

# Measurement of CO<sub>2</sub> and H<sub>2</sub>O concentration by laser Induced plasma fluorescence

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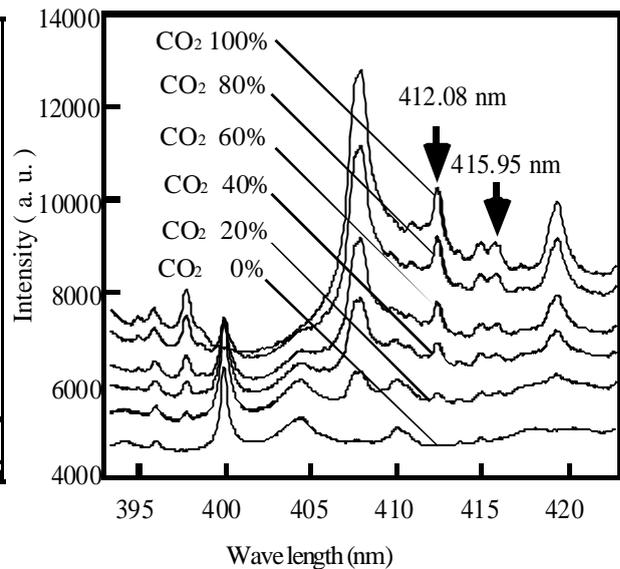
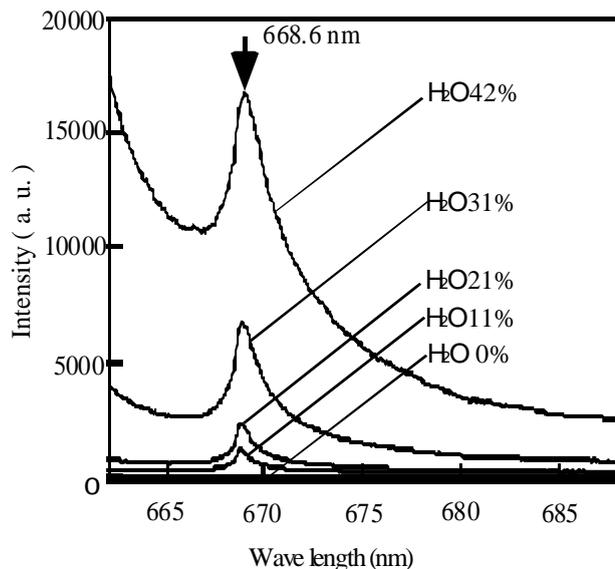
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## ABSTRACT

Since absorption bands of H<sub>2</sub>O and CO<sub>2</sub> do not exist within commercially available laser wavelength, conventional laser induced fluorescence technique could not be applied for the concentration measurements. In the present paper, nonintrusive techniques for H<sub>2</sub>O and CO<sub>2</sub> concentration measurements have been developed using a laser induced plasma fluorescence. It is based on the gas breakdown phenomena, which originates from the multiphoton ionization (MPI) and the absorption of laser radiation by electrons that gained sufficient energy to ionize the gas. This technique is verified experimentally varying gas concentrations of H<sub>2</sub>O and CO<sub>2</sub> at atmospheric pressure condition. In Fig. 1, the fluorescence emission spectrum of H<sub>2</sub>O<sup>+</sup> is presented in the wave region of 662-688 nm, varying the H<sub>2</sub>O volumetric concentration 0 to 42%. As water vapor concentration increase the fluorescence intensity on 668.6 nm band tends to increase. In Fig. 2, the relative fluorescence emission spectrum of CO<sub>2</sub><sup>+</sup> of 412.08 nm and 415.95 nm bands are shown varying CO<sub>2</sub> volumetric concentration, 0 to 100%. The fluorescence of 412.08nm and 415.95nm bands linearly increases with increase of CO<sub>2</sub> concentration, whose characteristics is different from H<sub>2</sub>O. The effect of laser beam energy on the fluorescence intensities has also been made clear. It has been demonstrated in this study that although gas breakdown is a complicated phenomena, ND:YAG laser intensity approximately over 350 mJ would induce fluorescence of ionized gas molecules, H<sub>2</sub>O<sup>+</sup> and CO<sub>2</sub><sup>+</sup>, which could be applied for the measurement of H<sub>2</sub>O and CO<sub>2</sub> concentrations, respectively. The present method has demonstrated its



validity at atmospheric pressure condition which is encountered in many thermo-fluid facilities.

Fig. 1. Effect of H<sub>2</sub>O concentration on the 668.6 nm H<sub>2</sub>O<sup>+</sup> fluorescence spectrum

Fig. 4. Effect of CO<sub>2</sub> concentration on the 412.08 nm and 415.95 nm CO<sub>2</sub><sup>+</sup> fluorescence spectrum



## 1. INTRODUCTION

Water vapor plays an important role in many technological aspects since it is one of fundamental species encountered in various thermo-fluid facilities. Carbon dioxide is one of the major greenhouse gases and of final production species of combustion processes. In spite of the considerable importance and interest in concentration measurements or detections of CO<sub>2</sub> and H<sub>2</sub>O, only a few techniques provide measurements without disturbing the fluid. These are based on optical methods.

Although laser induced fluorescence has large signal intensity and has been applied to the measurements of various chemical species, commercially available laser light wavelength does not coincide with the absorption bands of CO<sub>2</sub> and H<sub>2</sub>O that induce fluorescences. Laser Raman scattering method has been applied to the measurement of various chemical species including CO<sub>2</sub> and H<sub>2</sub>O at atmospheric pressure premixed hydrocarbon-air flames (Bechtel et al., 1981). The Raman technique, however, has small signal level compared to that of LIF. Diode laser has been utilized for combustion measurements of CO<sub>2</sub> and H<sub>2</sub>O (Mihalcea et al., 1998). Diode laser-based absorption diagnostics, however, could not measure local concentrations since the measurement detect the absorption integrated along the laser beam.

Remarkable phenomena could be seen in the high-intensity irradiation of molecules above threshold ionization. Molecules irradiated by a strong light field may absorb additional photons above the ionization threshold and the photoelectrons absorb radiation. Classical studies for the investigations of ionized states, H<sub>2</sub>O<sup>+</sup> and CO<sub>2</sub><sup>+</sup>, was conducted without using laser. Optical spectrum of H<sub>2</sub>O<sup>+</sup> has been measured by voltage discharge (Lew et al., 1972) and Helium 58.4 nm radiation (Brundle et al., 1968). Emission spectra between 288 and 458 nm from the photoionization of CO<sub>2</sub> by 58.4-nanometer Radiation has been obtained (Wauchop et al., 1971).

Laser induced ionized states are formed based on the breakdown phenomena, in which molecules are transformed explosively to a plasma by a focused pulsed laser beam. Molecules with high-intensity light has received special attentions and engendered a certain amount of understanding. The detail phenomena could be found in extensive reviews (Radziemski et al., 1989, DeMichelis., 1969). There have been relatively few investigations of high-intensity laser radiation effects in CO<sub>2</sub> molecule. The effects on H<sub>2</sub>O molecules have not been studied so far in author's knowledge.

The multiphoton ionization spectroscopy was recorded using ND:YAG laser-pumped dye laser system under pressure condition of  $2 \times 10^{-5}$  Torr (Wu et al., 1989). Resonance-enhanced multiphoton ionization-photoelectron spectra of CO<sub>2</sub> was obtained via several Rydberg states (Wu et al., 1991A, Wu et al., 1991B). Nonresonant multiphoton ionization method has been applied in ultrahigh vacuum pressure measurement (Sekine et al., 1993). These measurement are conducted in ultrahigh vacuum pressure conditions (Wu et al., 1989, Wu et al., 1991A, Wu et al., 1991B, Sekine et al., 1993). The present paper develops techniques for the measurement of H<sub>2</sub>O and CO<sub>2</sub> concentrations employing a ND:YAG laser induced fluorescence spectrum from H<sub>2</sub>O<sup>+</sup> and CO<sub>2</sub><sup>+</sup> molecules, respectively, under atmospheric pressure conditions.

## 2. MEASUREMENT OF H<sub>2</sub>O CONCENTRATION

The concentration measurements were conducted in a cell in which the water vapor mixed with Helium flew through. Schematic view of the experimental apparatus is depicted in Fig.1.

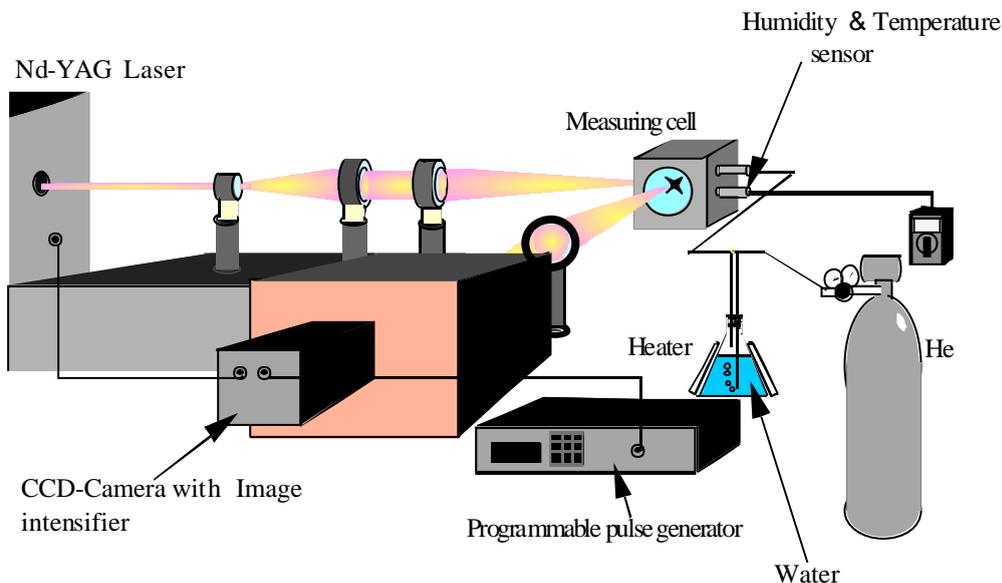


Fig. 1. Schematic view of experimental apparatus

Four fused silica windows are placed at the sides of the measuring cell. The temperature of the H<sub>2</sub>O/He mixture gas was kept constant at 363 K after H<sub>2</sub>O vapor was mixed with Helium by bubbling. The water vapor (H<sub>2</sub>O) concentration was controlled by the temperature at the bubbling section. Humidity and temperature sensors are placed inside the measuring section inside the cell. The water vapor was excited by a ND: YAG laser (Continuum, Power Light 9030) third harmonic light of 355nm wavelength. The maximum intensity of the laser light is 400 mJ/pulse. The beam was firstly expanded to form a parallel beam of 44mm diameter and focused into the cell with a 81.1mm focal length lens. The pulse energy of the laser beam was varied in the range of 158 to 360 mJ/pulse which was monitored by a Joule meter. The fluorescence from water vapor was viewed at right angles to the incident light and the fluorescence spectrum was analyzed by a spectrometer equipped with image intensifier and CCD camera. The system could detect approximately 30nm band width of the LIF spectrum.

In Fig. 2, the fluorescence emission spectrum of H<sub>2</sub>O<sup>+</sup> is presented in the wave region of 662-688 nm, varying the H<sub>2</sub>O volumetric concentration 0 to 42%. Total pressure of the mixed gas, Helium and water vapor, was kept at atmospheric pressure condition. The pulse energy of the laser light was fixed at 360 mJ / pulse. The fluorescence spectrum is recorded as a summation of 30 laser shots. No corrections have been made for the optical devices such as spectrometer and CCD camera response. As water vapor concentration increase the fluorescence intensity on 668.6 nm band tends to increase. The fluorescence intensity does not increase in proportion to the water vapor concentration. The 668.6 nm band originates from the H<sub>2</sub>O<sup>+</sup> transition, 7-0,  $\Delta^p P_{3,N-2}(3)$  ( Wehinger et al., 1974) .

The concentration measurement could be conducted by measuring the fluorescence intensity of the band which depend on the water vapor concentration. The effect of laser pulse energy on the fluorescence intensities of 668.6 nm band is shown in Fig. 3. The water vapor concentration is 42 %. Pulse energy varied in the range, 158 to 360 mJ/pulse. The fluorescence intensities are not linear to the pulse energies. The increasing rate of 668.6 nm band when pulse energy is raised over 350 mJ/pulse is extremely large. It may relates to the complicated process of multiphoton ionization and absorption of laser radiation by electrons that induces excited state of H<sub>2</sub>O<sup>+</sup>.

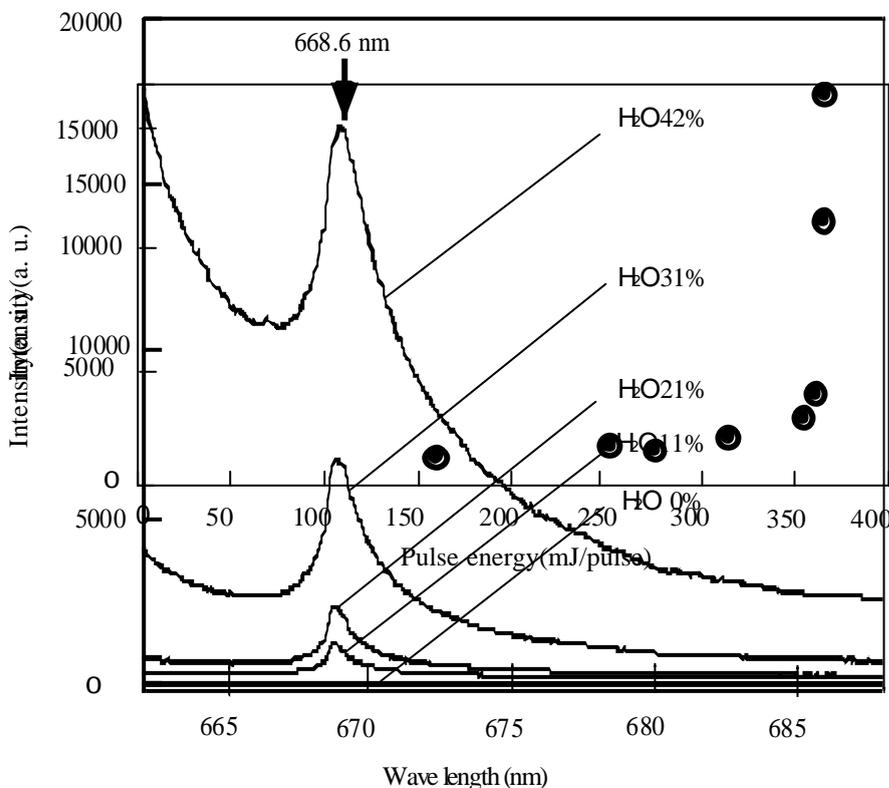


Fig. 2. Effect of H<sub>2</sub>O concentration on the 668.6 nm H<sub>2</sub>O<sup>+</sup> fluorescence spectrum

Fig. 3. Effect of laser light energy on the fluorescence intensity of 668.6 nm band.

The principle applied in the present work might be a complicated one and not be clearly understood. Nonetheless, the experimental result shows that fluorescence intensity clearly depends on the water vapor concentration. Gas breakdown phenomena, multiphoton ionization (MPI) to supply electrons and absorption of laser by electrons that ionize the H<sub>2</sub>O molecules to upper states to induce fluorescence, occurs by the present simple method to focus laser light to the measuring point.

### 3. MEASUREMENT OF CO<sub>2</sub> CONCENTRATION

CO<sub>2</sub> concentration measurement was conducted using a similar apparatus mentioned in H<sub>2</sub>O measurement. CO<sub>2</sub> gas was mixed with N<sub>2</sub> gas and introduced into the measuring cell. The CO<sub>2</sub> concentration was controlled by flow meters. The experiment was conducted at atmospheric pressure condition.

In Fig. 4, the relative fluorescence emission spectrum of CO<sub>2</sub><sup>+</sup> of 412.08 nm and 415.95 nm bands are shown varying CO<sub>2</sub> volumetric concentration, 0 to 100 %. The pulse energy is 360 mJ / pulse. The fluorescence of 412.08nm and 415.95nm bands linearly increases with increase of CO<sub>2</sub> concentration, whose characteristics is different from H<sub>2</sub>O (Fig. 2). Both bands originates from the  $A^2\Pi - X^2\Pi$  transitions (Pease et al., 1976). The effect of laser pulse energy on both 412.08nm and 415.95nm fluorescence intensities are depicted in Fig. 5. The CO<sub>2</sub> concentration is 50 %. The fluorescence intensity is not linear to the pulse energy, which shows the same tendency observed in H<sub>2</sub>O case.

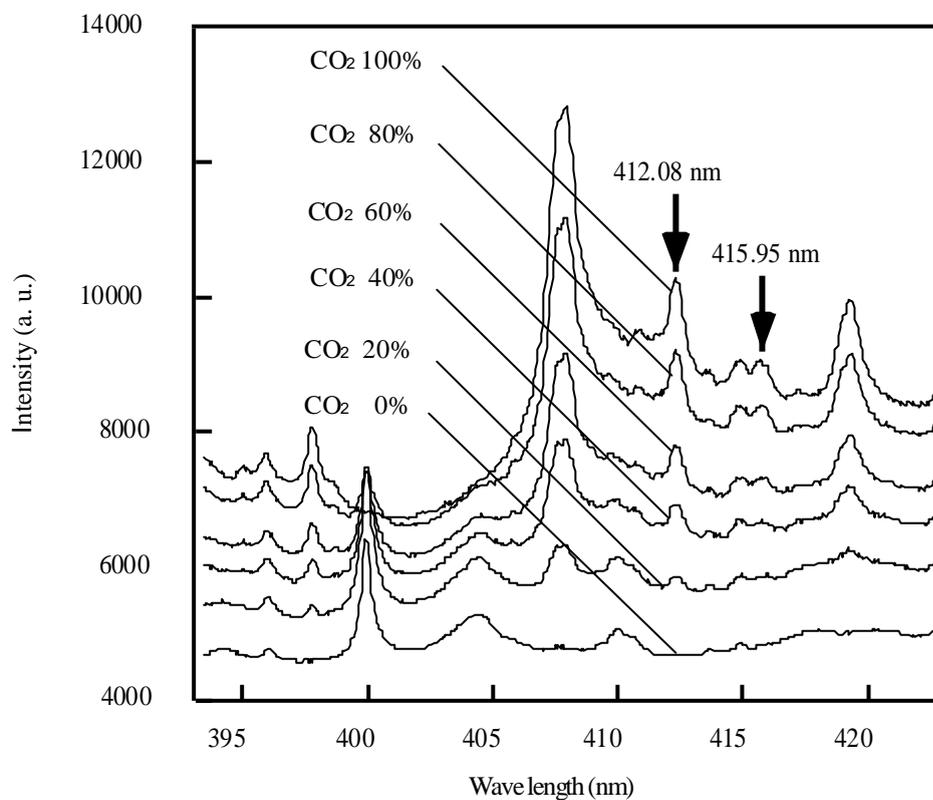


Fig. 4. Effect of CO<sub>2</sub> concentration on the 412.08 nm and 415.95 nm CO<sub>2</sub><sup>+</sup> fluorescence spectrum

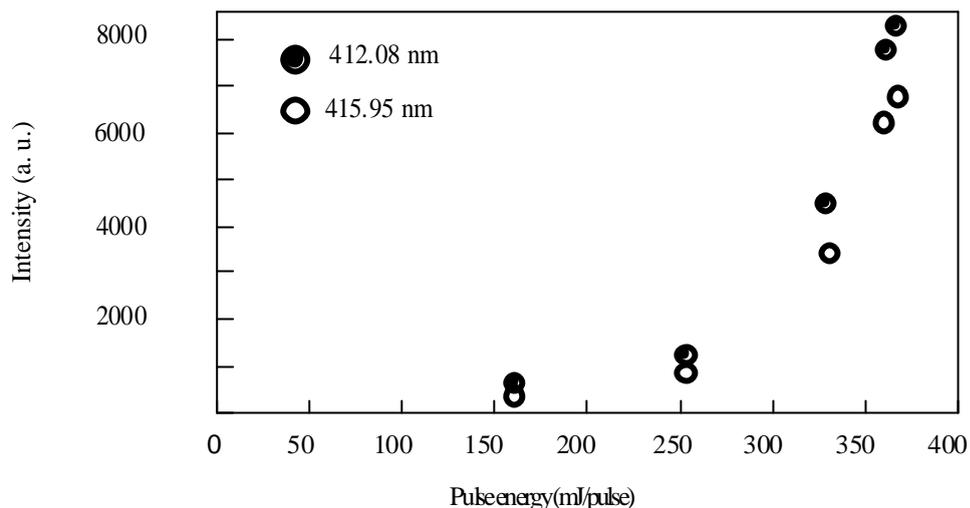


Fig. 5. Effect of laser light energy on the fluorescence intensity of 412.08 nm and 415.95 nm bands.

#### 4. CONCLUSION

Although gas breakdown is a complicated phenomena, ND:YAG laser intensity approximately over 350 mJ would induce fluorescence of ionized gas molecules,  $\text{H}_2\text{O}^+$  and  $\text{CO}_2^+$ , which could be applied for the measurement of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  concentrations, respectively. The present method has demonstrated its validity at atmospheric pressure condition which is encountered in many thermo-fluid facilities. Other effect on the present method, i.e., temperature dependence and elucidation of the detailed process to induce fluorescence, may be needed in further studies.

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