

The Spectra of Phosphorus

Part I. The Spectra of Neutral and Singly Ionized Phosphorus

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Investigation of the discharge emitted by a Geissler tube containing phosphorus vapor has resulted in the revision and extension of previous work on P I and P II. Twenty-two new terms classifying thirty-six lines of P I have been located. These lines also appear in a 25-ampere carbon arc containing calcium phosphide. The ionization potential is lowered tentatively from 11.1 to 10.9 volts and reasons are given for believing that this last value is still a few tenths of a volt too high. Term separations are in good agreement with values calculated by the method

of Goudsmit and Humphreys. Isoelectronic sequences with S II, Cl III, and A IV indicate that some changes in S II classifications are necessary. Fifty-two new terms have been located in P II. These classify 194 lines in both the Schumann and visible regions of the spectrum. Nearly all of the expected singlet terms have been found. More than twenty intersystem combinations allow the singlet and triplet sequences to be located accurately with respect to one another. The P II ionization potential is 19.56 volts which is lower than the previously accepted value.

GENERAL AND EXPERIMENTAL

THE spectra emitted by phosphorus vapor in a Geissler tube discharge have been measured by means of the two-meter normal incidence vacuum spectrograph¹ of the Carnegie Institution of Washington which is located in the Spectroscopy Laboratory of the Massachusetts Institute of Technology. The electrical equipment consisted of a 25,000-v transformer connected to an external spark gap and four Leyden jars. In a discharge of this type the phosphorus quickly polymerizes into a very stable yellow brown substance of low vapor pressure. To keep the element in the discharge it was therefore necessary to distil the (yellow) phosphorus into the tube between the capillary and the back electrode. Spectrograms were taken of phosphorus in helium and phosphorus in argon. The same source was photographed in the visible region of the spectrum by using a 21-foot grating in the same laboratory. No new lines were found and lines classified in this region have been taken from Geuter.² Because of the stigmatic qualities of a normal incidence spectrograph a partial segregation of the lines into the various stages of ionization was possible. The short lines appearing only in the capillary arise from P III and P IV, the longer lines arise from P I and P II. It has been possible to extend the classification of P I, P II,

and P III, while a series of intersystem combinations has been found for P IV. No lines of higher stages of ionization were found. The higher spectra will be described in parts of this paper which will follow shortly. It is hoped that extensions to even higher stages of ionization will be made by means of the grazing incidence spectrograph at Uppsala.

NEUTRAL PHOSPHORUS—P I

The spectrum of neutral phosphorus appeared quite strongly in the discharge hitherto referred to. It has been possible to identify twenty-two new terms (in some cases tentatively) and to classify thirty-six new lines. A twenty-five ampere vacuum arc using calcium and copper phosphides in carbon electrodes was run in order that some of the weaker lines might be verified as belonging to P I. In this source a few P II lines appeared but could easily be recognized. Because of the many-line spectrum which appears in this region, arising from impurities in the carbon, it was impossible safely to carry the analysis any further. The lines here classified appear in both the arc and the Geissler tube exposures.

Table I contains a list of all terms so far identified in P I with their separations as calculated according to the method of Goudsmit and Humphreys.³ It will be seen that in most cases

* Irving Langmuir Fellow, American-Scandinavian Foundation.

¹ Compton and Boyce, *Rev. Sci. Inst.* **5**, 218 (1934).

² Geuter, *Zeits. f. Wiss. Phot.* **5**, 1 (1907).

³ Goudsmit and Humphreys, *Phys. Rev.* **31**, 960 (1928). In the above calculation a_2 has been neglected with respect to A^1 .

TABLE I. *Theoretical and observed term separations.*

P I	CALC.	OBS.	P I	CALC.	OBS.
$s^2p^2 \cdot s \ ^4P_{1/2-3/2}$	157.6	4s 151.2 5s 146.7	$s^2p^2 \cdot p \ ^4D_{3/2-5/2}$	131.5	134.9 202.2
			$\ ^2D$	263.0	57.1
	263.0	4s 249.1 5s 322.1	$s^2p^2 \cdot d \ ^4P_{1/2-3/2}$	-78.8	-76.6
			$\ ^2P$	-131.5	-108.0
			$\ ^2P$	-157.6	+141.6
			$\ ^4D_{1/2-3/2}$	26.3	—
$s^2p^2 \cdot p \ ^2P_{1/2-3/2}$	315.0	297.6	$\ ^2P$	43.7	41.1
	78.8	16.8	$\ ^2D$	61.3	—
	131.5	183.9	$\ ^2D$	87.4	—
	157.6	117.2	$\ ^4F_{3/2-5/2}$	87.4	75.1
	78.8	76.6	$\ ^2F$	245.2	298.7

here as in the analogous spectra N I, O II, and S II the agreement is quite good. As in O II³ the greatest deviation appears in some of the doublets. The $3d \ ^2P$ which shows the largest discrepancy is quite close to the corresponding $\ ^4P$. The $4p \ ^2D$ has been identified by Kiess⁴ on the basis of a single transition and therefore should be regarded as a tentative value. The $5s \ ^4P$ terms must also be regarded as tentative assignments for this same reason, although in all cases these

and only these sets of lines satisfy both separation restriction as set by the theory of Goudsmit and Humphreys and absolute term values as predicted by the irregular doublet law. In all cases except the $3d \ ^4D$ the lines identified were the only P I lines within several thousand cm^{-1} . Kiess' X term is here designated as $(^1D) \ 4s \ ^2D_{3/2, 5/2}$ in which term the separation should theoretically be zero. The terms which he has designated as $3d \ ^2P$ form according to their intensities an inverted doublet and hence the J values have been reversed. The separation is that which one should expect for the sp^4 configuration and is negative and slightly less than the separation for $p^24s \ ^2P$. This term is peculiar in that it shows no combination with the metastable $s^2p^3 \ ^2D$. These terms were originally found by Miss Saltmarsh⁵ and identified in terms of our modern nomenclature by McLennan and McLay.⁶ Because of the new Schumann region measure-

⁵ Saltmarsh, Phil. Mag. 47, 874 (1924).

⁶ McLennan and McLay, Trans. Roy. Soc. Canada (3) 21, 63 (1927).

⁴ Kiess, Bur. Standards J. Research 8, 393 (1932).

TABLE II. *Complete term table P I.*

$3s^23p^3 \ ^4S_{3/2}$		§0.00	$(^3P)4p \ ^2P_{0,1/2}$	§67,970.2	117.2
$3s^23p^3 \ ^2D_{3/2}$	§11,361.7	14.8	$\ ^2P_{0,3/2}$	§68,097.9	
$\ ^2D_{5/2}$	§11,376.5		$(^3P)4p \ ^2S_{0,1/2}$	68,473.2	
$3s^23p^3 \ ^2P_{0,1/2}$	§18,722.4	25.7	$(^3P)3d \ ^2F_{5/2}$	70,391.3	298.7
$\ ^2P_{3/2}$	§18,748.1		$\ ^2F_{7/2}$	70,690.0	
$(^3P)4s \ ^4P_{1/2}$	151.21	§55,939.23	$(^3P)3d \ ^4D_{1/2}$	—	
$\ ^4P_{3/2}$	249.09	§56,090.59	$\ ^4D_{3/2}$	70,637.5	41.6
$\ ^4P_{5/2}$	249.09	§56,339.68	$\ ^4D_{5/2}$	70,778.6	
$(^3P)4s \ ^2P_{1/2}$	§57,876.8	297.6	$\ ^4D_{7/2}$	—	
$\ ^2P_{3/2}$	§58,174.4		$sp^4 \ ^2D_{5/2}$	71,168.3	-34.3
$sp^4 \ ^4P_{5/2}$	-180.2	59,533.4	$\ ^2D_{3/2}$	71,202.6	
$\ ^4P_{3/2}$	-105.0	59,713.6	$(^3P)3d \ ^4P_{5/2}$	-108.0	72,386.6
$\ ^4P_{1/2}$		59,818.6	$\ ^4P_{3/2}$	-76.8	72,494.6
$(^1D)4s \ ^2D_{3/2, 5/2}$	65,156.6		$\ ^4P_{1/2}$		72,571.4
$(^3P)4p \ ^4D_{0,1/2}$	76.6	§65,373.6	$(^3P)3d \ ^2P_{1/2}$	72,741.9	141.6
$\ ^4D_{3/2}$	134.9	§65,450.2	$\ ^2P_{3/2}$	72,883.5	
$\ ^4D_{5/2}$	202.2	§65,585.1	$sp^4 \ ^2S_{1/2}$	72,943.3	
$\ ^4D_{7/2}$		§65,787.3	$(^3P)3d \ ^2D_{5/2}^?$	73,248.1	75,064.6?
$(^3P)4p \ ^4P_{0,1/2}$	16.8	§66,343.4	$(^3P)5s \ ^4P_{1/2}$	146.7	75,211.3?
$\ ^4P_{3/2}$	183.9	§66,360.2	$\ ^4P_{3/2}$	322.1	75,533.4?
$\ ^4P_{5/2}$		§66,544.1	$\ ^4P_{5/2}$		
$(^3P)4p \ ^2D_{3/2}$	66,813.1	57.1			
$\ ^2D_{5/2}$	66,870.2?				
$(^3P)4p \ ^4S_{3/2}$	67,908.6	§66,834.5			
$sp^4 \ ^2P_{3/2}$		-217.6			
$\ ^2P_{1/2}$	68,126.2				

§ Terms from Kiess modified on the basis of new measurements.

TABLE III. Classified lines in P I.

<i>I</i>	$\lambda(\text{vac})$	$\nu(\text{cm}^{-1})$	COMBINATION	<i>I</i>	$\lambda(\text{vac})$	$\nu(\text{cm}^{-1})$	COMBINATION
3	1323.918 ¹	75,533.4	3 <i>p</i> 4 <i>S</i> ^o — 5 <i>s</i> 4 <i>P</i> _{5/2}	1	1834.866	54,499.9	3 <i>p</i> 2 <i>P</i> _{3/2} — 3 <i>d</i> 2 <i>D</i> _{3/2}
3	1329.587 ¹	75,211.3	— 5 <i>s</i> 4 <i>P</i> _{3/2}	1	1844.326	54,220.3	3 <i>p</i> 2 <i>P</i> _{1/2} — <i>sP</i> ⁴ 2 <i>S</i>
2	1332.186	75,064.6	— 5 <i>s</i> 4 <i>P</i> _{1/2}	1	1845.165	54,195.7	3 <i>p</i> 2 <i>P</i> _{3/2} — <i>sP</i> ⁴ 2 <i>S</i>
8	1377.954	72,571.4	3 <i>p</i> 4 <i>S</i> ^o — 3 <i>d</i> 4 <i>P</i> _{1/2}	8	1847.215	54,135.6	3 <i>p</i> 2 <i>P</i> _{3/2} — 3 <i>d</i> 2 <i>P</i> _{3/2}
8	1379.413	72,494.6	— 3 <i>d</i> 4 <i>P</i> _{3/2}	8	1851.144	54,020.6	3 <i>p</i> 2 <i>P</i> _{1/2} — 3 <i>d</i> 2 <i>P</i> _{1/2}
8	1381.472	72,386.6	— 3 <i>d</i> 4 <i>P</i> _{5/2}	2	1852.032	53,994.7	3 <i>p</i> 2 <i>P</i> _{3/2} — 3 <i>d</i> 2 <i>P</i> _{1/2}
2 <i>d</i>	1412.857	70,778.6	3 <i>p</i> 4 <i>S</i> ^o — 3 <i>d</i> 4 <i>D</i> _{3/2}	12	**1858.924	53,794.6	3 <i>p</i> 2 <i>D</i> _{3/2} — (1 <i>D</i>)4 <i>s</i> 2 <i>D</i> _{3/2} , 5/2
1	1415.678	70,637.5	— 3 <i>d</i> 4 <i>D</i> _{5/2}	12	**1859.401	53,780.8	3 <i>p</i> 2 <i>D</i> _{5/2} — (1 <i>D</i>)4 <i>s</i> 2 <i>D</i> _{3/2} , 5/2
7	1491.357	67,053.0	3 <i>p</i> 4 <i>S</i> ^o — 3 <i>d</i> 4 <i>P</i> _{5/2} [†]	2 <i>d</i>	1864.376	53,637.2	3 <i>p</i> 2 <i>P</i> _{3/2} — 3 <i>d</i> 4 <i>P</i> _{3/2} [†]
7	1493.030	66,977.9	— 3 <i>d</i> 4 <i>P</i> _{3/2} [†]				
0	1616.248	61,871.7	3 <i>p</i> 2 <i>D</i> _{5/2} — 3 <i>d</i> 2 <i>D</i> _{3/2}	2	1905.456	52,480.9	3 <i>p</i> 2 <i>P</i> _{1/2} — <i>sP</i> ⁴ 2 <i>D</i> _{3/2}
1	1625.450	61,521.4	3 <i>p</i> 2 <i>D</i> _{3/2} — 3 <i>d</i> 2 <i>P</i> _{3/2}	2-	1906.424	52,454.2	3 <i>p</i> 2 <i>P</i> _{3/2} — <i>sP</i> ⁴ 2 <i>D</i> _{3/2}
1	1625.825	61,507.2	3 <i>p</i> 2 <i>D</i> _{5/2} — 3 <i>d</i> 2 <i>P</i> _{3/2}	3	1907.663	52,420.2	3 <i>p</i> 2 <i>P</i> _{3/2} — <i>sP</i> ⁴ 2 <i>D</i> _{3/2}
1	1629.191	61,380.2	3 <i>p</i> 2 <i>D</i> _{3/2} — 3 <i>d</i> 2 <i>P</i> _{1/2}	6	**2024.127	49,404.0	3 <i>p</i> 2 <i>P</i> _{1/2} — <i>sP</i> ⁴ 2 <i>P</i> _{1/2}
6	1671.070	59,841.9	3 <i>p</i> 2 <i>D</i> _{3/2} — <i>sP</i> ⁴ 2 <i>D</i> _{3/2}	6	**2025.202	49,377.8	3 <i>p</i> 2 <i>P</i> _{3/2} — <i>sP</i> ⁴ 2 <i>P</i> _{1/2}
1	1671.546	59,824.9	3 <i>p</i> 2 <i>D</i> _{5/2} — <i>sP</i> ⁴ 2 <i>D</i> _{3/2}	8	**2033.104	49,185.9	3 <i>p</i> 2 <i>P</i> _{1/2} — <i>sP</i> ⁴ 2 <i>P</i> _{3/2}
6	1671.720	59,818.6	3 <i>p</i> 4 <i>S</i> ^o — <i>sP</i> ⁴ 4 <i>P</i> _{1/2}	10	**2034.146	49,160.7	3 <i>p</i> 2 <i>P</i> _{3/2} — <i>sP</i> ⁴ 2 <i>P</i> _{3/2}
2	1672.032	59,807.5	3 <i>p</i> 2 <i>D</i> _{3/2} — <i>sP</i> ⁴ 2 <i>D</i> _{3/2}				
6	1672.499	59,790.8	3 <i>p</i> 2 <i>D</i> _{5/2} — <i>sP</i> ⁴ 2 <i>D</i> _{3/2}	10	*2136.142	48,813.4	3 <i>p</i> 2 <i>D</i> _{3/2} — 4 <i>s</i> 2 <i>P</i> _{3/2}
12	1674.661	59,713.6	3 <i>p</i> 4 <i>S</i> ^o — <i>sP</i> ⁴ 4 <i>P</i> _{3/2}	11	*2136.875	46,797.3	3 <i>p</i> 2 <i>D</i> _{5/2} — 4 <i>s</i> 2 <i>P</i> _{3/2}
12	1679.730	59,533.4	3 <i>p</i> 4 <i>S</i> ^o — <i>sP</i> ⁴ 4 <i>P</i> _{5/2}	12	*2149.787	46,516.2	3 <i>p</i> 2 <i>D</i> _{3/2} — 4 <i>s</i> 2 <i>P</i> _{1/2}
00	1683.002	59,417.6	3 <i>p</i> 2 <i>D</i> _{3/2} — 3 <i>d</i> 4 <i>D</i> _{3/2}	11	**2153.630	46,433.2	3 <i>p</i> 2 <i>P</i> _{1/2} — (1 <i>D</i>)4 <i>s</i> 2 <i>D</i> _{3/2} , 5/2
11	1685.957	59,313.5	3 <i>p</i> 2 <i>D</i> _{5/2} — 3 <i>d</i> 2 <i>F</i> _{7/2}	12	**2154.761	46,408.9	3 <i>p</i> 2 <i>P</i> _{3/2} — (1 <i>D</i>)4 <i>s</i> 2 <i>D</i> _{3/2} , 5/2
10	1694.055	59,030.0	3 <i>p</i> 2 <i>D</i> _{3/2} — 3 <i>d</i> 2 <i>F</i> _{5/2}				
1	1694.498	59,014.5	3 <i>p</i> 2 <i>D</i> _{5/2} — 3 <i>d</i> 2 <i>F</i> _{5/2}	0	*2224.047	44,963.1	3 <i>p</i> 2 <i>D</i> _{5/2} — 4 <i>s</i> 4 <i>P</i> _{3/2}
6 <i>d</i>	*1719.333	58,168.9	3 <i>p</i> 4 <i>S</i> ^o — 4 <i>s</i> 2 <i>P</i> _{3/2}	0	*2236.430	44,714.1	3 <i>p</i> 2 <i>D</i> _{5/2} — 4 <i>s</i> 4 <i>P</i> _{3/2}
12	*1774.942	56,339.9	3 <i>p</i> 4 <i>S</i> ^o — 4 <i>s</i> 4 <i>P</i> _{5/2}	1	2243.189	44,579.4	3 <i>p</i> 2 <i>D</i> _{3/2} — 4 <i>s</i> 4 <i>P</i> _{1/2}
12	*1782.830	56,090.6	— 4 <i>s</i> 4 <i>P</i> _{3/2}				
12	*1787.686	55,938.2	— 4 <i>s</i> 4 <i>P</i> _{1/2}	0	2433.680	41,090.0	3 <i>p</i> 2 <i>P</i> _{1/2} — <i>sP</i> ⁴ 4 <i>P</i> _{1/2}

¹ Note added after submission of manuscript.

In rechecking the list of wave-lengths for possible impurities I find that the two lines 1323.918 and 1329.587A listed in the P I classifications are coincident with two lines in the Carbon I and Carbon II spectrum respectively. While in both cases the lines are relatively stronger than other lines of equal intensity in the carbon spectra it is felt that doubt may reasonably exist as to the validity of the tentative assignment for the P I 4*s* 4*P* set of terms. With these terms missing it is, of course, impossible to calculate an ionization potential from the available data although the I.P. as formerly published must still be too high.

² This list contains all lines classified in the Schumann region.

³ Classifications from McLennan and McLay (6) and from Kiess (4).

⁴ Lines have had their former identifications changed in this investigation.

[†] Wave-lengths from Kiess (4).

ments it has proven necessary to shift all of the formerly published terms by about 4.5 cm. A complete term table will be found in Table II where these modifications have been made. If the tentative 5*s* 4*P* set of terms be used to calculate an ionization potential one obtains 88,560 cm⁻¹ which is rather lower than the former value. Edlén⁷ has plotted the ionization potentials for the first two short periods. The single discrepancy in his curves occurs at P I where the I.P. is too high. The new value 10.9 volts while still high appears to be rather better.

The former ionization potential was calculated by Kiess⁴ using the ground 3*s*²3*p*³ 4*S* and the metastable 2*P* and 2*D* and similar terms arising from the 3*s*²3*p*²4*p* configuration. Such series deviate considerably from simple Rydberg series inasmuch as the ground terms arising from equivalent electrons always show much too large a quantum defect. When higher members of the

3*s*²3*p*²*ns* series can be found the accurate I. P. obtained will undoubtedly be lower than that given here. In P II the corresponding change has resulted in a lowering of the I.P. by 0.2 volt.

In Table IV the results of the irregular doublet law for this isoelectronic sequence are assembled. The term which shows the greatest disagreement is the (3*P*)3*d* 2*D*. The same disagreement is found in the N I isoelectronic sequence, i.e., the differences decrease instead of increase with decrease in atomic number of the element. The (3*P*)3*d* 4*P* and 2*P* also require special mention. In Cl III these terms are well above the 4*D*, 4*F* and 2*D*, 2*F* terms of the same configuration. In S II the 4*P* has been assigned a value by Bartel and Eckstein⁸ on the basis of its infrared combinations with 4*p* terms. This 4*P* is not in agreement with these new assignments in P I. Professor Bowen has kindly informed me that he has provisionally identified this multiplet otherwise.

⁷ Edlén, *Zeeman Verhandelingen* (Martinus Nijhoff, The Hague, 1935), p. 88.

⁸ Bartel and Eckstein, *Zeits. f. Physik* 86, 77 (1933).

TABLE IV. Irregular doublet law for P I isoelectronic sequence.

P I	$s^2p^3\ ^2P_{3/2} - sp^4\ ^2P_{3/2}$			
	49,260	31,767		
S II	81,027	25,194 × 2		
Cl III				
A IV	131,325			
P I	$s^2p^3\ ^4S_{3/2} - sp^4\ ^4P_{5/2}$		$s^2p^3\ ^4S_{3/2} - 3d\ ^4D_{5/2}$	
	59,533	19,862	70,779	43,352
S II	79,395	19,125	114,231	37,618
Cl III	98,520	19,044	151,849	
A IV	117,564			
P I	$s^2p^3\ ^4S_{3/2} - 3d\ ^4P_{3/2}$		$s^2p^3\ ^4S_{3/2} - 3d\ ^4F_{3/2}$	
	72,387	58,432	66,977	43,336
S II	130,819	48,676	110,313	36,437
Cl III	179,495		146,750	
P I	$sp\ ^2D_{5/2} - 3d\ ^2D_{5/2}$		$3p\ ^2P_{3/2} - 3d\ ^2P_{3/2}$	
	61,871	42,541	54,135	61,308
S II	104,412	60,511	115,443	40,489
Cl III	164,923		155,932	
P I	$s^2p^3\ ^4S_{3/2} - 5s\ ^4P_{5/2}$		$3p\ ^2D_{5/2} - (1D)4s\ ^2D_{5/2}$	
	75,533	275	53,780	232
S II	150,996	389	106,647	326
Cl III	246,139	496	170,270	413

The value given by Bowen⁹ is the one tabulated in Table IV. It will be seen that the agreement is satisfactory. Ingram¹⁰ has classified a single term in S II as $(^3P)3d\ ^2P_{3/2}$ the term with $J = \frac{1}{2}$ being unknown. It appears that this term is also too low on the basis of the P I and Cl III assignments and that the 2P , of which the electron configuration is unknown, which lies at 139,845.6 ($J = \frac{1}{2}$) and 140,015.7 ($J = 3/2$) is the correct one. Table IV also uses this value for these terms. The agreement is not so satisfactory as is the case with the 4P . These terms are, however, manifestly irregular. The 2P separation in S II is thus seen to be positive as in P I instead of negative. In Cl III, however, the term is negative as it should be.

This classification of P I includes all of the strong lines which appear in the arc with the exception of two at $\lambda 1491.357$ and $\lambda 1493.030$. (Intensity in each case 7.) The position and separation of these lines is consistent with the classification $s^2p^3\ ^4S - (^3P)3d\ ^4F_{3/2, 5/2}$. As might be expected, terms arising from this classification show no combination with the $s^2p^3\ ^2D$ or 2P .

While the above transitions do not occur in the first short period one does find $s^2p^3\ ^4S - (^3P)3d\ ^2F$ which is fairly strong. This transition arises, however, because of perturbation between the $(^3P)3d\ ^2F$ and the $(^3P)3d\ ^4D$. No such perturbations appear to be present here.

SINGLY IONIZED PHOSPHORUS—P II

The term table of P II has been enlarged by the addition of fifty-two terms including both singlet and triplet terms. The two systems are accurately located with respect to one another as among the 194 new lines classified there appear more than twenty intercombinations. Bowen's former classification of the $3d$ triplet terms have been considerably altered. These alterations are strengthened by several facts. New data on other members of this isoelectronic sequence indicate that the old values for the $3d\ ^3P$ term were too high and that the 3P and 3D should probably overlap. This has been found to be the case. As a result only the assignment of J values to the new terms appears to be of physical significance, the L values being somewhat arbitrary. The present assignments are supported, however, by the discovery of two higher terms $5d\ ^3P$ and $6d\ ^3P$ showing definitely that the terms as here assigned go to the $^2P_{3/2}$ P III limit instead of the 2P_1 limit. This is according to the Hund theory as the 3D terms should approach the lower limit. It will be noticed from Table VII that, as in Si I, the quantum defects increase at first for these terms but gradually approach a constant value. The L values in the $4d$ triplets were originally given the present assignments because of the intensity of their combinations with $4p\ ^3S$. The terms assigned to the $4d\ ^3P$ combine much more strongly than do those attributed to 3D . This assignment is substantiated by the restrictions set by the two limits in P III. A search has been made for the $3d\ ^3F$ by means of its (forbidden) combinations with the ground 3P_2 and metastable 1D_2 . The two terms given were found in this manner. They cannot be substantiated by combinations with the set of new high even levels, however, as the region of the spectrum in which the lines would lie has been very inadequately measured. Certain of these transitions

⁹ Bowen unpublished material.

¹⁰ Ingram, Phys. Rev. 32, 173 (1928).

appear in the lines listed by Déjardin¹¹ but as the measurements are valid only to an Angstrom they have not been listed. In other cases, notably the $6s\ ^3P_1$, where the reality of the terms has been established by other lines in Geuter's list Déjardin's measurements have been used.

In Bowen's original classification two terms were identified as belonging to the $3d\ ^3P$ group. Of these terms the first now proves to be $sp^3\ ^3S_1$. The second here designated as 1° appears to show combinations among the set of new high even terms. Two of the resulting lines 4561.93 and 4522.92A have been assigned by Déjardin¹¹ to P III; hence the validity of this term is somewhat in doubt. One other line has been assigned to P III in the same manner—2229.241. All other lines classified in Table IX either have been assigned to P II definitely or P III provisionally.

The set of high even terms listed separately may be expected to contain the $4f$ and $5p$ singlets and triplets as well as terms arising from the p^4 configuration. Since so many of these terms have been found, whose validity cannot be questioned because of the large number of lines classified by each, it would appear that terms approaching the P III 4P limit are also included. While quartet terms are known in P III no intercombinations have been found to connect them with the doublet system and hence the limit may be quite far from that provisionally assigned by Bowen.¹² For this reason no general attempt has been made to assign electron configurations to these terms although certain of the singlets have been provisionally classified on the basis of their strongest combinations. It must be realized, however, that the division of terms arising from the $4f$ configuration into singlets and triplets has, as Edlén¹³ has shown in his oxygen classification no significance whatsoever.

The limit has been calculated by fitting a Ritz formula to the $s\ ^1P$ and $s\ ^3P$ terms. The singlet series approaches a limit only 188 cm^{-1} above the 2P_3 term of P III instead of 560 cm^{-1} . The 3P_3 terms approach a limit which is 609 cm^{-1} higher. Thus while the triplet series would indicate a limit of $158,653\text{ cm}^{-1}$ the singlet series limit is lower. The best value for the ground state is

thus $158,550\text{ cm}^{-1}$. This lowers Bowen's value of the ionization potential from 19.8 volts to 19.56 volts. It is possible that a full knowledge of the $4f$ terms will change this value by a small amount.

The present triplet assignments are in satisfactory agreement with the irregular doublet law as may be seen from Table X. The singlet terms, however, have with one exception not been found in S III so that no complete comparison is possible. The three 1P_1 terms arising from the $s^2p\cdot s$ configurations can be calculated, however, from the separations of the corresponding triplet terms by Houston's¹⁴ method. How well this is verified in this and other terms in this isoelectronic series may be seen from Table V.

It will be seen from Table X that the low metastable 1D in S III provisionally identified by Bowen¹⁵ is substantiated by the new value in

TABLE V.

	SI I		P II			CI IV	
	$4s\ ^1P_1$	$5s\ ^1P_1$	$4s\ ^1P$	$5s\ ^1P_1$	$6s\ ^1P_1$	$4s\ ^1P_1$	$5s\ ^1P_1$
calc.	24,773	10,737	69,672	34,087	20,514	211,788	116,037
obs.	24,773	10,895	69,657	34,116	20,491	211,772	116,105

TABLE VI. Forbidden transitions of possible astrophysical importance in P II.

CLASSIFICATION	ν	λ
$^3P_1 - ^1S_0$	21,410 cm^{-1}	4,669A
$^1D_2 - ^1S_0$	12,704	7,869
$^3P_1 - ^1D_2$	8,706	11,483
$^3P_2 - ^1D_2$	8,403	11,897

TABLE VII. Rydberg denominators in P II.

A. TERMS TO $^2P_{1/2}$ P III						
TOTAL QUANTUM NUMBER	$s\ ^3P_1$	$p\ ^3D_2$	$d\ ^3D_2$	$d\ ^3F_3$	$P\ ^3S_1$	
$n=3$			2.8372	2.570		
$n=4$	2.4722	2.8196	3.7837	3.6242	2.8902	
$n=5$	3.5367				3.8956?	
$n=6$	4.565					
B. TERMS TO $^2P_{3/2}$ P III						
Total QUANTUM NUMBER	$p\ ^3P_2$	$d\ ^3P_2$	$s\ ^1P_1$	$p\ ^1S_0$	$p\ ^1P_1$	
$n=3$	1.6879	2.8129				
$n=4$	2.8779	3.7295	2.5003	3.0242	2.9426	
$n=5$		4.6828	3.5579	4.0723?	3.9468?	
$n=6$		5.6833	4.5644			
	$p\ ^1D_2$	$d\ ^1P_1$	$d\ ^1D_2$	$d\ ^1F_3$	$f\ ^1D_2$	$f\ ^1F_3$
$n=3$		2.9413	2.8739	2.1925		
$n=4$	2.9284	4.0039	3.8577	4.0064	4.0294?	4.0415?
$n=5$	3.9460					
$n=6$						

¹¹ Déjardin, Can. J. Research 7, 556 (1932).

¹² Bowen, Phys. Rev. 31, 34 (1928).

¹³ Edlén, Zeits. f. Physik 93, 726 (1935).

¹⁴ Houston, Phys. Rev. 33, 297 (1929).

¹⁵ Bowen, Phys. Rev. 46, 377 (1934).

P II. The 1S_0 term, however, appears to be incorrect. The forbidden transitions in P II which might be expected in nebulae or novae are listed in Table VI. They do not correspond to any of the present unknown lines found in such sources.

It will be noticed that in the ions that are iso-electronic with Si I low odd terms are predicted which arise from the electron configurations sp^3

and $s^2p \cdot 3d$. From the first configuration we get $^1P^0, ^1D^0, ^3S^0, ^3P^0, ^3D^0$ and from the second $^1P^0, ^1D^0, ^1F^0, ^3P^0, ^3D^0, ^3F^0$, terms. The singlet and triplet P 's and D 's have been the subject of some controversy particularly in Si I and P II as it has been impossible to be sure which terms arise from which of the two possible configurations. In the first short period of the periodic table this

TABLE VIII. Term table P II.

$3s^23p^2\ ^3P_0$		§158,550.0	3P_1		§53,246.4
3P_1	166.6	§158,383.4	3P_2	247.3	§52,999.1
3P_2	303.7	§158,079.7	$3d\ ^1D_2^0$	52,586.9	
$3s^23p^2\ ^1D_2$	149,677.4		$4p\ ^3S_1$		§52,547.5
$3s^23p^2\ ^1S_1$	136,973.6		$3d\ ^1F_3^0$	51,186.5	
$sp^3\ ^3D_1^0$		§93,298.2	$4p\ ^1D_2$	50,625.8	
$^3D_2^0$	21.1	§93,277.1	$3d\ ^1P_1^0$	50,178.2	
$^3D_3^0$	34.8	§93,242.3	$4p\ ^1P_1$	50,132.6	
$sp^3\ ^3P_2^0$	-48.8	§81,785.1	$sp^3\ ^3S_1^0$		§48,295.1 ($3d\ ^3P_1^0$)
$^3P_1^0$	-11.2	§81,736.8	10_2	164.6	§48,258.7? ($3d\ ^3P_2^0$)
$^3P_0^0$		§81,725.6	$20_2, 3$		48,093.1?
$sp^3\ ^1D_2^0$	80,839.2		$4p\ ^1S_0$	47,435.2	
$4s\ ^3P_0^0$		§71,951.0	$5s\ ^3P_0^0$	111.3	§35,204.6
$^3P_1^0$	146.1	§71,804.9	$^3P_1^0$	435.3	§35,093.3
$^3P_2^0$	381.0		$^3P_2^0$		§34,658.0
$4s\ ^1P_1^0$	69,656.5	§71,423.9	$5s\ ^1P_1^0$	34,116.2	
$3d\ ^3F_2^0$		66,641?	$4d\ ^3F_2^0$	174.6	33,594.1
$^3F_3^0$	184	66,457?	$^3F_3^0$	262.1	33,419.4
$^3F_4^0$		—	$^3F_4^0$		33,157.3
$sp^3\ ^1P_1^0$	55,751.6	§55,383.3	$4d\ ^3D_3^0$		31,216.4
$4p\ ^3D_1$	173.5	§55,209.8	$^3P_0^0$	232.5	§31,181.3 (x_0)
3D_2	328.7	§54,881.1	$^3P_1^0$	349.9	§30,948.8 (X_1)
3D_3		§54,917.7	$^3P_2^0$		§30,598.9 (x_1)
$3d\ ^3P_2^0$	-123.1	54,794.6	$^3D_2^0$	-45.5	§30,659.8 (x_2)
$^3P_1^0$		54,614.2	$^3D_1^0$		§30,614.3 (x_3)
$^3D_1^0$	117.4	§54,496.8 ($3d\ ^3D_1$)	$4d\ ^1D_2^0$	28,938.0	
$^3D_2^0$	48.2	§54,448.6 ($3d\ ^3D_2$)	$4d\ ^1P_1^0$	26,820.9	
$3d\ ^3P_0^0$		54,331?	$4d\ ^1F_3^0$	26,785.6	
$4p\ ^3P_0$	78.1	§53,324.5	$6s\ ^3P_0^0$	53	21,117
			$^3P_1^0$	514	21,064
			$^3P_2^0$		20,550
			$6s\ ^1P_1^0$	20,491.6	19,458.1
			$5d\ ^3P_2^0$		13,030.2
			$6d\ ^3P_2^0$		

HIGH EVEN TERMS				HIGH EVEN TERMS			
		j VALUE	PROBABLE TERM DESIGNATION			j VALUE	PROBABLE TERM DESIGNATION
1	28,924.5?	1	$5p\ ^3S_1?$	11	26,467.6	2	$4f\ ^1D_2?$
2	28,310.4	2		12	26,415.9	2, 3	
3	27,723.8	1, 2		13	26,386.4	2	
4	27,631.1	2	$5p\ ^1D_2?$	14	26,343.1	2	
5	27,600.4	2		15	26,314.0	3	$4f\ ^1F_3?$
6	27,580.0	1	$5p\ ^1P_1?$	16	26,195.3	2, 3	
7	27,229.5	2		17	26,178.8	1	
8	26,948.1	1, 2		18	26,153.0	2	
9	26,916.9	2		19	25,908.5?	0, 1	$5p\ ^1S_0?$
10	26,897.9?	?		20	25,131.2?	1	

TABLE IX.—Continued.

<i>I</i>	λ (vac)	ν (cm ⁻¹)	CLASSIFICATION	<i>I</i>	λ (vac)	ν (cm ⁻¹)	CLASSIFICATION
10	*1301.878	76,812.1	$3p\ ^3P_0 - sp^3\ ^3P_1^0$	5d	††965.43	103,581	$\{3p\ ^3P_2 - 3d\ ^3D_0^0$
8	1294.645	77,241.3	$3p\ ^3P_2 - sp^3\ ^1D_2^0$	5	964.940	103,633.3	$3p\ ^3P_1 - 3d\ ^3P_1^0$
6	1289.590	77,544.0	$3p\ ^3P_1 - sp^3\ ^1D_2^0$	2	963.815	103,754.3	$3p\ ^3P_2 - 3d\ ^3D_0^0$
5	1284.352	77,860.3	$3p\ ^1D_2 - 4s\ ^3P_1^0$	1	963.627	103,774.5	$3p\ ^3P_0 - 3d\ ^3P_1^0$
0	1278.094	78,241.5	$3p\ ^1D_2 - 4s\ ^3P_2^0$	3	962.576	103,887.9	$3p\ ^3P_1 - 3d\ ^3D_1^0$
10	§§1249.818	80,011.6	$3p\ ^1D_2 - 4s\ ^1P_1^0$	3	962.133	103,935.7	$3p\ ^3P_0 - 3d\ ^3D_1^0$
10	1231.178	81,223.0	$3p\ ^1S_0 - sp^3\ ^1P_1^0$	1	961.062	104,051.5	$3p\ ^3P_1 - 3d\ ^3P_0^0$
1	1204.302	83,035.7	$3p\ ^1D_2 - 3d\ ^3F_2^0$	1d	945.17	105,800	$3p\ ^3P_1 - 3d\ ^1D_2^0$
0	1201.67	83,218	$3p\ ^1D_2 - 3d\ ^3F_3^0$	1	910.876	109,784.4	$3p\ ^3P_2 - sp^3\ ^3S_1^0$
10	*1159.085	86,274.9	$3p\ ^3P_2 - 4s\ ^3P_1^0$	1	910.587	109,819.2	$3p\ ^3P_2 - 1^0$
10	*1156.968	86,432.8	$3p\ ^3P_1 - 4s\ ^3P_0^0$	1	908,361	110,088.3	$\{3p\ ^3P_1 - sp^3\ ^3S_1^0$
10	*1155.020	86,578.6	$3p\ ^3P_2 - 4s\ ^3P_1^0$	1	908,050	110,126.0	$3p\ ^3P_2 - 2^0$
10	*1153.997	86,655.3	$3p\ ^3P_2 - 4s\ ^3P_2^0$	1	907,841	110,151.4	$3p\ ^3P_1 - 1^0$
10	*1152.803	86,745.1	$3p\ ^3P_0 - 4s\ ^3P_1^0$	1	907,841	110,151.4	$3p\ ^1S_0 - 4d\ ^1P_1^0$
3	1152.134	86,795.4	$3p\ ^1S_0 - 3d\ ^1P_1^0$	1	906,987	110,255.1	$3p\ ^3P_0 - sp^3\ ^3S_1^0$
10	*1149.960	86,959.5	$3p\ ^3P_1 - 4s\ ^3P_2^0$	1	865,436	115,548.6	$3p\ ^1D_2 - 4d\ ^1F_3^0$
1	1130.925	88,423.2	$3p\ ^3P_2 - 4s\ ^1P_1^0$	0	813,768	122,885.1	$3p\ ^1D_2 - 5s\ ^1P_1^0$
1	1124.945	88,893.2	$3p\ ^3P_0 - 4s\ ^1P_1^0$	0	813,082	122,988.8	$3p\ ^3P_1 - 5s\ ^3P_1^0$
1B	1091.42	91,624	$3p\ ^3P_2 - 3d\ ^3F_2^0$	0	811,901	123,167.7	$3p\ ^3P_2 - 5s\ ^3P_2^0$
2	1093.627	91,438.9	$3p\ ^3P_2 - 3d\ ^3F_3^0$	0	811,080	123,292.4	$3p\ ^3P_1 - 5s\ ^3P_1^0$
10	†1064.783	93,915.8	$3p\ ^1D_2 - sp^3\ ^1P_1^0$	0	*810,237	123,420.6	$3p\ ^3P_2 - 5s\ ^3P_2^0$
2	1030.049	97,082.8	$3p\ ^1D_2 - 3d\ ^1D_2^0$	0	808,241	123,725.4	$3p\ ^3P_1 - 5s\ ^3P_1^0$
10	1015.458	98,480.1	$3p\ ^1D_2 - 3d\ ^1F_3^0$	0	*784,803	127,420.5	$3p\ ^3P_2 - 4d\ ^3D_2^0$
00	977.258	102,327.1	$3p\ ^3P_2 - sp^3\ ^1P_1^0$	1	*784,479	127,473.1	$\{3p\ ^3P_2 - 4d\ ^3P_2^0$
0	974.36	102,633	$3p\ ^3P_1 - sp^3\ ^1P_1^0$	0	*783,750	127,591.7	$3p\ ^3P_2 - 4d\ ^3D_1^0$
3B	972.807	102,795.3	$3p\ ^3P_0 - sp^3\ ^1P_1^0$	1B	*782,977	127,717.6	$3p\ ^3P_0 - 4d\ ^3P_0^0$
00	972.19	102,860	$3p\ ^1S_0 - 5s\ ^1P_1^0$	1B	*782,630	127,774.2	$3p\ ^3P_1 - 4d\ ^3D_0^0$
3	969.355	103,161.3	$3p\ ^3P_2 - 3d\ ^3P_2^0$	1			$3p\ ^3P_1 - 4d\ ^3D_1^0$
3	968.179	103,286.6	$3p\ ^3P_2 - 3d\ ^3P_1^0$				
			$\{3p\ ^3P_1 - 3d\ ^3P_2^0$				
5	966.519	103,464.0	$\{3p\ ^3P_2 - 3d\ ^3D_1^0$				

§ Since classifying these lines I have discovered that they appear in Moore, *A Multiplet Table of Astrophysical Interest* (Princeton, New Jersey).

† This list contains all lines classified in the Schumann Region.

* These lines have been classified by I. S. Bowen, *Phys. Rev.* **29**, 510 (1927).

§§ The classification of this line was originally suggested to me by Dr. Bowen.

†† The second order of this line coincides exactly with C I 1930,900; hence the separation could not be accurately measured.

‡ This line coincides with a line of P IV. The other members of this multiplet are very weak in my exposures.

D lines measured by Déjardin, *Can. J. Research* **7**, 556 (1932).

S lines measured by Saltmarsh, *Proc. Roy. Soc.* **A108**, 332 (1925).

III lines have been classified in P III but are assigned by Déjardin to P II.

B lines blend with other lines classified as P II.

r lines shade to red

Vb and vb very broad.

u lines not sharp.

s lines sharp.

difficulty does not occur as there, for example, electron transitions of the type $2s^22p^2 \rightarrow 2s2p^3$ may be clearly distinguished from those of the type $2s^22p^2 \rightarrow 2s^22p3d$ inasmuch as in the latter case the total quantum number changes from 2→3. It appears from the present data that Kiess¹⁶ assumption in Si I, that the designation here given (and as originally given by Fowler¹⁷) should be reversed, is not valid. The fact that the $sp^3\ ^1D\ ^3D$ combine with the $4f$ terms is not sufficient evidence for his proposed change because of the term sequences found which start with the $3d$ terms. The $4d\ ^3F$ terms which are known in P II and S III can without question be grouped with those here designated as $4d\ ^3D$ and 3P . In the C I isoelectronic sequence the $3d$ terms are almost hydrogen like; it is therefore more than likely that the large quantum defects associated with the $sp^3\ ^3D$ in P II and S III preclude the

other possibility. Two electron jumps of the type $sp^4 \rightarrow 4f$ are furthermore quite common and might therefore be expected in Si I and P II.

TABLE X. Irregular doublet law.

	$3p\ ^3P_2 - 3d\ ^3D_3$	$3p\ ^3P_2 - 3d\ ^3P_2$	$3p\ ^3P_2 - sp^3\ ^3S_1$
Si I	54,033	56,280	(80,300)*
P II	103,633	103,161	109,784
S III	146,915	142,294	137,231
Cl IV	186,005	180,302	163,380
	$3p\ ^3P_2 - sp^3\ ^3P_2$	$3p\ ^3P_2 - sp^3\ ^3D_3$	
Si I	50,277	45,099	19,738
P II	76,296	64,837	18,430
S III	97,914	83,267	18,261
Cl IV	118,915	101,528	
	$3p\ ^3P_1 - 3p\ ^1S_0$	$3p\ ^3P_2 - 3p\ ^1D_2$	
Si I	15,318	6,076	2,327
P II	21,410	8,403	2,084
S III	5,324 × 2	10,487	1,938
Cl IV	32,058	12,425	

* Estimated value.

¹⁶ Kiess, *Bur. Standards J. Research* **11**, 775 (1933).

¹⁷ Fowler, *Proc. Roy. Soc.* **A123**, 422 (1929).

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his original classifications. Since coming to Sweden the analysis has been greatly aided by Professor Manne Siegbahn's kindness in opening his laboratories and library to my use. Docent Bengt Edlén has been very helpful in discussing several difficult points. I wish also to thank the American Scandinavian Foundation for having given me the opportunity of continuing this work at Uppsala.

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The Periodic Emission of Light from a Discharge Tube Excited at High Frequency

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An investigation was made of the character of the light emitted by a discharge tube containing air at low pressure when the tube was driven by a high frequency oscillator. A vacuum photoelectric cell operated with an alternating driving potential of high frequency was used as a receiver. It was found that the light was fluctuating in character even when the driving frequency was as high as 10 megacycles per second, and that the average illumination lagged behind the driving potential by an angular amount which for the higher frequencies was a considerable fraction of a

cycle. This indicated that the light emitted from the excited atoms persisted after excitation for a time which was of the order of magnitude of 5×10^{-8} second. By using various path lengths between the source and the receiver the apparatus was also used to make a rough determination of the velocity of light. The result obtained agreed with the accepted value of light velocity within the experimental error of the apparatus, which was approximately 5 percent.

THE purpose of this research was to study the fluctuating light produced when a discharge tube was driven by a high frequency alternating current. The discharge tube was of the ordinary Geissler type with cold electrodes. It had a constricted capillary, 5 cm long and 1 mm in diameter, and contained air at low pressure. The high frequency source was a 50-watt Hartley oscillator.

As a preliminary experiment a tube of this type was driven at various frequencies up to 10^7 cycles per second, and the discharge observed visually in a rotating mirror. Below 3×10^6 cycles per second the light from the tube was seen to be definitely of a flickering variety, but at higher frequencies it was not possible to rotate the mirror fast enough to distinguish flicker.

In order to extend the observations to higher frequencies a high vacuum photoelectric cell was used as a receiver of the light. The polarizing

potential for the cell was alternating in character, and was derived either from the oscillator driving the discharge tube, or from an oscillator of exactly double the frequency. Either of these methods of operating a photoelectric cell causes it to be "dead" during half of each cycle, and hence if light which flickers at the same frequency as that at which the cell is driven falls on the cell, the photoelectric current should depend on the relative phase of the light and the polarizing potential.

In the method using a single oscillator, the oscillator was coupled to two tuned circuits, one driving the discharge tube and the other the photoelectric cell. The circuit driving the tube was in series with an 800-volt storage battery, so that the tube was actually driven by an a.c. superimposed on a d.c. The purpose of the battery was to neutralize one-half of the a.c. wave, and thus cause the discharge to occur only once per complete cycle instead of twice. Re-