

THE SERIES SPECTRA OF THE STRIPPED ATOMS OF PHOSPHORUS (P_V), SULPHUR (S_{VI}), AND CHLORINE (Cl_{VII})

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

ABSTRACT

Spectra of stripped atoms, sodium to chlorine.—Grating spectrograms of order three to eight have been obtained of the hot-spark spectra of these elements, which have yielded more accurate values for the $(3p_2 - 3p_1)$, $(3s - 3p_2)$ and $(3p_1 - 3d)$ terms of Al_{III} , Si_{IV} , P_V and S_{VI} , and have enabled the identification and determination within about 5 frequency units (1) of 18 series lines of P_V , and thence of the 14 most important term values $(3s \text{ to } 6f'')$, (2) of 11 series lines of S_{VI} , and 10 corresponding term values $(3s \text{ to } 5f')$, and (3) of the first doublet of the principal series of Cl_{VII} at 800.70 and 813.00 Å. The position of this doublet was first predicted by use of the method developed in a previous paper,¹ based on observed regularities in these spectra. Further evidence is presented for the fact that both the regular and the irregular doublet laws of x-ray spectra, hold also throughout the field of optics. A plot of $\sqrt{\nu/R}$ for the stripped atom levels as a function of atomic number gives approximately straight lines (Moseley law), those for the $3s$, $3p$ and $3d$ terms and for the $4s$, $4p$, $4d$ and $4f$ terms being approximately parallel (irregular doublet law). The doublet separations $d_1 d_2$, however, do not fit well into the relativity doublet law, the ratio of observed to theoretical values decreasing from about .8 for S_{VI} to less than .2 for Si_{IV} , while Al_{III} and Mg_{II} are anomalous, d_1 having a greater frequency than d_2 . The general similarity of the spectra of all these elements is strikingly shown in spectrograms on which appear the "D" doublet of Na and the corresponding "D" doublets of the stripped atoms of Mg, Al, Si, P, S, and Cl in the second, third, fourth, fifth, sixth and seventh orders, respectively, all near 5600 Å, that for Na being farthest from the mean position. The frequencies of all the known terms found for the stripped atoms of Na to S, are collected in a table. Ionization potentials of P_V and Si_{IV} , computed from the $3s$ levels of P_V and S_{VI} , come out 64.7 and 87.6 volts.

I. METHOD OF PROVING THE EXISTENCE IN OUR HOT SPARKS OF THE STRIPPED ATOMS OF THE WHOLE SECOND ROW OF ELEMENTS OF THE PERIODIC TABLE, FROM SODIUM THROUGH CHLORINE.

IN a preceding article¹ we have shown (1) that both the regular and the irregular doublet laws developed for the interpretation of x-ray spectra hold also throughout the whole field of optics, and (2) that this discovery puts into our hands a new method for predicting with certainty (a) the precise frequencies or wave-lengths which must be emitted by an atom of a given stage of ionization, and (b) the precise doublet-separations to be expected in these frequencies.

¹ Bowen and Millikan, *Phys. Rev.* **24**, 209 (1924)

By the application of this method we have now proved that our hot-sparks have the power of completely stripping all the valence electrons from the whole group of atoms from sodium through chlorine, thus reducing all of the atoms of this series to one single electronic structure in which, however, the effective nuclear charge increases from one in sodium to seven in chlorine.

Tables I and II represent the revision and extension of Tables V and VI of the preceding article. Table I exhibits the application of the relativity, or regular doublet law, to this series of similar atomic structures, and Table II exhibits in a similar way the applicability of the irregular doublet law to this same series.

TABLE I
($3p_2-3p_1$) separations of stripped atoms Na_I to Cl_{VII}

	$\Delta\nu$	$Z-s$	s
Na_I	17.18	3.550	7.450
Mg_{II}	91.55	5.394	6.606
Al_{III}	234.00	6.820	6.180
Si_{IV}	461.84	8.084	5.916
P_V	794.82	9.259	5.741
S_{VI}	1267.10	10.404	5.596
Cl_{VII}	1889.5	11.496	5.504

The way in which the position of these stripped-atom-lines was predicted from the irregular doublet law of Table II and their doublet separations from the regular doublet law of Table I, has been heretofore detailed for the atoms from sodium through sulphur. The exact values given in these tables differ slightly from those previously published for

TABLE II

	$3s-3p_2$	Diff.	2nd diff.	$3p_1-3d$	Diff.
Na_I	16956.17			12199.48	
		18713.25			23529.96
Mg_{II}	35669.42		701.14	35729.44	
		18012.11			26308.34
Al_{III}	53681.53		408.15	62037.78	
		17603.96			26585.63
Si_{IV}	71285.49		240.03	88623.41	
		17363.93			26131.82
P_V	88649.42		147.31	114755.23	
		17216.62			25557.64
S_{VI}	105866.04		81.43	140312.87	
		17135.19			
Cl_{VII}	123001.23				

the reason that new and very much better plates have been taken in the case of all these atoms save Na and Mg, and in consequence the present tables contain data of a considerably higher order of precision than that of preceding tables. The separations, from aluminum through sulphur, in the present table have all been taken upon spectra of order from three to eight and may be relied upon to one frequency unit. On account of

this increase in precision the present tables are to be regarded as not merely extending but rather completely replacing the old ones.

To show the power of the method it is to be observed from Table II that the column of 2nd differences progresses systematically by a factor a little more than $\frac{1}{2}$ (quite accurately .58), so that it was possible to predict where the first term of the principal series of the stripped atom of chlorine would lie to within considerably less than 15 frequency units which here corresponds to *one tenth of an angstrom*. We used aluminum electrodes with NaCl in their cores and obtained at once in both the first and second order a definite line of intensity 2 or 3 *at exactly the right place, namely, at wave-length 813.00 A.*

Next, from the progression of the values of the screening constant s in Table I it was seen that this constant for the stripped chlorine must have a value very close to 5.5. Substitution of this value in the equation $\Delta\nu = .108(Z-s)^4$ gave a value of $\Delta\nu$ which could not be in error by more than one-tenth angstrom. *At precisely the predicted distance from the ($3s-3p_2$) line, the position of which had been predicted from Table II, our plate showed a new and sharp chlorine line, at $\lambda 800.70A$, of the same intensity as its companion.*

This then completes the stripping of all the valence electrons from the whole row of the seven different atoms which in the periodic table intervene between neon and argon. This stripping reduces all of these atoms to the same electronic structure which is possessed by neon.

II. PHOTOGRAPHIC EXHIBITION OF SIMILARITY OF STRIPPED ATOM SPECTRA

Although there is identity of the electronic structure of the stripped atoms of Na, Mg, Al, Si, P, S and Cl the central charge pulling upon the radiating electron increases in going from sodium through chlorine in the ratios 1, 2, 3, 4, 5, 6, 7, provided the screening of the 10 electrons in the K and L shells is perfect.

These atoms should then all possess the same spectrum as that of sodium, save that the "D" doublet in going from Na to Cl should increase in frequency in view of the irregular doublet law (Table II), in the ratios 1, 2, 3, 4, 5, 6, 7. Hence, if this "D" or sodium doublet were observed in its first order for sodium, second order for magnesium, etc., down to the seventh order for chlorine, it should be found in the same spectral position for the whole seven stripped atoms. Because, however, the screening is not perfect, and therefore the irregular doublet law is not exact (see Table II), the actual spectral positions of these "D" doublets

will lack somewhat of coincidence, sodium being the farthest out as Table II shows.

Plate I shows this whole series of "D" doublets, for the stripped atoms Na to Cl, all taken in the same narrow region on the plate—between $\lambda = 5600$ and $\lambda = 5900$ —and with an unchanged position of the grating. This plate shows how beautifully the first order of the sodium, the second of the magnesium, the third of the aluminum, the fourth of the silicon, the fifth of the phosphorus and the sixth of the sulphur fall into the same narrow region of the spectrum. It was impossible to get the chlorine in the seventh order and consequently its position, as obtained from first and second order photographs, is merely indicated.

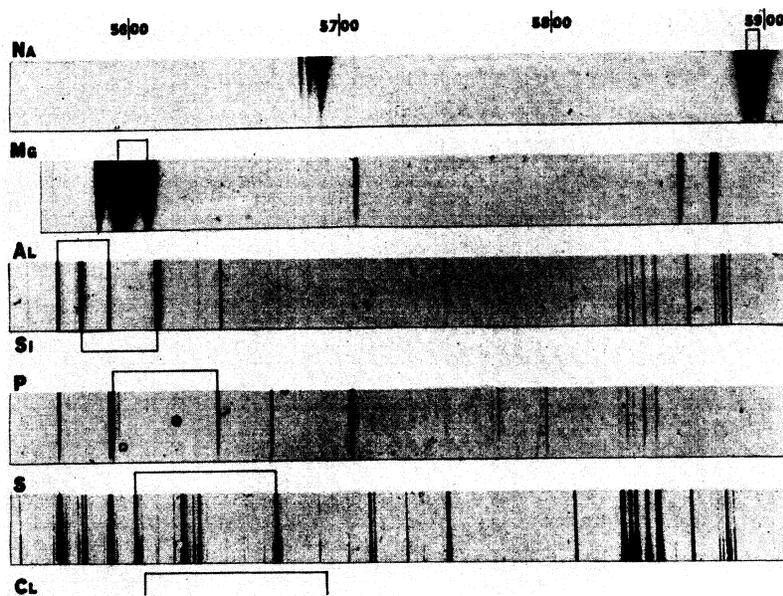


Plate I. Photographic exhibition of similarity of stripped-atom spectra.

Although the frequency separation of the components of this "D" doublet increases rapidly in going from Na to Cl (regular doublet law), the large increase in wave-length separation shown in the photographs is due primarily to increasing spectral orders, for since $d\lambda = d\nu/\nu^2$, $d\lambda$ does not increase with anything like the rapidity of $d\nu$. It will be understood that the "D" doublet is in every case the pair of lines indicated by the brackets.

III. THE SERIES OF THE STRIPPED ATOMS OF
PHOSPHORUS P_V AND SULPHUR S_{VI}

The positions of the principal lines due to jumps between the hydrogen-like terms (circular or nearly circular orbits) in the spectrum of the stripped atom of phosphorus can be predicted by means of the procedure which we have previously exposed in the case of the stripped atom of boron.² Thus, the 5*f'* orbit is a circle, the energy value of which should

TABLE III
Spectrum of stripped phosphorus P_V

Intensity	λ (I.A. vac.)	ν	$\Delta\nu$		Term values
2	542.52	184325.0	815.2	3 <i>p</i> ₂ -4 <i>s</i>	3 <i>s</i> 524491.19
2	544.93	183509.8		3 <i>p</i> ₁ -4 <i>s</i>	4 <i>s</i> 251540.66 5 <i>s</i> 147858.7
3	673.92	148385.6	788.26	3 <i>d</i> -4 <i>f</i>	3 <i>p</i> ₁ 435046.95
4	865.475	115543.49		3 <i>p</i> ₂ -3 <i>d</i>	3 <i>p</i> ₂ 435841.77
5	871.420	114755.23		3 <i>p</i> ₁ -3 <i>d</i>	4 <i>p</i> ₁ 220055.11
					4 <i>p</i> ₂ 220339.02
2	997.637	100236.86	277.84	3 <i>d</i> -4 <i>p</i> ₁	3 <i>d</i> 320295.0
2	1000.410	99959.02		3 <i>d</i> -4 <i>p</i> ₂	4 <i>d</i> 179101.1
15	1118.015	89444.24	794.82	3 <i>s</i> -3 <i>p</i> ₁	4 <i>f</i> 171909.4
12	1128.039	88649.42		3 <i>s</i> -3 <i>p</i> ₂	5 <i>f</i> 110036.5
0	1385.11	72196.4		4 <i>p</i> ₁ -5 <i>s</i>	5 <i>f'</i> 109818.4
1	1447.92	69064.6		4 <i>d</i> -5 <i>f</i>	6 <i>f'</i> 76278.5
2	1610.54	62091.0		4 <i>f</i> -5 <i>f'</i>	6 <i>f''</i> 76255.2
2	2425.08	41235.75	279.50	4 <i>p</i> ₂ -4 <i>d</i>	
2	2441.63	40956.25		4 <i>p</i> ₁ -4 <i>d</i>	
2	2962.26	33758.0		5 <i>f</i> -6 <i>f'</i>	
3	2979.45	33563.2		5 <i>f'</i> -6 <i>f''</i>	
5	3176.06	31485.55	283.91	4 <i>s</i> -4 <i>p</i> ₁	
3	3204.96	31201.64		4 <i>s</i> -4 <i>p</i> ₂	

be almost exactly 5² times that of the 5*f'* orbit of sodium, or (5/3)² times the 5*f'* orbit of aluminum. Since this latter term value is known from Paschen's work,³ we could compute the former at once to about one part in five thousand by this method. It could be obtained still more accurately by extrapolating to phosphorus from the progression shown in

² Bowen and Millikan, Proc. Nat. Acad. 10, 199 (1924)

³ Paschen, Ann. der Phys. 71, 142 (1923)

the $5f'$ terms in Table VII. In this way $5f'$ for stripped phosphorus was found to be $25 \times 4392.74 = 109818.4$ correct within about ± 5 .

The jump $4f-5f'$ can be predicted quite accurately from a similar extrapolation on the $4f$ term. This locates the $4f-5f'$ line to a fraction of an angstrom and enabled us to identify unambiguously the line of measured wave-length 1610.54 Å as the $4f-5f'$ line. Adding this observed frequency to the $5f'$ term fixed the $4f$ term at 171,909.4.

TABLE IV
Spectrum of stripped sulfur SVI

Intensity (I.A. vac.)	λ	ν	$\Delta\nu$		Term values	
0	388.91	257128.9	1256.6	$3p_2-4s$	$3s$ 710264.2	
0	390.82	255872.3		$3p_1-4s$	$4s$ 347264.0	
1	464.63	215225.0	1229.3	$3d-4f$	$3p_1$ 603131.1	
1	706.503	141542.2		$3p_2-3d_2$	$3p_2$ 604398.2	
2	712.693	140312.9		34.5	$3p_1-3d_1$	$4p_1$ 308625.9*
0	712.868*	140278.4			$3p_1-3d_2$	$4p_2$ 309083.5*
5	933.418	107133.1	1267.1	$3s-3p_1$	$4f$ 247612.1	
4	944.590	105866.0		$3s-3p_2$	$5f'$ 158159.5	
0	1117.91	89452.6		$4f-5f'$		
1	2588.12*	38638.1	457.6	$4s-4p_1$		
0	2619.14*	38180.5		$4s-4p_2$		

* Added to proof, January 27, 1925.

Exactly similar analysis identified the $3d-4f$ line as the line of measured wave-length 673.92 Å and then fixed the $3d$ level as in the table.

The $(3p_1-3d)$ is the first term of the diffuse series and its wave-length could be predicted accurately from the progression (irregular doublet law) shown in Table II. These considerations show that the measured line at $\lambda = 871.420$ Å is the line sought. The regular doublet-separation law of Table I then fixes the 865.475 line as $3p_2-3d$.

Thus by a combination of the regular and irregular doublet laws for the non-hydrogen-like terms and the simple Bohr theory for the hydrogen-like ones the whole group of results contained in Table III has been worked out. All these results have been checked by the use of the older methods represented in the Rydberg formula.⁴

⁴ In Table III the wave-lengths from 2400 up are taken from Geuter's data given in Kayser, vol. 6, p. 246. These are reduced to I. A. (vacuum).

A precisely similar analysis applied to the stripped atom of sulphur has been responsible for the assignment of lines and the computation of term-values shown in Table IV for the spectrum of the stripped atom of sulphur. The fixing of the 3s levels of P_V at 524491.19 (Table III) and of S_{VI} at 710264.2 (Table IV) fixes the *ionizing potential* of P_V at 64.7 volts and that of S_{VI} at 87.6 volts.

Table V contains the observed wave-lengths and the frequencies, determined as already indicated, of the two components of the "D" doublet of the stripped atom of chlorine.

TABLE V
Lines of stripped chlorine Cl_{VII}

Intensity (I.A. vac.)	λ	ν	$\Delta\nu$	
3	800.70	124890.7	1889.5	3s-3p ₁
2	813.00	123001.2		3s-3p ₂

IV. THE FREQUENCY SEPARATION OF THE d_1d_2 DOUBLETS FROM MAGNESIUM THROUGH SULPHUR

The data which we published in Table V of our preceding article¹ upon the 3d and 4d orbits in Mg_{II} and Al_{III} and the 4f orbits in Al_{III} and Si_{IV} showed that the relativity formula predicted accurately the observed separations, or in other words that the value of the screening constant s came out 10 within the limits of observational error.

But when upon our new plates, taken with high resolution, we studied the 3d and 4d terms in Si_{IV}, P_V, and S_{VI} this agreement broke down. Thus the relativity formula predicts a separation of the 3d₁3d₂ levels in phosphorus of 22.5 frequency units (see column 4 Table VI). When,

TABLE VI
d₁d₂ doublets for stripped atoms NaI to S_{VI}

	By direct measurement	3d ₂ -3d ₁ Principal minus diffuse	From theory .036(Z-10) ⁴	By direct measurement	4d ₂ -4d ₁ Principal minus diffuse	From theory .0152(Z-10) ⁴
NaI			.036			.0152
Mg _{II}	-.99	-.91	.576			.243
Al _{III}	-2.28	-1.70	2.92	-1.28		1.23
Si _{IV}		1.57	9.2		.08	3.9
P _V		6.32	22.5		4.41	9.5
S _{VI}	34.5	37.75	46.6			19.7

however, the (3d-4f) line 673.92 was observed in the fifth order it could not be seen to be a doublet at all despite the fact that our high resolution should have revealed it. This could only mean that the doublet was

actually much too narrow to fit the relativity equation. This doublet should also have appeared in the $(3p_1-3d)$ line at 871.420 Å with a separation of .17 Å (for this is the equivalent at this point of 22.5 frequency units), and also in the $(3d-4p_1)$ line at 997.637 Å with a separation of .22 Å. Though these lines were obtained in the seventh and third orders respectively they showed no resolvable doubling.

The actual separation could be obtained as follows: It is well known that in the diffuse series the separation of the two strongest components is equal to the difference of the p_1p_2 separation and the d_1d_2 separation. Hence a fairly good estimate of the d_1d_2 separation, which we could not directly observe, could be obtained from the difference between the observed diffuse separation and the true p_1p_2 separations as obtained from the principal series. As will be seen from Table III the difference between these two separations, namely $(3s-3p)=794.82$, and $(3p-3d)=788.26$ is 6.56, while the difference between $(4s-4p)=283.91$ and $(3d-4p)=277.84$ is 6.07. These two numbers agree fairly well and their mean, namely 6.32, is taken as the true $3d$ separation and is so recorded in Table VI. *It will be seen that this d_1d_2 separation, thus fairly reliably obtained, is less than one third of the separation predicted by the relativity equation, namely, 22.5.* The reason that this method succeeds when a direct observation of doubling fails is found in the fact that it is possible to set on the center of gravity of a line with an error not greater than a thirtieth of the width of the line.

In a similar way all the numbers in the 3rd and 6th columns of Table VI were obtained from measurements of this sort upon our own plates, except in the case of $3d_1-3d_2$ for Mg, which was taken from Fowler's book (p. 120), and $4d_1-4d_2$ for Si, which was taken from one of Fowler's papers.⁵ The numbers in the second and fifth columns are those used in Table V of our preceding article, and represent Fowler's and Paschen's direct measurements, respectively.

The negative signs used with the Mg and Al separations signify that d_1 has, quite anomalously, a larger term value than d_2 . This had been previously pointed out by Paschen.⁶ It means that in Mg and Al the separation of the two principal components of the diffuse series is, altogether anomalously, greater than the true p_1p_2 separation.

It will be seen that the departures of the separations predicted by the relativity-doublet formula and shown in columns 4 and 7, from the observed separations in columns 2, 3, 5, and 6, are quite unambiguous,

⁵ Fowler, Proc. Roy. Soc. **103**, 423 (1923)

⁶ Paschen, Ann. der Phys. **71**, 151 (1923), footnote.

although by the time sulphur is reached the observed separation seems to be rapidly nearing the theoretical value, as it might be expected to do since the observed and theoretical values are known to agree moderately well in the x-ray field.

The foregoing behavior of the *d* doublets, then, while it is clearly not predicted by the relativity equation yet seems to be tending to conformity with that equation.

TABLE VII
Comparison of frequencies of series terms for stripped atoms Na_I to S_{VI}.

	$\frac{N}{R/N^2}$	= 3 12192.78	4 6858.44	5 4389.40	6 3048.19
<i>s</i>	Na/1	41449.0	15709.5	8248.3	5077.3
	Mg/4	30316.9	12865.6	7120.3	4517.3
	Al/9	25494.89	11476.82	6535.29	
	Si/16	22756.83	10633.65	6168.72	
	P/25	20979.65	10061.63	5914.35	
	S/36	19729.56	9646.22		
<i>p</i> ₁	Na/1	24475.7	11176.1	6406.3	4151.3
	Mg/4	21376.6	10154.0	5949.6	3909.2
	Al/9	19504.01	9526.85	5664.93	
	Si/16	18272.62	9105.53	5471.16	
	P/25	17401.88	8802.20		
	S/36	16753.64			
<i>d</i>	Na/1	12276.2	6900.4	4412.5	3061.9
	Mg/4	12444.3	6988.8	4461.6	3091.6
	Al/9	12611.00	7074.30	4508.72	3119.96
	Si/16	12733.65	7131.84	4539.22	
	P/25	12811.80	7164.04		
	S/36	12856.59			
	Na/1		6860.4	4390.4	3043.
	Mg/4		6866.8	4394.3	3051.2
	Al/9		6871.28	4397.61	3053.83
	Si/16		6874.19	4399.97	3055.97
	P/25		6876.38	4401.46	
	S/36		6878.11		
<i>f</i> ^{''}	Na/1			4388.8	
	Mg/4				3048.7
	Al/9			4391.80	3050.30
	Si/16			4392.31	3050.84
	P/25			4392.74	3051.14
	S/36			4393.32	
<i>f</i> ^{''}	Na/1				3046.3
	Mg/4				
	Al/9				3049.64
	Si/16				3049.81
	P/25				3050.21

V. COMPARISON OF SERIES TERMS OF Na_I, Mg_{II}, Al_{III}, Si_{IV}, P_V, and S_{VI}

For convenience of reference and comparison we have arranged in Table VII all of our series terms in the form previously used by both

Fowler and Paschen. This form is dictated by the consideration that for remote orbits all of these stripped atoms should have term values which are proportional to the square of the effective nuclear charge, so that if these term values are divided by the squares of the numbers 1, 2, 3, 4, 5, 6, respectively, the same number should result.

In the present table the Na, Mg, and Al terms are taken directly from Paschen.³ The silicon follows Fowler's identification, but the term values have been recalculated with the use of new experimental data of our own and also with the use of the Rydberg constant which is appropriate to silicon, Fowler having used the hydrogen value of this constant. The remaining data are calculated from Tables III and IV of this paper.

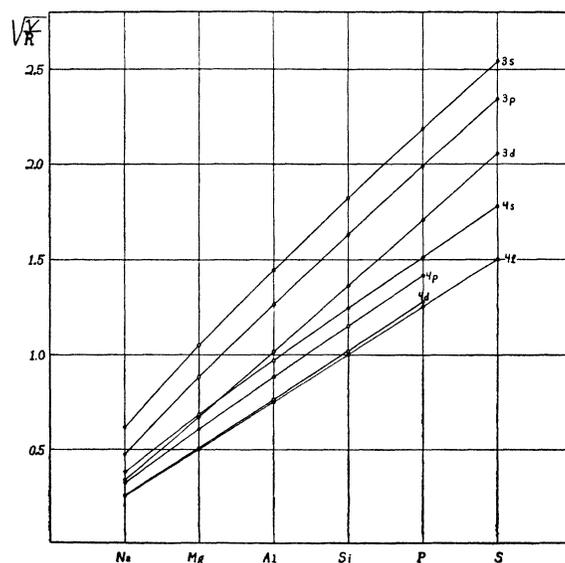


Fig. 1. Moseley's law in the field of optics.

This whole comparison may be very beautifully made graphic in precisely the way in which Moseley first exhibited the relations between atomic number and x-ray spectra. Indeed, no more striking demonstration of the fact that x-ray laws hold throughout the *optical* region as well can be made than is found in Fig. 1. In this figure we have plotted all our stripped atom levels, corresponding to the second row of the periodic table, in a Moseley diagram. That these optical levels follow the *Moseley law* is exhibited by the linear relation everywhere found between $\sqrt{\nu/R}$ and atomic number. That they follow the irregular doublet law is shown by the parallelism of the 3s, 3p, and 3d lines, all of which have constant screening differences, corresponding as they do to 3_1 , 3_2 , and 3_3 orbits,

respectively. Quite similarly, the irregular doublet law appears in the near parallelism of the $4s$, $4p$, $4d$, and $4f$ lines, which correspond to 4_1 , 4_2 , 4_3 , and 4_4 orbits, respectively. The lack of perfect parallelism in all these cases we interpret, as in our preceding papers, as due to decreasing perfectness in the screening, and a fortiori therefore, to the difference in the screening between differently shaped orbits, as the radiating electron's distance from the nucleus decreases relatively to the screening electrons' mean distance. The diagram thus furnishes a very satisfactory graphical illustration of the extension of two of the three x-ray laws, namely, the Moseley law and the irregular doublet law into the field of optics. That it fails to illustrate the extension of the third, or regular doublet law, is merely due to the fact that the regular doublet separations are so small as not to be visible at all upon a drawing of this scale.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA.
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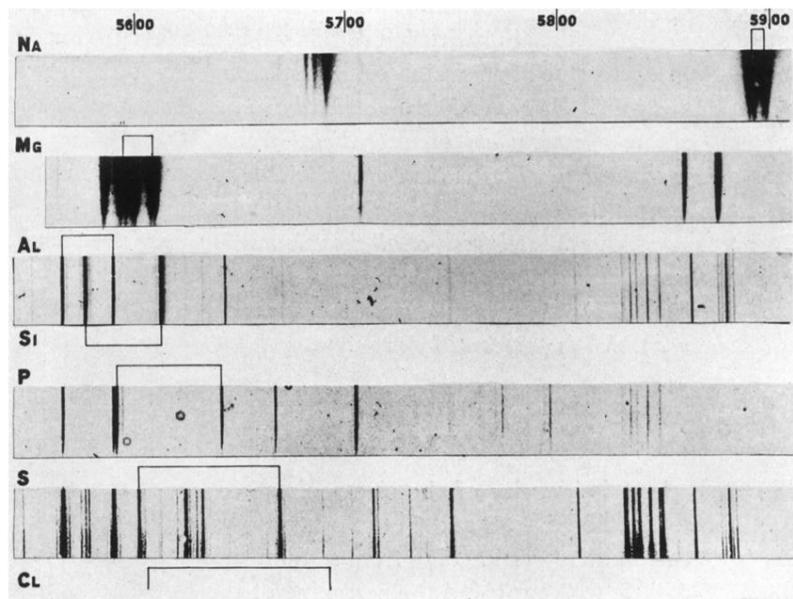


Plate I. Photographic exhibition of similarity of stripped-atom spectra.