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E. G. Myers, A. Wagner, H. Kracke, and B. A. Wesson

Department of Physics, Florida State University, Tallahassee, Florida 32306-4350, USA

By measuring the cyclotron frequency ratios of $^3He^+$ to HD^+ and T^+ to HD^+, and using HD^+ as a mass reference, we obtain new atomic masses for ^3He and T. Our results are M[^{3}He] = 3.016 029 322 43(19) u and M[T] = 3.016 049 281 78(19) u, where the uncertainty includes an uncertainty of 0.12 nu in the mass reference. Allowing for cancellation of common systematic errors, we find the *Q*-value for tritium beta-decay to be (M[T] – M[^{3}He])c^2 = 18 592.01(7) eV. This allows an improved test of systematics in measurements of tritium beta-decay that set limits on neutrino mass.

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Study of the shape of the tritium beta-decay spectrum near its maximum energy endpoint provides a direct laboratory method for setting an upper-limit to electron (anti-) neutrino mass [1]. Results of the Mainz and Troitsk experiments have set limits of $m(\nu_e) <$ 2.3 eV and $m(\nu_e) <$ 2.05 eV (95% C.L.) respectively [2,3], while an order of magnitude improvement is expected from the ongoing, large-scale tritium beta decay experiment KATRIN [4]. In principle, neutrino mass could be inferred directly from the difference between the maximum electron kinetic energy and the tritium beta-decay *Q*-value, defined as the mass difference between isolated atoms of T and ^{3}He. However, even in KATRIN, due to limitations of energy resolution and statistics near the endpoint, the highest sensitivity to neutrino mass is obtained from fitting the electron spectrum several eV below the endpoint, corresponding to relativistic neutrinos. The fit to the electron spectrum then produces a value for $m(\nu_e)^2$, and also for E_0, the endpoint corresponding to *zero* neutrino mass. Hence, an independent value for the mass difference between ^{3}T and ^{3}He is not used directly in obtaining neutrino mass. However, allowing for all processes that modify the energy of the electrons transmitted through KATRIN, including, for example, collisions and excitation of daughter-molecule final states, E_0 should correspond to the atomic mass difference. Hence, comparison of E_0 with the T – ^{3}He mass difference provides an independent test that the energy loss processes in KATRIN are understood. This understanding is necessary since the width of the overall energy transmission function in KATRIN correlates directly with the determination of $m(\nu_e)^2$ [5]. Since the absolute calibration of the KATRIN high voltage system is at the 50 meV level [6], well below the 1 eV uncertainty of existing values for the ^{3}T-^{3}He mass difference [7,8], improved atomic mass measurements of tritium and helium-3 are indicated. A further motivation is that the masses of their nuclei, the triton and the helion, are regarded as fundamental constants [9].

Cyclotron frequency ratios: - We determined the atomic masses of ^{3}He and T from measurements of the cyclotron frequency ratios (CFRs) $f_c(HD^+)/f_c(^3He^+)$ and $f_c(HD^+)/f_c(T^+)$. Pairs of single ions, either HD^+ and $^3He^+$, or HD^+ and T^+, were simultaneously trapped in an 8.53 tesla Penning ion trap maintained at 4.2 K [10,11]. The ions were created in the trap by injecting a pulsed, externally collimated, molecular beam of HD, ^{3}He, or T_2 through a hole in the upper end-cap, overlapping a pulsed, 900 eV, ~50 nA electron beam. Unwanted ions were removed by selective excitation of their axial motion, and then reducing the potential of the lower end-cap till they collided with its surface.

Typical ion lifetimes were several days for HD^+ and $^3He^+$, and many weeks for T^+. There was no indication of the subsequent production of unwanted ions in the trap, as might occur due to the beta-decay of tritium adsorbed onto the electrode surfaces [12]. We chose HD^+ as the mass reference in preference to H_3^+ because the fractional uncertainty of the CODATA mass of the proton is 9 x 10^{-11}, versus 3.8 x 10^{-11} for the deuteron [9], and because we could make HD^+ more easily in the Penning trap.

An ion in a Penning trap has two transverse circular motions, the (trap-) modified-cyclotron and magnetron modes, and a harmonic axial motion parallel to the magnetic field [13]. In this work only the axial mode was detected. This was done via the image current induced in a high quality-factor (28,000) superconducting tuned circuit, with a resonance frequency near 685 KHz, connected between the ring and upper end-cap. This current was detected using a dc-SQUID. Following pulsed excitation of the ion's axial motion, the damped-exponential ring-down current was recorded and analyzed, producing a measurement of phase, frequency and amplitude. Data was usually taken with the ion detuned 30 Hz below the detector resonance, increasing the damping time to around 4 s and thus improving the frequency and phase resolution. The cyclotron and magnetron modes were detected and damped by coupling them to the axial mode, using rf-drives at frequencies close to $f_{ct} - f_z$ and $f_z + f_m$, where f_{ct}, f_z, and f_m are the frequencies of the ion's modified-cyclotron, axial, and magnetron modes, respectively [14]. These coupling drives, and also the cyclotron drive, were applied to one half of one of the trap compensation electrodes – the electrodes whose main function is to null the trap's quartic electrostatic field imperfection, which is usually denoted as C_4 [13].

We measured the cyclotron frequency of one ion, centered in the trap, using the "pulse-and-phase" method [15]. Meanwhile, the other ion was held in a cyclotron orbit of 1.07(2) mm radius to reduce pertubations to the mode frequencies of the inner ion due to coulomb interaction [11,16-19]. In the pulse-and-phase method, f_{ct} is determined from the phase accumulated by the freely evolving modified-cyclotron motion. First, the ion was centered in the trap by bringing it to resonance with the detection circuit to damp its axial motion. Pi-pulses close to $f_{ct} - f_z$ and $f_z + f_m$ were used to reduce the radii of the cyclotron and magnetron modes. The ion was then excited to a cyclotron radius of approximately 45 μm, by applying a 20 or 22 ms rf drive pulse at close to f_{ct}. After a delay, which we call the evolution time, T_{evol}, the cyclotron phase □ was "read out" by coherent transfer of the action from the cyclotron to the axial mode, using a pi-pulse. To avoid damage to components in the cryostat, the maximum input power was limited so that the pi-pulse time was between 750 and 850 ms. The resulting narrow bandwidth of the pi-pulse required careful setting of the coupling frequencies and automated adjustment of the trap voltage. To obtain a single value of the modified cyclotron frequency, f_{ct}, we used a series of pulse-and-phase measurements with 14 different T_{evol}, with the four longest near 10 s. The modified cyclotron frequency was then determined from $2\pi f_{ct} = d□/dT_{evol}$. The 14 f_z-values were averaged to provide a single f_z-value to correspond to this f_{ct}, while f_m was obtained using the procedure described in ref. [20]. The cyclotron frequency, f_c, that the ion would have in the magnetic field without the quadratic electrostatic potential, which is related to the mass of an ion through $2\pi f_c = qB/m$, was then found using the Brown-Gabrielse Invariance theorem, $f_c^2 = f_{ct}^2 + f_z^2 + f_m^2$ [21].

After a pair of 14 pulse-and-phase cycles the ions were interchanged. To do this, the former outer ion was re-centered by applying the cyclotron-to-axial coupling drive continuously, and linearly sweeping the trap voltage to keep f_z close to resonance with the coupling drive and detection circuit. This voltage sweep was needed to compensate for the −180 Hz shift in the axial frequency at 1.07 mm cyclotron radius. This shift was mainly due to the quadratic magnetic field imperfection in our trap, parameterized by the quantity B_2/B_0 [13]. Having re-centered the outer ion approximately half-way, the inner ion was driven out by applying the modified-cyclotron drive for 8 s, linearly swept down in frequency to compensate for the relativistic decrease in f_{ct}. Finally, the former outer ion was completely re-centered. Repeating this procedure over a run lasting up to 10 hours, ultimately limited by the need to refill a nitrogen dewar, typically produced around 20 interleaved measurements of f_c for each ion. To obtain the average CFR, the measurements of f_c versus time for the two ions were fitted with similar polynomials, thus partly allowing for common-mode variation in the magnetic field. An example of this cyclotron frequency data is shown in Fig. 1. Besides magnetic field fluctuations, the f_c data fluctuate due to phase noise caused by detection noise and the initial thermal cyclotron motion (rms radius approximately 11 μm), and due to variation in f_{ct} caused by variations in the cyclotron radius (see eqn. 1 below), also due to the initial thermal motion.

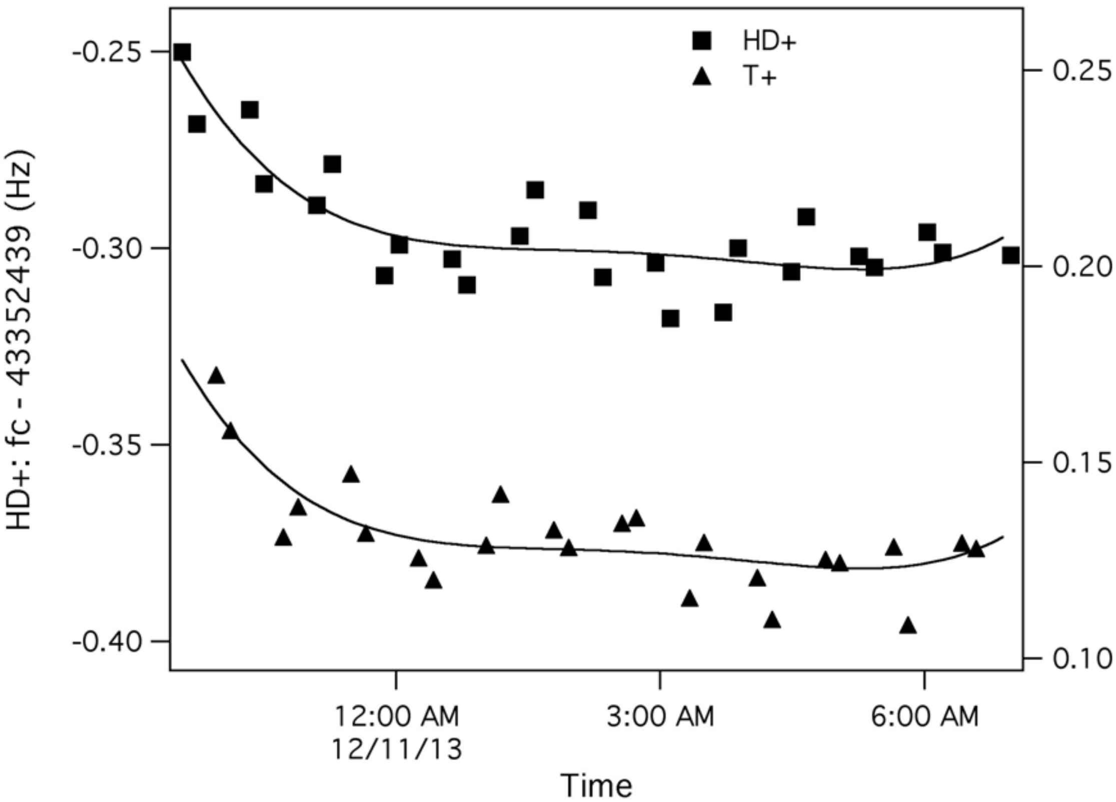

FIG. 1. Example of a single run of cyclotron frequency data for the ratio HD^+/T^+. The curves are a simultaneous least-squares fit using a 4th order polynomial, as determined using an *F*-test [22].

Analysis: - The CFRs from the individual runs used to obtain the atomic masses are shown in Fig. 2. These consist of 6 initial measurements of $HD^+/^3He^+$, 31 of HD^+/T^+, and a further 28 of $HD^+/^3He^+$. The averages of the two groups of $HD^+/^3He^+$ ratios agree within the statistical uncertainty. The uncorrected average ratios for the combined $HD^+/^3He^+$ data, and for the HD^+/T^+ data, are shown in the second column of Table 1. These were obtained by weighting the result of each run by $1/\sigma_i^2$, where σ_i is the statistical error for the *i*-th run returned by the simultaneous fit, as in Fig. 1. The reduced-chi-squared for the two average ratios were 1.26 and 0.90, respectively. The statistical uncertainties of the mean ratios were obtained from the σ_i using the usual formula, although for $HD^+/^3He^+$ we scaled by the square-root of the reduced-chi-squared. In addition, both uncertainties were increased by 10 ppt, added in quadrature, to take account of variations in the final averages due to different data cuts, and whether standard Gaussian or robust statistics were used in the fits to the f_c data. Data cuts were necessitated by the failure of some f_c points to phase-unwrap correctly. This occurred due to increased detector noise, or excessive variations of the axial and cyclotron frequencies, *e.g.* after refilling cryogens.

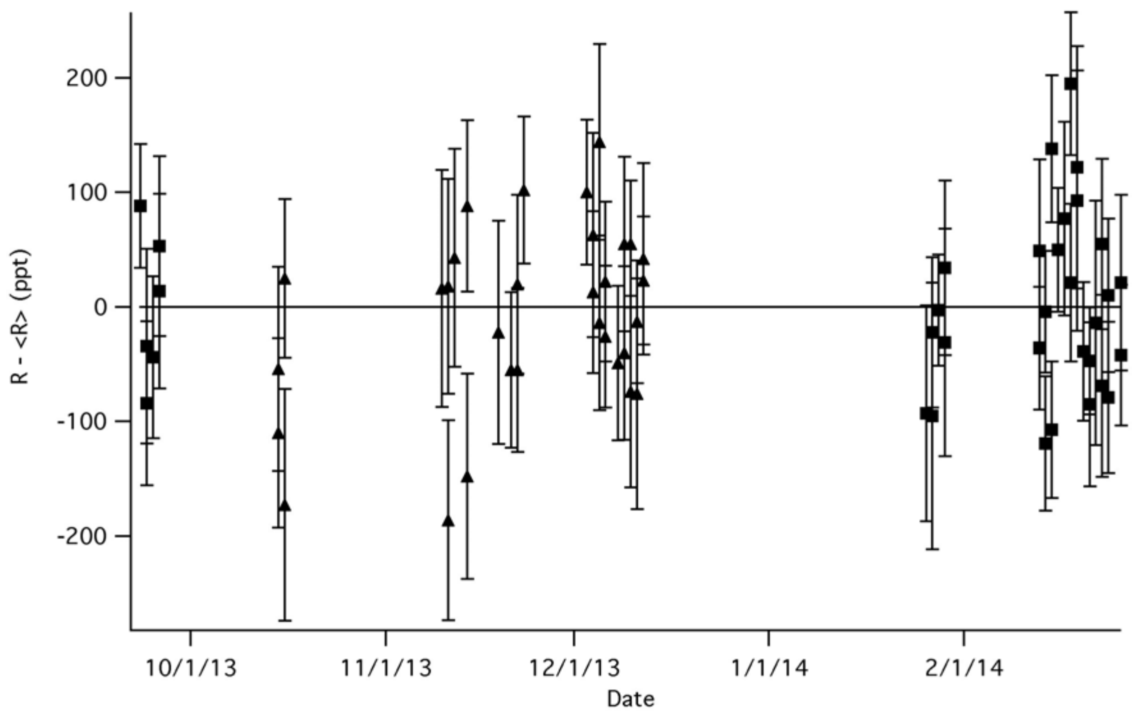

FIG. 2. Cyclotron frequency ratios from the individual runs. The *y*-axis shows the difference, in parts in 10^{12}, between the results of the individual runs for $HD^+/^3He^+$ (squares), and HD^+/T^+ (triangles), and their respective (uncorrected) weighted means, as given in the second column of Table 1.

TABLE I. Average cyclotron frequency ratios and systematic corrections for each ion pair. R_{unc} is the uncorrected CFR, with combined statistical and fitting uncertainty in parentheses, Δ_{imb} (in ppt) is the estimated correction for imbalance in the cyclotron radii, with uncertainty in parentheses. Δ_{pol} (in ppt) is the correction due to the polarizability of the HD^+ ion. R_{corr} (with total uncertainty in parentheses) is the corrected CFR and our final result for the inverse mass ratio.

Ion pair	R_{unc}	Δ_{imb} (ppt)	Δ_{pol} (ppt)	R_{corr}
$HD^+/^3He^+$	0.998 048 085 081(17)	−22(45)	94	0.998 048 085 153(48)
HD^+/T^+	0.998 054 687 216(17)	−22(45)	94	0.998 054 687 288(48)

Systematic errors: - The anharmonic shift to the modified cyclotron frequency due to special relativity, the quadratic imperfection in the magnetic field (B_2), and the quartic imperfection in the electrostatic potential (C_4) can be approximated by [19,23]

$$\frac{\Delta f_{ct}}{f_{ct}} = -\frac{1}{2}\left[\left(\frac{2\pi f_{ct}}{c}\right)^2 + \frac{B_2}{B_0}\right]\rho_c^2 + \frac{1}{2}\frac{B_2}{B_0}\left(a_z^2 - \rho_m^2\right) + \frac{3C_4}{4}\left(\frac{f_z^2}{f_{ct}^2}\right)\frac{\left(\rho_c^2 - 2a_z^2 + 2\rho_m^2\right)}{d^2} \quad (1)$$

where, ρ_c, a_z and ρ_m are, respectively, the cyclotron radius, axial amplitude, and magnetron radius during the cyclotron phase evolution period. From auxiliary measurements of the variation of f_z and f_{ct} with ρ_c and ρ_m, B_2/B_0 was determined to be $-1.16(2)\ \mathrm{x}10^{-7}\ \mathrm{mm}^{-2}$, while we were able to set the voltage on the compensation electrodes to achieve $|C_4| < 5 \times 10^{-5}$. The main contribution was hence from special relativity, slightly reduced by the B_2 gradient, producing an average shift of -7×10^{-10} for a cyclotron radius of 45µm, followed by a contribution of -4.5×10^{-10} from the axial motion interacting with the B_2 gradient, assuming an rms a_z of 90µm, corresponding to the (approximate) 27 K noise-temperature of our axial detector. Contributions from the magnetron motion (assuming an rms ρ_m of 11 µm), and from residual C_4, and also from the effective change in C_4 due to the coulomb interaction with the outer ion ($\Delta C_4 = 4.0(4) \times 10^{-5}$) were negligible.

The C_4 electrostatic field imperfection also affects the measurement of f_z, which occurs during the axial ring-down with initial amplitude of 360 μm. However, the resulting effect on the cyclotron frequency is < 5 x 10^{-11}.

Although the individual cyclotron frequencies are shifted at the level of 1 x 10^{-9}, the shift to the measured ratios is strongly suppressed. This is because the average values of ρ_c^2, a_z^2 and ρ_m^2 in eqn.1 are very similar for the two ions in each pair, since the trap voltages and cyclotron drive frequencies used for HD^+ and $^3He^+$ (or for HD^+ and T^+) differ by only 0.2%. For the data presented here, to avoid introducing imbalance between the cyclotron radii, a single waveform generator was used to generate the drive pulses that set ρ_c for both ions. As the frequency was changed between the ions, the variation of the drive amplitude external to the cryostat was measured to be less than 0.5%. However, the transfer function within the cryostat was not measured, leading to the possibility that a larger difference in drive amplitudes could exist at the trap electrodes (for historical reasons, the driveline contained filters optimized for much lower frequencies). To help quantify this, we obtained the ratios $\langle A_z(HD^+)\rangle/\langle A_z(^3He^+)\rangle$ and $\langle A_z(HD^+)\rangle/\langle A_z(T^+)\rangle$, where $\langle A_z(HD^+)\rangle$, etc., are the average amplitudes of the ring-down signals of all the pulse-and-phase measurements in a run, and then took the weighted average over all the runs for each ion pair. For the $HD^+/^3He^+$ and HD^+/T^+ ratios, these overall average axial-amplitude ratios were 0.969(3) and 0.971(3), indicating a small but significant imbalance.

Using a pair of ions with deliberately imbalanced cyclotron drive times of 18 and 22 ms we confirmed that the CFR and the A_z-ratio varied with ρ_c as expected. However, because we were unable to obtain adequate statistical precision at significantly larger or smaller ρ_c, we were unable to measure a shift in the CFR proportional to the nominal ρ_c^2, which would help verify that the observed A_z imbalance was due to an imbalance in the transfer function. (This was due to the poor signal-to-noise ratio at small ρ_c, and due to the combination of the increased noise on f_{ct}, and the increased shift to f_z during the pi-pulse at large ρ_c.) Lacking this confirmation, and because an amplitude change of 3% caused by a 0.2% change in drive frequency is larger than expected, we corrected our average CFRs by 50% of the shift implied by assuming the measured A_z-ratio is equal to the actual ρ_c ratio and eqn. 1. Conservatively, we assign an uncertainty equal to 100% of the maximum implied shift. This correction is shown in the third column of Table 1.

Many other systematics were considered, including effects of ion-ion interaction [17,18], variation in the equilibrium position of the ions interacting with the linear magnetic field gradient (B_1/B_0 = 1.4(0.3) x 10^{-8} mm^{-1}), frequency pushing of the axial frequency by the detector resonance, variation of axial frequency along the pulse-and-phase cycle, and heating of the trap by the rf-drives. These were estimated to affect the above ratios by <10^{-11} in total and are neglected. However, allowance must be made for the shift in the observed CFR due to the polarizability of the HD^+ molecular ion, which can be assumed to occupy the rotational groundstate in the 4.2 K environment of the trap. Using the expression in ref. [24] and the precise polarizability calculations of ref. [25] or [26], the observed $f_c(HD^+)$ is predicted to be reduced by a fraction 9.45 x 10^{-11}, with negligible uncertainty. The corresponding corrections to the CFRs are shown in the 4th column of Table 1.

Atomic masses and the mass difference between tritium and helium-3: - Using the 2010 CODATA values for the masses of the electron, proton and deuteron [9], combined with the groundstate energy of HD^+ relative to its separated constituents [25], we predict the atomic mass of the HD^+ ion to be 3.021 378 241 97(12) u, where the uncertainty is due to the uncertainty in the masses of the proton and deuteron. Combining this HD^+ mass with our corrected CFRs in Table 1, and the ionization energies of hydrogen and helium [27], we obtain new atomic masses of helium-3, tritium, and their nuclei. In Table 2 these are compared with results from the 2010 CODATA and from the 2012 Atomic Mass Evaluation [28].

TABLE II. Our results for the atomic masses of helium-3, tritium, and their nuclei, compared with the 2012 Atomic Mass Evaluation [28], which gives the atomic masses, and with the 2010 CODATA tabulation of fundamental constants [9], which gives the nuclear masses. The 0.19 nu uncertainty of our results is the combination of 0.15 nu due to our measured ratios, and 0.12 nu from the mass of HD^+ as obtained from the CODATA masses of the proton and deuteron.

Atom/ nucleus	This work (u)	AME/CODATA (u)	Difference (nu)
^{3}He	3.016 029 322 43(19)	3.016 029 320 1(25)	2.3(2.5)
helion	3.014 932 247 43(19)	3.014 932 246 8(25)	0.6(2.5)
^{3}T	3.016 049 281 78(19)	3.016 049 277 9(24)	3.9(2.4)
triton	3.015 500 716 47(19)	3.015 500 713 4(25)	3.1(2.5)

Whereas the difference in mass between HD^+ and either $^3He^+$ or T^+ is nearly 0.2%, the masses of $^3He^+$ and T^+ differ by only 6 x 10^{-6}. Because of this, and because for the $HD^+/^3He^+$ and HD^+/T^+ measurements we used nearly identical procedures, the effect of frequency dependence of the cyclotron drive transfer function, and other systematic effects, should be common and so have a negligible effect on the ratio of the two CFRs in Table 1. Hence, for the $T^+/^3He^+$ CFR, our final result is 0.999 993 385 00(24), where the uncertainty is entirely from statistics and fitting. From this, using the CODATA 2010 conversion between u and eV, we obtain the mass difference between atoms of tritium and helium-3: $M[T] - M[^3He] = 19\,959.34(7)$ nu = 18 592.01(7) eV/c^2. This is compared with previous values in Table III.

TABLE III. Our result for the mass difference between atoms of tritium and helium-3, in eV/c^2, compared with other measurements.

Source	$M[T]-M[^3He]$ (eV/c^2)
This work	18 592.01(0.07)
U. Washington 1993 [7]	18 590.1(1.7)
U. Stockholm 2006 [8]	18 589.8(1.2)
AME2012 [28]	18 591(1)

Conclusion: - Our new atomic mass for ^3He is in agreement with both the CODATA 2010 and the AME 2012 values. For T our result is more than one standard deviation higher than both previous values. (The CODATA results are derived from the measurements of the Stockholm group [8], while the AME2012 also includes the measurements by the Washington group [7], and data from measurements of tritium beta-decay). Due to cancellation of systematic errors, our value for the mass difference between T and ^3He has an estimated uncertainty below 0.1 eV/c^2, which is less than the uncertainties of the individual ^3He and T masses. This mass difference, which is equal to the *Q*-value for tritium beta-decay, and which is closely related to the "endpoint for zero neutrino mass", is 2.1(1.0) eV higher than the average of the previous mass measurements. Our estimated uncertainties improve upon previous results by more than an order of magnitude.

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