THE SECOND SPARK SPECTRUM OF SULPHUR, S III

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ABSTRACT

Analysis of the sulphur III spectrum.—With experimental data previously obtained the spectrum of sulphur III is analyzed. Most of the triplet terms predicted by the Hund theory are found and the strongest lines in both the visible and extreme ultra-violet regions are classified. The ground term $3s^23p^2\,{}^3P_0$ gives the ionization potential as 34.9 ± 0.4 volts. Complete term tables and a list of classified lines are given. The term $3s^23p\cdot4s^3P$ is anomalous, having a total separation of 450 while the p doublet of the ion is 950. The interval ratio of this term is 10 to 1, instead of the 2 to 1 give by Landé's rule. Combinations of this term with the ground term in the extreme ultra-violet are unusually weak.

IN A preceding paper[1] the spectrum of singly ionized sulphur was analyzed. With the same data it has been possible to classify most of the strong lines in the spectrum of the doubly ionized atom. Recently Gilles[2,3] has published a classification of most of the strong lines of the sulphur III spectrum in the visible and ordinary ultra-violet regions. Except for a few minor points our work is in agreement but as there are several very irregular features in the spectrum it seems worth while to repeat that part of the work which overlaps, particularly as, in these two analyses, two entirely different sets of experimental data were used. In addition to the identifications published by Gilles this paper includes a number of new terms. Most of these new identifications were made possible by the investigation of the extreme ultra-violet part of the spectrum.

The experimental work is described in the paper to which reference has been made.[1] Above 2000A two sets of data were employed. The strongest lines were photographed with a 7-meter concave grating in a Rowland mounting. The wave-lengths of the lines measured by this method are probably accurate to 0.02A. As only a few lines appeared on the plates below 3000A the spectrum in the ultra-violet was photographed with a Hilger quartz spectrograph E2. The wave-lengths determined by this instrument may be in error by 0.1 or 0.2A. The extreme ultra-violet spectrum was measured with a vacuum spectrograph with a grating of 1 meter radius. The probable error in these measurements is about 0.03A.

TERM VALUES

The spectrum of sulphur III is built up on the sulphur IV ion which has for its ground configuration[4] a ^2P term with a separation of 950. Addition of another electron gives a singlet system and a triplet system. All the

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[1] Ingram, Phys. Rev. **32,** 172 (1928).
[2] Gilles, Comptes Rendus **188,** 63 (1929).
[3] Gilles, Comptes Rendus **188,** 320 (1929).
[4] Millikan and Bowen, Phys. Rev. **25,** 600 (1925).

identifications so far made belong to the latter. Table I gives the terms expected according to the Hund theory. Terms which have been found are printed in bold face in the table.

TABLE I. *Predicted terms of S III.* Terms in bold face have been identified.

Electron Configuration	Prefix		Terms	
$3s^2 3p^2$	a		^3P	$^1D\,^1S$
$3s3p^3$	b	^5S	$\cdot\,^3S\,^3P\,^3D$	$^1P\,^1D$
$3s^2 3p \cdot 3d$	$3d$		$^3P\,^3D\,^3F$	$^1P\,^1D\,^1F$
$3s^2 3p \cdot 4s$	$4s$		^3P	^1P
$3s^2 3p \cdot 4p$	$4p$		$^3S\,^3P\,^3D$	$^1S\,^1P\,^1D$
$3s^2 3p \cdot 4d$	$4d$		$^3P\,^3D\,^3F$	$^1P\,^1D\,^1F$
$3s^2 3p \cdot 4f$	$4f$		$^3D\,^3F\,^3G$	$^1D\,^1F\,^1G$
$3s^2 3p \cdot 5s$	$5s$		^3P	^1P

TABLE II. *Term values of S III.*

	$3s^2 3p^2$			$3s^2 3p \cdot 4p$	
a^3P_0	282752		$4p^3D_1$	112976.05	
		300			297.30
a^3P_1	282452		$4p^3D_2$	112678.75	
		535			581.71
a^3P_2	281917		$4p^3D_3$	112097.04	
	$3s3p^3$		$4p^3P_0$	110114.68	
					154.50
b^3D_1	198729		$4p^3P_1$	109960.18	
		28			405.88
b^3D_2	198701		$4p^3P_2$	109554.30	
		51			
b^3D_3	198650		$4p^3S_1$	108709.76	
b^3P_0	[183978]not resolved from P_1			$3s^2 3p \cdot 3d$	
		-6			
b^3P_1	183984		$3d^3D_1$	135195.60	
		-19			140.69
b^3P_2	184003		$3d^3D_2$	135054.91	
					53.39
b^3S_1	144686		$3d^3D_3$	135001.52	
			$3d^3P_0$	139650.11	
	$3s^2 3p \cdot 4s$				20.20
$\cdot 4s^3P_0$	136049.72		$3d^3P_1$	139629.91	
		40.24			7.82
$4s^3P_1$	136009.48		$3d^3P_2$	139622.09	
		409.48			
$4s^3P_2$	135600.00			$3s^2 3p \cdot 4d$	
	$3s^2 3p \cdot 5s$		$4d^3F_2$	78167.11	
					491.86
$5s^3P_0$	72972.6		$4d^3F_3$	77675.25	
		152.7			489.92
$5s^3P_1$	72819.9		$4d^3F_4$	77185.33	
		771.5			
$5s^3P_2$	72048.4		$4d^3D_1$	76207.13	
					132.74
			$4d^3D_2$	76074.39	
					239.36
			$4d^3D_3$	75835.03	

Term combining with a^3P
x 145905

Gilles, in his paper, gives the value of the $4s^3P_2$ term as 135,600 which value has apparently been determined by means of a Rydberg formula from the two terms $4s^3P_2$ and $5s^3P_2$. According to Hund's theory of convergence to limits these terms go to the $^2P_{3/2}$ limit and hence Gilles' values are probably about 1000 too great when referred to the most stable state of S IV. However as the absolute values of the terms may be in error by an amount as great as this Gilles' value of $4s^3P_2$ has been adopted and the other terms evaluated on this basis.

Table II gives a complete list of term values. The P_1 and P_0 terms which I have assigned to the $s^2p.5s$ configuration Gilles has assigned to $s^2p.4d$.

TABLE III. *Classified lines of S III in the visible and ordinary ultra-violet regions.*

Int.	λ I.A. Air	ν	Triplets	Int.	λ I.A.Air	ν	Triplets
R0	4527.96	22078.83	$3dD_2-4pD_1{}^*$	Q4	3234.17	30911.0	$3dP_2-4pS_1$
R0	4499.29	22219.52	$3dD_1-4pD_1{}^*$	Q3	3233.24	30919.8	$3dP_1-4pS_1$
R2	4478.48	22322.76	$3dD_3-4pD_2{}^*$	Q3	3231.10	30940.3	$3dP_0-4pS_1$
R1	4467.83	22375.97	$3dD_2-4pD_2{}^*$	Q3	3185.16	31386.5	$4pP_2-4dF_2$
R4	4439.88	22516.83	$3dD_1-4pD_2{}^*$	Q3	3136.00	31878.6	$4pP_2-4dF_3$
R2	4418.87	22623.89	$4sP_2-4pD_1{}^*$	Q6	2985.98	33480.1	$4pP_2-4dD_2{}^*$
R5	4364.74	22904.46	$3dD_3-4pD_3{}^*$	R4	2964.80	33719.27	$4pP_2-4dD_3{}^*$
R7	4361.54	22921.26	$4sP_2-4pD_2{}^*$	R0	2961.83	33753.08	$4pP_1-4dD_1{}^*$
R5	4354.57	22957.95	$3dD_2-4pD_3{}^*$	R3	2950.23	33885.79	$4pP_1-4dD_2{}^*$
R5	4340.29	23033.48	$4sP_1-4pD_1{}^*$	R2	2948.34	33907.51	$4pP_0-4dD_1{}^*$
R7	4332.72	23073.73	$4sP_0-4pD_1{}^*$	Q6	2904.31	34421.5	$4pD_3-4dF_3$
R8	4284.99	23330.73	$4sP_1-4pD_2{}^*$	R0	2896.71	34511.83	$4pD_2-4dF_2$
R10	4253.59	23502.96	$4sP_2-4pD_3{}^*$	R2	2872.00	34808.75	$4pD_1-4dF_2$
R5	3985.97	25080.92	$3dD_1-4pP_0{}^*$	R5	2863.53	34911.71	$4pD_3-4dF_4$
R7	3983.76	25094.84	$3dD_2-4pP_1{}^*$	R4	2856.02	35003.50	$4pD_2-4dF_3$
R4	3961.55	25235.53	$3dD_1-4pP_1{}^*$	Q4	2797.39	35737.1	$4pS_1-5sP_0{}^*$
R9	3928.59	25447.25	$3dD_3-4pP_2{}^*$	Q6	2785.49	35889.8	$4pS_1-5sP_1$
R0	3920.37	25500.60	$3dD_2-4pP_2{}^*$	Q1	2778.82	35975.9	bS_1-4pS_1?
R4	3860.64	25895.13	$4sP_1-4pP_0{}^*$	Q5	2775.25	36022.2	$4pD_3-4dD_2{}^*$
R8	3838.32	26045.70	$4sP_2-4pP_2{}^*$	Q8	2756.89	36262.1	$4pD_3-4dD_3{}^*$
R5	3837.79	26049.30	$4sP_1-4pP_1{}^*$	Q5	2741.01	36472.1	$4pD_2-4dD_1{}^*$
R5	3831.87	26089.54	$4sP_0-4pP_1{}^*$	Q7	2731.10	36604.4	$4pD_2-4dD_2{}^*$
R6	3794.70	26345.09	$3dD_2-4pS_1{}^*$	Q7	2726.82	36661.9	$4pS_1-5sP_2{}^*$
R5	3778.91	26455.17	$4sP_1-4pP_2{}^*$	Q5	2721.40	36734.9	$4pP_2-5sP_1{}^*$
R1	3774.54	26485.80	$3dD_1-4pS_1{}^*$	Q7	2718.88	36769.0	$4pD_1-4dD_1{}^*$
R3	3750.74	26653.86	$3dP_1-4pD_1{}^*$	Q2	2713.28	36844.8	$4pD_2-4dD_3{}^*$
R5	3747.90	26674.05	$3dP_0-4pD_1{}^*$	Q2	2709.03	36902.6	$4pD_1-4dD_2{}^*$
R7	3717.77	26890.23	$4sP_2-4pS_1{}^*$	Q5	2702.76	36988.3	$4pP_1-5sP_0{}^*$
R2	3710.44	26943.34	$3dP_2-4pD_2{}^*$	Q5	2691.68	37140.5	$4pP_1-5sP_1{}^*$
R6	3709.37	26951.12	$3dP_1-4pD_2{}^*$	Q4	2680.47	37295.8	$4pP_0-5sP_1{}^*$
R5	3662.00	27299.73	$4sP_1-4pS_1{}^*$	Q7	2665.40	37506.7	$4pP_2-5sP_2{}^*$
R3	3656.61	27339.97	$4sP_0-4pS_1{}^*$	Q4	2636.88	37912.3	$4pP_1-5sP_2{}^*$
R6	3632.03	27524.99	$3dP_2-4pD_3{}^*$	Q7	2508.15	39858.1	$4pD_2-5sP_1{}^*$
R4	3387.12	29515.16	$3dP_1-4pP_0{}^*$	Q6	2499.08	40002.7	$4pD_1-5sP_0{}^*$
R4	3370.37	29661.84	$3dP_2-4pP_1{}^*$	Q6	2496.24	40048.1	$4pD_3-5sP_2{}^*$
R3	3369.47	29669.76	$3dP_1-4pP_1{}^*$	Q5	2489.59	40155.2	$4pD_1-5sP_1{}^*$
R4	3367.18	29689.94	$3dP_0-4pP_1{}^*$	Q5	2460.50	40629.9	$4pD_2-5sP_2{}^*$
R6	3324.85	30067.92	$3dP_2-4pP_2{}^*$	Q1	2442.62	40927.3	$4pD_1-5sP_2{}^*$
R4	3323.99	30075.70	$3dP_1-4pP_2{}^*$				

* Identified by Gilles.

The P_2P_0 separation of the $s^2p.5s$ term should be slightly less than 950, the doublet separation of the ion, and the separation of the P_2P_0 terms here found is 924. This, together with the fact that the members of the multiplets

follow the intensity rules nicely, supports the present assignment. In addition to these terms Gilles has found two others, P_2 which he assigns to $s^2p.4d$ and P_1 which he assigns to $s^2p.5s$. Each of these terms is identified on the basis of only two combinations and as the values of the terms, calculated from these combinations, differ by rather more than would be expected from the accuracy of the data they have been omitted from the table.

The ground term, $3s^23p^2\ {}^3P_0$, has a value of 282,752. This gives an ionization potential for the sulphur III ion of 34.9 volts. As the absolute values of the terms are uncertain to the extent of several thousand units this value may be in error by 0.3 or 0.4 volts. Gilles[3] has suggested that the PP' group at 850A which Bowen and Millikan[5] have assigned to S V may be $a^3P - 4s^3P$ of S III, since one of the P' separations is very near to the $4s^3P_2P_1$ separation. The present data in the extreme ultra-violet, however, show that this reassignment is not necessary. Furthermore the group at 850A, $3s3p^3P - 3p^2\ {}^3P$, is in an iso-electronic sequence and is given additional support by the closeness with which it follows the irregular doublet law.

CLASSIFIED LINES

Tables III and IV give a complete list of the classified lines in S III. Many of the combinations among the high terms have been identified by

TABLE IV. *Classified lines of S III in the extreme ultra-violet region.*

Int.	λ I.A. Vac.	ν	Triplets	Int.	λI.A. Vac	ν	Triplets
0	1390.67	71907.7	bP_2-4pD_3	2	735.24	136011	aP_2-x
0	1343.53	74430.7	bP_1-4pP_2	2	732.36	136546	aP_1-x
0	1343.25	74446.3	bP_2-4pP_2	0	730.74	136848	aP_0-x
0	1328.52	75271.5	$\{bP_1-4pS_1$	3	728.69	137233	aP_2-bS_1
			$\{bP_0-4pS_1$	3	725.86	137767	aP_1-bS_1
0	1328.12	75294.5	bP_2-4pS_1	3	724.29	138067	aP_0-bS_1
0	1202.10	83187.7	aP_2-bD_1	(masked by 702 O III)			$\{aP_2-3dP_2$
2	1201.71	83214.9	aP_2-bD_2				$\{aP_2-3dP_1$
4	1200.97	83266.2	aP_2-bD_3	3	700.29	142798	aP_1-3dP_0
3	1194.40	83724.0	aP_1-bD_1	3	700.15	142827	$\{aP_1-3dP_1$
4	1194.02	83750.9	aP_1-bD_2				$\{aP_1-3dP_2$
2	1190.17	84021.8	aP_0-bD_1	2	698.73	143118	aP_0-3dP_1
0	1166.13	85753.9	bD_1-4pD_1	0	685.35	145911	aP_2-4sP_1
1	1162.52	86020.0	bD_2-4pD_2	1	683.47	146312	aP_2-4sP_2
2	1155.34	86554.8	bD_3-4pD_3	0	683.07	146398	aP_1-4sP_0
1	1126.85	88743.1	bD_2-4pP_1	1	681.50	146735	$\{aP_0-4sP_1$
0	1126.48	88772.1	bD_1-4pP_1				$\{aP_2-3dD_1$
2	1122.42	89093.2	bD_3-4pP_2				$\{aP_1-4sP_2$
2	1021.32	97912.7	aP_2-bP_2	2	680.95	146853	$\{aP_2-3dD_2$
1	1021.10	97933.6	aP_2-bP_1	2	680.69	146910	aP_2-3dD_3
1	1015.76	98448.1	aP_1-bP_2	2	679.11	147252	aP_1-3dD_1
2	1015.51	98472.9	$\{aP_1-bP_1$	2	678.46	147392	aP_1-3dD_2
			$\{aP_1-bP_0$	2	677.75	147548	aP_0-3dD_1
3	1012.49	98766.7	aP_0-bP_1	0	485.22	206092	aP_2-4dD_3
				0	484.58	206365	aP_1-4dD_2

Gilles and these have been marked with an asterisk (*). The stronger lines, which have been measured on the large Rowland grating, are dis-

[5] Bowen and Millikan, Phys. Rev. **25**, 591 (1925).

tinguished by a capital R placed in the column of the intensities, and the frequencies of these lines are given to two decimals. The weaker lines, which were obtained only on the quartz spectrograph, are marked with a capital Q, and the frequencies given to one decimal. All such lines are to be considered as weaker than the R O lines and this fact must be borne in mind when intensities are being compared.

The line 3860.64 was previously classified as belonging to the sulphur II spectrum. Lines are predicted from the term values in S II and S III at 3860.61 and 3860.69, respectively, too close to be resolved, so that this line is doubtless a blend.

The line 2665.40 is identified as $4p^3P_2-5s^3P_2$. Bowen and Millikan[5] have identified this line as $4s^3S_1-4p^3P_0$ of S V and have used it to fix the $4p^3P_0$ level. As no other combinations with this level were observed the present identification may throw some doubt on the $4p^3P_0$ term of S V. The present assignment is very certain since five other combinations confirm it.

DISCUSSION

There are several very irregular features in this spectrum. The principal ones of these are connected with the $3s^23p.4s^3P$ term. Goudsmit[6] has developed the theory of multiplet separations. In this theory certain Γ values are defined which represent the energy differences between the various levels and the center of gravity of the multiple term. Also a Γ sum rule is formulated which states that "the sum of all Γ values belonging to a definite value of j is independent of the coupling." Now when we add an s electron to an ion in a ^2P state we get four levels, one with $j=2$, two with $j=1$, and one with $j=0$, and it follows from the Γ sum rule, as Goudsmit states in his paper, that "the separation of the s levels with $j=2$ and $j=0$ is exactly constant through the whole series of levels, and equal to the p doublet of the ion."[*] This condition should hold quite independently of the type of coupling between the electrons. The remarkable accuracy with which it usually holds is well illustrated by the case of the s levels in neon as has been pointed out by Goudsmit and Back.[7] Table V A illustrates this case. In Table V B are collected all the data which are available on the total separations of the s^3P terms of the spectra iso-electronic with S III, together with the doublet separations of the corresponding ions. It is at once obvious that the $4s^3P$ term of S III is anomalous, the separation being about one half of that which would be expected. The second term of the series appears to be perfectly regular.

This calls to mind a somewhat analogous case in the spectrum of N I. The ground state of the N II ion is a ^3P term of total separation 132.[8] Addition of an s electron gives a series of ^4P terms and a series of ^2P terms of which several members are known through the recent work of Compton

[6] Goudsmit, Phys. Rev. **31**, 946 (1928).

[*] Actually the screening effect of the added s electron may cause this total separation to be somewhat smaller. This is clearly illustrated by the data in Table V.

[7] Goudsmit and Back, Zeits. f. Physik **40**, 530 (1927).

[8] Bowen, Phys. Rev. **29**, 231 (1927).

and Boyce.[9] The theory of Goudsmit and Humphreys[10] predicts for this case, ^4P terms with total separation 117, and ^2P terms with separation 88. The comparison of the calculated and observed values is shown in Table V C. Here, again, the first member of the series, the $3s^4P$ term shows a marked deviation.

It should be remarked however that there is an essential difference between this case and that occurring in S III. In the N I case we have one level with $j = 5/2$ and two with $j = 1/2$, and the Γ sum rule may not be applied to predict the total separation of the ^4P term. Hence this separation is not independent of the coupling and it is only justified to apply the theory

TABLE V.
A. *Difference of levels with $j = 2$ and $j = 0$ in Neon I.*

Configuration	$j=2-j=0$	Configuration	$j=2-j=0$
$3s$	776.80	$9s$	780.73
$4s$	—	$10s$	779.95
$5s$	778.16	$11s$	780.16
$6s$	781.34	—	—
$7s$	780.13		
$8s$	780.98	Ne II $^2P_{3/2}, -^2P_{1/2},$	782 ± 3

B. *Total separation of s^3P terms.*

Terms	Si I	P II	S III	Cl IV
$4s^3P_0 - 4s^3P_2$	275	527	450	1446
$5s^3P_0 - 5s^3P_2$	283	546	924	—
$^2P_{1/2}, -^2P_{3/2},$ in ion	287	560	950	1495

C. *Total separation of s^4P and s^2P terms in N I.*

Terms	Obs.	Calc.	Terms	Obs.	Calc.
$3s^4P_{1/2} - 3s^4P_{5/2}$	81	117	$3s^2P_{1/2} - 3s^2P_{3/2}$	83	88
$4s^4P_{1/2} - 4s^4P_{5/2}$	118	117	$4s^2P_{1/2} - 4s^2P_{3/2}$	83	88
$5s^4P_{1/2} - 5s^4P_{5/2}$	114	117	$5s^2P_{1/2} - 5s^2P_{3/2}$	76	88
$6s^4P_{1/2} - 6s^4P_{5/2}$	117	117			

in case that the electrons are coupled according to the Russell-Saunders scheme. In S III however we have only one level with $j = 2$ and one with $j = 0$, and hence the total separation should be quite independent of the type of coupling.

Not only is the total separation of the $4s^3P$ term irregular, but the interval ratio is 409:40 or about 10 to 1 instead of the normal 2 to 1. A further abnormality occurs in the weakness of the combinations of this term with the ground term a^3P. Ordinarily, in other light elements, these lines are among the strongest in the whole extreme ultra-violet spectrum. A glance at the classified lines in Table IV shows, however, that they are here com-

[9] Compton and Boyce, Phys. Rev. 33, 145 (1929).
[10] Goudsmit and Humphreys, Phys. Rev. 31, 960 (1928).

paratively weak. The combination of a^3P with $4s^3P$ falls between those with $3d^3P$ and $3d^3D$ and is much weaker than either of the other multiplets.

It is, perhaps, worth remarking that the line $4s^3P_2 - 4p^3P_1$ is either entirely missing or else very weak. Gilles gives the line 3899.27 this designation but as it lies about 0.2A from the predicted position the identification is doubtful. In any case the intensity is only 1 on my scale while the other lines of the multiplet range from 4 to 8.

Bowen [11, 12] has identified the combinations of a^3P with $3d^3D$ and $3d^3P$ in P II and Cl IV which are iso-electronic with S III. Table VI gives the wave-numbers of the strongest lines of these multiplets. These should follow the irregular doublet law and the fact that the deviations are very large may indicate that some of the identifications need revision. The terms $3d^3D$ and $3d^3P$ seem quite certain in S III since they combine not only with a^3P but also with $4p^3S$, ^3P and ^3D.

TABLE VI. *Irregular doublets.*

Terms	P II		S III		Cl IV
$a^3P_2 - 3d^3D_3$	103726		146910		165401
		43184		18491	
$a^3P_2 - 3d^3P_2$	109823		142290		180735
		32467		38445	

In conclusion I wish to acknowledge the use of certain unpublished data of Dr. I. S. Bowen and to express my thanks to Dr. S. A. Goudsmit and Dr. O. Laporte for their helpful discussion. The experimental part of this work and a large part of the analysis were done at the California Institute of Technology and the remainder has been completed at the Univeristy of Michigan while the writer has been under appointment as a National Research Fellow.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MICHIGAN,
March, 1929.

Noted added to proof, April 24, 1929.—Considering the irregularity of the $4s^3P$ term it seems wise to add a few words giving the reasons for the indentification. These reasons are briefly as follows: (1) The position in the spectrum at which the multiplets involving the $4s^3P$ term should fall can be predicted from the iso-electronic spectrum of P II and also by analogy with the spectra of other elements in this part of the periodic table. The observed term agrees with these predictions to within about 1000 wave-numbers. (2) The three levels assigned to this term are undoubtedly real as can readily be seen from the number of combinations they give with $4p^3(SPD)$ and a^3P. There are no other levels to be expected in this region according to the Hund theory except those from the $s^2p \cdot 3d$ configuration. Of these ^3P and ^3D are found and ^3F could not possibly give the combinations given by the levels in question. By exclusion, therefore, the levels are assigned to $4s^3P$. (3) The $4s^3P$ level should combine with $4p^3(SPD)$ to give some of the strongest multiplets in the whole spectrum while among the unidentified lines are only three of intensity greater than 4. The multiplets involving $4s^3P$ are much stronger than this as can be seen from Table III.

[11] Bowen, Phys. Rev. **29**, 510 (1927).
[12] Bowen, Phys. Rev. **31**, 34 (1928).