Glow Discharge Plasma Properties of Gases of Environmental Interest

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Experiments in a low pressure glow discharge on gases of environmental relevance: CO$_2$, CO and O$_2$ are reported. We studied the various atomic processes: ionization, excitation and molecular dissociation with typical discharge parameters of $p \sim 0.6$ mbar, $I \leq 0.1$ A and $V \sim 1100$ Volts. We used visible and near UV spectroscopy to observe the emitted radiation on both electrodes on pure gases and hydrogen seeded mixtures. We also set up Langmuir probes in both electrodes.

1 Introduction

Low pressure linear discharges are a well known plasma producing device although highly anisotropic, non-homogeneous, non-equilibrium systems. The electron production and gas ionization at the cathode region, are complex mechanisms that make the balance of particles and current continuity still subjects of research [1-4]. The detailed understanding of those mechanisms are fundamental for industrial applications where large plasma volumes are required [4].

In this work we centered our attention in gases of environmental interest which oftenly show up in a plasma state in different physical scenarios such as: fusion research, in the presence of wall originated impurities in the after glow of the discharge, industrial processes where plasma etching is required and astrophysical plasmas present in comet tails, among others.

In this work we have concentrated in a comparative study of the discharge parameters namely, the various temperatures and the electron density. In particular, we discuss comparisons between Langmuir probe and spectroscopic measurements. We also propose a simple method to determine the molecular temperature of CO$_2^+$ using the Doppler width of an isolated line in the $\Lambda^2 \Sigma^+ \rightarrow X^2 \Pi$ double band of this molecular ion.

2 Experimental procedure

We used a low pressure glow discharge, with two 5 cm diameter brass electrodes separated 50 cm. Typical discharge parameters were, $p \sim 0.6$ mbar, $I \leq 0.1$ A and $V \sim 1100$ Volts. A pyrex tube was equipped with viewing ports with lines of sight along the axis of the discharge and at 45° to both anode and cathode front surfaces. To switch our line of sight between electrodes we toggle a mirror in an out of the system (Fig. 1). The same ports were used to slide and hold the Langmuir probes. Pure and mixed gases were available using an external manifold.

2.1 Spectroscopy

We have performed visible and near UV spectroscopy on radiation originated along the discharge axis and on both electrodes at 45° off axis. A f/10 quartz or glass lens focuses the light at the entrance slit plane. The space resolution on the electrodes is source limited, but it fulfills our goal of differentiating cathode and anode spectra. The spectrometer is a 1 m McPherson (MOD 2051) with a 1200 l/mm grating. Slit widths were varied between 10 and 100 $\mu$m, depending on the required resolution.
Figure 2. CO$_2$ discharge, spectral emission at anode and cathode. Comparison of the spectra of a CO$_2$ gas discharge measured at the cathode and anode electrodes in the region from 250 nm to 800 nm. Gas pressure: 0.6 mbar. Discharge current: 40 mA, 100 $\mu$m slit width. Second order lines were suppressed from the cathode trace for simplicity.

Optical emission spectroscopy (OES) shows a remarkable difference between cathode and anode emission for CO$_2$ under the same pressure (0.6 mbar) and discharge current(40 mA) conditions, see Fig. 2. From the central part of the cathode the spectrum exhibits the typical CO$_2^+$ near UV bands. There is also evidence of the presence of the so called Angström system (B$^1\Sigma^-$-A$^1\Pi$) for CO [6] and the characteristic OI (777 nm) multiplet (55 - 5P) emission. The typical ionization channel from CO$_2$ to CO$_2^+$ requires of an ionization energy $\approx$14 eV. Starting with CO$_2^+$ there are several channels that produce all the species present in the discharge and require between 5.8 and 8 eV for activation [7].

Near the anode only the Angström system from CO was observed but not the molecular emission from CO$_2$ -that mostly falls in the infrared-, neither the strong OI (777 nm) emission were present. All the positive ions were also absent since they stay in the most favorable region at the negative cathode. The presence of CO but weak OI lines near the anode may respond to CO molecules generated near the cathode that due to its higher ionization and excitation energies have a high probability to diffuse along the discharge. However, the presence of very weak bands in the region between 350-450 nm, that belong to CO$^+$ system, lead us to believe that CO and OI could also be produced along the discharge column.

Figure 3 shows a comparison for the emission spectra at the cathode from pure CO$_2^+$, CO and O$_2$ gas discharges, all at 0.6 mbar and 40 mA. Calibration lines from a He-Ne laser and from a Hg Lamp were taken simultaneously. The cathode emission from the CO gas discharge exhibits a typical molecular spectrum from CO [10] and again, no appreciable emission from OI was present (as in the anode emission from pure CO$_2$). The O$_2$ gas cathode emission presents several weak bands and the strong OI line at 777 nm.

2.2 Langmuir probe measurements

We measured the Langmuir probe I vs. V characteristic curve in both electrodes and for different gases. From those curves we inferred values for the electron temperature and density. It is important to mention that probe behavior differs significantly between situations where collisions can be ignored and those where they cannot. The effect of collisions is mainly to reduce the current collected by the probe due to diffusion of particles in the plasma region around it [8]. The condition to ignore collisions in the plasma is that $l \gg a$, where a is the probe radius and l is the electron mean free path. Thus, in our case, we are working with plasmas whose parameters are: electron temperatures ($T_e$) from 0.3 to 1 eV, and electron densities ($N_e$) from $3 \times 10^9$ cm$^{-3}$ to $2 \times 10^{10}$ cm$^{-3}$ approximately. For these values the mean free path goes from 7 to 30 cm. For $a = 5$ mm we the condition $l \gg a$ is fulfill and collision effects can be ignored.

The Langmuir probe, was positioned at 1 cm from the cathode surface along the axis. For classical low-pressure glow discharges, it is known that electrons in the usually sub-cm cathode fall region are not in equilibrium with the local electric field [9]. This fact was corroborated in our case by measuring the relatively constant DC potential between the anode and the Langmuir probe along several points of the discharge axis, up to a distance 3 to 4 mm away from both electrodes. As the gas pressure is elevated closer to the atmospheric pressure, the much increased collision between electrons and neutral particles significantly reduces the thickness of the cathode fall region to around 300 $\mu$m ($5 \times \lambda_D$) [3,4]. Over this narrow width, secondary electrons released from the cathode are unlikely to gain sufficient acceleration and reach equilibrium with the local electric field.

2.2.1 Electron temperature

Electron temperatures vs. current measured on the cathode (△) and anode (●) region of a pure CO$_2$ discharge, see figure 4, present a difference of 10% approximately. This can
be due to the unstructured (no striations) configuration observed during the discharge, which is dominated by the negative glow. When the discharge current was varied from 10 mA to 50 mA, for CO₂, the electron temperature was found to increase from 0.3 eV to 0.8 eV respectively. For a CO₂+H mixture with a breakdown parameter $p e l$ equivalent to the CO₂ case, the electron temperatures obtained were within the experimental uncertainty to the corresponding ones with CO₂ only. This result suggests that the molecular excitation process does occur along the whole plasma length.

![Image](image_url)

**Figure 4.** Measured electron temperatures inferred from Langmuir probe: ▲: pure CO₂ cathode; △: pure CO₂ anode; ⬤: CO₂+H mixture anode. ■: inferred from H-Balmer wavelength integrated intensities CO₂+H, cathode. The size of the symbols is proportional to the experimental uncertainties.

![Image](image_url)

**Figure 5.** Electronic densities inferred from Langmuir probe measurements as a function of the current. CO₂ discharge, ▲: cathode; △: anode. CO₂-H mixture, ⬤: anode. CO discharge, ⬤: cathode; ○: anode. Gas pressure: 0.6 mbar in all cases. The size of the symbols is proportional to the experimental uncertainties.

### 2.2.2 Electron density

The electron density was determined using the electron temperature value and the electron current saturation measured from the Langmuir probe I vs V curves. Electron current saturation values from 2.4×10⁻⁶ A to 16×10⁻⁶ A where measured for discharge currents between 10 to 50 mA respectively. For CO₂+H mixture, we observe that the electron temperature changed around 6%, compared with CO₂ experiment. On the other hand, the electron density (see Fig. 5), decreased by a factor of 4.2 for 40 mA, and 2.3 for 50 mA. That means, hydrogen gas increases the electron mobility in the mixture, reducing the electron density along the discharge column. For low current discharge, most of the power deposited in the ions is transferred to kinetic energy of the neutral gas. It is important to point out that we work with a stable glow discharge to avoid the onset of instabilities in the region near the electrodes, particularly in the cathode region, because this is the region of higher power density.

### 2.3 Cathode temperatures using light emission

#### 2.3.1 Electron temperature using H Balmer lines

The measured electron density values ~ 10⁹ cm⁻³ indicate that for the expected electron temperatures in a low pressure DC discharge, the system should be in a steady-state corona model (SSC) [11]. In such model the equilibrium is achieved by collisional excitation and spontaneous emission. The measured integrated intensity ratio between two lines of the same ionization stage in SSC depends only on the electron temperature, and is given by the following expression [12]:

$$\frac{I(\lambda_{ji})}{I(\lambda_{kl})} = \frac{X(T_e,0,j)B_{ji}}{X(T_e,0,k)B_{kl}}$$

(1)

$$X(T_e,0,j) = \frac{6.45 \times 10^{-4} f(0,j) e^{-\frac{T_e}{T}}}{} \chi(0,j) T_e^2 e^{-\chi(0,j) T_e} .$$

(2)

Where $j(k)$ and $i(l)$ are the upper and lower states of the transitions. $B_{ji}$ is the branching ratio for a specific transition from level $j$ to level $i$, to the total transition probability from level $j$. $X(T_e,0,j)$ is the excitation rate coefficient for the electron impact excitation from the ground state to level $j$.

In a mixture CO₂+H (80% CO₂ and 20% H) the electron temperature inferred from the different ratios of the wavelength integrated intensity for the Balmer series H₆, H₅ and H₄ was 0.35 ± 20% eV. The lower value, obtained by this method, in comparison to the Langmuir probe measurements is due to the radial gradient that is sample along the 45° line of sight.

#### 2.3.2 CO₂⁺ temperature

Determination of molecular or molecular ion temperatures in a linear discharge using the radiated emission, is typically done by measuring [3] the relative intensities distribution of the line components in the molecular band and then match it to a model where there is only one fitting parameter, the temperature. An alternative method is to find an isolated line within the molecular band, which are rarely found in molecular spectra, and measure its Doppler width, which is a very demanding measurement resolution-wise.

Even with very small amounts of CO₂ the double band of CO₂⁺ centered at $\lambda = 288.3$ and $\lambda = 289.6$ nm is always present (Fig. 2). At the center of each band there is a very conspicuous and differentiated sharp line, surrounded by the
various negative (R branch) and positive (P branch) components (Fig. 6). Although the origin of these two central components is not certain [7], they seem to belong to the Q branch ($\Delta J=0$).

We measured the profile of the central component at 288.3 nm with a narrow slit 10 $\mu$m (0.01 nm instrumental full width at half maximum), and found that the full width of the line was above the instrumental width. We then fitted a synthetic profile resulting from the convolution of the instrument function (0.01nm) and a gaussian that takes into account the Doppler contribution. We obtained a Doppler full width of 0.005 nm from the best match between the synthetic and experimental profile (Fig. 6), and inferred an upper limit of 2.5 eV for the CO$_2^+$ temperature.

Figure 6. The relative intensity spectrum (dotted line) of one of the CO$_2^+$ ($\Lambda^2\Sigma^+ \rightarrow X^2\Pi$) bands centered at $\lambda$ 288.3 nm. The figure shows an expanded view of the center portion of the band with the well differentiated and isolated central component (Q-branch head). The best synthetic profile fit (solid line) to the central component indicates an upper limit of 2.5 eV for the CO$_2^+$ temperature. Å units were used for convenience.

3 Conclusions

OES measurements have confirmed that this type of gas discharge is optically very active near the cathode (negative column) due to the high energy electrons produced there. For the discharge in CO$_2$, the presence of CO$_2^+$, CO and OI emissions shows that there is enough energy for the activation in the cathode of the respective ionization and dissociation processes. Observations at the anode indicate the possibility that CO could be produced along the plasma column as well. We have measured the electron temperatures and densities using a Langmuir probe for different gases and discharge regions (anode and cathode). These results are consistent with the probe sampling the main column of the discharge at about 1 cm from each electrode. We have derived electron temperatures CO$_2$+H mixture, near the cathode, using a SSC equilibrium atomic model and the measured wavelength integrated intensity ratios of the Balmer lines of Hydrogen. We also inferred an upper limit for the temperature of CO$_2^+$ at the cathode from the Doppler width of the Q branch of the 288.3 nm CO$_2^+$ band. A better determination of this temperature, using this method, will require a more systematic investigation.

References