Further Analysis of the N_2^+ Bands

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The $\Delta v=3$ sequence of the $^2\Sigma-^2\Sigma$ N_2^+ bands has been photographed in the second and third orders of a 21 foot grating. Rotational analyses have been made of the (4,7), (5,8), (6,9) and (7,10) bands. The B values obtained fit the expressions previously given for B_v' and B_v'' quite well. The perturbation in the (5,8) band has been investigated. The present data on the perturbing $^2\Pi$ state are discussed. Additional measurements in the (13,15) band are also given.

Introduction

THE upper $^2\Sigma$ state involved in the $^2\Sigma-^2\Sigma$ N_2^+ bands is known to be perturbed at several points by a $^2\Pi$ state. With the aim of obtaining further data as to the perturbations between these two states and of extending the data on the two $^2\Sigma$ states, the investigation to be described below was undertaken.

Experimental Procedure

Merton and Pilley[1] found that a discharge taking place in helium, at a pressure of a few centimeters of mercury, to which a trace of nitrogen had been added resulted in strong excitation of the negative nitrogen bands while the positive nitrogen bands were virtually absent. This has been made use of here. The most suitable mixture of helium and nitrogen was found to be helium at a pressure of 3 cm of mercury and nitrogen at a pressure of 0.01 cm of mercury. The discharge tube was of the type customarily used for exciting the hydrogen continuous spectrum. A 0.4 kva transformer with a maximum voltage of 15,000 volts was used to excite the discharge. Placing four Leyden jars in parallel with the discharge tube helped considerably in increasing the enhancement of the N_2^+ bands.

Attention was concentrated on the $\Delta v=3$ sequence. Spectrograms were obtained on Eastman 40 plates in the second and third orders of a 21 foot grating mounted stigmatically. The dispersion for the second order in this region is 2.420A per mm and for the third order 1.317A per mm. The exposure times necessary were three and nine hours for the two orders respectively. An iron arc comparison spectrum was also placed on each spectrogram.

Rotational Analysis

A rotational analysis has been made of the (4,7), (5,8), (6,9) and (7,10) bands. Table I shows the assignments of the lines into the various branches. The lines are denoted by their K values as the spin-doubling is so small that the R_1 and R_2 or P_1 and P_2 lines are not resolved (in the absence of a perturbation) until higher K values are reached than those obtained by this method of excitation. Herzberg[2] has pointed out that the presence of a double head in the (5,8) band shows that there must be a perturbation in it. This is quite evident from the rotational analysis of the band. By means of this perturbation the determination of which are the T_1 and which are the T_2 levels is made for the $v'=5$ state. The relative intensity of two lines of a branch which have the same K value but different J values is in the ratio $K+1:K$, the line originating on the T_1 levels being the stronger. By means of microphotometer traces taken on the 40 : 1 ratio of a Koch-Goos recording microphotometer, it has been ascertained that the higher frequency line of the spin doublets (from $K=11$ on) in the R branches of the (5,8) band is the stronger. Furthermore this branch can be traced back to $K=0$ which would not be the case if it were the

[1] T. R. Merton and J. G. Pilley, Phil. Mag. **50**, 195 (1925).

[2] G. Herzberg, Ann. d. Physik [4] **86**, 190 (1928).

TABLE I. *Rotational assignments.*

	(4,7)			(5,8)			
K	*R*	*P*	*K*	R_1	R_2	P_1	P_2
0	20186.44		0	20368.02			
1	90.85	20179.14	1	74.50	20374.81	20360.83	
2	95.45	75.65	2	77.57	78.72	57.35	
3	200.47	72.88	3	79.05	82.14	56.53	20356.98
4	05.94	70.37	4	91.87	88.21	53.05	54.20
5	11.60	67.99	5	97.15	93.75	57.35	51.34
6	17.89	66.51	6	402.82	99.70	53.05	49.47
7	24.50	65.17	7	08.81	405.97	51.34	
8	31.34	64.27	8	15.29	12.61	49.95	46.88
9	38.62		9	21.95	19.69	48.54	45.96
10	46.27	63.51	10	29.25	26.96	48.18	45.60
11	54.28		11	36.72	34.64	48.18	45.60
12	62.65	64.27	12	44.68	42.70	48.18	45.60
13	71.38	65.17	13	52.86	51.10	48.18	46.54
14	80.51	66.51	14	61.58	59.85	49.47	
15	89.93	67.99	15	70.47	68.98	50.69	48.91
16	99.71	69.85	16			52.29	50.69
17	309.65	72.25	17			54.20	52.67
18	20.35	74.96	18			56.53	55.05
19	31.37	78.08					
20	42.45	81.45					
21		85.28					
22		89.43					
23		93.98					
24		98.84					
25		203.85					
26		09.45					
27		15.43					
28		21.20					

	(6,9)			(7,10)	
K	*R*	*P*	*K*	*R*	*P*
0	20502.97		0		
1	07.10	20496.00(?)	1	20585.71	20574.50
2	11.42	93.57(?)	2	89.24	71.75
3	16.42		3	94.29	68.74
4	21.39	87.11	4	98.76	
5	26.76	84.68	5	603.48	
6	32.44	82.75	6	08.35	61.10
7	38.50	81.23	7	13.63	59.28
8	44.81	80.10	8	19.03	57.31
9	51.41	79.14	9	24.69	55.95
10	58.31	78.12	10	30.57	54.40
11		78.12	11	36.54	53.54
12	73.11	78.12	12	42.82	
13	81.02	78.12	13		
14	89.24	79.14	14	56.01	52.28
15	97.67	80.10	15	62.89	
16	606.51	81.23	16	69.98	51.41
17	15.47	82.75	17	77.31	50.58
18	24.69	84.68	18	84.33	50.58
19	34.24		19	92.25	50.58
20	44.54		20	700.15	50.58
21	56.01		21	08.87	50.58
22	69.98				
23	84.33				

TABLE II. Lower state combination differences. The values of $\Delta_2F''(K)=R(K-1)-P(K+1)$ are given for the various vibrational levels as determined by the present analysis. The values for $v''=8$ are the average of $\Delta_2F_1''(K)$ and $\Delta_2F_2''(K)$. The values of Coster and Brons are also included for $v''=8$ and 9.

K	$v''=7$	$v''=8$	$v''=8$ (C & B)	$v''=9$	$v''=9$ (C & B)	$v''=10$
1	10.79	10.67	10.93	9.40	9.78	
2	17.97	17.90	17.88		17.19	16.97
3	25.08	24.52	24.62	24.31	24.49	
4	32.48	30.83	30.94	31.74	31.37	
5	39.43	38.78	38.84	38.64	38.60	37.66
6	46.43	45.81	46.09	45.53	45.43	44.20
7	53.62	52.85	52.91	52.34	52.34	51.04
8		60.14	60.25	59.36	59.46	56.33
9	67.83	67.06	66.95	66.69	66.31	64.63
10		74.09	74.18	73.29	73.27	71.15
11	82.00	81.36	81.32	80.19	80.22	
12	89.11	88.32	88.39		87.17	
13	96.14	95.21	95.07	93.97	94.19	90.54
14	103.39	102.18	102.27	100.92	100.68	
15	110.66	109.22	109.32	108.01	108.09	104.60
16	117.68	116.29		114.92	114.95	112.31
17	124.75			121.83	121.92	119.40
18	131.57				128.81	126.73
19	138.90				135.80	133.75
20	146.09				142.67	141.67
21	153.02				149.59	
22					156.59	
23					163.55	

R_2 branch. The branches have been designated accordingly.

Table II gives the values of $\Delta_2F''(K)$ and Table III the values of $\Delta_2F'(K)$. B_v has been computed from these tables for the various vibrational states involved.[3] The values obtained for B_v are given in Table IV, as are the values determined by Childs[4] and by Coster and Brons.[5] Coster and Brons have given the following expression for B_v'':

$$B_v''=B_0''(1-0.0104v'') \qquad (1)$$

and the writer[6] has given the following expression for B_v':

$$B_v'=B_0'(1-0.0101v'-0.00072v'^2). \qquad (2)$$

TABLE III. Upper state combination differences. The values of $\Delta_2F'(K)=R(K)-P(K)$ are given for the various vibrational levels as determined by the present analysis. The values for $v'=5$ are those obtained from the unperturbed R_2 and P_2 branches, that is $\Delta_2F_2'(K)$. The values of Coster and Brons for $v'=4$ are also included in this table.

K	$v'=4$	$v'=4$ (C & B)	$v'=5$	$v'=6$	$v'=7$
1	11.71	11.53		11.10	10.21
2	19.80	19.48		17.85	17.49
3	27.59	27.17	25.16		26.55
4	35.57	35.49	34.01	34.28	
5	43.61	43.23	42.41	42.08	
6	51.38	51.24	50.23	49.69	47.25
7	59.33	58.99		57.27	54.35
8	67.07	66.98	65.73	64.71	61.72
9		74.79	73.73	72.27	68.74
10	82.76	82.74	81.36	80.19	76.17
11		90.60	89.04		83.00
12	98.38	98.45	97.10	94.99	
13	106.21	106.40	104.56	102.90	
14	114.00	114.23		110.10	104.60
15	121.94	122.14	120.07	117.57	
16	129.86	129.93		125.28	
17	137.40	137.93		132.72	126.73
18	145.39	145.52		140.01	133.75
19	153.29	153.31			141.67
20	161.00				149.57
21					158.29

Values computed from these two expressions are also included in Table IV. The course of the B values is shown in Fig. 1.

PERTURBATIONS

The T_1 levels of the $v'=5$ level undergo perturbation in the region of low K values. The point of maximum perturbation is at $J=4\frac{1}{2}$ and $5\frac{1}{2}$.

TABLE IV. The values of B_v' and B_v'' as determined by Childs, by Coster and Brons and by the writer. Values are in cm^{-1}.

	B_v'				B_v''			
v	Childs	C & B	Parker	calc.	Childs	C & B	Parker	calc.
0	2.0725	2.074		2.074	1.9224	1.920		1.920
1		2.047		2.052	1.9016	1.900		1.900
2		2.024		2.028		1.879		1.880
3		2.000		1.998		1.861		1.860
4		1.971	1.965	1.966		1.841		1.840
5			1.942	1.932		1.817		1.820
6			1.895	1.895		1.808		1.800
7			1.852	1.854			1.782	1.780
8		1.810		1.813		1.770	1.760	1.760
9				1.765		1.740	1.740	1.740
10		1.710		1.715			1.73	1.720
11				1.664				
12				1.608				
13			1.545	1.549				
14								
15							1.62	1.620

[3] The first two $\Delta_2F_2'(K)$ values of the $v'=5$ state have not been used as there is some indication that a perturbation may exist in the levels involved.

[4] W. H. J. Childs, Proc. Roy. Soc. **A137**, 641 (1932).

[5] D. Coster and H. H. Brons, Zeits. f. Physik **73**, 747 (1932).

[6] A. E. Parker, Phys. Rev. **44**, 90 (1933).

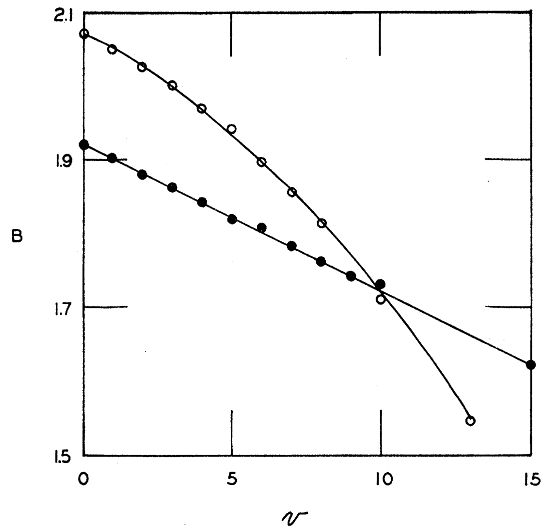

FIG. 1. Plot of B_v' (circles) and B_v'' (dots) against v. The solid lines represent Eqs. (1) and (2).

The separation of the T_1 and T_2 levels is given in Table V. The values are the average separations of the P_1 and P_2 lines and of the R_1 and R_2 lines except from $K=9$ through 14 where the separation of the R lines alone is used as the values obtained from the corresponding P lines are inaccurate, these P lines forming the head of the band. Fig. 2 is a plot of the separation of the T_1 and T_2 levels. There is a possibility that the first three T_2 levels are also perturbed but this cannot be said definitely to be true.

TABLE V. Separation of the T_1 and the T_2 terms of the $v=5\ {}^2\Sigma_u^+$ level. Two values are given when two lines are observed in the perturbed branch which have the same J value. The separations are given in cm^{-1}.

K	T_1-T_2		K	T_1-T_2	K	T_1-T_2
2	−0.31		7	3.10	12	2.08
3	−1.15		8	2.84	13	1.98
4	−3.09	6.04	9	2.68	14	1.77
5	−6.81	3.62	10	2.26	15	1.67
6	3.40		11	2.29	16	1.51
					17	1.48

Childs[4] has observed several perturbations in the $v=0$ level of the ${}^2\Sigma_u^+$ state. These are explained by him as arising from two consecutive vibrational levels of the ${}^2\Pi$ state perturbing the $v=0\ {}^2\Sigma_u^+$ level at $K=39$ and 66 respectively. It is reasonable to assume that $B_v=1.50\ cm^{-1}$ for

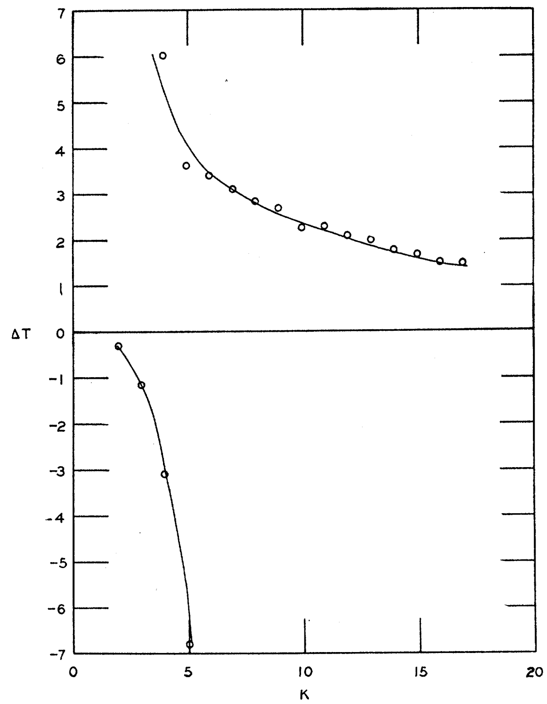

FIG. 2. The perturbation in the $v=5\ {}^2\Sigma_u^+$ level. The separation of the T_1 levels from the T_2 levels is plotted against K.

these two ${}^2\Pi$ vibrational levels. Childs has extrapolated to $K=0$ and computed the separation of the $v=0\ {}^2\Sigma_u^+$ state and the ${}^2\Pi$ level perturbing it at $K=39$ and found the separation to be 900 cm^{-1}. The next ${}^2\Pi$ level may be estimated to be 1570 cm^{-1} higher and this level perturbs the $v=1\ {}^2\Sigma_u^+$ level as well. The separation of the two ${}^2\Pi$ levels perturbing the $v=1$ and 3 ${}^2\Sigma_u^+$ levels is found to be approximately 4620 cm^{-1}. The ${}^2\Pi$ level which causes the next perturbation that in the $v=5\ {}^2\Sigma_u^+$ level is found to lie 4290 cm^{-1} higher. While that perturbing the $v=8\ {}^2\Sigma_u^+$ level lies 5870 cm^{-1} still higher. Fig. 3 illustrates the relative positions of the levels of the two states.

If we assume that the expression for the course of the ${}^2\Pi$ vibrational levels is of the form

$$G(v)=\omega_e(v+\tfrac{1}{2})-x_e\omega_e(v+\tfrac{1}{2})^2, \qquad (3)$$

we can from the separations compute $x_e\omega_e$. The average value obtained is 18 cm^{-1}. This must be taken as a maximum value for the effect of further terms in the expression for $G(v)$ would be

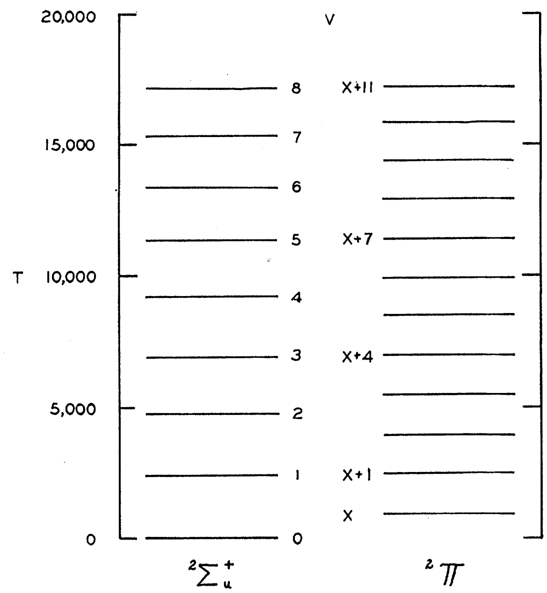

FIG. 3. Course of the $^2\Pi$ vibrational levels relative to the $^2\Sigma_u^+$ levels as determined from the perturbations. The first perturbed $^2\Pi$ level is denoted by x and the subsequent perturbed levels are also indicated by the appropriate designation.

to decrease $x_e\omega_e$, if they are of the same sign as the higher coefficients of the $G(v)$ expressions for the two $^2\Sigma$ states of N_2^+. As can be seen from these two $^2\Sigma$ states the theoretical expressions of Kratzer[7] do not hold sufficiently well to permit of estimating either ω_e or D_e from the values deduced for $x_e\omega_e$ and B_v.

Certain additional lines are frequently observed at points of perturbation. Such is the case in the (5,8) band. For two R_1 lines are observed for both $J''=3\frac{1}{2}$ and $4\frac{1}{2}$ and two P_1 lines for $J''=6\frac{1}{2}$. These are given in Table VI.

Some of the plates obtained showed the (13,15) band very well developed. Hence this band was remeasured on one of the second order plates. The region of the perturbation showed several additional lines whose assignments are given in Table VII. There is no need for a figure to illustrate this perturbation as it is quite similar to that shown in Fig. 2. From the microphotometer traces taken of the perturbed region in the P branches it is evident that the perturbed lines are the weaker. That this is the case for the lines furthest removed from the point of maximum perturbation indicates that the perturbed levels are the T_2 levels. One would expect though, by analogy to the perturbations in the $v=1$ and 5 levels, that the perturbation would be in the T_1 levels, only one set of levels being perturbed.

The author wishes to thank Professor W. W. Watson who suggested the problem for his interest in the research.

[7] Cf. Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 27.

TABLE VI. Additional lines in the (5,8) band.

R branches *J*	*K*		*P* branches *J*	*K*	
$2\frac{1}{2}$	3	20382.14	$5\frac{1}{2}$	6	20349.47
$3\frac{1}{2}$	3	79.05	$6\frac{1}{2}$	6	42.69
		88.21			53.05
$3\frac{1}{2}$	4	20388.21			
$4\frac{1}{2}$	4	81.38			
		91.87			

TABLE VII. Additional lines in the (13,15) band.

K	P_2	P_1	P_2
10	21005.82	21006.36	
11	00.92	01.70	
12	20995.94	20996.71	
13	90.63	92.02	
14	84.62	86.70	20989.41
15	79.56	81.42	83.55
16		76.01	77.30
17	66.96(?)	70.53	71.16
18		64.67	65.73
19		58.64	59.49