Spatially-resolved spectroscopic diagnostics of a miniature RF atmospheric pressure glow discharge jet in argon

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Abstract: The influence of operating conditions (power and flow rate) on the spatially-resolved $T_e$ and population density of first excited levels is investigated in a miniature RF Ar glow discharge jet at atmospheric pressure. Ar metastable density as high as 1x10\textsuperscript{19} m\textsuperscript{-3} have been measured close to the jet exit, with a $T_e$ around 0.7 eV. Rotational temperatures of OH(A) and N\textsubscript{2}(C) feature a large difference with the actual gas temperature.

Keywords: optical emission and absorption spectroscopy, collisional-radiative model

1. Introduction

Small-scale cold atmospheric plasma sources are of increasing interest for a wide range of applications, from biomedical and surface treatment to plasma chemical functionalization [1-3]. A number of configurations for sustaining the plasma at atmospheric pressure have been developed, and miniature jets are amongst the most popular due to their applicability to a number of treatments and remarkable features. The plasma jet needs to be hot enough to produce the reactive species desired for effective treatment, and also to be near room temperature, leaving heat-sensitive substrates unharmed. However, to implement these plasma sources in real applications, advanced diagnostics are needed to characterize and optimize their properties under various operating conditions (e.g. feed gas and precursor, power, flow rate).

In this study, non-invasive diagnostic approaches, namely optical emission spectrometry (OES) and optical absorption spectrometry (OAS), are applied on an Atmospheric Pressure Glow Discharge jet (APGD-j) operated with Ar as the main plasma gas. Spatially-resolved metastable and resonant population density of Ar atoms (1s states in Paschen notation) are estimated from OAS measurements, performed using a standard low-pressure Ar-lamp. Using these population results, a collisional-radiative model for Ar\textsuperscript{2}p states along with Ar\textsuperscript{2}p-to-1s emission line intensities are used to estimate the spatial profile of the electron temperature ($T_e$) as a function of power and Ar flow rate. The rotational temperatures from OH(A) and N\textsubscript{2}(C) systems was also recorded and compared with thermocouple measurements of the gas temperature.

2. Experimental setup and methods

The APGD-j used in this investigation has been designed and built at the Plasma Processing Laboratory as a next generation of the original design of Léveillé and Coulombe [4]. A schematic of the APGD-j is shown in Fig. 1. The device consists of a coaxial geometry featuring a RF-powered capillary electrode at the center, a grounded nozzle to induce high gas velocities, two gas lines, one for reactive gas injection into the capillary electrode and one for the plasma forming gas injection in the annulus formed by the two coaxial electrodes.

The grounded outer electrode is made of stainless steel while the inner capillary electrode, adjustable in axial position, is made of brass. This electrode is held in place by an O-ring located between two compressed PTFE sleeves. Argon is used as the plasma forming gas, with a flow rate ranging from 5 to 8 standard liters per minute (L/min). The RF power is delivered from a 13.56 MHz 300 W generator (Cesar Generator Model 1312 Advanced Energy) equipped with an automatic matching network (Dressler VM1000 A). Typical breakdown and sustaining voltages, measured with a Tektronix P5100 passive probe, are \textasciitilde 400 V and \textasciitilde 200 V peak-to-zero, respectively. The RF power was set at 40 W. The glow discharge is located inside the torch and the visible part of the jet where all the analysis is performed in this paper is the plasma afterglow.

OAS measurements are performed using a 25 cm focal length spectrometer (Acton SpectraPro 2750) equipped
with a PiMax camera (Princeton Instruments PI-MAX 1024x256). The 1200 grooves/mm grating, blazed at 300 nm, provides a spectral resolution of 0.22 nm. A schematic of the absorption setup is presented in Fig. 1. The light emitted by the Ar lamp is collected by a first lens (100 mm focal), and goes through a first iris to ensure that a parallel beam is obtained, with a well-controlled diameter (here 0.5 mm). The beam is then absorbed by the plasma and, after a second iris, is collected by the optical fiber with the second lens (100 mm focal).

OES measurements are performed using the same spectrometer, but with a different light collection arrangement: the light emitted by the discharge region is collected using a confocal microscope system with two lenses of focal lengths of 50 mm and 100 mm, respectively. With this optical setup, the magnification is 0.5. A 200 μm-diameter optical fiber, located at the focal point of the imaging lens, is connected to the entrance slit of the spectrometer. Considering the magnification, the spatial resolution is 400 μm. The typical spectrum presented in Fig. 2 shows the Ar emission lines as well as N2 and OH rotational bands used in this study.

![Fig. 2. Emission spectrum of the Ar plasma jet (afterglow), 0.6 mm from the torch nozzle end, integrated over 2 ms.](image)

In both OES and OAS, the light is collected from the center of the plasma channel, perpendicular to the discharge axis. The integration time varies between 2 ms to 10 s; each spectrum is an accumulation of 10 to 1000 samples depending on the signal level, in order to ensure an adequate signal-to-noise ratio.

### 3. Collisional radiative model

In order to obtain the spatial distribution of $T_e$ along the jet axis, the measured Ar I emission lines are compared to the predictions of a collisional-radiative (C-R) model. In this model, the emission intensity of a given Ar I line emanating from a specific Ar $2p$ state is assumed to be given by $I_{\lambda} = f(\lambda) \Theta_{\lambda} [\text{Ar}^*]$, where $f(\lambda)$ is the response of the monochromator and detector, $\Theta_{\lambda}$ is the escape factor (assumed equal to 1; optically thin medium), $A_{ij}$ is the Einstein coefficient for spontaneous emission (taken from NIST database [5]), and $[\text{Ar}^*]$ is the number density of the Ar excited state emitting at wavelength $\lambda$. The population and depopulation processes for the $2p$ levels considered in the model are presented in Fig. 3.

![Fig. 3. CR model framework for Ar $2p$ levels.](image)

The steady state rate balance equations are solved to obtain the population of $2p$ excited levels with respect of $T_e$ (assuming Maxwellian energy distribution function)

$$\frac{d}{dt} [Ar_p] = \left( k_1 + k_2 \left( \frac{[Ar_p]}{[Ar_s]} \right) \right) [Ar_s] n + \sum_k k_{ij} [Ar_{ij}] [Ar_j] - \sum_k A_{ij} [Ar_{ij}] - v_{rel} \rho$$ (1)

In equation 1, $k_1$ denotes the electron-excitation from ground state and $k_2$ from $1s$ levels; $k_{ij}$ and $k_{ji}$ represent the atom-induced energy transfer processes among the $2p$ manifold. The second to last term of equation 1 incarnates all possible spontaneous radiative decays to lower levels. The last term includes all other collision losses with neutral atoms. The model is not solved for the $1s$ level populations since these levels are highly involved in quenching with impurity atoms (due to the open air configuration). Moreover, molecular ions can also significantly contribute in populating and depopulating these levels. Thus, due the complexity of the processes involved, the uncertainty in the determination of $1s$ levels population from the model is high. This further introduces large uncertainty in $2p$ level population and thereafter, in extracted plasma parameters. The $1s$ level population is therefore used from OAS measurements, and the neutral density is obtained from standard gas law.

Eight well-resolved and intense enough $2p_j-1s_i$ emission line measurements (750-850 nm range) are used in the optimization procedure with corresponding model intensities, in order to extract the $T_e$ values. The inclusion of a higher number of lines improves the analysis by averaging out the uncertainties on cross-sections. In the present work, the ‘minimum scatter’ approach proposed by Donnelly et al [6] is adopted to retrieve $T_e$. 

![Diagram](image)
4. Results

OAS is often employed for measuring metastable and resonant atom densities in reduced pressure discharges assuming Gaussian line profile. However, at atmospheric pressure, the pressure broadening of the emission lines could be significant [7]. Thus, an analysis is carried out assuming a more generic Voigt line profile. A significant difference (at least one order of magnitude) in Ar excited state population is observed between the Voigt and the Gaussian profile. The Ar atom has two metastable (1s₂, 1s₃) and two resonant levels (1s₄, 1s₅): Ar-I line at 750.39 nm and 840.82 nm for 1s₂; 794.82 nm for 1s₃, 751.47 nm, 810.37 nm and 842.47 nm for 1s₄ and 763.51 nm and 811.53 nm for 1s₅ are used in the present OAS analysis.

Figure 4 presents a typical absorption profile. The 0 mm position is defined as the output plane of the APGD-j nozzle. Visually, the jet appears ~4 mm-long at 5 L/min to ~6 mm-long at 8 L/min. The spatial step size is fixed at 0.2 mm, even though the spatial averaging is set by the iris opening to 0.5 mm. For distances larger than 2 mm and all flow rates, the absorption of lines are not strong enough to be used in the calculations.

![Figure 4. Axial distribution of the measured absorption at 5 L/min and 40 W.](image)

At 5 L/min and 40 W, the population of excited states at the exit of the nozzle is \( \sim1\times10^{19} \text{ m}^{-3} \) for 1s₂, \( \sim3\times10^{18} \text{ m}^{-3} \) for 1s₃, \( \sim1\times10^{19} \text{ m}^{-3} \) for 1s₄, and \( \sim3\times10^{18} \text{ m}^{-3} \) for 1s₅. These numbers decrease by two order of magnitude 2 mm away from the nozzle exit. The results are shown in Fig. 5. A similar population behaviour is observed for other Ar flow rates, but the decay rates increase with the flow.

Using these 1s-population results, the collisional-radiative model is used along with the Ar absolute emission line measurements to estimate the spatial structure of \( T_e \) as a function of the Ar flow rate. Results presented in Fig. 6 show that at various flow rates (5, 6 and 8 L/min with fixed power of 40 W), a rapid decay of \( T_e \) is observed when moving away from the nozzle. One also notices that the decay rate seems to increase with the Ar flow rate. In all cases, \( T_e \) is around 0.7 eV at the nozzle exit.

![Figure 6. Axial distribution of \( T_e \) at various Ar flow rates.](image)

To ensure compatibility with temperature-sensitive applications, the plasma jet temperature is monitored. The gas temperature profile is first estimated using the OH and N₂ rotational band emissions acquired with the OES setup over the 300-400 nm range. The observed transitions are the second positive system of nitrogen (\( \text{N}_2(C^3\Pi_u) \rightarrow \text{N}_2(B^3\Pi_g) \), \( \Delta \nu = 1, 2, 3 \)) and the OH transition (\( \text{OH}(A) \rightarrow \text{OH}(X) \)). The Specair software [8,9] is used to model the experimental OES results and to determine the corresponding molecule rotational temperature. Unlike with the collisional-radiative model, the population of states of a molecule is determined by the value of the rotational temperature set in Specair. The results, presented in Fig. 7, show a rotational temperature ranging from 500 to 1000 K, both for OH(A) and N₂(C).
Fig. 7. Axial distribution of the excitation temperature of OH(A) and N₂(C) obtained using Specair and gas temperature measured with a thermocouple, at 5 L/min and 40 W.

These temperatures are then compared with a 1-mm RF-shielded thermocouple located in the plasma jet. The gas temperature measured by the thermocouple ranges from 30 to 60 °C, 5 mm away from the nozzle exit. Thus, OH(A) and N₂(C) molecules feature a non-equilibrium temperature. Their high excitation temperature most likely results from the collisions with the Ar metastable: First, since the energy of the Ar metastable is close to the excitation energy levels of OH(A) and N₂(C) and second, due to the high density of Ar metastable.

5. Conclusion

In this investigation, non-invasive diagnostic have been used on an APGD-j to study the Ar metastable density, as well as the electron and gas temperatures. OAS results revealed an Ar metastable density as high as ~1x10¹⁹ m⁻³ for the 1s₂ level 0.2 mm away from the APGD-j nozzle exit. The 1s population then decreases by two orders of magnitude over a distance of 2 mm. These results coupled with spatially-resolved OES measurements and a collisional-radiative model were used to estimate the evolution of T_e along the jet axis. At 40 W and from 5 to 8 L/min of Ar flow, T_e is around 0.7 eV at the nozzle exit and rapidly decreases to 0.4 eV over 2 mm.

The temperature of the gas measured with a thermocouple has been compared to the excitation temperatures of OH(A) and N₂(C) fitted using the Specair software. The large difference between the species excitation temperatures and the gas temperature highlights the non-equilibrium nature of the jet.

In future experiments, operation in different plasma-forming gases is foreseen, e.g. Helium. The injection of reactive gases in the plasma afterglow through the capillary electrode, like O₂ and various organosilicon precursors, will expand the possible applications of the APGD-j.

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7. References