

THE INFRA-RED RADIATION OF NITROGEN

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ABSTRACT

Extension of the first positive group of nitrogen bands. An investigation of the infra-red portion of the first positive group of nitrogen bands by thermocouple and prism has extended that group to the region of 1.5μ . The broad radiation maxima corresponding to the 0, +1, and +2 sequences have been broken up into individual bands. Their observed maxima occur at the positions calculated from the known vibration levels of this group. For higher accuracy the region from 7500 to 10500A was photographed under a dispersion of 9A per mm with neocyanin plates. The bands were recorded as far as 10500, the beginning of the 0 sequence. The measurements of the heads and principal lines within this range are given in tables. From these results values for the bands of the 0 sequence are found, and those of the -1 and -2 sequences are improved.

Reassignment of vibration numbers. The new data point very definitely to a modification of the assignment of vibration quantum numbers as previously made by Birge, in that the lowest final level should be dropped, and the other vibration quantum numbers should be diminished by one. The evidence pointing to this as the more probable assignment is discussed.

Oxygen triplet $\lambda 9265$. Incidentally, the hitherto unresolved O triplet at 9265A appeared clearly resolved on these plates. The wave-lengths were measured as: 9265.67, 9262.61, and 9260.31.

INTRODUCTION

THE considerable progress made in recent years towards unravelling the very complex spectrum of nitrogen has made the further extension of that spectrum beyond the region of the visible very desirable. Such an extension on the side of the infra-red is particularly inviting because the beautiful regularity of the bands at the red limit of the visible might be expected to continue into the adjacent region. These bands, from the green through the yellow and red, belong to the first positive group of nitrogen, now universally ascribed to the neutral N_2 molecule. The visible spectrum of this group has been adequately investigated, particularly by Deslandres,¹ Von der Helm,² and under high dispersion by Birge.³ The last named also gives the measurements of the most conspicuous lines or groups of lines between $\lambda 6800$ and $\lambda 7650$ as obtained by a Hilger constant deviation spectroscope. Croze,⁴ using a prism spectrograph of small dispersion detected ten other bands and measured their heads.

Turning now to radiometric methods, Pfund⁵ got the energy curve of the first positive group from $.59$ to 1.2μ . It showed the most marked maxi-

¹ Deslandres, *Comptes rendus*, **134**, 747 (1902).

² Von der Helm, *Zeits. f. Wiss. Phot.* **8**, 405 (1910).

³ Birge, *Astrophys. Jour.* **39**, 50 (1914).

⁴ Croze, *Ann. d. Physique* **1**, 97 (1914).

⁵ Pfund, *Jour. Opt. Soc. Amer.* **9**, 193 (1924).

imum of the entire system at $.90\mu$ and two decided maxima beyond at 1.06 and 1.20μ respectively. The various sequences of the group could not be analyzed into individual bands with his apparatus. Yet from a theoretical standpoint the individual bands are of primary interest. Hence it was thought worth while to refine methods of investigation for the purpose of getting as much as possible of the detailed structure of these higher sequences of the group.

I. THERMOCOUPLE METHOD

Apparatus. A powerful source was a primary requisite. Hence the discharge tube was made of generous proportions. It was of the usual type for this kind of work, shaped like the Greek letter Π , from the central section of which (50 cm in length) the light was taken end-on. It was made of Pyrex, was 1.5 m in over-all length, of 18 mm bore, and supplied with cylindrical iron electrodes 15 cm long and of 2 cm diameter.

Nitrogen, obtained by bubbling air through a solution of pyrogallie acid to remove the oxygen, was fed into the tube continuously through a fine capillary, its supply being so adjusted with the exhaustion as to give the greatest brilliancy of discharge. A 5 KVA transformer applied about 2000 volts to the tube, and the current through the tube when making a run was about 0.7 ampere.

An auto-collimating prism spectrometer was built up. The arrangement will be clear from Fig. 1. The light entering the slit S_1 placed at the focus of

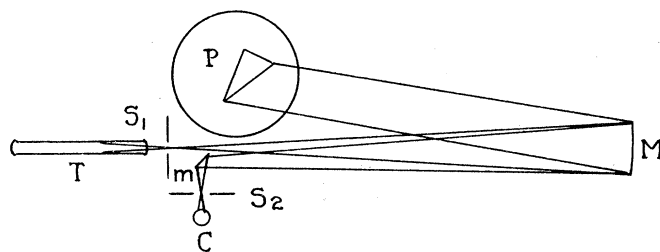


Fig. 1. Diagram of apparatus.

the concave mirror M was reflected as a parallel beam to the 30° reflecting glass prism P . Here, after refraction and reflection, it returned to the mirror M , thence, after a further reflection at m , was focused on the second slit S_2 and fell upon the thermocouple C placed immediately behind it. The dispersion of this system varied from about 140\AA per mm in the region of 7000\AA , to 450\AA per mm at $15,000\text{\AA}$. The mirror was of 10 cm aperture and 90 cm focal length. The prism had a 10 by 10 cm reflecting surface, and was mounted on a spectrometer table of very delicate adjustment, the turning of the table being read on a graduated scale by an optical system 250 cm long. The entire spectrometer system,—slits, prism table, mirrors and thermocouple,—was mounted on a single I -beam.

The detector was a three-junction compensating vacuum thermopile kindly made for me by Professor Pfund.⁶ Preliminary trials indicated the

⁶ Pfund, Phys. Zeits. 13, 870 (1912).

absolute necessity of shielding it from all stray radiation, air currents, minute changes of temperature, etc. Hence great pains were taken to house it properly. A double housing of good insulating material was provided, and every possibility of stray radiation on the second slit was guarded against. Still further asbestos shields protected the whole system from the heat of the discharge tube.

The galvanometer was a high sensitivity Leeds and Northrup instrument giving a 19 mm deflection per microvolt at 1 m distance, and with a period of about 12 seconds. It was operated at a scale distance of about 3.5 m. The leads connecting it with the thermopile were shielded from magnetic disturbances by being run through metal conduits, and the galvanometer was

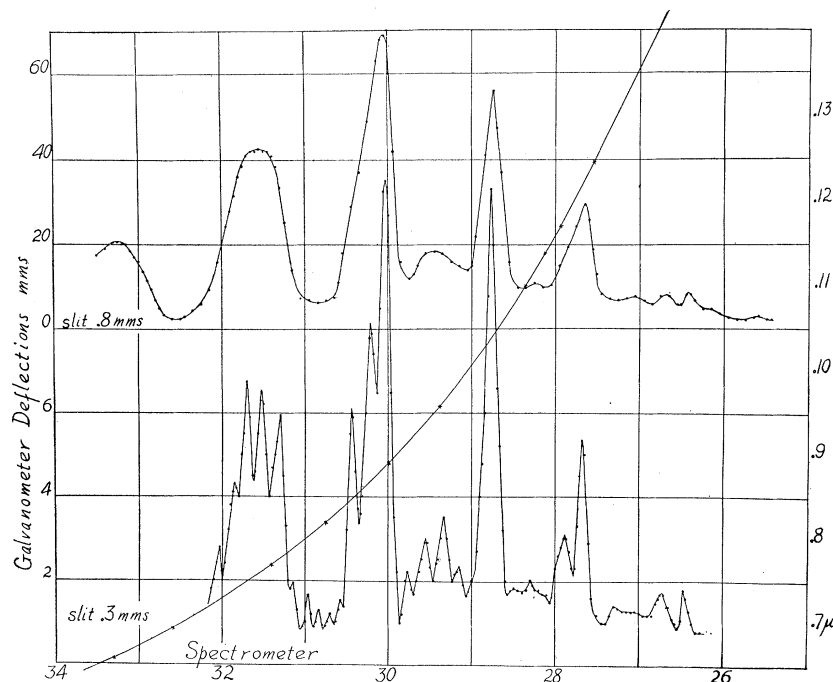


Fig. 2. Radiation curves of the first positive group of nitrogen.

protected as much as possible by thorough insulation from even gradual changes in temperature. The entire arrangement gave a combination of sensitivity and stability that was almost ideal.

In making a set of readings the discharge was run intermittently, each discharge lasting 15 secs. which was ample time to bring the galvanometer to its full deflection. This enabled the tube to be run at current densities which if steady would have caused the glass to soften. After each run the spectrometer table scale was calibrated anew from the strong lines of Na and K in this region. Light from an arc containing these substances was focused on the slit directly through the discharge tube.

Results. A general survey of the field with wide slits (0.8 mm) gave the upper curve of Fig. 2, which, except for the small maxima on the right and

the one at $.95\mu$, is very like the curve obtained by Pfund. Narrowing the slits to 0.3 mm brought out the band structure of these general maxima as shown in the lower curve of Fig. 2. Of the larger maxima of the preliminary curve only that at 1.04μ remains unresolved. This could not be made to show structure with the use of the prism. The maximum at 1.20μ could be broken up only into two minor ones at 1.183 and 1.222μ respectively. The last group of bands recorded by Croze is seen to consist of three intensely strong bands beginning at 0.89μ followed by several very weak ones. The next group or sequence comprises one band at 1.042μ of as great intensity as any of the spectrum, and somewhat separated from four weak bands that follow. Of the two following sequences only two or three bands could be located with certainty.

To determine if possible the more detailed structure of these higher maxima a plane grating of 15,000 lines per inch was substituted for the prism.

TABLE I
Radiation maxima for higher sequences of first positive group.

Seq. $n' \rightarrow n''$ Δn	Calculated Maxima (μ)	Prism				Structure by Grating	Int.	Remarks
		Princ. Max.	Int.	Minor Max.	Int.			
-2	5→3 4→2 3→1 2→0	0.736 .747 .761 .775	7 10 10 9					Partly due to O
-1	7→6 6→5 (5→4) 4→3 3→2 2→1 1→0			0.787 .802 .811 .822 .833	2 3 3 4 3			Argon N series lines Partly due to O
0	5→5 4→4 3→3 2→2 1→1 0→0	.9146 .9375 .9617 .9873 1.0143 1.0429		0.917 .939 .963 .988	3 5 5 2			
			1.042	16			{ 1.035 3 1.041 5 1.043 5 1.046 3	
+1	3→4 2→3 1→2 0→1	1.1043 1.1418 1.1820 1.2253		1.108 ?	2			Oxygen
			1.183	4			{ 1.174 1 1.178 1 1.182 1 1.187 1	
			1.222	7			{ 1.210 1 1.218 1 1.222 2 1.229 2	
+2	1→3 0→2	1.4107 1.4789		1.41 1.47	2 2			

Since this gave a dispersion of less than 20A per mm the slit could now be widened to 1 mm. This broke each of the unresolved maxima of the lower curve of Fig. 2, at 1.042, 1.183 and 1.222 μ , into four peaks as shown in the column "Structure" in Table I. Since the spectrum was normal the second order Balmer lines could be conveniently used for calibration.

Since under this high dispersion the galvanometer readings were hardly sufficient to be accurately read except in the regions of maxima, a light-sensitive thalofide cell was tried in the hope of its being a more sensitive detector. It was operated on a battery circuit of 80 volts, the dark deflection being balanced out in the galvanometer by a potentiometer method. Since the cell shows fatigue and gradual recovery, readings were taken at regular intervals of 45 secs. A high resistance short period galvanometer was substituted for this part of the work. The region of greatest sensitivity for the thalofide cell is from 0.9 to 1.2 μ . While the deflections in this region were greater than with the thermocouple, the stability was less; drift due to slow changes in the resistance of the cell was almost unavoidable. The results, however, checked the previous work unmistakably.

The energy maxima for the various bands as averaged from the results of the several runs are given in Table I. The possible error is 0.002 μ , and for the last two sequences even greater. The values under "Calculated Maxima" are those deduced by Birge⁷ from his analysis of the vibration levels for this group, except that $\frac{1}{4}$ the wave-number interval between successive first heads was added to obtain the approximate position of the maximum intensity of the band. The initial and final vibration quantum numbers, n' and n'' , used for band designation differ slightly throughout from those given by Birge, and will be justified in Part III. The oxygen lines are quite pronounced in the spectrum. They were detected as sharp narrow peaks with the grating and account for the shift of the centre of gravity of the .850 and .772 bands.

II. PHOTOGRAPHIC METHOD

The accuracy of the photographic method is so far superior to that of the thermopile, that it is desirable for purposes of analysis to have photographic results as far out as possible. The intensity of some of the bands of these higher sequences assured good photographic results even under fairly high dispersion. The region, therefore, from 7500 to 10,500A was investigated by this method.

An auto-collimating plane grating spectrograph previously described⁸ was used. It gave a dispersion of 9A per mm in the first order. Tube and excitation were as described in Part I, except that for continuous running the current through the tube was reduced to about 0.5 amperes. Also greater purity of the nitrogen was obtained by bubbling the air through a mixture of KOH and pyrogallol and then removing the water vapor by tubes of P₂O₅. Though this did not prevent the strongest O lines from registering, it did eliminate their over-exposure and halation otherwise present.

⁷ Birge, private communication. Equations of n'' and n' functions were later published in Birge and Spomer, Phys. Rev. **28**, 259 (1926), Eqs. (8) and (9).

⁸ Poetker, Phys. Rev. **30**, 418 (1927).

Neocyanin plates were used hypersensitized by an ammonia bath.⁸ Exposures averaged 15 hours for the range from 7500 to 9000A, and a full day for the range beyond. The slit widths used were about 0.02 mm and 0.1 mm respectively.

Results. Fig. 3 shows one of the plates for the lower range. Comparison with the radiation curve of Fig. 1 brings out the beautiful correspondence with the results obtained by thermocouple. The sensitivity of the neocyanin plates is falling off rapidly at 8800A which accounts for the apparently diminished intensity of the band beginning at 8912A. Though many of the lines are still incompletely resolved, a single band in this region shows on these plates about 125 lines. If more closely examined by superposition, the first three bands of this complex, at 8912, 8722, and 8542A, will be found to be very similar in detailed structure, and with well-defined heads, as in the sequences of lower wave-length. Distinctive heads or close similarity of structure can hardly be recognized in the next two bands, though this improves again in the ones that follow. The stronger lines that interrupt the regularity of the bands at various places include the strong oxygen doublet and triplet at 8446 and 7775A, the nitrogen series lines (especially those of the 'P⁴P' group in the vicinity of 8200A), and finally about eight fairly intense argon lines.

The heads of the bands and the more intense lines were accordingly measured on my plates. In general, this could be done for the lower range to within 0.04 or 0.05A, except perhaps where several lines were fused into one. The method followed was that adopted in previous work on the hydrogen infra-red.⁸

The wave-lengths and wave-numbers of about 125 of these lines are given in Table II. In many cases the line given is the first member of a close doublet or triplet. The lines known as not belonging to the molecular spectrum have been omitted for the sake of brevity. The intensities are only visual estimates, and allowance must be made in the last two bands for the diminished sensitivity of the plates.

I have arranged in Table III what seems to be the series of first heads, and possibly of the second and fourth, for this sequence. Similar first differences are found to exist between several other prominent lines in the first three bands and again in the last two (at 8047 and 7896A), but they cannot be traced across the intervening two with equal certainty. This might be interpreted as indicating that all these bands do not belong to the same sequence, but are partly fragmentary traces perhaps of an entirely different system; still on the other hand, the general regularity of all the other bands in the whole region makes this alternative unlikely.

For the following sequence, from 9000 to 10,500A, it is much harder to get satisfactory results. Beyond 8940A, as was evident from the thermocouple investigation, the spectrum is quite weak. This coupled with the greatly reduced sensitivity of the neocyanin makes the plates under high dispersion too weak for reproduction. The bands appear to be equally com-

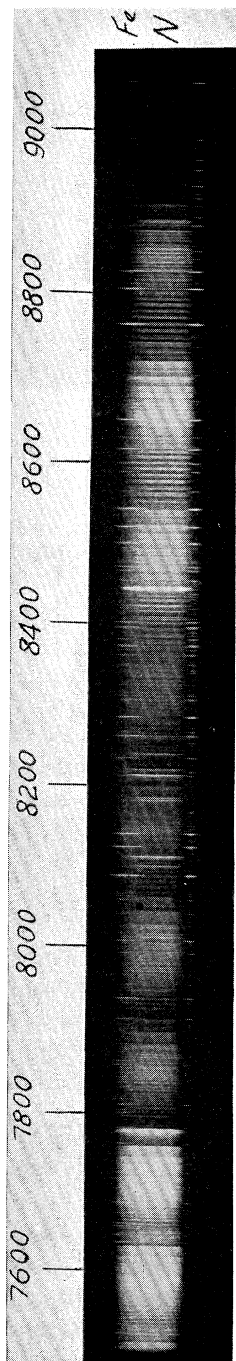


Fig. 3. Infra-red portion of first positive group of nitrogen.

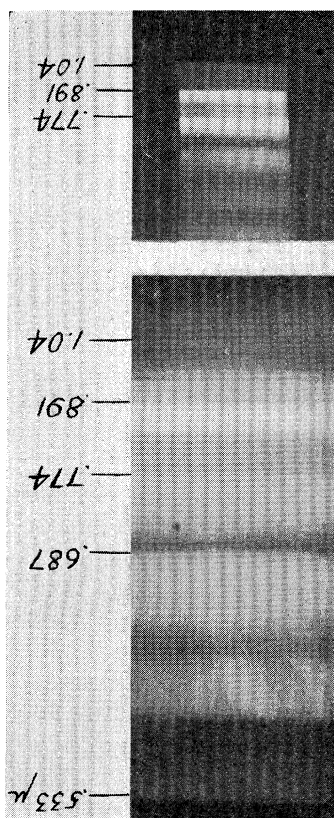


Fig. 4. First positive group of N showing new sequence extending from 10500A to 9000A. (Mag. 4x).

Fig. 5. Same under lower dispersion. (Mag. 6x).

TABLE II

Wave-lengths and wave-numbers of principal infra-red lines of nitrogen spectrum. In the second column the numbers are visual estimates of the intensities, while the letters denote the character of the lines; b, broad, perhaps multiple; h, hazy, diffuse; v, shades towards violet; r, shades towards red.

λ (I. A. air)	Int.	ν (vac.)	λ (I. A. air)	Int.	ν (vac.)	λ (I. A. air)	Int.	ν (vac.)	λ (I. A. air)	Int.	ν (vac.)
8936.60	2	11186.87	8504.82	2	11754.81	8137.10	2	12286.02	7828.07	3	12771.03
11.57	3r	11218.29	00.59	2	60.66				24.27	3	77.24
10.68	3	19.41	8496.88	2	65.79	30.85	2b	95.46	20.50	2	83.39
8892.08	3	42.88				13.13	2h	12322.31	02.39	2	12813.07
91.04	3	44.19	88.11	3	77.95	8097.07	2	46.76	7792.04	2	30.08
			68.15	3v	11805.72	78.84	2	74.62			
79.27	3h, r	59.10	62.12	2	14.13	64.47	2	96.67	7769.44	2	12867.40
72.31	2	67.93	11.18	2	85.68				53.05	3	94.61
71.17	3	69.38	10.29	3	86.93	47.26	2b	12423.18	39.56	3	12917.08
67.82	3	73.64				32.55	2	45.93	30.22	4	32.72
62.53	3	80.37	03.96	2b	95.88	30.23	2	49.52	18.55	3	52.24
			8397.10	2	11905.61	29.07	2	51.32			
58.75	2	85.18	86.31	2	20.92	19.38	2	66.37	17.59	3	53.85
52.74	4	11292.84	79.94	2	29.99				15.48	3	57.40
31.38	4	11320.15	74.70	2	37.45	8007.63	2	12484.66	02.44	3	79.33
8792.30	2	70.47				7999.92	2	96.70	7677.72	3	13021.12
75.35	4v	92.43	69.02	1b	45.55	89.58	2v	12512.86	76.85	3	22.59
			63.14	3b	53.95	82.13	2	24.54			
44.95	4b	11432.04	51.45	2	70.68	76.51	2	33.37	69.68	3	34.77
22.28	3	61.75	41.48	1	84.99				64.05	3	44.35
03.31	3	86.73	32.87	2	97.37	72.17	2	40.19	60.80	3b	49.88
8691.33	4	11502.56				68.31	2	46.13	54.52	3	60.59
75.46	3	23.60	8326.16	1	12007.04	59.37	3b	60.36	44.19	3	78.24
			8299.06	2h	46.25	39.20	2	92.27			
66.40	3	35.65	84.51	1	67.41	12.17	1	12635.29	7638.57	2	13087.86
60.81	3h	43.10	74.80	1	81.57				26.13	3h, r	13109.21
54.55	3b	51.45	05.59	1	12183.47	11.27	2	36.72	13.00	3	31.82
45.48	3v	63.56				7896.28	2	60.71	03.96	3	47.43
39.45	3v	71.64	04.62	1	84.91	81.93	2	83.76	7592.97	3	66.46
			8187.38	2	12210.57	79.72	2	87.32			
8607.84	4v	11614.13	82.14	1	18.39	65.36	2	12710.48	89.91	2	71.77
8595.58	3	30.70	76.36	2	27.02				72.27	3	13202.45
78.47	3	53.89	72.78	2	32.38	58.07	3b	22.28	53.31	3	35.59
63.48	3	74.29				55.76	1	26.02	36.90	3	64.41
41.73	2	11704.02	63.65	1	46.06	50.76	2	34.12	35.90	3	66.17
			58.43	2	53.90	40.85	2	50.21			
23.15	2	29.53	57.63	2	55.10	33.66	3	61.92	31.06	3	74.69
11.64	3	45.39	48.21	2b	69.26						

plex, so that with the widening of the slit the individual lines are somewhat run together. In the band at 1.04μ about 30 lines or groups of lines could be distinguished and measured. The most noticeable feature about this part of the spectrum is that the characteristic heads of great intensity seem to have given way to a more uniform and gradual distribution. As a result the banded structure is almost lost under high dispersion, and under low, the accuracy of measurement is considerably reduced.

Some small spectrograms were taken with a small constant deviation Hilger spectroscope from the other end of the central portion of the discharge tube. Fig. 4 is an enlargement of a typical plate. It reveals the 1.04μ band quite clearly and brings out very well the even banded structure of the region just beyond the 8900A maximum. Filters cut out the spectrum below 8500A in this plate except for a one minute exposure.

Fig. 5 is an enlargement of the spectrum obtained with a still more powerful prism spectrograph. The exposure is only 8 minutes, but this was repeatedly sufficient to register these bands between 9000 and 10,500A, though the plates are of very low sensitivity in this region.

I have used the small Hilger spectrograms to get the approximate positions of the heads and the maxima of the bands for this sequence (Table IV). From the results obtained with the same instrument in hydrogen an

TABLE III
Series of first, second and fourth heads of -1 sequence.

$n' \rightarrow n''$	$\lambda(\text{air})$ I. A.	Int.	ν (vacuo)	First Difference	Second Difference
7→6	7896.28	2	12660.71		
6→5	8047.26	2	12423.18	237.53	.74
5→4	8204.62	1	12184.91	238.27	1.09
4→3	8369.02	1	11945.55	239.36	2.17
3→2	8541.73	2	11704.02	241.53	1.74
2→1	8722.28	3	11461.75	242.27	1.19
1→0	8911.57	3	11218.29	243.46	
7→6	7879.72	2	12687.32		
6→5	8030.23	2	12449.52	237.80	1.15
5→4	8187.38	2	12210.57	238.95	.94
4→3	8351.45	2	11970.68	239.89	1.26
3→2	8523.15	2	11629.53	241.15	1.65
2→1	8703.31*	3	11486.73	242.80	1.05
1→0	8892.08	3	11242.88	243.85	
7→6	7858.07	3	12722.28		
6→5	8007.63	2	12484.66	237.62	.98
5→4	8163.65	1	12246.06	238.60	.42
4→3	8326.16	1	12007.04	239.02	2.23
3→2	8496.88	2	11765.79	241.25	.94
2→1	8675.46	3	11523.60	242.19	1.04
1→0	8862.53	3	11280.37	243.23	

* Coincident with a N series line but more intense than such series line should be.

TABLE IV
Approximate positions of maxima and heads of 0 sequence.

$n' \rightarrow n''$	$\lambda(\text{air})$ I. A.	Maxima $\nu(\text{vac.})$	First Diff.	$\lambda(\text{air})$ I. A.	Heads $\nu(\text{vac.})$	First Diff.
5→5	9133	10946		9180	10890	
4→4	9362	10679	267	9409	10625	265
3→3	9599	10415	264	9657	10352	273
2→2	9860	10139	276	9927	10071	281
1→1	—	—	545	—	—	542
0→0	10420	9594		10491	9529	

accurate dispersion curve was available, but the extremely low dispersion (700A per mm in this region) and the hazy outlines of the banded structure make the most careful measurements rather rough. To compensate if possible for this, the results of Table IV were averaged from a half-dozen plates. The second band of the sequence was too faint to be measured on any of these plates.

In this upper range under high dispersion about 200 lines or groups of lines could be clearly measured. I give the more prominent of these in Table V. Because of their faintness, the width of the slit used, and the use of a low

TABLE V
Wave-lengths and wave-numbers of principal infra-red lines of nitrogen spectrum.
Notation same as in Table II.

λ (I. A. air)	Int.	ν (vac.)	λ (I. A. air)	Int.	ν (vac.)	λ (I. A. air)	Int.	ν (vac.)	λ (I. A. air)	Int.	ν (vac.)
10498.4		9522.6	1058.3	2	9745.5	9593.7		10420.6	9157.3	2b	10317.3
90.8		29.5	48.7	2	54.7	77.6		38.2	52.3	2	23.2
86.1		33.8	41.8	2	61.2	59.3		58.2	48.7	2	27.5
75.7		43.3	28.3		74.1	55.3		62.5	44.9	1	32.1
71.5		47.1	07.5		94.0	53.2		64.8	41.1	1	36.6
65.4		52.6	10191.5		9809.4	9550.5	b	10467.8	24.1	2	57.0
61.1		56.6	44.5		54.8	45.1	b, h	73.7	17.3	2	65.2
57.4		60.0	40.3		58.9	37.4		82.2	12.0	1	71.5
53.3		63.7	33.4		65.6	06.6		10516.1	04.5	1	80.6
48.4		68.2	16.7		81.9	9491.9	1	32.4	9099.3	2	86.8
42.1		74.0	07.9		90.5	82.7	2b	42.6	96.2	2	90.6
37.5		78.2	10097.3		9900.9	34.8	1	96.2	92.6	2	94.9
24.4		90.2	14.5		82.8	17.6	1	10615.5	88.7	1	99.7
20.9	2	93.4	9940.2		10057.4	13.2	2	20.5	80.2	2	11010.0
16.3	2	97.7	34.5		63.2	09.8	3b, h	24.3	58.3	2	36.6
12.9	2	9600.8	9920.6		10077.3	05.8	2	28.8	9049.5	3b	11047.3
04.2		08.8	14.5		83.5	9397.6	1	38.1	45.7	2b	51.9
10397.1		15.5	9868.4		10130.6	92.2	4	44.2	37.4	2	62.1
95.3		17.1	64.4		34.7	86.2	3	51.0	33.3	2b, h	67.1
90.4		21.7	20.0		80.5	76.3	2	62.3	19.6	1	83.9
87.8		24.1	17.5		83.1	56.0	2	85.4	10.1	2	95.6
83.3		28.3	15.2		85.5	42.5	2	10700.8	06.2	2	11100.4
73.2	2	37.6	9704.8		10301.4	26.2	3	19.5	03.9	1	03.3
65.9	2	44.4	9697.7		09.0	22.7	2	23.6	00.4	1	07.6
59.6	2	50.3	88.4		18.8	19.1	2	27.7	8975.8	2b	38.0
10356.0	2	9653.6	86.3		21.0	9296.4	2	53.9	59.7	1	58.0
49.1	2	60.1	69.1		39.4	86.6	2	65.3	53.8	2	65.4
47.0		62.0	67.4		41.2	57.5	2	99.1	52.1	2	67.5
39.9		68.7	65.1		43.7	9196.9	2b	10870.2	48.2	2b, h	72.4
37.0		71.4	45.0	b	65.2	94.4	2b	73.2	41.7	2	80.5
16.4	2	90.7	41.6	b	68.6	9182.0	2	10887.9			
05.3		9701.1	35.7	b	75.2	78.5	3	92.0			
10271.0	2	33.5	33.6		77.5	74.9	2	96.3			
66.1	2	38.1	25.4	b	86.3	70.9	2	10901.1			
62.3	2	41.7	23.2	b	88.7	66.6	3	06.2			

power eye-piece in the comparator telescope in their measurement, the accuracy is considerably reduced, and since the error in some cases may amount to several tenths of an angstrom, only one decimal place is carried. The intensities, where added, are merely to indicate some relative distinction.

III. DISCUSSION

Birge⁹ has made an assignment of the vibrational quantum numbers for the bands of the first positive group of nitrogen, as well as for the second and

⁹ Birge, Phys. Rev. **23**, 294 (1924).

fourth. He has incorporated his results in the recent Bulletin of the National Research Council on Molecular Spectra in Gases, where he gives in Fig. 10 (p. 126) a comprehensive diagram of the vibrational energy levels and the bands involved in these groups. It was with the idea of checking this assignment by finding and measuring the bands it predicted in the extension of the first positive group in the infra-red that the present work was undertaken.

It has already been remarked that the assignment of vibration quantum numbers here proposed differs slightly from that previously suggested by Birge. The change was adopted as the only satisfactory way of reconciling several flaws in what was otherwise a perfect agreement between theory and experiment, prediction and observation. The reconciliation is effected by dropping the 0 level of the Birge assignment for the final (so-called *A*) levels. This involves that the Δn characterizing the sequences be diminished by one in each case, the green bands thus being the -5 sequence, the yellow bands the -4 , and the newly resolved batch at 1.04μ the 0 sequence. Had better data been available Birge would undoubtedly have made the same assignment.

The reasons for considering this the more probable assignment may be briefly summarized as follows:

1. The band whose head was measured by Croze as $\lambda 9108$ and which was designated as the $0 \rightarrow 0$ transition by Birge is conspicuous for its absence. And yet this $0 \rightarrow 0$ transition should theoretically be the strongest band of the entire group. The head of the weak band present lies considerably farther out. The only strong line I can find on my plates in this neighborhood is one which invariably measures up as $\lambda 9122.6$ and which, I am confident, is the argon line measured (radiometrically) by Meissner¹⁰ as $\lambda 9123.00$. Hence even this could not have been on Croze's plates since he used chemically prepared nitrogen.

2. On the other hand, the band with its maximum at 1.042μ is as strong as any in the whole group—being equalled in intensity only by the band at $8912A$. This fits in very well with its new assignment as the $0 \rightarrow 0$ transition.

3. The intensity distribution according to the new assignment of the whole group of bands is more symmetric, more in accord with the distribution found in other systems, and especially with that of the similar second positive group of this same neutral N_2 molecule. This intensity distribution for the higher sequences is given in Fig. 6. Comparison with Birge's Fig. 13¹¹ will indicate several points of close similarity between this and the distribution for the second positive group, especially the sudden drop after the initial member in the intensity curve of the 0 sequence.

4. Again, the absence in Birge's diagram¹¹ (Fig. 10, p. 126) of the bands due to transitions to the 0 final level in the very complete green and yellow sequences is rather suggestive of its non-existence. On the other hand, the established presence of such bands (Croze's 7887 and Birge's 6968) in the red and deep red sequences would be conclusive evidence for its existence.

¹⁰ Meissner, *Phys. Zeits.* **17**, 549 (1916).

¹¹ Birge, *Molecular Spectra in Gases*, p. 135.

But the assignment of these bands to their former places made them at best sad misfits in the sequences concerned, as is evidenced by their respective abnormally high and low first differences.¹² Only the first two bands of the -2 sequence were included in my recent plates, but fortunately I had an old plate from some preliminary work under lower dispersion (18A per mm) extending well down into this sequence. It was not particularly good, but

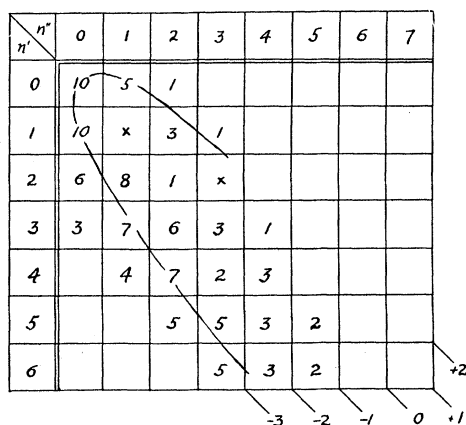


Fig. 6. Intensity distribution of first positive group of nitrogen.

using known N series lines, O and A lines present, the bands in question could be measured with sufficient accuracy for a decisive test of their assignment. For in this part of the spectrum the bands are sharply defined and unmistakable. I give in Table VI the series for the first and second heads as roughly measured from this plate. The error may easily amount to several tenths of an angstrom, but the values are better than data so far available,

TABLE VI
Series of first and second heads of the -2 sequence.

$n' \rightarrow n''$	$\lambda(\text{air})$ I. A.	$\nu(\text{vac.})$	First Diff.	$\lambda(\text{air})$ I. A.	$\nu(\text{vac.})$	First Diff.
7→5	7164.6	13953.7		7152.2	13977.9	
6→4	7273.0	13745.7	208.0	7260.9	13768.5	209.4
5→3	7386.5	13534.5	211.2	7374.0	13557.4	211.1
4→2	7504.0	13322.6	211.9	7491.0	13345.7	211.7
3→1	7626.13	13109.21	213.4	7613.00	13131.82	213.9
2→0	7753.05	12894.61	214.60	7739.56	12917.08	213.74

and the table is given to show how forced is the inclusion of the $\lambda 7896$ band in the -2 sequence; the first difference would jump from 215 to 234, an

¹² Birge, *Astrophys. Jour.* **39**, 50 (1914), see Table IV.

excess of about 18 cm^{-1} . As for the $\lambda 6968$ band, Birge's¹² table indicates sufficiently its misplacement. But it is doubtful whether this is a real band. Again using an old plate (panchromatic), I found that only one of the three heads given by Birge for this band had anything corresponding to it on the plate, a line at 6966A , which was evidently to be attributed to argon. Not even under low dispersion could anything like a clear-cut band be detected here.

These reasons seem to me conclusive evidence in favor of the modified assignment.¹³ For the rest, my findings, as is evident from the tables, confirm the general analysis of the genesis of this first positive group of nitrogen, and add new data for the more accurate determination of the relative vibration term values. The initial bands of either the -1 or -2 sequence suggest themselves by their regularity for a study of the quantum analysis of the individual bands, but no attempt has been made to attack this problem which has so far resisted all efforts at its solution.

It has been mentioned that the stronger oxygen lines were present on these plates. An additional remark on the $\lambda 9265$ triplet might be made. As is well known, it is the first member of the first subordinate series, 2^3P-3^3D . I am not aware of its having been clearly resolved before. Paschen gives it as $\lambda 9264.28$ and lists it as shading towards violet. The three components were clearly distinguishable on a number of my plates. The measurements averaged from several plates are given in Table VII. These give the aver-

TABLE VII
Oxygen triplet $\lambda 7265$

$\lambda(\text{air}) \text{ I. A.}$	Int.	$\nu(\text{vacuo})$	Designation
9265.67	3	10789.57	$2^3P_2-3^3D_{1, 2, 3}$
9262.61	2	10793.13	$2^3P_1-3^3D_{1, 2, 3}$
9260.31	1.5	10795.81	$2^3P_0-3^3D_{1, 2, 3}$

age term value for 3^3D as 12,415.17. The intensities are only relative visual estimates.

The experimental work of this investigation was done at Johns Hopkins University, and, in conclusion, I should like to express my thanks for the courtesy there shown me, and in particular to Dr. Pfund for making me the thermocouple and suggesting the investigation.

MARQUETTE UNIVERSITY,
MILWAUKEE, WIS.
September 1, 1927.

¹³ These results were communicated to Prof. Birge, who concurs in the new assignment.

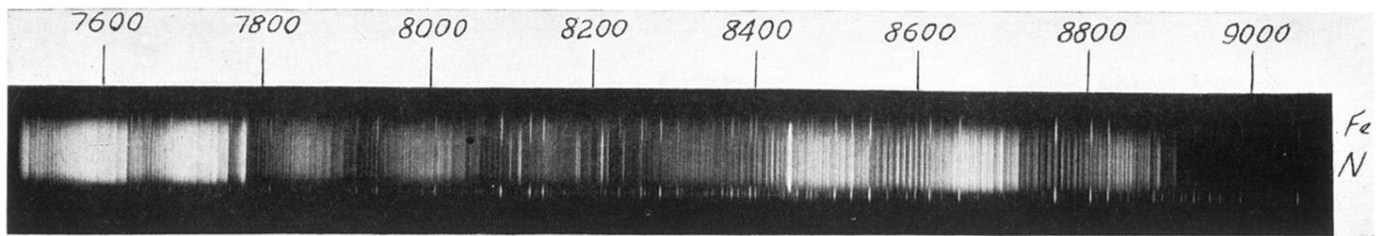


Fig. 3. Infra-red portion of first positive group of nitrogen.

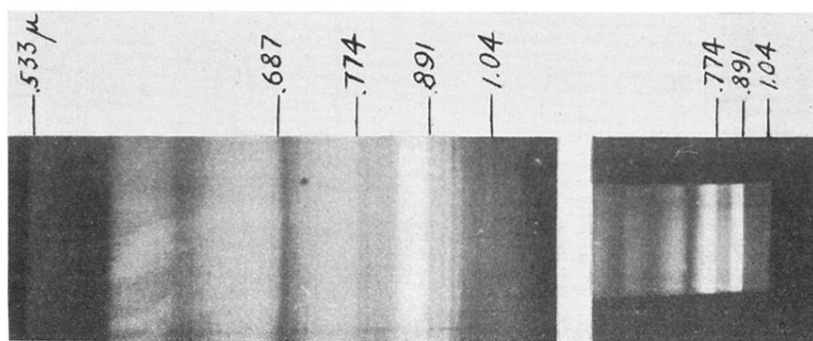


Fig. 4. First positive group of *N* showing new sequence extending from 10500A to 9000A. (Mag. 4x).

Fig. 5. Same under lower dispersion. (Mag. 6x).