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# SPECTROSCOPIC ANALYSIS OF NITROGEN ATMOSPHERIC PLASMA JET

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We performed uv-visible spectroscopy of the inside of a jet nozzle and along the plasma jet plume to identify the constituent particles and estimate the rotational temperature. Inside and near the nozzle, the emissions from atomic nitrogen and high energy states of molecular nitrogen (for example, second positive system and first negative system) are observed. At a position far from the nozzle, the emissions from low energy states of molecular nitrogen (first positive system and Vegard-Kaplan system) and nitric oxide due to the residual and influent oxygen are observed. The behavior of relatively low excited state of $N_2$ including metastable state and nitric oxide closely relates to the characteristics of the long plume plasma jet. The rotational temperature is approximately 5000 K inside the jet nozzle and decreases along the plasma jet plume. At a position far from the jet nozzle, it is necessary to estimate the gas temperature from the emission band of nitric oxide that several bands should be considered.

Keywords: plasma jet, atmospheric pressure, nitrogen, uv-visible spectroscopy, rotational temperature

## 1. Introduction

Plasma processing is one of the most important industrial technologies. Cold processing plasmas are generally in the state of non-equilibrium in which electrons are in a high temperature state. On the other hand, ion and gas temperatures are low in cold processing plasma. As a result, little damage is caused to materials, and the reaction rate is high. Hence, cold plasma processing is the key industrial technology, however it requires vacuum environment. Non-equilibrium plasmas at atmospheric pressure are studied for various applications. Atmospheric plasmas have great advantages in that reactions can be progressed to a high speed without vacuum systems. Recently, the atmospheric plasma jet [1] has been applied to various industrial technologies. The plume length of a plasma jet is often limited to approximately 20 mm. If the plasma jet plume is elongated, its application area would expand widely. We have succeeded in elongating the plume of a nitrogen plasma jet to 200 mm by purging air from the environment surrounding the plasma jet [2].

To investigate the characteristics of the nitrogen atmospheric plasma jet, it is necessary to clarify the constituent particles of the plasma jet plume and plasma parameters. Spectroscopic measurements are the most commonly used tools for characterizing plasmas and for better understanding of physical and chemical processes.

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The neutral gas plays an important role similar to an electron and an ion in plasma processing. The gas temperature must be measured to understand the characteristics of the process plasma. The gas temperature can be evaluated from the rotational temperature of the molecules. The rotational temperature is estimated from the profile shape of the uv-visible emission spectra.

In this study, we have performed space-resolving uv-visible spectroscopy inside a jet nozzle and along the plasma jet plume. From the results of the spectroscopic measurements, the behavior of constituent species, that are molecular nitrogen, atomic nitrogen, and nitric oxide, is discussed, and the rotational temperature of the constituent particles is analyzed as an indicator of the gas temperature.

## 2. Experimental Apparatus

A schematic view of the plasma jet is shown in Fig. 1. The plasma device is an atmospheric pressure plasma jet (Openair PFW10, Plasmatreat), which consists of a conical inner electrode and a grounded outer electrode with a nozzle of 4 mm inner diameter. The inner electrode is coupled to a stepped high-frequency pulse current power supply, 180 - 270 V, 3 - 7 A and 13 - 19 kHz, through a high voltage transformer. Working gas is fed into the annular space between the two electrodes and flows spirally. The gas used in this experiment is pure nitrogen

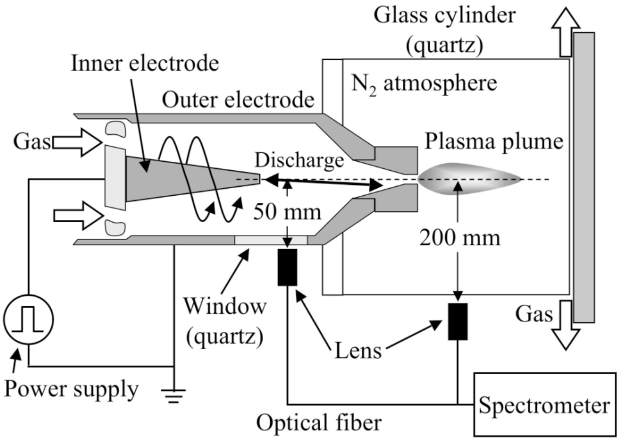


Fig. 1. A schematic view of the atmospheric plasma jet and the experimental set up.

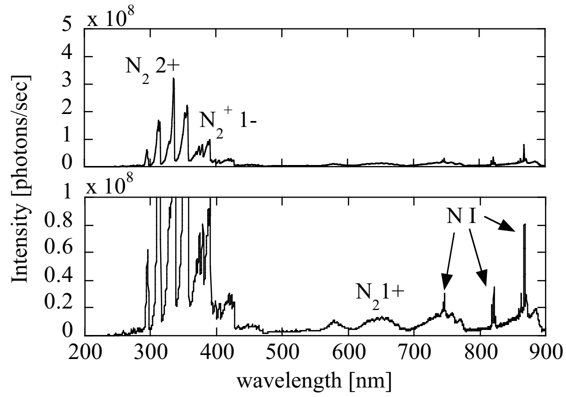


Fig. 3. Emission spectra observed just outside the jet nozzle (0 mm). The downside figure shows the zoom of weak emissions. N I: the emissions from atomic nitrogen.

(99.99%) with a flow rate of 30 L/min. The input power is approximately 1.5 kW. To shield the plasma head from the environmental air, a quartz glass cylinder (inner diameter: 220 mm, height: 300 mm) and a cap are attached to the nozzle.

The spectroscopic diagnostic system consists of a collimator lens (ϕ = 5 mm, f = 10 mm), an optical fiber, and a Czerny-Turner spectrometer equipped with a linear CCD detector array (HR4000CG, Ocean Optics). The CCD array has 3648 pixels with 8x200 μm pixel size. The measurable wavelength range is 200 to 1100 nm, and the wavelength resolution is approximately 0.75 nm. This system is absolutely calibrated by a standard lamp.

The spectroscopic measurement was performed inside the jet nozzle, and the collimator lens is installed in 50 mm from the center of the jet nozzle. In this position, the diameter of the discharge column is approximately 4 mm. Moreover, the spectra were measured just outside the jet nozzle (0 mm), 10, 50, and 100 mm from the top of the jet nozzle, and the collimator lens is placed in 200 mm from the center of the plasma plume. The diameters of plasma plume in each position are about 4, 15, 30, and 40 mm.

## 3. Experimental Results and Discussion

The long plume plasma jet was observed by optical emission spectroscopy to investigate the behavior of atomic and molecular nitrogen and other constituent species. In Fig. 2, the emission spectra are shown at a wavelength range of 200 nm to 900 nm, which is observed inside the jet nozzle. The emission lines shown in Fig. 2 are assigned as transitions of molecular nitrogen. The first positive system ($N_2$ ($B^3\Pi_g$-$A^3\Sigma_u^+$) transitions) is in the 500 - 900 nm range (e.g., 580 and 654 nm), and the second positive system ($N_2$ ($C^3\Pi_u$-$B^3\Sigma_g$) transitions) is in the 300 - 500 nm range (e.g. 337 and 354 nm). The characteristic spectrum of the first negative system ($N_2^+$ ($B^2\Sigma_u^+$-$X^2\Sigma_g^+$) transitions) is shown at 391 nm [3].

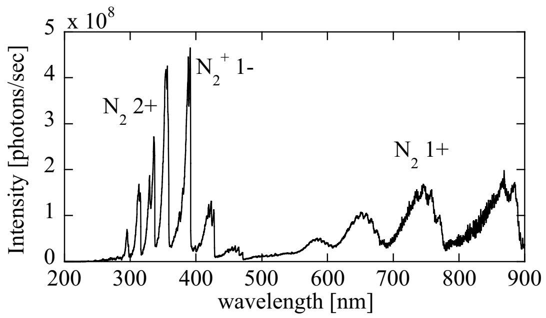


Fig. 2. Emission spectra observed inside the jet nozzle. $N_2$ 1+: $N_2$ first positive system, $N_2$ 2+: $N_2$ second positive system, $N_2^+$ 1-: $N_2$ ion first negative system.

The emission spectra just outside the jet nozzle (0 mm) are shown in Fig. 3. A spectrum similar to that inside the jet nozzle was obtained. However, there is a characteristic difference in that emissions from atomic nitrogen were observed. This fact suggests that atomic nitrogen is generated and excited near the exit of the jet nozzle. The discharge path in the jet nozzle is from the top of the inner electrode to near the exit of the jet nozzle. The dissociation of molecular nitrogen requires large energy, at least 10 eV. Therefore, it is thought that the high energy electrons are generated near the exit of the jet nozzle.

In Fig. 4, the emission spectra observed at (a) 10 mm, (b) 50 mm, and (c) 100 mm from the jet nozzle are shown. The emission lines shown in Fig. 4 are the first positive system, the nitric oxide β system (NO ($B^2\Pi$-$X^2\Pi$) transitions) in the 300 - 400 nm range, and the γ system (NO ($A^2\Sigma^+$-$X^2\Pi$) transitions) in the 200 - 300 nm range [4]. The strongest line is observed at 335 nm in Fig. 4(a) and 4(b). It is thought that some emission bands overlap each other in this line. The conceivable bands are the Vegard-Kaplan (V-K) system ($N_2$ ($A^3\Sigma_u^+$-$X^1\Sigma_g^+$) transitions), the NO-β, and the NO-γ system. The upper levels of these transitions of molecular nitrogen are relatively low energy states and are populated through cascade transitions from the second positive system or collisions between the vibrationally excited nitrogen

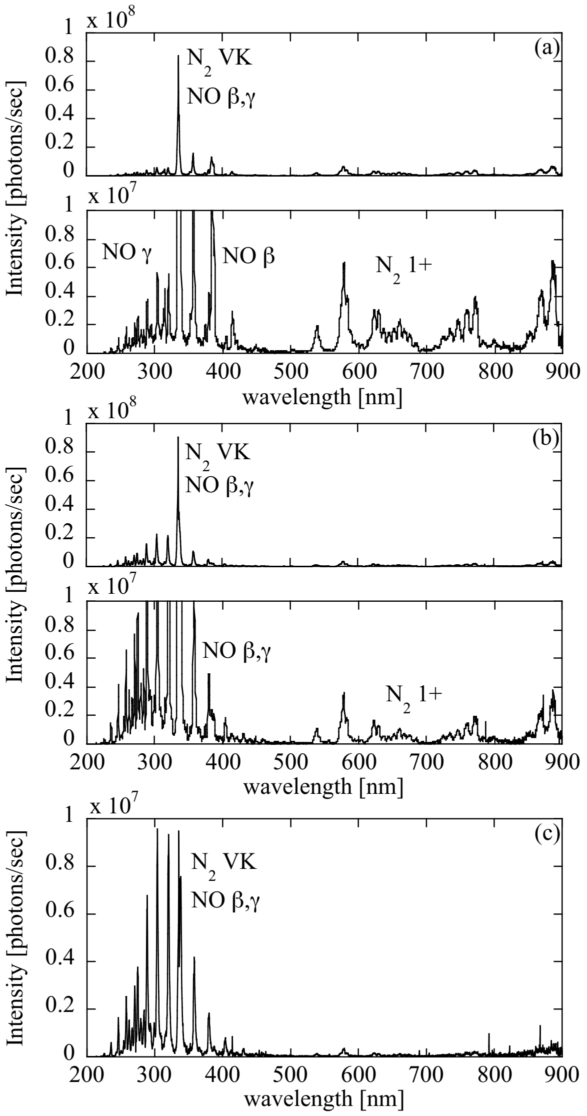


Fig. 4. Emission spectra observed at the distance of (a) 10 mm, (b) 50 mm and (c) 100 mm from the jet nozzle. The downside figure of (a) and (b) shows the zoom of the weak emission. $N_2$ VK: $N_2$ Vegard-Kaplan system, NO β,γ: NO β and γ system.

molecules. Especially, the upper level of the V-K system is the $N_2$ ($A^3\Sigma_u^+$) metastable state, and this state plays important role for non-equilibrium nitrogen discharge [5]. Those emissions expand along with gas flow. It is thought that generation and transport of relatively low electronically excited state of $N_2$ including metastable state closely relates to the behavior of the long plume plasma jet.

The emissions from nitric oxide are observed at the position far from the jet nozzle. It is thought that the nitric oxide is generated from the residual oxygen in the glass cylinder and the oxygen that flows in from the exit of working gas. Emissions from nitric oxide are the dominant spectra at 100 mm from the jet nozzle. This result shows that a large part of the energy reaching this position is used to produce and excite the nitric oxide. It is thought that the behavior of nitric oxide is important to surface

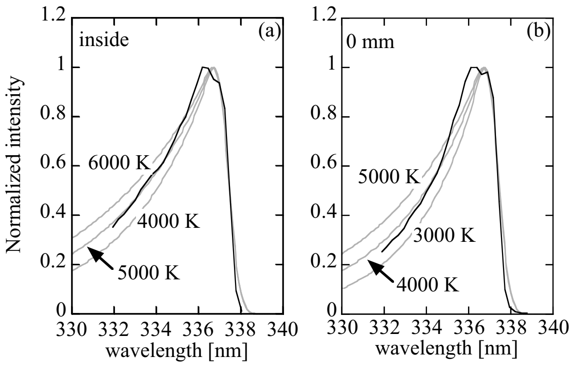


Fig. 5. Normalized intensity of second positive (0,0) band observed (a) inside and (b) 0 mm (black line) with calculated intensity profiles at each rotational temperature of 3000 K, 4000 K, 5000 K and 6000 K (gray lines).

modification at the position far from the jet nozzle.

The gas temperature is able to be evaluated from the rotational temperature of the molecules. The rotational temperatures of nitrogen and nitric oxide have been estimated from the uv-visible emission spectra of each position.

Figure 5 shows the normalized intensity of the second positive (0,0) band (337.1 nm) (a) inside the jet nozzle and (b) 0 mm with the calculated intensity profiles of each rotational temperature. In Fig. 5, the black line represents the normalized intensity and the gray lines indicate the calculated intensity profiles.

Inside the jet nozzle, which is the discharge region, the rotational temperature of molecular nitrogen is approximately 5000 K. From this result, it is thought that the generated discharge in the jet nozzle is an arc discharge. On the other hand, the rotational temperature is 3000 - 4000 K at 0 mm. In this position, the observed spectrum includes emissions from the discharge plasma that leaked outside the jet nozzle, and the emissions from the plasma plume. Therefore, it is thought that the region near the exit

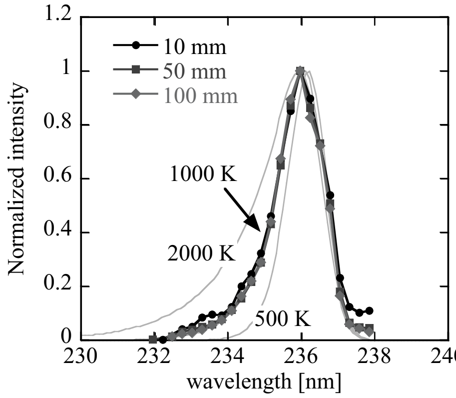


Fig. 6. Normalized intensity of NO-γ (0,1) band observed at 10, 50, and 100 mm from the jet nozzle (dark lines) with calculated intensity profiles at each rotational temperature of 500 K, 1000 K, and 2000 K (gray lines).

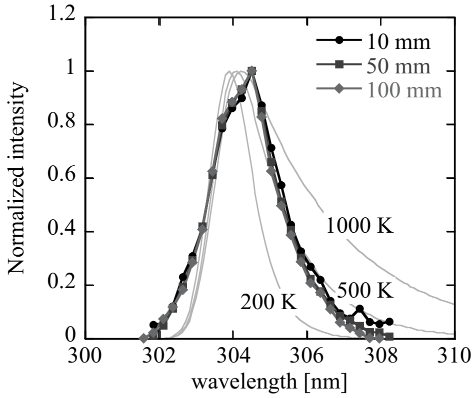


Fig. 7. Normalized intensity of NO-β (0,7) band observed at 10, 50, and 100 mm from the jet nozzle (dark lines) with calculated intensity profiles at each rotational temperature of 200 K, 500 K and 1000 K (gray lines).

of the jet nozzle is the transitional region from the discharge plasma to the afterglow plasma, and the rotational temperature reflects the effects of both plasmas.

At the position far from the jet nozzle, the second positive (0,0) band was not observed. The NO-γ (0,1) band (236.3 nm) was used to estimate the rotational temperature. In Fig. 6, the normalized intensities of the NO-γ (0,1) band at 10, 50, and 100 mm from the jet nozzle are represented. The calculated intensity profiles at the rotational temperatures of 500 K, 1000 K, and 2000 K are also shown in Fig. 6.

From Fig. 6, the rotational temperature of the nitric oxide is approximately 1000 K in the region far from the jet nozzle. It is thought that the rotational temperature is lower than the rotational temperature at 0 mm. However, it is expected from the experiments on the surface modification and from the measurements of gas temperature [5] that the gas temperature is lower than this result in this region. Moreover, the rotational temperature is hardly changed as a function of the distance from the jet nozzle. This means that the rotational temperature of this level of nitric oxide does not reflect the gas temperature. The other band was then analyzed to investigate the behavior of the rotational temperature of nitric oxide. Figure 7 shows the normalized intensity of the NO-β (0,7) band (304.3 nm) at 10, 50, and 100 mm from the jet nozzle and the calculated intensity profiles with the rotational temperatures 200 K, 500 K, and 1000 K.

From Fig. 7, the rotational temperature of NO-β system (0,7) band is approximately 500 K. This result is reasonable for the gas temperature. However, this temperature is different from the rotational temperature estimated from the NO-γ (0,1) band. This fact shows that there is a level of nitric oxide that the rotational excited state is not in thermal equilibrium with that of another level. Therefore, it is necessary to estimate the gas temperature from the emission band of nitric oxide that several bands are considered.

## 4. Summary

Spectroscopic measurements were performed to identify the constituent particles and estimate the rotational temperature of a nitrogen atmospheric plasma jet with a long plume. Spectroscopic measurements revealed that the particles with relatively high energy excited states exist only inside and near the jet nozzle. Especially, the high energy electrons concentrate near the exit of the jet nozzle. At the position far from the nozzle, nitric oxide due to the residual and influent oxygen and relatively low excited state of the nitrogen molecule play an important role in determining the behavior of the long plume plasma jet. The rotational temperature inside the jet nozzle is approximately 5000 K, and the rotational temperature of nitrogen decreases along the jet plume. At positions far from the jet nozzle, the gas temperature is able to be evaluated from the rotational temperature of the excitation level of nitric oxide. However, it is necessary that several bands be considered in the case of nitric oxide.

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