Study of the Temperature Dependence of Electron-Ion Recombination in Nitrogen*

W. H. KASNER
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania
(Received 7 July 1967)

The temperature dependence of the afterglow decay of electrons and ions from microwave discharges in nitrogen-neon gas mixtures has been studied using combined microwave and mass-spectrometric techniques. Under conditions where N_2^+ is the only significant afterglow ion species, i.e., at nitrogen pressures less than 10^{-2} Torr, and for neon pressures in the range 15 to 40 Torr, the afterglow is controlled by the recombination of N_2^+ ions and electrons. Over the temperature range studied, 205 to 480°K, the recombination coefficients exhibit no significant temperature dependence and can be represented by the constant value $\alpha(N_2^+) = (2.7\pm0.3)\times10^{-7}$ cm³/sec. At any given temperature the results show no systematic dependence on the nitrogen or neon gas pressure over the ranges indicated. Temporal mass analysis indicates similar decay rates for the N_2^+ ions and for the electrons over the major portion of the afterglow.

I. INTRODUCTION

In recent years there has been considerable interest in predicting free-electron lifetimes in various regions of the ionosphere following ionizing events, such as solar flares. An important process in determining the electron loss rate is the recombination of electrons with the positive ions present in the upper atmosphere. It has been reasonably well established from analysis of ionospheric observations[1] and from laboratory experiments[2] that the recombination coefficient α may be as large as 10^{-8} to 10^{-6} cm³/sec and that the capture process is most probably dissociative recombination, i.e.,

$$(XY)^+ + e \rightleftarrows (XY)^*_{\text{unstable}} \rightleftarrows X^* + Y + \text{kinetic energy}, \quad (1)$$

where the superscripts + and * indicate ionized and excited states, respectively.

Since no adequate theoretical calculations of the rate of the dissociative recombination reaction[3] are available, appeal is generally made to laboratory measurements of the recombination coefficients in the atmospheric gases[4] of interest. In nearly all cases these recombination studies have been conducted by observing the decay of the afterglow which persists after the termination of an active discharge. In such afterglow studies it is frequently difficult to achieve conditions in which electron-ion recombination is predominant, with various electron and ion production, ion conversion, electron attachment, and other electron and ion loss processes, notably diffusion, being adequately small. In addition, mass-spectrometric observations[5,6] have shown that it is difficult to prevent the formation of polyatomic ions such as N_3^+, N_4^+, and O_3^+ in these atmospheric gas studies. As a consequence, many of the previous recombination studies may *not* apply to the ion assumed to be present, e.g., N_2^+, leading to much confusion in the literature.[7–13]

In several of the reported nitrogen recombination studies[11–15] the measurements have been extended over a range of temperatures. Most of these studies were conducted without the benefit of mass analysis or any *a priori* knowledge concerning the identity of the dominant ion species. Therefore, as indicated in Sec. II, it is difficult to evaluate the effects resulting from impurities which can be driven off the cavity walls at elevated temperatures. An additional uncertainty arises from the fact that the relative concentrations of the various nitrogen ion species that may be present in the afterglow can change with temperature, giving an erroneous temperature dependence to the measured recombination coefficients.

The present paper describes the techniques which have been used in the determination of the temperature dependence of the coefficients for recombination of mass-identified N_2^+ ions and electrons. A description of the combined microwave-mass-spectrometer system

* This research has been supported in part by the Air Force Weapons Laboratory, Research and Technology Division, Air Force Systems Command, U. S. Air Force, Kirtland Air Force Base, New Mexico.

[1] See, for example, D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A187**, 261 (1946); H. S. W. Massey, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1952), Vol. 1, p. 395; T. M. Donahue, Planet. Space Sci. **14**, 33 (1965); E. E. Ferguson *et al.*, J. Geophys. Res. **70**, 4323 (1965).

[2] See, for example, the review by M. A. Biondi, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1963).

[3] D. R. Bates, Phys. Rev. **77**, 718 (1950); **78**, 492 (1950).

[4] See, for example, M. A. Biondi and S. C. Brown, Phys. Rev. **76**, 1697 (1949); A. C. Faire and K. S. W. Champion, *ibid.* **113**, 1 (1959); R. C. Gunton and T. M. Shaw, *ibid.* **140**, A756 (1965); M. H. Mentzoni, J. Appl. Phys. **36**, 57 (1965).

[5] W. H. Kasner, W. A. Rogers, and M. A. Biondi, Phys. Rev. Letters **7**, 321 (1961).

[6] W. H. Kasner and M. A. Biondi, Phys. Rev. **137**, A317 (1965).

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

[8] A. C. Faire, O. T. Fundingsland, A. L. Aden, and K. S. W. Champion, J. Appl. Phys. **29**, 928 (1958).

[9] A. C. Faire and K. S. W. Champion, Phys. Rev. **113**, 1 (1959).

[10] R. B. Bryan, R. B. Holt, and O. Oldenberg, Phys. Rev. **106**, 83 (1957).

[11] E. P. Bialecke and A. A. Dougal, J. Geophys. Res. **63**, 539 (1958).

[12] M. H. Mentzoni, J. Geophys. Res. **68**, 4181 (1963).

[13] R. Hackam, Planet. Space Sci. **13**, 667 (1965).

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

[15] L. Frommhold and M. A. Biondi, Bull. Am. Phys. Soc. **12**, 217 (1967).

used for the creation of the ionized gas and for the study of the subsequent decay of electron and ion species in the afterglow is given in Sec. II. A short discussion of the methods used to minimize the reactions which compete with recombination in the afterglow is also presented. The results of the present measurements and a comparison with previous published works are presented in Sec. III.

II. APPARATUS AND EXPERIMENTAL TECHNIQUES

The present investigation is an extension of a previously reported room-temperature ($\approx$300°K) study of electron-ion recombination in nitrogen.[6] Since most of the experimental apparatus has already been described in detail, the present discussion will be concerned primarily with the facilities and techniques required for operation as a function of gas temperature.

The essential parts of the experimental apparatus are shown schematically in Fig. 1. The rectangular microwave cavity, shown in dark outline, is constructed of stainless steel and is iris coupled to a 3000-Mc/sec microwave system. Under the normal operating conditions of these experiments, a pulse of microwave power of approximately 2-msec duration is used to create a discharge in the cavity. In the afterglow which follows the termination of the discharge, standard experimental techniques[6,16,17] are used to measure the shift in the resonant frequency of the cavity and, subsequently, to determine the electron density decay rate.

Some of the positive ions which diffuse to the cavity walls pass through the small orifice located opposite the coupling iris and are focused into a small radio-frequency mass spectrometer. By suitably pulsing the voltages applied to the secondary electron multiplier located at the output of the mass spectrometer, it is possible to measure the temporal decay rates of the ion currents diffusing to the cavity walls during the afterglow.

For the elevated temperature studies of electron-ion recombination, the microwave cavity is heated by a small "clam-shell" electric furnace (not shown in Fig. 1). A heavy layer of thermal insulating material (Marinite) is used to minimize the heat loss. The metal wall thickness in sections of both the rf mass spectrometer housing and the waveguide have been reduced to approximately 0.020 in. to further minimize the heat losses from the cavity. It has been necessary to provide an auxiliary heater winding at the end of the cavity adjacent to the rf mass spectrometer housing in order to maintain a nearly uniform cavity temperature. For the low-temperature studies the cavity is cooled by "dry-ice" packed around a heavy-walled copper cylinder which is in good thermal contact with the flanges at both ends of the cavity. In all cases the cavity temperature is monitored by thermocouples attached to it at various points. The observed temperature is always uniform over the walls of the cavity to within $\pm$5°C.

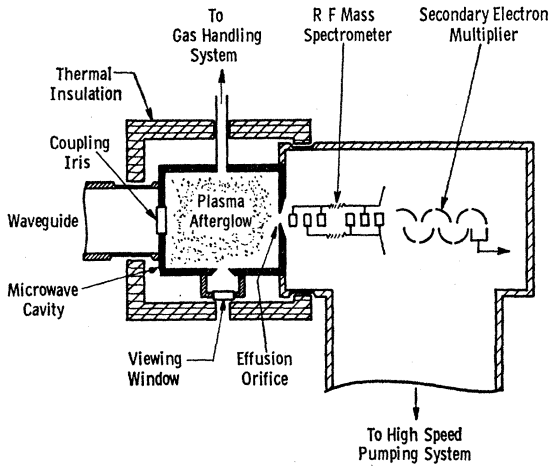

FIG. 1. Simplified sketch of the microwave cavity and rf mass spectrometer system used to monitor the ion currents diffusing to the cavity walls.

In these studies no attempt has been made to precondition the gas before it enters the cavity, i.e., the gas was not heated, or cooled, to the cavity temperature. The gas flow rates are such that the average residence time in the cavity for a given sample of gas is approximately 100 sec. Since this time is very much longer than the thermal diffusion time in the cavity, it is reasonable to assume that the gas is in thermal equilibrium with the cavity walls.

For reasons to be presented later these afterglow decay studies have been conducted using mixtures of nitrogen and neon gases, the neon serving primarily as a buffer. In a typical experiment the nitrogen pressure might be 10^{-4} to 10^{-3} Torr while the neon pressure is in the range 15 to 40 Torr. Since the neon gas density is many orders of magnitude higher than the nitrogen density it is quite evident that the neon must be very pure, otherwise its contaminants may produce undesired ions[6] which compete with the recombination process under study. To meet the required purity standards it has been necessary to extract the neon gas from the liquid phase, the advantage being that at the normal neon liquid boiling temperature, 27.3°K, the partial pressures of the undesirable contaminants[6] are below the detection limits of the experiment.

To further reduce the effects of impurities, the vacuum system has been designed so that various components, i.e., the cavity, rf mass spectrometer, and gas handling system, can be baked out at high temperatures, 400°C, the resulting background pressures, at room temperature, being less than 10^{-8} Torr. These bakeout procedures have not been entirely satisfactory. It has been observed that significant concentrations of impurity ions of mass 16 to 18 appear in the afterglow when the cavity is heated to temperatures exceeding

[16] M. A. Biondi, Rev. Sci. Instr. **22**, 500 (1951).
[17] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

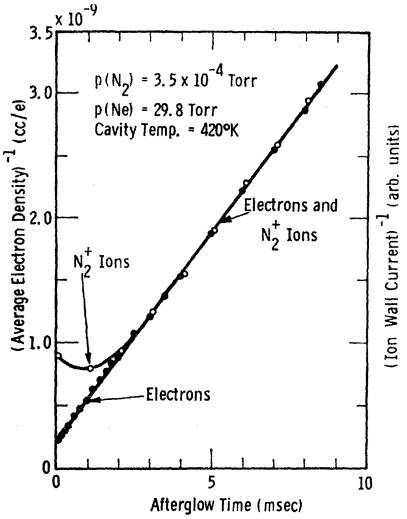

FIG. 2. Reciprocal electron density and reciprocal N_2^+ ion wall currents as functions of time in the afterglow of a nitrogen-neon microwave discharge.

approximately 100°C. It is presumed that these ions represent water vapor and its fragments which are given off by the components of the cavity. It has been possible to reduce the impurities to an acceptable level by first heating the cavity to temperatures 50 to 75°C above the desired operating temperature for extended periods of time, 48 to 72 h. This technique has been used successfully for operating temperatures up to approximately 200°C.

In the analysis of the afterglow decay it is necessary to consider several competing reactions, i.e., diffusion, ion conversion, electron attachment, etc., as well as the electron-ion recombination reaction which is being studied. A simple interpretation of the afterglow decay in terms of electron-ion recombination can usually be obtained only if one is able to eliminate, or at least minimize, these competing reactions. Assuming that the afterglow is dominated by a single positive ion species and that it contains no significant concentrations of negative ions, one can invoke the condition of quasineutrality and write the electron continuity equation in the simple form

$$\partial n_e(\mathbf{r},t)/\partial t = -\alpha n_e^2(\mathbf{r},t)\,, \qquad (2)$$

where α is the recombination coefficient and $n_e(\mathbf{r},t)$ is the electron density. The solution to the continuity equation is the well-known relation

$$1/n_e(\mathbf{r},t) = [1/n_e(\mathbf{r},o)] + \alpha t\,. \qquad (3)$$

The experimental results presented here were analyzed on the basis of this simple relation. We have followed the usual procedure in microwave afterglow studies[4] and assumed that the electrons and ions are distributed uniformly throughout the cavity, thereby permitting one to make a simple correlation between the "average electron density" and the measured shift of the resonant frequency of the cavity.[18]

The first step in the recombination studies is to ensure that the afterglows are dominated by a single positive ion species whose identity has been established. Previous studies[5,6] with the present apparatus have shown that the ions N^+, N_2^+, N_3^+, and N_4^+ can be present in the afterglow of a nitrogen discharge. The relative concentrations of these ions depend on the experimental conditions, i.e., the gas pressure and the discharge power level and pulse length. However, the parent molecular ion N_2^+ is the dominant species if the nitrogen pressure is kept below approximately 10^{-2}–10^{-3} Torr. The microwave system does not function properly at such low pressures, therefore, it has been necessary to add a neon buffer gas to achieve these experimental conditions. The ionization potential of neon is sufficiently high that under a wide range of conditions one observes only ions of the minority nitrogen constituent.

The use of the neon buffer gas can, under some circumstances, introduce an additional complication into the analysis of the afterglow decay. This results from the fact that the formation of N_2^+ ions via the Penning reaction with neon metastable atoms can persist into the afterglow and, if the neon metastable atom concentration is sufficiently high, constitute an undesirable competing reaction to the electron-ion recombination process. Optical absorption studies[6] have shown that for sufficiently long discharge pulse, >2 msec, the neon metastable atom concentration in the early afterglow becomes undetectable and the corresponding perturbing influence on the electron density decay rate, i.e., the departure from the behavior predicted by Eq. (3), becomes insignificant.

III. RESULTS AND DISCUSSION

The reciprocal plots of the electron density and N_2^+ ion wall currents shown in Fig. 2 give an example of the experimental data obtained in these afterglow studies in nitrogen-neon gas mixtures. The N_2^+ ion wall currents, i.e., the currents measured at the output of the rf mass spectrometer system, have been plotted in arbitrary units in order to normalize them to the electron density at an afterglow time of 3 msec. This procedure has been adopted since there is no convenient way to correlate these ion wall currents with the density of the N_2^+ ions in the volume of the cavity. The ion wall currents corresponding to the observed minority species N_3^+ and N_4^+ are not shown in Fig. 2. In the present studies the ion wall currents for the minority species are always less than 5% of the corresponding N_2^+ ion

[18] A discussion of the errors incurred in the measured recombination coefficients resulting from a choice of two rather different electron density distribution functions, i.e., a fundamental mode diffusion distribution and a uniform distribution is presented in Appendix A of Ref. 6. For the present experimental configuration the values of the recombination coefficients corresponding to these two distribution functions differ by only 5%.

wall currents throughout the entire afterglow. Therefore, one would not expect any ion conversion reactions between these species and N_2^+ to significantly alter the observed N_2^+ ion decay rate.[19] In addition, the electron density decay rate should not be appreciably altered by recombination with these minority ion species.

In Fig. 2 it is noted that the reciprocal of the electron density does increase linearly with time throughout the afterglow, thus indicating, according to Eq. (3), that recombination is the dominant loss mechanism. The slope of this straight line gives a measure of the desired recombination coefficient. One also observes that, except during the early afterglow, the decay of the N_2^+ ion wall current follows the electron density decay. It is important to note that the similarity in the temporal decay rates for the electrons and N_2^+ ions occurs *only* under "good" recombination conditions, that is, when there is clear N_2^+ domination of the afterglow and when there is no detectable neon metastable atom concentration in the afterglow. The existence of similar decay rates for both electrons and N_2^+ ions has been verified at each temperature for which data are presented.

It is our contention that the attainment of similar decay rates for the electron density and ion wall currents in recombination studies is a useful experimental condition. This similar behavior implies that there are no significant reactions which preferentially deplete either the electrons or the positive ions. Furthermore, one can say that there are not likely to be any significant concentrations of undetected ion species. This last point is particularly important in cases where negative ions are likely to be present, for example, in the study of oxygen or nitric oxide. Since the observed N_2^+ ion wall currents are proportional to the gradients of the N_2^+ ion density near the cavity wall, the existence of similar electron and ion decay rates seems to imply that the spatial distribution of the electrons and N_2^+ ions in the cavity does not change its form radically during the afterglow. The discrepancy in the observed decay rates in the early afterglow indicates that 2 to 3 msec are required to establish the final form of the afterglow wall gradients.

A theoretical analysis of afterglow decays involving electrons and a single positive ion species and including both diffusion and recombination loss processes has been published by Gray and Kerr.[20] These computations were carried out for widely different conditions, i.e., initial electron and ion spatial distributions, cavity-filling factor, and ratio of initial recombination loss rate to initial diffusion loss rate β and for both spherical and infinite cylindrical geometries. These computations indicate that reliable experimental estimates of electron-ion recombination coefficients can be obtained from linear $1/n_e$ versus time plots if the linear region extends over a sufficient range of the electron density, roughly an order of magnitude. The data shown in Fig. 2 easily fulfill this condition.

The theoretical analysis also provides correction factors which can be applied to the apparent recombination coefficients, i.e., the slopes of the linear $1/n_e$ versus time plots, to compensate for (a) the real diffusion of particles to the cavity walls and (b) the temporal variation of the electron density distribution in the cavity. These correction factors can be obtained in two different ways, i.e., from a determination of the range of electron density f over which a plot of $1/n_e$ versus time is linear[21] and from a determination of β using the expression[22]

$$\beta=\alpha n_0\Lambda^2/D_a. \tag{4}$$

In this expression n_0 is the initial electron density at the center of the cavity, Λ is the fundamental diffusion length of the cavity, and D_a is the ambipolar diffusion coefficient for the ion species in question. The second scheme for computing correction factors can be particularly useful in those cases where it is difficult to make a proper determination of the "f factors," for example, when there are competing reactions occurring in the early afterglow which cause a deviation from a straight-line behavior in the $1/n_e$ versus time plots.[23] Both correction schemes have been used in the present case and, as shown later in Fig. 4, the final results are quite similar.[24]

In determining the correction factors we have used the Gray and Kerr analysis for a spherical geometry and for an initial diffusion distribution of electrons and ions. This choice of parameters was based on some recent computations by Frommhold[25] which indicate that the proper correction factors for our particular cavity and mode of excitation are quite close to those corresponding to the spherical geometry.

The experimental studies of the recombination of N_2^+ ions and electrons have been carried out for a range of nitrogen and neon gas pressures. The pressure limits, which are somewhat dependent on the cavity tempera-

[19] It is assumed that the relative densities of the ions in the volume of the cavity are reasonably well approximated by the relative ion wall currents for the respective ions.

[20] E. P. Gray and D. E. Kerr, Ann. Phys. (N. Y.) **17**, 276 (1962).

[21] See Fig. 12 of Ref. 20.

[22] See Eq. (13) and Figs. 11 and 13 of Ref. 20.

[23] Consider, for example, the data shown in Fig. 5 of Ref. 6 which correspond to the presence in the early afterglow of a variable electron and ion production term, i.e., Penning ionization by neon metastable atoms. In this case the "β values" which one would compute for the different curves are all nearly equal; whereas, the corresponding "f factors" differ by as much as a factor of 3.

[24] In computing β it has been assumed that the ionic mobility μ_+ for N_2^+ ions diffusing in neon is independent of temperature. Under this condition it can easily be shown that $D_a \propto T_{\text{gas}}^2$. [See, for example, S. C. Brown, *Basic Data of Plasma Physics* (John Wiley & Sons, Inc., New York, 1959), p. 91.] The value of D_a used in the computation of β was obtained from Ref. 5. It should be noted that the values of the correction factors obtained by this technique were not strongly dependent on the particular temperature dependence assigned to D_a.

[25] L. Frommhold (private communication). In his analysis Frommhold has computed electron and ion decay rates, including both diffusion and recombination loss processes, for several real three-dimensional configurations, including our particular rectangular cavity.

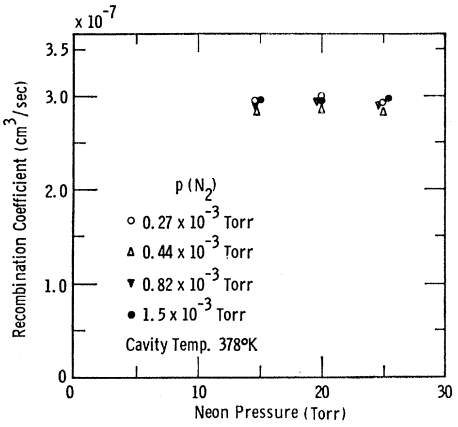

FIG. 3. Nitrogen and neon pressure dependences of observed recombination coefficients.

ture, are determined by the appearance of significant departures from the conditions for recombination control of the afterglow as specified above. At room temperature the nitrogen and neon pressure ranges are 10^{-4} to 10^{-3} Torr and 15 to 30 Torr, respectively.[6] An example of the results obtained in the recombination studies for various gas pressures is shown in Fig. 3. One notes that there is no systematic dependence on either the nitrogen or the neon gas pressures. Since similar results have been obtained at each cavity temperature, we conclude that the recombination process under study is a two-body reaction involving only N_2^+ ions and electrons.

In the microwave discharges in nitrogen-neon gas mixtures the dominant mechanisms for the production of N_2^+ ions are (a) direct inelastic collisions with energetic electrons and (b) collisions with neon metastable atoms, the Penning reaction. The neon density is 4 to 6 orders of magnitude larger than the nitrogen density; therefore, the majority of inelastic collisions with electrons having energies greater than that corresponding to the neon metastable levels, i.e., 16.6 eV, will lead to excitation of neon rather than ionization of nitrogen. The energetics of the subsequent ionization of nitrogen molecules via the Penning reaction does not permit excitation above the first three or four vibrational levels of the N_2^+ ground electronic state. The direct production of N_2^+ ions by electron impact involves, in most cases, the low-energy electrons (less than 16.6 eV); hence, only the lower vibrational levels of the N_2^+ ions will be excited by this mechanism. It is therefore reasonable to assume that the results of the present work correspond to the recombination of electrons with N_2^+ ions which are in low, possibly $v=0$, vibrational states.

A summary of the temperature-dependent recombination measurements in nitrogen-neon gas mixtures covering the approximate range 200 to 480°K is presented in Fig. 4. Each of the points in this plot represents the average of several measurements corresponding to a range of nitrogen and neon gas pressures. The solid circles result from the application of the Gray and Kerr corrections as determined from the extent of the linear ranges in the $1/n_e$ versus time plots, i.e., the "f corrections." The open circles, corresponding to the same experimental data, were obtained by using correction factors based on computed values of the parameter β. With the exception of the data corresponding to the lowest temperature, 205°K, the "β-correction" scheme consistently yields slightly lower values for the recombination coefficients. In most cases the two sets of results agree to within the sums of their respective standard deviations.

The measured coefficients for the recombination of N_2^+ ions and electrons show very little dependence on the gas temperature. The solid line in Fig. 4, corresponding to a constant value of $(2.7\pm0.3)\times10^{-7}$ cm^3/sec, is in agreement with our previously published[6] room-temperature ($\approx$300°K) result.[26] The uncertainty limits of this quoted value encompass all the results, both open and solid circles, presented in Fig. 4. The dotted line, which is proportional to $T^{-0.1}$, represents an upper limit to the temperature dependence which can be assigned to the combined experimental results, if one uses a single power term and weights all points equally. It is apparent from Fig. 4 that a temperature-independent recombination coefficient for N_2^+ ions and electrons, the solid line, provides a better fit to either set of results especially in the temperature range above 300°K. The over-all confidence limits which one can assign to the absolute magnitudes of the measured recombination coefficients is approximately $\pm10\%$. The relative variation of the recombination coefficients as a function of temperature should be more accurate than this since essentially the same systematic errors are present at each temperature.

Temperature-dependent studies of volume recombination in nitrogen covering the approximate range 90 to 3200°K have been published in the recent literature.[11–15] A summary of these published results is shown in Fig. 5. Even though the experimental techniques which have been used are quite similar in most respects, there still remain large discrepancies in the results. It is rather difficult to properly evaluate all the experimental results shown in Fig. 5 since, in many cases, there is no direct information regarding the reaction under study.

The work of Sayers[14] represents the only other nitrogen recombination study in which a mass spectrometer was used to identify the recombining positive-ion species. His experimental method differs from the others

[26] The previously published value, $\alpha(N_2^+)=(2.9\pm0.3)\times10^{-7}$ cm^3/sec, was based on the use of Gray and Kerr correction factors corresponding to a compromise between the infinite cylindrical and spherical geometries. When the more appropriate correction factors for the spherical geometry are used, this value must be reduced by approximately 7%.

in one important aspect, i.e., a Langmuir probe was used to measure the electron density and the electron temperature. His measured recombination coefficient for N_2^+ ions and electrons corresponding to an electron temperature of 3200°K is 1.1×10^{-7} cm³/sec.

The nitrogen recombination studies reported by Frommhold and Biondi[15] also utilize a different experimental technique. In particular, they use various constant microwave fields to heat the electron gas to temperatures T_e in the range 300 to 3000°K. The heavy particles, i.e., the neutral gas and positive ions, are not effected by these microwave fields and hence remain at ambient room temperature (≈300°K). In their studies Frommhold and Biondi use a mixture of nitrogen and neon gases whose proportions are quite similar to those used in the present experiments. The mode of plasma excitation is also quite similar to the present one; thus, it is reasonable to assume that their results correspond to the recombination of N_2^+ ions and electrons. The agreement between their measured recombination rate at room temperature and our published value for N_2^+ [6] lends support to this assumption. One would not expect the intensity level of the microwave heating fields to influence the discharge condition or to affect the gas composition by driving impurities off the cavity walls; thus, the same ion species should dominate their afterglows at all electron temperatures. The closest simple power law which fits the experimental results obtained by Frommhold and Biondi over the entire range $300\leqslant T_e\leqslant 3000$°K is $T_e^{-1/3}$ (indicated by the solid line sketched in Fig. 5). At high electron temperatures their results appear to be in reasonable agreement with those obtained by Sayers.[14] The observed temperature dependence is not in good agreement with the present results over the common temperature range, 300–500°K. It is not clear that one should necessarily expect to find the same temperature dependence in these two experiments since the degree of excitation of the recombining ion species can differ. In the microwave heating experiments the relative populations of the vibrational states of the afterglow ion species should not depend to any significant degree on the effective electron temperature; whereas, in the present case the relative populations of these vibrational states are directly influenced by changes in the bulk gas temperature.

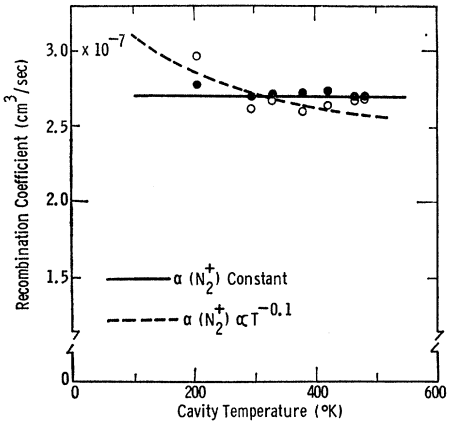

FIG. 4. Observed temperature dependence of the recombination coefficients for N_2^+ ions and electrons. The solid and open circles correspond to the use of the "f-correction" and "β-correction" schemes, respectively.

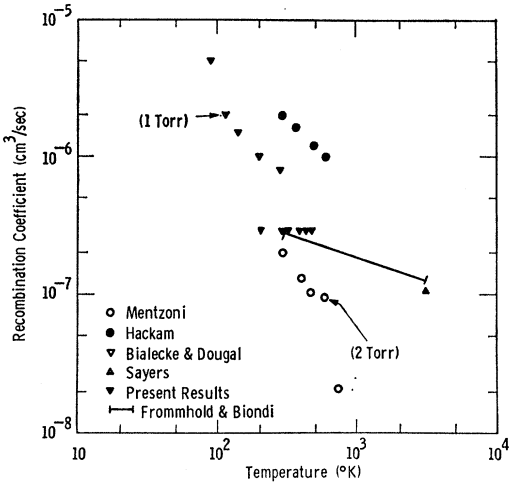

FIG. 5. Summary of recent studies of the temperature dependence of electron-ion recombination in nitrogen. The results of Mentzoni and of Bialecke and Dougal exhibit strong pressure dependences. The data presented in these cases correspond to the indicated pressures.

Some of the results of the temperature-dependent studies of recombination in nitrogen reported by Bialecke and Dougal,[11] by Mentzoni,[12] and by Hackam[13] for the combined temperature range 92 to 735°K are also presented in Fig. 5. Both Bialecke and Dougal[11] and Mentzoni[12] report that their measured recombination coefficients exhibit a strong dependence on the nitrogen pressure. The examples of their results shown in Fig. 5 correspond to the indicated nitrogen pressures. One notes that the recombination coefficients reported by these groups all exhibit comparable temperature variations, i.e., of the order of T^{-1} to $T^{-3/2}$. However, the large discrepancies in the absolute values suggest that this agreement may be somewhat fortuitous. The nitrogen gas pressures (0.2 to approximately 10 Torr) used in the experiments reported by these groups correspond to a pressure range in which our studies of nitrogen,[5] nitrogen-helium,[5] and nitrogen-neon[5,6] gas mixtures indicate that the predominant afterglow ions are N_3^+ and N_4^+ rather than N_2^+; thus, it seems probable that these reported afterglow studies involve more than a single nitrogen ion species. In connection with the present work some afterglow studies were conducted in nitrogen-neon mixtures under conditions where the ion species N_2^+, N_3^+, and N_4^+ were all present. It was observed that the concentrations of the more complex ions, N_3^+ and N_4^+, relative to N_2^+ decreased by more than an order of magnitude as the gas temperature was

increased from 300 to 500°K, the nitrogen and neon gas densities being maintained at constant values. Thus, it is conceivable that at least a part of the observed temperature dependence reported by these groups may be due to changes in the relative concentrations of the positive-ion species. Without the benefit of mass analysis it is difficult to assess the significance of this effect.

ACKNOWLEDGMENTS

The author wishes to thank the members of the Atomic and Molecular Sciences Directorate, especially M. A. Biondi and A. V. Phelps, for their interest and helpful suggestions concerning this research project. The author is also indebted to L. Frommhold for providing results of his computer calculations prior to publication.

PHYSICAL REVIEW VOLUME 164, NUMBER 1 5 DECEMBER 1967

Saturation Effects in Stimulated Rayleigh-Wing Scattering*

R. M. HERMAN
Department of Physics, Pennsylvania State University, University Park, Pennsylvania
(Received 30 June 1967)

The phenomenon of stimulated Rayleigh-wing scattering in anisotropic molecular liquids is analyzed. Representative combinations of polarization for the incident and scattered light are considered. It is shown that in regions where the focused laser beam is intense, saturation occurs in the molecular response to external optical fields, in that perfect alignment of the individual liquid molecules in the optical fields is approached. Accordingly, the nonlinear amplification associated with the stimulated radiation is reduced. The results of the analysis qualitatively explain several important recent observations which are in conflict with previous theroretical predictions. For example, it is shown that the nonlinear gain is considerably greater when the incident light is circularly polarized (the stimulated radiation being circularly polarized in the reverse sense) than it is when the incident light is linearly polarized. Despite saturation, sufficient amplification exists in the former case to allow the efficient conversion of incident to stimulated Rayleigh light at moderate power levels.

I. INTRODUCTION

THE phenomenon of stimulated Rayleigh-wing scattering in intense light beams has received attention by several authors[1–4] in the past two years. The most complete discussion of the theory for this phenomenon has been given by Bloembergen and Lallemand.[2] However, there have been several recent observations by Wiggins, Cho, Foltz, and Rank[5] which cannot successfully be explained using existing theory. It is the purpose of the present paper to give explanation to these new phenomena.

Spontaneous Rayleigh-wing scattering arises by virtue of the ability of intense optical fields to orient liquid molecules having large polarizability anisotropies. In their treatment, Bloembergen and Lallemand predict that the largest component of nonlinear polarization is parallel to the direction of linear polarization of the incident (laser) light. They found the effective nonlinear polarization at the displaced frequency ω_R to be given by the expression

$$P_{11}^{\mathrm{NLS}}(\omega_R)=\frac{N_0[(\alpha_{11}-\alpha_{22})^2+(\alpha_{22}-\alpha_{33})^2+(\alpha_{33}-\alpha_{11})^2]}{90kT}\times\left(\frac{n^2+2}{3}\right)^4\left(|E_R|^2E_R+\left\{1+\frac{1-i\omega\tau}{1+\omega^2\tau^2}\right\}|E_L|^2E_R\right),\quad(1)$$

where the incident radiation field is

$$\tfrac{1}{2}\{E_L\exp[i(\mathbf{k}_L\cdot\mathbf{r}-\omega_Lt)]+E_L^*\exp[-i(\mathbf{k}_L\cdot\mathbf{r}-\omega_Lt)]\};$$

the outgoing Rayleigh-scattered field is

$$\tfrac{1}{2}\{E_R\exp[i(\mathbf{k}_R\cdot\mathbf{r}-\omega_Rt)]+E_R^*\exp[-i(\mathbf{k}_R\cdot\mathbf{r}-\omega_Rt)]\};$$

N_0 is the number of scattering molecules per cm^3; α_{11}, α_{22}, and α_{33} are the principal components of the polarizability tensor, with $\alpha_{11}>\alpha_{22}>\alpha_{33}$; k is Boltzmann's constant; and T is the temperature in °K. The effective dielectric relaxation time is τ, while the frequency displacement $(\omega_L-\omega_R)$ is denoted by ω. The factor $[(n^2+2)/3]^4$ represents the local-field correction,[6] n being the index of refraction at ω_L (or ω_R).

* This research has been supported in part by the U. S. Office of Naval Research.

[1] D. I. Mash, V. V. Morozov, V. S. Starunov, and I. L. Fabelinskii, JETP Pis'ma v Redaktsiyu **2**, 41 (1965) [English transl.: JETP Letters **2**, 25 (1965)].

[2] N. Bloembergen and P. Lallemand, Phys. Rev. Letters **16**, 81 (1966).

[3] C. W. Cho, N. D. Foltz, D. H. Rank, and T. A. Wiggins, Phys. Rev. Letters **18**, 107 (1967).

[4] R. Y. Chiao, P. L. Kelley, and E. Garmire, Phys. Rev. Letters **17**, 1158 (1966).

[5] T. A. Wiggins, C. W. Cho, N. D. Foltz, and D. H. Rank, Bull. Am. Phys. Soc. **12**, 686 (1967).

[6] N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965), Chap. 3.