FREQUENCY EQUILIBRATION AND THE LIGHT-SHIFT EFFECT FOR BLOCK IIR GPS RUBIDIUM CLOCKS

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Abstract

Over the past several years, evidence has grown indicating that rubidium (Rb) vapor-cell frequency standards exhibit a long "frequency equilibration" period following activation. Though frequency equilibration can have important implications for diverse timekeeping systems, the mechanism driving the behavior is not well understood and has been the subject of debate. Here, we investigate this phenomenon, as well as frequency aging, for a number of Block IIR GPS Rb clocks. Consistent with previous work, we find that all six Rb clocks in the study showed a frequency equilibration phenomenon with time constants ranging from 98 to 584 days. Further, all clocks displayed a strong correlation between clock frequency and light intensity during equilibration. Significantly, five of the GPS clocks displayed small light-intensity jumps (~ 0.3%) that could be correlated with small jumps in clock fractional frequency (~ 3x10^{-13}); these were used to estimate the various clocks' light-shift coefficients. The broad range of equilibration time constants and the light-shift coefficient determinations cast doubt on the two mechanisms most often cited to explain frequency equilibration: helium permeation through the resonance cell's glass envelope, and the intensity-dependent light-shift effect. Additionally, the light-shift coefficient determinations cast doubt on the intensity-dependent light-shift effect as the driver of frequency aging.

INTRODUCTION

When a rubidium atomic clock is activated, the temperature of the lamp, filter cell and resonance cell increase, and as a consequence the alkali vapor density in each of these clock elements increases. Due to the light-shift [1] and position-shift [2] effects, these variations in alkali density give rise to a clock frequency change that proceeds until the clock's temperature has reached steady state. As illustrated conceptually in Figure 1a, the clock "warms up" to its true steady-state temperature conditions within a few days. Following this warm-up period, the clock frequency continues to change, though now at a much-reduced rate, and this slower frequency variation has often been termed frequency "aging." However, over the past several years evidence has accumulated suggesting that the frequency-aging rate is not constant following clock activation. Rather, the aging rate changes over a period of months, until after about 6 months to a year of continuous operation, the clock frequency displays what may best be described as the clock's "true" frequency aging: a very linear and very slow frequency change with time [3,4]. As illustrated conceptually in Figure 1b, we distinguish between these two regimes of long-term,

deterministic, frequency-change behavior by reserving the term frequency aging for the steady-state linear process that takes place well into the clock's operating life, and by defining a new term, clock-frequency "equilibration," as the temporal change in clock frequency that occurs between clock warm-up and true aging.
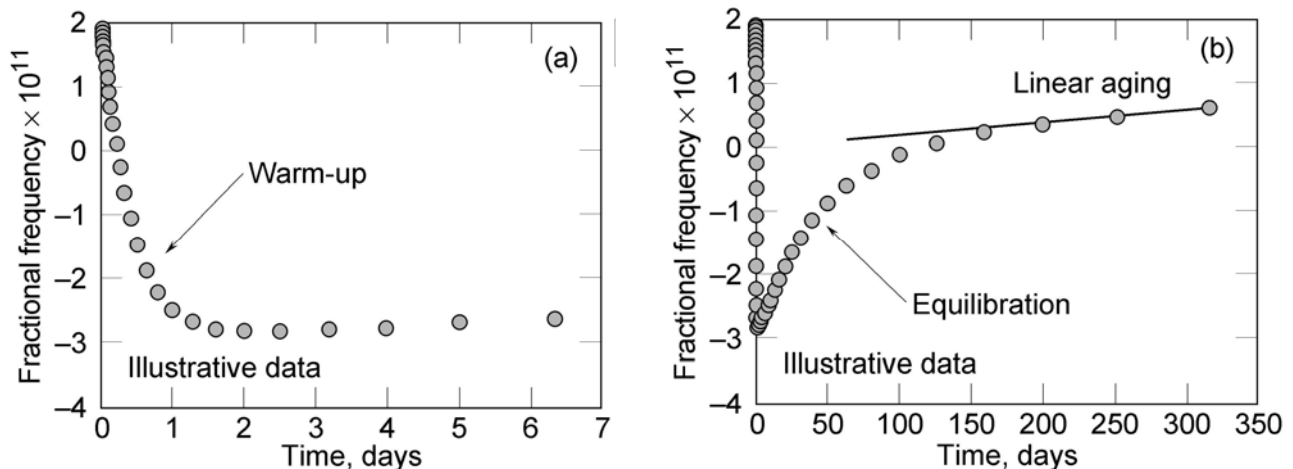

Figure 1. Illustration of the nominal temporal change of a rubidium clock's frequency with time. As shown in (a), within the first few days the clock warms up, and thereafter displays a slow frequency variation with time. On a longer timescale however, as illustrated in (b), the rate of frequency change after warm-up generally changes, until after a number of months the clock reaches its steady-state frequency-aging rate. To distinguish these two long-term, deterministic, frequency-changing processes, we reserve the term frequency aging for the clock's behavior well into its life and define the term frequency "equilibration" as illustrated in Figure 1b.

From the operational perspective of a timekeeping system, the issues of vapor-cell clock equilibration and frequency aging can be fairly important. For example, in situations where diverse spacecraft clocks are slaved to a master satellite Rb clock **[5]**, good constellation timekeeping requires a master satellite whose Rb clock has completed equilibration and whose frequency-aging rate is low. Consequently, there is a need to: 1) discover the underlying mechanism(s) driving frequency equilibration, 2) develop strategies to speed up the equilibration process, 3) discover the underlying mechanism(s) of frequency aging, and 4) eliminate or slow to insignificance the frequency-aging rate. In the next section, we describe measurements of frequency equilibration using long-term data from Block IIR GPS Rb clocks. We then use the data to test the validity of two mechanisms most often cited as explanations for frequency equilibration; the results show that both proposed mechanisms are problematic. Finally, we consider frequency aging of the Block IIR Rb clocks, and show that an intensity-dependent light-shift mechanism cannot explain frequency aging in these devices.

ON-ORBIT MEASUREMENTS OF FREQUENCY EQUILIBRATION

The Rb clocks onboard GPS Block IIR satellites are arguably among the best Rb clocks ever built **[6]**. Moreover, their activation on orbit corresponds to something of a "fresh start," since the clocks have

experienced significant vibration and acceleration during launch, thereby moving the pools of alkali metal in the lamp, filter cell, and resonance cell to random locations. With the help of Dr. M. Epstein of ITT Industries and Mr. T. Dass of Lockheed Martin, we were able to obtain daily averages of Rb clock frequency and lamp intensity for six Block IIR Rb atomic clocks following their activation. (For completeness, we note that these clocks correspond to a separated filter-cell design **[7]**.)

Figure 2 shows the frequency history of one of the Block IIR Rb clocks (i.e., the operational clock onboard SVN-54, which was activated on 8 February 2001). The clock clearly shows frequency equilibration, reaching its steady-state linear frequency aging after roughly 2 years of operation. Figure 3 shows the aging-removed fractional frequency as a function of time since activation, along with the relative lamp intensity. All of the other Block IIR Rb clocks showed essentially identical behavior to that displayed in Figures 2 and 3, in particular the very clear equilibration behavior and strong lamp-intensity/clock-frequency correlation.
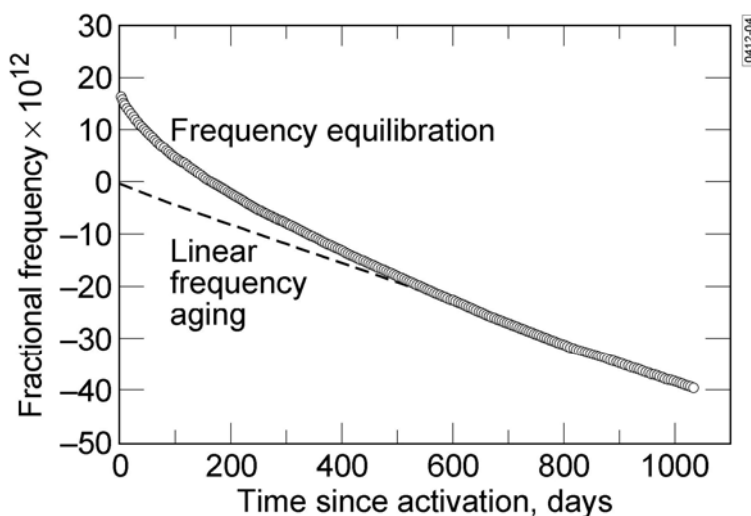

Figure 2. Fractional frequency history for the Rb atomic clock onboard the GPS satellite SVN-54. This clock was activated on 8 February 2001.

In order to quantify the equilibration process, we first removed the steady-state linear frequency aging from the clocks' frequency data, as in Figure 3. Then, using the aging-removed fractional frequency data, $\Delta y(t)$, from months one through eight following activation, we fit the data to an exponential function: $\Delta y(t) = \Delta y_o \exp(-t/\tau_{EQ})$. Additionally, we determined the linear regression coefficients between lamp intensity change, $\Delta I(t)$, and clock fractional frequency change, $\Delta y(t)$, for the equilibration period; this was termed $\delta y/\delta I_{EQ}$. The values of Δy_o, τ_{EQ} and $\delta y/\delta I_{EQ}$ for these clocks are collected in Table I, along with the correlation coefficients, r, for the Δy versus ΔI scatter plots.
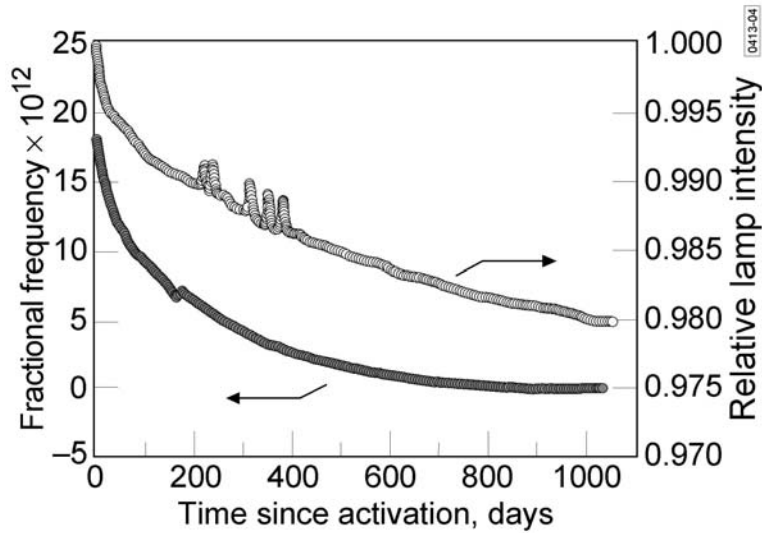
Figure 3. Aging-removed fractional frequency and relative lamp intensity history for the Rb clock onboard the GPS satellite SVN-54.

Table I. Measured clock parameters. $\delta y/\delta I_{EQ}$ corresponds to the linear regression slope for the scatter plot of fractional frequency vs. lamp intensity during the equilibration period; τ_{EQ} is the equilibration period's time constant, determined by least squares fit of $\Delta y(t)$ to an exponential, and $\alpha_{LS}\Phi$ is the light-shift coefficient of the clock. For completeness, correlation coefficient values, r, for the clock-frequency/lamp-intensity scatter plot are given.

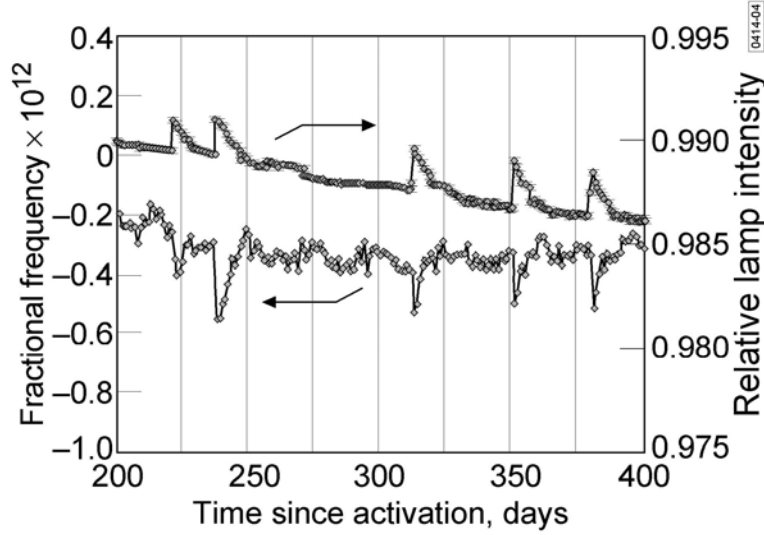| Clock	Linear Frequency Aging Rate	Δy_o x 10^{11}	τ_{EQ} (days)	$\left(\dfrac{\delta y}{\delta I}\right)_{EQ}$ $(10^{-11}/\%)$	$\alpha_{LS}\Phi$ $(10^{-11}/\%)$
SVN-41	-3.7×10^{-14}/day	+ 1.2	162.1 ± 0.4	4.0 ± 0.1 (r = 0.93)	-0.214 ± 0.009
SVN-43	-2.2×10^{-14}/day	+ 2.4	584 ± 11	5.1 ± 0.1 (r = 0.97)	
SVN-44	-3.5×10^{-14}/day	+ 1.2	307 ± 4	0.79 ± 0.04 (r = 0.81)	-0.10 ± 0.02
SVN-46	-1.9×10^{-14}/day	+ 1.6	98 ± 2	0.77 ± 0.01 (r = 0.99)	-0.088 ± 0.007
SVN-51	-3.5×10^{-14}/day	+ 1.7	300 ± 1	1.61 ± 0.05 (r = 0.97)	-0.17 ± 0.02
SVN-54	-3.7×10^{-14}/day	+ 1.4	235 ± 2	1.42 ± 0.02 (r = 0.98)	-0.139 ± 0.006

Figure 4. For the Rb clock onboard GPS satellite SVN-54, this figure shows jumps in the lamp intensity that coincide with jumps in the clock's frequency. We attribute this behavior to the intensity-dependent light shift effect as discussed in the text.

In five out of six cases, the GPS satellite clocks also displayed relatively sudden changes in lamp intensity that coincided with sudden changes in the clock's fractional frequency. A set of these is shown in Figure 4 for the SVN-54 Rb clock. As is well known, a Rb clock's frequency is determined, to a considerable extent, by the lamp intensity and lamp spectrum through the light-shift effect. Specifically, defining f_o as the clock's nominal frequency, $f_o \sim I_o \Phi$, where I_o is the lamp's nominal light intensity at the entrance to the resonance cell and Φ corresponds to the spectral overlap between the lamp's emission spectrum and the atom's Doppler-broadened absorption spectrum **[8,9]**. Defining Δy_{LS} as the change in the clock's fractional frequency due to a change in the light's characteristics, we have

$$\Delta y_{LS} = \alpha_{LS} \left(\frac{\delta I}{I_o} \right) \Phi\left(\{x_j\}\right) , \tag{1}$$

where α_{LS} is the partial derivative of the clock's fractional frequency with respect to the relative light intensity impinging on the resonance cell, and the x_j are parameters that can alter the spectrum of the lamp's emission line (e.g., filter cell temperature, lamp temperature, etc.). For ease of discussion, we refer to $\alpha_{LS}\Phi$ as the intensity-dependent light-shift coefficient.

Since the changes displayed in Figure 4 correspond to a period in the clock's operation that is well past the clock's warm-up, we presume that these changes were solely due to the intensity-dependent light shift effect (i.e., all δx_j are negligible over the period of time of the frequency jump). Consequently, with data like those of Figure 4 we were able to evaluate $\alpha_{LS}\Phi$ for five of the Block IIR Rb clocks. This was accomplished by first removing the equilibration in clock frequency and the slow variation in lamp intensity from the two sets of data by fitting each to third-order polynomials. The purpose of this data manipulation was to keep the frequency-equilibration phenomenon from unduly influencing the $\alpha_{LS}\Phi$ determinations. The results are collected in Table I, where it should be noticed that the values of $\alpha_{LS}\Phi$ all

have the same sign and are of essentially the same magnitude. We note that the average value of our intensity-dependent light-shift coefficient for the Block IIR Rb clocks (i.e., $\langle \alpha_{LS} \Phi \rangle = -1.4 \times 10^{-12}/\%$) is in agreement with an independent determination of this parameter [10].

ANALYSIS OF TWO POTENTIAL FREQUENCY EQUILIBRATION MECHANISMS

INTENSITY-DEPENDENT LIGHT-SHIFT EFFECT

Given the correlation between lamp-intensity and clock-frequency during equilibration, Coffer and Camparo hypothesized that frequency equilibration is driven by the intensity-dependent light-shift effect [3]. While the data of Table I are qualitatively consistent with this conjecture, the data are nonetheless problematic for the Coffer-Camparo hypothesis. Most telling is the comparison between the $\delta y/\delta I_{EQ}$ regression coefficients and the intensity-dependent light-shift coefficients, $\alpha_{LS}\Phi$, collected in Table I. In all cases, the $\delta y/\delta I_{EQ}$ values and the $\alpha_{LS}\Phi$ values have opposite signs. Additionally, the light-shift coefficients are about an order of magnitude smaller than the $\delta y/\delta I_{EQ}$ values. Thus, it seems unlikely that the intensity-dependent light-shift effect drives frequency equilibration in the vapor-cell atomic clock.

HELIUM PERMEATION

Bloch *et al.* have recently argued that frequency equilibration might arise from helium permeation through the glass walls of the resonance cell [11]. When a resonance cell is fabricated, it is filled with a pool of liquid Rb metal along with some tens of torr of a heavy noble gas (e.g., Kr) and/or a molecular buffer gas (e.g., N_2) [12]. As a whole, the buffer gas acts to slow the rate of Rb/wall collisions, which destroy hyperfine polarization and, hence, have a detrimental effect on the atomic clock's signal. The molecular species has the added effect of quenching resonance fluorescence [13], which is important for clock operation, since the re-absorption of resonance fluorescence can destroy hyperfine polarization through a competitive optical-pumping process [14]. Though glass is relatively impermeable to Kr and N_2, so that the vapor densities of Kr and N_2 in the resonance cell are constant over a clock's lifetime, Bloch *et al.* noted that this is not the case with regard to helium and the borosilicate glasses commonly used for atomic clock resonance cells.

During a resonance cell's tenure on the Earth, atmospheric He slowly (albeit non-negligibly) permeates through the glass envelope of the resonance cell. Since the partial pressure of He in the atmosphere is 3.98×10^{-3} torr [15], and since the pressure-shift coefficient of He is 1.05×10^{-7}/torr [16], this increasing pressure of He in the resonance cell will cause a time dependent variation in the clock's output frequency with a positive slope and with a maximum fractional change of 4.2×10^{-10}. In space, any He that had permeated into the resonance cell must permeate out, which again results in a time-dependent change in the clock's frequency, displaying in this case a negative slope.

As seen by the data collected in Table I, our results provide some support for this mechanism: space data show equilibration phenomena with a negative slope, and the magnitude of the fractional-frequency equilibration changes (i.e., $|\Delta y_o|$) are all less than 4.2×10^{-10}. However, if this mechanism is examined more critically [17], by considering He permeation through the glass walls of a spherical resonance with inner diameter 2a and outer diameter 2b, we find that on-orbit

$$P_a(t) = P_a^0 \exp[-\kappa\eta\Gamma t] \ . \tag{2}$$

Here, $P_a(t)$ is the He pressure inside the clock's resonance cell as a function of time; P_a^0 is the He pressure inside the resonance cell at the end of the Rb clock's tenure within the Earth's atmosphere; $(\kappa\eta\Gamma)^{-1}$ is the He permeation time constant; κ is the He permeation coefficient of the glass; Γ is a geometrical factor for the resonance cell, given by $b/[a^2(b-a)]$; and η is a thermodynamic factor given by $3P_{STP}(T/T_{STP})$. As noted by Riley [18], the resonance cells of the Block IIR GPS clocks are composed of a borosilicate glass, Corning 7070. Consequently, extrapolating Altemose's values of κ for this type of glass to the resonance cell's operating temperature (i.e., 65 °C) [19], we get $\kappa = 1.76 \times 10^{-10}$ [(cm^3 @ STP/sec)(mm/(cm^2 cm-Hg))]. Then, if we equate the surface area of the Rb clock's cylindrical resonance cell with the surface area of a sphere, we get b = 0.89 cm. Using these values of κ and b, we computed He permeation time constants. These are shown in Figure 5 with $(\kappa\eta\Gamma)^{-1}$ plotted as a function of the resonance cell's thickness, (b-a).
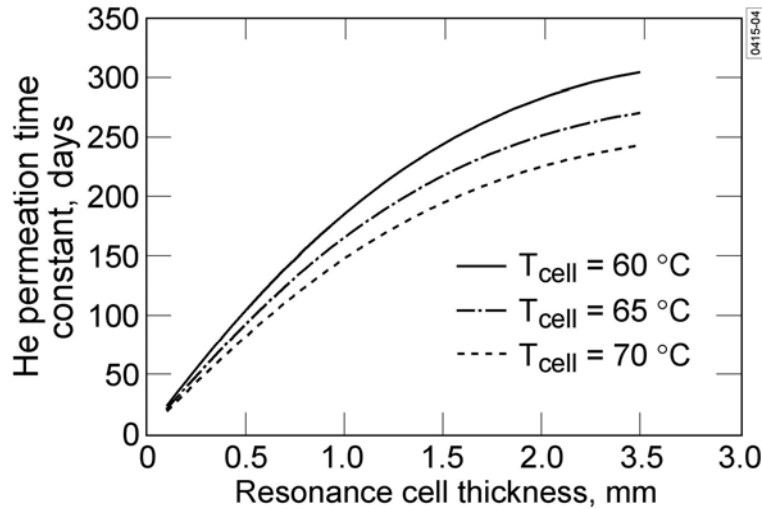

Figure 5. Time constant for He permeation through a Corning 7070 glass resonance cell as a function of glass thickness. Several curves are shown, corresponding to different operating temperatures of the resonance cell.

The results of Figure 5 highlight a significant problem for the helium permeation mechanism of Bloch *et al.* According to the data of Table I, the frequency-equilibration time constants for the Block IIR Rb clocks ranged from 100 to 600 days. However, from the results presented in Figure 5, it would be extremely difficult to account for such a broad range of time constants with the helium permeation mechanism: the Block IIR Rb clocks all come from the same manufacturer; they all have the same design; and they all employ the same type of glass for their resonance cells. Of course, it is known that alkalies diffuse into and react with glass [20], and this could affect the solubility of He within the glass and, hence, the permeation coefficients of different resonance cells. Nevertheless, in the absence of additional experimental results, we must consider the broad range of frequency equilibration time constants as problematic for the helium permeation hypothesis.

Notwithstanding the issue of time constants, there is an additional difficulty with the He permeation mechanism. According to the data of Table I, there appears to be a significant correlation between lamp-

intensity and clock-frequency during equilibration. If He permeation into (or out of) the resonance cell drives frequency equilibration, then this correlation is either accidental, or it is driven by He permeation into (out of) the lamp and/or filter cell. The lamps of the Block IIR Rb clocks are composed of Corning 1720 glass [18], whose He permeation coefficient is roughly three orders of magnitude smaller than the Corning 7070 glass of the resonance cell [19]. Further, permeation of 4 mtorr of He into the lamp would have a negligible effect on the lamp's output intensity [21]. Thus, it seems unlikely that He permeation into (or out of) the lamp envelope could account for the correlation between clock frequency and lamp intensity during equilibration. With regard to the filter cell, the Doppler broadened widths of the Rb^{85} D_1 and D_2 absorption lines are 554 and 565 MHz, respectively, at the filter cell's operating temperature of 85 $^{\circ}C$ [18]. In comparison, 4 mtorr of He only contributes ~ 90 kHz to the pressure-broadened widths of these absorption lines [22]. It, therefore, seems unreasonable to assume that He permeation into (or out of) the filter cell could affect the detected lamp intensity. Consequently, unless the clock-frequency/lamp-intensity correlation during equilibration is coincidental, the correlation poses an additional problem for the helium permeation mechanism.

FREQUENCY AGING

In addition to frequency equilibration, researchers have often speculated on the light-shift effect as a mechanism for frequency aging:

$$A = \frac{\delta[\Delta y_{LS}]}{\delta t} \cong \alpha_{LS}\frac{d\Phi}{dt} + \alpha_{LS}\Phi\left(\frac{\dot{I}(t)}{I_o}\right) = \dot{\beta}_{LS} + \beta_{LS}\left(\frac{\dot{I}(t)}{I_o}\right); \qquad (3)$$

here, for convenience, we have defined $\beta_{LS} = \alpha_{LS}\Phi$. (Note that $I(t) \cong I_o$ as demonstrated by the data of Figure 4.) In particular, as illustrated above, very slow changes in the lamp's light intensity have been observed, and it has been hypothesized that these must affect the clock's frequency through the light-shift effect, thereby giving rise to frequency aging. This tidy picture was confounded in the mid-eighties, however, when Volk and Frueholz demonstrated that $\left|\beta_{LS}\left(\dot{I}(t)/I_o\right)\right| << |A|$ for one high quality Rb clock [10]. Of course, it is certainly reasonable to argue that Volk's and Frueholz's sample-of-one result corresponded to the exception rather than the rule. Furthermore, as mentioned by Camparo [23], there is always the possibility that $\dot{\beta}_{LS}$ is non-zero. Consequently, given the present empirical situation, it must be admitted that the light-shift effect remains a viable candidate for the frequency-aging mechanism, though the situation is certainly confused.

In order to study the light-shift effect as a possible mechanism for frequency aging, we employed the light-intensity/clock-frequency jumps illustrated in Figure 4 to estimate β_{LS} at various times during the clocks' operating histories. These estimates for several of the satellite clocks are shown in Figure 6, and the linear fit values of $\dot{\beta}_{LS}$ for all five of the satellite clocks are collected in Table II. Also shown in Table II are estimates of $\beta_{LS}\left(\dot{I}(t)/I_o\right)$ for the satellite clocks; these were obtained by employing an average value of β_{LS} for each clock, and using data well past equilibration to estimate $\left(\dot{I}(t)/I_o\right)$.
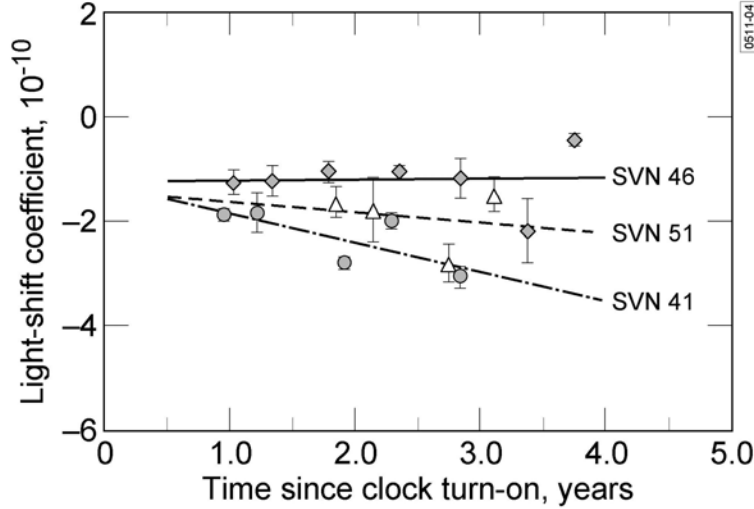
Figure 6. Light-shift coefficients, β_{LS}, as a function of time since clock activation on orbit: circles correspond to the clock onboard SVN 41; triangles correspond to the clock onboard SVN 51, and diamonds correspond to the clock onboard SVN 46. Data points correspond to the periods in the data record where an unambiguous determination of the light-shift coefficient could be made based on correlated frequency and light-intensity jumps.

Table II. Estimated linear frequency aging rates for six Rb atomic clocks onboard Block IIR GPS satellites. Aging rates were determined by linear least-squares fit over either 275 days or 189 days of data, and the 1-sigma uncertainties are for the fit by itself assuming only measurement noise, σ_{fit}, and the influence of random-walk frequency noise over the fit interval, σ_{RW} [24]. To determine σ_{RW}, we assumed a worst-case long-term Allan deviation of $\sigma_y(\tau) = 1.3 \times 10^{-16} \tau^{1/2}$ for all the clocks [6].

GPS Satellite	Estimated Frequency Aging Rate: $\hat{A} \pm \sigma_{fit} \pm \sigma_{RW}$ (10^{-14}/day)	$\beta_{LS}\left(\dfrac{i(t)}{I_o}\right)$ (10^{-14}/day)	$\dot{\beta}_{LS}$ (10^{-14}/day)
SVN-41	$-3.745 \pm 0.009 \pm 0.004$	$+0.056 \pm 0.004$	-15.3 ± 7.7
SVN-43	$-2.231 \pm 0.003 \pm 0.004$		
SVN-44	$-3.484 \pm 0.006 \pm 0.004$	$+0.046 \pm 0.012$	$+8.8 \pm 14.7$
SVN-46	$-1.880 \pm 0.004 \pm 0.004$	$+0.047 \pm 0.004$	$+0.4 \pm 6.1$
SVN-51	$-3.502 \pm 0.004 \pm 0.005$	$+0.026 \pm 0.003$	-5.2 ± 20.0
SVN-54	$-3.714 \pm 0.004 \pm 0.005$	$+0.094 \pm 0.004$	$+22.4 \pm 29.3$

As evidenced by the data collected in Table II, our results are consistent with the Volk-Frueholz finding. The lamps' intensity changes are too small to account for frequency aging via the light-shift effect; moreover, they are of the wrong sign. However, regarding a possible frequency-aging role for the light-shift coefficient, β_{LS}, our results are less definitive. In particular, Figure 7 shows the various clock values of $\dot{\beta}_{LS}/A$. Though the uncertainty of the $\dot{\beta}_{LS}/A$ estimates is large for the individual satellite clocks, it is possible to construct a weighted mean value, $\langle\dot{\beta}_{LS}/A\rangle$, for the sample [25], since all of these clocks are identically constructed and operate under identical conditions. In this way we obtain the intriguing result $\langle\dot{\beta}_{LS}/A\rangle = 1.7 \pm 1.5$. We must note, however, that even with this weighted mean value, we cannot reject the hypothesis $\langle\dot{\beta}_{LS}/A\rangle = 0$ with anything better than a 0.87 probability. (In Figure 7, the shaded region corresponds to the 95% confidence interval for the value of $\langle\dot{\beta}_{LS}/A\rangle$.)
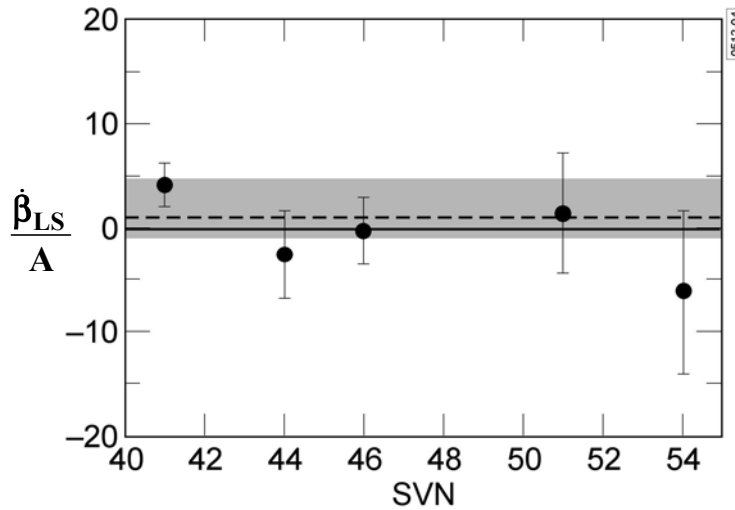

Figure 4. For each of the space vehicles, the ratio of the estimated derivative of the light-shift coefficient, $\dot{\beta}_{LS}$, and the linear frequency-aging rate, A; the dashed line corresponds to $\dot{\beta}_{LS}/A = 1$. The shaded region in the figure represents the 95% confidence interval for the weighted mean of all the space-vehicle ratios.

CONCLUSIONS

In summary, we have used on-orbit data from Block IIR GPS rubidium clocks to investigate frequency equilibration and frequency aging in these devices. As reported previously [26], frequency equilibration appears to be a generic phenomenon in Rb clocks, though the mechanism driving the process is not well understood. Using the GPS data, we analyzed the intensity-dependent light-shift effect and helium permeation as potential mechanisms driving equilibration. Unfortunately, both mechanisms were problematic in explaining our observations. At the present time, it is unclear what process actually drives frequency equilibration.

With regard to our frequency-aging studies, though more work is clearly required on what it will be convenient to refer to as the "$\dot{\beta}_{LS}$-hypothesis," it is reasonable to speculate on how a non-zero derivative of the light-shift coefficient might arise. One likely explanation for $\dot{\beta}_{LS} \neq 0$ posits a slow change in spectral overlap between the lamp's emission lines and the atom's absorption lines (i.e., $\dot{\Phi} \neq 0$). Since the lamp's emission spectrum is a sensitive function of alkali density, it might be that slow changes in the lamp's operating temperature change the spectral overlap [27]. Alternatively, alkali reaction with the lamp's glass envelope could lead to the production of volatile and reactive species that coat the liquid pool of metal within the lamp, thereby reducing the alkali vapor pressure [28]. Similarly, outgassing of reactive species (e.g., O_2 or H_2O) could lead to a reduction of alkali density [29]. Filtering of the lamp lines, either by a separate filter cell or within the clock's resonance cell, also affects the spectral overlap, and therefore changes in filtering action could lead to a non-zero value of $\dot{\beta}_{LS}$. These changes in filtering action could again be driven by temperature variations in the filter and/or resonance cell. Finally, given the inhomogeneous nature of the light shift in the vapor-cell atomic clock [30], any variations in the resonance-cell region where atomic signal is generated [31] could give rise to an affect that appears as a non-zero $\dot{\beta}_{LS}$. Notwithstanding these uncertainties, based on the results presented here, further investigation of the $\dot{\beta}_{LS}$-hypothesis seems warranted.

ACKNOWLEDGMENTS

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QUESTIONS AND ANSWERS

BILL RILEY (Hamilton Technical Services): Maybe some of you know that I was involved with these clocks, and so Jim and I have discussed this matter at length. And I will be brief here. I just wanted to mention a couple of things.

The best fit that I have seen to these aging characteristics is a diffusion fit, a square-root of time fit. And that suggests to me that there might be some underlying physics that is of the nature of a diffusion process. I have argued that it is not light shift, and so that part of what you have said I agree with very much.

But I just want to mention one other possibility that has been my favorite, and that is in the absorption cell, you have nitrogen gas. And it is very possible, in fact likely, that that gas could diffuse or in some other way be taken out of the gas phase and trapped into the rubidium film or the glass of the absorption cell. Nitrogen has a positive pressure-shift coefficient, so the rest of it causes the frequency to go down and that is the way every one of these clocks goes in a very consistent way. And so, it is another factor to put on your list of possibilities.

BOB GRAHAM (Sandia National Laboratories): Now, I understand that most of the work has been done on GPS clocks, but on your laboratory clocks, is this equilibration period just on the initial turn-on of the rubidium; or, if you would have powered down for some period of time and bring it back up, would it still show equilibration? Or is that something, again, just on initial power-up?

JIM CAMPARO: I think it is just on initial power-up. We actually wondered about ourselves. And so we turn the clock off over this period. We turned it off for 15 days/two weeks; turned it on. So there it was, and then turned it off again here for maybe 50 days. And turned it on again.

So it looks to me that whatever is going on here just continues, even if it is not powered. Notice that the light intensity did not continue to come down; it sort of stopped and picked up where it left off.

This was another indication to us that the light intensity effect was not driving equilibration. It may be correlated with it, but you would have expected this to come down – if this kept going, this would have kept going as well. So in the laboratory clocks, it looks like it has something to do with initial turn-on.

And one problem, and I think that Robert brought this us at the last PTTI, because these were commercial clocks that we had simply purchased, we did not know anything about their burn-in history. So that is really an uncertainty here in terms of where are we really starting. And we say the equilibration time constant is 10 days to 50 days; you probably have to think, well, what did the manufacturer do to it as well?

But those were just preliminary studies to get us going, to see what is going on.

RON BEARD (U.S. Naval Research Laboratory): I might make a comment on that. I think we have seen under our conditions that if you go in and out of vacuum, this reoccurs.

CAMPARO: Really? Well, I hate it. I would point to helium propagation.

BEARD: I am not opposing that; I am making an observation.

CAMPARO: Let me also that what we did with our laboratory clocks is we decided you cannot run them in vacuum; but we put them in vacuum. Pumped it down to 10^{-6} torr.

And we have had them in there for about maybe 4, 6 months – I cannot remember the full time. And, yes, we have been pulling them out periodically and just looking at them. And the idea is that if it is helium permeation, then we should be getting all that helium out while they are in vacuum. So that after a year, when we pull them back into the atmosphere, we will see the helium go back in, and we will see the equilibration begin again.

So we have got that study going on. A long term in and out of vacuum, basically.

HUGO FRUEHAUF (FEI-Zyfer): Early in the nineties at Efratom, we did some research on hydrogen as well. And hydrogen effects seem to be similar to helium, except you needed a hundred times the density. And the exit rate, then, for the hydrogen molecule will be different than the exit rate for helium. So I would not give up yet on any kind of gas absorption.

CAMPARO: For which? The aging or the equilibration?

FRUEHAUF: For the aging.

CAMPARO: For the aging. So, are you saying that atmospheric hydrogen would be coming in and out of the cell?

FRUEHAUF: Just like helium. Except at a different – it requires more hydrogen atoms to do the same thing helium atoms do.

CAMPARO: And that is because it is in a molecular form. Do you know if anybody has got measurements of permeation rates through various glasses for hydrogen molecules?

FRUEHAUF: Yes, I will have to think about it. I have to remember what we did actually.

CAMPARO: Well, let me give you my card and then maybe you can e-mail me that information. I would love to take a look at it.

FRUEHAUF: We actually estimated our drift rate of our rubidiums based on helium and hydrogen. We did not have a helium-proof glass. And in this particular case, which is interesting, we actually continued to use glass – we didn't worry about absorbing helium and hydrogen, because it actually had a positive aging effect with our standard. And it offset some our negative aging effects that we could not control.

CAMPARO: One thing I do want to mention, though, is that at previous PTTIs, I presented frequency aging for Milstar clocks. And those are showing very good aging rates of the same order of magnitude, parts in 10^{14} per day, but the coefficient is different. It is positive.

So a buffer gas permeation effect – that would be similar in all clocks, which would mean all rubidium clocks would have to show the same sign, either negative in space or positive in space. And so then a problematic issue: Why is it that the Milstar rubidium clock shows a positive frequency-aging rate on orbit, whereas the GPS clocks were showing these – did I get that right? In any case, the sign is different for the two clocks.

FRUEHAUF: For our Efratom clock, the hydrogen and helium had a positive aging effect. And I believe the difference is the vapor pressure of the nitrogen, that's my opinion.

MARC DAMASHEK (Department of Defense): Can you accelerate this testing by putting these things in a pressure chamber, rather than waiting for things to outgas at atmospheric pressure?

CAMPARO: Well, I worry a little bit about doing that because, as you said, if you put it in a pressure chamber, what you are doing is you are intentionally driving helium in. And you know that is going to work. I mean, if you put …

DAMASHEK: Not necessarily helium, though. Whatever gas that is in question.

CAMPARO: I think what that will tell you is that would give you an estimate of the permeation coefficient through the glass. But one thing you are trying to look at is, is there enough getting in over time. So if you did, let's say, an atmosphere of helium, well, compared to 4 millitorr in the atmosphere, you are talking – what – five to six orders of magnitude difference. So the rate is going to go way up. Basically, you are going to get that much more in.

And you know you will get a pressure shift, because people have measured the pressure shift's coefficients. Like seven hundred hertz per torr. So we are trying to do is do it under the actual conditions, and that means we are going to have to wait. But then we do not have to be concerned about, are we sort of artificially making an effect appear for us?

So I think we have just chosen the long-term approach, because then we do not have any of those questions to worry about. But yes, we have gone through those ideas.