

Atomic Oxygen Density in the Effluent of an RF-Excited Atmospheric Pressure Plasma Jet: Measurements, Modelling, Mechanisms

S. Reuter¹, K. Niemi², V. Schulz-von der Gathen², H.F. Döbele¹

¹ Institute for Laser and Plasma Physics, Universität Duisburg-Essen, D-45117 Essen, Germany

² Institute for Experimental Physics II, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Contact: Stephan.Reuter@uni-due.de

In this work a plane-parallel 13.56 MHz RF-excited atmospheric pressure plasma jet (APPJ) operated with 2 m³/h helium feed gas containing 0.5 % molecular oxygen is investigated. The effluent leaving the discharge through the jet's nozzle contains very few charged particles and a high oxygen radical density in the order of 10¹⁶ cm⁻³. Space resolved ground state atomic oxygen density in the effluent is measured with two-photon absorption laser induced fluorescence (TALIF) spectroscopy. In order to understand the underlying mechanisms of atomic oxygen production and annihilation in the effluent, the measured atomic oxygen density is compared with chemical model calculations. Model calculations from earlier investigations by Jeong et al. [1] are refined by taking into account the actual gas temperature distribution in the effluent of the jet.

1. The Atmospheric Pressure Plasma Jet (APPJ)

The atmospheric pressure plasma jet is a capacitively coupled radio frequency excited plasma source, which can be operated at ambient conditions. The feed gas consists of helium and small admixtures of molecular gas, here oxygen, in the order of 1%. The total gas flux of the jet is in the order of 2 m³/h. The effluent leaving the discharge through the jet's nozzle contains very few charged particles and a high concentration of radicals (O; O₃; O₂^{*}...) at a low gas temperature (below 80°C, see figure 1), making the jet ideally suited for treatment of thermally sensitive surfaces.

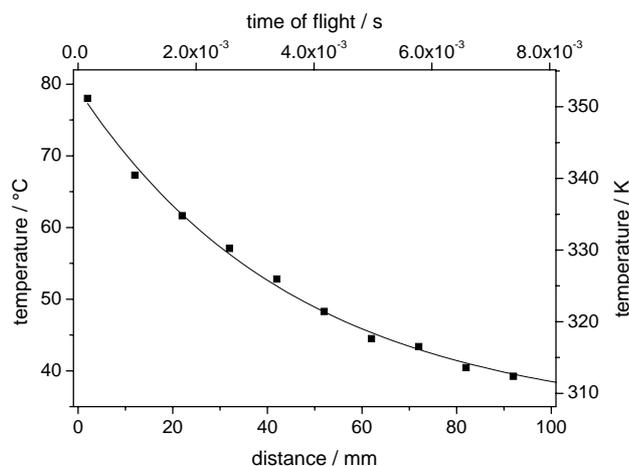


Fig. 1: On-axis temperature profile of the effluent measured with a thermocouple for 150 W RF power and 2 m³/h helium flux with an admixture of 0.5% O₂.

The originally concentric setup [2] was modified to a planar setup, which consists of two water cooled planar stainless steel electrodes (length 80 mm, width 40 mm), one of which is grounded, while the other is driven by a 13.56 MHz RF power source. The electrode gap is 1.1 mm. The discharge is a homogeneous glow discharge in α -mode. The applied RF power ranges from 20 to 200 Watt. Outside this range the discharge is either unstable at lower power, or it constricts into a high power density discharge of small dimension (γ -mode) at higher power, and thus destroys the electrodes surfaces.

In earlier investigations of the effluent, Jeong et al. [1] predicted an atomic oxygen density in the order of 10¹⁶ cm⁻³ from results of OES, UV absorption measurements, and chemical model calculations. In the present study, direct measurements of the atomic oxygen density in the effluent of the planar APPJ are presented. The measured oxygen density is compared with calculations based on the chemical model as used by Jeong et al.. Furthermore, this chemical model is refined by taking into account measurements of the actual gas temperature distribution in the effluent (figure 1).

2. Space Resolved Measurements of the Ground State Atomic Oxygen Density in the Effluent

2.1 Diagnostic Setup

According to previous measurements on the concentric version [3; 4], the atomic oxygen density distribution in the effluent of the planar APPJ has been determined by two-photon absorption laser

induced fluorescence (TALIF) spectroscopy. The APPJ was placed in a recipient filled with one atmosphere of helium. A frequency doubled Nd:YAG laser pulsed at 10 Hz is used to pump a dye laser, equipped with a frequency tripling unit, in order to obtain the tunable UV radiation at about 225 nm for two-photon excitation of ground state oxygen atoms. The fluorescence of the oxygen atoms (~845 nm) is detected perpendicular to the exciting laser beam with a photomultiplier (Burle C31034A modified for pulsed operation).

2.2 TALIF Calibration

Fluorescence signals from the excited oxygen atoms in the effluent of the APPJ were calibrated by comparison with xenon TALIF measurements in the same diagnostic setup. For this purpose the recipient was filled with a known amount of xenon. The xenon fluorescence signal and the oxygen fluorescence signal were both normalized to the squared laser pulse energy. At atmospheric pressure, the decay of the oxygen fluorescence signal is dominated by collisional quenching. For calibration of the measured fluorescence radiation, the quenching loss has to be taken into account. The jet was operated in a helium atmosphere, in order to exclude additional collision partners. The quenching coefficients for the collision partners involved (He with O; O₂ with O; and Xe with Xe) were determined in [4]. Self-quenching of atomic oxygen can be neglected. Figure 2 shows the map of the absolute atomic oxygen density in the effluent measured perpendicular to the electrode gap.

3. Chemical Model Calculations of the Ground State Atomic Oxygen Density in the Effluent

In order to understand the processes responsible for production and annihilation of atomic oxygen in the effluent, ground state atomic oxygen density measured by TALIF spectroscopy is compared with calculations based on the chemical model. For the model calculations six species are taken into account: helium, ozone, molecular and atomic oxygen, as well as the metastable oxygen molecules O₂(¹Δ_g) and O₂(¹Σ_g⁺). All other metastable and charged species can be neglected, because they are quickly lost in collisions. The reactions listed in table 1 were found to be the dominant reactions taking place in the effluent [1] and are used for chemical modelling in the present work.

Table 1: Chemical reactions and rate constants [1]

	reactions	rate constants
R ₁	O + O + M → O ₂ + M	$5.2 \times 10^{-35} e^{(900/T)*}$
R ₂	O + O ₂ + M → O ₃ + M	$1.85 \times 10^{-35} e^{(1057/T)*}$
R ₃	O + O ₃ → O ₂ + O ₂	$1.5 \times 10^{-11} e^{(-2250/T)}$
R ₄	O ₂ (¹ Δ _g) + O ₃ → O + 2O ₂	$6.01 \times 10^{-11} e^{(-2852/T)}$
R ₅	O ₂ (¹ Σ _g ⁺) + He → O ₂ + He	1×10^{-17}
R ₆	O ₂ (¹ Σ _g ⁺) + O → O ₂ + O	8.0×10^{-14}
R ₇	O ₂ (¹ Σ _g ⁺) + O ₃ → O + 2O ₂	1.5×10^{-11}

For details see text.

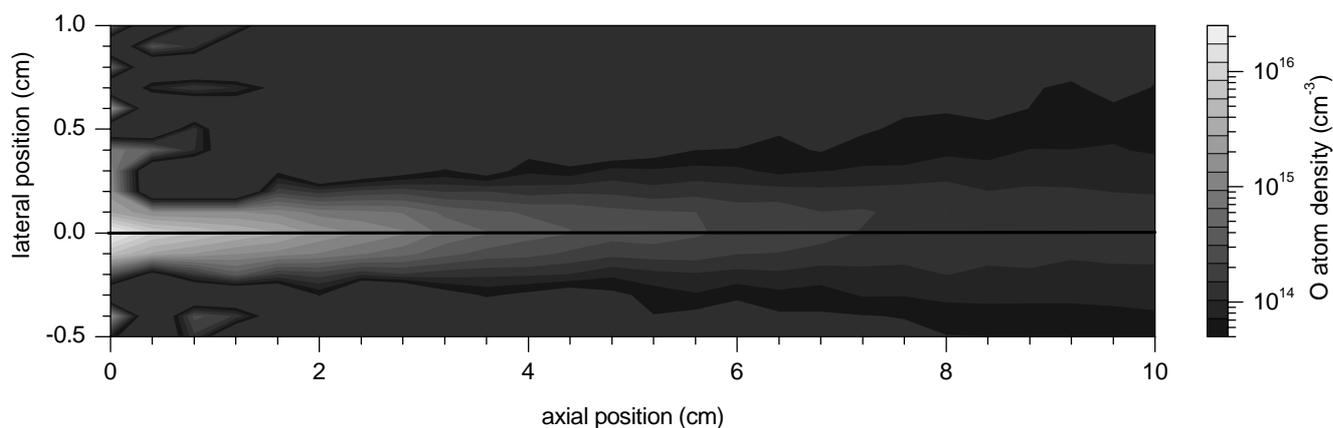


Fig. 2: Atomic oxygen density map of the effluent measured by TALIF spectroscopy for 150 W RF power and 2 m³/h helium flux with an admixture of 0.5% O₂.

The unit for the rate constants is $\text{cm}^2\text{molecules}^{-1}\text{s}^{-1}$ for the two-particle reactions, and $\text{cm}^6\text{molecules}^{-2}\text{s}^{-1}$ for the three-particle reactions marked with *. T is the gas temperature in Kelvin. The collision efficiencies for the third collision partner in reaction R_1 is 0.62 in case of helium, and 1.15 in case of O_2 . For reaction R_2 the collision efficiency is 1 in case of O_2 as third collision partner, 0.54 for helium, 0.13 for O, and 2.27 for O_3 . The material balance for each of the six species considered in the model is

$$\frac{dn_X}{dt} = \sum_i k_i n_X n_Y \left(\sum_j c_j n_Z \right) \quad (1)$$

where n_X (n_Y) is the concentration of species X (Y), and k_i is the rate of reaction i that either produces or consumes X (Y), and n_Z is the concentration of collision partners in a three body reaction which remains unchanged; c_j are the respective collision efficiencies in case of a three body reaction.

Helium plays an important role as collision partner in the reactions. The helium density, however, remains unaltered. Therefore, the differential equation for helium is redundant. The remaining five coupled first order differential equations were solved numerically for a given set of starting parameters.

4. Comparison of Measurements with Model Calculations and Modification of the Model

In the following, the results from the model calculations are compared with the TALIF measurements. The measured on-axis atomic oxygen density distribution is plotted in figure 3 as a function of distance or time of flight, respectively, when assuming a gas flux of ~ 12.5 m/s.

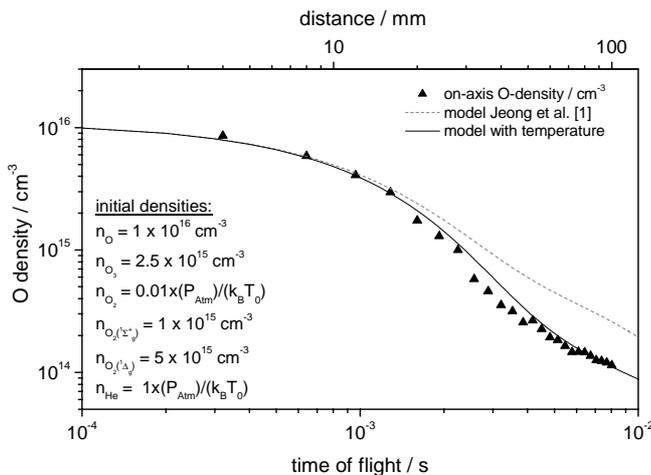


Fig. 3: On-axis atomic oxygen density (\blacktriangle) taken from figure 2 in comparison with model calculations from the unaltered model (----) and from the modified model (—) taking into account the temperature distribution from figure 1.

The initial densities of the six species presented in figure 3 were chosen according to the actual experimental conditions and the measurements (for He and O), and according to measurements on the comparable APPJ investigated in [1] (for O_3 , $\text{O}_2(^1\Sigma_g^+)$ and $\text{O}_2(^1\Delta_g)$). Thus the only parameter varied was the molecular oxygen admixture.

Results from calculations using the unaltered model of Jeong et al. are represented by the dashed grey line in figure 3. To achieve agreement of the model with the measured data, it was necessary to assume a molecular oxygen admixture of 1 % instead of the actual 0.5 % admixture in the measurements. Obvious deviation of the model calculation from the measured atomic oxygen density distribution occurs at larger distance to the nozzle.

We have modified the model by taking into account the actual on-axis gas temperature distribution in the effluent of the APPJ as measured in figure 1. The results are plotted as black solid line in figure 3. Obviously, a much better agreement between model calculations and measurements is reached.

Up to now, diffusion and radiation effects have been neglected. Diffusion enhances the decrease of the on-axis O-density in the downstream flow. We presume that taking into account diffusion and radiation effects will result in further improvement, particularly with regard to the accordance of the initial O_2 admixture in the experiment and the chemical model.

5. References

- [1] J.Y. Jeong, J. Park, I. Henins, S.E. Babayan, V.J. Tu, G.S. Selwyn, G. Ding, R.F. Hicks. *J. Phys. Chem. A* **104** (2000), 8027
- [2] S. Wang, V. Schulz-von der Gathen, H.F. Döbele, *Appl. Phys. Lett.*, **83** (2003), 3272
- [3] K. Niemi, S. Reuter, V. Schulz-von der Gathen, H.F. Döbele, *Proceedings of the 17th ESCAMPIG* (2004), 157
- [4] K. Niemi, V. Schulz-von der Gathen, H.F. Döbele, *Plasma Sources Sci. Tech.* **14** (2005), 375