

# SPECTRUM OF ACTIVE NITROGEN IN THE SCHUMANN REGION

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Plate I

**ABSTRACT** A review of the theories of active nitrogen is given. Experiments by the authors to study the emission and absorption spectrum of the afterglow in the Schumann region with one metre normal incidence vacuum spectrograph are described. Spectroscopic evidence which is produced, is against the atomic hypothesis and supports the molecular nature of the phenomenon.

The phenomenon of afterglow of nitrogen was discovered by E. P. Lewis (1900) by passing condensed electric discharges in tubes through which nitrogen was flowing. He observed that the gas continued to glow with a yellow colour as it came out of the region of discharge. The luminosity, however, steadily diminished until it entirely disappeared. The nitrogen in this form is capable of reacting with several substances very easily and vigorously and has, therefore, been given the name of active modification of nitrogen by Lord Rayleigh (1904) who has done a great deal of experimental work to elucidate its nature.

At one time Lord Rayleigh believed that the constitution of active nitrogen was similar to that of ozone. Under the action of the discharge some of the  $N_2$  molecules decompose into atoms and combine with molecules to give what may be called tri-nitrogen ( $N_3$ ), according to the equation



and further that  $N_3$  combines with  $N_1$  to form  $2N_2$ ,



and in doing so radiates light.

As the change of volume experimentally observed in the process of conversion is, however, quite different from that expected on this basis, and further the more recent measurements of Wrede on pressure changes also do not support it, the hypothesis so far has not found any favour.

Saha and Sur (1924) then put forward a new hypothesis. According to them the Lyman-Birge-Hopfield bands lying in the vacuum region arise from a level which is metastable and the energy content of the molecule in this state was considered to be of the order of 8 volts or so. Saha and Sur suggested that

the excited molecule parts with its energy by a collision of the second type with another molecule which when it returns to the normal state gives rise to the phenomenon of afterglow. At the time when this suggestion was made, knowledge of the molecular spectrum of nitrogen was very meagre and therefore in the light of the analysis of the band spectrum of nitrogen which he carried out, Birge (1924) modified this hypothesis, and to the extent that an energy-content of 11.4 volts was assigned to the metastable state. He also suggests that the function of impurities which are found to be necessary for the production of active nitrogen, is to absorb the free electrons, which would otherwise permit an easy and direct passage to the normal state.

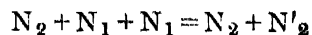
From an analogy with active hydrogen which is known to be atomic hydrogen, a handy explanation suggests itself that active nitrogen is also atomic in nature. Indeed, Lewis had suggested that chemical and luminescence phenomena are due to the energy set free by the recombination of two atoms. This would mean that the molecule formed by the recombination of two atoms possesses the energy of dissociation in the form of the energy of excitation.

For obvious reasons with our present-day knowledge of molecules such an idea without further modification would not be tenable. Sponer (1925), therefore, tried to explain away the difficulties by introducing the hypothesis that the discharge dissociates the molecule into two atoms, and when two of such atoms recombine in the presence of a third particle, phenomena associated with the active stage occur. The extraordinarily long life of the afterglow is thus due to the rare occurrence of such collisions. The third partner in such collisions may be a normal nitrogen molecule or any other foreign molecule or atom which takes up the dissociation energy which is liberated and given out eventually as radiation. The strongest bands in active nitrogen have their upper states corresponding to  $\nu' = 11, 12$  of the  $B(^3\Pi)$  of  $N_2$  and are situated in the visible region giving rise to the golden yellow colour of the afterglow. According to Spener, therefore, the energy of excitation of these bands corresponds to the heat of dissociation of  $N_2$ .

The three body collision hypothesis did not come in direct contradiction with any experimental facts. Indeed, it is supported by the decay curves which indicate that the decay of the afterglow is either a bimolecular or a trimolecular reaction. But as further spectroscopic data became available, the value 11.6 volts assigned by Spener for the dissociation of  $N_2$  molecule in two atoms in  $^4S$  states, was found to be too high.

These circumstances led Cario and Kaplan (1929) to develop a new hypothesis, which was really a modification and combination of the previous views, for it required the presence of metastable atoms and metastable molecules as well as a three body collision. According to this hypothesis, atomic nitrogen is formed by the discharge. As two such atoms combine in a three body collision with a molecule of nitrogen, dissociation energy amounting to 9.5 volts is liberated and this is sufficient either to take the molecule to the metastable state (which requires only 8 volts) or to excite any other atom (the third body) taking part in the

collision, but is not sufficient to excite the afterglow. The necessary equation is as follows:

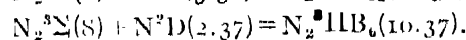
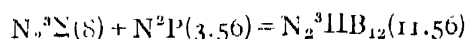


$N'_2$  indicates the nitrogen molecule in the metastable state ( $A^3\Sigma$ ). When two such excited molecules  $N'_2$  collide together, an energy of 16 volts goes towards the dissociation of one of the two molecules and is used up in changing the two atoms from a normal state to a metastable state. Thus



$N'_1$  and  $N'_1$  indicate two metastable atoms. The total energy of 16 volts is more than sufficient to dissociate a molecule which requires only 9.5 volts. The rest 6.5 volts is divided between the two atoms, each one being loaded with an amount of energy nearly 3.3 volts. Compton and Boyce have shown from spectroscopic investigations that for the nitrogen atom, the two metastable states ( $^2D$  and  $^2P$ ) have the energy-values of 2.37 and 3.50 volts respectively.

According to Cario and Kaplan (1920) the afterglow is given out when a metastable molecule collides with a metastable atom of either type. Thus



These are excited levels involved in the production of the afterglow corresponding to 11.56 and 10.37 volts, giving rise to certain bands of the first positive system selectively intensified.

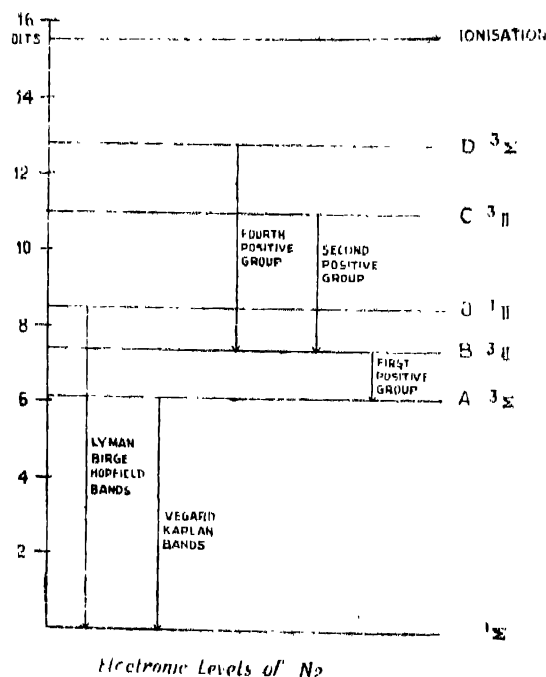


FIG. 1

In the light of further work on the analysis of the molecular spectrum of  $N_2$  and also on the basis of the work done by Okubo and Hamada (1933a) on

the excitation of spectrum by active nitrogen it becomes at once apparent that this hypothesis needs modification. According to the original theory of Cario the values of energies available in active nitrogen were 8.0 ( $A^3\Sigma$ ), 10.37 ( $B_6^3\Pi$ ) and 11.56 ( $B_{12}^3\Pi$ ). The lines observed by Okubo and Hamada have an excitation potential of 9.5 volts or less.

The discovery of Vegard-Kaplan (1930) bands (Fig. 1) also put the question of energy values in doubt. Vegard observed bands in solid nitrogen which he later also associated with certain bands in the spectrum of Aurora Borealis. Kaplan (1930) by designing a special discharge tube showed that they could be observed in  $N_2$  gas and after working out the vibration analysis proved conclusively that the lower state of this system corresponds to the normal state of the molecule. The value for  $A^3\Sigma$  thus comes out as 6.14 volts. In the light of these works, the energy values of  $A^3\Sigma$  and  $B^3\Pi$  are modified to 6.14 and 7.34 volts respectively.

As a result of series of experiments carried out in oxygen-nitrogen mixtures excited by rapidly interrupted weak discharges Kaplan has obtained an afterglow which has been called by him Auroral afterglow to differentiate it from the usual Lewis-Rayleigh phenomenon. It gives the auroral green line due to oxygen  $\lambda 5577$  ( $^1S_0 \rightarrow ^1D_2$ ). According to Kaplan the metastable nitrogen molecules in  $A^3\Sigma$  state are present only in the Auroral glow and not in the Lewis-Rayleigh glow. When the pressure is high the Auroral glow gives out in addition the forbidden lines of nitrogen corresponding to  $^2P \rightarrow ^4S$  and  $^2D \rightarrow ^4S$  transitions, proving the existence of metastable nitrogen atoms in the afterglow. The metastable nitrogen atoms are not produced directly but are supposed to be produced by the dissociation of the molecules.

Kaplan and Rubens (1940) have studied the behaviour of the Auroral glow with time and have observed that the intensity of the forbidden line  $\lambda 3467$  ( $^2P \rightarrow ^4S$ ) increases with time in the early phase of the afterglow. To explain this, they have postulated the existence of some molecules whose number increases with the time elapsed and their rapid predissociation causes the appearance of the forbidden lines. These temporal effects have also been observed in nitrogen-helium mixtures and the large intensity of the forbidden line has been explained as due to either the prevention of diffusion of metastable nitrogen atoms to the walls or the increased predissociation of molecular nitrogen in the presence of helium.

Hebb and Sponer (1941) have now proposed a modification of the old triple collision hypothesis, according to which the energy of the afterglow is stored partly as the energy of dissociation of nitrogen molecule into normal atoms and partly as the excitation energy of metastable  $^2D$  atoms. A  $^2D$  atom recombines with a normal atom in the presence of a third body directly into  $B^3\Pi$  state which is the upper state of the afterglow bands.

From the review of the present theories of active nitrogen which has been given above, it would appear that the view, that atoms of nitrogen in some state are present in active nitrogen, is generally finding favour. This hypothesis,

however, up to this time lacks a direct experimental confirmation. It may be mentioned that Cario (1934) and Kaplan (1934) have cited the results of Wrede (1929) and others on the observation of the pressure changes due to the diffusion of the products of the discharge, in support of their hypothesis of the presence of atoms of nitrogen. But, as has been pointed out by Saha and Mathur (1936), these experiments only prove the existence of these entities in the region of the discharge and it remains an open question whether they are also present in active nitrogen in the side tube. Kichiu and Acharya (1929) did not succeed in getting any line of nitrogen at 8200 on their plates though such long exposure were given that even the weakest bands of the first positive group were clearly visible up to 8900. The experiments described in the present paper were undertaken to photograph the spectrum of the afterglow of nitrogen in the Schumann region at about  $\lambda$  1700 Å where the resonance lines of atomic nitrogen due to the transitions  $2p^3-2p^2 3s$ ,  $2p^2 3d$  are situated.

E X P E R I M E N T A L

Nitrogen obtained from a commercial cylinder is collected in a large glass jar provided with a side tube at the bottom and placed in a water trough. By means of a tube put at the top it could be drawn out and passed through freshly cut chips of phosphorus contained in a bottle in order to remove traces of oxygen. After passing successively through calcium chloride tower, a phosphorus pentoxide tube and a capillary tube for partial regulation of the stream, the nitrogen entered the discharge tube provided with three electrodes ( $E_1$ ,  $E_2$ ,  $E_3$ ),  $E_3$ ,  $E_2$  being connected together and earthed. The gas is excited by a condensed

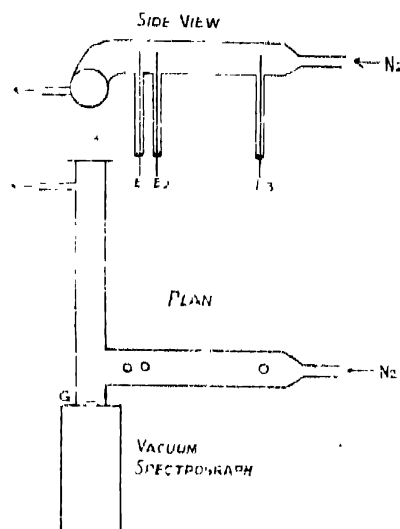


FIG. 2

discharge provided by a 16000-volt transformer with capacity and spark gap. The special construction of the discharge tube is shown in Fig. 2. The

end G is sealed on to the one-metre vacuum grating spectrograph of this laboratory. The passage between the slit and the tube is closed with a fluorite plate. The observation tube, about 30 cms. long, is collimated with respect to the spectrograph and is put in such a way that no light of the discharge enters the slit. The gas is drawn out by an oil pump which sends the gas back to the reservoir. A number of stop-cocks are put in the circuit for adjustment of pressure, etc. The arrangement is perfectly automatic and needs looking after only occasionally. Exposure is started after the gas has attained the characteristic yellow colour of active nitrogen as observed by the first positive group. The vacuum spectrograph has a dispersion of about 17.5Å per millimetre in the first order and is adjusted to take spectrum between 100Å and 2000Å in one exposure. In the present case the fluorite plate restricted the short wave-length limit to about 1250Å. The Schumann plates used were prepared in this laboratory.

Several photographs of the spectrum of active nitrogen with varying lengths in one case extending to 53 hours of exposure were taken. In none of these plates was there even the slightest trace of the lines of atomic nitrogen. The experiment of course cannot be advanced as an argument against the hypothesis Cario and Kaplan according to which the atoms of nitrogen may exist in metastable state  ${}^2D$  and  ${}^2P$  of  $2p^3$  configuration and may not exist in any of the states belonging to the configuration  $2p.2s$ . But it does show that the analogy of the parallel properties of active hydrogen and active nitrogen cannot be stretched too far, inasmuch as active hydrogen shows Balmer lines strongly and would, if the experiment were tried, also show the Lyman series.

A crucial test should be to observe the absorption spectrum of active nitrogen in the Schumann region where the resonance lines of atomic nitrogen are situated. According to Cario and Kaplan's theory, active nitrogen is composed of atoms in the states  $2p^3$  ( ${}^2D$ ,  ${}^2P$ ) and the absorption experiment should show the following multiplets in reversal ;

| $2p^3$        | $2p^2.3s$ | ${}^2P_{3/2}$ 31156 | ${}^2P_{1/2}$ 31230 | ${}^2D$ 17701 |
|---------------|-----------|---------------------|---------------------|---------------|
| ${}^2D$ 98143 |           | 1492.0              | 1494.7              | 1243.2        |
| ${}^2P$ 88537 |           | 1742.7              | 1745.3              | 1411.9        |

The apparatus employed to test this point was essentially the same as described before. The phosphorus bottle was, however, dispensed with and in addition more effective drying arrangements were used. For continuous spectrum the radiations from a hydrogen discharge tube taking 90 ma. at 1500 volts was used. This tube was sealed end-on to the tube through which the afterglow was streaming, and to avoid the mixing up of the two gases a fluorite window was provided. A fluorite window was also sealed on to the slit of the spectrograph. The length

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of the afterglow, through which the radiations from the hydrogen tube passed and fell on the slit of the one-metre vacuum grating spectrograph, was about 14 cms. The glow was very bright and was steadily maintained at a pressure of about 7 mm. The electrodes of the discharge tube near the spectrograph were carefully earthed, so that the afterglow streamed through a field-free space. The active nitrogen was formed by a condensed discharge from a 20,000 volts transformer taking about 300 watts. The Schumann plates used were prepared in the laboratory and an exposure of five hours was found to be enough.

RESULTS

Plate 1 shows two of the spectrograms taken. "a" shows the discharge alone from the hydrogen without any active nitrogen. This particular spectro-

*List of the fourth positive bands of CO observed in active nitrogen*

| $\lambda$ in Å<br>Observed by<br>authors | Observed by<br>Knauss | Assignment by<br>Birge<br>( $v'$ , $v''$ ) | $\lambda$ in Å<br>Observed by<br>authors | Observed by<br>Knauss | Assignment by<br>Birge<br>( $v'$ , $v''$ ) |
|--|-----------------------|--|--|-----------------------|--|
| 2202.3                                   |                       | 5-14                                       | 1724.5                                   | —                     | 4-0  |
|  | 2101                  | 2-11                                       | 1713.3                                   | —                     | 0-3  |
|  | 2171                  | 5-13<br>1-10                               | 1705.7                                   | —                     | 3-5  |
| 2150.9                                   | —                     | 4-12                                       | 1670.7                                   | 1669                  | 1-3  |
| 2068.0                                   | —                     | 4-11                                       | 1654.3                                   | 1653                  | 0-2  |
| 2044.9                                   | —                     | 3-10                                       | 1649.0                                   | 1648                  | 3-4<br>6-6                                 |
| 2034.1                                   | —                     | 6-12                                       | 1631.2                                   | —                     | 2-3<br>5-5                                 |
| 2010.6                                   | —                     | 5-11                                       | 1613.4                                   | —                     | 4-1  |
| 1991.0                                   | —                     | 4-10                                       | 1597.3                                   | 1597                  | 0-1  |
| 1970.2                                   | —                     | 3-9  | 1577.3                                   | 1574                  | 2-2<br>5-4                                 |
| 1931.3                                   | —                     | 1-7  | 1561.4                                   | 1558                  | 1-1<br>4-3                                 |
| 1914.8                                   | —                     | 0-6<br>7-11                                | 1543.5                                   | 1542                  | 3-2  |
| 1898.4                                   | —                     | 3-8  | —  | 1528                  | 5-3  |
| 1879.0                                   | —                     | 2-7  | —  | 1496                  | 6-3  |
| 1859.2                                   | —                     | 1-6  | —  | 1493                  | 5-1  |
| 1811.1                                   | 1810                  | 2-6  | —  | 1464                  | 1-1  |
| 1792.2                                   | 1793                  | 1-5  | —  | —                     | 6-2  |
| 1775.1                                   | —                     | 0-4  | 1411                                     | 1410                  | 6-1  |
| 1730.2                                   | —                     | 1-4  |  |                       |  |

gram was taken with an exposure of 3 hours. The continuous spectrum goes right upto the beginning of the Lyman  $H_2$  bands starting at 1674 and can still be observed at 1550A. It is perfectly free from any emission lines. Spectrogram "b" is that of the light after passing through the afterglow. The usual  $\gamma$ - and  $\delta$ -bands of NO and the fourth positive bands of CO observed by Knauss (1928) are clearly visible in emission but there is absolutely no trace of any absorption of nitrogen lines and we are definitely of the opinion that an increase of the length of the absorbing column would not bring out the looked for absorption lines, as in the present experiment the whole of the region of the strongest intensity in the afterglow was being utilized for absorption.

Attention may be drawn to the presence of the 4th positive bands of CO on our plates. No CO was introduced in the tube containing active nitrogen, as was done by Knauss. These bands must, therefore, be attributed to the combination of the traces of oxygen present as impurity with the carbon from greases, etc.

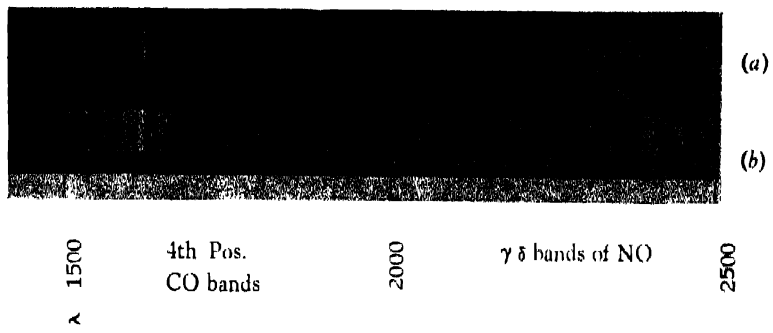
The list given above comprises of most of the bands of the fourth positive group of CO observed by Knauss and in addition gives a large number of bands not recorded by him. Knauss mentions that he experienced great difficulty in photographing these bands and as the intensity was very low the slit had to be kept very wide. In our experiments the bands come out easily and with short exposures. The accuracy of measurements for most of the bands is within 1A. The conclusion of Knauss that only those bands of CO are developed in the afterglow whose initial vibration states run from 1 to 6, is confirmed by observation on much larger number of bands recorded in the present work. This fixes up the excitation energy between 8.0 and 9.0 volts.

#### DISCUSSION

The absence of absorption lines of nitrogen in the  $^2D$  and  $^2P$  states does not support the theory of Cario and Kaplan mentioned before, nor the more recent speculation of Hebb and Sponer (1941). This result, however, appears to support the viewpoint of Saha and Mathur that the atoms occur only in the region of the discharge and the two excited atoms of nitrogen form an extremely stable state of the molecule which produces the L. R. afterglow on collision with neutral molecule. This view is essentially the same as proposed by Debeau, (1942) a short while ago, in consequence of some experiments on pressure changes in the afterglow.

In this experiment, electrodeless discharge in a bulb containing nitrogen at .5 m.m. pressure, produced active nitrogen in another connected bulb, and at the same time increased the pressure of the system to almost double its value before passing the discharge. On cooling a small portion of the active nitrogen bulb by liquid air, the intensity of the afterglow increased near the cooled portion and within thirty seconds completely disappeared from the entire bulb. The pressure of the system, however, was reduced to its value before the discharge. On removing the liquid air, the pressure regained its double value and the glow





reappeared first at the cooled portion and subsequently filling the bulb. The large pressure changes have been ascribed to the complete dissociation of nitrogen molecules. The products of dissociation consist of atoms in the normal state possessing energy equal to 7.35 volts and the excited metastable atoms in the  $^2D$  state. The recombination of these atoms forms a collision complex loaded with 9.8 volts energy. This complex on colliding with neutral nitrogen molecules raises them to certain levels of  $B^3\Pi$  state, which give rise to the afterglow. To explain the effects of liquid air he assumes that the life of these complex molecules increases with decrease of temperature, a corresponding decrease occurs in the number of atoms and causes the large reduction of pressure observed. The increased concentration of (NN) complex at the cooled surface is responsible for the increased intensity of the glow, which soon disappears due to the scarcity of more atoms to form the collision complex. The reverse process occurs on removing the liquid air.

This interesting experiment of the freezing out of the active component of the afterglow supports the recent hypothesis of Saha and Mathur (1936). The (NN) complex of Debeau is really identical with the proposed "some stable state of molecule loaded with an energy content of 9.8 volts" of Saha and Mathur. This "extremely stable molecule" or the (NN) collision complex loaded with about 10 volts energy, having a long life time, persists in the afterglow space, collides with neutral nitrogen molecules giving rise to the active nitrogen phenomenon. In our experiments with the Lewis-Rayleigh glow the excitation of a large number of CO bands of the fourth positive group, and  $\gamma$  and  $\delta$  bands of NO, clearly showed the activity of the afterglow. But the non-appearance of any emission or absorption lines of atomic nitrogen, in our plates definitely proves the absence of  $^2D$ ,  $^3P$  atoms in the afterglow. In view of this spectroscopic evidence against the atomic hypothesis, we conclude that the afterglow phenomenon of Lewis-Rayleigh is primarily due to the activity of some unknown molecular state of nitrogen. This would also appear to be supported by the experiments of Kneser recently confirmed by Lord Rayleigh (1940b) that a definite increase in the luminosity of this afterglow is obtained by the introduction of neutral nitrogen molecules.

It may be that under the conditions for the excitation of forbidden lines in the Auroral glow of Kaplan this particular molecular state predissociates to form the required excited atoms. But of course no evidence for or against such a supposition is provided by the present experiments. That atoms are present in the region of the discharge does not lead us very far, because they must be present even without the formation of active nitrogen. The chief problem, therefore, from the point of view of the phenomenon of active nitrogen is the identification of the stable molecular state of Saha and Mathur or the molecular complex of Debeau.

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