

SERIES SPECTRA OF CHLORINE, Cl_{II}, Cl_{III}, Cl_{IV}, Cl_V, AND OF Si_{II}, P_{III} AND S_{IV}

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ABSTRACT

Series spectra of chlorine.—Twenty-six lines are classified in Cl_{II}, eighty-eight in Cl_{III}, twenty-six in Cl_{IV} and seventeen in Cl_V. Twenty-one term values are fixed in Cl_{III}.

Series spectra of Si_{II}, P_{III} and S_{IV}.—Five lines are identified in Si_{II} in addition to those previously known. Fifteen additional lines are classified in P_{III} and thirteen in S_{IV}.

I. CLASSIFICATION OF CHLORINE SPECTRA

IN PREVIOUS papers by Millikan and Bowen,¹ several of the lines of Cl_V, Cl_{VI} and Cl_{VII} were classified. Paschen² has identified a few of the quintets of Cl_{II} and Hopfield³ has called attention to four triplet groups in Cl_{II} occurring in the extreme ultra-violet region.

In the present article several additional lines are classified in Cl_V and twenty-six lines of the triplet system of Cl_{IV} are identified. Nearly ninety lines are assigned as arising from transitions between various terms of the quartet and doublet systems of Cl_{III}. For Cl_{II} new measurements have been obtained on the lines observed by Hopfield and these, along with a few additional lines, are given their series designation.

TABLE I
Series lines of Cl_{II}

Int.	I. A. Vac.	ν	Series designation	Int.	I. A. Vac.	ν	Series designation
Triplets				5	788.742	126784.2	aP_2-3nD_3
				4	788.985	126745.1	aP_2-3nD_2
1	634.250	157667.	aP_2-P_1	3	793.345	126048.6	aP_1-3nD_2
1	635.882	157262.	aP_1-P_0	3	793.473	126028.2	aP_1-3nD_1
2	636.626	157078.	aP_2-P_2	3	795.357	125729.7	aP_0-3nD_1
1	637.070	156969.	aP_1-P_1				
1	638.278	156672.	aP_0-P_1	3	888.060	112605.	aP_2-4kS
1	639.458	156382.	aP_1-P_2	3	893.550	111913.	aP_1-4kS
				2	895.953	111613.	aP_0-4kS
4	707.450	141352.7	aP_2-D_3				
3	709.173	141009.3	aP_2-D_2	4	1063.77	94005.3	aP_2-bP_1
0	710.540	140738.0	aP_2-D_1	4	1067.95	93637.4	aP_1-bP_0
4	712.682	140315.0	aP_1-D_2	5	1071.03	93367.9	aP_2-bP_2
2	714.063	140043.7	aP_1-D_1	3	1071.77	93304.0	aP_1-bP_1
3	715.602	139742.5	aP_0-D_1	4	1075.22	93003.9	aP_0-bP_1
				3	1079.07	92672.7	aP_1-bP_2

¹ Bowen and Millikan, Phys. Rev. 25, 295, 591, 600 (1925).

² Paschen, Ann. d. Physik 71, 559, (1923).

³ Hopfield, Phys. Rev. 26, 282 (1925).

TABLE II
Series lines of Cl_{III}

Int.	I. A. Vac.	ν	Series designation	Int.	I. A. Air	ν	Series designation
Quartets							
4	572.693	174614.	$aS-4kP_3$	1	2796.37	35750.1	$4mS-4nD_3$
3	574.408	174092.	$aS-4kP_2$	2	2805.17	35638.0	$4mS-4nD_2$
3	575.582	173737.	$aS-4kP_1$	6	3104.46	32202.4	$4kP_1-4mS$
1	930.94	107418.	bP_3-4mS	8	3139.34	31844.7	$4kP_2-4mS$
1	936.28	106806.	bP_2-4mS	9	3191.45	31324.7	$4kP_3-4mS$
0	939.31	106461.	bP_1-4mS	6	3283.41	30447.4	$4kP_2-4mP_3$
1	943.22	106020.	bP_3-4mP_3	7	3289.80	30388.3	$4kP_1-4mP_2$
1	946.97	105600.	bP_3-4mP_2	3	3300.95	30285.6	$4kP_1-4mP_1$
1	948.72	105406.	bP_2-4mP_3	8	3329.06	30030.0	$4kP_2-4mP_2$
2	953.40	104888.	bP_2-4mP_1	9	3340.42	29927.8	$4kP_{3,2}-4mP_{3,1}$
5	1005.280	99474.8	$aS-bP_1$	6	3387.60	29511.0	$4kP_3-4mP_2$
6	1008.777	99129.9	$aS-bP_2$	9	3602.10	27753.7	$4kP_3-4mD_4$
7	1015.023	98519.9	$aS-bP_3$	8	3612.85	27671.4	$4kP_2-4mD_3$
I. A. Air							
3	2231.16	44805.7	$4mD_2-5kP_3$	7	3622.69	27596.0	$4kP_1-4mD_2$
7	2253.07	44370.1	$4mD_3-5kP_3$	7	3656.95	27337.5	$4kP_1-4mD_1$
2	2255.64	44319.5	$4mD_1-5kP_2$	7	3670.28	27238.1	$4kP_2-4mD_2$
5	2268.95	44059.6	$4mD_2-5kP_2$	7	3682.05	27151.1	$4kP_3-4mD_3$
5	2278.34	43878.0	$4mD_1-5kP_1$	6	3705.45	26979.6	$4kP_2-4mD_1$
7	2283.93	43770.6	$4mD_4-5kP_3$	3	3741.70	26718.2	$4kP_3-4mD_2$
4	2291.38	43628.3	$4mD_3-5kP_2$	Doublets			
4	2291.81	43620.2	$4mD_2-5kP_1$	4	I. A. Vac.	586.874	aD_2-4kD
5	2379.47	42013.3	$4mP_2-5kP_3$	4	587.078	170335.	aD_3-4kD
5	2403.32	41596.4	$4mP_3-5kP_3$	0	613.643	162961.	aD_2-P_2
7	2416.42	41371.1	$4mP_1-5kP_2$	1	613.874	162900.	aD_3-P_2
4	2422.47	41267.6	$4mP_2-5kP_2$	2	617.630	161909.	aD_2-P_1
5	2442.47	40929.7	$4mP_1-5kP_1$	3	621.027	161024.	aD_2-4kP_2
6	2447.14	40851.7	$4mP_3-5kP_2$	4	621.280	160958.	aD_3-4kP_2
6	2448.58	40827.6	$4mP_2-5kP_1$	3	623.768	160316.	aD_2-4kP_1
5	2486.91	40198.4	$4mS-5kP_3$	1	630.380	158634.	aP_1-4kD
1	2533.95	39452.3	$4mS-5kP_2$	1	630.746	158542.	aP_2-4kD
1	2562.52	39012.4	$4mS-5kP_1$	2	661.414	151191.	aP_1-P_2
3	2468.37	40500.2	$4mD_1-4nD_2$	2	661.836	151095.	aP_2-P_2
2	2477.29	40354.4	$4mD_2-4nD_3$	3	666.040	150141.	aP_1-P_1
2	2481.77	40281.6	$4mD_3-4nD_4$	1	666.500	150038.	aP_2-P_1
4	2484.27	40241.2	$4mD_2-4nD_2$	2	669.949	149265.	aP_1-4kP_2
5	2504.23	39920.4	$4mD_3-4nD_3$	3	670.383	149169.	aP_2-4kP_2
4	2510.92	39814.0	$4mD_3-4nD_2$	3	673.127	148560.	aP_1-4kP_1
5	2519.45	39679.2	$4mD_4-4nD_4$	1	673.598	148457.	aP_2-4kP_1
2	2542.65	39317.3	$4mD_4-4nD_3$	I. A. Air			
5	2661.65	37559.6	$4mP_2-4nD_3$	5	3244.44	30813.1	$4kP_1-4mP_1$
3	2662.29	37550.5	$4mP_1-4nD_2$	6	3259.32	30672.5	$4kP_1-4mP_2$
6	2665.54	37504.7	$4mP_3-4nD_4$	7	3320.57	30106.7	$4kP_2-4mP_1$
3	2669.52	37448.8	$4mP_2-4nD_2$	5	3336.16	29966.0	$4kP_2-4mP_2$
5	2691.52	37142.8	$4mP_3-4nD_3$	8	3748.81	26667.6	$4kP_1-4mD_2$
1	2699.79	37029.0	$4mP_3-4nD_2$	4	3850.81	25961.2	$4kP_2-4mD_2$

TABLE II continued
Term values

aS	321936.	$5kP_1$	76984.5	$4mD_1$	120862.6
		$5kP_2$	76543.6	$4mD_2$	120604.0
		$5kP_3$	75798.8	$4mD_3$	120170.9
bP_1	222461.			$4mD_4$	119568.4
bP_2	222806.				
bP_3	223416.	$4mS$	115997.5	$4nD_2$	80363.6
		$4mP_1$	117914.4	$4nD_3$	80250.9
$4kP_1$	148200.	$4mP_2$	117812.0	$4nD_4$	79889.8
$4kP_2$	147842.2	$4mP_3$	117394.8		
$4kP_3$	147322.1				

TABLE III
Series lines of Cl_{IV}

Int.	I. A. Vac.	ν	Series designation	Int.	I. A. Vac.	ν	Series designation
Triplets							
3	463.011	215978.	aP_1-4kP_2	3	607.088	164721.	aP_0-bS
3	464.292	215382.	aP_0-4kP_1	4	608.903	164230.	aP_1-bS
4	464.861	215118.	aP_2-4kP_2	4	612.070	163380.	aP_2-bS
3	465.350	214892.	aP_1-4kP_1	4	831.431	120274.6	aP_0-bP_1
3	466.132	214532.	aP_1-4kP_0	3	834.659	119809.4	aP_1-bP_0
3	467.194	214044.	aP_2-4kP_1	5	834.840	119783.4	aP_1-bP_1
				5	834.967	119765.2	aP_1-bP_2
				4	840.808	118933.2	aP_2-bP_1
3	549.219	182077.	aP_0-3nP	6	840.933	118915.5	aP_2-bP_2
2	550.706	181585.	aP_1-3nP				
3	553.297	180735.	aP_2-3nP	5	973.212	102752.5	aP_0-bD_1
				6	977.560	102295.5	aP_1-bD_2
2	599.733	166741.	aP_0-3nD	4	977.901	102259.8	aP_1-bD_1
3	601.499	166251.	aP_1-3nD	7	984.952	101527.8	aP_2-bD_3
3	604.590	165401.	aP_2-3nD	4	985.749	101445.7	aP_2-bD_2

The lines, thus classified, are collected in Tables I, II, III and IV. In these tables the usual notation is used for the term type. The electron configuration for an n -valence-electron system is indicated as follows:

Configuration	Designation
s^2p^{n-2}	a
sp^{n-1}	b
p^n	c
$s^2p^{n-3}.s$	k
$s^2p^{n-3}.p$	m
$s^2p^{n-3}.d$	n
$s^2p^{n-3}.f$	q

All electrons are in three-total-quantum-number orbits in the first three configurations. For the remaining cases the total quantum number of the excited electron is indicated in the usual way by a numeral preceding the letter.

The term values in Cl_{III} are fixed by making the $3kP_1$ and the $4kP_1$ terms follow the Rydberg formula.

The only lines requiring special mention are a^3P-b^3P , a^3P-b^3D , a^3P-3n^3P , a^3P-3n^3D of Cl_{IV} . In an earlier analysis of P_{II}^4 these groups were found and, by means of the irregular doublet law, definitely correlated with the same

⁴ Bowen, Phys. Rev. 29, 510 (1927).

TABLE IV
Series lines of Cl_v

Int.	I. A. Vac.	ν	Series designation	Int.	I. A. Vac.	ν	Series designation
Quartets							
3	676.785	147757.4	bP_1-cS	3	629.354	158893.	aP_1-bP_2
3	679.257	147219.7	bP_2-cS	4	633.186	157931.	aP_1-bP_1
4	683.171	146376.2	bP_3-cS	4	635.323	157400.	aP_2-bP_2
				3	639.226	156439.	aP_2-bP_1
Doublets							
1	390.07	256364.	aP_1-4kS	4	681.924	146643.9	aP_1-bS
1	392.39	254848.	aP_2-4kS	4	688.933	145152.0	aP_2-bS
5	538.032	185863.	aP_1-3nD_2	4	883.127	113234.0	aP_1-bD_2
6	542.297	184401.	aP_2-3nD_3	4	894.340	111814.3	aP_2-bD_3
3	542.395	184367.	aP_2-3nD_2	1	894.910	111743.1	aP_2-bD_2

groups in Si_I which had been observed by Fowler.⁵ The terms were then assigned to the electron configurations in the same way that Hund⁶ had assigned the corresponding levels in Si_I. Since then data have become available that fix the position of the lines caused by these electron jumps ($sp^{n-1} \rightarrow s^2p^{n-2}$ and $s^2p^{n-3} \cdot d \rightarrow s^2p^{n-2}$) in nearly all stages of ionization of all atoms of the second row of the periodic table. A study of the frequencies of these lines, relative to the frequencies of the corresponding lines in the first row of the periodic table, shows that the assignment of the configuration in Si_I and P_{II} should be interchanged, i.e., the b terms should be designated as $3n$ terms and vice versa. In the present table of Cl_{IV} these lines are given their correct assignment and therefore do not correspond to the designations in Si_I and P_{II}.

II. ADDITIONAL LINES IN THE SPECTRA OF THREE-VALENCE-ELECTRON SILICON, PHOSPHORUS AND SULPHUR

Fowler,⁵ Saltmarsh,⁷ and Millikan and Bowen¹ have classified many of the lines of Si_{II}, P_{III} and S_{IV}. Most of these lines could be assigned to jumps caused by the excitation of the p electron. In each case there were found also a p' term and an x term which the Hund theory has since accounted for as terms of the sp^2 configuration. In Si_{II} this x term is evidently the 2D term and in P_{III} and S_{IV} the 2S term. A study of new data for these elements reveals various lines due to combinations with the 2D term in P_{III} and S_{IV}

TABLE V
Series lines of Si_{II}

Int.	I. A. Vac.	ν	Series designation
Quartets			
1	1246.75	80208.5	bP_1-cS
1	1248.43	80100.6	bP_2-cS
1	1251.17	79925.2	bP_3-cS
Doublets			
1	1304.41	76663.0	aP_1-bS
2	1309.28	76377.8	aP_2-bS

⁵ Fowler, Phil. Trans. **225**, 1 (1925).

⁶ Hund, Zeits. f. Physik **33**, 345 (1925).

⁷ Saltmarsh, Proc. Roy. Soc. **A108**, 332 (1925).

and the 2S term in Si_I . This completes the identification of all doublet levels predicted by the Hund theory for the sp^3 configuration. These and several other new lines in the spectra of these ions are given in Tables V, VI and VII.

TABLE VI
Series lines of P_{III}

Int.	I. A. Vac.	ν	Series designation	Int.	I. A. Vac.	ν	Series designation
Quartets				3	964.234	103709.3	bD_3-4qF
2	972.828	102793.1	bP_1-cS	10	1334.835	74915.6	aP_1-bD_2
3	974.772	102588.1	bP_2-cS	10	1344.335	74386.2	aP_2-bD_3
3	977.884	102261.6	bP_3-cS	3	1344.850	74357.7	aP_2-bD_2
Doublets				2	1501.53	66598.7	bD_2-4mP_2
1	568.07	176035.	aP_1-5kS	3	1502.24	66567.3	bD_3-4mP_2
1	569.90	175469.	aP_2-5kS	2	1504.65	66460.9	bD_2-4mP_1
1	581.86	171863.	aP_2-4nD	2	1618.605	61781.4	$3nD_2-4qF$
				2	1618.925	61769.2	$3nD_3-4qF$
Term Values							
bP_1	134296.3	bD_2	168415.7	$4qF$	64678.8		
bP_2	133920.7	bD_3	168386.3				

TABLE VII
Series lines of S_{IV}

Int.	I. A. Vac.	ν	Series designation	Int.	I. A. Vac.	ν	Series designation
Quartets				3	852.716	117272.3	bD_2-cP
3	798.265	125271.6	bP_1-cS	3	853.135	117214.7	bD_3-cP
3	800.470	124926.6	bP_2-cS	6	1062.672	94102.4	aP_1-bD_2
4	803.975	124381.9	bP_3-cS	6	1072.992	93197.3	aP_2-bD_3
Doublets				4	1073.522	93151.3	aP_2-bD_2
4	836.286	119576.3	bD_3-4mP_2	1	1138.227	87855.9	$bS-cP$
4	837.447	119410.5	bD_2-4mP_1	1	1286.063	77756.6	bP_1-cP
				2	1296.640	77122.4	bP_2-cP
Term values							
bP_1	247923.5	bD_2	287439.5	cP	170173.		
bP_2	247297.5	bD_3	287393.3				

As only new lines and levels are included in these lists, they should be considered supplementary to the earlier tables. The relation between the notations used in the earlier articles¹ and the present one is as follows:

Old	New	Old	New
$3p_1$	aP_2	$5s$	$5kS$
$3p_2$	aP_1	$4p_1$	$4mP_2$
x	bS	$4p_2$	$4mP_1$
$3p'_1$	bP_2	$3d_1$	$3nD_3$
$3p'_2$	bP_1	$3d_2$	$3nD_2$
$4s$	$4kS$	$4d$	$4nD$

The wave-lengths of the S_{IV} lines are taken from unpublished determinations made by Mr. Ingram at this laboratory.

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