Mid-infrared dual frequency comb spectroscopy based on fiber lasers for the detection of methane in ambient air

F Zhu\(^1\), A Bicer\(^1\), R Askar\(^1\), J Bounds\(^1\), A A Kolomenskii\(^1\), V Kelessides\(^2\), M Amani\(^2\) and H A Schuessler\(^1,3\)

\(^{1}\) Department of Physics and Astronomy, Texas A&M University, College Station, TX 77843–4242, USA
\(^{2}\) Petroleum Engineering Program, Texas A&M University at Qatar, Doha 23874, Qatar
\(^{3}\) Science Department, Texas A&M University at Qatar, Doha 23874, Qatar

E-mail: zhf@physics.tamu.edu

Received 10 March 2015
Accepted for publication 19 March 2015
Published 5 August 2015

Abstract
We utilize mid-infrared dual frequency comb spectroscopy for the detection of methane in ambient air. Two mid-infrared frequency comb sources based on femtosecond Er: fiber oscillators are produced through difference frequency generation with periodically poled MgO-doped lithium niobate crystals and stabilized at slightly different repetition rates at about 250 MHz. We performed dual frequency comb spectroscopy in the spectral range between 2900 cm\(^{-1}\) and 3150 cm\(^{-1}\) with 0.07 cm\(^{-1}\) resolution using a multipass cell of ~580 m path length, and achieved the sensitivity about 7.6 \times 10^{-7} cm\(^{-1}\) with 80 ms data acquisition time. We determined the methane concentration as ~1.5 ppmv in the ambient air of the laboratory, and the detection limit as ~60 ppbv for the current setup.

Keywords: mid-infrared, dual frequency comb spectroscopy, infrared spectrometer (Some figures may appear in colour only in the online journal)

1. Introduction
Since the invention of frequency combs [1], mid-infrared (MIR) frequency comb sources and their spectroscopic applications are being developed actively to facilitate their potential applications in many areas of science and technology [2, 3], especially in the range from 3 to 4 μm, which not only is relatively transparent in the atmosphere, but also contains strong fundamental absorption features of methane, acetylene, ethane, propane and many other more complex hydrocarbons. Broadband MIR frequency combs provide high brightness and frequency precision for many spectroscopic applications, in particular for the spectroscopic methane detection in real time monitoring [4], which is of demanding interest for the natural gas industry, environmental science, atmospheric and geoscience research. Broadband MIR frequency comb sources have been demonstrated using difference frequency generation (DFG) between a frequency comb and a continuous wave (CW) laser [5], DFG between two frequency combs [6, 7], and with optical parametric oscillators (OPO) [8–14]. Different versions of MIR frequency comb spectroscopies have been developed since the invention of the frequency comb, such as dual frequency comb spectroscopy (DFCS) [2, 5, 10, 14], cavity enhanced Fourier transform spectroscopy [8, 11, 12], MIR upconversion spectroscopy [6], and MIR virtually imaged phase array spectroscopy [9, 13]. To increase the detection sensitivity, a multipass cell [6, 8] or a high finesse cavity [11–13] has been employed to effectively increase the interaction length between the detection target molecules and the MIR frequency combs. In particular, several MIR DFCS schemes were demonstrated with high concentration methane gas cells [5, 10, 14]. The stabilized MIR combs based on DFG between a CW laser and frequency combs, which were locked to sophisticated frequency references, provided comb-teeth resolved spectral measurements of methane around 3.4 μm [5]. However the relatively narrow bandwidth and microwatt power levels limited the applications for sensitive and real time multi-target...
gas detection. The OPO sources provided hundred milliwatt power and broad spectra, but the repetition rates or the carrier-envelope offset frequencies were not fully controlled, which led to distorted spectral measurements [10, 14].

In this work, we performed MIR DFCS for methane detection in a multipass cell with two DFG MIR high-power frequency comb sources. Both sources are based on femtosecond Er:fiber oscillators with stabilized repetition rates at ~250 MHz [7]. We implemented the MIR DFCS with a novel multipass cell of ~580 m interaction length to detect the trace amount of methane in ambient air.

2. Experimental setup

A simplified diagram of the experimental setup is presented in figure 1.

Two MIR DFG combs (Menlo Systems, MIR Comb) based on femtosecond Er-doped fiber oscillators with repetition rates locked to frequencies at ~250 MHz and referenced to a Rb frequency standard (Stanford Research, PSR10) are used. One advantage of these DFG sources is the passive carrier-envelope-offset (CEO) frequency stabilization. Since the pump and signal fields originate from the same source, the generated idler field is carrier-envelope phase slip free. Hence by stabilizing the source repetition rates, the MIR frequency combs are stabilized. In previous work, we characterized the DFG MIR comb1 by the measurement of spectrum and the interferometric autocorrelation trace and the verification of the coherence of the MIR comb with heterodyne beat experiments [7]. The MIR comb1 has ~120 mW output power, covering a spectral range from 2.8 to 3.6 μm (2700 cm⁻¹ to 3600 cm⁻¹). The pulse duration is ~80 fs. The MIR comb2, employing a higher power Yb-doped fiber amplifier, generates an MIR comb of ~300 mW with a similar spectrum and pulse duration.

After mode matching lenses, the sensing MIR comb2 is split by a 50 : 50 beam splitter. The transmitted portion consists of signal pulses, which are coupled into the multipass cell; the reflected part could be guided back with a mirror and serves as a reference. The signal pulses outgoing from the multipass cell and the reference pulses are recombined on the same 50 : 50 beam splitter and overlap with pulses from the local oscillator (LO) MIR comb1 on a 92 : 8 beam splitter. The combined pulses are aligned and focused on a liquid nitrogen cooled HgCdTe (MCT) detector with 100 MHz bandwidth (Kolmar Technology, KMPV11-0.1-JI/AC100). By using neutral density filters and beam splitters, the total incident power on the detector is adjusted to be less than 2 mW, above which the detector starts to show signs of saturation, and the powers of signal and reference from sensing MIR comb2 and the power from LO MIR comb1 are roughly equal.

The multipass cell has a confocal design, the radii of curvatures of the two 50 × 50 mm² mirrors are 1 m, and so is the distance between these two mirrors. Both mirrors are divided into 3 parts, two 25 × 25 mm² squares, and one 25 × 50 mm² rectangle. In one of the square parts, a hole of 5 mm diameter serves as the entrance and exit for the laser beam. The subsequent spots are aligned using the corresponding mirror mounts according to the design. After all six mirror parts are aligned, the spot patterns are formed on the mirrors, such that the laser beam exits the multipass cell after bouncing between the mirrors with 579 reflections, thus the effective path length is ~580 m. The mirror coating has two high reflection regions, one is in the MIR range (>99.85%, 3100 ~ 3600 nm) and the other is in the red visible range (>99.9%, 670 ~ 680 nm) (Layertec GmbH). For the alignment purpose, we use a visible red diode laser to adjust the multipass mirrors and to achieve the simulated spot patterns, as shown in figure 1(d). Then the MIR beam replaces the red laser beam by moving up the flip mirror and is aligned through two pinholes to enter the multipass cell. The output of the multipass cell is around 1.0 ~ 2.0 mW, depending on the humidity because of the water vapor absorption.

3. Results

We lock two femtosecond DFG MIR combs with slightly different repetition rates at \( f_1 = 249998, 633 \text{ Hz and } f_2 = 250000, 122 \text{ Hz, thus the difference is } \delta f = 1489 \text{ Hz.} \) In the time domain, when a pulse pair from two sources overlaps in time, the center burst of an interferogram is formed. Subsequent pulse pairs impinge on the detector with linearly increasing time delay. As a result, the detector records an interferogram formed by many pulse pairs of various delays. Because pulse pairs repeatedly move through each other, a new interferogram starts to form as soon as the previous is completed in \( 1/\delta f \approx 0.672 \text{ ms.} \) We record the interferogram train with an oscilloscope (Tektronix, MDO4104B-3) at a sampling rate of 250 MSPS with ~10 bit resolution. The maximum record length is 20 Mega points, corresponding to 80 ms, or ~118 complete interferograms. We first block the reference pulses, and record an interferogram train with only signal pulses out of multipass cell and LO pulses. The recorded 80 ms interferogram can be fast Fourier transformed to a comb-teeth resolved spectrum with a simple software phase correction. The magnitude and phase radio frequency (RF) spectra are presented in figure 2.

Because of the passive CEO frequency stabilization, the DFG MIR frequency combs have a simple form of \( \nu_r = m f_r, \) where \( \nu \) is the optical frequency in MIR, \( m \) is an integer, and \( f_r \) is the source repetition rate. For the measurements in the frequency domain, the individual comb lines from two sources beat between \( (N + 2)f_r, Nf_r, \) where \( N \) is an integer between ~347600 and ~377600, and down convert the MIR optical frequency information at about 87 ~ 95 THz to RF at about 18 ~ 63 MHz with a simple formula \( Nf_r - (N + 2)f_r \approx \nu_r \approx f_{RF}. \) Thus, the optical up conversion follows \( f_{RF}f_r, \delta f_r, 2f_1, 2f_2, \delta f_1. \) The measured complex spectrum of the signal is \( S(\nu) = S(0)\exp[-\alpha(\nu)L/2 - i\phi(\nu)], \) where \( S(0) \) is the complex spectrum of the reference, \( \alpha(\nu) \) is the molecular absorption coefficient, \( L \) is the path length of the multipass cell, \( \phi(\nu) \) is the phase shift.

Because of the pressure broadening in the ambient air and spectral overlaps, the methane or water absorption features have several GHz linewidths, as follows from figure 2(b).
Data acquisition and Fourier transform

Figure 1. The experimental setup includes two MIR comb sources, mirrors and lenses allowing to couple the MIR comb2 into the multipass cell, one 50:50 beam splitter (BS) to split the reference and signal pulses, one 92:8 beam splitter to combine pulses from two comb sources, and an MCT photodetector with electronics for data acquisition. The spectra measured with a scanning monochromator are shown in inset (a) for MIR comb1 (cyan) and MIR comb2 (red). Interferometric autocorrelation traces are shown in inset (b) for MIR comb1 (cyan) and (c) for MIR comb 2 (red). The absorption features in the spectra are due to water vapor in the laboratory environment. Spot patterns on the mirrors of the multipass cell with the visible red laser are shown in inset (d) and are produced when the alignment red laser is introduced with the flip mirror off. The entrance/exit hole of 5 mm diameter can be seen in the top left part of the right side mirror.

Figure 2. Fourier transformed magnitude (black) and unwrapped phase (green) RF spectra from an 80 ms signal interferogram train with a software phase correction: (a) broad range from 18 to 63 MHz, (b) zoomed in narrow range from 40.25 MHz to 40.45 MHz. The phase is only perceptible and plotted at comb teeth positions, since the RF signals between comb teeth are simply noise and therefore has a random phase between $-\pi$ to $\pi$. Because of the broad absorption features, the absorption dips can be observed in (a). The discrete comb lines with a spacing of $\delta f_r = 1489$ Hz can be observed in (b).

High resolution spectra show more noise in the baseline, especially when normalized with the reference taken at different time. Hence we take advantage of the $1/\delta f_r$ time window by interleaving the reference and signal interferograms together, and relax the spectral resolution to match the absorption features to increase the signal to noise ratio (SNR) and save the...
data acquisition and processing time. To achieve this, we unblock reference pulses from the sensing comb and spatially overlap them with signal pulses. Since the signal and reference pulses have different optical paths, the signal pulse has \( \approx 1.93 \mu s \) effective time delay due to the multipass cell and trails the closest reference pulse by \( \approx 1.4 \) ns, corresponding to \( \approx 0.23 \) ms laboratory time, which reflects the mutual slipping speed of the pulse pair and is scaled with the factor \( f_{\text{ref}}/\delta f_{\text{ref}} \). We averaged the 118 recorded interferograms into one, as shown in the red plot of figure 3.

For the averaged interferogram, two rectangular apodizing windows of 80 \( \mu s \) centered at signal and reference interferogram peaks are used. After the FFT and the up conversion from RF to MIR, the normalized spectra can be retrieved from signal and reference spectra. With an 80 \( \mu s \) apodizing window, the RF resolution is 12.5 kHz. Thus the up converted MIR resolution is \( \approx 2.1 \) GHz or \( \approx 0.07 \) cm\(^{-1}\), which is sufficient to resolve the absorption features in ambient air. The normalized spectra of the absorbance \( \alpha(v)L \), the phase shift \( \phi(v) \), and a comparison with the absorbance simulation from the HITRAN database \([17]\) are presented in figure 4.

Besides water and methane, no significant absorption features were observed for other species. The absorption features from methane are quite consistent, while the water absorption changes with indoor humidity. To reduce the water concentration, we built a glass container to cover the multipass cell and used desiccants to dry the air in it. In general, the experimental results show good agreement with the simulations from the HITRAN database despite inconsistencies largely caused by challenges associated with the air sample, such as additional scattering from airborne particles, overlapped spectral features, and saturated peak absorptions. By evaluating the root mean square noise \( \sigma \) from the normalized absorbance spectrum at the central high power spectral positions where no absorption signal is detected, the sensitivity of the measurement is determined to be \( \alpha_{\text{min}} = \sigma/L \approx 7.6 \times 10^{-7} \) cm\(^{-1}\). The SNR is about \( \approx 150 \) for water and \( \approx 75 \) for methane at the center of the measured spectral range for the most intense and isolated lines. Due to the reduced comb powers at both outer edges of the spectrum, the SNRs at these regions are lower. From this measurement,
and the $3\sigma$ detection limit of methane is estimated to be ~60 ppbv.

We evaluate the DFCS quality factor, which is the product of the SNR and the number of resolved spectral elements normalized by the square root of the total acquisition time [18]. With a SNR ~100, in 80 ms acquisition time, we obtain the number of resolved spectral elements as 250 cm$^{-1}$/0.07 cm$^{-1}$–3600 and the experimental quality factor ~$1.3 \times 10^6$ Hz$^{1/2}$, which is similar to the value of previous work [5, 18].

4. Discussion and summary

Although the repetition rates of the DFG MIR comb sources are locked to the Rb frequency standard, and the MIR frequency comb coherence properties are demonstrated, currently the mutual coherence of both combs is not well maintained, and it requires software phase correction to fully resolve comb teeth in the spectrum. The possible reason is that the low-bandwidth servo to stabilize the repetition rates to the Rb frequency standard does not compensate for the short-term instabilities of the combs. With a better frequency standard and locking electronics to improve the short time stability, or by locking the MIR frequency combs to a MIR CW laser source, which is frequency stabilized, a fully comb-tooth resolved and accurate spectrum without any software phase correction is expected.

In the current setup, the recording length is limited by the maximum storage length of the oscilloscope. According to the Allen deviation analysis of current data, the detection limit can be further improved with a longer data record, or real time correction, or an averaging approach [15]. The current detector and internal pre-amplifier have a 4 mV root mean square noise and begin to show saturation behavior at ±400 mV; the low detector dynamic range of about 100 is currently the major factor to limit the performance [18]. With a lower noise detector and improved detector dynamic range, a lower detection limit can be achieved.

In summary, we employed MIR DFCS for the real time detection of methane in ambient air with a multipass cell of ~580 m path length. We determined that the methane concentration in the ambient air of the laboratory ~1.5 ± 0.1 ppmv. The minimum detection limit for the current setup is ~60 ppbv with 80 ms data acquisition time.

Acknowledgments

We thank the Robert A Welch Foundation for funding provided under grant No. A1546. This publication was made possible by the NPRP award NPRP 6-465-1-091 from the Qatar National Research Fund (a member of The Qatar Foundation). The statements made herein are solely the responsibility of the authors.

References