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Emission Spectra of Nitrogen in the Vacuum Ultraviolet*

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The emission spectra of nitrogen have been photographed in the vacuum ultraviolet under high resolution. Selected bands of the $b' {}^1\Sigma_u^+ - X {}^1\Sigma_g^+$ and the $a' \Pi_g - X {}^1\Sigma_g^+$ systems have been analyzed and new rotational and vibrational constants obtained. The observed Λ -type doubling of the $a' \Pi_g$ state was used to determine that the F_c' doublet component lies above the F_d' component. Rotational perturbations were found in the $v=0$ level of the $a' \Pi_g$ state, and in the $v=0$ and 1 levels of the $b' {}^1\Sigma_u^+$ state. Vibrational perturbations were found in the $v=4, 5$, and 6 levels of the $b' {}^1\Sigma_u^+$ state and a new predissociation at $v=4, J=9$ was observed. The new predissociation limit lies at 13.233 eV and is equally compatible with either the 9.756 eV or the 7.373 eV ground-state dissociation energy.

I. INTRODUCTION

THE band systems $b' {}^1\Sigma_u^+ - X {}^1\Sigma_g^+$ and $a' \Pi_g - X {}^1\Sigma_g^+$ of the nitrogen molecule are of special interest because they provide a good source of vibrational and rotational data on the ground state as well as on the excited states.

The $b' - X$ bands were first observed in emission by Birge and Hopfield.¹ Watson and Koontz² made the first rotational analysis of this system and identified the upper state as ${}^1\Pi$, based on incompletely resolved rotational structure. Tschulanowsky³ was able to show that the upper state must be ${}^1\Sigma_u^+$, which was conformed by Setlow.⁴ Worley⁵ reported four incompletely resolved bands (4-0, 5-0, 6-0, 7-0), observed in absorption.

The $a - X$ bands were first observed in emission by Lyman⁶ and later studied under low resolution by Birge and Hopfield¹ and Sporer⁷ in both emission and absorption. Appleyard⁸ carried out the first rotational analysis (on the 5-13 and 5-14 bands) and showed the transition to be ${}^1\Pi - {}^1\Sigma$ in type; additional bands were analyzed by Watson and Koontz² and Spinks.⁹ The above workers assumed the upper state of the $a - X$ bands to be ${}^1\Pi_u$. However, Herzberg¹⁰ has shown that the upper state must be ${}^1\Pi_g$ and the transition must be a weak one permitted only by magnetic dipole selection rules.

Until recently, rotational Raman data^{11,12} and the rotational data on the nitrogen ground state obtained

from electronic spectra have been in disagreement. Stoicheff¹³ has remeasured the rotational and vibrational Raman spectra under high dispersion; his results are compatible with the ground state data obtained from electronic bands,^{3,9} but a rather large extrapolation from higher quantum numbers is required.

In the present work, new $b' - X$ and $a - X$ bands have been photographed under high resolution and analyzed, giving more reliable rotational and vibrational constants. A number of perturbations have been found and a new predissociation limit was observed at the $J=9, v=4$ level of the $b' {}^1\Sigma_u^+$ state.

II. EXPERIMENTAL

The $b' - X$ and the $a - X$ bands of nitrogen were photographed in emission in the first order of a 21 foot normal incidence vacuum spectrograph¹⁴ from 920 to 1700 Å. A newly ruled Bausch and Lomb concave grating (30 000 lines per inch with a 150 by 45 mm ruled surface) was employed, giving a dispersion of 1.33 Å per mm. Under favorable conditions lines 0.70 cm⁻¹ apart were clearly resolved, corresponding to a resolving power of 90 000. Ilford Q2 and "Experimental SWR" Eastman photographic plates were employed.¹⁵

The $a - X$ bands were readily excited in an electrodeless discharge of 1% nitrogen mixed with argon or neon. The discharge was excited by a Raytheon microwave generator (CMD-5, "Microtherm") which supplies 2450 Mc/sec at 125 watts. The $b' - X$ bands were readily excited in the same manner and could also be produced in mixtures of 1% nitrogen with helium or in pure nitrogen alone. The electrodeless discharge tube consisted of a 20 cm length of capillary tubing (6 mm i.d.) attached, end-on, to the spectrographic slit. No window was employed in the discharge tube and the gases flowed through the slit into the spectrographic tank. The $a - X$ bands were excited at pressures of 3-16 mm; the $b' - X$ bands appeared most strongly at 3 mm pressure. Exposure times with a slit width of 10μ

* This work was assisted in part by the Geophysics Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command, under Contract No. AF12(604)-1019 with the University of Chicago.

¹ R. T. Birge and J. J. Hopfield, *Astrophys. J.* **68**, 257 (1928).

² W. W. Watson and P. G. Koontz, *Phys. Rev.* **46**, 32 (1934).

³ W. M. Tschulanowsky, *Bull. Acad. Sci. U.R.S.S.* **1**, 1313 (1935).

⁴ R. B. Setlow, *Phys. Rev.* **74**, 153 (1948).

⁵ R. E. Worley, *Phys. Rev.* **64**, 207 (1943).

⁶ T. Lyman, *Astrophys. J.* **33**, 98 (1911); *Spectroscopy of the Extreme Ultraviolet* (Longmans Green and Company, New York, 1928), second edition, pp. 82, 113.

⁷ H. Sporer, *Z. Physik* **41**, 611 (1927); *Proc. Natl. Acad. Sci.* **13**, 100 (1927).

⁸ E. T. S. Appleyard, *Phys. Rev.* **41**, 254 (1932).

⁹ J. W. T. Spinks, *Can. J. Research* **20**, 1 (1942).

¹⁰ G. Herzberg, *Phys. Rev.* **69**, 362 (1946).

¹¹ C. E. Miller, *J. Chem. Phys.* **6**, 902 (1938).

¹² F. Rasetti, *Phys. Rev.* **34**, 367 (1929).

¹³ B. P. Stoicheff, *Can. J. Phys.* **32**, 630 (1954).

¹⁴ For a brief description, see P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.* **23**, 1895 (1955).

¹⁵ This is a new emulsion and is of excellent quality.

TABLE I. Wave numbers of the $b'-X$ bands.

J	0-11 $\nu_0=79629.7$		0-12 $\nu_0=77618.2$	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$
5		79599.39		77588.55
6	79619.42	589.44	77608.96	578.86
7	612.64	578.24	602.10	567.54
8	604.59	565.44	594.45	555.33
9	595.21	551.65	585.54	541.86
10	584.82	536.33	575.31	526.95
11	572.92	519.89	563.69	510.79
12	559.62	502.06	550.94	493.43
13	545.07	482.92	536.93	474.70
14	529.25	462.52	521.42	455.07
15	512.05	441.18	504.96	433.78
16	493.53	417.96	486.82	411.48
17	474.07	393.88	467.85	388.00
18	452.79	368.35	448.12	363.09
19	429.95	341.47	425.93	336.23
20	406.92	313.08	403.27	309.56
21	383.48 ^a	283.84	378.30 ^a	280.59
22	355.63	252.99	353.10	250.56
23	327.81	221.68 ^a	326.54	220.56 ^a
24	299.06	187.28	298.21	186.52
25	268.70	152.44	270.56	152.75
26	236.98	116.36	238.39	

J	1-7 $\nu_0=88711.8$		1-8 $\nu_0=86583.0$	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$
12	88628.58 ^a	88568.94 ^a		86425.04 ^a
13	612.28 ^a	549.80 ^a		403.76 ^a
14	593.94	527.54 ^a	86469.14	380.62 ^a
15	574.98	503.88 ^a	451.34	355.49
16	554.19	478.74	431.17	328.65
17	532.01	452.05	409.44	301.83
18	508.42	423.90	386.52	272.86
19	483.20	394.04	361.75	242.43
20	456.59	363.11	335.80	210.98
21	428.28	330.48	308.23	177.33
22	398.80	296.63	279.79	142.66
23	367.64	260.98	249.58	106.39
24	335.16	223.90	218.04	69.04
25			184.64	29.87
26			149.86	
27			113.58	85989.55
28				947.42
29			37.34	904.01
30			85997.68	

J	1-9 $\nu_0=84483.6$		1-11 $\nu_0=82372.8$		2-8 $\nu_0=87315.4$	
	$R(J)$	$P(J)$	$R(J)$	$P(J)$	$R(J)$	$P(J)$
2				80364.34		
3				358.14		
4				350.78		
5				341.94		
6	84452.18		80362.01	332.06		
7	442.06		355.36 ^a	320.58		
8	84456.46 ^a	416.82	347.62 ^a	308.00		
9	447.40 ^a	402.50 ^a	339.42 ^a	294.20 ^a		
10	430.79 ^a	386.62 ^a	323.80 ^a	279.44 ^a	87264.38	87216.20
11	420.32 ^a	370.38 ^a	313.54 ^a	263.97 ^a	250.90	198.25
12	406.56 ^a	346.76 ^a	300.84 ^a	241.37 ^a	236.59	179.17
13	391.03 ^a	328.62 ^a	286.33 ^a	223.79 ^a	220.23	158.80
14	374.23	307.93 ^a	270.41	203.91 ^a	202.81	136.32
15	356.01	285.19 ^a	253.34	182.71 ^a	183.96	113.17
16	336.37	261.19	234.86	159.16	163.59	88.52
17	315.61	235.64	215.04	135.08	141.72	62.74
18	293.15	208.61	193.68	109.46	118.64	34.78
19	269.28	180.19	171.24	82.45	93.90	5.70
20	244.15	150.43	147.66	54.05	68.65	86975.20
21	217.62	119.57	122.36	24.58	41.14	943.52
22	189.26		96.12	79993.73	11.68	909.97
23	159.78	53.18	68.28	961.55	86981.48	875.54
24	129.05	17.73	39.06	927.87	949.72	839.18
25	97.36	83980.97	8.83	892.88		
26	63.28	943.25	79977.09	856.64		
27	28.25	903.74				
28		862.72				
29	83953.75	820.19				

^a Perturbed region (see Sec. VA of text).

varied from a few minutes up to 12 hours, the longer exposures being necessary for the region below 1100 Å.

Certain NI, NII, OI, H, HeII, and CI lines, whose wavelengths have been accurately measured,¹⁶ were used as standards. From the agreement of combination differences in various bands, the probable relative error

¹⁶ P. G. Wilkinson, J. Opt. Soc. Am. **45**, 862 (1956).TABLE II. Rotational constants for the $X^1\Sigma_g^+$, $b'^1\Sigma_u^+$ and $a^1\Pi_g$ states.

v	$X^1\Sigma_g^+$		$b'^1\Sigma_u^+$		$a^1\Pi_g$	
	B_v ^a (cm ⁻¹)	$D_v \cdot 10^6$ ^b (cm ⁻¹)	B_v ^a (cm ⁻¹)	$D_v \cdot 10^6$ ^b (cm ⁻¹)	B_v ^a (cm ⁻¹)	$D_v \cdot 10^6$ ^b (cm ⁻¹)
0	1.9897 ^d	5.75	1.151 ₅	11.04	1.608	5.91
1			1.146	11.37	1.592	5.96
2	1.954	5.73	1.142	11.69	1.579 ^f	6.00
3	1.936	5.72	1.137	12.02	1.551 ^f	6.05
4	1.918	5.71			1.538 ^f	6.09
5	1.902	5.70	1.15 ^e		1.521 ^f	6.13
					1.522 ^f	
6	1.882	5.69			1.507 ^f	6.18
7	1.865	5.68				
8	1.845	5.67				
9	1.828	5.66				
10						
11	1.792	5.64				
12	1.778	5.63				

^a W. W. Watson and P. G. Koontz [Phys. Rev. **46**, 32 (1934)] obtained the following rotational constants: $B_0''=1.998$, $B_1''=1.96$, $B_2''=1.93$, $B_3''=1.88$, $B_4''=1.91$, $B_5''=1.83$, $B_6''=1.82$.

^b The D_v values were calculated from the expressions:

$$D_0 = D_e + \beta_e(v + \frac{1}{2}); \quad D_e = 4B_e^3/\omega_e^2; \quad \beta_e = D_e \left[\frac{8\omega_e x_e}{\omega_e} - \frac{5\alpha_e}{B_e} - \frac{\alpha_e^2 \omega_e}{24B_e} \right]$$

G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 108.

^c W. W. Watson and P. G. Koontz (see reference a) obtained the following rotational constants: $B_0'=1.632$, $B_1'=1.61$, $B_2'=1.59$.

^d B. P. Stoicheff, Can. J. Phys. **32**, 630 (1954).

^e The $v'=5$ level is strongly perturbed (see text).

^f J. W. T. Spinks, Can. J. Research **20**, 1 (1942).

in the standards proved to be less than ± 0.002 Å. In the plate reduction, deviation corrections to the usual linear dispersion equation were applied and in no case amounted to more than 0.015 Å. The relative error in wave number determination amounted to ± 0.1 cm⁻¹ near 1000 Å and ± 0.06 cm⁻¹ near 1700 Å. The absolute wave number error may be as high as ± 0.5 cm⁻¹.

III. ROTATIONAL ANALYSIS

The primary interest was to obtain more consistent ground-state B_v values from $v''=2$ to $v''=12$ since the available data for these levels are in considerable disagreement.^{2,8,9,11-13} Additional data on the $b'^1\Sigma_u^+$ and $a^1\Pi_g$ states were obtained. The evaluation of the constants B' and B'' was done graphically from experimentally determined $\Delta_2 F''(J)$ and $\Delta_2 F'(J)$ values on the P and R branches by methods outlined by Herzberg.¹⁷ These methods allow the experimental determination of D' and D'' also but with the presently available dispersion, the accuracy was not great (20-30%). Accordingly, D' and D'' were computed from the vibrational constants.¹⁸ All of the bands in both systems show the expected intensity alternation (even J strong, odd J weak).

A. The $b'^1\Sigma_u^+$ State

In the $b'-X$ system rotational analyses were carried out for the well resolved 0-11, 0-12, 1-7, 1-8, 1-9, 1-11, and 2-8 bands, which yielded reliable values of B' and B'' . The observed wave numbers in these bands

¹⁷ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), pp. 181-185.¹⁸ See reference 17, p. 108.

TABLE III. Molecular constants for the $b' {}^1\Sigma_u^+$, $a' {}^1\Pi_g$, and $X {}^1\Sigma_g^+$ states.

State	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e	r_e (\AA)	$D_e \cdot 10^6$ (cm^{-1})	$\beta_e \cdot 10^9$ (cm^{-1})	Transition Designation	ν_{00} (cm^{-1})
$b' {}^1\Sigma_u^+$	751.64	4.82	1.154	0.0048	1.4443	10.88	325	$b' - X$	103 672.1
$a' {}^1\Pi_g$	1693.90	13.97	1.617	0.0173	1.2202	5.89	44	$a - X$	68 948.3
$X {}^1\Sigma_g^+$	2357.78	14.08 ^b	1.999	0.01802	1.0971	5.75	9.2		

^a Calculated values. See note b, Table I.

^b $\omega_e y_e = -0.02 \text{ cm}^{-1}$.

are presented in Table I. For the less well-resolved 3–5, 1–6, and 2–6 bands, reasonable values of $B' - B''$ were also obtained. Band head measurements were made on 28 other bands which were either badly overlapped or poorly resolved. The agreement of the combination differences, $\Delta_2 F'(J)$ and $\Delta_2 F''(J)$, in appropriate bands indicated the correctness of the analysis.

The rotational constants, B_v' and D_v' , for the b' state are presented in columns 4 and 5, respectively, of Table II and B_e is shown graphically in Fig. 1. The data represent an extension of the work of Tschulanowsky,³ and Setlow⁴ in that values for B_2' and B_3' are now available. The equilibrium values, $B_e' = 1.154 \text{ cm}^{-1}$ and $\alpha_e = 0.0048$ are somewhat larger than the previous determinations, and hold only for the first four vibrational levels; correspondingly, a somewhat smaller equilibrium distance, r_e , is obtained (Table III).

B. The $a' {}^1\Pi_g$ State

In the $a - X$ system rotational analyses were carried out for the 0–2, 0–3, 0–4, and 1–5 bands which showed well-resolved P -, Q -, and R -branches, even near the band head. The observed wave numbers in these bands are presented in Table IV. The rotational constants, B_v' , determined from the combination relation, $\Delta_2 F''(J) = R(J) - P(J)$,¹⁹ are presented in Table II, column 6, and in Fig. 2 (circles) along with the data of Spinks (crosses).⁹ The rotational constants for this

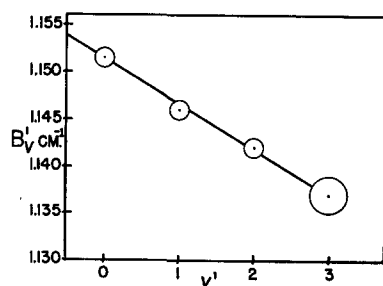


FIG. 1. The rotational constant, B_v' , as a function of v' for the $b' {}^1\Sigma_u^+$ state of nitrogen. The levels above $v' = 3$ are strongly perturbed.

¹⁹ The B_v' determined in this way is only one, namely $(B_v')_d$ of two B_v' 's, the other being $(B_v')_e$; one is obtained from the other by using the combination defect. However, the Λ -type doubling is so small below $J = 35$ that the two B_v' 's differ by less than 0.00001 cm^{-1} . Within the present experimental accuracy, it is immaterial whether B_v' is determined from the R and P , the Q and P , or the R - and Q branches. For the 0–2 and 1–5 bands, in which the R -branch was less well resolved and partly obscured by atomic emission lines, it proved to be slightly more advantageous to determine B' and B'' from the combination relations $\Delta_1 F'(J) = Q(J+1) - P(J+1)$ and $\Delta_1 F''(J) = Q(J) - P(J+1)$.

state given by Watson and Koontz² are several percent higher (Table II, footnote c). The equilibrium values are $B_e = 1.617 \text{ cm}^{-1}$ and $\alpha_e = 0.01703$; the equilibrium distance, r_e , (Table III) is somewhat larger than the earlier determination in conformity with the lowered B_e' .² The agreement of the upper state combination differences in the 0–2, 0–3, and 0–4 bands was quite satisfactory, which is an indication of the correctness of the analysis.

Herzberg¹⁰ has concluded that the $a - X$ transition must be a magnetic dipole ${}^1\Pi_g - {}^1\Sigma_g^+$ transition, and not ${}^1\Pi_u - {}^1\Sigma_g^+$, as previously supposed.^{2,8,9} This conclusion was based on the electron configuration of the nitrogen molecule, the experimental appearance pressures of the bands in absorption, and indirect evidence involving other systems combining with the $a' {}^1\Pi_g$ state. Due to the Λ -type doubling in this state, the combination differences obtained from the R and Q branches in a given band should not agree exactly with those computed from the Q and P branches. For $a' {}^1\Pi_g - {}^1\Sigma_g^+$ transition, the combination defect, $\epsilon = [R(J) - Q(J) - Q(J+1) + P(J+1)]$ may be either positive or negative, depending on whether the F_d' Λ -component lies lower than the F_c' , or vice versa. In Table V, average values for $R(J) - Q(J)$, in column 2, and $Q(J+1) - P(J+1)$, in column 3, are shown. The majority of the values given are the averages of 8 measurements on the 0–3 and 0–4 bands from three different photographic plates, and none of the lines involved are blended lines. The values of ϵ (column 4) have a probable error of $\pm 0.05 \text{ cm}^{-1}$ and show a consistent negative sign toward high J values. In the region above $J = 34$, ϵ becomes abnormally large owing to a perturbation which will be discussed in Sec. VB. The negative value of ϵ fixes the order of the Λ components of the $a' {}^1\Pi_g$ state (at least in the perturbed region): the F_d' component (symmetric and positive for odd J and antisymmetric and negative for even J) lies below the F_c' component (antisymmetric

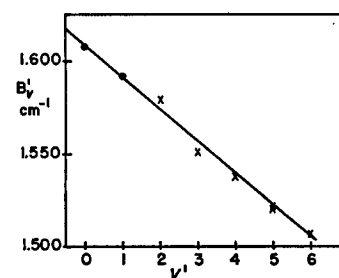


FIG. 2. The rotational constant, B_v' , as a function of v' for the $a' {}^1\Pi_g$ state of nitrogen. The small circles represent the new data reported and the crosses the data of Spinks.

TABLE IV. Wave numbers of the $a-X$ bands (BH—band head; ν_0 —band origin).

J	0-2 $\nu_0=64319.98$ BH 64329.04			0-3 $\nu_0=62047.63$ BH 62057.26		
	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$
2				62047.09	62041.32 ^a	62057.26 ^a
3				43.94	34.12 ^a	57.26 ^a
4				41.32 ^a	26.77	57.26 ^a
5				38.13	21.85	57.26 ^a
6				34.12 ^a	14.85	57.26 ^a
7		74287.67		29.47	7.16	55.68
8		269.71		24.24	61998.66	53.18
9		260.12		18.31	989.48	50.64
10		249.97		11.85	979.10 ^a	46.09
11	64274.62	239.07		4.62 ^a	969.00 ^a	43.09
12	266.07	227.48		61996.47 ^a	958.14 ^a	38.13
13	257.15	214.20		988.06	946.35 ^a	33.12
14	247.16	202.04		979.10 ^a	933.73	28.70
15	236.88	188.68		969.00 ^a	921.19	20.20
16	225.79	174.64		958.14 ^a	906.78	12.70
17	214.20	159.81	64272.06	946.35	892.14	4.62 ^a
18	202.04	144.26	262.40	934.92	877.13	61996.47 ^a
19	188.68	127.52	252.49	922.26	861.51	987.29
20	174.64	110.33	241.75	909.08	845.06	976.61
21	159.81		230.49	895.24	828.01	965.85
22	144.26		218.32	880.81	810.27	954.49
23	128.87	55.26	203.62	865.72	791.17	942.52
24	64112.10	64035.24	64192.14	61849.80	61772.97	61929.93
25		14.67	177.85	833.36	752.36	916.67
26		63993.53	163.11	816.16	733.01	902.64
27	58.50	971.63	147.43	798.43	712.05	887.93
28	38.61	948.92	131.18	779.88	690.31	872.69
29	18.48	925.78		760.88	668.10	856.65
30	63997.54	901.72		741.09	645.21	840.16
31	975.80	877.23		720.70	621.66	822.81
32	953.79	851.70		699.53	597.37	804.70
33	930.77	825.46		677.72	572.45	785.76
34	907.11	798.74		655.36	546.98	766.45
35				632.14	520.21 ^b	746.61
36				608.60 ^b	493.35 ^b	726.07
37				583.71 ^b	464.89 ^b	705.27 ^b
38				558.65 ^b	433.82 ^b	682.59 ^b
39				533.08 ^b	400.89 ^b	660.11 ^b
40				507.05 ^b	368.40 ^b	636.81 ^b
41				478.95 ^b		612.62 ^b
42				451.11 ^b		588.34 ^b

J	0-4 $\nu_0=59803.48$ BH 59813.60			1-5 $\nu_0=59254.55$ BH 59264.53		
	$Q(J)$	$P(J)$	$R(J)$	$Q(J)$	$P(J)$	$R(J)$
1				59264.53		
2				264.53	59258.70 ^a	
3				261.23 ^a	251.82	
4				255.75 ^a	242.20	
5		59775.76		248.87	232.72	
6		769.47		242.20 ^a	223.18	
7		762.72		237.42 ^a	214.06	59261.23 ^a
8		755.00		232.72	208.45	263.05
9		747.01		227.11	198.32	258.70 ^a
10	59771.54	737.87		220.87	189.35	255.75 ^a
11	763.79	727.27		214.06	179.13	251.82 ^a
12	755.00	716.61		206.84	168.13	247.85
13	747.01	705.31		198.32	157.00	242.20 ^a
14	737.87	693.30		189.35	145.03	237.42 ^a
15	728.81	680.72		179.13	132.44	
16	719.18	667.47	59773.51	169.95	119.26	224.16
17	708.41	653.73	766.04	159.38	105.46	
18	696.93	639.22	757.93	148.18	90.97	
19	685.24	624.25	749.40	136.36	76.03	
20	672.71	608.50	740.01	123.84	60.36	
21	659.64	592.23	729.95	110.70	44.25	
22	645.83	575.41	719.18	96.87	27.28	
23	631.32	557.77	708.41	82.62	9.72	
24	616.50	539.58	696.93	67.48	58991.48	
25	600.90	520.80	685.24	51.99	972.83	
26	59584.71	59501.43	59671.07	59035.51	58953.57	
27	567.91	481.36	657.29	18.64		
28	550.25	460.70	642.88	1.23		
29	532.17	439.50	628.09	58983.10		
30	513.50	417.64	612.45	964.49		
31	494.17	395.08	596.32	945.27		
32	474.14	371.88	579.42			
33	453.49	348.20				
34	432.25					
35	410.51					
36	387.96					

^a Blended line.^b Perturbed region (see Sec. VB of text).

and negative for odd J and symmetric and positive for even J). The normal Λ -type doubling is small and does not affect the present accuracy of the rotational constants.

TABLE V. Combination differences and combination defect in the 0-3 and 0-4 bands of the $a-X$ system.

J	$R(J)-Q(J)$	$Q(J+1)-P(J+1)$	ϵ
18	61.00	60.99	0.01
19	64.16	64.08	0.08
20	67.30	67.27	0.03
21	70.46	70.42	0.04
22	73.60	73.55	0.05
23	76.84	76.78	0.06
24	80.31	80.42	-0.11
25	83.31	83.26	0.05
26	86.41	86.39	0.02
27	89.53	89.62	-0.09
28	92.60	92.66	-0.06
29	95.96	96.03	-0.07
30	98.93	99.04	-0.11
31	102.12	102.26	-0.14
32	105.15	105.25	-0.10
33	108.24	108.47	-0.23
34	111.39	111.68	-0.29
35	114.47	115.25	-0.78 ^a
36	117.47	118.82	-1.55 ^a
37	121.56	124.83	-3.27 ^a
38	123.94	132.19	-8.25 ^a
39	127.03	138.65	-11.62 ^a

^a Perturbed region.(C) The $X^1\Sigma_g^+$ Ground State

In Fig. 3 is plotted the function $B_v = B_0 + \alpha_e(v + \frac{1}{2})$ with $\alpha_e = 0.01802$ for the various B_v values listed in Table II. The results found here (circles) are in reasonable agreement with Tschulanowsky⁸ (crosses) and also with Spinks⁹ and in very good agreement with B_0 obtained by Stoicheff¹³ (solid circle), but disagree considerably from Watson and Koontz² (Table II, footnote a). The values obtained for B_e (1.999 cm⁻¹) and α_e (0.01802) (see Table III) agree closely with the Stoicheff data¹³ (1.998₄ cm⁻¹ and 0.01803).

IV. VIBRATIONAL ANALYSIS

In Table VI are listed the observed band heads (column 2) of the $b'^1\Sigma_u^+ - X^1\Sigma_g^+$ system, and the band origins (column 3) either computed from the band heads or determined from the rotational structure. Using band heads to compute band origins undoubtedly introduces an error but probably not exceeding ± 0.5 cm⁻¹. From the Franck-Condon principle one would predict additional bands not listed in the table. Most of

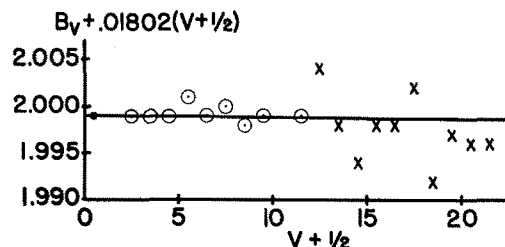


FIG. 3. Graphical determination of B_v'' for the $X^1\Sigma_g^+$ ground state of nitrogen. The small solid circle is the value of Stoicheff, the larger open circles represent the data of this work, and the crosses represent the data of Tschulanowsky.

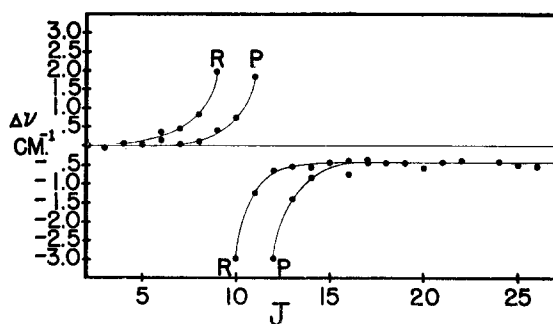


FIG. 4. The perturbation in the $v'=1$ level of the $b' {}^1\Sigma_u^+$ state. The observed minus the calculated positions of the rotational lines of the 1–11 band are plotted against J . Maximum perturbation occurs at $J'=10$ and 11. The frequency shift never returns to zero even for high J indicating perturbation by a ${}^1\Pi_u$ state.

these bands have been found but are overlain by stronger bands so badly that the band heads cannot be measured.

The vibrational constants for the $b' {}^1\Sigma_u^+$ and $X {}^1\Sigma_g^+$ states are given in Table III. These constants were determined from this work alone and accurately represent all the lower state vibrational levels and the upper state levels with quantum numbers $v'=0, 1, 2$, and 3. The ground-state constants obtained are only slightly different from those given by Stoicheff.¹³ The vibrational constants of the b' state agree well with those given by Setlow.⁴

The identification of the 4–0, 5–3, 5–4, 6–4, 6–5, and 6–8 $b'-X$ bands may be considered uncertain since these bands are out of position (using the vibrational constants of Table III) as follows: $v'=4$ about 41 cm^{-1} , $v'=5$ about 50 cm^{-1} , and $v'=6$ about 27 cm^{-1} , all too high. The assumption of vibrational perturbations in these levels is reasonable since: (1) the observed bands have a structure very much like the $b'-X$ bands with $v'=0$ to 3; (2) the positions of the levels agree well with those obtained by Worley⁵ from absorption data; (3) $B'-B''$ (0.765) obtained for the 5–4 band is reasonable although it results in a B_5' (1.15 cm^{-1}) which appears a little high; (4) a predissociation has been found in the $v'=4$ level (Sec. VI); and (5), the bands do not fit into the vibrational scheme of any other known electronic state. It must be admitted, however, that there are other observed emission bands in this region (near 1000 Å) which have not yet been identified.

The vibrational constants in Table III for the $a' {}^1\Pi_g$ state were obtained from the combined data of this work and that of Spinks,⁹ and are only slightly larger than his values.

V. PERTURBATIONS

A. The $b' {}^1\Sigma_u^+$ State

Setlow⁴ observed a small perturbation in the $v'=1$ level at $J'=10$ and identified the $p' {}^1\Sigma_u^+$ state as the perturbing state. This perturbation is very evident in our 1–8, 1–9, and 1–11 bands which are well resolved.

In Fig. 4, the deviations of the P and R branch lines of the 1–11 band from the calculated positions are shown in the region near the perturbation. All of the rotational lines in the perturbed region have a slightly lowered intensity as determined from microphotometer traces. The greatest energy shift occurs at $J'=10$ and 11. When the rotational branch lines for low J values are used as a basis for the perturbation plot (as in Fig. 4), it is found that the branch lines for the higher J above the perturbed region do not return to this zero line but are shifted downward by 0.45 cm^{-1} . This indicates that the perturbing electronic state must be ${}^1\Pi_u$ ²⁰ rather than $p' {}^1\Sigma_u^+$, as previously supposed.⁴ It is suggested that this perturbing state may be the Rydberg state, c , observed by Worley⁵ at 104316.1 cm^{-1} and tentatively identified as $c' {}^1\Pi_u$. The maximum perturbation in the b' state lies at an energy of 104552.6 cm^{-1} ; $J'=10$ in the $v'=1$ level of Worley's Rydberg state c is computed to lie at 104548 cm^{-1} . Herzberg¹⁰ has suggested that Worley's state $c' {}^1\Pi_u$ and Gaydon's state $p' {}^1\Sigma_u^+$ ²¹ may be identical. However, since the character of the p' state has been determined definitely as ${}^1\Sigma_u^+$, the identification of Worley's state c as the cause of the perturbation in $b' {}^1\Sigma_u^+$ is uncertain. It must be pointed out, furthermore, that the rotational structure of the Rydberg bands involving state c has not been completely resolved⁵ and that the rotational constants are not known accurately.

Tschulanowsky³ observed that in the $v'=0$ level, invariably $P23$ and $R21$ were either missing or unusually weak. This was confirmed in the present work, and, in addition, a definite positive shift of 2.35 cm^{-1} of both lines from the normal course of the branches was ob-

TABLE VI. Observed bands of the $b'-X$ system. Band origins were determined from rotational structure unless otherwise noted.

Band $v'-v''$	Band head (cm^{-1})	Band origin (cm^{-1})	Band $v'-v''$	Band head (cm^{-1})	Band origin (cm^{-1})
0–0	103673.8 ^a	103670.8 ^c	2–0	105169 ^b	
0–3	96825 ^a		2–2	100434 ^a	
0–4	94553 ^a		2–4	96005.6	96002.6 ^c
0–5	92309 ^a		2–6	91604.4	91601.4
0–7	87972.5	87969.3 ^c	2–7	89447.5	89444.4 ^c
0–8	85844.5	85841.2 ^c	2–8	87318.6	87315.4
0–9	83745.1	83741.8 ^c	2–9	85219.3	85216.1 ^c
0–10	81675.6	81672.3 ^c	2–10	83149.2	83145.9 ^c
0–11	79633.1	79629.7	3–0	105874.8	105871.9 ^c
0–12	77621.6	77618.2	3–5	94513.2	94510.2
1–0	104430 ^b		3–6	92309 ^a	
1–1	101994 ^a		3–7	90165 ^a	
1–5	93058.4	93055.3 ^c	3–8	88041.2	88038.0 ^c
1–6	90870.8	90867.6	4–0	106632.5	106622.4
1–7	88714.9	88711.8	5–3	100434.3	100431.3 ^c
1–8	86586.2	86583.0	5–4		98181.7 ^a
1–9	84486.9	84483.6	6–4	98841 ^a	
1–10	82416.7	82413.4 ^c	6–5	96650.2	
1–11	80375.5	82372.8	6–8	90165 ^a	

^a Band overlapped by another emission band.

^b Band very weak; position of band head uncertain.

^c Band origin determined from band head measurement.

²⁰ See reference 17, p. 288.

²¹ A. G. Gaydon, Proc. Roy. Soc. (London) **182**, 285 (1944).

served (Table I). Since no other lines are affected, the energy resonance must be rather sharp and so the difference in the B values in the b' state and the perturbing state must be fairly large. The experimental data do not suggest whether the perturbing state is Π or Σ . However, the $v'=3$ level of Worley's⁵ $b^1\Pi_u$ state lies at 103554 cm^{-1} and using Worley's $B_3'=1.412\text{ cm}^{-1}$ and $D_3'=23.10\cdot 10^{-6}\text{ cm}^{-1}$ (calculated from the vibrational constants and B_3'), the energy of the $J'=22$ level may be calculated as 104262 cm^{-1} . Since the perturbation in b' was observed at 104251 cm^{-1} , it seems possible that $b^1\Pi_u$ is the perturbing state although the rotational constants are not known with sufficient accuracy to make a definite decision.

B. The $a^1\Pi_g$ State

In Sec. III B it was stated that the Λ -type doubling in the $a^1\Pi_g$ state increased rapidly above $J=34$ due to a perturbation. In the $0-3$ band it was possible to follow the branches to rather high quantum numbers. The rotational energy functions F_e' and F_d' , corresponding to the two Λ components were computed in the following manner. The function $\Delta_2 F''(J)=R(J-1)-P(J+1)$ was determined from the experimental data (Table IV), and, from this, the rotational energy function in the ground state, $F''(J)$, was found by summing over the even and odd $\Delta_2 F''(J)$ values separately. The relation, $F''(J)=BJ(J+1)$, was used to compute the energy of $F''(1)$ in order to start the odd set summation. The upper state rotational energy functions then follow from the relations: $F_e'(J)=Q(J)+F''(J)-v_0$ and $F_d'(J+1)=R(J)+F''(J)-v_0$, where v_0 is the band origin of the $0-3$ band. In order to show the Λ -type doubling on a suitable scale, F_e' and F_d' were divided by $J(J+1)$ and the results plotted against $J(J+1)$ (Fig. 5). In the region below $J(J+1)=1332$ ($J=35$), $F/J(J+1)$ is a straight line with a slope of $D_0'=6\cdot 10^{-6}\text{ cm}^{-1}$ while above 1332 the splitting between components F_e' and F_d' becomes rapidly larger and a positive deviation from the usual rotational energy relation, $F(J)=BJ(J+1)-DJ^2(J+1)^2$, is noted for both components. Since both components are affected, it is concluded that the perturbing state cannot be $a^1\Sigma_g$ state,

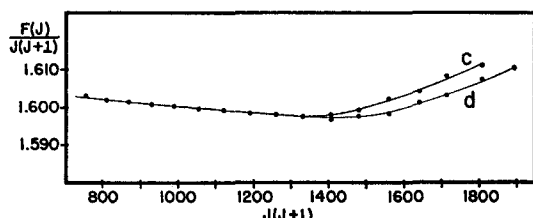


FIG. 5. Λ -type doubling in the $a^1\Pi_g$ state. The functions $F_e'(J)/J(J+1)$ (curve c) and $F_d'(J)/J(J+1)$ (curve d) are plotted as a function of $J(J+1)$ for the $v'=0$ level. The abnormally large splitting and the upward curvature at high J values are due to a perturbation discussed in the text.

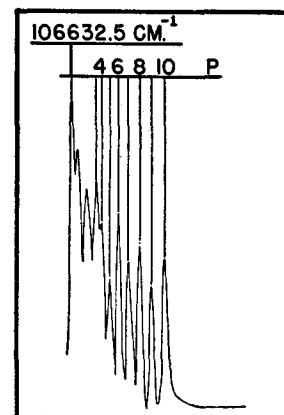


FIG. 6. Predissociation in the $4-0$ band of the $b'^1\Sigma_u^+\rightarrow X^1\Sigma_g^+$ system. The P branch breaks off suddenly above $P(10)$. The last line in the R branch is $R(8)$ which is blended with $P(3)$. The intensity alternation should be noticed.

but must be either Π_g or Δ_g . No further identification is now possible.²²

VI. PREDISSOCIATION IN THE $b'^1\Sigma_u^+$ STATE

All the observed emission bands of the $b'-X$ system are well developed except the $4-0$ band. Figure 6 shows a microphotometer tracing of the $4-0$ band, which breaks off abruptly at $P(10)$. From the measured position of $P(10)$, 106529.41 cm^{-1} , and B_0'' (1.990 cm^{-1}), the position of $R(8)$, the corresponding R branch line, may be calculated to be 106605.02 cm^{-1} which is in satisfactory agreement with the position of the blended line $P(3)$ (Fig. 6), 106605.3 cm^{-1} . It should be noticed that the observed intensity alternation from $P(4)$ through $P(10)$ is destroyed at $P(3)$ indicating a blend of $P(3)$ with $R(8)$. The breakoff indicates a predissociation between $J'=9$ and $J'=10$ with an energy (above $J''=0$, $v''=0$ of the ground state) of $106758\pm 13\text{ cm}^{-1}$ ($13.233\pm 0.002\text{ ev}$). Worley⁴ did not report a predissociation in the $4-0$ band, obtained in absorption. (One might have expected a broadening of the rotational lines to be observed.) This along with the observation that a breaking off in emission occurs only in the $v'=4$ level suggests that the predissociation is a relatively weak one.

There are three other predissociations in nitrogen: in the $a^1\Pi_g$ state at $78843\pm 50\text{ cm}^{-1}$,²³ in the $B^3\Pi_g$ state at 79384 cm^{-1} ,²⁴ and in the $C^3\Pi_u$ state at 97944 cm^{-1} .^{25,26} Consideration of all these predissociation limits does not uniquely determine the dissociation energy of the ground state of nitrogen, but does restrict the choice to either 7.373 ev (59484 cm^{-1}) or 9.756 ev (78709 cm^{-1}), depending upon the excitation energy of the dissociation products (23). The most recent experimental evidence on the dissociation energy of N_2^+ ,²⁷ combined with the

²² Perturbation by $B^3\Pi_g$ (which has the same electron configuration as $a^1\Pi_g$ (10), and is the only known Π_g or Δ_g state nearby) is, from energy considerations, not possible.

²³ A. E. Douglas and G. Herzberg, Can. J. Phys. **29**, 294 (1951).

²⁴ A. van der Ziel, Physica **1**, 353 (1934).

²⁵ A. Budo and I. Kovacs, Z. Physik **109**, 393 (1938).

²⁶ G. Büttgenbender and G. Herzberg, Ann. Physik **21**, 577 (1935).

²⁷ A. E. Douglas, Can. J. Phys. **30**, 302 (1952).

ionization potentials of the nitrogen atom and molecule, appears to favor the higher value (9.756 eV) as the dissociation energy of N_2 . This value is also supported by studies on the detonation velocities of C_2N_2 ²⁸ and predissociation in NO .²⁹ If the higher value be accepted, then predissociation of the $a^1\Pi_g$ state (and of the $B^3\Pi_g$) must be caused by interaction with a slightly stable $^5\Sigma_g^+$, which dissociates into two 4S (ground state) atoms.³⁰ This process is not incredible when one considers that the $a^1\Pi_g$ is metastable since it cannot combine with the ground state except by emission of magnetic dipole radiation.

The products of the 13.233 eV predissociation might be $^4S+^2D$, $^4S+^2P$, $^2D+^2D$, $^2D+^2P$, or $^2P+^2P$ nitrogen atoms, which lead to possible values of 10.849, 9.658, 8.465, 7.274, and 6.073 eV for the dissociation energy ($^2D-2.383$ eV, $^2P-3.574$ eV). The lowest value may be definitely eliminated since this is smaller than the sum of the observed vibrational quanta in the ground state (6.6 eV).³¹ The $C^3\Pi_u$ predissociation has been shown to be equal to an exact dissociation limit (12.139 eV) (26) which leads to possible ground-state dissociation energies of 9.756, 8.565, and 7.373 eV. Dissociation energies computed from the other predissociations may be somewhat higher but should not be lower than any of these values. Therefore, in the $b'^1\Sigma_u^+$ predissociation, the 7.274 eV value may be eliminated leaving only 10.849,

9.658, and 8.465 eV which must be related to the exact dissociation energies, 9.756, 8.565, and 7.373 eV, respectively. Since the 8.565 eV dissociation energy (corresponding to our 9.658 eV limit) has been definitely excluded,²³ only the limits at 10.849 and 8.465 eV need be considered. The former involves dissociation into $^4S+^2D$ atoms, the latter into $^2D+^2P$ atoms, and in each process a potential hill can best be understood if the predissociation considered is an accidental one, i.e., perturbation by a predissociating state. The relatively weak character of the predissociation indicates that it probably is a "forbidden" intercombination process ($\Delta S \neq 0$).

Of the other known predissociating states of N_2 ($a^1\Pi_g$, $B^3\Pi_g$, $C^3\Pi_u$) only $C^3\Pi_u$ can perturb $b'^1\Sigma_u^+$ and since above 12.363 eV the C state is predissociated, a radiationless transition is possible from b' into diffuse rotational states of $C^3\Pi_u$ at 13.233 eV. Thus, the potential hill can be accounted for as well as the relative weakness of the predissociation ($\Delta S=1$). The predissociation of $b'^1\Sigma_u^+$ is thus compatible with either the 9.756 or the 7.373 eV value for the dissociation energy of nitrogen.

ACKNOWLEDGMENTS

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²⁸ Kistiakowsky, Knight, and Malin, J. Am. Chem. Soc. **73**, 2972 (1951).

²⁹ Y. Tanaka, J. Sci. Research Inst. (Tokyo) **43**, 160 (1949).

³⁰ G. Cario and L. H. Reinecke, Abhandl. braunschweig. wiss. Ges. **1**, 8 (1949).

³¹ R. Herman, Ann. phys. (11) **20**, 241 (1945).