Ultra-Sensitive CO-LITES Detection at the Parts per Quadrillion Level

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ABSTRACT

Researchers from Harbin Institute of Technology, China have developed a gas sensor for carbon monoxide (CO) using light-induced thermoelastic spectroscopy (LITES). The ultra-sensitive design enables CO detection in the parts per quadrillion (ppq) range using a multi-pass cell with a double helix pattern generated using an artificial fish swarm algorithm as well as a polymer-modified round-head quartz tuning fork with a low resonant frequency. The system achieves CO detection at concentrations as low as 23 parts per trillion (ppt) and 920.7 ppq by extending the integration time of the sensor. With a compact design, high signal-to-noise ratio, and a long gas absorption path the CO-LITES sensor provides a new standard in gas detection sensitivity for applications including semiconductor manufacturing, hydrogen fuel cells, planetary exploration, and other fields needing highly sensitive trace gas detection.

SENSITIVE GAS DETECTION

The ability to detect trace gases in industrial, environmental, energy, and scientific research applications can help avoid major consequences that these low concentrations of gases can cause. A highly sensitive technology can help advance semiconductor manufacturing, energy innovation, and interplanetary exploration. When producing semiconductor chips, even trace impurities within the electron gases can negatively impact the yield and reliability. When dealing with energy innovation, trace carbon monoxide (CO) by-products of fuel cells can degrade the performance of the fuel cell or cause failure. Interplanetary exploration requires sensitive sensors in the search for life and understanding planetary atmospheres and the gases they hold.[1] Whether it's energy efficiency, manufacturing, or exploration, trace gases in the parts per trillion (ppt) or even in the parts per quadrillion (ppq) could have a significant impact on safety, performance, health, or the environment.

For highly sensitive measurements and detection, laser absorption spectroscopy (LAS) has gained traction among many researchers. LAS uses lasers tuned to specific gas absorption lines to detect a particular gas and to quantify the concentration of the trace gas. Because of its rapid response and high sensitivity, further developments have produced quartz-enhanced photoacoustic spectroscopy (QEPAS), advantageous due to its small size, low cost, and high Q factor. Using LAS, or some form of LAS, can provide ultra-high sensitivity gas detection for a variety of applications in the manufacturing, energy, and exploration fields.

PROBLEMS AND GOALS

Although QEPAS has significant advantages compared to other non-laser absorption techniques, there is a notable drawback of its design that can become problematic. In the QEPAS design, a quartz tuning fork (QTF) must be used to detect changes from the laser passing through the gas environment, detecting thermal or acoustic signals. When the QTF is submerged in acidic or corrosive gases, the QTF's surface can become damaged, affecting the sensitivity and properties of the QTF.

Another issue of the design of QEPAS is the short absorption path restricting further advancement of detection capabilities. As the Beer-Lambert Law dictates, a longer path length of the light from the laser corresponds to a stronger absorption of that light from the gas through which it passes. If the gas absorption path is increased, the detection capability of the system can be improved. This is harder to achieve with the shorter path length design of QEPAS, and the exposed QTF makes the technique restrictive in its range of applications.

To solve these issues, light-induced thermoelastic spectroscopy (LITES) can invert gas information from thermoelectric signals from the QTF which can change depending on the stimulation of the laser light and how much is absorbed after passing through the sample gas. This provides a non-contact method for sensitive gas detection. However, the typical two-mirror multi-pass cell (MPC) used with LITES to increase the effective optical path length can be limited in precision. Three-mirror MPCs can be used but may have complex optical structures to fully unlock the potential for ultra-sensitive gas sensors.

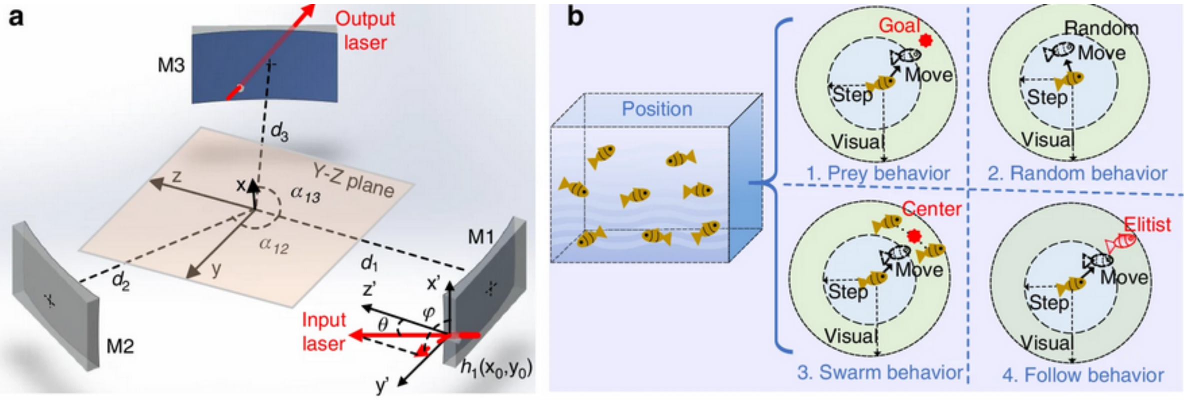

Figure 1. a) Structure model of three-mirror MPC. d: distance between mirror and origin. α: angle between mirrors; θ: the angle between the incident laser and the z axis; φ: the angle between the projection of the incident ray in the x-y plane and the x axis. $h_1(x_0, y_0)$: coordinates of laser entry hole. b) Theoretical model of artificial fish swarm algorithm (AFSA) design algorithm. Position: $P=[d_1, d_2, d_3, x_0, y_0, \theta, \varphi]$, seven-dimensional position information for fish swarm.[1]

METHOD

Researchers from the Harbin Institute of Technology, China have developed an ultra-sensitive light-induced thermoelastic spectroscopy (LITES) system based on an intelligent algorithm-optimized multi-pass cell (MPC) and low-frequency quartz tuning fork (QTF) for carbon monoxide (CO) detection. To increase absorption through longer optical path length (OPL) and to design an optimized MPC to better balance OPL with volume, researchers employed an artificial fish swarm algorithm (AFSA) (**Figure 1**). The AFSA was used to optimize the geometric structure of the MPC with a three-mirror model with a double helix structure by determining the path the laser light takes through the gas sample and mirror reflections. It is difficult to greatly extend the OPL without creating an extensive volume and a large system to contain it. By iteratively adjusting the parameters of the mirror placement, angles, and spacing, the AFSA maximized path length while keeping the cell compact and minimizing optical losses. The OPL/V ratio of the novel MPC using the AFSA was 25.8 m/165.8 mL which results in a highly dense pattern of spot distribution on the mirrors in a compact design. The simulated and measured distribution of the double helix pattern can be seen in **Figure 2**. This can increase gas-light interaction time leading to high sensitivity without increasing the physical size of the system.

To improve the standard commercial-grade QTF with high resonant frequency (f_0), researchers needed to reduce the f_0 to increase the energy accumulation time which would contribute to improving the detection sensitivity of the sensor.[1] The parameters that affect the f_0 include the thickness and length of the fork fingers, elasticity, and density of the QTF. Researchers customized a QTF by increasing the length from 3.9 mm to 9.1 mm, decreasing the width from 0.36 mm to 0.25 mm, adding round heads to enhance stress during vibration, and using gold electrodes to improve oxidation and corrosion resistance.[1] To further improve the design, the QTF was coated with polydimethylsiloxane (PDMS) (**Figure 3**) to reduce heat diffusion and increase the stress

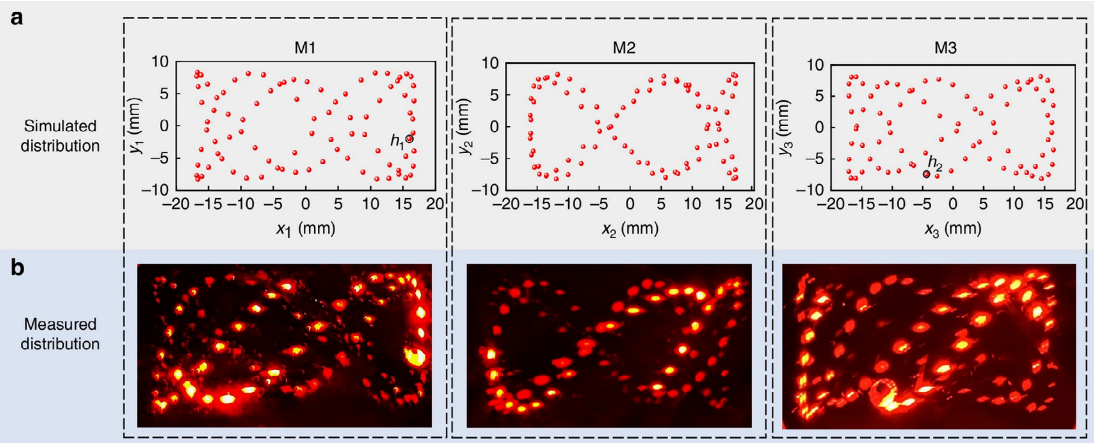

Figure 2. Double helix pattern of three-mirror MPC. Simulated (a) and Measured (b) distribution of double helix pattern.[1]

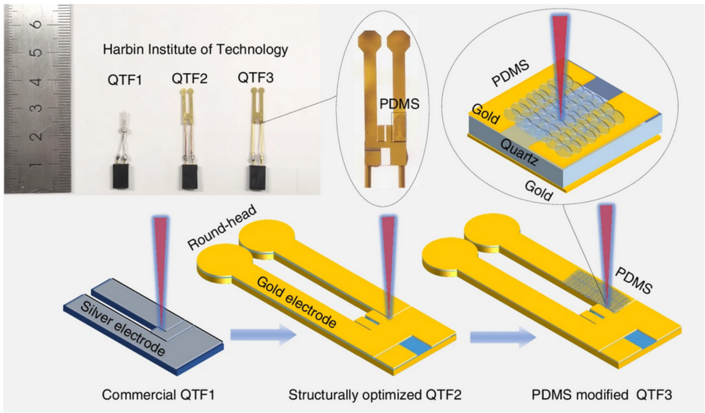

Figure 3. Schematic diagram of QTF optimization. Insert: real picture of different QTFs. QTF1: commercial QTF with high f_0. QFT2: structurally optimized QTF with low frequency and round head. QFT3: PDMS modified low-frequency QTF with P-Q-G sandwich structure. PDMS polydimethylsiloxane, a polymer material with low Φ and high β.[1]

during vibration. The PDMS, with low effective thermal conductivity and high thermal expansion coefficient, effectively increases the local temperature and stress of vibration which is a vast improvement from the commercial QTF.[1] With the polymer-coated QTF, f_0 was reduced by 70% from ~32.8 kHz to ~ 9.5 kHz.

To verify that both the optimized MPC and QTF can be used in LITES, an absorption line of CO was selected at 4587.64 nm as a target line for the experiment (Figure 4). A distributed feedback (DFB) quantum cascade laser (QCL) with a center wavelength of 4.69 µm was used as the excitation source and temperature controlled at 35ºC. With an input current of 301 mA, the output power of the laser reached 145 mW and passed through apertures before reaching the MPC with the double helix spot pattern. Inside the MPC the laser is reflected 259 times before exiting and being focused on the three QTFs with different characteristics to test the sensor performances.

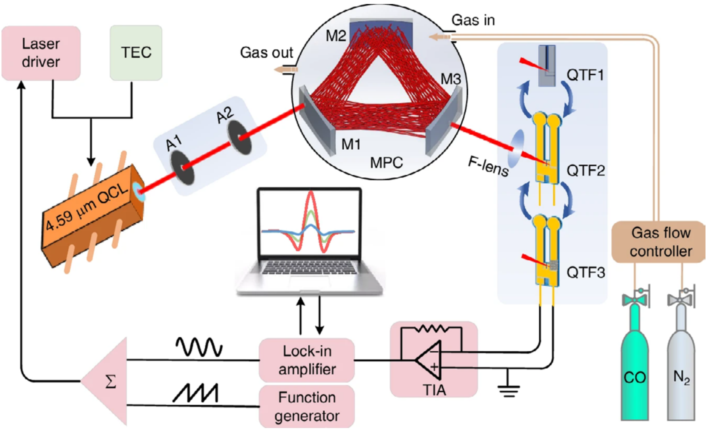

Figure 4. Schematic diagram of CO-LITES sensor based on intelligent algorithm optimized MPC with double helix pattern and PDMS modified round-head QTF with low f_0. F-lens focusing lens, TIA transimpedance amplifier, A1 and A2 two apertures used to determine the incident angle of the laser beam.[1]

Wavelength modulation spectroscopy (WMS) was used to suppress the background noise with ramp and sine waves set to the resonant frequencies of the respective QTFs. The noise of each QTF could be found using the relationship between the second harmonic (2*f)* signal amplitude and the current modulation depth and is used to determine the total signal-to-noise ratio (SNR). With the determined SNR values for each QTF, the minimum detection limit (MDL) can be calculated: MDL = C/SNR, where C is the gas concentration.

RESULTS

To fully test each QTF and the entire LITES system, researchers first determined the noise for each QTF by experimenting on 1 ppm CO in the optimized MPC. The noise values were found to be 957 nV, 834 nV, and 852 nV for QTF1, QTF2, and QTF3, respectively. Based on the *2f* signals, and the resulting noise levels, the SNRs for the three QTFs were calculated to be 4106.58, 15215.83, and 43485.92, respectively. QTF2 and QTF3, the optimized QTFs, achieved great improvement compared to the commercial QTF1. The structurally optimized QTF2 had an SNR over 3.71 times better, and the PDMS-modified QTF3 was 10.59 times higher than the commercial-grade QTF1.

The MDL was calculated to be 23 ppt for the CO-LITES sensor based on QTF3. The relationship between CO concentration and the *2f* signal can be seen in **Figure 5**. Different concentrations of CO were tested, and the signals of the CO-LITES sensor were directly proportional to the respective concentrations. As shown in that figure, the high R^2 value of 0.99 for the linear fitting indicates the CO-LITES had an excellent linear response to the ultra-low CO concentration.[1] By adjusting the average integration time to 500 seconds, the MDL of the CO-LITES sensor was improved to 920.7 ppq.

For this novel CO-LITES sensor, the mid-infrared QCL was utilized with an AFSA optimized three-mirror MPC with a double helix to significantly improve the absorption of CO in a relatively compact design. By optimizing the QTF by PDMS, researchers were able to achieve the highest detection sensitivity reported in LITES sensors.[1] Other real-world applications tested include CO concentration on the campus of Harbin Institute of Technology and CO concentration of human breath.

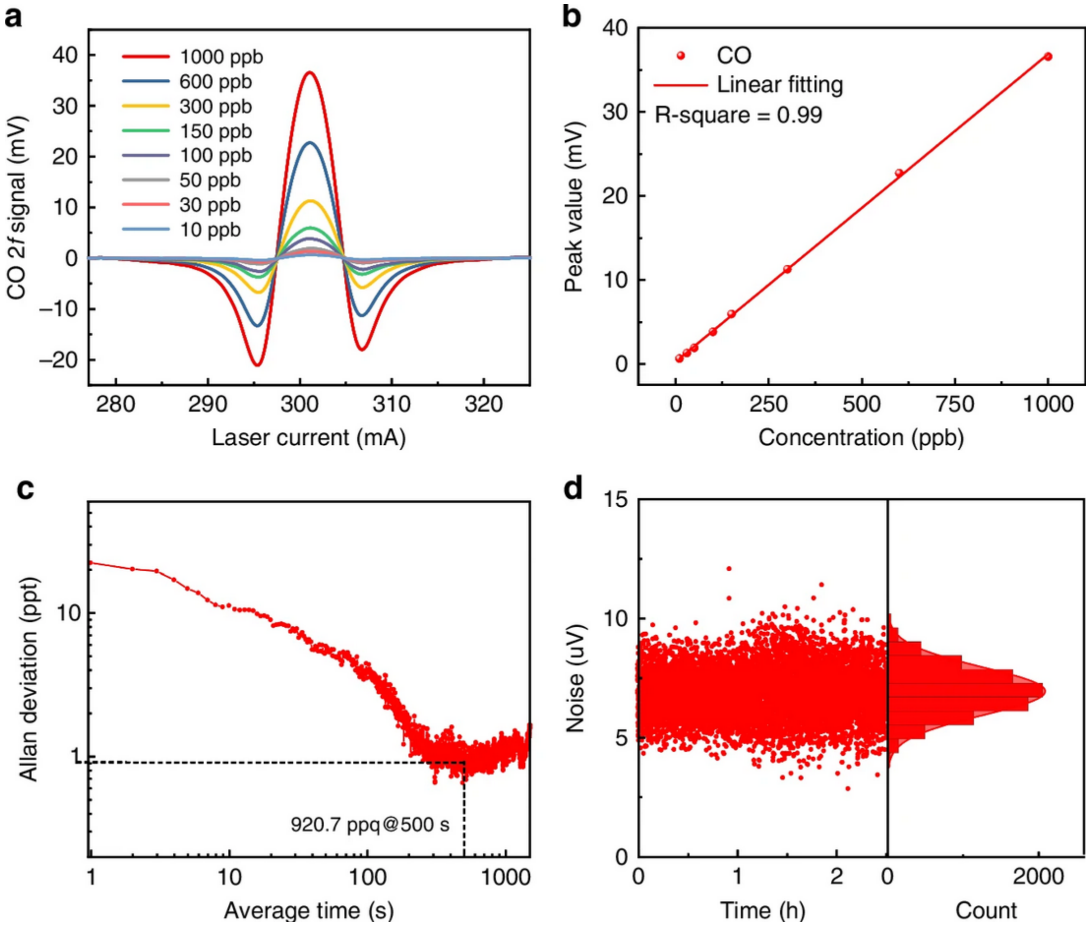

Figure 5. Performance of CO-LITES sensor based on optimized MPC and QTF3. a) 2*f* signal of the CO-LITES sensor with different CO concentrations. b) The linear relationship between 2*f* signal amplitude and CH_4 concentration. c) Allan variance analysis for CO-LITES sensor. d) Continuous noise detection in the sensor and corresponding normal distribution.[1]

By achieving ppq-level sensitivity, researchers designed a CO-LITES sensor that could revolutionize CO detection and measuring applications in urban environmental monitoring, semiconductor manufacturing, interplanetary exploration, and human health assessment.

WAVELENGTH'S ROLE

In the CO-LITES gas sensing system, achieving ultra-high sensitivity in the ppq level for CO detection relies heavily on laser wavelength and output stability. Since the system detects CO absorption at a narrow spectra line, any drift or instability in wavelength could directly affect signal accuracy and detection limits.

Researchers used the QCL1500 LAB quantum cascade laser driver for its high precision control at low noise levels. With the ability to maintain a narrow linewidth, the QCL1500 LAB provided consistent laser current to the QCL for maximum signal-to-noise ratio while minimizing jitter and current inconsistencies.

Alongside the current control, the laser temperature also required precise regulation as small temperature changes can shift the laser's center wavelength. With the TC10 LAB temperature controller, researchers could maintain the laser temperature at 35ºC with stability as low as 0.0009ºC. This ensured that the current modulation from the driver, not thermal drift, changed the laser wavelength.

The QCL1500 LAB and TC10 LAB enabled consistent and repeatable scans, maintaining constant current and stable temperature to the QCL for ultra-sensitive CO detection using the LITES design. These benchtop instruments with intuitive touchscreens provided the high-performance needed for this novel gas sensing system to achieve ppq gas detection.

REFERENCES

1. Sun, H., Qiao, S., He, Y., Sun, X., Ma, Y. Parts-per-quadrillion level gas molecule detection: CO-LITES sensing. *Light: Science & Applications*, **14**, 180 (2025). https://doi.org/10.1038/s41377-025-01864-4

USEFUL LINKS

- QCL1500 LAB Product Page
- TC10 LAB Product Page

PERMISSIONS

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Figures 1 - 3 were cropped and the captions for Figures 1 - 3 were modified. No changes were made to the other captions or images. They are presented here in their original form.

PRODUCTS USED
QCL1500 LAB, TC10 LAB

KEYWORDS
CO-LITES, quartz tuning fork, QTF, spectroscopy, carbon monoxide, CO, gas sensing, QCL, QCL driver, temperature controller, parts per quadrillion, ppq, semiconductor manufacturing, energy innovation

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REVISION	DATE	NOTES
A	June 2025	Initial Release