Quartz enhanced photoacoustic sensors for trace gas detection in the IR and THz spectral range

Pietro Patimisco^{1,2}, Simone Borri², Angelo Sampaolo¹, Miriam S. Vitiello³, Gaetano Scamarcio^{1,2}, and Vincenzo Spagnolo^{1,2}

¹Dipartimento Interateneo di Fisica, Università e Politecnico di Bari, Via Amendola 173, I-70126 Bari, Italy, v.spagnolo@poliba.it

²IFN-CNR UOS Bari, via Amendola 173, 70126 Bari, Italy

³NEST, CNR-Istituto Nanoscienze and Scuola Normale Superiore, Piazza San Silvestro 12, I-56127 Pisa, Italy

Abstract Quartz-enhanced photo-acoustic spectroscopy (QEPAS) is one of the most robust and sensitive trace-gas detection techniques, which in the mid-IR range offers the advantage of high sensitivity, compactness and fast time-response. One of the main features of the photoacoustic techniques is that no optical detection is required. Thus, the use of the QEPAS technique in THz range would allow to avoid the use of low-noise but expensive, bulky and cryogenic bolometers. The results obtained in the development of QEPAS sensors for trace gas detection of several chemical species, employing mid-IR and THz laser sources will be reviewed. Normalized noise equivalent absorption coefficients (NNEA) down to 10⁻¹⁰ cm⁻¹W/Hz^{1/2} and part per trillion concentration detection ranges have been attained.

Introduction

The development of compact optical sensors for trace gas sensing is of interest for a number of applications, including atmospheric chemistry, volcanic activity, industrial processes, and medical diagnostics (Sigrist 2003). Conventional photoacoustic spectroscopy (PAS) is a well-established trace gas detection method based on the photoacoustic effect (Elia et al 2009). In this method, light energy absorbed by a gas is converted to heat that generally occurs via molecular collision-induced non-radiative relaxation of excited states. This absorption causes the gas to expand. If the light is chopped or modulated, the expansion produces pressure waves that can be detected using a microphone. The common approach used to detect the acoustic signal utilizes an acoustic resonator filled with the gas. In this way the absorbed laser power is accumulated in the acoustic mode of the resonator. In order to obtain an optimal acoustic signal, the laser modulation frequency is typically selected to match the first acoustic resonance of the cell, given by the equation f = v/2L, where v is the speed of the sound and L is the length of the cell. Most often the Q factor is in the range 40-200 and f = 1000 - 4000 Hz. Ideally, PAS is a background-free technique because only the absorption of modulated laser radiation generates an acoustic signal. However, background signals can originate from nonselective absorption of the gas cell windows and external acoustic noise, which can be reduced by means of a proper isolation of the cell from any mechanical vibrations. Quartz-enhanced photoacoustic spectroscopy (QEPAS) sensors are based on a recent approach to photoacoustic detection which employs a quartz tuning fork as an acoustic transducer (Kosterev et al 2002, Elia et al 2009). In this way, the common approach is inverted: the absorbed energy is not accumulated in the gas but in the sensitive element, i.e. the tuning fork. These quartz tuning forks have recently become widely used for atomic force and optical near field microscopy and therefore their properties have been carefully analyzed. A standard tuning fork (S-QTF) used in electronic watches for timepiece applications has a resonant frequency close to $f_0 = 32,768$ (i.e. 2^{15}) Hz. The mode at this frequency corresponds to a symmetric vibration mode where the prongs move in opposite directions. S-QTF has tipically $Q \approx 100,000$ or higher when it is encapsulated in vacuum and a $Q \approx 8,000$ at atmospheric pressure. At this resonant frequency, QEPAS devices result in a high immunity of to background acoustic noise as a consequence of the following behavior and the ambient acoustic noise density approximately follows a 1/f dependence, so it is very low above 10 KHz. In addition, sound waves emanating from a distant source tend to apply a force in the same direction upon the two tuning fork prongs, not exciting the piezoelectrically active mode in which the two prongs move in opposite directions.

Mid-IR QEPAS

To detect a trace gas, modulated laser radiation is directed between the tines of the tuning fork and absorbed by the gas which gives rise to an acoustic pressure. This pressure wave excites a resonant vibration of the tuning fork thereby generating an electrical signal via the piezoelectric effect, thanks to thin gold or silver films deposited on the quartz surfaces. The electrical signal can be measured as either a voltage or a current, depending on the electronic circuit used. The majority of reported QEAPS sensors include a spectrophone (the module for detecting laser-induced sound) consisting of a S-QTF and a microresonator composed of a pair of thin metal tubes (Kosterev et al 2005a, Kosterev et al 2005b, Lewicki et al 2007, Kosterev et at 2010, Liu et al 2010, Dong et al 2011, Dong et al 2012). It was shown that the microresonator yields a signal gain of at least one order of

2

magnitude. The sensor including optical pathlength is very small (a few mm in length) and can be located within a larger sample volume.

The generation of a photoacoustic wave involves the energy transfer from internal to translational molecular degrees of freedom. If a ro-vibrational state is excited, a collision-induced vibrational to translational (V-T) or rotational to translational (R-T) relaxation are followed. The V-T or R-T energy transfer times for a particular molecule is dependent on the presence of other molecules and intermolecular interactions. The QEPAS measurements that are usually performed at a detection frequency of ~32 kHz are more sensitive to the energy relaxation rate compared to the conventional PAS (which is commonly performed at < 4 kHz frequency). In case of slow V-T or R-T relaxation with respect to the modulation frequency, the translational gas temperature cannot follow fast changes of the laser induced molecular vibrational excitation. Thus the generated photoacoustic wave is weaker. On the other hand, in case of fast energy relaxation processes, the amplitude of the photoacoustic signal is not affected by the relaxation time. Thus for fast-relaxing excited energy levels the photoacoustic signal S is given by:

$$S_0 \propto \frac{F \alpha P Q}{f_0} \tag{1}$$

where α is the absorption coefficient, *P* is the exciting radiation power, and *F* is a micro-resonator enhancement factor included in this equation to account for a particular QEPAS sensor design.

In addition, the Q factor depends on the pressure P and can be expressed as:

$$Q = \frac{Q_{vac}}{1 + Q_{vac}a\sqrt{P}}$$
(2)

where Q_{vac} is the quality factor in vacuum and *a* is a parameter dependent on a specific quartz tuning fork design. From Equ. (2), it is clear that the Q-factor decreases at higher pressure but, on the other hand, the energy transfer in energy relaxation processes is faster at higher pressure, resulting in more efficient sound excitation. In addition, merging of closely spaced absorption lines should be taken into account at higher pressures and broader linewidth than desirable can limit the gas spectral selectivity. So, the operating pressure is an important parameter to choose.

Due to this intrinsic coupling of strain and charge displacement, the tuning fork can be modeled both electrically and mechanically. Thus, the tuning fork can be described as a circuit with a capacitance C, a resistance R, and an inductance L. A generally accepted way of observing the tuning fork electrical response is to utilize a transimpedance amplifier with a feedback resistance R_F . Feedback maintains a zero voltage between the tuning fork electrodes. Thus, the resonant frequency is related to the electrical parameters,

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{1}{LC}} \tag{3}$$

and the Q-factor

$$Q = \frac{1}{R} \sqrt{\frac{L}{C}}$$
(4)

while the impedance at resonance was equal to its resistance.

It is verified in many experiments that the QEPAS spectrophone noise is primarily determined by the thermal noise of QTF. The QTF noise measured at the transimpedance amplifier output at the resonant frequency f_0 is equal to the thermal noise of the equivalent resistor R:

$$\frac{\sqrt{\langle v_N^2 \rangle}}{\sqrt{\Delta f}} = R_F \sqrt{\frac{4KT}{R}}$$
(5)

where $\sqrt{\langle v_N^2 \rangle}$ is the root-means-squared (rms) voltage noise at the transimpedance amplifier output, Δf is the detection bandwidth, *K* is the Boltzmann constant and *T* is the tuning fork temperature.

Different QEPAS configurations have been demonstrated, two of them exploit a longitudinal acoustic resonance in an organ pipe type micro resonators (mR). The first of them was originally proposed by Kosterev et al. (Kosterev et al 2005a) in which the light come through the QTF and the two co-axial adjacent resonator tubes and is used in most of the reported QEPAS sensors. The second was reported by K. Liu et al (Liu et al 2009) and called "Off- Beam (OB) QEPAS". In this second configuration the mR is a single tube with a small opening in the middle, and a QTF is coupled to the mR by putting it outside the mR tube near the opening. Very recently, Y. Cao et al. (Cao et al 2012), demonstrate evanescent-wave PAS, which uses tapered optical micro/nano fibers (OMNFs) for photoacoustic signal generation. An OMNF is threaded through the gap between the two prongs of a QTF. Light is guided along the OMNF with a very small beam size, and no precise optical alignment is needed. Modulated light from a single longitudinal mode laser is transmitted to the OMNF, and the evanescent field is absorbed by the target gas, generating an acoustic pressure wave that is detected by the QTF. Finally, an innovative spectroscopic technique, the modulation cancellation method (MOCAM) that relies on the use of two QEPAS sensors have been demonstrated for isotope, gas temperature and concentration measurements (Spagnolo et al 2011a, Spagnolo et al 2011b, Spagnolo et al 2012)

Several chemical species, such as NH₃, NO, CO₂, N₂O, CO, CH₂O, etc.. have been detected with QEPAS sensors, using laser emitting in the 1-10 µm spectral

range (Kosterev et al 2005b, Lewicki et al 2007, Phillips et al 2007, Schilt et al 2009, Curl et al 2010, Kosterev et al 2010, Liu et al 2010, Spagnolo et al 2010, Dong et al 2011, Spagnolo et al 2011b, Dong et al 2012, Spagnolo et al 2013a, Spagnolo et al 2013b) and the results reported so far are summarized in Table 1.

Table 1.	QEPAS	detection	of trace	gases.
----------	-------	-----------	----------	--------

Molecule (Host)	Fre- quency cm ⁻¹	Pressure, torr	NNEA, cm ⁻¹ W/Hz ^{1/2}	Power, mW	NEC, ppmv
H ₂ O (N ₂)**	7306.75	60	$1.9 \cdot 10^{-9}$	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	$4.6 \cdot 10^{-9}$	50	0.16
$C_2H_2(N_2)^*$	6523.88	720	$4.1 \cdot 10^{-9}$	57	0.03
NH ₃ (N ₂)*	6528.76	575	$3.1 \cdot 10^{-9}$	60	0.06
$C_2H_4(N_2)^*$	6177.07	715	$5.4 \cdot 10^{-9}$	15	1.7
CH ₄ (N ₂ +1.2% H ₂ O)*	6057.09	760	$3.7 \cdot 10^{-9}$	16	0.24
N_2H_4	6470.00	700	$4.1 \cdot 10^{-9}$	16	1
$H_2S(N_2)^*$	6357.63	780	$5.6 \cdot 10^{-9}$	45	5
HCl (N ₂ dry)	5739.26	760	$5.2 \cdot 10^{-8}$	15	0.7
CO ₂ (N ₂ +1.5% H ₂ O)*	4991.26	50	$1.4 \cdot 10^{-8}$	4.4	18
CH ₂ O (N ₂ :75% RH)*	2804.90	75	$8.7 \cdot 10^{-9}$	7.2	0.12
CO (N ₂ +2.2% H ₂ O)	2176.28	100	$1.4 \cdot 10^{-7}$	71	0.002
CO (propylene)	2196.66	50	$7.4 \cdot 10^{-8}$	6.5	0.14
N ₂ O (air+5% SF ₆)	2195.63	50	$1.5 \cdot 10^{-8}$	19	0.007
NO (N ₂ +H ₂ O)	1900.07	250	$7.5 \cdot 10^{-9}$	100	0.003
C ₂ H ₅ OH (N ₂)**	1934.20	770	$2.2 \cdot 10^{-7}$	10	90
C ₂ HF ₅ (N ₂)***	1208.62	770	7.8 · 10 ⁻⁹	6.6	0.009
NH ₃ (N ₂)*	1046.39	110	$1.6 \cdot 10^{-8}$	20	0.006
SF_6	948.62	75	$2.7 \cdot 10^{-10}$	18	$5 \cdot 10^{-5}$

* - Improved microresonator

** - Improved microresonator and double pass through ADM

*** - With amplitude modulation and metal microresonator

NNEA - Normalized Noise Equivalent Absorption coefficient

NEC – Noise Equivalent Concentration for available laser power and 1 second constant time, 18 dB/oct filter slope

The normalized noise equivalent absorption coefficient measured to date using QEPAS are better than the best conventional PAS results and experimental study of the long-term stability of a QEPAS sensors showed that the sensors exhibit low drift, which allows long term data averaging thus allowing significant improvement of the signal-to noise ratio in concentration measurements. In mid-IR range $(4-12 \ \mu m)$, continuous wave quantum cascade laser (QCL) sources capable of

thermo-electrically cooled, room-temperature operation, single mode emission with mode-hop-free frequency tuning, high power (tens to hundreds of mW), and intrinsic narrow emission linewidth are the best performing light sources and are commercially available. In combination with these laser sources, QEPAS offers the advantage of high sensitivity (part-per-billion (ppb) detection limits), large dynamic range, compact set-up, fast time-response and simple optical alignment. Very recently, a record detection limit of 50 part per trillion (ppt) has been reported for SF₆, corresponding to a normalized noise equivalent absorption (NNEA) value of $2.7 \cdot 10^{-10}$ W·cm⁻¹·Hz^{-1/2}, employing an external cavity QCL and a single mode mid-IR hollow-core waveguide (Patimisco et al 2012, Spagnolo et al 2012, Patimisco et al 2013a, Spagnolo et al 2013a, Spagnolo et al 2013b) with internal core diameter of 300 µm for guiding the laser beam.

THz QEPAS

QEPAS technique is an excellent candidate for high performance gas spectroscopic techniques at long wavelength, i.e. in the THz range, mainly for two reasons: i) no optical detection is required, allowing to avoid the use of expensive, bulky and cryogenic bolometers; ii) QEPAS signal strongly depends from the energy relaxation rates of the absorption gas species. In gas absorption processes that occur in the THz range, R-T relaxation rates are involved, and it was demonstrated that R-T relaxation rates are up to three order of magnitude faster with respect to V-T one (Flygare 1968) commonly involved in the mid-IR absorption. Thus the possibility to work with fast relaxing transition levels allows to operate at low pressure, so taking advantages of the very high QTF Q-factors (see Eq. 2) and enhancing the selectivity of the QEPAS sensor systems. In the last few years, the rapid growth of THz QCLs is stimulating a resurgence in THz spectroscopic application. In fact, THz QCL can provide single-mode emission with considerable frequency tunability and with output powers up to one hundred mW in continuous wave operation at cryogenic temperatures. In addition, THz QCLs have recently demonstrated interesting performances in high resolution molecular spectroscopy, mainly thanks to their frequency stability. Despite this, the extension of the QEPAS technique to the THz spectral region has been delayed, mainly due to the difficulty of a proper focalization of the THz laser beam between the prongs (300 µm distance for S.QTF). Indeed, one of the main criticism in QEPAS experiments is represented by the laser beam waist between the prongs of the fork. The laser beam has not to touch the prongs, otherwise an undesirable non-zero background due to the laser contribution arises. This background is often several times larger than the thermal noise level of QEPAS sensor, limiting the detection sensitivity (Spagnolo et al 2010, Dong et al 2011). For this reason we adopted a custom-made quartz tuning

6





Fig. 1 Schematic of Custom quartz tuning fork (C-QTF) and standard quartz tuning fork (S-QTF).

The prong spacing is $\sim 800 \ \mu\text{m}$. The single prong is L = 17.7cm long and 1.4 cm wide, with a thickness of 0.8 mm. In order to employ C-QTF in a QEPAS sensing system we have to verify that it behaves like a S-QTF in terms of resonance frequency and quality factor. The in-plane resonance frequencies of the tuning fork can be found analytically by considering one prong of the fork as a cantilever beam. In the fundamental mode of oscillation, the times move in opposite directions and the center-of-mass of the fork remains unchanged. The frequency of the vibration modes of a single beam are obtained by solving the classical Euler-Bernoulli equation, including clamped-free boundary condition. Thus the resonance frequencies can be predicted by the following equation:

$$f_n = \frac{\pi G}{8L^2} \sqrt{\frac{E}{\rho}} n^2 \tag{6}$$

where G is the radius of gyration of the beam cross section that for a bar with rectangular cross section is equal to $1/\sqrt{12}$ times the thickness, E is the elastic Young modulus and ρ is the density of the quartz. The first four solutions of Eq. 6 (E = $0.72 \cdot 10^{11}$ N/m² and $\rho = 2650$ Kg/m³) for C-QTF and S-QTF (3.2 mm long and 0.33 mm wide) are shown in Table 2.

Table 2 n values and the resonant frequencies for the S-QTF and the C-QTF fork employed inthis work, calculated from Equ. (6).

n	f _n (Hz) – S-QTF	f _n (Hz) – C-QTF
1.194	31978	4118
2.988	200263	25786
5	560764	72204
7	1099097	141520

A control electronics unit (CEU) is used to determine the equivalent electrical parameters of the quartz tuning fork and to estimate the quality factor Q, the resonant frequencies f_n and the resistance of the C-QTF. Two resonance frequencies at $f_{n=1} = 4.245$ kHz and $f_{n=3} = 25.4$ kHz have been observed at atmospheric pressure in pure N₂, as reported in Fig. 2. These two resonant frequencies can be easily ascribed to the first and the third in-plane resonance (see Table 1). The discrepancies from the theoretical values, calculated under vacuum conditions, are due to damping effects of the ambient gas, additional weight of the electrode gold layers, dependence of the elasticity modulus of quartz on the crystallographic axes orientation and deviations in geometry between the modeled and the real C-QTF.



Fig. 2 Frequency profiles measured at atmospheric pressure in pure N₂.

To study the damping effects induced by the environmental gas on the quality factor, we measured the resonant frequency f_1 and f_3 and the respective quality factor Q_1 and Q_3 as a function of the N₂ pressure. In Fig. 3 are shown the experimental results. f_1 (f_3) versus the gas pressure is linear in the whole investigated pressure range 10-700 torr, as theoretically predicted (Patimisco et al 2013), with a slope of $-1.19 \cdot 10^{-3}$ Hz/torr ($-4.49 \cdot 10^{-3}$ Hz/Torr) and the intercept value is 4246.3 Hz (25404.5 Hz), which gives the resonant frequency in the vacuum. The Q_1 (Q_3) factor pressure dependence shows an exponential behavior, as predicted in eq. 2, and rapidly decreases with the gas pressure. The best fit parameters obtained using Equ. (2) are: a = $1.98 \cdot 10^{-6}$ Torr⁻¹ and $Q_0 = 146350$ for Q_1 , and a = $8.73 \cdot 10^{-7}$ Torr⁻¹ and $Q_0 = 13180$ for Q_3 .



Fig. 3 QTF resonance frequency f_1 measured as a function of the N₂ gas pressure (a); f_3 measured as a function of the N₂ gas pressure (c); solid lines are linear fit to the data. Q₁ factor measured as a function of the N₂ gas pressure (b); Q₃ factor measured as a function of the N₂ gas pressure (d); solid lines are the best fits obtained by using Equ. (2).

THz QCL-based QEPAS sensor

A picture of the THz QCL-based QEPAS sensor is shown in Fig. 4. A THz QCL is used as the excitation source for generating the QEPAS signal. It is a single-mode bound-to-continuum QCL emitting at 3.93 THz (76.3 μ m), driven in CW mode and mounted on the cold finger of a continuous-flow cryostat equipped with polymethylpentene (TPX) windows. 90° off-axis paraboloidal gold mirrors are used to collimate/focalize the THz beam. At 6° K, the laser optical frequency can be scanned over a 0.025 cm⁻¹ by applying a low-frequency (10 mHz) voltage ramp up to 1 V to the external analog modulation input of the QCL current supply, with laser output powers up to 180 μ W. A sinusoidal dither at frequency f₁ or f₃ is contemporarily added to the low-frequency voltage ramp, to obtain up to 0.01 cm⁻¹

9

optical frequency modulation. The signal generated by the quartz tuning fork is amplified by a custom designed transimpedance amplifier ($R_f = 10 \text{ M}\Omega$). Subsequently the signal is demodulated by a lock-in amplifier (Stanford Research Model SR830) and digitalized by a USB data acquisition card (National Instruments DAQ-Card USB6008), which is connected to a personal computer. By means of a pyroelectric camera (mod. Spiricon Pyrocam III-C), we measured a focused beam waist of ~ 430 µm after the second parabolic mirror (see Fig. 4) well below the gap between the QTF prongs (~ 800 µm). As a results, in the THz QEPAS experiments almost all of the laser beam were transmitted through the C-QTF without touching it.



Fig. 4 THz QCL-based sensor.

We selected methanol as the target gas molecule. Methanol is widely used as a solvent, detergent or even denaturant additive for industrial ethanol. The selected methanol absorption line was the (v=1, K=6, J=11) \rightarrow (1, 5, 10) rotational translational transition, falling at v_{line} = 3.9289 THz (131.054 cm⁻¹) with line-strength S = 4.28 \cdot 10⁻²¹ cm/mol in HITRAN units. Gas mixtures with different methanol concentrations in pure N₂ have been obtained by diluting methanol vapors, collected from a reservoir held at the vapor pressure (P = 120 Torr at 300K), with pressurized N₂. Instead, for measurements at low concentrations, we used a certified 100 ppm methanol/N₂ gas mixture.

To find the optimal operating conditions in terms of QEPAS signal-to-noise ratio, we investigated the effects of gas pressure and modulation amplitude. The optimal sensor operating conditions were found to occur by using the first resonant frequency f_1 of the C-QTF (see Fig.2), and at a gas pressure of 10 Torr and a modulation amplitude of 600 mV (Patimisco et al 2013b). Under this operating conditions, the linearity and detection sensitivity of the methanol channel were evaluated by measuring its response to varying methanol concentration in pure N_2 . In Fig. 5 is shown a spectral scan of the certified 100 ppm methanol sample (the lowest concentration tested) in N_2 at 10 torr.



Fig. 5 QEPAS acquisition of a methanol/N2 sample with a certified concentration of 100 ppm and lock-in integration time of 3 sec.

The data in Fig. 5 are collected by setting the lock-in amplifier time constant to 3 seconds and the filter slope to 12dB/oct, corresponding to an equivalent noise related bandwidth of $\Delta f_{lock-in} = 0.05558$ Hz. It was verified that with such integration parameters the observed spectral lines were not distorted by the lock-in detection. The total fundamental noise also includes the feedback resistor noise and the operational amplifier noise, integrated over the full lock-in detector bandwidth. However, the power density of these noise sources is usually low and therefore expanding the detection bandwidth beyond the tuning fork response does not significantly increase the noise level. The extracted tuning fork thermal noise, by using Equ. (5), is ~ 0.12 μ V (R corresponding at f_1 is 6.5 M Ω). For 100 ppm methanol concentration the experimentally measured noise level (rms of short term point-topoint scatter) was in the $\pm 25 \,\mu$ V range, several time larger than the thermal noise level. The QEPAS

peak signal for 100 ppm methanol concentration results \sim 170 μ V, thus the corresponding Noise Equivalent Concentration (NEC) is \sim 15 ppm.

High-resolution QEPAS scans of a methanol/ N_2 calibrated mixtures with different methanol concentrations with lock-in integration time of 500 ms are shown in Fig. 6.



Fig. 6 Spectral scan of three representative methanol concentrations at 0.75%, 3.22% and 4.32% at 10 torr using N_2 as the diluting gas, obtained by a current modulation of f_1 , a peak-to-peak voltage amplitude of 600 mV and a lock-in integration time of 0.5 sec. The background signal has been removed.

We found a clear not-zero background signal: we verified that it is stable over at least one hour and this permit an efficient background subtraction by post processing of the spectra, thus improving the resolution, but also increasing the overall measuring time.

To verify the linearity of the THz QEPAS signal as a function of the methanol concentration, the sensor was operated in the locked mode, i.e. with the THz QCL frequency set to the center of the absorption line. The experimental data are easily linearly fitted, confirming the linearity of the system response to the concentration (Borri et al 2013, Patimisco et al 2013b). In order to characterize long-term drifts and establish signal averaging limits, we performed an Allan analysis in terms of the QEPAS signal at zero methanol concentration (pure N₂) (Borri et al 2013). For this analysis, the laser frequency was locked to the methanol absorption line at 131.054 cm⁻¹, and pure carrier gas N₂ was introduced into the housing where the C-QTF is placed. For 4 s averaging time (and related bandwidth of 0.04169 Hz) we achieve a detection sensitivity of 7 ppm, corresponding to a normalized noise equivalent absorption coefficient (NNEA) of $2.7 \cdot 10^{-10}$ cm⁻¹ W/Hz.

Conclusions

In this work we have reported an overview on the results obtained using QEPAS technique for trace gas sensing. Mid-IR quantum cascade lasers represent the ideal radiation sources for QEPAS gas sensing thanks to their excellent spectroscopic and technical properties, i.e., narrow linewidth, tunability, reliability and room-temperature operation. We described also the first THz QEPAS sensor employing a THz quantum cascade laser operating in continuous-wave and a custom-made quartz tuning fork. The normalized noise equivalent absorption coefficient obtained is comparable with the best result obtained in the mid-IR and in strong competition with the sensitivities achieved with the most performing cryogenic bolometers. THz QEPAS detection limit can be further improved by employing THz QCL with higher emission power (> 100 mW has been already demonstrated (Williams et al 2006)) and selecting molecules such as HF, H₂S, OH, NH₃, HCN, having absorption strengths larger than 10^{-19} cm/mol, potentially pushing down to the part per trillion concentration the QEPAS detectivity range.

References

- Borri S, Patimisco P, Sampaolo A, Beere HE, Ritchie DA, Vitiello MS, Scamarcio G, and Spagnolo V (2013) THz quartz enhanced photo-acoustic sensor. Appl Phys Lett in press.
- Cao Y, Jin W, Ho LH, and Liu Z (2012) Evanescent-wave photoacoustic spectroscopy with optical micro/nano fibers. Opt Lett 37: 214-216.
- Curl RF, Capasso F, Gmachl C, Kosterev AA, McManus B, Lewicki R, Pusharsky M, Wysocki G, and Tittel FK (2010) Quantum cascade lasers in chemical physics. Chem Phys Lett 487: 1–18.
- Dong L, Spagnolo V, Lewicki R, and Tittel FK (2011) Ppb-level detection of nitric oxide using an external cavity quantum cascade laser based QEPAS sensor. Opt Express 19: 24037– 24045.
- Dong L, Lewicki R, Liu K, Buerki PR, Weida MJ, and Tittel FK (2012) Ultra-sensitive carbon monoxide detection by using ECQCL based quartz-enhanced photoacoustic spectroscopy. Appl Phys B 107: 275–283.
- Elia A, Lugarà PM, Di Franco C. and Spagnolo V (2009) Photoacoustic Techniques for Trace Gas Sensing Based on Semiconductor Laser Sources. Sensors: 9616-9628.
- Flygare W H (1968) Molecular relaxation. Accounts of Chem. Res. 1, 121-127
- Kosterev AA, Bakhirkin YA, Curl RF, Tittel FK (2002) Quartz-enhanced photoacoustic spectroscopy. Opt Lett 27: 1902-1904.
- Kosterev AA, Tittel FK, Serebryakov DV, Malinovsky AL, and Morozov IV (2005a) Applications of quartz tuning forks in spectroscopic gas sensing. Rev Sci Instrum 76: 043105.

- Kosterev AA, Bakhirkin YA, and Tittel FK (2005b) Ultrasensitive gas detection by quartzenhanced photoacoustic spectroscopy in the fundamental molecular absorption bands region. Appl Phys B 80: 133–138.
- Kosterev AA, Buerki PR, Dong L, Reed M, Day T, and Tittel FK (2010) QEPAS detector for rapid specral measurements. Appl Phys B 100: 173–180.
- Lewicki R, Wysocki G, Kosterev AA and Tittel FK (2007) QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at 8.4 µm. Opt Express 15: 7357–7366.
- Liu K, Guo XY, Yi HM, Chen WD, Zhang WJ, and Gao XM (2009) Off-beam quartz-enhanced photoacoustic spectroscopy. Opt Lett 34: 1594-1596.
- Liu K, Yi H, Kosterev AA, Chen WD, Dong L, Wang L, Tan T, Zhang WJ, Tittel FK, and Gao XM (2010) Trace gas detection based on off-beam quartz enhanced photoacoustic spectroscopy: optimization and performance evaluation. Rev Sci Instrum 81: 103103.
- Patimisco P, Spagnolo V, Vitiello MS, Tredicucci A, Scamarcio G, Bledt CM, and Harrington JA (2012) Coupling external mid-IR quantum cascade lasers with low loss metallic/dielectric waveguides. Appl Phys B 108: 255-260.
- Patimisco P, Spagnolo, V, Vitiello MS, Scamarcio G, Bledt CM, and Harrington JA (2013a) Low-loss hollow waveguide fibers for mid-infrared quantum cascade lased sensing applications. Sensors 13: 1329-1340.
- Patimisco P, Borri S, Sampaolo A, Beere HE, Ritchie DA, Vitiello MS, Scamarcio G, and Spagnolo V (2013b) Quartz enhanced photo-acoustic gas sensor based on custom tuning fork and terahertz quantum cascade laser. Analyst submitted
- Phillips MC, Myers TL, Wojcik MD, and Cannon BD (2007) External cavity quantum cascade laser for quartz tuning fork photoacoustic spectroscopy of broad absorption features. Opt Lett 32: 1177-1179.
- Schilt S, Kosterev AA, and Tittel FK (2009) Performance evaluation of a near infrared QEPAS based ethylene sensor. Appl Phys B 95: 813–824.
- Sigrist W (2003) Trace gas monitoring by laser photoacoustic spectroscopy and related techniques (plenary). Rev Sci Instrum 71: 486-490.
- Spagnolo V, Kosterev AA, Dong L, Lewicki R, and Tittel FK (2010) NO trace gas sensor based on quartz-enhanced photoacoustic spectroscopy and external cavity quantum cascade laser. Appl Phys B 100: 125-130.
- Spagnolo V, Dong L, Kosterev AA, Thomazy D, Doty JH, and Tittel FK (2011a) Modulation cancellation method for measurements of small temperature differences in a gas. Opt Lett 36: 460-462.
- Spagnolo V, Dong L, Kosterev AA, Thomazy D, Doty JH, and Tittel FK (2011b) Modulation cancellation method in laser spectroscopy. Appl Phys B 103: 735-742.
- Spagnolo V, Dong L, Kosterev AA, and Tittel FK (2012) Modulation cancellation method for isotope ¹⁸O/¹⁶O ratio measurements in water. Opt Express 20: 3401-3407.
- Spagnolo V, Patimisco P, Borri S, Scamarcio G, Bernacki BE, and Kriesel J (2013a) Part-pertrillion level SF6 detection using a quartz enhanced photoacoustic spectroscopy-based sensor with single-mode fiber-coupled quantum cascade laser excitation Opt Lett 37: 4461-4463.
- Spagnolo V, Patimisco P, Borri S, Scamarcio G, Bernacki BE, and Kriesel J (2013b) Midinfrared fiber-coupled QCL-QEPAS sensor. Appl Phys B DOI 10.1007/s00340-013-5388-3 in press.
- Williams BS, Kumar S, Hu Q, and Reno JL (2006) High-power terahertz quantum-cascade lasers. Electron Lett 42: 89-90.