Investigations on the Generation of Atomic Oxygen Inside a Capacitively Coupled Atmospheric Pressure Plasma Jet

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Abstract. Inside a miniaturized capacitively coupled cold atmospheric pressure plasma jet operated at a helium base gas flow with a minor molecular oxygen admixture atomic oxygen is created. The build up of atomic oxygen along the discharge channel and its further decay in the effluent is investigated by means of xenon calibrated two photon laser induced fluorescence spectroscopy (TALIF). The longitudinal and the transversal atomic oxygen distribution is measured from the discharge core through the transition area into the effluent. A particular emphasis is set on the influence of collisional quenching at elevated pressures.

1. Introduction
Cold jet-like plasma devices gained tremendous importance, not only in the field of medical application [1]. Reactive oxygen species such as atomic oxygen are supposed to be of major importance regarding wound treatment and germ reduction [2]. Though atomic oxygen densities have been measured in the effluent, investigations of its creation within the discharge are often limited due to small sizes and encapsulation of discharge devices. The miniaturized microscaled atmospheric pressure plasma jet provides excellent access for active and passive optical diagnostics within the discharge core. Atomic oxygen densities in the free effluent [3] of few $10^{14}\text{ cm}^{-3}$ and first independent density measurements in the discharge core [4] - more than one order of magnitude higher - show the importance of the transition area between plasma and charge free effluent. An improved, extended device with a prolonged gas flow channel allows a continuous observation of particle densities from the beginning of the discharge far into the effluent avoiding the creation of vortices and backflow of outer atmosphere.

2. Discharge device and experimental setup
The 13.56 MHz driven jet (figure 1) consists of two rectangular steel electrodes of 40 mm length, 1 mm thickness and 1 mm distance of which one is powered and the other one is grounded. BK7 glass spacers of same size and shape form an electrically isolated continuation of the discharge gap. Quartz glass panes cover the channel from both sides confining the gas flow of 1.5 slm $He$ and 9 sccm $O_2$ to a channel of $1 \times 1 \text{ mm}^2$ cross section. The discharge is mounted on a three axis stepper motor controlled stage within a steel chamber allowing a precise scanning of the discharge through the fixed focus of the optical setup (figure 2). A frequency tripled Nd:YAG...
laser pumped dye laser is used to generate nanosecond UV laser pulses at around \( \lambda = 225 \text{ nm} \) for two-photon excitation of atomic oxygen (\( 2p^4 P_{2,1,0} - 3p^3 P_{1,2,0} \)). The laser beam is focused into the center of the chamber and fluorescence light at \( \lambda = 844 \text{ nm} \) is imaged into a cooled, gated infrared sensitive photo multiplier. Resolution is limited transversally by the focal beam diameter of < 200 \( \mu \text{m} \) and longitudinally by the 0.5 mm slit in front of the PMT. A fast UV-Diode provides reference to the laser pulse energy and is recorded together with the PMT signal by a digital storage oscilloscope (HP 54510A, 250 MHz, 1 Gs s\(^{-1}\)) and instantly evaluated on a PC. Absolute calibration is performed by comparative measurements on xenon reference densities. Details on the calibration process can be found in [5, 6].

3. Results

A signal map of \( 1 \times 55 \text{ mm}^2 \) (\( \Delta x = 0.1 \text{ mm} \) and \( \Delta z = 0.5 \text{ mm} \)) can be seen in (figure 3). The jet was operated at 12 W generator power, 1 mm electrode distance, 1.5 slm helium and 9 sccm molecular oxygen admixed. Due to the small cross section of the channel in comparison to its length, the channel has to be precisely aligned to the manipulator axis (\( \Delta x \) and \( \Delta y \) may not shift more than 0.1 mm along the entire channel) to perform on axis measurements. Alternatively, the manipulator position must be adjusted respectively.

3.1. Spatial profiles

Figure 4 shows the normalized signal distribution in transversal direction (between electrodes) at different positions along the discharge channel. A convex profile can be found for each longitudinal position. This is dominantly caused by geometric shadowing of the fluorescence light by the electrodes. For calibration, a uniformly distributed xenon reference density inside
The build up of a plateau can be seen from density distribution can be assumed uniform as well, within the detection limits. An important issue for the applied TALIF calibration technique is the collisional de-excitation of excited oxygen atoms since the density ratio of atomic oxygen and xenon is proportional not only to the PMT signal ratio but also to the ratio of effective branching ratio \( a_{ij} \) of the observed excited states \( < i > \) of oxygen and xenon respectively \( a_{ij} = \frac{A_{ij}}{\sum_{k<l} A_{kl} + \sum_{q} n_q k_{eq}} \). Here \( A_{ij} \) denotes the transition probability into a lower state, \( n_q \) density and \( k_{eq} \) the quenching rate of species \( q \) with that state. At atmospheric pressure this collisional de-excitation can easily exceed photonic de-excitation. Thus, it is of major importance to know its amount for a reliable calibration. For the effluent, usually data from low to mid pressure measurements is extrapolated and only the major colliding species are taken into account, since the available database is still very limited [3, 4, 5, 6]. Since \( \sum_{k<l} A_{kl} + \sum_{q} n_q k_{eq} = \tau_{eff} \) equals the effective lifetime of the respective excited state, we investigated the decay behaviour of the PMT signal for each measurement and compared it to the theoretical value with only helium atoms and bi-molecular oxygen in the ground state as colliders. For this we extrapolated mid pressure measurements of \( k_{He} = 0.017 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) and \( k_{O2} = 9.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) from [5]. Varying the molecular admixture to the helium base gas flow (figure 6), we find excellent agreement with the assumed theoretical value down
to \( \approx 5 \) ns converging to the bandwidth limit of the used oscilloscope (250MHz). These life time measurements confirm that under our conditions it is reasonable for the effluent area \((z = 42\) mm) as well as for the plasma core \((z = 35\) mm) to restrict the considered quenching species to only \( He \) and \( O_2 \) in their ground state and to apply values extrapolated from low or mid pressure data.

4. Concluding remarks
We found that atomic oxygen density inside a miniaturized capacitively coupled cold atmospheric pressure plasma jet builds up converging exponentially into an equilibrium plateau within the plasma itself and decaying also exponentially within the effluent. The corresponding rise and decay constants are an important parameter to compare to theoretical models of the oxygen chemistry in such atmospheric plasma jets. The transversal density distribution can be found to be uniform within the detection limits. Also, assumptions of collisional de-excitation for the atmospheric pressure range could be confirmed within the bandwidth limit of the used oscilloscope.

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