ART. X. — *Wave-lengths and Structural Relation of Certain Bands in the Spectrum of Nitrogen;* by E. E. LAWTON, Ph.D.

WHILE engaged upon a study of the spectrum of nitrogen, it became necessary to photograph in juxtaposition the solar spectrum and the spectrum given by the capillary portion of a nitrogen Plücker tube, which had been exhausted to about 1^{mm}. Upon investigating, it was found that so little has been done on this spectrum in recent years that most of the measurements of the wave-lengths of the lines in the spectrum are far inferior in precision to the measurements which can be made with the instruments now available.

The measurements of Ångström and Thalén,* Boisbaudran,† and Hasselberg,‡ expressed in Ångström units, give only one decimal place; in general, the error varies from 0·2 to 0·5 of that unit. Deslandres§ has published a table of wave-lengths of nearly the whole negative spectrum; but these results give only one decimal place. Ames‖ and Hermesdorf¶ have also studied the same spectrum. Ames, however, measured only the second line in each band, while Hermesdorf obtained the wave-lengths of six bands, particularly those of the band with its head at λ 3577. The other bands measured have their heads at λ 3805, 3755, 3710, 3536, and 3371. These measurements have been obtained with a strong dispersion, and the accuracy of measurement is given as 0·01 Ångström unit. Hermesdorf's accurate investigation of the wave-lengths of a part of the spectrum is the only one that the writer has been able to find in the literature that brings our knowledge of the wave-lengths apace with the present instruments. Hence, the object of the present work has been to extend, if possible, our knowledge in this direction.

My own results have been obtained from measurements made on photographs taken with a large concave Rowland grating, which is installed in Sloane Physical Laboratory. The grating has 20,000 lines per inch, and a radius of 21·5 ft. By means of an adjustable shutter the spectrum given by the capillary part of a Plücker tube, such as is ordinarily used in spectroscopic analysis, was placed side by side with the stand-

* Acta Soc. Upsala, iii, 1875.
† "Spectres Lumineux."
‡ British Association Reports, p. 188, 1886.
§ Comptes Rendus, ci, p. 1256, 1885; ibid., ciii, p. 375, 1886; Annales de Chem. et de Phys., xv, p. 5, 1888.
‖ Phil. Mag., p. 58, 1890.
¶ Annalen der Physik, xi, p. 161, 1903.

ard spectrum. The solar spectrum, with Rowland's values, was used as the standard, and the unknown wave-lengths were obtained by interpolation. The nitrogen tube had been exhausted to about 1^{mm}. Many photographs were obtained with exposures varying from forty-five to ninety minutes, the longer time always giving the best results. These photographs* show for this spectrum a complicated structure. The heads of bands lie toward the red, with the tails extending up the spectrum, and the lines of the bands are degraded on the side toward the head. Each band offers at the head an intense triplet. In the bands measured, the second and third lines of this triplet are clearly doubles, and it is quite probable that the head of the band which forms the first line of the triplet is a double also.

Considering a single band—near the head there is a confusion of lines showing no regularity of intensity; but as the lines become more and more remote from the head, the lines are seen to be grouped in series of threes, or triplets, and while the distance between the lines of a single triplet diminishes the distance between triplets increases. The lines of each triplet show the same intensity, which gradually diminishes with an increase of distance from the head until they finally disappear, or, as is sometimes the case, become hidden in the next band. The irregularity of intensity shown by the lines near the head has been pointed out by Deslandres,† using the band λ 3577, as due to several secondary series, if I may be permitted to call them such, which are quite distinct from those series of lines which form the triplets of the tail. To these secondary series belongs the strong triplet seen in the head of each band. In the same paper Deslandres considers that the third line of the triplets in the tail is a double, but I have seen no indications that this is so, and neither do Hermesdorf's‡ measurements indicate this to be the case.

The second group of this spectrum extends from λ 5000 to λ 3000 and is made up of five series of bands.§ All except the lower part of this group has been photographed during this investigation. The first attempt to secure a photograph of the lower part showed some faint lines at about λ 4600, but a later attempt proved unsuccessful, owing to the weakening of the tube. Eye observations, however, showed some strong lines in this lower region. Using the photographic method, some good plates of the region λ 4200 to λ 3000 have been

* It may be worthy of remark here, as a matter of interest, that there are no telluric lines in the solar spectrum corresponding to the lines of this nitrogen spectrum. Nothing more than what might be termed accidental coincidences were observed.

† Comptes Rendus, cxxxviii, p. 317, 1904.

‡ Loc. cit.

§ Comptes Rendus, ciii, p. 375, 1886.

obtained. At λ 4059 and λ 3998 there are two bands which present beautifully the phenomena of triplets. Just above there is a group of six bands which overlap each other in such a way as to entirely obliterate the triplets.

The wave-lengths of the bands beginning at λ 4059 and λ 3998 have been measured and the results are given below. The stronger dispersion has made it possible to measure nearly a hundred more lines in these two bands than did the early observers. The measurements have been made with the aid of a micrometer-microscope especially arranged for the purpose, and in each case measurements have been made by setting on the center of intensity of the lines. Each result given in the table is the mean of at least eight measurements. Taking $10^{-7\,\mathrm{mm}}$ as the unit, the precision of measurement should be at least equal to 0·01 of that unit, except in the case of the extreme triplets, which being rather faint, the setting is more uncertain. The measurements of the wave-lengths follow.

Wave-lengths of the bands beginning at 4059·458 and 3998·419.

4059·458	4053·790	4046·227
·207	·347	4045·781
·015	·107	·446
4058·895	4052·898	·350
·694	·730	·016
·511	·370†	4044·727
·403	·271†	·336
·084	4051·987	4043·873
4057·883	·657	·185
·576	·291	4042·927
·351	·059	·744
·119	4050·863	·399
4056·979	·482†	·208
·628	·268†	4041·853
·504	·179	·571
·266	4049·781	·200‡
·030	·167	4040·815
4055·831	4048·943	·509
·524	·442	4039·902
·359	4047·959	·189
·077	·597	4038·731
4054·639	·164	4037·780
·408*	4046·964	·447
·245	·679	4036·981
4053·896	·494	·281

* Very faint.
† A heavy double.
‡ Faint and difficult to measure.

4035·655	4025·869	4015·792
4034·938	·361	4013·991
·374	4024·004	·556
·065	4023·552	·199
4032·883	·072	4011·333
·326*	4021·613	4010·879
4031·771	·175	·534
4030·779	4020·704	4008·589
·236	4019·160	·151
4029·672	4018·730	4007·830
4026·580	·317	4005·774
·099	4016·641†	·394
4027·589	·195	4004·984
4026·357		

3998·419	3989·126	3978·229
·289	3988·978	3977·941
3997·946	·681	·557
·696	·587	·224
·591	·331	3976·774
·360	3987·839	·351
·138	·281	·072
3996·959	3986·993	3975·521
·829	·498	·251
·505	·043	3974·918
·048	3985·687	·563
3995·889	·282	·314
·608	·037	3973·680
·494	3984·802	3972·961
3994·617	·284	·378
·382	3983·884	3971·781
·151	·543	3970·938
3993·639	·418	·393
·372	·131	3969·821
·258	3982·831‡	3968·864
3992·912	·405	·338
·512	·001	3967·801
·180	3981·569	3966·693
3991·997	·274	·130
·540	3980·883§	3965·689
·335	·492	3964·474
·077	·285	3963·990
3990·907	3979·934	·487
·496	·643	3962·157
·376	·222	3961·681
·059	3978·904	·212
3989·802	·565	3959·792
·426	·397	·347

* This line hazy and setting uncertain.
† All the triplets above this were very faint.
‡ Very broad line and difficult to measure.
§ Very faint.

3958·870	3954·017	3949·259
3957·392	3952·254	3948·826
3956·932	3951·866	3946·972
·482	·457	·562
3954·892	3949·694	·173
·419		

To Deslandres* we owe most of our knowledge of the laws governing the bands in the nitrogen spectrum, and the lines in a band. These laws, three in number, are briefly as follows:

1. In a given band the interval 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,

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

where a and b are constants, and n is a series of positive integers.

2. When two or more 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 line in a single band.

With these laws as a basis, Deslandres† has, quite recently, investigated the band at λ 3577 in the second group of the negative spectrum. He finds that there are seven series of lines and all can be expressed by the formula

$$N = A\left(m + \frac{p}{q}\right)^2 + c$$

where A, c, p, q, are constants, and m a series of integers. The application of the formula to the wave numbers of a band is not given by Deslandres, hence the above measurements furnish an opportunity for the application of the formula. Taking the band beginning λ 3998, the formula has been applied to the triplets of the tail. The constants have been determined by the method of trial and error giving the following formulæ:

1st line of triplet.

$$N = 2501{\cdot}457 + 0{\cdot}0251257(m + 0{\cdot}85)^2$$

2d line of triplet.

$$N = 2502{\cdot}145 + 0{\cdot}025296(m + 0{\cdot}5)^2$$

3d line of triplet.

$$N = 2502{\cdot}786 + 0{\cdot}02490(m + 0{\cdot}5)^2$$

* Comptes Rendus, ciii, p. 375, 1886. Annales de Chemie et de Physique, xv, p. 5, 1888.

† Comptes Rendus, cxxxviii, p. 317, 1904.

The results as calculated by these formulæ are given in the following tables:

1st line of the triplet.

	Calculated $N = \frac{1}{\lambda}$	Observed $N = \frac{1}{\lambda}$	Difference
m = 15	2507·769	2507·623	+0·146
16	2508·591	2508·467	+ ·124
17	2509·462	2509·387	+ ·075
18	2510·384	2510·328	+ ·056
19	2511·357	2511·300	+ ·057
20	2512·380	2512·383	— ·003
21	2513·452	2513·469	— ·017
22	2514·575	2514·601	— ·026
23	2515·749	2515·776	— ·027
24	2516·972	2517·000	— ·028
25	2518·246	2518·297	— ·051
26	2519·571	2519·611	— ·040
27	2520·945	2520·992	— ·047
28	2522·370	2522·403	— ·033
29	2523·845	2523·878	— ·033
30	2525·460	2525·385	+ ·075
31	2526·945	2526·916	+ ·025
32	2528·571	2528·514	+ ·057
33	2530.247	2530·201	+ ·046
34	2531·973	2531·842	+ ·131
35	2533·749	2533·588	+ ·161

2d line of the triplet.

m = 15	2508·222	2508·155	+0·067
16	2509·032	·978	+ ·054
17	·892	2509·861	+ ·031
18	2510·702	2510·776	— ·074*
19	2511·763	2511·758	+ ·005
20	2512·776	2512·788	— ·012
21	2513·838	2513·863	— ·025
22	2514·958	2515·042	— ·084†
23	2516·115	2516·157	— ·042
24	2517·329	2817·384	— ·055
25	2518·594	2518·642	— ·048
26	2519·909	2519·947	— ·038
27	2521·275	2521·350	— ·075
28	2522·692	2522·710	— ·018
29	2524·159	2524·181	— ·022
30	2525·677	2525·669	+ ·008
31	2527·246	2527·211	+ ·035
32	2528 864	2528·817	+ ·047
33	2530·532	2530·450	+ ·082
34	2532·244	2532·120	+ ·124
35	2534·024	2533·851	+ ·173

* Broad line with the center of intensity uncertain.
† A second measurement verified this result.

3d line of the triplet.

	Calculated $N = \frac{1}{\lambda}$	Observed $N = \frac{1}{\lambda}$	Difference
$m = 14$	2508·021	2507·969	−0·052
15	·778	2508·754	+ ·024
16	2509·565	2509·535	+ ·030
17	2510·412	2510·407	+ ·005
18	2511·308	2511·300	+ ·008
19	2512·294	2512·252	+ ·042
20	2513·244	2513·255	— ·011
21	2514·296	2514·317	— ·021
22	2515·391	2515·394	— ·003
23	2516·537	2516·560	— ·023
24	2517·732	2517·763	— ·031
25	2518·977	2519·006	— ·036
26	2520·272	2520·287	— ·015
27	2521·617	2521·631	— ·014
28	2523·011	2523·030	— ·019
29	2524·455	2524·480	— ·025
30	2525·949	2525·973	— ·024
31	2527·493	2527·498	— ·005
32	2529·083	2529·073	+ ·010
33	2530·730	2530·713	+ ·017
34	2532·423	2532·398	+ ·025
35	2534·160	2534·101	+ ·059

It is seen from these results that the formula applies fairly well to the third line of the triplet, but the agreement between the calculated and observed values is not so good in the case of the other two lines. Another thing to be noticed is that values of N for small values of *m* do not exist. The same result was obtained by the writer when Deslandres'* formula was applied to the measurements of Hermesdorf. If the residuals are plotted, they show in each case that the curve approximates a parabolic form. Considering the complex structure of the nitrogen spectrum, the agreement is as close as could be anticipated, and it is evident that it will require a more complicated formula, than has as yet been proposed, in order that the residuals may be brought within the limits of observation.

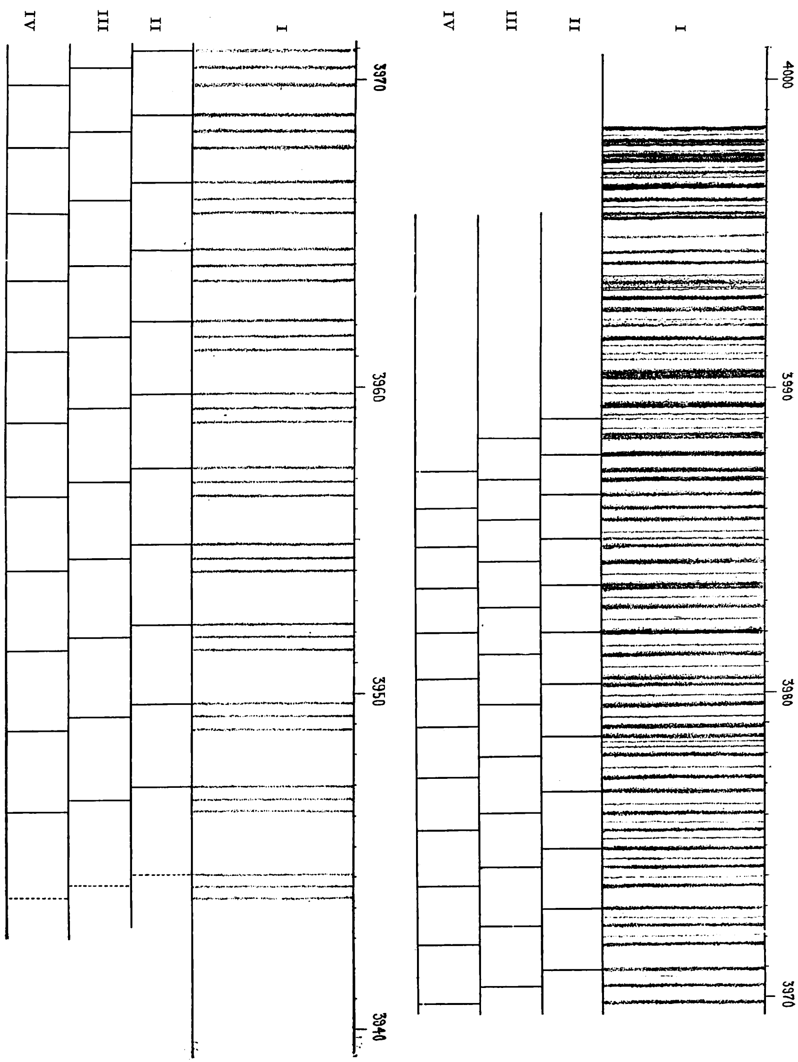
The points of chief interest which have been brought out by the foregoing are:

1. The wave-lengths of the lines of the bands beginning λ 4059 and λ 3998 have been measured, nearly half of them for the first time; and all the lines have been measured with a degree of precision hitherto not attained for this portion of the spectrum.

2. Application has been made of Deslandres' formula to the band λ 3998, and the constants determined giving as close an agreement between the calculated and the observed values as can be expected, considering the complex nature of the spectrum.

* Loc. cit.

Accompanying this article is an enlarged drawing of the band λ 3998. The drawing is made to scale; and the intensity of the different lines indicated in the drawing. (I) is the band itself (last triplet estimated, too faint for measurement). (II), (III) and (IV) show the triplets resolved into series.



In conclusion, it is a pleasure to acknowledge my indebtedness to Professor Arthur W. Wright, who obtained the excellent photographs used in this investigation, and whose kind criticisms and advice were continually of great assistance.