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# LIF spectroscopy of OH radicals in a micro-flow DC discharge in Ar and He with a liquid electrode

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**Abstract.** The laser induced fluorescence spectroscopy on a micro-flow discharge with water electrode is carried out in order to investigate OH radicals. The transitions  $P_2(6)$ ,  $P_1(4)$  and  $P_2(3)$  branches of  $X^2II$ ,  $\nu'' = 0 - A^2\Sigma$ ,  $\nu' = 1$  transition are used. Laser-induced fluorescence is used in order to estimate density of OH radicals and density of water vapor in a core of the plasma. Sputtering yield of  $H_2O$  from the liquid electrode is calculated based on experimental data. It is revealed that plasma core consists of 8-10% of water in both Ar and He discharges. The density of OH radicals in the micro-flow He plasma is higher than in the glow discharge with liquid electrode and in Ar micro-flow discharge due to constriction of the positive column and different mechanism of the OH radical production.

## 1 Introduction

Cold atmospheric pressure plasmas (CAPPs) are chemically active media in which non-equilibrium reactions occur near room temperature. Whereas CAPPs are typically generated in gas mixtures containing noble gases or in ambient air, they can also be produced in bubbles in liquids

or in the gas phase above a liquid surface. In recent years the interest in non-thermal plasmas in or in contact with liquids has increased significantly [1]. Intensive chemical reactions and energy transfer mechanisms at the plasma-liquid interface and the intensive evaporation makes the physics of these discharges complex and the diagnostics challenging. The micro-flow discharge above water surface is one of the examples of plasma in contact with liquid

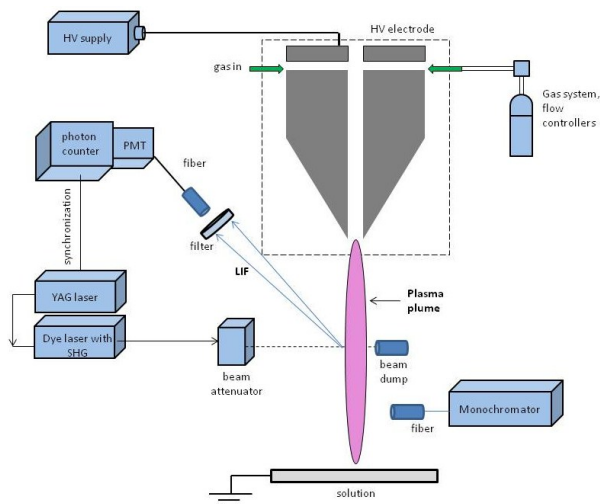
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where composition of gas phase can be controlled by external flow of feed gas. Several groups performed a study of the micro-flow atmospheric pressure glow discharge with liquid electrodes in various gases [2,3]. However, the study is mainly focused on electric characteristics and optical emission spectra, while the density of OH, as the most important active species, has not been measured. On the other hand, the LIF spectroscopy has been successfully applied to atmospheric pressure plasmas and flames in order to measure the absolute densities of active species and gas temperature [4,5]. This paper deals with the LIF spectroscopy of OH radicals in micro-flow plasma with liquid electrode.

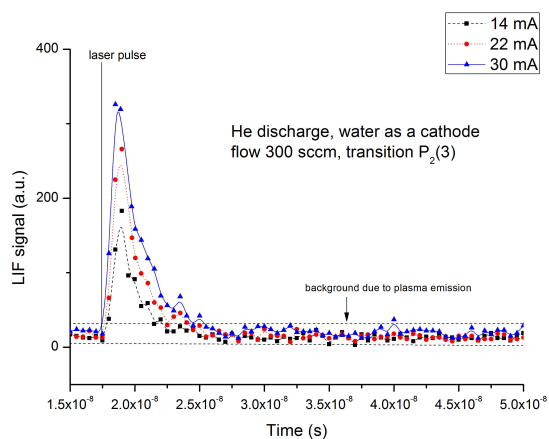
## 2 Experimental set-up

The experimental setup for LIF diagnostics is similar to one used recently [5] for glow discharge investigations. The experimental arrangement is shown in Fig. 1. A direct current discharge is generated between a metal electrode and a liquid surface (distilled water). A cone shaped stainless steel metal electrode with a top angle of 40 with a rounded and polished tip is attached to micrometer screw above liquid reservoir on 8 mm distance. Direct current discharge is generated by applying a positive or negative high voltage to the metal electrode and voltage is adjusted between 1.5-2.5 kV in order to reach desirable current. The metal electrode has a narrow uptake with a diameter of 0.5 mm where the flow of gas (Ar or He purity 99.99 %) with a flow rate of 300 sccm is applied. Due to low quenching rate of OH radicals by He or Ar it was

possible to use LIF technique on  $X^2\Pi, \nu''=0 - A^2\Sigma, \nu'=1$  transition around 285 nm. Three branches,  $P_2(6)$ ,  $P_1(4)$  and  $P_2(3)$  are excited by the laser around 285 nm that leads to population of OH(A) level. Radiative decay of those excited species to ground state OH(X) results to formation of laser-induced fluorescence signal around 309 nm which is proportional to density of OH radicals. The Sirah Cobra-Stretch dye laser with second harmonic generation (SHG) unit, pumped by a pulsed Nd :YAG laser on 532 nm working on 10 Hz has been used in order to excite OH radical. The linewidth for this arrangement is about  $0.03 \text{ cm}^{-1}$  (constructor data) and the pulse width is 8 ns. The Rhodamine 590 in ethanol is used as a laser dye. The maximum available energy per pulse with this configuration is 10 mJ and size of the beam in the detection volume is  $1.5 \times 5 \text{ mm}^2$ . The energy of the beam can be attenuated from  $50 \mu\text{J}$  up to  $1 \mu\text{J}$  using beam splitters and grey filters to reach conditions where the LIF signal depends linearly on the laser pulse energy. In this article we attenuated the energy per pulse is in the range of 0.05 mJ. The fluorescence is collected at 8 cm from the positive column of the glow discharge and led to a Hamamatsu R928 photomultiplier tube (PMT) after passing the optical bandpass filter with a central wavelength of 309 nm and spectral full width at half maximum (FWHM) of 10 nm. The LIF signal is accumulated by a SR430 photon counter at the frequency of the YAG:Nd laser during 1000 pulses.



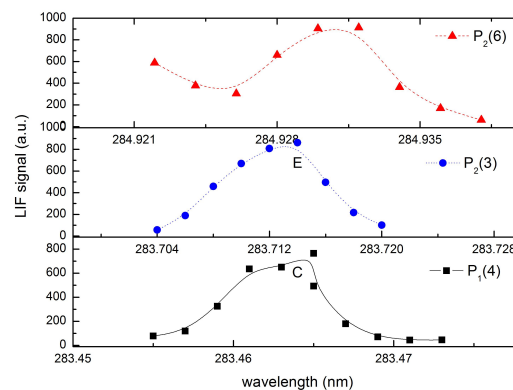
**Fig. 1.** Experimental set-up for the LIF measurements of OH radicals



**Fig. 2.** LIF signal as function of the discharge current, He is used as feed gas, excited transition  $P_2(2)$

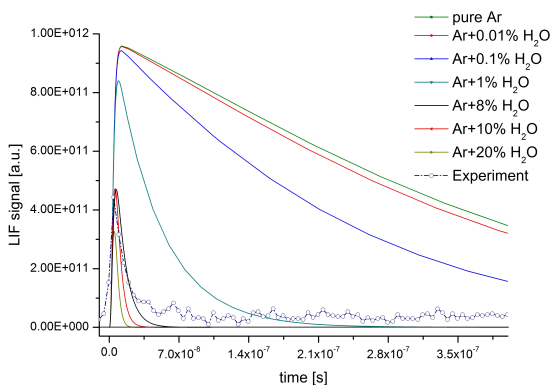
### 3 Results and discussion

Typical time resolved LIF signal for He discharge is presented on fig.2 for the case of excitation of  $P_2(3)$  transition. The example of the spectra of 3 transitions  $P_2(6)$ ,  $P_1(4)$  and  $P_2(3)$  obtained by the scan of the laser wavelength and used for OH radicals registration is presented on fig. 3 for the case of He discharge at 25 mA with water as an cathode.



**Fig. 3.** High resolution scans of excited transitions  $P_2(6)$ ,  $P_1(4)$  and  $P_2(3)$  (scans of transitions are stacked) for He discharge with water as a cathode at 25 mA discharge current

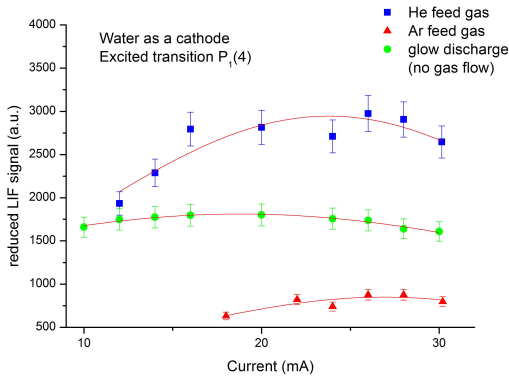
Due to high spectral resolution of the laser it was possible to discriminate the excitation of 3 different transition of OH radicals by set the laser wavelength to maximum of specific transition. From simulation of the LIF spectra in LASKIN it was found that the use of filter 309 nm (10 nm FWHM) allows us to detect all lines of OH radicals produced by radiative decay of the pumped transition. As known, the radiative decay time of excited OH radicals without quenching (e.g. in low pressure flames or plasmas) can be estimated as 780-1500 ns depending on the transition [6], but due to high pressure of atmospheric pressure plasmas and presence of different colliders (water vapor,  $N_2$ ,  $O_2$ ,  $O_3$ ,  $OH(X)$ ) the LIF signal decay has to be much faster. In both Ar and He discharge we observed decay of the LIF signal with a characteristic time of 30-40 ns (resolution of the registration system is 5 ns). The main quencher in the plasma core is  $H_2O$  because of high cross-section of OH radicals quenching by  $H_2O$  by compare with other species presented in the positive column [7,



**Fig. 4.** The comparison of the time resolved LIF signal with results of the simulation for Ar discharge at current of 25 mA

8] . Mainly  $\text{H}_2\text{O}$  is produced by thermal evaporation and sputtering of the liquid electrode. Other mechanisms of  $\text{H}_2\text{O}$  generation e.g. by gas phase recombination can not play significant role because of low density of recombining species (ionization degree of the plasma is  $10^{-3} \div 10^{-4}$ ) [1] . Amount of water vapor can be estimated by comparison of experimental time resolved LIF signal with results of the simulation where density of water vapor is varying. Fig. 4 presents results of simulation in LASKIN, transition  $\text{P}_2(6)$  for the case of Ar plasma and comparison of the results with experiments (discharge at 25 mA). It is revealed that the best agreement can be achieved with 8% of  $\text{H}_2\text{O}$  in the discharge and 10% of  $\text{H}_2\text{O}$  in He plasma. As it was shown [3,10] the dominant ion in the glow discharge with liquid electrolytes is  $\text{H}_3\text{O}^+$  with the density of about  $10^{19} \text{ m}^{-3}$  where density of other ions  $\text{O}_2^+$ ,  $\text{Ar}^+$ ,  $\text{He}_2^+$  is at least order of magnitude smaller. Because of high electrical field the ions can have energy up to 1.2-2 eV depends on used gas (Ar or He) especially when they reach liquid surface. At known current density of 5-

$10 \times 10^{-2} \text{ A/cm}^2$  we can calculate the flux of ions on the surface of liquid electrode which should be equivalent to the sputtering yield multiplied on flux of  $\text{H}_2\text{O}$  molecules from core of the micro-flow glow discharge to surrounding gas phase which we can estimate based on measured gas temperature from emission spectroscopy (1500-1800 K) and density of water in the plasma, for more details see [9] . The estimated water vapor concentration gives the sputtering yield in He plasma around 0.2  $\text{H}_2\text{O}/\text{ion}$  and around 0.12  $\text{H}_2\text{O}/\text{ion}$  in a case of Ar micro-flow discharge. The estimated value is order of magnitude higher than one measured in glow discharge between metal electrodes probably due to lower energy of ions required to sputter water molecules from surface of the liquid electrode. It is necessary to note that measured by present technique sputtering yield is an integrated value over the ion energy distribution function. Unfortunately, no experimental or simulation data on the ion energy distribution function are available in the literature and so only an integrated value of the sputtering yield can be calculated. With known density of water vapor, three steps model of the LIF excitation can be used [4,5] in order to evaluate absolute density of the radicals. Unfortunately, the model requires the calibration of the detection system by the Rayleigh scattering which is under progress now. Without calibration of the LIF technique only relative value of the LIF signal can be analyzed. Fig. 5 presents LIF signal as an integral of experimental timeresolved signal and also best 2-order polynomial fitting of data for discharge with water as a cathode in Ar, He and also in glow



**Fig. 5.** Reduced LIF signal vs current of the discharge for Ar, He micro-flow discharge and glow discharge above water surface

discharge without gas flow for transition  $P_1(4)$  as a function of the current. Presented signal is reduced to 1 mJ of the beam energy and divided on the size of the plasma as follow:  $LIF\ signal/E_{laser} [mJ] * (R_{plasma} / \text{Beam horizontal size})$  in order to take in to account the volume of the discharge where OH radicals are produced. We considered that the main quencher in both Ar and He plasmas is  $H_2O$ . The cross-section of OH quenching by  $H_2O$  is  $\sigma_Q = 79.8 \pm 7.1 \text{ \AA}^2$  which is much higher than negligible cross-sections of quenching by He and Ar:  $\sigma_Q = 0.004 \pm 0.001 \text{ \AA}^2$  and  $\sigma_Q = 0.047 \pm 0.008 \text{ \AA}^2$  respectively [11]. So because of similar mechanism of OH(A) quenching the LIF signal in Ar and He plasmas can be considered as directly proportional to the density of OH radicals in the core of the discharge but up to now no absolute density of radicals can be presented due to absence of a calibration. Remarkable difference in the density of radicals in He micro-flow plasma can be explained by different mechanism of OH radicals production. In the glow discharge or Ar micro-flow

discharge with liquid electrode the main reactions of OH radicals generation are electron dissociation of water and dissociative recombination of water ions. Argon metastables (energy 11.6 eV) can also generate OH(A) in collisions with  $H_2O$  with  $k \approx 10^{-16} \text{ m}^3\text{s}^{-1}$  [12] with furthermore fast deexcitation to state OH(X). In He discharge due to the higher energy of He metastables (19.8 eV lowest energy), they will mainly ionize water instead of production of OH(A) [13] and radicals OH(X) will be formed by electron dissociative recombination to  $H_2O^+(H_3O^+)$  with  $k \approx 10^{-14} \text{ m}^3\text{s}^{-1}$  [10,14].

## 4 Conclusions

The ground-state OH radicals in an atmospheric pressure micro-flow discharge in He and Ar with a liquid electrode are detected by the LIF technique. Decay of LIF signal is used in order to provide information on the density of water vapor in a core of the plasma. The density of OH radicals in He micro-flow discharge is higher than one in Ar micro-flow (almost 6 times higher) or glow discharge (almost 2.2 times higher) in air due to difference in a mechanism of OH(X) production in He plasma resulting in higher dissociation of  $H_2O$  into OH(X).

## 5 Acknowledgement

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