Tritium–Helium-3 Mass Difference Using the Penning Trap Mass Spectroscopy

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The atomic masses of both ^{3}H and ^{3}He have been measured with a Penning trap mass spectrometer that utilizes a frequency-shift detector to observe ion cyclotron resonances. Present resolution exceeds 1 part in 10^9 and is limited only by the stability of the magnetic field. The leading systematic shift (at $\lesssim 1$ part in 10^{10}) is due to the residual quadratic **B** field dependence. The atomic masses have been combined to yield $\Delta Mc^2(^3\mathrm{H}-{}^3\mathrm{He}) = 18\,590.1(1.7)$ eV. The excellent agreement with recent results from β spectrometers lends strong support for new limits on the neutrino's rest mass.

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Not since the development of Smith's rf mass spectrometer [1] in 1971 has a "new" device shown the potential for making mass measurements with significantly greater resolution (> 10). The Penning trap mass spectrometer (PTMS) ideally provides an environment essentially void of unwanted interactions which has a potential accuracy that exceeds 0.1 part per billion (ppb). Past examples of the use of this device include the measurements of the e^-/e^+ mass ratio [2] at 130 ppb, the p^+/e^- mass ratio [3] at 20 ppb, the $\bar{p}/p$ mass ratio [4] at 42 ppb, the H_2-D mass difference [5] at 6 ppb, the $^3He^+/H_2^+$ mass ratio [6] at 4 ppb, the proton's atomic mass [7] at 3 ppb, the D_2-^{4}He mass difference [8] at 1.3 ppb, and now the CO^+/N_2^+ mass ratio [9] at 0.1 ppb.

In the present research, this device has been used to independently measure the atomic masses of both ^{3}H and ^{3}He (to a precision of 0.5 ppb or better) in order to determine ΔM. This mass difference is particularly interesting because of its use in the determination of the possible nonzero rest mass of the electron's antineutrino. The measurement history of ΔM before 1991 was marked by a significant lack of consistency within the corresponding standard deviations of the various measurements. However, it now appears that the overall picture of agreement has been greatly improved. In particular, the present measurement helps to eliminate an important degree of freedom in the fit to the β-decay spectrum and in fact can be taken to indicate that final-state calculations are indeed being correctly carried out in these experiments.

Many aspects of the University of Washington Penning trap mass spectrometer have been extensively described in earlier publications [10–12] and will only be discussed briefly here. The device uses a compensated [11] (five-electrode) Penning trap, consisting of two end caps and a main ring electrode that are hyperbolas of revolution along the **B** field axis of a 6-T superconducting solenoid. When the trap is appropriately biased at potential $V_0 \sim 50$–80 V, a trapped ion (electrically driven by an axial rf field) will execute harmonic motion at the frequency $\nu_z \propto (qV_0/m)^{1/2} \sim 4$–$5$ mHz, where q/m is the ion's characteristic charge-to-mass ratio. The remaining two electrodes allow us to fine tune the linearity of the dc electric field such that ν_z may be resolvable to about 10 ppb (limited by the stability of V_0). A field-emission electrode, aligned with **B**, produces a folded electron beam which is capable of producing multiply charged ions. The ion's driven motion, detected as a voltage across a high-Q tuned circuit, is amplified and mixed with the output of the original drive source in order to generate a dc error signal that can be integrated and fed back to the main ring electrode. In this way, the ion's axial resonance is "frequency locked" to the drive oscillator. The resulting correction voltage is the "frequency-shift signal" that is used to monitor the particle's noncentered position by means of residual anharmonic terms in the trapping field.

Approximately (30–40)% of the data obtained in this comparison were obtained using a small "quadring" Penning trap [10] which has the main ring electrode split into four equal parts. The remaining data were taken in a 2×-larger trap which does not have a quadring, but does have the guard electrodes split into equal halves. In either case, the cyclotron motion is excited by applying an rf electric field across an opposing pair of electrodes at $\nu_c' = \nu_c - \nu_m$, where $\nu_c = qB/m$ and ideally, $\nu_m = \nu_z^2/2\nu_c'$. Figure 1 shows a sequence of single C^{4+} resonances, using this frequency-shift detector, taken about every 25 min in the larger trap. Presently, such data can be taken (manually) about 5 times more rapidly by first removing the previous excitation energy (in ~ 1 min) through the use of a sideband drive at $\nu_c' - \nu_z$ which couples the hot cyclotron motion to the strongly damped axial resonance [12] at ~ 4 K. Typical resolution is 0.2 ppb which arises from the power broadening of the very narrow resonances.

The cyclotron detection scheme requires a trigger-type signal, and the basic condition for narrow resonances is that the ion is always prepared in the same low energy, well-centered equilibrium position prior to excitation. Upon frequency sweeping of the rf drive, significant energy is absorbed only when the weak drive is near or within the residual cyclotron linewidth. In fact, it can be shown that with our axial resolution, only a small cyclotron energy, $E_c \approx 10^{-9} mc^2$, is required for initial observation.

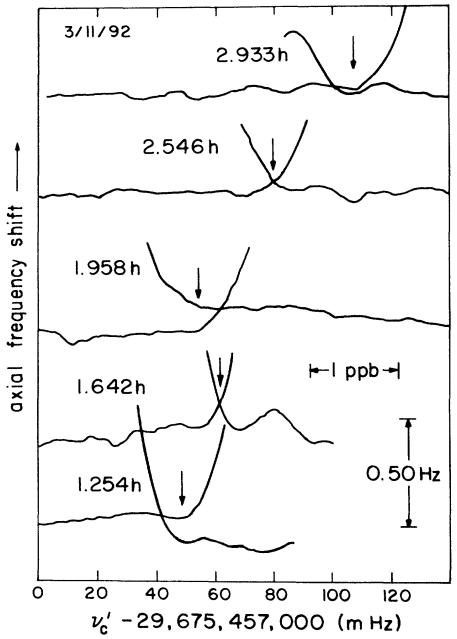

FIG. 1. Ion cyclotron resonances (ICR) for a single C^{4+} ion, observed via anharmonicity-induced axial frequency shifts. Each resonance is bracketed in both directions by traces which are preceded by strong ν_c'-ν_z coupling.

Using the analysis by Moore *et al.* [13], we find that the first-order electric and magnetic perturbations to the *free-space* cyclotron frequency are given by

$$\frac{\Delta\nu_c}{\nu_c} = \left(\gamma - \frac{\beta\alpha^2}{4}\right)E_z - \left(\frac{\beta\alpha^4}{4} - \frac{1}{mc^2}\right)E_c + 2\gamma E_m , \quad (1)$$

where $\alpha \equiv \nu_z/\nu_c' \sim 1/8$ and E_z, E_c, and E_m respectively represent the equilibrium energies of the axial, cyclotron, and magnetron motions. The quantity γ is proportional to the quadratic term in the magnetic field ($\gamma \approx 1 \times 10^{-8}$/eV for singly charged ions) and β is proportional to the highest-order nonharmonic term in the electric field ($\beta \approx 3 \times 10^{-6}$/eV also for singly charged ions). From Eq. (1), we find that, prior to excitation, the E_z and E_c terms produce negligible shifts, < 0.01 ppb. Thus, the dominant term is due to the magnetron energy, which was measured on one occasion in the larger trap to be $-18(5)$ meV for a single C^{6+} ion. For this quite favorable case, the shift $\Delta\nu_c/\nu_c \lesssim 5 \times 10^{-11}$, though for singly charged tritium, it is still expected to be $\lesssim 1 \times 10^{-10}$.

To determine ΔM, it is desirable to load ^{3}He immediately after ^{3}H. However, because of the accumulated β decay of tritium within the lattice of a tritium-soaked titanium wafer, the same enclosed source contains both atoms. To liberate ^{3}He (when initially at 4 K), about 30 J of energy is often needed; however, to load ^{3}H, at least 200 J of energy is required. As a result, the magnetic field is unstable (see Fig. 2) due to the temperature rise

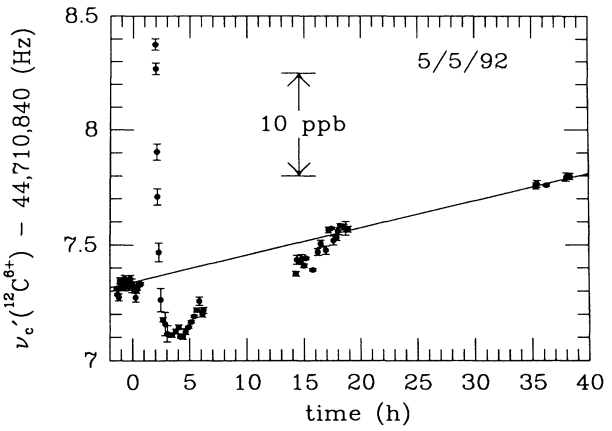

FIG. 2. Field variation from 80 J of energy added to the trap (from 1.08 through 1.50 h), monitored via ν_c' of a single $^{12}C^{6+}$ ion. Gradual return to equilibrium takes ~ 20 h.

of the electrodes whose temperature-dependent susceptibility causes the net field to vary with time. Since carbon is naturally occurring and is easily desorbed from the trap electrodes by the ionizing electron beam, we often find it convenient to use C^{4+} for field calibration. Figure 3 shows a typical run which consists of first measuring $\nu_c'(^3H^+)$ for several hours and then calibrating with C^{4+} for several more hours. The magnetron frequency is also measured by the same frequency-shift detector and the free space cyclotron frequency is recovered by taking all three normal mode frequencies in quadrature [14], after accounting for the image-charge shift [15] associated with the number of trapped ions. The solid line shown in Fig. 3 represents the weighted average of all the data, with a least-squares fit of the m/q ratio that allows the calibration data to be plotted on the same scale. The resolution is ~ 1 ppb and is typical for a 10–14 h run due

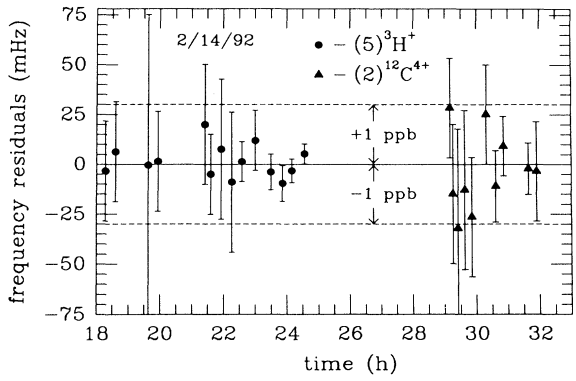

FIG. 3. Fitted residuals for the comparison of five $^3H^+$ ions with two $^{12}C^{4+}$ ions, relative to $\nu_c'(^3H^+) = 29,747,923,260$ mHz. Carbon data (triangles) are plotted on the same graph with tritium data (circles) after being scaled by fitted m/q ratio.

TABLE I. Summary of all ^{3}He and ^{3}H runs for both traps.

Ionic ratio	m/q ratio	$\delta M = M - A$(nu) [a]
$^3He^+/O^{6+}$	0.883 862 582 57(138) [b]	16 029 301.3(48)
$^3He^+/C^{4+}$	0.994 684 330 62(110) [b]	16 029 312.1(33)
$^3He^+/C^{4+}$	0.994 684 331 13(86) [b]	16 029 310.5(26)
$^3He^+/C^{4+}$	0.994 684 332 23(98) [b]	16 029 307.2(30)
$^3He^+/C^{4+}$	0.994 684 330 45(104) [b]	16 029 312.6(32)
$^3He^+/C^{4+}$	0.994 684 332 97(653) [c]	16 029 304.9(198)
$^3He^+/C^{4+}$	0.994 684 332 25(246) [c]	16 029 307.1(75)
$^3He^{2+}/C^{4+}$	1.989 730 597 90(96) [c]	16 029 310.5(15)
$^3He^{2+}/C^{6+}$	1.326 365 867 42(143) [c]	16 029 309.8(32)
$^3H^+/C^{4+}$	0.994 677 753 68(237) [b]	16 049 262.6(72)
$^3H^+/C^{4+}$	0.994 677 752 40(172) [c]	16 049 266.5(52)
$^3H^+/C^{4+}$	0.994 677 751 68(80) [c]	16 049 268.7(24)
$^3H^+/C^{4+}$	0.994 677 752 37(75) [c]	16 049 266.6(23)

[a] 1 nu $\equiv 10^{-9}$ u.
[b] Quadring trap.
[c] 2×-larger trap.

to residual field instability.

Table I lists all the runs for both ^{3}He and ^{3}H. Column 2 shows the fitted m/q ratio and column 3 gives the atomic mass after correcting for lost electrons. Helium-3 was used extensively to check on possible systematics by varying the charge state of either the ion of interest or the calibration ion. Note also the excellent agreement between the two traps: The weighted average for the quadring trap is 3016 029 309.63(1.42) nu, whereas the 2×-larger trap yields 3016 029 310.26(1.35) nu. The uncertainty associated with the electron's mass [16] is ±0.013 nu which is negligible as are the uncertainties due to the individual electron binding energies [17]. The total weighted average for the ^{3}He runs has a normalized $\chi^2 = 0.73$ which does not suggest any sizable systematic error. The resulting atomic mass excesses ($\delta M = M - A$ where A denotes atomic number) for the data shown in Table I are

$$\delta M(^3\mathrm{He}) = 16\,029\,309.98(98)\ \mathrm{nu}\,,$$
$$\delta M(^3\mathrm{H}) = 16\,049\,267.25(1.54)\ \mathrm{nu}\,. \qquad (2)$$

These are in excellent agreement with the accepted values [18]: 16 029 297(23) and 16 049 265(23) nu, respectively. The atomic masses shown in Eq. (2) may be combined to yield the mass difference, 19 957.27(1.82) nu, which corresponds to $\Delta Mc^2 = 18\,590.1(1.7)$ eV when the appropriate conversion unit [16] is used. This result can be compared with the recent values listed in Table II which are given roughly in chronological order. The agreement is now quite reasonable for all β spectrometers as far back as 1985 after being corrected for final-state spectra by Kaplan *et al.* [28]. In addition, Si-detector measurements have been corrected for a chemical shift of +10(3) eV estimated by Redondo and Robertson [25]. Note the excellent agreement with the five most recent β-spectrometer values [35–39]. The present result is also in excellent agreement with the rf-spectrometer values after a reevaluation by Audi, Graham, and Geiger [19]. However, the agreement is not very good with previous ion cyclotron resonance (ICR) spectrometer results [22–24,27], though the weighted average of these four experiments yield 18 590.0(1.4) eV with a reduced $\chi^2 = 12.9$. For all the results in Table II, the weighted average is 18 590.62(67) eV with a reduced $\chi^2 = 3.0$. Such averages assume a certain randomness in the distribution of possible systematic errors and a reduced $\chi^2 \gg 1$ indicates that systematic errors must indeed exist. In such cases, the er-

TABLE II. Recent measurements of the ^{3}H-^{3}He mass difference.

ΔMc^2 (eV)	Method	Authors	Year	Ref.
18 590(10)	rf mass spectrometer	Smith *et al.*	1975	[19,20]
18 579(12)	rf mass spectrometer	Smith *et al.*	1981	[19,21]
18 584(4)	ICR doublet	Nikolaev *et al.*	1984	[22]
18 599(2)	ICR doublet	Lippmaa *et al.*	1985	[23]
18 582(3)	ICR doublet	Talrose *et al.*	1985	[24]
18 590(8)	Si(Li) implantation	Simpson *et al.*	1985	[25,26]
18 581(3)	ICR doublet	Gorshkov *et al.*	1986	[27]
18 603(10)	β spectrometer	Fritschi *et al.*	1986	[28,29]
18 599(4)	β spectrometer	Boris *et al.*	1987	[28,30]
18 603(5)	β spectrometer	Kawakami *et al.*	1987	[28,31]
18 586(6)	Si(Li) implantation	Brudanin *et al.*	1988	[25,32]
18 589.0(2.6)	β spectrometer	Staggs *et al.*	1989	[33]
18 595(6)	Bremsstrahlung	Budick *et al.*	1991	[34]
18 590.6(2.0)	β spectrometer	Robertson *et al.*	1991	[35]
18 590.9(3.0)	β spectrometer	Kawakami *et al.*	1991	[28,36]
18 591.0(2.0)	β spectrometer	Holzschuh *et al.*	1992	[37]
18 590.7(3.0)	β spectrometer	Bonn *et al.*	1992	[38]
18 589.0(2.0)	β spectrometer	Stoeffl *et al.*	1992	[39]
18 590.1(1.7)	PTMS	Present work	1992	

ror in the weighted mean does not properly reflect the systematic errors. Nevertheless, the present work strongly supports the validity of the final-state calculations used in β-decay experiments to extract the upper limit for the neutrino's rest mass. In the past, such calculations were a possible source for apparent inconsistencies.

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[1] L. G. Smith, Phys. Rev. C **4**, 22 (1971).
[2] P. B. Schwinberg, H. G. Dehmelt, and R. S. Van Dyck, Jr., Phys. Lett. **81A**, 119 (1981).
[3] R. S. Van Dyck, Jr. *et al.*, Bull. Am. Phys. Soc. **31**, 244 (1986).
[4] G. Gabrielse *et al.*, Phys. Rev. Lett. **65**, 1317 (1990).
[5] A. G. Marshall *et al.*, in Proceedings of the Fortieth American Society on Mass Spectrometry Conference on Mass Spectrometers and Allied Topics, Washington D.C. (to be published), MOA945.
[6] D. Hagena and G. Werth, Europhys. Lett. **15**, 491 (1991).
[7] F. L. Moore *et al.*, Bull. Am. Phys. Soc. **34**, 99 (1989).
[8] Ch. Gerz, D. Wilsdorf, and G. Werth, Z. Phys. D **17**, 119 (1990).
[9] V. Natarajan *et al.*, in Proceedings of the Sixth and Ninth AMCO Conference, Bernkastel-Kues, Germany, 1992 (to be published).
[10] R. S. Van Dyck, Jr., P. B. Schwinberg, and S. H. Bailey, in *Proceedings of the Sixth AMCO* (Plenum, New York, 1980), p. 173.
[11] R. S. Van Dyck, Jr. *et al.*, Appl. Phys. Lett. **28**, 446 (1976); G. Gabrielse, Phys. Rev. A **27**, 2277 (1983).
[12] R. S. Van Dyck, Jr., D. L. Farnham, and P. B. Schwinberg, J. Mod. Opt. **39**, 243 (1992); also Phys. Scr. **46**, 257 (1992).
[13] F. L. Moore *et al.*, Phys. Rev. A **46**, 2653 (1992).
[14] L. Brown and G. Gabrielse, Phys. Rev. A **25**, 2423 (1982).
[15] R. S. Van Dyck, Jr. *et al.*, Phys. Rev. A **40**, 6308 (1989).
[16] E. R. Cohen and B. N. Taylor, Rev. Mod. Phys. **59**, 1121 (1987).
[17] C. E. Moore, National Standards Reference Data Series—34 (U.S. GPO, Washington, DC, 1970), p. 1.
[18] A. H. Wapstra and G. Audi, "The 1986 Audi-Wapstra Mid-Stream Mass Evaluation" (distributed by P. Haustein at Brookhaven National Laboratory, 1986).
[19] G. Audi, R. L. Graham, and J. S. Geiger, Z. Phys. A **321**, 533 (1985).
[20] L. G. Smith and A. H. Wapstra, Phys. Rev. C **11**, 1392 (1975).
[21] L. G. Smith, E. Koets, and A. H. Wapstra, Phys. Lett. **102B**, 114 (1981).
[22] E. N. Nikolaev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 441 (1984) [JETP Lett. **39**, 534 (1984)].
[23] E. Lippmaa *et al.*, Phys. Rev. Lett. **54**, 285 (1985).
[24] V. L. Talrose and E. N. Nikolaev, *Advances in Mass Spectrometry 1985* (Wiley, New York, 1985), p. 343.
[25] A. Redondo and R. G. H. Robertson, Phys. Rev. C **40**, 368 (1989).
[26] J. J. Simpson, W. R. Dixon, and R. S. Storey, Phys. Rev. C **31**, 1891 (1985).
[27] M. V. Gorshkov *et al.*, Metrologia (Russ.) **8**, 10 (1986); INIS Atomindex **18**, No. 070401 (1987).
[28] I. G. Kaplan *et al.*, Phys. Lett. **161B**, 389 (1985).
[29] M. Fritschi *et al.*, Phys. Lett. B **173**, 485 (1986).
[30] S. D. Boris *et al.*, Phys. Rev. Lett. **58**, 2019 (1987); Pis'ma Zh. Eksp. Teor. Fiz. **45**, 267 (1987) [JETP Lett. **45**, 333 (1987)].
[31] H. Kawakami *et al.*, Phys. Lett. B **187**, 198 (1987).
[32] V. B. Brudanin *et al.*, INIS Atomindex **22**, No. 061054 (1988).
[33] S. T. Staggs *et al.*, Phys. Rev. C **39**, 1503 (1989).
[34] B. Budick, J. Chen, and H. Lin, Phys. Rev. Lett. **67**, 2626 (1991).
[35] R. G. H. Robertson *et al.*, Phys. Rev. Lett. **67**, 957 (1991).
[36] H. Kawakami *et al.*, Phys. Lett. B **256**, 105 (1991).
[37] E. Holzschuh *et al.*, in Proceedings of the 1992 Rencontres de Moriond, edited by J. Tran Thanh Van (Editions Frontières, Gif-sur-Yvette, to be published).
[38] J. Bonn *et al.*, in Proceedings of the Sixth and Ninth NFFS AMCO Conference (Ref. [9]).
[39] W. Stoeffl (private communication).