Editors' Suggestion

Mass Difference of Tritium and Helium-3

Moisés Medina Restrepo and Edmund G. Myers
Department of Physics, Florida State University, Tallahassee, Florida 32306-4350, USA

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From cyclotron frequency ratios of $HD^+/^3He^+$, HD^+/T^+, and $T^+/^3He^+$ we measure the mass difference between atoms of T and ^3He to be $1.995\,940\,8\,(23) \times 10^{-5}$ u, corresponding to a Q value for tritium β decay of 18 592.071(22) eV. This enables an improved check on systematics of β decay experiments that set limits on neutrino mass. Using the HD^+ mass calculated from the atomic masses of the proton and deuteron as given by Rau *et al.* [Nature **585**, 43 (2020)], we also obtain improved atomic masses for the triton and helion (considered to be fundamental constants), namely, 3.015 500 716 066 (39) and 3.014 932 246 957 (38) u.

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Twenty-five years after the discovery via neutrino oscillations that neutrinos have mass [1], their absolute masses are still unknown, a situation that impacts both particle physics and cosmology [2]. The least model-dependent method of setting limits on absolute neutrino mass is the study of the electron spectrum of tritium β decay near its end point. The KATRIN Collaboration, operating a large-scale magnetically collimated electrostatic filter spectrometer with a gaseous tritium source, has already published a limit on effective electron-neutrino mass $m(\nu_e) < 0.8\ \mathrm{eV}/c^2$ (90% confidence) and aims for a reduction to $< 0.2\ \mathrm{eV}/c^2$ before completion [3–5]. At the same time, the Project-8 Collaboration is developing the novel technique of measuring electron energy via the detection of cyclotron radiation, with the eventual goal of $m(\nu_e) < 0.04\ \mathrm{eV}/c^2$ using an atomic tritium source [6,7]. In both these experiments, due to the very small number of events within $m(\nu_e)$ of the true end point, the information on neutrino mass is obtained from fitting the electron spectrum over a range extending more than 10 eV below the end point. Over this range, the neutrinos are relativistic and the analyses yield values for $m(\nu_e)^2$ and also the "end point for zero neutrino mass," E_0. After making corrections for recoil and electronic and molecular binding energies, E_0 can be related to the tritium β-decay Q value, defined as the mass difference between atoms of T and ^3He. Although E_0 is not used directly in determining $m(\nu_e)^2$, the comparison of the Q value from a Penning trap mass difference measurement with E_0 from the neutrino mass experiments provides an independent check of the electron spectroscopy. In the case of KATRIN, this includes all processes that affect the electron energy from the source to the retarding potential, including surface potentials, space charge, and scattering. Understanding these processes is important since spectral broadening, particularly due to spatial and temporal source potential variations, is a significant source of systematic error [5,8].

Our group has previously measured the T-^{3}He mass difference with an uncertainty of $0.07\ \mathrm{eV}/c^2$ by measuring the cyclotron frequency ratios (CFRs) $HD^+/^3He^+$ and HD^+/T^+ [9]. (HD^+ was used as an intermediary because T^+ and $^3He^+$ have such similar masses, with fractional difference approximately 6.6×10^{-6}, that they are difficult to manipulate independently in a Penning trap.) However, our $HD^+/^3He^+$ CFR disagreed by more than 4 combined standard deviations with results from another group. Specifically, results for m_d and m_h (the mass of the helion, i.e., the nucleus of helium-3) published by the University of Washington (UW) mass spectrometry group [10], combined with the then CODATA m_p (also derived mainly from UW results) [11], produced a value for the mass difference $m_p + m_d - m_h$ greater than that obtained from our $HD^+/^3He^+$ CFR by 0.79(18) nu. Since this discrepancy could undermine the credibility of our measured tritium Q value, we remeasured the $HD^+/^3He^+$ ratio with a rebuilt apparatus and improved procedures, obtaining a result in agreement with our 2015 result [12,13]. Further, since then, the discrepancy in $m_p + m_d - m_h$ has been partly resolved by new measurements of m_p [14] and m_d [15] by the MPIK-Mainz-GSI Collaboration. If these replace the CODATA [11] and UW [10] values, $m_p + m_d - m_h$ from measurements directly against ^{12}C differs from the value from the $HD^+/^3He^+$ ratio of [9] by 0.35(15) nu and from that of [12] by 0.26(9) nu.

Nevertheless, given these remaining discrepancies and the possibility that future tritium β-decay experiments may determine E_0 to better than 0.07 eV, we considered it appropriate to finally apply our improved apparatus and techniques to new measurements with tritium, which we report here. The improvements include a reduction in the quadratic magnetic field inhomogeneity by more than a factor of 30, an improved detector for the axial motion of the ion—which enabled smaller and variable cyclotron radii in the cyclotron frequency measurements, improved

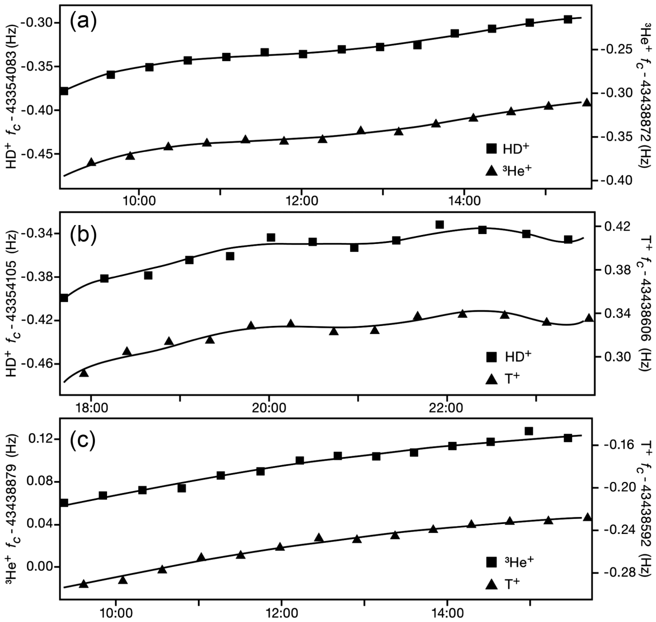

FIG. 1. Examples of cyclotron frequency versus time data for runs of (a) $HD^+/^3He^+$, (b) HD^+/T^+, and (c) $T^+/^3He^+$.

radio-frequency switching, and an increase in the "parking" radius of the outer ion. In addition, we have now developed methods for making and manipulating pairs of ions of very similar mass in our Penning trap, enabling us to carry out a direct measurement of the $T^+/^3He^+$ CFR. This resulted in an increase in precision and a cross-check against systematic errors. Our new result for $M[\mathrm{T}] - M[^3\mathrm{He}]$ agrees with our previous result, but has a factor of 3 smaller uncertainty. We also reconfirm our earlier values for $m_p + m_d - m_h$. Combined with the most recent values for m_p and m_d from direct measurements against ^{12}C [15] (but also utilizing a measurement of m_d/m_p [16,17]), our new CFRs yield improved atomic masses for the triton and helion, which are considered to be fundamental physical constants.

Our measurements used a Penning trap [18–20] with hyperboloidal electrodes with characteristic size $d =$ 5.5 mm, in a highly uniform 8.53 T magnetic field produced by a superconducting magnet. The trap was enclosed in a copper can surrounded by liquid helium that filled the bore of the magnet. The trap has a set of compensation electrodes that can null the quartic electrostatic potential imperfection C_4 [18], hence making the axial motion of a single ion highly harmonic. The ion's axial motion can then be detected (and damped) via the image current induced in a high-Q (34 000) superconducting tuned circuit with resonance frequency near 688.5 kHz, connected across the end caps of the trap and inductively coupled to a dc superconducting quantum interference device [21]. Ions were made inside the trap by electron beam ionization of a pulsed molecular beam of HD, ^{3}He, or T_2 which entered the trap through a 0.5 mm diameter hole in the upper end cap. Unwanted ions were removed by selectively exciting their axial motions and then lowering the potential on the lower end cap until they reacted with its surface, while the desired ions' axial motions were damped by bringing them to resonance with the tuned circuit. In the case of unwanted $^3He^+$ ions produced while making T^+ from T_2 contaminated with ^{3}He, we first separated the ions in axial frequency by selectively exciting their cyclotron motion and then applying a large C_4. Over the course of the data taking we used six HD^+, five $^3He^+$, and two T^+ ions, with trapped ion lifetimes (limited by collisions with neutrals) varying from days to months.

The two ions in the pair whose CFR was to be measured were trapped simultaneously, one at the center of the trap and the other in a 2 mm radius cyclotron orbit (1.1 mm was used in [9]). The cyclotron frequency of the ion at the center of the trap was measured using the "pulse-and-phase" technique [22]. In this method, the trap-modified cyclotron frequency f_{ct} (near 43.4 MHz) is obtained by exciting the ion's cyclotron motion using a resonant drive pulse, then allowing the cyclotron phase to evolve for time T_{evol}, and then mapping the final phase onto the axial motion using a "classical π pulse" at the cyclotron-to-axial coupling frequency [23]. The resulting axial ringdown signal is then digitized and Fourier transformed to yield its frequency f_z and phase ϕ. We repeat the pulse-and-phase sequence 14 times (which we call a pulse-and-phase cycle), with T_{evol} from 0.1 to 10 or 15 s, and extract f_{ct} from $d\phi/dT_{\mathrm{evol}}$. The corresponding f_z is obtained by averaging the 14 measurements of f_z over the cycle. The "true cyclotron frequency," $f_c = (1/2\pi)qB/m_{\mathrm{ion}}$, is then obtained by combining f_{ct}, f_z, and the magnetron frequency f_m, in the invariance theorem $f_c^2 = f_{\mathrm{ct}}^2 + f_z^2 + f_m^2$ [18]. (f_m was obtained to adequate precision from a single measurement using a variant of the pulse-and-phase method). To optimize the determination of ϕ and f_z, the damping time was increased during the pulse-and-phase measurements by setting f_z about 80 Hz above the coil resonance frequency, and the ringdown signal was acquired for 8 s.

After a measurement of f_c on one ion, the ions were interchanged. The outer ion was recentered using a continuous cyclotron-to-axial coupling drive, while its axial motion was damped by interaction with the detection circuit. The inner ion was swept out using a down-chirped cyclotron drive. (More details are given in the Supplemental Material [24].) The recentering and sweep-out process took 6 min. The pulse-and-phase cycle, including magnetron-to-axial pulses to prevent increase in the magnetron motion, and also axial cooling of the outer ion, took 8 min. A single experimental run lasted 6–7 h and yielded up to 15 alternate measurements of f_c of each ion. The run time was limited by the hold time of a liquid nitrogen Dewar that shields the Penning trap insert and the need to reset coupling frequencies and voltages to allow for drifts of the magnetic field and the detector's resonant frequency.

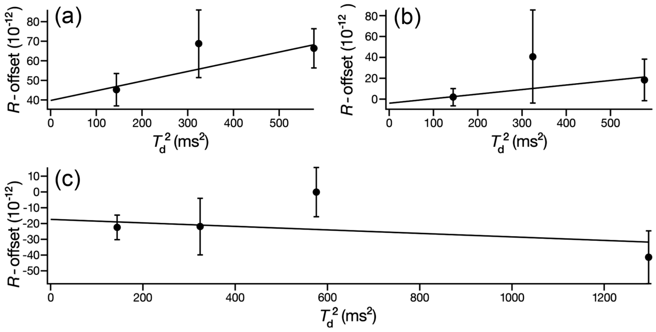

FIG. 2. Averaged cyclotron frequency ratios versus the square of the cyclotron drive time: (a) $HD^+/^3He^+$, (b) HD^+/T^+, and (c) $T^+/^3He^+$. The fits shown are independent straight line fits to each of the ratios. The offsets used in (a)–(c) are 0.998 048 085 000, 0.998 054 687 200, and 0.999 993 384 990, respectively.

The CFR was obtained by our usual procedure of fitting both ions' f_c versus time data to a common polynomial with a constant offset, with the optimum fit order obtained using an F test [25]. Examples of cyclotron frequency data for the three ion pairs $HD^+/^3He^+$, HD^+/T^+, and $T^+/^3He^+$ are shown in Fig. 1. For some runs, where $\lesssim 50$ nT jumps in the ambient magnetic field occurred due to current switching in a magnetic spectrograph in a nearby accelerator area, we corrected both ions' f_c data using the output of a fluxgate magnetometer (see Supplemental Material [24]). Our results are based on a total of 84 runs of $HD^+/^3He^+$, 74 of HD^+/T^+, and 79 of $T^+/^3He^+$, with additional runs to calibrate the cyclotron drives and investigate systematic errors. The typical statistical uncertainty of a single run from the polynomial fit was 4 to 5×10^{-11}. In addition to magnetic field noise, poorer statistical precision for some runs was caused by intermittent electromagnetic interference contaminating the axial signal.

For most of the measurements, we used a cyclotron radius ρ_c of 22 μm resulting in a relativistic shift to the individual cyclotron frequencies of -2.0×10^{-10}. Although, ideally, this shift should cancel in the CFRs, to allow for possible frequency-dependent systematic differences between the drive amplitudes applied to the ions, we also used ρ_c of 33 and 44 μm for all three pairs and, additionally, 66 μm for $T^+/^3He^+$. (The attenuation of the drive train from the frequency synthesizer to the drive electrode is frequency dependent due to imperfect impedance matching and due to a transformer filter in the cryogenic electronics, which, for historical reasons, was optimized for 5 MHz and not 43 MHz.) This was done by keeping the amplitude setting of the frequency synthesizer producing the cyclotron drive constant and varying the drive time T_d from 12 to 36 ms. We then modeled each of the three CFRs using $R_i(T_d) = R_i(0) + a_i T_d^2$, where a_i are constants allowing for cyclotron drive imbalance, with $i = 1, 2, 3$ corresponding to the $HD^+/^3He^+$, HD^+/T^+, and $T^+/^3He^+$ ratios, respectively. Our results for the averaged CFRs plotted against T_d^2 are shown in Fig. 2.

Given that f_{ct} for the $^3He^+$ and T^+ ions differs by only 287 Hz in 43.4 MHz, one might assume a model in which the slopes of $HD^+/^3He^+$ and HD^+/T^+ versus T_d^2 are equal and that of $T^+/^3He^+$ is zero. Performing a simultaneous fit with these constraints to all the data shown in Fig. 2 then gives a $T^+/^3He^+$ CFR of 0.999 993 384 971(5), with an overall reduced χ squared of 0.70. However, since reduced weight should be given to points with larger ρ_c where the absolute shifts are larger and to be cautious in our error estimation, we instead allow all three ratios to vary independently with respect to cyclotron drive time. The resulting (uncorrelated) $R_i(0)$ and their uncertainties, which combine uncertainties due to statistics and systematic imbalance in the relativistic mass shifts, are shown in the second column of Table I. The result of the direct measurement of the $T^+/^3He^+$ CFR, $R_3(0) = 0.999\,993\,384\,973(9)$, is in good agreement with the above simultaneous fit result and the result of using HD^+ as an intermediary, $R_1(0)/R_2(0) = 0.999\,993\,384\,975(17)$, showing the consistency of our results. We note, in contrast to our recent measurements on H_2^+/D^+ [16,17], because here the pulse-and-phase measurements used the same axial frequencies, we expect no significant systematic difference in the relativistic mass shifts due to initial ion temperature.

A second systematic shift, which is only significant for the $HD^+/^3He^+$ and HD^+/T^+ CFRs, results from the change in average position due to the change in ring voltage between the ions, combined with a linear magnetic field gradient. The required correction, see Supplemental

TABLE I. Uncorrected CFRs from the fits in Fig. 2, the corrections for the average position shift (Δ_{AP}), and for the polarizability of HD^+ (Δ_{Pol}), and the final, corrected, and least-squares adjusted (LSA) CFRs. The final CFRs are equal to the inverse of the mass ratios. The correlation coefficients between the final ratios are $r_{12} = 0.67$, $r_{13} = 0.36$, and $r_{23} = -0.46$.

Ion pair	CFR from fit	Δ_{AP}	Δ_{Pol}	Final LSA CFR
$HD^+/^3He^+$	0.998 048 085 039 8(114)	$-1.5(4) \times 10^{-12}$	$9.43(1) \times 10^{-11}$	0.998 048 085 131 8(92)
HD^+/T^+	0.998 054 687 196 3(132)	$-1.5(4) \times 10^{-12}$	$9.43(1) \times 10^{-11}$	0.998 054 687 290 2(97)
$T^+/^3He^+$	0.999 993 384 972 7(86)	$\ll 10^{-13}$	$\ll 10^{-13}$	0.999 993 384 973 2(77)

TABLE II. Result for the tritium β-decay Q value (mass differences between atomic T and ^{3}He) compared with previous values. Units are eV/c^2.

Source	$M[\mathrm{T}] - M[^3\mathrm{He}]$
This Letter	18 592.071(22)
Previous work (2015) [9]	18 592.01(7)
KATRIN (2022) [5]	18 591.49(50)
University of Washington (1993) [35]	18 590.1(17)
University of Stockholm (2006) [36]	18 589.8(12)

Material [24], is shown in the third column of Table I. HD^+ has a relatively large polarizability in its ground rovibrational state [26], which produces a significant shift to its cyclotron frequency [27]. The required correction to the CFR is shown in the fourth column of Table I. Applying the polarizability and equilibrium position corrections and then carrying out a least-squares adjustment gives the three correlated final CFRs shown in the last column of Table I. These are our best estimates of the inverse mass ratios.

Many other sources of systematic uncertainty were considered [20]. Although already allowed for by the fits versus T_d^2, shifts to the CFRs due to differences in axial, cyclotron, and magnetron amplitudes, combined with the trap potential imperfections characterized by C_4 ($<2\times10^{-5}$), C_6 ($1.4(2)\times10^{-3}$), and the quadratic and quartic magnetic imperfection B_2/B_0 ($-3.7(7)\times10^{-9}$ mm^{-2}), B_4/B_0 ($3(1)\times10^{-10}$ mm^{-4}) can be estimated to affect the CFRs by $<10^{-12}$ [20,28]. The effects of the ion's image charge in the trap electrodes [29] and interaction with the detector were also negligible. The effects of ion-ion interaction [28,30,31] were $<10^{-12}$. This was the case for the ratios involving HD^+, where the axial frequencies were separated by approximately 670 Hz, but also for the direct $T^+/^3He^+$ measurements, where the axial frequencies were separated by approximately 18 or 22 Hz, depending on whether the $^3He^+$ or T^+ was centered, the main part of the separation being due to trap field imperfections affecting the outer ion. More details are given in the Supplemental Material [24].

Using the mass of the electron [32] and ionization energies of ^{3}He, T [33], and HD^+ [34], the corrected mass ratios in Table I can be converted into mass differences between atoms or their nuclei without any loss of precision. From the $T^+/^3He^+$ ratio we obtain the atomic mass difference $M[\mathrm{T}] - M[^3\mathrm{He}] = 1.995\,940\,8(23)\times10^{-5}$ u. Converting to energy units [32], this implies a Q value for tritium β decay (neutral atom to neutral atom) of 18 592.071(22) eV. In Table II this is compared with previous results and the result obtained from the tritium β-decay end point E_0 as recently measured by KATRIN [4,5]. Our new result agrees at the 1σ level with our previous result and the KATRIN end point result, but is 2.2(1.0) eV/c^2 above the average of the earlier Penning trap results of [35,36].

In Table III we compare our new value for $m_p + m_d - m_h$ with our previous results [9,12], the result from m_d and m_h of [10] combined with the then accepted m_p [11], and the result using the more recent m_p and m_d of the MPIK Collaboration [15], but still with m_h from [10]. Our new result is in good agreement with our previous results and reduces the uncertainty by a factor of 2.5. However, it is in 5σ disagreement with the recent results for m_p and m_d [15] combined with the result for m_h from [10]. Using as a reference the HD^+ mass obtained from m_p and m_d given in Table 2 of Rau *et al.* [15], namely, $M[HD^+] = 3.021\,378\,241\,561(26)$ u, we obtain new atomic masses of ^{3}He and T and their nuclei. In Table IV these are compared with the current Atomic Mass Evaluation [37] and CODATA values [32], respectively. (These are mainly based on the $HD^+/^3He^+$ and HD^+/T^+ ratios from [9,12] and do not use m_h from [10].) The decrease of our values relative to CODATA 2018 for the nuclei reflects the reduced deuteron mass of [15] compared to [10], which affects the mass of HD^+. Otherwise, the different results are in good agreement.

TABLE III. Result for the $m_p + m_d - m_h$ mass difference compared with previous values.

Source	$m_p + m_d - m_h$ (u)
This Letter	0.005 897 432 161(28)
Florida State Univ. 2017 [12]	0.005 897 432 191(70)
Florida State Univ. 2015 [9]	0.005 897 432 097(145)
UW m_d,m_h [10]; CODATA10 m_p [11]	0.005 897 432 889(107)
MPIK m_p,m_d [15]; UW m_h [10]	0.005 897 432 450(50)

TABLE IV. Atomic masses of helium-3 and tritium, and their nuclei compared with the Atomic Mass Evaluation (AME) 2020 (atoms) and CODATA 2018 (nuclei). Our results assume a HD^+ mass of 3.021 378 241 561(26) u as obtained from [15]. The correlation coefficient between our tritium and helium-3 (or triton and helion) masses is 0.82.

Atom	This Letter	AME 2020
Helium-3	3.016 029 321 963(38)	3.016 029 321 967(60)
Tritium	3.016 049 281 372(39)	3.016 049 281 320(81)
Nucleus	**This Letter**	**CODATA 2018**
Helion	3.014 932 246 957(38)	3.014 932 247 175(97)
Triton	3.015 500 716 066(39)	3.015 500 716 210(120)

In conclusion, by measuring the cyclotron frequency ratios $HD^+/{}^3He^+$, HD^+/T^+, and $T^+/{}^3He^+$, we have obtained a Q value for tritium β decay with 1σ uncertainty of 22 meV. This agrees with the previous most precise measurement [9], but has a factor of 3 smaller uncertainty. By confirming the previous measurement and reducing the uncertainty, this result is valuable for both the KATRIN and Project-8 experiments, as well as future absolute neutrino mass experiments. We also obtain a more precise value for the cross-check mass difference $m_p + m_d - m_h$, which agrees with our previous results [9,12], but due to the reduced uncertainties, now disagrees by 5σ with the same mass difference from measurements of m_p, m_d [15], and m_h [10] directly against ^{12}C. Assuming the validity of the recent values of m_p and m_d [15], we obtain atomic masses of the helion and triton with fractional uncertainties of 13 ppt.

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