Testing the Stability of Fundamental Constants with the ^{199}Hg$^+$ Single-Ion Optical Clock

S. Bize,* S. A. Diddams, U. Tanaka,† C. E. Tanner,‡ W. H. Oskay, R. E. Drullinger, T. E. Parker, T. P. Heavner, S. R. Jefferts, L. Hollberg, W. M. Itano, and J. C. Bergquist§

Time and Frequency Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305

(Received 30 December 2002; revised manuscript received 27 February 2003; published 18 April 2003)

Over a two-year duration, we have compared the frequency of the ^{199}Hg$^+$ $5d^{10}6s\,^2S_{1/2}(F=0) \leftrightarrow 5d^96s^2\,^2D_{5/2}(F=2)$ electric-quadrupole transition at 282 nm with the frequency of the ground-state hyperfine splitting in neutral ^{133}Cs. These measurements show that any fractional time variation of the ratio $\nu_{\mathrm{Cs}}/\nu_{\mathrm{Hg}}$ between the two frequencies is smaller than $\pm 7 \times 10^{-15}$ yr^{-1} (1σ uncertainty). According to recent atomic structure calculations, this sets an upper limit to a possible fractional time variation of $g_{\mathrm{Cs}}(m_e/m_p)\alpha^{6.0}$ at the same level.

DOI: 10.1103/PhysRevLett.90.150802 PACS numbers: 06.30.Ft, 32.30.Jc, 32.80.Pj

The development of string theory models aiming at a unified description of gravity and quantum mechanics has renewed interest for improved experimental tests of Einstein's Equivalence Principle (EEP). Indeed, a common feature of these models is that they allow for, or even predict, violations of EEP [1]. These include violation of the universality of free fall as well as variation of fundamental constants with time and space. Interestingly, a recent analysis of the spectrum of quasars [2] suggests that the fine-structure constant α may have changed over the cosmological time scale (10^{10} yr). The Oklo reactor analysis [3,4], on the other hand, puts a stringent limit to possible variation of α on the geological time scale (10^9 yr). Owing to their high accuracy, comparisons between atomic frequency standards based on different atomic species and/or types of transitions provide one of the best ways to perform laboratory tests of the stability of fundamental constants. Present and future efforts to improve atomic frequency standards, in both the optical and the microwave domains, will improve these tests, leading to significant constraints on theoretical work aimed at a unified theory.

In this Letter, we describe frequency comparisons conducted over a two-year period between a ^{199}Hg$^+$ single-ion optical clock and a ^{133}Cs fountain atomic clock that set a new stringent limit to a possible variation of fundamental constants. The theoretical background is given first. We then describe the experiment and conclude with the results of the test.

In the experiment, the frequency ν_{Hg} of the ^{199}Hg$^+$ $5d^{10}6s\,^2S_{1/2}(F=0) \leftrightarrow 5d^96s^2\,^2D_{5/2}(F=2, m_F=0)$ electric-quadrupole transition at $\lambda = 282$ nm is compared to the frequency ν_{Cs} of the ground-state hyperfine transition $6S_{1/2}(F=3, m_F=0) \leftrightarrow 6S_{1/2}(F=4, m_F=0)$ in neutral ^{133}Cs. Including relativistic and many-body effects, ν_{Hg} can be expressed as $\nu_{\mathrm{Hg}} \simeq R_y F_{\mathrm{Hg}}(\alpha)$, where $R_y = R_\infty c$ is the Rydberg constant expressed as a frequency, and $F_{\mathrm{Hg}}(\alpha)$ is a dimensionless function of the fine-structure constant $\alpha = e^2/4\pi\varepsilon_0\hbar c$. Similarly, the hyperfine frequency of cesium can be approximated by $\nu_{\mathrm{Cs}} \simeq g_{\mathrm{Cs}}(m_e/m_p)\alpha^2 R_y F_{\mathrm{Cs}}(\alpha)$, where g_{Cs} is the ^{133}Cs nuclear g factor [5] and m_e/m_p the electron-to-proton mass ratio. $F_{\mathrm{Hg}}(\alpha)$ and $F_{\mathrm{Cs}}(\alpha)$ are calculated in [6,7]. With numerical values from [7], we find

$$\alpha \frac{\partial}{\partial \alpha} \ln F_{\mathrm{Hg}}(\alpha) \simeq -3.2, \tag{1}$$

$$\alpha \frac{\partial}{\partial \alpha} \ln F_{\mathrm{Cs}}(\alpha) \simeq +0.8. \tag{2}$$

Therefore, sequential measurements of the ratio $\nu_{\mathrm{Cs}}/\nu_{\mathrm{Hg}}$ actually test the stability of the product of fundamental constants $g_{\mathrm{Cs}}(m_e/m_p)\alpha^{6.0}$. The sensitivity to variation of individual constants needs to be known to only (1–10)% in order to adequately describe the constraints of this comparison. It is therefore justified to omit higher-order terms in the expression of the hyperfine splitting of ^{133}Cs, such as finite nuclear size. The high sensitivity of the Hg$^+$ vs Cs frequency comparison to a change of α arises from the large relativistic effects encountered in heavy atoms combined with the negative sign of the relativistic effects in ^{199}Hg$^+$. These factors make the ^{199}Hg$^+$ $^2S_{1/2} \leftrightarrow {}^2D_{5/2}$ optical transition one of the best choices for a search of a variation of α [7].

The ^{199}Hg$^+$ single-ion optical frequency standard has been described previously [8,9] and only the main features are outlined here. A single ^{199}Hg$^+$ ion is stored in a radio-frequency (rf) spherical Paul trap held at a cryogenic temperature (4.2 K). It is laser cooled to near the 1.7 mK Doppler limit using the strongly allowed $^2S_{1/2}(F=1) \leftrightarrow {}^2P_{1/2}(F=0)$ transition at 194 nm, as shown in Fig. 1. After a cooling and state preparation phase (~16 ms), the ion is left in the $^2S_{1/2}(F=0)$ lower state of the clock transition. The cooling laser is then switched off and the probe laser light at 282 nm is directed onto the ion for a typical duration of $T = 50$ ms. The cooling laser is turned on again to determine the ion's internal state using the technique of electron shelving [10,11]. The 194 nm fluorescence photons emitted by the ion are counted for 15 ms. The absence of

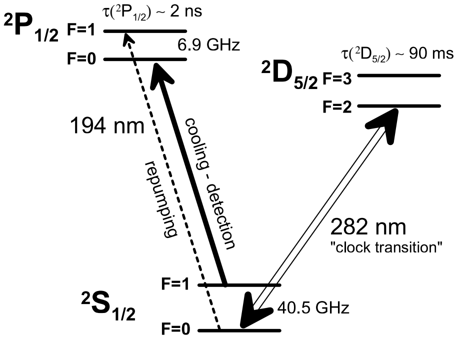

FIG. 1. Partial level scheme of $^{199}\mathrm{Hg}^+$. The 194 nm $^2S_{1/2}(F=1) \leftrightarrow {}^2P_{1/2}(F=0)$ transition is used for Doppler cooling, state preparation, and detection. The 282 nm electric-quadrupole transition from the ground state $^2S_{1/2}$ $(F=0)$ to the metastable $^2D_{5/2}$ $(F=2, m_F=0)$ state provides the reference for the optical clock frequency.

scattered photons indicates that the ion has been excited to the $^2D_{5/2}(F=2)$ state by the 282 nm probe laser. Similarly, a typical count rate of $\sim$6000 s^{-1} from the ion indicates that it has remained in the $^2S_{1/2}(F=0)$ state after the probe period. When the ion is detected in the $^2D_{5/2}$ excited state ($\tau_{D_{5/2}} \approx 90$ ms), the 194 nm is left on until scattered photons are detected again, indicating that the ion has spontaneously decayed to the $^2S_{1/2}$ state. A new interrogation cycle is then started.

The 282 nm radiation used to probe the clock transition is obtained by frequency doubling 563 nm light from a dye laser in a deuterated ammonium dihydrogen phosphate (AD*P) crystal, as shown in Fig. 2. The light from the dye laser is stabilized to a resonance of a stable high-finesse ($\mathcal{F} \sim 200\,000$) Fabry-Pérot cavity. Two acousto-optic modulators (AOM1, AOM2) driven by precision rf sources shift and fine-tune the frequency of the 563 nm radiation so as to match the frequency of the 282 nm radiation to the $S-D$ resonance frequency. By compensating the predictable linear drift of the stable reference cavity ($\sim$500 mHz s^{-1}) using AOM1, we realize an interrogation oscillator with a fractional frequency instability of 3×10^{-16} between 1 and 10 s, corresponding to a linewidth of 640 mHz at 282 nm [8]. For our typical probe time $T = 50$ ms, the observed linewidth is Fourier-transform limited with a full width at half maximum of $\sim$16 Hz, much larger than the frequency fluctuations of the probe laser during the probe pulse time. Under these conditions, the fluctuations of the measured transition probability and, hence, the frequency stability of the Hg^+ frequency standard, are limited mainly by atomic quantum projection noise [12].

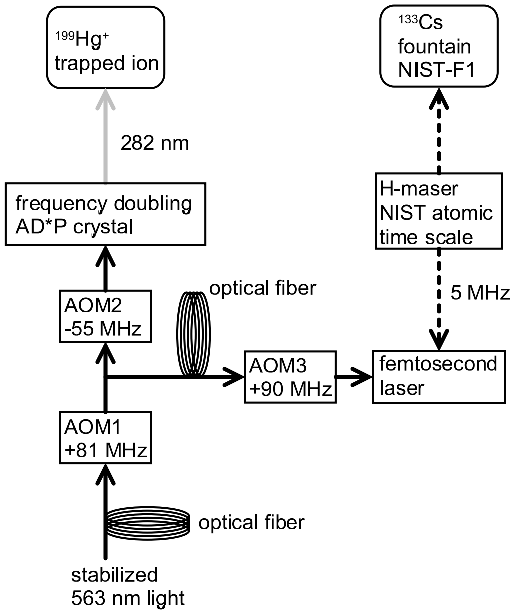

FIG. 2. Experimental setup for the absolute measurement of the frequency of the $^{199}\mathrm{Hg}^+$ optical clock in terms of the SI second defined by the ground-state hyperfine splitting of ^{133}Cs.

In our trap, the radial and axial secular frequencies are 1.1 and 2.2 MHz, respectively. Both frequencies are much higher than the recoil frequency $\nu = h/2m\lambda^2 \approx$ 12.6 kHz, where m is the ion mass and h is the Planck constant. The observed spectrum therefore consists of a central feature at the $^2S_{1/2}(F=0) \leftrightarrow {}^2D_{5/2}(F=2, m_F=0)$ transition resonance frequency, which is free of the recoil frequency shift, together with vibrational sidebands at integer multiples of the trap secular frequencies [11]. The spectrum also exhibits features corresponding to the carrier and vibrational sidebands of the $^2S_{1/2}$ $(F=0) \leftrightarrow {}^2D_{5/2}(F=2, m_F=\pm 1, \pm 2)$ "Zeeman components." Typically, the frequency difference between the clock transition and the first Zeeman components is $\sim$6 MHz, which corresponds to a quantization magnetic field $B \approx 0.3$ mT.

In order to lock the frequency of the probe laser to the atomic resonance, a square-wave frequency modulation is applied to the 563 nm beam using AOM2 so as to probe the carrier of the clock transition alternately on each side of the resonance. Typically, 24 measurements are averaged on each side of the resonance to find the transition probability. The difference between these two transition probabilities reveals the detuning between the center frequency of the probe laser and the center of the atomic resonance. This error signal is used in a digital servo loop that steers the average frequency of the probe laser to the center of the atomic resonance, applying frequency corrections to the synthesizer driving AOM1. The time constant of this servo loop is on the order of $\tau_{\mathrm{loop}} \sim 15$ s. The analysis of the frequency corrections indicates that, for $\tau > \tau_{\mathrm{loop}}$, the fractional frequency instability of the probe light stabilized to the atomic resonance is (5–7) $\times$ $10^{-15}\tau^{-1/2}$, in good agreement with the quantum-limited instability expected for our experimental conditions (trap secular frequencies, ion temperature, and measurement cycle time).

In order to compare the Hg^+ optical frequency standard to other frequency standards, some fraction of the

563 nm light at the output of AOM1 is launched into a 180 m long optical fiber and delivered into a separate room where it is frequency shifted by AOM3. AOM3 is used to actively cancel the optical path length fluctuations of the fiber in order to preserve the high degree of coherence of the light [13,14].

The frequency of the 563 nm light is measured with an optical frequency comb generated by a mode-locked Ti:sapphire laser whose femtosecond pulses are spectrally broadened in a microstructure fiber [15–18]. The optical spectrum at the output of the fiber consists of equally spaced, phase-coherent modes with frequencies $f_n = nf_r + f_0$, where f_r is the repetition rate of the mode-locked laser, n is an integer, and f_0 is a frequency offset caused by the difference between the phase and group velocities in the laser cavity. The repetition rate is typically $f_r \sim 1$ GHz and the spectrum spans more than one octave from ~520 to 1170 nm. The repetition rate is detected directly with a fast photodiode. The offset frequency f_0 is detected by the self-referencing method, where the frequency-doubled red part of the comb $2f_n = 2nf_r + 2f_0$ is heterodyned with the blue part of the comb $f_{2n} = 2nf_r + f_0$. We also detect the beatnote f_b between the 563 nm light and the closest mode of the optical frequency comb $f_m = mf_r + f_0$ (m is known from previous coarse measurements of the Hg^+ $S - D$ transition frequency). In practice, f_0 and f_b are phase locked to precision rf sources by acting on the cavity length and the pump power of the femtosecond laser, respectively. Finally, f_r is measured by counting the low-frequency beatnote between f_r and a third rf synthesizer.

In order to perform absolute optical frequency measurements in terms of the SI second, all synthesizers and frequency counters are referenced to the 5 MHz output of a hydrogen maser with a typical fractional frequency instability $\sim 2 \times 10^{-13}\tau^{-1/2}$ for measurement times $1\ \mathrm{s} < \tau < 10^5$ s. The maser itself is part of an ensemble of five masers and three commercial cesium clocks used to realize the local NIST atomic time scale, which is in turn periodically calibrated using the NIST-F1 cesium fountain primary standard [19], as well as international cesium standards. The frequency of the reference hydrogen maser is known within four parts in 10^{15} with respect to the ground-state hyperfine splitting of $^{133}\mathrm{Cs}$ [19]. As shown in recent investigations [20,21], the additional noise and inaccuracy from the optical frequency comb itself is negligible at this level. It is thus possible to perform absolute measurements of the frequency of the Hg^+ optical standard (together with the frequency of each component of the optical comb) with a fractional frequency uncertainty of 4×10^{-15}. Typically, measurements are performed for 2 h, leading to a statistical (type A [22]) fractional frequency uncertainty of 2.4 parts in 10^{15}, which corresponds to a 2.5 Hz uncertainty on the frequency of the 282 nm stabilized light.

The full evaluation of all systematic effects of the Hg^+ optical standard is still under way. At the present time, 10 Hz is a conservative upper bound for its total systematic (type B) uncertainty, as shown by the following preliminary analysis of systematic shifts. The second-order Zeeman frequency shift of the clock transition is given by $\delta\nu_Z = K_Z^{(2)} B^2$, $K_Z^{(2)} = -18.925(28)\ \mathrm{kHz\,mT^{-2}}$ [23]. The typical field $B \approx 0.3$ mT corresponds to a second-order Zeeman frequency shift $\delta\nu_Z \sim -1.7$ kHz. Therefore, the 1.5×10^{-3} fractional uncertainty on coefficient $K_Z^{(2)}$ leads to a 2.6 Hz uncertainty on the clock frequency. For the same value of the bias magnetic field, the sensitivity of the clock frequency to field fluctuations is $11\ \mathrm{Hz}\,\mu\mathrm{T}^{-1}$. In our unshielded environment, B-field fluctuations up to $\pm 0.2\ \mu$T have been observed, leading to a 2.2 Hz uncertainty. Since the field strength setpoint varied by up to a factor of 2, the field was measured and corrected for daily. The most troublesome frequency shift is the electric-quadrupole shift $\delta\nu_Q$ due to the coupling between the atomic electric-quadrupole moment in the upper $^2D_{5/2}(F = 2, m_F = 0)$ clock state with electric field gradients due, for example, to stray charges on the trap electrodes. We expect that $|\delta\nu_Q| < 1$ Hz [23] and note that the use of two successive versions of the trap electrodes (gold and molybdenum surfaces) have led to no detectable change of the clock frequency. However, in the absence of the full evaluation, we have placed the conservative estimate of ±10 Hz on the shift. Similarly, the background pressure of helium (the only species remaining with significant pressure at 4.2 K) has been changed by more than 1 order of magnitude (estimated by measuring the ion heating rate due to background collisions) without producing any detectable frequency shift. Empirically, this implies that the He background pressure shift is smaller than 1 Hz. At a temperature of 300 K, the blackbody radiation shift is -0.08 Hz, and it is considerably lower in the 4.2 K cryogenic environment [23]. At the Doppler cooling limit of 1.7 mK, the second-order Doppler shift due to thermal motion is -0.003 Hz. Finally, by compensating the stray static electric field, systematic shifts related to the trapping oscillating electric field (second-order Doppler shift due to micromotion, ac Stark shift) are made smaller than 0.1 Hz [24].

Over a period of two years, we have performed 20 measurements of the $^{199}\mathrm{Hg}^+$ $S - D$ transition frequency with respect to the $^{133}\mathrm{Cs}$ ground-state hyperfine splitting. Figure 3 shows these measurements, corrected for the second-order Zeeman frequency shift, with their statistical (type A) error bars. The absolute frequency of the Hg^+ optical standard is given by the weighted average of these data: $\nu_{\mathrm{Hg}} = 1\,064\,721\,609\,899\,143.7(1.1)$ Hz. The total statistical uncertainty is only 1.0 Hz. A linear fit gives a slope of $-0.24 \pm 1.3\ \mathrm{Hz\,yr^{-1}}$. Measurements in Fig. 3 clearly show a reproducibility better than 10 Hz at 1.06×10^{15} Hz, the most stringent comparison of optical and microwave frequencies until now. The uncertainty

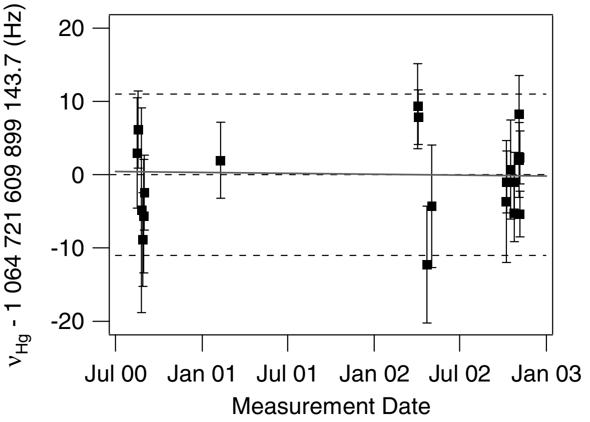

FIG. 3. Absolute frequency measurements of the ^{199}Hg$^+$ $^2S_{1/2}(F = 0) \leftrightarrow {}^2D_{5/2}(F = 2)$ transition with respect to the ^{133}Cs ground state hyperfine splitting defining the SI second. The plot shows the deviation of each measurement from the weighted average value with its statistical $\pm 1\sigma$ error bar and the linear fit (solid). The total systematic uncertainty is represented by the dashed lines at ±11 Hz.

of the measurement is dominated by the 11 Hz total systematic uncertainty obtained by adding in quadrature the 10 Hz Hg$^+$ clock uncertainty and the 4 Hz hydrogen maser uncertainty. With a 10^{-14} fractional uncertainty and a measurement period of two years, our measurement constrains a possible fractional variation of ν_{Cs}/ν_{Hg} at the level of $\pm 7 \times 10^{-15}$ yr^{-1} (1σ uncertainty).

This result can be interpreted as constraining a possible fractional variation of $g_{Cs}(m_e/m_p)\alpha^{6.0}$ at the same level: $\pm 7 \times 10^{-15}$ yr^{-1}. Assuming that any change in this quantity is due to the $\alpha^{6.0}$ factor, we derive an upper bound for a possible linear variation of the fine-structure constant: $|\dot{\alpha}/\alpha| < 1.2 \times 10^{-15}$ yr^{-1}, a factor of 30 improvement over [6]. However, there may be a significant change of g_{Cs} or m_e/m_p due to possible variation of the strength of the strong and electroweak interactions. In fact, recent theoretical work argues that within the framework of a grand unified theory a fractional variation of α is necessarily accompanied by a fractional variation of m_e/m_p that is ~38 times larger [25]. Comparisons between two optical clocks might test the stability of α alone [7]. One interesting possibility is to compare the ^{199}Hg$^+$ $S - D$ transition to the 657 nm $^1S_0(m = 0) \leftrightarrow {}^3P_1(m = 0)$ transition in neutral ^{40}Ca [15,26]. With an independent constraint to the stability of α, comparisons involving hyperfine transitions, such as the present ν_{Hg} (optical) vs ν_{Cs} comparison or the ν_{Rb} (microwave) vs ν_{Cs} comparison [27,28], will test the stability of the strong and electroweak interactions. Reference [5] investigates in more detail possible laboratory tests of the stability of fundamental constants.

We thank Robert Windeler, Thomas Udem, Murray Barrett, Jun Ye, and David Wineland for their contributions to this work. This work was partially supported by the Office of Naval Research and Timing Solutions, Inc. C. E. T. was also supported by DOE and NSF.

---

[*] Present address: BNM-SYRTE, Observatoire de Paris, 61 Avenue de l'Observatoire, 75014 Paris, France. Electronic address: sebastien.bize@obspm.fr

[†] Present address: Graduate School of Engineering Science, Osaka University, Osaka 560-8531, Japan.

[‡] Permanent address: Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556.

[§] Electronic address: berky@boulder.nist.gov

[1] T. Damour, F. Piazza, and G. Veneziano, Phys. Rev. Lett. **89**, 081601 (2002).
[2] J. K. Webb *et al.*, Phys. Rev. Lett. **87**, 091301 (2001).
[3] A. I. Shlyakhter, Nature (London) **264**, 340 (1976).
[4] T. Damour and F. Dyson, Nucl. Phys. **B480**, 37 (1996).
[5] S. G. Karshenboïm, Can. J. Phys. **78**, 639 (2000).
[6] J. D. Prestage, R. L. Tjoelker, and L. Maleki, Phys. Rev. Lett. **74**, 3511 (1995).
[7] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. A **59**, 230 (1999).
[8] B. C. Young, F. C. Cruz, W. M. Itano, and J. C. Bergquist, Phys. Rev. Lett. **82**, 3799 (1999).
[9] R. J. Rafac *et al.*, Phys. Rev. Lett. **85**, 2462 (2000).
[10] H. Dehmelt, Bull. Am. Phys. Soc. **20**, 60 (1975).
[11] J. C. Bergquist, W. M. Itano, and D. J. Wineland, Phys. Rev. A **36**, 428 (1987).
[12] W. Itano *et al.*, Phys. Rev. A **47**, 3554 (1993).
[13] L.-S. Ma, P. Jungner, J. Ye, and J. L. Hall, Opt. Lett. **19**, 1777 (1994).
[14] B. Young *et al.*, in *Proceedings of the 14th International Conference on Laser Spectroscopy*, edited by R. Blatt, J. Eschner, D. Leibfried, and F. Schmidt-Kaler (World Scientific, Singapore, 1999).
[15] Th. Udem *et al.*, Phys. Rev. Lett. **86**, 4996 (2001).
[16] R. Holzwarth *et al.*, Phys. Rev. Lett. **85**, 2264 (2000).
[17] S. A. Diddams *et al.*, Phys. Rev. Lett. **84**, 5102 (2000).
[18] S. A. Diddams *et al.*, Science **293**, 825 (2001).
[19] S. R. Jefferts *et al.*, Metrologia **39**, 321 (2002).
[20] Th. Udem, J. Reichert, R. Holzwarth, and T. W. Hänsch, Opt. Lett. **24**, 881 (1999).
[21] S. A. Diddams, L. Hollberg, L.-S. Ma, and L. Robertsson, Opt. Lett. **27**, 58 (2002).
[22] B. Taylor and C. Kuyatt, *NIST Technical Note 1297* (U.S. Government Printing Office, Washington, DC, 1994).
[23] W. Itano, J. Res. Natl. Inst. Stand. Technol. **105**, 829 (2000).
[24] D. J. Berkeland, J. D. Miller, J. C. Bergquist, W. M. Itano, and D. J. Wineland, J. Appl. Phys. **83**, 5025 (1998).
[25] X. Calmet and H. Fritzsch, Eur. Phys. J. C **24**, 639 (2002).
[26] J. Helmcke *et al.*, in Proceedings of the 2002 CPEM Conference [IEEE Trans. Instrum. Meas. (to be published)].
[27] S. Bize *et al.*, in *Proceedings of the 6th Symposium on Frequency Standards and Metrology* (World Scientific, Singapore, 2001), p. 53.
[28] H. Marion *et al.*, preceding Letter, Phys. Rev. Lett. **90**, 150801 (2003).