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Sensitive Detection of H_2 Molecules by Two-Photon Excited Laser-Induced Fluorescence

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Abstract. The sensitive detection of H_2 molecules was demonstrated by means of two-photon excited laser-induces fluorescence spectroscopy with a narrow-band ArF excimer laser. A detection limit of $2\times10^{14}\,\mathrm{cm}^{-3}$ was obtained with an excitation power of ~ 150 kW. This is already comparable with that obtained by the coherent anti-Stokes Raman scattering (CARS). This technique was successfully applied to measure a spatial distribution of H_2 in a town-gas burner.

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Spatially and temporally resolved, uni-directional detection of H_2 molecules is important in such fields as fundamental chemical process and plasma engineering. For the purpose, laser-induced fluorescence (LIF) is one of the most powerful technique among various methods. Recent advances of vacuum ultra-violet (VUV) lasers make it possible to apply LIF to the detection of light atoms and molecules, such as H [1] and CO [2], and so on, which have resonance lines in VUV wavelength region shorter than 190 nm. As for H_2, however, since its resonance lines lie below 106 nm, where just LiF has residual transmission, the application of usual LIF has many technical problems.

The difficulty caused by the use of VUV radiation in the one-photon excited LIF can be overcome by the two-photon excited LIF (TPLIF), which has another advantage that it is free from the stray-light problem. On the other hand, TPLIF needs a tunable, high-power light source for a sensitive detection, due to its relatively small absorption cross section. Fortunately, in the case of H_2, two-photon transitions from the ground state to the electronically excited E, F state are in the tunable range of an ArF excimer laser. Excited H_2 molecules decay to the lower states by emitting the near infrared fluorescence, or are ionized by absorbing another ArF laser photon. The former process has been used to study a collisional and radiative property of the E, F state [3], and more recently the latter process for the detection of H_2 by observing an ionization signal directly or by the opto-galvanic effect in a discharge [4].

In this paper, we have investigated the sensitive detection of H_2 with TPLIF excited by a narrow-band ArF excimer laser, and discussed its detection limit. A detection limit of $2\times10^{14}\,\mathrm{cm}^{-3}$ has been achieved with an ~ 150 kW excitation power, as described in Sect. 2.1. It is already comparable with that obtained by the coherent anti-Stokes Raman scattering (CARS) [5]. Then, TPLIF was successfully applied to measuring a spatial distribution of H_2 in a town-gas burner, as described in Sect. 2.2.

1. Experimental Apparatus

The experimental setup used is shown in Fig. 1. The ArF laser was a homemade auto-ionization type, and produced about 100 mJ on a free-running mode. A narrow-band and tunable operation was achieved by

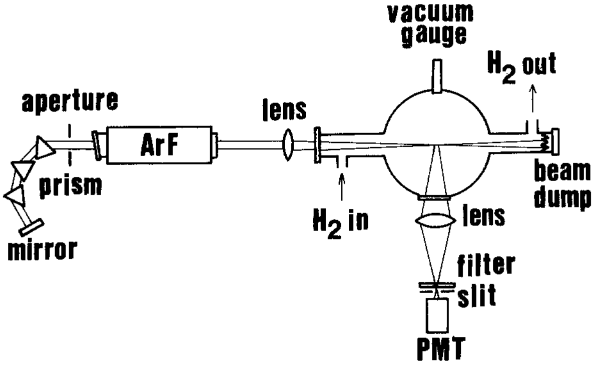

Fig. 1. Experimental set-up

inserting three 60° prisms made of quartz into the laser cavity, which was formed with an Al-coated total reflector and a CaF_2 optical flat window. An aperture with a diameter of 5 mm was used to decrease a beam divergence. A tunable range was about 1 nm. The spectral width was roughly estimated to be 0.01 nm by observing a fluorescence signal under scanning the laser wavelength. An output energy at the center of the tuning range was ~15 mJ. The tuning spectrum contained several dips due to an intra-cavity absorption by the Shumann-Runge band of molecular oxygen. However, even the $Q(1)$ transition, which is the nearest one to an absorption band, was at the edge of a dip. Therefore, in the following experiments special care was not made for achieving an oxygen-free optical path.

An output beam was focused with a quartz lens with a focal length (f) of 150 mm into an observation chamber. The laser energy was further decreased to 2 mJ at the observation volume. H_2 gas was sealed off at a pressure higher than 200 mTorr, and then continuously flowed below 200 mTorr. The pressure was monitored with an ionization vacuum gauge or a calibrated thermal conductivity gauge. Generated near-infrared fluorescence was collected with a lens ($F=2$), and detected with a photo-multiplier tube (PMT, Hamamatsu HTV R943-02) at a right angle to the laser beam. A color glass filter (Toshiba R680) was inserted in front of the PMT to reject an intense fluorescence light generated at an entrance window or a beam dump by the ArF laser beam. A viewing dump was also used. The signal from the PMT was displayed on an oscilloscope, and all measurements were performed on a single-shot basis.

For flame experiments, H_2 gas chamber was replaced with a town gas burner. In this case, a monochromator (Nikon G250, $f=250$ mm) was used in the detection system to avoid a saturation of the PMT due to the background light from the flame. The bandwidth of the monochromator was set at ~9 nm.

2. Results and Discussions

2.1. Pure H_2 Gas Experiment

A typical excitation spectrum for the $E,F \leftarrow X$ transitions is shown in Fig. 2. Four Q-branch transitions starting from the rotational level of $J=0$ to $J=3$ in the lowest vibrational level were observed. A spectral width of the ArF laser was estimated to be ~0.01 nm from the spectral width of the excitation spectrum. At the room temperature, the $Q(1)$ transition provides the largest signal, since the populational fraction of ~70% of H_2 exists in the $J=1$ level of the ground vibrational level and the wavelength of the $Q(1)$ transition is nearly at the center of the tuning range of the ArF laser. A pressure dependence of the TPLIF signal was measured by fixing the laser wavelength on the $Q(1)$ transition. The results are summarized in Fig. 3. A tendency of the saturation observed at a high pressure of H_2 is due to the self-quenching of the excited state. It was confirmed based on a rate-equation analysis that the experimental results explained well with the reported quenching constant in [6].

A detection limit of 5 mTorr ($\sim 2 \times 10^{14}$ cm^{-3}) was obtained with an excitation power of only ~150 kW. The detection limit is already comparable with that achieved by CARS, in spite of a relatively low excitation power. CARS signal is proportional to the square of a molecular density, dissimilar to the linear dependence of TPLIF. Therefore, it can be said that TPLIF is superior to CARS regarding to the trace detection. The lowest signal level in Fig. 3 corresponded to ~10 photo-electrons per pulse. This value roughly coincides with that predicted from the rate equation analysis, in which the experimental conditions were taken into account. The analysis also shows that further improvements of the detection limit down to 10^{12} cm^{-3} would be possible by increasing an excitation power up to 10 MW, and/or by narrowing the spectral width of the ArF laser to the Doppler width of H_2. Recently the stimulated emission followed by two-photon excitation of H_2 at a pressure of around 10 Torr has been observed at an excitation power level of 10 MW [7]. At a high pressure around 1 Torr it causes error in a density measurement, but at a low pressure of less than mTorr the present estimate will be scalable. Thus, TPLIF with a narrow-band ArF laser is a simple and powerful method for a sensitive detection of H_2.

A detection limit of the present method depends on a gas temperature due to a change of the populational fraction in each rotational level. However, a decrease of the population fraction of the $J=1$ level is only about a factor of 3, when a temperature is elevated up to

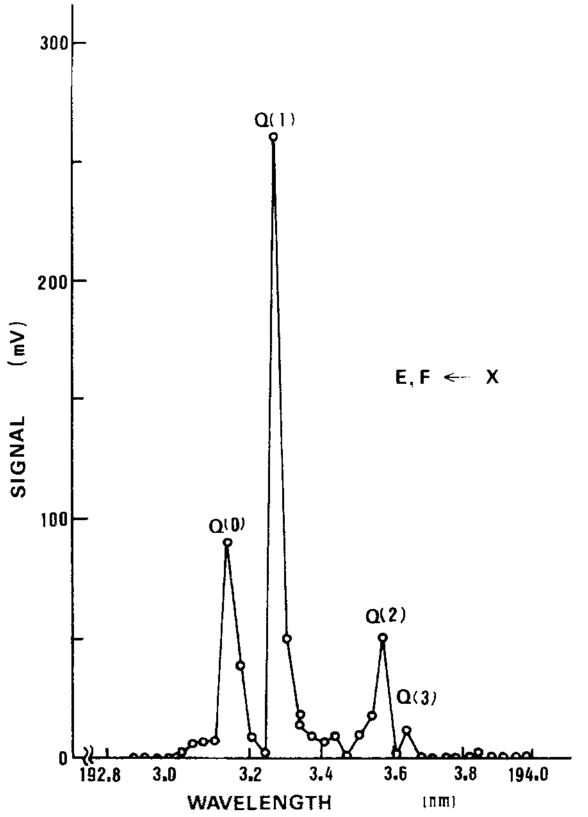

Fig. 2. Two-photon excitation spectrum of H_2 molecules at a pressure of 60 Torr

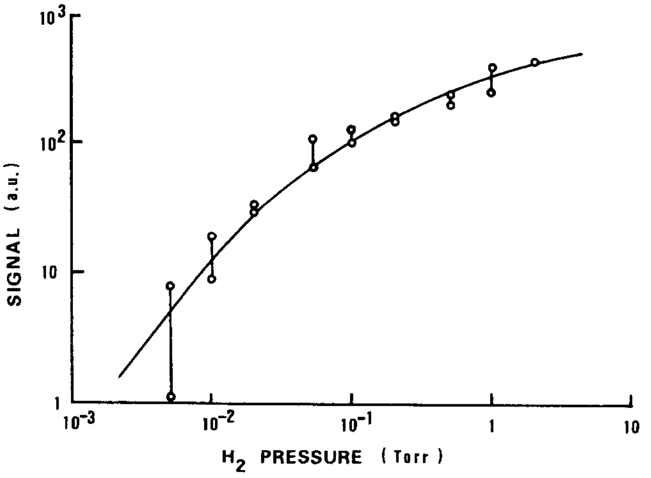

Fig. 3. Fluorescence signal as a function of H_2 pressure

1500 K. Therefore, the present method will be applicable to H_2 gas at a temperature of less than 1500 K without a considerable sacrifice of the sensitivity. A gas (rotational) temperature can also be determined by observing the fluorescence signals for an excitation of each Q-branch.

2.2. *Flame Experiment*

As an application of the present method, a spatial distribution of H_2 molecules in a flame of a town-gas burner was measured. This method might be interesting because the molecular oxygen can be measured simultaneously with the same experimental set up [8,9]. The measurements were performed across the flame at a height of 5 mm above the burner nozzle. H_2 molecules were excited via the $Q(1)$ transition, and the fluorescence was observed at the $R(1)$ transition through a monochromator. A measured horizontal distribution of the fluorescence signal is shown in Fig. 4. The result in Fig. 4 is not corrected against a temperature distribution in the flame. Under the present experimental condition, however, the result in Fig. 4 is roughly reflecting the distribution of H_2 molecules, since the temperature was believed not to be high ($\sim 1000°$C or less). The spatial profile was roughly the same as a dark inner cone of the flame.

An absolute calibration of the observed fluorescence signal to a density is difficult mainly due to an unknown quenching rate of the E, F state in the flame environment. Salmon and Laurendeau demonstrated to control the loss process from the excited state by the photo-ionization over the quenching process in their H atom detection in a flame, to perform quenching-independent fluorescence measurements [10]. Under the quenching-independent condition, an absolute density can be easily determined by calibrating an optical system with a pure H_2 gas at a known pressure. Since the third photon can ionize the excited H_2 in the E, F state in the present experiment, the same technique will be applicable. The photo-ionization

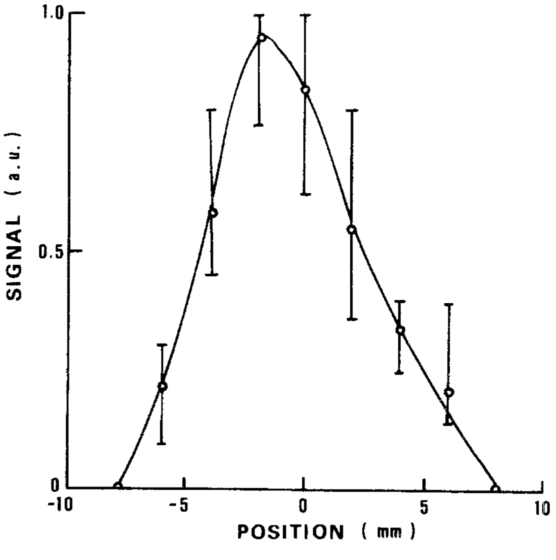

Fig. 4. Spatial distribution of fluorescence signals across the flame of a town-gas burner

cross section from the E,F state is $2.6 \times 10^{-18}\,\mathrm{cm}^2$ [11]. The quenching constant is unknown, but for reference let us take the quenching constant of $7 \times 10^8\,\mathrm{s}^{-1}$ [6], which is for a pure hydrogen at 10 Torr and a room temperature. In this case, an excitation intensity of more than 3 $\mathrm{GW/cm}^2$ is required, in order to dominate the loss process by the photo-ionization by an order of magnitude. At such a high power, another problem could occur. Actually, when an excitation intensity was increased by an order of magnitude from the present experiment by using a focusing lens with a focal length of 50 mm, the optical breakdown in the flame was observed. Therefore it was a critical problem to achieve the photo-ionization dominant condition under this experiment.

3. Conclusion

In conclusion, we have demonstrated that TPLIF with a narrow-band ArF excimer provides a simple and sensitive detection method for molecular hydrogen. Further investigations on the absolute calibration, and the possibility of the temperature measurement are now in progress.

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References

1. T. Kajiwara, M. Inoue, T. Okada, M. Maeda, K. Muraoka, M. Akazaki: Rev. Sci. Instrum. **56**, 2213–2216 (1985)
2. M. Maeda: Jpn. J. Appl. Phys. **24**, 717–722 (1985)
3. D.J. Kligler, J. Bokor, C.K. Rhodes: Phys. Rev. A **21**, 607–617 (1980)
4. E.W. Rothe, G.S. Ondrey, P. Andresen: Opt. Commun. **58**, 113–117 (1986)
5. G. Marowsky, A. Gierulski, B. Dick, U. Sowada, R. Vehrenkamp: Appl. Phys. B **39**, 47–53 (1986)
6. D.J. Kligler, C.K. Rhodes: Phys. Rev. Lett. **40**, 309–313 (1978)
7. H.F. Döbele, M. Höri, M. Röwekamp: Appl. Phys. Lett. **49**, 925–926 (1986)
8. G.A. Massey, C.J. Lemon: IEEE J. QE-**20**, 454–457 (1984)
9. M.P. Lee, P.H. Paul, R.K. Hanson: Opt. Lett. **11**, 7–9 (1986)
10. J.T. Salmon, N.M. Laurendeau: Opt. Lett. **11**, 419–421 (1986)
11. A. Cohn: J. Chem. Phys. **57**, 2456–2458 (1972)