Quartz tuning fork with improved sensing performance for Terahertz quartz-enhanced photoacoustic sensors

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Abstract

We report on a quartz-enhanced photoacoustic (QEPAS) sensor for methanol (CH₃OH) detection employing a novel quartz tuning fork (QTF), specifically designed to enhance the QEPAS sensing performance in the terahertz (THz) spectral range. The QTF was employed in a QEPAS sensor system using a 3.93 THz quantum cascade laser as the excitation source in resonance with a CH₃OH rotational absorption line located at 131.054 cm⁻¹. A minimum detection limit of 160 ppb in 30 seconds integration time, corresponding to a normalized noise equivalent absorption NNEA=3.75×10⁻¹¹ cm⁻¹W/Hz^½ was achieved, representing a nearly one order of magnitude improvement with respect to previous reports.

1. Introduction

Spectroscopic techniques for trace gas sensing and monitoring have shown a great potential for non-invasive chemical analysis requiring high sensitivity and selectivity. While trace gas detection in the near-infrared (IR) and mid-IR ranges demonstrated excellent performance, the use of far-IR or terahertz (THz) radiation for sensing purposes is still underdeveloped. New technological innovation in photonics is now enabling THz research to be applied in an increasingly wide variety of application fields, such as medical diagnostic, environmental monitoring, homeland security and defense, industrial quality and process control [1]. Several toxic gases such as hydrogen cyanide, hydrogen chloride, hydrogen iodine show their strongest absorption features in the THz spectral range, related to rotational energy level transitions. Furthermore, the detection of explosives and narcotics can be realized in the THz spectral range.

Recently, quartz-enhanced photoacoustic (QEPAS) based sensors operating in the THz range were reported [2-4], allowing to overcome many issues associated with THz spectroscopy, such as the use of cryogenic systems for the detection of THz radiation and complex signal analysis. QEPAS is based on the detection of acoustic waves produced by the absorbing gas target by means of piezoelectric quartz tuning fork (QTF) acting as an acousto-electric transducer [2]. The merits of QEPAS include high detection sensitivity and selectivity as well as fast time-response using a compact and relatively low-cost acoustic detection module. Since rotational level transitions are up to three orders of magnitude faster with respect to mid-IR vibrational levels, the THz spectral range is particularly suited for the QEPAS sensing technique. The fast relaxation time characteristics of THz transitions allow low-pressure sensor operation, providing a high QTF resonance Q-factor, and thereby a large QEPAS signal [2].

2. Experimental results

The extension of QEPAS into the THz range was made possible by the realization of a custom-made QTF [3-4] having the similar geometry as the commercial 32.78 kHz-QTF, but a size six times larger, with a prong length L=20.0 mm, prong width T=1.4 mm and a crystal thickness w=0.8 mm. The QTF prongs are separated by a ~ 1 mm gap that is required to focus a THz laser beam between the prongs without illuminating them. This approach is necessary since the standard commercial QTF design is optimized for timing purposes and not suitable for spectroscopic applications in the THz spectral range. In a previous study, we identified the QTF resonance frequency, quality factor and electrical resistance as the three main figures of merit in terms of sensing performance and correlated them with the prongs sizes and geometry [5]. Based on this study, we realized a new generation QTF optimized for THz QEPAS spectroscopy and successfully employed such a new QTF in a H_2S THz QEPAS sensor system [6].

We present here recent experimental results for methanol (CH₃OH) detection obtained by implementing a new custom fabricated QTF into a QEPAS sensor system based on a THz quantum cascade laser and a comparison of the

acquired data with those achieved for the first THz QEPAS demonstration [2,3]. The same rotational absorption line at $131.054~\rm cm^{-1}$ (3.93 THz) and a laser modulation amplitude of 600 mV as reported in Refs. [2, 3] was employed. High-resolution QEPAS scans of a CH₃OH:N₂ calibrated mixtures with different concentrations are shown in Fig. 1, together with a spectral scan acquired when pure N₂ flows inside the acoustic detection module (ADM) [7]. The lock-in integration time was set to 3 seconds for all measurements. A performance comparison of two generations of OTFs was carried out.

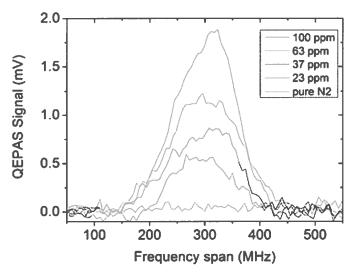


Fig. 1. QEPAS spectral scans of gas mixture containing different concentrations of methanol in N_2 at a gas pressure of 10 Torr acquired with a 3 seconds lock-in integration time. The spectral scan obtained with pure N_2 in the ADM at the same operating conditions is also depicted.

A minimum detection limit of 160 ppb with a 30 seconds integration time was obtained using the new QTF design. The corresponding normalized noise equivalent absorption (NNEA) coefficient was 3.75×10^{-11} cm⁻¹W/Hz^{1/2}, a record value for QEPAS sensing and nearly an order of magnitude better with respect to the results previously obtained employing a QTF based on a standard design [7]. These results clearly demonstrate that the new QTF geometry provides a significantly better sensor system performance with respect to standard QTF geometry. The next design improvement will be the implementation of a novel single tube micro-acoustic resonator system, which will lead to a \sim two orders in magnitude increase in detection sensitivity resulting in a THz QEPAS CH₃OH sensor detectivity of a few ppbs.

3. References

- [1] A.I. McIntosh, B. Yang, S.M. Goldup, M.Watkinson and R.S. Donnan, "Terahertz spectroscopy: a powerful new tool for the chemical sciences?", Chemical Society Reviews 41, 2072 (2012).
- [2] P. Patimisco, G. Scamarcio, F.K. Tittel, V. Spagnolo, "Quartz-Enhanced Photoacoustic Spectroscopy: A Review", Sensors 14, 6165 (2014).
- [3] S. Borri, P. Patimisco, A. Sampaolo, H. E. Beere, D. A. Ritchie, M. S. Vitiello, G. Scamarcio, and V. Spagnolo, "Terahertz quartz enhanced photo-acoustic sensor", Appl. Phys. Lett. 103, 021105 (2013).
- [4] P. Patimisco, S. Borri, A. Sampaolo, H. E. Beere, D. A. Ritchie, M. S. Vitiello, G. Scamarcio, and V. Spagnolo, "Quartz enhanced photo-acoustic gas sensor based on custom tuning fork and terahertz quantum cascade laser", Analyst 139, 2079 (2014).
- [5] P. Patimisco, A. Sampaolo, L. Dong, M. Giglio, G. Scamarcio, F. K. Tittel, and V. Spagnolo, "Analysis of the electro-elastic properties of custom quartz tuning forks for optoacoustic gas sensing", Sensor and Actuators B 227, 539 (2016).
- [6] V. Spagnolo, P. Patimisco, R. Pennetta, A. Sampaolo, G. Scamarcio, M.S. Vitiello and F.K. Tittel, "THz Quartz-enhanced photoacoustic sensor for H₂S trace gas detection", Optics Express 23, 7574 (2015).
- [7] Sampaolo, P. Patimisco, M. Giglio, M. S. Vitiello, H.E. Beere, D.A. Ritchie, G. Scamarcio, F.K. Tittel and V. Spagnolo, "Improved tuning fork for terahertz quartz-enhanced photoacoustic spectroscopy", Sensors 16, 439 (2016).
- [8] H. Zheng, L. Dong, A. Sampaolo, H. Wu, P. Patimisco, X. Yin, W. Ma, L. Zhang, W. Yin, V. Spagnolo, S. Jia, and F. K. Tittel, "Single-tube on-beam quartz-enhanced photoacoustic spectroscopy", Optics Letters 41, 978 (2016).