

Hydrogen Visualization Using Multi-photon Ionization

Masahiro FUKUTA*

Ryugo HAYANO**

Masaki HORI**

Hideo NOBUSUE*

Takatsugu KOYAMA*

Jun TANAKA*

ABSTRACT

Research has been conducted on a hydrogen visualization technology in order to provide support to the process of research and development on fuel cell vehicles by “making invisible hydrogen visible.” The project eschewed conventional approaches such as indirect measurement of hydrogen using chemical sensors or substitute gases. Instead, it attempted to directly detect hydrogen, and to enable visualization of the state of diffusion of hydrogen in space.

The use of a laser was selected from among a variety of hydrogen detection methods, as its use is considered to be effective in detection at low concentrations. The project focused on a principle by means of which, contrary to conventional fluorescence analysis, fluorescence would occur even if the laser light for excitation did not match the absorption wavelength, and proposed a theory for hydrogen detection.

Results confirmed that the use of the principle of multi-photon ionization enabled direct fluorescence and detection of hydrogen. In addition, results suggested that the technology has the potential to be employed to visualize the changes in the state of diffusion of hydrogen in space as the flow rate changes, enabling analysis and measurement of the state of hydrogen diffusion.

1. Introduction

Honda is conducting R&D to promote more widespread use and enable mass production of vehicles powered by fuel cells, which the company regards as the ultimate next-generation clean powerplant, in order to provide an alternative to fossil fuels, reduce exhaust emissions, and ameliorate the automotive contribution to global warming.

Fuel cell vehicles use hydrogen as fuel, and therefore necessitate technologies enabling monitoring of the flow and motion of hydrogen, which have not previously been necessary in gasoline vehicles. The first item of research has been a hydrogen visualization technology enabling hydrogen flow and motion to be directly monitored.

Conventional fluorescence analysis methods are available for the visualization of gases, but they are ineffective in the case of hydrogen atoms. Research has therefore been conducted on camera imaging following the direct excitation and subsequent light emission of hydrogen atoms. However, an excitation energy of 13.6 eV or higher is necessary for hydrogen atoms to emit light, necessitating the use of large-scale devices.

A hydrogen visualization technology employing a single laser and using multi-photon ionization has therefore been developed to enable direct light emission from hydrogen atoms⁽¹⁾.

2. Development Goals

Looking towards the advent of the coming hydrogen society, the goal of the project was established as the realization of a visualization technology which would “make invisible hydrogen visible.”

The development concept for the hydrogen visualization technology was as follows:

- (1) Able to directly detect hydrogen
- (2) Able to visualize the concentration distribution of hydrogen when it is diffused in space

3. Background to Use of Multi-photon Ionization Method

3.1. Selection of Method for Detection of Hydrogen

Table 1 shows the methods generally used to detect hydrogen⁽²⁾. Hydrogen disperses rapidly in space, and its

* Automobile R&D Center

** The University of Tokyo

Table 1 Summary of evaluation of technologies

Technique	Distinguishing characteristic	Applicability
Passive sonar	Turbulent airflow (ultrasound)	Demonstrated Low spatial resolution Sensitivity depends on pressure and aperture
Raman-spontaneous	Allowable energy levels	H ₂ : Sensitivity of 2% demonstrated He: None - monatomic, therefore no vibration
Raman-CARS	Allowable energy levels	H ₂ : Sensitivity of 10 ppm demonstrated He: None - monatomic, therefore no vibration
Rayleigh doppler	Molecular/atomic velocities	Theoretically applicable for both H ₂ and He
Indirect thermal	Temperature	Limited by clutter?
Shearography	Index of refraction	Sensitivity limited by clutter

concentration subsequently diminishes. Different methods detect hydrogen on the basis of sound waves, temperature, mass, index of refraction, and band gaps. Among these methods, the CARS method achieves a lower limit concentration of 10 ppm. Given this, it was considered that a measurement method using an optical laser would be effective in enabling detection at low concentrations.

3.2. Calculation of the Lower Limit Concentration for Hydrogen Detection

As Table 2 shows, at normal temperature and pressure, hydrogen is a colorless, transparent, and odorless gas. Its diffusion coefficient in the atmosphere is $7.78 \times 10^{-5} \text{ m}^2/\text{s}^{(2)}$. These characteristics make it challenging to study the flow and motion of the gas. Substitute gases can be employed to enable study of flow and motion, but the fact that their mass differs from that of hydrogen means that accurate values are not obtained. The necessary lower limit of concentration for a hydrogen visualization technology to enable the flow and motion of hydrogen to be studied was calculated.

The percentage concentration of hydrogen when it diffuses in a large area at a diffusion coefficient of $D \text{ m}^2/\text{s}$ over a distance of $r \text{ m}$ for a time of $t \text{ sec}$ is shown by the following differential equation⁽²⁾:

$$\frac{\partial C(r, t)}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C(r, t)}{\partial r} \right) \quad (1)$$

Equation (2) is a model of the diffusion of hydrogen at a flow rate of $\phi \text{ ml/min}$ from an ideal punctiform hole.

$$C(r, t) = \frac{\phi}{4\pi Dr} \operatorname{erfc} \left[\frac{r}{\sqrt{4Dr}} \right] \quad (2)$$

Equation (3) shows the equilibrium concentration after the elapse of infinite time.

$$C(r) = \frac{\phi}{4\pi Dr} \quad (3)$$

Figure 1 shows equilibrium concentrations for

Table 2 Comparison of physical properties of gasoline and hydrogen

	Gasoline	Hydrogen
State at normal temperature	Liquid	Gas
Color	Orange	Colorless
Odor	Irritating odor	No odor
Diffusion coefficient in atmosphere [cm ² /sec]	0.05	0.778

hydrogen diffusing into the atmosphere from an ideal punctiform hole at various flow rates ($\phi \text{ ml/min}$) over a distance $r \text{ m}$, at a diffusion coefficient of $D_{\text{H}_2\text{-Air}} = 7.78 \times 10^{-5} \text{ m}^2/\text{s}$, a temperature of 25°C and a pressure of 101.3 kPa .

Calculation of the lower limit concentration for hydrogen detection assumed the use of a commercially available laser, and the distance at which it was able to approach an ideal punctiform hole was set at 5 mm , corresponding to the radius of the laser. The lower limit for the controllable flow rate was set at 0.01 ml/min .

The hydrogen concentration at a flow rate of 0.01 ml/min and distance of 5 mm was calculated to be approximately 40 ppm . With this as the lower limit

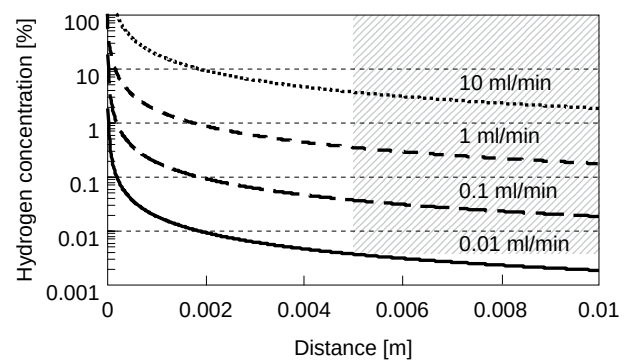


Fig. 1 Concentration of hydrogen at steady state

concentration for detection, it would be possible to detect the diffusion of hydrogen in the shaded section of Fig. 1.

3.3. Issues of Hydrogen Detection by Fluorescence Analysis

In standard fluorescence analysis, it is necessary to use a laser wavelength that matches the absorption wavelength of the band gap of the atoms or plasma being studied. Because of this, the wavelength of the laser light should be changed according to the gas that is to be detected. In the case of hydrogen, even when the laser wavelength corresponds to the absorption wavelength of the band gap, the band gap of a hydrogen atom is 13.6 eV or more, while the absorption wavelength is 120 nm or less, in the extended vacuum ultraviolet range. Light in the extended vacuum ultraviolet range is instantly absorbed and attenuated in the atmosphere, making it challenging to focus the laser on the area of detection.

Multiple lasers are necessary in order to address this issue, making the equipment used in the method very large.

Raman-CARS and spontaneous Raman are also known as methods enabling optical measurements of gases. However, these methods are only useful for gases with molecules that can be made to vibrate or can be rotationally excited by laser beam irradiation. In the case of hydrogen molecules, irradiation by a laser beam with intensities of 13.6 eV or higher at a wavelength that does not match the absorption wavelength will result in the molecules dissociating. As a result, hydrogen will be present in its atomic state, and will not be able to be detected. This made it necessary to develop a method differing from conventional fluorescence analysis methods.

3.4. Resolution of Issues Using Multi-photon Ionization

Figure 2 shows the results of a hydrogen atom ionization test using the second harmonic wave of an Nd-YAG laser⁽³⁾. At intensities of 10^{13} W/cm² and higher, 100% of the hydrogen atoms were ionized. When the ionized hydrogen stabilized, excitation energy was released and fluorescence was produced.

The results shown in Fig. 2 led to a focus on the phenomenon of fluorescence of the atoms occurring even if the wavelength of the incident laser was not equivalent to the absorption frequency of the band gap, and the proposal of a theory concerning the detection of hydrogen concentration by means of this phenomenon. Figure 3 shows a model of this theory.

A laser with an energy density of 10^{13} W/cm² or higher in the perpendicular section of the optical axis irradiates the gas being measured. Even if the wavelength of the irradiating laser does not match the absorption wavelength, the use of a high-directivity, high-photon density laser results in simultaneous absorption of multiple photons, as shown by the multiple arrows, Y1, in Fig. 3. This excites

the atoms from normal energy levels to a continuous state, ionizing them. This is the phenomenon of multi-photon ionization⁽⁴⁾.

After the gas being measured has been excited in this way, the molecules de-excite from an upper energy level to lower energy level 2 or 1, as shown by arrows Y4, Y3, and Y2 in Fig. 3. When this occurs, the gas produces specific types of fluorescence, A and B. It was therefore considered that the quantification of fluorescence A and B would enable the concentration of the gas being measured to be calculated, and the flow and motion of the gas to be visualized by means of imaging.

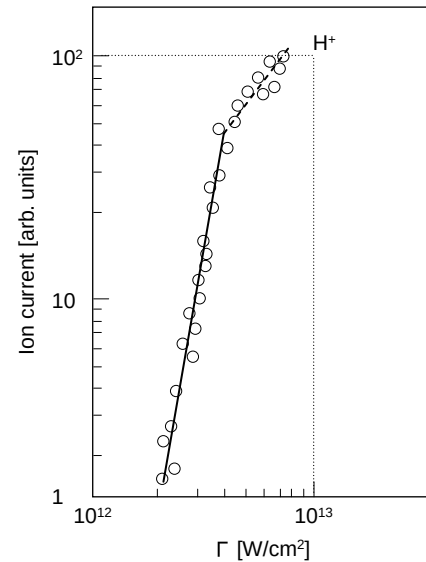


Fig. 2 Log-log plot of H^+ from H_2 as function of laser intensity Γ

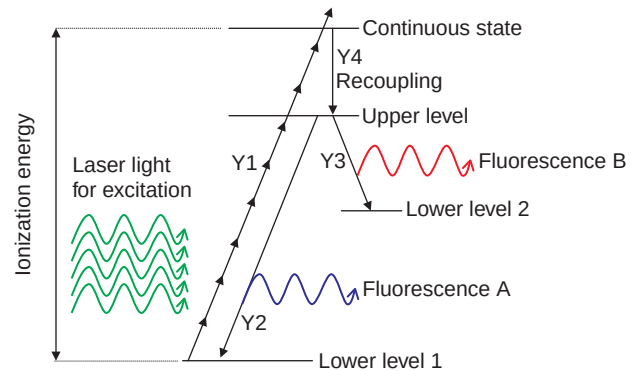


Fig. 3 Model of multi-photon ionization

4. Realization of Hydrogen Visualization Technology

The development of a high-peak laser with an energy density of 10^{13} W/cm² or higher in the perpendicular section of the optical axis was the key issue in the

realization of the principle of multi-photon ionization. With a standard laser energy density of 10^6 W/cm², the necessary laser strength would be from 100 to 1 000 000 times higher than that used in standard fluorescence spectroscopy.

In addition, because the principle indicated that all of the gas at the focal point of the beam would ionize and fluoresce, if a CCD camera was simply used without any extra considerations, the fluorescence produced by all the gas at the focal point would be photographed. This would represent an impediment to visualization, because the results would not clearly indicate where the hydrogen was present. The next sections will discuss the measures used to resolve these issues.

4.1. Achievement of Increased Laser Energy Density

The equation employed to calculate the rate of hydrogen fluorescence per pulse (N) in the development of a high-peak strength laser with an energy density of 10^{13} W/cm² or higher is shown below⁽⁵⁾.

$$N \propto \left(\frac{P}{hvA\Delta t} \right)^\alpha \times (n_{H_2}AL) \times \sigma(\theta) \times (\Omega \times \varepsilon_0 \times \varepsilon_d) \times \Delta t \quad (4)$$

Laser power: P [J]

Energy per photon: hv

Laser focal area: A [m²]

Pulse width: Δt [sec]

Concentration: n_{H_2} [%]

Thickness: L [1/m³]

Probability of fluorescence: $\sigma(\theta)$ [m²]

Solid angle: Ω [sr]

Efficiency of optical system: ε_0

Efficiency of detection equipment: ε_d



Fig. 4 Pulse compressor

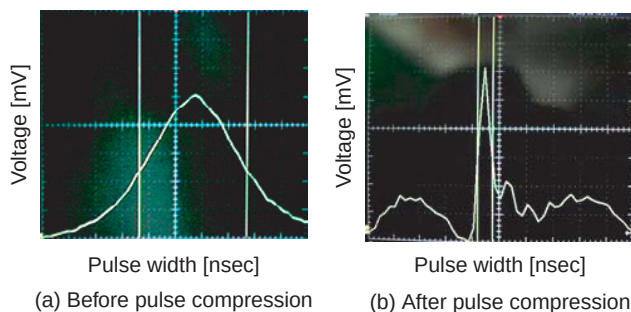


Fig. 5 Test of pulse compression

As Eq. (4) shows, as the laser power is increased, the focal area is restricted and the pulse width is shortened, increasing energy density.

Laser power depends on the wavelength of the irradiating beam, and higher energy per photon is effective. From this perspective, in the case of an Nd-YAG laser with a fundamental wave of 1 064 nm, the 213 nm fifth harmonic wave would be effective. However, conversion using a nonlinear optical crystal results in conversion loss, reducing total energy. The 532 nm second harmonic wave was therefore selected as being more effective from the perspective of total energy.

The pulse compressor shown in Fig. 4, which uses liquid as a medium, was developed and employed to compress the pulse width. Focusing the beam by means of a concave mirror and using the phenomena of backwards Brillouin scattering and stimulated Brillouin scattering enabled the pulse width to be compressed as shown in Figs. 5(a) and (b).

A lens that narrowed the focus area was developed and employed in order to increase energy density.

4.2. Imaging Hydrogen Fluorescence

A bandpass filter was constructed that would filter everything but the wavelength representing the characteristic emission spectrum of hydrogen from the irradiating laser light and all the fluorescence produced by the gas at the focal point of the laser (Fig. 6). This spectroscopic technique enabled only the characteristic emission spectrum of hydrogen to be imaged.

Tests of the wavelength filtering performance of the bandpass filter were conducted. In Fig. 7(a), the fluorescence produced by all the gas at the focal point of the laser is measured, but the application of the bandpass filter enables only the characteristic emission spectrum of hydrogen to be measured, as shown in Fig. 7(b).

4.3. Overview of Hydrogen Visualization System

The developed hydrogen visualization system is made up of three major sub-systems. The sub-sections below provide an overview of these sub-systems.

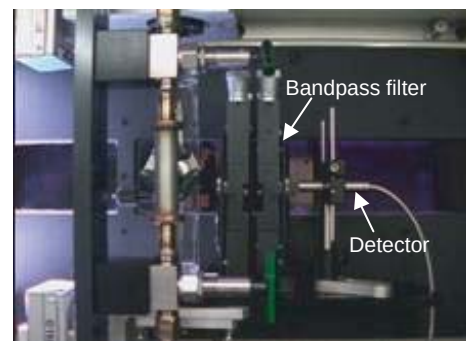
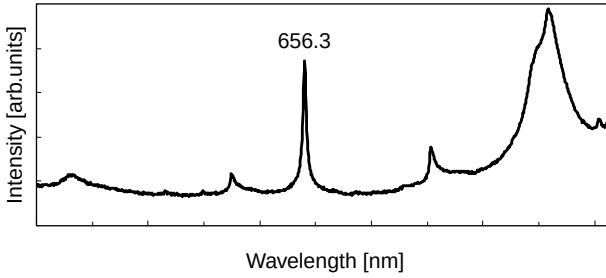


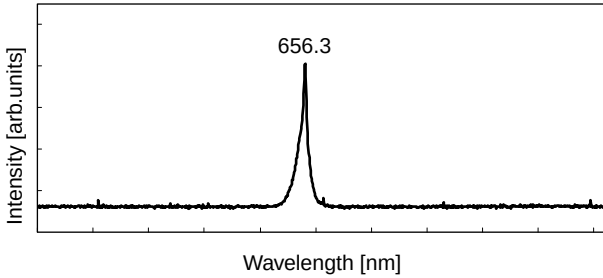
Fig. 6 Bandpass filter

4.3.1. Multi-photon ionization generating system

The multi-photon ionization generating system is shown in Fig. 8(a). A Q switch Nd-YAG laser enabling a top-hat beam profile to be obtained is employed. The laser has a wavelength of 532 nm, an energy of 425 mJ, a repeat cycle of 10 Hz and a pulse width of 6 nsec. An optical phase conjugator is incorporated in the center of the post-oscillation beam path. The optical phase conjugator maintains the energy density distribution of the pulse laser by means of optical inverse transformation of the laser light. The system also employs, as an optical amplifier, a pulse compressor that compresses the pulse width. A focusing lens is positioned at the end of the beam path.



(a) Before application of bandpassfilter: All wavelength



(b) After application of bandpass filter: Only characteristic wavelength of hydrogen

Fig. 7 Test of bandpass filter performance

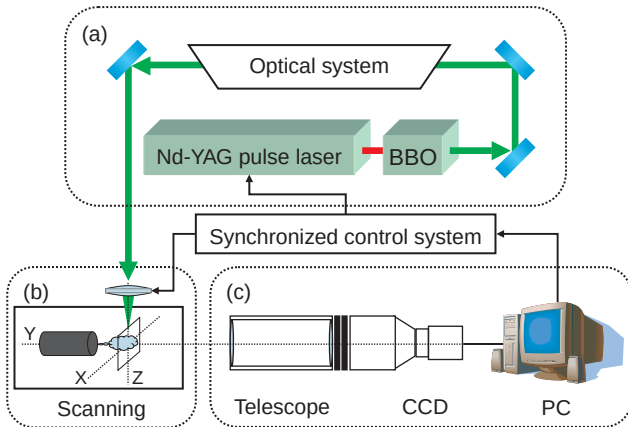


Fig. 8 Outline of hydrogen visualization system

4.3.2. Scanning system

The scanning system is shown in Fig. 8(b). This is composed of a mechanism for shifting the focal point of the laser (a focusing lens and mirrors incorporated into a robot) and a mechanism for adjustment of the measurement environment. Planar measurement is enabled by opening the exposure of the CCD camera in the imaging system and shifting the focal point of the laser without changing the strength of the laser across the range of measurement. This has enabled planar imaging of the flow and motion of hydrogen.

4.3.3. Imaging system

The imaging system is shown in Fig. 8(c). It is made up of an apochromat telescope, a bandpass filter and a CCD camera. The system is shielded from the irradiating laser light and stray light, and the CCD camera therefore images only the characteristic emission spectrum of hydrogen produced at the focal point of the laser. The use of a Peltier device has enabled the CCD sensors to be cooled to below -30°C in order to reduce thermal noise. This has increased the sensitivity of the sensors by approximately 1 000-fold against sensors at normal temperature, enabling imaging of even faint fluorescence. A PC conducts image processing of the data obtained by the camera, and synchronously controls the various systems.

5. Verification and Testing Using Hydrogen Visualization System

5.1. Verification of the Principle of Multi-photon Ionization

The developed system was used to verify the principle of multi-photon ionization. For the tests, hydrogen enclosed at 101.3 kPa within a silica tube was irradiated with an Nd-YAG laser at a wavelength of 532 nm, 100 mJ of energy and pulse width of 2 nsec.

The fluorescence of the hydrogen at the focal point of the laser was studied, as shown in Fig. 9. Figure 10 shows the results of a qualitative analysis conducted using a spectrometer. The wavelength of the fluoresced light is 656.3 nm, the characteristic wavelength of hydrogen.

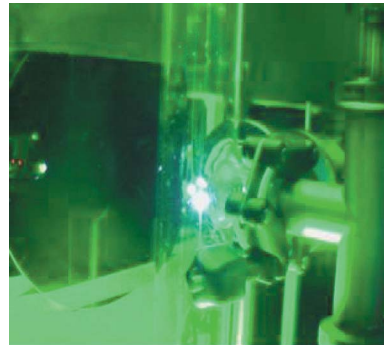


Fig. 9 Moment of hydrogen fluorescence

This result verifies the fact that the multi-photon ionization method is able to directly produce fluorescence of hydrogen atoms.

Next, a test was conducted to determine the lower limit hydrogen concentration that could be detected. Hydrogen was enclosed at known concentrations in a silica tube at 101.3 kPa. The hydrogen was irradiated by the laser under identical oscillating conditions as employed in the previous test. Figure 11 shows results obtained as the concentration of the hydrogen was shifted towards lower concentrations. A sensitivity of up to 30 ppm of hydrogen was verified by the spectrometer.

5.2. Tests of Hydrogen Visualization

Tests of visualization of hydrogen dispersing from a single hole were conducted in order to verify the ability of the system to determine the distribution of hydrogen concentration when dispersed in space. A hole with a diameter of 5 mm was pierced in the center of a stainless steel flange 40 mm in diameter and 5 mm in thickness. The hydrogen was dispersed in a planar direction from the hole, and was irradiated in a perpendicular direction by a laser positioned 5 mm from the end of the flange as shown in Fig. 8(b). The range for imaging was set at a 60 mm square, and the exposure of the CCD camera was open from the first to the last laser pulse. The laser was pulsed at vertical intervals of 5 mm and horizontal intervals of 2 mm. The hydrogen was dispersed at flow rates of 25 ml/min and 50 ml/min.

The results of the tests are shown in Figs. 12(a) and

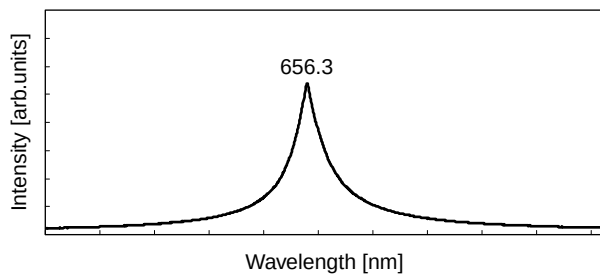


Fig. 10 Characteristic wavelength of hydrogen

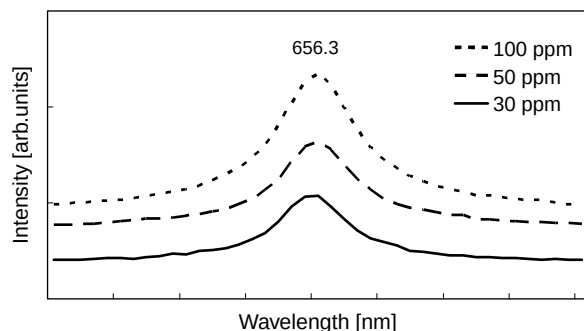


Fig. 11 Minimum limit for detection of hydrogen concentration

(b). These results indicate that it is possible to photograph and visualize hydrogen dispersing upwards from a single hole. The colored portions of the images are hydrogen fluorescence produced by the laser. The color bars in Fig. 12 show the relative hydrogen concentration. Figures 12(a) and (b) also indicate that it is possible to visualize changes in hydrogen dispersion that occur with changes in the flow rate.

5.3. Tests of Application of Hydrogen Visualization System

Next, in order to test the performance of the system in visualizing the flow and motion of hydrogen under conditions more closely approximating reality, tests were conducted of the visualization of hydrogen dispersing from multiple holes.

As shown in Fig. 13(a), 12 holes of approximately 30 μm in diameter were pierced in an H-shaped pattern in a stainless steel vacuum flange of 100 mm in diameter and 10 mm in thickness. Hydrogen was dispersed from each hole at 1 ml/min, for a total of 12 ml/min.

The hydrogen was irradiated by a laser positioned 5 mm from the end of the flange, using identical oscillating conditions to those employed in the previous tests. The results are shown in Fig. 13(b).

The results indicate that the system is able to visualize the dispersion of hydrogen not only from a single hole, but from multiple holes.

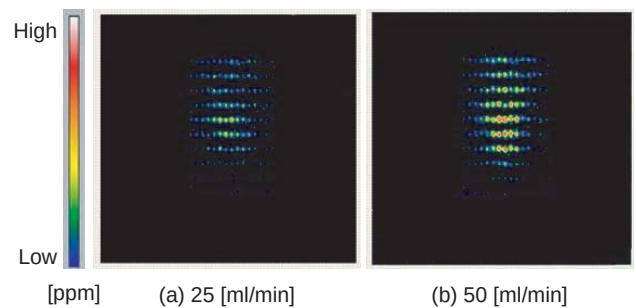
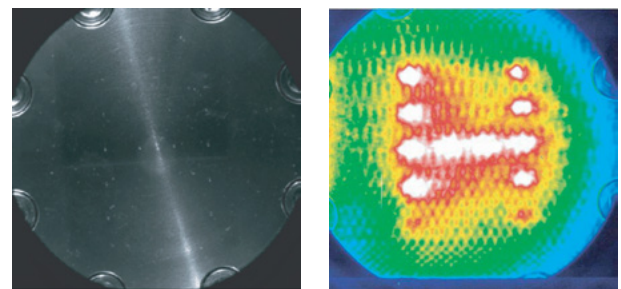


Fig. 12 State of hydrogen diffusion from single point



(a) Stainless steel vacuum flange

(b) Visualization of "H"

Fig. 13 State of hydrogen diffusion from multiple points

6. Conclusion

Using the multi-photon ionization method, the research discussed in this paper has taken the first step towards the important achievement of enabling visualization of hydrogen. The following knowledge was obtained.

- (1) The project demonstrated that the principle of multi-photon ionization could be used to enable direct fluorescence and detection of hydrogen.
- (2) It was possible to image and visualize the concentration distribution of hydrogen dispersed in space using a CCD camera.
- (3) Tests verified that the developed system was able to visualize changes in the state of dispersion of hydrogen occurring as a result of changes in the flow rate.
- (4) The results of the project suggest that the multi-photon ionization method can be employed in technologies for the analysis and measurement of hydrogen dispersion.

References

- (1) WO 2006/006628 A1
- (2) Seller, R. G., Wang, D.: Assessment of Remote Sensing Technologies for Location of Hydrogen and Helium Leaks, NASA, NAG10-0290 (2000)
- (3) LuVan, M., Mainfray, G., Manus, C., Tugov, I.: Multiphoton Ionization of Atomic and Molecular Hydrogen at 0.53μ , Physical Review. A, Vol. 7, Issue 1, p. 91-98 (1973)
- (4) Weyl, G. M.: Physics of Laser-Induced Breakdown: An Update, Laser-Induced Plasmas and Applications, Marcel Dekker, p. 1-59 (1989)
- (5) Hori, M.: Proof of Principle Experiment, University of Tokyo, 11p. (2003-2005)

■ Author ■



Masahiro FUKUTA



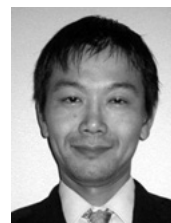
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