# Recent Advances and Applications of Mid-Infrared based Trace Gas Sensor Technology

F. K. Tittel, Y. Bakhirkin, A. Kosterev, R. Lewicki, S. So, G. Wysocki and R.F. Curl

Rice Quantum Institute, Rice University, 6100 Main St., Houston, TX 77005, USA

## ABSTRACT

Recent advances in the development of sensors based on infrared quantum cascade lasers for the detection of trace gas species is reported. Several selected examples of applications in environmental and industrial process monitoring as well as in medical diagnostics using quartz enhanced photoacoustic spectroscopy and laser absorption spectroscopy will be described.

**Keywords:** Laser spectroscopy, Quartz Enhanced Photoacoustic Spectroscopy, Mid Infrared Quantum Cascade Laser, External Cavity configuration

## 1. INTRODUCTION

There is an increasing need in many chemical sensing applications ranging from environmental science to industrial process control as well as medical diagnostics for fast, sensitive, and selective trace gas detection based on laser spectroscopy. The recent availability of continuous wave (cw) near infrared diode lasers-, mid-infrared quantum cascade and interband cascade distributed feedback (QC and IC) DFB lasers as mid-infrared spectroscopic sources addresses this need. A number of spectroscopic techniques have been demonstrated. For example, the authors have employed infrared DFB QC and IC lasers for the detection and quantification of trace gases and isotopic species in ambient air by means of direct absorption, cavity-enhanced, and photoacoustic spectroscopy. These spectroscopic techniques offer an alternative to non-spectroscopic techniques such as mass spectrometry (MS), gas chromatography (GC) and electrochemical sensors. The sensitivity and selectivity that can be achieved by both techniques (excluding electrochemical sensors) are similar, but the sensor response time, instrumentation size and cost of ownership for spectroscopic techniques can be advantageous as compared to MS-GC spectrometry.

## 2. CHEMICAL SENSING BASED ON TUNABLE THERMOELECTRICALLY COOLED CW QUANTUM CASCADE LASERS

The development of laser spectroscopic techniques strongly relies on increasing the availability of new tunable laser sources. For applications in the mid-IR molecular fingerprint region, QCLs have proved to be convenient and reliable light sources for the spectroscopic detection of trace gases.[1] Spectroscopic applications usually require single-frequency operation. This is achieved by introducing a DFB structure into the QCL active region or by placing a laser source into external cavity configuration. However, the range of wavelength tuning of the emitted laser radiation is limited by the DFB structures. Typically the maximum thermal tuning range of DFB-QCLs is $\sim 2$ cm$^{-1}$ achieved by laser current injection control or 10 cm$^{-1}$ by varying the temperature of the QCL chip. The development of bound-to-continuum QC

lasers[2] has led to device structures with intrinsically broader gain profile, because the lower state of the laser transition is a relatively broad continuum. A luminescence spectrum of 297 cm$^{-1}$ FWHM (full width at half maximum) at room temperature was observed for $\lambda \approx 10$ µm QCL devices employing bound-to-continuum transitions.[3] To take advantage of the broadband gain of such QCLs, an external cavity (EC) configuration can be used for wavelength selection.[4,5] Recently, even broader gain profiles with FWHM of ~350 cm$^{-1}$ were achieved by using a heterogeneous quantum cascade structure based on two bound-to-continuum designs emitting at 8.4 and 9.6 µm.[6] The development of a QC laser spectrometer for high resolution spectroscopic applications and multi species trace gas detection in the mid-IR based on the design and implementation of a novel EC-QCL architecture was described by Wysocki et al.[4]
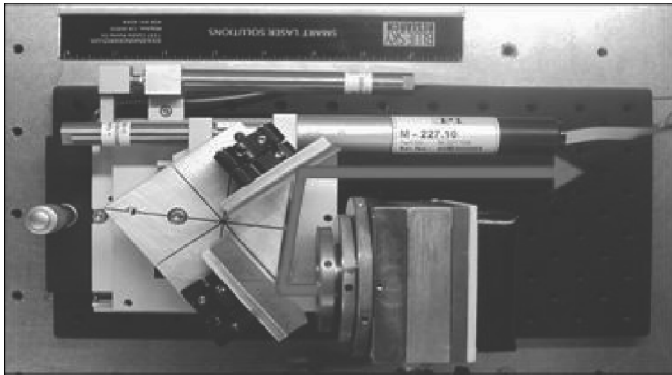


Fig. 1. Compact tunable external grating cavity quantum cascade laser

Figure 1 depicts the instrument configuration of an improved and miniaturized version of the source first reported in 2005. In this new design the collimated laser output beam is incident on the diffraction grating. The first order of diffraction beam provides feedback to the QCL and the zeroth order beam is used as the output for spectroscopic measurements. For a gain medium operating at ~5.3 µm in an EC-QCL architecture a total tuning range of ~155 cm$^{-1}$ was achieved by only changing the diffraction grating angle (Fig.2a). A continuous mode-hop free fine tuning range of ~ 2.5 cm$^{-1}$ can be obtained anywhere within the total tuning range by employing a piezo-activated cavity mode tracking system. The compact EC-QCL device equipped with the mode-tracking system provides independent control of the EC length, diffraction grating angle and laser current. For a 5.3 µm Fabry-Perot chip inserted in our EC configuration 11 mW of maximum optical power was obtained in a cw mode (see Fig. 2a) at quasi room temperature of -30$^{\circ}$C. The system performance and spectroscopic application capability was demonstrated by studying the fundamental absorption bands of both nitric oxide (NO) (Fig. 3) and a broadband absorbing molecule such as $C_2H_5OH$ (ethanol) with an unresolved absorption spectrum (Fig. 2b). The wide wavelength tunability of 155 cm$^{-1}$ and a narrow laser linewidth of <30 MHz, that allowed resolving spectral features separated by less than 0.006 cm$^{-1}$, makes such an EC-QCL an excellent light source suitable for high resolution spectroscopic applications and multiple species trace gas detection. As an example of high resolution spectroscopy, the mode hop free scan of NO at 1875.8 cm$^{-1}$ in the Q branch was recorded at a reduced pressure of 5 Torr for 5% NO in $N_2$ and is depicted in Fig. 3b. Access to the Q(3/2) transition of NO at 1875.8 cm$^{-1}$ allowed us to perform spectroscopic measurements of this molecule using a highly sensitive, selective and zero background method of laser magnetic resonance (LMR) spectroscopy.

The flexibility of the sensor arrangement makes it possible to use it with other QC lasers at other wavelengths without changing the EC configuration.[7] A QCL emitting at 8.4 µm resulted in a wavelength tuning range of 182 cm$^{-1}$ from 7.77 µm to 9.05 µm (Fig. 4a). This represents a total tuning range of 15.3% of the central QCL wavelength. The thermoelectrically cooled QCL operated at -30$^{\circ}$C and generated a maximum optical power of 50 mW in cw mode. High resolution spectroscopy with mode hop free tuning can be performed over a spectral range of up to 1.75 cm$^{-1}$ anywhere within the total effective active tuning range. A 8.4 µm EC-QCL sensor platform was used to acquire the respective spectra of two broadband absorbing molecules (Freon 125 and acetone) which are presented on Fig. 4b.[8]
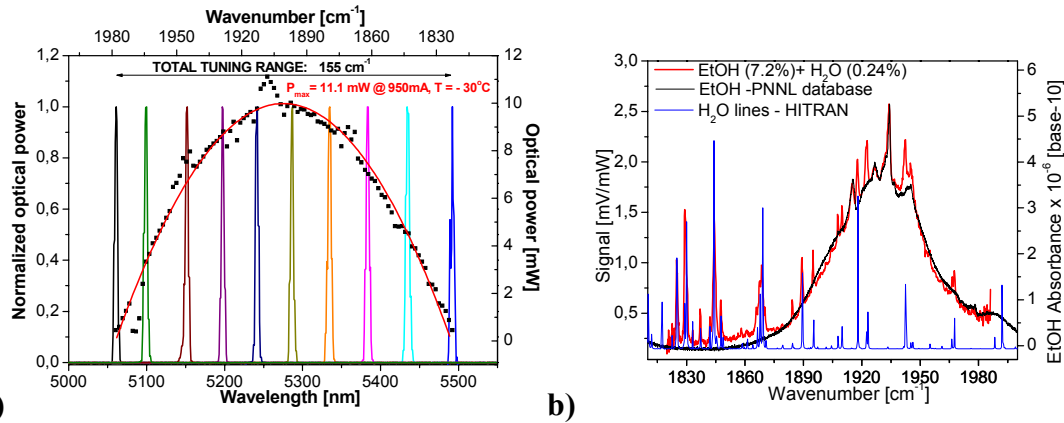
Fig. 2. a) Frequency tuning range and corresponding optical power of a 5.3 μm CW EC-QCL operating at 950mA and -30°C, b) Photoacoustic spectrum of gas mixture consisting of 7.2% ethanol and 0.24% H2O in $N_2$ as a buffer gas measured at atmospheric pressure using the 5.3μm EC-QCL (red line). Absorption spectra of ethanol (black line) and water vapor (blue line) obtained from the PNNL database and the HITRAN database respectively are plotted for comparison.
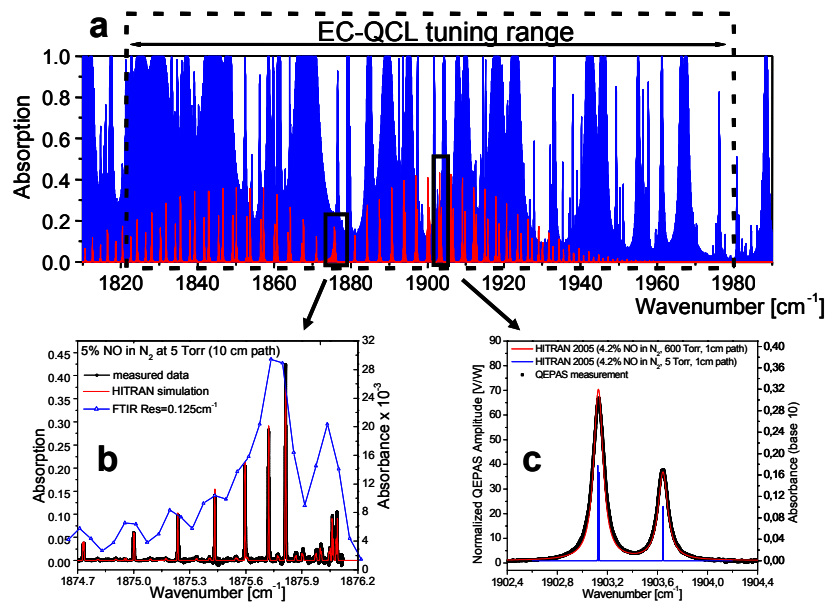


Fig. 3. a) Simulated absorption spectrum of nitric oxide at atmospheric pressure (in blue) and for 1 ppm NO (in red) for a 286m path length within the 5.3μm EC-QCL tuning range ($H_2O$ mixing ratio = 0.6%, $CO_2$ mixing ratio = 380 ppm, P=760 Torr, T= 276K), b) Direct absorption spectrum of the NO Q-branch recorded for 5% NO in $N_2$ at 5 Torr (black line) compared to a simulated HITRAN spectrum (red line) for the same conditions and to a high resolution FTIR spectrum (blue line), c) a QEPAS spectrum recorded for 4.2% NO in $N_2$ at ~1903$cm^{-1}$ (the strongest transition in the fundamental NO R-branch).
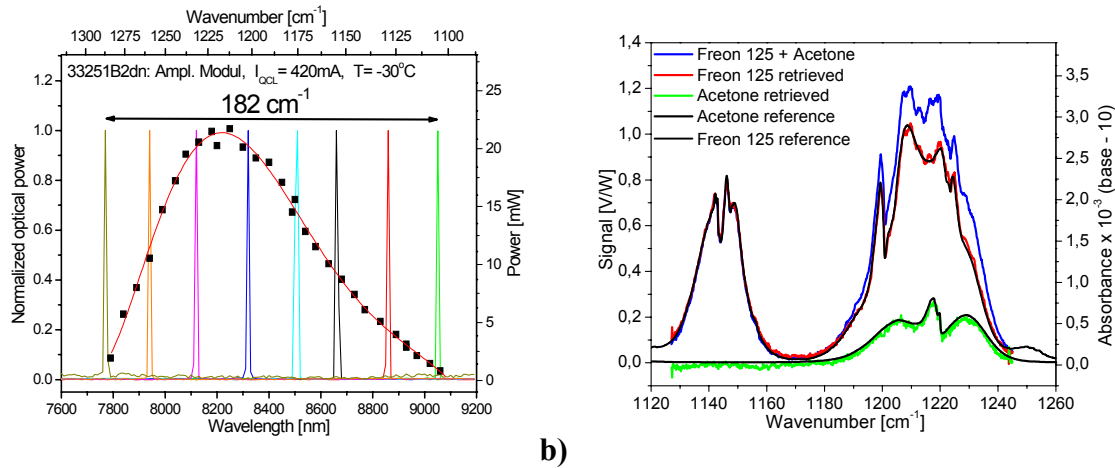
Fig.4. a) Frequency tuning range and corresponding optical power of a 8.4 μm CW EC-QCL operating at 420mA and -30°C, b) Photoacoustic spectrum of a Freon 125 and acetone mixture normalized to optical power plotted together with retrieved component spectra of Freon 125 (red line) and acetone (green line). The retrieved Freon 125 and acetone spectra were fitted using reference spectra from the PNNL spectroscopic database shown as a black line.

## 3. TRACE GAS DETECTION BASED ON LASER PHOTOACOUSTIC SPECTROSCOPY

Photoacoustic spectroscopy (PAS), based on the photoacoustic effect, in which acoustic waves result from the absorption of laser radiation by a selected target analyte in a specially designed cell, 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 absorption is detected. Light absorption results in a transient temperature effect, which then translates into kinetic energy or pressure variations in the absorbing medium via non-radiative relaxation processes that can be detected with a sensitive microphone. PAS is ideally a background-free technique, since the signal is generated only by the absorbing gas. However, background signals can originate from nonselective absorption of the gas cell windows (coherent noise) and external acoustic (incoherent) noise. PAS signals are proportional to the pump laser intensity and therefore, PAS is most effective with high power laser excitation. A sensitivity of 8 ppmv was demonstrated with only 2 mW of modulated diode laser power in the $CH_4$ overtone region.[9,10] The recent availability and implementation of high power cw DFB-QCL excitation in the fundamental absorption region leads to considerably improved trace gas detection sensitivity. 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.[11,12] 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 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 variety of packaged quartz crystals for use in timing applications is commercially available. Readily available low-frequency quartz elements are quartz tuning forks (QTF) intended for use in electronic clocks as frequency standards. These QTFs resonate at 32 768 ($2^{15}$) Hz in vacuum. A typical QEPAS absorption detection module (ADM) consisting of a QTF equipped with a micro-resonator is shown in Fig. 5. Only the antisymmetric vibration of a QTF (i.e. when the two QTF prongs bend in opposite directions) is piezo-electrically active. The laser beam is focused between the prongs of the QTF and its wavelength is modulated at $f_m = f_0/2$ frequency, where $f_0$ is the QTF resonant frequency. A lock-in amplifier is used to demodulate the QTF response at $f_0$. Spectral data can be acquired if the laser wavelength is scanned. To increase the effective interaction length between the radiation-induced sound and the QTF, an acoustic gas-filled resonator can be added similarly as in the traditional PAS approach. Acoustically, a QTF is a quadrupole, which results in excellent environmental noise immunity. Sound waves from distant acoustic sources tend to move the QTF prongs in the same direction, thus resulting in no photoacoustic response. Advantages of QEPAS compared to conventional resonant photoacoustic spectroscopy include QEPAS sensor immunity to environmental acoustic noise, a simple absorption detection module design, no spectrally selective element is required, applicable over a wide range of pressures, including atmospheric pressure and its

capability to analyze small gas samples, down to 1 mm$^3$ in volume.
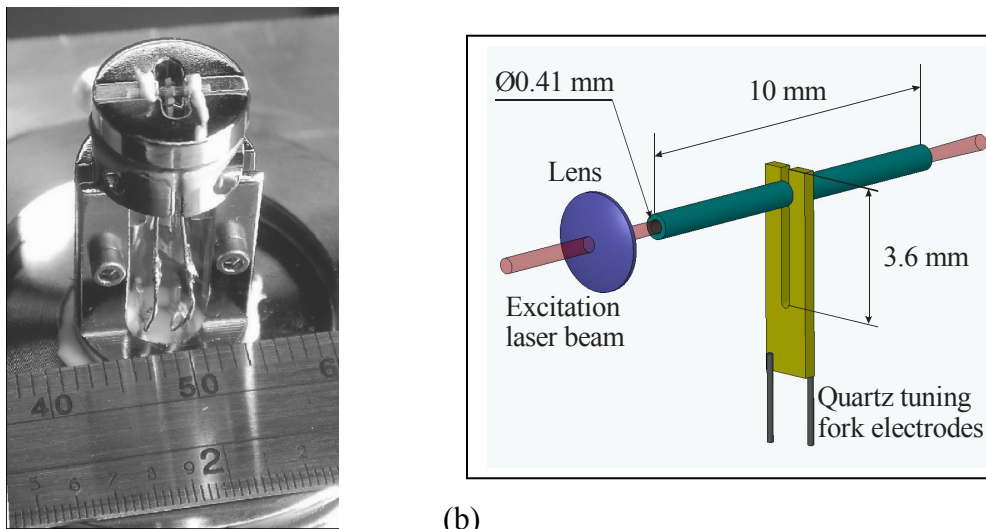


Fig. 5 (a) Photo of a QEPAS absorption detection module (ADM) with micro-resonator; (b) Schematic QEPAS ADM consisting of a quartz tuning fork (QTF) and an acoustic micro-resonator (two tubes on both sides of the QTF). All the elements except for the focusing lens are shown to scale.

QEPAS has already been demonstrated in trace gas measurements of $NH_3$,[13] $CO_2$,[14,15] $N_2O$,[16] HCN,[17] CO in propylene[18] and $CH_2O$.[19,20] The measured normalized noise equivalent absorption coefficient for $H_2O$ is $1.9\times10^{-9}$ cm$^{-1}$ W/Hz$^{-1/2}$ in the overtone region at 7306.75 cm$^{-1}$ is the best among the tested trace gas species to date using QEPAS and is indicative of fast vibrational–translational relaxation of the initially excited states. An experimental study of the long-term stability of a QEPAS-based $NH_3$ sensor[12] showed that the sensor exhibits very low drift, which allowed data averaging over >3 h of continuous concentration measurements.

Wojcik et al.,[21] demonstrated the performance of a novel infrared photoacoustic laser absorbance sensor for gas-phase species using an amplitude- modulated (AM) QCL and a quartz tuning fork microphone. A photoacoustic signal is generated by focusing 5.3 mW of a Fabry–Perot QC laser operating at 8.41 μm between the tines of a quartz tuning fork which served as a transducer for the transient acoustic pressure wave. The sensitivity of this sensor was calibrated using the infrared absorber Freon-134 a by performing a simultaneous absorption measurement using a 31cm absorption cell. The power and bandwidth normalized noise equivalent absorption sensitivity (NEAS) of this sensor was determined to be $2.0\times10^{-8}$ cm$^{-1}$ W/Hz$^{-1/2}$, which translates into noise equivalent concentration of 40 ppbv for the available QCL laser power and a data acquisition time of 1 s. We obtained a NEAS coefficient of $7.92\times10^{-9}$ cm$^{-1}$ W/Hz$^{-1/2}$ for Freon 125 measurements using the same AM technique with our 8.4 μm EC-QCL spectroscopic source. A minimum detection limit (1σ) of 9 ppb was obtained at 1208.62 cm$^{-1}$. Instead of amplitude modulation implemented by switching the QCL on and off, AM modulation can also be realized with an additional quartz tuning fork (QTF). The piezo electric element vibrates and acts as a mechanical chopper at 32 kHz frequency by applying voltage to the QTF electrodes. This minimizes the QCL chirp associated with the driver current modulation (Fig. 3c).

## 4. SUMMARY

Compact, sensitive, and selective gas sensors based on near infrared and mid infrared semiconductor lasers have been demonstrated to be effective in numerous real-world applications. These applications include such diverse fields as environmental monitoring (e.g. CO, $CO_2$, $CH_4$ and $H_2CO$ are important carbon gases in global warming and ozone depletion studies), industrial emission measurements (e.g. fence line perimeter monitoring in the petrochemical industry, combustion sites, waste incinerators, down gas well monitoring, gas pipeline and compressor station safety), urban (e.g. automobile traffic, power generation) and rural emissions (e.g. horticultural greenhouses, fruit storage and rice agroecosystems), chemical analysis and process control for manufacturing processes (e.g. semiconductor, pharmaceutical, food), detection of medically important molecules (e.g. NO, CO, $CO_2$, NH3, $C_2H_6$ and $CS_2$), toxic gases, drugs, and explosives relevant to law enforcement and public safety, and spacecraft habitat air quality and planetary atmospheric science (e.g. such planetary gases as $H_2O$, $CH_4$, CO, $CO_2$ and $C_2H_2$).

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