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OPTICAL EMISSION SPECTROSCOPY OF ABNORMAL GLOW DISCHARGE IN NITROGEN-METHANE MIXTURES AT ATMOSPHERIC PRESSURE

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Abstract. The abnormal glow discharge was studied in electrode configuration corresponding to gliding arc arrangement with interelectrode gap of 2 mm at the discharge power up to 300 W in nitrogen-methane mixtures (0.5–2.5 % of methane) at atmospheric pressure. Both gases had purity better than 99.999 % and the whole system was evacuated before measurement to suppress oxygen traces. Optical emission spectra were taken in dependence on applied power and gas mixture composition. Nitrogen and CN radical spectra as well as atomic lines of hydrogen and carbon were identified. The vibrational temperatures of 2300–8000 K were determined from the spectra of nitrogen second positive, CN violet and C_2 spectral systems. Rotational temperature calculated from nitrogen second positive and CN violet 0-0 bands varied in the interval of 1200–4800 K depending on the experimental conditions.

1. INTRODUCTION

The Cassini space mission to Saturn and the release of its Huygens probe onto its largest moon, Titan, has led to a wealth of data on the atmospheric and surface composition of Titan, presenting us a set of unexpected results including the observation of hydrocarbon lakes – the first liquid 'seas' on a solar system body outside the Earth; and the observation of anions in the upper atmosphere (ionosphere) (Vuitton et al. 2009). In order to understand the physical and chemical processes leading to such observed phenomena, additional laboratory simulations are required.

The dense atmosphere of Titan is mostly composed of N_2 with a few percent of CH_4. The presence of clouds and strong convective motions are a particular feature of Titan's lower atmosphere. Charged particles, originating from the Saturnian magnetosphere, can accumulate on droplets within the clouds of the troposphere. Neutralization of these charged particles leads to discharges within the clouds which can induce chemical reactions in the Titan troposphere (Vinatier et al. 2007).

Most of experimental works have been performed predominantly in DBD, glow, microwave, RF and corona discharges, which are considered to be a good environment for the study of electron-molecule and ion-molecule reactions. To understand the molecular kinetics, energy distribution under the discharge conditions is needed. The optical emission spectroscopy is one of the ways how to obtain such information.

2. EXPERIMENTAL SET UP

The experimental set up is shown schematically in Fig. 1. The reactor was equipped by fused silica window situated 10 cm from the discharge perpendicularly to the gas flow through the reactor for the protection of thin layers deposition.

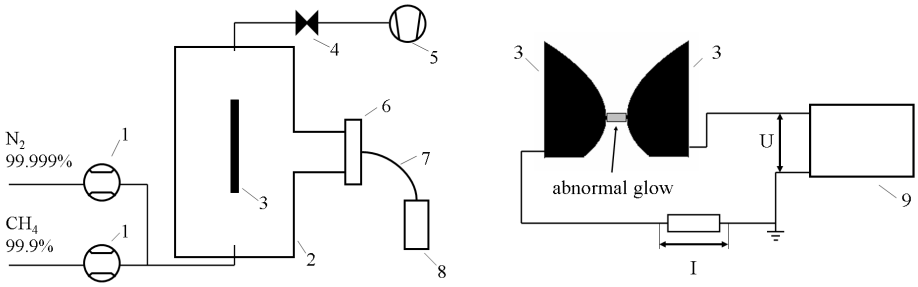

Figure 1: Simplified scheme of the experimental device: 1 – mass flow controller; 2 – discharge reactor; 3 – stainless steel electrode; 4 – vacuum valve; 5 – rotary oil pump; 6 – fused silica window; 7 – optical quartz fiber; 8 – spectrometer; 9 – HV power supply.

The Jobin Yvon TRIAX 550 spectrometer with CCD detector was used to monitor light emission from N_2/CH_4 plasma. The measurements were carried out in flowing regime of a total flow rate of 200 Sccm. The flow rates for both CH_4 and N_2 channels were regulated using MKS mass flow controllers. The discharge electrode system had a standard configuration of a classical gliding arc. A pair of stainless steel holders was positioned in parallel to the iron electrodes but in this case plasma was not gliding due to the low flow rate. Therefore stable abnormal glow plasma occurred between the electrodes at their shortest distance of 2 mm and formed plasma channel with diameter of 1 mm. With decreasing current (40–15 mA) the voltage was slightly increasing from 350 V to 400 V. Electrical parameters were measured by Tektronix oscilloscope using high voltage probe (1:1000) and non inductance resistor. The discharge was powered by DC HV source. The present experiments were performed for different N_2:CH_4 ratios in range from 0.5 % to 2% CH_4 in N_2 at atmospheric pressure. The whole device was prevacuated before measurement by rotary oil pump to keep the system as oxygen free.

3. RESULTS

The following molecular spectral systems were recognized in the spectra: second positive system of neutral N_2 ($C\ ^3\Pi_u \rightarrow B\ ^3\Pi_g$), first negative system of N_2^+ ion ($B\ ^2\Sigma_u^+ \rightarrow X\ ^2\Sigma_g^+$), CN violet ($B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$) and red systems ($A\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$), and C_2 ($^3\Pi \rightarrow X\ ^3\Pi$) Swan bands. Besides them the strong atomic H^α line, weak H^β, C (247 nm, measured in the second order) and N^+(399.5 nm) atomic lines have been recognized. The relative emission intensities for the selected emission bands are shown in Fig. 2.

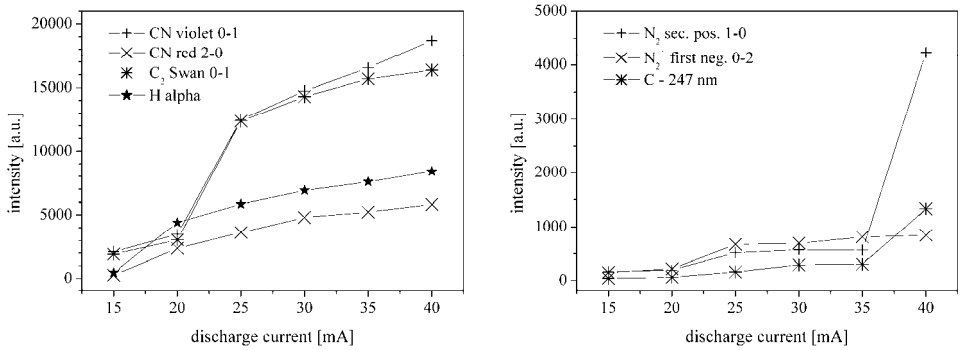

Figure 2: Emission intensities of selected bands in 2% CH_4 in N_2 mixture.

A slightly enhanced presence of N_2^+ ions in comparison to N_2^* molecules shows that the degree of plasma ionization increased with applied energy, in parallel with the number of free electrons. The high emission intensity of C_2 Swan system suggests the high decomposition degree of CH_4 into C than C_2 species, which is confirmed by the absence of emission lines of CH radicals.

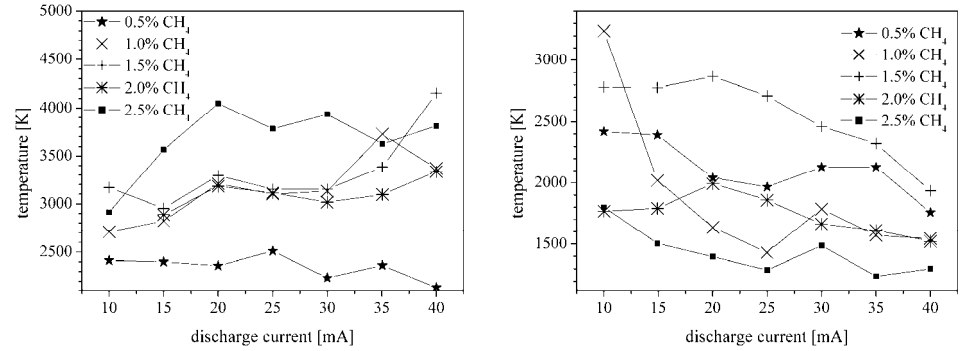

Figure 3: Rotational temperatures calculated from nitrogen second positive (left) and CN violet (right) 0-0 bands.

The N_2 rotational temperatures were calculated from CN violet 0-0 band (measured with high resolution using 3600 gr/mm grating) and from the nitrogen second positive 0-0 band (measured using 1200 gr/mm grating). The results are shown in Fig. 3. Temperature calculated from nitrogen spectrum varied in range from 2700 up to 3700 K. Its dependence on the discharge current had no function-

al behavior but it increased with the CH_4 molar ratio. The CN rotational temperature decreased with increasing current in range from 3200 to 1200 K. The CN rotational temperature increased with methane content in the gas mixture.

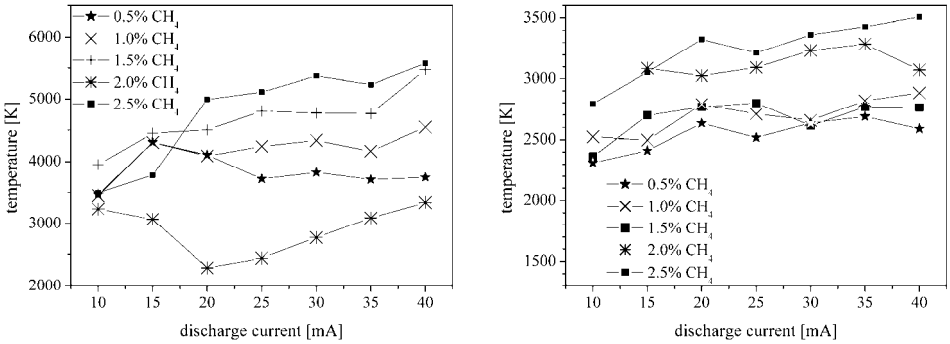

Figure 4: Vibrational temperatures calculated from the nitrogen second positive $\Delta v = -1$ sequence (left) and C_2 Swan system $\Delta v = +1$ sequence (right).

Vibrational temperatures were calculated from all nitrogen, CN and C_2 spectra. The results for nitrogen second positive and C_2 Swan systems are shown in Fig. 4. Bands and lines with signal/noise ratio better than 5 were used for the calculations, the other were omitted. The average uncertainty of calculated values was between 10 and 15 %. The vibrational temperature of nitrogen C state increased both with methane content and applied energy. The data obtained at 2.0% of methane in reaction mixture were probably irrelevant because they significantly differed from the others. The vibrational temperature of carbon diatomic molecule increased both with carbon content and applied power without any irregularities. The vibrational temperature (4800–6200 K) of N_2^+ ion decreased with increasing CH_4 content and increased with current, with a rapid fall at 40 mA. The plasma power and CH_4 molar ratio had a significant effect on the CN vibrational temperature, which reached values from 4200 to 6500 K and was more or less directly proportional to the current.

Acknowledgements

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