Trace gas sensing based on multi-quartz-enhanced photothermal spectroscopy

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1. Introduction

Optical gas sensing methods have been widely used in trace gas detection due to their advantages of short response time, high sensitivity and selectivity, non-invasive and real-time detection [1,2]. Optical gas sensors can be divided into three groups: i) direct absorption spectroscopy based sensors, such tunable diode laser absorption spectroscopy (TDLAS); ii) cavity-enhanced absorption spectroscopy (CEAS) based sensors; iii) photothermal spectroscopy based sensors. Usually optical gas sensing techniques have a fast response time of <1 s. When compare the detection performance among different sensors, normalized noise equivalent absorption parameter (NNEA) is the best indicator. In the above three different kinds of optical gas sensors, TDLAS and CEAS can reach a minimum NNEA of \(\sim 10^{-9}\) cm\(^{-1}\) W/\(\sqrt{\text{Hz}}\) and \(10^{-12}\) cm\(^{-1}\) W/\(\sqrt{\text{Hz}}\), respectively [3]. However, for these two techniques, significant increase in the optical pathlengths is always required, which means high cost and bulky. Quartz-enhanced photothermal spectroscopy (QEPAS) and quartz-enhanced photothermal spectroscopy (QEPST) are identified as advanced techniques, which offer several advantages such as a wide dynamic range, simplicity, a compact size and no optical detectors are needed. The minimum NNEA for QEPAS is \(\sim 10^{-11}\) cm\(^{-1}\) W/\(\sqrt{\text{Hz}}\) [4]. QEPAS was first reported in 2002 [5]. In QEPAS, a quartz tuning fork (QTF) with the merits of small volume, high quality factor and low price is used as an acoustic wave detector [6]. When the modulated laser passes through the gas, the QTF prongs vibrate due to the photothermal effect discovered by A.G. Bell and the charge is generated via the piezoelectric effect of quartz [7,8]. The metal film coated on the surface of the QTF is used to collect the generated electrical charges [9]. Due to the advantage of high sensitivity and compact structure, QEPAS is widely used today in the detection of numerous gases [10–17]. The QTF in QEPAS sensor needs to be placed inside the gas analyte [18]. This feature limits its application in some fields [19,20], for example, the measurement of hydrogen chloride (HCl), because the metal film of QTF would be corroded when HCl encounters water vapor, and hence the life of QTF would be reduced. Furthermore, QEPAS is difficult to meet some applications requiring remote detection, such as for combustion diagnosis.

QEPST is an alternative method for trace detection, which was first reported in 2018 [21]. It is also named light-induced thermoelastic spectroscopy (LITES) [22,23]. QEPSTs can overcome the above defects in QEPAS and achieved a better detection sensitivity. In QEPST, after being absorbed by the target gas the laser beam is transmitted to the surface of QTF. Part of the laser energy is absorbed by the target gas, and as a result a photothermal energy is generated, which can induce elastic deformation and mechanical vibration in the QTF. When the laser is modulated at the
to the resonance amplification of the QTF. Finally, the mechanical motion is converted into an electrical signal through the piezoelectric effect of the QTF. QEPTS is identified as an advanced technique. It has been demonstrated that QEPTS can provide a better detection sensitivity than QEPAS under the same conditions [21, 22]. Compared to the QEPAS technique, QEPTS is a non-contact measurement method and therefore can be used for remote and standoff trace gas detection. Furthermore, it shows superiority when compared to usually used technique of TDLAS. When compared to an optical detector used in TDLAS, a QTF is much cheap, tiny and independent to the laser wavelength. Hence, a QTF is especially attractive for QEPTS gas sensing in the >10 μm spectral region, where optical detectors are expensive and difficult to acquire.

Until now all the QEPS sensors only use a single QTF to detect the photothermal signal. If multiple QTFs can be used at the same time, the amplitude of the signal detected by each QTF can be added together and hence the detection performance of QEPTS can be improved significantly.

In this paper, a novel QEPTS gas sensing method based on multiple QTFs detection was demonstrated for the first time. We called this technique multi-quartz-enhanced photothermal spectroscopy (M-QEPTS). In this M-QEPTS, two QTFs were used to verify the superiority of this technique. A simple chemical etching method was used to improve the laser absorption and transmission. Acetylene (C2H2) was selected as the target analyte due to its particularly interest in polyethylene production and power transformer arc fault monitoring [24].

2. Experimental setup

The experimental configuration of M-QEPTS is shown in Fig. 1. According to the HITRAN database [25], a strong absorption line of C2H2 located at 1530.37 nm (cm/mol) with a line intensity of 1.21 × 10−20 cm/mol was adopted. A distributed feedback (DFB), continuous wave (CW) fiber-coupled diode laser with output power of 10.62 mW was used as the excitation source. In the M-QEPTS sensor system, wavelength modulation spectroscopy (WMS) with 2nd harmonic (2f) detection was utilized for the concentration detection. A sinusoidal wave at half of the resonant frequency of the used QTF was applied to a direct current ramp with a frequency of 25 mHz to achieve laser wavelength modulation. The ramp was used to scan across the absorption line of C2H2. The modulated laser beam emitted from the fiber was collimated by a fiber collimator (FC). The collimated laser beam was injected to a gas absorption cell which was 20 cm in length and equipped with two windows made of calcium fluoride (CaF2) on each side. Commercially available QTFs with a resonance frequency of 30.72 kHz were employed in the M-QEPTS sensor system. However, one of the limiting factors of this M-QEPTS method is that the optimal laser focusing position of a QTF is at the root of the two prongs of QTF, where the thermal stress field is the strongest [22], but usually a metal film acting as electrode is deposited on the surface of QTF, which has high reflectivity and prevents the absorption and transmission of the light to the QTF. Therefore, it is necessary to remove the metal films to reduce the reflectivity and maximize the absorption for the QTFs in the M-QEPTS technique. After passing through the cell, the laser beam was focused by a lens with focal length of 40 mm onto the surface of QTF1. Metal films at the optimal laser focusing position with a diameter of 1 mm on both sides of QTF1 were carefully removed by using chemical etching method of nitric acid so that the laser beam can pass through QTF1 with high transmission. Furthermore, the electrodes were not destroyed. The metal film on the surface of QTF was carefully removed by using nitric acid with a concentration of 65% v/v. A pipettor was used to transport nitric acid to the QTF. After a few seconds (less than 5 seconds), the chemical reaction between metal film and nitric acid was completed. Then the QTF was washed by high concentration ethanol to remove the residues on the surface of QTF. The corroded position of QTF is shown in the inset of Fig. 1. Subsequently, a lens with focal length of 20 mm was employed to focus the transmitted laser beam from QTF1 onto the surface of QTF2. The front surface of QTF2 was also reduced for optimum absorption. After adding the piezoelectrical signals generated by QTF1 and QTF2 together in the M-QEPTS system, the electrical signal was transferred to a lock-in amplifier which was employed to demodulate the 2f signal generated by the QTFs. The integration time of the used lock-in amplifier was 1 second.

3. Experimental results and discussions

In this M-QEPTS sensor system, two QTFs with optimized shaped surfaces were used to receive the laser and generate electrical signals. The difference of resonant frequency f between QTF1 and QTF2 must be slight (less than 0.100 Hz) in order to obtain the strongest response for the whole system (QTF1 + QTF2). After chemical etching, the resonant frequency of QTF was measured by adopting an electrical excitation approach. Fig. 2 shows the output voltage signals as a function of input signal frequency. The obtained signal amplitudes were Lorentzian fitted which can be used to calculate f1, f2, f3 and the quality factors Q1, Q2, Q3 for QTF1, QTF2 and QTF1 + QTF2, respectively. The calculated results were f1 = 30713.309 Hz, f2 = 30713.374 Hz, f3 = 30713.372 Hz and the detection bandwidth Δf1 = 2.57 Hz, Δf2 = 2.33 Hz, Δf3 = 2.67 Hz. Therefore, based on the formula Q = Δf/Δf, Q1 = 12236.38 Hz, Q2 = 13181.71 Hz, Q3 = 11503.14 Hz were obtained, respectively. The equivalent resistance of QTF was also investigated as R1 = 165.13 kΩ, R2 = 168.52 kΩ and R3 = 79.06 kΩ. The obtained parameters are listed in

![Fig. 1. Schematic diagram of M-QEPTS based on two corroded QTFs.](image-url)
Table 1. It can be seen that the $f$, $Q$, and $R$ did not have an obvious change after the chemical etching was applied due to the etched area with a very small diameter of 1 mm. The measured $f$ of QTFF1, QTFF2 and QTFF1 + QTFF2 after etching were almost the same (the difference between QTFFs was 0.065 Hz, less than 0.100 Hz), which was advantageous for the M-QEPTS technique. In the following experimental operations, the frequency of the sinusoidal wave for modulation was set as $f/2 = 15356.686$ Hz in order to obtain the strongest response for QTFF1 + QTFF2.

In order to improve the $2f$ signal amplitude when utilizing WMS with 2nd harmonic detection, the laser wavelength modulation depth should be optimized. A 2% $\text{C}_2\text{H}_2$ in nitrogen ($\text{N}_2$) gas mixture was selected as the target analyte. The $2f$ signal generated from QEPTS sensor employing QTFF1 as a function of the laser wavelength modulation depth is depicted in Fig. 3. The highest $2f$ signal amplitude was obtained when the modulation depth was 0.18 cm$^{-1}$, which indicated the optimum condition. This optimal 0.18 cm$^{-1}$ modulation depth was chosen in the following measurements.

The measured $2f$ QEPTS signals for QTFF1, QTFF2 and QTFF1 + QTFF2 are shown in Fig. 4. The $2f$ signal amplitudes were 650.05 $\mu$V, 372.56 $\mu$V, 983.44 $\mu$V for sensors employing QTFF1, QTFF2 and QTFF1 + QTFF2, respectively. Although QTFF1 was modified by nitric acid on both surfaces to reduce the reflectivity, the transmission for $1.53 \text{ cm}$ laser was ~ 60%. Therefore, the $2f$ signal level of QTFF2 was only 57% of QTFF1. In this M-QEPTS system, two QTFFs generated piezoelectric signals simultaneously but the signal level of 983.44 $\mu$V for the M-QEPTS sensor employing QTFF1 + QTFF2 was less than the sum of employing QTFF1 and QTFF2 (1022.61 $\mu$V), respectively. This difference came from the following fact. The modulation frequency of the laser current was half of the resonance frequency of the M-QEPTS sensor (QTFF1 + QTFF2).

However, due to the difference of resonant frequency among QTFF1, QTFF2 and QTFF1 + QTFF2, the respective response for QTFF1 and QTFF2 can not be the strongest for the same modulation frequency. The M-QEPTS sensor resulted in a 1.51 times signal enhancement compared to a sensor employing a single QTFF1. Before etching the QEPTS sensor employing a standard QTFF1 was also investigated. From Fig. 4, it can be seen that compared with the standard QTFF1 the etched QTFF1 resulted in a ~ 1.30 times signal improvement. The etching in QTFF not only improves the signal level but also increases the laser transmission, which is benefit for the following QTFF in M-QEPTS technique.

To verify the linear concentration response of such M-QEPTS sensor system, the 2% $\text{C}_2\text{H}_2$ gas was diluted with pure $\text{N}_2$ down to 100 ppm. Two mass flow controllers with a mass flow uncertainty of 3% was adopted to produce different $\text{C}_2\text{H}_2$ concentration levels. The measured $2f$ signal amplitude as a function of $\text{C}_2\text{H}_2$ concentration based on a calibration with a gas dilution system is shown in Fig. 5 (a), which resulted in a linear calibration function. The obtained R-square was 0.992 based on a linear fitting process, which indicates that the M-QEPTS sensor system had an excellent linearity concentration response. The injection current of the DFB diode laser was adjusted to ensure that the emission wavelength was consistent with the absorption line of $\text{C}_2\text{H}_2$. The continuous measurement of $2f$ signal level of M-QEPTS sensor system when different $\text{C}_2\text{H}_2$ concentration was used is shown in Fig. 5 (b). The error bars and small deviations were partially due to the uncertainty in the gas mixture concentration and system 1$\sigma$ noise.

The noise level for the M-QEPTS sensor was measured when the absorption cell was filled with pure $\text{N}_2$. The measured noise for sensors employing QTFF1, QTFF2 and QTFF1 + QTFF2 are depicted in Fig. 6, respectively. The standard deviation of the signal was used as the amplitude for the noise, so that the 1$\sigma$ noise levels for sensors employing QTFF1, QTFF2 and QTFF1 + QTFF2 were 47.79 $\mu$V, 47.57 $\mu$V and 47.80 $\mu$V, respectively. There was no obvious difference in noise levels when using

| QTFF No. | Resonant frequency $f$ (Hz) | $Q$ factor | Resistance $R$ (k$\Omega$) |
|----------|-----------------------------|------------|---------------------------|
| QTFF1    | 30713.977                   | 1284.25    | 160.35                    |
| (Before etching) |                          |            |                           |
| QTFF1    | 30713.309                   | 1223.38    | 165.13                    |
| (After etching) |                     |            |                           |
| QTFF2    | 30714.005                   | 1394.56    | 162.27                    |
| (Before etching) |                     |            |                           |
| QTFF2    | 30713.374                   | 1318.71    | 168.52                    |
| (After etching) |                     |            |                           |
| QTFF1 + QTFF2 | 30713.372                 | 11503.14   | 79.06                     |
a single QTF and multiple QTFs. Based on the measured signal and noise levels, limit of detection (LoD) of 1.47 ppm, 2.55 ppm and 0.97 ppm for sensors employing QTF1, QTF2 and QTF1 + QTF2 were obtained, respectively, according to the formulae LoD = C/SNR, where C is analyte concentration and SNR is signal to noise ratio. The detailed characteristics of the sensors were summarized in Table 2. Compared with QEPTS employing a single QTF, a M-QEPTS sensor resulted in an improved detection performance.

In the calculation of LoD, the integration time \( \tau \) of the QEPTS sensor system was 1 second. Therefore, fundamental white noise dominated the system. The detection limit of a QEPTS sensor can be improved by averaging over a long time scale. The long-term stability of such M-QEPTS sensor system was investigated by performing an Allan deviation analysis [26, 27]. When white noise dominates the measurements the Allan plot follows the \( 1/\tau \) slope. Pure \( \text{N}_2 \) was filled into the gas cell. The measurement was performed for more than two hours and the result is displayed in Fig. 7. The minimum in the Allan deviation corresponds to the instrumental detection limit at the optimum integration time. For an optimum integration time of 200 s, the LoD can reach 0.19 ppm, indicated the instrumental detection limit. System drifts start to dominate when the integration time was larger than 200 s.

4. Conclusion

In conclusion, a trace gas detection scheme of M-QEPTS method was demonstrated for the first time. Different from traditional QEPTS sensor employing a single QTF as a photothermal detector, two QTFs were used in M-QEPTS to increase the signal amplitude by adding the generated piezoelectric signals from each QTF. The coating film in the area of the QTF where photothermal effect is maximized was removed by using a chemical etching method in order to improve the laser absorption and transmission. The difference of resonance frequency between the two corroded QTFs was less than 0.100 Hz, indicating that this was a suitable method that could be used in a M-QEPTS sensor. \( \text{C}_2\text{H}_2 \) was selected as the target analyte and a 1.53 \( \mu \text{m} \) diode laser was adopted as the excitation source. Compared with QEPTS sensor using a single QTF, M-QEPTS sensor employing two QTFs had a signal enhancement of 1.51 times. As a result, LoD of 0.97 ppm was obtained. Using an Allan variance analysis, the LoD can be improved to 0.19 ppm with an optimum integration time of 200 s. The M-QEPTS sensor performance can be further improved with an increased number of QTFs. Furthermore, the increased transmission at the root position of the QTF prongs and reduced difference of resonance frequency among QTFs are also advantageous for enhancing the M-QEPTS sensor performance.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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