tysonite as the magnetic theory becomes increasingly refined through the development of improved experimental data on individual principal susceptibilities, etc., permitting more drastic tests and presumably requiring more complicated potentials than the simple ones used in the first approximations.

In conclusion, we do not wish to give any impression of finality to the rhombic potential represented in (43). It does seem to work better than the triclinic, and is fully as compatible with the known facts of the crystallographic structure. The departures from axial symmetry involved in (43) are rather large, and it is possible that they can be reduced by considering still more complicated potentials, notably those involving simultaneously both triclinic and staggered rhombic terms. Another possible modification is to have the z axis of the rhombic system spiral about the optic axis instead of being parallel to the latter. Then to compute the susceptibility in any given direction, a three-dimensional aver-

aging process is required, rather than a two-dimensional one as in (38) for the directions perpendicular to the optic axis and none at all for the parallel direction. The attractive feature of this modification is that it makes the magneton number deduced from saturation greater than that deduced from (17) even in the case of the parallel component, thus tending to alleviate the discrepancy between the two methods emphasized in section 4. Furthermore, the effect of the matrix elements of the crystalline potential and of the moment which are non-diagonal in the inner quantum number j ought really to be considered if the separation of $F_{5/2}$ and $F_{7/2}$ in cerium is only 1600 cm^{-1}, as reported by Brunetti and Ollano.[27] However, it appears useless to make elaborate calculations based on these various ideas until better experimental data are available for the perpendicular component.

[27] R. Brunetti and Z. Ollano, Zeits. f. Physik **75**, 415 (1932).

Nitrogen Molecular Spectra in the Vacuum Ultraviolet

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Nitrogen molecular spectra in the region from 900A to 2300A have been photographed with a 10-foot vacuum spectrograph giving a dispersion of 5.5A/mm. Partial rotational quantum analyses have been made for several bands of the $a^1\Pi_u \rightarrow {}^1\Sigma_g^+$ system yielding the constants $B_0' = 1.632 \pm 0.002$, $B_0'' = 1.998 \pm 0.002$, $\alpha' = 0.021$, $\alpha'' = 0.018$. Many new bands in a nitrogen band system with an origin at 1847A discovered by Hopfield in a condensed discharge in a helium-nitrogen mixture are reported. This system is due to N_2^+, having the same lower state as that of the first negative system. The rôle of the helium is discussed. Birge and Hopfield's b' progression is found to consist of Q branches only with $B' = 1.147$. Several new N_2 ground state progressions among the bands in the 900A–1300A interval are presented.

INTRODUCTION

SEVERAL band systems assigned to the N_2 or N_2^+ molecules lie in the vacuum ultraviolet. The vibrational structure of the prominent $a^1\Pi_u \rightarrow {}^1\Sigma_g^+$ system, which extends through the whole Schumann region, has been investigated in detail by Birge and Hopfield.[1] Their analysis yielded accurate vibrational energy data for these two N_2 states, but the dispersion of their

spectrograph was insufficient to reveal the rotational structure of the bands. That the upper state of this system is really $^1\Pi_u$ has been proved by Appleyard[2] who has made a rotational quantum analysis of the (5,13) and (5,14) bands which may be photographed with a spectrograph in air. The only determination of the rotational energy constant B_0 for the normal $^1\Sigma_g^+$ state, however, has been that of Rasetti[3]

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

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

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

from the rotational Raman spectrum of nitrogen gas. An analysis of the rotational structure of bands at the origin of this system was therefore thought to be desirable.

Among the large number of emission bands of N_2 in the interval from 900A to 1300A Birge and Hopfield[1] recognized three normal state progressions (their b, b' and c series). We have investigated this region in the nitrogen molecular spectrum with considerably higher dispersion with a view to creating further order in this complex of bands. Finally, a considerable increase in the number of bands in an interesting N_2 system with an origin at 1846A discovered by Hopfield[4] in a helium-nitrogen mixture is reported, revised vibrational quantum assignments are given showing that the emitter is the N_2^+ molecule with the lower electronic state identical with the lower state of the first negative nitrogen bands, and the probable energy transfer from helium ions is discussed.

EXPERIMENTAL PROCEDURE

The 10-foot, normal incidence, vacuum spectrograph used in this work was constructed in the shop of the Sloane Laboratory, following somewhat the design given by Sawyer[5] for a one-meter vacuum spectrograph. The grating is of speculum metal, 15,000 lines to the inch, giving a dispersion of 5.5A per mm in the first order. The plate-holder covers the entire vacuum region up to 2300A. We have used Schumann plates of our own manufacture, employing the process given by Hopfield and Appleyard[6] with entire satisfaction. Development with Eastman D-76 borax developer for $1\frac{1}{2}$ minutes is recommended. As wave-length standards we have taken revised values for the 1200A and 1134A NI triplets kindly furnished us by Dr. J. C. Boyce, the value 1742.749A for NI as determined by Hopfield, and the 1215A and 1025A H lines. The 1134A triplet is also present in the second order on all of our spectrograms.

As light source either a Π-shaped air-cooled tube 80 cm long and 2.5 cm diameter with an

internal capillary of 1 cm diameter and 30 cm length mounted close to the slit with a current of 100 milliamperes or a water-cooled tube of 1 cm internal diameter and 30 cm length carrying 300 milliamperes was used. A constant flow of gas from a cylinder of nitrogen or helium passed through a capillary, a hot copper oxide tube and a liquid air trap into the discharge tube and thence through the slit into the body of the spectrograph. The pressure in the discharge tube was usually about 0.1 mm, while in the spectrograph the pressure was less than 0.01 mm. The liquid air served to eliminate effectively the CO spectrum, so that the only impurity bands on the spectrograms are some rather weak NO bands at the long wave-length end. It was found that the tank helium had a sufficient nitrogen content so that no additional nitrogen was needed for the mixture. Exposure times were usually about 24 hours with the air-cooled tube, the slit width being about 0.025 mm.

THE $a^1\Pi_u - {}^1\Sigma_g^+$ SYSTEM

In agreement with Appleyard[2] we find that the bands of this system are of the $^1\Pi \rightarrow {}^1\Sigma$ type. Since the normal state of N_2 is known to be $^1\Sigma_g^+$, this fixes the upper a state as $^1\Pi_u$. In the enlargement of the (0,4) and (1,5) bands in Fig. 1 the inner Q-branch head is easily seen, and one can observe at some distance from the head that the rotational lines fall into two branches, P and Q, each exhibiting alternating intensities. A partial rotational analysis of the (0,1), (0,4), (1,5), (1,6), (1,7) and (2,8) bands has been made. The incompleteness of the analysis is due to the impossibility of locating any R-branch lines in the heads of the bands or in the regions of the first lines of the P and Q branches, and to the fusion of many of the latter lines. Quantum assignments may be made for all of the available P and Q lines, however, on the basis of the comparison of the usual $Q(J)-P(J)$ and $Q(J)-P(J+1)$ combination differences between bands. Unfortunately there is exact superposition of successive P and Q lines in the range of intermediate and high J-values in most of the bands, a fact which limits the accuracy of the calculations of the rotational constants. Assignments of line frequencies for three of the bands as samples

[4] J. J. Hopfield, Phys. Rev. **36**, 789 (1930).
[5] R. A. Sawyer, J. O. S. A. and R. S. I. **15**, 305 (1927).
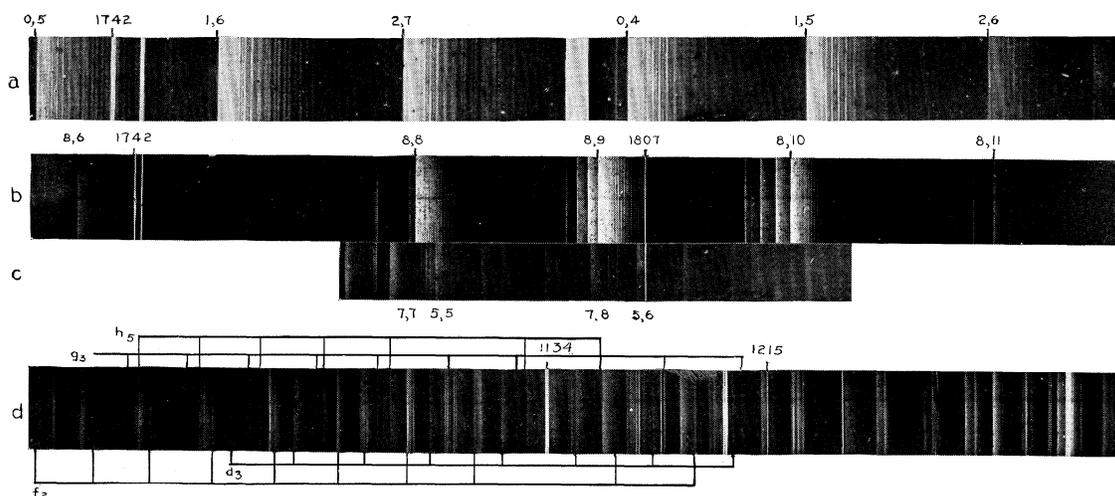[6] J. J. Hopfield and E. T. S. Appleyard, J. O. S. A. **22**, 488 (1932).

FIG. 1. (a) Enlargements (8.4 ×) of a $^1\Pi_u{\rightarrow}^1\Sigma_g{}^+$ N$_2$ bands. (b) N$_2{}^+$ system with origin at 1847A, Helium-nitrogen mixture. (c) Condensed discharge in nitrogen showing additional bands of lower v-values in N$_2{}^+$ system. (d) Short wavelength end of N$_2$ band spectrum showing ground state progressions.

are given in Table I. The more intense lines have even J'' numbering. Notice that the superposition of Q and P lines preserves the alternating intensities in the (0,1) band but destroys them in the (1,7) band. In the (0,4) band the two branches are not fused.

Application of the P–Q–R combination difference with the fragmentary measurements on portions of the R-branches indicate that the Λ-doubling in the Π state is very small. The rotational energy constants B_v' and B_v'' are then correctly given by the Q–P combination differences. The values so obtained are presented in Fig. 2. We include also Appleyard's values (the crosses) from his analysis of the (5,13) and (5,14)

bands. These indicate a departure of the B_v against v curve from linearity at high v values. Our analyses give $B_0' = 1.632$ cm^{-1} and $B_0'' = 1.998$ cm^{-1} with probable errors of ±0.002. This value of B_0'' for the normal state of N$_2$ is to be compared with Rasetti's value 1.992 ± 0.005 from the rotational Raman lines. From Fig. 2 it is evident that $\alpha' = 0.021$, $\alpha'' = 0.018$.

N$_2{}^+$ SYSTEM IN HELIUM-NITROGEN MIXTURES

Fig. 1(b) is a reproduction of a spectrogram obtained with a condensed discharge in tank helium. The most intense bands in this system were discovered by Hopfield[4] who pointed out that the bands showed the alternating intensities expected for N$_2$ bands. Hopfield apparently did not observe, however, the $\Delta v = +3$ and -2 sequences

TABLE I. *Assignments of frequencies in $a^1\Pi_u{\rightarrow}^1\Sigma_g{}^+N_2$ bands. Number following each frequency is estimated intensity.*

|	0,1		0,4		1,7	
J''	$Q(J)$	$P(J)$	$Q(J)$	$P(J)$	$Q(J)$	$P(J)$
14	66,542.7 4	66,493.0 5			54,852.1 3	54,807.3 3
15	29.0 2	79.6 2			44.0 2	795.6 3
16	19.6 4	63.9 4	59,734.4 4		36.1 3	83.8 3
17	507.1 2	48.8 2	24.2 2	59,668.7 2	27.0 1	71.6 3
18	493.0 5	33.0 4	14.5 4	54.2 0	16.9 3	59.2 3
19	79.6 2	416.0 2	704.6 2	41.1 2	807.3 3	45.7 3
20	63.9 4	398.3 4	692.2 4	27.2 1	795.6 3	31.2 3
21	48.8 2	79.9 2	80.0 2	612.1 2	83.8 3	16.9 2
22	33.0 4	61.4 3	66.1 1		71.6 3	701.4 2
23	416.0 2	40.6 2	51.2 1		59.2 3	686.1 2
24	398.3 4	22.2 3	37.2 2		45.7 3	69.3 2
25	79.9 2	300.9 1	20.9 0	539.5 1	31.2 3	48.6 2
26	61.4 3	278.0 3	603.5 2	18.8 0	16.9 2	34.8 2
27	40.6 2	56.2 1	588.3 1	00.5 0	01.4 2	
28	22.2 3	31.6 2	73.6 2			
29	300.9 1		56.2 1			
30	278.0 3					
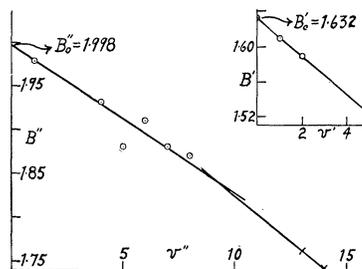
FIG. 2. B_v vs. v curves for a $^1\Pi_u$ and $^1\Sigma_g{}^+$ N$_2$ states. Circles indicate our data, crosses Appleyard's.

and the extension of the $\Delta v = +1$ and $+2$ sequences to more than four members. Furthermore, a condensed discharge in nitrogen brings out additional bands (those with $v' = 5$, 6 and 7 in Table II) in each of the main sequences on the long

TABLE II. *Assignments of band heads in the N_2^+ system. d indicates double assignment. All bands degrade to the red.*

v', v''	Int.	$\nu_{\mathrm{Obs.}}$	v', v''	Int.	$\nu_{\mathrm{Obs.}}$
8,11	4	48,553.7	10,11	5	52,472.6
9,12	3	48,729.5	11,12	3	52,585.3
10,13	2	48,912.5	12,13	0	52,695.0
11,14	1	49,097.6	13,14	0	52,809.1
6,8	0	50,134.6	2,2; 3,3	1 d	53,974.7
7,9	1	50,257.6	1,1; 4,4	1 d	53,985.1
8,10	10	50,391.5	0,0; 5,5	2 d	54,006.1
9,11	8	50,530.6	6,6	2	54,046.9
10,12	6	50,675.7	7,7	1	54,100.2
11,13	4	50,824.2	8,8	6	54,165.3
12,14	1	50,975.2	9,9	3	54,233.4
13,15	1	51,127.0	10,10	1	54,308.6
14,16	0	51,285.2	5,4; 6,5	1 d	56,050.4
15,17	0	51,426.8	7,6	1	56,074.0
5,6	1	51,996.4	9,8	1	56,138.7
6,7	2	52,073.1	10,9	1	56,180.6
7,8	2	52,160.5	11,10	0	56,224.2
8,9	9	52,261.7	7,5; 8,6; 9,7	3 d	58,078.9
9,10	7	52,363.1			

wave-length side of the bands intensified in the helium discharge. These additional bands are almost completely masked in the spectrum of the helium-nitrogen discharge by the rotational structure of the intensified bands which degrade to the red in apparent violation of the empirical rule that in band spectra with $\omega' > \omega''$ the bands degrade to the violet.

Having suspected that this band system was due to the N_2^+ molecule because of the action of the excited helium atoms (21.11 to 24.46 volts energy as compared to 15.65 volts for the I. P. of N_2), comparison of the observed $\Delta G(v'' + \frac{1}{2})$ values with those for the lower state of the first negative N_2^+ system as given by Coster and Brons[7] showed the two states to be the same.[8]

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

[8] J. Kaplan kindly informed us in a private communication during the course of the present work that he had already noticed the similarity of the lower state vibrational differences in Hopfield's data with those for the lower state of the N_2^+ bands in the visible, but that he had had difficulty in establishing the identity of the two states because of the most peculiar intensity distribution then resulting among the bands as given by Hopfield (no bands with $v'' < 8$ and no bands of wave-length shorter than 1779A).

There was the difficulty, however, that although the vibrational frequencies in the two states were very nearly equal, the $\Delta v = 0$ sequence seemed to begin with the (5,5) band. Calculation of the approximate positions of these missing bands by extrapolation of the course of the observed $\Delta G(v' + \frac{1}{2})$ values then showed that this sequence probably had a long-wave-length edge at about the (2,2) or (3,3) band and that the (0,0) and (5,5) bands should nearly coincide. Two additional bands have been found in this region on spectrograms taken with an uncondensed discharge in the helium-nitrogen mixture. Each of these agrees well within the experimental error with two of the predicted positions because of the reversal of direction in the sequence, and together with the use of the (5,5) band frequency also as (0,0) fills out the $\Delta v = 0$ sequence completely. There is no evidence of bands with $v < 5$ in the $\Delta v = +1$ or -1 sequences, however, and there remains to be explained the general lack of intensity among the bands of low v values.

TABLE III. *Additional normal state progressions at the short wave-length end of the N_2 emission spectrum.*

v''	d	Int.	e	Int.	f	Int.	g	Int.	h	Int.
1					107860.6	2	106606.5	1		
2					105548.8	1	104306.3	0		
3	98237.0	0			103270.0	1	102018.4	1		
4	95999.3	3			101044.9	2	99801.4	2 d		
5	93781.7	At.			98829.8	4	97591.1	2	101414.0	2
6	91597.7	3			96641.8	2	95398.4	0	99226.1	2
7	89449.2	3			94489.4	1	93247.0	3	97071.1	1
8	87322.0	4			92355.2	1	91136.3	1	94953.5	2
9	85218.7	3			90265.3	3	89027.6	2	92836.2	3
10	83150.7	2	83874.5	1						
11	81115.6	1	81831.5	1	86176.0	1	84942.4	1	88713.6	3 d
12			79814.4	3	84151.4	1	82899.7	3	86721.8	1
13			77836.0	2			80919.9	1	84710.4	1
14									82769.9	0

The assignment of frequencies of band heads in this system is given in Table II. For the range $v' = 0$ to 7 inclusive these frequencies fit the following formula:

$$\nu = 54,024 + 2173.2 \ (v' + \tfrac{1}{2}) - 10.43 \ (v' + \tfrac{1}{2})^2$$
$$- 0.017 \ (v' + \tfrac{1}{2})^3 - 2207.16 \ (v'' + \tfrac{1}{2})$$
$$+ 16.136 \ (v'' + \tfrac{1}{2})^2 + 0.040 \ (v'' + \tfrac{1}{2})^3,$$

where the lower state terms are those given for the first negative system. At $v' = 8$, strangely enough just at the energy where the intensification by the helium takes place, the second differences between the successive $\Delta G(v' + \frac{1}{2})$ values

jump to about 32 cm^{-1}. This sudden change in the course of the ΔG's makes it impossible to represent all of the bands in the system by the same formula.

In Fig. 3 we give the distribution of intensities among the bands of this N_2^+ system. The $v'=8$ level at which the enhancement of intensities due to the helium occurs is 2.05 volts above $v'=0$.

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0	2																
1		1															
2			1														
3				1													
4					1												
5					1	2	1										
6						1	2	2	0								
7						3	1	1	2	1							
8							3		6	9	10	4					
9								3	1	3	7	8	3				
10										1	1	5	6	2			
11											0		3	4	1		
12														0	1		
13															0	1	
14																	0

FIG. 3. Intensity distribution in the 1847A N_2^+ system.

Adding to this 6.67 volts for the energy of the (0,0) transition and 15.65 volts (I. P. of N_2) for that of the ground state of N_2^+ with respect to normal N_2, there results 24.37 volts for the total. The close agreement of this value with that for the I. P. of He, 24.46 volts, would indicate that collisions of the second kind between He ions and normal N_2 molecules are responsible for the large production of N_2^+ with this or slightly greater energy. Since, according to Lozier,[9] the heat of dissociation of N_2^+ in its ground $^2\Sigma$ state is 6.73 volts, the upper (apparently $^2\Sigma$, judging from the single-headed appearance of the bands) state of this system is in a favorable position in its lower vibrational levels for interaction with one of the several probable repulsion states arising from $N(^4S)+N^+(^3P)$ atoms. Such predissociation may be the cause of the very low intensity of bands with $v'<5$.

N_2 BANDS OF SHORTER WAVE-LENGTH

Between 900A and 1300A there are more than 150 emission bands of N_2. Among these Birge

and Hopfield[1] recognized three ground state progressions—their b, b' and c series—, each apparently coming from a different upper electronic level. With a certain condition of excitation of the discharge tube they noted the complete absence of the b' progression, and speculated as to the possibility of its being due to NO rather than to N_2 even though the vibrational intervals agreed fairly well with those of the N_2 normal state. Our higher dispersion spectrograms reveal clearly an alternating intensity among the rotational lines of these bands, however, which definitely decides in favor of N_2 as the emitter. Several of these b' bands seem to consist of but a single branch emanating from the head, and each has one rotational line at some distance from the head showing a marked intensity perturbation. Now if each of these bands consisted of an exactly superposed Q and P branch, as in some of the $a^1\Pi-^1\Sigma$ bands discussed above, one would expect that proceeding along some four or five bands in the progression the two branches would necessarily get out of step with each other. This is not the case. Furthermore, if superposed P and R branches were involved there should be two lines, separated by, say, four others since the fractional change in B is evidently large in these bands, showing the intensity anomaly. We therefore conclude that the b' progression consists of a set of single Q branches, the upper state being thus $^1\Pi_u$. This absence of P and R branches in a long progression of $^1\Pi-^1\Sigma$ bands forms a striking example of an already discovered type of predissociation.[10]

The frequency interval between each rotational line of these Q branches and the origin (head) divided by $J(J+1)$ should be a constant for each band (if $(D'-D'')J^4$ may be neglected) and equal to $B'-B''$. Numbering the perturbed line $J=25$ and the other lines accordingly in each band, these quotients are very constant. Then knowing B'' for each from the data for the $^1\Sigma$ ground state, we compute B' to be 1.148, 1.145 and 1.147 for the b' 14, b' 15 and b' 16 bands, respectively. The average of these, 1.147, one may assume to be B_0 for this $^1\Pi$ N_2 state lying 103,677.7 cm^{-1} above $v=0$ of the N_2 normal state.

[9] W. W. Lozier, Phys. Rev. 44, 575 (1933).

[10] R. deL. Kronig, Zeits. f. Physik 62, 300 (1930).

From the magnitude of this B_0 one would estimate that if other vibrational levels in this same $^1\Pi$ state existed they should be spaced at about 1400 cm^{-1} intervals. We list in Table III some further ground state progressions we have found among the N_2 bands in this region. One of these, that labelled d, is 1474 cm^{-1} above the b' level, and there are indications of excited state vibration frequencies of about 740 cm^{-1} and about 1250 cm^{-1}, but we have been unable to establish any upper state vibrational frequency definitely. Nitrogen absorption spectra taken at a number of rather low nitrogen gas pressures in

FIG. 4. Potential energy curves drawn with the aid of Morse functions for known N_2 and $N_2{}^+$ states.

the receiver of the spectrograph should aid greatly in the complete ordering of the N_2 levels in this higher frequency region. Experiments with this objective are in progress.

N_2 AND $N_2{}^+$ ELECTRONIC LEVELS

Lozier has shown[9] that the heat of dissociation D for the normal state of N_2 is 7.90 ± 0.02 volts. Kaplan[11] from his study of the energy relations between predissociation regions in the triplet band systems of nitrogen and the products of dissociation has pointed out that the energy of $v=0$ of the $A\ ^3\Sigma_u{}^+$ state must be $\geqq D-1\cdot2$ volts. This level must then come at or slightly higher than 6.7 volts above $v=0$ of the normal state. Placing it exactly at this energy, we may then plot the potential energy curves for all the known states of N_2 and $N_2{}^+$, for the first time placing the singlet and triplet levels in very closely their correct relative spacing. In Fig. 4 we present such a plot, the form and position of the curves having been computed with the aid of Morse functions. Since the b' level comes just above the energy of $^2D+^2D$ atoms, it may well be a repulsion curve from this limit which is responsible for the observed predissociation.

Note added in proof: The lowest $^3\Sigma_u$ curve in Fig. 4 was drawn according to the results recently published by J. Kaplan.[12] Kaplan's later revision of these results gives the $A\ ^3\Sigma$ state as the upper state of his new N_2 bands. The $^3\Sigma$ state arising from two ^4S atoms is therefore as yet undiscovered. Because of these new data on the $A\rightarrow X$ intercombination system, it may be necessary to use 7.4 volts for the heat of dissociation of N_2.[13] In that event all of the triplet levels in our Fig. 4 must be lowered by 0.5 volts.
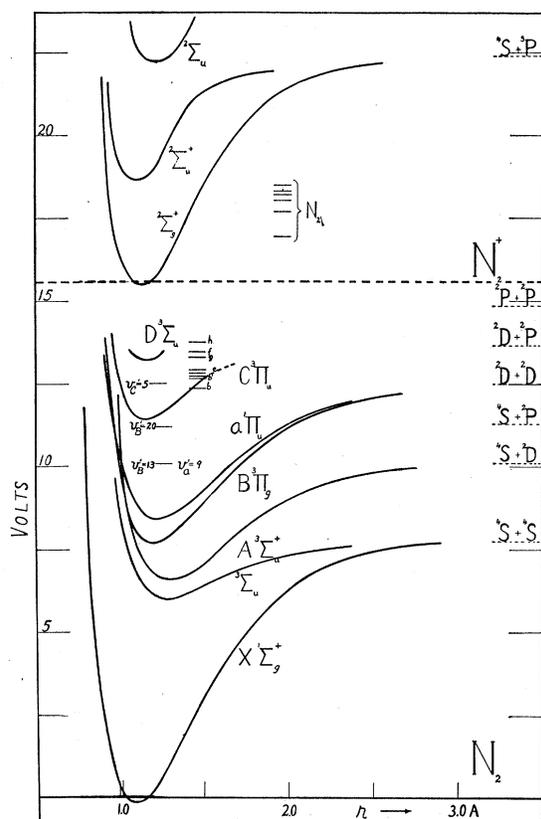
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[11] J. Kaplan, Phys. Rev. **42**, 97 (1932).
[12] J. Kaplan, Phys. Rev. **45**, 675 (1934).
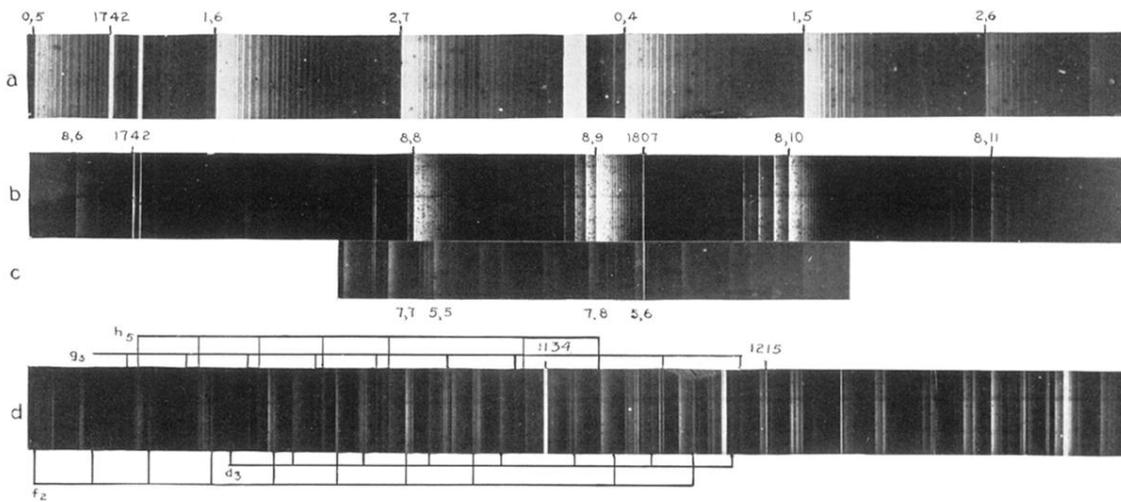[13] Cf. W. W. Lozier, Phys. Rev. **45**, 840 (1934).

FIG. 1. (a) Enlargements (8.4 ×) of $a\ ^1\Pi_u \rightarrow {}^1\Sigma_g^+$ N_2 bands. (b) N_2^+ system with origin at 1847A, Helium-nitrogen mixture. (c) Condensed discharge in nitrogen showing additional bands of lower v-values in N_2^+ system. (d) Short wavelength end of N_2 band spectrum showing ground state progressions.