Time-resolved atmospheric plasma investigation by molecular beam mass spectrometry

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Introduction

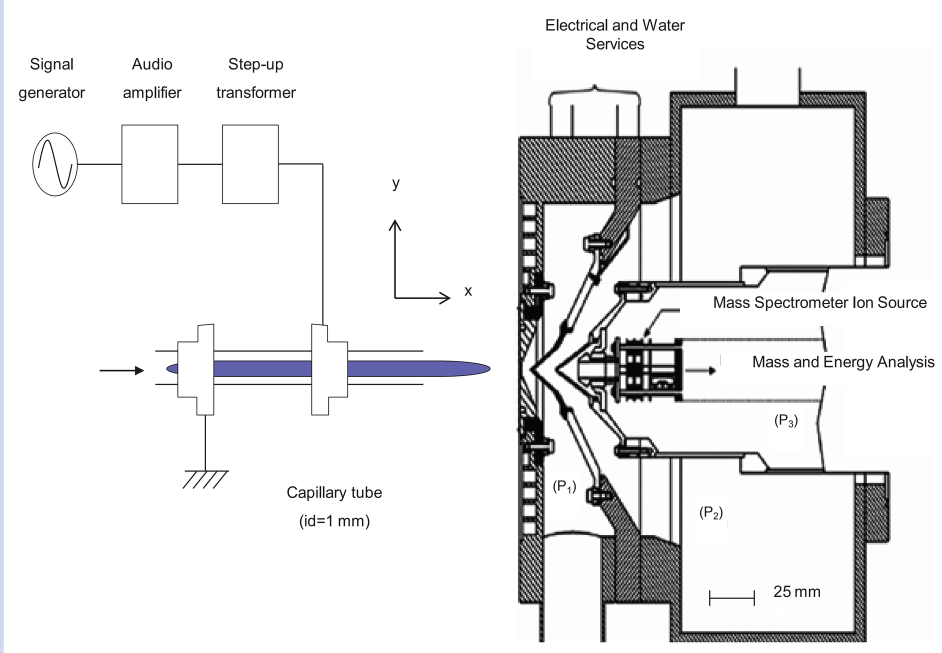
Atmospheric pressure plasma jets and its applications for material processing and biomedical treatment are of main interest recently in nonthermal plasma research [1]. Normally this kind of plasmas is operated at an excitation frequency of several tens of kilohertz (ac or pulsed mode) or in radiofrequency (rf) range. Detailed measurements obtained with ICCD images revealed that these jets are not continuous plasmas but consist of high velocity plasma packs/volumes referred to as ***"plasma bullets"*** [2-3]. Studies done with emission spectroscopy showed the evolution of the species along the trajectory of the bullets [4] but it is the first time that measurements of positive and negative ions generated in the plasma jet is presented by means of time-resolved molecular mass spectrometry (MBMS) [5].

The time-resolved measurements by molecular beam mass spectrometry reveals the evolution of the main species, positive and negatives, during the applied ac for the different repetition rate applied. The main positive species observed are O_2^+, O^+, N_2^+, N^+ and He^+. These positive ions were found to follow the applied voltage and for higher frequency or repetition rate we observe a decrease in the number of species present in the plasma. For negative ions there is a strong presence of O^-, OH^-, H_2O^-, H^-, $OH^-(H_2O)$ (see also [6]) and the behavior of these ions with respect to the repetition rate is different than for positive ions. At higher frequency the signal of negative ions tends to be constant in the active part of the applied voltage. That could be an indication of the origin of negative ions and it shows clearly that the dynamics and chemistry associated with positive and negative ions are different.

Experiment

The μ-plasma jet used in this study was made using a 15 cm long quartz tube of 1 mm (ID) and 3 mm (OD) on which two copper ring electrodes of 8 mm length were attached as shown in the drawing. The electrode close to the outflow was powered by high ac voltages over a range of frequencies. The power supply consisted of a sine wave oscillator (Farnell, LF1) driving a commercial audio amplifier (HQ power, VPA2350MB) with a voltage set-up transformer at the output stage to generate the required high voltages for discharge breakdown. The design allowed the separation and position of the ring electrodes to be changed on the glass tube to aid breakdown and optimise the visible jet length. A gap of 25 mm was chosen for all subsequent experiments.

The end of the μ-plasma jet was aligned with the center of the sampling orifice of the HPR-60 molecular beam mass spectrometer (MBMS) (Hiden Analytical Ltd., Warrington, UK) [5].



Results

ICCD images

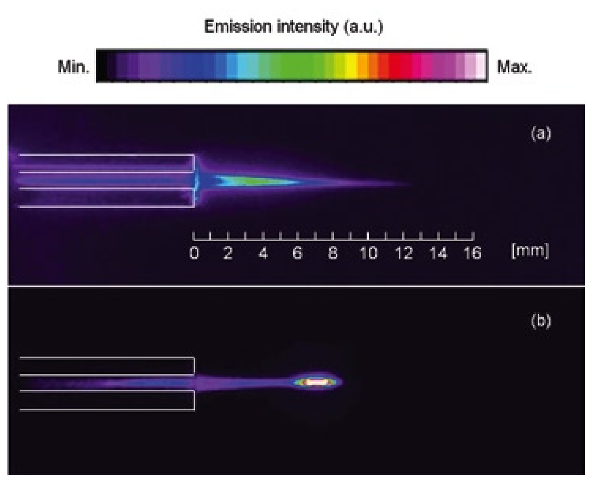
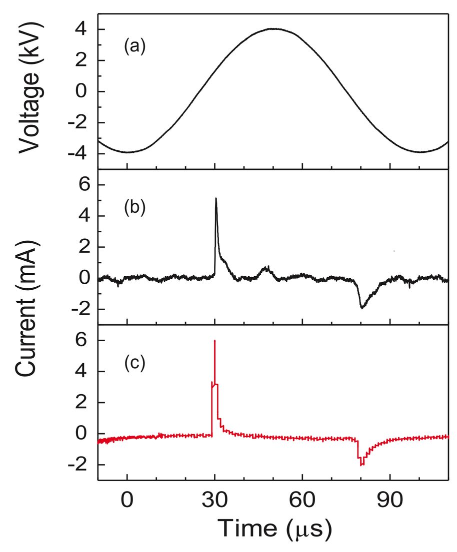


Image of a plasma plume driven 10kHz, 8 kV_{p-p} and 1.38 slm He.

Waveforms



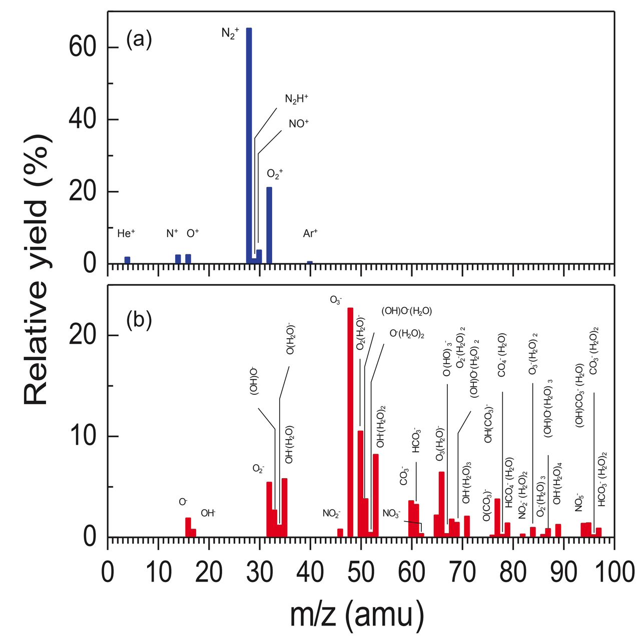
Plots of driving voltage (a), discharge current (b) and bullet current (c) at a 10kHz frequency

Positive and negative ions sampling of the micro plasma jet

Experiment conditions:

- AC voltage 8 kV_{p-p}
- Frequency 10kHz
- He (99.996%)
- Flow rate 1.38 slm
- Sampling orifice diameter 100μm
- Measurement position 7 mm
- Relative yield: $Y_i^r[\%] = \frac{Y_i^a}{\sum_i Y_i^a} x100$

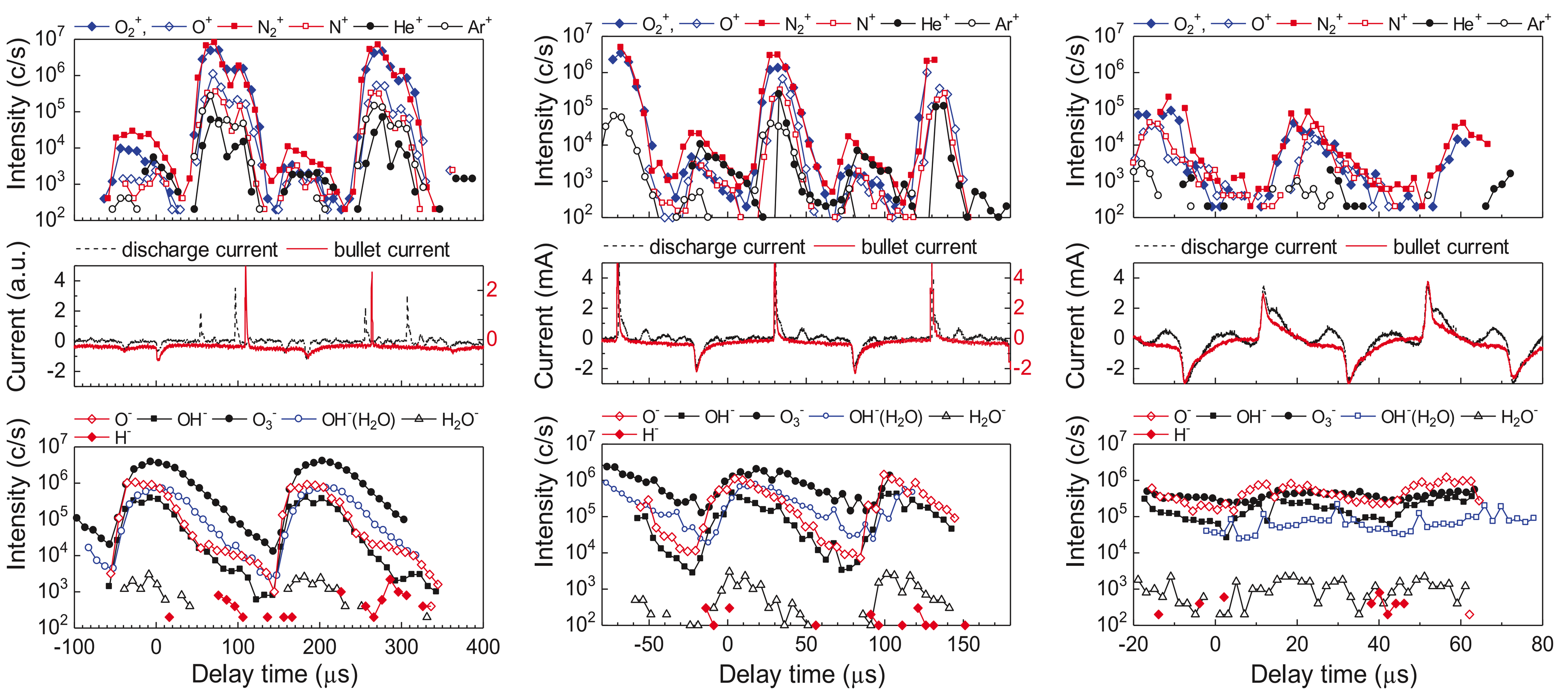
(where i is the reduced mass index of the ions)



Time-resolved measurements of the atmospheric micro plasma jet

The HPR-60 MBMS was operated in positive ion mode detection, with a time resolution of 10 μs, 5 μs and 2 μs corresponding to the plasma frequency of 5, 10 and 25 kHz, obtained by gating the detector using an internal gate signal synchronized to the driving voltage waveform. The time-resolved measurements were performed automatically by software.

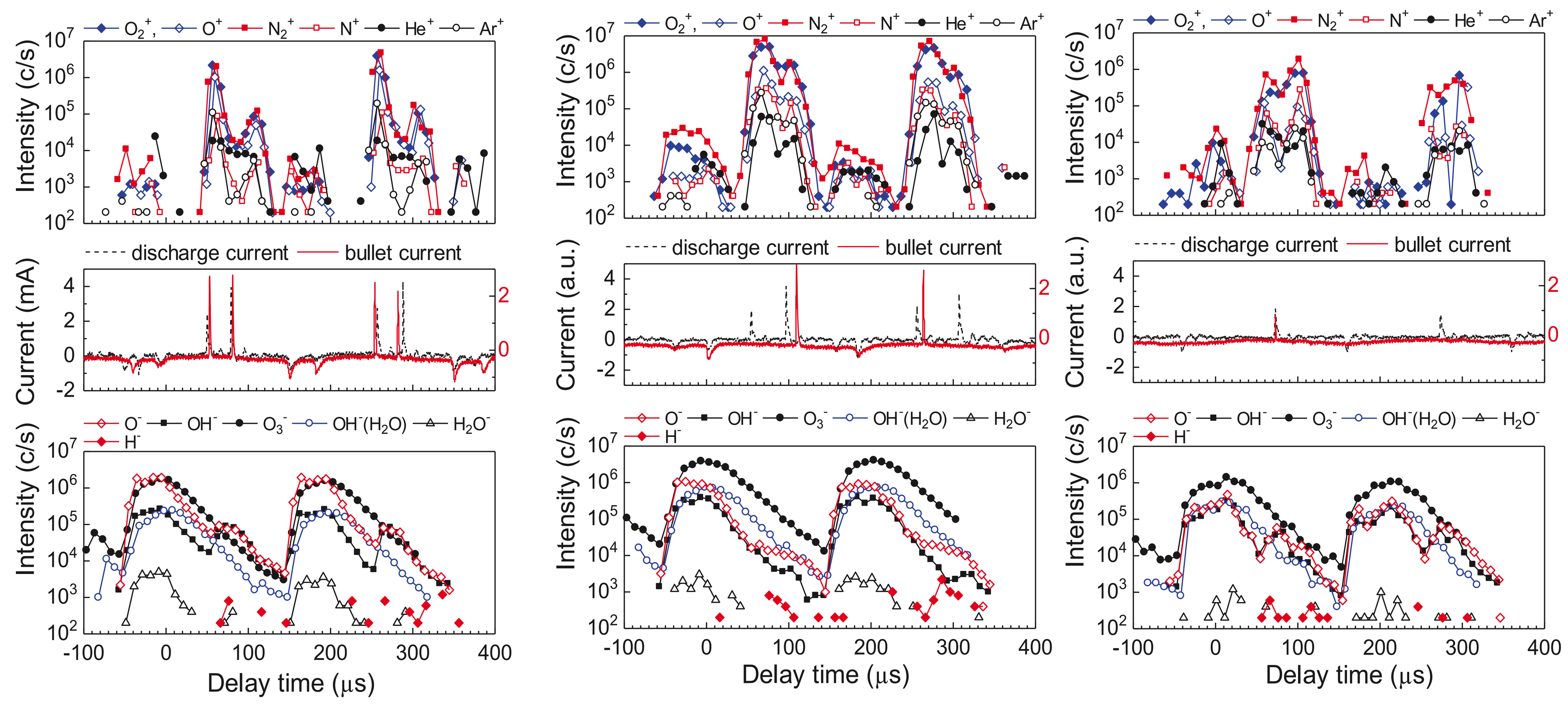
Time-resolved of positive and negative ion fluxes for selected species measured at a fix distance of 7 mm from the nozzle at different frequencies:



5 kHz **10 kHz** **25 kHz**

The ion fluxes are reduced at higher frequencies. At 25 kHz the negative ions respond less well to the voltage modulation, however the positive ions intensity show a clear modulation for the different frequencies. The N_2^+ and O_2^+ signal rises and falls following the modulation on the frequencies but atomic ions N^+ and O^+ are delayed around 10 μs. For the negative ions the atomic O^- and OH^- are measured before the heavier ions, this may be due to multi-step processes necessary for their creation and possibly longer travel time from the point creation to the mass spectrometer sampling orifice.

Time-resolved of positive and negative ion fluxes for selected species measured at a fix frequency of 10 kHz at different positions from the nozzle:



1 mm **7 mm** **11 mm**

In the positive voltage half cycle with an associated positive discharge current pulse there is a sharp rise in the positive ion concentration within about 10 μs. When two current peaks appear, in the positive or negative parts of the voltage cycle, the two peaks associated with he positive ion densities are correlated with the features in the current.

For the negative ions, their rise is correlated to the negative part of the voltage cycle. They behave like the positive ions but showing long time exposure, 100-150 μs and slow decays.

Conclusions

- Using time-resolved MBMS positive and negative ions have been detected in the output plume of an atmospheric plasma micro-jet operating in He at 5-25 kHz.
- Positive ions (O_2^+, $N_2^+$and He^+) are created on the positive and negative swings.
- The creation of negative ions (O^-, OH^-, O_3^-, H^-, $OH^-(H_2O)$ and $O_3^-(H_2O)$) is correlated only to the negative part of the voltage cycle but these species present a very long decay times .
- The temporal increase of the signal of both positive and negative ionic species in the mass spectra is correlated directly with the rise of the discharge and local bullets currents.

References

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