Characterization of a DBD plasma jet for soft ionization

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A source for soft ionization of organic molecules is presented in this paper. It is based on an atmospheric pressure dielectric barrier plasma jet, whereby the plasma is ignited inside a glass capillary surrounded by two ring electrodes. The length of the plasma jet depends on the applied gas and the gas flow. Pure He, Ne and Ar are used as operating gases. To characterize the mechanisms, which are responsible for soft ionization, spatially resolved optical emission spectrometry (OES) measurements were implemented. A special focus was put beside the emission of the different element lines also on the intensity variation of the N_2 and N_2^+ lines, which are involved in the ionization process.

1. Introduction

Miniaturisation is a common trend in analytical spectroscopy. Therefore, microdischarges are used, among others, as soft ionization source for mass spectrometry (MS) and ion mobility spectrometry (IMS) or as excitation source for optical emission spectrometry (OES). Dielectric barrier discharges (DBD) have some interesting advantages for this purpose. An overview is given by Meyer et al. [1, 2].

Michels et al. [3] introduced a DBD plasma jet used as soft ionization source for IMS and MS. Soft ionization refers to the formation of ions in gas phase with only little fragmentation. For identification in e. g. organic mass spectrometry non fragmented protonated molecular ions $[M + H]^+$ are more useful for the efficiency than fragments of ions [4].

In this paper the same plasma jet is further characterized with regard to the excitation mechanisms to improve succeeding measurements in the IMS. Spatially resolved optical emission measurements, with a focus on the elemental emission lines of the noble gases and N_2 and N_2^+, are carried out and will be shown in the following sections.

2. Experimental arrangement

This ionization source consists of a small glass capillary (i. d. 0.5 mm, o. d. 1 mm) on which the ring electrodes are tightly mounted with a distance of 10 mm and 1 mm from the open end. For mounting in the IMS or MS and for preventing direct arc discharges between the electrodes this arrangement is surrounded by a Teflon cage. A home-made high voltage generator providing an alternating voltage is connected to the electrodes. The plasma jet works reliably with an applied voltage of 5 kV at 20 kHz. The experimental arrangement is presented in Fig. 1.

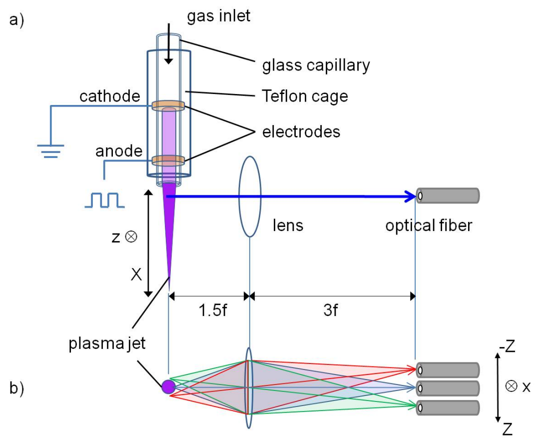

Fig. 1: Experimental arrangement for spatially resolved measurements a) top view, b) frontal view.

As operating gas for the plasma jet, helium, neon or argon, each with a purity of 99.999 % are used. To have the same jet length of about 10 mm, gas flows of 500 ml min^{-1}, 400 ml min^{-1}, 100 ml min^{-1} are used for helium, neon and argon, respectively. This different flows are needed, because the length of the plasma jet depends on the applied gas and on the gas flow. Furthermore, the amount of nitrogen diffusing from ambient air into the plasma jet is for the three noble gases the same [5]. For the spatially resolved measurements the optical and electrical parameters are not changed.

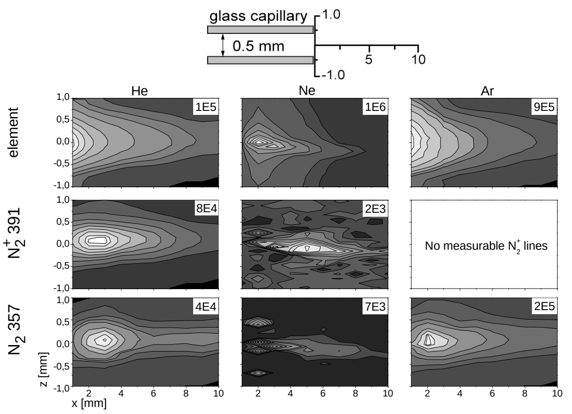

Fig. 2: Spatial density distributions of He, N_2^+ and N_2 measured in a He plasma jet compared with a Ne plasma jet and an Ar plasma jet, respectively. The maximum intensity is shown in the top right corner.

Along the plasma jet emission spectroscopic measurements were performed. Therefore, a hand held spectrometer (Ocean Optics, USB4000) operating in the visible spectral range (350 nm-950 nm) and an optical fibre (Ocean Optics, UV/VIS) with spectral range of 300 nm-1100 nm are used. The whole arrangement is mounted on translation stages to allow three dimensional adjustment. The emitted light is focussed with a lens (f=10 mm) on the optical fibre. For the measurement both optical parts are moved in 1 mm steps along the plasma jet in x-direction and for each x value in steps of 0.1 mm in vertical direction (z) spectra are recorded with an integration time of 500 ms.

3. Results and discussion

Fig. 2 presents the measurement results. Regarding the He plasma jet the intensity of the He 706 nm line has its maximum at the capillary exit, whereas the maxima for N_2^+ and N_2 appear with increasing x positions. The intensity maxima are nearly of the same scale. The energy transition levels are shown for all three working gases in Fig. 3. The excitation mechanism happens through Penning ionization. The upper level of the N_2^+ can be excited with the He metastables (He^M) which leads to a protonation of water clusters and a subsequent protonation of the analyte molecules $[M+H]^+$. The density population of the helium metastables cannot be exceeded by the population of the excited upper level of N_2^+. Hence the plasma jet should be arranged inside the IMS and MS to get the best efficiency.

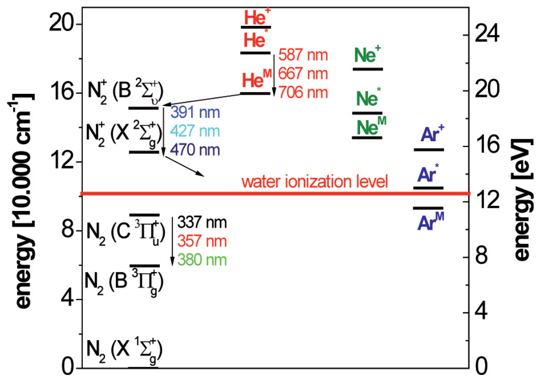

Fig. 3: Energy transition levels of helium, neon, argon, nitrogen and the water ionization level

In contrast, the intensity maximum of the neon emission lines (here shown for 703 nm) is distinctly outside the capillary region at x=2 mm. N_2^+ and N_2 could also be detected, but their intensities are about three orders of magnitude lower than the elemental emission lines. The energy levels of Ne^+, Ne^* and Ne^M are all above the N_2 level, so that N_2 should be observable. Although the Ne^+ density is much smaller than the metastable density the Ne^+ level is high enough so that N_2^+ can be excited.

In the case of argon the elemental lines, here shown for 811 nm, have also their maximum close to the capillary. But only the emission lines of N_2 can be observed. The intensity maxima are also of the same scale. The energy transition level of N_2^+ is too high, so that no emission can be discerned. Unlike the excitation mechanism in helium, the probability for Penning ionization of nitrogen is lesser for the argon plasma jet.

4. Outlook

This measurements show that the presented plasma jet with helium or neon can be used as soft ionization source for IMS or MS. Further measurements according to the excitation mechanisms and the improvement as soft ionization source are planned for the near future.

5. Acknowledgements

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6. References

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