Sensitivity enhanced NIR photoacoustic CO detection with SF$_6$ promoting vibrational to translational relaxation process

Yingying Qiao, Liping Tang, Yang Gao, Fengtao Han, Chenguang Liu, Lei Li *, Chongxin Shan

School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450001, China

**ARTICLE INFO**

**Keywords:**
- Photoacoustic spectroscopy
- Near-infrared light source
- Carbon monoxide sensor
- Vibrational to translational relaxation process
- Sulfur hexafluoride
- High sensitivity

**ABSTRACT**

A challenge for slowly relaxing carbon monoxide (CO) molecules detection using photoacoustic spectroscopy (PAS) is to promote the vibration-translation (V-T) relaxation process. Addressing this challenge, a sensitivity enhanced photoacoustic CO sensor with sulfur hexafluoride (SF$_6$) as the promotor is investigated and demonstrated. A 1568 nm near-infrared (NIR) laser diode and a customized optical amplifier are used as the excitation source to generate the photoacoustic signal. A differential photoacoustic cell is simulated and designed to obtain identical laminar flow distribution in the resonant cell to suppress the flow noise. The modulation frequency and added SF$_6$ volume ratio are optimized experimentally to achieve optimal sensitivity. Feasibility and performance of the CO sensor with a small amount of SF$_6$ as promotor is discussed and evaluated, obtaining a ~ 2 times improvement of signal value compared to the one with pure N$_2$ background and resulting in a minimum detection limit of 467.5 ppb for CO detection.

1. Introduction

Carbon monoxide (CO) is a colorless, odorless and highly toxic gas, which is emitted from the incomplete combustion of fossil fuels, organic compounds. Evidences show that excessive exposure to CO can cause dizziness, confusion, unconsciousness and even death [1]. A safe exposure limitation of 9 ppm CO concentration for an 8-h period has been adopted by the US Environmental Protection Agency (EPA) [2]. In addition, the concentration level of CO in exhaled human breath is regarded as a potential indicator for various diseases, such as oxidative stress, anemia and inflammation [3,4]. Therefore, reliable and highly sensitive CO detection is a critical requirement in many applications.

Photoacoustic spectroscopy (PAS) is one of the popular trace CO detection technologies because of its high sensitivity and excellent selectivity. It determines the CO concentration via monitoring the acoustic wave generated by the periodic photoacoustic excitation occurring within an absorbing gas [5]. The very basic element for the technology is the light source, which can be mainly classified as near-infrared (NIR) and mid-infrared (MIR) [6–9]. The absorption spectrum of gases located in NIR band is typically overtones of fundamental vibration in MIR band and hence can be significantly weaker [10]. However, the availability of high quality light source, elements and amplifiers from optical communication applications can counteract the disadvantage and obtain high signal to noise ratio (SNR). Additionally, the acoustic wave detector also is the key element of PAS. Up to now, microphone, quartz tuning fork, and cantilever as the acoustic wave detector has been widely researched [5,11,12]. Among them, the microphone has been well developed and has great advantages of stability, reliability, availability and cost. Hence, considering the practical application, the NIR PAS-based CO sensor with microphone as the acoustic wave detector is the best choice.

However, improving the sensitivity of the aforementioned sensor remains an ongoing challenge. There are two basic approaches currently being adopted to improve sensitivity. One is increasing the excitation light power [13–15], such as Yin et al. boosted the NIR light to ~ 10 W, resulting in a ppb-level CO detection sensitivity [16]; meanwhile, Yin et al. detected multicomponent by-products of SF$_6$ decomposition by amplifying the light power to 1.724 W, achieving a minimum detection limits (MDL) of 435 ppb for CO [17]; Mao et al. implemented an all-optical photoacoustic spectrometer using 1 W light source, and the obtained detection limits for CO was 4.6 ppm [18]. However, increasing power light source will lead to high power consumption, high cost, degraded light beam quality and complex cooling system which significantly limits the commercialization of the CO sensor. The other is promoting the vibration-translation (V-T) relaxation process [19,20], for example, Li et al. added 2.5% of water vapor into dry CO/N$_2$ mixture,
resulting a gain factor of ~ 8 on the peak value of the quartz-enhanced photoacoustic spectroscopy (QEPAS) spectra and achieving a ppb-level detection limit for CO [21]; Qiao et al. confirmed that a ~8 times PAS signal enhancement was obtained by adding water vapor in PAS sensor system, resulting a MDL of 9.8 ppm for CO [22]; Ma et al. also added the water vapor in dry CO/N₂ to improve the sensitivity of CO sensor, obtaining a 11-fold improvement of signal value compared to the one of a dry gas sample and resulting a MDL of 4.2 ppm [23]. Though, the water vapor is an extensively implemented promotor for PAS-based CO sensing, it is easy to condense into water droplets on the surface of the windows, wall of photoacoustic cell (PAC), and sensing probe of acoustic wave detector. The condensed water droplets may broaden the light beam, roughen the wall of the PAC, and worsen the performance of sensing probe, which will significantly impact the sensitivity and operating life of the PAS-based CO sensor. To solve the problem, SF₆ may be a promising candidate, because it is one kind of stable, non-flammable, and non-toxic gas, meanwhile, it has numerous vibrational and rotational levels, which raises the possibility of energy transfer in collisions with excited molecules and creates a ladder for subsequent multistep relaxation [24]. Previous studies have verified SF₆ is a great catalyst for CO₂ and N₂O measurement using in MIR QEPAS system, while has no influence on the CO detection for the same measurement system [24, 25]. We think the reason is the high working frequency of QEPAS which is usually around 32.7 kHz, it is too high to benefit from the promoted V-T relaxation process. CO is a kind of slowly relaxing molecule with the relaxation time constant of ~10 ms Torr in dry N₂ [26]. When the period corresponding to the working frequency is smaller than the relaxation time of CO molecule, the temperature in PAC cannot follow the rapid changes in the laser-induced molecular excitation rate which will cause heat accumulation and seriously impact the photoacoustic signal [27]. Moreover, the promoting ability of SF₆ for NIR CO detection has not been studied yet. Hence, it is worthy of analysis the promoting characteristic of SF₆ for NIR CO detection based on traditional PAS using microphone as the acoustic wave detector and working at low frequency.

In this paper, a highly sensitive PAS-based CO sensor with SF₆ enhanced V-T relaxation process working at NIR region was investigated and implemented for the first time. A continuous wave, distributed feedback (DFB) laser diode emitting at 1568.04 nm was used as the excitation source. A differential photoacoustic cell (DPAC) was designed and fabricated by 3D printing technology to reduce the flow noise. Two condenser microphones were embedded to detect the differential photoacoustic signal. SF₆ acting as the promotor was added in the PAS system to promote the V-T relaxation rate of the CO molecule. To suppress the absorption noise of window and wall, wavelength modulation spectroscopy and second-harmonic (2f-WMS) detection technique was utilized in this designed sensor. To achieve the optimal sensitivity, modulation frequency and added SF₆ volume ratio was optimized experimentally. Finally, the linear response relation between photoacoustic signals and gas concentrations was obtained by flowing through CO with different concentrations.

2. Experiment setup

2.1. Wavelength and excitation source selection

The principle of the PAS is to detect the acoustic wave signal generated by photoacoustic effect. For traditional PAS sensor, the acoustic signal is converted to electric signal by a sensitive microphone. The obtained electric signal UPAS at the weak absorption regime can be expressed as [28,29]:

\[ U_{PA} = S_{p} \cdot P(\lambda) \cdot C_{cell} \cdot \alpha(\lambda), \]  

(1)

where \( S_{p} \) is the microphone sensitivity (unit: mV/Pa), \( P(\lambda) \) is the excited light power at the chosen absorption line, \( C_{cell} \) is the photoacoustic cell constant which generally relates to the PAC geometry, modulation frequency of light and physical characteristic of carrier gas, \( \alpha(\lambda) \) represents the gas absorption coefficient. Obviously, the \( U_{pa} \) is directly proportional to absorption coefficient \( \alpha(\lambda) \) at the weak absorption regime when other parameter remains unchanged. So, to obtain high electric signal response, choosing strong absorption line is necessary. Meanwhile, to guarantee the excellent selectivity, the chosen absorption line must be free of interference from other potential background gases (such as SF₆, CO₂, H₂O, H₂S). According to the HITRAN database [30], the CO absorption spectrum in NIR is plotted in Fig. 1(a), it is shown that two main absorption bands locate in this region, one is near 1.56 µm, the other is near 2.33 µm. Though the absorption line is stronger near 2.33 µm, the power of the related DFB laser is just several milliwatts and there is no appropriate light amplification technique in this band. Hence, 1.56 µm band is a prefer choice to implement NIR CO detection. Specially, SF₆ molecule as the promotor shows no absorption lines in this band [9]. In addition, to avoid the interference of other gases, the absorption spectrum of CO₂, H₂O, H₂S is also analyzed, as shown in Fig. 1(b). Consequently, the absorption line of 1568.04 nm is chosen to implement CO detection.

2.2. Photoacoustic cell design

PAC is a core component of PAS sensor, which is used to generate resonant acoustic wave. As shown in Eq. 1, the cell constant \( C_{cell} \) is also a key parameter for improving the photoacoustic signal, and it can be expressed by [31]:

\[ C_{cell} = \frac{k \cdot (\lambda - 1) \cdot l \cdot Q}{f \cdot V} \]  

(2)

where \( k \) is the geometrical correction factor; \( \gamma \) is the ratio of specific heats at constant pressure and volume; \( l \) is the resonant cell length; \( Q \) is the quality factor which can be calculated by the ratio of the resonance frequencies \( f_{r} \) and the full width at half maximum (FWHM) of the acoustic resonance; \( f \) is the selected measurement frequency which is usually the resonant frequency for the purpose of obtaining optimum sensitivity; \( V \) is the volume, which is directly proportional to the \( R^2 \) (\( R \) is the radius of the resonator) for the cylindrical resonator. Based on the Thermoviscous acoustic module of COMSOL, we analyzed the frequency response and Q of a differential photoacoustic cell (DPAC). The results indicated that the acoustic pressure in the DPAC increased with the R decreasing for the same frequency, while the Q decreased with the R decreasing. The Q as a function of R is shown in the Fig. 2(a), meanwhile, the acoustic pressure of different frequency in the DPAC for different R is shown in the Fig. 2(b).

So far, various types of PAC have been investigated and proposed in the field of trace gas detection [32–34]. Given the analysis results shown in Fig. 2, a typical DPAC (the 3D schematic diagram is plotted in Fig. S1, Supplementary material) which is composed of two identical channels with length of 30 mm and diameter of 6 mm is designed and simulated, as shown in Fig. 3(a). Compared to other PACs [35–37], the resonant frequency is designed to be around 3 kHz, which is within the response bandwidth of microphone and large enough to reduce the 1/f noise. For the purpose of reducing windows absorption and turbulence noise, two buffer volumes with length of 15 mm and diameter of 30 mm are attached to both end of the resonant cell. Meanwhile, to determine the location of the gas inlet and outlet, simulations based on Finite Element Method (FEM) are implemented to obtain the laminar flow distribution which is beneficial to reduce flow noise in the resonant cells (shown in Fig. 3(b)). It is can be seen from Fig. 3(b) that the asymmetric flow velocity distribution appears with the flow rate increasing, which means the related noise cannot be suppressed well by the designed DPAC at large flow rate. Finally, frequency sweeping results of the acoustic pressure integration in the designed DPAC is depicted in Fig. 3(c). It shows that the peak of first-order longitudinal mode appears in the
middle of the resonant cell where two microphones with same frequency response sensitivity are embedded to detect the acoustic wave signal.

2.3. Experimental set-up

The experimental set-up composed of a gas dilution system, a DFB laser, a 3D-printed DPAC which is made of photosensitive resin, and data processing module is depicted in Fig. 4. To reduce the coherent noise caused by window and wall absorption, the 2f-WMS technique is usually adopted. So a superposed signal which contains a sinusoidal signal with frequency of $f_o/2$ ($f_o$ is the first-order longitudinal resonant frequency of the DPAC) and a low frequency ramp signal of 0.05 Hz is generated by a digital arbitrary waveform generator (Fluke 294) to modulate the laser wavelength (ILX Lightwave LDX-3232). A 1568.04 nm DFB laser diode (G&H E0067929) and a customized EDFA is used as the excitation source to generate and boost the light to ~ 1 W. During the experiments,

![Photoacoustics 25 (2022) 100334](image-url)
the dilution process, the pure N$_2$ was added in 500 ppm CO/N$_2$ mass flow controllers (MFC, MF-200 C, INHA) and a gas mixer. During gas mixtures. The used gas dilution system is composed of three identical cylinders of pure N$_2$, pure SF$_6$ and 1000 ppm CO/N$_2$ gas mixtures. The use of gas dilution system is composed of three identical mass flow controllers (MFC, MF-200 C, INHA) and a gas mixer. During the dilution process, the pure N$_2$, pure SF$_6$ and 1000 ppm CO/N$_2$ gas mixture flow through three identical MFCs, respectively. Then, they are fed into a gas mixer simultaneously to homogenize the gas mixture. To reduce the time of gas exchange and suppress the flow noise as far as possible, the total flow rate is controlled at 200 sccm during the experiments.

During the concentration calibration experiments, three standard gas cylinders of pure N$_2$, pure SF$_6$ and 1000 ppm CO/N$_2$ are connected to a gas dilution system to generate different concentrations of CO/N$_2$/SF$_6$ gas mixtures. The used gas dilution system is composed of three identical mass flow controllers (MFC, MF-200 C, INHA) and a gas mixer. During the dilution process, the pure N$_2$, pure SF$_6$ and 1000 ppm CO/N$_2$ gas mixture flow through three identical MFCs, respectively. Then, they are fed into a gas mixer simultaneously to homogenize the gas mixture. To reduce the time of gas exchange and suppress the flow noise as far as possible, the total flow rate is controlled at 200 sccm during the experiments.

3. Results and discussion

Many researchers have verified that the modulation frequency has significantly impacts on the performance of PAS-based sensor [29,38]. Hence, it will be optimized to obtain high-sensitive CO detection in the following experiments. Additionally, SF$_6$ with different volume ratio will be added in CO/N$_2$ gas mixture to research the improvement effect on sensitivity of NIR PAS-based CO sensor.

For the purpose of determining the optimal modulation frequency, the frequency response of DPAC was analyzed by measuring the peak-to-peak values of photoacoustic signal during a wide frequency range at atmospheric pressure and room temperature. In the experiments, we analyzed several kinds of frequency response when 0%, 2%, 3%, 4% SF$_6$ was added in 500 ppm CO/N$_2$ gas mixture. The frequency responses of these gas mixtures were plotted in Fig. 5. Results showed that the optimal modulation frequencies for these gas mixtures were 1557 Hz, 1503 Hz, 1461 Hz, and 1432 Hz corresponding to the resonant frequencies of 3114 Hz, 3006 Hz, 2922 Hz and 2864 Hz (the modulation frequency was half of the resonant frequency in 2$f_0$ demodulation method). Compared to the simulation, the difference in resonant frequencies in the experimental data could be attributed to the gas density variation, change of bulk viscosity and speed of sound. This was due to pure N$_2$ used in the simulation, while SF$_6$/CO/N$_2$ with different volume ratio used in the experimental set-up. Besides this, the resonant frequency decreased with the volume ratio of SF$_6$ increasing.

In present work, the 1568.04 nm absorption line was selected and thus a related DFB laser diode was chosen as the excitation source. In order to compensate the weak strength of absorption line, a customized EDFA was utilized to boost the output power to ~ 1 W. Considering the measurement flow rate of 200 sccm, the saturation effect of the designed sensor could be neglect in our experiments. To verify the improvement effect of SF$_6$ on PAS-based NIR CO sensor, SF$_6$ with different volume ratio was added in 500 ppm CO/N$_2$ gas mixture. The experiments were carried out at atmospheric pressure and room temperature. Then, the amplitudes of the 2$f$ photoacoustic signals were recorded as a function of the SF$_6$ volume ratio at corresponding resonant frequency as shown in Fig. 6(a). Obviously, an approximately 2 times improvement of signal value with 2% SF$_6$ adding in was obtained compared to the one without SF$_6$ adding in. Meanwhile, with the SF$_6$ volume ratio increasing, the values basically remained constant. This implied that the improvement of signal values did not depend on the modulation frequency decrease or gas physical characteristic change when the volume ratio of added SF$_6$ was smaller than 4%. Fig. 6(a) inset was the 2$f$ signal of 500 ppm CO in pure N$_2$ and 2% SF$_6$/N$_2$, it is clear that the signal in 2% SF$_6$/N$_2$ was...
narrower than that in pure N₂. This reason could be owed to the enhanced V-T relaxation process of CO molecule when a small amount of SF₆ was added in the sensor. The enhanced V-T relaxation process could accelerate the heat release process which was beneficial to reduce the signal aliasing. Moreover, the amplitudes of the 2 f photoacoustic signal when a 2% SF₆ was added in CO/N₂ gas mixture with different concentration were also analyzed at the modulation frequency of 1557 Hz (the resonant frequency of DPAC in pure N₂) and 1503 Hz (the resonant frequency of DPAC in 2% SF₆/N₂), respectively. As shown in Fig. 6(b) inset, compared to the results of 1503 Hz, the sensitivity at the modulation frequency of 1557 Hz did not seriously deteriorate, which was contributed to the wide frequency response range. This indicated that the dither of modulation frequency, and small resonant frequency shift caused by the concentration change of added SF₆ could not significantly impact the performance of the designed sensor. In conclusion, the modulation frequency of 1503 Hz was selected to implement the following experiments, and a 2% SF₆ is added in to improve the sensitivity of the designed PAS-based NIR CO sensor.

Finally, CO/N₂ gas mixtures with different concentration ratio were produced by a gas dilution system and fed into the DPAC, meanwhile, a 2% SF₆ as the promotor was added in each gas mixture to calibrate the system. Additionally, CO/N₂ gas mixtures were also measured as reference. A 1-s time constant was set for the Lock-in amplifier to demodulate the photoacoustic signal at the 2 f mode (the bandwidth is 0.25 Hz). The measurements were carried out at atmospheric pressure and room temperature. As plotted in Fig. 7, the mean 2 f signal amplitudes were recorded as a function of different concentration levels. Results confirmed that an excellent linearity response to the CO concentration levels was obtained, and the sensitivity with 2% SF₆ adding in rose from 68 μV/ppm to 130 μV/ppm. Compared to the system with pure N₂ background, a gain factor of ~ 2 on the sensitivity was obtained. The photoacoustic signals by filling pure N₂ and 2% SF₆/N₂ were also recorded to evaluate the corresponding noise level, respectively. The results showed that the standard deviations (1σ) of the noise for these two kinds of background gas was 78.01 μV and 60.77 μV corresponded to a MDL of 1147.2 ppb and 467.5 ppb. Table 1 shows the comparison of the main indexes for the two kinds of background gas.

4. Conclusion

In this report, a highly sensitive NIR PAS-based CO sensor with SF₆ enhancing the V-T relaxation process was developed and demonstrated. A DFB laser diode emitting at 1568.04 nm and a customized EDFA was selected to generated ~ 1 W light beam, which could compensate the weak absorption line strength. Meanwhile, to further improve the sensitivity of the designed sensor, SF₆ was introduced as the promotor. Experimental results verified that the SF₆ held the ability of improving the sensitivity of NIR PAS-based CO sensor. And a gain factor of ~ 2 for photoacoustic signal value was achieved by adding 2% SF₆ in the sensing system. With optimizing the modulation frequency, a MDL of 467.5 ppb was obtained. Compared to the sensors which improve the sensing performance by increasing the light power, the proposed sensor in this report has advantages of simple construction, relatively low power consumption. Considering that no absorption lines for SF₆ locate in NIR (the absorption spectrum of SF₆ is depicted in Fig. S2, Supplementary material), the measuring sensitivity of many other slowly relaxing gas molecules (such as N₂O, CO₂, NO, HCN) whose overtone absorption band locates in NIR region will be beneficial from the SF₆ promotor in PAS system. Hence, the proposed methodology opens up a new avenue for improving the sensitivity of NIR PAS-based sensors.

Table 1

| Background Gas | Sensitivity (μV/ppm) | Noise 1σ (μV) | MDL (ppb) |
|----------------|----------------------|---------------|------------|
| N₂             | 68                   | 78.01         | 1147.2     |
| 2% SF₆/N₂      | 130                  | 60.77         | 467.5      |
**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Acknowledgment**

This work was supported by the National Natural Science Foundation of China [Grant numbers 62025047, 62027816, and 62105294], the National Key Scientific Instrument and Equipment Development Project of China [Grant number 6202780147], the Henan Provincial Key Science and Technology Research Project [Grant numbers 162102210018] and the Zhengzhou Collaborative Innovation Major Project [Grant numbers 18XTZX12008].

**Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.pacs.2022.100334.

**References**

[1] D. Pinto, H. Moer, J.P. Waclawek, S. Dello Russo, P. Patimisco, V. Spagnolo, B. Lendl, Parts-per-billion detection of carbon monoxide: a comparison between quartz-enhanced photoacoustic and photothermal spectroscopy, Photoacoustics 22 (2021), 100244.

[2] US EPA, Carbon Monoxide National Ambient Air Quality Standards: Scope and Methods Plan for Health Risk and Exposure Assessment, 2009.

[3] J. Ma, Y. Dou, H. Zhang, S. Thijssen, V. Kuntsevich, G. Ouellet, M. Deffenbaugh, V. Spagnolo, Methane, ethane and propane detection using a compact quartz enhanced photoacoustic sensor and a single interband cascade detector, Sens. Actuators B Chem. 262 (2019) 952–960.

[4] Z. Lang, S. Qiao, Y. He, Y. Ma, Quartz tuning fork-based demodulation of an acoustic signal induced by photo-thermo-elastic energy conversion, Photoacoustics 22 (2021), 100272.

[5] Y. Qiao et al. Photoacoustics 25 (2022) 100334.
Yingying Qiao received her Ph.D. degree in Electronic Science and Technology from Beijing University of Posts and Telecommunications (BUPT), Beijing, China, in 2019. She is currently a lecturer in the School of Physics and Microelectronics, Zhengzhou University, Zhengzhou, China. Her current research interests include fiber-optic sensors and photoacoustic trace gas sensors.

Liping Tang received the Bachelor of Engineering degree in School of Physics from Zhengzhou University in 2019. She is currently pursuing the Master of Engineering degree in School of Physics from Zhengzhou University. Her research interests are sensing trace gases with photoacoustic spectroscopy.

Yang Gao received the B.Eng. degree in telecommunication engineering from the Beijing Institute of Technology, Beijing, China, in 2014, and the Ph.D. degree in radio physics from the University of Birmingham, Birmingham, U.K., in 2018. After graduating from the University of Birmingham, he joined Zhengzhou University, Zhengzhou, China, as a Lecturer. He is also an Honorary Research Fellow with the Emerging Device Technology Group, University of Birmingham. Yang’s current research interests include integrated microwave-photonic circuits, passive/active devices and systems.

Lei Li received the B.S. degree in electronic and information engineering from the Jilin University, Changchun, China, in 2004. He is currently pursuing the Ph.D. degree in radio engineering from the Institute of Acoustics, Chinese Academy of Sciences, Beijing, China. His current research interests include machine learning and signal processing.

Chongxin Shan is Professor at the School of Physics and Microelectronics, Zhengzhou University, Zhengzhou, China. He received his Ph.D. degree from Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences in 2004. His current activity is focused on diamond photoelectric materials and devices.

Fengtao Han received the B.S. degree in electronic and information engineering from the Jilin University, Changchun, China, in 2018. He is currently pursuing the master’s degree in instrumentation engineering at Zhengzhou University, Zhengzhou, China. His current research interests include integrated microwave-photonic circuits, passive/active devices and systems.