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Transient Spark in N_2-CO_2 Mixture above Water Surface at Atmospheric Pressure*

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Abstract: The electrical and optical properties of a DC-driven streamer-to-spark transition discharge named Transient Spark (TS) operating above the liquid water in N_2-CO_2 mixtures at atmospheric pressure were studied. Despite the DC applied voltage, TS has a pulsed character with very short (~100 ns) high current (~1 A) pulses, with repetition frequency 1–10 kHz. The emission of N_2 2-nd and 1-st positive, N_2^+ 1-st negative, CN violet and red, OH (A-X) and NH (A-X) systems, as well as atomic N, O, H, and C lines were detected. The non-equilibrium character of TS was confirmed by comparisons of the calculated vibrational (3100–5500 K) and rotational (500–1300 K) temperatures. This research is related to the theory of origins of life, since it enables a better understanding of processes leading to the formation of amino acids precursors, such as CN, HCN or NH species, under conditions simulating lightning strokes into water in the Earth's primitive atmosphere.

1. Introduction

Plasma, unlike gases that are usually chemically inert at standard conditions, posses chemical activity due to high energy of free electrons, excited particles, ions and radicals present. Atmospheric pressure plasmas in air generated by electrical discharges represent therefore considerable interest for a wide range of environmental, bio-medical and industrial applications, such as air pollution control, waste water cleaning, bio-decontamination and sterilization, or material and surface treatment [1–8]. New types of discharges are still being developed and studied, with a focus on efficiency, power requirements, stability, reliability and simplicity. For this reason we study a relatively novel type of streamer-to-spark atmospheric pressure transition discharge, named the transient spark (TS) [9, 10].

The TS is a DC-driven self-pulsing discharge with the repetition frequency 1–10 kHz. The TS is initiated by a streamer transforming to a short spark current pulse. Spark discharge usually generates thermal plasma, but the TS spark current pulses are sufficiently short (~10–100 ns) to avoid plasma thermalization. Non-equilibrium plasma generated during the spark phase of the TS is highly reactive, since the electron density as high as 10^{17} cm^{-3} can be achieved [11]. The TS has already been successfully tested for several environmental and bio-medical applications [12–15], and extensive fundamental research of TS in air and argon using several electrical and optical diagnostic methods has been performed [10, 11, 16–19].

Here, we present a study of transient spark in N_2-CO_2-H_2O gas mixture. The mixture can represent a simplified flue gas from the natural gas combustion. Study of plasma induced chemistry in this mixture can be also interesting for CO_2 lasers and a research of

*) *Dedicated to Prof. V. Martišovitš 75-th anniversary*

various extraterrestrial atmospheres (Mars, Titan, etc.). Moreover, this mixture also represents a model primitive atmosphere of the Earth relevant for the pre-biotic synthesis of organic species needed for further evolution of life [20, 21].

Chemistry induced by various electrical discharges in this mixture was therefore studied recently [22–29]. The objective of these studies was either the basic research of plasma induced chemistry, utilization of CO_2, which is the dominant contributor to the enhanced greenhouse effect and global climate change, or the formation of organic species, especially amino acids. Synthesis of reported organic species [27, 28] from this mixture by electrical discharges is very interesting from the viewpoint of the theory of origins of life. However, there are still many questions to answer, e. g. possible reaction pathways leading to the formation of amino acids and their radicals, or other organic compounds from this inorganic mixture.

Besides measurements of electrical discharge parameters, we performed an optical emission spectroscopy (OES) study of TS in the UV-VIS regions. The OES technique is widely used for plasma diagnostics, because it provides valuable information on excited atomic and molecular states. It enables to determine the rotational, vibrational, and electronic excitation temperatures of various plasma species, and thus the level of non-equilibrium and the gas temperature [30, 31]. In addition, it enables us to identify many radicals and active atomic or molecular species and so gives insight in the plasma chemical processes. This may help understanding and optimizing of processes leading to the formation of amino acids precursors, such as CN, HCN or NH_x species in the N_2-CO_2-H_2O mixture.

2. Experimental set-up

A DC high voltage power supply connected via a series resistor (R = 1.64–9.84 MΩ) limiting the total current was used to generate a positive TS discharge. The discharge voltage was measured by the high voltage probe Tektronix P6015A and the discharge current was measured using the current probe Pearson Electronics 2877 (1V/A) or a 1 Ω shunt, both linked to the 200 MHz digitizing oscilloscope Tektronix TDS2024.

The discharge reactor was a box made of acryl equipped with a quartz window transparent in the UV-VIS region. A stainless steel needle was used as a high voltage (HV) electrode, and a planar copper electrode was used as a low voltage (LV) grounded electrode. The distance between electrodes was 10 mm.

The experiments were carried out at room temperature and atmospheric pressure in N_2-CO_2-H_2O mixture. The concentration of CO_2 (c_{CO2}) in the N_2 carrier gas varied from 0 to 100 vol. %, while the total gas flow was kept at 0.32 l/min. Liquid water was directly in the reactor. The LV planar electrode was submersed, and the discharge was generated above the water surface. The distance between the HV electrode and the water surface was approximately 6 mm.

The UV-VIS spectra were obtained by an optical system leading to a dual-channel emission spectrometer Ocean Optics SD2000 (200–1100 nm, resolution 0.6–0.7 nm). The experimental set-up is depicted in Fig. 1.

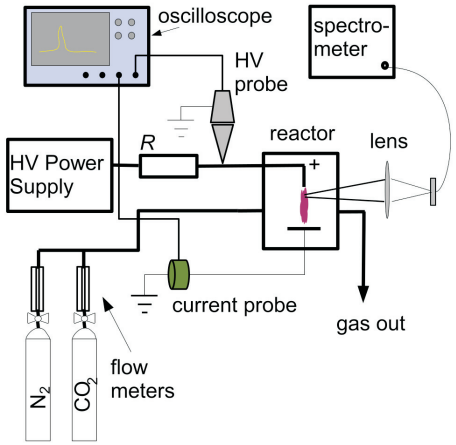

Fig. 1. Schematic of the experimental set-up.

3. Results and discussion

3.1. Electrical characteristics of TS

When a high voltage U_o applied to the stressed needle electrode was progressively increased, we first observed a streamer corona. As a characteristic threshold voltage (U_{TS}) was achieved, a transition to TS occurred. We found that U_{TS} increased almost linearly from about 7 to 13.5 kV as the CO_2 concentration in nitrogen increased from 0 to 100 vol. %.

The TS is initiated by a streamer that transforms to a short spark pulse. During the spark phase of TS, the internal capacity (C) discharges, the current given by

$$I \approx -C\frac{dU(t)}{dt} \tag{1}$$

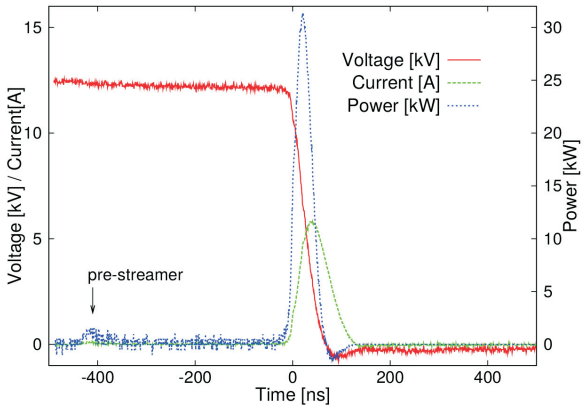

Fig. 2. Typical TS voltage and current waveforms, and calculated power, c_{CO2} = 50 vol. %, f = 1.75 kHz.

reaches a high value (~1 A), and the voltage drops to almost zero. The duration of the TS spark current pulse is usually in order of tens of nanoseconds, thanks to the small value of C (~10–50 pF). Fig. 2 shows typical waveforms of a TS pulse, together with the calculated power. The streamer preceding the TS pulse is also visible.

After the short spark pulse, C is recharged by a growing potential U on the stressed electrode. The potential U grows in time t according to the following equation:

$$U(t) = U_0[1 - \exp(-t / RC)], \tag{2}$$

where U_0 is the voltage on DC HV power supply.

As soon as U_{TS} is reached again, a new spark pulse appears preceded by a new streamer. This occurs in time $t = T$, given according to the (2) by:

$$T = RC \ln\left[\frac{U_0}{U_0 - U_{TS}}\right]. \tag{3}$$

From the equation (3) we get the characteristic repetition frequency f of the transient spark current pulses:

$$f = \frac{1}{T} = \frac{1}{RC \ln\left[\frac{U_0}{U_0 - U_{TS}}\right]}. \tag{4}$$

For typical R and C, the repetition frequency f is in the order of several kHz.

As f extends a certain value, TS may transform into a pulse-less glow discharge (GD) regime with a constant current of a few mA. Both TS and glow discharge regime are described in more detail in [9, 10, 32]. The transition between TS and GD is controlled by the external resistance R, the distance between the electrodes, and the gas flow rate. Moreover, it is also influenced by the gas composition. In the studied mixture, the threshold TS repetition frequency for transition to the GD generally increases with increasing CO_2 concentration.

Since TS is based on periodic charging and discharging of C, this parameter is important for the description and characterization of TS. We therefore calculated C by fitting the obtained current waveforms with the current calculated as the negative derivate of the measured voltage waveforms. We found that C = 32 ± 5 pF and it does not depend on the

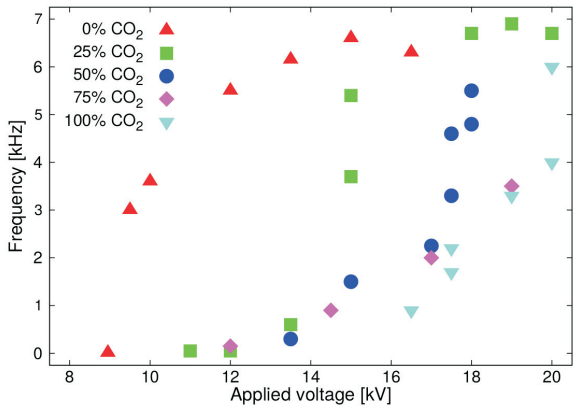

Fig. 3. Dependence of discharge frequency f on applied voltage U_o, R = 4.92 MΩ.

composition of the treated gas and the discharge frequency. It is mostly determined by the length of the HV cable connecting the HV electrode with the external ballast resistor *R*.

Based on equation (4), the TS repetition frequency can be controlled by U_o, and the increase of U_o above the threshold value leads to a monotonous increase of *f* (Fig. 3). However, the measured frequency is not absolutely regular. When U_o only slightly exceeds a threshold value for the appearance of the first TS pulses, the discharge frequency is very low and irregular. The actual value of U_{TS} slightly varies around its mean value from pulse to pulse. Moreover, the U_{TS} is not a constant for given gas mixture, but it changes with increasing TS repetition frequency (Fig. 4).

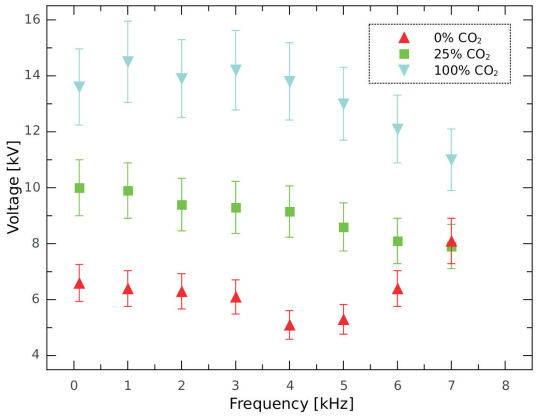

Fig. 4. The characteristic TS discharge voltage U_{TS} as a function of repetition frequency *f*.

In air, we previously observed almost linear decrease of U_{TS} with increasing *f* [16, 17]. This was attributed to the heating of the gas in the gap and the decrease of the neutral particles density. This enables U_{TS} to decrease while the reduced electric field *E*/*N* remains constant. The dependence of U_{TS} on f is more complicated in N_2-CO_2-H_2O mixture with TS generated above the water surface (Fig. 4). We also observed the increase of U_{TS} with increasing *f*. There are probably more effects influencing the behavior of U_{TS}. The gas heating with increasing *f*, resulting into the decrease of *N*, most probably also increases water vapor density. In mixtures with high CO_2 contents relatively high amount of CO can accumulate [28]. These changes in the composition of the treated gas then influence U_{TS}.

Knowing U_{TS} is very important for the description and characterization of TS. Several other discharge parameters, such as the total charge Q_p, and the energy delivered to the discharge gap per pulse (E_p) are functions of *C* and U_{TS}. They can be expressed as

$$Q_p = CU_{TS}\,, \tag{5}$$

$$E_p = \tfrac{1}{2}C(U_{TS})^2\,. \tag{6}$$

Finally, it is possible to calculate the power input to plasma P_{in} from E_p:

$$P_{in} = E_p \times f\,. \tag{7}$$

Power input thus increased with increasing TS frequency and increasing CO_2 concentration (Fig. 5), since U_{TS} was higher in CO_2 rich mixtures.

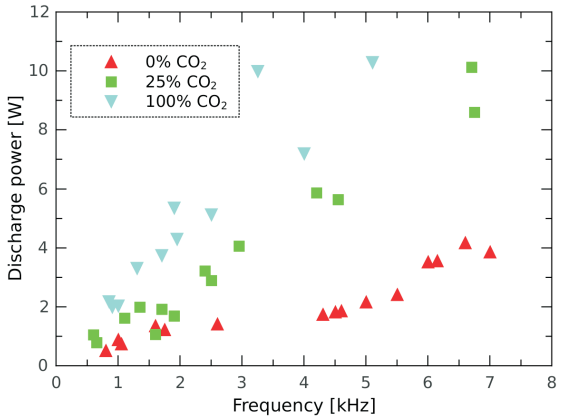

Fig. 5. The characteristic TS discharge voltage U_{TS} as a function of repetition frequency f.

Since both Q_p and E_p increase with increasing U_{TS}, it is not surprising that the amplitude of the TS current pulses (I_{max}) also grows with growing U_{TS} (Fig. 6). The I_{max} is thus typically higher in CO_2 rich mixtures where U_{TS} is higher. Moreover, these higher current pulses are also narrower, because the full with at the half of the maximum of TS spark pulses increases with the decreasing I_{max} (Fig. 7).

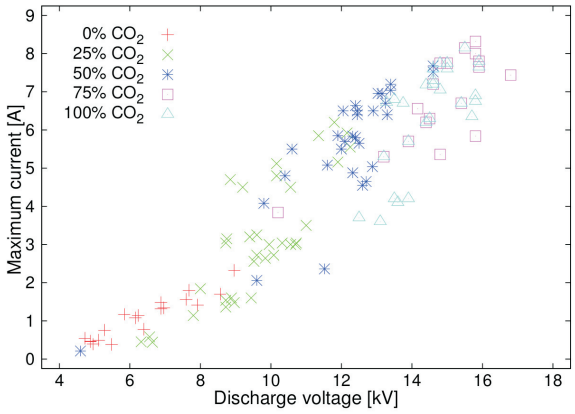

Fig. 6. Amplitude of the TS spark current pulses I_{max} as a function of U_{TS}.

3.2. Optical Emission Spectroscopy of TS

In the UV and VIS emission spectra of TS (Fig. 8 and 9), the strongest bands observed can be attributed to the emission of N_2 2-nd positive system ($C^3\Pi_u - B^3\Pi_g$) and CN violet ($B^2\Sigma^+ - X^2\Sigma^+$) systems. The emission of N_2 1-st positive system ($B^3\Pi_g - A^3\Sigma^+$), N_2^+ 1-st negative system ($B^2\Sigma^+ - X^2\Sigma^+$), OH ($A^2\Sigma^+ - X^2\Pi_i$) system, NH ($A^3\Pi - X^3\Sigma^-$) system, and atomic N, O and C lines was also observed.

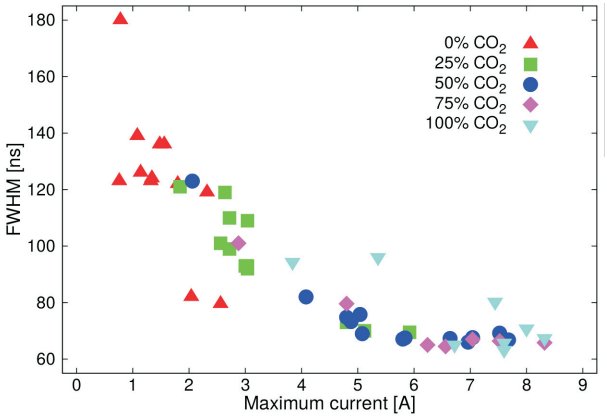

Fig. 7. Full width at half maximum (FWHM) of TS spark current pulses as a function of their amplitude.

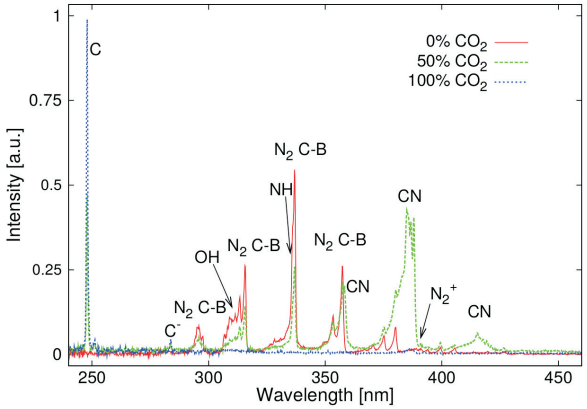

Fig. 8. Typical UV spectra of TS for selected CO_2 concentrations, f = 2.5 kHz.

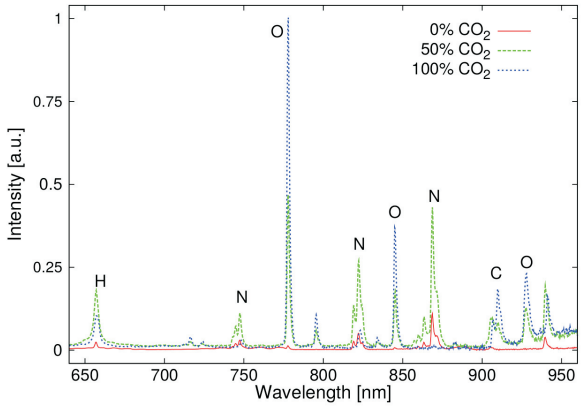

Fig. 9. Typical VIS spectra of TS for selected CO_2 concentrations, f = 2.5 kHz.

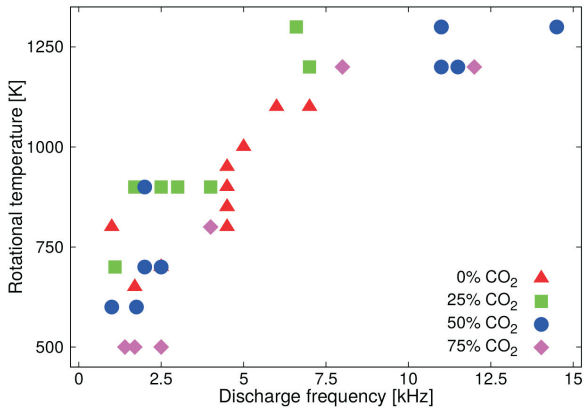

Fig. 10. Rotational temperature (T_r) calculated from the N_2 second positive system as a function of TS repetition frequency.

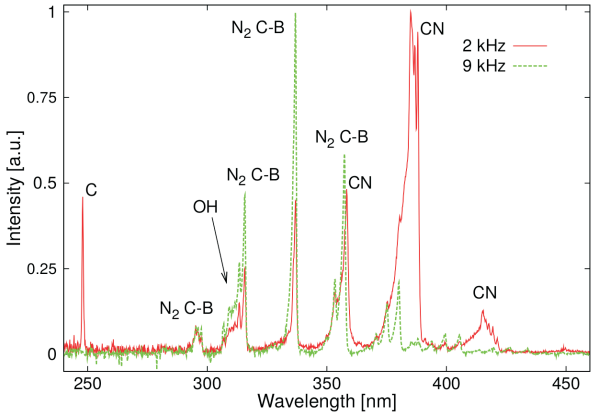

Fig. 11. Normalised UV spectra of TS at repetition frequency 2 and 9 kHz, c_{CO2} = 50 vol. %.

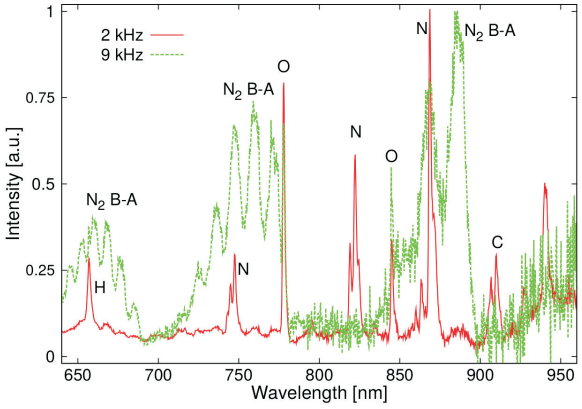

Fig. 12. Normalised VIS spectra of TS at repetition frequency 2 and 9 kHz, c_{CO2} = 50 vol. %.

The N_2^+ and atomic lines indicate plasma with high electron temperature and a high level of non-equilibrium. Non-equilibrium conditions were also confirmed by calculated vibrational (T_v) and rotational (T_r) temperatures, obtained by fitting the experimental N_2 2-nd positive system spectra with the simulated ones (we used Specair program [30]). The typical measured temperatures were: T_r = 500–1300 K (Fig. 10), T_v = 3100–5500 K.

The intensity of individual lines and emission systems changed as a function of c_{CO2} and TS frequency. For example, Fig. 8 and 9 show the obtained UV and VIS spectra as functions of c_{CO2} at f = 2.5 kHz. We can observe the increase of the intensity of C lines and the decrease of N_2 2-nd positive system as c_{CO2} increases. The intensity of CN emission reached a maximum in the mixture with 25 vol. % CO_2. However, it was not possible to compare absolute intensities from the measurements in different mixtures even at the same f, because the discharge "spatial distribution" changed with c_{CO2} as well [33]. The spectrometer's integration time varied from 0.2 to 2 s during the experiments, i.e. we collected emission integrated from at least several hundreds TS pulses, and the discharge in N_2 occupied much smaller volume than in 50 vol. % CO_2. Thus, the amount of the collected light from the focal point was much larger in N_2 than in the mixtures with CO_2, where only a certain fraction of the TS pulses contributed to the recorded spectra. Moreover, the discharge changed its appearance also as a function of f, especially in CO_2 containing mixtures, where the discharge contracted to smaller volumes as f increased.

We can thus only compare the ratio of various lines and emission systems at given frequency and given CO_2 concentration. For example, we found that the TS repetition frequency increase was accompanied by a significant difference between the obtained spectra (Fig. 11 and 12). At 2 kHz, CN emission dominated over N_2 2-nd positive system, and atomic lines (C, N, O) were clearly visible, whereas at 9 kHz, atomic lines disappeared and N_2 1-st and 2-nd positive systems dominated in the spectra.

4. Conclusions

We presented extensive investigations of transient spark discharge in N_2-CO_2-H_2O mixture at atmospheric pressure (with water electrode). Thanks to the very short spark pulse duration (<100 ns) given by a small internal capacity of the circuit generating TS and a limiting series resistor, the plasma cannot reach LTE conditions. On the other hand, the periodic streamer-to-spark transition provides non-equilibrium conditions with fast electrons resulting in strong chemical effects. Thus, TS represents a simple way for the generation of a pulsing discharge at high frequency with a DC power supply.

In the N_2-CO_2-H_2O mixture, TS generates CO, N, C, O, OH, CN and NH radicals, and N_2^+ ions. Some of these species may play an important role in the synthesis of amino acids and other organic species associated with the possible chemical evolution of life on the Earth. The efficiency of their production depended on the electrical parameters of the discharge and relative concentration of CO_2. The low frequency mode (~3 kHz) with stronger and shorter current pulses probably generated higher concentrations of radicals, as indicated by the emission intensity of atomic lines.

In future, we plan to perform time-resolved optical emission spectroscopy study of TS in N_2-CO_2-H_2O mixture to prove our hypothesis that the emission of atomic lines occurs

mainly during the spark phase of the TS discharge, and that they are related to the electron-ion dissociative recombination reactions.

Acknowledgement

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