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High Energy States of N_2^+ and N_2*

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The rotational structure of the $C-X$ bands of N_2^+ has been analyzed. A rotational perturbation appears in the $v=0$ level of the C state. Evidence is presented against postulating a vibrational perturbation in the $v=0$, $v=1$ levels of this state. Construction of potential curves using the new rotational data shows that previous assignments of vibrational levels are incorrect. A new vibrational numbering is proposed, which is in conformity with the Franck-Condon principle. The use of the Franck-Condon principle in predicting intensities in collisions of the second kind has been verified. Measurement of the rotational structure of the $c-X$ bands of N_2 shows that the c state is the $v=1$ level of the b' state. The vibrational analysis confirms this identification, as does the intensity distribution. Perturbations between states p' and b' are discussed. Evidence is cited to show that the c state of Worley is identical with the p' state of Gaydon.

A. THE $C-X$ SYSTEM OF N_2^+

1. Introduction

THE more intense bands of the N_2^+ spectrum around 1860A were discovered by Birge and Hopfield.[1] They were first identified by Watson and Koontz,[2] using a ten-foot normal incidence spectrograph having a dispersion of about 5.5A/mm. The bands represent transitions from an upper electronic state $C\,^2\Sigma_u^+$ to the ground state of N_2^+, $X\,^2\Sigma_g^+$. In addition, Watson and Koontz found many weaker bands, using a condensed discharge in pure nitrogen. The strong bands, on the other hand, are brought out by a condensed discharge in helium containing nitrogen as an impurity. Additional weak bands were discovered by Takamine and co-workers.[3] No bands were found with upper vibrational quantum number v', less than 5 (using the assignments given by Watson and Koontz). Moreover, the intensity distribution was by no means normal. Levels with $v'=8$ or more were strongly enhanced. The explanation for this intensity anomaly was given by Watson and Koontz in pointing out that collisions of the second kind between ionized helium atoms and N_2 in the ground state would raise unexcited N_2 to the $v=8$ level of $C\,^2\Sigma_u^+$ of N_2^+. An additional point of interest was an observed discontinuity of about 6 cm^{-1} in vibrational levels at $v'=8$.

In an effort to understand this discontinuity more fully, the rotational structure of this system of bands has been measured. Moreover, a rotational analysis of these bands supplies evidence concerning the validity of the Franck-Condon principle as applied to collisions of the second kind.[4]

2. Data

The plates used were those obtained by Watson and Koontz. The vibrational analysis and intensity distribution are given in their paper. The bands measured, together with accompanying information, are given in the following tables.

All bands except 5–6 show only the P branch resolved. The 5–6 band shows one line of the R branch. All bands show the expected alternation of intensities, even though the P branch is blended with lines of the returning R branch. This is simply due to the fact that the returning R lines have higher K values than the P lines with which they blend, and hence are of lower intensity. The intensity alternation then has the same character as the P branch; lines with even K are strong. Since none of the bands shows evidence of a Q branch, it is reasonable to suppose that the transition involved is $^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$. The lower state of this transition,

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[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] T. Takamine, T. Suga, and Y. Tanaka, Sci. Pap. I.P.C.R. **36**, 437 (1939).

[4] R. E. Meyerott, Phys. Rev. **71**, 553 (1947).

TABLE I. Observed rotational lines of the $C-X$ bands of N_2^+ (in cm^{-1}).

Band 5–6	K_P		K_P
51,983.0	$R(0)$	51,939.6	8
973.2	2	926.8	10
962.6	4	913.5	12
951.9	6	906.8	13
Band 8–9	K_P		K_P
52,240.3	2	52,084.3	20
231.0	4	070.8	21
225.9	5	057.5	22
219.6	6	042.8	23
213.7	7	028.1	24
206.2	8	012.0	25
198.7	9	51,997.2	26
190.9	10	981.0	27
181.9	11	964.1	28
173.6	12	946.8	29
165.3	13	929.6	30
154.4	14	910.8	31
142.9	15	893.0	32
132.7	16	872.0	33
121.8	17	854.9	34
109.4	18	834.8	35
097.3	19	813.8	36
		772.3	38

TABLE II. Summary of values of B' and ν_0 for the $C\,{}^2\Sigma_u{}^+$ state of N_2^+ (in cm^{-1}).

v'	B'	Estimated error	Measured from band	ν_0
5	1.62	0.02	5–6	51,979.1
	1.62	0:03	5–5	53,995.0
7	1.513	0.002	7–5	
8	1.492		8–6	58,070.2
	1.493		8–8	54,155.5
	1.492		8–9	52,248.2
	1.493		8–10	50,376.2
	1.494		8–11	48,540.1
	av. 1.493	0.001		
9	1.480	0.003	9–11	50,516.3
10	1.476	0.002	10–12	50,660.7
11	1.472	0.003	11–12	52,573.7
	1.469	0.002	11–13	50,809.1
	av. 1.470	0.002		

$D' = 2.0\times 10^{-6} \pm 20$ percent
(determined from bands 8–8, 8–9, and 8–10)

the ground state of N_2^+, has been measured by Coster and Brons.[5] Since B'' is known, we may find B' from $B'-B''$ as found from measurements on one branch. Since all the bands show essentially the same structure, the complete data for only two typical ones are presented (see Tables I and II).

The accuracy of these measurements depends, of course, upon those of the ground state. Judging from the internal consistency of the results, the ground state B values are certainly good to within the errors of these measurements.

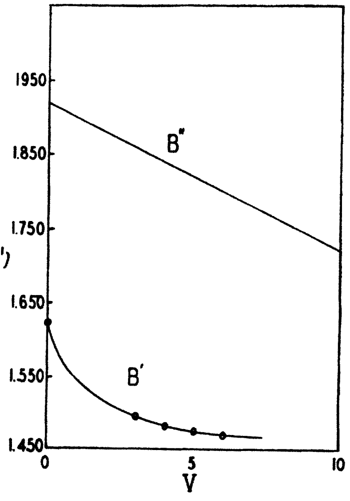

FIG. 1. B_v *versus* v for the C and X states of N_2^+.

A plot of B_v *versus* v is shown in Fig. 1. The vibrational numbering is in accord with the reassignment given below. For $v' > 8$ this is the usual straight line. Below this there is a marked deviation from the usual course. The explanation for this is not clear. Perhaps it is due to a perturbation by one of the many repulsive states of N_2^+ in this region. It is interesting to note that the discontinuity in the $B_v - v$ curve occurs where there is a suspected discontinuity in the vibrational structure.

3. Discussion of Results

From a knowledge of the B values one can compute approximate potential curves using a Morse function. For the ground state of N_2^+ the data of Coster and Brons were used. The potential curves are shown in Fig. 2a. The equilibrium separation for the ground state of N_2, about 1.1A, is indicated by the vertical line.

If the Franck-Condon principle is to be obeyed, transitions should take place straight up and down for the more intense bands, or, quantum mechanically, the larger the overlap integral, the more intense the transition. A cursory glance at these potential curves will show that if they are correct the Franck-Condon principle does not hold. For instance, a transition from $v' = 5$ would have a maximum somewhere in the neighborhood of $v'' = 12$, not $v'' = 5$ as

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

observed. Likewise transitions from other levels are also at variance with observed intensities. Another anomaly exists in the method of excitation of the $v=8$ level. The mechanism of this excitation is as follows. The ionization potential of N_2 is 15.53 volts (see Worley[6]). This represents a transition from the ground state of N_2 to the ground state of N_2^+. The energy of the $v'=8$ level above the ground state of N_2^+ is 8.72 volts. Thus this excited level is 24.30 volts above the ground state of N_2. Transitions from this level are strongly enhanced in a discharge in helium, which has an ionization potential of 24.46 volts. Thus a collision of the second kind between ionized helium atoms and N_2 in the ground state can excite the $v'=8$ level and a few higher ones, while the helium takes the extra electron and goes to its ground state without radiation. Because of the rather close energy resonance, one would expect that the cross section for this process would be large. Thus the distance of closest approach of ion and molecule is large. We might expect the Franck-Condon principle to hold for a collision of this sort. The potential curves in Fig. 2a indicate that an upward transition from the N_2 ground state to the $v'=8$ level is not too probable. It is even less so for the levels $v'=9$, 10, 11, which are also enhanced, although not as much as $v'=8$.

If we wish to bring the observed emission intensities into agreement with those predicted by the Franck-Condon principle, it is necessary to change the vibrational numbering of the upper state. The proper change to make is from $v'=5$ to $v'=0$, and so on. This reassignment does not conflict with observed data, since, using the previous vibrational assignment, no transitions from $v'<5$ are observed. While this renumbering will change the vibrational constants slightly, it will not alter the general shape of the potential curve for the upper $C\,^2\Sigma_u^+$ state. Thus the new potential curve is derived from the old one simply by a shift of five vibrational levels, as shown in Fig. 2b.

The transition from $v'=3$ to the ground state of N_2^+ is indicated by the right-hand solid line. This transition should have maximum intensity for $v''=9$, 10. Such is indeed the case. A subsidiary maximum representing a transition from the left side of $v'=3$ to the ground state should appear around $v''=0$, 1. These bands are not observed, perhaps because of the masking effect of the prominent $a-X$ system of N_2. According to the new numbering, transitions from $v'=1$ will have maximum intensity for $v''=6$ and $v''=1$. Again this agrees with observation. Similar analyses for other transitions yield results in accordance with observation. The one striking anomaly seems to be the intensity of the 3–6 band. One would expect this band to have a rather low intensity. It does not. This band has been given the triple assignment 2–5, 3–6, 4–7. Of the three possibilities, the 2–5 transition seems to have the greatest transition probability, especially if one recalls that the deviation toward higher B values (smaller r) seems to set in at this point (see Fig. 1). If this band is assigned to the transition $v'=2\rightarrow v''=5$, we then find B_2 (the previous B_7)$=1.513$ cm^{-1}. This point falls on the B_v *versus* v curve of Fig. 1.

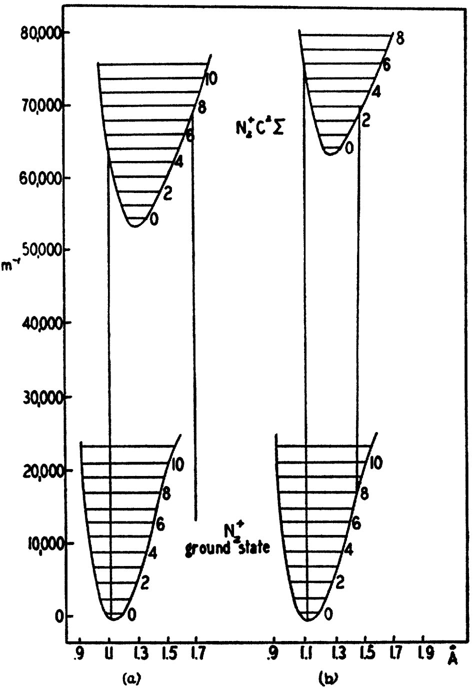

FIG. 2. Potential energy curves for the C and X states of N_2^+: (a) Previous vibrational assignments; (b) corrected assignments.

To obtain agreement between the Franck-Condon principle and the observed intensities,

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[6] R. E. Worley, Phys. Rev. **64**, 207 (1943).

Table III.

Spectrogram	Gas	Pressure	Current	Exposure time
1	100% N_2	0.05 mm Hg	25 ma	24 hr.
2	100% N_2	0.3	35	20
3	100% N_2	0.5	200	8

it has been necessary to change the vibrational numbering of the upper state. The level enhanced by collisions of the second kind with helium ions is now $v'=3$. In this collision N_2 in the ground state (internuclear distance 1.1A) is raised to the C state of N_2. Because of the width of the ground state eigenfunction, the probability of the transition to the $v'=3$ level is appreciable, especially in the case of a close energy resonance as we have here. The enhanced levels above $v'=3$ are not in such close energy resonance, but in these cases the overlap of the eigenfunctions is larger and hence the transition probability is still relatively large. Thus the population of the C state by collisions of the second kind also seems to obey the Franck-Condon principle. The vibrational states $v'=0$, 1, 2 are probably populated by collisions of the second kind between N_2 in the ground state and the metastable $a\,^1\Pi_g$ state of N_2. Again these transitions obey the Franck-Condon principle.

The discontinuity in the rotational structure is probably due to a perturbing state. The perturbation manifests itself in an increase in B'. This means that the perturbation increases with the value of K, and since the rotational level spacing is increased above normal, the perturbing state lies below the $v'=3$ level. The perturbing state must be a Π-state.

For perturbations between Π- and Σ-states, as is the case in this work, no vibrational perturbation should appear. This implies, however, that band origins are used in computing vibrational constants. Such is not the case for the majority of bands in the $C-X$ system. Band heads have been measured. A comparison of the band origins calculated from the heads with the measured origins shows differences as high as 3 cm^{-1}. Because of inaccuracies in the data and the presence of a rotational perturbation, one is justified in concluding that the vibrational perturbation does not exist.

B. THE b' AND c STATES OF N_2

1. Introduction

A system of bands in the far ultraviolet, found by Birge and Hopfield,[1] was tentatively identified by them as a transition from an upper electronic state b' to the ground state of N_2, designated $X\,^1\Sigma_g^+$. Watson and Koontz[2] were able to confirm this identification by rotational structure analysis. They obtained $B'=1.147$ cm^{-1} and identified the upper state as $^1\Pi$. Subsequently Tschulanowsky,[7] working with high members of the ground state progression, showed that the upper state was not $^1\Pi$ but $^1\Sigma_u^+$. He obtained $B'=1.144$ cm^{-1}. The latter worker also found the $v=1$ ($B=1.142$ cm^{-1}) level of the b' state, and was thus able to identify Watson and Koontz's d and e states as vibrational levels 2 and 3, respectively, of b'.

The results of the above investigators thus indicate four vibrational levels of the b' state. The ground state progression from $v'=0$ extends from $v''=4$ through 21. The progression from $v'=1$, on the other hand, only goes from $v''=18$ through 21. The short length of this progression is surprising, especially since the progression from $v'=2$ is about three times as long. In general one would expect the $v'=1$ progression to be somewhat similar to that from $v'=0$.

If the positions of these missing bands are calculated, they fall in the approximate position of another ground state progression observed by Birge and Hopfield, the progression from the state designated as c. The $0-0$ band of this progression has been tentatively identified in absorption by Worley,[6] who obtained $B'=1.92$ cm^{-1} for the upper state. Thus this state cannot possibly be the $v'=1$ level of b'.

There is one additional factor to note. The c state, as observed in emission by Birge and Hopfield, extends from lower state vibrational numbers 5 through 13. The length of this progression is very difficult to account for on the assumption that Worley's c state is the same as Birge and Hopfield's c state. In an effort to straighten out these difficulties, spectrograms in the vacuum ultraviolet were taken of a discharge in pure nitrogen.

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[7] W. M. Tschulanowsky, Bull. Acad. Sci. U.R.S.S. 1, 1313 (1935).

2. Experimental Procedure

The instrument used for the present investigation was a grazing incidence spectrograph using a 15,000 line per inch grating of twenty-one foot radius of curvature. The dispersion was about 1A per mm. A description of this spectrograph will be given elsewhere. The light source was a condensed discharge in a π-shaped water-cooled discharge tube 30 cm long and of internal diameter 1.0 cm. Three spectrograms were obtained. The pertinent information for each spectrogram is given in Table III. The nitrogen flowing continuously through the discharge tube and then into the spectrograph (maintained at a pressure of less than 10^{-4} mm Hg) was tank nitrogen passed over hot CuO. Hydrogen and oxygen showed up as atomic lines on all plates. The slit width was about 0.025 mm. The plates used were Eastman 103-0 U.V. sensitized, developed in D-19.

Spectrograms 1 and 2 were essentially the same. They showed little rotational structure. Spectrogram 3 showed a well developed rotational structure. Portions of the spectrograms are shown in Fig. 3.

3. Method of Analysis

The plates were reduced by assuming that the wave-length was a quadratic function of plate distance. The unknown constants were found using the standard lines given by Boyce.[8] Wave-lengths found from this expression were then corrected by use of a correction curve. If the wave-length range is about 150A, the maximum correction is of the order of 0.010A. The limitations of this method lie in the scarcity of readily available standard lines in the vacuum ultra-violet.

Let us tentatively identify the progression in the neighborhood of that due to the c state as caused by transitions from the $v=1$ level of the b' state. The rotational structure of these bands was measured on all three plates. The measurements agreed to within a few tenths of a wave number. Averages of the three spectrograms are reported.

4. Rotational Structure

Since the rotational structure of none of the bands measured was completely resolved, it was only possible to measure $B'-B''$. Thus to find B' we must know B''. To evaluate B'' the data

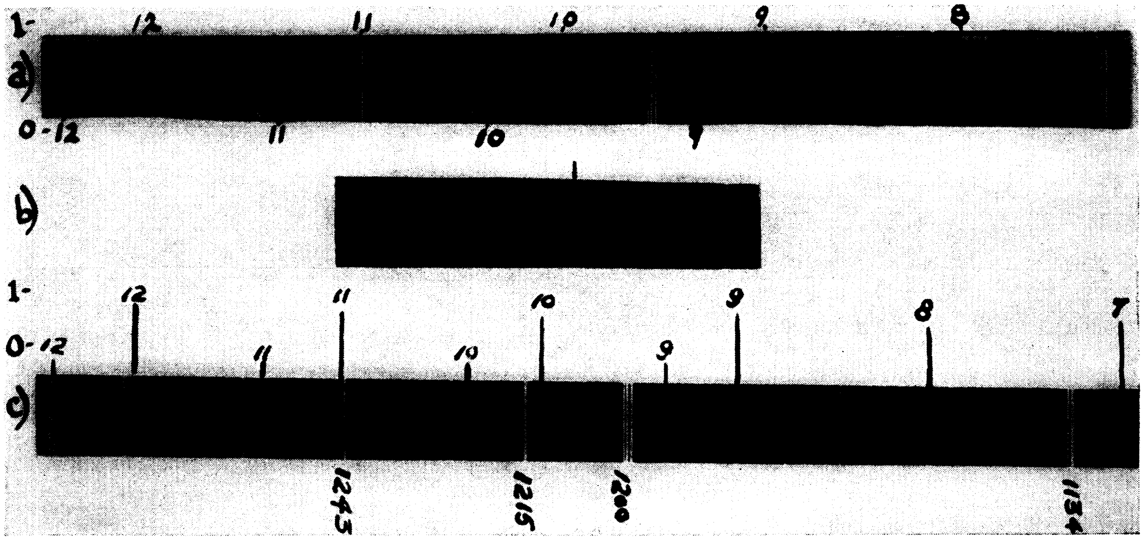

FIG. 3. Spectrograms of the $b'-X$ system of N_2; (a) Spectrograms 1 and 2 (actual size)—note the intensity alternation in the b_0' progression and the peculiar intensity distribution of the b_1' progression; (b) enlargement (3.4×) of the 1-9 band to show rotational structure; (c) Spectrogram 3—focus not as good as in spectrograms 1 and 2, but much higher intensity. Note the many rotational lines as compared with a.

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[8] J. C. Boyce, Rev. Mod. Phys. 13, 1 (1947).

TABLE IV. Observed and calculated rotational lines of the $b'-X$ system of N_2 (in cm^{-1}).

Observed	Obs.- calc.	J_P	Calculated	J_R	Calculated	Remarks
Band 1–7						
88,714.4						head, all lines
666.5	−1.2	6	88,667.1	9	88,669.0	*ss* diffuse
654.3	−1.8	7	654.7	10	656.8	*s*
641.0	−0.6	8	640.8	11	643.1	
625.8	−1.4	9	625.5	12	628.0	
612.3	0.9			13	611.4	
609.2	0.6	10	608.6			
593.0	0.6	11	590.4	14	593.4	*s*
580.2	5.3			15	574.9	? *ss*
568.2	−2.5	12	570.7			*s*
552.1	0.2	13	549.6	16	553.0	
530.5	2.3	14	527.0	17	530.7	
504.1	−1.5	15	503.0	18	506.9	
479.5	0.6	16	477.5	19	481.6	
453.1	−0.4	17	450.6	20	454.9	
425.9	2.3	18	422.1	21	426.7	
394.7	−0.8	19	392.3	22	397.1	
224.4	6.1	24	215.3	27	227.3	?
Band 1–8						
86,586.1						head
542.6	2.2	6	86,539.5	9	86,542.3	*s*
529.1	−0.3	7	527.3	10	530.5	*ss*
516.0	1.1	8	513.7	11	517.2	
502.2	1.0	9	498.7	12	502.5	
484.5	0.8	10	482.3	13	486.4	
468.1	0.6	11	464.5	14	469.0	*s*
455.0	−4.9			15	450.1	*ss*
444.1	−1.1	12	445.2			*ss*
429.3	1.4	13	424.2	16	429.8	diffuse from
405.3	0.9	14	402.6	17	408.1	here on
382.5	−0.5	15	379.2	18	384.9	
357.5	1.2	16	354.3	19	360.4	
302.7	0.1	18	300.3	21	307.1	
275.6	−0.3	19	271.1	22	278.3	
Band 1–9						
84,485.9						head
455.5	1.8	5	84,452.1	8	84,455.3	
443.3	0.9	6	441.6	9	445.3	*s*
430.6	−1.1	7	429.7	10	433.8	*ss*
418.2	0.8	8	416.4	11	421.0	
404.8	−1.5			12	406.8	
397.7	−4.1	9	401.8			?
385.7	−1.1	10	385.7	13	391.2	
372.6	1.3	11	368.3	14	374.3	*s*
358.5	2.5			15	356.0	? *ss*
346.7	−2.8	12	349.5			*ss*
339.5	3.2			16	336.3	?
327.6	−1.8	13	329.4			
307.4	−2.0	14	307.9	17	315.2	
288.5	−0.4	15	285.0	18	292.8	
260.5	−0.2	16	260.7			
242.7	−1.0	17		20	243.7	
211.9	−2.1	18	208.1	21	217.2	
190.5	−1.3			22	189.2	
152.8	0.9	20	149.9		159.9	
Band 1–10						
82,415.0						head
391.7	0.4	4	82,390.2	7	82,393.6	
374.5	2.2	6	370.8	9	374.9	*s*
361.7	−0.5	7	358.7	10	363.9	*ss*
347.7	0.1	8	345.7	11	351.6	
338.2	0.6			12	337.6	
318.6	0.6	10	315.7	13	322.5	
303.0	−0.6	11	306.1	14	298.7	*s*
290.8	3.0			15	287.8	*ss*
279.0	−1.3	12	280.3			
240.1	0.6	14	239.5			
194.4	1.4	16	193.0			
Band 1–11						
80,377.5						head
349.7	0.3	4	80,352.0	8	80,348.1	
341.0	0.0	5	343.3	9	338.6	*s*
335.4	2.2	6	333.2			
324.4	−1.5	7	321.8	10	327.9	*ss*
309.6	0.5	8	309.1			
299.0	−1.1	9	295.1	12	302.6	
280.7	0.9	10	279.8			
264.6	1.3	11	263.3			*s*
254.7	−0.1			15	254.8	*ss*
243.6	−2.4	12	245.3			*ss*
225.2	−1.0	13	226.2			
205.0	−0.6	14	205.6			
195.6	0.1			18	195.5	
182.1	−1.8	15	183.9			*ss*
176.4	3.4			19	173.0	
161.9	1.1	16	160.8			
148.0	−1.3			20	149.3	
136.2	−0.2	17	136.4			
109.3	−1.4	18	110.7			
095.5	−1.3			22	096.8	
081.4	−2.3	19	083.7			
054.5	0.1	20	054.4			
042.5	−0.2			24	042.7	
023.7	−2.2	21	025.9			
79,994.3	−0.6	22	79,994.9			
977.7	−0.7			26	79,978.4	
963.5	1.9	23	961.6			
925.4	−3.8	24	929.2			
893.9	−1.9	25	895.8			
872.5	−4.9			30	877.4	?
857.7	−0.7	26	858.4			
777.6	−4.7	30	782.3			?
Band 1–12						
78,364.8						head
352.6	−1.2	2	78,354.5	6	78,352.4	
339.6	−0.5	4	341.1	8	338.1	
330.3	−1.0	5	332.5	9	329.0	*s*
323.4	0.7	6	322.7			
315.2	−3.7			10	318.7	*s*
299.0	−0.1	8	299.1			
294.7	0.5			12	294.2	
271.2	0.6	10	270.6			
256.2	1.8	11	254.4			*s*
245.6	−2.5			15	248.1	*ss*
233.6	−3.4	12	237.0			*ss*
217.4	−0.9	13	218.3			
197.0	−1.3	14	198.3			

of Appleyard,[9] Rasetti,[10] Spinks,[11] Tschulanowsky and Watson and Koontz were used to obtain a least squares solution for B''. The result of this computation yields for the ground state of N_2:

$$B_0 = 2.0007 \pm 0.0027 \text{ cm}^{-1},$$
$$\alpha = 0.01869 \pm 0.00017 \text{ cm}^{-1}.$$

The analysis of the $v' = 0$ bands presents nothing new except a confirmation of Tschulanowsky's designation of this state as a Σ-state. The previous designation of Π by Watson and Koontz was due to an almost exact superposition of the P and R branches in the bands which they measured.

Since the data for the $v' = 1$ level are of some interest, they are presented in detail. Tables IV, V and VI give the observed and calculated wave numbers of the rotational lines of the various bands. The calculated values used in finding the observed-calculated values are taken as the center of the P and R branch lines. Strong lines are weighted twice.

The lines with even J are observed to be strong, except in the blending of weak and

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[9] E. T. S. Appleyard, Phys. Rev. **41**, 254 (1932).

[10] F. Rasetti, Phys. Rev. **34**, 367 (1929).

[11] J. W. T. Spinks, Can. J. Research **20**, 1 (1942).

strong lines in the P and R branches. Unusually strong lines are indicated by s or ss. Blends of the two branches are, in general, diffuse.

Tschulanowsky gives for the b' state

$$B_0' = 1.144 \text{ cm}^{-1}, \quad B_1' = 1.142 \text{ cm}^{-1}.$$

The close agreement with our values is good reason for assigning the bands observed in this work to the b' state.

5. Vibrational Structure

As a further check on the assignment of these bands to the $b'-X$ system, let us consider the vibrational structure. The present data plus those of Tschulanowsky and Watson and Koontz are shown in Table VI. All wave numbers refer to band origins. For the bands of $v'=2$, 3, the origins have been calculated from band head measurements. This undoubtedly introduces an error.

The bands measured in this work fit so well in the Deslandres table that there can be no doubt that they are the vibrational level $v=1$ of the b' state.

To find the vibrational constants of this state, the following procedure was adopted. The energy levels of the ground state of N_2 are rather well known. Knowing these values, the energy of each vibrational level of state b' measured from $v=0$ of the ground state may be found. We thus obtain the following vibrational energies with their probable errors (see Table VII). Solution gives:

$$E_0 = 103{,}678.9 \pm 0.3 \text{ cm}^{-1},$$
$$\omega_0 = 746.9 \pm 0.6 \text{ cm}^{-1},$$
$$\omega_0 x_0 = 4.82 \pm 0.23 \text{ cm}^{-1}.$$

These values are in good agreement with those of Tschulanowsky except for E_0 (he gives 103,767.1 cm^{-1}). However, Tschulanowsky's value for E_0 is obtained by an extrapolation from his data, and since the N_2 ground state ΔG *versus* v is no longer a straight line in the region of these data, the extrapolated value of E_0 is bound to be wrong.

If terms in v^3 are included, the vibrational constants change quite radically.

6. Discussion of Results

TABLE V. Summary of data on $b'\ {}^1\Sigma_u^+$ state of N_2 (in cm^{-1}).

Band	B'	Probable error	ν_0	Remarks
0–10			81,672.0	
0–11	1.149	0.020	79,632.2	
0–12	1.158	0.015	77,618.6	
0–13	1.151	0.010	75,634.7	
0–14	1.143	0.003	73,679.0	
0–15	1.140	0.003	71,744.4	beyond accurate plate calibration
av.	1.143	0.002		
1–7	1.146	0.008	88,711.7	
1–8	1.143	0.003	86,583.4	
1–9	1.145	0.010	84,484.2	
1–10	1.141	0.008	82,412.7	
1–11	1.144	0.003	80,374.2	
1–12	1.137	0.008	78,362.9	
1–13			76,380.0	
av.	1.143	0.001		

We may now use the accumulated spectroscopic data to construct potential energy curves for the b' and ground state of N_2. These potential energy curves are shown in Fig. 4. The potential energy curve for b' has been found using a Morse function, which is a rather good approximation near the potential minimum. In the ground state, however, we are interested in the shape of the potential curve up to $v=21$. Over this range a Morse curve is badly in error. The broken line curve is a Morse function for the ground state of N_2, while the solid line gives a corrected potential curve as given by Hulbert

TABLE VI. Deslandres table for the system $b'-X$ of N_2.

$v'' \backslash v'$	0		1		2		3
4					95,996.3		
5					93,778.8		
6					91,594.8		
7			88,711.7	734.5	89,446.2		
8			86,583.4	735.6	87,319.0		
9			84,484.2	731.4	85,215.6		
10	81,672.0	740.7	82,412.7	734.8	83,147.5	723.8	83,871.3
11	79,632.2	742.0	80,374.2	738.1	81,112.3	715.9	81,828.2
12	77,618.6	744.3	78,362.9				79,811.1
13	75,634.0	746.0	76,380.0				77,832.6
14	73,679.2						
15	71,755.9						
16	69,863.4						
17	67,992.9						
18	66,163.5	741.6	66,905.1				
19	64,358.4	740.6	65,099.0				
20	62,583.2	741.6	63,324.8				
21	60,839.3	739.8	61,579.1				

TABLE VII. Vibrational energies of the b' state (in cm^{-1}).

Energy	First difference	Second difference
$E_0 = 103{,}678.8 \pm 0.4$		
	742.5 ± 0.6	
$E_1 = 104{,}421.1$ 0.5		11.4 ± 1.5
	731.1 1.4	
$E_2 = 105{,}152.4$ 1.3		7.0 2.1
	724.1 1.6	
$E_3 = 105{,}876.5$ 1.0		

and Hirschfelder.[12] The difference is appreciable for high vibrational states.

An important point to note in the upper state is the large spread in the eigenfunction (about 1.2–1.7A). Because of this width, we obtain a very long $v'=0$ ground state progression, extending from $v''=4$ through 21. The ground state progression from the $v'=1$ level should be of about the same length, although in this case there should be some bands missing at the center of the progression. If we assume that the Birge and Hopfield c state is $v=1$ of b', then the observed bands are 1–5 through 1–14, and 1–18 through 1–21. Thus again we get good qualitative agreement. The observed intensity maximum is around $v''=9$. This also agrees qualitatively with the Franck-Condon principle.

If we apply the Franck-Condon principle to $v=2$, 3, we would predict additional bands, especially in the neighborhood of 2–20 and 3–5, 3–20. It is planned to look for these bands at a later date.

We conclude that qualitatively the intensity distribution is given by the Franck-Condon principle, thus offering another check on the identification of the vibrational levels of the b' state.

One additional point should be noted. To obtain the emission spectrum $b'-X$ it is necessary to populate state b from the ground state of N_2. Since the vibrational levels in the ground state are about one quarter of a volt apart, by far the great majority of the N_2 molecules are in the zero vibrational state. The probability of an upward transition $v''=0 \rightarrow b$ is rather small, because of the very low value of the overlap integral. Also any absorption of light representing a downward transition from b' to a high vibrational level of the ground state will be vanishingly small because of the small population of these high lying levels. Thus the observed intensity will depend primarily on transitions from $v''=0$ to the b' state. Since the probability of these transitions is small, we would expect the over-all intensity of these bands to be small compared with other electronic transitions. This point is verified by noting that in emission the intensity of the $b'-X$ system is not too far from the intensity of the $a-X$ system of bands. But, as shown by Herzberg,[13] the $a-X$ transition is a forbidden transition in that it is $g-g$, and it thus has a smaller intensity than an electric dipole transition by a factor of 10^4.

It now remains to correlate the $v=1$ level of the b' state with other observed states. There are three other known states of N_2 of about the same energy. They are:

(a) p' (Gaydon[14])
$E = 104{,}327.9\ \mathrm{cm}^{-1}$ $B = 1.93\ \mathrm{cm}^{-1}$
(b) c (Worley)
$E_R = 104{,}365.6$ $B = 1.92$
$E_Q = 104{,}316.1$

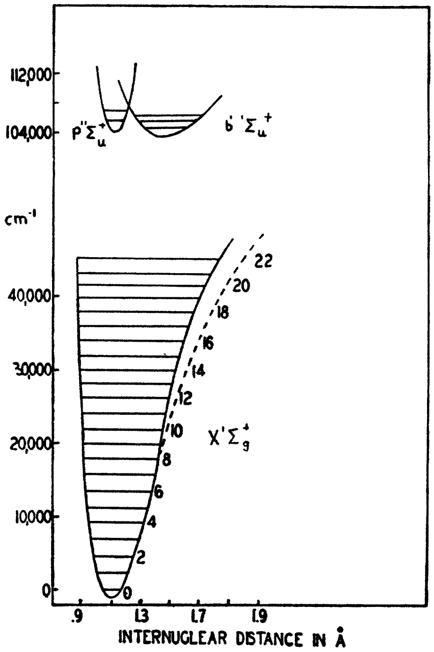

FIG. 4. Potential energy curves for the b' and X states of N_2.

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[12] H. M. Hulbert and J. O. Hirschfelder, J. Chem. Phys. 9, 61 (1941).

[13] G. Herzberg, Phys. Rev. 69, 362 (1946).

[14] A. G. Gaydon, Proc. Roy. Soc. A182, 286 (1944).

(c) c (Birge and Hopfield)
$E_R = 104{,}394.6$
$E_Q = 104{,}318.7$

As far as states p' and c (Worley) are concerned, the B values preclude any possibility of their being $v=1$ of b'. Furthermore, it seems highly probable that these states are identical, now that Worley's c state cannot be identified with the rather long ground state progression of $v'=1$. If Gaydon's data, verified by Janin,[15] are used to calculate the position of the head of the $0-0$ band of $p'-X$ and also the position of the first strong lines of the P branch, one obtains:

$$\nu_{\text{head}} = 104{,}377 \text{ cm}^{-1}, \quad \nu_P = 104{,}320 \text{ cm}^{-1}.$$

The agreement between these values and Worley's c state is good, especially since the head is formed by lines somewhere around $J=30$, where the intensity has begun to fall off. It should be noted that the observation of the transition $c-X$ in emission is almost impossible, because of the large self-absorption.

The difficulty in correlating Birge and Hopfield's c state with the first vibrational level of b' lies in their observation of the $c-X$ system as double-headed bands. These measurements were taken at low dispersion (15A per mm) and thus would be expected only to reproduce the gross features of these bands. In our higher dispersion spectrograms, the $v'=1$ progression appears as two unusually strong lines surrounded by many weak ones, the intensity falling off away from these lines. Qualitatively one would expect that under low dispersion these bands would appear as symmetrical doublets, as observed by Birge and Hopfield.

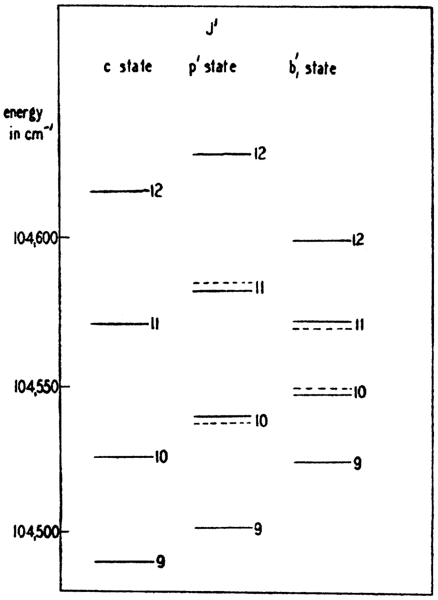

FIG. 5. Perturbing levels of the p' and b' states. For comparison, the rotational levels of the c state are shown. If this state is distinct from p', then a different set of perturbations in b' would be found.

TABLE VIII. Rotational levels of the p' and b' states (in cm⁻¹).

J	(p' state)	(b' state)	Diff.
9	104,501.7	104,524.0	22.3
10	104,540.2	104,546.8	6.6
11	104,582.7	104,572.0	−10.7
12	104,629.0	104,599.4	−29.6

7. Perturbations between p' and b'

The explanation of this intensity anomaly follows. Gaydon's p' state (or Worley's c state) is a ${}^1\Sigma_u{}^+$ state and thus has the proper symmetry to perturb the $v=1$ level of b', which is also ${}^1\Sigma_u{}^+$. Perturbation will only occur for equal J values in the two states. Moreover, to be noticeable, the energy difference between the two states must be small. The rotational levels of the p' state are given by:

$$\nu = 104{,}327.9 + 1.93J'(J'+1),$$

while the rotational levels of $b'(v=1)$ are given by:

$$\nu = 104{,}421.1 + 1.143J'(J'+1).$$

Table VIII gives the calculated values for rotational levels 9, 10, 11, and 12.

According to Table VIII, we would expect maximum perturbation for $J'=10$, 11, with rapidly decreasing effects on either side of these values. Moreover, since the perturbation depends on the overlap of the eigenfunctions involved, we would expect a rather small effect, since the overlap integral is small, as in the case of the ground state and b'. Figure 5 shows the perturbed (broken-line) and unperturbed positions of these levels.

The probability of a transition from the ground state ($B=2.007$ cm⁻¹) to the p' state ($B=1.93$ cm⁻¹) is high, since the internuclear separation

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[15] J. Janin, Ann. d. Physik 1, 538 (1946).

is about the same for the two states. Because of the perturbation between p' and b', we expect the perturbed levels of b' to have a population above normal. Thus transitions from these levels will not only be displaced, but will show up as unusually strong lines. Note that lines originating from these levels in the R branch are $J_R=9$, 10, while those in the P branch are $J_P=11$, 12.

Because of the blending of the two branches near the head, it is not possible to detect any perturbation in this region. However, the strong intensity lines agree well with those for $J_R=9$, 10. The line with $J_R=10$ is by far the most prominent. This, however, may be due to better line separation.

An examination of Table IV shows that in all cases the measured energy for the lines $J_P=11$ is greater than the calculated value, while the reverse is true for $J_P=12$. The average observed minus the calculated value of $J_P=11$ is 2.6 ± 0.8 cm^{-1}, while for $J_P=12$ the difference is -2.5 ± 0.5 cm^{-1}. This is in good qualitative agreement with prediction. The $J_P=12$ lines are the stronger.

An additional factor to note is the large deviations shown for the lines assigned as $J_R=15$. These lines are also unusually strong, as are their neighbors $J_P=11$, 12. It appears probable that the assignment $J_R=15$ is incorrect. The lines should be assigned to transitions from the $J=10$, 11 levels of the p' state.

The average difference between these lines and the perturbed $J_P=11$ lines is 11.4 ± 0.8 cm^{-1}. The $J=10$ level of the p' state is 11.8 cm^{-1} lower than the corresponding level of b', and gives rise to a line 11.8 cm^{-1} lower than $J_P=11$. This agrees well with the predicted value 11.4 cm^{-1}. The average difference from the perturbed $J_P=12$ line is 11.6 ± 0.4 cm^{-1}. The $J=11$ level of the p' state is 15.7 cm^{-1} higher than the corresponding level in b', and gives rise to a line 15.7 cm^{-1} higher than $J_P=12$. Again this agrees well with the calculated value, 11.4 cm^{-1}. Because of the proximity of these two lines, originating in the p' state, they are not resolved, but appear as a single line of high intensity.

Transitions from the p' state to high vibrational levels of the ground state would not ordinarily be possible because of the very small value of the overlap integral, but as a result of the mixing of first approximation eigenfunctions, the overlap integral for the perturbing and ground state may have an appreciable value. The large population of the p' state would then imply an appreciable intensity for these lines. Confirmation of the above interpretation is supplied by the works of Gaydon and Janin. The former, in analyzing the transitions from the p' state to the $a\,{}^1\Pi_g$ state, remarks that the rotational structure cannot be analyzed beyond $J'=10$ because of the strong perturbations at this point. Janin's data for the p' state (which he called c) also show perturbations for these levels. Tschulanowsky also shows perturbations for $J'=10$, 11, although he had no unusually strong lines, since the right-hand side of the potential curve from which his transitions take place is not overpopulated, as is the left, because of the short life of these levels. He observes no transitions from the p' state, since, again, such transitions would involve much larger changes in internuclear distances than are observed here.

We have seen that there are two groups of strong lines in the bands arising from transitions $v=1$ of b' to the ground state. The centers of these groups are about 40 cm^{-1} and 120 cm^{-1} from the band heads. The violet edges of these groups are about 35 cm^{-1} and 110 cm^{-1} from the heads, or at

$$\nu=104{,}386\text{ cm}^{-1},\quad \nu=104{,}311\text{ cm}^{-1}.$$

These values are in good agreement with Birge and Hopfield's values for the two heads of their c system.

8. Conclusions

Birge and Hopfield's c state is in reality the $v=1$ level of the b' state. Since Worley's c state would produce a different set of perturbations than are observed here, we believe that this state is identical with Gaydon's p' state.

9. Acknowledgments

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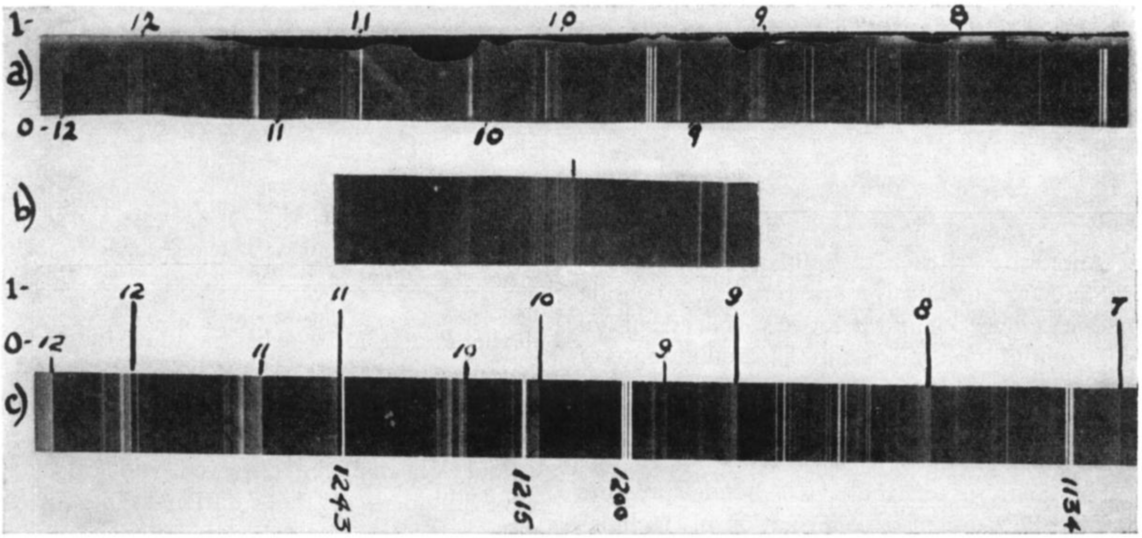

FIG. 3. Spectrograms of the $b'-X$ system of N_2; (a) Spectrograms 1 and 2 (actual size)—note the intensity alternation in the b_0' progression and the peculiar intensity distribution of the b_1' progression; (b) enlargement (3.4×) of the 1–9 band to show rotational structure; (c) Spectrogram 3—focus not as good as in spectrograms 1 and 2, but much higher intensity. Note the many rotational lines as compared with a.