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THE AFTERGLOW IN AIR

By Joseph Kaplan
University of California at Los Angeles

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Abstract

It was observed that on passing a weak discharge through the air glow the β bands of nitric oxide were very strongly excited. These bands possess several very interesting properties. They correspond to a transition from the B to the X level of the molecule and the transition B_0-X_0 is very improbable because of the large difference in nuclear separation. These bands have never been reported as being intense in electric discharges and they have been obtained with considerable intensity only in active nitrogen. This present experiment is therefore the first one in which these bands have been observed with great intensity in an electric discharge. The β bands, as observed in the present experiments, correspond to transitions only from the B_0 to the various X vibrational levels, whereas in the afterglow of active nitrogen they correspond to transitions from several B levels to the various X levels. This difference indicates that there are at least two possible methods for exciting these unusual bands and they have been discussed in brief by Kinsey and the author. They are excitation by recombination, and excitation by collisions of the second kind.

Introduction

THE problem of afterglows has been attacked in a great many different, ways in recent years. Of the various afterglows that have been studied the one receiving the most attention has been the afterglow in active nitrogen. The reason for the widespread interest in active nitrogen is readily understood when one considers the many interesting phenomena that have been observed in connection with it. These extend from the field of excitation of spectra by active nitrogen to that of surface chemistry. And because of the large range of action of active nitrogen it has been interesting both as a tool and as a problem in itself. In the present communication it is proposed to discuss some aspects of a much less studied and apparently far less interesting afterglow. The afterglow referred to is the one that is observed when almost any type of discharge is passed through air at pressures around 0.5 mm.

This afterglow was first observed by E. P. Lewis[1] and also studied by R. J. Strutt[2] during those years in which he made many very valuable contributions to the problem of afterglows. The spectrum of the air glow has not been studied to any great extent and there are no published photographs of it. Herzberg,[3] and independently the author,[4] have photographed the spectrum of the glow and found it to be continuous. Herbzerg has reported a

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[1] E. P. Lewis, Ann. d. Physik (4) **2**, 459 (1900).

[2] R. J. Strutt, Proc. Phys. Soc. **23**, 66 (1911).

[3] Herzberg, Zeits. f. Physik **46**, 878 (1927).

[4] Kaplan, Proc. Nat. Acad. Sciences **14**, 258 (1928).

maximum in the red and a decrease of intensity toward the violet. In addition to the continuous spectrum in the visible, the writer has reported the excitation of the OH band at 3064A. This band was undoubtedly excited by the active species in the afterglow, but as yet there is no basis for definitely discussing the process of excitation, since no experimental or theoretical work regarding the energy of the active species has appeared. Part of the purpose of the present work was to begin experiments designed for the purpose of studying in more detail than has been done, the nature of this afterglow.

Recently, Herzberg[3] and others have revived interest in the air glow by applying to its study a few of the methods that had been used in connection with the nitrogen afterglow. Herzberg has studied the effect of varying the relative amounts of oxygen and nitrogen in the discharge in which the afterglow was produced and also the influence of the condition of the walls of the containing-vessel. Other papers by Majewska,[5] Majewska and Witold[6] and Bernard Lewis[7] report work on the effect of surfaces, the rate of decay of the afterglow and on the mutual effects of nitrogen and oxygen on their afterglows. As the last title suggests, the continuous afterglow in air and in other mixtures of oxygen and nitrogen, has been ascribed to oxygen and several recent writers have suggested that it may simply be a recombination spectrum of atomic oxygen. It is not the purpose of this paper to discuss this point and it will be left for another communication. There is however no conclusive evidence in favor of the recombination hypothesis although the continuous spectrum makes that hypothesis a tempting one.

Another method of attack has recently been applied to the air afterglow by the author. The method, briefly, consists of allowing the active material to pass from the discharge in which it was formed into another discharge through which a very feeble current from a small spark coil is passing. The spectrum in the auxiliary tube is studied and the effect of the active material is noted. Recently Bay and Steiner[8] have applied this method to active hydrogen, active nitrogen and to a modification of oxygen to which they refer as active oxygen. They used external electrodes and electrodeless ring discharges whereas in the present experiments internal electrodes were used. The method was first used by the author in an attempt to excite atomic nitrogen lines in active nitrogen and it yielded some very interesting results. In the following a brief account will be given of some of the results of the present work.

Experimental Method

The afterglow was produced by passing an uncondensed discharge from a 1 kw Thordarsson transformer, giving 20,000 volts in the secondary, through various mixtures of oxygen and nitrogen. The pressure of the gas in the discharge was 0.5 mm and this has been found to be the best pressure

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[5] Majewska, Zeits. f. Physik **50**, 372 (1928).

[6] Majewska and Witold, Zeits. f. Physik **48**, 137 (1928).

[7] B. Lewis, J.A.C.S. **51**, 654 (1929); B. Lewis, J.A.C.S. **51**, 665 (1929).

[8] Bay and Steiner, Zeits. f. Phys. Chemie **3**, 149 (1929).

for the production of the afterglow. It is interesting to note that 0.5 mm is also about the optimum pressure for the production of atomic hydrogen and active nitrogen. The active material was allowed to pass into another discharge tube, having internal electrodes, and a weak discharge from a small spark coil was allowed to pass through this tube. The spectrum of this discharge was photographed on a Hilger E2 spectrograph and also on a small Gaertner instrument. The auxiliary discharge was sufficiently weak as to make it necessary to expose for about ten hours on the Hilger instrument in order to obtain reasonably intense plates. It is apparently the weakness of the auxiliary discharge that makes the method a valuable one in the study of active materials from discharges.

EXPERIMENTAL RESULTS

Several interesting results were obtained but the only one that is to be here discussed is the excitation of the β bands of nitric oxide. A preliminary note on these results was published in the letter column of the Physical Review.[9] The excitation of these bands with considerable intensity was certainly the most striking effect of the introduction of the active material into the weak discharge. The β bands are of special interest first because they have been obtained with considerable intensity only in the nitrogen afterglow and secondly, because of the large change in moment of inertia between the two levels that are involved in the excitation of these bands.

The β bands were first obtained by E. P. Lewis[10] in active nitrogen. The present experiments are the first ones in which these bands have been excited with great intensity in an electrical discharge. Furthermore, these seem to be the first spectroscopic results, other than the continuous spectrum that was discussed earlier, that have been gotten from the air glow. In what is to follow, the origin of the β bands will be discussed and several questions of interest will be raised.

DISCUSSION

The β bands correspond to the transition from the B level to the X electronic level of the molecule. The X level is the normal level and both the B and X levels are now thought to be $^2\Pi$ levels. Although there will be no occasion in this discussion to refer to the electronic configuration of the two levels involved the older method of identifying the two levels will not be used and they will be referred to as the $^2\Pi$ levels. It is proposed here also to use v instead of n for the vibrational quantum number in accordance with a suggestion contained in a letter[11] on band spectrum notation that was recently circulated.

The values of ω_0 for the two $^2\Pi$ levels are 1030 cm^{-1} for the upper one and 1892 cm^{-1} for the lower level. Consequently one should expect an intensity distribution among the bands that is typical of a molecule whose moments

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[9] Kaplan, Phys. Rev. **34**, 165 (1929).

[10] E. P. Lewis, Phys. Rev. (1) **18**, 125 (1904); Astrophys. J. **20**, 49 (1904).

[11] O. W. Richardson, Trans. Farad. Soc. **25**, 628 (1928).

of inertia in the upper and lower states differ greatly. Barton, Jenkins and Mulliken[12] have studied the intensity distribution among the β bands that were excited in active nitrogen, and they have found that the principal features of the intensity distribution agree with the predictions of the Condon theory. They have also noted some interesting and definite discrepancies between theory and experiment and the occasion will arise later in the paper for mentioning them.

In the present experiments the most intense β bands correspond to the $v'=0$ progression. Transitions from higher $^2\Pi$ levels are either very weak or entirely absent in the discharge. Birge[13] has pointed out that the $v'=0$ progression in the β bands, as excited by active nitrogen, was very intense relative to the higher progression. In the present experiments they seem to be relatively even more intense than they are in active nitrogen. The similarity between the two methods of excitation as indicated by the above point may be interpreted as showing that the mode of excitation in the present experiments may be exactly the same as that occurring in the afterglow of nitrogen. It is not proposed to discuss here the relationship between the excitation of the β bands and the nature of the afterglow. That will be discussed elsewhere. The present experiments have suggested several questions as to the possible ways in which the β bands can be excited and it is those questions that will be briefly discussed here.

The absence of the β bands from the spectra of ordinary discharges through mixtures of nitrogen and oxygen or through nitric oxide, is of course readily accounted for by the Condon theory and is due to the large change in moment of inertia during the transition $B^2\Pi^0 \rightarrow X^2\Pi^0$. The most probable transition from the $X^2\pi^0$ level by electron impact would probably result in dissociation of the molecule. Now according to ideas advanced by R. J. Strutt, NO_2 is formed in the air afterglow by the oxidation of NO by ozone. It is possible therefore that highly vibrating nitric oxide molecules are formed by the decomposition of NO_2 in the weak discharge and it is these molecules that are excited by electron impact to yield molecules in the $B^2\Pi^0$ level. It is difficult of course to see just why this level should be favored both by this process and by the one in active nitrogen. It is also difficult to reconcile the above suggestion with the absence or weakness of other than the $v'=0$ progressions.

Before calling attention to two other possible modes of excitation another unique property of the β bands will be mentioned. Barton, Jenkins and Mulliken have called particular attention to the fact that progressions higher than $v'=4$ are absent from the β bands excited in active nitrogen. This is especially striking since in absorption bands up to $v'=5$ have been observed. The above mentioned fact may give the clue to the explanation of the excitation of these bands in both afterglows.

The energy necessary for the excitation of the $^2\Pi^0$ level from the normal state of the molecule is 5.65 volts. The energy of recombination of NO is

[12] Barton, Jenkins and Mulliken, Phys. Rev. **30**, 175 (1929).

[13] R. T. Birge, Molecular Spectra in Gases, p. 141.

now thought to be about 6.6 volts.[14] Consequently it is possible that the energy of recombination of the nitrogen and oxygen atoms is used to excite the β bands. There are several ways in which this energy transfer can be made and a detailed discussion of these possibilities will be given elsewhere. The interesting point to note here is that when it is necessary to excite a molecular level, in which the separation of the two atoms is much larger than in the initial level, there are ways, in which that can be done, that do not involve a transition from the normal to the excited level. In the present case instead of an increase in separation between the nitrogen and oxygen atoms, as would occur if the excitation were from $X^2\Pi^0 \rightarrow B^2\Pi^0$, there is a decrease in separation arising from the recombination of the two atoms. This may account for both the absence of progressions higher than $v' = 4$ in the case of active nitrogen, and for the unusual intensity of the $v' = 0$ progression in the present experiments as well as in active nitrogen.

One other method remains and attention has already been called to this in an earlier note by Kinsey[15] and the writer. This method is based on the hypothesis that the excitation of bands by collisions of the second kind does not necessarily obey the Condon theory and that large changes in the separation of two atoms can arise when the excitation is brought about in this way. The presence of metastable molecules in active nitrogen makes the above postulate a plausible one, although the energy of the metastable molecules is such as to make difficult the immediate explanation of the several peculiarities in the bands to which attention has been called. There are hardly enough data on the excitation of bands by collisions of the second kind to warrant any hypotheses, but the possibilities are interesting.

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[14] Birge, Trans. Farad. Soc. **25**, 707 (1929).

[15] Kinsey and Kaplan, Phys. Rev. **33**, 114 (1929).