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Sensitive measurements of trace gas of formaldehyde using a mid-infrared laser spectrometer with a compact multi-pass cell

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HIGHLIGHTS

- A compact multi-pass cell with a pair of cylindrical mirrors for sensitive detection of trace gases in emission from combustion was constructed.
- The cell path-length was 9.8 m and its volume was 0.13 L.
- The cell was applied to detection of formaldehyde (HCHO), which is harmful to the environment.

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ABSTRACT

A compact multi-pass cell with a pair of cylindrical mirrors for sensitive detection of trace gases in emission from combustion was constructed. The cell path-length was 9.8 m and its volume was 0.13 L. Each mirror shape was a square with a side length of 25.4 mm and the mirrors were placed 100 mm apart. The cell was applied to detection of formaldehyde (HCHO), which is formed during fuel combustion and is harmful to the environment. The direct absorption spectrum in the range 2979.06–2981.2 cm^{-1} was recorded with a mid-infrared distributed feedback (DFB) interband cascade laser. The recorded spectrum of HCHO was in good agreement with a spectrum simulated using the HITRAN 2012 database. An absorption line at 2979.663 cm^{-1} (4.26×10^{-21} cm^2 $molecule^{-1}$ cm^{-1}, ν_5, 11_{84}–10_{73}), which showed the strongest absorption in the emission frequency range of the DFB interband cascade laser, was selected for HCHO detection. We also confirmed that there were no interferences of absorption peaks of major combustion products in the selected HCHO absorption peaks. At a signal-to-noise ratio of two and 3 kPa using *2f* wavelength modulation spectroscopy at less than 1 MHz bandwidth, the limit of detection for HCHO was 73 ppb by volume.

1. Introduction

Real time measurements of trace gases using laser absorption spectrometry (LAS) provide important information for reducing emissions of gases from fossil fuel combustion. The measurement sensitivity for LAS is dominated by the concentration of the measured gas, the absorption cross section of absorbing species, and the total light path length, based on the Beer-Lambert law. For high-sensitivity measurements, it is desirable to combine advanced spectroscopy techniques, such as wavelength modulation spectroscopy (WMS) [1] and cavity ring-down spectroscopy [2], with strong ro-vibrational molecular transitions.

Optical cells with long path lengths can be used for high-sensitivity measurements of trace gases. Studies using long path cells have been performed in a number of areas, including atmospheric measurements, combustion processes, and portable emission measurement systems (PEMS) for on-board real-time measurements of automobile exhaust. Many fields require compact measuring devices, and the compact multi-pass cell has become important. Especially, for PEMS for measuring automobile exhaust, the compact cell with a long path length is required, because a small size pump can be set for the small size cell, which leads to saving electricity consumption used in the total system. The most frequently used multi-pass cells are the White cell [3] and the Herriott cell [4]. Cells with denser spot patterns and smaller size than the White and the Herriott cells have been produced with two cylindrical mirrors [5–8]. Hao et al. developed a model for a cell with two cylindrical mirrors [5]. Silver investigated the behavior of a multi-pass cell, including light patterns and beam density, when one cylindrical mirror was rotated with respect to the other mirror [6]. Based on the model of Hao et al., Kasyutich

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et al. constructed a cell with a path length of 15.18 m using cylindrical mirrors (∅76 mm) spaced 110 mm apart [7]. More recently, Das et al. developed a cell with a path length of 50.31 m using 40 mm diameter mirrors spaced 88.9 mm apart [8]. A compact dense-pattern multi-pass cell has been constructed using two concave spherical mirrors to give an effective optical path length of 26.4 m [9].

For trace gas measurements, the selection of a measurement wavelength that coincides with the ro-vibrational molecular transitions for fundamental vibrational modes in the mid-infrared region is essential because these transitions show strong absorptions. Advances in semiconductor laser technology, including development of high-quality narrow bandwidths, have contributed to the success of trace gas measurements in the mid-IR region [10–12]. The 3 μm wavelength region is particularly important as it contains the C–H and O–H vibrational modes, which show strong absorptions. There are few light sources that are suitable for the 3 μm region, and quasi-phase-matched difference-frequency generation systems have been widely used [13]. Recently, distributed feedback (DFB) interband cascade lasers, which directly emit light in the 3 μm region with narrow line width of less than 1 MHz and good stability, have been used for high sensitivity measurements of trace gases. The 3 μm region is important for high sensitivity measurements of hydrocarbons in combustion emission, because there are many hydrocarbon absorption bands in the 3 μm region [14]. For example, formaldehyde (HCHO) is one of the important intermediate species in the oxidation of the hydrocarbons [15], and is present in industrial exhaust gas [16]. Because HCHO is harmful to the environment, measurements of HCHO are very important for environmental monitoring. Several studies have conducted measurement of HCHO using LAS in the mid-infrared region [17–21]. Lundqvist et al. measured HCHO at 3493 nm and their detection limit was 1 ppm [17]. Wang et al. observed HCHO at high temperatures in shock tube kinetic study at 3453 nm [21]. HCHO measurements with WMS and the multi-pass cell were also performed at 3.6 μm [18,19] and 5.68 μm [20]. Detection limit was achieved to be 6 ppb [19] at 2778.5 cm^{-1} (3.1×10^{-20} cm^2 - $\mathrm{molecule}^{-1}$ cm^{-1}, ν_1, $5_{50}-5_{51}$).

In this study, a compact multi-pass cell was developed using two cylindrical mirrors separated by a distance of 100 mm, which gave an effective path-length of 9.8 ± 0.1 m. This cell was coupled with a mid-IR DFB interband cascade laser in the 3.3 μm range and applied to measurements of trace gaseous HCHO. A second derivative (2*f*) WMS technique was used to detect HCHO. To utilize the spectroscopic measurements system for the PEMS for measuring HCHO in combustion exhaust, the compact optics system (45 cm × 45 cm square) was constructed with keeping the high-sensitive level to detect HCHO in combustion exhaust (~ ppm level) [16].

2. Development of the multi-pass cell

The theory behind a multi-pass cell with two cylindrical mirrors has been described by Kasyutich and Martin [7]. A schematic diagram of the multi-pass cell is shown in Fig. 1. A cell such as this uses a cylindrical mirror M_1 with a focal length f_1 and a central input/output hole. An *xy*-plane is set at the central hole of M_1, and a horizontal axis against the *xy*-plane is defined as the *z*-axis. The position $z = 0$ is at the center of the hole in M_1, and a cylindrical mirror M_2 with a focal length f_2 is set at $z = d$ and placed parallel to M_1 at a rotational angle $\beta \neq 0$. An input beam is introduced into the cell through the hole in M_1 at an angle α in the *xz*-plane. When the radii of the curvatures of the two cylindrical mirrors, the distance between the mirrors, and β are adjusted adequately, the *N*th reflected beam exits the cell at an angle $-\alpha$ on the *xz*-axis through the hole in M_1. The parameters for determining the beam patterns (e.g. radii of the curvatures, mirror placement distance, and β) can be obtained by calculating the ray matrix formalism [22].

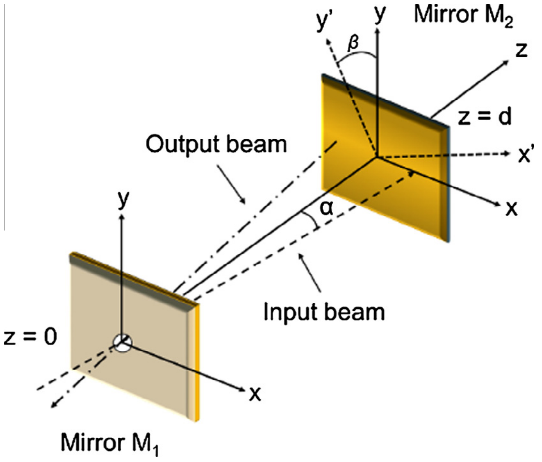

Fig. 1. Geometry of the cell with two cylindrical mirrors.

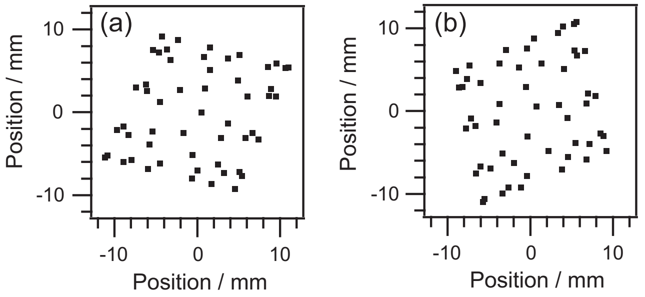

Fig. 2. Calculated spot pattern of 106 passes on (a) mirror M_1 and (b) mirror M_2 at $d = 100$ mm, $f_1 = f_2 = 100$ mm, $\beta = 53.8°$ and $\alpha = 4°$.

Using this theory, we constructed a compact multi-pass cell equipped with two 25.4 mm square cylindrical mirrors that gave a path length of 9.8 ± 0.1 m. Calculated spot patterns expected for 106 passes (total path length = 10.6 m) with cylindrical curvatures of $f_1 = f_2 = 100$ mm, $\alpha = 4°$ and $\beta = 53.8°$ are shown in Fig. 2(a) for M_1 and 2(b) for M_2 at $d = 100$ mm. The diameter of the central hole of M_1 was 4 mm, and light passed through this. Both M_1 and M_2 were coated with gold and had reflectivity of 97%. Because the light intensity of the output reduces exponentially with the number of reflections, high-reflectivity mirrors are required to achieve very long optical path lengths with sufficient light intensity. Although it is necessary to count the number of spots to determine the path length, this is difficult in practice. In this case, the laser intensity was modulated, and the phase shift induced by the path in the cell was measured as described previously [8]. The same procedure was performed and the path length was determined by the phase difference between the input and output beams, which gave a path length of 9.8 ± 0.1 m. There was a discrepancy between the measured and the calculated path lengths, which arose from the precision of the curvatures of the cylindrical mirrors or the parallelism of the two mirrors. Mirror mounts made of stainless steel were used. M_2 was set in a rotating mirror holder in the cell so that β (Fig. 1) could be adjusted. The cell body was made of quartz glass so that spots on the mirrors could be visualized.

3. Experiments

The experimental apparatus is shown in Fig. 3. A 3.356 μm DFB interband cascade laser (Nanoplus, Gerbrunn, Germany) with a