Quartz-tuning-fork enhanced photothermal spectroscopy for ultra-high sensitive trace gas detection

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Abstract: A gas sensing method based on quartz-tuning-fork enhanced photothermal spectroscopy (QEPTS) is reported in this paper. Unlike usually used thermally sensitive elements, a sharply resonant quartz-tuning-fork with the capability of enhanced mechanical resonance was used to amplify the photothermal signal level. Acetylene (C2H2) detection was used to verify the QEPTS sensor performance. The measured results indicate a minimum detection limit (MDL) of 718 ppb and a normalized noise equivalent absorption coefficient (NNEA) of 7.63 × 10⁻²¹ cm⁻¹ W/√Hz. This performance demonstrates that QEPTS can be an ultra-high sensitive technique for gas detection and shows superiority when compared to usually used methods of tunable diode laser absorption spectroscopy (TDLAS) and quartz-enhanced photoacoustic spectroscopy (QEPAS). Furthermore, when compared to an optical detector, especially a costly mercury cadmium telluride (MCT) detector with cryogenic cooling used in TDLAS, a quartz-tuning-fork is much cheap and tiny. Besides, compared to the QEPAS technique, QEPTS is a non-contact measurement technique and therefore can be used for standoff and remote trace gas detection.

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1. Introduction

Laser photothermal spectroscopy is an alternative to traditional laser absorption spectroscopy. When the laser output energy is absorbed by a medium, a change of the thermal state of temperature and other thermodynamic temperature-dependent parameters occur. Therefore, laser photothermal spectroscopy is based on measuring the parameters related to the changes of the medium in its physical and thermodynamic states, such as temperature, pressure, refractive index and the acoustic wave [1]. Laser photothermal spectroscopy has the merits of a zero-reference and a signal enhancement by increasing of the laser excitation power, which distinctly differs from laser absorption spectroscopy such as tunable diode laser absorption spectroscopy.

Usually pyroelectric crystals, bolometers and mechanical transducers are used as thermally sensitive elements in direct temperature measurements. Due to the advantage of a high quality factor (Q value ~100,000 in vacuum, ~10,000 at a standard atmospheric pressure), a quartz-tuning-fork (QTF) has been proved to be a hypersensitive force sensor that can be used for atomic force microscopy [2–4], near-field scanning optical microscope [5,6], femto-newton force sensing [7], alternating gradient magnetometer [8], magnetic force microscopy [9], electric field intensity distribution detection [10] and trace gas detection [11,12].

In this letter, we describe a quartz-tuning-fork enhanced photothermal spectroscopy (QEPTS) method for ultra-high sensitive trace gas detection. A QEPTS sensor consists of four parts: (i) a QTF receiver that collects the light, which is reflected, absorbed and
transmitted by the QTF; (ii) the photothermal energy generated by light absorption is transformed into a mechanical motion by the QTF (thermoelastic expansion due to photothermo-elastic conversion); (iii) the resonant QTF enhances the mechanical motion; and (iv) the QTF converts the mechanical vibration into an electrical signal due to the piezoelectric effect. The detector of the QTF in QEPTS is placed without a surrounding target gas. Therefore, QEPTS is a non-contact measurement technique and can be used for standoff and remote trace gas detection, which differs from quartz-enhanced photoacoustic spectroscopy [13–17]. Acetylene (C$_2$H$_2$) was chosen as the analyte to verify the reported sensor performance due to its important applications in the detection of fault gases in transformers [18] and in ethylene streams for polyethylene production [19].

2. Experimental setup

The experimental configuration of QEPTS is shown in Fig. 1. A 1.53 µm continuous wave, distributed feedback (CW-DFB) fiber-coupled diode laser (Agilecom Photonics Solutions, China) was used as the laser excitation source. A commercially available QTF with a resonance frequency $f_0$ of ~32.76 kHz is typically employed in many QTF based sensors [20–24]. In order to improve the signal amplitude a QTF with $f_0$ of 30.72 kHz (Jingyuxing Technology, China) was utilized, since the effective integration time of the QTF is inversely proportional to its resonant frequency [25]. The QTF was mounted on a high precision XYZ translator (SIGMAKOKI, Japan). The measured Q factor, resonant frequency and equivalent electrical resistance of QTF at 1 atm were 12136, 30.71 kHz and 114 kΩ, respectively.

Wavelength modulation spectroscopy (WMS) with 2nd harmonic detection was utilized for sensitive trace gas concentration measurements. Modulation of the laser current was performed by applying a sinusoidal modulation to the direct current ramp of the diode laser at half of the QTF resonance frequency. The piezoelectric signal generated by the QTF was detected by a low noise transimpedance amplifier (CDP, Russia) with a 10 MΩ feedback resistor and converted into a voltage, which was transferred to a lock-in amplifier for demodulation of the 2nd harmonic signal ($2f$). A 4000 ppmv (parts in 10$^6$ by volume) C$_2$H$_2$ in nitrogen (N$_2$) gas mixture was filled into an absorption cell of 20 cm in length and with CaF$_2$ windows attached to each end of the cell. After passing through the absorption cell the laser beam was focused onto the QTF using a plano-convex CaF$_2$ lens (L) with a 40 mm focal length. The laser beam size at the focal point was calculated to be ~36 µm.

![Fig. 1. Schematic diagram of the experimental setup. FC: fiber collimator; W: CaF$_2$ window; L: CaF$_2$ plano-convex lens; TA: transimpedance amplifier; ADC: analog-to-digital converter; Le1 = 6 mm; Le2 = 3.9 mm; Wd = 0.6 mm; Th = 0.36 mm.](image-url)
3. Results and discussion

A C$_2$H$_2$ absorption line located at 6534.37 cm$^{-1}$ with a line intensity of $1.2 \times 10^{-20}$ cm$^{-1}$/(mol$\cdot$cm$^{-2}$) according to HITRAN database was used [26]. When the diode laser emission wavelength reached this absorption line the output power of the diode laser was 15 mW and the optical power intensity on the QTF was $\sim$14.7 W/mm$^2$ at this condition. The C$_2$H$_2$ concentration measurements were carried out at atmospheric pressure and room temperature. The laser wavelength modulation depth was set to 0.14 cm$^{-1}$. The impact of $\Delta Y$ between the laser beam and the top of QTF prongs on QEPTS signal level was investigated and the experimental results are shown in Fig. 2(a). The measurements were carried out when the laser beam was focused on the front and the side of the QTF, respectively, which is depicted in Fig. 2(b). The integration time of lock-in amplifier for the QEPAS sensor was 1 s.

![Figure 2](image-url)

From Fig. 2(a), it can be seen that the 2$f$ signal level for Line A was the strongest when compared to those for Line B and Line C at the same $\Delta Y$. Most of the QTF area is coated with a silver layer, as shown in Fig. 2(b), which acts as an electrode and has a high reflectivity for the laser beam. A part of the path of Line A has no coating which means that more photons are absorbed by the QTF and resulted in a higher signal amplitude. A small section with no silver layer coating on the QTF side produced a sudden change of the signal for Line C, which verified the above analysis. When $\Delta Y<$3.9 mm, the 2$f$ signal amplitude increased with increasing $\Delta Y$. This can be explained as follows. In a static state approximation due to the photo-thermo-elastic conversion effect, the QTF prong is bent to an angle with a certain degree at the point where the laser is applied and the deviation of its tip is directly proportional to the distance between the tip and that point. Therefore, the basis of the prongs is the area where the maximum strain and stress occur. Hence this is the optimal position ($\Delta Y = 3.9$ mm) of the laser that maximizes the excited vibrational mode of the QTF, resulting in the highest QEPTS signal level. When $\Delta Y$ is $>3.9$ mm, with increasing of $\Delta Y$, the area of thermal diffusion becomes larger and the heat at the QTF’s prongs became less due to the larger transmission loss. The temperature gradient in the QTF’s prongs decreases and the thermal wave is attenuated. These experimental results and analyses were verified by the theoretical simulation depicted in Fig. 3, which is based on the finite element method (FEM) simulation tool COMSOL Multiphysics 5.1.

Two main eigenmodes of in-phase and anti-phase are associated with the QTF vibration. The QTF in QEPTS was excited following the anti-phase mode based on the simulation
depicted in Fig. 3, which implies that the prongs vibrate symmetrically (opposite in phase). The absorption ratio of the used laser by the QTF for Line B was about 0.1% based on the simulation.

Fig. 3. Calculated temperature and displacement fields of the QTF. (a) Two-dimensional temperature and displacement fields at different values of $\Delta Y$ of 1.0 mm, 3.9 mm and 5.6 mm, respectively when the laser beam was focused on the center of QTF’s prong (See line B shown in Fig. 2). (b) Three-dimensional temperature and displacement fields at $\Delta Y = 5.6$ mm when the laser beam was focused on the center of QTF’s prong.

Fig. 4. QEPTS signal amplitude for Line A at $\Delta Y = 3.9$ mm. (a) C$_2$H$_2$-QEPTS signal amplitude as a function of modulation depth. (b) C$_2$H$_2$-QEPTS signal amplitude as a function of C$_2$H$_2$ concentrations with a modulation depth of 0.18 cm$^{-1}$. 

The laser wavelength modulation depth was optimized to further improve the 2f QEPTS signal amplitude. The dependence of the QEPTS signal amplitude as a function of the laser wavelength modulation depth for Line A at ΔY = 3.9 mm is shown in Fig. 4(a). The QEPTS signal amplitude increased with the modulation depth, but when the modulation depth was >0.18 cm⁻¹, the signal amplitude started to decrease. A maximum signal level of 23.5 mV was obtained when the modulation depth was 0.18 cm⁻¹. To verify the linear concentration response of the QEPTS based C₂H₂ sensor platform, the 4000 ppm C₂H₂:N₂ gas mixture was diluted with dry N₂ down to 500 ppm C₂H₂ concentration levels. The measured QEPTS signal amplitude as a function of C₂H₂ concentrations is plotted in Fig. 4(b). The calculated R-square value is equal to ~0.99 after a linear fitting procedure, which indicates that the QEPTS sensor system has an excellent linearity response of the C₂H₂ concentration levels.

To investigate the laser power response of C₂H₂-QEPTS sensor, an adjustable optical attenuator was placed between the fiber collimator and C₂H₂ absorption cell. The optical output power of diode laser was varied from 50 μW to 15 mW. The measured 2f signal amplitude as a function of the laser power is depicted in Fig. 5. The calculated R-square value of a linear fit of the 2f signal is equal to ~0.99, which implies that the reported C₂H₂-QEPTS sensor exhibits an excellent linearity response of the excitation laser power levels. The insert in Fig. 5 shows that a strong 2f signal level was obtained when even a weak laser power of 50 μW was used.

The background noise level was determined when pure nitrogen was filled inside the absorption cell. The results are shown in Fig. 6 and the 1σ noise level was 4.22 μV. Based on the above measurements, a minimum detection limit (MDL) of 718 ppb was achieved, which even is significantly better than the recently reported result of 200 ppm based on the tunable diode laser absorption spectroscopy method using a C₂H₂ absorption line located at 1534.095 nm with a line intensity of 0.9 × 10⁻²⁰ cm⁻¹/(mol·cm⁻²) and an optical absorption length of 15 cm [27]. The calculated normalized noise equivalent absorption coefficient (NNEA) was 7.63 × 10⁻⁹ cm⁻¹ W/√Hz for this C₂H₂-QEPTS sensor, which is also superior to the recently reported result of 3.54 × 10⁻⁸ cm⁻¹ W/√Hz for the quartz-enhanced photoacoustic spectroscopy method based C₂H₂ detection [28].
4. Conclusion

In conclusion, an ultra-high gas sensing method of quartz-tuning-fork enhanced photothermal spectroscopy (QEPTS) was demonstrated. Unlike usually used thermally sensitive elements, a sharply resonant QTF with the capability of enhanced mechanical resonance was used to amplify the QEPTS signal level. C2H2 detection was used to verify the QEPTS sensor performance. Finite element modelling was adopted to simulate the temperature and displacement fields of QTF in QEPTS to support the experimental results and the analyses. The optimum position of the diode laser beam in the QTF and the optimum modulation depth of laser wavelength were investigated. The reported QEPTS sensor has an excellent linearity response of the C2H2 concentration and optical power levels. The measured MDL of 718 ppb and a NNEA of $7.63 \times 10^{-9}$ cm$^{-1}$W/√Hz, which are significantly better than the recently reported results of 200 ppm and $3.54 \times 10^{-8}$ cm$^{-1}$W/√Hz based on the tunable diode laser absorption spectroscopy and the quartz-enhanced photoacoustic spectroscopy methods, respectively, and demonstrated that QEPTS is an ultra-high sensitive technique for trace gas detection. Furthermore, compared to an optical detector, especially an expensive mercury cadmium telluride (MCT) detector with cryogenic cooling, used in tunable diode laser absorption spectroscopy, a QTF is less costly ($<$1) and tiny. Moreover, QEPTS is a non-contact measurement technique which differs from quartz-enhanced photoacoustic spectroscopy. When a custom QTF with large prong size of 20 mm in length and 2.5 mm in width [29] is used to reduce the sensitivity of the laser focused position and facilitate laser beam alignment, it can be used for standoff and remote detection of explosive and toxic gases. The QEPTS performance can be further improved significantly if the QTF is sealed in vacuum due to a ~10-fold enhancement of the Q factor and a reduced noise level.

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