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Sensitivity improvement of midinfrared gas sensing system using single-wavelength quantum cascade laser and hollow-waveguide gas cell

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Abstract. The configuration of a gas analysis system using the combination of a single-wavelength quantum cascade laser and a hollow-optical-fiber gas cell was optimized to improve measurement sensitivity. On the basis of theoretical calculation, a 6-m looped fiber gas cell was introduced into the system to more sensitively measure the concentration of nitric monoxide (NO) gas. High-precision measurement is achieved by precisely scanning the wavelength of the laser around the sharp absorption peak of NO gas. Concentrations of NO gas as low as 100 ppb were successfully measured. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: 10.1117/1.OE.56.8.080503]

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For applications including environment monitoring, industrial quality control, and breath analysis for medical diagnosis, detecting gases with a concentration of sub-ppm to ppb order is frequently necessary. To satisfy this necessity, a variety of gas sensors based on semiconductor devices, microstructured materials, microgravimetric or calorimetric sensors, and so on have been proposed and developed.^{1,2}

Among these gas sensors, optical sensors offer the advantages of fast response and high sensitivity with minimal drift.³ In place of conventional multipass gas cells, hollow-core waveguides such as photonic crystal fibers (PCF),⁴⁻⁶ photonic bandgap fibers (PBGF),⁷⁻⁹ and glass-capillary hollow-optical fibers (HOF) with an inner metal coating^{10,11} have been used as a gas cell because a long optical path is obtained with an extremely small sample volume. Likewise, midinfrared absorption spectroscopy for detecting fundamental molecular vibration has received attention because of the development of quantum cascade lasers (QCLs), which emit much higher power than the lamp sources used so far. Midinfrared QCLs enable the development of a robust, compact, and highly sensitive gas-sensing

system.¹²⁻¹⁴ Various groups have developed gas-sensing systems by combining a midinfrared QCL and hollow-core waveguides.^{15,16} Table 1 summarizes the data shown in the literatures. In this letter, we propose a gas sensing system using an HOF as a gas cell and a single-wavelength QCL as a light source for robust, inexpensive, and highly sensitive gas sensing.

A previous study showed that there is an optimum length for an HOF used as a gas cell. It is determined by the transmission loss of the fiber and the absorption coefficient of the sample gas.¹⁰ Sub-ppm concentrations of nitric monoxide (NO) gas were successfully measured with a system comprising a Fourier-transfer infrared spectrometer (FT-IR) and a hollow-optical-fiber gas cell with a length of 2 m. Although most of the QCL-based gas-sensing systems proposed so far have used wavelength tunable lasers to obtain the absorption spectra of the target gas, such lasers are usually very expensive, and ones having an external cavity sometimes have environmental disturbance problems such as vibration. In this letter, we report the development of a robust, inexpensive, and highly sensitive gas-sensing system that uses a monolithic QCL that emits a single wavelength in the mid-infrared region. High-precision measurement is achieved by precisely scanning the QCL wavelength around the sharp absorption peak of the target gas.

Figure 1 shows a schematic of the measurement setup. The QCL (Hamamatsu, L12015) is a pulsed distributed feedback (DFB) laser with an oscillating wavelength of 5.26 μm , an emission linewidth of 0.2 cm^{-1} , a peak power of 50 mW, and a repetition frequency of around 120 kHz. The emitting wavelength was calibrated using an FT-IR with a resolution of 0.125 cm^{-1} . The laser beam is focused on the input end of the HOF used as a gas cell by an aspheric ZnSe lens with a focal length of 4.8 mm, and the output beam from the fiber is detected by an InSb detector. The input end of the fiber is sealed by a metal sleeve with a ZnSe window, and the sample gas flows into the fiber through the sleeve with a flow rate of 100 ml/min and the bore of the fiber is held in atmospheric pressure.

We used an HOF with an inner diameter of 2 mm to reduce the coupling loss at the input end because the beam quality of a QCL is usually low, which causes a high coupling loss as a result of the generation of higher order modes in the fiber. The fiber uses flexible polycarbonate tubing as a base, and silver film is formed on the inside of the tubing.¹⁷ The fiber also has a dielectric thin film on the top of the silver film to reduce the loss at the target wavelengths caused by the optical interference effect of the dielectric thin layer. To form fibers longer than 2 m, we connected fibers with lengths of 1 and 2 m by using plastic sleeves, and the fiber was looped with a radius of 20 cm.

We first investigated the optimum length of the HOF. Because of the transmission loss of the fiber, there is an optimum length giving the highest signal-to-noise ratio (SNR) in a hollow-fiber-based gas-sensing system.¹⁰ Under the assumptions that the power of the input light is P_0 and that the noise power spectrum is N , the SNR of the spectrum measured with an HOF with length l and an attenuation constant of α_L is expressed as

$$\text{SNR}(\lambda) = \frac{P_0(\lambda)[1 - e^{-2\alpha(\lambda)cl}]e^{-2\alpha_L(\lambda)l}}{N(\lambda)}, \quad (1)$$

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Table 1 Data shown in literatures that use a hollow waveguide as gas cell.

Fiber type	Literature	Light source	Wavelength	Fiber size (dia., length)	Sample gas	Concentration
PCF	Ref. 5	ASE	1530 nm	62 μm , 25 m	C_2H_2	0.5%
PBGF	Ref. 7	LED	1550, 1300 nm	10 μm , 10 m	C_2H_2	10 mbar
	Ref. 8	Tunable LD	1400 to 1700 nm	12 mm	CH_4	10 ppm
	Ref. 9	Super-cont. source	3 to 3.8 μm	50 μm , 5 to 7 m	C_2H_2	0.9 ppm
HOF	Ref. 10	FT-IR	5.2 μm	2 mm, 2 m	NO	<1 ppm
	Ref. 11	FT-IR	13 to 15 μm	2 mm, 0.5 m	C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_6\text{H}_4(\text{CH}_3)_2$	<100 ppb
	Ref. 15	External-cavity QCL	7.7 to 8.2 μm	2 mm, 0.5 m	$\text{CH}_3\text{CH}_2\text{Cl}$, CHCl_3	ppb order
	Ref. 16	External-cavity QCL	7 to 7.8 μm	0.5 mm, 3 m	VOC's	ppm order
This letter		DFB-QCL	5.2 μm	2 mm, 6 m	NO	100 ppb

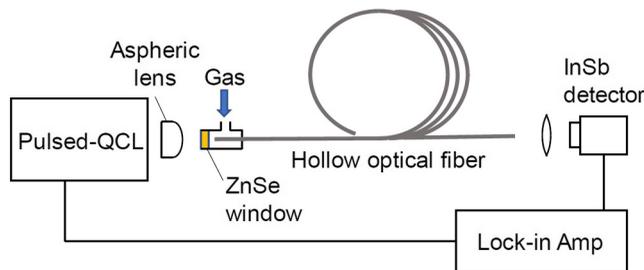


Fig. 1 Schematic of measurement setup.

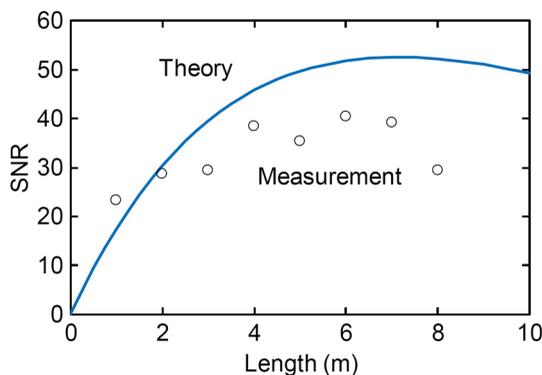


Fig. 2 Theoretical SNR of analysis system for NO gas with 2-mm-diameter hollow-fiber gas cell as function of fiber length. Open circles are SNRs of measured spectra obtained with different fiber lengths.

where α and c are the absorption constant and the concentration of sample gas, respectively. This equation shows that SNR depends on the absorption of the gas and the attenuation loss of the fiber because $P_0(\lambda)/N(\lambda)$ is inherent to the measurement system. From the results of a preliminary experiment, we found that the P_0/N of our system was nearly constant in the 5.26- μm wavelength region and was around 1370. From this value and from the attenuation loss of the fiber, which is around 2.5 dB/m, we calculated the SNR as a function of the fiber length, and the result is shown in Fig. 2. In the calculation and the following experiments, we used NO as the sample gas because it is frequently

used in atmospheric monitoring and breath analysis. We set the attenuation constant of NO at a wavelength of 5.26 μm to 5.68 cm^{-1} on the basis of the results of the preliminary experiment. From this calculated result, we found that the maximum SNR is obtained with a fiber length of around 6.5 m. We also found that this optimum length does not change with the gas concentration when it is lower than 10 ppm. This optimum length should change if the attenuation constant α_L is different from that of the fiber used in our system. For the fiber with lower attenuation constant, the optimum length should be larger.

In the gas analysis experiment, to obtain the spectral shape of the absorption peak of NO gas, the oscillation wavenumber of the QCL was first scanned from 1903.1 to 1903.2 cm^{-1} by changing the operating temperature of the Peltier-cooled QCL from 23.3°C to 24.3°C in 0.02°C steps. By using this wavelength-scan-based method, one can perform more precise measurement compared to common QCL-based methods using a fixed single wavelength because one can collect information on such as baseline fluctuation. Figure 3 shows the absorption peak spectra of 1-ppm NO gas measured with 1- and 6-m fibers and with nitrogen gas used as a background spectrum. The dots are measured data and the solid line is a Gaussian curve that was fitted to the measured data and it took around 3 min to obtain a single spectrum in the measurement. With this scanning range, only one absorption peak was observed at around 1903.14 cm^{-1} for both fibers. We confirmed that this peak was one of the absorption peaks of NO by measurement using FT-IR. By comparing the data shown in Figs. 3(a) and 3(b), it is found that the SNR was much higher with the 6-m fiber. The measured SNRs for different fiber lengths are shown in Fig. 2. The SNR was maximized with a fiber length of 6 m, as expected from theoretical calculation although the measured SNRs were somewhat lower than the theoretical ones. This discrepancy may be due to the bending losses of the fibers and the coupling losses between the fibers connected by plastic sleeves.

Figure 4 shows the calibration plots for NO gas measurement with different fiber lengths. The open circles are average intensities of the absorption peak for three measurements and it is seen that the absorbance linearly increased with the

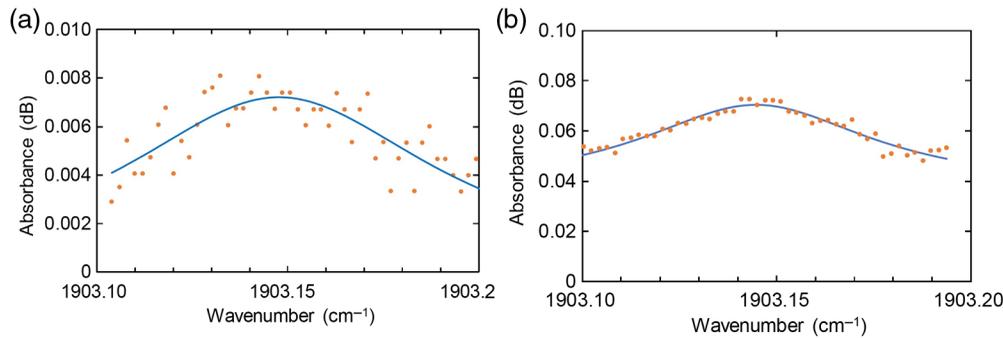


Fig. 3 Absorption peak spectra of 1-ppm NO gas measured with fiber gas cells with lengths of (a) 1 and (b) 6 m.

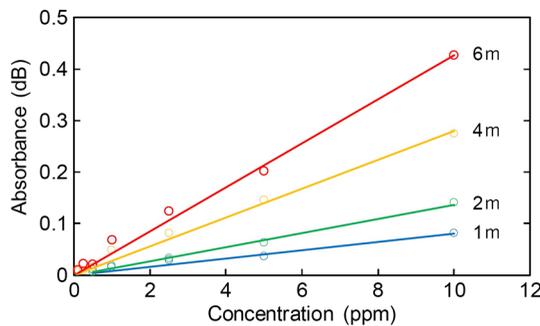


Fig. 4 Calibration plots for NO gas measurement with different fiber lengths.

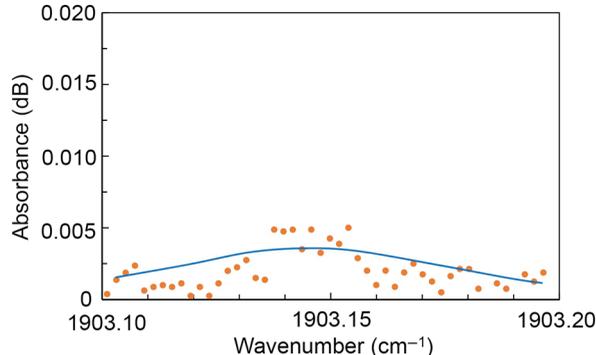


Fig. 5 Absorption peak of 0.1-ppm NO gas measured with 6-m gas cell.

fiber length. From this result, we found that the measurement error for a 1-ppm concentration with the 6-m fiber gas cell was around 10%.

Figure 5 shows the absorption peak of 0.1-ppm NO gas measured with the 6-m gas cell. Although the SNR of measured data was lower than those shown in Fig. 3, a peak is seen at around 1903.15 cm^{-1} . We confirmed that the concentration as low as 100 ppb was successfully detected and this was the lowest detection limit of our measurement system.

In conclusion, optimization of the configuration of a gas analysis system using the combination of a single-wavelength DFB-QCL and a hollow-optical-fiber gas cell improved measurement sensitivity. The introduction of a 6-m looped fiber gas cell enabled measurement of sub-ppm

concentrations of NO gas. High-precision measurement is achieved by precisely scanning the QCL wavelength around the sharp absorption peak of the target gas. Concentrations of NO gas as low as 100 ppb were successfully measured. However, in our present system, it takes around 3 min to obtain a single spectrum. This is mainly because the system should wait for the temperature being stabilized after changing it stepwise. Therefore, it is expected that the measuring time is drastically shortened by changing the temperature continuously. This is possible because the time for obtaining data for detecting power is very short ($<10 \text{ ms}$) and we are now working on improvement of our system.

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