Univerzita Komenského v Bratislave

Fakulta matematiky, fyziky a informatiky

RNDr. Gabriel Horváth

Autoreferát dizertačnej práce

Laboratory simulation of Titan's atmosphere by electrical discharges

na získanie akademického titulu philosophiae doctor

v odbore doktorandského štúdia:
Fyzika plazmy

Bratislava 2011

Dizertačná práca bola vypracovaná v dennej forme doktorandského štúdia na Katedre experimentálnej fyziky, Fakulty matematiky, fyziky a informatiky v Bratislave

Predkladateľ: **RNDr. Gabriel Horváth**
Katedra experimentálnej fyziky
Fakulta matematiky, fyziky a informatiky
Univerzita Komenského
Mlynská dolina F2
84248 Bratislava

Školiteľ: **Doc. RNDr. Miroslav Zahoran, Csc.**
Katedra experimentálnej fyziky
Fakulta matematiky, fyziky a informatiky
Univerzita Komenského
Mlynská dolina F2
84248 Bratislava

Oponenti: **doc. Ing. Ivan Hotový, DrSc**.; ME ÚEF FEI - E118, Slovenská technická univerzita v Bratislave, Fakulta elektrotechniky a informatiky, Ilkovičova 3, 812 19 Bratislava.

Dr. Michal Stano PhD; FMFI UK, Mlynská dolina F2, 84248 Bratislava.

Prof. Nicholas Braithwaite; Head of the Department of Physics & Astronomy, The Open University, Walton Hall, MK7 6AA, United Kingdom.

(meno a priezvisko oponenta s uvedením jeho titulov a hodností
a názov ustanovizne, s ktorou je oponent v pracovnom pomere)

Obhajoba dizertačnej práce sa koná ..... o ..... h
pred komisiou pre obhajobu dizertačnej práce v odbore doktorandského štúdia vymenovanou predsedom odborovej komisie .....
(uviesť dátum vymenovania)

Študijný odbor, názov študijného programu doktorandského štúdia: **4.1.6 Fyzika plazmy**

na .....
(presná adresa miesta konania obhajoby dizertačnej práce)

Predseda odborovej komisie:
Prof. Dr. Štefan Matejčík DrSc
Katedra experimentálnej fyziky
FMFI UK v Bratislave
Mlynská dolina F2
842 48 Bratislava

TABLE OF CONTENTS

1.INTRODUCTION 4
2. EXPERIMENTAL RESULTS AND DISCUSSION 5
2.1 SIMULATION EXPERIMENTS IN CORONA DISCHARGES 5
2.1.1 Analysis of neutral gas- and solid products 7
2.1.2 Analysis of negative ions 9
2.2 SIMULATION EXPERIMENTS IN INNOVATIVE CH_4-N_2 ROD-TO-PLANE PACKED BED DBD DISCHARGE 10
2.2.1 Analysis of neutral gas products 11
2.3 SIMULATION EXPERIMENTS IN CH_4-N_2 GLIDING ARC DISCHARGE 13
2.3.1 Analysis of neutral gas products 14
3. CONCLUSIONS 16
REFERENCES 19
A) List of peer-reviewed articles related to the PhD thesis: 20
B) List of conference articles related to the PhD thesis: 20
C) Oral presentations at international conferences: 23
C) Citations of articles related to the PhD thesis: 24

1. INTRODUCTION

The presence of organic chemistry and the possible existence of primitive life on foreign planets has influenced the work of researchers across many different scientific disciplines. The Voyager and Cassini-Huygens space missions sent to the outer planets of our Solar system have shown that Saturn's largest satellite, Titan is one of the most fascinating extraterrestrial solar bodies. Although Titan is classified as a moon, it is larger than both Mercury and Pluto. Its atmosphere is characterized by a higher density and atmospheric pressure than Earth's atmosphere however, it is mainly composed of nitrogen, methane and organic trace species such those hydrocarbons and nitriles which are the necessary precursors of amino acids, themselves important building elements for formation of life. Therefore researchers sometimes call Titan as "the cradle of life" because Earth's prehistoric atmosphere and surface is believed to have been similar [1].

In 1980 the Voyager space probe reached Titan in order to collect data about its atmosphere and surface, since liquid methane/ethane lakes were suspected by the astronomers. Unfortunately, the atmosphere seemed to be impenetrable and the only photos that could be taken were of Titan's mystery atmosphere and some spectroscopic measurements in the upper atmosphere.

Cassini and its Huygens package (which landed on Titan's surface in 2005) has revealed an enormous amount of information about the composition of Titan's atmosphere and confirmed that its surface is covered with organic lakes and rivers. However, understanding the physical and chemical mechanisms that dominate the organic chemistry that such observations revealed needs further research. The dissociation of methane and nitrogen together with subsequent hydrocarbon formation in the upper atmosphere is due to UV-radiation coming from space and heavy ionic species released from Saturn's magnetosphere, while in the lower atmosphere electrical activity and discharges initialize an organic chemistry. Therefore researchers have sought to carry out experiments to mimic these planetary conditions in the laboratory. This thesis is dedicated to the simulation of the organic chemistry in atmospheric pressure nitrogen-methane plasma discharges that may be used to explore Titan atmospheric chemistry. The main aim of this thesis is to understand the effect of different types of plasma on major physical/chemical processes in N_2-CH_4 discharges.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1 SIMULATION EXPERIMENTS IN CORONA DISCHARGES

[*ATTACHMENTS 1-3*]

These papers describe our very first experiments made in CH_4-N_2 corona discharges during my scientific missions to the Open University and Hiden Analytical in England. Due to compatibility requirements a wire-to-cylinder (coaxial) corona was designed to be placed in a FTIR spectrometer, while a point-to-plane corona electrode configuration has been chosen to be connected to the sampling entrance of a QMS spectrometer.

The main aims of this project were as follows:

- identification of neutral gaseous products formed in a cylindrical CH_4-N_2 corona discharge using FTIR spectroscopy.
- identification of solid products formed at the electrodes in a cylindrical CH_4-N_2 corona discharge using SEM-EDS analytical technique.
- identification of major negative ions releasing from a point-to-plane corona using high sensitivity QMS technique.
- monitoring and analysis of Current-Voltage characteristics in both corona configurations.
- qualitative comparison of discharge products with trace organic species detected in Titan's lower atmosphere.

Coaxial corona design. The active length of the corona reactor volume was 70 mm but the total optical length of the reactor was larger (100 mm) due to electrode holder rings at the both end of the chamber (Fig. 1). A wire electrode made of stainless steel and having diameter of 0.125 mm was centered in a brass tube having inner diameter of 16 mm. The wire electrode was connected to a high voltage and the outer electrode was grounded (also due to safety reasons). This cylindrical body was capped by KBr spectroscopic windows that allowed the IR beam through the electrode gap. This construction was then completed by inlet and outlet pipes that allowed the flow of CH_4-N_2 gas mixture through the cell. This design allowed us to record real-time evolutions of the discharge products formed after irradiation of the CH_4-N_2 gas mixture in flow-stopped regime. The need for in-situ measurements of product evolution was necessary due to the low productivity of corona in static regime.

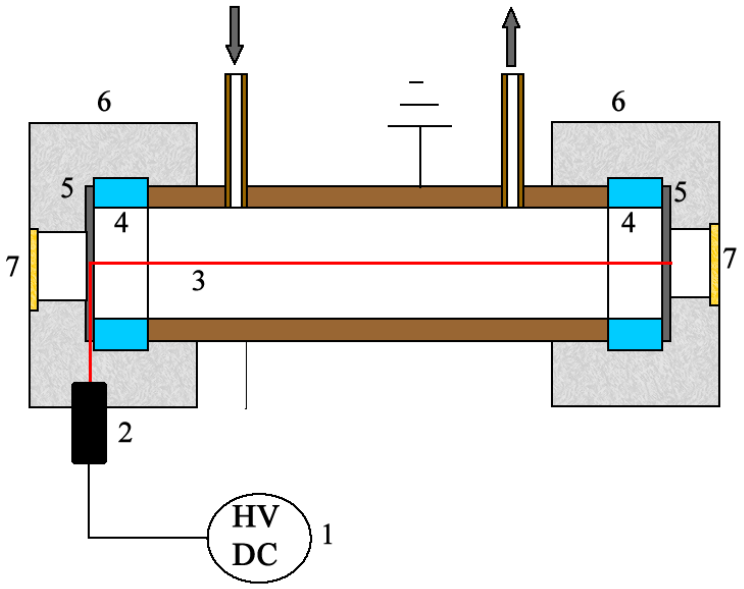

Fig. 1. Schematic diagram of the cylindrical corona used. 1 – DC HV power supply; 2 – external HV feedthrough for the wire electrode; 3 – wire electrode centered in the cylindrical gap; 4 – Teflon rings separating grounded cylinder electrode (brown color) and HV electrode holders; 5 – HV electrode holders; 6 plexiglas body; 7 – KBr spectroscopic windows allowing FTIR analysis.

Point-to-plane corona design. In this case the high voltage electrode was a stainless steel needle oriented perpendicularly to the sampling entrance of a molecular beam mass spectrometer. Therefore this metallic entrance body represented the grounded planar electrode. The discharge body was made of brass equipped with a Plexiglas needle holder connected to the top of this chamber. Inlet and outlet pipes were welded to the outer side wall. The distance between the needle and the planar electrode was set to 8 mm in order to ensure the same inter-electrode distance as in case of coaxial corona. This discharge configuration had a constant volume of 80 cm^3. Ionized products formed in the discharge could be then pumped through the tiny sampling orifice of diameter 0.2 mm (Fig 2).

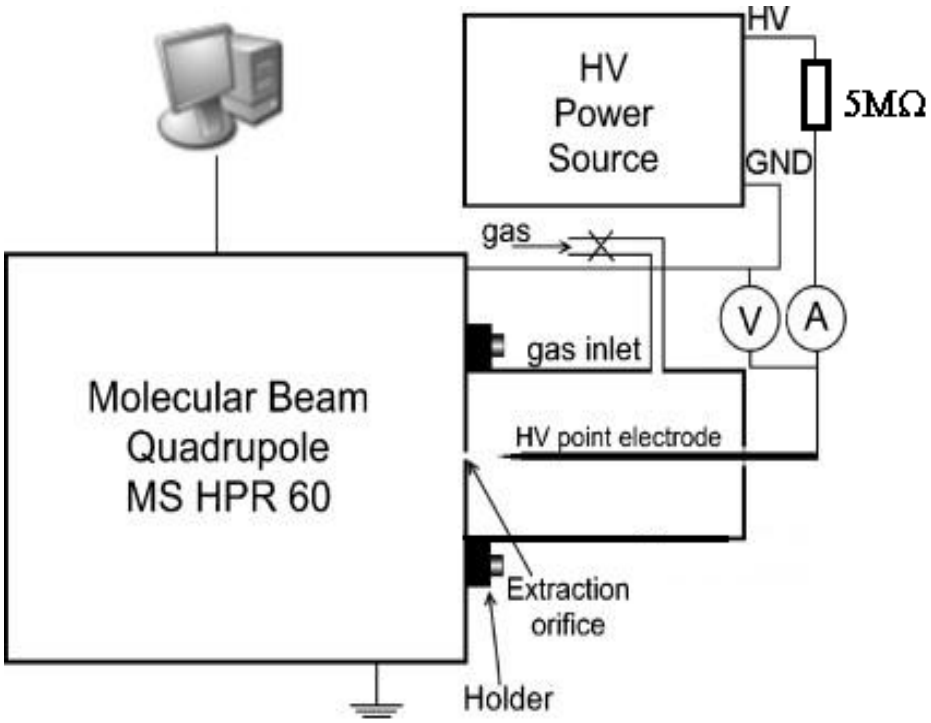

Fig. 2. Schematic diagram of point-to-plane corona design and experimental setup. The corona reactor was specially designed and built on the molecular beam quadrupole mass spectrometer manufactured by Hiden Analytical Ltd.

2.1.1 Analysis of neutral gas- and solid products

[*ATTACHMENTS 1-2*]

We have explored the formation of the chemical species produced in a coaxial corona discharge fed by a mixture of N_2 and CH_4 at atmospheric pressure and ambient temperature (both gases having quoted purities of 99.995%). The gaseous CH_4-N_2 (2:98) mixture in the wire-to-cylinder corona was prepared by MKS mass flow controllers with valves on the inlet/exhaust closed to use the reactor in static regime (see Fig 1 in ATTACHMENT 1). The CH_4-N_2 gaseous mixture was irradiated by corona plasma in a flow stopped static regime. The discharge was operated by a DC high voltage power supply (Glassman) at a constant voltage 6.6 kV for 12-14 minutes, the wire electrode was connected to a high voltage and the main electrical parameters such as discharge current and voltage were measured using high accuracy Fluke multimeters. The cylindrical discharge reactor was equipped with spectroscopic KBr windows and placed in the sample compartment of a Nicolet FTIR spectrometer and the IR beam passed through the drift region of the corona. Concentrations of the detected organic compounds were estimated from measured FTIR absorbance data using well known absorption cross-section values for the molecules and adopting the widely used Lambert-Beer formula. Solid products,

deposited on the wire electrodes, were examined using TESCAN VEGA TS 5136 MM Scanning Electron Microscope and INCA x-sight Energy Dispersive X-ray Microanalyser.

A small amount (0.2%) of CH_4 was decomposed after 12 min of treatment. After 12-13 min the discharge was stopped due to the formation of a yellow deposit on the wire electrode. 2% of CH_4 in N_2 caused a rise in the breakdown voltage of the discharge (in comparison with pure N_2 corona discharge) and led to a reduction in the observed discharge current. Simple organics were found to be the major products formed in this CH_4-N_2 corona discharge including C_2H_2, C_2H_6 and HCN: all species that have been detected in Titan's atmosphere by the Cassini-Huygens probe [2]. It should be mentioned that HCN was to be found the most dominant product which is in good agreement with the real constitution of Titan's lower atmosphere.

The temporal evolution of gaseous products C_2H_2, HCN and C_2H_6 was also measured. Analysis of these products showed a nearly linear increase with time during the first 10 minutes of the discharge after which saturation was observed. After 12–13 min a solid orange deposit was observed to form on the central wire electrode, these deposits built up until the thickness of deposit reached a critical value after which the necessary conditions for a stable corona discharge could not be sustained and instead a spark discharge was formed. The spark channels melted the deposit at certain points then formed small craters on the deposit surface which could be clearly distinguished by SEM–EDS analysis (see Fig. 4a,b in ATTACHMENT 2). EDS-analysis of the electrode surface showed that the C/N ratio in the deposit had an average value of 2.84, while the edges of mentioned craters showed a C/N ratio with a value 9.8. Such composition is similar to that observed in other N_2-CH_4 discharges (see ATTACHMENT 2) and is believed to be an analogue of the aerosol and dust observed in Titan's atmosphere being composed of chemical species commonly known as 'tholins' [2].

Deeper analysis and structural characterization of these craters, however, provided an **unexpected contribution** of corona discharge experiments. Mapping such features proved that the spark channels consisted of streamers and secondary electron avalanches. In other words, the measured average crater radius was surprisingly equal to the theoretical radius r_H of a streamer head near the active electrode surface. The observed head radius r_H ~25μm only slightly differed from the theoretical value of r_H = 23.3μm calculated (see equation (9) in the thesis), thus supporting the validity of classical streamer theory. Townsend coefficient α needed for such calculations was estimated by equation (1):

$$\frac{\alpha(x)}{p} = A\exp\left(-\frac{B}{\frac{E(x)}{p}}\right) \qquad (1)$$

where parameters *A, B* (valid at given pressure *p*) were taken from [3] and *x* is in our case the radius of ionization region (~500μm). Since the requirement for streamer formation is $E_o \sim E^*$, streamer head radius can be simply described as $r_H = 3/\alpha$. Electron density n_e in the streamer head was estimated as $n_e = 9.10^{13}$ cm^{-3}.(see equation (10) in the thesis) Moreover, secondary mini-craters distributed at the border of a primary crater (see Fig. 4b in ATTACHMENT 2) are clearly caused by secondary electron avalanches which started to develop in the front of the streamer head.

2.1.2 Analysis of negative ions

[*ATTACHMENT 3*]

We have also explored the formation of negative ions extracted from a point-to-plane coaxial corona discharge fed by a mixture of N_2 and CH_4 with small amount of Ar admixture (CH_4:N_2:Ar = 2:96:4) under the same experimental conditions as described in 2.1.1. However, in this case the corona chamber was aligned opposite the sampling entrance of a HPR60 (Hiden Analytical Ltd.) molecular beam mass spectrometer (Fig. 2).

From an astrophysical/planetary science point of view perhaps the most significant result of our studies was the detection of the CN^- anion which has been found to be the most dominant negative ion in the discharge and is believed to be the precursor of the heavier negative ions detected such as C_3N^- and C_5N^-. The most likely pathway for the formation of such molecular anions is H-loss dissociative electron attachment to HCN, HC_3N and HC_5N formed in the discharge. These same anions have also been detected in Titan's atmosphere and our experiments provided some novel interpretation of the electrochemistry and physical mechanisms active in Titan's atmosphere.

2.2 SIMULATION EXPERIMENTS IN INNOVATIVE CH_4-N_2 ROD-TO-PLANE PACKED BED DBD DISCHARGE

[*ATTACHMENT 4*]

Experiments conducted in corona discharges have provided us with information about processes within CH_4-N_2 plasmas where the mean electron energy reaches values up to 10-20 eV. Such electron energies are caused by the high electric fields generated by the shape wire/point electrodes. However the concentration of electrons in a corona is relatively low due to the small active plasma volume. Therefore investigations of atmospheric discharges producing electrons with lower energies are important for understanding plasma chemical processes in different conditions. We therefore designed a packed bed DBD (Dielectric Barrier Discharge) plasma reactor in order to investigate plasma chemical processes resulting from low energy electrons (1-10 eV).

DBD design. This discharge reactor-design had an unusual electrode geometry (Fig. 3). The main reactor body was a coaxial chamber made of stainless steel, with a length and diameter of 58 and 44 mm, respectively.

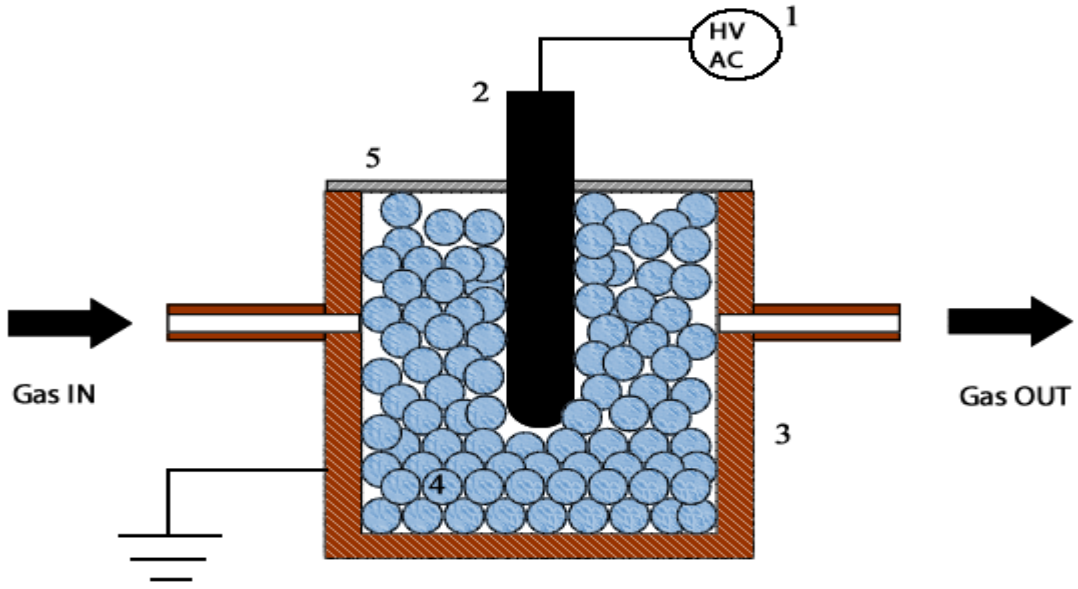

Fig. 3. Schematic diagram of the DBD reactor design. 1 – DC HV power supply; 2 – HV rod electrode with a shaped end; 3 – outer cylindrical electrode; 4 – borosilicate glass balls; 5 – electrode holder made of Plexiglas.

The bottom was closed by a stainless steel plate. A centered stainless steel rod acted as the central electrode (length = 50 mm) placed 8 mm from the bottom and had a diameter of 8 mm. The end of this electrode was curved having a radius 4 mm, in order to avoid sparking. The discharge gap was filled with borosilicate glass balls (diameter of the pellets was 6 mm). Inlet and outlet connections were fixed onto the outer side wall of the chamber.

The rod electrode was connected to an AC high voltage (f = 11.3 kHz, $U_{pk\text{-}pk}$ = 20&25 kV) whilst the reactor body was grounded. This construction allowed the formation of a non-uniform cold plasma in the discharge gap, where the pellets increased the active plasma surface. This innovative electrode design was believed to significantly improve catalytic surface processes in contrast with commercial cylindrical packed DBD discharges. In addition to the coaxial electric field around the rod an additional semi-spherical electric field occurred at the end of the rod electrode which highly increased the occurrence of microdischarge filaments.

Experiments were carried out at atmospheric pressure and at ambient temperatures. The measurements were carried out in flowing regime over the range from 25 to 200 sccm, with mixing ratios between 2 and 10% methane in nitrogen (both gases having quoted purities of 99.995%). The gas mixture was introduced into the reactor using MKS mass flow controllers. The discharge was typically ignited for between 30 and 60 min during which time the nascent reactor temperature (as measured by thermocouples on the reactor walls) did not rise above 300 K. The discharge was operated at two fixed voltages (20 and 25 kV peak-to-peak), a fixed frequency 11.3 kHz and over a wide range of discharge currents (up to 90 mA peak-to-peak) using a power supply system consisting of an oscillator, a Behringer amplifier and a homemade transformer. The voltages were monitored by a digital Tektronix TDS 3032B oscilloscope using a home-made HV probe and the current waveform was measured on a 10 Ohm resistor connected to the grounded part of the circuit. The discharge power could then be calculated from the measured current–voltage waveforms. A schematic diagram of the simple experimental setup can be found in [ATTACHMENT 4].

2.2.1 Analysis of neutral gas products

The DBD reactor was connected to an infra-red gas cell equipped with KBr windows and placed in a Nicolet Nexus FTIR spectrometer. The spectra were recorded at a

resolution 2 cm^{-1}, which provided the necessary conditions for a qualitative analysis of the products. The gaseous product concentrations were calculated using the Beer-Lambert formula with the necessary IR absorption cross-section data drawn from standard databases [89].

FTIR spectral measurements of the products formed in the DBD discharge revealed that the main chemical products were C_2H_2, HCN and C_2H_6 produced by dissociation of CH_4, with small but significant traces of NH_3 (see details about product yields in ATTACHMENT 4). The formation of NH_3 was assigned to the catalytic reactions active on the large surface area of dielectric balls. Similarly to corona experiments, HCN was found to be the most dominant product after plasma irradiation with C_2H_2 and C_2H_6 being the next most dominant species. Such results may also provide some insight into the chemical processes prevalent in the atmosphere of Titan. The discharge productivity for HCN and NH_3 was estimated as a function of specific input energy μ measured in unit kJ/L. Therefore measurements were conducted over a range of μ from 1 up to 30 kJ/L. The input energy μ has a significant effect on both HCN and NH_3 synthesis: the larger the value of μ, the more HCN and NH_3 were synthesized and with increasing initial CH_4 content the yields of HCN and NH_3 both increased (Fig. 5 in ATTACHMENT 4).

During the operation of the discharge a solid brown-yellowish deposit was formed on the central rod electrode and the dielectric pellets. Unfortunately due to the large size of the electrode the deposit could not be analyzed via SEM-EDS technique, since the rod electrode could not fit into the sample holder of SEM chamber.

2.3 SIMULATION EXPERIMENTS IN CH_4-N_2 GLIDING ARC DISCHARGE

[*ATTACHMENTS 5-6*]

Because both the corona and DBD discharges are commonly known as strongly non-thermal plasmas, further experiments were suggested using a gliding arc discharge which is a transition state between non-thermal and thermal plasma (see Chapter 4.3 in the thesis).

The apparatus used in these experiments is shown schematically in Fig. 4 (also see ATTACHMENTS 5-6]. The reactor was connected to the long path IR gas cell equipped with KCl windows and placed in a Nicolet Nexus FTIR spectrometer. Optical Emission Spectrometry (OES) using a Jobin Yvon Triax 550 spectrometer with a CCD detector was used to monitor the optical emission from the N_2/CH_4 plasma. The spectral response of this spectrometer was obtained using an Oriel radiation standard lamp. The 3600 g/mm grating was used for the rotationally resolved CN violet 0–0 band acquisition, all other spectra were measured with 1200 g/mm grating. The measurements were carried out in a flowing regime with a total flow rate of 200 sccm at ambient temperature and atmospheric pressure with CH_4 concentrations ranging from 0.5% to 2%.

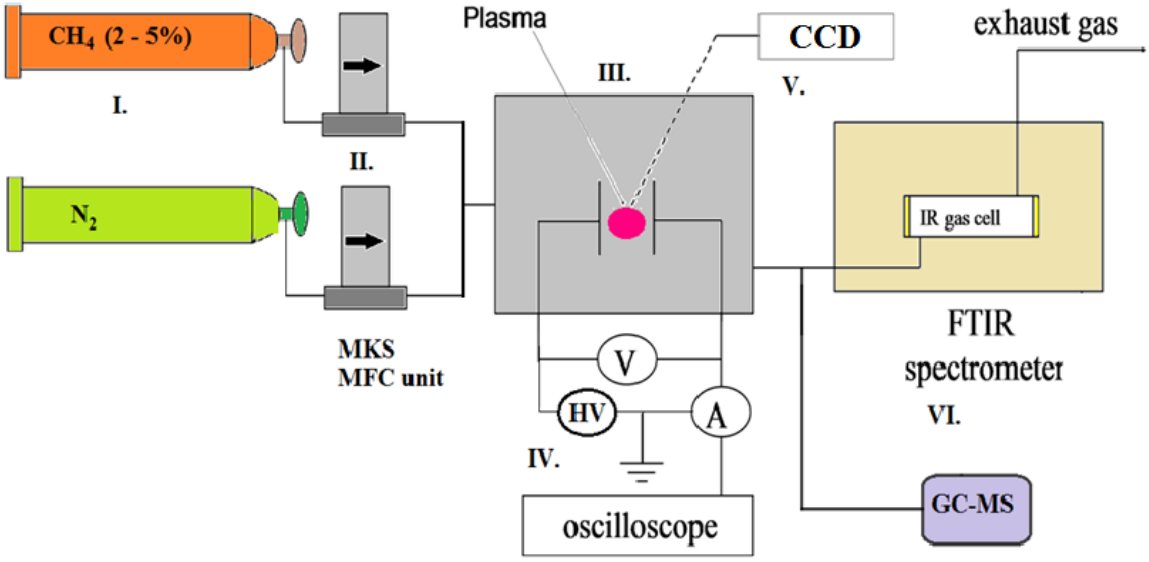

Fig. 4. Schematic diagram of experimental setup for gliding arc discharge: I. – gas cylinders; II. – mass flow controllers for setting required gas mixtures; III. – plasma reactor; IV. – HV power supply; V. – optical emission spectrometer for plasma radiation analysis; VI. – FTIR/GC-MS spectrometer for neutral product analysis.

The flow rates through the reactor for both CH_4 (purity 99.995%) and N_2 (purity 99.999%) were regulated using MKS mass flow controllers. The reactor chamber had a volume of 0.3 L. The discharge was typically operated for between 60 and 120 min during which time the nascent reactor temperature (as measured by thermocouples on the reactor walls) did not rise above 320 K.

Discharge design. The discharge electrode system had the standard configuration of a commercial gliding arc (see Fig. 4 in the thesis). A pair of stainless steel holders was positioned in parallel to the iron electrodes but in this case the plasma was not gliding due to the low flow rate and therefore stable abnormal glow plasma occurred between the electrodes at their shortest distance of 2 mm, forming a thin plasma channel with a diameter of 1 mm. The discharge was powered by a home-made DC HV source. Electrical parameters were measured using a Tektronix TDS 3032B oscilloscope with a homemade high voltage probe and a 10 Ω resistor for current measurement. Increasing the current from 15 to 40 mA saw the voltage slightly decrease from 400 V to 350 V, indicating an increase in the conductivity.

2.3.1 Analysis of neutral gas products

The formation of the chemical products produced in an atmospheric glow discharge fed by a N_2-CH_4 gas mixture was studied using a combined FTIR/GC-MS technique and Optical Emission Spectrometry (OES).

GC-MS analysis of the gaseous products showed that HCN, C_2H_2, CH_3CN are the major products in our CH_4-N_2 abnormal glow plasma. The yields of these compounds are such that HCN > C_2H_2 > CH_3CN. Thanks to the high sensitivity of GC-MS spectrometer, we could also detect low concentration products. Minor products detected using GC-MS were: ethane, ethene, cyanogens, propene, propane, propyne, propadiene, butenyene, butadiene, butadiyne, acetonitrile 2-propenenitrile, 2-propennitril, benzene and toluene.

FTIR-measurements revealed HCN and NH_3 to be the major products of the plasma with a smaller amount of C_2H_2, however, trace products detected by GC-MS analysis could be measured by FTIR due to optical sensitivity of long path infrared cell. All of these molecules have already been detected in Titan's atmosphere, thus improving our predictions about the main sources of Titan's organic plasma chemistry. Unfortunately, due to the sensitivity limitations of the chromatography, NH_3 could not be detected by the GC-MS technique.

In the recorded emission spectra the N_2 and CN bands were the most dominant. The spectra were composed of the following molecular spectral systems: the second positive system of neutral N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$), the first negative system of N_2^+ ion ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$), the CN violet ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$a) and red systems ($A^2\Sigma^+ \rightarrow X^2\Sigma^+$) and the C_2 Swan bands. Besides these the strong atomic H^α line, weaker H^β line and weak lines of C (247 nm - measured in the second order) and N^+(399.5 nm) were also detected. Using our OES study we could estimate the temperatures T_g, T_r and T_v which - together with the electrical parameters - allowed us to calculate the current and electron number densities in the discharge with typical values of 1.9-5.1 A/cm^2 and $n_e \sim 10^{13}$ cm^{-3}. Therefore, the continuous glow discharge was 'hot' with average $T_g \sim T_r$ ~2700-3700 K, since most of electron energy is converted into gas heating. Due to the measured values of T_g, the plasma was close to 'local thermodynamical equilibrium' but not close enough to assume a Maxwell distribution. Details of observed plasma chemistry and mechanisms are fully discussed in our articles [ATTACHMENTS 5-6].

3. CONCLUSIONS

This work presented in this dissertation thesis presents the potential for plasma technology to be exploited in a new cross-disciplinary research area *"Laboratory simulations of planetary atmospheres*". The main aim of this work was to synthesize the constitution of Titan's atmosphere in laboratory conditions by use of plasma discharges, because the aforementioned atmosphere is rich in organics and it is believed to be a mimic of the atmospheric conditions found on prehistoric Earth. The origin of such organic chemistry is veiled in the plasma chemistry generated by atmospheric electricity, energetic particles coming from Saturn's magnetosphere or ionosphere and UV radiation coming from the space.

Therefore, the major contribution and benefit of this PhD thesis is that it provides possible scientific explanations to the most highlighted biochemical questions "*What is the origin of life?*". Atmospheric pressure electrical discharges fed by various CH_4-N_2 gaseous mixtures developed in our laboratories were found to be a good environment to mimic organic plasma chemistry and astrophysical conditions of Titan's lower atmosphere (where the pressure is about 1 bar), since plasmas were found to be a good sources of electrons, UV radiation, furthermore ionized and excited species: all particles that also induce organic chemistry in Titan's atmosphere. Our long-term research programme was subdivided into 3 research areas, *i.e.* experiments carried out in CH_4-N_2 mixtures at atmospheric pressure and laboratory temperature in:

- *corona discharges*
- *dielectric barrier discharges (DBD)*
- *gliding arc discharges.*

The choice of such plasma sources is due to their different electron temperatures:

- **Corona discharge** – characterized by high energy electrons.
- **Dielectric barrier discharge (DBD) -** characterized by low energy electrons.
- **Gliding arc discharge** – characterized by lower difference between electron temperature and gas temperature

The results of this dissertation work can be summarized as follows:

Corona discharges fed by CH_4-N_2 mixture have been found to be the best "simulators" of Titan-like conditions, since they can also be easily formed between charged aeorosol particles in Titan's lower atmosphere. Our experiments provided an explanation about initial ionization parameters in such discharges, it has been determined that corona is characterized by high energy electrons with the mean electron energy reaching values up to 20 eV. However, mean electron concentration were quite low (only up to 10^{12} cm^{-3}), therefore it could be concluded that corona is weakly ionized plasma. The big advantage of this plasma was that the volume of corona sheet surrounding the thin wire/point electrode is smaller than the whole electrode gap by 3 orders of magnitude. This feature is believed to be a good analogue to the real plasma-to-gas volume ratio in Titan's atmosphere.

SEM-EDS analysis at the wire-electrode covered by fine deposit layer provided a fascinating observation. Since the formation of solid deposits blocks the necessary conditions for a stable corona the discharge could not be sustained and a spark discharge was generated that formed small craters at the deposit surface. The dimensions of these craters provided accurate data about the size of impacting spark streamers and the electron concentration in the streamer head. Measured and estimated values of streamer head diameter were 25 and 23.4 μm. Concentration of electrons in the streamer head reached values up to 10^{14} cm^{-3}.

FTIR analysis showed that the main measurable gaseous products formed in the CH_4-N_2 corona discharges were C_2H_2, C_2H_6 and HCN: all species detected in Titan by Cassini-Huygens space mission. The most dominant species was HCN which is also in good agreement with the real Titan's conditions. Mass spectrometric (QMS) measurements confirmed the high dominancy of CN^- anions: its abundance in the interstellar medium and also in Titan's atmosphere is relatively high. In consequence, CN^- anion is believed to be the precursor of the heavier negative ions detected in lower densities such as C_3N^- and C_5N^-. Our experiments also verified that the most likely pathway for the formation of such molecular anions is H-loss dissociative electron attachment to HCN, HC_3N and HC_5N molecules formed in corona discharge.

Further contributions and benefits of this thesis are simulation experiments made in an innovative self-designed rod-to-plate DBD discharge which provided us with information on heterogeneous surface processes. From an astrophysical and astrochemical

point of view these experiments simulated conditions near the surface of Titan. This type of discharge is typically known as cold plasma and the mean electron energies are in range 1-10 eV, which – in contrast to corona discharge – ensured the conditions needed for plasma chemistry processes induced by low energy electrons and particles.

FTIR analysis showed that the main detectable products formed in this CH_4-N_2 DBD discharge were C_2H_2, C_2H_6, HCN and NH_3: again, all species observed in Titan's atmosphere. The detection of NH_3 was assigned to heterogeneous effects: ammonia is typically formed via catalytic reactions, in our case formed on the large surface area provided by the dielectric pellets placed in the electrode gap. Our results may explain why NH_3 is found in higher concentrations in Titan's atmosphere near its surface. Therefore NH_3 found at higher altitudes is a result of a particle penetration from lower altitudes.

Our DBD experiments also provide a plausible low-cost industrial alternative for NH_3 productions using DBD discharge fed by nitrogen and natural gas. However the investigation of industrial relevance of such plasmas was not an object of our present research plan but optimization of this technology may be the topic of a future collaborative research.

The contributions and benefits of experiments in CH_4-N_2 gliding arc discharge are linked to in the high sensitivity of the analytical techniques used which allowed us to probe questions relevant to constitution of Titan's atmosphere. Experiments made in CH_4-N_2 gliding arc discharge helped us to mimic and understand conditions where electron temperature and concentration is higher than in case of corona and DBD discharges, for example in the case of energetic lightning in Titan's atmosphere. The main products formed in this CH_4-N_2 plasma have been analyzed by high sensitivity FTIR/GC-MS analysis that allowed us to determine trace products as well. Results showed that the main products were acethylene, hydrogen cyanid, acetonitril and other minor constituents such ethane, ethene, cyanogens, propene, propane, propyne, propadiene, butenyene, butadiene, butadiyne, acetonitrile 2-propenenitrile, 2-propennitril, benzene and toluene. All these species have also been detected in Titan's atmosphere and are believed to be precursors of higher important organics such DNA nucleotids.

As a consequence of the presented results we can conclude that all of the investigated discharges are good analogues for the organic plasma chemistry active in Titan's atmosphere. Future experiments should explore similar discharge experiments at lower pressures (down to 10^{-2} mbar) and temperatures (down to 98 K) which is the

temperature at Titan's surface) in order to experimentally simulate processes in Titan's upper atmosphere.

REFERENCES

[1] http://www.solarviews.com/cap/sat/titanrot.htm

[2] Brown HB, Lebreton J-P and Waite JH. Titan from Cassini-Huygens, *ISBN 978-1-4020-9214-5* (2009).

[3] Raizer Y P, Gas Discharge Physics, Springer-Verlag (1991) ISBN 3-540-19462-2.

A) List of peer-reviewed articles related to the PhD thesis:

1. Corona discharge experiments in admixtures of N2 and CH4:A laboratory simulation of Titan's atmosphere, **Horvath G**., Skalny J.D. , Mason N.J. and Zahoran M., *IOP-Plasma Sources Sci. Technol.* **18** (2009) 034016.

2. Negative ions formed in N2/CH4/Ar discharge - A simulation of Titan's atmosphere chemistry, **G. Horvath**, N.J. Mason, M. Zahoran, S. Matejcik, Y. Aranda Gonzalvo, *Eur. Phys. J. Appl. Phys*, **49**, 13105 (2010).

3. Packed bed DBD discharge experiments in admixtures of N_2 and CH_4, **G. Horvath**, J. D. Skalny, J. Orszagh, R. Vladoiu, N. J. Mason, M. Zahoran and S. Matejcik, *Plasma Chemistry and Plasma Processing*, **Vol. 30,** Issue 5 (2010), Page 565 (2010).

4. Organic chemistry of NH_3 and HCN induce atmospheric abnormal glow discharge in N_2-CH_4 mixtures, **G. Horvath**, F. Krcma, L. Polachova, K. Klohnova, N J Mason, M. Zahoran and S. Matejcik, *Eur. Phys. J. Appl. Phys*., **Vol. 53,** No. 1**,** ap100191 (2011).

5. Methane decomposition leading to deposit formation in a DC positive CH_4-N_2 corona discharge, **G. Horvath**, N J Mason, M. Zahoran and S. Matejcik, *Plasma Chemistry and Plasma Processing* **31**(2), pp. 327–335. (2010).

B) List of conference articles related to the PhD thesis:

6. Formation of solid deposits on high voltage corona discharge electrode in positive corona discharge fed by mixture of CH_4 and N_2, Horvath G., Skalny J.D. , Mason N.J. and Zahoran M., *HAKONE XI* Oléron Island September 7-12, 2008.

7. corona discharge experiment in mixtures of N_2 and CH_4 – laboratory simulation of titan's atmosphere G. Horváth , J. D. Skalný, N. J. Mason , M. Záhoran, *ESCAMPIG* Granada 2008 July, Book of abstracts.

8. Deposition of Solid Products of CH_4+N_2 Reactions in Positive Corona Discharge on Electrodes G. Horváth, J. D. Skalný, M. Záhoran, J. Országh, N. J. Mason,

WDS'08 Proceedings of Contributed Papers, Part II, 11–15, 2008. ISBN 978-80-7378-066-1 © MATFYZPRESS.

9. Laboratory simulation of Titan's atmosphere in positive coaxial corona discharge, Horvath G., Skalny J.D., Mason N.J. and Zahoran M., *II. CESPC* August 31 – September 4, 2008, Brno Czech Republic, pp 169.

10. Positive corona discharge in N_2+CH_4 mixture at atmospheric pressure, G. Horváth, J. D. Skalný, N. J. Mason, M. Záhoran, J. Országh, *Publ. Astron. Obs. Belgrade No.* **84** (2008), 341-342, ISSN 0373-3742.

11. Simulating chemical processes in Titan's atmosphere using a positive corona discharge fed by a mixture of CH_4 and N_2, Horvath G., Skalny J.D. , Mason N.J. and Zahoran M., *EANA'08 8th European Workshop on Exo-Astrobiology* 1-3 September 2008, p4.4.

12. Negative ions in N_2/CH_4/Ar plasma-a simulation of Titan's atmosphere chemistry, G. Horvath, Y. Aranda-Gonzalvo, N. J. Mason, M. Zahoran, S. Matejcik, *17th Conference of Slovak Physicists Proceedings (CD ROM), Bratislava* (2009) ISBN 978-80-969124-7-6. - pp. 131-132.

13. Positive corona discharge experiment in admixtures of N_2 and CH_4 - A simulation of Titan's atmosphere, G. Horváth, N. J. Mason, M. Zahoran, S. Matejcik, *8th Workshop on Frontiers in Low Temperature Plasma Diagnostics, Brno* : (2009) 83.

14. Simulácia elementárnych procesov atmosféry Titanu v elektrických výbojoch, G. Horvath, N. J. Mason, M. Zahoran and S. Matejcik, *Československý časopis pro fyziku*. - ISSN 0009-0700. - Zoš. 59, č. 4 (2009), s. 265-268.

15. Simulation of Titan's atmosphere in positive corona discharge fed by admixtures of N_2 and CH_4 - an analysis of gaseous and solid products, G. Horváth, J. D. Skalny, N. J. Mason, M. Zahoran, J. Orszagh, *17th Symposium on Application of Plasma Processes* (CD ROM). – Bratislava ISBN 978-80-89186-45-7. - S. 221-222.

16. Packed bed coaxial dbd discharge in ch_4-n_2 mixtures - mimic of titan's lower atmosphere, G. Horvath, N.J. Mason, M. Zahoran and S. Matejcik, *The 20th*

European Conference on the Atomic and Molecular Physics of Ionized Gases in Novi Sad, 13.-17. 2010, ISBN 2-914771-63-0.

17. FTIR analysis of stable gaseous products in N_2-CH_4 atmospheric glow discharge G. Horvath, F. Krcma, L. Polachova, N. J. Mason, M. Zahoran and S. Matejcik, *37th EPS Conference on Plasma Physics, , Dublin 21.-25. 2010*, 4-page papers. ISBN 2-914771-62-2. - S. P1.315.

18. Gliding arc discharge in CH_4-N_2 gas mixture - Laboratory mimic of Titan's atmosphere, G. Horvath, L. Polachova, F. Krcma, M. Zahoran, S. Matejcik, N. J. Mason, *37th EPS Conference on Plasma Physics, Dublin 21.-25. 2010*, 4-page paper, P1.315.

19. Formation of NH_3 and HCN in atmospheric glow discharge fed by gaseous CH_4-N_2 mixture**,** G. Horvath, L. Polachova, F. Krcma, K. Klohnova, M. Zahoran, S. Matejcik and N. J. Mason, *EPSC Abstracts* **Vol. 5**, EPSC2010-171, *2010; European Planetary Science Congress 2010 September, Rome - Italy.*

20. An optical emission spectroscopy of atmospheric glow discharge between shaped electrodes in CH_4-N_2 discharge, G. Horvath, L. polachova, F. Krcma, K. Klohnova, N. J. Mason, M. Zahoran and S. Matejcik, *Conference HAKONE XII Kúpeľná Dvorana, Trenčianske Teplice. 12.-17.9.2010, Slovakia,* ISBN 978-80-89186-72-3. p. 260-264.

21. Titan's atmosphere chemistry simulation in atmospheric glow discharge, L. polachova, G. Horvath, F. Krcma, K. Klohnova, N. J. Mason, M. Zahoran and S. Matejcik, *Conference HAKONE XII Kúpeľná Dvorana, Trenčianske Teplice. 12.-17.9.2010, Slovakia*, ISBN 978-80-89186-72-3.

22. Optical emission spectroscopy of abnormal glow discharge in nitrogen-methane mixtures at atmospheric pressure, F. Krcma, K. Klohnova, L. Polachova, G. Horvath, *Publ. Astron. Obs. Belgrade* No. **89** (2010), 371-374.

23. Plasma Discharges as a probe of chemical processes in planetary atmospheres N. J. Mason, M. K. Duffy, G. Horvath, J. Orszagh, *18th Symposium on Application of Plasma Processes* (CD ROM). - Bratislava 2011, ISBN 978-80-89186-77-8, pp 25-33.

24. Optical emission spectroscopy of atmospheric pressure discharges in nitrogen-methane gas mixtures, F. Krcma, G. Horvath, L. polachova, K. Klohnova, *18th Symposium on Application of Plasma Processes* (CD ROM). - Bratislava 2011, ISBN 978-80-89186-77-8, pp 46-50.

25. Simulation of Titan's atmosphere processes using DC gliding arc discharge, L. polachova, G. Horvath, F. Krcma, K. Klohnova, N. J. Mason, M. Zahoran and S. Matejcik, *18th Symposium on Application of Plasma Processes* (CD ROM). - Bratislava 2011, ISBN 978-80-89186-77-8, pp 185-188.

26. Organic abundances in atmospheric pressure N_2-CH_4 discharges, G. Horvath, L. polachova, F. Krcma, K. Klohnova, N. J. Mason, M. Zahoran and S. Matejcik, *18th Symposium on Application of Plasma Processes* (CD ROM). - Bratislava 2011, ISBN 978-80-89186-77-8, pp 257-261.

27. Study of plasma chemistry in atmospheric CH_4-N_2 gliding arc discharges by GC-MS and SEM-EDS spectroscopies, G. Horvath, L. polachova, F. Krcma, K. Klohnova, N. J. Mason, M. Zahoran and S. Matejcik, *European Winter Conference on Plasma Spectrochemistry 2011*, p. 142.

C) Oral presentations at international conferences:

2007 November – Symposium "Ozotech" in Bratislava: *Influence of humidity on ozone concentration in negative corona discharge fed by oxygen*

2008 July – 19th ESCAMPIG in Granada: *Corona discharge experiment in mixtures of N_2 and CH_4-laboratory simulation of titan's atmosphere* ***(Invited Hot Topic lecture!)***

2009 January - 17th Symposium on Application of Plasma Processes in Liptovsky Jan: *Simulation of Titan's atmosphere in positive corona discharge fed by admixtures of N_2 and CH_4 - An analysis of gaseous and solid products*

2009 November - The Informal Titan Ion Chemistry Meeting, Prague - *Simulating Titan's atmosphere using electrical discharges*

2010 January 2010 - WG3/Mulhouse follow up meeting, Open University in Milton Keynes, United Kingdom - *Titan's atmosphere chemistry simulation in electrical discharges.*

2010 October – COST-The Chemical Cosmos, Action Annual Conference in Grenoble, France – *Atmospheric pressure discharge measurements in CH4-N2 gaseous mixture – A contribution to the mici of Titan's atmosphere chemistry*

2011 October - COST-The Chemical Cosmos, Action Annual Conference in Valletta, Malta – *Plasmas and Titan's atmosphere*

C) Citations of articles related to the PhD thesis:

1. **Horvath G**, Skalny Jan D, Mason N J, Klas M, Zahoran M, Vladoiu R and Manole M. Corona discharge experiments in admixtures of N_2 and CH_4: a laboratory simulation of Titan's atmosphere. *Plasma Source S;cience and Technology*, Vol. **18**, Issue 3, 034016 (2009).

   Cited by:

   a. Ndiaye AA and Lago V, *Plasma Source Science and Technology*, Vol. **20**, Issue 1, 015015 (2011).
   b. Es-Sebbar E, Gazeau MC, Benilan Y, Jolly A and Pintassilgo CD, *Journal of Physics D-Applied Physics*, Vol. **43**, Issue 33, 335203 (2010).
   c. Loureiro et al, 2011 Plasma Sources Sci. Technol. 20 024007.

2. **Horvath G**, Aranda-Gonzalvo Y, Mason NJ, Zahoran M and Matejcik S. Negative ions formed in N_2/CH_4/Ar discharge - A simulation of Titan's atmosphere chemistry. *European Physical Journal – Applied Physics*, Vol. **49**, Issue 1, 13105 (2010).

   Cited by:

   a. Gichuhi WK, Mebel AM and Suits AG. *Journal of Physical Chemistry A*, Vol. **114**, Issue 51, 13296 (2010).
   b. S. Carles et al, Icarus Volume 211, Issue 1, January 2011, Pages 901-905.

3. **Horvath G**, Mason NJ, Polachova L, Zahoran M, Moravsky L and Matejcik S. Packed Bed DBD Discharge Experiments in Admixtures of N_2 and CH_4. *Plasma Chemistry and Plasma Processing*, Vol. **30**, Issue 5, 565 (2010).

   Cited by:

   a. Ndiaye AA and Lago V, *Plasma Source Science and Technology*, Vol. **20**, Issue 1, 015015 (2011).
   b. Gautier T, Carrasco N, Buch A, *ICARUS* **213** Issue: 2 (2011) 625-635.