

Experimental considerations of absorption spectroscopy of rubidium

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Introduction:

There are widely reported discrepancies in ¹²⁹Xe-Rb SEOP measurements compared to existing theoretical frameworks¹⁻³. The rubidium vapour density, [Rb], is a key parameter governing performance and is typically modelled using equilibrium vapour curves, calculated from measured optical cell wall or oven temperatures, T. The form of the Rb equilibrium vapour curve given by Killian⁴ is

$$[\text{Rb}]_{sat} = \frac{10^{\left(a - \frac{b}{T}\right)}}{k_B T} \cdot 10^{-1} m^{-3}, \qquad (\text{Eq. 1})$$

where *a*=10.55 and *b*=4132K. Lower Rb densities have been reported in continuous-flow polarisers^{3,5}, and work optimising the Rb vapour density distribution still needs to be done. The aim of this work was to measure Rb vapour densities in a small static cell using absorption spectroscopy (AS) for various conditions.

Path length correction:

The curvature of the cell leads to small changes in the path length off-centre of the cell for AS performed transverse of the cell. The mean path length can be calculated as a chord in a circle as

$$\bar{l} = \frac{1}{r_b} \int_0^{r_b} 2\sqrt{(r_{cell}^2 - x^2)} dx.$$
 (Eq. 4)

Evaluating Eq. 4 gives

$$\overline{l} = \frac{r_{cell}^2}{r_b} \cdot \arcsin\left(\frac{r_b}{r_{cell}}\right) + \sqrt{(r_{cell}^2 - r_b^2)}. \text{ (Eq. 5)}$$

For our conditions: $r_{cell} = 2.13$ cm, $r_b = 1.06$ cm, $\bar{l} = 4.07$ cm



Fig. 3: Path length correction for a curved optical cell.



Method:

Absorption spectroscopy was used to probe Rb D1 and D2 absorption lines to determine Rb vapour density (Fig. 1). Transmission, I, was measured (Fig. 2) and the absorbance, $\ln(I_0/I)$, where I_0 is a reference transmission spectrum taken at a cell temperature of 20°C (zero [Rb]), was fitted to a Lorentzian of the form⁶

$$S(\nu) = \frac{A + 2\pi T (\nu - \nu_0)}{(\nu - \nu_0)^2 + \left(\frac{\gamma}{2}\right)^2} + B.$$
 (Eq. 2)

Rb density was then calculated as

$$[Rb] = \frac{1}{r_0 cfl} \frac{2A}{\gamma}.$$
 (Eq. 3)

Preliminary measurements were performed on the cell straight from Rb filling in the glovebox (containing 1.001bar Ar), in the absence of a pumping laser. Rb density build up from 20°C to an oven temperature of 150°C (Fig. 5) as well as equilibrium Rb density for different cell temperatures were measured (Fig. 6). The cell was then filled to 1.47bar, with a gas mixture of 3%Xe, 10%N2, 87%He at 20°C and Rb vapour densities were measured in the presence of a D1 pumping laser [emission wavelength 794.77nm, Gaussian FWHM= 0.2nm, flux = $2.7W/cm^2$ (120W, 7.5 cm circular beam)], as shown in Fig. 7.



Fig. 4: Mean path length vs beam radius, normalised to the cell width and cell radius respectively.



Fig. 5: Rb density vs time for a set oven temperature of 150°C, for the Ar-filled cell in the absence of the pumping laser. The oven was switched on at time=0s.





Fig. 1: Experimental setup consisting of a halogen bulb, collimating lens and optical fibre placed either side of the optical cell (a) with and (b) without the D1 pumping laser on. This was performed longitudinally (not pictured) as well as transversely to the optical cell.



Fig. 6: Rb density vs cell temperature for the Ar-filled cell in the absence of the pumping laser. Fitting Eq. 1 to mean Rb density gives $a=9.861 \pm 1.461$ and *b*=(4311 ± 575)K.

Fig. 7: Rb density vs cell temperature for the 3%Xe mix-filled cell in the presence of the pumping laser. Measurements were taken with the laser (black) and immediately after blocking the laser (blue and red). Fitting Eq. 1 to mean Rb density with the laser blocked gives $a=7.517 \pm$ 0.439 and *b*=(3404 ± 177)K.

Discussion and Conclusions:

Fitting Eq. 1 to mean Rb densities from both the D1 and D2 line absorbances in Fig. 7 • gives $a=7.517 \pm 0.439$ and $b=(3404 \pm 177)$ K. These values lie within 2σ of values obtained from Fig. 6, showing good agreement between [Rb] in the presence and

Fig. 2: (a) Transmission spectra for cell temperatures of 20°C and 125°C, for the Ar-filled cell in the absence of the pumping laser. Corresponding absorbance at the (b) Rb D1 line and (c) Rb D2 line.

absence of the pumping laser.

- Equilibrium [Rb] were an order of magnitude lower than calculated Killian⁴ saturation levels for all conditions investigated, consistent with previously reported values³.
- Rb densities calculated from absorbance at the Rb D1 line were consistently higher than those calculated from absorbance at the Rb D2 line by ~ 10 to 50%.
- Further work is needed to understand and characterise the discrepancy in [Rb] \bullet measurements observed in this work.

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References:

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