Accurate Atomic Masses for Fundamental Metrology

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We have measured the atomic masses of ten species with a typical accuracy of 10^{-10} by comparing the cyclotron frequencies of 20 different pairs of alternately trapped ions. The mass of ^{28}Si provides a possible route to realizing an atomic standard of mass. The neutron separation energies for ^{15}N and ^{13}C determined from these mass measurements suggest the need to recalibrate γ-ray energies in the 2 to 13 MeV range, and may lead to an independent determination of both the fine structure constant α and the molar Planck constant $N_A h$ with a precision approaching 10^{-7}.

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The long observation time and well-understood dynamics associated with a single charged particle in a Penning trap [1] have made possible some of the most precise measurements in physics [2]. Recently, mass comparisons have been made by cyclotron resonance of ions in a Penning trap with a relative accuracy of $\sim 10^{-10}$ for both doublet [3] and nondoublet [4] ion pairs. This has improved the level of precision of mass spectrometry by at least an order of magnitude, ushering in a regime where mass comparisons have important implications in the area of fundamental constants and metrology.

In this paper, we report a table of atomic masses of nine isotopes and the neutron with accuracies as high as 7×10^{-11}, which is based on a series of 20 pairwise mass comparisons [5]. Several classes of self-consistent checks verify that the quoted uncertainties are accurately estimated [6]. The atomic mass of ^{28}Si is measured accurately enough to enable ongoing precision studies of the density and lattice spacing of silicon to replace the present artifact kilogram with an atomic mass standard. This level of precision also allows us to determine mass differences associated with neutron capture reactions with an accuracy of 10^{-7}. This can provide calibration energies for γ rays and may lead to an independent measurement of the fine structure constant α and the molar Planck constant $N_A h$ with this accuracy.

The experimental apparatus and procedure for measuring ion mass ratios have been described earlier in the literature and are briefly outlined here. The Penning trap consists of a uniform magnetic field (8.5 T), together with a weak quadrupole electrostatic field which confines the ions axially. The harmonic axial motion of a single trapped ion is observed with a high-Q resonant circuit and an rf SQUID detector [7]. The cyclotron mode is coupled to the axial mode with a diagonally oriented quadrupole rf field tuned to the difference frequency of the two modes. Pulses of this field are used to exchange the amplitudes and phases of these modes coherently, allowing the phase of the cyclotron mode to be measured [8]. The cyclotron frequency $\omega_c = qB/mc$ (where q is the charge, B is the magnetic field strength, m is the mass, and c is the speed of light) is obtained by directly pulsing the cyclotron mode and measuring the accumulated phase as a function of time [9].

A mass ratio is determined by comparing the cyclotron frequencies of two ions, repeatedly alternating between the ions (Fig. 1). The difference cyclotron frequency is obtained by fitting the data with a low-order polynomial to model the field drift. The random variability of the magnetic field dominates the uncertainty in the difference frequency. These field fluctuations were found to have a nearly Gaussian distribution with an rms deviation of 2.6×10^{-10} per single cyclotron frequency measurement [5]. To account for the non-Gaussian aspect of the

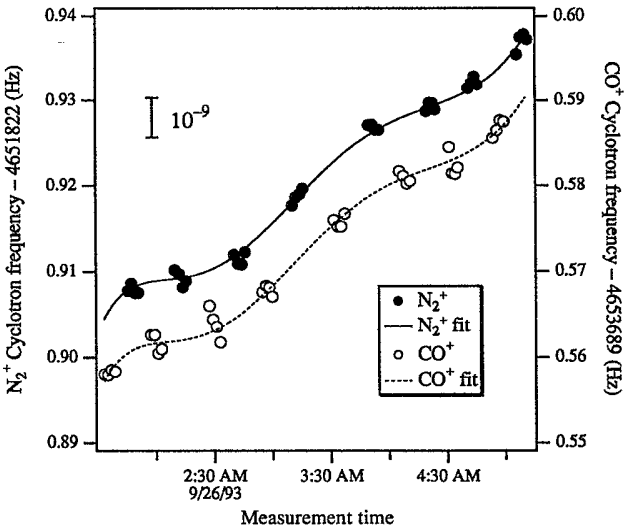

FIG. 1. Typical cyclotron frequency data. In order to model the field drift, measurements are alternated between the two species. A polynomial is fit simultaneously to both sets of data to determine the frequency difference. The curve fitting is based on a robust statistical estimator, and a statistical test is used to specify the order of the polynomial. In the above case, a sixth order polynomial was specified, and the best estimate of the ratio CO^+/N_2^+ is 0.999 598 887 60(8).

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field fluctuations, the polynomial fit is based on a robust statistical estimator which rejects outliers in a smooth and consistent manner [10]. The resultant uncertainty in the mass ratio is typically 1×10^{-10} per one night run. This random error from field fluctuations dominates any expected systematic errors, which are calculated to be 10^{-11} or less for doublets [6].

Atomic masses are expressed relative to ^{12}C, which is defined to have a mass of exactly 12 atomic mass units (u). In order to convert ion mass ratios to mass differences of neutral isolated atoms, chemical binding energies and ionization potentials are taken into account. The heats of formation for molecular ions and the neutral atoms in the ideal gas phase at 0 K are used to calculate these energies [11]. Afterwards, the atomic masses are found by performing a global least squares fit to the entire set of mass differences. The fit produces a covariance matrix which directly yields the uncertainty in the atomic mass (with respect to ^{12}C) and allows uncertainties to be calculated for quantities involving correlated isotopes [6].

Table I lists atomic masses measured with this experiment, along with the accepted values from conventional mass spectrometry [12] and the results from other Penning trap experiments [13–15]. The latest 1993 atomic mass evaluation [16] contains some data from Penning trap experiments, including preliminary values [17] of some results reported here. Our latest results are consistent with our preliminary results, except for a 1.5σ adjustment in the ^{14}N mass [6]. Our Penning trap results are a factor of 10–1000 more precise than the non-Penning-trap values and, with the exceptions of ^{16}O [13] and ^{20}Ne [14], are in good agreement with the other Penning trap values.

The mass ratio measurements that underlie the atomic masses in Table I were selected to allow several types of checks for systematic errors [6]. To illustrate, measurements of redundant doublets which give the same mass difference from different ion pairs agreed within error (e.g., the ratios O^+/CH_4^+, $CO^+/C_2H_4^+$, and $CO_2^+/C_3H_8^+$ all determine the mass difference C+4H-O). This provides a very stringent test of our doublet comparison technique since the experimental conditions (trap voltage, cyclotron frequency, and chemical energies) vary by over a factor of 2 in the measurements. In addition, the ratios have been chosen so that at least two completely independent groups of mass ratios enter into the determination of all atomic masses in the table, making it impossible for a single mistaken mass ratio to remain undetected. These checks, together with the observed reduced χ^2 value of 0.74 for the global fit used to determine the masses, indicate that there are no undetected systematic errors at the level of the reported uncertainties, and that these uncertainties accurately reflect the true statistical uncertainties in the results.

Precise atomic masses have an important contribution to metrology. The kilogram is the only fundamental metrological unit still defined in terms of an artifact (the platinum-iridium prototype at Bureau International des Poids et Measures in Sèvres, France). This definition has well-known limitations [18], including the possibility of temporal drift, loss or destruction, and comparison with standards of much lower density. An attractive alternative is to replace the prototype kilogram with a stable, universal, atomic-based mass standard [19], since Penning trap mass comparisons are accurate to 10^{-10}, a greater precision than that with which macroscopic masses can be compared. This could be accomplished by specifying the Avogadro constant N_A as a defined quantity, in which case 1 g would be defined to be one-twelfth the mass of N_A ^{12}C atoms.

In practice, realizing the kilogram by this approach would probably first be achieved using an ultrapure silicon crystal whose lattice constant is determined by direct length measurements. The density of such a crystal has been compared to density standards based on the prototype kilogram to measure N_A with an accuracy of

TABLE I. Atomic mass table. Atomic masses (in u) are listed as determined from this experiment, from the 1983 atomic mass evaluation [12], and from other Penning trap experiments [13–15]. The numbers in parentheses indicate the error in the rightmost figures. For the purpose of comparison, zeros have been added so that the numbers of digits are equal.

Atom	Mass (this work)	Non-Penning-trap values [12]	Other Penning trap values
^1H	1.007 825 031 6 (5)	1.007 825 035 0 (120)	1.007 825 032 6 (10) [13]
n	1.008 664 923 5 (23)[a]	1.008 664 919 0 (140)	1.008 664 918 7 (26) [13]
^2H	2.014 101 777 9 (5)	2.014 101 779 0 (240)	2.014 101 776 9 (11) [13]
^{13}C	13.003 354 838 1 (10)	13.003 354 826 0 (170)	13.003 354 840 4 (41) [13]
^{14}N	14.003 074 004 0 (12)	14.003 074 002 0 (260)	14.003 074 005 6 (18) [13]
			14.003 074 014 0 (190) [14]
^{15}N	15.000 108 897 7 (11)	15.000 108 970 0 (400)	...
^{16}O	15.994 914 619 5 (21)	15.994 914 630 0 (500)	15.994 914 626 3 (30) [13]
^{20}Ne	19.992 440 175 4 (23)	19.992 435 600 0 (22000)	19.992 440 691 0 (900) [14]
^{28}Si	27.976 926 532 4 (20)	27.976 927 100 0 (7000)	27.976 926 570 0 (3000) [15]
^{40}Ar	39.962 383 122 0 (33)	39.962 383 700 0 (14000)	...

[a]The neutron mass is determined in combination with a measurement of the deuteron binding energy [29], which is mainly responsible for the stated uncertainty.

1.1×10^{-6} [20], the major source of error being the uncertainty in the isotopic abundances of silicon. It is anticipated that modifications (that include using a crystal made from precisely weighed quantities of isotopically enriched silicon [21]) would allow a precision of 10^{-8} or better to be attained in the future [22]. The potential for improvement is reflected in a recent measurement of the silicon lattice constant to 3×10^{-8} [23]. Realizing the kilogram with this accuracy would then be a practical alternative to the artifact mass standard. The previous non-Penning-trap value of $M(^{28}\mathrm{Si})$ was accurate to 2.5×10^{-8} and would have been a limitation in the accuracy of N_A. The atomic mass of ^{28}Si reported in this paper is accurate to 7×10^{-11} and would not be a limitation for realizing the kilogram by this method.

Measuring atomic masses at the 10^{-10} level allows mass differences to be determined with relative precision of 10^{-7}, since ion doublets typically differ in mass by 10^{-3}. With this accuracy, atomic mass differences have important contributions to the field of fundamental constants. By Einstein's relationship, $\Delta E = \Delta m c^2$, the energy released in a nuclear process can be measured as a difference in the mass of the initial and final nuclei. Neutron separation energies determined with the help of mass spectrometry have been used to calibrate γ-ray energies in the 2–13 MeV range [24]. In particular, the $^{14}\mathrm{N}(n,\gamma)$ neutron capture spectrum has a rich variety of γ rays and is an important basis for calibration, along with the accurately known 2.2 MeV deuteron binding energy from $^{1}\mathrm{H}(n,\gamma)$:

$$^{14}\mathrm{N} + n \rightarrow {}^{15}\mathrm{N} + \gamma_1 + \gamma_2 \ (10.8\ \mathrm{MeV}),$$

$$^{1}\mathrm{H} + n \rightarrow {}^{2}\mathrm{H} + \gamma_3 \ (2.2\ \mathrm{MeV}).$$

Subtracting to eliminate the neutron mass yields the energy balance equation:

$$\Delta E = hc/\lambda^* = m(^{14}\mathrm{N} + {}^{2}\mathrm{H}\text{-}{}^{15}\mathrm{N}\text{-}{}^{1}\mathrm{H})\,c^2,$$

where λ^* is the effective wavelength $(\lambda_1^{-1} + \lambda_2^{-1} - \lambda_3^{-1})^{-1}$, after accounting for nuclear recoil. The mass difference $^{14}\mathrm{N} + {}^{2}\mathrm{H}\text{-}{}^{15}\mathrm{N}\text{-}{}^{1}\mathrm{H}$ represents a net energy release of 8.6 MeV, about 6×10^{-4} of the total rest mass involved. There is also a similar pair of reactions involving $^{12}\mathrm{C}(n,\gamma)$ and $^{1}\mathrm{H}(n,\gamma)$ which requires a measurement of the mass difference $^{12}\mathrm{C} + {}^{2}\mathrm{H}\text{-}{}^{13}\mathrm{C}\text{-}{}^{1}\mathrm{H}$. In this case, only 2.7 MeV is released, resulting in a larger relative uncertainty in the measured value of the mass difference.

Table II lists the measured values of the above mass differences from our experiment, along with previous results by conventional mass spectrometry [25]. The mass differences $^{12}\mathrm{C} + {}^{2}\mathrm{H}\text{-}{}^{13}\mathrm{C}\text{-}{}^{1}\mathrm{H}$ and $^{14}\mathrm{N} + {}^{2}\mathrm{H}\text{-}{}^{15}\mathrm{N}\text{-}{}^{1}\mathrm{H}$ are now accurate to 4×10^{-7} and 1×10^{-7}, respectively, and are about a factor of 10 more accurate than the prior values. The $^{12}\mathrm{C}(n,\gamma)$ mass differences are in good agreement; however, the $^{14}\mathrm{N}(n,\gamma)$ mass differences do not agree, differing by 9 times the reported uncertainty in the prior value.

TABLE II. Mass differences for determining α and $N_A h$. The mass differences associated with the neutron capture reactions $^{12}\mathrm{C}(n,\gamma)$ and $^{14}\mathrm{N}(n,\gamma)$ determined by this experiment and by conventional mass spectrometry [25] are listed. The new results area a factor of 10 more accurate and show considerable disagreement in the value of $^{14}\mathrm{N} + {}^{2}\mathrm{H}\text{-}{}^{15}\mathrm{N}\text{-}{}^{1}\mathrm{H}$.

Mass difference	This work [nu]	Ref. [25] [nu]
$^{14}\mathrm{N} + {}^{2}\mathrm{H}\text{-}{}^{15}\mathrm{N}\text{-}{}^{1}\mathrm{H}$	9 241 852.7 (0.9)	9 241 780 (8)
$^{12}\mathrm{C} + {}^{2}\mathrm{H}\text{-}{}^{13}\mathrm{C}\text{-}{}^{1}\mathrm{H}$	2 921 908.2 (1.1)	2 921 911 (12)

The current γ-ray energy calibration [24] is based on the prior value of the $^{14}\mathrm{N} + {}^{2}\mathrm{H}\text{-}{}^{15}\mathrm{N}\text{-}{}^{1}\mathrm{H}$ mass difference [25], which is inconsistent with the value reported here. Unlike our Penning trap measurement, which is based on at least two independent sets of mass ratios to verify its accuracy, the earlier result was based on a single mass comparison. The improved mass difference obtained by Penning trap mass spectrometry increases the accuracy of the energy calibration and suggests that an 8 ppm revision of this calibration is necessary. Recent γ-ray energy measurements have also indicated the need for such an adjustment [26].

If an accurate absolute measurement of λ^* were made at the 10^{-7} level, it could be combined with our measurement of the corresponding atomic mass difference ΔM (in u) to obtain fundamental constants. The molar Planck constant $N_A h$ follows from equating the photon energy and mass difference Δm (in kg) [27]:

$$E_\gamma = hc/\lambda^* = \Delta m c^2,$$

$$\rightarrow N_A h = \lambda^* \Delta M c \times 10^{-3}.$$

The Avogadro constant $N_A = 10^{-3}\Delta M/\Delta m$ appears as the conversion factor between mass expressed in atomic mass units and in SI units.

This procedure of "weighing a γ ray" also has been proposed for determining the fine structure constant α, which could be expressed as [27]

$$\alpha^2 = \frac{2R_\infty}{c}\left(\frac{h}{m_e}\right) = \frac{2R_\infty}{c}\left(\frac{M_p}{M_e}\right)\frac{N_A h}{M_p} \times 10^3.$$

The Rydberg constant R_∞, the proton-electron mass ratio M_p/M_e, and the proton atomic mass M_p are known to 4×10^{-11}, 2×10^{-8}, and 5×10^{-10}, respectively. Measuring λ^* and ΔM with a relative accuracy of $\sim 10^{-7}$ therefore would determine α to this level of precision.

A collaboration of researchers, led by E. G. Kessler, Jr. at NIST and using the High Flux Reactor in Grenoble, France, is undertaking precision experiments to measure absolute γ-ray wavelengths [28]. Already, the 2.2 MeV γ-ray wavelength for $^{1}\mathrm{H}(n,\gamma)$ has been determined by this group with an accuracy of 1.0×10^{-6} [29]. It is anticipated that λ^* will be measured for the above $^{14}\mathrm{N}(n,\gamma)$ process with an accuracy of $\sim 2 \times 10^{-7}$ [30],

which is comparable to the precision of our measurement of ΔM.

Other experiments to determine the fine structure constant measure h/m by equating the momenta of waves (h/λ) and particles (mv). Krüger *et al.* have determined h/m_n to 4×10^{-7} by measuring the wavelength and velocity of a neutron beam [31]. Weiss, Young, and Chu have determined h/m_{Cs} with an accuracy of 1×10^{-7} using atom interferometry to measure photo recoil [32]. Combined with the atomic masses M_n and M_{Cs}, these values of h/m determine α. An accuracy exceeding 10^{-8} is expected for h/m_{Cs} in the future, which would therefore require an improved measurement of M_{Cs}, now known to 2.2×10^{-8} [16]. The values of α determined by these experiments and by weighing γ rays could be compared to results from other branches of physics, most accurately from the Penning trap measurement of the electron $g - 2$ anomaly combined with QED theory [33]. This would provide an independent check on the physics underlying the different experiments [34].

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