Recent Advances in Infrared Semiconductor Laser based Chemical Sensing Technologies

F.K. Tittel, R.F. Curl, L. Dong, J.H. Doty, A.A. Kosterev, R. Lewicki, D. Thomazy, and G.Wysocki

Abstract Recent advances in the development of sensors based on the use of quantum cascade lasers (QCLs) for the sensitive, selective detection, quantification and monitoring of both small and large molecular gas species with resolved and unresolved spectroscopic features respectively will be described.

1 Introduction

Quantum cascade (QC) lasers and interband cascade (IC) lasers are convenient mid-infrared sources for ultra sensitive and highly selective trace gas monitoring as the result of recent advances in their fabrication. They can be fabricated to operate over a wide range of wavelengths from $\sim 3\mu$m to $\sim 20\mu$m. Continuous wave (cw) QCL devices capable of thermo-electrically cooled, room-temperature operation with a number of important practical features, including single mode emission with mode-hop free frequency tuning, high power (tens to hundreds of mW), and intrinsic narrow emission line width are commercially available in the $\sim$ 4–12 μm spectral region [1]. These spectral characteristics permit the development of compact, robust trace gas sensors [2–4]. For example, the Rice Laser Science group has explored the use of several methods for carrying out infrared laser absorption spectroscopy (LAS) with mid-infrared QCL and ICL sources, which include multipass absorption spectroscopy [2], cavity ring down spectroscopy (CRDS) [5], integrated cavity output spectroscopy (ICOS) [6], as well as photoacoustic spectroscopy (PAS) and quartz-enhanced photoacoustic spectroscopy (QEPAS) [1, 7–9]. These spectroscopic techniques permit the detection and quantification of molecular trace gases

F.K. Tittel, R.F. Curl, L. Dong, J.H. Doty, A.A. Kosterev, R. Lewicki, and D. Thomazy
Rice University, Houston, TX 77005, USA, e-mail: fkt@rice.edu

G.Wysocki
Princeton University, Princeton, NJ 08544, USA , e-mail: gwysocki@princeton.edu

with demonstrated detection sensitivities ranging from ppmv to pptv levels depending on the specific gas species and the detection method employed.

2 Overview of mid-infrared QCL and ICL based breath analyzers

High optical power and single frequency operation with good spectral purity and wide wavelength tunability of the laser source are the most critical characteristics for high performance chemical sensors. Single frequency operation is usually achieved by introducing a distributed feedback (DFB) structure into the QCL or ICL active region in order to favor a particular axial mode. Typically the maximum tuning range of DFB-QCLs, achieved by changing the laser injection current, is 3-4 cm^{-1}. This can be increased to $\sim$ 20 cm^{-1} by varying the temperature of the QCL chip. Because of the limited tuning range and the precision required in the fabrication of an embedded DFB structure, obtaining a DFB-QC laser that operates at precisely the desired wavelength is technically challenging. However, once obtained at the right wavelength, a mid-infrared DFB-QCL has a significant advantage of being very compact and robust making it for monitoring of a specific trace gas with resolved rotational structure from small molecular species. However a DFB-QCL with its limited spectral tuning range is not useful for monitoring a gas with a congested rotational spectrum, since it is difficult to scan far enough to ascertain the band profile of such an absorption band. However, the spectral width of the QCL optical gain profile is usually significantly broader than 20 cm^{-1} and therefore QCLs can provide in fact a much broader wavelength tuning range. Recent advances have resulted in very broad gain profiles. The bound-to-continuum QC laser design first proposed by Blaser et al. [10] and the heterogeneous QC structure first demonstrated by Gmachl et al. as a super-continuum QCL [11], are the most promising structures in terms of broadband emission, and have been further developed for wide single mode frequency tuning spectroscopic applications [12–15].

To take advantage of the broadband gain of such QCLs, an external cavity (EC) configuration can be used to obtain single mode operation at any wavelength within the laser gain profile. A widely tunable QC laser spectrometer implementing a novel EC-QCL architecture for high resolution spectroscopic applications and multi species trace-gas detection was demonstrated with a thermoelectrically cooled Fabry-Perot gain medium operating in a continuous wave mode at $\lambda \sim 5.28$ μm [14]. Such an instrument employs a piezo-activated cavity mode tracking system for mode-hop free operation. The mode-tracking system provides independent control of the EC length, diffraction grating angle and QCL current. The QCL gain medium allowed a coarse laser frequency tuning range of $\sim$ 155 cm^{-1} and a high resolution (better than 0.001 cm^{-1}) continuous mode-hop free fine tuning within a range of up to 2 cm^{-1} with a maximum available optical power of $\sim$ 11 mW. Commercial pulsed and cw, room temperature mid-infrared EC-QCLs are available
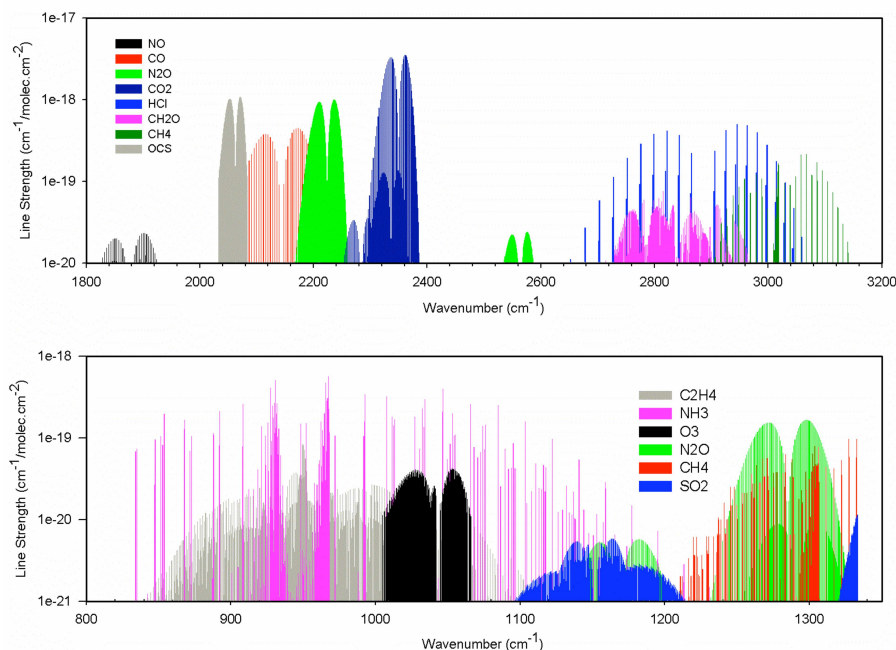
Fig. 1 Mid-infrared HITRAN simulation of absorption spectra of simple molecules.

from Daylight Solutions, Inc. with output powers ranging from 30 to 350 mW and frequency tuning ranges from 60 to 430 cm^{-1} fron 4.3–10.5 μm [1].

Detection sensitivity, selectivity and response time are the primary requirements for trace gas sensing. For small molecules with resolved rotational structure, optimum specificity is obtained by choosing an absorption line that is free of interference from other gases that might be present in the target sample (See Fig. 1). Furthermore, reducing the gas sample pressure sharpens the absorption line without reducing the peak absorption until the linewidth begins to approach the Doppler width. This sharpening of the absorption line also significantly improves selectivity. To obtain the best sensitivity both a strong molecular absorption line must be selected and a long effective optical pathlength must be used. High measurement precision and accuracy requires that absorption from baseline variations and laser power fluctuations can be identified. The first requirement is best met by choosing a line in a fundamental absorption band as this will be stronger than overtone or combinations bands. An effective long optical pathlength can be obtained by using multipass cells or cavity enhancement techniques. For sharp absorption lines, noise associated with laser power fluctuations can be greatly reduced by averaging rapid scans over an absorption line or by a wavelength modulation technique. The need to distinguish absorption from baseline variations is the most challenging. Every long

pass sensor configuration exhibits accidental etalons, which typically have widths comparable to the absorption line width. In principle, these can be removed by evacuating the cell, replacing the sample gas by a gas without absorption (ie "zero air" such as ultra pure nitrogen) and then dividing the sample trace by this background trace. This approach assumes that accidental etalons do not shift their pattern during the process of sample replacement.

Large molecules do not have resolved rotational structure as mentioned previously. Molecules with four heavy atoms or low frequency vibrational modes typically cause congested spectra. Because there is no nearby baseline to compare with, one way to detect absorption is also by pumping the sample out and replacing it with zero air. For weak absorptions expected for trace gas concentrations this imposes severe limits on long-term power stability of the laser source, the absence of low frequency laser noise, and baseline stability. Without a sharp rotational spectral component, the required long-term power stability is typically ~ 1 in 10^4. Furthermore in the mid-infrared fingerprint region, where many gases absorb, there may be other gases contributing to a broad absorption putting selectivity in jeopardy. An advantage of photoacoustic spectroscopy is that power and baseline stability requirements are reduced.

3 Photoacoustic spectroscopy (PAS) and Quartz-enhanced photoacoustic spectroscopy (QEPAS)

PAS is based on the photoacoustic effect, in which acoustic waves are produced by the absorption of modulated laser radiation by target trace gas species. By the use of an acoustic cell, which is acoustically resonant at the modulation frequency this is an effective method for sensitive trace gas detection. In contrast to other infrared absorption techniques, PAS is an indirect technique in which the effect on the absorbing medium and not the direct light attenuation is detected. Light absorption results in a transient temperature effect, which translates into pressure variations in the absorbing medium that can be detected by a sensitive microphone. PAS is ideally a background-free technique, since only the absorbing gas generates the signal. However, background signals can also originate from nonselective absorption of the gas cell windows (coherent noise) and external acoustic (incoherent) noise. PAS signals are directly proportional to the pump laser power and therefore maximum detection sensitivity can be realized conveniently with thermoelectrically cooled (TEC), high power QCLs and ICLs.

A novel approach to photoacoustic detection of trace gases, utilizing a quartz tuning fork (QTF) as a sharply resonant acoustic transducer, was first reported in 2002 [1, 6, 8, 16–18]. The basic idea of quartz enhanced photoacoustic spectroscopy (QEPAS) is to invert the common PAS approach and accumulate the acoustic energy not in a gas-filled acoustic cell but in a sharply resonant acoustic transducer. A natural candidate for such a transducer is crystal quartz, because it is a low-loss piezoelectric material. A nearly optimum commercially available quartz transducer
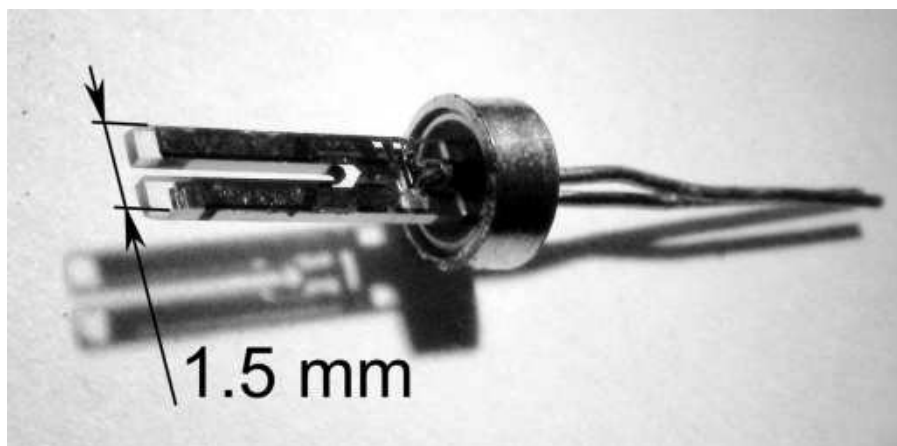
Fig. 2 Photograph of a quartz tuning fork. QTFs of this geometry are used in most QEPAS studies carried out at Rice University
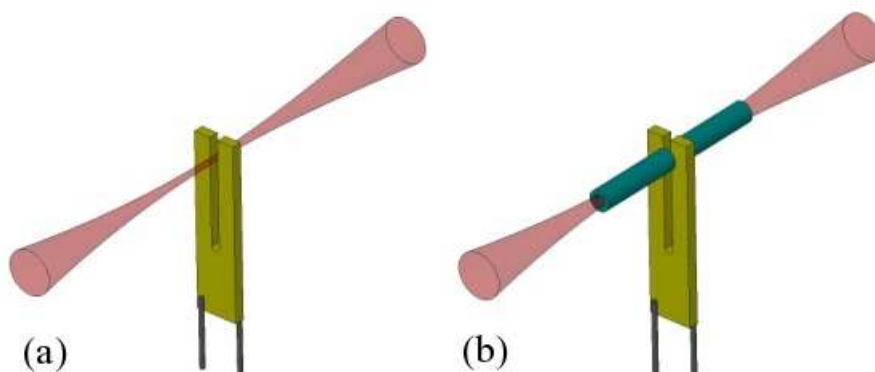

Fig. 3 QTF based spectrophones: (a) simplest configuration, (b) improved configuration with an acoustic resonator formed by two pieces of rigid tubing.

can be found in a quartz tuning fork (QTF) shown in Fig. 2. Commercial QTFs typically resonate at 32,768 (2^{15}) Hz developed as frequency standards for electronic clocks. A QEPAS absorption detection module or spectrophone consisting of a QTF equipped with an acoustic micro-resonator is depicted schematically in Fig. 3. In its simplest configuration (Fig. 3a) the laser radiation is focused between the prongs of the QTF and its wavelength is modulated at $f_m = f_0/2$ frequency or its intensity is modulated at $f_m = f_0/2$ frequency (where f_0 is the QTF resonant frequency) depending respectively on whether wavelength modulation or amplitude modulation of the excitation laser is used. The acoustic wave at f_0 induced by absorption of the

laser by the gas becomes the driving force to excite the anti-symmetric fundamental mechanical vibrations of the QTF prongs (i.e. the two QTF prongs move in opposite directions). Sound waves from distant acoustic sources tend to move the QTF prongs in the same direction, which results in zero net piezo-current thus making this element insensitive to such excitation. The electrical signal produced by this piezo-electrically active mode of vibration is picked up two pairs of electrodes deposited on the QTF prongs and measured using lock-in detection at f_0. Spectral data can be acquired by scanning the laser wavelength. To increase the effective interaction length between the radiation-induced sound and the QTF, a gas-filled acoustic micro-resonator consisting of two pieces of rigid tubing (See Fig. 3b) can be added to confine the optically generated acoustic vibrations in the gas. It was shown experimentally that the configuration (Fig. 3b) yields up to 30 times improvement of the signal-to-noise ratio (SNR) compared to configuration (Fig . 3a) depending on the gas composition and pressure. Sensor dimensions remain small, because the combined microresonator tubes length is in the 5–10 mm range, with a tube inner diameter of 0.4–0.8 mm. Therefore, most QEPAS based sensors utilize the configuration depicted in Fig. 3b. Other QEPAS spectrophone configurations are also possible, such as for example off-beam QEPAS [19].

Advantages of QEPAS compared to conventional resonant photoacoustic spectroscopy include a small sensor size comparable to the size of the excitation laser, sensor immunity to environmental acoustic noise (sensitivity is limited by the fundamental thermal QTF noise), a simple and low cost absorption detection module (spectrophone), a high Q factor (typically $\sim 10^5$ at atmospheric pressure), a large dynamic range (10^9) from thermal noise to breakdown deformation, wide temperature range up to 700K where the piezoelectric effect of quartz vanishes and the capability to analyze small gas samples, down to a few mm3 in volume. QEPAS allows excellent noise equivalent concentration levels (ppm to ppt). Considerable experimental and analytical progress has been made with QEPAS since 2002. Recently we have investigated the effect of humidity and 2-tube microresonator effects on detection sensitivity of different chemical species, in particular the diameter, length of the microresonators for QEPAS.

Applications include concentration measurements of single and multiple trace gas species for applications in such diverse fields as environmental monitoring, industrial process control and medical diagnostics [3].

The pressure corresponding to optimum sensitivity depends upon the V-T energy conversion cross-section of the gas of interest. It was experimentally found that this optimum pressure for fast-relaxing molecules with resolved optical transitions is $\sim$ 50 Torr, which also ensures Doppler-limited spectral resolution. For slow to relax gases such as NO or CO, this optimum pressure is higher. Most QEPAS sensors to date are based on $2f$ wavelength modulation (WM) spectroscopy, which allows suppression of coherent acoustic background that may be created when stray modulated radiation is absorbed by nonselective absorbers such as the gas cell elements and QTF itself. In this case, the noise floor is determined by thermal noise of the QTF [20]. For QEPAS $2f$ WM spectroscopy the laser wavelength must be modulated at half the resonant frequency of the QTF.

QEPAS excitation can also be performed in an amplitude modulation (AM) mode, although in this case a coherent acoustic background is also present. This background is directly proportional to the laser power reaching the spectrophone. Therefore, the sensitivity limit is no longer determined by the QTF thermal noise alone but also by the laser power fluctuations and spurious interference features. The AM mode must be used if the absorption feature of interest is spectrally so wide that fast modulation of the laser wavelength across this feature is not possible. This is often the case for large or heavy molecules, when individual rotational-vibrational transitions are not resolved and absorption bands look unstructured.

4 QCL Chemical trace gas sensing applications

Detection and identification of molecules with broad unstructured features requires wide spectral coverage, which can be achieved by using external cavity (EC) QCLs. First QEPAS measurements involving EC-QCL were reported in [14, 15]. For example, an EC-QCL tunable in the 1120-1240 cm^{-1} spectral range was used to quantify trace concentrations of freon 125 (pentafluoroethane) and acetone in nitrogen, added individually or simultaneously. Optical excitation modulation was achieved via 50% duty cycle on-off modulation of the laser injection current. A normalized noise equivalent absorption coefficient, (NNEA) $= 2.64 \times 10^{-9}$ $cm^{-1}W/Hz^{1/2}$ corresponding to ppbv levels, but separate measurements of coherent acoustic background in pure nitrogen and its subsequent subtraction from the signal was required.

Current modulation of an EC-QCL broadens its line width, preventing its use for high resolution spectroscopy. In order to preserve the intrinsically narrow line of a cw EC-QCL, its radiation must be modulated externally at ~ 32.7 kHz. One of the simplest way to carry out such a modulation is by using a second QTF as a mechanical chopper. With such a technique, it was possible to acquire high resolution AM QEPAS spectra of NO lines in N_2 at 600 Torr [21]. The voltage amplitude required to drive a QTF at its maximum sweep is $< 20V$ at resonance. If the QEPAS measurements are performed at reduced pressure and the chopping QTF is at the atmospheric pressure, there will be a mismatch of resonant frequencies. Such a mismatch can be corrected by adding a capacitor in series with the chopping QTF, which will up-shift its resonance frequency.

Significant progress has been made in the real time ammonia detection in exhaled human breath with both a distributed feedback and tunable external cavity quantum cascade laser based QEPAS sensor shown in Fig. 4 operating at ~ 10.5 μm. Ammonia is associated with liver and kidney disorders. NH_3 concentration levels exhaled from the lung by healthy subjects are typically of the order of hundreds ppb, whereas elevated levels (> 1 ppmv) indicate significant disease pathology.

Another application example of state-of-the-art QCL and ICL technology based on infrared laser absorption spectroscopy (LAS) is the opportunity to detect both in situ and remotely trace gases of specific interest to the International Atomic Energy Agency (IAEA), Vienna charged with the detection and verification of nuclear ma-
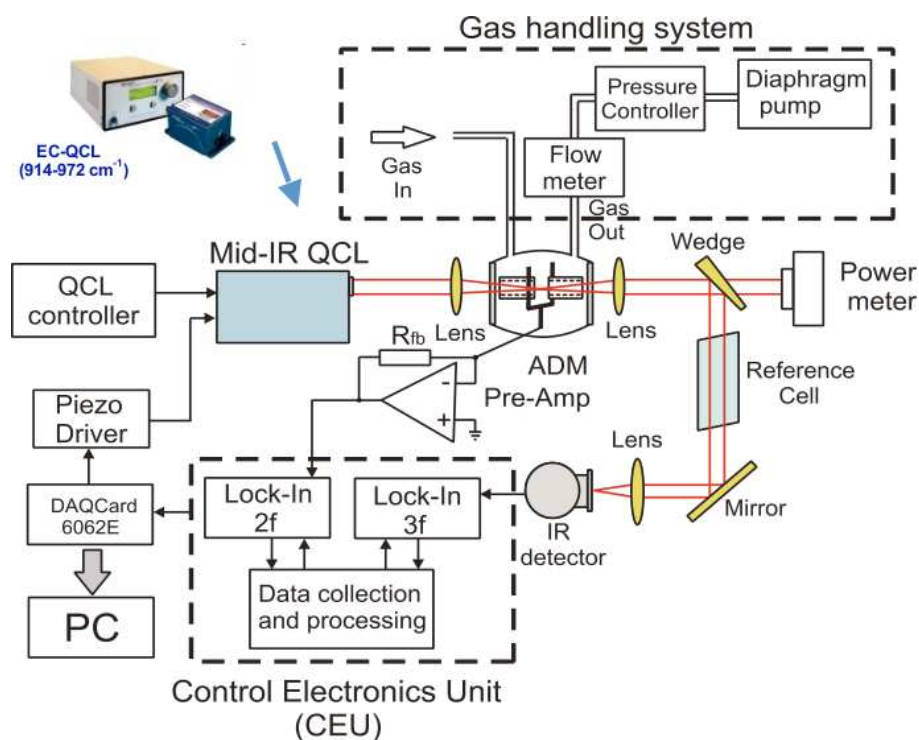
Fig. 4 Real-time breath sensor architecture for ammonia detection.

terials and activities on a global basis. LAS has been proposed as a spectroscopic technique that is capable of accurate uranium enrichment determinations of UF_6 samples [22] The current status of development of a cw, room temperature DFB QCL based spectroscopic source operating at 7.74 μm (1291 cm^{-1}) for use in field deployable sensor plaform will be described.

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