



# Methane, ethane and propane detection using a compact quartz enhanced photoacoustic sensor and a single interband cascade laser

Angelo Sampaolo<sup>a,b</sup>, Sebastian Csutak<sup>c</sup>, Pietro Patimisco<sup>a,b</sup>, Marilena Giglio<sup>a,b</sup>, Giansergio Menduni<sup>a,d</sup>, Vittorio Passaro<sup>d</sup>, Frank K. Tittel<sup>b</sup>, Max Deffenbaugh<sup>c</sup>, Vincenzo Spagnolo<sup>a,b,\*</sup>

<sup>a</sup> PolySense Lab - Dipartimento Interateneo di Fisica, Politecnico and University of Bari, Via Amendola 173, Bari, Italy

<sup>b</sup> Rice University, Department of Electrical and Computer Engineering, 6100 Main Street, Houston, TX, 77005, USA

<sup>c</sup> Aramco Service Company, 16300 Park Row Dr, Houston, TX, 77084 USA

<sup>d</sup> Photonics Research Group, Dipartimento di Ingegneria Elettrica e dell'informazione, Politecnico di Bari, Via Orabona 4, Bari, 70126, Italy

## ARTICLE INFO

### Keywords:

Quartz-enhanced photoacoustic spectroscopy  
Gas sensing  
Methane  
Ethane  
Hydrocarbons  
Interband  
Cascade laser

## ABSTRACT

Hydrocarbon detection in the gas phase represents a powerful tool to guide oil exploration and production operations for the oil & gas industry. This application requires highly sensitive, selective and robust spectroscopic techniques. In this work, a quartz-enhanced photoacoustic sensor system designed to detect methane (C1), ethane (C2) and propane (C3), employing a single interband cascade laser emitting in the spectral range 3.342–3.349  $\mu\text{m}$ , is reported. Detection levels in the part-per billion concentration range for C1 and C2 and a few parts per million for C3 were achieved. Measurements at both low and atmospheric pressures were carried out for mixtures simulating typical downhole hydrocarbon concentrations.

## 1. Introduction

Optical gas sensors typically operate in the near-IR or mid-IR spectral ranges where the strongest absorption features occur. Interband cascade lasers (ICLs) covering the 3–4  $\mu\text{m}$  range [1,2] have led to new opportunities for trace detection of the main hydrocarbon gases [3,4]. Indeed, the fundamental absorption bands of methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), ethylene ( $\text{C}_2\text{H}_4$ ), propene ( $\text{C}_3\text{H}_6$ ) and acetylene ( $\text{C}_2\text{H}_2$ ) are located in the  $\lambda = 3\text{--}4\text{ }\mu\text{m}$  spectral range [5]. For the petrochemical industry, the monitoring of hydrocarbons such as methane, ethane and propane represents one of the most efficient ways to predict production outputs, estimate reserves and assess raw material quality of source rocks and reservoirs [6].

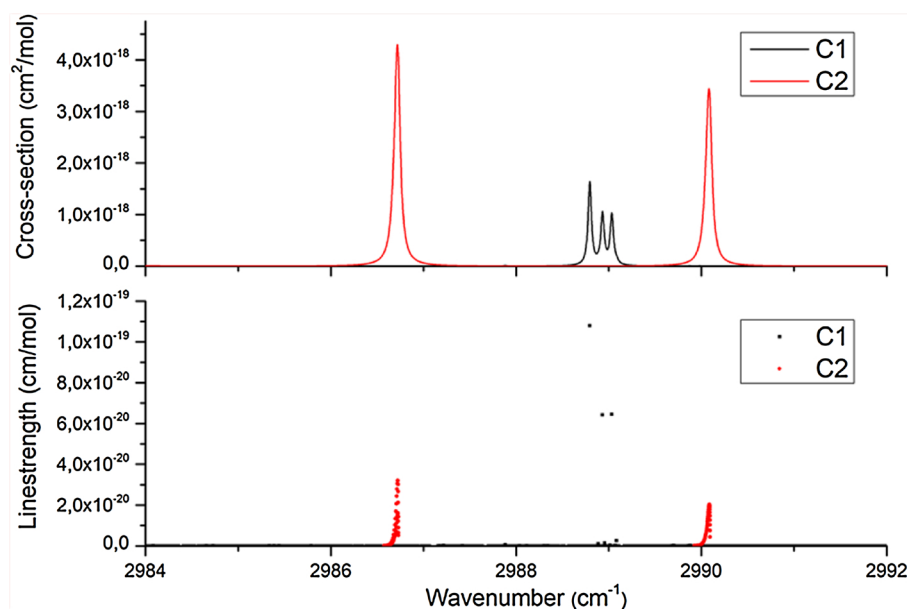
Among the main spectroscopic detection techniques, Quartz Enhanced Photoacoustic Spectroscopy (QEPAS) has proven to be a perfect candidate for in-situ and real-time trace gas detection, because of an unmatched level of compactness, extremely high sensitivity (down to parts per trillion [7]), immunity to environmental noise and its proven reliability, ruggedness and in-situ operation [8–14]. This technique exploits quartz tuning forks (QTFs) as optoacoustic transducers to convert an acoustic signal into an electrical signal via quartz piezoelectric properties [8,9]. The laser light must be focused between

the QTF prongs and modulated at its resonance frequency (or sub-harmonics). When the laser emission wavelength is resonant with an absorption level of a target gas analyte, the process of periodical heating-relaxation induced by absorption of the modulated light produces pressure waves, i.e. sound. These sound waves produce a deflection of the QTF prongs and the induced strain field is converted into an electrical signal by the QTF. The QEPAS technique does not require any optical detector and is insensitive to the laser wavelength, thereby the same acoustic detection module can operate in any spectral range from UV [15] to THz regime [16,17].

In this work, we report a compact QEPAS sensor prototype for trace gas detection of methane, ethane and propane (also referred in the text as C1, C2, and C3, respectively) by using a single ICL source operating in the spectral range 3.342–3.349  $\mu\text{m}$ . While  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  detection characterized by well-defined absorption peaks in the ICL operating range was straightforward, propane detection required a preliminary detailed study of the characteristic broadband absorption profiles which merge with the  $\text{C}_2\text{H}_6$  background signal in the ICL tuning range. A detailed study of gas mixtures containing both  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  allowed us to set up a fitting procedure capable to retrieve both hydrocarbons concentration levels with high precision. Mixtures of C1/C2 were also analyzed to verify that no cross-talk between methane and

\* Corresponding author at: PolySense Lab - Dipartimento Interateneo di Fisica, Politecnico and University of Bari, Via Amendola 173, Bari, Italy.

E-mail address: [vincenzoluigi.spagnolo@poliba.it](mailto:vincenzoluigi.spagnolo@poliba.it) (V. Spagnolo).



**Fig. 1.** Top panel: absorption cross-sections at 50 Torr pressure for methane (black curve) and ethane (red curve) in the range 2984–2992  $\text{cm}^{-1}$  simulated using the Hitran database [5]. Bottom panel: C1 (black dots) and C2 (red dots) corresponding line strengths. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

ethane is observed. For  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  we reached a detection limit of few parts per billion (ppb)-level, while for  $\text{C}_3\text{H}_8$  we achieved a few parts per million (ppm) detection limit.

## 2. Selection of C1 and C2 spectral range for QEPAS operation

As a first step, we identified the spectral region that can be covered with a single ICL source, containing well resolved  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  absorption features and characterized by absorption cross-sections in the  $10^{-18}$  ( $\text{cm}^2/\text{mol}$ ) range.

In Fig. 1  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  absorption cross-sections and related line strengths are plotted in the range 2984–2992  $\text{cm}^{-1}$  using data from the HITRAN database [5].

These spectra were simulated for pure  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  at 50 Torr. At this pressure, the absorption line broadening due to collisions is low enough to allow distinguishing the fine structure of the absorption bands. Within a spectral range of 3.5  $\text{cm}^{-1}$  there are two Lorentzian-like absorption lines of  $\text{C}_2\text{H}_6$ , composed by several lines marked in red dots, as shown in the lower panel of Fig. 1, and in the middle three partially merged lines of  $\text{CH}_4$ . Even though the line strength of a single  $\text{CH}_4$  transition is higher with respect to the two  $\text{C}_2\text{H}_6$  transitions, the collisional broadening at a pressure of 50 Torr or higher gives rise to two isolated  $\text{C}_2\text{H}_6$  absorption features with a cross-section larger than the three-fold C1 structures. The spectral separation between the  $\text{CH}_4$  three-lines structure and the two  $\text{C}_2\text{H}_6$  lines guarantees a non-interfering detection of both species.

## 3. QEPAS sensor configuration

The identification of target lines represented in Fig. 1 led to a specific ICL design commercialized by Nanoplus, with a central emission wavelength of 3345 nm (2989  $\text{cm}^{-1}$ ). The ICL current dynamic range is  $I = 15\text{--}70$  mA and the optimal operating temperature range is from  $T = 5^\circ\text{C}$  to  $T = 15^\circ\text{C}$ . The ICL is mounted in a standard TO66 package equipped with a collimating lens (see Fig. 2). The beam emerging from the lens has a nearly perfect Gaussian power distribution with a diameter of 3 mm. A maximum power of  $\sim 11$  mW was measured at  $T = 5^\circ\text{C}$  and  $I = 70$  mA with an electric power consumption of 0.273 W.

The high quality of the laser beam allowed operation with a standard 32 kHz QTF (prong spacing of 0.3 mm and length of 3 mm) mounted in an on-beam double tube configuration, constituting the

spectrophone of the QEPAS sensor system. The acoustic detection module (ADM) consists of a cylindrical chamber with gas-in and gas-out connectors and two optical ZnSe windows. The spectrophone is positioned inside the ADM. The employed spectrophone shows a quality factor of  $Q = 2100$  at atmospheric pressure and a resonance frequency for the QTF fundamental flexural in-plane mode of  $f_0 = 32,741.5$  Hz.

The collimated light exiting the ICL is focused by a ZnSe lens (L1) through the ADM; L1 has a focal length of 7.5 cm and a transmittivity of 95% at 3345 nm. A gas line connects the ADM to the pump on the outlet side and to a pressure controller located at the inlet side. The pressure controller maintains the downstream pressure of the targeted gas mixture into the ADM. The mixtures are generated by flow controllers and a constant water concentration of 1.7% was provided by a Nafion humidifier inserted on one of the gas line. The light exiting from the ADM is re-collimated using a ZnSe lens (L2) and collected by a VIGO detector (model PVI-3TE-3.4) with a detectivity of  $7.0 \times 10^{11} \text{ cm}\cdot\text{Hz}^{1/2}\cdot\text{W}^{-1}$ , current responsivity  $\geq 0.8 \text{ A}\cdot\text{W}^{-1}$  and time constant  $< 200$  ns was used for monitoring the laser power and for alignment purpose. The piezoelectric current generated by the photoacoustic excitation is converted into a voltage signal and amplified by a factor 30 using a transimpedance amplifier (with a feedback resistor of 10 M $\Omega$ ) and then sent to the Control Electronics Unit (CEU). The CEU is used to determine the main QTF parameters: the electrical resistance  $R$ , the quality factor  $Q$ , and the resonance frequency  $f_0$ . It is also used to transfer the signal coming from the transimpedance amplifier to a lock-in amplifier. The output analog signal from the lock-in amplifier is then digitalized by a National Instruments DAQ card (USB 6008) connected to a personal computer. LabVIEW-based software acquires the temporal evolution of the QEPAS signal and the response of the pyroelectric detector. All measurements were performed by using an integration time of 100 ms and acquisition time of 300 ms.

## 4. Sensor calibration for methane detection

We investigated the full ICL dynamic range to retrieve the most convenient experimental conditions for C1–C2 detection in the current scan mode. A mixture of 1000 ppm of  $\text{CH}_4:\text{N}_2$  and a mixture of 1000 ppm of  $\text{C}_2\text{H}_6:\text{N}_2$  were analyzed. 2f-wavelength modulation (WM) was employed as the detection scheme since it is characterized by a background-free signal [18]. The ICL injected current  $I$  was modulated at half of the resonance frequency  $f_0/2$  and the QEPAS signal was demodulated at the resonance frequency  $f_0$  (2f-signal). Usually, the

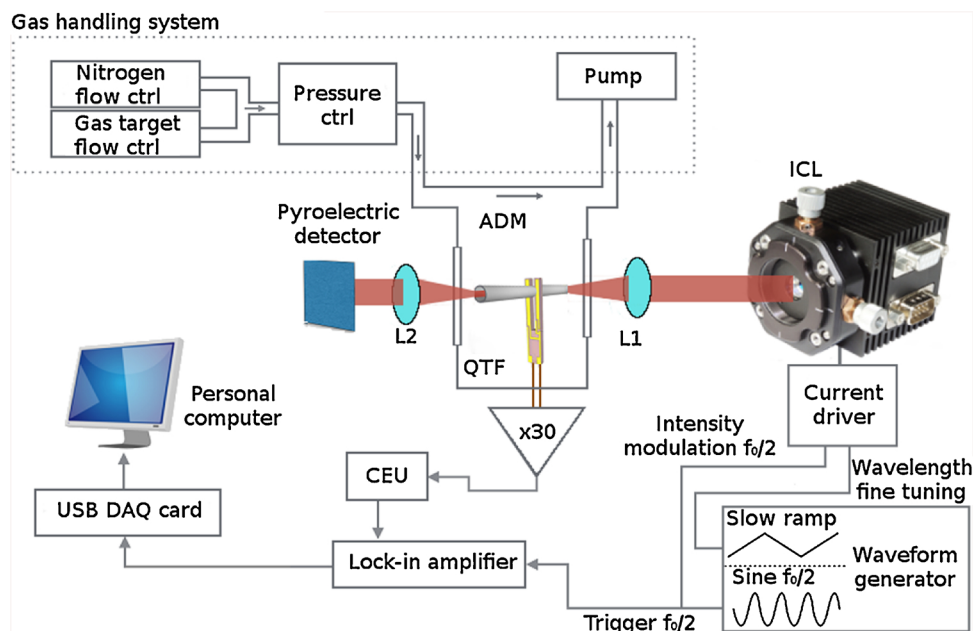


Fig. 2. Schematic of the experimental apparatus. CEU - control-electronic-unit; ADM - acoustic detection module; L1, L2 –ZnSe lenses; ICL – intercascade laser.

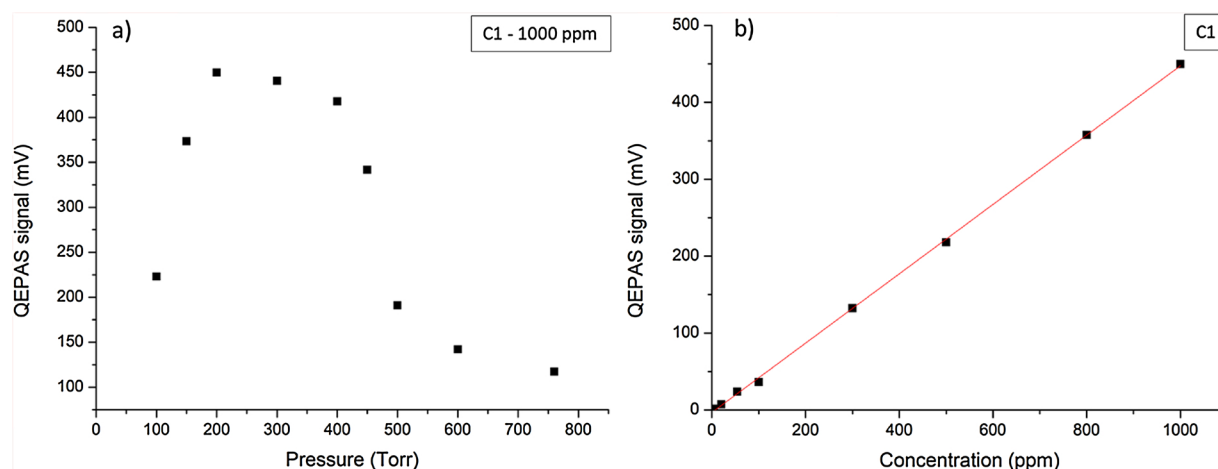


Fig. 3. a)  $2f$ -signal peak values related to  $\nu_3^{C1}$  at their optimum modulation depth for different pressures ranging from 100 Torr to atmospheric pressure; b) linearity of the  $2f$ -signal peak values obtained at 200 Torr over a range of C1 concentrations from 4 ppm to 1000 ppm in pure  $N_2$ .

current sinusoidal excitation and the QEPAS signal are out of phase. For this reason, the demodulation of the QEPAS signal occurs at a detection phase  $\varphi_i$  maximizing the demodulated signal amplitude. The main results from this investigation showed that by operating at an ICL temperature of 15 °C, the laser emission wavelength is resonant with the  $C_2H_6$  absorption line located at  $2986.25\text{ cm}^{-1}$  ( $\nu_2^{C2}$ ) at a laser current of  $I = 65.5\text{ mA}$ , while to target the strongest  $CH_4$  absorption line peak at  $2988.8\text{ cm}^{-1}$  ( $\nu_3^{C1}$ ) and for the  $C_2H_6$  line located at  $2990.1\text{ cm}^{-1}$  ( $\nu_2^{C2}$ ) the injected current must be set at  $I = 48\text{ mA}$  and  $I = 35\text{ mA}$ , respectively. Thus, all three transitions  $\nu_2^{C2}$  can be excited by keeping the laser operating temperature fixed at 15 °C and exploiting the ICL current dynamic range. Once the ICL operating conditions to target the selected  $CH_4$  and  $C_2H_6$  absorption lines were identified, the full sensor calibration procedure was performed. The QEPAS response to the excitation of  $\nu_3^{C1}$  at different pressures was recorded. The data reported in Fig. 3a correspond to the  $2f$ -QEPAS peak signals obtained by operating in the wavelength modulation configuration and optimizing the modulation depth for each different operating pressure. For methane the strongest response to photoacoustic excitation was achieved at a gas pressure of 200 Torr and a modulation amplitude of 130 mV peak-to-peak ( $V_{p-p}$ ).

The detection phase  $\varphi_1$  maximizing the QEPAS signal related to  $\nu_3^{C1}$  excitation was  $99.91^\circ$ . These operating parameters were used for all the following C1 measurements.

Once determined the best operating conditions in terms of gas pressure and modulation depth, the  $2f$ -signal peak signals at different C1 concentrations were recorded. Different  $CH_4$  concentrations in the range 4–1000 ppm were generated, starting from a certified 1000 ppm  $CH_4$  in  $N_2$  mixture and using pure  $N_2$  as diluting gas. By keeping fix the total flow of the mixture at 50 sccm, the uncertainty of the  $CH_4$  concentration was estimated from the nominal values of the accuracy of the two mass flow meters, one dedicated to the methane and the other one to pure nitrogen. The error estimated for the minimum concentration level of 4 ppm of  $CH_4$  is  $\pm 1.6\text{ ppm}$ .

The data reported in Fig. 3b demonstrate a good linearity for the  $CH_4$  sensor over a wide range of concentrations from 4 ppm to 1000 ppm. A linearity coefficient of  $0.46\text{ mV/ppm}$  was derived from the linear fit and a negligible intercept with  $1-\sigma$  noise fluctuations of  $0.073\text{ mV}$ .

In Fig. 4a and b are shown two representative acquisitions of  $CH_4$  signal for 1000 ppm and 4 ppm, respectively.

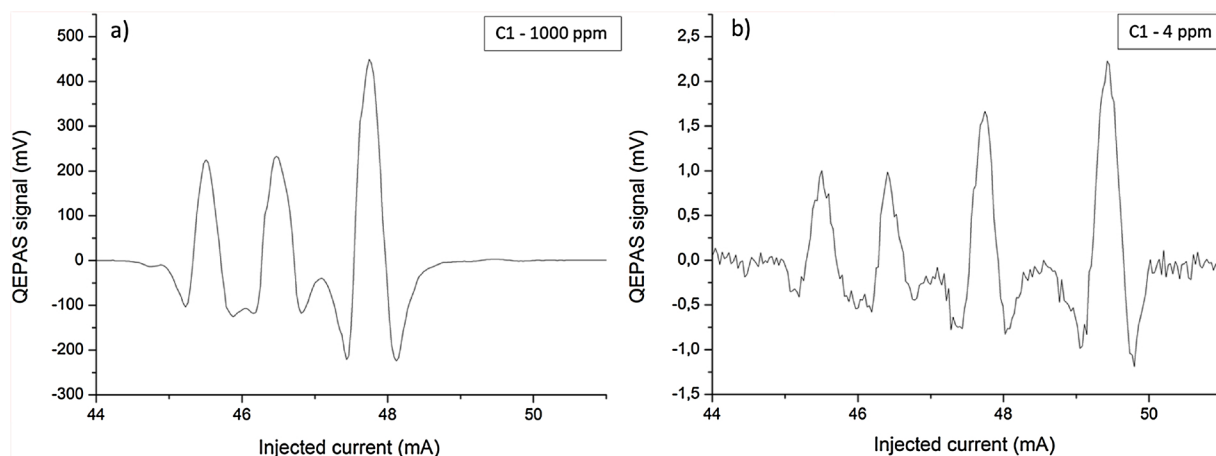


Fig. 4. a)  $2f$ -signal corresponding to a humidified mixture of 1000 ppm-C1:N<sub>2</sub>; b)  $2f$ -signal corresponding to a humidified mixture of 4 ppm-C1:N<sub>2</sub>.

In Fig. 4b it is clearly visible that a water absorption line falling at  $2988.61\text{ cm}^{-1}$  [5], corresponding to at a laser injected current  $I = 49.5\text{ mA}$ , with a line strength of  $1.1 \cdot 10^{-22}\text{ cm/mol}$ , gives rise to a  $2f$ -signal with a peak value of  $\sim 2.25\text{ mV}$ . This signal is barely visible in Fig. 4a due to the much higher CH<sub>4</sub> concentration. A very good correspondence between the absorption features listed in the Hitran database [13] and the  $2f$ -QEPAS signal structures due to methane absorption was found. The background signal not involving gas absorption lines has comparable  $1\text{-}\sigma$  noise fluctuations at different CH<sub>4</sub> concentrations. Allan deviation analysis [18] shows that for a 1 s integration time the detection limit for methane is  $\sim 90\text{ ppb}$ . This is a value well below the sensitivity needed for a sensor aimed at hydrocarbon detection at a well site, where C1 concentrations are expected to be generally well above the ppm scale.

## 5. Sensor calibration for ethane detection

Interesting results were observed when the sensor was calibrated for ethane detection. Line  $\nu_2^{C2}$  was targeted for determining the sensitivity of the sensor with respect to C<sub>2</sub>H<sub>6</sub>. The calibration procedure for C<sub>2</sub>H<sub>6</sub> is similar to the one illustrated in the previous section and the QEPAS response at different working pressures was investigated at a C<sub>2</sub>H<sub>6</sub> concentration of 100 ppm. The optimum gas mixture pressure, located at 300 Torr, provides a QEPAS signal only  $\sim 1.3$  times higher with respect to the value recorded at the atmospheric pressure (Fig. 5a), differently from methane where at 1 atm the QEPAS signal decreased by

$\sim 70\%$  with respect to the maximum signal recorded at 200 Torr. This means that the C<sub>2</sub>H<sub>6</sub> sensor works efficiently also at atmospheric pressure which is advantageous for in-situ applications.

We observed that 200 Torr is the optimum working pressure for methane and the pressure controller has proven to have the smallest fluctuations at this pressure. Moreover, since the QEPAS signal at 200 Torr from  $\nu_2^{C2}$  is  $\sim 4\%$  smaller with respect to the highest signal recorded at 300 Torr (see Fig. 5a), a pressure of 200 Torr was chosen for performing the measurements for both CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. For C<sub>2</sub>H<sub>6</sub> the optimum modulation depth results  $V_{p-p} = 130\text{ mV}$  and detection phase  $\varphi_2 = 166.15^\circ$ . The C<sub>2</sub>H<sub>6</sub>-calibration curve is shown in Fig. 5b and the linearity of the QEPAS response was demonstrated from 100 ppm down to 2 ppm, with a linearity coefficient of  $5.54\text{ mV/ppm}$  and a negligible intercept. Different from methane, ethane shows a broadband background absorption signal due to the presence of several absorption features with a small linewidth in the ICL operation spectral range. This can easily be noticed by comparing the signal at 1000 ppm for methane (see Fig. 4a) with the signal at 100 ppm for ethane (see Fig. 6a).

By comparing Fig. 6a and b, it can be noticed that the broadband background absorption levels off as the ethane concentration decreases. At 200 Torr and 2 ppm ethane concentration, the  $1\text{-}\sigma$  signal value calculated far from the  $\nu_2^{C2}$   $2f$ -peak is  $0.14\text{ mV}$ , only about two times the noise level measured for a 1000 ppm CH<sub>4</sub>:N<sub>2</sub> mixture. Allan deviation analysis [19] shows that for a 1 s integration time the detection limit for ethane is  $\sim 7\text{ ppb}$ . This represents a record for the QEPAS technique

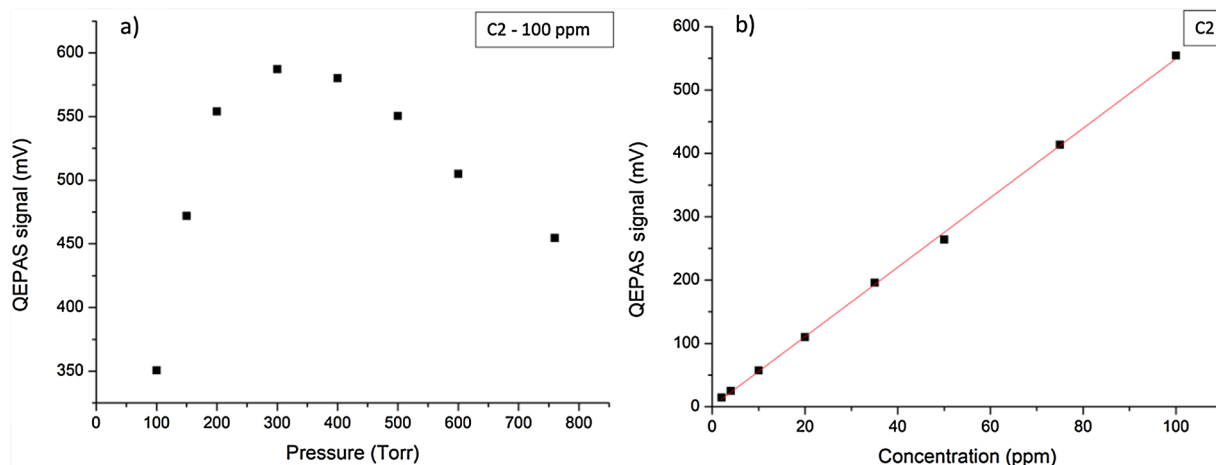


Fig. 5. a)  $2f$ -signal peak values related to  $\nu_2^{C2}$  at optimum modulation depths for different pressures, from 100 Torr to atmospheric pressure; b) linearity of the  $2f$ -signal peak values obtained at 200 Torr for a range of C2 concentrations from 2 ppm to 100 ppm in pure N<sub>2</sub>.

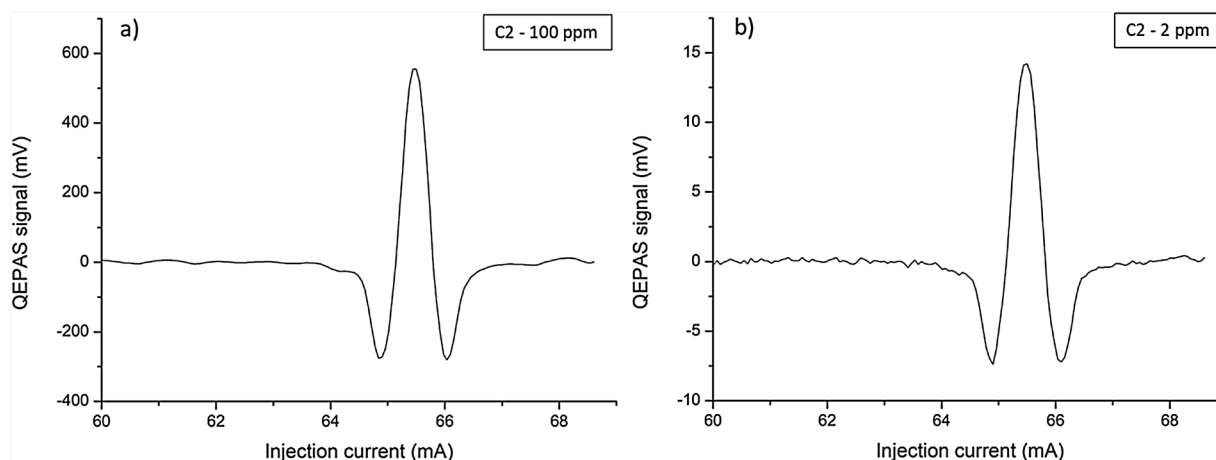


Fig. 6. a) 2f-signal corresponding to a humidified mixture of 100 ppm-C<sub>2</sub>:N<sub>2</sub>; b) 2f-signal corresponding to a humidified mixture of 2 ppm-C<sub>2</sub>:N<sub>2</sub>.

and opens the way to the implementation of QEPAS sensors for exploration and identification of ethane reservoirs, an application of strong interest for petrochemical and plastic industries.

## 6. Sensor performance and analysis of C1/C2 mixture

Considering the previous results, an unbalanced wet mixture containing 990 ppm CH<sub>4</sub>, 10 ppm C<sub>2</sub>H<sub>6</sub>:N<sub>2</sub> was used to perform the first test of a fast C1/C2 detection scan. In the upper panel of Fig. 7, the QEPAS signal acquired for an ICL current span from 20 mA to 70 mA at T = 15 °C is displayed.

The working pressure was fixed at 200 Torr and the modulation amplitude at 130 mV<sub>p-p</sub>. The second derivative profile of ethane absorption features  $\nu_1^{C2}$ ,  $\nu_2^{C2}$  and the second derivative shape of the three-lines structure from methane are clearly visible. The spectral separation is coherent with the absorption cross-section graph for both CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> simulated using the Hitran database and shown in the lower panel of Fig. 7. In order to maximize the QEPAS response of the CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> lines, the optimal detection phases identified for each gas were used

during the current scan in the proximity of the related absorption features. A  $\nu_3^{C1}$  2f-signal peak of 455 mV and a  $\nu_2^{C2}$  2f-signal peak of 63 mV were obtained as expected from the sensor calibration. Furthermore, the full spectral scan over the ICL dynamic range showed the presence of barely visible water line at I = 59 mA, different from the one previously observed at I = 49.5 mA.

The detection scheme is versatile, because in one single current scan CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> can be independently detected at sub-ppm scale and can also deal with unbalanced mixtures in which the methane concentration is two orders of magnitude or even higher in concentration with respect to ethane. More interesting is a comparison between two or more broadband absorber molecules that can be found in downhole mixture compositions.

## 7. Propane detection and analysis of broadband absorbers spectra

In this section a detailed study of propane (C3) will be presented. In particular, consideration will be given on how its broadband spectrum interacts with the C2 background signal. Since propane absorption lines

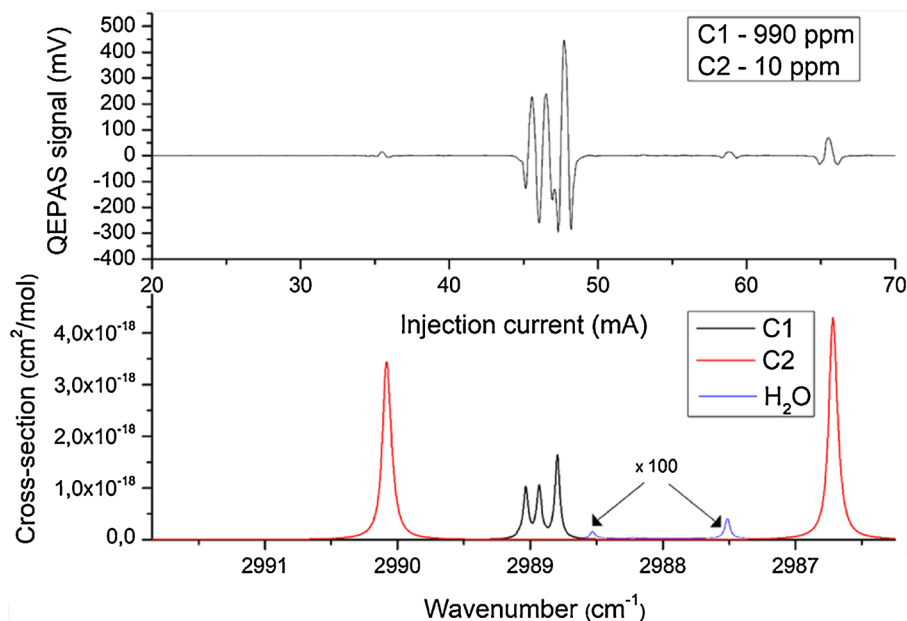
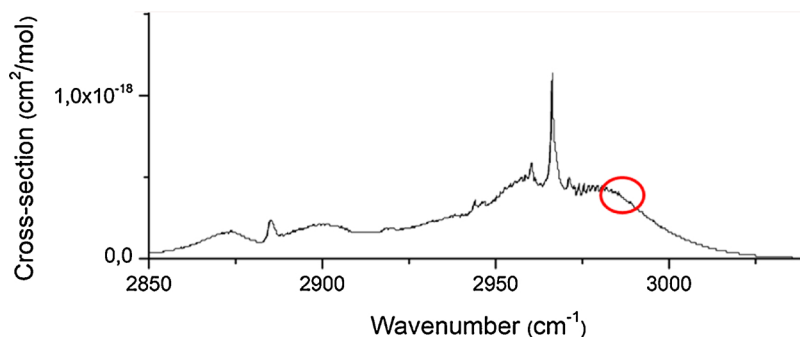


Fig. 7. Top panel: QEPAS 2f-signal for a humidified mixture of 990 ppm-C1 and 10 ppm-C<sub>2</sub>:N<sub>2</sub> with an adjusted detection phase of  $\nu_3^{C1}$  ( $\varphi_1$ ) and  $\nu_2^{C2}$  ( $\varphi_2$ ). Bottom panel: absorption cross-section for C1 and C2 obtained using the Hitran database [5]. Two weak H<sub>2</sub>O absorption features are also shown (blue curve) by multiplying the related cross-sections by a factor of 100. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).





**Fig. 8.** Cross-section of propane in the range 2850–3100 nm, using PNNL database [20]. The red circle highlights the spectral range corresponding to the ICL tuning range. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

in the 2–4  $\mu\text{m}$  range are not listed in the Hitran database, the PNNL database [20] was taken as reference to analyze the QEPAS measurements obtained for a mixture of 1000 ppm of  $\text{C}_3\text{H}_8:\text{N}_2$ . In Fig. 8 the absorption cross-section of  $\text{C}_3\text{H}_8$  in the spectral range 2850–3100 nm is shown.

The  $\text{C}_3\text{H}_8$  absorption cross-sections in the ICL tuning range (see the red circle in Fig. 8) are almost five times lower in linestrength than  $\nu_2^{C2}$  ( $1.26 \cdot 10^{-18} \text{ cm}^2/\text{mol}$ ) at atmospheric pressure. Nevertheless, the lack of sharp Lorentzian-like features like  $\nu_2^{C2}$  or  $\nu_3^{C1}$  leads to a photoacoustic excitation intensity in a wavelength modulation configuration that is low. In order to increase the  $\text{C}_3\text{H}_8$  WM QEPAS signal, all the measurements were carried out at atmospheric pressure, where multiple absorption lines merge to build a spectrum composed of well-separated bands. The lock-in phase maximizing the  $\text{C}_3\text{H}_8$  QEPAS signal was  $\varphi_3 = 107.25^\circ$ . In Fig. 9 the QEPAS spectra related to the  $\text{C}_3\text{H}_8$  absorption bands spectra measured at atmospheric pressure and for different  $\text{C}_3\text{H}_8$  dry concentrations, ranging from 1000 ppm to 200 ppm in pure  $\text{N}_2$ , are plotted.

These spectra were obtained by scanning the laser injected current from 20 mA to 70 mA at  $T = 15^\circ\text{C}$  and employing a modulation depth of 300 mVpp. Fig. 9b demonstrates the linearity of photoacoustic response as a function of the  $\text{C}_3\text{H}_8$  concentration, extracted for the peak of the QEPAS spectrum  $\nu_4^{C3}$  located at  $I = 61.3 \text{ mA}$ . The linearity coefficient is 0.0191 mV/ppm. The detection limit, extracted via an Allan deviation analysis of the QEPAS  $\nu_4^{C3}$  peak signals, results in  $< 3 \text{ ppm}$  for a 1 s integration time. It was verified that each peak of the  $\text{C}_3\text{H}_8$  spectrum exhibits a linear QEPAS response with  $\text{C}_3$  concentrations, as observed in Fig. 9a). The QEPAS signal measured for a pure  $\text{N}_2$  mixture

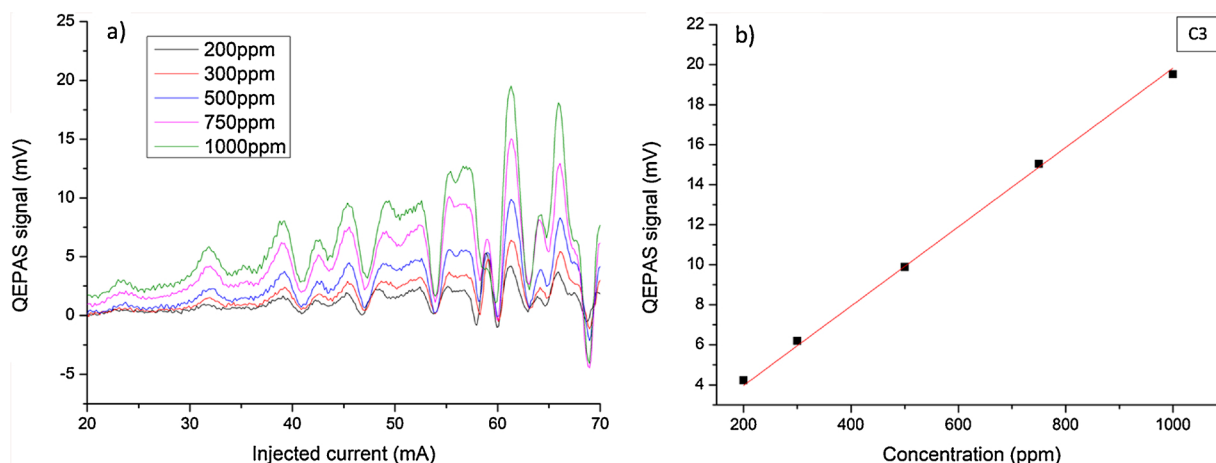
is flat within the ICL current dynamic range and comparable with the noise level. A flat background noise and QEPAS signal scaling linearly with the gas target concentration are mandatory requirements to compare  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  backgrounds. The QEPAS signal  $Y(\lambda)$  acquired for a mixture of  $n$  gases ( $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$ ) for a given wavelength spectrum can be assumed to be the sum of the QEPAS signals related to the individual gases:

$$Y(\lambda) = \sum_{i=0}^n A_i X(\lambda)_i = A_2 X(\lambda)_{C2} + A_3 X(\lambda)_{C3} \quad (1)$$

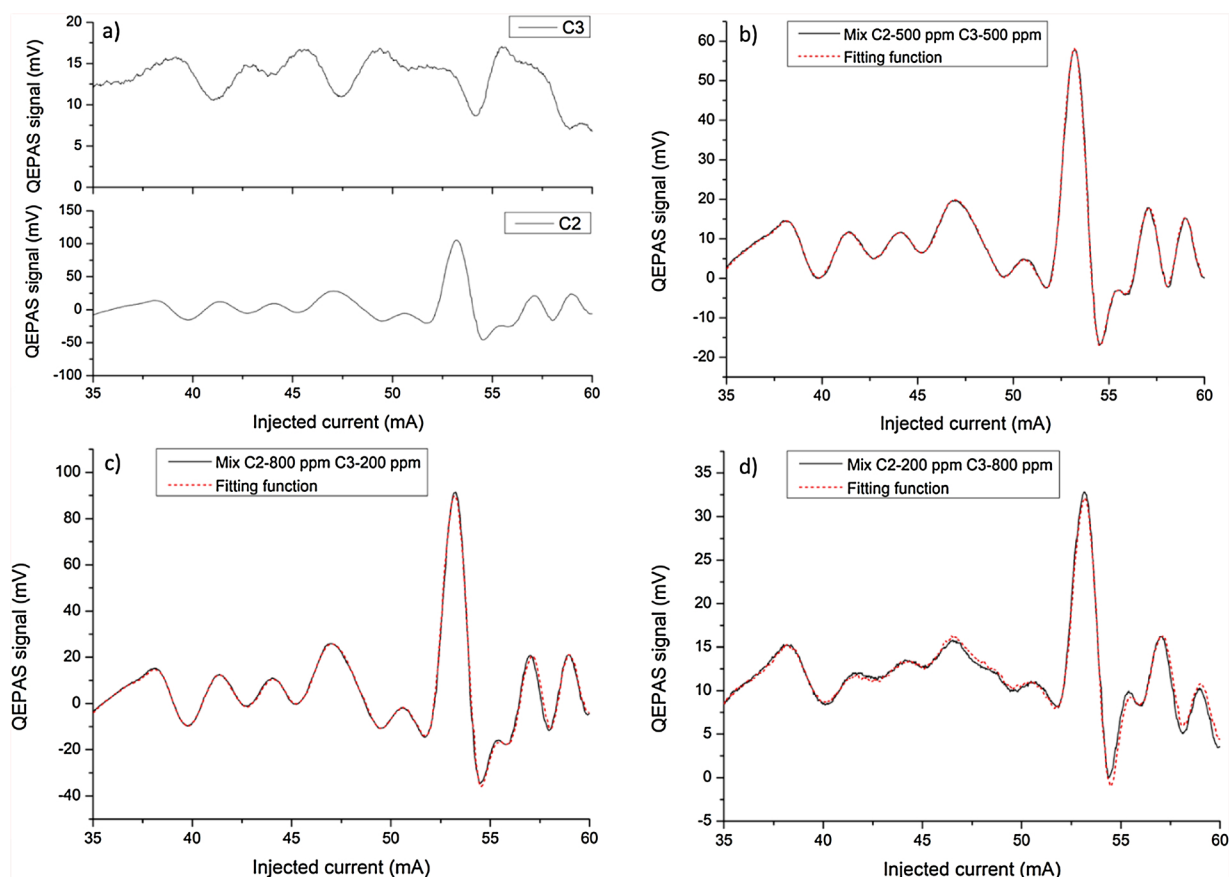
where  $Y(\lambda)$  is the acquired QEPAS signal (in mV),  $A_i$  is the concentration of the  $i$ -th gas (in ppm) and  $X_i$  the related QEPAS spectrum, in mV/ppm unit [21]. If the operating temperature is set to  $15^\circ\text{C}$ , the laser emission wavelength is related to the drive current. In order to discriminate both contributions in  $\text{C}_2$ - $\text{C}_3$  mixtures, an injected current range from 35 to 60 mA was selected, in which range no strong  $\text{C}_2\text{H}_6$  features are present and both  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  absorption broadband backgrounds can be easily compared (see Fig. 10a). The detection phase used for these measurements is the one maximizing the  $\text{C}_3$  QEPAS signal, i.e.,  $\varphi_3 = 107.25^\circ$ : in this way we also slightly reduced the intensity of the  $\text{C}_2$  background signal. However, it was verified that the  $\text{C}_2$  background signal detected at  $\varphi_3$  is still linear as function of  $\text{C}_2$  concentrations. The reference QEPAS spectra used for the fitting procedure using Eq. 1 are the  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  signals recorded at 1000 ppm in pure  $\text{N}_2$  concentration, therefore Eq. 1 becomes:

$$Y = a X_{1\%}^{C2} + b X_{1\%}^{C3} \quad (2)$$

where  $a$  and  $b$  are the fraction of 1000 ppm of the reference spectra. The first validation test of this multi-gas detection approach was made using



**Fig. 9.** a) 2f-QEPAS spectra measured for different  $\text{C}_3$  concentrations from 1000 ppm to 200 ppm in pure  $\text{N}_2$  at atmospheric pressure and using a modulation depth  $V_{p-p} = 300 \text{ mV}$ , in the laser current range 20–70 mA; b) linear fit (red line) of the 2f-signal peak values (black square dots) related to the absorption feature falling at  $I = 61.3 \text{ mA}$  for a range of  $\text{C}_3$  concentrations from 1000 ppm to 200 ppm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



**Fig. 10.** a) Top panel: 2f-signal for 1000 ppm-C<sub>3</sub>:N<sub>2</sub> acquired in the laser injected current range 35–60 mA. Bottom panel: 2f-signal for 1000 ppm-C<sub>2</sub>:N<sub>2</sub>; b) 2f-signal for a dry mixture containing 500 ppm of C<sub>2</sub> and 500 ppm of C<sub>3</sub> in pure N<sub>2</sub>; c) 2f-signal for a dry mixture containing 800 ppm of C<sub>2</sub> and 200 ppm of C<sub>3</sub> in pure N<sub>2</sub>; d) 2f-signal for a dry mixture containing 200 ppm of C<sub>2</sub> and 800 ppm of C<sub>3</sub> in pure N<sub>2</sub>.

dry mixtures composed of: i) C<sub>2</sub>-500 ppm, C<sub>3</sub>-500 ppm in pure N<sub>2</sub> (mix#1); ii) C<sub>2</sub>-800 ppm, C<sub>3</sub>-200 ppm in pure N<sub>2</sub> (mix#2); iii) C<sub>2</sub>-200 ppm, C<sub>3</sub>-800 ppm in pure N<sub>2</sub> (mix#3).

In Fig. 10b–d the QEPAS spectra and the related fits for all the three gas mixtures are shown. The calculated concentration values are listed in Table 1. In brackets the 95% confidence interval uncertainties are reported.

The differences between the fitting parameters, i.e. the calculated C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> concentrations, and the nominal concentrations expected remains below 5% and are mainly due to uncertainties in the certified gases flows used for producing the mixtures (especially for flows as low as 8 sccm, as used in our experiments). The obtained results successfully demonstrate the feasibility to perform photoacoustic C<sub>2</sub>/C<sub>3</sub> gas detection by fitting the QEPAS spectra measured for the gas mixtures. Among different valid approaches such as multivariate analysis or machine learning, a fitting procedure based on a linear combination of reference spectra still represents the most straightforward strategy. Since in the investigated spectral range, C<sub>1</sub> is characterized by well isolated absorption peaks and no background, we successfully determined CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> concentrations in humidified and dry gas mixtures respectively, using pure nitrogen as gas carrier. The next

step will be a detailed investigation of C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub> mixtures in a large dynamic range of concentration from several % to few ppb. Subsequently, butane will be added to the gas mixture in order to analyze gas samples as similar as possible to the natural gas composition. All these tasks aim to monitor natural gas sample compositions in situ and in real time for petrochemical applications.

## 8. Conclusions

Hydrocarbon concentration monitoring is essential for the oil & gas industry and the possibility to measure in real time methane and ethane as well as propane concentrations will represent a breakthrough for estimating reserves and assist in petrochemical exploration and drilling. In this paper, we demonstrated that a QEPAS sensor is capable of simultaneous detection of methane, ethane and propane using a single ICL source operating around 3.3 μm. The QEPAS sensor achieved an ultimate detection limit of 90 ppb, 7 ppb and 3 ppm for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>, respectively, for a 1 s integration time. Propane has never been detected previously using QEPAS and the detection limit achieved for ethane represents a record value for the QEPAS technique [22]. We also demonstrated the possibility to detect CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> at

**Table 1**  
Actual and calculated C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> concentration for the investigated gas mixtures.

Mixture	Actual C <sub>2</sub> H <sub>6</sub> concentration [ppm]	Actual C <sub>3</sub> H <sub>8</sub> concentration [ppm]	Calculated C <sub>2</sub> H <sub>6</sub> concentration [ppm]	Calculated C <sub>3</sub> H <sub>8</sub> concentration [ppm]
1	500	500	487.02 ( ± 1.4)	520.00 ( ± 2.5)
2	800	200	828.98 ( ± 3.8)	208.01 ( ± 6.8)
3	200	800	199.98 ( ± 1.7)	831.47 ( ± 2.9)

atmospheric pressure, thereby avoiding the use of pressure controller systems. Further improvements will be achieved by implementing new generations of QTFs [23], overtone modes operation [24,25] and new micro-resonator systems [26,27]. The final goal will be the development of a QEPAS sensor capable to perform CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> real-time measurement for upstream, midstream and downstream petrochemical sectors, and achieve the capability to detect butane.

## Acknowledgements

The authors from Dipartimento Interateneo di Fisica di Bari acknowledge the financial support from THORLABS GmbH, within the joint-research laboratory PolySense. Frank K. Tittel acknowledges the support by the Welch Foundation under Grant No. C0568.

## References

- [1] J. Meyer, I. Vurgaftman, Quantum and interband cascade lasers, *Opt. Eng.* 49 (2010) 111101.
- [2] I. Vurgaftman, R. Wei, M. Kamp, J.R. Meyer, C.L. Canedy, C.S. Kim, N. Kim, W.W. Bewley, C.D. Merritt, J. Abell, S. Höfling, Interband Cascade Lasers, *J. Phys. D Appl. Phys.* 48 (2015) 12.
- [3] C. Zheng, W. Ye, N.P. Sanchez, A.K. Gluszek, A.J. Hudzikowski, C. Li, L. Dong, R.J. Griffin, F.K. Tittel, Infrared dual-gas CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> sensor using two continuous-wave interband cascade lasers, *IEEE Photonics Technol. Lett.* 28 (2016) 2351.
- [4] L. Dong, F.K. Tittel, C. Li, N.P. Sanchez, H. Wu, C. Zheng, Y. Yu, A. Sampaolo, R.J. Griffin, "Compact TDLAS based sensor design using interband cascade lasers for mid-IR trace gas sensing," *Opt. Exp.* 24 (2016) A528.
- [5] L.S. Rothman, I.E. Gordon, Y. Babikov, A. Barbe, D. Chris Benner, P.F. Bernath, M. Birk, L. Bizzocchi, V. Boudon, L.R. Brown, A. Campargue, K. Chance, E.A. Cohen, L.H. Coudert, V.M. Devi, B.J. Drouin, A. Fayt, J.M. Flaud, R.R. Gamache, J.J. Harrison, J.M. Hartmann, C. Hill, J.T. Hodges, D. Jacquemart, A. Jolly, J. Lamouroux, R.J. Le Roy, G. Li, D.A. Long, O.M. Lyulin, C.J. Mackie, S.T. Massie, S. Mikhailenko, H.S.P. Muller, O.V. Naumenko, A.V. Nikitin, J. Orphal, V. Perevalov, A. Perrin, E.R. Polovtseva, C. Richard, M.A.H. Smith, E. Starikova, K. Sung, S. Tashkun, J. Tennyson, G.C. Toon, V.G. Tyuterev, G. Wagner, J. Quant. Spectrosc. Radiat. Transf. 130 (2013) 4–50.
- [6] J.G. Speight, *The Chemistry and Technology of Petroleum*, CRC Press, Boca Raton, 2014.
- [7] V. Spagnolo, P. Patimisco, S. Borri, G. Scamarcio, B.E. Bernacki, J. Kriesel, Part-per-trillion level SF<sub>6</sub> detection using a quartz enhanced photoacoustic spectroscopy based sensor with single-mode fiber-coupled quantum cascade laser excitation, *Opt. Lett.* 37 (2012) 460.
- [8] P. Patimisco, G. Scamarcio, F.K. Tittel, V. Spagnolo, Quartz-enhanced photoacoustic spectroscopy: a review, *Sensors* 14 (2014) 6165.
- [9] P. Patimisco, A. Sampaolo, L. Dong, F.K. Tittel, V. Spagnolo, Recent advances in quartz enhanced photoacoustic sensing, *Appl. Phys. Rev.*, *Appl. Phys. Rev.* 5 (2018) 011106.
- [10] A.A. Kosterev, F.K. Tittel, D. Serebryakov, A. Malinovsky, A. Morozov, Applications of quartz tuning fork in spectroscopic gas sensing, *Rev. Sci. Instrum.* 76 (2005) 043105.
- [11] A. Sampaolo, P. Patimisco, M. Giglio, L. Chieco, G. Scamarcio, F.K. Tittel, V. Spagnolo, Highly sensitive gas leak detector based on a quartz-enhanced photoacoustic SF<sub>6</sub> sensor, *Opt. Exp.* 24 (2016) 15872–15881.
- [12] M. Jahjah, W. Kiang, N.P. Sanchez, W. Ren, P. Patimisco, V. Spagnolo, S.C. Herndon, R.J. Griffin, F.K. Tittel, Atmospheric CH<sub>4</sub> and N<sub>2</sub>O measurements near Greater Houston area landfills using QCL-based QEPAS sensor system during DISCOVERY-AQ 2013, *Opt. Lett.* 39 (2014) 957.
- [13] P. Patimisco, A. Sampaolo, H. Zheng, L. Dong, F.K. Tittel, V. Spagnolo, "Quartz enhanced photoacoustic spectrophones exploiting custom tuning forks: a review," *Adv. Phys. X* 2 (2016) 169–187.
- [14] H. Wu, L. Dong, H. Zheng, Y. Yu, W. Ma, L. Zhang, W. Yin, L. Xiao, S. Jia, F.K. Tittel, Beat frequency quartz-enhanced photoacoustic spectroscopy for fast and calibration-free continuous trace-gas monitoring, *Nat. Comm.* 8 (2017) 15331.
- [15] S. Böttger, M. Köhring, U. Willner, W. Schade, Off-beam quartz-enhanced photoacoustic spectroscopy with LEDs, *Appl. Phys. B* 113 (2013) 227.
- [16] V. Spagnolo, P. Patimisco, R. Pennetta, A. Sampaolo, G. Scamarcio, M.S. Vitiello, F.K. Tittel, THz Quartz-enhanced photoacoustic sensor for H<sub>2</sub>S trace gas detection, *Opt. Exp.* 23 (2015) 7574.
- [17] A. Sampaolo, P. Patimisco, M. Giglio, M.S. Vitiello, H.E. Beere, D.A. Ritchie, G. Scamarcio, F.K. Tittel, V. Spagnolo, Improved tuning fork for terahertz quartz-enhanced photoacoustic spectroscopy, *Sensors* 16 (2016) 439.
- [18] P. Patimisco, A. Sampaolo, Y. Bidaux, A. Bismuto, M. Schott, J. Jiang, A. Muller, J. Faist, F.K. Tittel, V. Spagnolo, Purely wavelength- and amplitude-modulated quartz-enhanced photoacoustic spectroscopy, *Opt. Exp.* 24 (2016) 25943.
- [19] M. Giglio, P. Patimisco, A. Sampaolo, G. Scamarcio, F.K. Tittel, V. Spagnolo, Allan Deviation Plot as a tool for quartz-enhanced photoacoustic sensors noise analysis, *IEEE Trans. Ultrason. Ferroelect. Freq. Control.* 63 (2016) 555.
- [20] <http://vpl.astro.washington.edu/spectra/>.
- [21] I.T. Sorokina, K.L. Vodopyanov, *Solid-State Mid-Infrared Laser Sources*, Springer-Verlag, Berlin Heidelberg, 2003.
- [22] C. Li, L. Dong, C. Zheng, J. Lin, Y. Wang, F.K. Tittel, Pbpy-level ethane detection using quartz-enhanced photoacoustic spectroscopy with a continuous-wave, room temperature interband cascade laser, *Sensors* 18 (2018) 723.
- [23] P. Patimisco, A. Sampaolo, L. Dong, M. Giglio, G. Scamarcio, F.K. Tittel, V. Spagnolo, Analysis of the electro-elastic properties of custom quartz tuning forks for photoacoustic gas sensing, *Sens. Act. B Chem.* 227 (2016) 539.
- [24] F.K. Tittel, A. Sampaolo, P. Patimisco, L. Dong, A. Geras, T. Starecki, V. Spagnolo, Analysis of overtone flexural modes operation in quartz-enhanced photoacoustic spectroscopy," *Opt. Exp.* 24 (2016) A682.
- [25] A. Sampaolo, P. Patimisco, L. Dong, A. Geras, G. Scamarcio, T. Starecki, F.K. Tittel, V. Spagnolo, Quartz-enhanced photoacoustic spectroscopy exploiting tuning fork overtone modes, *Appl. Phys. Lett.* 107 (2015) 231102.
- [26] H. Zheng, L. Dong, A. Sampaolo, H. Wu, P. Patimisco, X. Yin, W. Ma, L. Zhang, W. Yin, V. Spagnolo, S. Jia, F.K. Tittel, Single-tube on-beam quartz-enhanced photoacoustic spectroscopy, *Opt. Lett.* 41 (2016) 978.
- [27] H. Zheng, L. Dong, A. Sampaolo, P. Patimisco, W. Ma, L. Zhang, W. Yin, L. Xiao, V. Spagnolo, S. Jia, F.K. Tittel, Overtone resonance enhanced single-tube on-beam quartz enhanced photoacoustic spectrophone, *Appl. Phys. Lett.* 109 (2016) 111103.

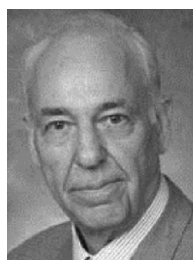


**Pietro Patimisco** obtained the Master degree in Physics (cum laude) in 2009 and the PhD Degree in Physics in 2013 from the University of Bari. Since 2013, he is a Post-Doctoral Research associate at the University of Bari. He was a visiting scientist in the Laser Science Group at Rice University in 2013 and 2014. Dr. Patimisco's scientific activity addressed both micro-probe optical characterization of semiconductor optoelectronic devices and photoacoustic gas sensors. Recently, his research activities included the study and applications of trace-gas sensors, such as quartz-enhanced photoacoustic spectroscopy and cavity enhanced absorption spectroscopy in the mid infrared and terahertz spectral region, leading to several publications, including a cover paper in *Applied Physics Letter* of the July 2013 issue.



**Angelo Sampaolo** obtained his Master degree in Physics in 2013 and the PhD Degree in Physics in 2017 from the University of Bari. He was a visiting researcher in the Laser Science Group at Rice University in 2016 and 2017. Since May 2017, he is a Post-Doctoral Research associate at the University of Bari. His research activity has included the study of the thermal properties of heterostructured devices via Raman spectroscopy. Most recently, his research interest has focused on the development of innovative techniques in trace gas sensing, based on Quartz Enhanced Photoacoustic Spectroscopy and covering the full spectral range from near-IR to THz. His achieved results have been acknowledged by a cover paper in *Applied Physics Letter* of

the July 2013 issue.



**Frank K. Tittel** obtained his bachelor, master, and doctorate degrees in physics from the University of Oxford in 1955 and 1959, respectively. From 1959 to 1967, he was a Research Physicist with General Electric Research and Development Center, Schenectady, New York. Since 1967 he has been on the faculty of the Department of Electrical and Computer Engineering and Biomedical Engineering at Rice University in Houston, TX, where he currently an Endowed Chaired Professor. Current research interests include various aspects of quantum electronics, in particular laser spectroscopy and laser applications in environmental monitoring, atmospheric chemistry, industrial process control, and medical diagnostics. Dr. Tittel is a Fellow of the

IEEE, Optical Society of America, the American Physical Society and SPIE.





**Vincenzo Spagnolo** obtained the PhD in physics in 1994 from University of Bari. From 1997 to 1999, he worked as researcher of the National Institute of the Physics of Matter (INFN). Since 2004, he works at the Technical University of Bari, formerly as assistant professor and, starting from 2015, as associate Professor of Physics. He is the director of the joint-research lab PolySense created by Technical University of Bari and THORLABS GmbH. His research interests include optoacoustic gas sensing and spectroscopic techniques for real-time device monitoring. His research activity is documented by more than 160 publications and two filed patents. He has given more than 40 invited presentations at international conferences and workshops.

Prof. Spagnolo is senior member of the SPIE and senior member of OSA.



**Marilena Giglio** received the M.S. degree (cum laude) in Applied Physics from University of Bari, Italy, in 2014, discussing the results obtained during a five months internship at the Academic Medical Center of Amsterdam, The Netherlands. Since 2014, she is pursuing a post-degree master in mechatronics and is currently a Research Assistant in the Physics Department of the University of Bari. Her research activity has included Optical Coherence Tomography (OCT) as an imaging technique for thin tissues and the analysis of the parameters of speckle distribution in OCT B-scans. Recently, her research activity has focused on the development of gas sensors based on Quartz-Enhanced Photoacoustic Spectroscopy.