Broadband detection of methane and nitrous oxide using a distributed-feedback quantum cascade laser array and quartz-enhanced photoacoustic sensing

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ARTICLE INFO

Keywords:
Broadband gas detection
Quartz-enhanced photoacoustic spectroscopy
Methane
Nitrous oxide
Distributed-feedback quantum cascade laser array

ABSTRACT

Here we report on the broadband detection of nitrous oxide (N₂O) and methane (CH₄) mixtures in dry nitrogen by using a quartz-enhanced photoacoustic (QEPAS) sensor exploiting an array of 32 distributed-feedback quantum cascade lasers, within a spectral emission range of 1190−1340 cm⁻¹ as the excitation source. Methane detection down to a minimum detection limit of 200 ppb at 10 s lock-in integration time was achieved. The sensor demonstrated a linear response in the range of 200−1000 ppm. Three different mixtures of N₂O and CH₄ in nitrogen at atmospheric pressure have been analyzed. The capability of the developed QEPAS sensor to selectively determine the N₂O and CH₄ concentrations was demonstrated, in spite of significant overlap in their respective absorption spectra in the investigated spectral range.

1. Introduction

Gas spectroscopy finds applications in breath analysis, industrial process control, environmental monitoring, geochemistry and leak detection [1–3]. Spectroscopic techniques capable of implementing wide spectral range analysis allow the detection of broadband absorber gases, such as greenhouse and volatile organic compounds, and measurements of complex gas mixtures of interfering components [4]. Among the optical sensing techniques, photoacoustic spectroscopy (PAS) and quartz-enhanced photoacoustic spectroscopy (QEPAS) are particularly suitable for broadband detection since the responsivity of the employed detecting element is wavelength-independent. In PAS the acoustic waves generated by the non-radiative relaxation of the gas target molecules excited by a modulated laser light are detected by a sensitive microphone. Typically, the PAS signal is amplified by tuning the modulation frequency to one of the acoustic resonances of the photoacoustic cell [5]. In QEPAS a quartz tuning fork (QTF) is employed as a sharply resonant acoustic transducer and the QEPAS signal is amplified by modulating the laser light at one of the in-plane flexural modes of the QTF [6]. Both techniques have demonstrated high sensitivity in concentration [5–9]. Typically, single mode distributed-feedback (DFB) diode lasers have been employed as a light source to target a single, interference-free absorption line, thus demonstrating high selectivity. Apart from specific cases in which two or more absorption lines can be covered within its dynamic current range [10,11], DFB lasers do not represent the optimal choice for multi-gas detection. Quantum cascade lasers (QCLs) in external-cavity configuration (EC-QCLs) are commonly employed to cover wide mid-infrared spectral ranges and have been exploited for the detection of several greenhouse and harmful gases [12]. For broadband gas detection (over a ~ 40 cm⁻¹ wide spectral range), EC-QCLs have been employed for acetylene and TNT detection with PAS [13] and for Freon 125 detection with a QEPAS sensor [14]. Compared to DFB laser sources, EC-QCLs are bulky and suffer from gratting mechanical instability which generates alignment-
and laser instability-related noises [15]. An alternative broadband emission laser source can be realized by using an array of DFB-QCLs monolithically grown on a single semiconductor chip, combining the compactness of a single chip, the wide tunability range of an array of devices and the pulse-to-pulse stability, spectral purity, and tuning reproducibility of DFB-QCLs [16]. Recently, a DFB-QCL array with 32 DFB-QCLs was employed as the excitation source in a QEPAS sensor for broadband detection of N₂O at atmospheric pressure in the 1190–1340 cm⁻¹ spectral range, with a sensitivity suitable for atmospheric monitoring [17,18]. In the investigated spectral range, N₂O exhibits two ∼50 cm⁻¹ wide absorption bands composed of several ~1 cm⁻¹ equally separated absorption lines whose smooth envelope results in a P- or R- branch [19,20].

In this work, we investigated the performance of the DFB-QCL array-based QEPAS sensor in the detection of methane (CH₄) to test the sensor capability to detect and recognize the absorption features of a gas presenting an irregular spectrum within the source emission spectral range [21]. The feasibility of broadband multi-gas detection was investigated, by analyzing mixtures of N₂O and CH₄ with strongly overlapping absorption bands. To avoid the influence of water vapor on the analytes energy relaxation rate [22], altering the spectra intensity, all measurements were performed in pure, non-humidified N₂. Our analysis demonstrated the capability of discriminating the contributions of a gas species from another one, even in the case of strongly overlapping absorption spectra. A quantitative estimation of the concentrations of the two gas species in the mixture was obtained by fitting spectra of mixtures with a linear combination of reference spectra of N₂O and CH₄, at a fixed concentration in N₂.

2. Laser source spectral characterization and beam profile analysis

The employed laser source consists in a monolithic array of 32 individually addressable distributed-feedback quantum cascade lasers grown on a single semiconductor chip and operated in pulsed mode, as described in [15,17,21]. Thermoelectric cooler and laser pulser boards are embedded in a single unit controlled by a LabVIEW-based software. As a first step, the spectral emission of the employed laser source was analyzed by using a Fourier-transform interferometer (FTIR-Nicolet 6700) with a spectral resolution of 0.125 cm⁻¹ in a rapid-scan mode. In Fig. 1(a) the normalized emission spectra of the devices composing the monolithic QCL array are reported for a TEC temperature of 25 °C, a drive voltage properly set for each device in order to ensure the highest optical power output (18.0–20.0 V), a repetition frequency of 33 kHz and a pulse-width of 300 ns resulting in a duty cycle of 1 %.

The overall emission spectrum of the QCL array covers a range 150 cm⁻¹ wide from 1190 cm⁻¹ to 1340 cm⁻¹. Each device in the array shows a single-mode output, whose peak emission wavenumber and linewidth were determined by fitting the spectrum with a Gaussian curve. As a representative, the FTIR measured spectrum of the QCL number 15 is reported at a driving voltage of 18 V in Fig. 1(b) together with its best Gaussian fit. The emission peak occurs at 1253.4 cm⁻¹ with a linewidth of 1.3 cm⁻¹. By repeating the measurements and the fit procedure for all the QCLs, a spectral spacing between adjacent devices lower than 5 cm⁻¹ was measured, while the linewidths ranged between 1.1 cm⁻¹ and 1.5 cm⁻¹. Narrower spectral lines (down to < 0.2 cm⁻¹) can be obtained by reducing the pulse durations. However, this also leads to a reduction of the average power if the repetition rate is kept constant to match the resonance of the quartz tuning fork. Since the QEPAS signal is proportional to laser average power, this is not advantageous. Mode hop-free tuning of the lasers’ optical frequency with the operating temperature was also verified in the 15 °C–50 °C range. The temperature tuning coefficient was calculated by linearly fitting the peak wavenumber as a function of the operating temperature. The optical frequency temperature tuning of the device number 15 is reported in Fig. 1(c) together with the best linear fit. A tuning coefficient of -0.09 cm⁻¹/°C was measured for all the devices in the array, resulting in an overall tuning of each QCL optical frequency of 3.15 cm⁻¹ within the investigated temperature range. Next the spatial quality of the QCL beams was investigated. The beams exiting the QCL array package were collected by a ZnSe focusing lens having a 25.4 mm diameter, a 50 mm focal length and an anti-reflection (AR) coating in the 7–12 μm spectral range. The beam profile of each device was acquired in the lens focal plane by a pyroelectric camera (Ophir Spiricon Pyrocam III-C) composed of an array of 124 × 124 100μm-side square pixels. Devices from number 1 to number 19 shown on the camera as a secondary spot, ~ 1 mm distant from the fundamental one, caused by stray light in the laser package. An updated design is currently being engineered to mitigate this issue. As representative, the three-dimensional far field image of the device number 15 is shown in Fig. 2(a). The secondary spot is 6 times less intense and appears 900 μm far from the highest peak.

In an on-beam QEPAS configuration, the laser source beam must be focused between the QTF prongs. When light hits the QTF prongs a background optical noise is generated. Therefore, multimode and/or poor spatial quality beams drastically affect the ultimate detection sensitivity of a QEPAS sensor. With the QCL array employed in this work, a spatial filter was used to suppress all secondary spots. Although hollow-core waveguides (HCWs) have been demonstrated to act as efficient low-loss single mode delivery spatial filters in the mid-infrared
spectral range, the observed shifts of the focused beams when switching from one device to another do not permit the use of an HCW, since realignments become necessary when switching the QCLs [23,24]. Instead, a 2 mm-diameter pinhole was positioned between the laser source and the focusing lens, allowing all the secondary spots to be cut off while preserving the fundamental mode Gaussian shape and intensity, as shown in Fig. 2(b) for device 15. Once the secondary spots are removed, beam radii of 260–300 μm in the x-direction and of 290–340 μm in the y-direction were measured in the lens focal plane by fitting all beam profiles with a Gaussian function in both directions. By considering also shifts in position of all primary spots, an overall illuminated area of 600 × 800 μm² was identified, represented by a dashed line-rectangle in Fig. 2(c). Hence, a 1 mm-prong spacing custom QTF (labelled as QTF #4 in [25]) was selected to reduce as much as possible the possibility that beam tails hit the QTF.

3. Experimental setup

The architecture of the broadband detection QEPAS sensor is depicted in Fig. 3. As discussed in the previous section, the laser beam is spatially filtered by a pinhole and then focused through the acoustic detection module (ADM) by means of the ZnSe focusing lens.

The ADM is composed of a gas cell, equipped with two ZnSe windows for the laser input and output, a pair of connectors for gas inlet and outlet and a QTF acoustically coupled with two 1.52 mm-internal diameter and 5.3 mm-long micro-resonator tubes in an on-beam configuration. A power-meter is set behind the ADM for optical power measurement and monitoring. At atmospheric pressure, the spectrophone composed of a QTF and micro-resonator tubes exhibits a first overtone flexural mode resonance curve peaked at \( f = 25,390.63 \) Hz with a full-width half-maximum value of 2.41 Hz, resulting in a quality factor of 10,530. The laser pulser is externally triggered by a waveform generator to set the pulse repetition rate at \( f \). For all QEPAS measurements, a 300 ns pulse-width was used, resulting in a 0.75 % duty cycle, while the QCL driving voltage was set to the value ensuring the highest optical power for each device. The QTF current signal is converted into a voltage signal by a 10 MΩ feedback resistor pre-amplifier and then demodulated by a lock-in amplifier at the frequency \( f \) with a 100 ms integration time. The demodulated signal is digitized by a DAQ card and acquired by a LabVIEW-based software with a sampling time of

![Fig. 2](https://example.com/fig2.png)  
**Fig. 2.** (a) QCL number 15 focused 3D beam profile. (b) Same QCL beam profile filtered by a 2-mm pinhole. (c) QCL number 15 2D spatially filtered beam profile. The two yellow areas represent the positions of the QTF prongs, spaced by 1 mm. The array overall illuminated area is highlighted with a red dashed line. All dimensions are represented in scale.

![Fig. 3](https://example.com/fig3.png)  
**Fig. 3.** Schematic of the experimental apparatus. WFG – waveform generator; DAQ – data acquisition board; TEC – temperature controller; PRE-AMP – Pre-amplifier; PC – personal computer; QCL ARRAY – quantum cascade laser array; P – pinhole; L – focusing lens; ADM – acoustic detection module; QTF – quartz tuning fork; mR – micro-resonator tubes; PM – power-meter; GC1, GC2 – gas cylinders.
300 ms.

The target gas flows from the gas cylinder GC1 through the ADM by using a vacuum pump. The gas flow rate and pressure in the ADM are set by controllers at 30 sccm and 760 Torr, respectively. A hygrometer (not shown in figure) was placed in-line to monitor the absence of humidity in the line and check any presence of undesired water vapor. Gas mixtures with a second gas species contained in the gas cylinder GC2 are obtained by appropriate setting the rate parameter of the flow controllers mounted on the two branches of the Y-shaped gas line.

4. Methane broadband detection

Within the emission wavelength range of the employed DFB-QCL array, methane exhibits an uneven absorption spectrum composed of several lines differing in line-strength and in wavenumber spacing. QEPAS measurements were performed by switching the QCLs in sequence while keeping the devices operating temperature fixed at 25 °C (fixed temperature acquisition mode-FTAM). All measurements were performed by using the lock-in phase N = 57.3°, maximizing the demodulated signal amplitude of the methane peaks. The QCL output power varies for each device. For this reason, a preliminary measurement of the array optical power was performed as a function of light wavenumber, by recording the output power while switching the devices in sequence. The obtained curve was then normalized to 1 with respect to the highest value. This curve will be referred hereafter as FTAM optical power calibration curve. QEPAS signals obtained for a certified concentration of 1000 ppm of CH$_4$ in GC1 were normalized to the FTAM optical power calibration curve. The resulting QEPAS spectrum is shown in Fig. 4 (black squares).

The FTAM QEPAS spectrum reproduces the highest intensity peak at 1306.10 cm$^{-1}$ as well as several side features. For each device, a 1σ noise level of ~2 μV was estimated when pure N$_2$ is flowing in the ADM. This suggests that the background optical noise related to light-induced photothermal effects on QTF prongs does not change when switching between different devices. Therefore, the selected QEPAS sensor architecture, i.e. the use of the pinhole together with a 1mm-prong spacing QTF, allows the QEPAS sensor alignment conditions to be preserved while switching among the devices.

The QEPAS sensor linear responsivity with the methane concentration was verified in the 200–1000 ppm range, by diluting the 1000 ppm CH$_4$N$_2$ certified concentration with pure nitrogen. The measurements obtained in fast acquisition mode for 400, 600, 800 and 1000 ppm CH$_4$ concentrations are shown in Fig. 4, together with the spectra recorded when pure N$_2$ was flowing in the ADM. The area underneath the spectra was calculated using the rectangles approximation and plotted as a function of the CH$_4$ concentration in the inset of Fig. 4. A slope of 0.036 mV·cm$^{-1}$/ppm was extracted by linearly fitting the data points in the graph. The fit exhibits an intercept of 1.74 mV·cm$^{-1}$, comparable with the area of 2.6 mV·cm$^{-1}$ measured underneath the pure nitrogen QEPAS spectrum. For the lowest concentration, i.e. 200 ppm CH$_4$N$_2$, an area of 7.87 mV·cm$^{-1}$ was calculated. The standard deviation $σ_{Area}$ of the area underneath the QEPAS spectrum can be obtained by using the propagation of uncertainty law:

$$σ_A = \sqrt{\sum (\frac{δA}{δN})^2 σ_N^2 + (\frac{δA}{δS})^2 σ_S^2}$$

where N and S are the ith rectangle base and height. The parameter $σ_N$ is the FTIR error, while $σ_S$ is the 1σ noise of the QEPAS signal. The QEPAS signal for each QCL exhibits a 1σ noise level of ~2 μV. By neglecting the FTIR error contribution, $σ_{Area}$ is proportional to 1σ and the extracted value is 0.05 mV·cm$^{-1}$. The sensor minimum detection limit (MDL) can be defined as the methane concentration corresponding to an area under the spectrum equal to $σ_{Area}$. Based on these considerations, an MDL of 1.27 ppm was estimated. 1σ noise of the QEPAS signal can be further reduced by integrating the signal over longer times. An Allan-Werle deviation analysis was performed to calculate 1σ noise as a function of the signal integration time [26]. For a 10 s lock-in integration time, the methane MDL was estimated to improve down to 200 ppb, ~ 9 times lower than the methane concentration in atmosphere [27].

The methane spectrum was also measured by employing a higher-resolution acquisition mode which consists in tuning the operating temperature of each QCL within the 15 °C–50 °C range, in steps of 3 °C, corresponding to a spectral resolution of 0.27 cm$^{-1}$, and driving the devices one by one, in sequence (temperature tuning acquisition mode-TTAM). A preliminary measurement of the TTAM optical power calibration curve was performed. QEPAS signals obtained for a certified concentration of 1000 ppm of CH$_4$N$_2$ in GC1 were normalized to the TTAM optical power calibration curve. The resulting QEPAS spectrum is shown in Fig. 5 (black dots) together with a simulation of the absorption spectrum of 1000 ppm of CH$_4$N$_2$ obtained by using the HITRAN database [28].

QEPAS measurements well reconstruct the highest intensity peak centered at 1306.10 cm$^{-1}$. Compared to Fig. 4, five equally spaced absorption features on the right side of the highest peak are now distinguishable and well reconstructed. However, the large QCLs emission linewidth, combined with the ~5 cm$^{-1}$ spacing and the 1 ~4 cm$^{-1}$ width of the methane absorption peaks, results in a QEPAS spectrum less
sharp than the simulated absorption coefficient spectrum, for all the five absorption features. On the left side, the absorption features are so spectrally dense that it is hard to distinguish among them. Narrower emission linewidth (attainable with shorter laser current pulse-widths) would allow a better reconstruction of the absorption features, but the reduction of the average optical power would negatively affect the ultimate detection sensitivity of the sensor. In this mode, the spectrum acquisition time is 14 times longer, but the resolution step decreases from 4−5 cm−1, depending on the optical frequency difference between adjacent devices, to 0.3 cm−1, thus allowing a more accurate peaks reconstruction.

5. Methane/nitrous oxide mixtures broadband detection

The results and the sensitivities obtained so far demonstrate that the DFB-QCL array-based QEPAS sensor can be considered as a valid tool for broadband detection of one single gas species in nitrogen. A further investigation is needed to demonstrate the feasibility of broadband multi-gas detection, particularly in the case of overlapping absorption features belonging to different gas species. This is the case for nitrous oxide and methane. The absorption spectrum of N₂O has been reported in [17], where FTAM and TTAM QEPAS measurements well mimic the simulated spectrum of the P- and R-branches. These two nearly-Gaussian envelope bands overlap with uneven absorption features of CH₄ [28], within the array emission spectral range. For this experiment, three different N₂O/CH₄ mixtures in N₂ were used. A concentration of 1020 ppm of N₂O:N₂ in GC2 was mixed with three concentrations of CH₄:N₂ in GC1, containing 1900 ppm, 1000 ppm and 300 ppm of methane, in order to obtain three gas mixtures composed of a fixed concentration of 510 ppm of N₂O and a concentration of 150 ppm, 500 ppm and 950 ppm of CH₄ in N₂, respectively. Keeping the concentration of one gas species constant, it is possible to investigate how the presence of the second gas species (CH₄) can affect the overall spectrum profile.

FTAM QEPAS measurements were performed, using a lock-in phase φ fixed at 57.31°. Reference spectra measured for 510 ppm of N₂O:N₂, R(N₂O), and 1000 ppm of CH₄:N₂, R(CH₄), are shown in Fig. 6(a) and (b), respectively, while the QEPAS spectra obtained for the three different mixtures are plotted in Fig. 6(c). All spectra are normalized to the optical power calibration curve.

The presence of methane in all three mixtures clearly affects the smooth envelope of the two N₂O nearly-Gaussian absorption bands, whose QEPAS reference spectrum R(N₂O) in Fig. 6(a) is consistent with the measurements presented in [17]. By considering R(CH₄), three spectral features centered at 1266.04 cm−¹, 1306.10 cm−¹ and 1330.35 cm−¹ are clearly distinguishable. As the methane concentration increases, the presence of these bands become clearer in the mixture spectrum. In addition, in the mixture N₂O:510 ppm-CH₄:950 ppm, a fourth spectral feature addressable to the methane contribution arises at 1251.60 cm−¹. Besides this qualitative analysis, a quantitative estimation of the amount of the two gas species in the mixture can be obtained by supposing the ith mixture spectrum, Mᵢ(ν), as the linear combination of the two reference spectra R(N₂O) and R(CH₄). MATLAB-based software was developed to retrieve the N₂O and CH₄ concentrations in all three mixtures. The results obtained for the three gas mixtures, together with related standard errors, are summarized in Table 1.

The discrepancy between the calculated and the nominal concentration for methane decreases at higher CH₄ concentrations as well as the relative standard errors, considering its increasing contribution on the QEPAS spectrum. The discrepancy between the calculated and the nominal concentrations is below 5 % for both gases, except for methane in mixture 1, where the discrepancy is ∼ 6.5 %. The relative standard error of the calculated concentrations is lower than 3 % for the two gases in all the mixtures, except for the relative standard error of 6.2 % estimated for methane in mixture 1, where absorption features of methane are hardly recognizable. The obtained results prove the robustness of the QEPAS technique for a fast broadband detection of gas mixtures. However, the capability of the sensor to recognize the influence of methane absorption features on the two N₂O absorption bands is expected to improve as the acquisition spectral resolution is increased. Therefore, measurements were repeated in the TTAM configuration. The reference spectra and the three mixtures spectra are shown in Fig. 7(c).

The spectra in Fig. 7(c) clearly show the different contributions of the two gaseous components in the mixtures, with several methane peaks becoming visible from the N₂O P- and R-branches, even at the lowest CH₄ concentration. The N₂O and CH₄ concentrations in the three mixtures were also calculated by using the MATLAB-based software and the results are reported in Table 2.

The discrepancy between the nominal and the calculated concentration of nitrous oxide and methane is lower than 5 % for all the mixtures. Moreover, the relative standard errors of the concentrations improved of a factor ∼ 2 compared to the values reported in Table 1. Compared to FTAM, TTAM measurements provide spectra with more recognizable absorption structures that can be associated to the single gas components in the mixture. Ultimately, the fitting procedure allows N₂O and CH₄ concentrations to be retrieved with a comparable level of accuracy for both acquisition modes and a higher precision is obtained in the case of operating in TTAM.

6. Conclusions

In this work we demonstrated the feasibility of broadband absorber multi-gas detection by employing a QEPAS sensor based on a DFB-QCL
array as the excitation source. The sensor architecture was determined by the spectral and beam profile characteristics of the array, leading to the choice of a 1 mm-prong spacing custom QTF as the acoustic resonator for the QEPAS sensor. The uneven methane spectrum was reconstructed within the light source emission spectral range with a spectral resolution of 0.27 cm$^{-1}$ and 4−5 cm$^{-1}$. A methane detection sensitivity of 200 ppb was achieved with a 10 s lock-in integration time and a linear responsivity with a CH$_4$ concentration in the 1000−200 ppm range was verified. Multi-gas broadband detection was then demonstrated by analyzing three different N$_2$O/CH$_4$:N$_2$ mixtures in dry nitrogen within the DFB-QCL array emission spectral range. Despite the absorption spectra overlap within the whole investigated spectral range, the concentration of both gas species can be retrieved with an accuracy equal or even higher than 95% while the precision is strongly affected by the spectral resolution of the acquisition. The two modes could be used in combination: the fast acquisition mode to determine the presence of a gas species and a slow one to retrieve its concentration with a high precision. The proof-of-concept presented in this paper represents a starting point for the development of sensors aiming at environmental monitoring of broadband greenhouse gases. In the future, investigations on the effect of relative humidity and additional interferents on the N$_2$O/CH$_4$ spectra will be performed, and multivariate analysis, like partial least squares regression, will be implemented for signal processing.

**Funding**

This work was supported by THORLABS GmbH, within the joint-research laboratory PolySense, the National Natural Science Foundation of China [Grants #61622503, 61575113], the National Science Foundation (NSF) [ERC MIRTHE, NSF NetS R3H685], the Robert Welch Foundation [C0586] and the US Army [W911SR-16-C-0005].

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| Table 1 | Nominal and calculated N$_2$O and CH$_4$ concentration for the three investigated gas mixtures analyzed with FTAM QEPAS. |
|---------|---------------------------------------------------------------|
| i | Nominal N$_2$O concentration (ppm) | Nominal CH$_4$ concentration (ppm) | Calculated N$_2$O concentration (ppm) | Calculated CH$_4$ concentration (ppm) |
| 1 | 510 | 150 | 503.1 ± 3.5 | 159.8 ± 9.9 |
| 2 | 510 | 500 | 510.9 ± 4.7 | 504.8 ± 13.2 |
| 3 | 510 | 950 | 516.5 ± 6.6 | 947.6 ± 18.6 |

| Table 2 | Nominal and calculated N$_2$O and CH$_4$ concentration for the three investigated gas mixtures analyzed in TTAM. |
|---------|---------------------------------------------------------------|
| i | Nominal N$_2$O concentration (ppm) | Nominal CH$_4$ concentration (ppm) | Calculated N$_2$O concentration (ppm) | Calculated CH$_4$ concentration (ppm) |
| 1 | 510 | 150 | 520.9 ± 1.8 | 157.4 ± 4.6 |
| 2 | 510 | 500 | 504.6 ± 2.9 | 484.5 ± 7.2 |
| 3 | 510 | 950 | 509.8 ± 3.9 | 954.8 ± 9.7 |

Fig. 7. (a) 510 ppm N$_2$O:N$_2$ and (b) 1000 ppm CH$_4$:N$_2$ TTAM QEPAS reference spectra; (c) TTAM QEPAS signal normalized to the optical power calibration curve for three dry mixtures containing 510 ppm of N$_2$O and 150 ppm of CH$_4$ (blue dots), 500 ppm of CH$_4$ (red triangles) and 950 ppm of CH$_4$ (green squares), respectively.
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