Compact and sensitive mid-infrared all-fiber quartz-enhanced photoacoustic spectroscopy sensor for carbon monoxide detection

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Abstract: A compact and sensitive quartz-enhanced photoacoustic spectroscopy (QEPAS) based sensor for carbon monoxide (CO) detection was demonstrated by using a mid-infrared all-fiber structure as well as a 3D-printed acoustic detection module. An all-fiber configuration has advantages of easier optical alignment, lower insertion loss, improvement in system stability, reduction in sensor size and lower cost. The 3D-printed acoustic detection module was introduced to match the mid-infrared all-fiber structure and further decrease the sensor volume, which resulted in a small size of 3.5 cm$^3$ and a weight of 5 grams. A 2.33 μm distributed feedback fiber-coupled diode laser was used as the laser excitation source. A custom quartz tuning fork (QTF) with a small-gap of 200 μm was used as the acoustic wave transducer in order to improve the signal level of the QEPAS sensor. An acoustic micro resonator was utilized as the acoustic wave enhancer. The gas pressure and laser wavelength modulation depth were optimized, respectively. Water vapor was used to accelerate the vibrational-translational relaxation rate of the targeted CO molecule. Finally, a minimum detection limit (MDL) of 4.2 part per million (ppm) was achieved, corresponding to a normalized noise equivalent absorption (NNEA) coefficient of 7.4 × 10$^{-9}$ cm$^{-1}$W/$\sqrt{\text{Hz}}$. An Allan deviation analysis was used to evaluate the long-term stability of the reported CO-QEPAS sensor system. With an integration time of 150 s, the MDL was improved to be 1.3 ppm.

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1. Introduction

Carbon monoxide (CO), a colorless and odorless gas, which is highly poisonous to humans and animals since it has a 200-times stronger bonding ability with hemoglobin than oxygen-[1]. CO constitutes the largest fraction of pollutants which are produced primarily in the incomplete combustion of carbon-containing materials used in industrial manufacturing, petrochemical refining and other applications [2,3]. In medicine, CO in exhaled human breath plays as an effective physiological tracer for diverse diseases including asthma, anemia and Alzheimer’s [4–7]. In addition, the CO concentration can be interpreted to indicate combustion efficiency. Hence, the sensitive detection of CO shows the critical requirement in combustion, medical and environmental fields.

Various techniques were developed for trace gas detection. Direct laser absorption spectroscopy has the advantages of the high sensitivity, highly selective and fast response time [8]. In [9], CO concentration was measured using direct laser absorption spectroscopy at measurement speeds of 100 kHz in a harsh environment of detonation tube. Laser photoacoustic spectroscopy (PAS) based on the photoacoustic effect discovered by Bell [10]
is another sensitive trace gas detection technique. When the laser output is absorbed by a gas sample, the absorbed energy is transformed to heat energy by non-radiative processes, and will result in an increase of the local temperature and pressure in the sample. Therefore, the absorption of a modulated laser beam in a gas sample leads to the generation of an acoustic wave. The intensity of the acoustic wave is related to the sample concentration which can be detected by a sensitive acoustic wave detector. Usually a microphone was utilized as the acoustic wave detector. Quartz-enhanced photoacoustic spectroscopy (QEPAS) is a promising trace gas detection technique which was first reported in 2002 [11]. QEPAS using a sharply resonant quartz tuning fork (QTF) as detector possesses the advantages of a high quality factor (Q factor), a large dynamic range, a small size and a low cost. The QTF is immune to environmental noise because only when the two prongs bend in opposite directions the QTF is piezoelectric active. A QTF with its small dimension enables an acoustic detection module with a small volume. Due to the above merits of high sensitivity, selectivity, large dynamic range and compactness, QEPAS has been applied in the quantitative analysis of a large number of trace gas species [12–21].

Usually CO detection based on three different CO transitions, the fundamental vibrational band (ν) near 4.6 μm [22–24], the first overtone band (2ν) near 2.33 μm [25,26] and the second overtone band (3ν) near 1.57 μm [27]. Costly quantum cascade lasers (QCLs) are usually applied for the fundamental vibrational band. Cost-effective diode lasers can cover the CO 2ν and 3ν absorption band and the absorption line strength of the 2ν band is approximately 10^2 times stronger than the one of the 3ν band. Therefore, the absorption line within the 2ν band is usually applied as a compromise between sensitive detection and low-cost requirement. In [25,26], a diode laser emitting at 2.33 μm was used for CO detection based on the QEPAS technique. A block optical collimator and focusing lens were adopted for laser beam propagation which limits the development of miniaturization of the QEPAS sensor. Furthermore, a discrete optical lens reduces the stability of the sensor system.

In the near infrared optical communications field, the gradient index (Grin) lens is a common micro optical element which is designed to focus the near-infrared Gaussian beam or serve as a collimator. The Grin lens possesses the advantages of a small volume, a flat end face and a self-focusing property as well as facilitates in coupling to other elements. Replacing a block optical collimator and the focusing lens with a Grin lens reduces the volume of the QEPAS system significantly. However, there does not exist a commercially available Grin lens to deliver diode laser radiation in the mid-infrared region beyond 2 μm.

In this paper, a strong absorption line of 2330.19 nm located at the 2ν band was chosen for sensitive CO detection. A 2.33 μm continuous wave (CW), distributed feedback (DFB) diode laser was used as an excitation source. A mid-infrared fiber-coupled Grin lens was fabricated for the first time for laser delivery to construct an ultra-compact all-fiber QEPAS sensor system. An all-fiber configuration has the advantages of easier optical alignment, lower insertion loss, improvement in system stability, reduction in sensor size and lower cost. A 3D printing technique was introduced to fabricate a small size acoustic detection module to match the mid-infrared all-fiber structure and further decrease the sensor volume. A custom QTF with a small-gap of 200 μm was utilized as the acoustic wave transducer to avoid energy losses of the acoustic wave and therefore improve the signal level of the QEPAS sensor. The performance of the CO-QEPAS sensor was investigated and optimized.

2. Experimental setup

2.1. Preparation of mid-infrared fiber-coupled Grin collimator

An ion exchange method is a convenient way to produce a Grin profile in glass [28,29]. In order to satisfy the requirements of the Grin lens, the formula of the glass follows the principles which should be taken into account primarily: (1) the optical properties, such as the refractive index and light absorption, should meet the design requirements; (2) a
reasonable melting temperature; (3) an appropriate viscosity at elevated temperature; (4) a high ion exchange coefficient and (5) chemical stability at normal and elevated temperatures. Based on these five requirements the base glass ingredients were as follows: SiO$_2$(60-65%), Na$_2$O(9-18%), TiO$_2$(7-13%), B$_2$O$_3$(4-8%), ZnO(4-5%) and TiO$_2$(2-3%).

![Fig. 1. Schematic of the fiber-coupled Grin collimator.](image)

The schematic of the fiber-coupled Grin collimator (FGC) is shown in Fig. 1. In practical applications, the Grin lens should be used together with a fiber stub and attach them to a borosilicate glass sleeve by gluing with an ultraviolet adhesive. The adopted Grin lens is a cylinder with a diameter of 1 mm and a length of 2.39 mm. The refractive index of the lens and the gradient constant at the wavelength of 2.33 $\mu$m were measured to be 1.588 and 0.326, respectively. The effective focal length of the Grin lens is 1.1 mm. The beam waist is ~60 $\mu$m and the working distance was calculated to be 9 mm, which is much larger than the required length for QEPAS sensor. With an oblique face angle of 8°, less optical reflection occurs. Therefore, the influence of the reflected laser on the laser source and system can be reduced. The numerical aperture and the fiber core diameter of the fiber pigtail (Nufern model SM-1950) were 0.2 and 7 $\mu$m, respectively. The transmittance of the mid-infrared fiber-coupled Grin lens at 2.33 $\mu$m was ~90%.

2.2. 3D-printed acoustic detection module

The schematic diagram of the design and the assembled configuration of the 3D-printed acoustic detection module are shown in Fig. 2. Photopolymer (type: Somos 8000) was used as the material in the 3D printing fabrication process. The FGC and the acoustic detection module were glued by vulcanized rubber. The acoustic micro resonators (mRs), formed by two metal tubes with a 5 mm length is considered as the optimal photoacoustic enhancer which has the ability of accumulating acoustic energy. The QTF was fixed when the vertical distance between the laser beam and the free ends of the QTF were adjusted to be 0.5 mm in order to obtain the maximum signal enhancement. The distance between the QTF prongs and the mRs was ~30 $\mu$m. The laser beam should pass through the groove of the QTF without touching in order to avoid optical background noise. The total volume and the mass of the photoacoustic detection module were only 3.5 cm$^3$ and 5 grams, respectively, which is highly competitive with the previous reported QEPAS-based CO sensing systems [25–27].

![Fig. 2. Design and the assembled configuration of the 3D-printed acoustic detection module.](image)
Usually in a traditional QEPAS sensor system, a precise optical alignment is required due to the usage of many discrete optical elements and small size acoustic components. For example, in [30], a complicated visualization system employing a microscope was used for the optical alignment. In this QEPAS system, due to the all-fiber structure and 3D-printed acoustic detection module, the optical alignment was much easier. Furthermore, in the traditional QEPAS sensor system, optical collimating lens, focusing lens and window should be used. Compared with that only one fiber-coupled Grin lens was employed in this QEPAS sensor system, the reduced number of optical elements decreased the optical loss. Furthermore, no obvious deformation for the 3D-printed acoustic detection module was observed for more than one year.

2.3. Experimental setup

The CO-QEPAS gas sensor was constructed with a 3D-printed acoustic detection module and the experimental setup is shown in Fig. 3. The energy of the acoustic waves generated in photoacoustic spectroscopy will diminish rapidly as the distance from the generation point of the acoustic wave increases [31]. Instead of a standard QTF with a gap of 300 \( \mu \text{m} \), a custom QTF with a small-gap of 200 \( \mu \text{m} \) was employed to improve the signal level of the QEPAS sensor. The length, thickness and width for the prong of the custom small-gap QTF were 3.42 mm, 0.44 mm and 0.3 mm, respectively. The deformation for the QTF prong caused by the acoustic wave was simulated using Finite Element Modeling (FEM) COMSOL software. The calculated maximum displacement for the small-gap QTF with 200 \( \mu \text{m} \) gap and the standard QTF with 300 \( \mu \text{m} \) gap were \( 1.96 \times 10^{-10} \text{ mm} \) and \( 1.82 \times 10^{-10} \text{ mm} \), respectively. This further confirmed the advantage of small-gap QTF. However, when the excitation sources with poor beam quality such as light-emitting diodes (LEDs) are used in QEPAS sensors, the large beam diameter and divergence angle make the light beam hard to pass through the small gap between the two prongs of QTF which will result in additional optical noise. Wavelength modulation spectroscopy (WMS) with a second harmonic (2\( f \)) detection technique was utilized for sensitive CO detection. A ramp voltage was applied to the laser driver in order to scan the laser wavelength across the absorption line of CO, while a sinusoidal dither was employed at half of the QTF resonant frequency (\( f_0 = 30.768 \text{ kHz}, \text{ in vacuum} \)). The lock-in amplifier (Zurich Instruments, model MFLI) demodulated the piezoelectric signal generated from QTF into a second harmonic signal. A 5\% CO:N\(_2\) target gas was flushed into the 3D-printed acoustic detection module. A needle valve and flow meter were used to set and monitor the gas flow through the QEPAS sensor system at a constant rate of 120 mL/min. An external humidifier was added at the inlet of the QEPAS system to improve the CO vibrational-translational (V-T) relaxation processes. A pressure controller (MKS Instruments, Inc., Type 649B) and a vacuum pump were employed to control and maintain the pressure in the sensor system.
The CO absorption lines in the 2.3 μm first overtone absorption band at a temperature of 300 K and a standard atmospheric pressure, according to the HITRAN 2016 database [32] are shown in Fig. 4. This simulation shows that a R(8) line in R branch located at 2330.19 nm (4291.50 cm$^{-1}$) is one of the strongest CO lines at ~2.3 μm. Furthermore, this CO line is free from spectral interference of water vapour (H$_2$O) and nitrogen (N$_2$). A 2.33 μm continuous wave (CW), DFB fiber-coupled diode laser (Model #: KELD1G5BAAH, NEL Corp., Japan) was used as the laser excitation source. The DFB-CW diode laser wavelength can be tuned to cover this absorption line by changing the laser injection current at a constant TEC temperature of 19 °C. When the laser wavelength was tuned to target the CO absorption line the optical power was ~3.7 mW. After the laser beam passed through the QTF gap and micro resonators the power was 3.3 mW.

3. Results and discussion

Firstly, the CO-QEPAS sensor was operated at atmospheric pressure (P = 760 Torr). In this case the sensor volume could be reduced because the pressure controller and vacuum pump become redundant. The integration time of the lock-in amplifier for the CO-QEPAS sensor system is important because the signal-to-noise ratio (SNR) and detective bandwidth is
related with it. Usually the SNR increases and the detective bandwidth decreases when integration time increases. Therefore, a reasonable integration time should be chosen in order to ensure that the QEPAS sensor had a large SNR, fast response for CO concentration measurements and appropriate detective bandwidth. From this point of view, a 1 s integration time was adopted in the experiments. The SNR and detective bandwidth of CO-QEPAS sensor as a function of integration time was performed and shown in Fig. 5. In this investigation, the CO-QEPAS signal level was measured when the laser wavelength modulation depth was set to 0.36 cm$^{-1}$. The background signal was detected when the 3D-printed acoustic detection module was flushed with ultra high purity nitrogen (N$_2$). It can be seen from Fig. 5 that when the integration time is 1 s the CO-QEPAS sensor had a SNR of 212 and detective bandwidth of 78 mHz.

In case of slow vibrational-translational (V-T) relaxation such as in the CO molecule, the thermal waves in the gas cannot follow fast changes of the laser induced molecular vibration excitation. Thus, the generated photoacoustic wave is weaker than it would be in case of fast
V-T energy equilibration [27]. Water vapor is a high-performance catalyst that is used to accelerate the V-T relaxation rate of the targeted CO molecule and will result in a higher detected amplitude of the CO-QEPAS signal. Therefore, a specialized gas humidifier was used to humidify the CO:N₂ gas mixture uniformly. The gas humidifier is a tube-in-shell moisture exchanger which transfers water vapor between a liquid water service system and a gas flow system. The water is absorbed into the shells of the Nafion tube and is then transferred as a vapor to the dry gas flow. This transfer is driven by the discrepancy in the partial pressures of the water vapor on opposite sides. The control of the humidity is achieved by varying the temperature of the circulating water. The dependence of the corresponding $2f$ signal amplitude on the water vapor concentration is plotted in Fig. 6. The maximum concentration of water vapor was 1.53%. In this condition, the signal achieved a 11-fold improvement compared to the one of a dry gas sample with a signal value of 0.12 mV.

![Fig. 7. The resonant frequency and Q factor of the QTF with acoustic mRs as a function of pressure.](image)

![Fig. 8. The CO-QEPAS signal as a function of the pressure and modulation depth.](image)

In order to obtain the maximum $2f$ QEPAS signal, on one hand, the gas pressure must be chosen appropriately. The resonant frequency and Q factor of QTF were first investigated when the pressure was changed. In the measurement, a sweep signal generated by a signal generator was sent to one pin of the QTF. An oscilloscope was used to detect the response of the QTF by receiving signal from the other pin of QTF. Thus, the QTF’s resonant frequency $f_0$ can be obtained in a peak amplitude. The Q-factor was calculated by the equation of
$f_0$/FWHM, where FWHM was the full width at half maximum of the frequency response curve for the QTF. The measured results for the QTF with acoustic mRs are shown in Fig. 7. It was found that the resonant frequency and Q factor increased when the pressure decreased. On the other hand, in WMS-$2f$ detection, an appropriate modulation depth can achieve a significant improvement of the signal level. The variation of the CO-QEPAS signal amplitude as a function of the pressure and modulation depth was experimentally investigated and is depicted in Fig. 8. It can be seen that the optimum gas pressure is 300 Torr and at this condition the amplitude of the CO-QEPAS signal increases until the laser wavelength modulation depth reached 0.10 cm$^{-1}$. The curve began to decrease when the modulation depth was greater than this value. Therefore, the optimum modulation depth of the laser wavelength was 0.10 cm$^{-1}$ for P = 300 Torr. The CO-QEPAS signal as a function of the water vapor concentration at pressure of 300 Torr and modulation depth of 0.10 cm$^{-1}$ is shown in Fig. 9. The maximum signal enhancement was obtained when the water vapor with concentration of 1.53% was injected.

![Image](image.png)

**Fig. 9.** The CO-QEPAS signal as a function of the water vapor concentration at pressure of 300 Torr and modulation depth of 0.10 cm$^{-1}$.

The measured $2f$ CO-QEPAS signal at a modulation depth of 0.10 cm$^{-1}$ and P = 300 Torr is shown in Fig. 10(a). Figure 10(b) depicts the background signal when pure N$_2$ was used. The 1σ background noise was 0.17 μV and is primarily determined by fundamental thermal noise of the QTF. Based on the data depicted in Fig. 10 the 1σ minimum detection limit (MDL) of the CO-QEPAS sensor is 4.2 ppmv which was better than the reported results of 43.3 ppm [26] and 120 ppm [33] at the 2.3 μm region using QEPAS method and a DFB laser. The calculated normalized noise equivalent absorption coefficient (NNEA) was $7.4 \times 10^{-9}$ cm$^{-1}$W/$\sqrt{\text{Hz}}$. 
Fig. 10. Signal amplitude: (a) 2f CO-QEPAS signal obtained with a pressure of 300 Torr and modulation depth of 0.10 cm$^{-1}$; (b) pure N$_2$ for noise determination.

To evaluate the long-term stability of the reported CO-QEPAS sensor with a mid-infrared all-fiber structure and a 3D-printed acoustic detection module, an Allan deviation analysis was performed. The 3D-printed acoustic detection module was flushed with pure N$_2$ at a constant flow rate, and the measurements lasted for more than two hours which is depicted in Fig. 11. It is observed that a MDL of 1.3 ppm can be obtained with an integration time of 150 s. System drifts start to dominate when the integration time was larger than 150 s. The integration time of 150 s demonstrated that the mid-infrared all-fiber structure had an excellent stability when compared with the QEPAS system using discrete block optical elements which possessed an optimum integration time of 70 s [14].

Fig. 11. Allan deviation analysis for the CO-QEPAS sensor system with a mid-infrared all-fiber structure and a 3D-printed acoustic detection module.

4. Conclusions

In conclusion, a sensitive and compact CO-QEPAS sensor based on a mid-infrared all-fiber configuration was demonstrated for the first time. An all-fiber configuration has the
advantages of easier optical alignment, lower insertion loss, improvement in system stability, reduction in sensor size and a lower cost. A 3D printing technique was introduced to fabricate a small size acoustic detection module to match the mid-infrared all-fiber structure and further decrease the sensor volume. The 3D-printed acoustic detection module consists of a small volume of 3.5 cm³ and the weight of the QTF, the fiber-coupled Grin collimator and the mRs was only 5 grams. A custom QTF with a small-gap of 200 μm was utilized as the acoustic wave transducer to avoid acoustic wave energy losses and therefore improve the signal level of the QEPAS sensor. An acoustic micro resonator consisting of two mRs with a length of 5 mm was utilized as the acoustic wave enhancer. The gas pressure and laser wavelength modulation depth were optimized to be 300 Torr and 0.10 cm⁻¹, respectively. Upon adding 1.53% water vapor to accelerate the V-T relaxation rate of the targeted CO molecule, a 11-fold enhancement of the QEPAS signal amplitude was achieved. Finally, a MDL of 4.2 ppm for CO detection was obtained with a 1 s integration time, which corresponds to a NNEA of 7.4 × 10⁻⁹ cm⁻¹W/√Hz. An Allan deviation analysis was used to evaluate the long-term stability of the reported CO-QEPAS sensor system. With an integration time of 150 s, the MDL was improved to be 1.3 ppm. The sensor’s sensitivity could be improved even further if the concentration of the water vapor is increased.

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