Optical diagnosis of high pressure non-thermal plasma

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Abstract. Optical diagnosis of high pressure plasma is one of the most powerful tools for investigating chemical reaction mechanisms in the high pressure plasma region. The authors developed various optical measurement systems by using tunable lasers, such as (two-photon-)laser-induced-fluorescence, coherent-anti-Stokes Raman scattering, time evolution of optical emission imaging and others for detecting O₃, O, OH, N, NO* and other radicals in atmospheric pressure plasma. Outline of basic measuring techniques developed by the authors for high pressure plasma diagnosis are explained and real examples of plasma diagnosis are demonstrated in this paper. For example, density distributions of single nitrogen (N) and excited nitrogen molecule (N₂(A)) below the discharge needle generated by the pulse plasma suggest that single N might be generated in the secondary streamer, while N₂(A) might be generated in the primary streamer, and single N decomposes NO more than N₂(A).

1. Introduction
The high pressure plasma has been developed for more than 40 years by late Prof. Masuda, at the University of Tokyo and many researchers have learned by him, including Prof. Wu and all Japanese invited speakers. Our common target is the environmental protection and providing a new tool for biological handling. Related with the ESP (Electrostatic precipitation) technology [1], DeNOx [2, 3] and DeSOx processes for combustion flue gas cleaning by using the non-thermal plasma were developed [4-7]. Moreover, combined with the ozone-hole protection and sick-house syndrome, VOC (volatile organic compounds) removal from the air by the plasma has been also developed by many researchers [8-14]. Recently high pressure glow-like plasma is also investigated for cleaning, mechanical plasma processing (cleaning, cutting, polish), and biological or medical processing tools. However, still now, the high pressure plasma process has been never understood. What kinds of radicals play any role in the process? It is not so easy to identify that radical behaviour generated by the plasma.

The authors’ group has developed various kinds of optical radical measurement systems by using UV tunable (variable wavelength) laser systems. UV absorption measurement with a nanosecond UV laser can detect the ozone generation with time resolution of nanoseconds and spacial resolution of mili-meter in the streamer. Laser-Induced Fluorescence (LIF) technique can detect various kinds of radicals with the time resolution of nanoseconds which cannot be observed as the direct optical images without the discharge excitation. Several radicals, such as O, N, OH and excited N₂ were observed by LIF techniques in the non-thermal plasma. Those results are listed in table 1.

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2. Streamer image and ozone generation for pulse discharge

2.1. Streamer of pulse discharge
The needle to plate streamer discharge image was observed by a gated nanosecond ICCD camera or
streak camera where submicrosecond high voltage pulse was applied. Some examples are shown in
figure 1 in the nitrogen and oxygen mixture condition. The streamer is usually divided into two parts.
The sphere-like bright point runs from the needle point to the plate for the positive pulse application.
The streamer speed is pretty high, (10 – 20 nanoseconds for 13 mm gap which means that the velocity
of the primary streamer is about 1 mm ns⁻¹). Then the bright secondary streamer progresses from the
needle point to the flat plate. A streak camera picture is also shown in figure 2 where the brightness is
shown at the same sensitivity indicating the secondary streamer is long and much bright.

| Active species | Measuring method | Ref.  |
|----------------|------------------|-------|
| O₃            | Photo absorption | 15    |
| OH            | LIF              | 16,17 |
| O             | LIF              | 18    |
| N             | LIF              | 19    |
| N₂(A)         | LIF              | 20    |
| NO            | LIF              | 21    |
| O₂(V)         | LIF              | 22    |
| N₂(V)         | CARS             | 23    |
| Temperature   | LIF              | 17    |

Figure 1. Streamer development after the pulse energization.

Figure 2. Streak photo of streamer.
2.2. Ozone generation
UV light is easily absorbed by the ozone gas and we can know the ozone generation in the streamer as shown in figure 3 where a strong excimer laser of 248 nm was used for observation of the ozone. It is obvious that the ozone is surely generated in the streamer. If we estimate the ozone region of about 1 mm in diameter, the ozone concentration in the streamer region is about 3,000 ppm at maximum. If we check the ozone generation area exactly, most ozone is generated in the secondary streamer region which is shown in figure 4. The ozone generation is mostly near the needle electrode and that pattern is very similar to the secondary streamer photo emission as shown in figure 4. In previous simulation and streak camera measurements reported by others suggested that the most ozone should be generated in the primary streamer because the electron energy in the primary streamer is much larger (about 10 eV) than that in the secondary streamer (about 1 eV = electron Volt). Our results are far from that estimation but might be because the electron density is much large in the secondary streamer region and the electron energy is also more than a few eV estimated our new simulation.

![Figure 3](image3.png)

**Figure 3.** Ozone generation in the streamer by UV absorption.

![Figure 4](image4.png)

**Figure 4.** Ozone distribution compared with the streamer illumination.

2.3. Optical emission spectroscopy (OES)
Optical emission spectroscopy is also very effective in observing various radicals generated by the pulse discharge but the illumination is limited by the discharge excitation only. Some data for the Corona discharge, barrier discharge and plasma jet will be demonstrated at the conference. One example of the OES of the plasma jet (gas flow is 40 l min⁻¹ and the discharge power is roughly 500 W) where upper position is just below the outlet of the plasma jet and lower level is about 40 mm below the jet is shown in figure 5. The centre is about 309 nm and spectra width is about 20 nm.
Figure 5. Optical emission spectra of the plasma touch near 310 nm.

2.4 Others
Schlieren image can also show the molecular density perturbation by the plasma-discharge, especially shock wave can be displayed well.

3. LIF Observation

3.1. What is LIF
One example of the electron energy level of OH radical related with LIF (Laser-Induced Fluorescence) is shown in figure 6. In the figure, the horizontal position means distance from the other atom (between O and H). \( \nu \) means vibration mode (electron energy level is separated by the quantized vibration mode of two atoms) and each level is also separated by the rotational mode. Some of excited electrons from the ground state (\( X^3\Pi \)) to upper state (\( A^3\Sigma \)) lose their energy by predissociation and quenching. So \( A^3\Sigma \) state electrons are easily lose energy by predissociation, and the quenching effect is rather negligible which means LIF of OH is not affected by the composition of surrounding gas but the sensitivity of OH is rather small. On the other hand, LIF signal of OH excited by 281 nm laser is very large (sometimes, more than 1,000) but the absolute value comparison among OH radical densities in different mixture of oxygen and nitrogen, for example. In the case of rare gas, OH density of ppb can be detected.

| laser wavelength (nm) | detected radical          |
|-----------------------|---------------------------|
| 205                   | H                         |
| 207                   | N                         |
| 211                   | N                         |
| 226                   | NO, O                     |
| 243                   | H                         |
| 248                   | \( \text{NO}_x \), OH, \( \text{O}_2^* \) |
| 254                   | Hg                        |
| 281                   | OH                        |
| 292                   | H                         |
| 308                   | OH                        |
| 336                   | NH                        |
| 388                   | CN                        |
| 473,512,563           | C2                        |
| 607                   | \( \text{N}_2\text{vib} \) |
At present, various wavelength lasers are used as LIF exciting lasers. Typical laser wave lengths and detected radicals are shown in table 2 where gothic means that we tested.

![Figure 6. Electron energy level for OH radicals related with LIF.](image)

![Figure 7. Example of Laser-Induced Fluorescence measuring system.](image)

One example of our experimental setup is shown in figure 7 for NO and O measurement where a dye tunable laser system is used as a laser source in this figure. For LIF signal imaging, a high sensitive gated Image-Intensified CCD Camera (IICCD) with narrow band pass filter is used.

### 3.2. LIF examples

#### 3.2.1. NO image

Ground state NO is sensitive for 226 nm laser irradiation where the experimental system is in figure 8. Sample gas is nitrogen with 50 ppm NO which flows slowly from left to right in sight. Because of optical reason, the viewing area is circle like and a sheet pattern laser beam is only at the centre position (bright area of original gas: 50 ppm). Left isolated picture is a streamer illumination.
photo just at the discharge (during pulse). Pulse width is about 500 ns but nothing occurs just after the pulse discharge. About 30 microseconds later, a slight decay of NO (black area) can be detected as a string which becomes large with time and right side becomes dark which means most NO might be decomposed. At 5 ms after the discharge, right side is mostly dark (left side is new NO supplied from left side. At 20 ms later, all gas is exchanged and fresh NO is detected. What (radicals) decompose NO after the discharge? The life time of that radical should be much longer than milliseconds. For analyze that, some new experiments have been done.

![LIF image of NO after the pulse Corona discharge.](image)

**Figure 8.** LIF image of NO after the pulse Corona discharge.

3.2.2 OH radicals We tested two different OH LIFs. One is used tunable excimer laser of 248 nm which is very strong of 450 ml/pulse and it is possible to take LIF picture. Figure 9 shows OH LIF image after the pulse corona discharge. Each picture is taken at different discharge but it is apparent that OH is generated in the streamer. From the LIF signal intensity by calculation with photomultiplier sensitivity, detecting solid angle and transition ratio, we can estimate the OH density, if OH density distribution is assumed. We can also observe the decay time of OH radicals and simulation including 14 reactions can suggest the original OH density. Time decay of OH signal is shown in figure 10 with simulation curves [24]. Simulation curve (theory 100 ppm) fits experimental data mostly and we can estimate the concentration of OH at this data should be about 100 ppm. From the estimation calculation by the transition coefficient is also about 100 ppm and both data are in good agreement. This error range is sometimes 50 % but we can say the order is the same. Those LIF signals are separately observed with each oscillation mode. If at that timing, OH energy might be equilibrium, we can estimate the gas temperature from the Boltzmann plot as shown in figure 11. Log plot of LIF signal intensity gradient versus electron energy difference shows the temperature. After some time delay from the discharge, OH radical temperature change with time can be observed. OH temperature is very different for the gas composition. From figure 11 and other data, we can know the gas temperature change with time after the discharge as shown in figure 12. OH gas temperature increases with time after the discharge and be maximum at about 40 or 50 microseconds and decreases after that time. In this experiment, back ground (balance) gas is nitrogen and humidity is roughly close to 100 %. Just after the discharge, highly excited states of higher vibration mode might be produced by the high energy electron impaction and high electric field. After several tens microseconds, many collisions
transfer the high energy to oscillation mode and ground state molecular temperature might be increase. Without the oxygen, that energy transfer is not so large but a little bit oxygen molecules enhance that transfer so much. More oxygen cannot increase the temperature so much but that reason is not yet known still now. Anyway, peak gas temperature might be close to 1,000 K which may enhance oxidation process so much.

The authors constructed a practical VOC decomposition plasma reactor and the relation between the real TCE (trichloro-ethylene) decomposition efficiency and OH temperature. Some data will be presented at the Conference.

Figure 9. (a) Corona streamer and (b) OH LIF images excited 248 nm.

Figure 10. OH LIF signal decay after the pulse discharge (281 nm laser).
3.2.3. Atomic oxygen

The atomic oxygen shows two-photon-assisted laser-induced fluorescence (TALIF) which energy level is shown in figure 13. As shown in figure 13, two photons were absorbed at the same time meaning strong photo density is essential (TALIF signal proportional to the square of photon density. If photon density is too strong, photo-desorption (laser beam decomposes O₂ molecule and generates atomic oxygen) occurs and real atomic oxygen signal cannot be separated from that signal. We must be care for that error. Atomic oxygen distribution from the corona needle point to the flat plate is shown in figure 14 where most atomic oxygen is generated in the secondary streamer which is in good agreement with the ozone generation profile. Uniform atomic oxygen generated by the primary streamer is also recognized from the zero position (just below the needle). Former simulation suggested that the decomposition of oxygen molecule, O₂, needs about 5 eV energy and that electron energy can be generated only in the primary streamer. However, these results and our recent simulation suggested that a several eV electrons are produced also in the secondary streamer and they can also contribute to decompose oxygen molecule to atomic oxygen.

![Figure 11. Log plot of OH LIF signals versus electron energy level difference when humidity is roughly 50 % and charging voltage is 28 kV observed at 3.6 mm below the discharge needle.](image1)

![Figure 12. OH gas temperature change with time after the discharge for different gas and discharge conditions of 28 kV or 32 kV when oxygen concentration is 20 % or 2 %.](image2)

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![Figure 13. Energy level of atomic oxygen related to TALIF.](image3)
Figure 14. Atomic oxygen profile from the needle point (observed by TALIF).

Figure 15. Atomic nitrogen distribution observed by TALIF (207 nm) for pulse corona.

3.2.4. Atomic nitrogen LIF signal of atomic nitrogen is also detected by TALIF where the exciting laser wavelength is 211 or 207 nm which is a little bit smaller than that for atomic oxygen but the energy level is quite similar to figure 14 and an experimental system is also roughly the same as that for an atomic oxygen TALIF measurement. One example of N atom distribution by TALIF is shown in figure 15 for in pure nitrogen and in air. That N distribution is also similar to the atomic oxygen distribution and the atomic nitrogen is also generated mostly in the secondary streamer where all signal is the integration of all TALIF except the distance from the needle point because the laser beam is a sheet pattern of 1 mm thickness. We simulate the time-decay by the parameters of the atomic nitrogen concentration and the streamer diameter, the atomic nitrogen concentration is 300 ppm and a streamer width is 240 micrometer in nitrogen with 200 ppm NO. If in the pure nitrogen, the nitrogen atom density is 300 ppm and the streamer diameter is 200 micrometers. That diameter determined by TALIF time decay is in good agreement with the light illumination measurement of the streamer diameter. That pretty high concentration of the atomic nitrogen is rather too large compared with the former reported simulation results, but our recent simulation results supports rather high atomic nitrogen and the decomposition of NO by the plasma might be due to that atomic nitrogen effect, although many papers suggested the NO decomposition by excited nitrogen molecule, maybe N2 (A), is dominant, which will be discussed in next section.
3.2.5. N₂ (A) We use N₂ (A'Σ⁺_u) - LIF, that is, the transition to N₂ (B³Π_g). Indeed, about 618nm laser beam is selected for many different wave lengths (transitions). That energy diagram is shown in figure 16.

LIF signal (N₂ (A)) distribution below the needle point is shown in figure 17 with discharge photoemission intensity. As shown in the figure, the photo-illumination is very strong just under the needle point and might be due to the secondary streamer propagation. On the other hand, N₂ (A) signal is roughly constant from the needle to the ground flat plane suggesting that most N₂ (A) is generated in the primary streamer region which is rather constant from the needle to the plane. If we estimate several equations for N₂ (A) decay with time for different gas composition, we can estimate the absolute density of that excited metastable N₂ (A). Example of that log-decay plot for N₂/O₂ mixture gas is shown in figure 18.

In pure nitrogen, typical concentration of N₂ (A) by about 20 kV pulse for 13 mm gap discharge is about 1-5×10¹³ cm⁻³ which is rather very small compared with previously estimated density of 10¹⁵ cm⁻³ of N₂ (A) which decompose NO in N₂ plasma.

![Figure 16. Energy diagram of nitrogen molecule [25].](image1)

![Figure 17. Axial distribution of N₂(A) metastable observed by LIF from the needle point to the plate with the light illumination intensity.](image2)

![Figure 18. Deca plot of N₂(A) at 6 mm below the needle point.](image3)

4. Raman Scattering
If the photon collides the molecule, most photon is scattered elastically but a little bit photon is scattered inelastically (energy loss or gain). Raman scattering is one of that. Photon energy loss or
gain is due to the molecular quantum mode (vibration of plural atoms). The merit of Raman scattering is that it does not need narrow special photon energy but short wavelength is preferable because the collision cross section is proportional to 4 powers of frequency. Sensitivity is not so large and detection is not so easy. Moreover, Raman scattering does not occur for single atom molecules (no atom vibration mode). Raman shift (shift of inelastic energy loss) is dependent not only on the molecule but also their mode which means exciting state can also be measurable. The authors observed Raman for hydrogen molecules and water molecules after the discharge explosion with time.

Recently the authors also succeed to observe CARS (coherent-anti-Stokes Raman scattering) which needs at least two laser beams as shown in figure 19. Higher vibrating mode density of nitrogen was observed by this measurement after the pulse plasma.

![Figure 19. CARS experimental setup.](image)

5. Conclusions
Some of our recent activities on high pressure plasma by using laser technology are demonstrated in this paper and recent other results will be discussed at the conference.

In air plasma condition, atomic nitrogen, oxygen and OH radical behaviours are a little bit understood by using the laser diagnosis; especially laser-induced-fluorescence technique is very effective to observe many radicals at any timing and temperature or density can be estimated by LIF only. It was surprising that
(a) Ozone is mostly generated not in the primary streamer but in the secondary streamer;
(b) Decomposition of NO and other reactions, atomic nitrogen works so much and density of metastable N$_2$ (A) is rather small in our experiment.

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