Recombination and Afterglow in Nitrogen and Oxygen*

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Measurements were made on pure N_2, using standard microwave cavity techniques, of the coefficient of electron recombination, α. Pressures ranged from 3 to 30 mm Hg. Spectrograms were obtained of the afterglow. Higher vibrational levels of the second positive bands are enhanced relative to those obtained from electronic excitation. Goldstein-Kaplan bands, the green bands of Gaydon, and the Herman bands in the range 7000–9000 A were also relatively much stronger. The (0,0) first negative band was observed 1500 microseconds after the end of the discharge. Light intensity measurements by means of a photomultiplier tube showed a peculiar behavior of the relative intensities of the first positive and second positive bands. The number of photons emitted was large as compared to the number of electron-ion pairs recombining.

In the afterglow of oxygen the only light observed was the (0,0) atmospheric band and weak radiation in the region 3500 A to 4500 A, which is thought to be a continuum. The continuum decreases in intensity as though it were the result of a two-body process.

INTRODUCTION

IN preceding papers electron-ion recombination was explored by the following three observations which were concurrently made after interrupting an electric discharge: the density of free electrons, the spectrum emitted, and the absolute intensity of the light emitted. Any one of these observations helped in the interpretation of the other two. The present paper extends these combined observations to the atmospheric gases, nitrogen and oxygen, which are of particular importance because they determine the survival of free electrons in the ionosphere. It is of additional interest that here is a short-duration afterglow of nitrogen which is to be compared with the other well-known types of afterglow.

Purified nitrogen or oxygen in quartz bottles were placed in a 10-cm microwave cavity and a discharge produced by a 10-microsecond pulse of microwave power. The electron density was determined from the shift of resonance frequency of the cavity; the spectra recorded on spectrographs, using a rotating slotted wheel; and the absolute light intensity measured by a photomultiplier tube with appropriate filters. Readings were made during the afterglow with delay times up to 5000 microseconds after termination of the discharge. The experiments reported in the present paper form a continuation of the work of Holt[1] and others. These authors used the method first described by Brown[2] and his co-workers.

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[1] Holt, Richardson, Howland, and McClure, Phys. Rev. **77**, 239 (1950); P. Dandurand and R. B. Holt, Phys. Rev. **78**, 331 (1950); Johnson, McClure, and Holt, Phys. Rev. **80**, 376 (1950).

[2] Brown, Biondi, Herlin, Everhart, and Kerr, Technical Report No. 66, Research Laboratory of Electronics, Massachusetts Institute of Technology, 1948 (unpublished); Phys. Rev. **75**, 1700 (1949), and **76**, 1697 (1949).

I. MEASUREMENTS ON NITROGEN

(a) Electron Densities

Let α represent the coefficient of electron recombination, defined in the usual way by the equation

$$dn/dt = -\alpha n^2,$$

where n = number of electrons/cm^3. Integrating, we obtain

$$1/n = (1/n_0) + \alpha t.$$

Hence a plot of $1/n$ *versus* t yields a straight line for a recombination process.

With moderate discharge voltages one single value, α_1, was observed for each of the three pressures used. With a more intense discharge the later portion of the plot of $1/n$ *versus* t became a straight segment of smaller slope, showing the production of an ion of lower rate of recombination, α_2 (Fig. 1). Four samples of nitrogen contaminated with CN yielded similar results though it required higher power to produce the second rate of recombination. The results for pure nitrogen are listed in Table I.

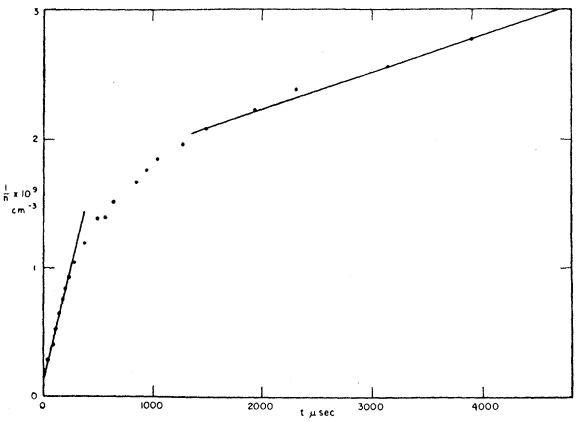

FIG. 1. Electron density n in the N_2 red glow as a function of time. $p=15$ mm Hg; $\alpha_1=3.1\times10^{-6}$ cm^3 sec^{-1}; $\alpha_2\leqslant 3.2\times10^{-7}$ cm^3 sec^{-1}.

TABLE I. Recombination coefficients in nitrogen.

p (mm Hg)	$10^6 \times \alpha_1$ (cm^3 sec^{-1})	$10^6 \times \alpha_2$ (cm^3 sec^{-1})
29	6.1	1.4
16	2.8	0.3
6.4	2.3	0.9

The variations in α with pressure are real. Even the values from the samples contaminated with cyanogen follow the same curves, that is, α_1 increasing with increasing pressure, while α_2 has a minimum at a pressure of 16 mm Hg.

(b) Spectra

Observations were made through a rotating wheel whose slits gave a "shutter speed" of about 100 microseconds, with a repetition period of about 2000 microseconds. It was practicable to use delays ranging from 50 to 1500 microseconds after the end of the discharge. Exposure times ranged up to 43 hours. The sample at a pressure of 6.4 mm Hg gave the most intense light and was therefore used most frequently. A wide-aperture Hilger quartz spectrograph was used for the ultraviolet and visible, and a Kipp liquid-prism spectrograph for the red and infrared.

The spectra were divided into three classes: that emitted during the discharge, presumably the result of electron bombardment; that emitted during the afterglow of a weak discharge, hereafter termed the "blue glow"; and that emitted during the afterglow of a strong discharge, hereafter termed the "red glow".[3]

The red glow would naturally contain, as an admixture, those processes properly belonging to the low-power discharge, since the exciting source was not monoenergetic. The great merit of the afterglow photographs is that the spectra resulting from recombination and association processes are not obscured by the much more intense electronic excitation. Judging from the light intensities during and just after the discharge, one hundred times as much light is produced by electronic excitation as by the afterglow processes.

No lines which could be ascribed to atomic nitrogen were ever observed, either allowed or forbidden.

No second positive bands had the same appearance in both types of glow. Compared with the direct discharge there was a somewhat higher rotational temperature, and a much greater relative intensity of the bands with higher upper vibrational numbers. Indeed, the distribution nearly approached that expected from equal population of upper vibrational states.

[3] When observed as a continuous discharge, excited by a continuous-wave radio-frequency source, the strongly excited glow is characterized by strong first positive bands, weak second positive bands, strong first negative bands, and the development of CN as an impurity. In the same bottle the weakly excited glow has the relative intensities of the first and second bands reversed, the first negative bands disappear, the CN disappears, and NO bands, in particular the γ series, appear as the impurity.

The first positive bands were much stronger relative to the second positive bands in the red glow than in the blue glow. They became relatively stronger with increasing delay time after the end of the discharge. However they never assumed the distinctive character of the Lewis-Rayleigh afterglow, but maintained the same familiar shape as when excited electronically.

The (0,1) and (0,0) first negative bands were weak in the afterglow, but stronger, relative to the second positive bands, than during the discharge. However, the (0,0) band was still observed 1500 microseconds after the end of the discharge, though, of course, it is a fully-allowed transition whose upper state is 3.2 ev above the ground state of N_2^+, and whose lifetime is much less than 1500 microseconds. This afterglow is presumably related to the "auroral afterglow" described by Kaplan,[4] but is observed within much shorter time intervals after the discharge. Kaplan describes the occurrence of the N_2^+ bands but does not state the law of their decay. Related observations are reported by Herman and Herman.[5]

Two prominent features were the green bands of Gaydon and all of the Goldstein-Kaplan bands observed hitherto.[6]

Several of the Vegard-Kaplan bands were observed. Though relatively very weak at 150 microseconds, at a delay of 1500 microseconds their intensities were comparable to that of the (0,0) first negative band. A few extremely weak NO bands were recorded. Their strength increased with increasing delay time.

Very strong bands in addition to the first positive bands were observed in the region 6900 A to 8500 A. Measured from an unsatisfactory plate, the wavelengths of their red edges, which may well be the proper edge to use, are as follows: 8081 A, 7841 A, 7614 A, 7543 A, 7464 A, 7080 A, and 7020 A, with an error of about 15 A. The dominant intensity of these bands in the short-duration afterglow indicates a preferred position of the energy levels involved. Unfortunately, the afterglow is much too weak a source to allow an investigation with high resolving power. These bands are identical with those discovered by Herman[7] in a weak discharge through nitrogen of low temperature. They were investigated in more detail by Carroll and Sayers.[8] The bands are located in the same wavelength range as the first positive bands and, at low dispersion, show the same appearance. Some of the bands nearly coincide with members of the first positive group.

[4] J. Kaplan, Phys. Rev. **42**, 807 (1932); **45**, 671 (1934); **51**, 143 (1937); **54**, 176 (1938).

[5] R. Herman, Compt. rend. **220**, 593 (1945); R. Herman and L. Herman, J. phys. radium **10**, 132 (1949).

[6] A. G. Gaydon, Proc. Roy. Soc. (London) **56**, 85 (1944). J. Kaplan, Phys. Rev. **46**, 326 and 534 (1935); J. Kaplan, Phys. Rev. **47**, 193 (1935); J. Kaplan and S. M. Rubens, Phys. Rev. **60**, 163 (1941).

[7] R. Herman, Compt. rend. **233**, 738 (1951).

[8] P. K. Carroll and N. D. Sayers, Proc. Phys. Soc. (London) **A66**, 1138 (1953). See plate 12.

(c) Light Intensities

The absolute intensity of the light was measured with a 1P28 photomultiplier tube which could be gated on and then off after a period of 50 microseconds, and whose gate could be delayed a known time after the end of the discharge. The absolute calibration was made by Mr. A. Redfield of this laboratory who determined the output per microwatt of light of 3400 A wavelength. Knowing the variation of the sensitivity of the phototube with wavelength and the character of the observed spectrum, one could calculate the number of photons emitted per second in the visible and ultraviolet.

If the light is emitted as the direct result of the recombination of two active particles (not necessarily electron and ion), then a plot of $I^{-\frac{1}{2}}$ *versus* time would be a straight line where I is the intensity. This also assumes that the character of the spectrum remains constant, or else the variation of sensitivity of the photomultiplier tube with wavelength would alter the curve. Such straight lines were observed with pure nitrogen at 6.4 mm Hg.[9]

The two dominant features of the spectrum in the range of the 1P28 are the first and second positive bands. The response due to the former was isolated by a cutoff filter. That due to the latter was obtained simply by measuring the total intensity since its maximum emission and the maximum sensitivity of the 1P28 nearly coincide. A proof of this was obtained from measurements with an ultraviolet filter.

The intensity of the first positive bands, when plotted as $I^{-\frac{1}{2}}$ *versus* t, yielded straight lines of equal slope for both the red and the blue glows. This implies that they are the result of a two-body reaction, which is probably an association of two nitrogen atoms, and the same process for each strength of excitation [but see Sec. I(*d*)].

The second positive bands yielded a straight line, when so plotted, during the blue afterglow, but not during the red. In fact, at times greater than 1000 microseconds in the red glow, the absolute intensity was less than that of the more weakly excited blue glow, though initially it was stronger.

In the samples of higher pressure the lines began to curve, but similar features were observed: the first positive bands decayed according to similar curves in both red and blue glows, the two curves merely being displaced in absolute intensity; the second positive bands of the red glow were initially stronger than those of the blue glow, but became absolutely weaker at longer delay times.

Each photon of second positive light is presumably followed by a photon of first positive light, since their lower and upper states, respectively, are the same state. Therefore if both their plotted intensities yielded straight lines of equal slope, this could be interpreted as one association process. If the second positive intensity yielded a straight line while the line of the first positive was curved, this could be interpreted as an additional association process whose atoms initially form the upper state of the first positive bands. However, neither of these possibilities explains the observations.

The absolute measurement of intensities leads to the result that the number of photons emitted is large as compared with the number of combining electron-ion pairs. For the detail the reader is referred to the thesis of R. B. Bryan.

(d) Discussion

Table I shows the rates of electron disappearance for pure nitrogen in the range of pressures from 6.4 to 29 mm Hg. The data show that after a *weak* discharge at any pressure the recombination is described by a rate constant α_1, which presumably measures the rate of recombination $N_2^+ + \epsilon$. If this process would occur, according to Bates,[10] by dissociative recombination, $N_2^+ + \epsilon \rightarrow N' + N'$, it would not depend on the pressure. Actually the rate increases with the pressure which may indicate a certain contribution of triple collisions.

After a *strong* discharge an additional process indicates the recombination of a species of lower rate of recombination. We guess that this species consists of atomic ions, N^+. It is known that an intense discharge partly dissociates the nitrogen as is evident from the production of "active nitrogen." It is true that only a small percentage of the molecules can be dissociated by an energy of 1 kw acting through 10 μsec (energy input per nitrogen molecule about 6×10^{-3} ev). However, charge exchange is expected to transfer the ionized state from N_2^+ to N^+ (ionization energies 15.6 and 14.5 ev, respectively) as in a well-known experiment of Biondi[11] in which 0.1% of argon in helium finally carries the whole ionization.

The data of Table I confirm the unexpected pressure dependence of α which is better evident in the data of Biondi and Brown.[2] The coefficient α seems to be constant, as expected for dissociative recombination, below a pressure of about 5 mm Hg. Above this limit α is increasing with increasing pressure. This effect is not well explained. Loeb and Kunkel[12] consider the simplified case of two ions (in our case N^+ and N_2^+) *in equilibrium* and so predict a curve representing $\alpha(p)$ which, however, shows a curvature opposite to that observed. So many secondary events (e.g., recombination of N+N and N^++N, charge transfer creating more N^+ at the expense of N_2^+) complicate the process that no unique interpretation seems possible. The

[9] In the samples contaminated with CN, the nitrogen spectrum rapidly decayed leaving only a cyanogen spectrum whose intensity distribution was that of cyanogen excited by active nitrogen, though the nitrogen spectrum was not that of the Lewis-Rayleigh afterglow.

[10] D. R. Bates, Phys. Rev. **77**, 718 (1950) and **78**, 492 (1950). M. A. Biondi, Phys. Rev. **83**, 1078 (1952).

[11] M. A. Biondi, Phys. Rev. **83**, 1078 (1951).

[12] L. B. Loeb and W. B. Kunkel, Phys. Rev. **85**, 493 (1952).

thorough discussion given by Massey[13] would explain a pressure effect by the action of triple collisions. According to Massey's estimate we calculate the contribution of triple collisions to α as 2×10^{-9} instead of the observed contribution of about 3×10^{-7}. One cannot explain the discrepancy by attributing the third-body effect to electrons or ions, because these particles would raise the value of α right after the interruption of the discharge. Such an effect is not observed.

Next we want to interpret the emission of light. The first guess that the observed light is due to the recombination of ions and electrons is untenable. The number of photons emitted in one band system is one or two orders of magnitude larger than the number of electrons disappearing at the same time. The discrepancy is still larger when one makes the plausible assumption that not each combination process generates a photon. The ratio of photons emitted to electrons disappearing changed with time.

The obvious second guess is that two free N atoms in a triple collision form an excited N_2 molecule. This guess, too, is untenable. Firstly this process has an energy limit of 9.76 ev and, therefore, fails to explain the excitation of the N_2^+ bands. Secondly this is the process claimed for the Lewis-Rayleigh afterglow[14] which is easily recognized by its characteristic intensity distribution. This is not observed here. Furthermore, the Lewis-Rayleigh afterglow lasts much longer.

Next the short duration of the afterglow leads to the guess that metastable atoms or molecules survive long enough to produce the light. But this simple idea is not compatible with the result that the emission of one quantum is due to the disappearance of two active particles.

We suggest a combination of these assumptions. One may assume that the two active particles forming a molecule consist of normal and metastable atoms, the metastable ones surviving from the discharge. A triple collision may lead to the formation of excited N_2 molecules whose rotation and vibration contains energies differing from the standard values produced by electron impact. For the explanation of the N_2^+ bands one may assume a survival of ionized molecules. But since their concentration after, say, 1500 microseconds must be extremely small, a more complicated process is indicated, for example, as suggested by Mitra,[15] the recombination of two metastable atoms, $N(^2D)+N(^2P)\rightarrow N_2^+ +$electron. The energy made available by this process exceeds that required for ionization by 0.18 ev. One must make the additional assumption that the ions so produced are excited by collisions with metastable atoms or molecules.

II. MEASUREMENTS ON OXYGEN

(a) Electron Densities

For the numerical results we refer to the paper of Biondi and Brown.[2] Only one value of α was observed (not, as in nitrogen after strong excitation and a certain delay, another smaller value). This result agrees with the above interpretation attributing the delayed effect in *nitrogen* to atomic ions. In *oxygen*, as opposed to nitrogen, the atom has the higher ionization energy, and hence is expected to neutralize promptly by charge transfer and to leave the ionization concentrated in the molecular species.

(b) Spectra

Unlike nitrogen, very little light is emitted in the observed region of the oxygen afterglow.[16] In the whole range of 2000 A to 9000 A, the only light observed by means of the spectrograph was the (0,0) transition of the atmospheric bands, whose intensity was comparable to that of the strongest emissions from nitrogen. No trace was observed of the (0,1) or (1,0) transitions.

An attempt was made to photograph light in the region 3500–4500 A, which according to the photomultiplier tube had an integrated intensity about that of the nitrogen afterglow after a delay of 1500 microseconds. A plate three times as sensitive as one which was successful in nitrogen was exposed for as long a time (14 hours), with the slit opened up to a width of one millimeter. Nevertheless, no blackening was observed. It is probable that the light is spread over a wide spectral range, and may even be a continuum.

(c) Light Intensities

As noted in the foregoing, very little light is observed in the afterglow. Though the direct discharge is itself dim, the intensity drops by a factor of 10^2 to 10^4 immediately. Nevertheless, the decay of light intensity could be measured for 400 to 600 microseconds in the afterglow, and a plot of $I^{-\frac{1}{2}}$ *versus* time yielded a good straight line with small scatter, indicating that the light was an immediate result of the disappearance of two active particles. Unfortunately the slope of this line depends on two factors, the coefficient of recombination, α, of the two particles and the probability that any one recombination generates a quantum. This complication prevents a simple interpretation of the slope. By means of various filters it was determined that most of the light, say 80%, was between the limits 3500–4500 A.

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[14] J. Berkowitz and G. B. Kistiakowsky, J. Chem. Phys. **25**, 457 (1956).
[15] L. K. Mitra, Phys. Rev. **90**, 516 (1953).
[16] L. M. Branscomb, Phys. Rev. **86**, 258 (1952).