Raman spectroscopy of molecule densities in Hydrogen-Air mixture premixed gas ignited by spark discharge

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Abstract—**For investigating the electrostatic ignition process of hydrogen-oxygen mixture, the densities and dynamics of H_2, O_2 and H_2O molecules are measured in incipient spark-ignited hydrogen-oxygen flame using Raman spectroscopy. A single-pulse narrow-band tunable KrF excimer laser is used as a vibrational Raman scattering source. The hydrogen-oxygen mixture is ignited with a capacitive spark discharge with energy of several times higher than the minimum ignition energy. It is shown that the H_2 and O_2 densities rapidly decrease after the spark discharge (us time scale), at the same time combustion byproduct H_2O density increases. These data are essential to clarify the kinetics of electrostatic ignition process.**

I. INTRODUCTION

Hydrogen generates power by reaction with oxygen. It is clean and promising energy source without exhaust of carbon dioxide. We can reduce the dependence on fossil fuel by using hydrogen energy. Hydrogen is sensitive to electrostatic discharge (ESD) compared with other inflammable gases. The minimum ignition energy (MIE) of a hydrogen–air mixture is only 0.019 mJ, whereas that of other flammable gases such as petrol, methane, ethane, propane, butane, and benzene is usually on the order of 0.1 mJ according to Lewis and von Elbe [1]. Therefore, the assessment of electrostatic hazard for hydrogen is urgent because hydrogen is used in fuel cells and fuel cell vehicles. However, the assessment has not yet been sufficiently achieved. In spite of the fact that the principle of spark ignition has long been known and used in the automobile industry, there are few measurements of molecule densities at the initial stage of ignition [2].

In this study, we measured the molecule densities of H_2, O_2 and H_2O in hydrogen-oxygen premixed gas using the capacitive spark discharge, the KrF excimer laser as a vibrational Raman scattering source.

II. EXPERIMENT

A. Ignition energy [3]

MIE is an important parameter in the assessment of electrostatic hazard. It has been measured for various flammable gases including hydrogen [1]. MIE is usually measured using capacitive spark discharge whose electrical circuit is shown in Fig. 1, because the capacitive spark is the most frequent electrostatic ignition source in practice. The capacitor C is charged up to voltage V, then the charge stored in the capacitor is discharged in a test chamber filled with an explosive mixture. MIE is defined as the lowest discharge energy required for ignition, where the discharge energy is defined as $CV^2/2$ [1].

Fig. 1 shows the electrical circuit for generating the capacitive spark. C_c is the capacitance of the ceramic capacitor connected in parallel to the spark gap and C_e is the capacitance of the electrodes. The carge stored in the capacitor $C = C_c + C_e$ is discharged at the spark gap. C_c is measured with an LCR meter (Kokuyo, KC-536). C_e is determined to be 1.7pF with an error of 10% at our previous experiment[3].

The spark discharge occurs between needle-to-needle electrodes placed in the center of the chamber. The needles are made from tungsten and have a 1mm diameter and a 40° tip angle. The gap distance can be adjusted with a micrometer. In this measurement, we fixed the gap distance in 2mm, which determined to be without causing interference with the focused laser beam.

Fig. 2 shows 6types previous measurements of the minimum ignition energy (MIE) of Hydrogen-oxygen-nitrogen mixture gas ignition which included our 2 types measurements. In this work, we determined to be the ignition energy as 75uJ with an error of 10%, because of the minimum ignition energy under $O_2 / (O_2+N_2) = 1.00$ in 2mm gap distance is around 45uJ.
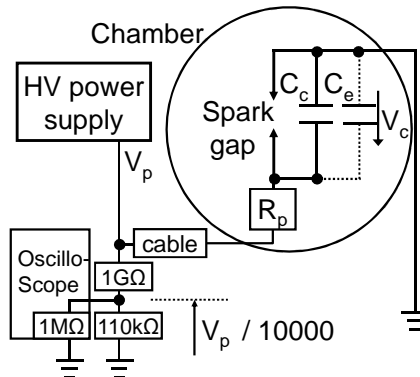

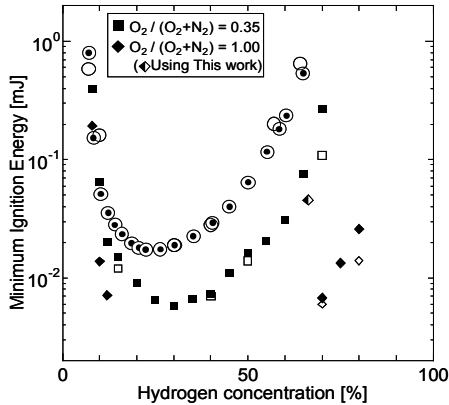Fig. 1. Electrical circuits for capacitive spark circuit

Fig. 2. MIE of H_2-O_2-N_2 mixture for various H_2 and O_2 concentrations:
Our previous measurement [6] under $O_2 / (O_2+N_2) = 0.21$ is ⊙ symbol.
Lewis and von Elbe measurements [1] under $O_2 / (O_2+N_2) = 0.21$ is ○ symbol,
$O_2 / (O_2+N_2) = 0.35$ is □ symbol, and $O_2 / (O_2+N_2) = 1.00$ is ◇ symbol the caption

B. Raman scattering [5 - 8]

It is well known that spontaneous elastic and inelastic scattering of light can be used as a potentially powerful probe of combustion systems. UV Raman spectroscopy has proved to be successful for turbulent combustion measurements. A major advantage compared with visible Raman scattering is the strong increase of the scattering cross section with inverse fourth power of wavelength of the incoming radiation proves advantageous in using excimer lasers in Raman spectroscopy for combustion diagnostics applicationst. That is indeed possible to take meaningful raman spectra with a single laser pulse. Nevertheless, even under those optimized excitation conditions, data averaging over more than one laser pulse may be inevitable. However, there are difficult for data averaging because of using the once premixed gas ignition, capacitive spark discharge and single pulse laser. We demonstrate choosing only a few data for molecule densities time changing in this work. Using the narrow-band tunable KrF excimer laser as the vibrational Raman scattering source (the center wavelength is 248.5nm) , the each H_2, N_2, O_2, H_2O species measured wavelength are shown in table I.

TABLE 1: RAMAN-SHIFTING APPROXIMATE STOKES Q BRANCH[5-8]

Species	Approximate Stokes Q branch wavelength range [nm]
H_2	276.5 - 277.7
O_2	256.8 - 258.4
N_2	263.4 - 264.0
H_2O	271.7 - 272.2

Raman scattering intensity I_R is the output signal proportional to the Molecule density N, focused laser intensity I_L and raman cross section σ. As we described previously, raman cross section increase with inverse fourth power of laser wavelength. Table II shows each species' vibrational raman cross section numbers.

$$I_R \propto \sigma I_L N$$
$$\sigma \propto \frac{1}{\lambda^4} \tag{1}$$

C. Optical setup

Fig. 3 shows the experimental systems.The laser is triggered after an adjustable delay following the end of the discharge pulse. By changing the delay time within the discharge pulse and the laser trigger from 3 [us] to 300 [us], which as same as the post discharge time. Because of the lasing mechanism has the 2.73 [us] delay time within the trigger and laser emission, the post discharge time begins to 3[us].

We placed a half-wavelength plate through the laser beam to adjust the parallel polarization to rotate 90 degrees around. Moreover, we placed the cylindrical lens right before the chamber to intensify the laser intensity I_L which cross-section size is 1mm $\times$ 6mm at the center of the spark gap.

Our imaging spectrograph is CHROMEX 500IS IMAGING SPECTROGRAPH which Focal length is 500 [mm] and the slit size is 200 [um]. The Raman scattering light is transmitted by the spectrograph to ORIEL InstaSpec V ICCD camera that is located on the spectrograph's exit plane. The images were processed in a PC.

In this experiment, we use hydrogen-oxygen premixed gas whose hydrogen concentration is 66% in volume. This combination ratio accomplishes complete combustion.

Liquid butyl acetate (BuAc.) which absorbs well at 248nm and at shorter wavelengths, filterd the light that entered our spectrometer. They simultaneously acquired Stokes vibrational Raman of H_2, O_2, H_2O and N_2 and LIF from OH and O_2.Without the BuAc, their spectrometer could not adequately reject Rayleigh light.
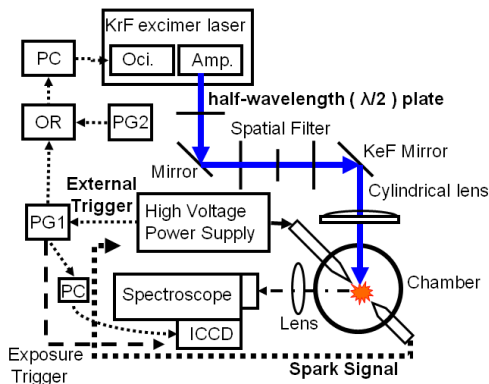

Fig. 3. Experimental systems

III.   RESULTS AND DISCUSSION

Figure 4 show the spectra of the Raman signal, which post discharge times are from 50 to 250 [us]. Each measurement time's Raman signal intensity is standardized by the intensity of the post discharge time 3[us]. Hydrogen Q stokes branch raman signal intensity at 277[nm] was decreasing, and water vapor raman signal intensity at 272[nm] was increasing. The Back ground base signal intensity were increasing at post discharge time from 150 [us] to350 [us]. It was caused by OH ($A^2\Sigma$ - $X^2\Pi$) emission.
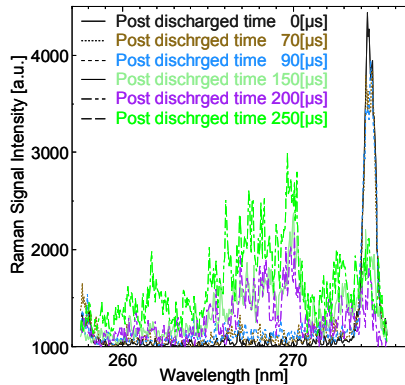

Fig. 4. The spectra of Raman scattering signal from 50 to 250 [us] post discharge times.

Fig. 5 is the time alternation of each molecule's raman signal intensity plotted by Fig. 4. As shown on the Equation(1), the Raman signal intensity proportional to the Molecule density. The Raman scattering signal intensity in Fig.4 and Fig.5 means the density of each molecules. In this work, we assumed the laser intensity I_L as fixed all experiment. Each plot was averaged over 5 measurements. Hydrogen broke out decreasing at 100[us] within 50[us]. Water vapor increased after 100[us]. Oxygen was moderate decreasing at 100[us]. It was different from hydrogen decreasing.
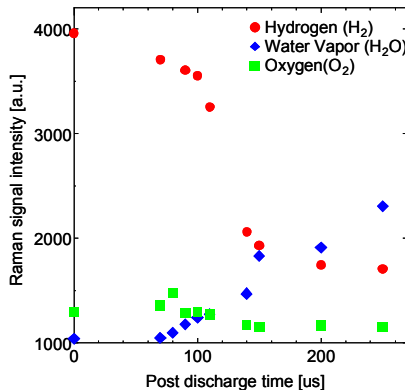

Fig. 5. The Raman signal Intensity of hydrogen, water vapor and oxygen from 3 to 300[us] post discharge time.

IV. CONCLUSION

We demonstrated measuring H_2, H_2O, O_2 molecule densities in hydrogen-oxygen pre-mixed gas using capacitive spark discharge and Raman scattering. Hydrogen decreased within 100 -150 [us], water vapor increased from 100[us].

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