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Two- and three-body electron–ion recombination in carbon dioxide

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Abstract. The electron–ion recombination rate in carbon dioxide was measured as a function of electric field strength and gas pressure. The separate effects of two- and three-body recombination was observed, and the respective rate constants obtained. The results indicate that three-body recombination is dominant at low field strengths for gas pressures above 1 atm, whereas two-body recombination is dominant at high field strengths.

1. Introduction

Of all the electron transport coefficients in gas discharges, electron–ion recombination is the least well documented. Nevertheless, recombination can represent the dominant loss mechanism for high pressure, high current discharges for which the electron densities can be high. We present here measurements of the electron–ion recombination rate in pure carbon dioxide in the range 2 to 20 Td (1 Td = 10^{-17} V cm^2). Measurements of the recombination rate in carbon dioxide are of particular importance to the carbon dioxide laser.

Warman *et al* (1979) recently measured the electron–ion recombination rate for a variety of pure gases. In all cases, they observed a dependence of the recombination rate on gas pressure. This result can be interpreted in terms of the effects of both two- and three-body recombination. However, their experimental results were obtained under field-free conditions, and it is not clear *a priori* how applicable their results are to the conditions in electric discharges in which an electric field can be significant. Our results confirm the effects of both two- and three-body recombination at low field strengths. However, we will show that at moderate and high field strengths, the two-body recombination rate is dominant, even at pressures of a few atmospheres.

2. Experimental details

The experimental technique adopted for our study follows that used by Douglas-Hamilton (1973) to measure the electron ion recombination rate in nitrogen. In this technique, the carbon dioxide gas (Air Products Coleman grade, purity 99.99%) is contained in a stainless steel discharge chamber (figure 1). No further purification of the gas is needed, although the sample is changed frequently to maintain the stated purity.

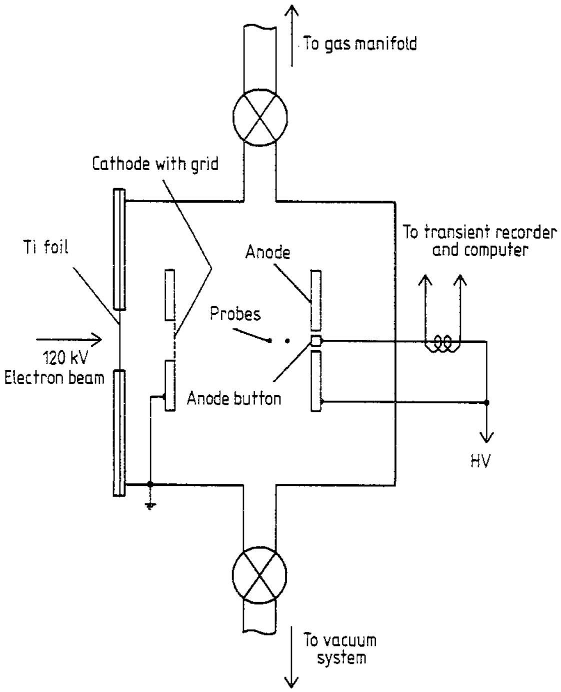

Figure 1. Schematic diagram of the experimental apparatus.

The sample cell is evacuated to less than 10^{-6} Torr between fills. In all cases, the gas temperature is kept at 293 K.

Measurements of the electron–ion recombination rate are made by producing a pulsed e-beam sustained discharge in the gas sample. The electron beam voltage is supplied by a four-stage Marx bank whose total capacity is 0.5 μF. During the experiments, we found that the results were not dependent on the Marx bank voltage, and all the results presented herein were obtained by using an e-beam voltage of 120 kV. The high voltage is fed to a thoriated tungsten filament, which can be heated by a current in excess of 20 A before the high voltage pulse is applied. The pressure in the electron beam chamber is maintained at less than 10^{-6} Torr.

After passing through a thin (0.008 in) titanium foil, the high energy electrons deposit their energy in the gas and create secondary plasma electrons in the process. All electrons are collected on a circular, 7 in diameter, anode maintained at some positive applied voltage with respect to the foil. A Pearson coil (Model 4100) is used to measure that portion of the current that is collected on a central button 5.65 cm^2 in area. By avoiding edge effects in the spatial distribution of the discharge, a reliable current density can be inferred. The output of the coil is attenuated and fed to an AEL 9300 transient recorder with a 10 ns resolution.

Probe wires mounted in the discharge volume (Ganley *et al* 1976) are used to measure the electric field between the anode and cathode. Corrections can thus be made for the cathode and anode fall voltages. In practice, the anode fall voltage was found to be negligible, and the applied anode voltage was used to determine the electric field. In contrast, the cathode fall voltage was quite significant, generally of the order of 10 to 20% of the applied voltage.

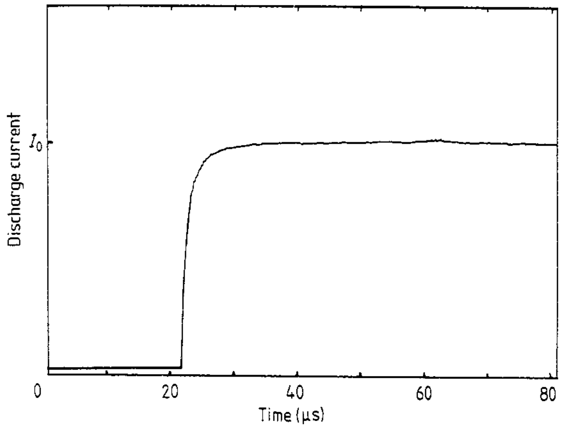

Figure 2. Typical current pulse. The horizontal scale is 10 μs per division.

Figure 2 shows a typical discharge current pulse. Measurements of the anode current with and without gas in the discharge cell indicate that the beam current is less than 0.1% of the total discharge current. Therefore, the beam electron density in comparison with the plasma electron density could be neglected and the discharge electron density represented by the differential equation

$$\frac{\mathrm{d}n_e}{\mathrm{d}t} = S - (\beta - \alpha)n_e - \gamma n_e^2 \tag{1}$$

in which S is the source term resulting from the ionisation of the gas by the electron beam, β the electron attachment coefficient, α the ionisation coefficient, and γ the electron–ion recombination coefficient. Extraction of the recombination coefficient, γ, can be accomplished by using the following measurements.

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

$$S = \left(\frac{\mathrm{d}n_e}{\mathrm{d}t}\right)_{n_{e0}=t=0}. \tag{2}$$

(2) Once the steady-state condition has been achieved, the electron density reaches its constant peak value n_{e0}, so that

$$\left(\frac{\mathrm{d}n_e}{\mathrm{d}t}\right)_{n_{e0}} = S - (\beta - \alpha)n_{e0} - \gamma n_{e0}^2 = 0 \tag{3}$$

from which

$$\gamma = \frac{S/n_{e0} - (\beta - \alpha)}{n_{e0}}. \tag{4}$$

The peak electron density is obtained from the peak current through the current density relation

$$J_0 = n_{e0}eW \tag{5}$$

in which e is the electronic charge, and W the electron drift velocity, which has been calculated from a Boltzmann code (Leland 1979) and confirmed experimentally in our laboratory (Sierra *et al* 1981). The attachment rate β and ionisation rate α are also taken from the same Boltzmann code and have also been confirmed experimentally. In practice, both β and α are negligible in comparison with S/n_{e0} and have no appreciable effect in the calculations of γ.

3. Results

The raw data for the electron–ion recombination rate are shown in figure 3 as a function of the reduced field strength, E/N. Measurements were made over as wide a range of E/N and gas pressure as possible consistent with maintaining a stable discharge. Each point represents the average of a number of individual measurements. For all four gas pressures studied, a steady decrease in the recombination rate with increasing E/N is evident. There is, however, a marked dependence of the recombination coefficient on gas pressure, particularly for the low field strengths. Figure 4 shows the recombination rate as a function of pressure for four different field strengths. It is apparent that the pressure dependence can be represented by a recombination rate, which is indirectly proportional to the pressure. Thus,

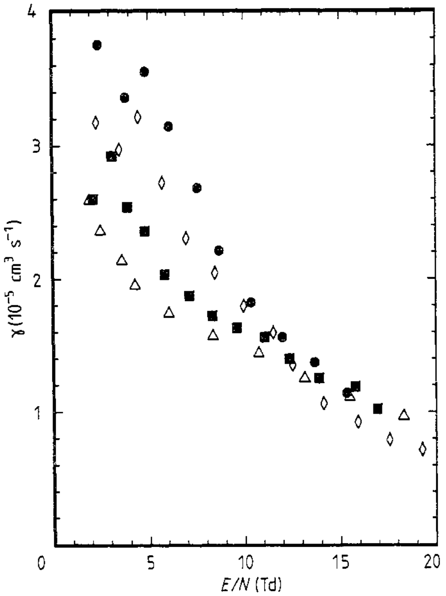

Figure 3. Electron–ion recombination rate in carbon dioxide as a function of the reduced electric field at four gas pressures (Torr): △ 100, ■ 200, ◇ 400, ● 600.

$$\gamma = \gamma_2 + \gamma_3[CO_2] \tag{6}$$

in which $[CO_2]$ is the density of carbon dioxide molecules. This result can be interpreted as the separate effects of the recombination of carbon dioxide ions in two- and three-body reactions as follows:

$$CO_2^+ + e \rightarrow \text{neutral products} \tag{7a}$$

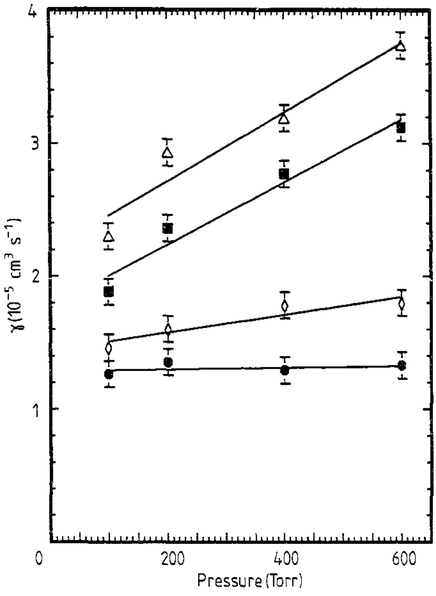

Figure 4. Electron–ion recombination rate for carbon dioxide as a function of gas pressure. Measurements taken at reduced field strengths (Td) of: △ 3, ■ 5, ◇ 10, ● 13.

and

$$CO_2^+ + e + CO_2 \rightarrow \text{neutral products} \qquad (7b)$$

with rates γ_2 and γ_3 respectively. Figure 5 shows the two- and three-body rates as functions of E/N as determined from the slope and intercept of curves similar to those

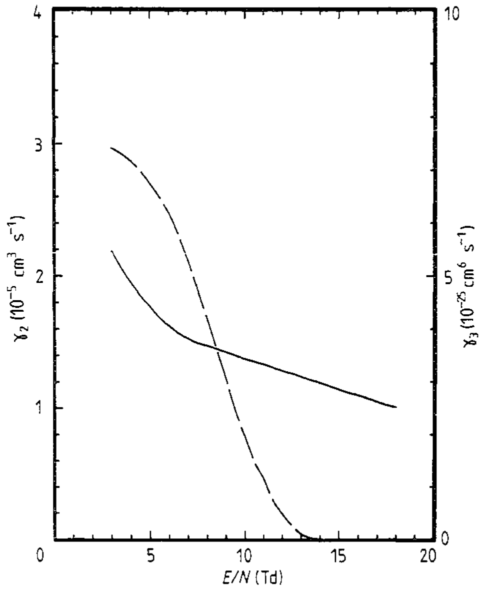

Figure 5. Two- and three-body recombination rates for carbon dioxide as a function of the reduced electric field. He: CO_2:N_2 = 0 : 1 : 0. Full curve, γ_2; dashed curve, γ_3.

in figure 4. The two-body rate appears to be relatively insensitive to E/N, in that it falls only slowly as the field strength increases. In contrast, the three-body rate falls rapidly and becomes essentially zero above 12 Td.

The recombination rates obtained in the study are larger than those previously obtained for mixtures of carbon dioxide, helium and nitrogen. Denes and Lowke (1973) estimated a rate of only 10^{-8} cm^3 s^{-1}, independent of field strength or gas composition. More recently, Homann *et al* (1978) and Nundy *et al* (1981) obtained values in the range of 10^{-7} to 10^{-6} cm^3 s^{-1} in mixtures of He : N_2 : CO_2 in the ratio of 8 : 1 : 1. It is not clear *a priori* what effect the presence of helium and nitrogen has on the electron–ion recombination rate of the bulk gas. The results presented here indicate that the recombination rate falls rapidly as helium and nitrogen are added to the discharge. If one approximates the recombination rate of the mixture to an average of the rates for the individual ions, weighted according to the relative number densities, the low rate for the 8 : 1 : 1 mixture indicates that carbon dioxide ions occur with low concentrations in the discharge, even after the relative partial pressures of the constituent gases in the mixture are taken into consideration.

4. Conclusions

We measured the recombination rate of electrons and ions in carbon dioxide as functions of the reduced electric field strength and of the gas pressure. The separate effects of two- and three-body recombinations were observed, and the respective rate constants measured as a function of the reduced electric field strength, E/N, in the range of 2 to 20 Td.

The results are of importance to high pressure discharges containing carbon dioxide, as in carbon dioxide lasers. At low electric field strengths, the three-body recombination rate becomes dominant for gas pressures of 1 atm and above. In contrast, at field strengths above 12 Td, two-body recombination is dominant even for pressures of a few atmospheres.

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