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# Formation of positive ions in hydrocarbon containing dielectric barrier discharge plasmas

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Dedicated to the memory of Ioana Alexandra Rusu, colleague, teacher, and friend, who passed away on December 2015.

**Abstract**

Low temperature atmospheric pressure plasma devices are suitable experimental solutions to generate transitory molecular environments with various applications. In this study we present experimental results regarding the plasma chemistry of dielectric barrier discharges (DBD) in helium - hydrogen (0.1%) - hydrocarbons (1.2%) mixtures. Four types of hydrocarbon gases were studied: methane ($CH_4$), ethane ($C_2H_6$), propane ($C_3H_8$), and butane ($C_4H_{10}$). Discharge diagnosis and monitoring was assured by electrical measurements and optical emission spectroscopy. Molecular beam mass spectrometry is engaged to sample positive ions populations from two different plasma sources. Dissociation and generation of higher-chain and cyclic (aromatic) hydrocarbons were discussed as a function of feed gas and discharge geometry. We found a strong influence of these parameters on both molecular mass distribution and recombination processes in the plasma volume.


*Keywords:* Atmospheric pressure plasma; Hydrocarbons; Positive ions mass spectrometry

## 1. Introduction

Carbon based chemical diversity in certain interstellar regions is a certitude since the discovery of first detection of a molecule in space, the methylidyne radical (CH), back in 1941. Since that observation, many more organic molecules (of around 157 in total, up to date Interstellar & Circumstellar Species, 2016; Millar, 2015) are observed in specific regions of molecular clouds, i.e. the hot molecular cores, regions that show appropriate thermodynamic parameters for chemical synthesis (Herbst, 2005). Earth-based experiments to simulate chemical processes in specific regions of interstellar space and to study reaction rates are developed continuously. Some widely used experiments are based on crossed molecular beams, selected ion flow tube, pulsed laser photolysis, ice and grains analogues exposed to UV radiation, atoms and ion beams (Blitz and Seakins, 2012; Smith, 2011; Armentrout and Baer, 1996; Gerlich and Smith, 2006). From all proposed experiments to explain the chemical diversity of hot molecular cores and to explore the reaction mechanisms, plasma based processes are of particular interests. Those experiments that may assure binary collisions are able to explore imposed chemical processes in various gases and to

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determine accurately rate coefficients and other parameters useful for theoretical studies (Rowe and Marquette, 1987; Rowe et al., 2014; Méndez et al., 2006; Carrasco et al., 2011). Nevertheless, high pressure plasmas (binary and ternary collisions, high collision frequency, reaction branching) are also used to explore some reaction pathways and to generate stable and transient molecular populations. Results of such experiments are useful to understand the chemistry of specific atmospheres and tholins production (Cable et al., 2012; Imanaka et al., 2004; Torokova et al., 2015; Plankensteiner et al., 2007), as investigated by flyby missions, such as Cassini flyby of Titan and the more recent New Horizons flyby of Pluto. Moreover, the Rosetta mission and the 2014 tracking of the 67P/Churyumov-Gerasimenko comet, revealed a rich chemical diversity in the coma region. Using the ion mode, the following positive ions were detected: $CN^+$, $C_2H_2^+$, $C_2H_3^+$, $HCN^+$, $CO^+$, $C_2H_5^+$, $HCO^+$, $CO_2^+$ (Fuselier et al., 2015). Equally, the neutrals detection pointed a series of volatile compounds: water, carbon monoxide and carbon dioxide, hydrocarbons, oxygenated species, nitrogen and sulphur bearing species (Le Roy et al., 2015).

The atmospheric or sub-atmospheric pressure plasma experiments for astrochemistry purposes are valuable resources to study complex molecular environments and relatively not expensive experimental techniques. In specific plasma conditions and experimental arrangements it was studied the ion chemistry of planetary atmospheres (Sabo et al., 2014; Navarro-González and Ramírez, 1997; Horvath et al., 2010), chemistry of hydrocarbons/nitrogen mixtures (Thejaswini et al., 2011, 2014), formation of enol and keto species (Wang et al., 2008). The gas plasma temperature monitored by rotational band analysis of nitrogen molecular ions for atmospheric pressure plasmas generated in barrier discharge configuration is usually near room temperature (Chiper et al., 2004; Topala et al., 2009; Wertheimer et al., 2012). With regard to mass characterization of chemical compounds present in plasma volume and on surfaces, mass spectrometry is a widely used technique, applied mainly for low pressure plasmas. Nevertheless, molecular beam mass spectrometry is an alternative to study atmospheric pressure plasmas, with reliable results (Große-Kreul et al., 2015). Moreover, recent reports show that dielectric barrier discharges can be also used as ambient sampling chemical ion source for different types of materials, even for specific trace compounds, such as TNT and RDX (Chen et al., 2010; Yang et al., 2012; Usmanov et al., 2013; Wright et al., 2013; McKay et al., 2014; Chauvet et al., 2014). As most atmospheric pressure discharges generate pulsed plasmas, with considerable spatial non-homogeneity and very short mean free path, allowing efficient recombination processes, the sampling process of charged species is difficult to achieve. Recent studies pointed that these difficulties may be overcome using appropriate plasma generation solutions, based on dielectric barrier discharge principle or RF discharges. Positive and negative ions studies applied for atmospheric pressure plasmas have shown a rich chemical environment based on water clusters, for helium feed discharge with air or water impurities (Bruggeman et al., 2010; Oh et al., 2011; McKay et al., 2013; Oh et al., 2015) or even gaseous oligomers (Benedikt et al., 2013; Oh and Bradley, 2013), if the discharge is feed with noble gases mixed with polymerisable molecules. We discuss here the results obtained in atmospheric pressure plasma feed with helium-hydrogen-hydrocarbons gas mixture. Two configurations used to generate DBD plasma in complex gas mixtures were analyzed by molecular beam mass spectrometry, configured to sample positively charged molecular ions from plasma volume: direction of molecular beam parallel with inter electrode electric field and perpendicular to inter electrode electric field, close to powered electrode and to the grounded one.

## 2. Experimental part

### 2.1. Plasma reactors

Hydrocarbon containing plasmas at atmospheric pressure were studied using two different plasma reactors based on dielectric barrier discharge principle: AC high voltage is applied on a power electrode, with at least one dielectric layer present in the overall discharge circuit. A stainless steel cylindrical chamber attached to the mass spectrometer sampling end orifice (Fig. 1) is used to isolate the electrode assembly from laboratory atmosphere, having coupled a dry vacuum pump and a turbo molecular pump. Before each experiment the pressure in the plasma reactor chamber is maintained at $10^{-2}$ mbar by using plasma reactor pumping system. After that, the reactor pumping system is switched off and the controlled gas mixture is obtained by filling the reactor up to atmospheric pressure ($10^3$ mbar). The plasma chamber is attached to the mass spectrometer body and the gas or plasma ions can be

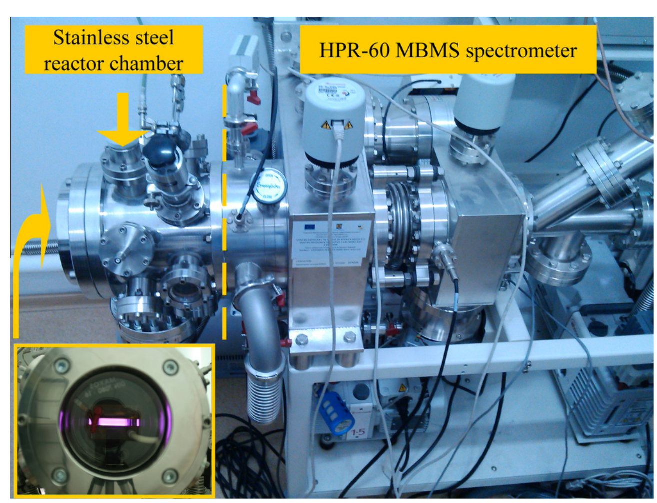


Fig. 1. Stainless steel cylindrical chamber attached to HPR60 Molecular Beam Sampling Mass Spectrometer System.