

## FREQUENCY MEASUREMENTS OF $\text{Al}^+$ AND $\text{Hg}^+$ OPTICAL STANDARDS

W. M. ITANO,\* J. C. BERGQUIST, T. ROSEN BAND, D. J. WINELAND, D. HUME,  
C.-W. CHOU, S. R. JEFFERTS, T. P. HEAVNER, T. E. PARKER,  
S. A. DIDDAMS, AND T. M. FORTIER

*Time and Frequency Division  
National Institute of Standards and Technology  
Boulder, CO 80305, USA*

*\*E-mail: itano@boulder.nist.gov*

Frequency standards based on narrow optical transitions in  $^{27}\text{Al}^+$  and  $^{199}\text{Hg}^+$  ions have been developed at NIST. Both standards have absolute reproducibilities of a few parts in  $10^{17}$ . This is about an order of magnitude better than the fractional uncertainty of the SI second, which is based on the  $^{133}\text{Cs}$  hyperfine frequency. Use of femtosecond laser frequency combs makes it possible to compare the optical frequency standards to microwave frequency standards or to each other. The ratio of the  $\text{Al}^+$  and  $\text{Hg}^+$  frequencies can be measured more accurately than the reproducibility of the primary cesium frequency standards. Frequency measurements made over time can be used to set limits on the time variation of fundamental constants, such as the fine structure constant  $\alpha$  or the quark masses.

*Keywords:* aluminum ion; mercury ion; optical frequency standards; time variation of fundamental constants; trapped ion frequency standards.

### 1. Introduction

Frequency is the physical quantity that can be measured the most accurately and reproducibly. Atomic frequency standards are based on transitions between the quantized energy levels of atoms. Since atoms of a particular type, for example  $^{133}\text{Cs}$ , are identical, atomic frequency standards based on the same atomic transition should have the same frequency. For this reason, their actual frequencies can have some physical significance, in contrast to frequencies based on macroscopic objects, such as quartz crystals or electromagnetic cavities, or astronomical cycles. Since 1967, the SI (Système International) unit of time has been defined in terms of an atomic transition frequency. To be more precise, the SI second was defined

as 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of  $^{133}\text{Cs}$ .<sup>1</sup>

In practice, frequency standards based on the same atomic resonance frequency do not agree exactly because of errors introduced, for example, by motion (Doppler shifts), by external fields that shift the frequencies, or by errors in the apparatuses used to determine the frequencies. The reproducibilities of atomic frequency standards have steadily improved. At the time when the SI second was redefined in terms of the cesium transition, frequency standards based on cesium were accurate to about one part in  $10^{12}$ . Currently the accuracy of cesium standards is about 3.3 parts in  $10^{16}$ .<sup>2</sup>

There is nothing in principle to prevent an atomic frequency standard from being more reproducible than the best cesium standards. However, it is impossible to express a frequency in SI units (Hz) any better than the accuracy of cesium standards, because they define the SI unit of time. This limit does not apply to the measurement of a frequency *ratio* between two different frequency standards.

Frequency standards based on optical transitions in the mercury ion and the aluminum ion have been developed at the National Institute of Standards and Technology (NIST). Both are based on narrow optical transitions in single trapped ions. According to estimates of their systematic uncertainties, both the mercury and aluminum standards are more reproducible than the primary cesium frequency standards. Details of these devices have been published previously, so only brief descriptions will be given here.

Until relatively recently, the accurate measurement of optical frequencies was difficult, involving complex chains of frequency-doubled and frequency-mixed lasers. Now, with the self-referenced femtosecond laser frequency comb, the linkage of optical to microwave frequencies, or optical to optical frequencies, is relatively simple.<sup>3-5</sup> A self-referenced femtosecond laser frequency comb generates a series of discrete, equally frequency-spaced modes. The mode spacing,  $f_{\text{rep}}$ , is given by the repetition rate of a mode-locked laser, typically around 1 GHz. The frequency of an individual mode can be expressed as  $f(m) = f_0 + m \times f_{\text{rep}}$ , where  $m$  is an integer. The offset frequency  $f_0$  is measured by a method called self-referencing. If the heterodyne beat frequency  $f_{\text{beat}}$  between an optical frequency standard and the nearest tooth of the optical comb is measured, then the frequency of the standard is known in terms of  $f_0$ ,  $f_{\text{rep}}$ , and  $f_{\text{beat}}$ , provided the integer  $m$  is known. This provides a link between the optical frequency and the frequencies,  $f_0$ ,  $f_{\text{rep}}$ , and  $f_{\text{beat}}$ , which can be referenced to a microwave frequency standard. To measure the ratio of two optical frequencies, one tooth of the

comb can be locked to one of the frequencies, and the beat note of the other frequency with the nearest tooth of the comb can be measured. The ratio of the two frequencies can then be measured without being limited by the accuracy of the cesium frequency standards.

## 2. $\text{Hg}^+$ frequency standard

The mercury ion frequency standard is based on the transition from the ground  $5d^{10}6s\ ^2S_{1/2}$  state to the metastable  $5d^96s^2\ ^2D_{5/2}$  state. The metastable state has a natural lifetime of around 90 ms, giving this transition a  $Q$  (frequency divided by the natural linewidth) of around  $6 \times 10^{14}$ . The transition was first proposed for use as an optical frequency standard by Bender *et al.*<sup>6</sup> in 1976. The transition was observed by Doppler-free two-photon absorption of a cloud of trapped  $^{198}\text{Hg}^+$  ions.<sup>7</sup> The transition was later observed in a single trapped  $^{198}\text{Hg}^+$  ion by single-photon electric-quadrupole absorption.<sup>8</sup> Doppler broadening is eliminated for single-photon absorption by confinement of the ion to a region smaller than the wavelength of the radiation.<sup>9</sup> Line broadening due to the magnetic field fluctuations is reduced by use of the ( $F = 0$ ) to ( $F = 2, m_F = 0$ ) hyperfine-Zeeman component in  $^{199}\text{Hg}^+$ , which has only a quadratic Zeeman shift. The 282 nm resonance has been observed with a linewidth as low as 6.7 Hz.<sup>10</sup>

The basic methods used for laser cooling, state preparation, and detection of the clock transition have been described previously.<sup>10-12</sup> The 194 nm  $5d^{10}6s\ ^2S_{1/2}$  to  $5d^{10}6p\ ^2P_{1/2}$  transition is used for Doppler laser cooling and laser-induced-fluorescence detection. To determine whether the 282 nm clock transition has been driven, 194 nm radiation is applied. If 194 nm fluorescence is observed, then the transition out of the ( $F = 0$ ) ground state did *not* occur. With the frequency of the laser servo-locked to the atomic resonance, the apparatus functions as a frequency standard. With the aid of a self-referenced femtosecond laser frequency comb, the frequency of the  $\text{Hg}^+$ -stabilized laser has been compared to microwave or other optical frequency standards.<sup>12-20</sup>

The various contributions to the systematic uncertainty of the mercury ion frequency have been evaluated or estimated.<sup>17,20</sup> The second-order Doppler shift due to thermal motion is reduced by laser cooling to near the Doppler cooling limit. The second-order Doppler shift due to rf micromotion is minimized by compensation of the stray electric fields.<sup>21</sup> The static magnetic field is periodically measured by observing the resonance line of a first-order magnetic-field-dependent Zeeman component of the  $^2S_{1/2}(F = 0)$  to  $^2D_{5/2}(F = 2)$  line. The frequency shift due to the interaction of the

atomic quadrupole moment with a static electric field gradient is canceled by switching the magnetic field direction between three mutually perpendicular directions.<sup>17,22</sup> The blackbody radiation shift is negligible, because the trap is operated at liquid helium temperature. An AC Zeeman shift due to unbalanced rf currents in the trap electrodes has been estimated and found to be small.<sup>20</sup> We plan to evaluate the AC Zeeman shift in the present trap by measuring the frequency of the ground-state hyperfine transition and comparing it to the accurately measured transition frequency at zero magnetic field.<sup>23</sup> The total fractional systematic uncertainty, given by the quadrature sum of the individual terms, is estimated<sup>20</sup> to be  $1.9 \times 10^{-17}$ .

### 3. Al<sup>+</sup> frequency standard

The 267 nm transition from the ground  $3s^2\ ^1S_0$  state to the  $3s3p\ ^3P_0$  state has a  $Q$  of  $1.45 \times 10^{17}$ , making it attractive as the basis of a frequency standard. However, there is no strongly allowed transition available for laser cooling and fluorescence detection. The strongly allowed 167 nm  $3s^2\ ^1S_0$  to  $3s3p\ ^1P_1$  transition would be usable for laser cooling and state detection, but narrowband tunable lasers are not readily available at that wavelength.

To get around the lack of a suitable transition for cooling and detection, Wineland proposed to simultaneously trap an auxiliary ion, which could be laser cooled and optically detected at a more convenient wavelength.<sup>24</sup> Because the two ions are coupled through the Coulomb interaction, the  $^{27}\text{Al}^+$  “clock” ion is also cooled. Further, the superposition state of the clock ion can be transferred to the auxiliary ion, making use of the fact that they share a vibrational degree of freedom. That is, if the state of the clock ion is  $(\alpha|S\rangle + \beta|P\rangle)$ , the state of the auxiliary ion becomes  $(\alpha|1\rangle + \beta|2\rangle)$ , where  $|1\rangle$  and  $|2\rangle$  are two of the ground-state hyperfine sublevels. This makes it possible to detect whether the clock ion has been driven to the metastable state by observing the fluorescence of the auxiliary ion. The use of this detection method, called quantum logic spectroscopy,<sup>26</sup> represents an early, and arguably the first, application of the techniques of trapped-ion quantum logic<sup>25</sup> to a practical device.

The basic methods were demonstrated with a  $^{27}\text{Al}^+$  clock ion and a  $^9\text{Be}^+$  auxiliary ion, by use of the  $^{27}\text{Al}^+\ ^1S_0$  to  $^3P_1$  transition.<sup>26</sup> More recently, the  $^{27}\text{Al}^+\ ^1S_0$  to  $^3P_0$  transition has been observed.<sup>27</sup> Details of the methods used to frequency-lock a laser to the  $^{27}\text{Al}^+\ ^1S_0$  to  $^3P_0$  resonance have been published.<sup>20,27,28</sup>

The total fractional systematic uncertainty of the  $\text{Al}^+$  frequency standard is  $2.3 \times 10^{-17}$ . The various contributions are discussed in detail elsewhere.<sup>20,27</sup> The greatest part of the systematic uncertainty is due to the second-order Doppler shift, from both the thermal motion and the micromotion. The linear Zeeman shift is cancelled by observing Zeeman components with reversed  $m_F$  and averaging the frequencies. The blackbody radiation shift is unusually small for an optical frequency standard because of a fortuitous cancelation between the  $^1S_0$  and  $^3P_0$  quadratic Stark shifts.<sup>29</sup> The fractional frequency shift at 300 K is  $(-8 \pm 3) \times 10^{-18}$ . At the normal operating temperature of the frequency standard, it is  $(-12 \pm 5) \times 10^{-18}$ .

A second  $\text{Al}^+$  frequency standard that makes use of a physically larger trap has been constructed. Because the heating rate of trapped ions has been shown to scale roughly as  $d^{-4}$ , where  $d$  is the distance to the nearest electrode, this should reduce second-order Doppler shifts. Also, the auxiliary ion used for cooling and detection is  $^{25}\text{Mg}^+$  rather than  $^9\text{Be}^+$ . The fact that the mass is closer to that of the  $^{27}\text{Al}^+$  clock ion makes the cooling more efficient. In the second trap, a narrower linewidth of the clock transition of 2.7 Hz has been observed.<sup>30</sup> The two  $\text{Al}^+$  frequency standards have been operated simultaneously. In these preliminary measurements, the frequency difference was  $(-2 \pm 3) \times 10^{-17}$ .<sup>30</sup>

#### 4. $\text{Hg}^+$ - $\text{Al}^+$ frequency comparisons

The  $\text{Hg}^+$  and  $\text{Al}^+$  frequency standards have been operated simultaneously. If one tooth of the femtosecond comb is phase-locked to one of the standards, and the heterodyne beat frequency between the other standard and the nearest tooth is measured, the frequency ratio of the two standards can be obtained in a way that does not depend on the accuracy of any microwave frequency standards used as references. The instability of the frequency ratio is described by an Allan deviation  $\sigma_y(\tau)$  (fractional error for a measurement duration  $\tau$ ) of  $3.9 \times 10^{-15} \tau^{-1/2}$  for  $\tau > 100$ , where  $\tau$  is expressed in seconds.<sup>20</sup> Both standards are thought to contribute approximately equally, in an uncorrelated manner, to the instability of the ratio, so the fractional frequency instabilities of both standards are given by  $\sigma_y(\tau) = 2.8 \times 10^{-15} \tau^{-1/2}$ . The reproducibility of the ratio is better than the accuracy of the primary Cs frequency standards. The weighted mean of the measurements of the ratio of the  $\text{Al}^+$  and  $\text{Hg}^+$  frequencies  $f_{\text{Al}}/f_{\text{Hg}}$  is 1.052 871 833 148 990 438 (55), where the uncertainty is expressed in units of the least significant digit and corresponds fractionally to  $5.2 \times 10^{-17}$ .<sup>20</sup>

## 5. Time variation of the fundamental constants

It is of interest to see whether the ratios of atomic frequency standards based on different transitions and different atoms remain constant over time. If a drift in one of these ratios is observed, this might be due to a time variation of fundamental constants, such as the fine structure constant  $\alpha$ , the strong interaction coupling constant  $\alpha_s$ , or the ratios of the masses of elementary particles.<sup>31-33</sup>

The ratios of the frequencies of electronic transitions in atoms are mainly dependent on  $\alpha$ . Measurements of the frequency ratio  $f_{\text{Al}}/f_{\text{Hg}}$  over a period of about a year show a slope of  $(-5.3 \pm 7.9) \times 10^{-17}/\text{year}$ , consistent with zero, within the experimental uncertainty. Calculations of the dependence of the atomic transitions on  $\alpha$ <sup>34,35</sup> allow us to infer a fractional rate of change  $(1/\alpha)(d\alpha/dt) = (-1.6 \pm 2.3) \times 10^{-17}/\text{year}$ , consistent with zero, within the experimental uncertainty.

Atomic hyperfine transition frequencies are dependent not only on  $\alpha$  but also on nuclear parameters, such as the nuclear magnetic moment and the nuclear size, which depend on the strong interaction. It is convenient to parameterize the strong-interaction coupling in terms of the dimensionless ratio  $X_q = m_q/\Lambda_{\text{QCD}}$ , where  $m_q = (m_u + m_d)/2$  is the average of the up- and down-quark masses, and  $\Lambda_{\text{QCD}}$  is the quantum chromodynamics scale.<sup>36,37</sup> The drift of the ratio of the <sup>87</sup>Rb and <sup>133</sup>Cs hyperfine frequencies has been measured to be  $(-5.2 \pm 7.9) \times 10^{-17}/\text{year}$ .<sup>38</sup> The dependence of the hyperfine frequencies on  $\alpha$  and on  $X_q$  have been calculated.<sup>36,37</sup> By use of these calculations, the <sup>87</sup>Rb-<sup>133</sup>Cs and Al<sup>+</sup>-Hg<sup>+</sup> frequency ratio drift data can be used to place a limit on the fractional rate of change of  $X_q$  of  $(1/X_q)(dX_q/dt) = (0.3 \pm 2.5) \times 10^{-14}/\text{year}$ , consistent with zero.<sup>37</sup>

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## References

1. J. Terrien, *Metrologia* **4**, 41 (1968).
2. S. R. Jefferts, T. P. Heavner; T. E. Parker; J. H. Shirley, *Proc. SPIE* **6673**, 667309 (2007).
3. S. A. Diddams, D. J. Jones, J. Ye, S. T. Cundiff, J. L. Hall, J. K. Ranka, R. S. Windeler, R. Holzwarth, T. Udem, and T. W. Hänsch, *Phys. Rev. Lett.* **84**, 5102 (2000).

4. D. J. Jones, S. A. Diddams, J. K. Ranka, A. Stentz, R. S. Windeler, J. L. Hall, and S. T. Cundiff, *Science* **288**, 635 (2000).
5. R. Holzwarth, T. Udem, T. W. Hänsch, J. C. Knight, W. J. Wadsworth, and P. S. J. Russell, *Phys. Rev. Lett.* **85**, 2264 (2000).
6. P. L. Bender, J. L. Hall, R. H. Garstang, F. M. J. Pichanick, W. W. Smith, R. L. Barger, and J. B. West, *Bull. Am. Phys. Soc.* **21**, 599 (1976).
7. J. C. Bergquist, D. J. Wineland, W. M. Itano, H. Hemmati, H.-U. Daniel, and G. Leuchs, *Phys. Rev. Lett.* **55**, 1567 (1985).
8. J. C. Bergquist, W. M. Itano, and D. J. Wineland, *Phys. Rev. A* **36**, 428 (1987).
9. R. H. Dicke, *Phys. Rev.* **89**, 472 (1953).
10. R. J. Rafac, B. C. Young, J. A. Beall, W. M. Itano, D. J. Wineland, and J. C. Bergquist, *Phys. Rev. Lett.* **85**, 2462 (2000).
11. W. M. Itano, J. C. Bergquist, A. Bruschi, S. A. Diddams, T. M. Fortier, T. P. Heavner, L. Hollberg, D. B. Hume, S. R. Jefferts, L. Lorini, T. E. Parker, T. Rosenband, and J. E. Stalnaker, *Proc. SPIE* **6673**, 667303 (2007).
12. L. Lorini, N. Ashby, A. Bruschi, S. Diddams, R. Drullinger, E. Eason, T. Fortier, P. Hastings, T. Heavner, D. Hume, W. Itano, S. Jefferts, N. Newbury, T. Parker, T. Rosenband, J. Stalnaker, W. Swann, D. Wineland, and J. Bergquist, *Eur. Phys. J. Special Topics* **163**, 19 (2008).
13. S. A. Diddams, T. Udem, J. C. Bergquist, E. A. Curtis, R. E. Drullinger, L. Hollberg, W. M. Itano, W. D. Lee, C. W. Oates, K. R. Vogel, and D. J. Wineland, *Science* **293**, 825 (2001).
14. T. Udem, S. A. Diddams, K. R. Vogel, C. W. Oates, E. A. Curtis, W. D. Lee, W. M. Itano, R. E. Drullinger, J. C. Bergquist, and L. Hollberg, *Phys. Rev. Lett.* **86**, 4996 (2001).
15. 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, *Phys. Rev. Lett.* **90**, 50802 (2003).
16. W. H. Oskay, W. M. Itano, and J. C. Bergquist, *Phys. Rev. Lett.* **94**, 163001 (2005).
17. W. H. Oskay, S. A. Diddams, E. A. Donley, T. M. Fortier, T. P. Heavner, L. Hollberg, W. M. Itano, S. R. Jefferts, M. J. Delaney, K. Kim, F. Levi, T. E. Parker, and J. C. Bergquist, *Phys. Rev. Lett.* **97**, 020801 (2006).
18. T. M. Fortier, N. Ashby, J. C. Bergquist, M. J. Delaney, S. A. Diddams, T. P. Heavner, L. Hollberg, W. M. Itano, S. R. Jefferts, K. Kim, F. Levi, L. Lorini, W. H. Oskay, T. E. Parker, J. Shirley, and J. E. Stalnaker, *Phys. Rev. Lett.* **98**, 070801 (2007).
19. J. E. Stalnaker, S. A. Diddams, T. M. Fortier, L. Hollberg, J. C. Bergquist, W. M. Itano, M. J. Delaney, L. Lorini, W. H. Oskay, T. P. Heavner, S. R. Jefferts, F. Levi, T. E. Parker, and J. Shirley, *Appl. Phys. B* **89**, 167 (2007).
20. T. Rosenband, D. B. Hume, P. O. Schmidt, C. W. Chou, A. Bruschi, L. Lorini, W. H. Oskay, R. E. Drullinger, T. M. Fortier, J. E. Stalnaker, S. A. Diddams, W. C. Swann, N. R. Newbury, W. M. Itano, D. J. Wineland, and J. C. Bergquist, *Science* **319**, 1808 (2008).

21. D. J. Berkeland, J. D. Miller, J. C. Bergquist, W. M. Itano, and D. J. Wineland, *J. Appl. Phys.* **83**, 5025 (1998).
22. W. M. Itano, *J. Research National Institute of Standards and Technology* **105**, 829 (2000).
23. D. J. Berkeland, J. D. Miller, J. C. Bergquist, W. M. Itano, and D. J. Wineland, *Phys. Rev. Lett.* **80**, 2089 (1998).
24. D. J. Wineland, J. C. Bergquist, J. J. Bollinger, R. E. Drullinger, and W. M. Itano, in *Proceedings of the 6th Symposium on Frequency Standards and Metrology*, P. Gill ed. (World Scientific, Singapore, 2002) pp. 361–368.
25. D. J. Wineland, C. R. Monroe, W. M. Itano, D. Leibfried, B. E. King, and D. M. Meekhof, *J. Research National Institute of Standards and Technology* **103**, 259 (1998).
26. P. O. Schmidt, T. Rosenband, C. Langer, W. M. Itano, J. C. Bergquist, and D. J. Wineland, *Science* **309**, 749 (2005).
27. T. Rosenband, P. O. Schmidt, D. B. Hume, W. M. Itano, T. M. Fortier, J. E. Stalnaker, K. Kim, S. A. Diddams, J. C. J. Koelemeij, J. C. Bergquist, and D. J. Wineland, *Phys. Rev. Lett.* **98**, 220801 (2007).
28. D. B. Hume, T. Rosenband and D. J. Wineland, *Phys. Rev. Lett.* **99**, 120502 (2007).
29. T. Rosenband, W. M. Itano, P. O. Schmidt, D. B. Hume, J. C. J. Koelemeij, J. C. Bergquist, and D. J. Wineland, in *Proc. 20th European Time and Frequency Forum* (2006) pp. 289–292; preprint: arXiv:physics/0611125v2.
30. C.-W. Chou, D. B. Hume, and T. Rosenband, unpublished work.
31. S. N. Lea, *Rep. Prog. Phys.* **70**, 1473 (2007).
32. S. G. Karshenboim and E. Peik, *Eur. Phys. J. Special Topics* **163**, 1 (2008).
33. V. V. Flambaum, *Eur. Phys. J. Special Topics* **163**, 159 (2008).
34. V. A. Dzuba, V. V. Flambaum, and J. K. Webb, *Phys. Rev A* **59**, 230 (1999).
35. E. J. Angstmann, V. A. Dzuba, and V. V. Flambaum, *Phys. Rev. A* **70**, 014102 (2004).
36. V. V. Flambaum and A. F. Tedesco, *Phys. Rev. C* **73**, 055501 (2006).
37. T. H. Dinh, A. Dunning, V. A. Dzuba, and V. V. Flambaum, *Phys. Rev. A* **79**, 054102 (2009).
38. S. Bize, P. Laurent, M. Abgrall, H. Marion, I. Maksimovic, L. Cacciapuoti, J. Grnert, C. Vian, F. Pereira dos Santos, P. Rosenbusch, P. Lemonde, G. Santarelli, P. Wolf, A. Clairon, A. Luiten, M. Tobar, and C. Salomon, *J. Phys. B* **38**, S449 (2005).