Laser-induced fluorescence of metastable $N_2(A^3\Sigma_u^+)$ in various gases pulsed positive corona discharge

Yoshiyuki Teramoto, Ryo Ono, and Tetsuji Oda

***Abstract*—The absolute density of metastable $N_2(A^3\Sigma_u^+)$, the rate constant of the reactions of $N_2(A^3\Sigma_u^+)$ with various molecules and one-dimensional distribution of that excited nitrogen molecules are observed after the pulsed positive corona discharge in various gasses of 1 atmospheric pressure by using the laser-induced fluorescence (LIF) . The $N_2(A^3\Sigma_u^+, v=0)$ state is excited to N_2 (*B*, v"=4) state by the laser irradiation. That excited state drops to (*A*, v"=1) state emitting 676nm light as the fluorescence. The discharge occurs from needle to plane electrode with the gap distance of 12 mm. When discharge voltage is 21.5 kV, the absolute density $N_2(A^3\Sigma_u^+)$ near the needle point just after the discharge is estimated to 10^{14}cm^{-3} by that fluorescence intensity. The observed one-dimensional distribution of the $N_2(A^3\Sigma_u^+)$ suggests that is mostly generated in the primary streamer channel.**

I. Introduction

Application of non-thermal plasma, disposal of environmental pollutants (e.g. nitric oxide from cars and factories), has been attracting attention. One characteristic of non-thermal plasma is that it effectively produces reactive radicals, however in non-thermal plasma there is a lot of unsolved mechanism of radical production. If a breakthrough is achieved in the dissolution of the mechanism of radical production and target radicals are effectively produced, then the effectiveness of the disposal of environmental pollutants will be improved.

The excited nitrogen has rather long lifetime and excites various atoms and molecules inducing various kinds of strong chemical reactions such as the ozone generation, OH radical formation and so on.

$$N_2(A^3\Sigma_u^+) + H_2O \rightarrow N_2 + H + OH. \quad (1)$$

Above all, the nitrogen metastable $N_2(A^3\Sigma_u^+)$ has the characteristic of a long radiative lifetime(2 s) and can reserve high-energy (6.2 eV) for a long time [1, 2]. It induces various reactions; $N_2(A^3\Sigma_u^+)$ produces free electrons by penning ionization:

$$N_2(A^3\Sigma_u^+) + N_2(a^1\Sigma_u^-) \rightarrow N_2(X^1\Sigma_g^+) + N_2(X^2\Sigma_g^+) + e. \quad (1)$$

And yields atomic oxygen by reaction with molecular oxygen:

$$N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2 + O + O. \quad (2)$$

Heretofore, the density of $N_2(A^3\Sigma_u^+)$ was measured using the indirect measurement method[3]. For example, $N_2(A^3\Sigma_u^+)$ excites the ground state NO($X^2\Pi$) to NO($A^2\Sigma^+$) state in the afterglow as:

$$N_2(A^3\Sigma_u^+) + NO \rightarrow N_2 + NO(A^2\Sigma^+). \quad (3)$$

NO($A^2\Sigma^+$) emits fluorescence within 200ns. Therefore, the density of NO($A^2\Sigma^+$) is correlated with that of $N_2(A^3\Sigma_u^+)$, and as a result the $N_2(A^3\Sigma_u^+)$ density can be estimated from the light emission intensity arising from the NO($A^2\Sigma^+$) molecules.

Simek [4, 5] also measured absolute density of $N_2(A^3\Sigma_u^+)$ in N_2 pulsed positive corona discharge using the ratio of emission intensities from the excited N_2 and NO($A^2\Sigma^+$) molecules. The $N_2(A^3\Sigma_u^+)$ density was estimated to be of the order of 10^{14}cm^{-3}.

Tochikubo and Arai [6] simulated the propagation of positive corona discharge and the $N_2(A^3\Sigma_u^+)$ density. They simulated one pulse of repetitive positive dc corona discharge. The discharge condition was as follows: 10-mm point-to-plane gap, applied voltage of 15 kV, and 40 mA peak current. In NO(300 ppm)/N_2 mixture, the $N_2(A^3\Sigma_u^+)$ density was calculated to be of the order of 10^{16} cm^{-3}. That result differs greatly from that of Simek.

The authors observed spatial distribution of $N_2(A^3\Sigma_u^+)$ in the pulsed positive corona discharge by measuring two-dimensional distribution of the NO-γ band ($A^2\Sigma^+ \rightarrow X^2\Pi$) emission and showed that $N_2(A^3\Sigma_u^+)$ is mainly produced in the primary streamer channel. The $N_2(A^3\Sigma_u^+)$ is far from ozone, atomic oxygen, OH radicals, and NO molecules that are mainly produced in secondary streamer channel [7].

The metastable $N_2(A^3\Sigma_u^+)$ plays important roles in atmospheric pressure discharge. Therefore, rate constants of the reactions of $N_2(A^3\Sigma_u^+)$ with various molecules under atmospheric pressure are important for the simulation of discharge. However, rate constants are mostly measured under low pressure[8, 9].

In this paper, we measure the density of $N_2(A^3\Sigma_u^+)$ using LIF in various gases generated in the positive pulse corona discharge atmospheric pressure. Direct measurement of $N_2(A^3\Sigma_u^+)$ suggests that $N_2(A^3\Sigma_u^+)$ is mainly produced in the primary streamer channel and absolute density of $N_2(A^3\Sigma_u^+)$ is estimated. We obtain the rate constants of the reactions of $N_2(A^3\Sigma_u^+)$ with various molecules from decay of $N_2(A^3\Sigma_u^+)$ density after discharge. These results give us further understanding on $N_2(A^3\Sigma_u^+)$ kinetics.

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II. EXPERIMENTAL

A. Pulsed corona discharge

The discharge occurs between a point-to-plane gap with 12 mm gap length. Fig.1 shows the electrical circuit for generating the discharge pulse. The charge stored in the 860 pF capacitor is discharged using the spark gap switch. R_p is 470Ω. The discharge voltage, V, is defined by the charging voltage of the capacitor. The voltage at the point electrode is measured with a high-voltage probe (Tektronix P6015A), and the current flowing through the plane electrode is monitored with a Rogowski coil (Pearson Electronics, Model-2878). Typical voltage and current waveforms are shown in Fig.2. The discharge occurs in a box-shaped reactor having a volume of 80 × 80 × 80mm^3. During the experiment, N_2 flows through the reactor at a rate of 2L/min under atmospheric pressure. The discharge repetition rate is 1 pps.

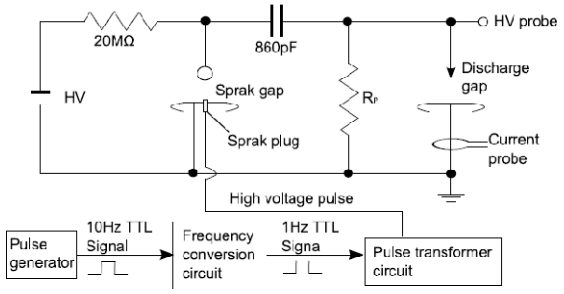

Fig. 1. High voltage circuit

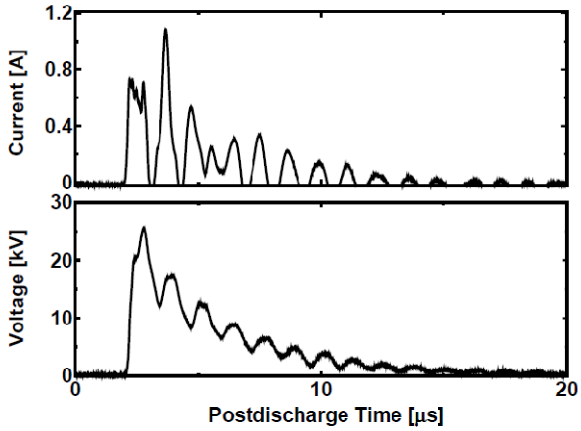

Fig. 2. Voltage and current waveforms. V = 21.5 kV

B. Laser-induced fluorescence

The LIF measurement of $N_2(A^3\Sigma_u^+)$ has been developed in low-pressure discharge, where the first positive system ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) of N_2 has been used for excitation and fluorescence bands. Our experiment also uses the first positive system(FPS). The $N_2(A^3\Sigma_u^+, v'' = 0)$ state is excited to $N_2(B^3\Pi_g, v' = 4)$ by a 618-nm dye laser irradiation, then the fluorescence from $(B^3\Pi_g, v' = 4)$ to $(A^3\Sigma_u^+, v'' = 1)$ is measured with a photomultiplier tube (PMT) through an optical bandpass filter (676 ± 5 nm). Figure 3 shows the beam path within the discharge gap. The cross section of the laser beam is a 2 × 2 mm^2 rectangle. When measuring one dimensional distribution of $N_2(A^3\Sigma_u^+)$, using cylindrical lens the width of the laser beam changes from 2mm to 20mm. $N_2(A^3\Sigma_u^+)$ fluorescence from the observation volume, defined in Fig.3, is detected with the PMT from the direction perpendicular to the laser beam. The distance between the anode tip and the center of the beam is defined as z, as shown in Fig.3 By changing z, one-dimensional distribution of $N_2(A^3\Sigma_u^+)$ density is measured. The laser energy is 0.8 mJ. It is checked that no saturation occurs at this laser energy.

Namely, the LIF signal intensity is proportional to the laser energy around 0.8 mJ. Fig.4 shows cross section of the laser beam from ICCD camera and one-dimensional distribution of laser intensity. The laser intensity is about uniform within the 20mm. In this experiment, the laser beam can cover the entire volume of the discharge. The laser is triggered after an adjustable delay following the end of the discharge pulse.

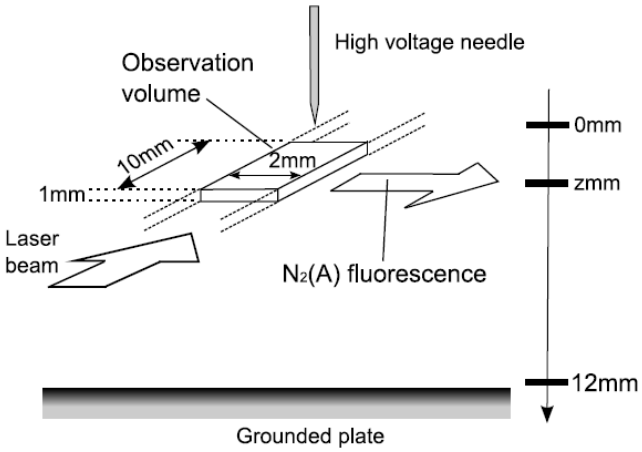

Fig. 3. Beam path and observation volume for LIF measurement.

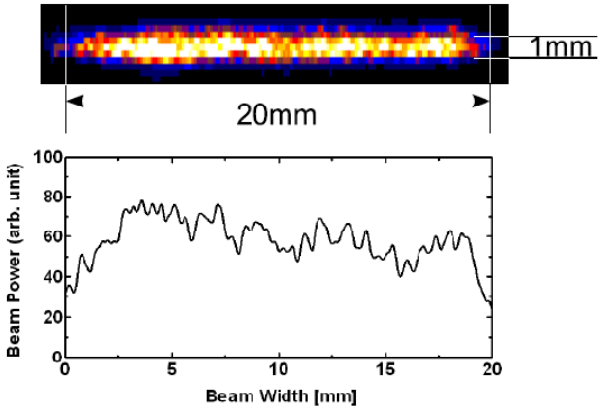

Fig. 4 Cross section of laser beam and one-dimensional distribution of laser intensity

By changing the delay time between the discharge pulse and the laser trigger, the temporal variation in the $N_2(A^3\Sigma_u^+)$ density after discharge is obtained. To reduce the effect of the shot-to-shot fluctuation in the laser power, the results are averaged over 256 discharge pulses.

Fig.5 shows a theoretical spectrum of LIF, which is calculated for T =400K and rotational level. It shows the laser at 618.801nm, which is the peak signal excited of the many rotational levels.

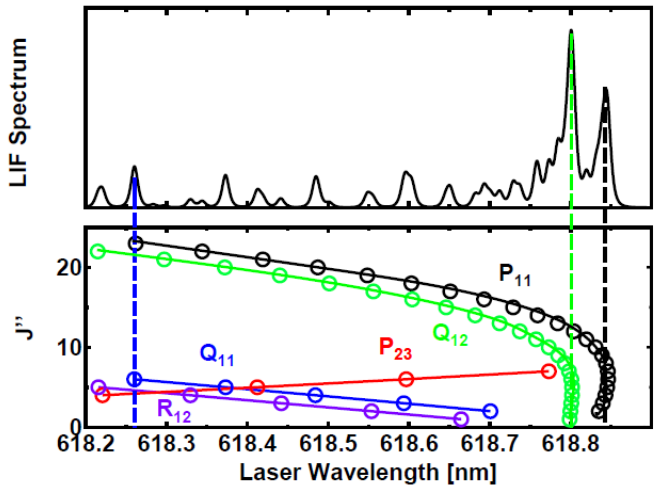

Fig. 5 theoretical spectrum of LIF and rotational level.

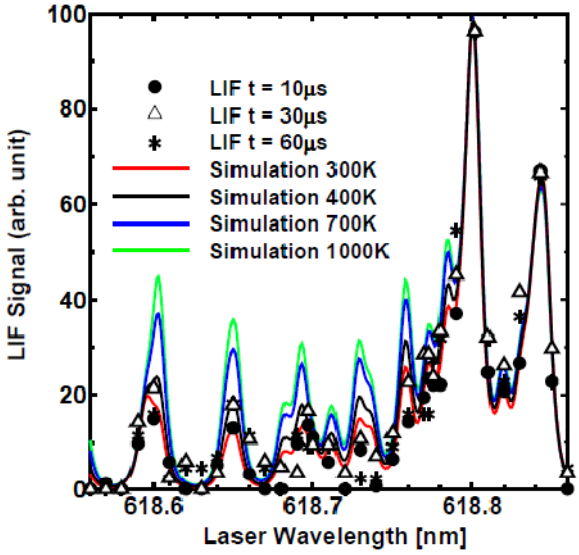

Fig. 6 Measured and theoretical LIF excitation spectra. Measured spectrum is obtained near the anode tip (z = 1mm) at 10, 30 and 60μs after discharge.

III. Results and Discussions

A. *One-dimensional distribution of $N_2(A^3\Sigma_u^+)$*

The peak signal intensity at 618.801nm changes by rotational temperature, because density of rotational level depends on temperature. Therefore, we measured rotational temperature of $N_2(A^3\Sigma_u^+)$ at z = 1mm and z = 6mm in the afterglow from spectral distribution. Fig.6 shows LIF excitation spectra near the anode tip (z = 1mm) at 10, 30 and 60μs after discharge obtained by sweeping the laser wavelength and theoretical spectra calculated with temperatures of 300, 400, 700 and 1000K. LIF excitation spectra are about agreement with theoretical spectrum of 300K and 400K. At z = 6mm the result is almost the same. From those results, the gas temperature within the gap is regarded as being constant at room temperature after discharge. LIF of $N_2(A^3\Sigma_u^+)$ in pulsed corona discharge. Fig.7 shows a one-dimensional distribution of $N_2(A^3\Sigma_u^+)$ within the gap at applied voltages (21.5, 20, 18.5kV). It is measured at 4μs after discharge, because there is electromagnetic noise within 4μs after discharge. The result shows that the density of $N_2(A^3\Sigma_u^+)$ is increased by applied voltage and $N_2(A^3\Sigma_u^+)$ is observed in the primary streamer propagation area. It indicates $N_2(A^3\Sigma_u^+)$ is mainly produced in the primary streamer channel, not in the secondary one. That result agrees with the prediction based on the light emission intensity of NO-γ.

B. *Absolute density of $N_2(A^3\Sigma_u^+)$*

Absolute density of $N_2(A^3\Sigma_u^+)$ can be calculated by two approaches. First, calculated from LIF intensity. The absolute density of $N_2(A^3\Sigma_u^+)$ is determined using a three-level model. Absolute density of $N_2(A^3\Sigma_u^+)$ near the anode tip is 6×10^{13}cm^{-3} at just after discharge. The other approach is using the slope of the reciprocal plot at $N_2(A^3\Sigma_u^+)$ recombination[10]. It is known that, $N_2(A^3\Sigma_u^+)$ decreases mainly by the recombination reaction in the N_2 discharge [10].

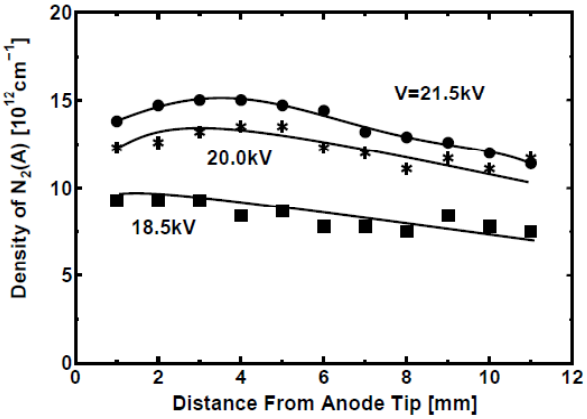

Fig. 7 one-dimensional distribution of $N_2(A^3\Sigma_u^+)$

It is known that, $N_2(A^3\Sigma_u^+)$ decreases mainly by the recombination reaction in the N_2 discharge [10]. The result is absolute density near the anode tip is 1×10^{14}cm^{-3} at just after discharge. In the middle of the gap, it is 6×10^{13}cm^{-3}. On the basis of these results, the density of $N_2(A^3\Sigma_u^+)$ produced by pulsed corona discharge under atmospheric pressure in N_2 at 21.5kV is an order of between 10^{13} and 10^{14}cm^{-3} , and density of $N_2(A^3\Sigma_u^+)$ near the anode tip is higher than that of the rest of discharge volume.

C. *Rate constant of $N_2(A^3\Sigma_u^+)$ with various molecules*

Decay of $N_2(A^3\Sigma_u^+)$ is measured in background mixes of N_2/O_2, N_2/NO_2, N_2/NO, N_2/H_2O and N_2/CO at z = 1 and 6mm. When the background is N_2/H_2O, we couldn't measure it at z = 6mm, because LIF signal is weak. Fig.8 shows the decay of $N_2(A^3\Sigma_u^+)$ in N_2/O_2 at z = 1mm. Fig.9 shows the decay rate that is obtained from slope of Fig.8. Slope at z = 1mm is almost the same at z = 6mm. Intercept at z = 1mm is larger than at z = 6mm; that indicates density of $N_2(A^3\Sigma_u^+)$ near the anode tip is

higher than that of the rest of discharge volume.

Rate constant of reaction (4) is calculated from the slope of Fig.9, when $N_2(A^3\Sigma_u^+)$ decreases mainly by the reaction (4),

$N_2(A^3\Sigma_u^+) + O_2 \rightarrow$ products. (4)

Results are $k = 3.7\times10^{-12}cm^3s^{-1}$ at z = 1mm and $k = 3.7\times10^{-12}cm^3s^{-1}$ at z = 6mm.

In other background gases, we also calculated rate constant. Table.1 shows rate constant of the reactions of $N_2(A^3\Sigma_u^+)$ with various molecules in the present experiment and in other works which are measured under low pressure[11]. Rate constants of $N_2(A^3\Sigma_u^+)$ with various molecules in this experiment are 2 or 3 times larger than reference value(300K). Gas temperature can be regarded as error cause. If rate constants are dependent on temperature, there is the possibility that rate constants at 400K are larger than at 300K. However, we can not obtain reference value of temperature dependence.

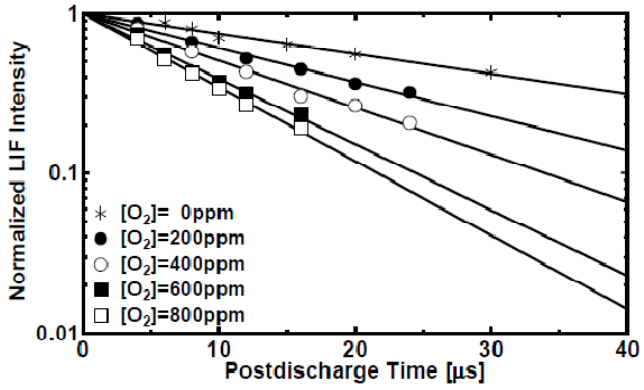

Fig. 8. Decya of $N_2(A^3\Sigma_u^+)$ in N_2/O_2

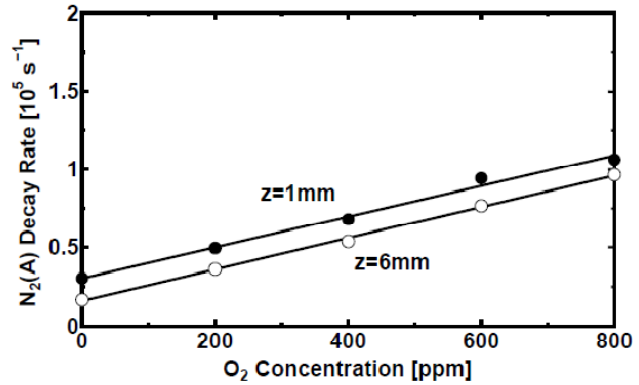

Fig. 9. Decay rate of $N_2(A^3\Sigma_u^+)$ in N_2/O_2

Table.1. Rate constant of the reactions of $N_2(A^3\Sigma_u^+)$ with various molecules

Reaction	$k(z=1)$	$k(z=6)$	k
$N_2(A^3\Sigma_u^+)+O_2 \rightarrow$ *products*	3.7×10^{-12}	3.7×10^{-12}	2.5×10^{-12}
$N_2(A^3\Sigma_u^+)+NO_2 \rightarrow N_2+NO(X^2\Pi)+O$	4.8×10^{-11}	4.4×10^{-11}	1.3×10^{-11}
$N_2(A^3\Sigma_u^+)+NO \rightarrow N_2+NO(A^2\Sigma^+)$	6.6×10^{-11}	6.9×10^{-11}	6.4×10^{-11}
$N_2(A^3\Sigma_u^+)+H_2O \rightarrow N_2+H+OH$	$\leq 9.8\times10^{-14}$	–	5.0×10^{-14}
$N_2(A^3\Sigma_u^+)+CO \rightarrow$ *products*	3.8×10^{-12}	3.7×10^{-12}	1.6×10^{-12}

units of $cm^3\ s^{-1}$

IV. Conclusion

The density of metastable $N_2(A^3\Sigma_u^+)$ was measured after the pulsed positive corona discharge in various gasses of 1 atmospheric pressure by using LIF. The observed one-dimensional distribution of the $N_2(A^3\Sigma_u^+)$ suggests that is mostly generated in the primary streamer channel. When V=21.5kV, the $N_2(A^3\Sigma_u^+)$ absolute density near the anode tip, which is calculated from LIF intensity and slope of recombination, is about $10^{14}cm^{-3}$ at just after discharge. Rate constants of the reactions of $N_2(A^3\Sigma_u^+)$ with N_2/O_2, N_2/NO_2, N_2/NO, N_2/H_2O and N_2/CO in this experiment are 2 or 3 times larger than reference value (300K).

Acknowledgment

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