

Trace Methane Detection Based on Raman Spectroscopy Using a High Finesse Optical Resonator

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A Raman spectroscopy-based gas sensor employing a high-finesse simple diode laser pumped external cavity, Power Build-up Cavity (PBC), has been developed. Results show that a compact 10-cm-long PBC includes a simple diode-laser-pumped external cavity could achieve an intra-cavity power of 40 W with a photon lifetime of up to 29 μ s. Raman scattering light from trace methane in the PBC was detected by a photo multiplier tube and a bandpass filter. Good linearity of the detected Raman signal was obtained in the 90-500 ppm methane concentration region with a response time of 1 sec.

Key Word: Raman spectroscopy, Methane detection, Gas sensor, Rayleigh scattering, Power Build-up Cavity

1. Introduction

Sensitive and fast-response trace gas detection techniques are required in various industrial fields for leak detection, combustion diagnostics, monitoring of environmental pollutant gas and so on.

We have studied Raman spectroscopy based trace gas detection with a simple high-finesse optical resonator. When applying the Raman scattering process to trace gas detection, it is possible to design a multi-gas sensor with a very simple configuration since one pump laser can generate Raman scattering of multi-molecules. However, a disadvantage of Raman spectroscopy is its extremely small scattering cross section, which is 10^{-3} ~ 10^{-5} times as large as those in absorption spectroscopy. High peak power pulsed lasers such as YAG lasers,¹⁾ excimer lasers,^{2,3)} have generally been employed as pump sources to generate detectable Raman scattering intensities for gaseous species. Short-wavelength lasers⁴⁾ are also employed because the Raman cross section is proportional to the fourth power of the pump laser frequency.

We have developed a compact Raman scattering-based gas sensor that incorporates a low power diode laser pumped Power Build-up Cavity (PBC) with a high finesse value⁵⁾ as a light source. A compact, non-dispersive Raman gas detection scheme can be realized using an optical band pass filter.

In this paper, we report on characteristics of methane detection by this newly developed Raman spectroscopy-based gas sensor.

2. High-finesse Power Build-up Cavity (PBC) and experimental details

The PBC in this paper can maintain a high power intra-cavity beam with no feedback, no active control of cavity length and

no temperature control. Such experimental schemes can generate high intra-cavity intensities at a power level ranging from several tens to a hundred Watts. To maintain stable and high intra-cavity power, TEM₀₀ transverse-mode operation in the resonator is required. An appropriate optical arrangement between two coupled resonators can allow single transverse mode operation.⁶⁾ Such optical design results in spectral broadening of up to the hundred gigahertz for long-term operation. Actually, that value is broader than general laser spectroscopic light source employed in fluorescence and absorption spectroscopy in which narrow-linewidth light source is required for highly resolved measurements of ro-vibrational spectra to detect specific species. However, vibrational Raman spectra of environmental gaseous species appear with their wavelength shifts, typically from 500 cm^{-1} to 5000 cm^{-1} away from the pump laser wavelength. The frequency separation between adjacent Raman shifted spectra due to the environmentally important gaseous species are mostly wider than 50 cm^{-1} . Such large spectral separation in Raman spectroscopy permits the identification of species, even if a laser source with relatively broadened spectra of $\sim 20 \text{ cm}^{-1}$ are employed.

2.1 Experimental details

The PBC consists of a pump diode laser (Sacher Lasertechnik: SAL-670-C, residual reflectivity is $<10^{-4}$, center wavelength 675 nm), a graded index (GRIN) lens (MELLESGRIT: 06LGT114), and a couple of high-reflectivity mirrors (RESEARCH ELECTRO-OPTICS: S7B-10CC, reflectivity at 675 nm is between 99.94 % and 99.999 %, plano/concave shape, radius of concave curvature of 0.1 m). Figure 1 shows two independent resonators located close together in this particular set-up. One composes that the back facet of the diode laser and mirror 1 (M1) to form resonator 1 (R1). The other composes one pair of highly reflective mirrors, M1 and M2, to form resonator 2 (R2). Careful alignment of the optical axis results in a finesse as high

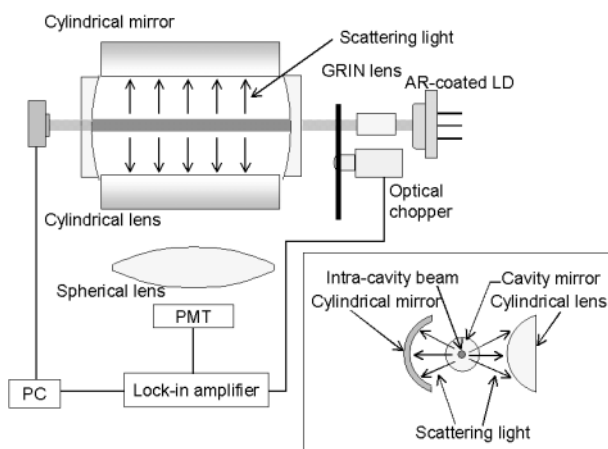


Fig. 1 Experimental set up of Raman-spectroscopy-based methane detection. Radially generated scattered light is collected by the cylindrical mirror and lens and focused on the PMT. The detected signal is amplified by a lock-in amplifier that synchronizes modulation frequency using optical chopper. The figure on the right shows an axial view of the collection optics. A pair of cylindrical mirrors and lens are located both sides of the intra-cavity beam.

as 10300. R2 serves as a small gas chamber for Raman spectroscopy.

2.2 Measurement of PBC photon lifetime

A pair of 99.999 % reflective mirrors were used for photon lifetime measurement. Leakage light passing through mirror M2 is measured by a high-speed photo diode (New Focus; 1621 M) to monitor intra-cavity power decay. The intra-cavity beam is modulated by an optical chopper (Scitec Instruments Ltd: Model 300 CD) with 500 Hz inserted between the GRIN lens and mirror M1. To examine the influence of Rayleigh scattering, the decay time is measured in cases where N₂ or He fills the chamber incorporated R2 of PBC. N₂ and He were fed into the gas cell through a 0.5 mm in-line particle filter prior to the gas chamber to reduce contamination performing as intra-cavity loss.

2.3 Methane detection experiment

In the methane detection experiment, scattered light from the intense intra-cavity beam is collected by a gold-coated cylindrical mirror and cylindrical lens as shown on the right side of Fig. 1. Rayleigh and Mie scattering components of collected light are rejected by a bandpass filter (Andover Corporation; 840FS10-25) located in front of the detector. Only the Raman scattering is able to pass through the bandpass filter and onto the detector since the transmission wavelength is fixed at the Raman shifted wavelength of methane. The Raman wavelengths of methane pumped by the 675 nm wavelength of PBC are an 840 nm. The detector is a 28 mm diameter side-on Photo Multiplier Tube (PMT) (Hamamatsu Photonics; H8249-102, active area: 4 mm

× 25 mm) for which the rectangular active area enables effective detection of Raman light from source with a line-contour-reducing background noise. The detected signal, referred to as the mechanical chopper modulation frequency, is amplified by a lock-in amplifier (Stanford Research Systems: SR830DSP).

3. Results and discussion

3.1 PBC photon lifetime and intra-cavity power

The photon lifetime in an optical cavity representing intra-cavity loss has a significant impact on intra-cavity power. The accuracy of the Raman gas sensor investigated in this report must be very sensitive to changes in intra-cavity power. For this reason, the photon lifetime of the cavity was examined with two different ambient gases.

Obtained intra-cavity power measured using leakage light through mirror M2 was estimated to be 40 W. Since the cross-sectional area of the intra-cavity beam was $6.36 \times 10^{-5} \text{ cm}^2$, the peak power density reached $6.29 \times 10^5 \text{ W/cm}^2$.

Measured and theoretical photon lifetimes are summarized in Table 1. As shown there, the photon lifetime greatly varies with the ambient gas species. The photon lifetime is expressed as

$$t_p = \frac{1}{c \left\{ \left(\frac{a}{n} \right) + \left(\frac{1}{2nL} \right) \ln \left(\frac{1}{R_1 R_2} \right) \right\}}, \quad (1)$$

where, t_p is photon lifetime, c is the speed of light, a is the intra-cavity loss per unit length, n is the refractive index, L is the cavity length and R_1 , R_2 are the reflectivity of the cavity mirrors. In theory, the variation of photon lifetime mainly depends on Rayleigh scattering. However, there were differences between calculated and experimental values, due to residual intra-cavity loss other than Rayleigh scattering. This additional residual cavity loss could have been caused by imperfect filtering of included contaminations in the sample gas. It might also have been due to degradation of the cavity mirrors by accretion of contamination. Thus, intra-cavity power variation should be carefully monitored together with Raman signal for the calibration of gas concentration.

3.2 Methane detection experiment

Optical detection techniques for trace methane have been widely studied based on absorption spectroscopy.^{7,8)} This methane detection experiment was conducted to characterize the newly developed Raman scattering-based gas sensor. Raman scattering characteristics of methane exhibit very attractive properties with both a relatively large cross section and a large frequency shift. Methane has two major Raman shifted spectra, ν_1 and ν_3 , whose shifts are 2914 cm^{-1} and 3020 cm^{-1} , respectively. In this experiment, ν_1 was selected since the cross section of ν_1 was approximately double that of ν_3 . The spectral distance of these spectra pumped by 675 nm was larger than 7 nm in the 840 nm wavelength region. This is easy to distinguish by employing bandpass filter, even if the light source emits a relatively

Table 1 Raman scattering cross sections and photon life times.

Molecule	Rayleigh scattering cross section [cm ²]	Intra-cavity loss [1/cm] (Calculation)	Intra-cavity loss [1/cm] (Experiment)	Residual intra-cavity loss [1/cm]
N ₂	2.00×10^{-27}	5.38×10^{-8}	2.22×10^{-7}	1.68×10^{-7}
He	2.78×10^{-29}	7.50×10^{-10}	7.22×10^{-8}	7.14×10^{-8}

Table 2 Raman spectrum characteristics of methane.

Spectrum	Cross section [$10^{-48}\text{cm}^6/\text{sr}$]	Raman shift [cm^{-1}]	Wavelength pumped by 675nm [nm]
$\text{CH}_4(\nu_1)$	43.2	2914	840.3
$\text{CH}_4(\nu_3)$	24.3	3020	847.8

broad linewidth.

The developed methane sensor has been characterized by using atmospheric pressure gas mixtures containing 90 to 500 ppm methane diluted with N_2 gas as a buffer. The time constant of the lock-in amplifier was the reasonably fast response of 1 sec. Figure 2 shows that the optical scattering signal increased proportionally with increased methane concentration. Major sources of background signal were derived from Rayleigh scattering and stray light from the cavity mirrors, mirror holders and GRIN lens. The results show that the background signal was effectively rejected, thus the developed non-dispersive Raman measurement system could selectively detect the weak Raman signal.

The collection efficiency of generated Raman scattering is calculated as follows. Theoretical Raman scattering power: P_{th} is expressed as

$$P_{\text{th}} = \sigma N S I h^9, \quad (2)$$

where, Raman scattering cross section $\sigma = 1.25 \times 10^{-29} \text{ cm}^2$, the number of molecules per unit volume $N = 2.69 \times 10^{19} \text{ cm}^{-3}$, cross section of incident light $S = 6.36 \times 10^{-5} \text{ cm}^2$, the power density of incident laser $I = 6.29 \times 10^5 \text{ W/cm}^2$ and the effective imaged length of laser beam on the detector $h = 5 \text{ cm}$. Calculated Raman power generated by pure methane at 1 atm in this experiment was 67.6 nW at 840 nm. On the other hand, we can calculate detected Raman power: P_{ex} from the detector signal. It is expressed as

$$P_{\text{ex}} = \frac{s}{Atp}, \quad (3)$$

where, the voltage of the Raman signal for pure methane at 1 atm $s = 3.55 \times 10^3 \text{ V}$ in this experimental set up, the transmission of collection optics and the bandpass filter $t = 0.58$, the amplitude of the lock-in amplifier $A = 1995$, and the radiant sensitivity of PMT at 830 nm $p = 7.4 \text{ V/nW}$ in this experiment. The

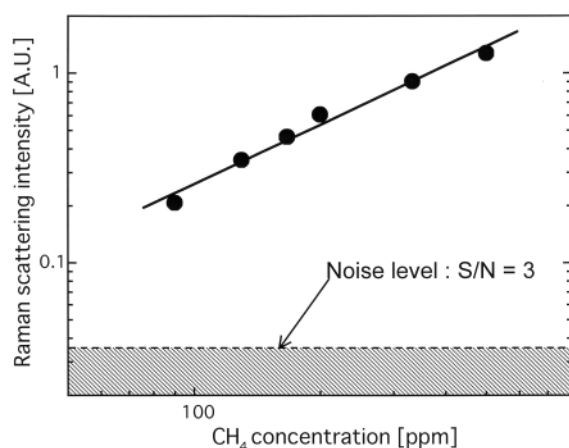


Fig. 2 Raman scattering intensity depends on methane concentration. Good linearity was shown in the 90 to 500-ppm concentration range.

collected Raman power was found to be 0.41 nW. Therefore, the collection efficiency of Raman scattering was 0.6 %. In the previous experiment, which employed an optical-fiber-coupled dispersive spectrometer, the collection efficiency was only 0.029 %.⁷⁾ Thus, a simple non-dispersive detection scheme could achieve improved collection efficiency.

4. Conclusion

In this study we investigated the performance characteristics of newly developed non-dispersive Raman-spectroscopy-based gas sensor employing PBC. Intra-cavity power was varied mainly due to Rayleigh scattering of the buffer gas species in the cavity. Accordingly, careful monitoring of intra-cavity power was required in case of trace gas concentration analysis using PBC as a spectroscopic light source. Realtime trace methane detection of less than 100 ppm was successfully demonstrated with a response time of 1 sec. Good linearity was also observed from the 90 to 500-ppm concentration range using a simple side collection optics whose collection efficiency was approximately 0.6 %. This system has been improved 60 times in comparison with previous experiments employing optical-fiber-coupled spectrometers. Technical problems of the sensor for field application are intra-cavity loss, a decrease in the signal-to-noise ratio, and degradation of the cavity mirror reflectivity by particles included in the sample gas. We inserted a 0.5 μm particle filter into gas delivery system, which was very effective in removing particles from normal laboratory air for at least one month of operation. However, complete rejection is impossible, so the admissible amount and size of particles should be carefully considered.

Such a Raman gas sensor may be very attractive for other trace gas detection, such as hydrogen detection, in situations where it is difficult to apply absorption spectroscopy.

References

- 1) I.A. Veselovskii, H.K. Cha, D.H. Kim, S.C. Choi, and J.M. Lee: *Appl. Phys. B* **71** (2000) 113.
- 2) Keith D. Evans, S. Harvey Melfi, Richard A. Ferrare, and David N. Whiteman: *Appl. Opt.* **36** (1997) 2594.
- 3) Wm.S. Heaps and J. Burris: *Appl. Opt.* **35** (1996) 7128.
- 4) S. M. Adler-Golden, N. Goldstein, F. Bien, M. W. Matthew, M. E. Gersh, W. K. Cheng, and F. W. Adams, *Appl. Opt.* **31** (1992) 831.
- 5) D. A. King and R. J. Pittaro: *Opt. Lett.* **23** (1998) 774.
- 6) S. Ohara, S. Yamaguchi, M. Endo, K. Nanri, and T. Fujioka: *Opt. Rev.* **10** (2003) 342.
- 7) H. Ashizawa, S. Ohara, S. Yamaguchi, M. Takahashi, M. Endo, K. Nanri, T. Fujioka, and F. K. Tittel: *Jpn. J. Appl. Phys.* **42** (2003) 1263.
- 8) D. Richter, D. G. Lancaster, R. F. Curl, W. Neu, and F. K. Tittel: *Appl. Phys. B* **67** (1998) 347.
- 9) M. J. Pelletier: in *Analytical applications of Raman spectroscopy*. Ed. M. J. Pelletier (Blackwell Science, London, 1999).