Measurements of OH in atmospheric pressure argon microwave plasmas

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Abstract: Hydroxyl radical is measured as function of distance, flux and microwave power in atmospheric pressure argon microwave plasma expanding in air. Employing mass spectrometry and optical emission spectroscopy the plasma jet was characterized and the conditions for maximum production of OH were determined. The kinetics of OH was discussed and its relationship with other radicals like as H_2O_2, H_2O, H_3O and NO, was addressed.

Keywords: Atmospheric pressure plasma, mass spectrometry, optical spectroscopy, hydroxyl radical.

1. Introduction

The last two decades witnessed a rapid growing of atmospheric pressure plasmas (APP) applications in a considerable widespread domain like environmental, processing of biomass, biology, medicine, foods, agriculture and material processing [1], thanks to their design versatility, ease of implementation, low-cost and unique chemical composition. The complexity and richness of APP chemistry is a challenge today for the understanding of the production and loss of various radicals present in this medium. Accurate knowledge of these very reactive plasmas is needed to tailor a given plasma source to a specific application. As an example of paper discussing the complexity of physics and chemistry of water containing plasmas we may cite the review article and roadmap of plasma-liquid interactions [2]. The authors put in relief the physical and chemical mechanisms leading to complex interaction between plasma and liquid at plasma-liquid interface resulting in reactivity in the liquid. Little knowledge is available for the kinetics of the water vapor containing plasmas including electron collisions with important species like as OH and H_2O_2. The OH radical is one of the most oxidative species produced in water containing plasmas and have key hole in H_2O_2 production which is another very reactive radical. The OH radical is highly oxidative because it has unpaired electrons which tend to transfer to other molecules. It is the most oxidant specie in the atmosphere and the Nobel Prize winner Paul Crutzen coined the term “detergent of the atmosphere” to describe the important cleansing role of OH [3]. In fact, most of the trace gases found in the troposphere are oxidized by OH into water-soluble products that are washed by rain and/or snow. OH has a high oxidation potential of 2.8 eV, higher than O_3 (2.07 eV) and H_2O_2 (1.78 eV). The production of OH in plasmas is mainly due electron-ion dissociative recombination with water ion and hydronium and electron collisions with water as well as metastables and thermal dissociation of H_2O.

Atmospheric-pressure plasmas are a novelty in medicine because it may generate many radicals in a controlled manner for low-cost treatment of damaged cells or tissues. The OH radical cause cell injury when they are generated in excess in living systems and its effect in bacteria killing was demonstrated by many authors [4].

An emerging and important application of APP is the remediation of organic contaminated soil. By a variety of sources the soil can be polluted, of which the following routes may be considered the most important: contamination from industrial waste emission, contamination from agricultural production, sewage irrigation and atmospheric deposition. The chemical elements responsible for these contaminants are primary recognized to be volatile organic compounds, pesticides, like dichlorodiphenyltrichloroethane (DDT), and polycyclic aromatic hydrocarbons (PAHs). APP is an excellent source to generate strong oxidizing free radical OH which play dominant role in oxidation of DDTs and PAHs. For phenol contaminated soils, for example, H_2O_2 cannot degrade the phenol molecules by direct oxidation, but by producing OH from reactions with other active species present in the medium, plasma may promote the degradation of organics [5].

In this work the production and loss channels of OH in an atmospheric-pressure plasma jet generated by a Surfatron launcher expanding in air is studied. A microwave power generator of 2.45GHz was employed to feed a Surfatron surface-wave launcher. The power was varied between 30W and 100W, flux of 2.5 SLM and 5.0 SLM and the gas used to produce the discharges was argon. Employing mass spectrometry (MS) measurements, the main neutral and positive ions along the jet are measured as function of operating parameters of the plasma. Axial variation of plasma parameters n_e, T_e, and T_g in was measured by optical emission spectroscopy (OES).

2. Experimental apparatus

The experimental set-up used for optical spectroscopy diagnostics was detailed in a previous publication [6]. As shown in figure 1, the experimental apparatus includes the plasma source, the mass spectrometer and data acquisition system for measurements.

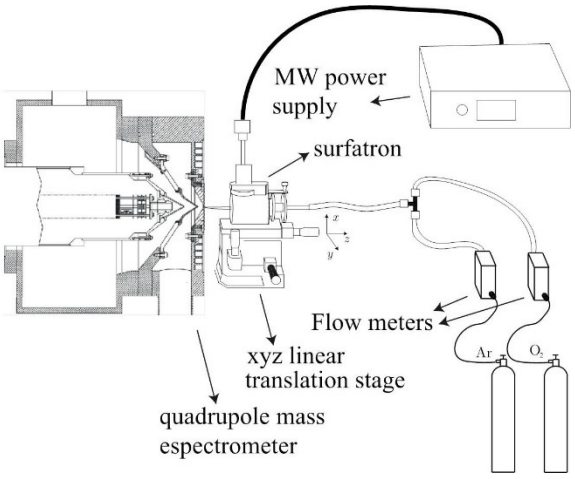

Figure 1. Arrangement employed in mass-spectrometer diagnostics.

The plasma source is a surface-wave launcher Surfatron operating at 2.45 GHz provided by a solid-state power supply of 200W. The alumina (Al_2O_3) tube placed inside the Surfatron cavity was fed by a continuous flow of argon gas with a purity of 99.999%. The mass flow meter was connected to a multi-channel flow controller and remotely operated. The discharges studied in this work are created in an alumina tube of inner diameter 2 mm and outer diameter 4 mm used to guide the gas inside the Surfatron. The discharge occupied all the internal volume of the tube and expanded in air. The light emitted by the discharge was collected by an optical fiber longitudinally and transversely. The surface-wave launcher, the power supply and the fiber positioning system were mounted on an optical table with tuned damping. Light was conducted through a line-to-spot optical fiber bundle specially designed for UV-vis measurements. The fiber was coupled to the entrance slit of a Horiba Jobin-Yvon monochromator iHR550, Czerny-Turner, with a 550mm focal length. A holographic grating of 1800 gmm^{-1} was used in the measurements of light within the visible range. In the UV range, a 2400 gmm^{-1} holographic grating was used instead. A 13.5 μm pixels Horiba CCD Synapse was used as the detector. The monochromator and the CCD were computer controlled. In the laboratory the temperature and humidity were monitored and remained stable along the experiments. The molecular beam mass spectrometer (MBMS) used for MS diagnostics was a quadrupole-based mass spectrometer (QMS) system, the HPR-60 MBMS (from Hiden Analytical Ltd) with an energy analyzer for resolved ion-energy distribution measurements; see figure 1. It consists of a three-stage differentially pumped inlet system separated by aligned skimmer cones and turbo-molecular pumps. As the molecular beam enters the mass spectrometer it transitions from atmospheric to the reduced pressure region where it undergoes a supersonic expansion. The shock waves create regions of large pressure, temperature, and velocity gradients, which can affect the chemical species present within the mass spectrometer. The HPR-60 is designed with conical skimmer cones that sample the molecular beam within a zone of silence, a region that has not been disturbed by the formation of shock waves and has an unmodified chemistry. The measured ion composition is representative of that produced in the plasma.

3. Results

To analyze the main production and loss mechanisms of OH the plasma source need to be characterized. Gas and electron temperature, ionization degree and electron density are important data once these plasma properties can significantly change according to discharge condition and affect the radical production mechanisms.

To determine the gas temperature we analysed the intensity distribution of the ultraviolet $OH\ (A\ ^2\Sigma^+, v' = 0 \longrightarrow X\ ^2\Pi, v" = 0)$ band, Q_1 branch. From this analysis we estimated the rotational temperature, which gives an approximate measure of the translational temperature. More details about the method may be found in [6]. The electron density was estimated using the H_β (486.13 mm) line broadening. Since water is present in the atmosphere and as an impurity in the Ar gas, hydrogen atoms are produced through molecular dissociation in the discharge by electron impact. The electron temperature was estimated using a collisional radiative model based on the method proposed in [6], which was extended to consider a more realistic electron energy distribution function (EEDF) and the deactivation of the 2p states by collision with heavy species. This method takes as experimental input four emission lines originating from 2p states, namely $2p_2$, $2p_4$, $2p_6$ and $2p_{10}$ (Paschen notation). It assumes that the plasma is optically thin for the transitions considered and the mechanism of excitation and de-excitation is governed by electronic excitation and de-excitation by quenching collisions and radiative emission.

The ionization degree ranges from 1 x 10^{-5} to 5 x 10^{-5} while the gas temperature ranges between 425K to 625K. The maximum in electron density is around 11 mm in the jet with densities from 1 x 10^{17} m^{-3} to 5.5 x 10^{17} m^{-3}. In the range of power and flux employed in the present experiments the electron temperature varied from 0.6 eV to 1.3 eV.

The understanding of the kinetics of the intermediate short-lived radical OH and the stable H_2O_2 depends not only on the knowledge of other species such as H_2O, but also on the subsequent chain and end reactions. In order to investigate the mechanisms of OH production, we analyzed the mass spectrometric results of recorded measurements of neutrals and ions.

Figure 2 shows the density of OH, H_2O, H_2O_2, H_3O and NO as function of distance when the plasma is excited by 100W of microwave power.

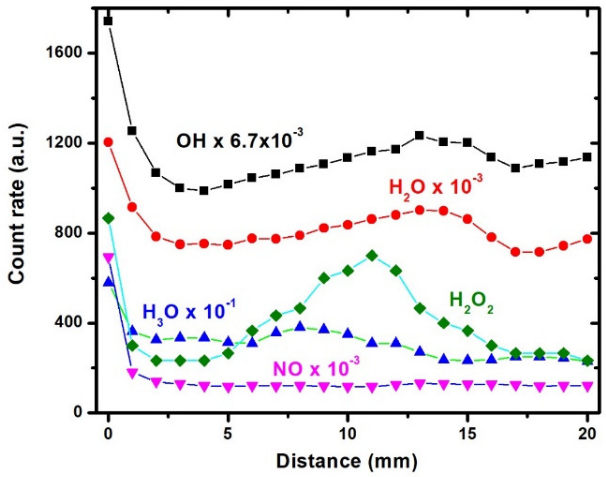

Figure 2. Mass flux of neutral radicals as function of distance; microwave power of 100 W and flux of 5.0 SLM. OH (filled square), H_2O (filled circle), H_2O_2 (filled diamond), H_3O (up filled triangle) and NO (down filled triangle).

The OH intensity initially decreases after Surfatron exit until a minimum at 3 mm growing after to a maximum at ~ 12 mm corresponding the maximum density of electrons. As n_e maximum is at ~ 11 mm, electron-ion recombination should be the most important mechanism for OH production in this region, while at the Surfatron exit the electric power density is high and electron dissociation may also be an important reaction for production of hydroxyl radical. Water has the same profile trend of OH once this radical is produced from H_2O and ions H_2O^+ and H_3O^+. Hydrogen peroxide is produced from reaction between two OH molecules and a third-body and lost mainly by collisions with electrons and with O, H atoms and argon metastables.

H_3O has high density along the plasma due to water hydration reactions which has high reaction coefficient ~ 10^{-15} m^3s^{-1}. NO is formed by reactions of metastable nitrogen $N(^2D)$ with N_2O with reaction coefficient of 2.2 x 10^{-18} m^3s^{-1} [7].

Figure 3 shows the evolution of most important ions as function of distance for a microwave power of 100 W and flux of 5.0 SLM of Ar. As can be seen the ion Ar^+ presents the highest intensity followed by H_2O^+ and NO^+. The ions in general present a maximum near the jet nozzle region where the electric power density is high and a second maximum near 11 mm corresponding the maximum of electronic density as can be seen in figure 3. ArH^+ and OH^+ have count rates about two orders of magnitude lower than Ar^+.

Figure 4 presents the OH intensity as function of distance from the Surfatron cavity and power. A maximum of OH count rate for power of 100 W occurs at 5 mm from the Surfatron exit while for 150 W the intensity continuous grows until distance of 10 mm after which a small decrease is observed.

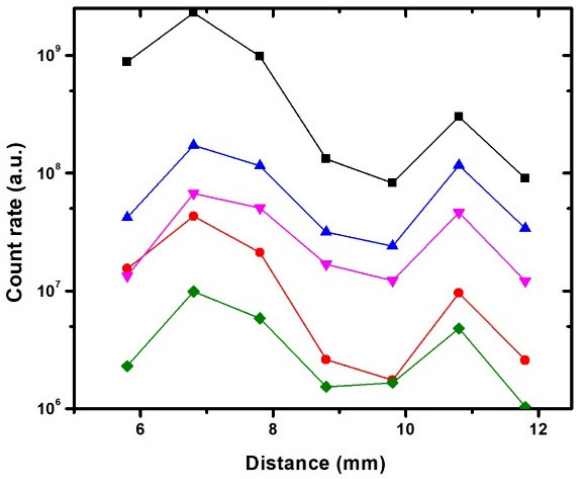

Figure 3. Ionic species as function of distance; microwave power of 100 W and flux of 5.0 SLM. Ar^+ (filled square), ArH^+ (filled circle), OH^+ (filled diamond), H_2O^+ (up filled triangle) and NO^+ (down filled triangle).

The main negative ions detected in similar experiments were NO_2^-, OH^- and O^- [8].

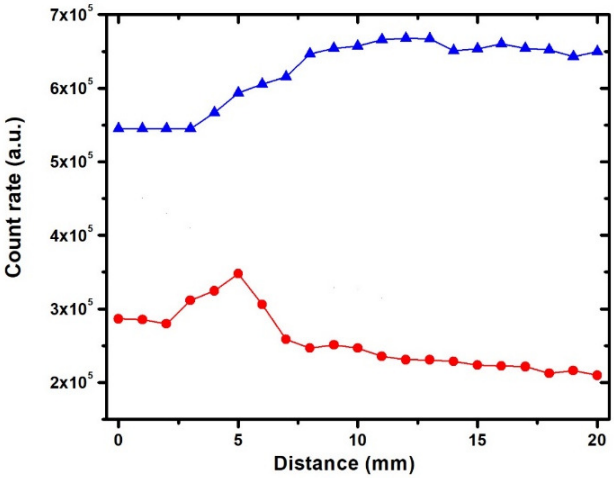

Figure 4. OH as function of distance; flux of 2.5 SLM, 100 W (filled circle) and 150 W (up filled triangle).

Figure 5 shows the OH mass flux intensity as function of flux and distance for 100 W of microwave power delivered to the Surfatron. The flux was varied from 2.5 to 7.5 SLM. As the flux increases the maximum intensity of the OH moved to higher distances. This occurs because the point of turbulence development gets closer to the jet nozzle as the flux increases favoring the injection of the H_2O into the plasma. This effect improves the mixing of ambient air particles with the effluent plasma jet in the region near the nozzle forming H_2O^+ and H_3O^+ ions but the position of maximum electron density

gets closer to the plasma tip as the flow increases. The resulting net balance of ionization and dissociative electron attachment is the profile presented in figure 5.

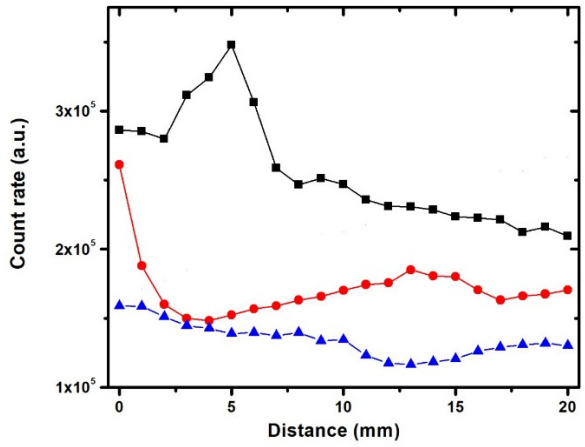

Figure 5. OH as function of distance; power of 100 W and flux of 2.5 SLM (filled square), 5.0 SLM (filled circle) and 7.5 SLM (up filled triangle).

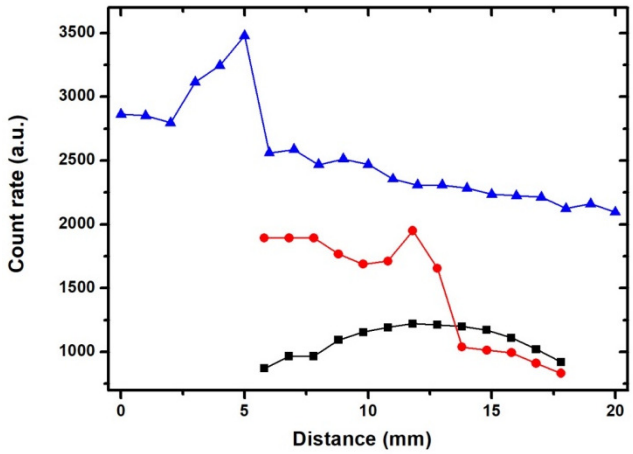

Figure 6. OH as function of distance, power of 100 W and 2.5 slm of Ar (up filled triangle); 2.48 slm Ar-0.02 slm O_2 (filled circle) and 2.42 slm Ar-0.08 slm O_2 (filled square).

Figure 6 shows the importance of O_2 in the formation of OH. Oxygen participates directly in the formation of OH mainly by reactions of O, H and O(^{1}D) species with H_2O and H_2O_2. Destruction occurs mainly in collisions of OH with O atoms, with a reaction coefficient of ~ 1.5 x 10^{-17} m^3s^{-1}. As can be seen the addition of O_2 leads to the destruction of OH putting in evidence the importance of reaction with oxygen atoms.

4. Conclusion

Mass spectroscopy and optical emission spectrometry were employed to study the formation of OH radical in an atmospheric pressure argon microwave discharge expanding in air. It was shown that hydroxyl radical mass flux intensity initially decreases after Surfatron exit until a minimum at 3 mm growing after to a maximum at ~ 12 mm corresponding the maximum density of electrons. OH intensity tends to increase like the electron density and gas temperature, in the range of powers and fluxes investigated. Electron-ion recombination is the most important mechanism for OH production in this region. At the Surfatron exit the electric power is maximum and electron dissociation may be an important reaction for production of hydroxyl radical. Water has the same profile trend of OH. This behavior is of course related to production of hydroxyl radical which is produced from H_2O and ions H_2O^+ and H_3O^+. Hydrogen peroxide is produced from reaction between two OH molecules and a third-body and lost mainly by collisions with electrons and with O, H atoms and argon metastables. The most populated ions were, as function of distance, Ar^+, ArH^+, OH^+, H_2O^+ and NO^+. OH intensity was found to be dependent on the gas flux. As the flux of argon in the plasma increases the maximum intensity of the OH moved to greater distances. OH maximum intensity for power of 100 W occurs at 5 mm from the Surfatron exit while for 150 W the intensity continuous grows until distance of 10 mm after which a small decrease is observed.

5. Acknowledgement

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