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Optical Emission Spectroscopy Study of Transition Discharges in N_2/CO_2 Mixture at Atmospheric Pressure

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Abstract

The emission from new type of streamer-to-spark transition type discharge in N_2/CO_2 mixtures as a function of CO_2 concentration was studied. Emission of N_2 2nd and 1st positive systems, CN violet system, and atomic N, O and C lines were detected. The aim was better understanding of processes leading to the generation of CN.

Introduction

Chemistry induced by atmospheric pressure DC discharges burning to the water surface in N_2-CO_2-H_2O mixtures was studied recently [1, 2]. This gaseous mixture represents a model pre-biotic atmosphere of the Earth and a simplified flue gas from the stoichiometric combustion of the natural gas. The aim of these studies was the formation of organic species, especially amino acids, and the CO_2 decomposition.

For better understanding of processes leading to CN formation, we performed Optical Emission Spectroscopy (OES) study of discharges in this mixture. OES gives valuable information on excited atomic and molecular states, enables to determine the rotational and vibrational temperatures and thus gives insight in an ongoing plasma chemistry. As the first step, we analyzed the discharges in dry N_2/CO_2 mixture, which is presented here.

Experimental set-up

All experiments were carried out at room temperature in atmospheric pressure N_2/CO_2 mixtures (from 0 to 100 vol. % of CO_2), with the total gas flow from 0.08 to 0.32 l/min. The experimental set-up consisting of a discharge reactor and electric and optical circuits is depicted in Fig. 1.

DC high voltage power supply connected via a 9.82 MΩ series resistor limiting the total current was used to generate the discharge. We used filamentary discharges of transition type initiated by a streamer named 'Spontaneously Pulsing Transition Discharge' (SPTD) or 'Transient Spark' [3]. The voltage at the reactor was measured by the high voltage probe Tektronix P6015A and the discharge current was measured using the current probe Pearson Electronics 2877 (1V/A) linked to the 200 MHz digitizing oscilloscope Tektronix TDS2024. The UV-VIS spectra were obtained by a compact emission spectrometer Ocean Optics SD2000 (200 – 1100 nm, resolution 0.4 – 1.7 nm).

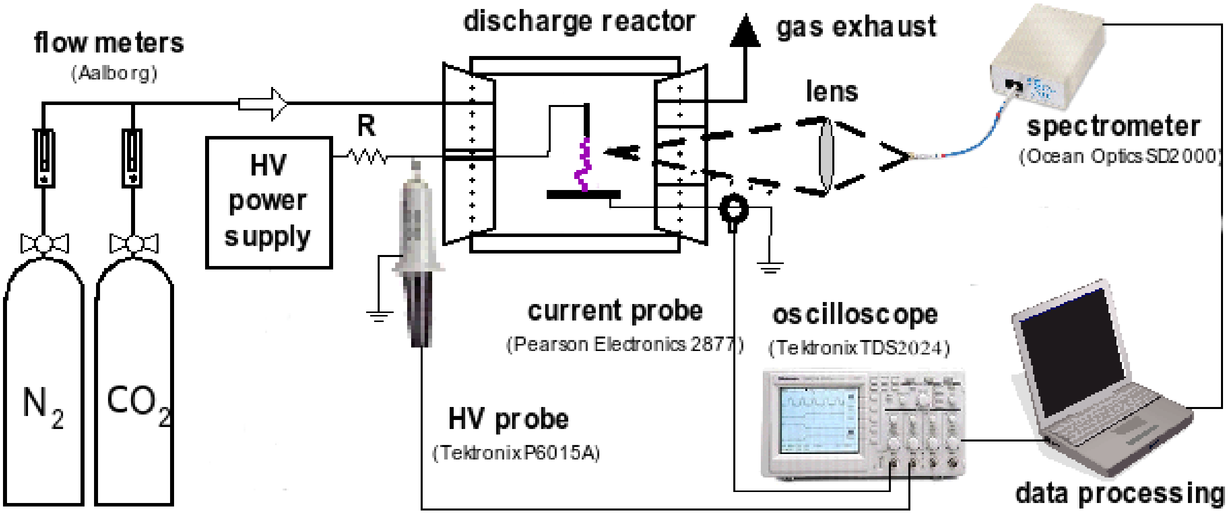

Fig. 1 – Scheme of the experimental set-up.

Results and discussion

The strongest lines observed can be attributed to the emission of N_2 2nd positive system ($C^3\Pi_u - B^3\Pi_g$) and CN violet ($B^2\Sigma^+ - X^2\Sigma^+$) system. The emission of N_2 1st positive system ($B^3\Pi_g - A^3\Sigma^+$), N_2^+ 1st negative system ($B^2\Sigma^+ - X^2\Sigma^+$), and atomic N, O and C lines were also observed, indicating plasmas with high electron temperatures with a high level of non-equilibrium. Non-equilibrium conditions were confirmed also by calculated vibrational (T_v) and rotational (T_r) temperatures (Fig. 2), obtained by fiting the experimental spectra of N_2 2nd positive system with the simulated ones (we use Specair simulation program [4]). The typical measured temperatures are: T_r = 400-800 K, T_v = 2100-2800 K.

It is possible to calculate T_v and T_r from CN violet system as well. We found that T_v and T_r of CN is much higher, around 11000 and 6000 K, respectively. Such high temperatures are unrealistic in a cold plasma and are in total disagreement with T_r and T_v measured from N_2. A possible explanation is that CN $B^2\Sigma^+$ excited state is not populated by electron impact but results from chemical reactions creating CN species. Vibrational and rotational distributions may be therefore non-Boltzmann and thus T_v and T_r are not defined.

The concentration of CO_2 (c_{CO2}) influences the intensity of individual emission lines directly (concentration of reactants), as well as indirectly, since it changes the discharge parameters. During our emission experiments, we kept the frequency of current pulses constant, but the waveforms of current and voltage changed with changing c_{CO2}. As a result, we found that in order to study the emission intensity as a function of c_{CO2} (Fig. 3), it is necessary to normalize the obtained spectra by the input energy. However, this is just an approximation, since it does not sufficiently reflect the changes of electron's energy as a function of c_{CO2} in our discharge.

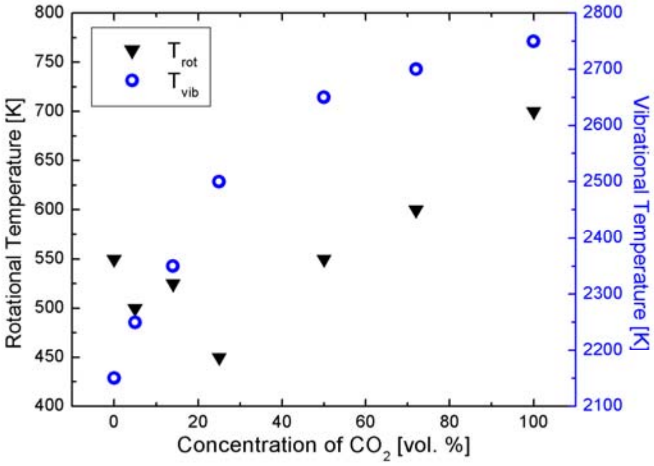

Fig. 2 – T_r and T_v as functions of c_{CO2}.

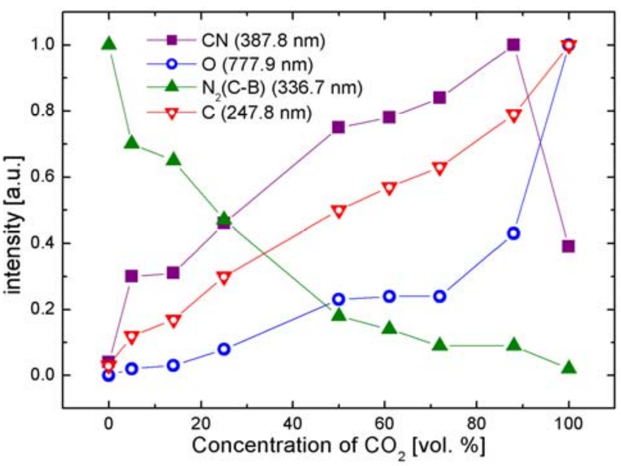

Fig. 3 – Emission intensities of selected species normalized to the input energy.

Conclusions

The transient spark discharge generates non-equilibrium cold plasma with high energy of electrons, which can dissociate N_2 and CO_2 to generate N and C species. The pathways leading to the synthesis of CN require further investigation, but they are certainly produced by more than one reaction. Moreover, CN was observed also in 'pure' CO_2 and N_2, since even minor impurities (e.g. CH_x) play an important role.

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