# THE EXISTENCE OF METASTABLE MOLECULES IN ACTIVE NITROGEN

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Abstract

It has been shown in the present experiments that active nitrogen contains, among other things, metastable molecules of nitrogen possessing about 8 volts energy. The evidence that is presented to prove this statement is the excitation of the fourth positive group of nitrogen simultanesously with the quenching of the afterglow by a mild electric discharge. The main spectroscopic characteristics of a condensed discharge have been reproduced by simply introducing active nitrogen into a weak discharge. The relation of these phenomena to the structure of the nitrogen molecule is discussed.

SUGGESTIONS that the characteristics of the afterglow in active nitrogen could be wholly or partially explained by the existence of metastable molecules of nitrogen possessing about eight volts energy, have been made by Saha and Sur,[1] Birge,[2] Kaplan and Cario[3] and others. The only basis for the existence of metastable nitrogen molecules was for a long time the fact that one could offer them as an explanation of the nitrogen afterglow. Recently however as a result of the study of the electronic states in molecules by Hund, Mulliken,[4] and Birge and from the study of the spectrum of nitrogen in the far ultra-violet by Sponer,[5] independent reasons have been found for postulating the existence of metastable nitrogen molecules.

The most recent assignment of electronic states by Mulliken calls the $X$ or normal level of nitrogen a $^1S$ level and the first electronic level at about eight volts either a $^3S$ or a $^3D$ level. One would therefore expect this level to be a metastable one because of the high improbability of a transition between a singlet and a triplet level. The absence of this transition is proved by the failure of repeated efforts to observe the bands that would arise in the transition $A$-$X$. It seems therefore that one is justified in assuming that this first level is metastable.

The purpose of the present communication is to present experimental evidence as to the existence in the afterglow of these metastable nitrogen molecules.

Active nitrogen can lose part of its afterglow when a weak discharge is passed through the glowing gas. This was first observed by Strutt.[6] Since the observation of this phenomenon very little mention has been made of it in spite of the fact that it has probably been often observed. In the present

[1] Saha and Sur, Phil. Mag. **48,** 421 (1921).
[2] Birge, Nature **114,** 642 (1924).
[3] Kaplan and Cario, Nature **121,** 906 (1928).
[4] Mulliken, Phys. Rev. **32,** 186 (1928).
[5] Sponer, Proc. Nat. Acad. Sci. **13,** 100 (1927).
[6] Strutt, Proc. Roy. Soc. **A91,** 303 (1922).

experiments attention was called to this effect purely by accident. An obvious experiment to try in the study of active nitrogen is the behavior of the gas under the action of electronic bombardment. If the active nitrogen is atomic then the atomic lines ought to be excited when a discharge is passed through it. Since an ordinary uncondensed discharge through molecular nitrogen does not excite any of the arc lines of nitrogen in the visible or near ultra-violet, it is apparent that the excitation of these lines when a mild discharge is passed through active nitrogen would be a very good indication that atomic nitrogen is present in the afterglow. Attention should however be called to the fact that a negative result in such an experiment would not be a proof that atomic nitrogen is absent. The lowest known electronic level in molecular nitrogen has an excitation potential of about eight volts. This value is lower than the energy necessary to excite any of the visible arc lines of nitrogen. It is quite possible, therefore, that in a mixture of atomic and molecular nitrogen the arc lines would be only feebly excited. The experiment was however tried in the hope that a positive result would follow.

In the present experiments active nitrogen was produced by passing a condensed discharge through streaming commercial nitrogen. The pressure was about 0.5 mm, at which pressure the production of the glowing gas was very great. Commercial nitrogen contains oxygen in amount sufficient to provide the impurity that has been found to be necessary in order that glowing active nitrogen be produced. The active gas was allowed to diffuse into another bulb through which a mild discharge could be passed. The spectra of these discharges were photographed on a small quartz Hilger spectrograph. In order to determine the effect of the presence of active nitrogen, photographs were taken both with and without the presence of active nitrogen.

In addition to the above method of producing active nitrogen, air, instead of commercial nitrogen was used in the discharge tube. Earlier experimenters invariably reported that the presence of more than about two percent oxygen was fatal to the production of the active gas. Since then, most experimenters have assumed that this was correct and no doubt with the many possible experimental conditions that can arise, the early experiments were correct. The author[7], however, was able to produce active nitrogen by passing a condensed discharge through air. The resulting afterglow which was blue in color differed spectroscopically from the better known straw yellow afterglow in that the first positive bands of nitrogen were greatly weakened because of the presence of the oxygen. Simultaneously with the author Herzberg[8] also reported the production of active nitrogen in mixtures of oxygen and nitrogen in which the percentage of oxygen was as high as that found in air.

We now go on to describe and to discuss the results of the above experiments. Before doing so, however, it may be well to state that the results were indentical for the active nitrogen produced from air and for that produced from commercial nitrogen. The most outstanding effect of a mild discharge through active nitrogen was the excitation of the fourth positive

[7] Kaplan, Proc. Nat. Acad. Sci. **14**, 258 (1928).

[8] Herzberg, Zeits. f. Physik **46**, 878 (1928).

group of bands of the nitrogen molecule. This group of bands was first observed by Strutt[9] under rather striking conditions. Strutt found that one of the main differences between a condensed and an uncondensed discharge in nitrogen was the excitation of the fourth positive group in the former. Later work showed that it originated on the highest known electronic level of the molecule. The 0–0 band in this group requires 14.8 volts for its excitation. Since, in order to obtain active nitrogen in any appreciable quantity, it is necessary to use a condensed discharge rather than an uncondensed one, this difference between the two discharges, suggested to Sponer[10] the following idea. All of the known fourth positive bands originate on the $D$ level that has zero as its vibrational quantum number. Bands arising on higher $D$ levels have not been observed, suggesting that the binding in this state is so weak that dissociation occurs quite readily. A discharge, in which these bands are highly excited, should therefore, according to Sponer, abound in atoms and this is cited as an argument that active nitrogen is primarily atomic nitrogen.

We can however, from the present experiments, discuss the excitation of the fourth positive group from an entirely new point of view. The result which we are going to discuss is the excitation of the fourth positive group when the afterglow is weakened by a mild discharge. It is apparent that the simplest interpretation that one can give to this phenomenon is, that when the discharge is passed through active nitrogen, there is present a modification of the nitrogen molecule which possesses more energy than the normal molecule. It is this modification, which is excited by the weak discharge to give the $D$ level of the molecule. The conclusion is a reasonable one when one considers that when active nitrogen is present the $D$ level is excited, whereas when active nitrogen is absent, the same discharge is unable to excite this level. The presence of a small amount of active nitrogen is sufficient to bring out strongly the fourth positive group at the same time that the afterglow itself is being weakened. In the following we will discuss the connection between these two facts.

We concluded in the last paragraph that an excited modification of the nitrogen molecule must be present in the afterglow. For several reasons the first electronic level is suspected to be the one in which the modified molecule finds itself. There are several reasons for thinking that the first or $A$ electronic level is a metastable one and these have been given in the earlier part of the paper. In a paper which is to appear elsewhere, Cario and the author base an hypothesis as to the nature of active nitrogen on the presence, among other things, of these metastable nitrogen molecules in the afterglow. The results of the present experiments are proposed as experimental evidence for the presence of metastable molecules in the glow. In brief, the quenching of the glow by a mild discharge is explained as being due to the excitation of metastable molecules to higher electronic levels by the mild discharge.

[9] Strutt, Proc. Roy. Soc. **A85,** 377 (1917).
[10] Sponer, Zeits. f. Physik **34,** 622 (1925).

It was mentioned above that the active nitrogen that was used in the present experiments was formed in one of two ways and that the results were the same for both "varieties" of active nitrogen. Without discussing this point in detail it is possible to point out its significance. In the active nitrogen that is produced from air the visible afterglow is considerably weaker than in that produced from relatively pure nitrogen. The excitation of the fourth positive bands in this case however shows that metastable molecules are present in both the active nitrogen produced from air and in that produced from the commercial nitrogen and that the presence of the metastable molecules alone is not sufficient to give rise to the visible glow. This is in agreement with the recent ideas on active nitrogen presented by Cario and the writer.[3]

In addition to the excitation of the fourth positive bands, Strutt[9] observed several other differences between the condensed and the uncondensed discharges through nitrogen. The second positive group of nitrogen corresponds to transitions between the $C$ and the $B$ electronic levels. Strutt observed that this group was considerably enhanced in a condensed discharge, relative to the rest of the spectrum. The same result was found in the mild discharge through active nitrogen. In addition, it was noted that several of the bands were especially enhanced, i.e., the intensity distribution among the bands themselves was changed. This change in the intensity distribution among the bands could not be traced to the enhancement of any one upper level.

Strutt[9] also observed that the $\gamma$ bands of nitric oxide, which are strongly excited in the uncondensed discharge, are almost completely absent from the condensed discharge. This was also found to be true for the mild discharge through active nitrogen. The phenomenon of the weakening of the $\alpha$ bands in the condensed discharge has of course been reproduced in the present experiments since the effect of the mild discharge is to weaken the visible afterglow.

It is worthy of note therefore that we have reproduced the main spectroscopic characteristics of a condensed discharge through nitrogen by simply passing active nitrogen into a very weak uncondensed discharge. We may therefore account for these spectroscopic characteristics of a condensed discharge by ascribing them to the presence of active nitrogen in the condensed discharge itself. In this way we have accounted for the excitation of the fourth positive bands in the condensed discharge as well as for some of the other characteristics of the discharge. The quenching of the $\alpha$ bands in the weak discharge as well as in the condensed discharge shows that metastable molecules play an important role in the excitation of the afterglow spectrum. One can conclude that a change in the intensity distribution of the second positive group of nitrogen should arise, if one considers the Franck-Condon[11] curves for the various electronic levels that are involved in the excitation and emission of these bands. The binding* in the upper level of these bands, the $C$ level, is approximately the same as that of the normal level of the molecule,

[11] Condon, Phys. Rev. **28**, 1182 (1926).

* By binding we refer to the value of $r_0$, which increases as the binding is weakened.

the $X$ level. On the other hand the binding in the metastable $A$ level is considerably weaker than that in either of these other levels. Consequently, if we assume that in the condensed discharge and in the mild discharge in active nitrogen, the metastable molecules are excited by electron impact to the upper levels of the second positive group, one would expect a change in the intensity of these bands.

Considerations similar to those given above for the second positive group can be brought forward in discussing the excitation of the fourth positive group. As yet, no detailed analysis has been made of the fourth positive group. Consequently we do not know the value of $\omega_0$ for the $D$ level. We can however indirectly make some conclusions regarding this and in that way discuss the excitation of these bands.

The strongest band in the fourth positive group is the one corresponding to the transition $D_0-B_2$. The two bands next in intensity are those that arise in the $D_0-B_1$ and the $D_0-B_3$ transitions. A distribution of intensity, in which the strongest band is not the $0-0$ band, is characteristic of groups that arise in transitions between two levels in which there is a difference in binding. The binding in $B$ level can be measured by the value of $\omega_0$, which is 1718 cm$^{-1}$. Consequently the value of $\omega_0$ in the $D$ level must be either slightly greater than this or slightly less and there are two arguments which show that the value is slightly greater.

First, the binding in the normal level of the molecule is given by $\omega_0=2345$ cm$^{-1}$. If therefore, the binding in the $D$ level were stronger than that in the $B$ level, then it would have to be nearly equal to that in the $X$ level and we should expect that electrons possessing the necessary energy should be able to excite these bands quite readily. Duncan,[12] who tried to excite these bands by direct electron impact, succeeded in doing so, showing therefore that the binding in the $X$ level differs only slightly from the binding in the $D$ level. We can conclude from this therefore that the binding in the $D$ level must be stronger than that in the $B$ level. Further, the fourth positive bands are degraded toward the violet and therefore the moment of inertia in the upper level must be less than that in the lower level. From the rule of Birge and Mecke, that $I_0\omega_0$ is nearly constant, it can be concluded that the binding in the $D$ level is stronger than that in the $A$ level. It is seen therefore that the conditions of excitation of the fourth positive group cannot be explained on the basis of the Franck-Condon curves.

It is possible however to explain the excitation of the fourth positive group in a very simple manner. One can ascribe the absence of the fourth positive group in ordinary discharges to the small number of electrons that have energy enough to excite these bands. When active nitrogen is present however, electrons of as low as 6.8 volts velocity are able to excite the fourth positive bands and the probability of exciting them is therefore much greater. The value of 6.8 volts is the difference between the energy of the nitrogen molecule in the metastable $A_0$ level and its energy in the $D_0$ level. In this

[12] Duncan, Astrophys. J. **62**, 145 (1926).

way we have accounted not only for the excitation of these bands but also for the role of metastable molecules in this process.

The effect of heat on the afterglow has been reported elsewhere.[3] An experiment similar to the one above was tried when the active nitrogen was heated. The effect of heating was to destroy the afterglow but not to destroy completely the activity of the gas. The "dark modification" of active nitrogen that remained was still able to excite the $D$ lines of sodium and it is this modification through which a mild discharge was allowed to pass. It was found that when a mild discharge was passed through heated active nitrogen, there was no excitation of the fourth positive bands, showing therefore that metastable molecules were absent from the "dark" afterglow. The observation that the sodium $D$ lines were excited in this dark afterglow whereas the NO bands were not excited, fits in with the above result. Elsewhere, the spectroscopy of active nitrogen will be discussed and this point will therefore not be considered here.

By photographing the afterglow both in the visible and in the ultra-violet when a mild discharge is passing through it, it was found that both the visual bands of the afterglow and the $\beta$ and $\gamma$ bands of nitric oxide were quenched by the discharge. Now, it is known that the $\beta$ bands of NO are excited strongly only in active nitrogen. Consequently the entity, that is quenched by the mild discharge, must take part not only in the excitation of the $\alpha$ bands of $N_2$, but also in the excitation of the $\gamma$ and $\beta$ bands of NO. It can be concluded therefore that metastable molecules must play an important role in the nitrogen afterglow and these experiments are presented as an experimental proof of this statement.

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