

RELATIONS BETWEEN DOUBLETS OF STRIPPED ATOMS IN FIVE PERIODS OF THE PERIODIC TABLE

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ABSTRACT

Principal and diffuse doublets of stripped atoms in five periods of the periodic table from Li I to O VI, Na I to Cl VII, K I to Mn VII, Rb I to Zr IV, and Cs I to Pr V. —Combining the data now available for the one-electron systems of the second, third, fourth, fifth and sixth periods certain regularities are found to exist between the successive elements in each period and between corresponding elements in successive periods. These regularities are found by the application of the regular and irregular doublet laws. For the long periods which involve more penetrating orbits extrapolations of Z_i and s_i (Landé's formula) prove to be better guides in identifying doublets of the higher members of a sequence although extrapolation of s (Sommerfeld's formula) is entirely satisfactory for the sequences in the short periods. Using the former we have been led to correct our previous identifications of the principal doublet of Ce IV. The tighter binding of the d electron over both the s and p electrons starting with Sc III, Yt III, and La III in the three long periods is especially well brought out by the Moseley type of diagram. Evidence is presented to indicate that the unexcited state of Ce IV involves a $5d$ rather than a $4f$ electron. New data are given for V V, Cr VI and La III.

WHEN all of the orbital electrons of an atom of an element, in excess of those possessed by an atom of the rare gas next preceding it in the periodic table, are removed, such an atom is said to be "stripped" of its outer shell of electrons. Emission lines resulting from transitions between energy levels that arise from the return of the first of these "stripped" off electrons are often referred to as spectra of one-electron systems. In such a system the energy levels always have a doublet character. To distinguish from the spectra of lower states of ionization these spectra of one-electron systems are designated, for example, in the third period as Na I, Mg II, Al III, etc.

Paschen¹ and Fowler² identified many lines in the spectra of sodium, magnesium, aluminum, and silicon as belonging to the various series for one-electron systems of these elements. Landé³ was the first to point out the similarity between the first doublet of the principal series of these elements and the regular doublets of the x-ray spectra. This correlation between x-ray spectra and optical spectra led him to the correct assignment of the various k 's and j 's of the x-ray levels K_I , $L_{I,II,III}$, $M_{I,II,III,IV,V}$, etc. Assuming that the selection principle holds for the intra-atomic x-ray levels as well as it does for the optical spectra of the alkalis and the alkaline earths, de Broglie and Dauvillier⁴ pointed out that the $L_{II}L_{III}$ doublet is analogous to the p doublet of the alkalis, and that they therefore have the same azimuthal

¹ Paschen, Ann. d. Physik **71**, 142 (1923).

² Fowler, Proc. Roy. Soc. A**103**, 413 (1923); Phil. Trans. Roy. Soc. **225**, 1 (1925).

³ Landé, Zeits. f. Physik **16**, 394 (1923).

⁴ de Broglie and Dauvillier, Jour. d. Physique et le Radium, [VI] **5**, 1 (1924).

quantum number. Bowen and Millikan⁵ have shown that not only the regular doublet (relativity doublet) law but also the irregular doublet law may be applied to the one-electron systems of the second and third periods. With the aid of these laws they have been able to identify lines in "hot-spark" spectra of one-electron systems from Li I to O VI and from Na I to Cl VII. By applying these same doublet laws to the one-electron systems in the fourth fifth and sixth periods starting with K I and Ca II, Rb I and Sr II, and Cs I and Ba II we have been able⁶ to identify the first pair of lines of the principal series for elements as far as Mn VII, Zr IV and Pr V, and also certain lines belonging to the diffuse series.

The values of $(\Delta\nu/\text{const.})^{1/4}$ and of s (*screening constant*) given in columns 3 and 4 of Table I have been determined by Bowen and Millikan and the authors from Sommerfeld's formula for regular doublets.⁷

For the sake of comparison we have computed values of Z_i and s_i columns 5 and 6 of Table I, from Landé's formula for penetrating orbits,⁸

$$\Delta\nu = \frac{R\alpha^2(Z-s_a)^2(Z-s_i)^2}{n^3k(k-1)} = \frac{R\alpha^2Z_a^2Z_i^2}{n^3k(k-1)}.$$

Although it is doubtful what physical significance can be attached to these quantities, (s , Z_i , and s_i), they served admirably as guides in predicting approximately the principal doublet separations and together with the irregular doublet law made it possible to identify with certainty the lines belonging to these doublets.

For the less penetrating orbits of the short periods the extrapolations from values of s were entirely satisfactory, although it is evident that nearly, if not equally, as satisfactory results might have been obtained by extrapolating from values of Z_i or s_i . However, for the more penetrating orbits, as for example in the sixth period, the latter extrapolation is a more reliable guide. The value of s as previously reported by us⁶ for Ce IV showed no irregularity in the progression of this screening constant for the caesium-like sequence, and consequently we felt that our identifications for the Ce IV doublet were correct. Recently in computing the values of Z_i it was suspected that the frequency separation of this doublet was not large enough as the curve for Z_i for this sequence exhibited a marked change in slope between La III and Ce IV. Since we had selected these lines from data given by Exner and Haschek and by Eder and Valenta for the spark spectrum of cerium, photographs were taken in this laboratory using a high-voltage spark between graphite electrodes cored with cerium nitrate. Plates taken in this way reveal a large number of lines nearly all of which belong to the first and second spark spectrum. There are, however, on the plates, which cover a range of about

⁵ Bowen and Millikan, Phys. Rev. **24**, 209 (1924); **25**, 295 (1925); **26**, 150 (1925); **27**, 144 (1926).

⁶ Gibbs and White, Proc. Nat. Acad. of Sci. **12**, 448, 551, 588, 675 (1926); Phys. Rev. **29**, 359 (1926).

⁷ Sommerfeld, *Atombau*, 4th German Ed. p. 420.

⁸ Landé, Zeits. f. Physik **25**, 48 (1924).

600A, two lines appearing to have come only from the tips of each electrode, ($\lambda_{vac} = 2779.07$ and $\lambda_{vac} = 2457.59$) that stand out from all the rest. This type of *short line*, as is well known, is characteristic of high states of ionization. Hence we conclude that these two lines, constitute the $6^2S_1 - 6^2P_{1,2}$ doublet of Ce IV. Neither of these lines is listed by Exner and Haschek or by Eder and Valenta. The frequency separation, as thus definitely identified, yields a value of 56.05 for Z_i which is much more consistent with those of the preceding elements of this sequence, than 55.52 obtained from our previous identifications. See Table I.

TABLE I. *Regular doublet law.*

Atom	$\Delta\nu$	$(\Delta\nu/\text{const})^{1/4}$	s	Z_i	s_i
Second period ($2^2P_1 - 2^2P_2$)					
Li I	0.338	0.981	2.02	0.93	2.07
Be II	6.61	2.06	1.94	2.06	1.94
B III	34.4	3.12	1.88	3.14	1.86
C IV	107.4	4.14	1.86	4.18	1.82
N V	259.1	5.16	1.84	5.21	1.79
O VI	533.8	6.18	1.82	6.24	1.76
Third period ($3^2P_1 - 3^2P_2$)					
Na I	17.18	3.55	7.45	7.66	3.34
Mg II	91.55	5.39	6.61	9.56	2.44
Al III	234.0	6.82	6.18	10.91	2.09
Si IV	461.8	8.08	5.92	12.08	1.92
P V	794.8	9.26	5.74	13.15	1.85
S VI	1267.1	10.40	5.60	14.23	1.77
Cl VII	1889.5	11.50	5.50	15.29	1.71
Fourth period ($4^2P_1 - 4^2P_2$)					
K I	57.7	5.96	13.04	14.85	4.15
Ca II	222.8	8.36	11.64	17.24	2.76
Sc III	474.3	10.09	10.91	18.29	2.71
Ti IV	817.5	11.57	10.43	18.99	3.01
V V	1264.7	12.91	10.09	19.54	3.46
Cr VI	1821.5	14.15	9.85	19.98	4.02
Mn VII	2464.7	15.25	9.75	20.19	4.81
Fifth period ($5^2P_1 - 5^2P_2$)					
Rb I	237.60	10.04	26.96	31.23	5.77
Sr II	801.46	13.60	24.40	34.81	3.19
Yt III	1553.7	16.05	22.95	36.29	2.71
Zr IV	2484.9	18.05	21.95	37.10	2.90
Sixth period ($6^2P_1 - 6^2P_2$)					
Cs I	554.0	14.23	40.77	49.55	5.45
Ba II	1690.9	18.81	37.19	53.88	2.12
La III	3095.7	21.76	35.24	55.52	1.48
Ce IV	4707.0	24.30	33.70	56.05	1.95

The line previously selected by us⁶ for Pr V at $\lambda = 2295.4$, listed by Exner and Haschek as a spark line of praseodymium, is in all probability a carbon line. We have taken several photographs, using first graphite and then tin electrodes cored with praseodymium oxalate and with praseodymium chloride, but with unsatisfactory results. The lines we have measured for the principal doublet are very weak and rather uncertain and therefore they have not been included in the tables.

How closely the irregular doublet law (i.e. the linear progression of frequency with atomic number for transitions involving no change in total quantum number) is followed, is shown in Fig. 1 for all five periods. It is therefore possible to use the irregular doublet law to predict the approximate wave-numbers, i.e. the location in the spectrum, for succeeding elements in any sequence.

In computing term values Bowen and Millikan utilized the hydrogenic nature of circular orbits, a procedure which in general is suitable for the lighter elements. In the long periods, however, we have used a method sug-

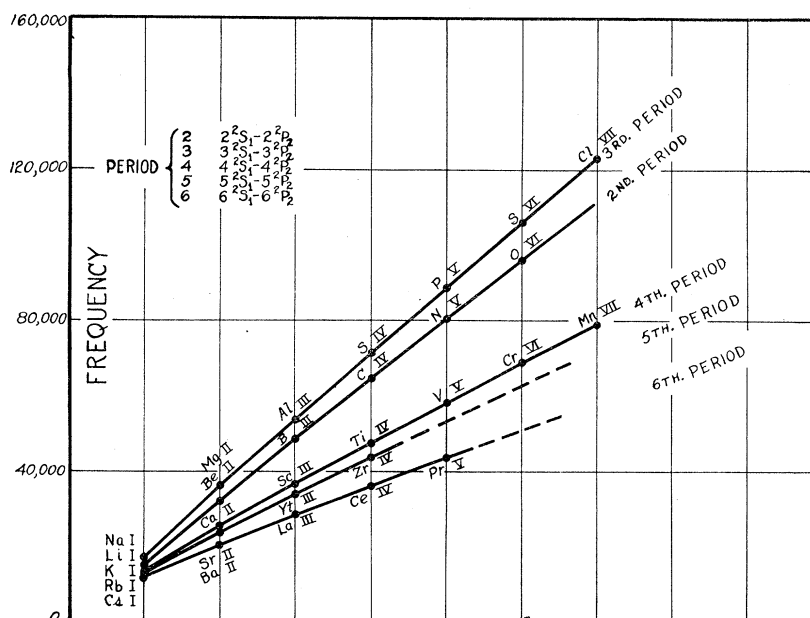


Fig. 1. Linear progression of frequency with atomic number (irregular doublet law).

gested by Hartree⁹ for penetrating orbits which yields results that are fairly accurate. Term values computed in this way differ very little from those obtained by the ordinary methods that can be applied when several members of a series are known.

From Fig. 2 it may be seen that term values of any sequence when plotted on a Moseley diagram show very nearly a straight line relation. A consequence of the irregular doublet law is that $\Delta(\nu/R)^{1/2}$ for any sequence should be independent of atomic number. As shown in Fig. 2 this relation is especially well followed for the *S-P* levels in all five periods. Although there is a marked change in the initial slope of the 2D_3 lines between the third and fourth periods there is a gradual increase in the downward curvature of the line itself in going from one period to the next. The 2F_4 lines also show this increase in curvature in going from one sequence to the next but instead of

⁹ Hartree, Roy. Soc. Proc. A106, 552 (1924).

TABLE II. *Wave-lengths and frequencies of lines not previously reported.*

λ	ν	Diff.	Transitions
Vanadium V			
481.657	207617}	620	$3^2D_2-4^2P_2$
483.099	206997}	1270	$3^2D_3-4^2P_2$
484.621	206347}		$3^2D_2-4^2P_1$
1716.74	58250}	1265	$4^2S_1-4^2P_1$
1680.26	59515}		$4^2S_1-4^2P_2$
286.36	349211}	634	$3^2D_2-4^2F_3$
286.88?	348577}		$3^2D_3-4^2F_4$
820.89	121819}	1267	$4^2P_1-5^2S_1$
829.52	120552}		$4^2P_2-5^2S_1$
506.11	197585}	1268	$4^2P_1-6^2S_1$
509.38	196317}		$4^2P_2-6^2S_1$
Chromium VI			
335.20	298311}	957	$3^2D_2-4^2P_2$
336.30	297354}	1822	$3^2D_3-4^2P_2$
337.28	296489}		$3^2D_2-4^2P_1$
Lanthanum III			
2216.83	45109.4}	1602.8	$5^2D_2-6^2P_2$
2298.50	43506.6}	3094.9	$5^2D_3-6^2P_2$
2380.13	42014.5}		$5^2D_2-6^2P_1$

Wave-lengths and frequencies of lines not previously reported are given in Table II, for vanadium V, chromium VI, and lanthanum III.

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