Buffer Gas Experiments in Mercury (Hg+) Ion Clock

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Abstract—**We report measured buffer gas collision shifts of the 40.507347996xx GHz mercury ion clock transition using inert helium, neon, and argon gases and getterable molecular hydrogen and nitrogen gases. The frequency shift due to methane was also examined. At low partial pressures methane gas did not impact the trapped ion number but was observed to strongly relax the population difference in the two hyperfine clock states thereby reducing the clock resonance signal. A similar population relaxation was also observed for other molecular buffer gases (N_2, H_2) but at much reduced rate.**

I. INTRODUCTION

In recent years, mercury ion (^{199}Hg$^+$) clock technology has demonstrated excellent inherent stability, reaching ~3 x 10^{-16} long-term frequency stability with continuous, free running operation [1]. This type of ion clock utilizes a combined, quadrupole and multipole, extended linear ion trap (LITE) technology wherein the trapped ions are moved between trapping regions for optical pumping and the microwave interrogation [2]. The excellent stability performance together with the practical design considerations makes this clock standard attractive for some of spaceflight applications including GPS satellites.

At JPL we are currently developing a trapped ion technology with a small volume appropriate for a space clock with a reduced frequency stability requirement (~10^{-15}/day) than the ground-based ones [3]. The initial small prototype developed at JPL used a traditional four electrode quadrupole linear ion trap. This system demonstrated excellent signal to noise leading with a short-term stability at 5x10^{-14}/$\tau^{1/2}$ in a small volume and low mass. A second prototype clock with a small multipole trap to minimize the second order Doppler shift [4] is currently in development and undergoing initial tests at JPL.

One crucial aspect of ^{199}Hg$^+$ LITS/LITE clock technology is the use of a buffer gas to increase ion loading efficiency and counter ion heating from the rf trapping fields. This passive ion cooling method eliminates the uses of lasers and accompanying complex optical elements incorporated in laser cooled atomic clocks. Traditionally, helium buffer gas has been used at ~10^{-5} Torr to confine Hg ions at near room temperature. An RF discharge lamp containing ^{202}Hg isotope is used to state-select the trapped ^{199}Hg$^+$ ions by means of optical pumping. In order to maintain a high constant helium buffer gas pressure while minimizing other gases, a high throughput mechanical turbo-pump together with temperature controlled, high rate helium leak has been used for most of our ground-based systems. While this provided the needed UHV environment and stable helium pressure this system is not sufficient to meet mass, power, size, and operability considerations of a space clock [6].

Two buffer gas / vacuum pump combination are currently being considered for possible operation of a small space-born clock. One approach uses a small getter pump with a fixed amount of inert buffer gas. Two issues that must be understood are the long term buffer gas pressure stability and possible evolution of non-getterable gas that could potentially adversely affect clock stability or operation. A second approach is to use a miniature ion pump and a calibrated micro-leak buffer gas that is not inert (inert gas can shorten ion pump life very quickly).

II. SIGNIFICANCE OF BUFFER GAS EXPERIMENTS

The traditional quadrupole linear ion trap (LITS) standards are based on a four-rod configuration providing two dimensional radial confinement along the axis using a pair of opposing rf fields. The two ends are capped-off by dc fields to provide axial confinement. The three major perturbations in the Hg$^+$ ion clock transition are the dc Zeeman magnetic shift, second order Doppler shift, and the collision pressure shift [5]. Second order Doppler shift arises from the thermal ion motion and space-charge repulsion within the ion cloud, balanced against the inward directed rf trapping force generated by ion micro-motion. Collisions between an ion and buffer gas or background gas atom/molecule produces a momentary shift of the ion clock transition frequency, the net effect which is linear with respect to the gas partial pressure.

The constancy of buffer gas pressure can impact clock stability performance via both collision and ion number dependent (second order Doppler) effects. The choice of the buffer gas, therefore, should be aimed to achieve the largest signal (ion number) with the least pressure collision shift.

In addition to the buffer gas, there can be other residual gases such as water, nitrogen, oxygen, or methane that may outgas from the vacuum system or gases such as carbon monoxide and carbon dioxide that may be produced as byproducts of electron emitters in the system. The pressure collision shift from evolving gases and background gases may be reduced to a sufficiently small level by baking the system to a high temperature for a long period of time; nevertheless, it is important to quantify what degree of frequency shift these residual gases can produce.

III. BUFFER GAS EXPERIMENTS

A pressure collision shift experiment for a given buffer gas is conceptually simple and straightforward. To vary the

background pressure one would either, introduce ultra purity gas via a variable leak valve at a constant pump speed, or introduce gas through a constant leak rate and vary the pump speed. The $^{199}Hg^+$ ion clock resonance would then be tracked as the test buffer gas pressure is varied.

In practice, however, it is not this simple, especially for measurements performed in a four electrode, quadrupole trap. In order to isolate ion number dependent shifts from the pressure collision shift, the ion number must be held constant throughout the buffer gas pressure test range. Even if this can be accomplished, ions heat up at low buffer gas pressures and the second-order Doppler shifts quickly overrides the pressure collision shift [6]. A more ideal system to carry out the pressure collision shift measurements is in a multipole ion trap configuration because of its inherent insensitivity to ion number variations [4, 6].

At higher buffer gas pressures, the ion lifetime may be affected from interactions with other residual gas; most evident when the pumping speed is varied in order to control the buffer gas pressure. Attention must also be given to the possibility of the presence of a background gas such as methane. Methane has been observed to relax the population difference in the two hyperfine clock states without affecting the trapped ion number. Since the ion number is often estimated from the resonance signal strength, one must distinguish the loss/gain of resonance signal from the variations in the ion number.

At the time these buffer gas measurements were performed a multipole trap such as used in [6] was not available. The measurements were instead performed in the small quadrupole space clock prototype without magnetic shielding. The ground state hyperfine energy levels of $^{199}Hg^+$ clock transition, $^2S_{1/2}(F=0, m=0)$ to $^2S_{1/2}(F=1, m=0)$, is a function of magnetic field as,

$$f(B) = 40.507347997 \text{ GHz} + 97.2 \text{ } B^2 \text{ [Hz/G}^2] . \tag{1}$$

The buffer gas experiment needed to be carried out in a magnetically quiet environment in order to isolate the magnetic sensitivity from the pressure collision shift. To separate field effects pressure reference point was selected for each test gas, and after each measurement at a test gas pressure (and the corresponding frequency shift), the pressure was brought back to the original reference point to check for a possible magnetic shift during the measurement. A few measurements were averaged for each pressure point in this way lasting about 10 to 15 minutes each. Also, if there were losses in the ion number by moving to a different pressure, this procedure provided the opportunity for ion number to build back up to the original equilibrium level for the next measurement.

For molecular gas (H_2, N_2, CH_4) shift measurements, Hg^+ ions were cooled principally by background neon buffer gas at fixed pressure, and the test gas varied to measure the relative collision shift. This was performed in order to eliminate the large second order Doppler shift at low buffer gas pressures, thereby substituting the usage of a multipole trap system. This technique allowed for measurements at much lower gas pressures than what would otherwise be impossible.

IV. RESULTS

Figure 1 shows frequency shifts of $^{199}Hg^+$ clock transition observed in the small LITS by varying helium, neon, and argon buffer gas pressures. Buffer gases were of ultra high purity grade and had a constant leak rate through a capillary (Vacuum Technology Inc.). For these three inert buffer gases the partial pressures were changed by use of a variable valve into a system evacuated by a mechanical turbo pump. The nonlinear negative shift at lower pressures is interpreted to be the 2nd order Doppler frequency pulling resulting from an increase in the average trapped ion cloud temperature. At higher pressures the ion cloud is in thermal equilibrium with the vacuum walls and linear slope is interpreted to be the collision pressure shift of clock transition. These characteristic shifts have been observed previously in both quadrupole linear [5] and spherical [7] traps, but in multipole trap [6] it showed negligible 2nd order Doppler effects at lower pressures because of reduced inherent sensitivity to ion number variations.
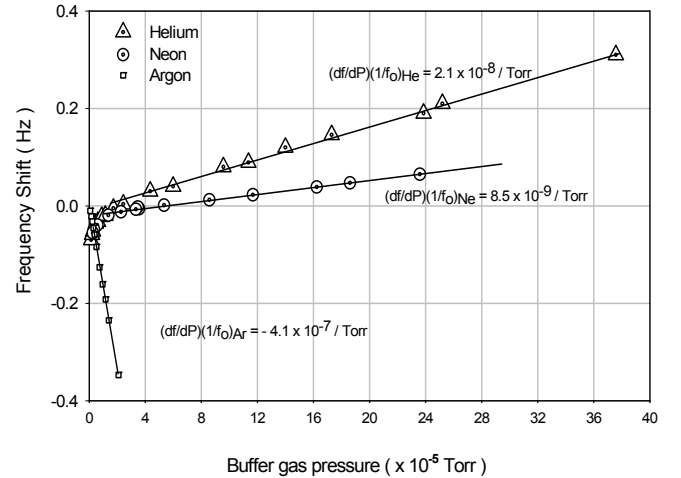

Figure 1: Helium, neon and argon collision shifts in the small linear ion trap. Note the effect of ion heating at low buffer gas pressures.

The obtained fractional frequency collision shifts of the 40.5 GHz clock transition are $(df/dP_{He})(1/f) = 2.1 \times 10^{-8}$/Torr for helium, $(df/dP_{Ne})(1/f) = 8.5 \times 10^{-9}$/Torr for neon and $(df/dP_{Ar})(1/f) = -4.1 \times 10^{-7}$/Torr for argon. Data taken from nonlinear regions have been excluded for this fit. It is clear from figure 1 that the operating buffer gas pressure be chosen to be above the low pressure turn-down regime.

Neon may be a better choice as a buffer gas than argon or traditional helium since the frequency shift is about 2.5 times less sensitive to changes than helium and 50 times less than argon. In the small clock prototype the optimum operating pressure for neon was found to be $\sim 3 \times 10^{-5}$ Torr to maximize the clock resonance signal size. Buffer gas pressure values shown in figure 1 have been corrected to take into account of

ion gauge sensitivity for each gas (Granville Phillips series 350 ion gauge controller). The multiplying correction factor for each gas is 5.56 for helium, 3.33 for neon and 0.78 for argon.

In addition to inert helium, neon and argon gases, we also considered molecular hydrogen and nitrogen as potential buffer gases that could be used in combination with a miniature ion pump. The effect of methane was also examined as a potential residual gas that could interact with trapped Hg ions.

For these measurements neon, because of its low collision shift, was used as the primary buffer gas at a fixed pressure around 3×10^{-5} Torr. Small quantities of H_2, N_2 and CH_4 were individually introduced via a precision sapphire leak valve to vary the pressure. The fractional frequency shifts of the 40.5 GHz clock transition of these molecular gasses (Figure 2) were measured to be $(df/dP_{H2})(1/f)= -1.0 \times 10^{-6}$/Torr for hydrogen, $(df/dP_{N2})(1/f)= -1.9 \times 10^{-6}$/Torr for nitrogen and $(df/dP_{CH4})(1/f)= -3.6 \times 10^{-5}$/Torr for methane. In order to resolve small changes in the partial pressures from the much larger background neon pressure, we aligned the calibration of a residual gas analyzer (SRS) to the ion gauge using nitrogen
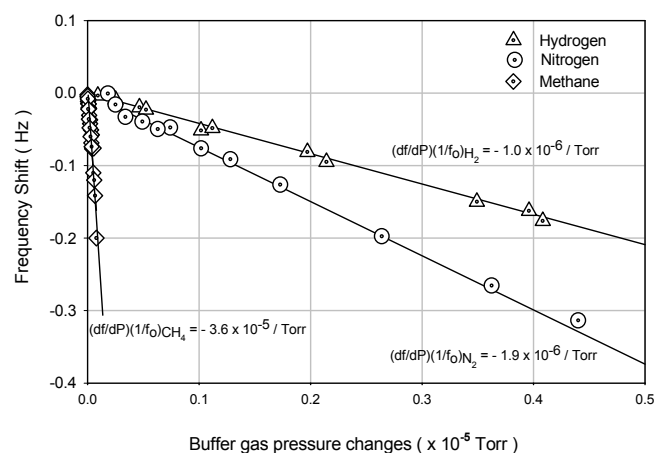

Figure 2: Hydrogen, nitrogen and methane gas collision shifts in the small linear ion trap. The effect of second order Doppler shift at low pressure is not observed due to the presence of 3×10^{-5} Torr of neon buffer gas.

buffer gas then used the ion gauge sensitivity for each gas (Gas correction factors are 1.00 for nitrogen, 2.2 for hydrogen and 0.71 for methane) as an approximation. The ion gauge was not absolutely calibrated though the measurements do provide relative collision shift sensitivity df/dP for each buffer gas. Figure 3 shows the collision shift measurements for inert gases and the molecular gases on a single plot.

Methane, in addition to having a very large collision shift, was observed to significantly reduce the coherent clock resonance. At partial methane pressure $>1 \times 10^{-7}$ Torr, clock resonance signals were nearly distinguished and resonance tracking was not possible. The confined ion number was found to be almost entirely preserved, and the loss of the clock
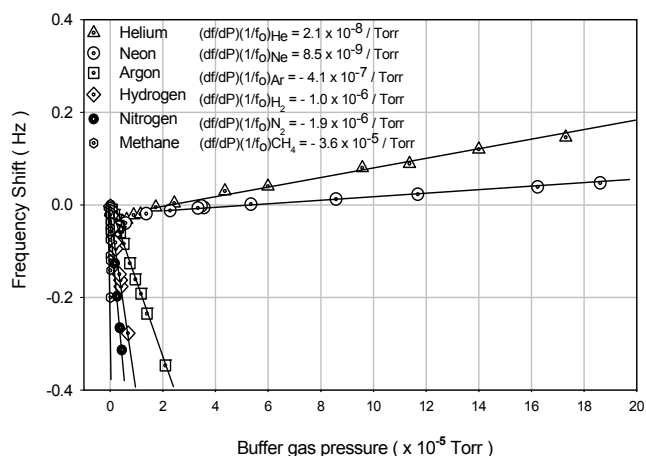

Figure 3: Combined collision shift data with inert buffer gases and the molecular gases.

signal is interpreted to be the population equalization of hyperfine clock states of $^{199}Hg^+$ ions, normally optically pumped by a ^{202}Hg lamp. This behavior was demonstrated in Figure 4 where we observed 194nm fluorescence beginning with an empty trap then as $^{199}Hg^+$ ions loaded by turning on the electron emitter. After loading ions for a designated time, T_l the fluorescence is observed for a T_i to determine the trap life of the ions. After T_i the ions are then dumped from the trap. For this data the background buffer gas was primarily neon at 3×10^{-5} Torr as before, except that different levels of methane were bled into the system to observe the ion fluorescence changes. In Figure 4 two curves, one with pure neon buffer gas (a), and one with neon plus the varying amounts of methane (b), are superimposed to show the
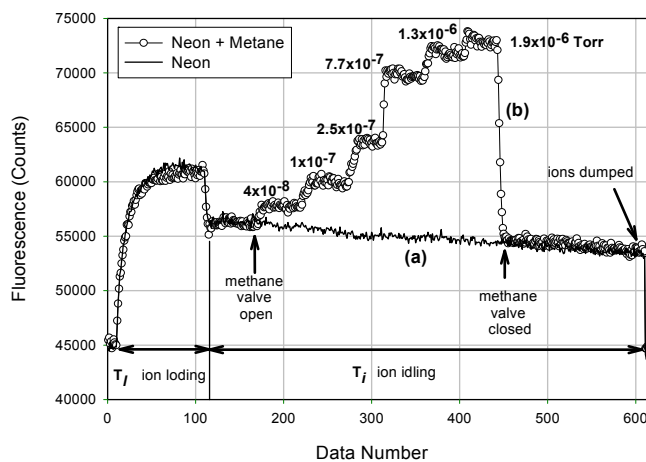

Figure 4: (a) Observed fluorescence when ions are loaded and dumped in a neon buffer gas environment with $P_{Ne} = 3 \times 10^{-5}$ Torr. (b) with step changes of partial pressure of methane gas. The step increases in the fluorescence are interpreted as relaxation of ^{199}Hg ion clock states by collisions with methane molecules.

relaxation behavior of hyperfine clock states by the presence of methane. The step increases in the fluorescence for curve (b) are interpreted to be caused by the relaxation of $^{199}Hg^+$ ion clock state-selection via collisions with methane molecules. Light from ^{202}Hg lamp then tries to repopulate the relaxed states of trapped $^{199}Hg^+$ ions by means of optical pumping resulting in the increased fluorescence. Prior to dumping the ions in both (a) and (b), where the level of methane is zero in the system, the level of ion fluorescence is approximately the same, indicating that the ion number is preserved in the presence of methane indicating the ion lifetime is not largely effected. This relaxation effect was also observed with both hydrogen and nitrogen though to a much lesser degree.

Another interesting interaction occurred during the collision shift measurement of hydrogen buffer gas. We found that hydrogen, presumably by interactions with the heated HgO powder, greatly increased the neutral Hg level in the system. The corresponding increases in the neutral Hg levels to changes in the hydrogen partial pressure at typical HgO oven temperature (~180 ^{o}C) had a time constant of several minutes, making the collision shift measurement for hydrogen difficult. We resorted to turning off the HgO oven and performing the experiment from residual Hg deposited on the system wall, often sufficient for several days.

V. SUMMARY

We have determined collision shifts of several buffer gases being examined for possible use in a ^{199}Hg ion clock for space. Among inert gases (He, Ne, Ar) we identified neon as a least shifting gas that is 2.5 times less sensitive to the pressure changes than the traditional helium buffer gas. All molecular gases (N_2, H_2, CH_4) tend to shift the frequency larger than the inert gases and exhibit relaxation of hyperfine clock states, with methane showing the largest effect. A promising vacuum pump/buffer gas combination for a miniature space Hg ion clock is a getter pump system with fixed amount of high purity neon buffer gas. The vacuum system and components must be thoroughly baked-out to rid the system of residual gas such as methane. This combination is being configured on the prototype clock and will be tested for long-term stability. Future plans also are to measure the collision shifts of other common UHV gases such as carbon monoxide (CO) and carbon dioxide (CO_2), both of which may be present when hot electron emitters are present.

ACKNOWLEDGMENTS

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