Analyzing plasma-chemical processes in RF-excited atmospheric pressure plasmas using VUV and visible optical emission spectroscopy

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Abstract: Atmospheric pressure RF discharges operated in helium with admixtures of nitrogen can generate a continuous afterglow. Emission spectra in the ultra-violet wavelength range of the plasma discharge and high-resolution spectra in the visible wavelength range of the afterglow are measured to deduce energy transfer mechanisms.

Keywords: atmospheric pressure RF discharge, nitrogen afterglow, plasma chemistry, VUV spectroscopy

1. Introduction

Non-thermal atmospheric pressure plasma jet devices efficiently generate reactive species at low gas temperature such as atomic oxygen or nitric oxide. Hence, they are commonly used for surface modification and biomedical applications [1]. However, to tailor species densities, detailed knowledge and a profound understanding of the plasma-chemical processes and energy transport in the discharge is crucial. Nitric oxide, for example, can be formed by nitrogen metastables reacting with an oxygen molecule or an oxygen atom [2,3]. Historically, low pressures at around 10 Torr were used for generating these plasmas. The loss and production processes of active nitrogen species in this pressure region are well-understood. Long-living nitrogen metastable states ($A^3\Sigma_u^+$) with a lifetime of the order 2-7 ms control the emission via pooling and resonant energy transfer processes.

However, at atmospheric pressure, population mechanisms differ from low pressure processes [4]. In contrast to streamer discharges, plasma jet sources do not require a pulsed operation but allow for a more convenient, continuous observation of the afterglow [5,6,7]. This is due to the direct correspondence of effluent extension to afterglow time depending on the gas flow rate.

Here, we present spatially resolved optical emission measurements of excited molecular and atomic nitrogen species. In addition to high-resolution visible range spectra with spatial resolution in the afterglow, we show vacuum-ultra-violet (VUV) spectra of the plasma discharge.

2. Experimental Setup

The atmospheric pressure plasma jet is operated using plane parallel electrodes with capacitively coupling and radio frequency excitation. The discharge is confined in a quartz capillary with a cross-section of 1 mm x 1 mm using helium as feed gas (2 slpm) with admixtures of nitrogen up to 1%. The plasma region has a length of 30 mm, the effluent emission is still visible in a distance of 150 mm. A schematic of the atmospheric pressure jet and the plasma emission is shown in Fig. 1.

The spectrometers used are a pm-resolution echelle spectrometer (LLA, ESA 4000) and a Seya-Namioka design VUV monochromator (McPherson, Model 302) in combination with a sodium salycilate detector. The light in the visible range was collected using a collimating lens system allowing for a spatial resolution of 2 mm along the x-axis and was guided into the spectrometer using an optical fibre. VUV emission was collected in extension of the x-axis, thus not allowing for any spatial resolution.

3. Results and discussion

Fig. 2 shows a relatively calibrated emission spectrum of the afterglow region at a spatial distance of 3 mm from the plasma jet exit in the visible wavelength range measured using the echelle spectrometer. Weak helium atomic lines

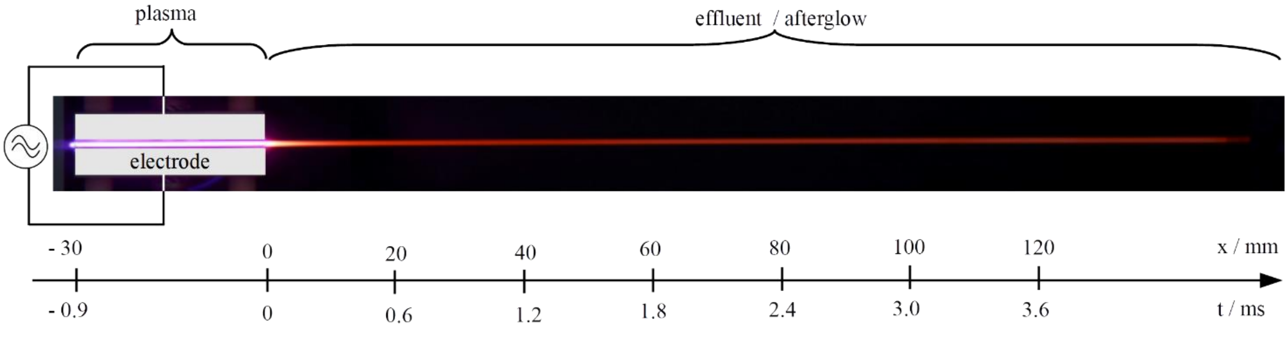

Fig. 1. Experimental setup showing the capacitively coupled atmospheric pressure plasma jet and the Helium-Nitrogen afterglow.

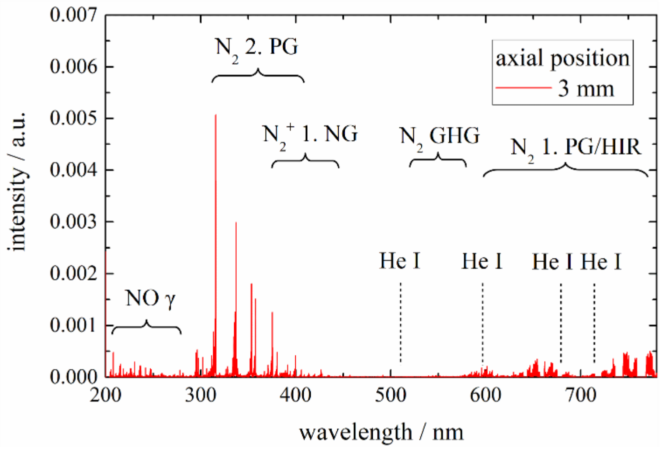

Fig. 2. Emission spectrum of the Helium-Nitrogen afterglow region in the visible and UV range.

are only visible in the plasma region at 501.6, 587.6, 667.8 and 706.5 nm. Nitrogen atomic lines were not observed in the spectra, neither in the plasma region nor in the afterglow. The spectrum is dominated by the rotational band structures of first positive and second negative system of nitrogen. The γ-band of nitric oxide (NO) is visible in the range 200 – 300 nm and originates from oxygen and water impurities in the discharge channel. Emission in the wavelength range 500 – 600 nm due to Gaydon-Herman green system and 600 – 800 nm due to the first positive system and Herman infrared system of molecular nitrogen only appear in the later afterglow region.

The relative emission intensity of several of these band structures is plotted as a function of axial position in the plasma and in the afterglow region in Fig. 3. Axial positions below 0 mm are inside the plasma discharge. Note the logarithmic scale. The plot shows that the emission in the plasma discharge is dominated by emission of the second positive nitrogen bands. Upon entering the afterglow region, the emission decays extremely fast. In contrary to helium, the NO emission is decreasing inside

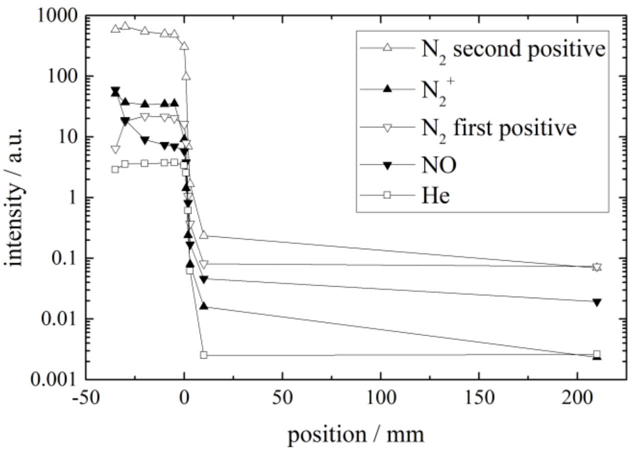

Fig. 3. Emission intensity of several molecular bands in dependence of spatial position in plasma and afterglow region. Note the logarithmic scale.

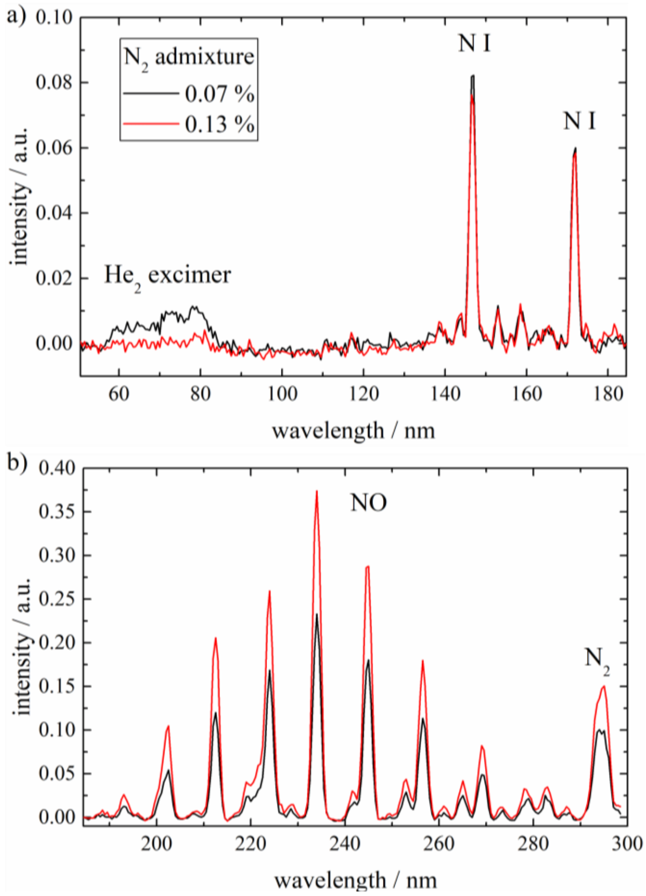

Fig. 4. Emission spectrum of the Helium-Nitrogen discharge in the vacuum ultra-violet range.

the discharge channel. Surprisingly, there is no atomic nitrogen emission (e.g. 745 nm) visible in the plasma discharge nor the afterglow region even if it is attributed an important role in the downstream region [8].

However, Fig. 4 a) and b) show an emission spectrum of the VUV emission of the plasma discharge region. In the wavelength region 50 – 85 nm, the helium excimer emission continua are visible. At 149.0 and 174.1 nm, atomic nitrogen emission lines verify the presence of atomic nitrogen in the plasma discharge and the NO γ-band bridges the visible and the VUV wavelength region.

With increasing nitrogen admixture, the helium excimer emission as well as nitrogen atomic emission lines decrease steeply. In contrast, NO bands increase with increasing nitrogen admixture. This opposite behaviour is clearly displayed in Fig. 5 by comparing the atomic nitrogen lines and one exemplary NO band head. For readability, the emission intensity of NO was divided by a factor of 5. Atomic nitrogen in the plasma is mainly produced by electron impact reactions (linear dependence on N concentration) and destroyed by three-body recombination of two nitrogen atoms (quadratic dependence). As the admixture increases, the N atom concentration increases until it is limited by recombination [8]. Nitric oxide can be produced by three-body collisions of atomic nitrogen and

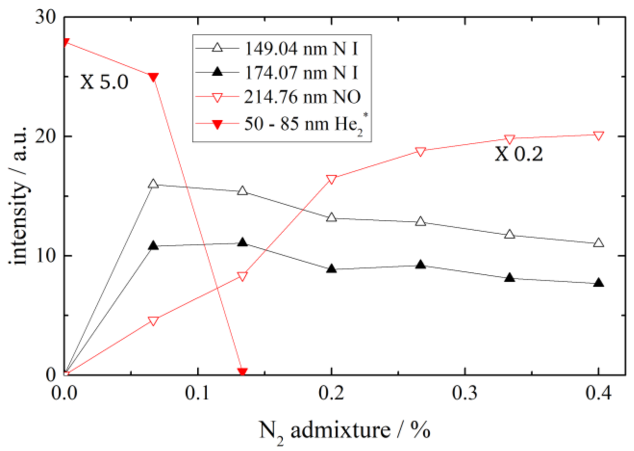

Fig. 5. Effect of nitrogen admixture on the emission intensity of atomic nitrogen lines.

oxygen or a two-body collision of nitrogen metastables and atomic oxygen. The behaviour observed in Fig. 5 indicates that the latter one is the dominant pathway.

4. Conclusion and Outlook

Nitrogen reaction kinetics inside a helium plasma discharge and afterglow were observed using optical emission spectroscopy in the VUV and visible wavelength range. The measurements qualitatively confirm that nitrogen metastables and atomic nitrogen play a role in the energy transport in the helium-nitrogen afterglow. The dominant NO generation pathway is presumably via two-body collisions of nitrogen metastables and atomic oxygen. The influence of gas flow rate, discharge power and nitrogen admixture will be further investigated. Rotational temperatures will be calculated using theoretical fits to the emission spectra.

5. References

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