Mass spectrometry of excited species produced in an atmospheric pressure plasma

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Abstract: A threshold ionization molecular beam mass spectrometer (TIMBMS) is used as diagnostic tool to study an atmospheric pressure cold plasma jet fed with a mixture of helium and other gases, in order to identify and measure the species produced. The final aim is the understanding of the reaction chemistry involved in atmospheric plasmas.

Keywords: mass spectrometry, threshold ionization, cold atmospheric plasma

1. Introduction

Cold atmospheric pressure plasmas are studied for a large range of applications, as biomedical applications, chemical analysis, nanosynthesis or decontamination. To optimize the production of species according to the application needs, the understanding of the plasma chemistry is an important challenge. Indeed, these plasmas are highly collisional and the wide range of species involved make the interpretation of the mechanisms difficult.

Mass spectrometry is a powerful diagnostic tool allowing the detection of different species and absolute densities measurements. Here, a threshold ionization molecular beam mass spectrometer (TIMBMS) will be coupled to an atmospheric pressure plasma source to investigate the species produced within an He plasma with admixtures of small quantities of other gases (O_2, N_2, H_2O, CH_4, CO_2...) to better understand the reaction chemistry. A special attention is paid to the admixture of CO_2. It belongs to greenhouse gases and represents a challenging field of research with the aim of CO_2 conversion in industrial applications and sustainable carbon cycles.

2. Experimental setup

The mass spectrometer used in this work has been already described in several papers [1-3]. It consists of a quadrupole mass spectrometer, Pfeiffer HiQuad QMG700 (mass range: from 0 to 3000 Th), coupled with a homemade atmospheric pressure interface, illustrated in Fig. 1. This system is used for the study of neutral species.

The interface is composed of a differential pumping system. The plasma species are sampled through an orifice of 100 µm; they travel through 3 stages with decreasing pressure before reaching the mass spectrometer. The interface is designed to facilitate the formation of a molecular beam. This method avoids the wall collisions and thus minimizes the attenuation of the beam signal. Moreover, to improve the signal-on-background ratio, and thus the limit of detection, a chopper is placed behind the orifice. It consists of a rotating skimmer. By subtracting the signal obtained when the chopper is open (a bunch of species is sampled) with the one obtained when it is closed (the species are blocked), we can measure the signal only coming from the species.

When the species reach the mass spectrometer, they are ionized in the ionizer by electron impact. Typically, the electron energy is 70 eV. Nevertheless, this energy doesn't allow to discriminate the contributions of different species. Indeed, as function of the excitation level of a species, the ionization energy will be changed. With the threshold ionization (TI) mode, the energy of the electrons can be tuned. Then, it is possible to measure the higher excited states of species without measuring the ones ionized from the ground state. It is also possible to avoid unwanted dissociative fragmentation.

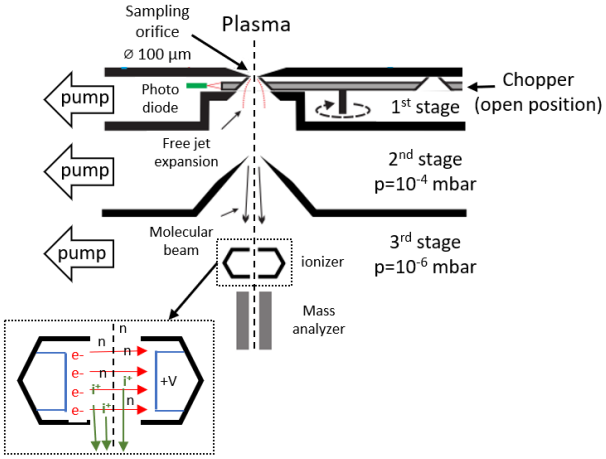

Fig. 1. Schema of the TIMBMS

Absolute density measurements can be achieved via a calibration realized with a calibration gas with known densities. The calibration gas is preferably chosen with a similar mass as the species of interest to neglect the mass dependent transmission factor in the MS ($F(m_i, m_{cal}) \approx 1$ in this case). The density of the species of interest (n_i) can be calculated from the density of the calibration gas (n_{cal}), the ratio of the measured signal (S_i/S_{cal}) and the ionization cross sections (σ_{cal} and σ_i).

$$n_i = F(m_i, m_{cal}) \cdot \frac{S_i \cdot \sigma_{cal}}{S_{cal} \cdot \sigma_i} \cdot n_{cal} \qquad (1)$$

The mass spectrometer is directly coupled to a cold atmospheric pressure plasma jet source allowing the direct sampling of the produced species within the plasma or the effluent part. The plasma source is powered with an RF power supply. The source is fed by a flow of He with small admixtures of other gases.

3. Previous results

Cold atmospheric pressure plasmas are a chemically rich environment suitable for a large range of applications. For some of them, small admixtures of gas are added to the discharge to produce the desired species. The reaction chemistry becomes more complex and the need of a better understanding more important.

With a mass spectrometer, we can obtain information about the composition of a plasma: ions, stable species, reactive species and vibrationally excited species.

To understand the chemistry involved in an He plasma with small amounts of other gases (O_2, N_2, H_2O, CH_4, CO_2...), TIMBMS will be used to study the reaction products sampled from the plasma.

This work is based on previous studies realized with a microplasma jet. In these cases, the added gases were O_2 [4], N_2 [3] and H_2O [5], and the species were sampled from the effluent part.

An example of measurement taken from [3] is shown in Fig. 2. The measurements were performed at a mass-to-charge ratio of 28, corresponding to N_2^+. When the plasma is off, N_2 is ionized from the ground state by the ionizer, the ionization potential of N_2 is 15.6 eV. Small amounts of N_2^+ are detected below this energy, due to the electron energy distribution. When the plasma is on, the signal is shifted to lower energy. This shift illustrates the production of vibrationally excited N_2. Because of their higher excited level, the energy needed to ionize them is lower than from the ground state. Thus, it is possible to determine the highest vibrational level, up to vibrational quantum number 7.

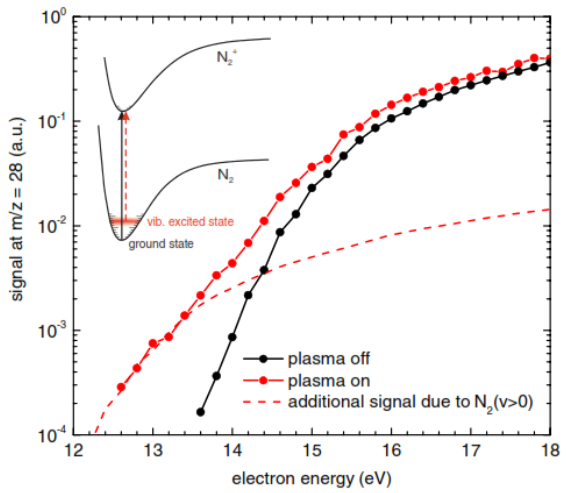

Fig. 2. TIMBMS measurement of N_2 in the effluent part of a microplasma jet fed with He and 0.25% N_2 (from [3])

The threshold ionization mode is also powerful to study dissociated species, for example atomic nitrogen [6]. N can be ionized in the ionizer with a threshold energy above 14.5 eV. But to avoid the detection of N^+ created by dissociative ionization of N_2 in the ionizer, the ionization energy should not reach 24.3 eV. The measurements of N^+, m/z =14, by varying the electron energy, are shown Fig. 3.

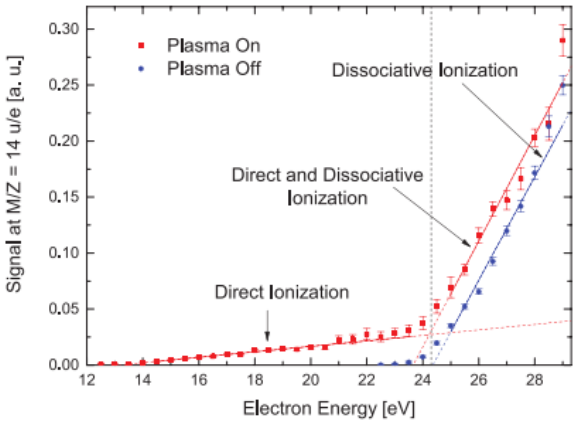

Fig.3. TIMBMS measurement at m/z = 14 in the effluent of a microplasma jet fed with He and 0.25% N_2 (from [6])

4. Outlook

A threshold ionization molecular beam mass spectrometer is directly coupled to a cold atmospheric pressure plasma jet source fed with He and small amount of additional gas. We want to determine the composition within the plasma. This study aims to a better understanding of the underlying phenomena happening in cold atmospheric plasmas. A special focus is on the admixture of CO_2 and the study of the dissociation of CO_2 in CO.

5. References

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