

Article

A Sulfur Hexafluoride Sensor Using Quantum Cascade and CO₂ Laser-Based Photoacoustic Spectroscopy

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Abstract: The increase in greenhouse gas emissions is a serious environmental problem and has stimulated the scientific community to pay attention to the need for detection and monitoring of gases released into the atmosphere. In this regard, the development of sensitive and selective gas sensors has been the subject of several research programs. An important greenhouse gas is sulphur hexafluoride, an almost non-reactive gas widely employed in industrial processes worldwide. Indeed it is estimated that it has a radiative forcing of 0.52 W/m². This work compares two photoacoustic spectrometers, one coupled to a CO₂ laser and another one coupled to a Quantum Cascade (QC) laser, for the detection of SF₆. The laser photoacoustic spectrometers described in this work have been developed for gas detection at small concentrations. Detection limits of 20 ppbv for CO₂ laser and 50 ppbv for quantum cascade laser were obtained.

Keywords: sulfur hexafluoride; photoacoustic spectroscopy; sensors

1. Introduction

Air pollution is one of the main environmental problems of the XXIst Century. After the publication of the Intergovernmental Panel on Climate Changes (IPCC) Report in 2007 [1], global warming is considered to be the responsible for climate changes in the planet [2-10] and for bringing significant consequences to human society.

The same Report highlights sulfur hexafluoride (SF_6) as an important greenhouse gas, as it has a radiative forcing of 0.52 W/m^2 , an atmospheric lifetime of 3,200 years and a Global Warming Potential (GWP) of 23,900. Sulfur hexafluoride is almost non-reactive and therefore it is widely employed for insulation and current interruption purposes in electric power transmission and distribution equipment. It is also used in the magnesium industry to protect molten magnesium from oxidation and potential violent burning, in semiconductor manufacturing to create circuitry patterns on silicon wafers and as a tracer gas for leak detection [11].

In trace-gas analysis of chemical species in the atmosphere, besides sensitivity and selectivity the response time is of increasing interest for the real-time detection of temporal concentration changes. In order to achieve the necessary sensitivity and selectivity, the use of high-resolution laser techniques in IR and near-IR (NIR) fingerprint region is of special interest. The methodologies based on the photothermal techniques, mainly photoacoustic spectroscopy, have suitable characteristics for trace gas detection. Actually several laser-based methods have been reported because they are very sensitive [12-14]. For instance, photoacoustic spectroscopy is widely used in the detection of several gases in the ppbv and sub-ppbv concentration range [15-19].

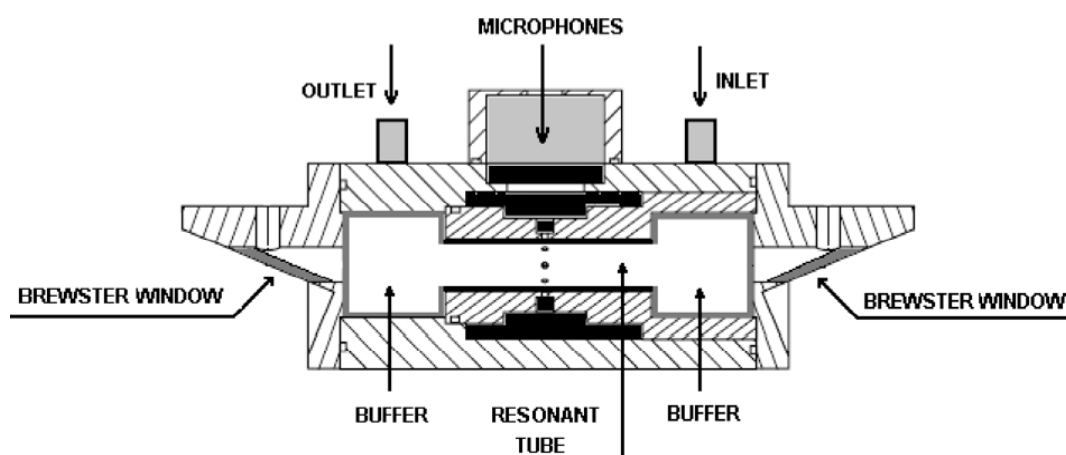
A homemade CO_2 laser photoacoustic spectrometer has been developed to monitor gas emissions of several sources [20]. A continuous wave CO_2 infrared laser tunable over 80 different lines, between 9.2 and 10.6 μm , has been employed at the emission line of 10P(16) as excitation source for sulfur hexafluoride gas detection [21-23].

With the recent development of quantum-cascade lasers (QCLs), compact solid-state radiation sources are available, covering the important infrared (IR) region with specific molecular absorption lines. In addition, spectral regions known as atmospheric windows can be selected in which water vapor has a very low absorption coefficient. Another important advantage of QCLs in practical applications is that they work at 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 and 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 [24].

Pulsed quantum-cascade distributed-feedback (QC-DFB) lasers provide quasi room temperature operation, combined with 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 [24-29].

Figure 2. Diagram showing the design of the resonant photoacoustic cell used.



The measurement was performed initially using a 1.1 ppmv certified gas mixture of ethylene in N_2 flowing into the cell at a rate of 5 L/h. The ethylene gas is used as a calibrator in CO_2 laser photoacoustic spectroscopy. The acoustic signal is detected by a microphone that generates an electric signal. This electric signal, in turn, is pre-amplified and then detected by a Lock-In amplifier (Stanford SR850). The Lock-In response is registered in a microcomputer. A continuous wave CO_2 infrared laser (Lasertech Group Inc.,—LTG, model LTG150 626G), tunable over about 80 different lines between 9.2 and 10.6 μm and delivering a power of 1.9 W at the emission line of 10P(14), was employed as the excitation source. At this power level, no saturation effect of the photoacoustic signal was observed. The CO_2 laser lines can be swept by a step motor controlled by the microcomputer. Within this spectral region many small molecules show a unique fingerprint. The photoacoustic instrument used in this work has been developed for gas detection at small concentrations. All measurements were made at room temperature.

Calibration and sensitivity measurements of our photoacoustic cell were performed obtaining the cell constant C in the Equation (1) below. This was carried out taking a certified mixture of 1.1 ppmv of ethylene in N_2 and diluting it in nitrogen until the lowest detected concentration of 16 ppbv. Thus, a calibration curve relating the PA signal and the ethylene concentration was obtained. As this function has a linear behavior we can extend this linearity to ppmv levels. This calibration line follows the expression:

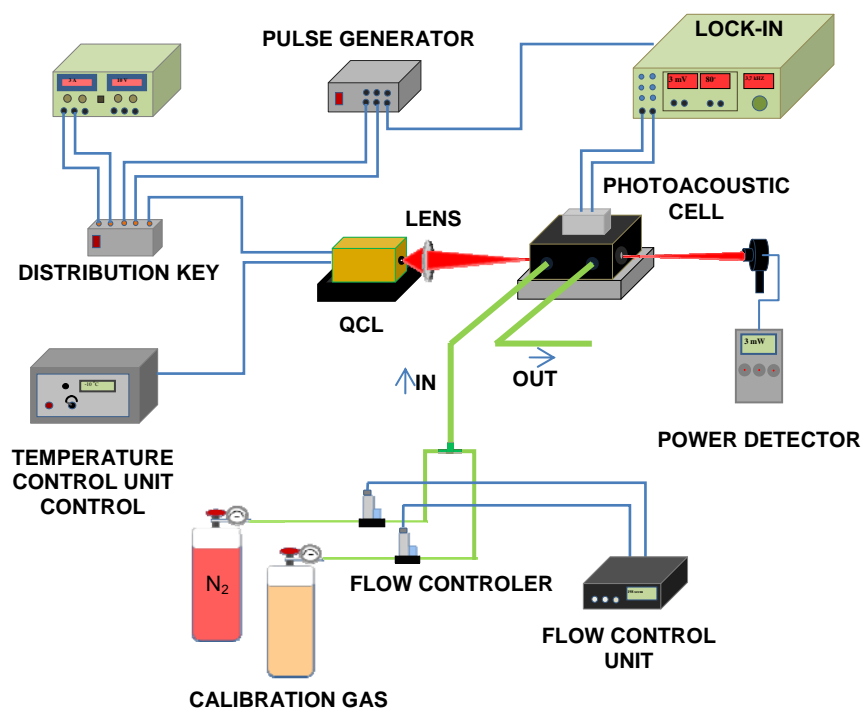
$$S_i = C \cdot P_i N_{tot} c_{ref} \sigma_i \quad (1)$$

The constant C is the so-called cell constant and it depends, like the detection sensitivity, on the cell geometry, the microphone responsivity and on the nature of the acoustic mode [32,33]. The absorption cross section σ of ethylene is well known at the 10P (14) ($k = 949.51 \text{ cm}^{-1}$) CO_2 laser line ($\sigma = 170 \times 10^{-20} \text{ cm}^2/\text{molecules}$). P_i represents the laser power at wavelength λ_i and c_{ref} is the concentration of the gas. N_{tot} is the total number density of molecules in the mixture and was considered to be typically $2.5 \times 10^{19} \text{ molecules/cm}^{-3}$ at room temperature [32]. Hence, the C constant value was then obtained from the Equation (1), which yielded $C = 40.2 \text{ V cm/W}$.

2.2. QC Laser Photoacoustic Spectroscopy

The experimental set up employed for the detection limit determination of the analyzed gas is illustrated in Figure 3. As radiation source, a pulsed quantum cascade laser furnished by Alpes Lasers was used. The laser (model #sb186 DN) emits in the range of 10.51–10.56 μm and can reach a power of 3.7 mW.

Figure 3. Experimental set up.



The laser wavelength can be turned over the given range by diode temperature, which is determined by a temperature control unit. The pulsed QCL light beam, with a repetition rate of 400 kHz and a pulse duration of 50 ns (duty cycle of 2%), was gated by an external transistor-to-transistor logic (TTL) signal at 3.8 kHz to excite the first longitudinal acoustic mode of the resonant differential photoacoustic cell [18,19]. A germanium lens (focus ~ 30.7 mm and diameter ~ 10.35 mm) was employed to focus the QCL radiation through the cell. The differential cell 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 were equally detected by the microphones placed on each of them, but only the microphones placed in the tube crossed by the laser could detect the pressure changes induced by the absorption of modulated radiation. Thus the photoacoustic signal is obtained as the difference of the microphones signals measured in the two tubes.

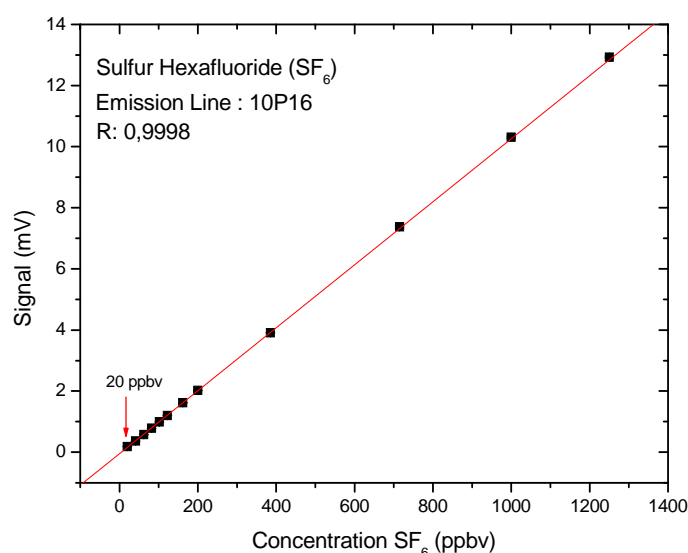
The laser power was monitored by a power detector (OPHIR, 3A-SH-ROHS) and the gas flows were controlled by two electronic mass flow controllers (model MKS 247, 50 sccm and 300 sccm). The PA data analysis was performed by the lock-in technique using a lock-in amplifier (model

Stanford SR 850 DSP) with a time constant of 300 ms. The theoretical model adopted was the same as used in the CO₂ laser photoacoustic system.

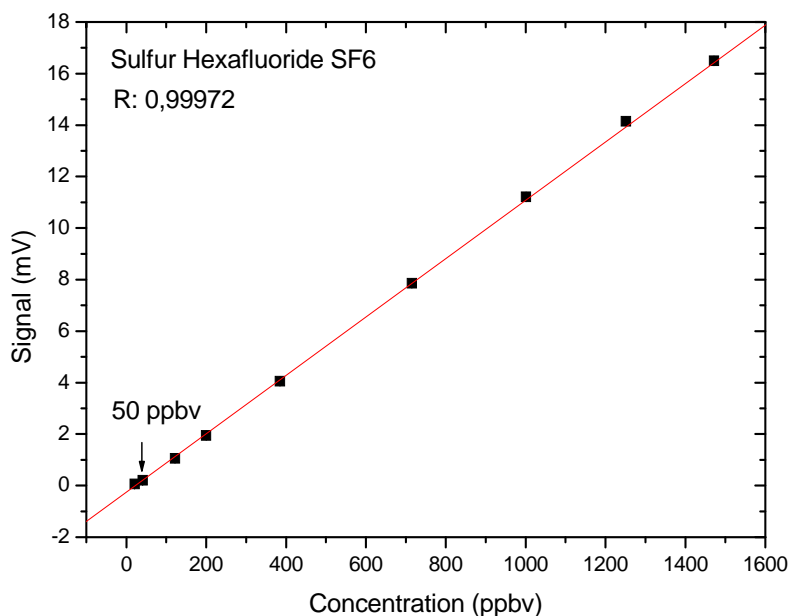
3. Results and Discussion

The continuous wave infrared CO₂ laser, delivering a power level of 1.5 W, was employed as an excitation source at the emission line of 10P (16), $\lambda = 10.5 \mu\text{m}$. The initial concentration of 5 ppmv of SF₆ was diluted with pure nitrogen (zero gas) down to the lowest concentrations detected by the system. The acoustic and electronic noises were determined by blocking the laser light while keeping all other devices running. The value of the noise signal was typically 30 μV . As expected, a linear dependence of the photoacoustic signal on the sulfur hexafluoride concentration was observed. The measured PA signals and the fitted straight line are shown in (Figure 4). The smallest measured concentration was 20 ppbv for sulfur hexafluoride. As this function has a linear behavior we can extend this linearity to ppmv levels.

Figure 4. Calibration curve for sulfur hexafluoride.



The pulsed quantum cascade laser (QCL), delivering a power of 1.12 mW at the wavelength of 10.5 μm , was used to excite the sulphur hexafluoride molecules. To determine the detection limit of the system, a dilution of a standard mixture of 5 ppmv of SF₆ in N₂ was carried out. Small concentrations of the gas were synthesized by using two electronic mass-flow controllers, one for N₂ (with full scale control of 200 sccm) and another for the investigated gas (SF₆) (with full scale control of 50 sccm). The electronic mass-flow controllers were connected in parallel to the gas inlet of the photoacoustic cell, and the initial SF₆ concentration of 5 ppmv was diluted with pure nitrogen (zero gas) down to the lowest concentrations detected by the system. The acoustic and the electronic noise were determined by blocking the laser light while keeping all other devices running. The value of the noise signal was typically 0.3 μV . As expected, a linear dependence of the photoacoustic signal on the sulfur hexafluoride concentration was found. The measured PA signals and the fitted straight line are shown in (Figure 5). The smallest measured concentration of sulfur hexafluoride was 50 ppbv. As this function has a linear behavior, we can extend this linearity to ppmv levels.

Figure 5. Calibration curve for sulfur hexafluoride.

While the QCL provided a detection limit of 50 ppbv, the CO₂ laser reached a limit of 20 ppbv, therefore proving to be more sensitive. However, 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, whereas CO₂ lasers are large, unstable and expensive in comparison. For this reason, QCLs are ideal for the development of compact trace gas analyzers that are also suitable for field measurements. We present an experimental setup where the QCLs is coupled to a differential photoacoustic cell that produces a photoacoustic signal with noise 100 times smaller (0.3 μ V) when compared with the photoacoustic cell used in the experiment with CO₂ laser (30 μ V). With the development of QCLs with continuous emission, rather than pulsed, greater power is provided, and along with proper alignments to optimize the laser beam it will be possible to achieve detection limits comparable to those obtained with the CO₂ laser.

For practical applications (industrial environments) that involve measurements in the atmosphere, the method proposed in this work must consider the presence of some chemical species that can alter the concentrations obtained for the SF₆ gas, such as CO₂ and water vapor. Thus one must use KOH and CaCl₂ filters so as to eliminate the possible interference from those species [34]. The typical concentration of SF₆ observed in the atmosphere is about 7 pptv, determined by NOAA (National Oceanic & Atmospheric Administration), on Mauna Loa, Hawaii, U.S.A. [35]. This value can be increased up to hundreds of ppbv to ppmv in certain processes and leaks in industrial environments.

4. Conclusions

The Photoacoustic Spectroscopy using CO₂ and quantum cascade lasers has proved to be extremely sensitive and selective for the detection of sulfur hexafluoride. This methodology allows measurements in anthropogenic sources that can reach concentrations higher than 20 ppbv, when using

the CO₂ laser, and higher than 50 ppbv when using the pulsed quantum cascade distributed-feedback (QC-DFB) laser. These results are very promising and encourage further research.

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References

1. IPCC. *Report of Working Group I. Climate Change 2007*. The Physical Science Basis: Paris, France, February 2007.
2. Hansen, J.; Sato, M.; Kharecha, P.; Beerling, D.; Berner, R.; Masson-Delmotte, V.; Pagai, M.; Raymo, M.; Royer, D.L.; Zachos, J.C. Target Atmosphere CO₂: Where Should Humanity Aim. *Open Atmos. Sci. J.* **2008**, *2*, 217-231.
3. Gillett, N.P.; Stone, D.A.; Stott, P.A.; Nozawa, T.; Karpechko, A.Y.; Hegerl, G.C.; Wehner, M.F.; Jones, P.D. Attribution of Polar Warming to Human Influence. *Nat. Geosci.* **2008**, *1*, 750-754.
4. Sander, B.D. Forced and Unforced Ocean Temperature Changes in Atlantic and Pacific Tropical Cyclogenesis Regions. *PNAS*, **2006**, *103*, 13905-13910.
5. Emanuel, K. Increasing Destructiveness of Tropical Cyclones over the Past 30 Years. *Nature* **2005**, *436*, 686-688.
6. Kurz, W.A. Mountain Pine Beetle and Forest Carbon Feedback to Climate Change. *Nature* **2008**, *452*, 987-990.
7. Greene, C.H.; Monger, B.C.; McGarry, L.P. Some Like It Cold, Northern Shrimp Stocks Thrive When Climatic Conditions Lead to Cold Bottom Waters. *Science* **2009**, *324*, 733-734.
8. Meinshausen, M. Greenhouse Gas Emission Targets for Limiting Global Warming to 2 °C. *Nature* **2009**, *458*, 1158-1163.
9. Allen, M.R.; Frame, D.J.; Huntingford, C.; Jones, C.D.; Lowe, J.A.; Meinshausen, M.; Meinshausen, N. Warning Caused by Cumulative Carbon Emissions towards the Trillionth Tonne. *Nature* **2009**, *458*, 1163-1166.
10. World Meteorological Organization. Available online: http://www.wmo.int/pages/index_en.html (accessed on November 2009).
11. *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990/2008*; U.S. Environmental Protection Agency: Washington, WA, USA, April 2010.
12. Sigrist, M.W. Trace Gas Monitoring with Infrared Laser-Based Detection Schemes. *Appl. Phys. B* **2008**, *90*, 289-300.
13. Rocha, M.V.; Sthel, M.; Silva, M.G.; Schramm, D.U.; Vargas, H. Greenhouse Gases Detection with Quantum Cascade Laser Photoacoustic Spectroscopy. In *Proceedings of Air & Waste Manager's 103rd Conference*, Calgary, Canada, June 2010, in press.
14. Cristescu, S.M.; Persijn, S.T.; Hekkert, S.L.; Harren, F.J.M. Laser-Based Systems for Trace Gas Detection in Life Sciences. *Appl. Phys. B* **2008**, *92*, 343-349.

15. Nagele, M.; Sigrist, M.W. Mobile Laser Spectrometer with Novel Resonant Multipass Photoacoustic Cell for Trace-Gas Sensing. *Appl. Phys. B* **2000**, *70*, 895-901.
16. Miklos, A.; Hess, P.; Bozóki, Z. Application of Acoustic Resonators in Photoacoustic Trace Gas Analysis and Metrology. *Rev. Sci. Inst.* **2001**, *4*, 1937-1955.
17. Sthel, M.S.; Schramm, D.U.; Faria, R.T., Jr.; Castro, M.P.P.; Carneiro, L.O.; Ribeiro, W.S.; Vargas, H. Photoacoustic Spectroscopy-Based Analysis of Gas Samples in A Bus Station. *J. Phys. IV France*, **2005**, *125*, 881-883.
18. Lima, J.A.P. Photoacoustic Detection of NO₂ and N₂O Using Quantum Cascade Lasers. *Appl. Phys. B* **2006**, *85*, 279-284.
19. Da Silva, M.; Miklos, A.; Hess, P. Photoacoustic Measurement of N₂O Concentration in Ambient Air with a Pulsed Optical Parametric Oscillator. *Appl. Phys.* **2006**, *82*, 329-336.
20. Schramm, D.U.S.; Sthel, M.S.; Silva, M.G.; Carneiro, L.O.; Junior, A.J.S.; Vargas, H. Application of Laser Photoacoustic Spectroscopy for The Analysis of Gas Samples Emitted by Diesel Engines. *Inf. Phys. Technol.* **2003**, *44*, 263-269.
21. Gondal, M.A.; Dastageer, A; Shwehdi, M.H. Photoacoustic Spectrometry for Trace Gas Analysis and Leak Detection Using Different Cell Geometries. *Talanta* **2004**, *62*,131-141.
22. Gondal, M.A; Baig, M.A.; Shwehdi, M.H. Laser Sensor for Detection of SF₆ Leaks in High Insulated Switch Gear Systems. *IEEE Trans. Dielectrics Eletrical Insulations.* **2002**, *9*, 421-427.
23. Gondal, M.A.; Yamani, Z.H. High Sensitive Electronically Modulated Photoacoustic Spectrometer for Ozone Detection. *Appl. Opt.* **2008**, *46*, 7083-7090.
24. Kosterev, A.A.; Curl, R.F.; Tittel, F.K.; Rochat, M.; Beck, M.; Hofstetter, D.; Faist, J. Chemical Sensing with Pulsed QC-DFB Lasers Operating at 15.6 μm. *Appl. Phys. B* **2002**, *75*, 351-357.
25. Meyer, T.; Braun, M.; Lambrecht, A. Fast Gas Spectroscopy Using Pulsed Quantum Cascade Lasers. *J. Appl. Phys.* **2003**, *93*, 3158-3160.
26. Silva, M.G.; Vargas, H.; Miklós, A.; Hess, P. Photoacoustic Detection of Ozone Using Quantum Cascade Laser. *Appl. Phys. B* **2004**, *78*, 1513-1516.
27. Curl, R.F.; Capasso, F.; Gmachl, C.; Kosterev, A.A.; McManus, B.; Lewicki, R.; Pusharsky, M.; Wysocki, G.; Tittel, F.K. Quantum Cascade Lasers in Chemical Physics. *Chem. Phys. Lett.* **2010**, *487*, 1-18.
28. Baptista F.M.; Da Silva, M.G.; Sthel, M.S.; Schramm, D.U.; Vargas, H.; Miklos, A.; Hess, P. Ammonia Detection Using Quantum-Cascade Laser Photoacoustic Spectroscopy. *Appl. Opt.* **2006**, *45*, 4966-4971.
29. Zeninary, V.; Grossel, A.; Joly, L.; Decarpenterie, T.; Grouiez, B.; Bonno, B.; Parvitte, B. Photoacoustic Spectroscopy for Trace Gas Detection with Cryogenic for Trace Gas Detection with Cryogenic and Room-Temperature Continuous-Wave Quantum Cascade Lasers. *Cent. Eur. J. Phys.* **2010**, *8*, 194-201.
30. Killinger, D.A.; Mooradian A. *Optics and Laser Remote Sensing Springer Series in Optical Science*; Springer-Verlag: Berlin, Germany, 1988.
31. Measures, R.M. *Laser Remote Chemical Analysis*; John Wiley & Sons: New York, NY, USA, 1988.
32. Thony, M.; Sigrist, W. New Developments in CO₂-Laser Photoacoustic Monitoring of Trace Gases. *Infrared Phys. Technol.* **1995**, *36*, 585-615.

33. Bijnen, F.G.; Reuss, C.J.; Harren, F. Geometrical Optimization of a Longitudinal Resonant Photoacoustic Cell for Sensitive and Fast Trace Gas Detection. *J. Rev. Sci. Inst.* **1996**, *67*, 2914-2923.
34. Pereira, T., Almeida, P.S.G.; Da Silva, M.G.; Vargas, H. Gas Diffusion in ‘Golden’ Papaya Fruit at Different Maturity Stages. *Postharvest Biol. Technol.* **2009**, *54*, 123-130.
35. *National Oceanic and Atmospheric Administration Earth System Research Laboratory—Global Warming Division*. Available online: <http://www.esrl.noaa.gov/gmd/hats/insitu/cats/conc/mlosf6>.

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