

Carbon dioxide detection using NIR diode laser based wavelength modulation photoacoustic spectroscopy

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A photoacoustic sensor using a laser diode emitting near 1573 nm in combination with a dual-microphone resonant photoacoustic cell has been developed for carbon dioxide trace gas analysis at atmospheric pressure. Wavelength-modulation scheme and $1f$ detection for CO₂ concentration measurements in Ar are demonstrated. The noise equivalent absorption sensitivity of NEAS(1σ) = 1.01×10^{-8} Wcm⁻¹/Hz^{1/2}, corresponding to a detection limit of 30 parts in 10⁶ by volume (ppmv) for a 100 s integration time and 4.5 mW average laser power. The photoacoustic response of CO₂ dependence on the buffer gases with different mixture ratio of Ar and N₂ was investigated. Finally, the possibility to make use of the sensor for measurements of ambient CO₂ is also presented.

Keywords: photoacoustic spectroscopy, NIR diode laser, wavelength modulation, CO₂ detection.

1. Introduction

With the rapid development of global industrialization and mechanization, automotive emissions are a major source of urban atmospheric pollution. High levels of pollutants such as carbon monoxide, nitrogen oxides, hydrocarbons and particulates are emitted from motor vehicles and can lead to health and environmental problems. Moreover, carbon dioxide is one of the most important minor components in the atmosphere and the second green house gas after atmospheric water, and it contributes greatly to the global warming of the atmosphere [1]. As a result of human activity (in particular combustion), its concentration has continuously increased during the last century [2]. This issue, of fundamental importance for the present and the future of mankind, constitutes the first climate change of anthropogenic origin. Therefore, its monitoring

has far-reaching implications for global control of the environment and for industrial, medical, and geophysical purposes [3].

Nearly one hundred years after Alexander Graham Bell's discovery in 1880, photoacoustic spectroscopy (PAS) awoke from a long sleep. Especially the introduction of lasers as radiation sources has led to rapid development of photoacoustics in the last ten years. Hence, it has gradually improved in utility with the gradual improvement in PAS theory and the great progress in the properties of suitable light sources, sound transducers and highly sensitive detectors.

Semiconductor diode lasers were first developed in the mid-1960s and found immediate application as much needed tunable sources for high-resolution laser spectroscopy commonly referred to as tunable diode laser absorption spectroscopy (TDLAS). Tunable diode laser photoacoustic spectroscopy (TDLPAS) is a widely recognised method for its excellent performance in trace gas monitoring and analysis from ppm down to ppb levels [4–6]. This technique provides many advantages such as high selectivity and sensitivity, on-line, real time and contactless measurements in a compact experimental arrangement. Since the sensitivity of this technique scales with the optical power, extremely high sensitivity is generally required with high power lasers, such as gas lasers (CO and CO₂ lasers) or solid state lasers [7, 8]. Recently, tunable laser diodes emit typical powers of several to several tens of milliwatts. It is worth noting that they have been developed, offering room temperature operating, fast response, narrow linewidth, continuous tunability, compact size and cost-effectiveness.

Although diode laser based (non-photoacoustic) spectroscopic methods can also achieve equivalent detection limits, at high concentrations the absorption signal begins to saturate [9]. Thus, they cannot provide the necessary high dynamic range unless special electronics is applied. In contrast to these methods, diode laser based photoacoustics has the potential to meet all the requirements discussed above with its simple construction and automatic operation, linearity over more than four orders of magnitude [10, 11]. In addition, unlike traditional IR long-path spectroscopic technologies, a number of high reflectivity mirrors are not used here, making the system mechanically very stable. Photoacoustics is a spectroscopic technique in which the signal is usually measured by means of microphones. This detection scheme has the advantage that the magnitude of the detected signal is proportional to the absorbed laser power and that the sensor (*i.e.*, the microphone) itself has a wavelength-independent responsivity. The same sample cell can thus be used at different wavelengths as long as the window material used to seal off the cell is transparent at the wavelengths of interest.

In this work, we report on our recent efforts in the development of a compact sensor for CO₂ monitoring in air. The system is based upon a distributed-feedback (DFB) diode laser operating at 1.573 μm, in coincidence with the R14 CO₂ absorption line with an intensity factor of $1.727 \times 10^{-23} \text{ cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2})$, as reported on the HITRAN2004 database [12]. This line is found to be free of interference from other

atmospheric gases (CO , H_2O , CH_4 , *etc.*). The research was motivated by the need for a simple, sensitive, inexpensive and spectrally selective device for monitoring trace amounts of CO_2 in ambient air, because this gas is often one of the major impurities in industrial processes and it plays a crucial role in biological systems. A dual-microphone resonant photoacoustic (PA) cell, in conjunction with wavelength modulation spectroscopy and 1st harmonic detection, has been carefully implemented to reach a detection limit of 30 ppm, with a 100 s integration time and average laser power of 4.5 mW. Finally, the possibility to make use of the sensor for measurements of ambient CO_2 is presented.

2. Experimental

2.1. Measurement setup

The experimental setup is shown schematically in Fig. 1. The pigtailed DFB (distributed feed-back) diode laser used is current-tunable over 1 cm^{-1} (tuning rate $\sim 0.02 \text{ cm}^{-1}/\text{mA}$) for each temperature point with a centre emission wavelength at 1573 nm (NTT Electronics corporation), has a power output of a few mW, and a line-width of 2 MHz and a side mode suppression ratio greater than 30 dB. The laser is operated with an ILX LDC-3724B driver at pre-selected temperatures. The laser wavelength is tuned by feeding an external voltage ramp to the driver. Sinusoidal small-amplitude modulation was applied to the injection current of the DFB laser. The modulation sweeps the laser line back and forth across the absorption line.

At 1573 nm CO_2 has a fairly weak vibrational combination band. One of the strongest lines of this band at room temperature is the rotational line R14 at 6358.654 cm^{-1} having a line intensity of $1.727 \times 10^{-23} \text{ cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$, primarily which is found

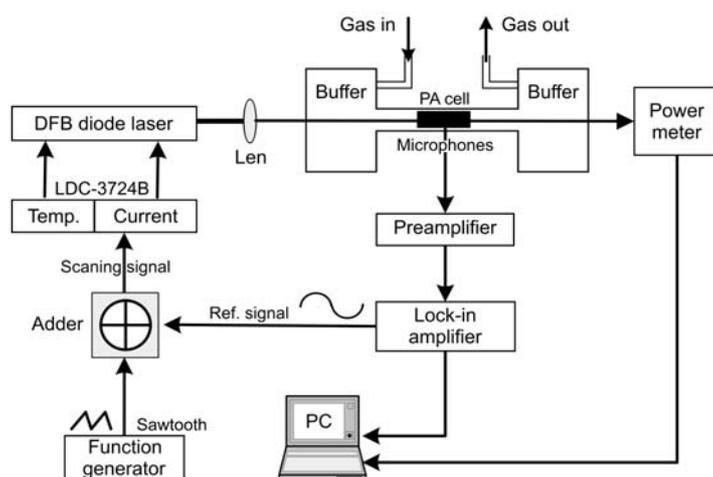


Fig. 1. Experimental arrangement for the photoacoustic measurements.

to be free of interference from other atmospheric gases, especially H₂O. Thus the DFB diode laser was tuned to the excitation of CO₂ into the corresponding ro-vibrational state for whole experiments.

Absorption spectra are obtained by sweeping the laser wavelength over absorption features of CO₂ using a low-frequency triangular waveform. An ac modulation current is superimposed onto the sweep signal to modulate the laser emission wavelength for the purpose of harmonic detection, where the detection frequency is usually the PA cell resonant frequency, *i.e.* the reference frequency times the harmonic detection number, with the purpose of amplifying the acoustic signal and increasing the signal-to-noise ratio (SNR).

The radiation from the diode laser was collimated and directed through the cylindrical photoacoustic cell axes. The transmitted power was simultaneously monitored with a power meter. The induced photoacoustic signals were detected using sensitive microphones (Mode MA211, sensitivity 50 mV/Pa). All the modulated signals were pre-amplified by a preamplifier (EG&G, Model 5113) with a bandpass filter set at 30 Hz–30 kHz and a gain factor 100. Subsequently the signals are demodulated by a lock-in amplifier (Stanford Research, SR830), then a PC-based data acquisition card was used to acquire the PA signal from the lock-in amplifier sampling at 20 kS/s with 16-bit resolution. A simultaneous TTL trigger signal from the triangular ramp function generator is used to start each acquisition and acquire 4096-points per laser scan. The computer stores individual laser scans and performs a running coverage of 100 sequential scans (about 100 s measurement time) to improve SNR. Control of all electronics, signal acquisition, and data analysis is provided through a LabWindows/CVI-based graphical user interface software program run on a PC.

2.2. Characteristics of the photoacoustic detector

The photoacoustic detector is a cylindrical PA cell equipped with double microphones. The PA cell is built out of duralumin and consists of a central cylindrical tube of radius $R = 6.5$ mm and length $L = 100$ mm acting as an acoustic resonator and two large buffer volumes sealed at either end with BK7 windows. The two microphones are installed at the center of the resonator and faced to each other, since they have the same responsivity around the resonance frequency of the PA cell, the two channel PA signals are directly added and pre-amplified, then demodulated by a lock-in amplifier. The PA cell had gas inlet and outlet valves, and was connected to a gas-sampling line and a pressure gauge.

Firstly the PA cell quality factor and frequency response are investigated. The PA cell was first evacuated with a vacuum pump and then filled to a range of sample pressures with a certified 1% of CO₂/Ar gas mixture. The first-derivative ($1f$) CO₂ spectra were recorded. The magnitude of the $1f$ signal, taken as the difference between the maximum and minimum points of a spectrum, was measured as

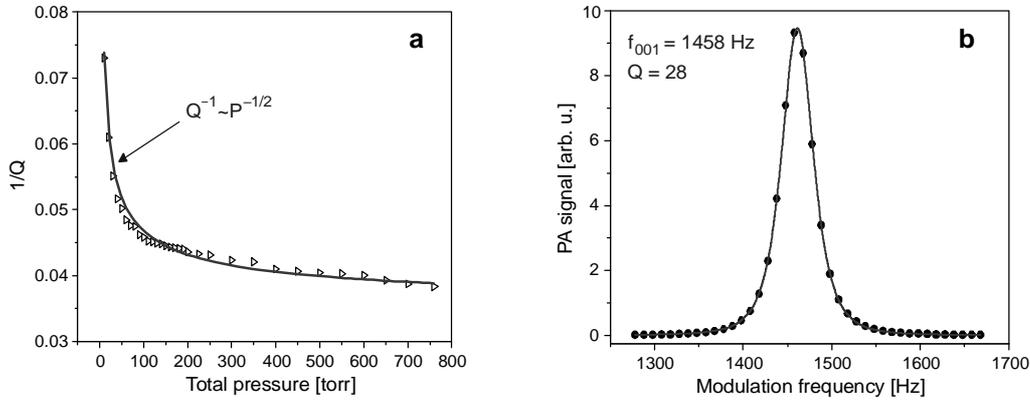


Fig. 2. The Q -factor as a function of the sample total pressure in the PA cell and its fit according to the theoretical expression as Eq. (11) in reference [14] (a), the resonance profile of the PA cell at atmospheric pressure and room temperature, the solid line is Lorentzian fit to the resonance profile (b).

the frequency of the sinusoidal laser modulation component was varied around the first longitudinal resonance frequency of the PA cell. The modulation parameters (modulation amplitude, modulation frequency) were optimised at each pressure to achieve the strongest PA signal [13], but the triangular function remained constant throughout, with a frequency of 1 Hz and an amplitude of $\pm 1V_{p-p}$. The resonance profiles were fitted with Lorentzian functions. The Q -factor was calculated for each resonance profile using $Q_j = f_j/\Delta f$, where f_j is the resonance frequency of the cell and Δf is the full width at half maximum (FWHM) of the resonance profile, and is shown as a function of sample pressure in the Fig. 2a. The amplification of the PA signal increased with sample pressure, up to a maximum of 28 at 1 atm, and the first longitudinal acoustic resonance frequency occurred at 1.458 kHz, shown in the Fig. 2b. For the first longitudinal mode of a cylindrical resonator according to equation:

$$\omega_j = \pi c \sqrt{\left(\frac{\alpha_{mn}}{R}\right)^2 + \left(\frac{k}{L}\right)^2}$$

where $c = (\gamma RT/M)^{1/2}$, while $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the constant of perfect gases, M – the molar mass of the gas, and T – the temperature [14]. The resonance frequency is calculated to be about 1.470 kHz for a sound velocity $c = 294 \text{ m/s}$. The discrepancy between theoretical and experimental value may be caused by drifts of the gas temperature. For the response of the Q -factor, we achieved good agreement with the theoretical expression as Eq. (11) in reference [14], which gives $Q^{-1} \sim P^{-1/2}$ dependence, and revealed that losses of acoustic energy take place mainly near the walls rather than in the bulk volume.

3. Results and discussion

To the best of our knowledge, if the relaxation is slow compared to the modulation rate ($\omega\tau \gg 1$), then the photoacoustic sound generation is suppressed. Hence, the ability to detect a molecular species by means of PAS does not only depend on its optical absorption strength but is also influenced by the relaxation processes [15–17].

3.1. The influence of molecular relaxation dynamics on PA signal intensity

First of all we observed that the PA response of CO_2 depends on the buffer gas. Figure 3 shows the PA signal intensity as a function of different mixture ratio of Ar and N_2 , whereas, the CO_2 concentration was kept constant throughout at 1%. Obviously, the PA signal intensity increased with the increment of mixture ratio of Ar. When using similar CO_2 concentration (1%), the PA signal intensity was enhanced

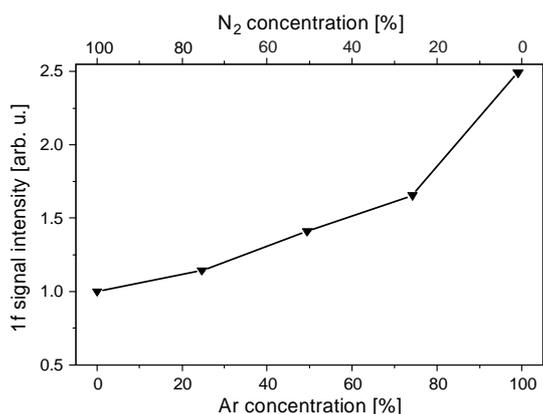


Fig. 3. PA signals as a function of different mixture ratio of Ar and N_2 , the CO_2 concentration was kept constant throughout at 1%.

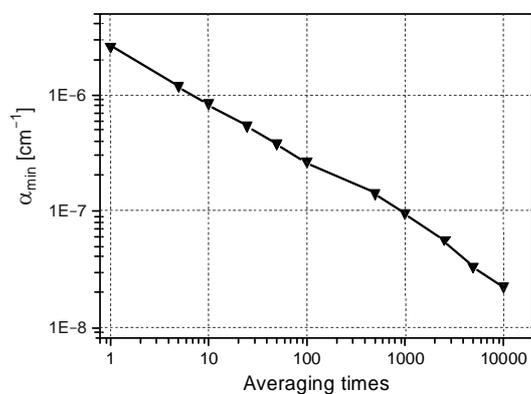


Fig. 4. Noise equivalent absorption coefficient plots as a function of averaging time.

approximately 2.5 times in 99% Ar, as compared to 99% N₂. This phenomenon can be attributed to the molecular relaxation effect [18], *i.e.* a resonant energy transfer between the excited state of CO₂ and the nearby vibration level of N₂, resulting in a very slow thermalization of the light energy, thus it drastically reduces the efficiency of PA signal generation. This was firstly demonstrated in CO₂ laser based PA measurements in the 10 μm wavelength range when CO₂ laser radiation is absorbed by CO₂ mixed in N₂ [19, 20]. Recently a similar observation at 1.43 μm has also been made by VERES *et al.* [21]. The suppression of the PA signal in N₂ is caused by molecular relaxation to a metastable state of N₂. Molecular relaxation at 1573 nm is also evident, as the same vibration of a CO₂ molecule has its overtone here.

3.2. Optimization of the data acquisition time

As we all know the stability of the sensor is an important issue, especially in spectroscopic technique measurements. One way to characterize the long-term drifts and establish the signal averaging limits is to measure the Allan variance of time sequences of the PA signal [22], which was originally introduced for determining frequency stability but can also be used for spectroscopic instruments [23]. Figure 4 depicts the minimum detectable absorption coefficient α_{\min} as a function of different averaging times. Obviously, α_{\min} is linear with the averaging times within multi-hour, which verifies that with noise remains the dominant source of noise. For comparison, trace gas sensors based on direct optical absorption detection usually exhibit drifts that do not allow useful data averaging for time periods longer than 100–200 s [24, 25]. In view of the optimal averaging, the time is too long for real applications, where small response time is required. And signal averaging is also necessary for the SNR improvement, so an integration time of 100 s was selected for the detection-limit experiments.

3.3. CO₂ detection limit

Based on above measurements, in the detection-limit experiments, we measured the PA absorption of the test mixture (CO₂ and Ar) at a constant overall gas pressure of 1 atm and in the stopped-flow mode. In this measurement a certified 312.5 ppm CO₂/Ar mixture was diluted with argon of 99.999% purity. The modulation amplitude was first optimised to maximise the PA signal intensity. However, this configuration was not optimal due to the high noise level associated with the residual IM and low level signals. The modulation amplitude was therefore rather chosen to maximise the SNR instead of the PA signal intensity. The laser power about 4.5 mW was measured as it exited the PA cell using a power meter. At each concentration the measured 1f spectrum is an average of 100 individual spectra corresponding to a measurement time of about 100 s. The dependence of PA signal and PA signal subtracted background noise at the first longitudinal resonance frequency on CO₂ concentration are shown in Fig. 5. The background noise level was obtained by

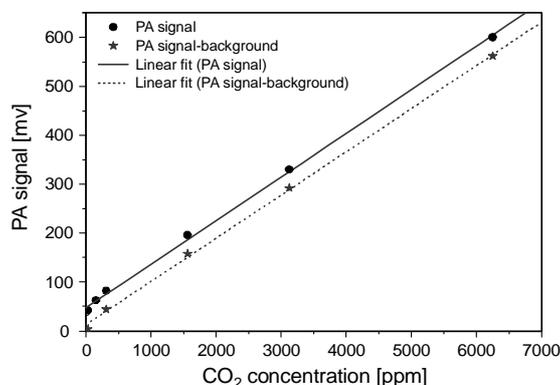


Fig. 5. PA signal demodulated at $1f$ as a function of CO_2 concentration. The dot and the pentacle correspond to the PA signal and the PA signal subtracted background noise, respectively. The line is the result of a linear fit. The noise-equivalent detection limit is about 30 ppm.

the average over 100 s of the PA signal recorded with pure Ar. A linear fit to the data gives a noise equivalent (1σ) detection limit of ~ 30 ppm. A more generally useful measure of absolute sensor performance is the power-normalized and bandwidth-normalized noise equivalent absorption sensitivity (NEAS). For this benchmark quantity yields a NEAS (1σ) is $1.01 \times 10^{-8} \text{ W cm}^{-1} \text{ Hz}^{1/2}$.

A comparison of detection limits with other laser-based detection systems employed for monitoring CO_2 is not straightforward, in view of rather different experimental configurations and definitions of sensitivity and sometimes lack of specific information. However, a comparison is made here with some recently reported systems employing PA detection schemes. LEWICKI *et al.* [26] used quartz-enhanced PAS and reported a detection limit of NEAS (1σ) = $1.4 \times 10^{-8} \text{ cm}^{-1} \text{ W/Hz}^{1/2}$ for CO_2 using the R18 line of the $2\nu_1 + \nu_3$ band at 4991.26 cm^{-1} , for a diode laser power of 3.9 mW at $2 \mu\text{m}$ and an optimized gas pressure of 50 torr. This corresponds to minimum detection limit (1σ) of 18 ppm for a 1 s lock-in-time constant. FISCHER *et al.* [27] demonstrated a resonance PA system equipped with 4 microphones using a tunable solid state $\text{Cr}^{2+}:\text{ZnSe}$ laser emitting at wavelengths between $2.2 \mu\text{m}$ and $2.8 \mu\text{m}$ with an average output power up to 500 mW, and achieved a detection limit of 0.2 ppm for CO_2 at atmospheric pressure, but the total time needed for the recording of a full spectrum of 0.5 cm^{-1} was about 1–2 h. As it is well known, in the mid-IR region the molecules absorption line strength is about two–three orders of magnitude higher than in the near-IR band, because of the presence of fundamental absorption band for most atmospheric molecules rather than absorption of overtone and combination bands. Most recently, LAURILA *et al.* [28, 29] reported a normalized detection sensitivity of $2.2 \times 10^{-9} \text{ cm}^{-1} \text{ W/Hz}^{1/2}$ realized with a DFB diode laser at 1572 nm with 34 mW power by using a novel cantilever-based PA system, resulting in a noise-equivalent detection limit (1σ) for CO_2 in Ar of 4.6 ppm and of sub-ppm employing a fiber power amplifier. Obviously the sensitivity achieved for

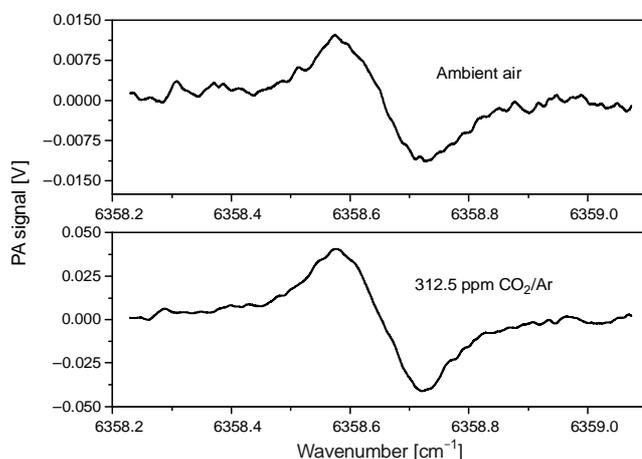


Fig. 6. Measured $1f$ PA spectra of ambient air and certified 312.5 ppm CO_2/Ar mixture at atmospheric pressure with a 100 s measurement time. The average laser power is about 4.5 mW.

the cantilever pressure transducer is superior to that obtained using the cell designs containing capacitive microphones. However, consideration of other factors such as cost, instrument robustness and thermal stability may favour the use of PA cells incorporating microphones rather than cantilevers. A PA cell containing a cantilever and associated interferometric detection system remains significantly more expensive and complicated than a device equipped with a capacitive microphone. These high sensitivities, however, involve rather sophisticated and costly instrumental refinements, whereas our main objective has been to develop a relatively simple, robust and economic measurement system for an industrial application rather than to further enhance the sensitivity. Our experiments may not have reached the optimum performance levels of the dual-microphone cell, because of residual ambient noise under realistic conditions of a working laboratory, rather than limiting performances of noise-isolated experiments.

As an example of application of our PA system to gas monitoring, the $1f$ PA spectra of ambient air and certified 312.5 ppm CO_2/Ar mixture are shown in Fig. 6. The good SNR of ambient air may be attributed to the presence of water vapor. Water vapor is known to be an efficient relaxation promoter for the energy stored in relatively slow relaxing CO_2 vibrational states or trapped in a long living N_2 vibrational state [21].

From the preliminary analysis of the SNR, it seems that the sensitivity offered by our sensor is quite satisfied to meet applications of industrial and environmental processes monitoring, and breathing diagnostics *etc.* In a laboratory environment the standard deviation over a period of several hours was below 1% relative to the typical concentrations in ambient air without any realignment. However, more detailed examinations of the long-term stability of the calibration and effects of electronic drift have still to be done.

4. Conclusions

Photoacoustic concentration measurements of ambient CO₂ near 1.573 nm have proved the feasibility for trace gas analysis at atmospheric pressure. The noise equivalent absorption sensitivity of NEAS (1σ) = 1.01×10^{-8} Wcm⁻¹/Hz^{1/2}, corresponding to a detection limit of 30 parts in 10⁶ by volume (ppmv) for a 100 s integration time and 4.5 mW average laser power. For industrial applications, where a sensitivity in the ppm range is sufficient, the detection scheme described here may be the most suitable choice. The impact of molecular relaxation effect on the photoacoustic response of CO₂ detection with different buffer gases is firstly investigated. Finally, the possibility to make use of the sensor for measurements of ambient CO₂ is presented. From the preliminary analysis of the results, it seems that the sensitivity offered by our sensor is relatively high. This is mainly explained by the weakness of the investigated absorption line and the relatively low laser power. Moreover, it should be noted that the pressure decrease in the PA cell is accompanied by a pronounced decrease of the sound noise level and an increase of the spectral resolution because of the narrowing of the absorption lines at low pressures. In future, the measurement setup can be further improved by optimizing the total gas pressure and system stability, and using multi-pass PA cell configuration or microphone arrays [30], accordingly much shorter integration time will only be needed.

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