Absolute Frequency Measurements of the Hg$^+$ and Ca Optical Clock Transitions with a Femtosecond Laser

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The frequency comb created by a femtosecond mode-locked laser and a microstructured fiber is used to phase coherently measure the frequencies of both the Hg$^+$ and Ca optical standards with respect to the SI second as realized at NIST. We find the transition frequencies to be $f_{\text{Hg}} = 1\,064\,721\,609\,899\,143(10)\,$Hz and $f_{\text{Ca}} = 455\,986\,240\,494\,158(26)$ Hz, respectively. In addition to the unprecedented precision demonstrated here, this work is the precursor to all-optical atomic clocks based on the Hg$^+$ and Ca standards. Furthermore, when combined with previous measurements, we find no time variations of these atomic frequencies within the uncertainties of $|\langle \Delta f_{\text{Hg}}/\delta t \rangle|/f_{\text{Hg}} \leq 8 \times 10^{-14} \,$yr$^{-1}$, and $|\langle \Delta f_{\text{Ca}}/\delta t \rangle|/f_{\text{Ca}} \leq 30 \times 10^{-14} \,$yr$^{-1}$.

Optical standards based on a single ion or a collection of laser-cooled atoms are emerging as the most stable and accurate frequency sources of any sort. However, because of their high frequencies ($\sim 500$ THz), it has proven difficult to count cycles as required for building an optical clock and comparing to the cesium microwave standard. Only recently, a reliable and convenient optical clockwork fast enough to count optical oscillations has been realized. Here, we report an optical clockwork based on a single femtosecond laser that phase coherently divides down the visible radiation of the Hg$^+$ and Ca optical frequency standards to a countable radio frequency. By this means we determine the absolute frequencies of these optical transitions with unparalleled precision in terms of the SI second as realized at NIST. Indeed, for the Hg$^+$ standard, the statistical uncertainty in the measurement is essentially limited by our knowledge of the SI second at $\sim 2 \times 10^{-15}$. The high precision and high demonstrated stability of the optical standards combined with the straightforward femtosecond-laser-based clockwork suggest Hg$^+$ and Ca as excellent references for future all-optical clocks. Additionally, the comparison of atomic frequencies over time provides constraints on the possible time variation of fundamental constants. When combined with previous measurements, the current level of precision allows us to place the tightest constraint yet on the possible variation of optical frequencies with respect to the cesium standard.

The Hg$^+$ and Ca systems have recently been described elsewhere, so we summarize only the basic features. The heart of the mercury optical frequency standard is a single, laser-cooled $^{199}$Hg$^+$ ion that is stored in a cryogenic, radio frequency spherical Paul trap. The $^2S_{1/2}(F = 0, M_F = 0) \leftrightarrow ^2D_{5/2}(F = 2, M_F = 0)$ electric-quadrupole transition at 282 nm [Fig. 1(a)] provides the reference for the optical standard. We lock the frequency-doubled output of a well-stabilized 563 nm dye laser to the center of the quadrupole resonance by irradiating the Hg$^+$ ion alternately at two frequencies near the maximum slope of the resonance signal and on opposite sides of its center. Transitions to the metastable $^2D_{5/2}$ state are detected with near unit efficiency since the absorption of a single 282 nm photon suppresses the scattering of many 194 nm photons on the strongly allowed $^2S_{1/2} \rightarrow ^2P_{1/2}$ transition. Usually, 48 measurements are made on each side of the resonance prior to correcting the average frequency of the 282 nm source. If an asymmetry between the number of excitations detected on the high- and low-frequency sides is found, then the frequency of the probe radiation is adjusted to minimize the asymmetry. In this way, we steer the frequency of the 282 nm source to the center of the $S \rightarrow D$ quadrupole resonance with an imprecision that decreases as the square root of the measurement time. In Fig. 1(b) we show an example of a normalized spectrum that was obtained from multiple bidirectional scans through the resonance during the lock-up, where the probe time was 20 ms. Most often, the frequency was locked to resonance with a 10 ms interrogation period, which provided a fractional frequency instability reaching $3 \times 10^{-15} \tau^{-1/2}$ for an averaging time $\tau$ measured in seconds.

The calcium standard is based on a collection of $\sim 10^7$ laser-cooled $^{40}$Ca atoms held in a magnetooptic trap. The 423 nm $^1S_0 \leftrightarrow ^1P_1$ transition is used for Doppler cooling and trapping the atoms to a residual temperature of $\sim 2$ mK, while the 657 nm $^1S_0(M_J = 0) \leftrightarrow ^3P_1(M_J = 0)$ clock transition (400 Hz natural linewidth) is used for the frequency standard [Fig. 2(a)]. We excite the clock transition with a four-pulse Bordé-Ramsey sequence (pulse duration $= 1.5 \, \mu$s) with light from a continuous wave (CW) frequency-stabilized diode laser. Using a shelving detection technique similar to that employed in the Hg$^+$ system, near-resonant 423 nm pulses (5 $\mu$s duration) are used before and after the 657 nm excitation to determine the fraction of atoms transferred from the ground state. Figure 2(b) shows...
Bordé-Ramsey fringes taken at a resolution of 960 Hz. This system has demonstrated a fractional frequency instability of $4 \times 10^{-15}$, when probing sub-kilohertz linewidths. For the measurements presented here the Ca spectrometer was operated with linewidths ranging from 0.96 to 11.55 kHz which are integer subharmonics of the recoil splitting.

The recent introduction of mode-locked lasers to optical frequency metrology greatly simplifies the task of optical frequency measurements. The spectrum emitted by a mode locked laser consists of a comb of regular spaced continuous waves that are separated by the pulse repetition rate $f_r$. The frequency of the $n^{th}$ mode of the comb is given by $f_n = nf_r + f_o$ where $f_o$ is the frequency offset common to all modes that is caused by the difference between the group- and the phase-velocity inside the laser cavity. Whereas $f_r$ can be measured by direct detection of the laser output with a photodiode, $f_o$ is measured by heterodyning the harmonic of a mode $f_n = nf_r + f_o$ from the infrared wing of the comb with a mode $f_{2n} = 2nf_r + f_o$ from the blue side of the comb. While an octave spanning comb can be produced directly from a mode-locked laser, launching the longer pulses from a commercially-available femtosecond laser into an air-silica microstructure fiber also produces a frequency comb that spans an octave. Via nonlinear processes in the fiber, additional equally spaced and phase-locked modes in the comb of regular spaced continuous waves that are separated in time via two single mode optical fibers that are 130 m and 10 m long, respectively. Approximately 2 mW of CW light from each fiber is mode-matched with the appropriate spectral region of the frequency comb to generate a beat signal $f_b$ with a nearby mode. This beat note is amplified and measured with a radio frequency counter. The optical frequency is then expressed as $f_{opt} = f_o + mf_r + f_b$, where $m$ is a large integer uniquely determined for each system from previous coarse measurements of $f_{opt}$.

We detect cycle slips in both of the phase-locks by monitoring $f_r$ and $f_o$ with additional counters. We selectively discard any measurement of $f_{opt}$ for which the measured $f_o$ or $f_r$ deviate from the expected value by more than $1/\tau_{gate}$, where $\tau_{gate}$ is the counter gate time in seconds. We avoid miscounts of $f_b$ by using an auxiliary counter to record the ratio $r$ between $f_b$ and $f_b/4$, where the division by 4 is implemented digitally. Any measurements of $f_b$ where the auxiliary counter gives a result that does not satisfy $(r - 4) * f_b < 10/\tau_{gate}$, are discarded. We rely on the assumption that the two counters recording $f_b$ and $r$, if in disagreement, do not make the same mistake. For each data point the three additional counters ($f_r$, $f_o$ and $r$) are started before the counting of $f_b$, and operated with 50 ms longer gate times to ensure temporal overlap.

Figure 3 summarizes the frequency measurements of $f_{opt}$ made between Aug. 16 and Aug 31, 2000, and Fig. 4 summarizes the Ca measurements made from Oct. 26 to Nov. 17, 2000. All measurements are corrected daily for the second-order Zeeman shift and for the offset of the reference maser frequency. The uncertainty for the Zeeman correction is $< 1 \times 10^{-15}$ for the Hg$^+$ system and $< 2.5 \times 10^{-15}$ in the Ca system. The frequency of the maser is calibrated by comparing to the local NIST time scale (5 hydrogen masers and 3 commercial cesium clocks), which in turn is calibrated by the local cesium fountain standard (NIST-F1) as well as international cesium standards. This resulted in a fractional uncertainty in the frequency of the reference maser of about $1.8 \times 10^{-15}$ for the measurements.

The weighted mean of our measurements of the Hg$^+$ clock transition is $f_{Hg} = 1 \times 64271209899143$ Hz, where the statistical uncertainty of 2.4 Hz is near the fractional frequency instability of the reference maser ($\sim 2 \times 10^{-13}$ at 1s, decreasing to $\sim 4 \times 10^{-16}$ at a few days). Since we have not made a full evaluation of the Hg$^+$-standard, we only estimate the total systematic un-
certainty to be 10 Hz. The dominant systematic contribution to the uncertainty of the \( S - D \) transition frequency is believed to be the electric-quadrupole shift of the \( ^2D_{5/2} \) state arising from coupling with the static potentials of the trap. In our spherical Paul trap, where the confinement of the ion uses no static applied fields, the maximum quadrupole shift should be less than 1 Hz (or a fractional frequency shift \(< 10^{-15}\) [2, 3]). In principle, it is possible to eliminate the quadrupole shift by averaging the \( S - D \) transition frequencies for three mutually orthogonal orientations of a quantizing magnetic field of constant magnitude. In the present experiment, we have measured the \( S - D \) frequency for various field values, but we have made no attempt to eliminate the quadrupole shift by using three orthogonal fields of constant magnitude. No shift of the resonance frequency is observed within the precision of these measurements. We anticipate that the uncertainties of all systematic shifts in the Hg\(^+\) system can be reduced to values approaching \( 1 \times 10^{-18} \) [1, 2, 3].

For the Ca data shown [Fig. 1], an additional correction is applied each day to account for a frequency shift caused by residual phase chirping on the optical Ramsey pulses produced by amplitude modulating an acoustooptic modulator (AOM). The phase chirping produced a resolution dependent frequency shift on the order of 100 Hz for 11.5 kHz wide fringes but only 10 Hz for 0.96 kHz wide fringes. On each day, the Ca frequency was measured for \( \sim 30 \) minutes at each of several fringe resolutions, and the zero-intercept of a linear fit to the data was used as the corrected frequency. On the last 3 days of experiments, we were able to reduce this shift by a factor of \( \sim 3 \) with improvements to the RF pulses that drive the AOM’s. The statistical uncertainty for each day’s measurement (typically 8 Hz) is smaller than the uncontrolled systematic uncertainties in the the Ca frequency. The largest systematic uncertainty stems from incomplete knowledge of the angular overlap of the counterpropagating beams in the Ca spectrometer, combined with a transverse drift velocity of the cold Ca ensemble. This leads to a residual first-order Doppler shift with a magnitude \(< 15 \) Hz (except on Nov. 16 where a large drift velocity led to a \( \sim 52 \) Hz uncertainty). Other significant uncertainties include our lack of knowledge or control of electronic offsets and baseline asymmetries (< 12 Hz), wavefront curvature (< 10 Hz), and cold-atom collisional shifts (< 10 Hz). Taking all known systematic uncertainties in quadrature gives a confidence level of \( \sim 26 \) Hz for the measured mean value as indicated by the dashed lines in Fig. 1.

Figure 2 also shows the good agreement between our measurement and the most recent value measured with a harmonic frequency chain [2, 3], which provides a degree of confidence in the reproducibility of the Ca standards. An additional measure of the Ca frequency can be made by using the present absolute measurement of Hg\(^+\) and our earlier measurement of the 76 374 564 455 429(40) Hz gap between \( f_{Hg} \) and Ca standard [27]. This yields a value \( f_{Ca} = 455 986 240 494 143(40) \) Hz in good agreement with the present absolute measurement of \( f_{Ca} \).

Finally, these results also provide data on the relative time variability of atomic frequencies. S. Karshenboim has recently reviewed the implications of such comparisons and their contribution toward constraining the possible time variation of fundamental constants [28]. In this regard Hg\(^+\) and Ca are two of the most interesting cases to study. Comparing our present measurement of \( f_{Ca} \) to measurements made by PTB in 1997 gives \((\partial f_{Ca}/\partial t)/f_{Ca} = (+2 \pm 8) \times 10^{-14} \) yr\(^{-1}\). Similarly, combining this result with our May 2000 measurement of \( f_{Hg} \) with respect to \( f_{Ca} \) provides an initial baseline constraint on the time variation of \( f_{Hg} \) of \((\partial f_{Hg}/\partial t)/f_{Hg} = (-7 \pm 30) \times 10^{-14} \) yr\(^{-1}\). Here we use the defined unit of time based on the frequency of the Cs hyperfine interval and assume that any time dependence is slow and dominantly linear over the relevant time scale. At our present level of precision we find no evidence of any relative time variation between these three frequency standards, two optical and one microwave.

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FIG. 1: (a) Partial level scheme for $^{199}$Hg$^+$. The 194 nm radiation is used for Doppler cooling, state preparation and detection. The 282 nm transition from the ground state $^2S_{1/2}(F = 0, M_F = 0)$ to the metastable $^2D_{5/2}(F = 2, M_F = 0)$ state provides the reference for the optical clock frequency. (b) A typical spectrum of the 282 nm clock transition obtained under lock conditions is shown. Here, the excitation pulse length was 20 ms, and the measured linewidth is Fourier transform limited to about 20 Hz at 563 nm (40 Hz at 282 nm).
FIG. 2: (a) Simplified diagram of the relevant energy levels in the Ca standard. (b) Optical Bordé-Ramsey fringes with a 960 Hz (FWHM) resolution. The total averaging time to generate this figure was 20 s.

FIG. 3: A chronological record of the average daily frequency of the $^{199}\text{Hg}^+$ clock transition measured on six days over a 15 day period representing 21 651 s of total measurement time. The error bars represent statistical fluctuations. The dashed lines represent an estimated systematic uncertainty of ±10 Hz in the Hg$^+$ system in the absence of a full evaluation.
FIG. 4: The filled squares are the measured Ca frequencies on ten days over a 23-day period representing 38 787 s of total measurement time. The inner and outer error bars for each day represent the statistical and total uncertainties, respectively. The dashed-lines show the 26 Hz systematic uncertainty assigned to the mean. The open triangle is the PTB measurement reported in Ref. [26], and the open circle is the Ca frequency calculated from the present Hg\(^+\) result and our previous measurement of the 76 THz gap between Ca and Hg\(^+\) [27].