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Absorption spectroscopy with femtosecond frequency comb lasers for breath analysis

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Abstract

An optical setup based on a frequency comb laser and a multipass optical cell has been developed for breath analysis. The frequency comb laser is a broadband Er⁺ fiber laser beam in a range spanning from 1500 nm to 1700 nm. The multipass optical cell is formed by six highly reflective confocal mirrors to achieve a long optical path of 300 m in a cell of only 0.5 m in length. For testing the optical setup, the absorption laser spectroscopy measurements in the near IR of the gases CO₂, CO, and CH₄ were carried out. In the case of CH₄ a signal to noise ratio of 120 was obtained, yielding an estimated sensitivity of 6 ppmv. The dispersion of the femtosecond laser pulse in a multipass cell filled with methane gas at atmospheric pressure was studied. In the case of 1.64 μm and after 600 reflections, the femtosecond laser pulse was temporally broadened and the laser pulse duration changed from 108 fs to 326 fs. To compensate for this broadening, dispersive mirrors with suitable parameters are being proposed.

Keywords: Frequency comb laser, Breath analysis, Laser spectroscopy

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1. Introduction

Sensitive laser absorption spectroscopy is considered to be a powerful tool for the detection of trace gases. As such laser absorption spectroscopy has applications not only in physics and chemistry but also in biology, environmental monitoring, and medicine. In the later field the analysis of the human breath is very useful for diseases detection and monitoring. Breath analysis is a non-invasive method for monitoring the volatile organic compounds present in an individual's exhaled breath and is one of the clinical tests that can be used for early disease detection. The advantages of breath analysis in comparison to blood or urine analysis includes it is non-invasive, easily repeated, and does not cause any infections. For disease early detection is very important a quick non- invasive method such as the breath analysis because it could mean the difference between life and death.

Normal human breath contains a few atmospheric molecules, e.g., water (H₂O), carbon dioxide (CO₂), molecular nitrogen (N₂), molecular oxygen (O₂), in relatively high concentrations, several volatile organic compounds (VOCs), e.g., acetone (C₃H₆O), isoprene (C₅H₈), propanols (C₃H₈O), etc., at the parts per million (ppm) or sub ppm levels, and about four hundred major VOCs (of more than 1,000 breath compounds) at the ppb or parts per trillion (ppt) levels (Jansson et al., 1969; O'Neill et al., 1988; Pauling et al., 1971). Qualitative and quantitative analysis of parts per trillion (ppt) to ppb concentrations of gaseous target analytes is always challenging. The diagnostic potential of breath analysis has been recognized for centuries. The original research can be found within the writings of Hippocrates (Risby & Solga, 2006). However, the first published quantitative analysis was not possible until 1784 when Lavoisier examined carbon dioxide in breath (Tan & Hu, 2004). By the 1950s, separation of individual gas molecules became possible with gas chromatography (Morgan, 1961). In general, there are several methods of trace molecular detection that have been used for breath analysis, including: optical detection (Crosson et al., 2002; Kosterev et al., 2001), Gas Chromatography (GC) combined with Mass Spectroscopy (MS) (Di Francesco et al., 2005; Wood et al., 2006) and electronic noses (Machado et al., 2005; Polikar et al., 2001).

Optical detection can be considered as a general method for breath analysis. The unique absorption spectrum of each molecule allows accurate identification and concentration measurements of a single molecule in the presence of many others.

As the time goes the laser technology becomes less expensive and more compact, the number of optical detection systems designed to detect biomarkers has increased. The tunable laser diodes that working in the near infrared (NIR) could measure the ratio of stable isotopes of carbon (Tazoe et al., 2011). Another NIR system detects methylamine to study its correlation with liver and renal diseases (Marinov et al., 2007). Quantum cascade lasers, operating in the mid-infrared, have been used to detect ammonia (NH_3) for diagnosis of renal failure (Manne et al., 2006). Breath nitric oxide (NO) for diagnosing asthma has been detected using tunable diode laser absorption spectroscopy (Cao et al., 1992; Stepanov et al., 1999). Tunable diode and quantum cascade lasers were used to detect carbon monoxide (CO) in breath using absorption spectroscopy (Moeskops et al., 2006; Stepanov et al., 1996) and cavity ring-down spectroscopy (Fritsch et al., 2007). NH_3 in breath was measured using photo-acoustic spectroscopy (Narasimhan et al., 2001). Cavity-ring down spectroscopy has been used to enable rapid breath NH_3 detection (Banik & Mizaikoff, 2020). Furthermore, cavity enhancement techniques permit highly sensitive detection in a matter of seconds (Doussin et al., 1999; Scherer et al., 1997; Ye et al., 1998). Such techniques are of interest for possible monitoring of kidney function and efficacy of dialysis. Finally, both quantum cascade and lead salt lasers have been used to detect ethane (C_2H_6) which is produced in lipid peroxidation and by some forms of cancer (Dahnke et al., 2001; Patterson et al., 2007; Skeldon et al., 2006).

Although all of these optical detection systems provide high selectivity and sensitivity, the number of molecules that can be monitored by a single system is limited. Recently, broad bandwidth optical frequency combs have been used for trace detection in such way that several molecules can be monitored simultaneously in a single shot (Diddams et al., 2007; Gherman & Romanini, 2002; Gohle et al., 2007; Thorpe et al., 2007; Thorpe et al., 2006). The frequency-comb laser systems allow access to broadband spectral region spans from UV to far infrared via nonlinear conversion (Maddaloni et al., 2006; Okuno et al., 2006; Tauser et al., 2004).

In this work, the broad spectrum of a mode-locked fiber laser was coupled to an optical multipass gas cell to enhance the detection sensitivity of trace gases. High

spectral resolution of ± 0.05 nm was achieved within the entire 1500 - 1700 nm spectral region. The relevant spectrum covers many biomarkers, such as ethane (C_2H_6) 1680-1700 nm, acetone (C_3H_6O) 1670-1680 nm, methane (CH_4) 1630-1690 nm, ethylene (C_2H_4) 1620-1660 nm, carbon dioxide (CO_2) 1540-1640 nm, carbon monoxide (CO) 1560-1600 nm, ammonia (NH_3) 1500-1540 nm and methylamine (CH_5N) 1500-1530 nm. In the preliminary measurement and in order to test the optical setup only the first overtone absorption spectra for CO_2 , CO and CH_4 gases were recorded.

2. Material and Methods

2.1. Experimental setup

The optical setup is shown in Fig. 1. It consists of the multipass system, the M-fiber femtosecond laser and a spectrum analyzer. The multipass cell is composed of six high reflective mirrors from Layertec GmbH. All six mirrors that form the cell have a broadband dielectric coating with a reflectivity higher than 99.995% in the wavelength range from 1500 nm to 1700 nm. The front confocal mirror M3 has a 2 mm diameter hole through which the light beam enters and exits. Each side of the multipass is formed by three confocal mirrors each with radius of curvature of 500 mm. Two of the mirrors are a square with dimensions of $25\text{ mm} \times 25\text{ mm}$, while the third mirror has a rectangular shape with dimensions of $25\text{ mm} \times 50\text{ mm}$. Together the three mirrors form a square with dimensions of $50\text{ mm} \times 50\text{ mm}$ and act as reflectors on each side of the cavity. Each mirror can be tilted independently in the horizontal and vertical planes to change the number of reflections. Also the position of each mirror can be adjusted independently in the horizontal and vertical directions. The gaps between the mirrors are minimized in such a way that the mirrors can be tilted without touching each other. To achieve precision tilt control, micrometer adjustable rotation stages were attached to the sides of the mirrors. For fine adjustment of displacement, the precision rotation stages were fixed to XYZ translation stages. The volume occupied by the beams depends on the space between the mirrors and it has about $50\text{ mm} \times 50\text{ mm}$ cross section and is 500 mm long, yielding a total volume of 1.25 liters.

The used laser system is a broadband femtosecond laser from Menlo Systems GmbH having an output power of 200 mW and covering the spectral range from

1500 nm to 1700 nm. In addition, mode matching of the input beam to the cell configurations was carried out in such a way that the beam diameter remained the same for a round trip in the cell.

The spectrum of the input and output beams was measured by an Optical Spectrum Analyzer (Yokogawa AQ6375). It covers the range from 1200 nm to 2400 nm and has a high sensitivity which enables measurements of powers as low as -70 dBm. It used a double-pass monochromator structure to achieve a wavelength resolution of ± 0.05 nm and a wide close-in dynamic range (55 dB). These advantages of the spectrum analyzer allows closely located signals near the noise limit to be observed.

The alignment of the multipass optical cell was achieved with the help of an infrared InGaAs camera from Hamamatsu (Model C10633) which has a spectral sensitivity from 900 nm to 1700 nm and a quantum efficiency of 80% at 1500 nm. Once the alignment is achieved, the beam exits after 600 reflections the same hole where the beam enters the multipass cell and its power is measured by a power meter. The transmission efficiency (power of the exit beam/power of the input beam) of the multipass cell reached about 80%. This is close to the theoretical transmission efficiency of about 90% obtained from the known reflectivity of the mirrors and the number of passes. The difference between the theoretical and measured transmission efficiency is mainly due to losses from the spots that were close to the gaps between the mirrors.

The sensitivity of the optical system was tested by measuring the absorption spectra of CH₄, CO, and CO₂. These molecules have overtone absorption bands that fall within the range of the used laser radiation (1500 nm to 1700 nm). In order to sample desired gas mixtures the multipass system is placed in a plexiglass enclosure at atmospheric pressure of ambient air. The enclosure has three ports, one is used for admitting the gases through leak valves for each gas and the second port pump the gas. The third port has an optical window for the input and output laser beams.

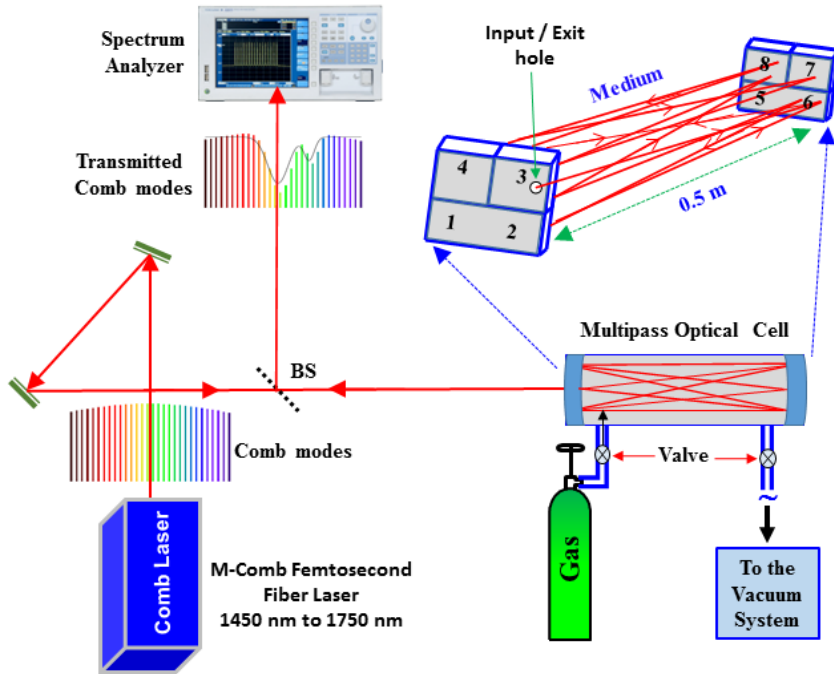


Fig.1. Schematic diagram of the optical setup; BS- beam splitter.

3. Results

When the gases were leaked into the cell the absorption spectra of CH₄, CO and CO₂ gases were obtained and are displayed in comparison with the laser spectrum (LS) where no gases as shown in Fig.2.

The total multipass absorbance α is obtained from $\alpha = -\ln \left[\frac{I}{I_0} \right]$ where I is the light intensity remaining after absorption (the exit beam intensity) and I_0 is the output intensity in the absence of the absorber (when the mirror losses are small it is close to the input beam intensity). For small losses variations $\delta I_0 \approx \delta I$ and when they are determined independently one can write for the variation of the absorbance $\delta \alpha \approx 2 \frac{\delta I}{I}$ (Cui et al., 2012; Steyert et al., 2001). The signal to noise ratio, $S/N = \alpha / \delta \alpha$, by taking into account that $\alpha \propto (n+1)$ and that $I_0 (\approx I) \propto R^n$, where R is the reflectance per pass and n is the number of reflections, can be expressed in the form

$\frac{S}{N} = \frac{\alpha I}{2 \delta I} \propto \frac{(n+1)}{2 \delta I}$ (Rothman et al., 2009). The S/N ratio is obtained by integrating the area under the spectral peak which is the signal S and dividing S by the integral of the intensity over a corresponding amount of area where no signal is detected, which is the noise N. The minimum detectable number density of absorbing molecules ΔN is given by (Cui et al., 2012) as $\Delta N \geq \frac{\alpha}{\sigma L (S/N)}$. This means that to achieve the highest sensitivity to gas concentrations the absorption path length L and the signal to noise ratio should be as large as possible, and the transitions with a large absorption cross section σ are preferable. The total absorbances α of CH₄, CO and CO₂ gases can be obtained from the observed data shown in Fig. 2 and are plotted as a function of the wavelength as shown in Figs. 3-5. In comparison with the HITRAN database spectra.

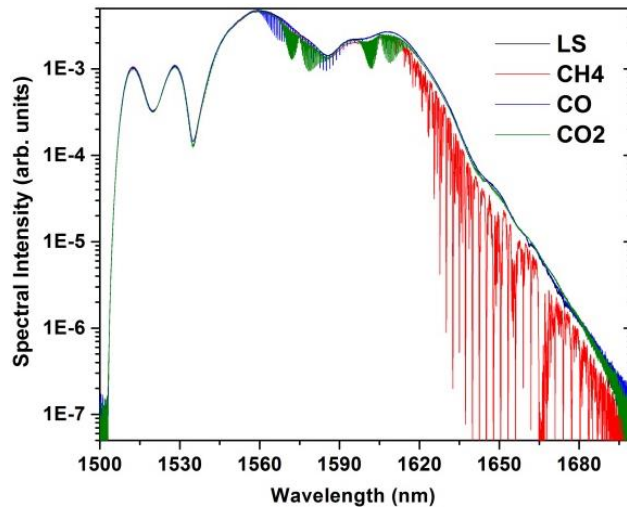


Fig.2. The measured absorption spectra of CH₄, CO and CO₂ gases displayed in comparison with the laser spectrum (LS).

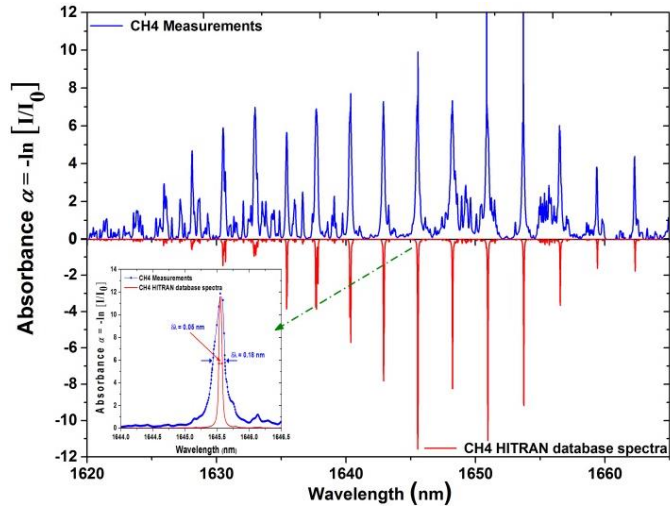


Fig.3. The total absorbance α of CH₄ gas as a function of the wavelength. Only the central portion of the spectrum containing a strong absorption band is shown with spectra calculated with the HITRAN database (red, inverted for clarity). The inset shows the absorption line of CH₄ having the highest absorbance at $\lambda = 1645$ nm in comparison with the HITRAN database spectra.

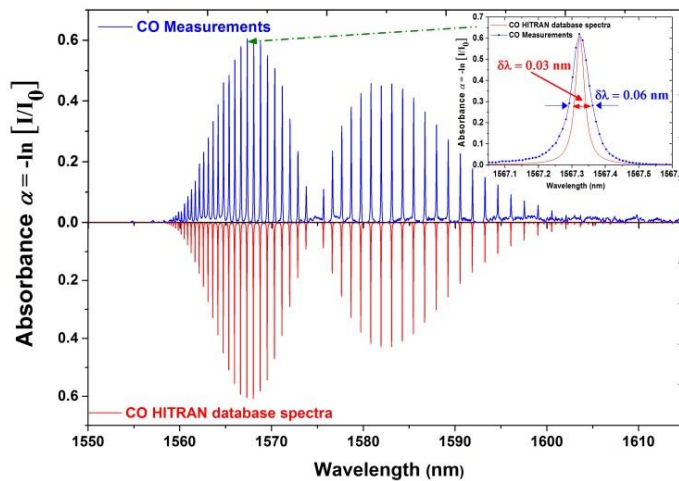


Fig.4. The total absorbance α of CO gas as a function of the wavelength is shown with spectra calculated with the HITRAN database (red, inverted for clarity). The inset shows the absorption line of CO having the highest absorbance at $\lambda = 1567$ nm in comparison with the HITRAN database spectra.

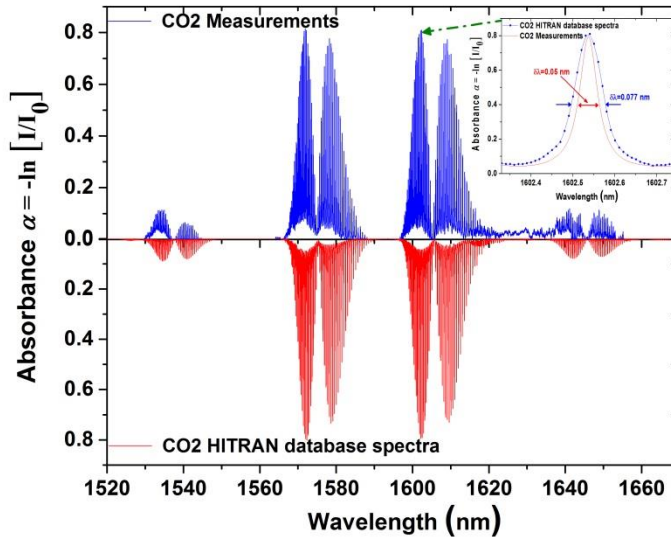


Fig.5. The total absorbance α of CO₂ gas as a function of the wavelength is shown with spectra calculated with the HITRAN database (red, inverted for clarity). The inset shows the absorption line of CO₂ having the highest absorbance at $\lambda=1602.5$ nm in comparison with the HITRAN database spectra.

To determine the maximum sensitivity of the developed optical setup the absorption spectrum of CH₄, CO and CO₂ gases were analyzed quantitatively. From the measured absorption spectrum of the CH₄ (Fig.3) the absorption line having the highest absorbance was selected at $\lambda=1645$ nm, where $\alpha = -\ln [I/I_0] = 12$. From the known absorption cross section [39] $\sigma = 17 \times 10^{-21}$ cm²/molecules and the optical path length $L=314$ m, we can find the number density of CH₄ molecules $N(\text{CH}_4/\text{cm}^3) = (\alpha)_\lambda / [\sigma(\text{cm}^2/\text{molecules})_\lambda L(\text{cm})] = 2 \times 10^{16}$ molecules/cm³ and the corresponding concentration of 800 ppmv. The observed absorption spectrum of the CH₄ in comparison with the HITRAN database spectra in Fig.3 exhibits a high S/N of about 120. The measured signal is broadened by the resolution of the spectrum analyzer. The spectra were measured without any averaging in 25 s per spectrum of 250 nm bandwidth with 0.05 nm resolution and 0.01 nm sampling interval. The minimal detectable number density of absorbing molecules ΔN is then about 1.6×10^{14} molecules/cm³, i.e. 6 ppmv. In a similar way

as CH₄ the minimal detectable number densities of CO₂ and CO were found to be 640 and 320 ppmv. To increase the sensitivity and decrease the minimal detectable number density of absorbing molecules ΔN , the absorption optical path length L and the signal to noise ratio should be as large as possible and the transitions with a large absorption cross section σ are preferable. For example, in the case of CH₄, the absorption line around 3300 nm has a large absorption cross section ($\sigma = 1.5 \times 10^{-18}$ cm²/molecules). Then by using our optical setup, the minimal detectable number density of absorbing of CH₄ molecules ΔN is decreased from 6 ppm to 60 ppbv which is lower than the reported value in (Moskalenko et al., 1996) by a factor of 10.

4. Conclusions

In this paper the development of an optical setup based on a multipass cell for breath analysis has been described. A multipass optical cell was used to provide a large optical path length. Direct absorption measurements of CO₂, CO and CH₄ gases have been performed using a broadband frequency comb femtosecond fiber laser in the spectral range from 1500 to 1700 nm. The absorption spectra for CO₂, CO and CH₄ were recorded using a spectrum analyzer and showed good S/N.

In the case of CH₄, S/N ≈ 120 was found, yielding an estimated theoretical sensitivity of 6 ppmv, which can be further improved by increasing the number of reflections. The optical apparatus is portable and can be used for a wide range of applications, including environmental monitoring, combustion processes, breath analysis and fundamental atomic and molecular physics studies.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no conflict of interest.

Competing interests The authors declare no competing interests.

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