

## RELATIONS OF PP' GROUPS IN ATOMS OF THE SAME ELECTRONIC STRUCTURE

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## ABSTRACT

**Pp' groups of spectral lines.**—(1) *For two-valence-electron atoms.* A quintuplet of nearly equally spaced lines (really an unresolved sextuplet) has now been found for all the two-valence electron spectra which have been studied by the method of hot-spark spectroscopy, namely for the series Mg<sub>I</sub>, Al<sub>II</sub>, Si<sub>III</sub>, P<sub>IV</sub>, S<sub>V</sub>, Cl<sub>VI</sub>, and for Be<sub>I</sub>, B<sub>II</sub>, C<sub>III</sub>, N<sub>IV</sub> and O<sub>V</sub>. In both of these series, this pp' group has been definitely shown to arise from an electron jump from the lowest p to the lowest s orbit, combined with a simultaneous jump of the other electron between the p<sub>1</sub>, p<sub>2</sub>, p<sub>3</sub> orbits. The frequency differences between groups of successive atoms obey the irregular doublet law, showing that the jumps are between levels of the same total quantum number. (2) *For three-valence-electron atoms.* A new quadruplet pp' group has been discovered for all the atoms of this type studied, Al<sub>I</sub>, Si<sub>II</sub>, P<sub>III</sub>, S<sub>IV</sub>, Cl<sub>V</sub> and C<sub>II</sub>, N<sub>III</sub>, O<sub>IV</sub>. The relative intensity of this group increases with the effective nuclear charge, from Al<sub>I</sub> to Cl<sub>V</sub>. This group is proved to be due to the return of one of the s electrons after displacement to a p position combined with the simultaneous interchange of the p electron between the p<sub>1</sub>, p<sub>2</sub> orbits. This group also obeys the irregular doublet law. These groups are of exceptional theoretical interest because their existence proves that the energy changes due to the simultaneous jumping of two electrons between orbits, are integrated into monochromatic radiation. The mechanism by which such an integration takes place is at present a complete mystery:

**Multiplicity of ionization potentials.**—The ionization potential must depend on the state in which the ionized atom is left after removing an s electron, for example, and will differ according as the p electron is left in the p<sub>1</sub>, p<sub>2</sub>, p<sub>3</sub> or P orbit.

## 1. HISTORICAL INTRODUCTION

THE so-called pp' group of spectral lines was noticed and carefully compared in the spectra of calcium and strontium by Rydberg<sup>1</sup> in 1894, and a corresponding group was first observed in barium in 1914 by Popow.<sup>2</sup> It was only, however, in 1921 that Götze<sup>3</sup> first interpreted these groups in Ca, Sr, and Ba as corresponding to electronic jumps into the p<sub>1,2,3</sub> levels from a group of theretofore unknown triplet levels which he designated as p' levels. This designation was adopted because a study of the lines missing out of the possible nine combinations between two triplet groups showed that the p' levels corresponded to the same inner

<sup>1</sup> Rydberg, Wied. Ann. **52**, 119 (1894).

<sup>2</sup> Popow, Ann. der Phys. **45**, 147 (1914).

<sup>3</sup> Götze, Ann. der Phys. **66**, 285 (1921).

quantum numbers as the  $p$  levels, and also because the Zeeman effect observed in these lines corresponded to the predictions of Landé's<sup>4</sup> theory for jumps from one  $p$  level to another.

The exceptional interest of these groups from the standpoint of theory arises from the discovery that when a series of them possessing ordinary spectral series relationships had been found in calcium the term values corresponding to the more remote  $p'$  terms of this series were actually *less than zero*. This is shown by the following numerical values of  $p'$  terms:  $4p' = 10800$ ,  $5p' = 750$ ,  $6p' = -5000$ ,  $7p' = -8300$ , and  $8p' = -10,000$ . The last two of these were worked out by Russell and Saunders.<sup>5</sup> This discovery was made independently by Wentzel<sup>6</sup> and by Saunders and Russell.<sup>7</sup> The negative terms of this series mean that the observed frequency corresponding to a jump from  $6p'$  to  $4p$ , for example, is actually larger than that corresponding to a jump from infinity to  $4p$ . In other words, the observed emitted energy (frequency) is larger than the total energy which the electron has to lose in jumping from infinity to the  $4p$  level. *This additional energy can then only be obtained from the simultaneous jump of some second electron, the total readjustment in energy due to the two jumps being just sufficient to produce the observed frequency.* This suggestion was first made by Bohr.<sup>8</sup>

The significance of this discovery does not lie in the demonstration that the emitted frequency corresponds to the total change in the energy of the atom because of electronic readjustments rather than to the change in energy of some particular electron. For it has long been recognized that the change in position of one electron must of necessity cause a readjustment of the whole electron family within an atom, and also that the emitted radiation must therefore be equivalent to the total energy change. That it is indeed the total energy change in the atom that determines the radiation has been especially clearly demonstrated in the study of band spectra. The significance of the foregoing discovery in the  $pp'$  group lies rather in the proof for the first time brought to light that *two electrons, both of which are in unstable quantum states, may simultaneously perform two definite quantum jumps and integrate these combined jumps into a single monochromatic radiation.*

As to the precise nature of these two jumps this much is definitely known. (1) One of the two jumping electrons, henceforth designated

<sup>4</sup> Landé, *Zeits. f. Phys.* **5**, 231 (1921).

<sup>5</sup> Russell and Saunders, *Astrophys. J.*, **61**, 38 (1925).

<sup>6</sup> Wentzel, *Phys. Zeits.* **24**, 106 (1923); **25**, 182 (1924).

<sup>7</sup> Saunders and Russell, *Phys. Rev.* **22**, 201 (1923).

<sup>8</sup> Bohr, lecture at Göttingen, 1922. See *Phys. Zeits.* **24**, 106, footnote 1.

as the first, *ends*, or comes to rest, in the lowest vacant  $p$  level, i.e. in the case of calcium in one of the levels  $4p_{1,2,3}$ ; in the case of magnesium in one of the levels  $3p_{1,2,3}$ ; in the case of beryllium in one of the levels  $2p_{1,2,3}$ . This is known because of the 6 lines of the group (these are reduced to 5 in our photographs because with our resolution the two middle ones overlap) certain ones show precisely the separation found in the normal  $p_{1,2,3}$  levels, and these separations occur in such an order as to show that the jump is *to* rather than *from* this group. (2) This same first electron jumps *from* some triplet  $p$  level, as is shown by the relation mentioned in the first paragraph. (3) The other of the two jumping electrons, henceforth designated as the second, *ends*, or comes to rest, in the lowest vacant  $S$  level, i.e.  $4S$  in calcium,  $3S$  in magnesium,  $2S$  in beryllium; for if it did not do so, the normal triplet separation could not appear exactly in a  $pp'$  group, since this normal separation is produced only when this second electron is in the  $4S$  level.

The level *from* which this second electron jumps was thought by Wentzel from his study of calcium to be  $3d$ , since he thought that he found the difference between  $4s$  and  $3d$  of the spark spectrum of calcium to be equal to the amount by which the limit of the  $p'$  terms was different from zero. Russell and Saunders<sup>5</sup> have recently come to the same conclusion. Despite the excellent quantitative agreement found by these observers, the following experimental study of the  $pp'$  group shows that this choice as to the second electron jump cannot be the correct one, *for the cases here studied*, though it may be correct for calcium.

## 2. THE IRREGULAR DOUBLET LAW AND THE $PP'$ GROUP

As is shown in preceding papers, the development of hot-spark spectroscopy has for the first time given us a means of comparing the radiating properties of a long series of light atoms of like electronic structure, such as is constituted by the series of the seven stripped atoms from sodium through chlorine. Letting one electron return to the last six of these atoms gives rise to another series of atoms of like electronic structure which in a previous paper<sup>9</sup> we have called a two-valence-electron series.

Now, previous studies of two-valence-electron systems have revealed a characteristic  $pp'$  group in them all. Thus, this group is found in the arc spectrum of barium, strontium, calcium, magnesium, and beryllium, and in the spark spectrum of aluminum, all of which are two-valence-electron systems. We therefore looked for this group in the spectra of the aforementioned two-valence-electron series and found it at once in the

<sup>9</sup> Bowen and Millikan, Phys. Rev. **25**, 591 (May 1925).

spectrum of every element of the series Mg<sub>I</sub>, Al<sub>II</sub>, Si<sub>III</sub>, P<sub>IV</sub>, S<sub>V</sub>, and Cl<sub>VI</sub>, as is shown in Table I.

We then made a similar study of the other two-valence-electron series accessible to our spectroscopic region, viz., Be<sub>I</sub>, B<sub>II</sub>, C<sub>III</sub>, N<sub>IV</sub>, O<sub>V</sub>, and found it in every element of this series also, as shown in Table II. How unmistakably this *pp'* group stands out on all our plates with its 5 nearly equally-spaced lines, the middle one being always much stronger than the others because it is actually two overlapping lines, may be seen from a glance at Plates I and II.

TABLE I

*pp'* groups in the two-valence-electron systems, Mg<sub>I</sub> to Cl<sub>VI</sub>

	$\lambda$ (I.A., vac.)	$\nu$	Diff.
Mg <sub>I</sub>	2777.503	36003.56	} 20727.94
	2779.084	35983.08	
	2780.639	35962.96	
	2782.226	35942.44	
	2783.782	35922.35	
Al <sub>II</sub>	1760.12	56814.3	} 20295.5
	1761.96	56755.0	
	1763.95	56690.9	
	1765.81	56631.2	
	1767.75	56569.1	
Si <sub>III</sub>	1294.52	77248.7	} 20050.7
	1296.73	77117.1	
	1298.93	76986.4	
	1301.13	76856.3	
	1303.34	76726.0	
P <sub>IV</sub>	1025.58	97506.0	} 19948.5
	1028.13	97264.2	
	1030.53	97037.1	
	1033.14	96792.4	
	1035.54	96567.9	
S <sub>V</sub>	849.25	117751.1	} 19942.6
	852.19	117345.0	
	854.81	116985.6	
	857.83	116573.2	
	860.46	116216.9	
Cl <sub>VI</sub>	724.13	138096.8	} 19942.6
	727.54	137449.5	
	730.31	136928.2	
	733.89	136260.2	
	736.76	135729.4	

The series of differences between the central member of each group, as displayed in column 4, shows how accurately linear is the progression of frequency with atomic number in going down either the series from Be<sub>I</sub> to O<sub>V</sub>, or that from Mg<sub>I</sub> to Cl<sub>VI</sub>. This means that *these pp' groups follow the irregular doublet law*, and this in turn means, as shown in a preceding paper<sup>9</sup> that *the jumps involved must take place between levels of*

the same total quantum number. In the case of the  $Be_I$  to  $O_V$  series the jumps in question are definitely limited to jumps between the  $2s$  and  $2p$  levels since there are no other levels of total quantum number 2. This eliminates the possibility of the jump proposed by Wentzel from a  $d$  to an  $s$  level, and with it the selection principle which he invented to make such a jump possible. It eliminates with equal definiteness the theory proposed by Landé<sup>10</sup> that in  $pp'$  groups the second electron always jumps between orbits of different total quantum number. In other words, the proof is complete and definite that the two electron jumps that combine to give off the  $pp'$  radiations are, in the  $Be_I$  to  $O_V$  series, (1) a jump of the first electron between two of the three levels designated as  $2p_1$ ,  $2p_2$ , and  $2p_3$ , and (2) a jump of the second electron from one of the  $2p$  levels to the  $2s$  level.

TABLE II

$pp'$  groups in the two-valence-electron systems,  $Be_I$  to  $O_V$

	$\lambda$ (I.A., vac.)	$\nu$	Diff.
$Be_I$	2651.343	37716.73	} 23858.8
	2651.438	37715.39	
	2651.507	37714.40	
	2651.585	37713.29	
	2651.652	37712.34	
$B_{II}$	1623.66	61589.2	} 23480.8
	1623.86	61581.7	
	1624.08	61573.2	
	1624.25	61567.0	
	1624.46	61558.9	
$C_{III}$	1174.96	85109.0	} 23267.2
	1175.31	85084.2	
	1175.72	85054.0	
	1176.03	85031.6	
	1176.40	85005.1	
$N_{IV}$	922.02	108457.5	} 23171.2
	922.57	108392.9	
	923.18	108321.2	
	923.68	108262.6	
	924.31	108188.8	
$O_V$	758.76	131794.0	}
	759.52	131662.1	
	760.50	131492.4	
	761.21	131369.8	
	762.18	131202.6	

Since the  $pp'$  group has in all two-valence-electron systems essentially the same structure, it is a natural inference that it always arises from the two jumps just mentioned. If in calcium, for example, the second electron jumps from a  $3d$  to a  $4s$  orbit, as Wentzel and also Russell and Saunders have suggested, then there is here a violation of the selection

<sup>10</sup> Landé, Zeits. f. Phys. **7**, 149 (1924).

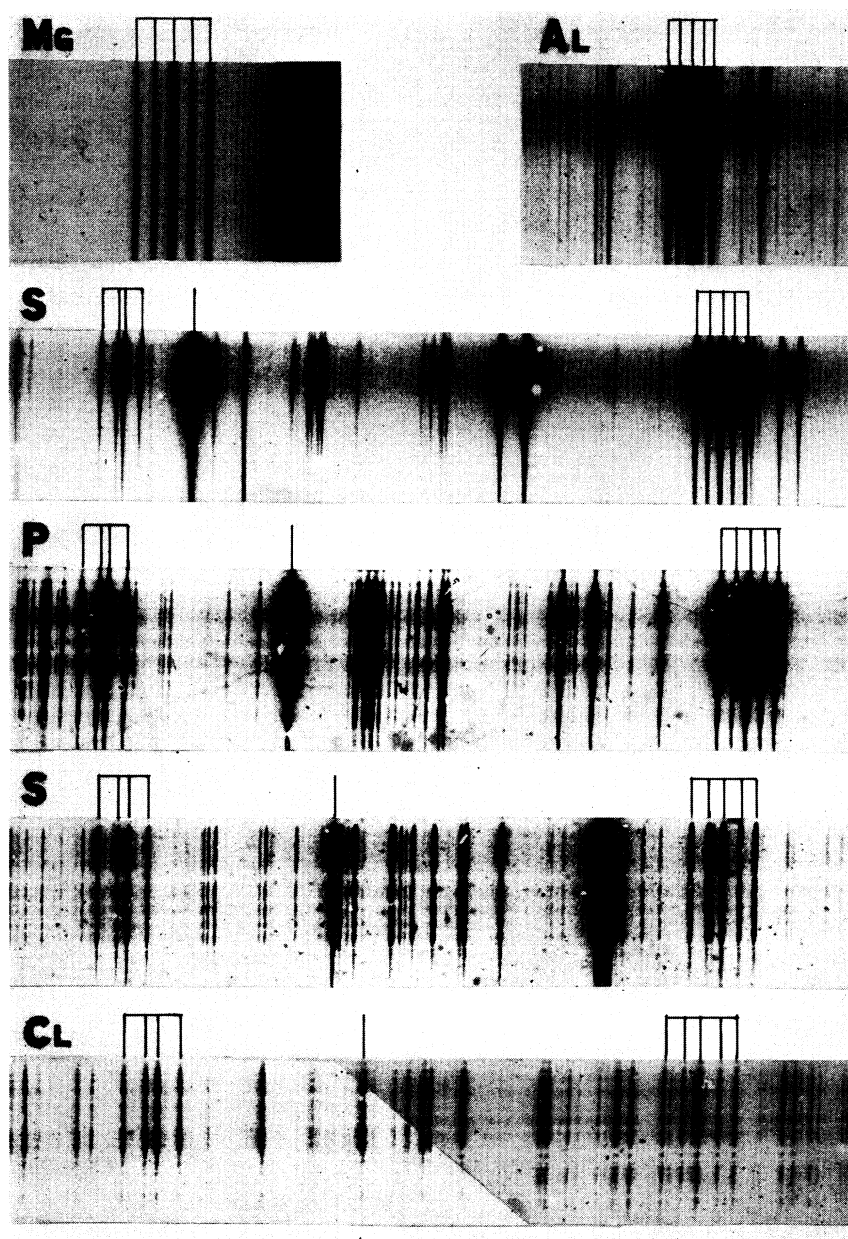


Plate I

principle which has been found to hold for all single electron jumps in the field both of optics and of x-rays, and which the present experiments prove to be valid for two-electron jumps as well, namely, that azimuthal quantum numbers can change only by plus or minus one. This is a difficult assumption to make, and one that is rendered more difficult by the entire absence in calcium of a second  $pp'$  group corresponding to the second electron jump from  $4p$  to  $4s$  such as we have proven to exist in our whole series of two-valence-electron systems. It is certainly to be expected that in calcium too there will be this regular  $pp'$  group in addition to the one attributed by Wentzel to the  $3d$  to  $4s$  jump, but no such second group is found.

TABLE III

*Comparison of frequencies of  $pp'$  group with  $(3S-3P)$  Jump*

	$3S-3P$	$pp'$
Mg <sub>I</sub>	35051.4	35962.96
Al <sub>II</sub>	59845.1	56690.9
Si <sub>III</sub>	82878.9	76986.4
P <sub>IV</sub>	105190.4	97037.1
S <sub>V</sub>	127144.0	116985.6
Cl <sub>VI</sub>	148949.2	136928.2
Ca <sub>I</sub>	23652.4	23254.66
Sr <sub>I</sub>	21698.4	20895.5
Ba <sub>I</sub>	18060.2	10843.5

A partial check upon the foregoing conclusion is obtained as follows: Since the double jump giving rise to this  $pp'$  group always involves the jump from a  $p$  to an  $s$  orbit, and since the second jump which is to be added either positively or negatively to this is quite small on account of the closeness of the  $p_{1,2,3}$  levels to one another it is to be expected that the  $pp'$  frequency will always be nearly the same as that corresponding to the jump from the  $p$  to the  $s$  level, i.e., nearly the same as the frequency of the first term of the principal series. Table III shows that this prediction is verified as closely as could be expected in view of the fact that the jump from the  $P$  to the  $S$  level will, of course, not involve quite the same energy after a nearby electron has shifted its position as before that shift has taken place.

The foregoing conclusion can be verified visually by reference to Plate I, for it states simply that the  $pp'$  group will always appear on any spectral plate close to the first term of the principal series. This is marked upon Plate I, by a single vertical line above it.

In order to permit of a simultaneous two-electron jump of any kind it is necessary that both of the two jumping electrons be at a given instant in a displaced position, i.e., in the particular case under consideration,

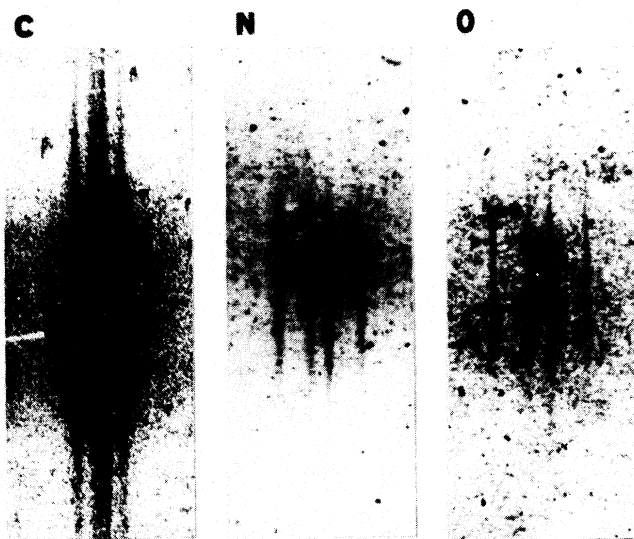
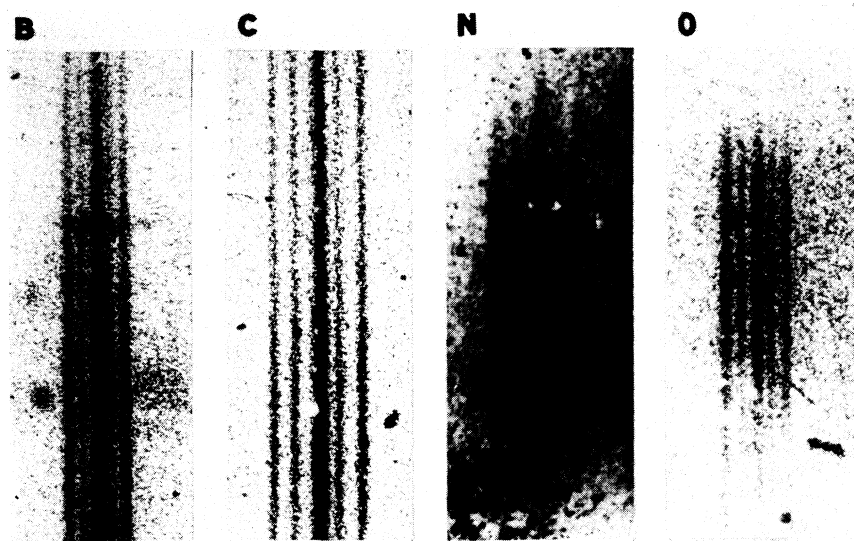


Plate II



that the first electron be in one of the  $2p_{1,2,3}$  levels at the same time that the second electron is in some  $2p$  level. If these two displacements are not the result of a single act, it is necessary that the first electron be held in a metastable position until another act can displace the second electron. The  $2p_1$  and  $2p_3$  levels are indeed metastable, but the  $2p_2$  level is definitely not so. Now *the approximate equality in the intensities of the lines of the  $pp'$  groups shows that all three of the levels  $2p_{1,2,3}$  are equally metastable, i. e. equally likely to be the seat of one of the two jumping electrons, when the double jump occurs*—a conclusion in accord with the observation, by Green and Peterson,<sup>11</sup> that lines originating in the  $2p_{1,2,3}$  levels are absorbed in equal intensity. *We conclude then, that it is one single act that displaces two  $s$  level electrons to the two  $p$  levels, from which they jump simultaneously in the production of the  $pp'$  group.*

### 3. PREDICTION OF $PP'$ GROUPS IN THREE-VALENCE-ELECTRON SYSTEMS

Having just shown that when two electrons are found at the same time in the  $p$  levels, they give rise to a  $pp'$  group through the simultaneous jumping of the second of them to an  $s$  level while the first jumps between two of the  $p$  levels, it is pertinent to inquire whether the same sort of phenomenon should not occur whenever in a three-valence-electron system, for example, two of the three valence electrons get at the same time into  $p$  levels; for the situation is then in every respect identical with that discussed in section 2, save for the presence of the third electron in an  $s$  orbit. This last fact ought not to modify in any way the general character of the events to be expected in the return of the two displaced electrons to their normal positions. Thus, the  $pp'$  group for a two-electron system was found when both the electrons were displaced to the  $3p$  level, at least one and probably only one being in the triplet level. Its structure and position showed that one electron returned to the  $3s$  level while the other either remained in its position or else jumped to any other triplet  $p$  level that the selection principle for inner quantum numbers permitted.

In the three-electron system under consideration we have exactly the same situation (two electrons in the  $p$  levels, one of which can return) save for the fact that there is one other electron which remains *all the time* in the  $s$  position and hence modifies by virtue of its field, the energies, or term values of all adjacent positions. We should therefore expect to find here a  $pp'$  group having an energy approximately equal to the difference between that of the  $s$  and  $p$  levels, but since odd-electron sys-

<sup>11</sup> Green and Peterson, *Astrophys. J.* **60**, 301 (1924).

tems always give rise to doublets in place of the triplets characteristic of even-electron systems, the new  $pp'$  group here being predicted ought to be a quadruplet, for this is the structure that would correspond to the four possible combinations between the two  $p'$  levels and the two normal  $p$  levels. The electron which does not return to the  $s$  level can either retain the same inner quantum number or change to the other possible one. In the two-electron system it had the choice of either remaining of the same inner quantum number or changing to a second or third possible one. In the present three-valence-electron case all of the four possible jumps are permitted by the selection principle.

From the foregoing analysis it will be seen that the predicted  $pp'$  quadruplet should reveal in the separation of its components the normal  $p_1p_2$  separation and a second slightly different  $p_1'p_2'$  separation. Further, it is to be expected (1) that this predicted quadruplet  $pp'$  group will be a characteristic of all three-valence-electron atoms, and (2) that since it is produced by a double jump between levels of the same total quantum number, its frequency will progress with atomic number in accordance with the irregular doublet law.

TABLE IV

$pp'$  groups in the three-valence-electron Systems, CII to OIV

	$\lambda$ (I.A., vac.)	$\nu$	Diff.	
C <sub>II</sub>	903.63	110664.8	} 35203.7	
	903.98	110621.9		
	904.17	110598.7		
	904.48	110560.8		
N <sub>III</sub>	685.04	145976.9		} 34533.7
	685.55	145868.4		
	685.86	145802.4		
	686.39	145689.8		
O <sub>IV</sub>	553.33	180724.0	}	
	554.07	180482.6		
	554.52	180336.1		
	555.23	180105.5		

#### 4. THE DISCOVERY OF QUADRUPLLET $pp'$ GROUPS

The predictions of the preceding section are verified in every detail by the data presented in Tables IV and V, and by the series of spectrograms shown in Plates I and II. A glance at the plates shows how characteristic of the three-valence-electron system is this quadruplet  $pp'$  group. That it has not been recognized before is due simply to the fact that this group in general falls in the extreme ultraviolet where preceding observers have been unable to do systematic work. Only in the case of

aluminum are the data in Table IV taken from another observer (Paschen<sup>12</sup>) who, however, did not recognize this quadruplet since it was very weak and partially obscured by other strong lines.

TABLE V  
*pp' groups in the three-valence-electron systems, Al<sub>I</sub> to Cl<sub>V</sub>*

	$\lambda$ (I.A., vac.)	$\nu$	Diff.
Al <sub>I</sub>	1762.79	56728.3	27101.8
	obscured		
	1766.31	56615.2	
	1768.95	56530.9	
Si <sub>II</sub>	1190.42	84004.0	25133.9
	1193.31	83800.5	
	1194.50	83717.0	
	1197.42	83512.9	
P <sub>III</sub>	913.99	109410.7	24441.4
	917.14	109035.2	
	918.69	108850.9	
	921.86	108476.0	
S <sub>IV</sub>	744.92	134242.8	24111.2
	748.40	133618.6	
	750.23	133292.3	
	753.76	132668.6	
Cl <sub>V</sub>	629.33	158899.1	
	633.18	157933.0	
	635.31	157403.5	
	639.24	156435.7	

Upon our own plates the  $pp'$  group for Al<sub>I</sub> is too faint to observe. It appears in increasing strength as the nuclear charge increases, as is shown in Table VI. The reason for this is as follows: Since the  $s$  electrons in Al<sub>I</sub> are bound much more tightly than the  $p$  electron, the latter will in general be entirely removed before any of the  $s$  electrons are disturbed.

TABLE VI  
*Increase of intensities of pp' groups with effective nuclear charge*

	Frequency		Intensity	
	$pp'$	$p_2$	$pp'$	$3p-3d$
Al <sub>I</sub>	56615.2	48280.91	2	15
Si <sub>II</sub>	83717.0	131818.	3	7
P <sub>III</sub>	108850.9	243332.1	5	5
S <sub>IV</sub>	133292.3	381541.4	5	6
Cl <sub>V</sub>	157403.5	542000.(est.)	6	4

When, however, the  $p$  electron has been entirely removed the atom has become a two-valence-electron system and hence any jump to an  $s$  level will correspond to a two-valence-electron series and not to the three-valence-electron series. Thus in aluminum the  $p$  electron is gone so much of the time that the characteristic three  $pp'$  electron lines are hard

<sup>12</sup> Paschen, Ann. der Phys. **71**, 544 (1923).

to find. With increasing effective nuclear charge the energy required to remove the *p* electron continually increases relative to the energy required to lift an *s* electron to the *p* position, and hence the latter jump becomes more and more frequent.

This follows clearly from the fact that the *s* to *p* change is an irregular doublet, and hence increases linearly with *z*, while the total energy of *p* varies as the square of the effective nuclear charge. In Table VI, the last two columns give the relative intensities of the *pp'* groups and the strongest lines due to jumps into the *3p* level from the *3d* level. Column 2 gives the energy necessary to transfer one of the *s* electrons to the *p* level, while column 3 gives the energy necessary to transfer the *p* electron to infinity.

5. SIGNIFICANCE OF PP' GROUP IN THREE-VALENCE-ELECTRON SYSTEM

In a three-valence-electron system it is known from absorption experiments in aluminum vapor, for example, that in the normal state two of the valence electrons are in the *3s* level and the third in a *3p* level. About

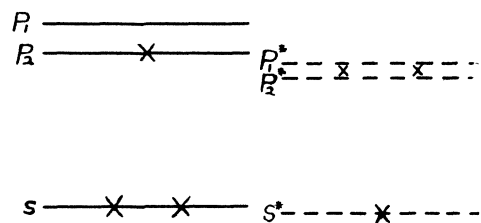


Fig. 1

these three occupied outer orbits (levels) are then arranged the series of virtual orbits in jumping between which the third electron produces the ordinary series of arc lines. This series of orbits is diagrammatically represented by the continuous lines of Fig. 1. When, now, one of the *3s* electrons absorbs energy and is thus elevated to a *3p* orbit its removal from the *s* level changes the field-strength everywhere about the nucleus so that the new series of virtual orbits is now in displaced positions, as represented by the dotted lines. These new orbits are here designated as  $3p_1^*$ ,  $3p_2^*$ , etc.

When, now, one of the two electrons in a *p* position jumps back to the vacant *s* position the  $3p^*$  levels cease at once to exist, the  $3p_1$ ,  $3p_2$  etc. positions reappearing instantly. Hence, a jump of one electron from a *3p* to a *3s* position is necessarily accompanied by a shift of the other *3p* electrons from a  $3p^*$  level to a *3p* level. But when this shift takes place the existence of four lines in the *pp'* group shows that the electron which is forced out

of a  $3p^*$  orbit by the jerking of that orbit out from under it, so to speak, may make the shift to a  $3p$  orbit in four different ways: by changing (1) from  $3p_1^*$  to  $3p_1$ , or (2) from  $3p_2^*$  to  $3p_2$  without change in inner quantum number, or (3) from  $3p_1^*$  to  $3p_2$  or (4) from  $3p_2^*$  to  $3p_1$  with change in inner quantum number. The two central lines of the quadruplet  $pp'$  group correspond to the first and second of these changes, the two outer lines to the third and fourth. The fact that the two central lines are not coincident shows that the energy change from  $3p_1^*$  to  $3p_1$  is not quite the same as from  $3p_2^*$  to  $3p_2$ . This is to be expected from the difference in the fields in which the  $p$  and the  $p^*$  orbits lie in virtue of the change of position of an  $s$  electron.

#### 6. MEANING OF IONIZATION POTENTIAL IN MULTIVALENT ATOMS

It is obvious from the foregoing discussion that the  $3s$  term value cannot be obtained by simply adding to the  $3p$  term value in the arc spectrum the frequency of any member of this quadruplet  $pp'$  group. It may be obtained as follows.

Assume that an  $s$  electron is completely removed from the atom. The atom will then be an ionized system with one electron in the  $s$  position and the other in the  $p$  position. The atom can then be brought back to normal by allowing this  $p$  electron to fall into the  $s$  position, thus emitting the first term of the principle series of the spark spectrum. Then if the second electron returns to its normal position it will emit a total energy equal to the term value of the lowest  $p$  orbit of the arc spectrum. But the total energy emitted in restoring the atom must be equal to that necessary to ionize it, i.e. necessary to remove an  $s$  electron. This is at once seen to be for aluminum equal to  $(3s-3p)$  spark spectra plus  $3p$  arc spectra. This is, then, the  $3s$  term value.

The question, however, at once arises as to whether to take one of the triplet  $p$  levels or the singlet  $P$  level in this computation. This forces on us a somewhat more general conception of the meaning of ionization potential as not merely the energy that must be given to an electron to remove it from an atom, but as the total energy given to an atom when a certain one of its electrons is removed. This, of course, will depend upon the state in which the atom is left and hence will be different according as the  $p$  electron is left in the  $p_1$ ,  $p_2$ ,  $p_3$  or  $P$  orbit, so that there may be, and probably are, as many as four ionization potentials for the lowest  $s$  level of these elements, depending upon whether in the readjustment of the position of the  $p$  electron, which follows upon the removal of an  $s$  electron, this  $p$  electron goes in the process of the readjustment into

one or the other of the four levels which are open to it. Measurements of ionization potentials have not yet been made with enough care to test this theory. In thallium, in which the separation of the  $p_1$ ,  $p_2$ ,  $p_3$  levels is relatively large, a measurable difference in ionization potentials might be obtained.

## 7. SUMMARY AND CONCLUSIONS

The fundamental significance of the two electron jumps which are dealt with in this paper lies in the new light which they throw upon the problem of the relation between the energy of ether waves (radiant energy) and atomic or subatomic energy (material energy).

These experiments constitute new proof of the futility of the 19th century attempt to find the origin of monochromatic ether waves in the vibratory motion of charged particles of any sort. Within the past ten years, an atom or molecule has been definitely shown, first by relationships discovered in band spectra, and second by two-electron jumps of the sort herein discussed, to have the capacity of integrating any sort of a complex subatomic or submolecular shudder into a monochromatic ether wave the frequency  $\nu$  of which is determined by  $h\nu = E_1 - E_2$ ,  $E_1$  and  $E_2$  representing the total energy before and after the shudder respectively. The facts of band-spectra show that this integrating process can combine into one emitted frequency a change (1) in the energy of rotation of the two nuclei of a diatomic dumb-bell shaped molecule, (2) in the vibration of these two nuclei along their line of connection, or (3) in the kinetic or potential energy of one of the electronic constituents of the system.

The present experiments along with the studies of Wentzel and of Russell and Saunders, which they supplement, prove conclusively that two electrons may simultaneously change their energies within an atom and integrate their joint energy-change into an emitted monochromatic ether wave. The mechanism by which such an integration takes place is thus far a complete mystery. We are here in the presence of one of the ultimate phenomena of the physical world. The contribution of these experiments to the understanding of this phenomenon consists simple (1) in the proof which they furnish that the particular two-electron jumps which are here integrated are (a) a jump of one electron from a  $p$  to an  $s$  position, and (b) a simultaneous jump of another electron from one  $p$  position to another  $p$  position; (2) in the evidence which they bring to light that every one of a long series of two-valence-electron systems is characterized by essentially the same sort of an easily recognizable

sextuplet  $pp'$  group, this sextuplet appearing without essential modification in such different two-valence-electron systems as  $\text{Be}_I$  to  $\text{O}_V$  and  $\text{Mg}_I$  to  $\text{Cl}_{VI}$ ; (3) in the discovery that a three-valence-electron system is similarly characterized by a quadruplet  $pp'$  group which is found in all the three-valence systems that we have studied; (4) in the proof herein furnished that the variation of the frequency of  $pp'$  groups with atomic number follows the irregular doublet law and hence that the group is formed by jumps between levels of the same total quantum number.

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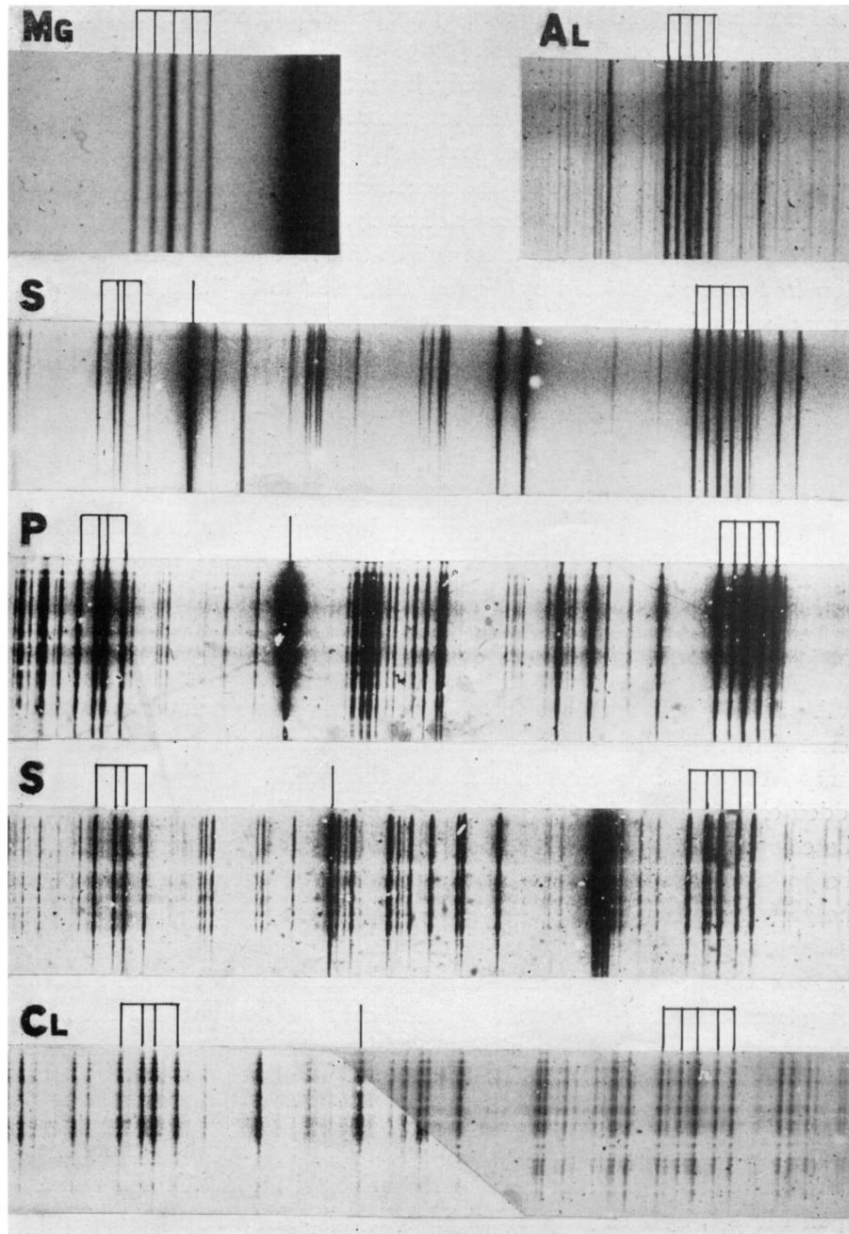


Plate I



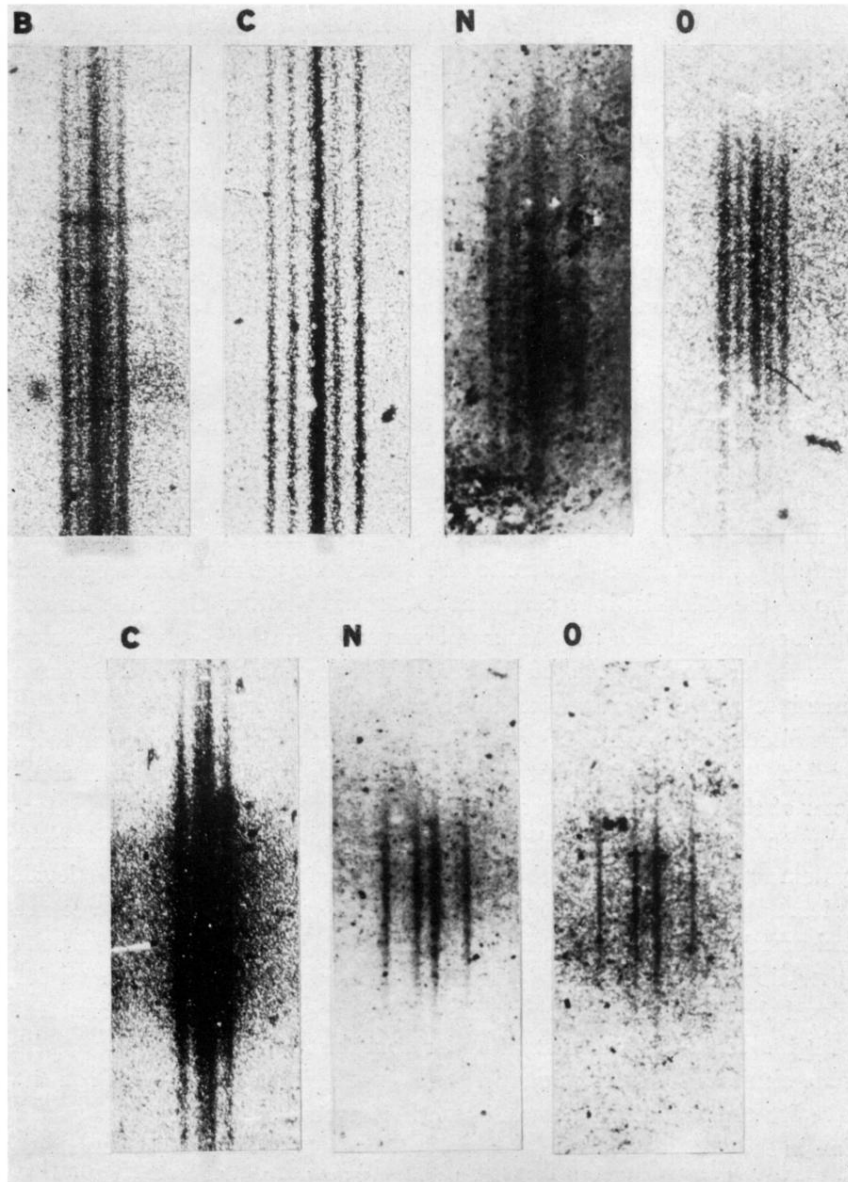


Plate II