Indian J. Phys. 54B, 388-425 (1980)

High resolution studies of nitrogen second positive system at laser threshold

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Abstract: Nitrogen second positive system was excited using a segmented electrode transvorsely excited nitrogen laser tube just below and just at laser threshold. Bands were photographed on a vacuum Ebert grating spectro-trograph at a dispersion ranging from 0.09 to 0.16 Å/mm. About 15 bands were very well resolved and found suitable for a detailed rotational analysis. With the resolution used the Λ components of the P and R branches of $C^3\pi_0$ - $B^3\pi_0$ transition and the R branch in the $C^3\pi_1$ - $B^3\pi_1$ transition could be easily identified. The results obtained are presented.

1. Introduction

The second positive system of nitrogen molecule in the ultraviolet region is a well studied band system. Study of the rotational structure of these bands started in the 1920's by Mecke and Lindau (1924), Lindau (1924, 1924a) and Hulthen and Johansson (1924, 1924a), Herzberg (1931) attributed a sharp cut off of the rotational levels in v' = 4 to a predissociation. A detailed rotational analysis of this system by Coster, Brons and Van der Ziel (1933), Guntsch (1933) and Buttenbender and Herzberg (1935) firmly established that the transition was ${}^{3}\pi - {}^{3}\pi$. Costor, Brons and Van der Ziel (1933) analysed six bands and they could resolve the Λ -doublets in the R_1 branches of these bands. Coster, Van Dijk and Lameris (1935) observed some bands at high resolution and gave line positions of the (0-0) band for higher J values (J = 40-91). Bude (1935) developed a general formula for term values for 3π states in intermediate coupling between Hund's cases (a) and (b) and derived revised equilibrium rotational and spin splitting constants for the $B^3\pi_q$ and $C^9\pi_u$ states. Janin (1946) observed new branches in some bands and discussed perturbations. Carrol and Sayer (1953) added five new bands in the region 5031-5452 Å. Later Dieke and Heath 388

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Figure 1. Rotational structure of the (2-1) band of the $C^3\pi_u - B^4\pi_g$ system of the strongen molecule in the 19th order.

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Figure 2. Rotational structure of the (0-0) band of the $C^3\pi_u - H^3\pi_g$ system of the nitrogen molecule in the 18th order.

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Figure 3. Rotational structure of the (0-1) band of the $C^2\pi_u - B^3\pi_g$ system of the mitrogen molecule in the 17th order.

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Figure 4. Rotational structure of the (0-2) band of the $C^3\pi_u - B^3\pi_y$ system of the nitrogen molecule in the 16th order. The intense band head structure in the second strip from top corresponds to the (0-0) band in the 18th order.

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Figure 5. Rotational structure of the (2-6) band of the $O^3\pi_u - B^3\pi_g$ system of the nitrogen molecule in the 14th order.

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Figure 6. Rotational structure of the (1-5) band of the $C^3\pi_u - B^3\pi_g$ system of the nitrogen molecule in the 14th order.

Nitrogen second positive system

(1959) studied this system in a greater detail at a dispersion of 0.6 Å/mm. They have analysed the rotational structure of the (1-1), (0-0), (2-3), (2-4), (1-3), (1-4), (0-3), (4-8), (3-7) and (1-7) bands and obtained the Λ -doublets of the P and R branches of the ${}^{3}\pi_{ou}-{}^{3}\pi_{og}$ and that of the R branch of the ${}^{3}\pi_{1u}-{}^{3}\pi_{1g}$ transitions.

 $C^3\pi_{\mathbf{u}}-B^3\pi_{\theta}$ stimulated omission lines in a nitrogen pulsed laser have been observed by Kaslin and Petrash (1966), Kasuya and Lide (1967), Parks *et al* (1968), Tocho *et al* (1974) and more recently by Petit *et al* (1978).

A comprehensive summary of the work done on nitrogen molecule till 1977 is given by Lofthus and Krupenie (1977).

We have studied recently the rotational structure of the (0-0), (0-1) and (1-0) bands under electron beam excitation and under laser discharge conditions. The results obtained will be published separately.

Owing to the importance of the nitrogen molecule both in the fields of lasers and that of spectroscopy it was thought worthwhile to reinvestigate the second positive system of the nitrogen molecule under higher resolution and dispersion than was done earlier. Accordingly the rotational structure of the (0-0), (0-1), (0-2), (0-3), (1-0), (1-2), (1-3), (1-4), (1-5), (2-0), (2-1), (2-4), (2-5), (2-6) and (3-1) bands has been studied in various higher orders of a vacuum Ebert grating spectrograph and the results obtained are presented in this paper.

2. Experimental

The nitrogen second positive system was excited using a segmented electrode transversely excited nitrogen laser tube just below and just at laser threshold. The discharge tube was filled at a pressure of 18 torr of nitrogen in the flowing condition. Spectra were taken on a 7.3 m vacuum Ebert spectrograph in 14th to 20th orders at dispersions ranging from 0.16 Å/mm to 0.09 Å/mm on Kodak I-O plates at the Herzberg Institute of Astrophysics, NRC, Canada. Exposure times varied from 2 minutes to 1 hour and this was found sufficient to obtain the rotational lines with reasonably good intensity. Measurements were made using a Carl-Zeiss Abbe Comparator in IIT Kanpur having a least count of one micron. Wavelengths and wavenumbers of the rotational lines were calculated using the program of John John's of the Herzberg Institute of Astrophysics, Canada on an IBM 1401 computer in IIT Kanpur. The measurement of the rotational lines are accurate to ± 0.01 cm⁻¹.

The results reported in this paper on the (0.0) band are obtained under excitation conditions just below the laser threshold of the 0, 0 band while those on other bands are obtained under excitation conditions of just above the laser threshold of the (0.0) band.

J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P_{3} (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹)
0				29678.06				
1	29671.69			$81.53 \\ 81.67$	29678.89			
2	68 99	29664.82		85.41 85.57	82.63			29669.12
3	66.38	62.295	29658.40	89.59 89.79	87.29 * 87.38	29686.55	29672 98	70.52
4	64.38	60 17	56.38	94.11 94 32	92.29* 92.47	92.29		
5	62.48	58.40	54.72	98 96 99.20	97.76 97.90	98.48	76.05	74.65
6	60.93	56.97	53.55	$29704.18\\04.43$	29703.60* 03.77	29705.00	78.06	77.37
7	59.62	65.93	52 78	$09\ 77\ 10.02$	10.02	11.89	81.17	80 .43
8	58.57	55.23	52 50	15 71 15.99	$16.46 \\ 16.63$	19.13	83.57	83.95
9	58.03	54.98	52.50	$\begin{array}{c} 22.04 \\ 22 \ 32 \end{array}$	$23.48 \\ 23.64$	26.75	87.76	
10	57.88	55.23	53.02	28.75 29.04	30 85 31.02	34.69	90.73	
11	29657.65 57.88	29655.56	29653.90	$29735.83 \\ 36.13$	29738 61 38,79	29743.02		

Table 1a, 's. The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (0-0) band of the nitrogen second positive system

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J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	<i>R</i> ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q2 (cm ⁻¹)	Q ₃ (cm ⁻¹)	_
12	58.18 58.40	56 38	54.98	43.32 43.61	46.75 46.90	51.66			Nit
13	$59.08 \\ 59.25$	57.65	56.97	51.19 51·48	55.25 55.43	60.72			roge
14	$\begin{array}{c} 60.17 \\ 60.42 \end{array}$	59.25	58.67	$59.46 \\ 59.75$	64 25 64 28	70.08*			n s
15	61-79 61-98	61.26	61-26	68·10 68·38	73·40* 73 51	79-84			econ
16	63-59 63 87	63.59	64.82	77 12 77·43	83·00* 83·16	89.91			nd p
17	65-98 66-18	66·54	68.82	86·53 86·73	92·98* 93·10	29800-38			osit
18	68-82 68-99	69-49	72.39	96 29 96 58	29803·33* 03 46	11.16			ive
19	71.69 71.98	72.98		$\begin{array}{r} 29806 \ 41 \\ 06 \cdot 733 \end{array}$	14 09* 14·15	22.35			syst
20	75-08 75-29	76 85	79-07	$17.03 \\ 17.29$	25 12* 25·21	33-85			em
21	78 89 79 07	81-17		27.97 28.19	36-65	45.79			
22	83∙04 83∙24			39 29 39-53	48 40	58.02			
23				$29850.96 \\ 51.13$	29860-63				
24				63·05 63·31	73.14	83.67			
25				75.44		96-89			

Table 1 (Contd.): The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (0-0) band of the nitrogen second positive system

(a) The Λ dlublings observed in the P₁, R₁ and R₂ branches of the (0-0) band are listed in the table. Those marked* are resolved and reported in the present work for the first time

(b) Guntsch (1933) reported Δ doublets for $R_1(2)$, $R_2(4)$ to $R_1(38)$ and $P_1(2)$ to $P_1(38)$

J	P ₁ (cm ⁻¹)	P2 (cm ⁻¹)	P ₃ (cm ⁻¹)	R_1 (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹)
)								
	27966-07			27976-12 76.33	27972·37			
1	63.80	27959-18		80·24 80·44	76-98		27966-54	27963-87
•	61-47	56.92	27953-36	84·61 84·75	81.99	27981-64	67-62	6 5·60
	59-42	55-20	51.52	89·22 89·41	87-53	87.53	69· 33	67.72
	57-81	53.87	50 34	94·26 94 49	93·15 93·31	93-93		70-12
	56·59	52-59	48-44	99-64 99-88	99·18 99·35	28000-69		73-25
7	55.20	51-64	48-91	$28005 \cdot 15 \\ 05 \cdot 42$	28005-66 · 05-81	07.89		76-45
8	54-12	51-16	48·91 、	11·07 11·33	12-38 12-57	15.43		80.24
	54-25	51-35	49.84	18.25 18.53	19-89 20-08	23.42		
0	54-44	52.02	50·34	25.31	27.64	31.78		

Table 2. The vacuum wave numbers, J assignments and the Δ -doubling of the rotational lines in the (0-1) band of the nitrogen second positive system

J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R_1 (cm ⁻¹)	R ₂ (cm ⁻¹)	R3 (cm ⁻¹)	Q ₂ (em ⁻¹)	Q ₃ (cm ⁻¹)
11	27954-58 54-77	27952-59	27951-35	28032-77 33-06	28035-81 35-98	28040-55		
12	54.77	54-12	52-97	39.62 40.20	44·36 44·53	49-68		
13	56·75 56·92	55-65	55·20	48-96 49-24	48·96 49·24	59.22		
14	58·42 58-59	57-81	57.64	57-67 57-96	57-67 57-96	69-13		
15	60·47 60·65	60-47	60-84	66-83 67-11	72-54 72-68	79.47		
16	62-97 63-15	63·34	64-28	76-43 76-68	82·73 82-88	90-18		
17	65·86 66·07	66.77	68-15	86-39 86-58	93-48	28101-37		
18	69·16 69·33	70.52	73·01	96·83 97·09	28104-33	12.79		
19	72-86 73-01	74.70	76-45	28107-61 07-85	15-80	24.70		
20	76-98 77-14	79-31	81-99	18-82 19-09	27.57	37-01		
21	81·46 81·64			30-53				
22	86-31 86-53							

Table 2. (Contd.) The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (0-1) band of the nitrogen 18 second positive system

J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R_1 (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q_2 (cm ⁻¹)	Q ₃ (cm ⁻¹)
0								
1	26290-27			26300·04* - 00·16				
2	87.60	26287.80		03.66*	26300-55		26290·27	
3	85-40	80-76	26276-98	03-80 08-13 08-32	05-93* 06-01	26305·19	91-43	
4	83-52	79-37	75.71	13-00 13-22	11-38* 11-47	11.47	93·49	26291-43
5	81-84	77-81	74.46	18.27 18.49	17·24* 17·39	18-12		94·50
6	80·64	76-98	73.83	23·90 24·16	23·57* 23·74	25-21		97-02
7	79-84	76-45	₽ 73·66	29·96 30-23	30·35* 30·53	32.72		
8	79-48	76-37	74.00	36·47 36·73	37·57* 37·74	40·63		26305-20
9 	79-37	76.75	74 .80	43-37 43-66	45·22* 45·39	48-97		
10	79.84	77-51	76.07	50·73 51·03	53-22* 53-49	57.72		
11	80-64	78-85	77-51			66-60		

Table 3°, ^b. The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (0-2) band of the 1 itrogen second positive system

J	P ₁ (cm ⁻¹)	P2 (cm ⁻¹	P3 (cm ⁻¹	R_1 (cm ⁻¹)	R ₂ (cm ⁻¹	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (em ⁻¹)	
12	81-84* 81-99	80· 64	80.07	66 88 67-12	70-88* 71-04	76·53 86·60			
13	83-52* 83-71	83.52	82.80	75·58 75 86	80-35* 80-56				
14	26285.67* 85·86	26285.40	26285 86	26384.78 85•08	26390.24* 90·39	26397.05			
15	88·15* 88·36	88.69	89.55	94-45 94-73	26400-59* 00-72	26408·03			
16	91·06* 91·23	92·09	93·49	26404-57 04-84	11·39* 11·50	26419-33			
17	94·50* 94·70	96.12	98-04	15·16 15·36	22.62* 22.76	31-13			
18	98-61* 98-81	26300-85	26303-66	26-20 26-47	34·28* 34·40	43.33			
19	26302-82	05-20	07-97	37·72 37·95	46·44* 46·54	55-99			
20	[07·36* 07-57	10.42	13-91	49-63 49-88	58·97	69-08			
21	12-69	16.35	20.27	62·02 62·26	72-11				
22	18.49*	22.60	27.03						
23	24.68	29.31	34 24						
24	31·31* 31·52		41.86						
25	38.39								

Table 3 (Contd). The vacuum wave numbers. J assignments and the A-doudling of the rotational lines in the (0-2) band of the nitrogen second positive syrtem

(a) The Λ-doublings observed the P₁, R₁ and R₂ branches of the (0.2) band are listed in the Table. Those marked * are resolved and reported in the present work for the first time.
(b) Lindau (1924a) reported Λ-doublets for R₁(3) to R₁(10), R₁(12) to R₁(15) and R₁(17) to R₁(25).

J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R_1 (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q_3 (cm ⁻¹)
0				24649-06				
1	24642-76			52-65	24649-61		24642-48	
2	40.30	24636-33		56-72 56-85	54.09			24640.57
3	38.10	34-12	24630·33	61-17 61-31	59-06 59-16	24658-39		42.38
4	36.33	32.40	28.73	66·07 66·27	64-53 64-67	64-67	46·92 43·36	44 ·75
5	34-91	31-14	27.73	71-41 71-61	70-51 70-67	71-41		48-36
6	33-92	50.33	27.30	77·18 77·43	77-00 77-18	78·7 4		
7	33-40 '	30-11	27-44	83·45 83·71	83-98 84-17	86-51		56.72
8	33·16 33·27	30.33	28-09	90·19 90·45	91-48 91-66	94.74		
9	33·40 33·53	30.99	29.28	97·40 97·67	99·47 99·65	24703·46		
10	34·12 34·28	32.18	30-99	24705-09 05-39	$24707.93 \\ 08.12$	12-69		
11	35·31 35·47	33.92	33-16	13·25 13·64	16·89 17·08	22-28		
12	36·96 37·12	36.03	35-87	21-99 22-28	26·35 26·52	32-36		

Table 4⁹. The vacuum wavenumbers, J assignments and the Λ -doubling of the rotational lines in the (0-3) band of the nitrogen second positive system

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J (cm ⁻¹)	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R_1 (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹)
13	24639-06 39-23	24638.74	24639.06	24731·17 31·48	24736-29 36-49	24742.97		·····
14	41-69 41-86	41 .68	41.86	40-82 41-16	46-69 46-86	53-96		
15	44·75 44·93	45.55	46 92	51·03 51·34	57·56 57·75	65-30		
16	48·36 48·48	49-61	51-58	61·66 61·97				
17	52-32 52-65	54-26	56.72	72-82				
18	56·85 57·02	59-16 59-30	62-38					
19	61-87	64.94	68·49					
20	67.54							

Table 4⁹. (Contd.) The vacuum wavenumbers, J assignments and the A-doubling of the rotational lines in the (0.3) band of the nitrogen second positive system

(b) Lindau (1924a) repirted A-dlublets fir R₁(4), R₁(6) tl R₁(8), R₁(10) tl R₁(15) and R₁(17) tl R₁(22). Dieke and Heath (1959) reported the A-doublets for R₁(1) to R₁(41) and P₁(8) to P₁(46). They also reported A-doublets in P₂(20), P₂(40), P₂(41), R₂(2) to R₂(25), R₂(31) and R₂(35)

J	P ₁ (cm ⁻¹)	P_2 (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹)
0				31673-02				
1	 31666 ∙69			76·38* 76·53			31665-58	
2	63-93			80·14* 80·33			66-23	31662-87
3	61.38	31656.58	31652-31	84·14* 84·36	31681.30	31679-97	67-06	64-15
4	59-13	54·31	50.00	88·48* 88·69	86-04* 86-17	85.52	68-25	65-83
б	57-05	52.31	48-18	93-09* 93-31	91·25* 91·39	91-39	69-84	67.86
6	55 ·2 5	50-60	46.76	98·01 98 28	96·77* 96·96	97.57	71.97	70-29
7	53·76	49.43	46.74	31703·26* 03·55	31702·68* 02·84	31704·10	73.94	73.02
8	52-48	45.72	45-06	08·88 09·14	0 9·14	10·9 4		
9	51-73* 51-53	47.98	44-81	14·77* 15·07	15·50* 15·67	18.07	80-67	
10	50•74* 50•91	47 58	44.81	21.03 21.34	22·40* 22·56	25.51		

Table 5°, b. The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (1-0) band of the nitrogen secondpositive system

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J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q₂ (cm ^{−1})	Q3 (cm~1)
11	50·38* 50·60	47.58	45.26	27-64 27-95	29·64* 29·80	33.26		
12	50-59* 50-74	47.98	46.00	34·58 34·90	37·22* 37·37	41-18		
13	31650.90*51.14	31648-72	31646.76	31741-88 42-19	$31745 \cdot 11* 45 \cdot 26$	31749-53		
14	51-54* 51-75	49.75	48-45	49-53 49-82	53·34* 53·49	58.50		
15	52·48* 52·67	51.12	50-38	57·51 57·80	61-87* 62-01	67-49		
16	53-77* 54-02	53-77	52.48	65-84 66-14	71·35* 71·52	76-78		
17	55·38* 55·62	54·88	5 1 ·88	74·50 74·78	80.10	86-42		
18	57·38* 57·59	57-38	57 ·59	83-49 83-77	89-58	96-35		
19	59 ·64* 59·86	60-06	60-68	92-82 93-12	99 ·44	31806·63		
20	62·27* 62·48	63·0 4	64 ·15	31802-22 02-67	31809.58	17.26		
21	65·20* 65·42	66-23	67-86	12·54 12·76	20.04	28-11		

Table 5 (Contd.). The vacuum wave numbers, J assimments and the Λ -doubling of the rotational lines in the (1-0) band of the nitrogen second positive system

,	P_1 (cm ⁻¹)	P_2	P ₃	R_1	R_2	R_3 (cm ⁻¹)	Q_2	Q_3
22	68•25* 68·58	70-10	71.97	22.87	30·84	39-34	(022)	(021)
23		74-16	76-09	33·54 33·90	42 ·10	50·87		
24	7 4 ·83	78-52	80.33	44·62 44·80	53.53	62.70		
25	79.56	83-30		55·89 56·22	65.32	74-89		
26				67.88	77-35			

Table 5. (Contd) The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (1-0) band of the

(a) The Λ -doublings observed in the P_1 , R_1 and R_2 branches if the (1-6) band are listed in the table. These marked * are resloved and reported in the present work for the first time

(b) Coster, Brons and Van der Ziel (1933) reported A-doublets in $P_1(6)$, $P_1(8)$ and $P_1(10)$ to $P_1(26)$

J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R2 (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (em ⁻¹)	Q₃ (cm ^{−1})
0				28291-21 91-46				
1	28285-17			94-88 95-04				
2	82.58	28277-94		98·78 98·95	28295 -53	28293-87	28284 ·99	28281-62
3	60.22	75-53	28302-98	28302-98 03-18	99-27	86-24	86·24	83-16
4	77-94	73 55	69·34	07-55 07-78	05·30* 05·42	28304-87	87.47	85-17
δ	76·45	71-96	67-91	12-51 12-72	10-85* 10-99	11.15	89-43	87.64
6	75·10	70-78	67-01	17-84 18 07	16.84* 16.99	17.84		90-57
7	73.96	70.02	66-58	23·20 23·44	24·10* 24·25	24.96		93·54
8	73.35	69-6 0	66-58	29·61 29·91	30·04* 30·23	32.43		
9	73·09	69 60	67.01	$36.13 \\ 36.45$	37·25* 37·45	40.32		
10	72 94* 73 09	70.02	67-91	43·05 43·37	44-89*	48.56		

19 Table 6 ^{a,b}. The Vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (1-2) band of the nitrogen second positive system

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J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹)
11	73·35* 73·55	70-90	69-17	50·37 50·70	52·9 3* 53·11	57.20		
12	74·10* 74·32	72.15	70.78	58·13 58·45	61·38* 61·54	66.06		
13	28275-33* 76-89	28273.83	28273-09	28366-29 66-60	28370·21* 70·39	28375.75		
14	77-10	75.89	75.33	74.87	79.46*	$85 \cdot 48 \\ 75 \cdot 19$	79-61	
15	78-88* 79-08	78-34	78-59	83·86 84-18	89·08* 89·25	95-68		
16	81·25* 81·46	81-25	81.86	93·29 93·59	99.15	28406-21		
17	84-04* 84-24	84-53	85.32	$28403 \cdot 12*$ $03 \cdot 41$	$28409.65 \\ 09.79$	17.19	17-19	
18	87·24 87·47	87.85	89.75	13·35 13·65	20·52* 20·61	28.50		
19	90 84 91·04	92.38	94.31	24·04 24·27	31-72* 31-81	40-24		
20	94·88 95·04	96-85	99-27	35.23	43·36	<u> </u>		
21	99·27 99·44	28301-78	28304·62	46·54* 46·81	55.36	64 ·89		

Table 6 (Contd.). The vacuum wave numbers, J assignments and the Λ -doubling of the rotational lines in the (1-2) band of the nitrogn second positive system.

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	P ₁ (cm ⁻¹)	P ₂ (cm ⁺¹)	P₃ (cm ^{−1})	R ₁ (em ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q_2 (cm ⁻¹)	Q ₃ (cm ⁻¹)
22	28304·15	07.07	10.43	58.43	67.78	77-80		
23	09·30 09·51	13.30	16.60	70.67	70-67	80.7	91-11	
24	14·90 15·12	22.66	22.66	83-71	91-91			
25	20·96 21·37	25.47						
26	27·51 27·66							

(a) The Λ -doublings observed in the P_1 , R_1 and R_2 branches of the (1-2) band are lasted in the table. Those marked * are resolved and reported in the present work for the first time.

(b) Lindau (1924a) reported Λ -doublet in $R_1(3)$ to $R_1(20)$, $R_1(22)$ to $R_2(28)$ and $P_1(18)$ to $P_1(20)$, $P_1(23)$ to $P_1(27)$ and $P_1(29)$.

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J	$\begin{array}{c}P_1\\(\mathrm{cm}^{-1})\end{array}$	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R_1 (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹)	- 7
0				26643 91 44·05					enka
1	26637.79			47·52 47·67			26636·85		teswa
2	55-26	26630-68		51-46 51-63	26648-26	26646-28	37.79	26634-34	ırlu,
3	32.97	28-38	26624·12	55·76 55·95	53-16	51.84	38 85	36-05	Mu
4	31-09	26.95	22-38	60 45 60 59	58-29 58-45	57-91	40.87	38-20	rtiy a
5	29.48	25.13	21-18	65·55 65·78	64·03 64·18	64-40		40.87	nd 1
6	28-38	24-12	20 53	71.06 71.33	70-22 70-39	71.33		44.05	dasu
7	27-55	23·57	20.86	76·86 77·28	78·76 77·01				
8	27.14	23.57	20.70	83·35 83·66	83-96 84-14	86.56		51-63	
9	27.30	23.88	21 ·51	90·16 90·47	91·51 91-71	94.80			
10	27.55	24-61	22.79	97-42 97-73	99·52 99-70	26703-46			

Table 7°,^b. The vacuum wave numbers, J assignments and the Λ -doubling of the rotational lines in the (1-3) band of the nitrogen seco positive system

5	Q ₃ (cm ⁻¹)	Q2 (cm ⁻¹)	R ₃ (cm ⁻¹)	R ₂ (cm ⁻¹)	R_1 (cm ⁻¹)	P ₃ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₁ (cm ⁻¹)	J
			12.55	26707·96 08·14	26705-13 05-44	24.61	25.94	28.09 28.26	11
016 00			21-89	$16.85 \\ 17.02$	13-28 13-61	26.70	27.55	29•31* 29•48	12
conu			26732-11	$\begin{array}{r} 26726 \ 19 \\ \mathbf{26\cdot 34} \end{array}$	26721-89 22-23	26629·31	26 629·78	26630-89* 31-09	13
pos			42-39	35 ·94* 36·08	30·96 31·27	32.32	32-32	32·97* 33·17	14
uve			53-17	46·12* 46·27	40- 46 40-77	36.05	35-44	35-44* 35-66	15
syste			64 34	57-35* 57-48	$50.45 \\ 50.81$	40 00	38.85	38-39 * 38∙60	16
em			76 ∙00	68-65* 68-77	60·87 61·13	44-41	42.78	41∙68* 41∙99	17
			88·02	79-40	71.71 72.02	49-25	47.86	45·59* 45·78	18
			26 800·51	91-43	83-02 83-29	54-56	52.04	49-84* 50-07	19
			13-44	26803.74	94-47 94-94	60-28	57-20	54·56 54·75	20
			26-40	17-09	26806·99* 07·22	66·46	62.93	59-67 59-91	21
₽ _									· · · · · · · · · · · · · · · · · · ·

Table 7 (Contd.). The vacuum wave numbers, J assignments and the Λ -doubling of the rotational lines in the (1-3) band of the nitrogen second positive system

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		p				p		
	(cm ⁻¹)	(em ⁻¹)	(cm ⁻¹)	(cm^{-1})	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
2	64-40		73.18	19-63		40.30		
3	69-02		80-13	32.72				
ŧ			87.58					
5	77-80	82-54						
8		84.69						

(a) The Λ -doublings observed in the P_1 , R_1 and R_2 branches of the (1-3) band are listed in the table. Those marked * are resolved and reported in the present work for the first time.

(b) Lindan (1924a) reported Λ -doublets in $E_1(3)$ to $R_1(20)$, $R_1(22)$ to $R_1(25)$ and $P_1(20)$, $P_1(21)$, $P_1(23)$ and $P_1(25)$.

P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (em ⁻¹)	R_2 (cm ⁻¹)	R_{3} (cm ⁻¹)	Q2 (cm ⁻¹)	Q ₃ (cm ⁻¹)
			25025.55				
25019-43			29·12 29·24	25025.55		25018-50	,
16-91	25012.39		33·12 33·24	30.01	25028.10	19-43	2501 6-08
14-72	10-18	25005-95	37-51 37-72	34·85 34·96	33.70		17.79
12-98	08-53	04-40	42-33 42-54	40·27 40·39	39-91		20·23
11.55	07-28	03-43	47·60 47·81	46·17 46·33	45.64	24.76	23-12
10-53 10-64	06.44	03.01	53·29 53·57	52-59 52-75	53-86		26.54
09-88 09 95	06.24	03-16	59•47 59•70	59·47 59-70	61.54		
09·72 10·18	06-51	03-82	66-09 66-40	66-88 67-06	67-69		
$09.95 \\ 10.18$	07-13	05.01	73·18 73·51	74-77 74-96	78-31		
10·64 10·85	08-28	06-69	80·79 81-11	85·14 83·32	87-37		
$11.81 \\ 12.05$	09.95	08-88	88·86 89·19	92·00 92·16	96 ·90		
13-43 13-62	12.10	11.55	97-44 97-70	25101·33 01·51	25106-77		

Table 8°. The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (1-4) band of the nitrogen second positive system.

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J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q3 (cm ⁻¹)
13	15-50 15-68	14.72	14.72	25106-49 60-77	11·13 11·31	17.40		
14	25018-03 18-22	25017.86	25018-22	25116-04 16-36	25121·41 21 57	25128-32		
15	21-05 21-25	21.45	22.59	26-06 26-35	$32 \cdot 17$ $32 \cdot 30$	39.69		
16	24·55 24·76	25-44	27.13	36-57 36-89	42.52	51.51		
17	28.50 29.72	30-01	32-23	47·59 47·89	55.19 55.29	63.80		
18	32·93 33·12		37.79	59-07 59-38	67-29	76.54		
19	37·79 38·06	40 . 63	43.84	71-04	80-05	89.71		
20	43·26 43·84		50.29	83-69	93 ·10	25203-47		
21	49·15 49·36	[53·05	57-33	96-42		17.68		
22	55.65	59-95	64-88	25209-91	25220.71			
23	-		72.79	23-81				
24	69-69							

Table 8. (Contd.). The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (1-4) band of the nitrogen second positive system.

(b) Dieke and Heath (1959) reported A-doublets in P1(8) to P1(23) to P1(41), P2(18), P2(23) to P2(37), P2(40), R1(2) to R1(25), R2(3) to R2(35) and $Q_2(3)$ to $Q_2(6)$.

Q₃ (0m ^{−1})	Q_2 (cm ⁻¹)	R 3 (cm ⁻¹)	R_2 (cm ⁻¹)	R ₁ (cm ⁻¹)	P3 (cm ⁻¹)	P2 (cm ⁻¹)	P ₁ (cm ⁻¹)	J
								0
				23439.95				1
			2344 0·73	43-95		23423.08	23427.57	2
23428.76			45.82	48-28 48-47	23416-86	21.07	25.55	3
			51-29	53-30 53-46	15-46	19.52	23.84	4
	23436-21	234 57·9	57·40 57-51	58- 66 58-80	1414·73	18-47	22.6 0	5
38-14	38.76	65-38	63-99 64-15	64-50 64-83	14.57	17.92	21.89	6
			73-39 71-34	70-95 71-19	15.01	17.92	21-48	7
		81-86	78-84	77-85 78-17	15.99	18.39	21-48 21-65	8
		90.85	87·05 87·25	85-27 85-59	17.55	19-42	22-25	9
		23500.31	$95 \cdot 81$ $95 \cdot 98$	$93 \cdot 21 \\ 93 \cdot 52$	19.63	20-94	23-08 23-25	10
		10-29	$23505 \cdot 11$ 05 25	$23501.65 \\ 01.97$	22-25	23.08	24.60 24.79	11

20 Table 9. The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (1-5) band of the nitrogen second positive system

J	P ₁ (cm ⁻¹)	P_2 (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q2 (cm ⁻¹⁻	Q ₃ (cm ⁻¹)
12	26-60 26-82	25.55	25.45	10·57 10·95	14.84	20.62		
13	29·1 2 29·3 0	28.76	29-12	20·12 20·45	25-1 3	31.86		
14	23432 15 32 35	2343 2·35	23433·17	23530·14 30·44	23535∙87 36∙06	23543-26		
15	35-68	36-54		40.69				
16	39·7 2 39·95	41.13						
17	44·30 44·59							
18	48·28 48·47							

Table 9 (Contd.). The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (1-5) band of the introgen second positive system

7	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P3 (cm ⁻¹ [R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q₃ (cm−¹)
0				33614-56			······································	
1	33607-15			17-77 17-95	33613-18		33606·24	
2	05-43	33599-84		21-43 21-56	17.20		06-86	
3	02.79	97-15	33592-10	25-21 25-48	21-43	33619-55		33603-98
4	33600-09 00-40	9 4-74	89.78	29·32 29·57	26.13	24-83	08-19	05-43
5	33598-13	§ 92.60	87-81	33.65 33.9 3	30·99 31·10	30-39	11-40	07-15
6	96-08 96-21	90·6 5	\$ 86.07	38·26 38·57	36-25			09-25
7	94·28 94·44	89.14	84.73	43 14 43·46	41·71 41·84	<u>42</u> ·35		11-61
8	92·72 92·91	87-81	83.70	48·32 48·67	47·52 47 66	48·6 7		14-92
9	91-42 91-62	86-84	83.00	53·77 54·12	53-63 53-77	55.35		
0	90-44 90-65	86-07	82.61	59·54 59·90	59-90 60-07	62-21		
1	89-27 89-85	85.70	82-49	65-58 65-92	66-62 66-77	69·36		

Table 10. The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (2-0) band of the nitrogen second positive system

J	P_1 (cm ⁻¹)	P ₂ (cm ⁻¹)	P_3 (cm ⁻¹)	R_1 (cm ⁻¹)	R_2 (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q3 (cm ⁻¹)
12	89-14	85.55	82-61	71·92 72·26	73-55 73-66	76.74		
13	33588-83	33585 .70	33583 17	33678-57 78-89	3 36 80-90	33684·43		
14	88.83	86.07	83.92	85•50 85•84	88.31	92-33		
15	89-14	86-84	84.97	92·71 93·04	96·17	33700.57		
16	89-78 99-00		86-27	33700·27 00·57	33704· 14	08-98		
17	90.65	89-27	87.81	05·09 08·40	12-53			
18		90-6 5			21.06	26.67		
19		9 2 ·72		24-60	29-97	35-89		
20				33.55	39.07	45.34		
21				42.24	48.51			

Table 10(Contd.). The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (2-0) band of the nitrogen second positive system

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J	P_1 (cm ⁻¹)	P 2 (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	$Q_{\mathfrak{s}}$ (cm ⁻¹)
0				31907.67				
1	31903-05			11-53			31901-10	
2	100-2 0	31894-82		15-66	31912·16		01-78	31897-78
3	31897.78	92·24	31887-17 20-06	19-82	16.59	31914-63	02-59	9 9-00
4	95-53	89-95	85-01	24-46 24-69	21.30	20-06	03-67	31900- 6 4
5	93 ·43	87.94	83 27	28-92 29-21	26·36 26·50	25-85	04-94	02·59
6	91·54 91·67	86-32	81·74	33-73 34-03	31·77 31·93	31-93		
7	89-95 90-14	84 -70	80.04	38·83 39·15	37.53 37.71	38.35		0 7-67
8	88-71 88-88	84-00	79.70	44.27 44.60	43-63 43-80	45.02		
9	87·67 87-94	83-27	79.70	50·03 50 34	50·03 50·21	52-02		
10	86-93	82-96	79-70	56.11 56.42	56·76 56·96	59·3 0		
11	86-32 86-60	82-92	80-04	$62.51 \\ 62.85$	63-89 64-03	66-91		
12	86-02 86-32	83 -27	80.72	69·25 69·59	71·23 71·39	74.75		

Table 11. The vacuum wave numbers, J-assignments and the A-doubling of the rotational lines in the (2-1) band of the nitrogen second positive system

J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R3 (cm ⁻¹)	Q2 (cm ⁻¹)	Q ₈ (cm ⁻¹)
13	86 93			76-69	79.05			
14	87·16 87·34	84.70	8 2-82	83·75 84·09	86-92 87-06	91-44		
15	87-94 88-18	86-02	83-99	91·44 91·82	95-3 5	32000·2 0		
16	89-08 89-30	87.67		99·55 99·87	32003 .90	90 -26		
17	90-52 90-76	89-48		32 008∙02 08-28	12.96	18-73		
18	82·24 92·54	91.67		16-84	22.01	28.32		
19	94-41 94-82			25·74 26·10	31.73	38-32		
20	97-01 97-56			35·11 35·44	41.57	48.56		
21	99-81			44.82	51·76	59-13		
22				55-12	62.21	69-94		
23				65-43	72.96			

Table 11 (Contd.). The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (2-4) band of the nitrogen second positive system

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· · ·	P ₁ cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R_3 (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹)	-
0				26967-14					- ~
1 26	960-05			70·47 70·69	26966-16		26959-20		Vitro
2	58 -41	26953·07		7 4 -38 74-56	70· 4 7	26967-78	60-05	26956-09	gen
3	56·04	50.83	26945·84	78 57 78·80	75· 20	7 3 ·30	61-03	57-70	secon
4	54-23	48-98	44.21	83·18 83·44	80·28 80·40	7 9·21		59.77	d po
5	52·60 52·69	47.55	43.05	88·15 88-44	85·92 86-06	85· 66		66-44	sitiv
6	51-35 51-53	46-57	42.37	93-54 95-85	91-99 92-15	92.50		65-57	ુ કપ્રક
7	50-49 50-65	45.84	42·20	99.35	98·51 98·68	99·77		6 9·14	tem
8	49-88 50-14	4 <i>5</i> ·99	42.51	27005-49 05-91	27005·49 05·67	27007-48			
9	49-88 50-14	46-17	43-28	12-21 12-54	12-89 13-09	15-58			
0	50·14 50·37	36-88	44 ·50	19·30 18-66	20-71* 20-93	24.09			
1	50-8 3 51-04	48.08	46-17	26-82 27-19	29·02 29 20	33-03			
2	51·94 52·15	i 49 ∙65	¥ 48-27	[34·80* ↓ 35·14	37·73* 37·90	42-32			41

Table 12". The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (2-4) band of the nitrogen second positive system

J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹)
13	26953·43 53·73	26951·75	26950-83	27043·20 * 43·57	27046-86* 47-03	27052-06		
14	55-37 <u>*</u> 55-61	54·23	₽ 53·43	52 06 ⁴ 52·37	56·38	62-20		
15	57·70* 57·98	57-17		61·30* 61-67	66-48	72.78		
16	60·47* 60·78	60· 1 7		71-04* 71-39	76.78	83-74		
17	63·76* 64·01	64·25		81·23* 81·65	87.63			
18	67·42* 67·65	68-45			98·80	27106-87		
19	71-47	73-14		27102·82* 14·64	27110-60	19·07		
20				14.93	22-64			
21	79 .63							

Table 12^c (Contd.). The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (2-4) band of the nitrogen second positive system

(a) The A-doublings observed in the P1, R1 and R2 branches of the (2-4) band are listed in the table. These marked * are resolved and reported in the present work for the first time.

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J	P ₁ (cm ⁻¹)	P2 (cm ⁻¹)	P₃ (cm ^{−1})	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q2 (cm ⁻¹)	Q3 (cm ⁻¹)
0				25377.63			/	
1				81-22	25375-98		25369-12	
2	25369-12			85·07 85·24	80.57	25378·53		25366-76
3	66-90	25356-79	25356-79	89-37 89-59	86.09	84-16	72-23	68·54
4	65.22	55-26	55 ·26	94·09 94·33	91·32* 91·43	90-31		7 _a .85
5	63-83	54-31	4 · 3 15	99·51 99·80	97·13* 97·26	96·94	76·85	
6	62.75	53-90	53.90	$25404 \cdot 81 \\ 05 \cdot 11$	25403-40* 03-56	25404-0 4		77-09
7		57.44	54·03	10·84 11·15	10·17* 10·36	11.62		
8	61-96 62-15	57-81	54.66	17·34 17·66	17·43* 17·66	19-63		85.31
9	62-15	58-47	55.81	24·26 24·61	25·16* 25·36	28-12		
10	62-60 62-75	59•5 6	57· 44	31.67 32.04	33·37* 33·56	37.02		,

Table 13°, c. The vacuum wave numbers, J assignments and the Λ -doubling of the rotational lines in the (2-5) band of the Nitrogen second positive system

second posit	second positive system											
J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R2 (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹				
11	63·65 63·83	61-18	59-56	39·58 39·93	42·05* 42·24	46-42						
12	65·10 65·32	63.18	62·15	47·96 45·33	51·22* 51·41	56-20			,			
13	67·07* 67·30	65.76	65.22	56·82 57·19	60·84* 61·02	66 51						
14	69·50 69·74	68 74	69.86	66-19 66-51	70.91	77.18			_			

Table 13 (*Contd*). The vacuum wave numbers, J assignments and the Λ -doubling of the rotational lines in the (2-5) hand of the nitrogen second positive system

(a) The Λ-doublings observed in the P₁, R₁ and R₂ branches of the (2-5) band band are listed in the table. Those marked * are res lved and reported in the present work for the first time

(b) Lindau (1924) reported A doublets in $R_1(2)$ to $R_1(16)$, $R_1(16)$, $R_1(19)$ $P_1(11)$, $P_1(12)$, $P_1(14)$, $P_1(20)$, $P_1(21)$ and $P_1(25)$ to $P_1(28)$



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J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q3 (cm-*)	
0				23816-48					
0				23816-48					_
1				20.35	23816-18		23810-10		
2		23803-15		24.76	20-90 21-05		10.70		
3	23807-44	01-36	23796-81	23829·27 29·47	26.05 26.21	23824·19	12-37		
4	05-19	00.13	95-44	34·12 34·38	31·45 31·57	50-51	14-13	23811-06	
5	03.87	23798-89	94.69	39·42 39·70	37-37 37-59	37.37	16-66	14-13	
6	03.15	98-47	94.54	45·21 45·52	43·95 44·12	44.71	18-43	17-73	
7	02-81 02 61	98.15	94-97	51·49 51·79	50-98 51-19	52-61		21-91	
8	02·81 02·61	99 ·06	95·9 4	58-24 58 57	58-57 58-75	60.96			
9	03·35 03·71	99.89	97.48	65-50 65-84	66-63 66-82	69.82			
10	04-09 04-30	23801-36	99-52	73·24 73·61	75·19 75·39	79.12			
11	05·53 05·79	03.35	23802-11	81-51 81-87	84·29 84·48	88.91			

Table 14. The vacuum wave numbers, J assignments and the Λ -doubling of the rotational lines in the (2-6) band of the nitrogen second positive system

J	P ₁ (cm ⁻¹)	P2 (cm ⁻¹)	P₃ (cm ^{−1})	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q_2 (cm ⁻¹)	Q₃ (cm ^{−1})
12	23807·44 07·67	23805-80	23805-19	23890-31 90-66	23893-88 94-07	23899 24		<u> </u>
13	09·85 10·10	08.92	08.81	99-60 99-97	23903-99 04-16	23910 00		
14	12-76 12-88	12.37	12.86	23909-42 09-78	14·58 14·74	21.33		
15	16 18 16-46	16.18	17.55	19·77 20·10	25·70 25·89			
16	20.07 20-35	20.58	22.63					
17	24·50 24·76	25.05	28 25					
18	29.48	29.69						

Table 14(Contd.). The vacuum wave numbers, J assignments and the Λ -doubling of the rotational lines in the (2-6) band of the nitrogen second positive system

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J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R ₂ (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q3 (cm ⁻¹)
0				33784.54				
1	3 3778·29			87.64	33782-26		33775.58	
				87.87				
2	75.57	33768-75		91.15	85.84		7 5 ·58	
				91 41				
3	73-12	66.06	33759-12	94-87	90.08	33787 14	76-41	33771-74
				95-13				
4	70-67	63-63	57.80	98·78	94 ·50	92.28		73-12
	70.44			99·14				
5	68-15 68-01	61-43	55-67	33802·94 03·34	99·34	97.70	79-02	74.86
6	66.06	5 9·51	53-96	07-31	33804·24	33803-34		76-83
7	63·95	57-80	52.53	11-98 12-36	09·52 09·68	09-52		79.02
8	62-49 62-24	56-40	51-40	16-92 17-31	15-10 15-39	15-39		81-40

Table 15. The vacuum wave numbers, J assignments and the A-doubling of the rotational lines in the (3-1) band of the nitrogen second positive system

J	P ₁ (cm ⁻¹)	P ₂ (cm ⁻¹)	P ₃ (cm ⁻¹)	R ₁ (cm ⁻¹)	R_2 (cm ⁻¹)	R ₃ (cm ⁻¹)	Q ₂ (cm ⁻¹)	Q ₃ (cm ⁻¹)	-
9	33761-06 60-81	33755-27	33750-59	33822·12 22·49	33820·91 21·09	33821-78			renka '
10	59 51 59·14	54-38	50.05	27·58 27·97	27·03 27·16	28.38			utesw
11	58·87 58·61	53-78	49-78	33·34 33·57	33-24	35-24			arlu,
12	57·80 57·45	53-46	49.78	39·34 39·73	40-07	42·21			M_u
13	57·45 57·19	53-27	50.05	45·66 46·00	47-01	49 64			rty (
14	57·19 57·45	53-46	50-59						and
15	57-47 57-49	31-40							Basu
16	57·45 57·80	54-62	52.33						•
17	57·80 58·12	55.65	53.78						
18	58-12	56-81							
19	58-62 58-87								
20	59·82 60·09								

Table $1^{\xi}(Contd.)$. The vacuum wave numbers, J assisnments and the Λ -doubling of the rotational lines in the (3-1) band of the nitrogen second positive system

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3. Results

The $C^3\pi_u - B^3\pi_d$ electronic transition is expected to give rise to P_1 , R_1 , P_2 , R_2 , Q_2 , P_3 , R_3 and Q_3 branchos belonging to the F_1 , F_2 and F_3 components of the above transition. An examination of the rotational structure of each of the (0-0), (0-1), (0-2), (0-3), (1-0), (1-2), (1-3), (1-4), (1-5), (2-0), (2-1), (2-4), (2-5), (2-6) and (3-1) bands revealed the presence of all the branches. In addition, due to Λ -doubling each one of the branches is expected to be doubled. However, the Λ -components of the P_1 , R_1 and R_2 branches could only be resolved under the present resolution and dispersion. The Λ -components in the rotational lines of the (0-1), (2-0), (1-5), (2-1), (2-6) and (3-1) bands are being reported for the first time.

The rotational structure of the (0-0), (0-3), (1-3), (1-4) and (2-4) bands was earlier reported by Dieke and Heath (1959). Our measurements agree with theirs within experimental errors. Further for the bands (1-3) and (2-4) the present work reports larger number of rotational lines. In the present work, the Λ -components belonging to a number of rotational levels of the P and Rbranches of F_1 and the R branch of F_2 could be identified and J assignments could be made for the individual branches. The rotational structure and analysis of (1-5), (2-1) and (2-6) bands is being reported for the first time. Vacuum wavenumbers along with the J assignments of all the fifteen bands studied here are presented in tables 1 to 15. A reproduction of the rotational structure of the (2-1), (0-0), (0-1), (0-2), (2-6) and (1-5) bands is given in figures 1 to 6.

4. Analysis

As we are dealing here with rotational states which are intermediate between case (a) and case (b), it is nocessary to take into account the decoupling of the spin from the inter-nuclear axis through the influence of the rotation of the molecule as well as the Λ -doubling which is the incipient decoupling of the orbital angular momentum (Dieke and Heath 1959). Following the initial work of Hill and Van Vleck (1928) and Van Vleck (1929), Budo (1935) and Hobb (1936) have worked out the necessary details for the 3π states, Budo without taking the Λ -doubling into consideration and Hebb treating the more general case. The results obtained have been applied by the authors to the N₂ molecule.

Since the coupling in the N_2 molecule lies between case (a) and case (b), the multiplet splitting is small and in such a case it is meaningful to consider all the rotational levels of the same J (but with different F) together and the rotational constant B_v can be calculated making use of the fact that for J > 2 the sum of the term values of six states belonging to one value of J is independent of the interactions and is equal to

Const. + $[6J(J+1)-2]B_v$

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neglecting the term involving D_v (Dieke and Heath 1959). Hence in order to evaluate the rotational constants the average values of the P and R lines of the ${}^{3}\pi{}^{-3}\pi$ transition have been obtained and the $\Delta_2 F$ values have been calculated from the following combination relations (Herzberg 1950)

$$\Delta_2 F''(J) = R(J-1) - P(J+1)$$

$$\Delta_2 F'(J) = R(J) - P(J).$$

Thus wherever more than one band is observed with common upper or lower vibrational level, the corresponding average $\Delta_2 F$ values have been calculated. The $\Delta_2 F$ values obtained have been then used to calculate the rotational constants of the various levels using the relation (Herzberg 1950)

$$\Delta_2 F = 4B_{\nu}(J + \frac{1}{2}) - 8D_{\nu}(J + \frac{1}{2})^3.$$

The molecular constants B_{e} , α_{e} , β_{e} , γ_{e} and D_{e} have been calculated using a relations (Herzberg 1950)

$$\begin{split} B_v &= B_e - \alpha_e(v+\frac{1}{2}) + \gamma_e(v+\frac{1}{2})^2 \\ D_v &= D_e + \beta_e(v+\frac{1}{2}). \end{split}$$

The constants have been obtained using a least square fit program with a IBM 1401 computer. An attempt has been made to estimate the value of H_v but no meaningful values could be obtained because of the low J values involved in the present work. The rotational constants B_v and D_v are given in Table 16 and the constants B_e , α_e , β_e , γ_e and D_e are given in Table 17.

Table 16. The rotational constants B_v and D_v of the $B^3\pi_g$ and $C^{9}\pi_u$ states of nitrogen molecule $B^3\pi_g$

	Prese	nt work	Dieko's work
•1	B., 11050	D.	R.
2	(om-1)	(cm ⁻¹)	(cm ⁻¹)
0	1.62843	5.76×10 ⁻⁶	1.62849
1	1.61286	10.52×10^{-6}	1.61047
2	1.59082	$3.61 imes 10^{-6}$	1.59218
3	1.56810	$5.40 imes10^{-6}$	1.57365
4	1.55526	$7.25 imes 10^{-6}$	1.55509
5	1.53533	$5.87 imes 10^{-6}$	1.53676
6	1.51368	$8.46 imes 10^{-6}$	1.51787
		$C^3\pi_u$	
	Prese	nt work -	Dieke's work
v	B_v	D_v	B_v
	(cm ⁻¹)	(cm-1)	(cm ⁻¹)
0	1.81498	6×10-6	1.8149
1	1.79351	6.57×10^{-6}	1.7933
2	1.76826	9.02×10^{-6}	1.7694
3	1.74314	$2.87 imes 10^{-6}$	1.7404

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Table 17. The rotational constants, B_t , a_t , β_t and γ_t of the $B^3\pi_g$ and $O^3\pi_a$ states of the nitrogen molecule. All values are in cm⁻¹

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	Prosen	t work	Dicke'	s Work
	$B^3\pi_g$	$C^3\pi_u$	$B^{3}\pi_{g}$	$O^{3}\pi_{u}$
Be	1.63858	1.8262	1.63748	1.8247
a	0.01882	0.02195	0.01794	0.01868
β_{e}	4.1×10-6	1.40×10^{-6}		
γe	$5.06 imes 10^{-6}$	3.17×10^{-4}	7.38×10^{-5}	2.28×10^{-8}
D_{ϵ}	3.71×10^{-6}	$5.30 imes10^{-6}$		

Acknowledgments

One of the authors (P.V.) is thankful to Dr. D. A. Ramsay, the Herzberg Institute of Astrophysics, National Research Council, Ottawa, Canada for giving him the necessary research tacilities for this work and to Dr. Werner Goetz for his efficient and extensive help with experiments.

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