Photoacoustic spectroscopy-based ppb-level multi-gas sensor using symmetric multi-resonant cavity photoacoustic cell

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ABSTRACT

In this paper, we propose and experimentally demonstrate a symmetric multi-resonant cavity photoacoustic cell (MR-PAC) with dual microphones detection, based on multi-resonator photoacoustic spectroscopy (MR-PAS). The designed photoacoustic cell contains three interconnected acoustic resonators to facilitate simultaneous control of three lasers for multi-gas sensing. Two microphones are symmetrically located at both sides of photoacoustic cell to implement two-point detection. The length of acoustic resonator is about 50 mm to minimize the photoacoustic cell, and the resonant frequency is around 3000 Hz. Feasibility and performance of the MR-PAC was demonstrated by simultaneous detection of C_2H_2, NO and CF_4 using a near infrared diode laser and two mid infrared quantum cascade lasers. The minimum detection limits (MDLs) of C_2H_2, NO and CF_4 are 480 ppb, 260 ppb and 0.57 ppb respectively with a 1 s integration time at normal atmospheric pressure. This minimized MR-PAS system is promising for the portable multi-gas sensing.

1. Introduction

Photoacoustic spectroscopy (PAS) gas sensing technology based on the principle of photoacoustic effect has developed rapidly in recent years, because of the advantages of high sensitivity, free from background light interference and convenient for multi-gas sensing [1,2]. Compared with non-resonant PAS, resonant PAS can realize resonant amplification of photoacoustic signals, greatly improve the sensitivity of gas sensing, and promote the development of PAS gas sensing technology [3]. Some new acoustic sensing methods have also been discovered to replace traditional acoustic microphones to improve sensitivity. Wu et al. reported a 3.3 μm inter-band cascade laser (ICL) in the quartz-enhanced photoacoustic spectroscopy (QEPAS) system to improve sensing sensitivity [4]. Fu et al. used cantilever enhanced photoacoustic spectroscopy technology in combination with optical microphones to carry out high sensitivity detection of CH_4 [5]. Xiao et al. achieved ultra-sensitive ppb-level CH_4 detection using a double channel differential T-type photoacoustic cell and optical microphones [6].

Beside acoustic sensing method, the sensitivity of photoacoustic spectroscopy gas sensing is also affected by photoacoustic cell. The traditional H-type resonant photoacoustic cell usually only uses the first

resonant frequency and is generally used to detect a single gas. However, multi-gas sensing can also be achieved by selecting several frequencies near the resonant frequency [7]. Huang et al. reported a spherical acoustic resonant cavity using the first three resonant frequencies to detect three gases [8]. Besson et al. reported a multi-resonant cavity photoacoustic cell (MR-PAC), in which three independent acoustic resonators of different lengths are arranged side by side in the photoacoustic cell, each using a microphone to detect acoustic signals [9]. This type of photoacoustic cell has a large volume and requires a microphone for each resonant cavity. Liu et al. innovatively reported a MR-PAC, where three acoustic resonators are interconnected and the acoustic signals generated in the three resonators can be detected using only one microphone. This structure has a smaller volume of photoacoustic cells and advanced sensitivity for multi-gas sensing [10]. It is worth further developing this kind of MR-PACs for the simultaneous gas sensing.

In this paper, we propose and experimentally demonstrate a symmetric multi-resonant cavity photoacoustic cell (MR-PAC) with dual microphones detection, based on multi-resonator photoacoustic spectroscopy (MR-PAS), and realize the ppb-level multi-component gas detection. The designed photoacoustic cell contains three interconnected acoustic resonators to facilitate simultaneous control of three
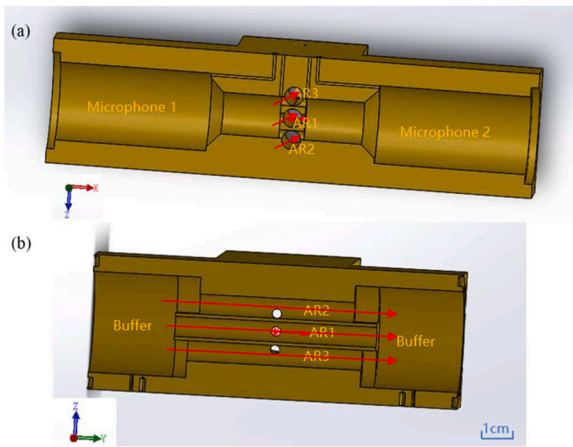

Fig. 1. (a) Sectional view of microphones. (b) Sectional view of acoustic resonators. The red lines in (a) and (b) indicates the direction of lasers.

lasers for multi-gas sensing. Two microphones are symmetrically located at either side of the photoacoustic cell to implement two-point detection, allowing the enhancement of SNR. The length of acoustic resonator is about 50 mm to minimize the photoacoustic cell, and the resonant frequency is around 3000 Hz. Feasibility and performance of the MR-PC was demonstrated by simultaneous gas sensing of C_2H_2, NO and CF_4 using a near infrared diode laser and two mid infrared quantum cascade lasers. The minimum detection limits (MDL) of C_2H_2, NO and CF_4 are 480 ppb, 260 ppb and 0.57 ppb respectively, with a 1 s integration time at the normal atmospheric pressure.

2. Photoacoustic spectroscopy principle

The principle of PAS contains the Beer-Lambert law and the photoacoustic effect. The Beer-lambert law describes the absorption of laser by gas molecules. According to the Beer-Lambert law, when a probe laser passes through a gas medium and is absorbed by gas molecules, the transmitted laser power can be expressed by Eq. (1):

$$I(v) = I_0(v)\exp[-\alpha(v)CL] \tag{1}$$

where $I(v)$ stands for the output laser intensity and $I_0(v)$ for the input light intensity. Where v is the frequency of laser, $\alpha(v)$ is the linear function of gas absorption spectra, C is the concentration of the gas, and L is the absorption path-length.

Photoacoustic effect describes how lasers excite acoustic waves. Gas molecules absorb laser energy and transition to transition to excited state, and then release energy in the form of heat through intermolecular collision, causing an increase in gas temperature. When the absorbed laser is periodically modulated, gas generates acoustic waves due to periodic temperature changes. When the photoacoustic cell work at resonant frequency, the photoacoustic signal can be expressed by Eq. (2):

$$S_{PA} = c_{cell} \quad C\alpha P_{light} \tag{2}$$

Where S_{PA} is the pressure of photoacoustic signals and P_{light} is the laser power where c_{cell} stands for the cell constant of the photoacoustic cell, which represents the ability of the photoacoustic cell to convert laser signals into acoustic signals, and only related to the structure of the photoacoustic cell.

3. Simulation of photoacoustic cell

Fig. 1 shows the dual microphone MR-PAS designed in this article. The photoacoustic cell consists of three cylindrical acoustic resonators that provide different acoustic resonance frequencies. Principally, the dimensions of the cells were comprehensively optimized, considering the photoacoustic conversion efficiency and the SNR of the system, as well as the fabrication capability. The length of acoustic resonator 1 (AR1), acoustic resonator 2 (AR2) and acoustic resonator 3 (AR3) is 60 mm, 50 mm, and 46 mm respectively, and the radius is 3 mm. Channels with a radius of 1.4 mm penetrate each acoustic resonator as channels connecting the acoustic resonator and microphones (microphone 1 and microphone 2). The entire length of the photoacoustic cell
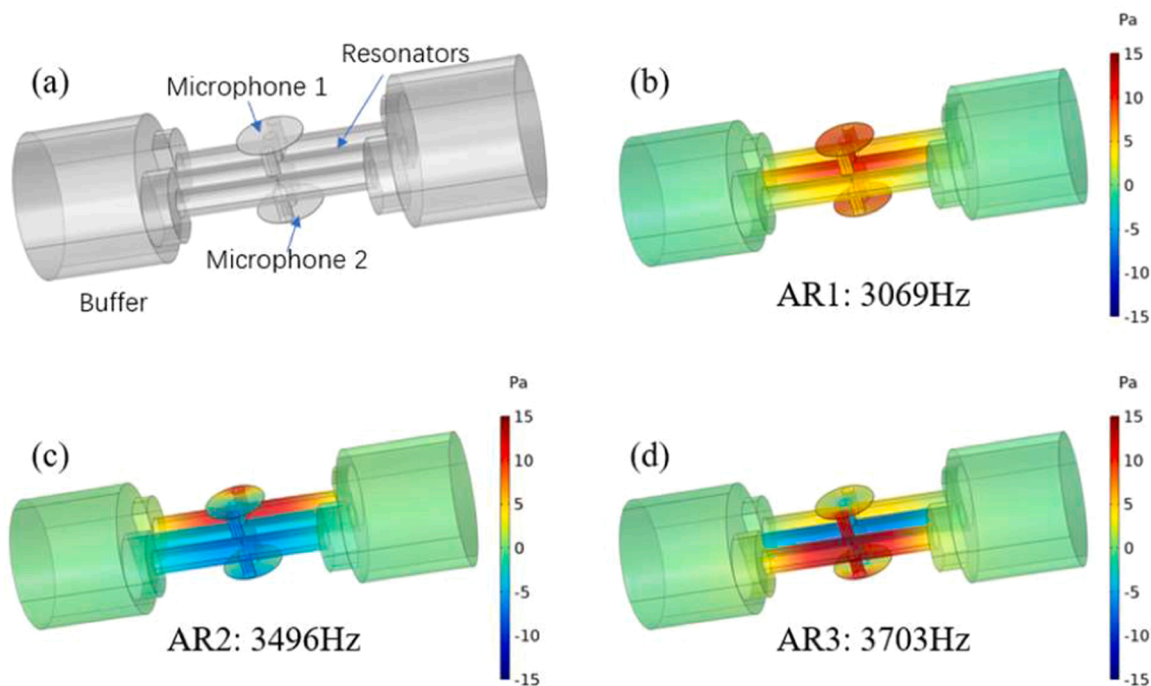

Fig. 2. Finite element model of the MR-PAC with dual microphones. (a) 3D model; (b), (c) and (d) the 1st longitudinal acoustic standing wave patterns of AR1, AR2 and AR3.
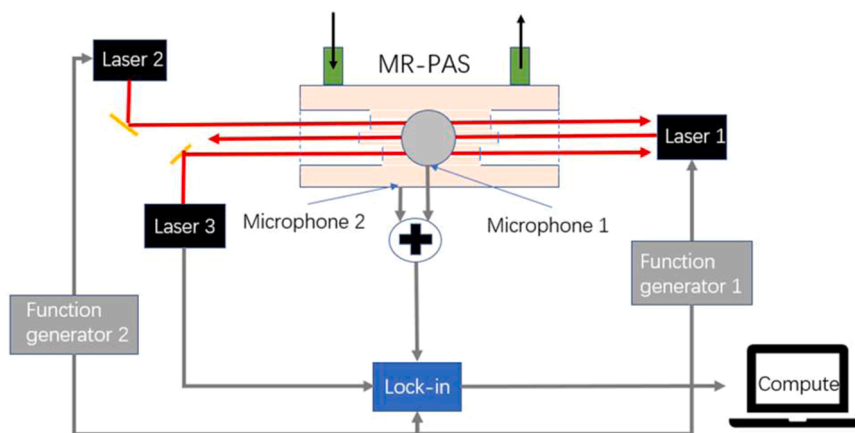
Fig. 3. Schematic diagram of the experimental device of the dual microphones MR-PAS.

is 110 mm, which is about half of that in the literatures. Dual microphones detect acoustic signals simultaneously to improve sensitivity.

Fig. 2(a) shows the 3D model of the MR-PAC with dual microphones. A finite element model is constructed to simulate the 1st longitudinal acoustic standing waves in the photoacoustic cell, as shown in Fig. 7(b), (c) and (d). In the finite element model, the material used is air, the temperature and the pressure are set to 298.15 K and 1 atm respectively. The resonant frequencies are about 3069 Hz (AR1), 3496 Hz (AR2), 3703 Hz (AR3).

As illustrated in Fig. 2, under the resonant condition of someone resonator, acoustic standing wave also exists in the other two resonators. This effect is more pronounced in the resonators at AR2 and AR3. It is analyzed that AR2 and AR3 form a structure like the spring oscillator because of the interconnectivity of the three resonant cavities through channels. This effect can be suppressed by reducing the diameters of the channels that connects the microphone with the resonator. Nevertheless, tiny channels may hinder the transmission of acoustic waves and affect the sensitivity.

It is worth noting that the diameter of the channels connecting acoustic resonator and microphones has increased from 0.8 mm to 2.8 mm in the experiments. The noise floors measured in the experiment were reduced to about a quarter. Through experimental verification, the diameter of the channels in this work is optimized as 2.8 mm.

4. Experimental setup

Feasibility and performance of the MR-PAC with dual microphones was demonstrated by simultaneous detection of C_2H_2, NO and CF_4, with the absorption wavelengths of 1532 nm, 5253 nm, and 7793 nm respectively. Fig. 3 shows the schematic diagram of the experimental setup, where laser 1 (WSLS-956010C1424–42) is an infrared distributed feedback (DFB) laser used for C_2H_2 detection, laser 2 (self-made instrument, Institute of Semiconductor, Chinese Academy of Sciences) and laser 3 (self-made instrument, Institute of Semiconductor, Chinese Academy of Sciences) are mid-infrared quantum cascade lasers (QCLs) used for NO and CF_4 detection respectively. The wavelength modulation spectroscopy and second-harmonic detection (WMS-2 f) is applied to laser 1 and laser 2 [11]. Laser 3 is a pulsed laser, so intensity modulation mode is adopted for it. Function generator 1 and function generator 2 (AWG, RIGOL DG800) offer high frequency sine wave superimposed low frequency triangle wave (10mHz) to drive the lasers. The acoustic signal generated in the photoacoustic cell is detected by microphone 1 and microphone 2 (CRY334). The sum of the two signals is demodulated by the lock-in amplifiers (LIA, Zurich Instruments, MFLI 500KHz) with a 1 s integration time.

The mixture gas of C_2H_2, NO and CF_4 is passed into the photoacoustic cell to be detected. The concentration of each gas is determined by the

Table 1
Experimental parameters of the MR-PAS.

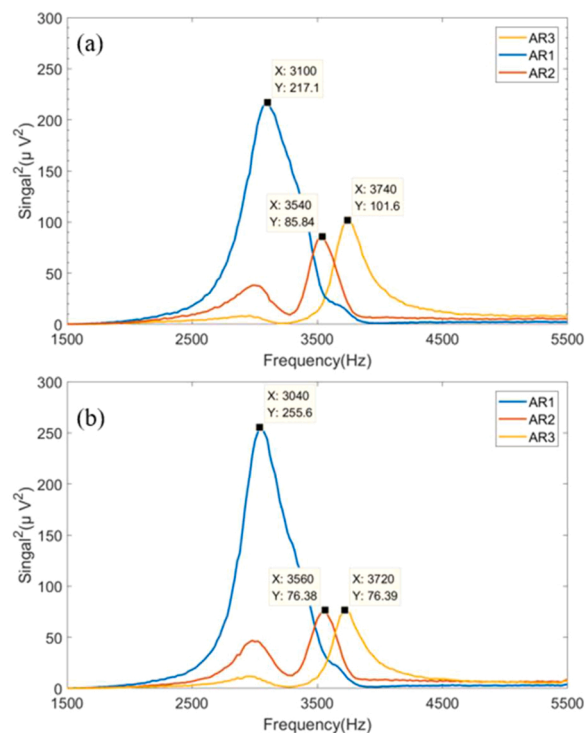| parameter	AR1	AR2	AR3
Length, mm	60	50	46
Molecule	C_2H_2	NO	CF_4
Target line, nm	1532	5253	7793
Modulation frequency, Hz	1520	1760	3730
Laser power, mW	40	14.2	8.2

Fig. 4. Frequency responses of the acoustic resonators in MR-PAC: (a) microphone 1; (b) microphone 2.

gas mixing ratio. The initial concentrations of C_2H_2, NO and CF_4 are 1000 ppm, 2026 ppm and 2000 ppm respectively. Table 1 shows the relevant experimental parameters of the dual microphones MR-PAS.

5. Results and discussion

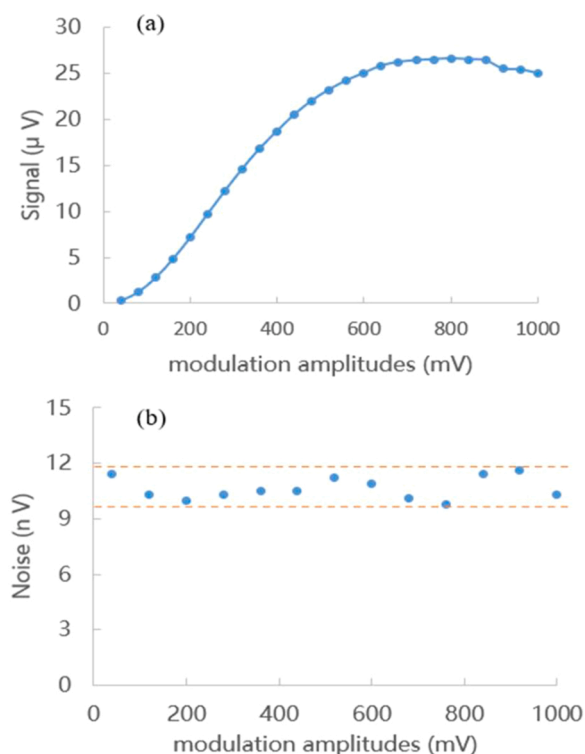Fig. 4 shows the frequency responses of three acoustic resonators.

Fig. 5. Relationship of (a) second harmonics and (b) noise to modulation amplitude.

chambers at both ends, the frequency response of someone cavity will also exhibit resonant responses corresponding to the other two cavities theoretically. The central cavity (the blue curve in Fig. 4) is nearby to the two adjacent cavities, hence the frequency responses of the two adjacent cavities (red and yellow curves in Fig. 4) would exhibit the two peaks in the experiments. The modulation frequencies of the three lasers are 1520 Hz (f/2), 1760 Hz (f/2) and 3730 Hz (f) sequentially.

The amplitude of the second harmonic signal is related to the modulation amplitude. Fig. 5 shows the relationship between the second harmonic and noise of C_2H_2 and the modulation amplitude of laser 1. The second harmonic amplitude reaches maximum with the appropriate modulation amplitude, and the noise amplitude is basically unchanged. The modulation amplitude is 600 mV in this experiment.

Fig. 6 shows the amplitudes of second harmonics of C_2H_2, NO and CF_4 at different concentrations. The response of the dual microphones
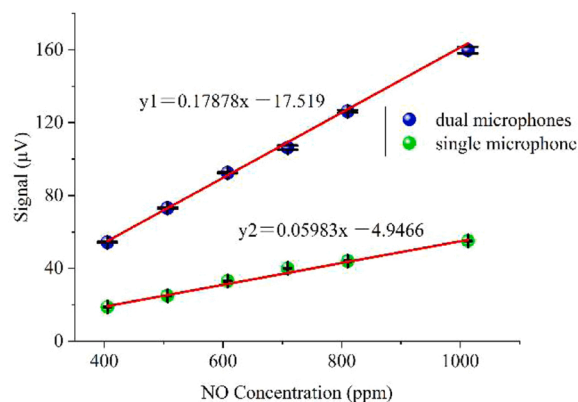

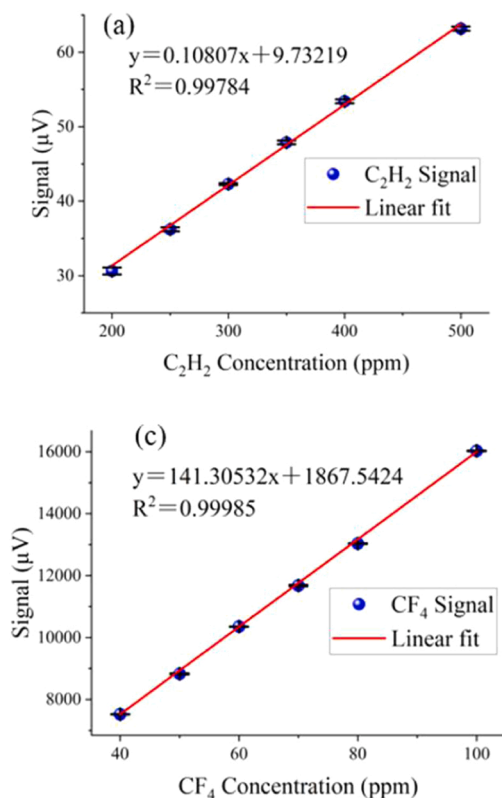**Fig. 7.** Responses of NO detection with dual microphones compared to single microphone.

The difference in resonant frequency detected by two microphones is caused by the different installation positions of the microphones. Because the three resonant cavities are interconnected by buffer

Fig. 6. The response of the dual microphones MR-PAS to (a) C_2H_2, (b) NO and (c) CF_4. (d) Second harmonic signal waveform of different concentrations of NO.
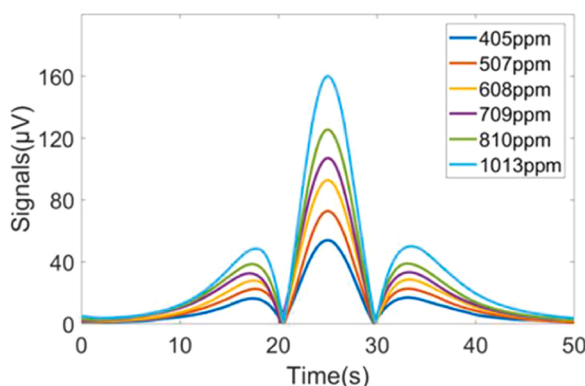
Table 2
Principle and performance of photoacoustic spectroscopy for multi-gas sensing.

Molecules	Wavelength (nm)	Principles and methods	MDL (ppm)	Ref.
CO_2	2004	non-resonant PAS with	140	[12]
CH_4	1391	infrared thermal radiation	4.4	
H_2O	1396	source	1.3	
H_2O	1368	QEPAS with three quartz	1.3	[13]
CH_4	1653	tuning forks	79	
C_2H_2	1532		5	
CH_4	1653	Single MR-PAS	0.2	[10]
CO_2	2004		12	
H_2O	1396		0.1	
CH_4	1653	PAS with time division	0.3	[14]
NH_3	1512	multiplexing	0.1	
H_2O	1368	BF-QEPAS	0.059	[15]
CO	4566		0.01	
CH_4	3599		40.75	
C_2H_2	1532	Symmetric MR-PAS with	0.48	This
NO	5253	dual microphones	0.26	paper
CF_4	7793		0.00057	

MR-PAS experiment system to C_2H_2, NO and CF_4 are 0.10807 μV/ppm, 0.17878 μV/ppm and 141.305 μV/ppm respectively. The noises floor of C_2H_2, NO and CF_4 are 0.0522 μV, 0.0465 μV and 0.0809 μV respectively. The minimum detection limits (MDL) of C_2H_2, NO and CF_4 are derived to be 480 ppb, 260 ppb and 0.57 ppb respectively, by calculating the ratio of noises and responsivity. Because the absorption coefficient of CF_4 is significantly higher than C_2H_2 and NO at the selected wavelengths, the MDL of CF_4 is suggestively lower.

In order to verify the dual microphone detection method to improve the sensitivity, a single microphone MR-PAS for NO detection is designed and compared. Fig. 7 shows the responses of NO with dual microphones and with single microphones. The responsivity of NO with dual microphone and with single microphone are 0.17878 μV/ppm and 0.05983μV/ppm respectively and the noise are 0.0465 μV and 0.0332 μV respectively, so the MDLs are derived to be about 260 ppb and 560 ppb respectively. The slopes using dual microphones indicates the responsivity is almost three times than that of single microphone, maybe caused by the sensitivity of the single microphone.

For comparison, the characteristics of some reported multi-gas sensing systems based on PAS are summarized in Table 2. The MDLs of C_2H_2, NO and CF_4 in this paper reach ppb level with a 1 s integration time and could be further enhanced with increased integration periods. Moreover, the size of the symmetric MR-PAC in this paper is minimized and only about half of the size compared to Ref [10].

To be noted, in order to achieve the simultaneous detection of acoustic waves from three resonant cavities, we connected the three cavities through the millimeter-diameter channels. This would reduce the resonant amplification effect of the photoacoustic cells and reduce the acoustic sensitivity. Nevertheless, if the diameters of the channels are reduced, the transmission loss of generated acoustic waves from the resonant cavities to the microphone as well as the fabrication challenges for the photoacoustic cell will increase. In the experiment, we have attempted to solve the issue by optimizing the size of the channels.

6. Conclusion

In summary, a symmetric multi-resonant cavity photoacoustic cell (MR-PAC) with dual microphones detection, based on multi-resonator photoacoustic spectroscopy (MR-PAS) is proposed and experimentally demonstrated. Two microphones are symmetrically placed at either side of photoacoustic cell to enhance sensitivity. The length of acoustic resonator is about 50 mm to reduce the size of the photoacoustic cell, and the resonant frequency is around 3000 Hz. The minimum detection limits (MDL) of C_2H_2, NO and CF_4 are 480 ppb, 260 ppb and 0.57ppb respectively with a 1 s integration time at normal atmospheric pressure. The designed multi-gas photoacoustic cell has a small volume, which is conducive to portable multi-gas sensing. Simultaneous detection of more kinds of gases can be achieved and enhanced by increasing the number of acoustic resonators and the integration time.

Data Availability

Data will be made available on request.

References

[1] S. Schilt, L. Thevenaz, M. Nikles, L. Emmenegger, C. Huglin, Ammonia monitoring at trace level using photoacoustic spectroscopy in industrial and environmental applications, Spectrochim. Acta A Mol. Biomol. Spectrosc. 60 (2004) 3259–3268, https://doi.org/10.1016/j.saa.2003.11.032.

[2] Y. Pan, L. Dong, X. Yin, H. Wu, Compact and highly sensitive NO2 photoacoustic sensor for environmental monitoring, Molecules 5 (2020) 1201, https://doi.org/10.3390/molecules25051201.

[3] C.F. Dewey, R.D. Kamm, C.E. Hackett, Acoustic amplifier for detection of atmospheric pollutants, Appl. Phys. Lett. 23 (1973) 633–635, https://doi.org/10.1063/1.1654774.

[4] H. Wu, L. Dong, X. Yin, A. Sampaolo, P. Patimisco, W. Ma, L. Zhang, W. Yin, L. Xiao, V. Spagnolo, S. Jia, Atmospheric CH₄ measurement near a landfill using an ICL-based QEPAS sensor with V-T relaxation self-calibration, Sens. Actuators B Chem. (2019), 126753, https://doi.org/10.1016/j.snb.2019.126753.

[5] L. Fu, P. Lu, C. Sima, J. Zhao, Y. Pan, T. Li, X. Zhang, D. Liu, Small-volume highly-sensitive all-optical gas sensor using non-resonant photoacoustic spectroscopy with dual silicon cantilever optical microphones, Photoacoustics 27 (2022), 100382, https://doi.org/10.1016/j.pacs.2022.100382.

[6] H. Xiao, J. Zhao, C. Sima, P. Lu, Y. Long, Y. Ai, W. Zhang, Y. Pan, J. Zhang, D. Liu, Ultra-sensitive ppb-level methane detection based on NIR all-optical photoacoustic spectroscopy by using differential fiber-optic microphones with gold-chromium composite nanomembrane, Photoacoustics 26 (2022), 100353, https://doi.org/10.1016/j.pacs.2022.100353.

[7] H. Wu, X. Yin, L. Dong, K. Pei, A. Sampaolo, P. Patimisco, H. Zheng, W. Ma, L. Zhang, W. Yin, L. Xiao, V. Spagnolo, S. Jia, F.K. Tittel, Simultaneous dual-gas QEPAS detection based on a fundamental and overtone combined vibration of quartz tuning fork, Appl. Phys. Lett. 110 (2017), 121104, https://doi.org/10.1063/1.4979085.

[8] Q. Huang, Y. Wei, J. Li, Simultaneous detection of multiple gases using multi-resonance photoacoustic spectroscopy, Sens. Actuators B Chem. (2019) 369, https://doi.org/10.1016/j.snb.2022.132234.

[9] J. Besson, S. Schilt, L. Thevenaz. Sub-ppm Multi-gas Photoacoustic Sensor, Pergamon-Elsevier Science LTD, 2006, pp. 899–904, https://doi.org/10.1016/j.saa.2005.10.034.

[10] K. Liu, J. Mei, W. Zhang, W. Chen, X. Gao, Multi-resonator photoacoustic spectroscopy, Sens. Actuators B Chem. 251 (2017) 632–636, https://doi.org/10.1016/j.snb.2017.05.114.

[11] B. Deng, C. Sima, Y. Xiao, X. Wang, Y. Ai, T. Li, P. Lu, D. Liu, Modified laser scanning technique in wavelength modulation spectroscopy for advanced TDLAS gas sensing, Opt. Lasers Eng. 151 (2022), 106906, https://doi.org/10.1016/j.optlaseng.2021.106906.

[12] Z. Gong, K. Chen, Y. Yang, X. Zhou, Q. Yu, Photoacoustic spectroscopy based multi-gas detection using high-sensitivity fiber-optic low-frequency acoustic sensor, Sens. Actuators B Chem. 260 (2018) 357–363, https://doi.org/10.1016/j.snb.2018.01.005.

[13] Q. Zhang, J. Chang, Z. Cong, Ji Sun, Z. Wang, QEPAS sensor for simultaneous measurements of H2O, CH4, and C2H2 using different QTFs, IEEE Photonics J. 10 (2018), https://doi.org/10.1109/JPHOT.2018.2880187.

[14] Y. Jiang, T. Zhang, G. Wang, S. He, A dual-gas sensor using photoacoustic spectroscopy based on a single acoustic resonator, Appl. Sci. 11 (2021) 5224, https://doi.org/10.3390/app11115224.

[15] H. Wu, L. Dong, H. Zheng, Y. Yu, W. Ma, L. Zhang, W. Yin, L. Xiao, S. Jia, Frank K. Tittel, Beat frequency quartz-enhanced photoacoustic spectroscopy for fast and calibration-free continuous trace-gas monitoring, Nat. Commun. 8 (2017) 1, https://doi.org/10.1038/ncomms15331.

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