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Detection of Greenhouse Gases Using the Photoacoustic Spectroscopy

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1. Introduction

Global warming is one of the main environmental problems of the XXI Century. It is generated by the intensive use of fossil fuels that leads to the so-called greenhouse effect (Meinshausen et al., 2009; Allen et al., 2009; Sthel et al., 2010; Hansen et al., 2008; Hansen & Makiko, 2004; Rosenzweig et al., 2008). It causes climate changes (Steffen et al., 2004; Solomon et al., 2009; Kevin et al., 2006; Kurz et al., 2008; Greene et al., 2009; Nathan P et al., 2008; Siddall et al., 2009; Sander et al., 2006; Emanuel, 2005; Peza & Simmonds, 2005; Janssen, 1998; Mann et al., 1998) and produces significant damages to the human society and biodiversity, such as the melting of the poles with the consequent increasing of oceans level, the intensity increasing of hurricanes, extreme events, changes in the rainfall patterns (floods, desertification), oceans acidification and biodiversity decreasing. Recently, the Intergovernmental Panel on Climate Change (IPCC) report (IPCC, 2007), published in February 2007, indicated based on meteorological studies, that the earth's global average temperature rose about 0.8°C in the last 150 years, mainly due to human activities. The global atmospheric concentrations of carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) have risen considerably as a result of human activities since 1750. Increases in global carbon dioxide concentration are primarily due to the use of fossil fuels and changes in the use of the soil through practices such as deforestation, biomass burning and biomass decomposition. Practices such as logging, peat decomposition and burning and other techniques employed in the modern agriculture are resulting in an increased concentration of methane and nitrous oxide. While the global atmospheric concentration of carbon dioxide has increased from a pre-industrial value of about 280 ppmv to 379 ppmv in 2005, the global atmospheric concentration of methane (CH₄) has increased from a pre-industrial value of about 715 ppbv to 1774 ppbv in 2005 and the global atmospheric concentration of nitrous oxide has risen from pre-industrial value of about 270 ppbv to 319 ppbv in 2005.

Therefore, it is necessary to use suitable analytical techniques to identify the atmospheric components and to determinate their trace concentrations. A trace sensor of atmospheric pollutants must meet a set of fundamental requisites. High selectivity is necessary to

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distinguish the gas species present in a multicomponent gas mixture, such as air, and high sensitivity is essential to detect very low concentrations of substances. A large dynamic range is important to monitor the gas components at high and low concentrations using a unique instrument. In addition, a good time resolution ensures the possibility of on-line analyses controlled by a computer. Photoacoustic spectroscopy meets these requirements that enable this technique to offer important advantages in pollutant gas monitoring.

In conventional spectroscopy, the absorption of radiation is measured from the power transmitted through the sample. On the contrary, in photoacoustic spectroscopy, the absorbed radiation power is determined directly via its heat and hence the sound produced in the sample. This methodology is based on the so called photoacoustic effect which consists on the generation and detection of pressure waves (sound) inside a resonant cell, where the gas samples are placed. These samples are exposed to the incidence of modulated radiation, absorbing it at determined wavelengths. The resonant absorption of radiation generates a modulated heating in the sample and, therefore, a sound signal is produced (photoacoustic effect) and detected by highly sensitive microphones coupled, inside the cell. These microphones convert the sound signal into an electric signal, which is filtered and detected by a lock-in amplifier. Photoacoustic spectroscopy is widely used for the detection of several gases in the concentration range of ppbv and sub-ppbv (Mothé et al., 2010; Berrou et al., 2010; Sthel et al., 2011; Harren et al., 2008; Thomas, 2006; Rocha et al., 2010; Elia et al., 2009; Sorvajärvi et al., 2009; Sigrist et al., 2008; Angelmahr et al., 2006; Filho et al., 2006; Schramm et al., 2003; Harren et al., 2000; Miklos et al., 2001; Gondal, 1997; Repond & Sigrist, 1996; Sigrist, 1994a, 1994b). There are some types of trace gas detection systems based on continuous wave (CW) CO₂ laser, optical parametric oscillator (OPO) in combination with photoacoustic spectroscopy and quantum cascade laser (QCL). These experimental arrangements are efficient in the detection of greenhouse gases and their precursors.

2. Photoacoustic spectroscopy

Currently, photoacoustic spectroscopy has been consolidated as an effective option for trace gases analysis for high sensitivity trace gases analysis (detection limits in the range of sub-ppbv and ppbv), good selectivity, possibility of in situ measurements and continuous flow systems associated with the possibility of non-destructive analysis are attributes that allow photoacoustic to be a powerful analytical tool for gases monitoring. The photoacoustic effect consists on the generation of sound waves from the absorption of a pulsed modulated radiation. It was discovered in 1880 by Alexander Graham Bell (Bell, 1880). This discovery raised the interests of other researchers, such as John Tyndall (Tyndall, 1881), Wilhelm Röntgen (Röntgen, 1881) and Lord Rayleigh (Rayleigh, 1881). However, the lack of equipment (radiation sources, microphones, amplifiers, etc.) prevented the immediate development of this new research field, and soon the photoacoustic effect has become a mere scientific curiosity, remained virtually forgotten for over half a century.

In the late 1930s, Viengerov (Viengerov et al., 1938) introduced an infrared absorption photoacoustic system to analyze gases infrared absorption. Then, Luft (Luft, 1943) improved the sensitivity of this technique, allowing absorption measurements of gaseous species in the concentration range of ppmV (10^{-6}). Since the 1960s, the development of

Lasers, sensitive microphones and lock-in amplifiers permitted this technique to have a great technical development. In 1968, L. B. Kerr and J. G. Atwood conducted the first photoacoustic experiments using Laser as the radiation source (Kerr & Atwood, 1968). Using a continuous wave CO₂ laser as excitation source, they achieved a minimum absorption coefficient of $1.2 \times 10^{-7} \text{ cm}^{-1}$ of CO₂ diluted in nitrogen. In 1971, L. B. Kreuzer, using a HeNe laser operating on 3.39 μm , attained a detection limit of 10ppbv of methane diluted in nitrogen (Kreuzer, 1971). Kreuzer, N. D. Kenyon and C. N. K. Patel used CO₂ and CO lasers as radiation sources to perform photoacoustic measurements of many trace gases (Kreuzer et al., 1972). The use of a photoacoustic cell operating at in resonant mode, associated with the modulation of the excitation beam in the acoustic resonance frequencies of the cell, was introduced in 1973 by CF Dewey Jr., RD Kahn and CE Hackett (Dewey et al., 1973). The success achieved by these pioneering studies provided a great interest in the application of photoacoustic spectroscopy in trace gases analysis in many scientific areas, especially in pollutant gas studies.

Advances in laser technology allowed the development of new infrared radiation sources continuously operating in a wide range of wavelengths, especially in the mid-infrared region. Among these new Lasers, the most promising for gas sensing are the optical parametric oscillator (OPO) and the quantum cascade laser (QCL). The combination of these new radiation sources with photoacoustic cell optimized settings (differential photoacoustic cell, intra-cavity arrangements or multi-pass) enabled major advances in trace gases photoacoustic detection.

2.1 Photoacoustic effect in gases

The photoacoustic signal generated and detection in gases been studied mainly by Kreuzer (Kreuzer, 1971) and revised and expanded by several authors(Harren & Reuss, 1997; Miklos & Hess, 2001; Hess, 1992; West, 1983; Meyer & Sigrist, 1990). Molecular absorption of photons results in the excitation of molecular energy levels (rotational, vibrational and electronic) degrees freedom. The excited state loses its energy by radiative processes, such as spontaneous or stimulated emission, and/or by collisional relaxation, in which the state energy is transformed into translational one.

In the case of vibrational excitation, radiative emission and chemical reactions do not play an important role, because the radiative lifetimes of vibrational levels are long compared with the time needed for collisional deactivation at pressures used in photoacoustic. Furthermore, the photon energy is too small to induce chemical reactions. For 1 atm pressure, the vibrational-translational non-radiative decay time is typically around 10^{-6} - 10^{-9} s, whereas the radiative lifetime is between 10^{-1} and 10^{-3} s (Hess, 1983). Thus, in practice, the absorbed energy is completely released as heat, appearing as translational (kinetic) energy of the gas molecules.

By modulating the intensity or the wavelength of the incident radiation, the sample local heating and expansion become periodic. If radiation intensity is modulated (without optical saturation), the heat density in the sample (H) is directly proportional to the volumetric density of molecules (N), to the absorption cross section of the absorbing molecule (σ) and to the incident laser radiation intensity (I_0). Therefore, the gas heat production is given by:

$$H(\mathbf{r}, t) = N\sigma I_0 e^{i\omega t} \quad (1)$$

The sample pressure oscillations (p) are related to the heat production by the following equation:

$$\nabla^2 p - \frac{1}{v^2} \frac{\partial^2 p}{\partial t^2} = -\frac{\gamma - 1}{v^2} \frac{\partial H}{\partial t} \quad (2)$$

where v , γ , and H are the sound velocity, the adiabatic coefficient of the gas, and the heat density deposited in the gas by light absorption, respectively. All dissipative terms of heat diffusion to the cell walls and viscosity were despised.

For many applications, this simplified approach is sufficient, although in some cases, more stringent treatment that takes into account relaxation effects is necessary. Since the amplitude of the acoustic waves produced depends on both the nature of the absorbing gases and their concentrations, the photoacoustic detection allows qualitative and quantitative analysis of gas mixtures.

The acoustic wave is generated in places where light is absorbed by the monitored species. The photoacoustic signal $S(\lambda)$ produced by a single absorbing gaseous species diluted in a non absorbing gas can be expressed as:

$$S(\lambda) = CP(\lambda)N_{\text{tot}}c\sigma(\lambda) = CP(\lambda)\alpha(\lambda)c \quad (3)$$

Where C is the cell constant, which depends on the cell geometry, the microphone responsivity and on the nature of the acoustic mode, $P(\lambda)$ is the laser power at the wavelength λ , N_{tot} is the total density of molecules, considering a pressure of 1013hPa and a temperature of 20°C, $N_{\text{tot}} \approx 2.5 \times 10^{19}$ molecules/cm³, c and $\sigma(\lambda)$ are, respectively, the concentration (mole fraction) and the absorption cross section of the absorbing molecule and $\alpha(\lambda) = N_{\text{tot}}c\sigma(\lambda)$ is the so called gas absorption coefficient (cm⁻¹).

Using equation 3, it is possible to determine the minimum detectable gas concentration in the photoacoustic spectrometer, through:

$$c_{\text{min}} = \frac{S_{\text{min}}}{N_{\text{tot}}CP\sigma} = \frac{S_{\text{min}}}{CP\alpha} \quad (4)$$

where $S_{\text{min}}(\lambda)$ is the minimum detectable signal, which is usually measured by passing a flow of non-absorbing inert gas (usually nitrogen or synthetic air) in the photoacoustic cell. The minimum signal is produced by the various sources of noise, which are always present in photoacoustic detection, determining its limitations. The most common sources of noise in photoacoustic systems include acoustic signals caused by the windows heating, the absorption and scattering of radiation on the cell resonator walls, by molecules adsorbed on them, the noise caused by the gas flow and electronic noise.

We can notice that the signal is obtained at a given wavelength, which is specific for the molecule we wish to detect. Moreover, the obtained signal is directly proportional to the concentration of the absorbing gas. Thus, it is possible to obtain the concentration as a function of the generated signal.

In order to determine the concentration of various gaseous species in a multicomponent sample, the photoacoustic signal can be obtained for different wavelengths, corresponding to the absorption of each analyzed component. In this case, the signal can be obtained by the relation:

$$S(\lambda_i) = CP(\lambda_i)N \sum_{j=1}^n c_j \sigma_{ij} \quad (5)$$

with $i = 1, 2, \dots, m$ and $j = 1, 2, \dots, n$ e $m \geq n$. Here, $P_i = P(\lambda_i)$ represents the laser power at wavelength λ_i and c_j is the concentration of the component j with absorption cross section σ_{ij} at λ_i . This equation solution for each gas species concentration is given by:

$$c_j = \frac{1}{CN} \sum_{i=1}^m (\sigma_{ij})^{-1} \left(\frac{S_i}{P_i} \right) \quad (6)$$

Where $(\sigma_{ij})^{-1}$ is the inverse matrix of the matrix σ_{ij} . The success of this method in multicomponent mixture analysis strongly depends on the nature of the matrix σ_{ij} (Sigrist, 1994a; Meyer et al., 1988). The trivial case is represented by a diagonal matrix (σ_{ij}) , where a set of wavelengths λ_i can be selected and the absorption by a single gas component occurs in each λ_i . However, this ideal case without interference between the absorptions due to different gas species in a multicomponent mixture hardly occurs. Instead, considerable effort is needed to discriminate the various components, as well as to identify any unexpected component. Iterative algorithms using least squares regression and based on prior knowledge of the absorption cross sections (σ_{ij}) have been developed to fit the photoacoustic spectrum of multicomponent samples (Moeckli, 1998).

2.2 Lasers as radiation sources

The selectivity required for the identification of the components of a gaseous mixture is achieved in spectroscopy when lasers are employed. Due to its high radiance, narrow linewidth and wide spectral range of emission, lasers are indeed suitable for trace gas monitoring. They allow a selective detection of different gases in trace level concentration (lower limit: parts per trillion by volume) even when there is overlapping of spectrum lines from different molecules. It is known that for molecules, absorption spectra in the near infrared (NIR) and the infrared (IR) ranges work as fingerprints, that is, they are unique for each molecular species. Currently, there are commercially available lasers that emit in these regions, for example, semiconductor lasers (DFB diode lasers) and gas lasers (CO and CO₂), respectively. The great advantage of using these light sources is the resulting high spectral resolution.

Promising new sources of light are the quantum cascade lasers (QCL). These lasers emit in the mid-IR range, where the molecules have higher absorption coefficients, and operate at room temperature. Since the photoacoustic signal intensity is also a function of the molecular absorption coefficients, the low power these lasers emit is hence compensated. Another important feature and advantage of these lasers is the high spectral resolution. Furthermore, the emission wavelength can be selected to match two, or more, absorption lines of a given molecule. Third generations of extremely promising lasers are the Optical Parametric Oscillator lasers (OPO).

2.2.1 CO₂ laser

The use of tunable CO₂ lasers (Patel, 1964), through the scanning of its emission wavelengths (9-11 μ m) ensures the exploration of the so-called molecular fingerprint, enabling the identification and simultaneous monitoring of several gaseous compounds with a single instrument. Figure 1 shows the absorption spectra of ozone (O₃), ammonia (NH₃) and ethylene (C₂H₄), for the emission range of a CO₂ laser. As gas lasers have high power (> 10 watts) and the signal intensity is directly proportional to the emitted light power, its use results in sensitivities in the range of pptv. Nevertheless, these lasers have two disadvantages, they are large and expensive and thus its use is limited to laboratories.

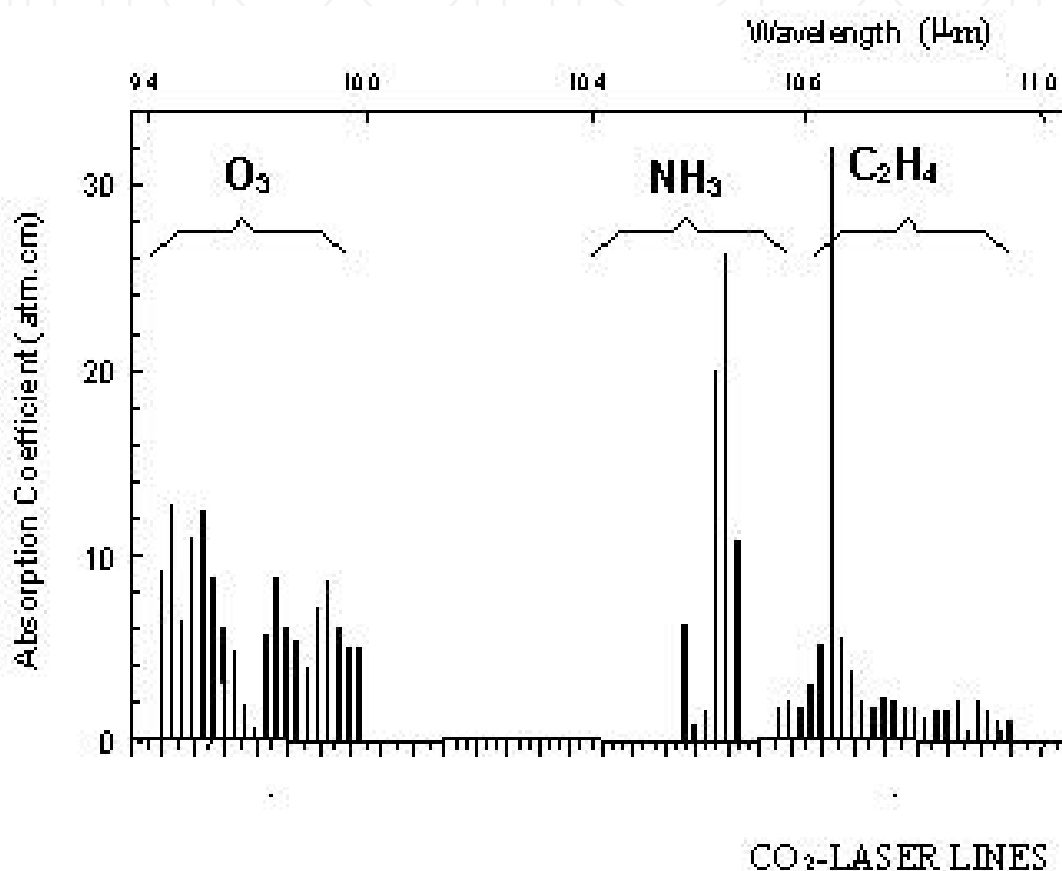


Fig. 1. Fingerprints of ozone (O₃), ammonia (NH₃) and ethylene (C₂H₄) corresponding to the emission lines of a CO₂ laser.

2.2.2 Quantum Cascade Laser (QCL)

The quantum cascade laser (QCL), introduced by Faist (Faist, et al., 1994,1997), represents an excellent source of radiation for trace gas monitoring. Although providing output power well below the CO₂ laser (a few mW), this source has some advantages such as compact size, continuous emission, high spectral resolution and the possibility of being operated near room temperatures.

In addition, they can be manufactured to operate in a wide range of wavelengths, from 3 to 24 μ m. Among its applications, we highlight the environmental monitoring, industrial process control, besides chemical and biomedical applications. (Beck et al., 2002)

The QCL laser coupled with a photoacoustic detector has been successfully used to measure the concentration of different gases which absorb radiation in the mid- infrared spectral region, such as ozone (Silva et al., 2004), ammonia (Baptista-Filho et al., 2006), and NO₂ and N₂O gases. (Lima et al, 2006; Grossel et al., 2007)

This type of laser is part of the family of semiconductor lasers, with the particularity of using quantum transitions within the same band. A quantum cascade laser comprises a series of alternate thin layers of two different materials. This configuration enables different electrical potentials to be established across the device, so that electrons can get trapped in these sites, called quantum wells. Thus, a series of sub-bands with different energies is created inside the conduction band.

When stimulated, the electrons undergo transitions and quantum tunneling to a lower energy sub-band, and consequently photons are emitted. A single electron can perform several transitions, that is, issue multiple photons. (Gmachl et al., 2001; Beyer et al., 2003)

Another important characteristic of quantum cascade lasers is that the wavelength can be determined by the thickness of the layers, rather than being determined by the energy difference between bands. The thickness and refractive index change by setting different temperatures turning the wavelength (Kosterev et al., 2002; Curl et al., 2010; Kosterev et al., 2002).

2.2.3 The Optical Parametric Oscillator laser (OPO)

An interesting optical process that has been used to produce near- and mid-infrared radiation is the optical parametric generation. In 1962, Armstrong et al and Kroll described the fundamental theory of the optical parametric generator and three years later, Giordmaine and Miller demonstrated the operation of an optic parametric oscillator (Armstrong et al., 1962; Giordmaine & Miller, 1965). When an optically nonlinear crystal is submitted to electromagnetic fields of high density of energy such as those present in pulsed lasers, the electrons respond with significant displacement that gives rise to the contribution of the second-order nonlinear component for the electric polarization of a nonlinear medium. The mixing of two electromagnetic waves under condition of nonlinear polarization produces parametric effects such as second harmonic generation (frequency doubling), sum frequency generation and difference frequency generation. In the latter case (figure 2), when the nonlinear crystal is pumped by two input photons with wavelength at λ_p (pump photon) and λ_s (signal photon, $\lambda_s > \lambda_p$), the signal photon stimulates the conversion of a pump photon into a new signal and an idler photon with wavelength at $\lambda_i^{-1} = \lambda_p^{-1} - \lambda_s^{-1}$ (fulfilling the energy conservation principle). Of course, the efficiency of such conversion is limited to phase match between the pump and signal waves. This process of increasing the number of signal photons is known as optical parametric amplification (OPA) and thus it fundamentally differs from the amplification mechanism in laser since no population inversion and excited states take place. Theoretically, the remarkable advantage of OPA is the infinity possibility of combining two waves that generates a third wave with different wavelength. This fulfills the expected desirable feature of an excitation source for analytical spectroscopy application that is the broad wavelength tunability. Therefore, this makes the optical parametric phenomena of great significance to spectroscopy application in the sense

of allowing selective trace gas detection and thus analysis of multicomponents samples, such as the air. Although the finite width of the emission line may reduce the selectivity, for atmosphere application the broadening of the line width of detected specie due to the atmospheric pressure (Demtröder, 2003; Sigrist a, 1994) for itself reduces the significance of an ultra-narrow line width of an applied source.

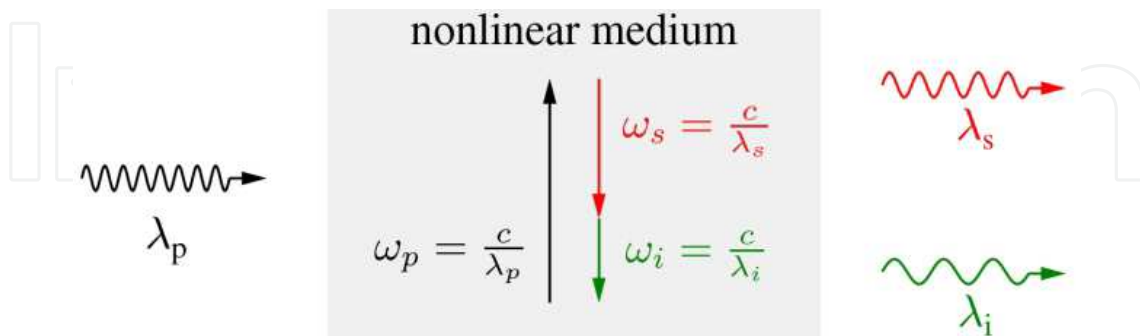


Fig. 2. Optical parametric process. The incident pump radiation with wavelength λ_p and circular frequency at ω_p is converted into signal and idler radiations with wavelength λ_s and λ_i and circular frequency at ω_s and ω_i , respectively. c is the velocity of the light in the medium.

The efficiency of the nonlinear conversion depends on the phase matching of the pump and signal waves. The dispersion of electromagnetic wave propagating through a crystal is directly related to the refractive index of the media that is different for each wavelength. Therefore the pump and signal wave move in and out of phase relatively to each other, limiting the quantity of generated signal photons. Consequently, initially the first issue was to find materials that provide phase matching for at least two wavelengths. The use of birefringent crystalline materials was the first key to fix the relative phase of the pump and signal waves. However, the available range of wavelengths that satisfies the phase-matching condition is limited to the variability of birefringent crystalline materials. More recently, the use of periodically poled lithium niobate (PPLN) has overcome this restriction. PPLN chips display an engineered inverted orientation of lithium niobate crystals that promotes a quasi-phase-matched combination of the pump and signal waves compensating the phase mismatch present in parametric interaction (Fejer et al., 1992; Tang et al., 1992).

For the optic parametric oscillator (OPO), the crystal is initially pumped by photons of only one wavelength λ_p . Based on the fundamental quantum uncertainty in the electric field (quantum noise), a pump photon (λ_p) propagating in a nonlinear optical crystal spontaneously breaks up spontaneously into two lower-energy photons with wavelength at λ_s (signal photon) and λ_i (idler photon) (Zhang et al., 1993; Zhou et al., 1998). This optic parametric process is called optic parametric generation (OPG). Afterwards, the created signal wave mixes with the pump wave under condition of nonlinearity resulting in new signal and idler waves (stimulated generation). To increase the number of signal and idler photons, the crystal is placed within an optic cavity formed by two mirrors (optical resonator). Single resonance is achieved when the signal wave is reflected back and forth in the optic cavity.

3. Detection of greenhouse gases: Experimental setups

3.1 CO₂ laser experimental setup

The methodologies based on photothermal techniques, mainly CO₂ laser photoacoustic spectroscopy, have suitable characteristics to detect trace gas, as high sensitivity and selectivity and possibility of in situ measurements. A CO₂ laser based photoacoustic spectrometer (Figure 3) can be used to detect volatile organic compounds (VOCs) emissions, such as ethylene (Demtröder, 2003; Fejer et al., 1992, Tang et al., 1992, Zhang et al., 1993). Ethylene is a reactive pollutant, since it is an unsaturated organic compound (Zhou et al., 1998). For this reason, this chemical species is a precursor for the generation of the tropospheric ozone (Da Silva et al., 2006), which is present in photochemical smog and directly affects human health. Besides, ozone is a powerful greenhouse gas, whose formation is greatly potentiated by the incidence of sun radiation and the presence of nitrogen oxides (NO_x) (Yu & Kung, 1999; McCulloch et al., 2005; Teodoro et al., 2010). According to the Intergovernmental Panel of Climatic Changes (IPCC), ozone has a positive radiative forcing of about 0.35 W/m², being, therefore, an important source of global warming.

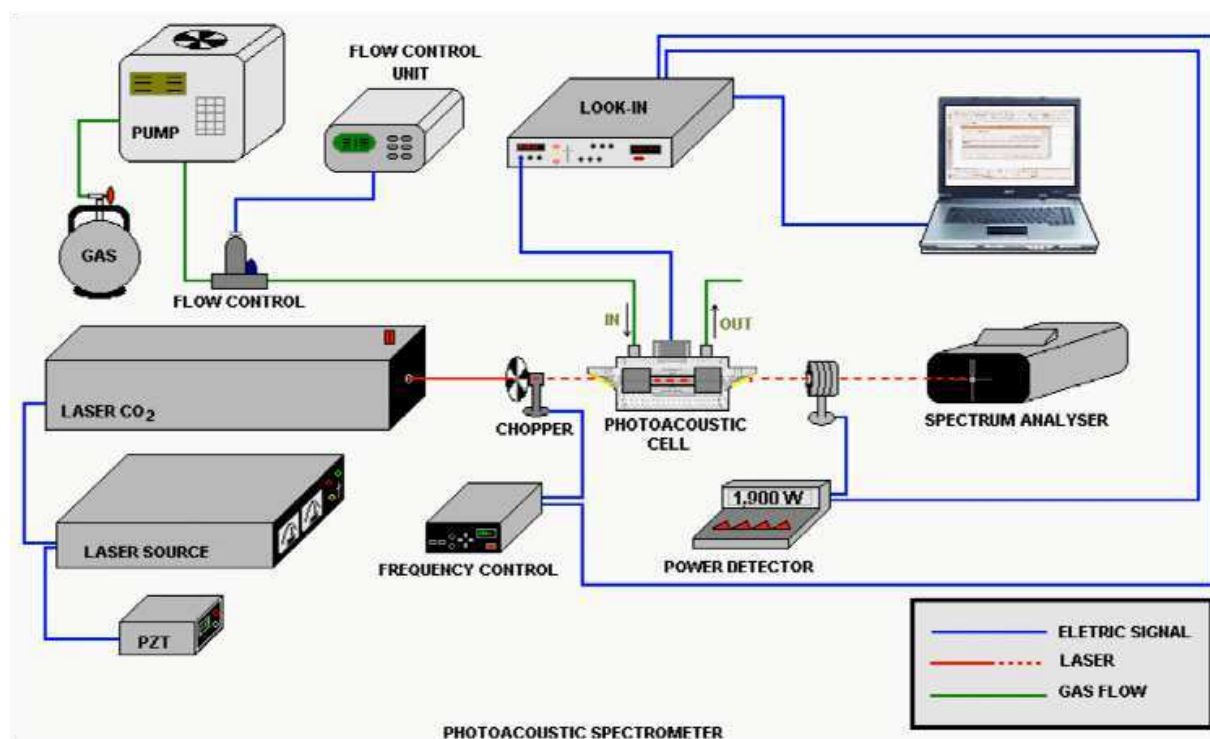


Fig. 3. Scheme of the photoacoustic experimental setup

To guarantee a refined detection of ethylene, the photoacoustic spectrometer is daily calibrated by submitting the cell to a flow of a certified mixture. This measurement was carried out using a certified gas mixture of 1.1 ppmV ethylene in N₂ flowing into the cell at a rate of 83.3 sccm (standard cubic centimeter). The acoustic signal is detected by a microphone that generates an electric signal. This electric signal is pre-amplified and then detected by a lock-in amplifier (Stanford SR850) with a time constant of 300 ms. The lock-in response is registered in a microcomputer. A continuous wave CO₂ infrared laser (LTG, model LTG150 626G), tuneable over about 80 different lines between 9.2 and 10.6 μm, with a

power of 1.9W at the emission line 10P(14) (10.53 μm), by internal PZT (Piezoelectric Transducer), is employed as the excitation source. At this power level, no saturation effects of the photoacoustic signal were observed. These lines can be swept by a step motor controlled by a microcomputer. Within this spectral region, many small molecules show a unique fingerprint. The photoacoustic instrument used has been developed for the detection of small concentrations of gases. All the measurements and the sample collection are made at room temperature. Therefore, the analysis of these samples is made for a number of n different species, rather than just one. This was accomplished by measuring the photoacoustic (PA) signal $S(\lambda_i)$ at a set of wavelengths λ_i ($i = 1, 2 \dots m$) chosen on the basis of the absorption spectra of the individual components to be detected. These individual absorption spectra were obtained from the HITRAN-PC database, which calculates the absorption cross sections (σ) of a given molecule at different wave numbers $k_i = 1/\lambda_i$ in a given interval. Thus, the expression used to determine the concentrations of a given component in the multicomponent gas mixture is the eq. (5). The absorption cross section σ_{ij} is related to the photoacoustic generation efficiency of each gas component for each CO_2 laser line. The sum is taken over the n components present in the sample.

3.1.1 Photoacoustic cell calibration and sensitivity measurements

The calibration and sensitivity measurements of the photoacoustic cell were performed by obtaining the cell coupling constant C in the eq (5). This was performed by taking a 1.1 ppmV certified mixture of ethylene in N_2 and diluting it in nitrogen until the least concentration achieved (about 16 ppbv) (Mothé et al, 2010). A linear dependence of the photoacoustic signal on the ethylene concentration could be proven and this linearity could be extended to ppmV levels. The absorption cross section σ of ethylene is well known at the 10P(14) (949.51cm^{-1}) CO_2 laser line ($\sigma = 170 \times 10^{-20} \text{cm}^2$). Hence, the C constant value was then obtained from the eq. (3), which yielded 40.2 V.cm/W . The unity of the cell coupling constant was furnished by the manufacturer of our photoacoustic cell (Prof. Markus W. Sigrist). Recent measurements made in greenhouse gas SF_6 , indicated that using the CO_2 laser, it was possible to achieve a detection limit of 20 ppbv. (Rocha et al., 2010)

3.2 Quantum Cascade Laser (QCL) experimental setup

With the recent development of quantum-cascade lasers (QCLs), compact, low-cost, solid-state radiation sources are available, covering the important infrared (IR) region with specific molecular absorption lines. In addition, spectral regions can be selected in which water vapor has a very low absorption coefficient, known as atmospheric windows. Another important advantage of QCLs in practical applications is that they work near room temperature, whereas diode lasers such as lead salt lasers, which emit in the fundamental IR region, have to be cryogenically cooled. Recent applications of QCLs clearly indicate their potential as tunable light sources in the mid-infrared, especially between 3 - 13 μm , with strong fundamental absorption bands. Current interest is based on the lack of other convenient coherent laser sources. In fact, it can be expected that QCLs will open new possibilities for real-time diagnostics of various molecular species in the 3-5 μm and 8-13 μm atmospheric windows. (Kosterev et al., 2002) Pulsed quantum-cascade distributed-feedback (QC-DFB) lasers provide quasi room temperature operation, combined with a high spectral selectivity and sensitivity, real time measurement capabilities, robustness, and compactness.

For this reason, QCLs are ideal for the development of compact trace gas analyzers that are also suitable for field measurements. In recent years the detection of a series of important trace gases has been demonstrated with these devices. (Faist, et al., 1994,1997; Beck et al., 2002; Silva et al., 2004; Baptista-Filho et al., 2006; Lima et al, 2006; Grossel et al., 2007; Gmachl et al., 2001; Beyer et al., 2003; Kosterev et al., 2002; Curl et al., 2010; Kosterev et al., 2002). By way of illustration we report on measurements of sulphur hexafluoride and methane with a homemade Laser Photoacoustic Spectrometer equipped with QC lasers and a Differential Photoacoustic Cell. The motivation of our research comes from the need for simple, sensitive, and spectrally selective devices for measuring traces of greenhouse gases in agriculture, automobile exhaust monitoring, power distribution facilities, cattle breeding and chemistry industries. The experimental set up employed in the detection limit determination of the analyzed gases is illustrated in Figure 4.

As radiation source, a pulsed quantum cascade is normally used. In this experiment two quantum cascade lasers were employed separately, each laser emission band matching the absorption lines of one of the specified molecules. The laser used in the detection of CH_4 , emits in the range of 7.71 - 7.88 μm and can reach a power of 5.6 mW (at lowest operating temperature of the laser), the one employed in the detection of SF_6 , emits in the range of 10.51 - 10.56 μm and can reach a power of 3.7 mW.

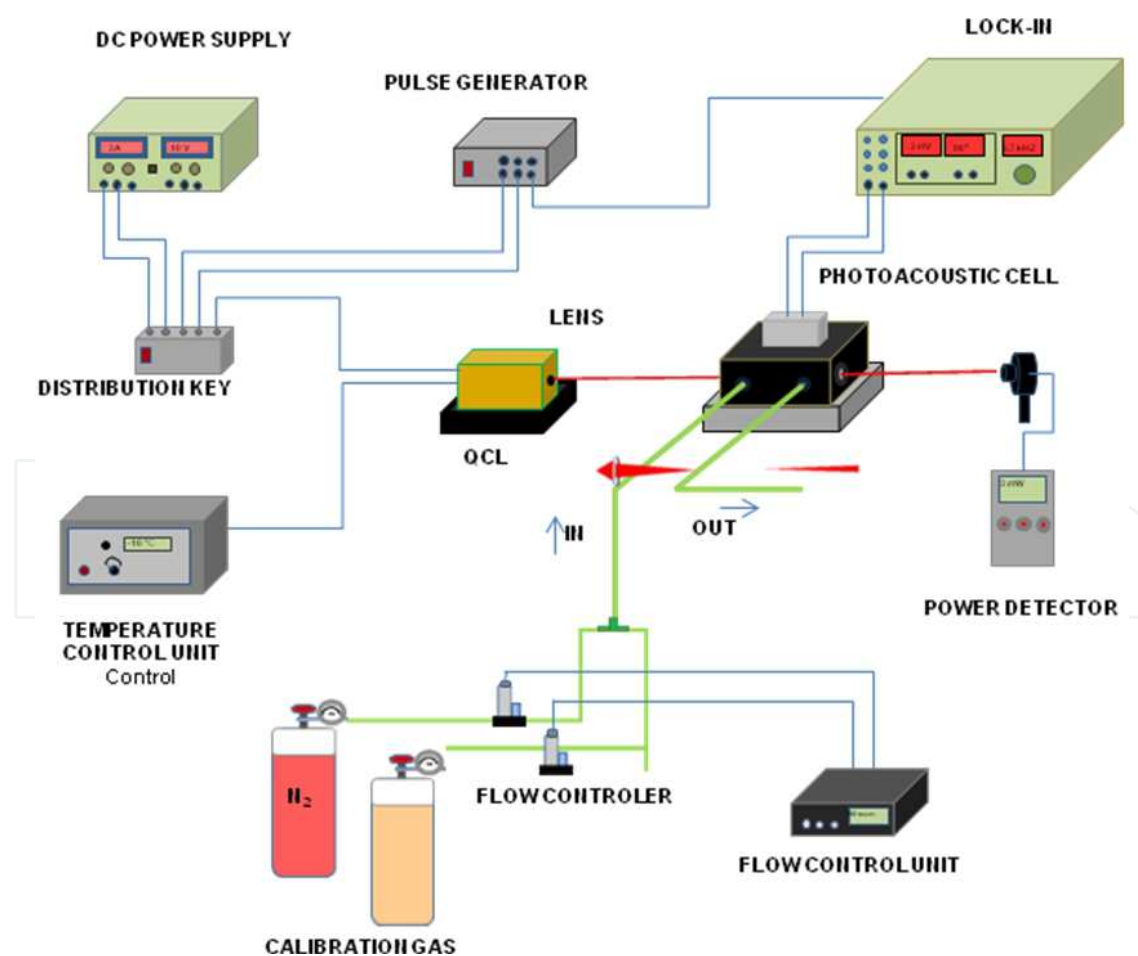


Fig. 4. Experimental set up using quantum cascade laser.

The laser emission lines are given according to the diode temperature, which is determined by a temperature control unit. The pulsed QCL light beam, with a repetition rate of 400kHz and a pulse duration of 50ns (duty cycle of 2%), is gated by an external transistor-to-transistor logic (TTL) signal at 3.8kHz to excite the first longitudinal acoustic mode of the resonant differential photoacoustic cell. A germanium lens (focus ~30.7 mm and diameter ~10.35mm) is employed to focus the QCL radiation through the cell. The cell (Miklos, 2001) has two resonant cylindrical tubes (5.5 mm in diameter and 4 cm in length) on whose edges are arranged acoustic buffers which reduce noise caused by gas turbulence and background signal produced by the heating in the cell windows when these are exposed to the radiation. The gas flow streams through both pipes and noise and background are equally detected by the microphones placed on each of them, but only the microphones placed in the tube crossed by the laser beam detect the pressure change induced by the absorption of modulated radiation in the gaseous sample containing the molecules under consideration. Thus the photoacoustic signal is obtained by simple differentiation of the signal produced by the microphones in the two tubes.

The laser power is monitored by a power detector (OPHIR, 3A-SH-ROHS) and the gases flows are controlled by electronic mass flow controllers (model MKS, 247), one of 50 sccm and one of 300sccm. The PA data analysis was performed by the lock-in technique using a lock-in amplifier (model Stanford SR_850 DSP) with a set data acquisition time constant of 300ms.

3.2.1 Calibration and sensitivity measurements

The following concentration measurements were performed keeping the temperature of each laser constant. At these emission lines the lasers power was 0.8 mW, feed current of 26.2 mA, for the laser used to measure CH_4 , and 1.12 mW, feed current of 25.3 mA, for the laser used to measure SF_6 . In such type of measurement, a high stability is observed during the entire experiment. In order to determine the detection boundaries of the gases of interest, a dilution of standard mixtures were carried out. Dilution experiments are depicted in figure 5 and figure 6. Small concentrations of the investigated gases were synthesized by using two electronic mass-flow controllers, one for N_2 (with full scale control of 200 sccm) and another for the investigated gas (CH_4 or SF_6) (with full scale control of 50 sccm). The electronic mass-flow controllers were connected in parallel to the gas inlet of the photoacoustic cell. The initial concentrations of 4.5 ppmv CH_4 and 5 ppmv SF_6 was diluted with pure nitrogen (zero gas) down to the lowest concentrations detected by the system.

The acoustic and electronic noise was determined by blocking the laser light while keeping all other devices running. The value of the noise signal was typically $0.300\mu\text{V}$. As expected (Eq.3), a linear dependence of the photoacoustic signal on the methane and sulphur hexafluoride concentration was found. The fitted straight line are also shown in Figures 5 and 6. The smallest measured concentrations were of 1.5 ppmv for methane and 49 ppbv for sulphur hexafluoride (Rocha et al., 2010 b). Although the smallest concentration of methane detected was of 1.5 ppmv, the strong linear slope of the fitted straight line allows us to estimate that the instrumentation has the sensitivity to detect concentration changes smaller than 1.5 ppmv. In recent measurements made with methane, it was possible to achieve an experimental detection limit of 50 ppbv, for this gas (Rocha et al, 2011). It is possible to estimate a detection limit of 30 ppbv methane, by extending the straight line until the noise limit, at a signal to noise ratio, in single pass (Grossel et al., 2007).

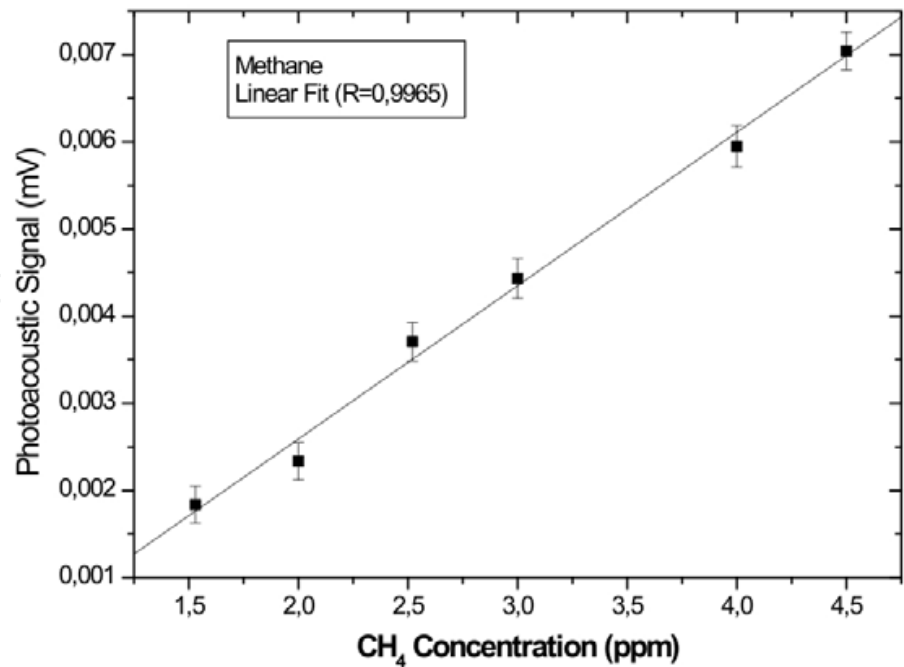


Fig. 5. Calibration curve for methane.

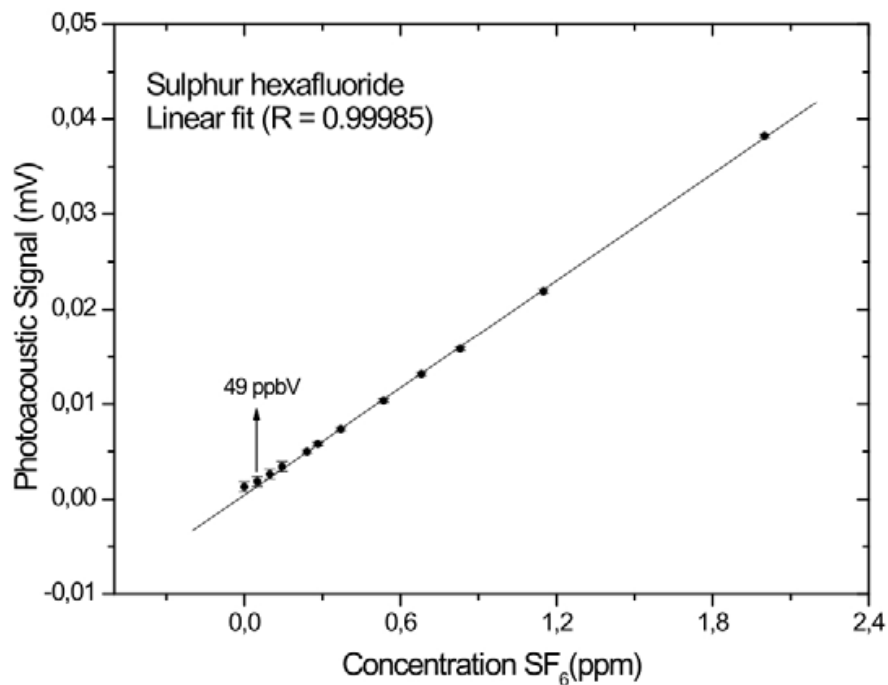


Fig. 6. Calibration curve for sulphur hexafluoride.

The photoacoustic spectroscopy with quantum cascade lasers has proved to be extremely efficient for the detection of greenhouse gases (Atkinson, 2000), being sensible and selective. In the case of the greenhouse gas methane, this methodology allows measurements in anthropogenic sources that emits methane in concentration higher than 1.5 ppmv and also atmospheric measurements, once it is estimated that the current average concentration of this gas in the atmosphere is of 1.7 ppmv. For sulphur hexafluoride the method is suitable

for concentrations greater than 49 ppbv, a concentration already detected by conventional equipments. Another important greenhouse gas is the nitrous oxide (N_2O) which can also be detected by quantum cascade laser (QCL), whose detection limit of 14 ppbv was obtained for this gas (Grossel et al, 2007).

3.3 OPO Laser experimental setup

Figure 7 shows a schematic diagram of an experimental setup for an OPO in a simple grazing-incidence grating configuration (GIOPO) (Yu & Kung, 1999). Two gold mirrors (M1 and M2) are used to produce an optical resonator. The pump light (1064 nm) is put into the resonator by 45° incidence on a third mirror (M3) coated for high reflection at 1064 nm and high transmission for signal and idler waves. A coated highly transmitting at 1064 nm lens (L1) is used to focus the pump beam at the middle of the PPLN crystal (C1) length. In the GIOPO configuration a grating (600/mm groove density) (G1) is placed at grazing incidence relative to the cavity axis. The grating serves as dispersing element. The diffracted first order off the grazing is reflected back into the cavity by M2 and used as injection seed. The zero order is out coupled from the resonator to be used as exciting light for photoacoustic spectroscopy. Before the beam reaches the photoacoustic detector, a highly reflecting mirror at 1064 nm is employed to eliminate the pump wave and a germanium element (Ge) is used to filtering the signal wave from the beam. This OPO configuration results in a typical linewidth of about 0.1 cm^{-1} and the idler wave covers a wavelength range between 2.4 and $4\text{ }\mu\text{m}$ with power average of some hundreds of miliwatts by either tuning the mirror M2 or changing the temperature of the crystal.

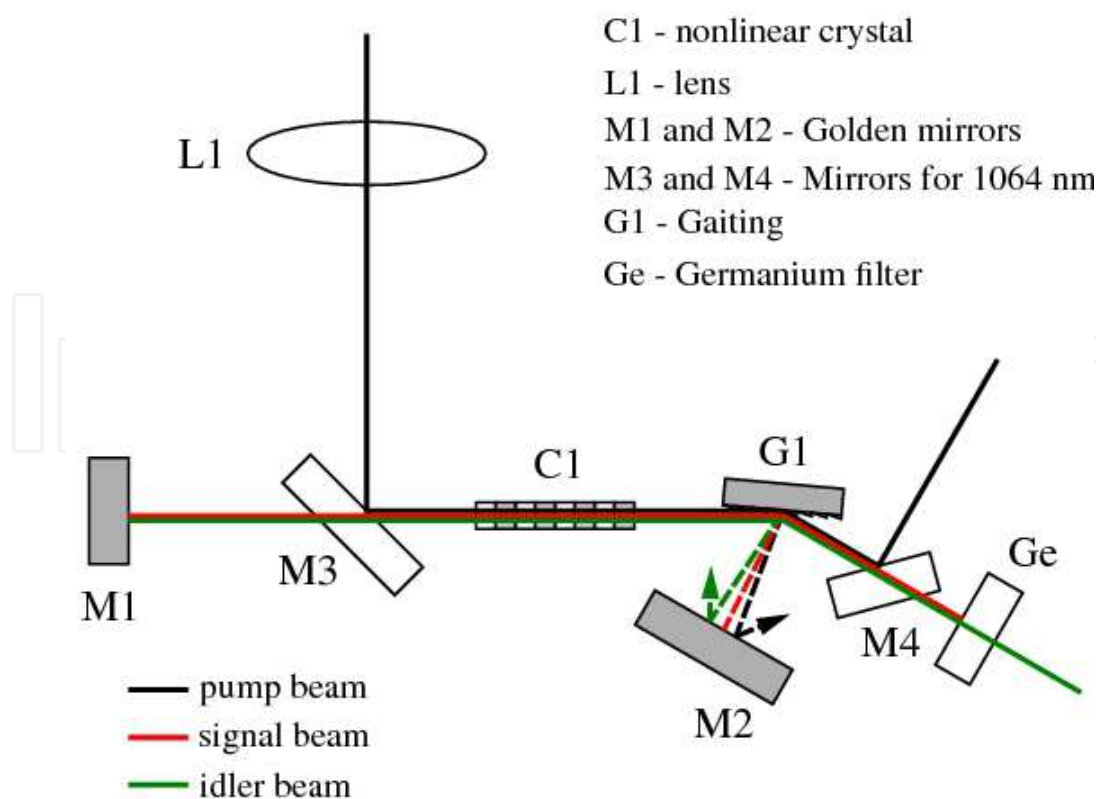


Fig. 7. Schematic setup for OPO with in a grazing-incidence grating configuration.

Owing to the wavelength tunability of the OPO, in recent years it has been shown the feasibility of using optical parametric oscillator as light source for trace gas detection of several chemical species of environmental appeal. Limits of part per billion for greenhouse gases have been demonstrated when OPO is combined with photoacoustic detection methods. Concentration limit of 60 ppbv (part per billion by volume) and 20 ppbv were estimated for nitrous oxides (N_2O) and methane (C_2H_4), respectively, when the OPO radiation is in amplitude modulated (Costopoulos et al., 2002, Liang et al., 2000). The sensitivity of the detection for methane can be improved when the technique of wavelength modulation of the OPO radiation, combined with multipass configuration, is employed. This modulation mode has the advantage of the suppression of the baseline caused by hits of the cell windows and the reflection on the mirrors. According to Nd *et al* , an ultimate sensitivity of 136 parts in 10^{12} for methane was estimated when the technique of wavelength modulation is used (Kung et al., 2004) [92].

Since the increase rate of greenhouse in the atmospheric air is higher than the sensitivity of an OPO setup, it gives rise in this way the possibility of using OPO devices to monitor the annual change of pollutants in atmospheric air. Detection of N_2O in ambient air was already carried out using photoacoustic spectroscopy. Applying the photoacoustic spectroscopy in combination with a pulsed grazing-incident optical parametric oscillator, concentrations of 311 ppbv were found for ambient samples collected at nearby roads (Da Silva et al., 2006).

4. Conclusion

The Photoacoustic Spectroscopy has proved to be extremely sensitive and selective for gas detection. Several experimental arrangements with laser sources have been presented to the detection of greenhouse gases and its precursors in the ppmv and ppbv range. Recent advances in radiation sources for photoacoustic detection of gases has been presented, such as the quantum cascade laser (QCL) and the optical parametric oscillator (OPO) system as well as improvements in the photoacoustic detector, like the differential photoacoustic cell and the simple resonant photoacoustic cell. Such progresses encourage the development of new researches in the field of atmospheric pollution.

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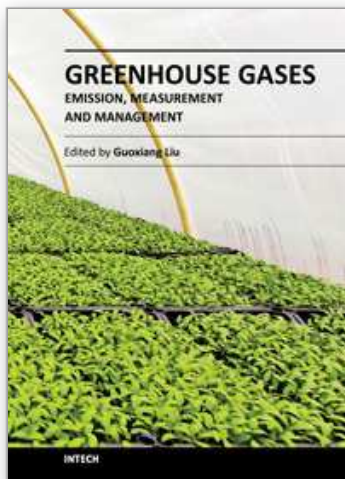
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Understanding greenhouse gas sources, emissions, measurements, and management is essential for capture, utilization, reduction, and storage of greenhouse gas, which plays a crucial role in issues such as global warming and climate change. Taking advantage of the authors' experience in greenhouse gases, this book discusses an overview of recently developed techniques, methods, and strategies: - A comprehensive source investigation of greenhouse gases that are emitted from hydrocarbon reservoirs, vehicle transportation, agricultural landscapes, farms, non-cattle confined buildings, and so on. - Recently developed detection and measurement techniques and methods such as photoacoustic spectroscopy, landfill-based carbon dioxide and methane measurement, and miniaturized mass spectrometer.

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