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C^{14}-N^{14} Mass Difference and Mass Excesses of Some Light Nuclides*

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Mass excesses of the nuclides H^1, D^2, C^{12}, C^{14}, N^{14}, O^{18}, and Ar^{40} were determined by measurement of 18 parent molecule ion doublets with the mass synchrometer. The C^{14}-N^{14} difference, 156.44±0.29 kev, was obtained from measurements on the doublets [$C^{14}O^{18}$-O_2], [$N^{14}O^{18}$-O_2], [$C^{14}H_4$-H_2O], [$C^{14}CH_2CO$], and [N_2H_4-O_2] and other doublets which give some of those above. This is in excellent agreement with the value of 156±1 kev obtained from determination of the C^{14} beta end point. The consistency of these data supports the 1 kev upper limit for the neutrino rest mass derived from the H^3-He^3 mass difference and the H^3 beta end point, and also supports the argument that mass synchrometer data are essentially free of systematic errors of the magnitude required to account for discrepancies between nuclear reaction and mass spectrographic mass excesses of C^{12} and O^{18}. Mass excesses of the light nuclides determined were slightly higher than recently published mass synchrometer data, but agreement was generally within 1 μMU.

INTRODUCTION

PRECISE measurement of the atomic masses of parent and daughter nuclides in systems undergoing β decay, taken with independently determined β spectra, provide an experimental approach to the determination of the upper limit of the neutrino rest mass. Alternatively, a theoretical value of zero rest mass may be accepted and then the atomic masses give an accurate value of the maximum β energy. Mass synchrometer determinations of the atomic masses of H^3 and He^3 have been published recently[1] and were used to establish an experimental upper limit of approximately 1 kev for the neutrino rest mass. The C^{14}-N^{14} mass difference appeared to be a particularly interesting subject because of the possibility of its measurement in several different parent molecule ions. This provides a better opportunity to uncover systematic errors and also permits the determination of mass excesses of stable light nuclides under very similar experimental conditions. Thus the C^{14} beta end point obtained from β spectra may be used as an external calibration to shed light on discrepancies between mass excesses of stable light nuclides determined from nuclear Q values and mass data.[2]

EXPERIMENTAL

A complete description of the mass synchrometer has been published by Smith and Damm.[3] Some recent modifications and the general operating procedure for mass difference determination are reported in a recent paper by Smith.[4] The only subsequent change in the mass synchrometer was narrowing of slits by a factor of 2, which gave half-width resolutions ranging between 30 000 and 40 000 for ions in the mass 20–32 region. Thermostatic control of magnet cooling water was installed to improve magnet stability.

Procedures for preparation and purification of the C^{14} and O^{18} containing compounds used in this work are given in the Appendix.

DISCUSSION OF RESULTS

The primary objective of this investigation was to determine by mass measurement the mass difference, C^{14}-N^{14}, and to compare this value with the maximum β energy in C^{14} decay. The C^{14}-N^{14} doublet is not resolvable with the mass synchrometer and it is not desirable to attempt precise mass measurements on atomic ions produced by electron impact. The required resolution for C^{14}-N^{14} is of the order of 100 000 or about three times better than generally available. The atomic ions are usually produced in low abundance with varying amounts of kinetic energy which destroys the advantage gained in the precise peak matching techniques. For these reasons the C^{14}-N^{14} mass difference was measured by taking the differences between the $C^{14}O^{18}$-O_2 and $N^{14}O^{18}$-O_2 parent molecule ion doublets and by finding similar differences from doublets involving $C^{14}H_4$-H_2O, $C^{14}C^{12}H_2$-CO, and N_2H_4-O_2, etc. Attempts to measure

TABLE I. Doublet values in μMU.

M	Doublet	ΔM_1[a]	ΔM_2[b]	ΔM_3[c]
18	$C^{14}H_4$-H_2O	23 987.12 ±0.23	23 986.72 ±0.39	
20	CD_4-ND_3	11 032.15 ±0.27	11 033.09 ±0.49	11 031.386 ±0.06
20	CD_4-D_2O	33 304.48 ±0.28	33 303.96 ±0.74	33 300.179 ±0.08
20	ND_3-D_2O	22 270.46 ±0.19	22 270.87 ±0.47	22 268.79 ±0.08
20	CD_4-H_2O^{18}	41 614.44 ±1.08	41 614.812 ±1.48	41 611.76 ±0.11
20	D_2O-$\frac{1}{2}Ar^{40}$	41 943.43 ±0.60	41 942.44 ±1.33	41 940.37 ±0.15
20	H_2O^{18}-$\frac{1}{2}Ar^{40}$	33 630.59 ±0.61	33 631.59 ±1.32	33 628.79 ±0.14
28	C_2H_4-N_2	25 164.34 ±0.29	25 164.20 ±0.88	25 160.86 ±0.4
28	N_2-CO	11 238.39 ±0.48	11 237.78 ±0.61	11 237.41 ±0.11
28	C_2H_4-CO	36 404.48 ±0.71	36 401.96 ±0.70	36 397.33 ±0.11
28	C_2H_4-$C^{14}CH_2$	12 416.05 ±0.52	12 415.24 ±0.86	
28	$C^{14}CH_2$-N_2	12 748.52 ±0.24	12 748.94 ±0.95	
28	$C^{14}CH_2$-CO	23 987.29 ±0.38	23 986.72 ±0.66	
32	NO^{18}-O_2	12 410.18 ±0.29	12 411.01 ±0.81	
32	$C^{14}O^{18}$-O_2	12 578.67 ±0.44	12 577.86 ±0.88	
32	N_2H_4-O_2	47 638.64 ±0.65	47 639.74 ±0.98	
32	N_2H_4-NO^{18}	35 227.72 ±0.43	35 228.73 ±1.30	
40	C_3H_4-Ar^{40}	68 945.91 ±0.83	68 944.92 ±1.65	68 940.69 ±0.31

[a] Experimental results.
[b] Adjusted values from least-squares analysis.
[c] Data of Smith, 1958.

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[1] L. Friedman and L. G. Smith, Phys. Rev. **109**, 2214 (1958).

[2] H. E. Duckworth, Revs. Modern Phys. **29**, 767 (1957).

[3] L. G. Smith and C. S. Damm, Rev. Sci. Instr. **27**, 638 (1956).

[4] L. G. Smith, Phys. Rev. **111**, 1606 (1958).

$C^{14}O^{16}$-C_2H_6 and $N^{14}O^{16}$-C_2H_6 at mass 30 failed because of the interference of $C^{12}O^{18}$ which was always present because of the natural abundance of O^{18}. The peak distortion arising from 0.2% $C^{12}O^{18}$ which was not completely resolved from $C^{14}O^{16}$ (the peaks are separated by ~1 mMU) was easily detectable and reliable superposition of $C^{14}O^{16}$ and C_2H_6 on the oscilloscope screen was not achieved. The doublets measured for determination of C^{14}-N^{14} are listed in Table I with values for ten other doublets which have been previously investigated. The purpose of the latter is to provide sufficient information for determination of the mass excesses of the light nuclides, H^1, D^2, C^{12}, N^{14}, O^{18}, and Ar^{40} from data gathered under experimental conditions similar to the C^{14}-N^{14} mass determination.

Table I contains sufficient information to compute the mass excess of D−2 from the cycle: $D-2=\frac{1}{4}(CD_4-\frac{1}{2}Ar)+\frac{1}{8}(CH_4-O)-\frac{1}{8}(C_3H_4-Ar)$. Mass excesses for the remaining stable light nuclides and C^{14} can readily be computed from the available data. A least-squares analysis of the data which yielded directly mass excesses of the seven nuclides was carried out using the BNL Remington Rand punched card computer. The results of this calculation are presented in Table II along with earlier data of Smith obtained from a similar computation. The adjusted values of the doublets presented in Table I were computed from the least-squares solutions.

TABLE II. Mass excesses in μMU.

Excess	Δ_1[a]	Δ_2[b]	Q Value
H^1-1	8146.365 ±0.278	8145.395 ±0.037	8145.2 ± 1.5[c]
D^2-2	14 743.730 ±0.370	14 742.216 ±0.044	14 740.3 ± 2.8[c]
$C^{12}-12$	3816.498 ±0.853	3815.75 ±0.11	3811 ± 7[d]
$C^{14}-14$	7693.992 ±0.776		
$N^{14}-14$	7527.142 ±0.515	7526.577 ±0.085	7519 ± 3[d]
$O^{18}-18$	4883.874 ±0.785	4882.06 ±0.11	4867 ±11[d]
$Ar^{40}-40$	24 909.954 ±1.841	24 911.88 ±0.28	

[a] Results of this study.
[b] Best values from mass synchrometer reported by Smith.
[c] A. H. Wapstra, Physica **21**, 367 (1955).
[d] See reference 8.

There is a systematic trend to higher values of doublet spacing from Smith's data recently published and our results in Table I. This trend is very similar in both direction and magnitude to one noted by Smith over a period of five years of work with the mass synchrometer. It was ascribed by him to the effect of surface charges producing small electric fields predominantly in the inward radial direction. This produces an error which increases with increased doublet spacing and which Smith found could be minimized by careful installation of a baffle to prevent the ion beam from striking walls of the source housing. Narrowing of slits, which was done subsequently, could produce an effect similar to the one obtained by installation of baffles. Another factor which probably had a more profound effect on surface charges was the use of quantities of gases containing radioactivity. The introduction of $C^{14}H_4$ or $C^{14}C^{12}H_2$ produced a noticeable improvement in resolution, which may be correlated with improved surface conductivity. The magnitude of shifts observed in the comparison of Smith's and our own data is approximately 1 μMU or less per 10 mMU doublet width. Exceptions to this are the C_2H_4-CO and C_2H_4-N_2 doublets which will be discussed in more detail below. The effect of this shift to wider doublet spacing on the mass excesses of the respective nuclides is shown in Table II. With the exception of O^{18} and Ar^{40} all mass excesses are increased by approximately 1 μMU. Ar^{40} and O^{18} are increased by 1.5 and 1.8 μMU, respectively. The comparison of O^{18} with old data is significant in view of the value[5] of 4867±11 μMU obtained from Q values for the O^{18} mass. The value reported herein is actually half way between Smith's data and Nier's value[6] of 4885.4 ±0.7 μMU and certainly confirms the mass spectrographic data.

The errors reported for the eighteen doublets in Table I are standard errors of the mean of individual readings and are considerably larger than Smith's errors. The precision of our data, while perhaps not the best obtainable from the mass synchrometer, is adequate for the purpose of obtaining C^{14}-N^{14} more accurately than available from beta end point data and for uncovering possible systematic errors which would account for discrepancies of mass data with Q-value mass excesses. The statistical treatment of the data in Table I permits a consistency test measured by the minimized sum of squares, $\chi^2=\sum_i(D_i-\Delta_i)^2/\sigma_i^2$, where D_i and Δ_i are, respectively, the adjusted and observed values, σ_i^2 the variances of the latter. The expected value of χ^2 is the number of doublets minus the number of independent quantities determined. In this case the expected value $\chi^2=18-7=11$ while the value computed from the data is 66. This error must be multiplied by $(66/11)^{\frac{1}{2}}$ or 2.2 for external consistency and indicates that the operating procedure followed did not permit sufficient randomization of all significant variables. This was also experienced by Smith and one must conclude that larger statistical errors in our work reflect a wider scatter of data rather than a more random sampling procedure.

Comparison of adjusted values and the original data in Table I gives 3.5×10^{-8} for the rms value of the ratio of adjustment required per mass unit for all eighteen doublets. An external precision of about one part in 30 million is thus expected from twenty measurements of a doublet. Smith's rms adjustment per mass unit gives a value of one part in 40 million for expected external consistency, in fair agreement with our results. Our data tend to scatter more widely from the mean than Smith's, but the average values determined indicate that the peak matching technique used is reliable to a precision of the order of one thousandth of a peak width.

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[5] Scolman, Quisenberry, and Nier, Phys. Rev. **102**, 1076 (1956).

[6] L. J. Lidofsky, Revs. Modern Phys. **29**, 773 (1957); C. S. Wu and A. Schwarzschild, Phys. Rev. **91**, 483(A) (1953), and private communication to L. J. Lidofsky.

TABLE III. C^{14}-N^{14} mass difference in μMU.

Doublet	Δm in μMU
1. $(C^{14}O^{18}\text{-}O_2)-(NO^{18}\text{-}O_2)$	168.49 ± 0.52
2. $(C^{14}H_4\text{-}H_2O)-\frac{1}{2}(N_2H_4\text{-}O_2)$	167.80 ± 0.46
3. $(C^{14}CH_2\text{-}CO)-\frac{1}{2}(N_2H_4\text{-}O_2)$	167.97 ± 0.50
4. $(C^{14}CH_2\text{-}N_2)-\frac{1}{2}(C_2H_4\text{-}N_2)$	166.35 ± 0.28
5. $\frac{1}{2}(C_2H_4\text{-}N_2)-(C_2H_4\text{-}C^{14}CH_2)$	166.12 ± 0.54
6. $(C^{14}O^{18}\text{-}O_2)+(N_2H_4\text{-}NO^{18})-(N_2H_4\text{-}O_2)$	167.75 ± 0.90
7. $(C^{14}H_4\text{-}H_2O)-\frac{1}{2}(N_2H_4\text{-}NO^{18})-\frac{1}{2}(NO^{18}\text{-}O_2)$	168.17 ± 0.44
8. $(C^{14}CH_2\text{-}CO)-\frac{1}{2}(N_2H_4\text{-}NO^{18})-\frac{1}{2}(NO^{18}\text{-}O_2)$	168.34 ± 0.46
9. $(C^{14}CH_2\text{-}N_2)-(N_2\text{-}CO)-\frac{1}{2}(N_2H_4\text{-}O_2)$	167.69 ± 0.63
10. $(C_2H_4\text{-}CO)-(C_2H_4\text{-}C^{14}CH_2)-\frac{1}{2}(N_2H_4\text{-}O_2)$	169.11 ± 0.94
11. $(C^{14}CH_2\text{-}H_2)-\frac{1}{2}(C_2H_4\text{-}CO)-\frac{1}{2}(N_2\text{-}CO)$	165.48 ± 0.89
12. $\frac{1}{2}(C_2H_4\text{-}CO)-\frac{1}{2}(N_2\text{-}CO)-(C_2H_4\text{-}C^{14}CH_2)$	167.00 ± 1.0
13. $(C^{14}CH_2\text{-}CO)-(N_2\text{-}CO)-\frac{1}{2}(C_2H_4\text{-}N_2)$	166.73 ± 0.89
Least squares	166.88 ± 0.93
From above, omitting C_2H_4 doublets	168.03 ± 0.31

The C^{14}-N^{14} mass difference can be determined from combination of doublets listed in Table III. The mass differences computed from mass excesses obtained from the least-squares analysis of all data and from selected doublets which omit all measurements against ethylene are also given in Table III. These data agree within the limits of estimated experimental error but inspection of Table III shows that doublets giving C^{14}-N^{14} fall into two groups: those which involve measurements on ethylene and the others. The average of values for C^{14}-N^{14} obtained from $[C^{14}O^{18}\text{-}O_2]-[N^{14}O^{18}\text{-}O_2]$ and the $C^{14}H_2$-$N^{14}H_2$ derived from $C^{14}H_4$, $C^{14}C^{12}H_2$, and N_2H_4 doublets are 168.08 μMU. The maximum deviation from this average is 0.46 μMU. If doublets containing ethylene are averaged the mass difference for C^{14}-N^{14} is 166.80 μMU, with a maximum deviation of 2.3 μMU. The avarage deviations are in both cases much smaller and the two values do not overlap within respective estimated error limits. The ethylene doublets scatter by 3.6 μMU, approximately four times the scatter of the other C^{14} doublets. This large scatter can be accounted for by assumption that all measurements against ethylene are a few μMU too large. For example, in doublets where $(C_2H_4\text{-}X)$ or $\frac{1}{2}(C_2H_4\text{-}X)$ is subtracted, the C^{14}-N^{14} difference is low. The tenth item in Table III, which gives 169.11 μMU for $C^{14}H_2$-$N^{14}H_2$, suggests a larger error on the C_2H_4-CO doublet than on the C_2H_4-$C^{14}CH_2$. This shows up at the 2.5 μMU difference of the measured value of C_2H_4-CO and its adjusted value. This adjustment is much larger than at any other doublet. Comparison of earlier determinations of C_2H_4-CO with our own shows a 7 μMU discrepancy, which is considerably larger than shifts on other doublets of similar width.

The anomaly in connection with measurements on ethylene is probably associated with the fact that the ethylene ion is both a parent molecule ion and a fragment ion which can be formed in good yield from a variety of higher molecular weight hydrocarbons. It is difficult to be sure that all ethylene precursor ions are eliminated and that the kinetic energy distribution for ethylene is really that of a parent molecule ion at the ion source temperature. This objection to ethylene as a compound for mass measurement applies generally to olefin ions and acetylenes as well. Isotopically tagged molecules are exceptions inasmuch as one would have to have saturated impurities of the proper isotopic constitution to set up a similar interference. Olefins and ethylene in particular are subject to an additional limitation in view of the fact that metastable transitions in which ethane, for example, loses a hydrogen atom gives rise to ions which are slightly heavier than $C_2H_4^+$. Such metastables would not necessarily be resolved from ethylene and could distort peak shapes, giving rise to high values for ethylene doublets. From the remarks above, it appears that there is sufficient basis for the rejection of ethylene doublets from the C^{14}-N^{14} determination. This gives 168.03 ± 0.31 μMU or 156.44 ± 0.29 kev for the C^{14}-N^{14} mass difference. Perhaps a significant aspect of the C^{14}-N^{14} determination is the manner in which it demonstrates the danger of a systematic error which would be detected only with difficulty through measurements of larger mass differences.

The value of 156.44 kev for C^{14}-N^{14} compares favorably with 156±1 kev selected by Lidofsky[6] as the best value for the maximum beta energy of C^{14}. Data summarized in Lidofsky's review range from 155±1 to 158.5±0.5 kev. This latter value of Pohm *et al.*[7] is approximately 2 kev high and is in disagreement both with mass data and other beta end-point determinations. These data are consistent with results of a study on the comparison of the T^3-He^3 mass difference and the T^3 beta end point. Here again the errors reported for the C^{14} beta end point are equal to or greater than the estimated error for the mass difference and is the limiting factor in setting a low upper limit for a neutrino rest mass.

The consistency of the C^{14}-N^{14} mass difference and the C^{14} beta endpoint data provide strong support for the argument that the other current mass spectrometer measurements are not only more precise than nuclear reaction data but also, where large discrepancies exist as in the cases of C^{12} and O^{18}, more accurate. Kettner[8] has analyzed the problem of adjustment of various nuclear reaction *Q*'s in the consistent computation of C^{12} and O^{18} mass excesses. This is useful in searching out nuclear reactions that are poorly determined or in error.

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[7] Pohm, Waddell, Powers, and Jensen, Phys. Rev. **97**, 432 (1955).

[8] M. E. Kettner, Phys. Rev. **102**, 1065 (1956).

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APPENDIX

$C^{14}O$, $C^{14}O^{18}$, and CO^{18}

These compounds were prepared by reduction of about 10 cc of the corresponding carbon dioxide by heating overnight in a sealed tube at 400°C with 40-mesh zinc. The zinc was pretreated with dilute acetic acid, then was washed and vacuum dried at 150°C. Tubes with a breakoff tip at one end were used, and after the reduction any water was frozen with a dry-ice slush and the contained gases pulled through a liquid nitrogen-cooled radiator trap by means of a Toepler pump, then the carbon monoxide was pumped into a container. The carbon dioxide in the radiator trap (about 25% of the original amount) was then recovered by distillation. This treatment gave carbon monoxide sufficiently free of the dioxide for the purposes of the experiment. For the O^{18} compounds, the appropriate carbon dioxide was first allowed to equilibrate with 1 cc of 90% H_2O^{18} by shaking overnight.

NO^{18}

About 10 cc of nitric oxide was shaken overnight with 1 cc of 25% H_2O^{18}, then the contents of the reaction vessel were frozen with liquid nitrogen. This was replaced with a dry-ice slush and the nitric oxide frozen into a sample manifold with liquid nitrogen, then passed through a 2-meter gas chromatography column packed with 25% G. E. Silicone oil No. SF-96 on C-22 firebrick and using helium at 30 cc/min as the carrier gas. The nitric oxide was trapped with liquid nitrogen, the helium pumped off and the sample distilled into a collecting bulb.

$C_2{}^{14}H_2$

Barium carbide was prepared from 1 g of shredded Ba metal (shredded under toluene with a coarse file) and 100 mg of 22% $BaC^{14}O_3$ by the method of Cox and Warne.[9] The reaction tube was cracked off and placed in a vessel on a vacuum line in which it could be treated with water. After evacuation, water was added and the evolved gases pumped through a trap cooled with liquid nitrogen. The trap was cooled with a dry-ice slush and the gases distilled into a sample manifold and passed through a gas chromatography column similar to that used for NO^{18}. The acetylene was trapped with liquid nitrogen, the helium pumped off and the product distilled into a breakoff tube. Acetylene with this isotopic content should not be stored for any appreciable length of time at room temperature, since a good deal of it is lost probably by radiation-induced polymerization.

$C^{14}H_4$

This was prepared by the reduction of $C^{14}O$ with H_2, using a nickel on Kieselguhr catalyst prepared from $Ni(NO_3)_2$ and Filter-Cel.[10] An apparatus was made in which the catalyst (about 0.5 g) was placed on a medium glass frit in a vertical tube which could be heated with a small ceramic furnace. A Toepler pump was provided at the bottom of the apparatus, along with a *T* stopcock with a joint on the side arm to accept gas collection bulbs. An open-end manometer was provided on the apparatus, and at the top a stopcock and joint which could be attached to a vacuum line. The catalyst was reduced in place by passing a stream of hydrogen through it while heating to 400°C. All joints were lubricated with high temperature Apiezon grease or wax. The system was then connected to a vacuum line and evacuated, with the $C^{14}O$ collection bulb in place above the Toepler pump. The system was closed and the $C^{14}O$ pumped into the main part of the system and the pressure measured as a drop of 80 mm on the manometer. The $C^{14}O$ was then taken back into the Toepler pump and hydrogen was introduced from the vacuum line to give a pressure drop of 250 mm on the manometer. The system was again closed off and the two gases were pumped up and down through the catalyst bed, which was heated to 250°C. After about 15 min of pumping, the pressure reading on the manometer was about one-half of its original value. The gases were then pumped back into the bulb which had originally contained the $C^{14}O$. These gases were then pumped through a radiator trap at liquid nitrogen temperature and into another collection bulb. The product contained about 3% H_2 and a trace (about 0.2%) of unreduced CO, but was satisfactory for use in these experiments.

The procedure for preparation of CD_4 is similar to that for $C^{14}H_4$ except for the use of D_2 and $C^{12}O$ as starting materials. The other materials used are commercially available chemicals.

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[9] J. D. Cox and R. J. Warne, J. Chem. Soc. **1957**, 1893.

[10] H. B. Adkins, *Reactions of Hydrogen* (University of Wisconsin Press, Madison, Wisconsin, 1937), p. 19.