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ABSTRACT

Large nonequilibrium polarizations on the order of 10% are achievable in the spin-1/2 isotopes $^3$He and $^{129}$Xe through a process called spin-exchange optical pumping (SEOP). Experiments utilizing hyperpolarized (HP) gases benefit from maximizing polarization and storage time. Interactions with other gas atoms and with the walls of the storage vessel limit the ultimate polarization and the longitudinal relaxation time. It is critical to understand the mechanisms governing the creation of HP gases and the interactions that cause relaxation. This thesis addresses the creation of HP $^3$He through a technique called hybrid SEOP and longitudinal relaxation in $^{129}$Xe due to the formation and breakup of $^{129}$Xe-Xe molecules.

The creation of HP $^3$He via SEOP is traditionally done using rubidium as the alkali metal intermediary. One drawback to this method is the time required to polarize the $^3$He, typically requiring 10-20 hours to achieve 40-50% polarization in enough gas ($\approx$1 L) for a single experiment. Two advances in SEOP have led to dramatic enhancements in efficiency: the use of spectrally narrowed diode laser arrays and hybrid SEOP, which employs both potassium and rubidium. We have combined these techniques to construct a dedicated $^3$He polarizing system capable of producing $>60\%$ $^3$He polarization in 0.5 bar·L of gas in valved and refillable glass cells in under 4 hours.

At gas densities typical for SEOP of $^{129}$Xe, fluctuations in the spin-rotation and chemical shift anisotropy interactions mediated by the formation and breakup of loosely bound $^{129}$Xe-Xe molecules have been identified as the primary intrinsic spin-relaxation mechanism, with $T_1$ limits of 4.6 hours for samples of pure Xe. We have shown that this relaxation mechanism can be suppressed at high magnetic fields, leading to longitudinal relaxation times of $\approx$ 100 h at 14.1 T. Further results
showed a near doubling of relaxation times with temperature increases from 293 K to 393 K, implying a maximum intrinsic relaxation time of \( \approx 9 \text{ h} \) at 393 K. At fields practical for SEOP (2.8 mT), we observed \(^{129}\text{Xe}\) relaxation times of nearly 5 hours in a 1 amagat Xe sample at 393 K suggesting a practical, low-field, noncryogenic storage system that will provide Xe hold times much longer than those currently available with standard techniques.
to Angie, Emilia and Charlie
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CHAPTER 1

INTRODUCTION

1.1 Research Introduction

As an undergraduate I saw for the first time an MRI image of lungs made with hyperpolarized $^3$He as the signal source (see Fig. 1.1). I was intrigued and wanted somehow to be involved with research that led to images like that. I soon found myself working in Brian Saam’s lab at the University of Utah the summer before my final year of my undergraduate education. I had the opportunity then to begin my studies of hyperpolarized $^3$He and $^{129}$Xe. Several years later after earning a master’s degree from the University of Oregon I returned to Salt Lake City to finish my education. My research focused on two aspects of hyperpolarized gases: how to create them and how they relax. The first year or so I spent studying hybrid spin-exchange optical pumping methods used to more efficiently produce HP $^3$He. I then turned my attention to a recently discovered relaxation mechanism important in samples of HP $^{129}$Xe. Together with Brittany Berry I was able to characterize relaxation due to the formation and breakup of loosely bound $^{129}$Xe-Xe molecules. Our increased understanding of intrinsic $^{129}$Xe relaxation mechanisms helped lay the foundation for a new low-field storage method for hyperpolarized $^{129}$Xe.

1.2 Overview of Hyperpolarized Noble Gases

It is possible to create large nonequilibrium polarizations exceeding 10% in gaseous samples of the spin-1/2 noble gases $^3$He and $^{129}$Xe. A sample of hyperpolarized (HP) gas has a polarization many orders of magnitude larger than that predicted by Boltzmann statistics, even at the multi-Tesla magnetic fields available from superconducting magnets. These HP noble gases are used regularly as the signal source for nuclear magnetic resonance (NMR) and magnetic resonance
imaging (MRI) experiments. HP gases are produced via two optical pumping methods: metastability-exchange optical pumping (MEOP)[1] in which $^3$He is polarized directly by the incident laser light, and spin-exchange optical pumping (SEOP)[2] where angular momentum from circularly polarized photons is transferred to $^3$He and $^{129}$Xe nuclei through the valence electron of an alkali metal intermediary. The work described here involves HP $^3$He and $^{129}$Xe produced via SEOP. The basic physics of spin-exchange optical pumping as well as the mechanisms responsible for relaxation of polarization to thermal equilibrium levels in HP gases will be outlined in this chapter.

1.2.1 History and Uses of Hyperpolarized Noble Gases

Optical pumping describes a process in which the population of a state in a given quantum system is driven to a nonequilibrium population level via selective absorption of resonant photons. This method was first described by A. Kastler in 1950[3], earning him the Nobel Prize in 1966. In 1961, M. Bouchiat, et al.
successfully demonstrated the production of HP $^3$He via SEOP[4]. Grover, et al. reported in 1977 the production of HP $^{129}$Xe and $^{131}$Xe as well as $^3$He by SEOP[5].

HP $^3$He and $^{129}$Xe each have important qualities that determine the feasibility of experiments utilizing these hyperpolarized gases. $^3$He is only $1.3 \times 10^{-4}$% abundant naturally[6]. It is, however, a byproduct of tritium decay, which means that the world’s nuclear weapons provide a steady yet poorly defined and expensive supply of $^3$He. One advantage of using HP $^3$He for nuclear magnetic resonance (NMR) experiments is its relatively long longitudinal relaxation time ($T_1$). A disadvantage of HP $^3$He is the length of time typically needed to polarize the gas: usually 10-20 hours are required to obtain 40-50% polarization in a useful volume of $^3$He($\sim 1$ L at STP). In 2001, Happer, et al. introduced a polarization method called hybrid SEOP[7] in which a mixture of potassium and rubidium is used as the alkali metal intermediary in place of pure rubidium. The feasibility of hybrid SEOP was demonstrated in 2003 by Babcock, et al.[8], with reports of polarizations exceeding 70% in a 25 cm$^3$ sealed cell containing $\approx 3.3$ atm $^3$He in less than 4 hours. Other work has more fully explained the process of spin-exchange optical pumping as well as explored mechanisms that limit the production of HP $^3$He leading to great improvements in efficiency[2, 9, 10].

$^{129}$Xe is 26.44% naturally abundant[6] and is readily available from Earth’s atmosphere. The work described in this thesis used xenon gas enriched to 86% $^{129}$Xe. Creation of HP $^{129}$Xe is intrinsically more difficult than $^3$He. The cross-section for depolarization of an optically pumped alkali vapor through collisions with xenon is large. This spin-rotation mechanism works to suppress the alkali polarization which in turn lowers the achievable $^{129}$Xe polarization. The electron cloud of a xenon atom is also very easily distorted by interactions with cell walls or other gas atoms. This leads to $T_1$ relaxation times often measured only in minutes for $^{129}$Xe. HP $^{129}$Xe can be produced in two ways: batch mode polarization or flow-through polarization. In batch-mode polarization a fixed amount of xenon gas in a valved cell undergoes SEOP. The polarized gas, which can be polarized to 10-20% is then transferred to the system of interest. A method involving the
polarization of $^{129}$Xe using a flow-through technique was introduced by Driehuys, *et al.*[11]. Recent developments by Hersman, *et al.* describe a very efficient flow-through polarizer[12]. Led by Geoff Schrank, our lab has actively pursued the construction of a similar xenon polarizer. The flow-through $^{129}$Xe polarizer operates at low total gas pressures, typically about 1 atm. A mixture of $\approx 90\%$ He, $\approx 10\%$ N$_2$ and $<1\%$ $^{129}$Xe flows through a 1.2 m polarizing cell. The mixture is lean in $^{129}$Xe due to the high spin-destruction cross section of Xe. The gas mixture and laser beam propagate in opposite directions which allows for the most efficient use of the incident light. Hersman’s group report $^{129}$Xe polarizations of 64% at a rate of 0.3 L/h, while our group has observed polarizations of 84±16% at a rate of 0.072 L/h and 44±5% at 0.6 L/h. Measurement cells can be attached to the flow-through polarizer and filled when HP $^{129}$Xe is needed. In some cases, however, it is desired to accumulate large quantities of polarized $^{129}$Xe. This is typically accomplished by flowing the mixture through a cold trap held in liquid nitrogen and placed in a moderate magnetic field ($\sim 0.1$ T). The xenon freezes while the rest of the mixture is unaffected. In this manner large amounts of HP $^{129}$Xe can be accumulated and stored. Under these conditions, $T_1$ of the $^{129}$Xe is 2.5 h[13]. However, the relaxation time of $^{129}$Xe near the freezing point is on the order of seconds and temperature gradients within the solid can lead to large polarization losses[13]. Care must be taken to avoid this issue. Hersman, *et al.* presented a method that maintains 90% or more of the initial polarization after a freeze/thaw cycle. It would, however, be potentially valuable to develop storage methods that do not involve cryogenic methods. In this work we will present results that could lead to a low-field $^{129}$Xe storage system that does not require freezing and thawing.

Recent advances in laser technology[14, 15] as well as a more thorough understanding of the nuances of the process of spin-exchange optical pumping as well as important relaxation mechanisms have made possible great improvements in efficiency of production of HP noble gases[2, 8, 9, 10].

The large polarizations of HP noble gases make them a very useful signal source in many applications. These include biochemistry, surface science, studies of
fundamental symmetries, neutron polarizers and spin filters and magnetic resonance imaging (MRI) of the lungs[16, 17, 18, 19, 20].

1.3 Spin-Exchange Optical Pumping

Spin-exchange optical pumping (SEOP) is the process by which angular momentum from circularly polarized photons is transferred to the nuclei of $^{129}$Xe and $^3$He via the valence electron of an alkali metal intermediary. A useful picture for describing SEOP is that of filling a series of two leaky buckets (see Fig. 1.2). The level to which the buckets can be filled depends on two things: the rate of water flow and the size of the holes in the buckets. In this picture the hose represents the laser, which is the source of water (angular momentum). The first bucket represents the alkali valence electrons, and the second bucket represents the noble gas nuclei. The level of water in the two buckets is the polarization of the system in question. Both buckets contain leaks which represent the various mechanisms responsible for the relaxation of the polarized valence electrons and noble gas nuclei. A deep understanding of both the mechanisms governing relaxation (the size of the holes) and the rate at which angular momentum is deposited in the system (the flow of water from the hose) is required for efficient use of HP noble gases. This thesis will address both aspects of the model. I will present the results of our work dealing with hybrid spin-exchange which is an effort to increase the efficiency of deposition of angular momentum into the $^3$He spin system. We will also discuss our studies of $^{129}$Xe relaxation, which have allowed us to begin thinking about improved storage methods for HP $^{129}$Xe greatly increasing the possibilities for use of the gas in various experiments.

1.3.1 Depopulation Optical Pumping

Depopulation optical pumping is the process through which the angular momentum of circularly polarized photons is transferred to the valence electrons of an alkali metal vapor. This process aligns, or polarizes, the alkali valence electrons. It is necessary to heat the cell to a temperature of 160-250°C to create a Rb vapor. Cells containing only Rb are heated to $\approx$165°C while hybrid cells typically require
Figure 1.2. Leaky bucket model for spin-exchange optical pumping.
SEOP temperatures $>200^\circ$C due to the suppression of Rb vapor pressure due to the presence of K\cite{21}. The incident laser light is tuned to 795 nm, which corresponds to the Rb D$_1$ (5S$_{1/2}$-5P$_{1/2}$) electric dipole transition. The circular polarization of the light imposes a selection rule of $\Delta m = \pm 1$ on the Rb valence electrons.

The process of depopulation optical pumping is depicted in Fig. 1.3. Right-circularly polarized light ($\sigma^-$) excites electrons in the spin-up ($m = +1/2$) sublevel of the Rb 5S$_{1/2}$ state into the spin-down ($m = -1/2$) sublevel of the Rb 5P$_{1/2}$ state. Collisional mixing with the noble gas atoms in the vapor equilibrates the relative populations in the sublevels of the 5P$_{1/2}$ excited state and the probabilities for transition to either of the 5S$_{1/2}$ sublevels become equal. This means that, on average, two incident photons are required to polarize a Rb atom.

The mechanism by which the excited Rb atoms decay to the ground state is important. If the atoms are allowed to decay radiatively, the emitted photon could be absorbed by a polarized Rb atom causing it to become depolarized. This process is called radiation trapping\cite{22}. A small amount of N$_2$ gas is added as a buffer gas, which acts to inhibit radiation trapping. The excited alkali atoms relax nonradiatively through quenching collisions by transferring energy and angular momentum into the vibrational and rotational degrees of freedom of the N$_2$ molecules. Quenching collisions repopulate the 5S$_{1/2}$ sublevels. The $m = -1/2$ sublevel is
transparent to the incident right-circularly polarized light and its population will increase until saturation is reached in tens of microseconds. Various relaxation mechanisms destroy the alkali polarization on a millisecond time scale and it is therefore required to continuously illuminate the spin-exchange cell with laser light to maintain the alkali polarization.

Mechanisms such as dipolar coupling of alkali atoms, spin-rotation interactions that couple the alkali electron spin and the rotational angular momentum of an interacting alkali-noble gas pair, and hyperfine interactions between the alkali electron spin and noble gas nuclear spin are responsible for relaxation of the polarized alkali vapor. Under the typical conditions found in spin-exchange optical pumping cells, alkali relaxation is dominated by two of these mechanisms. The first is the alkali-noble gas spin-rotation interaction, which causes relaxation of the polarized alkali electron spins. The second is the hyperfine coupling of the alkali electron spin to the noble gas nuclear spin, which is responsible for the transfer of angular momentum to the noble gas nuclei through spin-exchange.

1.3.2 Spin-Exchange

The quenching effect of N$_2$ removes the alkali relaxation mechanism of radiation trapping. The dominant remaining spin destruction mechanism is through a spin-rotation interaction with other atoms of any type in the cell. The spin-rotation interaction is described by the Hamiltonian

$$H_{sr} = \gamma \mathbf{N} \cdot \mathbf{S}, \quad (1.1)$$

where $\gamma$ is a coupling constant dependent on the internuclear atomic separation, $\mathbf{N}$ is the angular momentum of the interacting atoms about their center of mass and $\mathbf{S}$ is the alkali electron spin. In this interaction, the angular momentum of the alkali electron is transferred to the angular momentum of the pair of interacting atoms about their center of mass. This interaction does not polarize the noble gas nuclear spin and is analogous to a leak in the bucket shown in Figure 1.2.

The other dominant channel for the relaxation of the polarized alkali metal vapor is a transfer of angular momentum to the noble gas nuclei. This interaction
is called spin-exchange and occurs through hyperfine interaction and is described by the Hamiltonian first suggested by Herman[23]. The dominant term in the Hamiltonian is given by

\[ \mathcal{H}_{se} = -2\gamma_n\mu_n\mu_B \frac{8\pi}{3}\delta(r)\mathbf{S} \cdot \mathbf{I}, \]  

(1.2)

where \( \gamma_n \) is the nuclear gyromagnetic ratio, \( \mu_n \) the nuclear magnetic moment, \( \mu_B \) the Bohr magneton, \( \mathbf{S} \) the alkali electron spin, \( \mathbf{I} \) the nuclear spin and the distance between the electron and nucleus is given by \( r \).

Two types of interactions are responsible for spin-exchange between Rb and the noble gas nuclei \(^3\text{He}\) and \(^{129}\text{Xe}\): binary interactions and short-lived van der Waals molecules formed in three body collisions. The rate of spin-exchange due to the hyperfine interaction is given by[24]

\[ \gamma_{se} = [\text{Rb}] \left( \frac{\gamma_M \zeta}{[X]} + \langle \sigma_v \rangle_{se} \right). \]  

(1.3)

The first term describes spin-exchange in alkali-noble gas van der Waals molecules and is inversely proportional to the density of the third body in the collision. The constant \( \zeta \) depends on the polarization and isotopic composition of the Rb and \( \gamma_M \) depends on the rate of molecule formation and the interaction strength between the alkali and the noble gas. This term dominates in the case of Rb-\(^{129}\text{Xe}\) spin-exchange at low Xe pressures. The second term, due to binary collisions, is the velocity-averaged cross section for binary spin-exchange collisions, and is the dominant source of spin-exchange between Rb and \(^3\text{He}\) as well as \(^{129}\text{Xe}\) at higher pressures.

### 1.3.3 Noble Gas Polarization

The polarization of the noble gas nuclei as a function of time is given by

\[ P_{NG}(t) = P_A \frac{\gamma_{se}}{\gamma_{se}(1 + X) + \Gamma}(1 - e^{-(\gamma_{se} + \Gamma)t}), \]  

(1.4)

where \( P_A \) is the alkali polarization, \( \gamma_{se} \) is the spin-exchange rate, \( \Gamma \) is the noble gas relaxation rate and \( X \) is a phenomenological parameter describing an unexplained relaxation mechanism observed in \(^3\text{He}\)[25].
Under normal SEOP conditions, $P_A \approx 100\%$[8, 26]. The long time behavior of the $^3\text{He}$ polarization thus depends on the ratio $\frac{\gamma_{se}}{\gamma_{se}(1 + X) + \Gamma}$. In a cell with a relaxation rate which is small compared to the spin-exchange rate, $^3\text{He}$ polarizations would be expected to approach $P_A$ in the long time limit. Experimental evidence shows that $X$ appears to limit the achievable $^3\text{He}$ polarization to less than 80$\%$[26].

The polarization of $^{129}\text{Xe}$ is limited by the both the ratio of relaxation and spin-exchange rates and the alkali polarization. This is due to the fact that the highly polarizable electron cloud of the xenon atom leads to an enhance Rb spin-destruction rate and limits the achievable polarization of the Rb as well as the $^{129}\text{Xe}$.

### 1.3.4 Efficiencies

Efforts to understand and improve experiments utilizing spin-exchange optical pumping depend strongly on the understanding how efficiently the angular momentum from the circularly polarized photons is transferred to the noble gas nuclei. There are two measures commonly used to describe the efficiency of SEOP.

The first measure is called photon efficiency ($\eta_\gamma$) and is defined as the number of polarized nuclei produced per photon absorbed in the alkali vapor.

The second measure is the spin-exchange efficiency ($\eta_{se}$) and is defined as the ratio of the rate at which angular momentum is transferred to the noble gas nuclei to the rate at which angular momentum is lost by the alkali metal atoms through all possible channels (including spin exchange). The value of $\eta_{se}$ depends on the alkali metal used for spin-exchange. Recent work has shown that Rb-$^3\text{He}$ spin-exchange has an efficiency of $\approx 2\%$ under normal SEOP conditions[27]. This means that about 50 photons are required to polarize a single $^3\text{He}$ nucleus. K-$^3\text{He}$ spin-exchange is more efficient ($\approx 25\%$), requiring only four photons to produce a polarized $^3\text{He}$ nucleus[8]. This is due to the smaller K fine structure coupling which lowers the spin-destruction rate, or depolarization of the alkali through channels other than spin-exchange. The spin-exchange efficiency of Rb-$^{129}\text{Xe}$ is $\approx 7\%$[28].

Under ideal conditions, $\eta_\gamma = \eta_{se}$. The photon efficiency can never be larger than the spin-exchange efficiency. In practice the ratio $\eta_\gamma / \eta_{se}$ is always less than unity.
due to imperfections in optical pumping.

1.4 Hybrid Spin Exchange Optical Pumping

Given the increased efficiency of K-3He SEOP it would seem reasonable to expect potassium to be the alkali metal of choice in spin-exchange experiments. Rubidium, however, has mostly been used in this role. There are several reasons, both practical and physical, why Rb has been chosen historically.

One practical consideration is that of available lasers. There are many high powered lasers available at 795 nm, which is the wavelength of the Rb D$_1$ transition. It is considerably more difficult to find high powered lasers that operate at the K D$_1$ transition wavelength of 770 nm. Another practical consideration is the relative ease of working with Rb compared to K. Potassium has a higher melting point and requires much more effort and patience to distill into SEOP cells in a manner that will not damage the glass cells. Finally, the small splitting between the K D$_1$ and D$_2$ lines (3.4 nm) means that both transitions can be excited by the pumping laser, leading to lower alkali polarizations and less efficient production of HP $^3$He.

A method called hybrid spin-exchange optical pumping combines the benefits of K-3He spin-exchange with optical pumping of Rb[8]. In this case, a mixture of Rb and K is placed in the spin-exchange cell and optically pumped with a Rb (795 nm) laser. Optical pumping of Rb is much more efficient than that of K due to the much larger splitting between the Rb D$_1$ and D$_2$ lines (15 nm). This means that only the D$_1$ transition is excited and leads to Rb polarizations approaching 100%. The spin-exchange cross section between K and Rb is large, roughly 200Å$^2$[22], and the polarizations of the electron spins of the two alkali metals quickly reach a spin-temperature equilibrium[29]. Spin-exchange collisions with $^3$He then occur with both alkali species. The high spin-exchange efficiency of K-3He leads to high final $^3$He polarizations reached in less time than is typically needed for a Rb-only spin-exchange cell.

It is convenient to analyze hybrid SEOP in terms of the ratio of K to Rb in the vapor phase, represented by $\mathcal{D} \equiv [\text{K}]/[\text{Rb}]$. This work will present evidence that
the best combination of high $^3$He polarization and fast SEOP times are achieved for cells with $D$ values ranging from three to ten.

1.5 Noble Gas Nuclear Spin Relaxation

Hyperpolarized gases are in a state far from thermal equilibrium. There are several important mechanisms that provide pathways for HP gas to relax back to thermal polarization levels. This decay is described by a characteristic time constant $T_1$ given by:

$$\frac{1}{T_1} = \frac{1}{T_{1G}} + \frac{1}{T_{1\text{wall}}} + \frac{1}{T_{1\text{gas}}},$$

(1.5)

where $T_{1G}$ describes relaxation due to diffusion through magnetic field gradients, $T_{1\text{wall}}$ describes relaxation due to interactions with cell walls and $T_{1\text{gas}}$ gives the relaxation due to interactions between the noble gas nuclei with other nuclei in the gas. In all cases the relaxation rate is defined as $\Gamma \equiv 1/T_1$.

1.5.1 Gradient Induced Relaxation

Relaxation due to the diffusion of HP gas through magnetic field gradients is given by:

$$\frac{1}{T_{1G}} = D \left( \frac{\nabla B_\perp}{B} \right)^2,$$

(1.6)

where $D$ is the noble gas diffusion coefficient, $B$ is the longitudinal magnetic field and $\nabla B_\perp$ is the transverse gradient to the longitudinal field. This relationship is valid in the limit where the time required for an atom to travel across the cell is much longer than the Larmor period. This limit is easily met in our cells. The work described here took place in homogeneous fields created by well shimmed superconducting magnets or in carefully aligned Helmholtz coils. The gradient relaxation times in this work are on the order of 100s of hours or more meaning $T_{1G}$ is negligible and will not be considered further.

1.5.2 Wall Relaxation

Relaxation of HP noble gases due to interactions with cell walls is perhaps the least understood of all relaxation mechanisms. It is, however, in many cases the dominant relaxation mechanism. Efforts to gain a deeper understanding of wall
relaxation have been made difficult by wide variations seen in individual cells. It is not uncommon for cells made simultaneously to have measured relaxation times that differ by tens of hours. Historically, paramagnetic impurities at or near the cell surface have been believed to be responsible for wall relaxation of $^3$He \([31]\). $^3$He can also be absorbed into the glass cell walls and relax due to dipolar coupling to a magnetic dipole in the glass. Wall relaxation of HP $^3$He has been studied thoroughly by our research group over the last decade, and several important discoveries have been made that have allowed for more consistent production of cells with long $^3$He relaxation times\([32, 33, 34, 35, 36]\).

Relaxation of HP $^{129}$Xe due to interactions with cell walls is also poorly understood. Researchers have had success in extending the wall relaxation time of $^{129}$Xe cells by coating the cells with SurfaSil\([37]\) or dichlorodimethylsilane\([38]\). The coating inhibits relaxation due to interactions with paramagnetic impurities and magnetic dipoles on or below the cell surface. Relaxation of HP $^{129}$Xe occurs when the Xe atoms are adsorbed onto the coated cell surface or become trapped within the coating. It has been shown that in the low field limit ($< 100$ Gauss) that relaxation occurs through a dipolar coupling to protons in the SurfaSil coating\([38]\). This work will present evidence that wall relaxation can effectively be turned off at high (multi-Tesla) fields leading to extraordinarily long $^{129}$Xe relaxation times. We observed a magnetic decoupling of the relaxation of HP $^{129}$Xe as a function of field. The width of this decoupling is approximately 1 T which corresponds to a correlation time of $\approx 10$ ns. It is possible that this could be due to a coupling between the $^{129}$Xe nuclear spin to unpaired electrons in the cell coating.

The wall relaxation rate is independent of gas density under general SEOP conditions. This effect can be described by imagining a cell with a thin layer of spins within one mean free path of the cell wall. We further assume that there is a finite (and small) probability that a spin will relax in a collision with the wall. This means that on average some small fraction of the total magnetization of the hyperpolarized gas sample will be destroyed in a given collision. If, for example, the gas density was then doubled the rate of collisions with the wall would also double.
However, since the probability of relaxation due to a collision with the cell wall would remain constant, the fractional magnetization lost in a given time would be the same since there would be twice as many spins interacting with the wall. The density dependence of these two effects effectively cancels, leading to the observed independence of wall relaxation on density. This analysis is valid in the limit where $T_1$ is long compared to the diffusion time across the cell, a condition routinely met in our cells.

1.5.3 Gas Phase Relaxation Mechanisms

Relaxation of HP $^3$He due to dipole-dipole interactions with other $^3$He atoms is a well understood process[39]. The relaxation rate due to the modulation of the dipole-dipole interaction during collisions between $^3$He atoms is given by:

$$\frac{1}{T_{1dd}} = \frac{[^3\text{He}]}{744} \text{hours}^{-1},$$

(1.7)

where $[^3\text{He}]$ is the density of $^3$He in amagats. An amagat is defined as the density of an ideal gas at STP ($0^\circ$C and 1 atm). In a typical spin-exchange cell filled to 8 atm $T_{1dd}$ is 100 hours. The $^3$He work described in this thesis was done in a pressure regime ($\leq 8$ atm) where wall relaxation was the dominant mechanism.

1.6 $^{129}$Xe Intrinsic Relaxation Mechanisms

A large portion of this thesis describes important gas phase relaxation mechanisms of HP $^{129}$Xe. The mechanisms responsible for the relaxation of gas phase $^{129}$Xe can be divided into two categories: extrinsic and intrinsic relaxation. In general, the relaxation rate can be described as a sum of four terms

$$\Gamma = \Gamma_t + \Gamma_p + \Gamma_g + \Gamma_w$$

(1.8)

where the intrinsic mechanisms due to transient and persistent xenon dimers (discussed in section 1.6.1) are given by the first two terms. The last two terms describe extrinsic relaxation due to magnetic field gradients and interactions with the cell wall. This section will describe the pressure, temperature and field dependence of relaxation mechanisms relevant in the pressure and temperature regimes generally found in $^{129}$Xe SEOP experiments.
1.6.1 Xenon Dimers

The formation and breakup of $^{129}$Xe-$^{129}$Xe van der Waals molecules, hereafter referred to as xenon dimers, plays an important role in the intrinsic relaxation of HP $^{129}$Xe. It is important to distinguish between two types of dimers: transient and persistent. Transient dimers are the product of binary collisions. The lifetime of a transient dimer is given by the ratio of the atomic size to the relative thermal velocity of the interacting pair and is generally shorter than the time between collisions. Persistent dimers are formed in three-body collisions, and exist in a stable bound state until a subsequent collision with a third body, either xenon or another gas molecule in the mixture, breaks up the persistent dimer.

The existence of persistent xenon dimers was first proposed in 1959 by Bernardes and Primakoff who estimated their concentration to be 0.5% for a 1 amagat sample of Xe at room temperature\[40\]. This concentration is related to chemical equilibrium coefficient $K \equiv [Xe_2]/[Xe]^2$. From this it is possible to determine the fraction of persistent dimers in a Xe sample in the limit where $[Xe_2] \ll [Xe]$ with

$$\frac{2[Xe_2]}{[Xe] + 2[Xe_2]} \approx 2K[Xe]. \quad (1.9)$$

In 2003, Chann, et al. calculated the partition function of the internal rovibrational states of a Xe$_2$ molecule to find $K = 230 \text{ \AA}^3[14]$ giving a persistent dimer concentration of 1.2% in a 1 amagat, room temperature Xe sample.

It is possible to use the calculated Xe-Xe interatomic potential and kinetic theory to make estimates of the important kinetic parameters governing the formation and breakup of xenon dimers\[41, 42\]. These calculations, which are described in detail in Chapter 4, give a transient dimer lifetime of 2.85 ps and a persistent dimer lifetime of 115 ps in a 1 amagat Xe sample. The much longer lifetime causes persistent dimers to play a dominant role in the relaxation of HP $^{129}$Xe at low densities.

1.6.2 Relaxation Due to Transient Dimers

Over 40 years ago E. Hunt and H. Carr found that for densities above about 50 amagats the relaxation rate was linearly proportional to the xenon density with a
rate of $\approx 52 \text{ h}^{-1} \text{ amagat}^{-1}$[43]. The linear dependence of the relaxation rate on the xenon density is consistent with an interaction mediated by binary collision, the frequency of which increases linearly with density. The mechanism responsible for this relaxation is fluctuations in the spin-rotation (SR) interaction and is described by the Hamiltonian

$$\mathcal{H}_{\text{sr}} = c_K(R) \mathbf{K} \cdot \mathbf{N}, \quad (1.10)$$

where $c_K(R)$ is a coupling constant which depends on the distance $R$ between the interacting atoms, $\mathbf{K}$ is the $^{129}\text{Xe}$ nuclear spin and $\mathbf{N}$ is the angular momentum of the dimer. In the limit of weak interactions, given by $\langle c_K^2 N^2 \rangle / \hbar^2 \ll 1$, the relaxation rate due to fluctuations in the spin-rotation interaction is given by

$$\Gamma_{\text{sr}} = \sigma_{\text{sr}}(T) v_{\text{rms}}[\text{Xe}], \quad (1.11)$$

where $\sigma_{\text{sr}}(T)$ is the thermally averaged binary spin-relaxation cross section, which depends on both $T$ and $c_K(R)$, and $v_{\text{rms}}$ is the relative root-mean-square speed of the interacting Xe atoms. The work of Hunt and Carr was done before the advent of hyperpolarized gases and was therefore done at high gas densities in order to obtain a useful signal. Their data can be extrapolated down to standard SEOP density regimes to yield an expected relaxation time of $\approx 52$ hours for 1 amagat of xenon. This time was for many years assumed to be the limiting relaxation time at xenon densities of 1 amagat and below.

More recent work by Moudrakovski et al. confirmed the results of Hunt and Carr, but also extended it to the regime of large applied magnetic fields[44]. This work, which was carried out for $[\text{Xe}] > 20$ amagat and at applied fields between 4.7 T and 9.4 T, found a dependence of the $^{129}\text{Xe}$ relaxation rate as a function of xenon density proportional to the square of the applied field. Such a field dependence suggests that modulations of the chemical shift anisotropy (CSA) interaction also contribute to relaxation. The Hamiltonian governing this interaction is given by[45]

$$\mathcal{H}_{\text{csa}} = c_K(R) \mu_B \mathbf{K} \cdot \mathbf{\Theta} \cdot \mathbf{B}_0, \quad (1.12)$$

where $c_K(R)$ is the same coupling constant as in the SR interaction, $\mu_B$ is the Bohr magneton, and $\mathbf{\Theta}$ is the inertial tensor of the interacting pair of atoms.
An expression similar to Eq. 1.11 can be written for relaxation due to the CSA interaction, and the total relaxation rate due to transient dimers can be expressed as

\[ \Gamma_t = \Gamma_{t}^{sr} + \Gamma_{t}^{csa}. \]  

(1.13)

A complete theoretical explanation of relaxation due to transient dimers would require a reformulation of the binary spin-relaxation cross sections to include a factor of \(1/(1 + \Omega^2 \tau_c^2)\) where \(\tau_c\) is the correlation time and is on the order of the lifetime of a transient dimer and \(\Omega\) is the \(^{129}\text{Xe}\) Larmor frequency in an applied field \(B_0\) \((2\pi \times 11.87 \text{ MHz}/\text{T})[46]\). These terms were not included for work involving transient dimers since all work was done in the limit of \(\Omega^2 \tau_c^2 \ll 1\), which holds for all reasonable \(B_0\) since \(\tau_c \approx 10^{-13} \text{ s}\) for binary collisions. In this limit, known as the fast-fluctuation limit, the additional factor quickly approaches unity. In the fast-fluctuation limit the observed dependence of relaxation rate on applied field observed by Moudrakovski et al. is due entirely to the \(B_0^2\) dependence of the chemical shift anisotropy interaction.

### 1.6.3 Relaxation Due to Persistent Dimers

In 2002, the research group of T.G. Walker at the University of Wisconsin first presented evidence that at the lower xenon densities commonly used for SEOP experiments, relaxation due to fluctuations in the spin-rotation interaction was actually due to the formation and breakup of persistent dimers[47]. Their work revealed that, at low fields, the intrinsic \(^{129}\text{Xe}\) relaxation time was independent of xenon density, effectively mimicking wall relaxation. The relaxation rate was, however, dependent on the concentration of a second gas which served to influence the formation and breakup rate of persistent dimers without affecting the fraction of xenon atoms in molecules. Further, a limiting low-field, pure xenon \(T_1\) value was calculated to be \(\approx 4\) hours, over an order of magnitude shorter than the accepted value extrapolated from the work of Hunt and Carr[43].

Our research group extended the research of the Walker group to high applied magnetic fields. We showed that for xenon densities below \(\approx 1\) amagat and applied
magnetic fields \( \geq 1.5 \text{ T} \) a decoupling of the relaxation due to persistent dimers is observed. In this regime a dependence of the relaxation rate on gas density for a fixed gas composition is observed that agrees, with minor modifications, with the theory put forth by the Walker group\cite{47}. The relaxation rate due to the formation and breakup of persistent dimers is given by

\[
\Gamma_p = (2K[\text{Xe}]) (M^{sr} + M^{csa}) \left( \frac{\tau_p}{1 + \Omega^2 \tau_p^2} \right),
\]

(1.14)

The first factor, \( 2K[\text{Xe}] \), gives the fraction of Xe atoms bound in molecules. \((M^{sr} + M^{csa})\) gives the sum of the mean-squared interaction strengths of the spin-rotation and chemical shift anisotropy interactions during a molecular lifetime, otherwise known as the second moment of the interactions. The third factor gives the power spectrum of field fluctuations. The power spectrum is effectively a distribution function describing the field fluctuation frequencies experienced by a persistent dimer during its lifetime. If there is a significant frequency component at or near the Larmor frequency relaxation will occur\cite{46}. The term \( \tau_p \) is the correlation time of the fluctuations, which in this case is equal to the lifetime of the persistent dimers. The lifetime of a persistent dimer can be expressed in terms of the densities of the constituent gases in the mixture multiplied by the relevant molecular breakup coefficients for each gas. For a mixture of xenon and nitrogen gas this relationship is given by

\[
\frac{1}{\tau_p} = k_{\text{Xe}}[\text{Xe}] + k_{\text{N}}[\text{N}_2],
\]

(1.15)

where \( k_{\text{Xe}} \) and \( k_{\text{N}} \) represent the molecular breakup coefficients for xenon and nitrogen respectively.

The Walker group conducted their experiments at an applied field of 20.4 G. In this field limit the contribution to relaxation from the CSA interaction is vanishingly small and the \( \Omega^2 \tau_p^2 \) term in the power spectrum can also be neglected. Combining Eqs. (1.14) and (1.15) in the limit of low field and pure xenon gives

\[
\Gamma_p = \frac{2K M^{sr}}{k_{\text{Xe}}}. \]

(1.16)

In this expression all dependence of the persistent dimer modulated relaxation rate on xenon density has vanished.
At the higher applied magnetic fields at which our group worked neither the CSA interaction nor the $\Omega^2\tau^2_p$ term in the power spectrum could be neglected. We observed a dramatic decoupling of relaxation modulated by persistent dimers as total gas density was lowered for a fixed gas composition and fixed applied magnetic field.

1.6.4 Field Dependence of $^{129}$Xe Relaxation

There are two important interactions modulated by the formation and breakup of persistent dimers. The first is the spin-rotation interaction and is due to the precession of the $^{129}$Xe nuclear spin about magnetic fields created by the motion of electrons in the tumbling persistent dimer. The interaction strength $M^{sr}$ is independent of applied field and given by

$$M^{sr} = \frac{2\langle c_2^2N^2 \rangle}{3\hbar^2}. \quad (1.17)$$

The second interaction of importance is the chemical shift anisotropy interaction. The distribution of electron density in a molecular bond is inherently anisotropic and the local magnetic field experienced by the nuclear magnetic spin depends on the orientation of the bond with respect to the applied field. This effect is typically averaged out by the tumbling motions of a gas molecule, but cannot be discounted in strong fields when the nucleus in question exhibits a large chemical shift range. The chemical shift range for xenon is over 300 ppm, and it is expected that the CSA interaction will be of importance in $^{129}$Xe relaxation. This interaction depends on the square of the applied magnetic field $B_0$ and is given by

$$M^{\text{csa}} = \frac{2}{15} \frac{\mu_B^2B_0^2}{\hbar^5} \langle c_K^2 \Theta_\perp^2 \rangle. \quad (1.18)$$

We studied the intrinsic relaxation of HP $^{129}$Xe at magnetic fields of 1.5 T, 4.7 T, 8.0 T and 14.1 T. Measurements at multiple fields allowed for separation of the contributions from the SR and CSA interactions. The relative strengths of the SR and CSA interactions will be equal for an applied field of 16.6 T.
1.6.5 Temperature Dependence of $^{129}$Xe Relaxation

The persistent dimer modulated $^{129}$Xe relaxation rate depends on temperature through two factors: the relative fraction of xenon atoms bound in Xe$_2$ molecules and the mean time between molecular formation and breakup through a collision with another atom. In the fast-fluctuation limit ($\Omega^2 \tau_p^2 \ll 1$) Eq. (1.14) can be rewritten as

$$\Gamma_p = (2K[Xe])\tau_p(M^{st} + M^{csa}),$$

where the temperature dependent terms have been placed together.

The dimer concentration is related to the chemical equilibrium coefficient which is given by

$$K = \frac{1}{2} \left( \frac{h^2}{2\pi\mu kT} \right)^{3/2} Z_i,$$

where $h$ is Planck’s constant, $\mu$ is the reduced mass of the Xe$_2$ persistent dimer and $Z_i$ is the partition function of the dimer’s internal ro-vibrational states. The first portion of the equation is the ratio of the translational partition functions for a single dimer to that for two free Xe atoms in the classical limit of high temperature and low density[41]. The temperature dependence of $Z$ is assumed to be weak. This is likely a reasonable assumption since the internal partition function for a Xe$_2$ dimer consists of a sum of terms containing $e^{(-E_i/kT)}$ where $E_i/k$ is approximately 280 K[42].

The molecular lifetime $\tau_p$ is equal to the mean time between collisions and is inversely proportional to the relative thermal velocity of the interacting atom/molecule pair. For a gas described by a Maxwellian distribution the mean thermal velocity is given by

$$\bar{v} = \sqrt{\frac{8kT}{\pi\mu}},$$

where $\mu$ is the reduced mass of the interacting particles. The contribution to the temperature dependence of $\Gamma_p$ from the persistent dimer lifetime $\tau_p$ is therefore proportional to $T^{-1/2}$. When combined with the expected $T^{-3/2}$ dependence from the chemical equilibrium coefficient the persistent dimer modulated relaxation mechanism should be consistent with an overall dependence on $T^{-2}$. 
1.7 Thesis Summary

Three of the chapters in this thesis have either been published (Chapter 4) or will be submitted for publication (Chapters 3 and 5). These chapters remain in their submitted form. There may be some redundancy due to multiple explanations of the physics governing the creation of HP gases and the mechanisms responsible for relaxation, but I felt that periodic refreshers would benefit the reader.

Chapter 2 gives a brief overview of the experimental methods used in the work. The construction of spectrally narrowed diode laser arrays and spin-exchange cells is discussed as well as the measurements of noble gas polarization and the ratio of [K]/[Rb] in hybrid cells. Chapter 2 also includes an introduction to the nuclear magnetic resonance techniques used in this work.

Chapter 3 is an article that will be submitted to the Journal of Magnetic Resonance. We worked with hybrid spin-exchange optical pumping in a pressure regime where the alkali metal spin-destruction was dominated by $^3$He-alkali metal interactions. We found that the behavior of hybrid spin-exchange cells depends on $D$, defined as the ratio of K to Rb in the vapor phase at SEOP temperatures. The best combination of rapid spin-exchange and high final $^3$He polarization was realized in cells with $D$ ranging from 3-5.

Chapter 4 is an article that was published in the 15 December edition of Physical Review A. This work dealt with the relaxation of HP $^{129}$Xe due to the formation and breakup of persistent $^{129}$XeXe dimers at 8.0 T and densities less than 1 amagat. We verified that a large applied field suppressed persistent dimer modulated relaxation.

Chapter 5 is an article that will be submitted to Physical Review A. This chapter describes an extension of the work in chapter 4 to study persistent dimer modulated relaxation in HP $^{129}$Xe as a function of several applied fields and temperatures. This work allowed for a separation of the effects of the spin-rotation and chemical shift interactions as well as a confirmation of the predicted temperature dependence of $^{129}$Xe intrinsic relaxation. Results will be presented that could lead to vastly improve storage methods for HP $^{129}$Xe.
CHAPTER 2
EXPERIMENTAL METHODS AND PROCEDURES

2.1 Spectrally Narrowed Diode Laser Arrays

Several laser systems were used in this work, but all shared the same design. The laser used in the hybrid SEOP polarizer will be described in this section, a diagram of which is shown in Figure 2.1. The diode laser array (Quintessence Photonics Corporation, Sylmar, CA) operates at 795 nm and produces $\approx 40$ W of light. The first optical element is a microlens attached directly to the laser by the manufacturer which serves to reduce beam divergence along the fast-diverging axis. The laser is held at a fixed operating temperature of 18.25°C by a thermoelectric cooler (Ferrotec, Nashua, NH) in thermal contact with 20°C water circulated by a closed-loop chiller (PolyScience, Niles, IL).

Spectral narrowing of the laser output was obtained by following the methods outlined in references [15] and [51]. The light first passes through a 4x optical telescope which expands the beam onto a holographic diffraction grating (2400 lines/mm). The first order diffraction peak is reflected back into the laser resulting in a narrowing of the spectrum. The zeroth order peak continues through the optics train and is incident on the spin-exchange cell. The desired wavelength determines the angle of incidence on the diffraction grating according to Bragg’s law

$$\lambda = 2d \sin \theta$$

(2.1)

where $d$ is the line spacing of the grating and $\theta$ is the angle of incidence. An angle of 72.5° is required for a wavelength of 794.8 nm and a grating with 2400 lines/mm. The amount of feedback into the laser is controlled by a $\lambda/2$ waveplate placed within the 4x telescope. The half-wave plate controls the feedback intensity by rotating
the polarization of the linearly-polarized light from the laser with respect to the lines on the diffraction grating.

Following the grating is an IR mirror mounted on an assembly that co-rotates with the grating. This configuration allows for adjustment of the wavelength without moving the beam. The beam is then shaped by passing through a 150 mm plano-convex cylindrical collimating lens, a $\lambda/4$ waveplate and a spherical beam shaping lens. The focal length of the final lens determines the spot size at the optical pumping oven. Babcock et al. use a second telescope (10x) in place of the final spherical lens to minimize light divergence across the cell[15].

The power output of the laser was measured with a 30 W power meter (Thorlabs, Newton, NJ). Although the power meter was rated to only 30 W, we observed no change in the measured power with repeated measurements of up to 37 W. The laser used for hybrid SEOP delivered approximately 31 W to cell when spectrally narrowed and about 37 W when running in a broadband mode. The difference in power is due to the portion of light being fed back into the laser as well as the grating reflectivity of approximately 90%[52]. Using a PC based near-IR monochromator (USB 2000, Ocean Optics, Dunedin, FL), we measured the full-width at half-maximum (FWHM) of the broadband spectrum to be $\approx 2$ nm and the FWHM of the narrowed spectrum to be $\approx 0.3$ nm. The FWHM of the Rb absorption spectrum was $\approx 0.3$ nm for an 8.4 nm NTP cell (8.2 atm $^3$He and 0.2 atm N$_2$ buffer gas)[53]. Although narrowing the spectrum costs several watts of light, a much greater fraction of the light overlaps the central portion of the Rb absorption spectrum meaning more of the incident light is of the correct wavelength and fewer photons are wasted. It has been shown that the use of a spectrally narrowed diode laser array can improve the polarization levels of both $^{129}$Xe[54] and $^3$He[14] by 20-40 percentage points.
Figure 2.1. Optical elements in spectrally narrowed laser. Adapted from illustration by Jared Teter.
2.2 Spin-Exchange and Measurement Cells

The work described in this thesis was done in valved glass vessels (cells). Several variations of size and geometry were used, but all cells were patterned after those used historically in our lab[55]. While the overall cell design did differ, all cells contained common features. An illustration of a typical cell is found in Figure 2.2. In all cases, the body of the cell was connected to a valve via a long capillary. Nearly all cells contained one or more alkali metals which were distilled into the cell from a glass manifold through a tube (stem) located opposite the capillary and valve. NMR experiments were done with a coil placed around the cell stem.

Several cell body geometries and sizes were employed for the work described here, and the cells can be loosely divided into two types: polarization cells and measurement cells.

2.2.1 Polarization Cells

Two types of polarizing cells were used in this work. HP $^{129}$Xe was created exclusively in polarizing cells containing only Rb. Hybrid cells, or cells containing a mixture of Rb and K, were used for SEOP of $^3$He. The methods used for the preparation of new cells has been described in detail elsewhere[55] and will be summarized here.

New cells are attached to a glass manifold for bake-out and alkali distillation. A standard manifold for Rb-only cells contains a single retort designed to accom-
moderate an ampoule of Rb. An additional retort is added to a hybrid manifold to allow for the addition of K (see Fig. 2.3). The disparate melting points of the two alkali metals require selective distillation. Potassium has a higher melting point than rubidium and thus requires more time and patience during distillation.

The ratio $D$ of K to Rb in the vapor phase is a very important parameter in hybrid spin-exchange cells. Published reports place the optimal value of $D$ between 2 and 10[8, 26]. This work suggests that an optimum balance of high final $^3$He polarization and fast polarization times is reached for $D \approx 3 - 5$, although improvements in performance were observed in any cell containing K. Vapor density ratios in the optimal range require solid mixes that are very lean in Rb. Babcock et al. have shown that $D = 10$ requires a solid phase mixture that is roughly 30:1 K to Rb[8]. It was very difficult to rigorously control the relative amounts of alkali metals distilled into the cells. Efforts were made to distill approximately 400-500 mg of K into each cell. A small amount of Rb was then placed into the cell in the form of one or more opaque films coating the cell interior.

![Diagram of hybrid spin-exchange cell manifold](image)

**Figure 2.3.** Hybrid spin-exchange cell manifold. A manifold for Rb-only cells contains only one retort. Illustration by Jared Teter.
Hybrid cells of different geometries and sizes were used in this work. Spherical cells with 2” and 3.1” diameters were prepared as well as cylindrical cells with both hemispherical and optically flat ends. Similar polarization levels and pumping times were observed in all cells. Several cells can be seen in Figure 2.4. We noted a gradual discoloration in our hybrid cells over time, but no changes in spinup times or $^3$He polarizations were observed.

### 2.2.2 Measurement Cells

Wide variations in the relaxation behavior in a sample of cells is common in the field of hyperpolarized gas research. However, worthwhile relaxation experiments require consistent behavior in a single cell during its lifetime. In our initial attempts to study the molecular relaxation mechanisms in $^{129}$Xe we made measurements in the same cells in which the gas had been polarized. Over a series of several measurements we observed fluctuations up to a factor of two in the wall relaxation

![Figure 2.4](image)

**Figure 2.4**. Hybrid spin-exchange cells. We observed no apparent dependence on geometry. The discoloration observed did not affect cell behavior.
rate. Over time $\Gamma_w$ tended to increase until it reached a level comparable to intrinsic relaxation mechanisms. The total relaxation rate, given by $\Gamma_{\text{total}} = \Gamma_{\text{int}} + \Gamma_w$, is a sum of intrinsic and extrinsic rates. If $\Gamma_w$ becomes too large, small variations in $\Gamma_{\text{int}}$ become difficult to observe. It is unclear what causes this behavior, but we postulated the occurrence of a reaction at optical pumping temperatures of Rb with the cell coating that ultimately led to an irreversible increase in the wall relaxation rate.

The $^{129}\text{Xe}$ relaxation measurements described in this work were performed in 2.5 inch diameter spherical cells containing no alkali metal. The cells were further coated with dichlorodimethylsilane to inhibit wall relaxation[38]. Extremely robust and, more importantly, small wall relaxation rates were observed during a series of experiments lasting nearly 2 years in which the cells were repeatedly exposed to temperatures of 100°C.

### 2.3 $D$ Measurements

An important parameter in the study of K-Rb spin-exchange cells is $D$, defined as the ratio of [K] to [Rb] in the vapor phase. As noted in section 2.2.1, it was difficult to carefully control the relative amounts of alkali metals distilled into the cells. A direct and reliable method of measuring $D$ was therefore critical in the effective characterization of hybrid SEOP methods.

#### 2.3.1 Raoult’s Law

According to Raoult’s law, the partial pressure of a constituent metal above a mixture is lower than the vapor pressure of the pure metal at a given temperature[21]. In the case of a mixture of K and Rb, this effect is described by

$$[\text{Rb}] = f_{\text{Rb}}[\text{Rb}]_0,$$

and

$$[\text{K}] = f_{\text{K}}[\text{K}]_0 = (1 - f_{\text{Rb}})[\text{K}]_0,$$

where $f$ represents the mole fraction of the metal and the 0 subscript represents the vapor pressure of the pure metal. The vapor pressures of pure Rb and K are
given by the following expressions[56], although under standard SEOP conditions the actual densities can vary by a factor of two or more:

\[
[Rb]_0 = \left( \frac{7.25 \times 10^{16}}{T} \right) 10^{9.318-4040/T} \text{ cm}^{-3},
\]

\[
[K]_0 = \left( \frac{7.25 \times 10^{16}}{T} \right) 10^{9.408-4453/T} \text{ cm}^{-3}.
\]

(2.4)

(2.5)

It is possible to use Raoult’s Law to scale a \( D \) measurement at a given temperature to any desired temperature. For example, by combining Eqs. (2.2) and (2.3) and taking \( T = 200^\circ\text{C} \), \( D \) is given by

\[
D_{200^\circ\text{C}} = \left( \frac{[K]}{[Rb]} \right)_{100^\circ\text{C}} \left( \frac{[Rb]_0}{[K]_0} \right)_{100^\circ\text{C}} \left( \frac{[K]_0}{[Rb]_0} \right)_{200^\circ\text{C}},
\]

(2.6)

where the quantities with the 100C subscript were measured at 100°C as described below.

### 2.3.2 \( D \) Measurement Techniques

\( D \) was measured directly via white light absorption techniques. White light from a 50 W halogen bulb was incident on the cell and absorbed by the K and Rb atoms at their resonant transitions. After passing through the cell the light was directed into a PC based near-IR monochromator (USB 2000, Ocean Optics, Dunedin, FL). A diagram of the experimental setup is shown in Figure 2.5.

It was necessary to measure the ratio of K to Rb at a temperature below standard hybrid SEOP temperatures. At the elevated temperatures required for hybrid spin-exchange optical pumping (typically 200-250°C), the cells were optically

---

**Figure 2.5.** Experimental setup for \( D \) measurements.
dense. We choose 100°C since at this temperature the absorption ratios for the \( \text{D}_2 \) to \( \text{D}_1 \) transitions for both alkali metals were approximately 2, which is the theoretically predicted value for an optically thin vapor\(^{22}\).

Figure 2.6 shows the measured spectrum of cell 128A at 100°C. In each cell the \( \text{D}_1 \) and \( \text{D}_2 \) electric dipole transitions were observed for both K and Rb. A lorentzian was then fit to each of the peaks and the area under the peaks was obtained via a computer fitting and integrating routine. The ratio of the total area under the \( \text{D}_1 \) and \( \text{D}_2 \) lines for each metal was then calculated and used in Eq. (2.6) to scale the value of \( \mathcal{D} \) to the appropriate temperature. The \( \mathcal{D} \) values for the hybrid SEOP cells used in this work ranged from \(<0.1\) to \(>10\).

### 2.4 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a powerful experimental technique for probing systems on the atomic or molecular level. The work presented here was done nearly exclusively with NMR techniques, and short overview of the physics behind NMR and NMR techniques will be given.

#### 2.4.1 NMR Overview

Nuclear magnetic resonance allows for the study of magnetic systems that possess angular momentum. It is noteworthy that classical and quantum mechanical calculations give identical values for the NMR precession frequency. This section will discuss both derivations, starting with the classical case.

The magnetic moment of a nucleus \( \mu \) and its total angular momentum \( J \) are related by

\[
\mu = \gamma J, \quad (2.7)
\]

where \( \gamma \) is a constant called the gyromagnetic ratio. The gyromagnetic ratio is a constant with a unique value for each spin species. The equation of motion for a nucleus in a magnetic field \( \mathbf{H} \) is given by

\[
\frac{d\mu}{dt} = \mu \times \gamma \mathbf{H}. \quad (2.8)
\]
Figure 2.6. White light absorption spectrum for cell 128A with $D = 0.8$ at 100°C.
Eq. (2.8) is more easily dealt with when we transition to a rotating reference frame whose z-axis coincides with that of the stationary laboratory frame. The time derivative of a vector \( \mathbf{A} \) in a rotating frame is given by

\[
\frac{d\mathbf{A}}{dt} = \frac{\delta \mathbf{A}}{\delta t} + \mathbf{\Omega} \times \mathbf{A},
\]

where the first term describes time rate of change of the components of \( \mathbf{A} \) and the second term describes the time derivative of the unit vectors \( \hat{x}, \hat{y}, \) and \( \hat{z} \), where \( \mathbf{\Omega} \) is the angular velocity of the rotating frame. Using Eqs. (2.9) we can recast the equation of motion of \( \mu \) as

\[
\frac{\delta \mu}{\delta t} = \mu \times \left( H + \frac{\mathbf{\Omega}}{\gamma} \right).
\]

This is an equation identical in form to Eq. (2.8) with the exception that \( H \) has been replaced by an effective field \( H_{\text{eff}} \) defined as

\[
H_{\text{eff}} = H + \frac{\mathbf{\Omega}}{\gamma}.
\]

We can account for the behavior of \( \mu \) in a static field directed along the z-axis by setting \( \mathbf{\Omega} = -\gamma H_0 \hat{z} \). With this substitution \( H_{\text{eff}} = 0 \) and \( \delta \mu/\delta t = 0 \), and \( \mu \) is fixed in the rotating frame. In the laboratory frame, \( \mu \) is seen to rotate with an angular velocity of \( -\gamma H_0 \hat{z} \). This rotation has an angular frequency of \( \gamma H_0 \) and is defined as the Larmor frequency.

We now turn our attention to a quantum mechanical derivation of the behavior of a nucleus in a magnetic field. Again we note that \( \mu = \gamma \mathbf{J} \) where \( \mu \) and \( \mathbf{J} \) are now viewed as quantum mechanical operators and then define a dimensionless angular momentum operator \( \mathbf{I} \) with

\[
\mathbf{J} = \hbar \mathbf{I}.
\]

When a particle with a magnetic moment \( \mu \) is placed in a magnetic field \( \mathbf{H} \) it experiences a Zeeman interaction energy described by the Hamiltonian:

\[
\mathcal{H} = -\mu \cdot \mathbf{H}.
\]
It is conventional to define the direction of \( \mathbf{H} \) along the z-direction. This assumption, along with equations 2.7 and 2.12, allow the simplification of the Hamiltonian to:

\[
\mathcal{H} = -\gamma \hbar H_0 I_z.
\] (2.14)

The eigenvalues of \( I_z \) are defined as \( m \) where \( m = -I, ..., I \). Given these eigenvalues we can express the allowed energy states as

\[
E = -\gamma \hbar H_0 m.
\] (2.15)

The solutions to 2.14 give an energy spectrum with splittings equal to \( \gamma \hbar H_0 \). This system can be probed through a time-dependent excitation at a resonant angular frequency \( \omega \) that fulfills the condition

\[
\hbar \omega = \Delta E,
\] (2.16)

where \( \Delta E \) is the energy splitting between the initial and final Zeeman levels. A common method for study magnetic resonance is the application of an AC magnetic field perpendicular to the static field. This perturbation adds the following term to the Hamiltonian:

\[
\mathcal{H}_{\text{pert}} = -\gamma \hbar H_1 x I_x \cos \omega t.
\] (2.17)

The matrix elements \( \langle m' | I_x | m \rangle \) vanish unless \( m' = m \pm 1 \). This means that the only allowed transitions are between neighboring energy levels. This selection rule imposes the condition that

\[
\Delta E = \gamma \hbar H_0 = \hbar \omega \implies \omega_0 = \gamma H_0,
\] (2.18)

where the Larmor frequency \( \omega_0 \) is the same frequency found from the classical derivation. As is seen in equation 2.18, the Larmor frequency of a given spin depends both on its gyromagnetic ratio and the static field applied to the spin system. It is of interest to note that Planck’s constant no longer appears in the resonance condition.

Table 2.1 compares the properties of the spin-1/2 noble gas nuclei \(^3\)He and \(^{129}\)Xe to protons (\(^1\)H). It is important to note that both noble gas species of interest in this
Table 2.1. NMR properties of the spin-1/2 nuclei $^3$He and $^{129}$Xe compared to $^1$H. The magnetic moment of each nucleus is given in units of Bohr magnetons ($\mu_N$). These values were taken from reference [6].

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Larmor Frequency (MHz/T)</th>
<th>Magnetic Moment ($\mu_N$)</th>
<th>Natural Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>42.577</td>
<td>2.79270</td>
<td>99.984</td>
</tr>
<tr>
<td>$^3$He</td>
<td>32.434</td>
<td>-2.1274</td>
<td>1.3$x10^{-4}$</td>
</tr>
<tr>
<td>$^{129}$Xe</td>
<td>11.78</td>
<td>-0.7726</td>
<td>26.44</td>
</tr>
</tbody>
</table>

work have negative magnetic moments. If the moments were positive, the opposite helicity of circularly polarized light would be needed to pump the noble gas nuclei into the low energy state via spin-exchange optical pumping.

When a system of spins is placed in a magnetic field the spins align themselves with or against the field. Boltzmann mechanics tells us that there will be a slight excess of spins in the low energy configuration (aligned antiparallel to the field) than in the high energy configuration. The size of this imbalance is referred to as the polarization of the sample and is given by

$$P = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow}.$$  \hspace{1cm} (2.19)

Most NMR experiments are done with the Boltzmann thermal polarization which, in the high temperature limit, is given by comparing the magnetic energy of the spins to their thermal energy:

$$P \approx \frac{\gamma \hbar H_0}{2kT}.$$ \hspace{1cm} (2.20)

For a sample of liquid water at room temperature the thermal polarization is a few parts in a million. A NMR measurement takes its signal not from individual spins, but from the entire sample. This means that NMR signal strengths are proportional to the product of polarization and spin density. The high density of a water sample overcomes the low polarization and makes nuclear magnetic resonance possible. Gas phase NMR is much more difficult due to the much lower spin density in a gaseous sample. HP gases, however, have polarizations ranging from 10-70%, making NMR studies of low pressure gas samples feasible.
2.4.2 Alternating Magnetic Fields

Nuclear magnetic resonance is an inherently quantum mechanical concept. However, the fact that NMR experiments involve the behavior of an ensemble of spins in a macroscopic sample allows for the use of classical mechanics to describe magnetic resonance phenomena. A classical description of the effect of an alternating magnetic field on the spin system provides a more intuitive picture than a quantum mechanical explanation.

We first define the alternating field as

\[ H_1(t) = H_1(\cos \omega_z t \hat{x} + \sin \omega_z t \hat{y}) \]  

(2.21)

and then rewrite Eq. (2.8) to include the time-dependent term \( H_1(t) \)

\[ \frac{d\mu}{dt} = \mu \times \gamma [H_0 + H_1(t)]. \]  

(2.22)

At this point it is useful to again move to a frame rotating about the \( z \)-axis with an arbitrary frequency \( \omega_z \). In this reference frame the time dependence of \( H_1 \) vanishes, transforming it to a static field. \( H_0 \) is static in both frames. Following the same methods as in Section 2.4.1 with the assumption that \( H_1 \) is directed along the \( x \)-axis in the rotating frame and setting \( \omega_z = -\omega \) we can write

\[ \frac{\delta\mu}{\delta t} = \mu \times \gamma \left( H_0 - \frac{\omega}{\gamma} \right) \hat{z} + H_1 \hat{x}. \]  

(2.23)

Again this equation is identical in form with Eq. (2.8), but now contains an effective field given by

\[ H_{\text{eff}} = \left( H_0 - \frac{\omega}{\gamma} \right) \hat{z} + H_1 \hat{x}. \]  

(2.24)

In the rotating frame, the spin experiences a static field \( H_{\text{eff}} \) and precesses around the effective field at an angular frequency of \( \gamma H_{\text{eff}} \). It is interesting to consider the situation where the alternating field exactly fulfills the resonance condition of \( \omega = \gamma H_0 \). In this case the effective field is due completely to \( H_1 \) and the spins that are initially parallel to \( H_0 \) precess but always remain perpendicular
to $H_1$. The angle through which the spins precess depends on the length of time the alternating field is on and is given by

$$\theta = \gamma H_1 t_p,$$

(2.25)

where $t_p$ is the duration of the RF pulse. In NMR experiments this is referred to as the flip angle. Two commonly used pulses in NMR are a 90 degree pulse and a 180 degree pulse. A 90 degree pulse rotates the magnetization into the $x$-$y$ plane while a 180 degree pulse inverts the magnetization. After the pulse ends there will be component of the magnetization that is perpendicular to $H_0$ which will undergo precession at an angular frequency of $\gamma H_0$. This oscillating magnetic field can then be detected by a receive coil placed around the sample.

### 2.4.3 Important Time Scales in NMR

There are two important time scales governing NMR experiments. A convenient means of introducing these characteristic times is given by a set of equations called the Bloch equations[57] that provide a phenomenological description the magnetization (which is proportional to the polarization) of a sample as a function of time. The first Bloch equation describes the component of magnetization parallel to the static field, usually taken along the $z$–direction and is given by:

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} + \gamma (M \times H)_z.$$  

(2.26)

The time $T_1$ is called the spin-lattice relaxation time. It is the time constant that describes the exponential approach of the magnetization to thermal equilibrium. $T_1$ relaxation is caused by mechanisms that couple the spin system to the “lattice,” or outside world. When such a coupling exists, the spins will approach the lattice temperature. It does not matter if the system is approaching equilibrium from zero polarization or, in the case of hyperpolarized gases, far from thermal equilibrium. In both cases $T_1$ will be the same.

The other Bloch equations describe the time dependence of the $x$– and $y$– components of the magnetization and have the form:

$$\frac{dM_{x,y}}{dt} = \gamma (M \times H)_{x,y} - \frac{M_{x,y}}{T_2}.$$  

(2.27)
In thermal equilibrium, the magnetization in the $x - y$ plane, or the transverse magnetization, will approach zero. This relaxation process is governed by the time constant $T_2$. $T_2$ relaxation does not necessarily involve the transfer of energy to or from the lattice and may be very different from $T_1$.

Transverse relaxation can be pictured by considering the variation of magnetic field experienced by various members of a spin ensemble. The local magnetic field can vary due to spatial inhomogeneities in the static field or due to magnetic fields arising from the presence of other spins in the system. As seen in equation 2.18, the Larmor frequency of a spin depends on magnetic field and a spread in local fields over a sample causes a spread in Larmor frequencies. Some spins would have Larmor frequencies higher than average, while others would resonate at lower frequencies. If the spins were in phase at some initial time, the different rates of precession would soon cause a dephasing of the transverse magnetization. The time constant describing the dephasing in the transverse plane is defined as $T_2$. The effect of transverse relaxation is seen in Fig. 2.7 where the oscillating signal discussed in section 2.4.2 is damped. This is referred to as a free induction decay (FID) and forms the basis for many NMR experiments. Information about magnetic field inhomogeneities due to spin-spin interactions as well as a nonuniform applied field is contained in the shape of the envelope.

### 2.4.4 NMR Experimental Methods

The NMR measurements in this work were taken using a small transmit/receive coil that was placed either around the stem of the coil or below the body of the cell. Standard NMR techniques utilizing large pulse angles are undesirable when working with hyperpolarized gases. The magnetization tipped into the transverse plane by a pulse vanishes as the spins dephase. Care must be taken to minimize the amount of magnetization destroyed with each pulse. This can be accomplished by using small flip angles, exciting only a small portion of the sample or both. The coils were therefore designed to minimize the volume of the cell excited by each pulse. Efforts were made to always use small flip angles, but the small volume
Figure 2.7. A free induction decay for a sample with a single spin species. Note the decay of the sinusoidal signal due to nonuniform local fields experienced by individual spins. These inhomogeneities are due both to intrinsic spin-spin interactions as well as a nonuniform applied field.

excited by the coil allowed for larger pulse angles if necessary.

The bulk of the experimental work described in this thesis dealt with measurements of the polarization of a sample of HP gas, either during optical pumping while the polarization was increasing or after optical pumping when the polarization approached thermal equilibrium levels. In both types of measurements either the height of the FID or the area under the Fourier transform of the FID was periodically recorded. These measurements became the individual data points in measurements of the polarization transient or a $T_1$ measurement.
The data from optical pumping of a sample, or spin-up, were fit to

$$S(t) = S_0 \left(1 - e^{-t/\tau}\right), \quad (2.28)$$

where the quantity $\tau = (\gamma_{se} + \Gamma)^{-1}$ is known as the spin-up time. A representative $^3$He transient is given in Figure 2.8 for a Rb-only spin-exchange cell.

The data from $T_1$ measurements were fit to

$$S(t) = S_0 e^{-t/T_1}. \quad (2.29)$$

A typical $T_1$ measurement of a sample of HP $^{129}$Xe is seen in Figure 2.9. The improved signal provided by hyperpolarized gas allows for data to be acquired over three orders of magnitude in signal.

### 2.5 $^3$He Polarization Measurements

In this work it was necessary to determine the polarization of the hyperpolarized $^3$He. The most obvious method would be to compare the signals from a hyperpolarized and thermally polarized gas sample. This was, however, not feasible due to the inherently low thermal gas signal. We therefore compared the hyperpolarized gas signal to that from a sample of thermally polarized water containing CuSO$_4$ to lower $T_1$ to approximately 100 ms for signal averaging purposes. In the case where the samples have the same geometry and are probed at the same NMR frequency it is possible to determine the $^3$He polarization by comparing directly the ratio of the gas and water NMR signals. In the low flip angle limit the ratio is given by

$$\frac{S_g}{S_p} = \frac{P_g n_g \gamma_g^2}{P_p n_p \gamma_p^2}, \quad (2.30)$$

where $P$ is polarization, $n$ is the spin density, $\gamma$ is the gyromagnetic ratio[58]. The subscripts $g$ and $p$ represent gas and proton respectively. The thermal polarization level of the water and the respective spin densities can be calculated from first principles. Eq. (2.30) can be solved for $P_g$ to give

$$P_g = (3.76 \times 10^{-4}) \frac{f S_g}{p S_p}, \quad (2.31)$$

where $f$ is the NMR frequency in Megahertz, $p$ is the room temperature $^3$He pressure in atmospheres.
Figure 2.8. Polarization transient for $^3$He cell 8B. The data are fit to equation 2.28

$(\gamma_{se} + \Gamma)^{-1} = 3.41\pm0.04$ hr
Figure 2.9. A typical $T_1$ measurement. The data are fit to equation 2.29
CHAPTER 3

HYBRID SPIN-EXCHANGE OPTICAL PUMPING OF $^3$He

3.1 Preface

This chapter is an article that will be submitted to the Journal of Magnetic Resonance. It describes our efforts to make and characterize K-Rb hybrid SEOP cells. Hybrid spin-exchange optical pumping was first proposed by the research group of W. Happer in 2001[7]. This new method utilizes a mixture of K and Rb in the spin-exchange cells. It is exciting because it takes advantage of the high efficiency of K-$^3$He spin-exchange and ultimately allows for the creation of higher $^3$He polarizations in less time when compared to Rb-only SEOP.

Our research group has been actively studying hybrid SEOP since 2004 when Jared Teter made our first set of hybrid cells. These cells, which were made for our collaborators at Pacific Northwest National Laboratory, taught us that we had a lot to learn about making and using hybrid SEOP cells. A year or so later after trial, error and learning the hard way that plastic does not make a good cell stand and NMR coil form at 250°C we were consistently producing hybrid spin-exchange cells that were capable of producing usable amounts (0.5 L at NTP) of $^3$He polarized to levels greater than 50% in about 4 hours. Along the way I had the opportunity to assist in the construction of two externally narrowed diode lasers and install them in dedicated $^3$He polarizing systems as well as develop a method for determining the relative densities of K and Rb in our cells under normal SEOP conditions.

My coauthors on this paper were Rick Jacob and Kevin Minard, both of Pacific Northwest National Laboratory, and my advisor Brian Saam.
3.2 Abstract

Spin-exchange optical pumping (SEOP) is widely employed for generating hyperpolarized (HP) $^3$He gas in magnetic resonance imaging (MRI) applications. A drawback of SEOP is the time required to polarize $^3$He gas; existing polarizers typically require about 12-20 hours to achieve 40-50% polarization in enough gas ($\sim$1 L) for a single imaging study. Here, enhanced polarization rates with SEOP are reached through the combined use of a spectrally narrowed diode-array laser and hybrid (K-Rb) SEOP. Both variations to conventional SEOP are readily applied, and $>$50% polarization in 0.5 L (NTP) of $^3$He gas can be achieved in about 4 hours. We also find that the X factor, an unexplained relaxation mechanism that scales with alkali density and limits the achievable polarization, appears to be lower in hybrid SEOP vessels than in vessels containing Rb only.

3.3 Introduction

Magnetic resonance imaging (MRI) using hyperpolarized (HP) $^{129}$Xe and $^3$He gases is emerging as an important tool for visualizing respiratory structure and function[16, 59, 60]. For such applications, nuclear polarizations much larger than thermal equilibrium values are required to overcome low gas density and achieve sufficient imaging sensitivity[61]. Spin-exchange optical pumping (SEOP)[2], which involves transfer of angular momentum from laser photons to the nuclei of the gas via an alkali metal intermediary (usually Rb), is widely employed for achieving this so-called hyperpolarized state. When applied to $^3$He, 12-20 hours are normally required to achieve 40-50% polarization in enough gas for a single imaging study (typically of order 1 L at NTP), although polarizations as high as 20% in 3-5 hours have been reported in our laboratory at the University of Utah[55]. Others, for example, have reported 10-20% in 7 hours[62] and 30-40% in 10-15 hours[63]. Since testing and research normally require multiple experiments, the slow polarization rate of conventional SEOP represents a significant impediment to the further development of $^3$He MRI applications. Of course, the overall $^3$He production can be increased through the simultaneous operation of multiple polarizing units, but
this is often an impractical and/or costly solution.

Two recent advances in the physics of SEOP have dramatically increased achievable polarization rates and even polarization levels. First, hybrid SEOP\cite{7} takes advantage of the higher spin-exchange efficiency between $^3\text{He}$ and K\cite{2}. It has been reported, for example that hybrid (K-Rb) optical pumping increased the $^3\text{He}$ polarization rate by a factor of two in one instance\cite{8}. Second, it has been shown that the use of a spectrally narrowed diode laser array can improve the polarization levels of both $^{129}\text{Xe}$\cite{54} and $^3\text{He}$\cite{14} by 20-40 percentage points. Here we verify these recent reports and show that simultaneous application of the two techniques results in high levels of $^3\text{He}$ polarization ($> 60\%$) in as little as 4 hours. We also describe an apparatus that can be used to produce several liters of polarized $^3\text{He}$ per day.

Recent work reports the existence of a previously unrecognized relaxation mechanism that occurs during SEOP with a rate linearly proportional to the alkali metal density\cite{25}. This as yet undescribed mechanisms is referred to as the “X factor” and limits the achievable $^3\text{He}$ polarization. Given the assumption of unity or near unity alkali polarization, one would expect to observe $^3\text{He}$ polarizations approaching unity in the limit of long wall relaxation times. This condition is routinely met in SEOP cells, yet this level of $^3\text{He}$ polarization has not been seen. A lower value of X indicates a lower level of suppression and hence a higher achievable polarization. In this article we will report on our work with both Rb-only and hybrid SEOP cells. Our work suggests that the parameter X that describes the effect of this relaxation mechanism is lower in hybrid cells than in Rb-only cells.

### 3.4 Theory

Spin-exchange optical pumping is the process by which angular momentum is transferred from circularly polarized photons to the noble gas nuclei of interest via an alkali-metal intermediary. The circularly polarized photons are used to optically pump a vapor of alkali-metal atoms. The resulting spin-polarization is then transferred collisionally to the $^3\text{He}$ nuclei via a hyperfine interaction between
the $^3$He nucleus and the alkali valence electron.

One useful quantity for characterizing SEOP is the spin-exchange efficiency $\eta_{se}$, which is defined as the ratio of the rate at which $^3$He is polarized to the rate at which the alkali-metal polarization is destroyed and is given by

$$\eta_{se} = \frac{\gamma_{se}[^3\text{He}]}{\Gamma_{Rb}[\text{Rb}]},$$

where $\gamma_{se}$ is the spin-exchange rate, $[^3\text{He}]$ and $[\text{Rb}]$ are the $^3$He and Rb densities respectively and $\Gamma'_{Rb}$ is the spin-destruction rate for the polarized alkali metal vapor. In a K-Rb hybrid spin-exchange cell, the spin-exchange rate $\gamma_{se}^{K-Rb}$ is given by

$$\gamma_{se}^{K-Rb} = k_K[K] + k_{Rb}[\text{Rb}],$$

where $k_K$ and $k_{Rb}$ are the spin-exchange rate constants for K and Rb. The spin destruction rate $\Gamma'_{Rb}$ in a hybrid cell is further given by

$$\Gamma'_{Rb} = \Gamma_{Rb} + D\Gamma_K + q_{KR}[K],$$

where $\Gamma_{Rb}$ and $\Gamma_K$ are the spin-destruction rates for Rb and K, $D$ is the ratio of K to Rb in the vapor phase and $q_{KR}$ is defined as the spin-destruction rate constant for collisions between K and Rb.

Traditionally, Rb has been the alkali metal of choice for SEOP, in large part because of the existence of high powered lasers at 795 nm, which is the wavelength of the Rb D$_1$ ($5S_{1/2}-5P_{1/2}$) transition. Unfortunately, $\eta_{se}$ for the Rb-$^3$He pair is only about 2% at standard Rb SEOP temperatures ($\sim 180^\circ\text{C}$), meaning approximately 50 photons are required to produce a single hyperpolarized $^3$He nucleus[27]. It has been reported, however, that the spin-exchange efficiency for the K-$^3$He pair is an order of magnitude larger than that of Rb-$^3$He, likely requiring only 4 photons to polarize each $^3$He nucleus[8]. The increase in spin-exchange efficiency possible from spin-exchange optical pumping using K is often difficult to realize for two reasons. First, there are fewer powerful lasers available at the wavelength of the K D$_1$ transition (770 nm), although it is now possible to obtain 40 W diode laser arrays at 770 nm[26]. Second, the fine structure splitting between the K 4$P_{1/2}$ and
4\(P_{3/2}\) levels is only 3.4 nm, which is comparable to the width of the lasers typically used for optical pumping. The laser can thus excite both the K \(4S_{1/2}-4P_{3/2}\) (K D\(_2\)), and K \(4S_{1/2}-4P_{1/2}\) (K D\(_1\)) transitions which can lead to lower alkali polarizations as electrons in the desired \(M_J = +1/2\) sublevel of the ground state can be excited to the \(M_J = -3/2\) sublevel of the first excited state. By comparison, the D\(_1\)-D\(_2\) splitting in Rb is 15 nm, and this polarization suppression is not observed. This issue, however, can be overcome through the use of a spectrally narrowed laser whose width is small compared to the K fine structure splitting\[26]\.

Hybrid SEOP can be used to obtain the promised boost in efficiency from K spin exchange\[8\]. In hybrid spin-exchange, a mixture of K and Rb is optically pumped using a standard 795 nm Rb laser. Hybrid SEOP takes advantage of the increased spin-exchange efficiency of potassium and couples it with the relative ease of producing a highly polarized Rb vapor. The Rb fine structure splitting is 15 nm, so only the Rb D\(_1\) transition is excited by the incident laser light. This leads to higher attainable Rb polarization. The spin-exchange cross section between K and Rb is large\[22\], so the polarizations of the alkali metals quickly approach a spin-temperature equilibrium. Angular momentum is then transferred to the \(^3\)He nuclei via collisions with polarized alkali metal atoms. Spin-exchange between K and \(^3\)He is not more efficient due to a larger spin-exchange rate. In fact, the spin-exchange rate constants \(k_{\text{Rb}}\) and \(k_{\text{K}}\) are comparable\[47, 64\]. The benefit of K-\(^3\)He SEOP is due to the much smaller K spin-destruction rate \(\Gamma_{\text{K}}\). The cross-section for alkali-\(^3\)He spin-destruction depends strongly on the magnitude of the fine structure splitting, with smaller splittings leading to smaller spin-destruction cross sections and hence to smaller spin-destruction rates. The calculated Rb-\(^3\)He spin-destruction cross section is approximately an order of magnitude smaller than the calculated K-\(^3\)He cross section\[65\]. Experiments utilizing K for spin-exchange should lead to comparable increases in efficiency.

Eqs. (3.2) and (3.3) can then be used to rewrite Eq. (3.1) in terms \(\mathcal{D}\)

\[
\eta_{\text{se}} = \frac{(k_{\text{Rb}} + \mathcal{D}k_{\text{K}})[^3\text{He}]}{\Gamma_{\text{Rb}} + \mathcal{D}\Gamma_{\text{K}} + q_{KR}[\text{K}]}.
\] (3.4)
It is apparent from Eq. (3.4) that for large $D$, $\eta_{se}$ approaches the value for pure K. Work by the research groups of T.R. Gentile and T.G. Walker based on calculations of spin-destruction rates for alkali-alkali, alkali-$^3$He and alkali-$^2$N$_2$ interactions provides confirmation of the dependence of $\eta_{se}$ on $D$[26].

Recent work[25] has described the effect of a previously unknown and still unexplained relaxation process. This effect, which depends linearly on alkali-metal density and limits the achievable $^3$He polarization, is referred to as the X factor. The polarization of $^3$He due to SEOP can be expressed as

$$P_{\text{He}} = P_A \frac{\gamma_{K-Rb}^{K-Rb}}{\gamma_{se}^{K-Rb} (1 + X) + \Gamma (1 - e^{-t/\tau_{\text{up}}})},$$  

(3.5)

where $P_A$ is the alkali polarization, $\Gamma$ is the room temperature $^3$He relaxation rate and $k_A[A] = k_K[K] + k_{Rb}[Rb]$ and $\tau_{\text{up}}$ is the time constant for optical pumping and is called the spin-up time. The portion of Eq. (3.5) in parentheses describes the polarization transient for short SEOP times. The balance of the expression represents the saturated $^3$He polarization. Given the assumptions of of near 100% alkali polarization and small $^3$He relaxation rate, conditions routinely met in our cells with $T_1 (\Gamma = 1/T_1)$ values consistently exceeding 30 hours, the $^3$He polarization should be determined by the fraction in Eq. (3.5). $X$ is a phenomenological parameter inserted into the expression in such a way as to reflect that the slope of the $^3$He relaxation rate vs. alkali density is larger than the spin-exchange rate. The size of $X$ indicates the degree of suppression of $^3$He polarization with larger values of $X$ corresponding to larger suppression. There appears to be a correlation between $X$ and the surface to volume ratio of the pumping cell. The cause of the excess relaxation is unknown, but it could be due to a temperature dependent surface relaxation mechanism or perhaps to anisotropic spin-exchange.

### 3.5 Experimental Procedure and Results

The bulk of the work described here was done at University of Utah with the remainder done at Pacific Northwest National Laboratory. The design of the SEOP apparatuses used at both locations was essentially the same. In this paper we will
describe the polarizer used at the University of Utah. A dedicated polarizer was constructed at Utah for use at PNNL.

The essential elements of our SEOP apparatus include: a high-power diode-array laser, a laser cooling system, an optics train, glass vessels (cells) containing $^3$He gas and an alkali metal, and an oven for heating the cells during SEOP. Similar SEOP systems with non-narrowed lasers have been described previously[61, 55]. The total cost of the polarizer components described below was about $30k.

3.5.1 Spectrally Narrowed Diode-Array Laser

The diode-array laser (Quintessence Photonics Corporation, Sylmar, CA) used for this work operates at 795 nm and can produce 40 watts of light. A microlens, which is essential to reduce beam divergence along the fast-diverging axis, was attached by the manufacturer. The laser is cooled to an operating temperature of 18.25°C by a thermoelectric cooler (Ferrotec, Nashua, NH) in thermal contact with 20°C water circulated by a closed-loop chiller (PolyScience, Niles, IL). To spectrally narrow the laser, we followed the method clearly detailed in references[15, 51]. In summary, a 4x optical telescope, formed by a 76.2 mm primary lens and a 300 mm objective, focuses the laser light onto a 50 mm x 50 mm holographic diffraction grating (2400 lines/mm), see Figure 3.1. The grating, with the lines oriented vertically, reflects the first-order diffraction peak back into the laser resulting in the narrowing of the spectrum. For efficient narrowing the light must be directly reflected back into each originating emitter, so careful focus and alignment of the telescope and grating are critical. The desired wavelength of the narrowed spectrum determines the angle of incidence on the grating according to Bragg’s Law: $\lambda = 2d \sin \theta$, where $d$ is the grating line spacing and $\theta$ is the angle of incidence of the light with respect to the grating normal. Thus, for a laser spectrum centered at 795 nm and 2400 lines/mm grating, an angle of 72.5° is required. A $\lambda/2$ plate in a rotating assembly, placed either directly before or after the 76.2 mm lens, can be used to control the feedback intensity by rotating the polarization of the light incident on the grating. The grating and an IR mirror (50 mm diameter) are
Figure 3.1. Optics train for externally narrowed diode-array laser.

mounted on a co-rotating assembly. The IR mirror delivers the light through a 150 mm plano-convex cylindrical collimating lens, a spherical beam-shaping lens, and a $\lambda/4$ plate to an oven where it illuminates the glass cell. The focal length of the final spherical lens determined the beam size at the cell. We utilized cells of various sizes, each requiring a different lens to obtain the correct beam size. We note that Babcock et al. use a second telescope (10x) in place of the final spherical lens to minimize light divergence across the cell[15]. The interested reader may contact the authors for additional details, such as a parts list or design drawings. The PNNL system has been updated to two side-by-side lasers and a double oven, doubling polarization capacity.

The power output of the laser was measured with a 100 W power meter (Thorlabs, Newton, NJ). At a current of 50 A, the laser delivered about 31 W to the cell when spectrally narrowed and about 37 W broadband. The difference is due to the grating reflectivity, which is approximately 90%[52], and to the light reflected back into the laser. Using a PC based near-IR monochromator, we measured the full-width at half-maximum (fwhm) of the broad (non-narrowed) spectrum to be $\approx 2$ nm and the fwhm of the narrowed spectrum to be $\approx 0.3$ nm. The fwhm of the Rb absorption spectrum was $\approx 0.3$ nm for an 8.4 atm NTP cell (8.2 atm $^3$He and 0.2 atm N$_2$ buffer gas)[53]. Although narrowing the spectrum costs several watts of light, a much greater fraction of the light overlaps the central portion of the Rb absorption spectrum meaning that a more of the light is at the correct wavelength and can be absorbed by the Rb vapor.
3.5.2 Cell Preparation and Characterization

The preparation and geometry of the glass vessels (cells) used for SEOP are described in detail elsewhere[55] with several exceptions. In this work we made cells of several geometries and sizes: spherical cells (both 2” and 3.1” diameters), cylindrical cells with optical flats and cylindrical cells with hemispherical ends (1.25” and 2” diameters). Typically, new cells are attached to a glass manifold for bake-out and Rb distillation: this manifold requires a single retort to accommodate an ampoule of Rb. For hybrid cells, an additional retort for a K ampoule is added to the glass manifold near the Rb retort, thus forming a Y. This allows for selective distillation of each metal. We note that K has a higher melting point than Rb (63°C versus 39°C), so more care, patience and time are required during distillation to avoid overheating and potentially damaging the manifold. The ratio of K to Rb in the vapor phase, defined as \( D \), is an important parameter in the preparation of hybrid SEOP cells. The target ratio of K:Rb in the solid phase is roughly 30:1 which should result in a D value of 10 at 250°C[8]. However, Babcock et al. have shown mixtures more rich in Rb also give good results. Our work suggests an optimum balance of high final polarization and fast polarization time for a \( D \) value of about 5. We could not rigorously control the ratio but simply distilled approximately 400-500 g of K into each cell, followed by a small amount of Rb in the form of one or more opaque films coating the interior of the cell.

The inherent difficulty in controlling carefully the relative amounts of alkali metals distilled into the cells required a direct method of measuring \( D \) for effective characterization of hybrid SEOP methods. \( D \) was measured directly via white light absorption spectroscopy techniques using a PC based near-IR monochromator (USB 2000, Ocean Optics, Dunedin, FL). This measurement was done at low temperatures (100°C) since the cells were optically dense at SEOP temperatures. At this temperature, the absorption ratios of the D\(_2\) to D\(_1\) transitions for both alkali metals were approximately 2, which is the theoretically predicted value for an optically thin vapor[22]. According to Raoult’s law, the partial pressure of a constituent metal above a mixture is lower than the vapor pressure of the pure
metal at a given temperature\cite{21}. The actual densities depend on the mole fraction of each metal in the mixture and, in a K-Rb mixture, are given by

\[ [\text{Rb}] \approx f_{\text{Rb}}[\text{Rb}]_0, \quad (3.6) \]

and

\[ [\text{K}] \approx f_{\text{K}}[\text{K}]_0 = (1 - f_{\text{Rb}})[\text{K}]_0, \quad (3.7) \]

where \( f \) represents the mole fraction of the metal and the 0 subscript represents the vapor density above a pure metal at a given temperature. The pure vapor densities are given by\cite{56}

\[ [\text{Rb}]_0 = \left( \frac{7.25 \times 10^{16}}{T} \right) 10^{9.318 - 4040/T} \text{ cm}^{-3}, \quad (3.8) \]

\[ [\text{K}]_0 = \left( \frac{7.25 \times 10^{16}}{T} \right) 10^{9.408 - 4453/T} \text{ cm}^{-3}, \quad (3.9) \]

In reference \cite{26}, the alkali-metal densities from these expressions yielded spin-exchange rates that agreed with measured values to within 10%.

Applying Raoult’s law in the case of K-Rb spin exchange at a temperature of 200°C we can solve for \( \mathcal{D} \):

\[ \mathcal{D}_{200\text{C}} = \left( \frac{[\text{K}]}{[\text{Rb}]} \right)_{100\text{C}} \left( \frac{[\text{Rb}]_0}{[\text{K}]_0} \right)_{100\text{C}} \left( \frac{[\text{K}]_0}{[\text{Rb}]_0} \right)_{200\text{C}}, \quad (3.10) \]

where the quantities with a 0 subscript are the calculated vapor pressures at the given temperatures\cite{56} and the quantities without subscripts are the measured values. In each cell the D\(_1\) and D\(_2\) electric dipole transitions were observed for both K and Rb. The area under a lorentzian fit to each of the transitions was obtained via a computer fitting and integrating routine. The ratio of the total area under the D\(_1\) and D\(_2\) lines for each metal was then calculated and used as the first term in Eq. (3.10). The calculated \( \mathcal{D} \) values for the hybrid SEOP cells used in this work ranged from \(<0.1\) to \(>10\). We quote a 10% uncertainty in \( \mathcal{D} \), due to the uncertainty in the pure Rb and K vapor densities from Eqs. (3.8) and (3.9) as well as noise in our vapor density ratio measurements at 100°C.
3.5.3 Spin-Exchange Optical Pumping Characterization

Data was acquired from several cells to demonstrate the differences in the polarization rate between hybrid SEOP and nonhybrid SEOP. The results of our work can be found in Table 3.1. We measured the spin-up time $\tau_{\text{up}}$ (defined in Eq. (3.5)) and ultimate $^3$He polarization at a range of temperatures in each cell to determine the optimal SEOP temperature settings. The optimal temperature is the approximate temperature at which the $^3$He polarization reached the highest value most rapidly. Typically, hybrid cells require a higher oven temperature relative to that required for Rb-only cells to attain a sufficient Rb vapor pressure. Ideally, the optimal temperature is the maximum temperature at which 100% Rb polarization can be maintained with a given laser power.

Prior to optical pumping, cells were exposed to a variable strength 60 Hz AC magnetic field to destroy any remnant magnetization of magnetic sites in the cell walls due to prior exposure to large magnetic fields[66]. During SEOP, the rise of $^3$He signal was monitored using a 100 kHz (30 G) home-built LabView based spectrometer[67]. The spin-up time $\tau_{\text{up}}$ was extracted from a fit of the data to

$$S(t) = S_0(1 - e^{-t/\tau_{\text{up}}}).$$  \hspace{1cm} (3.11)

The $^3$He polarization was determined by comparing the NMR signal from a HP sample to the signal from a water phantom of the same geometry at thermal equilibrium. The water sample contained CuSO$_4$ to lower $T_1$ to approximately 100 ms for signal averaging purposes. The height of the HP gas FID from a small flip angle pulse was compared to a proton FID height from a water sample using the same NMR probe at 32.5 MHz. After compensating for different receiver gain settings, different pressures and densities as well as different gyromagnetic ratios, a direct comparison of the HP gas and phantom signals yielded the absolute polarization of the $^3$He.

In the case where the samples have the same geometry and are probed at the same NMR frequency it is possible to determine the $^3$He polarization by comparing
Table 3.1. $^3$He cells used in this work with the room temperature cell pressure $p$ in atm, the room temperature relaxation time $T_1$ and the optical pumping time $\tau_{up}$ given in hours, the maximum $^3$He polarization $P_{He}$, the optimum optical pumping temperature $T$ in °C, the vapor density ratio $D$, the X-factor and $V$ the volume in cm$^3$. Errors are given in parentheses for the least significant figure(s).

<table>
<thead>
<tr>
<th>Cell</th>
<th>$p$</th>
<th>$T_1$</th>
<th>$\tau_{up}$</th>
<th>$P_{He}$</th>
<th>$T$</th>
<th>$D$</th>
<th>$X$</th>
<th>$V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25A</td>
<td>6.7</td>
<td>48.7(1)</td>
<td>4.16(1)</td>
<td>0.487(20)</td>
<td>165</td>
<td>0</td>
<td>0.86(1)</td>
<td>47(2)</td>
</tr>
<tr>
<td>10B</td>
<td>7.1</td>
<td>52.9(1)</td>
<td>3.30(2)</td>
<td>0.466(20)</td>
<td>165</td>
<td>0</td>
<td>1.01(2)</td>
<td>66.1(3)</td>
</tr>
<tr>
<td>27A</td>
<td>8.1</td>
<td>20.8(4)</td>
<td>4.20(7)</td>
<td>0.489(20)</td>
<td>165</td>
<td>0</td>
<td>0.63(5)</td>
<td>51.1(3)</td>
</tr>
<tr>
<td>133A</td>
<td>3.8</td>
<td>32.5(1)</td>
<td>4.55(1)</td>
<td>0.496(20)</td>
<td>165</td>
<td>0</td>
<td>0.73(1)</td>
<td>120(6)</td>
</tr>
<tr>
<td>133B</td>
<td>3.0</td>
<td>19.8(1)</td>
<td>3.31(1)</td>
<td>0.349(15)</td>
<td>165</td>
<td>0</td>
<td>1.30(3)</td>
<td>120(6)</td>
</tr>
<tr>
<td>116A</td>
<td>5.9</td>
<td>46.5(2)</td>
<td>5.96(10)</td>
<td>0.706(30)</td>
<td>160</td>
<td>&lt;&lt; 0.1</td>
<td>0.24(3)</td>
<td>47.1(2)</td>
</tr>
<tr>
<td>129B</td>
<td>5.2</td>
<td>49.9(5)</td>
<td>2.61(13)</td>
<td>0.627(30)</td>
<td>190</td>
<td>0.20(5)</td>
<td>0.51(7)</td>
<td>45.0(2)</td>
</tr>
<tr>
<td>129A</td>
<td>5.2</td>
<td>46.9(5)</td>
<td>3.19(14)</td>
<td>0.694(30)</td>
<td>200</td>
<td>0.8(1)</td>
<td>0.34(5)</td>
<td>47(2)</td>
</tr>
<tr>
<td>128A</td>
<td>4.7</td>
<td>65.0(4)</td>
<td>6.62(10)</td>
<td>0.709(30)</td>
<td>200</td>
<td>0.8(1)</td>
<td>0.27(3)</td>
<td>213(10)</td>
</tr>
<tr>
<td>134A</td>
<td>4.9</td>
<td>33.8(1)</td>
<td>2.04(1)</td>
<td>0.577(30)</td>
<td>220</td>
<td>1.3(2)</td>
<td>0.63(1)</td>
<td>28.8(2)</td>
</tr>
<tr>
<td>122A</td>
<td>7.4</td>
<td>18.5(3)</td>
<td>1.84(1)</td>
<td>0.540(30)</td>
<td>220</td>
<td>1.5(2)</td>
<td>0.67(1)</td>
<td>47.2(2)</td>
</tr>
<tr>
<td>126A</td>
<td>5.1</td>
<td>34(1)</td>
<td>1.69(15)</td>
<td>0.631(30)</td>
<td>215</td>
<td>3.5(4)</td>
<td>0.51(8)</td>
<td>30.6(3)</td>
</tr>
<tr>
<td>124A</td>
<td>3.8</td>
<td>32(1)</td>
<td>1.83(9)</td>
<td>0.531(30)</td>
<td>240</td>
<td>5.0(5)</td>
<td>0.78(7)</td>
<td>56.0(5)</td>
</tr>
<tr>
<td>132A</td>
<td>4.7</td>
<td>27.7(1)</td>
<td>2.42(5)</td>
<td>0.518(30)</td>
<td>240</td>
<td>10(1)</td>
<td>0.76(4)</td>
<td>120(6)</td>
</tr>
<tr>
<td>132B</td>
<td>4.6</td>
<td>43(1)</td>
<td>2.34(4)</td>
<td>0.653(30)</td>
<td>240</td>
<td>&gt;10</td>
<td>0.45(2)</td>
<td>120(6)</td>
</tr>
</tbody>
</table>

directly the ratio of the gas and water NMR signals. In the low flip angle limit the ratio is given by

$$\frac{S_g}{S_p} = \frac{P_g n_g \gamma_g^2}{P_p n_p \gamma_p^2},$$

where $P$ is polarization, $n$ is the spin density, $\gamma$ is the gyromagnetic ratio[58]. The subscripts $g$ and $p$ represent gas and proton, respectively. The thermal polarization level of the water and the respective spin densities can be calculated from first principles. Eq. (3.12) can be solved for $P_g$ to give

$$P_g = (3.76 \times 10^{-4}) f \frac{S_g}{p S_p},$$

where $f$ is the NMR frequency in Megahertz, $p$ is the room temperature $^3$He pressure in atmospheres.

Each cell was optically pumped over a range of temperatures. Measurement of both the $^3$He polarization and $\tau_{up}$ at various temperatures served two purposes.
Figure 3.2. The observed plateau in obtainable $^3$He polarization in cell 132 B for a range of optical pumping temperatures suggests alkali polarization near 100%. At low temperatures, the wall relaxation rate begins to compete with the spin-exchange rate, and at high temperatures the alkali density increases to the point that the laser is unable to provide enough photons to maintain unity alkali polarization. Both mechanisms act to suppress $^3$He polarization. The plateau suggests that over that range in temperature the final $^3$He polarization is not limited by the alkali polarization or by wall relaxation. The curve is drawn to guide the eye and is not a fit to theory.
First, it allowed for the determination of the optimal pumping temperature for a cell. The polarization measurements also provided evidence for 100% alkali polarization, which was an important assumption made when discussing Eq. (3.5). As seen in Figure 3.2, we observed a plateau in obtainable $^3\text{He}$ polarization as a function of optical pumping temperature. The existence of the plateau is linked to the temperature dependence of the alkali density and the spin-exchange rate (see Eqs. (3.2), (3.8) and (3.9)), both of which increase with increasing temperature. The drop-off in $^3\text{He}$ polarization at both ends of the plateau can be described in terms of this temperature dependence. At low temperatures spin-exchange rate and the $^3\text{He}$ wall relaxation rate become comparable in magnitude which acts to suppress the attainable $^3\text{He}$ polarization. As SEOP temperatures increase, the alkali vapor density increases until the laser is unable to provide enough photons to maintain maximal alkali polarization, which again acts to suppress the $^3\text{He}$ polarization. On the plateau the $^3\text{He}$ polarization is independent of temperature suggesting that the noble gas polarization is not limited by the alkali polarization or by wall relaxation leaving only the X-factor as an explanation for $^3\text{He}$ polarizations less than 100%. The optimum pumping temperature for a given cell is the highest temperature still on the plateau. At this point the maximum achievable $^3\text{He}$ polarization and the fastest spin-exchange rate are simultaneously obtained. The values found in Table 3.1 are measured at the optimum SEOP temperature.

Assuming unity alkali polarization, the X factor can be found with

$$X = \frac{1}{P_{\text{He}}} - 1 - \frac{\tau_p \Gamma}{P_{\text{He}}}$$

(3.14)

where $\tau_p$ is the optical pumping time, $P_{\text{He}}$ is the $^3\text{He}$ polarization and $\Gamma = 1/T_1$ is the room temperature $^3\text{He}$ relaxation rate. Prior to exposure to high magnetic fields for polarization measurement we measured the room temperature $T_1$ for each cell. It was often difficult to again achieve this lifetime after the cells were degaussed. $T_1$ was therefore measured several times for each cell after thorough demagnetization. This value for $T_1$ was used for calculations of X. Values of X for all cells are found in Table 3.1. It is to be noted that the value of X is lower for all hybrid cells than
for any Rb-only cells, suggesting that the excess relaxation is less of a factor in SEOP cells containing both Rb and K.

3.6 Discussion

We present a description of the construction of a dedicated $^3$He polarizer including an externally narrowed diode laser array capable of producing usable amounts (0.5 L at NTP) of $^3$He polarized to levels greater than 50% in $\approx 4$ hours. A comparison of polarization performance between normal and hybrid cells (see Figure 3.3) shows that hybrid optical pumping (K-Rb) is primarily responsible for the increased polarization rate. We routinely exceed 50% polarization in hybrid cells, which was the previous broadband-laser polarization benchmark for cells of this size and pressure[55]. By comparison, researchers using metastability-exchange optical pumping (MEOP), which very efficiently polarizes $^3$He but only at low pressures ($\sim 1$ mbar), have produced several liters per hour of $>80\%$ polarized $^3$He, but complex and expensive equipment were used for compressing the gas up to a usable pressure[60, 61]. Others have dramatically simplified the compression stage of MEOP and have achieved 15% polarization in 1.1 L of gas in only 3 hours[68]. Through the combined use of narrowed diode lasers and hybrid spin-exchange, the production rate of SEOP is now more competitive with that of MEOP, particularly when practical implementation is considered.

We have constructed and characterized a series of valved, refillable K-Rb hybrid spin-exchange cells and compared their behavior to standard Rb cells. Hybrid spin-exchange optical pumping techniques take advantage of the increased efficiency of spin-exchange between K and $^3$He due to the lower spin-destruction rates inherent in K. The higher efficiency of spin-exchange for K-$^3$He means fewer photons are required to fully polarize a hybrid $^3$He cell. Figure 3.3 compares the polarization transients of a hybrid spin-exchange cell (132KRb) to a Rb-only cell (25Rb). Both cells have wall times longer than 40 hours, so the ultimate $^3$He polarization is not limited by wall relaxation. The hybrid cell reaches a higher polarization in a shorter time than the Rb-only cell. This behavior is generally observed in our hybrid
cells which typically produce polarizations >50% with spin-up times considerably shorted than those observed in Rb-only cells. The decrease in pumping time is due in large part to the elevated spin-exchange rate since hybrid SEOP generally requires higher pumping temperatures. The elevated $^3$He polarization level in the hybrid cell is due to both the increased efficiency of Rb-K SEOP as well as the lower observed values of X in hybrid cells.

We implemented a method to determine the density ratio $D$ of K to Rb in the vapor phase using white light absorptions spectroscopy methods. Our work suggests that the optimum combination of large $^3$He polarization and small $\tau_{\text{up}}$ is obtained for cells with $D \approx 3 - 5$, although the benefits of hybrid spin-exchange were observed in all cells containing K. We were unable, however, to determine a method to rigorously control the relative amounts of K and Rb distilled into our cells, but it is expected that with more experience it will become possible to more fully control $D$ in future cells.

In comparison to standard Rb spin-exchange cells, we observed marked improvements in $^3$He polarization in all hybrid spin-exchange cells regardless of $D$, with polarizations in some cases exceeding 70%. In general, the optical pumping time $\tau_{\text{up}}$ was lower in hybrid cells than in Rb-only cells, but in some cases with $D < 1$ we observed $\tau_{\text{up}}$ values exceeding those of even Rb-only cells. The cause of this increase in required optical pumping time is unknown.

Two methods of increasing the rate of production of HP $^3$He are discussed in reference [26]. One method is to increase the production rate by increasing the temperature which will lead to an improved spin-exchange rate. The transition to hybrid SEOP provides this production boost as hybrid cells are optically pumped at higher temperatures with correspondingly higher spin-exchange rates. This method has limitations when considering increasing the pumping temperature of a given cell. As seen in Figure 3.2, our work suggests that even moderate increases in temperature will lead to lower $^3$He polarization levels due to the inability of the available laser light to maintain high alkali metal polarizations.

The second method described to increase productivity is to increase the volume
Figure 3.3. Comparison of $^3$He transient for K-Rb hybrid spin-exchange cell and Rb-only cell. The hybrid spin-exchange cell reaches a higher ultimate $^3$He polarization with a shorter optical pumping time. Both cells have wall relaxation times longer than 40 hours and spin-up times ($\tau_{\text{up}}$) an order of magnitude smaller than the relaxation time. The ultimate $^3$He polarization is therefore not limited by wall relaxation. The SEOP temperature for cell 132Krb was 75°C higher than that of cell 25Rb leading to higher spin-exchange rates.
of gas polarized for a given laser power. We present evidence that this is indeed possible. We constructed cells with volumes ranging from 29 cm$^3$ to over 200 cm$^3$. With a few exceptions, the variation in $^3$He polarization and $\tau_{up}$ was small. For example, as seen in Table 3.1 we observed polarizations in cells 129B and 132B of $63 \pm 3\%$ and $65 \pm 3\%$ with $\tau_{up}$ values of $2.61 \pm 0.13$ hr and $2.34 \pm 0.04$ hr, respectively. However, the volume of cell 132B is 2.7 times larger than the volume of cell 129B meaning that nearly three times as much HP $^3$He is produced in essentially the same amount of time. A 120 cm$^3$ polarizing cell filled to 8-10 atm would provide approximately 1 L NTP of usable gas. Cell volumes approaching 1 L were reported in reference [26], suggesting that even larger volumes could readily be polarized with our polarizer.

We calculated values of $X$, the phenomenological parameter that describes the degree of “excess” relaxation present in a cell. Aside from the observation that $X$ appeared to be lower in most of our hybrid cells than in our Rb-only cells we noted no clear trends in the calculated $X$ values. The hybrid cells with seemingly large $X$ values did in general exhibit short $T_1$ values. Previous work found a correlation between $X$ and the surface to volume ratio of polarizing cells[25], but our results appeared to contain no such trend. It has been postulated that this effect could be due to a temperature dependent surface relaxation mechanism or anisotropic spin-exchange. More work remains to fully explain this phenomenon.

With the apparatus described in this work, it is possible to produce about 3 L (at NTP) of $>50\%$ polarized $^3$He per day in three separate polarizing runs (e.g., one cell can be polarized over night, and two hybrid cells can be polarized back-to-back in a few hours). This production rate can be doubled by addition of a second laser for under $\$10k$, since two lasers can easily share the optics table and most of the same equipment (i.e., chiller, 100 kHz spectrometer, etc.) except for the optics train. Indeed, the beam from a single, more powerful laser (e.g., 100 W) could be split to illuminate two separate cells, possibly at a further cost savings. With the addition of the additional laser, our apparatus could produce 6 L of gas per day with even larger volumes feasible with an increase in spin-exchange cell
size, thus making large-scale research projects and clinical $^3$He MRI more feasible.

We have shown that hybrid spin-exchange optical pumping techniques lead to increases in $^3$He polarization levels of 10-20 percentage points in valved, refillable cells. In general, hybrid spin-exchange cells also exhibit shorter spin-up times. The combination of high $^3$He polarization and short spin up times leads to an increase in the overall efficiency of production of HP $^3$He. Further optimization of cell construction techniques as well as a better understanding of the mechanisms responsible for the X-factor will lead to even greater improvements in performance making large-scale magnetic resonance experiments with hyperpolarized $^3$He possible.

### 3.7 Acknowledgments

Polarizer testing, fabrication and assembly, as well as cell fabrication and performance quantification, were conducted at the University of Utah. Further polarizer calibration and performance quantification were performed in the Environmental Molecular Sciences Laboratory (a national scientific user facility sponsored by the US Department of Energy’s Office of Biological and Environmental Research) located at Pacific Northwest National Laboratory (PNNL), and operated for the DOE by Battelle. Financial support was provided by NIH NHLBI RO1 HL073598, project 46109 of PNNL’s Laboratory Directed Research and Development (LDRD) program, and NSF PHY-0134980. The authors would like to thank D. Wiseman, J. Teter and S. Morgan for their roles in fabricating and testing equipment and cells, and G. Laicher for his help during assembly.
CHAPTER 4

NUCLEAR SPIN RELAXATION OF $^{129}$Xe DUE TO XENON DIMERS

4.1 Preface

In 2002, the research group of T.G. Walker identified and confirmed the existence of a previously unknown relaxation mechanism in hyperpolarized $^{129}$Xe: relaxation due to the spin-rotation interaction mediated by the formation and breakup of $^{129}$Xe-$^{129}$Xe molecules\[47\]. Their work, done in the limit of low applied magnetic field ($B_0 = 20.4$ G), identified molecular relaxation as the dominant intrinsic spin-relaxation mechanism in $^{129}$Xe samples of densities lower than 14 amagat, leading to a molecular relaxation time of 4.1 hours at atmospheric pressure. Relaxation due to persistent dimers is thus over an order of magnitude stronger than binary relaxation which was historically assumed to be the only important means of intrinsic spin relaxation in $^{129}$Xe.

We extended the work of Walker’s group to the regime of high applied magnetic fields (8.0 T) and low density (< 0.5 amagat). After much trial and error we were able to show that $^{129}$Xe intrinsic relaxation is caused by fluctuations in the spin-rotation and chemical shift anisotropy interactions modulated by the formation and breakup of $^{129}$Xe-$^{129}$Xe van der Waals molecules. Working in the double limit of low density and high applied field we observed a dramatic suppression of intrinsic relaxation mechanisms, leading to extremely long room temperature gas-phase $T_1$ measurements in $^{129}$Xe-$^2$N$_2$ samples. This work was published in the 15 December edition of Physical Review A and was authored by B.N. Berry-Pusey, B. Anger, G. Laicher and B. Saam. This paper outlines our first steps towards a more complete understanding of the mechanisms responsible for relaxation in samples.
of hyperpolarized $^{129}$Xe. Chapter 5 is a continuation of these efforts and together they point in the direction of potentially important advances in the methods used for the production and storage of hyperpolarized $^{129}$Xe.

4.2 Abstract

We have measured longitudinal nuclear relaxation rates of $^{129}$Xe in Xe-N$_2$ mixtures at densities below 0.5 amagats in a magnetic field of 8.0 T. We find that intrinsic spin relaxation in this regime is principally due to fluctuations in the intramolecular spin-rotation (SR) and chemical shift anisotropy (CSA) interactions, mediated by the formation of $^{129}$Xe-Xe persistent dimers. Our results are consistent with previous work done in one case at much lower applied fields where the CSA interaction is negligible and in another case at much higher gas densities where transient xenon dimers mediate the interactions. We have verified that a large applied field suppresses the persistent dimer mechanism, consistent with standard relaxation theory, allowing us to measure room temperature gas phase relaxation times for $^{129}$Xe greater than 25 hr at 8.0 T. These data also yield a maximum low-field $T_1$ for pure xenon gas at room temperature of 5.45±0.2 hr. The coupling strengths for the SR and CSA interactions we extract are in fair agreement with estimates based both on previous experimental work and on ab initio calculations. Our results have potential implications for the production and storage of large quantities of hyperpolarized $^{129}$Xe for use in various applications.

4.3 Introduction

The stable spin-1/2 isotopes $^3$He and $^{129}$Xe are readily polarized to levels exceeding 0.1 via spin-exchange optical pumping (SEOP) [2, 69], making them accessible to a wide variety of magnetic resonance experiments. As the name “hyperpolarized” suggests, the relative populations of nuclear-spin sublevels in these gases are well out of thermal equilibrium; therefore an understanding of longitudinal relaxation mechanisms (characterized by the time $T_1$) that limit both the achievable polarization and the sample storage time is critically important. Several recently published articles and references therein discuss the physics and applications of hyperpolarized
We are concerned here specifically with hyperpolarized $^{129}\text{Xe}$, which is also studied and used in a wide variety of applications, including recent examples in medical imaging [70], biochemistry [18], and surface science [19].

The gas-phase relaxation mechanisms may be divided broadly into intrinsic and extrinsic categories. The former are due to the presence of the other noble-gas atoms in the sample and include, for example, the dipole-dipole mechanism present during $^{3}\text{He}$-$^{3}\text{He}$ binary collisions that limits $T_1$ in a 1 amagat sample of $^{3}\text{He}$ to about 800 h [39]. (One amagat = $2.69 \times 10^{19}$ cm$^{-3}$, the density of 1 atm of an ideal gas at 0 °C. Unless otherwise noted, densities quoted here have been calculated from pressures measured at room temperature.) In practice, $T_1$ is usually limited by extrinsic mechanisms, including diffusion through external magnetic-field gradients [30, 71] and (more often) collisions with container (cell) walls. However, more recent work, including that presented here, indicates that intrinsic mechanisms are far more important in many practical experiments involving $^{129}\text{Xe}$ than previously assumed. We thus generally describe the $^{129}\text{Xe}$ gas-phase relaxation rate $\Gamma$ as the sum of four terms:

$$\Gamma = \Gamma_t + \Gamma_p + \Gamma_g + \Gamma_w,$$  \hspace{1cm} (4.1)

where the first two (intrinsic) terms are due, respectively, to transient and persistent xenon dimers (see below), and the last two (extrinsic) terms are due to gradient and wall relaxation, respectively.

4.3.1 Xenon Dimers

Intrinsic gas-phase $^{129}\text{Xe}$ relaxation is related to the van der Waals forces that govern the formation of xenon dimers, and herein we make an important distinction: *transient* dimers are formed in binary collisions, where the per-atom collision frequency $1/T_t$ is proportional to the xenon density [Xe] and the collision duration $\tau_t$ (a few picoseconds) depends on the details of the Xe-Xe interatomic potential; *persistent* dimers are formed by three-body collisions and exist in a stable bound state for a molecular lifetime $\tau_p$ until the next collision with another atom.
The possible existence of persistent dimers was suggested as early as 1959 by Bernardes and Primakoff [40], whose model can be used to estimated their concentration to be 0.5% for [Xe] = 1 amagat. The dimer concentration is related to the chemical equilibrium coefficient $K \equiv [\text{Xe}_2]/[\text{Xe}]^2$, from which we obtain the fraction of Xe atoms bound in Xe$_2$ molecules:

$$\frac{2[\text{Xe}_2]}{[\text{Xe}] + 2[\text{Xe}_2]} \approx 2K[\text{Xe}], \quad (4.2)$$

where the approximation is very good in the limit where $[\text{Xe}_2] \ll [\text{Xe}]$. Chann, et al. [47] calculated the partition function for the internal states of the Xe$_2$ molecule to arrive at $K = 230 \text{ Å}^3$, or a 1.2% persistent dimer concentration for [Xe] = 1 amagat.

The calculated properties of the Xe-Xe interatomic potential and simple kinetic theory [41] allow reasonable estimates of the relevant kinetic parameters to be made. Here we assume thermal and chemical equilibrium and that Xe gas is the only constituent. The results are summarized in Table 4.1. The velocity-averaged collision cross sections $\langle \sigma v \rangle_{\text{Xe}}$ and $\langle \sigma v \rangle_{\text{Xe}_2}$ are estimated as a product of relative rms speed and a classical target size. The target size is estimated as $\pi R_0^2$ for Xe-Xe collisions and $2\pi R_0^2$ for Xe-Xe$_2$ collisions, where $R_0 = 4.4 \text{ Å}$ [42] is the equilibrium separation of the atoms in Xe$_2$. The potential-well depth of $\approx 283$ K [42] indicates that room-temperature collisions are likely to break up persistent dimers; hence, the corresponding breakup rate $\tau_p^{-1} = k_{\text{Xe}}[\text{Xe}]$ can be estimated by assuming that the breakup coefficient $k_{\text{Xe}}$ for persistent dimers by Xe atoms is equal to $\langle \sigma v \rangle_{\text{Xe}_2}$. At 295 K and [Xe] = 1 amagat we obtain $\tau_p \approx 140$ ps, about two orders of magnitude longer than the transient dimers lifetime $\tau_t$. It is this much longer lifetime that causes persistent dimers (despite their low fractional abundance) to play a dominant role in $^{129}$Xe spin relaxation at low densities.

### 4.3.2 Previous Studies of $^{129}$Xe Intrinsic Relaxation

More than 40 years ago, Hunt and Carr demonstrated that $T_1^{-1}$ for $^{129}$Xe is linearly proportional to the xenon density [Xe] for densities above $\approx 50$ amagat [43].
Table 4.1. Estimates of kinetic parameters [41] for transient and persistent xenon dimers in pure xenon gas in thermal and chemical equilibrium. The cross sections are calculated using the appropriate value of relative rms speed, \( v_{\text{rms}} = (8k_B T/\pi \mu)^{1/2} \), where \( k_B \) is the Boltzmann constant, \( T \) is temperature, and the reduced mass \( \mu \) is 1/2 and 2/3 of the average (naturally abundant) Xe atomic mass for Xe-Xe and Xe-Xe\(_2\) collisions, respectively. The transient-dimer lifetime is calculated using \( v_{\text{rms}} = 3.08 \times 10^4 \text{ cm/s} \), appropriate for Xe-Xe binary collisions. The persistent-dimer lifetime is estimated under the assumption that all collisions break up the dimers and is about two orders of magnitude longer than the transient-dimer lifetime.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Formula</th>
<th>Value at 295 K, ([\text{Xe}] = 1 \text{ amagat})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenon density</td>
<td>([\text{Xe}])</td>
<td>-</td>
<td>2.687 \times 10^{19} \text{ cm}^{-3}</td>
</tr>
<tr>
<td>Xe(_2) equilibrium separation [42]</td>
<td>( R_0 )</td>
<td>( \pi R_0^2 v_{\text{rms}} )</td>
<td>4.4 Å</td>
</tr>
<tr>
<td>Depth of Xe(_2) potential well [42]</td>
<td>( \epsilon/k_B )</td>
<td>-</td>
<td>283 K</td>
</tr>
<tr>
<td>Vel.-avged. Xe-Xe cross section [42]</td>
<td>( \langle \sigma v \rangle_{\text{Xe}} )</td>
<td>( \pi R_0^2 v_{\text{rms}} )</td>
<td>1.9 \times 10^{-10} \text{ cm}^{3}/\text{s}</td>
</tr>
<tr>
<td>Vel.-avged. Xe-Xe(_2) cross section [42]</td>
<td>( \langle \sigma v \rangle_{\text{Xe}2} )</td>
<td>( 2\pi R_0^2 v_{\text{rms}} )</td>
<td>3.25 \times 10^{-10} \text{ cm}^{3}/\text{s}</td>
</tr>
<tr>
<td>Time between transient collisions</td>
<td>( T_t )</td>
<td>( ([\text{Xe}] \langle \sigma v \rangle_{\text{Xe}})^{-1} )</td>
<td>200 ps</td>
</tr>
<tr>
<td>Transient-dimer lifetime</td>
<td>( \tau_t )</td>
<td>( 2R_0/v_{\text{rms}} )</td>
<td>2.85 ps</td>
</tr>
<tr>
<td>Persistent-dimer lifetime</td>
<td>( \tau_p )</td>
<td>( ([\text{Xe}] \langle \sigma v \rangle_{\text{Xe}2})^{-1} )</td>
<td>115 ps</td>
</tr>
</tbody>
</table>

The dominant source of this intrinsic relaxation is fluctuations in the spin-rotation (SR) interaction, with the Hamiltonian:

\[
\mathcal{H}_{\text{sr}} = c_K(R) \mathbf{K} \cdot \mathbf{N},
\]

where \( K \) is the \(^{129}\)Xe nuclear spin, \( N \) is the angular momentum of the interacting pair of Xe atoms, and \( c_K(R) \) is the coupling energy at the distance \( R \) between the pair. The linear density dependence suggests that the fluctuations are caused by transient dimers. In the weak-interaction limit, for which \( \langle c_K^2 N^2 \rangle / h^2 \ll 1 \), the corresponding relaxation rate is [44, 47]

\[
\Gamma_{\text{sr}} = \sigma_{\text{sr}}(T)v_{\text{rms}}[\text{Xe}],
\]

where \( v_{\text{rms}} = (8k_B T/\pi \mu)^{1/2} \) is the relative rms speed of two interacting Xe atoms with reduced mass \( \mu \), and \( \sigma_{\text{sr}}(T) \) is the thermally-averaged binary spin-relaxation cross section, which is a function of temperature \( T \) and of \( c_K(R) \). This work was of necessity carried out at very high xenon densities (tens of amagats) using thermally
generated polarization. Extrapolating the data down to $[\text{Xe}] = 1$ amagat yields an intrinsic gas-phase $T_1$ for $^{129}\text{Xe}$ of $\approx 52$ hr. This was widely assumed to be the limiting value for several decades, even as SEOP made it common to work with much lower-density xenon samples.

Several years ago, Moudrakovski, Breeze, and co-workers [44] essentially confirmed the results of Hunt and Carr but also found a dependence of the slope of $T_1^{-1}$ vs. $[\text{Xe}]$ on the square of the applied magnetic field $B_0$ for $[\text{Xe}] > 20$ amagat and $B_0$ between 4.7 T and 9.4 T. This field dependence indicates an additional contribution to the intrinsic relaxation from fluctuations of the chemical shift anisotropy (CSA) interaction. The corresponding Hamiltonian may be written [45]:

$$H_{\text{csa}} = c_K(R)\mu_B \Theta \cdot B_0,$$  \hspace{1cm} (4.5)

where $\Theta$ is the inertial tensor of an interacting pair, $\mu_B$ is the Bohr magneton, and $c_K(R)$ is the same for both SR and CSA interactions. At such large values of $[\text{Xe}]$, the fluctuations were again reasonably presumed to be due to transient dimers. The total intrinsic relaxation rate due to transient dimers is then:

$$\Gamma_t = \Gamma_{t\text{sr}} + \Gamma_{t\text{csa}},$$  \hspace{1cm} (4.6)

where $\Gamma_{t\text{csa}}$ can be written in a form analogous to Eq. (4.4) with the appropriate cross section $\sigma_{\text{csa}}(T)$ depending on $B_0^2$. The cross sections (and the relaxation rates $\Gamma_{t\text{csa}}$ and $\Gamma_{t\text{sr}}$) become comparable for $B_0 = 12.5$ T.

Implicit in all of the work involving transient dimers is the assumption of the fast-fluctuation limit. A more complete formulation of the cross sections $\sigma_{\text{sr}}(T)$ and $\sigma_{\text{csa}}(T)$ would have both multiplied by a factor $1/(1 + \Omega^2\tau_c^2)$, where $\Omega$ is the Larmor frequency of the nucleus in the applied magnetic field $B_0$ [46]. (For $^{129}\text{Xe}$, the Larmor frequency $\Omega = 2\pi \times 11.78$ MHz/T.) The correlation time $\tau_c$ is on the order of the average duration of a binary collision $\tau_t$, or a few picoseconds. The fast-fluctuation limit corresponds to $\Omega^2\tau_t^2 \ll 1$, which clearly holds for any reasonable $B_0$. As expected in this limit, no dependence on applied field was observed up to 2.5 T in the earlier work of Hunt and Carr [43], and the field
dependence observed by Moudrakovski, et al. was due solely to the $B_0^2$ dependence of the CSA interaction strength.

A key development in understanding intrinsic gas-phase $^{129}$Xe relaxation came with the work of Chann, Nelson, and co-workers [47], who presented strong evidence that for lower gas densities typical of SEOP, the fluctuations in the SR interaction are predominantly mediated by the formation and break-up of persistent Xe dimers. Although the fraction of such molecules is small, their lifetime is about two orders of magnitude longer than the transient-dimer lifetime. In the double limit of weak interactions and fast fluctuations, the probability of a spin transition would thus be four orders of magnitude greater for persistent dimers. The further implications of this work are profound: in the low-field limit, the intrinsic $^{129}$Xe $T_1$ at low densities is independent of total gas density and depends instead only on gas composition, i.e., the relative concentrations of xenon and any other gases in the mixture that can serve as an effective third body for the formation and break-up of persistent dimers. Moreover, a maximum possible low-field $T_1$ for pure xenon gas at room temperature was deduced from these data to be $\approx 4$ hr, an order of magnitude smaller than the value extrapolated from the work of Hunt and Carr [43].

4.3.3 The Present Work

The purpose of the present work is to investigate $^{129}$Xe relaxation due to persistent dimers at high magnetic fields (8.0 T). All previous work has been carried out in the fast-fluctuation limit, for which the dimer lifetime (whether persistent or transient) is much shorter than the $^{129}$Xe Larmor period. As [Xe] is reduced below $\approx 1$ amagat, an applied field of 8.0 T decouples the relaxation due to persistent dimers; we show that one obtains in this regime a dependence of the rate on total gas density at fixed gas composition that is consistent with the theory of Chann, et al. [47], including the factor $1/(1 + \Omega^2 \tau_c^2)$, confirming that persistent and not transient dimers are primarily responsible for intrinsic $^{129}$Xe relaxation at these low gas densities. We are able to extract from our data reasonable estimates of molecular formation and break-up parameters, as well as the SR and
CSA interaction strengths. The SR interaction strength, properly parameterized 
according to Ref. [47], allows us to compute for comparison a maximum possible 
low-field $T_1$ for pure xenon gas at room temperature of $5.45 \pm 0.2 \text{ h}$, slightly larger 
than the result of Chann, et al. [47]. We further confirm both the role of magnetic 
decoupling and the presence of the CSA interaction at high field with several $T_1$ 
measurements for similar gas compositions and total densities in a lower 1.5 T 
applied field.

The silicone-coated borosilicate-glass cells used in these studies had very low 
wall-relaxation rates, which was essential in order to investigate the molecular 
effects with high precision. In fact, in the regime where wall relaxation dominates 
the contribution from persistent dimers, we have, to our knowledge, measured the 
longest longitudinal relaxation times for gas-phase $^{129}$Xe ever recorded, $> 25 \text{ hr}$ at 
8.0 T.

4.4 Theory

The relaxation rate $\Gamma_p$ of $^{129}$Xe due to persistent xenon dimers may be written 
[47]:

$$\Gamma_p = (2K[Xe])(M^{sr} + M^{csa})\left(\frac{\tau_p}{1 + \Omega^2\tau_p^2}\right),$$

(4.7)

where we have slightly rearranged Eq. 2 of Ref. [47] to form the product of three 
factors. The first factor is the fraction of Xe atoms bound in molecules in accordance 
with Eq. (4.2); the second factor $M^{sr} + M^{csa}$ is the sum of the SR and CSA mean-
square interaction strengths (second moments) during a molecular lifetime, where 
$M^{csa} \propto B^2_0$; and the third factor is the power spectrum of magnetic field fluctuations 
[46], where $\tau_p$ is the correlation time for the fluctuations, assumed to be equal to 
the molecular lifetime. (Here $\Gamma_p$ and $\tau_p$ correspond, respectively, to $\Gamma_{vdW}$ and $\tau_B$ 
in Ref. [47].) We note that it is immaterial whether the coherent rotation of the 
persistent dimers is interrupted by collisions that break up the molecule (with on 
average a new molecule created elsewhere by detailed balance) or by collisions that 
simply reorient its angular momentum. The inverse correlation time is actually the
sum of the rates for these two types of collisions; we call this total rate \( \tau_p^{-1} \), since it is likely that purely reorienting collisions are rare in such weakly bound molecules. For linear molecules, the second moments for SR [48] and CSA [49, 50] are given by

\[
M_{\text{sr}} = \frac{2\langle c_K^2 N^2 \rangle}{3\hbar^2},
\]
\[
M_{\text{csa}} = \frac{2\mu_B^2 B_0^2}{15\hbar^6} \langle c_K^2 \Theta_\perp^2 \rangle,
\]

where \( \Theta_\perp = \mu R^2 \) is the rotational inertia.

Chann, et al. conducted their experiments in an applied field \( B_0 = 20.4 \) G (\( \Omega = 2\pi \times 24 \) kHz), for which the CSA interaction is negligible and which corresponds to the fast-fluctuation (low-field) limit at all reasonable gas densities, thus reducing Eq. (4.7) to

\[
\Gamma_p = \frac{4K\langle c_K^2 N^2 \rangle}{3\hbar^2}[\text{Xe}]\tau_p
\]

For a pure xenon sample in chemical equilibrium, the formation and breakup rate per molecule is \( 1/\tau_p = k_{\text{Xe}}[\text{Xe}] \), where Xe atoms serve as the third body to provide kinetic energy, and \( k_{\text{Xe}} \) is the corresponding molecular breakup coefficient. Since \( [\text{Xe}]\tau_p \) is a constant, \( \Gamma_p \) is independent of \( [\text{Xe}] \) in the low-field limit. However, a second gas, capable of serving as a third body in the formation and breakup of molecules, can change \( \tau_p \) without affecting the fraction of Xe atoms bound in molecules. Chann, et al. found (and confirmed experimentally) that \( \Gamma_p \) depends on the relative gas composition but not on the total gas density at fixed composition.

For applied magnetic fields on the order of \( 10 \) T (\( \Omega = 2\pi \times 118 \) MHz) and gas densities on the order of 0.1 amagat or lower, we can no longer ignore the \( \Omega^2 \tau_p^2 \) term in the power-spectrum of Eq. (4.7). For fixed \( B_0 \), both the SR and CSA terms stay constant, and one should observe the magnetic decoupling of relaxation mediated by persistent dimers as the total gas pressure is lowered for a fixed gas composition. We worked exclusively with nitrogen as a second gas and measured \( \Gamma_p \) as a function of total gas pressure for three distinct relative compositions. (An alternative to our
experiment would be to vary the density of the second gas while holding \([Xe]\) fixed, which would lead to a maximum in the relaxation rate for \(\Omega \tau_p = 1\). We write the molecular breakup rate as

\[
\frac{1}{\tau_p} = k_\alpha [G] = k_{Xe}[Xe] + k_N[N_2],
\]

(4.11)

where \(k_N\) is the \(Xe_2\) molecular breakup coefficient for nitrogen and the total gas density \([G] = [Xe] + [N_2]\). The overall breakup coefficient \(k_\alpha\) is given by

\[
k_\alpha = \alpha k_{Xe} + (1 - \alpha)k_N,
\]

(4.12)

where \(\alpha = [Xe]/[G]\) is the fractional concentration of xenon. Under our conditions, where \([Xe]\) is small enough to ignore contributions from transient dimers and gradient relaxation is negligible (see Discussion below), the observed \(^{129}\)Xe relaxation is \(\Gamma = \Gamma_w + \Gamma_p\), where \(\Gamma_w\) is the wall relaxation rate. Using Eqs. (4.7) and (4.11) we can write \(\Gamma\) as a function of total gas density \([G]\) for a fixed concentration \(\alpha\):

\[
\Gamma([G]) = \Gamma_w + 2K(M^{st} + M^{csa})\left(\frac{\alpha k_\alpha [G]^2}{k_\alpha^2 [G]^2 + \Omega^2}\right).
\]

(4.13)

### 4.5 Experimental Procedure and Results

In order to examine molecular relaxation using Eq. (4.13), we require stable wall-relaxation rates, where \(\Gamma_w < \Gamma_p\). In our early attempts, stability of \(\Gamma_w\) was a problem. Relaxation measurements were done in the same cell that was used to polarize the Xe gas mixture. These cells are similar to those that have been fabricated and used to polarize \(^3\)He in our group [55]: They are 5.0 cm dia. spheres connected via a 10 cm length of capillary tubing (0.5 mm dia.) to a glass valve and side arm for refilling. A 4 cm length of 6 mm glass tubing (the stem) extends from the sphere opposite the capillary entrance. These cells were coated with dichlorodimethylsilane [38] to inhibit wall relaxation and contained a macroscopic amount of Rb metal (tens of milligrams) for optical pumping. Repeated measurements of the room-temperature wall relaxation rate in these cells at 8.0 T showed fluctuations of a factor of two or more. The changes were observed
to occur each time after a cell was pumped and polarized at 90 °C. After a cell was polarized several times, $\Gamma_w$ typically increased (though not necessarily monotonically) to a level comparable to $\Gamma_p$ or even larger. We infer that at optical pumping temperatures Rb reacted with the coating in a way that ultimately degraded the cell wall lifetime.

Thereafter, we switched to using two distinct types of cells: “pumping” cells and “measurement” cells. Eight different pumping cells (as described above) were used exclusively to generate hyperpolarized $^{129}\text{Xe}$. Periodically, we found it possible to rejuvenate cells with poor wall rates by removing the Rb, recoating the walls, and distilling in fresh Rb. Xenon gas was transferred from pumping cells to one of two measurement cells (designated “Oscar” and “Lloyd”). Measurement cells have a similar geometry to pumping cells and are also coated, but the spherical chamber has a larger 6.7 cm diameter. The smaller surface-to-volume ratio in these cells serves to further decrease the wall-relaxation rate. Measurement cells contained no Rb and were never heated above room temperature; they exhibited long and robust wall-relaxation times (> 20 hr).

Our high-vacuum gas-handling system was used to measure all cell volumes, as well as the ballast volumes used in gas transfer. The same system was also used to fill pumping cells with a precise amount of Xe and N$_2$, according to the chosen value of the Xe concentration $\alpha$. A known quantity of Xe atoms was first condensed into the stem of the cell, which was held at 77 K by immersing it in liquid nitrogen. Only the stem was immersed, the rest of the cell remained near room temperature (aided by a small styrofoam heat shield). While the Xe remained frozen, N$_2$ gas was admitted into the cell at the desired final partial pressure. After filling, the cell was allowed to return completely to room temperature and a final pressure was measured with a separate solid-state gauge (GE Novasensor, Model NPC-410-015A-3L). This final pressure was generally 1-2% higher than targeted; the discrepancy was interpreted as an excess of N$_2$ due to the fact that the cell was still somewhat colder than room temperature during filling because of proximity to the LN$_2$. This had the effect of slightly lowering the value of $\alpha$ compared to the
target value and introducing a small variation. We quote average values for $\alpha$ with an error range reflecting this variation.

Once filled, the gas in a pumping cell was polarized by SEOP with a frequency-narrowed [51] 20 W diode-laser array. The cells were placed in an oven and heated to 90 °C. The oven was located in a 1.5 T superconducting magnet with a 30 cm dia. horizontal bore. (The cell capillary protruded laterally outside of the oven so that the valve remained cool.) We found that the 1.5 T field generally decreased the $\Gamma_w$ of the pumping cell, thus increasing final polarization, as compared to the 30 G Helmholtz arrangement that we initially employed.

Once the Xe gas in a pumping cell was polarized, a known amount of gas was transferred from the pumping cell to a measurement cell, making use of a manifold and, in some cases, ballast volumes in order to achieve a desired total gas density $[G]$. A vacuum pump was used to clear dead spaces and avoid contact with atmospheric oxygen. The gas transfer was performed in the fringe field ($\approx 60$ G) of the 8.0 T vertical bore superconducting magnet; the measurement cell was then quickly placed into the NMR probe and the entire assembly secured in the magnet. The probe coil consisted of two elongated loops of wire (a few turns each) positioned on opposite sides of the stem. The coil was tuned to the $^{129\text{Xe}}$ Larmor frequency of 94.1 MHz. The NMR spectrometer incorporates a Tecmag Aries pulse programmer and digitizer with a homebuilt RF section. The longitudinal relaxation rate $\Gamma$ was measured by the periodic acquisition of the free-induction decay (FID) following the excitation pulse. Since only spins in the relatively small volume of the stem were excited, we were able to use large flip angles while destroying a negligible amount of the total spin magnetization over the course of the measurement. Either the initial height of each FID or the area of each Fourier-transform peak was plotted vs. time of acquisition. The plot was fit to an exponential decay to yield $\Gamma$. With the gas depolarized, the solid-state pressure gauge was used again to make a precise measurement of $[G]$. The process of filling and polarizing a pumping cell, transferring gas to a measurement cell, measuring $\Gamma$, and measuring $[G]$ was repeated for a range of values of $[G]$ from about 0.02 to 0.4 amagat, to yield $\Gamma$ vs.
for each value of \( \alpha \).

Plots of measured relaxation rate \( \Gamma \) at 8.0 T vs. total gas pressure [G] are shown in Fig. 4.1 for three different values of the Xe concentration \( \alpha \). In each case, the data are fit to Eq. (4.13) with \( \Gamma_w \), \( k_\alpha \), and \( 2K(M_{sr} + M_{csa}) \) as free parameters. The results are summarized in Table 4.2.

Figure 4.2 is a plot of \( k_\alpha \) vs. \( \alpha \). The data are fit to Eq. (4.12), yielding for the molecular breakup coefficients:

\[
\begin{align*}
  k_{\text{Xe}} &= (3.4 \pm 0.1) \times 10^{-10} \text{ cm}^3/\text{s}, \\
  k_N &= (1.9 \pm 0.2) \times 10^{-10} \text{ cm}^3/\text{s}.
\end{align*}
\]  

The values of \( \Gamma_w \) extracted from these fits are very small, corresponding to wall-relaxation times of 20-40 hr, thus allowing us to observe the dramatic effect of magnetic suppression of the molecular relaxation. The data point for \( \alpha = 0.712 \) and total gas pressure [G] = 0.0215 amagat (marked in Fig. 4.1 by an arrow) corresponds to a measured relaxation time of 25 hr. The wall relaxation time inferred from the theory exceeds 40 hr.

In a separate set of measurements, relaxation data were acquired in the measurement cell “Lloyd” for a fixed value of the xenon concentration \( \alpha = 0.712 \) in applied fields of both 8.0 T and 1.5 T at several additional values of the total gas density [G]. The 1.5 T data were acquired in the same way with a similar NMR spectrometer operating at \( \Omega = 2\pi \times 17.6 \text{ MHz} \). The magnet used was the same.

<table>
<thead>
<tr>
<th>Measurement Cell</th>
<th>( \alpha )</th>
<th>( 2K(M_{sr} + M_{csa}) ) ( (10^{-14} \text{ cm}^3/\text{s}^2) )</th>
<th>( k_\alpha ) ( (10^{-10} \text{ cm}^3/\text{s}) )</th>
<th>( \Gamma_w ) ( (10^{-5} \text{ s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lloyd</td>
<td>0.546(4)</td>
<td>2.43(23)</td>
<td>2.76(8)</td>
<td>0.76(5)</td>
</tr>
<tr>
<td>Lloyd</td>
<td>0.712(13)</td>
<td>2.66(15)</td>
<td>2.86(5)</td>
<td>0.64(3)</td>
</tr>
<tr>
<td>Oscar</td>
<td>0.823(8)</td>
<td>2.37(8)</td>
<td>3.14(5)</td>
<td>1.25(3)</td>
</tr>
</tbody>
</table>

Table 4.2. Free parameters extracted from the fits of the data in Fig. 4.2 to Eq. (4.13) for three values of the Xe concentration \( \alpha \). Errors are given in parentheses for the least significant figure(s). The near constancy of \( 2K(M_{sr} + M_{csa}) \) is evidence for the validity of the persistent-dimer theory of Chann, et al. [47].
Figure 4.1. Plot of $^{129}$Xe relaxation rate vs. total gas density at 8.0 T for three values of the concentration $\alpha = [\text{Xe}]/[\text{G}]$; the second gas is nitrogen in all cases. The fits are to the theory of Chann, et al. [47] as parameterized in Eq. (4.13) and including the CSA interaction. For each value of $\alpha$, the wall-relaxation rate $\Gamma_w$, molecular breakup coefficient $k_\alpha$, and the product $2K(M_{\text{sr}} + M_{\text{csa}})$ are extracted from the fits (see Table 4.2). The asymptotes at larger $[\text{G}]$ correspond to the density-independent rates observed in Ref. [47], where $k_\alpha^2[G]^2 \gg \Omega^2$. Relaxation due to persistent dimers is suppressed at low densities, where $k_\alpha[G] = \Omega$ for $[\text{G}]$ between about 0.05 and 0.1 amagats. The data point indicated by an arrow corresponds to a measured $T_1$ of 25 hr.
Figure 4.2. Plot of molecular breakup coefficient $k_\alpha$ vs. fractional xenon density $\alpha$. The fit is to Eq. (4.12) and yields molecular breakup coefficients $k_{\text{Xe}}$ and $k_{\text{N}}$ for xenon and nitrogen, respectively.
horizontal bore imaging magnet used to perform SEOP on the pumping cells. The cell was placed on top of a tuned surface coil inside of an aluminum box for shielding. For each value of $[G]$, the relaxation data were acquired consecutively at 1.5 T and then 8.0 T with the same gas, except for the lowest density $[G] = 4.9 \times 10^{-3}$ amagat, for which only data at 1.5 T could be acquired. The results are shown in Fig. 4.3. The theoretical curves show the dependence of the rate on $[G]$ for both $B_0 = 1.5$ T and $B_0 = 8.0$ T derived exclusively from the analysis of the separate 8.0 T data presented in Fig. 4.1; the method for arriving at these curves is discussed below.

### 4.6 Discussion

The present work provides strong confirmation of the theory presented by Chann, et al. [47] for relaxation of gas-phase $^{129}$Xe at low densities, particularly through the demonstration of the critical role played by persistent xenon dimers in setting an intrinsic lower bound to the relaxation rate and of high-field suppression of the molecular mechanism, as shown in Fig. 4.1. The role of transient dimers in our experiments was negligible: our largest xenon density was $[\text{Xe}] \approx 0.25$ amagat, for which the contribution to relaxation from transient dimers for $B_0 = 8.0$ T is $\Gamma_t \approx 1.7 \times 10^{-6}$ s$^{-1}$ [44], four to eight times smaller than the wall-relaxation rates extracted from our fits. The product of the chemical equilibrium coefficient $K$ and the total second moment $M^{sr} + M^{csa}$ (third column of Table 4.2) is dependent strictly on the physics of persistent-dimer formation and of the spin-relaxation interactions, respectively. They cannot be separated experimentally, but the fact that the product remains nearly constant for the three values of Xe concentration $\alpha$ is further evidence for the validity of the persistent-dimer theory. In further analysis below, we will make use of the weighted average

$$2K(M^{sr} + M^{csa}) = (2.44 \pm 0.03) \times 10^{-14} \text{ cm}^3/\text{s}^2. \quad (4.16)$$

The 1.5 T vs. 8.0 T data in Fig. 4.3 appear to demonstrate the correct dependence of $\Gamma_p$ on $B_0$, accounting for the different (and somewhat competing) degrees of both high-field suppression and contribution from the CSA interaction. If we
Figure 4.3. Plot of $^{129}$Xe relaxation rate vs. total gas density at two different applied magnetic fields and a fixed value of the xenon concentration $\alpha = 0.712$. All data were acquired using the measurement cell “Lloyd,” for which the wall-relaxation rate (intercept of both curves) is taken as $7.0 \times 10^{-6}$ s$^{-1}$. For each value of [G], the data were acquired consecutively at 1.5 T and then 8.0 T with the same gas, except for the lowest density point, for which only data at 1.5 T could be acquired. The curves are not fits to the data but rather are predictions derived entirely from the separate and independent data taken and displayed in Fig. 1 and Table 4.2. High-field suppression of the relaxation rate due to persistent dimers is stronger at 8.0 T for low densities, but the larger contribution to relaxation from the CSA interaction at 8.0 T eventually causes the curves to cross near [G] = 0.1 amagat, where the 1.5 T curve is already well into the limit $\Omega^2\tau_p^2 \ll 1$. The data point indicated by an arrow corresponds to a measured $T_1$ of $27.0 \pm 1.3$ h, the longest gas-phase $T_1$ ever reported for $^{129}$Xe.
make the reasonable assumption that the ratio $M_{\text{sr}}/M_{\text{csa}}$ is the same for persistent as for transient dimers (still in the weak-interaction limit in all cases), then we can use Ref. [44] to calculate the fraction $f$ of the total interaction strength that is due to SR to be

$$f = \frac{M_{\text{sr}}}{M_{\text{sr}} + M_{\text{csa}}} = (71.0 \pm 2.7)\% \text{ at } 8.0 \text{ T},$$

(4.17)

whereas $f \approx 1$ at $B_0 = 1.5 \text{ T}$. The theoretical curves in Fig. 4.3 have the form of Eq. (4.13). The intercept for both curves corresponds to $\Gamma_w = 7.0 \times 10^{-6} \text{ s}^{-1}$, which is the average of the two extracted values for $\Gamma_w$ from the two fits in Fig. 4.1 involving the same measurement cell “Lloyd” (see Table 4.2). We used Eqs. (4.14) and (4.15) to calculate $k_\alpha$ for $\alpha = 0.712$ and the weighted average in Eq. (4.16), where in the case of $B_0 = 1.5 \text{ T}$, $2\mathcal{K}(M_{\text{sr}} + M_{\text{csa}})$ was multiplied by $f(8.0T)/f(1.5T) \approx f(8.0T)$ to account for the much weaker CSA interaction at the lower field. The larger magnetic-field suppression combined with the presence of the CSA interaction for $B_0 = 8.0 \text{ T}$ causes the curves to cross near $[G] = 0.1 \text{ amagat}$. Near this crossing point, we measured almost identical $T_1$ values for the two applied fields of about 6 hr. Compared with this value, at the lower density $[G] = 0.017 \text{ amagat} T_1$ increases by about 25% at 1.5 T but by more than a factor of four at 8.0 T, due to the stronger magnetic suppression. The latter data point (marked with an arrow in Fig. 4.3) corresponds to a measured $T_1$ of $27.0 \pm 1.3 \text{ hr}$, which is to our knowledge the longest gas-phase relaxation time ever reported for $^{129}\text{Xe}$.

We have assumed in Fig. 4.3 that the wall relaxation rate $\Gamma_w$ is independent of $B_0$, at least for the two values of $B_0$ we investigated. The assumption is physically plausible because interactions due to wall collisions should be in the fast-fluctuation limit for all reasonable values of $B_0$, although the possibility of xenon dissolving into the surface coating [38] potentially complicates this picture. The assumption is also supported by how well the data fall on the curves, which we emphasize are not fits to this data but were derived exclusively from the independent 8.0 T data shown in Fig. 4.1 and Table 4.2. Finally, even allowing for some field dependence to $\Gamma_w$,
it is clear from the very low pressure 1.5 T data point \([G] = 4.9 \times 10^{-3} \text{ amagat}\),
where \(T_1\) is over 12 h, that the difference in relaxation rates for \([G] = 0.017 \text{ amagat}\)
could not be explained by a difference in \(\Gamma_w\) alone.

Using Eqs. (4.16) and (4.17), and the value \(\mathcal{K} = 230 \text{ Å}^3\) calculated in Ref. [47],
we can make an estimate of the SR interaction strength \(M^{sr} = 3.77 \times 10^7 \text{ s}^{-2}\). Using
Eq. (4.8) we obtain

\[
\sqrt{\langle c_K^2 N^2 \rangle} = h \times 1200 \text{ Hz.} \tag{4.18}
\]

This value falls between two estimates made by Chann, et al. [47], one of 820 Hz
based on their measurement of the low-field pure-xenon relaxation rate (see Eq. (4.22)
below) and the relationship between the SR coupling and the Xe-Xe chemical shift
[72, 73, 74], and the other of 1400 Hz based on the measured spin-relaxation rate
due to transient dimers in the applied-field regime where the CSA interaction is
negligible [43, 44]. These estimates and our result imply a value for \(c_K(R_0)/h\)
(where \(R_0\) is the equilibrium separation) of between 20 and 40 Hz, consistent with
\textit{ab initio} results of \(\approx 30 \text{ Hz}\) [42]. Using a similar argument and the fraction \(1 - f\) of
the total interaction strength that is due to CSA, along with Eq. (4.9), we estimate

\[
\sqrt{\langle c_K^2 R^4 \rangle} = h \times 240 \text{Hz Å}^2, \tag{4.19}
\]

which is consistent with \(c_K(R_0)/h \approx 10 \text{ Hz}\). We note that the CSA interaction is
related to the anisotropic chemical shift \(\Delta \sigma\) of the xenon dimer by [50]

\[
\Delta \sigma = \sigma_\| - \sigma_\perp = -\frac{\mu_B \Theta_\perp c_K(R)}{\gamma h^3}, \tag{4.20}
\]

where \(\gamma\) is the \(^{129}\text{Xe}\) gyromagnetic ratio. However, the extremely short correlation
times in the gas phase do not readily permit direct NMR measurements of \(\sigma_\|\) and
\(\sigma_\perp\).

Our values for \(k_{Xe}\) and \(k_N\) are quite reasonable compared to the estimates based
on kinetic theory. In fact, our estimated velocity-averaged cross section for collisions
between xenon dimers and xenon atoms is within 20\% of the value of \(k_{Xe}\) in Eq. 4.14
(see Table 4.1), supporting our assumption that most collisions result in the breakup of the weakly bound persistent dimers. We find nitrogen as a third body to be only about half as efficient as Xe, somewhat in disagreement with the results of Chann, et al. [47], who measured the ratio $k_N/k_{Xe}$ to be close to unity and deduced a breakup rate $k_{Xe} = 1.2 \times 10^{-10}$ cm$^3$/s, where the latter number is based on the calculated 820 Hz estimate for $\sqrt{\langle c_x^2 N^2 \rangle}/\hbar$ discussed above.

We can make a further comparison to the results of Chann, et al. [47] by considering the low-field limit ($\Omega^2 \ll k^2 [G]^2$) of Eq. (4.13). Ignoring the CSA interaction and using Eq. (4.8) we obtain

$$\Gamma([G]) = \Gamma_w + \frac{4K\langle c_x^2 N^2 \rangle \alpha}{3\hbar^2 k_\alpha}.$$  

(4.21)

In the limit where $\alpha = 1$ and $k_\alpha = k_{Xe}$, we obtain what is called $\Gamma_{\text{Xe} \text{vdW}}$ in Ref. [47], the low-field pure-xenon relaxation rate due to persistent dimers:

$$\Gamma_{\text{Xe} \text{vdW}} k_{Xe} = \frac{4K\langle c_x^2 N^2 \rangle}{3\hbar^2}.$$  

(4.22)

We can write an equivalent expression that is appropriate for our data using Eq. (4.17) to account for our 8.0 T applied field:

$$\Gamma_{\text{Xe} \text{vdW}} k_{Xe} = 2K(M^{sr} + M^{csa})f(8.0 \text{ T}).$$  

(4.23)

Using our values for $k_{Xe}$ and $f(8.0 \text{ T})$ in Eqs. (4.14) and (4.17), and the weighted average of $2K(M^{sr} + M^{csa})$ in Eq. (4.16), we find

$$\Gamma_{\text{Xe} \text{vdW}} = (5.1 \pm 0.2) \times 10^{-5} \text{ s}^{-1},$$  

(4.24)

which corresponds to a limiting low-field relaxation time for pure Xenon of $5.45 \pm 0.2$ h, slightly larger than the Chann, et al. value of $4.1 \pm 0.1$ h.

Relaxation due to diffusion of $^{129}$Xe through magnetic-field gradients in Eq. (4.1) should be negligible in our experiments. We confirmed this by displacing the entire cell and probe vertically by as much as 4 cm and recording the change in NMR frequency. We estimated a gradient of $\approx 3$ G/cm in the 8.0 T magnet. (The relative
gradients were even smaller in the 1.5 T magnet.) In the regime where the diffusion time across the cell is much longer than the Larmor period [30], gradient relaxation is given by:

\[ \Gamma_g = D \frac{|\nabla B_\perp|^2}{B_0^2}, \quad (4.25) \]

where \( \nabla B_\perp \) is the transverse magnetic field gradient and \( D \) is the Xe diffusion coefficient. Even in the fastest-diffusion case of a cell containing 0.01 amagat of pure xenon, Eq. (4.25) predicts \( T_1 > 10^8 \) s from this mechanism alone.

It is possible that there are contributions to our measured relaxation rates from persistent Xe-N\(_2\) dimers [75], producing another molecular term in Eq. (4.13) with a different chemical-equilibrium coefficient, interaction strength, and molecular lifetime. These molecules are somewhat more weakly bound, having well depth \( \epsilon/k_B \) between 200 K and 250 K [75]. In addition to the quality of our fits to a model involving only Xe\(_2\) dimers, we rely on the results and conclusions of Chann, et al. [47], where the asymptotic relaxation rate at high second-gas densities approached a common value (the wall-relaxation rate for the one cell employed) for Ar, N\(_2\), and He gases. This result is relevant because the well depth for Xe-He is exceedingly small at about 30 K; the asymptotic rates should have been different for the different second gases had the corresponding dimers played a significant role in relaxation. They were thus lead to conclude that Xe-N\(_2\) dimers are not contributing significantly to the measured relaxation rates, and there is no reason to expect this to change at higher applied fields.

It is likely that in some earlier work [44, 76] at lower xenon densities, \( \Gamma_w \) was inadvertently overestimated due to a significant contribution from the molecular mechanism. For example, Breeze, et al. [76] measured \( \Gamma^{-1} \approx 3 \) h in cells containing \( \approx 1 \) amagat of xenon and a relatively small amount of nitrogen, attributing virtually all of this relaxation to wall interactions. For this density and their applied field of 4.7 T, we would predict \( \Gamma_p^{-1} = 4.4 \) h; the actual wall relaxation time \( (\Gamma - \Gamma_p)^{-1} \) would then be almost 10 h.
Variations in the applied field $B_0$ and/or the total gas density $[G]$ at fixed xenon concentration $\alpha$ thus lead to changes in two distinct aspects of the relaxation due to persistent dimers: the rate of fluctuations compared to $\Omega$, and the relative strengths of the CSA and SR interactions. In the regime where $B_0$ is below several tesla, the fast-fluctuation limit $\Omega^2\tau_p^2 \ll 1$ (low field and high density, as in Ref. [47]) leads to an intrinsic relaxation that is independent of both $[G]$ and $B_0$. In the opposite limit of slow fluctuations (high field but still SR-dominated, and low density) the intrinsic relaxation is proportional both to $[G]^2$ and to $1/B_0^2$. In the regime where $B_0 > 10$ T, the CSA interaction begins to dominate, and relaxation in the fast-fluctuation limit, while still density independent, is now proportional to $B_0^2$. In the limit of slow fluctuations, the relaxation still depends on $[G]^2$ but becomes independent of $B_0$ as the effects of the CSA interaction and slow fluctuations cancel each other. We note that (according to our value for $k_{Xe}$) $\Omega\tau_p \approx 1$ for $B_0/[G] \approx 120$ T/amagat for pure xenon, so that the fast-fluctuation limit is readily attained for densities $\approx 1$ amagat, even for very large laboratory magnetic fields, and the fast-fluctuation limit always holds for $B_0$ at or below about 0.1 T, where the gas densities otherwise start to become too low to be detectable by NMR (even when hyperpolarized). Our data straddle both the transition from near-zero to moderate CSA interaction strength and the transition from the slow- to the fast-fluctuation limit. Finally for completeness we note that the contribution to relaxation from transient dimers (always in the fast-fluctuation limit and linearly dependent on $[Xe]$) becomes equal to that from persistent dimers for $[Xe] \approx 10$ amagats, with a $B_0^2$ dependence coming in at the largest applied fields.

The extraordinarily long $T_1$ values for gas-phase $^{129}$Xe measured here have potential implications for accumulating and storing large quantities of hyperpolarized xenon. We have fabricated cells with sufficiently low wall-relaxation rates ($< 1/20$ h$^{-1}$) that the maximum $T_1 \approx 5$ h due to the molecular mechanism for pure xenon samples can be realized in practice. Many designs for accumulation are based on storing hyperpolarized Xe frozen at 77 K [11, 12], where $T_1$ of the solid is only 2.5 h [77], and one must adequately address potential polarization
losses due to the freeze-thaw cycle. The use of an 8.0 T magnet in a practical device is clearly cumbersome, but there is strong evidence that the wall-relaxation rates in our cells do not increase by much for $B_0$ as low as 1.5 T. Much longer $T_1$ values are possible, although these are currently realized only for gas compositions that are lean in Xe and/or have total gas densities $\leq 0.1$ amagat. However, given that the Xe$_2$ potential-well depth $\epsilon/k_B$ is so close to room temperature, increasing the temperature by even a few tens of °C may significantly decrease the limiting relaxation rates due to persistent dimers and greatly improve prospects for a room-temperature accumulator at xenon densities approaching 1 amagat. Additional experiments to look for the $B_0^2$ dependence at relatively high applied magnetic fields would better sort out the contributions from the spin-rotation and chemical-shift-anisotropy interactions, as well as any variable wall-relaxation rate, in order to find the optimal field in which to operate a practical device.

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CHAPTER 5

INTRINSIC GAS-PHASE SPIN RELAXATION OF $^{129}\text{Xe}$

5.1 Preface

Shortly after we submitted the paper found in Chapter 4 we turned our attention to the next set of experiments needed to understand molecular relaxation in $^{129}\text{Xe}$. Our initial focus was on a set of relaxation measurements at 8.0 T at a range of temperatures from 293 K to 373 K. An exploration of the field dependence of relaxation was a possibility, but the temperature experiments seemed the most important. Our last paper had shown that the limiting low field, intrinsic relaxation time for a sample of pure xenon was over an order of magnitude shorter than previously expected. We knew that the formation of the $^{129}\text{Xe}-\text{Xe}$ molecules responsible for this relatively fast relaxation could potentially be suppressed by even a moderate increase in temperature. This effect was indeed seen when we observed an decrease in relaxation rate by nearly a factor of 2 when we increased the temperature from room temperature to 373 K.

Science, however, does not often happen the way it is planned. I certainly did not expect that our focus would soon be shifted to measuring $^{129}\text{Xe}$ relaxation rates at several fields ranging from 1.5 T to 14.1 T. We had realized that a combination of field and temperature dependent measurements would allow for the separation of the chemical equilibrium coefficient $\mathcal{K}$ and the spin rotation and chemical shift anisotropy mean-square interaction strengths $M^{sr}$ and $M^{\text{csa}}$. These experiments progressed nicely and we were able to measure some amazingly long relaxation times, including nearly 100 hours in a low density sample at 14.1 T. With every experiment the paper we planned to write got even better.
An experiment that was almost an afterthought shifted our focus once again. Given our more complete understanding of intrinsic relaxation along with our temperature dependent experiments we felt that it may be worthwhile to measure $T_1$ in 1 amagat pure Xe samples at low fields (2.8 mT) at room temperature and 373 K. We observed nearly a factor of two increase in the relaxation time in three cells with a maximum 373 K $T_1$ of nearly 5 hours. This was a remarkable result since it represented a factor of two increase in $T_1$ over the most common method used for storing HP $^{129}$Xe, cryogenic separation and storage in a moderate magnetic field ($\sim 0.1$ T). This method is mature and generally gives excellent results, but care must be taken when freezing and thawing the gas due to a $^{129}$Xe relaxation time on the order of seconds near the phase transition. Could these results be pointing towards a new storage system that could extend by a factor of two or more the hold time of HP $^{129}$Xe as well as avoid any issues associated with freezing and thawing? We report a $^{129}$Xe relaxation time of 5.75 hours at 373 K in a 5 inch diameter cell suggesting that such a storage system is very much a possibility.

5.2 Abstract

We have completed an extensive study of $^{129}$Xe longitudinal spin relaxation in the gas phase, involving both intrinsic and extrinsic mechanisms. The dominant intrinsic relaxation is mediated by the formation of persistent Xe$_2$ van der Waals dimers. The dependence of this relaxation on applied magnetic field yields the relative contributions of the spin-rotation and chemical-shift-anisotropy interactions; the former dominates at magnetic fields below a few tesla. This relaxation also shows an inverse quadratic dependence on temperature $T$; the maximum low-field intrinsic relaxation time for pure xenon at room temperature (measured here to be 4.6 h, in agreement with previous work) increases by more than 60% for $T = 100$ °C. The dominant extrinsic relaxation is mediated by collisions with the walls of the glass container. Wall relaxation was studied in silicone-coated alkali-metal-free cells, which showed long (many hours or more) and robust relaxation times, even at the low magnetic fields typical for spin-exchange optical pumping ($\approx 3$ mT).
The further suppression of wall relaxation for magnetic fields above a few tesla is consistent with the interaction of $^{129}$Xe with paramagnetic spins on or inside the surface coating. At 14.1 T and sufficiently low xenon density, we measured a relaxation time $T_1 = 99$ h, with an inferred wall-relaxation time of $170$ h. A prototype large storage cell (12 cm diam) was constructed to take advantage of the apparent increase in wall-relaxation time for cells with a smaller surface-to-volume ratio. The measured relaxation time in this cell at 3 mT and 100 °C was 5.75 h, approaching the 7.45 h intrinsic limit for this temperature. Such a cell (or one even larger) could be used to store hyperpolarized $^{129}$Xe produced by a flow-through polarizer/accumulator for up to three times longer than currently implemented schemes involving freezing xenon in liquid nitrogen.

5.3 Introduction

Noble-gas isotopes having non-zero nuclear spin may be optically polarized to levels approaching unity via the technique of spin-exchange optical pumping (SEOP) [2, 69], whereby the notoriously weak signal generated by nuclear moments is enhanced by several orders of magnitude. Even after several decades of work by many groups, hyperpolarized gases continue to be studied and applied in a wide variety of magnetic-resonance experiments; we cite a few recent examples [78, 79, 80]. In a typical implementation, circularly polarized laser light is incident on a glass cell containing a macroscopic amount of an alkali-metal (usually Rb), the noble gas, and a small quantity of nitrogen to promote collisional de-excitation of the excited states generated by resonant absorption of the laser light by the alkali-metal vapor at the first principle ($D_1$) electric-dipole transition [22]. (This corresponds to a wavelength of 795 nm for Rb.) The alkali-metal vapor density is controlled by adjusting the cell temperature from room temperature up to $\approx 500$ K in the presence of a macroscopic amount of alkali metal in the closed cell. The selection rule for absorption of circularly polarized light and collisional mixing of the excited-state magnetic sublevels lead to rapid and efficient spin polarization of the valence electron of the alkali-metal vapor. Collisions with noble-gas atoms then
lead to an exchange of angular momentum between the alkali-metal electron and the noble-gas nucleus. The time-dependent build-up of nuclear polarization $P_N(t)$ in such a sample that occurs while the laser is on given by:  

$$P_N(t) = \langle P_A \rangle \frac{\gamma_{se}}{\gamma_{se} + \Gamma} \left[ 1 - \exp \left( \frac{-t}{\gamma_{se} + \Gamma} \right) \right], \quad (5.1)$$

where $\langle P_A \rangle$ is the time- and volume-averaged alkali-metal polarization, $\gamma_{se}$ is the spin-exchange rate, and $\Gamma$ is the longitudinal relaxation rate of the noble gas due to all other mechanisms. It is clear from Eq. (5.1) that $\Gamma$ limits the ultimate nuclear polarization for a fixed value of $\gamma_{se}$, the latter being limited by available laser power and the photon efficiency (the number of polarized nuclei produced per photon absorbed in the cell volume) [8] for a given alkali-metal–noble-gas pair and laser/cell geometry, whereby one generally maintains $\langle P_A \rangle$ close to unity. An understanding of the mechanisms responsible for the relaxation rate $\Gamma$ is thus essential to the efficient production of hyperpolarized gases.

While SEOP is typically used to polarize either of the stable spin-1/2 noble-gas isotopes, $^3$He and $^{129}$Xe, we are concerned in this work specifically with the relaxation mechanisms that limit the polarization of $^{129}$Xe. The relaxation rate $\Gamma$ may be written [81]:

$$\Gamma = \Gamma_t + \Gamma_p + \Gamma_g + \Gamma_w, \quad (5.2)$$

where $\Gamma_i = \Gamma_t + \Gamma_p$ is the intrinsic rate due to the sum of contributions from transient and persistent Xe$_2$ dimers; and $\Gamma_e = \Gamma_g + \Gamma_w$ is the extrinsic rate due to the sum of contributions from atomic diffusion through gradients in the applied magnetic field [30, 71] and interactions with the cell surface (wall relaxation). In most cases involving SEOP of xenon, some combination of $\Gamma_p$ and $\Gamma_w$ dominates the relaxation. For xenon densities as low as 0.1 amagat, $\Gamma_g$ is usually negligible [81], although there is size limitation for hyperpolarized-xenon storage cells in a given Helmholtz geometry due to this mechanism (see Sec. 5.6.5). For xenon densities $\approx 1$ amagat and larger, $\Gamma_t$ sometimes makes a small but non-negligible contribution.

\footnote{In Eq. (5.1) we have ignored the anomalous excess relaxation that scales with alkali-metal density recently observed for SEOP of $^3$He [25].}
to the total relaxation rate. Based on the present and previous work [44, 47, 81], we have developed a semiempirical formula for the intrinsic relaxation rate $\Gamma_i^{-1}$ of $^{129}\text{Xe}$ as a function of xenon density $[\text{Xe}]$ (amagats), temperature $T$ (Kelvins), applied magnetic field $B_0$ (Tesla), and gas composition. This formula applies for $[\text{Xe}] > 0.3$ amagat at all reasonable values of $B_0$:

$$\Gamma_i = \frac{[\text{Xe}]}{56.1\text{ hr} \left( \frac{T_0}{T} \right)^{1/2} + \frac{1}{4.59\text{ hr} \left( \frac{T_0}{T} \right)^2} \left[ 1 + (3.65 \times 10^{-3})B_0^2 \right] \left( 1 + r \frac{[B]}{[\text{Xe}]} \right)^{-1}}$$

(5.3)

where the first term is due to persistent dimers and the second is due to transient dimers; $T_0 = 293$ K, $[B]$ is the density of a second gas in the mixture, and $r \equiv k_B/k_{Xe}$ is the ratio of the persistent-dimer breakup coefficient for the second gas to that for xenon. We have measured $r = 0.51$ for nitrogen, which, along with helium, is most often present with xenon in SEOP situations. For helium, Chann, et al. have measured $r = 0.25$. The transient-dimer term in Eq. (5.3) is based on the results of Moudrakovski, et al. [44]; we have estimated its temperature dependence by considering that, in the weak-interaction limit, the probability for a spin transition is approximately proportional to the rate of binary collisions and to the square of the collision duration. Hence, we should have $\Gamma_t \propto 1/v$, where $v \propto T^{1/2}$ is the mean thermal velocity of the xenon atoms. We have neglected here any relaxation due to binary collisions with other molecules besides xenon; to our knowledge, only relaxation due to paramagnetic oxygen has been measured[84]. The uncertainty in the relaxation time calculated from Eq. (5.3) is about 10%.

Longitudinal relaxation also plays a key role in the accumulation and storage of hyperpolarized gases. Storage times of several hours or more are directly relevant to applications such as magnetic resonance imaging (MRI), where the gas must often be transported to the MRI scanner with minimal polarization loss. In the case of $^{129}\text{Xe}$, a relatively long longitudinal relaxation time $T_1 \equiv \Gamma^{-1}$ is also important for the accumulation stage in a flow-through xenon polarizer [11, 12], the current state-of-the-art scheme for the versatile production of liter-quantities of highly polarized $^{129}\text{Xe}$ for any application. In these devices, a gas mixture lean in xenon is passed continuously through a glass cell, in which it is polarized by SEOP with a laser, and
subsequently frozen as a polycrystalline solid at 77 K in a liquid-nitrogen trap. This basic scheme has proven effective in dealing with the inherently low (7%) Rb-Xe spin-exchange efficiency, i.e., the rate at which angular momentum is transferred to the noble-gas nucleus divided by the rate at which it is lost by the alkali-metal atoms [28]. The source of this low efficiency is the strong spin-rotation interaction of the rubidium valence electron with the electron cloud of the xenon atom, whereby \( \langle P_A \rangle \) begins to plummet for xenon densities \([\text{Xe}] > 1\) amagat. Hence, \(^{129}\text{Xe}\) (unlike \(^3\text{He}\)) is not readily polarized in large batches at high density. Cryogenic accumulation of xenon as it flows out of the polarizing cell serves two purposes. First, it separates out the other gases, typically nitrogen and helium, making it possible to prepare pure xenon samples. Second, since most or all of the polarization survives the phase transition [12, 82], large quantities of hyperpolarized xenon can be accumulated from the low-density flow and stored for times on the order of \(T_1 \approx 2.5\) h at 77 K in an applied magnetic field \(B_0 \geq 0.1\) T [77] before being revolatilized. This method evolved, in part, because of the reliable 2.5 h storage time, although it became clear in later work the gas must be quickly and completely frozen to 77 K [12]; at higher temperatures, particularly those approaching the xenon melting point (161 K), relaxation rates increase dramatically due to vacancy diffusion in the solid [45], resulting in polarization losses in the freeze/thaw cycle.

Accumulation and storage of hyperpolarized xenon near room temperature in the gas phase is desirable in that it would eliminate the need for large magnetic fields, the cryogenic apparatus, and freeze/thaw cycles. The historical problem with this approach has been that \(^{129}\text{Xe}\) gas-phase relaxation is relatively fast and notoriously irreproducible, whereby wall relaxation plays a crucial role. Some progress was made in understanding wall interactions, particularly in cells treated with silane- or siloxane-based surface coatings in fields on the order of 1 mT [38, 37], where \(T_1 = 20-60\) min was observed. Others observed \(T_1 > 3\) h for some coated cells at 9.4 T, an indication that wall relaxation is suppressed at high field [44, 76]. These studies all had in common relatively small cells (1-3 cm dia.) that contained macroscopic amounts of rubidium along with the coating, meaning that the gas was
polarized by SEOP in the same cell in which $T_1$ was subsequently measured. While it is well known that $^3$He relaxation on uncoated glass is reliably suppressed by the presence of alkali metal [31, 83, 10], this is apparently not the case for $^{129}$Xe, where in fact, the interaction of the alkali metal with the surface coating, particularly when heated to 100 °C or more during SEOP can lead to erratic and generally increasing relaxation rates [81]. Evidence presented here and in our previous work [81] strongly indicates that wall relaxation in xenon cells is not relaxation-site limited at the usual SEOP densities, i.e., xenon atoms are not inhibited from interacting with wall sites due to their occupation by other xenon atoms. Hence, in the regime for which the wall contribution to $T_1$ is long compared to the mean time for a xenon atom to diffuse across the cell (easily realized in all of our experiments and most others), the wall-relaxation rate is independent of [Xe] and depends linearly on the surface-to-volume ratio $S/V$. This reasoning has led us to take a closer look at larger-diameter coated cells containing no alkali metal as a way of reducing the $^{129}$Xe gas-phase wall-relaxation rate.

Several years ago, Chann, et al. in the Wisconsin group first demonstrated gas-phase $^{129}$Xe relaxation due to persistent Xe$_2$ dimers [47]. These van der Waals molecules are formed in three-body collisions and have a mean lifetime $\tau_p \sim 1$ ns [47, 81] before being destroyed by another collision. The maximum relaxation time for a pure xenon sample due to this mechanism alone was shown to be $\approx 4$ h and independent of [Xe] for low applied magnetic field $B_0$ (a few millitesla). The density independence arises both because the fraction of xenon atoms bound in molecules and the molecular formation/breakup rate $\tau_p^{-1}$ have the same linear dependence on [Xe], and because the fast-fluctuation limit $\Omega^2 \tau_p^2 \ll 1$, where $\Omega$ is the $^{129}$Xe Larmor frequency, holds for all reasonable values of [Xe] and $B_0 < 1$ T; see Eq. (5.4) below. This density independence effectively mimics wall relaxation, and it has undoubtedly confounded some earlier work in measuring $\Gamma_w$, particularly since the minimum intrinsic rate $\Gamma_p$ is much larger than previously believed [44, 43]. Our group recently verified and extended this work at low [Xe] and $B_0 = 8.0$ T, which straddles the fast- and slow-fluctuation regimes. We showed that persistent-dimer
relaxation is strongly suppressed at this field for sufficiently low xenon densities ($\lesssim 0.1\ \text{amagat}$) and large magnetic fields. Indeed, we observed extraordinarily small gas-phase relaxation rates in our alkali-metal-free, coated cells, with measured $T_1$’s exceeding 25 h in some cases.

Continued progress in the understanding of gas-phase relaxation of $^{129}\text{Xe}$ is paving the way for significant improvements in cell performance vis-à-vis hyperpolarized gas production, accumulation, storage, and transport for the various applications. In this work, we have extended our study of this relaxation to a wide range of applied magnetic fields and temperatures, with an eye towards a large-diameter ($\geq 20\ \text{cm}$) coated cell that could store several liters of hyperpolarized xenon with a $T_1 \geq 7\ \text{h}$ in an applied magnetic field of $\approx 3\ \text{mT}$, tripling the storage time of solid xenon at 77 K and eliminating the need for high-field cryogenic accumulation. The work is divided into three main parts: (1) The study of the magnetic suppression of the persistent-dimer mechanism in a range of magnetic fields from 1.5 T to 14.1 T. These data allowed us to deduce the relative strength of the spin-rotation (SR) and chemical-shift-anisotropy (CSA) interactions via the $B_0^2$-dependence of the CSA contribution. This, in turn, generates an independent estimate for the maximum low-field pure-xenon relaxation time of $T_1 = 4.6\ \text{h}$. (2) The study of wall relaxation over the same range of $B_0$ and further on down to 3 mT. This is made possible by a thorough understanding of the persistent-dimer mechanism with which wall relaxation often competes. Wall-relaxation times in our alkali-metal-free coated cells varied from $\approx 10\ \text{h}$ at 3 mT to $> 100\ \text{h}$ at 14.1 T, suggesting a high-field decoupling of a wall mechanism that has to do with interactions of $^{129}\text{Xe}$ atoms with unpaired electrons at the surface or inside of the coating [38]. (3) The study of the temperature dependence of the persistent-dimer rate $\Gamma_p$ in the fast-fluctuation limit in the range of 20-100 °C. The inverse-square dependence of $\Gamma_p$ on temperature $T$ is consistent with our theoretical model and results in an increase of $\approx 60\%$ in the relaxation time due to persistent dimers at 100 °C compared to room temperature.
5.4 Theory

Intrinsic longitudinal relaxation of $^{129}$Xe gas in the SEOP regime of pressure and temperature is dominated by the SR [48] and CSA [49, 50] interactions modulated by the formation and breakup of persistent Xe$_2$ dimers in three-body collisions. The theory is discussed in detail in Refs. [47, 81]. In brief, the persistent-dimer relaxation rate is given by

$$\Gamma_p = 2K[Xe](M^{\text{sr}} + M^{\text{csa}})\left(\frac{\tau_p}{1 + \Omega^2\tau_p^2}\right),$$  \hspace{1cm} (5.4)

where $K \equiv [\text{Xe}_2]/[\text{Xe}]^2$ is the chemical equilibrium coefficient, $M^{\text{sr}}$ and $M^{\text{csa}}$ are the interaction strengths (second moments) of the SR and CSA interactions, respectively, and $\tau_p^{-1}$ is the molecular formation rate (equal to the breakup rate in chemical and thermal equilibrium). This equation can be reparameterized and added to the wall relaxation rate $\Gamma_w$ to obtain for the total relaxation rate:

$$\Gamma([G]) = \Gamma_w + 2\mathcal{K}(M^{\text{sr}} + M^{\text{csa}})\left(\frac{\alpha k_\alpha[G]^2}{k_\alpha^2[G]^2 + \Omega^2}\right),$$  \hspace{1cm} (5.5)

where $[G]$ is the total gas density, $\alpha \equiv [\text{Xe}]/[G]$ is the xenon concentration, and $k_\alpha$ is the molecular breakup coefficient for the particular gas composition. In this work, nitrogen is the only other gas in the mixture, and

$$\frac{1}{\tau_p} = k_\alpha[G] = k_{\text{Xe}}[\text{Xe}] + k_N[N_2],$$  \hspace{1cm} (5.6)

where $k_{\text{Xe}}$ and $k_N$ are the breakup coefficients for xenon and nitrogen as third bodies, respectively.

At high gas densities, in the fast-fluctuation limit of Eq. (5.5) $\Omega^2 \ll k_\alpha^2[G]^2$, the persistent-dimer relaxation rate is independent of $[G]$ for a given gas composition, as first observed by Chann, et al. [47] for $B_0 = 2.0$ mT and also by our group for $B_0 = 8.0$ T [81]. At lower densities the rate is suppressed due to the increasing relevance of the $\Omega^2$ term in Eq. (5.5). Whereas $M^{\text{sr}}$ is independent of the applied field $B_0$ [48], $M^{\text{csa}}$ is proportional to $B_0^2$. Hence, acquiring a set of relaxation curves as a function of $[G]$ that are fitted to Eq. (4.13), where each curve is at one of several values of $B_0$, allows $M^{\text{sr}}$ to be separated from $M^{\text{csa}}$. 
The temperature dependence to \( \Gamma_p \) comes predominantly through chemical equilibrium coefficient \( K \) and the mean persistent-dimer lifetime \( \tau_p \) in Eq. (5.4). The chemical equilibrium coefficient is given by [41]

\[
K = \frac{1}{2} \left( \frac{h^2}{2\pi \mu kT} \right)^{3/2} Z, \tag{5.7}
\]

where \( h \) is the Planck constant, \( k \) is the Boltzmann constant, \( Z = \sum_i (2N_i + 1)e^{-E_i/kT} \) is the partition function for the internal ro-vibrational states of the \( \text{Xe}_2 \) dimer, and \( \mu \) is its reduced mass. The portion of this expression that multiplies \( Z \) is the ratio of translational partition function for a single dimer to that for two free atoms in the classical high-temperature and low-density limit. We neglect here the weak temperature dependence of \( Z \) at room temperature and above, where \( T > E_i/k \approx 280 \text{ K} \) [42]. Classically, \( \tau_p \) is inversely proportional to the mean relative velocity of the gas molecules, which is proportional to \( T^{-1/2} \). We treat here only the fast-fluctuation limit, \( \Omega^2 \tau_p^2 \ll 1 \), relevant to high-density xenon storage cells in small magnetic fields. Since the product \( K\tau_p \) appears in this limit, we expect the relaxation rate \( \Gamma_p \) to depend on \( T^{-2} \). We have ignored here any temperature dependence of the collisional cross sections or of the interaction strengths \( M^{sr} \) and \( M^{csa} \).

### 5.5 Experimental Procedure

Many of the procedures described here are very similar or identical to those described in detail in our previous work [81]. Most of the measurements of the longitudinal relaxation time \( T_1 \) for \(^{129}\text{Xe} \) in xenon gas were done in a single borosilicate-glass (Pyrex) “measurement” cell, designated 113B. It is a 6.7 cm diam sphere connected via a 10 cm length of capillary (0.5 mm diam) to a glass valve and sidearm used for evacuation and refilling. A 4 cm length of 6 mm glass tubing (the stem) extends from the sphere opposite the capillary entrance. The cell contains no alkali-metal, but the interior was coated with dimethyldichlorosilane, which inhibits wall relaxation in a manner similar to silicone coatings previously introduced [37, 38].
Hyperpolarized xenon was generated in one of several “pumping” cells, which have a geometry similar to the measurement cells and also contain Rb metal for SEOP. Our high-vacuum gas-handling system [55] is used to measure cell volumes, evacuate cells, and to refill pumping cells with a precise mixture of xenon (isotopically enriched to 86%; Spectra Gases, West Branchburg, NJ) and nitrogen. Unless otherwise noted, the xenon concentration $\alpha = 0.91 \pm 0.02$ throughout this work, where the error reflects variation in multiple preparations of the mixture in the pumping cells. The effects of varying $\alpha$ are consistent with the theory presented above and were studied previously [81, 47].

Xenon gas, polarized by SEOP to $\approx 10\%$ in a pumping cell, was then transferred (at the known value of $\alpha$) to the measurement cell using a glass transfer manifold and mechanical vacuum pump for evacuating dead space. In the case of the 1.5 T and 8.0 T fields, the cell was immediately inserted into a NMR probe and the probe assembly was inserted into the magnet. In the case of the 4.7 T and 14.1 T fields, the polarized measurement cell was transported from the Department of Physics across campus in a portable 2 mT battery-powered solenoidal coil to an NMR facility in the Department of Chemistry. (Less than 10% of the magnetization was lost during transport.) All magnets (with the exception of the 1.5 T magnet) had a wide-bore (89 mm diam) vertical configuration. The probes were capacitively tuned saddle coils (one to two turns) placed along the stem of the cell; the respective resonance frequencies corresponded to the $^{129}$Xe gyromagnetic ratio of 11.8 MHz/T. In the 1.5 T field (provided by a 30 cm diam horizontal-bore imaging magnet), the cell was situated horizontally at the magnet isocenter with a surface-coil probe placed underneath it.

NMR measurements were conducted with an Aries (Tecmag) spectrometer with a homebuilt rf section (1.5 T and 8.0 T), Chemagnetics CMX200 (4.7 T), and Varian Infinityplus 600 (14.1 T). For measurements above room-temperature, the 8.0 T probe was insulated and heated with air flowing across a filament heater located away from the magnet. In addition, several low-field ($B_0 \approx 3$ mT) measurements were made using a homebuilt low-frequency spectrometer [58], whereby the cell and
NMR probe were placed in an oven (similarly heated with flowing hot air) located at the isocenter of a Helmholtz pair. In all cases the longitudinal relaxation rate $\Gamma$ was measured by periodic acquisition of a free-induction decay (FID) induced by a single rf pulse. A negligible fraction of the magnetization was destroyed by each pulse. Either the height or the area under the peak of each Fourier-transformed FID was plotted as a function of time and a least-squares fit was used to extract $\Gamma$.

5.6 Results and Discussion

5.6.1 Field Dependence at Room Temperature

The relaxation rate $\Gamma$ was measured as a function of total gas density $[G]$ for the four different magnetic fields. The data were fit in each case to Eq. (5.5) using the appropriate value of the Larmor frequency $\Omega$, with the wall-relaxation rate $\Gamma_w$ and the interaction-strength term $2K(M^{sr} + M^{csa})$ extracted as free parameters; see Table 5.1. Since the xenon concentration $\alpha$ and, hence, the breakup coefficient $k_\alpha$ are field-independent, the value

$$k_\alpha = (3.54 \pm 0.28) \times 10^{-10} \text{ cm}^3/\text{s},$$

was determined from a global fit to the four data sets, and this value was then used as a fixed parameter for each of the fits to the individual data sets. The plot in Fig. 5.1 shows the persistent-dimer rate $\Gamma_p = \Gamma - \Gamma_w$ plotted vs. $[G]$ for all four fields along with the respective best fits. The errors in the free parameters were, in general, underestimated by our non-linear fitting routines and had to be handled with some care. They were determined for a given field and temperature by allowing $k_\alpha$ to vary over its error range and observing the effect in the fit on $2K(M^{sr} + M^{csa})$ and $\Gamma_w$.

The effect of the CSA interaction is shown in Fig. 5.1 by the monotonic increase of the asymptotic high-density rate with increasing magnetic field. To determine the relative contributions of the SR and CSA interactions, the interaction-strength parameter $2K(M^{sr} + M^{csa})$ is plotted vs. the square of the applied field $B_0$ in Fig. 5.2. The data are consistent with a linear $B_0^2$ dependence. The slope and intercept from a linear least-squares fit yield, respectively,
Figure 5.1. Plot of the room-temperature $^{129}$Xe persistent-dimer relaxation rate vs. total gas density for a fixed xenon concentration $\alpha = 0.912$ at four different applied magnetic fields. The wall relaxation rate $\Gamma_w$ and the product $2\mathcal{K}(M^\text{sr} + M^\text{csa})$ are extracted from fits of the measured relaxation rates $\Gamma([G])$ to Eq. (5.5) for each field (see Table 5.1). The corresponding value of $\Gamma_w$ has been subtracted from all the data sets in this plot to show clearly the behavior of the persistent-dimer rate $\Gamma_p$: The high-density fast-fluctuation limit results in a density-independent relaxation rate (asymptote) that increases with field due to the increasing strength of the CSA interaction (see Fig. 5.2); the magnetic suppression of the persistent-dimer mechanism with decreasing density starts at higher densities and happens more gradually for higher fields. The field-independent molecular breakup coefficient $k_\alpha = (3.54 \pm 0.28) \times 10^{-10}$ cm$^3$/s was extracted from a global fit to all four data sets.
Table 5.1. Free parameters extracted from the fits of the data shown in Fig. 5.1 to Eq. (5.5). Errors are given in parentheses for the least significant figure(s).

<table>
<thead>
<tr>
<th>$B_0$ (T)</th>
<th>$2\kappa(M^{sr} + M^{csa})$ ($10^{-14}$ cm$^3$/s$^2$)</th>
<th>$\Gamma_w$ ($10^{-6}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>2.02(17)</td>
<td>18.5(9)</td>
</tr>
<tr>
<td>4.7</td>
<td>2.53(14)</td>
<td>4.1(5)</td>
</tr>
<tr>
<td>8.0</td>
<td>2.87(15)</td>
<td>3.70(8)</td>
</tr>
<tr>
<td>14.1</td>
<td>3.86(9)</td>
<td>1.60(19)</td>
</tr>
</tbody>
</table>

$$2\kappa M^{csa} = [(8.26 \pm 0.73) \times 10^{-17} \text{ cm}^3/\text{s}^2 \text{T}^2] B_0^2,$$  

$$2\kappa M^{sr} = (2.24 \pm 0.10) \times 10^{-14} \text{ cm}^3/\text{s}^2.$$  

The inset graph to Fig. 5.2 shows the fraction of the total interaction strength that is due to the SR interaction as a function of $B_0$; the SR and CSA interactions contribute equally for $B_0 \approx 16.5$ T. A correction to the empirical formula based on this result appears as a factor in the persistent-dimer term of the empirical formula in Eq. (5.3). Moudrakovski, et al. [44] made a similar measurement at very high xenon densities (> 30 amagat), in the transient-dimer regime, and found that the SR and CSA interactions contribute equally for $B_0 = 12$ T. Although our measurement was made at much lower density in the persistent-dimer regime, there is no apparent reason that the relative strength of the two interactions should be different in the two cases.

### 5.6.2 Minimum Low-Field Relaxation Rate

The result in Eq. (5.10) can be used to calculate the density-independent persistent dimer relaxation rate for pure xenon gas in the high-density low-field limit, where only the SR interaction contributes; this is almost always the relevant regime for SEOP. Here we follow the notation originally introduced by Chann, et al. [47] for this characteristic limiting rate:

$$\Gamma_{vdW}^{Xe} = \frac{2\kappa M^{sr}}{k_{Xe}}.$$  

We use the value of $k_{\alpha}$ in Eq. (5.8) and the value of the nitrogen breakup coefficient $k_N = (1.9 \pm 0.2) \times 10^{-10} \text{cm}^3/\text{s}$ measured in our previous work [81] in Eq. (5.6) to
Figure 5.2. Plot of $2K(M^\text{sr} + M^\text{csa})$ extracted from the fits in Fig. 5.1 (see Table 5.1) vs. the square of the applied magnetic field $B_0$. A linear fit to the data yields the relative contributions of the SR and CSA interactions as a function of $B_0$, as given in Eqs. (5.9) and (5.10), where the intercept is proportional to the field-independent spin-rotation interaction strength $M^\text{sr}$, which can then be used to deduce the limiting low-field pure-xenon relaxation rate due to persistent dimers; see Sec. 5.6.2. The inset graph shows the fraction of the total interaction strength due to SR as a function of $B_0$; the interactions contribute equally at $B_0 \approx 16.5$ T.
calculate $k_{Xe} = (3.70 \pm 0.31) \times 10^{-10} \text{cm}^3/\text{s}$. This represents only a small correction to our value of $k_\alpha$, since our samples are over 90% xenon. Finally, using Eqs. (5.10) and (5.11), we obtain

$$\Gamma_{\text{vdW}}^{Xe} = (6.05 \pm 0.57) \times 10^{-5} \text{ s}^{-1}, \quad (5.12)$$

corresponding to a relaxation time of $4.59 \pm 0.43$ h, which is the value that appears in the persistent-dimer term of Eq. (5.3). This value is in good agreement with 4.1 h measured by Chann, et al. [47]. It is smaller than 5.45 h deduced from measurements in our previous work [81]; however, most of this discrepancy can be traced to using different data to calculate the relative contributions of the SR and CSA interactions to the total interaction strength. Our previous work was done almost exclusively at $B_0 = 8.0$ T, where we took the measured rate and divided it by the fraction of the interaction strength that is due to the SR interaction in order to obtain a value appropriate in the low-field limit. This fraction was determined from the measurements of Moudrakovski, et al. [44], to be 71% at 8.0 T. A similar calculation based on the data presented here [see Eqs. (5.9) and (5.10)] yields an 81% contribution for the SR interaction at 8.0 T, which would lower the relaxation time in our previous work [81] to 4.8 h, in much better agreement with the present result.

### 5.6.3 Temperature Dependence

We observed a dependence of the relaxation rate on temperature with a decrease in relaxation rate with increasing temperature at both 1.5 T and 8.0 T. Figure 5.3 shows this temperature dependence in our 8.0 T data. The same behavior was observed at 1.5 T. It was expected that an increase in temperature would inhibit molecular relaxation mechanisms as molecular formation would be suppressed at elevated temperatures.

A more quantitative description of the temperature dependence of persistent-dimer modulated relaxation in $^{129}$Xe is found by measuring the relaxation rate at a fixed density over a range of temperatures. To this end, we performed a series of individual relaxation measurements in temperature range 20-100 °C at 8.0 T for...
Figure 5.3. Plot of measured 8.0 T $^{129}$Xe relaxation rates vs. total gas density as a function of temperature with xenon concentration $\alpha = 0.912$. The data are fit to Eq. (5.5) with $2\mathcal{K}(M^{ss} + M^{csa})$ as a free parameter. The wall relaxation rate $\Gamma_{\text{wall}}$ was measured at 293 K and is fixed to that value at higher temperatures. The contribution of wall relaxation is small at room temperature and will get smaller as temperature increases. Values for the molecular breakup coefficient $k_{\alpha}$ are extracted from global fits of data at each temperature.
\[ [G] = 0.35 \text{ amagat}, \text{ well into the density-independent fast-fluctuation limit. Relaxation due to transient dimers is negligible for this low density, but the measured rates at all temperatures have been corrected by subtracting the room-temperature wall-relaxation rate at 8.0 T (see Table 5.1). The higher-temperature points are likely over-corrected, since } \Gamma_w \text{ should become smaller at higher temperatures due to decreasing residence time on the coating, assuming that this time is governed by an Arrhenius relationship} [38]. \text{ However, the correction is small in any case, corresponding to a relaxation time of } \approx 75 \text{ h, so we use it as a best approximation at all temperatures. The corrected data are plotted in Fig. 5.4 vs. the inverse-squared absolute temperature. The one-parameter least-squares linear fit to this data (forced through the origin) supports the simple theory of a linear dependence of the persistent-dimer relaxation rate on } 1/T^2, \text{ which comes from the temperature dependence of the product } K\tau_p \text{ in the fast-fluctuation limit of Eq. (5.4). The slope of fitted line is } 6.2 \pm 0.2 \text{ s}^{-1} K^2. \text{ The slope can be corrected for the low-field limit by multiplying by 81\%, the fraction of the interaction strength due to SR at 8.0 T (see end of previous section and Fig. 5.2). Using the corrected slope to calculate } \Gamma_p \text{ at } T = 293 \text{ K yields } 5.85 \times 10^{-5} \text{ s}^{-1}, \text{ in good agreement with the minimum relaxation rate for pure xenon given in Eq. (5.12). We performed these measurements at 8.0 T to clearly separate } \Gamma_p \text{ from any temperature-dependent wall relaxation, but the results should be equally valid in the low-field limit and contribute to longer overall relaxation times at higher temperatures. Based on these results, we include the factor of } (T/T_0)^{1/2} \text{ in the persistent-dimer term of Eq. (5.3), which predicts an intrinsic maximum } T_1 \text{ for pure xenon of 7.45 h at } T = 100 \degree C.\]

### 5.6.4 Wall Relaxation

The extracted wall-relaxation rates } \Gamma_w \text{ in Table 5.1 decrease dramatically with increasing applied field. At 14.1 T, in the low-density regime where the persistent-dimer rate is highly suppressed, we measured } T_1 = 99.4 \text{ h for } [G] = 0.012 \text{ amagat. The wall-relaxation time extracted from the fit is an extraordinary 174 h. The plot of recorded NMR signal intensity vs. time for this measurement is shown in Fig. 5.5}
Figure 5.4. Plot of the $^{129}$Xe persistent-dimer relaxation rate $\Gamma_p$ at 8.0 T vs. $1/T^2$, where the absolute temperature $T$ ranges between 293 K and 373 K. The measured rates were corrected by subtracting the relatively small room-temperature wall-relaxation rate $\Gamma_w$. The quality of the one-parameter fit forced through the origin indicates that this simple inverse-square model for the temperature dependence of $\Gamma_p$ based on the arguments in Sec. 5.4 is reasonably valid at and above room temperature.
and shows that the slope actually trends slightly downward over the course of this measurement, corresponding to $T_1 = 105$ h for the first 50 h and $T_1 = 82$ h for the last 45 h. This may have to do with a gradual increase in oxygen concentration (due to very slow outgassing or leakage) into the cell over the course of the long measurement. If this gradual increase in relaxation rate were due solely to collisions with paramagnetic oxygen atoms, it would correspond to an oxygen partial pressure of $\approx 10^{-3}$ mbar [84] developing over the course of the measurement.

Figure 5.6 shows a plot of $\Gamma_w$ vs. $B_0$ at room temperature. In an attempt to obtain a more complete picture of the field-dependence of $\Gamma_w$, data were acquired for three additional values of the applied field $B_0$ made in an electromagnet (0.91 T, and 2.0 T) and a Helmholtz pair (2.8 mT). For these three data points, $\Gamma_w$ was not extracted from a fit. Instead, cell 113B was filled with nearly pure xenon ($\alpha \approx 1$) from a flow-through xenon polarizer (built in our laboratory) to a density $\approx 1$ amagat. In this density and magnetic-field regime, the persistent dimer rate $\Gamma_p = \Gamma_{\text{vdW}}^{\text{Xe}}$. According to Eq. (5.5), $\Gamma_w$ was then determined by subtracting our deduced value of $\Gamma_{\text{vdW}}^{\text{Xe}}$ in Eq. (5.12) from the measured rate for each of the three additional values of $B_0$.

We model the high-field wall relaxation as

$$\Gamma_w = M_w^w \left( \frac{\tau_c}{1 + \Omega^2 \tau_c^2} \right),$$

(5.13)

where $M_w^w$ is the strength of the wall interaction and $\tau_c^{-1}$ is its correlation time, presumed to be due to fluctuating paramagnetic spins at the surface. This is a simplified version of the model proposed by Driehuys, et al. [38] based on the expected field dependence of the relaxation due to the coupling of the $^{129}\text{Xe}$ spin $I$ with a wall spin $S$ [85], which contains additional terms in the power spectrum of Eq. (5.13) involving the Larmor frequency of the spin $S$ in addition to the $^{129}\text{Xe}$ Larmor frequency $\Omega$. In the range of applied field $B_0 < 10$ mT studied in that work, Driehuys, et al. [38] were able to fit their relaxation data to a sum of two terms involving protons and paramagnetic sites, respectively, as the spin $S$. They determined that $^{129}\text{Xe}$ relaxes due to coupling with the protons in the
Figure 5.5. Plot of NMR signal intensity vs. time for cell 113B at room temperature in an applied field of 14.1 T. The cell contains xenon at 12.0 mbar and nitrogen at 1.09 mbar. To our knowledge, this is by far the longest gas-phase relaxation time ever recorded for $^{129}\text{Xe}$ and results from the simultaneous suppression of the intrinsic persistent-dimer mechanism and the wall-relaxation mechanism at 14.1 T.
surface coating with an associated correlation time \( \tau_c \approx 8 \, \mu s \). The proton-induced relaxation, which was directly verified with a double-resonance experiment, cannot be explained by a simple adsorption model; rather, xenon atoms must be trapped within the coating for times \( \geq 8 \, \mu s \). The second term yielded a much shorter correlation time \( \tau_c \approx 8 \, \text{ns} \), which is a reasonable relaxation time for paramagnetic surface spins at room temperature.

For the much larger applied fields in our work, the relaxation due to protons is completely suppressed. For relaxation due to paramagnetic sites, the terms in the power spectrum involving the paramagnetic resonance frequency are negligible, due to the \( \approx 10^3 \) larger gyromagnetic ratio for electrons compared to \(^{129}\text{Xe} \), leading to the simple form of Eq. (5.13). A least-squares fit of the data to this functional form is also shown in Figure 5.6, and yields a correlation time \( \tau_c \approx 4 \, \text{ns} \) (corresponding to a characteristic decoupling field \( \approx 3 \, \text{T} \)), in reasonable agreement with the predicted correlation time for interaction with paramagnetic spins at the surface or inside of the coating.

### 5.6.5 Low-Field Storage Cells

To explore the implications of the above results for a practical low-field hyperpolarized xenon storage cell at ambient pressures, additional experiments were done at \( B_0 \approx 3 \, \text{mT} \) at both room temperature and \( T = 100 \, ^\circ\text{C} \). Again, the flow-through xenon polarizer provided nearly pure xenon (\( \alpha = 1 \)), and cells were filled to a density \( \approx 1 \, \text{amagat} \). We also used three additional alkali-metal-free coated cells. Two of these (designated 105B and 113A) were similar in size to cell 113B; the other was also similar except that its diameter (12.7 cm) is double that of the other cells. The cells all showed increases in the measured relaxation time \( T_1 \) of 50-100% at the elevated temperature. Our results are summarized in Table 5.2, which displays measured relaxation times \( T_1 \) and the inferred wall-relaxation times based on subtracting from the measured rate both \( \Gamma_p \) and \( \Gamma_t \) (the latter is a 10% correction at most), as calculated from Eq. (5.3). It is difficult to extract precise information concerning wall-relaxation times, particularly at the elevated temperature, since \( \Gamma_p \)
Figure 5.6. Plot of room-temperature $^{129}$Xe wall-relaxation rate $\Gamma_w$ as a function of applied magnetic field $B_0$. The points with small error bars are extracted from the density-dependence curves shown in Fig. 5.1; the weighted fit to Eq. (5.13) is almost entirely determined by these points. The other points result from single measurements on pure xenon in the fast-fluctuation limit, where the persistent dimer relaxation rate $\Gamma_{\text{vdW}}^{\text{Xe}} = (6.05 \pm 0.57) \times 10^{-5}$ s$^{-1}$ has been subtracted from the measured relaxation rate. The error propagation from this subtraction leads to much larger error bars. The fit yields a correlation time for the wall interaction of $\approx 4$ ns, consistent with interaction of $^{129}$Xe with fluctuating paramagnetic sites on or in the wall coating.
Table 5.2. Low-field relaxation times (in hours) of four cells at both room temperature and 100 °C. The first three have a diameter ≈ 6.7 cm and were measured at $B_0 = 2.8$ mT; the last cell has a diameter ≈ 12.7 cm and was measured at $B_0 = 3.1$ mT. The cells all contained pure xenon at the indicated density (in amagats). Uncertainties are given in parentheses for the least significant figure(s). The last two columns show the room-temperature wall-relaxation time derived from subtracting the relevant persistent- and transient-dimer rates [Eq. (5.3)] from the measured rate. The elevated temperature increases the measured $T_1$ by 50-100%.

<table>
<thead>
<tr>
<th>Cell</th>
<th>[Xe]</th>
<th>$T_1$ (293 K)</th>
<th>$T_1$ (373 K)</th>
<th>$T_1$(wall) (293 K)</th>
<th>$T_1$(wall) (373 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>105B</td>
<td>1.5(1)</td>
<td>2.40(5)</td>
<td>3.66(11)</td>
<td>5.8(8)</td>
<td>8.7(1.1)</td>
</tr>
<tr>
<td>113A</td>
<td>≈ 1.5</td>
<td>1.30(4)</td>
<td>2.45(5)</td>
<td>1.9(1)</td>
<td>4.0(2)</td>
</tr>
<tr>
<td>113B</td>
<td>1.1(1)</td>
<td>2.57(15)</td>
<td>4.53(13)</td>
<td>6.6(1.3)</td>
<td>14.5(3.0)</td>
</tr>
<tr>
<td>139</td>
<td>0.7(1)</td>
<td>3.40(22)</td>
<td>5.75(23)</td>
<td>16(7)</td>
<td>35(18)</td>
</tr>
</tbody>
</table>

and $\Gamma_w$ are comparable at these low fields (unlike at $B_0 = 8.0$ T) and both decrease with increasing temperature (see Sec. 5.6.3 above). However, it is clear that a significant improvement was realized for the cell with larger $S/V$; the measured $T_1$ in this cell of 5.75 h at $T = 100$ °C approaches our predicted limit of 7.45 h and is a factor of two or more longer than any previously recorded $^{129}$Xe relaxation time in the low magnetic fields typical of SEOP.

Even larger cells with a correspondingly larger xenon storage capacity are possible; the size will eventually be limited by magnetic field gradients far away from the center of a pair of Helmholtz coils, but this limit is not terribly stringent for xenon. As a guideline, we assume Helmholtz pair of radius (and separation) $R$ and a cell having radius no larger than $R/3$. We have estimated the gradient-induced relaxation for such a cell as

$$\Gamma_g \approx 0.01 \frac{D}{R^2}. \quad (5.14)$$

Although the calculation is done for an ideal Helmholtz geometry (actual gradients might be larger), the estimate in Eq. (5.14) applies only to the outer edge of a cell whose radius is as large as $R/3$, and so remains fairly conservative for the entire cell. For [Xe] = 0.1 amagat at (a conservative estimate of the density during the filling process), $D = 8.2 \times 10^{-5}$ m$^2$/s at 100 °C [87]. If we take $R = 0.50$ m, a 0.33 m diam spherical cell containing pure-xenon should have $\Gamma_g^{-1} \geq 85$ h from the
gradient mechanism alone; this time would increase by an order of magnitude as
the cell is filled to 1 amagat. Such a cell would have a 19 L storage capacity.

For completeness, we note that dilution of xenon with a second gas lowers
the rate $\Gamma_p$ significantly for those gases that can form and break up persistent
$\text{Xe}_2$ dimers with an efficiency comparable to Xe itself. Referring to Eq. (5.4), the
second gas decreases the persistent-dimer lifetime $\tau_p$ without changing the fraction
of xenon atoms bound in molecules. The effects of adding a second gas were studied
thoroughly by Chann, et al. [47] and in our previous work [81]. Nitrogen has
the largest breakup coefficient measured (besides xenon); $\Gamma_p$ is reduced by about
one-third for a 50-50 mixture. We have included the effects of a second gas in our
semi-empirical formula for the total intrinsic relaxation rate in Eq. (5.3).

In summary, we have presented a systematic study of both intrinsic persistent-
dimer relaxation and wall relaxation of $^{129}\text{Xe}$, including temperature and magnetic-
field dependence; we conclude that it should be possible to develop a xenon storage
cell that has a measured $T_1 \geq 7$ h at 3.0 mT and 100 °C for pure xenon at densities
up to a few amagats. These cells are silicone-coated but alkali-metal-free and show
relatively long and robust wall-relaxation times of up to tens of hours. They can be
utilized in state-of-the-art flow-through xenon polarizers, whereby storage times for
polarized xenon can be increased by a factor of three or more compared with state-
of-the-art cryogenic schemes, and cryogenic storage and associated freeze/thaw
cycles can be eliminated. We note that if producing pure hyperpolarized xenon
is required for a given experiment, then separation of xenon from other gases in the
mixture (which comes naturally with cryogenic accumulation) might be a limitation
of the room-temperature accumulation scheme proposed here. One approach would
be to use the cryogen for gas separation only, followed by immediate volatilization
and transfer to a storage cell. However, other cryogen-free separation schemes may
be possible: the use of a small gas centrifuge (on the order of 0.1 m diam) has
already been demonstrated for the continuous separation of methane from CO$_2$ on
the time scale of minutes [88, 89]; such a device utilizing suitable materials and/or
a surface coating that does not depolarize $^{129}\text{Xe}$ could presumably accomplish
continuous separation of xenon from the other much lighter gases typically found in a flow-through polarizer.

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REFERENCES


[86] See EPAPS Document No. TBD for a discussion of gradient-induced relaxation in a Helmholtz coil geometry. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.