TABLE I. Stochastic parameters computed by method A for electrons in N_2 at 300°K and 55 mm Hg as a function of E/P.

E/P (V/cm mm Hg)	v_D (10^5 cm/sec)	D (10^3 cm^2/sec)	$\langle E\rangle$ (eV)	$\langle\lambda\rangle$ (10^{-4} cm)	$\langle\mu\rangle$	f_r	$\langle\nu\rangle$ (10^{10} sec^{-1})
0.01	0.84	3.4	0.038	9.6	0.002	...	1.1
0.02	1.4	3.5	0.039	9.6	0.011	0.99	1.1
0.04	2.5	3.8	0.053	8.8	0.017	0.97	1.4
0.08	3.3	4.2	0.085	7.7	0.018	0.97	2.0

cosine of the collision angle is seen to be quite small in each case, indicating that a two-term expansion in μ should be adequate to represent the distribution function at these pressures and field strengths. This conclusion is also supported by the excellent agreement of the stochastic results with the Davydov distribution function for electrons in helium as demonstrated in Fig. 1, and is in agreement with earlier observation[13,35] that over the range of E/P investigated the Lorentz approximation is a satisfactory assumption. The present method also provides a simple tool for extending the investigation to higher E/P where the Lorentz approximation is no longer valid.

In addition to drift velocities, diffusion coefficients, and collision angles, a number of related parameters have been calculated and are also presented in Table I. These are the mean energy $\langle E\rangle$ of the stochastic distribution, the mean free path $\langle\lambda\rangle$ for the entire electron distribution, the fraction of energy f_r transferred to rotational excitation, and the mean collision frequency $\langle\nu\rangle$ for the entire electron distribution.

ACKNOWLEDGMENTS

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Recombination of Electrons and Molecular Helium Ions

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The recombination coefficient $\alpha(N_e,T_e)$ of He_2^+ is measured in helium afterglow plasmas (12 Torr$\leq p\leq$20 Torr; $t\gtrsim$1 msec) as a function of electron density and gas temperature under conditions where the temperature of electrons and ions equals that of the neutral gas (2.5×10^{12} cm$^{-3}\leq N_e\leq 2\times10^{13}$ cm^{-3}; 900°K$\leq T\leq$2200°K). The recombination coefficient is found equal to the theoretical collisional-radiative recombination rate of He^+. In spite of the high vibrational excitation of the recombining He_2^+, corresponding to the high gas temperatures, there is no evidence for dissociative processes. In particular, the time decay of the recombination light cannot be reconciled with collisional-dissociative recombination.

1. INTRODUCTION

STUDIES of the recombination of electrons and molecular ions have improved the knowledge of the structure of the participating molecular particles. In most ionized gases capable of forming molecular ions the recombination has been found to proceed by the fast dissociative mechanism[1]

$$(AB)^+ + e \rightarrow A + B. \quad (1)$$

This process occurs as a result of a radiationless transition to a repulsive state of the neutral molecule, which is formed by electron capture, leading to dissociation into (possibly excited) atoms. It has been pointed out especially by Ferguson *et al.*[2] that process (1) is unlikely to play an important role in helium plasmas, mainly because the recombination rate here is much smaller, and because the afterglow light resulting from recombination shows different characteristics.

The deionization in low-pressure ($p\lesssim$1 Torr) helium afterglow plasmas containing predominantly atomic ions has already been successfully explained by the collisional-radiative recombination process[3,4]

$$He^+ + e + e \rightarrow He + e, \quad (2)$$

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[3] E. Hinnov and J. G. Hirschberg, Phys. Rev. 125, 795 (1962).

[4] Reference 1, p. 253.

in which electron collisions contribute decisively to the formation and de-excitation of neutral atoms. The recombination coefficient α, defined by

$$(dN_i/dt)_{\text{rec}} = -\alpha N_e N_i \tag{3}$$

($N_{e,i}$ = concentration of electrons and ions), is, for this process, a function of plasma density and electron temperature.

Only recently have there been attempts to apply this scheme also to the analysis of afterglow experiments performed at higher pressures ($p \gtrsim 5$ Torr) where He_2^+ becomes the dominant ion. This interpretation has been based mainly on the optical characteristics of the afterglow: The line radiation could be attributed to the (collisional-radiative) recombination of atomic ions while the recombination of He_2^+ was found to result in the emission of bands,[5] in accordance with the collisional-radiative model. For the variation with pressure and time in the afterglow a correlation could be established between the band intensity and the He_2^+ concentration.[6] The dependence of the afterglow band emission on electron temperature[2] and electron density[7] was also found to follow approximately theoretical expectations. However, these experiments did not permit to measure directly the recombination coefficient as a function of density and temperature over an extended range of these parameters.

Such measurements appear necessary for a discrimination against other possible recombination mechanisms: Because of the proven existence of the Hornbeck-Molnar process[8]

$$A^* + A \rightarrow A_2^+ + e \tag{4}$$

in helium there is the question under which conditions the inverse mechanism, dissociative recombination (1), might become important, since it should then, in principle, also occur. More recently Collins and Robertson[9–11] have proposed that deionization might also take place by collisional-dissociative recombination if the molecule resulting from recombination possesses a repulsive state between the ionization level and the ground state. This process does not require a potential-curve crossing, as in process (1), since the unstable state may be populated by two-electron collisions from the continuum and superelastic electron collisions from higher excited states as in the collisional-radiative process. Model calculations have shown that this recombination process may exceed the collisional-radiative rate considerably, especially if the repulsive state is located close to the ionization level.[9] Collins and Robertson have also reported experimental evidence that this process may be effective in helium afterglows.[10,11] They found that the time decay of the line intensity at 10 830 Å (2^3S-2^3P) followed the slow decay of the band radiation rather than the much faster decay of the other helium lines. This was attributed to the formation of excited atoms by the dissociation of molecules in the $4p\sigma$, $^3\Sigma_g^+$ state and taken as an indication that this state should be repulsive. The occurrence of collisional-dissociative recombination resulting in excited helium atoms in the 2^3p state contradicts, however, the results of a recent theoretical paper by Mulliken[12] which indicates that the potential curves of the helium molecule between ground state and ionization level are not purely repulsive.

Unfortunately, the large number of reported measurements[13–21] of the recombination coefficient of He_2^+ have not allowed a positive identification of the dominant recombination mechanism. Most data obtained in afterglow experiments lie between $\alpha = 10^{-9}$ and 10^{-8} cm^3 sec^{-1} (measured mostly at plasma densities below 10^{11} cm^{-3}), and are therefore within the range of collisional radiative rates at and above 300°K (theoretical values for H^+ at 300°K: $\alpha \approx 1\times10^{-8}$ cm^3 sec^{-1} at 10^{11} cm^{-3}; $\alpha \approx 1.6\times10^{-9}$ cm^3 sec^{-1} at 10^{10} cm^{-3}).[4] However, for one or more of the following reasons many measurements are difficult to interpret: In afterglows where the decay is measured at low plasma densities (imposed by the use of a microwave cavity technique) it is difficult to exclude competing diffusion effects.[22] Moreover, the attempt to fit the measurements to the recombination solution $1/N_e \propto \alpha t$ is not meaningful if α depends on the density as in collisional-radiative recombination. A deduction of the recombination coefficient from the time variation of the afterglow-light intensity suffers from the lack of a general, simple theoretical relationship between plasma density and light intensity. This is a consequence of the importance of radiationless de-excitation induced by electron collisions. In particular, there is no strict theoretical foundation in the collisional-radiative model for the often assumed proportionality between light intensity and the product of electron and ion concentration.

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The greatest difficulty may arise in the determination of the electron temperature: Because of the energy feedback mechanism due to collisional-radiative recombination, which is enhanced by the presence of metastable states, it cannot be assumed, without verification, that the electron temperature remains at the temperature of the gas.[23,24] Electron heating is especially pronounced at low gas temperatures and should already be important at plasma densities as low as 10^{11} cm^{-3} when the gas is at room temperature.[24] In addition to afterglow electron-heating effects there may also be a heating of the neutral gas when initial plasma (or metastable) densities around 10^{11} cm^{-3} and higher are generated,[25,26] especially where high repetition rates are employed. (This effect may contribute to the often observed decrease of the initial plasma decay rate with increasing excitation-pulse length, which is usually only attributed to changes in the initial spatial plasma distribution.) The strong temperature dependence of the collisional-radiative recombination coefficient may be the most important reason for the wide variation (over two orders of magnitude) of the published α values.

Afterglow measurements of the recombination coefficient of He_2^+ covering an extended range of defined temperatures and densities are reported in this paper. The measured values do not differ significantly from the theoretical collisional-radiative recombination rates for atomic ions. In spite of the considerable vibrational excitation of the molecular particles, corresponding to the high gas temperatures at which the experiment is performed, no evidence is found for dissociative processes. In particular, the experimental results cannot be reconciled with the collisional-dissociative recombination mechanism, in accordance with Mulliken's theoretical model of the He_2^+ molecule.

2. EXPERIMENT

The experiments were performed at comparatively high plasma densities ($>10^{12}$ cm^{-3}) in a large discharge tube [Pyrex cylinder with tungsten electrodes, $L=52$ cm, $R=4.6$ cm (tube A)]. [At the lowest pressures a tube with the dimensions $L=90$ cm, $R=7$ cm (tube B) was used.] Because of the high absolute recombination rates at high plasma densities, diffusion was found unimportant down to the lowest pressures (0.25 Torr),[27] and the plasma losses due to gas impurities were also found negligible. After evacuation and bakeout (base pressure $<10^{-7}$ Torr) the tube was filled with research grade helium (Air Products and Chemicals Co.) and disconnected from the vacuum and gas handling system. The pressure range between 0.25 and 20 Torr was investigated. The pressure was measured with a Baratron gauge. The gas was partially ionized by a single-shot condenser discharge ($C=0.5$–2.5 μF, $U=5$–20 kV). The recombination rates obtained at low pressures, where He^+ is the dominant ion, were then compared with the rates at high pressures, where the majority of the ions is molecular. Since the magnitude of the collisional-radiative recombination coefficient of atomic ions is well established theoretically and experimentally the low-pressure measurements were considered as a test for the applied measuring techniques.

The electron density was determined by a free-space microwave method with a 70-GHz interferometer. Because of the large ratio between tube diameter and wavelength, enough "fringes" were obtained to allow a good time resolution in the density readout. For the evaluation it was assumed that the plasma filled the tube homogeneously; electron collisions were neglected.

The generation of plasmas of high densities causes a heating of electrons, of ions, and of the neutral gas so that time-resolved temperature measurements become necessary.[26] In addition, afterglow electron-heating effects have to be taken into account. For atomic hydrogen plasmas Bates and Kingston[24] have computed the quasiequilibrium temperatures which the electrons assume as a result of simultaneous heating and collisional cooling as a function of plasma density, gas density, and gas temperature. They arrived at the general result that the electron temperature will rise above that of the gas especially when the gas temperature is low and the plasma density is high. However, at sufficiently high gas temperatures, electrons, ions, and neutrals will reach approximately thermal equilibrium. This behavior follows from the strong temperature dependence of the recombination coefficient: With increasing gas (and electron) temperature the rate of recombination decreases and therefore the amount of energy released is also reduced. A qualitatively similar behavior is also expected for helium. This has been confirmed in earlier low-pressure (0.25–0.7 Torr) afterglow experiments[28] where the time-varying electron temperature was determined from the intensities of lines originating from high levels, whose populations are in Saha equlibrium with the free electrons.[3] The gas temperature was deduced from sound-velocity measurements. For the experimental range covered ($N_e \leq 10^{13}$ cm^{-3}, $T \geq 1000$°K) the electron temperature was found equal to the gas temperature, in agreement with calculations in which metastable effects were taken into account. It is interesting to note that intense discharges, which cause a substantial gas heating, provide relatively simple experimental conditions for measuring collisional-

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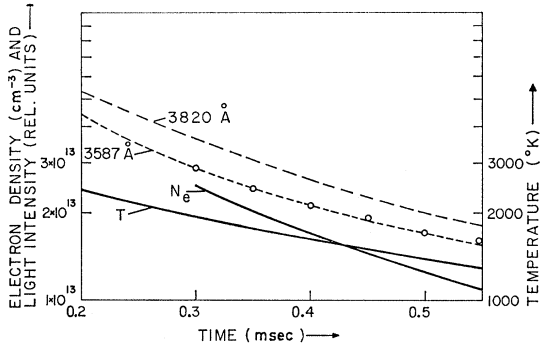

FIG. 1. Semilogarithmic plot of the time decay of (gas and electron) temperature T, electron density N_e, 3587 Å line (9^3D–2^3P) and 3820 Å line (6^3D–2^3P) (tube B, $p=0.25$ Torr, 1 μF, 9 kV). Points are calculated according to (6) from experimental N_e and T values. The T decay causes the 3587 Å line to decay with approximately the rate of N_e.

radiative recombination because in this case the charged particles remain at the temperature of the gas. Discharges where the gas is at room temperature, on the other hand, are not subject to such an easy analysis because the electrons may assume elevated temperatures which may be difficult to determine.

On the basis of the experimental results described below the energy balance for the electron gas at higher pressures (with He_2^+ as the dominant ion) is not expected to differ much from the low-pressure case (He^+). It can therefore be assumed that thermal equilibrium between electrons, ions, and neutrals should exist in the high-pressure case in about the same experimental range for which it has been established in the previous low-pressure measurements. Under these circumstances problems in determining the electron temperature directly (for example, from the relative intensities of rotational transitions[29–31]) are avoided and the measurement is reduced to a comparatively simple determination of the gas temperature.

The acoustic method to determine the time-varying gas temperature has already been described in detail elsewhere.[26] It makes use of the fact that pulsed gas discharges produce, in general, pressure perturbations which reduce to standing sound waves in the afterglow. The frequencies of the modes of oscillation depend, for a given gas, on container geometry and gas temperature, which can be computed from

$$\omega_n k_n^{-1} = (\gamma kT/m)^{1/2}, \tag{5}$$

where ω_n is the angular frequency, $k_n = 2\pi/\lambda_n$ is the wave number, γ is the ratio of specific heats c_p/c_v, k is Boltzmann constant, T is the gas temperature, and m is the mass of the gas atoms. The acoustic oscillation causes a density modulation of the electron gas which can be detected with microwaves. In this experiment a 9-GHz microwave interferometer operating in reflection was used to monitor the sound waves, which caused a phase modulation in the totally reflected beam (plasma frequency >9 GHz). For the temperature determination only the two lowest transverse modes possible in a cylinder were used ($k_1R=1.84$; $k_2R=3.83$). Methods to identify the modes have been discussed by Born and Buser.[26] At low pressures only one or both of these modes were excited strongly. At higher pressures, where the attenuation is low, care had to be taken to maintain the cylindrical symmetry of the discharge current to avoid a strong excitation of higher modes. This required, in some cases (at $p=12.5$ and 16.4 Torr), application of a weak preionization current (≈ 1 mA). Preionization improved also the homogeneity of the initial plasma distribution. It was ascertained that in these cases the preionization current had no effect on the plasma decay.

For the conditions of the experiments the temperature decay was always slower than the plasma decay. By varying the discharge power it was then possible to perform the measurements, within a certain range, at different density-temperature combinations. This allowed to compare the recombination rates, obtained in discharges of different pressures, at equal preselected values of density and temperature. Electron densities between 2.5×10^{12} and 2×10^{13} cm^{-3} and temperatures ranging from 750 to 2200°K could be covered.

The afterglow was also investigated optically. The time variation of several selected lines and bands was measured with a Jarell Ash grating monochromator with photophotomultiplier. The time decay of the total light (defined by the spectral response of the S-4 cathode used, ≈ 3000 to 6000 Å) was also recorded. The discharge in tube A was usually observed "end on" along a path (pathlength 52 cm) close to the cylinder axis. The slit width was varied according to the experimental conditions. For most lines in the visible a resolution of 5 Å or less was chosen. For the selected spectral bandwidth the band emission next to the measured lines was always negligible. Band radiation was monitored with a resolution of about 30 Å. As expected, the measured time decay of the lines or bands did not depend on the slit setting. For the measurement of the 2^3S–2^3P line at 10830 Å a photomultiplier with S-1 response was used. Here the slit was set as wide as permissible by the band radiation next to the line (≈ 60 Å). Because of the high light output of the intense discharges used in the present experiment, and the long sampling path, the line could be observed almost unaffected by photomultiplier noise late (~ 1.5 msec) into the afterglow.

3. DISCUSSION OF RESULTS

The composition of the decaying plasma was deduced from the light output. The low-pressure afterglow (≤ 1 Torr) consists practically exclusively of lines. With increasing pressure atomic ions are converted faster into molecular ions whose recombination leads to the emis-

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sion of bands of the excited He_2 molecule.[32,33] For a rough quantitative evaluation of this conversion process it is useful to establish an approximate relation between concentration of electrons and atomic ions and line-radiation intensity. A simple result can only be expected for the radiation from highly excited states, formed by recombination, whose population densities N_n are in a Saha equilibrium with the free electrons because of the high energy-exchange rate by electron collisions. The time behavior of the lines originating from these high states is then also described by the Saha equation which may be written in logarithmic form as

$$\ln I_n(t) = \ln N_e(t) + \ln N_i(t) - \tfrac{3}{2}\ln T_e(t) + E_n/kT + \text{const} \quad (6)$$

(I_n = intensity of the line originating from the nth level, assumed proportional to N_n, N_e = electron density, N_i = density of atomic ions, T_e = electron temperature, E_n = energy of nth level, measured from the ionization level). Only if the electron temperature does not change with the time will the intensity become a simple function of electron and ion density of the form

$$I \propto N_i N_e^p, \quad (7)$$

with $p=1$. A decay of the temperature with time, however, will result in an apparent value of $p<1$, with p now generally a function of time. Because of the strong influence of T_e in Eq. (6), p is quite sensitive to T_e time variations. This temperature effect was verified in a low-pressure (0.25-Torr) discharge where the analysis in terms of Eq. (6) is simplified because the number density of atomic ions is equal to the electron density. Figure 1 shows the measured decay of two lines together with the time variation of electron density and gas temperature, which in this case was found equal to the electron temperature. The upper level of the 9^3D–2^3P transition (3587 Å) was in Saha equilibrium with the electrons. [The n^3D–2^3P (n=8–10) transitions were used for a determination of T_e.] Using the measured $T_g = T_e$ and $N_e = N_i$ values the time decay of this line was calculated from Eq. (6) (points in Fig. 1), giving excellent agreement with the experimental data (broken line). Without the effect of the decaying electron temperature the line intensity would be expected to decay with twice the rate of N_e; the rapid T decay results in approximately equal decay rates of I and N_e ($p \approx 0$).

It should be noted that the decay of the lines considered here cannot be described by a value of $p=2$ in Eq. (7) contrary to what might at first be expected for the three-body recombination process (2). This is a consequence of the role of electron collisions in the depopulation of excited states. Because of the relative importance of these radiationless transitions the number of emitted photons is no longer proportional to the number of recombination events as the electron density (and energy) changes with time. At the relatively high electron densities at which the present experiment was conducted electron collisions also affect strongly the decay of the lines originating from lower n levels [whose populations are no longer described by the Saha equation (6)] leading to decay rates which are similar to the rates of the lines following Eq. (6). The 3820 Å line (6^3D–2^3P) is shown in Fig. 1 as an example for this behavior. The population of the upper level of this transition was found to deviate from the Saha value for times later than 0.2 msec. Similar decay rates were also found for most other lines starting from lower n values. The evaluation of the conversion of atomic ions at the higher pressures was, therefore, based on the empirical result that, at the high electron densities of the present experiments, most lines decay according to Eq. (7) with $0 \lesssim p \lesssim 1$. This result differs from the situation at low electron densities where the effect of electron collisions is reduced and p therefore approaches a value of 2.[7]

At higher pressures the decay of the line radiation relative to the electron density is much faster because of the conversion of atomic ions into molecular ions by triple collisions with neutral atoms:

$$He^+ + He + He \rightarrow He_2^+ + He. \quad (8)$$

The conversion rate ν is defined by

$$(dN_i/dt)_{\text{conv}} = -\nu(T) N_i N_n^2, \quad (9)$$

where $N_{i,n}$ is the concentration of atomic ions and neutrals. Compared with the rate expressed by Eq. (9), the conversion by the Hornbeck-Molnar process (4) can be neglected at the high pressures considered here. Niles and Robertson[33] found that $\nu(T)$ is inversely proportional to the absolute temperature, with $(\nu T) = 3.19 \times 10^{-29}$ sec^{-1} °K cm^6. They checked this temperature dependence experimentally in the range between 77 and 450°K.

Figure 2 shows experimental results for a discharge at 12.5 Torr (at 0°C). Here the electron temperature is again equal to the gas temperature. The 4472 Å line (2^3P–4^3D) represents the decay of most lines. [In this experiment the lines originating from high levels whose decay is determined by the Saha equation (6) could only be observed 0.6 msec into the afterglow because of the strong competing band radiation. For early times these lines showed again approximately equal decay rates with the strong lines emitted from atoms in lower excited states, as in the low-pressure case of Fig. 1.] For the conditions at the time $t=1.0$ msec in Fig. 2, for example, Eq. (9) predicts a conversion rate $1/\tau = [d(\ln N_i)/dt]_{\text{conv}} = 3 \times 10^3$ sec^{-1}. This result was obtained by extrapolating the ν value of Niles and Robertson to the much higher temperature (1750°K) of the present experiment. [The atom density was assumed equivalent to the fill pressure. This appears justified because the discharge

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TABLE I. Recombination coefficient α obtained at different gas pressures p: (a) at an electron density of $N_e=2.5\times10^{12}$ cm^{-3} and gas temperatures T_g around 1000 °K, (b) at $N_e=5\times10^{12}$ and $T_g\approx1250$ °K. The fourth line lists theoretical electron temperatures T_e which correspond, for the theoretical collisional-radiative recombination rates of H^+, to the measured N_e and α values. The values in the last column have been averaged over the results taken at the different pressures.

			(a) $N_e=2.5\times10^{12}$ cm^{-3}			
p (Torr)	0.25	2.7	12.5	16.4	20	Average
α (cm^3 sec^{-1})	8.3×10^{-10}	5.7×10^{-10}	5.3×10^{-10}	5.4×10^{-10}	5.6×10^{-10}	6.3×10^{-10}
T_g (°K)	900	1000	1100	1100	900	1000
T_e (°K)	1000	1100	1100	1100	1100	1080
			(b) $N_e=5\times10^{12}$ cm^{-3}			
p (Torr)	2.7	7.3	12.5	16.4	20	Average
α (cm^3 sec^{-1})	4.8×10^{-10}	6.2×10^{-10}	5.5×10^{-10}	4.6×10^{-10}	3.3×10^{-10}	5.2×10^{-10}
T_g (°K)	1250	1200	1250	1300	1250	1250
T_e (°K)	1300	1220	1250	1300	1400	1290

tube was disconnected from the vacuum system so that gas heating could not force part of the gas out of the discharge tube. Besides, the heat dissipation by heat conduction was too slow for generating substantial temperature and density gradients (except close to the walls) during the afterglow time of interest (assuming a homogeneous initial temperature distribution).] The decay of the 4472 Å line in Fig. 2 allowed to deduce only an approximate value of the conversion rate because of the uncertain ratio between line intensity and electron and ion density characterized by the exponent p in Eq. (7). Assuming a value $p\leq1$ yields, again at 1 msec, $1/\tau\geq3\times10^3$ sec^{-1}. ($p=0$ would yield about 6×10^3 sec^{-1}, but, because of the slower temperature decay compared to the case in Fig. 1, p might be expected closer to 1.) This value is in good agreement with the result obtained from (9). Within the stated uncertainty the experiment confirms then the proportionality between ν and $1/T$ also at high temperatures. For the experimental conditions considered ($p=12.5$ Torr, $T=1750$°K) the atomic ion concentration is then expected to drop below 10% of the total ion density within 0.4 to 0.7 msec (provided the recombination rate of molecular ions does not exceed that of atomic ions, as will be shown below). In general, the line-decay measurements suggested that molecular ions should dominate the afterglow at least for times later than 1 msec at temperatures below 2000°K, if the pressure is higher than 12 Torr. This parameter range was used for the determination of the recombination coefficient of He_2^+.

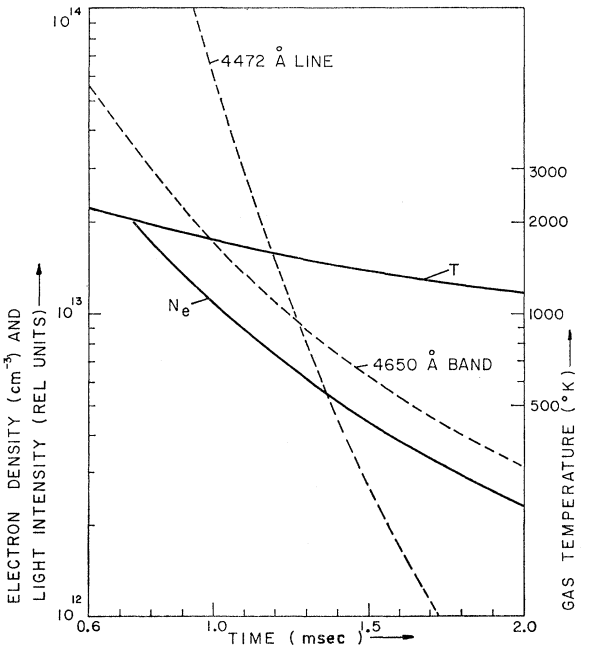

FIG. 2. Semilogarithmic plot of the time decay of gas temperature T, electron density N_e, 4472 Å line (2^3P–4^3D) and 4650 Å band. (Tube A; $p=12.5$ Torr; 1 μF, 15 kV). The rapid decay of the 4472 Å and other lines reflects the conversion of atomic into molecular ions.

Additional qualitative support for the dominance of molecular ions in the case of Fig. 2 can be derived from the time decay of the band emission at 4650 Å, which shows, for the times considered (>0.8 msec), a much closer correlation with the electron density decay than the line radiation does. It should be pointed out, however, that the measurement of the band decay may have been modified by self-absorption which, because of its time variation, might cause an apparent slower decay. The experimental setup with which the data of Fig. 2 were taken (tube A) did not permit measurement of the degree of self-absorption. However, afterglow experiments conducted under similar conditions[34] ($N_e\approx10^{13}$ cm^{-3}) have shown that a considerable degree of (time-varying) self-absorption at 4650 Å has to be expected. Because of the lack of a complete theoretical model for recombination of molecular ions no attempt was made to explain the exact relation between band emission and density of electrons and molecular ions.

Although the strongest lines could be observed late into the afterglow (~2 msec) even at the highest pressure under investigation (20 Torr) indicating the presence of a certain number of atomic ions, it could be shown that line radiation amounted only to a small fraction of the total recombination light. In Fig. 3 the

[34] W. S. Bickel and C. R. Burnett, J. Opt. Soc. Am. 55, 1504 (1965).

TABLE II. Recombination coefficient α as a function of electron density N_e and gas temperature T_g, averaged over the results obtained at various gas pressures. Second line in each field lists theoretical electron temperature as in Table I, third line lists pressures at which data were taken at each N_e-T_g combination. In the upper right part of the table $T_e \approx T_g$; in the lower left (separated by the line) $T_e > T_g$ because of afterglow electron-heating effects.

N_e (cm^{-3}) \ T_g (°K)	750	1000	1250	1500	1750	2200
2.5×10^{12}	$\alpha=10.5\times10^{-10}$ cm^3 sec^{-1} T_e=960 °K p=1.2; 2.7; 7.3; 12.5; 20 Torr	*6.3×10^{-10}* *1080* *0.25; 2.7; 12.5; 16.4; 20*	*4.0×10^{-10}* *1200* *7.3; 12.5; 16.4*			
5×10^{12}	9.6×10^{-10} 1120 1.2; 2.7; 7.3; 12.5	5.8×10^{-10} 1250 0.25; 12.5; 20	*5.2×10^{-10}* *1290* *2.7; 7.3; 12.5; 16.4; 20*	*2.9×10^{-10}* *1500* *7.3; 12.5; 16.4*		
1×10^{13}	6.4×10^{-10} 1400 1.2; 2.7; 7.3; 12.5	5.6×10^{-10} 1450 0.25; 1.2; 12.5; 20	4.9×10^{-10} 1490 0.25; 7.3; 12.5; 16.4; 20	*3.8×10^{-10}* *1570;* *2.7; 7.3; 12.5; 16.4; 20*	*2.3×10^{-10}* *1780* *7.3; 12.5; 16.4*	
2×10^{13}					*3.1×10^{-10}* *1900* *0.25; 2.7; 16.4*	*1.4×10^{-10}* *2280* *7.3; 12.5; 16.4*

the decay of the 4472 Å line and of the 4650 Å band is compared with the time variation of the total light (~3000–6000 Å). After about 0.8 msec the band radiation decays with the rate of the total light. This may be considered as further proof for the dominance of the recombination of molecular ions under these conditions.

The recombination coefficients α in afterglow plasmas dominated by He_2^+ were measured as a function of electron density and gas temperature. These values were then compared with the collisional-radiative recombination rates of He^+ measured at equal densities and temperatures, but at low pressures. Table I contains typical results for two different density-temperature combinations. The first three lines show the pressures and the measured values of the recombination coefficient α with the corresponding gas temperatures. The data at $p>12$ Torr were taken between 1.4 and 2.0 msec for the $N_e=2.5\times10^{12}$ cm^{-3} case, and around 1 msec for $N_e=5\times10^{12}$ cm^{-3}. The fourth line provides a comparison with the theoretical collisional-radiative recombination coefficients of He^+ (which are practically equal to the values[4] for H^+). The theoretical numbers are expressed in terms of the electron temperature at which, for the measured plasma density, the measured value of α should be obtained. These T_e values were determined by graphical interpolation from the tables of Bates *et al.*[35] Table I indicates that the recombination coefficient shows little variation with pressure. In particular, no systematic change can be detected as the pressure is increased. Similarly, the theoretical T_e values do not vary significantly. The absolute values of T_e agree with the measured gas temperatures within the expected experimental accuracy. At low pressures line-ratio measurements have already confirmed independently that electron and gas temperatures at these plasma densities and gas temperatures are indeed equal.[28] The recombination measurements at low pressures give, therefore, the correct magnitudes of α for He^+, and the data do not seem to be affected significantly by errors which might arise, for example, because of deviations of the actual spatial density and temperature profiles from the assumed homogeneous distributions.

As will be discussed below, the energy balance for the electron gas in the high-pressure case is not expected to differ much from the low-pressure experiments so that

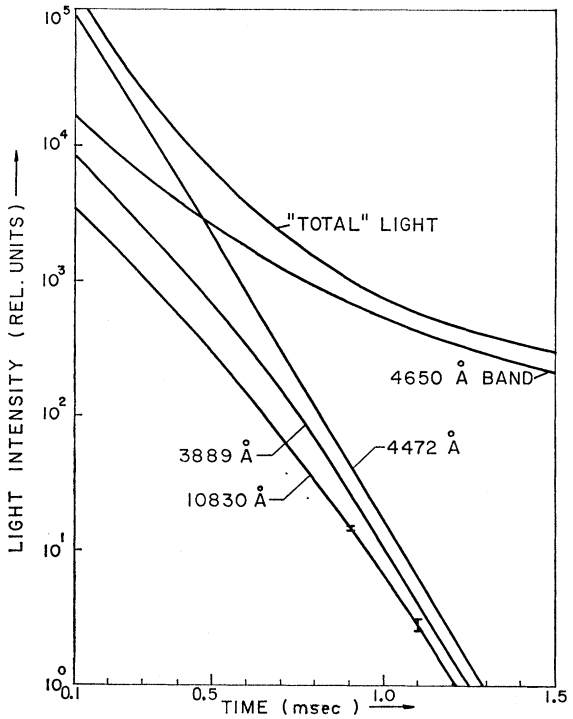

FIG. 3. Semilogarithmic plot of the time decay of the lines at 4472 Å (2^3P–4^3D), 3889 Å (2^3S–3^3P), and 10 830 Å (2^3S–2^3P), compared with the band at 4650 Å and the total light, integrated over the spectral range from ~3000 to ~6000 Å. Error bars indicate peak-to-peak photomultiplier noise. (Tube A, p=20 Torr; 1 μF, 19 kV). The slow initial decay of the 3889 and 10 830 Å lines can be explained by time-varying self-absorption. At late times (>1 msec), when self-absorption becomes negligible, all lines decay with similar rates.

[35] D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. (London) **A267**, 297 (1962).

thermal equilibrium between electrons, ions, and neutrals can also be expected for the conditions at the high pressures (>12 Torr) in Table I. The pressure independence of the measured recombination coefficients indicates that the recombination of He_2^+ is also of the collisional-radiative type, and that α is about equal to the value of atomic ions. Pressure independence was found for the whole density-temperature range investigated, so that it was convenient to average the measured results for equal density-temperature values, as it was done in the last column in Table I. These averaged results are listed in Table II. In addition to recombination coefficient and theoretical electron temperature, (e.g., the value computed from the tables of Bates *et al.*[35]) the pressures at which the data were taken are listed in each field. The upper right and lower left space of the table could not be covered as the experimental range was restricted by the simultaneous temperature and density decay during the afterglow. The data are divided into two groups by the heavy line: At high gas temperatures, especially at lower densities (upper right in Table II), the theoretical temperature values deduced from Ref. 35 correspond to the measured gas temperatures. Since in this range electron and gas temperatures are in fact equal, the experimental results show directly that He_2^+ recombines by collisional-radiative recombination with rates that are practically equal to that of atomic ions.

At lower gas temperatures and higher plasma densities (lower left in Table II) the measured loss rates are smaller than the theoretical values if the comparison is based on the measured gas temperatures. In this range the electron temperature therefore seems to exceed the gas temperature as is expected theoretically.[24] Again, the recombination coefficient, and so the theoretical electron temperature, was found to show no systematic variation with pressure.

To understand this behavior it is necessary to compare the electron heating and cooling mechanisms of the low-pressure case (He^+) with the situation at higher pressures (He_2^+). It can be shown that the amount of energy released is not sufficient to raise the ion temperature significantly above that of the gas under the conditions of the experiment ($T_i \approx T_n$). The energy gain of the electrons can then essentially be estimated, for a certain afterglow time, from a single equation.[28]

$$d(\tfrac{3}{2}N_e k T_e)/dt = -E_1(dN_i/dt)_{\rm rec} + E_2 c_{em} N_e N_m - (T_e - T_i)(c_{ei}/A)N_e N_i - (T_e - T_n)c_{en} N_e N_n \quad (10)$$

[$N_{e,i,n,m}$ = concentration of electrons, (atomic or molecular) ions, neutral atoms, and (atomic or molecular) metastables (2^3S or $2^3\Sigma$); $T_{e,i,n}$ = temperatures of electrons, ions, and neutrals, $E_{1,2}$ = average energies released per recombination and by collisional de-excitation of metastables, c_{em} = coefficient for superelastic electron-metastable collisions; $c_{ei,en}$ = energy transfer coefficients for electron-ion and electron-neutral collisions, A = atomic weight of the ion]. The positive terms on the right-hand side of Eq. (10) describe the heating due to recombination and de-excitation of metastables by superelastic electron collisions. The negative terms represent the cooling of the electrons by collision with ions and neutrals. The metastables are essentially generated by recombination and destroyed by superelastic electron collisions, according to

$$dN_m/dt = -a(dN_i/dt)_{\rm rec} - c_{em} N_e N_m, \quad (11)$$

where a is of the order of unity ($\approx \frac{3}{4}$).[28,36] The rates on the left-hand sides of Eqs. (10) and (11) are negligibly small compared to the right-hand-side terms, so that the electron temperature is determined by

$$0 \approx -(E_1 + aE_2)(dN_i/dt)_{\rm rec} - (T_e - T_n)N_e[(c_{ei}/A)N_i + c_{en}N_n]. \quad (12)$$

The heating rate [first term in Eq. (12)] is not expected to differ significantly for the recombination of atomic ions or molecular ions, since, in addition to the recombination rate, E_1 and E_2 should be approximately equal. The cooling rate by Coulomb collisions with He_2^+ ($A=8$) is weaker by a factor of 2 compared with the atomic case ($A=4$). However, this is approximately balanced by the stronger electron-neutral interaction at higher pressures. This may be demonstrated by a numerical example: For $N_i = 1\times10^{13}$ and $T_e = 1000$°K at low pressures ($p<1$ Torr) the Coulomb rate $(c_{ei}/A)N_e N_i \approx 3.2\times10^3$ erg cm^{-3} °K^{-1} sec^{-1}; the electron-neutral energy exchange is negligible. At a pressure of 15 Torr the exchange rate between electrons and molecular ions drops to 1.6×10^3, but now the cooling by neutrals $c_{en}N_e N_n \approx 2.0\times10^3$ erg cm^{-3} °K^{-1} sec^{-1} has to be added. Most important for the temperature balance is the strong temperature dependence of the recombination rate [$(dN_i/dt)_{\rm rec} \propto T_e^{-9/2}$]. A change in the cooling term (or in E_1 and E_2) in Eq. (12) by a factor x is then balanced by a small temperature adjustment by a factor of only $x^{2/9}$. For these reasons no great variation of the electron temperature with pressure is to be expected for the experiment. In particular, the condition $T_e = T_n$ which was found for the parameter range of the upper right space of Table II at low pressures is then also expected to hold at higher pressures.

Equation (12) gives also the correct absolute increase of the electron temperature over that of the gas for the parameters of the lower left space of Table II. Taking the case $N_e = 1\times10^{13}$, $T_g = 750$ °K, $T_e = 1400$ °K as an example, one obtains (for He^+, Coulomb collisions only) a value of $E_1 + aE_2 \approx 14$ eV as the energy released per recombination event. This is close to the expected value since $E_1 \approx 1$ eV,[23,24,37] $E_2 \approx 20$ eV, and $a \approx \frac{3}{4}$. For the high-pressure case (He_2^+) a similar result is obtained. One may therefore conclude that the data in the lower left

[36] R. W. Motley and A. F. Kuckes, in *Ionization Phenomena in Gases*, edited by H. Maeker (North-Holland Publishing Co., Amsterdam, 1962), Vol. I, p. 651.

[37] M. A. Gusinow, J. B. Gerardo, and J. T. Verdeyen, Phys. Rev. 149, 91 (1966).

space in Table II can also be explained by collisional-radiative recombination of He^+ at low pressures and of He_2^+ at higher pressures. All measurements indicate that the recombination rate of He_2^+ is about equal to that of He^+.

Approximately equal collisional-radiative recombination rates for He^+ and He_2^+ are also expected theoretically. Stabler has performed model calculations where he replaced the discrete term scheme by a continuum of bound states thereby maximizing the collisional de-excitation rates.[38] He concluded that the rate for molecular ions should not be significantly larger than that for atomic ions. He also considered in detail the influence of rotational excitation on the electron-capture mechanism.[29] The large capture rates which he found indicate that the rotational temperature may be closely coupled to the electrons as well as to ions and neutrals. However, due to the small energy differences associated with rotational and vibrational transitions only low-energy electrons are captured into very weakly bound states. The high probability of reionization from these levels makes it unlikely that the initial capture mechanism affects the net recombination rate.

Although the experiment described here was performed at relatively high plasma densities the result should also be of importance for more tenuous plasmas. The theoretical coefficients for collisional-radiative recombination at densities between 10^{11} and 10^9 cm^{-3} at 300 °K lie between 1×10^{-8} and 4×10^{-10} cm^3 sec^{-1} (which is of the order of the rates observed in most experiments). The smallest absolute value of the recombination coefficient found in the present experiment ($\sim10^{-10}$ cm^3 sec^{-1}) can be considered as an approximate upper limit for other recombination mechanisms (for example, of the dissociative type) at any plasma density, since the coefficient for such processes should only exhibit a weak temperature dependence[39] (and no density dependence).

The agreement between measured recombination rates and theoretical collisional-radiative values is, in itself, not yet sufficient proof for the absence of the collisional-dissociative mechanisms in He_2^+ plasmas. If, according to the interpretation of Collins and Robertson,[10,11] excited atoms in the 2^3P state were indeed formed by the dissociation of excited helium molecules the potential curve of He_2 which was assumed repulsive to explain this effect would be too far from the ionization level to enhance the recombination rate appreciably over that of collisional-radiative recombination.[9] Only the emission of the 10 830 Å (2^3P–2^3S) line should then indicate whether molecular dissociation or recombination of the decreasing fraction of atomic ions is the main source for the population of the 2^3P state.

First, the influence of self-absorption on the decay of lines terminating in the metastable 2^3S level was measured with a mirror technique.[40] This experiment was performed at a low pressure (0.3 Torr) in tube B. The discharge power was again chosen so that initial plasma densities above 10^{13} cm^{-3} were obtained. The 3889 Å (3^3P–2^3S) line was found to decay slower than the lines whose self-absorption was negligible. However, when corrected for the time-varying absorption the 3889 Å line followed exactly the decay of the other strong lines. In this experiment the decrease of the self-absorption from 68 to 56% (path length 14 cm) within 300 μsec led to an apparent increase of the decay-time constant of 20% over that of the other lines. The metastable density corresponding to the measured absorption was found to follow Eq. (11).

The conditions at higher pressures are represented by Fig. 3. Here the decay of three atomic lines (2^3S–2^3P, 2^3S–3^3P, 2^3P–4^3D) is compared with the band emission at 4650 Å, and with the emission of the spectrally integrated (3000–6000 Å) light. The high light level of the intense discharge allowed to monitor the 10 830 Å line late into the afterglow at the slit setting used (resolution$\approx$60 Å). The error bars at late times show the peak-to-peak photomultiplier noise. The readout accuracy was accordingly better than indicated by the bars. The 4472 Å line represents the majority of the lines with no self-absorption. The fast decay relative to the band emission is again caused by the conversion of atomic ions by the process (8) discussed above. As in Fig. 2, the electron density followed approximately the decay of the 4650 Å band. The gas temperature was around 1000 °K.

The setup with which the data of Fig. 3 were obtained (tube A) did not permit direct absorption measurements. However, the slow decay of the lines terminating in the 2^3S level at early times can again be explained if an initial self-absorption of more than 80% of 3889 Å line and more than 90% for the 10 830 Å line is assumed (pathlength 52 cm). These values compare well with the initial fractional absorption found in the low-pressure case if the difference in path lengths of the two setups is taken into account.[41] The larger difference between the slopes of the lines with self-absorption (10 830 and 3889 Å) on the one hand and without self-absorption (4472 Å) on the other hand in Fig. 3 indicates that, compared to the low-pressure case, the fractional absorption decreases much faster with time. This is expected from the fast conversion of atomic ions by the process (8). The corresponding fast decrease of the recombination rate of atomic ions, the source of 2^3S metastables, leads, according to Eq. (11), to a rapid decay of the density of atomic metastables. The similar time decay of the 3889 and 10 830 Å lines suggests

[38] R. C. Stabler, in *Ionization Phenomena in Gases*, edited by P. Hubert and E. Cremieu-Alcan (Paris, 1963), Vol. I, p. 449.
[39] L. Frommhold and M. A. Biondi, Bull. Am. Phys. Soc. **12**, 217 (1967).
[40] R. G. Buser and J. Kainz, J. Opt. Soc. Am. **55**, 12 (1965).
[41] A. C. G. Mitchell and M. W. Zemanski, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1954), p. 120.

absorption as the only cause for the slow initial time decay of these lines. The slight difference is to be attributed to the greater oscillator strength of the 2^3S–2^3P transition which causes a stronger absorption of the 10 830 Å line lasting to later afterglow times.

The similar initial decay rates of the 10 830 Å line (and also of the 3889 Å line) with that of the band emission cannot be taken as support for the assumption that molecular dissociation might be a source for the 2^3P states (and 3^3P states). At early times (<0.5 msec) the afterglow is dominated by atomic ions. This follows from the theoretical conversion rate of atomic ions into molecular ions according to Eq. (9), which agrees with the rate which can be deduced from the decay of lines (without self-absorption) relative to the electron density. The dominance of atomic ions in generating the afterglow at early times is also indicated by the fact that the 4472 Å line in Fig. 3 decays then with a similar rate as the total light. Except for the effect of the time-varying self-absorption, the 10 830 Å line should exhibit, at early times, the same time variation as the other atomic lines, since collisional-radiative recombination of He^+ should then be by far the most important populating mechanism of the 2^3P state.

If the dissociation of excited molecules resulting from the recombination of molecular ions should be primarily responsible for the population of the atomic 2^3P states then this would have to be expected for late times ($\gtrsim 1$ msec), when the recombination of He_2^+ is dominant (indicated by the similar decay of the 4650 Å band and the total light). However, Fig. 3 shows that then the 10 830 Å line (and the 3889 Å line), now unaffected by absorption, decays with the same fast rate as the other lines, and not with the rate of the molecular band emission. It can so be concluded that the 2^3P (and 3^3P) state is formed exclusively by the recombination of the small, decreasing fraction of atomic ions which are present even at late afterglow times.

This result contradicts Robertson and Collins's interpretation of afterglow experiments which were performed on a flowing-gas stationary afterglow discharge.[10,11] They found a similar decay of the 10 830 Å line and the 4650 Å band over a distance away from the ionizing source which corresponds to a short time period (60 to 170 μsec) in the early afterglow. The measurements revealed a self-absorption of 18% for the 10 830 Å line and 2% for the 3889 line, but the time variation of the absorption and its effect on the apparent decay of the line intensity was not discussed. However, if the line decay, as was apparently assumed, was unaffected by the time change of the absorption one would expect the 10 830 Å line to decay initially with the faster rate of the other atomic lines, since a certain time is required for the conversion of atomic ions into molecular ions. The fact that such a steeper initial decay does not show up in their data seems to indicate that time-varying absorption may have been important in their experiments, too.

4. CONCLUSIONS

The present experiments show that He_2^+ recombines by collisional-radiative recombination. The recombination rates are about equal to that of atomic ions. Dissociative processes are negligible. This result is particularly interesting since it was obtained at high gas temperatures where a considerable fraction of the molecular particles should be in vibrationally excited states. At temperatures above 2000 °K, a fraction of more than 5% of the population of the vibrationless ground state has to be expected in vibrational levels 0.5 eV above the $v=0$ state. In view of the high collisional population rate of the vibrational states[2] a dissociation even from weakly populated v levels could cause a substantial increase of the net recombination rate. Moreover, the resulting atoms in excited states should have an influence on the time decay of the lines originating from these states. Neither effect has been observed. This implies not only that the He_2 molecule does not possess purely repulsive states between ionization level and ground state, but also that the minima of all potential curves must have depths of not much less than of the order of 1 eV. This result agrees, for the $3p\sigma\ ^{1,3}\Sigma_g^+$ and $2\sigma\ ^{1,3}\Sigma_u^+$ levels, with experimental investigations of the He_2^+ band systems,[42] where discrete spectra for vibrational states as high as $v=4$ and $v=5$ have been observed. The present experiment also indicates that the Hornbeck-Molnar process must lead to vibrationally very highly excited molecular ions since the inverse process, dissociative recombination, does not play an important role at the high gas temperatures of this experiment. The data presented here confirm the results of Mulliken's theoretical work on the structure of the He_2 molecule[12,43]: In this model the potential curves of the higher Rydberg states ($n\geq 4$) possess deep minima because their dissociation asymptotes are located close to the ionization limit for the helium atom. The $n=3$ (and $4f\sigma$) states are rendered stable due to the existence of large, broad maxima in the potential curves.

ACKNOWLEDGMENTS

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[42] M. L. Ginter, J. Chem. Phys. **42**, 561 (1965).
[43] R. S. Mulliken, J. Am. Chem. Soc. **88**, 1849 (1966).