THE SPECTRUM OF SULPHUR, S II

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ABSTRACT

One hundred and eighty-three lines are classified in the spectrum of S II. Thirty-three terms of the quartet system and thirty-six of the doublet system are determined and correlated with the electron configurations by means of the Hund theory. The *ionization potential* of the S II ion is fixed at 23.3 ± 0.1 volts.

EXPERIMENTAL WORK

THE sulphur spectrum above 2000A was obtained by passing a condensed discharge through H_2S gas. At higher pressures the Balmers eries predominated but as the pressure was reduced towards the limiting value at which a discharge could sustain itself the hydrogen lines became relatively weak and the sulphur spectrum came out with great intensity. When the self induction of the discharge circuit was reduced to a minimum the lines of S II, III, IV and V appeared strongly on the plates. Insertion of sufficient self induction into the circuit to reduce the frequency of oscillation, and hence the instantaneous value of the current, to about one-tenth its former value completely suppressed all these except the S II lines. The visible and ordinary ultra-violet regions were photographed by means of a 7 meter concave grating in a Rowland mounting. In the ultra-violet these observations were supplemented by a plate taken on a Hilger quartz spectrograph E2. In the extreme ultra-violet the spectrum of a hot spark was photographed on a vacuum spectrograph with a grating of one meter radius. The exactness with which the data fit the series relationships gives a check on the accuracy of the measurements. The probable errors, estimated in this way are: for

TABLE I. *Predicted terms of S II.*

Electron configuration	Prefix	Terms	Prefix	Terms	Prefix	Terms
s^2p^3	a	^4S				
	a	$^2D\,^2P$				
sp^4	b	^4P				
	b	$^2P\,^2D\,^2S$				
S III ion s^2p^2		^3P		^1D		^1S
S II $s^2p^2\cdot ms$	ms	^4P				
	ms	^2P	ms'	^2D	ms''	^2S
$s^2p^2\cdot mp$	mp	$^4S\,^4P\,^4D$				
	mp	$^2S\,^2P\,^2D$	mp'	$^2P\,^2D\,^2F$	mp''	^2P
$s^2p^2\cdot md$	md	$^4P\,^4D\,^4F$				
	md	$^2P\,^2D\,^2F$	md'	$^2S\,^2P\,^2D\,^2F\,^2G$	md''	^2D
$s^2p^2\cdot mf$	mf	$^4D\,^4F\,^4G$				
	mf	$^2D\,^2F\,^2G$	mf'	$^2P\,^2D\,^2F\,^2G\,^2H$	mf''	^2F

the measurements on the large grating about 0.02A, on the quartz spectrograph about 0.3A, and on the vacuum spectrograph about 0.03A. Some of the weaker lines have been taken from old data appearing in Kayser's Handbuch der Spectroscopie. The probable error in these measurements appears to be about 0.2A.

Predicted Terms

The spectrum of sulphur II should be similar to that of oxygen II containing a doublet and quartet system. Table I gives a summary of the predictions of the Hund theory. The notation used is standard excepting for the introduction of primes on the letter referring to the orbit of the excited electron. Unprimed terms are based on the ^3P state of the S III ion, singly primed terms on the ^1D state and doubly primed terms on the ^1S state. Those terms which have been observed are in bold face in the table.

Term Values

Two members of both the series of terms ms^4P and ms^2P, $m=4$, 5, have been detected, thus making possible the determination of the term values and of the ionization potential. In fixing the terms $4s^4P$, and $4s^2P$, an increase of effective quantum number of 1.02 between the terms $4P$ and $5P$ has been assumed. This assumption is arbitrary except insofar as it is justified by analogy with the terms of O II and of other light elements. The term values calculated on this assumption are about 700 cm^{-1} less than those determined by an ordinary Rydberg formula. The combination of the $4s^4P$ term with the low ^4S term in the extreme ultra-violet fixes the ground term of the S II ion at 188824.5 cm^{-1} giving an ionization potential of 23.3 ± 0.1 volts. The complete list of term values is given in Table II. Since no intercombinations

Table II. *Term values.*

		s^2p^3			
a^4S_2	188824.5	a^2P_2	163934.5	a^2D_3	173623.9
		a^2P_1	163983.1	a^2D_2	173655.4
		sp^4			
b^4P_3	109429.7	b^2P_2	82908.36		
b^4P_2	109066.6	b^2P_1	82463.28		
b^4P_1	108856.5				
Terms based on S III ^3P				Terms based on S III ^1D	
		$s^2p^2\cdot 4s$			
$4s^4P_3$	78556.17	$4s^2P_2$	75045.88	$4s'^2D_3$	66977.31
$4s^4P_2$	78993.17	$4s^2P_1$	75570.00	$4s'^2D_2$	66978.87
$4s^4P_1$	79264.00				
		$s^2p^2\cdot 5s$			
$5s^4P_3$	37828.16	$5s^2P_2$	36596.42		
$5s^4P_2$	38293.29	$5s^2P_1$	37123.21		
$5s^4P_1$	38566.02				
		$s^2p^2\cdot 4p$			
$4p^4S_2$	57795.79			$4p'^2P_2$	44883.79
				$4p'^2P_1$	45018.43
$4p^4P_3$	58690.48	$4p^2P_2$	55107.43		
$4p^4P_2$	58966.43	$4p^2P_1$	55238.70	$4p'^2D_3$	47798.45
$4p^4P_1$	59036.81			$4p'^2D_2$	47757.24
$4p^4D_4$	60225.45	$4p^2D_3$	57320.17	$4p'^2F_4$	48188.00
$4p^4D_3$	60591.48	$4p^2D_2$	57866.26	$4p'^2F_3$	48277.33
$4p^4D_2$	60848.28				
$4p^4D_1$	60999.51				

Terms based on SIII ^3P				Terms based on SIII ^1D	
		$s^2p^2\cdot 3d$			
$3d^4F_5$	78058.19	$3d^2P_2$	70360.37		
$3d^4F_4$	78316.02				
$3d^4F_3$	78511.37	$3d^2D_3$	69212.27		
$3d^4F_2$	78647.67	$3d^2D_2$	69265.17		
		$3d^2F_4$	73221.76		
		$3d^2F_3$	73703.11		
		$s^2p^2\cdot 4d$			
$4d^4P_3$	33005.80			$4d'^2G_5$	24171.53
$4d^4P_2$	32795.14			$4d'^2G_4$	24169.63
$4d^4P_1$	32676.09				
$4d^4D_4$	35410.80	$4d^2D_3$	29679.53		
$4d^4D_3$	35541.51	$4d^2D_2$	29841.18		
$4d^4D_2$	35622.66				
$4d^4D_1$	35670.67				
$4d^4F_5$	36208.98	$4d^2F_4$	31903.37		
$4d^4F_4$	36519.60	$4d^2F_3$	32385.52		
$4d^4F_3$	36729.90				
$4d^4F_2$	36864.80				
Terms combining with a^2D, a^2P, of s^2p^3 configuration					
$^2P_2$	48491.26	$^2P_1$	48661.7	^2x	55147.9
	48491.6				

between the doublet and quartet systems have been detected the term values given in the two systems have not been determined accurately relative to each other.

Description of Table III

Table III gives a complete list of all the lines which have been classified in S II. In the first column is given the intensity of each line on a scale running from 0 to 10. Since the photographs were taken on different spectrographs the intensities are not in all cases comparable. The intensities of lines measured on the large grating spectrograph are prefixed by the letter *R*, the intensities of those taken from Kayser's tables are prefixed by *K*, and of those measured on the quartz spectrograph by *Q*. In general lines marked *K* are weaker than 0 lines on the *R* scale and those marked *Q* are weaker than either the *K* or *R* lines. Lines below 2000A are measured on the vacuum spectrograph. The second column of the table gives the wave-lengths, the third the wave-numbers, and the fourth and fifth the series designation in the quartet and doublet systems respectively.

Table III. *Classified lines of S II.*

Int.	I. A. Air	ν	Quartets	Doublets
R1	5819.22	17179.68		$4sP_2-4pD_2$
R3	5664.73	17648.21	$3dF_2-4pD_1$	
R4	5659.95	17663.11	$3dF_3-4pD_2$	
R6	5646.98	17703.68		$4sP_1-4pD_2$
K2	5645.70	17707.68	$4sP_3-4pD_2$	
R5	5640.32	17724.58	$3dF_4-4pD_3$	
R8	5639.96	17725.71		$4sP_2-4pD_3$
R1	5616.63	17799.34	$3dF_2-4pD_2$	
R6	5606.11	17832.74	$3dF_5-4pD_4$	
R1	5578.85	17919.88	$3dF_3-4pD_3$	
R4	5564.94	17964.67	$4sP_3-4pD_3$	
K1	5558.91	17984.14		$4pP_2-5sP_1$
R1	5556.01	17993.54	$4sP_2-4pD_1$	
K3	5536.76	18056.12	$3dF_2-4pD_3$	
R1	5526.22	18090.54	$3dF_4-4pD_4$	
K3	5518.76	18115.00		$4pP_1-5sP_1$
R5	5509.67	18144.88	$4sP_2-4pD_2$	
R5	5473.59	18264.49	$4sP_1-4pD_1$	
R10	5453.81	18330.72	$4sP_3-4pD_4$	
R9	5432.77	18401.71	$4sP_2-4pD_3$	
R5	5428.64	18415.72	$4sP_1-4pD_2$	
K3	5400.83	18510.54		$4pP_2-5sP_2$
R5	5345.67	18701.54		$4s'D_2-4p'F_3$
R7	5320.70	18789.31		$4s'D_3-4p'F_4$
R4	5212.61	19178.92		$4s'D_3-4p'D_3$
K2	5201.35	19220.45		$4s'D_3-4p'D_2$
R2	5201.00	19221.73		$4s'D_2-4p'D_2$
K1	5125.78	19503.82	$4pS_2-5sP_2$?	
R2	5103.30	19589.72	$4sP_3-4pP_2$	
R0	5047.28	19807.14		$4sP_2-4pP_1$
R5	5032.41	19865.67	$4sP_3-4pP_3$	
R3	5014.03	19938.49		$4sP_2-4pP_2$
R4	5009.54	19956.36	$4sP_2-4pP_1$	
R1	5006.71	19967.64	$4pS_2-5sP_3$	
R3	4991.94	20026.72	$4sP_2-4pP_2$	
R0	4942.47	20227.17	$4sP_1-4pP_1$	
R5	4925.32	20297.60	$4sP_1-4pP_2$	
R4	4924.08	20302.71	$4sP_2-4pP_3$	

TABLE III. (continued)

Int.	I. A. Air	ν	Quartets	Doublets
R2	4917.15	20331.33		$4sP_1-4pP_1$
R0	4901.30	20397.07	$4pP_3-5sP_2$	
R0	4900.47	20400.53	$4pP_2-5sP_1$	
R1	4885.62	20462.53		$4sP_1-4pP_2$
R0	4835.81	20673.30	$4pP_2-5sP_2$	
R3	4824.03	20723.79		$4pD_3-5sP_2$
R2	4819.55	20743.05	$4pP_1-5sP_2$ (Blend)	$4pD_2-5sP_1$
R9	4815.52	20760.41	$4sP_3-4pS_2$	
R3	4791.97	20862.43	$4pP_3-5sP_3$	
R2	4763.34	20987.82		$3dD_2-4p'F_3$
R3	4755.07	21024.32		$3dD_3-4p'F_4$
R0	4729.45	21138.21	$4pP_2-5sP_3$	
R7	4716.25	21197.37	$4sP_2-4pS_2$	
R0	4700.19	21269.80		$4pD_2-5sP_2$
R4	4668.59	21413.77		$3dD_3-4p'D_3$
R5	4656.75	21468.21	$4sP_1-4pS_2$	
R3	4648.14	21507.98		$3dD_2-4p'D_2$
R5	4552.37	21960.44		$4s'D_2-4p'P_1$
R6	4524.96	22093.46		$4s'D_3-4p'P_2$
R2	4524.65	22094.98		$4s'D_2-4p'P_2$
K1	4508.93	22172.03	$4pP_1-4dF_2$?	
K1	4492.32	22254.01	$4pS_2-4dD_3$	
R3	4486.63	22282.21	$4pD_2-5sP_1$	
R6	4483.42	22298.16	$4pD_3-5sP_2$	
R7	4463.58	22397.28	$4pD_4-5sP_3$	
R4	4456.39	22433.41	$4pD_1-5sP_1$	
R3	4432.37	22554.98	$4pD_2-5sP_2$	
R2	4431.00	22561.95		$3dP_2-4p'D_3$
K2	4402.64	22707.28	$4pD_1-5sP_2$	
R3	4391.81	22763.28	$4pD_3-5sP_3$	
R1	4333.84	23067.76	$4pP_3-4dD_2$	
R4	4318.64	23148.95	$4pP_3-4dD_3$	
R6	4294.39	23279.67	$4pP_3-4dD_4$	
R1	4291.43	23295.72	$4pP_2-4dD_1$	
R4	4282.60	23343.75	$4pP_2-4dD_2$	
R4	4278.51	23366.07	$4pP_1-4dD_1$	
R5	4269.72	23414.17	$4pP_1-4dD_2$	
R6	4267.76	23424.93	$4pP_2-4dD_3$	
R4	4230.94	23628.78		$4p'D_3-4d'G_4$
R4	4217.19	23705.82	$4pD_4-4dF_4$	
R4	4189.68	23861.59	$4pD_3-4dF_3$	
R5	4168.37	23983.46	$4pD_2-4dF_2$	
R10	4162.64	24016.47	$4pD_4-4dF_5$ (Blend)	$4p'F_4-4d'G_5$
R2	4162.29	24018.49		$4p'F_4-4d'G_4$
R10	4153.05	24071.92	$4pD_3-4dF_4$	
R5	4146.90	24107.62		$4p'F_3-4d'G_4$
R8	4145.05	24118.38	$4pD_2-4dF_3$	
R8	4142.24	24134.74	$4pD_1-4dF_2$	
R2	4050.08	24683.92	$4pD_4-4dD_3$	
R6	4032.77	24789.87	$4pS_2-4dP_3$	
R7	4028.74	24814.67	$4pD_4-4dD_4$	
R1	4009.35	24934.67		$4pD_3-4dF_3$
R1	4007.77	24944.50		$3dF_4-4p'F_3$
R2	4003.87	24968.80	$4pD_3-4dD_2$	
R5	3998.74	25000.84	$4pS_2-4dP_2$	
R6	3993.49	25033.70		$3dF_4-4p'F_4$
R5	3990.90	25049.95	$4pD_3-4dD_3$	
R4	3979.81	25119.75	$4pS_2-4dP_1$	
K3	3970.67	25177.58	$4pD_2-4dD_1$	
K2	3963.09	25225.72	$4pD_2-4dD_2$	
R0	3950.39	25306.82	$4pD_2-4dD_3$	
R2	3946.94	25328.94	$4pD_1-4dD_1$	
K1	3944.91	25342.00		$3dP_2-4p'P_1$
K1	3939.75	25375.20	$4pD_1-4dD_2$	

TABLE III. (continued)

Int.	I. A. Air	ν	Quartets	Doublets
R7	3933.25	25416.80		$4pD_3-4dF_4$
R3	3932.29	25423.30		$3dF_4-4p'D_3$
R5	3931.90	25425.82		$3dF_3-4p'F_3$
R1	3931.50	25428.41		$4pP_2-4dD_3$
R0	3924.07	25476.56		$3dP_2-4p'P_2$
R6	3923.43	25480.71		$4pD_2-4dF_3$
K1	3918.16	25514.99		$3dF_3-4p'F_4$
R1	3906.95	25588.19		bP_2-4pD_3
R5	3892.28	25684.63	$4pP_3-4dP_3$	
R4	3860.64	25895.13	$4pP_3-4dP_2$	
R0	3859.21	25904.72		$3dF_3-4p'D_3$
R2	3853.08	25945.93		$3dF_3-4p'D_2$
R3	3850.91	25960.55	$4pP_2-4dP_3$	
R1	3809.65	26241.70	$4pP_1-4dP_2$	
R1	3802.61	26290.29	$4pP_2-4dP_1$	
Q1	3734.8	26767.9		$4sP_2-4p'F_3$
R1	3672.11	27224.58		bP_1-4pP_1
R4	3669.03	27247.43		$4sP_2-4p'D_3$
K1	3663.36	27289.58		$4sP_2-4p'D_2$
K1	3654.52	27355.63		bP_1-4pP_2
R1	3638.17	27478.54		$4pD_3-4dD_2$
R4	3616.90	27640.13		$4pD_3-4dD_3$
Q5	3613.1	27669.4		bP_2-4pP_1
R3	3595.98	27800.93		bP_2-4pP_2
R3	3594.45	27812.76		$4sP_1-4p'D_2$
R3	3567.16	28025.53		$4pD_2-4dD_2$
Q3	3329.3	30027.6		$4sP_2-4p'P_1$
R1	3314.47	30162.09		$4sP_2-4p'P_2$
Q4	3272.3	30550.8		$4sP_1-4p'P_1$
Q3	3257.9	30685.5		$4sP_1-4p'P_2$
Q2	3015.7	33150.3		$4pD_3-4d'G_4$
Q1	2886.9	34628.9		$bP_2-4p'F_3$
Q3	2670.0	37442.4		$bP_1-4p'P_1$
Q1	2660.3	37578.8		$bP_1-4p'P_2$
Q1	2638.1	37894.5		$bP_2-4p'P_1$
Q2	2629.1	38024.7		$bP_2-4p'P_2$
	I. A. Vac			
5	1259.53	79394.8	aS_2-bP_3	
5	1253.79	79757.9	aS_2-bP_2	
3	1250.50	79968.0	aS_2-bP_1	
3	1234.14	81028.0		aP_2-bP_2
0	1233.36	81079.3		aP_1-bP_2
1	1227.45	81469.9		aP_2-bP_1
1	1226.70	81519.5		aP_1-bP_1
2	1131.65	88366.5		aP_2-4sP_1
2	1131.05	88413.1		aP_1-4sP_1
1	1125.00	88888.6		aP_2-4sP_2
1	1124.39	88937.3		aP_1-4sP_2
3	1102.32	90717.7		aD_3-bP_2
2	1096.57	91193.2		aD_2-bP_1
1	1031.34	96961.3		$aP_2-4s'D_{3,2}$
1	1030.87	97004.9		$aP_1-4s'D_2$
2	1019.53	98084.7		aD_2-4sP_1
2	1014.42	98578.0		aD_3-4sP_2
0	1014.09	98610.2		aD_2-4sP_2
2	1000.48	99952.3		aD_2-3dF_3
2	996.00	100401.9		aD_3-3dF_4
0	968.37	103265.9		aD_3-3dP_2
1	957.88	104397.5		$\begin{cases} aD_3-3dD_3 \\ aD_2-3dD_2 \end{cases}$
3	937.69	106644.8		$aD_3-4s'D_{3,2}$
3	937.41	106676.6		$aD_2-4s'D_{3,2}$
1	919.24	108785.8		aP_2-x

TABLE III. (continued)

Int.	I. A. Air	ν	Quartets	Doublets
3	918.82	108835.0		aP_1-x
3	912.74	109560.7	aS_2-4sP_1	
3	910.49	109830.3	aS_2-4sP_2	
3	906.87	110269.0	aS_2-4sP_3	
1	867.50	115273.7		aP_2-P_1
1	867.15	115320.5		aP_1-P_1
1	866.23	115443.3		aP_2-P_2
0	865.87	115491.1		aP_1-P_2
2	843.82	118508.5		aD_2-x
0	800.04	124993.9		aD_2-P_1
0	799.14	125134.6		aD_3-P_2
0	798.92	125168.8		aD_2-P_2
0	707.86	141271.0		aD_2-4dF_3
0	705.62	141720.1		aD_3-4dF_4
0	694.71	143944.9		aD_3-4dD_3
1	641.81	155810.0	aS_2-4dP_3	
0	640.93	156023.7	aS_2-4dP_2	
0	640.41	156149.9	aS_2-4dP_1	

No intercombinations between the doublet and quartet systems have been identified. The reason is doubtless that the data available in the present work did not include accurate measurements on the weaker lines among which such intercombinations are to be expected. Table IV gives a list of

TABLE IV. *Unclassified lines of S II.*

Int.	I. A. Air	ν	Int.	I. A. Air	ν
1	5142.33	19441.04	2	4185.90	23883.02
2	5027.19	19886.30	5	4174.25	23949.67
0	5011.61	19948.12	4	4173.97	23951.28
2	4779.09	20918.65	2	3860.11	25898.68
3	4561.87	21914.71	4	3831.37	26092.95
4	4549.56	21974.01	3	3783.13	26425.66
6	4464.44	22392.96	1	3678.11	27180.17
2	4431.00	22561.95	2	3385.79	29526.76
2	4259.15	23472.28	1	3371.87	29648.65
3	4257.39	23481.98	1	3368.07	29682.10
1	4193.50	23839.73	0	3356.40	29785.30

the only unclassified lines which can be definitely ascribed to S II. The group of lines in the region of 4200A probably involves the high $^2(S\ P\ D\ F\ G)$ terms of the $s^2p^2\cdot 4d$ configuration but it has not been possible to resolve them into multiplets. One line requires special mention, 4162.64, one of the strongest lines in the spectrum. It is without question the leading line of the multiplet $4p^4D$–$4d^4F$ and probably masks the line $4p'^2F_4$–$4d'^2G_5$ which should also be a strong line very close to this position. This line has been used to fix both the $4d^4F_5$ and $4d'^2G_5$ levels. The assumption of this value of the $^2G_5$ level gives an inverted G term of separation 1.90 cm^{-1}, a very reasonable value since in O II this term is inverted and has a separation of 1.2 cm^{-1}.

No terms from the configuration $s^2p^2\cdot 4f$ have been detected. Both the quartet and doublet terms based on the ^3P state of S III should be hydrogenlike and hence have term values in the neighborhood of 27000. The doublet terms based on the ^1D term of S III should lie at about 15000. The combination of these terms with the terms of the $s^2p^2 \cdot 4d$ configuration will give faint lines in the red or infra-red whereas the combinations with the observed terms of the $s^2p^2 \cdot 3d$ configuration will give faint lines in the ultra-violet near 2000A where they might easily be missed.

Strong doublet lines in the extreme ultra-violet should arise from combinations between the low ^2D and ^2P terms and the doublet terms of the $s^2p^2 \cdot 4s$ and $s^2p^2 \cdot 3d$ configurations. These lines have been identified. The low terms should also combine strongly with the ^2P, ^2D and ^2S terms of the sp^4 configuration. An inverted ^2P term of separation 445 cm^{-1} at 82000 cm^{-1} which combines with the $s^2p^2 \cdot 4p$ doublet terms is doubtless the ^2P term of this group. Another ^2P term near 48000 and an unclassified term, x, at 55147.9 give strong lines in the extreme ultra-violet in combination with the low doublet terms.

One component P_2, of the $s^2p^2 \cdot 3d$ ^2P term could be definitely fixed by combinations with the $s^2p^2 \cdot 4p$ terms and with a^2P_2. The lines given by the P_1 member are doubtless too weak to be detected.

I am indebted to Dr. I. S. Bowen for the identification of two important multiplets in the extreme ultra-violet, a^4S_2–b^4P_{321} and a^4S_2–$4sP_{321}$ which were taken from unpublished data of his.

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