

Two-photon absorption laser induced fluorescence study of repetitively pulsed nanosecond discharges in atmospheric pressure air

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Nanosecond repetitive discharges generated by high voltage pulses in a pin-to-pin electrode configuration in atmospheric pressure air are currently used to stabilize lean flames, for the purpose of reducing pollutant concentrations. The goal of this work is to gain an understanding of the plasma-flame stabilization mechanism. Two-photon absorption laser induced fluorescence was employed here for the measurement of atomic oxygen, that is considered to be the key species for stabilization mechanism. Time resolved measurements of the atomic oxygen number density during plasma formation and decay were performed. The hypothesis that the plasma creates reactive O via a two-step mechanism is partially demonstrated.

I. Introduction

ATMOSPHERIC pressure air plasmas are widely used for surface treatment and activation, exhaust gas control, aerodynamic flow control, plasma assisted combustion, and destruction of toxic compounds [1]. The efficiency of these processes strongly depends on the energy requirements of the plasma sources employed. Here, we used a nanosecond repetitively pulsed (NRP) discharge generated in a pin-to-pin electrode configuration in atmospheric pressure air, characterized by energy requirements of a few W/cm³ for electron densities of about 10¹² cm⁻³. Corona, diffuse and filamentary regimes of NRPP discharges have been observed, depending on the applied voltage (5-8 kV), repetition frequency (2-30 kHz), gas temperature (300-1000 K), air flow rate (1-17 m/s), and gap distance (1-7 mm). The goal of the present study is to characterize the production of O atoms in the filamentary regime.

The small plasma volume (1-5 mm³) and short lifetime of plasma species (tens of nanoseconds) limit the available diagnostic methods. Electrical measurements and emission spectroscopy have been carried out in order to determine the energy deposited into the discharge and the spatial and temporal evolution of air plasma excited state species [2].

According to the chemical kinetic model presented in [3] the formation of atomic oxygen in the discharge is a two-step mechanism. Excited molecular nitrogen N₂(A,B,C) formed by electron-impact excitation reacts with molecular oxygen to produce atomic oxygen. This process is accompanied by heating of the gas. To validate the kinetic model, the densities of ground state atomic oxygen as well the excited electronic states of N₂ must be measured.

Here we present measurements of the ground state atomic oxygen in the plasma discharge and post-discharge using Two-Photon Absorption Laser-Induced Fluorescence (TALIF). This advanced diagnostic technique has been employed earlier for measurements of oxygen in low-pressure discharges [4,5] and for atmospheric-pressure dielectric barrier discharges [6].

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II. Experimental

Direct absorption from the O ground state at 112 nm is not possible since we have open-air plasma systems (at 112 nm vacuum system is required). Moreover, a single-photon transition is forbidden. Continuous wave Cavity Ring Down Spectroscopy (cw-CRDS), a very sensitive technique that can allow the detection of weak or even optically forbidden transitions, was initially considered for probing the ground state by measuring the forbidden dipole transition ($^3P \rightarrow ^1D$). However, the calculated absorbance was found to be 10^{-8} , that is right at the lower end of the detection limit of cw – CRDS. After detailed calculations, it resulted that the suitable solution is oxygen detection using TALIF with two-photon absorption at 225 nm and fluorescence at 844 nm.

Figure 1 shows a schematic of the TALIF setup and the atmospheric pressure air discharge. The pulses were produced by a solid-state generator (FID Technologies FPG 10-30MS) that supplies pulses with rise/fall times of 5 ns, a flat top of 10 ns at greater than 90% of the maximum voltage into an open circuit. These discharges are non-thermal plasmas (gas temperatures ~ 1000 K, electron temperatures ~ 20000 K) characterized by low energy requirements (a few W/cm³) for high electron densities (about 10^{12} cm⁻³).

The 225-nm laser radiation was produced as follows. The second harmonic (532 nm) of a Nd:YAG laser (Continuum Precision PL 8010) was used to pump a tunable dye laser (Continuum ND 6000) at a slightly longer wavelength (around 570 nm). The dye was then doubled and mixed with the residual 1064 nm from the Nd:YAG laser to obtain the sum frequency 225 nm. The output energy per pulse was up to 3 mJ for the 6-ns pulse duration, 0.1-cm^{-1} laser width and 10-Hz repetition frequency. The resulting uv radiation was divided by a beam splitter (BS). The largest part ($> 90\%$) intersected the middle of the plasma and focused 3 cm after by an $f=35$ cm lens, and then measured by a power meter (Astral AD 30). The other portion of the beam was detected by a uv ultrafast photodiode (PD UV) (Alphas, UPD-200-UD, 200 ps rise time) and monitored by a digital oscilloscope (LeCroy, 2 GHz bandwidth).

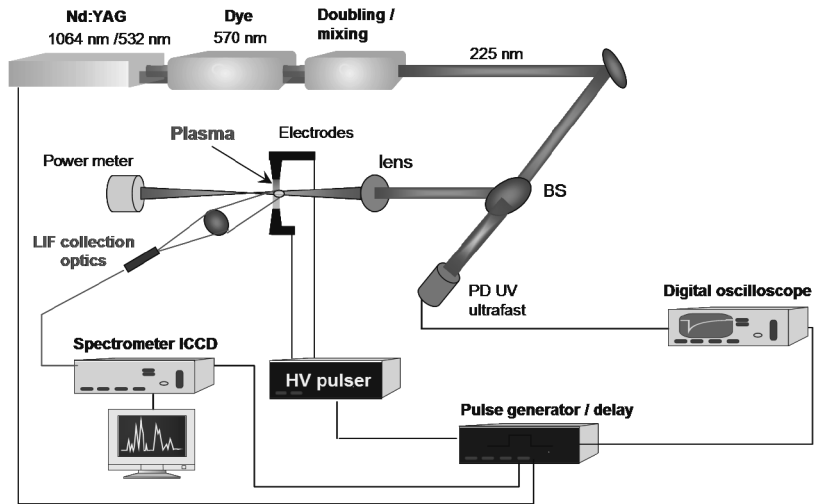


Figure 1. Schematic of the TALIF experimental setup. The laser system and the pulsed discharge were synchronized (ns time accuracy) with detection systems (ICCD spectrometer and UV photodiode).

The fluorescence optics (LIF) were placed to collect light perpendicular to the plasma channel and the laser beam. Two off-axis parabolic mirrors (effective focal length 10 cm and 20 cm, respectively) were used to collect light into a 2-m fiber and send it to the input slit of a half-meter spectrometer (Spectra Pro 2500i), equipped with a fast ICCD camera (Princeton instruments, PI-max). The fluorescence volume was considered, in first approximation as the intersection of the three cylinders, i.e. the plasma, the laser and the cylinder delimited by the solid angle of the collection system. The volume size was chosen smaller than the plasma diameter (< 1 mm), in order to allow for the future calibration of the O fluorescence signal to the fluorescence of a Xe cell. The detection system allowed time resolved measurements down to 2 ns. The O fluorescence was recorded at 844.6 nm either using the spectrometer working in first order or employing an interference filter centered at 840 nm (Semrock FF01-840) and the spectrometer in zeroth order. The last configuration allows for better signal noise ratio, however at the cost of reduced spectral selectivity. The measured fluorescence spectra were then recorded by a PC with Labview.

Synchronization of the plasma discharge with the laser, LIF and PD detection systems was achieved with a Berkeley Nucleonics (BNC) 555 four-channel pulse delay generator (1 ns RMS jitter). The BNC triggered the flash lamp, Q-switch of the Nd:YAG laser and detection systems at 10 Hz, and the discharge at 10 kHz with appropriate delays. Depending on the data quality, up to 200 numerical averages of fluorescence spectra and laser intensity profile were performed.

III. Results

In order to convert experimental data into absolute concentrations, a kinetic model for oxygen was considered. The electronic states of oxygen are shown in Figure 2. The evolution of the population densities in the levels involved for a TALIF experiment can be described by a system of rate equations [7,8]. The two-photon excitation rate represents the number of electrons per second which are excited from level 1 to level 2, and depends on the effective two-photon absorption cross section, $\sigma^{(2)}$, and the square of the photons flux, Φ^2 . The photoionisation rate depends on the photon flux, Φ , and on the excited state photoionisation cross section, σ_{pi} . The fluorescence rate is the Einstein coefficient for the spontaneous emission, A_{23} , in case of just one channel of fluorescence. If fluorescence branches into several emission channels, then the fluorescence rate is $A = \sum_k A_{vk}$, with the summation over all transitions to lower levels for which spontaneous emission is allowed.

Because the experiment is carried out at atmospheric pressure, one of the most important processes of the depletion of level 2 is mostly the quenching by collisions with N_2 and O_2 , which are the dominant species. The quenching rate, Q , is given by $Q = \sum_p k_p n_p$ where n_p is the collision partner number density and k_p is the corresponding quenching coefficient [4].

The time variation of the particle densities in the excited state $n_2(t)$ and in the ground state $n_1(t)$ is described by the system of equations:

$$\frac{dn_1(t)}{dt} = -R_v(t) n_1(t) \quad (1)$$

$$\frac{dn_2(t)}{dt} = R_v(t) n_1(t) - [A + Q + \Gamma(t)] n_2(t) \quad (2)$$

where $R_v(t)$ is the excitation rate and $\Gamma(t)$ is the ionisation rate. The two-photon excitation rate $R_v(t)$, is given by:

$$R_v(t) = \sum_{J'=0}^2 G^{(2)} \hat{\sigma}^{(2)}(J' \leftarrow 2) g(\Delta\nu) \left(\frac{I(t)}{h\nu} \right)^2 \quad (3)$$

where $G^{(2)}$ is the photon statistic factor which takes into account the intensity beating of the stochastic multimode excitation field, $\hat{\sigma}^{(2)}$ is the integrated two-photon absorption cross-section ($\hat{\sigma}^{(2)} g(\Delta\nu) = \sigma^{(2)}$), $g(\Delta\nu)$ describes the normalized profile ($\int_{\nu} g(\Delta\nu) d\nu = 1$) of the two photon excitation, $I(t)$ is the laser intensity and $h\nu$ the photon energy.

The sum of integrated two-photon absorption cross-sections over the three components, the transitions ${}^3P_{(J=2)}$ ($E_1 = 0 \text{ cm}^{-1}$) ${}^3P_{(J=2,1,0)}$ ($E_2 = 88631 \text{ cm}^{-1}$),

$$\sum_{J'=0}^2 G^{(2)} \hat{\sigma}^{(2)}(J' \leftarrow 2) = \sum_{J'=0}^2 \int_{\nu} G^{(2)} \sigma^{(2)}(J' \leftarrow 2) d\nu \quad (4)$$

was measured by Bamford et al. [8] and calculated by Saxon et al. [9] to be $2.6 \times 10^{-35} \text{ cm}^4$.

In the non-saturation regime, i.e. negligible depletion of level 1, and for minor ionization processes, from the rate equations (1) and (2) the time integrated number density of the fluorescence atoms is given by:

$$N_F(\lambda) = \frac{A_{23}}{A+Q} G^{(2)} \hat{\sigma}^{(2)} g(\Delta\nu) \frac{1}{(h\nu_{225nm})^2} n_1 I_0(t)^2 dt \quad (5)$$

where $\frac{A_{23}}{A+Q}$ is the branching ratio representing the ratio of the fluorescence atoms (at 846 nm) to those that are

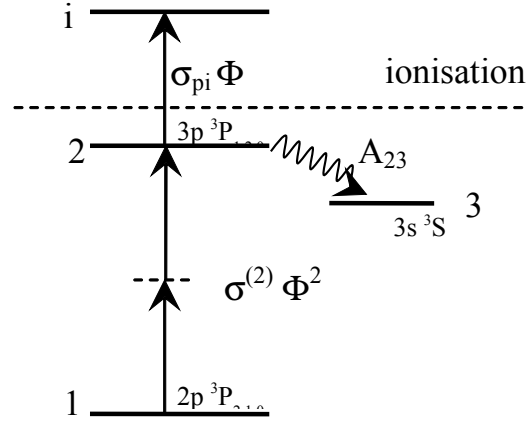


Figure 2. Energy levels for the two-photon absorption laser induced fluorescence.

quenched or fluorescence in other emission channels. The population of the ground state can be obtained from:

$$n_1 = \frac{\int_{\text{time}} \int_{\text{wavelength}} S_{TALIF}}{D(V, n_F, \gamma, \Delta\Omega) h\nu_{844nm} \frac{A_{23}}{A+Q} G^{(2)} \hat{\sigma}^{(2)} g(\Delta\nu) \frac{1}{(h\nu_{225nm})^2} \int I_0(t)^2 dt} \quad (6)$$

where S is the time-integrated fluorescence signal wavelength, D is the LIF recording characteristic and accounts for collection volume, solid angle, transmission of the fibre, filter and spectrometer, and the sensitivity of the ICCD.

If the parameter D is kept constant during the plasma parametric studies, the fluorescence signal normalized to the square of the laser intensity is directly proportional to the ground state concentration. Absolute densities can be obtained if all parameters in equation (6) are measured. A convenient method proposed in the literature [4,5,7] is the calibration using a Xe reference gas cell of known concentration. Xe has very close wavelength two-photon absorption and fluorescence transition systems, i.e. 224 nm and 835 nm, respectively. Thus the sensitivity of the detection system is practically the same. From the literature values of the spectroscopic properties of Xe and O (branching ratios, cross sections) the absolute O density, n_o , is obtained as:

$$n_o = \chi \frac{S_o}{S_{Xe}} n_{Xe} \quad (7)$$

where n_{Xe} is the Xe density, S_o and S_{Xe} are the time and wavelength integrated O and Xe fluorescence signals, which are normalized to the squared laser intensity. χ is a constant that accounts for the branching ratios, two-photon absorption cross-sections and two-photon absorption profile functions of O and Xe. At present, only relative measurements have been performed. An absolute calibration is planned in the near future.

The ground state of the atomic oxygen is a triplet $^3P_{2,1,0}$ with corresponding energies 0, 159 and 227 cm^{-1} , respectively. Consequently the fluorescence signal is proportional to the population of the sublevel from where the two-photon absorption takes place. Since the separation energies are smaller than the kinetic energy of plasma heavy particles, the population distribution mechanism is governed by collisions. Hence, the distribution of population over the triplet follows an equilibrium Boltzmann distribution. The total oxygen number density, N_{total} , is given by:

$$N_{total} = n_1 \frac{\sum_i g_i \times e^{-\frac{E_i}{kT}}}{g_1 \times e^{-\frac{E_1}{kT}}} \quad (8)$$

where n_1 is the measured concentration of the level with statistical weight g_1 and energy E_1 , and g_i and E_i are the statistical weights and energies of all O electronic levels. Here, the two-photon transition was chosen from 3P_2 sublevel. At a gas temperature of 1000 K, about 61 % of the O population is to be expected in 3P_2 state.

A sample oxygen TALIF signal is shown in Figure 3. A signal noise ratio of about hundred was obtained for a 20-second averaging time. The output laser intensity was

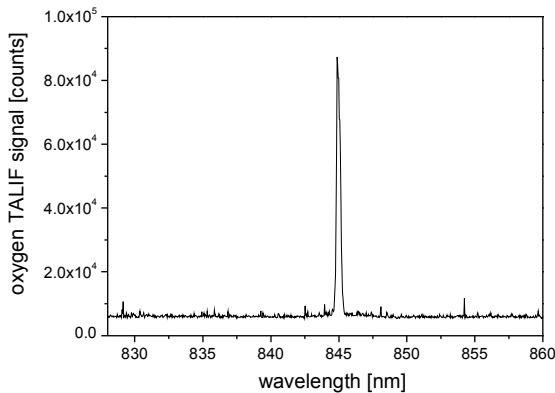


Figure 3. Sample of the oxygen fluorescence signal measured using the spectrometer with a fast ICCD.

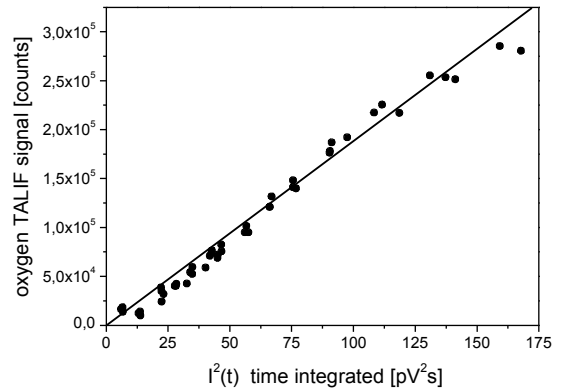


Figure 4. Oxygen fluorescence signal function of the time integrated squared laser intensity.

slightly changing in time and it was monitored by the fast photodiode for the normalization purpose. If no important depletion of the ground state (n_1) occurs then, based on (5), a linear dependency of the fluorescence signal function of the squared laser intensity should be obtained. In figure 4 the measured fluorescence signal function of intensity squared, $I^2(t)$, time integrated is represented. A non-saturation regime is observed. All TALIF measurements were performed for this range of intensities. In order to obtain fluorescence signals independent on laser intensity all further measurements were normalized to the quantity $I^2(t)dt$. The fluorescence signals were therefore directly proportional to the concentration of O in the ground state, (n_1).

Our particular interest for atomic oxygen is because it plays a very important role in combustion, as it is the oxidant of the fuel, and as its recombination is a source of heat during the first tens to hundreds of microseconds following the application of the discharge.

Based on the chemical kinetic model, we have obtained indications that one important pathway of atomic oxygen formation is via a two-step mechanism:

- Step 1: electron-impact excitation: $N_2(X) + e \rightarrow N_2(A) + e$
- Step 2: dissociative quenching: $N_2(A) + O_2 \rightarrow N_2(X) + O + O$

The latter process is accompanied by heating of the gas, over very short time scales of order 100 ns. Therefore, the NRPP discharge should increase the O production, and the heat released should enhance the combustion efficiency. In order to further validate the chemical kinetic model, time resolved measurements of atomic oxygen by TALIF and $N_2(A)$ by Cavity Ring Down Spectroscopy (CRDS) were performed.

In Figure 5 the temporal evolution of the normalized fluorescence signal between two discharge events (one plasma cycle) is represented. The discharge repetition frequency was 10 kHz. The discharge quickly increases the production of O species. The background O concentration due to the production from previous pulses increases by a

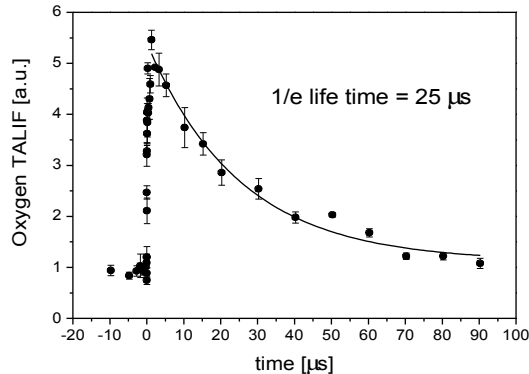


Figure 5. Temporal evolution of the oxygen fluorescence normalized to the squared intensity during one plasma cycle.

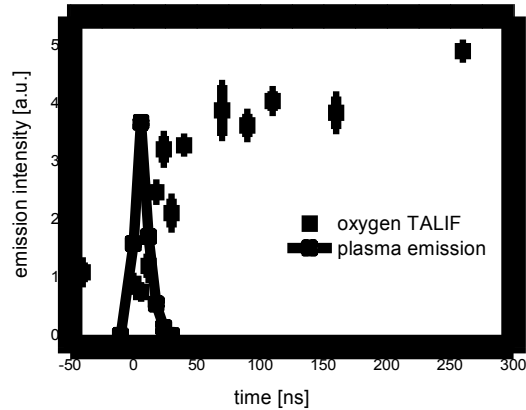


Figure 6. Temporal evolution of the oxygen fluorescence during the first 300 ns and the excited oxygen emission generated by plasma.

factor of about 5.5. Then, after the end of the 10-ns pulse, the O concentration decreases due to recombination. The $1/e$ life time of atomic oxygen after plasma creation was found to be about 25 μ s.

A zoom over the first 300 ns after the pulse is shown in Figure 6. The characteristic time of the discharge is shown by the emission of excited atomic oxygen generated by the discharge. This emission was recorded at 844.6 nm with the same detection system as for fluorescence except that the laser was turned off. Emission from the plasma was present for about 15 ns. An important aspect shown by TALIF data is that most of the atomic oxygen is produced only about 20 ns after the discharge event and over a period of about 100 ns. After 100 ns, the atomic oxygen continues rising slowly. These measurements are in good agreement with the model which predicts similar time variations. Future experiments are planned to compare the absolute densities the model. The relative TALIF measurements have to be converted by calibrating using Xe fluorescence spectra as shown in the literature [4,5,7].

The excited $N_2(A)$ molecules were measured by CRDS for further validation of the kinetic model. Only a brief description is given here. More details of the experimental results will be published elsewhere [10,11]. Emission from the excited $N_2(A)$ species could not be detected because the $N_2(A) \rightarrow N_2(X)$ is a forbidden dipole transition. Instead, the population of $N_2(A)$ electronic level could be probed by absorption, i.e. via the $N_2(A) \rightarrow N_2(B)$

transition. However, the expected absorbance was calculated to be 10^{-5} , which is below the limit of detection of a direct absorption technique that typically can resolve absorbances down to 10^{-3} . The solution chosen was to employ a pulsed CRDS technique, a highly sensitive diagnostic method, for transitions around 770 nm. The measured absorbances were then converted into concentrations based on the line strengths calculated using the spectral radiation code SPECAIR [12]. The $N_2(A)$ concentration during plasma decay is shown in figure 7. From preliminary data, the $1/e$ life time was found to be about 100 ns. This corresponds to the formation time of the atomic oxygen.

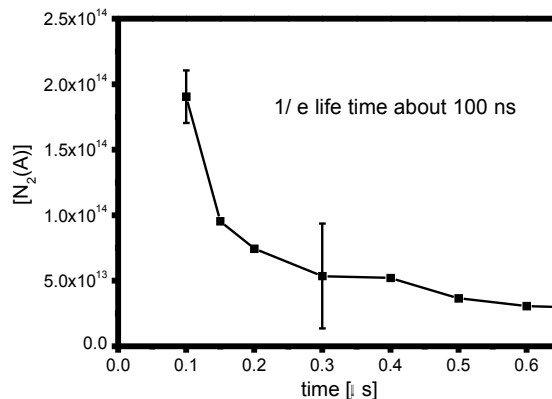


Figure 7. $N_2(A)$ concentration measured by CRDS during the plasma decay. The $1/e$ life time is found about 100 ns.

IV. Conclusions

Relative measurements of atomic oxygen densities generated in air at atmospheric pressure by nanosecond repetitively pulsed discharges were performed using TALIF. Time-resolved measurements were obtained with resolution as short as 6 ns. The $1/e$ life-time of the O atoms after the discharge was found about 25 μ s. It was observed that oxygen is produced by the plasma about 20 ns after the discharge event and its concentration increases rapidly during the first 100 ns. The production time of O was compared with the loss time of $N_2(A)$ obtained from preliminary CRDS measurements. The $1/e$ life time of $N_2(A)$ was found to be about 100 ns, which is comparable with the characteristic time of oxygen production. The proposed two step mechanism for the oxygen production is partially demonstrated. For further validation of the model absolute oxygen densities measurements using Xe calibration have to be done. The results obtained are valuable for the understanding of discharge behavior, the induced plasma chemistry, and also for the validation of the kinetic model-

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