A Partial Analysis of Drift
in the Rubidium Gas Cell Atomic
Frequency Standard

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Abstract

Uncorrected frequency drift in the rubidium (Rb) vapor atomic frequency standard can be a significant source of time error for systems based on this standard, and has thus drastically limited this standard's range of application. Not only are the origins of this drift not well understood, but its characteristics have never been fully documented. As a first step in correcting this situation we have reviewed the available experimental data concerning drift, and have arrived at a consistent set of general Rb clock drift characteristics: 1) on an individual standard the sign of the drift coefficient may be variable; 2) the magnitude and sign of the drift coefficient are typically only stable over a period of roughly three months, and 3) the general Rb clock drift coefficient is $(5 \pm 2) \times 10^{-12}$/month. Using these characteristics we then discuss eleven possible mechanisms capable of inducing drift. It is found that only four of these mechanisms are consistent with the drift characterization: 1) a temperature-induced pressure shift mechanism, 2) a quadratic Zeeman shift mechanism, 3) a spectrum dependent light shift mechanism, and 4) a position shift mechanism. It is suggested that these four mechanisms receive more theoretical and experimental attention to see if any one of them is capable of explaining all the vagaries of Rb clock frequency drift.

I.   Introduction

For various precise frequency applications in the field, either onboard satellites, aircraft or in manpacks, the rubidium (Rb) gas cell atomic frequency standard is particularly attractive due to its low weight and moderate power consumption. Additionally, recent experimental studies have shown that Rb gas cell standards can achieve frequency stabilities that rival those of cesium (Cs) beam standards [1], which makes them even more attractive for field use. Cs standards, however, typically do not display frequency drift, which is a deterministic variation of an oscillator's frequency output [2]. Alternatively, Rb gas cell standards generally display fractional frequency drifts ($\delta f/f_o$, where f_o is the clock's nominal frequency) of $\sim 10^{-13}$/day. If uncorrected the magnitude of this drift coefficient represents a potential problem for precise time keeping and frequency control, and thus drastically limits the standard's range of application.

Basically, there are two ways of treating drift in an oscillator without resorting to a frequency comparison between oscillators: one can "blindly" correct for it (either by predicting the appropriate frequency change based on a knowledge of the oscillator's past history, or by employing a predetermined correlation between drift and a monitored clock parameter), or one can eliminate it. For example, assume that temperature affects an oscillator's frequency because a critical resistor somewhere in the circuit has a large temperature coefficient. In this particular case temperature would be defined as the parameter that <u>drives</u> drift via a <u>mechanism</u> of resistor temperature sensitivity. Thus, barring the potentially dangerous situation of blind prediction, by monitoring oscillator temperature one could correct for the expected frequency change through the use of some predetermined algorithm; alternatively, one could replace the temperature sensitive resistor with a less sensitive one. Both of these procedures, however, require knowledge of the clock parameters that drive drift (e.g., temperature) and knowledge of the mechanism(s) by which drift occurs (e.g., resistor temperature sensitivity).

Unfortunately, when one surveys the sparce Rb clock drift literature, one is beset with a variety of seemingly unrelated drift coefficient measurements and hypotheses. This situation is not so much the fault of the various authors, as it is an indication of the complexity of the question. The end result of this confusion, however, is that there is no clear consensus as to the general characteristics of Rb clock drift; or even if general characteristics of drift, valid for Rb standards as a class, exist. Obviously, given this situation it is not surprising that there is no agreement as to the general mechanism(s) of Rb clock frequency drift, and hence the parameters that drive drift.

The purpose of the present study is therefore twofold. First, it is our intent to obtain a consistent set of general Rb clock drift characteristics based on the available data, and to clearly state the assumptions regarding drift contained within this characterization. We then plan to investigate a range of possible drift mechanisms to see if any are consistent with this general drift characterization. It is our hope that the surviving set of plausible mechanisms will help to guide further experimental research into drift, so that eventually an unambiguous understanding of the mechanism(s) of Rb clock drift and the parameters that drive drift will emerge.

II. Outline of Gas Cell Standard Operation

Before proceeding to our main topic, it will be advantageous to briefly describe the operation of the gas cell standard. Figure 1 shows the basic physics package elements of an optically pumped gas cell atomic frequency standard: the lamp, the filter cell, the resonance cell and the photodetector. In combination, the lamp and filter cell produce a spectral emission that preferentially excites atoms in the resonance cell out of one of the $5^2S_{1/2}$ ground state hyperfine multiplets. For example, the optical emission lines corresponding to transitions from F=2 (i.e. transition numbers 3 and 4 in Fig. 1b) may be effectively blocked by the filter cell, so that only those atoms in the F=1 hyperfine multiplet can absorb light. Since an excited atom can decay from the $5^2P_{3/2}$ or $5^2P_{1/2}$ state into either ground state hyperfine multiplet, the successive action of several optical absorptions and reemissions will lead to a transfer of population from one hyperfine multiplet into the other. Furthermore, since this process of optical pumping depopulates the optically absorbing hyperfine multiplet, the equilibrium light intensity transmitted by the resonance cell and detected by the photodiode will be at a maximum. If microwaves of the appropriate frequency, 6835 MHz, are now applied to the cavity, atoms in the overpopulated hyperfine multiplet will be induced into returning to the optically absorbing hyperfine multiplet. This appropriate frequency is then detected as a decrease in the light intensity transmitted by the resonance cell as shown in Fig. 2. Since the Q of the atomic interaction with the microwaves is 10^7-10^8, the decrease in transmitted light intensity can be used to discriminate against very small changes in the 6835 MHz microwave frequency.

In the gas cell standard, however, the center frequency of the clock signal ν_{atomic} does not correspond to the free atom's hyperfine resonance frequency ν_o. Various perturbations occurring in the resonance cell shift ν_{atomic} from its unperturbed value. If these perturbations were static, then the difference between ν_{atomic} and ν_o would simply represent a constant offset $\delta\nu$. This offset would affect the standard's applicability as a primary standard, but not as a secondary standard. Unfortunately, there are compelling reasons for believing that this offset is not static. Thus, as ν_{atomic} varies slowly in time, it can cause a slow variation in the clock's output frequency; in other words it can induce drift. In the following sections we will analyze a number of atomic perturbations that lead to the difference between ν_{atomic} and ν_o; we will consider how these offsets might vary slowly in time, and we will determine the consistency of these time varying offsets with the drift characterization.

III. Drift Characterization

In order to obtain a characterization of the rubidium clock's frequency drift, the literature of the past twenty years was surveyed. Several studies stood out as being exceptional drift researches [3]-[9], and average drift

coefficients, D_{avg}, obtained from their results are collected in Table I; to obtain the average drift coefficient magnitudes the drift values from these studies were weighted by the number of months of observation for a particular value of drift. Since these drift studies include results on frequency standards with different design approaches to the Rb physics package, a characterization of drift resulting from their comparison should be representative of the Rb standard's drift in general.

Regarding the data collected in Table I, there is a clear distinction between average drift coefficient magnitudes measured prior to 1967, and average drift coefficient magnitudes measured more recently:

$$\frac{D_{avg} \ (prior \ to \ 1967)}{D_{avg} \ (post \ 1967)} \approx 5 \pm 3. \tag{1}$$

This observation suggests that somewhere around 1967 the magnitude of the Rb clock's drift coefficient improved by roughly a factor of two industry wide, and has stayed nearly constant to the present day. Since the mid-sixties seem to be the time period when the switch from vacuum tube electronics to solid state electronics in the Rb clock was occurring [4], it may be that this dramatic decrease in the drift coefficient magnitude can be attributed to an improvement in the electronics of the clock. In our further considerations of drift coefficient values we will therefore only employ post 1967 data.

If we consider the coefficients collected in Table I the following statements can be made.

1) Even though these frequency standards are of different design, and span the past twenty years of Rb clock manufacture, within a factor of 2-3 they all exhibit the same average drift coefficient magnitude. Thus, the clock parameters that drive drift must not be associated with the clock characteristics that differentiate these standards. In particular, this observation argues against a purely electronic mechanism for drift (e.g., an a.c. or d.c. instability in the servo demodulator), since the electronic design and components of these standards can be expected to differ significantly. Thus, this observation suggests that the mechanism of drift must somehow be associated with a variation in the center frequency of the clock's atomic signal. Furthermore, this observation suggests that the same mechanism(s) is responsible for drift in all Rb frequency standards.

2) The magnitude of the drift coefficient and even its sign are in general only stable for a period of roughly three months. Thus, it could be argued that the process associated with drift is not deterministic at all, but is in fact the result of some very low frequency noise. However, for the present purposes the distinction between a truly deterministic process and noise is of no consequence. We are only interested in characterizing the behavior of the frequency change that is labelled as drift, so that an analysis of the mechanisms that might drive this frequency change may be undertaken.

It should be noted that not all Rb clocks exhibit this variation of the drift coefficient [10]. If, however, one were to assume that drift is due to a single mechanism, operative in all standards, then this observation would nonetheless be indicative of a general frequency drift characteristic. Specifically, we would require that any candidate mechanism be capable of accounting for a change in sign of the drift coefficient. Alternatively, if drift was assumed to be due to several independent mechanisms, then one might account for variations in the drift coefficient's sign by postulating an oscillation in the relative importance of two oppositely signed drift mechanisms (i.e. the sign of an individual drift mechanism would not have to be variable). Thus, the implications of this observation in an analysis of drift mechanisms can only be assessed in terms of some general assumption regarding the nature of Rb clock frequency drift. This assumption will be discussed subsequently.

3) Computing an average drift coefficient for the Rb standard in general yields.

$$D_g = (4.5 \pm 2.2) \times 10^{-12}/\text{month}. \tag{2}$$

Thus, since drift coefficients are in general stable for periods of roughly three months the total fractional frequency changes resulting from drift must at least be on the order of $1\text{-}2 \times 10^{-11}$. Additionally, by considering the minimum drift coefficient magnitudes collected in Table I, one finds that in general the best that one can expect from the Rb standard with regard to drift is roughly $(1.4 \pm 0.8) \times 10^{-12}/\text{month}$ for a period of approximately two months. Any plausible drift mechanism must be capable of accounting for these magnitudes.

IV. Postulates Regarding the Nature of the Drift Mechanism(s)

Before proceeding to the discussion of potential drift mechanisms, it is necessary to explicitly state our initial assumptions regarding the nature of the drift mechanism(s). Basically, these assumptions or postulates fall into six categories which are primarily differentiated by the number and universality of the mechanisms responsible for drift. In order of complexity these candidate postulates are:

1) Drift is due to a single universal mechanism: all Rb clocks have the same single drift mechanism.

2) Drift is due to several mechanisms, but only one mechanism is ever responsible for drift in a particular clock.

3) In a particular clock drift is due to several independent mechanisms, but these several mechanisms occur universally.

4) In a particular clock drift is due to several independent mechanisms, and different combinations of mechanims are responsible for drift in different clocks.

5) In a particular clock drift is due to several synergistic mechanisms (i.e., the total effect of the mechanisms is greater than the sum of their independent effects), but these mechanisms and their synergism are universal.

6) In a particular clock drift is due to several synergistic mechanisms, and there is no relation between the synergism existing in one clock and that existing in any other.

Obviously, if postulates 5 or 6 reflected the realities of drift an understanding of drift would be a very difficult task. However, since at present there is no experimental evidence to suggest a synergism among potential mechanisms of drift, or even a theoretical understanding of how such a synergism could arise, we will ignore this possibility in the following analysis of potential drift mechanisms. Furthermore, since the previous characterization lead to the conclusion that the mechanism(s) of drift is the same in all standards (i.e. the mechanism(s) is universal) postulates 2 and 4 are seen to be inconsistent with experiment and may thus be rejected. Left with only postulates 1 and 3, there is unfortunately no criteria, either experimental or theoretical, for determining the more realistic. Thus, for the sake of simplicity we will choose postulate 1 as our "working" postulate for the present study, remaining cognizant of the fact that at some point experience may force us to abandon this postulate in favor of postulate 3.

V. Drift Mechanisms

As previously mentioned the mechanism of drift in the Rb frequency standard is believed to result from a time varying shift in the atomic signal's resonance frequency. In the previous section we were able to list some of the characteristics of this shift; now, in the present section we want to determine plausible atomic frequency shift processes for drift. The processes to be considered are collected in Table II, and each of these will be dealt with in turn. Our method will be to determine drift characteristics based on the individual shift processes (mechanisms), and to compare these expected characteristics with those discussed in the previous section. In this way we will find that out of the list of eleven processes, there are only four plausible mechanisms of drift. For clarity the eleven processes are grouped into three categories: 1) a category in which atomic frequency shifts are due to collisional processes, 2) a category in which atomic frequency shifts are due to electromagnetic field interactions, and 3) a category in which atomic frequency shifts are due to miscellaneous processes.

A. Collisional Shifts

1) The Wall Shift — In the hydrogen maser collisions of H atoms with the container walls produce a significant shift of the hyperfine resonance frequency [11]. One might imagine that a similar effect is also present in the Rb gas cell standard, and that variations in the wall's characteristics account for drift. However, in the Rb gas cell standard the glass walls of the resonance cell are typically bare. Thus, wall collisions are extremely depolarizing, and very near the wall's surface the hyperfine polarization is essentially zero [12]. As a result of the depolarizing nature of the walls, the resonance cell typically contains several torr of some inert buffer gas to slow diffusion to the walls, and the rubidium atoms are typically considered

as frozen in place due to the presence of this buffer gas. Since none of the microwave signal can come from regions near the wall's surface, it is unlikely that a wall shift exists in the passive Rb standard. Thus, the wall shift is a highly unlikely mechanism of drift.

2) Pressure Shifts - When an alkali atom is in the presence of a buffer gas atom or molecule, the alkali experiences a variation in the energy level spacing associated with the clock transition. This effect is referred to as the pressure shift effect [12], and is responsible for the dependence of the clock's transition frequency on buffer gas density. If T_s is the temperature at which the resonance cell was filled with the buffer gas for the measurement of α_p (i.e. the pressure shift coefficient), then the fractional frequency shift due to this mechanism may be written in the form [13]:

$$\left(\frac{\delta\nu}{\nu_o}\right)_{PS} = \alpha_p[BG]kT_s, \tag{3}$$

where [BG] is the number density of buffer gas atoms or molecules in the resonance cell. However, due to the fact that the buffer gas density in the immediate vicinity of an alkali atom is governed by a Boltzmann factor [14], α_p is expected to display a slight temperature dependence. Expanding α_p about the nominal resonance cell temperature T_o to first order in a Taylor series, Eq. (3) becomes

$$\left(\frac{\delta\nu}{\nu_o}\right)_{PS} = [\alpha_p(T_o) + \beta(T_o)(T-T_o)][BG]kT_s, \tag{4}$$

where $\beta(T_o) = (d\alpha/dT)_{T=T_o}$. Thus, the clock frequency can be expected to show a sensitivity to both resonance cell temperature and buffer gas density as a result of this mechanism. If either parameter were to change slowly in time, then this mechanism might account for drift. Below, we consider three specific pressure shift situations.

2a) Permeation Pressure Shift - Since helium has a fairly large coefficient for permeation through certain types of glass [15], one could imagine that atmospheric helium diffuses into the resonance cell, and that the diffusion process results in a time varying atomic resonance frequency. Recently, Goldberg et al. demonstrated the potential importance of this mechanism [9]. Helium has a fractional frequency shift coefficient of +1.05 x 10^{-7} per torr [12], and since the partial pressure of He in the atmosphere is ~ 4 mtorr [16], the total fractional frequency shift one would expect is 4 x 10^{-10}. This magnitude is consistent with our characterization of drift, implying that over a three month interval ~100 μtorr of He diffuses into the resonance cell. However, after three months the preceding characterization leads us to expect a change in sign of the drift coefficient. With the present mechanism this could only occur if He began to diffuse out of the resonance cell. Ignoring any exotic changes in the He pressure gradient across the glass interface, this process is thermodynamically forbidden. Thus, though the magnitude of this permeation-pressure-shift mechanism appears reasonable, it cannot account for the characteristic change in sign of the

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drift coefficient. Note, however, that if the nature of drift satisfied the third drift postulate, then this process could not be so easily rejected.

(2b) The Adsorption Pressure Shift - In this mechanism of drift we consider the fact that at the nominal resonance cell temperature T_O there is an adsorbed layer of buffer gas molecules on the inner surface of the resonance cell. The amount of buffer gas that is adsorbed is typically represented by the degree of surface coverage $\theta(T,P)$ [17], which is the surface density of the adsorbed buffer gas at a particular temperature and pressure, $\sigma(T,P)$, normalized to the surface density of a monolayer σ_m:

$$\theta(T,P) = \frac{\sigma(T,P)}{\sigma_m} . \tag{5}$$

Thus, a change in either cell temperature or pressure will change the degree of surface coverage, and hence the number of buffer molecules in the gas phase. Since the number density of buffer gas molecules has a direct influence on the clock frequency via the pressure shift effect, variations in θ could be related to drift.

For a cylindrical resonance cell of radius r_c it is fairly easy to show that the change in buffer gas density that results from a change in the degree of surface coverage is given by the expression:

$$\Delta[BG] = -\frac{2\Delta\sigma}{r_c} = -\frac{2\,\sigma_m\Delta\theta}{r_c}. \tag{6}$$

Thus, the change in the adsorption pressure shift can be written:

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{APS} = -\alpha_p k\, T_s\, \left(\frac{2\sigma_m}{r_c}\right)\left[\theta(T,P)-\theta(T_o,P_o)\right], \tag{7}$$

where $\theta(T_o,P_o)$ is the degree of surface coverage in an operating rubidium frequency standard at nominal temperature and pressure. Expanding $\Delta\theta$ to first order in a Taylor series, Eq. (7) becomes

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{APS} = -\alpha_p k\, T_s\, \left(\frac{2\sigma_m}{r_c}\right)\left[\left(\frac{\partial\theta}{\partial P}\right)\Delta P + \left(\frac{\partial\theta}{\partial T}\right)\Delta T\right]. \tag{8}$$

If we now assume that any change in buffer gas pressure is due to a change in the resonance cell temperature, then from the ideal gas equation of state we have

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{APS} = -\alpha_p k\, T_s\, \left(\frac{2\sigma_m}{r_c}\right)\left[\left(\frac{\partial\theta}{\partial P}\right)\frac{P_o}{T_o} + \left(\frac{\partial\theta}{\partial T}\right)\right]\Delta T. \tag{9}$$

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In order to determine $\theta(T,P)$ and its temperature dependence for quantitative analysis of Eq. (9), we can consider the test case of nitrogen adsorption on pyrex. (We will assume that a nominal buffer gas pressure is ten torr.) For nitrogen the parameters required for this pressure shift effect are: $\alpha_p = 7.6 \times 10^{-8}$ per torr [12] and $\sigma_m = 6.2 \times 10^{14}$ cm^2 [17]. Hobson has studied this problem in detail [17], and using his procedure for calculating the adsorption isotherm [18], [19], the data of Table III was obtained. This data yields the values:

$$\frac{\partial \theta}{\partial P}\Big|_{P=P_o} = + 7.7 \times 10^{-5} \text{ per torr} \tag{10a}$$

and

$$\frac{\partial \theta}{\partial T}\Big|_{T=T_o} = - 1.1 \times 10^{-5} \text{ per degree.} \tag{10b}$$

Assuming a nominal clock temperature of 70°C, a cell radius of 1.35 cm [20], and a cell filling temperature for the α_p measurement (T_s) of 25°C, yields

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{APS} = - 1.9 \times 10^{-14} \text{ per degree.} \tag{11}$$

From this value we conclude that in order for this mechanism to account for drift the resonance cell temperature would have to vary by roughly 250 degrees per month. This is completely unreasonable, and so we consider this mechanism as inconsistent with our characterization of drift.

2c) The Temperature-Induced Pressure Shift - As mentioned previously the pressure shift coefficient can display a temperature sensitivity which is due to a buffer gas density distribution in the immediate vicinity of the alkali atom. Thus, if the buffer gas temperature should change by ΔT, then there will be a resonance frequency shift

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{TIPS} = \beta(T_o)[BG]kT_s\Delta T. \tag{12}$$

From Vanier et al. [13] we have for our nitrogen test case

$$\beta(T_o) = + 7.6 \times 10^{-11} \text{ per (torr} \cdot \text{°C)} \tag{13}$$

which, on assuming a nominal buffer gas pressure of ten torr, yields

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{TIPS} = + 7.6 \times 10^{-10} \text{ per °C.} \tag{14}$$

Thus, for this temperature-induced pressure shift to account for drift, temperature changes of roughly six millidegrees per month would be required. Since aging rates for thermistors can be as large as 26 millidegrees per month

[21], and since oscillations in temperature would force a change in sign of the drift coefficient, this effect seems to be a plausible mechanism for drift.

It should be mentioned, however, that this temperature sensitivity (after correcting for mixtures of buffer gas [13]) is somewhat larger than a state-of-the-art clock's resonance cell temperature coefficient [22]. One explanation for this discrepancy could be that the resonance cell temperature coefficient represents a sum of very many different temperature dependent shift mechanisms, of which the pressure shift is only one. In particular, the inhomogeneous light shift [20] has a very complicated temperature dependence, and how this manifests itself in the resonance cell temperature coefficient is not at all clear. It might be that over relatively large temperature variations (several degrees) the inhomogeneous light shift partially compensates for the pressure shift. Thus, though the above calculation indicates the potential seriousness of the temperature-induced pressure shift mechanism, more work needs to be done in order to better understand the phenomenon.

3)   The Spin-Exchange Shift - Basically, as its name implies alkali spin exchange phenomena are typically associated with an exchange of valence electron spin orientation during an alkali-alkali atomic collision. In a spin-exchange collision it is customary to imagine the spins of the two interacting rubidium atoms, $\vec{s}_1$ and $\vec{s}_2$, as precessing about their resultant $\vec{S} = \vec{s}_1 + \vec{s}_2$ [12]. If the individual spins precess by 180°, then the spin $\vec{s}_1$ will have been transferred to atom number 2 and vice versa; the spins will have been exchanged. If the spins do not precess by exactly 180°, then not only will the probability for spin exchange be reduced, but there will be a shift in the Rb atom's 0-0 hyperfine transition frequency. The fractional frequency shift that results from spin-exchange has the form [23]-[25]

$$\left(\frac{\delta\nu}{\nu_o}\right)_{SE} = \frac{\gamma_{ex}}{2\pi\nu_o} \frac{\lambda}{4\sigma_{ex}} \left[\rho(2,0) - \rho(1,0)\right], \tag{15}$$

where γ_{ex} is the collisional spin-exchange rate, λ/σ_{ex} is the ratio of the spin-exchange shift parameter to the spin-exchange cross section, and $[\rho(2,0)-\rho(1,0)]$ is the population difference between the two $m_F = 0$ Zeeman sublevels; for simplicity we will denote this population difference by r in what follows. Employing the value of λ/σ_{ex} appropriate for hydrogen-hydrogen spin-exchange [25] [26], since this value is not known for rubidium; and setting $\gamma_{ex} = N \bar{v} \sigma_{ex}$, where N is the rubidium number density (cm^{-3}) and $\bar{v}$ is the relative velocity between two Rb atoms, we have

$$\left(\frac{\delta\nu}{\nu_o}\right)_{SE} = 1.3 \times 10^{-21} \, Nr. \tag{16}$$

In this expression we have assumed that the clock has a nominal operating temperature of 65°C, and we have taken $\sigma_{ex} = 1.9 \times 10^{-14} \, cm^2$ [27].

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From Eq. (16) it is apparent that if either the Rb number density or the population difference varies, the spin-exchange shift will be altered. Thus, variations in either one of these parameters could potentially be responsible for drift. If we let $\Delta(\delta\nu/\nu_o)_{SE}$ be the alteration of the spin-exchange shift resulting from variations in either N or r, we have

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{SE} = 1.3 \times 10^{-21} \left[r\Delta N + N\Delta r\right]. \tag{17}$$

To simplify this formula further, we can use Killian's formula for N [28]:

$$N = \frac{P_o}{kT} \exp(-9514/T), \tag{18}$$

where T is the temperature in degrees Kelvin and $P_o = 3.55 \times 10^{10}$ dynes/cm^2, to find that $N = 4.5 \times 10^{11}$ cm^{-3} at 65°C. Furthermore, we can employ the clock model of Camparo and Frueholz [29] to estimate r for a Rb clock under normal operating conditions: $r = 8.5 \times 10^{-3}$. Using these results in Eq. (17) we have

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{SE} = 4.9 \times 10^{-12} \left(\frac{\Delta N}{N} + \frac{\Delta r}{r}\right). \tag{19}$$

If we first assume that the alteration of the spin-exchange shift is due entirely to variations in the 0-0 hyperfine population difference (i.e. the term $\Delta r/r$), then in order to account for the total 3 month drift related shift in the 0-0 hyperfine transition frequency of the clock, $\Delta r/r$ would have to be ~ 3. Since calculations based on the clock model of Camparo and Frueholz [29] indicate that $\Delta r/r$ would only be about 0.4 for a 20% change in the lamp's light intensity, it seems unreasonable to expect $\Delta r/r$ ~3 over a 3 month time interval. Thus, if spin-exchange is associated with drift, it appears that it must contribute through variations in the Rb number density (i.e. the term $\Delta N/N$) [30].

From Killian's formula for N (Eq. 18) it is clear that N is very sensitive to the clock's operating temperature. Thus, if we imagine that variations in N are related to clock temperature variations, then we can expand N in a Taylor series about the nominal clock operating temperature T_o to obtain an expression for $\Delta N/N$. Thus, in first order

$$\frac{\Delta N}{N} = (9514-T_o) \frac{\Delta T}{T_o^2} = 8.0 \times 10^{-2} \Delta T \tag{20}$$

so that

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{SE} = 3.9 \times 10^{-13} \Delta T. \tag{21}$$

In order to account for drift, the above formula suggests that ΔT would have to vary on the order of 12°C per month. This is unrealistic, and so we must consider spin-exchange as a highly unlikely drift mechanism.

B. Electromagnetic Field Shifts

4) **The Bloch-Siegart Shift** - In the Rb gas cell frequency standard an oscillating magnetic field in a microwave cavity is responsible for inducing atomic hyperfine transitions [11]. This oscillating field can be imagined as two counter-rotating fields, only one of which is responsible for inducing the hyperfine transitions. The other rotating component of the oscillating field produces a fractional frequency shift on the order of [31]

$$\left(\frac{\delta \nu}{\nu_o}\right)_{BS} = \left[\frac{\mu_o |B_z|}{2h\nu_o}\right]^2 \tag{22}$$

where μ_o is the Bohr magneton, $|B_z|$ is the magnitude of the oscillating magnetic field and $h\nu_o$ is the atomic hyperfine energy level spacing. Assuming an average power of ten microwatts supplied to a minimum volume TE_{111} microwave cavity with a Q of 100, the maximum value of $|B_z|$ in the resonance cell is ~ 1 mG [20]. This results in a maximum fractional frequency shift of 1×10^{-14}, which is too small to account for the total 3 month drift related shift.

5) **The Quadratic Zeeman Shift** - Due to the finite strength of the hyperfine interaction, the rubidium clock transition has a slight magnetic field sensitivity. This sensitivity is called the quadratic Zeeman shift, and has the general form:

$$\left(\frac{\delta \nu}{\nu_o}\right)_{QZ} = \frac{1}{2}\left(\frac{g_e \mu_o}{h\nu_o}\right)^2 B^2 = 8.41 \times 10^{-8} B^2, \tag{23}$$

where g_e is the electron g-factor and B is the magnetic field strength in gauss. Assuming a nominal clock magnetic field of 0.1 gauss, Eq. (23) implies that the full quadratic Zeeman shift in a typical Rb frequency standard is 8.4×10^{-10}. Since this total shift is roughly 50 times greater than the total drift related change in the clock's frequency, one could account for drift by postulating a very small relative change of the clock's magnetic field.

In order to quantify the required relative magnetic field change, we can expand Eq. (23) in a Taylor series about some nominal clock field strength B_o. Then to first order one has

$$\Delta\left(\frac{\delta \nu}{\nu_o}\right)_{QZ} = \left(\frac{g_e \mu_o}{h\nu_o}\right)^2 B_o \Delta B, \tag{24}$$

or

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{QZ} = 1.7 \times 10^{-9} \left(\frac{\Delta B}{B_o}\right). \qquad (25)$$

To account for the typical drift rate of 5×10^{-12}/month, Eq. (25) implies that $\Delta B(t)/B_o$ must be on the order of 0.3%/month, and that the total relative change in the magnetic field over a three month interval must be roughly 1%. Though this change in the clock's magnetic field may seem large, it is nevertheless plausible. Therefore, until magnetic field stability data becomes available, we retain the quadratic Zeeman shift as a viable mechanism of drift.

6) The Intensity Dependent Light Shift - One of the most important physical processes that occurs in the Rb frequency standard is the light shift effect [32]. Qualitatively this effect can be understood as arising from an atomic perturbation associated with the interaction of an induced atomic dipole moment P with the oscillating electric field of the light E [33]. Since the dipole moment is induced by the same oscillating electric field (i.e. $P = \alpha E$, where α is the atomic polarizability), the shift in frequency is proportional to $|E|^2$ or the light intensity coming from the lamp. One could thus expect that slow variations in the lamp's intensity produce drift. Volk and Frueholz [34], however, conclusively showed that for one frequency standard this shift could not be associated with drift. Therefore, the candidacy of this shift as a source of drift must be rejected, since it would violate our assumption that drift is associated with a universal mechanism.

7) The Spectrum Dependent Light Shift - Though we discussed and rejected the light shift due to intensity fluctuations as a possible mechanism of drift, it must be remembered that the light shift is also a function of the spectral profile of the lamp lines entering the clock's resonance cell. Thus, one could imagine a drift mechanism whereby the light intensity did not change, but the optical spectrum did. In order to estimate the characteristics of this type of mechanism, we consider the light shift coefficient associated with the Separated Filter (SF) design of the Rb frequency standard [32]. This is reasonable in light of our hypothesis that drift is due to a universal mechanism regardless of the clock's design.

According to Vanier et al. [32] in the SF design the light shift of the clock has the form:

$$\left(\frac{\delta\nu}{\nu_o}\right)_{LS} = \frac{\theta_F I_o(T_o)}{\nu_o} \left[(T_F - T_o) - K_F(T_F - T_o)^2\right], \qquad (26)$$

where θ_F is a constant giving the change in the light shift coefficient with filter cell temperature, $I_o(T_o)$ is the light intensity entering the resonance cell at a filter cell temperature T_o (where the light shift is independent of light intensity), T_F is the operating temperature of the filter cell and K_F is a constant giving the relative change in light intensity with filter cell temperature. Since we are only interested in spectral changes we consider the case where $K_F = 0$:

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$$\left(\frac{\delta \nu}{\nu_o}\right)_{LS} = \frac{\theta_F I_o(T_o)}{\nu_o} \left(T_F - T_o\right). \qquad (27)$$

Expanding Eq. (27) in a Taylor series about the filter cell temperature T_F yields

$$\Delta\left(\frac{\delta \nu}{\nu_o}\right)_{LS} = \frac{\theta_F I_o(T_o)}{\nu_o} \Delta T. \qquad (28)$$

From Vanier et al. [32] we have that $\theta_F I_o(T_o)/\nu_o$ is on the order of $1.8 \times 10^{-10}/°C$. Thus, in order to account for drift this mechanism would require that temperatures in the clock change on the order of 25 millidegrees per month. Since this is very close to the aging rate observed for certain types of thermistors (~ 26 millidegrees per month) [21], we conclude that the spectrum dependent light shift is a reasonable drift mechanism deserving of further investigation.

C. Miscellaneous Shifts

8) **The Second Order Doppler Shift** – In the cesium beam frequency standard an important shift that must be accounted for in order to obtain high precision is the second order Doppler shift [11]. This shift is just the relativisitic time dilation that occurs for atoms moving relative to the laboratory rest frame. For atoms in a vapor the value of the fractional frequency shift associated with this process is

$$\left(\frac{\delta \nu}{\nu_o}\right)_D = \frac{3kT}{2mc^2} \qquad (29)$$

where $3kT/2$ is just the average thermal energy of the atoms and mc^2 is their rest mass energy. Since the shift is temperature dependent, one can account for changes in sign of the drift coefficient by postulating both positive and negative temperature excursions about some nominal temperature T_o. However, the magnitude of this fractional frequency shift in a typical Rb frequency standard is only ~ 5×10^{-13}, which is less than the total 3 month drift related shift. Thus, this shift must be rejected as a possible source of drift.

9) **The Position Shift** – As a consequence of the work of Risley and Busca [35], it is now known that variations in the microwave power supplied to a Rb clock cavity can shift the clock frequency; this effect does not arise because of the Bloch-Siegart shift that was discussed previously. In a typical gas cell standard a buffer gas in the resonance cell effectively freezes the atoms in place. Therefore, individual atoms experience different optical and microwave field strengths, and hence contribute to the total clock signal to varying degrees. One can thus imagine that the clock signal is dominated by a small spatial region in the resonance cell, and that the shift in the clock signal frequency will be dominated by the region's local values of light intensity (i.e. light shift) and magnetic field strength (i.e.

quadratic Zeeman shift). If the microwave power varies, the dominant spatial region will also change, and hence there will be a variation in the clock signal frequency due to the fact that atoms in the new spatial region will typically experience a different light intensity and/or a different magnetic field strength. It is this shifting of dominant spatial regions that is defined as the position shift effect. Thus, though microwave power is one parameter that determines the position shift, any other parameter like cell temperature that can cause a change in this dominant spatial region also determines the position shift. Though present attention will focus on the microwave power's influence, it should be noted that other parameters may be just as important.

Clearly, a proper analysis of this mechanism requires a fairly sophisticated model of the Rb gas cell frequency standard. However, it is possible to obtain a very rough estimate of this shift's plausibility as a drift mechanism by employing the experimentally determined coefficient of Risley and Busca [35]. This coefficient was not measured in a commercial standard, but for their particular experimental arrangement; therefore the following analysis can only be regarded as order of magnitude. In any event we have:

$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{PS} = 2.5 \times 10^{-11}\ \Delta P, \tag{30}$$

where the change in microwave power entering the cavity ΔP is expressed in dbs. Again, employing our characteristic of drift this coefficient implies that the microwave power entering the cavity would have to change by roughly 0.2 db per month (4%/month), and would have to be capable of roughly a 0.6 db (12%) total change. These values appear to be reasonable, especially given the crude nature of our estimate. Thus, we consider the position shift as a viable drift mechanism.

It should be noted that what is really important in the position shift effect as originally considered by Risley and Busca is not the power entering the cavity, but the energy stored in the cavity. Thus, this "classical" (i.e. microwave power dependent) position shift effect arises because of a variation in the product QP, where Q is the microwave cavity quality factor and P is the average power entering the cavity. We could, therefore, account for drift with the classical position shift by postulating a 4% per month variation in the microwave cavity Q; this might arise because of rubidium migration on the inner surface of the resonance cell. Thus, the fact that the classical position shift can be effected by either power variations or cavity Q variations should not be ignored.

V.   Summary

Drift in the rubidium gas cell atomic frequency standard represents a serious impediment to this standard's more widespread use. As a first step in altering this situation we have cataloged the available data on drift, used this data to obtain a consistent characterization of Rb clock frequency drift in general, and have then used this characterization to analyze potential drift inducing atomic frequency shifts. The conclusions of this analysis are summarized in Table II, where a set of four plausible drift mechanisms are identified: 1) a temperature-induced pressure shift mechanism, 2) a quadratic

Zeeman shift mechanism, 3) a spectrum dependent light shift mechanism, and 4) a position shift mechanism. Though these four mechanisms....were deemed plausible on the basis that postulate 1 is correct (i.e. that drift is due to a single universal mechanism) the validity of the above analysis is not unduly constrained by the choice of the working postulate. If postulate 3 should in reality be true, the above analysis and conclusions would still be valid, with the exception that one would want to tentatively add helium permeation to this list.

Before the problem of drift in the Rb gas cell atomic frequency standard is solved, much more work needs to be done. In particular, each of the four mechanisms cited above should be analyzed both experimentally and theoretically in more detail. Furthermore, it is necessary to determine if any <u>one</u> mechanism can account for all the vagaries of drift, or if our working <u>drift</u> postulate (postulate 1) must be abandoned in favor of postulate 3. Finally, though an attempt was made to identify all possible mechanisms of drift, there is no guarantee that the list assembled for the present study is complete. For example, Vanier [36] has noted that when the optical package of a clock is unmounted and then remounted, the clock frequency changes. Consequently, it cannot be said with absolute certainty that the true mechanism of drift is contained within the list of plausible mechanisms cited above. This list, however, represents a starting place, and it is hoped that the present study will initiate and facilitate further research into this poorly understood phenomenon.

Acknowledgments

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$$\Delta\left(\frac{\delta\nu}{\nu_o}\right)_{SE} \approx 6 \times 10^{-10} \; (\Delta N/N + \Delta r/r).$$

Thus, variations in Δr of only 2% per month could lead to a significant frequency drift rate.

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Table: I. Summary of Rb Gas Cell Clock Drift Data.

Frequency Standard Type	Number Studied	Avg. Drift Magnitude	n_o*	Sign of Drift	Approx. Minimum Drift Magnitude	n_m**	Date	Reference
Varian R-20	3	1.3×10^{-11}/mo.	2	+ & −	1.1×10^{-12}/mo.	2	1966	Ref. 3
General Technology 304-B	1	4.6×10^{-11}/mo.	3	+ & −	5.4×10^{-12}/mo.	3	1966	Ref. 3
?	2	2.6×10^{-11}/mo.	2	+ & −	6.0×10^{-13}/mo.	4	1966	Ref. 4
Modified Varian R-20	3	1.9×10^{-12}/mo.	2	+ & −	1.4×10^{-12}/mo.	2	1968	Ref. 5
Hewlett-Packard hp 5065 A	2	3.0×10^{-12}/mo.	4	+ & −	1.0×10^{-12}/mo.	5	1969	Ref. 6
Efratom FRK-L	2	6.6×10^{-12}/mo.	1	?	2.1×10^{-12}/mo.	1	1978	Ref. 7
Efratom FRK-H	4	6.7×10^{-12}/mo.	3	+ & −	2.1×10^{-12}/mo.	1	1978	Ref. 7
Hewlett-Packard hp 5065 A	3	3.4×10^{-12}/mo.	2	?	2.1×10^{-12}/mo.	2	1978	Ref. 7
Rohde and Schwarz	1	5.1×10^{-12}/mo.	1	?			1978	Ref. 7
Rockwell-Efratom GPS	1	6.9×10^{-12}/mo.	7	+			1984	Ref. 8
EG&G Prototype	2	6.0×10^{-12}/mo.	4	?	4.8×10^{-13}/mo.	1	1984	Ref. 1
EG&G Prototype	1	1.3×10^{-12}/mo.	4	?	4.2×10^{-13}/mo.	1	1985	Ref. 9

* n_o is the average number of months for observing a particular value of drift.

** n_m is the number of months for which the minimum magnitude of drift was observed.

?: unknown

Table II

Possible mechanisms of drift and their plausibility based on a comparison of a mechanism's prediction and the drift's characterization.
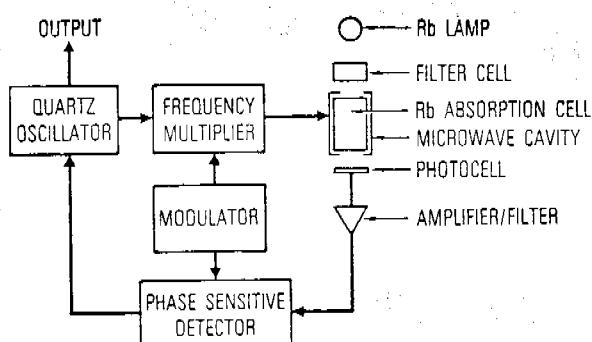
Mechanism	Plausible	Implausible
The Wall Shift		*
The Permeation Pressure Shift		*
The Adsorption Pressure Shift		*
The Temperature-Induced Pressure Shift	*	
The Spin-Exchange Shift		*
The Bloch-Siegart Shift		*
The Quadratic Zeeman Shift	*	
The Intensity Dependent Light Shift		*
The Spectrum Dependent Light Shift	*	
The Second Order Doppler Shift		*
The Position Shift	*	

Table III

The degree of surface coverage for nitrogen on pyrex as a function of temperature T ($^\circ$C) and pressure P(torr).

P \ T	40	60	80	100
9.5	1.18×10^{-3}	8.36×10^{-4}	6.20×10^{-4}	4.78×10^{-4}
10	1.24×10^{-3}	8.80×10^{-4}	6.53×10^{-4}	5.03×10^{-4}
10.5	1.30×10^{-3}	9.24×10^{-4}	6.85×10^{-4}	5.28×10^{-4}

## 1a)
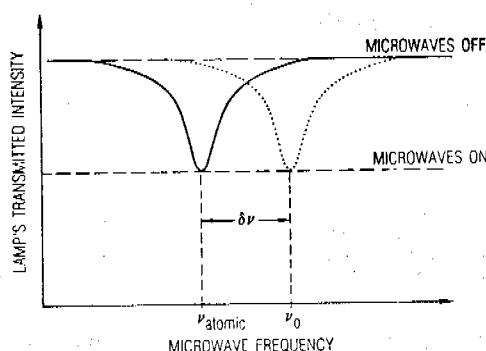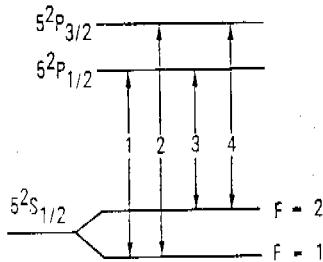
a) Schematic diagram of a passive rubidium gas cell frequency standard, where the ground state hyperfine splitting of Rb^{87} is used as a reference to stabilize the frequency of a quartz-crystal oscillator. In combination the lamp and filter cell produce a spectral emission that preferentially excites atoms in the resonance cell out of one of the $5^2/S_{1/2}$ ground state hyperfine multiplets.

1b)

b) Energy level diagram of Rb^{87} showing the radiative transitions of interest. If as an example it is assumed that the lamp and filter cell only excite transitions 1 and 2, then as a result of the optical pumping process, the atomic population in the F=1 hyperfine level will decrease.

Figure 2.

Diagram of the atomic resonance signal used to stabilize the quartz-crystal oscillator. In the absence of microwaves with a frequency corresponding to the $5^2S_{1/2}(F=2) - 5^2S_{1/2}(F=1)$ atomic transition, the lamp's transmitted intensity is maximized due to the optical pumping process. However, when microwaves of the appropriate frequency, $_{atomic}$, are applied to the microwave cavity, atomic population is returned to the optically absorbing ground state hyperfine multiplet. Thus, the lamp's transmitted intensity decreases. Since the Q associated with this atomic resonance is on the order of $10^7 - 10^8$, the resonant decrease in transmitted intensity can be used to discriminate against very small changes in the microwave frequency applied to the cavity. Note, that as a result of various atomic perturbations the resonance frequency of atoms in the clock, ν_{atomic}, is shifted slightly with respect to the resonant frequency these atoms would have in empty space, ν_0. The magnitude of this offset is denoted by $\delta\nu$.

QUESTIONS AND ANSWERS

MR. ROBINSON: I have a comment that I wanted to make. The simplified way of describing these gas cell standards versus the vacuum cell standards is that in the gas cell standard you have an inhomogeneous line width. The line shape is dependent on every unit absorber in that cell. In the vacuum cell we hope that we have a homogeeous line shape because a given atom averages all over that cell in making a transition. The importance of these two things is that the systematic effects that you so nicely delineated here for the gas cell and the systematic effects that appear in the vacuum cell are almost entirely orthogonal. They are completely different. The physics that you can talk about on the same basis, but these two devices are suspiciously closely looking alike but systematically are very different. That is one of the reasons that we have not been able to "wring out" this vacuum cell. Some of the same effects are going to limit both of them. In a lot of the cases, however, the effects that are really important in one device do not effect the other.

MR. CAMPARO: I think that that is true. One point that struck me while you were giving your talk was that the wall shift could be a source of drift. In my paper wall shift isn't a source of drift, I could eliminate it immediately. Then I realized that, of course, if you've got a coated wall, you have atoms that hit the wall but still contribute to the signal. In a buffer gas clock, there is absolutely no signal coming from the wall. When an atom hits the wall, it is dead and doesn't contribute to the signal. There is no wall shift in the buffer-gas gas cell frequency standard. If you have a wall coating you could have a large wall shift effect. I want to clarify one thing. The gas cell frequency standard is not necessarily inhomogeneously broadened. If you've got any degree of microwave power broadening then that sort of homogenizes things. Its the inhomogeneous character of where the signal comes from that people usually talk about as being an inhomogeneity in the typical gas cell frequency standard.

DAVID ALLAN, NATIONAL BUREAU OF STANDARDS: I want to add just a couple of data points. In the case of the GPS rubidium, as I am sure you are aware, the drift actually changes sign with temperature. As the rubidiums go through an eclipse you can see the drift reverse. In the case of NAVSTAR 8, we saw this nice third order term where the drift very beautiful changed in magnitude or decreased in size with time. One wonders if that is not the same effect, but with the very tight temperature control, one may have a drift in a thermistor which gradually changes the temperature over a long term and hence decreases the drift. If that were the case, should NAVSTAR 8 rubidium have lived on, which it didn't, you could have actually seen the drift reverse sign, instead of asymptoting to zero. We will not be privy to that data, apparently. We have a large data set at NBS of the earlier stages of the rubidium studies in which we showed one of the mechanisms for this sign reversal. The physics in the cell is very complex as you know, but the inner oven heater element is a heat dissapating transistor which is very close to the physics package. If you look at it carefully, there is actually a magnetic coupling loop due to the heating current of that heating transistor. It is close enough to effect the magnetic field and cause a Zeeman shift on the rubidium as a function of the environmental temperature. We have the data set on that if it is of use to you.

MR. CAMPARO: One of the problems associated with the study of drift is that there two things that are important. One is the mechanism of drift, is it a

quadratic Zeeman shift, i.e. what is the mechanism? The other is, what is the driver? The driver could appear to be a temperature effect as in your example, but actually the driver is a magnetic field effect. There is another subtlety involved in all of this. You have to separate mechanism from driver. Once you understand the mechanism, you can maybe get an idea of what the drivers are. Just understanding the mechanism is not the end of the story, either.

FRED WALLS, NATIONAL BUREAU OF STANDARDS: The transistor heater is more complex because the case is Kovar so there are hysteretic effects with the magnetic driver.

MR. CAMPARO: That is why I think that the first step is to try to understand the mechanism of frequency drift. Then you might lead the studies into the nature of the driver.

MICHAEL GARVEY, FREQUENCY AND TIME SYSTEMS: Did your data set of hardware that you looked at include enough variety in design that that is not a factor?

MR. CAMPARO: I don't think that the physics package is that different. It is a simple design, lamp, resosnant cell, photodetector. One of the major differences in design is integrated filter cell and separated filter cell. We did have those two types in the data. My feeling is that it was the electronics and the circuit designs associated with different clocks.