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Diagnostics on an atmospheric pressure plasma jet

K. Niemi¹, St. Reuter², L. Schaper¹, N. Knake¹, V. Schulz-von der Gathen¹,
T. Gans³

¹Institute for Application oriented Plasma Physics, CPST, Ruhr-University Bochum,
Germany
²Institute for Experimental Physics, University Duisburg-Essen, Germany
³Centre for Plasma Physics, Queen’s University Belfast, Northern Ireland

E-mail: t.gans@qub.ac.uk

Abstract. The atmospheric pressure plasma jet (APPJ) is a homogeneous non-equilibrium 
discharge at ambient pressure. It operates with a noble base gas and a percentage-volume 
admixture of a molecular gas. Applications of the discharge are mainly based on reactive 
species in the effluent. The effluent region of a discharge operated in helium with an oxygen 
admixture has been investigated. The optical emission from atomic oxygen decreases with 
distance from the discharge but can still be observed several centimetres in the effluent. 
Ground state atomic oxygen, measured using absolutely calibrated two-photon laser induced 
fluorescence spectroscopy, shows a similar behaviour. Detailed understanding of energy 
transport mechanisms requires investigations of the discharge volume and the effluent region. 
An atmospheric pressure plasma jet has been designed providing excellent diagnostics access 
and a simple geometry ideally suited for modelling and simulation. Laser spectroscopy and 
optical emission spectroscopy can be applied in the discharge volume and the effluent region.

1. Introduction

There is rapidly growing interest in non-thermal atmospheric pressure plasmas, especially diffuse 
homogeneous glow discharges, starting with the publications by Bartnikas [1,2] and Okazaki [3-5] and 
co-workers in the late 1980s. These non-equilibrium discharges have drawn considerable attention due 
to their enormous potential for technological applications. High concentrations of radicals, suitable for 
many applications preferably in surface modifications, can be provided without the requirement of 
complicated and expensive vacuum systems. The absence of streamer-like micro-discharges, as known 
from dielectric barrier discharges, and a low gas temperature allow application to sensitive surfaces. 
Many of these discharges operate in a mixture of a noble gas, preferably helium, and a small 
molecular component - depending on the application envisaged. A variety of applications have already 
been demonstrated, e.g., in semiconductor technology, art restoration, and biomedicine.

The discharge concept adopted here is the Atmospheric Pressure Plasma Jet (APPJ) introduced by 
Selwyn, Hicks and co-workers [6] in 1998. This technically relatively simple capacitively coupled 
device (figure 1) is typically operated at an excitation frequency of 13.56 MHz and an electrode 
speaking of about 1 mm. The length and width are usually a few centimetres. The mixture of noble and 
molecular gas is flushed through this discharge area at a high flow rate in the order of m³h⁻¹. The 
effluent can be easily applied for treatments of various substrates. Many application experiments have 
been performed by Selwyn and co-workers demonstrating the ability of depositing and removing
silicon oxide layers, to remove tungsten layers, and to clean surfaces from biological contamination [7-9].

Figure 1: Typical set-up of a radio-frequency atmospheric pressure plasma jet.

Investigations on discharge phenomena have been mainly concentrated on electrical characterisation of the discharge [10-12]. On the basis of model calculations the electron density within the discharge is estimated to be in the order of $10^{11}\text{cm}^{-3}$. Outside the discharge area the ion density was measured to be one order of magnitude lower, even close to the nozzle [7]. Further experiments have investigated the operation regimes of the discharge. At low powers the discharge is characterised as a typical $\alpha$-mode discharge, while at higher powers it turns into $\gamma$-mode [13]. The discharge then becomes inhomogeneous showing bright concentrated discharge columns and can even become ohmic. The distinction between these two modes is not precise in literature. However, a few approaches from the modelling and simulation side, based on drift-diffusion approximation in a fluid picture, have been presented recently [14,15]. In general this condition is designated as “arching mode”. Reducing the power shows a strong hysteresis requiring much lower power before the homogeneous discharge recovers [10-12]. Parameters determining the onset of the transition into the inhomogeneous mode are manifold. Apart from the rf power and frequency the electrode separation, the gas flow, and the admixture of the molecular component influence the mode transition. A typical limit of the molecular admixture is of the order of 1%.

It has been demonstrated recently that the homogeneous operation is also possible with argon as a base gas [16]. In this case the power operation range is significantly narrower than with helium. The discharge ignites at higher power with hotter effluent and becomes unstable earlier.

In the following measurements of excited species and ground state atomic oxygen in the effluent region are presented. In particular, absolutely calibrated measurements of atomic oxygen using two-photon absorption laser induced fluorescence (TALIF) under atmospheric pressure conditions are discussed. These measurements show that the understanding of energy transport mechanisms from the discharge region into the effluent region is crucial. The design of a new micro-APPJ ($\mu$-APPJ) allows excellent optical access to the discharge volume as well as the transition region to the effluent. This will allow detailed investigations of the discharge dynamics and energy transport mechanisms to the effluent region.
2. Absolutely calibrated TALIF measurements of atomic oxygen

In this section we discuss quantitative, spatially resolved TALIF measurements of atomic oxygen ground state densities in the effluent of an APPJ with concentric geometry, operated with O\textsubscript{2}/He. The results are based on a TALIF calibration scheme with xenon [17,18]. The method of TALIF calibration with noble gases for the determination of absolute atomic ground state densities has been introduced by Goehlich et al. [19]. It represents a technically simple alternative to the use of atomic reference sources like the flow-tube reactor with titration [20]. The method is based on comparative TALIF measurements using a noble gas as a reference with a two-photon resonance spectrally close to that of the atomic species to be quantified. Xenon is well suited for the purpose of the present measurements - calibration of atomic oxygen - as shown in figure 2.

\[
\frac{S_O}{S_{Xe}} = \frac{n_O \sigma^{(2)}_O T_O \eta_O a_O}{n_{Xe} \sigma^{(3)}_{Xe} T_{Xe} \eta_{Xe} a_{Xe}}
\]

with the fluorescence signal \(S\) (integrated over fluorescence wavelength, excitation wavelength and interaction time), the effective branching ratio \(a\) of the observed fluorescence transition, the transmission \(T\) of the detection optics and the detector’s quantum efficiency \(\eta\) for the fluorescence wavelength, and the two-photon excitation cross section \(\sigma^{(2)}\).

Figure 2: Two-photon excitation schemes of atomic oxygen and xenon.

Several rules have to be observed: the conditions of excitation and detection should be as similar as possible for both the oxygen and xenon transitions; this includes the properties of the laser output and the optical set-up. Only the unsaturated quadratic signal response allows a quantitative comparison. The various saturation effects (ground state depletion, photo-ionization out of the excited state, amplified spontaneous emission (ASE) via fluorescence channels or artificial particle generation, e.g. by photo-dissociation) exhibit rather complex intensity dependences with individual thresholds; therefore, the laser intensity has to be kept as low as possible. The unknown atomic ground state density \(n_O\) is then related to the reference gas density \(n_{Xe}\) by:
Collisional quenching, especially with increasing pressure, reduces the effective branching ratio of a spontaneous transition $i \rightarrow k$:

$$a = \frac{A_{ik}}{A_i}$$

where $A_i$ denotes the effective decay rate including quenching:

$$A_i = \sum_k A_{ik} + \sum_q k_{iq} n_q$$

Here, it becomes obvious that knowing the relevant quenching coefficients $k_q$ and the densities of the corresponding quenching partners $n_q$ is essential, in particular under atmospheric pressure conditions when collisional de-excitation can be dominant.

The effective decay rates and, therefore, the required quenching coefficients can be determined from the temporal behavior of the fluorescence decay after pulsed excitation with a short laser pulse [21]. The change of the fluorescence decay is illustrated in figure 3. It is obvious that the decay time and the integrated fluorescence signal decrease significantly with increasing density of the quenching partners. Under the conditions investigated molecular oxygen is the dominant quenching partner [22].

![Figure 3: Illustration of the change of the fluorescence decay due to quenching.](image)

A systematic variation of the density of quenching partners allows the measurement of quenching coefficients from the slope in a so-called Stern-Volmer plot [23]. Figure 4 shows a Stern-Volmer plot for the most relevant quenching partners expected in the APPJ operated with small oxygen admixtures in helium or argon, respectively.
In the following we discuss absolute measurements of atomic oxygen in the effluent region of an APPJ operated in helium with a 0.5% admixture of molecular oxygen; figure 5 displays the experimental set-up [18]. The vessel allows absolute calibration using xenon as filling gas. The majority species in the jet effluent are the feed gases helium and molecular oxygen. They represent the dominant colliders responsible for the strong and inhomogeneous quenching of the laser-excited O atoms. We can infer the effective quenching rate on the basis of measured quenching coefficients, since we know the dominant colliders responsible for quenching of the laser excited oxygen atoms as well as their density distributions.

Figure 4: Stern-Volmer plot for the determination of relevant quenching coefficients.

Figure 5: Experimental set-up for absolutely calibrated TALIF measurements of atomic oxygen.
The local effective quenching rate can be calculated on the basis of the measured room temperature quenching coefficients and the measured gas temperature field shown in figure 6 (a). The density distributions of both colliders are simply related to the gas temperature according to Dalton’s law for the case of constant (atmospheric) pressure and constant ratio of molecular oxygen to helium (according to the feed gas composition) throughout the jet effluent. The former is supported by the laminar flow conditions and the latter by the fact that we have a cold and weakly dissociated gas in which the (plasma-) chemically generated particles are still in a minority. The gas temperature was measured by a thermocouple.

The determination of the absolute atomic density is performed in the following way: in a first step, a two-dimensional fluorescence map of the jet effluent is recorded, where the on-resonance fluorescence signal is measured as a function of the axial and radial positions. Then, the calibration measurement is performed at one spatial position. The spectrally and temporally integrated fluorescence signal is measured as a function of the laser pulse energy. The analogous procedure is repeated for the case of xenon filling at the close-by Xe resonance. The fluorescence map data recorded on-resonance were converted into spectrally integrated data using the measured temperature distribution. The resulting map of the absolute atomic oxygen density for a helium flux of 2 m\(^3\) h\(^{-1}\), an O\(_2\) flux of 0.01 m\(^3\) h\(^{-1}\) (corresponds to an O\(_2\) admixture of 0.5%) and an RF power of 150 W is shown in figure 6 (b).

The atomic oxygen density and the gas temperature are highest close to the nozzle: \(2.8 \times 10^{15}\) cm\(^{-3}\) and 80°C, respectively. The atomic density decreases by nearly two orders of magnitude, and the gas temperature drops to 65°C over a distance of \(~10\) cm on-axis. The atomic density remains sharply concentrated within the nozzle cross section, although the temperature field indicates a slight beam divergence. Only the shape of the radial density distribution develops from a hollow profile, caused by the annular structure of the nozzle, to a centred one at far distances; the particular case of a flat-top density profile is found at \(~1\) cm. It is likely that the radial density drop at the beam border is considerably steeper because the laser beam with an estimated diameter of \(~4\) mm is not focused in the radial direction for the chosen orientation of a cylindrical lens. This cylindrical lens was chosen to avoid the above mentioned problem with laser dissociation. The situation is alleviated by the nonlinear character of the two-photon excitation process, which leads to an effective radial resolution of \(~2\) mm.

Figure 6: Gas temperature field (a) and map of absolute atomic oxygen density (b) in the APPJ effluent.
This observed distribution map of ground state atomic oxygen correlates well with the observed fluorescence of excited atomic oxygen. Figure 7 shows a measurement of excited atomic oxygen (777 nm) in the effluent. Fluorescence can be observed at distances of several centimeters from the nozzle of the discharge. These distances over which excitation survives, after excitation inside the discharge, are much larger than can be expected according to the natural lifetime. The energy transfer processes providing excited atomic oxygen relatively far (10 cm) outside the discharge are still being discussed. Possible explanations such as excitation by helium metastables are not convincing. Radiation in the UV and VUV wavelength ranges, however, has to be taken into account as a second energy transport mechanism for the excitation or production of excited atomic oxygen outside the discharge.

![Figure 7: Optical emission of atomic oxygen (777nm) in the effluent.](image)

3. The micro atmospheric pressure plasma jet (µ-APPJ)

The experiments described above clearly reveal that in order to understand the complex energy transport mechanisms in the APPJ, the connection between the effluent and the discharge region is of major importance. Investigations of the discharge dynamics and transport processes within the discharge volume are, therefore, essential. Figure 8 illustrates the complexity of energy dissipation in the discharge volume and energy transport processes to the effluent region. The plasma chemistry inside the discharge volume is strongly influenced by the dynamics of the plasma boundary sheaths in front of the electrodes and corresponding surface processes. The surface plays a key role in atmospheric pressure plasmas since the surface to volume ratio increases with decreasing discharge dimensions. Energy transport mechanisms to the effluent region include transport of radicals, excited particles, and radiation. It has been shown that the effluent region is practically free of charged particles [7]. A crucial parameter for the discharge dynamics and energy transport mechanisms is the gas flow velocity through the discharge volume.
Diagnostics access to the discharge volume of the standard APPJ is not possible due to electrode configurations. The standard APPJ shows a collinear geometry where no direct access is possible. A specifically modified version of the APPJ with reduced discharge volume of about 1x1x30 mm$^3$ (µ-APPJ) provides excellent diagnostic access, in particular for optical techniques. Figure 9 shows a sketch of the µ-APPJ and the set-up for optical diagnostics inside the discharge volume. Even diagnostics requiring a large observation angle, such as various laser diagnostics, can be applied to the µ-APPJ.
Figure 10 is a photograph of the µ-APPJ operated with a gas flow of 1 slm of pure helium and an rf-power of 10 Watt at 13.56 MHz applied to flat polished stainless electrodes. It shows the homogenous discharge region and the transition region to the effluent where the luminescence decreases.

![Figure 10: Photograph of the µ-APPJ operated in atmosphere with pure helium flow through the discharge volume.](image)

References

[1] J.P. Novak and R. Bartnikas, J. Appl. Phys. 62, 3605 (1987)
[2] J.P. Novak and R. Bartnikas, IEEE Trans. Plasma Sci. 19, 95 (1991)
[3] S. Kanazawa, M. Kogoma, T. Moriwiki, and S. Okazaki, J. Phys. D: Appl. Phys. 21, 838 (1988)
[4] K. Okazaki, T. Makabe, and Y. Yamaguchi, Appl. Phys. Lett. 54, 1742 (1989)
[5] T. Yokoyama, M. Kogoma, T. Moriwiki, and S. Okazaki, J. Phys. D: Appl. Phys. 23, 1125 (1990)
[6] V.J. Tu, et al., J. Vac. Sci. Technol. A 18, 2799 (2000)
[7] A. Schütze, J.Y. Jeong, S.E. Babayan, J. Park, G.S. Selwyn, and R.F. Hicks, IEEE Trans. Plasma Sci. 26, 1685 (1998)
[8] G.S. Selwyn, H.W. Herrmann, J. Park, and I. Henin, Contrib. Plasm Phys. 10, 573 (2001)
[9] S.E. Babayan, et al., Plasma Sources Sci. Technol. 10, 573 (2001)
[10] J. Park et al., J. Appl. Phys. 89, 15 (2001)
[11] J. Park et al., J. Appl. Phys. 89, 20 (2001)
[12] W.C. Zhu, B.R. Wang, Z.X. Yao and Y.K. Pu, J. Phys. D: Appl. Phys. 38, 1396 (2005)
[13] X. Yang, et al., Plasma Sources Sci. Technol. 14, 314 (2005)
[14] J. Shi and M.G. Kong, J. Appl. Phys. 97, 023306 (2004)
[15] J. Shi and M.G. Kong, IEEE Trans. Plasma Sci. 33, 624 (2005)
[16] S. Wang, V. Schulz-von der Gathen, H.F. Döbele, Appl. Phys. Lett. 83, 3272 (2003)
[17] K. Niemi, V. Schulz-von der Gathen, H.F. Döbele, J. Phys. D: Applied Physics, 34, 2330 (2001)
[18] K. Niemi, V. Schulz-von der Gathen, H.F. Döbele, Plasma Sources Sci. Technol. 14, 375 (2005)
[19] A. Goeshlich, T. Kawetzki, H.F. Döbele, J. Chem. Phys. 108, 9362 (1998)
[20] K. Niemi, T. Mosbach, H.F. Döbele, Chem. Phys. Letters 367, 549 (2003)
[21] A. Francis, U. Czarnetzki, H.F. Döbele and N. Sadeghi, Appl. Phys. Lett., 71, 3796 (1997)
[22] N. Sadeghi, D.W. Setser, A. Francis, U. Czarnetzki, H.F. Döbele, Journal of Chemical Physics, 115, 3144 (2001)
[23] T. Gans, C.C. Lin, V. Schulz-von der Gathen, H.F. Döbele, Phys. Rev. A. 67, 012707 (2003)