ARC SPECTRUM OF NITROGEN IN THE EXTREME ULTRA-VIOLET

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Abstract

Analysis and classification of lines in the arc spectrum of nitrogen.—Excitation of nitrogen by controlled electron impact was found to bring out many lines in the arc spectrum of nitrogen. These were observed with a vacuum spectrograph in the region from 500 to 1200A. The lines thus found, together with material of Hopfield, Bowen, and Fowler in the extreme ultra-violet, and of Merton and Pilley in the visible, and the multiplets already found by Kiess have led to a fairly complete analysis of the spectrum, in good agreement with the predictions of the Hund theory. The *ionization potential* is 14.48 volts, and the metastable levels ^2D and ^2P have energies corresponding to 2.37 and 3.56 volts respectively, in good agreement with the predictions of Kaplan and Cario from a study of active nitrogen.

THE analysis of the arc spectrum of nitrogen is rendered peculiarly difficult by several circumstances. Arc types of excitation tend to bring out principally the strong band systems which, in the far ultra-violet, may look like a system of lines and may mask arc lines. More strenuous excitation brings out spark lines. Most of the arc lines are in regions inconveniently far in the infra-red or the ultra-violet. Spectra obtained by Merton and Pilley[1] under peculiar conditions of excitation and by Kiess[2] in the near infrared enabled the latter author to work out the skeleton of the spectral structure involved in the near-visible region, comprising eight quartet and five doublet multiple levels. The quartet levels were specified with reference to the ionization limit, but the doublet levels were given only relative values, since no series were found.

In an abstract of a paper before the American Physical Society, Hopfield[3] announced the discovery of two doublet and two quartet series in the extreme ultra-violet and gave the formula for one of these series. He has recently very kindly furnished us with prints of the lantern slides which he showed at that time. Hopfield connected one quartet and one doublet series with the higher terms found by Kiess (although the following analysis shows the latter of these connections to be only partially correct and at least two of his series to involve misgrouping of lines).

We have photographed in our vacuum spectrograph the extreme ultraviolet spectrum of nitrogen excited by single electron impacts at voltages between 20 and 100 volts and have been able to work out the general structure of the entire nitrogen arc spectrum. Several details in this scheme are admittedly uncertain and provisional, but there can be little doubt about the correctness of the general structure, in view of the resemblance to the known

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[1] Merton and Pilley, Proc. Roy. Soc. **A107**, 411 (1925).

[2] Kiess, Jour. Opt. Soc. Am. **11**, 1 (1925).

[3] Hopfield, Phys. Rev. **27**, 801 (1926).

structure of O II and of the possibilities allowed by the Hund theory. There is particular interest attached to certain features of this analysis in relation to the peculiarities of "active" nitrogen.

Fig. 1 is a Grotrian diagram of the nitrogen atom. The Hund theory predicts five ground states: the lowest state $2p^4S_2$ and the four metastable ground states $2p^2D_{3,2}$ and $2p^2P_{2,1}$. Going to the $^3P_{3,2,1}$ limit are series of

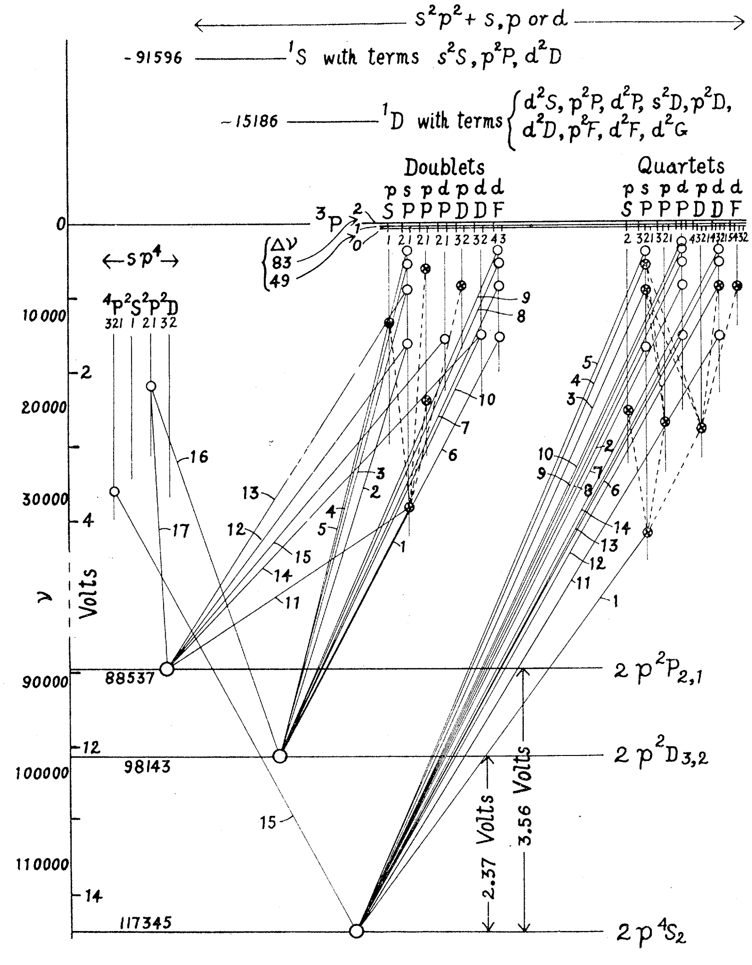

Fig. 1. Grotrian diagram of the nitrogen atom.

quartet and doublet terms. Other series of doublet terms go to the higher ^1D and ^1S limits. The normal electron configuration of the outer shell of electrons is s^2p^3. The foregoing excited states arise from the displacements of one of the p electrons. A less common mode of excitation involves the displacement of an s electron, for which the most significant terms are the four shown in the upper left corner of Fig. 1. The solid disks are the terms previously identified by Kiess, and the broken diagonal lines show the combinations on which his identification was based. The solid diagonal numbered lines are the ultra-violet combinations thus far identified.

TABLE I. *Identified terms*

(**Bowen[4]) (*Kiess[2])

Quartets		
$2p^4S_2$	117345	
$3s^4P_1$	34059*	34
P_2	34026*	47
P_3	33979*	
$4s^4P_1$	13724	50
P_2	13674	68
P_3	13606	
$5s^4P_1$	7532*	44
P_2	7487*	70
P_3	7417*	
$6s^4P_1$	4779*	45
P_2	4734*	72
P_3	4662*	
$7s^4P_3$	3211 ±	
$3p^4S_2$	20593*	
$3p^4P_1$	21868*	18
P_2	21850*	38
P_3	21812*	
$3p^4D_1$	22573*	23
D_2	22550*	37
D_3	22513*	51
D_4	22462*	
$3d^4P_1$	12481	26
P_2	12455	117
P_3	12388	
$4d^4P_1$	7022	28
P_2	6994	48
P_3	6946	
$5d^4P_2$	4471	35
P_3	4436	
$6d^4P_3$	3068	
$7d^4P_3$	2242	
$3d^4D_3$	12523	
$4d^4D_1$	7069*	
D_2	7124*	−54
D_3	7057*	66
D_4	6942*	115
$5d^4D_3$	4520	
$6d^4D_3$	3157	
$4d^4F_2$	7159*	18
F_3	7131*	35
F_4	7097*	56
F_5	7041*	

Doublets		
$2p^2D_{2,3}$	98143	
$2p^2P_{1,2}$	88537	
$3s^2P_1$	31239*	83
P_2	31156*	
$4s^2P_1$	13240	83
P_2	13157	
$5s^2P_1$	7340	76
P_2	7264	
$6s^2P_2$	4554	
$7s^2P_2$	3183	
$3p^2P_1$	19607*	36
P_2	19571*	
$5p^2P_1$	5082*	26
P_2	5056*	
$4p^2S_1$	10898*	
$4p^2D_2$	6855*	
D_3	6832*	23
$3d^2P_1$	12728	
P_2	12771	−43
$3d^2D_3$	12247	
$3d^2F_3$	12557	71
F_4	12486	
$4d^2F_3$	7066	62
F_4	7004	
$5d^2F_4$	4472	
$6d^2F_4$	3096	
	Terms from sp_4	
$sp^4\,{}^2P_1$	17671	−30
P_2	17701	
$sp^{44}P_1$	29176**	−18
P_2	29194**	−44
P_3	29238**	

Table I gives the values of the terms shown in Fig. 1. Kiess' values are given for his quartet terms, and also for his doublet terms except for a bodily shift from his arbitrary scale to a new scale determined from the computed series limits. The remaining terms are determined from a consideration of all the data at present available in the extreme ultra-violet region.

[4] Bowen, Phys. Rev. **29**, 231 (1927).

TABLE II. *Quartets from* $2p^4S_2=A$

No.	Combination	Calculated	Observed		Hopfield[5]		Note
1	$\mathrm{A}-3s^4P_1$	83286	83283	6	83286	3	a
	P_2	83319	83318	7	83320	4	
	P_3	83366	83369	7	83366	5	
2	$\mathrm{A}-4s^4P_1$	103621	103619	2	103739	1	
	P_2	103671	103673	3	103669	2	
	P_3	103739	103742	4	103736	3	
3	$\mathrm{A}-5s^4P_1$	109813	109818	0	109813	1	
	P_2	109858	109865	1	109856	2	
	P_3	109928	109926	2	109926	2	
4	$\mathrm{A}-6s^4P_1$	112566			112562	0	
	P_2	112611			112609	0	
	P_3	112683	112672	0	112680	1	
5	$\mathrm{A}-7s^4P_3$	114140 ±	114140 ±	00			
6	$\mathrm{A}-3d^4P_1$	104864	104878	2	104864	1 −	
	P_2	104890			104890	1	b
	P_3	105007	105010	2	105003	3	
7	$\mathrm{A}-4d^4P_1$	110323	110307	3*d*	110323	0	b
	P_2	110351			110351	1	c
	P_3	110399	110401	3*d*	110396	3	
8	$\mathrm{A}-5d^4P_2$	112874	?		112874	0	
	P_3	112909	112908	1	112910	2	b
9	$\mathrm{A}-6d^4P_3$	114277	114277	0.5			b
10	$\mathrm{A}-7d^4P_3$	115103	115103	00			b
11	$\mathrm{A}-3d^4D_3$	104822	104822	3	104823	1	
12	$\mathrm{A}-4d^4D_1$	110276					
	D_2	110221					
	D_3	110288	110307	3*d*	110296	0	c
13	$\mathrm{A}-5d^4D_3$	112825	112830	0.5	112821	1	
14	$\mathrm{A}-6d^4D_3$	114188	114188	0			d
15	$\mathrm{A}-sp^4\ {}^4P_1$	88169	88160	3	88185	2	e
	P_2	88151			88167	4	
	P_3	88107	88107	3	88123	6	

TABLE III. *Doublets from* $2p^2D_{2,1}=B$

No.	Combination	Calculated	Observed		Hopfield		Note
1	$\mathrm{B}-3s^2P_1$	66904	66900 B	2	66908	4	
	P_2	66987	66987 B	2	66996	6	f
2	$\mathrm{B}-4s^2P_1$	84903	84906	2	84919	1	
	P_2	84986	84984	2.5	85005	2	g
3	$\mathrm{B}-5s^2P_1$	90803	90798	00	90811	0	
	P_2	90879	90879	1	90883	0	
4	$\mathrm{B}-6s^2P_2$	93589	93589	0.5			
5	$\mathrm{B}-7s^2P_2$	94960	94960	00			
6	$\mathrm{B}-3d^2F_3$	85586	85575	2	85589	3	h
	F_4	85657	85646	2	85666	4	
7	$\mathrm{B}-4d^2F_3$	91077	91086	0	91073	0	
	F_4	91139	91134	2	91144	1	
8	$\mathrm{B}-5d^2F_4$	93671	93671	1			
9	$\mathrm{B}-6d^2F_4$	95047	95047	00			
10	$\mathrm{B}-3d^2D_3$						
	D_3	86896	85903	0*d*			i
16	$\mathrm{B}-sp^4\ {}^2P_1$	80466	80472 F	4			
	P_2	80436	80442 F	7			j

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[5] Hopfield (from unpublished data referred to in Ref. 3; also Hopfield and Liefson, Astrophys. J. **58**, 59 (1923).

TABLE IV. *Doublets from* $2p^2P_{1,\,2} = C$

No.	Combination	Calculated	Observed		Hopfield		Note
11	$C-3s^2P_1$	57298	57298 B	3	57296	8	
	P_2	57381	57381 B	3	57379	10	k
12	$C-4s^2P_1$	75297	75301 F	1			
	P_2	75380	75377 F	2			
13	$C-5s^2P_1$	81197	81321 F	4d			
	P_2	81273					l
14	$C-3d^2D_2$	76290	76283 F	5d			
	D_3						
15	$C-3d^2P_1$	75809	75809 F	2			
	P_2	75766	75766 F	5			m
17	$C-sp^4\,{}^2P_1$	70860					
	P_2	70830	70822 F	4	70827	2	n

Tables II, III and IV summarize the facts upon which the analysis is based.

NOTES ON TABLES

(a) These three lines are among the extreme ultra-violet standards determined by Bowen and Ingram,[6] whose measurements, together with Kiess' s^4P term values, were used to fix the value of the $2p^4S_2$ ground term.

(b) Hopfield's photographs, taken in the second order, resolve P_1 and P_2, which are just too close for us to separate. The reasons for identifying this and Nos. 7–10 as d^4P combinations are as follows. Kiess identified the $4d^4D$ and $4d^4F$ terms, and the s^4P terms are all accounted for. The only remaining terms on the Hund scheme, which could combine with the ground A state are of the type d^4P. The series Nos. 6–10 is therefore, by exclusion, ascribed to these terms. This is supported by the fact that such combinations should be stronger than those with d^4D or d^4F, and because, by analogy with O II, the d^4P terms should be higher than d^4D or d^4F, as is found to be the case in comparing with Kiess' $4d^4D$ and $4d^4F$ terms. Also the progressively smaller interval as we go to higher members indicates a d^4P series. The terms are not, however, inverted as in O II.

(c) The combinations of A with Kiess' terms $4d^4D_{1,2,3}$ give predicted lines at 110276, 110221, 110288 respectively. Our apparatus would probably not resolve the first and last of these from the $P_{1,2}$ lines. Hence probably all four lines are blended in our diffuse line 110307. We did not definitely find the other predicted lines 110186 and 110214 from Kiess' $4d^4F_{2,3}$ terms although there was a faint diffuse band very near this. Such ${}^4S$ with ${}^4F$ combinations would, however, be expected to be quite weak.

(d) An additional support of the classification of the series A, md^4P and A, md^4D is the fact that the strongest lines in each (associated with the P_3 and D_3 terms) have about the expected frequency separation 83 characteristic of the fact that d^4P_3 terms go to ${}^3P_2$ and d^4D_3 terms go to ${}^3P_1$ as limits.

(e) These ${}^4P_{1,2,3}$ levels were fixed from the values given by Bowen and Ingram as wave-length standards, and the identification of the term was first made by Bowen.[4]

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[6] Bowen and Ingram, Phys. Rev. **28,** 444 (1926).

(f) These lines lie beyond the range of our spectrograph. The lines marked "B" are from Bowen and Millikan.[7] For theoretical reasons elaborated later in the paper, we should expect that the experimental frequency separation in each doublet of this type should be 4 or 5 units too large. That this is so is a strong support of this phase of the analysis. This remark applies to lines 1–5 and 6–9. The discrepancy should be less in case of line 10.

(g) Here the discrepancy between our measurements and Hopfield's is quite large. However our values check well with a combination with Fowler's lines shown in lines 12 Table IV. Probably such discrepancies as these fall within limits of error of plate calibrations except in the case of lines measured with precision in higher orders.

(h) In O II these combinations are next in strength to those of $B-ms^2P_{1,2}$ and the d^2F levels are midway between the d^2D and the d^2P levels. The assignment here given makes this also true for N I.

(i) In O II the d^2D levels are higher and have smaller separation than either the d^2P or the d^2F levels. This suggests that this unresolved line is due to the assigned combination. Furthermore, the $3d^2P$ level (an inverted one) is already fixed by Kiess, and we find its combination in Table IV. We should expect the $B-d^2P$ combination to be the weakest of the three d doublet sets, and it is not surprising that we find it to be the missing one.

(j) These $sp^4\ {}^2P_{1,2}$ levels are fixed by analogy with O II, as having about the expected position and separation and as being inverted as shown by the intensities. F means that these lines were measured by Fowler and Freeman,[8] who listed them as probaly arc lines. We also found these lines strongly but unresolved. They came so near the edge of our plate, however, that our measurement of them is not accurate.

(k) These lines as well as the corresponding $B-3s^2P_{1,2}$, show reversal in some of Hopfield's photographs. B signifies that we have used Bowen's measurements in this region which our plates do not cover. Lines 12–15 show Fowler's measurements. (15) is calculated from Kiess' term value and shows excellent agreement. In the 13 and 17 the agreement is not so good, but there are certain reasons for this as follows:

(l) The observed value is some 50 wave-numbers larger than the calculated values, the line is diffuse and stronger than would be expected in view of the intensities of the two preceding members of the series. However the observed diffuse line must include the $C-4d^2P_{1,2}$ lines whose exact wave-numbers cannot be calculated since the term $4d^2P_{1,2}$ is not known. By comparing with the combinations of C with the $3d$ terms we should expect $C-4d^2P_{1,2}$ to lie at about 81350 and to be stronger than $C-5s^2P_{1,2}$. Consequently the observed diffuse line lies just in the midst of these four expected lines. Our resolving power should suffice to separate them. Our intensity was so low, however, that we could barely see something in this region but could not measure or resolve it, and hence we can only use Fowler's value.

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[7] Bowen and Millikan, Phil. Mag. **48,** 259 (1924).

[8] Fowler and Freeman, Proc. Roy. Soc. **A114,** 662 (1927).

Fowler states that his diffuse line is probably a group of several lines, and he is uncertain as to their arc or spark character.

(m) Classed by Fowler as probably arc lines. The correspondingly predicted combination of B with these d^2P levels was not observed, but would be expected to be relatively weak.

(n) Comparing with note (j) it is seen that, if the present identification is correct, there must be a relative error of about 14 wave-numbers between Fowler's measurements of 80442 (1243) and 70822 (1412). Also we should expect a weaker companion of 1412, which has not been reported. Fowler judges 70822 to be a spark line from its behavior, but has not fitted it into his spark classification.

Discussion

The metastable states. These are identified through connecting them with the $3s^2P_{1,2}$ states by the lines 1492, 1495 and 1742, 1745 which are the first members of two series of doublets converging to the $^3P_{0,1,2}$ limit. Hopfield correctly evaluated the latter series, although he could not correctly "label" it because his work antedated the Hund classification. The entire set of relations here has, however, remained in doubt for a reason which is actually a strong support of the classification. Consider the expected relations as shown by Fig. 2.

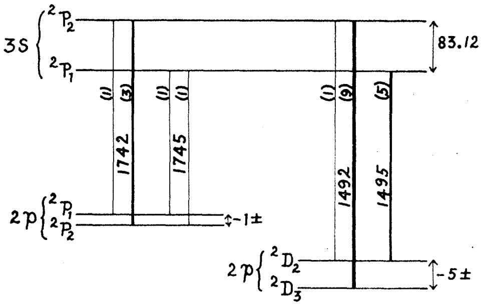

Fig. 2. Term diagram for nitrogen atom.

The upper P_1P_2 separation of 83.12 is known from the near visible lines analyzed by Kiess. The separations of the two lower pair of terms can be estimated approximately from analogy with O II, where the lower P_1P_2 separation is -4.5 and that of D_2D_3 is -19.8. We should therefore expect the corresponding separations in N I to be approximately -1 and -5 respectively, as shown in Fig. 2.

No spectrograph has yet been used, in this region of the spectrum, which could resolve lines as close as 1 or even 5 wave-numbers. Consequently the four predicted lines of the $2p^2P_{1,2}-3s^2P_{1,2}$ combination would appear as two lines, of relative intensities 2 and 1, and with a separation almost exactly 83.12. The $2p^2D_{2,3}-3s^2P_{1,2}$ combination of three lines would appear as two, of intensity ratio 2 to 1, but with separation about 5 units greater than 83.12. This is exactly what is found:

1742.740		1492.83	
57380.9		66986.9	
1745.260	82.8	1494.78	87.4
57298.1		66899.5	

Thus the argument which has been used against connecting both the 1742 and the 1492 pairs to the $3s^2P_{1,2}$ levels is, in the light of the predictions of the

Hund theory and of analogy with O II, really a convincing evidence of this connection. Similar considerations apply to the higher series combinations with these low levels.

Further evidence for this assignment of terms is found by applying the irregular doublet law. Knowing the low terms in O II to be ^4S 283028, ^2D 256200, ^2P 242558, and in N I the term ^4S 117345, we predict the other low N I terms ^2D 99983 and ^2P 91748. These are each within two or three percent of the values calculated from the strong 1742 and 1492 pairs, and there are no other lines in their vicinity.

Finally the fact that some of Hopfield's photographs show the 1492 and 1742 pairs in absorption would seem to complete the proof of this assignment. But there is still the following evidence.

Active nitrogen. Work in this laboratory by Kaplan and Cario,[9] on which a preliminary note has appeared in Nature, appears to give the complete explanation of this long-puzzling substance. Active nitrogen contains metastable molecules in the ^3S state[10] of energy about 8.2 volts and also metastable atoms of energies about 2.4 and 3.7 volts. The afterglow arises from excitation of the metastable molecules by the metastable atoms. The metastable molecules may be removed and the afterglow extinguished by passing the gas through a highly heated tube, but the 2.4 and 3.7 volt metastables are shown to persist and, beyond the heated region, to replenish the supply of metastable molecules by recombination,—thereby renewing the afterglow.

By investigating the intensities of spectra of various substances when excited by active nitrogen, Kaplan and Cario fixed the energies of the metastable atoms certainly within a few tenths of a volt of the values 2.37 and 3.56 given by the present analysis.

Accuracy of the series limits. For the series $A-ms^4P_3$ the quantum defects run regularly 3*s* 1.20, 4*s* 1.16, 5*s* 1.15, 6*s* 1.15, 7*s* 1.16±, and the calculated limit is about 117350. For the series $A-md^4P_3$ the quantum defects are more irregular: 3*d* 0.02, 4*d* 0.03, 5*d* 0.03, 6*d* 0.02, 7*d* 0.01 and the limit is calculated as about 117361. Hopfield calculated 117353, and Kiess 117345. We have arbitrarily used Kiess' limit as the one to which to refer our quartet terms. It appears, however, that a value about 8 or 10 units larger might be more accurate. Hopfield has already given the ionization potential as 14.48 volts.

For the doublet series, $B-ms^2P_2$ gives quantum defects; 3*s* 1.12, 4*s* 1.11, 5*s* 1.11, 6*s* 1.10, 7*s*1.13, and the estimated limit is about 98150. For the series $B-md^4F_4$ the quantum defects are very regular, 3*d* 0.03, 4*d* 0.04, 5*d* 0.05, 6*d* 0.06 with the estimated series limit 98143, which is probably the most accurate of the four.

These considerations show that the absolute scale of term values is probably accurate within about 10 units. No inter-system combinations between the doublet and quartet terms have been found (nor in O II), so that a direct tying together of the two systems is impossible. Consequently inter-system

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[9] Kaplan and Cario, Nature **121**, 906 (1928); also more detailed article soon to appear in Zeits. f. Physik.

[10] Sponer, Zeits f. Physik **34**, 622 (1925); Birge and Hopfield, Astrophys. J. (in print).

combinations are less accurately predicted from Table I than are intrasystem combinations.

Spark lines. Bowen[4] has identified a number of N II lines in the extreme ultra-violet. Of these, 18 lie between the extremes 533 and 1085, and therefore within the range of our plates (which took in the region 0–1250). We find all Bowen's lines, and with very satisfactory agreement in wave-lengths and intensities (except that we could not resolve several of his closest groups), except for one striking omission: we failed entirely to excite his strong group 644.633, 644.836, 645.180. Furthermore we have not succeeded in exciting spectra higher than the first spark in any gas thus far tried, i.e., N, Ne, A,[11] although we have gone to voltages well above those which should, energetically, be necessary. Consequently we have come to the provisional conclusion that single electron impacts do not disturb more than two electrons in an atom,—at least in the range of moderate energies. However this may be, the results indicate that Bowen's group 644–645 is due to some special condition of excitation of N II not present in our discharge. Fowler[12] has recently come to the same conclusion on other grounds, for he does not list this group but, instead, assigns weak lines near 776 to the combination suggested for 644–645 by Bowen. We find this line on our plates.

In conclusion we may say that the essential parts of the structure here proposed for N I seem to us to rest on quite convincing evidence, but the details in analyzing some close lines where no check in the near visible region is possible may require revision. We are at present experimenting with a novel type of discharge, with which we hope to discover some of the faint lines predicted by this analysis but not yet found.

Palmer Physical Laboratory,
Princeton, N. J.,
November 9, 1928.

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[11] Compton, Boyce, and Russel, Phys. Rev. **32,** 179 (1928).

[12] Fowler, Proc. Roy. Soc. **A118,** 44 (1928).