

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. 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 $|(\partial f_{\text{Ca}}/\partial t)/f_{\text{Ca}}| \leq 8 \times 10^{-14} \text{ yr}^{-1}$ and $|(\partial f_{\text{Hg}}/\partial t)/f_{\text{Hg}}| \leq 30 \times 10^{-14} \text{ yr}^{-1}$.

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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 [1–5]. However, because of their high frequencies (~ 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 [6–8]. 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 National Institute of Standards and Technology (NIST) [9]. 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 standards [1,4] 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 [1,4,10,11], so we summarize only the basic features. The heart of the mercury optical frequency standard is a single, laser-cooled $^{199}\text{Hg}^+$ 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 [1]. We lock the frequency-doubled output of a well-stabilized 563 nm dye laser to the center of the quadrupole resonance by ir-

radiating 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 $^2S_{1/2} - ^2P_{1/2}$ transition [12,13]. Because the fractional frequency instability of the probe laser is $\leq 10^{-15}$ for measurement times $0.1 \text{ s} < t < 10 \text{ s}$ [11], usually 48 measurements are made on each side of the resonance prior to correcting the average frequency of the 282 nm source. The resonance probe period was either 10 or 20 ms, but each measurement cycle was longer by the time used (for example) for state preparation (15 ms) and detection (10 ms), as well as the decay time ($\tau_D \approx 90 \text{ ms}$) of the metastable state if an excitation was made. A new interrogation cycle is begun when the 194 nm fluorescence intensity rises above a preset threshold level. This reduces dead time, since it would otherwise be necessary to wait more than the lifetime of

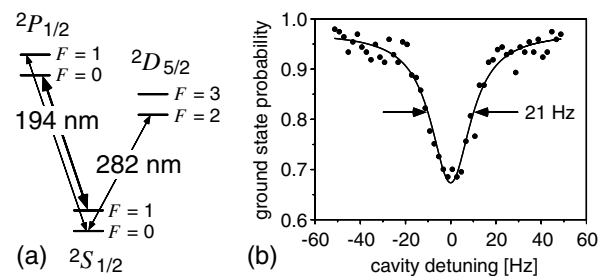


FIG. 1. (a) Partial level scheme for $^{199}\text{Hg}^+$. The 194 nm radiation is used for Doppler cooling, state preparation, and detection. The 282 nm transition from the ground state $^2S_{1/2}(F=0, M_F=0)$ to the metastable $^2D_{5/2}(F=2, M_F=0)$ state provides the reference for the optical clock 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).

the metastable state to ensure that the ion has returned to the ground state. 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 $S - D$ quadrupole resonance with an uncertainty that is less than 2×10^{-15} for averaging times $\tau \leq 30$ s and that decreases as $\tau^{-1/2}$ for $\tau > 30$ s [14]. In Fig. 1(b) we show an example of a normalized spectrum that was obtained from multiple bidirectional scans through the resonance during the lockup, where the probe time was 20 ms.

The calcium standard is based on a collection of $\sim 10^7$ laser-cooled ^{40}Ca atoms held in a magneto-optic trap. The 423 nm $^1S_0 \leftrightarrow ^1P_1$ transition is used for Doppler cooling and trapping the atoms to a residual temperature of ~ 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 μs) 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 μs 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 $4 \times 10^{-15} \tau^{-1/2}$, when probing subkilohertz linewidths [4]. 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 [6–8,15–17]. 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 $f_n = nf_r + f_o$ [18,19], where f_o is the frequency offset common to all modes that is caused

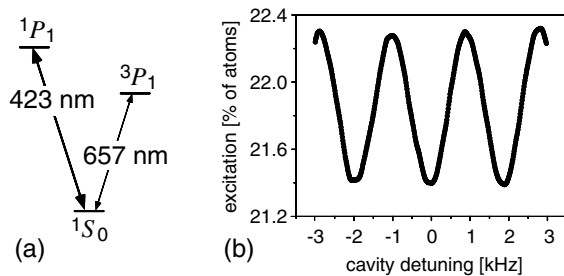


FIG. 2. (a) Simplified diagram of the relevant energy levels in the Ca standard. (b) Optical Bordé-Ramsey fringes with a 960 Hz (FWHM) resolution. The total averaging time to generate this figure was 20 s.

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 [7,8]. While an octave spanning comb can be produced directly from a mode-locked laser [20], launching the longer pulses from a commercially available femtosecond laser into an air-silica microstructure fiber [21,22] also produces a frequency comb that spans an octave. Via nonlinear processes in the fiber, additional equally spaced and phase-coherent modes are added to the comb. It has been demonstrated that this process of spectral broadening preserves the uniformity of spacing and spectral fidelity of the comb to at least a few parts in 10^{16} [8].

We couple approximately 200 mW average power from a femtosecond Ti:sapphire ring laser ($f_r \approx 1$ GHz) [23] into a 15 cm piece of a microstructure fiber that has a 1.7 μm core and a group velocity dispersion that vanishes near 770 nm [21]. This power is sufficient to increase the spectral width of the laser from 13 THz to more than 300 THz, spanning from ~ 520 to ~ 1170 nm. The infrared part of the comb from the fiber ($\lambda \approx 1060$ nm) is split off by a dichroic mirror and frequency doubled into the green portion of the visible spectrum with a 2 mm long KNbO_3 crystal. Following an adjustable delay line that matches the optical path lengths, the frequency-doubled light is spatially combined with the green part of the original comb using a polarizing beam splitter. A second rotatable polarizer projects the polarization of the combined beams onto a common axis so that they can interfere on a photodiode. This polarizer is also used to adjust the relative power of the two beams for optimum signal-to-noise ratio in the heterodyne signal. A small grating prior to the photodiode helps to select only that part of the frequency comb that matches the frequency-doubled light, thereby reducing noise from unwanted comb lines [19]. We phase lock both f_o and f_r to synthesized frequencies derived from a cavity-tuned hydrogen maser. Control of f_r is achieved with a cavity folding mirror that is mounted on a piezotransducer, while f_o is controlled by adjusting the 532 nm pump beam intensity with an electro-optic modulator [8]. When f_o and f_r are both phase locked, the frequency of every mode in the comb is known with the same precision as the reference maser.

The cw light from the Hg^+ (563 nm) and Ca (657 nm) spectrometers is transferred to the mode-locked laser system via two single mode optical fibers that are 180 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 $f_{\text{opt}} = f_o + mf_r + f_b$, 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 [24]. 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 $1/\tau_{\text{gate}}$, where τ_{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 $(r - 4)f_b < 10/\tau_{\text{gate}}$ are discarded. We rely on the assumption that the two counters recording f_b and r , if in agreement, 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 Hg^+ made between 16 August and 31 August 2000, and Fig. 4 summarizes the Ca measurements made from 26 October to 17 November 2000. All measurements are corrected 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 [9]), as well as international cesium standards. This resulted in a fractional uncertainty in the frequency of the reference maser of about 1.8×10^{-15} for the measurements.

The weighted mean of our measurements of the Hg^+ clock transition is $f_{\text{Hg}} = 1\,064\,721\,609\,899\,143$ 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 1 s, decreasing to $\sim 4 \times 10^{-16}$ at a few days). We have not yet made a full evaluation of the systematic uncertainties of the Hg^+ standard; however, we believe that 10 Hz

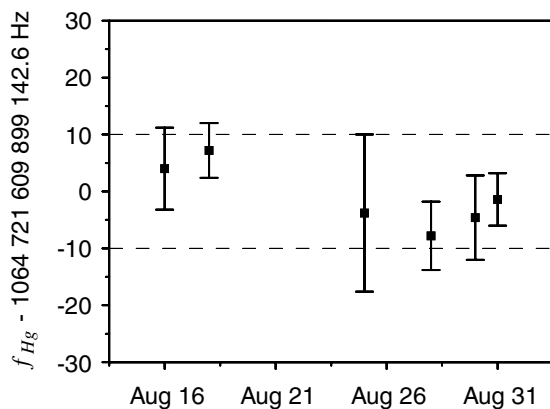


FIG. 3. A chronological record of the average daily frequency of the $^{199}\text{Hg}^+$ clock transition measured on six days over a 15 day period representing 21 651 s of total measurement time. The error bars represent statistical fluctuations. The dashed lines represent an estimated systematic uncertainty of ± 10 Hz in the Hg^+ system in the absence of a full evaluation.

is a conservative upper bound for the total systematic uncertainty. The largest systematic uncertainty is due to the interaction between the atomic quadrupole moment of the $^2D_{5/2}$ state and a static electric field gradient. In the currently used spherical Paul trap, no static field gradient is deliberately applied. A potential difference between the ring and the end cap electrodes of as large as 0.5 V due to contact potentials or stray charges, for example, would result in a quadrupole shift of only 1 Hz [25]. The magnetic field is evaluated before and after each run by measuring the frequency of one or more of the magnetic field dependent electric-quadrupole transitions. This results in an uncertainty of the second-order Zeeman shift of the clock transition of less than 0.5 Hz. The accuracy of this calibration has been verified by varying the magnitude of the magnetic field for successive runs. The blackbody radiation shift of the clock transition would be -0.08 Hz at 300 K and is considerably lower in the cryogenic trap environment of approximately 4 K. At the Doppler cooling limit, the second-order Doppler shift due to thermal motion is -0.003 Hz. Finally, the second-order Doppler shift due to residual micromotion caused by the trapping field is estimated to have a magnitude no greater than 0.1 Hz. We anticipate that the uncertainties of all systematic shifts in the Hg^+ system can be reduced to values approaching 1×10^{-18} [1,25].

For the Ca data shown (Fig. 4), 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 acousto-optic 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

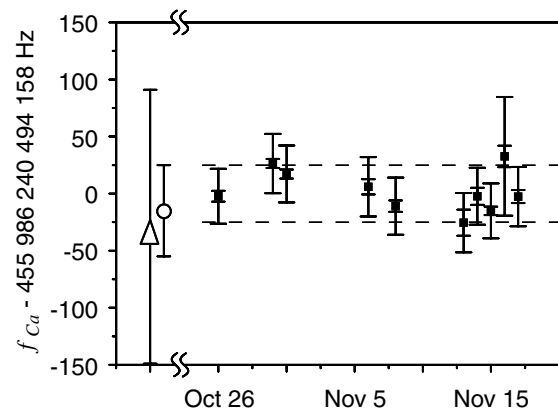


FIG. 4. The filled squares are the measured Ca frequencies on ten days over a 23 day period representing 38 787 s of total measurement time. The inner and outer error bars for each day represent the statistical and total uncertainties, respectively. The dashed lines show the 26 Hz systematic uncertainty assigned to the mean. The open triangle is the Physikalisch-Technische Bundesanstalt (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].

wide fringes. On each day, the Ca frequency was measured for ~ 30 min 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 three days of measurements, we were able to reduce this shift by a factor of ~ 3 with improvements to the rf pulses that drive the AOM's. With horizontal beams we can achieve < 20 Hz gravity-induced frequency shift, which can be readily quantified and eliminated simply by reversing the pulse sequence. The statistical uncertainty for each day's measurement (typically 8 Hz) is smaller than the uncontrolled systematic uncertainties in 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 16 November 2000, where a large drift velocity led to a ~ 52 Hz uncertainty). Other significant uncertainties include our lack of knowledge or control of electronic offsets and baseline asymmetries (< 12 Hz), wave front curvature (< 10 Hz), and cold-atom collisional shifts (< 10 Hz). Taking all known systematic uncertainties in quadrature gives a confidence level of ~ 26 Hz for the measured mean value as indicated by the dashed lines in Fig. 4. Again, for the Ca measurement we find that the stability is limited by the maser.

Figure 4 also shows the good agreement between our measurement and the most recent value measured with a harmonic frequency chain [26], 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 $f_{\text{Hg}}/2$ and the Ca standard [27]. This yields a value $f_{\text{Ca}} = 455\,986\,240\,494\,143(40)$ 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. 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 [26] gives $(\partial f_{\text{Ca}}/\partial t)/f_{\text{Ca}} = (+2 \pm 8) \times 10^{-14} \text{ yr}^{-1}$. Similarly, combining this result with our May 2000 measurement of f_{Hg} with respect to f_{Ca} [27] provides an initial baseline constraint on the time variation of f_{Hg} of $(\partial f_{\text{Hg}}/\partial t)/f_{\text{Hg}} = (-7 \pm 30) \times 10^{-14} \text{ yr}^{-1}$. 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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Note added.—Since the submission of this work a new measurement of the Ca clock transition was conducted at PTB with a femtosecond system similar to the one described here [29]. Although less precise, this most recent PTB measurement is in agreement with the value we report.

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