

The Spectra of Singly and Doubly Ionized Sulphur in the Region $\lambda\lambda$ 3300-4900 Å.

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VII. *The Spectra of Singly and Doubly Ionized Sulphur in the Region*
 $\lambda\lambda$ 3300—4900 *A*.

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[PLATES 4 and 5.]

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Introduction.

The atomic spectra of the elements of the oxygen group in various stages of ionization have been of increasing importance to spectroscopic theory in the last few years. Of

no less prominence is their astrophysical importance: in the determination of stellar radial velocities, and in the study of stars of spectral types O, B, and A, an accurate knowledge of wave-lengths in the high excitation spectra of these atoms is indispensable.

For these reasons it has been disappointing to find that the published data on sulphur, in particular, are of inadequate accuracy. The early observations of EDER and VALENTA* and of EXNER and HASCHEK† are incomplete and hardly reliable to 0·2 Å. Wave-lengths listed by BHATTACHARYYA‡ appear to be in error by amounts up to 0·5 Å., whilst INGRAM's measurements in S II§ include only the stronger lines, and in S III|| only those which have been classified. Recent work of comprehensive scope is due chiefly to L. and E. BLOCH¶ and to GILLES,** who unfortunately record many lines ascribable to impurities. In addition, the wave-lengths of their lines are sometimes in disagreement by as much as 0·1 Å.

It therefore seemed desirable to investigate the spectra S II and S III, beginning with the region of greatest astrophysical importance, viz., from λ 3300 to λ 4900 Å., and taking particular care not only to obtain accurate wave-lengths, but also to exclude all impurity lines.

Experimental Procedure.

Desiderata in the Method of Excitation.—In previous work on this subject, the source of radiation has usually been a discharge, electrodeless or otherwise, in the vapour of sulphur or of one of its compounds (usually H₂S or SO₂). The method of sealing a quantity of sulphur in an otherwise evacuated tube and obtaining sufficient vapour by applying heat is open to experimental objections in that the discharge requires an external stimulus for its maintenance and is liable to fortuitous interruption, and that a very high vacuum is required initially. Worst of all, it is evidently impossible with this method to eliminate all impurity lines, for any gaseous impurities originally present in the tube or subsequently evolved from the walls or electrodes must perforce remain there; many O II lines are present in the list given by L. and E. BLOCH, whilst over 10% of the lines listed by GILLES are attributable to impurities, chiefly oxygen and carbon. In these circumstances it seemed desirable to devise a method of excitation which would give the sulphur spectrum free from impurity lines, and also, if possible, work throughout, without attention, at relatively coarse vacua.

The Discharge Tube.—These requirements are met in the discharge tube shown in

* 'Denkschr. Akad. Wiss. Wien,' vol. 67, p. 108 (1899).

† "Die Spektren der Elemente bei normalem Druck," Leipzig u. Wien, F. Deuticke, 1911-12, vol. 3.

‡ 'Proc. Roy. Soc.,' A, vol. 122, p. 416 (1929).

§ 'Phys. Rev.,' vol. 32, p. 172 (1928).

|| 'Phys. Rev.,' vol. 33, p. 907 (1929).

¶ 'Ann. Physique,' vol. 12, p. 5 (1929).

** 'Ann. Physique,' vol. 15, p. 269 (1931).

fig. 1. It consists of the usual "end-on" type of Geissler tube modified by the introduction of a well W to contain the sulphur. Tubes A, B, whose axes are perpendicular to the plane of the diagram, serve for the admission and removal respectively of pure dry hydrogen. The discharge passes through the capillary C between the aluminium electrodes E, E', and is viewed through the window D attached to the end of the tube by sealing-wax. The body of the tube may be either of soda-glass or of pyrex. The material of the window is determined by the spectrum region to be examined and by the grating order in use; it may be of soda-glass, quartz, or pyrex.

Conditions of the Discharge.—The hydrogen was prepared electrolytically from an aqueous solution of pure barium hydroxide, and was dried over sulphuric acid and passed through phosphorus pentoxide before admission to the discharge tube. The sulphur was prepared from laboratory flowers of sulphur by repeated crystallization from carbon disulphide, the clear yellow crystals finally obtained being crushed and dried for a few hours in a stream of low-pressure hydrogen to remove possible occlusions of the solvent.

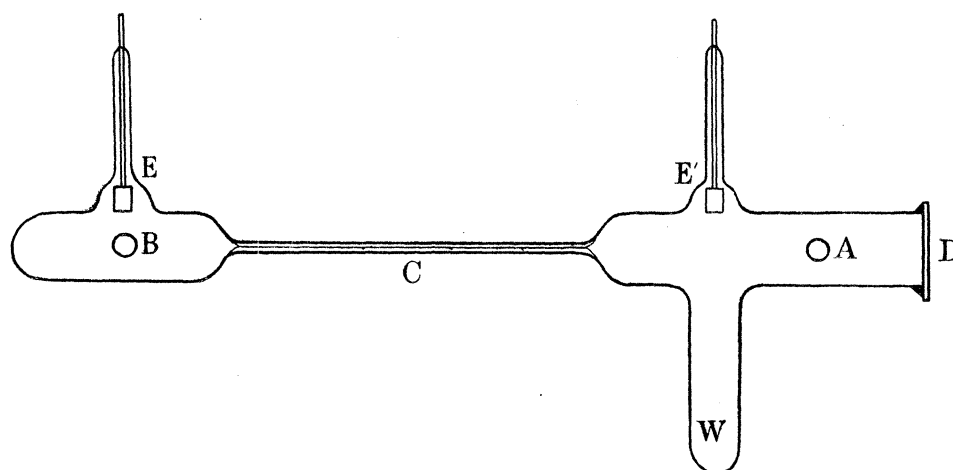


FIG. 1.

The experimental procedure adopted was as follows. After the introduction of the sulphur into the well W, the system was exhausted through B by means of a small rotary pump; then a continuous stream of hydrogen at low pressure was passed through the tube for the duration of the exposure. Under these conditions it was found that the hydrogen stream carried through the capillary just enough vapour from W to give a spectrum of fairly high intensity and excellent definition. When a higher sulphur pressure was required, the well was gently warmed. The long neck at A, together with the fact that the stream of gas carried the sulphur vapour away from the window, prevented serious fouling of the latter; an hourly touch with a small pointed flame sufficed to keep it clear.

The hydrogen pressure in the tube was maintained at about 1 mm. by continued exhaustion at B, the supply from the reservoir of the voltameter (which was at

approximately atmospheric pressure) being regulated by means of a fine capillary. The discharge was produced by an induction coil capable of a 5-inch spark between points in air at atmospheric pressure, fed from 20-volt D.C. mains through a mercury interrupter. A large Leyden jar and a variable spark-gap were used for the condensed discharge. The diameter of the capillary C varied from 0.5 to 1.5 mm. in different tubes. Under these conditions an uncondensed discharge produces the well-known bands of sulphur mixed with the secondary hydrogen spectrum, the colour of the discharge being a bright blue. On condensing the discharge its colour changes to a pale green; the bands disappear and their place is taken by the required line spectrum, attributed entirely in the region investigated (apart from the occasional impurity lines mentioned below) to singly and doubly ionized sulphur atoms.

The arrangement described above combines simplicity of operation with ease of construction. The continuous stream of hydrogen facilitates the discharge, allows the maintenance of a moderate gas pressure in the tube, and continually substitutes for the emitting sulphur ions in the capillary a fresh supply of clean vapour. The only hydrogen line registered was $H\beta$, though in any case the simplicity of the hydrogen line spectrum would obviate any confusion with sulphur lines. For short exposures (30 mins. or less) no impurity lines whatsoever could be detected, though for long exposures (four hours or so) the lines

$$\begin{array}{ll} \lambda\lambda 4075.869, 4414.888, 4649.148 & (\text{O II}); \\ 3919.061, 3920.773, 4267.02, 4267.27 & (\text{C II}) \end{array}$$

sometimes appeared. Since, however, these are among the strongest lines of their respective spectra, their presence caused no serious difficulty. A leak of any marked extent could be at once detected by the occurrence of multitudes of O II and N II lines.

The Spectrograph.—The spectrum was produced by means of a concave grating of 3 m. radius of curvature. The Eagle mounting employed gives, with this grating, a dispersion of 5.5 Å. per mm. in the first order. The plates used were 300 mm. long, so that the region investigated (1600 Å. in extent) could be photographed on one plate in the first order, or on three in the third order. For the purpose of wave-length measurements the whole region was photographed six times in the first order (6 plates), and three times in the third order (9 plates). Four hours' exposure in the first order was found sufficient to bring out the fainter lines at intensities high enough for accurate measurement. Since only the stronger lines were required on third order plates, four hours also sufficed for these. Each line was measured six times on first order plates, whilst certain of the strong lines were in addition measured three times on third order plates. The comparison spectrum used was that of iron; the International Astronomical Union instructions for the reproduction of the standard Pfund arc* were

* ' Trans. Int. Astr. Union, vol. 3, p. 12 (1929).

strictly followed, and the recommended values of the secondary standards of wavelength* were employed throughout.

Enlargements from a first order plate used for measurement purposes are reproduced in Plate 4, which gives a general view of the sulphur line spectrum in the region investigated. The positions of the stronger S III lines are indicated below each strip of the photograph, lines not otherwise marked belonging to S II.

Differentiation between S II and S III Lines.—The lines were assigned to their appropriate orders of ionization by comparing their characters and intensities under the action of different discharges. A strong discharge, whether produced by lengthening the spark-gap in series with the tube, increasing the primary voltage applied to the induction coil, or using a condenser of higher capacity, favours the appearance of S III lines. The most convenient method of experimental differentiation, however, was to increase the pressure of sulphur vapour in the discharge tube. Warming the tube with this object at first broadens the S II lines, and when carried to excess shifts some of them towards the red, whilst drawing out all of them into continuous patches of light. The S III lines remain throughout relatively sharp. In this connection it should be noticed that all the plates used for purposes of wave-length measurements were taken with the lowest sulphur pressure practicable, in order to keep the lines as sharp as possible. The intensity of the light emitted being thus reduced, exposures for such plates were in consequence rather long. Plates taken for classification purposes, however, with sulphur pressures gradually increasing, could be obtained in from 30 mins. to 5 mins.

Plate 5 (a), (b) shows the effect of increasing the sulphur pressure on the group of S II lines at λ 4270, the S III multiplet at λ 4350 remaining relatively sharp. Exposures (c), (d) illustrate the different behaviours of different S II multiplets in the spectra of high pressure discharges: the components of the multiplet $4s^2D^a - 4p^2P^a$ at λ 4550 broaden symmetrically, whilst those of $4p^4D - 5s^4P$ at λ 4450 show a marked red shift.

Term Notation.

The notation used is summarized in Table I; it follows the usual practice, as recommended by RUSSELL, SHENSTONE, and TURNER,† of prefixing each term symbol with the electronic configuration from which the term is derived. In representing each ion the symbols $1s^2 2s^2 2p^6$ referring to the “neon core,” *i.e.*, the inner configuration of completed K and L shells, are omitted.

Singly Ionized Atom, S⁺.—In the singly ionized atom, the ground configuration $3s^2 3p^3$ is formed by adding a $3p$ electron to the ground state $3s^2 3p^2$ of S III, and is represented by the symbol $3p$. The prefix $3p'$ is used for the second deepest configuration, $3s 3p^4$, derived by adding a $3p$ electron to the excited S III core $3s 3p^3$. In all transitions not involving this state, the configuration $3s^2 3p^3$ remains unchanged,

* *Ibid.*, vol. 3, Table I (1929).

† ‘Phys. Rev.’, vol. 33, p. 900 (1929).

TABLE I.—Predicted terms of S II and S III (observed terms are in heavy type).

Ion.	Electron Config.	Prefix.	Allowed Terms.		
Normal S III core S II ground S II excited Do. Do. Do. Do. Do. Do.	$3s^2 3p^2$	$3p$	$3P$	$1D$ $2D$	$1S$ $2P$ $2D^b$
	$3s^2 3p^3$	$3d$	$2P$ $2D$ $2F$	$2D^a$ $2F^a$ $2G^a$	$2S^b$ $2P^b$ $2D^b$
	$3s^2 3p^2 3d$	$4s$	$2P$ $2D$ $2F$	$2D^a$ $2F^a$ $2G^a$	$2S^b$ $2P^b$ $2D^b$
	$3s^2 3p^2 4s$	$4p$	$2S$ $2P$ $2D$	$2P^a$ $2D^a$ $2F^a$ $2G^a$	$2S^b$ $2P^b$ $2D^b$
	$3s^2 3p^2 4d$	$4d$	$2P$ $2D$ $2F$	$2P^a$ $2D^a$ $2F^a$ $2G^a$	$2S^b$ $2P^b$ $2D^b$
	$3s^2 3p^2 4f$	$4f$	$2D$ $2F$ $2G$	$2D^a$	$2S^b$ $2P^b$
	$3s^2 3p^2 5s$	$5s$	$2P$	$2D^a$	$2S^b$ $2P^b$
	$3s^2 3p^2 5p$	$5p$	$2S$ $2P$ $2D$	$2S^a$ $2P^a$ $2D^a$ $2F^a$ $2G^a$	$2S^b$ $2P^b$
Excited S III core S II excited	$3s 3p^3$	$3p'$	$3P$	$1P$ $1D$	$1D$
	$3s 3p^4$		$4P$ $2P$	$2S$	$2D$
Normal S IV core S III ground S III excited Do. Do. Do. Do. Do.	$3s^2 3p$	$3p$	$2P$	$1S$ $1D$	
	$3s^2 3p^2$	$3d$	$3P$ $3D$ $3F$	$1P$ $1D$ $1F$	
	$3s^2 3p 4s$	$4s$	$3P$	$1P$	
	$3s^2 3p 4p$	$4p$	$3S$ $3P$ $3D$ $3F$	$1S$ $1P$ $1D$	
	$3s^2 3p 4d$	$4d$	$3P$ $3D$ $3F$	$1P$ $1D$ $1F$	
	$3s^2 3p 4f$	$4f$	$3D$ $3F$ $3G$	$1D$ $1F$ $1G$	
	$3s^2 3p 5s$	$5s$	$3P$	$1P$	
	$3s^2 3p 5p$	$5p$	$3S$ $3P$ $3D$	$1S$ $1P$ $1D$	
Excited S IV core S III excited	$3s 3p^2$	$3p'$	$4P$ $3S$	$2P$ $2D$	$2D$
	$3s 3p^3$		$5S$ —	$3P$ $3D$ $3D$	$3D$

and can therefore be omitted without ambiguity, only the running electron being specified by its orbital designation before the term symbol. Thus, for example,

$$3s^2 3p^2 4s^2 P = 4s^2 P.$$

The ground state $3s^2 3p^2$ of S III gives, on application of the exclusion principle, three allowed terms, viz., 3P , 1D , 1S . Accordingly three parallel systems of S II terms are expected (in addition to the ground states), each built upon one of these three states of the normal core; such terms are known, however, only for the first two systems. They are distinguished by adding to the term symbol a superscript “*a*” for the terms built on the 1D state of the core, or a superscript “*b*” for the terms built on the 1S state of the core. Thus :

$$\begin{aligned} 3s^2 3p^2 (^3P) 4d^2 D &= 4d^2 D, \\ 3s^2 3p^2 (^1D) 4d^2 D &= 4d^2 D^a, \\ 3s^2 3p^2 (^1S) 4d^2 D &= 4d^2 D^b. \end{aligned}$$

This notation differs considerably from that previously used by INGRAM, who primes the letter referring to the electron configuration instead of distinguishing the terms : thus INGRAM’S $4s' 2D$ is identical with the $4s^2 D^a$ of the present investigation.

Doubly Ionized Atom, S⁺⁺.—In the doubly ionized atom the deepest two states are formed by adding a $3p$ electron to the ground ($3s^2 3p$) or excited ($3s 3p^2$) state of S IV, and are similarly represented by $3p$ and $3p'$ respectively. Transitions involving the remaining configurations leave the core $3s^2 3p$ unchanged, and it has therefore been omitted from the abbreviated notation. Thus :

$$3s^2 3p 4s^3 P = 4s^3 P.$$

The family of configurations based on the normal S IV core is here, however, only one-fold since the exclusion principle allows only one term, 2P , to the normal core; hence no system of attaching superscripts is here necessary.

As in S II, although the $3p'$ configuration contains terms derived from three of the allowed terms of an excited core, no confusion can at present arise by failing to distinguish their different origins by attaching superscripts. It might be mentioned, however, that GILLES has proposed the transition $3s 3p^2 4p^5 D \rightarrow 3s 3p^2 4s^5 P$ for a group of lines near λ 4100, but the identification lacks support from other combinations; whilst his claim to have established the term $3s 3p^2 4p^5 S_2$ rests upon the assignment of an oxygen line λ 4119.222 to S III.

The terms predicted by theory as arising from the deeper configurations of S II and S III are given in Table I, those which have been established being printed in heavy type.

Catalogue of Lines Observed.

Description of Table II.—The results of the investigation are given in Table II. In the first column appear the wave-lengths, measured in air in International Angstroms,

of all the sulphur lines recorded in the region examined, referred to the 1928 secondary standards (*loc. cit.*). Wave-lengths of the S III lines are separated from those of S II by slightly indenting the former ; it is hoped that this method will prove of convenience to practical spectroscopists by obviating the cross-reference necessary when two separate tables are given.

Wave-lengths given to 0·01 Å. represent the means of six values computed from all of the first order plates measured ; the precision attained is indicated by a probable error of $\pm 0\cdot007$ Å. It is felt that except for lines of intensity (00) the sixth figure is reliable, and even for them is rarely in error by more than unity. Support is lent to this claim by the accuracy with which the data fit the predictions of theory. Occasionally a line has not appeared on all six plates ; its wave-length is then given only to 0·1 Å. Seven-figure wave-lengths are given for lines which have been measured on third order plates, and therefore represent the means of three separately determined values. All lines of intensity greater than (4) appear amongst these (except λ 4189·71, which was considered too diffuse for inclusion), as well as several sharp ones of intensity (4) or less, which were also found measurable to this accuracy. The precision here attained is represented by a probable error of $\pm 0\cdot002$ Å., the listed seventh figure being therefore little more than an indication of the true one.

In order to eliminate any possibility of recording impurity lines, the wave-lengths in column 1 have been carefully compared with the published data for mercury, selenium, nitrogen, carbon, and oxygen, and with the list given in KAYSER'S "Hauptlinien der Linienspektra." No impurity lines other than the eight recorded above have, however, been detected on any plate used for wave-length measurements.

In the second column of Table II are recorded intensities on an arbitrary scale estimated by eye, very faint lines being listed as (00), and the strongest as (10). To this number is added for a diffuse line the letter "n," and for a specially sharp line the letter "s." The estimated intensities give a good indication of relative values over a short spectrum range, *e.g.*, in a single multiplet, but owing to variations in emulsion sensitivity do not necessarily provide accurate comparisons over extended regions.

The third column of Table II gives the wave-number of each line, to 0·01 cm^{-1} for lines of six and seven-figure wave-lengths, to 0·1 cm^{-1} for the others.

Where the multiplet classification of a line is known, it appears in column 4. Usually these classifications have been already announced (S II by INGRAM and L. and E. BLOCH ; S III by GILLES, *loc. cit.*), and are included here for the sake of completeness ; those classifications distinguished by an asterisk, however, have not hitherto been published.

The fifth column of Table II contains references to the notes collected together at the end of the table.

Complete lists of term values for both ions will be found in Table V, which is discussed later.

TABLE II.—List of Sulphur Lines (S II and S III) : $\lambda\lambda$ 3300—4900 A.

λ air (I.A.) S II S III.	Int.	ν (cm. ⁻¹).	Classification.		Notes.
			S II.	S III.	
4885.63	2	20462.49	$4s\ ^2P_{1/2} - 4p\ ^2P_{3/2}$		
4835.85	00	20673.13	$4p\ ^4P_{3/2} - 5s\ ^4P_{3/2}$		
4826.77	00	20712.02			
4824.07	3	20723.61	$4p\ ^2D_{5/2} - 5s\ ^2P_{3/2}$		
4819.60	} 2n	20742.83	$4p\ ^2D_{3/2} - 5s\ ^2P_{1/2}$		(e)
4819.60			$4p\ ^4P_{1/2} - 5s\ ^4P_{3/2}$		
4815.515	10	20760.43	$4s\ ^4P_{5/2} - 4p\ ^4S_{3/2}$		
4804.12	00	20809.67	$4s\ ^4P_{3/2} - 4p\ ^2D_{3/2}$		
4802.81	0	20815.34			
4792.02	3	20862.21	$4p\ ^4P_{5/2} - 5s\ ^4P_{5/2}$		
4779.11	2s	20918.57	$4s\ ^4P_{5/2} - 4p\ ^2D_{5/2}$		
4763.38	1	20987.65	$3d\ ^2D_{3/2} - 4p\ ^2F_{5/2}^a$		
4755.12	2	21024.10	$3d\ ^2D_{5/2} - 4p\ ^2F_{7/2}^a$		
4742.4	00	21080.5	$4s\ ^4P_{1/2} - 4p\ ^2D_{3/2}$		
4729.45	0	21138.21	$4p\ ^4P_{3/2} - 5s\ ^4P_{5/2}$		
4716.226	8	21197.48	$4s\ ^4P_{3/2} - 4p\ ^4S_{3/2}$		
4700.21	00	21269.71	$4p\ ^2D_{3/2} - 5s\ ^2P_{3/2}$		
4689.9	00	21316.5			
4681.32	00s	21355.54	$4s\ ^4P_{3/2} - 4p\ ^2D_{5/2}$		
4677.67	0	21372.20			
4668.58	3	21413.81	$3d\ ^2D_{5/2} - 4p\ ^2D_{5/2}^a$		
4664.4	00	21433.0			
4656.74	4	21468.26	$4s\ ^4P_{1/2} - 4p\ ^4S_{3/2}$		
4653.3	00	21484.1			
4648.17	2	21507.84	$3d\ ^2D_{3/2} - 4p\ ^2D_{3/2}^a$		
4624.11	1	21619.75			
4613.47	00	21669.61			(a)
4591.05	3n	21775.43			(f)
4590.8	00	21776.6	$*4p\ ^4P_{5/2} - 5s\ ^2P_{3/2}$		(r)
4561.88	2	21914.67			
4552.378	} 7	21960.41	$4s\ ^2D_{3/2}^a - 4p\ ^2P_{1/2}^a$		(e)
4552.378			$*4p\ ^4P_{5/2} - 4d\ ^4F_{5/2}$		
4549.547	5	21974.07			
4535.7	00	22041.2			
4533.3	00	22052.8	$4p\ ^4P_{3/2} - 5s\ ^2P_{3/2}$		(h)
4527.9	00	22079.1		$3d\ ^3D_2 - 4p\ ^3D_1$	
4524.946	6	22093.54	$4s\ ^2D_{5/2}^a - 4p\ ^2P_{3/2}^a$		
4524.68	2	22094.83	$4s\ ^2D_{3/2}^a - 4p\ ^2P_{3/2}^a$		
4518.9	00	22123.1	$4p\ ^4P_{1/2} - 5s\ ^2P_{3/2}$		(y)
4509.0	00	22171.7	$4p\ ^4P_{1/2} - 4d\ ^4F_{3/2}$		(y)
4504.22	00	22195.20			(h)
4499.3	00	22219.5		$3d\ ^3D_1 - 4p\ ^3D_1$	
4497.88	00	22226.48	$4p\ ^2D_{5/2} - 4d\ ^4D_{7/2}$		
4495.9	00	22236.3	$*4p\ ^4P_{3/2} - 4d\ ^4F_{5/2}$		
4492.3	00	22254.1	$4p\ ^4S_{3/2} - 4d\ ^4D_{5/2}$		
4486.66	3	22282.06	$4p\ ^4D_{3/2} - 5s\ ^4P_{1/2}$		
4485.62	00	22287.23			(b)
4483.424	6	22298.15	$4p\ ^4D_{5/2} - 5s\ ^4P_{3/2}$		

* Established during the present investigation.

TABLE II—(continued)

λ air (I.A.) S II S III.	Int.	ν (cm. $^{-1}$).	Classification.		Notes.
			S II.	S III.	
4482.48	0	22302.84			
4478.48	00	22322.76		$3d\ ^3D_3 - 4p\ ^3D_2$	
4467.8	00	22376.1		$3d\ ^3D_2 - 4p\ ^3D_2$	
4464.425	6	22393.04			
4463.582	7	22397.27	$4p\ ^4D_{7/2} - 5s\ ^4P_{5/2}$		
4456.43	2	22433.21	$4p\ ^4D_{1/2} - 5s\ ^4P_{1/2}$		
4450.73	00	22461.94			
4449.1	00	22470.2			
4439.87	1	22516.88		$3d\ ^3D_1 - 4p\ ^3D_2$	(d)
4437.8	00	22527.4			
4432.41	3	22554.78	$4p\ ^4D_{3/2} - 5s\ ^4P_{3/2}$		
4431.02	1	22561.85	$3d\ ^2P_{3/2} - 4p\ ^2D_{5/2}^a$		
4418.84	00	22624.04		$4s\ ^3P_2 - 4p\ ^3D_1$	
4411.34	00	22662.51			
4404.8	00	22696.2			
4402.86	0	22706.15	$4p\ ^4D_{1/2} - 5s\ ^4P_{3/2}$		
4395.5	00	22744.2			
4391.84	3	22763.13	$4p\ ^4D_{5/2} - 5s\ ^4P_{5/2}$		
4378.57	00	22832.11			
4369.96	0	22877.10			
4367.1	00	22892.1			(n)
4364.73	1	22904.51		$3d\ ^3D_3 - 4p\ ^3D_3$	
4361.53	2	22921.31		$4s\ ^3P_2 - 4p\ ^3D_2$	
4360.49	1	22926.78			
4356.9	00	22945.7			
4354.56	2	22958.00		$3d\ ^3D_2 - 4p\ ^3D_3$	
4351.7	00	22963.1			(d)
4342.84	00	23019.96	$*4p\ ^4D_{3/2} - 5s\ ^4P_{5/2}$		
4340.30	2	23033.43		$4s\ ^3P_1 - 4p\ ^3D_1$	
4333.84	0	23067.76	$4p\ ^4P_{5/2} - 4d\ ^4D_{3/2}$		
4332.71	4	23073.78		$4s\ ^3P_0 - 4p\ ^3D_1$	
4330.95	00	23083.15			(d)
4318.68	4	23148.74	$4p\ ^4P_{5/2} - 4d\ ^4D_{5/2}$		
4294.432	6	23279.44	$4p\ ^4P_{5/2} - 4d\ ^4D_{7/2}$		
4293.14	00	23286.45			
4291.45	1	23295.62	$4p\ ^4P_{3/2} - 4d\ ^4D_{1/2}$		
4284.991	5	23330.73		$4s\ ^3P_1 - 4p\ ^3D_2$	
4283.70	0	23337.76			(a)
4282.63	3	23343.59	$4p\ ^4P_{3/2} - 4d\ ^4D_{3/2}$		
4278.54	3	23365.91	$4p\ ^4P_{1/2} - 4d\ ^4D_{1/2}$		
4269.76	3	23413.95	$4p\ ^4P_{1/2} - 4d\ ^4D_{3/2}$		
4267.802	5	23424.70	$4p\ ^4P_{3/2} - 4d\ ^4D_{5/2}$		
4259.18	2	23472.11	$*4p\ ^2D_{5/2}^a - 4d\ ^2F_{7/2}^a$		(x)
4257.42	3	23481.82	$4p\ ^2D_{3/2}^a - 4d\ ^2F_{5/2}^a$		
4253.593	9	23502.94		$4s\ ^3P_2 - 4p\ ^3D_3$	
4249.92	0	23523.26	$4p\ ^2D_{5/2}^a - 4d\ ^2F_{5/2}^a$		
4236.0	00	23600.6			
4230.98	4	23628.56	$4p\ ^2D_{5/2}^a - 4d\ ^2G_{7/2}^a$		
4227.6	00	23647.8			
4221.61	0	23681.00			

* Established during the present investigation.

IONIZED SULPHUR IN THE REGION $\lambda\lambda$ 3300-4900 A.

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TABLE II—(continued)

λ air (I.A.) S II S III.	Int.	ν (cm. ⁻¹).	Classification.		Notes.
			S II.	S III.	
4217.23	3	23705.59	$4p\ ^4D_{7/2} - 4d\ ^4F_{7/2}$		
4213.5	00	23726.6	$*4p\ ^4D_{5/2} - 4d\ ^4F_{3/2}$		
4193.51	1	23839.68	$4s\ ^4P_{1/2} - 4p\ ^2P_{3/2}$		(f) (x) (e)
4189.71	} 6n	23861.30	$*4p\ ^2F_{7/2}^a - 4d\ ^2F_{7/2}^a$		
4189.71			$4p\ ^4D_{5/2} - 4d\ ^4F_{5/2}$		
4185.95	1	23882.73			
4182.14	00	23904.49			
4180.7	00	23912.7	$4p\ ^2F_{7/2}^a - 4d\ ^2F_{5/2}^a$		(p)
4178.83	00	23923.42			(d)
4175.21	0n	23944.17			
4174.300	6	23949.39			
4174.042	4	23950.87	$*4p\ ^2F_{5/2}^a - 4d\ ^2F_{7/2}^a$		(x)
4168.409	5	23983.23	$4p\ ^4D_{3/2} - 4d\ ^4F_{3/2}$		
4165.11	1	24002.23	$4p\ ^2F_{5/2}^a - 4d\ ^2F_{5/2}^a$		(a) (x)
4164.96	0	24003.09			(e)
4162.698	} 10	24016.14	$4p\ ^2F_{7/2}^a - 4d\ ^2G_{9/2}^a$		
4162.698			$4p\ ^4D_{7/2} - 4d\ ^4F_{9/2}$		
4162.39	2	24017.91	$4p\ ^2F_{7/2}^a - 4d\ ^2G_{7/2}^a$		
4153.098	10	24071.65	$4p\ ^4D_{5/2} - 4d\ ^4F_{7/2}$		
4148.91	1	24095.95			(a)
4146.94	3	24107.39	$4p\ ^2F_{5/2}^a - 4d\ ^2G_{7/2}^a$		
4145.100	9	24118.09	$4p\ ^4D_{3/2} - 4d\ ^4F_{5/2}$		
4143.9	00	24125.1			(p)
4142.291	8	24134.45	$4p\ ^4D_{1/2} - 4d\ ^4F_{3/2}$		
4127.54	0	24220.70			(p)
4125.4	00	24233.3			
4121.0	00	24259.1	$*3p'\ ^2P_{3/2} - 4p\ ^4P_{3/2}$		(g)
4112.28	00	24310.57			(p)
4111.56	3	24314.83			(p)
4104.99	0	24353.75			(d)
4099.44	1	24386.72			
4099.25	00	24387.85			
4095.17	0	24412.15			(i) (p)
4091.4	00	24434.6			
4087.9	00	24455.6			
4086.5	00	24463.9			
4084.9	00	24473.5			(d)
4064.45	2	24596.65			(p)
4062.48	00	24608.58			
4058.7	00	24631.5	$*4p\ ^2D_{5/2} - 4d\ ^4P_{5/2}$		(s)
4050.11	1	24683.74	$4p\ ^4D_{7/2} - 4d\ ^4D_{5/2}$		
4032.812	7	24789.61	$4p\ ^4S_{3/2} - 4d\ ^4P_{5/2}$		
4028.791	7	24814.36	$4p\ ^4D_{7/2} - 4d\ ^4D_{7/2}$		
4014.4	00	24903.3			
4009.39	0	24934.43	$4p\ ^2D_{5/2} - 4d\ ^2F_{5/2}$		
4007.78	0	24944.44	$3d\ ^2F_{7/2} - 4p\ ^2F_{5/2}^a$		
4003.89	1	24968.68	$4p\ ^4D_{5/2} - 4d\ ^4D_{3/2}$		
3998.79	3	25000.52	$4p\ ^4S_{3/2} - 4d\ ^4P_{3/2}$		

* Established during the present investigation.

TABLE II—(continued)

λ air (I.A.) S II S III.	Int.	ν (cm. ⁻¹).	Classification.		Notes.
			S II.	S III.	
3997.97	0	25005.65			(f)
3993.526	4	25033.47	$3d^2F_{7/2} - 4p^2F_{7/2}^a$		
3990.94	3	25049.70	$4p^4D_{5/2} - 4d^4D_{5/2}$		
3985.97	2	25080.93		$3d^3D_1 - 4p^3P_0$	
3983.77	3	25094.78		$3d^3D_2 - 4p^3P_1$	
3979.86	3	25119.43	$4p^4S_{3/2} - 4d^4P_{1/2}$		
3970.69	} 1	25177.44	$*4p^2D_{3/2} - 4d^4P_{5/2}$		(e)
3970.69			$4p^4D_{3/2} - 4d^4D_{1/2}$		
3963.13	2	25225.47	$4p^4D_{3/2} - 4d^4D_{3/2}$		
3961.55	2	25235.53		$3d^3D_1 - 4p^3P_1$	
3959.05	00	25251.47			(d)
3950.42	00	25306.63	$4p^4D_{3/2} - 4d^4D_{5/2}$		
3946.98	1	25328.68	$4p^4D_{1/2} - 4d^4D_{1/2}$		
3939.49	00	25376.84	$4p^4D_{1/2} - 4d^4D_{3/2}$		(m)
3933.294	9	25416.81	$4p^2D_{5/2} - 4d^2F_{7/2}$		
3932.54	0	25421.69			(d)
3932.30	2	25423.24	$3d^2F_{7/2} - 4p^2D_{5/2}^a$		
3931.938	3	25425.58	$3d^2F_{5/2} - 4p^2F_{5/2}^a$		
3931.55	0	25428.09			(z)
3928.615	6	25447.08		$3d^3D_3 - 4p^3P_2$	
3924.05	00	25476.69	$3d^2P_{3/2} - 4p^2P_{3/2}^a$		
3923.483	7	25480.37	$4p^2D_{3/2} - 4d^2F_{5/2}$		
3922.63	00	25485.91	$^2Y^o - 4d^2F_{7/2}^?$		(w)
3918.19	00	25514.79	$3d^2F_{5/2} - 4p^2F_{7/2}^a$		(g)
3911.32	1	25559.60			
3906.95	1s	25588.19	$3p'^2P_{3/2} - 4p^2D_{5/2}$		
3901.99	00	25620.72			
3899.27	00	25638.59			(o)
3892.321	5	25684.36	$4p^4P_{5/2} - 4d^4P_{5/2}$		(j)
3862.2	00	25884.7			
3860.64	} 3	25895.13	$4p^4P_{5/2} - 4d^4P_{3/2}$		(b) (e)
3860.64					$4s^3P_1 - 4p^3P_0$
3860.15	2	25898.41	$4p^2S_{1/2} - 5s^2P_{1/2}$		(g)
3859.26	0	25904.39	$3d^2F_{5/2} - 4p^2D_{5/2}^a$		(g)
3853.09	2s	25945.87	$3d^2F_{5/2} - 4p^2D_{3/2}^a$		
3850.93	2	25960.42	$4p^4P_{3/2} - 4d^4P_{5/2}$		
3850.0	00	25966.7			
3847.29	0n	25984.98			(d)
3845.21	00	25999.03	$*3d^4D_{5/2} - 4p^2F_{5/2}^a$		
3842.88	0	26014.80			
3842.34	0	26018.45			(d)
3838.316	6	26045.73		$4s^3P_2 - 4p^3P_2$	
3837.80	3	26049.23		$4s^3P_1 - 4p^3P_1$	
3831.85	2	26089.68		$4s^3P_0 - 4p^3P_1$	
3831.41	3	26092.68			
3827.25	00	26121.04			(g)
3818.9	00	26178.1			
3811.80	1n	26226.91			
3809.67	1	26241.57	$4p^4P_{1/2} - 4d^4P_{3/2}$		(g)
3802.65	1	26290.01	$4p^4P_{3/2} - 4d^4P_{1/2}$		

* Established during the present investigation.

TABLE II—(continued)

λ air (I.Å.) S II S III.	Int.	ν (cm. ⁻¹).	Classification.		Notes.
			S II.	S III.	
3794·69	2	26345·16		$3d\ ^3D_2 - 4p\ ^3S_1$	
3783·16	2	26425·45	$4p\ ^2S_{1/2} - 5s\ ^2P_{3/2}$		
3782·6	00	26429·4	$*3d\ ^4D_{7/2} - 4p\ ^2D_{5/2}^a$		
3780·64	00	26443·07			
3778·90	1	26455·24		$4s\ ^3P_1 - 4p\ ^3P_2$	
3776·80	00	26469·95	$*4p\ ^4P_{5/2} - 4d\ ^2F_{7/2}$		
3774·52	00	26485·94		$3d\ ^3D_1 - 4p\ ^3S_1$	
3750·74	1	26653·86		$3d\ ^3P_1 - 4p\ ^3D_1$	
3748·73	0	26668·15			
3747·90	3	26674·05		$3d\ ^3P_0 - 4p\ ^3D_1$	
3744·37	00	26699·20			(a)
3741·15	0	26722·18			
3738·21	00	26743·20			(g) (t)
3734·8	00	26767·6			(d)
3732·92	00	26781·09			
3730·64	1	26797·46			
3722·7	00	26854·6			
3717·775	6	26890·19		$4s\ ^3P_2 - 4p\ ^3S_1$	
3710·42	0	26943·49		$3d\ ^3P_2 - 4p\ ^3D_2$	
3709·371	5	26951·11		$3d\ ^3P_1 - 4p\ ^3D_2$	
3700·09	0	27018·71			(d)
3699·37	1	27023·97			(a)
3697·88	0	27034·86			(a)
3696·25	0	27046·78			
3688·8	00	27101·4			
3688·12	00	27106·40			
3680·7	00	27161·0			
3678·13	1	27180·02			
3672·14	2	27224·35	$3p'\ ^2P_{1/2} - 4p\ ^2P_{1/2}$		
3669·049	5	27247·29	$4s\ ^2P_{3/2} - 4p\ ^2D_{5/2}^a$		
3663·47	0	27288·78	$4s\ ^2P_{3/2} - 4p\ ^2D_{3/2}^a$		(k)
3662·005	4	27299·70		$4s\ ^3P_1 - 4p\ ^3S_1$	
3656·61	1	27339·97		$4s\ ^3P_0 - 4p\ ^3S_1$	
3655·7	00	27346·8			
3654·51	1	27355·68	$3p'\ ^2P_{1/2} - 4p\ ^2P_{3/2}$		(k)
3652·2	00	27373·0			
3638·15	0	27478·69			(a) (z)
3637·02	00	27487·23			
3632·022	6	27525·06		$3d\ ^3P_2 - 4p\ ^3D_3$	
3626·53	0	27566·74			
3625·91	00	27571·45			(c)
3622·68	00	27596·03			
3617·50	00	27635·55			
3616·916	5	27640·01	$4p\ ^2D_{5/2} - 4d\ ^2D_{5/2}$		(l) (z)
3613·03	0	27669·54	$3p'\ ^2P_{3/2} - 4p\ ^2P_{1/2}$		
3600·08	00	27769·27			(c)
3595·991	4	27800·78	$3p'\ ^2P_{3/2} - 4p\ ^2P_{3/2}$		
3594·462	3	27812·67	$4s\ ^2P_{1/2} - 4p\ ^2D_{3/2}^a$		
3584·18	0	27892·45			(c)
3582·3	00	27907·1			

* Established during the present investigation.

TABLE II—(continued.)

λ air (I.A.) S II S III.	Int.	ν (cm. ⁻¹).	Classification.		Notes.
			S II.	S III.	
3567·171	3	28025·45	$4p\ ^2D_{3/2} - 4d\ ^2D_{3/2}$		(z)
3549·72	1	28163·22			(a)
3540·30	00	28238·15			
3531·90	00	28305·31			
3499·2	00	28569·8			(v)
3497·340	5	28585·01			
3387·35	00	29513·16		$3d\ ^3P_1 - 4p\ ^3P_0$	(b)
3387·13	2	29515·08			
3385·81	2	29526·58			
3373·19	0	29637·05			
3372·48	0	29643·29			
3371·90	1	29648·38			
3370·38	2	29661·75	$3d\ ^3P_2 - 4p\ ^3P_1$	$3d\ ^3P_1 - 4p\ ^3P_1$	
3369·49	1	29669·59			
3368·09	1	29681·92	$3d\ ^3P_0 - 4p\ ^3P_1$		(u)
3367·18	2	29689·94			
3356·41	1	29785·21	$4s\ ^2P_{3/2} - 4p\ ^2P_{1/2}^a$	$3d\ ^3P_2 - 4p\ ^3P_2$	
3347·43	0	29865·11			
3341·88	0	29914·71			
3329·3	00	30027·7			
3324·87	4	30067·74			
3324·01	2	30075·52			
3314·50	0	30161·81	$4s\ ^2P_{3/2} - 4p\ ^2P_{3/2}^a$	$3d\ ^3P_1 - 4p\ ^3P_2$	

Notes on Table II.

- (a) Attributed by GILLES to S II.
 (b) Attributed by L. and E. BLOCH to S II.
 (c) Attributed by GILLES to S III.
 (d) Attributed by L. and E. BLOCH to S III.
 (e) Unresolved blend.
 (f) Not given by GILLES though listed by L. and E. BLOCH at high intensity.
 (g) Not given by L. and E. BLOCH though listed by GILLES.
 (h) GILLES gives the lines $\lambda\lambda$ 4533·3 (00), 4504·22 (00) with intensity (4), but they do not appear in the tables given by either INGRAM or L. and E. BLOCH.
 (i) GILLES gives the line λ 4095·17 as λ 4095·40.
 (j) GILLES gives the line λ 3892·321 as λ 3892·61.
 (k) GILLES gives an intensity (4) to each of the lines $\lambda\lambda$ 3663·47 (0), 3654·51 (1).
 (l) GILLES gives an intensity (1) to the line λ 3616·916 (5).
 (m) INGRAM lists λ 3939·49 as λ 3939·75.
 (n) GILLES lists λ 4367·1 (00) as λ 4366·91 (3).
 (o) GILLES gives an intensity (1) for the line λ 3899·27 (00) and classifies it as $4s\ ^3P_2 - 4p\ ^3P_1$. In fact it lies 1·2 cm.⁻¹ from the position predicted by calculation from these terms, which are well known from other combinations. No line has been detected at the true position.
 (p) A group of faint lines near λ 4100 can be arranged so as to give separations whose ratios approximate

closely to 4 : 3 : 2 : 1. On these grounds and on the admittedly inconclusive results given by their measured Zeeman effects, the lines have been tentatively assigned by GILLES to the transition $4s' \ ^5P - 4p' \ ^5P$ between quintet terms based on an excited S IV core. Since no further support for this identification has been found, the classifications have not been included in Table II.

(q) The line λ 3860·15 is classified by GILLES as $4p \ ^4P_{5/2} - 4d \ ^4P_{3/2}$, but lies $3\cdot2 \text{ cm.}^{-1}$ from its predicted position. The true line is masked by an S III line at λ 3860·64, within $0\cdot1 \text{ cm.}^{-1}$ of the calculated value.

(r) The line λ 4590·8 has very recently been given this classification independently by BARTELT and ECKSTEIN ('Z. Physik,' vol. 86, p. 77 (1933)).

(s) The line λ 4058·7 (00) is attributed by L. and E. BLOCH to the transition $4p \ ^2D_{3/2} - 4d \ ^2P_{3/2}$, but is $0\cdot7 \text{ cm.}^{-1}$ from its predicted position. Since the other two lines of the multiplet have not been detected, although their intensities should be respectively 5 and 10 times as great, this line has been classified as $4p \ ^2D_{5/2} - 4d \ ^4P_{5/2}$, which is predicted at $0\cdot01 \text{ cm.}^{-1}$ from the observed position.

(t) The line λ 3734·8 is attributed by INGRAM to the transition $4s \ ^2P_{3/2} - 4p \ ^2F_{5/2}^a$, but lies $1\cdot0 \text{ cm.}^{-1}$ from the position predicted by calculation from the two terms, whose values are known from other combinations to within $0\cdot1 \text{ cm.}^{-1}$.

(u) The line λ 3356·41 is $1\cdot5 \text{ cm.}^{-1}$ from the position calculated for $4p \ ^2S_{1/2} - 4d \ ^2P_{3/2}$, to which it is assigned by L. and E. BLOCH, whilst the fainter component of the doublet does not appear at all. The classification has therefore been abandoned.

(v) The line λ 3497·340 has been classified as $4p \ ^1D_2 - 4d \ ^1F_3$ by GILLES, but no support for the identification has been found.

(w) The classification of λ 3922·63 is due to L. and E. BLOCH. Since no other combinations with the term $^2Y^o$ as initial or final level have been detected in the region examined, the identification has been queried.

(x) The S III line λ 4164·96 is classified by GILLES as $4p \ ^2F_{5/2}^a - 4d \ ^2F_{7/2}^a$ of S II. For discussion on the classification of $\lambda\lambda$ 4259·18, 4189·71, 4174·042 as members of this multiplet see p. 321 and Table IV.

(y) GILLES has classified the lines $\lambda\lambda$ 4518·9, 4509·0 as members of the multiplet $4p \ ^4S - 4d \ ^4D$, whose calculated positions are, however, respectively $1\cdot8$ and $1\cdot3 \text{ cm.}^{-1}$ from these lines. For discussion see p. 319.

(z) INGRAM attributes the line λ 3638·15 to $4p \ ^2D_{5/2} - 4d \ ^2D_{3/2}$ of S II. For discussion of this multiplet and the value of the term $4d \ ^2D_{5/2}$ see p. 320.

Comparison of Wave-Lengths.

Comparison of the wave-lengths tabulated above with the results of other recent investigations shows that INGRAM's values are the only ones in good agreement with those of the present paper. In S III especially this agreement is very close (to $0\cdot01 \text{ Å.}$), possibly owing to the greater sharpness of these lines in discharges at moderate sulphur pressures. With the wave-lengths published by L. and E. BLOCH and by GILLES there is only fair agreement, *i.e.*, to about $0\cdot05 \text{ Å.}$, the distribution of differences being apparently a random one except in certain regions. Thus systematically high values occur in the BLOCHS' list in the region $\lambda\lambda$ 3935 — 4010 to the extent of about $0\cdot04 \text{ Å.}$, and in GILLES' list in the region $\lambda\lambda$ 4255 — 4285 to about $0\cdot05 \text{ Å.}$

INGRAM has recorded both S II and S III entirely free from impurities, being doubtless aided in this respect by employing as source a discharge through H_2S gas in a way somewhat similar to that of the present investigation. His lists are, however, far from complete. Unfortunately a large number of impurity lines appear in the more

comprehensive tables of both GILLES and L. and E. BLOCH. For example, the strong O II lines at

$$\begin{aligned} \lambda\lambda & 4251\cdot275 \text{ (6)} \\ & 4249\cdot435 \text{ (8)} \\ & 4247\cdot429 \text{ (5)} \\ & 4245\cdot570 \text{ (7)} \end{aligned}$$

are classed in both as S III and appear with exactly proportional intensities and wavelengths differing but slightly from those above.

The lines

$$\begin{aligned} \lambda\lambda & 4696\cdot27 \text{ (0)} \\ & 4695\cdot45 \text{ (1)} \\ & 4694\cdot12 \text{ (2)} \end{aligned}$$

classed by L. and E. BLOCH as belonging to S II appear as a very faint band 3 A. wide on some plates taken during the present investigation, and are here attributed to the "raies ultimes" of the neutral atom, viz., the second member of the principal series of quintets in S I: $4s^5S_2 - 5p^5P_{1,2,3}$. The same authors have listed in both S II and S III several high intensity lines of which no trace has been found here, yet which cannot at present be attributed with certainty to any particular impurity. These lines are given in Table III, together with several strong lines included in GILLES' list but not appearing on any plates taken during the present investigation. All these lines are of intensities far higher than would be needed for inclusion in Table II.

TABLE III.—Strong lines hitherto wrongly attributed to sulphur.

S II.		S III.	
L. and E. BLOCH.	GILLES.	L. and E. BLOCH.	GILLES.
4819·46 (4)	—	4247·66 (0)	4247·64 (1)
—	4279·02 (1)	3953·12 (4)	—
—	4266·90 (4)	3901·55 (7)	3901·55 (0)
4190·02 (2)	*4190·07 (2)	3841·40 (5)	—
†4180·12 (0)	†4180·13 (2)	3829·33 (5)	—
—	4150·78 (1)	3818·04 (8)	3818·00 (0)
‡4130·95 (3)	‡4130·90 (2)	3808·03 (7)	3808·10 (0)
—	4128·40 (2)	3767·92 (4)	—
3783·49 (3)	—	3675·85 (4)	—
3782·26 (5)	—	3599·88 (5)	—
3767·73 (2)	3767·68 (2)	—	3598·40 (1)
—	3445·44 (6n)	3545·57 (4)	—
—	3360·14 (3)	—	3511·29 (1)
		3502·19 (0)	3502·32 (2)
		3492·47 (0)	3492·58 (2)
		—	3491·67 (1)
		—	3480·63 (1)
		—	3462·87 (1)

* Erroneously classified as $4p^4D_{5/2} - 4d^4F_{5/2}$.
† Classified as $4p^2F_{7/2}^{\alpha} - 4d^2F_{7/2}^{\alpha}$. See Table IV.
‡ Classified as $3d^2F_{7/2} - {}^3X$.

It will be noticed that the majority of the lines are not common to both sets of observations; these may be confidently ascribed to impurities. As for the others, it should be remembered that for sulphur lines the numbers on GILLES' intensity scale are about one-half those used by L. and E. BLOCH; in Table III, however, with three exceptions, they are either very much less than half, or else at least double, those of the BLOCHS; the corresponding lines are therefore also probably due to impurities.

Of five new lines very recently reported in the more refrangible region of the S II spectrum by BARTELT and ECKSTEIN (*loc. cit.*), the strongest, λ 3792·46 (5), does not appear on any plate taken during the present investigation, although a faint line at λ 4590·73 (00) is presumably identical with that at λ 4590·8 (00) listed in Table II.

Modified Classifications.

Although the main object of this research was the establishment of accurate wave-lengths in the sulphur spectrum, the increased precision attained and the many new lines of low intensity found rendered it desirable to examine more closely the classifications already published, to complete as far as possible multiplets upon whose validity doubts might be cast by reason of the absence of their fainter members, and to improve the accuracy of the term values for both ions.

The wave-numbers of all but the very weakest lines being known to $0\cdot1$ cm^{-1} , all classified lines appearing more than $0\cdot2$ cm^{-1} away from their predicted positions have been subjected to a close scrutiny. As a result of this, several reassignments, as well as new combinations, appear amongst the transitions in Table II. Minor points arising from these classifications have been dealt with in the notes (*o*) to (*w*) appended to that table; those requiring further explanation, inasmuch as they involve considerable modifications in previously accepted results, are discussed below.

A term ${}^2X^\circ = 49338\cdot16$ cm^{-1} , with a J-value of $2\frac{1}{2}$ or $3\frac{1}{2}$, is assigned to S II by L. and E. BLOCH. In the region covered by the present communication the only published transition involving this term is at λ 4130·95 (3), classified by those authors as $3d\ {}^2F_{7/2} - {}^2X$. No trace of this line has been found during the present investigation, though its intensity should bring it well within the range of all the first order plates taken; nor does any wave-number difference between 2X and any other known term correspond even approximately to any line listed in Table II; owing to the lack of support from well-established lines in other regions, the term has therefore been omitted from the list of values given in Table V.

GILLES has classified three S II lines near λ 4500 as belonging to the multiplet $4p\ {}^4S - 4d\ {}^4D$, thus:

$$\begin{aligned} 4p\ {}^4S_{3/2} - 4d\ {}^4D_{5/2} &= \nu\ 22254\cdot1 & \Delta\nu &= 82\cdot4 \\ 4p\ {}^4S_{3/2} - 4d\ {}^4D_{3/2} &= \nu\ 22171\cdot7 & \Delta\nu &= 48\cdot6 \\ 4p\ {}^4S_{3/2} - 4d\ {}^4D_{1/2} &= \nu\ 22123\cdot1. \end{aligned}$$

The true separations of these $4D$ terms are, however, $81\cdot08$ and $48\cdot06$ respectively, as may be seen from the well-established multiplets $4p\ 4P - 4d\ 4D$ at $\lambda\ 4300$ and $4p\ 4D - 4d\ 4D$ at $\lambda\ 4000$. Moreover, in addition to the fact that the intensity distribution in the multiplet is irregular, the lines $\nu\nu\ 22171\cdot7$, $22123\cdot1$ have been satisfactorily classified elsewhere (see Table II), so that the proposed classifications for these must be rejected. The identification of $\nu\ 22254\cdot1$ with $4p\ 4S_{3/2} - 4d\ 4D_{5/2}$ has been retained since the agreement between its calculated and observed positions is within $0\cdot1\ \text{cm.}^{-1}$. The absence of the other two components need not appear surprising since this line is theoretically the strongest of the three but has an observed intensity of only (00).

The value of the term $4d\ 2G_{9/2}^a$ of S II must be fixed from the multiplet $4p\ 2F^a - 4d\ 2G^a$, since no other combination involving it is known. Its distance in frequency units from the known term $4d\ 2G_{7/2}^a$ at $24487\cdot79$ will be given by the interval between the known line $4p\ 2F_{7/2}^a - 4d\ 2G_{7/2}^a$ at $\nu\ 24017\cdot91$ and an unknown line $4p\ 2F_{7/2}^a - 4d\ 2G_{9/2}^a$, of estimated intensity (5) (the strongest line of the multiplet), near it. The original suggestion of INGRAM that this latter line forms a blend with a strong classified line at $\nu\ 24016\cdot14$ fixes the $4d\ 2G_{9/2}^a$ term at $24489\cdot56$. There seems no adequate basis for GILLES' more recent assignment of the value $24494\cdot7^*$ to this term, as this emendation would require the presence of the line $4p\ 2F_{7/2}^a - 4d\ 2G_{9/2}^a$ at $\nu\ 24011\cdot0$, whereas no line of such intensity is within $5\ \text{cm.}^{-1}$ of this position. The original value has therefore been retained.

The S II multiplet $4p\ 2D - 4d\ 2D$ should consist of four lines, recognition of three of which has been claimed by INGRAM :

$$4p\ 2D_{5/2} - 4d\ 2D_{5/2} = \nu\ 27640\cdot01$$

$$4p\ 2D_{5/2} - 4d\ 2D_{3/2} = \nu\ 27478\cdot69$$

$$4p\ 2D_{3/2} - 4d\ 2D_{3/2} = \nu\ 28025\cdot45.$$

The line at $\nu\ 27478\cdot69$ is, however, $0\cdot9\ \text{cm.}^{-1}$ from its predicted position, and also behaves in every way as an S III line ; it has therefore been so listed in Table II. The term $4d\ 2D_{5/2}$ has hitherto been used in the identifications of the above line $\nu\ 27640\cdot01$ as $4p\ 2D_{5/2} - 4d\ 2D_{5/2}$ and of the line $\nu\ 25428\cdot09$ as $4p\ 2P_{3/2} - 4d\ 2D_{5/2}$. The more accurate measures now available, however, show that these classifications are mutually exclusive, since by using the term value obtained from the former, the predicted position of the latter is found to lie $1\cdot0\ \text{cm.}^{-1}$ from the observed line. The classification of $\nu\ 25428\cdot09$ has therefore been omitted from Table II.

The terms $4d\ 2P_{3/2, 1/2}$ of S II have been claimed by L. and E. BLOCH on the evidence of four lines, only two of which have been found during the present investigation. Neither of these falls within experimental error at its predicted position, and one is

* An obvious misprint giving the term as $24394\cdot7$ has been rectified here.

more satisfactorily classified otherwise (see notes (s), (u) to Table II). The terms have therefore not been included in Table V.

Considerable doubt is thrown on the classifications due to L. and E. BLOCH of the $4p\ ^2D^a - 4d\ ^2F^a$, $4p\ ^2F^a - 4d\ ^2F^a$ multiplets of S II by the fact that in both the strongest lines are missing, though, judging by the ones found, they should be amongst the most intense lines not merely in their own neighbourhood, but also in the whole spectrum. The evidence adduced is unconvincing: the line λ 4180·12 attributed to $4p\ ^2F_{7/2}^a - 4d\ ^2F_{7/2}^a$ is not to be found on any plates taken during the present investigation—in this, and in being listed by GILLES and L. and E. BLOCH at totally different intensities, it exhibits all the characteristics of an impurity line. The line corresponding to $4p\ ^2F_{5/2}^a - 4d\ ^2F_{7/2}^a$ is not listed by L. and E. BLOCH, but this transition is assigned by GILLES to λ 4164·98, an S III line 2·3 cm.^{-1} from the calculated position. It therefore seems likely that the level common to both multiplets, viz., $4d\ ^2F^a$, has been wrongly valued. By assigning the value 24643·87 to the term $4d\ ^2F_{7/2}^a$, thus making the multiple level inverted with a separation of $-51\cdot15\ \text{cm.}^{-1}$, the two multiplets are completed in better agreement with the intensity rules,* and three strong lines are satisfactorily classified (see Table IV). The corresponding doublet level in O II is also inverted, with a separation of $-103\cdot2\ \text{cm.}^{-1}$.

TABLE IV.—Revision of two S II multiplets.

	$4p\ ^2D_{5/2}^a$ 48115·99	$4p\ ^2D_{3/2}^a$ 48074·50	$4p\ ^2F_{7/2}^a$ 48505·70	$4p\ ^2F_{5/2}^a$ 48594·72
	(2)		(6n)	(4)
$4d\ ^2F_{7/2}^a$	23471·11	—	23861·30	89·57 23950·87
24643·87	(23472·12)	—	(23861·83)	(23950·85)
	$-51\cdot15$	—	$-51\cdot40$	$-51\cdot36$
$4d\ ^2F_{5/2}^a$	(0)	(3)	(00)	(1)
24592·72	23523·26	$-41\cdot44$ 23481·82	23912·7	89·53 24002·23
	(23523·27)	(23481·78)	(23912·98)	(24002·00)

(Figures in brackets below the observed wave-numbers are values calculated from the terms; those above are intensities. The large error in ν 23861·30 is doubtless due to its nebulous character; it is a blend with $4p\ ^4D_{5/2} - 4d\ ^4F_{5/2}$.)

Revised Term Values.

The modifications rendered necessary by the more accurate measurements in Table II and the numerical considerations discussed above have been incorporated

* Convenient intensity tables have recently been published by White & Eliason, 'Phys. Rev.', vol. 44, p. 753 (1933).

in Table V, which gives a complete list of revised term values for both ions. The terms are given as far as is practicable in numerical order, odd and even terms being distinguished by printing the former in italics.

In S II, the sequences $ms\ ^4P$, $ms\ ^2P$ have been employed by INGRAM to arrive at

TABLE V.—Revised Term Values, S II and S III (odd terms in italics).
S II.

<i>3p</i>	$^4S_{3/2}$	<i>188824.5</i>		<i>3d</i>	$^2F_{5/2}$	<i>74020.39</i>	
<i>3p</i>	$^2D_{3/2}$	<i>173972.6</i>			$^2F_{7/2}$	<i>73539.19</i>	481.20
	$^2D_{5/2}$	<i>173941.1</i>	31.5	<i>3d</i>	$^4P_{5/2}$	<i>73007.5</i>	
<i>3p</i>	$^2P_{1/2}$	<i>164300.3</i>			$^4P_{3/2}$	<i>72954.1</i>	— 53.4
	$^2P_{3/2}$	<i>164251.7</i>	48.6		$^4P_{1/2}$	<i>72932.2</i>	— 21.9
<i>3p'</i>	$^4P_{5/2}$	<i>109429.7</i>	— 363.1	<i>3d</i>	$^2P_{3/2}$	<i>70678.00</i>	
	$^4P_{3/2}$	<i>109066.6</i>	— 210.1	<i>3d</i>	$^2D_{3/2}$	<i>69582.37</i>	
	$^4P_{1/2}$	<i>108856.5</i>			$^2D_{5/2}$	<i>69529.80</i>	53.57
<i>3p'</i>	$^2P_{3/2}$	<i>83225.48</i>	— 445.14	<i>4s</i>	$^2D_{3/2}^a$	<i>67296.30</i>	
	$^2P_{1/2}$	<i>82780.34</i>			$^2D_{5/2}^a$	<i>67295.01</i>	1.29
<i>4s</i>	$^4P_{1/2}$	<i>79264.00</i>	270.78	<i>4p</i>	$^2S_{1/2}$	<i>63339.18</i>	
	$^4P_{3/2}$	<i>78993.22</i>	437.05	<i>4p</i>	$^4D_{1/2}$	<i>60999.57</i>	151.28
	$^4P_{5/2}$	<i>78556.17</i>			$^4D_{3/2}$	<i>60848.29</i>	256.86
<i>3d</i>	$^4F_{3/2}$	<i>78647.67</i>	136.30		$^4D_{5/2}$	<i>60591.43</i>	366.04
	$^4F_{5/2}$	<i>78511.37</i>	195.35		$^4D_{7/2}$	<i>60225.39</i>	
	$^4F_{7/2}$	<i>78316.02</i>	257.83	<i>4p</i>	$^4P_{1/2}$	<i>59036.79</i>	70.36
	$^4F_{9/2}$	<i>78058.19</i>			$^4P_{3/2}$	<i>58966.43</i>	276.01
<i>4s</i>	$^2P_{1/2}$	<i>75887.17</i>	523.89		$^4P_{5/2}$	<i>58690.42</i>	
	$^2P_{3/2}$	<i>75363.28</i>		<i>4p</i>	$^2D_{3/2}$	<i>58183.50</i>	545.86
<i>3d</i>	$^4D_{1/2}$	<i>74662.30</i>	38.25		$^2D_{5/2}$	<i>57637.64</i>	
	$^4D_{3/2}$	<i>74624.05</i>	30.30	<i>4p</i>	$^4S_{3/2}$	<i>57795.74</i>	
	$^4D_{5/2}$	<i>74593.75</i>	48.36	(?)	$^2Y^o$	<i>57706.7 ?</i>	
	$^4D_{7/2}$	<i>74545.39</i>					

TABLE V—(continued).

S II—(continued).

<i>4p</i>	$^2P_{1/2}$	55555·97	131·29	<i>4d</i>	$^4P_{5/2}$	33006·13	—210·91	
	$^2P_{3/2}$	55424·68			$^4P_{3/2}$	32795·22		—118·91
(?)	2x	55465·1		$^4P_{1/2}$	32676·31			
(?)	$^2P_{1/2}$	48978·9	170·1	<i>4d</i>	$^2F_{5/2}$	32703·17	482·34	
	$^2P_{3/2}$	48808·8			$^2F_{7/2}$	32220·83		
<i>4p</i>	$^2F_{5/2}^a$	48594·72	89·02	<i>4d</i>	$^2D_{3/2}$	30158·05	160·42	
	$^2F_{7/2}^a$	48505·70			$^2D_{5/2}$	29997·63		
<i>4p</i>	$^2D_{5/2}^a$	48115·99	— 41·49	<i>4d</i>	$^2F_{7/2}^a$	24643·87	— 51·15	
	$^2D_{3/2}^a$	48074·50			$^2F_{5/2}^a$	24592·72		
<i>4p</i>	$^2P_{1/2}^a$	45335·89	134·42	<i>4d</i>	$^2G_{9/2}^a$	24489·56	— 1·77	
	$^2P_{3/2}^a$	45201·47			$^2G_{7/2}^a$	24487·79		
<i>5s</i>	$^4P_{1/2}$	38566·30	272·92	<i>5p</i>	$^4D_{1/2}$	24705·9	133·4	
	$^4P_{3/2}$	38293·38			$^4D_{3/2}$	24572·5		195·3
	$^4P_{5/2}$	37828·23			$^4D_{5/2}$	24377·2		325·4
<i>5s</i>	$^2P_{1/2}$	37440·67	526·84	$^4D_{7/2}$	24051·8			
	$^2P_{3/2}$	36913·83		<i>5p</i>	$^4P_{1/2}$	24545·2	38·1	
<i>4d</i>	$^4F_{3/2}$	36865·09	134·93	$^4P_{3/2}$	24507·1	142·1		
	$^4F_{5/2}$	36730·16		$^4P_{5/2}$	24365·0			
	$^4F_{7/2}$	36519·79						
	$^4F_{9/2}$	36209·25						
<i>4d</i>	$^4D_{1/2}$	35670·84	48·06	<i>5p</i>	$^4S_{3/2}$	23822·05		
	$^4D_{3/2}$	35622·78						
	$^4D_{5/2}$	35541·70						
	$^4D_{7/2}$	35410·98						

TABLE V—(continued).

S III.

$3p$	3P_0	282752	300	$3d$	3D_1	135195·68	140·67
	3P_1	282452			3D_2	135055·01	
	3P_2	281917	535		3D_3	135001·46	
$3p'$	3D_1	198729	28	$4p$	3D_1	112975·96	297·27
	3D_2	198701			3D_2	112678·69	
	3D_3	198650	51		3D_3	112097·06	
$3p'$	3P_2	184003	— 19	$4p$	3P_0	110114·73	154·50
	3P_1	183984			3P_1	109960·23	
	3P_0	183978	— 6		3P_2	109554·27	
(?)	x	145905		$4p$	3S_1	108709·81	
$3p'$	3S_1	144686			$4d$	3F_2	78167·11
$3d$	3P_0	139650·09	20·28	3F_3		77675·25	489·92
	3P_1	139629·81		7·74		3F_4	77185·33
	3P_2	139622·07		$4d$	3D_1	76207·13	132·74
$4s$	3P_0	136049·81	40·35		3D_2	76074·39	
	3P_1	136009·46			409·46	3D_3	75835·03
	3P_2	135600·00		$5s$	3P_0	72972·6	152·7
			3P_1		72819·9	771·5	
					3P_2	72048·4	

approximations to the terms $4s\ ^4P_{1/2}$, $4s\ ^2P_{1/2}$ respectively. The establishment of intercombinations between quartet and doublet terms by L. and E. BLOCH fixes at 317·17 the additive correction to be applied to his doublet terms to reduce them to the same basis as the quartet system, to which all the S II terms in Table V are referred. The limited range of the present investigation has made it necessary to supplement the S II term table by using INGRAM'S values for the terms $3p\ ^4S$, 2D , 2P ; $3p'\ ^4P$; and $3d\ ^4F$. The terms $3d\ ^4P$; $5p\ ^4S$, 4P , 4D are due to BARTELT and ECKSTEIN. With regard to these latter terms, it might be mentioned that quartet-doublet intercombinations between the terms $3d\ ^4D$ and $4p\ ^2D^a$, $^2F^a$ have been recognized amongst the many new lines of low intensity found on the first order plates taken here. This suggests

that the above terms $3d\ ^4P$ near 73000 cm.^{-1} should also combine with $4p\ ^2P^o$, $^2D^o$ to give groups of faint lines at $\lambda\ 3600$ and $\lambda\ 4020$ respectively. None of these has, however, been detected.

In S III, the value 135600 for $4s\ ^3P_2$ was derived by GILLES by applying a Rydberg formula to the two known members of the series $ms\ ^3P_2$. All the S III terms in Table V are referred to this level. Terms derived from the $3p$, $3p'$, $4d$, and $5s$ configurations are not involved in transitions giving lines in the region $\lambda\lambda\ 3300 - 4900$, so INGRAM'S values have been used in order to complete the table.

Acknowledgments.

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It is a pleasure to thank Professor A. FOWLER, F.R.S., who originally suggested the research, for his constant helpful interest and advice during its progress.

Summary.

The spectra S II and S III have been photographed in the first and third orders of a 10-ft. concave grating spectrograph from $\lambda\ 3300$ to $\lambda\ 4900$ Å. The source of radiation was a condensed discharge through a stream of low-pressure hydrogen containing adjustable amounts of sulphur vapour, the spectra due to the atom in different stages of ionization being distinguished from one another by suitably altering the experimental conditions.

The table given includes many new lines, and particular care has been taken to avoid listing impurities. The great majority of the lines measured are expressed to either $0\cdot01$ Å. or $0\cdot001$ Å., the probable errors being respectively $\pm 0\cdot007$ Å. and $\pm 0\cdot002$ Å.

Although the main object of the investigation was to establish accurate wavelengths for astrophysical application, the comprehensive nature of the results has enabled many new classifications to be made, whilst the increased precision attained has rendered necessary several reassignments amongst lines already classified. A table of revised term values for both ions is therefore included. Of the intense lines in the region investigated only three now await classification.

DESCRIPTION OF PLATES.

PLATE 4.

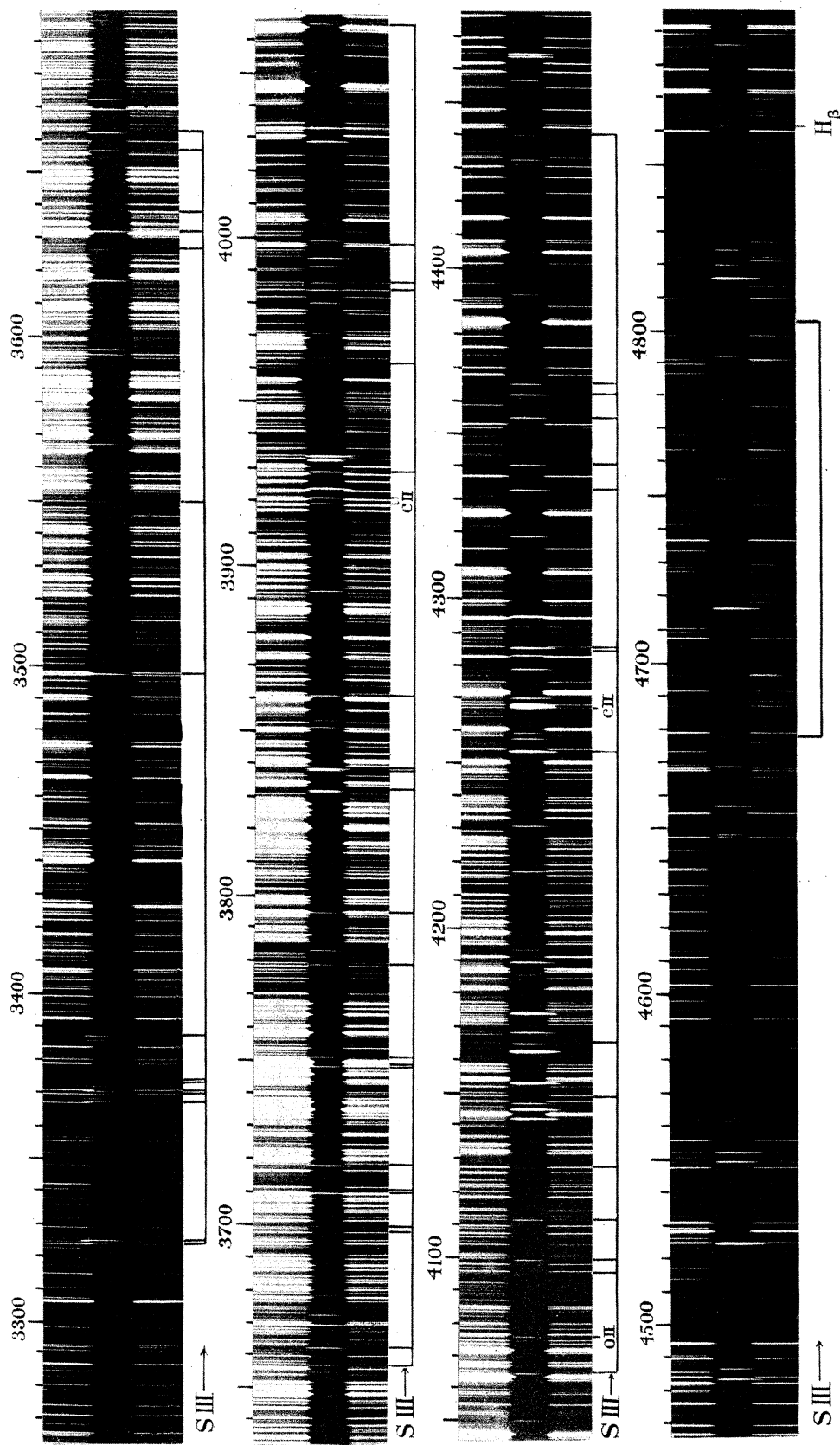
General view of the sulphur line spectrum, $\lambda\lambda\ 3300 - 4900$, from a photograph of the condensed discharge taken in the first order of a 10-ft. concave grating ($5\cdot5$ Å. per mm.). The sulphur pressure being low, the exposure required was four hours. The outer spectrum is an iron arc comparison. Except where otherwise stated, the vertical lines below each strip of the photograph indicate the positions of S III lines of intensities greater than (00). Lines not marked belong to S II.

PLATE 5.

Pressure effects in S II and S III, illustrated by means of enlargements from first order plates. (*a*) and (*d*) are of low pressure discharges and were obtained in three hours; (*b*) and (*c*) are of high pressure discharges and were obtained in 30 minutes. The outer spectra are iron arc comparisons.

(*a*), (*b*) show the experimental differentiation between lines due to atoms in successive stages of ionization. The S II lines (group at λ 4270) broaden with increasing pressure from (*a*) to (*b*), whilst the S III lines (group at λ 4350) remain relatively sharp.

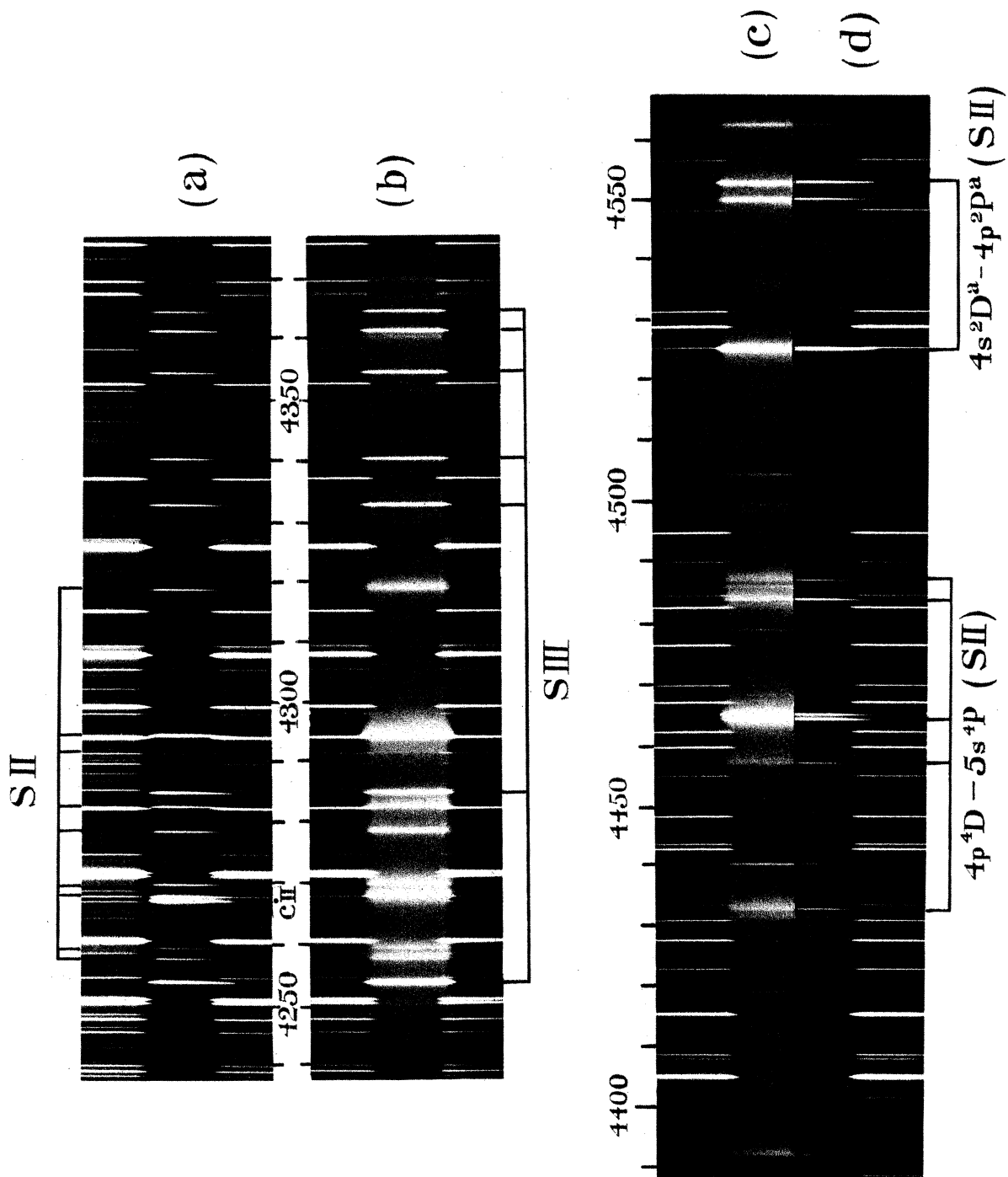
(*c*), (*d*) show the experimental classification of S II lines into related groups. The symmetrical broadening of the members of the multiplet $4s\ ^2D^{\circ} - 4p\ ^2P^{\circ}$ distinguishes them from lines belonging to the multiplet $4p\ ^4D - 5s\ ^4P$, which suffer marked red shifts when the sulphur pressure is increased from (*d*) to (*c*).



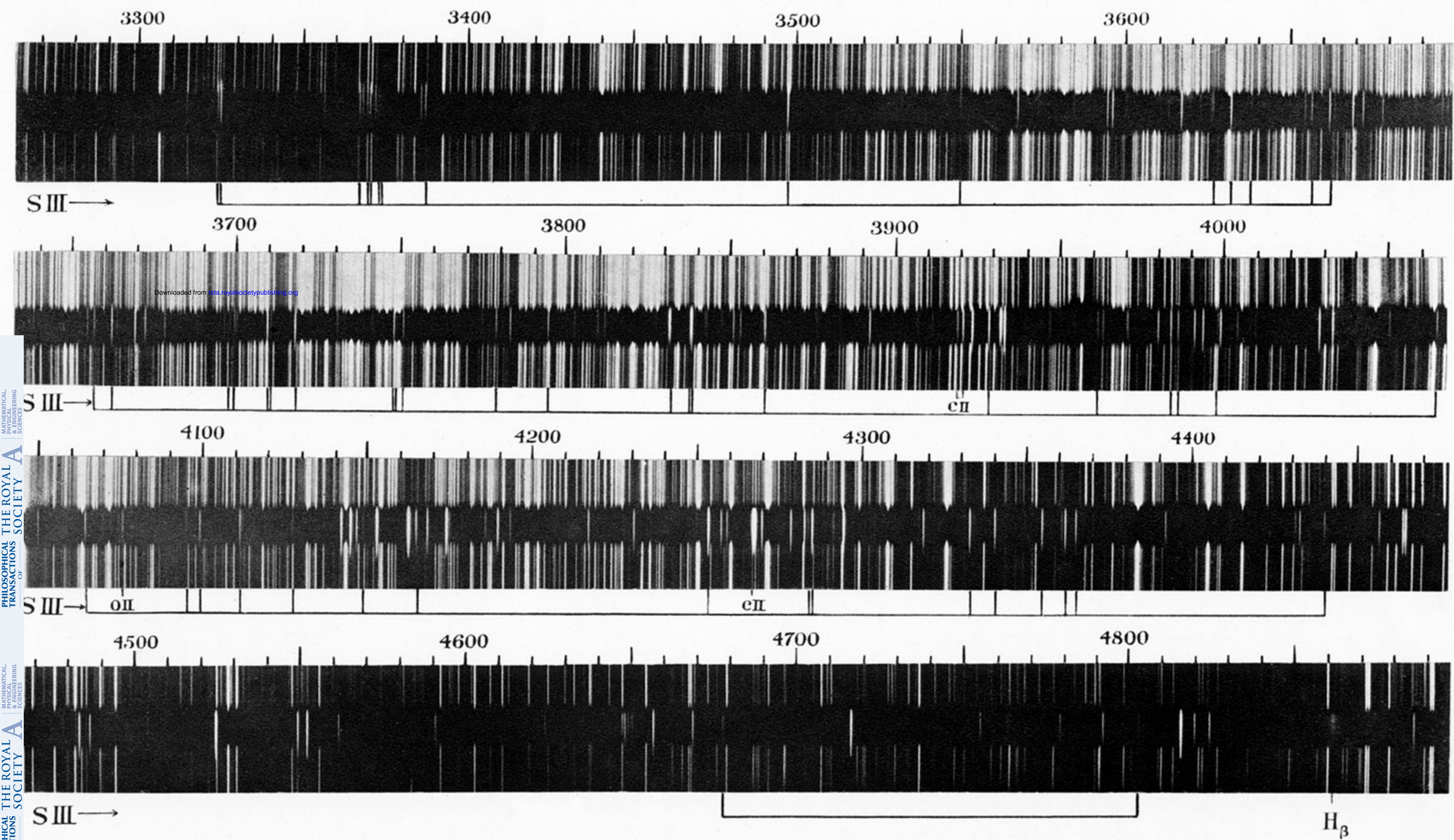
General view of the Sulphur line spectrum $\lambda\lambda$ 3300—4900 Å.

Hunter.

Phil. Trans., A, vol. 233, Plate 5.



Pressure effects in Sulphur.

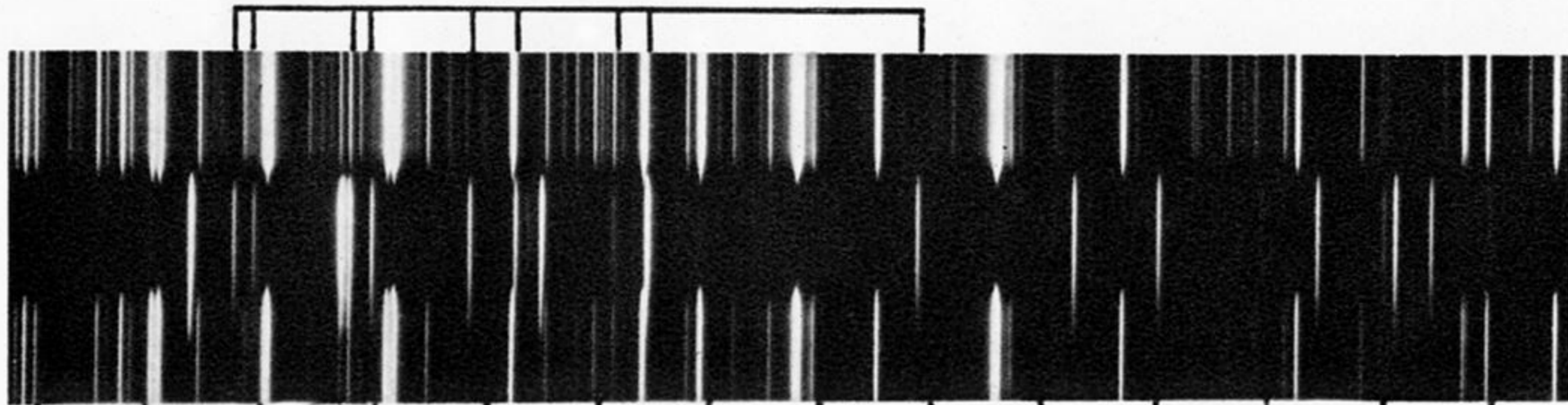


General view of the Sulphur line spectrum $\lambda\lambda$ 3300—4900 Å.

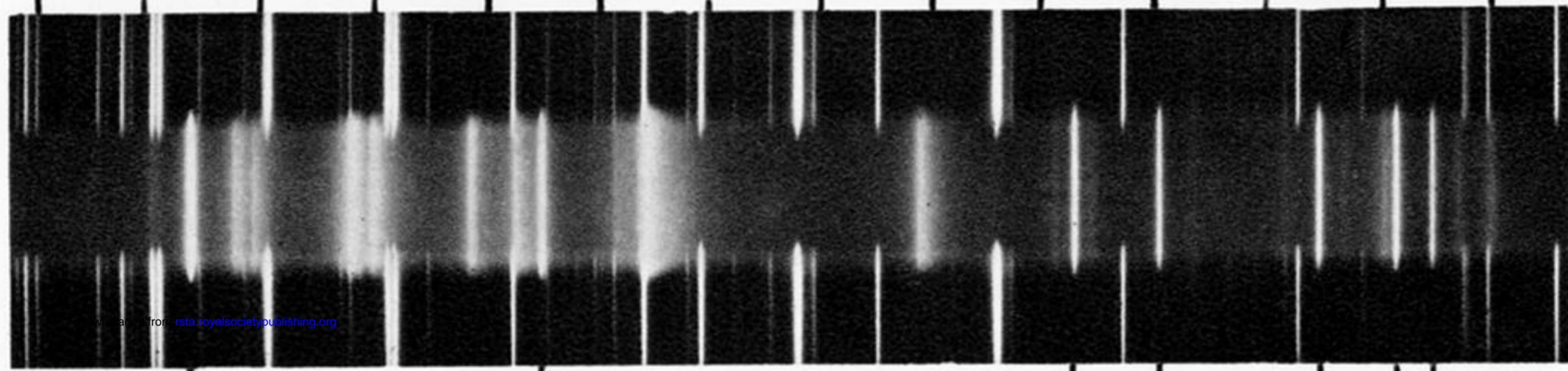
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S II

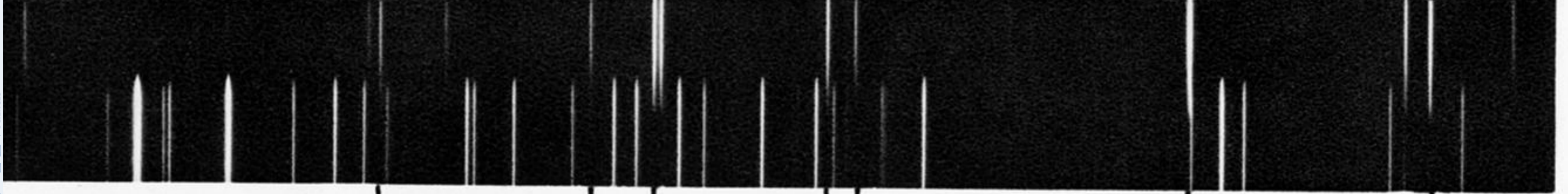
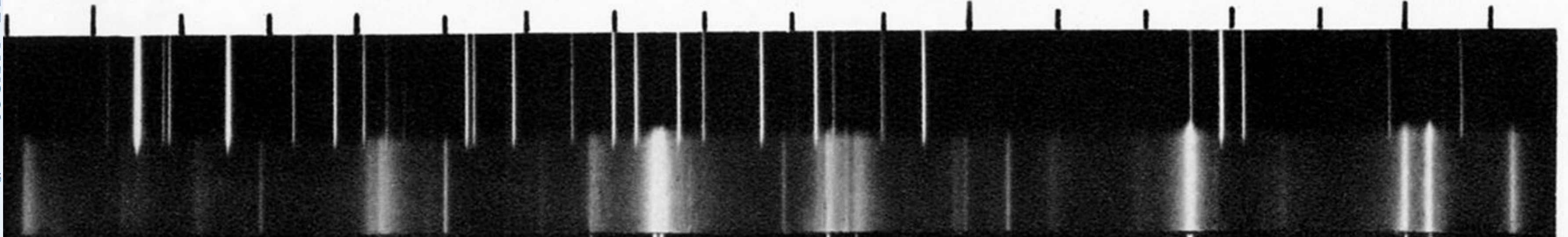


4250 c II 4300 4350



S III

4400 4450 4500 4550



$4p^4D - 5s^4P$ (S II)

$4s^2D^a - 4p^2P^a$ (S II)

Pressure effects in Sulphur.