Probing methane in air with a midinfrared frequency comb source

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We employed a midinfrared frequency comb source for methane detection in ambient air. The transmitted spectra over a bandwidth of about 500 nm were recorded with an optical spectrum analyzer under various experimental conditions of different path lengths. The normalized absorption spectra were compared and fitted with simulations, yielding quantitative values of concentrations of methane and water vapor in the ambient air. The 3σ detection limit was \(\sim 6.6 \times 10^{-7} \text{ cm}^{-1}\) in ambient air for a broad spectral range, achieved with a path length of \(\sim 590 \text{ m}\). This approach provides a broad spectral range, a large dynamic range, high sensitivity, and accurate calibration. The performed analysis of the residuals shows that an excellent agreement between the measured and calculated spectral profiles was obtained.

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1. INTRODUCTION

Midinfrared (MIR) gas-sensing techniques are being developed actively to fulfill the large demand in many fields of science and technology, such as environmental studies, medical diagnostics, geosciences, and energy industries [1,2]. In particular, the C–H stretching fundamental vibrational bands are in the wavelength range of \(3 \sim 4 \mu\text{m}\), and their unique spectroscopic fingerprints, which are present in a large number of molecular species, are utilized for the trace detection of methane, acetone, and many other complex hydrocarbons. These fundamental bands in the MIR are typically at least two orders of magnitude stronger than the respective overtone bands in the near infrared [3]; thus, the detection sensitivity of trace gases can be greatly enhanced with the MIR spectroscopic methods compared to the equivalent near infrared techniques in general.

Simultaneous detection of several gas species requires widely tunable continuous-wave laser sources or proper broadband pulsed laser sources. The broadband frequency comb sources in the MIR have emerged, and various methods of MIR frequency comb spectroscopy have been implemented for gas-sensing applications [3,4]: cavity-enhanced MIR frequency comb Fourier transform spectroscopy [5,6], MIR dual-frequency comb spectroscopy [7–10], virtual-image phased array spectroscopy with a MIR frequency comb [11–14], intracavity spectroscopy with a MIR frequency comb source [15], Vernier spectroscopy with a MIR frequency comb [16], MIR upconversion spectroscopy [17], and frequency agile MIR dual comb spectroscopy [18]. These MIR frequency laser sources emit coherent broadband pulse trains with high power, which facilitates propagation over long distances, cavity enhancement, and coherent detection.

In this paper, we utilized a MIR frequency comb source as a high-brightness laser source and coupled this radiation into a homebuilt multipass cell having a path length of \(\sim 584 \text{ m}\). The spectra were recorded with an optical spectrum analyzer (OSA). This detection scheme was also used for the trace gas sensing in open air with paths of up to \(\sim 40 \text{ m}\) in length.

2. EXPERIMENT SETUP

The schematic of the experimental setup is presented in Fig. 1. The MIR frequency comb source (Menlo Systems, Mid-IR Comb) is based on difference frequency generation with fiber lasers [19], the repetition rate is \(\sim 250 \text{ MHz}\), the pulse duration is \(\sim 80 \text{ fs}\), the output power is \(\sim 300 \text{ mW}\), and the spectral tuning range is from \(\sim 2.8 \mu\text{m}\) to \(\sim 3.6 \mu\text{m}\) when adjusting the optical delay between the pump and signal pulses. Following mode-matching lenses, the MIR beam was split by a 50:50 beam splitter, and the transmitted part was coupled into the
The composite mirrors are divided into three parts: two 50 mm composite mirrors with radii of curvatures of 1 m. The composite mirrors were then put into a chamber with input and output ports for high-reflection regions, one is in the MIR range (5.7–36 μm). The mirror coating has two different path lengths of about 580 m. The entrance and exit hole of 5 mm diameter can be seen in the top left part of the right-side mirror.

The confocal multipass cell consists of two 50 mm × 50 mm composite mirrors with radii of curvatures of 1 m. The composite mirrors are divided into three parts: two 25 mm × 25 mm squares and one 25 × 50 mm² rectangle. Both composite mirrors were mounted on plates connected by invar rods and separated by a distance of 1 m. The mirrors were then put into a chamber with input and output ports for gas circulation. In one of the 25 × 25 mm² square parts [top left part of right-side mirror in Fig. 1(a)], a hole of 5 mm in diameter serves as the entrance and exit. The laser beam enters the multipass cell from this hole and hits the mirrors on the opposite side; the subsequent spots are aligned using the corresponding mirror mounts according to a computer simulated pattern. After the alignments of all six mirrors, the designed spot patterns are formed, such that the laser beam exits the multipass cell from the same hole. The total number of bounces between the mirrors consists of 579 reflections; thus, the effective path length is about 580 m. The mirror coating has two high-reflection regions, one is in the MIR range (>99.85%, 3.1–3.6 μm) and the other is in the red visible range (>99.9%, 670–680 nm) (Layertec GmbH). During the alignment, we utilized a visible red diode laser to finely adjust the multispot mirrors and to obtain the desired spot patterns, as shown in Fig. 1(a). After alignment was achieved, a flip mirror was used to replace the red visible laser beam with the MIR beam. Two pinholes were used to align the MIR beam into the multipass cell. To calibrate the MIR spectroscopic measurement of room air, the multipass chamber was first flushed with compressed nitrogen gas and then filled with a calibrated gas.

To investigate the ambient air in the laboratory, two flip mirrors were used to let the laser beam bypass the chamber and couple into the same fiber. This arrangement results in a short free-space path length of ~3.3 m. To increase the path length of the open-air gas sensing for improving detection sensitivity, we used another flip mirror to steer the beam onto a large mirror of 40.6 cm diameter about 17.5 m away in our laboratory; the returned beam was collected with a Ritchey–Chretien telescope (Optical Guidance Systems, RC10) and coupled into a MIR fiber. Because both the large mirror and the telescope were not coated for the MIR, the reflectivity is relatively low, ~60% in the range of 2.9–3.6 μm. For ~300 mW MIR output, ~50 mW power was collected with the telescope, and ~30 mW power was coupled through another single-mode MIR fiber and sent to the OSA.

### 3. RESULTS AND ANALYSES

The recorded transmission spectra of ambient air with different open air path lengths, calibrated gas, and ambient air in the multipass cell are presented in Fig. 2. All spectra were recorded with a high-sensitivity setting using the internal chopper of the Yokogawa OSA AQ6376. Data acquisition requires about 8 min to record a single transmitted spectrum from 2900 nm to 3400 nm. The wavelength resolution was set to 0.10 nm with a sampling step of 0.02 nm. The specified noise floor is ~55 dBm/nm from 2200 nm to 3200 nm and ~50 dBm/nm from 3200 nm to 3400 nm. Since the Yokogawa OSA uses a Czerny–Turner double path monochromator with a path length of ~2.4 m, this additional path length of ~2.4 m room air was added to the total path length during the data analysis.

Depending on the conditions of the measurements, different powers were coupled through the MIR fibers and sent to the OSA. For the short path case, the power was ~120 mW for a total path length of ~5.7 m, including the free space and the OSA lengths. For the longer open air path with the telescope setup, the power coupled through fiber was ~30 mW, and the total path length was ~39.6 m. For the multipass setup, the total path length consisted of ~584.8 m from the multipass cell and ~6.4 m due to free space including the OSA. The calibrated gas was synthesized with ultrapure dry air containing a small amount of water vapor and thus much less water absorption than with ambient air in the multipass setup. The incoupled power for the OSA was ~1.3 mW with calibrated gas in the multipass chamber, larger than the power of ~1.0 mW measured with room air.

The magnitudes of the absorption features due to water vapor and methane under the broadband source envelope increased from a short path length to a long path length, and in the case of room air in the multipass, many water absorption peaks reached the noise floor. Still the Yokogawa OSA offers a large dynamic range and reliable linearity to analyze the strong absorption features, which are commonly present in atmospheric measurements. Data analysis shows that no other gas
MIR source spectra were adjusted to peak around 3300 nm. Because of different mirror coatings, the transmitted spectra show different envelopes: air (black), midpath in air with telescope setup (purple), multipass calibrated gas (pink) and air (green) from 2900 nm to 3400 nm are presented. The employed piecewise background fitting for the baseline emitted spectral envelope of the MIR light source. We fulfill a challenging task of removing the background, i.e., the analyses.

The transmitted spectra through piecewise baseline fitting in the spectral range from 3130 nm to 3400 nm for further increases at the high power spectral portion, we normalize in mirror coatings. Considering that the signal-to-noise ratio decreases at the low power portion of spectra, partly because of the differences in mirror coatings. The transmitted MIR spectra had slightly different shapes for different experimental settings, especially in the signal pulses. The transmitted MIR spectra had slightly different shapes for different experimental settings, especially in the signal pulses. The transmitted MIR spectra had slightly different shapes for different experimental settings, especially in the signal pulses. The transmitted MIR spectra had slightly different shapes for different experimental settings, especially in the signal pulses. The transmitted MIR spectra had slightly different shapes for different experimental settings, especially in the signal pulses. The transmitted MIR spectra had slightly different shapes for different experimental settings, especially in the signal pulses. The transmitted MIR spectra had slightly different shapes for different experimental settings, especially in the signal pulses. The transmitted MIR spectra had slightly different shapes for different experimental settings, especially in the signal pulses. The transmitted MIR spectra had slightly different shapes for different experimental settings, especially in the signal pulses.

To obtain the absorption spectra in open air, it is required to fulfill a challenging task of removing the background, i.e., the emitted spectral envelope of the MIR light source. We employed the piecewise background fitting for the baseline generation [13,20]. The transmitted spectra were divided into 5 ~ 10 nm portions, obvious absorption features were excluded, and the remaining spectra were individually fitted with a 5th-order polynomial to generate the baselines. The absorbances were calculated by subtracting transmitted spectra from baselines and converting the results to the natural logarithm scale.

We utilized the high-resolution transmission molecular absorption database (HITRAN) [21] for the simulations and for the comparisons with the experimental results. HITRAN provides a set of spectral parameters for each absorption line of each species, such as spectral line intensity, line center frequency, pressure-dependent linewidth, line shift, etc. Along with a Voigt line shape profile model, HITRAN parameters were used to calculate the absorbance of methane and water across the spectral range of interest with ambient temperature and pressure in the laboratory. Simulations were dependent upon the sampling of the Yokogawa OSA at 0.02 nm, and the simulated absorbance spectra had to be convoluted with the instrumental OSA resolution of 0.10 nm to match the experimental results. By varying the mole fractions of methane and water vapor, the residuals of the differences between simulations and experimental data were minimized with a least-squares fitting approach.

The normalized absorption spectrum measured with the telescope setup is presented in Fig. 3, together with the HITRAN simulations and corresponding residuals.

To further compare the experimental data, absorption spectra in the MIR range between 3234 nm and 3243 nm measured for different configurations are presented in Fig. 4, together with HITRAN simulations and corresponding residuals. It took about 9 s to record a single transmitted spectrum of 9 nm in bandwidth. The retrieved mole fractions of methane and water vapor in laboratory air under three different experimental conditions are presented in Table 1. We use 3σ of standard deviations of residuals to estimate the uncertainties of the retrieved mole fractions.

The highest sensitivity was achieved with the longest path length, and the 3σ detection limit was ~6.6 × 10⁻⁷ cm⁻¹ in ambient air for a broad spectral range between 3200 nm and 3400 nm with about the same power density level.

Many factors affect the uncertainties, i.e., noise contributions in residuals, including systematic etalon effects, pointing stability of the laser beam into the fiber, laser amplitude noise or drift, air turbulence, and mechanical vibration as well as mismatches between experimental line shapes and simulation models. In these three different experimental conditions, the dominant noise factors for the residuals are quite different. The short path normalized absorption spectrum is presented in Fig. 4(a) and shows the smallest noise evaluated by the standard deviation (σ = 0.0042) of the residuals because of the higher spectral power intensity, smaller air turbulence, and mechanical vibrations. The 0.01 absorbance ripple is dominated in the residuals of Fig. 4(a), indicating systematic etalon effects in the current experimental setup for short path length.

In Fig. 4(b) of the midrange telescope setup, the effects of air turbulence and mechanical vibrations contribute to the noise and show the largest noise (σ = 0.015) of the three configurations because of the long-distance separation between the 40.6 cm reflective mirror and 25.4 cm telescope. In Figs. 4(c) and 4(d), the standouts in the residuals are within the strong
absorption features of the spectral range, and are due to the mismatches between the measured spectral line shapes and absorption model used in the simulations. The residual magnitudes also reflect the decreasing of the signal-to-noise ratios because of the spectral power density reduction in the strong absorption regions. Especially in Fig. 4(d), the normalized absorbance of the water line shows a saturated peak, and in the transmitted spectrum of Fig. 2, many water line absorption dips reach the noise floor of \(-50\) dBm/nm in the presented wavelength range; thus, we cut the normalized absorption spectra above the absorbance value of \(\sim 5.0\) for the HITRAN simulations and in the concentration fitting process. Because of this approach, the residuals in Fig. 4(d) have a gap in the water vapor peak range. The methane fitting was not affected since

![Graph](image)

**Fig. 3.** Normalized absorption spectrum (black) for the \(\sim 39.6\) m path of indoor air in comparison to HITRAN simulations and corresponding residuals (black, bottom graph). The methane (red) and water vapor (blue) HITRAN simulations are presented in their negatives for clarity. The spectral range is between 3130 and 3400 nm, sampling is at 0.02 nm, and the resolution is 0.10 nm. The standard deviation (\(\sigma\)) of residuals for this global fit is \(\sim 0.025\), and there are clear spikes in the residuals near the absorption peaks due to mismatches between the measured line shapes and the absorption model used in the simulations. Because of the reduced spectral power density at the short wavelength range, the residuals show larger fluctuations in the range between 3130 nm and 3140 nm.

![Graph](image)

**Fig. 4.** Normalized absorption spectra (black) compared to HITRAN simulations and corresponding residuals in the range between 3234 nm and 3243 nm of four different experimental configurations. The methane (red) and water vapor (blue) HITRAN simulations are presented in their negatives for clarity. It took about 9 s to record a single transmitted spectrum of 9 nm in bandwidth with 0.02 nm sampling step and 0.10 nm resolution. In Figs. 4(a)–4(d), we present normalized absorption spectra of the laboratory air at ambient conditions with different total path lengths of 5.7 m, 39.6 m, and 591.2 m, respectively. In Fig. 4(c), the presented spectrum is evaluated for the calibrated gas in the multipass chamber, which has a low concentration of water vapor (less than 800 ppmv).
the absorbance of the methane peak is $\sim 4.5$, and the methane absorption dip in the transmitted spectrum does not reach the noise floor.

In Fig. 4(c), the absorbance spectrum of calibrated gas in the multipass chamber is presented. This data was obtained by first using compressed nitrogen to flush the multipass chamber for 10 min and then filling the chamber with the calibrated gas (Scott-Marrin, Inc). This results in a mixture consisting of 2.020 ppmv methane, 511 ppmv carbon dioxide, 2.001 ppmv carbon monoxide, and ultrapure air. The tolerances of gas components are ±2%. The absorption path length outside the chamber consisted of $\sim 4.0 \text{ m}$ of path length for the free space travel plus $\sim 2.4 \text{ m}$ path length from the OSA, together with the 1.96 ppmv methane and 18,100 ppmv water vapor concentration retrieved from Fig. 4(a). These parameters were used to evaluate the absorption outside the multipass chamber. The methane concentration of 2.020 ppmv was used for simulations of the calibrated gas inside the multipass chamber. In the simulation process, the path length of the multipass chamber was iterated to minimize the standard deviation of residuals by least-squares fitting. The retrieved path length inside the multipass chamber was 584.8 m, and considering a ±2% uncertainty of methane concentration for the calibrated gas, the estimated $\sim 580 \text{ m}$ path length is well within the retrieved path length, which is used in the evaluation of the room air in the multipass chamber.

The retrieved mole fractions of methane and water vapor presented in Table 1 are consistent. The water vapor of $\sim 18,000 \text{ ppm}$ corresponds to $\sim 60\%$ relative humidity, agreeing additionally with measured results of a relative humidity monitor (Omega, RH-USB). However, the Voigt line shape profile used in the simulations with the HITRAN parameters does not account for more complicated aspects of molecular spectroscopy, such as the coupling between energy states with close transitions (line mixing) and the speed-dependent effect of molecular collisions on the Doppler contribution to the line shape that could lead to inaccurate atmospheric retrievals. Also, the required convolution of instrumental resolution with HITRAN simulations may degrade the accuracy of the retrieved values. Thus, a more advanced absorption model needs to be developed for future work.

Compared to techniques involving two-dimensional virtual-image phased array spectroscopy with an MIR frequency comb for the open-air trace gas sensing [13], the traditional Czerny–Turner double path monochromator requires rotating the diffraction grating for a single photodiode detection; hence, it takes a longer time to acquire the same broadband spectrum. However, with an internal chopper and lock-in detection of the Yokogawa OSA, the sensitivity and dynamic range is greatly enhanced; this is particularly useful for the large absorbance conditions, e.g., breath analysis, such that strong water absorptions will not limit the performance of the experimental techniques.

### 4. CONCLUSIONS

A MIR frequency comb light source was utilized for broadband detection of multiple species in laboratory air under ambient condition. We demonstrated the detection of trace amounts of methane in the presence of much higher absorption water lines with a conventional OSA with three path lengths ($\sim 6 \text{ m}$, $\sim 40 \text{ m}$, $\sim 590 \text{ m}$) using three modified experimental setups. By using a piece-wise background fitting of transmitted spectra, the normalized absorbance spectra were obtained and compared to HITRAN simulations. Mole fractions of methane and water vapor at different conditions were retrieved and compared. Overall, this approach provides a broad spectral range, a large dynamic range, high sensitivity, and accurate calibration. The performed analysis of the residuals shows that an excellent agreement between the measured and calculated spectral profiles was obtained. The enhanced sensitivity of the long path length of the multipass chamber will facilitate the trace detection of more complex hydrocarbon molecules in various applications, such as breath analysis.

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