Sub-ppb Penning trap measurements of the masses of ^{133}Cs, ^{87,85}Rb, and ^{23}Na

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We report new values from Penning trap single ion mass spectrometry for the atomic masses of ^{133}Cs, ^{87}Rb, ^{85}Rb, and ^{23}Na with uncertainties ≤ 0.2 ppb, a factor of 100 improvement over the accuracy of previously measured values. We have found M(^{133}Cs)=132.905 451 931 (27) u, M(^{87}Rb)=86.909 180 520 (15) u, M(^{85}Rb)=84.911 789 732 (14) u, and M(^{23}Na)=22.989 769 280 7 (28) u. These values are important for new ppb-level determinations of the molar Planck constant $N_A h$ and the fine-structure constant α. With the measurement of ^{133}Cs we have increased the mass range for sub-ppb measurements by a factor of 3. From M(^{133}Cs) and other values we derive $\alpha^{-1} = 137.035\,992\,2\,(40)$.

The fine-structure constant α is one of the most fundamental and best-measured quantities in physics, but the discrepancies between different precision measurements of α are noteworthy [1]. The most precise value α_{g-2} (uncertainty = 3.8 ppb = 3.8 parts in 10^9) has been obtained from the measured values of (g-2) for the electron and positron and complex QED calculations [2,3]. Unfortunately, the next most precise measurements of α (24 ppb using the Quantum Hall effect [4,5] and 37 ppb via neutron interferometry [6]) disagree with the (g-2) value. Thus to test the unity of physics and QED there is a need for new ppb-level measurements to compare with α_{g-2}.

A high-precision route to α founded on simple physics with no complex calculations is based on the relationship between α and the molar Planck constant $N_A h$ [7],

$$\alpha^2 = \frac{2R_\infty}{c}\frac{10^3}{M_p}\frac{m_p}{m_e}(N_A h). \tag{1}$$

All the quantities linking α and $N_A h$ in Eq. (1) are known to high precision: R_∞ to 0.008 ppb [8,9], m_p/m_e to 2 ppb [10], and M_p (the proton mass in atomic units u) measured by our group to 0.5 ppb [11] (Van Dyck et al. have recently reported a value of M_p accurate to 0.14 ppb [12]). Thus an independent measurement of $N_A h$ to 2 ppb would determine α to 1.4 ppb, a precision sufficient to test α_{g-2}. The most complicated calculations for this method are the computation of the $2P_{1/2}$, $2P_{3/2}$ and 8D Lamb shifts to allow R_∞ to be obtained from measurements of the 1S-2S and 2S-8D transitions in hydrogen [9]. The largest calculational uncertainty contribution to R_∞ is 0.00026 ppb due to the 8D Lamb shift.

$N_A h$ can be determined by measuring the velocity v and de Broglie wavelength $\lambda_{dB} \equiv h/mv$ of a particle, since $\lambda_{dB} v = h/m = 10^3 N_A h/M$ where m is the mass of the particle in SI units. Kruger et al. exploited this method using neutron interferometry to measure h/m_n with 73 ppb precision [6]. Combining this with a precise measurement of M_n (from Penning trap measurements of $M[^2\mathrm{H}]$, $M[^1\mathrm{H}]$ and γ-ray measurements of the nuclear binding energy of ^{2}H [11], [13], [14]) gave a value of α with a precision of 37 ppb, again not sufficient to stringently test α_{g-2}.

It appears that measurements of $N_A h$ of much higher precision can be made by combining accurate atom interferometry measurements of h/m for alkalis with the ~ 0.1 ppb measurements of M possible using Penning traps. At Stanford atom interferometry is used to measure h/m_{Cs} via photon recoil [15] in terms of λ_{D1} (recently measured to 0.12 ppb at MPI Garching [16]). Although systematic effects in the photon recoil measurement currently limit the accuracy to 55 ppb (which would limit a determination of α to 28 ppb), the high precision achieved (22 ppb in 4 h) [17] shows promise for much better measurements of α. Moreover, advances in alkali BEC technology hold great promise for similar atom interferometry measurements on Na and Rb. With measurements of h/m_{alkali} in mind, we have measured the atomic masses of the stable alkali metal isotopes ^{133}Cs, ^{87,85}Rb, and ^{23}Na using Penning trap mass spectrometry. The previous mass accuracies for these species [18] (see Table IV) would have limited the accuracy of $N_A h$ to several tens of ppb.

There are additional motivations for our measurements. New values of $N_A h$ at the few-ppb level in combination with measurements of h (such as a recent 87 ppb measurement, expected to be improved by a factor of 10 [19]) can yield values of N_A with ppb-level accuracy. This would be of great interest since N_A links the atomic and SI units of mass [7]. Furthermore, Cs and Rb are used as reference masses for measurements of heavy radioactive nuclei which are important for modeling astrophysical heavy element formation [20], [21].

We obtain absolute atomic masses M from mass ratios relating the unknown mass to the atomic mass standard ^{12}C. Ion mass ratios are obtained from ratios of measured cyclotron frequencies $\omega_c = qB/mc$ where m and q

are the ion mass and charge. We make precise cyclotron frequency measurements on a single ion confined in an orthogonally compensated Penning trap [22] of characteristic size $d = 0.55$ cm placed in the $B = 8.5$ T field of a superconducting magnet. Use of a trapped single ion takes advantage of long observation times in the absence of perturbations from ion-ion interactions, and allows sub-ppb precision.

An ion in our Penning trap has three normal modes of motion: trap cyclotron, axial, and magnetron, with frequencies $\omega_c' >> \omega_z \approx 2\pi \times 160$ kHz $>> \omega_m$, respectively. The free-space cyclotron frequency ω_c is obtained from the following expression (invariant with respect to trap tilts and ellipticity) [22]:

$$\omega_c = qB/mc = \sqrt{(\omega_c')^2 + (\omega_z)^2 + (\omega_m)^2}. \tag{2}$$

We detect axial motion by coupling to a DC SQUID via a $Q = 5 \times 10^4$ superconducting resonant transformer. Detection damps the axial motion at a rate $\gamma_z \sim 1\ \mathrm{s}^{-1}$ and cools it to 4 K. The amplitude and phase of the undamped trap cyclotron mode are measured via coupling to the axial mode established by an RF quadrupole field at frequency $\omega_\pi = \omega_c' - \omega_z$ [23]. (This coupling is also used to cool the radial modes.) We obtain ω_c' from the phase accumulated in the cyclotron mode in a given time. Using the measured values of ω_c' and ω_z we calculate $\omega_m \approx (\omega_z^2/2\omega_c')(1 + 9/4\sin^2\theta_m)$ where $\theta_m = 0.16°$ is the measured angle between the B-field and trap axes (the effect of θ_m on a mass ratio is at most 0.002 ppb).

We measured the free-space cyclotron frequency ratios $r \equiv \omega_{c2}/\omega_{c1}$ listed in Table I. A cyclotron frequency ratio r was determined by a run of alternately measured clusters of ω_c of each of the two ions during the period from 1:30-5:30 am when the nearby electrically-powered subway was not running (Fig. 1). The measured free-space cyclotron frequencies exhibited a common slow drift. We fit a common polynomial $\Omega(t)$ plus a frequency difference to the data. From this we obtained the frequency ratio r_n and the uncertainty σ_n for a single night. The average order of $\Omega(t)$ was 3 and was chosen using the F-test criterion [24] as a guide.

Excluding the $Cs^{++}/C_5H_6^+$ data, the distribution of residuals from the polynomial fits had a Gaussian center with a standard deviation $\sigma_{resid} = 0.28$ ppb and a background ($\approx 2\%$ of the points) of non-Gaussian outliers, as in our earlier measurements [11]. As in [11] we chose to handle the non-Gaussian outliers using a robust statistical method to smoothly deweight them [25]. The observed random fluctuations of the measured free-space cyclotron frequency should limit the precision of a one-night (4 h) measurement of r_n to ~ 0.1 ppb. These fluctuations are due primarily to variations of the magnetic field, however for heavy ions with low ω_c uncertainty in ω_z can contribute significantly to uncertainty in ω_c. Thus stability of the trapping voltage is important. Our trap voltage exhibits long-term RMS fluctuations of only 100 ppb, and so contributes below 0.1 ppb uncertainty to a night's measurement. Observed variations in the axial frequency ~ 20 mHz are dominated by measurement error and contribute at most ~ 0.25 ppb to a single cluster for $Cs^{++}/C_5H_6^+$ (the residuals for $Cs^{++}/C_5H_6^+$ had $\sigma_{resid} = 0.44$ ppb mainly because of this).

As shown in Table I we measured each frequency ratio on more than a single night. For ratios involving Cs and Rb the measured r_n were distributed with scatter $> \sigma_n$ ($\chi^2_\nu \approx 5$). By contrast $\chi^2_\nu \approx 0.8$ for ratios involving Na. All earlier data taken using this apparatus [11] did not exhibit these excess night-to-night variations. Possible sources of this excess scatter are presented in Table II and discussed below.

The axial frequency ω_z is "pulled" by its coupling to the detector by an amount $\Delta\omega_z = (\gamma_z/\gamma_0)(\omega_z - \omega_0)$ where ω_0 and $\gamma_0/2\pi = 3$ Hz are the detector resonance frequency and FWHM. We adjusted ω_z to be equal to the slowly drifting ω_0 (typically ~ 50 mHz/hour), measured before each alkali ion cluster. We then used the measured values of ω_z and ω_0 ($|\omega_z - \omega_0|$ typically < 100 mHz) to correct the measured ω_z for the remaining pulling shift. Table II gives the rms difference in r_n for each night computed before and after applying this correction. The $\sim 30\%$ accuracy of our corrections implies that frequency pulling represents an error in our final ratios below 0.03 ppb and was not the source of the excess night-to-night fluctuations of r_n.

Relativistic mass variation and spatial imperfections $\Delta\vec{B} = -(B_2/2)\rho^2\hat{z}$ and $\Delta V/V_{trap} = -(3/16)(C_4/d^4)\rho^4$ [22] of the trap fields lead to radius-dependent shifts of the cyclotron frequency

$$\frac{\Delta\omega_c}{\omega_c} = \left(-\frac{\omega_c'^2}{2c^2} - \frac{B_2}{2B_0} + \frac{3\omega_m C_4}{2\omega_c d^2}\right)\rho^2 \tag{3}$$

For our trap $B_2/B_0 = 10^{-6}/\mathrm{cm}^2$ and $|C_4| < 10^{-4}$. Systematic differences in cyclotron orbit radii gave negligible systematic shifts in r except for Na^{++}/C^+ ($\Delta r/r = 0.035$ ppb). We adjusted the final ratio for this shift. To reflect uncertainty in the absolute radius ρ we assigned the adjustment a 50% uncertainty added in quadrature with the other uncertainties.

Table II gives the systematic shifts in r for differential displacements of ions from the geometric center of the trap (due to the electric field from fixed charge patches) in combination with B-field inhomogeneities. The z component of the patch electric field was measured with $< 10\%$ uncertainty by applying offset potentials and measuring the quadratic shifts in ω_z, as described in [26]. Na^{++}/C^+ experienced the largest systematic shift $\Delta r/r = 0.08$ ppb. We adjusted all ratios for this systematic shift and assigned the adjustment a 100% uncertainty added in quadrature with the statistical uncertainty to reflect uncertainty concerning the radial component of the charge patch electric field.

The systematic shifts in Table II are constant from night to night and also are much too small to explain the observed night-to-night scatter.

To test the hypothesis that the excess night-to-night fluctuations were due to improper choice of fit order for $\Omega(t)$ we computed r_n by a completely different method. A value of r was calculated for each cluster in a night by taking the ratio of its frequency to the frequency obtained by linear interpolation between the two neighboring clusters of the other ion type. The values of r for each cluster were averaged to yield a single value of r_n for each night. This "piecewise linear" method and the polynomial fits gave similar night-to-night variations in r_n, suggesting that the variations were not polynomial fitting artifacts.

We calculated the weighted average, for the polynomial fit and piecewise linear methods separately, of the values of r_n. There was no statistically significant difference between these averages $\bar{r}_{poly}$ and $\bar{r}_{pl}$ except for $Cs^{++}/C_5H_6^+$ (0.57 ppb disagreement) due to one night with anomalously constant magnetic field, which gave a small uncertainty and hence significantly higher weight to that night's r_n computed with the piecewise linear method. To account for any such discrepancies we quote the average $\bar{r} = (1/2)(\bar{r}_{poly} + \bar{r}_{pl})$ and a final uncertainty $\bar{\sigma}^2 = \tilde{\sigma}^2_{poly} + [(\bar{r}_{poly} - \bar{r}_{pl})/2]^2$ where $\tilde{\sigma}_{poly}$ is the uncertainty in the polynomial fits after the rescaling described in the following paragraph.

Ultimately we did not discover the origin of the night-to-night fluctuations of r_n for Cs and Rb. We therefore increased the quoted statistical uncertainties to ensure that they reflect the observed night-to-night scatter. For $Cs^{++}/C_5H_6^+$ and Cs^{+++}/CO_2^+, we increased each night's statistical uncertainty until $\chi^2_\nu = 1$ (from 6.6 and 4.9 respectively) for each ratio separately. For the Rb ratios we assumed that the night-to-night fluctuations were drawn from a common statistical distribution since the Rb measurements all had similar m/q. Therefore, we increased the statistical uncertainty on all the Rb r_n by a common factor to reduce the overall Rb χ^2_ν from 4.7 to 1. The resulting increased statistical uncertainties for $\bar{r}_{poly}$ are the $\tilde{\sigma}_{poly}$ used above. The Na ratios had no significant night-to-night fluctuations and required no adjustment of their uncertainties.

After correcting for a 93(1) μHz/e image-charge shift, we convert ion frequency ratios r to neutral mass ratios by accounting for missing electrons [18] and ionization and chemical binding energies [27]. These adjustments contribute $\leq$ 0.03 ppb uncertainty to the final neutral mass ratios. We neglect vibrational/rotational excitation due to ionization. Vibrational energy decays in msec (except for homonuclear species like C_2^+, where the decay time $\sim$ 1 min). Rotational energies ($\sim$ meV) can be ignored.

From the neutral mass ratios we obtained a set of neutral mass difference equations. We added to this the mass difference equations used to determine the atomic masses in [11]. Solution of this overdetermined set of linear equations gave the neutral masses of the alkali metals (see Table IV) with uncertainties σ_{od} as well as the previously published neutral masses with $\chi^2_\nu = 0.83$. The previously published masses were essentially unchanged and so are not reported. Uncertainties in M[^{16}O] and M[H] contributed < 0.1 ppb uncertainty to the alkali masses.

The use of two distinct reference ions gave a check on systematics by providing two independent values for each neutral mass (Table III). For Rb and Cs χ^2_ν is less than 1. However, because of the larger uncertainty on M[Cs] from $Cs^{++}/C_5H_6^+$ we quote a final uncertainty of 0.20 ppb $>$ ($\sigma_{od}(Cs) = 0.16$ ppb). For ^{87,85}Rb we quote $\sigma_{od}(^{87,85}\mathrm{Rb})$ as the final uncertainties. For the neutral masses from Na^{++}/C^+ and Na^+/C_2^+, the statistical uncertainties are 0.09 and 0.07 ppb respectively. The 0.2 ppb disagreement of the two values may be evidence for a systematic at the 0.1 ppb level. To reflect this we assigned M[^{23}Na] a 0.12 ppb uncertainty $>$ ($\sigma_{od}(Na) = 0.06$ ppb) which spans both independent measurements.

Table IV gives final values for M[^{133}Cs], M[^{87}Rb], M[^{85}Rb] and M[^{23}Na] obtained from the solution of the mass difference equations with uncertainties from the above discussion. Also included in Table IV are alkali masses from the 1993 mass evaluation [18]. Our values differ from the 1993 values by $\sim 1.5\sigma_{1993}$. Our value for M(^{133}Cs) lies within the uncertainty of the recent measurement of M(^{133}Cs) reported by the SMILETRAP collaboration [28]. Using R_∞ [8], m_p/m_e [10], the preliminary value of the photon recoil shift [17], f_{D1} for the photon recoil transition [29], and our values for M(^{133}Cs) and M_p we obtain $\alpha^{-1} = 137.035\,992\,2\,(40)$.

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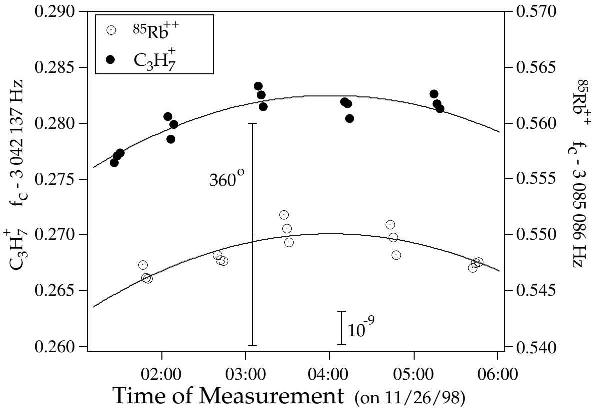

FIG. 1. Typical night of data. The solid line is a second order polynomial fit to the data. The 360° bar shows the magnitude in Hz of a 360° error in phase unwrapping.

TABLE I. Measured ion cyclotron frequency ratios, corrected for systematics.

A/B	$\frac{\overline{\omega}_c}{2\pi}$ (MHz)	Nights	$\omega_c[A]/\omega_c[B]$
$^{133}Cs^{+++}/CO_2^+$	2.968	5	0.992 957 580 983 (135)
$^{133}Cs^{++}/C_5H_6^+$	1.977	4	0.993 893 716 487 (427)
$^{87}Rb^{++}/C_3H_8^+$	2.994	2	1.013 992 022 591 (266)
$^{87}Rb^{++}/C_3H_7^+$	3.028	3	0.990 799 127 824 (174)
$^{85}Rb^{++}/C_3H_7^+$	3.064	2	1.014 106 122 230 (164)
$^{85}Rb^{++}/C_3H_6^+$	3.100	2	0.990 367 650 976 (285)
$^{23}Na^+/C_2^+$	5.578	2	1.043 943 669 690 (076)
$^{23}Na^{++}/C^+$	11.155	2	1.043 944 716 614 (098)

TABLE II. Random uncertainties (σ) and systematic shifts (Δ) for frequency ratios r **in ppt** (10^{-12}).

	$\frac{Cs^{+++}}{CO_2^+}$	$\frac{Cs^{++}}{C_5H_6^+}$	$\frac{Rb^{++}}{C_3H_x^+}$	$\frac{Na^+}{C_2^+}$	$\frac{Na^{++}}{C^+}$
$\sigma(r_n)/r$ axial frequency pulling	120	64	62	11	29
Δr/r relativity [a]	2	1	7	4	79
Δr/r B_2 [a b]	−2	−4	9	−13	−38
Δr/r C_4 [a b]	−1	−4	2	−9	−6
Δr/r different positions [c]	2	1	3	−19	−38

[a]These shifts in the ratio are due to systematic differences in the cyclotron radii ($\Delta\rho/\rho \approx 1\%$ to 7% with $\langle\rho\rangle = 230\ \mu$m). These differences arise from the variation with frequency of our cyclotron drive transfer function.
[b]$B_2 = 10^{-6}/\mathrm{cm}^2$ and $C_4 < 10^{-4}$.
[c]Shifts due to differential axial displacement (the largest being $\Delta z \approx 0.24\ \mu$m for Na^{++}/C^+) combined with the measured $B_1 = 1.6 \times 10^{-6}$ /cm.

TABLE III. Measured alkali masses from different routes.

Species	Ref. ion	Mass (u)	σ_M/M (ppb)	χ^2_ν
^{133}Cs	CO_2^+	132.905 451 931 (22)	0.17	0.003
	$C_5H_6^+$	132.905 451 934 (57)	0.43	
^{87}Rb	$C_3H_8^+$	86.909 180 540 (24)	0.28	0.92
	$C_3H_7^+$	86.909 180 511 (17)	0.19	
^{85}Rb	$C_3H_7^+$	84.911 789 737 (15)	0.18	0.45
	$C_3H_6^+$	84.911 789 717 (25)	0.30	
^{23}Na	C_2^+	22.989 769 278 9 (17)	0.07	2.97
	C^+	22.989 769 283 7 (22)	0.09	

TABLE IV. Measured neutral alkali masses.

Species	MIT Mass (u)	1993 Mass (u) [18]
^{133}Cs	132.905 451 931 (27)	132.905 447 000 (3000)
^{87}Rb	86.909 180 520 (15)	86.909 185 800 (2800)
^{85}Rb	84.911 789 732 (14)	84.911 792 400 (2700)
^{23}Na	22.989 769 280 7 (28)	22.989 769 660 0 (2600)