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Measurements of Dissociative Recombination and Diffusion in Nitrogen at Low Pressures

A. C. FAIRE AND K. S. W. CHAMPION*

Geophysics Research Directorate, Air Force Cambridge Research Center, Laurence G. Hanscom Field, Bedford, Massachusetts

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The measurements of recombination in nitrogen and nitrogen-helium mixtures by Faire, Fundingsland, Aden, and Champion have been extended using, in addition to the basic microwave techniques, a monochromator and photomultiplier to study the spectra emitted. Electron production in the afterglow due to helium metastable atoms has been investigated and the results have made it possible to correct, where necessary, the apparent value of the recombination coefficient of nitrogen ions in nitrogen-helium mixtures. In addition, the ambipolar diffusion coefficient in nitrogen has been determined. This has been used to correct for losses due to fundamental mode diffusion. The magnitude of higher mode diffusion losses is discussed and shown to be small in this experiment.

The average values of the recombination and diffusion coefficients determined by this experiment are, respectively, $\alpha=(4.0\pm0.3)\times10^{-7}$ cm^3 sec^{-1}, $D_ap=220\pm30$ cm^2 sec^{-1} mm Hg, with an electron temperature of approximately 400°K. For pressures below 4 mm Hg it was found that the value of α was independent of pressure.

INTRODUCTION

THE values of the recombination and diffusion coefficients in nitrogen have both an intrinsic scientific interest and a particular interest since nitrogen is a major constituent of the ionosphere and these coefficients contribute to the magnitude of the time rate of change of electron density and other properties of the ionosphere.

Since the development of new techniques of measurement of these coefficients during the past decade, a number of independent measurements have been made of the coefficient of dissociative recombination[1–4] in nitrogen. Despite the refined techniques used, there exists a considerable amount of scatter in the published data. The aim of the present investigation is to resolve these discrepancies as far as possible.

* Physics Department, Tufts University, Medford, Massachusetts.

[1] Faire, Fundingsland, Aden, and Champion, J. Appl. Phys. 29, 928 (1958).

[2] M. A. Biondi and S. C. Brown, Phys. Rev. 76, 1697 (1949).

[3] Bryan, Holt, and Oldenberg, Phys. Rev. 106, 83 (1957).

[4] J. Sayers, *Solar Eclipses and the Ionosphere* (Pergamon Press, Inc., New York, 1956), p. 212.

EXPERIMENTAL PROCEDURE

Faire *et al.*[1] extended their measurements of the recombination coefficient of nitrogen ions to lower nitrogen pressures by using an inert gas to reduce the diffusion losses. Helium was assumed to be the most satisfactory recoil gas since the first excited level is 19.8 ev above the ground state, whereas only 15.6 ev is required to ionize N_2. The present work includes an investigation of the limitation of helium as a passive recoil agent. The study has been made analytically using the electron density decay data, and also experimentally by means of a monochromator and photomultiplier. A functional block diagram of the experimental arrangement is shown in Fig. 1. A cylindrical microwave cavity was excited in the TM_{010} mode by pulses from a magnetron and the resulting field produced a discharge in a quartz bottle enclosed by the cavity. A klystron was used to measure the electron density in the afterglow in terms of the shift in resonant frequency of the TE_{111} mode of the cavity. In addition, a quartz monochromator and photomultiplier were used so that the time variation of intensity of individual spectral lines and bands could be studied. Measure-

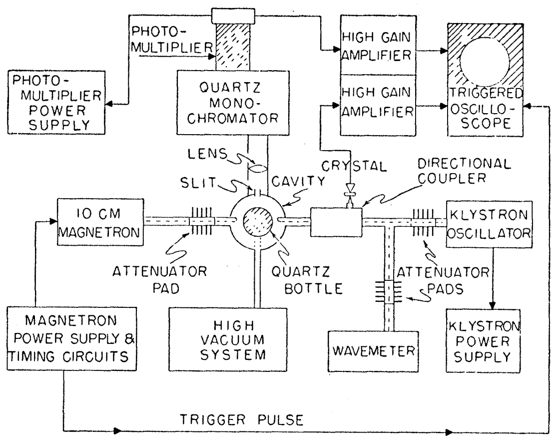


FIG. 1. Functional block diagram of experimental apparatus.

ments were made after the system had been carefully baked and evacuated to about 10^{-8} mm Hg, and then filled with spectroscopically pure nitrogen and also with mixtures of helium and nitrogen.

RESULTS

Nitrogen Only

Measurements were obtained with pressures of 0.9 mm Hg and higher. A typical electron density decay curve is shown in Fig. 2. It was found most satisfactory to plot the electron density on a logarithmic scale. On this plot, simple diffusion produces a straight line. With the experimental data it was found that the electron density decay curves tended to a straight line at sufficiently late times in the afterglow. This was taken to correspond to normal-mode diffusion loss.

The density decay curves were analyzed numerically, assuming that the decay could be represented by the sum of a linear and a square law term. That is,

$$\delta n/\delta t = -An^2 - Bn. \tag{1}$$

If it is assumed that recombination and fundamental mode diffusion are the predominant processes, then

$$A = \alpha, \quad B = D_a/\Lambda^2, \tag{2}$$

where α is the recombination coefficient, D_a is the diffusion coefficient, and Λ is the diffusion length of the quartz bottle. Table I shows the details of a typical calculation to obtain the values of α and $D_a p$ from measured values of electron density as a function of time in an afterglow. The electron losses due to recombination and diffusion were computed separately and added for comparison with the measured loss. The amount of agreement seen in this table is typical and appears to have reached the limit of the accuracy of the experimental data. A 10% change in the assumed value of either α or $D_a p$ gives a significant difference between the calculated and observed losses. If the change was made in the value of α the discrepancy would appear in the losses during the early intervals, and if the change was made in the value of $D_a p$ the discrepancy would appear in the losses during the later intervals of the afterglow.

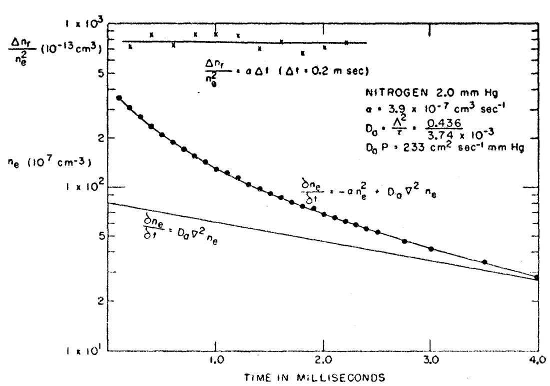


FIG. 2. Afterglow data in pure nitrogen.

In Fig. 2 are plotted the measured electron density decay curve, the calculated diffusion curve, and the calculated values of the recombination coefficient for successive 0.2-millisecond intervals. The relatively constant value of α as a function of time can be seen.

Table II shows typical measured values of α and $D_a p$ for afterglows in pure nitrogen, with various pressures and initial electron densities. If an appreciable portion of the electron loss attributed to recombination were due to a non-square-law process, such as higher mode diffusion,[5] then the apparent value of α would be a function of both electron density and pressure. However, the measured values of α are constant within the experimental error.

It might be pointed out that if diffusion effects are neglected in the calculation of the recombination coefficient, an apparent value for α is obtained which is approximately the same as the higher value (1.4×10^{-6} cm^3 sec^{-1}) reported in earlier work. The corrected value of α reported in this paper is nearer the approximate theoretical value of 10^{-7} cm^3/sec estimated by Bates.[6]

Nitrogen and Helium

To extend the measurements to lower pressures of nitrogen, helium was introduced as a recoil gas. Since the lowest excited level in He from which radiation can be emitted ($2p\,^3P$) is 5.3 ev above the ionization potential of N_2, it might be expected that no helium spectral lines would be emitted. However, in almost all discharges in nitrogen-helium mixtures, strong helium lines were observed. Figure 3 shows typical photographs of oscillograph traces of the intensity of six lines and bands as a function of time during the pulse discharge and ensuing afterglow.

[5] K. B. Persson and S. C. Brown, Phys. Rev. **100**, 729 (1955).
[6] D. R. Bates, Phys. Rev. **78**, 492 (1950).

TABLE I. Electron density decay in a nitrogen afterglow analyzed into recombination and fundamental-mode diffusion components. Nitrogen pressure = 1.2 mm Hg. The unit in all columns is 10^9 cm^{-3}, except where indicated. δn_R was calculated assuming $\alpha = 3.8\times10^{-7}$ cm^3 sec^{-1}. δn_D was calculated assuming $D_a p = 230$ cm^2 sec^{-1} mm Hg. $\delta t = 0.1$ msec for the first 20 entries, and 0.5 msec for the remainder.

Time (msec)	n_0	$1/n_0+\alpha\delta t$ (10^{-9} cm^3)	n (if recombination only)	δn_R	$n_0[1-(D_a/\Lambda^2)\delta t]$	δn_D	Calculated $\delta n_R+\delta n_D$	Exper. loss
0.1	2.31	0.471	...	...	...	...	...	...
0.2	2.05	0.526	2.13	0.18	2.21	0.10	0.28	0.26
0.3	1.81	0.590	1.90	0.15	1.96	0.09	0.24	0.24
0.4	1.61	0.659	1.70	0.11	1.73	0.08	0.19	0.20
0.5	1.45	0.728	1.52	0.09	1.54	0.07	0.16	0.16
0.6	1.32	0.796	1.38	0.07	1.39	0.06	0.13	0.13
0.7	1.19	0.878	1.26	0.06	1.26	0.06	0.12	0.13
0.8	1.09	0.955	1.14	0.05	1.14	0.05	0.10	0.10
0.9	0.99	1.048	1.05	0.04	1.04	0.05	0.09	0.10
1.0	0.92	1.125	0.96	0.03	0.95	0.04	0.07	0.07
1.1	0.84	1.228	0.89	0.03	0.88	0.04	0.07	0.08
1.2	0.78	1.320	0.82	0.02	0.80	0.04	0.06	0.06
1.3	0.72	1.427	0.76	0.02	0.75	0.03	0.05	0.06
1.4	0.67	1.531	0.70	0.02	0.69	0.03	0.05	0.05
1.5	0.62	1.651	0.65	0.02	0.64	0.03	0.05	0.05
1.6	0.58	1.762	0.61	0.01	0.59	0.03	0.04	0.04
1.7	0.54	1.890	0.57	0.01	0.55	0.03	0.04	0.04
1.8	0.50	2.038	0.53	0.01	0.52	0.02	0.03	0.04
1.9	0.47	2.166	0.49	0.01	0.48	0.02	0.03	0.03
2.0	0.44	2.46	0.46	0.01	0.45	0.02	0.03	0.03
2.5	0.32	3.32	0.40	0.04	0.35	0.09	0.13	0.12
3.0	0.24	4.36	0.30	0.02	0.26	0.06	0.08	0.08
3.5	0.19	5.45	0.23	0.01	0.19	0.05	0.06	0.05

The nitrogen bands shown constitute three of the strongest bands in the N_2 second positive system. The second positive system is readily excited and corresponds to the transition $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$. Incidentally, only N_2 bands and sometimes also N_2^+ bands were observed. This confirms that nitrogen in the molecular form predominated, as required by the assumption of dissociative recombination. The excited levels commonly obtained in the atoms resulting from dissociative recombination, *viz.*, ^2P and ^2D, are metastable levels. The nitrogen bands were observed to decay in the afterglow with a τ of about 50 μsec. This time may be partly due to instrumental time constants.

The helium lines shown represent, respectively, the singlet and triplet series. The steady increase in the intensity of these lines during the active discharge is probably associated with the growth of metastable atom concentration, since with low average electron energy the appropriate upper excited level is most readily reached by two steps, the intermediate one being the metastable level. In these particular curves the τ for the singlet decay is about 150 μsec and for the triplet decay τ is about 200 μsec, with a significant value for nearly 1.0 msec. in the afterglow. The triplet states predominate and have a longer decay constant, in agreement with the studies of Phelps.[7]

Afterglow Processes in Nitrogen-Helium Mixtures

In addition to ambipolar diffusion and dissociative recombination in the afterglows, other processes occur due to collisions of metastable helium atoms. A nitrogen molecule can be ionized by collision with a metastable helium atom.

$$He^m + N_2 \rightarrow He + N_2^+ + e + \text{K.E.} \quad (1)$$

The kinetic energy is 4.2 ev for a triplet metastable level and 5.0 ev for a singlet metastable level. As a result of conservation of momentum, almost all the kinetic energy is taken up by the electron. If one of these electrons collides with a metastable helium atom, it can raise it to an excited state from which it can radiate,

$$\begin{aligned} He^m + e + \text{K.E.} &\rightarrow He^* + e, \\ He^* &\rightarrow He^m + h\nu. \end{aligned} \quad (2)$$

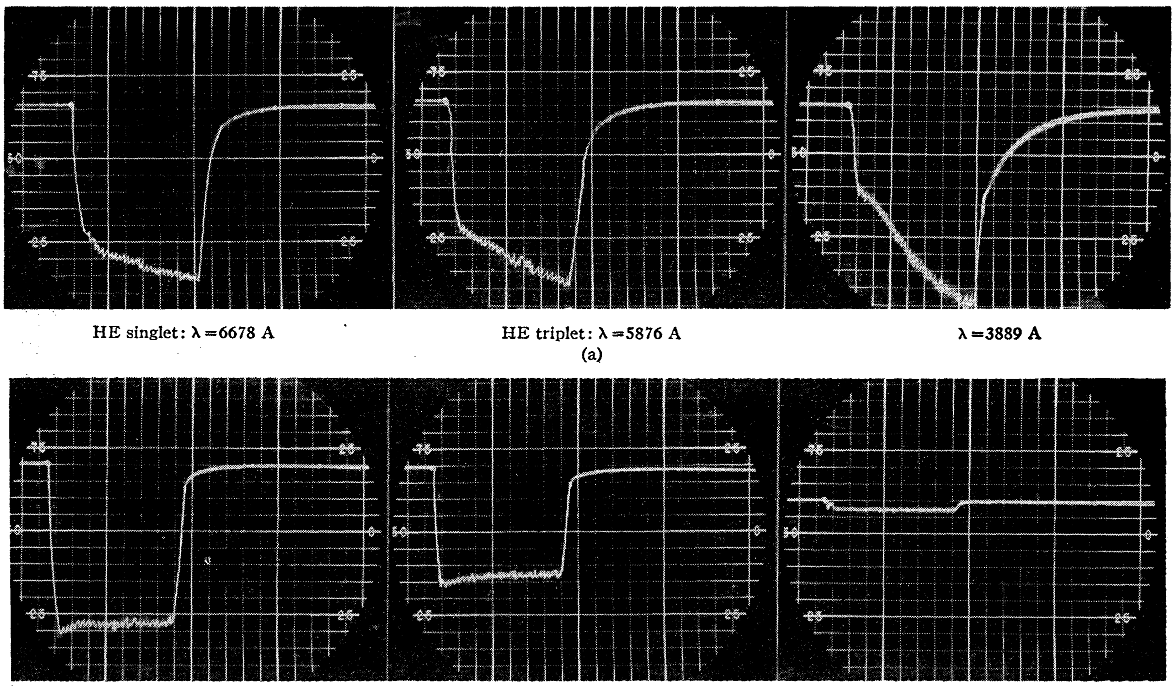
For example, the upper level for the 3889 A line is $3p\,^3P$, which is 3.2 ev above the triplet metastable level to which it returns after emission of this radiation. Similarly, the upper level for the 5876 A line is $3d\,^3D$,

TABLE II. Typical measured values of α and $D_a p$ for afterglows in nitrogen, with various pressures and initial electron densities.

Nitrogen pressure (mm Hg)	Initial[a] electron density (10^9 cm^{-3})	Measured value of α (10^{-7} cm^3 sec^{-1})	Measured value of $D_a p$ (cm^2 sec^{-1} mm Hg)
0.85	1.58	3.8	230
0.85	1.60	3.7	240
0.85	3.75	3.8	230
0.85	4.0	4.0	213
1.2	2.3	3.8	230
2.0	3.6	3.9	233
		3.8[b]	230[b]

[a] 0.1 millisecond after the end of the discharge pulse.
[b] Average values.

[7] A. V. Phelps, Phys. Rev. 99, 1307 (1955).



HE singlet: λ = 6678 A HE triplet: λ = 5876 A λ = 3889 A

(a)

N₂II pos: λ = 3577 A λ = 3371 A λ = 3159 A

(b)

FIG. 3. Intensity as a function of time of some of the bands and lines observed in the spectra from discharges in helium-nitrogen mixtures. The length of the active discharge is approximately 1.0 msec.

which is 3.3 ev above the triplet metastable level. The 5876 A line is emitted as a result of a transition to the $2p\,{}^3P$ level. The energy required to excite these lines in the afterglow is thus well within that acquired by electrons liberated by collisions of metastable atoms.

An approximate calculation shows that, during the interval 0.1 to 0.3 millisecond after the end of the ionizing pulse, approximately 10^7 to 10^8 cm^{-3} metastable helium atoms will be excited as a result of reaction (2) to levels from which they can radiate. Although the absolute intensity of the light emitted by excited helium atoms was not measured, this estimate is not inconsistent with the observed time variation of the intensity. Metastable helium atoms are lost in the afterglows as a result of diffusion and of reaction (1).

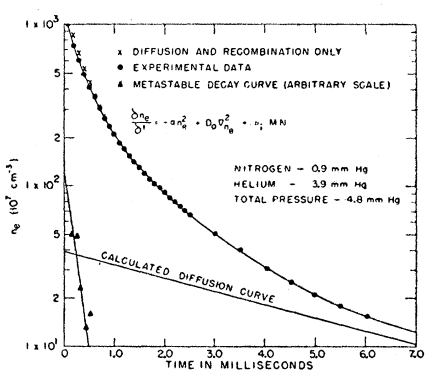


FIG. 4. Afterglow data in a nitrogen-helium mixture, nitrogen pressure 0.9-mm Hg. Coefficient of recombination $\alpha = 4.0 \times 10^{-7}$ cm^3 sec^{-1}.

Analysis of Afterglow Data

Figure 4 shows afterglow data obtained with a mixture of 0.9 mm Hg of nitrogen and 3.9 mm Hg of helium. The experimental values of electron density are shown as circles. From the spectroscopic data it was found that, with these conditions, the metastable atom density was negligible after 1.0 millisecond and so the electron density curve at later times in the afterglow was fitted assuming diffusion and dissociative recombination only. The electron densities were calculated for early times in the afterglow and where the computed values differed from the measured values, the former are indicated by crosses. It was assumed that the difference was due to electron production as a result of collisions with metastable atoms [reaction (1)]. The difference in electron density was plotted and the result was an approximately exponential decay. This was taken as evidence that the processes given above actually occur in the afterglows, and the line was assumed to be approximately proportional to the metastable atom density. Due to the two principal loss mechanisms of metastable helium atoms, the value of the time constant related to their decay is a complicated function of the relative nitrogen and helium pressures as well as the total gas pressure. Actual observed values of τ were in the range 50 μsec to 300 μsec.

It should be noted that with a nitrogen partial pressure of 0.9 mm Hg the effect on electron density of metastable helium atoms is small. In other words, with this pressure helium is a satisfactory recoil agent. Figure 5 shows data obtained with a nitrogen partial pressure of 0.085 mm Hg. At this pressure the density of metastable atoms is larger and their effect on the afterglow electron density is quite appreciable. Measurements were made with lower partial pressures, down to 1 micron of nitrogen, with increasing afterglow effects due to metastable atoms. This is demonstrated by the data in Fig. 6, which correspond to a nitrogen partial pressure of 0.011 mm Hg. The corrected value of the dissociative recombination coefficient was found to remain constant, within the experimental accuracy.

The average values of the coefficients determined by this experiment are

$$\alpha = (4.0 \pm 0.3) \times 10^{-7}\ \text{cm}^3\ \text{sec}^{-1},$$

$$D_a p = 220 \pm 30\ \text{cm}^2\ \text{sec}^{-1}\ \text{mm Hg},$$

with an electron temperature of approximately 400°K. (The corresponding value of $D_a p$ at 273°K is 150±30 cm² sec⁻¹ mm Hg.)

The value of 400°K for the afterglow temperature was calculated in the following way. During the one-millisecond ionizing pulse approximately 10 watts of microwave power was dissipated in the gas. Assuming that all this power was converted into heat the temperature of the gas would rise by approximately 100°K. A calculation of the rate of conduction of heat to the bottle walls by the gas shows only a 3°K drop in temperature during the 5-millisecond afterglow measuring interval. Thus the afterglow temperature was assumed to be 400°K and this gives a positive-ion mobility (at normal density) of 2.8 cm²/volt sec, which is in good agreement with the experimental value measured by Tyndall and Pearce[8] at 400°K, which (reduced to normal density) is 2.9 cm²/volt sec.

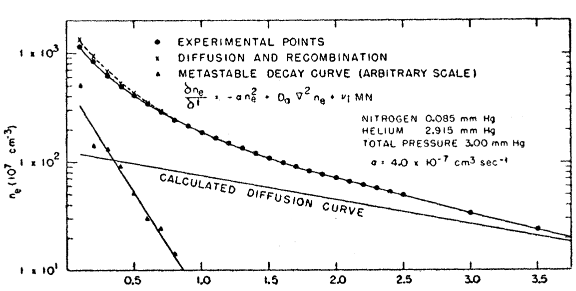


FIG. 5. Afterglow data in a nitrogen-helium mixture; nitrogen pressure 0.085 mm Hg.

[8] A. M. Tyndall and A. F. Pearce, Proc. Roy. Soc. (London) **A149**, 434 (1935).

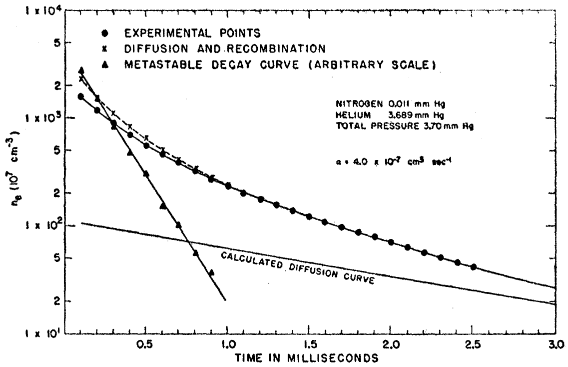


FIG. 6. Afterglow data in a nitrogen-helium mixture; nitrogen pressure 0.011 mm Hg.

The present value of α is consistent with that of Sayers[4] (1.1×10^{-7} cm³/sec with an electron temperature of 3200°K) if α varies as $1/T^{0.6}$. Now Bates[6] has developed an approximate theory for dissociative recombination whereby α varies as $f(T)/T^{1.5}$ and states that under favorable conditions $f(T) = \text{const} \times T$. In this case α would vary as $1/T^{0.5}$, in reasonable agreement with the above experimental value.

CONCLUSIONS

The coefficient of dissociative recombination in nitrogen was found to be independent of pressure, at least for all pressures below 4 mm Hg. This is in agreement with theory.[6] The apparent value of α observed by previous experimenters is reduced when corrections are made for diffusion losses. The value of the ambipolar diffusion coefficient of ions and electrons in nitrogen has been reported for the first time and appears to be in agreement with mobility measurements.

APPENDIX

Higher Diffusion Modes

When recombination is appreciable in a plasma, the distribution of electron density is no longer entirely in the fundamental mode, as determined by diffusion. Thus, in the decay of such an afterglow, there will be some loss of electrons in the form of higher-mode diffusion. Of particular interest in this connection is the magnitude of the higher-mode losses when compared with losses due to other processes active in the afterglow.

Although the calculation of the amplitude of the higher modes in any particular case, when both recombination and diffusion are present, is a complicated mathematical problem requiring the use of an electronic computer, it can be assumed that the actual amplitudes are less than those obtained with a uniform density distribution corresponding to recombination only. Thus both the time constants of the higher modes and a good estimate of their amplitudes can be obtained from a Fourier analysis of a uniform distribution of electron density.

The Fourier expansion of a one-dimensional square wave of maximum value N and zero value at the boundaries $(-h/2, +h/2)$ is

$$\frac{4N}{\pi}\left\{\cos\frac{\pi z}{h}-\frac{1}{3}\cos\frac{3\pi z}{h}+\frac{1}{5}\cos\frac{5\pi z}{h}-\frac{1}{7}\cos\frac{7\pi z}{h}+\cdots\right\}. \quad (3)$$

The corresponding expansion for cylindrical geometry, when the density is independent of θ and satisfies the additional boundary condition of being equal to zero when $r=r_0$, is

$$\frac{4N}{\pi}\left\{\cos\frac{\pi z}{h}-\frac{1}{3}\cos\frac{3\pi z}{h}+\frac{1}{5}\cos\frac{5\pi z}{h}-\frac{1}{7}\cos\frac{7\pi z}{h}+\cdots\right\}$$
$$\times\{1.604J_0(2.405r/r_0)-1.065J_0(5.52r/r_0)$$
$$+0.851J_0(8.66r/r_0)-0.73J_0(11.79r/r_0)\cdots\}. \quad (4)$$

Consider the case of a cavity containing a bottle that is sufficiently small so that the microwave measuring E field is essentially constant over the bottle. Then the change in resonant frequency is simply proportional to the average value of the electron density in the bottle. The effect of the higher modes on the electron density decay curves will be proportional to the average value of each mode over the bottle. The ratio of the integral of the $1.065\cos(\pi z/h)J_0(5.52r/r_0)$ term over the bottle to the integral of the fundamental term is 0.436. The ratio for the $(1.604/3)\cos(3\pi z/h)J_0(2.405r/r_0)$ term is 0.111. The magnitudes of the successive higher modes fall off steadily. The numerical values of the time constants of the higher modes depend on the value of the ratio h/r_0. In the present experiment, where $h/r_0=2.74$, it can be shown that $\tau_1/\tau_2=2.49$ and $\tau_1/\tau_2'=4.49$, where τ_1 is the decay constant of the fundamental mode and τ_2, τ_2' are the respective decay constants of the two higher modes considered above.

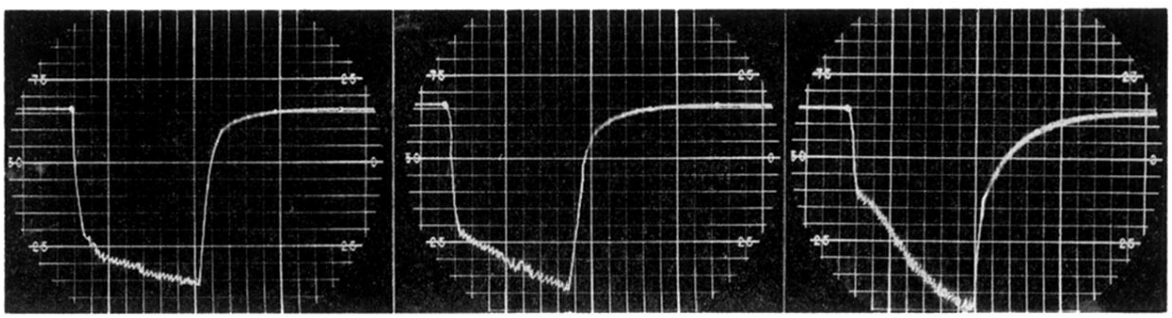
Because of recombination in the afterglow, more electrons are fed into the higher modes and they do not decay as quickly as if diffusion only were taking place. Nevertheless, the relative amplitudes of the higher modes must at all times be less than the values calculated assuming a uniform density distribution.

For typical afterglow data such as those plotted in Fig. 4, where both diffusion and recombination exist, an estimate of the amplitude of the first higher mode[9] is 0.2 of the amplitude of the fundamental mode, instead of 0.436 for a square distribution corresponding to recombination only. Including the effects of all higher modes, the factor would be approximately 0.5, corresponding to a density of 1.9×10^8 cm^{-3} at 0.1 msec in the afterglow. The measured density at this time was 1.0×10^{10} cm^{-3} and the difference between this value and that computed assuming only recombination and fundamental mode diffusion is 1.8×10^9 cm^{-3}. Thus higher modes would not contribute more than about 10% of this difference and it is necessary to assume that ionization produced by collisions of metastables accounts for the major part of the difference. This assumption is also necessary for consistency with the observed magnitude and time dependence of the helium spectral lines.

ACKNOWLEDGMENT

The authors gratefully acknowledge the fine laboratory and computational assistance provided by Miss Anna D. Gray of the Geophysics Research Directorate during the course of this work.

[9] The cavity was well matched to the coaxial line, the microwave ionizing field was approximately uniform across the bottle, and the pulse was sufficiently long (1 msec) for the plasma to reach steady-state conditions. Also, since recombination is negligible during the active discharge, the electron density during the discharge should be mainly in the fundamental mode. The light distribution from the discharge appeared to confirm this. As a result of recombination during the afterglow, some higher modes are introduced into the electron density distribution.



HE singlet: $\lambda = 6678$ A HE triplet: $\lambda = 5876$ A $\lambda = 3889$ A

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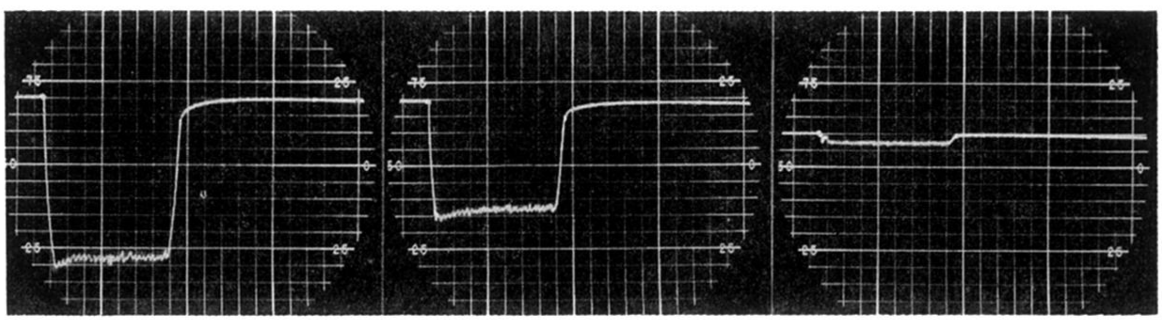

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FIG. 3. Intensity as a function of time of some of the bands and lines observed in the spectra from discharges in helium-nitrogen mixtures. The length of the active discharge is approximately 1.0 msec.