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Continuous-wave quantum cascade lasers absorption spectrometers for trace gas detection in the atmosphere

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Abstract

Mid infra-red absorption spectrometry based on continuous-wave distributed feedback (DFB) quantum cascade laser (QCL) is more and more widely used for trace gas detection and pollution monitoring. The main advantages of this technique are high sensitivity, high selectivity and a potential for extreme compactness. Various examples of trace gas detection for atmospheric detection will be presented in this paper. Commercial QCLs available on the shelves were first implemented. A cryogenic QCL emitting at 6.7 μm was used to demonstrate the detection of water vapor and its isotopes. A room-temperature QCL was then used to simultaneously detect methane and nitrous oxide at 7.9 μm . Recently, we have developed a room-temperature top grating DFB QCL designed around 4.5 μm for the demonstration of N₂O detection in the ppb range. Atmospheric applications of these spectrometers will be presented. The improvements of QCL performances make it now possible to develop instruments that are more and more compact and therefore compatible with in situ applications.

Keywords: Quantum cascade laser, Infrared gas detection; Atmospheric applications

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1 Absorption spectrometers for trace gas detection

Air pollution is currently a major environmental issue. Numerous chemical agents identified in urban and peri-urban atmospheres have a direct impact on the environment and/or on the human health as greenhouses gases (carbon dioxide, methane, nitrous oxide, ozone, CFCs ...) and Toxic Industrial Chemicals (TIC) (i.e. : Ammonia, Sulfur dioxide, Sulfuric acid...). For either the detection or the control of chemical agents, a flexible sensor adaptable to the variety of pollutants has to be developed. The main characteristics of this sensor must be:

- Very high sensitivity (in the ppb range);
- Capable to give fast measurements of pollutant densities (few seconds of acquisition);
- Portable device to make on site measurements (outdoor as well as indoor).

The currently available gas detection methods may be split into two groups, (i) direct methods, which monitor a physical parameter of the target gas, and (ii) indirect methods, which use a chemical reaction or indicator to assess the concentration of the gas being sensed. This division of methods may be further split into optical sensing techniques and non-optical techniques. Indirect methods are used in a variety of fashions depending on the specific need or application. They are usually based on low cost technologies while being able to reach sensitivity in the ppb range. The small size, low power consumption and relative durability of their designs lend themselves well to portable detection instruments. They are also used in a variety of fixed applications as well. However, they can be poisoned by exposure to adverse chemicals or conditions and can be sensitive to groups of gases rather than a specific gas in a group. They also may exhibit non-reversible behavior, which, in many cases, may be undesirable. In contrast, direct methods are generally very accurate and highly selective means of detecting gas and measuring their concentrations. For the most sensitive chemical analyses of gases, laboratory techniques such as gas chromatography (GC) or the combination of gas chromatography and mass spectrometry (GC/MS) are often applied. These techniques achieve both the highest sensitivity and high selectivity, but are complicated. Moreover, major disadvantages like long measurement time, the need for additional carrier gases, high instrument cost, high maintenance cost, limited detector lifetime and the need for frequently recalibration prevent these methods from being applied efficiently on a large scale and in various situations.

Direct spectroscopic optical methods are easier to implement and provide fast, robust, high sensitivity and selectivity since every molecule has a unique IR spectrum (fingerprint). Gas sensing based on Tunable Diode Laser Spectroscopy (TDLS) is an established technology that has progressed in parallel with the advances in near-infrared (NIR) semiconductor diode lasers in the 0.7-3 μm range [1-3]. TDLS has been the preferred technology for the purpose of gas detection in industrial applications (chemical emission monitoring, process control, high sensitivity trace detection). The robustness of TDLS makes it possible to manufacture sensors with long life time (20 years) that need no recalibration. However, NIR TDLS still shows some drawbacks which prevent to use it for in situ atmosphere detection : the use of NIR overtones much weaker than fundamental Mid Infra-Red (MIR) absorption lines limit their sensitivity and the size of the current high sensitivity systems does not make them transportable.

The use of QCL as a MIR source in TDL spectrometers permits to overcome these problems [4-8]. In recent years, the performance of QCLs has improved markedly and they are today the only semiconductor laser sources operating at room temperature in pulsed or continuous modes over the 3-12 μm wavelength range. This semiconductor technology has moreover a potential for extreme compactness, high lifetime, high reliability and low cost. QCLs were invented 15 years ago and have now reached a certain degree of maturity [9]. However, the business of QCLs is still in its infancy. There are today only two commercial companies in Europe which are really able to fabricate and deliver quantum cascade lasers (a Swiss SME called Alpes Laser founded in 1998 by one of the co-inventors of the device and Alcatel-Thales III-V Lab).

Single frequency operation of the laser is required for spectroscopy application. It is usually achieved by introducing a distributed feedback (DFB) structure into the QCL active region in order to favor a particular mode. Pulsed DFB QCLs are commercially available over the whole 4-10 μm range. Pulsed operation mode operation of those devices at Room Temperature (RT) on Thermal Electro Cooler (TEC) is now easily achieved. On the other hand, Continuous Wave (CW) RT operation lasers on TEC are more lab devices than product and their price is prohibitive. As the demand is going to rapidly increase, in particular due to the development of MIR gas sensing systems, the price should reduce in the near future.

The challenge of designing and fabricating single mode CW, RT QCL has been partially overcome using buried gratings. However, this technique is quite costly and heavy since it requires an overgrowth step. The use of surface metal grating to fabricate QCL DFB is a way to reduce cost [10]. Indeed, one major advantage of surface metallic grating is that no overgrowth is necessary. Moreover, by this approach we can achieve the cm^{-1} precision criterion over the device emission wavelength range. This has allowed pulsed DFB QCL with both a high output power and a high SMSR (Side Mode Suppression Ratio) to be demonstrated. We showed that robustness of top grating design is such that the fabrication yield can be very high (close to 100%) [11]. By reducing the difficulty of fabricating such diodes, costs would be automatically scaled down. The combination of this approach with improved heat dissipation processing has been used in this work to proceed toward continuous waves operation at $4.5 \mu\text{m}$.

In this paper we will present examples of realizations of direct absorption spectrometers based on quantum cascade lasers and applied to gas detection in the atmosphere: water vapor isotopes at $6.7 \mu\text{m}$, methane and nitrous oxide at $7.9 \mu\text{m}$ and nitrous oxide at $4.5 \mu\text{m}$. The schematic representation of such a spectrometer is presented in Fig.1.

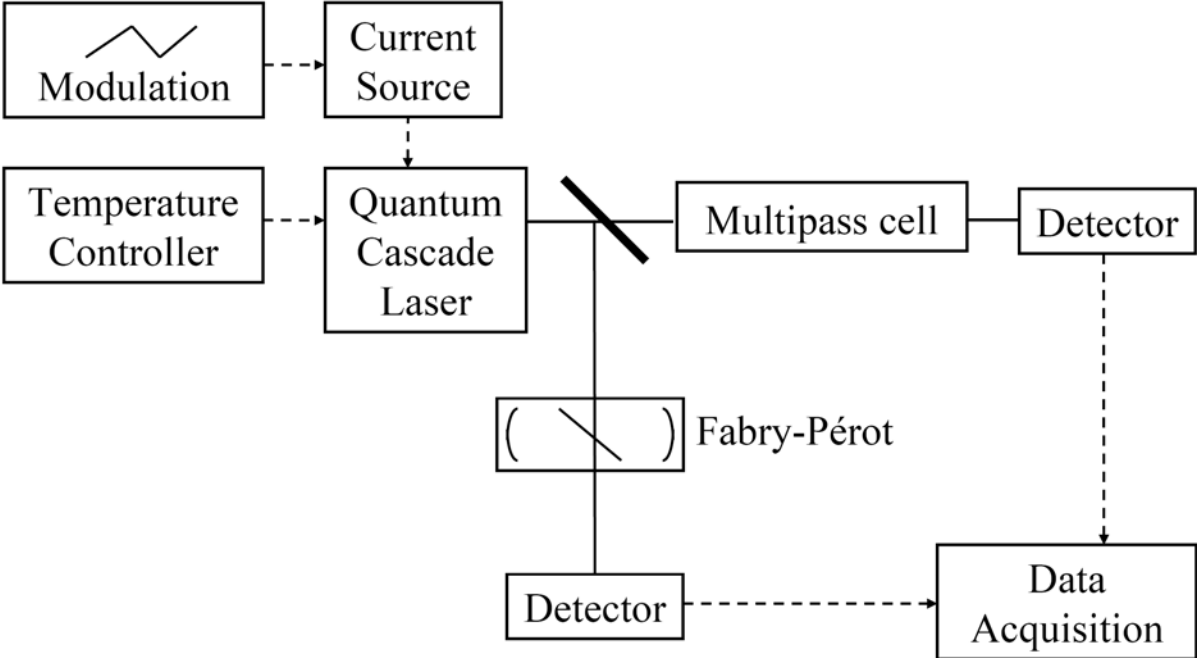


Figure 1: Schematic representation of a quantum cascade laser spectrometer

The QCL is driven by a temperature controller and a current source. The laser emission wavelength is scanned over the molecular transition by applying a triangular current ramp (typ. 100 Hz). The QCL beam is usually collected by a lens adapted to the laser wavelength and is separated into two parts by a beam splitter. The reflected beam is coupled with a Fabry–Pérot etalon used for relative frequency calibration. The second beam passes through a gas cell. The beams are focused onto two detectors adapted to the laser wavelength. Signals are further recorded and treated in order to obtain the atmospheric molecule concentrations. All measurements are usually made at room temperature. To retrieve the gas concentration for a particular line we applied a nonlinear least-squares fit to the molecular transmission, using a Voigt profile to model the line shape. The fitting procedure was described for example in [12].

2 H₂O isotopes detection with a 6.7 μm cryogenic QCL

The first spectrometer presented in this paper was developed in order to measure H₂O and its isotopologues. In the stratosphere, a constant increase in the amount of water vapor of roughly 1% per year is observed. Even if the stratosphere appears to be strongly dehydrated, a change in the weak content of H₂O could have a strong effect on the radiative and chemical equilibrium of the stratosphere and further alter ozone recovery. The coupling processes that transport and mix humid tropospheric air masses into the stratosphere, essentially in tropical regions where strong convective events occur, are largely unknown [13-15]. The in situ measurement of H₂O isotopologues can be helpful in addressing this issue, as water-vapor fractionation can be used for diagnosing the transport of an air mass through the upper troposphere (UT) and the lower stratosphere (LS) and associated dehydration mechanisms.

The developed spectrometer is represented in Fig. 2 [16]. The dimensions of this spectrometer are quite big: 160 cm x 60 cm x 60 cm. One reason is that the QCL from Alpes Lasers – Switzerland was housed inside a cryostat filled with liquid nitrogen every 8 h. The QCL works from 80 to 125 K, and the threshold current is 380 mA. The tunability range of the QCL is 1483.5 cm⁻¹ at T=124 K and I=710 mA to 1489 cm⁻¹ at T=87.4 K and I=400 mA. The average output power is #30 mW, the laser linewidth is approximately 3–4 MHz, and there are no mode hops over the tunability range. One scan of the laser emission wavelength with the temperature over selected water-vapor transitions goes from 1483 to 1487 cm⁻¹.

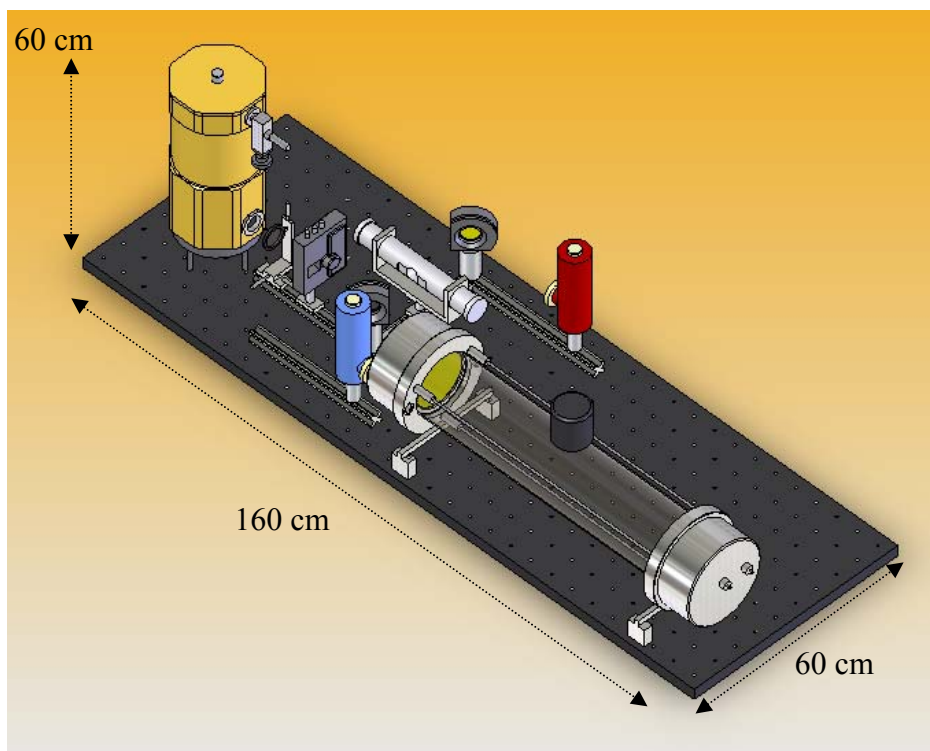


Figure 2: Three-dimensional view of the H₂O isotopologues set-up

Numerous water-vapor isotopologues absorption lines are reachable in the tunability range of the QCL device. The spectroscopic parameters used for the inversion process are taken from [17]. The second reason of the big size of the spectrometer is that the cell is a multipass White-type cell of 48 m effective length with BaF₂ windows. The total air pressure was measured with an uncertainty of 0.5% by an MKS baratron manometer with a 1000 Torr full scale. The air sample pressures vary from 15 to 75 Torr. We studied eight samples. One example of a recorded spectrum with the fitted Voigt profile and the residual below is presented in Fig. 3.

The tunability of the QCL enables it to reach many water-vapor isotopologues transitions. Some of these lines are used for the retrieval of the isotopologues concentrations. The concentrations derived from the fitting procedure are compared with the calculations based on the saturated vapor pressure in air at the temperature measurement and the partial water-vapor pressure obtained from a hygrometer. The concentrations obtained from the fitting procedure and those of the hygrometer are in quite good agreement for H₂¹⁸O and H₂¹⁶O. The HDO value is quite different, as explained below. The experimental H₂¹⁸O / H₂¹⁶O isotopic ratio is 2014 parts in 10⁶ whereas the standard value is 2006.

The experimental HDO / H₂¹⁶O isotopic ratio is 236 parts in 10⁶ whereas the standard value is 156. Our value seems not to be reasonable. However, the White cell used for the static measurements was used previously for intensity measurements of HDO in the laboratory [18]. The sample gases for the study of HDO lines consist of evaporation from various mixtures of liquid-enriched H₂O and liquid H₂O. So our cell was probably polluted by the outgassing of HDO trapped in the optical cell used during the previous laboratory experiment.

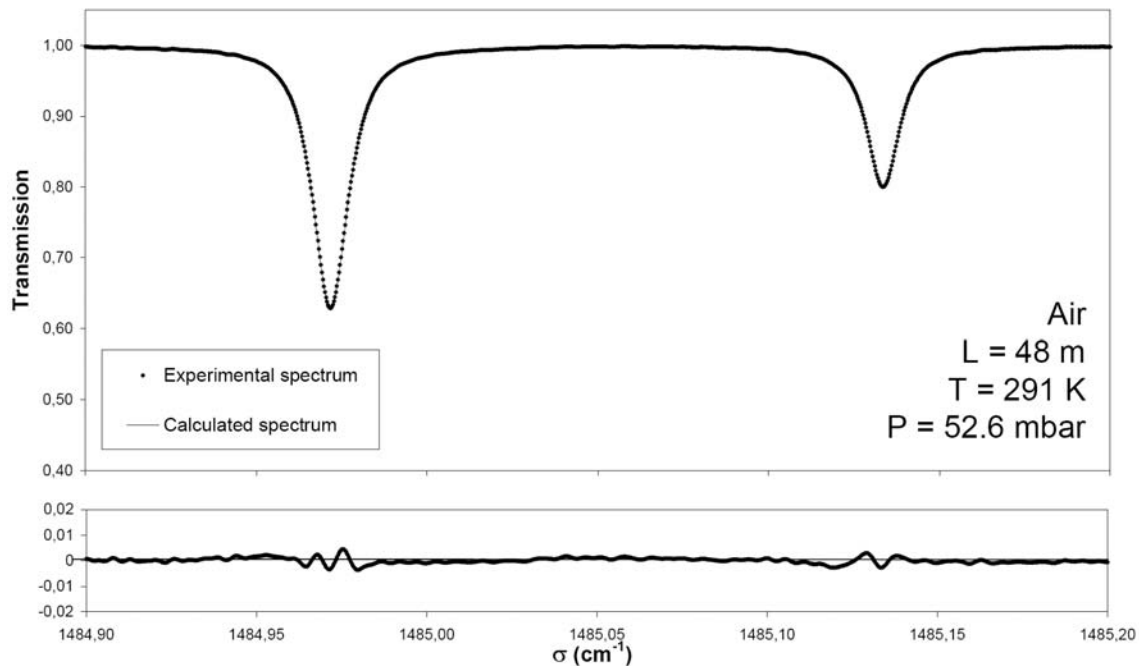


Fig. 3: Example of a recorded spectrum for air and fitted spectrum from 1484.9 to 1485.2 cm^{-1} . The (experimental minus calculated) residual is shown in the lower panel. The current excursion can cover two water vapor isotopologues, H₂¹⁸O and H₂¹⁶O within 1 s.

For measurements performed directly in the field, the problem of contamination of outgassed or trapped water vapor will be eradicated by use of an optical multipass cell operated open to the atmosphere. Nevertheless, this experiment has demonstrated that quantum cascade lasers are ideal sources for these challenging developments. These results have been obtained with a liquid-nitrogen cooled source however the same results may be obtained nowadays with a room-temperature cw source as it will be demonstrated in the next paragraphs. Thus the final idea of the work is to implement a laser source onboard the SDLA [1-2] balloonborne tunable diode laser spectrometer to investigate the mechanisms that control H₂O in the tropical tropopause layer.

3 CH₄ and N₂O detection with a 7.9 μm room-temperature QCL

The second spectrometer presented in this paper was developed in order to measure CH₄ and N₂O in the atmosphere. These two gases are well known to be involved in the global warming phenomenon. The global warming potentials of N₂O and CH₄ at 100 years on the horizon are 296 and 23 times larger than that of CO₂, respectively [19]. Worldwide, concentrations of CH₄ have increased by 148% and those of N₂O by 18% compared to the levels in preindustrial times. Globally, the soil–atmosphere exchange of greenhouse gases is thought to contribute roughly 30% and 70% to the annual emissions of CH₄ and N₂O, respectively [20].

A photograph of the developed spectrometer is depicted in Fig. 4 [21]. The RT QCL purchased from Alpes Lasers (Switzerland) emits in the 7.9 μm region on the ν₄ band of methane [17]. The dimensions of this spectrometer are always quite big: 120 cm x 80 cm x 40 cm. Since the availability of RT CW QCL, the size of the whole system is not anymore limited by the source. The current limitation comes mainly from the absorption multipass cell which is a new type of multiple-reflection cell (L = 140 m) presented in [22]. The QCL is mounted onto a copper substrate attached to a thermoelectric cooler and contained in a hermetically sealed enclosure (Alpes Lasers LLH). Heat produced by the cooler is removed by circulating water through the base of the enclosure. The QCL operates between −30 °C and +30 °C and the maximum current is 550mA. The temperature is controlled and stabilized by a model ILX LightWave temperature controller and the current source is an ILX Lightwave model LDX-3232. The tunability range of this laser is from 1265 cm^{−1} (T_{QCL} = −29 °C, I_{QCL} = 550mA) to 1274 cm^{−1} (T_{QCL} = −29 °C, I_{QCL} = 290mA). The QCL power is #30mW. The synthetic spectrum calculated in this region shows the best spectral window to simultaneously detect N₂O and CH₄. This spectral range is from 1270.7 to 1271.2 cm^{−1}. In this region N₂O and CH₄ lines are isolated enough, and there is no interference with water vapor lines. Pressure (MKS Baratron) and temperature (PT100) sensors permit measurements of these two important parameters for high resolution spectroscopy. The sample gas (outside the laboratory) is brought from atmospheric pressure to #40 mbar across the inlet orifice to reduce the pressure broadening of the absorption lines, increasing the distinctive nature of the absorbing species spectral signature. The system operates at a gas flow of 5 L/min. A dust filter is set at the inlet of the measurement head to protect the gas system and the mirrors of the cell from pollution. A WXT510 weather transmitter from Vaisala is used to measure thermodynamic conditions outside the laboratory.

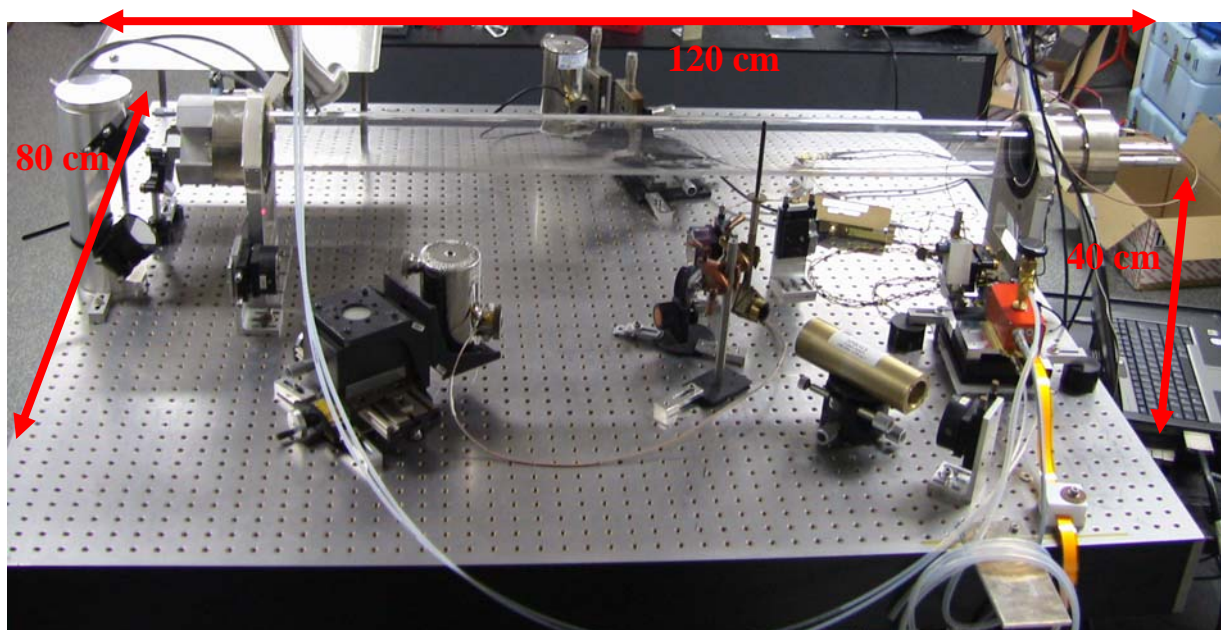


Figure 4: Photograph of the CH₄ and N₂O sensor set-up.

An example of a recorded spectrum is shown in Fig. 5. The line shape was modeled with a Voigt profile and the resulting residual is also displayed in Fig. 5. The residual features an M shape, which is typical when using the Voigt model approach. The fitting can be improved and the residual reduced by using profiles such as the Rautian–Sobel’man line shape functions. However the residual with the Voigt profile is < 1%. Moreover the use of more complicated profiles would increase the processing time with no significant improvement in the accuracy of the concentration retrieval [2].

Stability and laboratory tests of the instrument based on the Allan variance method have been realized [21]. The log–log plot of the Allan variance versus the integration time (τ) in seconds demonstrates that the Allan variance decreases and, hence, only the white noise is dominant up to 1280 s integration time. The variance minimum at $\tau_{\text{Allan}} = 1280$ s corresponds to a minimum σ_{Allan} of 0.5 ppb; and for CH₄ the variance minimum at $\tau_{\text{Allan}} = 1280$ s corresponds to a minimum σ_{Allan} of 3 ppb. These are the maximum precisions reachable, which satisfy the field measurement requirements asking for sensitivities to flux variability of 1 ppb for N₂O and 10 ppb for CH₄.

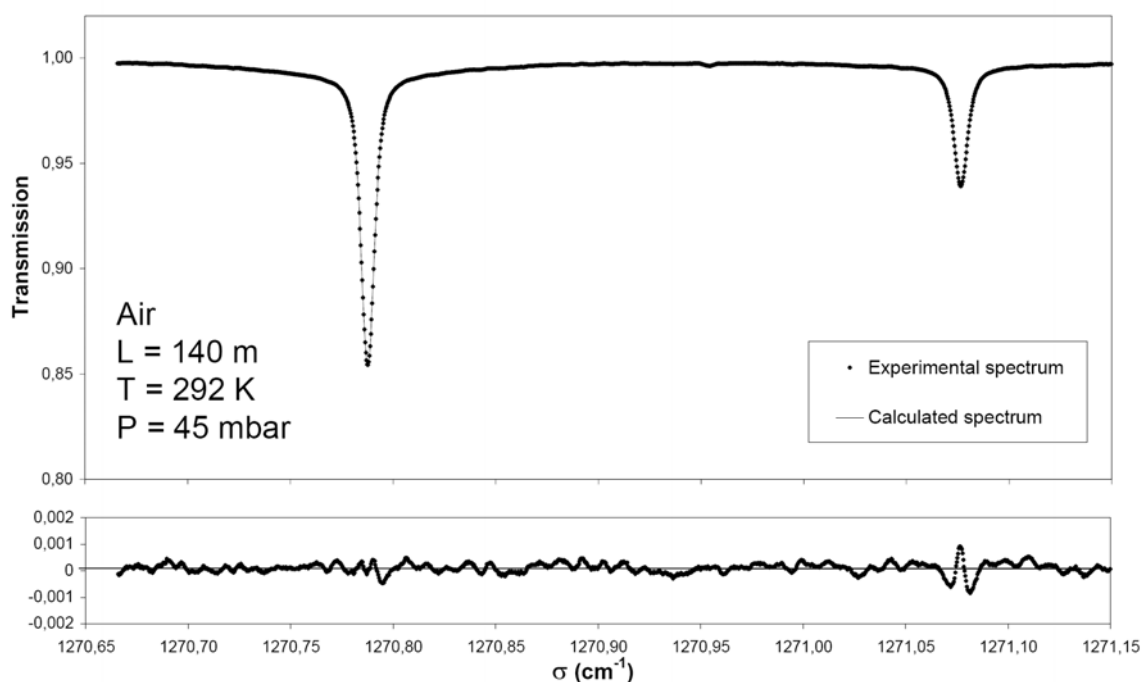


Figure 5: Example of a recorded spectrum for air and fitted spectrum from 1270.65 to 1271.15 cm^{-1} . The (experimental minus calculated) residual is shown in the lower panel. The current excursion can cover three lines within 1 s: one CH_4 line around 1270.78 cm^{-1} , a small H_2O line around 1270.95 cm^{-1} and one N_2O line around 1271.08 cm^{-1} . The retrieved volume mixing ratios are 1.92 ppm of CH_4 and 320 ppb of N_2O .

The instrument has been used to record a series of ambient air measurements. Ambient air samples were collected from outside the laboratory building. The spectrometer was located in the laboratory. A filter was put at the tube entrance to prevent dust entering the optical cell. The vegetation all around the laboratory was mainly a meadow with some oaks. N_2O and CH_4 concentrations have been monitored during a period of 1 day. The mean N_2O volume mixing ratio was 319 ppb and the mean CH_4 volume mixing ratio was 1.93 ppm, which are typical background troposphere boundary layer values. Over this one-day period, no cycle for N_2O nor CH_4 was observed. Moreover no correlation between concentrations and weather conditions at ground level were observed.

The instrument was further used to measure concentrations of CH₄ and N₂O when N fertilizer is added to the soil [21]. Added mineral N fertilizer is susceptible to gaseous loss via microbial denitrification, particularly if fertilization is accompanied by irrigation, which creates anaerobic microhabitats suitable for denitrifying bacteria. Denitrification can lead to the release of either N₂ or N₂O as gaseous end products. Thus the study of the time response of N₂O fluxes to a fertilizer addition in a soil sample is of high interest [23]. Each soil sample enriched with fertilizer was located in a closed chamber. The box containing the soil sample was then connected to the spectrometer. For this measurement 3.8 g of ammonium nitrate (33% N) were added to the soil sample (mass of 4 kg) that was previously saturated with water (this supply was equivalent to 300 kg of N.ha⁻¹). Then N₂O and CH₄ concentrations were monitored during a period of 9 h after the addition of a commercial fertilizer. The N₂O volume mixing ratio varies from 320 ppb up to > 800 ppb after 9 h. The CH₄ volume mixing ratio remains constant at #1.93 ppm. These experiments have demonstrated the capabilities of the developed instrument for a long time online atmospheric accurate measurement.

4 N₂O detection with a 4.5 μm room-temperature QCL from III-V lab

The third spectrometer presented in this paper was developed in order to measure N₂O in the atmosphere. It was particularly dedicated to N₂O measurements for agronomical studies because agricultural soils contribute substantially to this budget. N₂O emission occurs due to the use of mineral and organic fertilizers in agricultural activity, through the activity of microorganisms, and to the exhalations of human beings [24]. The production of N₂O by soils primarily occurs through two biological processes: (1) denitrification, the anaerobic microbial respiration using nitrate and nitrite as electrons acceptors [25] and (2) nitrification, the exothermic oxidation of ammonium to nitrite and nitrate [26]. A better understanding of the soil–atmosphere exchange is necessary to control N₂O emissions with new cropping systems.

N₂O emissions are very variable with time and space [27-28] and difficult to measure. Two main methods are available today [29]: (1) the static method that is based on the measurement of gas concentration within closed chambers that are put at the soil surface during a given period (typically 3 h) and (2) the micrometeorological method that is based on the measurement of the gradient of gas concentration in the atmosphere. Both methods require gas concentration measurements that are done either in the laboratory after atmospheric sampling or directly in the field. Available gas analyzers limit the possibility to measure the gas concentration on a wide scale and over a long period while modern atmospheric research on gas exchange between the biosphere and the atmosphere requires sensitive, reliable, and fast response chemical sensors. Therefore, techniques for fast and simultaneously sensitive trace gas measurements based on tunable diode laser absorption spectroscopy have been successfully applied to micrometeorological trace gas flux measurement techniques [30].

A photograph of the developed spectrometer is depicted in Fig. 6. This spectrometer is a faster and a more compact version of the previous described ones. The QCL especially developed in this work by Alcatel-Thales III-V Lab emits in the 4.5 μm region where a fundamental band of nitrous oxide is present. This wavelength region where nitrous oxide absorptions are stronger permits to reach the same kind of detection limit that the previous spectrometer (part 3 of this paper) but using a cell with a smaller path length. Thus the cell volume is also lower and may be refreshed more easily permitting fast measurements such as Eddy covariance measurements around 10 Hz. Moreover the dimensions of this spectrometer are now lower: 60 cm x 45 cm x 40 cm. Finally this instrument is now light enough to be transported and operated on in the field by two people and with energy autonomy to study spatial and temporal variability of fluxes as a function of these parameters.

The room-temperature QCL from Alcatel-Thales III-V Lab (France) is mounted onto a copper substrate attached to a thermoelectric cooler. Heat produced by the cooler is removed by circulating water through the base of the enclosure. The QCL operates between 10 °C and +50 °C and the maximum current is 520 mA. The temperature is controlled and stabilized by a model ILX LightWave temperature controller and the current source is an ILX Lightwave model LDX-3232. The tunability range of this laser is from 2235.2 cm^{-1} to 2239.5 cm^{-1} . The QCL power is #15 mW.

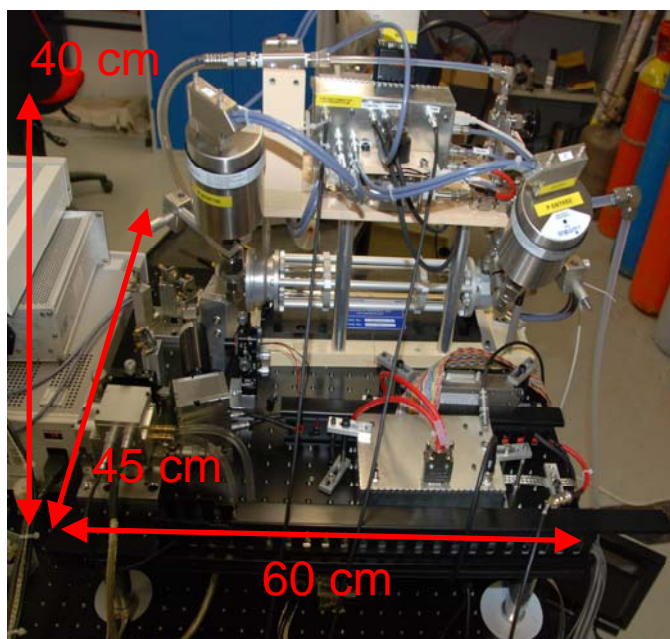


Figure 6: Photograph of the N₂O detector set-up.

The absorption cell ($L = 76$ m, $V = 0.5$ L) is a Herriott-type multiple-reflection cell from Aerodyne. The sample gas is brought from atmospheric pressure to #50 mbar to reduce the pressure broadening of the absorption lines, increasing the distinctive nature of the absorbing species spectral signature. The system operates at a gas flow of around 10 L/min. A dust filter is set at the inlet of the measurement head to protect the gas system and the mirrors of the cell from pollution. Pressure (MKS Baratron), temperature (PT100) and humidity (Farnell) sensors are used to measure thermodynamic conditions.

The N₂O line shape at 2238.36288 cm⁻¹ is modeled with a Voigt profile as described in Sections 2 and 3 to obtain the N₂O concentrations in air. A preliminary result of N₂O concentrations measured in air is presented in Fig. 7. The retrieved N₂O concentration is 318 ppbv +/- 2 ppbv. More precisely a dispersion of 1.46 ppb per 120 ms of measurement is achieved. If the time increases, the dispersion is then 0.15 ppb for a 12 s measurement. These results are sufficient to develop instruments that are very well adapted for measuring the N₂O fluxes on field, determining the factors (soil composition, soil temperature and humidity, quantity of fertilizer...) which favor the N₂O emission and showing the annual increase of N₂O concentration. For micrometeorological applications [31], the instrument is also capable of sampling high-frequency eddies, typically up to 10 Hz.

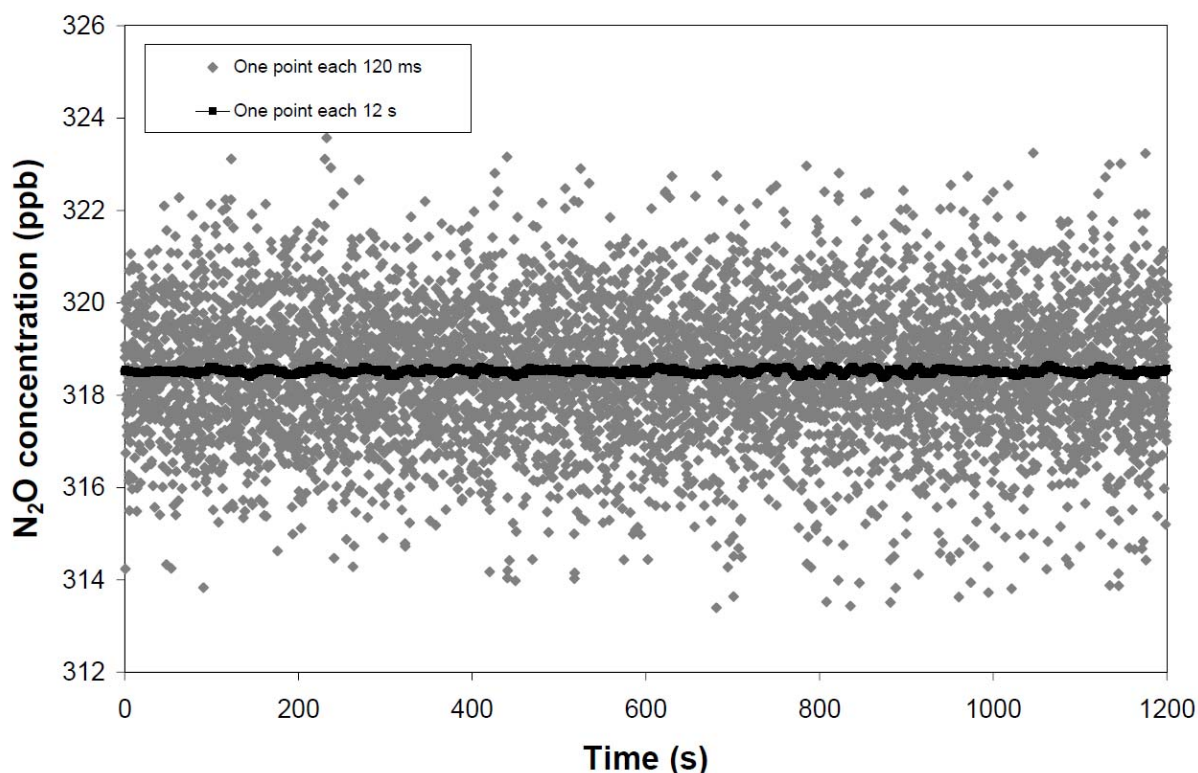


Figure 7: Retrieved N₂O concentrations in air with the III-V lab QCL spectrometer

5 Conclusion and outlook

Direct spectroscopic optical methods are easier to implement and provide fast, robust, high sensitivity and selectivity since every molecule has a unique IR spectrum (fingerprint). Thus continuous-wave quantum cascade laser spectrometers are more and more widely used for trace gas detection and pollution monitoring. Three examples of trace gas detection for atmospheric detection have been presented in this paper. A first cryogenic QCL spectrometer working at 6.7 μm was used to demonstrate the detection of atmospheric water vapor and its isotopes. A room-temperature 7.9 μm -QCL spectrometer was then used to simultaneously detect methane and nitrous oxide in air. These two spectrometers demonstrate that cw QCLs are ideal sources for trace gas detection in the atmosphere. Moreover QCLs are still in progress in terms of cw, RT, etc. Thus the spectrometer characteristics are also in progress and these spectrometers are more and more efficient and give reliable interesting measurements for various applications.

However the size of these spectrometers (typ. 120 cm x 60 cm x 40 m) mainly due to the multipass cell and to the laser source was still a brake to real in situ measurements. The third part of this paper presents a room-temperature QCL spectrometer which was used to demonstrate the detection of N₂O around 4.5 μm. With this kind of spectrometer which is more compact by using low volume cell and RT laser, in situ atmospheric applications can now be realized. The preliminary results demonstrated in this paper show the capabilities of the instrument for agronomical applications. The next step will be to use this spectrometer in fields and to automate it.

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