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Spatially resolved diagnostics on a microscale atmospheric pressure plasma jet

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Abstract
Despite enormous potential for technological applications, fundamentals of stable non-equilibrium micro-plasmas at ambient pressure are still only partly understood. Micro-plasma jets are one sub-group of these plasma sources. For an understanding it is particularly important to analyse transport phenomena of energy and particles within and between the core and effluent of the discharge. The complexity of the problem requires the combination and correlation of various highly sophisticated diagnostics yielding different information with an extremely high temporal and spatial resolution. A specially designed rf microscale atmospheric pressure plasma jet (µ-APPJ) provides excellent access for optical diagnostics to the discharge volume and the effluent region. This allows detailed investigations of the discharge dynamics and energy transport mechanisms from the discharge to the effluent. Here we present examples for diagnostics applicable to different regions and combine the results. The diagnostics applied are optical emission spectroscopy (OES) in the visible and ultraviolet and two-photon absorption laser-induced fluorescence spectroscopy. By the latter spatially resolved absolutely calibrated density maps of atomic oxygen have been determined for the effluent. OES yields an insight into energy transport mechanisms from the core into the effluent. The first results of spatially and phase-resolved OES measurements of the discharge dynamics of the core are presented.

1. Introduction

Non-thermal non-equilibrium atmospheric pressure plasmas are commonly characterized by reduced spatial dimensions of the confining structures, e.g. electrodes, stabilizing the discharge and preventing the transition to a ‘thermal’ discharge. Typical dimensions vary from a few micrometres up to a few millimetres. The wide range of these discharges is, therefore, often sub-summarized under the topic ‘micro plasmas’ [1–4].

High concentrations of atoms in the order of $10^{14}$ cm$^{-3}$ and a low gas temperature significantly below 100 $^\circ$C, suitable for many applications especially in localized modifications of sensitive surfaces, can be provided by jet-like devices without the requirement of complicated and expensive vacuum systems [5]. Many of these discharges operate in a mixture of a noble gas, preferably helium, and a small molecular component selected depending on the envisaged application [6]. Despite enormous potential for technological applications, the fundamentals of these stable homogeneous non-equilibrium plasmas at ambient pressure are only poorly understood. This is mainly due to the complexity of these discharges composed of electrodes in the close neighbourhood of the confining walls and a mixture of neutral and charged atomic and molecular gas components. Furthermore, radiation can play an important role in the discharge balance. Finally, these jets are divided into the core plasma where all plasma processes are driven and the effluent with applicable reactive gas components.

The discharge concept adopted here is the atmospheric pressure plasma jet (APPJ) introduced by Selwyn and co-workers [7] in 1998. This technically relatively simple capacitively coupled device is typically operated at an excitation frequency of 13.56 MHz and an electrode spacing...
of about 1 mm. A mixture of a noble gas as the base gas and a 1 vol% addition of a molecular component serves as the operating gas. A further increase of the molecular admixture is limited by the onset instability of the discharge. At gas flows of about 2 m³ h⁻¹ the resulting gas velocities are some 10 m s⁻¹. The atomic oxygen concentration in the effluent leaving the discharge ‘core’ of an APPJ at 150 W input power and 0.5 vol% O₂ admixture was measured to be n_O ≈ 10¹⁵ cm⁻³ [8]. These reactive oxygen species are supposedly responsible for the surface modifying properties of the jet [9, 10].

One phenomenon under discussion for these discharges is the stability range. At low powers the discharge behaves like a typical α-mode discharge, while at higher powers it turns into the γ-mode [11]. The discharge then becomes inhomogeneous, showing bright concentrated discharge columns that can even become ohmic. The distinction between these two modes is not precise in the literature. In general the constricted discharge is designated as the ‘arcing mode’. The stability range for homogeneous α-mode operation can be significantly reduced, e.g. if the base gas is changed to argon [12]. The mode transition of these discharges along with the related structure formation processes is extremely complex and is a major issue in understanding the fundamental discharge mechanisms. The investigation of the discharge dynamics and transport processes within the discharge volume is, therefore, essential. Due to the geometry and dimensions of the discharges in [7, 13](concentric or plane parallel with an exit cross section of 40 mm² at a slit width of 1 mm and a length of 100 mm) access to the discharge core is severely limited.

Here we present investigations on a specifically designed microscale atmospheric pressure plasma jet (μ-APPJ) (figure 1) with a reduced discharge volume of 1 × 1 × 30 mm³ between stainless steel electrodes and quartz glass side walls. The operation parameters of the μ-APPJ are scaled down from the ‘standard’ APPJ—where possible—to keep the devices comparable. This reduces the gas flow from a value of 1 m³ h⁻¹ down to 1 slm. The discharge is operated using helium as the base gas and oxygen admixtures. Typical transceiver powers for this device range from 5 to 20 W and result in gas temperatures in the effluent of about 30 °C.

The construction of the device provides excellent diagnostic access to the full length of the discharge volume and the interface to the effluent region, in particular for optical techniques. Figure 1 shows a sketch of the possible large detection solid angle necessary for laser fluorescence methods. For all presented measurements the nozzle at the end of the quartz windows defines the origin (zero position) of the z coordinate with the z axis in the direction of the gas flow.

In summary the device allows, for example, detailed investigations of the discharge dynamics, the constituents as well as particle and energy transport mechanisms from the discharge to the effluent. This complex system can only be approached by a combination of diagnostics dedicated to different quantities and regions. In the following we present a selection of measurements providing information on a limited sub-set of these. Optical emission spectroscopy (OES) in the visible and the (vacuum) ultraviolet ((V)UV) can yield information not only on the composition of the core plasma but also on radiation passing through the effluent. In the effluent atoms, generated in the core, undergo processes such as de-excitation or molecular recombination before they reach a surface to be treated. Knowledge of the absolute number densities and the spatial distribution of atomic ground state oxygen in the effluent is therefore essential. These quantities can be measured using two-photon absorption laser-induced fluorescence (TALIF) spectroscopy. The generation of the atoms in the core is mainly determined by the electrons. Phase resolved optical emission spectroscopy (PROES) yields an insight into the electron dynamics in that region, in particular into electron heating mechanisms and the plasma boundary sheath dynamics. This allows a direct comparison with simulation results. First conclusions are drawn based on the combination of results from the presented diagnostics.

2. OES in the UV and VUV

OES represents a technically simple diagnostic for micro-discharges regarding the limited access. Preliminary OES measurements in the effluent of a standard APPJ yielded the observation of emission from excited atomic oxygen (λ = 777 nm) transversely to the direction of the gas flow at a distance of 100 mm outside the plasma [12]. Regarding the lifetime of the emitting state of τ ≈ 27 ns and the gas velocity the excited state must be populated outside the discharge core. Electrons are not detectable in the effluent [14]. The possible candidates for excitation are collisions by metastables or radiation.

Here, we present spatially resolved time-integrated OES measurements in the UV and vacuum ultraviolet (VUV) in search for an energy transport mechanism that can provide this excitation energy [13, 14]. Helium and argon metastables can be excluded since they are subject to very fast two-step destruction processes via excited dimers at high pressures [15]. During this process radiation in the VUV is emitted (e.g. argon...
excimer continua). To deal with this question the radiation of the jet was directed through the air towards the entrance slit of a 25 cm monochromator closed vacuum tight with a 1 mm magnesium fluoride window. Spectra between 120 and 330 nm were taken with a solar-blind photomultiplier.

Figure 2 shows a set of spectra taken at the 2 mm distance of the entrance slit of the monochromator from the nozzle of the jet for increasing admixtures of 0–0.6% oxygen into a helium base gas. The main spectral features visible are an atomic oxygen line at $\lambda = 130$ nm, the Schumann–Runge bands of molecular oxygen at around 180 nm and for certain conditions NO and OH bands from impurities between 180 and 300 nm. Even the VUV radiation components are transported over distances of several centimetres into the surrounding atmosphere [13]. At this point it has to be realized that the radiation is transported in the jet’s ‘own’ atmosphere mostly consisting of helium. From figure 2 it can be seen that for small or no admixture of oxygen the NO and OH line emission is relatively strong in comparison with higher admixtures. The latter might derive from impurities or an inmixing of the surrounding atmosphere. For the same reason also the line of atomic oxygen might be dominant even for no oxygen admixed. An interesting point to note is the maximum of O emission at the 0.06% oxygen admixture. At this admixture the line emission of NO and OH is already strongly quenched. This means that the respective excitation and production mechanisms are suppressed. For small admixtures the production of atomic oxygen will follow the admixture but at some point the energy required for the rotational and vibrational excitation of the oxygen molecules will disturb the plasma itself. This can be correlated with the known increase in ignition power for plasmas with molecular admixtures. The decision whether the atomic oxygen densities also peak at around 0.06% by OES is difficult due to the model dependence of OES. Apart from characteristic cross sections the electron energy distribution function determining the excitation has to be known before conclusions can be drawn from the emission on the concentration of the ground state atom. For a method such as actinometry under atmospheric pressure conditions collisional de-excitation (‘quenching’) must be carefully checked and taken into account for the respective lines. One method to determine absolute ground state number densities for light atoms is TALIF spectroscopy. Atomic oxygen is supposedly the most important reactant in the effluent for applications. Therefore, the spatially resolved measurement of the absolute oxygen concentration in the effluent is of great importance also for the understanding of surface processes.

The radiation at 130 nm consisting of photons of about 9.5 eV in combination with metastable molecular oxygen might be a source of excited atomic oxygen outside the discharge core. For a more detailed analysis the radiation leaving the APPJ will have to be measured with an absolutely calibrated setup [5].

For a more detailed understanding of energy transport processes in the effluent knowledge of the concentration profiles of the constituents in the effluent and in the discharge core is indispensable. The main constituents are molecular oxygen including metastable O$_2$(b 1 $\Delta_g$) and ozone, atomic oxygen and helium atoms and will have to be measured to complete the picture. Ozone is accessible by UV absorption spectroscopy and some results for the APPJ are presented by Jeong et al [16].

3. Two-photon absorption laser-induced fluorescence

To quantitatively acquire the atomic oxygen ground state densities spatially resolved TALIF can be applied [17]. Here, this technique is based on the excitation of ground state atoms by simultaneous absorption of two laser photons at a wavelength of 225 nm and subsequent observation of the fluorescence at 845 nm in a perpendicularly oriented optical setup with a gated photomultiplier. By moving the APPJ in relation to the point defined by the overlap of the laser and the observation path a map of the fluorescence in the effluent area is determined. An absolute calibration is subsequently required to transform the fluorescence signals into a concentration map for the oxygen atoms. The method is based on comparative TALIF measurements using the noble gas xenon as a reference with a two-photon resonance spectrally close to that of the atomic oxygen to be quantified [8]. To allow this calibration the measurements are carried out in a helium filled vacuum-tight cell. For the measurements presented here the vessel is filled with the same gas mixture as the operating gas. With this, effects of the atmosphere backflow into the discharge which would also influence the calibration process are excluded. For a more general description of the TALIF technique we here refer to [18,19]. At atmospheric pressure several effects have to be taken into account. The most important ones are various saturation effects and artificial particle generation. The latter is of particular importance for mixtures with molecular components. At atmospheric pressure non-radiative de-excitation of excited states by collisions, so-called ‘collisional quenching’, can no longer be neglected. Quenching reduces the fluorescence lifetime of an excited state. The quenching rate for each specific state is dependent on the number density.
and the quenching cross section of each possible quenching partner in the discharge. This results in an additional temperature dependence of the calibration.

These measurements presented here have been carried out in the effluent of the µ-APPJ operating with He/O₂. For these conditions we can assume that only O₂ and He significantly influence the quenching since other species such as ozone or atomic oxygen are minority species. The setup and results are described in detail in another publication in this issue [20]. The resulting on-axis profile of the absolute atomic oxygen ground state density for a 1.4 slm helium flux containing 1% O₂ at an RF power of 15 W transceiver power is shown in figure 3. The measurements presented here are spatially resolved with a resolution of about 1 mm along the laser axis and 0.3 mm in the perpendicular direction. The starting point of the measurements is located 5 mm outside the cuvette to prevent reflections into the optical detection system. The atomic oxygen density and the gas temperature are the highest close to the nozzle: 2 × 10⁻¹⁴ cm⁻³ and 35 °C, respectively. From that point the atomic density decreases approximately exponentially by a factor of about 4 down to 6 × 10⁻¹⁵ cm⁻³ over a distance of about 2 cm. Beyond this distance the concentration on the axis only slightly decreases to about 4 × 10⁻¹⁵ cm⁻³ over the full accessible spatial range of 80 mm. The detection limit of the system is at about 2 × 10⁻¹³ cm⁻³ with an estimated error of about a factor of 2 mainly from uncertain cross sections. In combination with the OES measurements one possible explanation for the behaviour is the influence of UV radiation producing an approximately constant background while the fast drop may be explained by processes destroying atomic oxygen, e.g. by the production of ozone. Within the accuracy of UV absorption measurements the ozone concentration is in reasonable agreement with this argument.

The assumption of an exponential decay allows an extrapolation of the ground state density back to the nozzle, i.e. to the end of the plasma core. For this position the concentration is in the order of 1 × 10⁻¹⁵ cm⁻³ and can be taken as a first estimate of the densities inside the discharge core.

In the direction perpendicular to the effluent a range of ±10 mm is accessible for detection. In this region a spreading of the concentrated beam leaving the nozzle can be observed as shown in figure 4. An important result of these measurements is the concentration of the atomic oxygen density to the beam axis showing only a slight divergence raising the beam diameter from about 2 mm at the 5 mm distance from the nozzle to about 4 mm at 25 mm. Further details are presented in the paper by Knake et al in this issue [20]. Gas flow effects may be responsible for the density increase far off the beam axis close to the device. Within the limited accessible range a final conclusion cannot be drawn. Measurements of the ozone distribution in the effluent region done by UV absorption spectroscopy based on a Hg/Ar lamp yielded similar observations. This behaviour changes to a more turbulent behaviour in ambient air [13]. The observed distribution maps of ground state atomic oxygen correlate reasonably well with those resulting from measurements at a standard APPJ [8,14]. Deviations such as a higher average concentration and an even stronger concentration of the beam may be attributed to lower diffusion losses in the large device. We therefore assume that we can regard both discharges to be equivalent.

The measurements in the effluent prove the existence of ground state oxygen atoms far outside the jet as indicated by the observations by OES in the visible. The emission from the core discharge in the UV and VUV wavelength range still has to be taken into account as an energy transport mechanism for the excitation and production of excited atomic oxygen outside the discharge.

Parameter studies varying the admixture of molecular oxygen, input power and gas flow reveal, for example, a clear maximum of atomic oxygen production at a molecular admixture of 0.6% [20]. Observations in the VUV show a maximum atomic oxygen emission at significantly lower admixtures. To understand this behaviour plasma chemical and surface processes on the surrounding walls will have to be analysed in detail. Still, both diagnostics only give an indirect access to the production processes inside the discharge.

First successful preliminary TALIF measurements inside the discharge core show an atomic oxygen density in the order of 10¹⁶ cm⁻³. This corresponds to a degree of dissociation in the order of 20%. As a consequence of this high value the basic assumptions for the calibration have to be checked since atomic oxygen can become an important quenching partner. Other important features are the gas temperature...
and electronic excitation. The quenching cross section for atomic oxygen is known only approximately [21]. Methods of OES can be applied to solve the problems. Gas temperatures can be determined from ro-vibrational emission bands of the molecule. PROES as described in the following section can be applied to measure the effective lifetime of the specific state due to all present quenchers. From a variation of the partial gas pressure the effective quenching rate can be determined.

4. Space and phase resolved OES

PROES complements the other diagnostics by providing access to the dynamics of the excitation processes within the discharge core. Typically this dynamics is attributed to the mobile electrons. Since the excitation energies of the observable states of oxygen are usually close to the ionization limit and much higher than the dissociation energies information on these states also allows conclusions for these processes. The technique is based on measuring the population dynamics of excited states in rf discharges by analysing the fluorescence radiation with temporal resolution on a nanosecond time scale. For the experiments presented here an optical system is used that has already demonstrated its ability of allowing a deep insight into the electron dynamics of low-pressure low-temperature discharges [22].

The optical system is based on a high-repetition-rate, gateable and intensified charged coupled device camera (ICCD camera) with 576 × 384 pixels on a sensitive surface of 13.2 × 8.8 mm². The µ-APPJ is imaged with a magnification of about 4 onto the camera providing a spatial resolution of 6 µm per pixel. The phase resolved measurement is realized by synchronizing and delaying the camera gate (width of 3 ns) to the excitation frequency of 13.56 MHz. By this method one cycle of the excitation of about 74 ns is resolved into spatially resolved images of the discharge at 25 equidistant phase positions. The combination of inter-electrode profiles from all phase positions finally yields the spatio-temporal profile displayed in figure 5. The time axis indicates the start of each time interval. Here the location of the 1 mm wide inter-electrode cross sections is approximately 5 mm inside the discharge in the central region not influenced by effects of the nozzle.

The wavelength-integrated experiment presented was carried out for a pure helium flow of 1 slm at a transceiver power of about 25 W.

From this spatio-temporal map conclusions can be drawn on the electron kinetics within the discharge between the electrodes. A first observation is the excellent symmetry of the discharge showing three pairs of emission features (indexed as 1–3) of equal intensity and distance to the electrodes. The respective emission at the opposite electrode is displaced by 1–3) of equal intensity and distance to the electrodes. The combination of inter-electrode profiles from all phase positions finally yields the spatio-temporal profile displayed in figure 5. The time axis indicates the start of each time interval. Here the location of the 1 mm wide inter-electrode cross sections is approximately 5 mm inside the discharge in the central region not influenced by effects of the nozzle.

Figure 5. A phase and space resolved wavelength integrated emission profile showing the emission behaviour in one excitation cycle between the electrodes from the central region of the µ-APPJ in pure helium at a medium transceiver power. The intensity rises from bright to dark colours. The highest intensity is localized in the features indexed as 2 close to the electrodes localized at a ±0.5 mm distance from the discharge axis. The maxima are exaggerated for better visibility in this grey scale plot.

was previously observed in hydrogen rf discharges at low pressures [23]. A comparison with electron production structures for an α-mode discharge at atmospheric pressure modelled by Shi and Kong furthermore shows very good agreement in phase position and location of these emission structures [24]. This comparison is reasonable since excitation and ionization energies of helium are close enough (about 2 eV), so that it can be assumed that both processes are driven by the same group of electrons. The additional feature 3 appearing at this intermediate power input can be attributed to the onset of secondary electron amplification in the phase of increasing field strength. This excitation mechanism becomes dominant at higher transceiver powers changing the discharge into the γ-mode. This mode is characterized by a significantly higher gas temperature of about 75 °C as compared to 30 °C in the α-mode and a strong concentration of the emission including the danger of electrode destruction or—in the case of application—of the substrate.

For a more detailed insight into the electron excitation processes wavelength-resolved OES measurements are a prerequisite and in preparation. At atmospheric pressure the influences of quenching will additionally have to be integrated into the analysis [25].

5. Conclusions

Micro-plasma jets represent a very complex system consisting of various distinct regions such as core and effluent. While the core contains, apart from electrons and ions, neutral particles such as molecules and atoms, the effluent is predominantly composed of neutrals. OES measurements show that UV radiation with energies of about 10 eV from the core can transport energy into the effluent and excite and dissociate atoms and molecules. To verify this the measurement of the number densities of the gas constituents is necessary. Here we present spatially resolved results for the number density of atomic oxygen in the effluent measured using two photon-absorption laser-induced fluorescence spectroscopy. Atomic
oxygen can be detected with densities of some $10^{13}$ cm$^{-3}$ up to distances of 8 cm from the nozzle of the micro-jet. The results show a concentrated beam of oxygen atoms expanding several centimetres into the surrounding atmosphere. This proves the applicability of the micro-jet for localized treatment. Close to the nozzle the discharge oxygen atoms are rapidly destroyed and the density falls off from about $10^{15}$ to $10^{13}$ cm$^{-3}$ within 2 cm. First absorption measurements of ozone indicate that the main loss process for atomic oxygen is the formation of ozone. Detailed measurements of other components of the effluent such as ozone and metastables molecules required to complete the understanding are still in progress. Further calibrated measurements are also necessary for the analysis of the radiation coupling the effluent to the core.

The particles flowing into the effluent are generated in the discharge core. For an understanding of the relevant production and destruction processes in the core the determination of the particle densities is of eminent importance. The small dimensions of the discharge add additional complications to the measurements as described above by reflections, windows close to the laser focus, and so on. Preliminary TALIF measurements have been carried out yielding number densities two orders of magnitude higher than in the effluent. For the core discharge PROES shows that the discharge can be operated as a typical low-temperature $\alpha$-mode discharge. In this case processes inside the discharge are driven mainly by the electrons. PROES yields an insight into the electron dynamics of the micro-jet. A comparison of space (inter-electrode) and time resolved theoretical models of the ionization rate shows very good agreement. For further analysis yielding more insight into the electron energy distribution function wavelength selected measurements are prepared.

The results are clear indications that only a combination of suitable diagnostics with modelling will provide the necessary understanding of these micro-discharges. They furthermore reveal an urgent need for detailed spatially resolved measurements between the electrodes of the $\mu$-APPJ in order to understand the influence of wall effects on the core discharge, plasma chemical processes within it and in the effluent.

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