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Measurements of Six Light Masses

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The mass differences of 16 doublets involving the six atoms H, D, ¹⁴N, ¹⁶O, ³⁵Cl, and ³⁷Cl have been measured with a new rf mass spectrometer with considerably greater precision than was attainable with the mass synchrometer. By least-squares adjustment, best values of the mass excesses of these six atoms have been determined for which the estimated errors are materially less than for previously published values.

APPARATUS AND PROCEDURE

Design considerations were presented in 1960¹ of the rf mass spectrometer,² then being proposed, which was used in the work reported here. A brief description of the instrument and its early performance was presented in 1967.³

A doublet spacing is measured by alternately displaying its two peaks on an oscilloscope screen at a rate of about (but not exactly) 15 peak pairs per second, i.e., by the familiar technique of visual peak matching. To make the orbit distributions of the two types of ion as nearly identical as possible, all voltages are alternated between pairs of values inversely proportional to the ionic masses. The two frequencies alternately applied to the modulator are generated by separate oscillators covering the range from 50 to 500 mHz, each being phase-locked to a multiple of 10 mHz derived from the same crystal-controlled oscillator plus or minus the frequency of a frequency synthesizer referenced to this same 10-mHz crystal. Each frequency may be set and read with respect to the other to less than 0.1 Hz, i.e., to a precision of a few parts in 10¹⁰, which is quite adequate.

The two rf signals are fed to the modulator via tuned power amplifiers and tuned transmission lines. Each line contains a five-section low-pass filter to suppress overtones followed by a 3-dB pad and a tuning device known as a stub stretcher. The two tuners join, at a T, the single line leading to the modulator whose length is so adjusted that it is a quarter wavelength or very nearly so for one or both frequencies. This provides that a volt-

age node for one or both frequencies is at or very near the junction so that tuning adjustments to maximize both voltages at the modulator are very nearly independent. Of course, only one signal at a time is applied, the other being very completely suppressed by having the plate voltage removed from the last two of the three stages of the corresponding power amplifier by a fast-acting relay. These two relays, like those which control all dc voltages, are operated by a flip-flop circuit triggered by the sweep return signal from the display oscilloscope. Other switches similarly operated provide for differential gain control to set the peak heights accurately equal and for a 30 kHz square-wave signal to be applied to the second Y input of the oscilloscope on alternate sweeps. This signal splits the trace for one peak into two parallel traces between which the unsplit trace is centered by adjusting one synthesizer, as well as a number of other controls.

In order to display peaks, the frequency of the 10-mHz crystal oscillator may be swept by a small but adequate amount so that each frequency is swept by an amount proportional to that frequency. To avoid the small shift in either frequency that would otherwise result from phase slip in the phase detector of either phase-lock loop, an adjustable amount of sweep voltage is fed along with the phase detector output to the voltage-variable capacitor diode controlling each oscillator, of such magnitude that there is no sweep voltage discernable in said output and hence no phase slip in either phase detector. This means that each frequency would be swept the proper amount even if the gain of each loop were turned to zero. This

method of peak display has generally been utilized only for wide doublets such as those used in "calibration" measurements to correct for electric field effects as explained below.

An alternative method of displaying peaks used throughout this work for narrow doublets is to apply a small adjustable sawtooth voltage to the outer, insulated jaw of the phase-defining slit, thereby producing a small radial electric field between the jaws which varies in sawtooth fashion with time. Such a field changes slightly the cyclotron frequency of each ion. This method of display avoids any possibility of error caused by differential phase slip either in the main phase-lock loops or in other such loops in the synthesizers (both of which possibilities are indicated to be of negligible significance), since it obviates the necessity of varying either frequency with time. More importantly, it avoids potential small errors due to differential variation of rf voltage during two consecutive sweeps that might arise from slight differences in tuning of the two channels. Its chief disadvantage is that the amplitude of the swept electric field is exactly the same for the two ions and not inversely proportional to their masses, so that (a) the peaks do not have exactly the same width and (b) the match must be made with the peaks centered on the oscilloscope screen where the swept field is zero. These disadvantages are not significant for doublets as close as any re-

ported on here but are significant for wide "calibration" doublets.

From 10 to 26 measurements were made of each doublet spacing except $C_2H_4 - CO$, of which 63 were made. Ion energies ranged from 15.09 to 22.84 kV, orders from about 800 to 1200, and frequencies from 140 to 360 MHz. rms rf voltages on the central modulator plate between 100 and 150 V expanded the beam width at the phase-defining slit to 3 or 4 times the width (0.040 in.) of that slit. Typically, peak currents at the detector were in the neighborhood of 7×10^{-12} A. (The detector acts as a single-stage multiplier with a gain of about 7 so that effective currents were of the order of 5×10^{-11} A.) In most cases, readings for a given doublet were taken at different frequencies near a single value, small shifts being made and all circuits being tuned before each reading. Usually only one or two values of accelerating voltage were employed. No significant changes in values were observed in cases where considerably different voltages, frequencies, and orders were used. Nor was any effect on the match ever observed as ion currents were reduced by factors of from 10 to 100.

ACCURACY OF PEAK MATCHING

A basic and readily determinable source of error in the measurements is the "setting error" or accuracy with which the frequency difference between two peaks can be determined by the matching technique under a given set of operating conditions. This has been determined by measurements of the difference between the frequencies f_A and f_B generated by the two channels when a given order of a peak is matched with the same order of the same peak. Here no shift of voltages occurs between sweeps, and the expected value of $f_B - f_A$ is known to be zero provided there are no differential effects present (such as differences in rf waveform).

A series of 100 measurements of $f_B - f_A$ was made on the peak CO^+ under typical operating conditions and with typical noise originating from microphones, instabilities in ion current and magnetic field, etc. The accelerating voltage was 17.59 kV, and the frequency 249.53 MHz. The order was $(n + \frac{1}{2}) = 916.5$, while the peak was 1200 Hz wide at half maximum so that the half-width resolution was 208 000. After each match was made, the synthesizer in channel B was displaced different unknown amounts (several Hz or tens of Hz). The match was then reestablished by adjusting the other synthesizer. Thereafter the two frequencies f_B and f_A were read off and their difference deter-

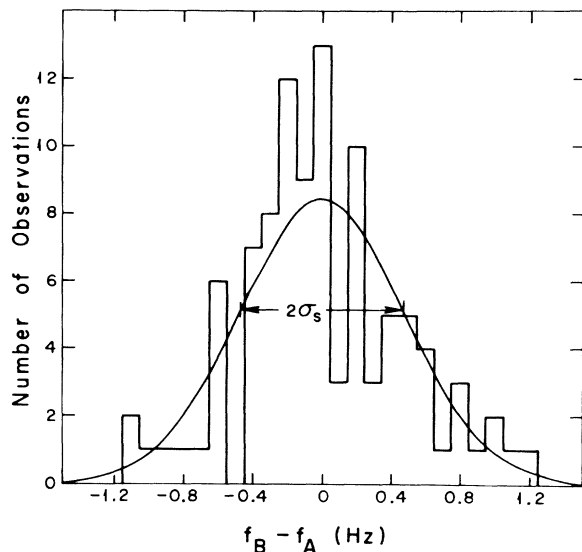


FIG. 1. Distribution of measurements of the difference in frequency of the two rf channels when a peak (CO^+) was matched with itself. The Gaussian curve has the same standard deviation, $\sigma_s = 0.473$ Hz, and area as the histogram. The peak was 1200 Hz wide at half maximum so that σ_s (for a single reading) is about $\frac{1}{2500}$ of a peak half width.

mined to the nearest 0.1 Hz. The results of this series of observations are shown in the histogram in Fig. 1, where it may be noted that not one of the 100 observations gives a value of $|f_B - f_A|$ greater than 1.2 Hz or $\frac{1}{1000}$ of the peak half-width. The standard error of a single reading is 0.473 Hz or about $\frac{1}{2500}$ of a peak half-width, while the mean value of the 100 readings is 0.010 ± 0.047 Hz. The expected normality of the distribution is indicated by its similarity to the normal or Gaussian distribution curve also shown in Fig. 1, which has the same standard deviation, $\sigma_s = 0.473$ Hz, and area as the histogram.

That the mean value is zero, well within the error of the mean, provides gratifying evidence that, at least under these rather typical conditions, no difference in wave form or other such effects are present. The absence of such effects in general is indicated by lack of evidence of any significant changes in values obtained for doublet spacings on interchange of the channels generating the two frequencies. This was not the case before a differential effect, due apparently to the 30-kHz square-wave signal getting into one power amplifier output through the switch circuits, was eliminated by proper shielding. In most, but not all, of the doublet measurements reported here, about half of the readings was obtained with channel A providing the larger frequency and half with channel B providing it.

Since the *standard* error of a single setting is but $\frac{1}{2500}$ of a peak width, then, for a resolution of 208 000, *so far as this error alone is concerned*, an unknown mass may be determined in terms of a known one in a single observation with a standard error of 1.9 parts in 10^9 . This extraordinarily small setting error may be compared with the observation made with the mass spectrometer where the *probable* setting error was about $\frac{1}{1000}$ of a half-width,⁴ or 3.8 times as large. The greater peak-matching precision of the new spectrometer appears to be due to a sharper oscilloscope trace, a more nearly square trace-splitting signal, and less, but still not negligible, noise. Because resolution in the measurements to be described ranged from 200 000 to 400 000, one would expect that, if setting error were the limiting factor, the mean of 10 measurements of a mass difference should have a standard error between about 3 and 6 parts in 10^{10} . That this is not the case is due, of course, to the presence of other greater sources of error. Their presence, at least with this spectrometer, would seem to make futile an attempt to reduce the setting error by use of a signal-averaging device, even if, as seems unlikely, such a reduction could thereby be achieved.

STRAY ELECTRIC FIELD EFFECTS

Before the instrument became operational, it was hoped that mass ratios perhaps as large as 2 could be measured with precision. No limitations on such measurements exist, because of limitations on the accuracy with which frequency ratios materially different from unity can be measured, as would very probably be the case with resistance or voltage ratios. However, such measurements of high precision have not been possible, because of difficulties in adjusting all voltages to pairs of values such that the distributions of orbits for the two types of ion are everywhere exactly the same. These difficulties, not important with the close doublets measured here, increase rapidly as the relative mass difference of the two ions increases above about 1 or 2%. The lack of identity of orbit distributions is shown by the fact that the two peaks are not the same functions of some of the (switched) electric fields, particularly those causing vertical bending of the beam, and often are not exactly congruent for any adjustment of parameters. This difference in orbits is undoubtedly caused by stray electric fields arising from electron space charge in the ion source and from contact-potential differences and surface charges on electrodes and walls, none of which vary in inverse proportion to mass. Considerable progress has been made in compensating for the effects of these stray fields by adding small adjustable, nonswitched voltages to the accelerating voltage and to the voltages applied to the eight curved electrostatic deflectors. Further progress is possible but attainment of the same precision for wide doublets as for narrow ones is undoubtedly not possible because of the impossibility of fully compensating for all stray fields by nonswitched ones of the same shape at all points of the orbits.

While differences of orbit distributions are not significant for close doublets not involving ions formed by molecular dissociation, small errors in the relative frequency difference caused by shifts of cyclotron frequencies by stray fields in the toroidal chamber in the magnetic field *are* important. In an attempt to compensate for these, a small radial electrostatic field is applied at the most critical part of the orbit by applying an adjustable nonswitched dc voltage to the inner jaw of the phase-defining slit. The proper setting of this voltage is determined by observing a wide doublet, usually involving two ions differing by one H or D atom or two H atoms, whose fractional spacing ($\Delta M/M$) is known with sufficient accuracy. While the sensitivity of the observed spacing to change of this voltage (the PD voltage) in-

creases in proportion to doublet spacing, the effects of the preceding paragraph tend to offset this and cause the uncertainty in the proper setting to increase above a fractional spacing (estimated now to be about 1, or 2%) that depends on how nearly identical one succeeds in making the orbit distributions.

Calibration runs to determine the proper PD voltages were made at mass numbers near each close doublet measured. They yielded values of this voltage between 0 and 0.25 V for all but a few

recent measurements of the doublet $C_2H_4 - CO$ at mass 28, for which measurements on the doublet $C_2H_4 - C_2H_3$ have yielded a value of about -0.22 V. It has been determined from measurements on a wide variety of doublets that a shift of 0.25 V in the PD voltage causes a shift in the fractional spacing of a doublet in frequency ($\Delta f/f$) and hence in measured mass ($\Delta M/M$) of 4.4 ppm for an ion energy of 20 kV. These measurements have also verified the theoretical prediction that the shift in fractional spacing is inversely proportional to ion energy.

TABLE I. Measured and adjusted (underlined) values in nu of the 16 doublets from which the six mass excesses of Figs. 2-4 were determined by least-squares adjustment. Errors given with values are external standard errors obtained by multiplying internal errors σ_r by the consistency factor 1.327. For the method of determining σ_r and the relativistic corrections made see text.

Eff. mass No.	Doublet	Adjusted and measured values (nu)	Corrections added (nu)				Error estimates (nu)			
			K.E.	$\Delta(BE)$	$-\Delta I_p$	$-\Delta I_p$	σ_m	σ_{sm}	σ_e	σ_r
1	H - 1	<u>7 825 029 \pm 5</u>								<u>3.85</u>
10.67	$\frac{1}{12}(C_9H_{20} - C_{10}H_2)$	7 825 027 \pm 10	2.00	2.14	~ 0	~ 2.14	4.63	2.88	5.51	7.20
2	D - 2	<u>14 101 771 \pm 10</u>								<u>7.62</u>
14	$\frac{1}{6}(C_5D_{12} - C_6D_6)$	14 101 771 \pm 15	5.45	1.59	-0.23	1.36	4.70	3.48	9.94	10.99
3	H ₂ - D	<u>1 548 287 \pm 4</u>								<u>2.86</u>
14	$\frac{1}{2}(C_2H_4 - C_2D_2)$	1 548 294 \pm 10	1.95	3.56	0.47	4.03	6.83	7.18	1.011	7.25
14	$\frac{1}{6}(C_6H_{12} - C_6D_6)$	1 548 285 \pm 4	0.61	2.81	-0.19	2.62	2.63	3.18	1.084	3.36
	Weighted mean	1 548 286 \pm 4					2.45	2.90	0.74	3.05
14	CD - N	<u>11 027 799 \pm 9</u>								<u>7.12</u>
14	$\frac{1}{2}(C_2D_2 - N_2)$	11 027 815 \pm 18	14.87	3.78	2.24	6.02	11.90	7.50	6.74	13.68
14	CH ₂ - N	<u>12 576 086 \pm 9</u>								<u>7.13</u>
14	$\frac{1}{2}(C_2H_4 - N_2)$	12 576 098 \pm 15	15.51	7.34	2.71	10.05	7.02	8.05	8.40	11.63
16	CD ₂ - O	<u>33 289 109 \pm 16</u>								<u>11.74</u>
28	C ₂ D ₂ - CO	33 289 129 \pm 33	52.13	6.17	2.81	8.98	17.91	9.15	17.51	25.06
32	C ₂ H ₄ D ₂ - CH ₃ OH	33 289 061 \pm 38	36.64	8.79	-0.83	7.96	18.70	10.01	21.80	28.74
	Weighted mean	33 289 100 \pm 25					12.96	6.76	13.41	18.88
16	CH ₄ - O	<u>36 385 683 \pm 16</u>								<u>12.02</u>
28	C ₂ H ₄ - CO	36 385 644 \pm 36	58.99	13.29	3.76	17.05	19.50	6.27	18.49	26.90
16	CH ₂ D - O	<u>34 837 396 \pm 13</u>								<u>10.16</u>
16	$\frac{1}{2}(C_2H_4D_2 - O_2)$	34 837 406 \pm 33	37.88	13.02	0.24	13.26	9.70	6.22	23.08	25.03
28	N ₂ - CO	<u>11 233 512 \pm 19</u>								<u>14.20</u>
28	N ₂ - CO	11 233 543 \pm 25	15.15	-1.39	-1.66	-3.05	17.30	12.47	6.87	18.62
36	C ₃ - H ³⁵ Cl	<u>23 322 256 \pm 30</u>								<u>22.74</u>
50	C ₄ H ₂ - CH ₃ ³⁵ Cl	23 322 239 \pm 34	16.92	14.98	0.63	15.61	20.70	17.80	14.84	25.48
40	C ₂ D ₈ - H ₃ ³⁷ Cl	<u>123 436 659 \pm 50</u>								<u>37.38</u>
52	C ₃ D ₈ - CH ₃ ³⁷ Cl	123 436 511 \pm 120	76.76	27.85	0.13	27.98	22.16	20.88	87.94	90.68
35	$\frac{1}{2}(C_5H_{10} - ^{35}Cl_2)$	<u>70 272 432 \pm 37</u>								<u>27.94</u>
42	$\frac{1}{2}(C_6H_{12} - CH_2^{35}Cl_2)$	70 272 506 \pm 64	30.93	29.98	0.59	30.57	21.00	12.21	43.84	48.61
72	C ₅ H ₁₂ - ³⁵ Cl ³⁷ Cl	<u>159 145 211 \pm 51</u>								<u>38.35</u>
86	C ₆ H ₁₄ - CH ₂ ³⁵ Cl ³⁷ Cl	159 145 171 \pm 120	85.09	65.58	0.99	66.57	43.30	26.45	79.81	90.80
37	$\frac{1}{2}(C_3H_6O_2 - ^{37}Cl_2)$	<u>52 487 096 \pm 37</u>								<u>28.24</u>
44	$\frac{1}{2}(C_4H_8O_2 - CH_2^{37}Cl_2)$	52 487 118 \pm 41	28.11	21.72	0.77	22.49	17.13	13.05	25.69	30.90

MEASURED VALUES AND ERROR ESTIMATES

Mean measured values (in nu) of 16 doublets at mass numbers from 28 to 128 are given in column 3 of Table I. Also given there (underlined) are best values of the 14 distinct mass differences represented by these 16 doublets. These were computed from best values of the mass excesses,

shown in Figs. 2-4, of the six atoms H, D, ^{14}N , ^{16}O , ^{35}Cl , and ^{37}Cl in terms of which all 14 differences are expressible and which were obtained by weighted least-squares adjustment. To each measured value obtained by equating $\Delta M/M$ to $\Delta f/f$ have been applied corrections for differences in (1) kinetic energy, (2) electron separation energy (i.e., ionization potential I_p), and (3) molecular

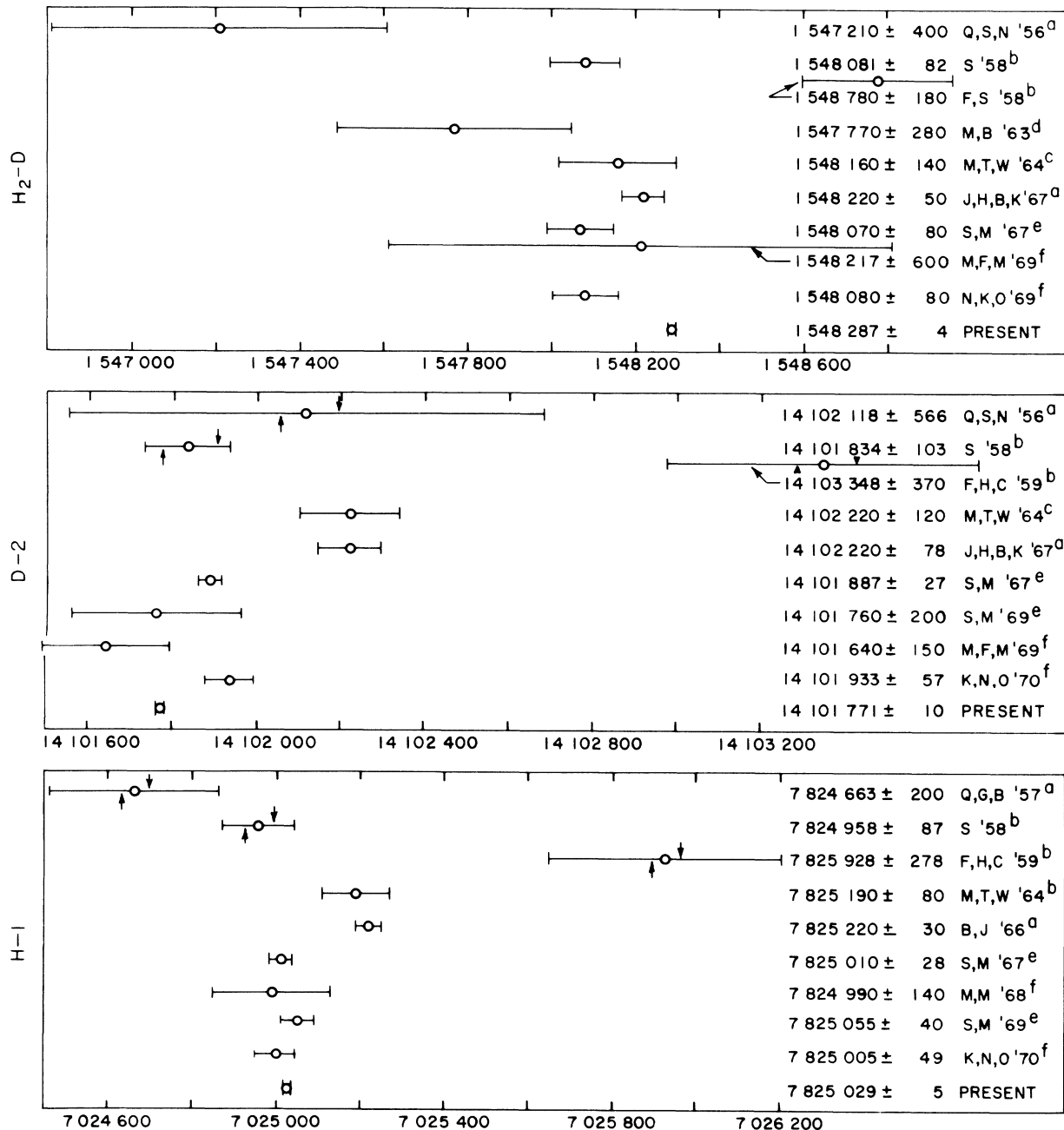


FIG. 2. Hydrogen isotopes. Present adjusted and previously published values in nu. References are given in Table II. Errors given for the present results and those of S '58 are external standard errors. Arrows indicate values obtained by using values of $16 - ^{16}\text{O}$ in S '58 (†) and M, T, W '64 (†) rather than the present value.

binding energy (BE). Thus, all values given represent masses of separated neutral atoms at rest in the gaseous phase or linear combinations thereof rather than differences of the masses of molecular ions in motion. Values in nu of these three corrections, as well as of the net binding-energy correction $\Delta(\text{BE}) - \Delta I_p$, are given in columns 4 to 7 of Table I.⁵

Errors of measured values given in column 3 of Table I are estimates of "external" error determined as follows. (1) The standard deviation σ_m of the mean of the readings for each doublet was determined. (2) The standard setting error σ_{sm} of each mean was determined from the resolution, the data of Fig. 1, the effective mass, and the number of readings. (3) An estimate σ_e of the uncertainty in each measured value corresponding to an uncertainty of 0.03 V in the proper setting of the PD voltage was determined. (4) The "internal" standard error σ_r of each mean measured value

was taken to be the resultant of σ_e and the larger of σ_m or σ_{sm} . Values of σ_m , σ_{sm} , σ_e , and σ_r are given in columns 8–11 of Table I. The weight factors used in the least-squares adjustment were proportional to σ_r^{-2} . (5) After the adjustment, the χ^2 of the distribution was found to be 14.08. This, of course, is the minimized sum of 14 squared terms, each being the ratio of the difference between the best and the measured value to the "internal" error (σ_r) of the latter. The "consistency factor" of the distribution or the square root of the ratio of χ^2 to its expected value ($14 - 6 = 8$) was then determined to be 1.327. All errors of present best, as well as measured, values in Table I and Figs. 2–5 are external errors, each being obtained by multiplying the corresponding internal error by this factor.

That χ^2 is greater than its expected value shows that errors, in addition to the internal errors estimated in the above manner, are present. While

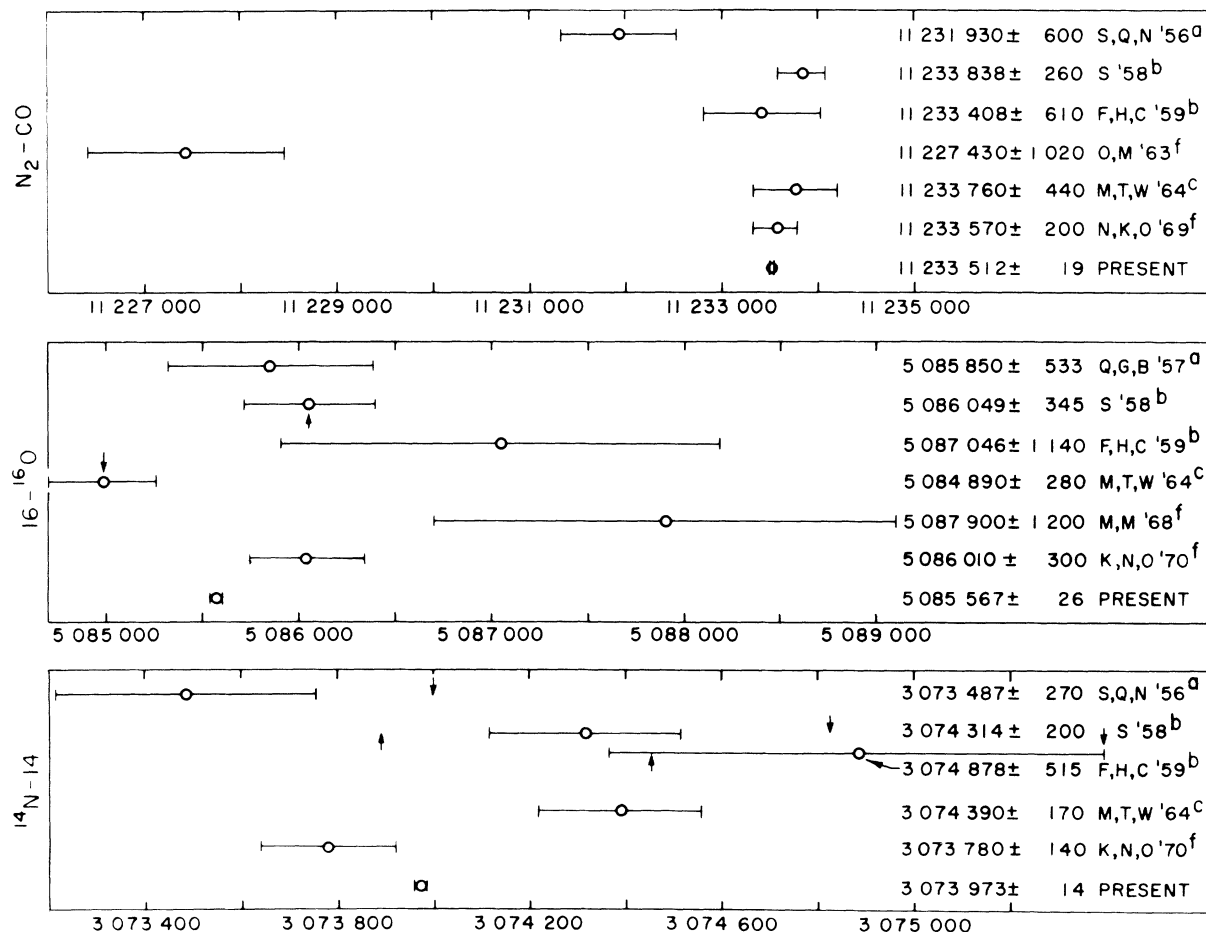


FIG. 3. Nitrogen and oxygen isotopes. Present adjusted and previously published values in nu. References are given in Table II. Errors given for the present results and those of Ref. S '58 are external standard errors. Arrows indicate values obtained by using values of $16 - ^{16}\text{O}$ given in Refs. S '58 (†) and M, T, W '64 (‡) rather than the present value.

it is possible that these arise entirely from electric field effects larger than have been allowed for, it seems likely that other sources of error are present as well, and that the assumption of the same uncertainty in the PD voltage for all doublets is not entirely correct. Because of current ignorance of such other errors and the extent to which they are accounted for in σ_m , the above treatment of multiplying the internal error by 1.327 seems preferable to increasing the allowance for σ_e alone, which might well result in giving too much weight to the narrowest doublets such as $H_2 - D$. It is of interest that, if one omits correction of experimental values for total binding energy, the value of χ^2 is 15.24. Thus, this correction results in an improvement in the consistency of the data which appears to be significant though it by no means fully accounts for the inconsistency of the uncorrected values.

It is also notable that, from the *experimental* values of Table I, one obtains $2(H-1) - (D-2) = 1548283 \pm 18$ nu, which is entirely consistent with the separately measured mean value $H_2 - D = 1548286 \pm 4$ nu.

COMPARISONS WITH OTHER RESULTS

In Figs. 2-5 are given both numerically and graphically all mass-spectrometric values⁸ pub-

lished since 1956 of the mass excesses and differences measured in this work along with present adjusted values and those obtained from the 1964 mass table of Mattauch, Thiele, and Wapstra (see Table II for complete listing of references used). All values published before 1960 have been converted from the scale $^{16}O = 16$ to the scale $^{12}C = 12$ by use of the present adjusted value of $16 - ^{16}O$. Arrows indicate values that would be obtained if one used either the value of $16 - ^{16}O$ from the mass table (downward arrows) or that obtained by the author with the mass synchronometer (upward arrows). Obviously, if one used an intermediate value for $16 - ^{16}O$, such as that of Quisenberry, Giese, and Benson, he would obtain a value lying between the two arrows in each case. Arrows are not shown for doublet values, because their variations with such changes in the conversion factor are negligible. Errors of values labeled S'58 are external errors obtained by multiplying those published by the consistency factor 2.35 (which, it will be noted, is considerably greater than that of the present, less-extensive set of doublets).

Figures 2-5 reveal quite satisfactory agreement between the author's present and mass-synchronometer results. Differences are less than 1 standard error for $H-1$, $D-2$, CH_2-N , $CD-N$, and CH_4-O ; between 1 and 2 standard errors for H_2-D , $^{14}N-14$, $16-^{16}O$, and N_2-CO ; and between 2 and

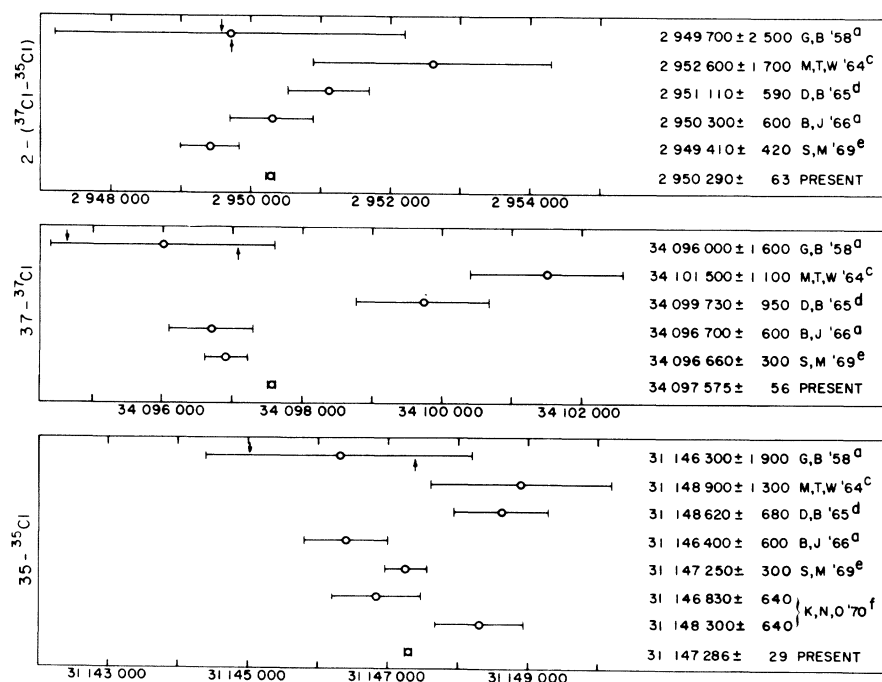


FIG. 4. Chlorine isotopes. Present adjusted and previously published values in nu. References are given in Table II. Errors of present results are external standard errors. Arrows indicate values obtained by using values of $16 - ^{16}O$ given in S '58 (†) and M, T, W '64 (†) rather than the present value.

3 for $\text{CD}_2 - \text{O}$. Of course, all values of each of the author's two sets, being adjusted, are exactly consistent, as are also all values of F,H,C '59 and those derived from the mass table.

Comparison of the values obtained with the mass synchrometer by Friedman and Smith and by Friedman, Henkes, and Christman, not only with the present values but with others as well, indicates strongly that systematic errors as well as considerably larger random errors than those in S '58 were present in this work. It is to be hoped that such errors largely canceled in values of the

small differences $\text{T} - {}^3\text{He}$ and ${}^{14}\text{C} - {}^{14}\text{N}$ that were the chief objectives of those two papers. Unfortunately, this cannot be guaranteed, since such errors might have changed from one run to another.

The present value of $\text{H} - 1$ agrees well with all values obtained at Argonne and Osaka but less well with either of the two Minnesota values or with that of the mass table. The present value of $\text{D} - 2$ agrees very well with the latest Argonne value and fairly well with values of M,F,M '69 and Q,S,N '56. It differs considerably from the latest

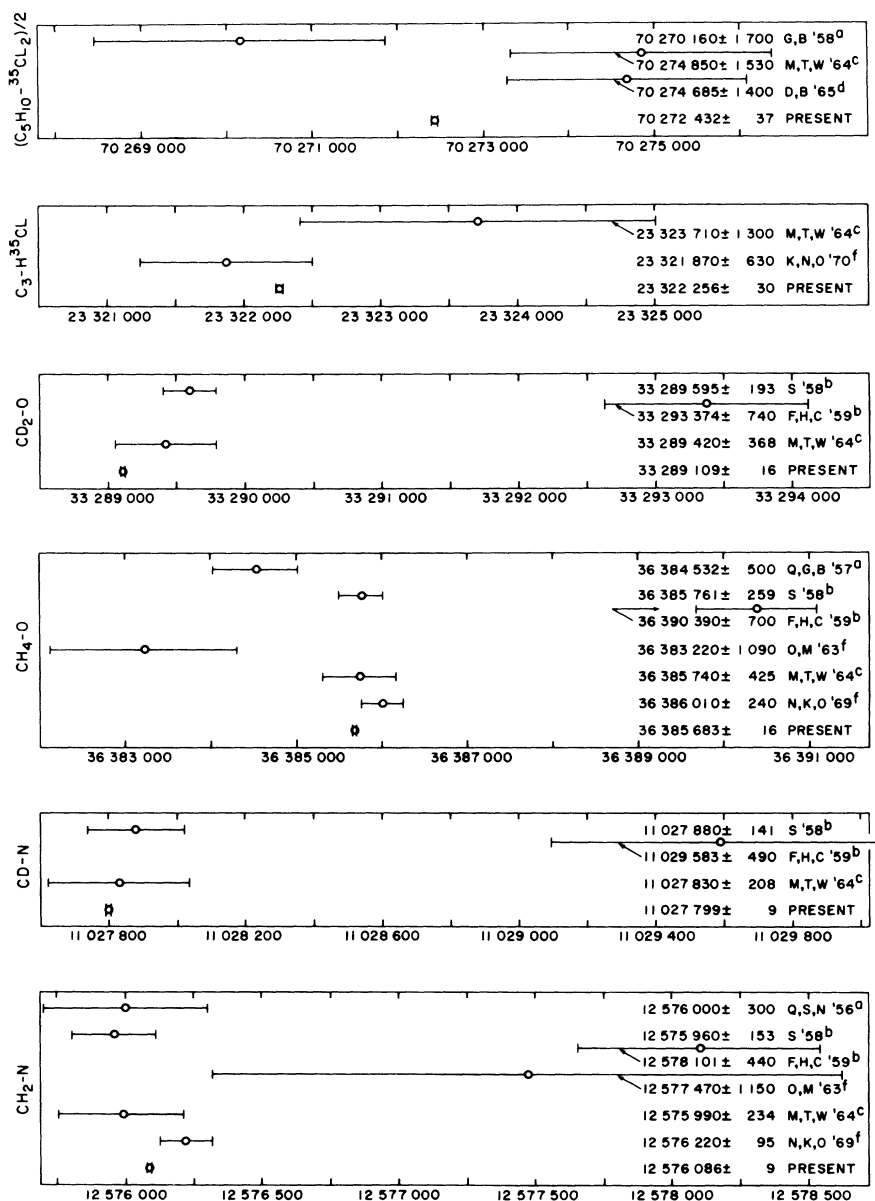


FIG. 5. Other doublets also measured by others. Present adjusted and previously published values in nu. References are given in Table II. Errors of present results and those of S '58 are external standard errors.

TABLE II. References for mass spectrometric values published since 1956 as shown in Figs. 2-5.

(a) Minnesota	(d) Harvard
<p>Q, S, N '56; K. S. Quisenberry, T. T. Scolman, and A. O. Nier, <i>Phys. Rev.</i> 102, 1071 (1956).</p> <p>S, Q, N '56; T. T. Scolman, K. S. Quisenberry, and A. O. Nier, <i>Phys. Rev.</i> 102, 1076 (1956).</p> <p>Q, G, B '57; K. S. Quisenberry, C. F. Giese, and J. L. Benson, <i>Phys. Rev.</i> 107, 1664 (1957). Values cited in Figs. 2, 3, and 5 from this paper have been used in obtaining those cited there from the preceding two papers.</p> <p>G, B '58; C. F. Giese and J. L. Benson, <i>Phys. Rev.</i> 110, 712 (1958).</p> <p>B, J '66; J. L. Benson and W. H. Johnson, Jr., <i>Phys. Rev.</i> 141, 1112 (1966).</p> <p>J, H, B, K '67; W. H. Johnson, Jr., M. C. Hudson, R. A. Britten, and D. C. Kayser, in <i>Proceedings of the Third International Conference on Atomic Masses</i> (see Ref. 3), p. 793.</p>	<p>M, B '63; P. E. Moreland and K. T. Bainbridge, in <i>Proceedings of the Second International Conference on Nuclidic Masses</i>, edited by W. H. Johnson, Jr. (Springer-Verlag, Berlin, Germany, 1964), p. 425.</p> <p>D, B '65; J. W. Dewdney and K. T. Bainbridge, <i>Phys. Rev.</i> 138, 540 (1965).</p>
(b) Brookhaven	(e) Argonne
<p>S '58; L. G. Smith, <i>Phys. Rev.</i> 111, 1606 (1958).</p> <p>F, S '58; L. Friedman and L. G. Smith, <i>Phys. Rev.</i> 109, 2214 (1958).</p> <p>F, H, C '59; L. Friedman, W. Henkes, and D. Christman, <i>Phys. Rev.</i> 115, 166 (1959).</p>	<p>S, M '67; C. M. Stevens and P. E. Moreland, in <i>Proceedings of the Third International Conference on Atomic Masses</i> (see Ref. 3), p. 673.</p> <p>S, M '69; C. M. Stevens and P. E. Moreland, in <i>Proceedings of the International Conference in Mass Spectroscopy, Kyoto</i>, edited by K. Ogata and T. Hayakawa (The University of Tokyo Press, Tokyo, Japan, 1970), p. 1296.</p>
(c) 1964 mass table	(f) Osaka
<p>M, T, W '64; J. H. E. Mattauch, W. Thiele, and A. H. Wapstra, <i>Nucl. Phys.</i> 67, 1 (1965).</p>	<p>O, M '63; K. Ogata and S. Matsumoto, in <i>Proceedings of the Second International Conference on Nuclidic Masses</i>, edited by W. H. Johnson, Jr. (Springer-Verlag, Berlin, Germany, 1964), p. 415.</p> <p>M, M '68; H. Matsuda and T. Matsuo, <i>J. Phys. Soc. Japan</i> 25, 950 (1968).</p> <p>M, F, M '69; H. Matsuda, S. Fukumoto, and T. Matsuo, in <i>Proceedings of the International Conference in Mass Spectroscopy, Kyoto</i>, edited by K. Ogata and T. Hayakawa (The University of Tokyo Press, Tokyo, Japan, 1970), p. 477.</p> <p>N, K, O '69; H. Nakabushi, I. Katakuse, and K. Ogata, <i>Mass Spectroscopy (Japan)</i> 17, 705 (1969).</p> <p>K, N, O '70; I. Katakuse, H. Nakabushi, and K. Ogata, <i>Mass Spectroscopy (Japan)</i> 18, 1276 (1970).</p>

Minnesota value and that of the mass table and somewhat from that of K,N,O '70. The present values of ^{14}N - 14, ^{16}O , and N_2 - CO agree a little better with the values of K,N,O '70 and N,K,O '69 than with those of S '58. That of ^{16}O is in fairly good agreement with the value obtained from a single doublet by Quisenberry, Giese, and Benson. The present values of both ^{35}Cl and ^{37}Cl favor the two sets of Minnesota values, the Argonne values, and the lower of the two Osaka values more than those of the mass table or of

Dewdney and Bainbridge.

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¹L. G. Smith, in *Proceedings of the International Conference on Nuclidic Masses*, edited by H. E. Duckworth (The University of Toronto Press, Toronto, Canada, 1960), p. 418.

²Construction and assembly of the spectrometer and associated equipment were financed by grants from the National Science Foundation.

³L. G. Smith, in *Proceedings of the Third International Conference on Atomic Masses*, edited by R. C. Barber

(The University of Manitoba Press, Winnipeg, Canada, 1967), p. 811.

⁴L. G. Smith and C. C. Damm, *Phys. Rev.* **90**, 324 (1953); **91**, 481 (1953).

⁵Ionization potentials were obtained from F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press Inc., New York, 1957). Binding energies of diatomic molecules were obtained from the *Handbook of Chemistry and Physics* (Chemical Rubber Publishing

Company, Cleveland, Ohio, 1970). For polyatomic molecules, binding energies were calculated on the assumption of the now fairly well established value of 170 kcal/mole for the heat of sublimation of carbon from data on heats of combustion and vapor pressures given in the latter reference.

⁶The author's mass-synchrometer values of excesses and differences involving the chlorine isotopes have been

excluded as being so much in error (presumably because of kinetic energy effects) as not to fall within the ranges of the plots of Figs. 4 and 5. Also excluded is the value $H_2 - D = 1553100 \pm 10300$ nu of Ref. O, M'63. Errors of combinations of mass table values are calculated without regard to their correlations and hence are somewhat larger than if correlations were taken into account.

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Approximation to the Relativistic Scattering Problem

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We extend the calculation of the relativistic phase-shift problem, as given before, to second order in \hbar by means of Miller and Good's modified WKB method. The scheme of Bertocchi, Fubini, and Furlan is used to avoid the divergences introduced in the second-order terms. The example indicates that the phase shifts are greatly improved at lower angular quantum numbers.

1. INTRODUCTION

This note is written to report some improvements over a previous paper¹ that result from taking into account the second-order contributions in \hbar . We use Miller and Good's² modified WKB method, choosing a solved problem to approximate the unsolved problem. The second-order terms were given in a previous paper.³ However, they are divergent at the lower limit. This divergent property at the lower limit for the high-order terms in \hbar is not new. It was discussed in the paper of Bertocchi, Fubini, and Furlan⁴ for the high-order terms in the ordinary WKB problem. They succeeded in avoiding the difficulty by means of contour integrals. In Sec. II, we discuss this in detail.

As an example, in Sec. III, we choose a point nucleus together with the pure Coulomb potential as the solved problem. We then solved for the phase shifts in a supposedly unsolved problem with another potential – for example, the shell distribution for the same amount of nuclear charge. These potentials are chosen for illustrative purposes. A comparison can readily be made with the numerical values for the phase shifts given by Ravenhall and Yennie.⁵ In Ref. 1, the uniform distribution of the nuclear charge was used as the solved part, and the shell distribution as the unsolved part. Because these two distributions are remarkably similar, our lowest-order-in- \hbar approach did yield some meaningful results. These results agree to the third decimal place for the phase shifts with

the numerical ones, which are accurate to the fifth decimal place. In the problem considered here, however, the agreement for the lowest order in \hbar is less good, especially for the first few phase shifts where the angular momentum quantum number is small. By carrying the calculation to the second order in \hbar , we see that substantially better agreement can be achieved. This fact actually is independent of the particular example chosen.

2. GENERAL THEORY OF THE RELATIVISTIC SCATTERING PROBLEM

From the Dirac radial equations at the high-energy limit, by taking the rest mass to be zero, we get

$$\frac{d}{dr}u - \frac{l+1}{r}u - \frac{W - V(r)}{\hbar c}v = 0, \quad (1a)$$

$$\frac{d}{dr}v + \frac{l+1}{r}v + \frac{W - V(r)}{\hbar c}u = 0. \quad (1b)$$

In the notation of Rosen and Yennie, these equations become

$$\frac{d}{dr}M = \frac{f(r)}{\hbar}N, \quad (2a)$$

$$\frac{d}{dr}N = \frac{-g(r)}{\hbar}M, \quad (2b)$$

with

$$M = u + v, \quad N = u - v,$$