Precise ^{3}H-^{3}He Mass Difference for Neutrino Mass Determination

E. Lippmaa, R. Pikver, E. Suurmaa, J. Past, J. Puskar, I. Koppel, and A. Tammik
Department of Physics, Institute of Chemical Physics and Biophysics of the Estonian Academy of Sciences, Tallinn 200 001, U.S.S.R.

(Received 30 July 1984)

The precise ^{3}H-^{3}He atomic mass difference has been measured by high-resolution (10^{-8}) ion cyclotron resonance in a 4.7-T magnetic field. The result of 18 599 ± 2 eV favors a nonzero electron antineutrino mass.

PACS numbers: 21.10.Dr, 14.60.Gh, 27.10.+h, 35.10.Bg

Precision measurement of the β spectrum of tritium near its end point is at present best suited for determining, or putting a useful limit on, the mass $m(\bar{\nu}_e)$ of the electron antineutrino. A sizable number of measurements of both the end-point energy and the corresponding ^{3}H-^{3}He atomic mass difference have been published by Bergkvist (18 651 ± 16),[1] Smith and co-workers (18 600 ± 7, 18 588 ± 7, 18 573 ± 7),[2,3] Lubimov *et al.* (18 603.6 ± 7),[4] Simpson (18 567 ± 5),[5] and Dixon *et al.* (18 594 ± 25).[6] Measurements of the β-decay spectrum of tritium in solid tritiated valine by Lubimov *et al.* indicated a nonzero electron antineutrino mass within the limits $14 \leq m(\bar{\nu}_e) \leq 46$ eV.[7] The more recent result is given as $m(\bar{\nu}_e) > 20$ eV at a 95% confidence level.[4] All β-decay measurements involve serious experimental problems and uncertainties connected with the geometry and chemistry of the high-activity source required; background problems in magnetic β spectrometers; radiation damage, annealing, and other solid state effects in cooled Si(Li) detectors[5,6]; uncertainties associated with ^{3}He$^+$ ionized-state interactions; and difficulties with β-spectrometer calibration.[6] Even the mass spectrometric ^{3}H-^{3}He mass difference of Smith[2] has been corrected downwards.[3] In view of these difficulties, a new experiment to study the β decay of free atomic tritium is underway.[8] An exact value of the ^{3}H-^{3}He mass difference would serve both as a point of reference and as a check for any $m(\bar{\nu}_e)$ from the β-decay data. Recently, the very high mass resolution achievable in high-field Fourier-transform ion cyclotron resonance (ICR) has been used for ^{3}H-^{3}He mass-difference determination by us[9] and by Nikolaev *et al.*[10] Both measurements were carried out in a 4.7-T field using a ^{3}He$^+$-to-^{3}H$^+$ signal-intensity ratio close to unity. The ion mass differences found, 18 588 ± 3 eV[9] and 18 573 ± 4 eV,[10] are simple averages of a few hundred mass doublets, assuming a Gaussian distribution of random errors. The atomic mass differences are larger by 10.9828 eV, the difference between the first ionization potentials of helium and tritium. The discrepancy between the two ion mass difference values can only in part be caused by a lower mass resolution, 1.5×10^{-7} instead of 1.3×10^{-8}, associated with the lower value[10] and the relatively high scatter of the data points found in these experiments must have other causes. We have carried out a systematic study of factors causing small line-shift errors in very-high-resolution ICR.

A superconducting solenoid with a 89-mm room-temperature bore, equipped with both superconducting and room-temperature shim coils, provided a highly homogeneous 4.7-T magnetic field and allowed to register single-scan ICR mass spectra with up to 10 ppb resolution (0.24 Hz full width at half height at 24 MHz). A rectangular $33\times33\times40$ mm^3 gold-plated McIver ICR cell with a tungsten cathode was placed in the center of the solenoid and Fourier-transform ICR spectra were registered using a Bruker Physik CXP-200 NMR spectrometer, equipped with a 24-bit Aspect-2000 computer for data accumulation, Fourier transformation, and Lorentzian or Gaussian fit of the doublet lines (see Fig. 1). The ICR cell was connected to the spectrometer preamplifier through a matched resonant circuit. The same pair of cell plates was used for excitation and signal reception. The line fitting accuracy was 0.001 Hz, but overall precision of a single run of 100 scans was lower due to the 8 to 80 ppb per hour random drift of the magnetic field, which, together with the 0.5-Hz line broadening due to digital filtering, led to the 1.0 to 1.5 Hz linewidths actually

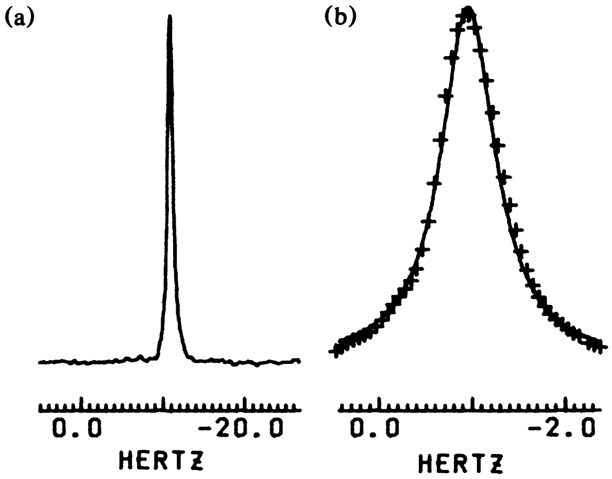

FIG. 1. (a) Line shape of the very-high-resolution ^{3}H$^+$ line with 0.35 Hz line broadening. (b) The Lorentzian fit.

used. Each data point shown in Fig. 3 is an average of twenty such runs. The standard deviation, based on these twenty values, was $\sigma = 0.02$ to 0.04 Hz for each data point shown. The line shapes contained some noise (signal-to-noise ratios of 1:20 to 1:100), but were nevertheless so symmetric that both Lorentzian and Gaussian fits yielded the same averages. A computer-controlled synthesizer in the NMR spectrometer console was used for ICR spectrum excitation and a Wavetek 178 swept waveform synthesizer for the axial resonance. The pulse sequences used for quench, ionization, rf excitation, axial resonance, grid and trap voltage switching, and free induction decay signal registration were generated by the CXP-200 pulse programmer and are shown in Fig. 2.

The vacuum system provided a 2×10^{-9} Torr vacuum and consisted of Nor-100 and 30 l/s Vacion ion pumps, connected to a nonmagnetic copper vacuum can containing the ICR cell, two Varian leak valves, and a Varian UHV ionization gauge. It could be removed from the superconducting magnet with a vertical bore and baked at 200 °C. Separate inlets through the leak valves provided a 1×10^{-10} Torr partial pressure of helium and 4×10^{-10} Torr of tritium. Ions were generated by a grid-switched 30 V or 90 V, 0.5-μA electron beam. Impurity ions were removed by an axial resonance rf pulse, swept from 10 to 150 kHz, and blanked while passing through the $^3H^+$ and $^3He^+$ resonances. The ions measured were excited to 3.6-mm-diam orbits by a 10-μs rf pulse at the doublet center frequency. A ±30% change in the orbit diameter had no influence upon the frequency differences measured, but smaller orbits lead to some line broadening by mutual space charge effects and larger orbits introduce significant relativistic corrections. The relativistic effects and corrections for the axial movement of ions do not exceed 0.2 eV for the trap voltages and ion-orbit diameters used and are thus insignificant. The ion mass differences and the $^3He^+$-to-$^3H^+$ line intensity ratios were calculated separately for each run from the Lorentzian fit parameters after the Fourier transformation, and averaged over twenty runs.

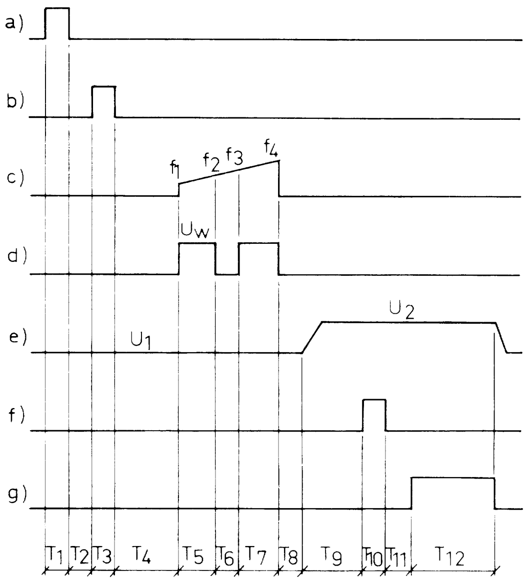

FIG. 2. The pulse sequences used in the experiments: (a) quench pulse, (b) ionization pulse, (c) axial resonance frequency sweep, (d) axial excitation pulse with blanking, (e) trap potential, (f) cyclotron resonance excitation pulse, (g) registration of the free induction decay.

The $^3H^+$-$^3He^+$ ion mass difference is given by

$$m_{^3H^+} - m_{^3He^+} = \frac{eN_A B(f_{^3He^+} - f_{^3H^+})}{2\pi f_{^3He^+} f_{^3H^+}}$$

$$= \frac{m_{^3H^+}}{f_{^3He^+}}(f_{^3He^+} - f_{^3H^+}),$$

where $m_{^3H^+}$, $m_{^3He^+}$ are ion masses in atomic mass units, e is ion charge in coulombs, N_A is Avogadro's number, B is the magnetic induction in tesla, and $f_{^3H^+}$, $f_{^3He^+}$ are the ICR frequencies in hertz.

Using the recent Avogadro number $N_A = 6.022\,0978 \times 10^{26}$ kmol^{-1} ±1 ppm, $e = 1.602\,1892\times10^{-19}$ C ±3 ppm, $m_{^3H^+} = 3.015\,500\,695$ amu ±20 ppb, $c = 2.997\,924\,58\times10^8$ ms^{-1} ±4 ppb, and the ICR frequency $f_{^3He^+} = 239\,359\,88$ Hz ±1 ppm, we get $(m_{^3H^+}/f_{^3He^+})\times(c^2/eN_A) = 117.351 \pm 0.001$ eV/Hz for the frequency-splitting–mass-splitting conversion coefficient.

The effective magnetic field B is averaged by the rapid cyclotron and axial motion of the trapped ions in the active zone of the cell and cannot be directly measured. Such averaging is highly efficient and leads to very narrow resonances, but even very small differences in the relative size and form of the $^3He^+$ and $^3H^+$ ion clouds cause significant deviations of the measured mass-doublet splitting from the true value. Different ionization mechanisms are the main cause of these artifacts. In contrast to $^3He^+$ ions which are formed upon electron impact with nearly thermal energies, the $^3H^+$ ions are produced in direct and helium-mediated dissociation processes with excess kinetic energy comparable with the trapping energy. These differences in ionization result in a different spatial distribution of the ions. The corresponding changes in doublet frequency splitting increase with the space charge which would otherwise influence both $^3H^+$ and $^3He^+$ ICR frequencies to the same degree.[11] At a low 30-V ionization voltage and long ionization times the results shown in Fig. 3(a) display a large spread of data points with a very pronounced dependence upon ion concentration and the ^3He-to-$^3H^+$ ratio. The curves

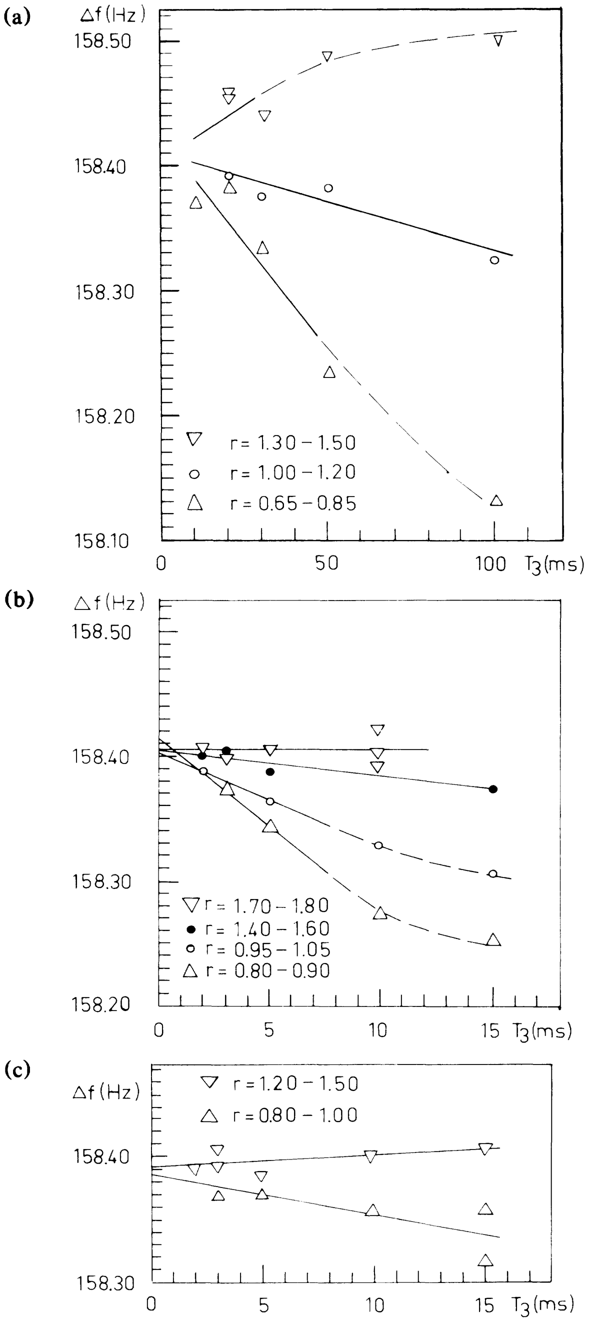

FIG. 3. The $\Delta f = f_{^3\mathrm{He}^+} - f_{^3\mathrm{H}^+}$ frequency difference vs ionization time plots for various signal intensity ratios $r = {}^3\mathrm{He}^+/{}^3\mathrm{H}^+$. (a) 30-V ionization voltage, $T_1 = 50$ ms, $T_2 = 20$ ms, $T_3 = 20$ to 100 ms, $T_4 = 10$ ms, $T_5 = 120$ ms, $T_6 = 24$ ms, $T_7 = 136$ ms, $T_8 = 100$ ms, $T_9 = 0.7$ s, $T_{10} = 10$ μs, $T_{11} = 140$ ms, $T_{12} = 3$ s, $U_1 = U_2 = 2$ V, $U_w = 0.3$ $\mathrm{V_{pp}}$, $f_1 = 12$ kHz, $f_2 = 72$ kHz, $f_3 = 84$ kHz, $f_4 = 152$ kHz. (b) 90-V ionization voltage, $T_3 = 2$ to 15 ms, $T_4 = 2.5$ s, $U_1 = 1$ V, $U_2 = 3.5$ V, $U_w = 0.14$ $\mathrm{V_{pp}}$, $f_1 = 8$ kHz, $f_2 = 50$ kHz, $f_3 = 58$ kHz, $f_4 = 105$ kHz, otherwise as in (a). (c) 90-V ionization voltage, $U_w = 0.24$ $\mathrm{V_{pp}}$, otherwise as in (b).

tend to converge in the vicinity of 158.41-Hz frequency difference, but the curvature and ion-ratio sensitivity are such that no meaningful extrapolation is possible. In the following two series of experiments a 90-V ionization voltage was used. In order to equalize the behavior of different ions after ionization, axial cooling was used. Resistive 50-kΩ rf loading was provided between the trap plates, but proved inefficient. Application of a low trap voltage ($U_1 = 1$ V) during the long delay time $T_4 \leq 2.5$ s followed by an adiabatic increase to a high value allowed the more energetic ions to leave the cell through the axial motion, thus providing cooling by selection, and largely equalizing the spatial distribution of the different ions in the cell. There is still some ion concentration and ${}^3\mathrm{He}^+$-to-${}^3\mathrm{H}^+$ ratio dependence, but the plots in Fig. 3(b) are much closer, more linear, and show a good asymptotic behavior by converging to 158.405 Hz at zero on concentration.

In the third series of experients [Fig. 3(c)] the cooling by selection was even more efficient and the asymptotic behavior was even more pronounced with the ${}^3\mathrm{H}^+$-${}^3\mathrm{He}^+$ frequency difference convergence point at 158.390 Hz.

An adiabatic raise of the trap voltage to $U_2 = 3.5$ V centers the ions in the most homogeneous magnetic and electric fields and is obligatory during free-induction signal registration for the best resolution, sensitivity, and good Lorentzian line shapes of the doublet lines. At 10^{-8} resolution and the shortest 2-ms ionization times only about twenty ions of a kind were present. The number of ions was calculated according to Comisarow[12] from the input resonant circuit parameters and the signal amplitude.

Our simple average ${}^3\mathrm{H}$-${}^3\mathrm{He}$ atomic mass difference 18 599 ± 3 eV[9] actually encompasses the precise difference value 158.40 ± 0.01 Hz, equal to 18 599 ± 1 eV, found in the experiments with axial equalization of the spatial distribution of tritium and helium ions. Since, however, the H_3^+ ions formed during the axial cooling and equalization process may have influenced the measured mass difference by up to 1 eV, it is prudent to leave ± 2 eV as an error estimate giving 18 599 ± 2 eV as the exact value of the atomic mass difference of tritium and helium-3.

The ${}^3\mathrm{H}$-${}^3\mathrm{He}$ atomic mass difference found in this study practically coincides with the first, uncorrected results of Smith and Wapstra, 18 600 ± 7 eV.[2] It is very close to the recent atomic mass differences, calculated from the tritium β-decay data, in particular those of Lubimov *et al.* (18 603.6 ± 7 eV)[4] and Dixon *et al.* (18 594 ± 25 eV),[6] and this is consistent with a nonzero electron (anti)neutrino mass. The exact value must await the results of exact measurements of atomic tritium β decay now in progress.

---

[1] K.-E. Bergkvist, Nucl. Phys. **B39**, 317, 371 (1972).

[2] L. G. Smith and A. H. Wapstra, Phys. Rev. C **11**, 1392 (1975).

[3] L. G. Smith, E. Koets, and A. H. Wapstra, Phys. Lett. **102B**, 114 (1981).

[4] V. A. Lubimov, S. T. Boris, A. I. Golutvin, L. P. Lapin, V. V. Nagovitsyn, E. G. Novikov, V. Z. Nozik, V. A. Solostchenko, I. H. Tikhomirov, and E. F. Tretyakov, in *Proceedings of the International Europhysics Conference on High Energy Physics, Brighton, July 1983,* edited by J. Guy and C. Costain (Rutherford-Appleton Laboratory, Chilton, Didcot, United Kingdom, 1984), p. 386.

[5] J. J. Simpson, Phys. Rev. D **23**, 649 (1981).

[6] W. R. Dixon, W. F. Davidson, R. S. Storey, and D. M. Rehfield, Phys. Lett. **108B**, 265 (1982).

[7] V. A. Lubimov, E. G. Novikov, V. Z. Nozik, E. F. Tretyakov, and V. S. Kosik, Phys. Lett. **94B**, 266 (1980).

[8] J. F. Wilkerson, T. J. Bowles, J. C. Browne, T. H. Burritt, J. A. Helfrich, D. A. Knapp, M. P. Maley, R. G. H. Robertson, and M. L. Stelts, Bull. Am. Phys. Soc. **29**, 665 (1984).

[9] E. T. Lippmaa, R. J. Pikver, E. R. Suurmaa, J. O. Past, J. H. Puskar, I. A. Koppel, and A. A. Tammik, Pis'ma JETP **39**, 529 (1984).

[10] E. N. Nikolaev, J. I. Neronov, M. V. Gorshkov, and V. L. Tal'roze, Pis'ma JETP **39**, 441 (1984).

[11] E. B. Ledford, Jr., S. Ghaderi, R. L. White, R. B. Spencer, P. S. Kulkarni, C. L. Wilkins, and M. L. Gross, Anal. Chem. **52**, 463 (1980).

[12] M. B. Comisarow, in *Ion Cyclotron Resonance Spectrometry II,* edited by H. Hartmann and K.-P. Wanczek, (Springer-Verlag, Berlin, 1982) p. 484.