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Spectroscopic Study of the "Brown" Coating Observed in Mercury rf-Discharge Lamps

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Abstract

Mercury (Hg) rf-discharge lamps employed in Hg$^+$ *atomic clocks can develop a “brown coating.” We have performed spectroscopic analyses of the coating in the UV, to study the coating’s absorbance at 194 nm, which is the wavelength of UV light used in Hg*$^+$ *atomic clocks for optical pumping and atomic signal monitoring. Our results indicate that the coating is a HgO material, which we believe is embedded in the lamp bulb’s glass matrix. The coating can have significant absorption at 194 nm, suggesting that further study of the coating is warranted to aid in the development of long-lived Hg*$^+$ *atomic clocks.*

I. Introduction

Recently, JPL completed a two year on-orbit technology demonstration of a mercury-ion (Hg$^+$) atomic clock (*i.e.*, the JPL Deep Space Atomic Clock or DSAC) [1]. The DSAC has a SWaP of 18 L, 16 kg, and 45 W, and consequently is well designed for Global Navigation Satellite System (GNSS) spacecraft like GPS. The excellent frequency stability of the device combined with its near-zero frequency drift rate suggests that this device could effectively take the clock out of a GNSS’s Signal-in-Space User-Range-Error [2].

In contrast to most next-generation atomic clocks for GNSS, the Hg$^+$ clock generates and monitors its atomic signal with an rf-discharge lamp as opposed to a laser [3]. The use of an rf-discharge lamp for signal-generation/monitoring is similar to the rubidium (Rb) atomic clock [4], which is presently flying on GPS and Advanced-EHF satellites [5]. As is now well-documented, the lamp in a Rb clock is a key physics-package component affecting clock lifetime and reliability [6,7]. Consequently, we expect the lamp in the Hg$^+$ atomic clock to also be a key component affecting clock lifetime and reliability.

In this report we describe a preliminary study of a “brown coating” that appears on the inside of the Hg lamp’s glass bulb after lamp operation. We show that this coating attenuates the intensity of the 194 nm UV light emitted by the lamp, which is required for Hg$^+$ clock signal generation/monitoring, and evidence suggests the coating is a HgO material.

II. General Description of the Hg$^+$ Clock

In order to put lamp coating-formation in context, it is worth briefly reviewing the Hg$^+$ clock’s operating principles [3], and in broad outline a schematic picture of the Hg$^+$ clock is presented in Fig. 1. The atomic system portion of the Hg$^+$ frequency standard consists of a ^{202}Hg rf-discharge lamp [8], a linear quadrupole rf-trap (*i.e.*, the “optical-pumping/signal-detection region”), a 16-pole rf-trap (*i.e.*, the “atomic signal generation region”) [9], a source of 40.5 GHz microwaves, and a photomultiplier tube that measures the Hg$^+$ fluorescence coming from the optical-pumping/signal-detection region [10].

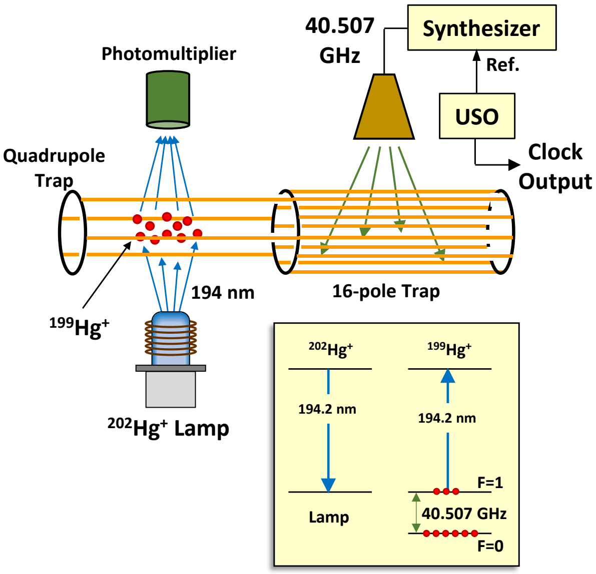

Figure 1: Illustration of the physics package components for JPL’s Hg$^+$ clock. USO stands for ultra-stable oscillator, and this will have an output frequency ~ 10 MHz.

Due to a coincidence of nature, 194 nm light from the ^{202}Hg$^+$ enriched rf-discharge lamp preferentially excites ^{199}Hg$^+$ ions out their F=1 ground-state hyperfine level [11]. The excited ions then spontaneously decay back to *either* the F=1 or F=0 ground-state hyperfine levels, emitting UV fluorescence that can be detected by a photomultiplier tube (PMT). After several absorption/emission cycles a fraction of the F=1 ^{199}Hg$^+$ ions will have been transferred into the F=0 state, where they remain since the ^{202}Hg$^+$ light is “off resonance” for the F=0 atoms. As a consequence of this “optical-pumping process” a population imbalance between the two hyperfine states is created, in contrast to normal thermodynamic equilibrium conditions where these two states are equally populated. The optical-pumping process is relatively fast (*i.e.*, seconds or faster), and occurs while $^{199}Hg^+$ ions are confined in the quadrupole trap region. Then, using electric fields the optically-pumped mercury ions are shuttled into the 16-pole rf-trap, where they are exposed to a 40.507 GHz microwave field.

The atomic line quality factor (Q) for the mercury ions' absorption of 40.5 GHz microwave radiation is very high, usually exceeding 10^{11} [1,12]. Thus, the ions may be employed as a very fine discriminator for microwave frequency variations. Specifically, if the microwave signal frequency does <u>not</u> match the ion's ground-state hyperfine splitting, then the ions will be unaffected by the microwaves while they are in the 16-pole rf-trap region. As a consequence, when the ions are shuttled back into the quadrupole-trap region most of the ions will still be in the optically pumped F=0 state, and the UV fluorescence detected by the photomultiplier will be at a low level. Alternatively, if microwaves <u>are</u> on-resonance and are absorbed by the ions in the 16-pole rf-trap region, then there will be a transfer of population from the F=0 state to the F=1 state. Consequently, when the ions are shuttled back into the quadrupole-trap region, the UV fluorescence detected by the photomultiplier will be at a high level. Thus, the UV fluorescence can be used to monitor the ions' absorption of microwaves, and the photomultiplier signal can be employed in a feedback loop to stabilize the frequency of an ultra-stable oscillator (USO) for precision timekeeping purposes.

From this discussion it should be clear that the Hg lamp is a critical component for the clock's proper functioning. The 194 nm lamplight effectively creates the atomic signal, and the 194 nm lamplight provides for monitoring of the Hg ions' absorption of microwave radiation. Consequently attenuation of the lamp's emission of 194 nm light by any coating that might form on the lamp glass will degrade the Hg^+ atomic clock signal.

III. Spectroscopic Experiment to Examine a Hg Lamp's "Brown Coating"

Figure 2 is a picture of a round-bottom Hg rf-discharge lamp produced by Precision Glass Blowing (PGB) for our Hg consumption studies after approximately 10 hours of operation [13].[*] A brown coating is clearly visible on the lamp bulb, and we note that no amount of cleaning of the lamp's exterior could remove the coating. We therefore believe that this coating is on the glass bulb's interior or within the glass matrix of the bulb. Further, it is interesting that the coating does not occur uniformly over the bulb. Rather, the coating appears to be most pronounced in a ring, though we should not assume that the coating is solely confined to this ring: the coating could exist throughout the glass bulb's interior, just at depths/concentrations not visible to the unaided eye. In this regard, we note that the lamp is operated by placing it within the coils of a cylindrical inductor, which supplies the rf-field for the discharge, and this may suggest that the coating's formation is related to that rf-field.

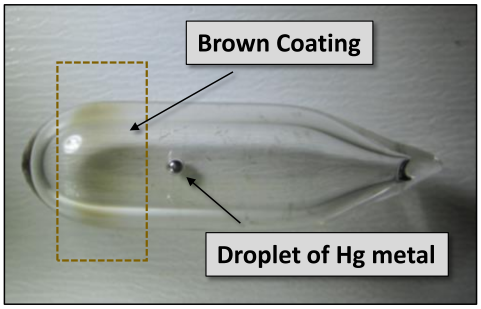

Figure 2: Picture of a natural isotope ratio Hg rf-discharge lamp manufactured by Precision Glass Blowing (PGB) with brown coating on glass bulb's interior (or within bulb's glass matrix). Normally, the droplet of Hg is placed at the bulb's cold point (right-most portion in figure), and the vapor-pressure from this droplet produces the Hg emission lines.

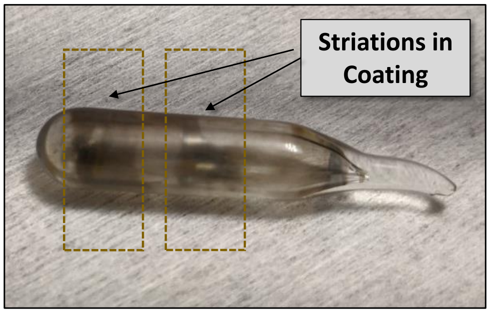

Figure 3: Picture of a ^{202}Hg enriched rf-discharge lamp manufactured in-house at JPL for use in their Hg^+ atomic clocks. Similar to the PGB lamp, operation results in a brown coating with a striated appearance.

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[*] This lamp was employed in our initial studies of Hg mass and lamp spectroscopy. Consequently, since we were beginning our experiments we did not have a good measure of the rf-power driving the lamp nor a good measure of the operating temperature of the lamp. Additionally, this lamp was fabricated by PGB under no special preparation procedures.

Figure 3 is a picture of a round-bottom Hg rf-discharge lamp manufactured in-house at JPL for use in their Hg^+ atomic clocks.[†] Again, a brown coating is clearly visible on the lamp bulb, and the density of the coating has striations. Similar to the PGB lamp, this suggests that formation of the coating may be related to the geometry of the rf-field that powers the discharge.

The spectrum of the PGB coating was first obtained using an Ocean Optics Model DH-2000-BAL fiber-coupled deuterium continuum light source and a McPherson Model 234 VUV spectrometer having a MgF_2 and aluminum coated 1200 groove/mm holographic grating. The entrance and exit slit widths of the spectrometer were set to 100 µm, which provided a spectral bandpass of 0.4 nm. All spectra were obtained while the monochromator was being flushed with nitrogen gas at 4 CFH to reduce the effect of oxygen gas absorption along the 400 mm internal path length of the monochromator.

The lamp was masked using black vinyl electrical tape before mounting it in front of the monochromator entrance slit. The tape mask served two purposes: it allowed us to confine the radiation transmitted through the lamp to only the region of the dark coating (or for comparison a clear section of the lamp), and it provided a means for securing the lamp to the entrance slit assembly with the lamp positioned as close to the slit as possible. A diagram and picture of the spectrometer setup is shown in Fig. 4.

The fiber from the deuterium light source was positioned close to the mounted lamp on the slit, so that the light from the fiber was directed through the mask opening and onto the slit, with a Hamamatsu R955 photomultiplier mounted at the exit slit. The spectrum was acquired by scanning the grating between 170 and 500 nm and recording the PMT photocurrent. The spectrum was recorded at discrete 5 nm intervals using a Keithley DAQ 6510 multimeter.

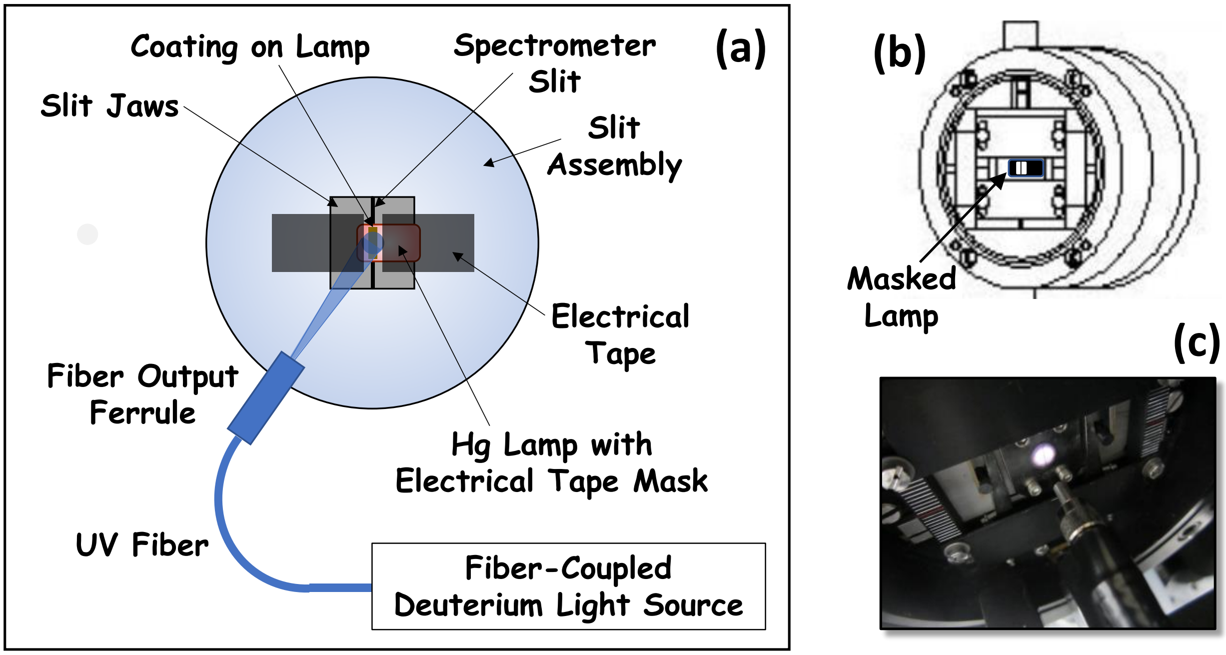

Figure 4: (a) Sketch of the spectrometer setup, where the lamp is masked and tapped over the monochromator entrance slits. (b) A second drawing illustrating the location of the lamp on the monochromator. (c) A photograph of the deuterium light source illuminating the entrance slits of the monochromator prior to attaching the lamp to the monochromator.

The spectrum of the PGB coating was also obtained with a BWTEK fiber-coupled spectrometer (Exemplar LS spectrometer module), which was examined the brown coating of the JPL lamp as well as the PGB lamp. The spectrometer has a resolution of 0.6 nm. UV fiber was employed to pass the deuterium light to the lamp, and also to collect the transmission through the coating

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[†] Since this lamp was loaned to Aerospace by JPL, we do not have a good estimate of its operating time nor the rf-power that created the discharge over that lifetime.

to the spectrometer. Placement of the two fiber ends near the lamp as illustrated in Fig. 5 allowed us to examine transmission through a portion of the lamp with little (if any coating) and a portion with significant coating. We note that the fiber transmission and spectrometer CCD have attenuated responsivity below 200 nm, which limits our signal-to-noise ratio at those wavelengths.

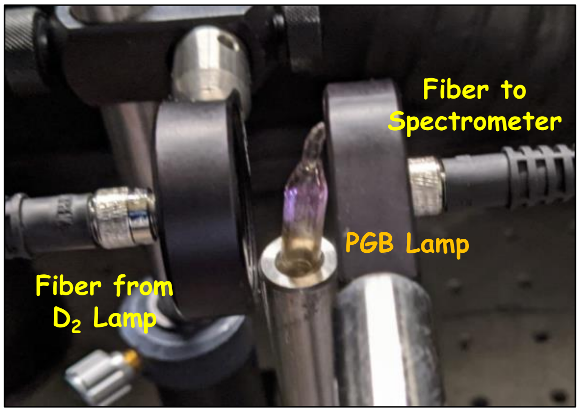

Figure 5: Picture of the setup to measure the absorbance of the brown coating using the BWTEK fiber-coupled spectrometer.

IV. PGB Lamp Absorbance

Figure 6 illustrates the transmission spectrum of the deuterium light source passing through the brown coating and through a clear portion of the lamp bulb. Similar spectra were observed using the BWTEK fiber-coupled spectrometer. Figure 7 shows the absorption spectrum, with absorbance A defined as

$$A = \mathrm{Log}_{10}\left[\frac{S_{\mathrm{Clear}}}{S_{\mathrm{Film}}}\right], \qquad (1)$$

where S is the generated photomultiplier current (or in the case of the BWTEK spectrometer the CCD output). Note that the peak of the absorption spectrum occurs at about 250 nm, and that $A_{194\ \mathrm{nm}} = 0.26$. Thus, if this particular coating were in the direct path of the 194 nm light used for optical pumping, the coating would effectively reduce the optical pumping rate by 45%. To put this in context, in the linear regime of optical pumping this reduction would result in a decrease in the signal-to-noise ratio (SNR) by a factor of about two.

To be clear, we are not saying that formation of this coating will definitely degrade the SNR of a Hg^+ clock by a factor of two. Specifically, we have assumed in this crude estimation that the coating is "in the direct path of the 194 nm light." This may not be completely fair if the lamplight is extracted from the bulb face, as Figs. 2 and 3 would suggest. Rather, our point is to highlight the fact that formation of the coating could have important consequences for Hg^+ clock longevity, depending on how and where the coating forms over a lamp's life and how long it takes the coating to form in a region that is in the direct path of the 194 nm light.

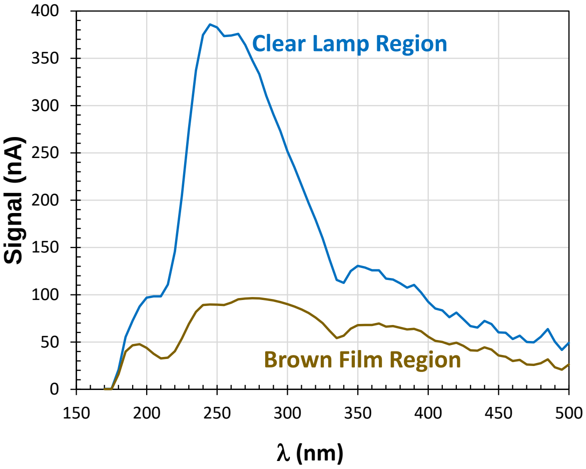

Figure 6: Transmission spectrum of the deuterium light source passing through a clear region of the PGB lamp and the brown coating region as measured with the McPherson monochromator.

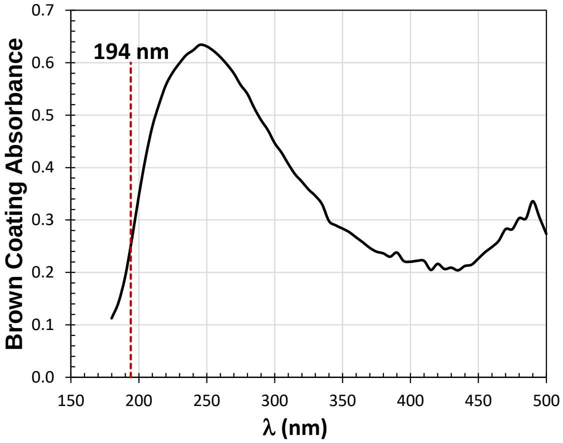

Figure 7: Absorption spectrum of the PGB round-bottom lamp's brown coating. The dashed line shows the absorbance at the Hg^+ resonance line used for optical pumping.

V. JPL Lamp Absorbance

Figure 8 shows the spectrum of the PGB lamp as well as the JPL lamp, here determined using the BWTEK fiber-coupled spectrometer. The results with this spectrometer for the PGB lamp are equivalent to those obtained with the free-space McPherson spectrometer, which provides confidence in the absorbance values.

Regarding Fig. 8, we want to be clear that in our opinion the difference in absorbance observed between the two lamps studied here is likely due to the much longer operation time of the JPL lamp compared to the relatively short 10-hour operating time of the PGB lamp. Due to small sample size and the unknown operation history of the JPL lamp, we cannot infer how HgO formation might relate to lamp quality or manufacturing processes. For us, the important point to focus on in Fig. 8 is that *brown coating formation appears to be a phenomenon endemic to Hg rf-discharge lamps*.

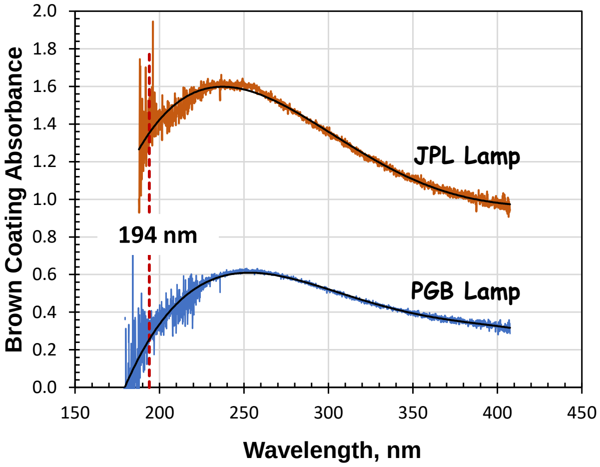

Figure 8: Absorption spectra of the PGB and JPL lamps. The fact that the JPL lamp's brown coating shows greater absorption than the PGB lamp is likely due to the longer operating history of the JPL lamp compared to the PGB lamp. The solid lines are 4th-order polynomial fits to estimate the absorbance at 194 nm.

Fitting the absorbance to a 4th-order polynomial (shown as the solid line in Fig. 8) we find that

$$A_{194\text{ nm}} = 0.26 \text{ for the PGB lamp}$$

$$A_{194\text{ nm}} = 1.35 \text{ for the JPL lamp}$$

The absorbance for the PGB lamp obtained with the BWTEK fiber-coupled spectrometer is equivalent to that obtained with the free-space McPherson spectrometer, and as noted above would result in a decrease in the Hg^+ clocks SNR by a factor of about two. For the JPL lamp, the 194 nm light would be reduced by a factor of 96%, reducing the SNR by a factor of about 20. Again to be very clear:

1. We don't want to imply that there is a problem with JPL lamps, and that their brown coating is more problematic than other Hg lamp brown coatings.
2. Nor do we want to imply that brown coatings will have such devasting effects on SNRs. The effect of the brown coating on the Hg^+ clocks SNR will depend on *where* the coating is relative to the path out of the lamp for 194 nm light as well as the coating's thickness at that location.

We only want to emphasize that the brown coating on Hg rf-discharge lamps is important for Hg^+ clock operation.

Clearly, as evidenced by Figs. 2 and 3 the brown coating on the JPL lamp seems thicker than that on the PGB lamp. The influence of coating thickness on the absorption spectrum is shown in Fig. 9, where absorbance values have been normalized to unit peak value. Also shown is a normalized absorption spectrum of HgO particles in a microemulsion template (*i.e.*, [HgO] = 6.25 mM for a CTAB microemulsion in water with CTAB = cetyltrimethylammonium bromide plus n-butanol/n-heptane) [14]. These particles have a size of ~ 10^2 nm.

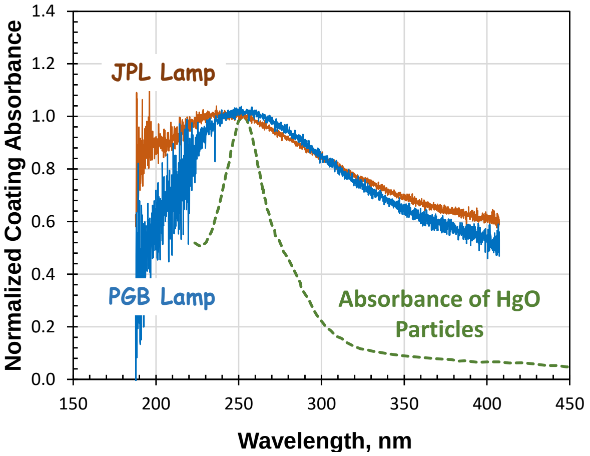

Figure 9: Normalized absorbance of the PGB and JPL lamps. The dashed curve is the absorption spectrum for 100 nm HgO particles in solution.

Note that the peak of the absorption spectrum for HgO particles in CTAB is identical to that of the brown coating in both lamps. The sole difference appears to be the width of the absorption spectrum. Since the width for the JPL lamp (*i.e.*, thicker coating) is greater than that of the PGB lamp (*i.e.*, thinner coating), one could easily extrapolate that an "ultrathin coating" (*i.e.*, 10^2 nm particles in solution) would be narrower still. Figure 9 gives evidence for this conclusion, and indicates that the brown coating in Hg rf-discharge lamps is indeed some form of HgO material.

VI. Discussion

The results presented here indicate that Hg rf-discharge lamps will form brown coatings after continued operation, and that the formation of this coating appears to be an endemic characteristic of Hg rf-discharge lamps. Further, the evidence indicates that this brown coating is some type of HgO material, which attenuates the 194 nm light necessary for atomic signal generation/monitoring in Hg^+ atomic clocks. However, this work has also raised a number of questions.

1. Is the brown coating on the inside surface of the lamp bulb, or is the HgO within the glass matrix? Evidence from Hg interactions with soda-lime glass

would suggest that the HgO is formed within the glass, likely resulting from Hg^+ bombardment [15].

2. Hg^+ impact with the glass surface as a primary step in the HgO formation process might explain why the coating appears to have a non-uniform spatial distribution. As noted above, the glass bulb is placed within the inductor coils of an oscillator circuit. Perhaps the spatial distribution of the rf-field within the discharge favors certain locations on the glass surface with more or less energetic Hg^+ bombardment.

3. Though we do not hypothesize major differences between the JPL and PGB lamps with regard to coating formation, it is nonetheless valid to ask if coating formation depends on lamp-glass type? (Both the JPL and PGB lamps were constructed from synthetic fused silica.) Are there some glass types that are more impervious to coating formation than others? HgO was seen to exist *within* the glass matrix for soda-lime glass, but is this true in general for all glass types and to the same extent in all glass types?

4. We do note that according to our measurements with Differential Scanning Calorimetry [DSC] [13] these lamps were filled with very different amounts of Hg: PGB lamp – 7 mg and JPL lamp – 2 μgms. Though the vapor pressure of Hg would be the same in the two lamps when operated at the same temperature, could it be that Hg film coating over the inner glass surface could be different in lamps filled with different amounts of Hg? Could it be that a Hg film assists/impedes coating formation?

5. How does coating formation depend on lamp operating characteristics?
    a. Lamp temperature, which controls the vapor pressure of Hg in the discharge.
    b. Discharge rf-power, which will control the formation rate of Hg ions and possible field conditions at the lamp bulb's glass walls.
    c. Lamp operating life.

6. Finally, can coating formation be mitigated by lamp processing procedures [16]?
    a. Can glass-bulb bakeout temperature and duration minimize the ability of HgO coating to form?
    b. Can scrubbing and/or polishing of the bulb's interior surface make coating formation more difficult?

Answers to these questions will require further investigation, and we are planning to address these questions in future research.

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