Comparison of Quartz-enhanced Photoacoustic Spectroscopy and Conventional Photoacoustic Spectroscopy based Detectors

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Abstract: Performance of quartz-enhanced photoacoustic spectroscopy and conventional photoacoustic spectroscopy based detectors applied to trace gas sensing was compared. Nitrogen with 10 ppmv of acetylene and a diode laser accessing 6529.17 cm⁻¹ absorption line were used.

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1. Introduction

Trace gas sensing based on photoacoustic spectroscopy (PAS) relies on detecting the sound generated in gas upon the absorption of electromagnetic radiation by analyte molecules [1]. Non-radiative relaxation processes, such as collisions with other molecules, lead to a local temperature increase. Pressure fluctuations following the thermal expansion can be detected in the form of acoustic waves. A critical part of a conventional PAS based gas detector is the cell in which the photoacoustic signal is generated and detected [2]. Common "gas-microphone cells" are cylindrical cavities with transparent windows. The microphone is coupled to the cavity by a thin hole in a sidewall of the cell. The absorbed laser power is accumulated in the acoustic mode of the cylindrical cavity for Q oscillation periods, where Q is the quality factor of the resonator.



Fig.1. Quartz tuning fork.

Quartz-enhanced photoacoustic spectroscopy (QEPAS) first reported in 2002 is based on a new approach to photoacoustic detection, which employs a quartz tuning fork (QTF) (Fig.1) as a resonant acoustic transducer [3]. A QEPAS sensor detects a weak acoustic pressure wave that is generated when optical radiation interacts with a trace gas. The pressure wave excites a resonant vibration of the QTF which is then converted into an electric signal by the piezoelectric effect. Thus, an electric signal proportional to the concentration of the absorbing gas is generated. A typical watch QTF with resonant frequency of ~ 32768 Hz has a Q factor of 100000 in vacuum and 13000 at atmospheric pressure.

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Merits of QEPAS compared to PAS include QEPAS sensor immunity to environmental acoustic noise, a simple absorption detection module design, and its capability to analyze trace gas in extremely small gas samples (~1 mm³). However, from the published results of photoacoustic gas sensing, it is not easy to compare the performance of QEPAS and PAS, since the reported results are obtained for different experimental conditions, including gas species, wavelength, pressure and flow. This study focuses on the characterization and comparison of the QEPAS and PAS detectors performed for the same experimental conditions.

2. Spectrophone design and experimental setup

A state-of-the-art differential photoacoustic cell [4] shown in Fig 2 (left) was used in this work. The cell is formed by two coupled cylindrical resonators ~90 mm in length and with an 8 mm diameter. The balanced configuration eliminates most of the coherent and incoherent acoustic noise.

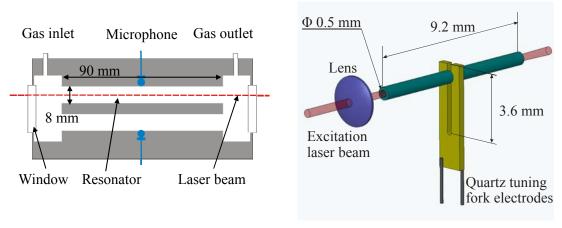


Fig.2. Structures of the tested acoustic cell (left) and QEPAS spectrophone (right)

The QEPAS spectrophone consists of a QTF and a microcresonator composed of a pair of thin tubes, as shown in Fig.2 (right). Such a microresonator yields a signal to noise ratio (SNR) gain of 10 to 20. The tubes are 4.4 mm long with a 0.5 mm diameter, which represent the experimentally optimized microresonator dimensions [5].

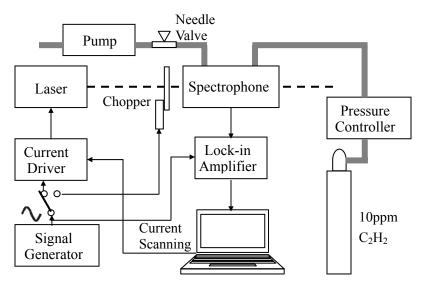


Fig.3. Schematic of the measurement system

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Figure 3 shows the schematic of the PAS and QEPAS measurement system. A 1.5μm DFB laser is used as the spectroscopic source. A signal generator controls the modulation of the optical radiation either by modulating the diode laser current, or by means of a mechanical chopper wheel. It also provides a reference signal to a lock-in amplifier. The laser beam enters the spectrophone (acoustic cell or QEPAS spectrophone) and is partially absorbed by C₂H₂ (at the 6529.17cm⁻¹ absorption line). The signal from the spectrophone is demodulated by the lock-in amplifier. A computer program is used to scan the diode laser current to obtain the absorption line profile as well as acquire the data from the lock-in amplifier. A 10ppm C₂H₂/N₂ cylinder is connected to a pressure controller which maintains a constant 1 atm. gas pressure in the spectrophone. A needle valve is used to adjust the gas flow, typically set to 100 sccm.

3. Experimental Results

Table 1. Comparison of QEPAS normalized NNEA with PAS NNEA

Spectrophone	Resonant acoustic	Modulation	NNEA*,
	frequency, Hz	method	$cm^{-1}W/\sqrt{Hz}$
Acoustic Cell	1770	Amplitude	3×10 ⁻⁹
Acoustic Cell	1770	Wavelength	4.64×10 ⁻⁹
QEPAS spectrophone	32760	Wavelength	3.45×10 ⁻⁹

^{*}NNEA- noise equivalent absorption coefficient

The C_2H_2 has a fast vibrational-translational (V-T) relaxation rate, which can be considered instantaneous on the $1/f_0$ time scale. Thus, the C_2H_2 monitoring results permit the evaluation of the intrinsic QEPAS detection sensitivity. Table 1 summarizes a comparative study of QEPAS and PAS sensitivity. The time constant of the lock-in amplifier in all experiments is set to 1s. A second order filter (12dB/oct) is selected, which results in a lock-in amplifier equivalent noise bandwidth of 0.25 Hz. In the 2f wavelength modulation mode, a QEPAS sensitivity of $3.45 \times 10^{-9} \text{cm}^{-1} \text{W}/\sqrt{\text{Hz}}$ is obtained which is slightly higher than the achieved PAS sensitivity of $4.64 \times 10^{-9} \text{cm}^{-1} \text{W}/\sqrt{\text{Hz}}$, but is somewhat lower than the amplitude modulation based PAS result. A sensitivity comparison for a slower V-T relaxation molecule, such as methane, is currently in progress.

4. References

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