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Thermalization of ^{199}Hg Ion Macromotion by a Light Background Gas in an RF Quadrupole Trap

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Abstract. The largest systematic uncertainty in the performance of atomic frequency standards using a cloud of ions stored in an rf quadrupole trap is the second-order Doppler shift which depends on ion temperature and trapping parameters. This paper presents evidence that cooling the ions by collisions with atoms of a background gas light compared to the ions results in the condensation of the ions into a cloud of almost uniform density determined by space charge versus potential well forces. In this condition the second-order Doppler shift is simple to calculate and is found to depend only on readily measured characteristics of the ion cloud. This along with already observed good signal-to-noise ratio shows that the frequency standard we have constructed using the hyperfine splitting of singly ionized ^{199}Hg with helium cooling can have an order of magnitude better performance in accuracy, stability, and reproducibility than presently available commercial cesium beam standards.

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Several investigations [1–4] have shown that the alkali-like hyperfine structure of singly ionized ^{199}Hg is a promising candidate for an atomic frequency standard with advanced performance. We have demonstrated that the intrinsic linewidth of the 40.5 GHz hyperfine splitting is smaller than 0.08 Hz [5]. Storing the ions in an rf quadrupole trap eliminates the first-order Doppler shift because it depends on the average vector velocity of the ions over the interogation time, and this average is zero. The fractional change in frequency due to the second-order Doppler shift, an effect of special relativity, is approximated by the ratio of kinetic energy to rest mass energy of an ion. It cannot be eliminated because the oscillatory motion of the ions in the field of the trap produces the force which confines them to the trap. It has long been known that the average ion energy under ultra-high vacuum conditions in an rf quadrupole trap is about 1/10 of the pseudopotential well depth as defined in the Dehmelt [6] model. A typical well depth is 20 eV which implies a fractional frequency shift for Hg ions of -1×10^{-11}. A useful advance in frequency standards would achieve a stability of about 2×10^{-14}. To reach this the Hg ion system would need its Doppler shift stabilized to 0.2%. The accuracy of the prediction of the magnitude of the shift bears directly on the system's accuracy and reproducibility as an absolute standard. For a frequency standard it is therefore desirable to keep the second-order Doppler shift at as low a value as possible, stabilize it, and find a satisfactory theory to account for its magnitude. In this paper we describe a model of the trapped ion cloud based on the assumption that the statistics of the macromotion can be characterized by a temperature. The model is particularly simple if the typical macromotion energy is much less than the well depth. In this case the second-order Doppler shift can be readily calculated. Ion macromotion cooling by a light background gas is then discussed. Finally some observations demonstrating cooling and confirming the thermalized ion cloud model are presented. These results are then analyzed in terms of the performance of frequency standards.

Analysis of a Thermalized Ion Cloud

We begin by considering the case in which the ion macromotion energy is, on the average, much smaller than the pseudopotential energy. The pseudopotential model [6, 7] provides an appropriate description of the trap as a three-dimensional parabolic well. The charge density will adjust itself so that the gradient of the total potential (pseudopotential plus space charge potential) is zero everywhere within the volume occupied by the ions. If the rf and dc voltages on the trap are adjusted so that the radial and axial macromotion frequencies of a single stored ion would be equal, then a cloud of ions is spherical and the number density n is uniform with a value given by

$$n = 3\varepsilon_0 m\omega^2/q^2\,, \tag{1}$$

where m is the ion mass, ω is the isotropic single ion macromotion frequency and q is the electron charge. The total number N of ions in the cloud and the cloud radius r_c are related by $N = 4\pi r_c^3 n/3$. Some typical numbers for stored Hg ions are $\omega = 2\pi \times 50\,\mathrm{kHz}$ and $n = 3.4 \times 10^4/\mathrm{mm}^3$. A cloud of 10^6 ions would have a radius of 1.9 mm.

The rf-induced micromotion is always present. Its amplitude and hence the ion kinetic energy is a simple function of position in the trap and the known trapping parameters. Using (1) an average kinetic energy and the implied second-order Doppler shift can be calculated for a given cloud size. One obtains

$$\Delta f/f = -(3/10c^2)\,(\omega N q^2/4\pi\varepsilon_0 m)^{2/3}\,. \tag{2}$$

Equation (2) gives the value of the Doppler shift integrated over the micromotion cycle and averaged over all positions in the cloud. If macromotion is completely absent, the resulting lineshape will be broadened by the spread in Doppler shifts and (2) will predict the first moment of the shifted line. At not too low a temperature sufficient macromotion will be present to average the spatially dependent Doppler shift for each ion during the period of microwave interrogation. In this case an unbroadened symmetric line results, and (2) predicts the shift for the line center.

Equation (2) shows that in the limit of small macromotion the second order Doppler shift can be controlled by stabilizing the ion number N and the single-ion macromotion frequency. Normalizing to typical values of ω and N for our experiments we obtain

$$\Delta f/f = -1.2 \times 10^{-12} (\omega/2\pi \times 50\,\mathrm{kHz})^{2/3} (N/10^6)^{2/3}\,. \tag{3}$$

Using a method recently suggested by Knight [8] we have extended the calculation to allow a non-zero macromotion temperature T in a spherical pseudopotential. A self-consistent calculation is used to find the ion number density function $n(r, z)$ which satisfies a Boltzmann distribution. The results we have obtained from this numerical calculation are shown in Fig. 1 for a cloud of 2×10^6 Hg ions in a spherical pseudopotential with $\omega = 2\pi \times 50\,\mathrm{kHz}$. At low temperatures the density approaches a rectangular distribution with the value of n given by (1), and at high temperatures the density approaches the gaussian distribution which has been observed experimentally in the absence of ion cooling [9–11].

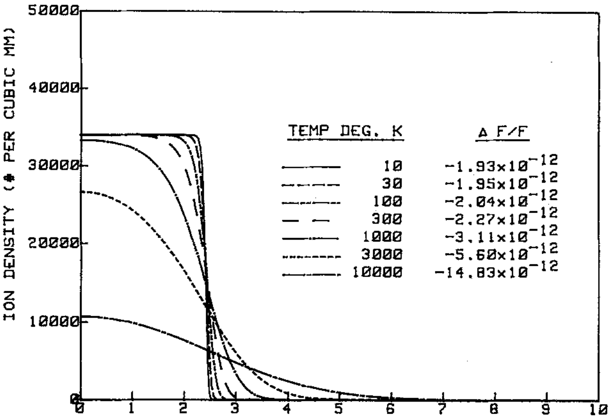

Fig. 1. Calculated number-density distributions for 2×10^6 $^{199}\mathrm{Hg}^+$ ions in a spherical effective potential with $\omega = 2\pi \times 50\,\mathrm{kHz}$. It is assumed that the ion cloud can be described by a temperature T. The tabulated data shows the calculated second-order Doppler shift $\Delta f/f$ for each temperature

The complete density distributions can be used to calculate the second-order Doppler shift. The modified number density weights the integral involved in calculating the average micromotion energy and thermal kinetic energy equal to $3kT/2$ is added. Data in Fig. 1 show how the calculated fractional shift varies with temperature for a typical Hg ion cloud. At 300 K the rate of change with temperature is 1.2×10^{-15}/K and the total shift is about 12% greater than for a cold cloud as given by (2). These results show that under the assumed conditions ($N = 2 \times 10^6$, $\omega = 2\pi \times 50\,\mathrm{kHz}$, $T = 300\,\mathrm{K}$) controlling N to $\pm 0.3\%$, ω to $\pm 0.3\%$ and T to ± 5 K would result in a stability of 1 part in 10^{14}.

Ion Cooling

Three methods of reducing the energy of ions in an rf quadrupole trap are known: laser cooling as done by Neuhauser et al. [12], radiative cooling, as described by Church and Dehmelt [13], and collision cooling with buffer gas molecules light compared to the mass of the stored ions as discussed by Major and Dehmelt [14]. The buffer gas technique seemed simplest and most appropriate for our application.

It was known [15, 16] that light buffer gases enhanced trapping lifetimes of heavy ions but the resulting energy distribution and the limits to the process were not known. These previous results indicated that a helium pressure of 10^{-5} Torr was effective for mercury ions. Major and Dehmelt's [14] calculation showed that the fractional energy loss per collision, $\Delta E/E$, would be

$$\Delta E/E = m_{\mathrm{He}}/m_{\mathrm{Hg}}. \tag{4}$$

The cooling rate is the product of $\Delta E/E$ and the collision rate $nv\sigma$. At 300 K and 10^{-5} Torr the helium density dominates with $n = 3\times10^{11}/\mathrm{cm}^3$. In a 20 eV deep trap before cooling Hg ions would have an energy of 2 eV and a velocity v, of the order of 10^5 cm/s as would the helium atoms at 300 K. Some idea of the cross-section, can be obtained from measurements of Hg ion mobility in helium [17]. For our purposes the cross-section can be obtained from the mobility with a simple mean free path theory, multiplying by a suggested factor of 4 to account for the inadequacy of that theory [18]. We take a value of $\sigma = 2.5\times10^{-15}\,\mathrm{cm}^2$ and obtain a collision rate $R = 75/\mathrm{s}$ and a cooling rate $(1/E)dE/dt = 3/\mathrm{s}$. The cooling rate is a measurable aspect of the ion image current signals discussed below. It thus appears that the technique might be turned around and used to measure cross-sections as was done in a similar Penning trap experiment on electrons [19]. In mobility measurements such as that referred to above, the ion mobility is measured versus the ratio of electric field to pressure, typically over a range of 1–100 V/cm/Torr. In our rf quadrupole experiment this ratio is of the order of 10^6. Perhaps this represents an opportunity for a considerable extension of measurements on ion-atom collisions.

We gleaned a useful hint from Wuerker et al. [20], one of the first published discussions of the rf quadrupole technique. They stored and observed by eye charged dust particles in varying background pressures. With single particles at low pressures they saw the expected superposition of harmonic motions at the rf drive frequency (micromotion) and at the pseudopotential well frequency (macromotion). When many particles were stored they initially saw confused and violent motion. On increasing the background pressure to several micrometers they observed the particles losing kinetic energy and condensing into a crystal like array determined by the balance of space charge and ion storage forces. The particles vibrated at their micromotion frequency about their equilibrium positions and there was no macromotion. The time required for condensation varied inversely with background pressure. We note that the many orders of magnitude difference in the charge to mass ratio makes it seem unlikely that mercury ions reach a phase of condensation as a crystalline solid.

First-Order Doppler Spectrum of Cooled Ions

The first-order Doppler spectrum of the ions takes a form first generally described by Dicke [21] due to their confinement and thermal motion. If we assume that the microwave excitation is a travelling wave, the phase ϕ, that an ion sees depends on its position as $\phi = \bar{k}\cdot\bar{r}$, where $\bar{k}$ is the wave vector of the microwave excitation. If the position of an ion is periodic in time with frequency F, it sees the microwave signal phase modulated at this frequency with a peak phase $1/2\,\mathrm{ka}\sin\theta$, where θ is the angle between the k vector and the normal to the plane of motion and a is the diameter of the region of confinement. A signal with periodic phase modulation has a spectrum with an unshifted carrier and sidebands uniformly spaced by the modulation frequency.

A cooled cloud of ions has a range of motional frequencies. The background density of mercury ions, neutral mercury, and helium is sufficiently low that the rate of collisions of the ions with the potential barrier at the edge of the ion cloud is much greater than the rate of ion-ion, ion-neutral, or ion-helium collisions. However, the mean time between collisions of the latter types is short compared with the interaction time with the microwave excitation. If the trap effective potential is spherically symmetric, the individual ions move in orbits that are unperturbed by collisions other than potential barrier collisions for many transits across the cloud. Angular momentum is conserved, and the motion takes place in planes that contain the center of the trap. If the cloud is fairly cool, the ions are essentially free between collisions with the potential wall and they are specularly reflected there. For a cloud diameter a and ion speed v, an ion passing through the center of the trap would simply bounce back and forth along a line through the center with a frequency $F_1 = v/2a$. Similarly an ion in a grazing path at the edge of the cloud would travel in a circular orbit of diameter a with frequency $F_2 = v/\pi a$. An ion traveling in any other possible path would have a frequency F between F_1 and F_2.

The ions do suffer many collisions with other ions, helium atoms and neutral mercury atoms during the interaction time with the microwaves. Therefore each ion sees all the thermal speeds and all the trajectories possible during the interaction time, which leads to a distribution in the effective modulation frequencies. The resulting spectrum that an ion sees is a sharp unshifted carrier with sidebands that are smeared by the speed distribution folded with the smearing due to trajectory distribution. If the peak phase angle is much smaller than one radian then most of the power is in the carrier and only the first order sidebands are appreciable. For a 4 mm diameter cloud $ka/2$ is about 1.7 radians and there is about a 10 dB loss in the carrier. The carrier attenuates quickly with cloud size for $a>2/k$.

Experimental Setup and Results

^{199}Hg ions are stored in an rf quadrupole trap. The z_0 dimension of the trap is 1 cm. The rf drive is about 750 V at 500 kHz and the dc potential which sets up the spherical pseudopotential is around 37 V. The resulting single ion macromotion frequency was 50 kHz. The trap is in a vacuum system whose base pressure is 10^{-8} Torr. Helium is admitted into the vacuum system through a quartz leak. The pressure can be conveniently varied from 10^{-8} to 10^{-4} Torr. We have described this system in greater detail elsewhere [21] and a similar system has been described by Jardino et al. [4].

The nuclear spin of ^{199}Hg is 1/2 so the ion has a hyperfine structure similar to hydrogen. We optically pump the ^{199}Hg ions with a ^{202}Hg ion lamp. The transition at 194.2 nm is between the $6S_{1/2}$ ground state and the $6P_{1/2}$ first excited state, analogous to the lower D line transition in sodium. The ^{202}Hg has no nuclear spin thus no hyperfine structure. Due to isotope shift the transition in ^{202}Hg is fortuitously resonant with the transition from the upper ground hyperfine state in ^{199}Hg. Decay from the $6P_{1/2}$ state is to both hyperfine states, but the effect of continued illumination with 202 light is to populate the lower hyperfine state in 199 at the expense of the upper. Applying resonance radiation at the hyperfine frequency tends to restore the population of the upper state. The photons from the $6P_{1/2}$ to $6S_{1/2}$ transition are observed to monitor the resonance. The hyperfine radiation is coherently synthesized from a crystal oscillator which with the feedback from the fluorescence signal can be locked to the hyperfine resonance to create a frequency standard. To avoid a frequency shift which would occur if the hyperfine and optical radiation were present simultaneously, we pulse them alternately.

The number of stored ions can be monitored by observing image currents induced in the trap electrodes by the motion of the ion cloud [23, 24]. Our variation of the technique is to apply a pulse of rf at the macromotion frequency to the cap electrodes of the trap and watch the free decay of the ion cloud oscillation damped by the buffer gas and other effects. This signal controls the current of the electron gun pulse which creates the ions thus closing the number loop. The frequency of the decaying ion cloud oscillation can also be measured and servoed through its dependence on the amplitude of the rf drive to the trap. The whole process of macromotion pulse, free decay, electron gun pulse, and return to thermal equilibrium must occur at a time other than when the hyperfine spectroscopy is being done so that the equilibrium assumptions are met. The ion trapping lifetimes must be long enough not to affect the assumptions.

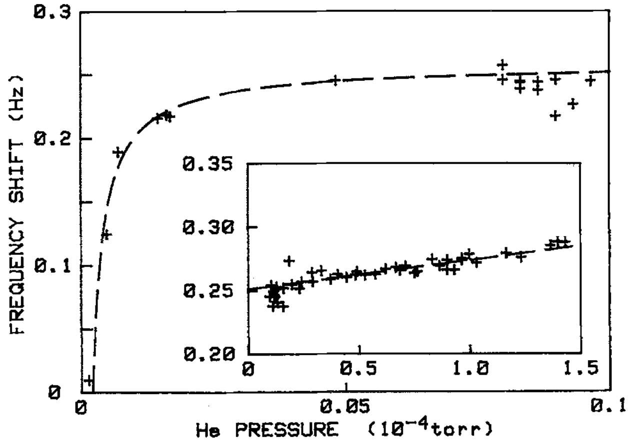

Fig. 2. Observed variation of the line-center frequency f as a function of the pressure p of the He cooling gas. The inset shows the points for pressures exceeding 10^{-5} Torr on a reduced scale. The dashed line represents a fit to the data given by $f=f_0+233\,p-5.5\times10^{-8}/p$ based on a simple model of the variation of cloud temperature with pressure and a linear collision shift. The zero of the vertical axis is arbitrary

As we expected, cooling the ions increased the ion storage time and the stored ion density while stabilizing the second-order Doppler shift. With a helium pressure of 1.5×10^{-5} Torr the storage time was about 2.5×10^{3} s under typical operating conditions. The spectroscopy cycle is about 3 s long and the ion number/frequency interrogation takes about 0.1 s, thus our assumption of a cooled cloud in equilibrium is met.

Figure 2 shows the variation of hyperfine frequency with helium pressure with the ion number and single ion macromotion frequency held constant. The measurement was made by comparing the frequency of the mercury standard to a cesium beam frequency standard stable to 10^{-13}. The pressure was measured with a Bayard Alpert ionization gauge with the reading corrected for helium [25]. No absolute calibration of the gauge was done. As the helium pressure rises to 10^{-5} Torr the frequency increases rapidly due to cooling of the macromotion and reduction of the micromotion shift as the ion cloud contracts. Above this pressure it appears that the macromotion has reached thermal equilibrium with the gas and further

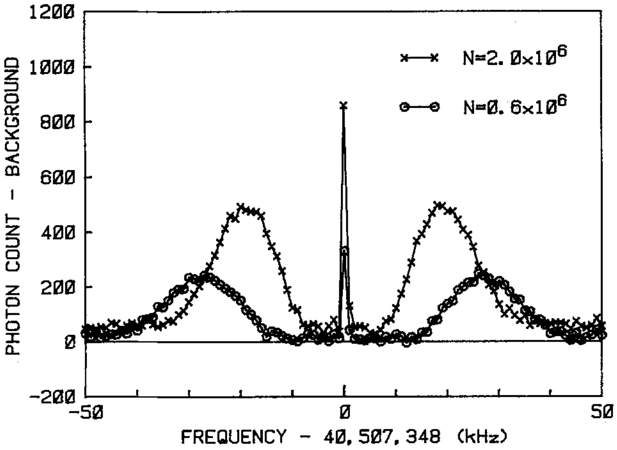

Fig. 3. First-order Doppler spectra of stored ^{199}Hg$^+$ ions for two different numbers of ions. The shape and position of the sidebands are consistent with the model of the cooled cloud. In neither case is any intensity seen at ±50 kHz from the line center, the single ion macromotion frequency

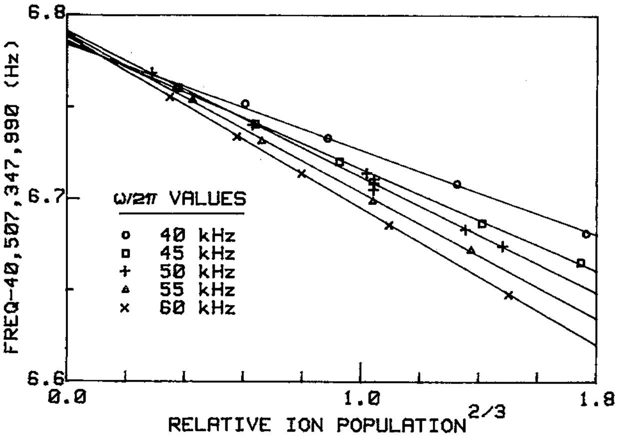

Fig. 4. Observed variation of the line-center frequency with relative ion population to the two-thirds power for various values of the macromotion frequency ω. The data is for approximately spherical clouds, and the frequency has been corrected for magnetic field and He pressure

increase in gas pressure has little effect. The small linear variation at higher pressure, a fractional shift of 5.7 $\times 10^{-9}$/Torr, we interpret as the well known collision or pressure shift of alkali hyperfine structure that has been observed in other atomic and ionic systems. The value is the same order as that observed in ^{137}Ba$^+$ in helium [26].

In Fig. 3 we show the first-order Doppler spectra for two different ion numbers, $N=0.6\times 10^6$ and $N=2\times 10^6$. There is no noticeable amplitude to be seen at 50 kHz from the center where sidebands due to the macromotion of uncooled ions would be. The peak frequency of the sidebands that are observed varies as $N^{-1/3}$ as would be expected if the ions were in motion at thermal energy ($T=300$ K) in the flat bottom potential, colliding with a spherical barrier at $r=r_c(N)$ as we hypothesize.

In Fig. 4 we demonstrate that the observed shift of the hyperfine frequency varies as 2/3 power of the ion number with the macromotion frequency as a parameter for five different macromotion frequencies. Extrapolating to zero ion population and correcting for the collision shift noted above and the ambient magnetic field, allows us to estimate the unshifted hyperfine frequency. As can be seen the intercepts agree to within $\pm 1\times 10^{-13}$, which is the limit of stability of our comparison standard.

Conclusions

The results presented above demonstrate the effectiveness of a light background gas in cooling a cloud of ^{199}Hg ions. The results of Fig. 4 are in good agreement with (2), accounting for the variation of second-order Doppler shift with the total stored charge. The results of Fig. 2 and 3 independently support our cold cloud, suppressed macromotion picture. Our overall error budgets indicate that a ^{199}Hg ion frequency standard using the buffer cooling technique can achieve a stability of 2.3×10^{-14} and an accuracy of 2.5×10^{-13} which is an order of magnitude improvement in both of these specifications over presently available commercial cesium standards. The knowledge that the ions are to be found in a compact uniform density cloud has proven useful in improving the optical design of the standard. We can forsee applications to atomic collision experiments and ion spectroscopy.

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