$$+[1 \rightleftarrows 2]|\varphi(\vec{r}_1\vec{r}_2)\rangle_{J=0} . \quad (16)$$

Combining all the results into a simple form it is found that nuclear motion corrections to the ^3P splittings can be expressed by modifying Eq. (15) to read

$$\begin{aligned} W_{J=0} &= W_p - 2C_e(1-3m/M) - 2C_Z(1-m/M) \\ &\quad - \tfrac{10}{3}D\,(1-3m/M) - 2C_{ZN}, \\ W_{J=1} &= W_p - C_e(1-3m/M) - C_Z(1-m/M) \\ &\quad + \tfrac{5}{3}D(1-3m/M) - C_{ZN}, \\ W_{J=2} &= W_p + C_e(1-3m/M) + C_Z(1-m/M) \\ &\quad - \tfrac{1}{3}D\,(1-3m/M) + C_{ZN}. \end{aligned} \quad (17)$$

C_{ZN} has been calculated numerically[6] using a 165-term Hylleraas wave function employing techniques similar to those of Ref. 5 with the result

$$C_{ZN} = -4.78236 \text{ MHz} . \quad (18)$$

Using this value of compute the splittings from Eq. (17) we find the nuclear-motion contributions

$$\begin{aligned} \Delta\nu_{01}(ZN) &= -10.707 \text{ MHz}, \\ \Delta\nu_{12}(ZN) &= +1.952 \text{ MHz}. \end{aligned} \quad (19)$$

It is clear that nuclear-motion corrections yield an important contribution to the splittings.

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Electron-Ion Recombination in Cryogenic Helium Plasmas*

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The electron-ion recombination coefficient measured in a cryogenic helium afterglow at a constant gas temperature of 4.2 °K at pressures between 0.075 and 1.25 Torr (neutral densities ranging from 1.7 to 28.7×10^{17} cm^{-3}) and at an electron temperature of 10 °K is $(40\pm6)\times10^{-6}$ cm^3 sec^{-1}. It varies with the electron temperature as $T_e^{-\chi}$, where $\chi=1\pm0.2$, and shows no dependence on electron density over the range we have covered from 5×10^8 to 2.5×10^{10} cm^{-3}.

I. INTRODUCTION

Goldan, Berlande, and Goldstein[1] were the first to note that the superimposition of a low-level microwave heating field on a cryogenic helium plasma results in a sudden important increase in its free-electron density. The electron density reverts very rapidly to its unperturbed value upon removal of the heating field. Subsequent analysis led Gerardo and Gusinow[2] to the conclusion that the behavior of a helium afterglow plasma near 77 °K is dominated by the presence of a large electron-source term; taking this term into account, they measured the electronic recombination coefficient of the dominant He_3^+ ion at a gas temperature near 77 °K.

Our observations in helium afterglow plasmas at a gas temperature of 4.2 °K are also consistent with the presence of a large electron-source term independent of the electron population. Our study of the electron-density dependence on low-power (a few tens of milliwatts) and on medium-power (a few watts) microwave heating fields enables us to deduce the electron-ion recombination coefficient in helium gas at electron temperatures between 10 and 200 °K. This recombination coefficient is independent of pressure and of electron density.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

The plasma was formed by a high-voltage (2–5 kV) moderate-current (20–100 mA) pulse of adjustable duration (5–100 μsec) in a cylindrical Pyrex tube having a diffusion length $\Lambda = 0.156$ cm (7.5 mm i.d., 45 cm long). High-purity helium gas provided by l'Air Liquide in 1-liter metal flasks was used; it was further purified by cataphoresis under a pressure of a few tens of Torr s during more than 24 h.[3] The whole experimental system in contact with ultrapure gases has typical ultrahigh vacuum performances[4]; the rate of rise of the pressure is lower than 10^{-12} liter Torr sec^{-1} after 24 h baking at 400 °C. Pressures are measured with a differential bellows manometer having a resolution of 5×10^{-3} Torr, together with a systematic error lower than 0.5% up to 200 Torr. The dimensions of the container and of the coupling tubes are such that pressure corrections due to thermomolecular effects at cryogenic temperatures are negligible.[5]

The plasma tube is enclosed inside a standard X-band waveguide used for diagnostics (inside dimensions, 2.286×1.016 cm^2). This assembly is itself contained inside a sealed cylinder filled with gaseous helium to ensure thermal contact with the walls. This cylinder fits inside a metallic Dewar filled with liquid helium for work around 4.2 °K. Temperature is measured at various points, and particularly on the external wall of the plasma tube, near the cathode and near the anode, by measuring the resistance of Speer radio-grade resistors calibrated at 77.1, 20.4, and 4.2 °K; intermediate temperatures are interpolated with an extension of the Clement-Quinnel formula.[5] In this work, the external temperature of the plasma tube was always between 4.2 and 4.3 °K, with or without plasma. The total power dissipated inside the plasma tube was kept low enough so as to have no visible effect on the liquid-helium boil-off rate (about 250 cm^3/h); doubling this power did not measurably affect the helium pressure inside the plasma tube, nor our experimental results. We thus estimate that the gas in which the plasma was created was in thermal equilibrium with the walls, i.e., at a temperature between 4.2 and 4.3 °K.

All the plasma diagnostics relevant to this work were made at X-band frequencies by using classical-interferometry techniques (see Fig. 1); we measure the phase shift and the attenuation of a low-power sensing microwave signal (1 μW at 8.77 GHz) by heterodyning at an intermediate frequency near 45 MHz.[6] We favor heterodyning over direct measurements because it gives a much better signal-to-noise ratio; furthermore, it is much easier to isolate the receiver from relatively high-level microwave heating pulses.

We have made a detailed computation of the relationship between the measured microwave parameters (phase shift and attenuation) and the corresponding plasma parameters (electron density n_e and collision frequency for momentum transfer ν). The solution for wave propagation was obtained in a partially filled waveguide by a variational method.[7] Parasitic reflections and losses due to the plasma container and to the plasma itself were taken into account as well as the corresponding distortion of the field lines. The propagation constant was nearly insensitive to the unknown radial-electron-density distribution under the present experimental conditions (small cylinder centered in a rectangular waveguide). At higher pressures, near 1 Torr at 4.2 °K, the collision frequency ν was not completely negligible compared to the angular frequency ω of the microwave field; we have taken this small correction into account, if and when necessary.

Basically, in this work, we follow by microwave diagnostics the response of the plasma to a microwave "heating" field which only affects directly the free electrons.[8] The frequency of the heating field was $f_h = 9250$ MHz. The power available to the plasma guide was known within 2%. The heating microwave was either pulsed (up to 10 W) or cw (up to 20 mW) or both simultaneously at independently adjustable levels.

Margenau has shown[9,10] that a microwave heating field at the angular frequency ω_h does not affect the Maxwellian character of the electron-energy distribution function provided $\nu^2/\omega_h^2 \ll 1$ when inelastic collisions are negligible. However, when a steady state is reached, the field raises the electron temperature by the value

$$\Delta T_e = \frac{M}{6k}\left(\frac{e}{m\omega_h}\right)^2 \langle E^2\rangle_{\rm av}, \tag{1}$$

where $\langle E^2\rangle_{\rm av}$ is the mean-square value of the electric field averaged over the plasma volume; k is Boltzmann's constant, e and m are the electron charge and mass, M is the mass of the neutral atoms; mks units are used throughout unless explicitly specified. This formula is valid when the thermal conductivity[11] of the plasma is high enough to ensure its thermal homogeneity, and when the sheath potential, which develops in the vicinity of the plasma boundary, is sufficient to greatly reduce electron-energy transport between the electron gas and the walls.[12] These conditions were largely met in this work.

We have related the mean-square electric field inside the plasma to its unperturbed value in a standard waveguide, taking into account the distortion of field lines due to the plasma and to its container.[6,7] This results in the following practical formula when ν^2/ω_h^2 is negligible:

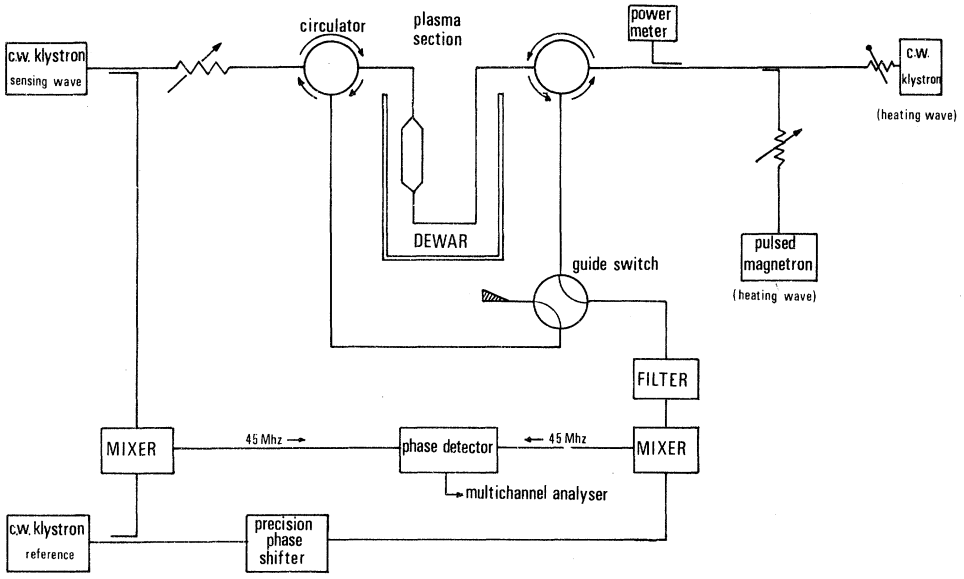

FIG. 1. Experimental apparatus.

$$\Delta T_e = C\,\frac{M}{6k}\left(\frac{e}{m\omega_h}\right)^2\,\frac{120\pi}{ab}\,\frac{\lambda_g}{\lambda_v}\,P_i\,, \qquad (2)$$

where P_i is the incident available power, λ_v and λ_g are the wavelengths corresponding to the angular frequency ω, respectively, *in vacuo* and in the perturbed waveguide, and where a and b are the inside dimensions of the guide. The explicit form of the correction factor C has been given elsewhere.[7] It depends on the glass permittivity and on the inside and the outside radii of the glass tube. It is equal to unity when the effect of the glass tube is neglected, but it is equal to 0.65 under our experimental conditions.

Validity of Eq. (2) was checked under a broad range of experimental conditions; steady-state electron-temperature increases measured by radiometry[13] or inferred from collision-frequency measurements are always in good agreement with their theoretical value. It should also be noted that the electron temperature very rapidly reaches its steady state after rapid application or removal of the heating microwave field, owing to the high values of the collision frequency in low-temperature helium; the corresponding time constant is less than 5 μsec in the worst case pertaining to this work ($p = 0.075$ Torr, $\Delta T_e = 100\,^\circ$K).

All our measurements were obtained by multichannel sampling with a 1-μsec time resolution, followed by phase-locked synchronous digital integration on 512 consecutive afterglows. The time between each consecutive afterglow was usually about 0.14 sec. The measured values for each channel at the end of each run were printed for manual analysis and were also punched on paper tape for digital treatment by a minicomputer. The over-all performance and stability of our experimental apparatus is illustrated by the excellent reproducibility of results over months.

III. QUALITATIVE DESCRIPTION OF PLASMA AT CRYOGENIC TEMPERATURES

Many authors have described the distinctive features of cryogenic afterglow plasmas either near liquid-nitrogen temperature (77 °K)[2,14-16] or near liquid-helium temperature (4.2 °K).[1,14] These plasmas are characterized (Fig. 2) by a very slow decay of the electron density n_e; this decay does not seem to be diffusion controlled, since it is quite nonlinear in a semilogarithmic plot. On the

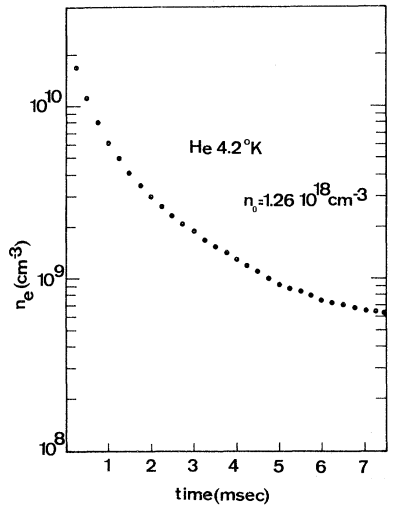

FIG. 2. Experimental semilog plot of n_e vs time at a gas pressure of 0.55 Torr at 4.2 °K.

other hand, a plot of $1/n_e$ as a function of time is reasonably linear. It is thus tempting to conclude that the plasma is recombination dominated, and to deduce from the slope of the $1/n_e$ plot vs time[17] a recombination coefficient α close to 10^{-7} cm^3 sec^{-1} for a helium plasma near liquid-helium temperature. This was done recently by Fugol *et al.*[14]

However, this conclusion is difficult to reconcile with the well-documented fact[1,2,15] that a very moderate pulsed microwave heating of the free electrons of the plasma—a few tens of °K—produces a strong electron-density enhancement; the electron density returns to its unperturbed state immediately after removal of the heating pulse. The transitions from the normal to the perturbed state and back to normal take place quite rapidly [Fig. 3(a)]. This observation, together with a simultaneous study of the recombination light-intensity variations associated with the heating pulse, led Kaplafka *et al.*[15] to the logical conclusion that an unidentified electron-source term was playing a major role in cryogenic afterglows. After a more detailed study, Gerardo and Gusinow[2] concluded that the experimental observations near 77 °K were entirely consistent with the existence of a slowly varying electron source in the afterglow, apparently independent of electron temperature and density, almost exactly balancing the loss of electrons by recombination (diffusion losses are usually negligible at low temperatures, even with a short diffusion length). They ascribed this source term to the presence of a large population of atomic and/or molecular metastable, slowly decaying with time through mutual collisions, producing electron-ion pairs,[18] and they also showed that measurements of the amplitude of the electron-density pulse, as well of its rise and fall times, yield values of the electron-ion recombination coefficient.

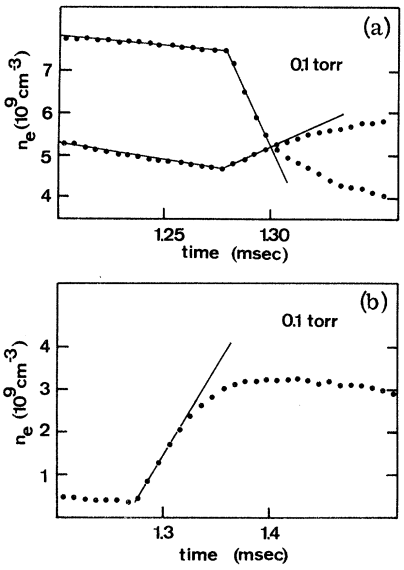

FIG. 3. Variation of the electron density with microwave heating. (a) Rise of the electron density when a low-power microwave field (a few tens of milliwatts) is incident on the plasma at 1.28 msec in the afterglow, and fall of the electron density when the pulse is terminated at 1.28 msec. (b) Rise of the electron density when a medium-power microwave pulse (a few watts) is terminated at 1.28 msec in the afterglow.

Our observations at liquid-helium temperature are qualitatively very similar to those of Gerardo and Gusinow over the pressure range we have covered, and are equally consistent with the presence of a slowly varying electron-source term in the afterglow. This leads to the following equation for the electron density n_e in the presence of a dominant ion species of density $n_i \cong n_e$:

$$\frac{dn_e}{dt} = -\alpha(T_e)n_e^2 + S(t) , \tag{3}$$

where $S(t)$ is the electron-source term; the electron-ion recombination coefficient is noted $\alpha(T_e)$ to underline its strong inverse dependence on electron temperature. It is easy to see from this equation that the electron density to first order tends to adjust itself so that $\alpha(T_e)n_e^2 \cong S(t)$; when the heating pulse raises the electron temperature, the corresponding decrease in the recombination coefficient is compensated by an increase in electron density which maintains the balance between production and losses. Defining the steady-state electron densities at time t, n_{eh}, and n_{eo}, respectively, with and without heating, $\dot{n}_{eh}$ and $\dot{n}_{eo}$ the corresponding slopes, and $\dot{n}_{er}$ and $\dot{n}_{ef}$ the initial slopes of the rising edge and of the falling edge of the electron-density pulse, also at time t, Eq. (3) yields the following values[2] for the recombination coefficients α at the unperturbed electron temperature T_e and at the electron temperature perturbed by microwave heating, $T_e + \Delta T_e$:

$$\alpha(T_e)n_{eo}^2 - \alpha(T_e + \Delta T_e)n_{eo}^2 = \dot{n}_{er} - \dot{n}_{eo} , \tag{4}$$

$$\alpha(T_e) = (\dot{n}_{eo} - \dot{n}_{ef})/(n_{eh}^2 - n_{eo}^2) , \tag{5}$$

$$\alpha(T_e + \Delta T_e) = (\dot{n}_{er} - \dot{n}_{eh})/(n_{eh}^2 - n_{eo}^2) . \tag{6}$$

In practice, the value of the couple $\alpha(T_e)$, $\alpha(T_e + \Delta T_e)$ is chosen as the best fit to these three simultaneous equations in order to minimize the effect of experimental noise.

We have devised another independent method of measurement of $\alpha(T_e)$. At neutral densities lower than about 7×10^{17} cm^{-3} (0.3 Torr at 4.2 °K), it is possible to raise the average electron energy to a sufficiently high value for ambipolar diffusion (which is linearly proportional to T_e) to become the dominant loss term during the heating pulse,

while still keeping inelastic electron-metastable collisions to a negligible level. This corresponds to electron temperatures between 5000 and 10 000 °K. When this microwave heating pulse is of sufficiently short duration, it has no measurable effect on the electron source term.[19] Immediately upon termination of this pulse, the source term causes the electron density to rise steeply at first towards its unperturbed value, since the electron density is initially very low; this makes the recombination term negligible in Eq. (3). The initial slope of the electron density is thus a direct measure of the source term $S(t)$ [Fig. 3(b)]. As the electron density rises, the recombination term becomes more and more important, up to the point where it is exactly balanced by the source term. It is thus sufficient to measure the source term $S(t)$ and the subsequent maximum electron density $n_{e(\max)}$ right after cessation of the high-power heating pulse to get an independent evaluation of the recombination coefficient

$$\alpha(T_e) = S(t)/n_{e(\max)}^2 , \tag{7}$$

where $S(t)$ and $n_{e(\max)}$ are measured at the same time in the afterglow. If our plasma model is consistent, recombination coefficients $\alpha(T_e)$ derived from Eq. (7) and from Eqs. (4)–(6) should agree within experimental error bars. Figure 4 shows that there is indeed a very satisfactory agreement.

The apparently continuous increase of the recombination coefficient with time is a general feature of afterglow plasmas in helium near 4.2 °K in the range of densities we have covered. We interpret this phenomenon as being due to the very slow relaxation of the electron-gas temperature towards neutral temperature. The corresponding heating effect is most probably due to the electron source term, which does not directly produce thermalized electrons; metastable-metastable collisions, depending upon whether they involve atomic or molecular states, produce electrons with an average kinetic energy of 15 or 9 eV.[20] Most of the energy of these electrons is directly released to the neutral gas,[21] but a small fraction ends up as an added energy of the electron gas. Although small, this effect is definitely not negligible in cryogenic plasmas where the neutral temperature is 4.2 °K. We have deduced the electron temperature from the electron-neutral collision frequency, assuming a nearly temperature-independent electron-neutral collision cross section[22]; such measurements show indeed the average electron energy to decay very slowly during the afterglow (Fig. 5); it does not fall below about 10 °K in the afterglow region with which we are concerned in this work. We shall see in Sec. IV how we have dealt with this fact.

The hypothesis that the source term $S(t)$ is independent of perturbations to the electron population plays a basic role in the methods of measurement outlined above. In fact, this might not be always true: Experimental evidence shows that there may be a small reaction of the electron density on the source term since electron-ion recombination may have a finite probability of giving as an "almost final" product molecular and/or atomic metastable states.[19,23,24] However, this effect has a negligible influence on the measurements reported in this paper. This is experimentally confirmed by the fact that there is no variation in our experimental results with substantial changes of the length of the heating pulse.

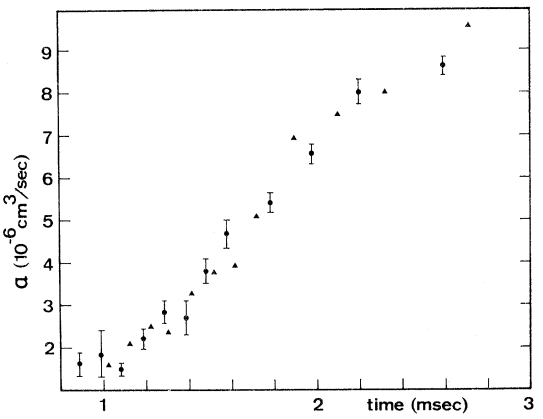

FIG. 4. Variation of the recombination coefficient with time in the afterglow at 0.1 Torr, 4.2 °K. Dots, deduced from low-level microwave heating through Eqs. (4) – (6). Triangles, deduced from medium-power heating through Eq. (7).

IV. DISCUSSIONS OF EXPERIMENTAL RESULTS

The recombination-coefficient measurements reported in the remaining part of this paper were always deduced from the shape of the electron-density pulse associated with low-power pulsed heating of the electron gas (40 mW at $f_h = 9.25$ GHz, corresponding to a differential heating $\Delta T_e = 125$ °K; measurements have also been made at other pulsed-power levels, with no detectable effect on results). Whenever possible, these values have been compared with recombination coefficients deduced from a direct measurement of the source term through the use of relation (7). The agreement was always satisfactory (Fig. 4). The duration of the heating pulse was varied from 0.2 to 1 msec, depending on experimental conditions. The measured recombination coefficient was independent of this duration, provided a steady state was reached (this is necessary for measuring n_{eh}).

Recombination-coefficient measurements correlated with electron temperatures deduced from electron-neutral collision-frequency measurements

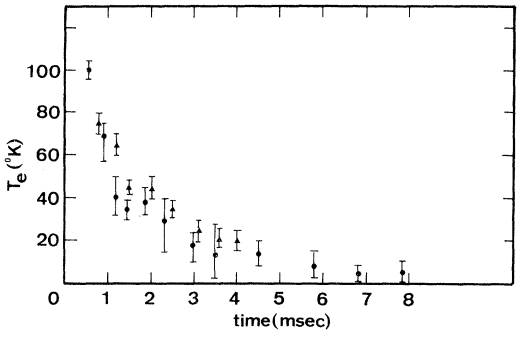

FIG. 5. Plot of electron temperature vs time (0.55 Torr, 4.2 °K) deduced from electron-neutral collision-frequency measurements (triangles) and from recombination coefficients (dots, see text and Figs. 6 and 7).

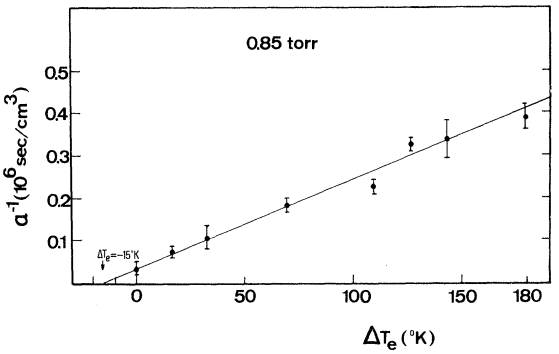

FIG. 6. Experimental values of α^{-1} as a function of ΔT_e.

indicated that α had roughly a $T_e^{-\chi}$ dependence with $\chi \cong 1$. To ensure a precise and self-consistent determination of the electron-temperature dependence of the recombination coefficient at a constant gas temperature of 4.2 °K, the plasma was also submitted to a continuous heating wave adjustable between 0 and 25 mW at the same frequency f_h, corresponding to electron-temperature variations from 0 to 80 °K. A combination of these two heating waves (cw and pulsed) thus enabled, at any given time in the afterglow, measurements of the recombination coefficient at continuously variable electron temperatures from the unperturbed value T_{eo} to a maximum value $T_{eo}+205$ °K.

Experimental plots of α^{-1} as a function of the total-electron temperature increase ΔT_e (Fig. 6) always fell very near straight lines of constant slope under our experimental conditions (neutral densities between 1.7 and 28.7×10^{17} cm^{-3}, time in the afterglow between 600 μsec and 15 msec, and electron densities between 2.5×10^{10} and 5×10^{8} cm^{-3}). The unperturbed electron temperatures were inferred from the abscissa of the interaction of these straight lines with the ΔT_e axis; they were in satisfactory agreement with the values deduced from electron-neutral collision-frequency measurements (Fig. 5). These observations are consistent with $\chi \cong 1$.

After determination of the absolute unperturbed electron temperatures, we made systematic plots in log-log coordinates of the experimental values of α vs T_e. These plots do not show any measurable variation with neutral or with electron density within error bars in the broad experimental domain we have covered (20/1 variations in neutral density and 50/1 variations in electron density). Figure 7 shows a few points at two pressures; all our experimental values fell very near the straight line of slope minus one corresponding to $\chi = 1$. Their scatter is typical of the random distribution of our experimental points around their average value. The lines of slopes -0.9 and -1.1 are also shown for reference.

Figure 8 gives the average value of the electron-ion recombination coefficient at a gas temperature of 4.2 °K and at an electron temperature of 10 °K, as deduced from log/log plots of α vs T_e analogous to those of Fig. 7 for various gas pressures. There is no significant pressure dependence over the whole experimental range.

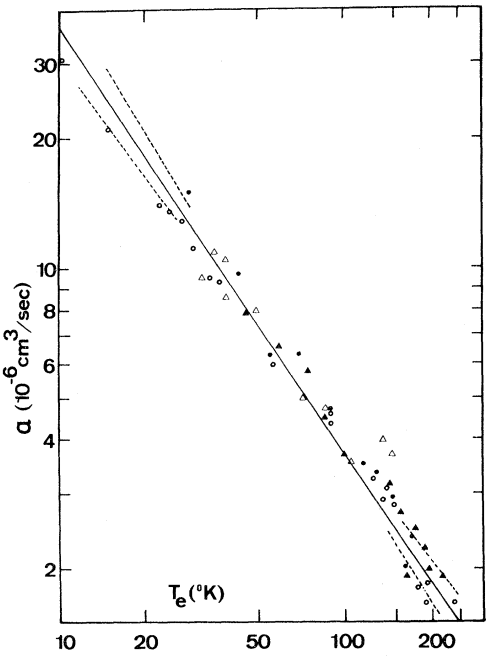

FIG. 7. Experimental log-log plot of α as a function of T_e; we have shown a small fraction of our results which we consider typical of the average scatter of the experimental points. Circles, 0.55 Torr; triangles, 0.18 Torr. Closed symbols are with heating, open symbols without heating.

This evidence suggests that the electron-ion recombination coefficient has the average value $\langle \alpha \rangle = 40 \times 10^{-6}$ cm^3 sec^{-1} at $T_e = 10$ °K, and that the electron-temperature dependence of this coefficient is $T_e^{-\chi}$, the exponent χ having the average value $\langle \chi \rangle = 1$ between $T_e = 10$ °K and $T_e = 200$ °K.

The main systematic errors on these measurements are related to systematic errors on the electron density n_e and on the electron temperature increase ΔT_e. These errors have been discussed elsewhere[7]; we estimate their total contribution to be no higher than 2% on n_e and 10% on ΔT_e. In view of these possible systematic errors and of the experimental scatter of the data, we estimate the total uncertainty on the measured recombination coefficient and on its electron-temperature dependence to be ±15% and ±20%, respectively.

V. CONCLUSION

The effective electron-ion recombination coefficient measured in a cryogenic helium afterglow at a constant gas temperature of 4.2 °K at neutral densities betwen 1.7 and 28.7×10^{17} cm^{-3} (pressures between 0.075 and 1.25 Torr at 4.2 °K) and at an electron temperature of 10 °K is $(40 \pm 6) \times 10^{-6}$ cm^3 sec^{-1}. It varies with the electron temperature as $T_e^{-\chi}$, with $\chi = 1 \pm 0.2$. The fact that the measured recombination coefficient is independent of pressure or of the time in the afterglow suggests that the dominant ion remains the same in all cases, or, alternatively, if there is ion conversion, that the recombination coefficients of the initial and of the final ions are very nearly the same. We have not yet attempted mass identification of the molecular ions present in an afterglow at 4.2 °K. He_3^+ [25] and He_4^+ seem the most likely candidates. They have both been identified in helium near 300 °K[23,26] and near 77 °K.[16,27] It is generally accepted that the He_3^+ ion is dominant near 77 °K. A lower He_4^+/He_3^+ density ratio has been measured[16] at 76 than at 300 °K under similar experimental conditions; following Gerber and Gusinow, one possible reason for this behavior would be the presence of an activation energy in some stage of the kinetic of He_4^+ formation. It is thus perhaps not unreasonable to expect a still lower He_4^+/He_3^+ density ratio at 4.2 than at 76 °K.

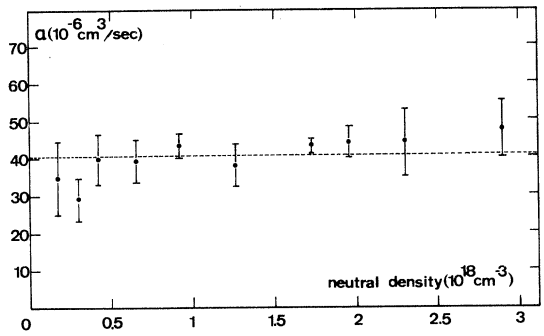

FIG. 8. Plot of the recombination coefficient at $T_e = 10$ °K and $T_0 = 4.2$ °K as a function of neutral density.

It is also to be noted that our measurements yield for the recombination coefficient at $T_0 = 4.2$ °K and $T_e = 80$ °K the value $(5 \pm 0.75) \times 10^{-6}$ cm^3 sec^{-1}, to be compared to the value $(3.4 \pm 1.4) \times 10^{-6}$ cm^3 sec^{-1} measured by Gerardo and Gusinow at $T_0 = T_e = 80$ °K. These two values are consistent within error bars. The same may be said for the values of the exponent χ describing the temperature dependence of the recombination coefficient. This would seem to indicate that recombination takes place on the same dominant ion (i.e., He_3^+) at gas temperatures of 4.2 and of 77 °K, and that the processes involved are the same.

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Composition Dependence of Ion Diffusion Coefficients in Gas Mixtures at Arbitrary Field Strengths*

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Expressions for the diffusion coefficient of ions in gas mixtures are obtained from momentum-transfer theory, and are given in terms of the diffusion coefficients and drift velocities of the ions in the pure component gases. Blanc's law holds exactly at all field strengths if the mean free time between collisions is independent of velocity (Maxwell model), but otherwise there may be either positive or negative deviations from Blanc's law at high fields. Such deviations are of comparable magnitude for the diffusion coefficients and the mobility, but are not identical. Specific cases of inverse-power potentials are treated in further detail, and some numerical examples are given for rigid-sphere interactions.

I. INTRODUCTION

The diffusion coefficients of ions in gases are proportional to their mobilities at low electric field strengths, but at high fields the proportionality breaks down and the diffusion coefficients usually increase more rapidly than the mobilities.[1] Moreover, the diffusion coefficient becomes anisotropic at high fields, the rates of diffusion parallel and perpendicular to the field direction being different. The purpose of this paper is to find an expression for the composition dependence of ion diffusion coefficients in gas mixtures at arbitrary field strengths in terms of the diffusion coefficients in the pure component gases. Although no data at present exist, measurements in mixtures introduce no new experimental difficulties, and the present work predicts interesting effects.

Since we seek only a composition dependence, we can use a simple momentum-transfer method used previously for finding the composition dependence of the ion mobility.[2] As a side result we make explicit a hidden assumption in the previous work, namely that the dependence of the momentum-transfer cross section on the drift velocity itself could be ignored. This has a distinct effect on the deviations from Blanc's law predicted for high fields.

At low fields, the analog of Blanc's law for ion mobilities holds to first order in the Chapman-Enskog approximation,

$$1/D = \sum_j (x_j/D_j) , \tag{1}$$

where D is the diffusion coefficient of the ion in the mixture, the x_j are mole fractions, and the D_j are the diffusion coefficients of the ion in the pure component gases at a number density the same as the total number density of the mixture. Higher Chapman-Enskog approximations yield only positive deviations from Blanc's law, but these are usually small.[3] For high fields we find that appreciable deviations from this linear rule can occur, and that the deviations are sensitive to the form of the ion-neutral interaction.

II. MOMENTUM-TRANSFER THEORY

The basic idea in a momentum-transfer calculation is that the momentum given to the ions by external forces must be balanced by the momentum the ions transfer to the neutral molecules by collisions, since the ions are not accelerated on the average. For mobility, the external force is obviously supplied by the electric field. For diffusion, the external force is regarded as coming from the gradient of partial pressure of the diffusing species.[4]