Vacuum Ultraviolet (VUV) Emission of an Atmospheric Pressure Plasma Jet (µ-APPJ) Operated in Helium-Oxygen Mixtures in Ambient Air

H. Bahre1, H. Lange2, V. Schulz-von der Gathen3, R. Foest2
1Ruhr-Universität Bochum, Inst. f. Experimentalphysik II, 44801 Bochum, Germany
2Leibniz Institut für Plasmaforschung und Technologie e.V.
17489 Greifswald, Germany

Abstract: The VUV emission of a µ-APPJ operated at 13.56 MHz in He with small O2 additions (<0.7%) is analysed between 115 nm and 230 nm. Two atomic emission lines at 115 nm ('D - 'D') and 130 nm ('P - 'S') dominate the spectra. Absolutely calibrated measurements of the VUV radiance provide line integrated radiances of 15 and 27 µW mm⁻²sr⁻¹ respectively for an oxygen admixture of 0.1 vol-% and at 4 nm distance from the nozzle. The axial dependence of the singlet line 115 nm can be described with a decay based on the absorption by atomic and molecular oxygen and ozone. The measurements demonstrate that VUV radiation with photons of 10 eV is transported through the afterglow of the plasma jet over the distance of > 1 cm.

Keywords: VUV emission, absolutely calibrated radiance, micro plasma jet

1. Introduction
Non-equilibrium atmospheric pressure micro plasma devices are known to produce intense UV and VUV emissions. Radiation within this wavelength range along with chemical reactivity caused by high densities of free radicals while maintaining low gas temperatures plays an essential role for applications as e.g. the modification of temperature-sensitive surfaces or the interaction of the plasma with biological material [1]. Micro plasma jets introduce a new range of applicability by adding the possibility of localized treatment [2]. The energy transport processes from the plasma core region into the chemically reactive effluent region are of particular interest as this region is targeted for technological exploitations. Means of energy transport are e.g. metastables or radiation transport by VUV photons with correspondingly high energy.

The vacuum ultraviolet (VUV) emission in the wavelength range between 115 nm and 230 nm is analysed and the effect of varying the oxygen admixture to the helium flow is studied. The absolute VUV radiance is presented.

The spectra presented in the current work originate from both the active discharge region and from the downstream afterglow region of the µ-APPJ. The intent of the VUV spectroscopy on the plasma jet is to characterize the spatially resolved and temporally averaged optical emission.

2. Experimental
Investigations on the plasma radiation are carried out at the so-called µ-APPJ, an especially designed micro scale version of the APPJ providing excellent access for optical diagnostics, in particular to the core plasma [3]. This core plasma is enclosed between two coplanar 1 mm wide stainless steel electrodes. The electrodes are located inside a quartz cuvette at 1 mm distance thus forming a 30 mm long discharge channel with a cross section of 1 mm². The electrodes extending out of the quartz cuvette form a nozzle of about 4 mm length. This µ-APPJ is operated with applied transceiver powers between 5 and 10 W at radio frequency (13.56 MHz) in pure He (1 slm) and mixtures with O2 (0.5%) expanding in open atmosphere. The gas velocity of this effluent is at about 20 ms⁻¹. At these conditions the discharge operates in the a-mode characterised by a weak homogeneous emission.

The optical spectra were obtained using a 0.5 m VUV scanning monochromater from Acton Research Corporation (VM 505) with a grating of 1200 G/mm blazed at 150 nm. A photomultiplier tube from Thorn/EMI (9635 QB) was used as detector of the VUV radiation. The optical emission was measured end on by placing the quartz cuvette in the axis of the optical system. The system consists of a measuring aperture, imaging mirror and entrance slit, which are located in a vacuum chamber with a pressure of 2*10⁻⁶ mbar [4]. The plasma jet was positioned in open air at different distances axially to the MgF2 window which seals the vacuum chamber. This window is located in close proximity to the measuring aperture (diameter 0.6 mm) and couples the VUV radiation into the vacuum chamber. The mirror in the vacuum chamber images the area of the aperture on the entrance slit of the monochromator, to define the emitting area. The set-up is also equipped with a deuterium lamp (Cathodeon, V03 with MgF2 window) calibrated by the Physikalisch Technische Fig. 1: Uncalibrated VUV spectrum of the µ-APPJ operated in a helium/oxygen mixture displaying atomic oxygen emission from low lying singlet and triplet states of atomic oxygen and Lyman-α from gas impurities.
Bundesanstalt (PTB) in units of radiance ($\mu$W/nm mm$^2$sr, spectral bandwidth of 1.6 nm, low cut off wavelength 115 nm). The emission of this lamp is transferred via the same optical components to the entrance slit of the monochromator alternatively, so that no geometric corrections are needed (to obtain absolute radiance values). The spectral response of the detection system is received by dividing the spectral scan obtained from the radiance data provided by the deuterium lamp. Dividing spectral scans measured from the plasma jet, by the response function described above, gives the absolute radiance end on from the jet. These output spectra correspond to the VUV radiation emitted from a 0.282 mm$^2$ area (defined by the aperture).

The entrance slit of the monochromator was kept at 1.0 mm to ensure the same spectral bandwidth of 1.6 nm during the measurements of the radiance. Better resolved (0.2 nm bandwidth) uncalibrated spectral measurements were performed with a reduced entrance slit width, for line identifications.

3. Results

Figure 1 shows an uncalibrated VUV section of the $\mu$-APPJ emission. The main contributions of VUV radiation are assigned to two oxygen atomic lines, the Lyman-$\alpha$ line, and parts of the Schumann-Runge bands. The weak emission of the latter is not shown in figure 1. The spectrum is dominated by the O I resonance line ($^3P - ^3S_o$) at 130 nm. The emission line at 115 nm ($^1D - ^1D_o$) ends in the lowest metastable state of the singlet system. The Lyman-$\alpha$ of atomic hydrogen at 121 nm is attributed to impurities of the working gases and desorbing from the walls.

The VUV emission can be observed for distances from the nozzle of the discharge up to several centimetres. This comparably far expansion is caused by the radiation propagating in the rare gas stream leaving the jet before it vanishes due to turbulence effects.

The radial and axial dependences of the O I lines, in particular the resonance line at 130 nm, are investigated for oxygen admixtures around 0.5%. Different decay mechanisms of observed lines are discussed.

By varying distance from the nozzle, total flow and composition i.e. oxygen admixture another series of measurements could be carried out.

The absolute value of the radiation is an important information for modelling of the complex radiative processes of the system. Figure 2 shows the absolutely calibrated radiances of the 3 observed VUV lines in units of $\mu$W/sr mm$^2$ in dependence on the oxygen admixture measured close to the nozzle at a distance of 4 mm. The helium flow was kept constant at 3 slm for these measurements.

As a first result it is found that the calibrated radiance ratio between the two oxygen lines is reversed. The singlet emission line at 115 nm is depending on the admixture about a factor of 3 stronger than the 130 nm resonance line. Radiances of about 10 $\mu$W mm$^{-2}$sr$^{-1}$ are measured for that resonance transition into the atomic oxygen ground state. This observation could be explained by the presence of a substantial amount of metastable oxygen atoms within the discharge core. The hydrogen line radiance is about one order of magnitude lower than the singlet emission.

The maximum radiance for all three lines is observed for lowest O$_2$ admixtures. It decreases with increasing admixtures. The general decay of the lines could either be attributed to changes of the excitation function of the discharge or additional absorption due to molecular oxygen. The singlet line shows a much stronger decay than the resonance line. This corresponds very well with the known strong quenching of the metastable oxygen $^1D$ state by molecular oxygen [5].

One of the most important advantages of micro plasma jets is the possibility of localized treatment of sensitive surfaces. Prerequisite for this application is a collimated effluent. It was demonstrated by TALIF spectroscopy that the oxygen atoms stay collimated after leaving the nozzle of the jet over distances of several centimetres [6].
confirmed by measurements scanning the radial emission profiles transversely to the electrodes at various distances from the nozzle. For these measurements the nozzle of the µ-APPJ is displaced towards the entrance aperture of the diagnostics system. Results are displayed in Fig. 3 for 4 and 10 mm distance from the nozzle for a gas flow of 1.5 slm Helium and an admixture of 0.1 vol-% oxygen. A width of the beam of about 0.8 mm is observed at both distances. This value is very close to the diameter measured by TALIF spectroscopy. Small deviations might be explained by a small misalignment of the jet’s axis towards the observation axis or an effect of the end-on measurement.

Fig. 4 shows the decay with distance of the singlet and triplet emission lines at 115 and 130 nm at a flow of 1.5 slm He with an admixture of 0.7 vol-% oxygen. The measurements were done starting at a distance of 4 mm from the discharge core defined by the glass cuvette up to 14 mm. It is obvious from fig. 4 that the singlet line at 115 nm (black circles) is absorbed rapidly within a distance of about 2 mm. Regarding the flow velocity of about 20 ms⁻¹ this corresponds to a decay time of 1 ms. The 130 nm triplet line shows a significantly different behaviour. The fluorescence decreases slowly to half maximum value over a distance of about 8 mm. Provided that absorption at this distance is mostly determined by the working gases the locally transmitted intensity can be calculated for both lines. For this estimation we assumed a constant molecular oxygen concentration of 0.7 vol-%. This is an acceptable approximation since outside the discharge core the ozone and atomic oxygen ground state densities have been measured to be below 1 percent of the molecular oxygen concentration. The associated profiles, measured by UV absorption [7] and with TALIF [6] respectively, have also been incorporated into the estimate of the respective contributions to absorption. The absorption coefficients for molecular oxygen and ozone were taken from Okabe [8]. For atomic oxygen the values were calculated via the absorption oscillator strength. The resulting atomic absorption is about an order of magnitude smaller than the other ones.

The respective theoretical decay behaviour for both lines is shown as red and black lines corresponding to the colour of the measured values. It appears that the absorption of the singlet line at 115 nm is well approximated by this coarse model. However, this is not the case for the triplet line at 130 nm. Here, additional contributions must be taken into account. One candidate could be metastable oxygen O₂,a¹Δg, yet its absorption coefficient at 130 nm is too low to provide a significant contribution [9].

4. Conclusions

Absolutely calibrated measurements of the VUV radiance of an RF micro plasma jet have been carried out and presented. Operated in helium with a vol-% admixture of molecular oxygen two atomic emission lines at 115 and 130 nm dominate the observed spectra. Radiance from other plasma components as molecular oxygen and hydrogen from impurities only constitute below 10 % of the total radiance in the wavelength region between 115 and 200 nm. The dominant transition observed at 115 nm is located in the singlet system of the atomic oxygen and ends in the lowest lying metastable state. (¹D). The observed exponential decay of the radiance outside the discharge core allows an estimate of the radiance inside to be about 50 μW mm⁻²sr⁻¹ for an oxygen admixture of 0.1 vol-%.

This emission contributes significantly to the total radiation of the discharge and in consequence influences its energy balance. The population of the metastable ground state is rapidly quenched in the effluent of the discharge by collisions with oxygen molecules. This is confirmed by the rapid absorption of the 115 nm emission line and the decay of the emission with increasing oxygen admixture.

The second important atomic oxygen VUV emission is a resonance line at 130 nm. The maximum radiance of this contribution is much less influenced by the amount of admixed oxygen. The radiation decay in the afterglow of the µ-APPJ cannot be explained solely from the absorption of oxygen constituents as atomic and molecular oxygen, ozone or metastable oxygen molecules. It is therefore assumed that at larger distances ambient air diffuses into the effluent and starts to determine the absorption.

In summary the measurements demonstrate that VUV radiation with photons of beyond 10 eV is transported through the helium atmosphere of the plasma jet afterglow to distances of centimetres.

This radiation is strictly localized to a diameter corresponding to the cross section of the micro jet. The energy and radiance of these photons is sufficient to break molecular bonds and has therefore to be taken into account for applications of the micro jet.
Acknowledgements
Support of this work by the DFG in the frame of the research group FOR1123 and project SCHU 2353/1 is gratefully acknowledged. The authors also would like to thank Mr. P. Holtz for technical support.

References