Enhancement of ^{129}Xe polarisation by off-resonant spin exchange optical pumping

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Abstract

A high power narrow line width (38W, 0.09nm FWHM) external cavity diode laser is investigated for rubidium spin exchange optical pumping of ^{129}Xe. This tunable photon source has a constant line width, independent of operating power or wavelength within a 1 nm tuning range. When using this laser, an increase in the ^{129}Xe nuclear polarisation is observed when optically pumping at a lower wavelength than the measured Rb electron D_1 absorption. The exact detuning from D_1 for the highest polarisation is dependent upon the gas density. Furthermore, at high power and/or high Rb density, a reduction of the polarisation occurs at the optimum wavelength as previously reported in SEOP studies of ^{3}He which is consistent with high absorption close to the cell front face. These results are encouraging for moderate high throughput polarisation of ^{129}Xe in the mid pressure range of (0.5-2.0 amg).

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I. INTRODUCTION

Hyperpolarised ^{129}Xe is used in a diverse range of applications including NMR [1] and MRI [2, 3]. In MRI, hyperpolarised ^{129}Xe has been used as an inhaled contrast agent to study the lung [4]. In addition, the chemical shift in ^{129}Xe depends upon the dissolved environment, giving a unique tool to probe gas dissolution pathways in chemical and biological system [5].

As gas phase NMR is inherently a low sensitivity technique, the success of these applications requires the production of gas with high polarisation in large volumes. The technique used to produce the gas polarisation is spin exchange optical pumping (SEOP) [6], where Rb is optically pumped on the D_1 electron transition ($^2S_{1/2}$ - $^2P_{1/2}$) and results in a highly polarised electron ground state. During interactions between the ^{129}Xe nucleus and the Rb atom there is a transfer of polarisation from the electron-nuclear spin through a Fermi contact interaction. The depolarised Rb electron is then repolarised via optical pumping and the process repeats, leading to a build-up of ^{129}Xe polarisation over time. Under steady state conditions the ^{129}Xe polarisation (P_{Xe}) is given by:

$$P_{Xe} = \frac{\gamma_{SE}}{\gamma_{SE} + \Gamma_{Xe}} P_{Rb} \tag{1}$$

where Γ_{Xe} is the ^{129}Xe relaxation rate and γ_{SE} is the spin exchange rate, which is intrinsic to the particular alkali metal-noble gas combination used and depends on the Rb density ([Rb]). For ^{129}Xe, γ_{SE} is pressure dependent; this is due to changes in the interaction time between the alkali metal and noble gas. At high pressure, these interactions are dominated by binary collisions and at low pressure by the formation and break up of van der Waals molecules [7]. P_{Rb} is the Rb polarisation, given by:

$$P_{Rb} = \frac{\gamma_{opt}}{\gamma_{opt} + \Gamma_{SD}} \tag{2}$$

where Γ_{SD} is the electron spin polarisation destruction rate, which is dependent upon the gas density and composition. γ_{opt} is the optical pumping rate given by:

$$\gamma_{opt} = \int I(\nu)\, \sigma(\nu)\, d\nu \tag{3}$$

where $I(\nu)$ is the photon flux at frequency ν and $\sigma(\nu)$ is the photon absorption cross

section for the Rb electron transition. Eqn. 1, 2 and 3 show that in order to achieve high P_{Xe}, three conditions need to be met: minimising the alkali electron relaxation and ^{129}Xe nuclear relaxation, maximising the absorbed photon flux and maximising the spin exchange rate.

The relaxation mechanisms are minimised by using high purity gas and coating the cell surface [8] to decrease the surface relaxation. Relaxation due to persistent dimers can be suppressed at high B_0 field [9], however this is not always practicable. The dependence of $\sigma(\nu)$ on gas density has been extensively studied by Romalis *et al.* [10]. For a gas mixture of 3% Xe, 10% N_2, 87% He, the absorption width (FWHM) at 70°C is 0.038 nm/amg [11] and the wavelength shift is 0.0062 nm/amg.

Commercially available lasers have typical line widths of the order 2 nm (for example, 60W FAP, Coherent, USA) and therefore to maximise the absorption, optical pumping is often performed at high gas pressures where the D_1 resonance is broadened due to collisions. For ^{3}He this is straight forward and ^{3}He is polarised at high gas pressure with a small quantity of nitrogen. Xe is less suited to this self pressure broadening technique due to its much higher spin destruction rate at high pressure and therefore optical pumping is typically performed in a gas mixture with a few percent Xe and nitrogen with the bulk being ^{4}He, which is added to pressure broaden the absorption line. This mode of operation has been used by a number of teams [12, 13]. One of the main limitations of this approach is laser heating, where elevated nitrogen temperatures of several 100°C have been observed[14], which limits the maximum attainable polarisation[15].

An alternative approach where ^{129}Xe is optically pumped at low pressure, has also been pursued by several teams [16, 17]. This exploits the faster spin exchange rates and lower self relaxation rates at low pressure. Impressive volume polarisation rates have been reported [16]. Low pressure polarisers use a long cell to increase the total light absorption and a Rb column to saturate the gas mixture prior to optical pumping. This results in a larger apparatus which has the added complication of driving the Rb through the system, thus requiring periodic replenishment of the glassware. These devices also utilise a narrowed laser due to the smaller absorption width at low pressure.

A number of groups have developed lasers with an external grating to narrow the emission [18–20]. These can achieve powers of several watts when narrowed, showing significant gains with polarisations $\approx$ 40% higher than 15 W unnarrowed sources [18]. Further developments

in narrowing have resulted in the use of diode laser arrays with ≥40 W [21] of narrowed power and with line widths ≈0.2 nm. These have been used to produce high polarisations of ^{3}He. Studies of ^{3}He SEOP have shown that the alkali polarisation saturates at ≈ 0.9 [22] when using unnarrowed (≈2 nm) sources and only narrowed sources produced $P_{Rb} \approx 1$. However at very narrow line widths the net optical pumping efficiency of ^{3}He decreases due to high absorption of the pumping light close to the front of the cell [23].

For ^{129}Xe SEOP, a diode stack [24] was recently used to produce a 90 W laser with 1.5nm FWHM which gave a production rate of 0.3 liters/hour with 64% polarisation. A similar development at low pressure (0.83 Bar) obtained a polarisation of 84% using 60 W (FWHM 0.3 nm) with a Xe partial pressure of 1.1 mBar and flow of 10 sccm. A further development by Nikolaou *et al*. [25] used a volume holographic grating (VHG) to narrow the laser to 0.27 nm with an output power of 27 W producing ≈10% polarisation when optimised. This work showed the surprising result that detuning from the D_1 resonance by -0.11nm significantly increased the achievable polarisation. This device was tuned in wavelength by changing the operating current, utilizing the temperature dependence of the VHG. This approach has the unfortunate side effect of coupling the laser wavelength and power. The use of an external cavity diode laser (ECDL), where the wavelength is altered by changing the external angle of the grating allows the decoupling of power and wavelength. This allows the systematic investigation of off resonant pumping under constant power and permits the separation of heating effects [13], as a function of power and/or wavelength.

The experimental work detailed in this paper explores the use of an ECDL for ^{129}Xe polarisation using a design which has been shown to routinely achieve $P_{Rb} \approx 1$ and $P_{He} >$ 70% for ^{3}He [26]. This device is the narrowest photon source at high power that has been used for Rb-Xe SEOP. Specifically the paper concentrates upon an investigation of the wavelength dependence of the optical pumping. Measurements of the Rb absorption, ^{129}Xe polarisation, laser emission spectra and power dependence are also presented in order to characterize the performance of these devices for ^{129}Xe optical pumping in the 0.8 - 2 amg [11] mid pressure range.

II. EXPERIMENTAL DETAILS

The apparatus consists of a large diameter (0.8 m) Helmholtz B_0 coil, which produces a field of 2.7mT. The optical pumping cell (Pyrex, 12 cm long, 5 cm diameter) is placed at the B_0 isocenter. The cell contains a small amount of Rb ($< 1\ g$) which was loaded into the cell in an inert (Ar) glove box using a heated pipette. The gas used was of varying density in the concentrations 3%Xe, 10%N_2 and 87%He, this was premixed and certified by the supplier (Spectra Gases, UK).

The cell was located in a non-magnetic oven built from calcium silicate and heated with an inline air process heater (750 W) fed from a compressed air line. The external cell temperature was measured using a three terminal resistance temperature detector (RTD) placed ≈2 cm from the cell. The cell was polarised by SEOP using an ECDL based on the design reported by Chann *et al*. [27] and using a modified external Littrow cavity. A 100 W diode laser (n-light, Vancouver, USA) was used. This was narrowed using a holographic grating (2400 lines/mm) (Edmund optics, USA). In addition, a beam splitter was placed in the cavity to limit the emission to the grating; this design is similar to that used to achieve high polarisation of ^{3}He [26, 28].

The laser, fluorescence and absorption measurements were performed using an Ocean Optics spectrometer (HR4000, resolution 0.02 nm) This was fibre coupled using a large diameter lens (2 cm) to capture the fluorescence signal. The absorption measurements were performed with a halogen lamp (150 W, white source) to illuminate the cell and normalised to the lamp intensity when the cell is cold (i.e.[Rb]=0), similar to the procedure used by Couture *et al*. [29]. The laser power was measured at the cell location using a large area power meter (Gentec - EO, Canada).

A home built NMR spectrometer [30] was used with a high bandwidth (1.25 MHz) digital I/O card to record the polarisation in the optical pumping cell. A series of in-situ NMR measurements were performed to measure the polarisation at various gas densities and temperatures. All data were corrected for the temperature dependence of the NMR coil sensitivity and calibrated to a ^{1}H sample [31]. All NMR measurements were performed in a static mode, i.e., no gas flow. Furthermore, to account for possible heating effects, each time the cell temperature or laser wavelength was changed the cell was left for 15 minutes before NMR measurement of the polarisation.

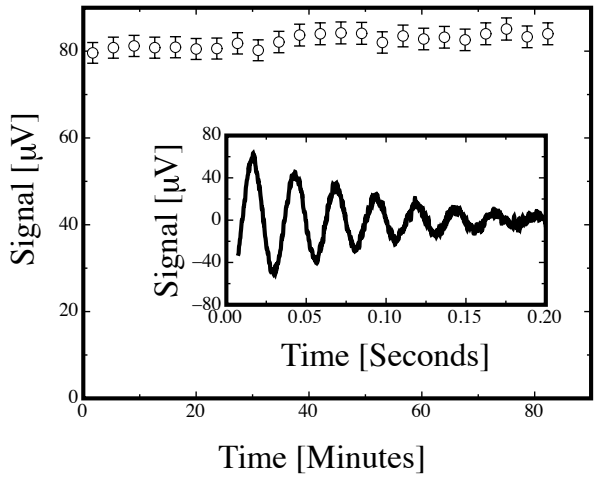

FIG. 1: Typical NMR data for a valved cell at 1.59 amg at 80°C with 38 W incident on the cell, each measurement is 10 averages with 10 seconds delay between each average, inset is a typical averaged FID obtained from this measurement.

In order to test the accuracy of the NMR system, a series of tests were performed. A typical FID is shown in the inset of figure 1; this was obtained with 10 averages and a 10 second delay between each average to allow for the optical pumping to replenish any polarisation lost due to RF depolarisation. The 10 second wait is an experimentally determined parameter, with waits of 10, 20 and 30 seconds having no additional effect on the obtained signal. The stability of the system was also tested with successive pulses being applied with a two minute delay between each 10 point average. The results are shown in figure 1, the value quoted is the initial FID intensity, $V_{pp}/2$ as defined in [30].

III. RESULTS

Firstly the laser system (ECDL) and Rb absorption were characterised. Shown in figure 2 (a) is a comparison between the bare (unnarrowed) diode array and the emission from the ECDL, demonstrating the increase in photons close to the D_1 resonance. The laser emission line width is ≈2 nm (FWHM) for the bare diode array and 0.09 nm (FWHM) when narrowed. Further investigation of the laser power and line shape dependence (typical spectra in figure 2 (b)) showed that the line width is constant with power. Measurements were also performed to check that the laser line width is constant with wavelength in the ≈ 1 nm tuning range; in this range the power change is negligible (≈ 2%). There exists a small amount of emission which is not narrowed, seen in figure 2 (a) as a small hump centered at

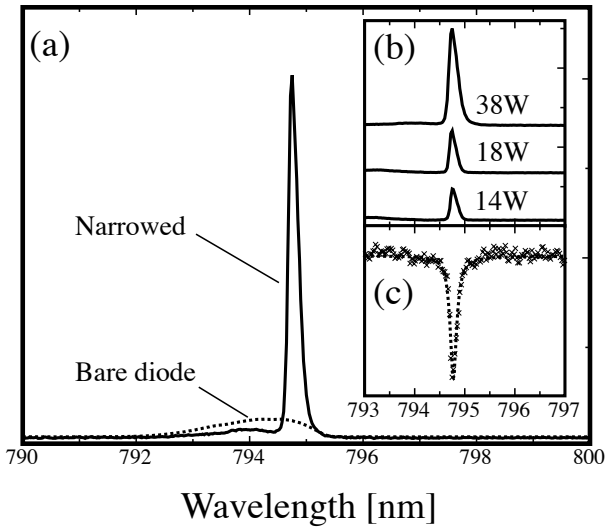

FIG. 2: (a) Comparison of the bare diode spectral profile before and after narrowing using the external cavity. In both cases the diode was driven at 110A and integrated intensities are shown normalised to output power. (b) Spectral output of narrowed laser as a function of power (current), offset for clarity and (c) absorption data for the D_1 line, measured using a lamp and monochromator

794 nm.

The absorption measurements were then performed on a valved cell, containing Rb and a fixed gas mixture (3% Xe, 10% N_2, 87% He) of varying density. Whilst the values for the D_1 absorption quoted by Romalis *et al.* [10] are of high accuracy, differences in calibration of the optical spectrometer may introduce a wavelength offset and therefore the Rb absorption was measured for a range of gas densities (0.6-2.6 amg) at 70°C with low absorption ($\approx 10\%$). A typical absorption spectrum is shown in figure 2 (c) for a gas mixture at 1.4 amg with a Lorentzian fit using the procedure detailed by Couture *et al.* [29]. The D_1 resonance was measured to be 794.77 ± 0.02 nm, with no observable shift with gas density within the range studied. This is attributed to the limited resolution of the optical spectrometer used and therefore must be less than 0.02 nm.

Following this characterisation, the polarisation in the optical pumping cell was measured by in-situ NMR. A range of total gas densities, cell temperatures and laser powers were investigated, the results of which are summarised in figure 3. A number of points are evident from these results; the first is that the optimum wavelength for maximum polarisation (P_{Max}) occurs at a lower wavelength than that of the D_1 absorption, agreeing with the observations of Nikolaou *et al.* [25] when using a VHG. Direct comparison with the absorption measurement gives a detuning of -0.06 nm at 1.59 amg. Secondly, when the cell temperature is raised to

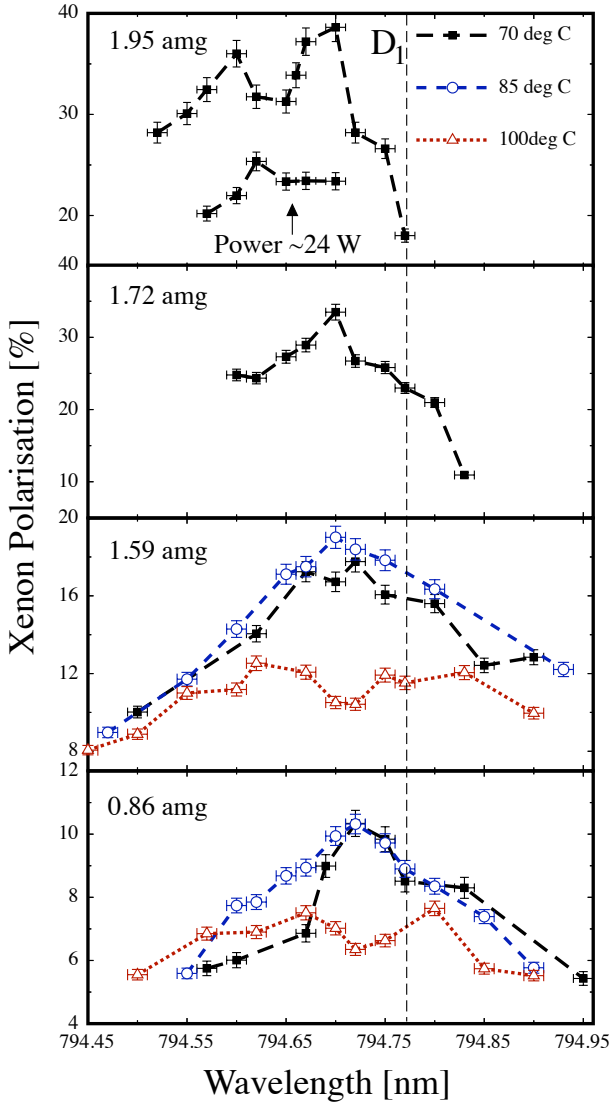

FIG. 3: NMR data for various temperatures and gas densities as indicated in the figure. All measurements at 38W except where noted. The vertical dashed line (D_1) indicates the center of the absorption as measured.

100°C (hence higher [Rb]) the polarisation starts to show a dip at the wavelength where P_{Max} was observed at lower temperatures. At 1.95 amg and 70°C, the polarisation has a dip at ≈794.65nm, which disappears at lower power, albeit with a reduced total polarisation. The polarisation is observed to increase with gas density, with the maximum gas density obtainable (1.95 amg) being limited by the cell design.

Finally the dependence of the ^{129}Xe polarisation on laser power was investigated. These results are shown in figure 4 for a gas density of 1.59 amg. In all cases no significant decrease in polarisation with increasing laser power was observed. At 794.72 nm and 85°C, close to

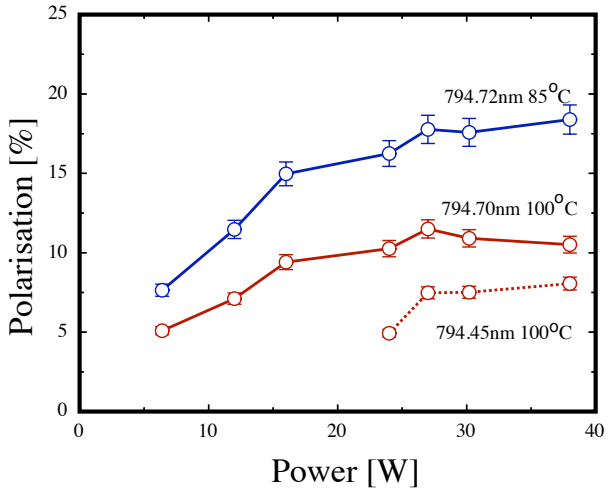

FIG. 4: Power dependence of ^{129}Xe for 1.59 amg at various temperatures and wavelengths (as indicated).

the saturation, the polarisation shows a non-linear increase with laser power, whilst at the higher temperature (100°C) the polarisation saturates at ≈ 25W.

IV. DISCUSSION

The ECDL demonstrated in this work has an emission which is tunable, stable in line width and power and for Rb-Xe SEOP represents the narrowest high power laser yet reported (38W, 0.09nm FWHM). Specifically, the laser line width is well matched to the absorption width of [Rb] for gas densities of 2 amg (0.08nm) in these mixtures. The maximum polarisation (P_{Max}) is however dependent upon the detuning of the laser emission from the wavelength of the measured D_1 Rb absorption line. For SEOP of ^{129}Xe the ECDL provides high levels of polarisation at a higher concentration (3%) than usually used (1%)[12]. The optimal detuning is dependent upon the total gas density and is larger than that predicted from the absorption measurements (figure 2) and by the measurements of Romalis *et al.* [10].

In the earlier work [25] it was argued that the cause of the off resonant effect is due to the change in the light intensity across the cell. When close to resonance the light is absorbed predominantly at the front face whilst off-resonant light penetrates much further through the cell yielding a higher volume averaged rubidium polarisation than the on-resonant case. This type of behavior would be expected to be symmetric around the measured D_1 absorption

line assuming that the absorption line itself is symmetric. This is not true in the case of this work and the dip in polarisation at high absorption/[Rb] is observed in this work however it is consistently shifted to lower wavelength. This is indicative of a new phenomenon the theory of which will require further study.

There is a trend in the data indicating that the optimum wavelength is dependent upon the gas density. To investigate this further cells suitable for working at larger gas densities are required and will be investigated further.

Additional measurements of the D_2 fluorescence at the far end of the cell showed a maximum in emission when pumping at 794.77nm, consistent with this being the peak of the D_1 resonance.

Direct measurement of the absorption during optical pumping conditions was not possible due to contamination of the probe by the pump beam. It should however be possible to assess the Rb polarisation using alkali metal polarimetry [32] under optical pumping conditions.

The further optimisation of these lasers will require a detailed investigation of all parameters (gas mixture and pressure, cell temperature/[Rb], laser wavelength and power) and specifically at realistic flow rates for high volume MRI/NMR studies. Moreover the high polarisation already demonstrated by this setup suggests that higher Xe partial pressures can be utilised to increase gas production, without having to resort to a low pressure system. This is encouraging for the construction of a compact mid pressure range batch/flow polariser for moderate-high gas production rate. Experimentally it is more time consuming to set up an ECDL than a VHG laser, however such a system does provide an ideal approach to determining the correct wavelength for a narrowed laser.

In summary, a narrow high power laser has been constructed and used to observe the off resonant behaviour previously reported by Nikolaou *et al.* [25]. The amount of detuning needed was different to that previously reported. This difference is attributed to the decoupling of the laser wavelength from the power which is achievable using an ECDL. Further investigation of these effects will require a detailed study of the alkali polarisation. Optimisation of this system will then need to be performed under typical flow conditions which are used to provide viable gas doses for imaging studies.

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