FREQUENCY COMPARISON OF Al^+ AND Hg^+ OPTICAL STANDARDS

T. ROSENBAND*, D. B. HUME, A. BRUSCH, L. LORINI†, P. O. SCHMIDT‡, T. M. FORTIER, J. E. STALNAKER§, S. A. DIDDAMS, N. R. NEWBURY, W. C. SWANN, W. H. OSKAY¶, W. M. ITANO, D. J. WINELAND, AND J. C. BERGQUIST

National Institute of Standards and Technology,
325 Broadway, Boulder, CO 80305
** E-mail: trosen@boulder.nist.gov*

We compare the frequencies of two single ion frequency standards: $^{27}Al^+$ and $^{199}Hg^+$. Systematic fractional frequency uncertainties of both standards are below 10^{-16}, and the statistical measurement uncertainty is below 5×10^{-17}. Recent ratio measurements show a reproducibility that is better than 10^{-16}.

Although single-ion optical frequency standards promise a potential accuracy of 10^{-18} or better,[1,2] this long-standing goal has not yet been realized due to various technical difficulties. Here we report progress for the NIST $^{199}Hg^+$ and $^{27}Al^+$ single-ion standards,[3,4] as their systematic fractional frequency uncertainty approaches 10^{-17}.

In these measurements, the fourth harmonics of two clock lasers are locked to the mercury and aluminum clock transitions at 282 and 267 nm respectively. An octave-spanning self-referenced Ti:Sapphire femtosecond laser frequency comb (FLFC)[5] is phase-locked to one clock laser, and the heterodyne beat-note of the other clock laser with the nearest comb-tooth is measured. The various beat-note and offset frequencies can be combined to yield a frequency ratio, which is independent of the Cs-based definition of the second, allowing this ratio to be measured even more accurately than the fundamental unit of time can be realized. In recent comparisons of the frequencies of the two clock lasers included here, an octave-spanning self-referenced fiber comb laser[6] has provided a second independent measure of

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†Present address: Istituto Nazionale di Ricerca Metrologica (INRIM), Torino, Italy
‡Present address: Institut für Experimentalphysik, Universität Innsbruck, Austria
§Present address: Department of Physics and Astronomy, Oberlin College, Oberlin, OH
¶Present address: Stanford Research Systems, Sunnyvale, CA

the frequency ratio.

The $^{27}Al^+$ $^1S_0 \rightarrow {}^3P_0$ standard, which uses Quantum Logic Spectroscopy[7] has been described previously.[4] Briefly, one $^{27}Al^+$ ion is trapped together with a $^9Be^-$ ion, which provides sympathetic cooling. The $^{27}Al^+$ clock state is mapped to $^9Be^-$ repetitively through their coupled motion, allowing for up to 99.94% clock state detection fidelity.[8] With the ability to detect the clock state comes the ability to detect state transitions, whose probability depends on the clock laser frequency. The clock laser is locked to the atomic transition by alternating between upper and lower slopes of the atomic resonance curve, and keeping the transition rates equal. At the operating field of 1 gauss, the Zeeman structure is split by several kilohertz, and the individual Zeeman components are well resolved. We alternate between the extreme states of opposite angular momentum ($m_F = \pm 5/2$), which allows compensation of magnetic field shifts up to second order.[4,9]

The accuracy of the aluminum standard is limited to 2.2×10^{-17} primarily due to uncertainties in the second-order Doppler shifts. For ions confined in Paul traps, there are two types of motion: secular motion, which is the harmonic motion of the trapped particle, and micromotion, which occurs when the ion is displaced from the rf-null of the confining field. Both types of motion have rms-velocities of about 1-2 m/s, with similar uncertainties. Excess micromotion results when slowly fluctuating electro-static fields in the ion trap displace the ion from the null position. These quasi-static fields are monitored and corrected by interleaving micromotion-test experiments with the clock interrogations. Tests are performed by monitoring the strength of radial-to-axial coupling of certain normal modes via $^9Be^-$,[10] and applying compensation voltages at the ion trap to minimize this coupling. With real-time corrections, the stray electric fields are nulled to (0 ± 10) V/m, allowing an estimate of the time dilation uncertainty.[11] The total fractional frequency clock shift due to the extreme case of a 10 V/m field along both radial directions is 3.2×10^{-17}, and we estimate the fractional frequency shift caused by residual (uncompensated) stray electric fields to be $(2 \pm 2) \times 10^{-17}$ when the clock is operating.

Secular mode heating[12,13] causes deviations in the secular kinetic energy from the Doppler-cooling limit. Among the 6 normal modes[a] of the $^{27}Al^+/^9Be^+$ ion pair, two radial modes with large amplitude on $^{27}Al^+$, and

[a] The two axial normal-mode frequencies are 5.80 MHz and 2.62 MHz, and the frequencies of the poorly damped radial modes are $\nu_x = 3.50$ MHz and $\nu_y = 4.64$ MHz. The other pair of radial modes, which is well damped, has frequencies of 14.06 MHz, and 13.02 MHz.

small amplitude on $^9Be^+$ are damped only weakly by the laser-cooled $^9Be^+$ ion. Prior to clock interrogation, we enhance this damping by twisting the ion-pair with a static electric field of about 300 V/m in order to begin each experiment at the Doppler-cooling limit. We also apply $^9Be^+$ -Doppler-cooling light continuously during each 100-ms clock interrogation, keeping the four well-damped modes at the Doppler-cooling limit. However, the two poorly damped radial modes have damping rates of $\gamma \approx 60$ s^{-1}, and heating rates of $\langle \dot{n}_x \rangle = 400 \pm 300$ quanta/s, and $\langle \dot{n}_y \rangle = 100 \pm 100$ quanta/s, leading to 6.6 ± 5 and 1.5 ± 1.5 excess motional quanta. The fractional clock shift per radial motional quantum is 8×10^{-19} for both modes, and at the Doppler-cooling limit both modes would contain 3 ± 1 quanta. Conservatively we estimate that the average total motional quantum number for the two radial modes during each clock interrogation is 14 ± 10 quanta, leading to a second-order Doppler shift of $(-1.1 \pm 0.8) \times 10^{-17}$.

Other important shifts are the blackbody radiation shift,[14] which is very small in $^{27}Al^+$,[15] and the quadratic Zeeman shift, which has been accurately calibrated by varying the magnetic field, and measuring the shift in the $^{27}Al^+$ /$^{199}Hg^+$ ratio, together with the linear Zeeman splitting ν_1 between the π-polarization-excited m=$\pm\frac{5}{2}$ lines. The resulting shift is $\nu_2 = \nu_1^2 \times 1.0479(7) \times 10^{-8}$/Hz.

Table 1. $^{27}Al^+$ $^1S_0 \rightarrow {}^3P_0$ and $^{199}Hg^+$ $^2S_{\frac{1}{2}} \rightarrow {}^2D_{\frac{5}{2}}$ shifts in units of 10^{-18} of fractional frequency. Evaluations of first-order Doppler shifts, background gas collisions, and the gravitational red shift are in progress.

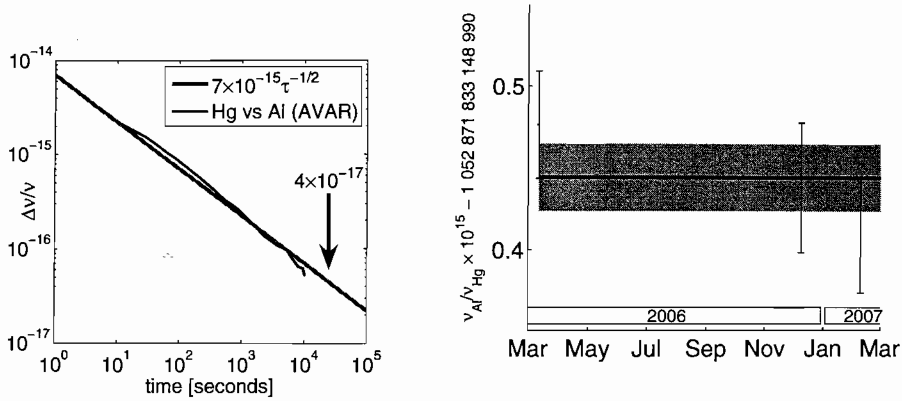
shift	$\Delta\nu_{Al}$	σ_{Al}	$\Delta\nu_{Hg}$	σ_{Hg}	limitation
Micromotion	-20	20	-4	4	static electric fields
Secular motion	-11	8	-3	3	Doppler cooling
Blackbody rad.	-12	5	0	0	DC polarizability
313 nm Stark	-7	2	0	0	polarizability, intensity
DC Quad. Zeeman	-685	0.5	-1203	5	calibration
AC Quad. Zeeman	0	0	0	10	trap magnetic fields
Electric quadrupole	0	0.5	0	10	B-field orientation
TOTAL	-735	22	-1210	16	

The $^{199}Hg^+$ ion standard is based on the $^2S_{\frac{1}{2}} \rightarrow {}^2D_{\frac{5}{2}}$ electric-quadrupole transition.[3] A 194 nm laser cools the ion to the Doppler-cooling limit via the allowed $^2S_{\frac{1}{2}} \rightarrow {}^2P_{\frac{1}{2}}$ transition, and a fiber laser frequency-quadrupled to 282 nm excites the clock transition. The clock state of the $^{199}Hg^+$ ion is measured directly via quantum jumps in the scattering fluorescence rate of the 194 nm laser.[16] Systematic uncertainties in the $^{199}Hg^+$ standard are listed in Table 1. Here the largest uncertainty is a possible quadratic Zeeman shift due to unbalanced rf-currents in the ion trap. The magnitude of this shift is conservatively estimated by assuming the worst case scenario; that all of the rf-currents flowing in the ring electrode (in the middle of which the ion is held) are fully unbalanced and travel in a half loop along one side of the ring only. The maximum rms-current ($I_{RF} < 1$ mA) at the site of the trap is set by the trap capacitance ($C < 70$ fF), the rf-frequency (12 MHz) and the maximum voltage applied (1100 V). This produces an rms-field of approximately 4×10^{-7} T at the center of the ring electrode for a ring diameter of 1 mm. A field of this magnitude causes a fractional frequency shift of the order 1×10^{-17}. The return path for the rf-current through the endcap electrodes ideally produces no net field at the center of the trap, but if they are unbalanced, then the field produced can only help compensate the field generated by the asymmetrical flow of rf-currents through the ring electrode. Otherwise, the rms-field produced at the site of the ion is less than 4×10^{-7} T. The electric-quadrupole shift, which has previously limited the accuracy of the $^{199}Hg^+$ standard is constrained below 10^{-17} by averaging over three orthogonal magnetic field directions.[17,18]

Second-order Doppler shifts are easier to control for $^{199}Hg^+$ than for $^{27}Al^+$, because the heavy mercury ion moves less in response ambient electric fields than the lighter aluminum ion does. Near the Doppler-cooling limit, the total time-dilation shift due to secular motion is $(-3 \pm 3) \times 10^{-18}$. Micromotion is carefully compensated,[11] leading to a similar shift of $(-4 \pm 4) \times 10^{-18}$. The quadratic Zeeman coefficient in $^{199}Hg^+$ was calibrated in an analogous way to that of the $^{27}Al^+$ standard. Here the shift is $\nu_2 = -\nu_1^2 \times 1.23564(37) \times 10^{-11}/\text{Hz}$, where ν_1 is the linear Zeeman splitting between the π-polarization-excited $m_F = \pm 2$ lines.

Both atomic clocks were operated simultaneously, while the FLFCs recorded their frequency ratio every second. Figure 1(b) shows Allan deviation (an estimate of the statistical measurement uncertainty vs. measurement duration) of a typical ratio measurement. For measurement durations τ greater than 100 s, the uncertainty is given by $7 \times 10^{-15}/\sqrt{\tau/s}$. A deviation from this slope at long measurement times, which would indicate fluctuating systematic shifts, has not been observed. Figure 1(a) shows the history of measurements of the ν_{Al^+}/ν_{Hg^+} ratio. While the systematic uncertainties in Table 1 are only valid for the last data point, the consistency of the earlier measurements provides confidence in the reproducibility of this result.

Currently, both standards are being evaluated for first-order Doppler shifts, which would appear if the ion motion was correlated with the probe



(a) (b)

Fig. 1. Fractional stability of the ratio ν_{Al^+}/ν_{Hg^+} (a). History of measurements of ν_{Al^+}/ν_{Hg^+} (b). Error bars are statistical, and the shaded area represents the statistical uncertainty of the weighted mean. These data points do not contain the complete set of systematic corrections listed in Table 1, and will be revised in the future.

beam. By probing alternately from opposite directions, such motion can be detected, and averaged away. Possible causes for such a shift would be stray charge buildup in the ion trap, which is correlated with the interrogation pulses, or correlated mechanical motion caused by shutters. We have not observed a direction-dependent shift for either standard.

Besides their obvious application to frequency metrology and precision time-keeping, more accurate atomic clocks might also help answer a fundamental question in physics. *Are the constants of nature really constant*, or are they changing in time, or dependent on the gravitational potential in which they are measured? Frequency ratio measurements of dissimilar atomic clocks can help answer these questions. In particular, the ratio of atomic resonance frequencies depends on the fine-structure constant α.[19,20] Repeated accurate measurements of the ν_{Al^+}/ν_{Hg^+} frequency ratio will provide constraints on present-day changes of the fine-structure constant.

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