Additions to Certain Spectra of Sulphur, Potassium and Calcium

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Twenty-seven lines have been classified in S III. These locate six of the important singlet levels accurately with respect to the known triplets. S VI has been completely revised. Fourteen new terms have been added which classify eighteen new lines. The revised ionization potential is 87.610 ± 0.003 volts. Two new singlet terms with intercombinations have been found in K VI and Ca VII. One new singlet term has been added to K IV and three terms to S VIII. Several of these last few spectra have been investigated in order to test the conclusions drawn from the previous paper in this issue of the Physical Review.

T has been possible to extend the classifications of certain sulphur spectra by means of spectrograms obtained in Professor Siegbahn's laboratory in Uppsala, Sweden. Previously published lists of sulphur lines¹⁻³ have also been used. Certain of the terms have already been published:4 it was impossible at that time to list the newly classified lines. The new results are given in Tables I and II.

The new measurements show that 6 cm⁻¹ must be subtracted from all terms higher than 140,000 cm⁻¹. Since these terms are very accurately known with respect to one another³ the new values are not listed. The $3s3p^23d$ ³D terms listed by L. and E. Bloch¹ are erroneous; the lines which they give as the $3s3p^3 {}^3D - 3s3p^23d {}^3D$ transitions are in reality the $3s^23p^2$ $^3P - 3s3p^3$ 3D transitions previously classified by Ingram.⁵ Slightly more accurate values for the sp^3 triplet terms have also been added.

Extensions have also been possible in the case of S VI. (Tables III and IV.) The Rydberg denominators have been determined by means of the Princeton tables.6 The absolute value of the ground state was obtained by setting n^* for $5g^{2}G$ equal to 4.9990. This value was extrapolated from the corresponding terms in the other members of the isoelectronic sequence.

It has also been possible to identify the $s^2 2 p^{5} {}^2 P - s p^{6} {}^2 S$ transition of S VIII. The lines

* Now at Central Technical Laboratory, Armstrong Cork Company, Lancaster, Pennsylvania. ¹L. and E. Bloch, J. de phys. 6, 441 (1935)

- ² L. and E. Bloch, Ann. de physique **12**, 5 (1929). ³ A. Hunter, Phil. Trans. Roy. Soc. London **233A**, 303 (1934).
- ⁴ H. A. Robinson, Nature 137, 992 (1936).
- ⁶ S. B. Ingram, Phys. Rev. 33, 907 (1929).
 ⁶ A. G. Shenstone, J. C. Boyce and H. N. Russell, Rydberg Interpolation Table (Princeton, N. J., 1934).

TABLE I. S III Classified lines.

INT.	λ(air)	ν(cm ⁻¹)	CLASSIFICATION	
7	4677.67	21,372.20	$4s {}^{1}P_{1} - 4p {}^{3}D_{1}$	
5	4613.47	21,669.61	$4s {}^{1}P_{1} - 4p {}^{3}D_{2}$	
0	4125.4	24,233.3	$4s {}^{1}P_{1} - 4p {}^{3}P_{0}$	
3	4099.25	24,387.85	$4s {}^{1}P_{1} - 4p {}^{3}P_{1}$	
00	3899.27	25,638.59	$4s {}^{1}P_{1} - 4p {}^{3}S_{1}$	
00	3008.82	33,226.0	$sp^{3} P_{1} - 4p D_{2}$	
1	2749.94	36,353.7	$sp^{3} P_{1} - 4p^{3}P_{2}$	
Î	2593.87	38,540.9	$\begin{vmatrix} 3p & 1 \\ 4p & ^{3}P_{1} - 5s & ^{1}P_{1} \end{vmatrix}$	
2	2422.91	41,260.14	$4p \ {}^{3}D_{2} - 5s \ {}^{1}P_{1}$	
1	2405.63	41,556.5	$4p \ ^{3}D_{2} = 53 \ ^{3}P_{1}$ $4p \ ^{3}D_{1} - 5s \ ^{1}P_{1}$	
•	2100.00	41,000.0	$+p D_1 - 55 T_1$	
1 0				
1 2	λ(vac)	ν(cm ⁻¹)	CLASSIFICATION	
8 2	1077 125	. 03 939 0	2,010 .210	
$\begin{array}{c} 5 & 2 \\ 00 & - \end{array}$	$1077.135 \\ 911.77$	92,838.9	$3p^{2} D_{2} - sp^{3} D_{2}$	
		109,677	$3p^{2} S_0 - sp^{3} P_1$	
	836.315	119,572	$-4s {}^{3}P_{1}$	
4 0	824.887	121,229	$-4s {}^{1}P_{1}$	
$ \begin{array}{c cccccccccccccccccccccccccccccccccc$	796.692	125,519	$3p^{2} D_2 - sp^{3} P_1$	
	788.984	126,745	$-sp^{3}S$	
4 1	738.474	135,414	$-4s \ ^{3}P_{1}$	
2 –	736.25	135,834	$-4s \ ^{3}P_{2}$	
L	733.92	136,255	$- 3d \ ^{3}D_{1}?$	
) -	733.34	136,362	$- 3d \ ^{3}D_{2}$	
$\dot{)}$ $\dot{-}$	732.98	136,492	$- 3d ^{3}D_{3}$	
$\begin{array}{c c}1 & 4\\1 & 3\end{array}$	729.529	137,075	$-4s P_1$	
	735.251	136,008	$3p^{2} {}^{3}P_{2} - sp^{3} {}^{1}P_{1}$	
50	732.376	136,542	${}^{3}P_{1} - {}^{1}P_{1}$	
$3 0n \mid$	730.783	136,840	${}^{3}P_{0} - {}^{1}P_{1}$	
2 0n	543.031	184,152	$3p^{2} S_{0} - 5s P_{1}$	
30	499.983	200,006	$3p^{2}D_{2} - 5s^{1}P_{1}$	

Intensities, col. 1 from L. and E. Bloch, reference 1.

Intensities, col. 2 from authors own measurements. All wave-lengths in vacuum from personal data except for those lines for which a dash is given in col. 2. Wave-lengths in air from references 2 or 3.

TABLE II. S III term table.

$s^{2}3p^{2} {}^{3}P_{0}$ ${}^{3}P_{1}$ ${}^{3}P_{2}$ ${}^{1}D_{2}$	0.0 297.2 832.5 11,320	$sp^{3} {}^{1}D_{2}$ ${}^{1}P_{1}$ $4s {}^{1}P_{1}$	104,159? 136,839 148,397.8	$sp^{3} \frac{^{3}D_{1}}{^{3}D_{2}}$ $\frac{^{3}D_{2}}{^{3}D_{3}}$ $sp^{3} \frac{^{3}P_{2}}{^{3}P_{1}}$	84,018.9 84,046.4 84,099.5 98,743.0 98,765.6
${}^{1}S_{0}$	27,163	5s 1P1	211,326.8	${}^{3}P_{0}^{1}$	(98,771)
				sp ³ ³ S	138,061.4

INT. λ (vac.) ν(cm⁻¹) CLASSIFICATION 3s 2S $-3p^{2}P_{1/2}$ 5§ 944.517 105,874 ${}^{2}\bar{P}_{3/2}$ 25 4 § 3 § 4 § 6 § 933.382 107,137 $3p \, {}^{2}P_{3/2} - 3d \, {}^{2}D_{3/2}$ 712.844 140.283 ${}^{2}P_{3/2}$ - ${}^{2}D_{5/2}$ 712.682 140.315 ${}^{2}D_{3/2}$ ${}^{2}P_{1/2}$ -706.480 141,547 $3d \, {}^{2}D_{3/2} - 4p \, {}^{2}P_{1/2}$ 650.4301 153,744 ${}^{2}\bar{P}_{3/2}$ ${}^{2}D_{5/2} - {}^{2}P_{2D} - 4f {}^{2}F_{2D}$ 1 648.628 154,172 10§ 8§ 6§ 6 3 2 464.654 215,214 $3d ^{2}D$ 390.859 3p 2P 3/2 - 4s 2S 255,847 $\frac{{}^{2}P_{1/2}}{3d \,{}^{2}D} - \frac{{}^{2}S}{5f \,{}^{2}F}$ 388.940 257,109 328.605 304,409 $\begin{array}{c} 3p \ {}^{2}P_{3/2} - 4d \ {}^{2}D_{5/2} \\ {}^{2}P_{1/2} - {}^{2}D_{3/2} \\ 3d \ {}^{2}D - 6f \ {}^{2}F \end{array}$ 290.132 344,671 345.911 289.092 $\frac{1}{3}$ 0n283.502 352,731 261.810 381.956 $-7f^2F$ $3d \ ^2D$ $\begin{array}{c} 3p \, {}^{2}P_{3/2} \, - \, 5s \, {}^{2}S \\ 3s \, {}^{2}S \, - \, 4p \, {}^{2}P_{1/2} \end{array}$ 251.905 396,975 2 4 249.271 401,170 ${}^{2}P_{3/2}$ 4 2 248.985 ^{2}S 401,631 227.845 439,895 $3p^2 P_{3/2} - 5d^2 D_{5/2}$ ${}^{2}P_{1/2}$ - ${}^{2}D_{2/2}$ 227.197 440,147 $3p \, {}^{2}P_{3/2} -$ 00 214.277 466,686 6s 2S 204.190 489,740 $3p^{2}P_{3/2}^{0} - 6d^{2}D$ 0n00n192.273 520,094 $3p^2P_{3/2}$ $-7d^{2}D$ $7a - 5p {}^{2}P_{1/2} {}^{2}P_{3/2}$ 192.560 522,030 ^{2}S 0n3s 192.480 522,248 ^{2}S 00 3s ^{2}S $6p^2P_{3/2}$ 00n171.327 583,679

TABLE III. Classified lines of S VI.

TABLE V.							
Int.	λ(vac.)		ν(cm ^{−1})		CLASSIFICATION		
$\begin{array}{c}2\\10 \ d.\\3\\3\end{array}$	48 45	01.649 88.120 2.667 9.013	20 22	9,343 4,868 0,913 2,711	$ \begin{array}{c} p^{2} {}^{1}D_{2} - sp^{3} {}^{3}S \\ p^{2} {}^{1}D_{2} - sp^{3} {}^{1}P_{1} \\ p^{2} {}^{3}P_{2} - sp^{3} {}^{1}P_{1} \\ p^{2} {}^{3}P_{1} - sp^{3} {}^{1}P_{1} \end{array} $		
TABLE VI. K VI term table.							
^ 3P	$\begin{array}{c c} s^2 p^2 {}^3P_0 & 0 \\ {}^3P_1 & 1131 \\ {}^3P_2 & 2924 \end{array}$		¹ S ₀		So	18,973 223,840	
TABLE VII.							
6 2 2 2 <i>Bl</i>			230,623 248,416 250,869 252,497		$\begin{array}{c} p^{2} {}^{1}D_{2} - sp^{3} {}^{1}P_{1} \\ p^{2} {}^{3}P_{2} - {}^{1}P_{1} \\ {}^{3}P_{1} - {}^{1}P_{1} \\ {}^{3}P_{0} - {}^{1}P_{1} \end{array}$		
TABLE VIII. Ca VII term table.							
$\begin{array}{c c c c c c c c c c c c c c c c c c c $) .	$s^{2}p^{2} {}^{1}D_{2}$ ${}^{1}S_{0}$ $sp^{3} {}^{1}P_{1}$		21,872 252,495		

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TABLE IV. S VI term table with Rydberg denominators.

3s 2S	710 1045	2.3585	2100	462,774§	1
35 23	710,194§	2.3383	3d 2D _{3/2}	402,7748	
4 s 2S	347,211§	3.3732	$^{2}D_{5/2}$	462,742§	2.9219
5s 2S	206,082	4.3785	$4d \ ^2D_{3/2}$	258,409 (23)	
6s 2S	136,371	5.3822	$^{2}D_{\delta/2}$	258,386	3.9101
3 p 2P1/2	604,320§ 1263		5a 2D3/2	164,173 (11)	
${}^{2}P_{3/2}$	603,057§	2.5595	${}^{2}D_{5/2}$	164,162	4.9056
4 p 2P1/2	309,030§ 457		6d 2D	113,317	5.9043
${}^{2}P_{3/2}$	308,573	3.5780	7d 2D	82,963	6.9007
$5p {}^2P_{1/2}$	188,164 218		$4f {}^2F$	247,541§	3.9949
${}^{2}P_{3/2}$	187,946	4.5846	5f 2F	158,346	4.9949
6 p 2P 3/2	126,515	5.5880	6f 2F	110,024	5.9923
5g 2G	158,088§	(4.9990)	7f 2F	80,799	6.9924

\$ Lines and terms previously classified: R. A. Millikan and I. S. Bowen, Phys. Rev. 25, 295 (1925).

are of intensity 0, wave-length 202.605A ($\nu = 493,571 \text{ cm}^{-1}$) and 198.550A ($\nu = 503,652 \text{ cm}^{-1}$). This indicates a separation of $-10,080 \text{ cm}^{-1}$ for the $p^{5} {}^{2}P$ which is in good agreement with prediction.

Minor additions to the singlet spectra of

K IV⁷⁻⁹ show that the lines λ 447.085 (ν =223,671 cm⁻¹) and λ 384.095 (ν =260,352 cm⁻¹) are in all probability the transitions $3p^{4} {}^{1}S_{0} - p^{3}3d {}^{1}P_{1}$, and $3p^{4} {}^{1}S_{0} - p^{3}4s {}^{1}P_{1}$ respectively. This places tentatively the $p^{4} {}^{1}S_{0}$ term at 37,778 cm⁻¹ ($p^{4} {}^{3}P_{0}$ =0).

Two of the singlet states of K VI⁴ have also been located: the lines classified are given in Tables V and VI.

The corresponding transitions in Ca VII^{7, 9} are given in Tables VII and VIII.

The additions to K IV and CaV II have been made jointly with Dr. George H. Shortley as part of the preceding paper in this issue of the *Physical Review*. They are listed here for convenience.

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⁷ Wave-lengths from E. Ekefors, Dissertation, Uppsala (1931). ⁸ I. S. Bowen, Phys. Rev. 46, 791 (1934).

⁹ A. E. Whitford, Phys. Rev. 46, 793 (1934).