

TRACE GAS MEASUREMENT USING IR LASER DIODES

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ABSTRACT

The properties of semiconductor laser diodes for trace gas measurements are reviewed. First, the modulation characteristics of these lasers are discussed. Then, two sensitive spectroscopic methods using a frequency-modulated near-IR laser are presented and their performance compared. In the $\lambda = 2 \mu\text{m}$ range, second-harmonic optical detection has shown a 20 times better detection limit than photoacoustic detection. The extension of these methods to longer wavelengths is finally discussed.

Keywords: laser diode, spectroscopy, wavelength modulation spectroscopy, photoacoustic spectroscopy, gas sensing

1. INTRODUCTION

The availability of fast and accurate instruments for gaseous pollutants monitoring at sub-ppm (parts per million) concentrations is of growing interest. Such measurements are of great importance for the monitoring of environment, the control of industrial processes and for the food industry. In environmental measurements, it is important to control the emission of atmospheric pollutants such as CH_4 , CO , CO_2 , SO_2 or NO_2 , which can produce severe effects on human health, on the growth of plants or can induce climatic changes. In industrial processes, it is necessary to control the amount of substances that can perturb the process, for example H_2O or NH_3 in the semiconductor manufacturing.

For best performance, trace gas detection instruments require an excellent sensitivity and a good selectivity, in addition to a fast response time. A high sensitivity is needed to reach ppm detection limits or better, whereas high selectivity is required to measure one species in the presence of a large and changing number of background substances. Conventional non-spectroscopic analytical methods for trace-gas measurement [1], such as chromatography, flame ionization or chemiluminescence, do not fulfil all these requirements, because they are not selective enough to differentiate between distinct species present in a gas compound. The related instrumentation is large and heavy, so that these methods are not suitable for *in-situ* measurements. In addition they cannot be used for real-time measurements owing to their long response time.

Laser-based spectroscopic measurements have the matching properties for this type of applications. Indeed, the most important atmospheric constituents have strong rotational-vibrational absorption bands in the mid-IR (3-20 μm), the so-called "fingerprint region". Since this absorption spectrum is proper to each molecule, spectroscopic methods allow highly specific detection of many substances [2].

In the mid-IR, there is unfortunately no suitable source for spectroscopic analysis of gas concentration. Lead-salt diode lasers give access to this spectral range, but they are limited by the need for cryogenic cooling, which is not acceptable for site applications. Furthermore, their emission spectrum is frequently multimode and their power is typically limited to several hundred of microwatts. Quantum cascade lasers are probably the sources of the future for spectroscopic measurements in the mid-IR [3]. Manufactured using the same technologically-matured semiconductor material as the usual IR lasers for telecommunications (GaAs, InP), they can be designed to emit at any wavelength in the 5-20 μm range. But they are currently operating only in pulsed mode and are still under development in different labs, so few of them are commercially available.

On the other hand, near-IR laser diodes based on the InGaAsP/InP technology developed for fiberoptics communications offer several attractive properties for spectroscopic applications [4]. In addition to the usual advantages of semiconductor

devices, such as compact size, reliability and low power consumption, they operate at room temperature with output power of several milliwatts. They can be manufactured to grant single frequency emission, which is necessary to obtain a good selectivity in spectroscopic applications. Single frequency emission is obtained using distributed feedback (DFB) lasers with a side mode suppression ratio (SMSR) better than 30 dB, which avoids stray absorption from interfering substances that may absorb at nearby wavelengths. These lasers are operating in the 1.3 to 2.0 μm range and their wavelength can be smoothly and continuously changed over several nanometers by varying either the laser temperature for coarse tuning or the injection current for fine tuning. One significant drawback of these devices is that the near-IR absorptions are overtones or combination bands that are one to several orders of magnitudes weaker than the strong fundamental bands in the mid-IR [5]. However their excellent modulation properties result in detection limits in the ppm range for many gases in environmental or industrial monitoring. In this paper, we will review the modulation properties of laser diodes and their applications to spectroscopic measurements. We will present two different techniques based on this modulation scheme to measure gas concentration using the same laser diode emitting at $\lambda = 2 \mu\text{m}$. The first, called tunable diode laser absorption spectroscopy (TDLAS), is an all-optical method based on the transmission of light through the analysed sample. In the second, called photoacoustic spectroscopy (PAS), the light absorbed in the sample is measured through an acoustic wave generated by the thermal relaxation of the molecules in an acoustic cavity. The principle of both methods will be presented and their performances will be compared.

2. MODULATION PROPERTIES OF LASER DIODES

Semiconductor laser diodes are easily current-modulated, resulting in both an intensity- and a frequency-modulation of the emitted field (IM and FM):

$$\begin{cases} i(t) = i_o + \Delta i \cos \Omega t & : \text{ current modulation} \\ I(t) = I_o + \Delta I \cos \Omega t & : \text{ intensity modulation (IM)} \\ \nu(t) = \nu_o - \Delta \nu \cos(\Omega t + \Psi) & : \text{ frequency modulation (FM)} \end{cases}$$

where i is the laser current, I the light intensity, ν the light emission frequency, Ω the modulation frequency and Ψ the phase shift between IM and FM.

At low modulation frequencies the dependence of the emission frequency ν on the injection current i is essentially due to a thermal effect: increasing the laser current dissipates more power, thus heats the laser. As the bandgap of the laser material decreases with increasing temperature, the laser wavelength increases accordingly. This thermal modulation is dominant at low frequencies and decreases up to frequencies comparable with the inverse thermal time constant, typically 1 MHz (Fig 1a). At higher frequencies, the wavelength is only modulated by changes in the charge density, which alters the refractive index. This mechanism has the opposite effect on the refractive index, so that the IM-FM phase shift Ψ is dependent on the modulation frequency (Fig. 1b): its value is about 0° at low frequency, than decreases above 10 Hz and reaches a value of approximately $-\pi/2$ at frequencies higher than 100 MHz [6].

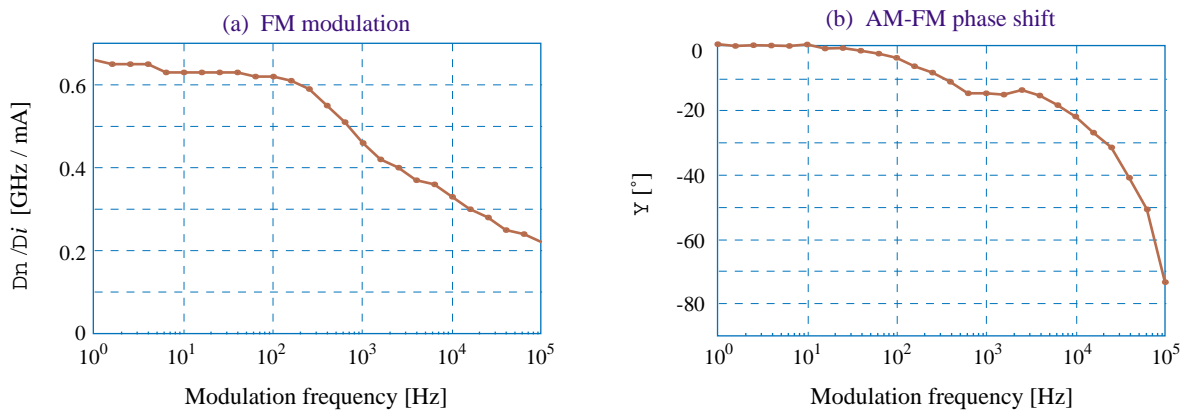


Figure 1. Frequency modulation efficiency (a) and IM-FM phase shift (b) in function of the modulation frequency for an InGaAsP/InP DFB laser diode emitting at $\lambda = 2 \mu\text{m}$.

3. TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY

3.1. Principle

A sensitive spectroscopic detection method called tunable diode laser absorption spectroscopy (TDLAS) uses the modulation properties of laser diodes [7]. High sensitivity is achieved by sinusoidally modulating the laser injection current at a frequency f (typically several tens of kHz), while slowly scanning (10 Hz) the laser emission line through the measured absorption line. Absorption of light by the molecules converts the frequency modulation into an intensity modulation, which is easily detected using a photodiode and a lock-in detection (Fig. 2).

The signal at any harmonics of the modulation frequency can be analysed, although only the three first overtones are usually used. In the case of low modulation depth with respect to the linewidth of the absorption profile, the detected signal at the n^{th} harmonic is approximately proportional to the n^{th} derivative of the absorption line. For this reason this method is also called derivative spectroscopy. Small asymmetries due to the residual amplitude modulation (RAM) of the laser are observed on the signals. The second harmonic ($2f$) signal has a zero baseline and a maximum close to the line centre. Its amplitude is directly proportional to the species concentration for weak absorbance. The third harmonic ($3f$) signal vanishes at the line centre and is used in a feedback loop to stabilise the laser emission frequency on the centre of the analysed absorption line. With no line-locking scheme, the laser emission frequency fluctuates over several tens of MHz, even though the laser is temperature-stabilised within 0.01°C . These fluctuations can perturb the concentration measurement using the $2f$ signal. Using line-locking, the laser is very stable and the concentration measurement, accordingly (Fig 3).

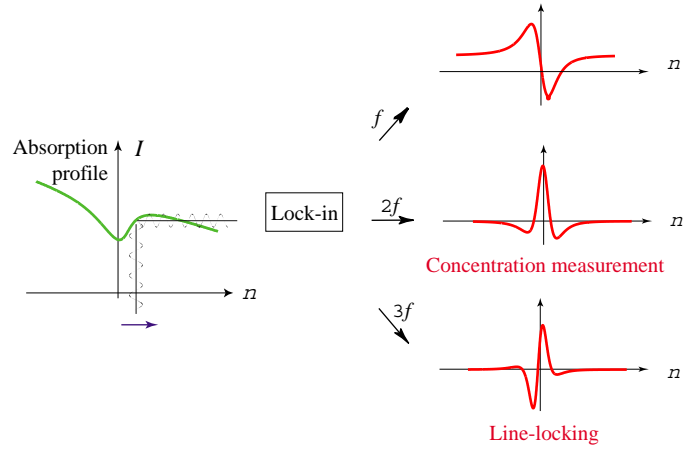


Figure 2. Principle of derivative spectroscopy with harmonic detection.

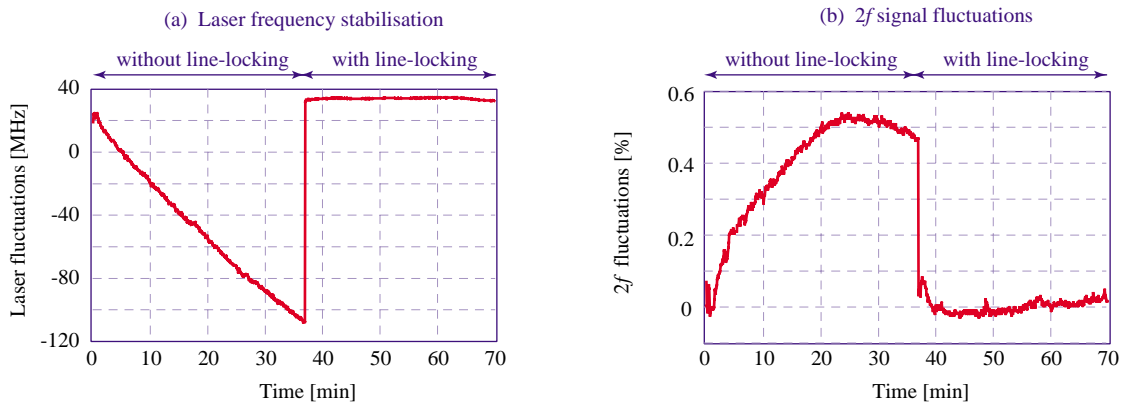


Figure 3. Effect of line-locking on the laser frequency stability (a) and on the second-harmonic signal (b).

3.2. Experiment

CO_2 concentration measurements have been performed at $\lambda = 2004 \text{ nm}$ (line R16) using an InGaAsP/InP DFB laser diode. The experimental system is shown in Fig. 4. The laser beam is first collimated by an AR-coated lens of 12 mm focal length, then is splitted in three parts: in the first, light is injected into a 100 m multipass cell; in the second, the beam goes through a 1 m linear cell and the third is a reference path. One of the cells is used for measurement, while the other is used to stabilise the laser frequency. Each beam is focused on an extended-wavelength InGaAs photodiode with a gold-coated off-axis

parabolic mirror (OAP). The three paths are matched so that their length outside the cells is equal. The signal of the reference path is subtracted from the two other before performing the lock-in detection. This subtraction scheme cancels the absorption of light due to the air outside the cells. In addition, this operation reduces the noise due to modulation non-linearities of the laser and increases the detection sensitivity, accordingly. The whole system is pre-aligned using a HeNe laser coupled into the set-up by a beamsplitter that is removed during the measurements. In addition, a wavemeter and a Mach-Zehnder interferometer are used to characterise the spectral properties and the modulation of the laser.

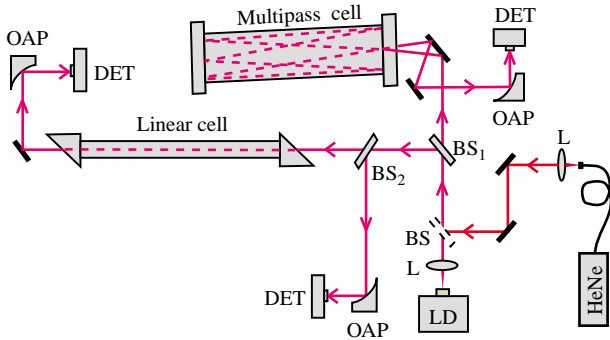


Figure 4. Experimental set-up.

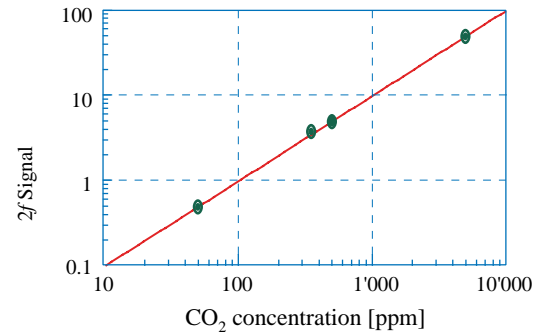


Figure 5. Response of the system in function of the CO₂ concentration.

Measurements of the $2f$ signal have been performed with different concentrations of CO₂ using the 1 m linear cell (Fig 5). From the measured signal to noise ratio (SNR), the minimal detectable concentration was determined to be 10 ppm with an optical power of only 70 μ W on the photodetector. This corresponds to a minimal detectable absorbance of $(\alpha L)_{\min} \cong 1.4 \cdot 10^{-4}$, where α is the linear absorption coefficient and L the absorption path length. As the detection limit depends on the optical power P reaching the detector, a light-intensity-independent value has been calculated for 1 W effective optical power: $(\alpha L P)_{\min} \cong 1 \cdot 10^{-8}$ W.

4. PHOTOACOUSTIC SPECTROSCOPY

4.1. Principle

Photoacoustic spectroscopy (PAS) differs from the previously discussed method as the energy absorbed in the analysed sample is determined directly and not through the detection of the transmitted light. It thus corresponds to a calorimetric technique. This method relies on the photoacoustic effect discovered one century ago by Graham Bell. In its simplest version (Fig 6) it occurs when an intensity-modulated laser beam propagates through a cell containing the gas to be analysed. If the laser wavelength coincides with an absorption line of the gas, a fraction of the incident radiation is absorbed in the sample. The subsequent nonradiative relaxation of the excited molecules produces a temperature variation and hence a pressure change in the cell. As the light is modulated, a periodic variation of pressure occurs. This acoustic wave, detected using a sensitive microphone, is proportional to the gas concentration [1, 8].

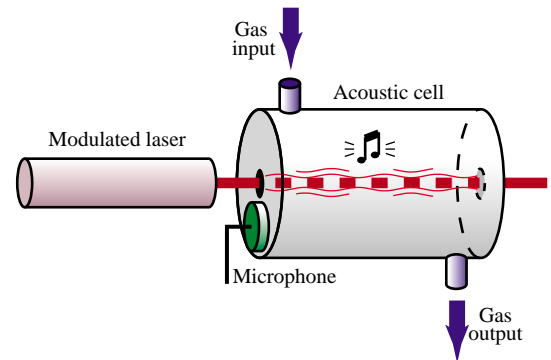


Figure 6. Basic principle of PA

The sensitivity of this method can be improved by carefully designing the photoacoustic cell. An optimum design results in a large signal to noise ratio, a small adsorption of the analysed gas from the cell walls and the possibility of measuring flowing gases for continuous monitoring. The performances are also improved if the laser modulation frequency corresponds to an acoustic resonance of the cell. In this case the acoustic wave is enhanced by the quality factor Q of the resonance.

4.2. Experiment

Our cell is made of a central cylinder of length $L = 12$ cm connected with two outer cylindrical buffer volumes used as acoustic filters (Fig. 7). The system is operating in the first radial mode of the central cylinder, which exhibits a resonance frequency of $f \approx 10.5$ kHz. The microphone is placed at the position of the maximum acoustic amplitude. The quality factor of the cell is better than 600 (Fig. 8).

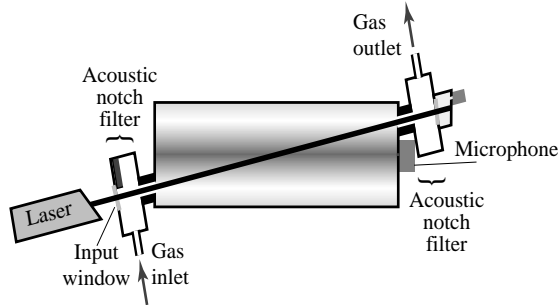


Figure 7. Schematic view of the PA cell.

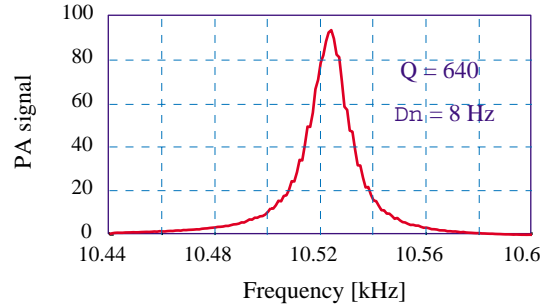


Figure 8. PA signal as a function of the laser modulation frequency.

The PA signal is proportional to the light intensity propagating through the sample (Fig. 9), but does not depend on the length of the absorption cell. For this reason this method has been used almost exclusively using intense CO or CO₂ lasers [1, 8]. We have nevertheless implemented it using a semiconductor laser diode with a much lower power ($P < 3$ mW) in order to make a quantitative comparison between the two methods discussed in this paper (TDLAS and PAS). The use of laser diodes offers furthermore some advantages over CO₂ lasers for photoacoustic spectroscopy:

- (i) The wavelength of laser diodes is continuously tunable, which allows to centre the laser emission on the analysed absorption profile, whereas for gas lasers only fortuitous coincidences between the laser line and the absorption profile can be used.
- (ii) CO₂ laser with mechanical choppers are limited to modulation frequencies of 5 kHz approximately, whereas laser diodes can be modulated at much higher frequencies, which allows to use PA cells of smaller size.
- (iii) The signal to noise ratio improves when frequency modulation is used instead of IM. Indeed, absorption by the cell windows contributes to the background noise (windows noise) in IM schemes. As this absorption is less wavelength-dependent, its derivative is near zero and does not contribute to the acoustic signal.

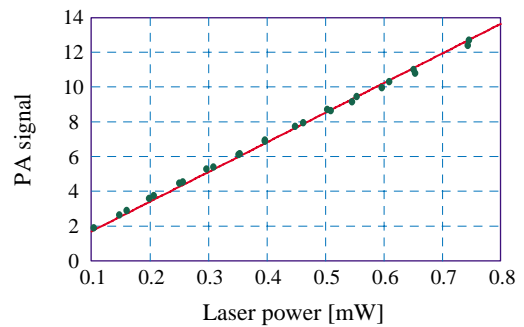


Figure 9. Dependence of the PA signal with the laser power

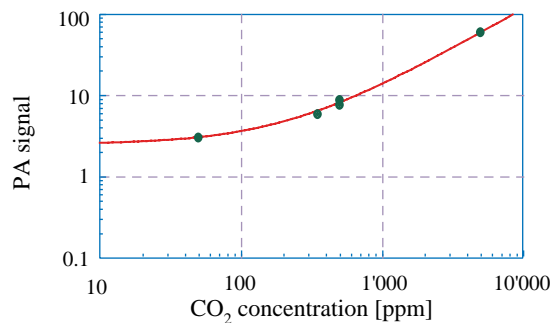


Figure 10. PA signal in function of the CO₂ concentration.

Photoacoustic experiments have been performed using the same laser diode and the same absorption line of CO₂ as previously (see part 3.2). The laser was frequency-modulated. When the laser frequency was slowly scanned through the absorption line, the detected photoacoustic signals were similar to those obtained with direct optical detection (derivative-type signals at the different harmonics of the modulation frequency). Measurements have been performed using first harmonic detection with different CO₂ concentrations in order to determine the sensitivity of the method (Fig. 10). The minimum detectable concentration was approximately 200 ppm with a laser power of 600 μ W inside the cell. This corresponds to a detection limit $\alpha_{\min} \approx 2.9 \cdot 10^{-5} \text{ cm}^{-1}$. As this value depends on the laser power, a light-intensity-independent value has been calculated by converting this value to 1 W effective light power: $(\alpha P)_{\min} \approx 1.8 \cdot 10^{-8} \text{ cm}^{-1} \text{ W}$.

5. CONCLUSION

Two different spectroscopic detection methods have been studied using the same semiconductor laser diode emitting in the $\lambda = 2 \mu\text{m}$ range. The sensitivity of these techniques has been determined using frequency modulation of the laser diode. A detection limit of 10 ppm of CO_2 was achieved on a 1 m path length using optical second harmonic detection, whereas a minimum detectable concentration of 200 ppm was reached using photoacoustic detection.

As the optical power and the path length were different between the two experiments, light-intensity-independent detection limits have been computed for the same path length ($L = 12 \text{ cm}$) for comparison purposes. A value of $(\alpha P)_{\text{min}} \cong 8.4 \cdot 10^{-10} \text{ cm}^{-1} \text{ W}$ was achieved using optical detection, while a value of $(\alpha P)_{\text{min}} \cong 1.8 \cdot 10^{-8} \text{ cm}^{-1} \text{ W}$ was reached using acoustical detection.

Optical detection showed thus a sensitivity approximately 20 times higher than the photoacoustic method. Furthermore, it must be added that the photoacoustic signal is independent of the length of the measurement cell, whereas the signal obtained using optical detection depends on the absorbance, which is the product of the linear absorption coefficient α with the absorption path length L . Consequently, the minimum detectable concentration achieved using optical detection can be improved by increasing the length of the measurement cell, by using a multipass cell for example, which is actually not possible for photoacoustic spectroscopy. For this reason, optical detection is a much promising technique than photoacoustic detection in the considered spectral range.

However, photoacoustic spectroscopy offers several advantages over optical detection at longer wavelengths, where the absorption lines are more intense. As a matter of fact, the sensitivity of photoacoustic spectroscopy is wavelength-independent, since an acoustic detection is performed as opposed to an optical detection. The same detection scheme can be used with different lasers emitting at any wavelengths and still have the same sensitivity. On the other hand, optical detection is strongly wavelength-dependent. In the near-IR, high performance photodetectors are available, thanks to the technology developed for the optical communications, giving to optical detection a higher sensitivity than photoacoustic detection. Other types of detectors are used at longer wavelengths: PbS (1-3 μm), PbSe (1-5 μm), InAs (1-4 μm), InSb (1-5.5 μm) or HgCdTe (5-12 μm). However, these detectors are getting more expensive, less sensitive and therefore less suitable as the wavelength increases, as they have to be operated at low temperature (multi-stage thermoelectrical or cryogenic cooling). Consequently, optical detection is less attractive at longer wavelengths, but remains extremely suitable at wavelengths shorter than approximately 4 μm . On the other hand, a higher sensitivity can be achieved using photoacoustic detection at longer wavelengths ($\lambda > 4 \mu\text{m}$). Fig. 11 shows the estimated detection limit as a function of wavelength for both methods. These figures were obtained on the basis of a reference detection limit at $\lambda = 2 \mu\text{m}$ and taking into account the typical spectral response of IR detectors.

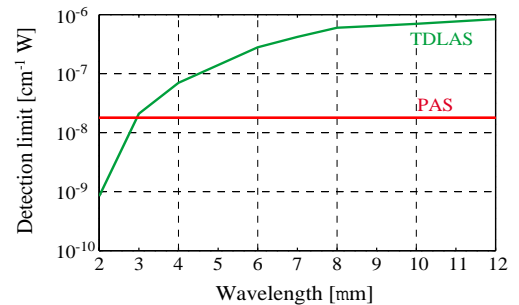


Figure 11. Estimated detection limit of optical and photoacoustic detection as a function of wavelength.

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