THE SERIES SPECTRA OF THREE-VALENCE-ELECTRON ATOMS OF PHOSPHORUS (P_{III}), SULPHUR (S_{IV}), AND CHLORINE (Cl_V)

By R. A. Millikan and I. S. Bowen

Abstract

Series spectra of three-valence-electron atoms of P, S and Cl.—By the methods of the preceding paper, 21 lines of P_{III} have been identified, 20 lines of S_{IV} and 10 lines of Cl_V, including a pp' group for each; also 10 term values of P_{III} have been determined and 10 term values of S_{IV}, including the x level.

Screening constants for one, two, and three valence electron systems are collected in a table for Na to Cl. The values increase regularly with the number of valence electrons and decrease with the atomic number, the difference decreasing as the atomic number increases.

HAVING obtained the characteristic lines and term values for stripped or one-valence-electron atoms from Na_I through Cl_{VII}, and then for two-valence-electron atoms from Mg_I through Cl_{VI}, we now apply the same methods to three-valence-electron atoms and seek the series lines of the atoms Al_I through Cl_V. These lines, according to Sommerfeld's rule, must be doublets.

As heretofore, the first predictions grow out of the irregular doublet law shown in Table I, in which both Al_I and Si_{II} are obtained from

TABLE I

Irregular doublets

	$3p_1-3d$ ν	Diff.		$4s-4p_2$ ν	Diff.
Al_I	32324.69	46731.31	Al_I	7601.57	8090.03
Si_{II}	79056.0	37265.1	Si_{II}	15691.6	7849.6
P_{III}	116321.1	34868.1	P_{III}	23541.2	8524.0
S_{IV}	151189.2	33200.4	S_{IV}	32065.2	
Cl_V	184389.6				

	$4p_1-4d$ ν	Diff.
Al_I	5967.76	13804.84
Si_{II}	19772.6	11143.7
P_{III}	30916.3	10757.5
S_{IV}	41673.8	

Fowler.[1,2] The difference between these two frequencies as shown in Table I fixes the position of P_{III} at 850A within say 50A. This falls into the region of the strongest phosphorus lines found, namely, the lines λ855.65 and λ859.69, and the separation of these two lines is seen in Table II to fit nicely into the progression exhibited by the regular doublet

TABLE II

Series lines of P_{III}

Int.	λ(I.A., vac)	ν	Δν		*Term values*	
2	848.65	117834.2		$3p_2-4s$	$4s$	125497.8
			559.4			
3	852.70	117274.8		$3p_1-4s$	$5s$	67292.8
4	855.65	116870.6		$3p_2-3d$		
			549.5		$3p_1$	242772.5
6	859.69	116321.1		$3p_1-3d$	$3p_2$	243332.1
4	913.99	109410.7			$4p_1$	101821.2
5	917.14	109035.2	559.8		$4p_2$	101957.8
5	918.69	108850.9	559.2	pp' group		
5	921.86	108476.0				
					$3d_1$	126450.0
5	998.03	100197.1		$3p_2-x$	$3d_2$	126461.4
			559.7			
5	1003.64	99637.4		$3p_1-x$	$4d$	70904.5
1	2420.47	41314.3		$x-4p_1$		
			136.4		x	143135.1
1	2428.49	41177.9		$x-4p_2$		
5	2884.75	34665.0		$4p_2-5s$		
			136.6			
5	2896.17	34528.4		$4p_1-5s$		
6	3220.23	31053.7		$4p_2-4d$		
			137.4			
6	3234.54	30916.3		$4p_1-4d$		
4	4058.53	24639.5		$3d_2-4p_1$		
6	4060.41	24628.1	136.8	$3d_1-4p_1$		
7	4081.18	24502.7		$3d_2-4p_2$		
7	4223.34	23677.9		$4s-4p_1$		
			136.7			
7	4247.87	23541.2		$4s-4p_2$		

law (see Table V). The corresponding line in sulphur is fixed with certainty as the strong doublet λ657.34, λ661.42. Quite similarly from Table I the corresponding line in chlorine is fixed at λ538.08 and λ542.33.

The next doublet to be expected with the same frequency separation as $3p-3d$ is $3p-4s$. The appearance of this separation in the doublet at

[1] Fowler, Report on Series in Line Spectra, 156—(Al)

[2] Fowler Nature **113**, 802 (1924)—(Si)

λ848.65, λ852.70 for P_{III} suggests such an identification, and further its position was predicted by comparison of the $3p-4s$ lines in two-valence-electron atoms. This also located the $3p_2-4s$ line shown in S_{IV}, the other component of which is obscured by the complex oxygen line at 554 A (see Table III).

Just as the pp' group in the two-valence-electron system was early recognized by its striking structure as well as through showing the characteristic $3p$ separation, so here the same two characteristics identified the pp' group listed under P_{III}, S_{IV}, and Cl_V (Tables II, III, and IV).

This same separation identified the $3p-x$ doublet for P_{III} and S_{IV}, the level from which the electron jumps being here denoted x because it cannot be fitted into either the s or the d series of levels. Fowler found

TABLE III

Series lines of S_{IV}

Int.	λ(I.A., vac)	ν	Δν		Term values	
2	551.17	181432.2		$3p_2-4s$	$4s$	200109.2
5	657.34	152127.8	938.6	$3p_2-3d$	$5s$	110531.0
6	661.42	151189.2		$3p_1-3d$		
					$3p_1$	380591.2
5	744.92	134242.8			$3p_2$	381541.4
5	748.40	133618.6	950.5			
5	750.23	133292.3	950.0	pp' group	$4p_1$	167824.0
5	753.76	132668.6			$4p_2$	168034.0
4	809.69	123503.9	950.1	$3p_2-x$	$3d_1$	229400.0
5	815.97	122553.8		$3p_1-x$	$3d_2$	229414.3
2	1108.36	90223.1	206.2	$x-4p_1$	$4d$	126151.6
2	1110.90	90016.9		$x-4p_2$	x	258037.5
0	1623.62	61590.7		$3d_2-4p_1$		
2	1624.00	61576.4	210.7	$3d_1-4p_1$		
2	1629.20	61380.0		$3d_2-4p_2$		
0	1739.03	57503.3	210.5	$4p_2-5s$		
1	1745.42	57292.8		$4p_1-5s$		
2	2387.72	41881.0	207.2	$4p_2-4d$		
3	2399.59	41673.8		$4p_1-4d$		
5	3098.36	32275.1	209.9	$4s-4p_1$		
3	3118.65	32065.2		$4s-4p_2$		

these x levels in Si_{II} and C_{II}, which are also three-valence-electron systems.

Similarly, the irregular doublet law of Table I fixed the positions of $4s-4p_2$ and $4p_1-4d$ lines and the equality of their doublet separations confirmed the identification.

The $3d-4p$ lines were obtained from the equation

$$(3p-3d)+(3d-4p)=(3p-4s)+(4s-4p),$$

and the $x-4p$ lines from

$$(3p-x)+(x-4p)=(3p-3d)+(3d-4p).$$

TABLE IV

Series lines of Cl_V

Int.	λ(I.A., vac.)	ν	Δν	
3	538.08	185846.0		$3p_2-3d$
			1456.4	
4	542.33	184389.6		$3p_1-3d$
2	564.30	177210.7		
2	565.47	176844.0	1507.0	
2	569.14	175703.7	1500.8	pp' group
2	570.31	175343.2		
6	629.33	158899.1		
6	633.18	157933.0	1495.6	
6	635.31	157403.5	1497.3	pp' group
5	639.24	156435.7		

The identification is again confirmed by the fact that these doublets all show the $4p$ separation (see Tables II and III). The $4p-5s$ doublet was identified just as was the $3p-4s$ doublet. In the case of S_{IV} there is a very slight uncertainty about the correct identification of $4p-5s$ because of the existence of two pairs very close together. Also the $4s-4p$ line in S_{IV} does not fit as well as is usual into the irregular doublet law.

The term values were obtained from the lines in the same way as in the case of the two-electron system presented in a preceding paper.

TABLE V

Screening constants for regular doublets, $3p_2-3p_1$

	Δν	$Z-s$	s_3	s_2	s_1
Na					7.450
Mg				7.130	6.606
Al	112.07	5.674	7.326	6.549	6.180
Si	287.	7.177	6.823	6.231	5.916
P	559.5	8.481	6.519	6.042	5.741
S	950.2	9.682	6.318	5.894	5.596
Cl	1500.2	10.853	6.147	5.770	5.504

Table V shows not only how well the relativity or regular doublet law works for triplets, but also how consistent and rational are the values it yields for the screening constant s (columns 4 to 6). Column 6 gives the values of s for one-electron systems (stripped atom doublets), column 5 for two-electron systems (triplets), and column 4 for three-electron systems (doublets). It will be seen that when a particular element is under consideration s for a two-electron system always comes out, as it should, between its values for a one-electron system and for a three-electron system.

TABLE VI

Comparison of term values

	$N=$ / $R/N^2=$	3 / 12192.78	4 / 6858.44	5 / 4389.40
S	Al/1		22933.27	10591.58
	Si/4		16580.8	8462.9
	P/9		13944.2	7477.0
	S/16		12506.8	6908.2
p_1	Al/1	48168.87	15316.48	8003.24
	Si/4	32882.8	12643.0	
	P/9	26974.7	11313.5	
	S/16	23787.0	10489.0	
d_1	Al/1	15844.15	9347.22	6043.31
	Si/4	13119.5	7700.0	
	P/9	14050.0	7878.3	
	S/16	14337.5	7884.5	
f	Al/1		6962.6	4451.5
x	Si/4	19124.5		
	P/9	15903.9		
	S/16	16127.3		

In Table VI are collected in the most convenient form for comparison all of the data now available on the term-values of three-valence-electron atoms. For this comparison, as is indicated in the table, the term-values are divided by 1, 4, 9, 16 in going from Al to S. In this table the silicon term-values have been obtained from Fowler's $3p$ term and from Sawyer and Paton's measured lines above 2000 A. In the case of P_{III} the lines above 2000 A necessary for our computations were taken from Geuter's work.[3]

Table VI shows greater irregularity than the corresponding table for two-valence-electron systems, and this in turn greater irregularity than the corresponding table for stripped atoms. It is not surprising that the

[3] Kayser, Spektroskopie, vol. VI, 246.

irregularities increase with increasing remove from the simple nucleus-electron system. At present we are not able to explain, however, why the d and x terms in the table all pass through a minimum in going from Al to S.

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