

## The Spectra of Phosphorus

### Part II: The Spectra of Doubly, Triply and Quadruply Ionized Phosphorus (P III, P IV, P V). Additions and Corrections to P II

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Data taken from spectrograms using a vacuum spark containing red phosphorus supplemented by spectrograms previously described have enabled a complete revision and extension of the spectra of P III, P IV, and P V. Certain quintet terms in P II have also been located. In P III nineteen new terms have been found which classify fifty-nine lines. Six of these terms replace previous terms which have proved erroneous. The ionization potential is found to be  $30.012 \pm 0.003$  volts. Tentative intercombinations between the doublet and quartet systems are given. In P IV twenty-three new terms have been found which

classify fifty-one lines. Several intercombinations have been located between the singlet and triplet systems. The various series are badly perturbed. The ionization potential is  $51.106 \pm 0.013$  volts. In P V fourteen new terms have been located which classify twenty lines. The series are very regular and give an ionization potential of  $64.698 \pm 0.003$  volts. The previous data have been entirely revised in view of new measurements and complete term tables as well as complete lists of lines now classified in the Schumann region are given.

IN Part I<sup>1</sup> of this paper data obtained from spectrograms taken at the Massachusetts Institute of Technology on the two meter vacuum spectrograph designed by Compton and Boyce<sup>2</sup> and built with funds obtained from the Carnegie Institute of Washington were described. Those spectra were obtained by means of a Geissler tube discharge in phosphorus vapor. Since that time additional spectrograms using a hot spark discharge between Be electrodes containing red phosphorus have been obtained with a one-meter grazing incidence vacuum spectrograph located in Professor Siegbahn's laboratory in the Physical Institute at Uppsala, Sweden. In the region where the new and old spectrograms overlap further information has been obtained concerning the segregation of the various lines into the stage of ionization to which they belong. The Uppsala hot spark equipment gives virtually no lines due to P II and none which may be attributed to P I. P III is generally weak but P IV and P V are much enhanced while the optical spectra of the *L* shell have now been traced as far as the Li I spectrum, P XIII.<sup>3</sup> These higher spectra will be described in detail

in the future. The new spectrograms have shown that several of the lines previously used to fix the tentative term designated as  $1_2^\circ$  in P II are in reality P III or P IV. This term which was listed tentatively is therefore not real and should be deleted from the P II term table. The tentative  $3d^3F$  and  $^1F$  terms must likewise be withdrawn as several lines which gave rise to them have now been found to fit other assignments. The line 4814.2A was included in the P II classification through an error and should also be deleted.

It is furthermore possible to classify three lines to give four new quintet terms in P II listed in Table I. The  $3s3p^3\ ^5S - 3s3p^24s\ ^5P$  transitions apparently are partially blended with other lines and will not be added at this time. The absolute value of the  $3s3p^3\ ^5S$  may be estimated at  $106,100\text{ cm}^{-1}$  by assuming a Rydberg denominator of 2.80 for the  $3s3p^23d\ ^5P_{5/2}$  (the limit is

TABLE I. *Ultraviolet quintet transitions in P II.*

INT.	$\lambda$ (vac.)	$\nu$ ( $\text{cm}^{-1}$ )	CLASSIFICATION
1	927.771	107,785.2	$3s3p^3\ ^5S^\circ - 3s3p^2 \cdot 3d\ ^5P_{1/2}$
1	928.550	107,694.7	$^5S^\circ - ^5P_{3/2}$
1	929.642	107,568.2	$^5S^\circ - ^5P_{5/2}$
		$3s3p^3\ ^5S_{3/2}^\circ$	$106,100.0$
		$3s3p^2 \cdot 3d\ ^5P_{1/2}$	$-1,685.2$
			$-90.5$
			$^5P_{3/2} - 1,594.7$
			$-126.5$
			$^5P_{5/2} - 1,468.2$

<sup>1</sup> H. A. Robinson, Phys. Rev. **49**, 297 (1935).

<sup>2</sup> K. T. Compton and J. C. Boyce, Rev. Sci. Inst. **5**, 218 (1934).

<sup>3</sup> These data were briefly presented to the American Physical society at Atlantic City in December, 1936 by the author.

$sp^2\ ^4P_{5/2}$  of P III). The separation of these terms is calculated to be  $-89.1\text{ cm}^{-1}$  and  $-125.1\text{ cm}^{-1}$  if we use the Goudsmit and Humphreys' equations.<sup>4</sup>

#### DOUBLY IONIZED PHOSPHORUS P III

The spectrum of P III has been treated by Bowen and Millikan<sup>5-7</sup> and Saltmarsh<sup>8</sup> in the Schumann and visible regions, respectively. The classifications due to Bowen have been confirmed and extended; several of the terms due to Miss Saltmarsh must be rejected. These terms are the  $s^26s$  and  $s^27s\ ^2S$ , the  $s^25p\ ^2P$  and the  $s^25d$  and  $s^26d\ ^2D$ . These terms were found by estimation from the quantum defects and were tied to the lower terms by two lines purporting to be the  $s^24p\ ^2P-s^25d\ ^2D$  transitions. On the basis of the new measurements the  $4p\ ^2P$  separation as given by this pair of lines was incorrect by  $10\text{ cm}^{-1}$  an error very much greater than the accuracy of the present measurements. The  $s^25p\ ^2P-s^26s\ ^2S$  transitions are furthermore necessarily P II lines<sup>9</sup> and were so classified in Part I ( $\lambda 6043.45$  and  $6024.14$ ). Certain other of the transitions involve lines which are coincident with lines in the argon spectrum. Since this element is an impurity in Geuter's<sup>10</sup> list these other transitions may likewise be open to question. It has furthermore been possible to extend these two series using only lines which may definitely be attributed to P III in both the visible and Schumann regions and to completely tie them in with the rest of the terms

TABLE II. Rydberg denominators in P III.  
Terms to  $3s^2\ ^1S_0$  in P IV.

TOTAL QUANTUM NUMBER	$3s^2\ ns\ ^2S$	$np\ ^2P_{3/2}$	$nd\ ^2D$	$nf\ ^2F$	$ng\ ^2G$
$n=3$		2.0600	2.7952		
4	2.8058	3.2804	3.7333	3.9089	
5	3.8323	4.4158	4.8010	4.9453	4.9999
6	4.8385		5.8050	5.9510	6.0009
7					6.9995

<sup>4</sup> S. Goudsmit and C. J. Humphreys, Phys. Rev. **31**, 960 (1923).

<sup>5</sup> R. A. Millikan and I. S. Bowen, Phys. Rev. **25**, 600 (1925).

<sup>6</sup> I. S. Bowen, Phys. Rev. **31**, 34 (1928).

<sup>7</sup> I. S. Bowen, Phys. Rev. **39**, 8 (1932).

<sup>8</sup> M. O. Saltmarsh, Proc. Roy. Soc. **A108**, 332 (1925).

<sup>9</sup> Desjardin, Can. J. Research **7**, 556 (1928).

<sup>10</sup> P. Geuter, Zeit. f. wiss. Phot. **5**, 1 (1907); (all phosphorus lines in this paper above 2500A taken from this paper except as otherwise noted).

without the ambiguities arising from the previous classification.

While most of the new terms found in this analysis are doublets certain additions have been possible in the quartet system. These terms arise from the  $3s3p4f$  configuration. It has not been possible to find the complete triad of  $^4DFG$  terms predicted by the Hund theory mainly because of the inability to completely determine several of the quartets arising from the  $sp\cdot p$  and  $sp\cdot d$  configurations.

Extra terms can be found which arise mainly from the displaced doublet system coming from configurations of the  $sp\cdot x$  type. A very intense search for these terms has revealed a number of dubious sets which do not combine among themselves as well as one might expect. The term listed as  $^21_{3/2}^{\circ}$  may be either the  $sp\cdot d\ ^2P_{3/2}$  or the  $sp\cdot d\ ^2D_{3/2}$ . These further identifications will not be published now pending further investigation in the visible.

The intercombinations given must be considered as tentative classifications. They are consistent with regard to position and intensity with the same transitions in Al I<sup>11</sup> and with certain new classifications in P IV. This latter point is discussed in detail in the following section of this paper. In view of the latest results on the analogous spectrum of N III<sup>12</sup> further intercombinations may be expected among the  $sp\cdot 4f$  and  $sp\cdot 5g$  doublets and quartets. Rydberg denominators for the doublet system are listed in Table II. The limit has been set by using the  $g$  series. The irregularity in the  $6g\ ^2G$  is analogous to a similar irregularity in N III. The new classifications comprise fifty-nine lines which locate nineteen new terms. These are listed in Table III and Table IV, respectively. The ionization potential works out to be  $30.012 \pm 0.003$  electron volts.

#### TRIPLY IONIZED PHOSPHORUS P IV

The original classification of this spectrum has been given by Bowen, Millikan<sup>7, 5</sup> and others.<sup>8</sup> In the original Geissler tube exposures this spectrum was fairly weak. The Uppsala spectrograms above 1000A are also of less intensity than

<sup>11</sup> F. Paschen, Ann. d. Physik **71**, 537 (1923); R. A. Sawyer and F. Paschen, Ann. d. Physik **84**, 1 (1927).

<sup>12</sup> B. Edlén, Zeits. f. Physik **98**, 561 (1936).

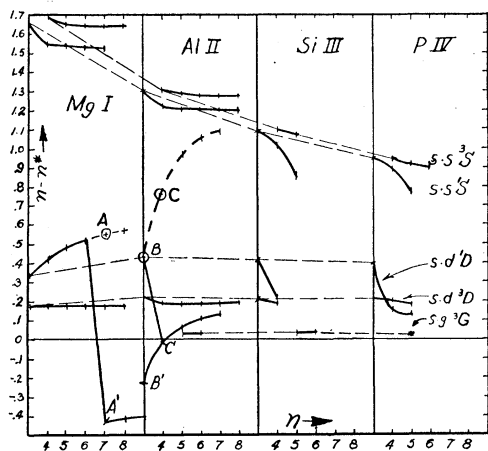


FIG. 1.  $n - n^*$  vs.  $n$  for the  $s$ ,  $d$  and  $g$  series of the Mg I-like isoelectronic sequence. The  $1D$  series is badly perturbed by the  $p^2 1D_2$  term which has inserted itself into the series. The dotted extensions give the series as in Bacher and Goudsmit. The perturbing term according to Shenstone and Russell† is the one at  $A$  and  $B$  (or  $C$ ). Removing this term the quantum defects continue from  $A'$  and  $B'$  (or  $C'$ ). The singlet then lies above the triplet as would be expected.

those below this limit due to the optical properties of the grazing incidence spectrograph. As a result certain lines (marked  $B$ ) in Table VII are taken from Bowen who was able to measure them with much greater accuracy than has been possible in this investigation. The group at 656A is badly mixed up with higher orders of strong oxygen lines and has also been taken from Bowen's work.

P IV is a Mg I-like spectrum having  $2p^6 \cdot 3s^2 1S_0$  as a ground state. Spectra of this type are notorious in giving series which are badly perturbed due to interactions between terms going to the  $2p^6 3s^2 S$  limit and terms going to the  $2p^6 3p^2 P$  limit in P V. These perturbations are still apparent in this case as may be recognized from the irregularities in the Edlén-type diagrams given in Figs. 1 and 2. In a diagram of this type the quantum defect ( $n - n^*$ ) is plotted against the total quantum number ( $n$ ) for the

TABLE III. *New classifications in P III.*

INT.	$\lambda$ (air)	$\nu$ (cm <sup>-1</sup> )	CLASSIFICATION	INT.	$\lambda$ (vac.)	$\nu$ (cm <sup>-1</sup> )	CLASSIFICATION
1	5203.85	19,211.2	$4d^2 D - 5p^2 P_{3/2}$	6	1618.665§	61,779.31	$2D_{3/2} - 2F$
8 II	4587.90	21,790.4	$4f^2 F - 5d^2 D$	9	1504.719§	66,457.6	$s p^2 2D_{3/2} - 4p^2 P_{1/2}$
8	3978.27	25,129.5	$4f^2 F - 5g^2 G$	10	1502.273§	66,565.8	$2D_{5/2} - 2P_{3/2}$
3	3283.20	30,449.3	$p^3 2D_{3/2} - 3d^2 D_{3/2}$	7	1501.551§	66,597.8	$2D_{3/2} - 2P_{3/2}$
2	3280.20	30,477.2	$4d^2 D - 5f^2 F$	5	1492.031	67,022.7	$4s^2 S_{1/2} - 2^1_{3/2} \circ ?$
3	3277.80	30,499.5	$p^3 2D_{5/2} - 3d^2 D_{5/2}$	0	1471.218	67,970.9	$3d^2 D - 2^1_{3/2} \circ$
1	2686.58	37,210.0	$4f^2 F - 6g^2 G$	2	1447.512	69,084.1	$4s^2 S - s p \cdot s^2 P_{3/2}$
II	2636.77	37,913.8	$s p^2 2P_{3/2} - p^3 2D_{3/2}$	2	1430.409	69,910.1	$s p^2 2S - p^3 2P_{3/2}$
7	2632.62	37,973.7	$2P_{3/2} - 2D_{5/2}$	1	1429.242	69,967.2	$2S - p^3 2P_{1/2}$
6	2611.05	38,287.3	$2P_{1/2} - 2D_{3/2}$	8	1381.633	72,378.1	$s p^2 2D_{5/2} - p^3 2D_{3/2}$
	$\lambda$ (vac.) <sup>l</sup>			10	1381.111	72,405.5	$2D_{3/2} - 2D_{3/2}$
1	2428.58§	41,176.3	$s p^2 2S - s^2 4p^2 P_{3/2}$	10	1380.464	72,439.4	$2D_{5/2} - 2D_{5/2}$
1	2420.52§	41,313.4	$2S - 2P_{1/2}$	5	1379.873	72,470.4	$2D_{3/2} - 2D_{5/2}$
0	2248.31	44,477.8	$4f^2 F - 7g^2 G$	1	1374.780	72,738.9	$3s3p3d^4 D_{7/2} - 3s3p4f^4 D_{7/2}$
1	1757.68	56,893.2	$3p^2 P_{3/2} - s p^2 4P_{5/2}$	3	1372.711	72,848.5	$4D_{5/2} - 4D_{3/2}$
0	1756.82	56,921.1	$2P_{1/2} - s p^2 4P_{1/2}$	1	1372.01	72,885.7	$4D_{3/2} - 4D_{5/2}$
1	1696.92	58,930.4	$4p^2 P_{3/2} - 5d^2 D$	0	1370.39	72,971.8	$4D_{1/2} - 4D_{3/2}$
1	1693.03	59,065.8	$2P_{1/2} - 2D$	0	1354.957	73,803.1	$4s^2 S_{1/2} - 5p^2 P_{3/2}$
0	1678.12	59,590.6	$4p^2 P_{3/2} - 6s^2 S$	3	1349.110	74,122.9	$3s3p3d^4 P_{1/2} - 3s3p4f^4 D_{3/2}$
00	1674.26	59,728.1	$2P_{1/2} - 2S$	0	1348.449	74,159.3	$4P_{1/2} - 4D_{1/2}$
3	1647.546	60,696.3	$s p^2 2P_{3/2} - p^3 2P_{3/2}$	0	1347.508	74,211.1	$3s3p3d^4 P_{3/2} - 3s3p4f^4 D_{5/2}$
2	1645.914	60,756.5	$2P_{3/2} - 2P_{1/2}$	3	1346.998	74,239.2	$4P_{3/2} - 4D_{3/2}$
1	1637.377	61,073.3	$2P_{1/2} - 2P_{3/2}$	10	1344.900§	74,355.0	$\left\{ \begin{array}{l} 3s3p3d^4 P_{5/2} - 3s3p4f^4 D_{7/2} \\ 3p^2 P_{3/2} - s p^2 2D_{3/2} \end{array} \right.$
2	1635.799	61,132.2	$2P_{1/2} - 2P_{1/2}$				
6	1618.944§	61,768.65	$3d^2 D_{5/2} - 4f^2 F$				

II, Blend with P II.

IV, Blend with P IV.

§, Lines classified by Bowen, references 5, 6 and 7.

† A. Shenstone and H. N. Russell, Phys. Rev. 39, 426 (1932).

d, Line double.

?, Line nebulous.

l, From here on this list contains all lines classified as P III.

several members of an isoelectronic sequence. When no perturbations are present the series show regularities along the sequence like that found for the  $s \cdot s \ ^3S$  series in Fig. 1. Every one of the other series shows evidence of some outside effect; in all cases the effect can be directly traced to terms in the displaced series. Table V lists the Rydberg denominators for the several series. The limit has been calculated by extrapolation of the  $3s5g \ ^3G$  from Al II.<sup>13</sup>

The extension of the singlet system as given here contains only lines which definitely belong to P IV. They have been carefully sorted out by using self-induction in the various circuits. The line at 843.984A appears to be an exception to this but it is closely surrounded by stronger

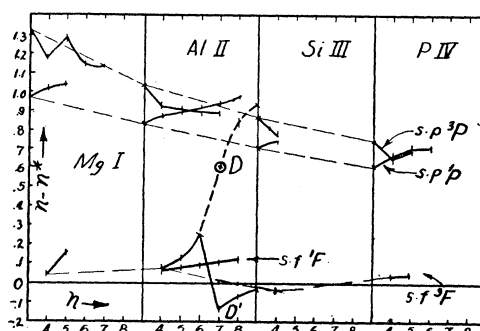


FIG. 2.  $n-n^*$  vs.  $n$  for the  $p$  and  $f$  series in the Mg I-like isoelectronic sequence. The  $^3F$  series is perturbed by the  $3p \cdot 3d \ ^3P$  which has inserted itself into the Al II series at  $D$ . Removing this term the quantum defect continues from  $D'$ . In this case the term displaces the series partly (Al II) upwards. The irregularities in the  $s \cdot p \ ^3P$  series are due both to the  $3p4s \ ^3P$  and  $3p3d \ ^3P$ .

TABLE III.—Continued.

INT.	$\lambda$ (vac.)	$\nu$ (cm <sup>-1</sup> )	CLASSIFICATION	INT.	$\lambda$ (vac.)	$\nu$ (cm <sup>-1</sup> )	CLASSIFICATION
15	1344.343§	74,385.8	$3p \ ^2P_{3/2} - sp^2 \ ^2D_{5/2}$ $3s3p3d \ ^4P_{5/2} - 3s3p4f \ ^4D_{5/2}$	1	909.846	109,908.7	$sp^2 \ ^2D_{5/2} - 2 \ ^1_{3/2} \ ^\circ$
1	1343.687	74,422.1	$3s3p3d \ ^4P_{5/2} - 3s3p4f \ ^4D_{5/2}$	8	859.667§	116,324.1	$3p \ ^2P_{3/2} - 3d \ ^2D_{5/2}$
2	1337.710	74,754.6	$3d \ ^2D_{5/2} - 5p \ ^2P_{3/2}$	0	859.411§	116,358.8	$sp^2 \ ^4P_{5/2} - 3s3p3d \ ^4P_{5/2}$
1	1337.498	74,766.5	$3d \ ^2D_{3/2} - \ ^2P_{3/2}$	1	858.139	116,531.2	$^4P_{5/2} - \ ^4P_{3/2}$
10	1334.866§	74,913.9	$3p \ ^2P_{1/2} - sp^2 \ ^2D_{3/2}$	2	856.963	116,691.2	$^4P_{3/2} - \ ^4P_{5/2}$
1	1325.509	75,442.7	$sp^2 \ ^2P_{3/2} - 2 \ ^1_{3/2} \ ^\circ$	5	855.618	116,874.6	$3p \ ^2P_{1/2} - 3d \ ^2D_{3/2}$
0	1318.91	75,820.1	$^2P_{1/2} - 2 \ ^1_{3/2} \ ^\circ$	1	854.855	116,978.9	$sp^2 \ ^4P_{3/2} - 3s3p3d \ ^4P_{1/2}$
00	1290.134	77,511.3	$sp^2 \ ^2P_{1/2} - sp \cdot s \ ^2P_{3/2}$	1	854.223	117,065.6	$^4P_{1/2} - \ ^4P_{3/2}$
0	1283.949	77,884.7	$^2P_{3/2} - \ ^2P_{3/2}$	0	853.346	117,185.8	$^4P_{1/2} - \ ^4P_{1/2}$
1	1210.600	82,603.7	$sp^2 \ ^2P_{1/2} - 5p \ ^2P_{3/2}$	5	852.679§	117,277.4	$3p \ ^2P_{3/2} - 4s \ ^2S$
2	1093.627	91,438.9	$sp^2 \ ^2S_{1/2} - 5p \ ^2P_{3/2}$	3d	848.636	117,836.2	$^2P_{1/2} - 4s \ ^2S$
4	1050.817	95,164.0	$sp^2 \ ^2D_{5/2} - p^3 \ ^2P_{3/2}$	1	848.445§	117,862.7	$sp^2 \ ^4P_{5/2} - 3s3p3d \ ^4D_{3/2}$
1	1050.518	95,191.1	$^2D_{3/2} - \ ^2P_{3/2}$	2d	848.023§	117,921.3	$^4P_{5/2} - \ ^4D_{5/2}$
4	1049.824	95,254.1	$^2D_{3/2} - \ ^2P_{1/2}$	3d IV	847.658§	117,972.1	$^4P_{5/2} - \ ^4D_{7/2}$
10	1003.592§	99,642.1	$3p \ ^2P_{3/2} - sp^2 \ ^2S$	0 IV	846.494§	118,134.3	$^4P_{3/2} - \ ^4D_{1/2}$
8	998.000§	100,200.4	$^2P_{1/2} - \ ^2S$	1 IV	846.125§	118,185.8	$^4P_{3/2} - \ ^4D_{3/2}$
4	977.888§	102,261.2	$sp^2 \ ^4P_{5/2} - p^3 \ ^4S$	1	845.656§	118,251.4	$^4P_{3/2} - \ ^4D_{5/2}$
3	974.776§	102,587.6	$^4P_{3/2} - \ ^4S$	1	845.047§	118,336.6	$^4P_{1/2} - \ ^4D_{1/2}$
3	972.807§	102,795.3	$^4P_{1/2} - \ ^4S$	1	844.635§	118,394.3	$^4P_{1/2} - \ ^4D_{3/2}$
1	964.251§	103,707.4	$sp^2 \ ^2D_{5/2} - 4f \ ^2F$	1 II	786.244§	127,186.9	$sp^2 \ ^4P_{5/2} - 3s3p4s \ ^4P_{2/2}$
1 IV	963.993	103,735.1	$^2D_{3/2} - \ ^2F$	1	785.392§	127,325.0	$^4P_{3/2} - \ ^4P_{1/2}$
5	921.863§	108,475.9	$3p \ ^2P_{3/2} - sp^2 \ ^2P_{1/2}$	1	783.752§	127,591.4	$^4P_{5/2} - \ ^4P_{5/2}$
5	918.706§	108,848.7	$^2P_{3/2} - \ ^2P_{3/2}$	1	782.977§	127,717.6	$^4P_{1/2} - \ ^4P_{3/2}$
4	917.130§	109,035.8	$^2P_{1/2} - \ ^2P_{3/2}$	1 II	781.726§	127,922.0	$^4P_{1/2} - \ ^4P_{5/2}$
5	913.989§	109,410.7	$^2P_{1/2} - \ ^2P_{1/2}$	1	581.898	171,851.4	$3p \ ^2P_{3/2} - 4d \ ^2D$
				00n	579.98	172,420	$^2P_{1/2} - \ ^2D$
				2nn	569.90 §	175,469	$3p \ ^2P_{3/2} - 5s \ ^2S$
				0	568.09	176,028	$^2P_{1/2} - \ ^2S$
				00	497.17	201,138	$3p \ ^2P_{3/2} - 6s \ ^2S$

<sup>13</sup> A recent extension of this (Mg I) isoelectronic sequence by Edlén (Zeits. f. Physik 103, 536 (1936)) includes the  $s \cdot 3d \ ^3D - s \cdot 4f \ ^3F$  transition for several of the more highly ionized elements.

TABLE IV. Complete term table for P III.

$s^2 3p \ ^2P_{1/2}^\circ$	243,290.0§			$s^2 5s \ ^2S_{1/2}$	67,249.0§		
$\quad \quad \quad \ ^2P_{3/2}^\circ$	242,730.4§	559.6		$s^2 4f \ ^2F^\circ$	64,636.8§		
$s p^2 \ ^4P_{1/2}$		206.5	186,370.7§	$3s 3p 4s \ ^4P_{1/2}^\circ$		185.9	58,836.6§
$\quad \quad \quad \ ^4P_{3/2}$		328.7	186,164.2§	$\quad \quad \quad \ ^4P_{3/2}^\circ$		405.9	58,650.7§
$\quad \quad \quad \ ^4P_{5/2}$			185,835.5§	$\quad \quad \quad \ ^4P_{5/2}^\circ$			58,244.8§
$s p^2 \ ^2D_{3/2}$	168,374.9§			$3s 3p 3d \ ^2 1_{3/2}^\circ$	58,435.9		
$\quad \quad \quad \ ^2D_{5/2}$	168,345.4§	29.5		$3s 3p 4s \ ^2P_{3/2}^\circ$	56,369.3		
$s p^2 \ ^2S_{1/2}$	143,088.8§			$s^2 5p \ ^2P_{1/2}^\circ$	—		
$s p^2 \ ^2P_{1/2}$	134,254.3§			$\quad \quad \quad \ ^2P_{3/2}^\circ$	51,650.5		
$\quad \quad \quad \ ^2P_{3/2}$	133,880.3§	374.0		$s^2 5d \ ^2D$	42,847.2		
$s^2 3d \ ^2D_{3/2}$	126,416.4§			$s^2 6s \ ^2S_{1/2}$	42,186.6		
$\quad \quad \quad \ ^2D_{5/2}$	126,405.1§	11.3		$s^2 5f \ ^2F^\circ$	40,383.6		
$s^2 4s \ ^2S_{1/2}$	125,455.5§			$s^2 5g \ ^2G$	39,507.3		
$s^2 4p \ ^2P_{1/2}^\circ$	101,914.3§			$3s 3p 4p \ ^4P_{1/2}$		116.9	33,351.1§
$\quad \quad \quad \ ^2P_{3/2}^\circ$	101,777.2§	137.1		$\quad \quad \quad \ ^4P_{3/2}$		250.3	33,234.2§
$p^3 \ ^2D_{3/2}^\circ$	95,967.6			$\quad \quad \quad \ ^4P_{5/2}$			32,983.9§
$\quad \quad \quad \ ^2D_{5/2}^\circ$	95,905.7	61.9		$3s 3p 4p \ ^4S$			31,950.6§
$p^3 \ ^4S^\circ$			83,575.4§	$s^2 6d \ ^2D$	29,307.2		
$p^3 \ ^2P_{3/2}^\circ$	73,182.8			$s^2 6f \ ^2F^\circ$	27,888.0		
$\quad \quad \quad \ ^2P_{1/2}^\circ$	73,123.0	— 59.8		$s^2 6g \ ^2G$	27,426.8		
$s^2 4d \ ^2D$	70,860.8§			$s^2 7g \ ^2G$	20,159.0		
$3s 3p 3d \ ^4P_{5/2}^\circ$		— 175.0	69,476.6§	$3s 3p 4f \ ^4D_{1/2}^\circ$		37.1	4,975.5
$\quad \quad \quad \ ^4P_{3/2}^\circ$		— 117.8	69,301.6§	$\quad \quad \quad \ ^4D_{3/2}^\circ$		29.0	4,938.4
$\quad \quad \quad \ ^4P_{1/2}^\circ$			69,183.8§	$\quad \quad \quad \ ^4D_{5/2}^\circ$		31.0	4,909.4
$3s 3p 3d \ ^4D_{1/2}^\circ$		53.3	68,029.2§	$\quad \quad \quad \ ^4D_{7/2}^\circ$			4,878.4
$\quad \quad \quad \ ^4D_{3/2}^\circ$		62.5	67,975.9§				
$\quad \quad \quad \ ^4D_{5/2}^\circ$		50.6	67,913.4§				
$\quad \quad \quad \ ^4D_{7/2}^\circ$			67,862.8§				

§ Terms from I. S. Bowen, references 5, 6, and 7. Slightly modified on the basis of new measurements.

higher order lines and may be obscured on the hot spark plates. Few singlet systems can be considered as definitely established in their entirety without some outside aid such as that gained from the Zeeman effect. It is nevertheless felt that the additions presented here with the possible exception of  $3p 3d \ ^1D_2$  and  $3p 3d \ ^1F_3$  may be considered to be well established. This part

of the classification has presented considerable difficulty due to the fact that in most cases the irregular doublet law breaks down due to the large perturbations mentioned before. The  $3p^2 \ ^1S_0$  and  $^1D$  are completely unidentifiable by this means. Some help is afforded by certain of the relations given by Bacher and Goudsmit.<sup>14</sup>

<sup>14</sup> R. Bacher and S. Goudsmit, Phys. Rev. **46**, 959 (1934).

TABLE V. Rydberg denominators in P IV.

TERM	n=3	4	5	6
$s^2 \cdot np \ ^3P_2$	2.2536	3.3382	4.3180	
$np \ ^1P_1$	2.3833	3.3464	4.3161	5.3138
$nd \ ^3P_2$	2.7940	3.8083	4.8494	
$nd \ ^1D_2$	2.6180	3.8648	4.8940	
$ns \ ^3S_1$		3.0608	4.0851	5.0945
$ns \ ^1S_0$	2.0586	3.1205	4.2396	
$nf \ ^3F_4$		3.9833	4.9826	
$ng \ ^3G$			4.9859	

TABLE VI. Irregular doublet law for  $3s^2 \ ^1S_0 - 3s3p \ ^3P$ , in P IV.

	$\nu$ (cm <sup>-1</sup> )	$\Delta\nu$
Mg I	21,870.7	15,583.1
Al II	37,453.8	15,303.8
Si III	52,757.6	15,289.0
P IV	68,146.6	

$$(sp^2)[^4P - ^2S] = (p^2)[^3P - ^1S] + \frac{1}{2}(sp)[^3P - ^1P]$$

$$p^2 \ ^1S \text{ calc. } -225,332 \text{ cm}^{-1}$$

$$\text{obs. } -220,474$$

$$(sp^2)[^4P - ^2D] = (p^2)[^3P - ^1D]$$

$$p^2 \ ^1D \text{ calc. } -250,604 \text{ cm}^{-1}$$

$$\text{obs. } -248,918$$

also eliminating  $p^3 \ ^4S$  from the two relations

containing it, we get:

$$(p^3)[^2D - ^2P] = \frac{2}{3}(p^2)[^1D - ^1S]$$

or numerically 22,790  $\equiv$  18,964.

Thus these three relations show that the inter-combination classifications in P III and the classification of these  $p^2$  singlet terms are mutually consistent. The discrepancies are of the

TABLE VII. New classifications in P IV.

INT.	$\lambda$ (air)	$\nu$ (cm <sup>-1</sup> )	CLASSIFICATION	INT.	$\lambda$ (vac.)	$\nu$ (cm <sup>-1</sup> )	CLASSIFICATION
I D	4291.1	23,298	$4d \ ^1D_2 - 5p \ ^1P_1$	1d	1205.513	82,883.5	$3s4p \ ^3P_0 - 3s5d \ ^3D_1$
3 d II	3728.66	26,811.7	$4d \ ^3D_2 - 5p \ ^3P_1$	1	1204.302	83,035.7	$\ ^3P_1 - \ ^3D_2$
5 II	3717.62	26,891.3	$4d \ ^3D_2 - 5p \ ^3P_2$	1	1203.410	83,097.2	$\ ^3P_2 - \ ^3D_3$
4	3717.02	26,895.7	$4d \ ^3D_1 - 5p \ ^3P_2$	1	1197.822	83,484.9	$3s4p \ ^1P_1 - 3s5d \ ^1D_2$
0	2547.8	39,237.6	$4p \ ^1P_1 - 4d \ ^1D_2$	1	1161.783	86,072.5	$3s4s \ ^1S_0 - 3s5p \ ^1P_1$
	$\lambda$ (vac.)*			4	1118.586	89,398.6	$3s3p \ ^1P_1 - 3p^2 \ ^1S_0$
8 II	2498.081	40,030.7	$3p3d \ ^3F_4 - 3s5g \ ^3G$	0	1116.915	89,532.3	$3s3p \ ^3P_2 - 3s3d \ ^1D_2$
1	2479.269	40,334.5	$\ ^3F_3 - \ ^3G$	1	1111.127	89,998.7	$\ ^3P_1 - \ ^1D_2$
0	2464.782	40,571.5	$\ ^3F_2 - \ ^3G$	1B	1101.65	90,773	$3s4s \ ^3S - 3p4s \ ^3P_0$
1 B	1910.18	52,351.1 §	$3s4p \ ^3P_2 - 3s5s \ ^3S$	2B	1098.183	91,059.5	$\ ^3S - \ ^3P_1$
1 B	1904.80	52,499.0 §	$\ ^3P_1 - \ ^3S$	2B	1093.318	91,464.7	$\ ^3S - \ ^3P_2$
Q	1902.62	52,559	$\ ^3P_0 - \ ^3S$	4B II	1091.442	91,621.9	$3s3d \ ^3D - 3p3d \ ^3P_2$
10	1888.652	52,947.8 §	$3s3p \ ^1P_1 - 3s3d \ ^1D_2$	3B	1088.608	91,860.4	$\ ^3D - \ ^3P_1$
1	1691.807	59,108.4	$3s4p \ ^1P_1 - 3s5s \ ^1S_0$	2B	1086.943	92,001.1	$\ ^3D - \ ^3P_0$
0	1673.759	59,745.6	$3s3p \ ^1P_1 - 3p^2 \ ^3P_0$	3	1072.528	93,237.7	$3s4s \ ^3S - 3s5p \ ^3P_2$
3	1640.476	60,957.9	$3s3p \ ^1P_1 - 3p^2 \ ^1D_2$	3	1073.373	93,164.3	$\ ^3S - \ ^3P_1$
Q 2	1614.85	61,925	$3p^2 \ ^1S_0 - 3s4p \ ^1P_1$	2B	1066.640	93,752.3	$3s3d \ ^3D - 3p3d \ ^3D_1$
4	1489.101	67,154.6 §	$3s3d \ ^3D - 3s4p \ ^3P_0$	3B	1065.554	93,847.9	$\ ^3D - \ ^3D_2$
4	1487.796	67,213.5 §	$\ ^3D - \ ^3P_1$	3B	1064.60	93,932	$\ ^3D - \ ^3D_3$
6	1484.506	67,362.5 §	$\ ^3D - \ ^3P_2$	8	1035.505	96,571.2	$3s3p \ ^3P_2 - 3p^2 \ ^3P_1$
1 II	1467.424	68,146.6	$3s^2 \ ^1S_0 - 3s3p \ ^3P_1$	8	1033.099	96,796.1	$\ ^3P_1 - \ ^3P_0$
1	1264.481	79,083.8	$3s4s \ ^1S_0 - 3p4s \ ^1P_1$	10	1030.511	97,039.2	$\ ^3P_{2,1} - \ ^3P_{2,1}$
				1	1028.093	97,267.5	$\ ^3P_0 - \ ^3P_1$
				4	1025.564	97,507.2	$\ ^3P_1 - \ ^3P_1$
				1	1006.218	99,382.0 §	$3s3d \ ^1D_2 - 3s4p \ ^1P_1$
				1 III	963.993	103,735.1	$p^2 \ ^1S_0 - 3p3d \ ^1P_1$

\* This is a complete list of all lines classified in the Schumann Region.  
 II, Blend with P II Lines.  
 III, Blend with P III Lines.  
 B, Wave-lengths from Bowen, reference 7.

Q, Wave-lengths from Queney, J. de phys. et rad. (6) 10, 299 (1929).  
 D, Wave-lengths from Desjardin, reference 9.  
 §, Lines classified by Bowen, reference 7.

same order of magnitude as those using these same relations in C, O and N spectra.

The intercombinations in P IV are well established. The line  $3s^2\ ^1S_0 - 3s3p\ ^3P_1$  obeys the irregular doublet law very well as may be seen in Table VI. This lends further support to the intercombination line classified by Bowen<sup>7</sup> in Si III.

Certain singlet-triplet distances may also be calculated by means of Houston's<sup>15</sup> equations. This is particularly true of the  $3s4p\ ^3P$  and  $^1P$ . In this case the singlet is predicted at 156,755 and found at 156,792  $\text{cm}^{-1}$ . The  $3s\cdot nd$  terms cannot be so tested and indeed do not obey these equations at all due to the large perturbations. The  $3p\cdot 4s\ ^3P$  separations indicate that the singlet should be lower than the triplet, as is found to be the case, although the separation observed does not check with that calculated.

<sup>15</sup> W. Houston, Phys. Rev. 33, 297 (1929).

This appears to be general in all such cases.<sup>16</sup> The new classifications comprise fifty-one lines locating twenty-three new terms. They are listed in Table VII and Table VIII, respectively. The ionization potential works out to be  $51.106 \pm 0.013$  electron volts (using  $1.2336 \times 10^{-4}$  as conversion factor).

#### QUADRUPLY IONIZED PHOSPHORUS P V

The original classification of this spectrum was given by Millikan and Bowen.<sup>17</sup> The main lines are relatively easy to excite and by means of the Uppsala equipment it has been possible to considerably extend the various series as well as to get better measurements for the lines already known. The earlier analysis has been completely substantiated but due to the new

<sup>16</sup> R. F. Bacher, Phys. Rev. 43, 264 (1933).

<sup>17</sup> R. A. Millikan and I. S. Bowen, Phys. Rev. 25, 591 (1925).

TABLE VII.—Continued.

INT.	$\lambda$ (vac.)	$\nu$ ( $\text{cm}^{-1}$ )	CLASSIFICATION	INT.	$\lambda$ (vac.)	$\nu$ ( $\text{cm}^{-1}$ )	CLASSIFICATION
25	950.662	105,189.9 §	$3s^2\ ^1S_0 - 3s3p\ ^1P_1$	6	756.510	132,186.0	$p^2\ ^1D_2 - 3p3d\ ^1P_1$
4	908.050	110,126.0	$p^2\ ^1D_2 - 3p3d\ ^1F_3$	0	680.570	146,935.7	$p^2\ ^1D_2 - 3p4s\ ^1P_1$
2	907.590	110,181.9	$p^2\ ^1D_2 - 3p3d\ ^1D_2$	0	649.69	153,920	$3s3d\ ^3D - 3s5f\ ^3F_3$
2	879.310	113,725.5	$3s3d\ ^3D - 3s4f\ ^3F_2$	2	648.507	154,201.3	$^3D - ^3F_4$
11	877.493	113,961.0	$^3D - ^3F_3$	2B	656.55	152,311	$3p^2\ ^3P_2 - 3p4s\ ^3P_2$
11	875.132	114,268.4	$^3D - ^3F_4$	2B	655.78	152,490	$^3P_1 - ^3P_1$
0	866.84	115,362 §	$3p^2\ ^3P_2 - 3p3d\ ^3P_2$	3B	654.86	152,704	$^3P_2 - ^3P_1$
3	865.04	115,602 §	$^3P_2 - ^3P_1$	1B	654.54	152,779	$^3P_1 - ^3P_2$
3	863.325	115,831.2 §	$^3P_1 - ^3P_2$	2B	653.51	153,020	$^3P_0 - ^3P_0$
1	861.552	116,069.6 §	$^3P_1 - ^3P_1$	2B	652.79	153,189	$^3P_1 - ^3P_1$
2	860.449	116,218.3 §	$^3P_1 - ^3P_0$	10	631.790	158,280.4	$3s3p\ ^3P_2 - 3s4s\ ^3S$
00	851.09	117,496 §	$3p^2\ ^3P_2 - 3p3d\ ^3D_1$	4	629.920	158,750.3	$^3P_1 - ^3S$
3	850.390	117,593.1 §	$^3P_2 - ^3D_2$	3	629.023	158,976.7 §	$^3P_0 - ^3S$
4	849.764	117,679.7 §	$^3P_2 - ^3D_3$	00n	522.02	191,564	$3s3p\ ^1P_1 - 3s4d\ ^1D_2$
6 III	847.658	117,972.1 §	$3p^2\ ^3P_1 - 3p3d\ ^3D_1$	2	472.957	211,435.6	$3s3p\ ^1P_1 - 3s5s\ ^1S_0$
5	846.999	118,063.8 §	$^3P_1 - ^3D_2$	0	445.194	224,621.2	$3s3p\ ^3P_2 - 3s4d\ ^3D$
1 III	846.494	118,134.3	$3s3d\ ^1D_2 - 3p3d\ ^1F_3$	0	444.249	225,099.0	$^3P_1 - ^3D$
2 III	846.125	118,185.8	$3s3d\ ^1D_2 - 3p3d\ ^1D_2$	1	415.815	240,491.6	$3s3p\ ^3P_2 - 3s5s\ ^3S$
2	845.995	118,204.0	$3p^2\ ^3P_0 - 3p3d\ ^3D_1$	0	415.022	240,951.0	$^3P_1 - ^3S$
1	843.984	118,495.6	$p^2\ ^1S_0 - 3p4s\ ^1P_1$	00n	412.90	242,189	$^3P_0 - ^3S$
25	827.932	120,782.9 §	$3s3p\ ^3P_2 - 3s3d\ ^3D$	6	388.315	257,522.9	$3s^2\ ^1S_0 - 3s4p\ ^1P_1$
20	824.726	121,252.4 §	$^3P_1 - ^3D$	0	359.628	278,065.1	$3s3p\ ^3P_2 - 3s6s\ ^3S$
20	823.181	121,479.9 §	$^3P_0 - ^3D$	4	312.443	320,058.3	$3s^2\ ^1S_0 - 3s5p\ ^1P_1$
3	776.366	128,805.2 §	$3s3p\ ^1P_1 - 3s4s\ ^1S_0$	0n	283.99	352,125	$3s^2\ ^1S_0 - 3s6p\ ^1P_1$
00n	765.28	130,671	$3s3d\ ^3D - 3s5p\ ^3P_2$				

measurements their ground state has been slightly changed. The Rydberg denominators have been determined logarithmically using the Rydberg constant for phosphorus in place of  $R_\infty$ . By extrapolation along the Na I isoelectronic sequence  $6h^2H$  has been set at  $n^* = 5.99960$ . The lines above 2000Å have been taken from Geuter<sup>10</sup> with the exception of 2440.75 and

2441.04 which were obtained by the author by means of the Hilger EI spectrograph located at M.I.T. In Geuter's list these transitions were represented by a single line and it was impossible to give the  $4d$  separation accurately. It should be noticed that the  $3d^3D$  separation as given is calculated from the difference of the  $4p^3P$  difference (as found from the lines 1,000.360 and

TABLE VIII. Complete term table—P IV.

$3s^2\ ^1S_0$	414,312.4§		$3s4d\ ^3D_1$		121,078.9§
$3s3p\ ^3P_0^0$		227.4	$346,400.8§$	5.4	
$\ ^3P_1^0$		468.4	$346,173.4§$	7.7	121,073.5§
$\ ^3P_2^0$			$345,705.0§$		121,065.8§
$3s3p\ ^1P_1^0$	309,122.5§		$3s4d\ ^1D_2$	117,654.6	
$3s3d\ ^1D_2$	256,174.2§		$3p3d\ ^1P_1^0$	115,985	
$3p^2\ ^3P_0$		243	$3s4f\ ^3F_2^0$		111,197
$\ ^3P_1$		468	$\ ^3F_3^0$	235	110,962
$\ ^3P_2$			$\ ^3F_4^0$	307	110,653
$3p^2\ ^1D_2$	248,168		$3s5s\ ^3S_1$		105,210.4§
$3s3d\ ^3D_{1, 2, 3}$			$3p4s\ ^1P_1$	101,234	
$3p^2\ ^1S_0$	219,723.9		$3s5s\ ^1S_0$	97,685.4	
$3s4s\ ^3S_1$			$3p4s\ ^3P_0^0$		96,650 §
$3s4s\ ^1S_0$	180,317.4§		$\ ^3P_1^0$	286	96,364 §
$3s4p\ ^3P_0^0$		58.6	$\ ^3P_3^0$	405	95,959 §
$\ ^3P_1^0$		148.6	$3s5p\ ^1P_1^0$	94,248.9	
$\ ^3P_2^0$			$3s5p\ ^3P_0^0$		—
$3s4p\ ^1P_1^0$	156,792.2§		$\ ^3P_1^0$		94,259
$3p3d\ ^1F_3^0$	138,042?		$\ ^3P_2^0$	73	94,186
$3p3d\ ^1D_2^0$	137,987?		$3s5d\ ^3D_3$		74,676.9
$3p3d\ ^3P_2^0$		—240	$\ ^3D_2$	—3.8	74,673.1
$\ ^3P_1^0$			$\ ^3D_1$	—2.8	74,670.3
$\ ^3P_0^0$		—140	$3s5d\ ^1D_2$	73,307.6?	
$3p3d\ ^3D_1^0$		97	$3s5f\ ^3F_2$		—
$\ ^3D_2^0$		82	$\ ^3F_3$		71,003
$\ ^3D_3^0$			$\ ^3F_4$	281	70,722
			$3s5g\ ^3G$		70,624
			$3s6s\ ^3S$		67,640
			$3s6p\ ^1P_1^0$	62,187?	

§ Terms from I. S. Bowen, references 5, 7, slightly modified on the basis of new measurements.



TABLE IX. Complete list of classified lines for P V.

INT.	$\lambda$ (air)	$\nu$ cm <sup>-1</sup>	CLASSIFICATION	INT.	$\lambda$ (vac.)	$\nu$ cm <sup>-1</sup>	CLASSIFICATION
3	3204.04§	31,201.61	4s <sup>2</sup> S - 4p <sup>2</sup> P <sub>1/2</sub>	8	544.914§	183,515.1	3p <sup>2</sup> P <sub>3/2</sub> - 4s <sup>2</sup> S
5	3175.14§	31,485.60	2S - 2P <sub>3/2</sub>	7	542.567§	184,309.0	2P <sub>1/2</sub> - 2S
3	2978.5 §	33,563	5g <sup>2</sup> G - 6h <sup>2</sup> H	8n	475.610	210,256.0	3d <sup>2</sup> D - 5f <sup>2</sup> F
2	2961.39§	33,758.09	5f <sup>2</sup> F - 6g <sup>2</sup> G	2n	410.073	243,859.0	3d <sup>2</sup> D - 6f <sup>2</sup> F
5	2440.75§	40,958.6	4p <sup>2</sup> P <sub>3/2</sub> - 4d <sup>2</sup> D <sub>5/2</sub>	8	390.700	255,950.9	3p <sup>2</sup> P <sub>3/2</sub> - 4d <sup>2</sup> D <sub>5/2</sub>
1	2441.04	40,953.7	2P <sub>3/2</sub> - 2D <sub>3/2</sub>	3	389.500	256,739.0	2P <sub>1/2</sub> - 2D <sub>3/2</sub>
2	2424.34§	41,235.80	2P <sub>1/2</sub> - 2D <sub>3/2</sub>	4	348.194	287,192.6	3p <sup>2</sup> P <sub>3/2</sub> - 5s <sup>2</sup> S
	$\lambda$ (vac.)			2	347.237	287,987.8	2P <sub>1/2</sub> - 2S
0B	1610.54§	62,089.1	4f <sup>2</sup> F - 5g <sup>2</sup> G	5†	328.768	304,165.9	3s <sup>2</sup> S - 4p <sup>2</sup> P <sub>1/2</sub>
2B	1447.92§	69,064.5	4d <sup>2</sup> D - 5f <sup>2</sup> F	5†	328.455	304,455.8	2S - 2P <sub>3/2</sub>
0B	1385.11§	72,196.3	4p <sup>2</sup> P <sub>1/2</sub> - 5s <sup>2</sup> S <sub>1/2</sub>	4	311.347	321,185.1	3p <sup>2</sup> P <sub>3/2</sub> - 5d <sup>2</sup> D
10	1128.006§	88,650.9	3s <sup>2</sup> S - 3p <sup>2</sup> P <sub>1/2</sub>	3	310.579	321,979.2	P <sub>1/2</sub> - 2D
15	1117.979§	89,447.1	2S - 2P <sub>3/2</sub>	1	296.112	337,710.0	3p <sup>2</sup> P <sub>3/2</sub> - 6s <sup>2</sup> S
3	1000.360§	99,963.2	3d <sup>2</sup> D <sub>3/2</sub> - 4p <sup>2</sup> P <sub>1/2</sub>	2	280.609	356,367.8	3p <sup>2</sup> P <sub>3/2</sub> - 6d <sup>2</sup> D
3	997.641§	100,235.6	2D <sub>5/2</sub> - 2P <sub>3/2</sub>	00	273.13	366,126	3p <sup>2</sup> P <sub>3/2</sub> - 7s <sup>2</sup> S
15d	871.396§	114,758.4	{ 3p <sup>2</sup> P <sub>3/2</sub> - 3d <sup>2</sup> D <sub>5/2</sub>	5*	264.938	377,447	3p <sup>2</sup> P <sub>3/2</sub> - 7d <sup>2</sup> D
			{ 2P <sub>3/2</sub> - 2D <sub>3/2</sub>	7	255.688	391,101.7	3s <sup>2</sup> S - 5p <sup>2</sup> P <sub>1/2</sub>
			{ 2P <sub>1/2</sub> - 2D <sub>3/2</sub>	7	255.596	391,242.4	2S - 2P <sub>3/2</sub>
15	865.435§	115,548.8	3d <sup>2</sup> D - 4f <sup>2</sup> F	3	229.832	435,100.4	3s <sup>2</sup> S - 6p <sup>2</sup> P <sub>3/2</sub>
10	673.888§	148,392.6		0	217.220	460,362.8	3s <sup>2</sup> S - 7p <sup>2</sup> P
				00	210.004	476,181.4	3s <sup>2</sup> S - 8p <sup>2</sup> P

§ Lines previously classified by Bowen.

B Wave-lengths from Bowen.

† Obscured by oxygen lines.

\* Obscured by 5×Be 88.

TABLE X. Complete term table and Rydberg denominators for P V.

3s <sup>2</sup> S <sub>1/2</sub>	524,462.9§	2.28710	3d <sup>2</sup> D <sub>3/2</sub>	320,265.8		
4s <sup>2</sup> S <sub>1/2</sub>	251,501.8§	3.30273	2D <sub>5/2</sub>	320,254.6§	11.2	2.92683
5s <sup>2</sup> S <sub>1/2</sub>	147,823.7§	4.30795	4d <sup>2</sup> D <sub>3/2</sub>	179,064.5		
6s <sup>2</sup> S <sub>1/2</sub>	97,306	5.3098	2D <sub>5/2</sub>	179,059.6§	4.9	3.91414
7s <sup>2</sup> S <sub>1/2</sub>	68,890	6.3105	5d <sup>2</sup> D	113,831.8		4.90920
			6d <sup>2</sup> D	78,649		5.9061
			7d <sup>2</sup> D	57,570		6.9031
3p <sup>2</sup> P <sub>1/2</sub>	435,811.2§					
2P <sub>3/2</sub>	435,016.6§	794.6				
4p <sup>2</sup> P <sub>1/2</sub>	220,301.6§		4f <sup>2</sup> F	171,867.6§		3.99526
2P <sub>3/2</sub>	220,017.6§	284.0	5f <sup>2</sup> F	110,004.2§		4.99387
5p <sup>2</sup> P <sub>1/2</sub>	133,361.2		6f <sup>2</sup> F	76,401.2		5.99226
2P <sub>3/2</sub>	133,220.5	140.7	7f <sup>2</sup> F	55,933		7.0034
6p <sup>2</sup> P <sub>1/2</sub>						
2P <sub>3/2</sub>	89,362.5					
7p <sup>2</sup> P	64,100		5g <sup>2</sup> G	109,778.5§		4.99901
8p <sup>2</sup> P	48,282		6g <sup>2</sup> G	76,246.1§		5.99832
I.P. = 524,462.9 × 1.2336 × 10 <sup>-4</sup>						
= 64.698 volts			6h <sup>2</sup> H	76,215.5§		(5.99960)

§ Terms previously classified by Bowen but modified slightly on the basis of new measurements.

997.641A) and that difference as known from the other pairs containing it. The difference cannot be accurately found from the pair at 871.396 and 865.435 inasmuch as the first line is really double. Twenty new lines have been classified. These locate fourteen new terms. The complete list of classified lines and the complete term table are listed in Tables IX and X, respectively. Using the conversion factor  $1.2336 \times 10^{-4}$  for changing  $\text{cm}^{-1}$  to electron volts the ionization potential is  $69.698 \pm 0.003$  volts.

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## The Correction of Continuous Spectra for the Finite Resolution of the Spectrometer

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The relation between the theoretical intensity function of a continuous spectrum and the intensity measured with an ionization chamber (or counter) and a spectrometer, is discussed. It is shown that while the problem of correcting the observed intensity for the finite resolution of the spectrometer does not always have a mathematically unique solution, the requirement that the theoretical intensity have a smooth graph is sufficient to make the solution practically unique. On this basis, an approximate

solution of the problem is given, which involves the first and second differences of a set of equally spaced measurements. A second method of solution is discussed which involves the scanning of a template of the measured intensity wave-length curve by a photoelectric cell connected to a recording galvanometer. This method has practical disadvantages but illustrates several theorems derived analytically in the earlier part of the paper.

## INTRODUCTION

THE problem of correcting the measurements of a continuous spectrum for the effect of the finite resolution of the spectrometer has apparently received little attention. It is known that if  $I(\lambda)$  is the intensity measured with an ionization chamber or counter, and  $\rho(\lambda)$  is the theoretical intensity, the two functions are connected by an equation of the form

$$I(\lambda) = \int_{-a(\lambda)}^{+a(\lambda)} \rho(\lambda + \xi) K(\lambda, \xi) d\xi. \quad (1)$$

The functions  $a$  and  $K$  are positive and have been determined for various types of instruments, but the general nature of the relation thus established between  $I$  and  $\rho$  has not been investigated.

Eq. (1) has usually been approximated by

$$I(\lambda) = \alpha(\lambda) \rho(\lambda), \quad (2)$$

$$\text{where } \alpha(\lambda) = \int_{-a(\lambda)}^{+a(\lambda)} K(\lambda, \xi) d\xi, \quad (3)$$

but there are cases in which this is not a sufficient approximation, e.g., some of the measurements of continuous beta-ray spectra made for the purpose of determining the mass of the neutrino.<sup>1</sup>

The validity of this approximation is readily estimated as follows: let  $\rho_+(\lambda)$  and  $\rho_-(\lambda)$  be the largest and smallest values, respectively, of  $\rho(\lambda + \xi)$  for  $|\xi| \leq a(\lambda)$ . Then it follows from the positiveness of  $K$  that

$$\alpha \rho_- \leq I \leq \alpha \rho_+. \quad (4)$$

<sup>1</sup> W. J. Henderson, Proc. Camb. Phil. Soc. 31, 285 (1935); E. M. Lyman, Phys. Rev. 51, 5 (1937).