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W.M. Hicks F.R.S.

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I. *The Series System in the Spectrum of Gold.*

By W. M. HICKS, *F.R.S.**

THE spectra of the copper group of metals are interesting in that, whilst they offer clear evidence of being built upon the same plan, they seem defective in representatives of the ordinary series lines and in some apparent deviations from relations indicated by other groups. They all show a pair of strong doublets in the ultra violet, a curious set of inverted D lines in the red—proved to belong to the D (or F) system by their Zeeman patterns—linked to associated lines by analogous *e* and *u* links, and S (2) doublets in the immediate ultra red also proved to belong to the S system by their Zeeman patterns. In copper and silver only two or three other lines have been assigned to S and D series, whilst in gold none have been allocated. The present communication attempts to throw some light on the series relations in gold. Although it does not pretend to be a thorough discussion of the material at disposal, certain definite results are arrived at, and some striking illustrations are afforded of general laws obtained in a series of papers published in the 'Transactions of the Royal Society' †.

* Communicated by the Author.

† "A Critical Study of Spectral Series," Trans. Roy. Soc. I., 210 A. p. 57 (1910).—II., 212 A. p. 33 (1913).—III., 213 A. p. 323 (1914).—IV., 217 A. p. 361 (1918); and V., read Jan. 23 (1919). References in the present paper are made in [], thus—[IV. p. —].

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The arc spectrum of gold has been touched upon by me in [III. p. 405] and the spark spectrum has been more fully discussed in its linkage relations in [IV.]. It does not afford data for the direct determination of series constants. The two strong lines usually taken to correspond to the P (1) doublet give the doublet separation to be looked for in the P, S, or D series. The mean from measures by Kayser and Runge, Exner and Haschek, and by Eder and Valentá gives $\nu=3815\cdot58$. The most reliable is that obtained from the inverse D set above referred to, viz., $\lambda\lambda=5064\cdot75, 6278\cdot37$ R.A., giving $\nu=3815\cdot54$. These two were the only sets giving the separation in K. R.'s original measures of the arc spectrum. Since then E. & H. have observed a line at $\lambda 4811\cdot81$, which K. R. appear to have missed and which has a separation $3815\cdot57$ with $\lambda 4665\cdot22$. Also Lehmann* has observed in the ultra red a line at $7509\cdot8$ giving with K. R.'s 5837 a separation of 3813 ± 13 , and allocated by him to S (2) —an allocation justified by their position relatively to the corresponding lines in Cu and Ag and by the Zeeman pattern for 5837 as determined by Hartmann. The Zeeman effects for certain lines have been observed by Michelson†, Purvis‡, and Hartmann§. They are given in the notation suggested by me || in the following list :—

	λ .	n .	Hartmann.	Purvis.
$D'_{22}(1)$	6278·37	15923·38	0/5 ?	
$p_1(1)-p_1(2)$	5957·24	16781·73	0/7½	
$S_2(2)$	5837·64	17125·54	4/8	
$D'_{11}(1)$	5230·47	19113·51	0/6½	
	4811·81	20776·50	0/5 ?	
	4792·79	20858·97	0/6	0/6
	4065·22	24592·07		0/3½
	3898·04	25646·81		0/6½
	3804·22	26279·28		0/6½
	3586·66	27873·33		0/5
	3122·88	32012·59		0/5
	3029·32	33001·33		3/6½
	2913·63	34311·67		0/6
	2748·30	36374·87		0/6½
$P_2(1)$	2676·05	37357·62		3+/6

* *Ann. d. Phys.* xxxix. p. 75 (1912).

† *Nat.* lix. p. 440 (1899).

‡ *Proc. Camb. Phil. Soc.* xiv. p. 217 (1907).

§ *Dissertation Halle* (1907). *Sc. Abstracts*.

|| *Phil. Mag.* xxxi. p. 171 (1916).

The inverse D set referred to are in W. N. :—

D_{12} —19738·92 **3815·52** —15923·38 (0/5) D_{22}
625·41

D_{11} —19113·51 ($0/6\frac{1}{2}$).

The Zeeman effect ($Z=5/10$) for the D_{12} was not observed, but the others definitely belong to a D (or possibly F) type. This and the corresponding sets in Cu, Ag are quite out of step with the normal D lines. The satellite separation 625, however, reproduces itself in a very striking manner in the spark linkages to which attention has been drawn in [IV. p. 385].

In [III. p. 405] an indirect attack on the problem was made by using the value of the δ as calculated direct from the atomic weight, $\delta=361\cdot8(W/100)^2=1406\cdot9$ and taking the lines 17125, 20858 as $D_{11}(2)$, $D_{22}(2)$, as they were in step with the undoubted corresponding D lines in Cu and Ag. Their separation is 3733·43, producing therefore a satellite separation of 82·11, with a weaker D_{12} line too faint to have been observed. The observed Zeeman pattern for 20858 is 0/6, which is that of a triplet D_{22} line, in place of 0/5 required for a doublet D_{22} , whilst 17125 is undoubtedly a S_2 line, although the pattern 4/8 as observed is not perfectly clear. Since then I have found that Rydberg in his original memoir had attached the same two lines also to D_{11} and D_{12} . It would appear that the $D_{11}(2)$ and $S_2(2)$ are almost coincident with 17125, as the supposition appears to be justified by the results.

The method adopted was to apply the laws (1) that the separation 3815 was due to a displacement by a multiple of the δ on the S or D limit, and (2) that the satellite separation of 82 was due to a displacement by an δ multiple in the D sequent. With this went the consideration that the limit would fall into step with those for Cu and Ag, and would therefore be of the order 30000 ± 1000 . The test (1) applied to these gave a series of possible limits between these values with Δ varying from 76 δ to 81 δ . To each of these test (2) was applied, with the result that only two of them were found to satisfy the condition, viz. :—

30819	$\Delta=76\delta$	sat. sep. due to $24\delta_1=6\delta$.
29465	$\Delta=81\delta$	„ „ $28\delta_1=7\delta$.

The fact that 29465 is in due step with Cu=31515, and
 B 2

$\text{Ag}=30644$, and some other considerations led to the adoption of the latter number. It was completely justified by the later discussion in [IV.], the links calculated on the foregoing data being found to be satisfied with great exactness.

Taking $\nu=3815\cdot56$, $D_1(\infty)=29465\cdot18+\xi$,
 $D_2(\infty)=33280\cdot74+\xi+d\nu$, the mantissæ are

$$D_1(\infty) \quad 929298-32\cdot739\xi,$$

$$D_2(\infty) \quad 815338-27\cdot273(\xi+d\nu),$$

giving

$$\Delta=113960-5\cdot466\xi+27\cdot27d\nu\pm1=81\delta,$$

whence

$$\delta=1406\cdot920\pm\cdot012-\cdot067\xi+\cdot336d\nu,$$

the $\pm$ ambiguities being due to uncertainties in final digits when using 7-fig. logarithms with 7-fig. numbers.

With 20858·97 for D_{22} , D_{12} is ν less, *i. e.* 17043·41. The mantissa of this satellite is $\cdot971410-119\cdot60(\xi+\nu)+26\cdot3p$, and of $D_{11}=17125\cdot54$ is $981279-120\cdot80\xi+16\cdot9p$, where $d\lambda=\cdot05p$ in each case, $\cdot05A$ being in each case K. R.'s estimate of their possible error. The difference of these is

$$\begin{aligned} &9872\pm1-1\cdot20\xi+16\cdot9p_1-26\cdot3p_2+119\cdot6d\nu \\ &=7\{1406\cdot920+3\cdot365\pm\cdot14-\cdot171\xi+2\cdot41p_1 \\ &\quad -3\cdot76p_2+17\cdot1d\nu\}=7\delta. \end{aligned}$$

The difference of the two values of δ is

$$3\cdot365\pm\cdot15-\cdot104\xi+2\cdot41p_1-3\cdot76p_2+16\cdot74d\nu, \quad (\text{A})$$

in which $d\nu$ is not greater than 0·1. The two values of δ therefore agree within quite easy limits of error, and the two results give no means of obtaining closer approximation. It is from this point that the present discussion starts. For this portion recourse must be had to the other general laws.

Now two well-established laws are that in the normal case (1) the mantissa of the extreme satellite of the first line in a D series is a multiple of Δ , whilst (2) the mantissæ of succeeding orders differ from one another by multiples of the *oun*. But in all the elements of this group the mantissa of D_{12} (2) is decisively not a multiple of Δ . The only explanation that appears to offer is that $m=2$ is not the first line, but that a set depending on $m=1$ exists in the far ultra red. The evidence for this will be considered below. For our immediate purpose it should be noticed that the two relations above necessitate that the mantissæ of D lines must

be multiples of the *oun* at least. Usually the *oun* is so small—or the multiple so large—that no further help to a closer approximation is attainable. In the case of Au, however, the *oun* is so large that the actual multiples could be uniquely determined if the limit were known within about unity ($\xi=1$). But in the present case the value of ξ with our present knowledge may be considerable, and there will necessarily be an ambiguity of a few units.

With the above values of Δ and δ ,

$$8\Delta + 49\frac{1}{2}\delta = 981326 \pm 8 - 47\cdot044\xi + 234\cdot7\,d\nu,$$

also mant. of $d_1 = 981279 - 120\cdot80\xi + 16\cdot9\,p_1$.

These are equal within possible errors as they stand, but ξ may be so large as to upset the agreement. If the multiple of δ_1 is y larger, $351\cdot7\,y$ must be added, and the condition of equality becomes

$$351\cdot7\,y + 47 \pm 8 + 73\cdot76\xi - 16\cdot9\,p_1 + 234\cdot7\,d\nu = 0. \quad (\text{B})$$

If condition A $\times 14$ be deducted from B the term in $d\nu$ disappears and

$$351\cdot7\,y + 75\cdot21\xi - 50\cdot6\,p_1 + 52\cdot6\,p_2 \pm 11 = 0,$$

$$\xi = -4\cdot67\,y \pm 1\cdot5 \quad (p \text{ having max. values } \pm 1).$$

Then $d\nu = 2 \pm \cdot02 - \cdot030\,y - \cdot14\,p_1 + \cdot23\,p_2 = 2 - \cdot030\,y \pm 4$.

The condition that $d\nu < 1$ is thus easily satisfied.

The results so far arrived at may be stated as follows :—

$$\left. \begin{aligned} \nu &= 3815\cdot56 + d\nu & d\nu &< 1 \\ \Delta &= 113960 - 5\cdot466\xi + x & x &\text{probably} < 10 \\ \delta &= 1406\cdot91 - \cdot0674\xi + \cdot0123\,x \\ \xi &= \pm 1\cdot5 - 4\cdot674\,y & y &= 0, \pm 1, \pm 2. \end{aligned} \right\} \quad (\text{C})$$

It may be noted that if y is as large as 2, ξ is altered by 9 and δ by $\cdot6$. This would make δ so different from that determined directly from the atomic weight as to render it improbable, though not impossible ($W = 197\cdot20 \pm \cdot07$). Certainly y cannot be so large as 3. The only possible limits would then seem to be

$$29465\cdot18 \pm 1\cdot5, \quad 29469\cdot85 \pm 1\cdot5, \quad 29474\cdot52 \pm 1\cdot5,$$

with corresponding smaller values. By the preceding considerations the choice of the limit has been considerably restricted.

To arrive at a closer determination, we may attempt to obtain a more complete allocation of the D series, and have

recourse to the existence of summation series if they show themselves. This type of series has been shown to exist in [V.]. If the wave-number of a given series of the hitherto recognized type is written as the difference of two sequents $A - \phi(m)$, it is there shown that in many cases at least a summation type $A + \phi(m)$ also exists. When this occurs the mean of two corresponding wave-numbers gives the exact value of the limit. Unfortunately, it is also shown that displacements sometimes appear concurrently, especially in the summation type which require some care in applying the condition. In this particular case a displacement of one *oun* in the limit produces a change in it of 10.76, and in the sequent a change which depends on the order m . For $m=2$, the lines just considered, it produces 2.90 in $d_1(2)$ and 2.93 in $d_2(2)$.

With the given D(2), the region in which D(3) is to be expected is narrowed down. The lines chosen were

$$[22496.77] \quad \mathbf{3815.56} \quad (2n) 26312.33 \pm .34$$

$$\mathbf{32.55 \pm .5}$$

$$(4) 22529.32 \pm .25,$$

in which the D_{12} line is, as before, too faint to be seen, and is interpolated as $26312 - \nu$. Its possible error is the same as that of 26312. The *oun* displacement on the sequent produces 1.228. Consequently $28 \delta_1$ produces 32.13, which not only reproduces the observed satellite separation but gives the same *oun* multiple as in $m=2$, and lends additional support to the allocations. With $D_{11}(2)=17125$ and $D_{11}(3)=22529$ with the limit 29465 the formula for D_{11} was determined and the wave-numbers up to $m=10$ calculated and compared with the observed lines. The result is given on the left hand of Table I. in which under any order the lines in succession correspond to D_{12} , D_{11} , D_{22} . A search was then made for the corresponding summation or **D** lines which was successful. The results are entered on the right hand. The middle column gives the means of the corresponding **D** and **D*** lines, which in the absence of displacement effects should be the true limits and the same in each order. They form the raw material for a closer discussion which follows. In the table calculated values are given in [], deduced values in italics.

* Summation series are denoted by clarendon type. The author has found it convenient in writing to use capitals reversed right and left, as in a looking-glass.

TABLE I.

<i>m.</i>	<i>I.</i>	λ .	O-C.	<i>n.</i>	<i>I.</i>	λ .	O-C.	<i>n.</i>
1		36550.5 33502.2 15264.1		<i>2735.94</i> <i>2984.82</i> <i>6557.90</i>	4 1 1	[1779.2] 1787.2 1666.0	.05 .25	[56203.77] 55953.45 (127, 94) 60024.01 (237, 14)
2	6	5887.64 4792.79	*	[17048.41] [17125.54 (75, 53)] 20856.97 (81, 143)	4 1 _n 2	2387.82 (-10.5) 2391.7 (-5.5) 2186.9	0 .05 -.06	44896.27 (7, 62) 44816.82 (33, 57) 45712.83 (43, 25)
3	4 2 _n	4487.44 3799.44	*	[22496.97] 2252.932 (256, 85) 26312.33 (9, 23)	1 1 2 _n	2743.27 2745.80 2483.4	.02	36442.22 (34, 136) 36408.65 (34, 34) 40255.38 (53, 50)
4	1 1	(25.) 3990.0 3470.47	-.02	<i>25034.17</i> 28806.40 (10, 152)	1	2646.98		37767.91 (60, 22)
5	2 2	3787.37 3310.34	-.40	[26384.50] 26396.23 (61, 28) 30199.89 (66, 18)	1 _n	2748.9 (-2.5)		36370.60 (20, 7)
6	1 2 2 _n	3675.11 3674.0 3223.03	.18	27202.44 (11, 8) 27210.66 (8, 8) 31017.94 (47, 10)	1 3	(b) 3145.77 (b) 3146.52		31736.68 (7, 69) 31729.42 (173, 7)
7	2	(-5), 3604.94	.00	<i>27742.70</i> (20, 27)	4 _n	3204.75		31194.82 (61, 97)
8	2 _n 1 _n	3557.13 3131.75	.2	28104.65 (70, 12) 31921.85 (14, 20)	1 3	3242.83 2885.68	.2	30828.51 (5, 116) 34643.91 (76, 26)
9	1 2 _n	(-36), 3528.25 3106.70	-.1	28366.99 (87, 39) 32179.38 (109, 27)	2 _n 5	3270.17 2907.18	.2	30570.84 (23, 30) 34387.78 (76, 13)

* Used for formula constants.

Let us take at first those data which depend directly on observed lines and do not require displacements for their interpretation. They are $D_{22}(2)$ and the whole set for $m=3$. Their means point quite definitely to limits in the vicinity of 29469 and 33285. In many portions of the Au spark spectrum the lines are excessively crowded, so that in those regions mere coincidences have little value as evidence. Fortunately, however, in these particular instances this is not the case. This is indicated by showing in brackets on the right of the lines the separation from the next observed lines on either side. In all the examples they are large, so that the combined evidence is convincing that the limits are close to the values given. It is striking, also, how closely they approximate to the second of the set of alternative values obtained above from quite independent considerations. It corresponds to putting $y = -1$ in the data under C, and makes them :

$$\left. \begin{aligned} \xi &= \pm 1.5 + 1.674 \\ \Delta &= 113935 + x \\ \delta &= 1406.60 + .0123 x \\ D_1(\infty) &= 26469.85 + \xi \\ D_2(\infty) &= 30285.41 + \xi. \end{aligned} \right\} \quad \xi = \pm 1.5 \quad (C')$$

The formula for D_{11} , re-calculated with the new limit, is

$$n = 29469.85 - N/\{m + .964130 + .033168/m\}^2.$$

It gives for $m=4 \dots 10$ wave-numbers of 25034.05, 26393.42, 27212.05, 27742.76, 28106.24, 28366.01, 28551.06. The question of the existence of lines corresponding to $m=1$ is of special importance for the reason mentioned above. Values extrapolated by the formula for $m=1$ rarely show any close agreement with observation, especially when, as now, they should occur in the far ultra red. In this case the law that the extreme satellite of the first line has its mantissa a multiple of Δ should give a very close approximate value for D_{12} and D_{22} . This mantissa must be greater than that of $D(2)$, and it is natural to take for the first experiment the multiple just larger—in this case 9Δ —and then seek for evidence as to its existence or not.

The value of 9Δ is $1.025370 + 9x$. This gives

$$D_{12} = 2733.70 + \xi + .237 x,$$

$$D_{22} = 6549.06 + \xi + .237 x.$$

Paschen, who has measured lines in the far ultra red for Cu and Ag, has unfortunately not dealt with Au, so that direct comparison with observation is not possible. There are, however, indirect methods which may be applied, viz., the possible existence of summation lines (far in the violet), the method of sounding as exemplified in [IV., V.], and the presence of Ritz combination lines. In addition the $d(1)$ sequents should be the limits of a doublet F series. The corresponding D lines should be at

$$D_{12} = 56206.00 + \xi - .237 x,$$

$$D_{22} = 60021.56,$$

of which the D_{12} should be considerably weaker than D_{22} , and a strong line intermediate to these should be expected as a representative of the D_{11} line. The separation of the D_{12} and D_{11} gives the doublet separation of the F series and should show a high occurrency. Fortunately we possess measures so far down in the ultra violet by Handke *, and amongst them is 60024.01 ± 3.6 of intensity 1, but no 56206. There are several strong lines in a suitable position for D_{11} , but 55953 gives a satellite separation of 250. This separation occurs so frequently throughout the whole spectrum as to fit in well with the condition for a D_{11} line. The whole set would then be arranged as follows:—

$2733.70 + \xi + .237 x$	$29471.07 + \frac{1}{2}\xi + .11 x \pm 1.8$	$[56208.45 \pm 3.6]$
252.55		255.00
$[2986.25 + 2\xi \mp 3.1]$	$29469.85 + \xi$	$(4) 55953.45 \pm 3.1$
$6549.06 + \xi + .237$	$33286.53 + \frac{1}{2}\xi \pm 1.8$	$(1) 60024.01 \pm 3.6$

A displacement of $28\delta_1$ or 7δ in the sequent produces a satellite separation of 258.03 , or $27\delta_1$ of 248.88 . The possible errors in the observed do not enable us to settle which is the more probable. We shall see later, when dealing with the F series, that these separations are reproduced. The appearance of the summation lines in the exact positions to be expected, their relative intensities, and with a satellite separation depending on the same own-multiple displacement as for orders $m=2, 3$, together form weighty evidence in favour of the existence of the $D(1)$ lines as calculated.

But we can obtain further evidence by sounding for the actual D lines themselves. This method has been developed in [V.] and depends on the linkage laws developed in [IV.]. The e, u, v links in Au are so large that they can stretch from

* Dissert. Berlin. The measures used are quoted from Lyman.

either of the above lines into the observed regions. Their values $e = p_2(1)(-2\Delta) - p_2(1)(2\Delta)$, $u = s(1) - s(1)(\Delta)$, $v = s(1)(-\Delta) - s(1)(\Delta)$ can be calculated from the values of Δ and $p(1)$ given above and with the $S(\infty) = 29469.85 + \xi$ are $e = 17252.31$, $u = 11340.77$, $v = 14534.05$, with respective changes 10.25, 9.17, 13.32 per oun-modification. It is shown in [IV.] that each series line is linked to long sets of other lines by these separations, and that successive e , u or e , v links are very common. If, then, to an unseen line n we observe another at say $e + n$, it is an indication—though not a proof—that the line n exists. If several such links are found together the evidence is greatly strengthened. When a link is added to a wave-number n it is written after it, if subtracted then it is written before it. Thus $2733.e = 19987$, or $e.19987 = 2733$. In the following the calculated values are given in [] and the observed set beneath (with separations from next observed lines as in Table I.)—

v , 2733.70. $v = [17667.75]$.

(4) 17675.53 (23, 16) **3814.84** (21490.37) = (3 r) 21499.65 ($-\delta_1$) (66, 41)

252.23

(1 n) 17927.76 (7, 31)

u , 2733.70. $u = [14074.47]$; 6549. $u = [17889.77]$.

outside obs.

(4 r) 17890.37 (11, 7)

.....

e , 2733.7. $e = [19986.0]$.

(2) 19988.97 (14, 112)

3816.59

(2 n) 23805.56 (45, 75)

[20240] not obs.

The v sounding gives a satisfactory complete set if the D_{22} be really an oun displacement on the D_2 sequent as indicated. The oun on d_2 produces a change of 9.285 and on d_1 of 9.155. As additional evidence for the $D_{22}(1)$, may be added the $e + v$ sounder, *i.e.*, the e sounder for the above set. We find $e(1) 38746.77 \pm 1.5 = 21494.46 \pm 1.5$. The next line to this is (1) 38757.29 ± 1.5 , which is equivalent to an oun displacement on the sequent, and is the corresponding line linked by e to 21504.98.

The u link is not large enough to reach the D_{12} , D_{11} lines. It indicates, however, as is seen, D_{22} . This line 17890 is also associated with two lines ahead by e and v links.

In the e sounding again we get a good indication. There is no observed line, however, corresponding to $D_{11}(1).e$. The nearest is (2 n) 20200.35 (100, 117). Numerically it is

$(2\delta_1)D_{11}(1)(2\delta_1).e$, giving $D_{11}(1).e=20240.18$. Although exact, the double displacement is of small evidential value unless supported by independent considerations.

In connexion with the third kind of tests I have noted the two combinations $d'_1(1)-\bar{d}_2(1)$, $d'_1(1)-d_1(1)$, where d' denotes the sequent for the inverse D set already referred to. Since $-D'_{11}(1)=p(1)-d'_1(1)$ and $D_{11}(1)=p(1)-d_1(1)$, it follows that $d'_1(1)-d_2(1)=D'_{11}(1)+D_{12}(1)=19113.53+2733.7=21847.2$; this is observed at $(2)21846.41$. So $d'_1(1)-d_1(1)=D'_{11}(1)+D_{11}(1)=19113.53+2986=22099$, which is observed at $(4n)22102.18$ within possible limits. With the first it would give the satellite separation as 255.77.

The cumulative evidence of these three independent considerations is convincing that the D(1) lines as suggested really exist, and that the rule for the extreme satellite mantissa is not broken in the case of Au, as it apparently was when the old observed D(2) line was regarded as belonging to the first set. The consideration of the F series which follows will give direct proof that the $d(1)$ sequence at least exists, but before taking up that question it is necessary to complete the discussion of the results of Table I. which raise points of importance not only in connexion with the properties of D series, but of those of displacement in general.

$m=2$. No direct lines are found for the weaker D_{12} and D_{13} , nor for D_{11} . Rydberg had allotted $(4)17050.97$ to D_{12} , but K. R. have pointed out that its separation from $D_{22}=20858$ is too large. The true value cannot deviate more than $.32$ from 17043.41 . This differs by $7.56\pm.46$ from 17050 . The own displacement on $d(2)$ produces 2.93 , so that 7.56 is as far as it can be from a value produced by $2\delta_1$ or $3\delta_1$ and much beyond the possible errors of $\pm.46$. The line in question therefore cannot be a simple displacement of $D_{12}(2)$. Since the own on the limit produces 10.76 , it may be $(\delta_1)D_{12}(2)(\delta_1)$, which is separated from D_{12} by $10.76-2.93=7.83$, but is probably unrelated to the D series. The D_{11} and satellite appear each displaced into at least two others. Thus

$$\begin{array}{llll} (4)41866.75+.87p & \text{as} & D(10\delta_1) & \text{gives} & D_{12}=41896.05+.87p \\ (2)41928.72+.87p & \text{,,} & D(-11\delta_1) & \text{,,} & D_{12}=48896.49+.87p \\ (1n)41798.68+1.7p & \text{,,} & D(5\delta_1) & \text{,,} & D_{11}=41813.18+1.7p \\ (5)41859.04+1.7 & \text{,,} & D(-16\delta_1) & \text{,,} & D_{11}=41812.64+1.7p \end{array}$$

For $m=3$ the satellite separation is due to $26\delta_1$ in line

with those for $m=1, 2$. All the set appear except the weak line D_{12} , and it is at the same time instructive to notice that there appear no signs of displaced lines. For $m=4$, on the contrary, there are possible representatives only of D_{22} and D_{23} , but there are clear evidences of extensive displacements. The calculated value for D_{11} is 25034.05. This has a u link to (4)36374.87, for which the Zeeman pattern has been observed by Purvis. It is represented by $0/6\frac{1}{2}$, the proper pattern for a D_{11} line. Displacement certainly alters the Zeeman pattern—witness, as an instance, the different forms for satellite lines. If this indication that linkage leaves the Z-patterns unaffected is sustained by further evidence, it would be of fundamental importance for spectral theory. The normal line 20534 itself appears split up into a number of others all showing displacements by an own multiple in the limit. We find in succession the lines in the following list, in which are given the suggested displacements, and the O-C values on the supposition that the true $D_{11}(4)$ should be 25034.24 :—

		O—C.
(1) 25012.07	$(2\delta_1) D_{11}$	.11
[25034.05]	[D_{11}]	.03
(1) 25045.39	$(-\delta_1) D_{11}$	— .06
(1) 25055.69	$(-2\delta_1) D_{11}$	.01
(1n) 25077.80	$(-4\delta_1) D_{11}$	— .08

The two lines suggested in the Table for D_{22} , D_{23} are probably not the normal, but may be displaced. They would give a satellite separation of 43.40, much too large to be in step with those for $m=1, 2, 3$. Here $28\delta_1$ would produce a separation of 17.5. The general disintegration of the $D(4)$ set would seem to be indicated by the existence of fragments of other sets in the neighbourhood. For instance, we find

(3n) 25170.53	29472.88	(1r) 33775.23
3813.70		3814.52
(1) 28984.23	33286.99	(1) 37589.75

Here 25170 has the normal limit.

In $m=5$, D_{22} is represented by two displaced lines, viz.,

(5) 36374.88 as $D_{22}(-3\delta)$	gives ... 70.52,
(1n) 36367.70 as $D_{22}(2\delta)$	gives ... 70.60,

but the first is $D_{11}(4)-u$, and is too strong to represent D_{22} . It forms a merely numerical coincidence.

In $m=6$, the displaced D_{12} , D_{22} would seem justified by their order of intensities and same displacement = δ .

In $m=7$, 3604.96 is exactly the calculated λ for $(\delta_1)D_1(7)$. But this line is also, as will be seen later, the combination $p_1(1)-p_1(7)$. The values coincide. Whether the observed is either or both there is nothing to decide.

$m=8$. The calculated D_{11} gives a better ν with D_{22} , and a closer value to the mean limit.

The foregoing discussion supports conclusively :

- (1) The value of the limit $S(\infty)=D(\infty)$ is 29469.85 ± 1.5 .
- (2) The existence of summation **D** series.
- (3) The existence of extreme ultra red **D** lines, depending very closely on 9Δ as the mantissa of the d_2 sequent.
- (4) A satellite separation about 249 or 258 due to displacements of $27\delta_1$ and $28\delta_1$.

With this limit and its uncertainty 1.5, and $\nu=3815.56+d\nu$, $d\nu < .1$,

$$\Delta = 113935 + 27d\nu - 5.46\xi = 113935 + x, \quad x < 10,$$

$$\delta = 1406.604 + .123x,$$

$$f(8\Delta) = 30017.06 - .251x,$$

$$f(9\Delta) = 26734.86 - .237x.$$

It should be remembered, however, that the value of the ν as determined from the $S(\infty)$ and the doublet or triplet separation appears often to show an indication of being very slightly smaller than when determined from **D** or **F** data, although the latter are very consistent amongst themselves. It is possibly due, if it is real, to a difference in the value of N between **P** and **D** sequences. In any case it is always extremely small. Here the value from **D** and **F** data would depend on the $D(1)$ lines, and we have no direct observations to give their values with sufficient exactness to test. So far as evidence is at disposal it must come from the sounding with e, u, v links given above, and these point to a slightly higher value of the **D** lines than those calculated. In fact, the following arrangement would fit all the sounding indications, within error limits. The observed lines are supposed to be corrected by amounts less than the possible

errors and are shown as alterations on the observed measures :—

	D.		D.	
	(2735·94	29469·85	[56203·77]	
3815·56	248·88		248·88	
	2984·82	29469·85	55953·45+1·44	($p= \cdot 5$)
	6551·30	33285·41	60021·04-4·68	($p=1\cdot 3$)

This would give $d_2(1) = 29469\cdot 85 - 2735\cdot 94 = 26733\cdot 91$. It may be taken as this with an uncertainty at present of ± 4 . This makes $\Delta = 111940$, $\delta = 1406\cdot 78$ or within the limits of the direct determination from $S(\infty)$.

The F and F series. These series have as their limits the first D_{11} , D_{12} sequents. With our new $D(1)$ lines or the d_2 sequent with a mantissa 9Δ ,

$$F_2(\infty) = d_2(1) = 26733\cdot 9 - 237x \quad x \text{ not } > 10.$$

The D satellite displacement of $27\delta_1$ gives a separation of $248\cdot 89$, or $28\delta_1$ of $258\cdot 05$. We should expect, therefore, doublet series with these separations on both sides of 26734 , appertaining to $F_1(\infty) = 26486$ or $26476\cdot 81$. We find on inspection a very large number indicating a profusion of displacements, and the lines in consequence so crowded that it is difficult to determine definitely whether numerical co-incidences correspond to real relationships or not. For our present purposes we desire to obtain the $F_2(1)$ lines. Now, like the d sequences the $f(1)$ sequence also has its source in a mantissa which is a multiple of Δ and at the same time is a large fraction approximating to unity. Here, then, the multiple can only be 9 or 8, or possibly 7 or 6—or there may be, as in the rare gases, several groups depending on both. In other elements we find indications of F satellites depending only on small displacements of order $2\delta_1$. Also the lower orders are often subject to very large Δ displacements. We proceed to discuss the two cases of 9Δ and 8Δ in order :—

Case I. $f(1) = N/(9\Delta)^2$. In this case $d_2(1)$ and $f(1)$ are identical and equal to $26733\cdot 96 \pm 2$. The expected lines should therefore be :

$$\begin{array}{ll} F_2(1) = 0 & F_2(1) = 53467\cdot 8 \pm 4, \\ F_1(1) = -248\cdot 89 & F_1(1) = 53218\cdot 9 \pm 4. \end{array}$$

$F_2(1) = 0$ would correspond to no oscillation and probably to instability, and lead to an expectation of displacement.

For direct evidence we must look, as before, for **F** lines in the ultra violet. There are no lines at the places indicated. The nearest are (6)53401·69 + 2·9 *p*, (−70, 183), and (2)53151·91 + 2·9 (−174, 32) with the proper separation of 249·78±. If they are the sought **F** lines the complete set would be :

$$\begin{array}{llll} \mathbf{F}_1 & -181\cdot9 + x & 26485\cdot0 & 53151\cdot91 \pm 2\cdot9, \\ \mathbf{F}_2 & 66 + x & 26733\cdot9 & 53401\cdot69 \pm 2\cdot9, \end{array}$$

with *x* of order ±4, depending on obs. errors 2·9 *p* and limit uncertainty. These are 66± less than the calculated values and can be explained by a +7 δ₁ displacement in the sequent, which produces a separation of 64·75. The *u*, *v* links are too small to reach into the observed region. We have no knowledge as yet as to how links should be attached to wave-numbers which formulæ give as negative, but we should expect doublet separations to be conserved. We should then look for lines, with added and with subtracted links as follows :—

$$\begin{array}{ll} \mathbf{F}_1 & e - 181\cdot9 + x = 17071\cdot8 + x, \quad -e - 181\cdot9 = 17435\cdot7 + x, \\ \mathbf{F}_2 & e + 66 + x' = 17319\cdot8 + x', \quad -e + 66 = 17187\cdot8 + x'. \end{array}$$

Now we find in this neighbourhood a large number of lines with all the signs of being *débris*, so to say, of a shattered system, viz., weak lines of the same nature and separated by multiples of the same numbers. Taking the lines as they occur in order they may be arranged as follows:—

<i>e</i> . F ₂ .	<i>e</i> . F ₁ .	
(1 <i>n</i>) 17178·50	(2 <i>n</i>) 17410·02	
9·3	29·57 = 6 × 4·93	(4) 17675·53 arc.
[17187·8 + <i>x'</i>]	[17435·7 + <i>x</i>]	[17684·6]
251·8 − <i>x'</i> (2 <i>n</i>) 17439·59	251·51	(1 <i>n</i>) 17691·10
	4·99	4·92
(1 <i>n</i>) 17444·58	251·44	(1 <i>n</i>) 17696·02
	11·48	4·19
		(1 <i>r</i>) 17700·21
		6·89
(3) 17456·06	251·04	(3 <i>r</i>) 17707·10
		4·39
		(3 <i>n</i>) 17711·49
		9·11
		(3) 17720·69

$F_1.e.$ $F_2.e.$ $(2n) 17269.10 = e + 15$

(4) 17050.97 arc.

20.8

64.84

 $[17071.8 + x]$ $[17319.8 + x']$
 $\left\{ \begin{array}{ll} 242.4 & (1n) 17562.23 \\ 254.1 & (3) 17573.91 \end{array} \right. 11.68$
262.1 $(1n) 17333.94$

15.79

 $(1n) 17349.73$ 251.2 $(1n) 17601.92$

6.23

 $(5) 17355.96$

It will be noticed, the same weak and nebulous character of the lines, the frequency of separations depending on multiples of 4.9, and also similar analogies in the two sets, *e.g.* the changes from a sharp line to a nebulous one with sep. 11.6 or in that neighbourhood at 17456, 17573. In relation to the whole set it should be remembered that we should expect the $27\delta_1$ or $28\delta_1$ displacements of the D series to be repeated on the limit, or on the f sequent. In this connexion the following data may be given :—

$+27\delta_1$	$-27\delta_1$	$+28\delta_1$	$-28\delta_1$
248.91	252.39	258.05	261.80

The effects are capable of so many interpretations that it is impossible to draw any certain conclusions. A few remarks, however, may not be out of place :—

- (1) $f(1)$ is taken as $d_2(1)(7\delta_1)$, so that the set are $d_1(1) \pm f(1)$ and $d_2(1) \pm f(1)$.
- (2) 17178 is either $e.(\delta_1)F_2$ or $e.F_2(-\delta_1)$.
- (3) In 17269 the original displacement of 64.8 is reproduced.
- (4) It is difficult to explain the differences 4.9 by our displacements. They could possibly be explained by the our if these series depended on a Rydberg constant $4N$, as in the enhanced series of the alkaline earths, and there are some independent indications pointing to this.
- (5) The important consequence to be drawn is that they afford evidence of the extreme disruption of a set, and of the nature of the complicated displacement systems called into play and which require disentanglement.

We might now attempt to allocate sets of lines to stand in the relation of higher orders to the series. They exist, but

I omit reference to them, as for the present purpose—that of illustration of method and the more exact determination of the gold ouu—the next set in which $f(1)$ depends on $N/(8\Delta)^2$ is preferable and is sufficient.

Case II. $f(1) = N/(8\Delta)^2$. Here $f(1) = 30017\cdot06 - \cdot251x$ with the ouu displacement producing a change of $11\cdot046$. With the $d(1)$ value $F(\infty)$, viz., $26734\cdot86 - \cdot237x$, the calculated values of the set for $m=1$ are

$$\begin{array}{lll} F_1 & -3531\cdot20 & 56502\cdot92 \quad \Gamma_1, \\ F_2 & -3282\cdot20 & 56751\cdot92 - \cdot488x \quad F_2. \end{array}$$

For the **F** lines only (1) $56744\cdot03 + 3\cdot22p$ is observed. It should be normally a strong line. There is a strong line at (5) $56721\cdot50$ separated by $22\cdot53$, and as $2\delta_1$ in the sequent produces $22\cdot09$ it is probably $F_2(1)(2\delta_1)$. The F_1 should be 56495 (not seen). But there is again a strong line (5) $56561\cdot09$, 66 ahead. This may be either $6\delta_1$ ($66\cdot27$) on the sequent or the $7\delta_1$ ($64\cdot0$) on the limit (similar to Case I.). The only interest in these at present is that if displaced **F** lines, the weakness of the normal ones is explained.

For evidence of the **F** lines we must again have recourse to sounding. The u links are too small to reach. The v links land close to a doublet with the proper separation, viz. :

$$(1n) 18217\cdot03 + \cdot15p \quad \mathbf{250\cdot53} \quad (3) 18467\cdot56 + \cdot15p,$$

with again several lines intensity (1n) near 18217 , suggesting other displaced lines with consequent weakness. Subtracting v gives as the **F** lines $3283, 3533\cdot51$. Treating the series as $N/(9\Delta) - N(8\Delta)$ gives—with the observed F_2 —

$$\begin{array}{lll} -3533\cdot51 & & [56493\cdot52] \\ \mathbf{250\cdot51} & & \mathbf{250\cdot51} \\ -3283\cdot00 & 26730\cdot52 + 1\cdot6p & 56744\cdot03 + 3\cdot22p. \end{array}$$

In the absence of observation in the ultra red this set cannot be considered as conclusive, although it satisfies the conditions. If it be taken as real, the observed $56744\cdot03$ is the value calculated above and should give the value of x . That is

$$\begin{aligned} 56744\cdot03 + 3\cdot22p &= 56751\cdot92 - \cdot488x, \\ \text{whence } x &= 16\cdot16 - 6\cdot60p. \end{aligned}$$

This gives a closer value to Δ as depending on the **D**, **F** data. If it is the same as from $S(\infty)$ and v , $x < 10$ or p should be about 1—or the observed measure of the **W**, **L** should be $\cdot1\text{ \AA}$ less. The possible error is certainly greater than this. Provisionally we will take $p=1$, $x=9\cdot5+x$, where now $x=0$

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if the ouns calculated from S and D are the same, but may be anything between ± 6 if not.

This makes $\Delta = 113951 - 6 \cdot 60p$,

from which $N/(9\Delta)^2 = 26731 \cdot 03 + 1 \cdot 56p$.

It will be noted that allowance being made for uncertainty in v this is the mean limit given by the observations. It points to the fact that the link is not modified and the observed line 18217 has suffered no displacement in the linking. If so, any differences occurring can only arise through observation errors. Take the natural supposition that the two determinations of the oun are the same. Then, as we have seen, p is about 1, say $\cdot 9$, so that $x = 10$. The link v is increased by $\cdot 98$ or say 1. The possible error in 18217 is $\cdot 15p'$. Hence $F_2 = -3282 \cdot 00 - \cdot 15p'$ and the mean limit is now $26732 \cdot 66 - \cdot 07p'$, as against the value directly calculated from $N/(9\Delta)^2$ of $26732 \cdot 43$, or exact equality.

This is not a mere meticulous refinement. The analysis is exact when the data are definite. The difficulty in general is that on account of the numerous displacements in two sequents, modified links, and other changes, the data themselves are subject to indefiniteness.

Before attempting to allot lines for higher orders it may be advisable to consider what we are to expect. The D and F systems of lines have much in common—indeed, it may ultimately be found on more complete knowledge that the f -are only another set of d -sequences. There is considerable evidence* that the d -sequences are not representable by a continuous mathematical expression, but that they may approximate to values so represented. In the F system, wherever they have been discussed in detail, this tendency is still more marked. There is indisputable evidence that what we should regard as a normal line is often accompanied by a number of others displaced in definite ways, that its intensity is then diminished, and, indeed, that it is itself, in that case, frequently absent. In some instances the whole set for a given order (m) may be absent and represented either by another strong set related to it by a displacement of several multiples of Δ †, or by a congery of *membra disjecta* displaced by various oun multiples. One is even tempted to suspect that the possible lines of a spectrum—at least in the D and F systems—are built up by the addition to the mantissa of successive multiples of the oun, and that the

* See, for instance, *Astro. J.* xliv. p. 229 (1916).

† *E. g.* alkaline earths [III. p. 383 *seq.*], the rare gases [V.].

intensities—or the chance of the particular configurations corresponding to those multiples existing—alter with each addition, rising to maxima under certain as yet unknown conditions. That sometimes such a displacement suddenly confers increased intensity is certainly true. This whole question is a most interesting one and of fundamental importance in any theory of spectral origins. Before it can be profitably discussed, however, a greatly increased collection of raw material bearing on this point must be obtained. The spectrum of gold seems especially promising for a more exhaustive investigation under this head.

In the following list many lines have been included to illustrate the effects of displacement as above indicated. Several of the individual illustrations are doubtless spurious and mere numerical coincidences. This may be specially the case with lines occurring in the region embracing W, N 25000 to 28000 (say, $\lambda\lambda$ 4000 to 3500), which is exceedingly crowded owing to this cause, containing as it does lines belonging to different sequents and different limits. It is, however, the number of such coincidences which give evidence as to the general existence of the displacement effect. Their consideration is, however, of importance from another aspect. A line associated by one of the usual links to an unseen one is evidence in support of the possible existence of the unseen, but it does not give the power in general of exactly determining its measure, owing to uncertain linkage modifications. On the other hand, an observed line satisfying a condition of displacement from a suspected one, gives no reliable evidence that such a suspected line can actually exist, but it does give evidence as to its theoretical measure, if it were capable of being emitted. This point is of importance in settling the mean limits as determined from the means of difference and summation lines, *i.e.* limit = $\frac{1}{2}(F + F)$, where one of the lines in question is determined by displacement from an observed set.

In the following table sets of lines have been allotted whose mantissæ in the different orders (*m*) are of the same order of magnitude—a condition which normal series lines must conform to. Also a considerable number of other lines have been added where they seem to show the presence of displacement, especially where what should be a strong line appears represented by a number of weak ones of similar character. Under each order is inserted the change produced in the sequent by the displacement of one oun. The corresponding change on the limit is 9.14. Deduced values are in ().

Lines of the F system, $F_2(\infty) = N/(9\Delta)^2$, $f(1) = N/(8\Delta)^2$.

$m = 1$.

Change per $\text{oun} = 11\cdot04$.

$v(1u) 18217\cdot03$	$-3532\cdot51$	
$v(3) 18467\cdot56$	250·51	
	$-3232\cdot00$	(1) 56744·03

$m = 2$.

Change per $\text{oun} = 3\cdot078$.

$(2\delta_1)v, (1) 28620\cdot74?$	$26731\cdot02 + 1\cdot6p$	
	$26484\cdot68$	(4) 39292·11
		350·14
		(2) 39542·25
		

$m = 3$.

Change per $\text{oun} = 1\cdot273$

$(1u) 19440\cdot01$		(5) 33522·63
19·41		72·96
$(\hat{v})(3) 19420\cdot60$	$26485\cdot25$	$(\hat{v}_1)(1) 33595\cdot59$
		248·88
$(2\hat{\delta}_1)(1u) 19649\cdot22$	$26732\cdot73$	(6) 33835·33

$m = 4$.

Change per $\text{oun} = 638$.

$(6u) 21928\cdot38$	45·35	(30990·61)
$(6u) 21973\cdot73$		
		(5) 30970·20 (−8δ)

A parallel set.

$(3u) 22001\cdot67$	$26485\cdot93$	(5) 30970·20 = F₁(4)(8δ)
251·56		
$(2u) 22253\cdot23$		

(1 _n) 23302.53 (1 _n) 23354.78 (1 _n) 23362.19 (1 _n) 23379.90 (2 _n) (3) 26638.60 (3) 26624.78 (3) 26595.17	$m = 5.$ Change per o <u>u</u> n = .370.	23362.19 257.17 (26619.36)	26482.17 242.78 (1) 29845.93	=	(3) 29550.83 (1) 29557.73 (δ) (1) 29638.67
(δ_1)(1 _n) 24213.43	$m = 6.$ Change per o <u>u</u> n = .22	(24204.29)	26480.05	(1 _n) 28755.79	18 39 (1 _n) 2877+16
A parallel set		14.61 (2 _n) 24228.04 249.13 are (2) 24477.17	26730.70	[287 45.10] (1) 28984.23	
	$m = 7.$	are (2) 24739.07 244.01 (3) 24983.08	26483.06 26729.80	(3) 28227.06 249.45 (28476.51)	(1 _n) 28430.17 9.78 (- δ)(1 _n) 28439.95
(1 _n) 25092.34 248 (1 _r) 25340.32	$m = 8.$	(1 _n) 25092.34 248 (1 _r) 25340.32	26482.83 26733.18	(7) 27873.33 252.7 (28126.04)	(- δ_1)(3) 28116.90

NOTES.— $m=2$. The F lines are in the unobserved red region. There appear no simple e, u, v links. That suggested is very problematical.

$m=3$. The separation $19\cdot41$ suggests $15\delta_1$ on the sequent, which gives $19\cdot09$. $2\delta_1$ on the limit gives $18\cdot24$ and is too far out. In connexion with F_1 , there appear several lines which suggest displacement.

$$\begin{array}{llll}
 & (5)33522\cdot63 & & \\
 \left\{ \begin{array}{l} (33586\cdot45)=F_1 \\ (1)33595\cdot59 \\ 32\cdot88 \end{array} \right. & \begin{array}{l} 72\cdot96 \\ (2r)33619\cdot33 \\ 33\cdot60 \end{array} & \begin{array}{l} 2\delta \text{ on limit gives } 73\cdot12 \\ (-\delta_1)F_1 \\ (-3\delta_1)F_1(-5\delta_1) \text{ gives } 33\cdot77 \end{array} & \\
 66\cdot48 & (2n)33652\cdot93 & (-6\delta_1)F_1(-10\delta_1) \text{ gives } 67\cdot54 \text{ for } 66\cdot48 & \\
 & 76\cdot62 & & \\
 & (4n)33729\cdot55 & &
 \end{array}$$

$m=4$. The only directly observed line is F_1 . A precisely similar line lies next before it separated by $45\cdot35$, which is $5\delta_1(=45\cdot70)$ on the limit. They are clearly associated, but whether in this way, or with concomitant displacement in the sequence cannot be definitely settled with this order $m=4$ as the change per oun in the sequent is so small.

$m=5$. Here again there appear several sets of displaced lines. The different separations $257, 242$, show that the sequents in the F_2 set are different from those of F_1 —in other words, the sequent in F_2 has experienced a change $\frac{1}{2}(257\cdot17-242\cdot78)=7\cdot20$. As $5\delta=20\delta_1$ produces $7\cdot40$, it may be this. It makes the actual separation $249\cdot98$.

$m=6$. The separation of the associated F_1 lines, $18\cdot39$, is exactly due to a $2\delta_1$ displacement on the limit.

The set given for $m=8$ is not in step for this order. The denominator of its sequent is $8\cdot872840$, and is smaller than we should expect, although it is possibly in step with a rapid decrease foreshadowed in $m=7$, and analogous with D lines of highest order in the alkalis. It is given, however, as illustrating the general remarks on these series above. As an example of another set in this neighbourhood may be taken :

$$\begin{array}{lll}
 & (1n)27972\cdot50 & \\
 & 245\cdot42 & \\
 (5)25249\cdot65 & 26733\cdot78 & (28217\cdot92) = (\delta_1)(3)28227\cdot06
 \end{array}$$

It may be noticed that there are in the foregoing many instances where displacement on the sequent produces a nebulous line, whilst on the limit it is sharp. We cannot say, however, whether this is a general rule. To indicate that the given lines are at least near positions for normal lines, the following values of the denominators calculated from them are given: 1.911560, 2.926185, 3.929447, 4.931517, 5.930130, 6.936977, 7.929360.

P and S Series.

It has generally been assumed that the strong pair in the ultra violet, whose W.N. are (10) 41172.94, (10) 37357.62 with separation 3815.32, form the first P doublet, in analogy with the strong violet pairs in Cu and Ag. Although at first sight this assumption would appear natural, it is easy to show that it cannot be sustained. In the first place—as was pointed out by Kayser and Runge in their original measures,—they are not in step with the Cu P and Ag P lines. The P_1 lines would run Cu, 30782; Ag, 30471: Au, 41172 with Au much larger instead of somewhat smaller than Ag. But the matter is definitely settled against the supposition when the question of the limit is considered. The rule that $S(\infty) = p(1)$ is always so closely observed that it may be considered as absolute. The rule that $P(\infty) = s(1)$, although never exactly fulfilled when $s(1)$ is extrapolated from the $s(m)$ formula, is also so very nearly followed that it should be regarded as holding very approximately. In the case of gold $S(\infty) = 29469.85 = N/(1.929145)^2$. If 41172 is $AuP_1(1)$, $P(\infty) = 70642.79 = N/(1.246015)^2$. The undoubted $S(2)$ lines (see below) give $s(2) = N/(2.545878)^2$. It is clear, therefore, that $s(1)$ cannot be $N/(1.246)^2$ or near it, so that 41172 cannot be $P_1(1)$, or belong to a principal series of the ordinary type. Nevertheless, if regarded as belonging to a series in which the separations diminish with ascending order, it is possible to arrange a set for whose real existence as a definite series some evidence can be adduced, apart from the fact that the set are reproducible by a formula of the ordinary type. I give the evidence, such as it is, premising that considerations to follow may throw doubt on its validity. The letter P' will be used provisionally to denote the series, as its type is undecided.

The value of $P(\infty)$ is $70642.79 + \xi$, and the denominator of the first sequent $= 2.940001 - 115.9\xi$. We should, therefore, expect to find $P'_1(2)$ with a denominator near 3.94 . . . , or wave number near 58000. Also we might hope to find evidence in support by the combination line $p(1) - p(2)$.

We find in this region several strong lines, the strongest being (5) 57954·22 ($\lambda=1725\cdot5$). This would make the combination line $p_1(1)-p_1(2)=16781\cdot28$, and we find it in the observed line (4) 16781·73 ($\lambda=5957$). We may, then, conclude with certainty that this allocation is correct. With these given lines for $m=1, 2$, the formulæ constants are given by

$$n = 70642\cdot79 + \xi - N / \left\{ m + \cdot950924 - 199\xi - \frac{021769 - 166\xi}{m} \right\}^2$$

This gives for $m=3 \dots 8$, the following wave numbers 63590·85, 66148·38, 67542·50, 68370·55, 68906·70, 69273·06, all in the ultra violet beyond the observed region. For evidence as to the existence of these, it will therefore be necessary to have recourse to sounding, and to testing for the existence of combination lines.

- $m=3$. The e link requires 46337·90. There is
obs. (3n) 46342·43 ± 2 . $d\lambda = -\cdot1$
 $p_1(1)-p_1(2)$ requires 22417·21 and is
not observed.
- $m=4$. The e requires 48896·1. There is obs.
(5) 48892·82. $d\lambda = +\cdot07$
The comb. requires 24975·44. There is
obs. (3) 24977·02.
This combination gives 66149·96. $d\lambda = -\cdot03$.
- $m=5$. The v requires 52608·45. There is obs.
(2) 52606·66. $d\lambda = \cdot04$
The comb. requires 26369, and is not
observed.
- $m=6$. The e requires 51118·2. There is obs.
(3) 51119·52. $d\lambda = -\cdot02$
The comb. requires 27197·6. There are
obs. (1) 27191·28, (1) 27202·44, of
which the latter may be $D_{12}(6)$, but
agrees well as a combination.
- $m=7$. The v requires 53972·65. Obs. (4) 53978·16. $d\lambda = -1$
The e requires 51654·4. Obs. (1) 51659·56. $= -1$
Both point to a common line 68911·7.
The comb. requires 27733·76. There is
obs. (2) 27731·94.
- $m=8$. The v requires 54339. Obs. (3) 54330·11.
The e requires 52020·3. Obs. (7) 52018·31,
but the latter is too strong to be accepted
as really related.
The comb. requires 28100·0. There is
obs. (2r) 28104·65, which is also pos-
sibly $D_{11}(8)$.

Several strong lines appear in positions suitable for $P'_2(2)$, and they are probably related. The line (4)56911.96, regarded as a P'_2 line, has its mantissa less than that of $P'_1(2)$ by $113800 + 389p_1 - 333p_2$. The lines are measured to the nearest unit in the first decimal point—consequently, if no observation errors are made, they are indefinite to the extent of .05, or in the above p_1 and p_2 are equally probable within ± 5 . The mantissæ difference is then with great probability exactly Δ , *i. e.* the same as for $P'(1)$. We might be tempted, therefore, to allocate it to the real $P'_2(2)$, were it not that the rule—so far as may be judged from the case in the alkalis—appears to be that this difference is not the same for successive lines, but that it is about $\cdot 8$ to $\cdot 9\Delta$ for $m \geq 2$, and is an own multiple also. This condition is satisfied by (4)56947.61 whose displacement from $P'_1(2)$ is 110106. As $78\frac{1}{2}\delta = \Delta - 2\frac{3}{4}\delta = 110076$, this satisfies the multiple law with no observation error. None of the lines in this neighbourhood appear to give observed combination lines with $P'_2(1)$. The nearest is (2)57191.88 requiring 19834.26 as against an observed (1n)19828.64, possibly within error limits, especially as these combination lines seem susceptible to change by the electric field in the arc. It would seem that the P'_2 lines here are represented by several associated lines, of which 56947.61 would appear to be the normal line.

In the following the estimated separations are based on the $78\frac{1}{2}\delta$ displacement.

$m=3$. Separation about 394 or less. This is satisfied by a v linked line and a combination, *viz.*:

$$(1)48254.39v = 63188.44.$$

$$p_2(1) - p_2(3) = (1)25834.32 \text{ gives } 63191.94 = P'_2(3).$$

$m=4$. Separation about 200. Satisfied by

$$(2n)38695.80.e = 65948.11.$$

$$p_2(1) - p_2(4) = (2)28595.47 \text{ gives } 65953.09 = P'_2(4).$$

$m=5$. Separation about 114.

$$(5)52476.9.v(-\delta_1) = 67424.28.$$

$$(2)50169.9.e = 67422.2.$$

$$p_2(1) - p_2(5) = (1)30067.59 \text{ gives } 67425.21 = P_2(5).$$

$m=6$. Separation about 70.

$$(2)51051.66.e = 68303.97.$$

$$p_2(1) - p_2(6) = (4n)30944.04 \text{ gives } 68301.66 = P_2(6).$$

$m=7, 8$. Separations about 48, 33.7.

The lines are collected in the following table, together with the deduced wave-lengths :—

	λ .	n .	$p(1) - p(m)$.
1 { 10 R	2676.05	37357.62	
10 R	2428.06	41172.94	
2 { 4	1756.0	56947.61	
5	1725.5	57954.22	(4) 16781.73
3 {	1582.48	63191.94	(1) 25834.32
	1572.5	63590.80	
4 {	1516.23	65953.07	(2) 28595.47
	1511.16	66149.96	(3) 24977.02
5 {	1483.12	67425.21	(1) 30067.59
	1480.5	67540.65	
6 {	1464.09	68301.68	(4n) 30944.04
	1462.75	68369.80	(1) 27202.44 ?
7 {			
	1451.28	68904.88	(2) 27731.94
8 {			
	1443.6	69272.38	(2r) 28104.65 ?

The considerable number of combination lines of a very common type $p(1) - p(m)$ strongly supports the supposition that the set form an actually related series. The question presents itself whether the objection raised as to the limit not being $s(1)$ can be met. In the foregoing treatment of the set as a P series, 29469 is $p(1)$, and the series is regarded as produced by deducting the sequence $p(m)$ from a limit 70642. We have shown that 70642 cannot be the true $P(\infty)$ or $s(1)$. This difficulty may, however, be possibly explained by regarding 70642 as composite—in other words, by regarding the series in question as linked to the true P series and $70642 = P(\infty) + \text{links}$ (that is, as forming a parallel series to the P). For instance, if it was the single e link the $P(\infty)$ would be $70642.79 - 17252.31 = 53390.68 = N/(1.4335)^2$, which is within possible reach of $s(1)$. In this connexion the large number of $-v$ links noted above in sounding is suggestive. To these may be added the following for the orders $m = 1, 2$, in which also the linkages $v + c$ are included :—

$$\begin{aligned}
 (2r) 21629.62 \quad \mathbf{4606.98} \quad (2n) 26236.60 \quad \mathbf{14936.34} \quad & 41172.94 \quad P'_1(1) \\
 (1) 37410.03 \quad \mathbf{4606.60} \quad (1) 42016.63 \quad \mathbf{14930.98} + 3.3p \quad & 56947.61 + 3.3p \quad P'_2(2) \\
 (1n) 38418.54 \quad \mathbf{4606} \quad + \quad & \mathbf{14929.68} + 3.3p \quad 57954.22 + 3.3p \quad P'_1(2)
 \end{aligned}$$

in which p is equally probable within ± 5 and possible within ± 2 . The linkage $v + c = 14934.05 + 4607.77 = 19541.82$ here indicated would give for the $P(\infty) = s(1)$ a value $70642.79 - 19541.82 : 51101 = N/(1.464 \dots)^2$. It is, in fact, a value obtained by an independent attack on the P problem undertaken below. It may be noted that by an explanation of this kind the combination lines given by the P' set will be the same as by a P set, and consequently $p(1) - p(m)$.

There is also another way in which the presence of the $S(\infty)$ in the 41172 pair may be accounted for, and in our present state of ignorance as to spectral constitution, it is advisable to consider it. It is to regard the 29469 as a limit and the pair as summation lines. Now it is curious that such a set can be found. They are

$$\left. \begin{array}{ll} (3)21558.05 & (4\delta) = \dots 81.86 \\ (3)21577.30 & (3\delta_1) = \dots 81.76 \\ (3)21589.65 & (-5\delta_1) = \dots 82.21 \end{array} \right\} \begin{array}{ll} (21581.94) & 29469.78 \\ & (10)37357.62 \end{array}$$

$$\begin{array}{ll} \mathbf{3814.83} & \mathbf{3815.32} \\ (1n)25396.77 & 33284.85 \quad (10)41172.94 \end{array}$$

Denoting the series by R for convenience, the R_1 is given as split up into at least three displaced lines. The sequent (37357—29469) has denominator 3.728865, so that the lines correspond to $R(3)$. The own displacement on the sequent produces 1.488. The three lines displaced from $R_1(3)$ as indicated give the same value for $R(3)$ within fractions of possible errors, and are of the same intensity and character. Indeed, they would seem to afford a striking illustration of the split up of a normal line of strong intensity (witness, the intensities of the R lines) into a number of weaker displaced ones*.

For $m = 4$ the denominator should be near 4.72, and the following set satisfying the conditions are found:

$$\begin{array}{lll} (1)24558.61 & 29467.36 & (34376.11) = (-6\delta_1)(10)34311.55? \\ \mathbf{3814.93} & & \mathbf{3815.88} \\ (3)28373.54 & 33282.76 & (2)38191.99 \end{array}$$

* There is, in fact, a whole successive group of similar character—in addition to the above may be added (3)21530.70 ($34\delta_1$) = $\dots 81.30$; (1)21542.49 ($26\delta_1$) = $\dots 81.18$; (3)21601.77 ($-13\delta_1$) = $\dots 82.43$, a mean from the six of 21581.79 making $\nu = 3815.0$.

The mean limits are both in defect by about 2·5, and the allocation of R_1 seems rather arbitrary. R_2 is much weaker than R_1 and can be accounted for by the presence of the displaced lines, thus :

$$\begin{array}{rcl}
 (2)38127\cdot63 & & \\
 \mathbf{64\cdot36} & 5\delta_1 \text{ on limit gives } 64\cdot30 & \\
 (2)38191\cdot99 & & \\
 \mathbf{12\cdot98} & \hat{e}_1 \quad , \quad , \quad 12\cdot30 & \\
 (4n)38204\cdot97 & &
 \end{array}$$

From the sets for $m=3,4$ and the given $S(\infty)$, the following formula is found :

$$n = 29469\cdot85 - N / \left\{ m + \frac{715861}{m} + \frac{0\cdot39012}{m} \right\}^2.$$

The positive term in $1/m$ points to the series being of the D or F type. With this the set for $m=5$ is found to be (O-C = -·3).

$$\begin{array}{rcl}
 (2)26112\cdot25(-4\delta) = \dots 19\cdot84 & & \\
 (\delta_1)(8)26130\cdot61 = \dots 19\cdot85 & \left. \begin{array}{l} \} 26119\cdot84 \quad 29471\cdot12 \quad (2)32822\cdot40 \\ \} \end{array} \right\} & \mathbf{3516\cdot13} \\
 & \dots & (1)36338\cdot53
 \end{array}$$

For $m=2$, R_1 comes into the ultra red, but the others are indicated, viz. :

$$\begin{array}{rcl}
 [14815\cdot91] & 29469\cdot60 & (44123\cdot29) = (1n)44130\cdot82(2\delta_1) \\
 \mathbf{3815\cdot56} & & \mathbf{3814\cdot20} \\
 (2n)18638\cdot98(-2\delta_1) = (18631\cdot47) & 33284\cdot48 & (1)47937\cdot49
 \end{array}$$

Any combination lines from these would fall in the ultra red region. There are thus considerable indications in favour of this second explanation, although perhaps not very convincing. Both cannot be correct and one, at least, is therefore spurious. I have inserted the second because it affords warning against relying on a few numerical coincidences, especially where, as in this case, so many of the lines are in crowded positions. At the same time, the second may be possibly the real solution, and the question may be left for solution in the future.

We may make the direct attempt to determine the P series without regard to the 41172, which, as we have seen, cannot

belong to a normal P. We require a doublet with separation 3815, such that the sum of the larger W.N. and 29469 shall show a mantissa within possible reach of $s(1)$. There are only two observed in the region involved, viz.:

(2n)17879.43	(3)17573.91
3816.92	3818.66
(6)21696.35	(6)21392.57

both spark lines not seen in the arc. They are possibly, therefore, both P doublets modified in some way, as is indicated also by the enlarged separations. Since $21696.35 + 29469.85 = 51166.20 = N/\{1.464071\}^2$, the $P(\infty)$ is near a possible $s(1)$. Both the limit 51166 and the line 21696 are near the values given by the $v+c$ linkage in the P' series. The lines given in the following table seem to give at least one set of P series. The pair for $m=2$ are both seen in the arc, but are enhanced in the spark. The formula for P_1 found from the first and second is

$$m = 51166.20 - N / \left\{ m + 978446 - \frac{.049298}{m} \right\}^2.$$

This gives for $m=3$, 44179.44 with $O-C = -.1$. For $m=4$, $n=46719.15$ the nearest observed line being (1n)46703.65.

For the first two orders any P lines would lie in the unobserved ultra violet. For $m=3$ there are seen two which serve for $P(3)$ lines, in which it may be noticed that the means give a larger limit than that assumed, but one in accordance with the enlarged separations observed. A displacement δ_1 in $S(\infty)$ increases ν by 2.17 to 3817.73 and $S(\infty)$ by 10.76. Hence $P(\infty)$ should be 51176.96, which duly appears for $P_2(3)$, $P_2(3)$:—

P.		P.
$m=1 \left\{ \begin{array}{l} (2n)17879.43 \\ (6)21696.35 \end{array} \right.$		Outside observed region.
$m=2 \left\{ \begin{array}{l} (8)37844.09 \\ (6)38595.88 \end{array} \right.$		„ „
$m=3 \left\{ \begin{array}{l} (4n)43892.19 \\ (4n)44181.90 \end{array} \right.$	$\begin{array}{l} 51175.60 + 1.7p \\ 51169.17 + 1.7p \end{array}$	$\begin{array}{l} (3)58459.02 \quad (-81, 123) \\ (4)58156.44 + 3.3p \quad (-200, 57) \end{array}$

The S Series. The $S(2)$ set are quite definitely 13309.98 (corrected from Lehmann's 13312.9 ± 13) and 17125.54, both from their analogous position with the $S(2)$ lines in Cu, Ag

and because the Zeeman pattern for 17125 is that of a S_2 line. It gives with the known $S(\infty)$ a denominator 2.545. We can now proceed in one of two ways, (1) either by using $51166 = P(\infty)$ as $s(1)$ or (2) by looking for a 3815 doublet in the region given by a denominator 3.54. Method (1), however, never gives a formula reproducing well other lines. Here it prophesies a line $S_1(3)$ at 20879. There is only one line in this neighbourhood, viz. (6)20858 already adopted as $D_{22}(2)$ and showing no companion at 3815 ahead. There is, however, in the 3.54 neighbourhood one doublet which satisfies the condition, although their Zeeman patterns, so far as they can be deduced from Hartmann's measures, are indeterminate. They are (3)20776.50 **3815.57** (6)24592.07. The resulting formula for S_1 is

$$n = 29469.85 - N / \left\{ m + .563932 - \frac{.036108}{m} \right\}^2.$$

The lines as indicated through this formula are given in the following table :—

S.	S.
	$m = 2.$
	Change per oun = 4.808.
(4)13309.98	29471.77 (1)45633.56 + 2.08p
3815.56	
(6)17125.54	
	$m = 3.$
	Change per oun = 1.723.
(5)20776.50	29469.44 (38162.38) { (2)38127.63 (-5 δ) = 62.09
3815.57	3815.45 { (5)38191.99 (17 δ_1) = 62.70
(10)24592.07	33284.95 (41977.83) { (4n)41960.21 (-10 δ_1) = 77.40
	{ (1n)41995.45 (10 δ_1) = 78.21
	$m = 4.$
	Change per oun = .814.
.....	
(δ_1)(1)27987.13 = 27974.23	33285.13 (5)38596.04

These wave numbers are 34.61 less than the calculated S_2 , but they give a very exact $\frac{1}{2}(S + S)$ and therefore indicate displaced $s(4)$. A displacement of 42 δ_1 on sequent gives 34.19. O-C = -.05.

$$m=5.$$

Change per oun = .448.

$$(2r)25922\cdot38 \quad O-C=-\cdot66 \quad \dots\dots$$

$$\mathbf{3818\cdot90}$$

$$(1)29741\cdot28 \quad \dots\dots$$

$$m=6.$$

$$(-\delta_1)(1)26310\cdot66 \quad =(26921\cdot42) \quad O-C=-\cdot24$$

$$\mathbf{3813\cdot38} \quad \mathbf{3815\cdot52}$$

$$(-\delta_1)(2r)30724\cdot04 \quad =(30736\cdot94)$$

This case is specially interesting as the observed lines treated as $(\delta_1)S$ give also the separation proper to the limit $(\delta_1)S(\infty)$.

Amongst the results obtained in the foregoing discussion of most importance to the general theory of spectral analysis may be mentioned :—

(1) The existence of a D set corresponding to order $m=1$ far up in the ultra red whose satellite mantissa conforms to the general rule of being a multiple of Δ . Gold therefore does not form an exception, as formerly appeared to be the case.

(2) The indication given of the existence of summation lines for P and S series. The evidence for these lines in [V.] is drawn from D and F series. In general, such lines for S and P will lie far down in the ultra violet, and this is, no doubt, one reason why they have not previously been recognized. The evidence here given must be sustained by further numerical coincidences obtained in other spectra before it is regarded as conclusive, but it is sufficient to render it extremely probable.

(3) The more accurate determination of the oun depending on $81\delta=\Delta=113951-6p$, where $\cdot1p$ angstroms is an observational error. This result gives

$$\delta=1406\cdot802-\cdot074p.$$

Taking the ratio of δ to $(W/100)^2$, where W is the atomic weight, to be $361\cdot75+\cdot05q$, the resulting value of the atomic weight of gold is

$$197\cdot2024-\cdot0052p-\cdot0136q.$$

The University,
Sheffield,

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