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EXPLORING THE SENSITIVITY LIMITS OF INTRA-CAVITY MEMS-BASED PHOTOACOUSTIC GAS SENSORS

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"DIMMI ETEOCLE, PARLA: PERCHÉ TI SOTTOMETTI
ALL'AMBIZIONE DEMONIACA,
LA DEA PIÙ MALIGNA? NON FARLO! IN LEI NON C'È GIUSTIZIA.
MEGLIO FARESTI, FIGLIO, A ONORARE L'UGUAGLIANZA,
CHE STRINGE LEGAMI
TRA LE CITTÀ, CASE E CASE, AMICI E AMICI,
L'UGUAGLIANZA CHE PER NATURA
IMPONE L'EQUILIBRIO TRA GLI UOMINI:
STA' ATTENTO! QUANDO C'È LO SCONTRO
TRA CHI È MENO E CHI È PIÙ,
ALLORA ARRIVANO I GIORNI DELL'ODIO."

*Giocasta si rivolge a suo figlio Eteocle,
per ricordagli cosa vuol dire pensare.
Euripide - La fenice*

Preface

December 27, 2024

Scientific effort and technological innovation are driving forces in addressing some of the most important challenges of our time, such as environmental monitoring, medical diagnostics, and industrial safety. Among all the possible optical techniques, photoacoustic spectroscopy (PAS) has emerged as a powerful method, gaining prominence for its flexibility, versatility, and scalability. The pressing demand for greater detection sensitivity levels, easier miniaturization, and more efficient operations, is pushing the boundaries of traditional PAS, requiring innovative approaches, advanced materials, and quantum technologies. In this framework, moved by the beauty of scientific exploration and relentless pursuit of knowledge, this thesis describes all the work conducted during the three years of PhD (January 2022 - January 2025). It aims at exploring the sensitivity limit of Micro Electro Mechanical (MEMS) based intra-cavity photoacoustic sensors, and proposing cutting-edge insights for a future *quantum-enhanced* approach.

I sincerely thank my supervisor, Dr. Simone Borri, for his guidance and support, all my colleagues for fostering a stimulating environment, and my family and friends for their unwavering encouragement.

Jacopo Peline

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I.1 Trace-gas sensors: from daily-life application to quantum sensing

The precise identification and quantification of trace gases in the air has emerged as a pivotal area of research and development, driven by the growing need for comprehensive and increasingly stringent control requirements. Generally speaking, regardless of the type, the operating principle of an optical trace-gas sensor lays its basis on a few ingredients and fundamental principles of molecular absorption spectroscopy [1, 2]. A tunable or broadband light source is exploited to address an absorption feature of one or more selected species highly diluted within a mixture. Following the interaction, the molecule will absorb the energy coming from the radiation, jumping to one excited state. After a certain time interval, whose duration depends on its relaxation dynamics, the molecule will undergo a de-excitation to the ground state, losing the previously acquired energy. Finally, by using a proper detection system, the absorption spectrum can be reconstructed, thus retrieving information about the trace-gas relative concentration within the mixture.

In this context, the most interesting and stimulating challenge, pushed both by a huge scientific effort and unceasing technological progress, is to provide innovative solutions and experimental approaches capable of pushing down the detection sensitivity, up to the classical limit or beyond. This aim must go through the achievement of two crucial aspects: (1) the maximization of the system's response to the addressed molecule, and simultaneously (2) the minimization of all the possible noise sources that may degrade the measurement, thus allowing to obtain the highest possible Signal-to-Noise Ratio (SNR). At the same time, however, sensitivity is not the only parameter estimating the overall efficiency of a sensor. Together with ultra-high detection sensitivity, and depending on the application, other important features are the response time, high stability, accuracy, and repeatability. All of these aspects are being widely addressed thanks to the availability of new and promising materials, instruments, and techniques.

As a consequence, over the decades this field of research has become increasingly interconnected to everyday life, finding applications in lots of sectors. One of the most

widespread and important implementations of gas sensing technology is related to environmental monitoring and air quality control [3–5]. Since the growing population requires an ever-increasing energy demand, the amount of polluting gases in the atmosphere is reaching critical values, sometimes even exceeding the limits imposed by the *World-Health-Organization global air quality guidelines* [6].

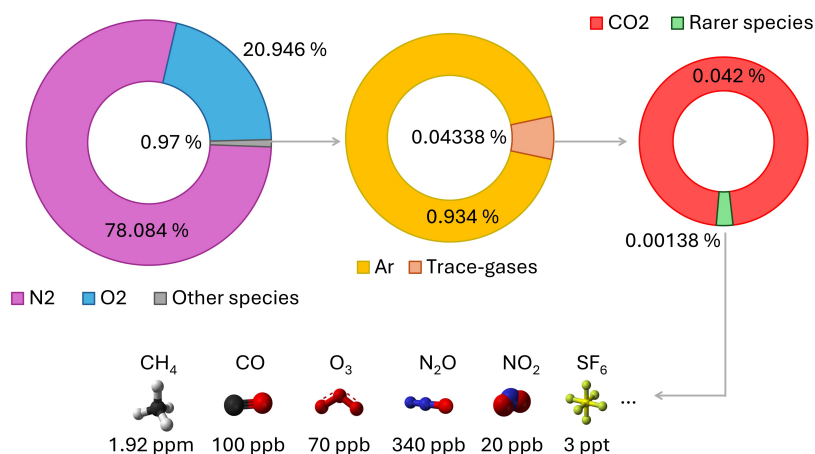


Figure I.1: Atmospheric gaseous composition, monthly update by the [NOAA Global Monitoring Lab](#).

Many species of interest and potentially dangerous for the environment (such as methane, carbon monoxide, carbon dioxide, nitrous oxide, nitrogen dioxide, ozone, sulfur hexafluoride, and so on) are highly dilute within the whole gaseous atmosphere, as shown in Figure I.1. That said, exploiting performing gas sensors is necessary to detect minimal variations from the associated limit values.

Exhaled breath analysis has emerged as a promising diagnostic tool, providing valuable insights into the individual's health. Gas sensing technologies provide performing and alternative solutions in this field. They are based on non-invasive systems that recognize the presence of a specific disease or metabolic disorder, by detecting the associated analytical marker [7–10].

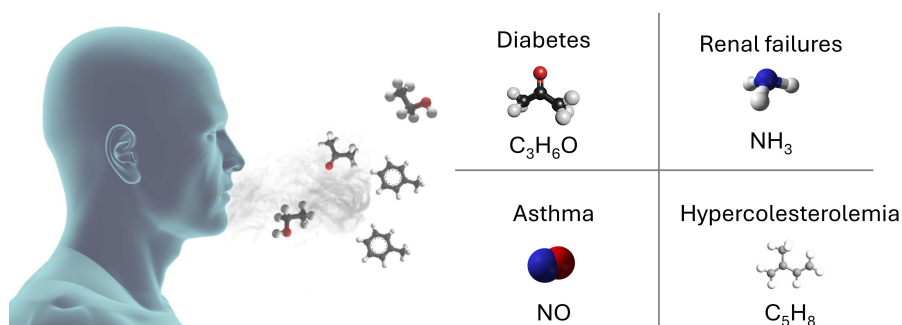


Figure I.2: Some examples of gas sensing applications for non-invasive exhaled breath analysis.

Figure I.2 reports some remarkable examples of breath analysis applications. Many examples in the literature report the implementation of gas sensors for trace-level

dimethyl ketone ($\text{C}_3\text{H}_6\text{O}$) detection, which represents a clear indicator of diabetes-related disease [11, 12]. Ammonia (N_3) is another important target molecule, whose excessive respiratory exhalation could be associated with kidney disease and renal failure [12, 13]. Finally, other two examples are the implementation of nitric-oxide (NO) [14, 15] and isoprene (C_5H_8) sensors [16, 17] for for asthma and hyper-cholesterolemia diagnosis respectively.

Another important application concerns the field of industrial process control [18, 19]. In this context, optical gas sensing technologies provide efficient solutions for detecting gas leakage or variation of toxic contaminants concentration in high-risk workplaces (such as steel mills, petrochemical plants, and so on), preventing the worker from being exposed to potentially dangerous environmental conditions [20]. Some examples regarding the exposure limits for typical toxic gases are reported in Table 1.

Table 1: Some examples of workplace exposure limits to toxic gaseous species.

Molecule	Chemical formula	Exposure limit EH40/2005 15 min (ppm)
Ammonia	NH_3	35
Arsine	AsH_3	0.05
Bromine	Br_2	0.2
Carbon monoxide	CO	0.2
Chlorine	Cl_2	0.5
Chlorine dioxide	ClO_2	0.3
Hydrogen cyanide	HCN	4.5
Hydrogen chloride	HCl	5
Hydrogen fluoride	HF	3
Hydrogen Sulfide	H_2S	10

Despite the very high technological level achieved, driven by the availability of increasingly new and performing materials, instruments, and techniques, continuing to invest scientific and economic efforts in this field should be a prerogative, with an eye towards novel configurations and alternative applications. Among all the different spectroscopic techniques such as non-dispersive infra-red (NDIR) spectroscopy [21, 22] or tunable diode laser spectroscopy (TDLS) [23, 24], some peculiar example have demonstrated the ability to push the detection sensitivity to extremely low levels. For example, Saturated Absorption Cavity Ring Down spectroscopy [25] (SCAR, or Sat-CRDS) enables the possibility to detect $^{14}\text{CO}_2$ at the part-per-quadrillion level, approaching the accelerator mass spectrometry (AMS) detection limit. This achievement introduced a paradigm change in radiocarbon detection for applications like environmental monitoring, cultural heritage, and pharmacology [26].

In this context, photoacoustic spectroscopy (PAS) [27, 28] has emerged as an

alternative but highly performing and promising approach for trace-gas sensing thanks to its relatively simple experimental implementation and high flexibility. For this reason, since its first and rudimentary analytical applications, this technique has emerged and forcefully asserted in all the above-mentioned daily-life applications (air [29], food [30], and water monitoring [31], medical diagnostic [32, 33], and so on). To date, the sensitivity level reached with photoacoustic-based setups is becoming more competitive, approaching the best performances obtained by the SCAR technique with the advantages of a much-reduced cost and higher scalability level. In this sense and perspective, PAS could meet all the requirements to be the best candidate for future *quantum-enhanced* trace-gas sensing, addressing exciting challenges such as single-molecule detection.

I.2 Physical principle of PAS

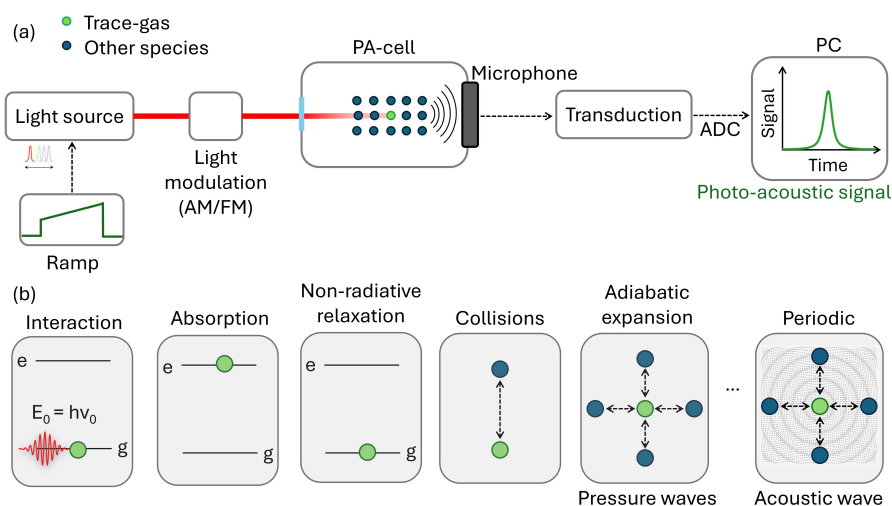


Figure I.3: (a): schematic representation of a typical photoacoustic spectroscopy-based setup for trace-gas sensing. (b): building blocks for the acoustic wave generation.

Photoacoustic spectroscopy offers an alternative to direct absorption schemes. The detected signal does not directly describe the absorption line of the trace gas but rather reconstructs it indirectly through different detection approaches. According to Figure I.3(a), a photoacoustic-based setup consists of a few ingredients and lays its basis on relatively simple physical principles [34, 35], briefly described in Figure I.3(b).

When the light source's wavelength is resonant with a molecular transition of the selected trace molecule, the latter will absorb the impinging energy, jumping to its associated excited state. When the preferred de-excitation dynamics is non-radiative, the relaxation to the ground state will occur by transferring the kinetic energy to the surrounding molecules through collisions, generating a pressure wave and a local thermal expansion of the sample. If the excitation beam is modulated (in amplitude or frequency) this phenomenon will be periodic, resulting in the generation of a sound wave. The latter is converted into a measurable signal, called the photoacoustic signal, by exploiting a proper microphone combined it with an efficient acoustic-to-voltage

transduction scheme. From this signal is then possible to estimate the sensor's final detection sensitivity.

The photoacoustic spectroscopy technique offers several unique advantages compared with common direct absorption setups. Being an indirect detection approach, no bulky photo-detectors are needed to measure the molecule's absorption spectrum, thus determining the high scalability of the entire system and the intrinsic high degree of flexibility. Firstly, since the choice of the excitation source is free from the limitations imposed by the narrow-bandwidth photo-detector response, a photoacoustic-based sensor can work properly in a potentially unlimited wavelength range, leading to high and easy broadband tunability. Secondly, the acoustic wave detection part can be implemented in many different and efficient ways, choosing between different types of high-performing microphones and alternative readout approaches.

Therefore, a photoacoustic setup can be thought of as a complex puzzle whose building blocks are interconnected and contribute together to the final sensitivity performances of the entire architecture. For this reason, this technique has firmly established itself as one of the most promising techniques in the field of trace gas sensing over the years, reaching results comparable with the most performing direct-absorption detection schemes.

I.3 Historical excursus and state-of-the-art

The photo-acoustic effect was discovered and studied for the first time by Alexander Graham Bell more than 125 years ago [36]. On 27 August 1880, he gave a lecture at the American Association for the Advancement of Science in Boston concerning the exploitations of the property of light in the transmission of speech. In this context, he presented a prototype called *Photophone*[37], consisting of guiding sunlight inside a selenium chamber connected with the electrical circuit of a telephone. When the sunlight is modulated via a voice-modulating mirror it changes the electric resistance of the selenium, resulting in the transmission of the voice inside the telephone circuit, and so in a successful propagation of sound in a solid sample.

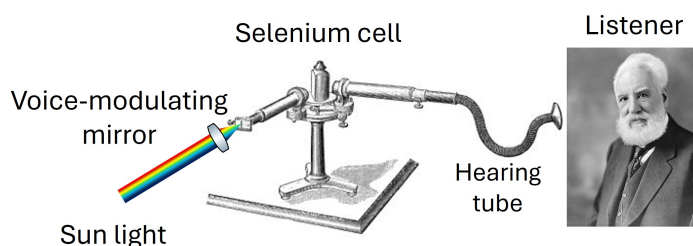


Figure I.4: Bell's *photophone*.

"...We are warranted in concluding that the nature of the rays that produce sonorous effects in different substances depend on the nature of the substances that are exposed to the beam."

A.G. Bell, J. Franklin Inst. 111,401–428 (1881).

The discovery of the photoacoustic effect brought great excitement to the scientific community, and several scientists started a deeper investigation into both theoretical aspects and their experimental implementations. The effort of Bell [38], John Tyndall [39], and Wilhelm Röntgen [40] highlighted that the photoacoustic effect was not limited only to solid bodies, but also to gaseous samples.

Despite the excitement of the early years, about 50 years passed before the first pioneering analytical applications of the photoacoustic effect. Mark Leonidovitch Veingerov reported the first attempt to exploit the photo-acoustic effect for small gas concentration detection [41]. In his experiment, he exploited black-body infrared radiation to excite CO_2 within pure N_2 , and a state-of-the-art capacitive microphone for the acoustic wave collection, obtaining a detection limit of around 0.2 % vol. At the same time, August Herman Pfund proposed a similar system for evaluating the concentration of CO_2 , CO , and CH_4 mixed in atmospheric air [42].

While theoretical dissertations on the photoacoustic effect continued to arouse the interest of the scientific community, mainly focused on the study of the vibrational relaxation rates and molecular energy transfer in gases [43, 44], the experimental breakthrough came in the 1960s with the birth of the laser. The possibility of employing high-power sources with much improved spectral purity, stability, and repeatability opened the doors to reach incredibly low trace-gas detection sensitivities. The first laser-assisted photoacoustic sensor was developed in 1968 by Edwing L. Kerr and Jhon K. Atwood [45]. Exploiting a 9.6 μm pulsed ruby laser and a lock-in amplification scheme, they reached a sensitivity at the part-per-million level for CO_2 in N_2 . Three years later L.B. Kreuzer was able to detect CH_4 in N_2 at the part-per-billion level with an intensity-modulated infrared HeNe laser [46]. In the following twenty years the great development of this new laser technology, together with increasingly sophisticated capacitive microphones and optimized photoacoustic cell geometry, allow the achievements of unprecedented results with conventional photoacoustic-based setups [47–50].

In the early 2000s, the scientific effort shifted its focus to the optimization of the acoustic transduction part, trying to propose alternative sensitive elements to microphones with the same (or even better) performance. Kosterev et al. [51] reported for the first time the study of a photoacoustic sensor using a quartz tuning fork (QTF) as an acoustic transducer, thus enabling a new technique known as Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS). QTF is a sharp resonator whose prongs are taken into oscillation if perturbed by the acoustic wave, and whose readout is all electrical thanks to the quartz piezo-resistivity. In the same years, Wilcken and Kauppinen [52] proposed a different photoacoustic sensing approach, known as Cantilever-Enhanced Photoacoustic Spectroscopy (CEPAS), based on a rectangular cantilever as the sensitive element integrated with an interferometric signal readout. Both these innovative approaches were thoroughly studied in recent years [53–55], reaching detection performances comparable with microphone-based PAS, but with the advantage of an easier miniaturization [56].

As in the case of direct absorption spectroscopy, also for photoacoustic spectroscopy the real step forward in achieving ultra-low detection sensitivities was to combine the advantages offered by the technique with an increase in the available optical power

given by optical resonators [57], enabling the Cavity-Enhanced photoacoustic spectroscopy. To date, conventional PAS, QEPAS, and CEPAS have demonstrated ppt-level and sub-ppt level detection sensitivities when used on selected target molecules characterized by strong transitions (i.e. large line-strengths) and fast relaxation dynamics, and of course integrated with high-finesse optical cavities [58–62].

Given these impressive results, future challenges should focus on parallel fronts. On one side, achieving the sub-ppt sensitivity on most of the molecules of interest for environmental, medical, and security applications. On the other side, proposing alternative approaches and developing novel tools to push the technique to its classical limits, with an eye to potential improvements towards *quantum-enhanced* photoacoustic spectroscopy.

I.4 Thesis overview

This thesis aims firstly to investigate the limits of the photoacoustic technique starting from a standard case of study, then it will be devoted to the development of new solutions, providing an alternative approach for the development of ultra-high trace-gas detection systems. Taking advantage of the great flexibility of PAS, the leading idea will be to identify the best choice for each crucial experimental component (i.e. the excitation source, the acoustic-to-voltage transducer, and the signal readout scheme), thus acting on the overall final performance.

Chapter 1 is divided into two parts. Starting from some basic concepts of laser-based spectroscopy, the first part (Section 1.1) provides an exhaustive theoretical recipe for the laser-based photoacoustic effect, highlighting the most important features to understand the phenomenon. The second part (Section 1.2) introduces the main experimental ingredients for developing a photoacoustic-based setup. Due attention is given to the laser excitation sources, among which two types of mid-IR lasers are proposed: Quantum Cascade Lasers (QCL) and Interband Cascade Lasers (ICL). Then, the analysis shifts to the detection part, analyzing the strengths and weaknesses of three possible choices for acoustic transduction: conventional microphones, quartz tuning forks, and silicon-based cantilevers.

Chapter 2 describes the development of a doubly-resonant cantilever-enhanced photoacoustic sensor. The first part focuses on the experimental setup, providing a detailed description of the PAS excitation laser source, the acoustic-to-voltage transducer, the doubly resonant configuration, and the signal readout scheme (Section 2.1). The second part of the chapter is devoted to discussing the experimental data (Section 2.2), and highlighting the main results (Section 2.3).

In Chapter 3, all the experimental efforts aimed at improving what was already achieved in Chapter 2 are illustrated. Firstly, the characterization of novel silicon-based Micro-Electro-Mechanical systems (MEMS) as alternative acoustic transducers is presented (Section 3.1). Summarized in the published article [63], this work aims at finding new geometry for acoustic transduction to overcome and replace the standard rectangular cantilever configuration. The second part describes the realization of a sub-ppb level trace gas sensor for N_2O , obtained via the coupling with one of the best performing investigated MEMS structures with a dual-tube acoustic resonator

(Section 3.2). This work is summarized in the published article [64]. In the last part, the spectrophone is coupled with an optical cavity, unveiling the ultimate detection sensitivity achieved (Section 3.3).

Chapter 4 describes parallel works carried on during my Ph.D activity, where the leading topic is analyzing the main noise features affecting the developed sensor, and proposing alternative schemes for their minimization in the view of a *quantum-assisted* approach for photoacoustic spectroscopy. The chapter's core is devoted to a comprehensive study of the excitation source emission. On one side, an experimental approach for frequency noise minimization is proposed, based on the coupling between the mid-IR QCL with an ultra-high finesse optical cavity (Section 4.1). On the other side, the intensity noise features of alternative mid-IR Interband and Quantum Cascade Lasers are studied via Balanced Homodyne detection (BHD), unveiling the possibility of obtaining a shot-noise limited emission for spectroscopic purposes (Section 4.2). The final part of the chapter switches to the other fundamental part of the sensor. In this sense, a preliminary overall noise performance investigation of the developed interferometric signal readout is presented, aiming at understanding the fundamental limitations for a future *quantum-enhanced* acoustic transduction (Section 4.3).

CHAPTER 1

Photoacoustic spectroscopy: theoretical recipe and experimental ingredients

The physical process describing the interaction between light and molecules is a fundamental concept for understanding the working principle of the photoacoustic effect. Despite the apparent simplicity, a big effort was needed to obtain a generalized theoretical picture [65–67]. Only through rigorous formalization is it possible to fully understand the phenomenon in all its key aspects: the excitation laser source, the molecular excitation and relaxation phenomena, the acoustic wave generation, and its transduction into a measurable signal.

This chapter provides an overview of the photoacoustic effect, proposing firstly a theoretical recipe, and then providing some experimental ingredients for its realization. After a brief introduction to laser-based spectroscopy (Section 1.1), the first part describes the theory behind the photoacoustic effect (Section 1.2). Starting from the equations of acoustics (Subsection 1.2.1), this section highlights the main parts of the photoacoustic signal generation: the heat generation (Subsection 1.2.2), the sound wave generation in free (Subsection 1.2.3) and in closed (Subsection 1.2.3) spaces, and the sound wave detection (Subsection 1.2.4).

The second part introduces experimental solutions for the realization of a photoacoustic-based setup (Section 1.3). A detailed discussion is devoted to the laser excitation source (Subsection 1.3.1), investigating as two main examples the Quantum Cascade (Subsection 1.3.1) and the Interband Cascade (Subsection 1.3.1) lasers. Then, the three types of widely used acoustic transducers are presented and described (Subsection 1.3.2): the condenser microphone, the quartz tuning forks, and the silicon-based cantilever.

The theoretical description developed in this chapter takes inspiration from the works presented in [65, 68–70] and in the textbooks [2, 71, 72].

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1.1 Pills of laser absorption spectroscopy

Laser Absorption Spectroscopy (LAS) consists of the interaction between a laser source and a target molecule. When the first one is tuned in wavelength to be resonant with a specific spectral feature, the second will absorb the incoming energy, experiencing a transition between two energy states. Since each molecular species shows a unique ensemble of transitions, this technique can provide a very affordable identification and quantification tool.

Although the processes of laser-molecule interaction are spread across the entire electromagnetic spectrum, the infrared and, in particular, the mid-infrared are regions of great interest in gas sensing applications. This is due to the presence of narrow and strong absorption transitions as a result of the quantized variation of rotational and vibrational states, namely the molecular bonds stretching and bending [73–75]. Also known as the *fingerprint region*, the mid-IR spectral region is typically characterized by the presence of overtones of fundamental vibrations in the near-IR. As an example, Figure 1.1 reports the simulated absorbance of some molecules of interest between 1 μm and 25 μm .

Any molecular transition can be described by a physical parameter, known as the absorption coefficient and defined as a function of the wave number k , the temperature T , and the gas pressure p :

$$\alpha(k, T, p)[\text{cm}^{-1}] = NS(T)f(k, k_0, T, p). \quad (1.1)$$

Here N represents the number density of the absorbing molecules, $S_0(T)$ is the single-molecule line-strength [$1/\text{cm}^{-1}$], while $f(k, k_0, T, p)$ is defined as the line-shape function [$\text{cm}/\text{molecule}$] with a central wave-number k_0 . N can generally be extracted from the ideal law of gasses as a function of the temperature and the pressure, while $S_0(T)$ can be calculated with the help of a simulation database such as HITRAN [76].

In the case of trace-gas detection the addressed molecules are highly diluted in a matrix, and the associated number density can be written as a function of the volume mixing ratio of the absorbing molecules as $N = c_m N_0$, where N_0 is the total number density of the molecules.

Additionally, if the interaction process occurs with multiple species, the total absorption coefficient will be a linear sum of the single contributions, as $\alpha = \sum^j \alpha_j$.

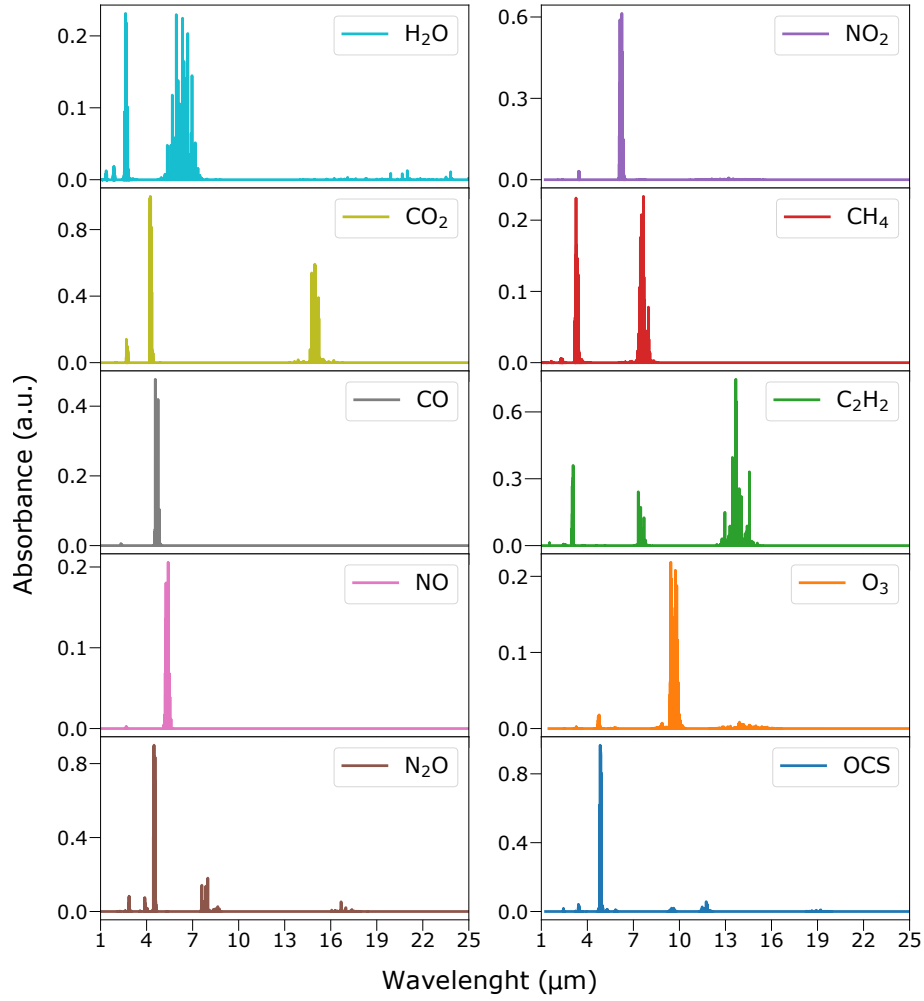


Figure 1.1: Absorbance for some molecule of interest in the mid-IR region: H_2O , CO_2 , CO , NO , N_2O , NO_2 , CH_4 , C_2H_2 , O_3 , and OCS . The simulations are performed at a pressure of 0.01 atm, a temperature of 20 °C, and with 1 mm of path length.

Regarding the spectral molecular line shape, its determination mainly depends on two different dynamical mechanisms describing the interaction with the impinging radiation. The first one, known as Doppler broadening [77], depends on the frequency shift of the incident radiation due to the Doppler effect. As a result, from the point of view of the molecules, the interaction process will be described by a broadening of the line shape. The latter broadening follows the molecule's velocity distribution and it can be described by a Gaussian function:

$$f_D(k, k_0) = \sqrt{\frac{\ln 2}{\pi}} \frac{1}{\Delta_D} e^{(-\ln 2) \frac{k - k_0}{\Delta_D}}. \quad (1.2)$$

Δ_D is the Doppler-limited Full-Width-at-Half-Maximum (FWHM), typically of the order of tens/hundreds of MHz in LAS experiment, and it can be written as:

$$\Delta_D = k_0 \sqrt{\frac{2k_B T \ln 2}{mc^2}}, \quad (1.3)$$

where m is the molecule's mass, c is the light speed, and k_B is the Boltzmann constant.

Together with Doppler broadening, the interacting molecules can undergo inter-molecular collisions, resulting in an energy exchange and a decrease in the excited state lifetime. This results in a shift in the central frequency and a pressure-dependent broadening, whose mechanism is described by a Lorentzian-type line shape written as [78]:

$$f_L(k, k_0) = \frac{1}{\pi} \frac{\Delta_L}{(k - k_0 - \Gamma)^2 + \Delta_L^2}, \quad (1.4)$$

being Γ the pressure-induced line shift, Δ_L the pressure-broadened FWHM, typically of the order of 3-GHz/atm for typical LAS experiments, while the central frequency shift is of the order of 30MHz/atm.

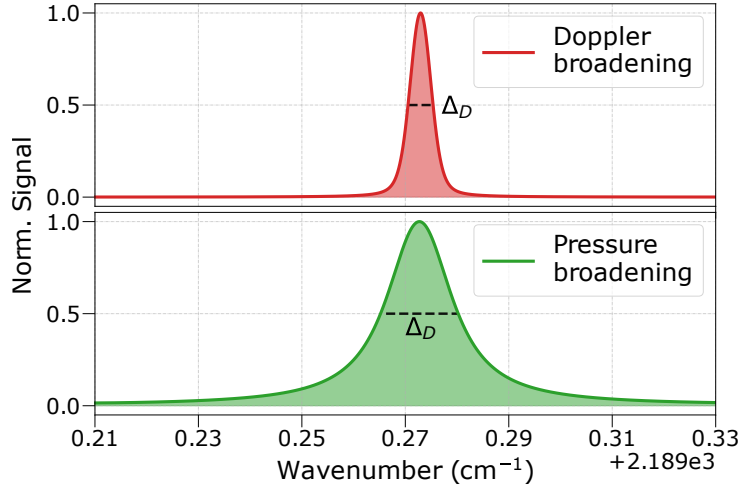


Figure 1.2: Examples of Doppler-broadened (a) and pressure-broadened line shapes (b) for a N_2O absorption line at 2189.273 cm^{-1} .

Even if the Doppler broadening has a much greater contribution at a lower-pressure regime, while the collisional broadening becomes more important at higher pressure, in reality, the two contributions are strictly correlated. For this reason, a complete and formal description of the phenomenon requires more sophisticated models. A famous example is the Voigt function [79], defined as a convolution of a Gaussian and a Lorentzian functions. More complex models were developed for more sophisticated measurements, such as the Hartmann-Tran profile [80].

As already discussed in the Introduction, the absorption phenomena can be observed by measuring directly the transmitted light, namely a direct approach, or measuring the variation in the state of the gas, referring to an indirect scheme. In the first case, the light must be collected via a photo-detector to measure the transmitted laser's optical power. According to the Beer-Lambert law [81, 82], when a laser beam transverses any absorbing medium, the associated optical power results exponentially attenuated according to the formula:

$$P_t = P_0 e^{-\alpha \mathcal{L}}, \quad (1.5)$$

where P_0 is the incident power, and $\mathcal{L}$ is the optical path length. In a typical direct absorption diode laser-based experiment the photo-detector records the transmitted

optical power as a function of the laser wavelength, resulting in the reconstruction of the absorption spectrum. Then, the spectrum can be used to obtain information about the number density N , or the associated mixing ratio c_m of the addressed trace gas in the medium. Usually, the latter is extracted by fitting the signal with a proper line-shape function and by computing the enclosed line area. The measurement and analysis methods are different in the case of an indirect approach such as photoacoustic spectroscopy, as the spectrum is not measured by analyzing the photo-detector output, but extracted via an acoustic-to-voltage transducer.

1.2 Theory of the photo-acoustic effect

The photoacoustic effect is only apparently a simple physical problem, being the combination of different building blocks. An efficient way to describe the theory behind this phenomenon consists of analyzing all the parts separately and putting them together in a unified and comprehensive picture. This section provides a brief overview of the main physical principle characterizing the PAS effect, starting from the equation of acoustics, moving to the description of the heat generation by light absorption and the acoustic wave propagation in the medium, ending up with the signal detection.

1.2.1 Equation of acoustics

The sound propagation within a gas sample can be defined as a perturbation of its equilibrium state [83], causing a change in its physical parameters as:

$$\begin{cases} p(\mathbf{r}, t) = p_0 + p_1(\mathbf{r}, t) \\ \rho(\mathbf{r}, t) = \rho_0 + \rho_1(\mathbf{r}, t) \\ T(\mathbf{r}, t) = T_0 + T_1(\mathbf{r}, t) \\ S(\mathbf{r}, t) = S_0 + S_1(\mathbf{r}, t), \end{cases} \quad (1.6)$$

being p , ρ , T , and S the pressure, mass density, temperature, and entropy respectively. In the limit of small perturbations, these four parameters can be linked via three linearized equations, respectively consisting of the mass conservation, the Newton second equation, and the entropy balance equation:

$$\begin{cases} \frac{\partial \rho_1}{\partial t} + \rho_0 \nabla \cdot \mathbf{v} = \varsigma \\ \rho_0 \frac{\partial v_1}{\partial t} + \nabla p = \mathbf{F} \\ T_0 \rho_0 \frac{\partial S_1}{\partial t} = H. \end{cases} \quad (1.7)$$

Here ς is the mass injection per unit volume and unit time, $\mathbf{F}$ is the force density, while H is the heat power density injection. Given that these terms are equally zero outside of the perturbing source region, and considering the acoustic movements outside this region irrotational and without changing in entropy, the equations in the system 1.7 can be combined in a unique wave equation, being equal to:

$$\frac{1}{c^2} \frac{\partial^2 p}{\partial t^2} - \nabla^2 p = \frac{\partial \zeta}{\partial t} - \nabla \cdot \mathbf{F} + \frac{(\gamma-1)}{c^2} \frac{\partial H}{\partial t}, \quad (1.8)$$

where γ is the adiabatic coefficient of the gas. According to this assumption, a sound wave within the gaseous sample can be generated by a time-dependent fluctuation of mass injection ($\partial \zeta / \partial t$, as happens in organ pipes), by space fluctuations of a force ($\nabla \cdot \mathbf{F}$, what happens when a speaker membrane is used), or by a fluctuation in the heat injection ($\partial H / \partial t$, the case of laser absorption by the molecule). Finally, by properly manipulating equation 1.8, it is possible to end up with the fundamental equation of photoacoustic:

$$\frac{\partial^2 p}{\partial t^2} - c^2 \nabla^2 p = S_{PA}(\mathbf{r}, t) = \frac{(\gamma-1)}{c^2} \frac{\partial H}{\partial t}. \quad (1.9)$$

The photoacoustic source term $S_{PA}(\mathbf{r}, t)$ is proportional to the time first derivative of the heat power density in the medium. This means that sound wave generation will occur only via the absorption of a modulated light beam by the gas. In fact, if the excitation beam hits the sample with constant optical power, the result will be only local heating without periodic pressure wave generation.

1.2.2 Heat generation by modulated light

Any kind of light source can lead to the generation of photoacoustic effects, such as sunlight, solid-state lasers, light-emitting diodes, and so on. As will be explained later, one of the most used sources in this type of application is Quantum Cascade Laser (QCL) [84–89], due to its direct emission at mid-IR to THz and thanks to several peculiarities such as compactness, high spectral purity, narrow free-running linewidth (500 kHz-1 MHz), and relatively high output power (10-100 mW). In almost all cases the excitation source should be collimated to ensure that the entire beam interacts with the molecules, minimizing the investigated volume without generating a signal background.

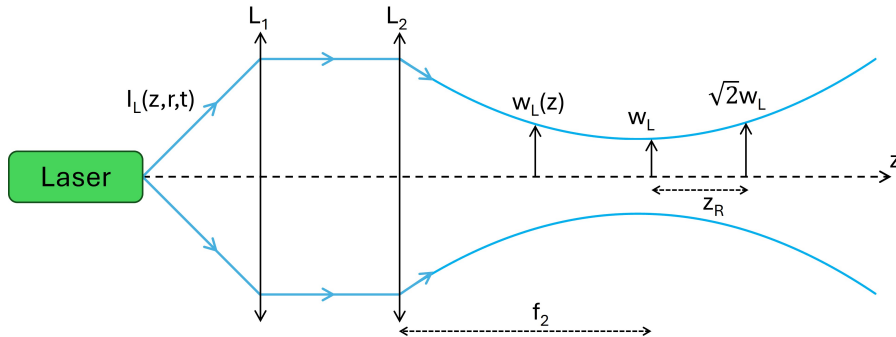


Figure 1.3: Laser beam profile characterizing by a Gaussian shape. In this example, the laser beam is collimated with the help of a focus lens.

In the case of a collimated and Gaussian beam (see Figure 1.3), the spatial intensity profile as a function of the radial distance $\mathbf{r}$ from the beam axis z can be described by

the relation:

$$I_L(r, z, t) = P(t) \frac{2}{\pi w_L(z)^2} e^{-2\left(\frac{r^2}{w_L(z)^2}\right)}. \quad (1.10)$$

Here $w_L(z)$ describes the distance from the propagation axis. The beam's shape is uniquely described by two parameters. The first one is the beam waist radius w_L , associated with a beam intensity reduced by a factor of $1/e^2$. The second one is the so-called Rayleigh parameter defined as:

$$z_r = \frac{M^2 \pi w_L^2}{\lambda_L(t)}, \quad (1.11)$$

being $\lambda_L(t)$ the laser's wavelength, and M^2 the beam propagation factor. Finally, these two parameters are intrinsically linked to each other via the following relation:

$$w_L(z) = w_L \sqrt{1 + \left(\frac{z}{z_r}\right)^2}, \quad (1.12)$$

In the infrared region, the radiative lifetimes of vibrational levels are longer than the ones associated with non-radiative collisional de-excitations in the typical pressure ranges exploited for the photo-acoustic effect (i.e. $10^1 - 10^2$ mbar). As a result, after interacting with the impinging energy, in most cases, the trace molecule relaxes to the ground state by transferring its kinetic energy to the surrounding molecules, with a connected heat release. According to references [69, 90], the heat production by light absorption can be explained using a simplified two-level model. The trace-gas concentration is split into two levels, being equal to $N_1(t)$ in the ground state and $N_2(t)$ in the excited state. During the process, the total concentration N has to be constant:

$$N = N_1(t) + N_2(t). \quad (1.13)$$

According to Einstein's rate equations [91, 92], the light absorption will determine a variation in the two-level population as:

$$\frac{d}{dt} N_2 + (k_{st} + k_{sp} + k_r) N_2 = k_{st} N_1, \quad (1.14)$$

where k_{sp} represent the spontaneous emission constant rate, while k_r include all the effects linked to the relaxation processes. The stimulated rate constant k_{st} is proportional to the absorption cross-section of the target trace-molecule σ and the photon flux φ :

$$k_{st} = \sigma \varphi = \frac{\sigma I}{h\nu}, \quad (1.15)$$

where I is the beam intensity, and $h\nu$ is the absorbed photon energy. Combining Equation 1.13 and 1.14 it is easy to end up with an equation rate where the contribution of N_1 is eliminated:

$$\frac{d}{dt} N_2 + (2k_{st} + k_{sp} + k_r) N_2 = k_{st} N. \quad (1.16)$$

Furthermore, the heat power density $H(\mathbf{r}, t)$ generated by the light absorption of

the targeted molecules can be expressed as follows:

$$H(\mathbf{r}, t) = k_{V-T} N_2(\mathbf{r}, t) h\nu. \quad (1.17)$$

Here k_{V-T} represents the rate constant of the associated vibrational-translational relaxation path. Since the photoacoustic signal $S_{PA}(\mathbf{r}, t)$ is defined as the time derivative of the heat power density (see Equation 1.9), it is evident that the photo-acoustic effect occurs when the concentration of the excited molecules is varying over time. This condition can be reached only by modulating the excitation laser beam. In general, two are the main modulation schemes adopted in a photo-acoustic setup, as shown in Figure 1.4.

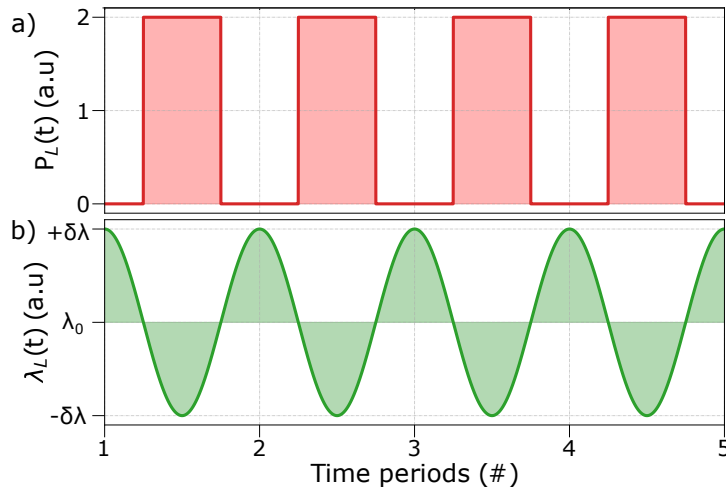


Figure 1.4: Examples of amplitude (a) and wavelength (b) modulation schemes. In the first case, the optical power is modulated via a square wave. In the second case, the laser's wavelength is periodically shifted by its carrier via a sine wave modulation.

The first one is known as amplitude modulation (AM) and consists of tuning the laser wavelength to the addressed trace-molecule transition and inducing an intermittent on and off of the beam at a given frequency f_0 . This intensity modulation can be obtained in two ways: (1) via a square or sine wave modulation of the laser pump (the driving current for semiconductor lasers like QCLs), (2) exploiting other optics technologies such as acousto-optic (AOM) or electro-optic (EOM) modulators. The second one is known as wavelength modulation (WM) and consists of scanning the laser wavelength around the absorption peak while keeping the optical power constant [93].

The following derivation considers the case of an excitation source with a constant light intensity I_0 periodically switched on and off at a time t' . Supposing that the radiation is switched on at a time $t = 0$, the equation rate 1.16 can be solved to find out the time evolution of the population in the excited level $N_2(t)$:

$$N_2(t) = \frac{(\sigma I_0 / h\nu)}{2(\sigma I_0 / h\nu) + k_{sp} + k_r} N \left(1 - e^{-\left(2\frac{\sigma I_0}{h\nu} + k_{sp} + k_r\right)t} \right). \quad (1.18)$$

According to Equation 1.18 the population in the excited state initially experiences an exponential growth. Since the relaxation dynamics are usually very fast (order

of nanoseconds), the system will suddenly achieve the equilibrium state, reaching a population number equal to:

$$N_2(t) = \frac{(\sigma I_0/h\nu)}{2(\sigma I_0/h\nu) + k_{sp} + k_r} N. \quad (1.19)$$

If the excitation source is switched off at the time t' (i.e. $I = 0$), the stimulated emission is stopped, resulting in the zeroing of the right side and of the first term in the bracket of the left side of Equation 1.16. As a consequence, by solving the rate equation, the population concentration in the excited state will undergo an exponential decrease:

$$N_2(t) = N_2(\tau) e^{-(k_{sp} + k_r)(t - t')}. \quad (1.20)$$

Hence, a periodic beam intensity modulation (on/off) will result in a periodic population variation of the excited state. According to Equation 1.17, the time derivative of the heat power density is proportional only with the time-dependent part of $N_2(\mathbf{r}, t)$. So, referring to Equation 1.9, the photoacoustic source term can be divided into two contributions: one is associated with the rising transient (laser on), $S_{PA}^+(\mathbf{r}, t)$, while the other one is related to the exponential decay of the excited state's population (laser off at $t = t'$), being $S_{PA}^-(\mathbf{r}, t)$ and with associated formulas:

$$S_{PA}^+(\mathbf{r}, t) = (\gamma - 1)k_{V-T}\sigma N(\mathbf{r})I_0 e^{-\left(2\frac{\sigma I_0}{h\nu} + k_{sp} + k_r\right)t}, \quad (1.21)$$

$$S_{PA}^-(\mathbf{r}, t) = -(\gamma - 1)k_{V-T} \frac{k_{sp} + k_r}{2\left(\frac{\sigma I_0}{h\nu}\right) + k_{sp} + k_r} \sigma N(\mathbf{r})I_0 e^{-(k_{sp} + k_r)t}. \quad (1.22)$$

The two latter equations are valid only if the switching time of the laser is shorter than the relaxation time associated with the target molecules' excited state. Since typical relaxation times of vibrational-translational transitions are of the order of microseconds or sub-microseconds [94–96], in AM photoacoustic-based setups the typical modulation frequency ranges spans hundreds of Hz to tens of KHz.

To sum up, the photoacoustic source term associated with an on/off intensity-modulated excitation beam is represented by the combination of a train of alternate exponential pulses, with slightly different amplitudes and decay constants due to the effect of stimulated emission.

A simplified view can be applied if the intensity of the excitation laser source is low enough to consider the stimulated emission much smaller than the other contribution, i.e. spontaneous emission and relaxation rates. Under these conditions, the term k_{st} can be neglected. The picture becomes even easier if the laser beam is intensity-modulated via a sine-wave function. In this case, its intensity can be divided into DC and AC parts:

$$I(\mathbf{r}, t) = I_{DC}(\mathbf{r}) + I_{AC}(\mathbf{r})e^{i\omega t}, \quad (1.23)$$

where ω is the modulation frequency. The evolution of the population in the excited

state $N_2(\mathbf{r}, t)$ can be resolved by the Equation 1.16 as follows:

$$N_2(\mathbf{r}, t) = \frac{\sigma N(\mathbf{r})}{h\nu} \frac{I_{DC}(\mathbf{r})}{k_{sp} + k_r} + \frac{\sigma N(\mathbf{r})}{h\nu} \frac{I_{AC}(\mathbf{r})}{k_{sp} + k_r + i\omega} e^{i\omega t} \quad (1.24)$$

Since the photoacoustic source is proportional to the time derivative of the heat source term, according to equations 1.9 and 1.17 only the AC term of the beam intensity will enter into the derivation of S_{PA} :

$$S_{PA} = \frac{(\gamma - 1)}{c^2} \frac{\partial}{\partial t} (k_{V-T} N_2(\mathbf{r}, t) h\nu) = i\omega(\gamma - 1) \frac{k_{V-T}}{k_{sp} + k_r + i\omega} \sigma N(\mathbf{r}) I_{AC}(\mathbf{r}) e^{i\omega t}. \quad (1.25)$$

As it is possible to see, the photoacoustic term is linearly proportional to the concentration of the absorbing molecule, $N(\mathbf{r})$, to the absorption cross-section of the addressed molecular transition, σ , and the intensity of the modulated excitation beam, $I_{AC}(\mathbf{r})$.

According to the latter Equation, the photoacoustic source term experiences a phase shift with the modulated beam, being equal to $\arctan[(k_{sp} + k_r)/\omega]$. Moreover, its amplitude shows a dependence on the ratio of the relaxation rates. Anyway, in most cases (especially in the infrared region of the electromagnetic spectrum), the vibrational-translational rate, k_{V-T} is the dominant one so that $k_r \simeq k_{V-T}$, and $\frac{k_{V-T}}{k_{sp} + k_r + i\omega} \simeq 1$.

1.2.3 Sound wave generation

In free space

Understanding the characteristics of the photoacoustic source term makes it possible to study the associated sound wave generation, by solving the non-trivial wave equation 1.8. One possibility refers to the Green's function method [94, 97], in which a function $G(\mathbf{r}, \mathbf{r}', t, \tau)$ (i.e. Green's function) is introduced to be the solution of the equation:

$$\frac{\partial^2 G}{\partial t^2} - c^2 \nabla^2 G = \delta(\mathbf{r} - \mathbf{r}') \delta(t - \tau). \quad (1.26)$$

In this case of study the Green's function represents the impulse response of the sound wave equation for a short excitation in a point $\mathbf{r}'$ at an instant of time τ . As a result, the solution of the wave equation $p(\mathbf{r}, t)$ associated with a given photoacoustic source term $S_{PA}(\mathbf{r}, t)$ can be obtained by solving the following two-dimensional integral:

$$p(\mathbf{r}, t) = \iiint G(\mathbf{r}, \mathbf{r}', t, \tau) S_{PA}(\mathbf{r}', \tau) dV' d\tau, \quad (1.27)$$

where the volume integral is extended within the sample region illuminated by the light beam and the time interval within the duration of the heat pulse. If the laser beam has a Gaussian profile, it will be characterized by a strong intensity variation only along the beam radius, neglecting the variation in the direction of propagation. Under these conditions, the photoacoustic source term can be easily described by choosing a cylindrical coordinate system where the z-axis coincides with the laser beam. In this radially symmetric two-dimensional space, the Green's function takes the following form:

$$G(r, r', t, \tau) = \frac{\Theta\left(t - \tau - \frac{r-r'}{c}\right)}{2\pi c^2 \sqrt{(t - \tau)^2 - \left(\frac{r-r'}{c}\right)^2}}, \quad (1.28)$$

being Θ the Heaviside function, whose general definition is:

$$\Theta(x - x_0) = \begin{cases} 1, & x - x_0 \geq 0 \\ 0, & x - x_0 < 0 \end{cases} \quad (1.29)$$

At this point, exploiting the last definition of Green's function in cylindrical coordinates, the solution of sound wave equation 1.8 at a generic distance r from the Gaussian laser beam can be obtained by solving the following integral:

$$\frac{\partial p(r, t)}{\partial t} = \frac{1}{2\pi c^2} \iint \frac{\Theta\left(t - \tau - \frac{r-r'}{c}\right)}{\sqrt{(t - \tau)^2 - \left(\frac{r-r'}{c}\right)^2}} S_{PA}(r', z, \tau) 2\pi r' dr' d\tau. \quad (1.30)$$

To simplify the discussion, let's imagine a laser with a beam radius $w_L(z)$ at a position z and dividing its cross-section into thin rings with radius r' and thickness $\Delta r' \simeq cT_P$, where T_P is the pulse duration expected to be sufficiently smaller so that the photoacoustic source term is approximately constant within each ring. If the laser illuminates the sample for an interval $\tau < T_P$, the absorption from the target molecules results in the generation of a heat pulse with duration $\tau < T_H$. Finally, the heat pulse will cause a simultaneous sound pulse in the whole spatial domain illuminated by the laser. In this view, each ring will be responsible for generating cylindrical pulses of sound separated by a time interval $\tau = \Delta r'/c$, until the last cylindrical pulse arrives at a time $t = T_H + r/c$. Hence, the final result will be the generation of a primary sound pulse in the point of observation with a total duration $T_S = T_H + w_L(z)/c$, roughly equal to the transit time of sound along the beam radius. Commonly, sound pulses generated by a laser with a radius of order of millimeters show duration in the μs range. However, their amplitude strongly depends on the beam radius, revealing an important decrease especially if the sound waves are detected outside the region illuminated by the optical beam (as it happens in most cases).

In a closed space

In all the experimental applications of photoacoustic spectroscopy, the sample gas is confined inside a closed space consisting of a small cell and two windows to allow the excitation laser to pass through and interact with the target molecules. In this case, the derivation of the sound wave pressure $p(\mathbf{r}, t)$ will be slightly different.

If the length of the cell is much smaller than the excitation source wavelength, i.e. $\lambda \gg L$, and considering the optical beam to be intensity modulated (AM), the spatial derivative of the sound pressure, $\nabla \cdot p$, can be neglected in the sound wave Equation 1.8. It is then possible to integrate the latter equation within the whole cell volume:

$$\int \frac{\partial^2 p}{\partial t^2} dV = \int S_{PA}(\mathbf{r}, t) dV. \quad (1.31)$$

The term on the right side can be directly integrated, while the term on the left side can be computed by considering the definition of S_{PA} in the case of an intensity-modulated beam with a sine-wave function given by Equation 1.25:

$$-\omega^2 pV = (\gamma - 1) \frac{k_{V-T}}{k_{sp} + k_r + i\omega} \sigma N \int I_{AC}(\mathbf{r}, t) e^{i\omega t} dV. \quad (1.32)$$

In this case of study, it is possible to assume that both the sound pressure wave and the absorbing molecule concentration N have no spatial dependence within the cell. The volume integral can be computed by splitting it into two parts: a surface integral in the coordinates (x,y) and a one-dimensional integral along the z-axis. The first one is, by definition, the optical beam power P_{AC} :

$$\int \left[\int I_{AC}(\mathbf{r}) dx dy \right] dz = \int P_{AC} dz. \quad (1.33)$$

Combining Equation 1.33 with the assumption that the absorption within the cell is governed by the Beer-Lambert law, the sound pressure wave inside the chamber will be:

$$p(t) = i \frac{(\gamma - 1) P_{AC}}{\omega V} (1 - e^{-\alpha L}) e^{i\omega t} \simeq i \frac{(\gamma - 1) P_{AC} \alpha L}{\omega V} e^{i\omega t}, \quad (1.34)$$

being $\alpha = \sigma N$ and supposing the V-T relaxations to be dominant compared to the other processes. It follows that, in the case of a small non-resonant cell, the sound pressure wave is proportional to the absorption coefficient of the trace-molecule investigated and to the beam optical power, but inversely proportional to the volume of the cell itself and the modulation frequency.

Without loss of generality it can be stated that in all the cases of studies where the interaction between the laser and the molecules is spatially confined, the generated pressure wave will always be characterized by this type of functional dependencies on the experimental parameters such as the optical power, the resonance frequency, the optical path length, and so on.

1.2.4 Sound wave detection

Once the acoustic wave is generated within the sample, a fundamental next step regards its detection. Since, as already mentioned, the sound pressure wave drastically decreases as the distance from the excitation source increases [98], a photoacoustic detector has to convert the periodic pressure variation induced by the sound wave generation into a measurable signal, playing the role of a transducer. The most common photoacoustic detectors are condenser microphones, quartz tuning forks, and cantilevers. Since the main target in trace-gas sensing applications is reaching high detection sensitivity, the photoacoustic detector has to be exploited in a configuration where the sound wave intensity is enhanced within a limited volume. For this reason, these detectors are often coupled with acoustic resonators of different geometry, such as Helmholtz [99, 100] single-tube [101] or dual-tube resonators [102].

Without going into the details of the peculiarities that distinguish each of these configurations, it is possible to state that the homogeneous acoustic wave equation of a resonator has a series of solutions called eigenmodes, $\epsilon_n(\mathbf{r})$, associated with discrete resonance frequencies f_n . They represent an orthogonal base within the resonator volume V , and they can be normalized as follows:

$$\int_V \epsilon_n(\mathbf{r}) \epsilon_m(\mathbf{r}) dV = V \delta_{nm}, \quad (1.35)$$

being δ_{nm} the Kronecker's delta. If the photoacoustic effect is caused by an intensity-modulated beam with a given modulation frequency Ω_{mod} , the sound pressure wave can be written as a series expansion of the resonator's eigenmodes as:

$$p(\mathbf{r}, t) = \left(A_0 + \sum_{n=1}^{\infty} A_n(\omega_n) \epsilon_n(\mathbf{r}) \right) e^{j\Omega_{mod}t}, \quad (1.36)$$

where $A_n(\omega_n)$ is the sound wave amplitude associated with the n_{th} resonator's eigenmode. Putting the latter definition of $p(\mathbf{r}, t)$ in the wave equation 1.8, integrating over the resonator's volume, and performing simple mathematical manipulations, it is possible to derive the expression for $A_n(\omega_n)$ as follows:

$$A_n(\omega_n) = \frac{\int_V \epsilon_n(\mathbf{r}) S_{PA}(\mathbf{r}, t) dV}{V \left(\omega_n^2 - \Omega_{mod}^2 + i \frac{\Omega_{mod} \omega_n}{Q_n} \right)}. \quad (1.37)$$

The term Q_n represents the n_{th} eigenmode's quality factor. It takes into account the mechanical response of the resonator to the perturbation induced by the acoustic wave. While the term $\left(\omega_n^2 - \Omega_{mod}^2 + i \frac{\Omega_{mod} \omega_n}{Q_n} \right)$ gives an estimation of the acoustic losses of the resonator near resonance.

If a photoacoustic detector is placed at a location $\mathbf{R}_M$ near the resonator it will detect a sound pressure wave equal to:

$$p(\mathbf{R}_M, t) = \left(A_0 + \sum_{n=1}^{\infty} A_n(\omega_n) \epsilon_n(\mathbf{R}_M) \right) e^{i\Omega_{mod}t}. \quad (1.38)$$

According to Equation 1.38 all the resonator's eigenmodes will, in principle, contribute to the detected photoacoustic signal. But if the laser is tuned to one specific and strong eigenmode, $\Omega_{mod} \equiv \omega_n$, the others will be neglected, resulting in a detected on-resonance photoacoustic signal equal to:

$$p(\mathbf{R}_M, t) \simeq A_n(\omega_n) \epsilon_n(\mathbf{R}_M) e^{i\omega_n t}. \quad (1.39)$$

It is also evident that the amplitude of the photoacoustic signal will depend not only on the mechanical response of the acoustic resonator but also on the mechanical response of the specific detector used. The total response will therefore be a convolution of the two contributions.

1.3 Basic ingredients for a photoacoustic-based sensor

Section 1.2 was devoted to providing a generalized theoretical recipe for the photoacoustic effect. As a natural step forward, the next section provides several experimental solutions for implementing a real photo-acoustic setup, focusing on both the excitation source and the acoustic transduction.

1.3.1 The excitation source

In principle, any type of modulated light source, such as sunlight [103], solid-state lasers [104], (LED) [105], hetero-structured laser [106], or even optical parametric oscillator (OPO) [107, 108], can be exploited as the excitation source. Among the immense possibilities offered, the mid-IR part of the electromagnetic spectrum is a region *par excellence* for trace-gas sensing applications [109, 110]. Thanks to the abundance of strong rovibrational or translational-vibrational molecular transitions of many key molecules (see Fig 1.1), mid-IR-based technologies have become one of the most used and efficient solutions for environmental monitoring [111–113], medical diagnostic [114], and even archaeological dating via $^{14}\text{CO}_2$ detection [115, 116]. This important development was driven by the birth of chip-scale and low-noise semiconductor mid-infrared lasers, which are Quantum Cascade and Interband Cascade Lasers.

The cascade process

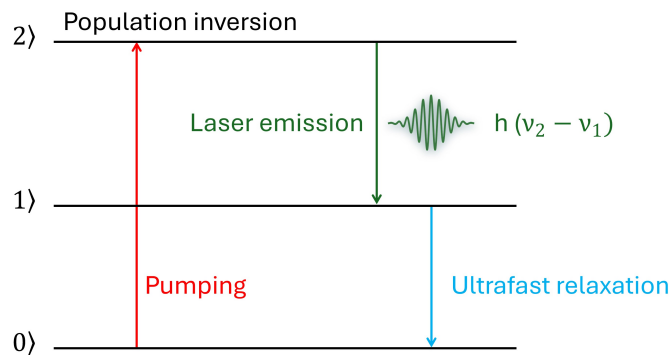


Figure 1.5: Schematic representation of laser emission from the simplest three-level system. The electron population inversion is obtained via the excitation from $|0\rangle$ to a meta-stable upper level $|2\rangle$. The laser emission occurs following the de-excitation from $|2\rangle$ to $|1\rangle$. The transition $|1\rangle$ to $|0\rangle$ typically follows non-radiative pathways.

Given the hetero-structured nature of both QCLs and ICLs, their emission relies on electronic transitions between the conduction and the valence bands inside the active medium [117]. The energy difference of the two bands, also known as *energy gap*, determines the wavelength of the emitted photons. To obtain laser emission from a bipolar diode, an inversion of the electron population must be verified. The easiest implementation, shown in Figure 1.5, is the three-level system: the injected electron is excited from the level $|0\rangle$ to the level $|2\rangle$ to obtain the population inversion and gain. the laser emission occurs following the radiative de-excitation from $|2\rangle$ to $|1\rangle$

and the recombination with the holes. Finally, the system comes back to its equilibrium state via a non-radiative relaxation from $|1\rangle$ to $|0\rangle$.

Each injected electron can (ideally) produce a single photon, resulting in a final output power from one of the two facets equal to [118]:

$$P = \frac{1}{2e} h\nu \eta (I - I_{th}), \quad (1.40)$$

where $h\nu$ is the photon energy, being equal to the energy gap between the two lasing levels, e is the electron charge, I_{th} the laser current threshold, while η is a parameter linked to some key property of the devices such as cavity length, losses, and reflectivity, the latter value laying between 0 and 1. The factor $1/2$ is introduced because the emission from the device can occur in both two facets of the device.

If the aim is obtaining an efficient mid-IR emission source, the exploitation of a standard bipolar structure is not convenient for two main reasons. Firstly, it is very hard to find a semiconductor structure characterized by a small enough energy band to be able to emit above $\simeq 3\mu\text{m}$. Secondly, according to Equation 1.40, the emitting power decrease when the wavelength increase ($P \propto \lambda^{-1}$), together with an increase of the loss factor η [117].

To overcome this limitation, semiconductor mid-IR laser source generally relies on the confinement of the electrons within several layers of semiconductor material (typically grown with molecular beam epitaxy techniques, MBE), allowing the generation of an active medium made by a series of nanometric-thickness layers of different chemical composition [119, 120]. This results in a variation of the electric potential seen by the injected electron during its propagation through the active medium. As a result, the electron will encounter a series of quantum wells, determining the division of the conduction band in discrete sub-levels. Thanks to this *hetero-structured cascade configuration*, characterized by the succession of active regions (for the laser emission) and injection zones (for the electron population inversion), each electron will contribute multiple times for the laser emission, enhancing the overall emitting power [117].

Quantum Cascade Laser

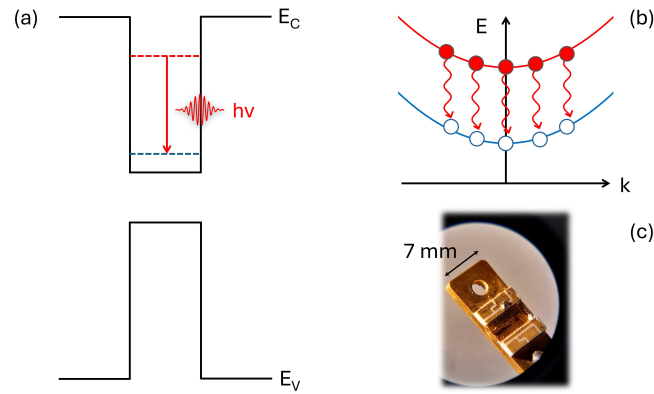


Figure 1.6: (a): Schematic representation of the QCL inter-sub-band transition. (b): electron transition between two inter-sub-band in the valence bond. (c): Photo of a QCLs obtained via an electronic microscope.

QCLs are chip-scale, uni-polar, and hetero-structured semiconductor lasers whose cascade processes are related to inter-sub-band transitions of the conduction band. The first prototype was proposed by J. Faist et al. in 1994 [121] alternating within the substrate layers of Indium-Gallium-Arsenide (InGaAs) and Indium-Aluminium-Arsenide (InAlAs) on a substrate of Indium phosphide (InP).

This peculiar architecture, schematized in Figure 1.6(a), allows the QCL to have peculiar and unique characteristics if compared with common semiconductor lasers.

1. First of all, since the laser emission occurs entirely within the conduction band and between two sub-bands, QCLs are devices characterized by very fast laser dynamics, typically of the order of pico-seconds.
2. Another figure of merit for QCL is related to their capability in covering an emission range from approximately $2.4\ \mu\text{m}$ up to $24\ \mu\text{m}$ [122, 123], with a wide range of emitting optical power from milliwatts up to the Watt.

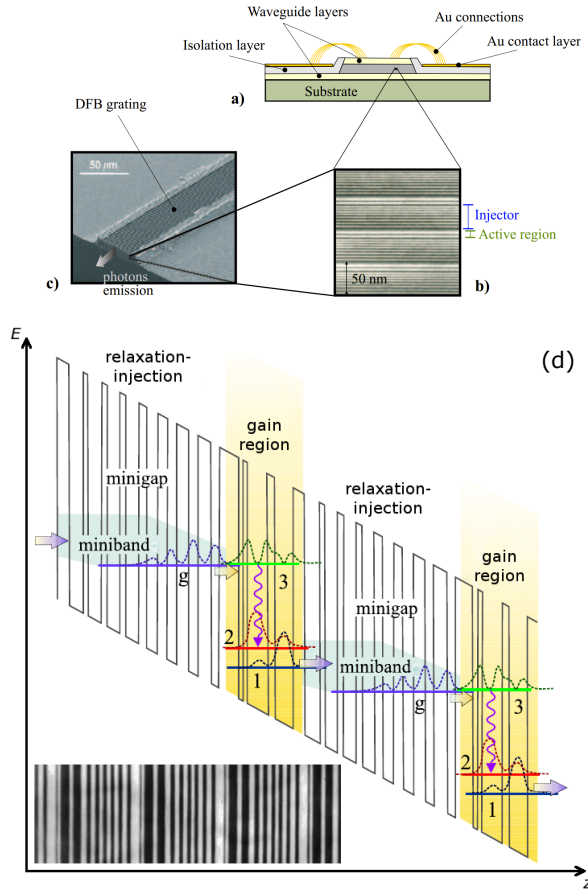


Figure 1.7: (a): Schematic representation of a QCL device from the facet. (b): zoom on the active medium where the succession of the quantum wells are visible, and (c): front view of the active medium. Both the images (b) and (c) were taken with an electronic microscope. (d): typical QCL's band structure made by a three-quantum-well vertical-transition architecture. The overall slope of the structure is determined by the application of an external electric field to obtain electron transport (depicted by the violet arrows) between the quantum wells. The evolution of the square moduli of the electron wave function is depicted alongside the lattice. Light regions are AlInAs barriers, while dark regions are GaInAs wells. All the four pictures were taken from [109, 117, 124].

Figure 1.7 (a) reports a typical structure of a QCL. The electrons are injected via

gold (AU) connections in the wave-guide, a complex structure of layers where the laser effect occurs. (see Figure 1.6(b)). The laser beam travels along the wave-guide and their facets are cut perpendicular forming the semi-reflective mirrors of the laser cavity (as shown in Figure 1.6(c)). The electron injected experience the N-stage cascade (typically between 10 and 100) of the heterostructure active medium. Each stage has a width of $\simeq 50$ nm and it is divided into an electron injection region and an active region. The combination of these structures forms super-lattices, whose theoretical description can developed by solving the associated Shrödinger equation. The solutions will be a discrete but complex system of energy levels. An in-depth description can be found in [109, 117, 124]. Once the injected electron undergoes a photon emission in the first active region, it will pass through the adjacent injection region and it will arrive at the second active region, thus emitting another photon with the same energy, direction of propagation, and phase of the previous one. It is therefore evident that, for an injected electron, the generated output power will be:

$$P = N_S \left[\frac{1}{2e} h\nu\eta(I - I_{th}) \right], \quad (1.41)$$

where N_S is the number of stages. Hence, the higher the number of cascade stages, the higher will be the output power of the device, up to a thousand times greater than the common diode laser at the same wavelength.

3. Additionally, a peculiarity that differentiates the QCL from common semiconductor lasers is the high spectral purity. If in a common semiconductor laser, the transition occurs between two bands with opposite curvature (one in the conduction band and one in the valence band), in the case of QCLs the two transition bands have the same curvature. As a consequence, their emission will be characterized by a constant frequency in the whole range of momentum k , as depicted in Figure 1.6(b). Accordingly, the spectral emission profile, centered on a given wavelength (or frequency) λ_0 , will be characterized by a narrow line-broadening for a specific timescale. In general, the laser linewidth, defined as the FWHM of the emission spectra, is affected by several contributions such as psychical mechanisms related to the electron dynamics or technical noise (current or temperature fluctuation). When only the first ones contribute to the laser emission profile the FWHM is defined as the *intrinsic line-width*, and it can be computed with the following equation, known as Shallwow-Townes formula [125]:

$$\Delta f_{LAS} = \frac{4\pi h\nu(\Delta f_c)^2}{P_{out}}, \quad (1.42)$$

where Δf_c is the resonator HWHM, and P_{out} the output power. Several theoretical works have predicted a very narrow linewidth for QCLs in the mid-IR and THZ range ($\simeq 1$ kHz) [126], and the first experimental result performed on a QCL emitting around $4.33 \mu\text{m}$ measured an intrinsic linewidth of around 510 ± 160 Hz [127].

However, in most of the experimental applications of QCLs, technical noise plays a crucial role. In fact, contributions such as temperature and emitted power fluctuations (mostly due to the supply instrumentation used for the laser current driving and the temperature stabilization), lead to a further spectral line broadening with numbers ranging from hundreds of kHz to a few MHz for time scales of 1-10 microseconds [128]. Anyway, several experimental strategies were developed to stabilize the laser frequency noise, and consequently decrease its spectral linewidth. Some examples are: locking the QCL to stable reference, such as optical resonators [129, 130], optical frequency combs (OFC) [131, 132], and so on. More details will be discussed in Chapter 4.

Taken together, all these features enable Quantum Cascade Lasers to become one of the leading technology in the field of high-precision [133, 134] and high-sensitivity spectroscopy [26, 135], finding a very important role also in trace-gas photoacoustic spectroscopy in continuous [104], pulsed [136], and comb [62, 137] emission regimes.

Interband Cascade Lasers

One year after the first experimental demonstration of a Quantum Cascade Laser, a new bipolar mid-IR hetero-structured semiconductor laser was developed by R.Q. Yang *et al.* [138]. Known as Interband Cascade Laser, it relies on the inter-band transition between the conduction and valence bands (such as traditional diode lasers) but combined with a cascade design of the active medium [139].

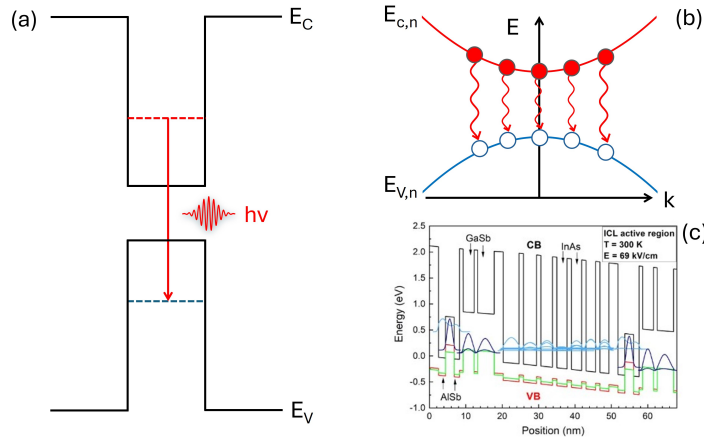


Figure 1.8: (a): schematic representation of the ICL inter-band transition. (b): electron transition between two inter-bands in the conduction and valence bands. (c): example of an ICL's super-lattice describing the cascade process. The latter figure is taken from Reference [140].

This feature allows the ICLs to have great flexibility in wavelength emission range thanks to active medium engineering, similar to what happens with QCLs. The inter-band transition schemes have the consequence of a much-reduced number of stages and, consequently, a lower overall emitting optical power (compared with QCLs) that can achieve maximum values of the order of mW at the current limit threshold. Additionally, the typical emission dynamics for ICLs are slower compared with QCLs, being of the order of nanoseconds. As a direct consequence, these devices require a low

power supply to work, thus providing significant advantages in energy consumption and heat dissipation. These features allow the ICLs to be very promising laser sources for outdoor in-field and far-field applications where the supplied energy resources are very limited [141, 142]. Furthermore, they can be easily designed in the spectral window between 3 μm and 4 μm , where the QCLs show very limited performances, thus making them particularly suitable for specific sensing applications, such as the strong C-H band detection [143, 144].

Without entering more details, and considering the above-described peculiarities, both ICL and QCL represent optimal solutions as the excitation source for the generation of the photoacoustic effect in a trace-gas detection setup, offering a huge flexibility in the wavelength range, a great possibility for further compactness reduction, and relatively high optical powers.

1.3.2 The acoustic-to-voltage transducer

Together with the laser excitation source, the acoustic-to-voltage transduction and readout parts play a crucial role in determining the ultimate detection sensitivity of a photoacoustic sensor. From the beginning of PAS, three different types of transducers were established as valid solutions: the condenser microphone and, more recently, the quartz tuning fork, and the silicon-based cantilever. This paragraph provides a detailed description of all three photoacoustic detectors, focusing on both the structural and mechanical features, but also on the associated readout method.

Condenser microphone

As already mentioned, in modulated photoacoustic-based schemes the sound wave generation ranges from hundreds of Herz up to several tens of kHz. For this range of frequency, standard condenser microphones are very well suited both for their response and for their ease of implementation. The first use of a condenser microphone as an acoustic transducer in a photoacoustic spectroscopy experiment was performed in 1940 by M.L. Veingerov [41]. For the next 60 years, the microphone has established itself as the only possible choice for the development of highly sensitive trace gas detection systems, enabling the so-called microphone-enhanced photoacoustic Spectroscopy (MPAS). Starting from the early 2000s other solutions came up in the market, but they remain a very good, compact, and low-cost choice. Nowadays, bulky and noisy microphones were replaced with chip-scale and much more performing solutions suitable for portable applications with low-power consumption. Some examples of compact microphones available on the market are reported in Figure 1.9, all of them are fabricated with Micro-Electro-Mechanical system technologies.

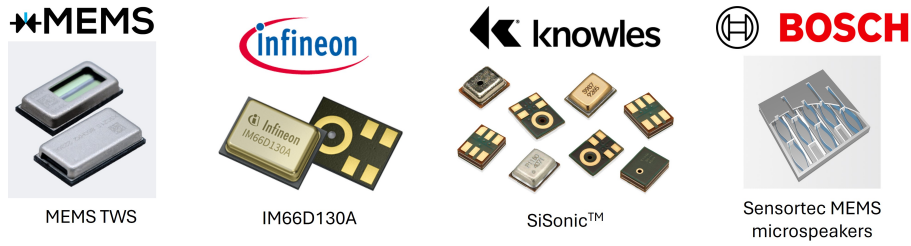


Figure 1.9: Some example of MEMS-based microphones. All of them are chip-scale and very suitable for compact sensing applications.

The basic principle of a microphone consists of forcing the movement of a thin membrane, typically made of gold-coated Mylar, silicon, or stainless steel, following its interaction with an impinging acoustic wave. The oscillation readout is all-electric and based on the principle of the condenser [145]. Two conductor plates are separated by a dielectric material (air in most cases): one plate is the membrane itself, and the other is an electrically polarized backplate. When the membrane oscillates the distance between the two plates changes, resulting in a capacitance change of the condenser. This variation is then converted into an analog or digital signal via a proper electronic readout, providing the photoacoustic signal. The detection sensitivity of the whole system depends mainly on the area of the two plates, their relative distance, and the membrane's material and thickness.

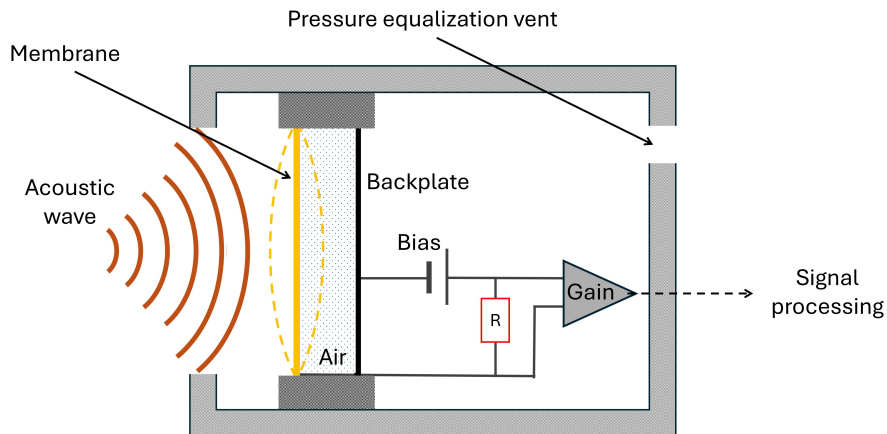


Figure 1.10: Schematic representation of the sound wave conversion using a conventional condenser microphone.

As shown in figure 1.10, the membrane divides two gas volumes, one is responsible for the sound wave propagation, while the other is the gas confined inside the condenser. Usually, the membrane is perforated to balance the low-frequency pressure waves between these two volumes. Furthermore, a vent is added at the back volume to equalize its pressure with the ambient air. Starting from this basic configuration, it is possible to modify the microphone's geometry to reduce the acoustic damping effect from the back volume [146].

In the case of a condenser microphone, the photoacoustic signal output is directly linked to the pressure, and the microphone detection sensitivity, named S_M , is often given in mV/Pa , or dB relative to 1 Pa, as a function of the frequency. In general, the sensitivity response of a given microphone is flat off-resonance, then shows a rapid

increase at the associated resonant frequency (ranging from 20 Hz to 20 kHz). For this reason, working in resonance is much better if the task is to exploit the best transduction efficiency of the microphone [147]. Furthermore, thanks to amplification and lock-in detection schemes, is possible to isolate the resonance from the off-resonance components, and consequently maximize the signal-to-noise ratio. On the other hand, working off-resonance can take advantage of the microphone flat response, a very important prerogative for high-sensitive and broad-band detection [62].

Quartz Tuning Fork

Following the development of the first quartz crystal oscillator by Walter G. Candy in 1921 [148], quartz tuning forks (QTF) were initially conceived as a low-cost and very compact component for the fabrication of quartz-based watches, and designed to work at a resonance frequency of $2^{15} = 32.768$ kHz [149, 150]. In 2002 Kosterev *et al.* [51] reported the first use of a miniaturized quartz tuning fork as the transducer in a trace-gas photoacoustic setup, enabling the QEPAS.

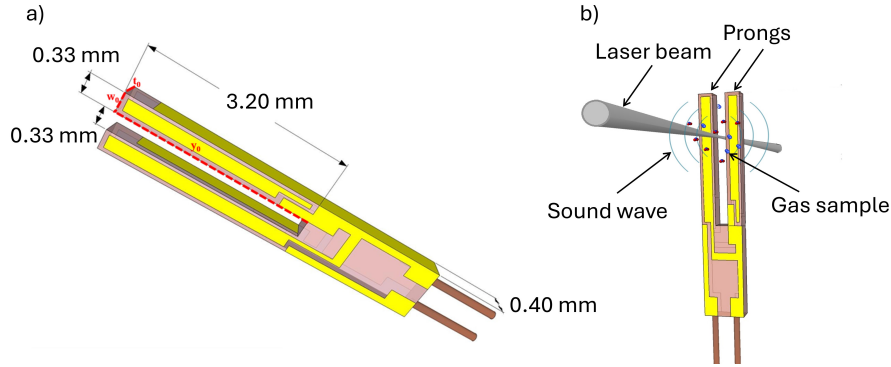


Figure 1.11: (a): Typical geometrical features of a standard QTF with prong dimensions $y_0 \times w_0 \times t_0$. (b): on-beam configuration, where the beam is focalized between the two prongs. The images are taken from reference [68].

A QTF is a sharp acoustic transducer exploited to detect weak photoacoustic excitation signals but with the advantages of using an extremely small gas volume confined between the two prongs [68]. In the on-beam configuration (Figure 1.11(b)) the laser beam is guided and focalized between the two QTF's prongs, spatially separated by a distance of the order of 0.2 mm to 0.5 mm. The sound wave generated following the trace-gas non-radiative relaxation will cause bending in the two QTF's prongs, and consequent charging thanks to the quartz piezo-electricity.¹

The prong's oscillation modes and the associated resonance frequencies can be modeled considering them as two rectangular slabs of dimensions $y_0 \times w_0 \times t_0$ and characterized by a free end and anchored to the QTF's base on the other side. Under the condition of constant elastic modulus, inertia, and cross-sectional area along the beam propagation, the (x, y) in-plane prongs vibration over time can be described by the Euler-Bernoulli beam theory [68, 151]:

¹The latter is a characteristic typical of many crystals lacking a center of inversion symmetry and consists of the generation of a charge displacement in the material's surface, and consequently, the generation of an induced electric field, if subjected to mechanical stress

$$\mathcal{E}\mathcal{M}\frac{\partial^4 y}{\partial x^4}(x,y) + \rho A \frac{\partial^4 y}{\partial t^4}(x,t) = 0, \quad (1.43)$$

being $\mathcal{M}$, $\mathcal{E}$ and ρ the inertia momentum, the Young modulus, and the density of the QTF fabrication material, while $A = w \times w_0$ is the in (x,y) QTF's dimension. Supposing that the prong's displacement can be separated in the x -dependent and the y -dependent components, Equation 1.43 can be solved by superimposing the boundary conditions, according to that the prong's displacements have to be zero at the clamp region, and the free-end cannot be subjected to a bending moment or a shearing force. Under these assumptions, and with few mathematical passages, it is possible to derive a generalized relation defining the set of QTF's resonant frequencies as:

$$f_n = \frac{\pi K}{8y_0^2} \sqrt{\frac{\mathcal{E}}{\rho}} N^2 = \frac{\pi K}{8y_0^2} \sqrt{\frac{\mathcal{E}}{\rho}} \left(\sqrt{\frac{\rho A}{\mathcal{E}\mathcal{M}}} \omega_n \right), \quad (1.44)$$

where $K = w_0/\sqrt{12}$, and ω_n the angular velocity. The applied Euler-Bernoulli model is valid only in vacuum conditions but, in all the experimental applications, the QTF is immersed within a viscous fluid medium. In this condition the harmonic oscillation of the prongs following the interaction with the acoustic waves will be affected by a damping phenomenon, leading to energy dissipation [152]. This effect must therefore be taken into account in the derivation of the QTF resonance modes, resulting in a modified and generalized Euler-Bernoulli equation [68, 153]:

$$\mathcal{E}\mathcal{M}\frac{\partial^4 y}{\partial x^4}(x,y) + (\rho A + \mu) \frac{\partial^4 y}{\partial t^4}(x,t) + C_d \frac{\partial y}{\partial t}(x,t) = 0, \quad (1.45)$$

where C_d defines the damping parameter and μ the mass per unit length. If the damping effect remains sufficiently small and if $\mu \ll \rho A$, the QTF resonant frequency will experience a shift $\delta f = -\mu/2\rho A$ compared with the in-vacuum condition.

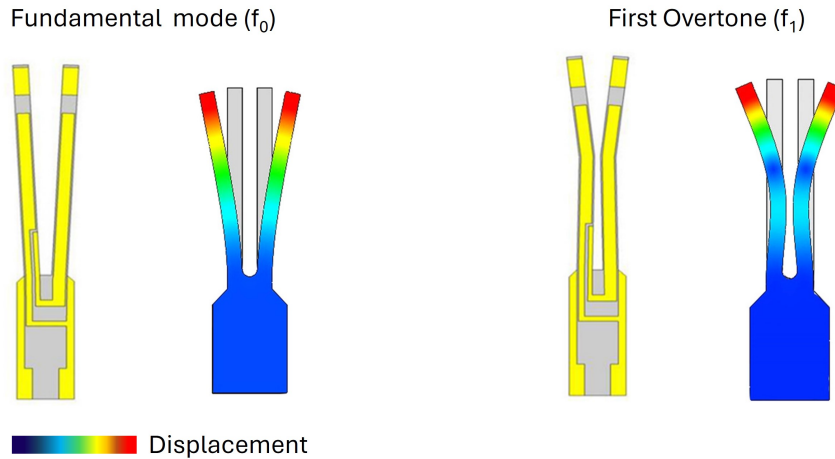


Figure 1.12: Graphical simulation of the first two resonant modes of a standard QTF, namely fundamental mode and first overtone. Next to the representation, a qualitative simulation of the displacement distribution along the structure is reported. In both cases, the highest displacement occurs at the free end, while the clamp region is immovable. Images from References [154] and [155].

Two examples, regarding the fundamental vibrational mode and the first flexural overtone of a standard QTF, are reported in Figure 1.12. In both cases the clamp

region remains immovable, while the prongs free-end (associated with the maximum displacement) oscillates in the opposite direction, allowing the QTF to be characterized by an anti-symmetric vibrational inactivity. The differences between these two modes can be summarized as follows: (1) the fundamental mode shows only one anti-node while there are two in the first flexural overtone, (2) the fundamental mode is characterized by lower resonance frequencies and quality factors (2879.55 Hz, and 12098.97, respectively in [154]) compared with the first overtone (17788.95 Hz and 31373.81 respectively [154]).

The damping losses negatively affect also the mechanical quality factor of the QTF. In fact, supposing the drag force of the surrounding gas to be dominant in the damping losses, the damping parameter can be approximated as $C_d \simeq \sqrt{p\xi}$, with ξ and p the fluid viscosity and pressure, respectively. At the same time, the influence of fluid damping on the quality factor can be defined in terms of the energy loss $1/Q(p)$ at the given pressure P [68]:

$$C_d = \frac{1}{Q(p)} - \frac{1}{Q_0}, \quad (1.46)$$

being Q_0 the QTF quality factor in vacuum. Combining Equation 1.45 and 1.46, the trend of the QTF quality factor as a function of the fluid pressure can be defined as:

$$Q(p) = \frac{Q_0}{1 + Q_0 b \sqrt{p}}. \quad (1.47)$$

The parameter b sums up the dependence of the quality factor on several factors such as the energy losses due to the viscosity of the fluid and the geometry of the QTF itself.

To date, many versions of QTF were developed aiming at overcoming the standard configuration and obtaining higher quality factors. This effort enables the exploitation of QTFs in a wide resonance frequency range optimal for the generation and detection of acoustic waves. After having pushed the techniques to the sensitivity limits imposed by the limited performance of the standard watch QTFs [156], the scientific effort shifted to the fabrication of a second generation custom QTFs. By properly modifying the dimensions (distance between the prongs, thickness, and so on) and proposing alternative shapes such as T-shaped QTF [152], it was possible to obtain an oscillating structure with reduced resonance frequencies, enabling a fundamental resonance mode down to $\simeq 3$ kHz.

The readout of the QTF's oscillations is all-electric. In fact, the piezo-electricity allows modeling the QTF as an equivalent electric circuit made by a capacitance C , a resistance R , and an inductance L . As reported in Figure 1.13, the acoustic wave responsible for the prongs oscillation is represented with an oscillating input voltage signal V_{in} . The QTF electric circuit allows retrieving an output voltage signal proportional to the force applied on the oscillating prongs. The signal acquisition passes through an ultra-low impedance amplifier, with a feedback resistor R_f typically of the order of $10M\Omega$, able to maintain at zero the voltage difference between the two free-ends so that the parallel capacitance C_p is neutralized [68].

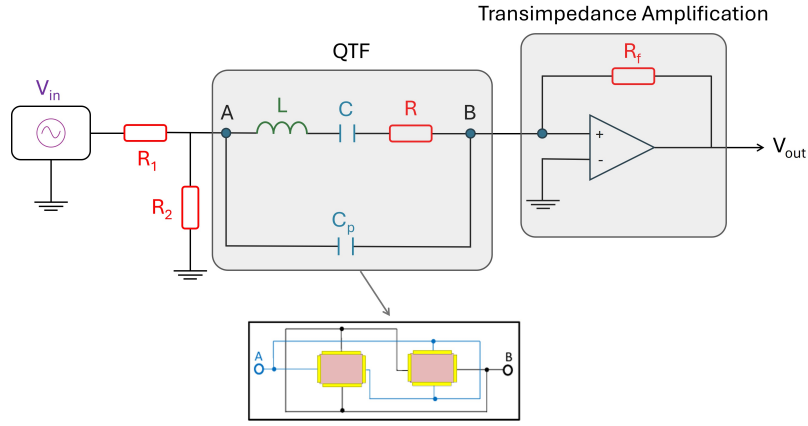


Figure 1.13: Scheme of a QTF with an RLC equivalent circuit. The oscillating signal V_{in} identifies the acoustic wave, treated as a voltage signal on the QTF's prongs. The output voltage signal is amplified via a trans-impedance amplifier feedback loop.

Furthermore, according to the theory of electric circuits, it is possible to easily compute both the resonant frequency and the quality factor (in vacuum condition) for the QTF RLC circuit as:

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{1}{LC}}, \quad (1.48)$$

$$Q = \frac{1}{R} \sqrt{\frac{L}{C}}. \quad (1.49)$$

One disadvantage of exploiting an electrical readout is the noise limitation imposed by the trans-impedance stage, but it can be neglected for the value of resistance R between 10 and 100 k Ω . Furthermore, a big problem could be the presence of parasitic charge in the circuit and electromagnetic interference. For this reason, QTFs must be engineered and efficiently shielded from the external environment (e.g. with a Faraday cage). Anyway, during the last two decades, QEPAS-based sensors have shown world-record performances in terms of detection sensitivity, approaching the sub-ppt level with a doubly resonant acousto-optical configuration [60]. A new perspective developing in this field concerns the exploitation of new material for the QTF fabrication such as Lithium niobate [157], paving the way to a new era for QEPAS spectroscopy.

Silicon-based Cantilever

One year after the first use of a QTF in photo-acoustic spectroscopy, Tomberg et al. propose an alternative approach based on the exploitation of a silicon-based cantilever as the acoustic-to-voltage transducer [52]. The latter is a rectangular structure in silicon with dimensions ranging from hundreds of microns to a few millimeters, and thickness of order of a few to tens of microns. Grown on a thicker substrate, it is anchored to only one side, while a gap Δ of the order of 5-15 μm separates the others [158], enabling a door-like architecture as reported in Figure 1.14(a). Such thin structures can be easily excited by external sound or vibration, especially at low frequencies. In fact, when the excitation source interacts with the trace gas, and the sound wave is generated following the photoacoustic effect, the local perturbation will induce an oscillation on

the cantilever's free end, whose amplitude will be proportional to the acoustic wave intensity.

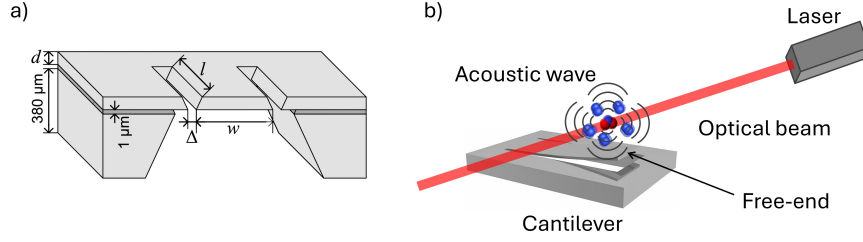


Figure 1.14: **(a)**: Typical geometrical features of a silicon-based rectangular cantilever [158], characterized by a length l , a base w , and a thickness d . **(b)**: working principle of cantilever sound wave's transduction. Here, the excitation source interacts with the trace gas, thus allowing the photoacoustic effect and leading to the cantilever's free-end oscillations.

The cantilever dynamics can be described by modeling it with a flexible rectangular bar bound to one side only and exploiting the Euler-Bernoulli formula. In particular, neglecting the effect of the frames and the surrounding environment, and for a homogeneous beam of uniform cross-section, the associated equation of motion $y(x,t)$ due to an external perturbation will be [159]:

$$\mathcal{E}I \frac{\partial^4 y}{\partial x^4}(x,t) + \rho_c A \frac{\partial^4 y}{\partial t^4}(x,t) = 0, \quad (1.50)$$

where $A = wd$ is the rectangular cross-section, ρ_c is the cantilever's density, and $\mathcal{M} = wd/12$ the associated inertia moment. In the case of silicon, the Young modulus is typically $\mathcal{E} = 169$ GPa, while $\rho_c = 2.33$ g/cm³. According to Equation 1.50, a general solution for the cantilever's longitudinal displacement $y(x,t)$ from the rest position can be written as:

$$y(x,t) = (a_1 e^{kx} + a_2 e^{-kx} + a_3 e^{ikx} + a_4 e^{-ikx}) e^{-i\omega t}, \quad (1.51)$$

being $k = \frac{2\pi}{\lambda}$ the wave-number and $\omega = 2\pi f$ the angular frequency. Without entering many details and inserting the general solution $y(x,t)$ in Equation 1.50, it is possible to end up with the following dispersion relation:

$$\mathcal{E}\mathcal{M}k^4 - \rho_c A \omega^2 = 0. \quad (1.52)$$

Since the cantilever is clamped to one side and free on the other, it is possible to introduce the following boundary conditions:

$$\begin{cases} y = 0, \frac{\partial y}{\partial x} = 0, & \text{if } x = 0 \\ \frac{\partial^2 y}{\partial x^2} = 0, \frac{\partial^3 y}{\partial x^3} = 0, & \text{if } x = L \end{cases} \quad (1.53)$$

It means that the deflection and the slope at the clamped end have to be zero, while both the momentum and the shear force at the free end should be zero [159]. In these conditions, it is possible to extrapolate the cantilever's eigenfrequency as:

$$f_{c,n} = \frac{1}{2\pi} \frac{\chi_n^2}{l^2} \sqrt{\frac{\mathcal{E}d^2}{12\rho_c}}, \quad (1.54)$$

where $\chi_0 = 1.8751$, $\chi_1 = 4.6941$, $\chi_2 = 7.8548$ and so on. In standard rectangular cantilevers exploited for photoacoustic-based sensors, the first vibrational mode $f_{c,1}$ occurs typically in the sub-kHz range. In principle, flexural or torsional vibration can also be excited in the direction perpendicular to the plane (x,y) , enabling the exploitation of higher resonance frequencies, in the order of tens of kHz. This makes these structures particularly suitable for addressing a variety of trace molecules with high sensitivity, characterized by slow and fast relaxation rates.

Compared with QTFs, silicon-based cantilevers work, in general, at lower resonant frequencies (between hundreds of Hz up to several kHz), and they are characterized by lower mechanical quality factors (up to a few thousand) due to the different geometrical structures and higher masses. Furthermore, if the QFT's transduction of the sound waves is performed electrically, the cantilever's displacement is typically carried out optically via interferometric readout [58, 158].

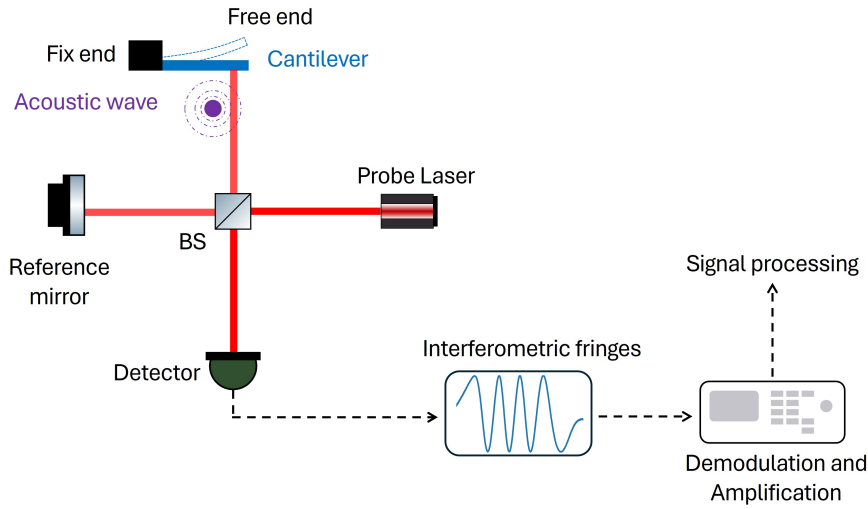


Figure 1.15: An example of an all-optical Michelson interferometric readout of the cantilever's oscillations.

An example of implementation refers to a Michelson-type interferometer, whose schematization is reported in Figure 1.15. A probe laser beam is divided into two identical parts via a 50/50 beam splitter: one arm ends up with a reference mirror, while the other one with the moving cantilever. The back-reflected beams are then recollected and detected via a photo-detector, generating interferometric fringes, whose amplitude is linearly proportional to the path difference between the two arms. By demodulating the interferometric output at the laser modulation frequency (via a lock-in amplifier), and performing signal processing, it is possible to retrieve the photoacoustic signal. The latter can be *on-resonance* when the modulation frequency is equal to the cantilever's resonance frequency, or *off-resonance* if the laser modulation frequency falls out the cantilever's mode. Furthermore, the cantilever's surface can be treated with a high-reflectivity coating (silver, gold, and so on) to maximize reflected beam intensity and, accordingly, the amplitude of the interferometric fringes.

Such configuration allows CEPAS-based instrument to become competitive, reaching detection sensitivities levels at the state-of-the-art. In particular, the best result reported in the literature was reached by Tomberg et al, where the sub-ppt detection

sensitivity was achieved by combining the advantages of the CEPAS techniques with the power enhancement given by an optical parametric oscillator OPO [58]. Furthermore, an important aspect that was strongly investigated in recent years concerns the possibility of miniaturizing the entire apparatus thanks to the exploitation of alternative fiber-optics interferometric readout methods [160–163].

CHAPTER 2

Exploring the sensitivity limit of a doubly-resonant cantilever-enhanced Photoacoustic sensor

The *fil rouge* behind all the research works performed during my PhD activity was based on conceptualizing and studying alternative approaches and novel ingredients for ultra-sensitive photoacoustic trace-gas detection. As a natural starting point, the first task was developing a conventional photoacoustic-based setup, exploiting the available ingredients deeply discussed in Chapter 1 and understanding the fundamental limitations. This approach allowed me first to become familiar with both the technique and the components, and then to think about new solutions, overcoming the emerging problems.

Based on these considerations, the following chapter investigates the performance of a cantilever-based photoacoustic sensor. The sensor was first characterized and tested in its basic configuration. Then, an advanced version based on a doubly-resonant acoustic and optic configuration was set up and studied, aimed at enhancing the final sensitivity. Section 2.1 is dedicated to the developed experimental setup. The latter is described firstly in a concise way (Subsection 2.1.1). Then the key parts are separately addressed in more detail: the excitation source (Subsection 2.1.2), the optical resonance (Subsection 2.1.3), the MEMS rectangular cantilever (Subsection 2.1.4), the doubly resonant approach (Subsection 2.1.5), and the balanced Michelson interferometric readout (Subsection 2.1.6). The second part of the chapter (Section 2.2) is devoted to a discussion of the experimental results. After having characterized the mechanical properties of the cantilever (Subsection 2.2.1), an in-depth analysis of the photoacoustic measurements is provided (Subsection 2.2.2). Finally, some conclusions close the Chapter with a little outlook about the following activities (Section 2.3).

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2.1 Experimental setup

2.1.1 A brief description

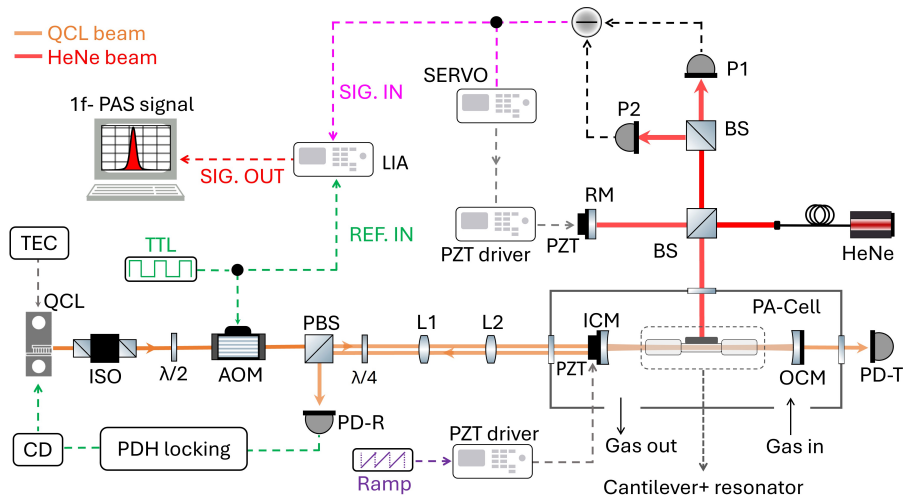


Figure 2.1: Schematic representation of the doubly-resonant cantilever-enhanced photoacoustic setup developed. TEC: temperature controller. CD: current driver. QCL: quantum cascade laser. ISO: optical isolator. $\lambda/2$: half wave-plate. AOM: acousto-optical modulator. PBS: polarizing beam-splitter. $\lambda/4$: quarter wave-plate. L1,2: focus lenses. PZT: piezo-electric ceramic material. ICM: input cavity mirror. OCM: output cavity mirror. PD-T: transmission photo-detector. PD-R: reflection photo-detector. HeNe: Helium-Neon laser. RM: reference mirror. BS: beam-splitter. P1,2: single-ended photo-detector. SERVO: servo controller. REF IN: reference input signal. SIG. IN: input signal. SIG. OUT: output signal.

Figure 2.1 shows a schematic representation of the experimental setup. A tunable, Continuous-Wave (CW), Distributed Feedback (DFB), mid-IR Quantum Cascade Laser provided by *Hamamatsu Photonics K.K.* acts as the excitation source, addressing a strong N_2O rovibrational transition. All the laser driving electronics, namely the temperature controller (TEC) and the current driver (CD), are embedded together in a modular controller provided by *ppq Sense S.R.L.* (QubeCL 52). The latter is characterized by a low bias current density-noise, enabling the QCL emission with

a free-running sub-MHz linewidth. Before entering the photo-acoustic cell (PA-cell) the laser beam passes through an optical isolator (ISO, COHERENT FM2 MID-IR 4.55 μm) to prevent optical feedback effects from the optical cavity. A half-wave plate changes the beam's polarization from horizontal to vertical to maximize the amount of light interacting with the acousto-optic modulator (AOM, ISOMET, M1208-G80-4). The latter is exploited for laser amplitude modulation, allowing the photo-acoustic effect generation within the PA-cell. Combining an 80-MHz RF and a digital modulation (TTL) at a given frequency f_0 , the AOM periodically deflects the interacting laser beam, resulting in an intensity modulation at f_0 . Two mode-matching lenses (L1, and L2), with focal lengths equal to 75 mm and 50 mm respectively, are interposed between the AOM and the PA-cell to ensure that the QCL beam waist falls in the center of the optical cavity, thus optimizing the coupling efficiency. The beam enters the PA-cell via a Zinc Selenide (ZnSe) wedged window and is coupled with a Fabry-Pérot optical cavity. The latter consists of two plano-convex mirrors with the same reflectivity $R = 0.9984$ and radius of curvature $RoC = 125$ mm. To stabilize the laser frequency at the fundamental cavity mode peak, thus also stabilizing the intra-cavity power, a Pound-Drever-Hall (PDH) feedback loop is implemented exploiting the cavity reflection signal collected via the photo-detector PD-R (Vigo Systems, PVI-4TE-5-1x1-TO8). The photo-detector PD-T is placed after the output cavity mirror (Vigo Systems, PVI-4TE-5-1x1-TO8), and serves only for alignment purposes.

The photo-acoustic effect is obtained by filling the PA-cell with the targeted gas and modulating the laser amplitude via the AOM while the QCL beam is locked to the cavity. Inside the cavity, the cantilever is coupled to a custom-made acoustic resonator, enabling an amplification of the generated sound waves. The resonator's mode and laser's intensity modulation frequencies were chosen to optimally match with the cantilever resonance frequency, enabling a doubly-resonant configuration.

The cantilever's oscillations are converted into a measurable voltage signal via a balanced Michelson interferometric readout. The interferometric output is demodulated at the cantilever's resonance frequency via a lock-in amplifier (LIA, MFLI, Zurich Instruments 500kHz/5MHz), allowing to retrieve the in-phase first harmonic (1-f) R -component of the signal ($R = \sqrt{X^2 + Y^2}$), providing good suppression of the off-resonance components not related to the photo-acoustic signal.

Additionally, during the measurements, a slow ramp ($f \simeq 2$ mHz) is sent to the PZT moving the input cavity mirror (ICM), resulting in a scan of the laser frequency through the molecular absorption line. Meanwhile, the laser frequency follows the cavity length variation by the PDH locking loop, retrieving the whole trace-gas absorption spectrum in a single acquisition.

The sample (N_2O highly diluted in pure N_2) slowly flows inside the PA-cell via a gas blender (GB-100, MCQ Instruments) with a flow rate equal to 20 standard cubic centimeters (sccm), and the pressure is controlled by a pressure controller (HiCUBE, PFEIFER).

2.1.2 The mid-IR, DFB-CW Quantum Cascade Laser

The QCL exploited in this work is a device from Hamamatsu, mounted on a butterfly housing, and characterized by a built-in DFB grating for single-mode emission. It is based on an InGaAs/InAlAs active medium with 25 stages and grown on an InP substrate. The active core is $1.325\ \mu\text{m}$ thick, and the laser waveguide is fabricated in an InP-based planar buried heterostructure geometry with a length of 2 mm. The uncoated out-coupling facet is characterized by a reflectivity of around 30 %, while the back facet can reach a reflectivity of above 98 % thanks to a HR-coating. Figure 2.2 reports a complete preliminary characterization of QCL's working parameters, i.e. wavelength and optical power, at different temperatures.

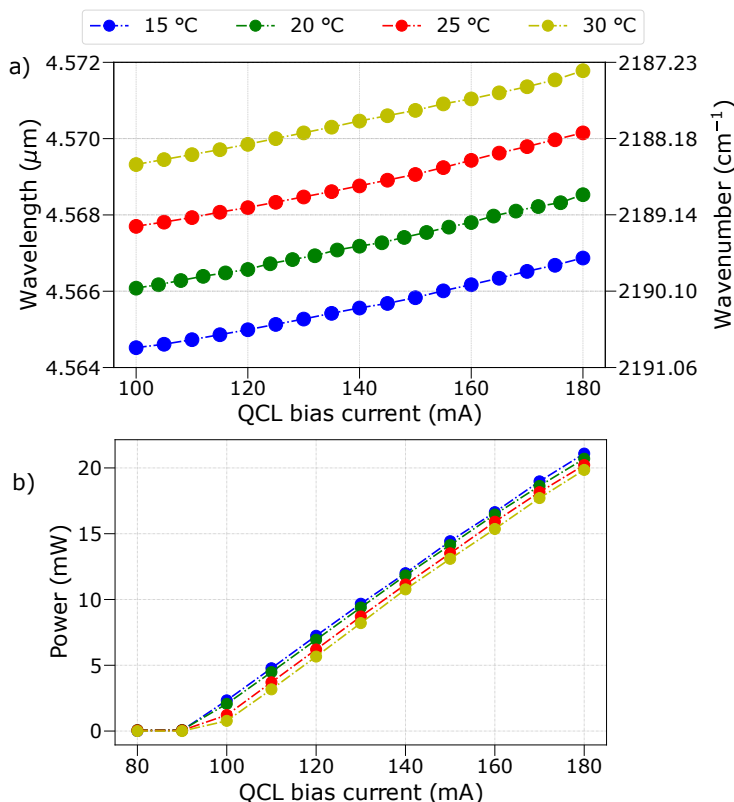


Figure 2.2: (a): Emission peak wavelength as a function of the QCL bias current at different working Temperatures. The data points were acquired with an optical FTIR spectrometer (Bristol) (b): QCL LIV within the same range of temperatures. The laser power was measured at the input of the optical cavity. The two graphs share the same color map, whose description is indicated in the upper part.

According to Figure 2.2(a), this laser excitation source can span a spectral region falling in the mid-infrared, from approximately $4.564\ \mu\text{m}$ at a bias current of 100 mA and a Temperature of 15 °C, up to $4.572\ \mu\text{m}$ at 180 mA and 30 °C, always in a single-mode operation. This behavior allows the system to access the *molecular fingerprint region* with relatively high available optical power (see Figure 2.2(b)), where several molecules of interest show strong rovibrational transitions, as already shown in the Figure 1.1.

Among all of them, nitrous oxide (N_2O) is a gas of interest for air pollution and environmental monitoring, with a Global Warming Potential (GWP) 273 times higher

than carbon dioxide for a 100-year timescale. Furthermore, N_2O is very suitable as a target molecule for photoacoustic spectroscopy experiments due to its highly stable response to potential changes in the gaseous matrix [164], making its rovibrational relaxation dynamics sufficiently fast even in pure N_2 [164, 165], when compared with other contaminants in the atmosphere such as ethane, carbon dioxide, or carbon monoxide. Moreover, N_2O was also selected as the target molecule because of the large literature about N_2O PAS detection, allowing for a direct comparison of the performance of our system with existing state-of-the-art sensors.

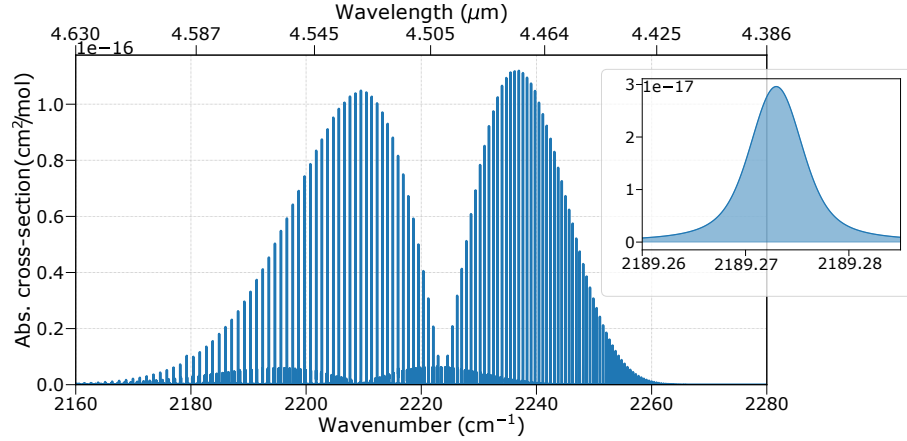


Figure 2.3: HITRAN simulation for N_2O absorption cross-section between 2160 cm^{-1} and 2280 cm^{-1} . **(Inset):** zoom at the addressed rovibrational absorption line, occurring at a wave number equal to 2189.273 cm^{-1} .

Accordingly, this molecule was chosen as the target gas in this work, diluted in pure N_2 at a nominal concentration of 10 part-per-million. Figure 2.3 reports a list of the spectral features of N_2O between 2160 cm^{-1} and 2280 cm^{-1} . Among all of them, by setting the QCL's temperature at 20°C and the bias current around 155-160 mA, it is possible to select a strong and well-isolated rovibrational transition, characterized by a wave number equal to 2189.273 cm^{-1} and a line-strength equal to $2.14 \times 10^{-19}\text{ cm/molecule}$ (depicted in the Inset of Figure 2.3).

2.1.3 The FP optical cavity and the PDH locking

A Fabry-Perot optical cavity is exploited to enhance the available laser power for the photoacoustic effect. It consists of two plano-convex mirrors with a reflectivity of 99.84 % placed at a distance $L=85\text{ mm}$, and it is characterized by a Free-Spectral Range (FSR) equal to 1.76 GHz. In vacuum condition, the associated Finesse $\mathcal{F}$ is:

$$\mathcal{F} = \frac{\pi}{1-R} \simeq 1963, \quad (2.1)$$

corresponding to an intra-cavity power enhancement of $G_{IC} = \mathcal{F}/\pi \simeq 625$.

Generally speaking, two fundamental prerogatives must be addressed to exploit the optical cavity's potential. The first is maximizing the coupling efficiency between the free-running laser beam and the fundamental cavity mode, and consequently reducing the contributions from higher-order modes, to ensure the highest possible power enhancement factor. The second is locking the laser frequency to the fundamental

2.1 Experimental setup

cavity mode, thus minimizing the frequency fluctuation and stabilizing the intra-cavity power over time.

It is important to note that, in general, mid-IR CW QCLs are characterized by a free-running linewidth in the 10^{-1} - 10^0 MHz range. Since the fundamental mode width of the used cavity is of the same order of magnitude, being equal to $\Delta c = FSR/F \simeq 0.89$ MHz, in the actual experimental configuration the optical resonance will lead only to an intra-cavity power buildup, and not to a sensible frequency stabilization and noise attenuation of the excitation source.

To comply with the first point, carefully selecting all the relative distances between the matching optics (i.e. the two-mode matching lenses after the AOM and the two cavity mirrors) is of crucial importance to ensure co-axiality between the QCL beam and the optical cavity. For this reason, a Python script was developed to choose the theoretically best mode-matching architecture. Leading on a 6-equation non-linear system, this program returns the optimal relative distances between the two mode-matching lenses and the optical cavity. The used configuration is reported in Figure 2.4.

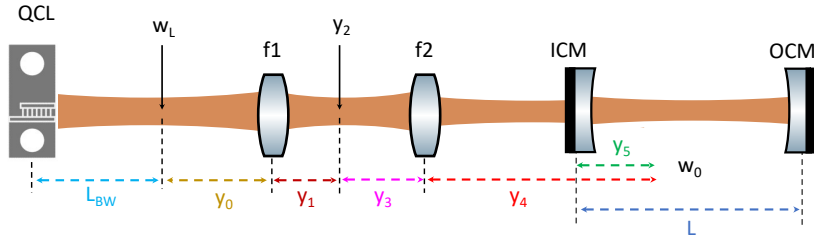


Figure 2.4: Schematic representation of the mode-matching architecture implemented. The following parameters are fixed: the free-running QCL beam waist position (L_{BW}) and radius (w_L), the distance between the QCL waist position and the first focus lens (y_0), the focus lengths (f_1 , and f_2), the optical cavity length (L), and the intra-cavity beam waist (w_0). All the other quantities are independent variables (y_1 , y_2 , y_3 , y_4 , y_5 , and y_6 .) that have to be extracted by solving a 6-equations non-linear system.

Both the free-running QCL beam waist position and radius, $L_{BW} = 100$ mm and $w_L = 0.9$ mm respectively, were experimentally measured via a knife-edge method [166], while the distance y_0 was fixed to 850 mm. The two lenses have focal lengths $f_1 = 50$ mm and $f_2 = 75$ mm respectively, and the cavity length is $L = 85$ mm. Given the refractive index and the radius of curvature of the two cavity mirrors respectively $n = 1.5$ and $RoC = 125$ mm, it is possible to estimate the associated focal length using the formula:

$$f_3 = RoC/(n - 1) = 250 \text{ mm}. \quad (2.2)$$

Starting from these values, it is possible to estimate a beam waist inside the optical cavity approximately equal to 0.29 mm. Finally, the six independent variables $y_{1,6}$ can be computed by solving the following 6-equations non-linear system:

$$\begin{cases} \frac{1}{y_2^2} - \frac{1}{w_1^2} \left[\left(\frac{1}{y_0/f_1} \right)^2 + \left(\frac{\pi w_1^2}{\lambda} \right)^2 \right] \frac{1}{f_1^2} = 0 \\ y_1 - f_1 - f_1^2 \left[\frac{y_0 - f_1}{(y_0 - f_1)^2 + (\pi w_1^2/\lambda)^2} \right] = 0 \\ \frac{1}{y_6^2} - \frac{1}{y_2^2} \left(\frac{1 - y_3}{f_2} \right)^2 + \left(\frac{\pi y_2^2}{\lambda} \right)^2 \frac{1}{f_2^2} = 0 \\ y_4 - f_2 - f_2^2 \left[\frac{y_3 - f_2}{(y_3 - f_2)^2 + (\pi y_2^2/\lambda)^2} \right] = 0 \\ \frac{1}{w_0^2} - \frac{1}{y_6^2} \left(\frac{1 - y_5}{f_3} \right)^2 + \left(\frac{\pi y_6^2}{\lambda} \right)^2 \frac{1}{f_3^2} = 0 \\ \frac{L}{2} - f_3 - f_3^2 \left[\frac{y_5 - f_3}{(y_5 - f_3)^2 + (\pi y_4^2/\lambda)^2} \right] = 0 \end{cases} \quad (2.3)$$

where λ is the laser wavelength. The results of the computation are: $y_1 = 52.10$ mm, $y_2 = 0.05$ mm, $y_3 = 89.01$ mm, $y_4 = 0.25$ mm, $y_5 = 472.08$ mm, and $y_6 = -44.74$ mm.

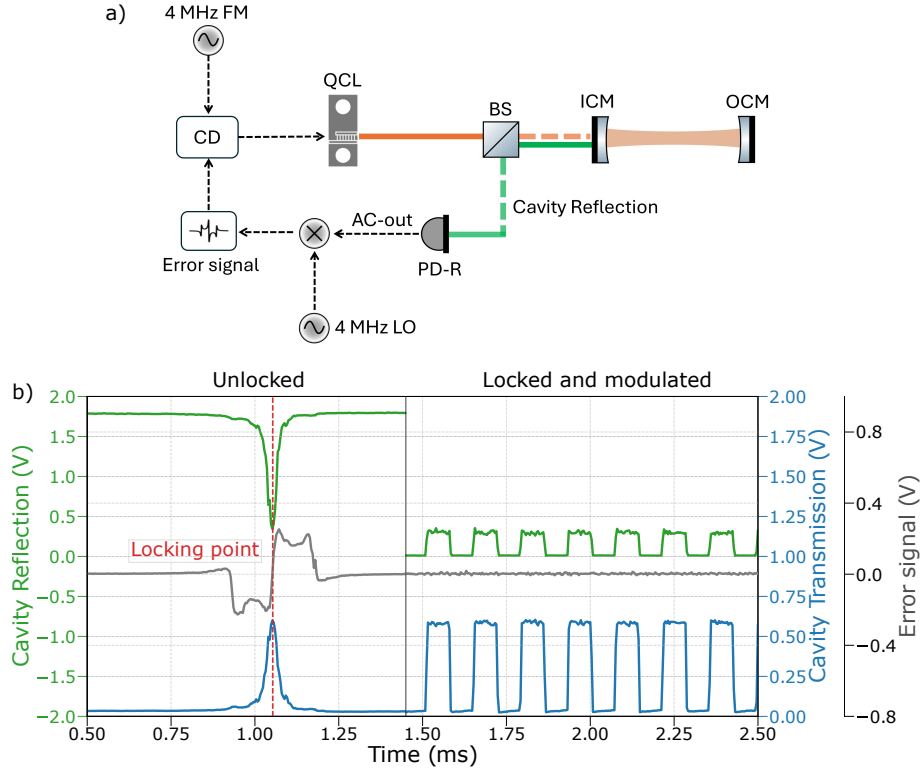


Figure 2.5: (a): schematic representation of the Pound-Drever-Hall laser-cavity locking feedback loop implemented in this work (b): optical cavity reflection (in green) and transmission (in blue) signals and PDH error signal (in grey). The red dashed line represents the laser-cavity locking point (corresponding with the transmission peak). The left side of the graph shows the reflection and transmission by the fundamental cavity mode in the unlocked configuration, while the right side of the graph reports the cavity transmission and reflection signals once the locking is achieved and the optical beam is intensity modulated. All the traces were collected with a laser current fixed at the N_2O absorption peak, and at a pressure of 0.2 mbar inside the PA-cell. All the traces were acquired with the use of an oscilloscope.

Concerning the second point, the intra-cavity optical power stabilization was obtained via a PDH laser-cavity locking feedback loop, a frequency stabilization technique widely used in cavity-enhanced spectroscopy experiments [167–171]. Its practical im-

plementation is shown in Figure 2.5(a).

A sine frequency modulation at 4 MHz is applied to the laser beam to generate first-order side-bands, as shown in the green (cavity reflection) and blue (cavity transmission) traces in the left part of the graph reported in Figure 2.5(b). The cavity reflection is collected via a photo-detector, and its AC-coupled output is mixed with a 4 MHz local oscillator (LO) and sent to the SERVO electronics for locking. A locking bandwidth of $\simeq 300$ kHz is achieved, ensuring a robust locking condition. Once the laser is locked to the cavity, the optical beam is intensity-modulated by the AOM at the cantilever resonance frequency, achieving the condition reported in the right part of Figure 2.5(c). The locking loop is robust enough to maintain the laser locked to the cavity even when the AOM is switched periodically on and off for laser intensity modulation.

A coupling efficiency of $\simeq 85\%$ can be computed by looking at the cavity transmission and reflection in locking conditions. Such a high value indicates that PDH locking strategy implemented is capable of coupling almost the entire optical beam in the cavity by narrowing the laser linewidth on the fundamental cavity mode, thus ensuring a high intra-cavity power available for the photo-acoustic effect.

2.1.4 The rectangular silicon-based cantilever

The acoustic-to-voltage transducer exploited in this work is a rectangular silicon-based MEMS cantilever, characterized by a 4 mm length, a 6 mm height, and a $10\ \mu\text{m}$ thickness. The fabrication process, summarized in Figure 2.6, was realized in the clean room of the Institute of Microelectronics and Microsystems of the Italian National Research Council (CNR-IMM) in Bologna.

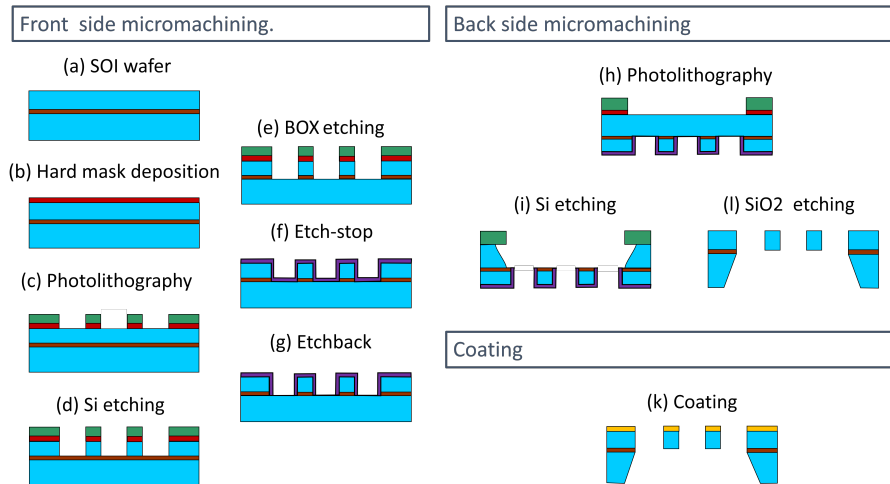


Figure 2.6: Graphical description of the cantilever's fabrication routine performed by (CNR-IMM) in Bologna.

The structure was fabricated in a silicon-on-insulator wafer (SOI) made up of a $10\ \mu\text{m}$ thick Si device layer and a $500\ \mu\text{m}$ thick Si handle layer separated by a $2\ \mu\text{m}$ thick buried SiO_2 (a). The structure's layout was created on the front side by photo-lithography and dry etching of the Si device layer through a $4\ \mu\text{m}$ -thick OIR-908 35 photo-resist on a $2.2\ \mu\text{m}$ -thick SiO_2 hard mask (b, c). The obtained Si trenches were uniformly coated by a 35 nm thick poly-silicon layer, which was afterward over-

oxidized to form a 180 nm-thick SiO_2 layer all around the patterned MEMS geometry. The surface was further coated with 1.5 μm SiO_2 deposited by LPCVD so that the resulting SiO_2 layer on the top surface was about 3.6 μm **(d)**. Then, a mask-less Inductively Coupled Plasma (ICP) etch-back step was performed to complete the removal of the previously deposited 1.7 μm -thick SiO_2 layer from the bottom of the trenches **(e)**. As a result, the trenches originating the MEMS structure were protected by a SiO_2 coating during the subsequent backside wet etching **(h)**, without creating any free-standing SiO_2 membrane between the released Si structures. In this way, possible problems coming from the cracking of this membrane after the release of the MEMS resonator were prevented.

After front-side micro-machining, pass-through holes were created in the handle layer from the backside of the wafer, to release the MEMS resonators and, simultaneously, to guarantee optical access to them for interferometric readout of their oscillation. The backside holes were opened by Si etching through the 3.5 μm thick back side SiO_2 **(f)**. The Si removal was achieved in two steps: first, with a Deep Reactive Ion Etching (DRIE) process up to 325 μm depth **(f)**; then, after wafer cutting **(g)**, using an anisotropic wet etching in Tetra-Methyl-Ammonium Hydroxide (TMAH) performed on diced chips **(h)**. The two-step etching allowed for secure chip separation by dicing saw. The structures were finally released by SiO_2 wet etching **(i)**. The MEMS reflectance was maximized by a 40 nm thick Ag layer evaporated on the front side **(k)**.

For the Si DRIE foreseen at steps **(c)** and **(f)** in the flow, a Bosch process providing a 5 $\mu\text{m}/\text{min}$ etch rate on Si was used. The gas mixture was made up of 300 sccm of Sulfur hexa-fluoride (SF_6) and 150 sccm of Octa-fluoro-cyclobutane (C_4F_8), at 0.027 mbar chamber pressure.

The Si anisotropic wet etching performed at step **(h)**, was carried out in a 5% wet and diluted aqueous TMAH solution with the addition of 0.5% wet ammonium peroxodisulfate, following the procedure described in [172]. The solution was uniformly heated at 90 °C and stirred at 1000 rpm. The etching duration, up to the complete release of the structures, exceeded 1h 40 min. For SiO_2 DRIE, 17 sccm C_4F_8 were fluxed in the chamber at 0.005 mbar pressure, resulting in an etch rate of about 0.25 $\mu\text{m}/\text{min}$. This process was used in steps **(c)** and **(e)**. A SiO_2 wet etching was performed at step **(i)** using either a commercial Buffered Oxide Etch (BOE) solution or hydrofluoric acid diluted in water.

LPCVD polysilicon was deposited at 610 °C in 80 sccm Silane (SiH_4) flow at 0.21 mbar. The deposition rate ranged between 11.7 nm/min and 13.7 nm/min. The polysilicon was wet oxidized at 1100 °C. These processes were used to fabricate the passivation coating shown in step **(e)**. LPCVD SiO_2 was deposited at steps **(b)** and **(d)** with the following parameters: 430 °C chamber temperature, 0.24 mbar chamber pressure, in a 82 sccm SiH_4 and 120 sccm O_2 gas mixture. The resulting SiO_2 deposition rate was around 1 $\mu\text{m}/\text{h}$.

To conclude, a compendium of the first six theoretical resonance frequencies of the investigated cantilever is reported. Each of them is associated with the corresponding mode's shape and displacement distribution. This preliminary analysis was performed via a Finite Element Method (FEM) in static conditions, aiming at obtaining a rough evaluation, and more information will be introduced later in Section 1.3.1.

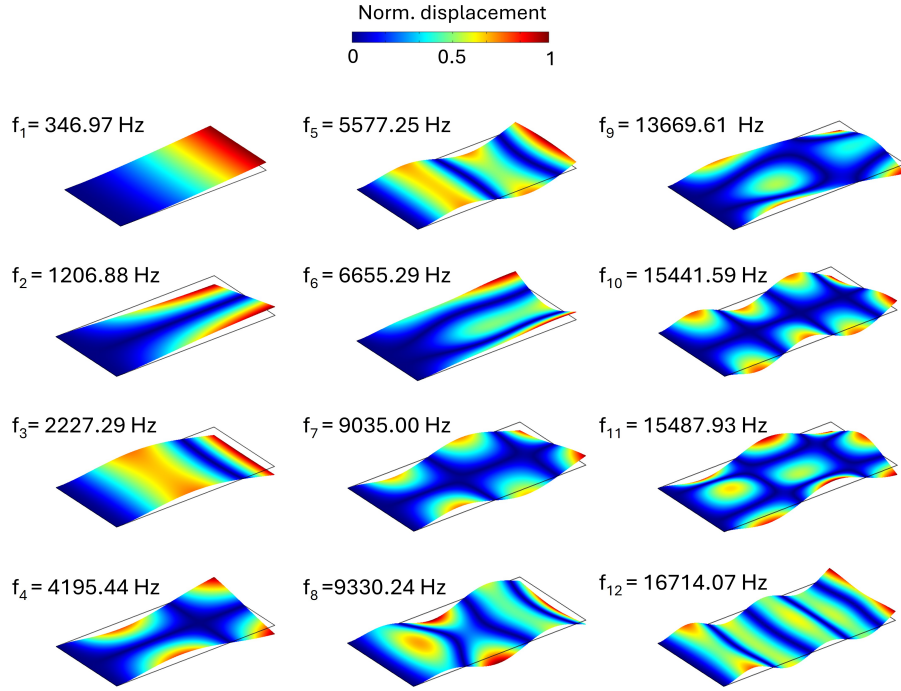


Figure 2.7: Simulations of the first twelve resonance modes of the used rectangular cantilever with dimensions 4×6 mm and thickness $10 \mu\text{m}$. For each mode, the color map describes the displacement distribution.

In this work, the cantilever is investigated in its fifth resonance mode, whose expected resonance frequency (in vacuum) is estimated to be 5577.25 Hz. This frequency range was taken into consideration to exploit an optimal working regime where two fundamental conditions can coexist: a sufficiently high signal-to-noise ratio marginally affected by the low-frequency environmental noise and an efficient acoustic wave generation capability.

2.1.5 The acoustic resonator

As well known from the literature, the confinement of a propagating sound wave within a proper geometrical architecture can induce a great amplification in its intensity [173]. So, a strategic way to increase further the photo-acoustic signal amplitude, and consequently the final detection sensitivity, is to couple the optical resonance (induced by the cavity) with acoustic resonance (achieved employing an acoustic resonator), obtaining a so-called doubly-resonant configuration. In this case, the PAS signal will be proportional both to the intra-cavity power buildup factor G_{IC} and to the acoustic amplification factor β_{AC} [60, 174]:

$$S_{PAS} = G_{IC} \times \beta_{AC} \times K \times P_{in}(\lambda) \times \alpha(\lambda) \times \epsilon_{RS}(f, \tau(p)), \quad (2.4)$$

where $P_{in}(\lambda)$ is the laser incident power, $\alpha(\lambda)$ the trace-gas absorption coefficient, and $\epsilon_{RS}(f, \tau(p))$ the so-call radiation-to-sound conversion efficiency which depends on the modulation frequency f and the relaxation time $\tau(p)$.

According to these assumptions, a custom-made transmission-type acoustic res-

onator was developed with a geometry theoretically optimized to match the narrow-bandwidth frequency response of the used cantilever.

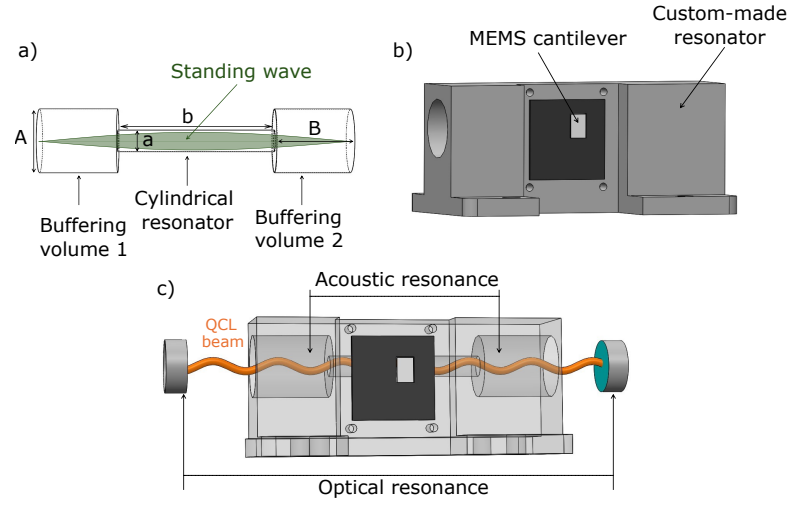


Figure 2.8: (a): geometrical features of the developed acoustic resonator. (b): 3D sketch of the MEMS cantilever mounted on the custom-made acoustic resonator. (c): working principle of the doubly-resonant configuration.

The device, depicted in Figure 2.8(a), consists of a cylindrical resonator with length and internal diameter $b = 37$ mm and $a = 5$ mm respectively, and two buffering volumes on both sides with a length $B = 18.5$ mm and diameter $A = 15$ mm. These dimensions were theoretically selected for an optimal acoustic amplification in the 5-kHz frequency range to match the cantilever's resonance mode. The MEMS cantilever is positioned at the resonator's midpoint, corresponding with the anti-node position of the generated acoustic wave (depicted in green). To maximize interaction between the cantilever and the impinging acoustic wave in a very reduced volume, the resonator has a small rectangular aperture in correspondence to the cantilever, as reported in Figure 2.8(b). Furthermore, the FP optical cavity was coupled co-axially to the acoustic resonator, obtaining the doubly-resonant configuration depicted in Figure 2.8(c).

2.1.6 Balanced Michelson interferometric readout

The cantilever's oscillations following the interaction with the generated acoustic waves are converted into a measurable voltage signal via a Balanced-Michelson interferometric readout [175], whose schematic representation is depicted in Figure 2.9.

A Helium-Neon laser emitting at 633 nm is exploited as the probe beam, and its polarization is controlled via the use of a first half wave-plate to maximize the input power. The beam is then divided into two identical paths with orthogonal polarizations via the use of a 50/50 polarizing beam-splitter (PBS): one is focused via a 100 mm focal lens on the free-end of the silicon cantilever (i.e. the portion affected by the highest displacement), while the other one ends with a reference mirror mounted on a PZT. Both the arms are equipped with a quarter wave-plate for balancing reasons. The back-reflected beams of the two arms are superimposed at the same PBS. Then the recombined radiation is split again by another beam splitter into two parts, again with orthogonal polarization, and detected by two identical Indium-Gallium-Arsenide

2.1 Experimental setup

photo-diodes (PD1 and PD2, FGA10, Thorlabs). Another quarter wave-plate is placed before the second PBS to ensure an equal splitting in the optical powers of the two arms.

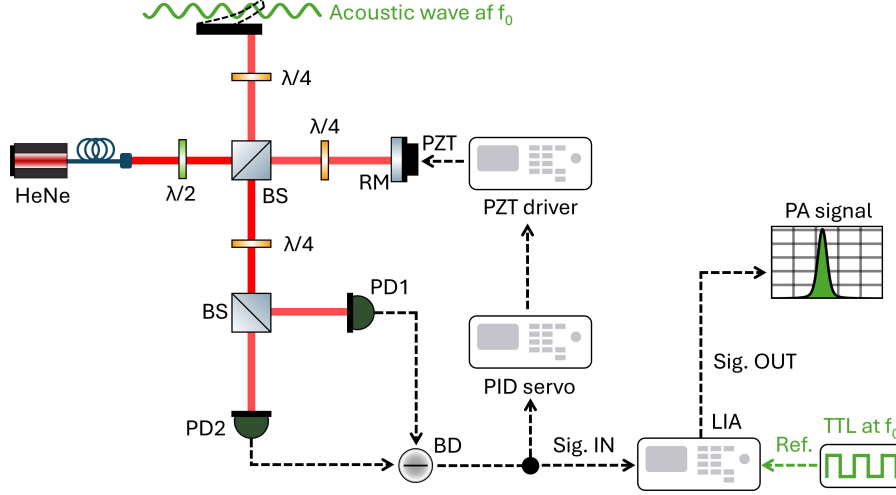


Figure 2.9: Schematic representation of the cantilever oscillation's readout via Balanced-Michelson interferometry.

When the cantilever is in rest condition, the two path lengths are adjusted to produce a zero interferometric signal. When the cantilever oscillates following the interaction with the generated acoustic wave, an imbalance occurs, resulting in the production of interferometric fringes. Hence, by measuring the amplitude of the fringes it is possible to access the amplitude of the cantilever's oscillations and retrieve information about the detection sensitivity of the system (in terms of minimum detectable trace-gas concentration). It is important to note that the interferometric detection system must be characterized by a sufficiently high bandwidth to resolve the fringes at the cantilever's resonance frequency.

Being $E_{a,b}$ the field amplitude of the back-reflected beams coming from the cantilever and the reference mirror respectively, and $\varphi_{a,b}$ the associated phases, and assuming the two recombined beams at the second PBS orthogonal polarized, the detected intensity at the two photo-detectors PD_{1,2}, in rest condition, will be [175]:

$$I_{1,2} = \frac{E_a^2 + E_b^2}{2} \mp E_a E_b \cos(\varphi_a - \varphi_b), \quad (2.5)$$

being the phase difference between the two arms equal to $\varphi_a - \varphi_b = 3\pi/2$. When the cantilever starts to oscillate, its contribution on the interferometric fringes can be modeled, with good approximation, with a harmonic on-resonance signal $\Phi(t, f)$ (i.e. at the cantilever's resonance frequency), and proportional to the photo-acoustic signal amplitude S_{PAS} :

$$\Phi(t, f) = S_{PAS} \sin(2\pi f t), \quad (2.6)$$

The intensity detected by PD_{1,2} will become proportional to it, with a fixed background equal to the total beam intensity:

$$I_{1,2} = \frac{E_b^2 + E_b^2}{2} \mp E_a E_b \cos\left(\frac{2\pi\Phi(t, f)}{\lambda}\right), \quad (2.7)$$

where λ is the probe beam's wavelength. To retrieve the photo-acoustic signal S_{PA} from the interferometric fringes it is also necessary to isolate the on-resonance component from the other off-resonance contributions. For this reason, the interferometric output (SIG. IN) is mixed with a TTL reference signal (REF. IN) at the cantilever's resonance frequency, and demodulated via a lock-in amplifier.

Apart from the off-resonance components, other factors could add noise to the demodulated signal output (SIG. OUT), affecting the final detection sensitivity. The first can be attributed to fast drift induced by acoustic and environmental noise that may affect the interferometer. The result will be an additional on-resonance oscillation component that the LIA can not filter out. A way to overcome this problem is to preliminary eliminate the common drifts from the two arms. For this reason, in the developed system the single-ended outputs $PD_{1,2}$ are sent into an electronic circuit that performs the difference between the two signals, enabling an interferometric balanced detection (BD). In this way, the differential signal intensity will be (in the presence of the cantilever's oscillations):

$$I_D = I_1 - I_2 = 2E_a E_b \cos\left(\frac{3}{2}\pi + \frac{2\pi\Phi(t, f)}{\lambda}\right) = 2E_a E_b \sin\left(\frac{2\pi\Phi(t, f)}{\lambda}\right). \quad (2.8)$$

The associated output is then demodulated to retrieve the PAS signal.

A second important contribution is associated with drifts (for example due to temperature variations) that may change the relative distance between the two arms, causing a continuous and unpredictable variation of the interferometric signal, and affecting both the accuracy and the repeatability of the measurement. To overcome this problem, implementing a control strategy for maintaining a stable working point during the measurement is necessary.

The best possible working point corresponds to the zero of the differential signal, a condition also called *zero working point* (ZWP). In this peculiar configuration, the slope of the interferometric fringes is the highest possible, resulting in the maximum displacement-to-amplitude conversion factor for the cantilever's oscillations [175]. This condition is reached by adjusting the length of the reference arm to achieve a zero differential signal with the cantilever at rest (i.e. no PAS signal). Then, a stabilization loop is closed to the PZT via a Proportional-Derivative-Integrative (PID) servo control to maintain a constant relative length between the two arms. In detail, part of the differential signal is sent to a servo controller (SERVO, New Focus LB1005), which generates an error signal. The latter is sent to the PZT acting on the RM, closing the loop, and correcting the mirror's position to reach the ZWP. Once this condition is achieved (see Figure 2.10), the instabilities in the interferometer readout falling in the locking bandwidth are canceled out, and the repeatability of the measurements is increased.

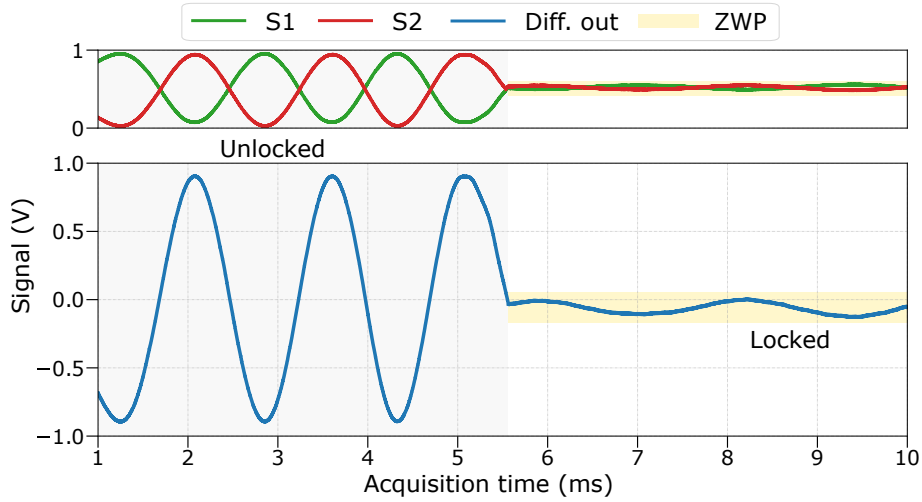


Figure 2.10: An example of the two single-ended outputs, reported in green and red respectively (upper panel). Differential interferometric output (in blue, lower panel). The first two detected beams are orthogonally polarized, so the differential output is twice the single-ended amplitude. In the left part of the graph (highlighted in grey) the interferometer is unlocked, while in the right part, the interferometer is locked, thus achieving the zero working point condition.

To highlight the advantages of the stabilized interferometer, the upper panel of Figure 2.11 shows an example of repeated 1f-PAS spectra acquisition over time in both the unlocked and locked conditions. When the interferometer is unlocked, the peak signal (blue data points in the lower panel of Figure 2.11) shows a large dispersion due to a continuous variation of the interferometer working point, resulting in changes in the relative lengths of the two arms. The dispersion is drastically reduced (up to $\sim 1.7\%$) when the interferometer is locked in the ZWP, improving the stability of the measurement and reaching a condition where the PAS signal amplitude is maximized.

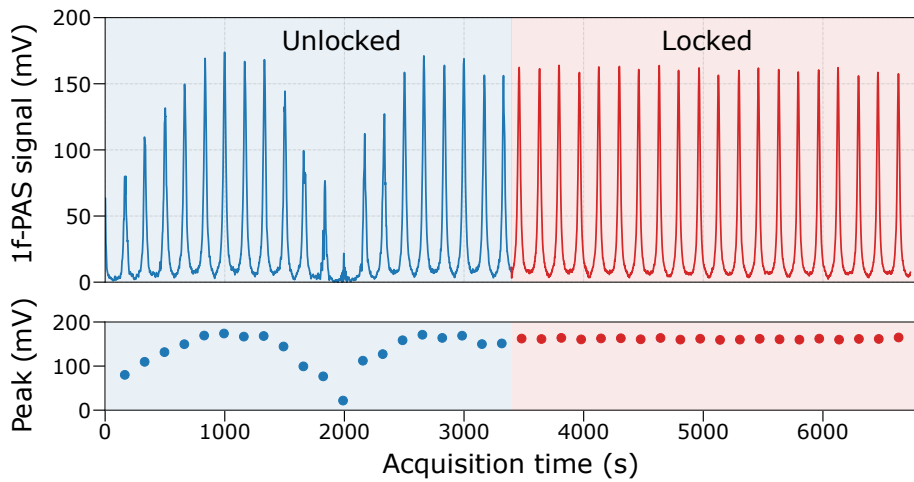


Figure 2.11: Continuous 1f-PAS spectra acquisition over time performed in unlocked (blue trace) and locked (red trace) configurations (upper panel). Associated peak signal trends (lower panel).

2.2 Results and discussion

The first part of this Section provides the acousto-mechanical characterization of the used silicon-based MEMS cantilever, investigating the quality factor and the resonance frequency as a function of the working pressure. The second part is devoted to the description of the photo-acoustic measurements.

2.2.1 Investigating the cantilever's acousto-mechanical properties

According to the theory, the resonant properties of an oscillating structure can be described by two fundamental parameters. The first one is the mechanical resonance frequency f_0 , defined as one of the natural frequencies at which the structure oscillates with the highest amplitude. The second is the quality factor Q , defined as the ratio between the stored energy and the energy lost per cycle of oscillation, and it gives information about the *under-damping* degree of the investigated structure. Regardless of the dimension and the geometry, when the structure is subject to an external perturbation, it will show a peculiar response in the Fourier frequency domain, characterized by a Lorentzian-type trend peaked at f_0 :

$$L(f) = L_0 + \frac{2A}{\pi} \frac{\Delta_f}{4(f - f_0)^2 + \Delta_f^2}, \quad (2.9)$$

where L_0 is an offset, A is a constant related to the structure's geometry, while Δ_f is the Full Width at Half Maximum (FWHM). The quality factor is then defined as $Q = f_0/\Delta_f$. Accordingly, a preliminary investigation of the cantilever's mechanical properties is a fundamental and necessary step for studying its performance as an acousto-to-voltage transducer.

Experimentally, the cantilever's resonant curve spectrum was obtained using the following routine, repeated for several sample pressure values. A step-wise measurement was performed fixing the laser current at the absorption line peak current and varying the intensity modulation frequency (i.e. the AOM on/off frequency) around the MEMS cantilever resonance predicted by the simulation. Each data point was collected with a 3 dB cut-off lock-in bandwidth set to 100 mHz and represents the mean value of the de-modulated R-component signal. The associated error was estimated by computing the 1σ standard deviation. In this way, the cantilever's Lorentzian resonance curve was reconstructed with measured data.

The theoretical background underlying this experimental approach, based on the voltage readout of the resonator's acousto-mechanical response, is identical to that expressed for the current readout in Equation (6) of Reference [176]. Additionally, even if the Quality factor, in general, is derived from the demodulated in-phase X -component of the signal, it is trivial to demonstrate that the X -component and the R^2 -component of the demodulated signal differ only by a constant multiplication factor (the demonstration is reported in Appendix A.1). That said, the resonance features (f and Q) can be evaluated using one component or the other because the associated FWHMs are the same. Hence the square of the R -signal was directly evaluated to suppress any error connected with any signal's phase change.

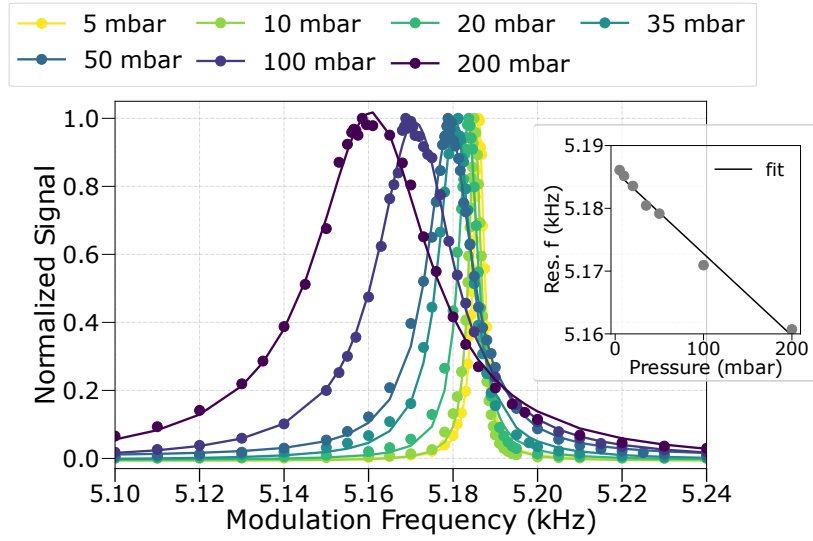


Figure 2.12: Normalized R^2 signal component (i.e. resonant curve spectra) of the rectangular MEMS cantilever at different pressure values. The solid lines represent the fit on each experimental data set performed using Equation 2.9. **Inset:** resonance frequency trend as a function of the sample pressure

Figure 2.12 shows the resonance curve spectra of the cantilever at different pressures of the gaseous sample ranging from 5 mbar to 200 mbar. As expected, the resonance frequency linearly decreases when increasing the pressure (see the **Inset** of Figure 2.12), while the FWHM increases, resulting in a progressive broadening of the cantilever's response. The combination of these two phenomena leads to a progressive decrease in the mechanical quality factor (reported in Figure 2.13), which follows the typical well-known trend [176, 177]:

$$Q(P) = B + \frac{cQ_0}{a + bQ_0\sqrt{P}} \quad (2.10)$$

where Q_0 is the quality factor in vacuum, which includes all the pressure-independent loss mechanisms (such as thermoplastic damping) [174], while B , a , b , and c are fitting parameters that take into account both the geometry of the MEMS and the viscosity of the surrounding fluid.

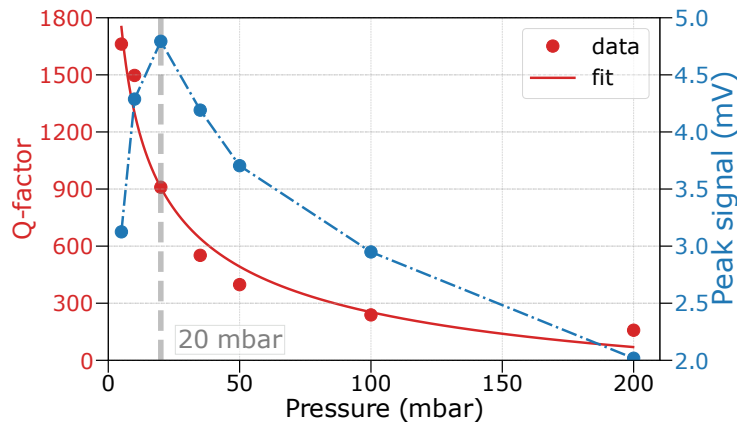


Figure 2.13: Quality factor (red data-points) and peak signal (blue data-points) as a function of the pressure. The red solid lines represent the fit on the experimental Q-factors following Equation 2.10.

According to this evidence, from a purely mechanical point of view, an optimal response of the oscillating structure is maintained at a low-pressure working regime. In fact, the quality factor shows a monotone degradation of around 90 % within the investigated pressure range (i.e. from a value of 1162 at 5 mbar it drops down to 158 at 200 mbar). At the same time, however, the generation and propagation of acoustic waves in a gas sample require a sufficiently high number of molecules in the sample, i.e. a sufficiently high sample pressure, thus affecting the overall acoustic-to-voltage transduction efficiency of the cantilever. Accordingly, another figure of merit to be considered is the photoacoustic peak signal as a function of the pressure. The latter was acquired in a single-pass configuration (i.e. without the optical cavity) and using 10 ppm of N_2O in N_2 as the trace-gas. During the measurements, the resonance frequency value was optimized for each value of pressure. The overall trend, represented by the blue data point in Figure 2.13, is affected simultaneously by these two mechanical and acoustic contributions. Despite a higher Q-factor, the PA peak signal is suppressed at low pressures by insufficient acoustic wave generation. It achieves a maximum value at the associated best working point, and then it decreases again monotonically with increasing pressure due to the quality factor cut-off. In our case, the best working point occurs at 20 mbar, where the PAS signal achieves its maximum value and where, at the same time, the mechanical quality factor remains sufficiently high (i.e. ≈ 909). According to this evidence, performing the photoacoustic measurements at a pressure of 20 mbar could guarantee a good trade-off between the two correlated (and opposite) trends.

2.2.2 Photo-acoustic measurements

The photoacoustic measurements, performed at a pressure of 20 mbar, were acquired in two different configurations: **(1)** single-pass, where the sensitivity enhancement is given only by the acoustic coupling between the cantilever and the custom-made acoustic resonator, and **(2)** cavity-enhanced, where both the acoustic and optical resonances affect the sensor's performances. In both cases, the 1-f PAS spectra were acquired at different values of incident laser power by varying the optical beam polarization state via the half wave-plate placed before the ISO. In the single-pass configuration, the 1f-PAS spectrum was acquired by applying a slow ramp (frequency 2 mHz) directly to the modulation input of the QCL driver. In the cavity-enhanced configuration, instead, the laser was locked to the cavity mode, and the slow ramp was applied to the PZT attached to the input cavity mirror.

Figure 2.14 shows the trend of the PAS peak signal as a function of the incident laser power in the two investigated configurations. In both cases, the laser power was measured in front of the PA-cell, at the N_2O absorption peak current. In the single-pass configuration, the signal shows good linearity with the increasing incident power ($R^2 = 0.984$, see Figure 2.14 **(a)**), confirming a well-known behavior in the literature [27, 68]. However, the scenario changes when the optical cavity comes into play. In fact, according to Figure 2.14 **(b)**, the system's response is linear only in the low-power range, up to approximately 2.5 mW (as reported in the **Inset**). This condition is lost at higher power, where the system enters a clearly non-linear regime.

The following paragraph will investigate this experimental observation, attributing it to an N_2O absorption line saturation due to the high intra-cavity power buildup.

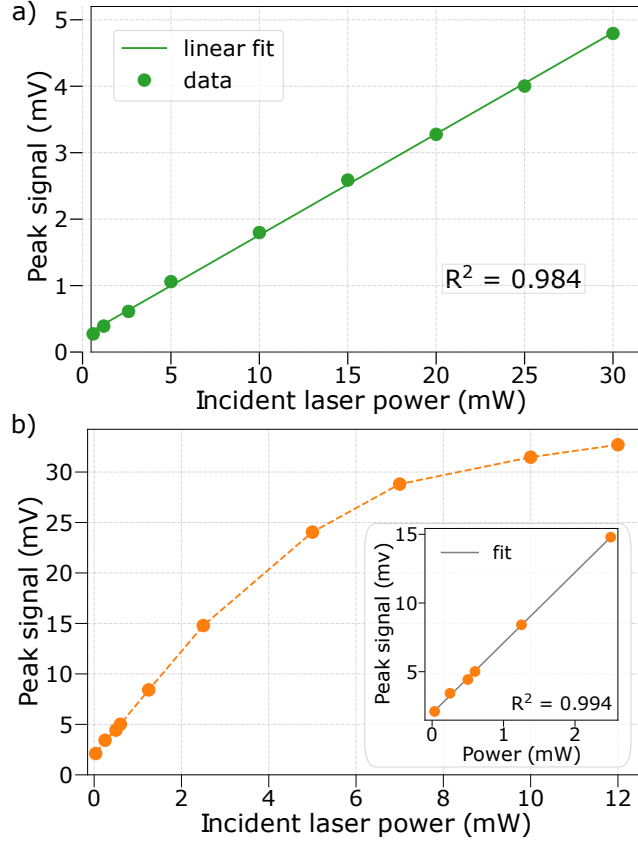


Figure 2.14: **(a)** 1f-PAS peak amplitude versus the incident laser power in single-pass configuration. The experimental data (in green) were fitted with a linear function (solid green line). **(b)** 1f-PAS peak amplitude versus the incident laser power in cavity-enhanced configuration. **Inset:** linearity at the low-power regime in cavity-enhanced configuration.

Saturation of the N_2O molecular transition

In the experimental working condition, i.e. 10 ppm of N_2O in pure N_2 at a pressure of 20 mbar, the addressed trace-gas rovibrational transition is affected by three main line-broadening mechanisms. The first one, already introduced in Section 1.1, is the Doppler effect and, according to equation 1.3, it contributes to a broadening of $\Delta_D \simeq 59.9$ MHz. The second one is related to collisional effects and is described by the pressure-depended coefficient $\Delta_p = C_p p$, where C_p [MHz mbar $^{-1}$] is the self-broadened HWHM obtainable from the HITRAN database of the given transition [178], and p the pressure. In our case of study, this effect introduces an additional line-broadening term $\Delta_p \simeq 41.8$ MHz. Finally, a third broadening contribution arises from transit time effects occurring during the interaction between the propagating excitation laser and the trace molecules. Assuming a Gaussian beam profile and confining its interaction with the trace molecules within the beam waist diameter, the transit-time broadening can be written as [179]:

$$\Delta_t = \frac{\bar{v}}{4\pi w_L}, \quad (2.11)$$

where $\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$ the averaged molecule's speed, k_B the Boltzmann constant (1.3806×10^{-23} J/K), T the temperature ($\simeq 296$ K), and m the mass of the molecule (N_2O , 7.3056×10^{-26} kg). Given a beam waist $w_L \simeq 0.3$ mm falling in the center of the optical cavity (see Subsection 2.1.3), and according to Equation 2.11, the transit-time effect is responsible for an additional $\Delta_t \simeq 1$ MHz broadening, much smaller than the other two.

For a *quantitative* analysis of the saturated signal, let's assume that the dominant contribution to the absorption line's saturation came from the molecules characterized by the same group velocity. In this sense, only the homogeneous line-broadening mechanism (i.e. Δ_p , and Δ_t) enters the definition of the saturation intensity I_s , the latter defined in a good approximation as [180]:

$$I_s = \frac{\hbar \omega_{LAS}}{2\pi c^2 A_E} \times (2\pi \Delta_p + 2\pi \Delta_t)^2. \quad (2.12)$$

Here $\omega_{LAS} = 2\pi f_{LAS}$ is the laser angular frequency, c the light velocity (2.9979×10^8 ms⁻¹), $\hbar$ the Planck constant (1.0546×10^{-34} Js), and A_E the Einstein coefficient of the transition obtainable from the HITRAN database. Given that $E_A = 1.031 \times 10^2$ s⁻¹ in our case of study, and solving Equation 2.12, a saturation intensity of $I_s \simeq 9.2$ W/mm² is expected at a pressure of 20 mbar.

Coming back to the experiment, let's consider the single-pass configuration. At the highest possible incident power (i.e. 30 mW) the associated power intensity, measured at the beam waist, will be:

$$I_{in} = \frac{P_{in}}{\pi \times w_L^2} = \frac{30 \times 10^{-3} \text{ W}}{\pi \times (0.3 \text{ mm})^2} \simeq 0.114 \text{ W/mm}^2. \quad (2.13)$$

Since $I_{in} \ll I_s$, no saturation effect will occur in the single-pass configuration. Moving to the cavity-enhance configuration, the optical cavity introduces a power buildup factor, proportional to the associated Finesse, being equal to:

$$G_{ic} = \frac{\mathcal{F}}{\pi} = \frac{1}{\pi} \frac{\pi}{[(1-R) + L\alpha]}, \quad (2.14)$$

where αL is the relative absorbance and describes the mirror loss coefficient due to trace-gas absorption within a light path of length L . This parameter can be calculated via the HITRAN simulation, adjusting the trace-gas concentration value within the matrix and setting L equal to the cavity length (i.e. $L = 85$ mm).

According to the simulation reported in Figure 2.15, the relative absorbance of the investigated absorption line (peaked at 2189.27 cm⁻¹), for a trace-gas concentration of 10 ppm at a pressure of 20 mbar, is equal to $\alpha L = 1.23 \times 10^{-3}$. Being the mirror's reflectivity equal to $R = 0.9984$ and according to Equation 2.14, a power buildup factor equal to $G_{ic} = 350$ is estimated. Hence, for an incident power of 12 mW, the intra-cavity laser power intensity at the beam waist can be written as:

$$I_{ic} = \eta_{CE} \times G_{ic} \times \frac{P_{in}}{\pi \times w_0^2} = 0.85 \times 354 \times \frac{12 \times 10^{-3} \text{ W}}{\pi \times (0.29 \text{ mm})^2} \simeq 12.7 \text{ W/mm}^2, \quad (2.15)$$

where $\eta_{CE} = 0.85$ is the coupling efficiency between the free-running QCL beam and the fundamental cavity mode (see the Subsection 2.1.3). The latter value exceeds the N_2O -line saturation intensity, justifying the saturation effect for an incident laser power of 12 mW.

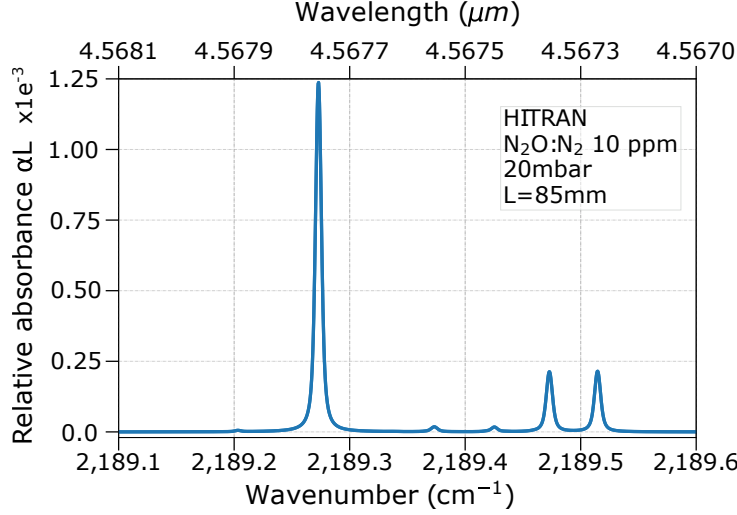


Figure 2.15: Simulated relative absorbance for a gas mixture consisting of 10 ppm of N_2O in pure N_2 and given an absorption path length of 85 mm at 20 mbar. These data were extracted from the HITRAN database.

Looking at the overall trend of the photoacoustic signal with optical power intensity is crucial for further justifying the hypothesis of absorption line saturation. Depending on the working pressure, the theoretical trend defining the detected absorption signal S from a gas sample as a function of the laser intensity I is characterized by two different physical laws:

$$S(I) = \frac{\alpha_0 I}{\left(1 + \frac{I}{I_s}\right)}, \quad \Delta_p \gg \Delta_D \quad (2.16)$$

$$S(I) = \frac{\alpha_0 I}{\sqrt{\left(1 + \frac{I}{I_s}\right)}}, \quad \Delta_p \ll \Delta_D \quad (2.17)$$

where α_0 is a fit parameter. Equation 2.16 characterizes a homogeneous line-broadening regime, where the pressure-dependent phenomena are much greater than the Doppler-limited ones. While Equation 2.17 belongs to the opposite condition, referring to an inhomogeneous regime. At 20 mbar the Doppler and the collisional line broadening contributions are similar ($\Delta_D \simeq 59.9$ MHz and $\Delta_p \simeq 41.8$ MHz), resulting in a *hybrid* condition where homogeneous and inhomogeneous dynamics are comparable. In this condition, a proper theoretical analysis is not trivial, and therefore it is necessary to shift to a working point where one of these two effects is dominant. Accordingly, the photoacoustic signal acquisition versus the incident power was repeated at a pressure of 1.5 mbar, where the pressure-dependent broadening, being equal to $\Delta_p \simeq 3.1$ MHz, is much smaller than Δ_D , and the associated saturation intensity is $I_s \simeq 0.088$ W/mm². This working condition allows access to a purely inhomogeneous regime, where Equation 2.17 can be considered as the expected trend for the saturated signal.

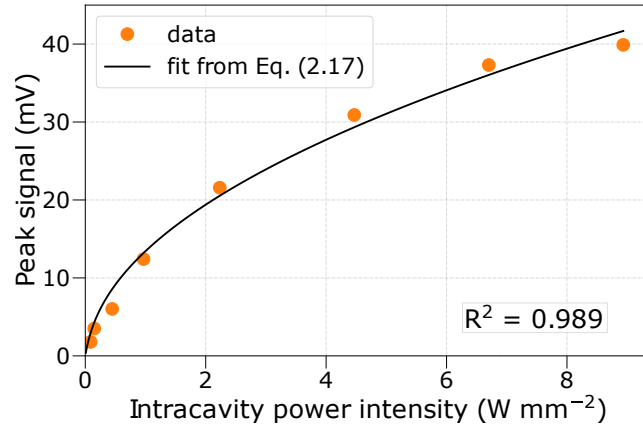


Figure 2.16: PAS peak signal as a function of the intra-cavity power intensity at 1.5 mbar (orange data point) fitted with Equation 2.17 (solid black line). The x-axis was converted from laser incident power to intra-cavity power intensity via Equation 2.15. The fitting process returns a value α_0 equal to 47.3 mVW/mm².

According to Figure 2.16 the data points (depicted in orange) agree with the theoretical trend (represented by the solid black line), as confirmed by a R^2 -value equal to 0.989, further supporting the saturation hypothesis.

1-f PAS spectra at 20 mbar

A fair comparison of the ultimate sensitivity achievable in the single-pass and cavity-enhanced configurations was done by taking into account the low-power regime of Figure 2.14 (b), where no saturation occurs. Furthermore, when the impinging power is decreased by a factor of 35 μ W, the associated intra-cavity intensity is only ≈ 0.037 W/mm², well below the saturation intensity level. According to this evidence, the analysis in the cavity-enhanced configuration was carried out maintaining the laser incident power at its lowest value of 35 μ W, while in the single-pass case, the incident laser power was kept at the highest possible (i.e. 30 mW).

Figures 2.17(a) and 2.17(b) show the 1-f PAS signal in single-pass and cavity-enhanced configurations, respectively. The evaluation of the system's performance can be obtained by estimating the minimum detectable concentration:

$$NEC = \frac{c_{tg}}{SNR}, \quad (2.18)$$

where c_{tg} is the trace-gas concentration within the mixture (i.e 10 ppm of N₂O in this case of study), and SNR is the ratio between the peak signal amplitude and the associated 1σ standard deviation of the noise level. While the peak signal values can be easily extracted from the two spectra (being equal to 4.79 mV in single-pass and 2.11 mV in cavity-enhanced respectively), the noise level can be obtained by acquiring a long-term trace at the associated laser current and performing an Allen-Werle deviation analysis.

The lower panels of Figures 2.18(a) and 2.18(b) report the noise traces acquired in the two analyzed configurations for an acquisition time of 1.2 hours. In both two cases, the lock-in 3dB cut-off bandwidth was set to 1 Hz (corresponding to a time constant equal to 0.08 seconds), the laser current was fixed at the N₂O absorption peak, and

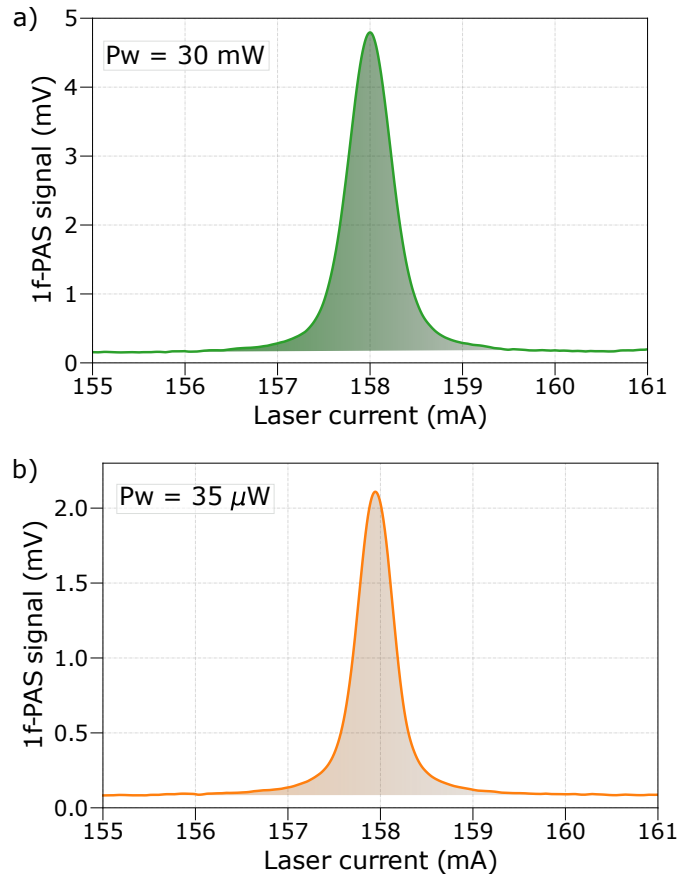


Figure 2.17: (a): 1f-PAS single-pass spectrum acquired at a pressure of 20 mbar and the highest incident laser power (i.e. 30 mW). (b): 1f-PAS cavity-enhanced spectrum acquired at 20 mbar and the lowest incident laser power (i.e. 35 μ W).

the chamber was filled with 20 mbar of pure N₂ to prevent any residual interaction between the target molecules and the excitation laser beam. Given 1σ values equal to 0.0123 mV for single-pass and 0.0073 mV for cavity-enhanced, the associated SNRs are 389.64 and 289.73 respectively, corresponding to NEC values equal to 25.67 ppb and 34.52 ppb. It follows that exploiting a doubly-resonant approach leads to similar performances with the single-pass scheme but with an impinging power around 1000 times below. To fairly compare the two configurations the NEC was converted into the Normalized Noise Equivalent Absorption coefficient (NNEA), normalizing for the incident laser power and the lock-in bandwidth. A detailed description regarding the derivation of the NNEA coefficient is reported in Appendix A.2. If in single-pass configuration a NNEA equal to $9.33 \times 10^{-9} \text{ cm}^{-1} \text{ WHz}^{-\frac{1}{2}}$ is obtained, in cavity-enhanced configuration the NNEA decreases by more than two orders of magnitude, down to $2.93 \times 10^{-11} \text{ cm}^{-1} \text{ WHz}^{-\frac{1}{2}}$.

Another important feature of a photoacoustic-based sensor is its long-term stability. It provides an estimation of how much the detection sensitivity of the system under examination can be improved by progressively increasing the averaging time. This test can be inferred employing the Allan-Werle deviation, which allows investigating drifts and determining the sensor signal averaging limits [181]. Designed for testing the frequency stability of a generic oscillator, the Allan deviation of an M -time series

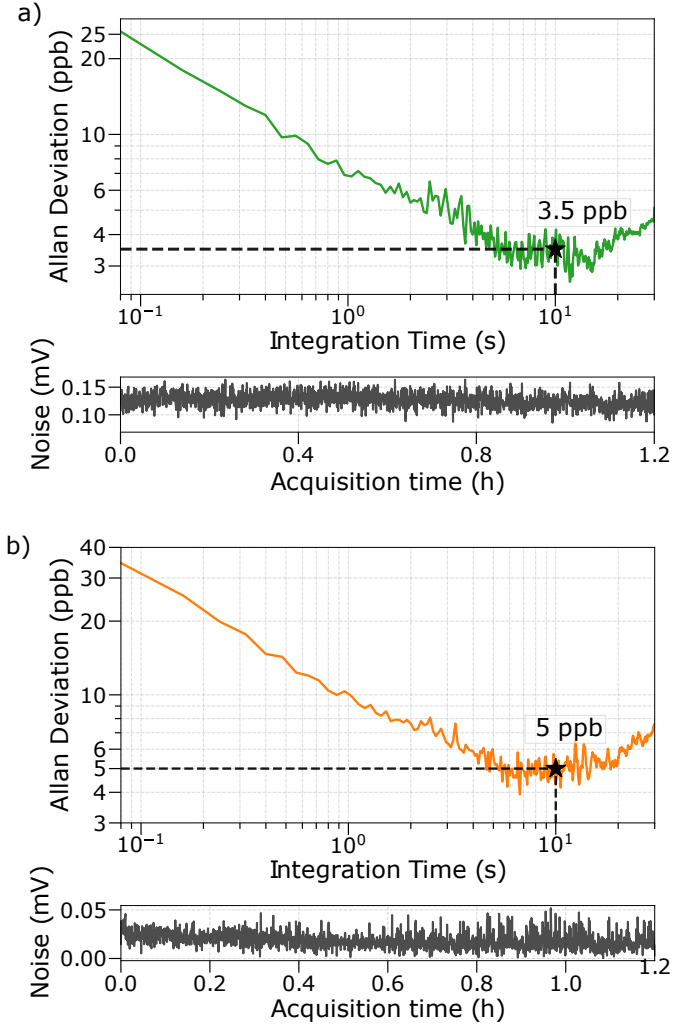


Figure 2.18: **(a)**: Long-term noise level acquisition (lower panel) and Allan-Werle deviation analysis (upper panel) performed in single-pass configuration at 20 mbar and 30 mW of incident laser power. **(b)**: Long-time deviation noise level acquisition (lower panel) and Allan-Werle deviation analysis (upper panel) performed in cavity-enhanced configuration at 20 mbar with 35 μ W of incident laser power. Both the measurements were performed by filling the chamber with 20 mbar of pure N_2 and setting the lock-in 3dB cut-off bandwidth to 1 Hz.

of experimental data acquired with an integration time τ_c is defined as [182]:

$$\sigma_y(\tau_c) = \sqrt{\frac{1}{M} \sum_{k=1}^M \frac{1}{2} (y_{k+1} - y_k)^2}. \quad (2.19)$$

To understand how $\sigma_y(t)$ varies with the integration time a Python script was applied to the long-time noise traces. The latter returns the trend of $\sigma_y(\tau_c)$ as a function of $k\tau_0$, where $k \in [1, M]$, and τ_0 is the lock-in amplifier integration time set for the measurement.

The results of the Allan-Werle deviation analysis are reported in the upper panels of Figures 2.18(a) (single-pass), and 2.18(b) (cavity-enhance). In both two cases, the minimum detection limit (MDL) is reached at around 10 seconds of averaging time, with corresponding values equal to 3.5 ppb for single-pass and 5 ppb for cavity-enhanced. Averaging for more time is no longer advantageous, as indicated by an increase in the

Allan deviation trends, preventing us from further increasing the minimum detection limit at a higher averaging time.

Cavity-Enhanced at higher pressure: retrieving the linearity

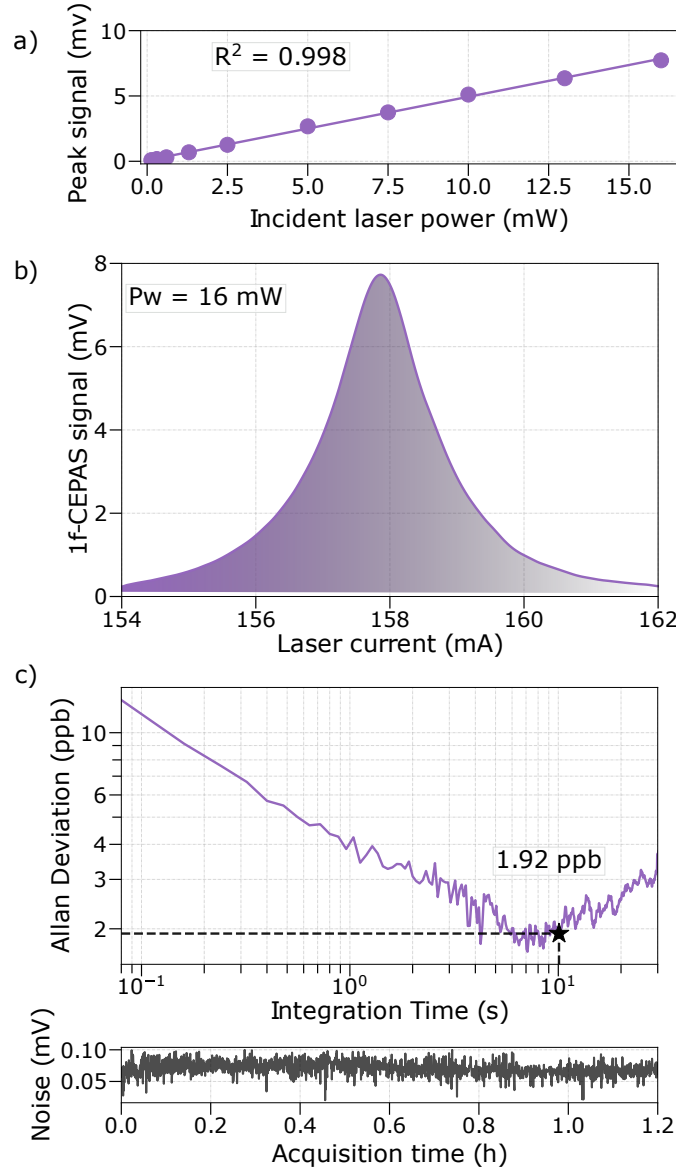


Figure 2.19: (a): Photoacoustic peak signal versus the laser incident power at 200 mbar. (b): 1-f PAS spectra acquired at 200 mbar with the highest laser incident power. (c): Associated Allan-Werle deviation analysis.

Working at high pressure could be beneficial in important applications, such as air-quality analysis and in-field applications, where the sensor is required to work in open air. In this regime, the system is affected by a quality factor degradation, but with the drawback of being no longer affected by the saturation even when working at higher laser power. In fact, increasing the working pressure leads the system to exit the diffusive regime and enter a new one. Here the contribution of the line broadening due to collision becomes non-negligible due to more important pressure-dependent effects.

This happens because the increase in pressure introduces in the gas sample a sufficiently high number of non-radiative collisional relaxation channels. As a consequence, the saturation intensity becomes sensibly higher for the same addressed line.

As reported in Figure 2.19(a), when the working pressure is increased from 20 mbar to 200 mbar, the linear regime is also retrieved in the cavity-enhanced configuration, as expected. In this case, the transit time coefficient C_t remains constant, but the collision coefficient C_{pp} becomes sensibly bigger (i.e. 418 MHz). Accordingly, the saturation intensity increases to $I_S = 898.9 \text{ W/mm}^2$, much larger than the highest intra-cavity power intensity, preventing the saturation effect.

Figure 2.19(b) shows the 1-f PAS spectrum acquired at the highest laser incident power, and Figure 2.19(c) reports the Allan-Werle deviation analysis with 200 mbar of pure N_2 . In this configuration, a MDL equal to 1.92 ppb was achieved for an averaging time of 10 seconds, corresponding to a NNEA value equal to $5.07 \times 10^{-9} \text{ cm}^{-1} \text{ WHz}^{-\frac{1}{2}}$. Although the best performance (both in terms of MDL and NNEA values) was obtained at the pressure of 20 mbar and at the lowest reachable incident power, this latter result demonstrates how the system developed in this work can be also very well suited to work in high-pressure regimes, enabling possible future application in in-field environmental monitoring experiments.

2.3 Perspectives

The developed system represents the starting point for further improvements that will be treated in the next chapter. When operated in its linear regime, the cavity-enhanced configuration demonstrated a sensitivity improvement by more than two orders of magnitude compared with the single-pass configuration. In particular, ppb-level detection with extremely low optical power (i.e. few tens of μW) opens the door to highly-sensitivity detection with low-power consumption devices, which is a fundamental prerogative for specific applications, such as in integrated systems.

To contextualize the achieved results, this work has to be compared with the state-of-the-art photoacoustic-based sensor's performance for the same target molecule (i.e. N_2O). In the actual configuration, concerning only the minimum detection limit, our system is very far from the best result reported in the literature, being a MDL of 0.7 ppt for an integration time equal to 210 seconds [61]. On the other hand, our system reaches performance at the same order of magnitude as the record value in terms of NNEA (i.e. $2.93 \times 10^{-11} \text{ cm}^{-1} \text{ WHz}^{-1/2}$ against $3.10 \times 10^{-11} \text{ cm}^{-1} \text{ WHz}^{-1/2}$ of [61]), having exploited an incident power three orders of magnitude lower (i.e. 35 μW against 65 mW of [61]). These considerations are summarized in Figure 2.20.

Moreover, our system demonstrated a very good MDL (≈ 2 ppb) at around 200 mbar, highlighting important potentiality for atmospheric pressure trace-gas detection applications. This is due to the beneficial effect of the cavity-enhanced configuration, which allows the mitigation of the quality factor degradation effect in the high-pressure regime. Finally, if properly exploited, the saturation effect at low pressure and high power could open the possibility of exploring unconventional regimes for PAS-based systems, paving the way (for example) to sub-Doppler high-resolution trace-molecule detection.

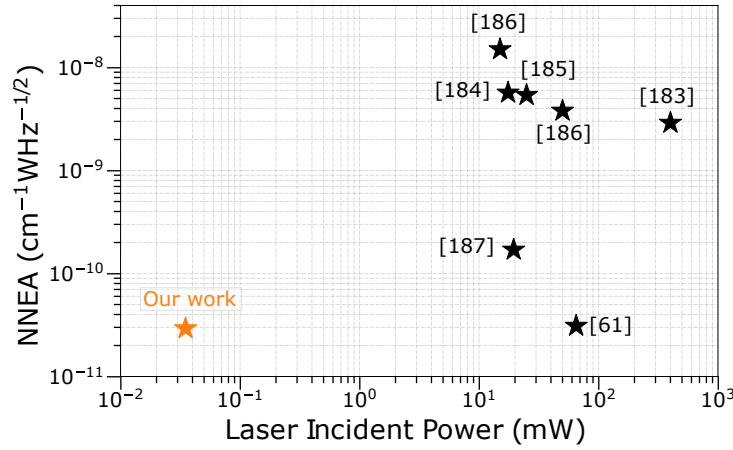


Figure 2.20: (a): Normalized Noise Equivalent Absorption coefficients for the state-of-the-art photoacoustic-based N_2O sensors with the associated laser incident power. The result achieved in this work is indicated with the orange (cavity-enhanced) stars.

The results achieved represent an excellent starting point for further developments and studies aimed at improving the ultimate detection sensitivity of the system. In this regard, the following chapter will describe all the efforts that were made to fulfill this purpose, and at the same time to propose valid alternatives. The journey will be divided into three main parts; **(1)** exploring new geometry for MEMS-based acoustic-to-voltage transducers, and performing a comparative analysis of their properties and performances, **(2)** choosing one promising structure among all of them and coupling it with proper acoustic wave confinement, and **(3)** repeating the doubly-resonant experiment with the improved components.

CHAPTER 3

Investigating alternative approaches for highly-performing photoacoustic-based sensing

The following chapter explores possible evolutions of the sensor reported in the previous one (Chapter 2). Taking as a starting point the experimental limits that have emerged, we chose to undertake an exploratory approach, aimed at studying alternative solutions to improve the PAS sensor working on its key components, such as the acoustic transducer. The first Section (3.1) is devoted to the characterization of novel geometries for silicon-based Micro-Electro-Mechanical Systems to be exploited as acoustic transducers in a trace-gas photoacoustic setup. Starting from the simulation and the design of the MEMS structures (Subsection 3.1.2), and a brief description of the experimental setup (Subsection 3.1.2), the discussion will move to the analysis of the experimental results. Firstly, the mechanical characterization is performed (Subsection 3.1.3) to estimate the resonance frequencies and the quality factors. Then the photo-acoustic response of each structure is investigated (Subsection 3.1.4) to find out the best-performing ones. The final part includes a summary and the conclusions (Subsection 3.1.5).

The second Section (3.2) describes the coupling between one of the most performing MEMS structures previously investigated and a dual-tube acoustic resonator, paving the way to achieve a sub-part-per-billion detection sensitivity. In this part a complete and detailed characterization of the spectrophone is reported, starting from the design (Subsection 3.2.1) and passing to the discussion of the results (3.2.2). The latter is focused on the fabrication material comparison of the dual-tube system (Subsection 3.2.2), the best geometry investigation (Subsection 3.2.2), and the spectrophone response in the best configuration (Subsection 3.2.2). Conclusion and outlook will be part of Subsection 3.2.3.

The last Section (3.3) describes the coupling of the dual-tube spectrophone with the optical cavity, unveiling the ultimate detection sensitivity that the system can achieve. Subsections 3.3.1 and 3.3.2 summarize the results, while Subsection 3.3.3 is devoted to general conclusions and perspectives.

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3.1 New silicon-based Micro-Electro-Mechanical systems as acoustic transducers

The work described in this section is summarized in our research article published in 2024 in *Photoacoustics (Elsevier)* [63], in collaboration with the *Italian Space Agency* (ASI) of Matera, the *Institute for Microelectronics and Microsystems* (IMM-CNR) of Bologna, and the *Chinese University of Hong-Kong*. Taking advantage of the immense possibilities offered by micro-electro-mechanical systems (MEMS), the main purpose is to propose novel and more performing geometries of silicon-based acoustic transducers for photoacoustic trace-gas detection, overcoming the standard rectangular shape.

As a starting point, five different geometries were designed to address different mechanical features (i.e. big elongation, high symmetry, and so on). After having theoretically simulated the expected resonance frequencies with Finite Element Methods (FEM), six different vibrational modes were chosen for the analysis. Via photoacoustic excitation, the resonance properties of the chosen modes were evaluated and compared with the simulated ones. Subsequently, the photoacoustic detection performances of each MEMS structure, in terms of Minimum Detection Limit Normalized Noise Equivalent Absorption, were estimated and compared. This systematic approach allowed the identification of the most promising structures in terms of geometry and detection performance.

3.1.1 Design and simulations of the MEMS structures

Silicon is a material with mechanical properties that make it ideal for MEMS structures fabrication [183]. Designing different structures with peculiar mechanical behavior is possible by carefully choosing the material (crystalline orientation, doping) and tailoring the geometry. In particular, material properties, mass, and suspension structures will determine the mechanical behavior of the silicon element, as well as the frequency spectrum of the mechanical resonance and the oscillator quality factor. In this case of study, for each designed structure the geometric parameters were varied and optimized to obtain resonance modes falling within the 1-10 kHz frequency range, which is typically an optimal range for the generation and propagation of the acoustic wave in a gaseous matrix. *Comsol multiphysics* was used for the *eigenfrequencies* analysis, simulating the natural frequency for each structure and the associated resonant mode's shape (i.e. the *eigenmode*) via Finite Element Method (FEM). The simulations were performed in static conditions, without adding any forcing or damping sources. The theoretical modeling of a damping force due to the generation of an acoustic wavefront is very complex because it has to consider some factors that are difficult to control experimentally, such as the interaction dynamics between the molecules of the gas matrix. For this reason, having a rough evaluation of each structure's mechanical properties is enough for our purposes.

Concerning the fabrication process, the reader can refer to Subsection 2.1.4. The next Figures (from 3.1 to 3.5) report a graphical representation of the MEMS structures under study, underlying their geometrical features and the investigated resonant mode's shapes. For all the structures, the regions bound to the substrate are colored in red. Furthermore, Tables from 3.1 to 3.5 report the first five predicted *eigenfrequency* of each structure, and the experimentally investigated ones are marked in bold red.

M1: *Three-arms spring*

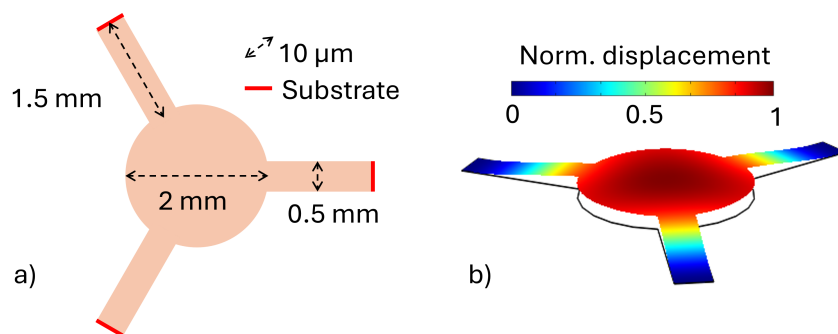


Figure 3.1: (a): geometrical features of the *three-arms spring* (M1). (b): displacement simulation associated with the investigated resonance (i.e. first mode).

This MEMS structure is made by a circular surface of 2 mm diameter anchored to the substrate via 3 symmetrically distributed arms of 1.5 mm length and 0.5 mm thickness. According to the simulation, the investigated resonance mode is characterized by a high distribution displacement symmetry.

3.1 New silicon-based Micro-Electro-Mechanical systems as acoustic transducers

Table 3.1: First five simulated resonant modes of the MEMS structure M1. The investigated mode is marked in red.

N ^o of mode	Resonance frequency (Hz)
1st	2051.569
2 nd	7697.581
3 rd	7740.631
4 th	19699.889
5 th	19808.108

M2: *Two-turn rectangular spring*

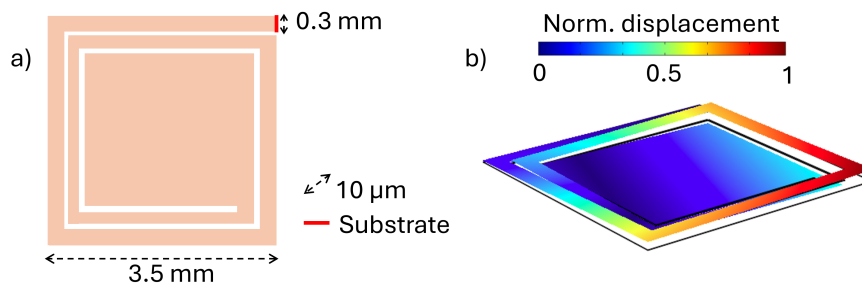


Figure 3.2: (a): geometrical features of the *two-turn* rectangular spring (M2). (b): displacement simulation associated with the investigated resonance (i.e. fifth mode).

The structure M2 is characterized by a square base of 3.5 mm length, from which a two-turn spring structure develops. A 0.3 mm segment is the only part anchored to the substrate.

Table 3.2: First five simulated resonant modes of the MEMS structure M2. The investigated mode is marked in red.

N ^o of mode	Resonance frequency (Hz)
1 st	293.318
2 nd	541.889
3 rd	576.023
4 th	1113.023
5th	1422.232

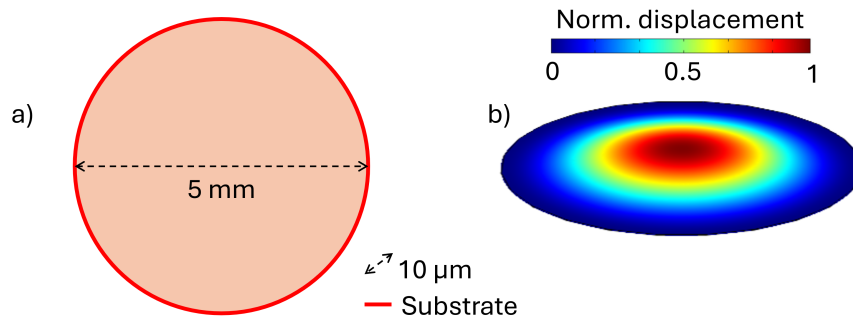
M3: Circular drum membrane

Figure 3.3: **(a)**: geometrical features of the *circular drum* membrane (M3). **(b)**: displacement simulation associated with the investigated resonance (i.e. first mode).

The structure M3 is a 5 mm circular membrane completely anchored to the substrate.

Table 3.3: First five simulated resonant modes of the MEMS structure M3. The investigated mode is marked in red.

N° of mode	Resonance frequency (Hz)
1st	12428.757
2 nd	20654.242
3 rd	20659.644
4 th	23605.760
5 th	30636.445

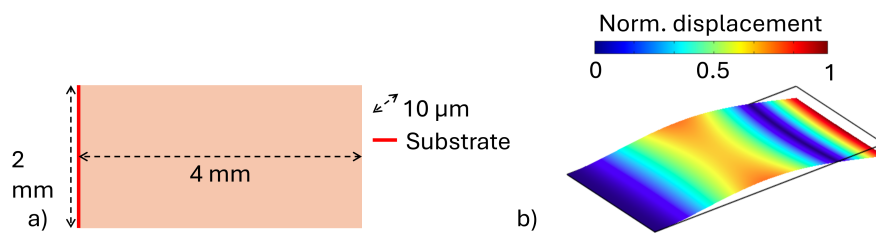
M4: Standard rectangular cantilever

Figure 3.4: **(a)**: geometrical features of the *standard rectangular* cantilever (M4). **(b)**: displacement simulation associated with the investigated resonance (i.e. third mode).

This structure is a standard rectangular cantilever, and it was introduced for a fair comparison with the other MEMS. It is characterized by a base of 2 mm and a height of 4 mm.

3.1 New silicon-based Micro-Electro-Mechanical systems as acoustic transducers

Table 3.4: First five simulated resonant modes of the MEMS structure M4. The investigated mode is marked in red.

N° of mode	Resonance frequency (Hz)
1 st	771.955
2 nd	3353.859
3rd	4821.055
4 th	10919.173
5 th	13559.519

M5: Racket-shaped cantilever

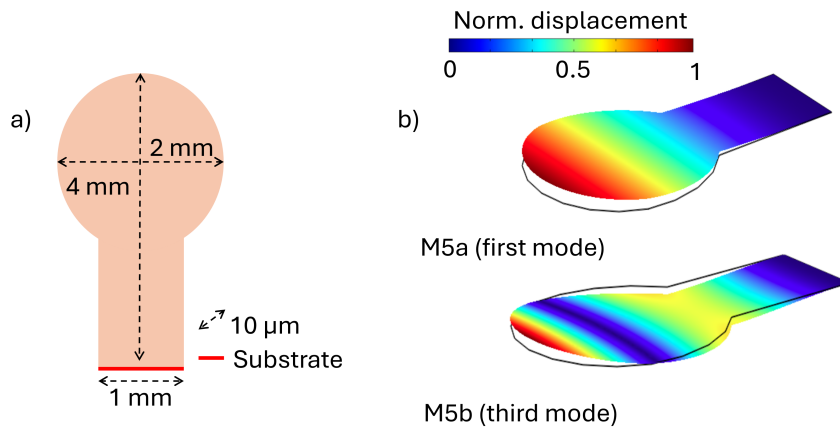


Figure 3.5: (a): geometrical features of the *racket-shaped* cantilever (M5). (b): displacement simulation associated with the investigated resonances (i.e. first mode and third mode).

This MEMS represents a variant of the standard rectangular cantilever. It is characterized by a thinner anchored base of 1 mm, ending up with a circular free-end of diameter equal to 2 mm.

Table 3.5: First five simulated resonant modes of the MEMS structure M5. The investigated modes are marked in red.

N° of mode	Resonance frequency (Hz)
1st	846.151
2 nd	3877.715
3rd	6846.171
4 th	20143.718
5 th	20568.494

The different geometries were selected to investigate and enhance a potentially wide range of acousto-mechanical features. For example, the MEMS structures M1 and M2 were properly designed to achieve high displacements following the interaction with the impinging acoustic wave. In particular, the *three-arms* spring (M1) is characterized by a very symmetric oscillation at the first resonance mode (see Figure 3.1(b)). In addition, the isolation provided by the three-arms architecture should determine good immunity from external mechanical vibration. Contrariwise, the *two-turn* rectangular spring (M2) was designed to maximize the unanchored area, determining excellent decoupling between its resonances and the substrate. Accordingly, the latter structure will be characterized by the ease of large oscillations even following small excitation, with the drawback of much lower displacement symmetry, negatively affecting the expected quality factor.

The *circular drum* membrane (M3) shows the opposite behavior. Since it is completely anchored to the substrate, the oscillation's amplitude is very reduced but the associated resonant modes are characterized by higher resonance frequencies (i.e. its first fundamental mode falls at an expected resonance frequency of 12428.757 Hz) and higher spatial symmetry. The structure M4 was designed according to the rectangular structure for standard CEPAS systems [158, 184], for comparison purposes with the other novel structures. Finally, the *racket-shaped* cantilever M5 represents a variation of the conventional rectangular shape, characterized by a thinner anchored base and larger free-end. This alternative architecture can provide potentially a better quality factor due to a different mass distribution, and more efficient acoustic collection due to the reduced intrinsic inertia. The first (M5a) and the third resonant modes (M5b) were investigated in this case.

3.1.2 Experimental setup

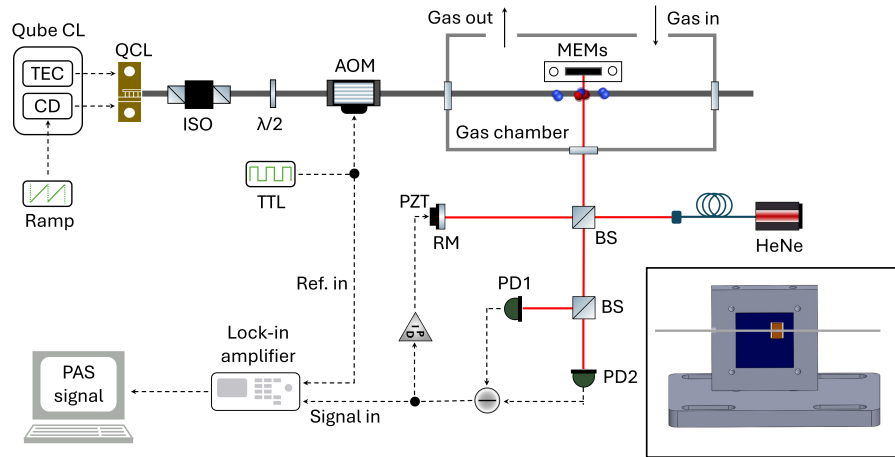


Figure 3.6: Schematic representation of the setup implemented for the MEMS structures characterization. TEC: temperature Controller. CD: current driver. QCL: Quantum Cascade Laser. ISO: optical isolator. $\lambda/2$: half wave-plate. AOM: acousto-optic modulator. HeNe: Helium-Neon laser. BS: beam splitter. PD: photo-diode detector. RM: reflective mirror.

The mechanical and photo-acoustic characterizations were performed with a simplified setup version described in Section 2.1, and its schematic representation is reported

in Figure 3.6. The measurements were carried out in a *bare* configuration, i.e. without acoustic and/or optical resonators.

Each MEMS was mounted on a custom-made anchoring system, whose 3D-rendering is shown in the Inset of Figure 3.6. This system allows keeping the MEMS coaxial to the mid-infrared beam (sketched in the figure in blurred gray), and as close as possible to the point-size sound wave source. Furthermore, each MEMS structure was properly aligned with both the readout beam (i.e. the HeNe) and the excitation laser (i.e. the QCL) as shown in Figure 3.7. The first one was aligned to hit the region affected by the highest displacement (according to the simulations) to maximize the acoustic-to-voltage transduction, except for the structure M2. The position of the QCL was experimentally optimized to simultaneously maximize the amplitude of the photo-acoustic signal and the associated signal-to-noise ratio.

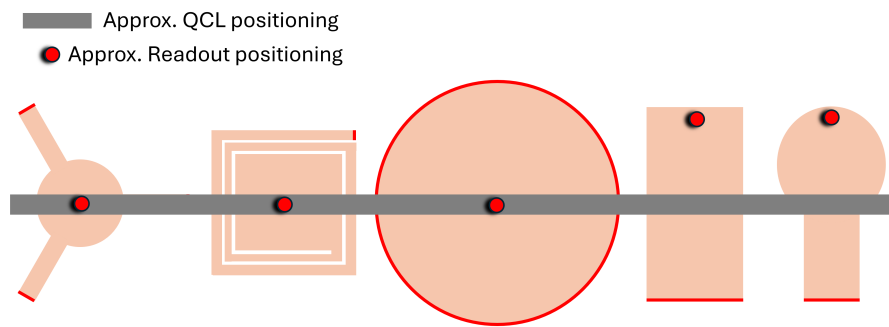


Figure 3.7: Excitation and readout beams positioning on each MEMS structure. The gray blurred line represents the approximated location of the mid-IR laser beam for the pressure wave generation. The red spot indicates the position where the He-Ne laser, used for the interferometric readout, hits the structures.

3.1.3 Mechanical response characterization

According to the experimental routine already discussed in Subsection 3.3.1, a complete characterization of the mechanical features of the investigated MEMS structures was preliminary performed within a pressure range from 5 mbar to 300 mbar.

As an example, Figure 3.8 reports the resonant curve spectra at a fixed working pressure of 20 mbar. To make the comparison more effective all the data were normalized to their respective peak values. Table 3.6 reports the investigated resonant mode, the comparison between the theoretical (f_{th}) and measured (f_0) frequencies, the percentage difference between these two latter values, the Full Width at Half Maximum (Δf), and the quality factor (Q) of the MEMS structure at 20 mbar.

M1 shows a percentage difference of around 43% between the simulated and the experimental resonance frequencies, while in all the other cases this difference lies between more acceptable values, from 1 % (for M2) and 22 % (for M3). This discrepancy is linked to a non-optimal release of M1 on its substrate during the fabrication process, leading to a final structure slightly different from the simulated one. All the MEMS resonances show a very narrow FWHM, from 2.3 Hz to 4.6 Hz, except for M3, whose measured mode width is 25.8 Hz. The structures M1, M2, M4, and M5 are all characterized by a geometry where the boundaries are only partially anchored

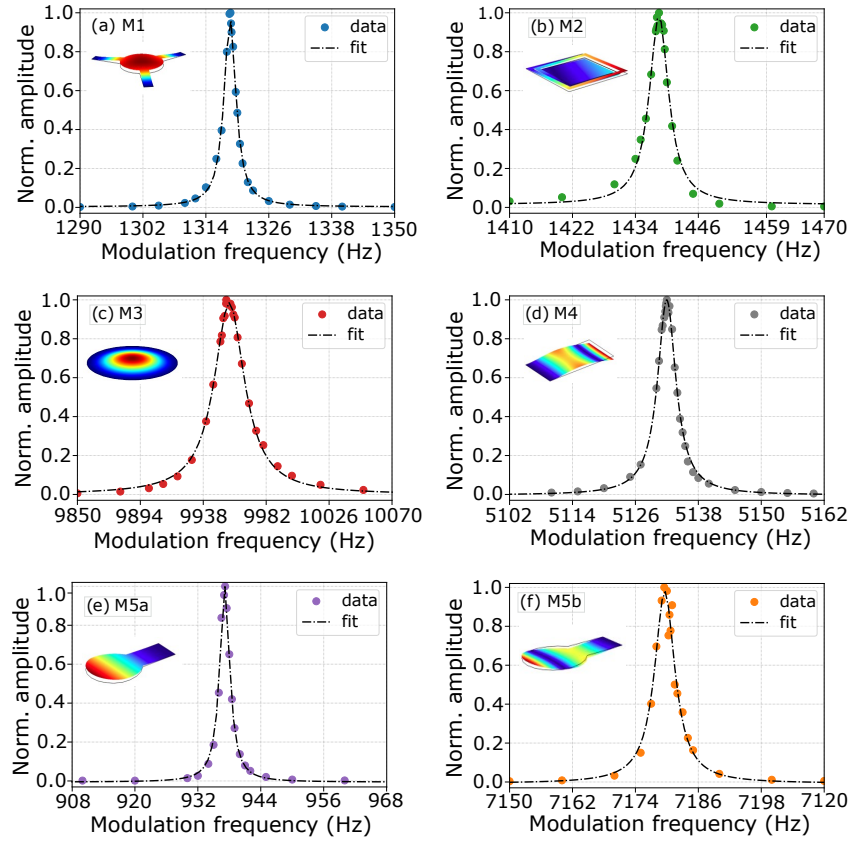


Figure 3.8: Normalized R^2 -component signals versus modulation frequency at a fixed working pressure of 20 mbar for (a) M1, (b) M2, (c) M3, (d) M4, (e) M5a, and (f) M5b. For each of them, the colored points represent the experimental data, while the dashed black line is the associated Lorentzian fit. Given the FWHM Δf and the central frequency f_0 as the fit results, then the Q-factor can be calculated as $Q = f_0/\Delta f$.

Table 3.6: Theoretical (f_{th}) and experimental (f_{ex}) resonant frequencies, percentage difference, Full Width at Half Maximum (Δf), and quality factor (Q) of the five studied silicon-based structure at a working pressure of 20 mbar. The theoretical resonant frequency was determined in vacuum conditions.

MEMS	f_{th} (Hz)	f_{ex} (Hz)	% diff.	Δf (Hz)	Q
M1	2051.6	1318.6	43.1	2.7	488
M2	1422.2	1438.5	1.14	4.6	313
M3	12428.8	9956.2	22.1	25.8	386
M4	4821.1	5132.0	6.25	4.3	1193
M5a	846.2	937.1	10.19	2.3	407
M5b	6846.2	7179.6	4.75	4.7	1528

to the substrate, while M3 is entirely anchored to it. This crucial difference impacts the response of the investigated structure to the pressure wave generated following the trace-gas non-radiative relaxation. In the first case (M1, M2, M4, and M5), the limited anchoring points allow the MEMS to oscillate with negligible perturbation of the substrate. Conversely, in the second case (M3), the oscillation corresponds to a

strong interaction between the MEMS and the substrate, resulting in a broadening of the resonance curve spectrum and, consequently, a degradation of the quality factor. Furthermore, at a pressure of 20 mbar, only M4 and M5b show Q-factor values above 1000 (1193 and 1528, respectively). Since the photo-acoustic signal is linearly proportional to the Q-factor, a higher signal-to-noise ratio (SNR) is expected for these two higher modes.

To conclude, Figure 3.9 reports the resonance frequency and the quality factor variations as a function of the working pressure respectively. In both cases, the experimental data follows the expected trend: the resonance frequency monotonically decreases as the pressure increases, while the quality factor is in accordance with the theoretical law defined in Equation 2.10.

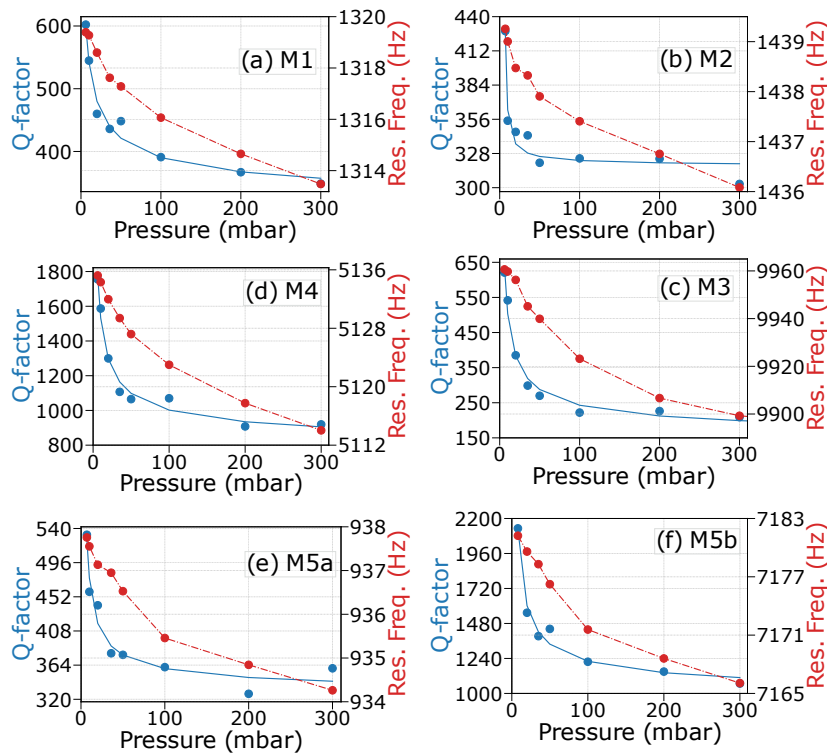


Figure 3.9: Resonance frequency (red data-points) and quality factor (blue data-points) versus the working pressure for: (a) M1, (b) M2, (c) M3, (d) M4, (e) M5a, and (f) M5b. The resonant frequency decreases when the pressure increases. The quality factor follows in all the cases the fit obtained by the Equation 2.10

3.1.4 Performance as acoustic transducers

Once the mechanical properties of the 5 different MEMS structures were characterized, the performances as acoustic transducers were investigated. For each of them, the 1f-PAS spectrum was acquired at different working pressures, ranging from 5 mbar to 300 mbar, and interrogating the strong N_2O rovibrational transition at 2189.273 cm^{-1} (i.e. the same exploited in the work of Chapter 2).

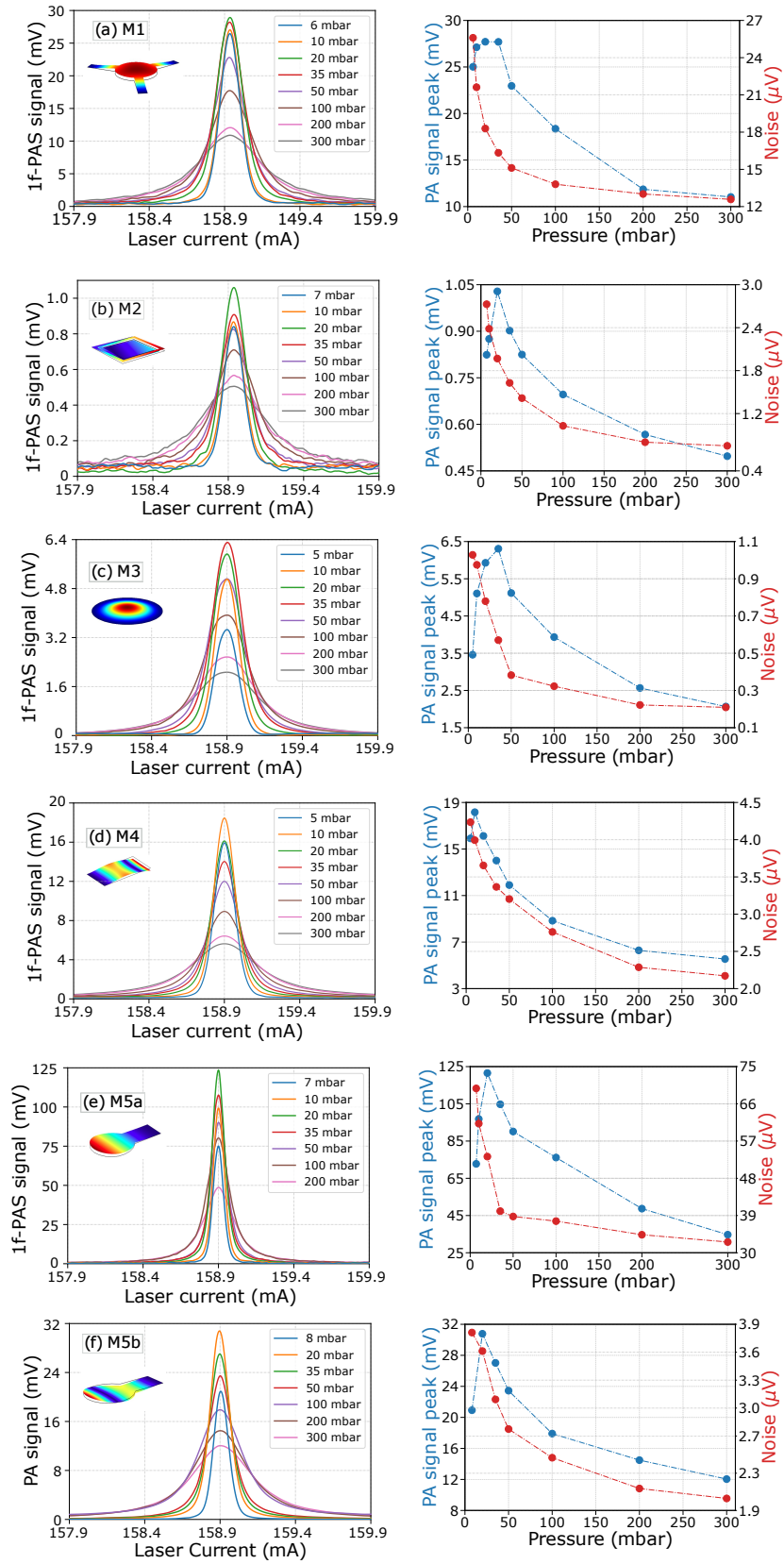


Figure 3.10: 1f-PAS signals at different pressures for: (a) M1, (b) M2, (c) M3, (d) M4, (e) M5a, and (f) M5b. Next to each graph, the relative trends of the signal peak amplitude (blue data points) and the noise level (red data points) are shown.

During the whole measurements, the trace-gas concentration was fixed at 200 ppm within pure N_2 , and the lock-in bandwidth was set to 0.1 Hz, corresponding with a time constant of 0.8 seconds. Figure 3.10 reports a compendium of the measurements.

The overall trend of the photo-acoustic peak signal in pressure (represented by the blue data points) behaves in a very similar way for all the investigated MEMS structures. More deeply, starting from 5 mbar, the PAS signal increases until it reaches a maximum value at relatively low pressures (within a range from 10 to 50 mbar), then it rapidly decreases at higher pressures following the quality factor degradation due to the damping losses increase. Another figure of merit is represented by the photo-acoustic noise level (red data points) that strongly affects the final detection sensitivity estimation. As expected, the noise monotonically decreases when the pressure increases in all six investigated cases, mainly due to the smaller *free* vibration amplitude of the structures at higher pressures.

Additionally, as a general trend, the noise level shows an inverse proportionality with the resonance frequency, justified by the combination of the electronic flicker noise that typically drops down as $1/f$ [185], and the acoustic noise usually more pronounced at lower frequencies. In fact, starting from a level of the order of tens of μV for a resonant frequency around 900 Hz (M5b, Figure 3.10(e)), the noise decreases by 2 order of magnitude for a resonant frequency around 10 kHz (M3, Figure 3.10(c)).

Once the signal-to-noise ratio is computed, it is possible to have access to the Noise Equivalent Concentration achieved by each structure as a function of the pressure. The experimental results are reported in Figure 3.11.

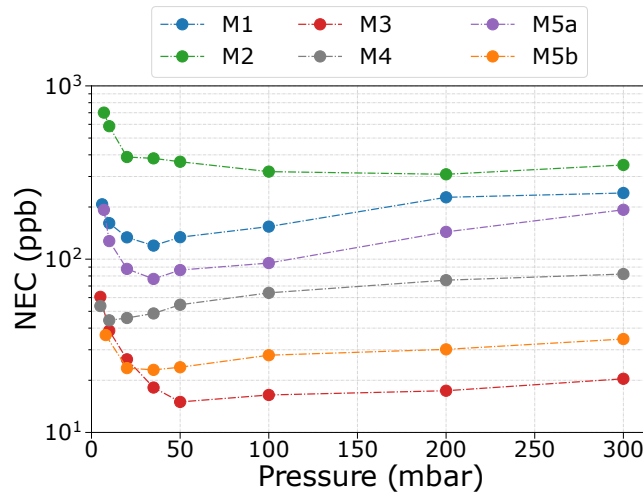


Figure 3.11: Noise Equivalent Concentration as a function of the working pressure for the different structures investigated. As reported in the legend: blue dots for M1, green dots for M2, red dots for M3, grey dots for M4, purple dots for M5a, and orange dots for M5b.

As a general trend, the NEC decreases as the resonance frequency increases. In fact, the structures M1, M2, and M5a, characterized by resonant modes at lower frequencies, show a NEC laying in the 100-1000 ppb range (blue, green, and purple curves in Figure 3.11, respectively). On the other side, all the other three investigated cases (M3 in red, M4 in grey, and M5b in orange), characterized by higher resonant frequencies (10 kHz, 5 KHz, and 7 kHz respectively), show one order of magnitude better sensitivities, with a MDL laying in the 100-10 ppb range, for 0.8 seconds of averaging time. This evidence

highlights how the detection sensitivity depends on a trade-off between the oscillation amplitude and the environmental noise affecting the structure's oscillations themselves.

As an explanatory example, it is possible to compare the performances of the *racket-shaped* cantilever (M5) when investigated in the first (M5a) and third (M5b) modes, at a fixed pressure of 20 mbar. According to Figures 3.10(e) and 3.10(f), a factor $\simeq 4$ between the PAS peak amplitude at 900 Hz and 7 kHz (122 mV and 27 mV respectively) was observed. This confirms that the fundamental resonant mode excitation leads to a bigger displacement when compared to its overtone, for the same-impinging pressure wave intensity. However, due to the larger environmental noise contribution at lower frequencies, the discrepancy between the photoacoustic peak amplitude is counterbalanced by the much lower noise level at 7 kHz (3.1 μ V compared to a value of 53.2 μ V obtained at 900 Hz), resulting in a higher signal-to-noise ratio, and consequently higher sensitivity.

3.1.5 Summary and Conclusion

In this section, novel geometries of silicon-based micro-electro-mechanical systems to be applied as acoustic transducers in a photoacoustic-based trace-gas setup were presented and investigated. After having chosen resonant modes expected to fall approximately into the 1-10 kHz frequency range, the mechanical properties and the photoacoustic responses were experimentally investigated.

Among all the six resonant modes investigated, the highest quality factors were recorded by the third resonant modes of the two cantilevers (M4, and M5b) lying respectively above 800 and 1000 within the investigated pressure range.

Regarding the photoacoustic response, this comparison highlighted that, as a general trend, better performances are achieved when the MEMS structures are operated at higher resonant frequencies, characterized by higher Signal-to-Noise ratios. This evidence is summarized in Figure 3.12, where the minimum detection limit (MDL) achieved by each MEMS structure is reported and re-arranged in ascending order with the resonance frequency.

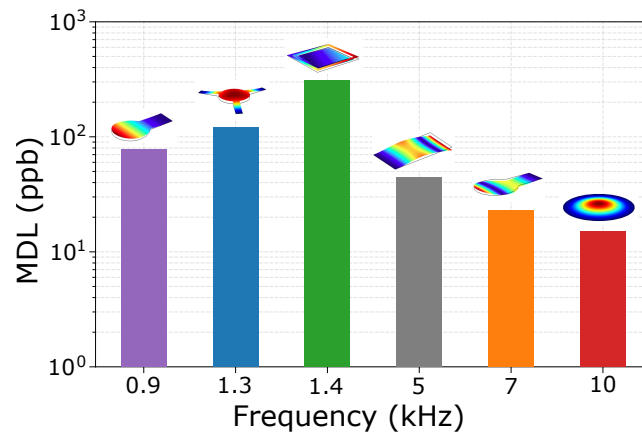


Figure 3.12: Minimum detection limit reachable by each MEMS structure sorted in ascending order with the resonant frequency.

The best performances were achieved with the *racket-shaped* cantilever in its third

mode around 7 kHz (M5b), and with the *circular drum* membrane at its first mode around 10 kHz (M3), showing similar sensitivity levels. Given a QCL impinging radiant power of approximately 16 mW, minimum detection limits of 23 ppb and 15 ppb were achieved with M5b and M3 respectively. The corresponding normalized NNEA coefficients are equal to $2.6 \times 10^{-8} \text{ cm}^{-1} \text{ WHz}^{-1/2}$ and $1.7 \times 10^{-8} \text{ cm}^{-1} \text{ WHz}^{-1/2}$ respectively. These values are comparable to the state-of-the-art of the main *bare* cantilever- and QTF-based photoacoustic sensing techniques [186, 187]. Furthermore, the structures M5b and M3 show a very limited deterioration of their sensitivity when operated at high pressure, up to 300 mbar (see Figure 3.11). This feature, together with their weak dependence on environmental noise, makes the structures M3 and M5b two good candidates for direct open-air sensing.

To conclude, the results discussed in this section open the doors to developing MEMS-based photoacoustic trace-gas setups with improved performance going beyond the state-of-the-art, exploiting advanced photoacoustic schemes where the use of acoustic [102, 173] and optical resonators [57, 60] is expected to further increase the sensitivity already achieved.

3.2 Achieving the sub-ppb detection sensitivity with a dual-tube MEMS-based spectrophone

The following section reports the work summarized in our published article in 2024 in *Photoacoustics (Elsevier)* [64], in collaboration with the *Italian Space Agency* (ASI) of Matera, and the *Institute for Microelectronics and Microsystems* (CNR-IMM) of Bologna. Taking as a starting point the results highlighted in Section 3.1, this section describes a novel spectrophone configuration, combining one of the best MEMS structures with a cost-effective and easy-to-build dual-tube resonator, allowing a further enhancement in the detection sensitivity through acoustic wave amplification.

Among the two best-performing structures investigated, i.e. the *circular drum* membrane and the *racket-shaped* cantilever, the choice fell on the second one for two reasons. Firstly, the *racket-shaped* cantilever is almost completely unanchored from the SOI substrate, except for the 1 mm smaller side (see Figure 3.5a), thus providing good independence of its resonant modes from any external contribution. This is not the case with the *circular drum* membrane, whose boundaries are completely anchored to the substrate (see Figure 3.3a). In this case, it was experimentally demonstrated that the first resonant mode's frequency undergoes a significant shift (within a range approximately from 16 kHz to 9 kHz) when changing the stress exerted by the screws fixing the entire structure (MEMS plus substrate) to the anchoring systems. Secondly, choosing a transducer resonant at around 7 kHz instead of 10 kHz allows for coupling an acoustic resonance geometry whose dimensions (i.e. internal diameter and length) are advantageous for easy coupling with the excitation laser beam. Net of a small difference in the minimum detection limits, and considering the two discussed fundamental technical aspects, the *racket-shaped* cantilever was considered the best choice. The work performed develops in three parts.

1. Four different dual-tube systems were realized, characterized by a similar geo-

metry (in length and internal diameter). Two were fabricated with plastic materials, commonly used in 3D printers and particularly easy to handle, while the other two are metallic tubes, widely exploited in QEPAS sensors [188]. Each of them was coupled with the *racket-shaped* MEMS structure to quantify the signal enhancement compared to the *bare* configuration (i.e. without any acoustic resonance).

2. Once having determined the best material, several dual-tube systems with different lengths and internal diameters were tested to find the best enhancement performance.
3. With the best couple of geometric parameters, the spectrophone's detection sensitivity was tested at a fixed trace-gas concentration and varying the sample pressure within a range from 8 mbar to 335 mbar. Finally, the long-term stability and the achievable minimum detection limit were analyzed at the best pressure working point (i.e. where the signal-to-noise ratio is the highest).

3.2.1 Spectrophone design

A proper acoustic resonator can be used to locally increase the amplitude of the pressure wave impacting the MEMS structure, leading to an increase in the spectrophone's sensitivity. The conventional and most used symmetry is cylindrical for laser-based photoacoustic techniques, developed in two possible variants. In the first case, the laser beam is accommodated between a single tube equipped with an aperture in correspondence with the sensitive element (single-tube configuration) [101, 161, 189], while in the second case, the laser beam passes through a pair of millimetric tubes, defining the so-called dual-tube configuration [102, 190].

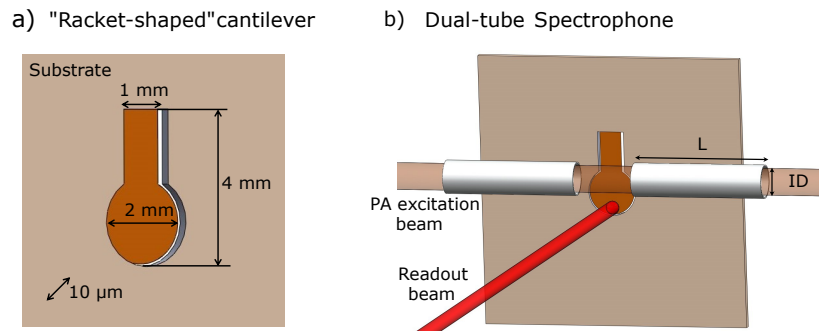


Figure 3.13: (a): front view of the "racket-shaped" cantilever and its associated dimensions. The oscillating structure is depicted in darker orange, while the substrate is colored in lighter orange. (b): front view of the assembled spectrophone, made by the coupling of the MEMS with a dual-tube acoustic resonator system. The laser beam exploited for the photo-acoustic effect (PA excitation beam, depicted in light orange) is aligned to cross co-axially the tubes, thus maximally exploiting the acoustic wave intensity enhancement. The readout beam used to convert the structure's oscillation into a measurable voltage signal via an interferometric readout is colored in red and aligned with the region affected by the highest displacement.

The spectrophone developed in this work, whose 3D sketch is depicted in Figure 3.13(b), takes its inspiration from the second configuration. This choice is justified by the fact that, in the case of a single-tube architecture, the experimental search for the best possible configuration associated with the sound wave intensity amplification

becomes more complicated due to a higher number of geometrical parameters to be simultaneously controlled (i.e. length, internal diameter, but also the shape and the geometrical dimensions of the aperture for the interaction between the sensitive element and the sound wave). Instead, in the dual-tube configuration, the experimental parameters to be checked are reduced to the internal diameter and the length. So, in the perspective of developing a systematic experimental characterization of the transducer-resonator acoustic coupling, and at the same time simplifying the manufacturing process, the dual-tube configuration is the best choice. However, exploring different geometric wave confinement for acoustic amplification could be a very interesting and challenging future activity to investigate.

According to the theory, the optimal length of each tube L_T is linked to the chosen MEMS resonance frequency f_0 , by the following equation [102]:

$$L_T = \frac{v_s}{2f_0} - \frac{16I_D}{3\pi} \quad (3.1)$$

where v_s is the speed of sound (equal to 343.4 ms^{-1} in air at a temperature of 20°C), and I_D is the resonator internal diameter. The optimal length of an open-ended tube differs from a closed resonator by a factor of $8I_D/3\pi$ for each aperture [191, 192]. This difference, known as open-end correction (OEC), takes into account the boundary conditions existing for a standing wave of a specific frequency inside the resonator: compared to the case of closed resonators, the anti-nodes appear slightly outside the tubes due to the interaction between the resonator and the external environment, reducing its optimal length. Although for each I_D there is a unique correspondence with the optimal length, there is no analytical methodology that links the chosen pair (L_T, I_D) to the effective acoustic enhancement, which thus has to be measured experimentally.

For this reason, the dimensions of the resonator's tube were preliminary chosen taking inspiration from published studies carried out with similar photoacoustic-based setups. In particular, in the work of *Patimisco et al.* [152], a pair of tubes with an internal diameter equal to 1.6 mm were exploited for the amplification of a 12.46 kHz sound wave. By operating a simple proportion, an internal diameter of approximately 2.77 mm and consequently, resolving Equation 3.1, a length of 19.18 mm represent good values for efficient amplification of our 7.18 kHz sound wave frequency.

In addition to the size, the fabrication material could also play a fundamental role in the amplification capability of the dual-tube system. Hence, a comparative analysis of these two properties is crucial. Accordingly, four different types of material were selected to quantify any differences in performance related to chemical-physical features or production defects. Two pairs were made via 3D printing/additive manufacturing in UV curing resin and Polylactic acid (PLA) via liquid crystal display (LCD) resin printer and filament printer respectively. The other two, made of stainless steel and brass, were fabricated with more common computerized numerical control (CNC) techniques and subtractive manufacturing.

Figure 3.14 shows the top and front-side view of the four types of resonators realized for the comparison, while Table 3.7 reports the associated length, internal diameter, and external diameter (measured with a digital caliper with a precision of 0.01 mm). A more accentuated surface roughness, due to the limitations of the manufacturing

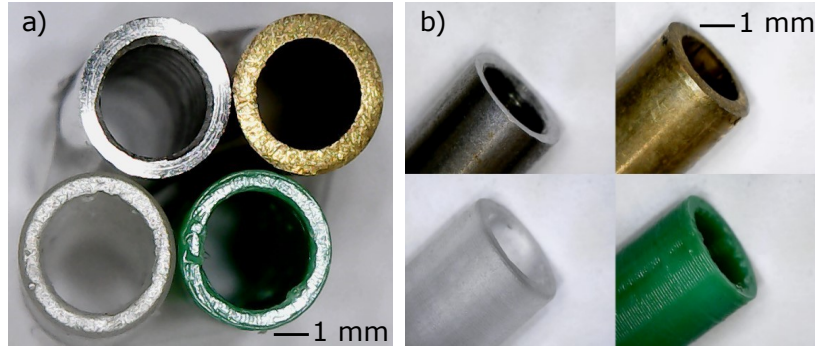


Figure 3.14: Top (a) and front-side views (b) of the four different resonators under investigation: stainless steel (top left), brass (top right), UV resin (bottom left), and PLA (bottom right).

Table 3.7: Material, length (L_T), internal diameter (I_D), and external diameter (E_D) of the four different resonators investigated. The small discrepancies between internal diameters depend on the manufacturing process of each material.

Material	L_T (mm)	I_D (mm)	E_D (mm)
Stainless steel	19.20	2.75	3.98
Brass	19.20	2.75	4.00
PLA	19.20	2.75	3.99
UV Resin	19.20	2.81	4.09

technique, can be observed for PLA resonators (machine resolution $200\mu\text{m}$). The surface roughness of the UV Resin tubes, although barely visible from the image, is slightly worse compared with one of the metal resonators, with a nominal machine resolution of $50\mu\text{m}$ (pixel size of the LCD display). According to this evidence, it is interesting to compare the overall performances of these four resonators to understand how the surface roughness affects acoustic wave amplification.

The experimental apparatus is the one already exploited for the MEMS structures characterization (whose details are reported in Subsection 3.1.2), but with one small complication, as reported in Figure 3.15.

Compared to the bare-MEMS configuration, in this case, the coupling between the *racket-shaped* cantilever and the dual-tube system has to be carefully performed, ensuring the maximization of the acoustic coupling. The experimental procedure consists of several steps, repeated for all the dual-tube systems investigated. Firstly, the QCL beam was properly aligned with the MEMS structure without the tubes to maximize the interaction between the circular free-end of the structure and the acoustic wave generated via the photo-acoustic effect. The second step concerns the insertion and alignment of the tube, coaxially with the QCL beam. To facilitate this operation the tubes were placed in the right position with the help of a *V-groove*. To ensure collinearity and to avoid any touching, the tubes were positioned at a distance of around $200\mu\text{m}$ from the *racket-shaped* MEMS with the help of a USB microscope.

A focal lens (FL, $f = 150\text{ mm}$) focalizes the beam at the center of the dual-tube system, thus making its radius inside the system considerably smaller than the tube's

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internal diameter (ranging from 2.75 mm to 3.34 mm). In fact, given a beam radius approximately equal to $\simeq 1$ mm when impinging the focal lens, the beam diameter in the middle of the tubes is reduced up to 0.43 mm, and at 20 mm from the middle (i.e. approximately at the tube entrance) is approximately equal to 0.51 mm. This confirms that there is no possibility that the beam will touch the tube's walls. Additionally, the tube-system alignment was performed with the help of a power meter (PM) placed just after the output window of the sample cell and aligned with the QCL beam. The optical power was measured firstly without the tubes, and then it was measured again once the tubes were positioned to monitor any variation due to the beam's interaction with the walls.

The chamber was filled via a gas cylinder containing 200 ppm of N_2O in pure nitrogen, while the working pressure was varied and managed via a vacuum pump (PFEIFFER DualGauge), a pressure controller (PFEIFFER HiCUBE) and a system of needle valves (not shown in Figure 3.15). In this way, it was possible to evaluate the acousto-optical response of the resonators–MEMS system for a constant concentration of the target gas and pressure. All the 1f-PAS spectra were acquired by setting the lock-in 3dB cut-off bandwidth to 0.1 Hz.

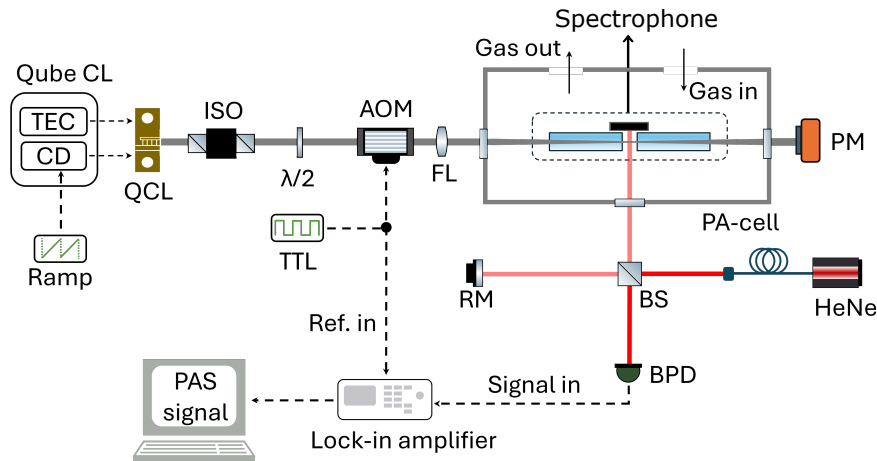


Figure 3.15: Schematic representation of the setup. QCL: Quantum Cascade Laser. CD: current driver. TEC: temperature controller. ISO: optical isolator. AOM: acousto-optical modulator. PM: power meter. He-Ne: Helium-Neon laser. RM: reference mirror. PZT: piezoelectric material BPD: balanced photo-detector. REF in: reference signal. For graphical reasons, the following components are not reported in the sketch: the gas pressure control system (a vacuum pump, a pressure controller, and a system of needle valves), and four- and half-wave plates used to balance properly the interferometric arms.

3.2.2 Result and Discussion

Material comparison

During the material comparison, the pressure inside the chamber was fixed to 300 mbar. The acquired 1f-PAS spectra in the four cases were compared to the one obtained with the *bare* configuration (i.e. without any acoustic resonance) in the same working condition.

According to Figure 3.16, starting from a peak value equal to 10.86 mV with the *bare* MEMS cantilever, peak values equal to 102.88 mV, 97.63 mV, 103.71 mV,

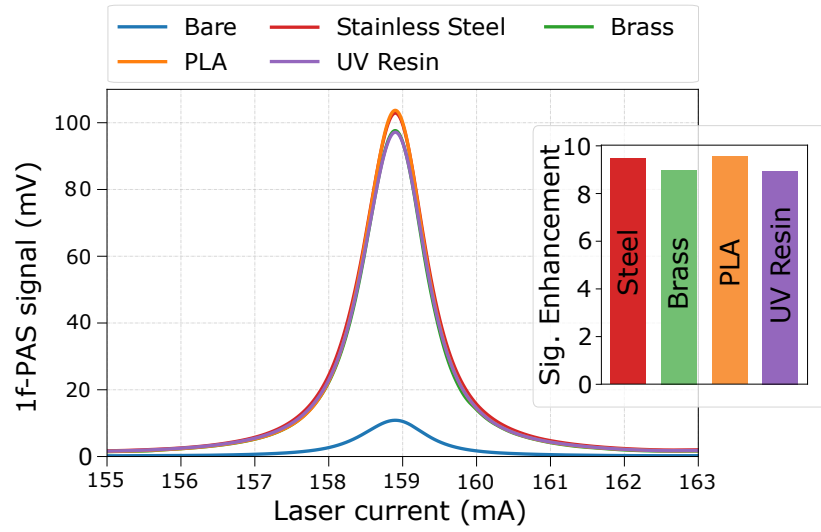


Figure 3.16: Comparison between the 1f-PAS spectra obtained with the dual-tube configurations of different materials (stainless steel in red, brass in green, PLA in orange, and UV RESIN in purple) and the 1f-PAS spectrum in the *bare* configuration (depicted in blue). For all the traces the sample pressure within the aluminum cell was fixed at 300 mbar. **Inset:** signal enhancements with the four investigated material. These values are defined as the ratio between the peak signals in dual-tube and bare configurations.

and 97.15 mV were measured adding the dual-tube resonator of stainless steel, brass, PLA and UV RESIN respectively. As reported in the Inset of Figure 3.16, each of them corresponds to a peak signal enhancement equal to 9.47, 8.99, 9.55, and 8.95 respectively. Discrepancies of less than 5% on the peak signal between the various materials investigated can be ascribed to slightly different positioning of the resonator tubes within the setup rather than a difference in signal enhancement due to the material itself. This evidence also highlights that the surface roughness due to the fabrication material does not play an appreciable role in determining the acoustic amplification performances.

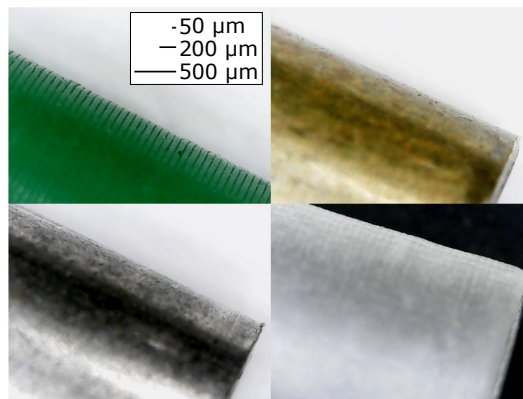


Figure 3.17: Surface roughness of each investigated tube observed via the USB microscope.

In this case of study, the surface roughness mainly depends on the type of processing. For additive techniques, the PLA is printed through a nozzle with a diameter of 400 μm , and the machine resolution is of the same order of magnitude, typically about half the size of the nozzle. While the UV Resin is polymerized through an LCD display

with a pixel size of $50\text{ }\mu\text{m}$. For the materials processed with subtractive techniques (i.e. brass and stainless steel), the roughness obtainable with a lathe and column drill is typically in the order of tens of micrometers or even less. A surface analysis using the USB microscope is shown in Figure 3.17, highlighting these critical issues of the printing technique. At the same time, however, the sound wavelength for a 7.18-kHz modulation frequency corresponds to 47.8 mm, i.e. three orders of magnitude greater than the worst surface roughness analyzed (i.e. $\approx 200\text{ }\mu\text{m}$ for PLA). It is evident that, in this experimental condition, the surface roughness does not have an appreciable influence on the sound wave propagation quality inside the tubes.

Best geometry investigation

Since the manufacturing material does not introduce appreciable differences in the amplification ability of the dual-tube system, the choice for the best geometry investigation fell on the UV Resin. In fact, if the subtractive techniques exploited for the metal tube fabrication are time-consuming and polluting, while the tubes made of PLA have very long production times (half an hour per pair), in the case of UV Resin it is possible to produce a high number of pairs of tube in a single one-hour processing.

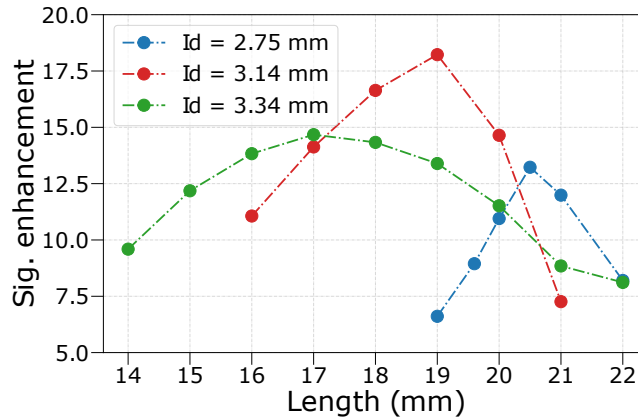


Figure 3.18: Comparison between the signal enhancement of the dual-tube configuration made of UV Resin with different lengths and internal diameters. The three data sets are obtained fixing the internal diameter (blue trace $I_D = 2.75\text{ mm}$, red trace $I_D = 3.14\text{ mm}$, and green trace $I_D = 3.34\text{ mm}$ respectively), and varying the single tube length.

To perform a comprehensive study, different sizes were investigated in addition to the set described in Table 3.7, all designed to operate in the 7-kHz amplification range. A summary is reported in Figure 3.18. For each pair of tubes, the 1f-PAS spectrum was acquired and the associated peak value was compared with the one obtained in the *bare* configuration, retrieving the signal enhancement factor. These measurements were performed on the same experimental condition of the material comparison.

Following the discussion of Section 3.2.1, as the internal diameter of the resonators increases, the associated optimal length decreases. In fact, if for an internal diameter of 2.75 mm the associated optimal length is equal to 20.5 mm, when I_D is increased to 3.34 mm, L_T decreases up to 17 mm. The greatest signal enhancement, equal to 18.22, was obtained with a pair of resonators with an internal diameter of 3.14 mm and a length of 19 mm. According to Equation (3.1), the expected optimal resonator length with $I_D = 3.14\text{ mm}$ and developed to amplify sound waves around 7.18 KHz should be

18.56 mm, highlighting that the experimental results are in good agreement with the theory.

Spectrophone's response with pressure

Mechanical characterization Before identifying the detection sensitivity, the mechanical properties of the spectrophone were experimentally investigated with the same routine introduced in Section 2.2.1. In general, when a transducer (the MEMS structure in our case) is coupled with an acoustic resonator, the overall mechanical response of the spectrophone is a convolution of the two independent contributions. As a result, the resonance curve spectrum of the system (transducer plus acoustic resonator) undergoes a broadening compared to the one associated with the transducer in a *bare* configuration, under the same experimental conditions.

This behavior was observed also in our case of study. As an explanatory example, Figure 3.9 reports a comparison between the resonant curve spectra of the MEMS structure in the *bare* configuration (in blue) and of the spectrophone (i.e. MEMS plus dual-tube resonator, in red) at a pressure of 300 mbar. To make the comparison more effective, the two curves were overlapped by changing the x-axis from resonance frequency to relative distance from the central frequency Δf .

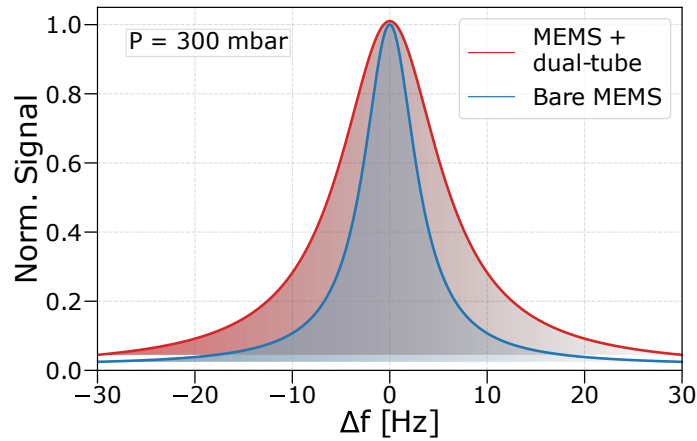


Figure 3.19: Resonant curve spectra of the MEMS structure in the bare configuration (blue curve) and of the spectrophone (MEMS + dual-tube system, red curve) at a pressure of 300 mbar.

When the *racket-shaped* cantilever is coupled with the dual-tube acoustic resonator the FWHM of the resonance curve spectrum increase from 6.49 Hz (in the *bare* configuration) to 12.38 Hz, resulting also into a Q-factor reduction from 1067.8 to 577.8. At the same time, the coupling with the acoustic resonator leads to a shift in the resonance frequency from 7.166 kHz to 7.152 kHz.

Photoacoustic measurements Given the best dual-tube configuration ($I_D = 3.14$ mm, $L_T = 19$ mm) the 1f-PAS spectra were acquired at several discrete pressure values ranging from 8 to 335 mbar, as reported in Figure 3.20

Comparing this latter trend with the one associated with the *bare* configuration, the coupling between the *racket-shaped* cantilever and the dual-tube system determines a shift of the best working point at higher pressure, as shown in Figure 3.21(a). In fact, if

3.2 Achieving the sub-ppb detection sensitivity with a dual-tube MEMS-based spectrophone

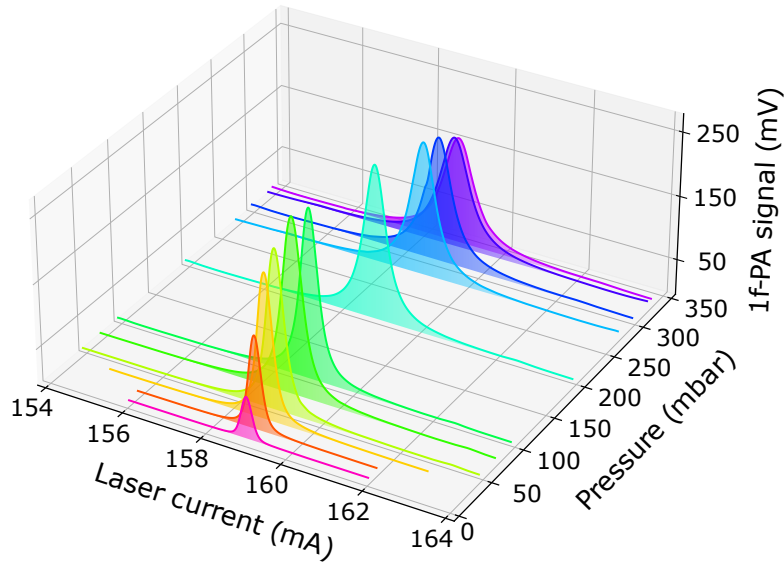


Figure 3.20: 1f-PAS spectra acquired with the best dual-tube configuration ($I_D = 3.14$ mm, $L = 19$ mm) as a function of the sample pressure.

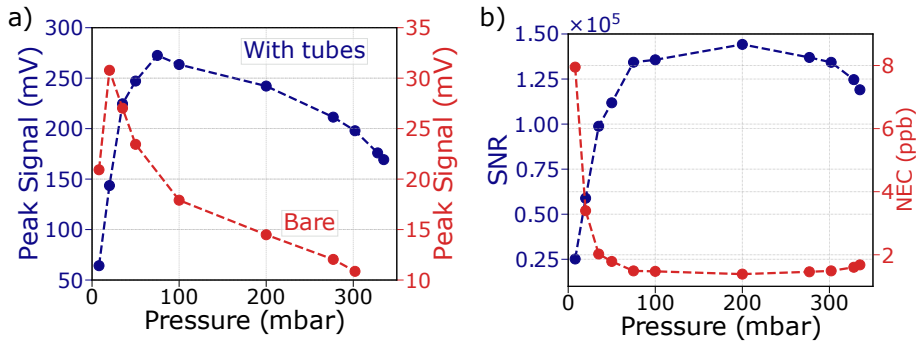


Figure 3.21: (a): peak signal values as a function of the pressure in dual-tube (blue trace) and *bare* (red trace) configurations. (b): SNR (blue trace), and NEC (red trace) trends as a function of the sample pressure for the dual-tube configuration, both obtained with a 3dB cut-off LIA bandwidth equal to 0.1 Hz

for the *bare* configuration the highest peak signal, equal to 30.78 mV, was measured at a pressure of 20 mbar, in the dual-tube configuration the best condition, associated with a peak signal equal to 272.52 mV, was found at a pressure of 75 mbar. This evidence can be attributed to the acoustic enhancement pressure dependence, based on the necessity of having a suitable number of molecules for its maximization. Furthermore, following an increase of the signal in the low-pressure range, after reaching its maximum peak value, it explores a decrease at higher pressure due to the well-known increases of the pressure-dependent viscous damping losses [193].

Then, for each value of pressure, a 60-second-long noise trace was acquired with the same 3dB cut-off LIA bandwidth used to collect the 1f-PA spectra (i.e. 0.1 Hz, corresponding to a lock-in time constant equal to 0.8 s), and the standard deviation was computed to retrieve the 1σ noise. In this way, it is easily possible to access both the SNR and the NEC. According to Figure 3.21(b), the SNR (blue trace) remains approximately constant within 75 mbar and 300 mbar, ranging from 1.343×10^5 to 1.247×10^5 . The highest value, equal to 1.442×10^5 , occurs at 200 mbar, where the

photo-acoustic signal amplitude degradation due to the damping effect and the overall noise level reduction effects reaches the optimal trade-off. With the latter pressure, the minimum value of the spectrophone's NEC (red trace) was reached, being equal to 1.39 ppb.

Finally, an Allan-Werle deviation analysis was performed to investigate the stability and the overall behavior of the spectrophone as a function of the integration time. A long-time trace was acquired by fixing the laser current at the N_2O absorption peak but filling the chamber with 200 mbar of pure N_2 to prevent the QCL beam interaction with any residual trace-gas spectral features. Furthermore, the 3B cut-off LIA bandwidth was set to 1 Hz during the acquisition, corresponding to an integration time of 0.08 s and a roll/off equal to 18 oct/decade. This choice allows investigating the sensor's performances in different time regimes, starting from its real-time response (i.e. at 0.08 seconds), up to an average response of 30 seconds. The results are reported in Figure 3.22.

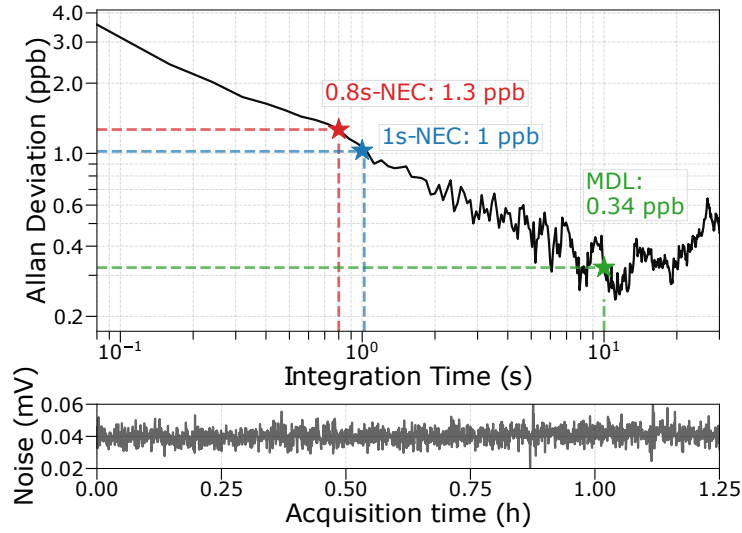


Figure 3.22: Long-time noise acquisition (lower panel), and associated Allan deviation analysis (upper panel) converted from noise level (mV) to noise equivalent concentration (ppb). The red star represents the point of the Allan deviation obtained at an integration time equal to 0.8 s, whose value is in accordance with the one estimated via the 1σ analysis setting the LIA to 0.1 Hz of 3dB cut-off LIA bandwidth (corresponding to a time constant of 0.8 s). The blue star represents the NEC obtained at 1 second of averaging time, while the green star is the MDL achieved when increasing the integration time up to 10 seconds.

At an integration time of 0.08 seconds (first point of the Allan-Werle deviation), the spectrophone achieves a NEC of 3.6 ppb, corresponding to a NNEA equal to $1.3 \times 10^{-9} \text{ cm}^{-1} \text{ WHz}^{-1/2}$. Moving to 0.8 seconds, the NEC reaches a value in agreement with the one obtained from the 1σ noise analysis (equal to 1.3 ppb, represented by the red star in Figure 3.22(b)), since they are both associated with the same integration time. Then, averaging up to 10 seconds allows the system to achieve a sub-ppb minimum detection limit, being equal to 0.34 ppb (green star in Figure 3.22(b)). Increasing further the integration time is no longer advantageous since the Allan deviation experiences an increase that worsens the overall performance at longer time scales, as already seen in Figures 2.18 (a) and (b).

3.2.3 Conclusions and outlook

With this work, a further step forward was taken, demonstrating how the combination of a novel and high-performing MEMS-based structure (i.e. the *racket-shaped* cantilever), with an easy-to-build acoustic resonator made by a dual-tube configuration, can represent a valid and performing alternative to conventional photoacoustic-based setups to achieve ultra-high detection sensitivity. As far as we know, this study reports record performances for single-pass photoacoustic-based trace gas sensors addressing the same target molecule (i.e. N_2O), in terms of both Normalized Noise Equivalent Absorption coefficient and Noise Equivalent Concentration at 1 second integration time, as summarized in Table 3.8.

Table 3.8: State-of-the-art single-pass photoacoustic sensors for N_2O detection. The last row marked in bold identifies the results achieved in this work. To make a fair comparison, NEC values at the same integration time (1 second) are reported, except for rows five and six. In these latter cases, the 1s-NEC values are neither declared in the main text nor deducible from the graphs presented.

Year	Wavelength (μm)	Power (mW)	NNEA ($\text{cm}^{-1}\text{WHz}^{-\frac{1}{2}}$)	NEC (ppb)	Integration time (s)
2013 [194]	4.61	400	2.9×10^{-9}	23	1
2014 [195]	7.83	250 **	N.A.	6	1
2021 [196]	4.47	100	N.A.	20	1
2021 [197]	4.53	17.5 **	5.69×10^{-9}	28	1
2022 [198]	4.52	25 **	5.4×10^{-9}	7	0.1
2023 [199]	7.84	77	N.A.	9	0.1
2024 [200]	4.56	100	1.5×10^{-8}	4 **	1
2024 [*]	4.56	15	1.3×10^{-9}	1	1

N.A.: data not available

[*]: this work

** : data extracted from the graphs of the related cited work.

In particular, this study demonstrates the possibility of achieving sub-ppb detection sensitivity with a compact and cost-effective spectrophone. These results open interesting perspectives for the development of compact sensors for in-field analysis. Future work can be focused on a further size reduction of the entire system, both testing new geometries and fabrication materials for the sample cell and developing alternative and more performing detection schemes to measure the photoacoustic signal. Furthermore, due to the dual-tube configuration's relatively simple but effective design and the possibility of 3D printing with a large variety of materials, it would be possible to plan the development of low-cost systems with easy integration with different MEMS classes, paving the way to the realization of high-performing trace-gas sensors in harsh environments and working condition up to atmospheric pressure.

However, taking into account the *fil rouge* behind my Ph.D thesis work, the natural and direct evolution of these results concerns the coupling of the developed dual-tube system with the optical cavity, to see if and how much the performance of the developed system has improved compared to the starting point described in Chapter 2, and understand how much the ultimate detection sensitivity can be pushed down. These topics will be explored in the next section.

3.3 Achieving the ppt-level detection sensitivity with the cavity-enhanced dual-tube MEMS-based setup

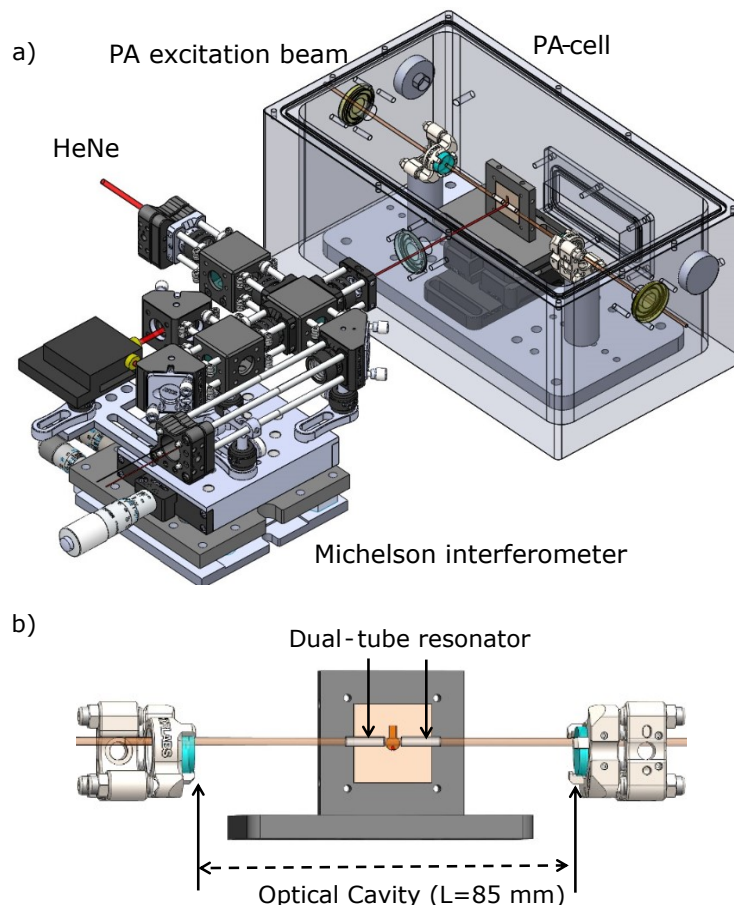


Figure 3.23: **(a)** Three-dimensional rendering of the sensor's core. **(b)**: coupling between the dual tube system and the optical cavity.

The schematic representation of the experimental setup is reported in Figure 3.23 in its 3D representation, highlighting the key components. To maintain consistency with all the work done so far, the same target gas, (i.e. nitrous oxide) and the same absorption line (i.e. $k_0 = 2189.2713 \text{ cm}^{-1}$, $S = 2.14 \times 10^{-19} \text{ cm/molecule}$) were addressed.

The whole interferometer was built on a compact cage system that guarantees good mutual stability between the optical elements. Furthermore, to facilitate the alignment phase, the system is equipped with many additional degrees of freedom (in the three-axis directions and their associated rotation) both on the interferometer and the MEMS structure, provided by a series of micro-metric translation stages. Given this highly stable configuration, which does not require any special mechanical insulation or temperature stabilization systems, when the interferometer is locked to its zero working point (see Subsection 2.1.6), very high repeatability in the photoacoustic signal measurement can be achieved.

3.3.1 Acousto-mechanical characterization

As discussed extensively, the selection of the optimal working pressure for the photoacoustic trace-gas detection must represent a trade-off between the two opposite coexisting trends: the increasing Q-factor with decreasing pressure, and the higher efficiency for the acoustic wave generation at higher pressures. The effect of the two competing effects is well summarized in Figure 3.24, where the 1f-PAS peak signal is reported as a function of the working pressure. Each data point in the figure was extracted by acquiring the 1f-PAS spectra at different pressures and the N₂O concentration within the mixture constant at 1 ppm.

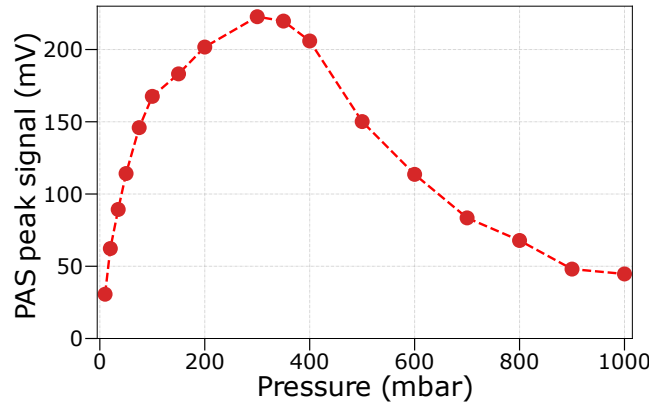


Figure 3.24: 1f-PAS peak signal versus the pressure in cavity-enhanced configuration.

As it is possible to see, despite the Q-factor degradation with pressure, the optimal system's response (corresponding to the maximum of the PAS signal) occurs at considerably high pressure, within a range of approximately 200-350 mbar. This evidence, together with the fact that the cavity-free system showed its best signal-to-noise ratio within a similar pressure range, as reported in Figure 3.21(b), allows it to work in a regime where the saturation effect is prevented. As a consequence, this configuration can leverage a full exploitation of the intra-cavity power build-up at the best possible pressure working point.

3.3.2 Retrieving the ultimate detection limit

As reported in Figure 3.25, the 1f-PAS spectra were acquired with and without the optical cavity at a gas pressure of 300 mbar and maintaining unaltered all the operating conditions except for the trace-gas concentration.

Considering the different concentrations of the gas mixtures in the two cases (i.e. 200 ppm without the optical cavity, and 1 ppm in cavity-enhanced configuration) and the associated peak values, the power buildup introduced by the optical cavity leads to an enhancement factor of approximately 260.

Additionally, the linear response of the sensor was tested at the working pressure of 300 mbar and varying the N₂O concentration in pure N₂ from 1000 ppb up to 20 ppb by progressively changing the relative percentage fractions via the gas blender. Each data point (depicted in red in Figure 3.26) represents the mean value of the 1f-PAS peak signal acquired at the addressed N₂O absorption peak current for 60 seconds. As

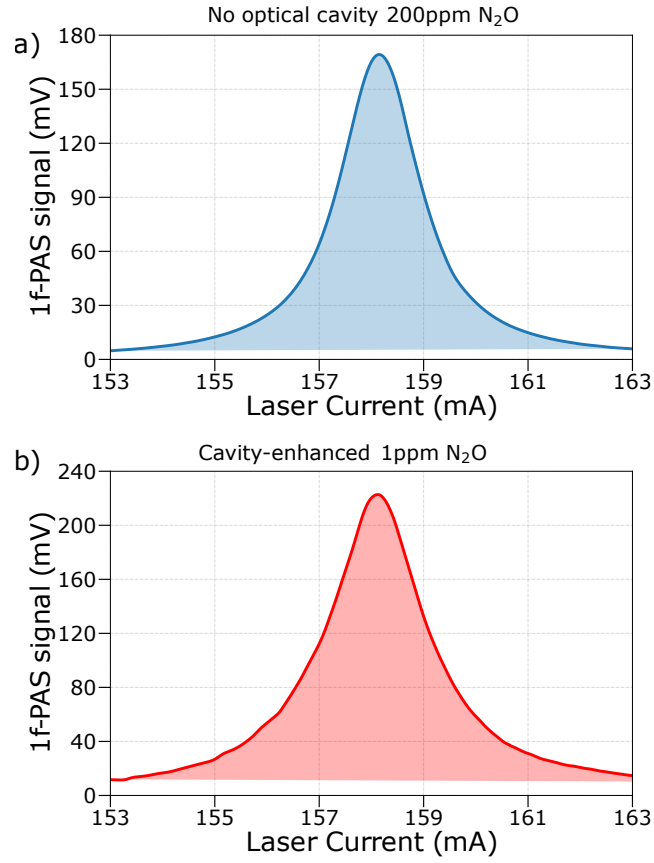


Figure 3.25: (a): 1f-PAS signal obtained without the optical cavity, at a working pressure of 300 mbar and with 200 ppm of N₂O in pure N₂. (b): 1f-PAS signal obtained in cavity-enhanced configuration, at a working pressure of 300 mbar and with 1 ppm of N₂O in pure N₂. Considering the difference in the gas mixture concentration, the peak signal enhancement factor between the two cases is approximately equal to 260.

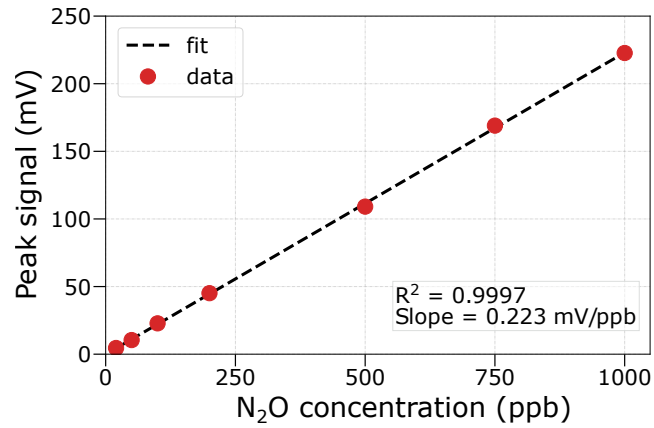


Figure 3.26: Photoacoustic peak signal versus acquisition time at different N₂O concentrations within a range between 1000 ppb and 20 ppb, measured at a pressure of 300 mbar. Each red data point represents the mean value associated with a 60-second acquisition. The black dashed line represents the linear fit applied to the data.

expected, the system follows a good linear response within the investigated range of concentrations, with a slope of 0.223 mV/ppb and an R-squared value of 0.9997.

3.3 Achieving the ppt-level detection sensitivity with the cavity-enhanced dual-tube MEMS-based setup

Again, the long-term stability was studied with an Allan-Werle deviation analysis. The acquisition was performed by filling the chamber with 300 mbar of pure N_2 to prevent any residual interaction with N_2O . The 3dB cut-off lock-in bandwidth was set to 1 Hz, with a time constant of 0.08 s and a roll of equal to 18 dB/octave.

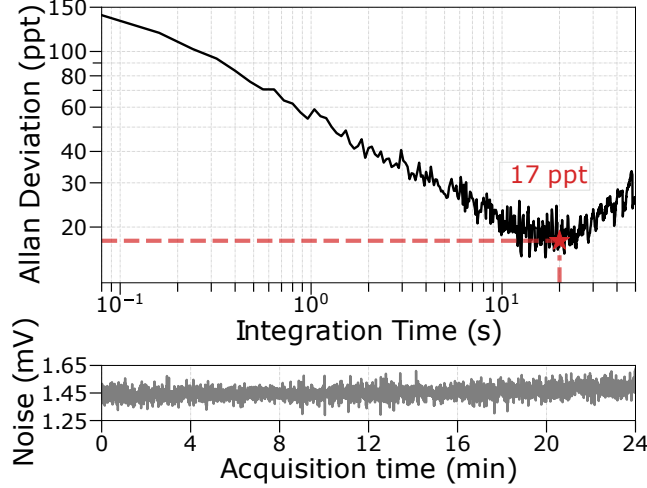


Figure 3.27: Long-time noise acquisition (lower panel) and associated Allan-Werle Deviation analysis (upper panel) directly converted from noise level (expressed in μV) to detection sensitivity (in part-per-trillion). The noise was acquired by filling the chamber with 300 mbar of pure N_2 and setting the 3dB cut-off LIA bandwidth at 1 Hz. The red star identifies the minimum detection limit of the sensor when averaging for 20 seconds.

The results, shown in Figure 3.27, highlight a NEC of 139 ppt at 0.08 seconds integration time (first point of the Allan-Werle plot), corresponding to a NNEA coefficient equal to $5.98 \times 10^{-11} cm^{-1} W Hz^{-1/2}$. The detection sensitivity can be further improved by averaging up to 20 seconds, reaching a MDL equal to 17 ppt. As already observed in the previous works (see Figures 3.22 and 2.19(e)), the overall stability of the system is maintained only up to $\simeq 20$ seconds when the Allan-Werle plot shows a plateau, and then it starts to increase. Additional investigations highlighted that the present limiting factor to the ultimate sensitivity can be attributed to instabilities in the optical power due to electrical noise introduced by the AOM. In this regard, a future challenge will be the study and implementation of alternative AOM-free photoacoustic-based schemes characterized by longer time stability, paving the way to decrease further ultimate detection sensitivity level.

3.3.3 General conclusions and perspectives

The work summarized in this Chapter represents a first attempt at combining new key elements for exploiting the flexibility of the PAS technique, reducing the ultimate detection limit from the part-per-billion level to the part-per-trillion. In this proof-of-principle configuration, our sensor already demonstrates the best performance among state-of-the-art QEPAS and CEPAS systems targeting the same gas species reported in the literature, and it is second only to a microphone-based sensor achieving a better NNEA (by a factor of 2) at the cost of a much higher averaging time, as reported in the summary table 3.9.

3.3 Achieving the ppt-level detection sensitivity with the cavity-enhanced dual-tube MEMS-based setup

Table 3.9: Comparison between the state-of-the art QCL-based N₂O photoacoustic sensors. The last row marked in bold identifies the result achieved in this work.

Wavelength (μm)	Transducer	MDL (ppb)	Integration time (s)	Power (mW)	NNEA ($\text{cm}^{-1}\text{WHz}^{-\frac{1}{2}}$)
4.56 [200]	QTF	0.24	210	93	1.50×10^{-8}
4.61 [194]	QTF	4	500	400	2.91×10^{-9}
4.53 [197]	Microphone	1	1013	33	5.69×10^{-9}
4.52 [198]	QTF	7	0.1	35	5.40×10^{-9}
4.59[201]	QTF	0.75	10	19.5	1.70×10^{-10}
4.56 [61]	Microphone	0.0007	200	65	3.10×10^{-11}
4.56 [*]	Cantilever	0.017	20	16	5.98×10^{-11}

[*]: this work

At present, the limiting factor to the sensitivity is attributed to AOM instabilities which affect the long-term stability and do not allow the system to push its detection sensitivity down to the sub-ppt level. Nonetheless, the achieved results and the large margins for future improvements given by the flexibility of the technique make us confident that our approach can be successful in the race toward ultra-high detection sensitivity with photoacoustic systems, paving the way to applications that can be addressed nowadays only by more complex, bulky, and expensive setups.

In the next chapter, a first insight into possible steps towards a *quantum-enhanced* PAS system will be provided. As it will be discussed, this still represents a hard challenge, but it could open the doors on unexplored lands so far.

Before introducing anything quantum, the smartest starting point passes through a detailed investigation of all the main noise contributions that could come into play, thus affecting the whole system's performance. Once a complete picture of the situation is available, then it is possible to start thinking about some solution to reduce the overall noise level, up to the classical limit or even beyond.

In this framework, the next chapter will be devoted to the description of additional works that I have performed during my Ph.D activity, all focused on analyzing the main noise source affecting our photoacoustic trace-gas sensors, and proposing experimental solutions to push them down, enabling a future *quantum-assisted* photoacoustic sensing. Two main key components will be analyzed:

1. The excitation source. In this case, both the frequency noise and the amplitude noise will be investigated. Regarding the first case, a technique for noise reduction will be proposed. In the second case, the amplitude noise of several mid-IR laser sources will be investigated, aiming at knowing if they can emit at the corresponding shot-noise level.
2. The acoustic-to-voltage transduction scheme. It could be, in principle, improved by exploiting the quantum property of light (such as the squeezing). However, before switching from a classical source (i.e. the HeNe laser) to a quantum one, it is essential to understand the limiting noise features affecting the readout.

CHAPTER 4

Towards *quantum-assisted* photoacoustic spectroscopy

As already stressed before, the availability of high-performance semiconductor lasers capable of generating mid-IR coherent light has provided a determinant boost to the development of optical technologies in this spectral region, enabling a large variety of applications. Among them, molecular spectroscopy and trace-gas sensing (both for direct and indirect detection schemes such as photoacoustic spectroscopy), are pivotal for the present and future challenges impacting many important applications. An important contribution in determining a boost forward to extreme sensitivity levels, approaching single-molecule detection, is expected by quantum technologies. In this sense, photoacoustic spectroscopy can benefit from several improvements driven by its intrinsic high flexibility. Among them, working on both the excitation source and the signal transduction and proposing alternative *quantum-enhanced* solutions can be the turning point toward a next-generation version of our sensor. However, this paradigm shift must undergo an intermediate step. To assess the feasibility of implementing such improvements and understand their potential contribution, addressing the limitations of the actual experimental setup is a fundamental prerogative. For this reason, a preliminary analysis of the noise features affecting both the excitation source and the transduction system can provide a clear answer.

This is the core purpose of the following chapter, in which some additional and related works performed during my Ph.D activity are described. The first part (Section 4.1) summarizes the activity carried on during a 6-month internship at *ppq Sense S.R.L.*, focused on the analysis of the frequency noise reduction of a mid-IR QCL when locked to a high-finesse optical cavity. Section 4.2 focused on another parallel activity, aiming at investigating the intensity noise features of mid-IR semiconductor lasers (Interband and Quantum Cascade Lasers) with different structures and probing shot-noise limited emission in this spectral region. Finally, Section 4.3 investigates the noise features affecting the transducer and the balanced interferometer. This last part aims to understand if the readout scheme currently in use in our sensor is limited by

the thermal noise, or if it is masked by additional contributions.

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4.1 Frequency noise reduction of a QCL locked to a high-finesse optical cavity

An essential requirement for trace-gas sensing applications is exploiting an excitation source characterized by a high spectral purity [202]. All the laser sources are plagued by frequency noise which can hinder their performance in precision applications. The latter manifests as fluctuations in the laser output frequency, which can arise from various sources, including thermal drift, mechanical vibrations, and quantum effects within the laser medium. To reduce this effect frequency stabilization and linewidth reduction techniques must be implemented.

Focusing on the laser sources exploited in our sensor, i.e. QCLs, several approaches were proposed to accomplish this complex task during the last two decades [203]. A valid method is the implementation of active feedback loop locking, involving real-time adjustments of the QCL frequency fluctuation by monitoring its output frequency. For this purpose, an external reference, such as a molecular absorption line [204, 205], an optical cavity [206–208], metrological optical sources [131, 209–211], or high-Q micro-ring resonators [129] has to be exploited as a stable reference. According to the specific method adopted, techniques like the Pound-Drever-Hall (PDH) or heterodyne detection can be used to generate an error signal reflecting the frequency deviation. This error signal is processed to adjust the laser parameters (e.g., current or temperature), thus stabilizing its output frequency.

The following Section is dedicated to the work I carried out during a collaboration with ppq Sense S.R.L, where I spent a six-month internship during my Ph.D period under the supervision of Dr. *Saverio Bartalini*. This company was founded by CNR-INO researchers and technicians following research on high-performance trace-gas sensors conducted in Florence. Its main efforts are devoted to the development of compact and reliable all-optical $^{14}\text{CO}_2$ sensors based on Saturated-Absorption Cavity Ring-Down

Spectroscopy, and to the realization of ultra-low noise and easy-to-use drivers for mid-IR Quantum Cascade Lasers¹. This collaboration was aimed to investigate how the exploitation of an optical cavity characterized by an ultra-high finesse affects the frequency noise properties and the linewidth of a mid-IR QCL. This work allowed me to become familiar with the laser frequency noise measurement technique, acquiring useful knowledge and skills to be further applied in the photoacoustic experiment.

4.1.1 Experimental setup

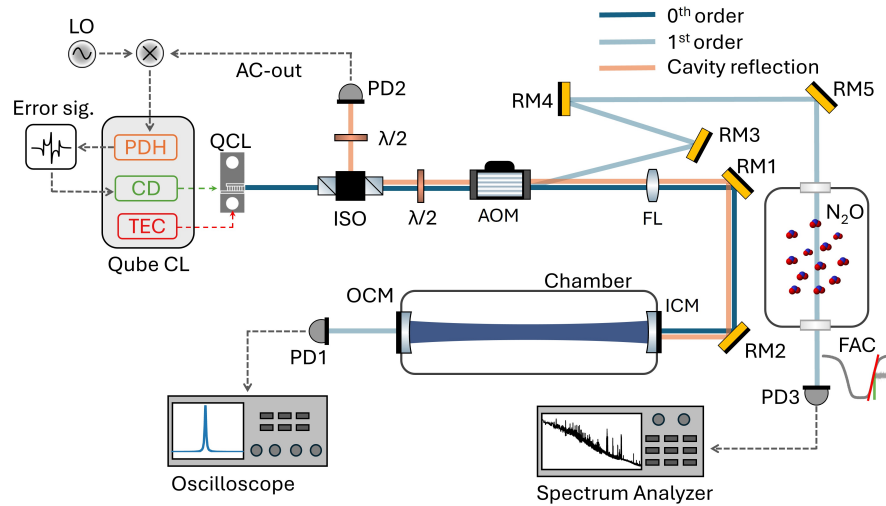


Figure 4.1: Schematic representation of the experimental setup used to unveil the frequency noise properties of the QCL.

Figure 4.1 reports a schematic representation of the setup. The tested DFB-CW Quantum Cascade Laser, provided by Hamamatsu Photonics K.K, has an emission wavelength between $4.52 \mu\text{m}$ and $4.53 \mu\text{m}$. All the laser driving electronics, i.e. Temperature controller (TEC), Current Driver (CD), and Poud-Drever-Hall (PDH) module, are embedded inside a custom-made driver (QubeCL) characterized by a nominal bias current noise density typically around $300 \text{ pA}/\sqrt{\text{Hz}}$. The optical beam passes through an optical isolator (ISO, COHERENT FM2 MID-IR $4.55 \mu\text{m}$) to avoid optical feedback to the laser itself, and through an acoustic-optical modulator (AOM, BRIMROSE 410-472-7070) maintained at a fixed temperature of 25°C via a water cooling circuit. A half wave-plate ($\lambda/2$) is interposed between these two optical components to retrieve the right beam's polarization state before interacting with the AOM. A 750 mm - CaF_2 focus lens is used to couple the 0th-order deflected beam (depicted in dark blue and corresponding to approximately the 95 % of the impinging light) inside a 1 m long high-finesse Fabry-Pérot optical cavity. The latter consists of two identical plano-convex mirrors with a radius of curvature of 3000 mm and a nominal reflectivity of 99.994 %. The optical cavity is embedded within an aluminum chamber equipped with a vacuum pump that maintains the pressure at $\approx 10^{-4} \text{ mbar}$. Two plane mirrors (RM1,2) are used to optimally align the laser beam with the cavity optical axis. The photo-detector (PD1, VIGO System, UM-I-6) placed after the output cavity mirror

¹Further information can be found in the company's website: <https://www.ppqsense.com/>

(OCM) acquires the cavity transmission peaks and allows a real-time checking of the optical beam coupling efficiency.

A PDH feedback loop is exploited for laser-cavity locking: the QCL beam is frequency modulated via a 4 MHz sine wave for the first order side-bands generation, and the cavity reflection coming from the input cavity mirror (ICM, depicted in orange) is guided back to the optical isolator and sent to a photo-detector (PD2, VIGO Systems, UM-I-6) after having adjusted its polarization state via a $\lambda/2$ wave-plate. The photo-detector AC-coupled output is mixed with a 4-MHz Local Oscillator (LO) to generate the error signal, and the latter is used to correct the frequency fluctuation of the optical beam, thus achieving stable locking. All the electronic parts of the feedback loop architecture are integrated within the PDH module of the QubeCL, providing an easy-to-use selection of the best locking parameters (i.e the pre-amplifier gain, two resistance values associated with the proportional R_P and the derivative R_D gain, and the capacitor for the integrative part closing the loop C_I).

Essentially, the main focus of the developed system is to evaluate how much the frequency noise fluctuation of the QCL beam can be decreased when locked to the high-finesse optical cavity, compared to the free-running condition. According to a well-established method, this task can be accomplished by acquiring the laser's power spectral density (PSD, in dBm) and converting it into Frequency Noise Power Spectral Density (FNPSD, in Hz^2/Hz) with the help of a discriminator for a linear frequency-to-amplitude conversion (FAC), which in our case is the slope of a strong molecular absorption line [127, 130, 204, 212].

To accomplish this request, the residual 1st-order deflected beam by the AOM (colored in dashed blue) is collected via a series of mirrors (RM3, 4, 5) and sent to a reference cell filled with pure N_2O . The transmitted light is collected by a photo-detector (PD3, VIGO System, UM-I-6), and its output is sent to a spectrum analyzer (Rohde&Schwarz, FSW26) for measuring the QCL's power spectral density both in free-running and locked conditions.

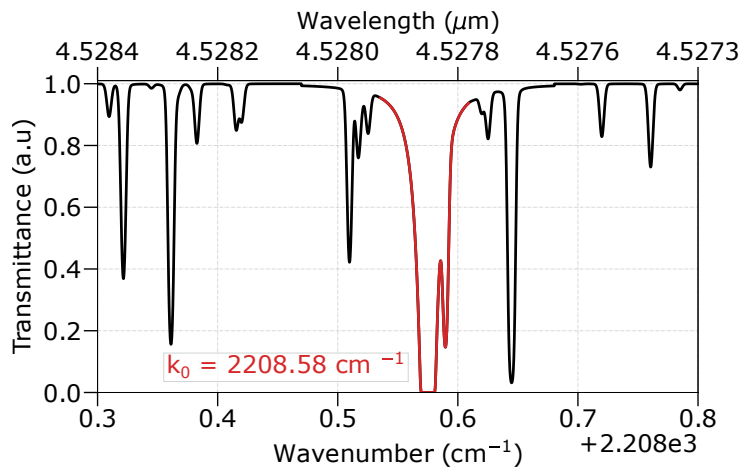


Figure 4.2: Simulated transmittance function of N_2O within the QCL working range. The spectral line exploited for the frequency-to-amplitude conversion is colored in red, and the associated peak wave number is reported.

The N_2O transition selected for the discrimination is reported in Figure 4.2. Characterized by a central wave-number equal to 2208.58 cm^{-1} and a line-strength of $9.23 \times 10^{-19}\text{ cm/molecule}$, it ensures a sufficiently high frequency-to-amplitude conversion factor. During the power spectral density acquisition, the laser temperature was set to 25°C , and the bias current was maintained at the center of the absorption line slope.

4.1.2 Result and discussion

Optical cavity characterization

A fundamental preliminary step before performing the noise measurements concerns the alignment of the laser beam with the optical cavity. Figure 4.3(a) reports the best alignment condition obtained with the free-running QCL to the cavity mode. The laser wavelength was scanned with a slow ramp ($f = 10\text{ Hz}$, $V_{pp} = 900\text{ mV}$) to observe, at the oscilloscope, one entire cavity Free-Spectral-Range, being equal to $c/2nL = 149\text{ MHz}$, where n is the refractive index of the gas sample. Looking at the transmission signal (depicted in blue) the laser beam is spread both on the fundamental cavity mode (whose amplitude is $\simeq 40\text{ mV}$) and on several higher-order modes. This happens because the typical spectral emission linewidth of a mid-IR free-running QCL (ranging between 0.5 and 1 MHz if supplied with low-noise drivers) is expected to be much higher than the fundamental mode width of this cavity. Accordingly, only a small fraction of the incoming laser beam will be coupled with the fundamental cavity mode, resulting in a free-running coupling efficiency by only $\simeq 5\%$, as demonstrated by the associated cavity reflection hole (orange trace).

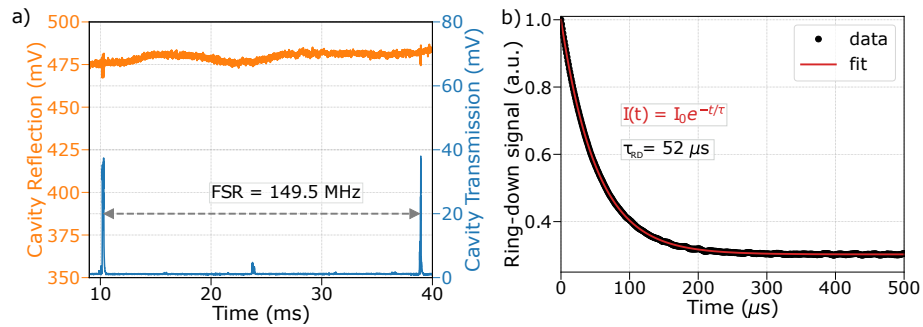


Figure 4.3: (a): QCL beam coupled with cavity modes of the High-Finesse optical cavity. (b): Ring-down time measurement on the fundamental cavity mode.

The cavity mode width can be estimated by evaluating the photon lifetime in the cavity, i.e. the time interval occurring before the photon exits the cavity. Also called ring-down time [213, 214], it can be measured with the following experimental routine. By triggering the AOM with the cavity transmission signal (i.e. the output of the photo-detector PD1) it is possible to switch off the light at the given cavity-filling threshold. Immediately the ring-down event occurs, and the cavity transmission signal is digitized and acquired. A Labview program allows setting all the experimental parameters and performing a real-time analysis routine [26].

Figure 4.3(b) reports an example of the ring-down measurement. The black data points were fitted with an exponential decay function, finding a ring-down time

$\tau_{RD} \simeq 52 \mu\text{s}$. From the latter value is possible to retrieve information about the cavity Finesse $\mathcal{F}$ and the cavity mode width $\Delta\nu$:

$$\mathcal{F} = \frac{c\pi}{L} \tau_{RD} = 48845 \quad (4.1)$$

$$\Delta\nu = \frac{1}{2\pi\tau_{RD}} = 3.06 \text{ kHz} \quad (4.2)$$

These results explain the low coupling with free-running QCL, being the cavity mode much narrower than the QCL free-running linewidth. The only way to increase the coupling is to reduce the frequency fluctuation of the laser beam via strong and stable active locking to the optical cavity.

Calibration

Before acquiring the QCL frequency noise spectral density in the two investigated configurations, the frequency-to-amplitude calibration was performed by exploiting the chosen absorption line as the discriminator. The latter was acquired via the photo-detector aligned with the reference cell (PD3) and collected via an oscilloscope. The calibration process consists of two fundamental steps, as reported in Figure 4.4.

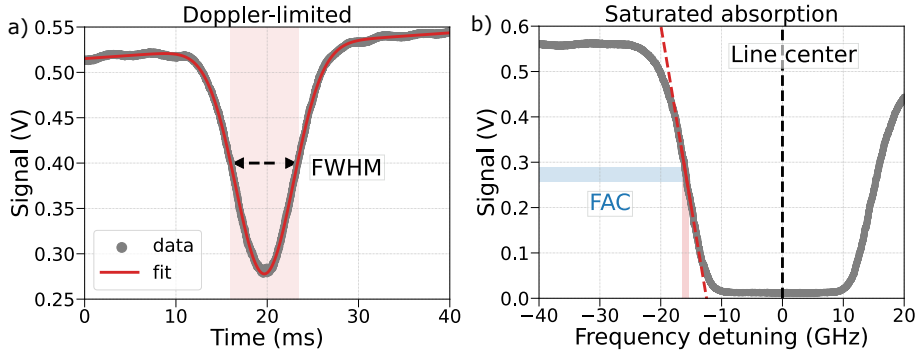


Figure 4.4: Calibration for the frequency-to-amplitude conversion. (a): Doppler-limited absorption N_2O line at 0.005 mbar. (b): Saturated N_2O absorption line at 0.2 mbar. The frequency-to-amplitude conversion factor in our case is $\alpha_{V/Hz} = 1.8 \times 10^{-8} \text{ VHz}^{-1}$. Both the traces were acquired with the use of an oscilloscope.

The first concerns a preliminary conversion of the x-axis from time acquisition to frequency. The conversion can be done by accessing the Doppler-limited absorption profile of the selected N_2O transition. This regime is reachable by decreasing the sample pressure to $\simeq 0.05$ mbar, where the absorption line shows the typical Gaussian shape (Figure 4.4(a)). In this condition, it is possible to fit the experimental data (colored in grey) with a Gaussian-type function plus a baseline (colored in red), retrieving the Full Width at Half Maximum (FWHM) in milliseconds as a parameter. In the Doppler-limited regime, the frequency linewidth Δ_D of a given spectral line can be analytically calculated via the Equation 1.3, which is reported again below:

$$\Delta_D = k_0 \sqrt{\frac{2k_B T \ln 2}{mc^2}}. \quad (4.3)$$

Given a central wavelength $k_0 = 2208.58 \text{ cm}^{-1}$ for the selected N_2O line discrimin-

ator, the associated Doppler-limited FWHM at the temperature of 296 K is $\Delta_D = 61.5$ MHz. By comparing the calculated Doppler-limited width (in MHz) with the one extracted by the fit, the millisecond-to-Hertz conversion factor can be easily obtained.

In the second step, the gas pressure has to be increased to access the saturated absorption regime (Figure 4.4(b)). This condition is necessary to achieve a condition where the discriminator slope is sufficiently high that the contribution of the frequency noise converted into intensity fluctuations is much larger than the direct contribution of the laser intensity noise [202]. By fitting the saturated absorption line slope with a linear function, as shown in Figure 4.4(b), it is possible to estimate the frequency-to-amplitude conversion factor (FAC).

Frequency Noise Power Spectral densities

The QCL FNPSDs (in free-running and locked conditions) were acquired by fixing the current at the center of the discriminator slope and maintaining the pressure of the N₂O reference cell at 0.2 mbar. Appendix A.3 describes the noise spectra acquisition routine and conversion from dBm to Hz²/Hz unit. Figure 4.5 reports the acquired FNPSD in the two analyzed configurations, depicted in grey and green respectively. The locked configuration was achieved with the best possible electronic parameters set for the Pound-Drever-Hall locking loop ².

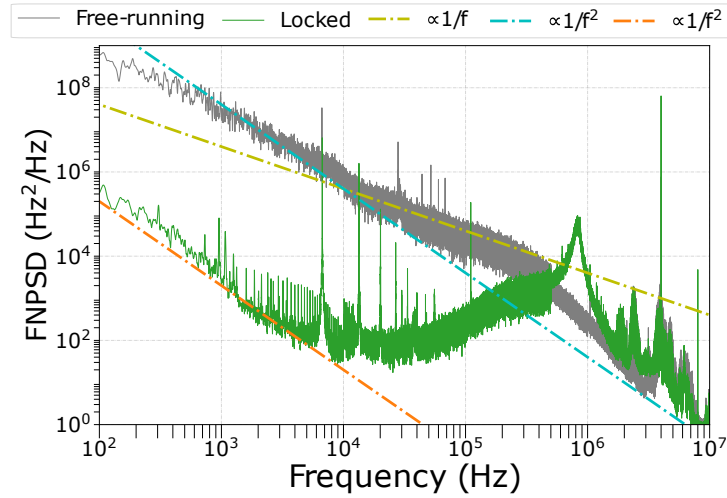


Figure 4.5: Frequency Noise Power Spectral Densities for free-running QCL (in grey) and locked QCL (in green). Both the $1/f$ and $1/f^2$ trends affecting the noise properties of the free-running QCL in the two different frequency windows are identified with dashed yellow and cyan lines.

The free-running QCL FNPSD shows a well-known $1/f$ trend dominating within a spectral region from 10 kHz to 300 kHz, the latter value ascribed to the QCL cut-off frequency. Below 10 kHz the device seems to have an excess of noise, well fitted by a $1/f^2$ trend, that could be associated with technical current-driver-related noise. Locking the laser to the optical cavity leads to a drastic frequency noise reduction in the low Fourier frequency range (up to approximately 500 kHz). In more detail, the 0.1-10 kHz spectral region is affected again by a $1/f^2$ trend, while in the 10-100 kHz

²The best possible locking condition was achieved by selecting the following electrical component for the PHD electronic module: Pre-Ampl Gain = 2.43, $R_P = 6.2k\Omega$, $R_D = 100\Omega$, $C_I = 1nF$.

the spectrum shows a flat response, reaching the highest noise reduction compared to the free-running QCL, being equal to more than three orders of magnitude. In the 100 kHz-1 MHz range, the FNPSD shows an increase up to a peak at around 900 kHz, corresponding with the PDH locking bandwidth. Finally, the spectrum overlaps with the free-running one at higher frequencies, being outside the locking bandwidth.

Starting from the acquired FNPSDs, an evaluation of the QCL linewidth narrowing can be done by exploiting two different methods.

Emission linewidth reduction

According to the theoretical picture introduced by *Elliot et al.* [215], the emission spectral line shape of a laser $S_E(\nu)$ can be derived by resolving the following two-step integration:

$$S_E(\nu) = 2 \int_{-\infty}^{\infty} e^{-i2\pi\nu\tau} \underbrace{\left[E_0^2 e^{i2\pi\nu_0\tau} \exp \left(-2 \int_0^{\infty} S_{\delta\nu}(f) \frac{\sin^2(\pi f\tau)}{f^2} df \right) \right]}_{\Gamma_E(\tau)} d\tau, \quad (4.4)$$

where $S_{\delta\nu}(f)$ is the FNPSD and E_0^2 the field intensity. The first integral, limited by the square brackets, consists of the electrical field auto-correlation function $\Gamma_E(\tau)$. The second step defines the Fourier transform of $\Gamma_E(\tau)$, leading to the determination of the spectral line shape $S_E(\nu)$. In the simplest case of pure white frequency-noise, i.e. $S_{\delta\nu} = S_0$, Equation 4.4 can be analytically solved, leading to a Lorentzian spectral line shape with a FWHM equal to πS_0 . In all the other cases, including ours, Equation 4.4 has to be solved via a numerical integration [202]. Once the spectral line shape is resolved, the associated FWHM Δf_{LAS} can be extracted.

An alternative and simplified approach for the laser linewidth estimation, valid for a generic frequency noise spectrum, was proposed [216]. The basic concept relies on the so-called β -separation line: defined as $\beta(f) = (8 \log(2)/\pi^2) \times f$, it divides the FNPSD into two regions with a very different impact on the linewidth. The noise components exceeding the β -separation line, i.e. $S_{\delta\nu} > (8 \log(2)/\pi^2) \times f$, will contribute to the laser linewidth defining the slow modulation area. Whereas, the noise components under the β -separation line, i.e. $S_{\delta\nu} < (8 \log(2)/\pi^2) \times f$, will define the fast modulation area and will have an impact only on the tails of the line-shape. Hence, the FWHM linewidth Δf_{LAS} will be approximated with the following equation:

$$\Delta f_{LAS} = \sqrt{8 \ln(2) A} \quad (4.5)$$

being A the area under the slow-modulation area. It should be noted that in both the two described approaches a cut-off frequency f_c , corresponding to a given linewidth observation time $\tau_0 = 1/f_c$, has to be introduced to prevent any divergence of A in the low-frequency range. This is fundamental in the case in which the investigated low-frequency range FNPSD is dominated by the $1/f$ flicker noise, or even by higher-order $1/f^n$ trend with $n \geq 2$. In our case of study, both approaches were tested to prove their mutual validity. A cut-off frequency of 100 Hz was chosen, corresponding to an observation time of 10 ms.

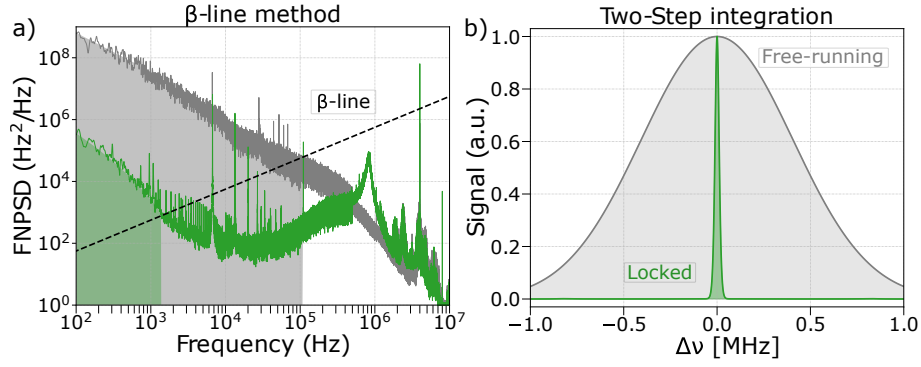


Figure 4.6: **(a)**: FNPSDs plotted with the β -separation line (in dashed black). The corresponding slow modulation areas are colored with light grey for the free-running and light green for the locked QCL. **(b)**: Results of the numerical integration for the QCL line-widths calculations. In both cases, the observation time is set to 10 ms.

Figure 4.6(a) reports the FNPSDs of the free-running and locked QCL plotted together with the β -separation line. For the free-running QCL the upper bound of the slow-modulation area, depicted in light grey, is equal to around 100 kHz. When the laser beam is locked with the optical cavity the latter value is decreased to around 2 kHz (light green). The two slow-modulation areas were numerically calculated with the trapezoid rule. The results highlight that starting from a free-running QCL linewidth $\Delta f_{LAS}^{free} \simeq 950$ kHz, the introduction of the laser-cavity locking allows a linewidth reduction of around 97 %, down to $\Delta f_{LAS}^{locked} \simeq 25$ kHz.

Regarding the integration method, a Python script was developed to retrieve the laser line shape and the associated FWHM linewidth. According to the result shown in Figure 4.6(b), the integration led to free-running and locked FWHM line widths respectively equal to $\Delta f_{LAS}^{free} \simeq 959$ kHz and $\Delta f_{LAS}^{locked} \simeq 29$ kHz. These values are in very good agreement with the ones obtained with the β -separation line method, confirming the mutual validity of the two approaches.

4.1.3 Conclusion and outlook

This work proved the possibility of exploiting a high-finesse optical cavity to reduce the frequency fluctuation of a mid-IR QCL by more than 90%. Besides the possibility of achieving a high coupling efficiency, having a low-frequency-noise emission is fundamental in improving the overall sensor's performance. Despite a significant reduction, the laser line width cannot be completely narrow at the fundamental cavity mode width (equal to approximately 3 kHz). This could be due to an excess of low-frequency noise that makes the QCL FNPSD away from the expected $1/f$ trend. The noise source, still unknown, could be attributed to several hypothetical origins: environmental/acoustic noise introducing instability in the whole experimental setup, electronic noise introduced by the laser driver, or intrinsic noise in the laser emission dynamics. Nevertheless, by taking care of all possible experimental parameters and reducing all the technical and environmental noise sources (for example by isolating the whole system from mechanical vibrations, or stabilizing the working temperature) a drastic frequency noise reduction can be achieved. To conclude, such results can be seen as a good starting point in the vision of substituting the optical cavity currently in

use in our trace-gas photoacoustic sensor with the one employed in this work. In fact, the much higher finesse (i.e. $\simeq 49000$ against $\simeq 2000$) can lead not only to a sensible frequency noise reduction but also to an impressive intra-cavity power build-up (up to 250 W for an impinging laser power of $\simeq 15$ mW), thus further enhancing the ultimate detection sensitivity.

4.2 Probing shot-noise limited emission from Interband and Quantum Cascade Lasers

In addition to the frequency noise introduced and investigated in the previous paragraph (Section 4.1), another fundamental noise source connected with any laser emission has to be investigated. Defined as intensity noise, it describes the power fluctuations around the central emission power of a laser source, and it can represent one of the key parameters for the ultimate sensitivity in laser-based sensing systems [217].

If the frequency noise spectra of mid-IR Quantum and Interband Cascade Lasers have been deeply investigated, only very few studies regarding the intensity noise features were reported in the literature [218–220]. Despite that, such an analysis could unveil if a chosen laser source can emit at the corresponding shot-noise level or if it can be characterized even by sub-shot-noise emission. In the context of trace-gas sensors, reaching this condition could be, on the one hand, a fundamental prerogative to minimize the noise contribution coming from the excitation source, thus increasing the detection sensitivity. On the other hand, such a condition could be a good starting point to improve further the overall performance of the sensors, testing the possibility of the source emitting in a sub-shot noise regime, where the standard quantum limit is overcome in favor of a quantum-enhanced configuration.

In this context, part of my PhD work was focused on characterizing the intensity noise of conventional and novel mid-IR Quantum and Interband Cascade Lasers (which are the most used mid-IR laser sources for spectroscopic applications), aiming at unveiling where and if they can emit at their corresponding shot-noise level. Summarized in two published articles [221, 222], all the measurements were carried out at the QCLab25 at the European Laboratory of Non-Linear Spectroscopy (LENS, Florence) under the supervision and the expertise of Drs. *Tecla Gabbrielli* and *Francesco Cappelli*, and exploiting a well-established technique known as Balanced Homodyne detection (BHD) [223–225]. The following section will summarize this activity, both focusing on a little bit of theoretical contextualization and on a detailed description of the experimental part.

4.2.1 Balanced Homodyne detection: theory

According to a quantum field representation, in a typical balanced homodyne detection scheme (schematized in Figure 4.7) the investigated light source (defined also as the local oscillator, LO) can be described via the field operator $\hat{a}$. The latter is split by a 50/50 beam splitter, and the outputs $\hat{a}_{2,3}$ are collected by two photo-detectors that convert the impinging optical power into a photo-current. If the two arms are identical in length and if the two photo-detectors have the same response (i.e. responsivity,

wavelength working range, electronic architecture, and so on), by performing the balanced difference between the output photo-currents $\hat{I}_{1,2}$ it is, in principle, possible to suppress any type of common noise sources such as correlated noise from the photon generation process, amplification, and so on.

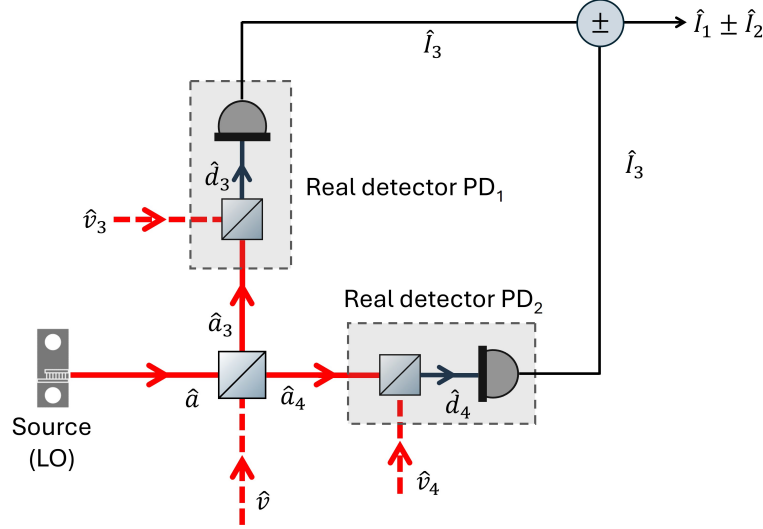


Figure 4.7: Theoretical schematization of a balanced homodyne detection scheme. The local oscillator (i.e. the source under examination) is represented via the field operator $\hat{a}$ and it is mixed with the vacuum field $\hat{v}$ at the beam splitter, and the two photo-detectors collect the output field. The latter is schematized with the coupling between a beam splitter and a detection unit, simulating the optical losses induced by the non-unity of the detector quantum efficiency η_{eff} . The output fields $\hat{a}_{3,4}$, obtained by mixing $\hat{a}_{3,4}$ with two vacuum fields $\hat{v}_{3,4}$ are collected by the two photo-detectors, and the output photo-currents $\hat{I}_{3,4}$ are summed and subtracted to obtain the local oscillator's photon statistics and the corresponding shot-noise level.

This measured balanced difference (in the time domain) is then converted into an Intensity Noise Power Spectral Density (INPSD) via a Fast Fourier Transform (FFT) analysis. The latter determines the ultimate noise level of the BH detector, which has to be compared with the associated theoretical INPSD shot-noise level, defined as:

$$INPSD_{sn} = 2e \frac{(V_1 + V_2)}{R_T}, \quad (4.6)$$

where e is the electron charge, $V_{1,2}$ are the first-stage trans-impedance DC-coupled outputs of the two photo-detectors, and R_T is the trans-impedance resistance value (supposed to be equal for both). Therefore, if the INPSD of the difference lies at the same level as the expected shot-noise level, it means that any extra classical noise affecting the measurement is efficiently canceled out, thus achieving the requested detection sensitivity by the standard quantum limit. At this point, the sum of the two photo-detector outputs (corresponding with the overall intensity noise power spectral density of the emitted radiation) can be computed and compared with the INPSD of the difference: if the sum and the difference lay at the same level it means the source under examination can emit at its corresponding shot-noise, unveiling the possibility to work at the standard quantum limit.

A fundamental prerogative for this kind of measurement is that the two photo-detectors must work in the linear responsivity regime to ensure a linear proportionality between the output voltage and the impinging optical power, preventing any saturation

effect. Only in this configuration, the photon statistics of the investigated light source can be reconstructed by the statistical properties of the two output photo-currents (such as mean values and variance). Ideally, no optical losses are considered or neglected. In a real configuration, a typical optical loss can be introduced by several factors, such as any attenuation of the local oscillator due to absorption and reflection from optical components during its propagation.

Another loss factor can be linked to the detection part. Ideally, a perfect photovoltaic detector generates an electron for each incident and absorbed photon. In a real configuration, only a part of them is effectively converted into a photo-current. As a consequence, the rate between incident photons and generated electrons, a parameter known as quantum efficiency (η_{qe}), is always lower than one, introducing an additional optical loss term. In quantum optics theory, these mechanisms can be modeled in a good approximation with a 50/50 beam splitter (characterized by a given reflection and transmission coefficients R and T) that couples the radiation with the vacuum field³. That's why in Figure 4.7 the state $\hat{a}$ is mixed with the vacuum state $\hat{v}$, generating as outputs the field $\hat{a}_{3,4}$:

$$\hat{a}_3 = R\hat{a} + T\hat{v}, \quad (4.9)$$

$$\hat{a}_4 = R\hat{v} + T\hat{a}. \quad (4.10)$$

At the same time, the two real photo-detectors $PD_{1,2}$ can be seen as the coupling between a 50/50 BS (where the output field $\hat{a}_{3,4}$ are mixed with the vacuum states $\hat{v}_{3,4}$ respectively) and a detection unit, as shown in Figure 4.7. In this case, schematizing the BS losses with transmission and reflection coefficients $T_L = \sqrt{\eta_{eff}}$ and $R_L = i\sqrt{1 - \eta_{eff}}$, the BS outputs $\hat{d}_{3,4}$ can be written as:

$$\hat{d}_3 = \sqrt{\eta_{eff}}\hat{v}_3 + i\sqrt{\eta_{eff} - 1}\hat{a}_3, \quad (4.11)$$

$$\hat{d}_4 = \sqrt{\eta_{eff}}\hat{a}_4 + i\sqrt{\eta_{eff} - 1}\hat{v}_4 \quad (4.12)$$

Given these assumptions, the loss budget associated with the BH-detection schemes should be taken into careful consideration for the right interpretation of the data. The detectors collect the two fields $\hat{a}_{3,4}$ giving as output the photo-currents as $\hat{I}_3 = \hat{d}_3^\dagger \hat{d}_3$ and $\hat{I}_4 = \hat{d}_4^\dagger \hat{d}_4$ respectively, proportional to the incident photon flux. Integrating the difference and the sum of the two photo-currents within a measuring time τ :

$$\mathcal{A}_{+,-} = \int_t^{t+\tau} (\hat{I}_3 \pm \hat{I}_4) dt', \quad (4.13)$$

³Referring to an ideal beam splitter with no losses and given the two input states $\hat{a}_{1,2}$, the output fields $\hat{a}_{3,4}$ will be given by the equation:

$$\hat{a}_3 = R\hat{a}_1 + T\hat{a}_2, \quad (4.7)$$

$$\hat{a}_4 = T\hat{a}_1 + R\hat{a}_2, \quad (4.8)$$

where R and T are the BS reflections and the transmission respectively, linked by the relations $\text{mod } R^2 + \text{mod } T^2 = 1$ and $RT^* + tR^* = 0$

it is possible to retrieve information about the photon statistics of the tested light. Since in this case the input state mixing with $\hat{a}_{3,4}$ is the vacuum field $\hat{v}_{3,4}$, the mean value of the photon number $\langle N_{+,-} \rangle$ and the associated variance $(\Delta N_{+,-})^2$ for the photo-current sum and difference will be [117]:

$$\langle N_+ \rangle = \eta \langle n \rangle, \quad (4.14)$$

$$(\Delta N_+)^2 = \eta^2 (\Delta n)^2 + \eta(1 - \eta) \langle n \rangle, \quad (4.15)$$

$$\langle N_- \rangle = 0, \quad (4.16)$$

$$(\Delta N_-)^2 = \eta \langle n \rangle. \quad (4.17)$$

Here $\hat{n} = \hat{a}^\dagger \hat{a}$ is the number of emitted photons by the local oscillator, and $\langle \hat{n} \rangle$ is the expectation value, while $\eta = \eta_1 \eta_{eff}$ takes into account the overall optical losses (η_1) during the light beam propagation and the detector's quantum efficiency (η_{eff}). According to this picture, the variance of the difference $(\Delta N_-)^2$ determines the shot-noise level of the investigated radiation collected with the BH-detection scheme. Hence, it is possible to state that the investigated light source is emitting at its corresponding shot-noise level only if the variance of the sum $(\Delta N_+)^2$ is equal to the variance of the difference. According to the Equations 4.15 and 4.17, this situation is accomplished when the source (i.e. the local oscillator) is a pure coherent state, for which the relation $(\Delta n)^2 = \langle n \rangle$ is valid.

Besides this conclusion, it is important to highlight the role played by the losses; when the local oscillator field is coupled with the vacuum field the variance of the sum will be characterized by an extra term proportional to the factor $(1 - \eta)$. If the loss is too high, the background noise could cover both the sum and the difference terms, thus limiting the overall sensitivity of the developed BH detector in measuring the LO shot-noise level [117]. Hence, net to the optical losses, the two photo-detectors should be selected to ensure the highest signal-to-noise ratio within their linear responsivity regime and avoid any saturation. This crucial information can be addressed by measuring the clearance of the detector, defined as the ratio between the INPSD of the difference and the detector background.

4.2.2 Results and discussion

This activity involved collaborations with international Universities and Institutes, such as the *Technischen Universität Wien* (TU Wien), the *Swiss Federal Institute of Technology in Zurich* (ETH Zurich), the *Nanosystems and Technologies GmbH*, and the *Hamamatsu Photonics K.K.* All the work described in this section is summarized in two research articles, one published in 2024 in *ACS Photonics* [221], and the other one available on arXiv [222].

The investigated lasers are representative of the main typologies of current state-of-the-art mid-IR semiconductor lasers: two single-mode distributed feedback (DFB)

devices (one QCL and one ICL), a comb-emitting Fabry–Pérot (FP) QCL, and a novel ICL, characterized by a non-conventional ring-shaped cavity architecture and a vertical emission. This choice allows us to apply such an investigation to the main typologies of current state-of-the-art mid-IR lasers, thus providing a complete overview.

1. FP QCL

The FP QCL was fabricated at ETH Zürich. The active medium was grown via molecular-beam epitaxy and comprises two gain stages composed of alternate layers of $\text{In}_{0.684}\text{Ga}_{0.316}\text{As}/\text{In}_{0.335}\text{Al}_{0.665}\text{As}$, resulting in 2 gain stages (one centered at $4.6\text{ }\mu\text{m}$, the other one at $4.3\text{ }\mu\text{m}$). The active region (AR1+AR2) has a total thickness of $2.1385\text{ }\mu\text{m}$, with 17 periods in AR1 and 18 in AR2. The laser wave-guide is 4.5 mm long and has one high-reflectivity (HR) coated facet (reflection of approximately 100%), while the other facet is uncoated and therefore characterized by a residual reflection of 27%.

2. DFB QCL

This laser, fabricated by *Hamamtsu Photonics K.K.*, is a twin of the QCL used as the excitation source in the photoacoustic experiments described in Chapters 2 and 3. The main structural features were already discussed in Subsection 2.1.2.

3. DFB ICL

The ridge DFB ICL was fabricated by *Nanoplus*. This device has a cavity length of $900\text{ }\mu\text{m}$ with a ridge width of $7.35\text{ }\mu\text{m}$ and a 6-stage active medium enclosed by 400 nm -thick GaSb separate confinement layers and InAs/AlSb superlattice cladding layers, which have a thickness of $3.5\text{ }\mu\text{m}$ and $2.0\text{ }\mu\text{m}$, respectively. A W-quantum well sequence was chosen to achieve a center gain wavelength of $4.5\text{ }\mu\text{m}$ ($2.50\text{ nm AlSb}/2.22\text{ nm InAs}/2.50\text{ nm In}_{0.35}\text{Ga}_{0.65}\text{Sb}/1.83\text{ nm InAs}/1.0\text{ nm AlSb}$). The laser has a 100% reflective coating in the back facet and the front facet is cleaved with a 30% reflectivity.

4. Ring-cavity ICL

The ring-cavity ICL was fabricated by the *TU Wien*. It was grown by solid-source molecular beam epitaxy (MBE) on an n-GaSb (100) substrate. The W-shaped AR with 6 periods follows the layer sequence $2.50\text{ nm AlSb}/1.92\text{ nm InAs}/2.40\text{ nm In}_{0.35}\text{Ga}_{0.65}\text{Sb}/149\text{ nm InAs}/1.0\text{ nm AlSb}$ for a target emission wavelength of $3.8\text{ }\mu\text{m}$. It is sandwiched between two 200 nm -thick GaSb separate confinement layers as well as a 3.5 and $2.0\text{ }\mu\text{m}$ InAs/AlSb lower and upper cladding, respectively. The epitaxial ICL structure was processed into ring-shaped cavities with a diameter of $\simeq 800\text{ }\mu\text{m}$ and a ridge width of $6\text{ }\mu\text{m}$ (circumference: approximately 2.5 mm) using state-of-the-art clean room fabrication techniques. Special attention was given to the sub-micro-metric size features of the implemented second-order DFB grating for vertical and single-mode light coupling, which was patterned through electron-beam lithography and as a next step etched around 1100 nm deep into the already existing waveguide with $\text{Cl}_2\text{-Ar}$ reactive ion etching.

Preliminary characterization

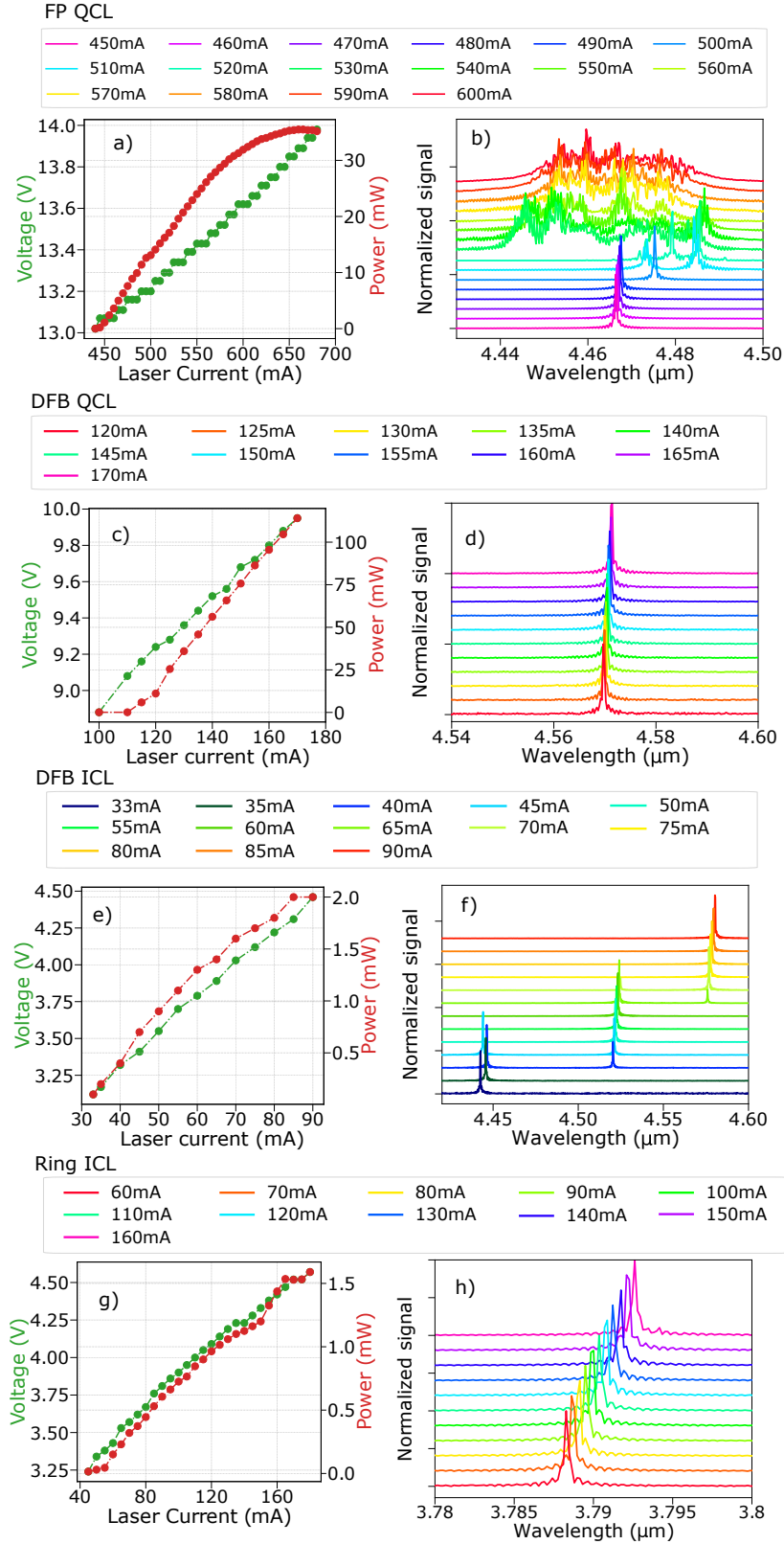


Figure 4.8: (a,c,e,g): Light-Intensity Voltage (LIV), and (b,d,f,h) Individually normalized emission spectra (acquired with an FTIR 721, Bristol) of the four investigated devices.

Before investigating the intensity features of the devices, a preliminary characterization was performed to unveil their working regime when operated at room temperature: the FP QCL, the DFB QCL, and the DFB ICL were tested at 20 °C, while the Ring-cavity ICL was set to 16 °C. This temperature range was chosen to ensure high enough optical emission power and a device's operation free of more sophisticated control systems (such as purging the laser with dry air/nitrogen to prevent water condensation at the laser facet from ambient humidity).

Figures 4.8(a,c,e,g) report the LIV curves of the devices, acquired in the region where all the lasers under investigation operate above the threshold, which is the region of interest for the intensity noise characterization. Figures 4.8(b,d,f,h) show the corresponding bias-dependent emission spectra measured with an optical spectrum analyzer (FTIR 721, Bristol), with a resolution of 6 GHz (i.e., 0.2 cm^{-1}). The y-scale is linear. The traces were normalized to their respective maximum peak and an offset was added in the y-direction to allow a good visibility of all the spectra within a single graph.

Immediately noticeable is the difference in the emission power between the two QCLs and the two ICLs. The FP QCL (Figure 4.8(a)) has a laser threshold around 450 mA and it reaches an emission power of 35 mW before its rollover at $\simeq 650 \text{ mA}$. Due to the shorter wave-guide, the DFB QCL (Figure 4.8(c)) shows a lower threshold a current operation ($\simeq 110 \text{ mA}$) and, at the same time, CW optical output power well beyond 100 mW for a bias current of $\simeq 170 \text{ mA}$. Hence, the bias voltage enabling their operations is quite high: well below 10 V within the entire lasing range for the FP QCL, and between $\simeq 8.8 \text{ V}$ and 10 V for the DFB QCL. Things are very different in the case of ICLs. For the DFB ICL 4.8(e) the lower number of cascade stages results in a lower threshold bias current of $\simeq 33 \text{ mA}$, and a reduced optical emission power with a maximum value of $\simeq 2 \text{ mW}$ at 90 mA. The same happens for the ring-cavity ICL 4.8(g), characterized by a lasing threshold of around 50 mA and a maximum optical output power of approximately 1.6 mW at 160 mA. In both cases, the energy consumption is significantly lower than the QCLs, achieving a maximum lasing voltage of $\simeq 4.5 \text{ V}$ and proving a good potentiality for in-field applications. Furthermore, a few mW of emitting power is (typically) enough for trace-gas sensing applications, especially if the radiation is coupled with an optical cavity for intra-cavity power build-up.

Moving to the optical emission spectra, the DFB QCL (4.8(d)) and the Ring-cavity ICL (4.8(h)) operate in a single-mode emission in the whole current range, at central wavelengths respectively equal to approximately $4.57 \mu\text{m}$ and $3.79 \mu\text{m}$. The DFB ICL (4.8(f)) shows a different behavior. Close to the threshold, the laser emits in a single mode regime around $4.44 \mu\text{m}$, then for currents between 40 mA and 50 mA the emission switch to a bi-color regime with modes peaked respectively at around $4.44 \mu\text{m}$ and $4.52 \mu\text{m}$.

Regarding the FP QCL, the situation is more complex (4.8(b)). Between the laser threshold and $\simeq 500 \text{ mA}$ the operation regime is single-mode, with a central wavelength slightly below $4.47 \mu\text{m}$. At around 510 mA a bi-color emission appears with peak centers at $\simeq 4.47 \mu\text{m}$ and $\simeq 4.48 \mu\text{m}$. Between 520 mA and 530 mA, the emission switches to a harmonic comb regime (i.e. characterized by a low number of

correlated modes) [226, 227]. Finally, the device operates as a standard dense QCL comb for higher currents.

Intensity Noise characterization

Experimental setup Measuring the intensity noise down to the shot-noise level in the MIR range is a non-trivial task. First, this technique requires high-bandwidth detectors since the eventual shot-noise limited emission could be hidden and dominated by $1/f$ or technical noise at low Fourier frequencies. Second, the dark noise (including electronic and background thermal noise contributions) has to lie sufficiently below the shot-noise level. The experimental setup developed for this purpose takes inspiration from the work by *Gabrielli et al.* [228], and Figure 4.9 shows a schematic representation.

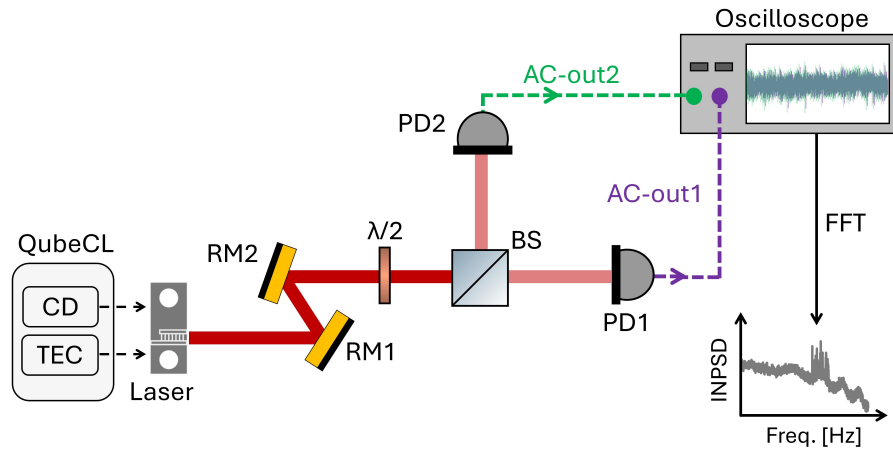


Figure 4.9: Sketch of the balanced homodyne detector for the intensity noise characterization of the investigated mid-IR devices.

The light source under examination is split into two identical paths via a 50/50 beam splitter and collected by two identical photo-detectors (PD1 and PD2). The optical beam polarization has to be controlled with a half-wave plate ($\lambda/2$) before the splitting, ensuring an equal distribution of power detected⁴. The two AC-coupled outputs (AC-out 1,2) are synchronously recorded by a 12-bit oscilloscope (Tektronix, MSO64) and analyzed in the time domain within a fixed time window and a given Sampling Rate (i.e. 31.25 Ms/s). Finally, a Python script computes the sum and the difference of the acquired signal. It converts them from the time domain to the frequency domain via a Fast Fourier Transform analysis (FFT), computing the Intensity Noise Power Spectral Density (INPSD) of the sum and the difference. Based on a differential measurement, this configuration provides a sufficiently large dynamic range and good common-mode noise suppression in the two arms, down to the corresponding shot-noise level.

A fundamental prerogative for this kind of measurement concerns the exploitation of two identical (as much as possible) photo-detectors whose working bandwidth falls within the laser's emission wavelength. Another important requirement for them concerns having a sufficiently high responsivity, defined as the conversion efficiency of

⁴In the case of the Ring-Cavity ICL the overall beam polarization is circular. For this reason, a quarter wave-plate ($\lambda/4$) is placed before the $\lambda/2$ wave-plate, thus retrieving a linear polarization

an input optical power signal into an output photo-current (or photo-voltage)⁵. Furthermore, the measurements have to be performed in the detector's linear-responsivity regime, avoiding saturation.

For the DFB QCL, the DFB ICL, and the FP QCL the BHD were performed using two commercial HgCdTe photovoltaic detectors (VIGO System, PVI-4TE 5-2x2-TO8-wAl203-36+MIP-10-250M) characterized by a nominal bandwidth of 180 MHz and optimized to work within the 4-5 μm spectral range⁶. The responsivity associated with their linear response regime is 1.48 A/W (measured at $\simeq 4.5 \mu\text{m}$), leading to a quantum efficiency of $\simeq 40\%$. The saturation intensity of each detector at this wavelength is $\simeq 1 \text{ mW}$. Hence, the incident power on the BS does not have to exceed $\simeq 2 \text{ mW}$ [228]. Due to the saturation limit, when using laser sources as powerful as the QCLs presented in this work, their radiation impinging onto the BS needs to be attenuated accordingly.

In the case of the Ring-Cavity ICL, the detection system consists of two commercial HgCdTe photovoltaic detectors (VIGO Photonics, PIP-UC-LS, PV-4TE-4-1x1) optimized to work within around 3.5-4 μm ⁷. Their are characterized by a nominal bandwidth of around 5 MHz and a saturation level of about 12 mW. The responsivity, measured at around 3.79 μm , is approximately 0.7 A/W, corresponding to a quantum efficiency of $\simeq 23\%$ ⁸. In all cases, the detectors are maintained at a fixed temperature of -73°C by a four-stage Peltier cooling system via a thermometric cooler controller (VIGO Systems, PTCC-01-BAS). Finally, all the lasers are driven by ultra-low-noise current drivers provided by ppq Sense S.R.L. to minimize any additional technical noise (nominal current noise density of $300 \text{ pA}/\sqrt{\text{Hz}}$).

Intensity Noise Power Spectral Density Figure 4.10 shows a compendium of the Intensity Noise characterization performed at a specific operating regime (i.e. laser temperature and current) of all the investigated devices. For the sake of completeness, it must be stated here that this characterization was applied to the four lasers throughout their corresponding operating range, and further information can be found in the related published articles [221, 222].

In the case of the two QCLs, it is reasonable to compare them in similar working conditions, i.e. reasonably above threshold and at relatively low emission power to limit the attenuation and to avoid saturation on the photo-detectors. According to these assumptions, the selected elected working conditions are $I = 490 \text{ mA}$ for the FP QCL (where the latter is still emitting in single-mode regime) and $I = 120 \text{ mA}$ for the DFB QCL, corresponding to a factor of 10% above the laser threshold I_{th} , i.e. $(I - I_{th})/I_{th} \simeq 0.10$. In both cases, an attenuation was required to avoid detector

⁵The detector responsivity is defined as $\mathcal{R} = \eta_{qe}\lambda e/hc$. η_{qe} is the associated quantum efficiency, e the electron charge, h the Planck constant, and c the light velocity.

⁶Additionally, these two detectors have a two-stage preamplifier consisting of a 2.2k Ω DC trans-impedance preamplifier stage and an AC-coupled second stage with a measured voltage gain of 26.5 V/V

⁷The electronic architecture of the detectors consists of two amplifier stages: a 6 k Ω DC preamplifier trans-impedance stage, and a second stage for which coupling (i.e., AC or DC) and gain can be chosen via a PC software (VIGO Photonics S.A., Smart Manager). In our case, the AC-coupled second stage is used to amplify the AC-voltage noise amplitude by a factor of 62 V/V. We fixed the gain to 20 via the Smart Manager control platform, but we also measured a minimum amplification amount between the 1st-stage output voltage and the 2nd-stage output voltage equal to 3.1 V/V when the AC gain is set to 1. The two factors (3.1×20 in our case) must be multiplied to retrieve the actual voltage amplification factor.

⁸The two photo-detectors have, in this case, slightly different responsive: $R1 = (0.704 \pm 0.007) \text{ A/W}$, and $R2 = (0.659 \pm 0.008) \text{ A/W}$.

saturation, being $\simeq 87\%$ for the DFB QCL and $\simeq 82\%$ for the FP QCL.

Contrariwise, no attenuation is needed for the DFB ICL, at the net of the isolator transmittance ($\simeq 70\%$). In this case, a laser current equal to 60 mA (well above the associated lasing threshold) was chosen for the intensity noise analysis, preventing the bi-color regime. Finally, the Ring-Cavity ICL was set to $I = 140$ mA, a condition associated with a sufficiently high incident power but away from the current limit.

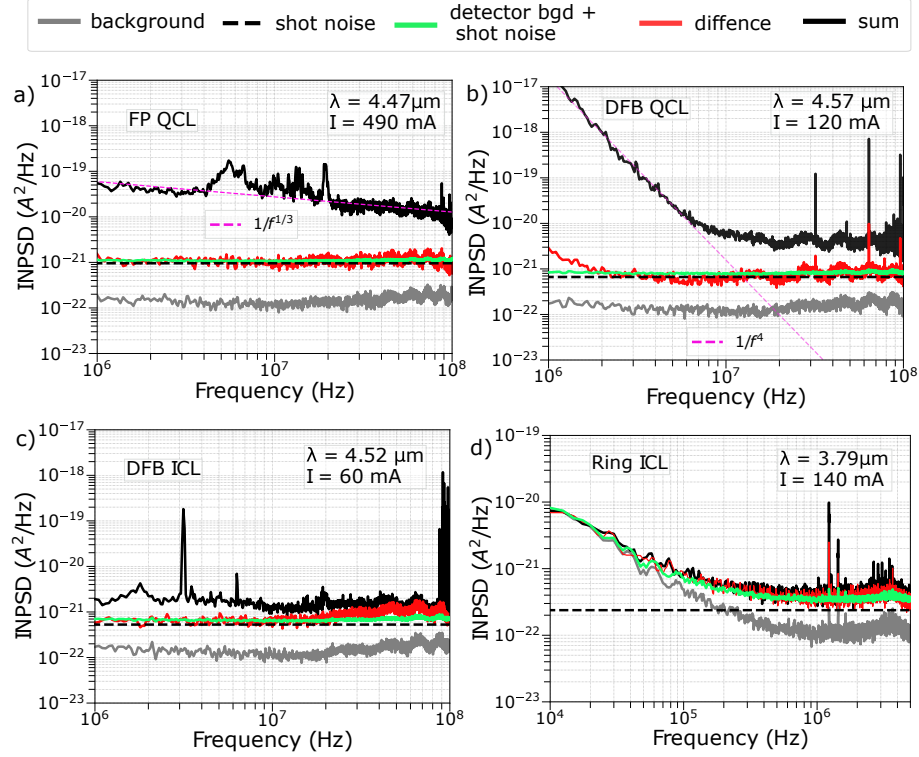


Figure 4.10: Compendium of the Intensity Noise Power Spectral density of the investigated devices: (a) FP QCL, (b) DFB QCL, (c) DFB ICL, and (d) Ring-Cavity ICL. The INPSD sum and difference signal traces are colored black and red, respectively. The dashed black line represents the theoretical shot-noise level, obtained from the DC-outputs of the detectors using Equation 4.6, while the detector background is shown in gray. The green line shows the sum of the theoretical shot-noise level and detector background noise, defining the *experimental* shot-noise level.

The INPSD of the difference signal (red traces) corresponds to a direct measurement of the shot-noise level. In all the cases, the INPSD of the difference signal overlaps with the green trace, corresponding with the *experimental* shot-noise and defined as the sum of the detector background noise (gray trace) and the theoretical shot-noise (dashed black line) computed from Equation 4.6. The INPSD of the sum signal (black trace) gives direct information about the intensity noise of the collected radiation, highlighting crucial differences and peculiarities among the four studied devices.

• FP QCL

A residual $1/f^{1/3}$ trend in the intensity noise is present within the entire tested Fourier frequency range of 1–100 MHz (dashed orange line in Figure 4.10(a)). This residual excess noise decays smoother than the typical $1/f$ trend shown by such devices [126, 229]⁹. This does not allow this QCL to achieve a shot-noise-limited emission in the investigated frequency range.

⁹This excess of noise, which deviates the measured INPSD from the flat white noise trend, is compatible

• DFB QCL

An excess of noise in the low Fourier-frequency range is present (Figure 4.10(b)) with a step decay following a $1/f^4$ ¹⁰. Above 10 MHz this excess noise becomes negligible, allowing a genuine analysis of the device's intensity noise features. As a general trend, in the analyzed working condition (i.e. $I_{LAS} = 120$ mA and $T = 20$ °C), the DFB QCL emission lies well above the corresponding shot-noise level. Visible but spurious peaks above 20 MHz are present, probably due to technical noise (associated with resonances in the supply chain ground loop).

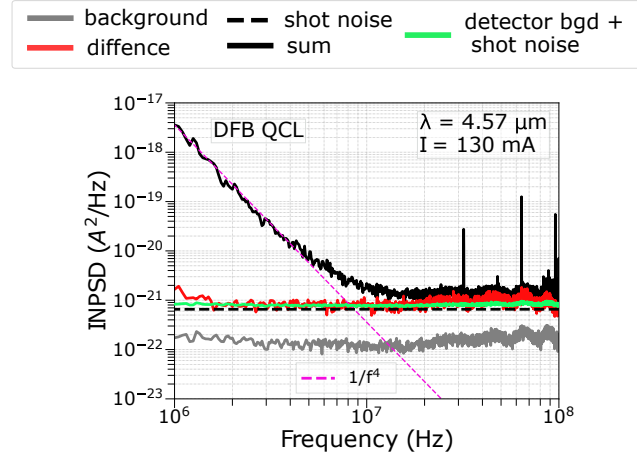


Figure 4.11: INPSD analysis for the DFB QCL at a current $I = 130$ mA and a temperature $T = 20$ °C

Additionally, it is interesting to notice that, when the DFB QCL is operated further from the threshold, a shot-noise limited emission can be obtained, at the cost of a higher attenuation level (96%) to avoid saturation on the detectors. Figure 4.11 reports an explanatory example: when the laser current is increased to 130 mA the measured intensity noise (i.e. INPSD of the sum) remains at the same level of the INPSD of the difference from $\simeq 20$ MHz to 100 MHz.

• DFB ICL

Compared with the two QCLs, this ICL shows much better performance (Figure 4.10(c)). The measured intensity noise is flat for the investigated Fourier-frequency range and tends to have a white noise behavior expected by a perfectly coherent source. In particular, the measured ICL radiation intensity noise flattens to the shot-noise level for Fourier frequencies above $\simeq 10$ MHz. A spurious peak around 3 MHz is present, not affecting the overall trend.

• Ring-Cavity ICL

The obtained data shows an INPSD of the sum signal superimposed with the INPSD of the difference trace (in blue) for the entire investigated Fourier frequency domain (Figure 4.10(d)). Up to 100 kHz all the traces are background

with the results found in [220], where an excess of noise causing this decay was linked to the following factors' combination: driving source noise and anomalously high-frequency noise of QCLs in combination with the alpha parameter.

¹⁰Among the factors that impact the excess of intensity noise in these devices [220], here the different laser packaging, being a butterfly, and the consequent use of a different driver, together with the higher wall-plug efficiency, have played a not negligible effect at low FFT frequencies

noise limited (they overlapped with the grey curve), but at higher frequencies, both the INPSD of the difference and the sum move sufficiently away from the background, reaching a maximum clearance equal to 6 dB at 1 MHz. This evidence highlights that such a device can benefit from a shot-noise-limited radiation up to 5 MHz. This behavior is expected to persist at higher frequencies, even if it is impossible to observe because of the limited dynamic range of the photo-detectors. Some spurious peaks also appear at around 1 MHz.

Relative Intensity Noise To conclude the analysis, the Relative Intensity Noise (RIN) was also investigated at different current values for all the investigated devices. Defined as the INPSD of the sum normalized to the squared of the total photo-current $(I_1 + I_2)^2$ measured by the photo-detectors, and the results are reported in Figure 4.12.

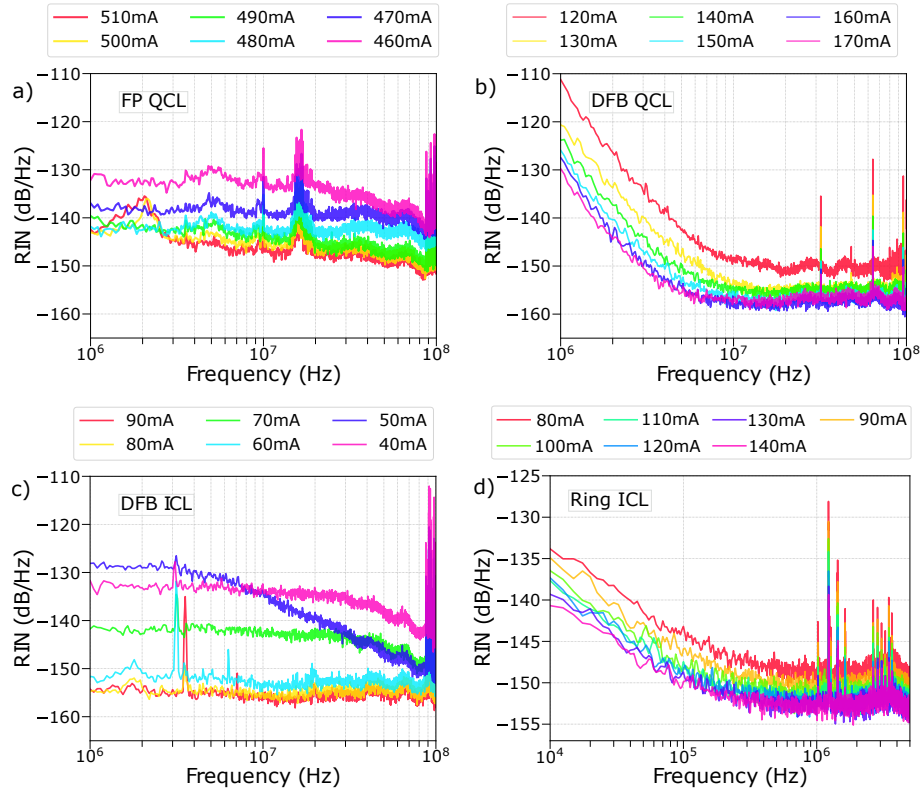


Figure 4.12: Relative Intensity Noise of the investigated devices: (a) FP QCL, (b) DFB QCL, (c) DFB ICL, and (d) Ring-Cavity ICL.

For the FP QCL (Figure 4.12(a)), a bias current range within 460 mA and 510 mA was analyzed, avoiding the comb emission regime. For this device, the RIN is higher when the laser is close to its threshold (pink curve). It starts to decrease with increasing current, reaching the lowest level for the tested currents of 510 mA. A similar behavior characterizes the DFB QCL, where the RIN exhibits a decreasing trend with increasing driving current (Figure 4.12(b)). Similarly to the reported INPSDs of the sum, each single RIN trace follows a steep decreasing trend reaching almost a white-noise plateau for frequencies above 10 MHz. Additionally, the measured RIN levels are compatible with the values estimated by theoretical prediction (being $\simeq -150 \div -160$ dB/Hz for QCL emitting in the range of 10-20 mW) [219].

Regarding the DFB ICL (Figure 4.12(c)), the expected decreasing trend for increasing the laser current in the corresponding RIN traces is broken in the two cases where the device undergoes a bi-color emission. In particular, a rise of the RIN appears by moving from the laser threshold ($I=40$ mA) to 50 mA, where a first mode jump occurs. Here a frequency cut-off of $\simeq 4$ MHz (well below the detector bandwidth of 5 MHz) is visible, and it can be attributed to a saturation effect connected with the high noise regime achieved in the bi-color emission. Another excess noise appears at 70 mA, in correspondence with the second mode jump. This interconnection between a bimodal or multi-modal emission and an increase in the overall intensity noise of the laser was already observed in other works [227, 230].

Finally, for the Ring-Cavity ICL (Figure 4.12(d)), the performance in terms of RIN is better if compared to previous state-of-the-art studies on room-temperature ICLs [231, 232]. In particular, at 140 mA, the Ring-cavity ICL RIN drops down to -153 dB/Hz, a value similar to the one found in [233] but obtained at a temperature of $\simeq -243$ °C. As an overall trend, the RIN follows the expected behavior.

4.2.3 Conclusion and outlook

This part of my PhD activity was dedicated to a thorough analysis of the intensity noise features of the most popular mid-IR sources, investigating the main typologies of state-of-the-art QCLs and ICLs at room temperature: a DFB ICL working in single-mode and bi-modal emission regimes, a single-mode DFB QCL, an FP QCL working in both single-mode and comb regime, and a novel Ring-Cavity ICL. A balanced homodyne detection scheme allows to study of the main peculiarities in terms of their intensity noise features. In the case of ICLs, for the DFB ICL the INPSD lies close to the shot-noise level in the whole tested frequency range and substantially achieves the shot-noise for high Fourier frequencies. For the Ring-Cavity ICL a standard quantum-limited emission can be achieved in the whole investigated frequency range (up to 5 MHz). A higher noise level characterizes the radiation from the two QCLs, operated at comparable working conditions of relative distance from the threshold and output power. In both cases, the measured INPSDs of the sum remain above the corresponding shot-noise level in the whole frequency range, thus marking a difference compared with the Interband devices. Nonetheless, in the case of the DFB QCL, a shot-noise-limited emission can be achieved by operating the laser further from the threshold at the cost of a higher attenuation.

To conclude, the results demonstrated the availability of obtaining mid-IR shot-noise-limited radiation from ICLs and, under certain conditions, from QCLs, paving the way to important improvements in the view of their application in high-sensitivity measurements (such as trace-gas sensing) where the intensity noise of the source represent a non-trivial limiting factor. The next step could be to continue investigating such sources to unveil their possibility of emitting in a sub-shot-noise regime.

4.3 Investigating the noise features of the acoustic-to-voltage transduction

Before investigating further improvements towards a *quantum-enhanced* system, a serious and comprehensive investigation of the noise source limiting the present performance is necessary also for the acoustic transduction and the detection part. In fact, it can be even stated that the ultimate noise limit reachable by a sensing system is governed also by the signal readout performance. In this regard, exploiting a shot-noise limited (or even sub-shot-noise) excitation source could show a real potential only if the overall intrinsic noise level of the readout scheme lays is not affected by additional *classical* noises (environmental, acoustic, and so on), a condition corresponding with its *standard quantum limit*. This is also true in our case of study, where a balanced Michelson interferometric readout was exploited for the acoustic-to-voltage transduction. In this framework, this section provides a brief investigation of the noise performances characterizing the developed interferometer, aimed at highlighting the ultimate potential in its actual configuration.

The acoustic-to-voltage transduction of the photoacoustic signal is proved by the interferometric readout of the MEMS structure's mechanical oscillations following the non-radiative relaxation of the investigated trace molecule. In this physical *picture* the ultimate *standard quantum limit* is associated with the MEMS thermal noise. Also known as Brownian noise, thermal noise arises from the random thermal motion of particles at the atomic level, governed by thermodynamic principles, and defines an intrinsic feature of a generic micro- or nano-mechanical structure [234–236].

Accordingly, it follows that a direct measurement of the noise features affecting the MEMS-based interferometric readout can give indirect but crucial information about its overall performance and limits. If the MEMS thermal noise is covered by additional classical features (such as technical, mechanical, or environmental noises) it means that the readout system is far from its *standard quantum limit*, thus hiding its ultimate potentiality. If the overall noise level lies at the MEMS thermal noise, it means that the readout scheme has reached its *standard quantum limit*. The latter condition is an essential prerogative to exploit the potentiality offered by having a shot-noise-limited PAS excitation source and could be also interpreted as a fundamental starting point towards several *quantum-enhanced* solutions. For example, by decreasing the overall temperature of the readout system and minimizing its fluctuation, it could be possible to reduce its overall thermal noise level to a condition where the use of a squeezed light source in the interferometric readout could be beneficial for a further improvement of the photoacoustic signal.

The following few pages will provide a brief description and discussion of the type of measurements performed, adding an important building block in this perspective Chapter.

4.3.1 Displacement power spectral density

According to the fluctuation-dissipation theorem (FDT), any dissipative process within a system will include fluctuations proportional to the system's temperature and dissipative

properties. In our case of study, the MEMS structure undergoes periodic oscillation due to the interaction with an on-resonance acoustic wave. In rest condition (i.e. without any PAS excitation process), the MEMS is affected only by Brownian motion whose dynamics can be described, in good approximation, by modeling it with a damped harmonic oscillator of effective mass m . Under these assumptions, its fluctuation dynamic is governed by the Langevin equation [234]:

$$m\ddot{x} + q\dot{x} + Kx = F_{th}, \quad (4.18)$$

where $\dot{x}$, $\ddot{x}$ are the first and second derivative of the harmonic oscillator position x , K is the spring constant, and q is the so-called velocity coefficient. F_{th} is a random force introduced by the Brownian motion with a white-noise power spectral density. Without going into many details, Equation 4.18 is easy to solve when moving from the time domain to the Fourier frequency domain, leading to a position (or displacement) power spectral density [m^2Hz^{-1}] of the damped oscillator equal to [234]:

$$|x(\omega)|^2 = \frac{4k_B T q}{(K - \omega^2)^2 + q^2 \omega^2}, \quad (4.19)$$

where $\omega = 2\pi f$ is the angular frequency. The spring constant K is linked to the oscillator resonance frequency by $\omega_0 = \sqrt{K/m}$, while the velocity coefficient can be derived by the oscillator quality factor Q as $q = m\omega_0/Q$. According to these two relations, the displacement power spectral density can be written as a function of two experimental parameters (i.e. $\omega_0 = 2\pi f_0$ and Q) that were already characterized in Subsection 3.1.3:

$$|x(\omega)|^2 = \frac{4k_B T \left(\frac{m\omega_0}{Q} \right)}{\left[(m\omega_0^2 - m\omega^2)^2 + \omega^2 \left(\frac{m\omega_0}{Q} \right)^2 \right]}. \quad (4.20)$$

4.3.2 Experimental approach and results

This theoretical formulation allows the development of a straightforward experimental routine to investigate the noise properties characterizing the interferometric readout system in the rest condition (i.e. without photoacoustic excitation). The *racked-shaped* MEMS cantilever was exploited for this characterization. In the first step, shown in Figure 4.13(a), the interferometer was properly aligned, maximizing the amplitude of the interferometric fringes. During this phase, the reference arm was moved via the PZT connected with a WFG, thus simulating the continuous movement of the MEMS, and optimally overlapping the two recombined beams. The calibration was obtained considering that the differential interferometric output peak-to-peak amplitude (i.e. V_{pp}) corresponds to a MEMS displacement of $\lambda/2$, where $\lambda = 633\text{nm}$ is the wavelength of the HeNe laser used for the readout, thus leading to the voltage-to-displacement coefficient $\alpha_{V/m} = \pi V_{pp}/(\lambda/2)$ at the *zero working point*, where the interferometric fringes slope is the highest.

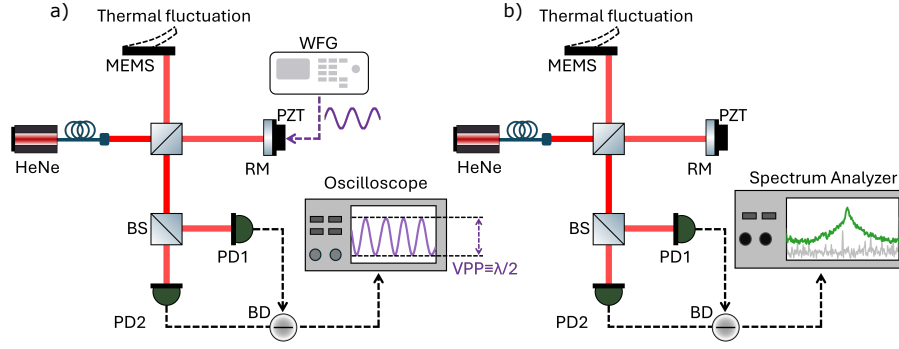


Figure 4.13: Experimental routine used for the interferometer displacement PSD measurement. (a): Interferometric fingers alignment and Voltage-to-displacement calibration. (b): PSD acquisition.

In the second step, the WFG was switched off, the interferometer was locked to the *zero working point* (see Subsection 2.1.6) and the differential interferometric output was acquired in the Fourier frequency domain via a spectrum analyzer (Tektronix, RSA 3303A), as reported in Figure 4.13(b). The frequency span was adjusted to acquire the PSD around the 7-kHz range, in order to investigate the *racket-shaped* MEMS resonance. Then, the acquired PSD (in dBm) was converted into Displacement PSD (DNPSD, in m^2Hz^{-1}) via the relation:

$$DNPSD = \left(\frac{10^{\frac{P[\text{dBm}]}{10}}}{1000} \right) \times \left(\frac{Z}{RBW} \right) \times \left(\frac{1}{\alpha_{V/m}} \right)^2, \quad (4.21)$$

where $Z = 50\Omega$ is the spectrum analyzer impedance. Finally, the acquired DNPSD was fitted using Equation 4.20, fixing all the parameters except for the temperature. As a result, the value of T extracted from the fit gives quantitative information about the noise level affecting the whole interferometric readout. In particular, if T is much higher than the ambient temperature (i.e. the one that characterizes the measurement system) it means that the interferometer is affected by additional noise features, hiding the MEMS thermal noise level. A deeper investigation of these noise sources must be performed in this case. If T is in the same order of magnitude as the ambient temperature, it means that the detection system is very close to or even at the thermal noise level for the MEMS structure, which is the optimal wanted condition.

The DNPSD measurements were performed for different working pressure values, fixing the RBW at 2 Hz. The effective mass m of the structure, being equal to $\simeq 5.3 \times 10^{-8}$ kg (about half of the real mass, i.e. $\simeq 9.13 \times 10^{-8}$ kg) was simulated by considering the effective measurement conditions (i.e. the MEMS structure displacement dynamics, the excitation point, and the interferometric beam size used for the oscillations readout). In Figure 4.14 a demonstrative acquisition at 100 mbar is reported. As it is possible to see, the experimental data (reported in orange) are quite well reproduced by the thermal noise fit (obtained from Equation 4.20), even if slight asymmetry persists in the tails of the resonance peak. A temperature of $\simeq 311$ K was extracted from the fit, a value in the same order of magnitude as the ambient temperature (i.e. $\simeq 298$ K).

This result confirms that the noise level of the acoustic transducer plus the readout system is very close to its fundamental limit (i.e. the MEMS structure thermal noise)

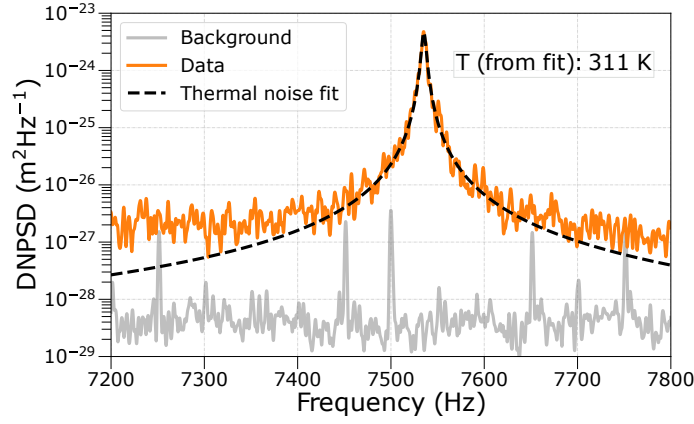


Figure 4.14: DNPSD of the *racket-shaped* MEMS cantilever at a pressure of 100 mbar (orange trace), fitted with the thermal noise function (black dashed line). The grey trace represents the spectrum analyzer's background.

in its actual configuration. As a further improvement, it could be useful to stabilize and even reduce the working temperature of the MEMS structure (which is embedded in the PA cell), thus preventing additional fluctuation beyond pure Brownian motion and further reducing the related noise level. With these precautions, we are confident that it could be possible to achieve a thermal-noise-limited readout, enabling the potentiality offered by the exploitation of a shot-noise-limited and frequency-noise-reduced excitation source for the photoacoustic excitation. Furthermore, this condition will also open a very interesting perspective concerning replacing the interferometric readout laser (i.e. the HeNe laser) with a non-classical source. In this sense, a very interesting and stimulating perspective could be implementing an interferometric readout with squeezed light [237], similar to what happens in gravitational wave detection experiments [238–241], to further reduce the readout noise and explore the possibility given by this *quantum-enhanced* regime.

Conclusion

Given its intrinsic high level of flexibility, compactness, and versatility, photoacoustic spectroscopy can be considered a leading technological solution for present and future challenges in all the possible declinations of highly performing trace-gas detection, such as environmental monitoring, medical diagnostic, and industrial process control. In this context, all the work carried out during my Ph.D. was devoted to exploring the sensitivity limits and investigating alternative configurations and improvements to this technique, also oriented towards future *quantum-enhanced* molecular sensing. The main achievements of my work can be summarized as follows.

- An important result relies on critical insight into the main aspects limiting the sensitivity performances of a doubly-resonant cantilever-enhanced photoacoustic sensor. On the one hand, the demonstrations of a ppb-level detection sensitivity using extremely low incident optical power (i.e. tens of μW) pave the way to potential and challenging in-field applications with low-power consumption solutions. On the other hand, the observation of N_2O absorption line saturation, opens interesting perspectives for high-resolution PAS-based spectroscopy applications.
- A fundamental step forward is taken by proposing novel silicon-based MEMS structures as alternative acoustic transducers, overcoming the traditional rectangular design. In this framework, the integration of one of the best-performing structures, i.e. the *racket-shaped* cantilever, with an advanced dual-tube acoustic resonance and with the optical cavity improves the detection sensitivity up to the ppt-level, with a NNEA value at the state-of-the-art for N_2O . All this effort marks an important step forward in the field of PAS detection, highlighting the scalability and adaptability of MEMS-based technologies and reinforcing their potential exploitation for future practical applications.
- Last but not least, pivotal steps in the view of a *quantum-assisted* approach for PAS were investigated. In particular, a preliminary but fundamental study of the main noise sources affecting the developed system was performed, proposing valuable solutions for their minimization, up to the corresponding standard quantum limit. An important focus is dedicated to the PAS excitation laser source,

investigating both its frequency and amplitude noise features. On the one hand, a key achievement is the demonstration of a significant frequency noise reduction for a mid-IR QCL by coupling with a high-finesse optical cavity, improving its spectral purity. On the other hand, another important result is the demonstration, via a balanced homodyne detection technique, of obtaining shot-noise limited mid-IR radiation from ICLs and, under certain conditions, from QCLs, leading to a potential reduction of the noise contributions coming from the radiation. This takes, consequently, to a maximization of the signal-to-noise ratio in PAS applications. Furthermore, these advancements can provide a robust framework to single out and exploit the quantum properties of light, such as squeezing or entanglement, to achieve sensitivities beyond classical limits. The last building block of this investigation provides a rigorous noise analysis of the transducer and signal-readout part. We demonstrate that in the actual configuration, it is possible to rely on a thermal-noise-limited MEMS-based interferometer, yielding a fundamental starting point in the view of overcoming the primary barriers and developing quantum-enhanced acoustic-to-voltage readout.

Therefore, the work and results achieved during these three years of Ph.D. must be framed in a wider future perspective. The integration of quantum technologies with a photoacoustic-based approach can hold great potential in pushing the trace-molecule detection sensitivity to unprecedented levels, beyond the state-of-the-art, but also in exploring exciting future challenges such as single-molecule detection. At the same time, continued progress in MEMS design, material science, and laser technologies must be considered equally important in the view of improving further the scalability and versatility of PAS systems. This could make them a forerunner solution for global challenges in science, industry, and environmental sustainability.

A.1	Proportionality between the R^2 and X components	131
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A.1 Proportionality between the $\mathbf{R}^2$ and $\mathbf{X}$ components

According to Reference [176], and switching from a current to a voltage readout of the photoacoustic signal, the in-phase (X) and out-of-phase (Y) voltage components of the signal can be written as:

$$X = \frac{V_0 \Delta_f^2 f^2}{\Delta_f^2 f^2 + (f - f_0)^2}, \quad (\text{A.1})$$

$$Y = \frac{V_0 \Delta_f f (f^2 - f_0^2)}{\Delta_f^2 f^2 + (f^2 - f_0^2)}, \quad (\text{A.2})$$

where V_0 is the maximum voltage value at the cantilever's resonance frequency f_0 according to these definitions, the R^2 signal component can be mathematically derived as follows:

$$\begin{aligned} R^2 = x^2 + Y^2 &= \frac{V_0^2 \Delta_f^4 f^4}{\left[\Delta_f^2 f^2 + (f - f_0)^2 \right]^2} + \frac{V_0^2 \Delta_f^2 f^2 (f^2 - f_0^2)^2}{\left[\Delta_f^2 f^2 + (f - f_0)^2 \right]^2} \\ &= \frac{1}{\left[\Delta_f^2 f^2 + (f - f_0)^2 \right]^2} [V_0^2 \Delta_f^4 f^4 + V_0^2 \Delta_f^2 f^2 (f^2 - f_0^2)^2] = \\ &= \frac{V_0^2 \Delta_f^2 f^2}{\left[\Delta_f^2 f^2 + (f - f_0)^2 \right]^2} = V_0 X. \end{aligned}$$

This demonstrates that the R^2 and the X signal components differ from each other only from the multiplicative constant V_0 .

A.2 NNEA coefficient derivation

The derivation of a definition for the Normalized Noise Equivalent Absorption Coefficient passes through the definition of the absorption coefficient $\alpha(\lambda)$ of a given molecule [242]:

$$\alpha(\lambda) = \frac{Sp}{k_B T} g(\lambda), \quad (\text{A.3})$$

where k_B is the Boltzmann constant, T the temperature, p the partial pressure of the targeted gas in the mixture, while S is defined as the line strength associated with the addressed absorption line, obtained referring to the HITRAN database [76], and $g(\lambda)$ represents the spectral line-shape. Assuming a Lorentian pressure-broadening regime [77], the line-shape value at the absorption peak wavelength λ_0 can be defined as:

$$g(\lambda_0) = \frac{1}{\pi \gamma_{air} p_{tot}}, \quad (\text{A.4})$$

where p_{tot} is the total pressure of the gas mixture and γ_{air} represents the air-broadening coefficient, a parameter typical for every molecule species. Then, given the minimum detectable concentration $c_{min} = p_{min}/p_{tot}$, it is possible to compute the so-called Noise Equivalent Absorption coefficient (NEA) as:

$$\alpha_{min} = \frac{Sp_{min}}{k_B T} \frac{1}{\pi \gamma_{air} p_{tot}} = \frac{S}{k_B T} \frac{c_{min}}{\pi \gamma_{air}} \quad (\text{A.5})$$

Finally, the Normalized Noise Equivalent Absorption (NNEA) coefficient can be computed via the following equation:

$$NNEA = \frac{P_{in} \alpha_{min}}{\sqrt{BW}} \quad (\text{A.6})$$

Where P_{in} is the incident laser power and BW the 3dB cut-off lock-in bandwidth. As it is defined, this experimental parameter allows the quantification of absolute sensor's performances, regardless of the type of molecular transition chosen, the available optical power, and the integration time, providing a fair comparison with the literature.

A.3 FNPSD derivation

The noise spectra acquisition routine for the free-running QCL and the locked QCL consists of several steps. To maintain a sufficiently high spectral resolution within the investigated frequency range (i.e. from 100 Hz to 10 MHz), the spectra were acquired in progressively larger frequency windows and varying the resolution bandwidth (RBW), as summarized in the Table below:

The spectrum analyzer provides the measurements in dBm units. So, to obtain the Frequency Noise Power Spectral Density it is necessary to go through the following two conversion steps:

$$P[W] = \frac{10^{\frac{P[dBm]}{10}}}{1000} \quad (\text{A.7})$$

Table 1: Different frequency time-window noise acquisition acquisitions and associated resolution bandwidth.

Frequency span	RBW [Hz]
0-10 MHz	100
0-3 MHz	50
0-1 MHz	30
0-500 kHz	20
0-100 kHz	100
0-10 KHz	10

$$VNPSD[V^2Hz^{-1}] = \frac{P[W]}{RBW[Hz]} \times Z[\Omega] \quad (A.8)$$

$$FNPSD[Hz^2Hz^{-1}] = VNPSD[V^2Hz^{-1}] \times \left(\frac{1}{\alpha_{V/Hz}} \right)^2, \quad (A.9)$$

where Z is the spectrum analyzer impedance, fixed at 50Ω .

List of abbreviations

1-f	First-Harmonic
Ag	Silver
AM	Amplitude Modulation
AOM	Acusto-Optic Modulator
ASI	Italian SPace Agency
BHD	Balanced Homodyne Detection
BOE	Buffered Oxide Etch
C ₂ H ₂	Acetylene
C ₃ H ₆ O	Di-methyl ketone
C ₄ F ₈	Octa-fluoro-cyclobutane
C ₅ H ₈	Isoprene
CH ₄	Methane
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CD	Current Driver
CEPAS	Cantilever-Enhanced Photo-Acoustic Spectroscopy
CNR-IMM	Institute of Microelectronics and Micro-systems of the Italian National Research Council
CNR-INO	National Institute of Optics of the Italian National Research Council
CW	Continuous Wave
DFB	Distributed Feedback
DRIE	Deep Reactive Ion Etching
EOM	Electro-Optic Modulator
FAC	Frequency-to-Amplitude Converter

FEM	Finite Element Method
FFT	Fast Fourier Transform
FWHM	Full-Width at Half-Maximum
FM	Frequency Modulation
FNPSD	Frequency Noise Power Spectral density
FP	Fabry-Perot
FSR	Free-Spectral Range
FTIR	Fourier-Transform Infrared Spectrometer
GB	Gas Blender
GWP	Global Warming Potential
H ₂ O	Water
HgCdTe	Mercury Cadmium Telluride
HITRAN	High Resolution Transmission
HR	High-Reflectivity
HWHM	Half-Width at Half Maximum
ICL	Interband Cascade Laser
InAlAs	Indium-Aluminium-Arsenide
InGaAs	Indium-Gallium-Arsenide
InP	Indium-Phosphide
ISO	Optical Isolator
ICP	Inductively Coupled Plasma
LAS	Laser Absorption Spectroscopy
LCD	Liquid Crystal Display
LED	Light Emitted Diode
LIA	Lock-in Amplifier
LIV	Laser-Light-Voltage
LO	Local Oscillator
LPCVD	Low Pressure Chemical Vapor Deposition
MDL	Minimum Detection Limit
MEMS	Micro-Electro-Mechanical Systems
Mid-IR	Mid-Infrared
N ₂ O	Nitrous Oxide
NDIR	Non-Dispersive Infrared Spectroscopy
NEA	Noise Equivalent Absorption
NEC	Noise Equivalent Concentration

N ₃	Ammonia
NNEA	Normalized Noise Equivalent Absorption
NO	Nitric Oxide
NO ₂	Nitrogen Dioxide
O ₂	Dioxygen
O ₃	Ozone
OCS	Carbonyl Sulfide
OFC	Optical Frequency Comb
OPO	Optical Parametric Oscillator
PAS	Photo-acoustic Spectroscopy
PDH	Pound-Drever-Hall
PSD	Power Spectral Density
PZT	Piezo-Electric Ceramic Material
QCL	Quantum Cascade Laser
QEPAS	Quartz-Enhanced Photo-Acoustic Spectroscopy
QTF	Quartz Tuning Forks
RBW	Resolution Band-Width
RIN	Relative Intensity Noise
ROC	Radius of Curvature
Sat-CRDS	Saturated Cavity Ring Down Spectroscopy
SCAR	Saturated-Absorption Cavity Ring Down Spectroscopy
sccm	Standard Cubic Centimeter
Si	Silicon
SF ₆	Sulfur hexa-fluoride
SiH ₄	Silane
SiO ₂	Silicon dioxide
SOI	Silicon-on-Insulator
TDLS	Tunable Diode Laser Spectroscopy
TEC	Temperature Controller
THz	Terahertz
TTL	Transistor-Transistor-Logic signal
TMAH	Tetra-Methyl-Ammonium Hydroxide
WFG	Wave-Form Generator
WM	Wavelength modulation
ZnSe	Zinc Selenide

List of abbreviations

ZWP	Zero Working Point
-----	--------------------

List of symbols

∇	Nabla operator
∇^2	Laplace operator
$ 0, 1, 3\rangle$	States of a three-level system
$\alpha(k, T, p)$	Absorption coefficient [cm^{-1}]
$\alpha_{\text{Hz/ms}}$	Millisecond-to-Hertz conversion factor [Hzms^{-1}]
$\alpha_{\text{V/Hz}}$	Frequency-to-amplitude conversion factor [VHz^{-1}]
$\alpha_{\text{V/m}}$	Voltage-to-displacement conversion factor [Vm^{-1}]
β_{AC}	Acoustic damping factor
γ	Adiabatic coefficient
Γ	pressure-induced line shift [Hz/atm]
$\Gamma_E(\tau)$	Laser electric field auto-correlation function
δ_{nm}	Kronecker's delta
Δc	Cavity mode width [Hz]
Δ_D	Doppler-limited FWHM [Hz]
Δf	MEMS response curve's FWHM [Hz]
Δ_L	Pressure-broadened FWHM [Hz]
Δf_{LAS}	QCL intrinsic line-width [Hz]
ϵ_0	Vacuum permittivity [Fm^{-1}]
$\epsilon_n(r)$	Resonator's eigenmodes
$\epsilon_{\text{RtS}}(f, \tau(p))$	Radiation-to-Sound conversion efficiency
η	QCL Loss factor $\in [0, 1]$
η_{CE}	Laser-cavity coupling efficiency
η_{qe}	Quantum efficiency $\in [0, 1]$
$\Theta(x - x_0)$	Theta's Heaviside function
λ	Wave-length [μm]

μ	Mass per unit length [kgm^{-1}]
ξ	Fluid Viscosity [$\text{kgm}^{-1}\text{s}^{-1}$]
$\rho(\mathbf{r}, t)$	mass density [kgm^{-3}]
ς	Mass injection per unit volume [kgm^{-3}]
σ	Molecule's absorption cross-section [cm^2/mol]
τ_{RD}	Optical cavity Ring-down time [μs]
φ	Photon flux
$\Phi_{a,b}$	Interferometric back-reflected beam phases
ω	Angular velocity [rads^{-1}]
$\hat{a}_i$	field operators, $i \in [1, 2, 3, 4]$
A_E	Einstein coefficient
$A_n(f_n)$	n – th sound wave amplitude
c	Light velocity in vacuum [ms^{-1}]
c_m	Mixing ratio
C_d	QTF damping parameter
C_p	Collision coefficient [MHzmbar^{-1}]
C_t	Transit time coefficient [MHz]
C_{tg}	Trace-gas concentration [ppX]
d	dipole momentum [Cm]
$\hat{d}_{3,4}$	Photo-detector output field operator
e	Electron Charge [C]
$\mathcal{E}$	Young modulus [Nm^{-2}]
$E_{a,b}$	Interferometric back-reflected field amplitudes
E_D	Single tube external diameter [mm]
f	Frequency (Hz)
$\mathcal{F}$	Cavity Finesse
$\mathbf{F}$	Force density [N^{-3}]
$f_{1,2}$	Focus lengths [mm]
f_3	Cavity mirror's focus length [mm]
$f(k, k_0, T, p)$	spectral line-shape function [cm^{-1}]
$f_D(k, k_0)$	Doppler-limited broadening line-shape [cm^{-1}]
$f_L(k, k_0)$	Pressure broadening line-shape [cm^{-1}]
f_{LAS}	Laser emission frequency [Hz]
f_n	Resonator's eigenfrequencies [Hz]
FSR	Free Spectral Range [Hz]

F_{th}	Random force by Brownian motion [N]
$G(\mathbf{r}, \mathbf{r}', t, \tau)$	Green's function
G_{IC}	Intra-cavity power enhancement
h	Plank constant [Js]
H	Heat power density injection [J^{-3}]
$I_{1,2}$	Detected interferometric back-reflected intensities
$\hat{I}_{1,2}$	Output photocurrent operators
I_D	Single tube internal diameter [mm]
$I_L(r, z, t)$	Intensity profile of a Gaussian beam
I_S	Absorption line saturation intensity [mWmm ⁻²]
K	Spring constant [N^{-1}]
k	wave-number [cm^{-1}]
k_B	Boltzmann constant [JK^{-1}]
k_r	Relaxation constant rate [s^{-1}]
k_{sp}	Spontaneous emission constant rate [s^{-1}]
k_{st}	Stimulated emission constant rate [s^{-1}]
k_{V-T}	Vibrational Translational relaxation rate [s^{-1}]
L	Cavity Length [mm]
$\mathcal{L}$	Optical path-length [mm]
L_{BW}	QCL beam waist position [mm]
L_T	Single tube length [mm]
m	Mass [kg]
$\mathcal{M}$	Inertia momentum [kgm^2]
M^2	Beam propagation factor
MDL	Minimum detection limit [ppX]
M_{mol}	Molar mass [$kgmol^{-1}$]
n	Refractive index
$\hat{n}$	Number operator
N	Molecules absorbing number density
NEC	Noise equivalent concentration [ppX]
N_S	QCL number of stages
p	Pressure [mbar]
P	Optical power [mW]
q	Velocity coefficient
Q	Quality factor

Q_0	Quality factor in vacuum
R	Mirror reflectivity
ROC	Radius of curvature [m]
R_T	Trans-impedance resistance [Ω]
$S(\mathbf{r}, t)$	Entropy [JK^{-1}]
$S_{\delta\nu}(f)$	Laser frequency noise power spectral density [$\text{Hz}^2\text{Hz}^{-1}$]
SNR	Signal-to-noise ratio
$S(P)$	Laser power saturation [mWmm^{-2}]
$S_{PA}(\mathbf{r}, t)$	Photoacoustic source term
$S(T)$	Single-molecule line-strength [cm/molecule]
T	Temperature [K°C]
V	volume [m^3]
$\hat{v}_i$	Vacuum field operator $i \in [1, 2, 3, 4]$
$V_{1,2}$	first-stage trans-impedance photo-detectors DC-outputs [V]
v_s	Sound velocity [ms^{-1}]
w_1	QCL beam waist radius [mm]
w_L	Beam waist radius [mm]
$ x(\omega) ^2$	Position (or displacement) power spectral density [m^2Hz^{-1}]
y_0	Waist position - the first focus lens distance [mm]
$y_{1,6}$	Variable of the mode-matching 6-equation system
Z	Spectrum analyzer impedance [Ω]
z_r	Rayleigh parameter

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Curriculum vitae & Publications list

Jacopo Pelini



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Personal Introduction

I am currently a third-year PhD student in Quantum Technologies, an international doctorate shared between the University of Naples *Federico II*, the National Research Council (CNR) of Italy, and the University of Camerino. My research activity is mainly focused on cantilever-enhanced photo-acoustic spectroscopy for ultra-high sensitive trace-gas detection. In parallel, I am interested in proposing novel photoacoustic-based experimental approaches, regarding both acoustic transduction and signal readout. My research interests also include the characterization of mid-infrared sources in terms of frequency and amplitude noise. I am also interested in exploiting such emitting devices in applications like Light Detection and Ranging (LIDAR).

Work & educational experiences

December, 2024 – today

- **RESEACH FELLOWSHIP (POSTDOC)**

Institute: National Institute of Optics (CNR-INO), Largo Enrico Fermi, 6, 50125 Firenze FI - Italy.

Project “Covert and Advanced multi-modal Sensor Systems for tArgetacqui-sition and reconnAissance” – CASSATA, GA 101121447 - CUP B53C23008400006.

Scientific director: Dr. Simone Borri

Research topics: Development of cavity enhanced photoacoustic for trace gas sensing.

January 1, 2022 – December 2024

- **PHD STUDENT OF THE DOCTORATE IN QUANTUM TECHNOLOGIES**

Institute: University "Federico II", C.so Umberto I, 40, 80138 Napoli, Italy; National Institute of Optics (CNR-INO), Via Nello Carrara 1, 50019 Sesto Fiorentino (FI) - Italy.

Thesis title (tentative) & supervisor: “Exploring the sensitivity limit of Cantilever-Enhanced photoacoustic spectroscopy” – Dr. Simone Borri.

Main goal: Development and characterization of highly-sensitive photoacoustic trace-gas sensors, identification of alternative approaches, and investigation of quantum-assisted configuration.

August, 2023 – February, 2024 (~7 months)

- **INTERNSHIP AT PPQ SENSE S.R.L**

Company: ppq Sense S.R.L, Viale L.Ariosto, 492B, 50019 Sesto Fiorentino, Florence .

Project description & supervisor: Coupling a QCL with a High-Finesse optical cavity for frequency noise reduction – Dr. Simone Borri & Dr. Saverio Bartalini

Main goal: Development of an experimental setup to test the frequency noise reduction of a mid-IR Quantum Cascade Laser coupled with a high-finesse optical cavity.

October 2019 – July 2021

- **MASTER IN PHYSICS, CURRICULUM PHYSICS OF MATTER, LM-17 (110/110)**

Institute: University of Perugia (Italy)

Thesis title & supervisor: “Vibrational properties of SARS-CoV-2 main protease as affected by potential antiviral inhibitors” – Prof. Alessandro Paciaroni.

March 2021 – July 2021

- **INTERNSHIP**

Institute: *Physics of DNA and Biosystems Laboratory*, Department of Physics and Geology, University of Perugia (Italy)

supervisor: Prof. Alessandro Paciaroni.

October 2016 – October 2019

- **BACHELOR DEGREE IN PHYSICS, L-30 (110/110)**

Institute: University of Perugia (Italy)

Thesis title & supervisor: “Neutron spectroscopy for the study of alternative moderators for the production of ultra-cold neutrons” – Prof. Andrea Orecchini.

Publications List

Peer-reviewed articles

1. Georg Marschick, **Jacopo Pelini**, Tecla Gabbrielli, Francesco Cappelli, Robert Weih, Hedwig Knotig, Johannes Koeth et al. [*Mid-infrared Ring Interband Cascade Laser: Operation at the Standard Quantum Limit*](#), ACS photonics 11, no. 2 (2024): 395-403.
2. **Jacopo Pelini**, Stefano Dello Russo, Inaki Lopez Garcia, Maria Concetta Canino, Alberto Roncaglia, Pablo Cancio Pastor, Iacopo Galli, Paolo De Natale, Wei Ren, Simone Borri, Zhen Wang, and Mario Siciliani de Cumis, [*New silicon-based micro-electro-mechanical systems for photo acoustic trace-gas detection*](#), Photoacoustics 38 (2024): 100619.
3. Stefano Dello Russo, **Jacopo Pelini**, Inaki Lopez Garcia, Maria Concetta Canino, Alberto Roncaglia, Pablo Cancio Pastor, Iacopo Galli, Paolo De Natale, Simone Borri, and Mario Siciliani de Cumis, [*Dual tube MEMS-based spectrophone for sub-ppb mid-IR photoacoustic gas detection*](#), Photoacoustics (2024): 100644.
4. **Jacopo Pelini**, Stefano Dello Russo, Mario Siciliani de Cumis, Zen Whang, Iacopo Galli, Inaki Lopez Garcia, Pablo Cancio Pastor, Maria Concetta Canino, Alberto Roncaglia, Naota Akikusa, Wei Ren, Paolo De Natale, and Simone Borri. [*A cavity-enhanced MEMS-based photoacoustic sensor for ppt-level trace-gas detection*](#), Sensors and Actuators B: Chemical (2025): 137313.

Submitted articles

5. Tecla Gabbrielli, **Jacopo Pelini**, Georg Marschick, Luigi Consolino, Irene La Penna, Jérôme Faist, Mathieu Bertrand et al., [*Shot-noise-limited emission from interband and quantum cascade lasers*](#), arXiv:2409.12732 (preprint, 2024) [Submitted to Optics Express, Optica publishing group]

6. **Jacopo Pelini**, Mario Siciliani de Cumis, Zhen Wang, Iacopo Galli, Inaki Lopez Garcia, Maria Concetta Canino, Pablo Cancio Pastor et al., *Trace-molecule detection below the part-per-trillion level with doubly-resonant cantilever-enhanced photoacoustic spectroscopy*, The European Conference on Lasers and Electro-Optics, p. ch₁₄₂. Optica Publishing Group, 2023.
7. **Jacopo Pelini**, Mario Siciliani de Cumis, Zhen Wang, Stefano Dello Russo, Iacopo Galli, Inaki Lopez Garcia, Maria Concetta Canino et al., *High-performance cavity-enhanced photoacoustic trace-gas sensing*, Quantum Sensing and Nano Electronics and Photonics XX, vol. 12895, pp. 60-63. SPIE, 2024.
8. **Jacopo Pelini**, Stefano Dello Russo, Arianna Elefante, Maria Concetta Canino, Alberto Roncaglia, Inaki Lopez Garcia, Pablo Cancio Pastor, Paolo De Natale, Simone Borri, and Mario Siciliani de Cumis. *Characterization of new silicon-based micro-electro-mechanical systems for photoacoustic trace-gas detection*, MOEMS and Miniaturized Systems XXIII, vol. 12899, pp. 18-22. SPIE, 2024.
9. Giacomo Insero, Francesco Cappelli, M. Siciliani de Cumis, **Jacopo Pelini**, Tecla Gabbrielli, Georg Marschick, Robert Weih et al., *Excess frequency noise in interband cascade lasers: towards narrower linewidth operation*, Novel In-Plane Semiconductor Lasers XXIII, vol. 12905, pp. 125-130. SPIE, 2024.
10. **Jacopo Pelini**, Mario Siciliani de Cumis, Zhen Wang, Stefano Dello Russo, Iacopo Galli, Inaki Lopez Garcia, Maria Concetta Canino et al., *High-performance cavity-enhanced photoacoustic sensing*, Laser Applications to Chemical, Security and Environmental Analysis, pp. LM1F-1. Optica Publishing Group, 2024.
11. Tecla Gabbrielli, **Jacopo Pelini**, Georg Marschick, Luigi Consolino, Irene La Penna, Jérôme Faist, Mathieu Bertrand et al, *Intensity noise of mid-infrared semiconductor cascade lasers: exploring shot noise-limited operation*, Novel In-Plane Semiconductor Lasers XXIII, vol. 12905, pp. 121-124. SPIE, 2024.

International conferences and symposia (oral or poster)

CONFERENCE (YEAR)	PLACE	CONTRIBUTE NAME & TYPE
PhD Program in Quantum Technologies 2022 Summer School (2022)	Catania (Italy)	<i>Trace-molecule detection below the ppt level with cavity-enhanced photoacoustic spectroscopy</i> Oral presentation
Quantum2022 Summer School on Quantum Optical Technologies (2022)	Trani (Italy)	<i>Combined acoustic and optical enhancement for sub-ppt Photoacoustic-based trace-molecule detection</i> Poster
Quantum2023 Summer School on Quantum Optical Technologies (2023)	Trieste (Italy)	<i>Towards sub-ppt trace-molecule detection with a doubly-resonant cantilever-enhanced photoacoustic sensor</i> Poster
CLEO- Europe/EQEC 2023 (2023)	Munich (Germany)	<i>Trace-molecule detection below the part-per-trillion level with doubly-resonant cantilever-enhanced photoacoustic spectroscopy</i> Oral
HRMS2023 (2023)	Dijon (France)	<i>High-sensitivity vibrational spectroscopy by a cantilever-enhanced photoacoustic sensor</i> Oral
SPIE Photonic West (2024)	San Francisco (USA)	<i>Characterization of new silicon-based micro-electro-mechanical systems for photoacoustic trace-gas detection</i> Oral presentation — <i>High-performance cavity-enhanced photoacoustic trace-gas sensing</i> Oral presentation

CONFERENCE (YEAR)	PLACE	CONTRIBUTE NAME & TYPE
Photon Hub: Frontier trace gas sensors addressing industrial challenges for the environment, health, safety, and security (2024)	Florence (Italy)	<i>Photo-acoustic Spectroscopy: a tool for highly sensitive trace-gas detection</i> Oral presentation
IQCLSW2024 (2024)	Isola d'Ischia (Italy)	<i>High-Performance Mid-Infrared QCL-based Cantilever-Enhanced photoacoustic sensor</i> Poster
FLAIR2024 (2024)	Assisi (Italy)	<i>A ppt level cavity-enhanced photo-acoustic sensor with a "racket-shaped" cantilever</i> Oral presentation — <i>Investigating the acousto-mechanical properties of novel MEMS structure for photo-acoustic spectroscopy</i> Poster — <i>3D-printed acoustic resonators for MEMS-based photoacoustic spectroscopy</i> Poster
CNR-INO Symposium (2024)	Florence (Italy)	<i>Performance investigation of cavity-enhanced photo-acoustic sensors</i> Poster
SPIE Photonic West (2025)	San Francisco (USA)	<i>A novel dual-tube spectrophone for sub-ppb cantilever-enhanced photoacoustic detection</i> Oral presentation

Awards

1. *Amat Mills* award for the best oral presentation. The 28th Colloquium on High-Resolution-Molecular Spectroscopy (HRMS2023 Dijon, France)

2. Best student poster Award by *Nature Photonics*. The International Quantum Cascade Lasers School and Workshop 2024 (IQCLSW2024 Ischia, Italy)
-

Informative

The undersigned Jacopo Pelini declares that all the facts reported in this curriculum correspond to the truth under and for articles 46 and 47 of the Presidential Decree 445/2000. The undersigned declares to be aware of the criminal penalties to be incurred in the event of a false declaration or containing data that no longer corresponds to the truth, as required by art. 76 of the Presidential Decree 28.12.2000, n. 445. The undersigned declares to be aware of art. 75 of the Presidential Decree 28.12.2000, n. 445, relating to the forfeiture of any benefits resulting from the provision issued, if the Administration, following a check, finds the content of the aforementioned declaration to be untruthful.



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