



Multi-pass cell-assisted photoacoustic/photothermal spectroscopy of gases using quantum cascade laser excitation and heterodyne interferometric signal detection

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Abstract

A heterodyne interferometer-based signal retrieval in photoacoustic/photothermal gas spectrometer using mid-infrared quantum cascade laser excitation is demonstrated. This new method for all-optical photoacoustic/photothermal signal detection allows for sensitivity enhancement using standard multi-pass cells, commonly used in absorption-based spectrometers. Two types of multi-pass cell are examined: a Herriott type with up to 33 passes and a White type with up to 46 passes. Good agreement between experimental results and numerical analysis is obtained.

1 Introduction

Photoacoustic spectroscopy (PAS) is a laser-based sensing technique frequently used for chemical analysis. PAS relies on photoacoustic (PA) effect that is generated in the sample due to absorption of light [1]. When source of radiation is modulated at audio frequencies, local temperature of the sample changes periodically and pressure waves are generated that can be detected with a sensitive microphone. To enhance the PA signal, an acoustic resonator can be used for sound energy buildup. Other commonly used approach relies on incorporating a quartz tuning fork that serves

as a resonant microphone with high quality factor [2]. In both cases, retrieved signal strongly depends on resonator enhancement factor which may drift, e.g., due to changes of sample composition, temperature, or pressure. In both techniques, an effective sensing volume is very small (e.g., $>10\text{ cm}^3$ for the conventional PAS cells and $>1\text{ mm}^3$ in quartz-enhanced PAS or QEPAS), which severely narrows possibilities for optical enhancement of the PAS signal. Several groups reported on PAS and QEPAS implemented with high-finesse optical cavities for effective optical power buildup [3, 4], which works well for sensitivity enhancement, but results in a quite complex and vibration-sensitive instrumentation. Standard multi-pass cell-based optical enhancement used in the conventional absorption-based methods (such as tunable diode laser absorption spectroscopy, TDLAS, or wavelength modulation spectroscopy, WMS) is not fully compatible with PAS. Implementation of multi-pass enhancement into PAS was briefly studied in [5, 6], but both cases required a design of custom PAS cell and only relatively small sensitivity improvements were achieved (e.g., in Ref [6] with 18 passes inside a Herriott-type cell, a signal amplitude was increased only by a factor of ~ 3.5).

Recently, fully optical methods for signal retrieval in PAS (or photothermal spectroscopy, PTS) have been explored. In this approach, locally induced changes of the sample's refractive index (due to local changes of temperature and pressure) are measured optically, usually using a secondary probe laser and an interferometric detection scheme. Refs [7, 8] reported an early demonstration of this

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approach utilizing a mid-infrared CO₂ laser for molecular excitation, and a HeNe laser (aligned collinearly with the infrared radiation) was used to probe resulting changes in the refractive index of the sample. Since these techniques rely on measuring refractive index over the entire interaction length of the probe beam with the optically excited sample, they are compatible with conventional multi-pass cells and long open-path configurations, which are not typically used in PAS/PTS. Recently, a few examples of optical-based detection of PA signal have been demonstrated to probe gas enclosed in a hollow-core fiber [9–11]. In Ref [12], we have introduced a heterodyne-based optical PA signal retrieval, which, in contrast to standard interferometric detection [9–11], does not require the setup to be stabilized and balanced for operation in quadrature and is fully compatible with various sensing arrangements, including open-path or inside hollow-core fiber. In addition, the optical-based signal detection in PAS allows for the excitation wavelength and the probe laser wavelength to be chosen independently, which enables implementation of mid-infrared sources to target the fundamental molecular ro-vibrational transitions, whereas high quality and efficient visible or near-infrared laser sources and detectors can be used for signal detection [11, 13].

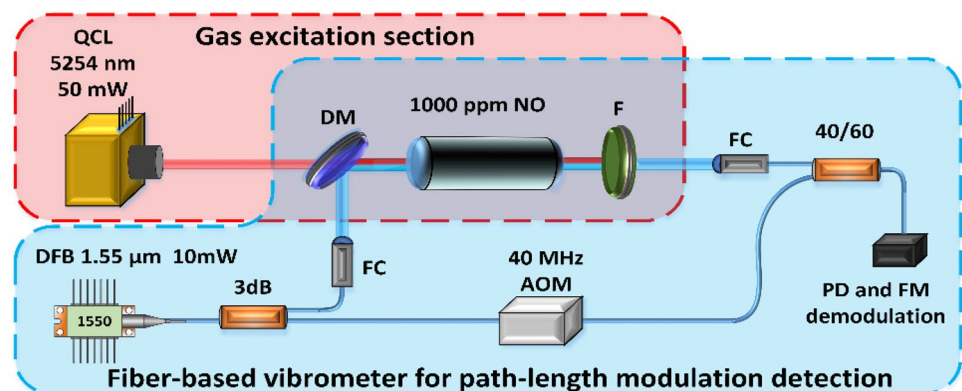
In this letter, we describe a heterodyne-based signal retrieval implemented in the mid-infrared molecular fingerprint region using a distributed feedback (DFB) quantum cascade lasers (QCLs) for photoacoustic/photothermal signal generation and standard telecom diode laser for interferometric signal detection. First, a single-pass detection of nitrous oxide with 5.25 μm QCL is presented. This configuration is subsequently modified to demonstrate application of a multi-pass cell for photoacoustic signal enhancement using 7.2 μm QCL to target molecular transition of methane. Here, we show what we believe is the first demonstration of a multi-pass cell enhanced mid-infrared PAS utilizing optical-based PA signal detection.

2 Experimental setup

2.1 Single-pass configuration

Figure 1 shows a schematic diagram of the experimental layout. It can be divided into two parts: (a) gas excitation section and (b) heterodyne interferometer section. A thermoelectrically cooled DFB QCL operating at 5.25 μm with an output power up to 50 mW was used as an excitation source. The laser wavelength was swept across target R7.5 transition of nitric oxide (NO) at 5254 nm (1903.16 cm^{-1}). The laser wavelength was modulated via sinusoidal modulation of the laser current with modulation frequency of $f_0 = 500$ Hz used to generate periodic PA signal (wavelength modulation depth was optimized experimentally to generate the strongest signal at the second harmonic of f_0). The interferometric detection section of the setup was built with telecom-grade fiber-coupled components. Light from a DFB fiber-pigtailed laser diode operating at 1550 nm was split with a 3 dB coupler to form two arms of the Mach–Zehnder interferometer. The first beam (‘reference’) was frequency-up-shifted by 40 MHz using an acousto-optic modulator (AOM, Gooch Housego, M040-8J-F2S). The second beam (‘probe’) was co-linearly combined with the emission from the QCL using a dichroic mirror and propagated through a 10 cm long gas cell filled with 1000 ppmv mixture of NO in N₂ at 760 Torr. After passing through the absorption cell, the excitation beam was blocked with a filter, while the probing beam was combined with the reference beam using a 40%/60% coupler. The combined beam was directed onto an InGaAs detector (Thorlabs, DET08CFC), where heterodyne beatnote at 40 MHz was detected. The electric signal was demodulated using an RF spectrum analyzer (Tektronix, RSA5000 series) and analyzed at $2 \times f_0 = 1$ kHz (the second harmonic of the wavelength modulation frequency). Due to limited heat transfer in the excited gas sample, the amplitude of photothermal signal deteriorates with increasing laser modulation frequency. However, phase-sensitive detection of signals in

Fig. 1 Schematic of the experimental layout. *QCL* quantum cascade laser; *DFB* distributed feedback telecom laser diode; 3 dB, 40/60—fiber couplers; *DM* dichroic mirror; *F* filter; *FC* fiber collimator; *PD* photodiode



sub-kHz frequency range is susceptible to additional noise sources. Therefore, optimal modulation frequency for the proposed photothermal configuration was determined experimentally, yielding highest SNR at demodulation frequency of 1 kHz.

When QCL wavelength is tuned across the NO absorption line, wavelength modulation results in periodic changes of the refractive index in the gas sample (due to the PA effect). Those changes produce modulation of the phase of the heterodyne beatnote that can be detected as frequency modulation of the carrier at 40 MHz. Consequently, PA signal can be retrieved through FM demodulation of the beatnote and its subsequent analysis at the second harmonic of the wavelength modulation frequency ($2 \times f_0$). Figure 2 shows a series of NO spectra recorded for various wavelength modulation amplitudes to optimize the modulation depth.

Spectra in Fig. 2 show that when the modulation depth increases, the PAS signal amplitude changes in a similar way as absorption signals commonly expected in the conventional wavelength modulation spectroscopy (WMS) systems and the peak signal exhibits local maximum at modulation index of ~ 2.2 . There is one significant difference with respect to a conventional WMS; namely PAS is fundamentally a baseline-free technique (no PA signal is produced without absorption), and thus, there is no baseline in the measured spectra despite relatively large wavelength modulation amplitudes. This is particularly important feature of the proposed detection technique, since it enables continuous

monitoring of the signal amplitude at single spectral point corresponding to the transition center.

2.2 Multi-pass configuration

The concept employing a multi-pass cell for sensitivity enhancement was tested using a DFB QCL operating at $\sim 7.2 \mu\text{m}$. Several molecular transitions were located within the tuning range of this laser including water vapor transitions suitable for isotopic ratio measurements [14] and strong absorption lines of hydrogen sulfide [15]. In this work, to demonstrate the multi-pass PA sensing concept, we have chosen to target transition of methane (CH_4) located in its ν_4 band near 1389 cm^{-1} . The schematic of the experimental setup is depicted in Fig. 3. Similar to the single-pass configuration discussed in the previous section, the QCL's output radiation was overlapped with light from a near-infrared laser diode ($\sim 1.55 \mu\text{m}$) using a dichroic mirror and this combined dual-color beam was later coupled into two different multi-pass cells (a Herriott-type and a White-type). The additional spool of fiber (SMF28) was added to the reference arm to ensure that the Mach–Zehnder interferometer had similar optical path length in both arms (since the probe laser is a simple telecom diode laser, any imbalance larger than few meters results in reduction of the heterodyne efficiency and increase in demodulation noise).

The Herriott-type multi-pass cell was built using two 1" concave mirrors placed 108 mm from each other (input

Fig. 2 Photoacoustic signal intensity registered for nine consecutive spectral acquisitions performed with different values of QCL's injection current modulation amplitude. The analyte was 1000 ppm of NO in N_2 under 760 Torr, enclosed in a 10 cm long gas cell

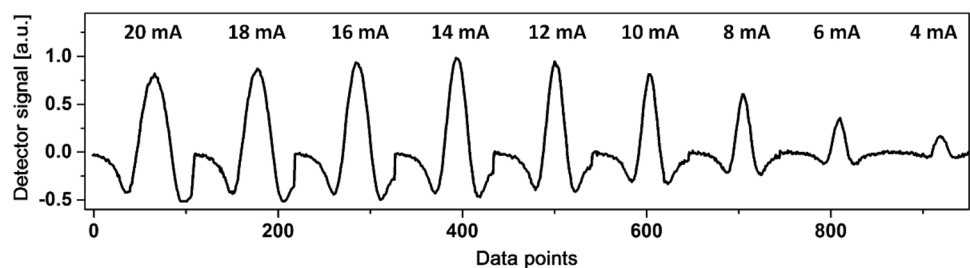
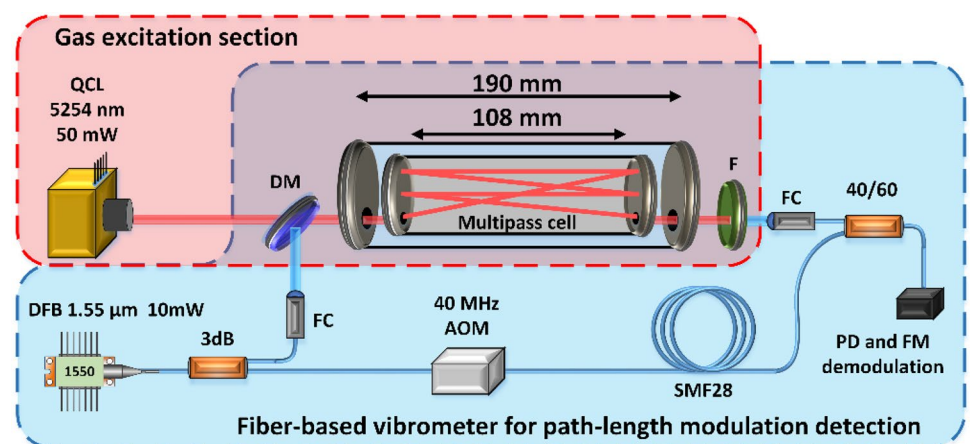


Fig. 3 Schematic of the experimental layout incorporating a multi-pass cell for interferometric detection of a PA signal. QCL quantum cascade laser, DFB distributed feedback telecom laser diode, X0/Y0 fiber couplers with specified splitting ratio, DM dichroic mirror, F filter, FC fiber collimator, PD photodiode



and exit holes were machined in both mirrors). The multi-pass cell was placed in a tight enclosure with a physical length of 19 cm (measured from the input to the output window). It could be configured to support three different path lengths: 19, 83, and 364 cm (1, 7, and 33 passes, respectively, obtained through axial rotation of the exit mirror). The optical path re-configurability was the key feature of the proposed measurement layout that enabled experimental verification of the linear path length enhancement of the PA signal amplitude. To ensure the same measurement conditions for each path length test, the spatial overlap of the excitation and the probe beam was not altered between the consecutive reconfigurations of the multi-pass cell. After each reconfiguration, only the output collimator was re-aligned to achieve maximum collection efficiency, which resulted in slightly different levels of the heterodyne beatnote for each optical path. However, this had no noticeable impact on the performance of the setup, since spectroscopic information is retrieved not from the amplitude but from the frequency of the beatnote which does not depend on the collected optical power at 1550 nm.

The Herriott cell was filled with a calibrated mixture of 1% of CH_4 balanced with N_2 at a pressure of 250 Torr. Figure 4 shows a raw detector signal acquired during a direct absorption measurement performed with the Herriott cell configured to 19 cm optical path length. The second harmonic PA signals registered using the fiber-based heterodyne interferometric setup for each Herriott cell configuration are presented in Fig. 5. These spectra have shapes similar to known from WMS technique and show clear dependence on the optical path length. However, in WMS-based measurements, baseline is often present in the second harmonic spectrum (mainly due to parabolic shape of the sample transmission, such as visible in Fig. 4). Spectra presented in

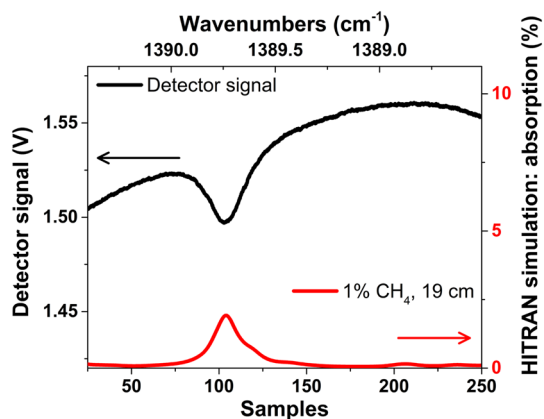


Fig. 4 Direct absorption measurement of a 1% CH_4 absorption line located near 1389 cm^{-1} in a Herriott cell configured to have 19 cm of total optical path length. Black graph represents measurement; red graph shows a HITRAN simulation of the targeted line

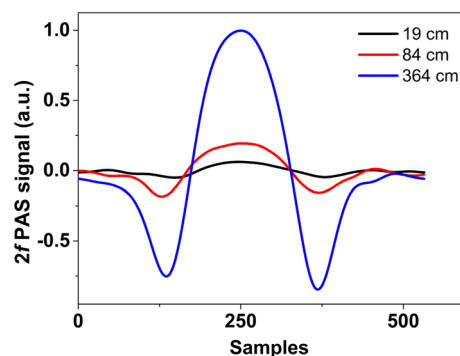


Fig. 5 $2f$ PAS signals registered for three different configurations of a Herriott multi-pass cell yielding a total gas–laser interaction length of 19, 84, and 364 cm

Fig. 5 confirm the baseline-free character of the PA measurement. The signal amplitude (at the center of the transition) as a function of path length is demonstrated in Fig. 6 and is consistent with the peak absorption calculated using the Beer–Lambert law with HITRAN database parameters (shown as a dashed line).

Similar experiments were performed using a White multi-pass cell with a base length of ~ 235 mm (from Pike Technologies). By adjusting the angle at which the input beams were coupled into the cell, the optical path lengths of 1.03, 2.87, 5.63, and 10.7 m could be obtained (4, 12, 24, and 46 passes, respectively). The target CH_4 transition was the same as in Herriott cell experiments. Due to longer path lengths achievable with the White cell, a lower concentration mixture of 3300 ppm of CH_4 balanced with N_2 was used (with similar pressure of 250 Torr). Figure 7 shows measured $2f$ PAS amplitude as a function of optical path length. Measured values are again in agreement

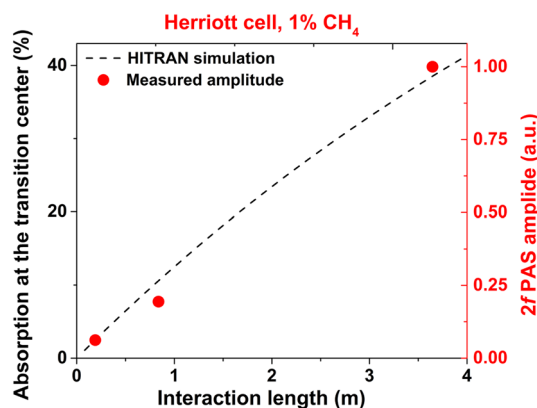


Fig. 6 $2f$ signal amplitude plotted as a function of optical interaction length for different Herriott multi-pass cell configurations (red dots). Black dashed line shows HITRAN-based simulation of the peak absorption

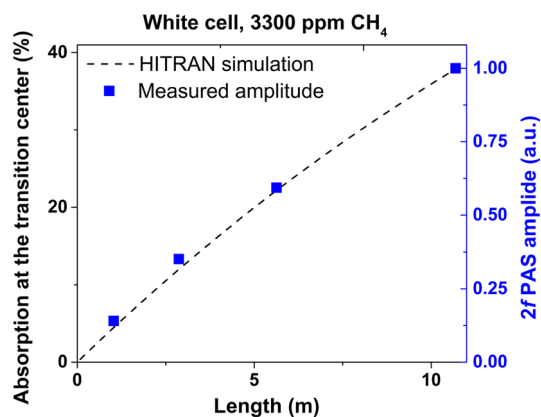


Fig. 7 $2f$ signal amplitude plotted in function of gas–laser interaction length for White multi-pass cell (blue dots). Black dashed line shows HITRAN-based absorption simulation

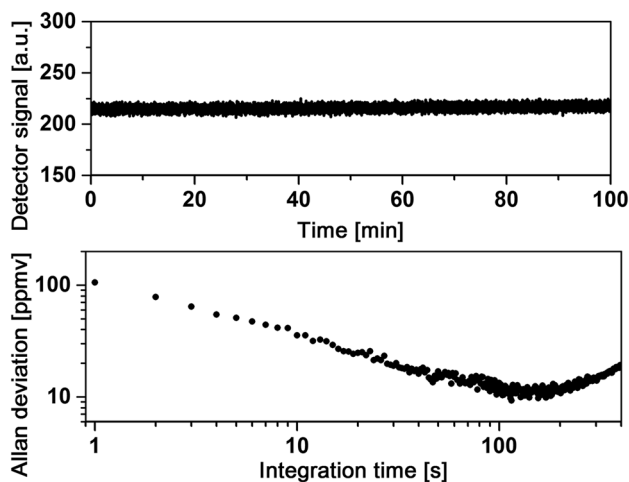


Fig. 8 Top: Long-term $2f$ signal measurements performed at the center of the transition of 1% CH₄. Bottom: Allan deviation analysis

with the peak optical absorption simulated at the transition center using HITRAN database.

Performance of the Herriot multi-pass-cell-assisted sensor configuration was estimated by performing a long-term measurement of $2f$ signal amplitude, while the QCL was parked at the center of the 1% CH₄ transition. Based on the gathered data, we calculated Allan deviation, which is plotted in Fig. 8, along with the raw signal amplitude. According to the gathered data, the configuration using a Herriott-type multi-pass cell was capable of reaching a minimum CH₄ detection limit of 10 ppmv at an integration time of 100 s. Further increasing of the integration time did not improve the detection limit, which is most likely due to long-term wavelength drift of the QCL (no line-locking was used in our experiment). We predict that the main source of noise in the system, limiting the

performance, was coming from mechanical and acoustic vibrations.

3 Conclusions

In this paper, a mid-infrared photoacoustic/photothermal spectroscopy with heterodyne-based interferometric signal retrieval was presented. We have demonstrated that this approach to PAS enables straightforward signal enhancement using standard multi-pass cells, frequently used in typical absorption-based spectroscopic instruments. Two types of multi-pass cells were used and good agreement with simulated absorption data from HITRAN database was obtained. This method can be further evaluated in a configuration utilizing a high-finesse cavity and open-path configurations for sensitivity enhancement. We suspect that the intra-cavity energy buildup would enable maximizing the PAS signal, leading to detection limits comparable with standard approach to PAS but with no need for using acoustic resonant cells.

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