Sensitive acetone detection with a mid-IR interband cascade laser and wavelength modulation spectroscopy

JINBAO XIA,1,2 FENG ZHU,1,3 ALEXANDRE A. KOLOMENSKII,1,7 JAMES BOUNDS,1 SASA ZHANG,1,2,8 MAHMOOD AMANI,4 LIAM J. FERNYHOUGH,5 AND HANS A. SCHUESSSLER1,6

1Department of Physics and Astronomy, Texas A&M University, College Station, Texas 77843-4242, USA
2School of Information Science and Engineering, Shandong University, Jinan, 250100, China
3School of Physics and Astronomy, Sun Yat-sen University, Zhuhai, Guangdong 519082, China
4Petroleum Engineering Program, Texas A&M University at Qatar, Doha, Qatar
5Department of Medical Education, Weill Cornell Medicine, Doha 24144, Qatar
6Science Program, Texas A&M University at Qatar, Doha 23874, Qatar
7alexandr@physics.tamu.edu
8sasazhang@sdu.edu.cn

Abstract: An efficient method for the detection of acetone, an important biomarker in exhaled breath, by utilizing wavelength modulation spectroscopy (WMS) with a mid-infrared distributed feedback interband cascade laser (DFB-ICL) is presented. The performance of the DFB-ICL laser is characterized, and its linewidth is measured to be (3.39 ± 0.15) MHz by beating the output with an auxiliary mid-IR frequency comb over 50 ms. The measured asymmetric acetone absorption profile with the center wavelength around 3367 nm is fitted by the pseudo-Voigt function. The phase shift between the intensity and frequency modulations is determined and used for processing the results. The sensor is tested by performing measurements with calibration mixtures of acetone in nitrogen, and the detection limits of 0.58 ppm and 0.12 ppm were determined with 1 s and 60 s signal averaging times, respectively. Our work shows that wavelength modulation spectroscopy with a DFB-ICL laser complemented by a multipass cell for higher sensitivity can be efficiently used for acetone detection and is promising for sensitive breath analysis.

© 2019 Optical Society of America under the terms of the OSA Open Access Publishing Agreement

1. Introduction

The development of a simple yet sensitive spectroscopic technique for detection of acetone as a prominent biomarker in exhaled breath is an important goal toward realization of diagnostics based on breath analysis. Human exhaled breath contains thousands of gaseous components having both endogenous and exogenous origins with the composition comprised of a mixture of inorganic gases such as COx and NOx, volatile organic compounds (VOCs) (e.g., isoprene, ethane, pentane, and acetone, etc.) and non-volatile substances (e.g., isoprostanes, peroxynitrite and cytokines) [1–4]. The specific breath components can be used as biomarkers to provide the patient’s current health status and a diagnosis of various possible diseases in the body. There are several volatile compounds used for breath tests, which have been approved by the FDA. Carbon monoxide (CO) is used for the neonatal jaundice [5]. The small intestine bacterial overgrowth syndrome can be detected by measuring the methane concentration [6]. Nitric oxide is used for monitoring the effects of asthma therapy [7].

Generally, the techniques for breath analysis can be categorized into several groups: mass spectrometry for real-time quantitative breath analysis, including gas chromatography with mass spectrometry (GC-MS), ion mobility spectrometry (IMS) and the fast flow and flow-drift tube...
techniques called selected ion flow tube mass spectrometry (SIFT-MS); proton transfer reaction mass spectrometry (PTR-MS) [8] and also chemical sensors (CS). Natale et al. characterized the solid-state gas sensors for breath analysis using the technologies of chemiresistor based on various sensing materials and optical spectroscopy [9], including laser absorption spectroscopy (LAS). Ben et al. demonstrated the potential application of laser spectroscopy for breath analysis by tunable diode laser absorption spectroscopy (TDLAS), laser photoacoustic spectroscopy (LPAS), cavity enhanced spectroscopy (CES) and optical frequency comb spectroscopy (OFCS) and applied the laser-based ethylene detector in the real clinical setting [10]. Compared to other techniques, laser absorption spectroscopy is characterized by high resolution, high sensitivity and real-time response. The cavity-enhanced absorption spectroscopy (CEAS) or cavity ring-down spectroscopy (CRDS) can achieve sensitivities of parts per billion (ppb) or even parts per trillion (ppt) and both have been used for detecting ammonia and nitrogen oxide. Manne et al. used CRDS with a quantum cascade laser at 10.3 µm for ammonia detection in breath, achieving a sensitivity of 50 ppb [11]. Kosterev et al. used CRDS with a quantum cascade laser at 5.2 µm to detect NO concentrations in the ppb range [12]. Thorpe et al. developed a cavity-enhanced optical frequency comb spectrometer to measure multispecies of CO₂, CO and NH₃ in exhaled breath simultaneously [13]. The real time ethane detection in human breath by cavity leak-out spectroscopy (closely related to cavity ring-down spectroscopy with pulsed lasers) was developed by Dahnke et al. with a 100 ppt detection limit at 5s integration time [14]. Being a simple technique, wavelength modulation spectroscopy (WMS) allowed real-time measurements of methane with a ppb-level detection limit by using a DFB laser at 1.64 µm [15], as well as CO and its isotopes with an ICL laser at 4.69 µm [16].

Acetone, as the breath marker of diabetes [17,18] and heart failure [19] is an ongoing research topic. The concentration values of acetone for healthy individuals vary from about 0.3 ppm to 1.0 ppm [20]. CRDS in the UV spectral range with the detection limit of few hundreds of ppb for acetone measurements has also been reported [21], although CRDS needs a more complicated experimental setup and signal processing, which is less practical for analysis in real time.

Recently, several mid-infrared (MIR) spectroscopic sensors for acetone detection were reported. The spectral measurements of acetone at ~7.4 µm with a widely tunable external-cavity quantum cascade laser were performed by Nadeem et al. [22] and have shown that WMS at second harmonic provides significantly lower detection limit (~15 ppmv with ~10 s integration time) compared to direct absorption spectroscopy. Reyes-Reyes et al. studied the exhaled acetone in patients with Type-1 diabetes using a quantum cascade laser for measuring the acetone signature within the spectral interval (8.0–8.7) µm [23]. Tuzson et al. developed the acetone detector using the pulsed external cavity surface emitting laser centered at 3.38 µm, achieving a detection limit of 14 ppb with an averaging time of 15 min [24]. It was noted that the used spectral interval furnishes relatively low interference from other gases.

In this work for detection of acetone a compact sensor with a MIR distributed feedback interband cascade diode laser (DFB-ICL) operating near the acetone absorption peak at ~3.37 µm in combination with WMS is presented. We characterized the tuning range, modulation phase characteristics, the linewidth of the laser used, and the shape of the selected absorption line. In the present WMS experiment, the laser tuning range was almost the same as the spectral width at half maximum of the absorption line, and to increase the spectral coverage, two scans at different diode temperatures were implemented. At last, to evaluate the sensor performance, we introduced a calibration gas into a home-built Herriot multipass cell and determined the sensitivity and detection limit of the sensor.

2. Experimental setup

The schematic of the experiment is shown in Fig. 1. The MIR laser is a single-mode DFB-ICL (Nanoplus, GmbH), emitting around 3270 nm that is used with a commercial laser current and
**Fig. 1.** The schematic of the experimental setup. DFB-ICL: distributed feedback interband cascade laser, M: flat mirrors, BS: beam splitter, HWP: half wave plate, RL: red alignment laser, OPM: off-axis parabolic mirror, ML: mode matching lenses, OG: optical grating, VP: vacuum pump, VG: vacuum gauge, DAQ: data acquisition card, SA: spectrum analyzer. PD1,2: HgCdTe detectors. The inset at the top left shows the reflection spots on the two mirrors of the Herriot cell.

**temperature controller (ILX Lightwave, LDC-3724).** The maximum output power of the laser is \(\sim 10 \text{ mW} \) at a current of 80 mA and a temperature of 25 °C, and the range can be tuned from 3361 nm to 3372 nm.

The output from the DFB-ICL was split into two beams by a 45/55 pellicle beam splitter (BS). The first beam (with \(\sim 55\%\) of the transmitted power), passing two mode matching lenses went into a Herriot cell for absorption spectroscopy. Two irises were used to assure the overlap of the beams of the red laser (He-Ne laser, used for alignment) and the MIR laser. The output beam from the Herriot cell was focused by an off-axis parabolic mirror with a focal length of \(f = 10.2 \text{ cm}\) on a four-stage thermoelectrically cooled photodetector PD2 (Mercury Cadmium Telluride, HgCdTe, photovoltaic detector, Vigo, PIP-20M-F-M4) with a bandwidth of 15 MHz. The Herriot cell had two concave gold-coated mirrors (Thorlabs, CM254). The diameter and focal length of each mirror are 5.1 cm and 20 cm, respectively. The average reflectivity of the mirrors is above 98.5% in the spectral range from 2 to 12 \(\mu\text{m}\). One of the Herriot cell mirrors had a center hole with a diameter of 4 mm. The laser beam was reflected \(n = 35\) times, thus with the cavity length \(L = 44 \text{ cm}\) providing the interaction length \(L_{\text{eff}} = L(n + 1) \sim 15.8 \text{ m}\). The two mirrors were mounted in an aluminum vacuum chamber. The size of the chamber was \(48 \times 15 \times 10 \text{ cm}^3\) with volume 7.2 L which can be reduced to the volume between the mirrors of 0.6 L. For the entrance and exit of the laser beam the chamber had a BaF\(_2\) window with AR coating, assuring a transmission above 94% in the spectral range 2-5 \(\mu\text{m}\), and wedged at 0.5° to avoid fringes from the etalon effect. Two valves were used to evacuate the chamber with a fore-pump and for introducing the gas sample. The reflection spots on the two mirrors of the Herriot cell are shown in the inset of Fig. 1.

Another beam for characterizing the IR laser parameters (with \(\sim 45\%\) of the initial beam power after the BS) was reflected by a flat mirror, went through a \(\lambda/2\) wave plate, and then was
overlapped with a MIR frequency comb that has a repetition rate of 250 MHz and is produced by difference frequency generation (DFG), covering the spectral range from 2.9 to 3.4 µm [25]. The overlapped beams were incident on a 25×50×9.5 mm ruled reflective diffraction grating (Thorlabs, GR2550-45031) with 450 lines/mm and blaze wavelength of 3.1 µm. The light of the first order diffraction was incident on the photodetector PD1 (Vigo, PIP-DC-200M-F-M4). The beat signal from the PD1 was acquired by a spectrum analyzer (Advantest Corp, R3132).

To control spectral measurements a LabVIEW program on the basis of the DAQ software with a multifunction I/O device (National Instruments, USB6361) was developed. The program controls the laser scanning and modulation, data acquisition, demodulation, lock-in amplification and the saving of the data. A detailed description of the software was presented in our previous work [15].

3. Laser calibration and characterization

3.1. DFB-ICL laser calibration

The spectral range of the laser can be tuned from 3361 nm to 3372 nm by changing the laser current from 20 mA to 80 mA and the temperature, as shown at three different temperatures 10 °C, 15 °C and 20 °C in Fig. 2(a). The tuning curves are similar, but shifted for different temperatures. The determination of wavelengths with a resolution of ∼0.14 nm (∼0.13 cm⁻¹) was performed with a spectrometer (Thermo Scientific Nicolet 8700 FT-IR, Thermo Fisher Inc.).

![Fig. 2. Characteristics of the ICL laser: (a) Wavelength tuning curves with currents changing from 20 mA to 80 mA at three different temperatures (data from Nanoplus). The slope of this dependence is increasing with the current from 0.09 to 0.16 nm/mA. (b) The laser output (measured by the photodetector voltage) for different scan frequencies at 15°C. (c) The laser output at scan frequency 1 Hz for different temperatures.](image-url)
The laser output measured with the PD1 at 15 °C for various currents is shown in Fig. 2(b). For different scan frequencies 1 Hz, 10 Hz and 20 Hz the dependences have somewhat different slopes, increasing with the scan frequency, and show about the same output at ~40 mA current. At a 1 Hz scan frequency, the laser output for different temperatures is depicted in Fig. 2(c), indicating that at higher temperature it is lower.

3.2. Linewidth measurement

A knowledge of the laser linewidth is important in high precision spectroscopy for studying detailed structures and dynamics in excited states of molecules [26] and measurements of path lengths of gas cells by an optical frequency domain reflectometer [27]. The phase fluctuations of the laser radiation broaden the spectral width of the laser line. The conventional method for laser linewidth measurement is a self-heterodyne technique, the principle of which is to analyze the power spectrum of the beat signal in a Mach-Zehnder interferometer that converts the optical frequency fluctuations of the laser into laser intensity variations. In the present work, the linewidth of the MIR ICL laser was measured through heterodyne beats between this CW laser and a stable frequency comb. The frequency comb is comprised of millions of narrow spectral lines with constant intervals equal to the repetition rate, which can be conveniently used as a frequency ruler for frequency measurements. Each comb line of a stabilized frequency comb has ultra-narrow linewidth.

The experimental setting of the linewidth measurement is shown in Fig. 1. The MIR comb repetition rate of $f_r \sim 250$ MHz was locked to a synthesizer with a GPS-disciplined Rubidium frequency standard by a home-made electronic circuit. The output power of the MIR comb is 300 mW with a 700 nm spectral range from 2.9 to 3.6 μm, which corresponds to >0.8 μW/ mode. The heterodyne beat signal was recorded in 50 ms and converted to the frequency domain by a fast Fourier transform (FFT) with a frequency resolution of 280 kHz. The measured beat signal is plotted in Fig. 3(a). The plot shows the peak from the repetition rate at 250 MHz, the beat signal with frequency $f_{b1} \sim 70.86$ MHz and another beat note at $f_{b2} \sim f_r - f_{b1} = 179.14$ MHz due to beating with both adjacent comb lines. We converted the beat signal intensity from a log scale to a linear scale and fitted the profile by a Lorentzian function as shown in Fig. 3(b). The width at the half maximum of the profile is the linewidth of the MIR ICL laser. As a result for the measured FWHM value of the MIR ICL laser we obtained $(3.39 \pm 0.15)$ MHz.

The above presented method uses a static linewidth measurement with fixed MIR ICL laser current. With the dynamic linewidth measurement by tuning the laser injected current [30] a somewhat different linewidth of 760 kHz was reported. The possible reason for the difference
with our result is as follows. The laser output wavelengths vary due to quantum noise and lasing conditions; consequently, the measured linewidth is dependent on the acquisition time. With a shorter acquisition time the measured linewidth of laser can become narrower. In our experiment, the acquisition time was 50 ms, while the reported acquisition time in [28] was from 67 µs to 1 ms.

4. Acetone measurement

4.1. Absorption band selection

The acetone absorption spectrum from the Pacific Northwest National Laboratory (PNNL) spectral database ranging from 1.5 µm to 10 µm for the (concentration × optical path) = 1 ppm×m with 0.06 cm⁻¹ resolution at temperature of 25 °C and pressure of 760 Torr is shown in Fig. 4. Strong fundamental absorption of the acetone molecule is mainly located in the MIR regions 3–4 µm, 5.5–6 µm, 7–7.5 µm and 8–8.5 µm. The two latter intervals suffer from overlaps with strong absorption bands of H₂O, and therefore, they are not well suited for acetone detection in the exhaled breath. In the interval 5.5-6 µm acetone has a relatively broad absorption band, which in view of the limited tuning range of diode lasers makes it more difficult to identify the contribution of this peak. Consequently, in our work the region 3–4 µm was selected for acetone detection.

![Fig. 4. The acetone spectrum in the wavelength interval from 1.5 µm to 10 µm from the PNNL database. The selected absorption band for the acetone detection is depicted in the inset: the strong absorption band is shown by the red line and the experimentally determined laser tuning dependence is shown by the black line (the limits of the tuning range are indicated by the two vertical dashed lines). The absorbances of CH₄ and H₂O for (concentration × optical path) of 2 ppm×m and 5% ×m, respectively, in the spectral range from 3.360 µm to the 3.372 µm are plotted in the inset (blue line is methane and green line is H₂O).](image-url)
detection, namely the wavelengths near 3.3 µm, as is shown in the left inset of Fig. 4. As this inset shows, the laser tuning range (black line) well overlaps with the strong acetone absorption band (from 3.360 µm to 3.372 µm, red line).

To assess the possible interferences of other gases on acetone detection, first, we note that the highest absorption intensity of the carbon dioxide absorption bands within the spectral interval of interest is \( \sim 2.2 \times 10^{-27} \text{ cm}^{-1}/\text{mole cm}^{-2} \) and is far less than the similar intensity of methane, which is \( \sim 5.8 \times 10^{-21} \text{ cm}^{-1}/\text{mole cm}^{-2} \), as follows from the HITRAN database [29]. The spectra of absorbance of H\(_2\)O and CH\(_4\) in the interval from 3.36 µm to 3.372 µm are shown in the right inset of Fig. 4 and were calculated for typical values of (Concentration \( \times \) Optical Path) COP(CH\(_4\)) \( \sim 2 \text{ ppm} \times \text{m} \) and COP(H\(_2\)O) \( \sim 5\% \times \text{m} \) that can be expected in exhaled breath. Thus the peak values of CH\(_4\) absorbance \( (\sim 0.001 \text{ at 3368.5 and 3370.0 nm}) \) are about 7 times higher than that of acetone \( (\sim 0.00015) \). The absorbance of H\(_2\)O at the peak \( \sim 3367.5 \text{ nm} \) \( (\sim 0.005) \) is about 30 times higher than for acetone. We note that interference of H\(_2\)O and CH\(_4\) lines can be significantly reduced by filtering the sample through a selective absorber, such as Ascarite II [30]. Furthermore, the interference can be minimized by using for measurements the wavelengths, where the absorption of H\(_2\)O and CH\(_4\) is weak. Then contributions of different gas components are separated by the location of their spectral peaks and can be distinguished by fitting with the spectral data from PNNL and HITRAN databases. In particular, the selected absorption band of acetone in the wavelength interval 3362–3371 nm is relatively broad compared to the absorption bands of CH\(_4\) at 3367.3 nm and 3370.1 nm, so in the spectral interval of interest the acetone absorption is observed as a broad gradual change of the signal, while the CH\(_4\) absorption would show up as sharp peaks.

To facilitate simulations the acetone absorption band was well approximated with a pseudo-Voigt function (Fig. 5), which is the linear combination of Lorentzian, \( L(x) \) and Gaussian, \( G(x) \),

\[
V_p(x) = y_0 + A \left[ m \times L(x) + (1 - m) \times G(x) \right], \tag{1}
\]

where the coefficient \( m \) determines the proportion in which Lorentzian and Gaussian functions are taken. In the equation above,

\[
L(x) = \frac{2}{\pi} \frac{w}{4(x - x_c)^2 + w^2}, \quad G(x) = \frac{\sqrt{4 \ln 2}}{\sqrt{\pi}w} \exp \left( -\frac{4 \ln 2}{\pi w^2} (x-x_c)^2 \right),
\]

Fig. 5. The peak of the acetone absorption band fitted by the pseudo-Voigt function; the graph at the bottom shows the residue, i.e. the difference between the acetone spectrum from the PNNL database and the fit function.
and the fitting parameters $y_0 = 3.64 \times 10^{-5}; m = 1.31, A = 4.23 \times 10^{-4} \text{ cm}^{-1}, w = 2.196 \text{ cm}^{-1}$ (the half width at half maximum, HWHM), $x_c = 2970.18 \text{ cm}^{-1}$ (the center wavelength from the PNNL spectroscopic data is $x_c = 2969.96 \text{ cm}^{-1}$) were found by the Levenberg-Marquardt algorithm.

4.2. Wavelength modulation spectroscopy and phase shift measurement

For spectral measurements we used WMS with 2f-detection. This is a powerful technique with high sensitivity. It is widely used for real-time measurements of trace gases and analysis of combustion processes in various industrial applications [31]. The injected current is modulated by the combination of a low frequency ramp voltage and a high frequency sine voltage. We assume that the incident laser intensity and frequency are modulated as described by the following equations:

$$I(t) = I + \Delta I \cos(\omega t),$$

$$v(t) = v + \Delta v \cos(\omega t + \psi).$$

Here, $I$ is the average laser intensity, depending on the injected current, $\Delta I$ is the modulation amplitude, $\omega = 2\pi f$, where $f$ is the modulation frequency, $v$ is the average frequency of the laser, $\Delta v$ is the frequency modulation amplitude, $\psi$ is the IM/FM phase shift. The amplitude of the WMS 2f-signal of the second harmonic $S_{2f}$ obtained with a lock-in amplifier is given in [32] as

$$S_{2f} = \frac{G}{2} \left\{ \left[ \frac{H_2 + \Delta I}{2f} (H_1 + H_3) \cos \psi \right]^2 + \left[ \frac{\Delta I}{2f} (H_1 - H_3) \sin \psi \right]^2 \right\}^{1/2},$$

where $G$ is a coefficient proportional to the system gain. $H_k (k = 1, 2, 3)$ are the components of the Fourier series expansion, which can be calculated as

$$H_k(\bar{v}, \Delta v) = -\frac{P\chi L S}{2\pi} \int_{-\pi}^{\pi} \varphi(\bar{v} + \Delta v \cos \theta) \cos k\theta d\theta,$$

where $\theta = \omega t$. $S$ and $\varphi$ are the spectral line strength, mainly dependent on the gas temperature $T$, and the line shape function, respectively; $P$ is the pressure of the gas mixture, $\chi$ is the mole fraction of the absorbing species and $L$ is the effective optical path length. Equations (4) and (5) show that for the signal amplitude $A_{2f}$ the following proportionality relation takes place

$$A_{2f} = \max(S_{2f}) - \min(S_{2f}) \propto GIPS\chi L.$$

The signal to noise ratio (S/N) can be expressed as

$$S/N = A_{2f}/\delta,$$

where $\delta$ is the background noise.

When the laser driving current is modulated by a sine signal, the laser radiation frequency as well as the laser power output are also modulated, however, their time dependences have a phase shift (Eqs. (2) and (3)), which influences the 2f-signal (Eq. (4)). Lytkine et al. developed the method based on the effect of “mirror reflection” for determination of this phase shift between the intensity modulation and frequency modulation (IM/FM) [33]. When scanning the spectrum with a sinusoidal modulation current, the absorption peaks occurring in the ascending part also appear in the descending part of the current sine wave. The presence of the phase shift results in the asymmetry of the signal shape, while the average wavelength is scanned up and down through the absorption peak. The importance of accurate accounting for the phase shift follows from the fact that it changes the detected signal in WMS through the residual amplitude modulation.
The illustration of the determination of the IM/FM phase shift is presented in Fig. 3(a), following Liu et al. [34] in the assumption that there is only one absorption peak within the scanning range. The black and red lines are the modulated current and modulated absorption signal, respectively. The time shift can be calculated as

$$\Delta t = \frac{1}{2} (t_1 + t_2 - 2t_c)$$  \hspace{1cm} (8)$$

where $t_c$ is the central time at the maximum amplitude of the modulation signal; $t_1$ and $t_2$ are the time differences relative to $t_c$ (see Fig. 6(a)). The phase shift is then $\psi = 2\pi f \Delta t$. This method can be extended to arbitrary number $N$ of absorption peaks, i.e. the phase shift expressed through the time differences of pairs is

$$\psi = 2\pi f \Delta t_N, \quad \Delta t_N = \frac{1}{2N} \sum_{k=1}^{N} \Delta t_k,$$  \hspace{1cm} (9)$$

where $\Delta t_k = (t_k' - t_c) - (t_c - t_k)$ again correspond to the time difference of k-th absorption peak pair.

In the experiment, an acetone sample with concentration of 200 ppm and the peak at 3.367 $\mu$m was used for the phase shift measurement by direct absorption spectroscopy, and the result is shown in Fig. 6(b). There is one pair of the absorption peaks (peak1 and peak2) in one period of the current scan for the up- and down-sweeps of the current.

In the experiment, we modulated the ICL-DFB laser by a sine signal with different frequencies and utilized an oscilloscope (Tektronix MDO4104B-3) with 100 MHz sampling rate to acquire the data. During the scan, the central time and the times for the centers of the absorption peaks were measured. The phase shift was determined from Eq. (9) for different modulation frequencies, as presented in Fig. 6(c). There were three modulation frequency intervals (separated by vertical lines), as indicated in the figure.

Fig. 6. The illustration to determining IM/FM phase shift: (a) The simulated sine signal with two absorption peaks on the positive and negative slopes of the current at the up- and down-sweeps. (b) The experimental peaks detected with a direct absorption spectroscopy at the positive and negative slopes of the current scan. (d) The phase shift variations for different modulation frequencies.
red dashed lines) showing different behavior: (1) with the modulation frequency increasing from 100 Hz to 500 Hz, the phase shift decreases from $0.15\pi$ to $0.05\pi$, (2) in the frequency interval from 500 Hz to 4 kHz the phase shift varies within the limits from $0.05\pi$ to $0.08\pi$, and (3) from 4 kHz to 50 kHz there is a trend of increasing of the phase shift. We note that a similar trend was observed in a previous study [35], where the phase shift was measured for the modulation frequency in the range from 100 Hz to 50 kHz.

4.3. Measurement of acetone

To validate the above S/N for WMS of acetone a calibrated 200 ppm acetone sample in a nitrogen gas mixture was used. In this measurement, the laser tuning range achieved by the current scan is about 6 nm, which is less than the whole spectral range of the acetone absorption band. To achieve a broader coverage of the absorption band, two scans at temperatures $T = 14.8^\circ C$ and $18^\circ C$ were carried out in the experiment, as shown in Fig. 7(a): the first scan covered the spectral interval from the 3362.3 nm to 3367.3 nm (interval A) and the second scan covered the interval from 3362.0 nm to 3369.3 nm (interval B). We note that for determination of the acetone concentration just one scan (A or B) was sufficient, which took only $\sim 1$ s. However, when the temperature was changed from the first value ($T = 14.8^\circ C$) to the second value ($T = 18^\circ C$) by the command sent with the LabVIEW software to the temperature controller through a GPIB card, the response time was only about 0.5 s. Thus, even when a broader wavelength coverage is used with switching of temperatures, the measuring time still meets the requirement for a real time measurement (less than $\sim 1$ minute) [36].

![Fig. 7.](image)

The $2f$-signal amplitude was normalized and plotted versus the amplitude of the modulated current in Fig. 7(b), which shows that the signal gradually increased up to 20 mA and then decreased. From Fig. 6(b) and the data of Fig. 8 we conclude that the signal-to-noise ratio in WMS is 50 times better than that of the direct absorption detection.

Consequently, the scanning current was selected from 40 mA to 60 mA and the modulation amplitude set to 20 mA, assuring that the injection current is less than the maximum laser current allowed. To assure the stability of the laser wavelength at each measuring spectral point, the scanning frequency was selected to be 1 Hz, while the modulation frequency of 10 kHz was high enough to significantly suppress the noise. The temperature stability was measured to be better than $0.1^\circ C$, and thus temperature variations did not noticeably affect the experimental results. The measured normalized $2f$-signal amplitude for the two scans in the spectral intervals A and B is shown in Fig. 8. The integration time for these measurements is 0.25 s, and the noise magnitude is less than the thickness of the lines. The blue dashed line shows the result of the
calculation with Eqs. (4) and (5) for a pseudo-Voigt profile using the set of parameters: \( x_c = 2969.96 \text{ cm}^{-1}, m = 1.31, \omega = 2.196 \text{ cm}^{-1}, m = 1.9 \), which better described the measured central part of the absorption band. From Eq. (7) we obtained an estimate for the signal-to-noise ratio \( \sim 100 \). The inset in Fig. 8(a) shows a portion of the measured curve with experimental points. The occurred differences is generated by the electronic circuits performing signal processing in real experiment and the approximation of small absorption in the simulation calculation.

4.4. Sensor evaluation

The acetone cross sections at different pressures were investigated in Ref. [37], showing that increasing pressure of synthetic air in the gas mixture has only small effect on broadening of the structure of the acetone absorption band. In order to evaluate the performance of the acetone sensor, a calibration measurement and a long-time experiment at 760 Torr were performed. In the calibration measurement, we pumped the chamber below \( 10^{-3} \) Torr and flushed it with pure nitrogen at 760 Torr for half an hour. First, the background signal was obtained. Then we sequentially filled the chamber with the calibration acetone gas mixtures having concentrations of 50 ppm, 100 ppm, 150 ppm and 200 ppm from the GASCO Company and obtained the \( 2f \)-signal. The dependence of the \( 2f \)-signal on the concentration is plotted in Fig. 9 and fitted by a straight line with the \( R \)-squared value of 0.997. The linear fit is as follows:

\[
C = (4790.8 \times V_{2f} - 6.15629) \text{ ppm.}
\]  

(10)

In this equation, \( C \) is the acetone concentration in ppm, and \( V_{2f} \) is the \( 2f \)-signal amplitude measured in V.
Fig. 9. The measured $2f$-signal at different concentrations of the calibration gas. It is well fitted by the linear dependence.

<table>
<thead>
<tr>
<th>Equation</th>
<th>$y = a + b \times x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adj. R-Square</td>
<td>0.99764</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.1563</td>
</tr>
<tr>
<td>A</td>
<td>3.1023</td>
</tr>
<tr>
<td>A</td>
<td>4790.88</td>
</tr>
<tr>
<td>A</td>
<td>116.56</td>
</tr>
</tbody>
</table>

Fig. 10. Results of the sensor tests: (a) The results for a 25 minutes continuous data acquisition with a 200 ppm acetone concentration mixture. (b) The histogram of the measured data points. (c) The Allan deviation of the measured data, showing the detection limits of 0.58 ppm and 0.12 ppm with averaging times of 1 s and 60 s, respectively.
To further evaluate the measurement precision of the sensor, a long-term continuous experiment was carried out with the 200 ppm calibrated acetone gas mixture at a total pressure of 760 Torr and room temperature. During continuous measurement for twenty-five minutes with 1s interval 1500 data points were obtained (Fig. 10(a)). The histogram of the measured data shows their distribution in Fig. 10(b). The distribution was fitted by a Gaussian profile and the HWHM value was determined to be 0.62 ppm. Thus, the relative error of the acetone concentration measurement is 0.3%. The uncertainty in the measured concentration value can be mainly attributed to electronic noise.

To investigate the detection limit and stability of the sensor, the Allan deviation analysis was performed, as depicted in Fig. 10(c). The results indicate that the sensitivity is about 0.58 ppm with 1s averaging time and reaches the optimal sensitivity of the sensor of 0.12 ppm, when the integration time is increased to 60 s. For integration times longer than the optimal one, the Allan deviation increases due to drift and the noise of the ICL laser and electronic components. The noise can be further suppressed to improve the sensor sensitivity by using a balanced detection.

5. Conclusions

In this paper an acetone sensor was developed in the mid-IR region, which has the high sensitivity, sufficient to detect acetone in the human breath. We characterized the mid-IR laser and the measured acetone absorption band at 3367 nm. The acetone absorption band was covered by two scans using WMS. With a long (about 25 minutes) continuous measurement at 200 ppm acetone concentration, a relative error of the measured value of about 0.3% was determined. A detection limit of 0.58 ppm with 1s averaging time and down to 0.12 ppm with 60 s time averaging was achieved, which should be sufficient for acetone concentration measurements in human breath (from about 0.3 ppm to 1.0 ppm for a healthy individual). To improve the sensor sensitivity, novel multipass cells with longer interaction lengths, as presented by K. Krzempek et al. [38] and K. Liu et al. [39] can be used in further experiments. For acetone measurements in human breath a pre-processing and reduction of the concentrations of CH$_4$ and H$_2$O in the sample should be considered to avoid their influence on the measured concentration values.

Funding

Welch Foundation (A1546); Qatar Foundation (NPRP 8-735-1-154); National Key Basic Research Program of China (2015CB921003); China Scholarship Council (CSC) (201506220056).

References


