Oxygen atomic density of atmospheric Ar plasma jet generated with syringe needle-ring electrodes

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Abstract: Atmospheric-pressure argon plasma jet is generated with syringe needle–ring electrodes in an 8 kHz sinusoidal excitation voltage. It is found that the rotational temperature of nitrogen is in the range of 333 - 373 K obtained by comparing the simulated spectrum with the measured spectrum at the $C^1\Pi_u \rightarrow B^3\Pi_g (\Delta v = -2)$ band transition, the electronic excitation temperature is in the range of 3187 - 3243 K determined by the Boltzmann’s plot method, and the oxygen atomic density is in the order of magnitude of $10^{16}$ cm$^{-3}$ estimated by the actinometry method, respectively.

1. Introduction

Recently, cold atmospheric-pressure plasma jets (CAPPJs) have received much attention owing to their attractive features that make them indispensable in a large number of applications, such as surface modification [1], thin film deposition [2-4], etching [5], sterilization [6-9], and biomedical and chemical decontamination [10-11]. One of the most prominent features of the CAPPJs is their enhanced plasma chemistry at low gas temperatures [12]. The CAPPJs can be generated using the different electrode configurations and the generators [13]. However, the discharge of CAPPJs is ignited in the inside of dielectric (such as quartz tube and Pyrex tube) rather than ambient air [5, 12-15]. It is due to the fact that the most of electrons are attracted by the oxygen in ambient air, which impede the electrons impacting the working gas to generate the plasma [16]. Wang et al. [17] observed that as the fraction of O$_2$ in radio-frequency (RF) driven He/O$_2$ plasma jet up to 3.2%, which causes the amplitude of the RF current to drop rapidly to its original value before the gas is ignited. In
addition, the quantification of O in discharge center of CAPPJs has been widely reported. But, few studies have reported the density of O radicals in downstream of a CAPPJ [18].

For these reasons, a specially designed Ar plasma jet is generated with syringe needle-ring electrodes by a sinusoidal excitation voltage at frequency of 8 kHz, and the oxygen atomic density in downstream of plasma plume is calculated by the actinometry method. The discharge of Ar plasma jet is ignited in ambient air, which reduces the dissipated power of plasma bullet through the inside of dielectric and the time of plasma bullet reached to the object to be treated.

2. Experimental setup

![Figure 1.](image)

Figure 1. Experimental setup of device (a) and discharge photograph (b) in peak applied voltage of 6.2 kV and Ar flow rate of 0.8 lpm.

A schematic of experimental apparatus and discharge photograph are shown in figure 1. The high voltage electrode is a syringe needle with an inner diameter of 1.2 mm, an outer diameter of 1.6 mm and a length of 51 mm, which is powered by a sinusoidal excitation voltage at 8 kHz. The syringe needle is inserted to a quartz glass tube and sealed tightly by wrapping Teflon tape on it. The quartz glass tube is an outer diameter of 3 mm, an inner diameter of 2 mm and a length of 38 mm. The bottom of quartz glass tube and the tip of syringe needle are in the same height. A copper foil of 7 mm wide is wrapped on the outside of quartz glass tube used as a ground electrode, which is in the position of 12 mm away from the tip of syringe needle. A quartz glass plate (thickness of 1 mm) is placed in the position of 5 mm away from the tip of syringe needle.

The working gas of Ar (99.999%) is injected through the syringe needle controlled by mass flow controller at flow rate of 0.8 lpm. The applied voltages are measured by using a high voltage probe (Tektronix P6015A), and its signals are recorded via a digital oscilloscope (Tektronix TDS 2012B). An optical fiber located in the position of 2 mm away from the quartz glass plate is used to collect the optical emission of the plasma plume and the signals are recorded by a spectrometer (Acton INS-300-122B) with a grating of 1200 grooves per millimeter and slit width of 20 μm. The discharge
image is obtained by a Nikon digital camera COOLPIX S600.

3. Experiment results and discussions

3.1 Optical emission characteristics

![Figure 2](image1.png)
![Figure 3](image2.png)

**Figure 2.** Optical emission spectrum 300 – 410 (a), 410 – 650 (b), and 650 – 900 nm (b) in peak applied voltage 6.2 kV and Ar flow rate of 0.8 lpm.

**Figure 3.** Excitation temperature as a function of peak applied voltage at Ar flow rate of 0.8 lpm and the inset graph is Boltzmann plot of excitation temperature at peak applied voltage of 6.2 kV.

The measured optical emission spectrum from 300 nm to 900 nm is shown in figure 2. As the results shown in figure 2, the plasma plume is dominated by the excited OH, N\textsubscript{2}, Ar, and O, in which the excited OH and O are active species. It is indicating that the Ar plasma jet can be used to sterilization [6-9], surface modification [1], etching [5], etc. The characteristic spectral lines 415.9 nm for the transition (3s\textsuperscript{2}3p\textsuperscript{5})5p \rightarrow (3s\textsuperscript{2}3p\textsuperscript{5})4s and 706.7, 714.7, 738.4, 751.5, 794.8, and 800.6 nm for the transition (3s\textsuperscript{2}3p\textsuperscript{5})4p \rightarrow (3s\textsuperscript{2}3p\textsuperscript{5})4s are chosen to determine the electronic excitation temperature $T_{\text{exc}}$ (K) under a Boltzmann approximation [19-22]. Figure 3 shows the variation in excitation temperature with peak applied voltage, and the inset graph is the Boltzmann plot of excitation temperature at peak applied voltage of 6.2 kV. Regarding the results in figure 3, as the peak applied voltage increases from 4.6 to 7.4 kV, the excitation temperature increases from 3187 to 3243 K. It is in well agreement with
the conclusion reported by Wei et al. [22].

Figure 4. Rotational temperature of $\text{N}_2$ vs peak applied voltage at Ar flow rate of 0.8 lpm and the inset graph is measured and simulated spectrum of the $C^1\Pi_u \rightarrow B^3\Pi_g (\Delta v = -2)$ band transition of $\text{N}_2$ from 368 nm to 382 nm at peak applied voltage of 6.2 kV.

Figure 4 shows the variation in rotational temperature versus peak applied voltage and the inset graph is measured and simulated spectrum of $\text{N}_2$ second positive system 0-2 transition at peak applied voltage of 6.2 kV. The rotational temperature $T_{\text{rot}}$ (K) is determined by comparing the simulated spectrum with the measured spectrum at the $C^3\Pi_u \rightarrow B^3\Pi_g (\Delta v = -2)$ band transition, which is much close to the gas temperature [12, 23]. As the results presented in figure 4, as the peak applied voltage increases from 4.6 to 7.4 kV, the rotational temperature increases from the 333 to 373 K. In peak applied voltage of 6.2 kV, the vibrational temperature $T_{\text{vib}}$ (K) is 1349 K, which is much higher than the rotational temperature. It is shown that the plasma plume is under extremely nonequilibrium condition.

3.2 Oxygen atomic density and nitrogen molecular density

The density of atomic oxygen can be determined by choosing the atomic oxygen line $\lambda = 844.6$ nm and the argon line $\lambda = 750.4$ nm [16, 24-25] and the applicable conditions of this actinometry method are as follows [24]:

1. The excitation cross sections have the same shape, particularly close to the threshold.
2. The population of excited levels from higher levels is negligible.
3. Two-step excitation, e.g., via metastables, is negligible.
4. There is no population of atomic levels via dissociation.
5. Radiationless de-excitation (quenching) of excited levels is negligible.

To improve the accuracy of calculation, the collisional induced quenching of the upper Ar ($2p_1$) and O ($3p^3P$) states in the argon gas is considered in this study. The intensity of argon line $\lambda = 750.4$ nm can be expressed as
The intensity of atomic oxygen line $\lambda = 844.6$ nm is given by

$$I(O) = C_0 h \gamma_0 A^{(O)}_j n_e k_{eq} n_0 (A_j^{(O)} + k_{Oq} n_{Ar})^{-1}. \quad (2)$$

Where the quantities $C$ contain all optical and geometrical Parameters; $h\gamma$ is the photon energy of respective transition; $A_j$ denotes the sum over all optical transition probabilities $A_j$ for the excited state, and is equal to the reciprocal of the natural lifetime $\tau_0$; $A_j$ is equal to $A_j = 1/\tau_0$, since the only optically allowed transition from each of the excited states is observed, respectively [25]. $n_e$, $n_O$, and $n_{Ar}$ represent the electron density, oxygen atomic density, and argon density, respectively, in which the argon density $n_{Ar}$ is determined by the ideal gas equation $n = p/kT_g$, where the gas pressure $p$ (Pa) takes the value of one atmospheric-pressure and the gas temperature $T_g$ (K) is obtained from the figure 4. $k_{Oq}$ and $k_{Arq}$ represent the quenching rate coefficients of the upper Ar $(2p_1)$ and O $(3p^3P)$ states in argon gas, respectively. Table 1 summarizes the data of radiative lifetimes and quenching rate coefficients for O $(3p^3P)$ and Ar $(2p_1)$ atoms taken from the literature [26-27].

| Reagent | Quenching coefficients $(10^{-10} \text{ cm}^3 \text{s}^{-1})$ |
|---------|----------------------------------------------------------|
| O$(3p^3P)$ | Ar$(2p_1)$ |
| Ar      | $0.14^a$  | $0.16^b$          |

The electron excitation rate coefficient $k_e$ is determined by integrating the cross sections over an assumed Maxwellian distribution

$$k_e = \int_0^\infty \sigma(\varepsilon) f(\varepsilon) \sqrt{\frac{2\varepsilon}{m_e}} d\varepsilon \cdot, \quad (3)$$

where $\sigma(\varepsilon)$ is the electron-impact cross section for excitation [28-29], and the variations in it versus...
electron energy are shown in figure 5. \( f(e) \) is the electron energy distribution function, and \( m_e \) is the electron mass. Taking the intensity ratio of Eq. 2 to Eq. 1, we obtain

\[
    n_{\Omega} = \frac{C_{\Omega}h\gamma_{\Omega}I_{\Omega}k_e^{(Ar)}a_{ij}^{(Ar)}}{C_{\Omega}h\gamma_{\Omega}I_{\Omega}k_e^{(O)}a_{ij}^{(O)}} n_{Ar}
\]

with

\[
    a_{ij}^{(Ar)} = \frac{A_{ij}}{A_i + k_{eq} n_{Ar}} \quad \text{and} \quad a_{ij}^{(O)} = \frac{A_{ij}}{A_i + k_{eq} n_{Ar}}.
\]

Eq. 4 is used to determine the density of atomic oxygen. Figure 6 shows the variation in oxygen atomic density with peak applied voltage. Regarding the result presented in figure 6, as the peak applied voltage increases from 5 to 7.4 kV, the oxygen atomic density increases from \( 1.26 \times 10^{16} \) to \( 1.48 \times 10^{16} \) cm\(^{-3}\). Besides, the curves of oxygen atomic density and electronic excitation temperature versus peak applied voltage (in figure 3) present a similar tendency, which is indicating that the oxygen atomic density increases with the electronic excitation temperature. It is in well agreement with conclusions reported by Qian et al. [16].

![Figure 5. Electron-impact excitation cross section of atomic oxygen \( \sigma_e \) and argon \( \sigma_e \).](image-url)
4. Conclusions

A cold argon plasma jet generated with syringe needle–ring electrodes in atmospheric-pressure has been studied. It is found that the excited Ar, N₂, OH, and O are existed in the plasma plume, and the rotational temperature, electronic excitation temperature, and oxygen atomic density increase linearly with peak applied voltage. In addition, the oxygen atomic density in the position of 5 mm away from the tip of syringe needle is in the order of magnitude of 10¹⁶ cm⁻³.

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