

# High Sensitive Gas Sensing with Low Power Consumption Quantum Cascade Lasers

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Gas sensing using Quantum Cascade Lasers (QCLs) as a light source is expected to offer a high sensitivity, a short measurement time, and a good portability compared to conventional sensing methods. We have studied low power consumption 7  $\mu\text{m}$  wavelength QCLs for realizing a portable sensing apparatus. The performance of our Distributed Feedback (DFB) QCL in gas sensing was evaluated by measuring the mid-infrared absorption spectrum. In this evaluation, a multi pass type gas cell was used for gas absorption, and for sweeping lasing wavelength of QCLs, the injection current of the DFB-QCL was swept. First, we measured the absorption spectrum of the room air, and found the absorption lines of water and methane to agree well with our simulation results. We then evaluated the sensitivity of the apparatus using a methane gas of a certain amount of concentration, and achieved a high sensing sensitivity of 17 ppb at a DFB-QCL power consumption of less than 3 W.

Keywords: semiconductor lasers, quantum cascade lasers, low power consumption, gas sensing, mid-infrared

## 1. Introduction

Recently, gas sensing is performed in various fields such as environmental protection, industrial process, agricultural analysis, medical care, and security and safety. In these fields, portable gas sensing apparatuses that enable high-sensitive, real-time, and/or on-site measurements are required. Figure 1 shows the correlation between the detection sensitivity and measurement time of existing gas sensing apparatuses. High-sensitive methods, such as Fourier transform infrared spectroscopy (FT-IR) and mass spectrometry, take time for measurement. Meanwhile, the sensitivity of non-dispersive infrared absorption (NDIR) and semiconductor sensors (considered to be real-time solutions) is only below about 0.1%. In addition, in the case of FT-IR and mass spectrometry, gas samples must be brought back to a laboratory for measurement; conducting on-site measurement is difficult. To overcome these problems, gas sensing using a quantum cascade laser (QCL), which is a kind of semiconductor laser, as a light source, has attracted much attention. This is because gas sensing using a QCL is expected to enable high-speed, high-sensitivity, and high-portability sensing, which has been difficult with conventional gas sensing methods. High-sensitive measurement is achieved primarily because QCLs can lase in the mid-infrared region (wavelength: 3–20  $\mu\text{m}$ ) as discussed below. Gaseous molecules absorb mid-infrared light and are subject to vibrational excitation. The wavelength at which absorption occurs depends on the molecules, and the absorption intensity depends on the gas concentration. Therefore, gas sensing can be achieved by measuring the absorption spectrum of the target gas. Many molecules have absorption lines in the mid-infrared region (i.e. fingerprint region of molecules), and absorption of mid-infrared light is much larger than the other wavelength regions due to absorptions by the fundamental vibrations of molecules. Besides, as named “atmospheric window,” absorption by water that is present in large amounts in the atmosphere is also low in the mid-infrared region. These

characteristics help achieve high-sensitive sensing. Furthermore, gases, ranging from those with low molecular weight and prevalent in the atmosphere to those consisting of complicated organic molecules, are subject to absorption at around 7–12  $\mu\text{m}$  in the mid-infrared region. Thus, gas sensing in the mid-infrared region is highly useful, and its applications in various fields have been actively examined. It should be noted, however, that until QCLs were developed, there had been few lasers that lased even at mid-infrared wavelengths. The mainstream solution was to use an FT-IR, which utilizes an interferometer and white light derived from ceramics, tungsten, or dispersive infrared spectroscopy in which a diffraction grating is used for spectrometry. QCLs can operate in a single mode by introducing a DFB structure with a diffraction grating into a chip.<sup>(1)-(4)</sup> This enables the measurement exclusively for the

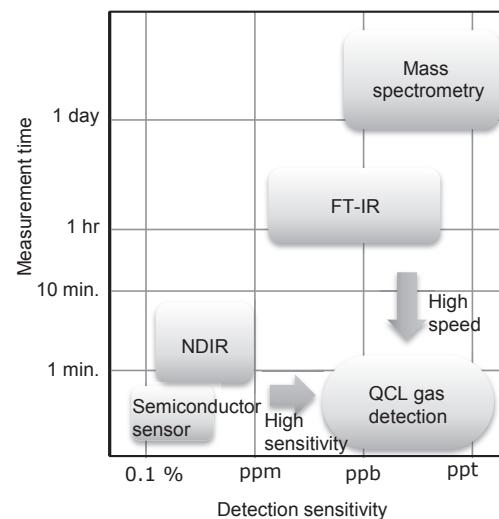


Fig. 1. Diagram of the correlation between detection sensitivity and measurement time of existing gas sensing apparatuses

absorption lines of target gases. It has been reported that the line width (i.e. the lasing wavelength fluctuation that affects the resolution of absorption line measurement) of QCLs is generally  $10^{-6}$  cm $^{-1}$  or less.<sup>(5)</sup> This means that the resolution of QCL-based gas sensing is considerably higher than that of FT-IR (several cm $^{-1}$ ). Thus, QCLs enable the measurement of absorption lines for respective molecules with high resolution even if the absorption lines of many molecules are present in the narrow region of mid-infrared wavelengths, achieving considerably high-sensitive measurement compared with conventional light sources.

Although QCLs offer an advantage in terms of the measurement mechanism of gas sensing as discussed above, commercially available QCLs have high power consumption of several W. Therefore, a large amount of power supply is required to operate QCLs, and most of the input power is released as heat, leading to the necessity for a large cooling system (e.g. a water-cooled system) to control the QCL temperature. For these reasons, portable gas sensors using QCLs have not been realized. To address this issue, we studied a reduction in power consumption of a QCL, and we have recently developed a low-power-consumption (< 1 W) QCL in the 7  $\mu\text{m}$  wavelength region.<sup>(6)</sup> This paper reports on the experimental results of the high-sensitive gas sensing using our low power-consumption DFB-QCL as a light source. For these experiments, we constructed our original gas-sensing measurement system as mentioned in the next section.

## 2. Gas Sensing Experimental Apparatus

Recently, various QCL-based gas sensing methods have been proposed.<sup>(7)</sup> To increase the sensitivity, it is necessary to increase the optical path length. We selected a method that employed a multiple reflection gas cell.

Figure 2 shows a schematic diagram of the gas sensing experiment apparatus. Light emitted by a 7  $\mu\text{m}$ -band DFB-QCL is collimated using a zinc selenide (ZnSe) lens, and then the beam diameter is reduced to about 2 mm with two parabolic reflectors. The beam is then led to a gas cell by using three flat mirrors for adjusting the optical axis. A Herriot type multi-reflection cell<sup>(8)</sup> is used as a gas cell. The two high reflectance mirrors placed on each end of the gas cell (distance between the mirrors: 0.32 m) causes 238 reflections to obtain a total optical path length of 76 m. To obtain such a long optical path, it is necessary to produce a beam with an adequately small diameter of 2 mm when it enters into the gas cell. The beam from the gas cell is detected by a liquid nitrogen-cooled HgCdTe photodiode (hereafter, “MCT detector,” as it is commonly used). Among the photodetectors for the mid-infrared region, the MCT detector has the highest sensitivity at the target wavelength region (7  $\mu\text{m}$ ). Its detection speed is high enough (in orders of  $\mu\text{ sec.}$ ) to respond to the DFB-QCL’s wavelength sweep. Thus, the MCT detector was optimal for this experiment. The output voltage from the MCT detector is measured using a multimeter and recorded in a computer. Regarding the DFB-QCL’s lasing wavelength, a barium fluoride ( $\text{BaF}_2$ ) window is arranged in front of the gas cell as a beam splitter, and the wavelength of the reflected light

from the beam splitter is monitored on a real-time basis using a wavemeter. The sample gas is introduced to the gas cell, and the flow rate is controlled using a mass flow controller and scroll pump. The pressure in the gas cell is measured using a vacuum gauge. When the gas pressure was maintained at 0.1 atm, the gas flow rate was approximately 290 sccm. The gas temperature is measured using a 100  $\Omega$  platinum resistance thermometer.

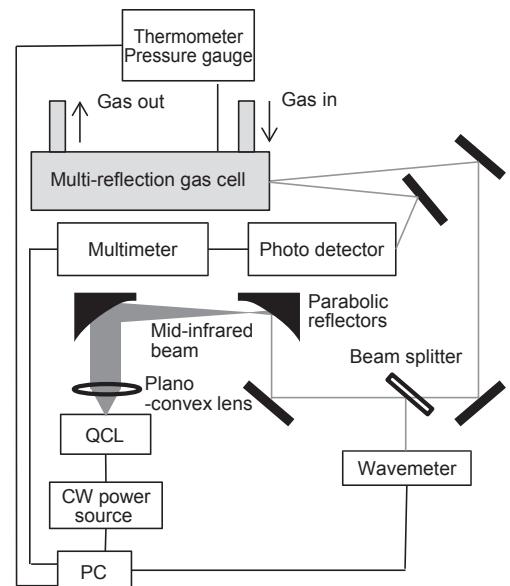


Fig. 2. Schematic diagram of the experimental apparatus

When the continuous wave (CW) current injected into the DFB-QCL is swept with its bottom temperature constant, the temperature of the QCL’s emission layer changes, resulting in sweeping of the lasing wavelength. In fact, the lasing wavelength of our DFB-QCL was measured with the CW current swept in the lasing region. Figure 3 shows the results. The sweep rate of the lasing wavelength was 0.23 nm/mA on average, and the sweep range was 30 nm. Based on this current-wavelength relation, we

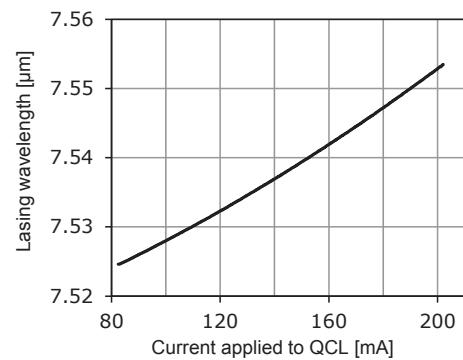


Fig. 3. Dependence of lasing wavelength on the current applied to DFB-QCL

measured the power of the transmitted light as a function of a wavelength by sweeping the current and measure the power of the light transmitted from the gas cell at each current level.

We carried out this measurement with the gas cell filled with the target gas, and then filled with nitrogen, which is inactive in the infrared region as a background. Then, dividing the intensity of the transmitted light of the target gas by that of nitrogen (background gas) at each wavelength, we can finally obtain an infrared absorption spectrum which is the absorption rate of the target gas as a function of wavelength.

### 3. Measurement Results

First, the absorption spectrum of the air in the laboratory was measured because (i) the air has drawn much attention as a target of gas sensing, (ii) numerous molecules present in the air are subject to absorption near the 7  $\mu\text{m}$  lasing wavelength of the DFB-QCL used in this research (as shown in Fig. 4), and (iii) air is safe and easy to handle.

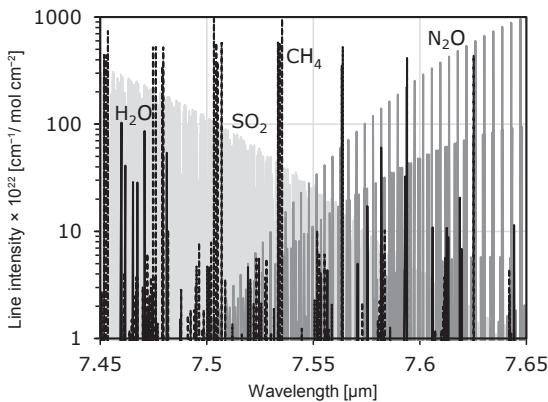


Fig. 4. Line intensity of absorption of molecules present in the air  
Source of numerical data: HITRAN<sup>(9)</sup>

As a result of measurement, many absorption lines were observed in the absorption spectrum as shown in Fig. 5 (a). To verify the measurement accuracy, the absorption spectrum was simulated using HITRAN,<sup>(9)</sup> which is often used as a database of mid-infrared absorption lines. The simulation results based on the optical path length, gas pressure, and temperature used in this measurement as well as the standard air composition (H<sub>2</sub>O: 1.190000%, CO<sub>2</sub>: 0.033000%, O<sub>3</sub>: 0.000002%, N<sub>2</sub>O: 0.000028%, CO: 0.000047%, CH<sub>4</sub>: 0.000148%, O<sub>2</sub>: 20.700001%, SO<sub>2</sub>: 0.000008%, NH<sub>3</sub>: 0.000001%, N<sub>2</sub>: 78.076466%) were compared with the actual measurement values. As shown in Fig. 5 (a), the simulation results agreed well with the actual measurement values in terms of the wavelengths of the absorption lines of gases contained in the air. Also, the simulation results broadly agreed with the actual measurement values in terms of the intensity of each absorption line. Based on the above discussion, we confirmed that

high-accuracy gas sensing is achieved using our DFB-QCL in the 7  $\mu\text{m}$  wavelength region. The maximum power consumption of the DFB-QCL during the measurement was as low as 3 W corresponding to the longest wavelength (i.e. corresponding to the largest injection current) as shown in Fig. 5 (b). These results confirm that our low power consumption DFB-QCL demonstrates sufficient performance as a light source for gas sensing. The differences in intensity between the experimental values and simulated values are presumably attributed to the difference between the air composition used for simulation (a standard model) and the actual air composition used in the actual measurement. In particular, the absorption by water that was frequently observed is considerably changed by the water composition fluctuation in the indoor air. Therefore, in the second step, a gas of a certain concentration was used as a sample to quantitatively verify the accuracy of this gas sensing measurement.

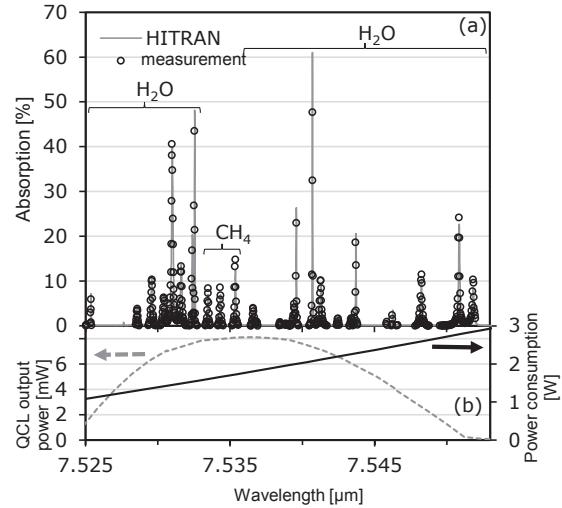


Fig. 5. (a) Infrared absorption spectrum of the room air  
○: Measurement results in this research  
Solid line: Simulation by HITRAN  
(b) Dependence of QCL optical output, power consumption, and sweep wavelength during absorption spectrum measurement (a)

Specifically, CH<sub>4</sub> diluted with N<sub>2</sub>, which is inactive in the infrared region, was used. Regarding the concentration, 1 ppm (actual concentrate of 1.01 ppm) CH<sub>4</sub> gas which is the lowest level of concentration among the commercially available CH<sub>4</sub> gases is adopted for this measurement. This concentration of the CH<sub>4</sub> gas was close to that of the air (1.48 ppm mentioned above) so that it seemed to be detected without difficulty using our measurement system.

Figure 6 shows the absorption spectrum of CH<sub>4</sub> (1 ppm) measured using the same method and DFB-QCL chip as in the abovementioned air measurements. The experimental values agreed well with the simulation results in terms of the wavelength, intensity, and absorption line width. Thus, we confirmed that gas concentration can be measured quantitatively using our low power consumption DFB-QCL.

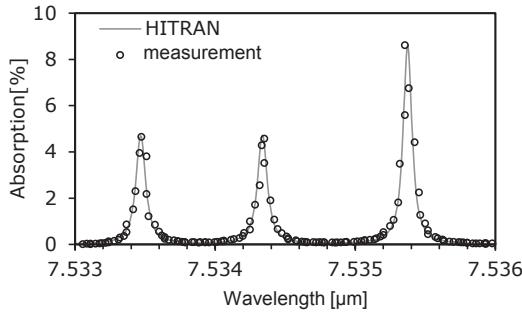


Fig. 6. Infrared absorption spectrum of  $\text{CH}_4$  diluted to 1.01 ppm using nitrogen  
 ○: Measurement results in this research  
 Solid line: Simulation by HITRAN

Next, we evaluated the gas sensing sensitivity using the abovementioned  $\text{CH}_4$  as a target gas. Here, an overview of the Allan variance evaluation,<sup>(10),(11)</sup> which is generally used to evaluate gas sensing sensitivity using a laser as a light source, is explained. The variance of the gas concentration obtained when repeated measurements are conducted at a fixed concentration is plotted against the integration time of each repeated measurement on a log-log scale. This is called an Allan plot. When the measurement error is derived solely from the frequency-independent white noise, the variance decreases with an inclination of  $-1$  against the integration time in the Allan plot. In a prolonged measurement, the drift of the measurement data becomes significant due to instability of the light source, detector, gas temperature, pressure, optical system, etc., resulting in increased variance. Thus, the variance becomes minimal at a certain integration time; the sensitivity at this point can be evaluated as the sensitivity limit of the measurement apparatus.

Figure 7 shows the Allan variance evaluation results for this apparatus. Figure 7 (a) shows the continuous measurement results of  $7.5355\text{ μm}$  absorption lines among the  $\text{CH}_4$  absorption lines that were observed in Fig. 6. These lines were measured repeatedly at an interval of 0.4 seconds. Figure 7 (b) shows the Allan plot derived from Fig. 7 (a). The stability without the influence of the drift was confirmed up to 100 seconds in the integration time. The minimum value was recorded at 102 seconds in the integration time; the concentration at this point was 17 ppb. Thus, the sensitivity limit of this entire apparatus was evaluated to be 17 ppb for  $\text{CH}_4$ . This result demonstrates a sensitivity as high as that in the previous QCL gas-sensing experiment reported by other research group.<sup>(7)</sup> Based on these results, we confirmed that our DFB-QCL with low power-consumption (3 W or less) could be used as a light source for a high-sensitive gas detection. The highest sensitivity was achieved at the integration time of 102 seconds, and a sensitivity of 60 ppb was achieved at the integration time of 0.4 seconds, which are short enough to enable real-time gas sensing.

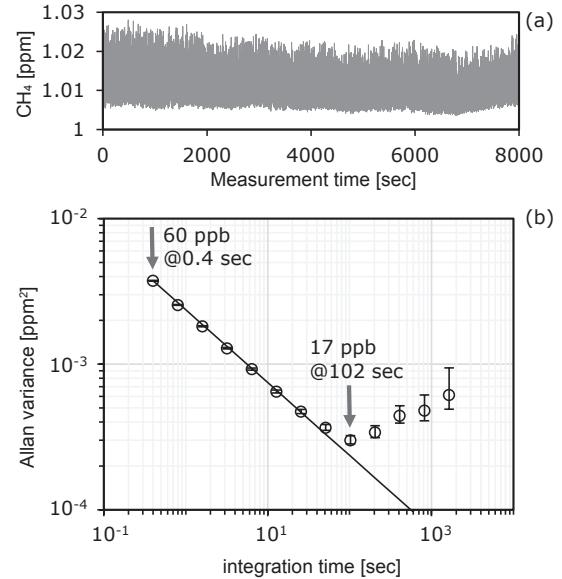


Fig. 7. Allan variance analysis during 1.01 ppm  $\text{CH}_4$  absorption measurement  
 (a) Changes during prolonged measurement  
 (b) Allan variance plot

#### 4. Conclusion

We evaluated the performance of our low power consumption DFB-QCL which had been developed as a light source for high-sensitive and portable gas sensors. The DFB-QCL achieved a high sensitivity detection of 17 ppb for  $\text{CH}_4$  with a low power consumption of 3 W or less. In the future, we will identify the contributing factors to the variance of measured gas concentration (e.g. light source output, wavelength, detector's sensitivity, sample gas pressure, and instability of gas concentration) in order to improve measurement systems and reduce measurement time.

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