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The Mass Differences of the Fundamental Doublets Used in the Determination of the Isotopic Weights C^{12} and N^{14}

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The values of the mass of C^{12} as determined by different observers, show a discrepancy well outside the corresponding probable errors. This mass is important since it is used in the determination of so many of the other isotopic weights. Fundamental to its determination is the mass difference $C^{12}H_4-O^{16}$. With the large spectrograph completed last year, a new determination of this mass difference has been made. In addition, the $C^{12}H_2-N^{14}$ mass difference has been checked by means of the doublets $C^{12}H_3-N^{14}H$ and $C^{12}H_4-N^{14}H_2$. These values together with the associated experiments are reported in the present paper.

I. INTRODUCTION

THE importance of the isotopic weight of C^{12} and consequently the mass difference of the fundamental doublet $C^{12}H_4-O^{16}$ which is used in its determination, has been discussed in a series of letters to *Nature* by Dr. Aston.[1] Since C^{12} is the most important substandard used in the determination of isotopic weights, and since there is a discrepancy between the value obtained by Dr. Aston[2] and that obtained by Bainbridge and Jordan, and later by others,[3,4] a careful study of the $C^{12}H_4-O^{16}$ doublet has been made on the new mass spectrograph.[5] A complete discussion of this discrepancy is included in Dr. Aston's papers as well as in a recent paper by Mattauch.[6]

Last year, shortly after the mass spectrograph was completed, a number of $C^{12}H_4-O^{16}$ doublets were obtained on one plate which gave a value for this mass difference approximately that of the average of the values reported to date, i.e., of the first four values listed in Table I.

Since this value differed appreciably from any of the others, and since at that time, all of the preliminary runs on the spectrograph had not been completed, a report of this mass difference was delayed until additional plates could be obtained. Although, since then, a large number of $C^{12}H_4-O^{16}$ doublets have been photographed on six different plates, some of these plates having been exposed only after radical variations were made, the resulting mass difference is essentially the same as that obtained from the first plate. For convenience in discussing the details of these separate experiments a schematic diagram of the mass spectrograph is shown in Fig. 1.

TABLE I. *The $C^{12}H^1_4-O^{16}$ mass differences in terms of 10^{-4} mass unit.*

Aston	360.1 ±1.6
Bainbridge and Jordan	364.9 ±0.8
Mattauch and Bonisch	364.06±0.40
Asada, Okuda, Ogata and Yoshimoto	364.2 ±0.9
Jordan	363.2 ±0.35*

* This error is three times the probable error computed from internal consistency of data.

II. EXPERIMENTAL DETAILS

A. Source

The discharge tube used was the usual cylindrical type in which a low pressure discharge was maintained by a unidirectional pulsating potential difference of fifteen to twenty kilovolts. An aluminum cathode of the Thomson type was mounted on the iron base which supports the discharge tube. The gas, in this case a mixture of methane, nitrogen and oxygen, was admitted into the tube within the cathode opening.

The discharge was collimated by means of a large water-cooled solenoid mounted on the front end of the analyzer magnet and carefully aligned so that its axis was parallel to the axis of the collimating slits S_1 and S_2 (Fig. 1).

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[1] F. W. Aston, Nature **137**, 357 (1936); **137**, 613 (1936); **138**, 1094 (1936); **139**, 922 (1937); **141**, 1096 (1938); **143**, 797 (1939).

[2] F. W. Aston, Proc. Roy. Soc. **A163**, 391 (1937).

[3] J. Mattauch, Zeits. f. tech. Physik **19**, 578 (1938); Physik. Zeits. **39**, 892 (1938).

[4] T. Asada, T. Okuda, K. Ogata and S. Yoshimoto, Nature **143**, 797 (1939). Proc. Phys. Math. Soc. Japan 22, 23 (1940).

[5] E. B. Jordan, Phys. Rev. **57**, 1072A (1940).

[6] J. Mattauch, Phys. Rev. **57**, 1155 (1940).

By means of this solenoid, field strengths of the order of 1000 gauss were maintained within the source region when a run was made. This field together with the opening in the aluminum cathode serves to align the narrow pencil-shaped beam of electrons passing from cathode to anode, and thus a maximum positive ion beam intensity is obtained at all times.

The most important feature of this arrangement is that it ensures uniform illumination of the image slit by all types of positive ions present. That this is an important factor was demonstrated in one experiment in which the solenoid and cathode were adjusted so that the core of the discharge made a slight angle with the axis of the collimating slits. After development, the photographic plate showed lines corresponding to the $N^{14}H^{1+}_2$ and O^{16+} ions, but no line corresponding to the $C^{12}H^{1+}_4$ ion, although a large portion of the gas in the discharge tube was methane. It is thus not hard to conceive of cases in which there would be a uniform illumination of the image slit by one ion corresponding to a given doublet pair, and only partial illumination by the other ion. One could even obtain matched doublets under such conditions, but the resulting error in the completed mass difference would be large. In addition to obviating these difficulties, the magnetic field tends to steady the discharge at all times.

B. Disperser magnetic field

Initially the pole pieces of the disperser magnet (indicated by the letter H_2 in Fig. 1) were first surface ground and then polished by hand. After assembly, the gap width (5 mm) was checked by means of a steel wedge and was found to be accurate to ±0.0005″. This gap width is 66 percent greater than that used in other instruments, and thus the percentage error due to small surface variations is correspondingly less. The angles which the end faces make with the top surface were estimated to be accurate to ±20 seconds of arc.

In spite of the many precautions taken in the original construction of this unit, it was later taken apart and thoroughly rechecked and resurfaced when it was found that the $C^{12}H^1_4-O^{16}$ mass difference differed slightly from previously reported values. Spectra taken before and after this change yielded values for the $C^{12}H^1_4-O^{16}$ mass difference which are in agreement within the small probable error computed from the internal consistency of the data.

C. Stray field

The integrated effect of the stray magnetic fields on each side of the pole pieces H_2 (Fig. 1), was initially calculated[7] and taken into account by cutting back the pole edges. Since the line breadth depends upon the accuracy of this correction, several runs were also made in order to find its value experimentally and at the same time to determine if there was any effect on the calculated mass differences due to these stray

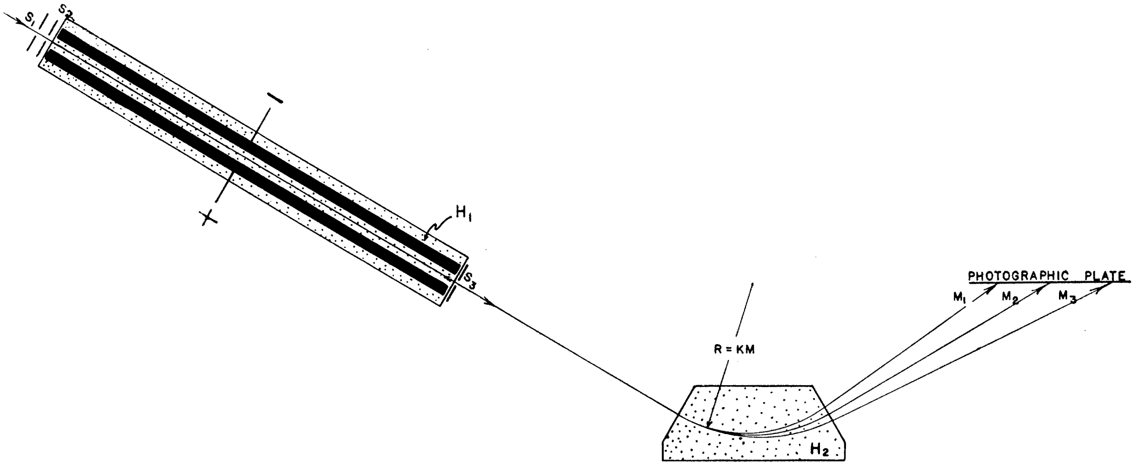

FIG. 1. Schematic diagram of apparatus.

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[7] I am indebted to Dr. Nye of this department for many helpful suggestions concerning this correction.

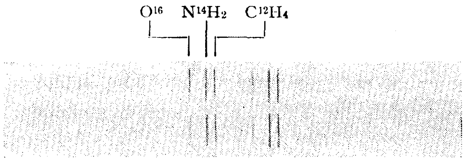

FIG. 2. $C^{12}H^1_4-N^{14}H^1_2-O^{16}$ matched triplet, natural size. $S_1=0.1$ mm, $S_2=0.04$ mm, $S_3=2$ mm.

fields. The allowed stray field correction and thus the effective dispersion of this magnet was altered by raising or lowering the disperser pole pieces relative to the rest of the spectrograph. After each change the apparatus was accurately realigned, the position of the photographic plate being kept the same throughout.

$C^{12}H^1_4-O^{16}$ doublets have been photographed for these pole pieces in two different positions. In one position the correction allowed for the effect of the stray field was 1.25 gap widths, and in the other 1.50 gap widths. The resulting mass differences for both cases were consistent and once again showed close agreement. These data also indicated that the best value for this stray field correction should be 1.65 gap widths, a value which is utilized in the present alignment.

D. Spectra

Local disturbances in the field of the instrument, if any, were minimized by photographing spectra at several different positions on each plate. When all six plates are considered, the range in distance over which useful doublets were obtained was 10 cm.

The dispersion lines used in the determination of the $C^{12}H_4-O^{16}$ mass differences were those corresponding to the $C^{12}H^{1+}_3$ ion at mass position fifteen and the $N^{14}H^{1+}_3$ ion at mass position seventeen. In some spectra a strong line corresponding to the $O^{16}H^{1+}$ ion was also present and, in such cases, was used in the determination as an additional check. These lines were identified not only by position, but also by taking exposures when only one gas was present in the discharge tube. Since deuterium has not yet been used in the spectrograph no lines due to its compounds were expected.

Another source of error, especially in the case of low resolving power instruments, is the presence of the $C^{13}H^1_3$ line. Unless it is completely resolved, this line although faint, is of sufficient density to distort seriously the shape of the $C^{12}H^1_4$ line and thus cause the resulting mass difference to be considerably lower than its true value. In the present instrument, it is separated from the $C^{12}H_4$ line by a distance of 0.4 mm.

In order to test the effect of slit S_3 (Fig. 1), doublets have been photographed for values of this opening from one to three millimeters. Although there was a slight broadening of the lines when the larger opening was used, the computed mass differences were in agreement in all three cases.

III. RESULTS

Figure 2 is a contact print of one of the mass sixteen triplets $C^{12}H^1_4-N^{14}H^1_2-O^{16}$.

In all, twenty-one doublets, obtained under the various conditions noted above, yielded a value for the $C^{12}H_4-O^{16}$ mass difference equal to 0.03632 mass unit. This value, together with those of the other observers previously referred to, is given in Table I.

It is interesting to note that Mattauch, whose value is closest to that reported in this paper, states in his last paper[6] that he has found a small systematic error which tends to lower the value he has reported for this doublet. He did not state the magnitude of this error, however, and up to the present time has not reported his later measurements. The combination check

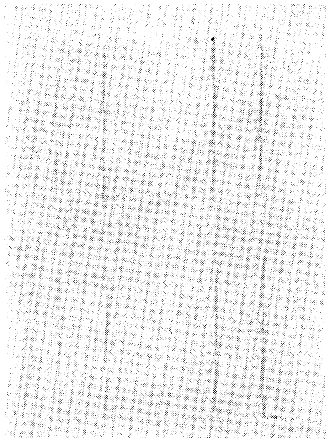

FIG. 3. $C^{12}H_3-N^{14}H$ doublets, enlarged 5 times. $S_1=0.10$ mm, $S_2=0.05$ mm, $S_3=2$ mm.

doublets which he has reported[6] also yield values lower than that obtained by direct measurement. From the $C^{12}H^1_2-N^{14}$; $N^{14}H^1_2-O^{16}$ doublet combination he obtains a value for the $C^{12}H_4-O^{16}$ mass difference equal to 0.036361 ±0.00004, and from the $C^{12}H_2-N^{14}$; $N^{14}_2-C^{12}O^{16}$ combination a value 0.036384±0.000061. Both of these values are in agreement with the value reported above by myself.

IV. The $C^{12}H^1_2-N^{14}$ Mass Difference and Check Doublets

In a recent letter to *The Physical Review*,[8] the mass difference $C^{12}H^1_2-N^{14}$ was reported and compared to the values obtained by other investigators. Since then a few check doublets at mass positions fifteen (the $C^{12}H_3-N^{14}H$ doublet) and sixteen (the $C^{12}H_4-N^{14}H_2$ doublet) have been photographed. These repeat the same mass difference respectively, one and two units higher. The value of the mass difference $C^{12}H_3-N^{14}H^1$ as obtained from five matched doublets is 0.012563. The agreement with the value 0.012560 previously obtained from measurements on doublets at mass position fourteen and already reported is very good. Enlarged spectra of this doublet are shown in Fig. 3, and a densitometer trace of one of them in Fig. 4.

Ten matched check doublets ($C^{12}H_4-N^{14}H_2$) at mass position sixteen were obtained on four different plates while attempting to obtain matched $C^{12}H_4-O^{16}$ doublets. These plates were exposed under different conditions as regards slit sizes, line focus, and plate position. A contact print of some of these spectra is shown in Fig. 2.

TABLE II. *Mass differences in terms of 10^{-4} mass unit.*

DOUBLET	$C^{12}H_2-N^{14}$	$C^{12}H_2-N^{14}H$	$C^{12}H_4-N^{14}H_2$
Mattauch and Bonisch	125.81 ±0.23	125.63 ±0.27	126.26 ±0.51
Jordan	125.60 ±0.15	125.63 ±0.13	125.50 ±0.13

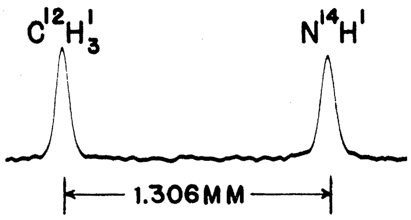

FIG. 4. Densitometer curve of one of the $C^{12}H_3-N^{14}H$ doublets.

These doublets yielded a value for the $C^{12}H_4-N^{14}H_2$ mass difference equal to 0.012550 ±0.000013.[9] Here again the agreement with the other two values as listed above is very good.

It is interesting to compare in Table II these values with those obtained by Mattauch and Bonisch[6] for the same doublets. The agreement is most excellent except in the case of the $C^{12}H_4-N^{14}H_2$ check doublet, for which Mattauch and Bonisch obtain a value somewhat higher than they do for the other two doublets.

Additional measurements on the $C^{12}H_4-O^{16}$ mass difference and check doublets used in its determination as well as other light element doublets are in progress.

The construction of the mass spectrograph was made possible by a grant to Professor Loomis and the author from the Graduate School Research Fund.

It is a pleasure to acknowledge the suggestions and aid received from Mr. Ernest Englund who was responsible for the construction of the instrument and who has aided in making the many mechanical changes discussed in this paper. I am also indebted to Professors Bartlett, Mott-Smith, Serber and Goldhaber for valuable suggestions. Valuable aid has also been received from Professor H. E. White of the University of California and Professor F. G. Dunnington of Rutgers University.

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[8] E. B. Jordan, Phys. Rev. **58**, 1009 (1940).

[9] This error is three times the probable error computed from internal consistency of data.

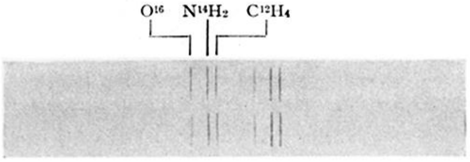

FIG. 2. $C^{12}H^1{}_4-N^{14}H^1{}_2-O^{16}$ matched triplet, natural size. $S_1=0.1$ mm, $S_2=0.04$ mm, $S_3=2$ mm.

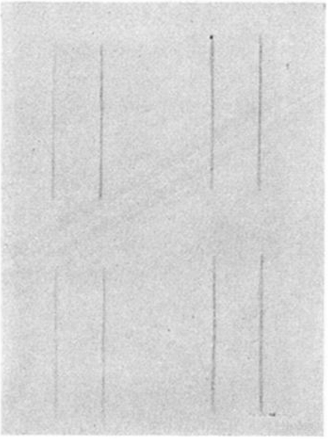

FIG. 3. $C^{12}H_3-N^{14}H$ doublets, enlarged 5 times.
$S_1=0.10$ mm, $S_2=0.05$ mm, $S_3=2$ mm.