# Quartz-enhanced photoacoustic spectroscopy

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A new approach to detecting a weak photoacoustic signal in a gas medium is described. Instead of a gas-filled resonant acoustic cavity, the sound energy is accumulated in a high-$Q$ crystal element. Feasibility experiments utilizing a quartz-watch tuning fork demonstrate a sensitivity of $1.2 \times 10^{-7}$ cm$^{-1}$ W/$\sqrt{\text{Hz}}$. Potential further developments and applications of this technique are discussed. © 2002 Optical Society of America

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Photoacoustic spectroscopy (PAS) is an established method of experimental physics. A review of its history and the present state of the art with respect to its use for chemical sensing in the gas phase is given in Ref. 1 A common approach to detecting the acoustic signal generated by the modulated laser radiation in a weakly absorbing gas utilizes an acoustic resonator filled with the gas.[1] The absorbed laser power is accumulated in the acoustic mode of the resonator for $Q$ oscillation periods, where $Q$ is the quality factor of the resonator. The signal is proportional to the effective integration time $t = Q/f$ (where $f$ is the resonant frequency). Most often the $Q$ factor is in the range 40–200, and $f = 1000$–$4000$ Hz. As an example, in the research reported in Ref. 2, $Q = 70$ and $f = 1250$ Hz, which yields $t = 0.056$ s. This is one of the highest reported values. Achieving longer values of $t$ in a gas-filled resonator is problematic because of intrinsic losses related to gas viscosity and other relaxation processes.

We suggest inverting the common approach to resonant PAS and accumulate the absorbed energy not in the gas but in the sensitive element (i.e., the microphone). A well-suited material for a resonant high-$Q$ microphone is piezoelectric crystal quartz. This material is mass produced and inexpensive; every electronic watch or clock is built around a high-$Q$ quartz crystal frequency standard. Usually it is a quartz tuning fork (TF) with a resonant frequency close to 32 768 (i.e., $2^{15}$) Hz. The mode at this frequency corresponds to a symmetric vibration (the prongs move in opposite directions). The antisymmetric vibration is piezoelectrically inactive. These quartz TFs have recently become widely used for atomic-force and optical near-field microscopy,[3,4] and therefore their properties have been carefully analyzed. A typical watch TF has a value of $Q \approx 20,000$ or higher when it is encapsulated in vacuum and of $Q \approx 8000$ at normal atmospheric pressure. Therefore the corresponding energy accumulation time at atmospheric pressure is $t \approx 250$ ms, which is a noticeably longer time than any practical gas-filled resonator can provide. Our purpose in this Letter is to explore the potential utility of photoacoustic spectroscopy that uses these TFs. We shall refer to the TF-based PAS as quartz-enhanced photoacoustic spectroscopy, or QEPAS.

An important feature of the QEPAS is its immunity to background acoustic noise, which is a consequence of the following behavior:

- The ambient acoustic noise density approximately follows a $1/f$ dependence and is very low above 10 kHz.
- The acoustic wavelength in air is ~1 cm at 32 kHz and is longer at lower frequencies. Therefore the sound waves emanating from a distant source tend to apply a force in the same direction upon the two TF prongs positioned at an ~1 mm distance. This does not excite the piezoelectrically active mode in which the two prongs move in opposite directions.
- The width of the TF resonance at normal pressure is ~4 Hz, and only frequency components in this narrow spectral band can produce efficient excitation of the TF vibration.

For the feasibility experiments described below a watch TF, R38-32.768-KHZ (Raltron) purchased from Newark Electronics, was used. The overall TF dimensions were 6 mm × 1.4 mm × 0.2 mm; each prong was 3.8 mm long and 0.6 mm wide. The gap between the prongs was 0.2 mm. Of central importance is the development of experimental configurations for efficiently coupling the photoacoustic signal to the TF. Several configurations for detecting the photoacoustic signal with this TF are shown in Fig. 1, and observations in which they are used are described. Figures 1(a) and 1(b) correspond to aiming the light at the tuning fork from different directions. Figure 1(c) presents a combination of a TF with a resonant sound tube.

An operational amplifier-based transimpedence preamplifier circuit (see, for example, Ref. 5) with a feedback resistor of 4.4 MΩ was used to detect a piezoelectric signal generated by the TF in the current mode. Such a circuit minimizes the influence of any parasitic parallel capacitance by maintaining the voltage between the TF electrodes close to zero. Noise of the TF coupled to a transimpedence amplifier was investigated in detail and reported in Ref. 6. The fundamental limitation of the TF sensitivity arises from thermal excitation of its symmetric mode, i.e., the energy $kT$ stored in its vibration. This excitation

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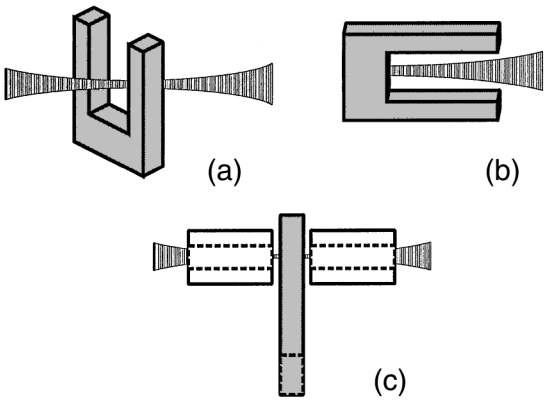


Fig. 1. Optical configurations for photoacoustic signal detection with a TF. (a) The laser beam is perpendicular to the TF plane. (b) The laser beam is in the TF plane. (c) An acoustic resonator (sound tube) is added to enhance the signal. The laser beam is directed through the tube. The pressure antinode is in the center at the location of the tuning fork between the two pieces of the tube.

manifests itself as a peak in the noise spectrum centered at the TF resonance frequency and with a width defined by the TF $Q$ factor. We observed this peak by using a network signal analyzer (SR780, Standford Research Systems). Another fundamental source of noise is a feedback resistor in the transimpedence amplifier circuit. This element creates a frequency-independent noise background.

The experimental arrangement that uses the configuration shown in Fig. 1(a) is presented schematically in Fig. 2. A TF was extracted from its original evacuated enclosure and placed in a 5-cm-long optical gas cell. To investigate different aspects of QEPAS we filled the gas cell with a TF with air–methane mixtures of various ratios. To excite a photoacoustic signal we used a distributed-feedback diode laser operating at $\lambda \sim 1.66$ $\mu$m. This laser was kindly provided by Carlo Sirtori (Semiconductor Lasers Group, Thales Research and Technology, Orsay, France). It was tunable with current or temperature from 5997 to 6001 $cm^{-1}$, thus covering a number of rovibrational lines in the $Q$ branch of the $2\nu_3$ overtone of the methane ($CH_4$). In most of our experiments the diode laser's temperature was set to +22.8 °C, so its frequency coincided with the peak absorption of the group of overlapping lines at 5999.5 $cm^{-1}$. A photodiode located after the gas cell was used for accurate positioning of the TF with respect to the laser beam and also to detect $CH_4$ absorption lines for initial laser frequency calibration. In QEPAS experiments the laser current was sinusoidally modulated at half the TF resonant frequency, giving rise to wavelength (and amplitude) modulation at the same frequency $f/2$. An absorption line in the gas was crossed twice during each modulation period, which generated acoustic waves at frequency $f$. The resonant frequency of the TF was determined from the position of the peak in its noise spectrum. Frequency $f$ was found to decrease linearly with increasing pressure at a rate of $k = -8 \times 10^{-3}$Hz/Torr. The laser diode current's modulation depth was adjusted to ensure maximum signal at $f$ without strong deterioration of spectral resolution. Most QEPAS experiments were carried out at a 375-Torr total pressure in the gas cell. This reduced pressure was chosen for better spectral resolution. At this pressure $Q \approx 13\,000$, and the noise voltage at $f$ after the transimpedence preamplifier was 1.1 $\mu V/\sqrt{Hz}$ rms. This measured noise is in good agreement with the experimental results and theoretical predictions of Ref. 6.

Goals of the first experiment were to verify the local nature of the QEPAS sensing technique and to find the most sensitive area in the configuration shown in Fig. 1(a). For a high signal-to-noise ratio and fast data acquisition the gas cell was filled with 100 Torr of $CH_4$, ambient air was added to 1-atm total pressure, and the lock-in time constant was set to 300 ms. It was found that the TF response is highest when the focal spot is centered between the TF prongs and positioned 0.7 mm below the TF opening (assuming the orientation shown in Fig. 2). When the focal spot was shifted sidewise to the area outside the TF, the phase of its response was inverted because the TF prong closest to the laser beam was pushed by an acoustic wave in the opposite direction. No laser-induced signal was observed at $f$ if the laser wavelength was tuned off the absorption line or if the cell was filled with pure nitrogen. This was so even when the laser beam directly hit the TF prong or its base.

The objective of a second set of experiments was to establish and compare QEPAS response for the three configurations shown in Fig. 1. The acoustic resonator in configuration 1(c) was made from stainless-steel capillary tubing (1.59-mm outer diameter and 0.51-mm inner diameter). The overall length of the two tube pieces plus the two gaps between tubes and the TF was 5.3 mm. This is half the wavelength of sound at $f = 32\,770$ Hz. The tube centers were positioned 0.7 mm below the TF opening to ensure the most efficient TF excitation. The noise level for all three configurations was the same and was determined by the fundamental limits set by thermal excitation of the TF and the feedback resistor noise. To generate a photoacoustic signal we filled the cell with ambient air doped with 6.7% $CH_4$ at a total pressure of 375 Torr. This provided a peak absorption

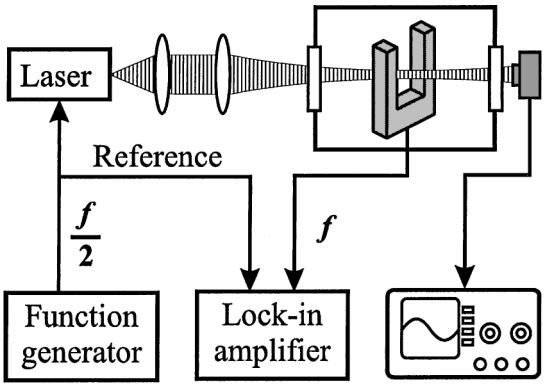


Fig. 2. Experimental setup. The distributed-feedback diode laser current is modulated at half the TF resonant frequency $f$.

**Table 1. Normalized Response of the TF-Preamplifier Unit and Normalized Minimum (SNR=1) Detectable Absorption Coefficient for Three Configurations Shown in Fig. 1**

| | Configuration | | |
|---|---|---|---|
| Performance | (a) | (b) | (c) |
| Responsivity [V/(W cm$^{-1}$)] | 1.24 | 5.03 | 9.45 |
| Detectivity (cm$^{-1}$ W/$\sqrt{\text{Hz}}$) | $8.8 \times 10^{-7}$ | $2.2 \times 10^{-7}$ | $1.2 \times 10^{-7}$ |

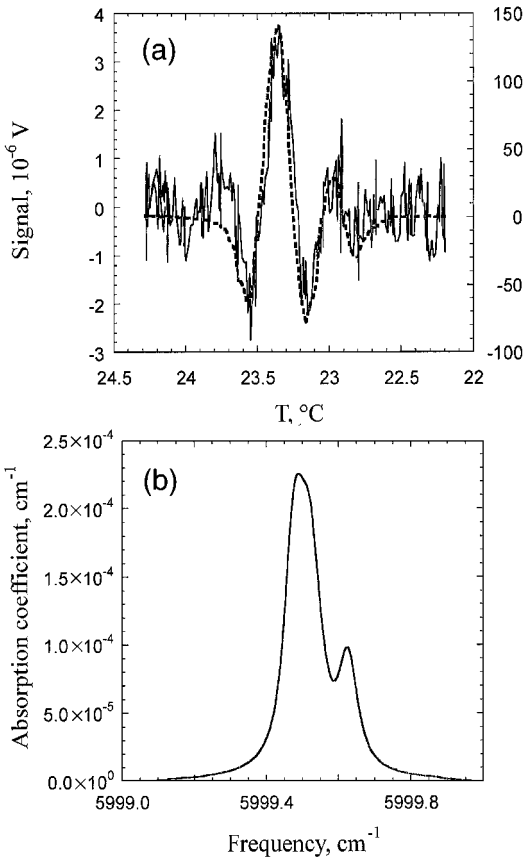


Fig. 3. (a) Two examples of spectral data acquired with the QEPAS technique. Total pressure in the gas cell is 375 Torr. The dashed curve and the solid curve depict 6.7% (right axis) and 0.17% (left axis) $CH_4$ concentrations, respectively. (b) Simulated $CH_4$ absorption at 0.17% $CH_4$ concentration in the same spectral region obtained from HITRAN'96 data.

coefficient $\alpha = 1.71 \times 10^{-2}$ cm$^{-1}$ at $\nu = 5999.49$ cm$^{-1}$. Results for the voltage responsivity of the system to the molecular absorption and the detection limits for the three configurations are listed in Table 1. The first row of the table lists the voltage signals from the transimpedence preamplifier normalized by the laser power and the gas absorption coefficient. This signal scales linearly with the feedback resistor; the results shown are for a feedback resistor of 4.4 MΩ. The second row gives the absorption coefficient that will result in a signal-to-noise ratio of 1 at a 1-W laser power level and a 1-Hz detection bandwidth.

Two examples of actual photoacoustic spectra recorded with the QEPAS technique in the configuration of Fig. 1(b) are presented in Fig. 3(a). These data were acquired with a laser power of ~2 mW and a lock-in amplifier time constant $\tau = 1$ s. We scanned the laser's optical frequency by changing its temperature. The thick dashed curve and the thin solid curve in Fig. 3(a) correspond, respectively, to 6.7% and 0.17% $CH_4$ concentrations in ambient air at a total pressure of 375 Torr. The absorption for the lower concentration, simulated from HITRAN'96 data,[7] is shown in Fig. 3(b).

These results demonstrate the QEPAS is capable of providing detectivity levels for absorption that are comparable with those of conventional PAS with a much simpler and more robust system. It is possible that the QEPAS sensitivity could be improved if a specially designed quartz crystal were used instead of a standard watch TF. Other modifications of crystal-enhanced PAS can be considered in which other means of detection of the crystal vibration are employed in place of the piezoelectric effect. For instance, vibrational deformation of the crystal might be detected by means of stress-induced birefringence in the crystal or by the interferometric methods.

QEPAS modules (TF plus preamplifier) are compact, inexpensive, and immune to environmental acoustic noise. A set of such modules can be used, for example, in multipoint gas-sensing applications. The central unit of such a sensor will contain the laser and all the associated electronics, and the laser power could be delivered to each QEPAS module via optical fibers. QEPAS also permits the spectroscopic analysis of extremely small gas samples. The minimum sample volume is ultimately defined by the gas volume between the TF prongs, which in our case was 0.15 mm$^3$.

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