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Absolute OH and O radical densities in effluent of a He/H₂O micro-scaled atmospheric pressure plasma jet

J Benedikt¹, D Schröder¹, S Schneider¹, G Willems¹, A Pajdarová², J Vlček² and V Schulz-von der Gathen¹

¹ Research Department Plasmas with Complex Interactions, Ruhr-Universität Bochum, 44780 Bochum, Germany
² Department of Physics, University of West Bohemia, Universitní 22, Plzeň, Czech Republic

E-mail: jan.benedikt@rub.de

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Abstract

The effluent of a micro-scaled atmospheric pressure plasma jet (μ-APPJ) operated in helium with admixtures of water vapor (≤ 10⁴ ppm) has been analyzed by means of cavity ring-down laser absorption spectroscopy and molecular beam mass spectrometry to measure hydroxyl (OH) radical densities, and by two-photon absorption laser-induced fluorescence spectroscopy to measure atomic oxygen (O) densities. Additionally, the performance of the bubbler as a source of water vapor in the helium feed gas has been carefully characterized and calibrated. The largest OH and O densities in the effluent of 2 × 10¹⁴ cm⁻³ and 3.2 × 10¹³ cm⁻³, respectively, have been measured at around 6000 ppm. The highest selectivity is reached around 1500 ppm, where the OH density is at ~63% of its maximum value and is 14 times larger than the O density. The measured density profiles and distance variations are compared to the results of a 2D axially symmetric fluid model of species transport and reaction kinetics in the plasma effluent. It is shown that the main loss of OH radicals in the effluent is their mutual reaction. In the case of O, reactions with other species than OH also have to be considered to explain the density decay in the effluent. The results presented here provide additional information for understanding the plasma-chemical processes in non-equilibrium atmospheric pressure plasmas. They also open the way to applying μ-APPJ with He/H₂O as a selective source of OH radicals.

Keywords: micro-scaled atmospheric pressure plasma jet, absolute radical densities, cavity ring-down laser absorption spectroscopy, molecular beam mass spectroscopy, two-photon absorption laser induced fluorescence spectroscopy, OH and O density profiles

(Some figures may appear in colour only in the online journal)

1. Introduction

Atmospheric pressure microplasmas with electrode separations from tens of micrometers up to one millimeter can be operated as non-equilibrium glow discharges. These discharges exhibit high electron temperatures at low gas temperatures and require no expensive vacuum systems. Hence, they are attractive for various applications such as treatment of temperature and vacuum sensitive materials, in vivo decontamination of skin and wounds, or even localized material synthesis [1, 2].

In recent years, a variety of microplasma jets has been developed [3, 4]. These can be subdivided into ‘direct’ jets where the active plasma expands, e.g. in the form of ionization waves within the gas flow, and devices where only a plasma afterglow is emitted [5, 6]. These microplasma jets are capable of delivering reactive species (neutrals, metastables, ions, electrons, vacuum-UV and UV photons) to a treated surface.
via the imposed gas flow resulting, for example, in inactivation of pathogens [7–9], deposition of thin films [10, 11], generation of nanoparticles [12], or etching of surface material [13]. Most of these microplasma jets are operated in noble gases with small admixtures of molecular gases as precursors. In particular, reactive oxygen species and reactive nitrogen species are believed to play a dominant role in plasma interactions with bacteria and cells/tissues [2, 9]. To understand and optimize these processes the absolute densities of these species must be known. The plasma chemistry can then be effectively studied and existing plasma-chemistry models can be validated. Moreover, the effect of plasma treatment on biological substrates can be better understood when the absolute fluxes of reactive species to the treated substrate are known. However, the experimental characterization of atmospheric pressure microplasmas is a challenging task due to the highly collisional conditions and their small dimensions. Fluxes of reactive oxygen species have been recently reported for ‘direct’ discharges for various target conditions and target materials, revealing strong influence e.g. of the conductivity of the target [14, 15]. Here, we report on quantitative measurements of O atoms and OH radicals in the field-free afterglow of a microscaled atmospheric pressure plasma jet (μ-APPJ) operated in helium under controlled admixture of small amounts of water vapor. The measurements of O atoms are performed by two-photon absorption laser-induced fluorescence (TALIF) spectroscopy, and OH radicals are detected by cavity ring-down laser absorption spectroscopy (CRDS) and molecular beam mass spectrometry (MBMS). The latter diagnostics is also used to absolutely calibrate the water concentration in the gas mixture. The O and OH densities as a function of water concentration and distance to the jet are reported and discussed.

2. Setup and diagnostics

2.1. μ-APPJ with bubbler system

The μ-APPJ is a capacitively coupled microplasma jet consisting of two stainless-steel electrodes (length 30 mm, width 1 mm) with 1 mm electrode distance, where the electrode gap is confined on both sides by quartz glass plates. A discharge is generated in the volume of $1 \times 1 \times 30 \text{ mm}^3$ by applying a radio-frequency (rf) voltage ($13.56 \text{ MHz}$, $P_{\text{applied}} < 30 \text{ W}$, $P_{\text{Plasma}} < 2 \text{ W}$) to one electrode, where the other one is grounded (see figure 1). This electrode–glass configuration and corresponding dimensions resemble very closely the recently introduced plasma-jet reference discharge, the COST-Jet [16]. The standard gas flow used is 1.4 slm helium (5.0 purity) with a small admixture of water vapor ($\lesssim 10^4 \text{ ppm}$). It has been shown that this microplasma jet, under selected conditions, is operated in a homogeneous α-mode glow [17] with typical plasma densities around $10^{11} \text{ cm}^{-3}$ [2, 18, 19]. This jet has already been used with He/O$_2$ and He/N$_2$ gas mixtures, where production of O, N, or O$_3$ has already been investigated by TALIF and MBMS [20–23]. The coordinate system used in this work has its origins (0,0,0) at the exit of the jet. The central axis along the electrodes will be referred to as the z-axis, and the inter-electrode direction as the x-axis, respectively.

The helium flow is controlled by mass flow controllers, and the water vapor at a given concentration is prepared in a bubbler system as described below.

The bubbler system consists of a glass bubbler which is filled with distilled water and cooled in an ice bath. The temperature of the distilled water as measured inside the bubbler by a K-type thermocouple is kept at 1.7 °C by this cooling. The concentration of water in the vapor above the liquid phase can be calculated with

$$c_{\text{H}_2\text{O, bubbler}} = \frac{P_{\text{H}_2\text{O, vapor}}(T)}{P_{\text{total}}}$$

and the water vapor concentration $c_{\text{H}_2\text{O, plasma}}$, which is injected into the plasma jet, is controlled by adding pure helium after the gas bubbler via a T-fitting and is

$$c_{\text{H}_2\text{O, plasma}} = \frac{1_{\text{He, bubbler}}}{1_{\text{He, bubbler}} + 1_{\text{He, dilute}}} \cdot c_{\text{H}_2\text{O, bubbler}}.$$ (2)

Here, $1_{\text{He, bubbler}}$ denotes the helium flow through the bubbler and $1_{\text{He, dilute}}$ the (pure) helium flow added via the T-fitting to dilute the water concentration, where the sum of both helium flows is set to 1.4 slm. In the ideal case, the measured bubbler temperature (1.7 °C here) can be used for calculation of the $P_{\text{H}_2\text{O, vapor}}(T)$ and the water concentration. To make sure that this is the case, MBMS diagnostics (for details see section 2.2) has been used to determine the absolute water concentration in the gas mixture, where the water signal has been calibrated by a large bubbler (400 ml) at room and at low temperatures. The measured data have proven that the water concentration in the He gas inside the plasma jet scales linearly with the helium flow through the bubbler, see figure 2. However, the measured concentrations correspond to an effective temperature of about 7 °C, which is higher than the measured 1.7 °C. This is probably due to too low a volume of liquid water in the bubbler (3 ml) and the short residence time of the He gas in contact with the liquid. The water concentration determined by MBMS is used in the following plots. Alternatively, it can be estimated by using 7 °C as the effective bubbler temperature.

The gas line after the bubbler is heated up to about 100 °C to avoid re-condensation of the water vapor to the liquid phase. It was observed that the plasma can become unstable if the gas line is not heated. The gas temperature decreases, however, back to values close to room temperature after the addition of the T-connector and before it is injected into the plasma jet.

2.2. Detection of OH radicals: CRDS

Absolute densities of the OH radical in the effluent of this μ-APPJ are detected and quantified by the CRDS setup shown in figure 3, where the laser light absorption as a function of the wavelength is measured. The laser light at about 308 nm for the absorption of the OH(X–A) transition is produced by a Nd:YAG pumped dye laser (Narrow Line, Radiant Dyes) with frequency doubling. Laser pulses 7–10 ns long are generated with a repetition frequency of 10 Hz. The spectral line-width
of the fundamental at 616.310 nm is about 0.002 nm according to the laser specifications. It is reduced by a factor of 2 due to the required frequency doubling to about 0.7 pm at 308.155 nm central wavelength of the OH(X-A) transition. As will be discussed later, the best fit of the measured absorption features is achieved with 1.4 pm of the spectral width, which is just a factor of two bigger than the ideal spectral width and which is also observed by other authors [24].

The CRDS principle is as follows: two high-reflectivity mirrors (CM1 and CM2 in figure 3, Laseroptik, plan-concave, \( r = 1000 \text{ mm} \)) are used to form an optical cavity of length \( L = 1125 \text{ mm} \). The mirrors are attached to a vacuum vessel filled with one atmosphere of helium to maintain a controlled atmosphere, and the \( \mu \)-APPJ is placed in the center. After passing the pinhole (PH), the laser pulse is coupled into the cavity through the CM1 mirror and starts to ‘ring’ there. Without any absorbing medium, the light intensity in the cavity decreases exponentially due to weak losses at each mirror reflection. The rate of decay can be measured as a decrease of the intensity of the light leaking out of the cavity through the mirror CM2. The transient signal is measured by a photomultiplier tube (PMT) (Hamamatsu R928) connected to a transient recorder card (100 MHz bandwidth, 500 Msamples s\(^{-1}\)). A narrow-band optical filter (BF, \( \lambda_{\text{central}} = 308 \text{ nm} \)) in front of the PMT blocks the emission from the plasma at other wavelengths. The decay time of the measured light intensity (ring-down time) decreases when an absorbing medium is present in the cavity. The ring-down time \( \tau \) of the measured transient can be written as [25]:

\[
\tau(\nu) = L \frac{1}{c(\ln(R_{\text{eff}}) + A)} = L \frac{1}{c(\ln(R_{\text{eff}}) + \sigma(\nu) \int_{0}^{d} n(x) \, dx)}
\]

(3)

where \( L \) is the cavity length, \( c \) is the light velocity, \( R_{\text{eff}} \) is the effective mirror reflectivity, \( \sigma(\nu) \) is the frequency-dependent cross section of the absorbing species, \( d \) is the length of the absorbing medium, \( \int_{0}^{d} n(x) \, dx \) is the line-integrated number density, and \( A \) is the absorption per pass in the cavity. The value of \( A \) can be easily calculated from the measured ring-down times \( \tau_{0} \) of the empty cavity and \( \tau \) of the cavity with absorbing species:

\[
A = \frac{L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_{0}} \right) \approx \sigma(\nu) \int_{0}^{L} n(x) \, dx.
\]

(4)

In the present case, the \( Q_{1}(3) \) peak at 308.154 nm of the OH(X-A) transition was selected for investigation, as it shows the highest absorption (see the measured data in figure 4). The energy of the applied laser pulse (about 8 \( \mu \)J energy before entering the cavity) was selected such that the saturation effects of the transition were avoided [26]. The respective absorption cross section of the \( Q_{1}(3) \) transition can be calculated from the effective cross section given by Dorn et al [27]. This value is valid for the line center of the natural Voigt profile calculated for \( T = 300 \text{ K} \) and \( p = 1013 \text{ hPa} \). When corrected for an increased temperature of about \( T = 350 \text{ K} \) and for the Boltzmann ratio considering the population of the excited states, the used cross section \( \sigma_{Q_{1}(3)} \) amounts to \((1.40 \pm 0.11) \cdot 10^{-20} \text{ m}^2\). The ratio is corrected assuming that the gas temperature equals the rotational temperature of the OH transition. The rotational temperature is determined by comparing the measured spectral absorption profile to a simulated one at \( T = 350 \text{ K} \) (LIFBase [28], including Doppler and pressure broadening and with spectral laser width of 1.4 pm)
as shown in figure 4. The error is ±50 K, mainly caused by the noisy background signal in the outer wings of the absorption profile.

The ring-down time of the empty cavity $\tau_0$ reflecting the background signal is on average about 620 ns for the present experiment (which corresponds to a reflectivity of the mirrors of around 99.4%). For each single measurement, the background signal has been recorded separately and is identical to the ring-down time values measured outside of the absorption features. To obtain a ring-down time, 100 transients are recorded on the 16-bit memory transient recorder card, each is fitted separately to an exponentially decaying function with a standard least-squares fitting routine, and the resulting ring-down times are averaged.

The number density of OH radicals is determined with the simplifying assumption that it is constant over the absorption length $d < L$ and zero elsewhere. $d$ is selected to be 1 mm as will be discussed later. Equation (4) is then further simplified to

$$A = \sigma_0(3) \cdot n_{OH} \cdot d. \quad (5)$$

The region under investigation can be scanned automatically by moving the jet by two stepping motors attached to the jet-holder in the vessel. Absolute values of OH density possess an
error of about 20%. The error is an estimation mainly of the high uncertainty of the cross section up to 16% [27]. Stochastic experimental errors are calculated from the 100 transients and illustrated by error bars in the respective figures.

2.3. Detection of OH radicals: MBMS

For measuring OH radicals in the effluent of the μ-APPJ with MBMS, we used the same differentially pumped sampling setup, which was used previously to measure O, O₃ and N radicals generated by the same jet with admixture of oxygen or nitrogen gases [20, 22]. Therefore, the details of the experimental setup will not be repeated here and the reader is referred to these previous works. Here just briefly: the gas from the plasma effluent is sampled through a small orifice (100 μm diameter) into the differentially pumped system with two pumping stages connected by an additional orifice. A molecular beam is formed from the sampling gas and passes the ionizer of the mass spectrometer in the second stage. The background signal in the mass spectrometer pumping stage is reduced and determined with help of a specially designed beam chopper with rotating skimmer [29]. MBMS allows measurements of absolute densities of reactive species, if properly conducted [30, 31]. Concentrations below 1 ppm can be measured for heavy species in helium with our setup. The proper calibration of the measurements, as explained below, as well as to realize the ambient helium atmosphere needed for the detection of OH radicals as shown in figure 3. The microplasma jet is mounted on a three-axis manipulator in order to measure space-resolved density distributions. The used coordinate system is indicated by black, dashed arrows and is identical to the one used in the CRDS measurements. Again, the region under investigation can be scanned automatically as to realize the ambient helium atmosphere needed for the detection of OH radicals as shown in figure 3. The microplasma jet is mounted on a three-axis manipulator in order to measure space-resolved density distributions. The used coordinate system is indicated by black, dashed arrows and is identical to the one used in the CRDS measurements.

The optical setup consists of two parts. On the one side, the incoming laser beam (ns-pulses) forms the y-axis. It is focused by a quartz lens to a minimal diameter of about 150 μm at the origin of the coordinate system. On the other side is the detection system, which images the laser focus by a lens on the photocathode of a photomultiplier tube (PMT) after passing an interference filter (FWHM = 1 nm at 844 nm) and a 1.5 mm wide pinhole (PH). Thus the fluorescence is detected perpendicular to the laser beam in the direction of the y-axis. The total spatial resolution of this particular optical setup is 0.15 mm in the x- and z-directions and 1.5 mm along the y-axis, as determined by the PH diameter (the fluorescence is imaged 1 : 1 on the PH). The y-resolution can be improved by taking a smaller PH diameter, but it was not possible in this case due to very low fluorescence intensity. As will be discussed later the full width at half maximum (FWHM) of the effluent containing O atoms is narrower (~ 1 nm) than the PH diameter. This fact has been considered in the absolute signal calibration.

2.4. Detection of O radical: TALIF spectroscopy

Atomic oxygen densities in the effluent of the microplasma jet are determined by TALIF [32]. In this technique two photons in the UV at 225.65 nm are absorbed simultaneously, exciting ground state oxygen atoms (2p3 P2) into the 3p3 P state. In the unsaturated regime with low laser energies the resulting fluorescence at 844.6 nm from the de-excitation into the 3s3 S0 state is proportional to the atomic oxygen ground state density and to the square of the laser pulse energy. A sketch of the setup is shown in figure 5. The complete setup, including the laser system, a vacuum-tight vessel and the signal-detecting system is described elsewhere [33].

The vessel and the laser system are not shown here for reasons of clarity. However, the vessel is needed for the absolute calibration of the measurements, as explained below, as well as to realize the ambient helium atmosphere needed for the detection of OH radicals as shown in figure 3. The microplasma jet is mounted on a three-axis manipulator in order to measure space-resolved density distributions. The used coordinate system is indicated by black, dashed arrows and is identical to the one used in the CRDS measurements. Again, the region under investigation can be scanned automatically by moving the jet through two stepping motors attached to the jet-holder in the vessel.

The optical setup consists of two parts. On the one side, the incoming laser beam (ns-pulses) forms the y-axis. It is focused by a quartz lens to a minimal diameter of about 150 μm at the origin of the coordinate system. On the other side is the detection system, which images the laser focus by a lens on the photocathode of a photomultiplier tube (PMT) after passing an interference filter (FWHM = 1 nm at 844 nm) and a 1.5 mm wide pinhole (PH). Thus the fluorescence is detected perpendicular to the laser beam in the direction of the y-axis. The total spatial resolution of this particular optical setup is 0.15 mm in the x- and z-directions and 1.5 mm along the y-axis, as determined by the PH diameter (the fluorescence is imaged 1 : 1 on the PH). The y-resolution can be improved by taking a smaller PH diameter, but it was not possible in this case due to very low fluorescence intensity. As will be discussed later the full width at half maximum (FWHM) of the effluent containing O atoms is narrower (~ 1 nm) than the PH diameter. This fact has been considered in the absolute signal calibration.
Laser-induced fluorescence needs to be absolutely calibrated. This can become exceedingly challenging at atmospheric pressure due to the fast quenching reactions of the excited states by the ambient gas species. The established procedure consists of a reference measurement in a defined xenon atmosphere, created in the closed vessel [32, 34]. It is described in detail for the particular experimental setup in a recent publication of the authors [33].

Quenching is accounted for neutral helium atoms and water molecules for an average gas temperature of 350 K [32, 35]. The number density of quenching water molecules in the effluent is assumed to equal the density admixed in the feed gas flow. This simplification implies a systematic error of less than 5% over the complete range of water admixture. Absolute density values possess an inherent reliability of about 30%, mainly due to the uncertainties in the determination of the two-photon absorption cross sections for atomic oxygen and xenon [32].

2.5. O and OH chemistry model in the effluent

Since the plasma is confined in the region between electrodes (transverse electric field is applied), no power is delivered to the effluent and the evolution of the species densities with the increasing distance to the jet is just a result of recombination reactions and diffusion losses to the surrounding helium gas (all experiments are performed in the controlled helium atmosphere). This evolution can be, therefore, rather easily modeled by a diffusive-convective transport with recombination reactions, where the initial species densities at the jet exit are the extrapolated experimental densities at \( z = 0 \). It is realized as a 2D axially symmetric model of the He gas flow and diffusive-convective transport of OH and O species, where chemical reactions are incorporated by coupled rate equations in the same way as in our previous models used to predict the O and O\(_3\) densities in the effluent of the He/O\(_2\) plasma [20, 36] or used to study the chemistry of hexamethyldisiloxane and its fragments in the plasma effluent [37]. A global gas temperature of 350 K is assumed and \( D_{\text{OH}} = 1.14 \times 10^{-4} \text{m}^2\text{s}^{-1} \) and \( D_{\text{O}} = 1.31 \times 10^{-4} \text{m}^2\text{s}^{-1} \) have been used as diffusion coefficients of OH [38–40] and O [38, 39, 41–43] in He, respectively.

The reaction of OH radicals with water molecules does not change the gas composition, because it is symmetric with \( \text{H}_2\text{O} \) and OH as products. Additionally, the reactions with possible O\(_2\) and N\(_2\) impurities, if present in the gas mixture, are extremely small and can be neglected as well. The obvious reactions which have to be taken into account are the reaction with O and reaction of two OH radicals [44–47]:

\[
\begin{align*}
\text{OH} + \text{O} &\rightarrow \text{O}_2 + \text{H}; \quad k_{350, \text{K}} = 3.29 \cdot 10^{-11} \text{cm}^3\text{s}^{-1} \quad (\text{R1}) \\
\text{OH} + \text{OH} &\rightarrow \text{H}_2\text{O} + \text{O}; \quad k_{350, \text{K}} = 1.40 \cdot 10^{-12} \text{cm}^3\text{s}^{-1} \quad (\text{R2}) \\
\text{OH} + \text{OH} + \text{He} &\rightarrow \text{H}_2\text{O}_2 + \text{He}; \quad k_{350, \text{K}} = 5.12 \cdot 10^{-12} \text{cm}^3\text{s}^{-1} \quad (\text{R3})
\end{align*}
\]

Rates are taken at 350 K gas temperature and for the latter instance (three-body \( \text{OH} + \text{OH} \) recombination) multiplied by the helium density at this temperature. The reaction rate constants have to be carefully selected from the literature. For the three-body reaction, the values in relevant plasma-related literature [46, 48] differ up to a factor 3.84 under one atmosphere and 300 K conditions, which influences significantly the resulting model densities. Therefore, an extensive literature search has been carried out [38–52] to identify the reaction rates determined in He as a bath gas and in the proper pressure range. For example, the effect of the bath gas for the \( \text{OH} + \text{OH} \) recombination reaction rate constant can be as large as 2.4. The values for N\(_2\) and He as bath gases are \( 6.9 \times 10^{-31} \text{cm}^6\text{s}^{-1} \) [52] and \( 3.7 \times 10^{-31} \text{cm}^6\text{s}^{-1} \) [51], respectively. The present model uses the values provided by the IUPAC Task Group. They periodically review the available values from experiments and theoretical predictions and update those on their website [48].

3. Results and discussion

3.1. Radial O and OH density distributions

Figure 6 compares the measured density profiles of OH (figure 6(a)) and O (figure 6(b)) species along the \( x \)-axis with the profiles obtained by the model. The modeled profiles both have FWHMs of 1 mm, which is clearly determined by the width of the gas flow, which is equal to the jet diameter. The short-lived species such as OH or O can be detected only in the fast helium flow, which has a diameter of 1 mm. It was also observed in the previous case for O atoms [53].

The measurements were carried out close to the nozzle (0.5 mm for TALIF and \( \geq 2 \) mm for CRDS). Both experimental profiles show a FWHM of about 1.8 mm, which is larger than the expected value. This is due to spatial resolution limits of both experimental techniques. For the TALIF setup, when measuring along the emitting gas beam in the transverse direction (\( x \)-axis) the laser-induced fluorescence, which corresponds to atomic oxygen distribution \( O_{\text{real}} \), is 1 : 1 imaged onto a PH with 1.5 mm diameter in front of the PMT. The measured profile is therefore a convolution of the real profile and the PH diameter. If assuming both profiles as Gauss functions with FWHMs of 1 mm and 1.5 mm, respectively, the FWHM of the resulting, measured profile can then be calculated as \( \text{FWHM}_{\text{O,measured}} = \sqrt{\text{FWHM}_{\text{O,real}}^2 + \text{FWHM}_{\text{PH}}^2} \) yielding a measured value of about 1.8 mm, corroborating that the width of the real O density profile is 1 mm.

The measured density profile of OH, which is also broader than the expected 1 mm, indicates that the laser pulse ringing in the cavity scans during its multiple reflections has a rather broad volume. With an effective diameter in the range of 1.5 mm, this gives again a broader profile like in the case of TALIF measurements. The absorption length \( d \approx 1 \) mm assuming a constant density is therefore used to calculate the OH density on the jet axis with the help of equation (5). The resulting value only differs by 2% from the value obtained by applying the calculated profile. As a further consequence, the OH profile can only be measured at distances \( \gtrsim 2 \) mm from the nozzle.
3.2. Influence of water concentration on species density

Figure 7 shows the OH radical density as a function of water concentration in a helium flow of 1.4 slm and at an applied voltage of 200 V RMS. The measurements were performed close to the jet nozzle, at \( z \geq 2 \) mm for the CRDS (the first point is set to \( z = 2 \) mm) and at \( z = 5 \) mm for MBMS.

Both diagnostics show the same trend. The OH density increases steeply in the range of small H2O admixtures below 3000 ppm and saturates slowly at water concentrations above 6000 ppm. Both diagnostics also provide very similar densities, especially when the fact is considered that the MBMS measurements were performed at 3 mm greater distance than CRDS. The species densities drop with increasing distance to the plasma (see section 3.3) and this decrease can explain the density difference. This excellent agreement between these two fundamentally different diagnostics makes us very confident about the absolute value of the OH radical density, which saturates at a level of approximately \( \times 10^{14} \) cm\(^{-3}\). The first and lowest OH density value of \( 2 \times 10^{13} \) cm\(^{-3}\), as obtained by CRDS, was measured without the water bubbler system being connected to the gas supply system and serves as an estimate for the OH density resulting from the water, which is present in the helium gas as an impurity. The water impurity concentration is very difficult to determine and we estimate it to be somewhere between 10 and 100 ppm. To prevent the plasma from changing to a constricted mode discharge, the voltage had to be reduced to 185 V RMS during this single measurement. By comparison to the COST-Jet this corresponds to an adsorbed power of about 0.5 W [16] and decreases with the admixture of a molecular gas in case the root-mean-square voltage is constant [54]. Since the used jet didn’t include the current and voltage probes incorporated into the electrode head of the COST-Jet, we decided to keep the voltage as a control parameter. The change of O density as measured by TALIF follows a slightly different trend as shown in figure 8. It also increases for water concentrations below 6000 ppm, but this increase is almost linear with small increases of the slope around 1500 ppm. The O density reaches its maximum of \( 3.2 \times 10^{13} \) cm\(^{-3}\) at about 6000 ppm, before it starts to decrease again as the water concentration increases further.

Comparing the absolute values, the OH radical has 14 times higher density than the O radical at 1500 ppm water concentration. The density ratio gets smaller as the water concentration increases to 6000 ppm, where the O density has its maximum and the OH density is just six times higher. The ratio of OH to O densities gets larger again as the water concentration increases.
concentration increases even further, because the OH density levels and O density decrease here.

The initial increase of O and OH densities can be explained by the increase of the water concentration, which is a precursor for these radicals. OH is a primary water dissociation product and therefore its density increase is highest at the lowest water concentrations. The O can also be produced in primary dissociation of water, but with a lower probability, because two O-H bonds have to be broken. The secondary O production processes (plasma dissociation of OH or reactions such as the reaction R2) will play, therefore, also an important role in its generation. It is also probably the reason for the change of slope at the water concentration of 1500 ppm, at which O density starts to grow faster and the OH density increase slows down with increasing water concentrations. The maximum densities are reached for both species at a water concentration of 6000 ppm. The leveling of the OH density and the decrease of the O density beyond this concentration is very probably caused by the fact that less power couples into the plasma under the increasing amount of molecular gas in the gas mixture (the applied root mean square voltage has been used as a controlled plasma parameter, not the absorbed power). The same effect has been observed for He/O2, He/N2, He/N2/O2, and He/N2/H2O gas mixtures [20–22, 55].

The \( \mu \)-APPJ with He/O2 gas mixture has been used in the past as a selective source of O radicals in the treatment of inorganic (SiO2-like films [37]) and also biologically relevant (bacteria, proteins, DNA molecules [56]) substrates. Considering the above presented results, the \( \mu \)-APPJ jet with He/H2O gas mixture could be used as a selective source of OH radicals, where the best operation condition seems to be a water concentration of 1500 ppm. The OH density is at \( \sim 63\% \) of its maximum density and it is 14 times larger than the O density, assuring therefore the best selectivity. The low water concentration will probably also result in low densities of other species such as HO\(_2\) or H2O2. Additionally, we expect that there will also be atomic hydrogen present in the gas mixture with density very similar to the OH density in case the water dissociation into OH + H is the main primary dissociation reaction. The densities of all these species should be measured in the future to obtain a reliable image of all plasma-chemical processes in this gas mixture. The OH concentration is under these conditions around 6 ppm, which means that the conversion efficiency of water into OH radicals is less than one percent (making the measurement of the water consumption by MBMS impossible). The water concentration of 6000 ppm is optimal, if not the highest selectivity in respect to the OH radical, but the highest oxidation effects of this plasma are asked, because both OH and O radicals have the highest densities under these conditions.

3.3. Axial decay of O and OH densities

The decay of the radical densities along the gas flow axis can reveal important information about recombination reactions and their effective lifetime. Figure 9 shows this decay for the OH radical as measured by CRDS and MBMS at similar water concentrations of 7230 ppm and 7980 ppm, respectively, measured with a helium flow of 1.4 slm and an electrode voltage of 200 Vrms. Figure 10 shows the O density decay for the same plasma parameters as measured by TALIF with water concentration of 7230 ppm. Additionally, radical density decays from the 2D axially symmetric model are added where two cases have been studied: first, a simple chemistry with just the three above-mentioned reactions involving OH, and second, an extended chemistry including additional reactions and species such as H, H2O or HO2. Details of the extended chemistry model are summarized in the appendix.

Regarding the OH, its density decay is governed by the OH + OH recombination (reactions R2 and R3). Additional reactions and species in the extended set of reactions result only in small changes in the modeled OH density decay, which follows almost perfectly the OH density as measured by MBMS. The OH density determined with CRDS starts at a similar density to the MBMS one, but it decays faster and reaches zero at around 22 mm. We explain this difference by
The measured O density drops faster than the OH density, and this decrease cannot be explained just by the O reaction with OH from the simple chemistry (reaction R1). Its initial fast decrease can only be reproduced if additional reactions of the O radical with other species in the gas mixture such as H, H₂O₂ or HO₂ are added to the model. Considering the reaction rate constants only, the O reacts the fastest (next to OH) with HO₂ \((\sim 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1})\). The reaction rate constant of O with H₂O₂ is four orders of magnitude smaller \((\sim 1.8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1})\) and with water is negligibly small \((\sim 10^{-22} \text{ cm}^3 \text{ s}^{-1})\). The measured O density deviates from the density decrease as predicted by the model at distances further than 5 mm. It seems that the density follows a faster decay trend compared to the model prediction and also compared to the decay at the first 5 mm behind the jet nozzle. This change in the trend is probably artificially caused by the difficulties in the calibration procedure of the TALIF diagnostics. The TALIF measurements have been performed in a closed chamber filled with helium and with gases originating from the plasma jet, and the possible effects are the fast reduction of the gas temperature to the room temperature and some impurities, which would both result in higher quenching and therefore underestimation of the real O density. As mentioned above, the non-radiative quenching of the excited state by each existing collision partner has to be taken into account. Therefore, the quenching effect of water in corresponding concentration, atmospheric pressure, and temperature of \(T = 350 \text{ K}\) has been considered. However, starting at 5 mm distance from the jet, the diffusion of the surrounding gas into the gas flowing from the jet starts to influence the gas mixture properties [33, 57]. This also means that the composition of the quenching partners is changing along the gas flow, hence locally enhancing the quenching. No attempt has been made to account for this effect in the calibration.

4. Conclusions

The densities of OH and O radicals in the effluent of a micro-scaled atmospheric pressure plasma jet (\(\mu\)-APPJ) operated in helium with controlled admixtures of water vapor \((\leq 10^4 \text{ ppm})\) have been measured by several absolutely calibrated diagnostic techniques. The experiments have been carried out under controlled conditions operating in a helium atmosphere. Also, the influences of fields, in particular in interaction with surfaces, have been obviated. An excellent agreement between OH densities as determined by MBMS and CRDS has been obtained, giving a large confidence in the absolute OH density values. The O densities have been determined by TALIF spectroscopy. The largest OH and O densities have been measured for water concentration at around 6000 ppm absolute values of \(2 \times 10^{14} \text{ cm}^{-3}\) and \(3.2 \times 10^{13} \text{ cm}^{-3}\), respectively. The highest selectivity has been reached around 1500 ppm, where the OH density is at \(\sim 63\%\) of its maximum value and it is 14 times larger than the O density. The measured density variations as a function of the distance to the jet have been compared to the results of a 2D axially symmetric fluid model of species transport and reaction kinetics in the plasma effluent. It could be shown that the mutual OH + OH reactions are the main loss channel of these radicals in the plasma effluent. On the contrary, the reactions with other species than OH and O have to be considered to explain the fast decay of O radical density in the plasma effluent. The results presented here provide additional information for understanding the plasma-chemical processes in the afterglow of non-equilibrium atmospheric pressure plasmas. They also open the way to apply the \(\mu\)-APPJ with He/H₂O as a selective source of OH radicals in a variety of plasma–substrate interaction studies. A further step will be the discrimination of surface-related processes.

Acknowledgments

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Appendix. Fluid model

It should be noted here that the chemistry model is used just as a supporting analysis tool, because the densities of the other unmeasured species had to be estimated to be able to perform the analysis. The species recombination and transport through the convection and diffusion has been modeled by a 2D axially symmetric fluid model in the same way as it was done in our previous publications for He/O2 and He/hexamethyldisiloxane/O2 gas mixtures [36, 37]. The plasma is not modeled, because only the recombination reactions in the effluent are needed to explain the decrease of species densities in the effluent. Following species (table A1) and reactions (table A2) have been included in the simple chemistry and in the extended chemistry.

The temperature used in the model was T = 350 K both for calculating helium density and reaction rates, if temperature-dependent. This is very probably an upper estimate of the gas density, because the plasma effluent can be touched by a finger without feeling any temperature increase. Additionally, the temperature will certainly decrease with the increasing distance to the plasma. A lower set temperature of 300 K in the model results in a slightly faster decay of the species densities (within the experimental errors of the densities measured), but with the same effects of the extended and simplified chemistry.

References


Table A1. Species and their diffusion coefficients and initial densities as used in the 2D axially symmetric model.

<table>
<thead>
<tr>
<th>Species i</th>
<th>Di (m² s⁻¹)</th>
<th>nini,i at z = 0 (cm⁻³)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>1.13 · 10⁻⁴</td>
<td>1.9 · 10¹⁴</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1.29 · 10⁻⁴</td>
<td>3.1 · 10¹³</td>
<td></td>
</tr>
<tr>
<td>HO₂</td>
<td>1.0 · 10⁻⁴</td>
<td>2.5 · 10¹⁴ (12 ppm)</td>
<td>Estimated values</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.0 · 10⁻⁴</td>
<td>1.5 · 10¹⁷</td>
<td>Multiplied value</td>
</tr>
<tr>
<td>H</td>
<td>4.0 · 10⁻⁴</td>
<td>1.9 · 10¹⁴</td>
<td>Dhl est., nini,H</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>1.0 · 10⁻⁴</td>
<td>2.5 · 10¹⁴ (12 ppm)</td>
<td>Estimated values</td>
</tr>
</tbody>
</table>

Note: The bold species are used in the simple set of chemistry reactions.

Table A2. Reactions and their reaction rate constants as used in the 2D axially symmetric model.

<table>
<thead>
<tr>
<th>Reactants Products</th>
<th>k (cm³ s⁻¹)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 OH + O</td>
<td>O₂ + H</td>
<td>3.29 · 10⁻¹¹</td>
</tr>
<tr>
<td>R2 OH + OH</td>
<td>H₂O + O</td>
<td>1.40 · 10⁻¹²</td>
</tr>
<tr>
<td>R3 OH + OH + He</td>
<td>H₂O₂ + He</td>
<td>5.12 · 10⁻¹²</td>
</tr>
<tr>
<td>R4 O + H₂O</td>
<td>OH + OH</td>
<td>3.38 · 10⁻²²</td>
</tr>
<tr>
<td>R5 O + HO₂</td>
<td>OH + O₂</td>
<td>5.12 · 10⁻¹¹</td>
</tr>
<tr>
<td>R6 O + H₂O₂</td>
<td>OH + HO₂</td>
<td>1.78 · 10⁻¹⁵</td>
</tr>
<tr>
<td>R7 OH + H₂O₂</td>
<td>H₂O + HO₂</td>
<td>1.8 · 10⁻¹²</td>
</tr>
<tr>
<td>R8 OH + H₂O₂</td>
<td>H₂O + O₂</td>
<td>9.8 · 10⁻¹¹</td>
</tr>
<tr>
<td>R9 H + H₂O₂</td>
<td>OH + H₂O</td>
<td>9.9 · 10⁻¹⁴</td>
</tr>
<tr>
<td>R10 H + H₂O₂</td>
<td>H₂ + HO₂</td>
<td>1.2 · 10⁻¹⁴</td>
</tr>
<tr>
<td>R11 H + HO₂</td>
<td>OH + O</td>
<td>8.1 · 10⁻¹¹</td>
</tr>
<tr>
<td>R12 H + HO₂</td>
<td>H₂ + O₂</td>
<td>5.7 · 10⁻¹²</td>
</tr>
<tr>
<td>R13 H + HO₂</td>
<td>H₂O + O</td>
<td>2.4 · 10⁻¹²</td>
</tr>
<tr>
<td>R14 OH + H + He</td>
<td>H₂O₂ + He</td>
<td>2.2 · 10⁻¹²</td>
</tr>
</tbody>
</table>

Note: The bold reactions are used in the simple set of chemistry reactions.
[54] Marinov D and St John Braithwaite N 2014 Plasma Sources Sci. Technol. 23 062005