Recombination and Ionization in a Molecular-Ion-Dominated Helium Afterglow*

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An intense source of free electrons has been observed to strongly influence the time history of the electron density in a high-pressure (> 15-Torr) helium afterglow. The electronic recombination coefficient α of molecular helium ions was measured by utilizing this source and was found to be over five times larger than the effective recombination coefficient obtained by equating the net loss rate of free electrons to the recombination loss rate in the usual manner. If α is assumed to be of the form $\alpha = \alpha_0 + k_p p$, then $\alpha_0 = 1.1 \times 10^{-8}$ cm^3 sec^{-1} and $k_p = 4.1 \times 10^{-10}$ cm^3 sec^{-1} Torr^{-1} over the pressure range from 15 to 56 Torr. A model is presented which indicates that ionizing metastable-metastable collisions are responsible for the source of free electrons.

I. INTRODUCTION

Experimental studies of electron–molecular-ion recombination in plasmas have been widely pursued ever since the introduction of microwave diagnostic techniques.[1] Recombination studies in helium have been plagued by a great many difficulties, which leave considerable uncertainty about the actual recombination rate as well as the recombination processes. Previously reported measurements[1,2] of the electronic recombination coefficient α for molecular helium ions at 300 °K have yielded values from less than 4×10^{-9} to 1.6×10^{-8} cm^3 sec^{-1}. Recently, Berlande *et al.*[3] examined the decay of electrons in the helium afterglow and fitted the results with a computer solution. After mitigating most of the problems that had plagued the earlier experiments, they found both a pressure dependence and an electron density dependence of the recombination coefficient. Collins *et al.*[4] observed an electron density dependence of the recombination coefficient that was significantly smaller than that observed by Berlande *et al.*

In all these previous experiments, the electronic recombination coefficient was obtained by observing the time decay of the electrons in the afterglow. We have discovered for the conditions of the experiment described in this paper that an intense source of free electrons strongly influences the observed electron decay in the helium afterglow and that this source probably played a role in all previous measurements of α in high-pressure He. We have remeasured the effective recombination coefficient α_{eff} which is obtained directly from the time history of the electrons in the afterglow and found it to be in reasonable agreement with the previously reported values of the electronic recombination coefficient. However, when we took into account the source term, the actual electronic recombination coefficient was found to be larger than α_{eff} by as much as a factor of 5. The correct electronic recombination coefficient for molecular helium ions was found to range from 1.7×10^{-8} to 3.3×10^{-8} cm^{3}sec^{-1} over the pressure range from 15 to 56 Torr.

In Sec. III of this paper the method used to measure the electronic recombination coefficient α of molecular helium ions is described. The technique is based on observation of the effects that quenching of the recombination has on the measured electron density and molecular radiation as was previously observed in a 77 °K helium-afterglow plasma.[5,6] The recombination coefficient is obtained in a manner similar to that reported in Ref. 6 on recombination in a helium plasma maintained at 77 °K. In Sec. V, we consider the particular source (metastable-metastable ionizing collisions) of the free electrons. General rate equations describing important phenomena in the helium afterglow are solved in order to determine if a consistent picture can be formed. If molecular metastables are assumed to enter into ionizing collisions with other metastables at about the same rate as atomic-metastable–atomic-metastable ionizing collisions, then agreement between the predicted rate of decay of electrons and the observed rate is found. For the conditions of this experiment, molecular ions resulting from the ionizing collisions are indistinguishable from atomic ions since the conversion of atomic ions to molecular ions is so rapid. Information on the radial distributions of electrons is described in Sec. IV. The gas and electron temperatures are estimated in Sec. VI along with the observed effects of elevated electron temperatures on the recombination coefficient.

II. EXPERIMENTAL APPARATUS

The bakable vacuum system used to evacuate the discharge tube utilized a mechanical pump and a three-stage oil diffusion pump. An oven was

used to uniformly heat the ultrahigh vacuum system to 300 °C during pumpout. An ultimate base pressure of 2×10^{-9} Torr was achieved after bakeout and electrode outgassing. The study was conducted with research-grade gas obtained from Cryogenic Rare Gas Laboratories, Inc. Before leaking the helium into the main discharge tube, the gas was cataphoretically purified. Tantalum electrodes were used in the cataphoresis tube. The cylindrical discharge tube was 12.8 cm in diameter with two tantalum cup electrodes approximately 27 cm apart. Preliminary work, which yielded the same results obtained with the above discharge tube, was performed with two other discharge tubes of 5-cm diameter and 25-cm separation between the electrodes. The essential difference between the two preliminary discharge tubes was that in one of the tubes the electrodes were formed from tantalum sheet and in the other tube, from molybdenum sheet. The electrodes were properly outgassed by (i) sputtering with a discharge of nominally 1 A at a gas pressure of 0.5–0.7 Torr, and (ii) induction heating of the electrodes with continuous pumping of the emitted gas.

The plasma in the discharge tube was produced by a current excitation pulse of 1.0–5.0 A. Excitation duration times were from 6 to 200 μsec. Since relatively very small currents will heat the electrons and affect the recombination loss rate, the excitation pulse must terminate completely. No detectable current was observed in the afterglow. For all repetition rates used in this experiment, the excitation pulse raised the average gas temperature by less than 15 °C as measured by the pressure rise in the discharge tube. With the use of a Fabry-Perot interferometer, the linewidth of the 5016-Å helium line was measured and, within the accuracy of the measurement (10%), the temperature did not change measurably with time in the afterglow. A maximum Doppler temperature of the helium gas atoms was determined to be less than 350 °K.

The electrons in the afterglow period during a selected time interval were heated with a current pulse of 0.1–1.0 A and nominally 200-μsec duration. In the preliminary experiment[7] the electrons were heated with a 6.2-GHz microwave source. Better accuracy in the present measurements was obtained because the electrons were more uniformly heated. The values of α reported here are near the lower limits of those reported earlier. (In the previous report,[7] the limits in column three of Fig. 1 and in the last equation of the article are presented incorrectly. The plus and minus signs should not have been included, since the smaller-sized numbers are the values of the limits.)

The light emitted from the discharge tube was monitored with a photomultiplier tube attached to the exit slit of a Spex monochromator (resolution 0.3 Å in first order). The optical system (which included the monochromator, 13-cm focal length lens, and associated optical bench) was mounted on a movable platform. The image of the axis of the cylindrical discharge tube was parallel to the slits of the monochromator. Thus, the discharge tube could be scanned in steps of about 1 mm (equal to whatever slipwidths had been chosen) for use in a numerical Abel inversion.[8] Time resolution was obtained by gating the photomultiplier tube on for nominally 50 μsec at a chosen time into the afterglow. The integrated pulse output was then read with a voltmeter.

The plasma electron density was measured with two free-space microwave interferometers. One of these interferometers was operated at 34.95 GHz and the other one was operated at several frequencies in the band from 22 to 26.3 GHz. Both interferometers were of conventional design[9] and each utilized high-gain transmitting and receiving horn antennas. The free-electron density in the helium afterglow was monitored in the smaller discharge tubes (5-cm diameter) with both the direction of propagation and the electric field vector of the microwaves oriented in a plane containing the axis of the discharge tube and with the electric field nominally at the Brewster angle of 62° relative to the normal to the axis of the discharge tube. The thickness of the wall of the larger discharge tube (13-cm diameter) was chosen to be nominally $\frac{1}{2}\lambda$ of a wavelength (minimum reflection condition) with the direction of propagation of the microwaves perpendicular to the axis of the discharge tube. With both systems described above, the rate of

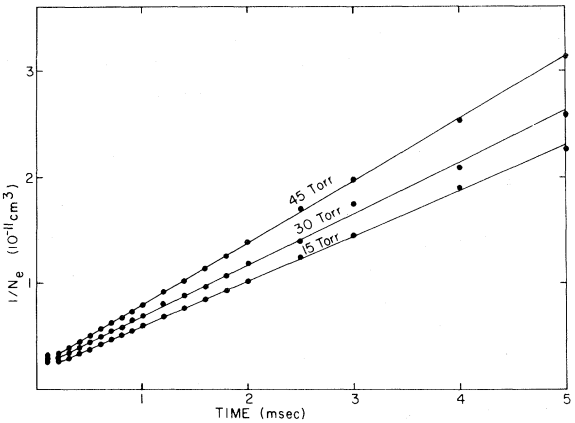

FIG. 1. Reciprocal of the measured electron density is plotted vs time into the afterglow. The dots are the experimental points. The slopes of the straight lines give α_{eff}.

decay of the free-electron density in the afterglow was observed to be the same. Most of the final results reported in this paper were obtained with the larger diameter discharge tube. Extraneous reflected signals were dissipated with the aid of a multitude of absorptive surfaces located near the discharge tube. The horn separation was maintained sufficiently large to ensure at least 18-dB insertion loss. This practice was followed in order to keep the effect of multiple reflections between horns to an acceptably low level. The reflected signals in this case resulted from the impedance mismatch into the receiving horn antenna.

The line electron density was evaluated from the phase shift introduced by the plasma in the conventional manner.[10] Both microwave systems yielded the same value of line electron density (i.e., the integrated electron density along the path of the traversing microwave signal) to within ± 7%. This maximum deviation from the mean resulted from measurements at several frequencies throughout the frequency band 22–26.5 GHz, at 34.95 GHz, and at many different horn separation distances[11] and horn orientations.

The conversion of phase shift to line electron density along a ray path requires detailed information about the field patterns of the transmitting and receiving antennas used in the interferometer system. Such information is not easily obtained, especially in laboratory situations where extraneous reflections are sometimes present and where gradients in the plasmas electron density cause refraction effects. We did not evaluate the field patterns, but we did follow the criterion set forth in Ref. 10. In addition some measurements of the index of refraction of a cylinder of Styrofoam ($n \approx 1.03$) of diameter equal to that of the plasma column indicated that the microwave phase shift was equal to that produced by a path along the diameter to within experimental accuracy.

The electric field intensity of the microwave sensing waves was held to sufficiently low values to ensure negligible heating of the electron gas. Indeed, the maximum microwave field intensity used in the study should not have increased the electron temperature by more than a few degrees.[12] It was substantiated that negligible heating occurred by observing that the molecular band radiation was not altered when the microwave sensing wave was operated in a pulsed mode.[13]

III. RECOMBINATION COEFFICIENT OF MOLECULAR HELIUM IONS AND ELECTRONS

The time rate of change of electron density when only a single ion species is present, in the absence of diffusion, and with a source S of free electrons, is given by

$$\frac{dN_e}{dt} = -\alpha N_e^2 + S \ , \tag{1}$$

where N_e is the free-electron density. This equation is a greatly simplified approximation to the set of coupled rate equations which in general describe the ions, electrons, and excited-state densities in a helium afterglow. Equation (1) is used in this section to simplify the discussion, but the detailed analysis will be treated later in order to indicate the source of the free electrons and to evaluate the diffusion effects.

Experimentally, it was observed that under the conditions of this experiment the electron density could be described by an equation of the form

$$\frac{1}{N_e} = \frac{1}{N_e^0} + \alpha_{\text{eff}}\, t \ , \tag{2}$$

where N_e^0 is the initial electron concentration and α_{eff} is the effective recombination coefficient. This empirical relation was found valid at all times and under all conditions except at very early times into the afterglow at low gas pressure (see Fig. 1). In Fig. 2, the measured values of α_{eff} are given as a function of background gas pressure p. We will present evidence in a later section that S describes ionizing metastable-metastable collisions and will show that the measured value of S is consistent with $dN_e/dt < 0$ only if $\alpha > \alpha_{\text{eff}}$. Since Eq. (2) was found empirically to be correct for the conditions of this experiment, the effective source term regardless of its origin is given by

$$S = (\alpha - \alpha_{\text{eff}})(1/N_e^0 + \alpha_{\text{eff}}\, t)^{-2} \ . \tag{3}$$

In order to measure the recombination coefficient α, the electrons were heated by applying a low-level current pulse during a specified time interval into the afterglow (see Fig. 3). (The initial increase of the electron density after the main pulse resulted from metastable-metastable ionizing collisions.[14]) The elevated electron temperature resulted in a

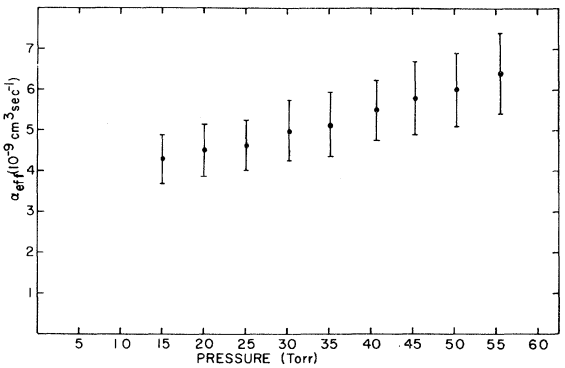

FIG. 2. Effective recombination coefficient α_{eff} obtained from curves similar to those in Fig. 1 is plotted vs pressure.

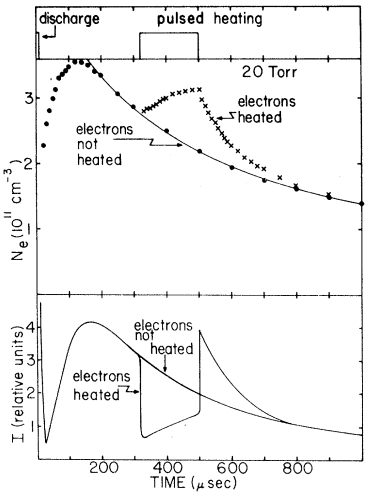

FIG. 3. Time sequences of the electron density N_e and the helium molecular radiation of the 4650-Å band. The start of the main discharge is referenced to zero time. During the heating pulse, *"I"* was quenched and N_e increased. Following the electron heating pulse, both I and N_e returned to the value which prevailed when the electrons were not heated.

reduction of the recombination coefficient. With sufficient electron heating, the electron density increased during the heating pulse. This is in agreement with Eq. (1) because, if S is assumed to be unchanged by the electron heating pulse and if α is greatly reduced, dN_e/dt can become positive and the electron density will then increase. Since the molecular light resulted from recombination of an electron and an ion, the quenching of recombination likewise quenched the molecular radiation (4650 Å in Fig. 3). As soon as the heating pulse was terminated the electrons cooled (< 10 μsec) and the recombination coefficient returned to its nonheated value. The electron density decayed at a rate faster than before the heat pulse was applied because the recombination term αN_e^2 was increased above its nonheated value while the source term was assumed to be unaffected. (This assumption will be discussed in more detail in Sec. V.) Since the rate of recombination of the molecular ions was greatly increased upon termination of the heating pulse, the molecular light increased rapidly (as quickly as the electrons cooled) and eventually decayed to the same value it had when the heating pulse was not applied. Likewise, the electron density asymptotically approached the value it assumed when no heating pulse was applied. These latter two observations are evidence that the newly created free electrons were derived from a source which was independent of electron temperature and could not have resulted from electron collisional ionization of ground state and excited atoms.

The rate equation governing the electron density N_{eH} following termination of the heat pulse is given by

$$\frac{dN_{eH}}{dt} = -\alpha N_{eH}^2 + (\alpha - \alpha_{eff})\left(\frac{1}{N_{eN}^0} + \alpha_{eff}\, t\right)^{-2}, \quad (4)$$

where the empirically determined form for S (assumed to be unchanged by the heating pulse) in Eq. (3) has been substituted into Eq. (1) and the notational change $N_e \rightarrow N_{eH}$ has been made in order to indicate that this is the electron density in the wake of the heating pulse. The time $t = 0$ is now referenced to coincide with a time 10 μsec after the cessation of the heating pulse and N_{eN}^0 is the electron density which was observed at this same time when no heating pulse was applied. At a given pressure, the value of α_{eff} was obtained by the fit of the data to Eq. (2) over the full time history of ~ 0.2–5 msec. With the measured value of N_{eN}^0 and initial value of N_{eH} at the new $t = 0$, the time history of N_{eH} was computed by a numerical computer solution to Eq. (4) for various values of α, and the best fit of the data to the computed curves yielded the recombination coefficient (see Fig. 4). The resulting value of α was found to be pressure dependent (see Fig. 5) and independent of N_e. We estimate that the absolute accuracy of the measured α's is $\pm 25\%$. The error bars in Fig. 5 represent only the precision of the measurements. If the recombination coefficient α is assumed to be of the form $\alpha = \alpha_0 + k_p p$, then $\alpha_0 = 1.3\times10^{-8}$ cm^{3}sec^{-1} and $k_p = 4.08\times10^{-10}$ cm^{3}sec^{-1}Torr^{-1}. We do not suggest that our data prove a pressure dependence that is

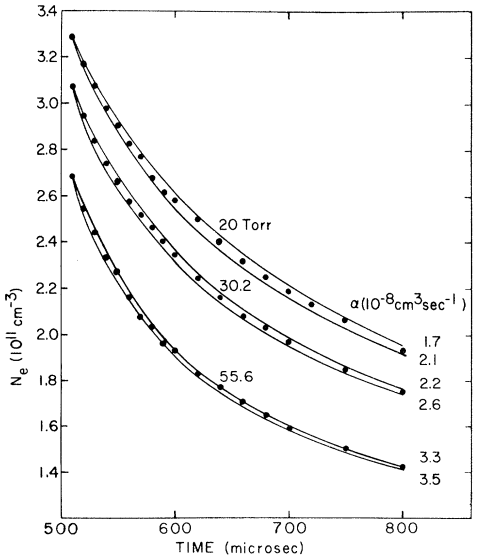

FIG. 4. Electron density following the heating pulse is plotted vs time. The heating pulse was on from 300 to 500 μsec in the afterglow period. Note that the ordinate in the plot does not begin at zero. The solid lines represent the solutions to Eq. (4) for different α.

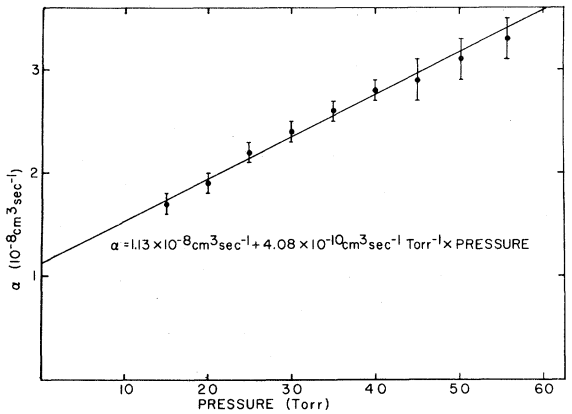

FIG. 5. Electronic recombination coefficient is plotted vs the pressure in the helium afterglow. The straight line is a fit to the data of the form $\alpha = \alpha_0 + k_p p$. The error bars represent only the limits to the fit of the curves exhibited in Fig. 4.

linear (although as evidenced by the data there is obviously some pressure dependence), and we do not imply that the projection of this linear fit to pressures less than 15 Torr is appropriate.

The analysis as presented above will yield the correct value of the electronic recombination coefficient for 300 °K molecular helium ions only if certain assumptions are valid. In addition, some corrections to the data may be necessary. The assumptions and possible reasons for corrections are listed along with the section in which they are discussed: (a) effect of heating pulse on S (Secs. V and VI), (b) radial distribution of particles (Sec. IV), (c) electron temperature and gas temperature (Sec. VI), (d) dependence of recombination coefficient α on electron density (Sec. IV), and (e) plurality of ion species (Sec. V). In addition, the actual form of the source term S is considered in Sec. V.

IV. MOLECULAR RADIATION

The relative intensity of the 4650-Å band of He_2 was compared to the electron density in order to assess the role of electron collisions in the recombination process to verify the near independence of α on N_e. If electron collisional recombination of He_2^+ is an important mechanism, it should be observable in the functional relationship of the intensity of the 4650-Å band relative to N_e. With the assumption that at a given pressure, a given fraction of the recombination events results in a photon in the 4650-Å band, the measured intensity I should be proportional to N_e^δ, where $2 < \delta < 3$. If I depends on N_e^2, then electron collisional recombination of He_2^+ is not an important recombination mechanism for the production of molecular light. In Fig. 6, an example of the experimental data is presented on a log-log plot of the measured intensities of the 4650-Å band vs the measured electron densities at different times into the afterglow. The slope of the straight line gives the power dependence of I on N_e. Over the pressure range 10–60 Torr and electron density range 4×10^{10} to 5×10^{11} cm^{-3}, δ varied from 1.95 to 2.1, with an average value of 2.04. This observation was independent of the discharge conditions and the discharge tube. A limited number of measurements on other bands at 3690 and 5730 Å indicated the same dependence. These results show that, within the range of our experimental parameters, the coefficient of recombination which results in molecular light does not depend upon the electron density. Likewise, we saw no indication of such a dependence in the direct measurements of α as described above.

In the above discussion, it has been assumed that the electron density uniformly filled the discharge tube. Over most of the region between electrodes, axial uniformity of the molecular radiation and hence of the electron density was obtained. However, since complete radial uniformity was not observed, we included this initial nonuniformity in the analysis of the data, along with the relation between line electron density and N_e. An Abel inversion on the emitted plasma light from a molecular band (usually 4650 Å) was performed by a numerical technique.[8] The intensity function was normalized to unity at the radial center of the discharge tube. The electron density function was

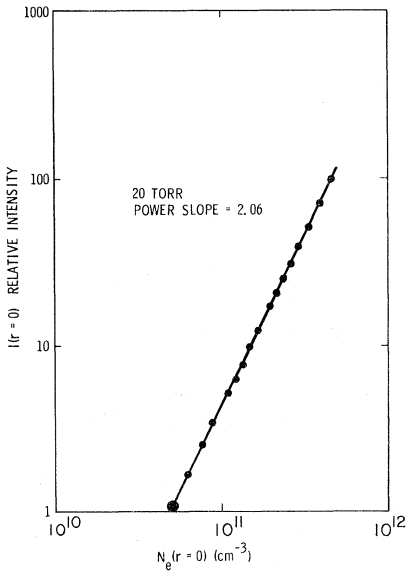

FIG. 6. Molecular radiation (4650 Å) is plotted vs the electron density at the center of the discharge tube. The slope of the curve indicates the power dependence of the radiation on the electron density. The estimated error is shown at the lowest and at the highest electron density by the size of the dots.

taken to be the square root of the intensity density function. The measured radial distribution was used as initial conditions in exact solutions of the general rate equations (Sec. V). However, since the distributions were nearly uniform over the full extent of the discharge tube, this had little effect on the results. Emphasis should be made here that these necessary effective corrections had already been minimized by the experimental techniques of maximizing the initial plasma uniformity. Conditions were readily obtained wherein the distributional effects greatly affected the time history of the measured electron density.

V. GENERAL RATE EQUATIONS

In the previously described measurements of the electronic recombination coefficient, we neglected to specify the source term for the production of free electrons. In an attempt to give a consistent picture of the molecular helium afterglow, we will assume that the source term S in Eq. (1) resulted from metastable-metastable ionizing reactions. The processes assumed to be active in the helium-afterglow plasma (pressure > 15 Torr) are given below:

$$M_1 + M_1 \xrightarrow{\beta_1} \mathrm{He}^+ + \mathrm{He} + e \quad \text{or} \quad \mathrm{He}_2^+ + e \ , \tag{5a}$$

$$M_2 + M_2 \xrightarrow{\beta_2} \mathrm{He}_2^+ + 2\mathrm{He} + e \quad \text{or} \quad \mathrm{He}^+ + 3\mathrm{He} + e \ , \tag{5b}$$

$$M_1 + M_2 \xrightarrow{\beta_{12}} \mathrm{He}_2^+ + \mathrm{He} + e \quad \text{or} \quad \mathrm{He}^+ + 2\mathrm{He} + e \ , \tag{5c}$$

$$M_1 + 2\mathrm{He} \xrightarrow{B} M_2 + \mathrm{He} \ , \tag{5d}$$

$$\mathrm{He}^+ + 2\mathrm{He} \xrightarrow{\gamma} \mathrm{He}_2^+ + \mathrm{He} \ , \tag{5e}$$

$$\mathrm{He}_2^+ + e + X \xrightarrow{\alpha_1} M_1 + X + \mathrm{He} \ , \tag{5f}$$

$$\mathrm{He}_2^+ + e + X \xrightarrow{\alpha_2} M_2 + X \ , \tag{5g}$$

$$\text{diffusion of } M_1, M_2, \mathrm{He}^+, \text{ and } \mathrm{He}_2^+ \ . \tag{5h}$$

The symbols M_1 and M_2 represent the atomic and molecular metastables, respectively. The other constituent particles are represented in the usual manner. The determining rate constants for each of the above reactions are represented by the symbols above the arrows. In Eqs. (5f) and (5g), the symbol X represents either an electron, an atom, or nothing. All processes are neglected for destruction of metastables except ionizing collisions with other metastables and conversion from atomic to molecular metastables. In particular, electron collisional depopulation of the atomic and molecular triplet metastables is not included because no permanent loss of the source term was observed following the heating pulse which increased the electron density and electron temperature as described in Sec. III. Collins and Hurt[15] made the same observation for similar heating levels. Note that $\alpha_1 + \alpha_2$ is not necessarily the total electronic recombination events will not result some of the recombination process will not result in a metastable particle. Although not explicitly included, the recombination of He_3^+ can arbitrarily be included in reactions (5f) and (5g) since the equilibrium concentration of He_3^+ relative to He_2^+ is proportional to pressure.[16] At lower pressures, Veatch and Oskam[17] observed only the atomic metastables resulting in atomic ions. However, Phelps[18] found that the molecular metastables are lost by mutual ionizing collisions or by superelastic collisions with electrons. If the mutual ionizing collisions of molecular metastables result in molecular ions, Veatch and Oskam would not have observed the reaction. For the conditions of our experiment, we are unable to distinguish between the first and second processes given in (5a)–(5c) because atomic ions are quickly converted to molecular ions via (5e).

The electronic recombination coefficient α is defined as

$$\alpha = \alpha_0 + k_e N_e + k_p p \ . \tag{6}$$

The three constants α_0, k_e, and k_p represent the recombination mechanisms

$$\mathrm{He}_2^+ + e \xrightarrow{\alpha_0} \mathrm{He}_2^* \quad \text{or} \quad \mathrm{He}^* + \mathrm{He} \ , \tag{7a}$$

$$\mathrm{He}_2^+ + 2e \xrightarrow{k_e} \mathrm{He}_2^* + e \ , \tag{7b}$$

$$\mathrm{He}_2^+ + e + \mathrm{He} \xrightarrow{k_p} \mathrm{He}_2^* + \mathrm{He} \quad \text{or} \quad \mathrm{He}^* + 2\mathrm{He} \ , \tag{7c}$$

respectively, for a high-pressure (p >15-Torr) helium afterglow. Recombination is defined in this paper to have occurred when an electron and an ion form a neutral particle, and that neutral particle reaches an energy level which has essentially zero probability of being ionized by a thermal plasma species without transfer of internal energy. We have assumed that process (7b) does not result in dissociation. Because of the observed dependence of the molecular radiation on electron density and because there was no indication of an N_e^3 term in the observed electron decay, process (7b) was assumed to be insignificant for the conditions of this experiment.

The differential equations describing M_1 and M_2 (which are also used as the density terms), the atomic-ion density N_1, and the molecular-ion density N_2 in the helium afterglow restricted to processes listed in Eqs. (5) are

$$\frac{dM_1}{dt} = -\beta_1 M_1^2 - \beta_{12} M_1 M_2 - B p^2 M_1 + \alpha_1 N_e N_2 + D_{M1} \nabla^2 M_1 \ , \tag{8a}$$

$$\frac{dM_2}{dt} = -\beta_2 M_2^2 - \beta_{12} M_1 M_2 + Bp^2 M_1 + \alpha_2 N_e N_2 + D_{M2} \nabla^2 M_2 \quad , \quad (8b)$$

$$\frac{dN_1}{dt} = -\gamma p^2 N_1 + \tfrac{1}{2} f_1 \beta_1 M_1^2 + f_{12} \beta_{12} M_1 M_2 + \tfrac{1}{2} f_2 \beta_2 M_2^2 + D_{N1} \nabla^2 N_1 \quad , \quad (8c)$$

$$\frac{dN_2}{dt} = -\alpha N_2 N_e + \gamma p^2 N_1 + \tfrac{1}{2}(1-f_1)\beta_1 M_1^2 + (1-f_{12})\beta_{12} M_1 M_2 + \tfrac{1}{2}(1-f_2)\beta_2 M_2^2 + D_{N2} \nabla^2 N_2 \quad , \quad (8d)$$

where f_1, f_2, and f_{12} represent the fraction of the reactions of type (5a)–(5c) which result in atomic ions. Numerical solutions of Eqs. (8) indicated that diffusion is insignificant for the conditions of of this experiment.

The Eqs. (8) cannot be treated in general because the values of $\beta_{12}, \beta_2, f_1, f_{12}$, and f_2 are not known and the reported value of β_1 may not be correct because of the influence of the second and fourth terms on the right-hand side of Eq. (8a). The study by Miller *et al.*[19] indicated that β_1 may be as much as 50% larger than the measured value[18,19] 1.8×10^{-9} cm^3 sec^{-1}. Since there is considerable uncertainty on this point, in the following discussion we will set β_1 equal to the measured value. The basic argument on the consistency of this model will not be affected even if this value of β_1 needs to be corrected by + 50%. At pressures of interest here, the conversion frequency of atomic ions to molecular ions is sufficiently rapid to permit setting the right-hand side of Eq. (8c) to zero. (At the lowest pressures of interest, the maximum ratio of N_1/N_2 was less than 0.07.) With this substitution, the set of Eqs. (8) can be solved numerically if it is assumed that atomic and molecular metastables are indistinguishable (i.e., $\beta_1 = \beta_2 = \beta_{12} = \beta$), although the solutions are still dependent on the value of the recycling parameter $K = (\alpha_1 + \alpha_2)/\alpha$. Analytic solutions are also possible if it is assumed that the time rate of change of N_e is given by $-\alpha_{eff} \times N_2^2$, which is in agreement with experimental results. In this spirit Eq. (8d) leads to the solution

$$(\alpha - \alpha_{eff})(1/N_e^0 + \alpha_{eff}\, t)^{-2} = \tfrac{1}{2}\beta M^2 \quad , \quad (9a)$$

which requires that the metastable density be expressed as $M = (1/M_0 + \beta_{eff}\, t)^{-1}$. Equations (8a) and (8b) lead to the following expression, again with the assumption of indistinguishable metastables:

$$(\beta - \beta_{eff})(1/M_0 + \beta_{eff}\, t)^{-2} = \alpha K (1/N_e^0 + \alpha_{eff}\, t)^{-2} \quad . \quad (9b)$$

Equations (9) yield the following relationships:

$$K = 2\left\{1 - \frac{\alpha_{eff}}{\alpha}\left[1 + \left(\frac{\alpha - \alpha_{eff}}{2\beta}\right)^{1/2}\right]\right\} \quad , \quad (10a)$$

$$(M/N_e)^2 = (\alpha - \alpha_{eff})(2/\beta) \quad , \quad (10b)$$

which agree with the solutions given by Stevefelt.[20] Thus if $\beta = 1.8\times10^{-9}$ cm^{3}sec^{-1} the measured values of α and α_{eff} require that $K \approx 0.7$. At pressures below 25 Torr, Eqs. (10) are consistent with our results either if molecular metastables also enter into ionizing collisions or if only atomic metastables are ionized by mutual collisions and $\alpha_1 \gg \alpha_2$. However, at pressures above 25 Torr the conversion of atomic metastables to molecular metastables becomes a significant term, and numerical solutions have shown that a plot of $1/N_e$ vs time would be linear as it was observed to be only if both atomic and molecular metastables enter into ionizing collisions. Thus our results indicate that atomic metastables and molecular metastables are essentially indistinguishable in mutual ionizing collisions. We emphasize, however, that our results do not necessarily indicate that $\beta_{12} = \beta_2 = \beta_1$. If the molecular ion helium afterglow is represented by Eqs. (8), then our results do indicate that molecular metastables enter into ionizing collisions with reaction rates on the order of 1.8×10^{-9} cm^{3}sec^{-1}.

For our analysis to be correct, the relation between the metastable density and the electron density as given by Eq. (10b) must be maintained in the afterglow. Measurements of atomic metastable densities by an absorption technique at the lower pressures where the expected density of molecular metastables is expected to be small indicated this relation was satisfied to within the accuracy of the measurements. The numerical solutions also indicated that this ratio is quickly attained in the afterglow under the conditions of this experiment regardless of the initial ratio produced during the excitation pulse if the metastable density is understood to equal the sum of the atomic and molecular metastable densities.

The above discussion indicates that a considerable fraction of the recombining ions produce metastables which in turn are involved in ionizing collisions. This is not consistent with the assumption that the source term S is independent of the intensity and the duration of the heating pulse. Since both the molecular light and the electron density following the heating pulse returned to the same value which each attained in the absence of heating, no permanent change in the magnitude of the source was observed. However, since metastables are formed in recombination, the source must necessarily be altered during the heating period. Since $M > N_e$ and the relative change in N_e during the heating period is small, the change

in the source which results from metastable-metastable ionizing collision does not significantly affect the results. This can easily be shown by a perturbation analysis. Thus using the subscript notation of Eq. (4), we find that $M_N^0 - M_H^0 < K(N_{eH}^0 - N_{eN}^0)$. With Eq. (10b), we find that the source term immediately following termination of the heating pulse S_H^0 relative to its value at this same time without application of the heating wave S_N^0 is

$$\frac{S_N^0 - S_H^0}{S_N^0} < 2K \frac{N_{eH}^0 - N_{eN}^0}{N_{eN}^0} \left(\frac{\frac{1}{2}\beta}{\alpha - \alpha_{eff}} \right)^{1/2}$$

For typical conditions investigated, the maximum change in the value of the source term due to the heating pulse is about 14%. This will result in an underestimation of α by about $\frac{1}{2}$ this percentage if we neglect alterations in the source. Detailed numerical solutions substantiate this perturbation analysis.

VI. TEMPERATURES

The average gas temperature T_g was estimated from the average pressure change with and without the excitation pulses. In all cases this amounted to less than a 5% increase above room temperature (300 °K).

The electron temperature T_e is maintained above the gas temperature by heating from the metastable-metastable reactions and superelastic collisions of electrons and metastables. The differential equation for the electron temperature is

$$\frac{d}{dt}(N_e \tfrac{3}{2} k T_e) = \tfrac{1}{2}\beta M^2 \langle \epsilon \rangle + \alpha_s N_e M \langle \epsilon_s \rangle - \tfrac{3}{2} k \frac{2m}{M} \nu (T_e - T_g) N_e \quad , \quad (11)$$

where k is Boltzmann's constant, m/M is the electron-to-atom mass ratio, ν is the elastic collision frequency of electrons and atoms,[21] α_s is the superelastic collision rate of electrons and atomic metastables, $\langle \epsilon \rangle$ is the average energy imparted to the electron gas by the hot electron produced in the M-M reaction, and $\langle \epsilon_s \rangle$ is the average energy imparted to the electron gas by the electron involved in the superelastic collision. The average energies $\langle \epsilon \rangle$ and $\langle \epsilon_s \rangle$ can be estimated by consideration of the partition of energy between the gas atoms and the background electrons. We estimate that

$$\langle \epsilon \rangle = \int_{kT_e}^{14.8} \frac{1}{1 + \Upsilon_{ee}(\epsilon)(2m/M)\nu(\epsilon)} \, d\epsilon \quad ,$$

where Υ_{ee} is the relaxation time for a test electron of energy ϵ in a background electron gas.[22] The value of $\langle \epsilon_s \rangle$ is evaluated similarly. When the time derivative of Eq. (11) is approximated by zero, the electron temperature can be estimated.

For the particular conditions of this experiment, the highest estimated elevation of the electron temperature was greatest at the lowest pressure (15 Torr) where at the earliest time of consequence it was estimated to be 33 °K. The maximum estimated correction necessary to deduce the 300 °K recombination coefficient from the measured value of α is a negative 17%. Above 20 Torr, the estimated error is negligible. Since we measured α at 15 Torr at different times into the afterglow (i.e., at different metastable densities) and detected no difference in α we concluded that the net effect of the electron temperature on the recombination coefficient was overestimated. The values given for α in Sec. III have not been corrected for elevated temperature although the error at the lowest pressure could be as large as a negative 10%.

The electron temperature during the heating pulse has also been estimated with the measured amplitude of the current heating pulse and the quasiequilibrium condition of the energy. For the conditions of this experiment, the largest electron temperature during heating was 1500 °K. If $\alpha \propto 1/T^n$, then the power of T can be calculated from a comparison of the calculated increase in electron density with the use of the rate equations in Sec. V and the observed increase during the heat pulse. This analysis indicated that $n \approx 1.0$. Measurements of the relative intensities of the molecular radiation with and without heating also indicated a power dependence on T of approximately 1.0.

VII. DISCUSSION AND CONCLUSIONS

The measured values of the electronic recombination coefficient reported in Sec. III are considerably larger than previously reported because an intense source of free electrons retards the rate of decay in a helium afterglow. The technique we used to obtain α did not depend upon a complete knowledge of the source. The basic assumption necessary was that the source term was unaffected by the low-level heating current. Such a source term can be described by metastable-metastable ionizing collisions if molecular metastables enter into the reactions along with atomic metastables. Only a fraction of the recombining electrons (0.68 ± 0.15) would then result in metastables which are involved in subsequent ionizing collisions.

The observed pressure dependence of α is evidently larger than can be explained by the collisional stabilization of bound electronic levels as described by Bates[23] or by the presence of He_3^+.[16] A uniquely molecular recombination process which needs to be given serious consideration is collisional stabilization of autoionizing levels with rotational and vibrational degrees of freedom. The

value of the recombination coefficient resulting from this radiationless transition $\alpha(rlss)$ can be calculated with the equation given by Bates.[24] For example, if the autoionization times are very small and the average impact parameter which can lead to stabilization is assumed to be 6 Å, then $\alpha(rlss)$ is 2.5×10^{-10} $cm^3 sec^{-1} Torr^{-1}$ for the level $He_2(n=10, v=1)$, where n and v are the principle and vibrational quantum numbers, respectively. Presumably the stabilization would be effected via a curve crossing in the He_3^* system. The multitude of possible autoionizing states and stabilization routes in the He_3^* system could together yield a significant route for recombination of He_2^+. A detailed calculation has not been performed for these rotationally and vibrationally excited states because of a lack of knowledge of all the autoionizing rates. Some autoionization rates will be smaller than the stabilization rates; thus the pressure dependence of $\alpha(rlss)$ will have a negative second derivative with pressure until a pressure is reached at which every radiationless transition is stabilized. This dependence of $\alpha(rlss)$ on pressure is consistent with our measurements and in this light α_0 could be due to complete stabilization of some radiationless transitions at the lowest pressure investigated (15 Torr).

The projected zero-pressure intercept α_0 of the total recombination coefficient may also be attributed to dissociative recombination of He_2^+. Because of the relatively weak atomic radiation, any significant dissociative recombination must terminate directly on an atomic level with principal quantum number 1 or 2.

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