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# Spatially resolved measurement of hydroxyl (OH) radical concentration in a microwave plasma jet by planar laser-induced fluorescence

**Abstract:** The spatially resolved concentration of OH radicals in the effluent of a microwave (MW) surfatron plasma jet was measured by planar laser-induced fluorescence. Two cases were compared – constant MW power and MW power modulated by 80 Hz. In both cases the maximal concentration was at the tip of the visible discharge, but for constant MW power the OH was spread over a larger volume. The maximum concentration in both cases was on the order of $10^{22}$ m$^{-3}$.

**Keywords:** modulated microwave power, spectroscopy, surfatron, LIF, OH

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## 1 Introduction

Microwave discharges (MD), i.e. electrical discharges excited by electromagnetic waves with frequencies in the microwave region (300 MHz – 300 GHz), are widely used for generation of quasi-equilibrium and non-equilibrium plasmas. These are useful for many applications: for generation of the active medium in gas discharge lasers, in light sources, in plasma chemistry, in analytical chemistry, *etc*. Microwave discharges can be operated not only in the continuous wave regime but also in the pulsed or modulated regime. Modulated discharge can have higher density of active particles (such as electrons, ions, excited particles, atoms, molecules, radicals, *etc*.) and lower gas temperature than the continuous wave plasma at the same mean power. These effects can be assigned to non-linear relation between the input power, electron temperature and gas temperature. It can be very useful not only for many applications including material processing but also for the studies of fundamental aspects of plasma physics [1-5]. The excitation power continuously modulated by a sinusoidal waveform instead of simple on-off pulsation has potential for several applications; such a design was tested in [6-8].

The measurement of OH concentration in discharges at atmospheric pressure is a still developing topic. In most published works, laser-induced fluorescence (LIF) has been used. A calibration must be performed to obtain quantitative results. In reported measurements of OH concentration in plasma jets, a calibration of the detector sensitivity by laser Rayleigh scattering [9-12] is usually used. In this case, the fluorescence quantum efficiency must also be determined by means of a fluorescence model. In environments with abundance of noble gases, where the excited OH radicals have relatively long lifetimes (hundreds of ns), a simple scheme with excitation to the $\nu' = 0$ state of the excited electronic state ($A^2\Sigma$) can be used. Expanding the laser to a plane (planar LIF or PLIF) and recording the fluorescence with a 2D detector can conveniently yield OH concentration measurement with very good spatial resolution. However, to obtain a reliable result, spatially dependent corrections should be introduced.

## 2 Experimental procedure

### 2.1 Experimental setup

The surface wave discharge was produced by applying microwave power to a gas flowing in a narrow discharge tube. A SAIREM GMP 20 KED (2.45 GHz) microwave generator was operated in amplitude modulated (AM)

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mode using a function generator. A sinusoidal AM envelope was selected (min. 150 W, max. 350 W) to supply a mean power of 250 W. Among the possible modulation envelopes, the sine was chosen as it was the simplest one, *i.e.*, it did not contain any higher harmonics. The microwaves were fed from the magnetron to the surface wave launcher – surfatron (SAIREM Surfatron 80 with integrated matching) [13] – *via* waveguide, ferrite circulator and coaxial cable. The matching was adjusted to maintain the reflected power below 10 W. The surfatron design consists of a coaxial resonant cavity with a narrow wave launching gap around a fused silica discharge tube (170 mm in length, 1.5 mm and 4 mm inner and outer diameter, respectively). The end of the discharge tube was 1 cm from the launching gap. It was fed with argon at a flow rate of 1.45 slm (standard liter per minute) set by a flow-controller. The humidity of argon gas was on the order of 0.05% (V). For ignition of the plasma a Tesla transformer was used. The discharge tube was externally cooled by compressed air (4 slm, humidity on the order of 0.5% (V)), whereas the generator, circulator and surfatron were cooled by water. Due to the high flow rate of the cooling air, the flow regime at the tip of the discharge was always turbulent. The humidity of the laboratory air was on the order of 1% (V).

A schematic of the optical setup is shown in Fig. 1. A frequency-doubled pulsed Nd:YAG laser (Quanta-Ray PRO-270-30) was used to pump a dye laser (Sirah PRSC-D-24-EG). The dye laser radiation was further frequency doubled to the wavelength of absorption, ca. 306.5 nm, in order to induce the transition R1(4) of the $A^2\Sigma^+(v' = 0) \leftarrow X^2\Pi(v'' = 0)$, absorption band. The manufacturer's documentation states the spectral width of the output laser line to be ca. 0.4 pm. The output beam polarization is horizontal, which is disadvantageous for the Rayleigh-scattering measurement used for calibration. Therefore, a Fresnel rhomb was used to turn the laser polarization to vertical. The laser was expanded to a sheet using a telescope – a horizontally oriented negative cylindrical lens for vertical expansion, a spherical positive lens for vertical collimation and horizontal shrinking and a vertically oriented cylindrical negative lens for horizontal collimation. The energy of each laser pulse was measured with a pyroelectric head and logged to the computer.

The fluorescence was measured with an ICCD camera (PI-MAX 1024RB-25-FG43, 16-bit grey-scale resolution, 1024 × 256 pixels) with an objective lens. The spatial resolution was around 80 µm per pixel. The fluorescence signal was much stronger than the spontaneous emission. Therefore, no wavelength filter was used and the spontaneous emission was subtracted as a background. To avoid the scattered laser light, the acquisition gate was set to start after the end of the laser pulse.

The detection limit of the presented method is estimated to be around $10^{18}$ OH radicals per $m^3$.

## 2.2 Measurement

The measurement procedure was thoroughly described previously [10,14]. The OH concentration $n_{OH}(x,y)$ can be calculated from the measurements of the spatially dependent fluorescence gain parameter $\alpha_F(x,y)$, and the spatially dependent lifetime of laser-excited OH $\tau(x,y)$ as

$$n_{OH}(x,y) = \frac{\alpha_F(x,y)}{\tau(x,y)A_{(v'=0)}(T_{OH})}\frac{E_{LRS}(y)}{M_{RS}(x,y)}\frac{p_{air}}{kT_{air}}\frac{4\pi\frac{\mathrm{d}\sigma_{RS}}{\mathrm{d}\Omega}}{\kappa\sigma_{abs}}\frac{1}{f_B(T_{OH})} \quad (1)$$

where $A_{(v'=0)}(T_{OH})$ is the mean emission coefficient obtained as a weighted average of the coefficients for the individual rotational transitions with weights given by the Boltzmann fractions of the respective upper rovibronic states, $M_{RS}(x,y)/E_{LRS}(y)$ is the Rayleigh scattering gain parameter, $p_{air} / kT_{air}$ is the concentration of the air particles during the Rayleigh scattering measurement expressed in terms of the pressure and temperature in the laboratory, $\mathrm{d}\sigma_{RS}/\mathrm{d}\Omega$ is the differential cross section for the Rayleigh scattering in the direction of the detector, $\sigma_{abs}$ is the cross section for absorption of a laser photon, $\kappa$=7.85×$10^{-11}$ s is the factor of the overlap of the laser line with the absorption line and $f_B(T_{OH})$ is the Boltzmann fraction of the lower state of the laser-induced transition.

Eq. 1 was derived under several assumptions. The approximation of single-exponential decay described by a single lifetime $\tau$ as well as the use of the mean emission coefficient $A_{(v'=0)}$ is based on the expectation that the rotational energy transfer (RET) in the excited vibronic state is very fast and the rotational thermal equilibrium is reached almost instantaneously. The fluorescence gain parameter $\alpha_{F(x,y)}$ can be used only if the laser power is kept sufficiently low and the stimulated emission rate is much lower than the rate of spontaneous and collision-induced deexcitation. Further, in Eq. 1 the temperature $T_{OH}$ is not spatially dependent. This assumption is not entirely correct. However, the results in [14] and rotational temperature measurements in the surfatron discharge suggest that the OH temperature varies only weakly: in the range 2000–2700 K over the region with significant OH presence. Calculations suggest that assuming a constant temperature of 2400 K introduces an uncertainty of less than 20%.

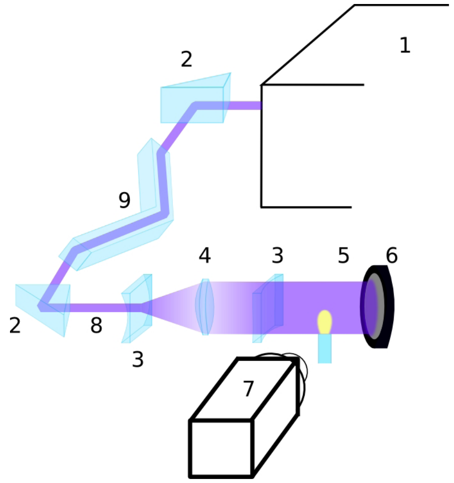


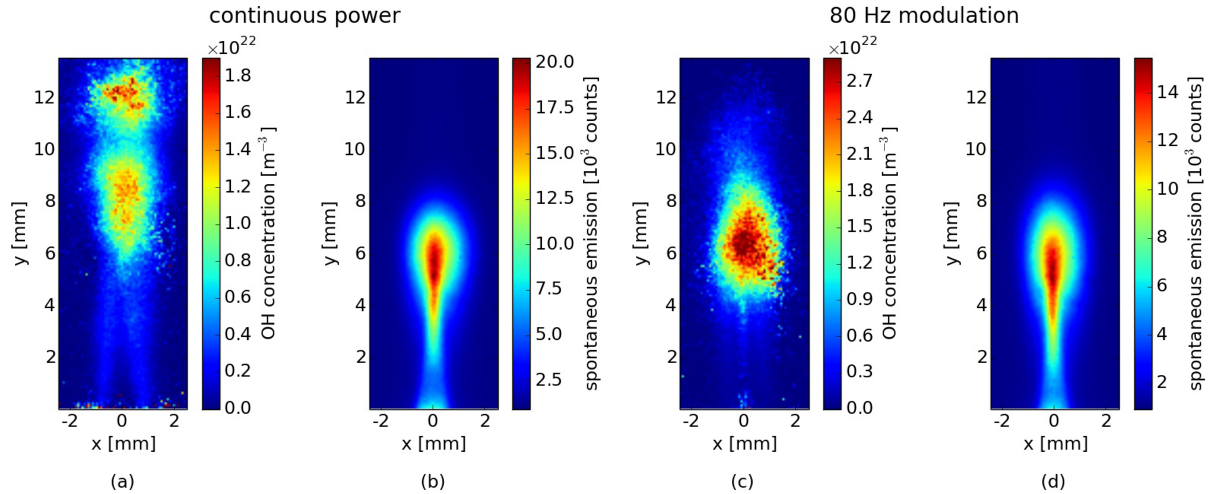
**Figure 1:** Experimental setup: 1 - dye laser with frequency doubling unit, 2 - right-angle prism, 3 - cylindrical negative lens, 4 - spherical positive lens, 5 - surfatron, 6 - laser power meter, 7 - ICCD detector, 8 - laser beam, 9 - Fresnel rhomb (turns polarization).

# 3 Results and discussion

In this work, the hydroxyl concentration was measured in the effluent of the surfatron discharge for both constant MW input power and MW input power modulated by 80 Hz. The left part of Fig. 2 depicts the spatial distribution of hydroxyl radical concentration (a) and spontaneous emission of the discharge (b) for constant MW power averaged through a series of measurements. The bottom margin of the picture approximately corresponds to the end of the surfatron nozzle. Since argon flowing through the surfatron contains some humidity as impurity, there are some hydroxyl radicals detected directly at the end of the surfatron nozzle. In this region hydroxyl radicals are concentrated close to the edge of the argon jet since the discharge inside the tube is ignited by a surface wave which does not penetrate to the central axis of the jet. With increasing distance from the end of the surfatron nozzle, the hydroxyl concentration increases and reaches a distinct maximum approximately 8 mm from the end of the tube. The position of the maximum hydroxyl concentration corresponds to the tip of the visible discharge (see part (b) of Fig. 2), which is similar to the situation in RF argon plasma jets [14]. This can be explained by the fact that the electric field intensity reaches its maximum at the discharge tip resulting in high electron energy and maximum dissociation rate in this region. Also, the OH radicals are formed mainly by dissociation of water molecules. In an environment with an abundance of argon, the OH loss processes are expected to be rather slow. Therefore its amount is expected to rise due to accumulation. Moreover, the amount of ambient air, which is the main source of humidity admixed to argon, is higher at the discharge tip than the amount of air admixed at any point of the active discharge located closer to the surfatron nozzle.

In the parts (c) and (d) of Fig. 2, the OH concentration and spontaneous emission of the discharge modulated by 80 Hz is shown. The influence of AM modulation on the microwave plasma jet was studied previously [5], where strong-pressure waves (sound), caused by periodic heating and cooling of the plasma, were observed. This direct observation was also supported by the fast camera imaging and time resolved emission spectroscopy. As the plasma filament is cooling down, the local pressure decreases and the gas flow is affected. The effective gas velocity can locally decrease or it can even be negative. This implies that the surrounding air can be sucked in. The opposite effect appears during the rising part of the modulation envelope. Heated gas expands and so the local flow velocity is higher than the average value. In effect, the modulation induced periodic changes in local temperature and pressure influence the gas flow and the back-diffusion of air into the working gas. As mentioned in the experimental setup description, the mean MW power supplied to the plasma is the same as in the unmodulated case. The shape of the visible modulated discharge is very similar to the preceding case. The maximal OH concentration is significantly higher in the modulated case, which is probably caused mainly by the fact that the region with considerable OH presence is more contracted. The LIF measurement corroborates the effect of modulations on the production of active species.

Since the quenching rate of excited hydroxyl radicals strongly depends on the type of species that collide with the excited radical, the amount of ambient air admixed to the argon flow can be calculated from the lifetime of excited hydroxyl radicals [14]. The resulting map of gas composition for discharge ignited by constant MW power is shown in the left part of Fig. 3. At the tip of the visible discharge the concentration of admixed air is approximately 15%. 10 mm above the end of the surfatron nozzle the admixed air concentration starts to increase sharply and it reaches more than 40% at a distance of 13 mm above the nozzle end. The admixed air supplies a lot of water molecules to the argon flow. This water-rich region coincides with the position of the second maximum of hydroxyl concentration placed approximately 12 mm from the surfatron nozzle end. These water molecules cannot be dissociated by electron impact since the amount of energetic electrons outside the active discharge is low. Therefore, we attribute this second maximum to



(a) (b) (c) (d)

**Figure 2**: OH concentration and spontaneous emission of the surfatron discharge for constant MW input power (on the left) and MW input power modulated by 80 Hz (on the right).

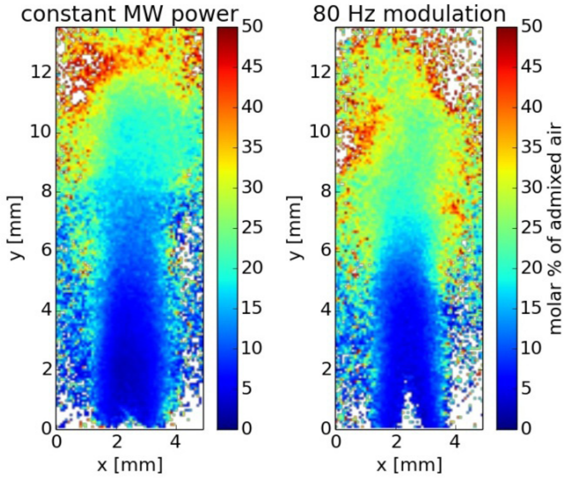


**Figure 3**: Maps of the gas mixing for the case of constant MW input power (on the left) and MW input power modulated by 80 Hz (on the right).

the dissociation of admixed water molecules by collisions with metastable argon atoms [9]. In the case of modulated MW power, the situation changes, as the region with significant amount of admixed air gets closer to the nozzle end. Together with the nonuniform velocity field of the effluent gas, this can result in the contraction of the region containing a significant amount of OH.

## 4 Conclusions

The spatially resolved concentration of OH radicals in the effluent of a microwave surfatron plasma jet was measured for constant MW power as well as for power modulated by 80 Hz. It is shown that the OH concentration profile is influenced by the modulation of the MW power. The maximal concentration of radicals was found on the tip of the visible discharge. In the case of constant MW power, a second maximum further from the jet nozzle was observed. The position of the second maximum was located in the region with sharply increasing concentration of ambient air admixing into the effluent gas. In the case of modulated MW power, the second maximum was not present. The maximal OH concentration was on the order of $10^{22}$ $m^{-3}$. The total amount of OH radicals was almost identical for both modulated and unmodulated cases.

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The plots in this article were produced with the help of the Matplotlib library [15].

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