

## THE ABSORPTION SPECTRUM OF SULPHUR DIOXIDE

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In some earlier work on sulphur dioxide<sup>1</sup> the author obtained an absorption spectrum, which exhibited marked changes with change of pressure and change in the length of the column of gas. The change in the absorption with the reduction in the absorbing medium consisted not merely in a reduction in the width of the region, but also in breaking up very wide absorption bands into narrow bands.

With a column of gas 207 cm in length and at a pressure of from one to three atmospheres the spectrum consisted of:

Narrow bands from  $\lambda$  3900 to 3333  
One wide band from  $\lambda$  3330 to less than 2100

At a pressure of 1.5 cm of mercury it consisted of:

Narrow bands from  $\lambda$  3226 to 3146  
One wide band from  $\lambda$  3134 to 2467  
Narrow bands from  $\lambda$  2456 to 2297  
One wide band from  $\lambda$  2290 to less than 2100

At a pressure of 0.13 cm it consisted of:

Narrow bands from  $\lambda$  3180 to 2970  
One wide band from  $\lambda$  2968 to 2715  
Narrow bands from  $\lambda$  2702 to 2269  
One wide band from  $\lambda$  2250 to less than 2100

When the length of the column of gas was reduced to 20 cm and the pressure was less than 1 cm of mercury, the whole spectrum consisted of narrow bands lying within the region  $\lambda$  3133 to 2200.

The changes in the spectrum produced by change of pressure suggested that with the gas at a suitable pressure and with spectral apparatus of greater dispersion the bands of the spectrum might be broken up into lines.

### OBJECTS OF INVESTIGATION

The present investigation was undertaken to determine whether the bands of absorption could be broken into lines and, if so, whether

<sup>1</sup> *Astrophysical Journal*, 23, 324, 1906.

a relationship existed between the wave-numbers of lines of similar physical character.

In the case of sulphur dioxide a special value is attached to the absorption spectrum and its resolution into lines, as its emission spectrum is so difficult to obtain, on account of the great tendency of the gas to dissociate, even when a very weak discharge is passed through it. So far its emission spectrum<sup>1</sup> is known only as a band spectrum with heads toward the ultra-violet, and its investigation has not been carried into wave-lengths less than 3270; the author, however, intends to make a further attempt in this direction at the first opportunity. No resemblance between the emission and absorption spectrum has yet appeared. This fact is true also of chlorine, but in the case of iodine, Konen has found that the absorption spectrum corresponds with the band emission spectrum from a vacuum tube.

#### APPARATUS AND MANIPULATION

The source of light was the spark of an alloy of cadmium and zinc mixed in atomic proportions; this light gives a continuous spectrum down to  $\lambda$  2100, provided a sufficiently long exposure is given and a suitable capacity is placed in parallel with the spark, across the terminals of the secondary of an induction coil.

The spectral apparatus was a concave Rowland grating, of 180 cm radius of curvature, with 15,028 lines to the inch (592 to the mm, approximately) and the width of the ruled surface 6.2 cm. The photographic plates used were Seed's No. 27 Gilt Edge on lantern-slide glass.

The gas was inclosed in steel tubes which had been thoroughly cleaned and their ends closed with quartz plates. At the beginning of the investigation, a tube 20 cm in length was used, but as the spectrum obtained was not well defined, a tube 80 cm long was adopted and better results were obtained.

The tube was exhausted by a Geissler pump and the pressures read by a McLeod gauge. The gas was obtained from liquid sulphur dioxide which had been redistilled, and care was taken that the gas used in the tube should be free from air; its high temperature of liquefaction ( $-10^{\circ}$  C.) insures its freedom from other gases.

<sup>1</sup> *Astrophysical Journal*, 23, 338, 1906.

The beam of light from the spark was made parallel by a quartz lens before entering the tube; on emergence it was brought by a second quartz lens to a focus on the slit of the grating apparatus. For comparison a photograph of the spectrum of the unabsorbed light of a second spark of the same alloy was taken immediately above or below that of the absorption spectrum of the gas. The beam from this second spark was made parallel by a third quartz lens and when required was brought between the end of the absorption tube and the second quartz lens which focused the light on the slit.

For determination of the wave-lengths of all the lines, measurements of the photographic plates were made in the usual way by means of a dividing engine; on the one used for this purpose readings could be made to 0.0001 mm, that is, to a greater degree of accuracy than that to which settings could be made on the absorption lines. The reduction factor was roughly 9.3 Å to 1 mm.

#### STANDARD LINES

Metallic lines of cadmium, zinc, lead, and iron were transmitted through the gas, the lead and iron appearing from impurities in the two other metals. Certain cadmium lines were used as standards of reference; intermediate lines of cadmium, zinc, lead, and iron were used for plotting a curve of errors, which was applied in the usual manner for the correction of the calculated values of the unknown lines. By using as lines of reference those transmitted through the gas, one avoids possible errors due to displacement of standard lines by want of perfect adjustment of another source. A further advantage in having the reference lines superposed on the spectrum to be investigated is that the plate can be placed under the microscope of the dividing engine, so that lines stretch continuously across the whole field of view, and this makes easier the exact adjustment of the cross-hair parallel to the lines.

The best values known of the wave-lengths of cadmium and zinc in the region in which this spectrum lies, namely  $\lambda$  2700 to  $\lambda$  3200, were those determined by Eder and Valenta;<sup>1</sup> these were based on

<sup>1</sup> *Normal-Spectren einiger Elemente zur Wellenlängenbestimmung im äussersten Ultraviolett*, 1899.

their own values of iron lines which were referred to Rowland's normals.

The last photograph for the present work was taken before the publication of Fabry and Buisson's iron standards<sup>1</sup> reached this country, March 1908; otherwise a photograph of iron lines would have been taken on the same plate as the absorption spectrum and measurements on these lines compared with those made on the lines of reference transmitted through the gas. It was considered that Fabry and Buisson's standards would form a more uniform basis for a relationship among wave-numbers, hence the wave-lengths of the standard lines were referred to these normals by the following plan. A curve was plotted having as abscissae wave-lengths of iron lines and as ordinates the ratios of Rowland's wave-lengths to those of Fabry and Buisson's of the same lines. From this curve was read off the ratio by which Eder and Valenta's wave-lengths must be divided to give their values referred to Fabry and Buisson's normals. The wave-lengths of the lines used for this curve are given in Table I, together with the ratio of their values as determined by Rowland and by Fabry and Buisson.

TABLE I

Rowland's Value*	Fabry and Buisson's Value	Rowland's $\lambda$
		Fabry and Buisson's $\lambda$
2435.247	2435.159	1.00003601
2506.994	2506.904	3590
2528.599	2528.516	3322
2679.148	2679.065	3098
2778.340	2778.225	4135
2813.388	2813.290	3483
2851.904	2851.800	3646
2912.275	2912.157	4052
2987.410	2987.293	3916
3075.849	3075.725	4032
3225.907	3225.790	1.00003627

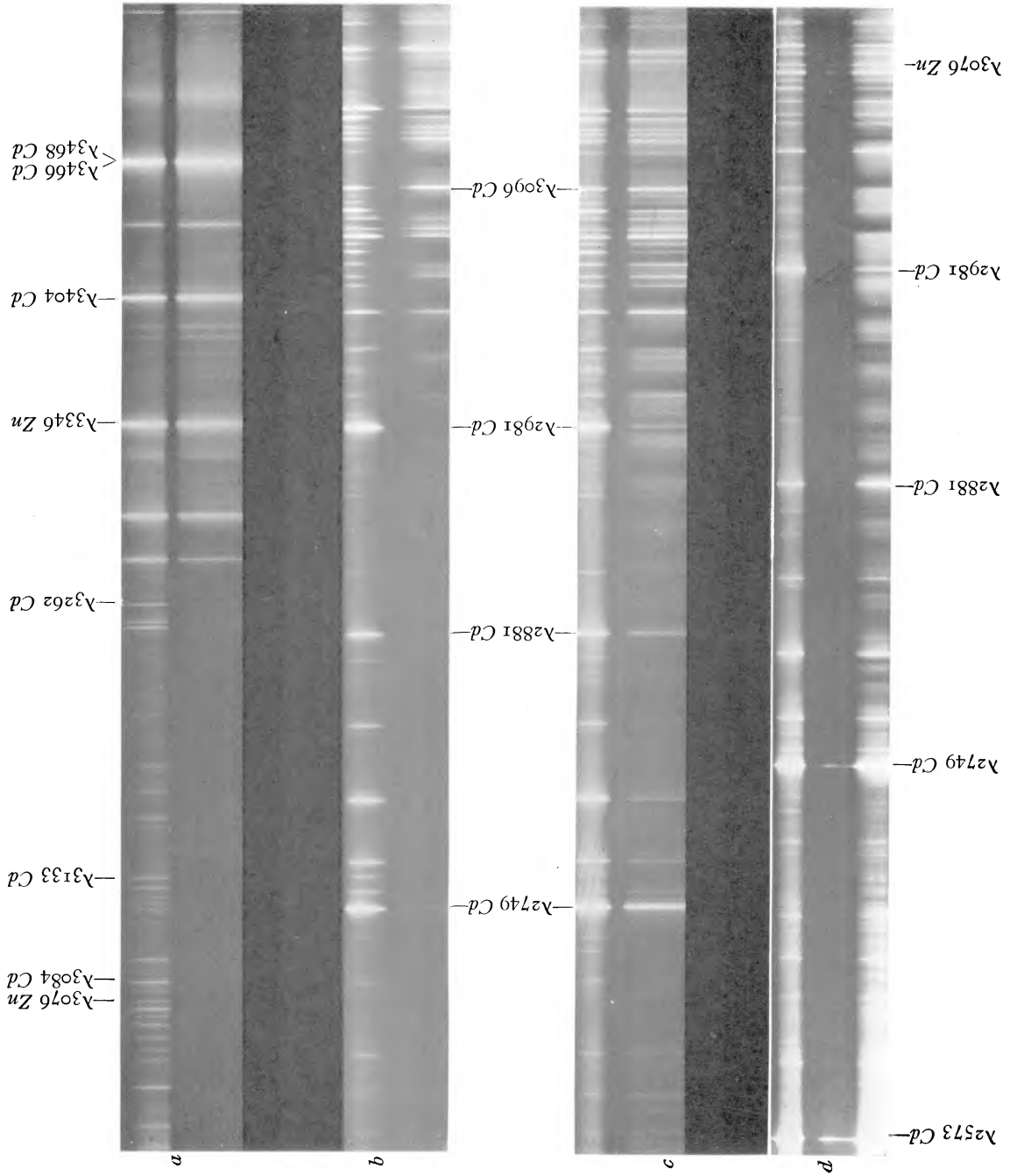
\* *Philosophical Magazine* (5), 36, 49, 1893.

The cadmium standards used for the regions lying between them have the following wave-lengths when referred to Fabry and Buisson's normals:

2707.05	3080.877
2833.073	3133.228
2996.049	

<sup>1</sup> *Journal de Physique* (4), 7, 169-193, 1908.

PLATE IX



ABSORPTION SPECTRUM OF SULPHUR DIOXIDE  
(All the fine lines are lost in the engraving)

DETERMINATION OF EXPERIMENTAL CONDITIONS FOR BEST DEFINITION

Photographs of the spectrum were taken first with a column of gas 20 cm in length and with the gas under various pressures and the plates were given different times of exposure. These experiments showed that the bands obtained in the earlier work could be broken into lines, but so far the lines were not well defined. The experiments were repeated with a column of gas 80 cm in length until conditions were found which gave the best-defined lines. These conditions were a column of gas 80 cm long, a pressure of about 1 mm, and an exposure of four hours. With smaller pressure the absorption was too weak to give clear lines; with greater pressure the bands were not completely broken up into lines. Similar effects were produced with different exposures; with too long an exposure, too much was transmitted; with too short an exposure, not sufficient light was transmitted to give clear lines.

RESULTS

The spectrum under different pressures is shown on Plate IX. The positives from which the reproductions are made are threefold enlargements of the original negatives. Much of the detail of the negatives is lost even in the positives, but for reproduction, enlargement was necessary, as it requires a magnifying glass to show the lines on the negatives.

The spectrum is shown on Plate IX under the following conditions:

Fig.	Length of Column of Gas	Pressure of Gas
<i>a</i>	20 cm	1 atmos.
<i>b</i>	80	3 mm
<i>c</i>	20	5
<i>d</i>	80	0.8

The spectrum was found to consist of about 590 lines lying between  $\lambda$  2707 and 3120; the absorption extended to shorter wave-lengths but the lines were much less clearly defined. The wave-lengths were determined as described above and expressed in Ångströms; the wave-numbers were then calculated as  $\frac{I}{\lambda} \times 10^8$  and therefore represent the number of vibrations executed while the wave is propagated through one centimeter. The wave-lengths,  $\lambda$ , of the lines, with their intensities,  $I$ , are given in Table II, the intensities being estimated by eye from 10, the greatest, to 1, the least.

TABLE II

$\lambda$	I	$\lambda$	I	$\lambda$	I	$\lambda$	I
2707.6	7	2780.85	7	2807.18	7	2829.79	8
10.28	6	81.43	8	07.56	7	30.38	9
22.33	8	81.96	6	08.03	6	30.85	10
25.84	7	82.50	6	08.41	6	31.38	10
26.22	7	82.98	6	09.30	6	31.83	10
26.73	7	83.47	7	09.66	6	32.24	10
28.04	5	84.01	7	10.07	7	32.78	10
28.56	5	84.52	7	10.3	7	33.47	9
29.03	5	84.93	7	10.73	8	33.86	9
33.42	8	85.22	7	11.03	7	34.27	9
35.66	7	86.38	6	11.51	8	34.79	9
36.61	7	86.69	6	11.88	7	35.15	9
37.48	6	87.02	6	12.28	8	35.58	8
37.86	6	87.30	6	12.70	7	35.91	8
38.61	6	87.72	8	13.20	7	36.23	8
39.2	8	88.24	8	13.60	7	37.46	8
39.92	6	88.66	8	14.21	8	37.85	8
40.46	6	88.96	9	14.57	8	38.19	8
40.8	6	89.50	9	14.85	8	38.63	8
41.18	6	90.06	9	15.35	9	39.02	7
41.65	5	90.58	8	15.80	9	39.33	7
42.0	6	91.06	8	16.1	9	39.79	6
42.3	5	91.40	7	16.5	9	40.20	7
42.84	5	91.82	7	16.93	9	40.55	7
52.94	2	92.14	7	17.22	9	41.00	7
53.43	3	92.68	7	17.59	9	41.61	7
53.91	3	93.07	7	17.99	10	42.06	7
54.4	4	93.37	7	18.46	10	42.46	7
55.02	4	93.86	6	18.71	10	43.15	8
59.12	5	94.32	6	18.97	10	43.60	8
60.02	5	94.74	6	19.26	9	43.99	8
60.69	5	95.13	6	19.65	9	44.40	8
61.32	5	95.58	6	20.13	9	44.74	8
61.97	5	95.93	7	20.48	9	45.27	7
62.80	5	96.65	8	20.79	9	45.60	7
63.39	5	97.13	9	21.12	9	45.91	7
64.29	5	97.62	9	21.53	9	46.31	7
64.75	6	98.08	8	21.78	9	46.81	8
65.24	7	98.91	7	23.42	6	47.27	8
65.75	6	99.31	7	23.76	6	47.68	9
66.16	4	99.70	6	24.16	7	48.16	9
66.52	4	2800.35	5	24.44	7	48.56	8
67.37	3	01.56	5	24.75	7	48.96	8
67.77	3	02.10	5	25.21	7	49.54	8
69.08	4	02.4	5	25.57	7	49.98	8
76.8	5	03.22	5	26.01	7	50.3	8
77.26	8	03.79	5	26.23	8	50.67	9
77.73	7	04.19	5	26.60	7	51.08	9
78.25	7	04.76	6	26.96	6	51.45	9
78.91	7	05.20	6	27.37	6	51.79	10
79.34	7	05.49	6	27.96	6	52.14	10
79.85	7	06.04	6	28.40	6	52.57	10
80.26	7	06.45	6	28.84	6	52.98	9
80.6	8	06.80	7	29.30	7	53.58	9

TABLE II—Continued

$\lambda$	I	$\lambda$	I	$\lambda$	I	$\lambda$	I
2853.92	9	2886.51	8	2920.2	8	2949.28	5
54.31	9	86.82	9	20.55	8	49.6	5
54.85	9	87.22	9	20.89	8	49.90	5
55.28	9	87.74	10	21.16	9	50.28	5
55.60	9	88.10	10	21.45	9	54.3	3
56.10	8	88.65	10	21.71	9	54.7	3
56.63	8	89.13	9	22.21	9	55.62	3
57.04	8	89.66	9	22.89	8	56.16	4
57.94	8	89.91	9	23.38	9	56.80	5
58.32	8	89.42	9	23.75	9	57.50	7
58.69	8	91.08	8	24.34	9	57.89	7
59.13	8	92.21	7	24.65	9	58.22	8
59.63	7	92.7	6	25.52	9	58.57	8
60.03	7	93.03	6	26.20	8	58.99	8
60.47	7	93.43	5	26.59	8	59.30	9
60.98	7	94.06	6	26.81	8	59.84	9
61.35	7	94.38	7	27.84	8	60.22	10
61.88	7	94.69	7	28.43	7	60.78	10
62.46	6	96.55	7	28.89	7	61.18	10
63.42	6	98.48	6	29.21	7	61.45	10
64.02	5	2906.27	9	29.56	6	61.98	10
64.9	7	01.15	9	30.01	6	62.40	10
65.64	8	01.56	8	30.33	6	62.83	9
65.98	9	01.96	8	30.69	5	63.27	9
66.5	10	02.62	8	31.10	5	63.72	9
66.82	10	03.30	8	31.72	5	64.82	8
67.38	10	04.37	8	32.95	4	66.04	8
67.87	10	04.8	7	33.50	4	67.40	5
68.62	9	05.20	8	34.69	3	68.05	5
68.97	9	05.81	8	35.11	4	68.34	5
69.21	9	06.14	8	35.52	4	69.09	5
69.66	9	06.49	10	36.38	5	69.76	5
70.31	9	07.17	10	37.2	5	70.51	3
70.76	9	07.90	10	38.07	10	71.70	1
71.32	9	08.2	9	38.5	10	72.91	1
72.19	8	08.6	9	39.10	9	73.57	1
72.72	8	08.98	8	39.63	10	74.33	1
73.1	8	09.86	8	40.06	9	74.8	1
73.72	8	10.13	8	40.41	9	75.89	1
74.1	8	12.04	5	40.79	9	78.2	8
74.43	8	12.36	5	41.18	9	78.55	8
74.95	8	13.28	5	41.57	9	79.13	9
75.55	8	13.55	5	41.97	9	79.85	8
76.92	6	14.3	4	42.83	9	81.66	5
77.62	5	15.25	4	43.40	9	81.99	5
78.01	6	16.1	5	43.93	9	83.40	6
78.35	7	16.53	6	44.39	9	84.79	6
79.86	5	16.82	7	44.82	9	86.13	5
82.73	3	17.42	8	45.64	9	88.02	4
83.5	3	17.74	8	46.09	9	88.77	4
83.79	4	18.31	9	46.65	8	89.46	3
84.4	4	18.94	8	47.23	8	90.27	2
85.1	5	19.35	7	48.55	6	93.8	2
85.93	8	19.66	7	49.00	5	98.0	5

TABLE II—Continued

$\lambda$	I	$\lambda$	I	$\lambda$	I	$\lambda$	I
2998.33	7	3021.18	10	3048.22	6	3083.21	5
99.0	9	21.62	9	49.46	6	84.02	6
99.56	9	22.15	9	49.82	5	85.63	7
99.81	10	22.68	9	50.46	4	86.20	7
3000.41	10	23.25	9	50.9	4	86.54	6
00.94	10	23.87	8	51.54	4	86.88	6
01.22	10	24.29	8	51.79	4	87.4	6
02.00	10	24.83	8	52.43	4	87.99	5
02.37	9	25.40	8	53.7	3	89.49	5
02.93	9	25.65	7	54.03	2	89.79	4
03.53	9	26.10	7	54.76	2	90.30	3
04.15	9	26.51	7	55.31	2	90.62	3
04.50	8	26.87	7	55.7	2	91.24	3
05.43	7	27.15	6	56.0	2	99.27	$\frac{1}{2}$
05.8	7	27.64	6	56.62	2	3101.2	3
06.2	5	28.19	6	57.15	2	03.0	$\frac{1}{2}$
06.55	4	28.72	6	57.73	2	04.16	1
06.96	4	29.25	5	58.38	2	05.29	2
07.40	4	29.87	5	61.72	7	05.81	2
07.99	3	30.4	5	62.48	8	06.36	5
08.58	3	33.8	3	63.11	8	06.89	5
09.35	3	34.7	3	63.7	8	07.43	4
09.87	3	35.2	3	64.10	7	08.08	2
10.33	2	37.1	2	64.4	8	08.66	1
10.87	2	37.6	2	65.46	8	09.26	1
11.42	2	38.0	2	65.71	7	09.86	3
12.29	2	38.5	2	66.49	7	10.73	3
13.00	2	39.5	3	67.0	6	11.18	1
13.56	2	40.07	4	67.76	6	11.77	1
13.88	2	40.8	3	70.02	2	12.27	2
14.82	1	41.43	10	70.57	4	13.61	2
15.28	1	41.79	10	71.20	4	14.18	2
15.86	1	42.03	10	75.31	3	16.1	2
16.59	2	42.40	9	78.3	3	16.9	1
18.1	2	43.14	9	79.0	3	17.3	1
18.83	8	44.0	8	79.74	3	17.8	1
19.26	8	44.96	8	80.31	3	18.2	1
19.63	9	46.00	8	81.5	3		
19.98	10	47.20	6	82.03	4		

## STRUCTURE OF THE SPECTRUM

A curve was plotted having wave-numbers as abscissae and intensities as ordinates (see Fig. 1). The regularity of this curve suggested a relationship between the wave-numbers of lines of relatively equal intensity. With this clue as a guide, it was found that 92 per cent of the lines could be arranged in groups or series of lines, in each of which the *first* differences of consecutive wave-numbers were approximately constant, or that each series of wave-numbers formed an

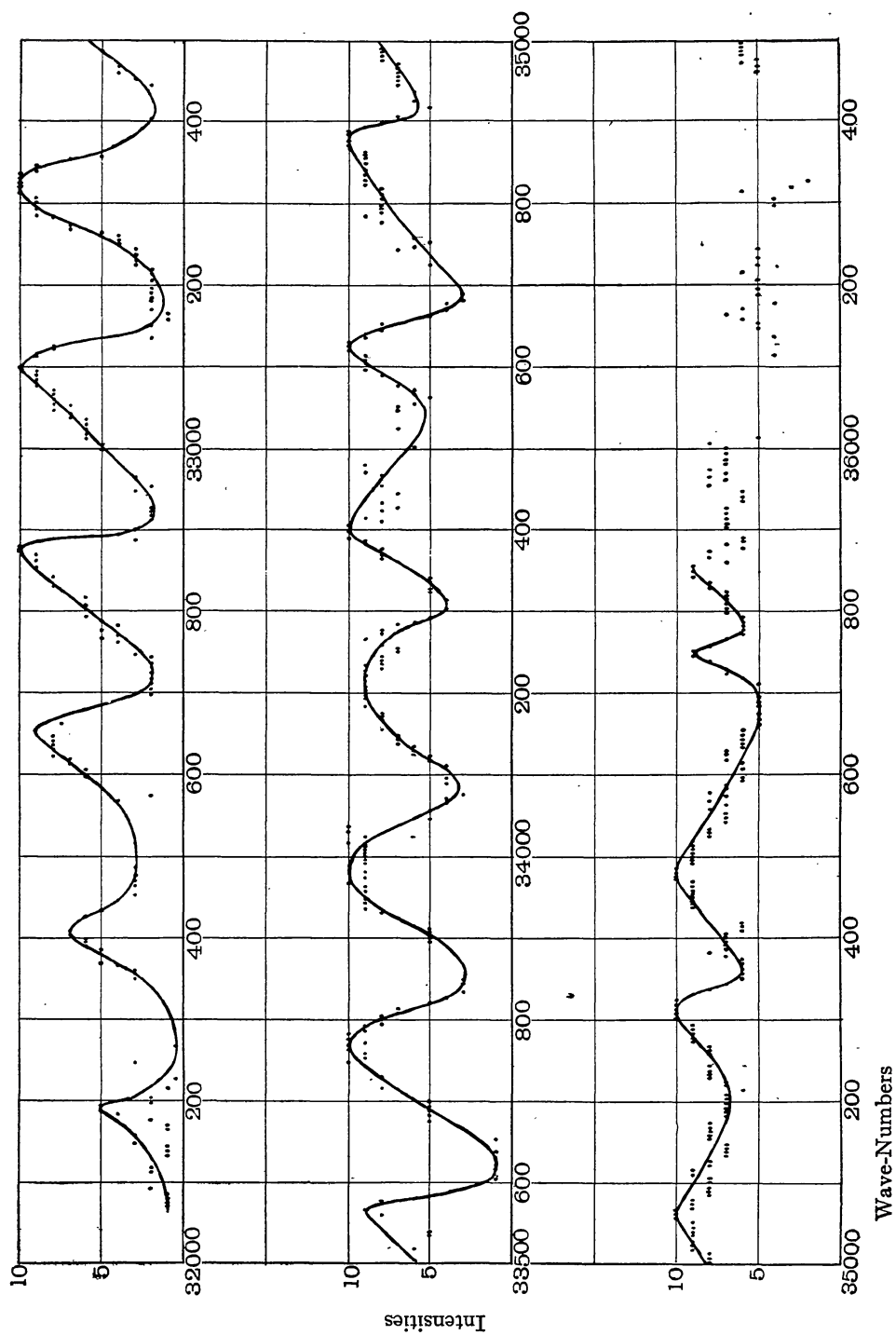


FIG. 1.—Curve of Wave-Numbers and Intensities of Absorption Lines

arithmetical progression; further, it was found that all these progressions, 44 in number, had approximately the same common difference, namely, 223. This equality of first differences is expressed by the simple equation:

$$N = a + bm \quad (1)$$

where

$N$  = wave-number

$a$  = constant

$b$  = the common difference

$m$  = the number of the term in its series,

= 1, 2, 3 . . . . .

It is to be noted that the spectrum of sulphur dioxide does not obey Deslandres' laws of equal *second* differences, between the lines of a band or between the heads of bands—laws which, as is well known, are expressed by a quadratic equation of the form

$$N = a + bm + cm^2,$$

where the first differences form arithmetical progressions. In the spectrum of sulphur dioxide the first differences are constant and the wave-numbers themselves form arithmetical progressions. Of the 586 lines in the region measured, only 47 do not appear in these 44 series; five of these 47 lines form a short series with the same mean common difference as the others; it is between series 43 and 44. In each series the greatest deviation of the common differences from their mean value is less than 1 per cent.

The 44 series of wave-numbers, with their first differences and intensities, are given in Table III; for convenience in reference, the wave-length of the line at the head of each column is inclosed in brackets above the column of differences. The wave-numbers which do not appear in this table are collected in Table IV, the five which form a short series being in the first column. In these tables  $N$  denotes the wave-number,  $D$  the first difference in wave-numbers,  $m$  the number of the term in the series, and  $I$  the intensity. Of the series found, that of lowest wave-numbers has been called the first; similarly for the terms in the series. Whether this series is really the first has not been determined; Plate IX shows that the spectrum extends into longer wave-lengths when the gas is at higher pressures,

but at these pressures measurable lines have not been obtained; hence it is undetermined whether or not the series extend into the region of longer wave-length. Thus the constant,  $a$ , in equation (1) has not been found. Apparently each series should have 23 terms, but none of the series is complete.

TABLE III

$m$	SERIES 44			SERIES 43			SERIES 42			
	I	N	D	I	N	D	I	N	D	
23										
22										
21				7	36680.8	(2726.22) 222.2				
20	5	36466	(2742.3) 223	5	36458.6					
19	5	36243.4					5	36231.6	(2760.02) 224.9	
18			2×225.3			3×223.9	8	36006.7	225.2	
17	6	35792.8		6	35786.9		6	35781.5	223.2	
16	8	35568.1	224.7	7	35563.3	223.6	8	35558.3		
15	7	35344.4	223.7	8	35338.3	225.0			2×224.0	
14	8	35121.4	223.0	9	35116	222	9	35110.4	224	
13	8	34896.2	225.2	9	34892.1	224	10	34886	224	
12			2×222.3	4	34669	223	5	34661	225	
11	8	34451.6		7	34443.6	225			2×224	
10	8	34229.6	222.0	9	34220.7	222.9	9	34212.7		
9	9	34004.5	225.1	9	33995.5	225.2	9	33990.8	221.9	
8	10	33781.3	223.2	9	33770.3	225.2	9	33767.2	223.6	
7	8	33558.7	222.6			2×223.7			2×223.8	
6	10	33335.4	223.3	10	33322.9		10	33319.7		
5				10	33099.6	223.3	9	33094.8	224.9	
4			3×224.7	10	32875.4	224.2	10	32872.8	222.0	
3	7	32661.4		9	32653.3	222.1			2×223.6	
2			2×223.3				6	32425.3	222.2	
1	1	32214.8					2	32203.1		
	Mean differences 223.7				223.8				223.8	

TABLE III—Continued

<i>m</i>	SERIES 41			SERIES 40			SERIES 39		
	I	N	D	I	N	D	I	N	D
23									
22	6	36896.6	(2710.28) 222.6						
21	7	36674.0	2 × 225.6						
20							6	36214.6	(2761.32)
19	5	36222.8	222.2						
18	7	36000.6	224.1	7	35993.9	(2778.25) 223.1			2 × 224.2
17	6	35776.5	223.5	6	35770.8		7	35766.3	224.6
16	7	35553.0	221.9	7	35546.7	221.6	7	35541.7	223.2
15	9	35331.1	225.6	10	35325.1	224.6	10	35318.5	225.1
14	8	35105.5	223.6	8	35100.5	225.5	8	35093.4	224.3
13	10	34881.9	2 × 225.5	10	34875.0	224.1	10	34869.1	225.2
12				8	34650.9	225	8	34643.9	222.9
11	8	34430.9	223.9	7	34426	223	8	34421.0	
10	9	34207.0	2 × 222.9	9	34202.6	221.7			
9				9	33980.9	224.5			
8	10	33761.2	222.8	9	33756.4	221.7			
7	5	33538.4	3 × 223.2	5	33534.7	223.6			9 × 223.6
6				10	33311.1	222.0			
5				9	33089.1	2 × 224.6			
4	9	32868.8	222.3						
3	8	32646.5	2 × 224.4	8	32640	2 × 224			
2							7	32408.3	
1	2	32197.7		5	32192.0				
	Mean differences 223.7			223.6			223.9		
	SERIES 38			SERIES 37			SERIES 36		
23									
22									
21									
20									
19							5	36194.8	(2768.80) 221.6
18	7	35979.8	(2779.34) 222.7				8	35973.2	222.3





TABLE III—Continued

m	SERIES 32			SERIES 31			SERIES 30		
	I	N	D	I	N	D	I	N	D
9	9	33948.5		9	33943.3		9	33936.8	221.8
8			2×222.6				8	33715.0	2×223
7	6	33503.2				3×223.4			
6			2×224.8	7	33273.1		7	33269	223
5	8	33053.5		7	33050.8	222.3	8	33045.8	
4	8	32830.0	223.5						2×224.4
3	6	32605	225			4×223.8	6	32597.1	
2	5	32383.6	221						
1	1	32162.0	221.6	3	32155.8				
Mean differences 223.0				223.0			222.9		
SERIES 29			SERIES 28			SERIES 27			
23									
22									
21									
20									
19	7	36163.2	(2765.24) 224.3	6	36156.6	(2765.75) 223.9	5	36151.2	(2766.16) 224.8
18	6	35938.9		6	35932.7	222.9	7	35926.4	
17			2×223.8	5	35709.8	223.6			2×223.0
16	9	35491.3	225.1	10	35486.2	224.1	10	35480.4	222.3
15	8	35266.2	222.5	8	35262.1	222.6	8	35258.1	223.4
14	9	35043.7	222.5	9	35039.5	222.9	9	35034.7	224.5
13	9	34821.2		8	34816.6		8	34810.2	221.0
12			2×222.5				8	34589.2	223.3
11	8	34376.3	221.4			3×222.9	8	34365.9	223.3
10	8	34154.9		7	34148.0	2×224.2	7	34142.6	
9									
8			3×222.2	5	33699.5	2×221.7			4×222.8
7	5	33488.2	223						
6	5	33265	224	4	33256.1	221.7	4	33251.3	222.3
5	7	33041.4	224.4	6	33034.4		6	33029.0	222.9

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TABLE III—Continued

<i>m</i>	SERIES 29			SERIES 28			SERIES 27		
	I	N	D	I	N	D	I	N	D
4	6	32817.0					6	32806.1	
3			2×224.6			3×223.2			2×223.4
2	5	32367.8		4	32364.7		3	32359.2	
			221.7			222.6			223.1
I	3	32146.1		I	32142.1		I	32136.1	
	Mean differences 223.2			223.0			223.1		
	SERIES 26			SERIES 25			SERIES 24		
	I	N	D	I	N	D	I	N	D
23									
22									
21							8	36584.2	(2733.42)
20									2×224.4
19	5	36146.5	(2766.52)				4	36135.4	
									222.6
18				7	35919.4	(2784.01)	7	35912.8	
						225.0			225.3
17			3×223.1	5	35694.4		5	35687.5	
						224.1			222.1
16	10	35477.2		9	35470.3		9	35465.4	
									222.6
15			2×224.6			2×223.8	8	35242.8	
									223.9
14	9	35028.1		9	35022.8		9	35018.9	
			223			224.7			225
13	8	34805		8	34798.1		8	34794	
						222.5			224
12			2×221	7	34575.6		6	34570	
11	8	34362.7				2×223.0			2×222
			223.8						
10	7	34138.9		6	34129.6		6	34125.9	
			223.9			223.0			223
9	6	33915.0		5	33906.6		5	33903	
			223.0						223
8	5	33692.0					5	33680.4	
			225.0						221.8
7	4	33467.0				3×222.8	4	33458.6	
			222.2						2×223.6
6	3	33244.8		3	33238.3				
			221.8			221.2			
5	6	33023.0		6	33017.1		6	33011.5	
						224.4			222.7
4				6	32792.7		5	32788.8	
						2×221.6			221.6
3			3×222.3				4	32567.2	
2	3	32356.0		3	32349.5				2×225.0
			225.1						
I	I	32130.9					2	32117.1	
	Mean differences 223.1			223.1			223.4		





ABSORPTION SPECTRUM OF SULPHUR DIOXIDE 329

TABLE III—Continued

m	SERIES 17			SERIES 16			SERIES 15			
	I	N	D	I	N	D	I	N	D	
4	3	32747		2	32743.6				$2 \times 222.5$	
3							3	32517.0		
2		$3 \times 223$			$3 \times 223$				$2 \times 223.5$	
I	I	32079		I	32074		I	32070		
	Mean differences 223.5				223.4				223.0	
	SERIES 14			SERIES 13			SERIES 12			
23										
22										
21	6	36524.9	(2737.86)							
20				4	36297.4	(2755.02)				
19			$3 \times 223.0$			$2 \times 224.4$				
18	9	35855.7		9	35848.7					
			223.5			220.9				
17	6	35632.2		7	35627.8		7	35622.9	(2807.18)	
			223.4			222.6			221.5	
16	6	35408.8		7	35405.2		7	35401.4		
			223.1			224.4				
15	7	35185.7		7	35180.8				$2 \times 224.2$	
			221.0			221.5				
14	7	34964.7		7	34959.3		7	34953.1		
			222.6							
13	7	34742.1								
12			$2 \times 225$			$3 \times 224.0$			$3 \times 223.1$	
11	5	34292		6	34287.3		7	34283.9		
			222			221.8				
10	4	34070.3		4	34065.5					
			221			222				
9	3	33849		3	33844				$3 \times 222.6$	
						223				
8			$2 \times 224$	I	33621.1		I	33616		
7	2	33402							$2 \times 223.1$	
			222							
6	2	33179.8				$3 \times 223$	2	33169.5		
									223	
5			$2 \times 222.0$	2	32952		3	32947		
						222			224	
4	2	32735.8		2	32729.9		2	32723		
3										
2										
I										
	Mean differences 222.9				223.0				223.1	
	SERIES 11			SERIES 10			SERIES 9			
23										
22										
21	6	36514.9	(2738.61)	8	36733.2	(2722.33)				
20										
19			$3 \times 224.5$			$4 \times 224.6$				



## ABSORPTION SPECTRUM OF SULPHUR DIOXIDE 331

TABLE III—Continued

<i>m</i>	SERIES 8			SERIES 7			SERIES 6		
	I	N	D	I	N	D	I	N	D
9	5	33820.4		7	33812.3		7	33807.9	
8									
7			$3 \times 223.4$			$4 \times 223$			$4 \times 223$
6	2	33150.1							
			224						
5	2	32926		2	32921		2	32916	
			222			224			
4	2	32704.0		2	32697				$2 \times 223$
3							3	32470.3	
									224
2							3	32246	
1									
	Mean differences 223.1			223.1			223.2		
<i>m</i>	SERIES 5			SERIES 4			SERIES 3		
	I	N	D	I	N	D	I	N	D
23									
22									
21				6	36480.7	(2741.18)	5	36474.4	(2741.65)
20									
19						$4 \times 224$			$3 \times 223.8$
18	7	35807.9	(2792.68)				7	35802.9	
			221.6						224.8
17	7	35586.3		7	35583		8	35578.1	
						222			222.4
16			$2 \times 222.2$	6	35361.2		6	35355.7	
						223.0			222.5
15	7	35142.0		7	35138.2		7	35133.2	
						220.0			
14				5	34916.0				$2 \times 222.0$
13			$4 \times 222.8$			$2 \times 223.4$	3	34689.3	
									224.1
12				9	34469.1		8	34465.2	
						224.6			225.1
11	7	34250.6		8	34244.5		8	34240.1	
									222.2
10			$2 \times 223.2$			$2 \times 222.2$	10	34017.9	
									222.6
9	8	33804.1		8	33800.1		8	33795.3	
									221.9
8			$2 \times 224$			$2 \times 224.1$	8	33573.4	
7	5	33356		7	33351.9				$2 \times 224$
			223						
6	2	33133					8	33125.4	
			222						225
5	2	32911					3	32900	
4			$2 \times 223$						
3	3	32464.3							
2									
1									
	Mean differences 222.9			223.5			223.4		

TABLE III—Continued

<i>m</i>	SERIES 2			SERIES I		
	I	N	D	I	N	D
23						
22						
21	6	36470	(2742.0)			
20						
19			3×224			
18	7	35799.1	224.9			
17	7	35574.2	224.0			
16	6	35350.2	223.2			
15	8	35127.0	222			
14	7	34905	2×222.5			
13				4	34676.7	(2883.79)
12	8	34459.5	223.4			2×221.9
11	8	34236.1	223.2	9	34233.0	224
10	9	34012.9		9	34009	223
9			2×223.0	9	33785.6	
8	9	33566.8	223			2×223.6
7	9	33344	223	9	33338.3	221.2
6	8	33120.7		9	33117.1	223.1
5				4	32894.0	
4			3×223			2×223.9
3	3	32452	225	4	32446.2	
2	$\frac{1}{2}$	32227				
1						
	Mean differences 223.3			223.1		

It is obvious from Table III that equality of the observed intensities is not rigidly held in the series; there is too great a probability of error between the observed and actual values to make strict conformity to such a condition needful.

TABLE IV

I	N	D	I	N	I	N	I	N	I	N
9	34000.0		7	36685.9	6	35644.4	9	34385	3	33450.8
		225.1								
10	33774.9		5	36656.4	10	35473.9	5	34336.5	4	33260.7
		2×223.0								
10	33328.8		5	36649.4	9	35455.0	9	34226.5	9	33112.8
		2×224.8								
10	32879.3		5	36643.1	6	35418.0	6	34134.8	7	33037.4
		2×222.8								
5	32433.7		8	36507	8	35382.8	5	34046	5	32999
			6	36312.0	9	35276.0	9	34024	3	32886
	Mean differ. 223.7		5	36206.0	8	35233.7	8	33930.2	8	32633
			5	36013	3	34680	5	33909.8	2	32573.1
			7	35985.3	9	34606.1	9	33791.8	3	32478
			7	35903.8	9	34597.1	5	33689		
			8	35864.9	9	34479.5	8	33577		

## ERRORS

1. *In wave-lengths.*—The wave-lengths were determined by measurements made on the lines on two plates, six measurements of one plate and four of the other. The difference between the mean values of the wave-length of any one line obtained from the two plates is in many cases less than 0.1, in the majority of cases less than 0.15, although in some cases this difference amounts to 0.2 Å. The following are examples of the mean values of wave-lengths obtained from the two plates:

Plate 26	Plate 28	Plate 26	Plate 28
2811.85	2811.91	2916.83	2916.82
2812.27	2812.28	2917.39	2917.44
2812.69	2812.72	2918.20	2918.41
2813.16	2813.23	2918.87	2919.01
2813.52	2813.68	2919.66	2919.66
2814.23	2814.19	2920.09	2920.28
2814.55	2814.58	2920.89	2920.88
2814.79	2814.90	2921.46	2921.45
2815.37	2815.33	2922.24	2922.17
2815.77	2815.82	2922.87	2922.91

2. *In wave-numbers.*—Let

$N$  = true wave-number,

$\lambda$  = true wave-length,

$\nu$  = error in  $N$ ,

$e$  = error in  $\lambda$ .

Then

$$\begin{aligned} N - \nu &= \frac{1 \times 10^8}{\lambda + e}, \\ &= N - \frac{e \times 10^8}{\lambda^2}. \end{aligned}$$

For the upper limit in the spectrum,  $\lambda = 3200$ , hence  $\nu = 10e$ ; for the lower limit  $\lambda = 2700$ , hence  $\nu = 13e$ ; thus an error of  $0.1 \text{ \AA}$  in  $\lambda$  corresponds to an error of 1 or 1.3 in  $N$ . Some of the lines, whose wave-lengths have been given to the second place of decimals and their wave-numbers to the first place, may not be correct to 1 in those places, but they have been left to the nearest calculated value there when the probable error in the mean value of the wave-length was only about 0.03. This was done because giving the wave-numbers to the units place only would have frequently doubled the error in the first differences. The close agreement with one another of the mean values of the common differences of the arithmetical progressions seems to justify this course in many cases. For lines with larger probable errors, wave-lengths are given only to the first place of decimals and wave-numbers to the units place.

3. *In intensity*.—The want of accuracy in estimation by eye of the relative intensities of lines is well recognized. The difficulty in such estimation increases greatly with the number of lines to be observed, which here amounts to nearly 600. Further, errors must be present in the estimated intensity of absorption of those lines, which occur very near a broad metallic line strong enough to be transmitted through the gas. For example, the intensity of wave-number 33538.4 would most probably be represented by a higher number if full allowance were made for the increased intensity of the background due to the breadth of the metallic line 2980.79. Fig. 1 shows the position of some of the metallic lines transmitted; the absence of absorption lines at some of these places suggests that they are hidden by the metallic lines. The plates show several metal lines broadened by the capacity required to produce the continuous spectrum.

#### SIMILAR REGULARITY IN OTHER SPECTRA

1. *In emission spectra*.—Equal first differences in wave-numbers have been found by: Ames<sup>1</sup> in zinc and cadmium between the

<sup>1</sup> *Philosophical Magazine* (5), 30, 33-48, 1890.

frequencies of the first and second and between the second and third lines of most of the triplets; Kayser and Runge<sup>1</sup> in tin, lead, arsenic, antimony, and bismuth; Rydberg in copper<sup>2</sup> and in the red spectrum of argon;<sup>3</sup> Kayser<sup>4</sup> in the elements of the platinum group; Snyder<sup>5</sup> in rhodium, in the lines measured by Kayser; Olmsted<sup>6</sup> in the oblique series of barium, strontium, and calcium; Messerschmitt<sup>7</sup> in the heads of those bands of selenium which lie in the ultra-violet region. In these spectra, with the exception of the last two named, the constant first difference is different for different groups of lines of the same element.

In contrast with the above spectra, Professor Wood<sup>8</sup> has found in the resonance spectrum of sodium vapor series of lines having equidistant wave-lengths.

2. *In absorption spectra.*—Friedrichs<sup>9</sup> found in the absorption spectrum of  $Mn_2Cl_7$ , two kinds of bands, arranged in groups, those of one kind strong, the other weak, the groups alternating with each other. A constant first difference appeared between the wave-numbers of the edges of the first bands of the strong groups; also between those of the weak groups, as follows:

STRONG GROUP		WEAK GROUP	
N	$\Delta N$	N	$\Delta N$
1896	76	1919	76
1972	76	1995	76
2048	76	2071	74
2124	77	2145	
2201	77		
2278			

<sup>1</sup> "Ueber die Spectren der Elemente," 7 Abschrift, *Abhandl. Berl. Akad.*, 1894.

<sup>2</sup> *Astrophysical Journal*, 6, 239-243, 1897.      <sup>3</sup> *Ibid.*, 6, 338-348, 1897.

<sup>4</sup> "Ueber die Bogenspectren der Elemente der Platingruppe," *Abhandl. Berl. Akad.*, 1897.

<sup>5</sup> *Astrophysical Journal*, 14, 179-180, 1901.

<sup>6</sup> *Zeitschrift für wissenschaftliche Photographie*, 4, 255-291, 293-333, 1906.

<sup>7</sup> *Ibid.*, 5, 249-278, 1907.      <sup>8</sup> *Astrophysical Journal*, 30, 339, 1909.

<sup>9</sup> *Zeitschrift für wissenschaftliche Photographie*, 3, 154-166, 1905.

Here the first differences are approximately the same for the two groups.

Another example of this structure in absorption spectra is in that of the vapor of paraxylene, found by Mies.<sup>1</sup> The approximately constant first differences are between the wave-numbers of the heads of bands, which are not resolved into lines; hence, as might be expected, there are comparatively large variations in the constants.

In an earlier work by Käbitz<sup>2</sup> on the spectrum of the vapor of  $\text{CrO}_2\text{Cl}_2$  this simple structure can be found. He found five series of *Absorptionstreifen* (broad lines) in this spectrum; his values of the wave-lengths with their first and second differences are quoted below in Table V. The writer has calculated their wave-numbers and placed them in columns parallel with those containing the wave-lengths. The first four columns are quoted from Käbitz' paper; for the fifth and sixth columns the present writer is responsible.  $n$  denotes the number of the line in the spectrum.

It is obvious from the fifth and sixth columns of this table that the *first* differences of the wave-numbers of these series are approximately equal; further, that this constant difference, namely 135, is approximately the same for all the series. Hence this spectrum does not obey Deslandres' third law.

TABLE V

SERIES I. PRINCIPAL SERIES					
$n$	$\lambda$	$D_1$	$D_2$	N	$\Delta N$
3	5846.5			17104	
8	5800.2	46.3	1.1	17241	137
13	5755.0	45.2	0.5	17376	135
18	5710.3	44.7	0.9	17512	136
23	5666.5	43.8	0.4	17648	136
28	5623.1	43.4	2.1	17784	136
33	5581.8	41.3		17915	131

Mean  $\Delta N = 135$

<sup>1</sup> *Zeitschrift für wissenschaftliche Photographie*, 7, 357-368, 1909.

<sup>2</sup> *Ueber die Absorptionsspectra der Chlorsäuren*, Dissertation, Bonn, 1904.

TABLE V—Continued

SERIES II. SUBORDINATE SERIES I						SERIES III. SUBORDINATE SERIES II					
<i>n</i>	$\lambda$	D <sub>1</sub>	D <sub>2</sub>	N	$\Delta N$	<i>n</i>	$\lambda$	D <sub>1</sub>	D <sub>2</sub>	N	$\Delta N$
4	5837.1			17132		5	5827.5			17160	
		45.3			134			46.1			137
9	5791.8		0.1	17266		10	5781.4		1.2	17297	
		45.2			136			44.9			135
14	5746.6		1.0	17402		15	5736.5		0.6	17432	
		44.2			135			44.3			136
19	5702.4		0.1	17537		20	5692.2		0.5	17568	
		44.1			136			43.8			136
24	5658.3		1.4	17673		25	5648.4		2.4?	17704	
		42.6			134			41.4			131
29	5615.8		1.3	17807		30	5607.0		0.6	17835	
		41.3			132			40.8			127
34	5574.4			17939		35	5567.2			17962	

Mean  $\Delta N = 135$

(Omitting the last) Mean  $\Delta N = 135$

SERIES IV. SUBORDINATE SERIES III						SERIES V. SUBORDINATE SERIES IV					
<i>n</i>	$\lambda$	D <sub>1</sub>	D <sub>2</sub>	N	$\Delta N$	<i>n</i>	$\lambda$	D <sub>1</sub>	D <sub>2</sub>	N	$\Delta N$
1	5865.9			17048		2	5855.3			17079	
		46.6			136			46.1			135
6	5819.3		0.4	17184		7	5809.2		0.8	17214	
		46.2			138			45.3			135
11	5773.1		1.3	17322		12	5763.9		0.9	17349	
		44.9			135			44.4			135
16	5728.2		0.5	17457		17	5719.5		0.7	17484	
		44.4			137			43.7			135
21	5683.8		0.9	17594		22	5675.8		0.9	17619	
		43.5			136			42.8			134
26	5640.3		0.6	17730		27	5633.0		0.8	17753	
		42.7			135			42.0			133
31	5597.6			17865		32	5591.0			17886	

Mean  $\Delta N = 136$

Mean  $\Delta N = 135$

CONCLUSION

The spectra of  $SO_2$  and  $CrO_2Cl_2$  exhibit a very simple and definite structure, which is built up of a number of series of lines characterized by equidistant frequencies, this equal distance having approximately the same value in every series; for  $SO_2$  it is 223, for  $CrO_2Cl_2$  it is 135. Thus the different members of the structure are simple in themselves,

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being expressed by arithmetical progressions, whose common difference is the difference in frequency. These members are united into a regular structure by the simple tie that the mean frequency difference of every series is approximately the same.

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