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Absorption Spectrum of N_2 in the Extreme Ultraviolet[1]

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The absorption spectrum of N_2 that corresponds to excited states in the range $12.2-17.0$ ev has been investigated at large dispersion. Data are presented for a very extensive Rydberg series of bands, which are interpreted and correlated with previous observations. The ionization potential of N_2 corresponding to the series limit is 15.577 volts. Absorption beyond this point is complete for a path of $\sim$0.5 mm atmos. From λ995 to λ815 the spectrum is well developed at $\sim$0.2 mm atmos. Here most of the absorption is due to bands that show an open rotational structure which could usually be analyzed to give values of $B'-B''$. Several such bands above λ920 are correlated with the known states b and b'. In general the internuclear distance, r_e', was found to increase with energy, up to values 40 percent larger than for the normal state. Vibrational constants are unexpectedly small ($\omega'/\omega''<\frac{1}{3}$), and the ratio ω'/B' is about half the nearly constant value (Birge-Mecke rule) found for all the lower states of N_2. There is some evidence that the coupling in a few of the more excited states represents a transition toward Hund's case d'.

INTRODUCTION

STUDIES of absorption in the extreme ultraviolet have furnished valuable information on the higher electronic states of diatomic molecules, but the existing data are still meager. My own investigation of the N_2 bands in the region λλ1015–730 has led to a number of interesting results, the details of which have not previously been published.

For purposes of orientation, the electronic scheme of the singlet states of nitrogen is given in Fig. 1. The a state was discovered from Lyman's[2] early measurements of the ultraviolet spectrum in 1911, and with the extension of this work in 1928 by Birge and Hopfield,[3] the states b, b', and c were added. In 1930, Hopfield[4] reported the absorption bands analyzed in this paper and gave data on two Rydberg series of bands at shorter wave-lengths. Both series, one in absorption and one in emission, have since been observed by others,[5] and the absorption series was interpreted by Mulliken[6] so as to give a spectroscopic value of the ionization potential of N_2. New ground state progressions reported in 1934 by Watson and Koontz[7] were designated d, e, g, f, and h, but of these Tschulanowsky[8]

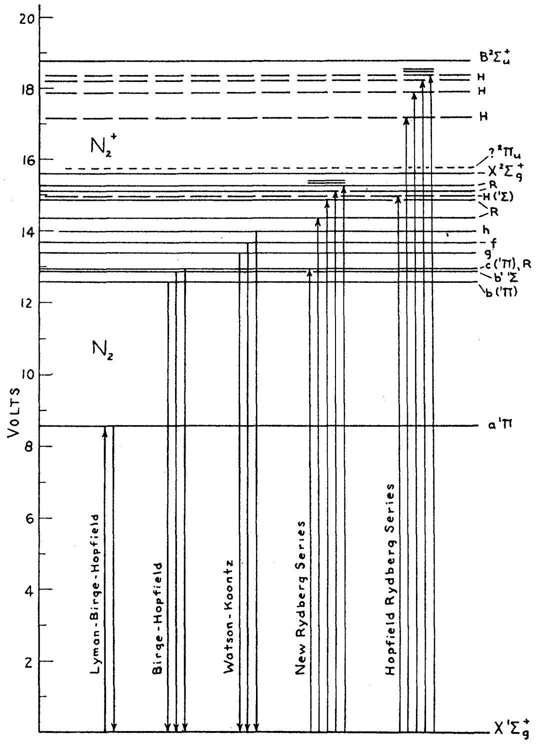

FIG. 1. Rydberg terms, and previously known singlet states, of N_2. The excited terms corresponding to the progressions of Fig. 2 lie between 12.5 and 15.3 ev (Fig. 4).

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[1] For further details, see R. E. Worley, Thesis, University of California, 1940. The present article includes revisions and supplemental material.

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[2] T. Lyman, Astrophys. J. **33**, 98 (1911).

[3] R. T. Birge and J. J. Hopfield, Astrophys. J. **68**, 257 (1928).

[4] J. J. Hopfield, Phys. Rev. **35**, 1133 (1930); **36**, 789 (1930). Cf. also ref. 3, p. 274.

[5] T. Takamine, T. Suga, and Y. Tanaka, Sci. Pap. Inst. Phys. Chem. Res. Tokyo **34**, 854 (1938).

[6] R. S. Mulliken, Phys. Rev. **46**, 144 (1934).

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

[8] W. M. Tschulanowsky, Bull. Acad. Sci. U.S.S.R. Classe d. sci. math. et nat., p. 1313 (1935). The results are briefly tabulated in ref. 1, p. 68a. Cf. also, W. M. Tschulanowsky and S. I. Gassilewitsch, Physik. Zeits. Sowjetunion **12**, 83 (1937).

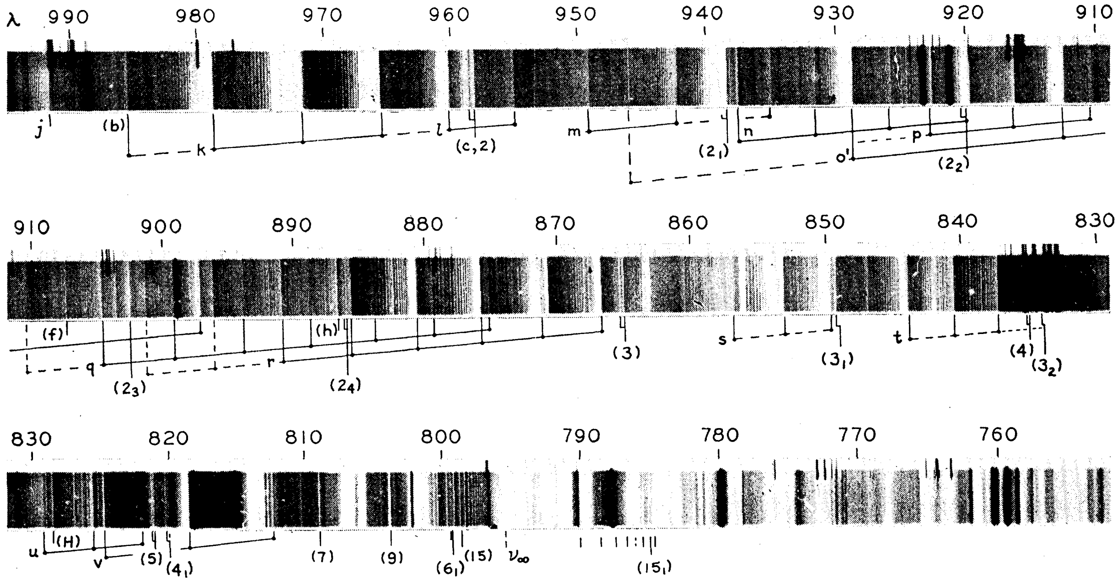

FIG. 2. Far ultraviolet absorption spectrum of N_2 (positive, 5.7×). Bands that have been grouped in progressions are joined by sloping lines. Rydberg bands of the main series ($v'=0$) are shown by parenthesized integers; subscripted integers refer to bands having $v'>0$.

ascribed d and e to the vibrational levels $v'=2$ and 3 of state b'. The Σ nature of this state was also established by Tschulanowsky, while the Π character of the a state is indicated by several investigations.[7, 9]

The first result of the present study was the announcement of a new Rydberg series[10] converging to the normal state of N_2^+. Some of the Rydberg terms are shown in Fig. 1, and it is now found that the lowest is the c state of Birge and Hopfield. Numerous bands that do not form obvious series of the Rydberg type will for convenience be referred to as "non-Rydberg." Several of these are interpreted as transitions to vibrational terms of states b and b', but the majority involve new electronic states. The partial rotational analysis obtained for many of the bands will be considered after discussing the Rydberg series.

EXPERIMENTAL

Apparatus

The vacuum spectrograph employed a three-meter grating of aluminized speculum, ruled 15,000 lines to the inch, and mounted at a grazing angle of 7.0°. This arrangement gave a dispersion of better than 2A/mm in the region investigated. The instrument was focused with precision, and correct grating apertures[11] were provided. An improved Lyman discharge tube used as source of the continuum has been described elsewhere,[12] but it may be noted here that the design largely avoids the usual mechanical difficulties, and that it was feasible to use a narrow slit (~0.02 mm) as required for good resolution.

Nitrogen used for absorption was prepared from sodium azide,[13] and stored in a large glass tank. Before an exposure, the spectrograph was thoroughly flushed, and the gas was then passed through in a slow, steady stream. As helium (purified) was generally used in the discharge tube, this gas was also present in the spectrograph. A condensed discharge through tank helium,

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[9] E. T. S. Appleyard, Phys. Rev. **41**, 254 (1932). Cf. also G. Herzberg and H. Sponer, Zeits. f. physik. Chemie **26**, 1 (1934), footnote p. 2.

[10] R. E. Worley and F. A. Jenkins, Phys. Rev. **54**, 305 (1938). The indicial lines above Fig. 1 of this reference are in error. These higher members of the series are shown well, also, on a plate taken by other workers (reference 25), who used a helium source.

[11] R. O. Anderson and J. E. Mack, J. Opt. Soc. Am. **24**, 292 (1934), with the earlier papers listed therein. References to slit illumination are included.

[12] R. E. Worley, Rev. Sci. Inst. **13**, 67 (1942).

[13] Erich Tiede, Ber. d. D. Chem. Ges. **49**, 1742 (1916). I found it safe to decompose powdered azide with a low bunsen flame, if the azide was held in a nearly horizontal Pyrex tube (2-mm wall), protected from the main system by elbows filled with glass wool.

which contained traces of argon in air, provided a good comparison spectrum.[12]

Plate Material

Data for the initial report of the new Rydberg series were taken from exposures made with an earlier form of discharge tube,[14] with nitrogen in the source as well as in the receiver, and the reduction was based on a few lines of O II and O V that appeared with the continuum. The subsequent improvement in technique netted a distinct gain in actual resolution and permitted a more accurate reduction of the data. Both Ilford Q II and Hilger Schumann plates were employed, but most of the final measurements are taken from a single Schumann plate of unusually fine definition, reproduced in Fig. 2. The equivalent path of N_2 in this case was about 0.2 mm atmos., or one two-thousandths of the path used by Birge and Hopfield[3] in photographing the $a-X$ absorption bands. The spectrum shows no trace of contamination by O_2,[15] and very few atomic absorption lines of significant intensity are present. Absorption by helium in the source so weakened the continuum below λ505 that its 2nd order caused no obscuration in the region studied.

A comparator with a least count of 1μ was used to measure all plates, and the reduction was effected by linear interpolation between values of λ calculated quadratically for each millimeter. A final correction was based on the comparison spectrum of the individual plate.[1] In view of the care taken, it is probable that the absolute error for absorption lines rarely exceeds 0.02A,[1] while the relative error was about a tenth as great in favorable cases. The uncertainty in the relative position of band heads was about 0.01A, as judged from the consistency of two sets of readings.

RESULTS

Measurements of band heads, and of regions of diffuse absorption, were carried out for the range λλ1015–734. Except for higher members of the main Rydberg series (Table II), these results are collected in Table I. An arbitrary symbol in the first column designates the group to which a band is assigned, while eye estimates of intensities (0 to 15) are given in the second. The third and fourth columns contain λ_{vac} and ν_{vac}, respectively. As explained later, it was in many cases possible to obtain $-C=B''-B'$ from the rotational structure [Eqs. (1) and (3)]. This value, and the ratio $r'/r''=(B''/B')^{\frac{1}{2}}$, are given in columns five and six.[16] Incidental remarks appear in the last column. Here the letters *V* and *X* refer, respectively, to longer (violet) and shorter (x-ray) wave-lengths, while the symbols (*d*), *d*, and *dd* represent increasing degrees of diffuseness of band heads. Data beyond the Rydberg series limit are arranged somewhat differently, as explained in the table. Most bands beyond $R_1(16)$, and those indicated by a dagger, were recently measured at the Mt. Wilson Laboratory, on a comparator kindly made available by Dr. A. S. King.

RYDBERG SERIES

Very striking in Fig. 2 is the group of closely spaced, converging bands, lying between λ801 and the O II emission line λ797. These are the higher members of the series, whose limit at λ795.8 is indicated by ν_∞. With the identification of its first five members—raising the number of reliably measured bands to over twenty—this molecular Rydberg series is the most extensive thus far reported. The bands are all shaded toward longer wave-lengths, and are characterized by absence of resolved rotational structure. Lower members—indicated by Rydberg integers, *m*, in parentheses—show two heads of about equal intensity, but these draw together and are unresolved beyond $m\sim 8$. Where measurable, both heads are listed in Table I [$R_0(m)$ and $R_0'(m)$], and their separation $\Delta\nu_h$ is given in Table II. In the latter table, wave numbers of the more prominent short wave-length heads are listed for all observed members of the series.

With the new data it was possible to improve slightly the value of the series limit ν_∞ and to derive a Ritz formula to fit all but a few heads

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[14] H. P. Knauss and S. S. Ballard, Phys. Rev. **48**, 796 (1935).

[15] The strong O_2 band λ983.1, faintly present on some of the earlier plates, is clearly absent. [Cf. W. C. Price and George Collins, Phys. Rev. **48**, 714 (1935).]

[16] Cf. ref. 37. An inferior digit in column five usually indicates an average deviation of at least 5 units in the last place.

TABLE I. Absorption bands of nitrogen, λλ1015–734 (Plate *B*59).

Group	Int.	$\lambda(A)$	$\nu(\text{cm}^{-1})$	$B''-B'$	r'/r''	Remarks
i	0^-	1015.37	98,486	—	—	Rotational structure not discernible.
—	0	08.95	9,113	—	—	Center of narrow, unshaded band. (N_2?)
i	0	08.52	9,155	—	—	Head (partially masked). Open rotational structure.
i	0^+	01.74_6	9,826	—	—	Head. Open rotational structure.
—	00	00.16_3	9,984	—	—	Faint, narrow band, shaded *V*. (N_2?)
—	0^-	994.23	100,580	—	—	Center of narrow, unshaded band. (N_2?)
		Preceding bands, from Plate *B*45 (higher pressure). Absent from Plate *B*59.				
j	2^+	991.853	100,821.4	0.54_5	1.17_3	
b, *k*	2	85.649	1,456.0	0.58	1.19	
k	10	78.87	2,158	0.58_5	1.19	(*d*) (Cf. Table IV.)
k	15	72.0_7	$2,87_3$	0.59	1.19	*dd*. Interpolated from Pl. *B*69 (lower pressure). (Cf. Table IV.)
k	12	965.63	3,559	0.580	1.187	(*d*) (Cf. Table IV.)
k(*l*)	7	0.206	104,144.4	0.508	1.158	
c $R_0'(2)$	3	958.625	$316._1$	0.077	1.020	$B''-B'$, estimated from $\Delta\nu_h$.
$R_0(2)$	2	8.170	365.6			
k(*l*)	2	5.076	703.7	0.52	1.16	
m	2	949.221	105,349.6	0.63	1.21	
[*o'*]	1	6.123	694.5	—	—	
m	3	2.386	106,113.6	0.64	1.21^+	
$R_1(2)$	8	938.57	545	—	—	(*d*)
. .	—	8.314	574.1	—	—	Strong blend in λ937.7. (Reference line.)
n	2	7.654	649.2	0.81	1.30	Apparent head. (Cf. Table IV.)
. .	0	7.20	70_0	—	—	Center of narrow, unshaded band on Pl. *B*45. (N_2?)
[*m*]	1	5.147	935.1	—	—	
n	1^-	1.727	107,327.6	0.83^-	1.31^-	
o'[*p*]	6	928.876	657.0	—	—	(*d*)
n	1	5.926	108,000.0	0.80_5	1.29_5	(*d*)
p	2	2.746	372.2	0.78_5	1.28_4	
—	½	0.73_2	609	—	—	Faint head (?).
$R_2'(2)$?	¼?	0.46	641	—	—	Questionable (overlaid).
$R_2(2)$; *n*	3^+?	0.04_1	$690._8$	—	—	Overlaid by λ919.8.
—	1^+?	919.846	713.9	—	—	
p	3	6.416	109,120.8	0.78	1.28	
o'	5	2.622	574.4	—	—	(*d*)
p[*q*]	1^-	0.475	832.8	—	—	
f	1	907.453	110,198.5	—	—	
q	2	4.731	530.1	0.88	1.34	
—	1	3.637	664.0	—	—	
$R_3(2)$	2	2.578	793.7	—	—	
[*r*]	1^-	1.352	944.5	—	—	
q	2	899.196	111,210.5	0.90	1.35	
o'	3	7.185	459.8	—	—	
[*r*]	1^+	6.192	583.3	—	—	(*d*)
q	1	3.863	873.9	0.92	1.36	
r	2	0.949	112,239.8	0.92_0	1.36_3	
q	½	888.81	51_0	—	—	Head very indistinct.
h	2	6.694	778.5	—	—	
$R_4'(2)$?	0^+	6.24_6	$835._5$	—	—	Line-like (questionable).
$R_4(2)$	¼	6.030	863.0	—	—	Line-like.
r	2	5.657	910.5	—	—	
q	½	3.90_6	$113,134._2$	0.9_4	1.38^-	
. .	—	2.966	254.7	—	—	Strong blend in λ880.7. (Reference line.)
r	4	0.723	543.1	0.93_5	1.37_2	(*d*) Rotational perturbation at λ882.5 (text)
q	¼	879.47	705	—	—	
r	3^+	5.869	114,172.3	0.94_5	1.37_9	(*d*)
q	¼	5.24	254			
r	3?	1.40?	758	0.94^-?	1.37	Obscured by λ870.7. (Cf. Table IV.)
—	1^+?	0.744	844.3	—	—	
r	3	866.761	115,372.1	0.91^+	1.36	(*d*) Seemingly overlies another band.
$R_0'(3)$	1	5.324	563.6	—	—	
$R_0(3)$	1	5.060	598.9	—	—	
—	1	3.171	851.9	—	—	
—	1^-	0.511	116,210.1	—	—	
(*s*)	2^+	856.98	689	0.88	1.34	Head indistinct. (Cf. Table IV.)
—	2^-?	6.004	821.8	—	—	Overlapped by λ853.2.
(*s*)	5	3.190	117,207.2	0.93_5	1.37	(*d*)
(*s*)	4	849.714	686.6	1.03?	1.44?	*d*, overlaid by λ849.3.
$R_1'(3)$	1^+	9.302	743.7	—	—	

TABLE I (*Continued*)

Group	Int.	λ(*A*)	ν(cm⁻¹)	$B''-B'$	r'/r''	Remarks
—	1^+	846.930	118,073.5	—	—	
(*t*)	3^+	3.972	487.3	0.8_3?	1.31?	
..	—	2.860	643.7	—	—	Last *V* line, region of irregular absorption.
..	—	2.05_5	$757._1$	—	—	*V* edge of complete absorption.
..	—	1.873	782.8	—	—	*X* edge, same. (Band head?)
(*t*)	3	0.552	969.4	—	—	
(*t*)	2^+	837.314	119,429.5	0.95_0	1.38_2	
$R_0'(4)$	1?	5.16_0	$737._6$	—	—	Obscured by O III emission line.
$R_0(4)$		4.951	767.6	—	—	
?	$\frac{1}{2}^+$	4.52	829†	—	—	*V* edge, O II line. Open rotational structure at ∼λ836 indicates head near this entry.
$R_2'(3)$?	$\frac{1}{2}$	4.11	888	—	—	Head indistinct.
—	$\frac{1}{2}$	2.00	120,192	—	—	
(*u*)	1^-	829.293	584.6	0.92	1.36	
H	1	8.550	692.8	—	—	
?	$\frac{1}{4}$	6.20	121,036†	—	—	Questionable head.
—	$\frac{1}{4}$	5.97_9	$068._5$			Questionable (overlaid).
(*u*)	1?	5.64_6	$117._3$			Open but confused structure, associated with one or both heads.
—	1?	5.575	127.7			
..	—	5.223	179.4			Line-like absorption.
(*v*)	1	4.76_4	$246._8$			*X* edge of narrow band. Weak absorption extends to preceding "line."
—	$\frac{1}{2}$	3.36	454			Interpolated from Pl. *B*45. (Open rotational structure.)
(*u*)	0	2.12	636			Interpolated from Pl. *B*45.
$R_0'(5)$	$\frac{1}{2}$	1.240	767.1			
$R_0(5)$	$\frac{1}{2}$	1.110	786.4			
$R_1'(4)$	$\frac{1}{2}^-$	0.234	916.4			
$R_1(4)$?	0^+	0.04_6	$944._4$			
—	3^+	818.66	122,151			*V* head interpolated from Pl. *B*69 (lower pressure). If single band, rotational structure is compact.
(*v*)		8.534	169.6			
..	—	5.689	595.7			Line-like absorption.
—	4?	3.6_3	90_5			Interpolated from Pl. *B*69 (lower pressure). Indication of rotational structure near λ814.5.
[$R_0(6)$]	—	3.515	923.3			Calc. position. Overlaid.
?	1^-?	3.33	952			Narrow band (?). Overlaid.
—	1?	3.02_9	$996._8$			Narrow band (?).
..	—	2.755	123,038.3			Center, narrow band (unshaded).
(*v*)	1	2.366	097.2			*X* edge, narrow band.
..	—	0.84	329†			Line-like absorption.
..	—	0.312	409.3			Line-like absorption.
$R_0'(7)$	1^-	808.96_7	$614._4$			Poorly resolved.
$R_0(7)$		8.90_9	$623._3$			
—	5	6.43	124,004			*d*. Questionable traces of rotational structure near λ807.5.
[$R_0(8)$]	—	5.901	084.7			Calc. position. Overlaid.
?	2	5.72_5	$111._8$			Probable head.
—		5.605	130.3			Definite head.
..	—	4.484	303.3			Line-like absorption.
$R_0(9)$	1^+	3.81_3	$407._2$			
$R_0(10)$	—	2.33	637			*V* edge of O IV emission line.
$R_0(11)$	—	1.21	811			Overlaid by diffuse absorption.
$R_0(12)$	$\frac{1}{2}^+$?	0.352	945.0			Tail, overlaid by diffuse absorption.
$R_0(13)$	$\frac{1}{2}^+$	799.681	125,049.8			
$R_1'(6)$?	0^+	9.47	083			
$R_1(6)$	0^+	9.38_0	$096._9$			
$R_0(14)$	$\frac{1}{2}$?	9.155	132.2			Tail, overlaid by $R_1(6)$.
$R_0(15)$	$\frac{1}{2}^-$	8.723	199.8			

For *R*(16) to *R*(26), see Table II. Following these bands on Plate *B*59 (Fig. 2) is a short region of strong, diffuse absorption, with a slight rise in background at ∼126,030 cm⁻¹. Weaker, general absorption extends a great distance toward shorter wave-lengths, with a weak maximum at ∼λ720. Above λ734 a number of structureless bands, many of them with diffuse heads but nearly all shaded to longer wave-lengths, are in evidence.

The following wave numbers refer to heads (*X* edges) of such bands, except as otherwise noted. The very narrow, faint bands that are members of the $v'=1$ Rydberg series are designated "$R_1(m)$." A rough estimate of the width of broad bands is given in the first column, and an index of completeness of absorption (1 to 5) is entered in the second. Bands that are in evidence on Plate *B*69 (lower pressure) are indicated by an asterisk. When they were measured only on this plate, the fact is indicated by a leading entry "*B*69," under "Remarks." Band widths and intensities refer always to plate *B*59.

TABLE I (*Continued*)

Width (cm^{-1})	Absorp. (*B*59)	ν(cm^{-1})	Remarks
—	—	125,789*	*B*69, line-like absorption (traces).
—	—	126,113*	*B*69, line-like absorption.
—	(4)	306*	*B*69, strong band. (Possible 2nd head, ~40 cm^{-1} toward *V*.)
—	—	437*	*B*69, narrow band. (Cf. next entry.)
—	3	454	*d*, *B*59. Indistinct edge of seemingly continuous absorption.
—	—	$481._1$	Narrow band.
—	—	$579._4$	$R_1(9)$.
150	5	$698._7$*	*d*. Extends to O IV 790.2; 790.1 is absent. (Diffuse on *B*69.)
—	—	$741._0$	Faint, narrow band.
—	—	$816._0$	$R_1(10)$.
—	—	$987._5$	$R_1(11)$.
—	—	$127{,}118._9$	$R_1(12)$.
120	4	251*	*d*. (Diffuse on *B*69.)
—	—	$306._1$	$R_1(14)$.
—	—	$373._7$	$R_1(15)$.
—	—	$428._7$	$R_1(16)$.
80	3^-	517	*dd*. This and next head, questionable.
50	3^-	603*	*dd*. (Strong, but diffuse, on *B*69.)
60	3^-	732	*dd*.
—	—	128,054*	*B*69, distinct head.
200	3	100	*d*. Masks previous head.
20^-	2	157	Center of narrow, diffuse band.
200	2	462*	Head (*V* edge of 3rd order C IV 259.47). (Weak on *B*69.)
(220)	(4)	94_2*	*B*69, strong band.
>140	3	129,082*	*d*. Masks previous band. (Faint, narrow, on *B*69.)
—	—	105	Faint, line-like absorption in wing of O V 774.5.
—	—	129	Sharp, line-like absorption, super-posed on O V 774.5 ("self-reversed" appearance).
(240)	(2)	581*	*B*69, head. (*V* edge of 4th order O V 192.91.)
—	—	651*	*B*69, head (?). (*V* edge of 4th order O V 192.80.)
40	1	980*	Center, diffuse band. (Very faint on *B*69.)
80	2^+	130,249*	*d*. (Very faint on *B*69.)
160	4	606	*V* edge (absent on *B*69).
		768*	*d*. *X* edge of same band. (Sharp, 15 cm^{-1} smaller, on *B*69.)
160	3	878	Diffuse *V* edge.
		984*	*B*69, weak head (sharp).
		131,034	Diffuse *X* edge.
—	—	069	Narrow band (sharp head).
—	—	44_4*	*B*69, head (?).
>230 (?)	5	477	Head, or *V* edge of O V 760.44. Absorption extends to O V 762.00; obscures O V 761.13.
—	—	543	Fine, line-like absorption (traces); "splits" O V 760.23.
>70 (?)	3	625	Sharp head (precedes edge of O V 759.44).
>80 (?)	3	910*	Sharp head.
60	3^-	132,135*	
100	2^-	373	Questionable (sharp, but overlaid).
(200)	(2)	59_0*	*B*69, diffuse head.
>70	2^-	657	Masks previous entry.
40	2	791*	(Very faint on *B*69.)
120	2	133,002*	(Traces, 100 cm^{-1} toward *V*, on *B*69.)
<10	—	076	Center, very narrow band.
20^-	1^+	118	Head, narrow band.
30	2	202	Head.
<10	—	240	Center, very narrow band.
100	2	37_0	Questionable head (overlaid).
>130	2^+	508*	Sharp head.
—	0^+	572	*V* edge of weak absorption.
100	2	688*	*V* edge, stronger absorption.
		792*	Head (*V* edge of 2nd order O III 373.80).
70	3	967*	*d*. Contrast, very poor beyond this point.
220	3	134,400	Head (?).
30	2	498	*V* edge (?).
		530	*X* edge.
—	—	671	Line-like absorption, traces.
—	—	723	Line-like absorption, traces.
10	—	775	Center, narrow band.
120 (?)	1	860	*d*. Head (?).
—	2^-	975	*d*. *V* edge (?).
>80 (?)	2^-	$135{,}61_0$*	Head (?). (Very faint on *B*69.)
>120 (?)	2	136,169*	Head. (Very faint on *B*69.)

within the accuracy of measurement.[17] The residuals shown in Table II under $\nu^{\text{obs}}-\nu^{\text{calc}}$ were obtained from

$$\nu^{\text{calc}}=125{,}665.8-R/(m+0.3450-0.1000/m-0.100/m^2)^2,$$

with $m=2, 3, \cdots$ and $R=109{,}735$ cm^{-1}. Inasmuch as the measurements on lower members do not represent band origins, the small discrepancies in these cases are of no consequence.

The region of continuous absorption that follows the series limit, Fig. 2, corresponds to unquantized photo-ejection of an electron from N_2, and the limit itself gives, very precisely, an ionization potential of N_2. Its value, namely, 125,666 cm^{-1} = 15.577 volts,[18] agrees perfectly with the ionization potential obtained less directly by Mulliken.[6] He pointed out that the upper terms of Hopfield's absorption series very likely approach the $^2\Sigma_u^+$ state of N_2^+ as a limit (evaluated below), and that subtraction of the electronic energy of the $^2\Sigma_u^+\rightarrow{}^2\Sigma_g^+$ emission system[19] of N_2^+ should accordingly give the position of the $^2\Sigma_g^+$ state of N_2^+ relative to the ground state of N_2. The result, in this case, is 151,247 − 25,566 = 125,681 cm^{-1} or 15.579 ev. The limit of the new series represents the *lowest* ionization potential of N_2, if, as is believed, $^2\Sigma_g^+$ is the normal state of N_2^+.[20]

This state, $^2\Sigma_g^+$, is reached from $X^1\Sigma_g^+$ of N_2 by removal of a σ_g2p electron,[21c, 22] whose excitation therefore gives rise to the Rydberg terms. These should be of Π type, as the double-headed aspect of the first few bands may be attributed to the presence of R and Q branches. The excited orbitals appear then to be $np\pi$ (Rydberg notation), with $n=3, 4, 5\cdots$, since $3p\pi$ is the lowest orbital to which σ_g2p (i.e., $3s\sigma$) could be excited and yet give a firmly-bound Π state. Thus it is probable that these Rydberg terms are of the form

$$KK(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u2p)^4(\sigma_g2p)\cdot(np\pi)^1\Pi_u,\quad n=3, 4, 5, \cdots.$$

No *series* of levels having the corresponding configuration $3s3p^2np$ is reported for the united atom Si I (below), but a single $3p^3D$ term is listed by Kiess.[23] Since the effective quantum number is of the same magnitude as for the first of the above molecular terms, the level $n=3(m=2$, Table II) is the lowest one to be expected in N_2.

As previously mentioned, this lowest Rydberg term has been identified as the c state of Birge and Hopfield,[3] who obtained the heads (0−0 band) by extrapolation. My direct measurements give a value 30 cm^{-1} smaller for the R head, but sensibly the same result for the Q head. The long wave-length (Q) heads of the $c-X$ emission bands were found by Birge and Hopfield to give the best fit in an ω_v formula, and this circumstance, together with the appearance of the bands, led them to favor type Π for state c. The fact that the two heads in each absorption band draw rapidly together with increasing n is doubtless due to uncoupling of the orbital mo-

TABLE II. Heads of the new Rydberg series.*

m	ν^{obs}	$\nu^{\text{obs}}-\nu^{\text{calc}}$	$\Delta\nu_h$	m	ν^{obs}	$\nu^{\text{obs}}-\nu^{\text{calc}}$
2	104,365.6	−4.4	$49._5$	14	125,132.2	+0.2
3	15,598.9	+6.4	35.3	15	199.8	+0.5
4	19,767.6	−1.1	(30)	16	254.9	+0.2
5	21,786.4	−3.6	19.3	17	300.7	−0.1
6	(Table I)	—	—	18	339.0	−0.5
7	23,623.3	+0.6	8.9	19	371.9	−0.5
8	(Table I)	—	—	20	400.8	+0.2
9	24,407	+1.1	—	21	424.1	−0.7
10	4,637	(−1.2)	—	22	445.6	−0.3
11	4,811	(−0.7)	—	23	465.0	+0.6
12	4,945.0	+0.3	—	24	480.7	+0.1
13	5,049.8	+1.0	—	25	494.4	−0.5
				26	506.4	(−1.2)

* The bands for $m=6$, 8, 10, and 11 occur in regions of strong and seemingly diffuse absorption, but in the last two cases approximate wave numbers can be given (cf. Table I). The second head for $m=4$ is obscured by an emission line (O III). At $m=9$ (remeasured), the appearance still suggests two heads, but they are unresolved.

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[17] The procedure was to first compute μ, in the Rydberg denominator, from the reliable measurements on bands for which it was sensibly constant ($m=12$ to 25), and for which the position of a band origin should, as shown below, be indistinguishable from that of its head. The value of μ so found (0.342) then led to a very consistent set of values of ν_∞ (a.d.∼0.3 cm^{-1}). However, in order to include the lower members of the series, the variation in μ has been expressed in a three-constant form, found by graphical approximation.

[18] The revised conversion factor is used. [R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941).]

[19] M. Fassbender, Zeits. f. Physik **30**, 73 (1924). D. Coster and F. Brons, Zeits. f. Physik **73**, 747 (1932).

[20] One cannot altogether exclude the possibility that $^2\Pi_u$, known to be near $^2\Sigma_g^+$, is the normal state. (Cf. the brief remarks relative to $^2\Pi_u$, several paragraphs below, and again under *Absorption*, λλ*818–800*.)

[21] R. S. Mulliken, Rev. Mod. Phys. (a) **2**, 60 (1930); (b) **3**, 89 (1931); (c) **4**, 1 (1932).

[22] G. Herzberg, *Molecular Spectra* (Prentice-Hall, New York, 1939).

[23] C. C. Kiess, J. Research Nat. Bur. Stand. **21**, 185 (1938) [R.P. 1124].

mentum of the excited electron from the resultant momentum of the molecular core. Such a transition from case b' to case d' coupling is exemplified by the $(np\pi)^3\Pi \rightarrow (2s\sigma)^3\Sigma$ Rydberg bands of He_2.[24] By analogy, the heads of the higher members of the present series should give the positions of band origins very closely.

It is not surprising that Birge and Hopfield reported $c-X$ bands only in emission, as their spectrogram of the $a \leftarrow X$ system shows almost complete absorption below λ1020. When account is taken of the much smaller equivalent absorption path used in my case and of the difference in dispersion and in the number of bands observed (cf. third paragraph below), the transition probability for $c \leftarrow X$ appears to exceed that for $a \leftarrow X$ by a factor of 10^3 or 10^4. A reliable comparison however can hardly be made without photographing both systems on the same instrument, preferably at normal incidence.

Tanaka and Takamine[25] have reported several $v'=1$ bands of the new Rydberg series, and from them obtained a mean value of 2171 cm^{-1} for $\Delta G'(\frac{1}{2})$, as compared to 2175 cm^{-1} for the limiting state $^2\Sigma_g{}^+$ of $N_2{}^+$. I have subsequently identified several of the $v'=1$ bands on my own plates, but at the pressure used many of those with $m>4$ are overlaid by diffuse absorption.[26] My own data on these bands, indicated in Table I by the symbol $R_1(m)$, lead to the values of $\Delta G'(\frac{1}{2})$ shown in Table III. The intervals for $m=6$, 10, and 11 are based on computed heads for $v'=0$, but the last four and most reliable entries are seen to agree excellently with the expected value.

In contrast to the $v'=0$ bands, the appearance of the $v'=1$ bands for $m=3$, 4, and 6 (unobscured) shows that in these cases the R head becomes prominent only for $m>4$. Hence for $m=3$ and 4, the interval $\Delta G'(\frac{1}{2})$ has been formed with the Q head of the $v'=0$ band, rather than with the R head. Similarly, a weak band at λ834.1, if interpreted as a Q head for $m=3$, $v'=2$, gives 2144 cm^{-1} for $\Delta G'(\frac{3}{2})$, as compared to 2143 cm^{-1} for $N_2{}^+$.

The case of $m=2$, state c, is of special interest. The Q head for $v'=1$ could not be measured, but if the R head is again prominent, an intense band at λ938.6, Fig. 2, is just at the position expected for $v'=1$. In addition, heads are found corresponding to $v'=2$, 3, and 4, while for 2 and 4 there is indication of a Q head as well. The values of $\Delta G'$ (R heads) given by the five bands thus identified[27] would be 2180, 2146, 2103, and 2069 cm^{-1}. From these values, and from the $\Delta\nu_h$ interval for $v'=0$ (Table II), it has been possible to estimate ω_e and B_e, and so to plot the potential curve of state c (Fig. 4). r_0 is found to be the same as for $^2\Sigma_g{}^+$ of $N_2{}^+$, and to differ only slightly from r_0''—a situation ideal for the development of an extensive Rydberg series.

Professor Mulliken has reminded me that in addition to the Rydberg terms just discussed, which converge to $^2\Sigma_g{}^+$ of $N_2{}^+$, one may expect others that converge to $^2\Pi_u$, believed to lie slightly above $^2\Sigma_g{}^+$.[21] According to Mulliken's estimate[21] of 1.15A for r_e of $^2\Pi_u$, the strongest bands should have $v'>0$. Their identification would evidently give definite information regarding the relative positions of $^2\Sigma_g{}^+$ and $^2\Pi_u$.[20]

In correspondence, Mulliken has suggested that $a^1\Pi$ may be the lowest of the Rydberg states (derived from $^2\Pi_u$ by the addition of a σ_g electron). Nearly all bands involving higher terms would then probably be masked by stronger absorption (cf. above). On the other hand, were o' (Table IV) the lowest state, identification of higher terms would appear feasible, although even here most of them would be expected to fall below λ797 where they would not show to advantage on my plates. A cursory survey of this possibility has yielded no conclusive results.

Hopfield's Rydberg Series

For certain large energies of excitation, analogous term series are predicted for N_2 and the

TABLE III. Values of $\Delta G'(\frac{1}{2})$, for the Rydberg terms.

m	$\Delta G'(\frac{1}{2})$	m	$\Delta G'(\frac{1}{2})$
3	2180	11	(2176)
4	2179	12	2174
6	(2174)	14	2174
9	2172	15	2174
10	(2178)	16	2174

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[24] W. E. Curtis, Trans. Faraday Soc. **25**, 694 (1929).

[25] Y. Tanaka and T. Takamine, Phys. Rev. **59**, 613 (1941). The work was done at Berkeley on the spectrograph described above, but the helium continuum was employed as source.

[26] In Fig. 2, the notation (m_v) refers to Rydberg bands other than those of the main series.

[27] This interpretation revises an earlier grouping of some of the bands (ref. 1) [cf. *Group o'*].

united atom Si I (14 electrons).[21,22] Examination of the known singlet terms of Si I[23,28] shows that only those of the $3pns\,^1P_u$ series bear a close resemblance to the excited states of Hopfield's absorption bands.[29] By considering the (two) singlet molecular states derivable from a term of the atomic series, in conjunction with the configuration of the $^2\Sigma_u{}^+$ state of $N_2{}^+$ approached by the terms of Hopfield's series, it appears that the upper states of these bands have the configuration

$$KK(\sigma_g 2s)^2(\sigma_u 2s)(\pi_u 2p)^4(\sigma_g 2p)^2 \cdot (ns\sigma)\,^1\Sigma_u{}^+, \quad n=4,\,5,\,6,\,\cdots.$$

Mulliken[6] had already suggested that the excited orbitals may be $ns\sigma$, but that if so, Hopfield's data start with $n=5$, whence another band would be expected at longer wave-lengths. This band should have an unresolved rotational structure ($r_e'\sim r_e''$) and should show a single head ($^1\Sigma-{}^1\Sigma$). With my high dispersion plates, it seemed worth while to look for it, even though Hopfield's other bands—diffuse in nature due to pre-ionization and situated in a region of general absorption—were not in evidence. By setting $m=1$ in the Rydberg formula[30] $\nu_m=151{,}249-R/(m+0.907)^2$, the calculated wave-length is found to be 825.94A. Two or three heads lie very near this position, and at least one (λ825.98) is of a suitable character except for its low intensity. However, by the analogy with Si I, the band sought would be displaced toward longer wave-lengths. This consideration as well as that of intensity leads me to favor the narrow band with a single, sharp head at λ828.55 (H—Fig. 2).

Besides the series in absorption, Hopfield[4] reported one in emission. This series is also clearly in evidence on the more recent plates of Tanaka and Takamine, as well as in an earlier reproduction.[5] The fact that corresponding absorption and emission bands approach each other and possess the same series limit,[31] together with the close analogy that exists between the terms of the latter series and the $3pns\,^3P_u$ terms of Si I,[32] suggests that the upper states of both series arise from the same electron configuration. As n increases, progressive uncoupling of the spin of the excited electron is expected, and the distinction between the predicted $^1\Sigma$ and $^3\Sigma$ states would diminish. Absence of low pressure absorption to the $^3\Sigma$ states may be attributed to selection rules, which would still operate to some extent. At the same time, the emission bands may be accounted for by supposing that conditions in the source—a condensed discharge in helium, with traces of nitrogen present—result in the transfer of N_2 molecules to the hybrid $^3\Sigma$ states. It would be of interest to examine other regions of the spectrum from the same source to detect if possible transitions between the proposed $^3\Sigma$ terms and known triplet states of N_2. The procedures developed by Kaplan[33] to investigate metastable states might also be of use in testing my suggestion.

NON-RYDBERG BANDS

In the region λλ995–818 are a large number of discrete bands that are stronger and far more prominent than those of the Rydberg series, excepting $c\leftarrow X$. Although likewise shaded toward longer wave-lengths, these bands show in most cases a comparatively open rotational structure, indicative of a large internuclear distance in the excited states. As would be expected, many of these bands appear to form vibrational progressions. The assignments, however, could not be made with assurance by means of the usual criteria, for besides the shortness of several progressions, and an extensive overlapping in the region λλ940–870, the values of $\Delta G'$ were often irregular. At large energies, where many electronic states lie close together, and where a transition toward case d' coupling may in some instances result in an unusual band structure,[34] this is not surprising. It was very fortunate, therefore, that the rotational constant B', which should be uniform for bands of one progression, could often be determined. Above λ865, nearly all of the groupings of Fig. 2, designated by small letters in accordance with precedent,[7,1] have been

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[28] A. Fowler, Proc. Roy. Soc. London **A123**, 422 (1929).

[29] Including the new band (below), the effective quantum numbers in Si I exceed those in N_2 by 0.20, 0.23, 0.24, 0.23, 0.24, (0.18) for $n=4$ to 9. (Ref. 1, p. 59.)

[30] This formula reproduces Hopfield's observations ($m=2$ to 6) with residuals of +11, −9, 0, 0, (+38) cm⁻¹.

[31] The formula $\nu_m=151{,}244-R/(m+0.107)^2$, with $m=3$ to 6, yields residuals (Hopfield's data) of −55, +1, 0, 0 cm⁻¹.

[32] For the $^3P_1$ levels, the effective quantum numbers are nearly identical (ref. 1).

[33] Joseph Kaplan, Phys. Rev. **54**, 176 (1938).

[34] Cf. ref. 21(b, c), §F3.

TABLE IV. Probable vibrational progressions of N_2 absorption bands.

Group	State	B'	ν_h	$\Delta\nu_h$
i	(Pl. B45)	—	98,486	
				669
		—	9,155	
				671
		—	9,826	
k,	$b\,^1\Pi$	1.41	101,454	
				698
		1.41	2,152*	
				709
		1.40	2,861*	
				693
		1.41_2	3,554*	
				588
l	(text)	1.48_4	4,142	
				560
		1.47	4,702	
m	(text)	1.36	105,347	
				764
		1.35	6,111	
				(822)
		—	(6,933)	
n	$b'\,^1\Sigma$	1.18	106,640*	
				686
		1.16^{+}?	7,326	
				672
		1.19^{-}	7,998	
				(691)
		—	(8,689)	
o'	(text)	—	(105,693)	
				(1962)
		—	7,655	
				1918
		—	9,573	
				1885
		—	11,458	
p	$^1\Pi$	—	(107,655)	
				(715)
		1.21^{-}	8,370	
				749
		1.21	9,119	
				712
		—	9,831	
q	$^1\Pi$	—	(109,831)	
				(697)
		1.11	10,528	
				681
		1.09	1,209	
				663
		1.07	1,872	
				63_8
		—	$2,51_0$	
				62_2
		1.05?	3,132	
				572
		—	3,704	
				55_0
		—	$4,25_4$	
r	$^1\Sigma$	—	(110,943)	
				(639)
		—	(1,582)	
				(657)
		1.07	2,239	
				670
		—	2,909	
				633
		1.06^{-}	3,542	
				629
		1.05^{-}	4,171	
				607
		1.06^{-}?	4,778*	
				592
		1.08	5,370	
More doubtful progressions				
s	$^1\Sigma$	1.11	116,683*	
				522
	$^1\Sigma$	1.06	7,205	
				479
	$^1\Pi$?	0.96?	7,684	
	$^1\Pi$?	1.1_6?	118,486	
				482
	—	—	8,968	
				460
	$^1\Sigma$	1.04	9,428	
				(460)
	(text)	—	(9,888)	
u	$^1\Sigma$	1.07	120,583	
				533
		—	1,116	
				519
		—	1,635	
v	—	—	121,245	
				923
		—	2,168	
				928
		—	3,096	

* Calculated from rotational data.

substantiated by this test. The groups o', s, t, u, and v are, as will be explained later, more questionable, but including these, it will be seen that very few bands are unaccounted for.

The assignments to progressions are shown in Table IV.[35] Where possible, the probable type of excited electronic state is indicated, and values of B' for individual bands are listed. Except for the o' group, or for bands affected by case d' coupling, $\nu_h-\nu_0$ is not expected to exceed 6 cm^{-1}; $\Delta G'$ is then given very closely by the interval between heads ($\Delta\nu_h$). The unusual smallness of these intervals will be considered later.

Determination of the Rotational Constant B'

Even with excellent definition, the rotational structure was not sufficiently resolved to permit an accurate determination of both B_v' and B_0'' by applying combination differences in the usual manner.[36] From selection rules, however, either a two-branch or a three-branch band structure is expected, while, because of unit nuclear spin of the N atom, there is an alternation of intensity in each branch, strong lines being associated with an even parity of J''.[21, 22] The simplicity of structure, combined with the feature of alternation as a guide in assigning J values, made it possible to evaluate the *difference* $B_v'-B_0''$ with considerable assurance. B_v' was then obtained from the previously known value of B_0''.[37]

As an illustration of the data available, Table V gives the measurements on one band of type $^1\Sigma-{}^1\Sigma$, and one of type $^1\Pi-{}^1\Sigma$.[38] It will be seen that for the most part, these data represent the positions of blends formed by two branches that run parallel in $^1\Sigma-{}^1\Sigma$ bands, or nearly parallel in $^1\Pi-{}^1\Sigma$ bands. This feature is typical, and the procedure usually followed in evaluating $B'-B''$ is based on the assumption that the measurements represent mean positions of the components in such blends or "line-pairs".[39] Only occasionally was it feasible to measure isolated branches, such as the R branch in bands of group k, or Q lines in one of the p bands.

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[35] The (rounded) data for Table IV, and for Table VI below, were obtained in the course of rotational measurements (Table V), when the cross hair was set on the estimated position of head-forming lines. These wave numbers of heads are consistently 1 to 3 cm^{-1} lower than those given in Table I.

[36] To effect a complete rotational analysis would doubtless require photographing the spectrum with a six-meter grating, ruled 30,000 lines to the inch, and surfaced for high reflectivity [G. B. Sabine, Phys. Rev. **55**, 1064 (1939)].

[37] In this paper, the value 1.992 cm^{-1} is used for B_0'' [F. Rasetti, Phys. Rev. **34**, 367 (1929)]. The value 1.998 cm^{-1} given by Watson and Koontz (ref. 7) was obtained from measurements of partially fused lines, with Λ-doubling neglected, while the value 1.994 cm^{-1} given by Tschulanowsky (ref. 8) depends on a long extrapolation.

[38] For more complete measurements, see ref. 1. (Estimates of line intensities given there in a few cases refer, actually, to the relative contrast of neighboring lines or blends.)

[39] Although the components were seldom resolved over the measurable range, their (computed) separation averaged about ten times the least count of the comparator. Hence mean positions could be read quite reliably, at least in that majority of cases in which the components were of equal parity in J, and thus of comparable intensity.

A preliminary value of $B'-B''$ was found from the slope of a plot of first differences, so adjusted as to reduce to zero near the band head. The procedure is illustrated in Fig. 3 for the $^1\Sigma-{}^1\Sigma$ band listed in Table V. Since $B''>B'$ in all these cases, the positive quantity $-C\equiv B''-B'$ is used. This graphical solution, as well as Eq. (1), below, assumes that terms beyond J^2 in the rotational energy functions may be neglected. The second difference in the wave numbers of any branch of a band is then $2(B'-B'')$, or $2C$.[40]

The final values of $-C$ listed in Table I were usually obtained algebraically, as follows. Let $\Delta\nu(J)$ represent the observed difference corresponding, in the case of $^1\Sigma-{}^1\Sigma$ bands, to the combination difference $\Delta_2F'(J)$, while the integer m gives the relative numbering of the lines in a blend ($J_R=J_P+m$ for any line-pair). $\Delta\nu(J)$ may then be equated to the mean of the differences $R(J)-P(J)$ and $P(J-m)-R(J+m)$. By substituting the usual quadratic expressions for the wave numbers of P and R lines,[41] and eliminating B' in favor of C, one finds

$$-C=\Delta\nu(J)/m(2J+1). \qquad (1)$$

The value of m, needed for application of Eq. (1), is most easily determined by noting that the appearance of a band as regards intensity alternation can be predicted from the preliminary value of $-C$. The alternation will be pronounced for m even, but hardly detectable for m odd. For exact coincidence, the width of blends, namely,

$$\Delta_{RP}(J)\equiv R(J_P+m)-P(J) \\ =[2B''+C(m+2)](2J+m+1),$$

must vanish. The values of $-C$ for the pertinent cases are: 0.996 and 0.664 for $m=2$ and 4, respectively; 0.797 and 0.569 for $m=3$ and 5. In the band λ991.9, for example, $-C\sim 0.55$ cm^{-1} (Fig. 3) and as no intensity alternation is observed one sees that m can only be 5. A tentative assignment of $J\equiv J_P$ is made by equating some specific first difference, taken from the plot, to the separation of successive lines in the P branch, namely, $P(J)-P(J+1)=2B''-2CJ$. Alternation, if present, furnishes a partial check, but in any case a correct assignment should lead by Eq. (1) to a series of consistent values of $-C$. The results found in this way not only provide a refinement upon the graphical solution, but give an indication of the uncertainty as well. Thus, in the example cited, a mean of 0.545 cm^{-1} was obtained with residuals averaging 0.005 cm^{-1}.

As a final check, or as a means of detecting questionable data, values of the band origin may be calculated from the revised value of $-C$ and the mean wave number, ν_J, of blends. For R–P pairs, with $J\equiv J_P$,

$$\nu_0=\nu_J-CJ(J+m+1) \\ -[(m+1)/2][2B''+C(m+2)]. \qquad (2)$$

Referring again to the band λ991.9, the 17 measurements of ν_J gave $\nu_0=100{,}816.1$ cm^{-1} with an average deviation of 0.4 cm^{-1}. The head should be formed by $R(2)$, 5.4 cm^{-1} beyond. Hence $\nu_h^{\text{calc}}=100{,}821.5$ cm^{-1}, as compared to $\nu_h^{\text{obs}}=100{,}821^-$ cm^{-1} (Tables I and V).

TABLE V. Sample rotational measurements.
λ991.87, $^1\Sigma-{}^1\Sigma$. No intensity alternation of $R-P$ blends: $J_R=J_P+5$.

J_P	ν^{obs}	Remarks	J_P	ν^{obs}	Remarks
—	100,819.9	Head.	12	110,698.3	
3	801.0	indistinct owing to strength of absorption	13	80.9	
4	792.9		14	62.7	components barely resolved
5	84.9		15	43.9	
6	76.1	sharp	16	24.1	
7	66.0		17	02.6	
8	54.6		18	579.3	
9	42.0		19	56.2	
10	29.1		$R(21)$	625.5	
11	14.6		$P(16)$	618.7	

λ965.65, $^1\Pi-{}^1\Sigma$. Marked intensity alternation of $P-Q$ blends: $J_Q=J_P+2$. R branch resolved for $J_R\geq 18$. (s designates a strong blend or line.)

J_P	ν^{obs}	Remarks	J_P	ν^{obs}	Remarks
—	103,557.4	Head.	24	103,127.5	s
(10)	455.7	blended with $R(15)$	25	(094.3)	mean (below)
(11)	39.7	blended with $R(16)$	26	59.3	s
(12)	23.6	blended with $R(17)$	27	—	
12	25.7	s	28	102,987.3	s
13	07.6		$Q(27)$	103,096.2	trace
14	388.6	s	$P(25)$	092.3	trace
15	68.2		J_R	ν^{obs}	Remarks
16	46.6	s (broad)	18	103,399.8	s?
17	23.4		19	79.4	
18	299.5	s	20	58.0	s?
19	73.9		21	36.3	
20	47.6	s	22	12.2	s?
21	19.2		23	287.2	
22	190.2	s $\Delta_{PQ}\sim$ 4.0 cm^{-1}	24	61.2	s?
23	59.3		25	31.0	

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[40] Cf. ref. 21, 22, or W. Jevons, *Report on Band Spectra* (The Physical Society, London, 1932).

[41] If the terms involving D' and D'' are included (ref. 40), the right-hand side of Eq. (1) will contain the correction $-2(D'-D'')J(J+1)$. Except for the k-group bands (below), there was no clear evidence for the need of such a term, but for $D'>D''$, its neglect will in general cause the value of $-C$ to be somewhat too large.

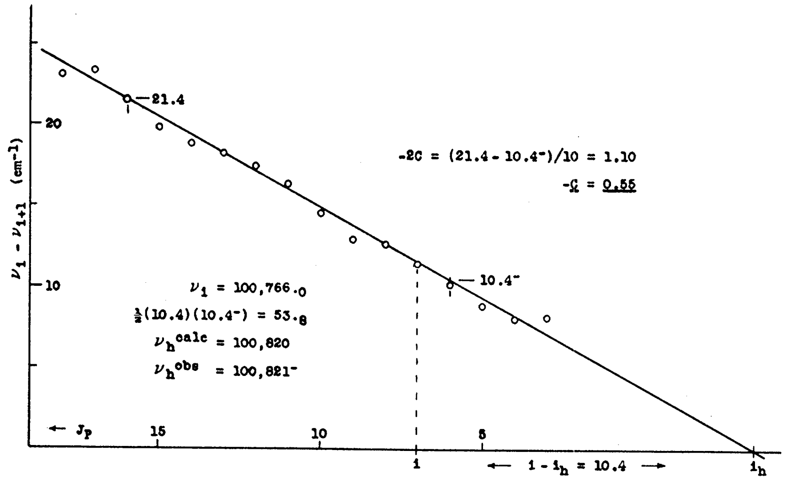

FIG. 3. First differences of $R-P$ blends for λ991.9($^1\Sigma-{}^1\Sigma$). The locus is tested by extrapolation to ν_h from an observed blend, ν_i, as illustrated:

$$\nu_h = \nu_i + \tfrac{1}{2}(i - i_h)\Delta\nu_{i-1}.$$

The J numbering may be obtained after approximating $-C$ from the slope (text).

The procedure for $^1\Pi-{}^1\Sigma$ bands was similar, although more involved. In this case, the graphical solution is subject to the ambiguity introduced by Λ-doubling,[40] and by the fact that the Q branch actually forms a different parabola from the P or R branch. Most frequently, measurable blends consisted of P–Q pairs,[42] and while P and Q lines do not run parallel at low J values, the algebraic method could be applied to advantage over the range encountered, usually $J_Q \sim 10$ to 25. Let $\Delta\nu(J)$ again represent the observed difference, equated in this case to the mean of $Q(J)-P(J)$ and $P(J-n)-Q(J+n)$, where n gives the relative numbering of the components in a blend ($J_Q = J_P + n$). In substituting the expression for P and Q branches, one now distinguishes between the two sets of rotational levels due to Λ-doubling by using B_d' and B_c', respectively. When these two constants are eliminated in favor of $q = B_d' - B_c'$,[22] and of $-\bar{C}$, the mean of $B''-B_d'$ and $B''-B_c'$, one finds

$$-\bar{C} + (q/4)(n+1)/J = [\Delta\nu(J) - nB'']/2nJ. \quad (3)$$

It is significant that for the values of J_P involved, the q term may be neglected without appreciable error, and that to this approximation $-\bar{C}$ is independent of the Λ-doubling.

The width of blends is in this case given by

$$\Delta_{QP}(J) = 2B''J + 2\bar{C}(n+1)(J+n/2) - q[J(J+n) + n(n+1)/2],$$

while band origins were computed from

$$\nu_0 = \nu_J - \bar{C}[J(J-1) + (n+1)(J+n/2)] + B''J + \tfrac{1}{2}q(n+1)(J+n/2), \quad (4)$$

where, as usual, J refers to the P component of a blend. The values of $-\bar{C}$ that minimize Δ_{QP} are here given only approximately ($J_P \gg n$, $q=0$). For $n=2$ (pronounced alternation), $-\bar{C} \sim 0.66$, while for $n=1$ (alternation absent), $-\bar{C} \sim 1.00$. It can be seen that in certain instances the slope of the first-difference curve, together with the presence or absence of alternation, not only gives the value of m or n for use in Eqs. (1) or (3), but provides a criterion of the band type—whether it is $^1\Sigma-{}^1\Sigma$ or $^1\Pi-{}^1\Sigma$.

The procedures just described are based on rotational formulae for bands involving states in which the coupling is not unusual. It is therefore of interest to note that in most cases they were found to be quite appropriate. In fact, it was only by the use of Eq. (3) that a reliable value of $-\bar{C}$ was found for bands of the prominent k group, of which λ965.6 (Table V) is the best example. Here the individual values found from Eq. (3) showed a pronounced trend with J, and only the average was in agreement with the plot of first differences. Since the J numbering was almost certainly correct ($J_Q = J_P + 2$, with even parity for strong blends), the observed trend could only be explained by including the term $DJ^2(J+1)^2$ in the rotational energy functions—a refinement that was applied only in the case of these intense bands, where the values of J encountered were

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[42] Difference in intensity of the components would render the method inaccurate for $R-Q$ pairs.

rather large ($J_Q = 12$ to 32). The significant correction to Eq. (3) consists of a term $-2(D'-D'')J^2$, to be added to the right member,[43] so that if the values originally found are plotted against J^2, they extrapolate to $-\bar{C}$ at $J^2=0$. In this case, $-\bar{C}$ was found to be 0.580 cm^{-1} instead of the original estimate of 0.61 cm^{-1}.[44] The slope, $2(D'-D'')$, was 5.3×10^{-5} cm^{-1}, in reasonable agreement with the harmonic oscillator approximation[22] of 3.4×10^{-5} cm^{-1}. The Λ-doubling in the upper state appears to be small, as a measured estimate of 4.0 cm^{-1} for $\Delta_{QP}(22)$ gave for q the rough value -0.001 cm^{-1}.

The same band, λ965.6, afforded a nice external check of consistency. As is seen in Table V, a number of resolved R-branch lines could be measured, and with these one may form the combination differences

$$\begin{aligned} R(J-1)-P(J+1) &= \Delta_2F''(J) \\ &= (2J+1)[2B''-D''(2J+1)^2]. \end{aligned}$$

Values of $P(J+1)$ were obtained from observed frequencies of P–Q blends corrected by $\frac{1}{2}\Delta_{QP}$, and the small constant D'' was taken as 0.6×10^{-5} cm^{-1} (harmonic oscillator approximation). The six available differences gave $B''=1.990$ cm^{-1}, with residuals averaging 0.008 cm^{-1}, in complete agreement with Rasetti's value of 1.992 ± 0.005 cm^{-1}.[45]

The v' Progressions

Before giving a brief account of the individual groupings of Table IV, it should be noted that an unambiguous correlation with known singlet states of N_2, Fig. 1, seemed rather unlikely. A large internuclear distance for the excited states led me not to expect the $0-0$ band in most cases; yet except for state b' (a is not considered here because of the lower $a\leftarrow x$ transition probability), levels with $v'>0$ had not previously been identified. Nevertheless it was found that a number of the bands could be attributed to vibrational levels of states b and b'. In order to present most simply the basis of correlation, and also to facilitate reference,[1] it has seemed best to retain the original group designations (k, l instead of b; n instead of b') in the following discussion. At the end, it is shown that two isolated bands of compact structure may probably be assigned to levels f and h.

Group i consists of three bands that appeared faintly only at perhaps twice the pressure used to photograph the other bands. Measurement of rotational structure was not feasible, but the intensities and intervals suggest the grouping.

Group j. The band at λ991.9 has been cited as an example of a $^1\Sigma-{}^1\Sigma$ transition. Although of moderate intensity, it is left uncorrelated with any other band, since the weaker one at λ985.6, designated j originally,[1] is here assigned to the k group.

Group k is the most prominent progression in the entire spectrum. It was just the high intensity of the bands that prevented measurement at intermediate J levels and thus led at first to erroneously large values of $-\bar{C}$. The appropriate correction explained for λ965.6 was applied to the other two strong bands, with satisfactory but less precise results.[46]

It may be seen in Fig. 2 that the head of the strongest band, λ972, is very diffuse. The absorption in fact extends some 50 cm^{-1} beyond the calculated position of the head, which agrees with the position shown on a plate taken at a reduced pressure. This distance seems too great to attribute to the wings of head-forming lines ($J_R=1$, 2, 3), but the peculiarity remains unexplained. A minor irregularity was observed also in the band λ978.9, where an unexpected line at 101,823 cm^{-1} appears to be $R(25)$, in abnormal strength.

The high intensity of the k bands suggests that in their case the $0-0$ transition should be observed, in spite of the large value of r_e'. The weaker band at λ985.65, while it does not fit perfectly into the usual sequence of ω_v and B_v

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[43] Following Herzberg (ref. 22), I have taken $D>0$.

[44] In view of the approximations involved in my treatment, least-squares solutions seem unjustified. However, if the corrective term is added to each apparent value of $-\bar{C}$, deviations from 0.580 cm^{-1} average less than 0.002 cm^{-1}. Use of the refinement in calculating ν_0 from the pairs $J_P=12$ to 26 led to values with an a.d. of only 0.2 cm^{-1}.

[45] In two bands of $^1\Sigma-{}^1\Sigma$ type, *viz.*, λ890.9 and λ857.0, combination differences were applied directly. In these cases B'' averaged 1.990 cm^{-1}, but the mean average residual was 0.025 cm^{-1}.

[46] The ratio of theoretical intensities (ref. 21) for the Q and P components of a pair was plotted for blends in the range of measurement, and found to vary between extremes of 1.8 and 0.6. Thus a quantitative basis for the use of mean wave numbers, above, was established for bands of the k group.

values,[47] is of nearly the strength expected. Its correlation with the *k* group would be of unusual significance, as its position agrees with that calculated by Birge and Hopfield[3] for the origin of the *b–X* system (985.52A). Three of the strongest bands in the entire spectrum would by this identification involve the levels $v'=1$, 2, and 3 of state *b*.

Group l. Relative intensities suggest that this pair of bands is a continuation of group *k* which otherwise would terminate abruptly. The original segregation of the *l* bands[1] was based on a sharp break in the sequence of ω_v and B_v values and on the fact that these bands, in contrast to those of group *k*, do not show intensity alternation in the rotational structure. Both effects, however, may be explained in terms of a perturbation resulting from the near approach of two electronic states of the same species.[22] The magnitude of Λ-doubling is in fact indicative of a perturbation. First attempts to analyze the band λ960.2 failed, but use of Eq. (3) to obtain the average of B_c' and B_d' with but slight dependence on doubling led to remarkably consistent results.[48] An estimate of pair widths then gave approximately -0.02 cm^{-1} for *q*. This large value would account for the observed absence of intensity alternation as it implies the blending of *P* and *Q* lines of different parity ($J_Q=J_P+3$). The band intensities, together with these considerations, thus make it reasonable to identify the upper terms of the *l* bands with the $v'=4$ and 5 levels of state *b*.

The perturbation may perhaps be attributed to $c^1\Pi$, as its potential curve, near minimum, is expected to approach closely that of state *b* near $v'=3$ (Fig. 4). There are still slight irregularities in the values of ω_v and B_v below $v'=3$, and the unprecedented intensity distribution reported by Birge and Hopfield[3] for the *b–X* emission bands ($v'=0$) remains unexplained. It should be remarked that the emission bands appear to be very narrow,[3, 8] whereas the value of r'/r'', Table I, suggests a pronounced shading.

Group m. The two measured bands, although of but moderate strength, show intensity alternation. However, the type of transition is still ambiguous, as the value of $-C$ shows that lines of the same parity (*P* and *R*, or *P* and *Q*) would form blends whether the upper state is $^1\Sigma$ or $^1\Pi$. Inclusion of a faint third band is plausible, but implies a large irregularity in $\Delta G'$ (Table IV).

Group n. The value of $-C$, taken in conjunction with the appearance of blends and the regularity of structure at low *J* values, clearly indicates a $^1\Sigma-{}^1\Sigma$ band type. It was found that the wave numbers of heads are in essential accord with predicted vibrational levels of state *b'*, shown in the upper row of Table VI. These values were obtained by using Birge and Hopfield's[3] calculated position of the $0-0$ band, in conjunction with Tschulanowsky's[8] vibrational function, *viz.*, $G(v')=745.42v'-4.16v'^2$. In the lower row, the wave numbers for $v'=2$ and 3 are those of levels *d* and *e*,[49] and the remaining four values represent *n* bands.[50] While the agreement is poor at $v'=4$, this may probably be attributed to inhomogeneity of the data, especially as the vibrational function is itself based on the work of different observers.[7, 8] My designation of the upper state as $^1\Sigma$ is in accord with Tschulanowsky's analysis of emission bands from the levels $v'=0$ and 1, but my value for *B'* is a few percent *larger* than his. Although the correlation is very plausible, it is to be noted that whereas the intensity at $v'=4$ would lead one to expect a band at smaller wave numbers, I find no indication of a head corresponding to $v'=3$, even on a plate (*B*45) taken at a higher pressure.

Group o'. Two of the bands formerly assigned[1] to a group designated *o* are now identified with vibrational terms of state *c*. The remaining two are included in group *o'*. This new arrangement is favored by a more uniform variation of intensity, while the large values of $\Delta G'$ are, as before, consistent with compactness of rotational structure.[51]

Group p. The first unobscured band, at λ922.7,

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[47] The faintness of λ985.6 prevented a reliable evaluation of B_v'.

[48] For $J_P=9$ to 17, the *spread* in calculated values of ν_0, Eq. (4), was but 0.2_5 cm^{-1} (least count of comparator).

[49] I have extrapolated levels *d*, *e*, *g*, *f*, and *h* from Watson and Koontz' data (ref. 7), by use of a least-squares solution for $\Delta G''$.

[50] The wave number of the last *n* band is presumably a few units smaller than that of the Rydberg head $R_2(2)$ used here. Note that an unassigned head at 108,712 cm^{-1} does not fit the *n* progression (Table IV).

[51] As r_e' is not much greater than r_e'', the *o'* minimum, Fig. 4, was located by assuming $v'=0$ for the strong band λ928.9. However, a much weaker band at λ946.1, since it about fits the progression, may well be the $0-0$ band. If so, the minimum should be lowered to 104,700 cm^{-1}, while $\omega_e\sim 2000$ cm^{-1}.

TABLE VI. Vibrational terms of state b'.

$b'\ ^1\Sigma$, v'	0	1	2	3	4	5	6	7
$\nu^{\text{calc}}-10^5$	3678	4419	5152	5877	6593	7301	8001	8692
$\nu^{\text{obs}}-10^5$	—	—	5147	5868	6640	7326	7998	(8689)

provided rather complete measurements, from which the Π character of the upper state was established. Near the head, P, Q, and R lines were blended ($J_Q=J_P+1$, $J_R=J_P+3$), but beyond $J_P=10$ the Q branch was resolved from R–P pairs. From the latter, $-C_d\equiv B''-B_d'$ was computed by Eq. (1), while with the added measurements of Q lines, $-\bar{C}$ could be found as well. Comparison indicates small Λ-doubling, as the values of $-C_d$ and $-\bar{C}$ were nearly equal. An unexplained feature is the intensity of some Q lines as compared to neighboring R–P blends, for in about half the cases, the computed ratio was inverse to that observed. In the next band only two or three Q lines were resolved, but a regular fluctuation in the first differences of measured blends could be attributed to alternation of intensity in the Q branch. The last band was fitted only by its intensity and position.

Group q. Although of but moderate intensity, these bands form a regular and fairly long progression. The strongest, at λ904.7, consisted of a series of blends of moderate intensity ($J_Q=J_P+1$), between which were faint but measurable traces of sharp lines (R branch). While it was not feasible to evaluate $-C_d$ accurately or to form a reliable estimate of q, measurements of R lines were used in connection with those of P–Q blends to confirm the value of $-\bar{C}$ given by Eq. (3). Measurements were carried out on three weaker q bands, but in these, a resolved R branch was not observed. Generally speaking, the computed intensities of successive blends agreed with observation.

Group r. At least six bands, several of them quite strong, comprise this group. The high intensity of the last two members, however, seems to be due to other, overlying absorption. A long parallelism of branches, and the values of $-C$ coupled with the width of blends and the alternation of intensity, point clearly to a $^1\Sigma-{}^1\Sigma$ band type. P and R branches were in fact measured separately in one case (λ890.9), but a precise determination of both rotational constants was not feasible.[45]

There is a marked perturbation of rotational structure in the band at λ880.7, that had not formerly been traced in detail. Diminished intensity, and confusion due to a q band at λ883.9, prevented following the branches beyond $P(20)$, but the sharp lines $R(17)$ and $P(19)$ both indicate a deviation of 10 cm^{-1} for the level $J'=18$ (term value $\sim 113{,}900+10$ cm^{-1}). However, when deviations of P and R lines were plotted separately against J', a considerably more rapid and larger rise was obtained for the R than for the P branch. Such an effect is not consistent with a single set of levels in the upper state, yet it seems to be too pronounced to attribute to incomplete resolution.[52]

The well-developed band at λ875.9 shows a few peculiarities. Besides two or three very faint irregular lines, and a broadening of the blend $R(17)$–$P(15)$, the pair $R(21)$–$P(19)$ is about twice the expected intensity, while $R(22)$–$P(20)$ is weakened. An overlapping q band prevented following the branches further. Measurements at low J values were not feasible in the case of λ871.4 due to overlying absorption, and the analysis of observable blends was unsatisfactory in that values of $-C$ consistent with the width of blends showed a distinct trend [Eq. (1)]. The average is lower than expected, and while the value of ν_h computed from it fits the ω_v sequence (Table IV), it is some 20 cm^{-1} larger than the apparent wave number. However, an analysis of resolved lines in the tail of the last r band corroborates the drop in $-C$, and in this case the observed and calculated heads agree closely.

Group s. A detailed examination of these three bands throws considerable doubt on the earlier grouping.[1] Whereas the first two can be analyzed as $^1\Sigma-{}^1\Sigma$ transitions, the third consists of a strong branch that appears to be formed by superposed P and R lines ($J_R=J_P+2$; $-C_d\sim 1.00$),

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[52] The perturbation was in evidence at the pair $R(15)$–$P(13)$, for which $\Delta_{RP}(\nu_R>\nu_P)$ was noticeably larger than expected. The increasing shift causes $R(17)$ to resemble an added line between $R(16)$–$P(14)$ and the blend ($\nu_P>\nu_R$) formed by $P(15)$ with $R(18)$. Finally, the intensity of $P(16)$ indicates near coincidence with $R(19)$. The deviation of $R(19)$ would then be about 30 cm^{-1}, whereas a smooth trend in the P branch predicts 15 cm^{-1} for $P(21)$. Besides these shifts, two or three irregular lines are doubtless to be attributed to the perturbation.

and of a weaker branch, presumably of Q type ($-C_c \sim 1.06$). This interpretation of the third band is supported by combination differences involving B'', but it implies a very large Λ-doubling and gives for ν_h^{calc} a value 30 cm^{-1} less than ν_h^{obs}.[53] These features suggest that the upper state may be of modified Π type (transition toward case d' coupling).[34]

In the second band, λ853.2, an abrupt termination of the strong blends is attributed to predissociation, with breaking off of the rotational levels at ~117,740 cm^{-1}. It appears that a narrow band, still in evidence on a plate taken at a lower pressure, obscures the pair $R(21)$–$P(19)$, but the P branch could be traced as far as a broadened line corresponding to $J'=22$.

Group t. Marked dissimilarities of structure suggest that the three or four bands involved[54] may not represent a true progression. Thus, blends in the first band are narrow in the tail, and broaden rapidly toward the head, while the next band is conspicuous for its remarkably incoherent appearance.[55] In contrast, the band at λ837.3 presents a beautifully simple structure that could be analyzed as a close blending of P and R lines.[56] However, the appearance of the last four unobscured lines in the tail [$P(17)$ to $P(20)$] indicates that the rotational levels of the upper state teminate with $J'=19$ (term value ~119,825 cm^{-1}). The lines in question are weaker and sharper than the preceding blends, and as they are displaced to lower wave numbers by about 3 cm^{-1} ($\frac{1}{2}\Delta_{RP}$), it seems clear that the R component is absent. It may be noted, also, that the blend $R(16)$–$P(14)$ is of half-normal intensity.

Group u. Rotational measurements were carried out for the band at λ829.3, and an open structure is evidently associated with one of the heads near λ825.6. A third head appears faintly on another plate ($B45$), from which its position has been estimated.

Group v. If intensity is any guide, a progression is indicated by the strong band at λ818.5. At the same time, incompletely resolved branches suggest an intermediate value for $\Delta G'$. The grouping of Table IV is thus plausible.

g, f, and h levels. These terms of Watson and Koontz[7] remain for possible correlation with absorption bands. Since the distribution of intensity among the emission bands from level g indicates that r_e' does not differ greatly from r_e'', the $0-0$ band might be expected in absorption—but no head is found at the position predicted (108,950 cm^{-1}).[49] On the other hand, there is good agreement between the f level (110,190 cm^{-1}) and the weak band with indication of fine structure at 110,198 cm^{-1}. This is true also of the h level (112,770 cm^{-})[1] and the unassigned band with poorly resolved structure at 112,778 cm^{-1}. However, as intensities among the $h-X$ emission bands lead one *not* to expect the $0-0$ transition in absorption, h appears to be a vibrational term with $v'>0$.

Absorption, λλ818–800. It is clear that a part of the strong and seemingly diffuse absorption at λλ813, 807, and 801, Fig. 2, is due to overlapping, as additional heads are revealed when the pressure is reduced.[25] On the other hand, there is no clear indication of rotational structure below λ818 (cf. Table I, λλ814.5, 807.5), a circumstance that may be attributed to insufficient resolving power only in those cases where $r_e' \sim r_e''$ (e.g., Rydberg bands). The diffuseness may then be due in part to photo-dissociation into repulsive states of N_2, while a possibility that the absorption at say λ801 (most diffuse) represents ionization into the $^2\Pi_u$ state of N_2^+ cannot yet be ruled out.[20]

Absorption below λ796. Even on my own plates, there are many measurable bands in this region (Table I). Only the weak $v'=1$ Rydberg bands (λλ790–785, Fig. 2) have been interpreted, but some of the others are probably related to the non-Rydberg bands (see discussion). An adequate treatment of the absorption here would evidently require plate material obtained at a reduced pressure, in this case by use of either the Lyman or the helium continuum.[12]

DISCUSSION[57]

A number of instances of peculiarities in rotational structure have been noted, particularly for

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[53] I refer here to the strong head at λ849.7, rather than to the weaker one at λ849.3 given in ref. 1.

[54] The fourth (see ref. 1), λ834.1, appears to be the Rydberg band $v'=2$, $m=3$, as noted previously.

[55] This may be due in part to overlapping (cf. Table I, λ841.9). In any case, there is an abrupt drop of intensity in the rotational structure at 118,644 cm^{-1}.

[56] An earlier suggestion (ref. 1) is incorrect.

[57] I am indebted to Professor Mulliken for suggesting many of the features brought out in this discussion.

bands of the r, s, and t groups. While some of these anomalies arise from perturbations or from predissociation, it is reasonable to suppose that others, of a more intrinsic sort, are manifestations of case d' coupling in the upper electronic states. It will be recalled that the higher members of the Rydberg series also give evidence of this type of coupling.

An unexpected feature of nearly all the progressions (we shall exclude here the Rydberg terms and state o') is the smallness of $\Delta G'$, or ω. The values are in fact about one-third that of the normal state, and on the whole ω decreases somewhat with increasing energy (Table IV). At the same time, the values of r_e' for these terms are 20 to 40 percent larger than in the ground state,[58] and the increase with energy is quite pronounced (Table I).

It is true that the r bands can be rearranged into two progressions such that every other band falls into one of them. (λ919.8 and λ907.5 (f) would be added to one group, and λ860.5 to the other, while λ870.7 would replace λ871.4.) The alteration would double ω, but the revised values are hardly as consistent as before, and as this was the only case where larger intervals seemed feasible, the modification is not favored.

In the case of state b, further evidence for a small value of ω is provided by the rotational structure, as the value found for D' (k bands) would agree very poorly with the theoretical expression, $4B^3/\omega^2$, if ω were doubled.

States having unusually small ω_e and large r_e are known for other molecules, e.g., for the upper state ($^1\Sigma_u{}^+$) of the Lyman bands of H_2. In discussing this case, Mulliken[59] has pointed out that the behavior is to be expected if the state is derived from two ions. Mulliken,[60] and Mulliken and Rieke,[61] have also shown that transitions characterized by a net transfer of charge between atoms may be expected to have high intensity, provided (diatomic molecules) the jump is of parallel type, i.e., with $\Delta\Lambda = 0$. Transitions from atomic to ionic (bonding to anti-bonding) orbitals are of just this type, and the intense Lyman bands provide a classical example.

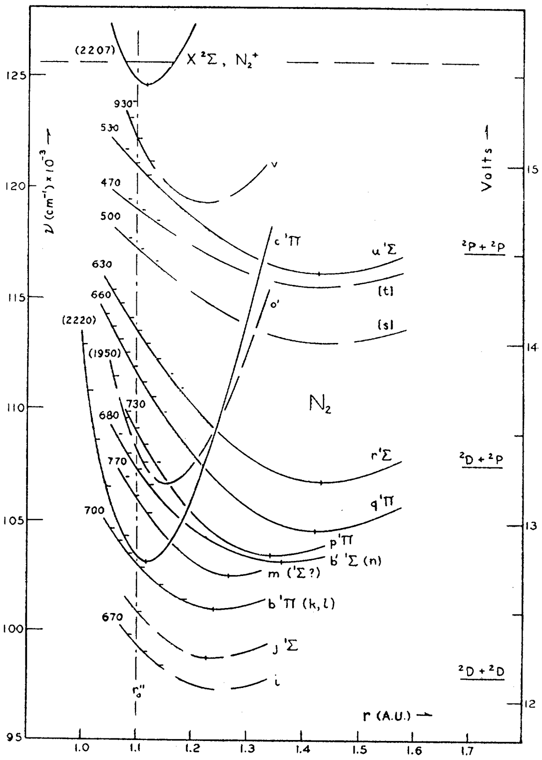

FIG. 4. Highly excited singlet states of N_2. The potential curves for states c and o' (ref. 51) were calculated by Dunham's method (ref. 62) on the basis of reasonable assumptions regarding B_e and α_e. At the left (parentheses) is shown the probable value of ω_e. Levels corresponding to observed bands are indicated by short, horizontal lines. In addition to c, there are of course the other, similar Rydberg states, converging to $X\,^2\Sigma$ of $N_2{}^+$. The shallower curves (except for i, j, and v) were sketched from a rough approximation in which only the first term of Dunham's expression was retained, with ΔG_v (shown at left end of curve) and B_v used in place of ω_e and B_e, respectively. Here v refers to the preferred levels ($r'_{\min}{\sim}r_0''$), with respect to which the minima have been located, vertically. Horizontally, I have arbitrarily used $0.95 r_v$ for r_e (short, vertical line). These curves were treated alike, save that for b' the minimum was raised to obtain conformity with Table VI. No correction was needed for b, the only case that permitted a direct check.

From these remarks, it appears that the $^1\Sigma$ states of N_2 considered here are similar to the ionic $^1\Sigma$ state of H_2. However, the ratio ω/B is in the latter case nearly the same as for the normal state of the molecule, whereas in N_2 it is less than half as great in some instances. These deviations from the empirical Birge-Mecke rule imply an unusual anharmonicity, such as occurs in the ionic $^1\Sigma^+$ state of LiH and of KH, where a unique combination of circumstances[59] results in nega-

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[58] Cf. F. A. Jenkins and R. E. Worley, Phys. Rev. **57**, 252A (1940). In the next to last line, "four times" should read "1.4 times."

[59] R. S. Mulliken, Phys. Rev. **50**, 1028 (1936).

[60] R. S. Mulliken, J. Chem. Phys. **7**, 14, 20 (1939).

[61] R. S. Mulliken and C. A. Rieke, *Reports on Progress in Physics* (The Physical Society, London, 1941), Vol. 8, p. 231. (Cf. §§4, 5.)

tive values of $x_e\omega_e$ and of α_e. The situation is not without precedent however in N_2. From an analysis of a considerable number of $b'-X$ emission bands, Tschulanowsky[8] found $\omega/B\sim650$ for state b', as compared to ~1100 for the five lowest states of N_2. Although $x_e\omega_e$ and α_e appear to be positive for $b'\,{}^1\Sigma$, my results (Table IV) indicate that $x_e\omega_e$ is negative for some of the other states.

Thus it appears that most of these non-Rydberg terms of N_2 possess both ionic characteristics and an unusual anharmonicity. Presumably they dissociate, or tend to dissociate, into ions N^++N^-, and are strongly influenced at large r by a Coulomb law of force. Although the detailed shape of the potential curves is not known, I have included a diagram, Fig. 4,[62] to illustrate their main features. The shallowness of the curves and the large values of r_e, as compared to the Rydberg states, is striking. I have not attempted to indicate the nature of the anharmonicity (see caption), nor to consider the mutual influence of neighboring terms, although such influence is doubtless pronounced in some instances.

It is remarkable that in a comparatively small energy range there should be so many states of ionic character, and it may be that some of those energetically farthest apart are configurationally similar (derived from atomic terms that differ only in n). On the other hand, one may suppose that the large values of r_e' are in some cases due to the excitation of *two* bonding electrons. The smaller stability at higher energies (Fig. 4), which led to an earlier suggestion[1] that the excited terms form series whose limits are unstable states of N_2^+, could be explained in this way. However, even though two-electron jumps may be quite strong in molecules,[60, 61] it is doubtful whether they would account for the intense absorption observed here.

Professor Mulliken informs me that the strength of the ${}^1\Pi-{}^1\Sigma$ bands cannot be explained in the way suggested above for the ${}^1\Sigma-{}^1\Sigma$ bands. Perpendicular type transitions ($\Delta\Lambda\neq0$) are expected to be intense only under special circumstances, as for instance when they bear a similarity to the strong atomic *s–p* jump. It is noteworthy, however, that in the present case, the $\Sigma-\Sigma$ and $\Pi-\Sigma$ transitions, both of which introduce a large change in the molecular bond, are well developed at the same, low pressure of nitrogen.

In conclusion, I wish to express appreciation to Professor F. A. Jenkins for valuable criticism in presenting the results; also to Dr. C. R. Jeppesen for experimental suggestions. For her help in preparing the manuscript, I am grateful to my wife.

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[62] Calculated by Dunham's method, see J. L. Dunham, Phys. Rev. **41**, 713, 721 (1932). [Cf. also J. Chem. Phys. **9**, 61 (1941).]

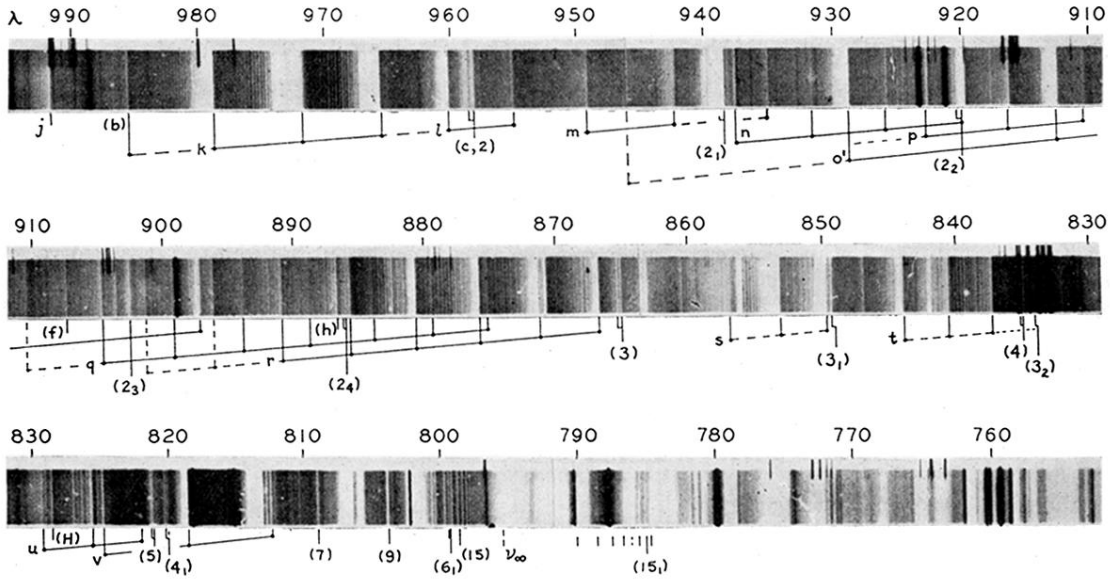

FIG. 2. Far ultraviolet absorption spectrum of N_2 (positive, 5.7×). Bands that have been grouped in progressions are joined by sloping lines. Rydberg bands of the main series ($v'=0$) are shown by parenthesized integers; subscripted integers refer to bands having $v'>0$.