

THE  
PHYSICAL REVIEW

---

THE SERIES SPECTRA OF TWO-VALENCE-ELECTRON  
ATOMS OF PHOSPHORUS ( $P_{IV}$ ), SULPHUR ( $S_V$ ),  
AND CHLORINE ( $Cl_{VI}$ )

BY I. S. BOWEN AND R. A. MILLIKAN

ABSTRACT

**Series spectra of two-valence-electron atoms of P, S, and Cl.**—In a previous paper,<sup>1</sup> the regular and irregular x-ray doublet laws were used to predict the spectra of stripped atoms, that is, atoms having only one valence electron. The method has now been applied to the spectra of two-electron atoms, since, although these spectra consist of triplets or singlets instead of doublets, the same laws apply to them. In this way 23 lines of  $P_{IV}$  have been identified, 17 lines of  $S_V$  and 6 lines of  $Cl_{VI}$ . With the help of the Ritz equation, 12 term values of  $P_{IV}$  and 8 of  $S_V$  were also determined. In a table are collected all known term values for two-electron atoms of Mg, Al, Si, P and S.

**Physical significance of the x-ray irregular doublet law.**—Spectral lines which give parallel curves on a Moseley diagram  $\sqrt{\nu/R}$  plotted as a function of atomic number) and which therefore follow this law, are produced by jumps between orbits of the same total quantum number but with different screening constants.

I. INTRODUCTION

THE present paper is merely a further illustration of the fecundity of the method for the identification of spectral lines which we have recently brought to light. This method grows out of the discovery that both the regular and the irregular x-ray doublet laws are also applicable throughout the whole field of optics<sup>1</sup> so long as a series of atoms of like electronic structure but varying effective nuclear charge is under observation. The irregular doublet law makes possible the prediction of the precise position of a particular line, while the regular doublet law foretells the character of its fine structure, i.e. the frequency separation of its components.

We have heretofore used the irregular doublet law only to predict the positions of lines belonging to a stripped-atom series, i.e. the series constituted by the stripped atoms of Li, Be, B, C, N, or of Na, Mg, Al,

<sup>1</sup> Bowen and Millikan Phys. Rev. **24**, 209 (1924)

Si, P, S, Cl. Such a series may be called a one-electron series since it has but one valence electron, which radiates as it jumps between the series of levels characteristic of the second quantum state of the lithium group or the third quantum state of the sodium group.

In the present paper we apply the same method to a two-electron system (one having two electrons in its outer shell). The irregular doublet law is here applicable precisely as in the case of the one-electron system. But while a one-electron system is characterized by lines the fine structure of which is a doublet, a two-electron system is characterized by a fine structure consisting of either triplets or singlets. Since, however, we have shown that the regular or relativity doublet law holds for triplets as well as for doublets, it is possible to predict with its aid the frequency separation of any two of the three lines of a triplet, and we have in this paper chosen for this purpose the two extreme lines, in this respect changing the procedure followed in a preceding paper in which we worked with the two more widely separated adjacent lines instead of the outside ones. In other words, we are now using the  $p_1p_3$  separation where we before used the  $p_1p_2$  separation.

## 2. SIGNIFICANCE OF THE IRREGULAR DOUBLET LAW

Before applying the irregular and regular doublet laws to the actual identification of lines produced by two-electron systems, it will be of interest to present the proof that whenever the frequency of a given spectral line is found to progress linearly with atomic number, i.e. to follow the irregular doublet law, this line must be produced by a jump between orbits of the same total quantum number.

The simple Moseley law

$$\frac{\nu}{R} = \left( \frac{Z - \sigma}{n} \right)^2$$

shows that when there is a jump between two orbits of different screening constants  $\sigma_1$  and  $\sigma_2$  and of total quantum numbers  $n_1$  and  $n_2$  the frequency  $\nu'$  produced by a jump between these orbits is given by the difference between two expressions of the foregoing form, viz.

$$\frac{\nu'}{R} = \left( \frac{Z - \sigma_1}{n_1} \right)^2 - \left( \frac{Z - \sigma_2}{n_2} \right)^2$$

or

$$\frac{\nu'}{R} = \frac{(n_2^2 - n_1^2)Z^2 - 2(n_2^2\sigma_1 - n_1^2\sigma_2)Z + n_2^2\sigma_1^2 - n_1^2\sigma_2^2}{n_1^2 n_2^2}.$$

This equation shows at once that if  $\nu'$  is to vary linearly with  $Z$  the coefficient of  $Z^2$  in the first term must be zero, i.e. that  $n_2$  must equal  $n_1$ .

If  $n_2$  is not equal to  $n_1$  the first term introduces a variation of  $\nu'$  with  $Z^2$ . In other words, the irregular doublet law signifies that there is a difference in screening constant between orbits of the same total quantum number.

Since the irregular doublet law also is equivalent to parallelism between the lines on the Moseley diagram corresponding to the two sets of levels the differences between which determine the irregular doublet, it follows that whenever such parallelism is found the levels between which it exists correspond in every case to the same total quantum number.

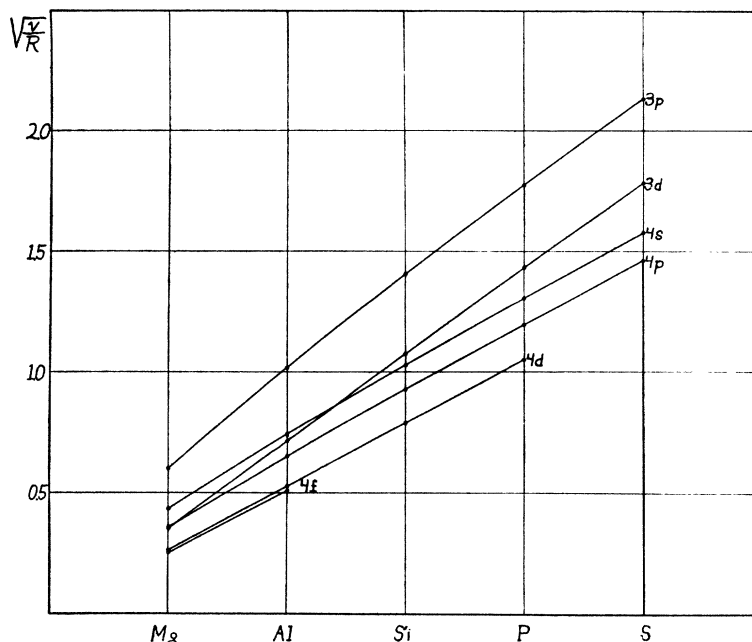


Fig. 1. Series spectra of two-valence electron atoms from  $Mg_I$  to  $S_V$ .

All the relations in this section are nicely illustrated by the Moseley diagram shown in Fig. 1, in which all the parallel lines have the same total quantum number while those corresponding to different total quantum numbers have definitely different slopes.

### 3. LINES AND TERM VALUES FOR $P_{IV}$ , $S_V$ , AND $Cl_{VI}$

With the aid of the irregular and regular doublet laws the lines and term values for  $P_{IV}$ ,  $S_V$ , and  $Cl_{VI}$  have been obtained as follows.

According to Fowler<sup>2</sup> the first term of the diffuse series of  $Mg_I$  has a wave-length at  $\lambda=3838.29$  and a frequency in vacuum of 26045.9.

<sup>2</sup>Fowler, Series in Line Spectra, p. 116.

According to Paschen<sup>3</sup> the corresponding line of Al<sub>II</sub> has a wave-length  $\lambda = 1724.95$  and a frequency 57972.7. According to Fowler<sup>4</sup> the corresponding line of Si<sub>III</sub> has a wave-length  $\lambda = 1113.76$ , which corresponds to the frequency 89786.0. These three frequencies constitute an approximately linear progression (irregular doublet law) as shown in Table I,

TABLE I  
*Irregular doublets*

	$3p_1-3d$ $\nu$	Diff.	$4s-4p_3$ $\nu$	Diff.	
Mg <sub>I</sub>	26045.9		Mg <sub>I</sub>	6650.4	
Al <sub>II</sub>	57972.7	31926.8	Al <sub>II</sub>	14153.13	7502.73
Si <sub>III</sub>	89786.0	31813.3	Si <sub>III</sub>	21853.5	7700.37
P <sub>IV</sub>	120779.9	30993.9	P <sub>IV</sub>	29655.5	7802.0
S <sub>V</sub>	150797.7	30017.8	S <sub>V</sub>	37506.4	7850.9
	$3S-3P$ $\nu$	Diff.	$4p_1-4d$ $\nu$	Diff.	
Mg <sub>I</sub>	35051.4		Mg <sub>I</sub>	6340.2	
Al <sub>II</sub>	59845.1	24793.7	Al <sub>II</sub>	16012.62	9672.42
Si <sub>III</sub>	82878.9	23033.8	Si <sub>III</sub>	26262.8	10250.18
P <sub>IV</sub>	105190.4	22311.5	P <sub>IV</sub>	36486.9	10224.1
S <sub>V</sub>	127144.0	21953.6			
Cl <sub>VI</sub>	148949.2	21805.2			

which should yield a frequency difference between Si<sub>III</sub> and P<sub>IV</sub> of about 31000 (see Table I), and this difference locates the first term of the diffuse series of P<sub>IV</sub> at a frequency value of about 121,000, i.e., at wave-length  $\lambda = 826$  A. We should then find a strong phosphorus triplet

TABLE II  
*Regular doublets*

	$3p_3-3p_1$ $\Delta\nu$	$Z-s$	$s$
Mg <sub>I</sub>	60.81	4.870	7.130
Al <sub>II</sub>	187.3	6.451	6.549
Si <sub>III</sub>	394.	7.769	6.231
P <sub>IV</sub>	696.3	8.958	6.042
S <sub>V</sub>	1128.1	10.106	5.894
Cl <sub>VI</sub>	1720.1	11.230	5.770

<sup>3</sup> Paschen, Ann. der Physik **71**, 544 (1923)

<sup>4</sup> Fowler, Nature **113**, 802 (1924)

at about this wave-length. Our plates revealed just such a strong triplet at  $\lambda\lambda 823.21, 824.76, \text{ and } 827.95$  (see Table III).

The regular doublet law (Table II) gives a progression of the separations of the most distant components which can be computed from the

TABLE III  
Series lines for P<sub>IV</sub>

Int.	$\lambda$ (I. A., vac.)	$\nu$	$\Delta\nu_p$	$\Delta\nu_d$	Term values
2	631.74	158293.0			$3p_1-4s$ 4s 187687.9
5	823.21	121476.4			$3p_3-3d$ 5s 105479.2
6	824.76	121247.8	> 228.6		$3p_2-3d$
6	827.95	120779.9	> 467.9		$3p_1-3d$ 3p <sub>1</sub> 345964.9 3p <sub>2</sub> 346432.8 3p <sub>3</sub> 346661.4
4	1025.58	97506.0			
4	1028.13	97264.2			
4	1030.53	97037.1			$pp'$ group 4p <sub>1</sub> 157825.3
4	1033.14	96792.4			4p <sub>2</sub> 157973.7
4	1035.54	96567.9			4p <sub>3</sub> 158032.4
3	1484.55	67360.5			$3d-4p_1$ 3d 225185.0
3	1487.85	67210.9	> 149.6		$3d-4p_2$ 4d <sub>1</sub> 121330.7
2	1489.16	67152.1	> 58.8		4d <sub>2</sub> 121338.4 4d <sub>3</sub> 121344.0
0	1904.97	52494.3			$4p_2-5s$
0	1910.35	52346.4	> 147.9		$4p_1-5s$
4	2725.67	36688.2			$4p_3-4d_3$
4	2729.61	36635.3	58.2		$4p_2-4d_2$
3	2730.00	36630.0	> 5.3		$4p_2-4d_3$
5	2740.13	36494.6			$4p_1-4d_1$
3	2740.71	36486.9	148.4 > 7.7		$4p_1-4d_2$
*		36481.6	> 5.3		
6	3348.67	29862.6			$4s-4p_1$
6	3365.39	29714.2	> 148.4		$4s-4p_2$
5	3372.06	29655.5	> 58.7		$4s-4p_3$
10	950.66	105190.4			$3S-3P$

\* Not observed.

values of  $s$  for Mg<sub>I</sub> Al<sub>II</sub> Si<sub>III</sub> in the last column, at about  $\Delta\nu=700$ , correct to about  $\pm 20$ . The observed  $\Delta\nu$  is 696.5, in altogether satisfactory agreement with the prediction.

The location of S<sub>V</sub> could now be predicted from the sequence of differences in Table I, the P<sub>V</sub>-S<sub>IV</sub> difference being at once seen to be

necessarily about 30,000 and therefore the frequency of  $S_V$  to be 150,800, with an uncertainty of say 200, which corresponds to a wave-length uncertainty of 1 angstrom. This definitely identified our strong line at  $\lambda 663.14$ ,  $\nu = 150797.7$  as the  $3p_1-3d$  line of  $S_V$ . The regular doublet law of Table II then predicted the separation of the extreme components of the  $3p-3d$  triplet shown in Table IV, with an uncertainty of  $\pm 20$  frequency units (0.1A).

TABLE IV  
Series lines for  $S_V$

Int.	$\lambda$ (I. A. vac.)	$\nu$	$\Delta\nu$		Term values	
1	437.37	228639.4		$3p_3-4s$	4s	273075.0
			427.9			
1	438.19	228211.5		$3p_2-4s$		
			757.8			
1	439.65	227453.7		$3p_1-4s$	$3p_1$	500497.7
					$3p_2$	501252.4
					$3p_3$	501618.2
3	658.25	151918.2		$3p_3-3d$		
			365.8			
4	659.84	151552.4		$3p_2-3d$	$4p_1$	235191.6
			754.7		$4p_2$	235480.7
4	663.14	150797.7		$3p_1-3d$	$4p_3$	235568.6
4	849.25	117751.1			3d	349700.0
4	852.19	117345.0				
5	854.81	116985.6		$pp'$ group		
4	857.83	116573.2				
4	860.46	116216.9				
1	873.20	114521.3		$3d-4p_1$		
			321.7			
1	875.66	114199.6		$3d-4p_2$		
4	2639.68	37883.4		$4s-4p_1$		
			289.1			
2	2659.98	37594.3		$4s-4p_2$		
			87.9			
1	2666.21	37506.4		$4s-4p_3$		
6	786.51	127144.0		$3S-3P$		

The corresponding  $Cl_{VI}$  line should fall at a frequency of 180,000 ( $\lambda 555$  A), but this triplet should be of weak intensity and this particular region is so studded with Cl and O lines, some of them strong, that certain identification upon our plates is practically hopeless.

These  $3p-3d$  lines were determined for  $P_{IV}$  by measurement in the 1st, 2nd, 4th, and 7th orders, and for  $S_V$  in the 1st, 2nd, 3rd, 8th, and 9th orders.

The location of the  $4p_1-4d$  and  $4s-4p_3$  lines for  $P_{IV}$  and  $S_V$  is made in precisely the same way with the aid of the irregular doublet law for  $4p_1-4d$  and  $4s-4p_3$ , as shown in Table I. In this table the  $4p_1-4d$  lines are taken from Fowler<sup>2</sup> for  $Mg_I$  and from Paschen<sup>3</sup> for  $Al_{II}$ . This gave

the first difference in the  $4p_1-4d$  sequence of Table I. From this difference we were able to identify the triplet  $\lambda\lambda 3791.13, 3796.18, 3806.60$  given by Sawyer and Paton<sup>5</sup> as the  $4p_1-4d$  Si<sub>III</sub> triplet, which when reduced to vacuum gives the frequency 26262.8 shown in Table I.

The  $4s-4p_3$  term for Si<sub>III</sub> was found in the same way to correspond to the Sawyer-Paton triplet  $\lambda_{air}=4552.50, 4567.66, 4574.66$ , which yields the vacuum frequency 21853.5 shown in the table.

The addition to this frequency of the nearly constant difference 7800 fixes unambiguously our strong line  $\nu=29655.5$  as  $4s-4p_3$  for P<sub>IV</sub> (see Table III), and a similar procedure identifies at once the strong sulphur triplet shown in Table IV as  $4s-4p$  for S<sub>V</sub>, and also fixes the third member of this triplet  $\lambda 2666.21, \nu=37506.4$ , as  $4s-4p_3$ . The consideration of the intensities of these particular triplet lines combined with the irregular

TABLE V  
Series lines for Cl<sub>VI</sub>

Int.	$\lambda$ (I. A., vac.)	$\nu$	
3	724.13	138096.8	
3	727.54	137449.5	
4	730.31	136928.2	$pp'$ group
3	733.89	136260.2	
3	736.76	135729.4	
4	671.37	148949.2	$3S-3P$

doublet law is quite sufficient for their identification, though they may also be checked with the aid of the regular doublet law, as used above with the  $3p_3-3p_1$  separations (Table II). It is only in the case of the S<sub>V</sub> triplet here considered that certain irregularities in the progressions raise in our minds a little question as to the certainty of the identifications.

The exceedingly strong  $3S-3P$  singlet lines in Tables III, IV, and V are indubitably fixed by their intensities and the exceedingly uniform progression that the irregular doublet law exhibits for these lines as shown in Table I.

Thus far the irregular doublet law has been our most certain guide, but it fails us entirely for the identification of the  $3p-4s$  triplets because these represent jumps between levels of different total quantum numbers and such jumps have been shown above not to follow this law. We actually identified these lines easily in S<sub>V</sub> by the agreement of their frequency differences with those of the  $3p-3d$  triplet, for  $3p-4s$  should be the next strongest line to  $3p-3d$ , having the same frequency difference.

<sup>5</sup> Sawyer and Paton, *Astrophys. J.* 57, 290 (1923)

In the case of  $P_{IV}$  only one component of the  $3p-4s$  line is shown because the others are obscured on our plates by other strong lines. This was, however, the only unidentified phosphorus line below 750 Å and further its position could be predicted within two or three angstroms by comparisons of the sequence of  $3p_1-4s$  lines in stripped atoms with the corresponding lines in two-valence-electron atoms.

The  $4p-5s$  lines in  $P_{IV}$  were identified by a precisely similar comparison aided by the fact that the separation here was of necessity the same as in  $4s-4p$ .

The  $3d-4p$  triplet has its position exactly predicted by the fact that  $(3d-4p) + (3p-3d) = (3p-4s) + (4s-4p)$  and all these except the first are already found.

TABLE VI  
*Comparison of term values*

$N =$		3	4	5
$R/N^2 =$		12192.78	6858.44	4389.40
<i>s</i>	Mg/1		20474.5	9799.3
	Al/4		15147.3	7942.64
	Si/9		12962.5	7096.0
	P/16		11730.5	6592.5
	S/25		10923.0	
<i>p<sub>1</sub></i>	Mg/1	39760.5	13820.0	7419.0
	Al/4	28570.3	11598.17	6535.34
	Si/9	24097.7	10522.5	
	P/16	21622.8	9864.1	
	S/25	20019.9	9407.7	
<i>d</i>	Mg/1	13714.7	7479.5	4704.1
	Al/4	14078.41	7595.02	4760.18
	Si/9	14121.4	7604.4	
	P/16	14074.1	7583.2	
	S/25	13988.0		
<i>f</i>	Mg/1		6994.8	4469.0
	Al/4		7109.90	4603.27
<i>f'</i>	Al/4			4419.45

The  $pp'$  group of lines that appear in Table III, IV, and V have been found with the indicated wave-lengths in the extreme ultraviolet. Precisely similar  $pp'$  groups have been previously found by Paschen and Götze<sup>6</sup> in  $Mg_I$  and  $Al_{II}$  and they were therefore to be expected in  $Si_{III}$ ,  $P_{IV}$ ,  $S_V$ , and  $Cl_{VI}$ , since these are all atoms of the same electronic structure.

In the case of the spectra of stripped atoms such as those with which we have been dealing in preceding papers, we have been able to start

<sup>6</sup> Paschen-Götze, *Seriengesetze der Linienspectren*, Julius Springer (1922)



with a circular orbit remote enough from the nucleus so that its term value could be computed at once from the corresponding term value in hydrogen. The identification and measurement of the lines then fixed all the other reported term-values. In the present case the  $f$  and  $f'$  terms were not in our data and resort had therefore to be made to the usual method of finding the absolute values of some particular terms through the aid of the Ritz equation.<sup>7</sup> The foregoing series of lines then gave all the rest of the term values recorded in Tables III and IV.

For convenience of reference and comparison we have exhibited in Table VI all of our series terms for these two-valence-electron atoms in the form adopted in a preceding article for our series of stripped atoms. As indicated, the actual term values have been divided for the purposes of this table by the square of the numbers 1, 2, 3, 4, 5. The  $3p_1$  value for silicon in this table was taken from Fowler's computation.<sup>4</sup> The other silicon values were obtained from this and our own data combined with that of Sawyer and Paton<sup>5</sup> mentioned above. In the case of phosphorus, Table III, the lines above 2000 Å were taken from Geuter.<sup>8</sup>

As will be seen from Fig. 1, the spectra of these two-valence-electron atoms follow the Moseley law quite as well as we have before shown those of the stripped atoms to do.

NORMAN BRIDGE LABORATORY OF PHYSICS,  
CALIFORNIA INSTITUTE OF TECHNOLOGY,  
PASADENA.  
February 5, 1925

<sup>7</sup> Fowler, Report on Series in Line Spectra.

<sup>8</sup> Kayser, *Spektroskopie*, vol. VI, p. 246.