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Spectroscopic measurements of nonequilibrium CO_2 plasma in RF torch

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ABSTRACT

This paper deals with the experimental study of the CO_2 dissociation in a RF plasma torch at low pressure. Experiments have been carried out for different initial conditions in order to study the influence of the pressure and the power on the plasma characteristics. Furthermore the emission spectroscopic measurements have been performed at four different locations to investigate the evolution of the plasma chemistry from the creation zone to downstream. The results have confirmed that the CO_2 plasma is in thermal and chemical nonequilibrium. For each condition, we have obtained the estimation of CO and O densities on their ground state from the chemiluminescent emission; and the rebuilding of experimental spectra has provided the species density on their excited states: O($3p^5P$), O($3p^3P$) and CO($B^1\Sigma^+$). The discussion of the experimental data has led to make out a description of the chemical processes for the CO_2 plasma under dissociation and has highlighted the main role of the vibrational excitation and relaxation on the kinetic mechanisms.

1. Introduction

Carbon dioxide has attracted much attention for many years because it is one of the simplest polyatomic molecules and it is present in a large number of fields. For example, on Earth, its behavior is carefully examined with respect to the global warming process. Otherwise the chemical kinetics of the molecule is of great interest in space community because carbon dioxide is one of the fundamental constituents of planetary atmospheres [1]; in particular it is the most abundant molecule in the atmospheres of Venus or Mars [2].

The first part of this work proposes the description of the experimental set-up, an inductive RF torch, and the spectroscopic diagnostic associated. Absolute spectroscopic measurements on a CO_2 plasma have been carried out for different initial conditions of mass flow rate, pressure and power at four different spatial locations within the plasma. The corresponding results are presented detailing each of the radiative contributions from 300 to 900 nm:

- A characteristic continuum due to chemiluminescent recombination reaction of CO and O is observed.
- Two strong lines corresponding to electronic transitions of atomic oxygen are detected: ($3p^3P \rightarrow 3^s3S$) and ($3p^5P \rightarrow 3s^5S$).
- CO bands systems are present on the whole range of wavelengths including the Angstrom system ($B^1\Sigma+ \rightarrow A^1\Pi$), the Triplet system ($d^3\Delta i \rightarrow a^3\Pi r$), the Asundi system ($a'3\Sigma+ \rightarrow a^3\Pi$) and the third positive system ($b^3\Sigma+ \rightarrow a^3\Pi$).
- The system of CO_2^+ ($A^2\Pi u \rightarrow X^2\Pi g$) is detected in the creation zone.

The last part of this paper proposes a brief overview of mechanisms referring to CO_2 dissociation and a synthesis of the results in order to describe the chemical scheme of the CO_2 plasma dissociation occurring in the RF torch.

2. Spectroscopic results

2.1. Experimental set-up

The experimental apparatus shown in Fig. 1 is an inductively coupled plasma source (ICPS). The reactor is made of quartz with the form of a cylinder having 60 mm in diameter at the coil location and 90 mm in diameter downstream by 700 mm high. The discharge power is supplied by an RF20 model radio-frequency generator from Advanced Energy Industries operating at 13.56 MHz. The maximum power delivered is 2 kW. The generator is connected to a matching network in order to tune the inductor consisting in a seven loops coil. The forward power delivered by the generator as well as that reflected from the load were measured by a wattmeter supplied with the generator. The gas is injected into the reactor according to a maximum flow rate of 1 slm and the discharged gas is removed by a dry primary pump

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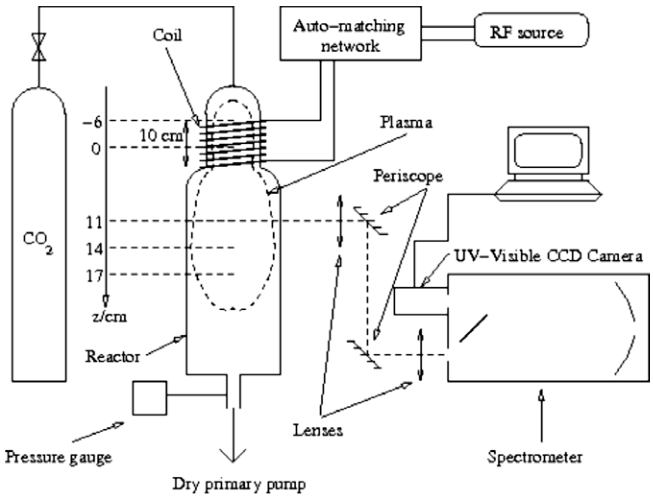

Fig. 1. Block diagram of the experimental device.

maintaining the plasma at a low pressure P (1–2 mbar). The experiments are carried out by changing both flow rate Q_S (0.1–0.3 slm) and power P_W (80–160 W) delivering to the plasma specific enthalpies E_m from 13.6 to 40.8 MJ/kg (Table 1).

The CO_2 plasma is studied using classical emission spectroscopy technique. The light emitted is collected perpendicularly to the flow by a periscope system whose lenses are interdependent. This optical scheme allows acquisitions at various longitudinal locations within the plasma and provides a spatial resolution of 0.1 mm. But this method does not propose local values because measurements integrate over the line of sight. The plasma is not radially homogeneous so the results presented in this paper are only average estimations of radiative flux and temperatures.

Table 1
Experimental conditions

Q_S (slm)	P (Pa)	P_w (W)	E_m (MJ/kg)
0.3	100	120	13.6
		140	15.9
		160	18.1
0.2	150	120	20.4
		140	23.8
		160	27.2
0.1	200	80	27.2
		100	34
		120	40.8

A SpectraPro-300i spectrometer is used with a 1200 g/mm grating blazed at 300 nm and an entry slit aperture of 50 μm wide, the FWHM being therefore 0.215 nm. The emission is then recorded using an ICCD camera PI-Max of Princeton.

The optical set-up has been calibrated in spectral intensity by means of a ribbon tungsten lamp (14 A, 2600 K) simulating device used as a quasi punctual source. This calibration has to provide an estimation of the radiative flux on the studied range of wavelengths 300–900 nm.

The luminosity of the CO_2 plasma is not very intense but, thanks to the stationary nature of the emission, this weakness is compensated by storing the signal in order to increase the signal-to-noise ratio. The stationary characteristic of the plasma also allows studying the evolution of the plasma chemistry through spatial measurements.

The nature of the irradiance in the reactor is of two distinct types: from the gas inlet to the middle zone of the loops ($z = 0$), i.e. the beginning of the plasma creation zone, a deep purple color plasma is present whereas downstream, in the relaxation zone, the flow is homogeneously fuzzy blue-white. Measurements are performed at the height −6 cm, 11, 14 and 17 cm (see Fig. 1).

All the spectra present the same characteristic bands of CO, atomic oxygen lines and a continuum-like shape. Intensity of both oxygen atomic lines at 777 nm and 844 nm are higher than intensity of CO bands and continuum. If the spectra obtained in the post discharge present the same global form whatever the operating conditions, they are significantly different from those of creation region. Fig. 2 presents two spectra obtained for the condition E_m=34 MJ/kg at the locations $z = -0.06$ cm (a) and $z = 11$ cm (b). Whatever the specific enthalpy delivered to the plasma, the emission in the creation zone is lower than in the post discharge; the ratio is about five for CO bands plus the continuum and three for atomic oxygen lines. Furthermore, the continuum-like shape looks also different since the maximum intensity for $z = -0.06$ cm is present at about 425 nm whereas it is at 450 nm for $z = 11$ cm. All the radiative systems that contribute to the emission are analyzed below.

2.2. CO + O chemiluminescence

Measurements of the radiative reaction of atomic oxygen and carbon monoxide have been performed in discharge flow tubes [3,4], in carbon monoxide flames [5–7] and in shock-tubes [8,9]. All the experimental spectra show a strong blue continuum, between 250 and 800 nm with a maximum intensity around 400 nm. This emission is due to the chemiluminescence accompanying the recombination of CO and O [10]:

$$CO(X^1\Sigma^+) + O(^3P) \rightarrow CO_2(X^1\Sigma_g^+) + h\nu \quad (1)$$

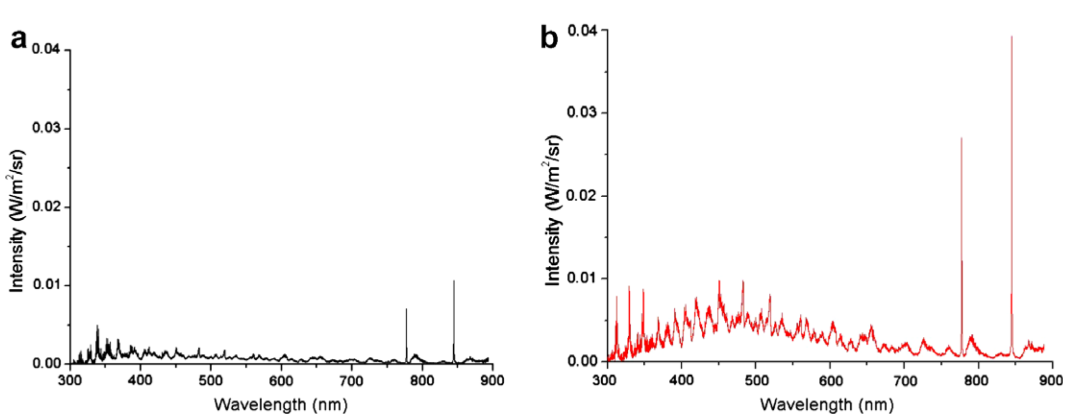

Fig. 2. Experimental spectra at E_m = 34 MJ/kg for (a) $z = -0.06$ cm and (b) $z = 11$ cm.