New Advances in Quartz Enhanced Photoacoustic Spectroscopy for Gas Sensing Applications

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***Abstract*—In this paper, we review the latest advancements in Quartz-Enhanced Photo-Acoustic Spectroscopy (QEPAS) for trace-gas sensing. Starting from the QEPAS basic physical principles, we analyze and discuss the influence of Quartz Tuning Forks (QTFs) geometry on their optoacoustic transducer performance. Subsequently, we provide an overview of the latest developments in QEPAS sensing technology employing custom QTFs and novel micro-resonator configurations. Finally, we report on a novel QEPAS approach allowing simultaneous dual-gas detection.**

Keywords-Quartz-enhanced photoacoustic spectroscopy; gas sensing; custom quartz tuning fork; acoustic resonators; dual-gas detection.

I. INTRODUCTION

In the last few years, gas sensing has gathered an increasing attention for both industrial applications and academia research. Examples of gas sensing applications are: industrial production (like methane/ethane detection in drilling) [1], automotive industry (like detection of polluting gases from vehicles) [2], medical applications (breath analysis) [3], indoor air quality supervision (like detection of carbon monoxide) [4], environmental monitoring (like greenhouse gas monitoring) [5].

A wide range of non-optical gas detection approaches have been proposed, like laboratory analytical equipment, semiconductor gas sensors and electrochemical devices [6]. Optical sensors can offer higher sensitivity [7], selectivity and long-term stability, and are characterized by a long lifetime and short response time, allowing real-time and in-situ detection.

Optical gas sensors are mainly based on Lambert-Beer's law of light absorption processes. Photoacoustic spectroscopy is one of the most sensitive optical sensing techniques. It is based on the detection of acoustic waves, generated as a consequence of the modulated absorption of light from a specific targeted gas. Absorbed light excites the gas target molecules into higher energy levels that relax non-radiatively and generate heat and thereby an increase of pressure in the localized region of the excitation light beam. The modulated absorption generates pressure waves, which can be detected by a microphone.

Quartz-Enhanced Photo-Acoustic Spectroscopy (QEPAS) is an alternative approach to photoacoustic detection of trace gas utilizing a Quartz Tuning Fork (QTF) as a sharply resonant acoustic transducer to detect weak photoacoustic excitation and allowing the use of extremely small volumes [8][9]. Such an approach removes restrictions imposed on the gas cell by the acoustic resonance conditions. QEPAS is a very sensitive technique, for several gases limit of detection of few parts per billion have been achieved [9]. A record sensitivity of 50 part per trillion (ppt) in 1sec integration time has been demonstrated for SF_6 detection [10], while implementing an intracavity-based QEPAS system a detection limit of 900 ppt in 1sec has been achieved for CO_2 trace detection [11][12]. Here, we review the latest advancements in QEPAS for trace-gas sensing. In Section II, we report on QEPAS sensing using custom QTFs, in Section III we discuss the results obtained using single-tube micro-resonator systems, and in Section IV we report on QEPAS results obtained using QTFs operating at the 1^{st} overtone flexural mode. We conclude the work in Section V.

II. QEPAS WITH CUSTOM QTFS

Prior to 2013, all the QEPAS sensors reported in the literature employed commercial standard QTFs operating at the fundamental in-plane flexural resonant mode, with a frequency of ~ 32.7 kHz. However, the standard QTFs structure and its operating frequency were optimized for timing purposes and not for spectroscopic applications. With the aim of determining the dependence of the QTF parameters and performance on their relevant dimensions and identify the optimal design for optoacoustic gas sensing, we designed and tested a set of QTFs with different values of spacing between the prongs, their length and thickness, and crystal thickness. A photograph of one of the realized QTFs is shown in Figure 1.

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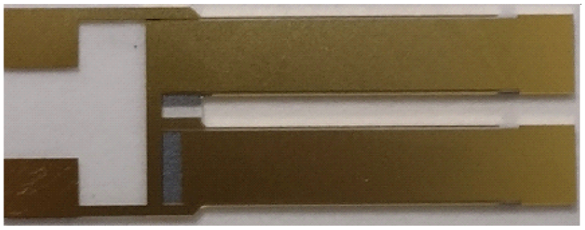

Figure 1. Photograph of custom QTFs. The space between the prongs is 1.5 mm.

We assessed the dependence of the resonance frequency, the related Q-factor, the fork stiffness, the spring constant, and the electrical resistance from the QTF dimensions [13][14]. We also identified the optoacoustic gas sensing figures of merit and studied their dependence from the QTFs relevant dimensions. For QEPAS applications, our results show that the QTF resistivity R should be kept low and the resonance Q-factor as high as possible. Both conditions can be obtained by increasing the QTF crystal thickness w and the ratio T/L between the prong thickness T and length L. However, the resonance frequency increases as T/L^2, and it should not exceed 40 kHz. Moreover, the smallest possible prong spacing must be chosen to enhance the amplitude of the acoustic wave incident on the internal prong surface, avoiding that the focused laser beam illuminates the QTF. Therefore, the optimal prong spacing selection is mainly determined by the wavelength of the exciting laser beam and its spatial quality.

III. SINGLE-TUBE MICRO-RESONATOR SYSTEMS

Acoustic micro-resonators are important components to improve the performance of QEPAS sensors [8][13]. Among the different QEPAS spectrophone configurations, the on-beam one showed the strongest acoustic coupling efficiency between the QTF and the microresonator (mR), resulting in an optimum signal to noise (SNR) gain factor of ~ 30 [9] for a standard 32 kHz-QTF. The on-beam spectrophone configuration consists of two stainless steel tubes with the QTF inserted between them. The possibility to operate with custom QTFs with a prong spacing of up to 1.5 mm, opens the way to the implementation of a single-tube mR configuration in an on-beam QEPAS spectrophone (SO-QEPAS configuration). By implementing the SO-QEPAS configuration we demonstrated that it is possible to achieve a signal-to-noise amplification factor of ~130 in comparison with the bare QTF [15].

IV. QEPAS WITH QTF OPERATING IN THE 1ST OVERTONE FLEXURAL MODE

In QEPAS sensing, the resonance frequency of the QTF must be limited below 40 kHz to ensure that the transfer of the excess energy absorbed by the target gas follows efficiently the fast modulation of the incident laser radiation [9]. The custom QTF we have realized are characterized by a fundamental resonance frequency up to one order of magnitude lower with respect to the standard 32 kHz-QTF [13][14]. However, the 1st overtone modes frequencies are also reduced with a decrease of the fundamental resonance frequency to ~ 3kHz. This opened the way to the implementation of QTF overtone flexural modes for QEPAS trace gas sensing.

A typical calculated vibration profile of the QTF prongs at the 1st overtone flexural mode for maxima displacements conditions is shown in Figure 2 as a function of the distance from the support base for the first overtone mode.

The 1st overtone flexural mode can be modeled as 2-coupled point-masses, each one positioned at an antinode and oscillating in counter-phase. The two antinodes identify the position of the maximum vibration amplitudes along the prong. When the focusing spot is located at the antinodes points of the vibration profile, where the maximum vibration amplitude is allowed, the QEPAS signal is maximized.

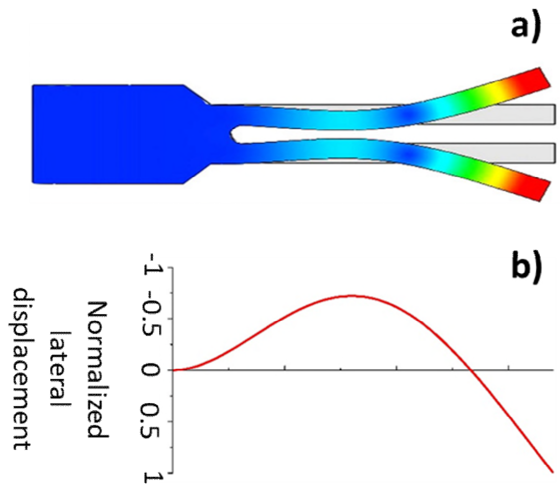

Figure 2. Deformation of the QTF prongs (a) and normalized lateral displacement for a QTF first overtone mode (b).

By optimizing the QTF design, it is possible to favor the first overtone flexural mode operation with respect to the fundamental mode one in terms of QEPAS signal [16],[17].

A. *Single-tube micro-resonator coupled with QTF 1st overtone flexural mode*

The length of the mR is correlated with the sound wavelength, given by $\lambda = v/f$, where v is the sound speed (343 m/s in air). Thereby, implementing dual-tube or single-tube mR for QTFs having resonance frequency < 10 kHz becomes challenging. As an example, for a frequency as low as 5 kHz, $\lambda = 6.86$ cm. The optimal length for a single-tube mR falls between $\lambda/2$ and λ, closer to $\lambda/2$., because of the mR acoustic coupling with the QTF [9]. These lengths make optical alignment challenging when operating with mid-IR and inhibits operations with a THz laser. However, since the 1st overtone frequency is about 6.2 times higher than the fundamental one, operating at the 1st overtone will require a significantly more than six times reduced mR length. The first demonstration of a QEPAS system implementing a QTF operating at the 1st overtone flexural mode and coupled with

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a single-tube mR is reported in [18]. Benefiting from the high overtone resonance frequency (17.7 kHz) and the quasi 1st harmonic acoustic standing waves generated in the SO-QEPAS configuration, the AmR length was reduced to 14.5 mm. The signal enhancement in the overtone resonance mode in this SO-QEPAS configuration leads to an overall sensitivity enhancement factor of ~380 with respect to the bare custom QTF operating in the fundamental resonance mode.

B. *Double antinode excited QEPAS*

Since the 1st overtone flexural mode can be modeled as 2-coupled point-masses, each one positioned at an antinode and oscillating in counter-phase, it can be possible to excite the two resonance antinode points of a custom QTF operated at the 1st overtone resonance mode simultaneously using one laser source and two dual-tubes mRs. This approach named double antinode excited quartz-enhanced photoacoustic spectroscopy (DAE-QEPAS) has been demonstrated for the first time in [19]. Two sets of acoustic mRs were optimized and assembled at two separated 1st overtone antinode points of the QTF to improve the spectrophone performance. With the two antinodes excited by one laser source, the DAE-QEPAS spectrophone attained a sensitivity gain factor of ~ 100 times and ~3 times with respect to the 1st overtone resonances of the bare custom QTF and a standard on-beam QEPAS spectrophone, respectively.

C. *Simultaneous dual-gas QEPAS detection*

QEPAS sensors require a proper design to perform chemical analysis of a multi-component gas mixture due to the fact that the QTF cannot recognize the molecular species responsible for the generation of the pressure waves. Very recently, this limitation has been overcome by realizing a dual-gas QEPAS sensing system based on a QTF frequency division multiplexing technique [20]. The QTF in a dual-gas QEPAS sensor is excited simultaneously at the fundamental and 1st overtone flexural modes by two independently modulated lasers. The two target gases are detected via demodulation of the custom QTF piezoelectric signal at the fundamental frequency f0 and the 1st overtone frequency f1, respectively, by means of two lock-in amplifiers. The capability of the QEPAS sensor to perform simultaneous dual-gas spectral detection was demonstrated by implementing a DFB laser source targeting an acetylene (C_2H_2) and a diode laser targeting a H_2O absorption line and reaching normalized noise equivalent absorption factors in the 10^{-7} $cm^{-1}\cdot W/Hz^{1/2}$ range. Further improvements of dual-gas QEPAS sensors performances will be achieved by adding dual- or single-tube acoustic micro-resonators to enhance the generated photo-acoustic wave intensity.

V. Conclusions

Recent developments in quart-enhanced photoacoustic spectroscopy were reviewed. Compared with a standard 32 kHz-QTF, the custom QTFs result in better sensing performance, considering also that they allowed to implement large prongs spacing (up to 1.5 mm) making the optical alignment less critical, especially with laser sources having limited spatial beam quality. The simultaneous reduction of the fundamental resonances modes down to 3 kHz in custom QTFs opened the way to the use of the 1st overtone mode for QEPAS sensing. Since the 1st overtone mode is characterized by two antinodes positions, new approaches, such as the double antinode excited QEPAS and simultaneous dual-gas detection by exciting simultaneously the QTF at the fundamental and the 1st overtone flexural modes, have been demonstrated.

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