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Precision mass ratio of $^3He^+$ to HD^+

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By measuring the cyclotron frequency ratio of $^3He^+$ to HD^+ directly, with confirmation from measurements using H_3^+ as an intermediary, we obtain $M[^3He^+]/M[HD^+] = 0.998\,048\,085\,122(23)$ and hence the mass difference $m_p + m_d - m_h = 0.005\,897\,432\,19(7)$ u. This result disagrees by more than four standard deviations with the value inferred from current precise literature values for the atomic masses of the proton, deuteron, and nucleus of ^3He.

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Precision measurements of the cyclotron frequency ratios (CFRs) of single ions in a cryogenic Penning trap yield atomic mass ratios with applications to fundamental constants and tests of fundamental physics [1]. In particular, due to the near cancellation of most systematic errors, the measurements of CFRs of ions of the same total mass number have the potential for the highest precision. In a previous paper [2] we reported measurements of the CFRs $HD^+/^3He^+$ and HD^+/T^+. The ratio of these ratios yielded the mass difference between tritium and ^3He, and hence the Q value of tritium beta decay, an important parameter for testing the systematics of current [3], and future [4], tritium beta-decay spectroscopy, aimed at setting laboratory limits on the mass of the electron antineutrino.

The individual $HD^+/^3He^+$ and HD^+/T^+ CFRs, of course, also relate the masses of ^3He and T to those of H and D [5]. Soon after the publication of Ref. [2], new results for the atomic masses of ^3He and D, obtained from direct measurements against ^{12}C, were published by the University of Washington (UW) group [6]. When these ^3He and D masses were combined with the Committee on Data for Science and Technology (CODATA2010) value for the mass of the proton [7] (which was mainly derived from an earlier result by the UW group [8], and a result from a group at the University of Stockholm [9]), there was an inconsistency with the CFR for $HD^+/^3He^+$ measured in Ref. [2]. Specifically, the equivalent mass difference, $m_p + m_d - m_h$, where, here, m_d and m_h are the masses of the deuteron and the helion (the nucleus of ^3He) taken from Ref. [6], and m_p is the mass of the proton from Ref. [7], was greater than the result derived from our 2015 $HD^+/^3He^+$ measurement [2] by 0.79(18) nu, where the number in parentheses is the combined standard uncertainty. This large discrepancy has sometimes been referred to as the "^3He puzzle," although it could also have been due to errors in the accepted values of m_p and m_d. And in fact, a new, more precise measurement of m_p has been recently published [10], with a result that is about three combined standard uncertainties lighter than the CODATA2010 value [7]. Using this new value for m_p, the discrepancy for $m_p + m_d - m_h$ with respect to our 2015 result [2] was reduced to 0.56(16) nu, however, this is still more than three standard uncertainties.

It was still unclear if this remaining inconsistency was the result of an underestimated error in the $HD^+/^3He^+$ result [2], or in the individual measurements of m_p, m_d, and m_h. This leads to difficulties in assigning the best values for m_p, m_d, and m_h in the CODATA adjustment of fundamental constants [11]. This problem is made more urgent by the proposed redefinition of the International System of Units (SI) in terms of fundamental constants. The discrepancy may also reduce confidence in the precise tritium Q-value result of Ref. [2], which is required for the validation of the ongoing measurements of electron neutrino mass by the Karlsruhe Tritium Neutrino Experiment (KATRIN) and future tritium beta-decay experiments [3,4,12]. Hence, having made significant improvements to our Penning trap mass spectrometer, enabling a reduction in statistical and systematic uncertainties, we have carried out new measurements of the $HD^+/^3He^+$ CFR. Our new CFR has half the uncertainty and is in good agreement with our previous result [2], hence validating the significantly smaller value for $m_p + m_d - m_h$, compared to that obtained by combining the results in Ref. [6] with those in Ref. [10], or Ref. [7].

To provide additional confirmation of our result for $HD^+/^3He^+$ we have also measured H_3^+/HD^+ and $H_3^+/^3He^+$. From the ratio of ratios, this gives another value for $HD^+/^3He^+$. We note that the measured CFRs involving H_3^+ cannot be simply used to relate m_d and m_h to m_p, since the H_3^+ can be in a metastable rotational level, with energy above the molecular ground state of a fraction of an eV [13]. It is hence also necessary to carry out the H_3^+/HD^+ and $H_3^+/^3He^+$ measurements using the same H_3^+ ion. This is discussed further in a related paper [14], where we also obtain lower limits on m_d and m_h with respect to m_p. By contrast, due to its body-frame dipole moment, the HD^+ can be assumed to be in its rovibrational ground state in the 4.2-K environment of our ion trap.

Since our apparatus and procedures have been described previously [1,2], here we present only an outline and indicate changes from our previous work. Our Penning trap mass spectrometer uses a single set of hyperboloidal electrodes, maintained at 4.2 K in extreme high vacuum, inserted into the bore of an 8.5-T superconducting magnet. Since the work of Ref. [2], the magnet cryostat was disassembled to repair a vacuum leak, and hence the magnet has been reenergized and reshimmed. This enabled the reduction of the quadratic magnetic field inhomogeneity, usually specified by the ratio B_2/B_0 [15], by a factor of 20 to $B_2/B_0 = -5.7(3) \times 10^{-9}\ \mathrm{mm}^{-2}$.

All information on the ions in the trap is obtained from detecting their axial motion via image currents induced in a superconducting resonant circuit, with a quality factor of

34 000 at 688 kHz, inductively coupled to a dc superconducting quantum interference device (SQUID). Compared to Ref. [2], this detection circuit has been improved by replacing the dc-SQUID and controller with one that uses a high-bandwidth flux-locked loop [16,17], which, with other improvements in grounding and shielding, has significantly reduced the noise at our detection frequency.

The ions were made inside the Penning trap by electron beam ionization using a nominal 10-nA, 900-eV electron beam from a field emission point (FEP). HD^+ and $^3He^+$ ions were made by injecting a 5-ms pulse of a tenuous molecular beam of the parent gas along the axis of the trap, in coincidence with the electron beam. In the case of H_3^+, which we assume is made by collisions of H_2^+ with H_2 [18], this procedure was ineffective. Instead, using the fact that H_2 can be liberated from surfaces impacted by the electron beam, H_3^+ ions were made by operating the FEP for periods of 30 s without injecting gas, but usually requiring ten or more tries. Successful production of a desired ion after making an attempt could be seen in real time from the signal from its large axial motion. After making a desired ion, the unwanted ions were removed using our usual procedures.

The largest source of statistical uncertainty in our CFR measurements is variation in the magnetic field. This makes it desirable to alternate between measurements of the cyclotron frequency of each ion in a pair as rapidly as possible. To achieve this, we simultaneously trap both ions, and alternate them between a large radius "parking" orbit and the center of the trap, where the cyclotron frequency measurement is carried out [19]. Due to the reduction of B_2, and due to improvements in our recentering procedure, we were able to recenter the outer ion from a cyclotron radius of 2.0 mm in 4 min, compared to 1.1–1.3 mm in a similar time previously.

The (trap-modified) cyclotron frequency of the inner ion was measured using the pulse-and-phase technique [20,21]. In this method, pulsed excitation of the cyclotron motion to a well-defined radius is followed by a variable delay to allow the cyclotron phase to evolve, after which, by using a pi pulse at the cyclotron-to-axial coupling frequency, the action of the cyclotron motion is phase coherently transferred to the axial motion. The modified cyclotron frequency is then obtained from the gradient of the final cyclotron phase with respect to evolution time. This is then combined with the axial and magnetron frequencies to obtain the true cyclotron frequency using the invariance theorem [15]. Due to the detector improvements, and with the axial frequency set 70 Hz above the detector resonance frequency, we were able to obtain a better signal-to-noise ratio using a cyclotron radius of 20–25 μm than we were able to obtain with a 45-μm cyclotron radius in Ref. [2], and with no ambiguities in phase unwrapping. Also, compared to Ref. [2], the switching of the cyclotron drive and cyclotron-to-axial coupling drives was improved, reducing the possibility of phase shifts due to drive signal leakage. Examples of the alternating cyclotron frequency data used to obtain the CFRs are shown in Fig. 1.

The results presented here were obtained from part of a data-taking campaign of over 120, 6–10 h runs, including tests of systematics, carried out from February to August 2017. The direct $HD^+/^3He^+$ measurements were made in February and June. The measurements of H_3^+/HD^+ and $H_3^+/^3He^+$, which used the same H_3^+ ion, and which provide a confirming value for $HD^+/^3He^+$, were obtained in March and April. Other measurements of H_3^+/HD^+ and $H_3^+/^3He^+$ were carried out using different H_3^+ ions and will be discussed in a companion paper [14]. In addition, we carried out measurements of H_3^+/H_2^+ to test for mass-dependent systematics.

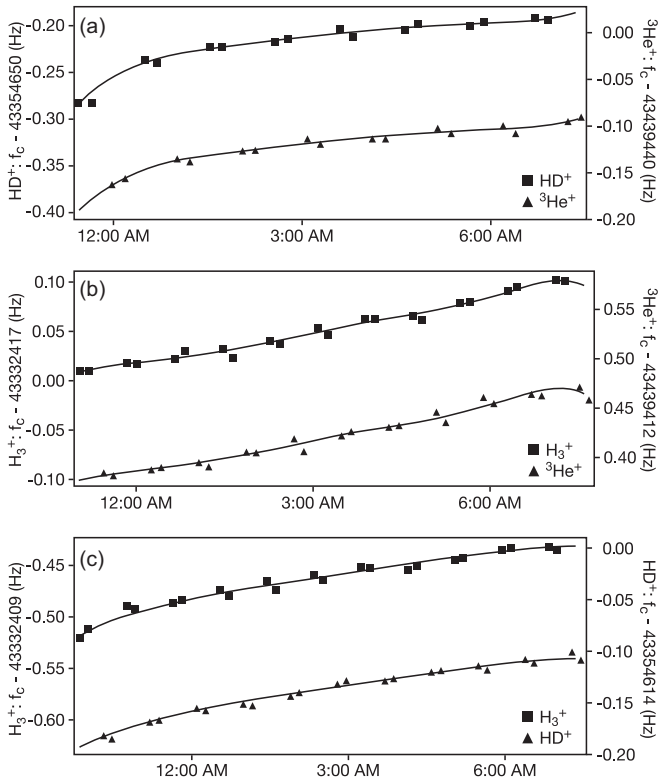

FIG. 1. Examples of cyclotron frequency data used to obtain ion mass ratios, (a) $HD^+/^3He^+$, (b) $H_3^+/^3He^+$, (c) H_3^+/HD^+. In each case the CFR is obtained from a fit of similar polynomials to the trap-modified cyclotron frequency data vs time.

Table I summarizes the average CFRs from which we obtain our $^3He^+/HD^+$ mass ratio. The first three columns indicate, respectively, the ion pair, the start and end date of

TABLE I. Average cyclotron frequency ratios and systematic corrections for the different ion pairs. "Dates" indicates the date of the first and last run used to form the average. "Runs" is the number of runs used in the average. R_{unc} is the uncorrected average CFR, with statistical uncertainty in parentheses. Δ_{imb} is the correction for imbalance in the cyclotron radii with uncertainty in parentheses. Δ_{pol} is the correction due to the polarizabilities of the HD^+ and H_3^+ ions (both Δ_{imb} and Δ_{pol} are in units of 10^{-12}). Note that the H_3^+ ion was in a metastable rotational level, and so its mass is increased by an unknown amount of order 0.5 eV/c^2 with respect to an H_3^+ ion in its ground state.

Ion pair	Dates	Runs	R_{unc}	Δ_{imb}	Δ_{pol}
$HD^+/^3He^+$	2/16–3/1	11	0.998 048 085 049(13)	−20(4)	94
$H_3^+/^3He^+$	3/9–4/9	13	0.997 536 905 750(10)	−26(5)	1
H_3^+/HD^+	4/13–4/21	13	0.999 487 820 978(11)	−4(1)	−94
$HD^+/^3He^+$	6/14–6/15	4	0.998 048 085 042(27)	−17(3)	94

data taking, and the number of runs. The fourth column gives the uncorrected average CFR, with each run weighted as $1/\sigma_i^2$, where σ_i^2 is the statistical uncertainty for the result of run i, as returned by the fits as in Fig. 1. The corresponding statistical uncertainty for the average is in parentheses. The fifth column gives the correction due to imbalance in the cyclotron radii, with statistical uncertainty in this correction (see below), while the sixth column gives the correction [22] due to the large polarizability of HD^+ in its rovibrational ground state [23,24], and the small polarizability of H_3^+ in its vibrational ground state [25,26], which contributes only 1×10^{-12} to the CFR.

As discussed previously [1,2], the cyclotron frequencies obtained from the pulse-and-phase technique are shifted due to special relativity and imperfections in the magnetic and electrostatic fields, combined with the amplitudes of the three normal modes [27]. The fractional relativistic shift for a cyclotron radius of 25 μm is -2.6×10^{-10}, while, using our measured values of B_2 and the electrostatic imperfection parameters C_4 and C_6 [15], the fractional frequency shifts due to field imperfections are in total less than 10^{-11}. Hence, the total systematic shifts to the cyclotron frequencies are reduced a factor of 4 compared to our previous work [2] and are dominated by special relativity. Because we measure CFRs between ions in a pair which differ in mass by at most 0.25%, and the ions are driven to nominally the same cyclotron radius using pulses of the same duration and same amplitude (within 0.3% at the frequency synthesizer), one expects the resulting amplitude-dependent shifts to the CFRs to be smaller than the fractional shifts to the individual cyclotron frequencies by two orders of magnitude. However, in our previous measurements of the $HD^+/^3He^+$ and HD^+/T^+ ratios [2], we observed that the axial amplitudes after the pulse-and-phase sequences, averaged over a whole run, showed an imbalance of about 3%, which implied a surprisingly strong frequency dependence of the cyclotron drive transfer function from outside the cryostat to the trap electrodes. In the current work we observed a similar imbalance in axial amplitude between ions in a pair, and that it varied linearly with the cyclotron frequency difference [28]. Moreover, in contrast to Ref. [2], we were able to obtain CFR measurements from runs using cyclotron radii (nominally the same for both ions in a pair) varying from approximately 20 to 60 μm. The observed variation in the measured CFR was consistent with the strong variation in transfer function. So, to correct for the cyclotron radius imbalance, we assume a correction given by $\Delta R = C T_{CD}^2 V^2 \Delta f_{ct}$, where T_{CD} is the cyclotron drive pulse length, V the voltage amplitude at the synthesizer, Δf_{ct} is the modified cyclotron frequency difference, and C is a parameter obtained by fitting to all the data in which the cyclotron radius was varied. This is the imbalance correction in column 5 of Table I.

A second source of systematic error is from differences in the average positions of the ions in the trap, due to the slightly different trap voltages used to bring the different ions in a pair to the same axial frequency, combined with a linear gradient in the magnetic field. To test for this, and also for any unknown systematic that depends on trap voltage, we measured the cyclotron frequency ratio between an H_2^+ and H_3^+ ion, the trap voltage for H_2^+ being nearly 2/3 that for H_3^+. On 6/3/2017, using a H_2^+ made that day, and a H_3^+ made 2 days earlier, and using cyclotron radii of 25(5) and 23(4) μm for the H_2^+ and H_3^+ ions, respectively, we measured the H_3^+/H_2^+ CFR to be 0.666 606 178 59(3)(10), where the first number in parentheses is the statistical uncertainty, and the second is the uncertainty in the relativistic shift due to the uncertainty in the cyclotron radii. This is in good agreement with the calculated ratio 0.666 606 178 6(2), obtained using the atomic masses of the proton [10] and electron [11], and energies of formation for H_2^+ [23,29] and H_3^+ [30,31]. Here, to allow for the fact that the H_2^+ could have been formed in one of several vibrational levels, with mean lifetimes of several days [29,32], we follow Solders *et al.* [9] by assuming an average excitation energy of 0.74(55) eV [33,34]. We also allow for the unknown rotational excitation of the H_3^+ by assuming a H_3^+ stored energy of 0.3(3) eV [13]. By appropriately scaling the difference between the measured and calculated H_3^+/H_2^+ CFR according to the difference in trap voltages, this result is consistent with any voltage-dependent shift of the ratios between the mass-3 ions being $<2 \times 10^{-12}$, and so negligible.

With the outer ion in a 2-mm-radius cyclotron orbit, the effect of the ion-ion interaction on the CFR is estimated to be less than 1×10^{-12} [19]. This was checked by carrying out 15 additional runs with a reduced outer ion radius of 1.1 mm, where ion-ion interaction effects would be expected to be larger by a factor of $(2/1.1)^5$. Averaged over all the relevant data, the shift in the average CFR for an outer ion radius of 1.1 mm, with respect to a radius of 2 mm, was $-4(11) \times 10^{-12}$, consistent with a negligible shift at 2 mm. We also considered shifts to the CFR caused by possible ion-differential heating of the trap electrodes by the rf drives during the recentering procedure, even though the drives are applied symmetrically for both ions [35]. This was investigated by asymmetrically varying the time the drives were applied for, and by introducing asymmetric delays, and found to be negligible for data taken under normal conditions. Several other sources of systematic error such as image charge shifts, ion-detector interactions, and systematic uncertainty in measuring the magnetron frequency were considered and found to contribute at below the 10^{-12} level. In addition, many instrumental tests were made, including tests of the phase coherence and frequency accuracy of the synthesizers.

From Table I we see that there is good agreement between the $HD^+/^3He^+$ CFRs measured in February and June. From their weighted average we obtain the ion mass ratio $M[^3He^+]/M[HD^+] = 0.998\,048\,085\,122(12)(4)$, where the first number in parentheses is the estimated statistical uncertainty, and the second is the uncertainty in the imbalance correction obtained from the fits to data in which the cyclotron radius was varied. If we take the ratio of the H_3^+/HD^+ and $H_3^+/^3He^+$ CFRs, we obtain $M[^3He^+]/M[HD^+] = 0.998\,048\,085\,115(15)(4)$, which is in very good agreement. Although it is tempting to average these two results, because we cannot be certain the H_3^+ did not undergo rotational transitions during the 6 weeks of data taking, we use the double ratio as a redundant check. Further, because we are still concerned about the relatively large cyclotron radius imbalance correction, and we wish to be conservative in our error estimation, we increase our systematic uncertainty to 100% of the imbalance correction.

TABLE II. Mass difference from our cyclotron frequency ratio compared with results from the literature. For "this work," the numbers in parentheses are the statistical, systematic, and total uncertainties; for the result obtained from Refs. [6,10], the number in parentheses is the total uncertainty, ignoring any possible correlations.

Source	$m_p + m_d - m_h$ (u)
This work	0.005 897 432 191(37)(60)(70)
Refs. [6,10]	0.005 897 432 660(67)
Difference	−0.000 000 000 469(97)

Hence, our final result for the ion mass ratio is

$$M[^3\mathrm{He}^+]/M[\mathrm{HD}^+] = 0.998\,048\,085\,122(12)(20)(23),$$

where the numbers in parentheses are the statistical, systematic, and total uncertainties, respectively. This is in good agreement with our previous result for the same mass ratio [2], 0.998 048 085 153(17)(45)(48). This agreement is even better if, to the result in Ref. [2], we apply 100% instead of 50% of the imbalance correction, as we now believe we should, resulting in 0.998 048 085 130(17)(45)(48).

Using theoretical values for the ionization energy of $^3\mathrm{He}^+$ [36] and the energy of formation of HD^+ [23] we can convert the $^3\mathrm{He}^+/\mathrm{HD}^+$ mass ratio to a mass difference between their nuclei. In Table II we show the mass difference $m_p + m_d - m_h$ obtained from our direct $\mathrm{HD}^+/^3\mathrm{He}^+$ CFR, compared with the result obtained from m_d and m_h given in Ref. [6], and m_p given in Ref. [10]. Using the value for u expressed in eV from CODATA14 [11], our value for the mass difference is equivalent to a Q value for the $d(p,\gamma)^3$He nuclear reaction of 5 493 423.264(65)(34) eV, where the uncertainties in parentheses are due to uncertainty in the mass difference and the conversion factor, respectively.

With an upgraded apparatus and extensive tests of systematics we have remeasured the $\mathrm{HD}^+/^3\mathrm{He}^+$ cyclotron frequency ratio, both directly and by using $\mathrm{H_3}^+$ as an intermediary. Our $\mathrm{HD}^+/^3\mathrm{He}^+$ CFR obtained by direct measurement agrees with the ratio of the $\mathrm{H_3}^+/\mathrm{HD}^+$ and $\mathrm{H_3}^+/^3\mathrm{He}^+$ CFRs measured with the same $\mathrm{H_3}^+$ ion. Our new result has half the uncertainty of, and agrees with, our previous result [2], which was one of two measurements required to obtain a precise Q value for tritium beta decay, and so revalidates the Q-value result. Our new value for the mass difference $m_p + m_d - m_h$ is still significantly smaller, by 0.47(10) nu, than that obtained from the most precise masses of these nuclei with respect to ^{12}C [6,10].

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