

Photoacoustic spectroscopy for trace gas detection with cryogenic and room-temperature continuous-wave quantum cascade lasers

Research Article

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Abstract:

The main characteristics that a sensor must possess for trace gas detection and pollution monitoring are high sensitivity, high selectivity and the capability to perform in situ measurements. The photoacoustic Helmholtz sensor developed in Reims, used in conjunction with powerful Quantum Cascade Lasers (QCLs), fulfils all these requirements. The best cell response is $\# 1200 \text{ V W}^{-1} \text{ cm}$ and the corresponding ultimate sensitivity is $\# 3.3 \times 10^{-10} \text{ W cm}^{-1} \text{ Hz}^{-1/2}$. This efficient sensor is used with mid-infrared QCLs from Alpes Lasers to reach the strong fundamental absorption bands of some atmospheric gases. A first cryogenic QCL emitting at $7.9 \mu\text{m}$ demonstrates the detection of methane in air with a detection limit of 3 ppb. A detection limit of 20 ppb of NO in air is demonstrated using another cryogenic QCL emitting in the $5.4 \mu\text{m}$ region. Real in-situ measurements can be achieved only with room-temperature QCLs. A room-temperature QCL emitting in the $7.9 \mu\text{m}$ region demonstrates the simultaneous detection of methane and nitrous oxide in air (17 and 7 ppb detection limit, respectively). All these reliable measurements allow the estimated detection limit for various atmospheric gases using quantum cascade lasers to be obtained. Each gas absorbing in the infrared may be detected at a detection limit in the ppb or low-ppb range.

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1. Photoacoustic spectroscopy for trace gas detection

The photoacoustic (PA) technique is being increasingly used for in-situ pollution monitoring. This has practical applications in a variety of areas: ambient air monitoring, the industrial environment, agricultural monitoring, medical diagnostics, etc. The main characteristics that must be achieved are a high sensitivity, a high selectivity and the

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ability to perform in situ measurements. The PA technique fulfils all these requirements: the technique is intrinsically sensitive, the use of laser sources allows selectivity, and the PA sensors are compact and robust set-ups. Many teams across the world are currently working with this technique. One can cite the Sigrist team from Switzerland currently developing, for example, the Differential Mode Excitation PhotoAcoustic (DEM-PA) technique [1], the Harren team from the Netherlands working with Optical Parametric Oscillators (OPOs) [2], the Tittel team developing the Quartz Enhanced PhotoAcoustic Sensor (QEPAS) [2, 3], the Hess team from Germany [4], the Szabo team from Hungary [5, 6], the Kauppinen team from Finland currently developing the cantilever system [7], the Ponomarev team from Tomsk – Russia [8], or the Li team from China [9].

The PA technique for trace gas detection consists of sending modulated radiation into a sample gas cell containing a microphone. Any absorbed radiation will be, in general, converted to thermal energy of the gas through collisions, thus leading to a modulated pressure detectable with a microphone. For low concentrations of absorbing molecules the PA signal is proportional to the response of the cell R_C , the microphone sensitivity R_M , the laser power W_0 , the gas concentration c , and the absorption coefficient of the gas K :

$$U = R_C \times R_M \times W_0 \times c \times K. \quad (1)$$

The potential of PA systems at atmospheric pressure is determined by parameters such as the responsivity:

$$R = R_C \times R_M \text{ (V} \cdot \text{W}^{-1} \cdot \text{cm)} \quad (2)$$

and the ultimate sensitivity:

$$\Lambda = \sqrt{U_n^2} / R(W \cdot \text{cm}^{-1} \cdot \text{Hz}^{-1/2}), \quad (3)$$

where $\sqrt{U_n^2} \text{ (V} \cdot \text{Hz}^{-1/2})$ is the root-mean-square value of total noise intensity.

The cell responsivity, and the ultimate sensitivity, may be experimentally determined when the PA cell contains a gas with a known concentration. The minimum detectable gas concentration at atmospheric pressure c_{min} may then be obtained by:

$$c_{min} = \Lambda / (W_0 \times K). \quad (4)$$

When constructing PA cells, the acoustic resonance in a cell volume is commonly used in, for example, excitation of longitudinal modes, radial modes or azimuthal modes. The resonant PA cells provide improvement in the signal to noise ratio (SNR) and the realization of a continuous

gas flow through the PA cell. The sophisticated design of resonant PA cells enables, in particular, the suppression of the external acoustic noise caused by the gas flowing through the cell.

The Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France), in collaboration with the Institute of Atmospheric Optics (IAO, Tomsk, Russia), has developed since 1997 a PA cell based on differential Helmholtz resonance for infrared gas detection in the gas flow mode of operation. This sensor makes it possible to amplify by a factor of 2 the signal amplitude and to significantly decrease the external acoustic noise. The design of the differential Helmholtz resonator PA sensor and a detailed examination of its characteristics were first presented in [10]. The PA detector consists of two 10cm long cells with two 10 cm long capillaries, in a total volume of less than 20 cm³. Various prototypes were produced: glass cells equipped with electret microphones and metal cells equipped with condenser microphones from Bruel&Kjaer used in conjunction with low-noise preamplifiers. The cell sensitivities have been successively improved up to $R \# 700 \text{ V W}^{-1} \text{ cm}$ [11]. Using a simple mirror at the end of the cell, thus increasing the path-length by a factor 2, the cell sensitivity increases up to $R \# 1200 \text{ V W}^{-1} \text{ cm}$. The noise limit is approximately 0.4 μV in the static mode with an integration time of 1 second. This limit increases by a factor 2 when using the sensor in the flow mode. The corresponding ultimate sensitivity is $\Lambda = 3.3 \times 10^{-10} \text{ W cm}^{-1} \text{ Hz}^{-1/2}$. The characteristics of this sensor are of the same order of magnitude as those found by other teams, for example the quartz resonator of the Tittel team which possesses an ultimate sensitivity of $\# 30\text{--}40 \times 10^{-10} \text{ W cm}^{-1} \text{ Hz}^{-1/2}$ [12, 13], and the cantilever tested on CO₂ whose ultimate sensitivity is $\# 1.5 \times 10^{-10} \text{ W cm}^{-1} \text{ Hz}^{-1/2}$ [14].

The best version of the Helmholtz sensor has been tested in conjunction with near-infrared diode lasers. The tested gas was methane and the reference concentrations were 100 ppm, 1000 ppm and 3% of methane in air. The room-temperature (RT) diode lasers (DL) from Sensor Unlimited (SU) and Anritsu (Anr) both emit in the 1.65 μm region on the R(3) absorption line of the $2\nu_3$ band of methane. The values of the corresponding experimental photoacoustic signals are represented in Fig. 1.

The black squares and circles correspond to the Sensor Unlimited and Anritsu results respectively. Fig. 1. demonstrates that the photoacoustic signal is proportional to the gas concentration. The experimental detection limit is obtained by extending the experimental line until it cuts the noise limit, *i.e.* 0.4 μV at a signal to noise ratio of 1. The SU limit is estimated as 1 ppm and the Anritsu limit as 0.15 ppm. This difference is due to the emitted power of

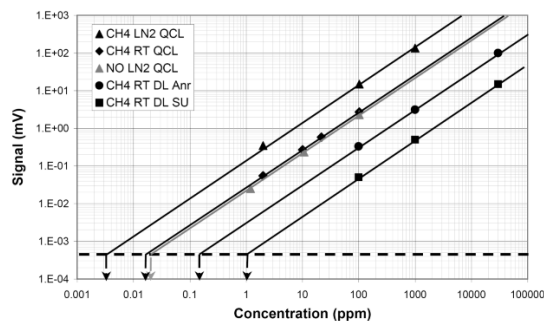


Figure 1. Photoacoustic signal *versus* gas concentration using various lasers. The signal is clearly proportional to gas concentration as expected in photoacoustic measurements. All the lines are parallel. The detection limits for all the gases and all lasers are estimated by extending the parallel lines until they cut the noise limit, *i.e.* 0.4 μ V at a signal to noise ratio of 1. Note that this figure demonstrates the high dynamic range of photoacoustic measurements: up to 6 orders of magnitude. See text for more details.

the lasers as expected by Eq. (1): around 1.5 mW for the SU laser and around 10 mW for the Anritsu laser.

Photoacoustic detection is an indirect method of measurement. The recorded signal is related to the heat created by the relaxation of excited molecules. At atmospheric pressure, the primary source of relaxation is collisions, where collisional relaxation times have to be much shorter than the period of laser modulation. This condition is generally well fulfilled in PA schemes, however a study by Schilt [15] has shown that PA measurements of methane in air can be affected by the resonant vibration to vibration energy transfer occurring in $\text{CH}_4\text{--O}_2$ collisions. The relaxation of the vibrational state of O_2 is very slow: collisional de-excitation time is 25 ms, which means that it is longer than the acoustic wave period in the cell. Schilt noted an unexpected parabolic response of his PA spectrometer *versus* methane concentration in dry air. On the other hand, water vapour is known to promote relaxation of O_2 [15, 16]. Calibration with dry air can lead to an under-estimation of the response of the cell, as the global response of a PA spectrometer is expected to increase with humidity in air. These effects were not observed when calibrating our PA sensor, even at the weaker methane concentration. This may be explained by a small contamination by water vapour in the cell and the weak frequency used (usual PA resonances are in the kHz range). None of our measurements on ambient air leads us to think to a calibration problem due to water vapour.

The results presented in this introduction are the best achieved with commercial diode lasers and the developed differential Helmholtz PA sensor. Thus the limitation of the diode lasers, in particular in terms of emitted power, is the main limitation of the gas detection limits to the

ppm range. The GSMA team has used new-generation Quantum Cascade Lasers to improve the gas detection limits. These lasers emit in the mid-infrared region thus permitting one to reach the strong fundamental absorption bands. Moreover these lasers are powerful. Those two qualities are very interesting for photoacoustic gas detection.

2. Gas detection with quantum cascade lasers

The Quantum Cascade laser (QC laser or QCL) is a semiconductor laser involving only one type of carrier and is based upon two fundamental phenomena of quantum mechanics, namely tunnelling and quantum confinement. Although the basic concept was proposed in the seventies, it took more than twenty years before an actual device was demonstrated in 1994 [17]. In conventional diode lasers, the light emission originates from the recombination of electrons and holes across the energy gap existing between the conduction and valence bands of the crystal. The energy separation between the two bands thus determines the lasing wavelength. The QC laser is based on a different approach. In a QCL there is no electron-hole recombination: electrons transitions between bound states created by quantum confinement in ultrathin alternating layers of semiconductors materials. The spacing between the steps depends on the width of the well, and increases as the well size is decreased. Thus the emission wavelength depends on the layer thicknesses and not on the bandgap of the constituent materials. This has allowed the realization of lasers with emission wavelengths across the mid-infrared range using the same base semiconductors than near-infrared lasers (GaAs/AlGaAs material system).

Due to problems of energy dissipation in the material, the first prototypes of continuous-wave QCLs emitted only at cryogenic temperatures, *i.e.* the temperature of liquid nitrogen (LN2). This proves detrimental to the ability to conduct *in situ* measurements, as illustrated in Fig. 2a. The QCL need to be installed within a large cryostat (# 40 cm high) that must be filled every 8 hours. The progression in QC laser technology has been exponential during the last ten years, with recent prototypes able to function at room-temperature (RT), and as a result the use of liquid nitrogen is no longer required. A typical QCL installed in a Laboratory Laser Housing from Alpes Lasers² is pre-

² www.alpeslasers.com

sented in Fig. 2b. The right part of Fig. 2b is identical to the right part of Fig. 2a, demonstrating the utility of RT QCL for conducting in situ measurements. In this set-up a short-focal ZnSe lens (diameter 25 mm, focal length 25 mm) is used to collect the laser beam. The Helmholtz PA sensor is installed just in front of the cryostat and a gold mirror is placed at the outside of the cell. The laser beam is usually focalised near the output of the cell. The acoustic signal is measured with two high sensitivity microphones (Bruel & Kjaer 4179) and sent on a lock-in amplifier (EG&G model 5301). Data are recorded on a laptop computer by a National Instrument acquisition card with a 10 or 1 Hz sampling rate.

The amplitude modulation of the laser beam uses a mechanical chopper rotating at the resonance frequency of the cell, *i.e.* 315 Hz. A slow linear current ramp tunes the laser across the target line with a typical amplitude of the ramp of 40 mA to 50 mA, which enables tuning to approximately 1 cm^{-1} . The integration time is usually set to 1 s, with scan duration of between 2 and 3 min. This solution was used for laboratory measurements because it is the most satisfactory from a spectroscopic point of view as it allows the direct fitting of a calculated spectrum to the experimental one in order to obtain the concentration. Another technique termed ‘on-off modulation’ is obtained by a modulation between the center of the line and a point out of the line, generally with a square waveform amplitude modulation of the laser. In this case the obtained signal is directly proportional to the concentration of the target molecules if the line is well isolated. This method is very efficient for the realization of an in situ sensor as it permits one to use a modulation of the QCL current driver instead of a mechanical chopper. Moreover, the value of the concentration in obtained in one measurement point *i.e.* in one second.

3. Liquid nitrogen and room-temperature quantum cascade lasers for CH₄ and NO detection

The developed PA sensor has been successively used with LN₂ and RT quantum cascade lasers in order to detect various gases in the atmosphere. In order to continue the work developed with diode lasers, we chose to continue with the detection of methane in air. The motivation behind this choice of gas was the need of gas companies which are confronted with the leak of methane from their gas distribution networks. The typical commercial methane detectors based on flame ionization are non-specific to methane, and other pollutants such as C₂H₄, C₃H₈ *etc.* may introduce false alarms. Moreover the flame

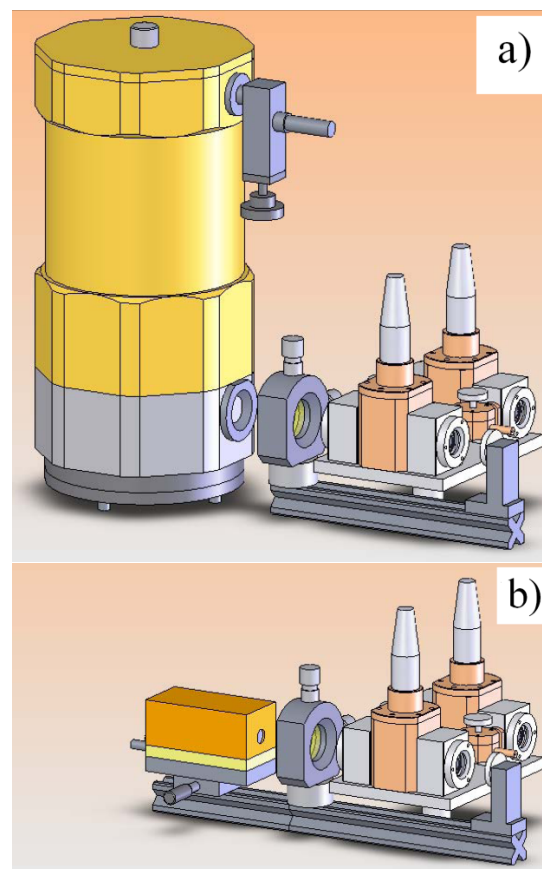


Figure 2. Photoacoustic sensor with cryogenic quantum cascade laser (a) and with room-temperature quantum cascade laser (b)

ionization technique requires the use of hydrogen which is highly combustible. A portable methane detector would prove a useful tool for gas companies, and the developed PA sensor described here fulfils the requirement.

The first QCL purchased from Alpes Lasers emits in the $7.9\text{ }\mu\text{m}$ region on the ν_4 band of methane [18]. Six transitions of this band between 1266 and 1273 cm^{-1} can be reached with a temperature ramp from 90 to 150 K. Heating is provided by a temperature controller (LakeShore 340). The QCL is driven to its working current with a ILX Lightwave LDC 3744B. Wavelength variation is obtained by a temperature ramp, at a working current of 500 mA. At this current the tuning rate of the QCL is $-0.09\text{ cm}^{-1}\text{ K}^{-1}$. The lines have intensities of about $6 \times 10^{-20}\text{ cm}^{-2}/\text{molecule cm}^{-1}$ according to the HITRAN database [19], *i.e.* about 20 times stronger than the R(3) line of the $2\nu_3$ band. The laser can operate at a power up to 80mW at a temperature of 80 K according to Alpes Lasers. However, as has been previously noted the cryostat window diaphragms a part of the beam, due to the

divergent nature of QCLs. Moreover, the methane line of interest is reached for a higher working temperature of the laser and some losses happen on the path of laser beam: absorption or reflections on the lens, or on the cell windows. This explains that the effective power in this experiment is only approximately 30 mW. The detection limit can be estimated, as for laser diodes, by extending the experimental line until it cuts the noise limit at a signal to noise ratio = 1: we find here a limit of 3 ppb. This result is demonstrated in Fig. 1 and was obtained with certified

mixtures of 2 ppm, 100 ppm and 1000 ppm of methane in air.

The experimental detection limit corresponds well to the theoretical value calculated from the laser diodes results, with the improvement of the absorption coefficient (due to stronger fundamental absorption line) and the increase of the incident power. All the characteristics of the diode and QC lasers, absorption wavelength and experimental and theoretical results are summarized in Tab. 1.

Table 1. Summary of the detection limits obtained with the photoacoustic sensor and various laser diodes (LD) or quantum cascade lasers (QCL) for the detection of atmospheric gases.

Gas	Wave number (cm^{-1})	Wave length (μm)	Absorption Coefficient (cm^{-1})	Laser Type	Laser Power (mW)	Calculated Detection limit (ppb)	Experimental Detection limit
CH ₄	6047	1.65	0.356	DL	1.6	1170	1 ppm
CH ₄	6047	1.65	0.356	DL	11	170	0.15 ppm
CH ₄	1270.78	7.87	7.28	QCL	32	2.9	3 ppb
NO	1857.27	5.38	13.2	QCL	2.8	18.0	20 ppb
CH ₄	1277.45	7.83	4.6	QCL	8	18.1	17 ppb

The second QCL also purchased from Alpes Lasers emits in the 5.4 μm region on the main absorption band of nitric oxide [20]. Nitric oxide is a very important molecule in atmospheric chemistry. It has been studied for years because of its role in the depletion of the ozone layer. NO is one of the main pollutants produced by combustion in industrial plants and transport exhausts, and its concentration at ground level has to be monitored due to its role in the formation of acid rains and smog. Moreover, interest for NO detection has been brought back by the discovery of its importance in human physiology, particularly in the cardiovascular system. NO can also be used as a marker of lung inflammations such as asthma. NO is also considered as a good marker to diagnose the inflammations of the lower airways and to evaluate the effectiveness of treatments.

The QC laser was operated between 100 and 150 K, at a current of 780 mA. Heating is provided by a temperature controller (LakeShore 340) and the QCL is driven to its working current with a ILX Lightwave LDC 3744B. The tuning range in this temperature scan extends from 1862 to 1857 cm^{-1} , which covers two doublets of the P branch of NO band: P(4.5) and P(5.5). The maximum output power of this laser was 9 mW, but it was generally operated at temperature above 140 K and the useful power was then

less than 3 mW. The detection limit is 20 ppb. This result is demonstrated in Fig. 1 and was obtained with certified mixtures of 1.2 ppm, 10 ppm and 100 ppm of nitric oxide in nitrogen. The experimental detection limit is in good agreement with what is expected when using previous calibration of our sensor (see Tab. 1). This result may be improved in a very simple manner. Continuous-wave QC lasers working at room temperature are now available at Alpes Lasers, in the 5.2 μm region, and show sufficient power to enable the construction of a NO PA sensor. When used with our sensor, such a device could lead to detection of NO in the low-ppb range.

The third QC laser from Alpes Lasers emits in the 7.9 μm region [21]. This QCL is a thermoelectrically cooled laser emitting between 1276 and 1283 cm^{-1} . The QCL operates between 243 and 303 K and the maximum current is 530 mA. The temperature and the current are stabilized by a model ILX LightWave 3744B temperature and current controller. The region reached with this laser is presented in Fig. 3. The strongest water line is a doublet at 1276.62 cm^{-1} . Two methane lines can be seen on this wavenumber region, at 1276.84 and 1277.47 cm^{-1} . According to the HITRAN database [19], the line intensity at 1277.47 cm^{-1} is a little bit weaker than the 1270.78 cm^{-1} one (see Tab. 1). The laser power is weaker as well: for

the methane measurements, the useful power was 8 mW for a working temperature of 283 K instead of 32 mW for the cryogenic laser. Photoacoustic signal is both proportional to the laser power and to the absorption coefficient. This means that in the same experimental conditions, a loss of sensitivity of a factor of around six with the RT laser compared to the cryogenic QCL was obtained. This drawback is offset by the obtained precision gain thanks to the absence of any strong water line overlapping the methane line. With the cryogenic laser, the water lines hide the N_2O lines in the same region, and it was impossible to fit the nitrous oxide concentration. On the contrary, with the RT laser, it was possible to quantify both methane and nitrous oxide. However, sensor calibration was not performed for the nitrous oxide and the response was estimated by using the calibration for methane and the spectroscopic data for N_2O of the HITRAN database. Some experimental and fitted spectra are presented in Fig. 3. This figure demonstrates the ability of the sen-

sor to detect methane and nitrous oxide in ambient air. The retrieved air concentrations for methane and nitrous oxide are given in the figure and are in very good agreement with the expected values in air (1.8 ppm for CH_4 and 320 ppb for N_2O).

The CH_4 detection limit is 17 ppb. This result is demonstrated in Fig. 1 and was obtained with certified mixtures of 2 ppm, 10 ppm, 20 ppm and 100 ppm of methane in air. The experimental detection limit is in very good agreement with what is expected when using previous calibrations of our sensor (see Tab. 1). The calculated N_2O detection limit using the spectroscopic data for N_2O of the HITRAN database [19] is 7 ppb. One can verify in Tab. 1 that the limiting factor for detection limit is the laser power. As for the NO results, a new-generation of continuous-wave QC lasers working at room temperature are now available. The increasing power of these lasers should permit the detection of CH_4 and N_2O in the low-ppb range.

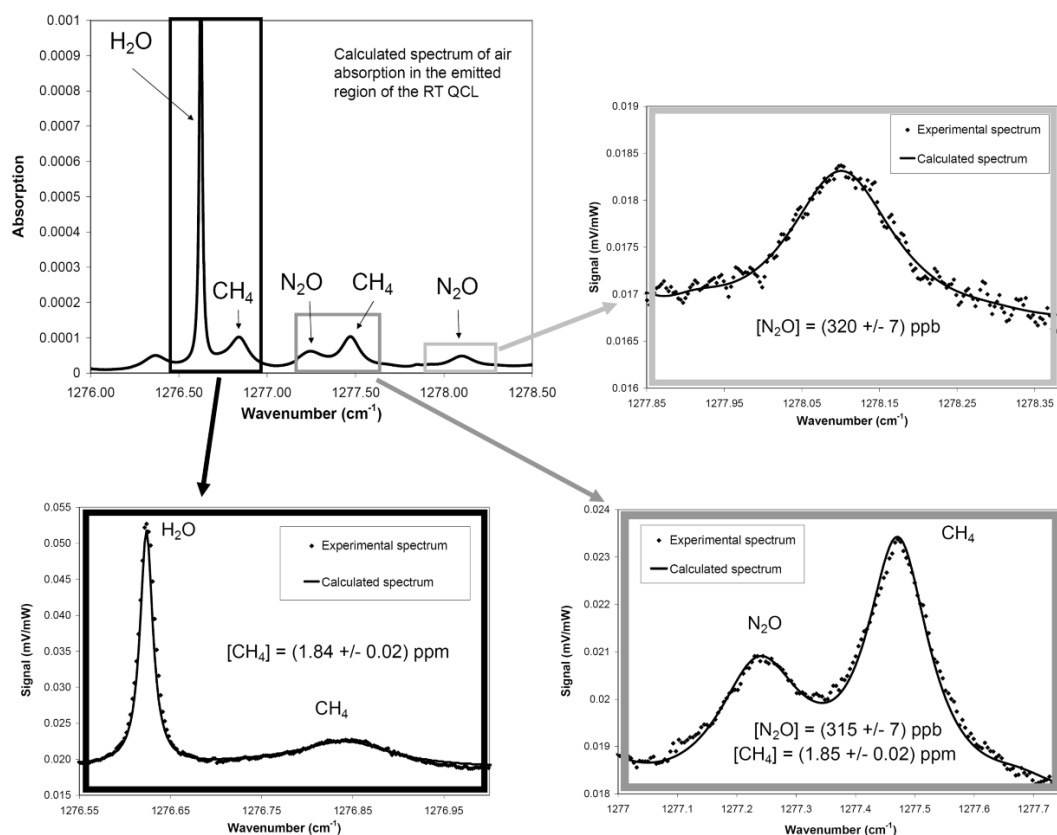


Figure 3. Calculated and experimental spectra of air absorption in the emitted region of the room-temperature quantum cascade laser. In the upper left a calculated absorption spectrum is shown, demonstrating that the whole region that can be achieved with the RT QCL. The black, gray and light-gray rectangles present examples of recorded PA signals (in mV/mW) with the corresponding calculated fitted spectra in order to obtain the atmospheric concentrations. Each experimental point is obtained in one second.

Table 2. Calculated detection limits using the developed photoacoustic sensor.

Gas	Wavelength (μm)	Absorption coefficient (cm^{-1})	Detection limit (ppb)
CO ₂	4.2	376	0.1
N ₂ O	4.5	99	0.3
CO	4.6	58	0.5
OCS	4.8	50	0.5
H ₂ O	5.9	25	1
NO ₂	6.1	15	2
SO ₂	7.3	4	7
C ₂ H ₂	7.4	13	2
HNO ₃	7.5	2	12
H ₂ O ₂	7.8	3.5	8
HOCl	8.0	4.5	6
COF ₂	8.0	3.5	8
O ₃	9.5	4	6
NH ₃	10.3	42	1
C ₂ H ₄	10.5	7.5	4

4. Quantum cascade laser photoacoustic spectrometry for the detection of atmospheric gases

We have demonstrated in previous sections that:

- our PA sensor gives reliable measurements: all lines in Fig. 1 are parallel, *i.e.* the cell responsivity is well known;
- the quantum cascade lasers are very good infrared sources for in situ gas detection.

This well-known comportment of the photoacoustic Helmholtz sensor allows the estimated detection limit for various atmospheric gases using quantum cascade lasers to be obtained. Tab. 2 gives calculated detection limits of gases absorbing in the infrared where QCLs exist.

The first column of this sensor is the detected gas. The second column corresponds to the best value of laser wavelength where the absorption coefficient (column 3) is the higher. The last column gives the estimated detection limit with the Helmholtz photoacoustic sensor considering a laser power of 25 mW, which is consistent with the traditional QCL power values. All the detection limits are in the ppb or sub-ppb range. These results are very interesting since the same instrument, *i.e.* the Helmholtz PA sensor, may be used for the detection of all these gases whatever the region. This is impossible with other

**Figure 4.** Photograph of the new glass cell photoacoustic spectrometer.

techniques for trace gas detection such as Cavity Ring Down Spectroscopy, where the mirrors of the cavity must be carefully chosen as a function of the laser wavelength emission.

Some of the detected gases may break up the sensor during the calibration procedure when using quite highly concentrated mixtures. For this reason we have developed a glass cell based on the previous metal model. A photograph of this prototype is presented in Fig. 4. Previous glass prototypes were used with small electret microphones and the cell responsivity was less than using Bruel&Kjaer microphones. This new prototype has the same dimensions as the metal variant, but combines the cheap glass material with high sensitivity and low-noise microphones. This type of cell will be easier to develop and to copy. We currently test this cell in term of responsivity. This value should be equivalent to those of the metal cell. It will soon be used with other QCLs for the detection of various gases.

5. Conclusion and outlook

The photoacoustic sensor developed by the Groupe de Spectrométrie Moléculaire et Atmosphérique (Reims, France), used in conjunction with cryogenic and room-temperature quantum cascade lasers, is an effective technique to detect atmospheric gases to the ppb level. The main advantages are an intrinsically high sensitivity, a large dynamic range and a comparatively simple experimental set-up. The feasibility of CH₄ or NO detection in air has been demonstrated. The improvements in quantum cascade lasers makes it possible to detect the desired gas with mid-infrared absorption.

The Helmholtz sensor used with QCLs has all the needed

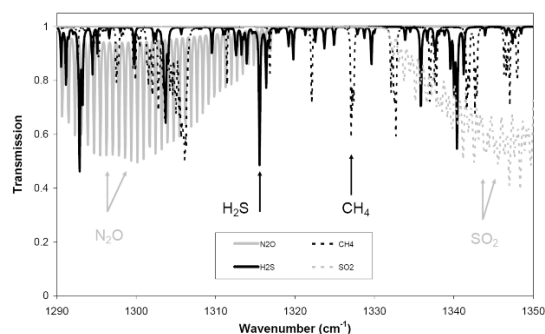


Figure 5. Calculated spectrum of 2 ppm of N_2O , 200 ppm of H_2S , 2 ppm of CH_4 and 2 ppm of SO_2 absorptions in the $7.6\ \mu\text{m}$ region. Arrows indicate the best lines to detect the gases without interferences from other gases. An external-cavity QCL emitting on $60\ \text{cm}^{-1}$ permit the simultaneous detection of many gases, a process which is impossible with a conventional QCL (max $6\ \text{cm}^{-1}$ emission).

characteristics for gas detection: high sensitivity, high selectivity and the possibility of in situ measurements. The only exception to this is a lack of high tuning. Conventional QCLs emit on $3\text{--}5\ \text{cm}^{-1}$ which is too weak for real multi-gas applications. The next step will be to improve the emission range of the quantum cascade lasers. This can be realized by using an external cavity with the laser [22, 23]. This kind of set-up will enable real multi-gas detection or the detection of bigger molecules such as Volatils Organic Compounds, explosives or pesticides whose infrared signature is larger than small molecules. For example, an external cavity quantum cascade laser emitting in the $10\ \mu\text{m}$ region could be capable of the simultaneous detection of ammonia, ethylene and carbon dioxide. Another external cavity QCL emitting in the $4.5\ \mu\text{m}$ region could help to simultaneously detect carbon monoxide, carbon dioxide, nitrous oxide and their isotopes. Finally in the $7.6\ \mu\text{m}$ region, the Helmholtz sensor used in conjunction with an external cavity QCL could simultaneously detect nitrous oxide, methane, sulfur dioxide and hydrogen sulfide. This last assertion is demonstrated in Fig. 5. An in situ sensor using this kind of laser would be very efficient, for example, in volcanic environments.

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