Intracavity Quartz-Enhanced Photoacoustic Sensor for Mid-Infrared Trace-Gas Detection

S. Borri1, P. Patimisco2, I. Galli1, D. Mazzotti1, G. Giusfredi1, G. Scamarcio2, P. De Natale1, N. Akikusa3, M. Yamanishi4, and V. Spagnolo2

1 CNR-INO UOS Sesto Fiorentino and LENS, via Carrara 1, 50019 Sesto Fiorentino FI, Italy
2 Dipartimento Interateneo di Fisica, Università e Politecnico di Bari and CNR-IFN, Via Amendola 173, 70126 Bari, Italy
3 Development Bureau Laser Device R&D Group, Hamamatsu Photonics KK, Shizuoka 434-8601, Japan
4 Central Research Laboratories, Hamamatsu Photonics KK, Shizuoka 434-8601, Japan

Author e-mail address: simone.borri@ino.it

Abstract: Quartz-enhanced photoacoustic spectroscopy (QEPAS) and cavity-enhanced spectroscopy are merged in a novel gas sensor. Thanks to the intracavity power build up, sensitivity is increased by more than a factor 100 with respect to standard QEPAS.

OCIS codes: (300.6360) Spectroscopy, laser; (140.5965) Semiconductor lasers, quantum cascade

The development of cost-effective, compact optical sensors for trace chemical species in the gas phase is, for our present society, a challenge in a wide variety of applications, including climate changes, homeland security, industrial processes control, workplace surveillance, and medical diagnostics. Since the advent of lasers, the development of high-sensitivity optical sensors followed three main criteria: i) selection of optimal molecular transition in terms of absorption strength and absence of possible interfering gases; ii) long optical absorption length and/or use of build up optical cavity; iii) efficient spectroscopic detection schemes.

Quartz-enhanced photo-acoustic spectroscopy (QEPAS) is one of the most robust and sensitive trace-gas detection techniques. It is based on the use of tiny quartz tuning forks (QTF) with a resonant frequency $f_0 \approx 32$ kHz as a transducer to detect laser absorption by a gas sample in a compact and relatively low-cost detection module [1]. Combined with quantum cascade laser (QCL) sources has demonstrated record sensitivities down to 50 part-per-trillion (ppt) concentration levels in 1 s for SF$_6$ [2]. Very recently the possibility of high-sensitivity gas detection in the THz region has been also demonstrated by employing a custom tuning fork [3,4].

QEPAS is characterized by a direct proportionality between the signal amplitude and the laser power available for gas excitation, so the higher the optical power focused between the QTF prongs, the lower the sensor detection limit. In order to fully exploit this feature, we developed a novel spectroscopic technique by merging standard QTF detection scheme and the power build up acting in a high-finesse optical resonator. The use of an optical cavity leads to further advantages: it behaves as a selective optical filter for the laser frequency, leading to more stable signals and better selectivity; matching of the laser beam to the TEM$_{00}$ cavity mode provides an excellent spatial profile for the intracavity radiation, thus effectively lowering the light-induced photoacoustic thermal noise.

A cw room-temperature quantum cascade laser (QCL) emitting at 4.3 μm was used, with an available power of ~3 mW at the input mirror of the cavity. An effective enhancement factor of ~250 has been achieved with a four-mirrors bow-tie configuration, corresponding to an intracavity laser power of ~0.75 W. The QTF was placed inside the cavity between two spherical mirrors, in correspondence of the beam waist (60 μm 1/e$^2$ radius). For spectral scans the QCL driving current was linearly tuned around the selected molecular transition by applying a slow voltage ramp to the current driver. A home-made electronic servo loop was used to lock the resonance of the cavity to the laser frequency for each step of the slow linear scan. In Fig. 1 a schematic of the apparatus is shown.

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<th>QCL</th>
<th>Optical resonator</th>
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<td>MML</td>
<td>OC</td>
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Fig. 1. Experimental setup. MML: mode-matching lens; IM: input mirror; OC: output coupler; PZT: piezo-electric transducer; PI: proportional-integral locking module; CEU: control electronic unit.
Spectral scans have been performed using a wavelength modulation (WM) approach and 2f detection: a sinusoidal dither at a frequency of f0/2 was applied to the QCL through a FET (field-effect transistor) controller and the spectroscopic signal was demodulated at f0 by means of a lock-in amplifier. Optimal amplitude modulation and gas pressure conditions (50 mbar) were chosen by maximizing the spectroscopic signal. The sensor was tested on the (001–000) P(42) ro-vibrational transition of CO2, centered at 2311.105 cm\(^{-1}\), having a linestrength S=4.749·10\(^{-19}\) cm/mol. Several spectral scans were recorded for different CO2 concentrations in the 50–860 ppb range. We verified the linearity of the sensor by plotting the signal amplitude versus the CO2 concentration. In Fig. 2a a representative spectrum for 90 ppb CO2:N2 sample is reported (50 mbar pressure, 1 s lock-in integration time constant). By analyzing the signal-to-noise ratio of the recorded spectra, we estimated a minimum detectable concentration of 1.2 ppb for 1 s integration time.

![Image](SM2E.5.pdf)

Fig. 2. a) Intracavity QEPAS spectral scan of a gas mixture containing 90 ppb of CO\(_2\) in pure N\(_2\) at P = 50 mbar, acquired with 1 s lock-in integration time constant. A signal-to-noise ratio of 75 was calculated by considering the 1-s noise fluctuations on the tails. b) Allan deviation plot of a 90-minutes long time acquisition of the signal with pure N\(_2\) in locking conditions.

The recorded spectra were compared with standard single-pass QEPAS measurements obtained under the same operating conditions, in terms of pressure and incident laser power, by removing the optical resonator. The comparison shows an improvement by a factor ~250, in very good agreement with the intracavity build-up factor.

In order to determine the best achievable sensitivity and long-term drifts of the sensor we performed the Allan variance analysis of a long time acquisition (90 minutes) of the signal with pure N\(_2\) (Fig. 2b). A minimum achievable sensitivity of 230 ppt at 9 s averaging time (0.011 Hz equivalent noise bandwidth) was found, corresponding to a minimum absorption coefficient \(\alpha_{\text{min}}=1.07 \cdot 10^{-9} \text{ cm}^{-1}\) and a normalized noise equivalent absorption (NNEA) of 3·10\(^{-10}\) W cm\(^{-1}\)Hz\(^{-1/2}\). For a comparison with the existing QEPAS sensors we have to consider that our sensor makes use of a bare tuning fork; by equipping the QTF with standard acoustic organ-pipe-type micro-resonators the sensitivity is expected to increase by at least one order of magnitude. Anyway, in its present configuration our spectrometer results to be competitive with the best cantilever-based sensors reported in literature, with the advantage of a simpler and robust detection module, and over one order of magnitude more sensitive than the best reported QEPAS-based sensors for CO\(_2\) detection (NNEA=4·10\(^{-9}\) W cm\(^{-1}\)Hz\(^{-1/2}\) [5]).

References


