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Electron–ion recombination in gas mixtures of helium, nitrogen, and carbon dioxide

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A study has been conducted to determine the electron–ion recombination rates in gas mixtures of helium, nitrogen, and carbon dioxide. Measurements were made as functions of electric field strength, gas pressure, and gas composition. In gas mixtures containing only nitrogen and carbon dioxide, the rates were dependent on pressure. This dependence is interpreted as being due to the separate effects of two- and three-body recombination processes. No pressure dependence was observed for mixtures containing helium. In such mixtures, two-body recombination appears to be dominant. Moreover the addition of relatively low concentrations of helium to the discharge leads to a dramatic change in the bulk recombination rate. Two possible explanations for this observation are suggested.

INTRODUCTION

Although volume electron–ion recombination represents the dominant electron loss mechanism in high-pressure, high-current gas discharges,[1] it is the least well documented of electron transport properties in discharge plasmas. To offset this neglect, we have measured the electron–ion recombination rates in carbon dioxide laser gas mixtures in terms of reduced electric fields (E/N), gas pressures, and gas mixtures.

The electron–ion recombination rate in pure carbon dioxide was measured under field-free conditions by Maier and Fessender[2] and by Warman *et al.*[3] and under discharge conditions by Littlewood *et al.*[4] In all three experiments, the investigators observed that the electron–ion recombination rate was dependent on the gas pressure. They interpreted this dependence as being due to the separate effects of two- and three-body processes:

$$CO_2^+ + e \rightarrow \text{neutral products} \tag{1}$$

and

$$CO_2^+ + CO_2 + e \rightarrow \text{neutral products} \tag{2}$$

with rate constants γ_2 and γ_3, respectively. They could then express the rate loss of electrons (density n_e) by recombination as

$$(dn_e/dt)_R = -\gamma n_e^2 \tag{3a}$$

$$= -(\gamma_2 + \gamma_3 N_{CO_2}) n_e^2 \tag{3b}$$

in which N_{CO_2} is the number density of carbon dioxide molecules, and the electron and ion densities are assumed to be equal.

In calculating the electron transport properties in gas mixtures of helium, carbon dioxide, and nitrogen, Lowke *et al.*[5] assumed a recombination rate constant of 10^{-7} cm^3 s^{-1} independent of all discharge parameters. Fenstermacher *et al.*[1] estimated a similar rate constant from their measurements of the electrical characterization of carbon dioxide laser gas discharges. Mills[6] showed, however, that the rate constant, rather than being independent of the discharge parameters, decreases monotonically with an increase in the electric field (E/N).

More recently, Homann *et al.*[7] and Nundy *et al.*[8] measured the electron–ion recombination rate in a single gas mixture, He:CO_2:N_2, 8:1:1. In their experiments, they monitored the voltage and current waveforms from short-pulse (duration less than 1 μs), self-sustained discharges. They then calculated the instantaneous electric field from the time-dependent voltage but did not make any corrections for the cathode fall voltage. They measured the effective recombination rate at a single gas pressure and did not investigate the pressure dependence of the recombination rate [Eq. (3b)].

EXPERIMENTS

For our investigation, we adopted the experimental technique used by Douglas-Hamilton[9] to measure the electron–ion recombination rate in pure nitrogen. By obtaining the data from a long pulse (100 μs), quasi-cw, e-beam sustained discharge, we avoided the major difficulties associated with fast discharges and were able to correct for the cathode fall voltage easily.

We placed the gas sample in a stainless steel discharge chamber, which we could evacuate to a background pressure of less than 10^{-6} Torr. Because the stated purities of the gases used were He:99.9999%, N_2: 99.999%, and CO_2: 99.99%, we made no attempt to purify them further, but changed the samples periodically to preserve their stated purity. In all cases, the gas temperature was 293 °K.

We initiated the discharge in a gas sample by irradiating it with a pulsed electron beam (Fig. 1) and supplied the electron beam voltage from a four stage Marx bank. During the experiments, we found that the results were not dependent on the Marx bank voltage. We obtained all the results by using an e-beam voltage of 120 kV with a pulse duration in excess of 100 μs. The electrons were emitted from a thoriated tungsten filament, which we could heat by using a current in excess of 20 A before we applied the high voltage pulse. The electrons accelerated under the influence of the applied voltage towards a thin (0.008 in.) titanium foil. After passing through the foil, they deposited their energy in the gas and created secondary electrons in the process. We applied a variable discharge voltage to a circular 7 in. diameter anode

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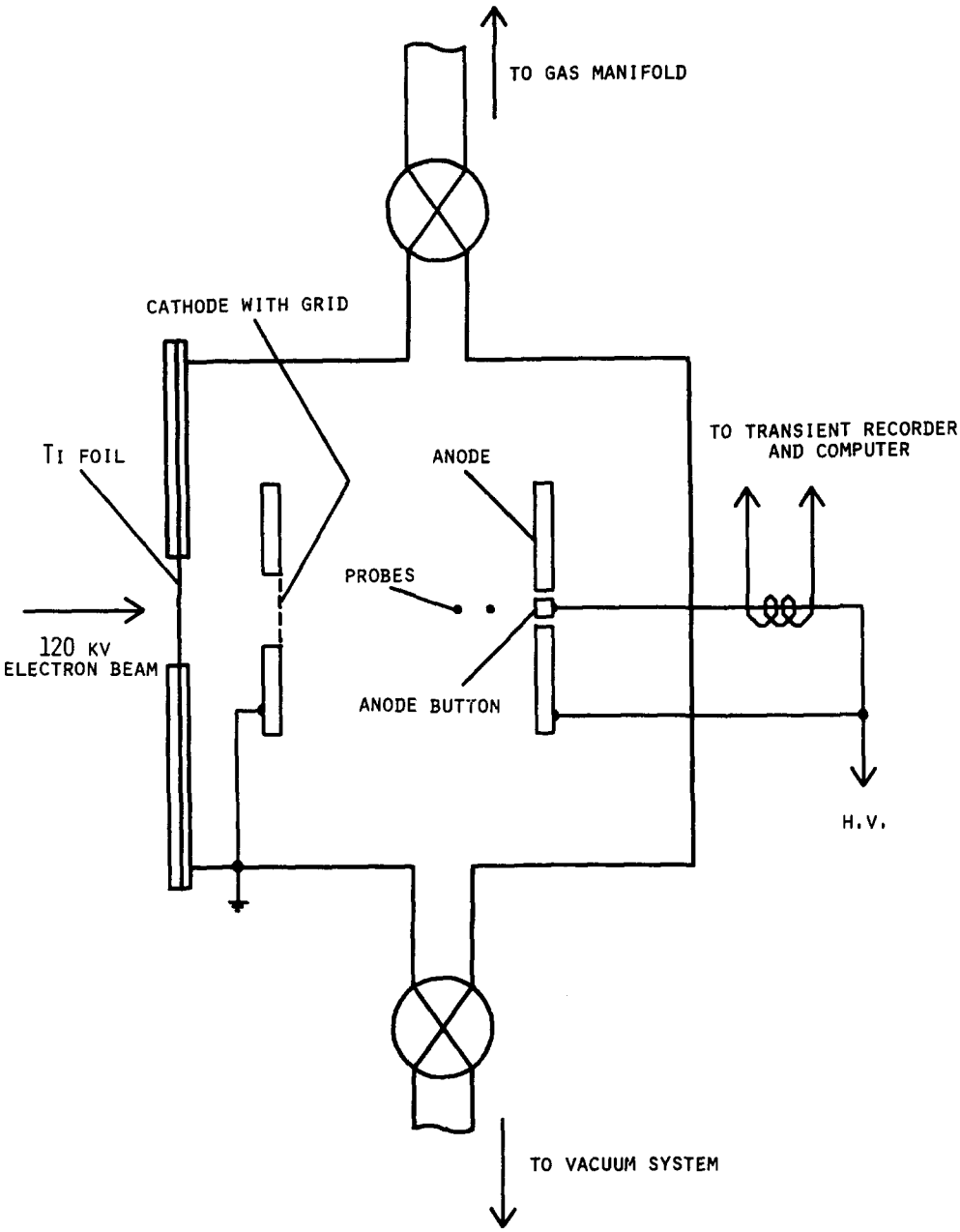

FIG. 1. Schematic of the experimental apparatus.

located up to 25 mm from a grounded cathode, and used a Pearson coil (model 4100) to measure that portion of the current that was collected by a central button 5.65 cm^2 in area and isolated from the rest of the anode except for external connections. By avoiding the edge effects in the spatial distribution of the discharge current, we could infer a reliable current density. We attenuated the output of the coil and fed it to an AEL 9300 transient recorder with a 10 ns resolution. This can be compared with a current risetime of approximately 10 μs. Our measurements of the anode current with and without gas in the discharge cell indicated that the beam current was less than 0.1% of the total discharge current.

We determined the electric field in the discharge by mounting probe wires across the discharge volume.[10] Thus, we could make corrections for the anode and cathode fall voltages. In practice, we found the anode fall voltage to be negligible and used the applied anode voltage to calculate the electric field. In contrast, the cathode fall voltage was quite significant and was generally of the order of 10% to 20% of the applied voltage.

By neglecting the beam–electron density in comparison with the plasma–electron density, we were able to represent the discharge electron density by using the differential equation

$$(dn_e/dt) = S - (\beta - \alpha)\, n_e - \gamma n_e^2 , \tag{4}$$

in which S is the source term resulting from ionization of the gas by the electron beam, β the electron attachment rate, α the ionization rate, and γ the electron–ion recombination

rate. We could also extract the recombination rate by using the following meausrements:

(1) The initial slope of the rising edge of the current waveform gives the source term S as

$$S = (dn_e/dt)_{n_e = t = 0} \cdot \tag{5}$$

(2) After the discharge attained the steady state condition, the electron density reached its constant peak value n_{e0} so that

$$(dn_e/dt)_{n_{e0}} = S - (\beta - \alpha)n_{e0} - \gamma n_{e0}^2 = 0 \tag{6}$$

from which

$$\gamma = \frac{S/n_{e0} - (\beta - \alpha)}{n_{e0}} \cdot \tag{7}$$

We could obtain the electron density in the discharge at any time from the current relationship of

$$J = n_e e W \tag{8}$$

in which e is the electronic charge and W the electron drift velocity. We took the electron drift velocity, attachment rate, and ionization rate from a Boltzmann code calculation.[11] In practice, both β and α are negligible in comparison with S/n_{e0} and have no appreciable effect in the calculations of γ.

RESULTS AND DISCUSSION

In our study, we measured the recombination rate for two separate mixtures of nitrogen and carbon dioxide and for five mixtures containing helium. In all cases, we made the measurements over a wide range of gas pressures and electric field strengths. The highest achievable electric field strength was limited by our ability to maintain spatially uniform discharges. Once a discharge became unstable, the current constricted to a narrow channel of undefined area, and we could not obtain meaningful results. The highest pressures were limited by the ability of the titanium foil to maintain the pressure differential between the gas cell and the e-beam chamber without rupturing, particularly during the intense heating occasioned by the deposition of part of the electron beam energy in the foil.

MIXTURES OF NITROGEN AND CARBON DIOXIDE

Figures 2 and 5 show the measured recombination rates in the He:CO_2:N_2, 0:4:1 and 0:1:1 mixtures, respectively. In both cases, the measured recombination rates were lower than that previously measured in pure carbon dioxide[4] but were in qualitative agreement with the much lower recombination rate for nitrogen.[9]

It is evident that the measured electron–ion recombination rate is dependent on the gas pressure, just as it is for pure carbon dioxide.[4] Figure 3 shows a plot of the recombination rate in the 0:4:1 mixture as a function of total pressure for four different electric field strengths. Each point is the average of many individual measurements. It is apparent that the recombination rate is linearly proportional to the pressure. We interpret this result as being due to the effects of two- and three-body processes similar to reactions (1) and (2). We obtained a similar set of curves for the 0:1:1 mixture and were able to resolve the two- and three-body rates for each mix-

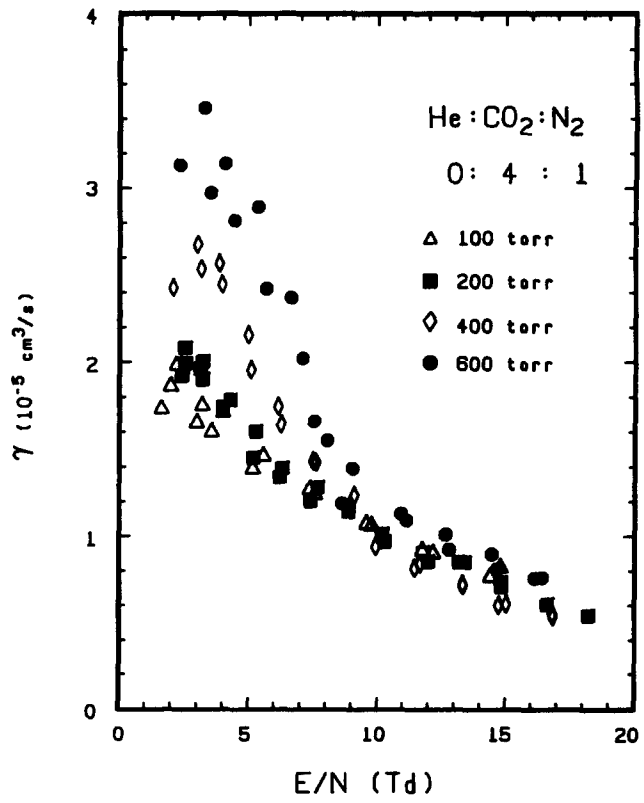

FIG. 2. Recombination rates in the He:CO_2:N_2 0:4:1 mixture.

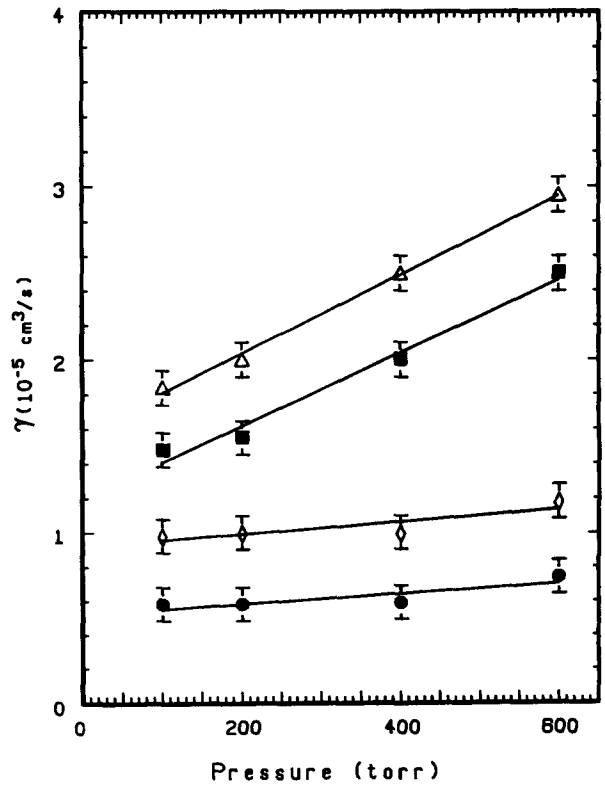

FIG. 3. Pressure dependence of the recombination rate in the He:CO_2:N_2 0:4:1 mixture. (△ 3 Td, ■ 5 Td, ◇ 10 Td, ● 13 Td.)

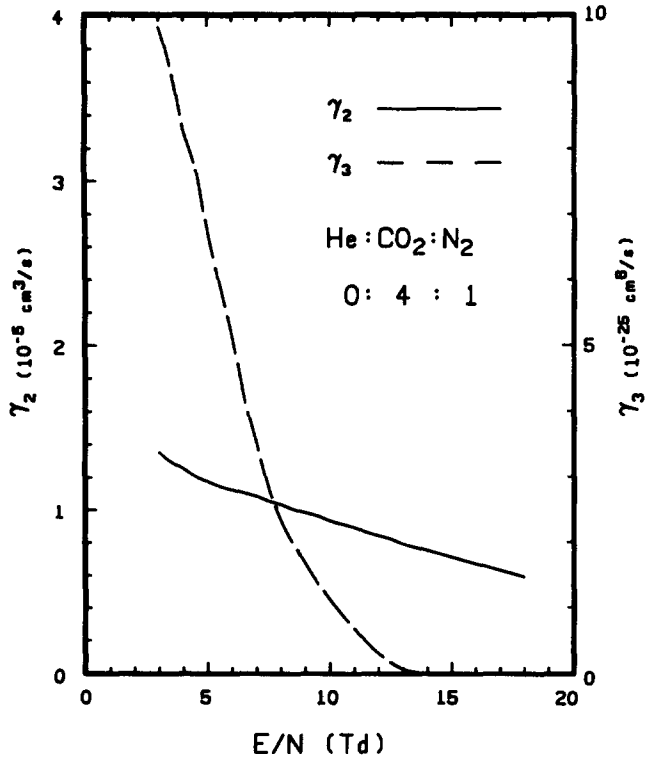

FIG. 4. Two- and three-body recombination rates in the He:CO_2:N_2 0:4:1 mixture.

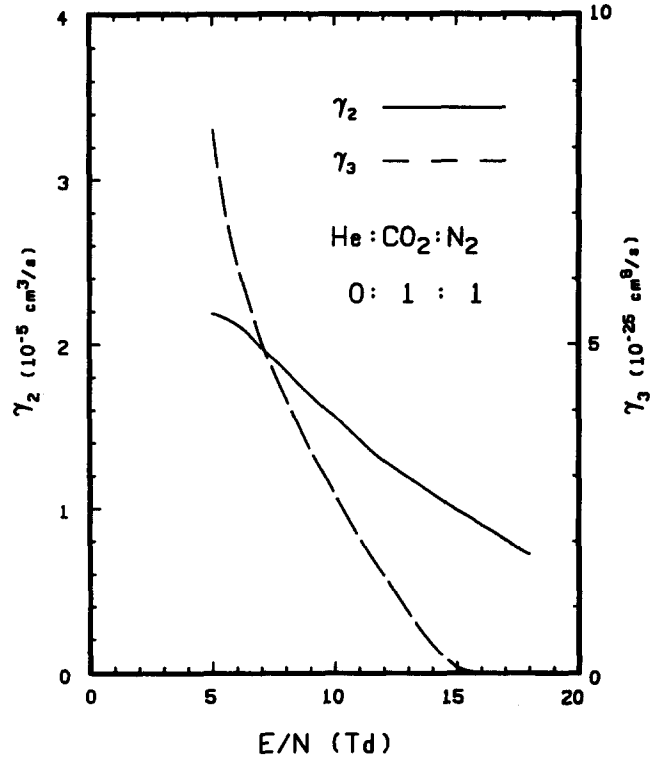

FIG. 6. Two- and three-body recombination rates in the He:CO_2:N_2 0:1:1 mixture.

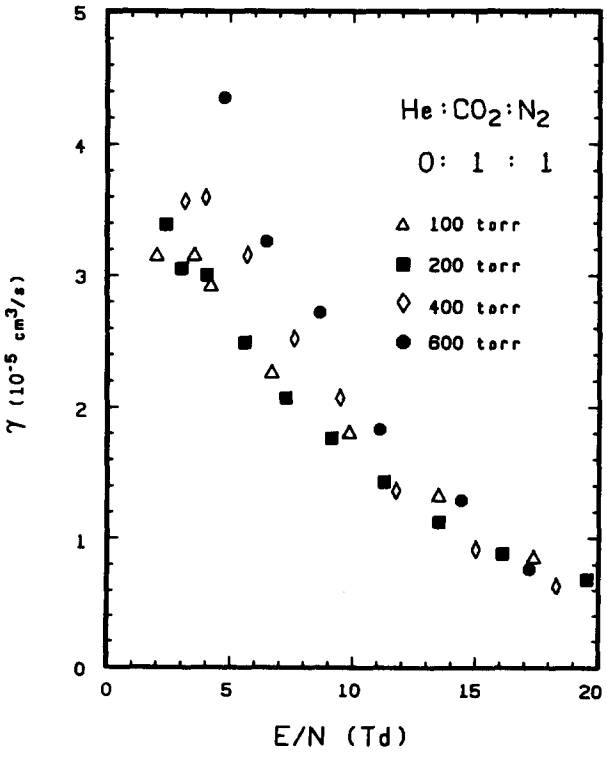

FIG. 5. Recombination rates in the He:CO_2:N_2 0:1:1 mixture.

ture from the intercept and slope of the curves, which are shown in Figs. 4 and 6.

MIXTURES OF HELIUM, NITROGEN, AND CARBON DIOXIDE

The recombination rates for the five gas mixtures containing He, N_2, and CO_2 are shown in Figs. 7 through 11. In contrast to the results we obtained for the mixtures of carbon dioxide and nitrogen, the recombination rates for the ternary mixtures show no pressure dependence up to the highest pressures studied. Such a result indicates that only two-body recombination is important at these pressures in ternary mixtures.

It might be expected that the dilution of the $CO_2 + N_2$ concentration by helium would lead to a reduction in the overall recombination rate. However in some cases the $CO_2 + N_2$ concentration remains high enough that a complete absence of a pressure dependence would not be expected. For example in the He:CO_2:N_2 1:1:1 mixture at 600 Torr total pressure, the combined CO_2 and N_2 partial pressure is 400 Torr, high enough for a significant three-body contribution to be observed at low E/N (see Fig. 5). It follows that the bulk properties are not simple functions of the individual partial pressures. Instead we suggest that the absence of three-body recombination similar to reaction (2) may result from the ineffectiveness of helium, a monatomic gas, as a three-body partner.

The data presented in Figs. 7 through 11 show that the addition of helium or nitrogen to the discharge significantly lowers the electron–ion recombination rate. The results are summarized in Fig. 12 in which we have plotted the recombination rate as a function of the helium percentage for fixed

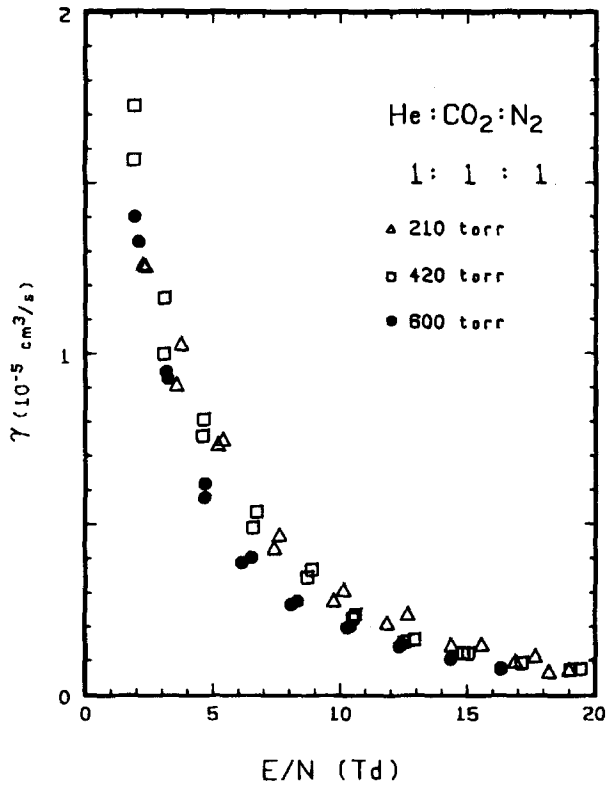

FIG. 7. Recombination rates in the $He:CO_2:N_2$ 1:1:1 mixture.

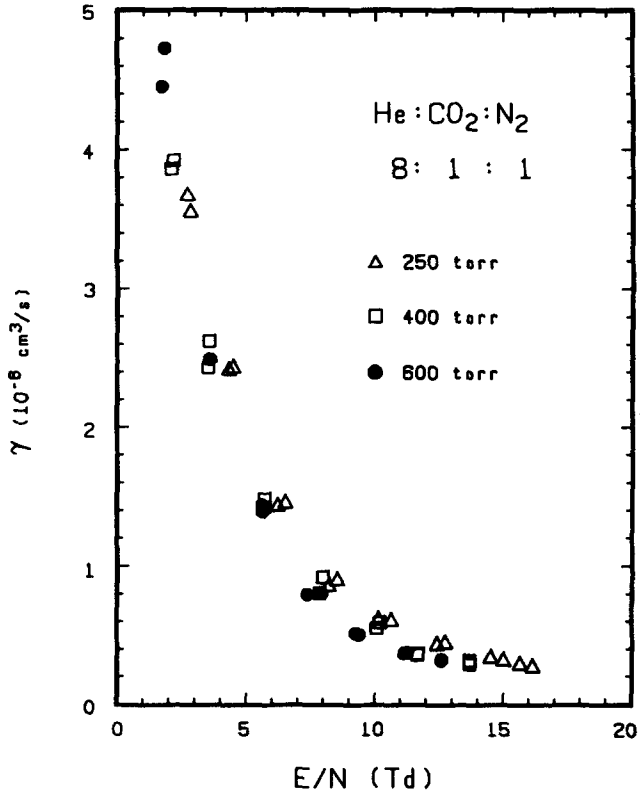

FIG. 9. Recombination rates in the $He:CO_2:N_2$ 8:1:1 mixture.

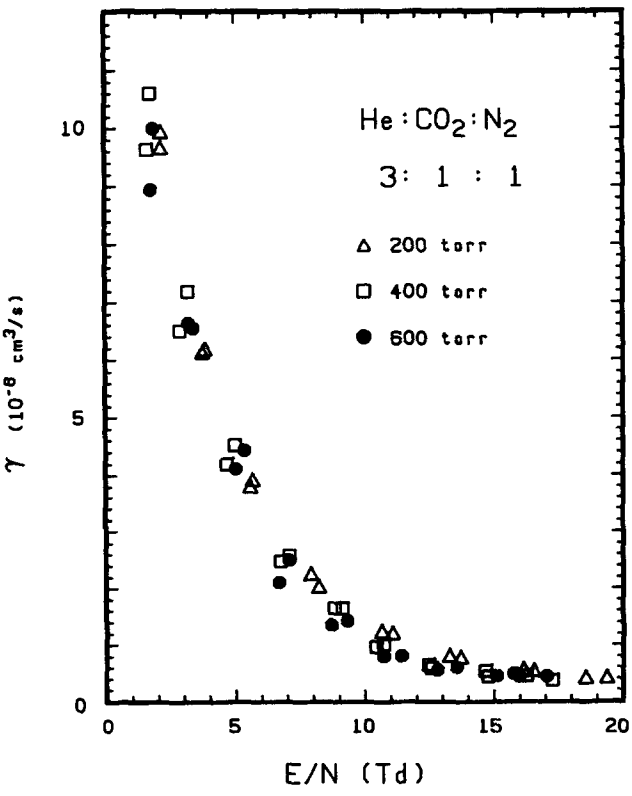

FIG. 8. Recombination rates in the $He:CO_2:N_2$ 3:1:1 mixture.

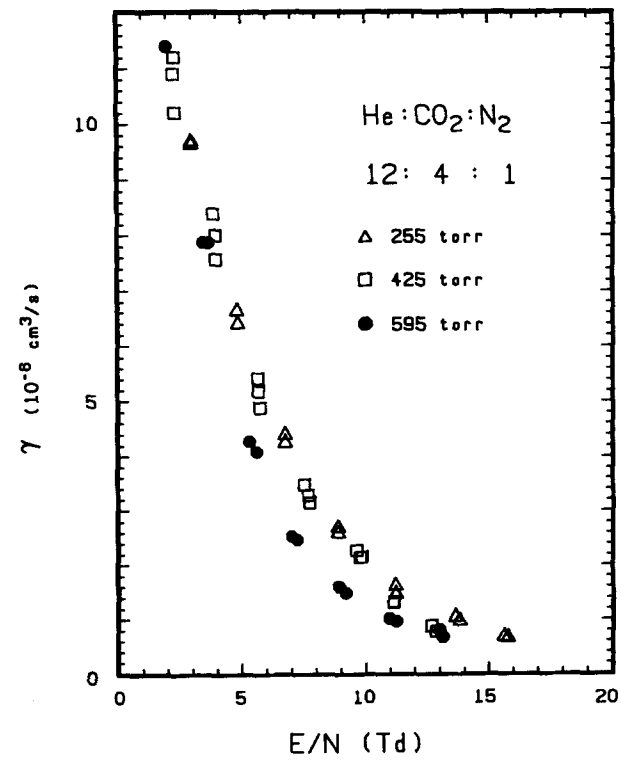

FIG. 10. Recombination rates in the $He:CO_2:N_2$ 12:4:1 mixture.

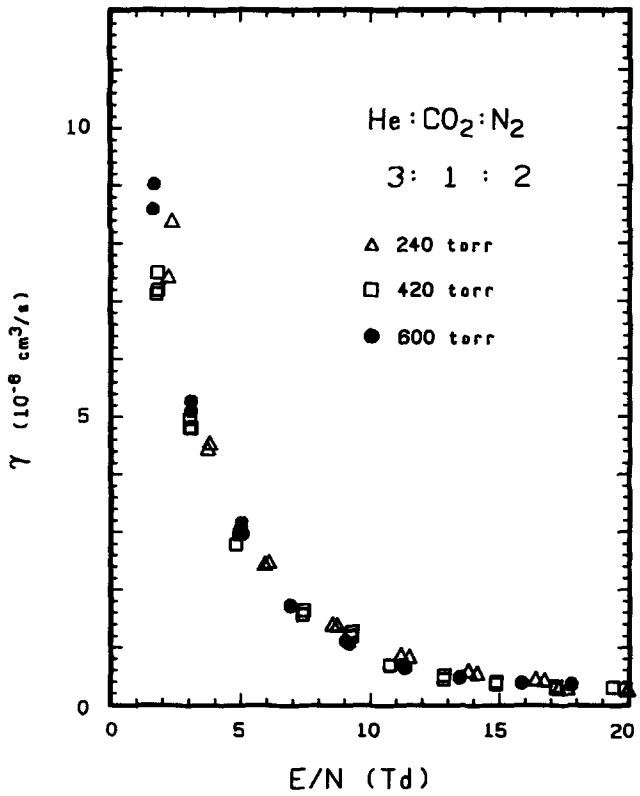

FIG. 11. Recombination rates in the He:CO_2:N_2 3:1:2 mixture.

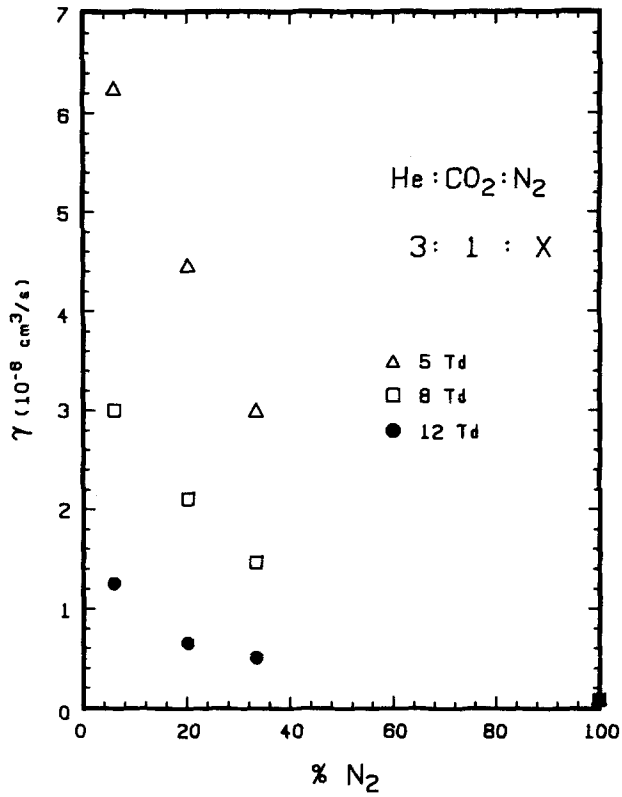

FIG. 13. Variation of the recombination rate with nitrogen concentration. None of the gas mixtures included in this figure show any dependence of the recombination rate on pressure.

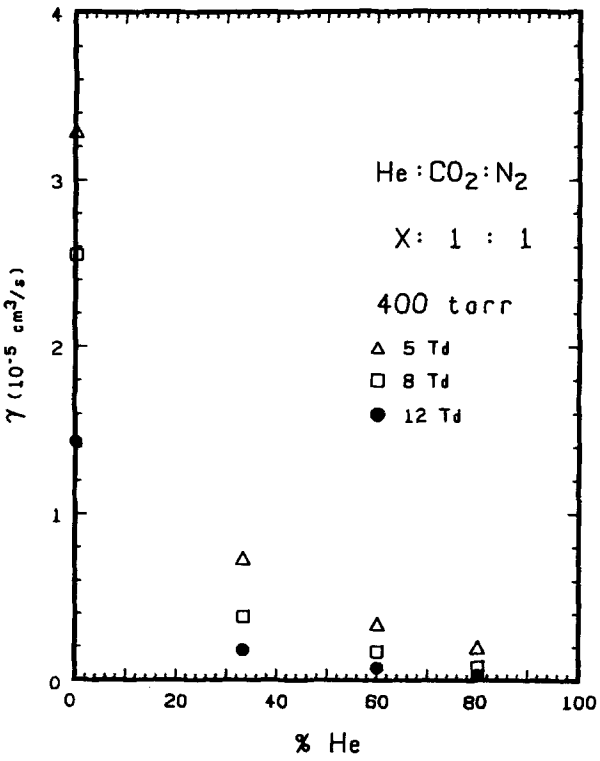

FIG. 12. Variation of the recombination rate with helium concentration. Since the recombination rate for the 0:1:1 mixture (0% He) is pressure dependent, the data in this figure is given at a pressure of 400 Torr. Similar graphs are obtained at other pressures.

proportions of nitrogen and carbon dioxide. In Fig. 13, the proportion of nitrogen is plotted as the abscissa. Also, we show in Fig. 13 the recombination rate for pure nitrogen.[9] The dependence on gas mixtures reflects the increasing proportion of species having low recombination rates. However, the fall in the recombination rate as helium or nitrogen is added to the discharge is much more dramatic than would be expected by simple dilution of the carbon dioxide concentration. Addition of only 30% of helium reduces the recombination rate by an order of magnitude. It should be stressed again, that the bulk recombination rate cannot be obtained by a simple average of recombination rates in the pure gases weighted by the relative partial pressures. Instead, the lower recombination rates in the dilute carbon dioxide mixtures reflect the increased complexity in the discharge kinetics. The change in gas composition through the addition of gases of high ionization potential, such as helium, leads to a change of the electron energy distribution towards higher energies at which the electron–ion recombination rate is low. Alternatively, the presence of diatomic ions, such as He_2^+, which must necessarily dissociatively recombine to atoms, might be expected to lead to lower recombination rates than in the mixtures for which the dominant ions are polyatomic, such as CO_2^+, for which the dissociation products can include one or more molecular species.

The results presented in this paper bear out the qualitative suppositions made by Lowke *et al.*[5] that the recombination rate should be expected to be dependent on the gas pressure and mixture and to decrease with increasing electron energy. We did not observe any change in the recombination rate for an order of magnitude change in the electron den-

sity. This is consistent with the data of Douglas-Hamilton[9] for pure nitrogen, which also show no electron density dependence, and with the Monte Carlo calculations of Morgan[12] for the case of pure carbon dioxide, for which only a small electron density dependence is predicted. In contrast, Homann *et al.*[7] did observe an electron density dependence, such that the product γn_e remains constant in the discharge. The reasons for this discrepancy are not obvious, although the density achieved by Homann *et al.* by using a self-sustained discharge (10^{12}–10^{14} cm^{-3}) are generally higher than either those reported by Douglas–Hamilton in nitrogen or those observed by us, with both parties using *e*-beam sustained discharges.

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