

Determination of the ^{133}Cs and Proton Mass Ratio Using Highly Charged Ions

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The ratio of the ^{133}Cs and proton mass has been determined by comparing the cyclotron frequencies of highly charged (about 40+) Cs, $^{12}\text{Cs}^{4+}$, and H_2^+ ions in a Penning trap. This ratio is determined to 131.945 355 91(24)(15), which is a tenfold improvement in accuracy over the previously determined value. This result may be used to improve the knowledge of the fine structure constant α , in a way which does not require detailed QED calculations.

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The fine structure constant α plays an important role in various fields of physics. It can be extracted from a number of different phenomena [1] like the fine structure in helium [2], the Lamb shift in hydrogen, the hyperfine structure in hydrogen and muonium [3], the quantum Hall effect, the Josephson effect [4], the ratio between the Planck's constant and the neutron mass [5], and the anomaly of the electron magnetic moment [6]. The most accurate value of α is extracted from a comparison of the experimental value of $g - 2$ for the electron and the value obtained from QED calculations. The relative uncertainty of this approach is 4 ppb [6]. Further improvements of the QED calculations may have to involve strong and weak interactions. It is, therefore, important to search for alternative methods, which do not require complex QED calculations and which have the potential to improve the accuracy of the fine structure constant still further. One such approach [7] is based on the following expression for the fine structure constant:

$$\alpha^2 = \left(\frac{2R_\infty}{c}\right)\left(\frac{h}{m_e}\right) = \left(\frac{2R_\infty}{c}\right)\left(\frac{h}{m_{\text{Cs}}}\frac{m_{\text{Cs}}}{m_p}\frac{m_p}{m_e}\right). \quad (1)$$

The Rydberg constant R_∞ is known with a relative uncertainty which is $< 2 \times 10^{-11}$ [8], while by definition the velocity of light is 299 792 458 m/s. The uncertainty in the m_p/m_e mass ratio is 2.2×10^{-9} [9]. If the remaining two ratios could be experimentally determined to a similar accuracy the uncertainty of the fine structure constant would be improved by a factor of about 2.

Penning trap mass spectrometers are capable of mass determinations with sufficient accuracy [10,11] to realize such a determination. It also appears to be possible to determine h/m_{Cs} with high accuracy from studies of recoiling Cs atoms after the absorption of photons. This ratio has been measured to a statistical precision $< 6 \times 10^{-8}$ at Stanford [7], and future significant improvements are probable. Also required for the determination of the h/m_{Cs} ratio is an accurate determination of the Cs D1 transition frequency, which is recently done to 1.2×10^{-10} at MPI Garching [12].

In a Penning trap mass spectrometer the mass of an ion is extracted from cyclotron frequency determinations.

The cyclotron frequency of an ion with mass m and charge qe moving perpendicular to a magnetic field B is given by the well-known equation,

$$\nu = \frac{qeB}{2\pi m}. \quad (2)$$

The q dependence of relation (2), which makes it possible to compensate a large mass with a high charge state to maintain a high frequency, motivates the use of the highly charged Cs ions (up to 42+) in this work.

Since it is not possible to determine the average magnetic field during a measurement with sufficient accuracy, the magnetic field dependence is eliminated by the use of a reference mass. In this work we have used $^{12}\text{C}^{4+}$ and H_2^+ . Denoting the two ion species, whose cyclotron frequencies are to be compared, with subscripts 1 and 2, their frequency ratio is given by the following equation:

$$R = \frac{\nu_1}{\nu_2} = \frac{q_1}{q_2} \frac{m_2}{m_1}, \quad (3)$$

provided that the change in the magnetic field between the measurements of the two frequencies can be neglected.

There are two different ways by which the mass ratio of ^{133}Cs and the proton can be derived from our measurements (throughout the remainder of the text ^{133}Cs is denoted Cs and ^{12}C by C). In the first method m_{Cs} is determined by using C^{4+} as mass reference. The mass ratio of Cs and the proton is then obtained by dividing the Cs mass with the most accurately determined proton mass available. The second method utilizes a determination of $\nu_{\text{Cs}}/\nu_{\text{H}_2^+}$ and the accurately known ratio of the H_2^+ and proton masses.

When calculating the atomic mass from the experimentally observed ion mass one has to account for the mass qm_e of the removed q electrons and their atomic binding energy E_B . Thus, the mass of atomic Cs becomes

$$m_{\text{Cs}} = m_{\text{Cs}^{q+}} + qm_e - \frac{E_B}{c^2}. \quad (4)$$

From Eqs. (3) and (4) the following relation is obtained:

$$m_{\text{Cs}} = \left(\frac{\nu_{\text{C}^{4+}}}{\nu_{\text{Cs}^{q+}}}\right)\left(\frac{q}{4} m_{\text{C}^{4+}}\right) + qm_e - \frac{E_B}{c^2}, \quad (5)$$

where $\nu(\text{C}^{4+})/\nu(\text{Cs}^{q+})$ is the experimentally measured frequency ratio (Table I), which is obtained by

TABLE I. The observed frequency ratios with statistical uncertainties. The frequency ratios of Cs and $^{12}\text{C}^{4+}$ are obtained by dividing the measured frequency ratios of ^{133}Cs and H_2^+ by those of $^{12}\text{C}^{4+}$ and H_2^+ .

	$\nu_{\text{Cs}}/\nu_{\text{H}_2^+}$	$\nu_{\text{Cs}}/\nu_{\text{C}^{4+}}$
36+	0.545 910 028 55(17)	0.812 579 730 10(25)
37+	0.561 076 500 69(12)	0.835 154 819 76(26)
38+	0.576 243 094 89(11)	0.857 730 091 10(17)
42+	0.636 910 719 78(14)	0.948 033 034 22(21)

dividing the experimentally obtained frequency ratio 0.671 823 340 32(27) of C^{4+} and H_2^+ by the frequency ratio of Cs^{9+} and H_2^+ , both ratios measured under identical experimental conditions.

The influence of the error in the electron mass on the mass of an ion is $<10^{-12}$ and can be ignored at the current level of precision. The ionization energies for elements with Z less than about 25 are accurately known [13], with an influence on the relative uncertainty of the atomic mass, which usually is $<10^{-11}$ and negligible. This is, for example, the case for C^{4+} for which the calculated binding energy is only 148.025 eV. The uncertainties are not given in the reference but if we take 0.1 eV as a very conservative estimate this corresponds to an uncertainty $<10^{-11}$. This results in a C^{4+} mass of 11.997 805 839 30(12) u. For heavier atoms like Cs, however, one has to rely upon calculated values. Using relativistic many-body perturbation theory, it is possible to calculate the total electron binding energies in K-, Ar- and Cl-like Cs ions with an uncertainty of about 10 eV [14]. The uncertainty contribution due to QED corrections is only about 1 eV (<1 part in 10^{11}). The binding energies for charge states 36+, 37+, and 38+ obtained this way are 27 416.4, 29 840.6, and 32 495.2 eV [15].

Dividing Eq. (4) with the proton mass and using the fact that $m(\text{H}_2^+)/m_p$ is a constant $k(\approx 2)$ which can be calculated with an accuracy of less than 0.1 parts per 10^9 (ppb) one obtains

$$\frac{m_{\text{Cs}}}{m_p} = qk \frac{\nu_{\text{H}_2^+}}{\nu_{\text{Cs}^{q+}}} + \frac{qm_e}{m_p} - \frac{E_B}{m_p c^2}. \quad (6)$$

The calculation of k involves atomic quantities, which are well known. The dominating uncertainty originates from the population distribution of the vibrational levels in H_2^+ , which has been measured and is also confirmed by calculations [16]. Taking this effect into account, the average ionization energy changes from 15.43 to 16.18 eV. This results in a mass increase of only 0.35 ppb. This value is experimentally confirmed, by comparing the cyclotron frequencies of the H_2^+ ions and the proton which gave the value 2.000 544 598 9(11) as compared to the calculated value 2.000 544 600 50(10).

The mass determinations have been performed in the Penning trap mass spectrometer SMILETRAP, which is described in more detail in [17,18]. The experiments were

performed using highly charged ions produced externally in the electron beam ion source CRYISIS [19]. About 10^8 charges are delivered from the ion source about once per second. Before capture in the measurement trap, the beam is charge/mass state separated in a 90° analyzing magnet. The ions are thereafter captured in a preparation trap (cylindrical geometry, room temperature environment, 0.2 T magnetic field), where the kinetic and potential energy is adjusted for optimal injection into the measurement trap. This second trap is situated in a room temperature environment, in a 4.7 T magnetic field, has a hyperbolic geometry, and is equipped with correction electrodes for reduction of trap imperfections. The excitation, which lasts 1 s, is tuned to the sum frequency of the reduced cyclotron frequency and the magnetron frequency ($\nu_+ + \nu_-$), which is equal to the true cyclotron frequency (ν_c) [20]. The detection is done by determining the time of flight to a multichannel plate detector. A full measurement cycle is completed in 1.5 min, including the reversal of ion species, thus making field shifts negligible. The size and limits of possible systematic errors have been investigated [18] using highly charged ions of ^{12}C , ^{14}N , ^{16}O , ^{20}Ne , ^{40}Ar , and singly charged H, H_2^+ , H_3^+ , all with accurately known masses.

The analysis of these measurements verifies the presence of two systematic errors, while a third systematic effect is suggested. The first effect is a frequency shift due to non-negligible kinetic energies, causing a relativistic mass increase. The second effect is a frequency shift correlated with the number of stored ions in the trap during excitation. The third hinted effect is a possible observed mass dependence on the charge to mass ratio (q/A) difference between the observed and the reference ion.

At present, we do not cool the ions. Instead we rely on a sequence of selection procedures that results in average kinetic energies which are <1 eV per charge. In the experiment, we observe the total mass of the ion which depends on the rest mass of the particle and its kinetic energy ($mc^2 = E_k + m_0c^2$). Thus it is possible to determine the rest mass from the experimentally observed mass if the kinetic energy during the observation is known. This energy is determined by applying a retardation potential on meshes placed in front of the detector [17,18]. As a conservative estimate of the relative uncertainty of the average kinetic energy, we take 50% of the maximal contribution, which is <0.5 ppb.

Since we are not able to precisely control the number of captured ions, the average number of simultaneously stored ions varies from 0.5 to about 1.5. We observe that the cyclotron frequency is reduced with the number of simultaneously stored ions. In previous studies [18], involving ions up to $^{40}\text{Ar}^{16+}$, the frequency reduction was ≈ 2 mHz/charge. In the case of Cs^{36-42+} , the effect is smaller. All four charge states consistently shift <0.6 mHz/charge (shift per highly charged Cs ion is <1.5 ppb). In experiments, where contaminant ions

were removed by strong excitation of ν_z , the effect is reduced. Also, the trap is situated in a room temperature environment, with cryo- and nonevaporative getter pumps placed some 30–90 cm away. In this region, the vacuum is better than 10^{-11} mbar. However, in the trap volume the charge recombination rates are consistent with a vacuum of low 10^{-10} mbar. Thus, these observations support the conclusion that this frequency shift is most likely caused by contaminant ions created by charge exchange reactions between highly charged ions and the rest gas in the trap. In the case where only *one* ion was detected there are two possible scenarios. Either, it is a contaminant ion and therefore unaffected by the excitation or it is a Cs ion and therefore not subject to shifts due to the presence of contaminant ions. Thus, the number dependence should not be present for only one ion in the trap. Accordingly, we only use data corresponding to one stored ion in the Cs mass evaluation. However, the detection efficiency is less than 100%. A contaminant ion might be present, although it is not detected. Therefore, the data are corrected to, on the average, one “real” ion in the trap. The detection efficiency for singly charged low energy ions (2 keV) is <0.4 . For higher energies the detection efficiency increases and is about 0.8 for singly charged 4.4 keV ions [21]. Therefore, we estimate the detection efficiency for 80 keV Cs ions to be 0.95, which however, is reduced to 0.8 by the analyzing grids in front of the detector. Returning to the difference in number dependence between Cs and previous measurements, we attribute this only partly to the higher detection efficiency of 80 keV Cs ions and mainly to the lower average number of simultaneously stored ions (factor of 2–3) than previously used. Remember that having only one Cs ion will not cause a shift. To have a shift, at least two Cs ions are required. If the probability of having 1 Cs ion is reduced to 0.3, the probability of 2 Cs ions is $0.3 \times 0.3 = 0.1$. Thus, when the count rate is reduced, the probability of having the number dependence shifting situation is reduced even more leading to a smaller shift. The ion number dependence of Cs^{36+} and Cs^{37+} is about 1.3 ppb/ion, which corresponds to a correction to the mass ratios less than +0.3 ppb. As a conservative estimate of the uncertainty, we at present take *the whole correction*.

When analyzing all our measurements [18], involving highly charged ions and H_2^+ ions, it was found that the observed frequency ratios indicate a q/A dependence. For a q/A -ratio difference of 0.28 (Cs^{36+} - H_2^+), the effect corresponds to +2.3(0.55) ppb. However, another test measurement using H_2^+ and H_3^+ (q/A difference = 0.17) gave a result of -0.2(0.45) ppb, suggesting a smaller q/A dependence. At present, we choose not to perform the correction but await the accumulation of further data. However, as a conservative estimate of this possible uncertainty we take a larger value. Thus, in the Cs/H_2^+ comparison this gives a maximum uncertainty

contribution, due to different q/A values of the two ion species, of 3.0 ppb while in the Cs/C comparison this effect gives an uncertainty contribution of 0.8 ppb (see Table II).

The resonance linewidth, expected for a Fourier limited process lasting 1 s, is about 0.9 Hz. However, due to the fact that the conversion from radial kinetic energy of the ion to flight time to the detector is not linear, the linewidth is increased to about 1.1 Hz [20]. A statistically significant additional broadening, which is not caused by magnetic field drifts, indicates the presence of a systematic error. For example, a test run using a 30%/70% mixture of $^4\text{He}^{2+}$ and $^{12}\text{C}^{6+}$ gave a linewidth broadening of 0.6 Hz and a shift of the center frequency of the $^{12}\text{C}^{6+}$ resonance with 6 ppb. Therefore, as a rule, we discard results for which the linewidth is larger than 1.15 Hz. The Cs 38+ and 42+ resonances were excessively broadened (<0.3 Hz) and shifted (≈ 4 ppb) away from the Cs 36+ and 37+ in a direction as if contaminant ions were present. The most probable explanation is a contamination originating from the ion source, which is not removed by our injection system. $^{14}\text{N}^{4+}$ and $^{16}\text{O}^{5+}$ have q/a ratios similar (not separable by our analyzing magnet) to Cs^{38+} and Cs^{42+} , respectively. Therefore, due to the *unacceptable linewidth*, the 38+ and 42+ measurements were discarded.

The observed cyclotron frequency ratios are given in Table I. Each charge state of Cs represents 12–15 hours of data acquisition. The C^{4+} data, which were obtained under identical experimental conditions during two different run weeks, correspond to a total running time of 30 hours.

In Table II we present the statistical and systematic uncertainties for the accepted measurements, while the ratios of the cesium and proton masses are presented with their uncertainties in Table III. The ratios with H_2^+ as mass reference are directly obtained, while the values for $^{12}\text{C}^{4+}$ as mass reference are obtained by dividing our determination of the Cs mass with the recent proton mass determination performed by the University of Seattle group

TABLE II. Individual uncertainties.

Uncertainties [ppb]	Ref. ion H_2^+		Ref. ion $^{12}\text{C}^{4+}$	
	Cs^{36+}	Cs^{37+}	Cs^{36+}	Cs^{37+}
Statistical (1σ)	3.11	2.14	3.14	2.18
Reference mass ^a	0.14	0.14
Electron binding energy ^a	0.08	0.08	0.08	0.08
Vibrational energy (H_2^+) ^a	0.1	0.1
Relativistic mass ^a	0.58	0.61	0.63	0.66
Ion number dependence ^a	0.40	0.38	0.41	0.39
q/A dependence ^a	2.99	2.89	0.82	0.72
Magnetic field drift	0.1	0.1	0.1	0.1
Total systematic	3.08	2.98	1.14	1.08

^aUncertainties are common for both charge states.

TABLE III. The ratios of the Cs and proton mass obtained for Cs charge states $36+$ and $37+$ with H_2^+ and $^{12}\text{C}^{4+}$ as mass reference ions. In the latter determinations, the proton mass $m_p = 1.007\,276\,466\,89(14)$ has been utilized [22].

q	$m(\text{Cs})/m(p)$; Ref. H_2^+	$m(\text{Cs})/m(p)$; Ref. $^{12}\text{C}^{4+}$
36+	131.945 355 75(41)(40)	131.945 355 82(41)(15)
37+	131.945 355 87(28)(39)	131.945 355 95(29)(14)
Average	131.945 355 83(24)(40)	131.945 355 91(24)(15)

[22]. The numbers within the first brackets represent the statistical uncertainty, while the numbers within the second brackets give the total systematic uncertainty obtained from Table II. Note that using H_2 or C as reference ions results in a m_{Cs}/m_p difference of only 0.5 ppb (also supporting a small q/A dependence). However, our claimed systematic uncertainty is 3.1 ppb using H_2^+ as mass reference and 1.2 ppb using C . Thus, we select the results which use $^{12}\text{C}^{4+}$ as mass reference as our best determination.

In conclusion, we have determined the Cs/proton mass ratio to be 131.945 355 91(24)(15) as compared to the more accurate value 131.945 355 994(60) obtained by the MIT group [23]. Although both groups use trapped ions in a Penning trap, the methods and therefore the involved systematic errors are very different (ours are undeniably larger). However, our value is an independent measurement, which verifies the Cs/proton mass ratio to an accuracy of about 2.2 ppb and which is accurate enough to allow for an improved determination of the fine structure constant, in which the uncertainties due to QED calculations are negligible.

From an analysis of all our previous experiments [18], it seems possible to increase the accuracy of the determination of the Cs proton mass ratio, using the present mode of operation, with a factor of 2–4. However, in order to significantly improve the accuracy beyond that value, additional measures are required, such as utilization of longer observation times, single ion operation, improved vacuum, and ion cooling.

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