ART. XX.—*On the Oxygen Absorption Bands of the Solar Spectrum*; by O. C. LESTER.* (With Plates II, III and IV.)

THE present research was undertaken with the object of investigating as fully as possible the structure and extent of the oxygen absorption spectrum. This includes a study of the relations existing between the lines of a band and also between the several bands, taking into account those groups above α which do not seem to have been considered before. In order to do this satisfactorily it was necessary to have very accurate measurements of the wave lengths. The best determinations previously made are those of Rowland and Higgs, but neither gives all the lines even of the groups A, B, and α . Rowland's measurements are nearly complete for B, but he gives only a few for the other two groups. Higgs gives A and B and up to the ninth pair of α , and although he and Rowland agree remarkably well in general upon B, judging from the few lines in A which both have measured the agreement is not so good, there being much greater discrepancies than one would expect from the accuracy claimed for their measurements. Hence it seemed worth while to make new determinations of all, or nearly all, the lines previously measured, and in addition many new lines are given. It is hoped, therefore, that the present determination of the wave lengths, taking into account the best previous results, have both extended and unified the measurements on these bands and rendered them, on the whole, more accurate; thus doing for the absorption spectrum of oxygen what a similar work of M. Eisig† has done for the line spectrum.

Because of the precision which it is possible to attain in the measurement of this spectrum, a careful study of the relations subsisting between the lines and bands furnishes an excellent test of the so-called laws of Deslandres for band spectra. They are briefly as follows:

1. In a given band the intervals from one line to the following in any series, calculated in vibration numbers, are in arithmetical progression, i. e., the lines are connected by a relation of the form

$$\frac{1}{\lambda} = N = a + bn^2$$

* Abstract of a thesis presented to the Philosophical Faculty of Yale University, June, 1904, for the degree of Doctor of Philosophy. The paper will appear *in extenso* in the September number of the *Astrophysical Journal*.

† M. Eisig: *Das Linienspektrum des Sauerstoffs*, Wied. Ann., li, 1894.

where a and b are constants and n takes on all integral values from 0 to n .

2. When several series arise from the edge of a band they are similar in all respects, and all bands belonging to the same substance have the same number of series.

3. In a series of bands the vibration numbers of the edges form a series similar to that of the lines in a single band.

These laws are the most general in their application that have yet been announced. Deslandres tested them on many spectra, although he never published details showing the exactness of agreement. Kayser and Runge* have obtained a general confirmation upon bands of many substances, including those of N, C, CO, CN, and I, but the laws do not apply equally well to all cases and occasionally appear to degenerate into mere interpolation formulæ. The difficulties in the way of obtaining more exact expressions for the laws are in measuring the wave lengths of bands accurately enough to warrant taking into account small variations of the reciprocals, and, in the case of the third law, in finding a long enough series of bands capable of precise measurement. Most of the bands hitherto investigated are in the upper part of the spectrum, where a small error in the wave length causes a large error in the reciprocal.

Measurement of Wave Lengths.

In the measurements of Rowland and Higgs to which reference is made above, both use the same unit, viz. 10^{-7} mm., and their results appear to be equally accurate. For those lines in B and α which both have measured and for which the agreement is .01 of a unit or closer, the value adopted in the present work is the mean of the two. In case the disagreement is greater than one would attribute to errors of observation, the value adopted is the mean of my own final result and the one which it confirms, provided such agreement is decidedly stronger with one than with the other. In some cases the mean of all three measurements was taken. For the large majority of the lines in A and α the values given are the means of my own and Higgs' results alone. Those of α' and α'' have not been given before. Since .01 of a unit is about the limit of accuracy in general, it has been thought best to retain only two decimal places in the wave lengths except in the case of B, where many of the lines are taken as Higgs and Rowland give them. It may be added further that the third decimal place rarely affects even the seventh place of the reciprocal.

* Ueber die Spektren der Elemente: Abhandl. der Berl. Akad., 1888-92.

The measurements of the stronger lines were made as usual with a micrometer microscope. Some of the weak lines had to be strengthened by a fine mark placed on the back of the negative. Others were measured from Rowland's charts, care being taken to set on the center of density of the lines. This last method is better for weak lines, although even here a fine mark must sometimes be used, as any magnification by the micrometer causes some of them to melt into the background.

The group a' was first noted by Jewell.* In the "head" or first band of this group, many of the lines appear double and some foreign lines seem to be present. The line 5789.40, which is the "chief line" of this band corresponding to similar lines in A, B, and a , has been assumed double, as it is in all the other bands. The only indication of being double actually shown is its greater intensity and a certain flatness of the intensity curve characteristic of close doubles. The uniformity of the two series also calls for a close double at this place.

The approximate positions of many of the lines in the group called a'' were calculated from relations established between the other groups, the observed values differing by less than .2 of a unit from the calculated. The lines are all extremely weak. Some, though not all of them, appear on negatives taken in zero weather, which indicates that they are not water-vapor lines. The first band of the group begins as usual with a double line, possesses a chief line and a final pair in its proper position, as a glance at the groups as shown in Plate III will show. Probably not all the lines present can be seen. Many are so faint as to be visible only on the charts and then only when they are held in particular positions with respect to the light. Some of the lines are stronger on the corresponding chart of Rowland's first series, which is more intense than the second. No attempt has been made to measure many of the lines of this group closer than the nearest half-tenth, which is readily done by estimation. Blunders and mistakes in calculation for all groups except A have been practically eliminated by the use of verniers made to fit Rowland's charts, which, in spite of irregularities in the map scales, enabled any but small mistakes to be detected at once.

* The Absorption Spectrum of Oxygen; *Astron. and Astrophys.*, xii, 1893.

TABLE I.

Note.—Each band contains two series which go by pairs. Consequently to obtain a single series of a band alternate numbers must be taken.

A		B	
First band.	Second band.	First band.	Second band.
7594·00	7621·27	6867·458	6884·080
95·27	23·53	68·457	86·004
94·28	24·77	67·794	86·982
95·55*	27·30	68·780†	89·183
94·81	28·52	68·337	90·144
96·06	31·28	69·338	92·614
95·55	32·49	69·144	93·559
96·79	35·47	70·130	96·282
96·51	36·65	70·220	97·197
97·74	39·86	71·180	6900·196
97·70	41·01	71·528	01·116
98·90	44·46	72·489	04·363
99·14	45·59	73·078	05·263
7600·30	49·27	74·039	08·785
00·80	50·40	74·888	09·677
01·95	54·33	75·830	13·449
02·65	55·45	76·953	14·331
03·80	59·62	77·878	18·365
04·73	60·73	79·275	19·245
05·87	65·14	80·173	23·542
07·05	66·25	-----	24·416
08·20	70·89	-----	28·986
09·57	71·97	-----	29·839
10·72	76·86	-----	34·669
12·33	77·92	-----	35·518
13·45	83·06	-----	40·584
15·32	84·11	-----	41·430
16·41	89·47	-----	46·770
----	90·50	-----	47·580?
----	96·11	-----	-----
----	97·13	-----	-----
----	03·02	-----	-----
----	7704·02	-----	-----
----	10·16	-----	-----
----	11·16	-----	-----
----	17·60	-----	-----
----	18·55	-----	-----

* Higgs gives also 95·42 and 95·66; probably outside edges of this line.

† These lines taken from Higgs' measurements, and from the uniformity of the series preceding they appear a little large.

‡ This line apparently double.

§ These lines constitute the so-called "chief line." Components difficult to measure accurately.

α		α'	
First band.	Second band.	First band.	Second band.
6276·81	6287·94	5788·33	5796·30
77·66	89·60	(88·55)§	97·76
77·03	90·42	89·00 (double?)	98·43
77·86	92·35	88·75	5800·18
77·52	93·15	89·40 (chief line)	00·83
78·29*	95·36	89·40	02·87
78·29	96·34	(89·71)	03·51
79·07	98·64	90·07	05·84
79·31	99·41	90·32 (double?)	06·47
80·08	6302·18	90·97	09·10
80·61	02·95	91·49	09·72
81·37	06·00	(91·78)	12·64
82·16	06·75	92·15	13·25
82·93	10·06	92·96	16·46¶
84·00	10·81	93·60	17·07
84·75	14·40	----	20·58
----	15·14	----	21·16
----	19·02	----	24·94
----	19·75†	----	25·52
----	23·92	----	----
----	24·64	----	----
----	29·10	----	----
----	29·82	----	----
----	34·55	----	----
----	35·26‡	----	----
----	40·28	----	----
----	40·98	----	----
----	46·27	----	----
----	46·96	----	----
α''			
First band.	Second band.		
5377·20	5384·27		
77·32	85·45		
78·00	86·05		
78·38 (chief line)	87·50 (double?)		
79·45 (double?)	88·10**		
80·00	{ 89·85 }		
80·20 (double?)	{ 90·45 } ††		
80·85 “	92·55 (covered)		
81·40	93·10**		
81·97	95·55		
	96·10		

* Chief line and evidently a close double. Higgs gives also 78·19 and 78·38, apparently the outer edges.

† End of Higgs' measurements. ‡ This line hidden by adjacent heavy line.

§ Lines bracketed do not appear to fit the series. Perhaps foreign.

¶ Covered by heavy line.

¶ Hidden by heavy adjacent line.

** Stronger on old chart.

†† Hidden by a group of five heavier lines, none of which actually cover the positions but the shading renders them invisible.

Relations between Lines and Bands.

The terms "head" and "tail" or "train" used to designate the two parts of the A, B, and α groups cannot be taken in this case in the usual sense of these terms as applied to band spectra, and are really misnomers. The spectrum is composed of two series of entirely separate bands instead of a single series, the so-called "heads" forming the first and the "tails" the second. The first series has the appearance of being nearly all "head" and the second all "tail," but the apparent crowding and confusion in the case of the former is due to the distance between the first few pairs being less than their width. That the "head" and "tail" are really separate bands is apparent from the following considerations.

Both "head" and "tail" begin with pairs of the same width, which decrease in width with increasing wave length in the same manner.

No series in a "head" or "tail" is a continuation of a series in the other as it should be if they were parts of the same band. Also, the first and second differences between homologous lines in the "heads" and "tails" form entirely different series as do the ratios of the homologous lines. Further, while there are no lines in places calculated for the tail series extended upward, faint lines appear to be in the proper places for an extension of the head, just as if the first band, instead of fading out gradually as the second does, should drop very suddenly in intensity on approaching the region occupied by the second. That this is apparently what happens is indicated also by the fact that the last line of what is usually considered the last pair in the "head" of B is scarcely half the intensity of its mate and in α is less than half. Extending the series of the first bands of B and α we find the following agreement between observed and calculated values.

B		α	
Observed.	Calculated.	Observed.	Calculated.
6879.28 } *	----	6284.00 } *	----
80.17 } *	----	84.75 } *	----
81.80	81.85	86.09	86.11
82.72†	82.72	86.88	86.84
84.65	84.67	88.48	88.49
85.54	85.52	89.20	89.20
87.75	87.74	91.14 (covered)	91.14
88.60	88.57	----	91.83
91.05	91.06	----	----
91.87	91.87	----	----
94.67	94.63	----	----
95.50	95.42	----	----

* Last pair of strong lines.

† Hidden by heavy adjacent line.

Indications that the first A band is continued beyond the last strong pair are not lacking though they are not so strong. The other groups are too faint for corresponding lines to be observed in them.

The geometrical relations of both lines and bands are clearly seen in Plates III and IV.

In most spectra it is the vibration numbers which are subject to regular laws rather than the wave lengths, but in this case it makes little difference so far as Deslandres' first law is concerned, which is taken. The first law is but a rough approximation, as is shown by the following application to the second series of the second band of B. The constant b is calculated from the sixth line.

$\frac{1}{\lambda}$ observed.	$\frac{1}{\lambda}$ calculated.	Diff.
14526.27	14526.27	0.00
520.15	524.84	+ 4.69
513.49	520.53	+ 7.04
506.29	513.36	+ 7.07
14498.65	14503.33	+ 4.68
490.42	490.42	0.00
481.70	474.65	— 7.05
472.45	456.00	— 16.45
462.72	424.49	— 38.23
418.53	319.67	— 98.76
406.26	292.92	— 123.34

The accuracy of the measurements would allow a variation of only a few hundredths in the last column. The fact is, Deslandres' constant b is not really a constant, at least for this spectrum, as the following values of b , calculated for the different lines of the above series, show:

$b = -6.12$ when $n = 1$	$b = -1.098$ when $n = 7$
—3.195 “	—0.993 “
—2.22 “	—0.911 “
—1.726 “	—0.846 “
—1.434 “	—0.792 “
—1.238 when $n = 6$	—0.748 “
	—0.710 when $n = 13$

The variations of b are the same for all the bands, except that for the second band series the initial values are always larger than for the first. Also, the values of b for homologous lines of the same band series are nearly constant.

If the values of b for any series are plotted as ordinates and the values of n as abscissæ, curves are obtained which at once suggest a much better law.

The bn -curve for sec. series, sec. band, Group B.

The curve, in form, is very nearly an equilateral hyperbola. Assuming it to be such we have

$$bn = k = \text{const.}$$

This, however, is not quite true, but if a correction is made as follows,

$$bn - \frac{n}{c} = k$$

then k is almost exactly constant. Substituting this value of b in Deslandres' formula we have

$$N = a + kn + cn^2.$$

That is, the correction for Deslandres' law is of the first order in n instead of being as usual of a higher order; the constant k is very large compared with c . Both c and k are different for the different series but their variations are small.

The increased accuracy of the new formula is shown by its application to the same series of B calculated above by Deslandres' law. The differences only are given here corresponding to the third column above.

0.00	+0.01	$k = 5.86$
+0.00	−0.04	$c = .2611$
+0.02	−0.07	
+0.05	+0.01	
+0.00	−0.02	
+0.02	−0.05	
+0.01	−0.16	

The second differences of the new formula are constant as they are in that of Deslandres, and it is evident from the near approach to constancy observed in the second differences of both N and λ , that some law based on this property is the true one. That the lines follow some very definite arrangement is seen from the smoothness of the bn -curves and from the smallness of the differences between the observed and calculated values. It is quite probable that the proposed formula will be found to represent the line series of other band spectra more closely than the old. This I have not as yet investigated. Assuming the proposed law to be exact we have on the other hand a criterion of the accuracy of the measurements of the wave lengths. It is quite likely that if the series were longer the formula would need an additional term, possibly one depending on the wave length. This is a matter for further investigation. The formula may have some theoretical importance also, as the formulæ so far deduced theoretically have not contained the first power of n .

Deslandres' second and third laws are only approximate for this spectrum but a correction for them could not be obtained with certainty, owing, in the case of the third law, to the shortness of the band series.

The points of chief importance in the foregoing discussion may be summarized as follows:

1. The general accuracy of the determination of the wave lengths in the groups A, B, and α has been greatly increased and the series which compose them considerably extended.

2. The band α' has been measured and its relation to the other groups studied for the first time, and in addition a new band α'' has been observed and studied at $\lambda = 5377.2$.

3. The oxygen absorption spectrum has been shown to consist of two distinct series of bands instead of one, the series of bands occurring in pairs just as do the series of lines in a band.

4. Deslandres' first law has been shown to be entirely inadequate to represent the line series of the several bands and a modification is proposed which gives results agreeing with the observed values to about the limit of error of the measurements.

In conclusion I wish to express my thanks to Prof. A. W. Wright, whose kindly interest and criticism have been of great benefit throughout this investigation, and through whose aid the excellent photographs of the spectrum were obtained.

Sloane Physical Laboratory, Yale University.
May 1, 1904.

EXPLANATION OF PLATES II TO IV.

PLATE II.

- 1.—A group ; Kirchhoff. Prismatic spectrum.
- 2.—A " ; Thollon. " "
- 3.—A " ; Langley. Grating spectrum.
- 4.—A " ; Piazzì Smyth. " "
- 5.—A " ; Cornu. " "
- 6.—A " ; Drawn from photographs with large Rowland grating in Sloane Laboratory. The last three pairs added from measurements of wave lengths. Comparison was made with Higgs' photographs of A which are probably the best yet taken. The drawing shows all details except the "secondary series." The eighteenth pair is cut off.

PLATE III.

The groups as represented in Plate III are drawn from the measurements of the wave-lengths. Beginning with A, they are arranged in order, one above the other, with the first lines of the second bands forming a straight line. This pyramid-like grouping of the bands is especially effective in showing the symmetrical arrangement of the pairs from group to group and their decreasing width from A to α .

PLATE IV.

The distance between the lines marked A and B is 4^{cm} , representing the distance in wave lengths between these two bands. The other horizontal lines are drawn at distances proportional to their distances in wave lengths from A. Plotted in this way the corresponding lines of the several bands fall almost exactly in a straight line, this being especially true for those lines whose wave lengths are most accurately measured.