

# Notes on the Rb Maser and the CPT Clock

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## 1 Introduction

I should summarize lots of stuff here including

- Rubidium density
- laser absorption
- some buffer gas stuff
- Vanier stuff

## 2 Rb Number Density

The CRC handbook of chemistry and physics (P4-124) gives an empirical formula for the vapor pressure of rubidium above the bulk as an expression of the form

$$\log_{10} p = A + B/T + \dots$$

with tables of coefficients. There is a discontinuity at the melting point of the rubidium and thus we have

$$p = \begin{cases} 10^{4.857-4215/T} & T < T_{\text{melt}} \\ 10^{4.312-4040/T} & T > T_{\text{melt}} \end{cases} \quad (1)$$

for the Rb pressure in atmospheres when the temperature is in kelvin and the melting point is 39.3°C. We can determine the number density by converting the pressure to Pascal and dividing by  $kT$ . In this section I have included both a table and a figure showing some relevant values.

There is also a somewhat more recent reference, *Vapour pressure of the elements*, A. Nesmeyanov, translated by J. I. Carasso, (Academic Press, 1963). This reference uses a similar formula,

$$\log_{10} p = A - \frac{B}{T} + CT + D \log_{10} T$$

where  $p$  is the pressure in Torr and  $T$  is the temperature in Kelvin. Once again two sets of coefficients are used to fit the data above and below the melting point of Rb at 39.3°C. These are

coefficient	A	B	C	D
solid	-94.04826	1961.258	-0.03771687	42.57526
liquid	15.88253	4529.635	0.00058663	-2.99138

The results for the two pairs of empirical relations are similar. However, the Handbook of Chemistry and Physics values are somewhat larger (roughly 25% in terms of density). Below is a table comparing the empirical functions of Nesmeyanov and the CRC, evaluated at temperatures of relevance to our clock and quantum optics experiments:

°C	Nesmeyanov		CRC	
	Torr	cm <sup>-3</sup>	Torr	cm <sup>-3</sup>
20	$1.7 \times 10^{-7}$	$5.7 \times 10^9$	$2.2 \times 10^{-7}$	$7.4 \times 10^9$
30	$5.0 \times 10^{-7}$	$1.6 \times 10^{10}$	$6.7 \times 10^{-7}$	$2.1 \times 10^{10}$
40	$1.3 \times 10^{-6}$	$4.2 \times 10^{10}$	$1.9 \times 10^{-6}$	$6.0 \times 10^{10}$
50	$3.5 \times 10^{-6}$	$1.0 \times 10^{11}$	$4.8 \times 10^{-6}$	$1.4 \times 10^{11}$
60	$8.5 \times 10^{-6}$	$2.5 \times 10^{11}$	$1.1 \times 10^{-5}$	$3.3 \times 10^{11}$
70	$2.0 \times 10^{-5}$	$5.5 \times 10^{11}$	$2.6 \times 10^{-5}$	$7.3 \times 10^{11}$
80	$4.3 \times 10^{-5}$	$1.2 \times 10^{12}$	$5.6 \times 10^{-5}$	$1.5 \times 10^{12}$
90	$9.1 \times 10^{-5}$	$2.4 \times 10^{12}$	$1.2 \times 10^{-4}$	$3.1 \times 10^{12}$
100	$1.8 \times 10^{-4}$	$4.8 \times 10^{12}$	$2.3 \times 10^{-4}$	$6.0 \times 10^{12}$
110	$3.6 \times 10^{-4}$	$9.0 \times 10^{12}$	$4.4 \times 10^{-4}$	$1.1 \times 10^{13}$
120	$6.7 \times 10^{-4}$	$1.6 \times 10^{13}$	$8.2 \times 10^{-4}$	$2.0 \times 10^{13}$
130	$1.2 \times 10^{-3}$	$2.9 \times 10^{13}$	$1.5 \times 10^{-3}$	$3.5 \times 10^{13}$
140	$2.1 \times 10^{-3}$	$5.0 \times 10^{13}$	$2.6 \times 10^{-3}$	$6.0 \times 10^{13}$
150	$3.7 \times 10^{-3}$	$8.4 \times 10^{13}$	$4.4 \times 10^{-3}$	$1.0 \times 10^{14}$

The values in this table and figure 1 are simply the evaluation of the functions cited in these references. We have not attempted to measure the density of rubidium vapors ourselves to test them. Note that in our vapor cells, we frequently have uncertainties in temperature of greater than 5°C making anything other than a very qualitative comparison difficult in any event.

### 3 Bulb Storage Time

The storage time of Rb atoms in a cell is determined by the ratio of bulb area to escape hole area times the mean path length across the bulb divided by the mean velocity. Additionally, and tube at the exit can increase the storage time due to its Claussing factor. I'll work out several of the pieces of this puzzle.

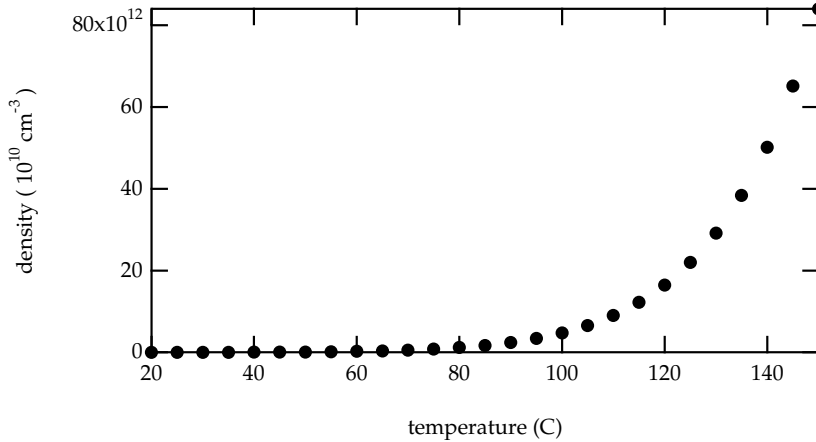


Figure 1: Rubidium vapor density as a function of the temperature of the bulk (solid or liquid) rubidium in the temperature range of interest to Rb clocks and quantum optics experiments. (The plotted points are from empirical function cited in Nesmeyanov evaluated at the stated temperatures.)

### 3.1 Mean path in a spherical bulb

*My notebook, 2/24/99, p69*

Atoms hitting the coated surface of the bulb stick briefly and then escape the surface with a distribution of directions given by the law of cosines ([1] p45)

$$dN = \frac{1}{\pi} N \cos \theta d\Omega \quad (2)$$

where  $d\Omega = \sin \theta d\theta d\phi$ . To determine the mean path inside a sphere, we need to average the path length of an atom leaving the surface of the bulb at an angle  $(\theta, \phi)$  from the normal and average over all angles using the cosine distribution of equation 2. As can be seen in figure 2, the path length for an atom leaving the surface at an angle  $\theta$  is given by  $l^2 = 2r^2 + 2r^2 \cos 2\theta$  where  $R$  is the radius of the sphere. By averaging over all angles

$$\langle l \rangle = \frac{\sqrt{2}}{\pi} R \iint \cos \theta \sin \theta d\theta d\phi [1 + \cos 2\theta]^{\frac{1}{2}}. \quad (3)$$

With a simple change of variables, this integral may be evaluated to

$$\langle l \rangle = \frac{4R}{3}.$$

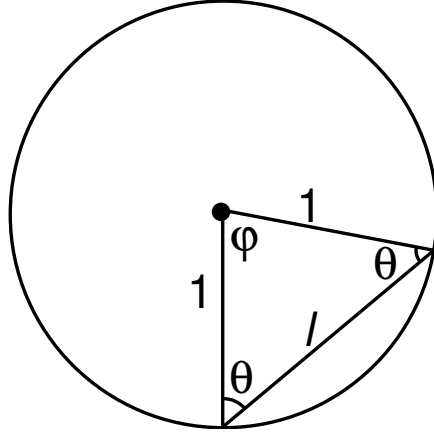


Figure 2: Path length,  $l$  for an atom leaving the surface at angle  $\theta$ .

### 3.2 Thermal Velocity

*My notebook, 1/27/99, p34. Corrected 11/20/02.* The mean velocity of the Rb atoms is found by calculating the expectation value of the norm of the velocity. We start with  $v^2 = v_x^2 + v_y^2 + v_z^2$  and the probability of finding a velocity  $v$  of

$$p(v) dv \propto 4\pi v^2 \exp\left(-\frac{1}{2}mv^2/kT\right). \quad (4)$$

(The extra factor of  $v^2$  comes from an integral over the angular components of velocity.) Thus, after proper normalization, the mean value of  $v$  is

$$\bar{v} = \int_0^\infty v p(v) dv = \sqrt{\frac{8kT}{\pi m}} \quad (5)$$

where  $m = 87 \cdot 1.7 \cdot 10^{-27}$  kg,  $k = 1.38 \cdot 10^{-23}$  J/K and, at room temperature,  $T = 313$ K. This leads to a mean thermal velocity

$$\bar{v} = 3 \cdot 10^4 \text{ cm/s}. \quad (6)$$

### 3.3 Storage Time

We can now determine the geometric storage time for Rb atoms in a spherical bulb of radius  $R$ . This is given by

$$T_{geom} = \frac{A_{sphere} \langle l \rangle}{A_{escape} \bar{v}} \quad (7)$$

which can be written as

$$T_{geom} = \frac{16R^3}{3r_{hole}^2 \bar{v}}. \quad (8)$$

For the single-bulb cells made by Raworth [2],  $R \approx 2$  cm and the exit hole radius,  $r_{hole} \approx 0.01$  cm. Therefore, the geometric lifetime is 14 seconds. In the maser bulb of the 1996 Mikoski double bulb, the radius is  $R = 1.7$  cm and the exit hole radius is  $r = 0.32$  cm leading to a storage time of 8.5 ms ignoring Claussing factors.

However, if we blindly apply the Claussing factor,  $\kappa$ , given by

$$\frac{1}{\kappa} = \frac{8 r_{hole}}{3 l} \quad (9)$$

for a cylindrical exit tube of radius  $r_{hole}$  and length  $l$  where  $r \ll l$  to the double bulb whose transfer tube has a length of 2.5 cm, we find that  $\kappa \approx 3$ . While Ramsey defines the Claussing factor in terms of the flux leaving an atomic beam oven, it should also apply to the storage time in a bulb. Therefore, the geometric storage time for the maser bulb,  $T_{geom} = 20$  ms.

## 4 Enriched Rubidium

*My notebook, 1/27/99, p35*

I'd like to summarize some of the information that is in my notebook on using isotopically enriched rubidium. First, you can apparently only buy enriched rubidium as RbCl. Rick Stoner did some research into vendors He determined that Isotec, a typical dealer of exotic gases, doesn't stock it any longer, however Oak Ridge (ORNL) and Trace Science International (located in Toronto, ON) sell it for \$11.05 and \$7.50 per mg respectively in quantities of 100 mg. Note that if we want 10 mg per cell, the cost is only twice that of a standard metal rubidium ampoule.

There are two techniques we've found in the literature for reducing the  $^{87}\text{RbCl}$  to pure rubidium. Bell, Bloom and Lynch [3] mix the RbCl with  $\text{CaH}_2$  under vacuum, warming it slightly. This produces Rb, CaCl and  $\text{H}_2$ . Others, including the JILA and Princeton folks use a similar procedure with metallic Ca instead of  $\text{CaH}_2$ . They take great cautions keeping the metallic calcium clean. Debbie Jin [4] bakes the Ca at  $400^\circ\text{C}$  under vacuum for four days before using it. The papers describing the  $\text{CaH}_2$  techniques appear more manageable. Therefore, we have decided to try that route.

There is a third technique which Hugh Robinson described. One could use Barium Azide instead of metallic calcium to reduce the RbCl. However, it is very dangerous.

Andreea, while visiting Princeton, quizzed one of the students about enriched Rb use. They rely on the metallic calcium

technique, but had some good news on efficiency issues. They warm the powders with a methane torch and cool the regions where they want the Rb to collect with nitrogen and from a few milligrams (maybe 10) of RbCl they collect enough Rb to see silver colored metal in the cool regions.

*My notebook, 2/1/99, p39* We ordered from Aldrich [5] natural abundance RbCl and CaH<sub>2</sub> (as well as some new tetracontane) for tests of these techniques. Rick has also ordered the enriched <sup>87</sup>RbCl from Trace Science International. Presently (4/21/99), we await the repair of our cell filling station before trying to test these techniques.

## 5 Wall Shifts

*My notebook, 2/1/99, p40* Following calculations by Hugh Robinson [6] (who is following KGR [7]) we can compare the wall shift and the line width of the hyperfine frequency to determine the phase shift per collision and the fraction of the linewidth due to wall collisions. The best results we have obtained, to date, are from a Raworth single bulb cell in which  $T_2 = 17$  ms and frequency shift from the natural rubidium frequency was  $\Delta\nu = -73$  Hz. The phase shift per collision is given by

$$\phi = t_c \cdot \Delta\omega_s \quad (10)$$

where  $t_c$  is the mean time between wall collisions and is given by  $l/\bar{v} \approx 90 \mu\text{s}$ . Therefore, the phase shift per collision,  $\phi = 0.04$  rad which is smaller than the 0.06 rad which Robinson determined. The FWHM broadening due to these phase shifts is

$$\Delta\nu_{\text{broad}} = \frac{\phi^2}{\pi t_c}. \quad (11)$$

For our transit time, this is only 6 Hz. However, we observe much broader lines of 19 Hz. This might be explained by non-uniform coatings.

## 6 Light Shifts

In preparing for a talk on the Dark state clock at MIT, I've been learning a little more about light shifts. The two key papers presenting initial measurements and basic theoretical understanding of light shifts were by Kastler [8] and Happer [9]. I've read through Kastler's paper which quotes data and analysis

Table 1: Summary of previously measured values of the light shift for various Rb clocks.

author	light	cell	clock	shift (Hz/MHz)
Davidovits [10]	lamp	buffer	maser	0.01
Hashimoto [11]	diode	buffer	passive	0.5
Robinson [12]	diode	coated	passive	0.025
Camparo [13]	diode	buffer	passive	0.4
Vanier [14]	diode	buffer	darkstate	60 Hz/GHz <sup>2</sup>

from Cohen-Tanoudji and Cangac but I haven't read Happer's (longer) article, yet.

The basic summary of light shifts is that there are two different sources of shifts: real and virtual transitions. The real transitions lead to shifts because the hyperfine frequency in the excited state is smaller than that of the ground state. Thus, less phase will accumulate and a negative frequency shift will occur. The virtual transitions are equivalent to the AC Stark effect. However, there is also some Clebsch-Gordon coefficient trickery lying in wait in Kastler's equations. Differing polarizations in the experiments listed in the table discussed below may explain why the answers vary.

Many people have measured light shifts in single bulb passive devices. Unfortunately they all seem to get different answers. This may be in part because they have slightly different experiments or because these numbers are hard to measure. A summary could state that the light shift numbers pile up around 0.5 Hz ( $\mu$ wave) / 1 MHz (optical) and around 0.02 Hz/MHz. I'll include a little table with more of these numbers.

## 7 Wall Coating Stability

Hugh Robinson published some results on the temperature dependence of tetracontane wall coatings [15]. Centered on the melting temperature of the tetracontane, he finds an "S" shaped curve with some hysteresis to it. Typical slopes on the wings of the curve are roughly 0.2 Hz/°C. There is an inflection point in the curve, right before the melt, where he proposes to operate at a temperature of 80°C. We haven't reproduced these measurements with our coatings, so we only have his measurements to go on.

Note also that if we don't operate at an inflection point, this temperature dependence places very rigid constraints upon the temperature control. To get  $10^{-15}$  fractional stability out of the clock, the wall coating must be held at a constant temperature to better than  $50\mu\text{K}$ . On the flip side, the value of this coefficient for buffer gases is usually much bigger. With the carefully chosen mixture of 10 Torr of an equal mixture of Ne and Ar, one gets the same temperature dependence with a total shift of several kHz (compared to a shift of only 75 Hz for the wall coating). Thus, if we can get close to an inflection point, we'll be doing much better than with a buffer gas cell. The reduced total shift also might improve the long term stability of the device against aging of the coating.

## References

- [1] N. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1956).
- [2] **Wilbur Scientific, Inc.**, 37 Leon St., Boston, MA 02155, Phone 536-2609, Charles Raworth does all of our standard glass blowing and some of the less critical quartz work, as well.
- [3] W. E. Bell, A. L. Bloom, and J. Lynch, "Alkali metal vapor spectral lamps", *Rev. Sci. Instrum.* **32**, 688 (1961).
- [4] B. DeMarco, H. Rohner, and D. S. Jin, "An enriched  $^{40}\text{K}$  source for fermionic atom studies", unpublished (1999), private communication from E. Cornell.
- [5] Aldrich Chemical Company, 1001 West Saint Paul Avenue, Milwaukee, WI 53233, <http://www.aldrich.com/>, cat. no. 381713.
- [6] H. Robinson and C. Johnson, "Narrow  $^{87}\text{Rb}$  hyperfine-structure resonances in an evacuated wall-coated cell", *Appl. Phys. Lett.* **40**, 771 (1982).
- [7] D. Kleppner, H. M. Goldenberg, and N. F. Ramsey, "Theory of the hydrogen maser", *Phys. Rev.* **126**, 603 (1962).
- [8] A. Kastler, "Displacement of energy levels of atoms by light", *J. Opt. Soc. Am.* **53**, 902 (1963).
- [9] B. Mathur, H. Tang, and W. Happer, "Light shifts in the alkali atoms", *Phys. Rev.* **171**, 11 (1968).

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- [10] P. Davidovits and R. Novick, “The optically pumped rubidium maser”, *Proc. IEEE* **54**, 155 (1996).
  - [11] M. Hashimoto and M. Ohtsu, “Experiments on a semiconductor laser pumped rubidium atomic clock”, *IEEE J. Quantum Electron.* **QE-23**, 446 (1987).
  - [12] W. K. Lee, H. Robinson, and C. E. Johnson, in *Proceedings of the 16th Precise Time and Time Interval Applications and Planning Meeting* (U.S. Naval Observatory, Washington, D.C., 1984), p. 91.
  - [13] C. Volk, J. Camparo, and R. Frueholz, in *PTTI 13* (PUBLISHER, ADDRESS, 1981), p. 631.
  - [14] J. Vanier, A. Godone, and F. Levi, “Coherent population trapping in cesium: Dark lines and coherent microwave emission”, *Phys. Rev. A* **58**, 2345 (1998).
  - [15] C. Rahman and H. Robinson, “Rb 0-0 hyperfine transition in evacuated wall-coated cell at melting temperature”, *IEEE J. Quantum Electron.* **QE-23**, 451 (1987).