Precision Penning Trap Comparison of Nondoublets: Atomic Masses of H, D, and the Neutron

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We compare the cyclotron frequency of two single ions in a Penning trap to obtain their mass ratio with a relative uncertainty close to 1×10^{-10}. We have developed methods, based on a classical implementation of the separated oscillatory fields technique, that extend this precision to mass ratios far from unity (nondoublets). This allows direct determination of the atomic mass of any ion by comparison to a C^+ ion. Using isotopically selected methane ions, we obtain the masses of H, D, and the neutron with up to 40 times improved precision over accepted values. We have checked our technique with known nondoublet ratios such as $M[N_2^+]/M[N^+]$.

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Single charged particles stored in Penning traps have been used for some of the most precise fundamental measurements in science [1]. Comparison of the masses of trapped ions is the first technique to achieve relative uncertainty smaller than 1 ppb ($=1\times10^{-9}$) and promises to introduce a new era in mass spectrometry [2]. Recent work by Van Dyck, Farnham, and Schwinberg [3] and our group [4,5] with accuracy close to 0.1 ppb has improved the precision of some atomic masses by 10–10^3 times over the standard nuclear mass table [6]. Here we report up to a fortyfold improvement in the atomic masses of H, D, and n, which are regarded as fundamental constants due to their importance in atomic and nuclear physics [7]. For example, the masses of H and D are important in ongoing experiments to compare the Lamb shifts in the two atoms [8].

The phenomenal accuracy of Penning trap mass measurements comes from the ability to precisely measure the cyclotron frequency of single ions trapped in a highly uniform magnetic field. In order to overcome systematic shifts in the frequency due to various imperfections in the trapping fields, precision work has heretofore been done on a doublet, i.e., two ions with nominally the same mass to charge ratio [2–4]. Differences in these shifts for the two ions are then scaled down by the factor $\Delta m/m$, which is usually below 10^{-3}.

In this paper, we report on a new technique that extends precision measurements of mass ratios to nondoublets, i.e., ion pairs with a mass ratio far from unity. This allows us to make a direct measurement of mass in atomic units (u) by comparison to a C^+ ion; moreover, this can be done in more than one independent way for a given atomic species as done here for the mass of D using CD_3^+ vs C^+ and CD_4^+ vs C^+. Nondoublet measurements also permit much more stringent checks on systematics using ratios such as $M[N_2^+]/M[N^+]$, which may be calculated with an accuracy of 1 ppt ($=1\times10^{-12}$) from the known electron mass and binding energies. Atomic masses have been previously obtained [3] by comparing a given ion to C^{n+}, with a suitable value of n to make a doublet; our technique works for arbitrary ratios and avoids potential systematics due to induced dipole shifts from the trap electrodes which affect the two ions differently if they have different charge states [9].

The ideal Penning trap consists of a strong, uniform magnetic field and a quadrupole electric field typically applied using three hyperboloidal electrodes. The motion of a single ion decomposes into three normal modes: an axial mode (at ω_z) along the magnetic field axis, and two radial modes—an electric field modified cyclotron motion (at ω_c') and an $\mathbf{E}\times\mathbf{B}$ magnetron drift (at ω_m)—perpendicular to it. In our 8.5 T field, these frequencies are, respectively, 160 kHz, 4.5 MHz, and 2.8 kHz for an ion of mass 28 u. The "free space" cyclotron frequency of the ion is recovered from [10,11]

$$\omega_c = \frac{qB}{mc} = \sqrt{\omega_c'^2+\omega_z^2+\omega_m^2} \tag{1}$$

by measuring the three normal mode frequencies to appropriate precision. Mass ratios are obtained by loading the trap with a single ion of one species, measuring its cyclotron frequency, and then repeating with a single ion of the other species. Temporal variation of the magnetic field and other smaller statistical uncertainties are averaged by alternately measuring the frequencies of the two ions a number of times.

Most of the details of our trap and detector are discussed elsewhere and will only be briefly reviewed here. We detect the presence of the ion only through its axial motion, by measuring the image current induced in the end caps. The axial mode is resonantly coupled to a high $Q(\sim25000)$ superconducting tank circuit by adjusting the trap voltage ($\omega_z\propto\sqrt{qV/m}$), and then detected with an rf SQUID [12]. We have developed a scheme of π pulses at the appropriate coupling frequency to *coherently* swap the action (i.e., $|\oint p\,dq|$) from an initially excited radial mode into the axial mode, which can then be cooled and detected [13]. We measure the cyclotron frequency from the phase accumulated in the cyclotron mode in a given length of time, using what we call our pulse and phase (PNP) technique. The cyclotron mode is excited to an amplitude a_c with a short duration pulse

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from a phase-locked source, allowed to evolve unperturbed for a known time, and finally coupled to the axial motion with a π pulse to determine its phase [2].

The leading sources of systematic error in these measurements come from the second-order spatial inhomogeneities in the magnetic and electric fields, usually designated B_2 and C_4, respectively [2,11], and the mass shift due to special relativity. All these effects cause a shift in the cyclotron frequency varying as a_c^2 (see Table I), but do not cause a systematic error for a doublet measurement if the values of a_c for the two ions are equal. Linear gradients in the magnetic field can also cause errors if the two ions have different equilibrium positions in the trap. The mean position of the ion is determined by the point at which the applied electric field cancels the stray fields due to surface potentials, which are probably caused by charged dielectric patches adsorbed on the trap electrodes. For a doublet, the applied fields needed to bring the two ions into resonance with our detector are so nearly the same that the shift in position causes less than 1 ppt error.

As seen from Table I, the error budget for nondoublets is very different. We will consider as our representative nondoublet the ions N^+ and N_2^+, whose mass ratio is exactly 2 except for some small (known) corrections. In order to eliminate the effect of relativistic mass shifts on this measurement, we need to measure the cyclotron frequency for the two species at the same tangential velocity, i.e., at amplitudes that differ by a factor of 2. The requirement on a_c for nulling the differential effects of B_2 and C_4 is not the same; hence these different sources of error cannot be nulled simultaneously. But this is not a serious problem since we can measure the B_2 and C_4 coefficients and correct for their effects to an accuracy of 20%, which causes negligible error at the 0.1 ppb level.

TABLE I. Systematic errors. The expressions in the second column give the effect of the different corrections on ω_c' to lowest order in the cyclotron amplitude, where $d=0.549$ cm is the characteristic size of our trap. The typical values (in ppb) shown in the third and fourth columns are with $a_c \approx 0.010$ cm for N^+ and with $a_c \approx 0.020$ cm for N_2^+, chosen to cancel the effect of relativity. The field inhomogeneities were shimmed to $B_2/B_0 = 0.7(2)\times 10^{-6}$ cm^{-2} and $|C_4| \leq 1.0\times 10^{-4}$. The last column gives an upper limit on systematic errors (in ppb) for this nondoublet comparison after correcting for the effects of B_2 and C_4.

Correction	Form of $\Delta\omega_c'/\omega_c'$	Value of $\Delta\omega_c'/\omega_c'$ N^+	N_2^+	Limit on systematic error
Magnetic	$-\frac{1}{2}\frac{B_2}{B_0}a_c^2$	−0.035	−0.140	~0.030
Electrostatic	$\frac{3}{2}\frac{C_4}{d^2}\frac{\omega_m}{\omega_c'}a_c^2$	0.007	0.119	~0.025
Relativity	$-\frac{1}{2}\frac{\omega_c'^2}{c^2}a_c^2$	−0.192	−0.192	~0.020

The problem with the mean position of the ion is much more serious. The trap voltage needed to bring N^+ into resonance with our detector is about 5 V, while we need 10 V for N_2^+. This can cause a significant difference in the position of the ion depending on the size of our surface potentials. We have taken great care to have a clean vacuum in order to minimize adsorbed patches when we cool our trap from room temperature to 4.2 K, and we also coat the surface of our electrodes with a graphite film to reduce the effect of surface potentials near the trap center [14]. In the axial direction, we have measured the effective stray potential to be about 22 mV by applying known offset voltages to the lower end cap and studying the resulting quadratic shift in ω_z. With our measured linear field gradient of about 1×10^{-6} cm^{-1}, this should cause a 2 ppb shift for the $M[N_2^+]/M[N^+]$ ratio. Indeed, we obtained a systematic difference of this order from the predicted value when we measured the ratio with our PNP technique. The systematic error remained after we repeated the measurement with the axial offset nulled (see Fig. 2), suggesting that there are radial components to the stray fields of the same order (which we cannot measure or null in our azimuthally symmetric trap).

This offset error is eliminated by measuring the frequencies of both ions with the same trap voltage applied. Thus, in our example, we have to measure ω_c for both N^+ and N_2^+ with 10 V on the trap, the voltage at which our PNP technique works for N_2^+. However, at 10 V, the axial frequency of N^+ is $\sqrt{2}$ times higher than the fixed frequency of our narrow band detector, and we cannot measure its cyclotron frequency with this method.

Our solution is to use the Ramsey separated oscillatory fields (SOF) technique [15], applied here in the classical regime, to store the cyclotron resonance information in the cyclotron *amplitude* in a nonresonant trap and then determine this amplitude after bringing the ion into resonance with the detector. Thus, to measure the frequency of N^+ at 10 V, we first excite its cyclotron mode with a short pulse from a signal generator. After a length of time T, during which the cyclotron motion evolves freely, we apply a second identical pulse to the ion. The resultant classical amplitude of the cyclotron oscillation (rather than the state amplitude of a quantum oscillator) then represents the interference between the ion's natural frequency and the drive frequency, and displays a characteristic Ramsey fringe pattern at the beat frequency, as shown in Fig. 1. In order to measure this amplitude, we change the trap voltage to 5 V, which brings N^+ into axial resonance with our detector, then apply the usual π pulse and detect the axial motion. We repeat this process for a series of interference times allowing us to determine the order of each Ramsey fringe unambiguously.

In order to obtain the free space cyclotron frequency for N^+ and N_2^+ as in Eq. (1), we need to know their axial frequencies. We can directly measure ω_z for N_2^+ on our detector, but for N^+ we infer it by scaling the value

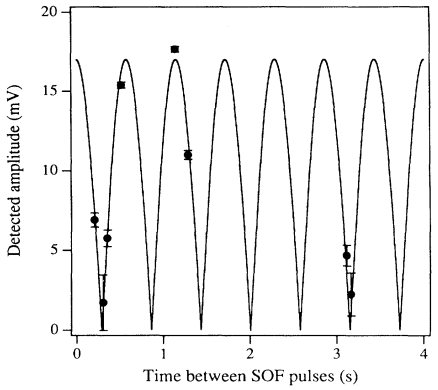

FIG. 1. SOF technique for determining ω_c'. For each point, the cyclotron mode was given two pulses centered at $\omega_c'/2\pi - 1.75$ Hz and separated by time T, and the resultant amplitude detected by changing the trap voltage to bring the ion into axial resonance and applying a π pulse. We can determine the order of each fringe unambiguously if the separation times are incremented by a factor less than 3. The precision measurement of ω_c' comes from points with $T = 50$ s.

TABLE II. Nondoublet ratios and atomic masses. In (a), we list the nondoublet ratios measured and the values obtained using the current nuclear mass table (see Ref. [6]). Note that the first two ratios (designated with an *) are known to a few ppt accuracy, and depend only weakly on the masses in Ref. [6]. In (b), we have converted the comparisons to C^+ into masses of H, D, and the neutron after correcting for binding energies.

(a)

Ratio	Measured	Accepted [6]
N_2^+/N^+	2.000 039 175 61(29)	2.000 039 175 424(1)*
Ar^+/Ar^{++}	2.000 027 454 12(36)	2.000 027 454 084(1)*
CH_4^+/C^+	1.335 957 033 78(23)	1.335 957 034 89(300)
CD_3^+/C^+	1.503 548 462 35(20)	1.503 548 462 71(400)
CD_4^+/C^+	1.671 397 950 39(31)	1.671 397 950 57(480)
Ar^+/Ne^+	1.998 902 121 05(30)	1.998 902 607 38(23000)

(b)

Species	Mass (nu)	Accepted [6]
H	1 007 825 031.7(7)	1 007 825 035.0(120)
D	2 014 101 777.9(6)	2 014 101 779.0(240)
n	1 008 664 923.4(23)	1 008 664 904.0(140)

of ω_z for N_2^+ with the square root of the mass ratio. The precision with which this scale factor needs to be known is much smaller than the ultimate precision, and we can use the mass values from the standard table [6].

We have tested our new technique for nondoublet mass comparisons, and the error analysis presented above, by performing measurements on two systems with known ratios, namely N_2^+/N^+ and Ar^+/Ar^{++}. In Fig. 2, the cyclotron frequencies of N^+ and N_2^+ are plotted as a function of time. The slow drift in the frequencies is attributed to variations in the magnetic field at the location of the ions. A polynomial fit was used to take out this drift before extracting the ratio. For a given N^+ ion, the frequency was measured both in an N_2^+ trap—using the SOF technique described above—and an N^+ trap with our conventional PNP technique. There is a clear systematic shift of order 3 ppb for the latter case which disappears with our new method. Both the measurements were performed with 22.5 mV axial offset in order to eliminate axial shifts in the equilibrium position of the ions. As seen from Table II, our claimed errors and the discrepancies from the known values are at the 0.15 ppb level.

Some of the useful measurements we have performed with this new technique are summarized in Table II. In Fig. 3, we show the results of a typical night of measurement on a nondoublet, Ar^+/Ne^+. Each ratio of neigh-

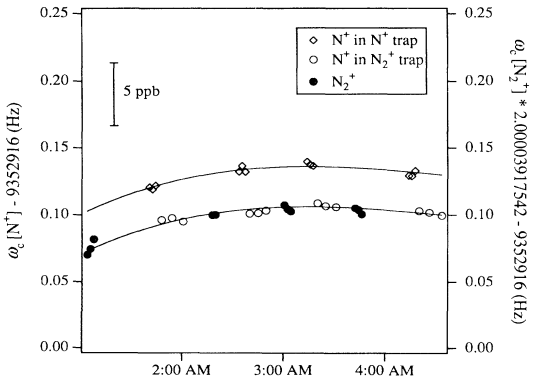

FIG. 2. Free space cyclotron frequencies for N^+ and N_2^+. The frequency for the same N^+ ion was measured both in an N^+ trap (with 5 V) and in an N_2^+ trap (with 10 V). The frequency for N_2^+ has been scaled by the known ratio of $M[N_2^+]/M[N^+]$, so that the plotted points for the two ions should line up if there are no systematic errors. The solid line is a third-order polynomial fit to the magnetic field drift.

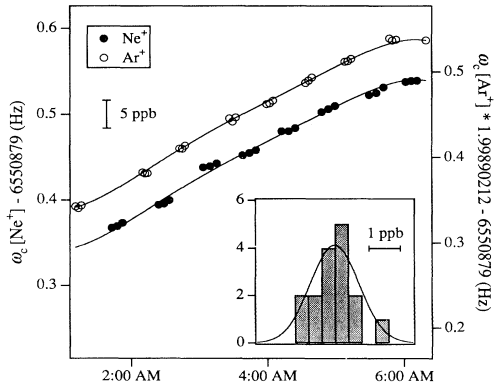

FIG. 3. Mass ratio measurement for a typical nondoublet Ar^+ vs Ne^+. The cyclotron frequency for Ne^+ was measured using the SOF technique in an Ar^+ trap. The magnetic field drift was taken out with a fifth-order polynomial fit. Each ratio of neighboring frequencies was taken as an independent measure of the mass ratio to obtain the histogram presented.

boring frequencies on the two ions, after removing the polynomial drift, is taken as an independent measure of the mass ratio. The average ratio remains robust as we increase the order of the fit polynomial, while the distribution approaches a Gaussian. We rarely go beyond sixth or seventh order, and the histogram presented here is for a fifth-order fit. There are no apparent non-Gaussian errors. If we do not take out the temporal drift, the average is nearly the same, but the distribution is bimodal as we obtain alternately high and low values for the ratio. For this particular comparison, we were able to perform an independent check on our measurement using the doublet comparison Ar^{++}/Ne^{+} [5], and the two results agree within their errors. The errors quoted in Table II are caused predominantly by magnetic field fluctuations around the slow drift, and are limited by how fast we can switch between the two ion species.

The comparisons to C^{+} have been converted to atomic masses of H and D. As mentioned earlier, the mass of D was obtained from two independent comparisons (using CD_3^{+} and CD_4^{+}) and their agreement is another check on our error estimates. Our new values are in good agreement with the standard nuclear mass table [6] but represent more than an order of magnitude improvement in precision. They can be combined with the average value of the deuteron binding energy [16] to yield the neutron mass; the improvement by only a factor of 6 is limited by the imprecision of the deuteron binding energy.

The precision masses of H and D reported here are useful for mass spectrometry in general since they can be used in a manner analogous to the smallest weights in a balance pan set. Once their masses are known, masses of other species can be determined just from doublet comparisons using compounds formed by adding suitable H and/or D atoms (e.g., CH_2^{+}/N^{+} or CD_2^{+}/O^{+}).

The improved level of precision demonstrated in this paper opens up several new experiments of fundamental interest. Measurement of the end point of the tritium decay spectrum to 0.3 eV can aid ongoing beta ray spectroscopy experiments to determine the rest mass of the electron neutrino [17]. An accurate knowledge of the binding energy of nuclei (in u) when combined with a precise wavelength measurement of the associated γ ray would yield the value of $N_A h$, and, in conjunction with the M_e/M_p ratio and the Rydberg constant, an independent value for α^2 [18].

Finally, we have achieved precision below 0.1 ppb in some cases while comparing doublets [5] and the error analysis in Table I shows that this should be possible for nondoublets, too, if we can get sufficient statistics in one run. Nevertheless, the size of our present field fluctuations will probably limit us around 0.05 ppb, and we feel the route to greatly increased precision lies in measuring the frequency of the two ions simultaneously [19].

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