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Photonic integration for opto–acoustic and opto–thermo–elastic sensing

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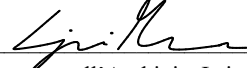
Il sottoscritto **Luigi Melchiorre**, nato ad **Acquaviva delle Fonti (BA)** il **28/09/1996**, residente in **Gioia del Colle (BA)**, via **Fratelli Rosati n. 25**, e-mail **l.melchiorre@phd.poliba.it**, iscritto al terzo anno del Corso di Dottorato di Ricerca in **Industria 4.0**, ciclo **XXXVIII**, essendo stato ammesso a sostenere l'esame finale con la prevista discussione della tesi dal titolo:

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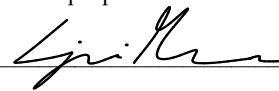
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DEGLI STUDI DI BARI
ALDO MORO

Ph.D. Candidate:

Luigi Melchiorre

*Photonic Integration for Opto–Acoustic and
Opto–Thermo–Elastic Sensing*

Thesis submitted for the degree of *Philosophiae Doctor*

Interuniversity Ph.D. Program in *Industry 4.0*

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Ph.D. Advisors:

Prof. Vincenzo Luigi **Spagnolo**, Ph.D.

Prof. Angelo **Sampaolo**, Ph.D.

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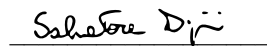


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LIST OF ACRONYMS AND ABBREVIATIONS

1f	<i>First harmonic or fundamental.</i>
2f	<i>Second harmonic.</i>
ADM	<i>Acoustic detection module.</i>
AlF ₃	<i>Aluminum fluoride.</i>
APC	<i>Angled physical contact.</i>
ARROW	<i>Anti-resonant reflecting optical waveguide.</i>
As ₂ S ₃	<i>Arsenic trisulfide.</i>
As ₂ Se ₃	<i>Arsenic triselenide.</i>
ASIC	<i>Application-specific integrated circuit.</i>
BaF ₂	<i>Barium fluoride.</i>
BB	<i>Broadband.</i>
BF	<i>Beat-frequency.</i>
C	<i>Carbon.</i>
C1	<i>Methane.</i>
C2	<i>Ethane.</i>
C ₂ H ₆	<i>Ethane.</i>
CEAS	<i>Cavity-enhanced absorption spectroscopy.</i>
CH ₄	<i>Methane.</i>
CMOS	<i>Complementary metal–oxide–semiconductor.</i>

CO *Carbon monoxide.*

CO₂ *Carbon dioxide.*

CHF₃ *Trifluoromethane.*

CRDS *Cavity ring-down spectroscopy.*

Cu *Copper.*

CVD *Chemical vapor deposition.*

DBR *Distributed-Bragg-reflector.*

DC *Direct-current.*

DFB *Distributed-feedback.*

FBT *Fused biconical taper.*

FC *Ferrule connector.*

FEM *Finite element method.*

FWHM *Full-width at half-maximum.*

H *Hydrogen.*

H₂O *Water vapor.*

H₂S *Hydrogen sulfide.*

HCF *Hollow-core fibers.*

HF *Hydrogen fluoride.*

HgCdTe *Mercury cadmium telluride.*

HTO *High-temperature oxide.*

I *Intracavity.*

ICL *Interband cascade laser.*

ICOS *Integrated cavity output spectroscopy.*

IFG *Indium fluoride glass.*

In₂O₃ *Indium oxide.*

InAlAs *Aluminum indium arsenide.*

InF_3 *Indium fluoride.*
 InGaAs *Indium gallium arsenide.*
 InP *Indium phosphide.*
 IR *Infrared.*
 LaF_3 *Lanthanum fluoride.*
 LED *Light-emitting diode.*
 LEL *Lower explosive limit.*
 LITES *Light-induced thermoelastic spectroscopy.*
 LP *Low-pressure.*
 LTO *Low-temperature oxide.*
 MDL *Minimum detection limit.*
 MFD *Mode-field diameter.*
 MEMS *Micro-electromechanical systems.*
 N_2 *Nitrogen.*
 NaF *Sodium fluoride.*
 NEP *Noise equivalent power.*
 NH_3 *Ammonia.*
 NICE *Noise-immune cavity-enhanced.*
 NNEA *Normalized noise-equivalent absorption.*
 NO *Nitric oxide.*
 O *Oxygen.*
 OA *Off-axis.*
 OEC *Open-end correction.*
 OF *Optical feedback.*
 OHMS *Optical heterodyne spectroscopy.*
 O_2 *Molecular oxygen.*

PAS	<i>Photoacoustic spectroscopy.</i>
PC	<i>Personal computer.</i>
PCF	<i>Power-confinement factor.</i>
PDK	<i>Process design kit.</i>
PIC	<i>Photonic integrated circuit.</i>
pp	<i>Peak-to-peak.</i>
ppb	<i>Parts-per-billion.</i>
ppm	<i>Parts-per-million.</i>
ppt	<i>Parts-per-trillion.</i>
Q	<i>Quality factor.</i>
QCL	<i>Quantum cascade laser.</i>
QCM	<i>Quartz crystal microbalance.</i>
QEPAS	<i>Quartz-enhanced photoacoustic spectroscopy.</i>
QTF	<i>Quartz tuning fork.</i>
R^2	<i>Correlation coefficient.</i>
RLC	<i>Resistor–inductor–capacitor.</i>
RMS	<i>Root-mean-square.</i>
SAW	<i>Surface acoustic wave.</i>
SCCM	<i>Standard cubic centimeters per minute.</i>
SEM	<i>Scanning electron microscopy.</i>
SF ₆	<i>Sulfur hexafluoride.</i>
Si	<i>Silicon.</i>
Si ₃ N ₄	<i>Silicon nitride.</i>
SiH ₂ Cl ₂	<i>Dichlorosilane.</i>
SiN	<i>Silicon nitride.</i>
SiNOI	<i>Silicon nitride-on-insulator.</i>

SiO ₂	<i>Silicon dioxide.</i>
SLR	<i>Sensitivity-to-loss ratio.</i>
SMO	<i>Semiconducting metal oxide.</i>
SnO ₂	<i>Tin oxide.</i>
SNR	<i>Signal-to-noise ratio.</i>
SOI	<i>Silicon-on-insulator.</i>
SrF ₂	<i>Strontium fluoride.</i>
SWG	<i>Subwavelength waveguide.</i>
SWIR	<i>Short-wave infrared.</i>
TCD	<i>Thermal conductivity detector.</i>
TDLAS	<i>Tunable diode laser absorption spectroscopy.</i>
TE	<i>Transverse electric.</i>
TEC	<i>Thermoelectric cooler.</i>
TEOS	<i>Tetraethyl orthosilicate oxide.</i>
USD	<i>United States dollar.</i>
UV	<i>Ultraviolet.</i>
VOC	<i>Volatile organic compound.</i>
V–T	<i>Vibrational–translational.</i>
WG	<i>Waveguide.</i>
WMS	<i>Wavelength modulation spectroscopy.</i>
WO ₃	<i>Tungsten oxide.</i>
ZBLAN	<i>ZrF₄–BaF₂–LaF₃–AlF₃–NaF.</i>
ZnF ₂	<i>Zinc fluoride.</i>
ZnO	<i>Zinc oxide.</i>
ZrF ₄	<i>Zirconium tetrafluoride.</i>

INTRODUCTION AND AIM OF THE DISSERTATION

The relentless advancement of modern society has created an unprecedented need for sophisticated sensing technologies capable of monitoring the complex interplay between human activities and environmental systems. As industrial processes become increasingly intricate, urban populations continue to expand, and regulatory frameworks demand ever-more stringent compliance measures, the ability to detect and quantify trace gases with high sensitivity and selectivity—using sensors that are both fast and compact—has emerged as a fundamental technological imperative. This dissertation presents an investigation of advanced photonic approaches for gas sensing, tracing an evolutionary path from innovative to established techniques through the development of novel sensing platforms that bridge the gap between laboratory-scale instrumentation and field-deployable systems.

The global significance of gas sensing technology extends far beyond academic curiosity, touching every aspect of modern life. In industrial processes, the detection of hazardous gas leaks can prevent catastrophic accidents and protect workers' health. Moreover, environmental monitoring networks rely on sensors to track greenhouse gas emissions, assess air quality, and provide data essential for climate modeling and policy development. In healthcare, breath analysis offers promising non-invasive diagnostic capabilities for diseases ranging from diabetes to cancer. The market dynamics reflect this societal importance, as the global gas sensor market is projected to reach USD 4.44–5.83 billion by 2030–2035, driven by compound annual growth rates approaching 10%. Nevertheless, existing technologies face fundamental limitations that constrain their effectiveness in addressing emerging challenges.

Traditional non-optical gas sensors, including electrochemical, semiconducting metal oxide, and catalytic devices, have served admirably in numerous applications where cost, simplicity, and proven reliability are paramount. However, these technologies suffer from inherent limitations, including cross-sensitivity to multiple gases, susceptibility to environmental conditions, material degradation over time, and insufficient sensitivity for trace-level detection. Conversely, laser absorption spectroscopy methods offer superior selectivity through the interrogation of molecular-specific absorption features and exceptional sensitivity through various enhancements of the light–gas interaction path length. Nevertheless, the complexity, size, and cost of traditional optical systems have largely confined their deployment to specialized laboratories and industrial applications, creating a technological gap between what is analytically possible and what is practically deployable.

This dissertation addresses this fundamental challenge through the systematic development and characterization of photonic sensing platforms that progressively bridge the gap between performance and practicality. The research trajectory begins with innovative enhancements to the established quartz-enhanced photoacoustic spectroscopy (QEPAS) technique, progresses through the development of fiber-integrated beam delivery systems for the mid-infrared spectral region, and culminates in the demonstration of semi-integrated sensing platforms that combine silicon nitride photonic circuits with quartz tuning fork transducers. This progression represents a coherent strategy for advancing gas sensing technology toward the ultimate goal of ubiquitous, high-performance chemical monitoring.

The dissertation is organized into four chapters, each addressing critical aspects of the photonic integration journey.

Chapter 1 provides an extensive review of gas sensing techniques, establishing the theoretical and practical context necessary for understanding the innovations presented in subsequent chapters. Beginning with a thorough examination of non-optical sensing approaches, the chapter elucidates both the enduring value and the fundamental limitations of traditional technologies. The discussion then transitions to optical sensing methods, with particular emphasis on tunable diode laser absorption spectroscopy that has revolutionized laboratory-based gas analysis. The chapter

concludes with detailed coverage of quartz tuning fork-based sensing systems, including QEPAS and light-induced thermoelastic spectroscopy (LITES), which form the technological foundation for much of the original research presented in this thesis.

Chapter 2 presents the development and characterization of beat-frequency QEPAS technique for *quasi*-simultaneous, multi-gas detection. This work addresses the critical limitation of conventional QEPAS systems that require time-consuming sequential measurements for multiple gas species. Through the implementation of frequency-detuned modulation strategies and *ad hoc* signal processing algorithms, the research demonstrates improvements in measurement speed while maintaining comparable analytical accuracy. The experimental validation using methane and ethane as target analytes provides compelling evidence for the practical utility of this approach in natural gas monitoring and environmental assessment applications.

Chapter 3 explores the integration of optical waveguides for mid-infrared gas sensing, focusing on the development of a novel indium fluoride glass fiber combiner that enables dual-gas detection using fiber-coupled interband cascade lasers. This research addresses the fundamental challenge of beam delivery in the molecular fingerprint region where absorption strengths are orders of magnitude greater than in the near-infrared. The successful demonstration of simultaneous carbon dioxide and nitric oxide detection, achieved using a single beam delivery system by alternately switching between laser sources, validates the potential of all-fiber architectures to create robust, alignment-free sensing systems suitable for harsh environmental conditions.

Chapter 4 presents the culmination of the integration journey through the development and characterization of semi-integrated sensing platforms combining silicon nitride waveguides with quartz tuning fork detectors. This work explores both conventional strip waveguide architectures and advanced subwavelength structures designed to enhance light-gas interaction while maintaining the advantages of chip-scale integration. The demonstration of both QEPAS and LITES detection within a unified platform architecture represents a significant advance toward the realization of mass-producible, high-performance optical gas sensors.

The research presented in this dissertation makes several significant contributions to the field of optical gas sensing:

INTRODUCTION AND AIM OF THE DISSERTATION

- the implementation of innovative signal processing approaches to dramatically improve the performance of established sensing techniques without requiring fundamental changes to hardware architecture;
- the feasibility of fiber-integrated beam-delivery systems for mid-infrared sensing applications, opening new possibilities for remote and distributed monitoring;
- the potential of semi-integrated photonic platforms to combine the sensitivity advantages of optical spectroscopy with the practical benefits of chip-scale integration.

These contributions collectively advance the state of the art in gas sensing technology while providing clear pathways for continued development toward fully integrated, mass-producible sensing systems.

CHAPTER 1

1. Gas Sensing Techniques

The rapid and in-field detection and quantification of gaseous species represents one of the most critical technological challenges of our time, with implications extending to every aspect of modern life [1,2].

Indeed, rapid industrialization and global modernization have led to unprecedented levels of gas emissions, creating both environmental and health challenges that demand sophisticated monitoring solutions [5,6]. In many real-world scenarios, gaseous pollutants released into the atmosphere do not remain confined to the vicinity of their source. Instead, they may form plumes that can extend several kilometers downwind, as illustrated in Figure 1.1, potentially affecting large populations far from the emission source [7,8].

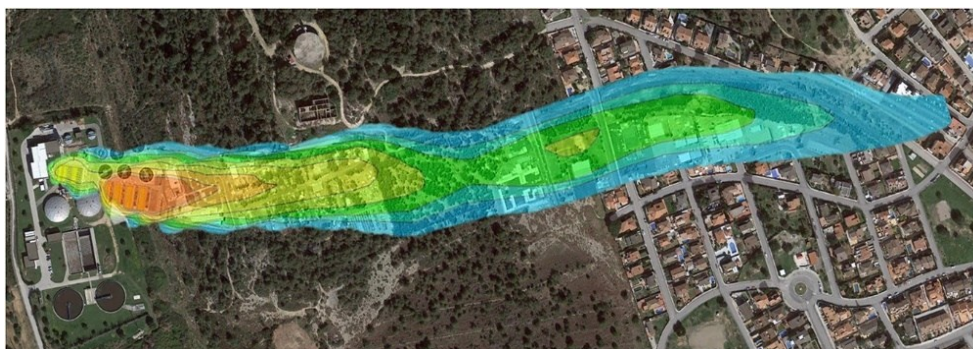


Figure 1.1. Time-averaged chemical plume emitted by an industrial site and reaching a nearby population [5].

This scenario underscores the need for distributed sensing networks, capable of tracking gas concentrations across wide geographical areas with high spatial and temporal resolution [9,10].

Over the past decades, the evolution of gas sensing technologies mirrors the broader trajectory of analytical instrumentation, from simple chemical indicators to sophisticated instruments capable of detecting trace molecules at the parts-per-trillion (ppt) level in complex mixtures [11,12]. This technological progression has been driven by increasingly stringent regulatory requirements, growing environmental awareness, and the recognition that many critical applications—from early human disease detection to atmospheric science—require sensitivity levels that push the boundaries of what is technically feasible [13–15].

The global gas sensor market reflects this technological and societal importance. Indeed, the market analyses consistently indicate robust growth, with monetary valuations estimated between USD 2.28–3.14 billion in 2024 and projections reaching USD 4.44–5.83 billion by 2030–2035 [16,17], driven by factors including environmental regulations, industrial safety requirements, and the proliferation of Internet-of-Things-based applications [18,19]. The Asia-Pacific region currently leads the market accounting for approximately 33.5% of global revenue, primarily due to rapid industrial expansion and substantial investments in smart infrastructure [18].

Despite these impressive market dynamics and technological advances, current gas sensing solutions still face some fundamental limitations that constrain their effectiveness in the development and deployment of next-generation applications. Gas sensors based on electrochemical, semiconducting metal oxide, and catalytic devices, while cost-effective and widely deployed, suffer from cross-sensitivity to multiple gases, susceptibility to environmental conditions, and material and performance degradation over time [21,22]. These limitations often lead to frequent calibrations and maintenance, making them unsuitable for remote deployment or applications requiring long-term stability [21]. Conversely, optical gas sensors offer superior selectivity and stability but have historically been largely confined to laboratory and specialized industrial environments due to their complexity, size, and cost [24,25].

By leveraging expertise and fabrication processes developed for the semiconductor and telecommunications industries, photonic integrated circuits (PICs) promise to deliver laboratory-grade optical sensing performance in chip-scale devices suitable for mass production and widespread deployment [26,27].

In this chapter, different gas sensing techniques are examined, starting from well-established non-optical methods, through advanced optical approaches to cutting-edge photonic integration strategies.

Section 1.1 examines non-optical gas sensing approaches and their operating principles, including electrochemical, semiconducting metal oxide (SMO), catalytic, thermal conductivity, and acoustic sensors. These devices continue to dominate many practical applications where their simplicity and low cost outweigh their limitations. Furthermore, hybrid approaches that combine optical and non-optical techniques are becoming increasingly important, requiring deep understanding of both domains [26].

Section 1.2 analyzes optical gas sensing techniques, exploring how the interaction between electromagnetic radiation and gas molecules unlocks high sensitivity and selectivity. The discussion covers fundamental spectroscopic principles before examining specific implementations, including tunable diode laser absorption spectroscopy (TDLAS), cavity-enhanced techniques, and photoacoustic spectroscopy (PAS), with particular attention to how each technique addresses some specific limitations of non-optical sensors while introducing new challenges.

Section 1.3 focuses on quartz tuning fork (QTF)-based optical configurations, specifically quartz-enhanced photoacoustic spectroscopy (QEPAS) and light-induced thermoelastic spectroscopy (LITES). The analysis examines both the fundamental physics underlying these approaches and their practical implementation in real-world sensors.

Section 1.4 explores photonic integrated approaches for gas sensing, examining how miniaturization and integration can overcome the size, cost, and complexity barriers that have often limited optical sensors to specific applications. The discussion covers material platforms, integration strategies, and the critical challenge of creating and maintaining sufficient light–gas interaction in micro- and nanoscale devices.

1.1. Non-Optical Gas Sensing Approaches

Non-optical sensing methods rely on the detection of gases through their physical or chemical interactions with sensing materials and continue to serve critical roles in applications ranging from industrial safety to environmental monitoring.

These gas sensors can be broadly categorized based on their transduction mechanisms, and each category has evolved to address specific sensing challenges, resulting in a diverse ecosystem of technologies with complementary strengths and weaknesses. By analyzing their operating principles, performance characteristics, and application domains, this section examines five major categories: (i) electrochemical, (ii) SMO, (iii) catalytic, (iv) thermal conductivity, and (v) acoustic wave gas sensors.

Electrochemical sensors, such as those shown in Figure 1.2, represent one of the most mature and commercially successful gas sensing technologies, accounting for over 21% of the global gas sensor market [27].

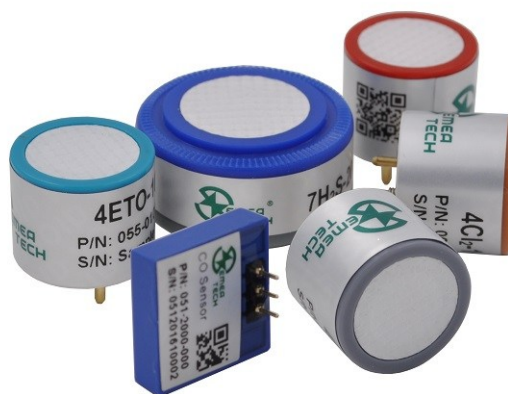


Figure 1.2. Example of electrochemical gas sensors for hazardous gas detection [28].

Their widespread adoption stems from a combination of sensitivity, selectivity, and practicality suitable for many real-world applications [29]. These sensors operate by measuring electrical currents generated when target gas molecules undergo oxidation or reduction reactions at specially designed electrode surfaces [30].

Figure 1.3 shows the basic architecture of an electrochemical sensor consisting of three (or four) electrodes—working, counter, and reference—immersed in an electrolyte solution and separated from the gas sample by a selectively permeable membrane [31].

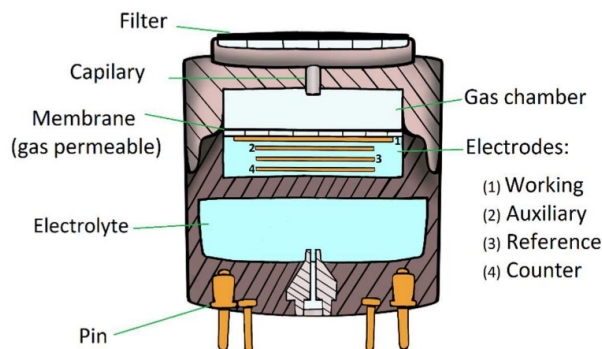
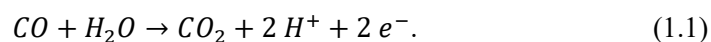


Figure 1.3. Components of a four-electrode electrochemical sensor for detection of air-polluting gases [32].

This configuration creates an electrochemical cell where the target gas undergoes a specific reaction at the working electrode, generating a current proportional to the gas concentration. The reference electrode maintains a stable electric potential, while the counter electrode completes the circuit and balances the reaction occurring at the working electrode [33].

The fundamental operating principle relies on Faraday's law, which relates the transferred electrical charge to the amount of chemical species reacted [34]. For example, carbon monoxide (CO) molecules diffusing through the membrane are oxidized at the working electrode according to:



Equation 1.1. Carbon monoxide oxidation reaction.

The electrons released in this reaction flow through an external circuit, creating a measurable current directly proportional to the CO concentration in the gas sample. Theoretically, the selectivity of this process can be extremely high, as the electrode potential can be controlled to enhance specific reactions while suppressing interfering ones from other gases [35].

The performance of electrochemical sensors depends critically on several design factors. The choice of electrode materials determines which gases can be detected and at what efficiency. Platinum and gold are common choices for their catalytic properties and chemical stability, though research continues into nanostructured materials that offer enhanced surface area and catalytic activity [37,38]. Electrolyte composition

affects both the types of reactions possible and the operating temperature range of the sensor. Aqueous electrolytes provide high ionic conductivity but limit the operation to moderate temperature and humidity ranges, while solid polymer electrolytes enable wider operating conditions at the cost of reduced sensitivity [38].

The gas-permeable membrane serves multiple critical functions beyond simply allowing the target gas to reach the electrode. By controlling diffusion rates, it establishes the linear relationship between gas concentration and sensor current. It also provides selectivity by excluding certain interfering species based on molecular size or chemical properties [39]. Modern membranes often incorporate multiple layers with different properties to optimize these competing requirements [40].

Electrochemical sensors offer several compelling advantages that explain their commercial success. They can operate at room temperature, consuming minimal power—typically just microwatts—making them ideal for portable and battery-powered instruments [41]. Their response is inherently linear over wide concentration ranges, simplifying calibration and improving accuracy. Many designs achieve excellent selectivity through careful choice of electrode potential and membrane properties. The technology is mature and well-understood, enabling reliable mass production at reasonable cost.

However, these sensors also face significant limitations that restrict their use in certain applications. The finite lifetime—typically one to three years—results from gradual electrolyte evaporation, electrode degradation, or membrane fouling [42]. This necessitates periodic replacement, increasing operational costs and limiting deployment in remote locations. Cross-sensitivity to interfering gases remains a challenge, particularly for sensors targeting gases with similar oxidation potentials. Environmental factors strongly influence performance, with temperature affecting reaction kinetics and humidity potentially diluting the electrolyte or affecting membrane properties. Response times, while adequate for many applications, are relatively slow (typically 30 to 90 s to reach 90% of the final value) compared to optical methods [43].

SMO sensors, such as those shown in Figure 1.4, constitute another major category of gas detectors, operating on the principle that the electrical conductivity of certain metal oxides changes dramatically upon exposure to reducing or oxidizing gases [44].

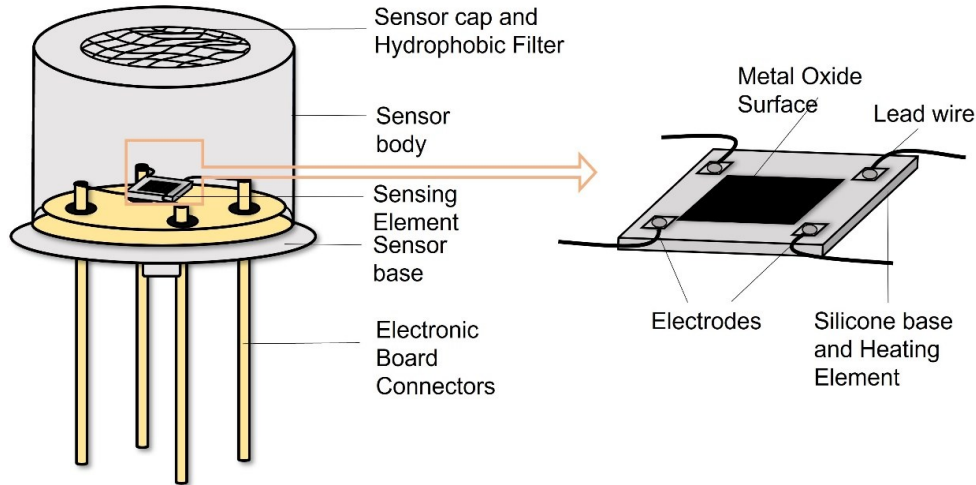


Figure 1.4. The working principle of semiconducting metal oxide sensors [45].

This class of sensors has found widespread application due to their high sensitivity, simple construction, and ability to detect a broad range of gases [46].

At temperatures typically between 200 °C and 500 °C [47], oxygen (O_2) molecules from the ambient atmosphere adsorb onto the metal oxide surface, extracting electrons from the conduction band of the material. This creates a depletion layer near the surface, in turn increasing the electrical resistance of the material. When reducing gases such as CO, hydrogen, or volatile organic compounds (VOCs) are exposed to the surface, they react with the adsorbed O_2 releasing electrons back to the conduction band, thus decreasing resistance [48]. Conversely, oxidizing gases like nitrogen dioxide or ozone extract additional electrons, further increasing resistance [49].

The commonly used sensing materials include tin oxide (SnO_2), zinc oxide (ZnO), tungsten oxide (WO_3), and indium oxide (In_2O_3) [50]. Each material exhibits a different sensitivity to various gases and operates optimally at different temperatures. The choice of the material significantly influences sensor characteristics, with SnO_2 being the most widely used due to its good sensitivity to many gases and relatively stable operation. The sensing performance can be further increased by adding noble

metal catalysts like platinum or palladium, which enhance sensitivity to specific gases and lower operating temperatures [51].

The relationship between gas concentration and sensor resistance typically follows a power law behavior [52]:

$$R = A \cdot c^n, \quad (1.2)$$

Equation 1.2. Power law relationship in semiconducting metal oxide-based sensors.

where R is the sensor resistance, A is a constant depending on the sensor material and operating conditions, c is the gas concentration, and n is the sensitivity exponent, which typically ranges from 0.3 to 1.

SMO sensors provide high sensitivity to many gases, often detecting concentrations down to sub-parts-per-million (sub-ppm) levels [53]. Their simple construction enables low-cost mass production, and they exhibit long operational lifetimes of five to ten years under proper conditions. Response times are relatively fast, typically ranging from seconds to minutes, allowing *quasi*-real-time monitoring. The robust solid-state construction withstands mechanical shock and vibration better than sensors with liquid components.

However, SMO sensors also exhibit fundamental limitations that significantly impact their utility. Poor selectivity represents perhaps the most serious drawback; indeed, most SMO materials respond to multiple gases, making it difficult to identify specific species in mixed gas matrices [54]. The high operating temperature required for sensing results in substantial power consumption, up to 1 W in continuous mode [55]. This not only limits battery life in portable applications but also creates safety concerns in explosive atmospheres. Environmental factors, particularly humidity, strongly affect sensor response, often requiring complex compensation schemes [56]. Long-term baseline drift necessitates frequent recalibration to maintain accuracy. Certain compounds, particularly silicones and sulfur-containing species, can poison the sensor surface, causing permanent sensitivity loss [57].

Catalytic sensors, like those shown in Figure 1.5, also known as pellistors or catalytic bead sensors, detect combustible gases through the heat generated during catalytic oxidation [58].

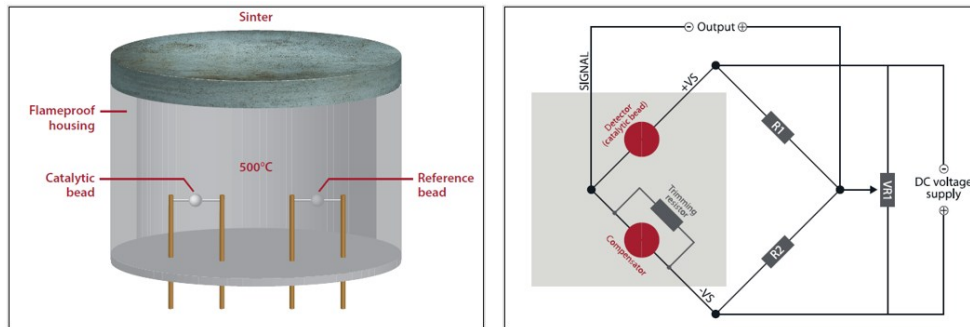


Figure 1.5. The working principle of catalytic sensors [59].

These sensors have been the mainstay of combustible gas detection for decades, particularly in industrial safety applications where reliable detection of explosive atmospheres is critical. Their operating principle, while conceptually simple, involves sophisticated engineering to achieve the sensitivity and stability required for life-safety applications.

The basic architecture consists of two matched elements: an active detector element coated with a catalyst (typically platinum or palladium) and a reference element with an inert coating [60]. Both elements are heated to temperatures where catalytic combustion occurs, typically ranging from 300 °C to 500 °C, and incorporated into a Wheatstone bridge circuit for differential measurement [61]. This matched-pair design provides compensation for environmental factors such as ambient temperature changes, humidity variations, and thermal losses, which would otherwise cause significant measurement errors.

When combustible gas molecules expose the catalytic surface of the detector element, they undergo flameless oxidation, releasing heat that increases the temperature of the element. This temperature rise increases the electrical resistance of the element, creating an imbalance in the Wheatstone bridge. The reference element, exposed to the same ambient conditions but lacking catalytic activity, does not experience temperature change from gas exposure, allowing the bridge circuit to output a signal proportional to the gas concentration while rejecting common-mode environmental effects.

The catalytic oxidation process follows well-established chemical kinetics, with the reaction rate depending on gas concentration, catalyst activity, and operating

temperature [62]. At low concentrations, the response is approximately linear, as the heat generated is proportional to the number of gas molecules oxidized. At higher concentrations, the response may become non-linear due to O₂ depletion near the catalyst surface or heat transfer limitations. Most catalytic sensors are calibrated to measure gas concentrations up to the lower explosive limit (LEL), providing a safety margin before dangerous conditions develop [63].

These sensors excel in several important aspects. They provide broad-spectrum response to virtually all combustible gases, eliminating the need for gas-specific sensors in many applications. Furthermore, the technology offers inherent fail-safe operation, since if the catalyst is poisoned or the element fails, the signal decreases rather than giving false alarms. Good accuracy and repeatability for gas concentrations up to the LEL make them suitable for safety-critical applications [64]. The relatively simple construction enables cost-effective manufacturing and maintenance, and catalytic sensors provide stable long-term operation when properly maintained, with some installations operating reliably for many years.

However, catalytic sensors also face significant limitations because they require sufficient O₂ to support combustion, typically at least 10–12%, which can be problematic in confined spaces or inert atmospheres [65], and the catalyst is susceptible to poisoning by various compounds, including silicones, lead compounds, and sulfur species, which can cause permanent sensitivity loss [66]. Moreover, high power consumption required for heating limits battery life in portable instruments and the non-selective response to all combustible gases prevents identification of specific species in mixtures. Finally, catalyst activity naturally degrades over time, requiring periodic calibration and eventual replacement.

Thermal conductivity detectors (TCDs), such as those shown in Figure 1.6, measure gas concentrations based on differences in thermal conductivity between the target gas and a reference gas, typically air [67].

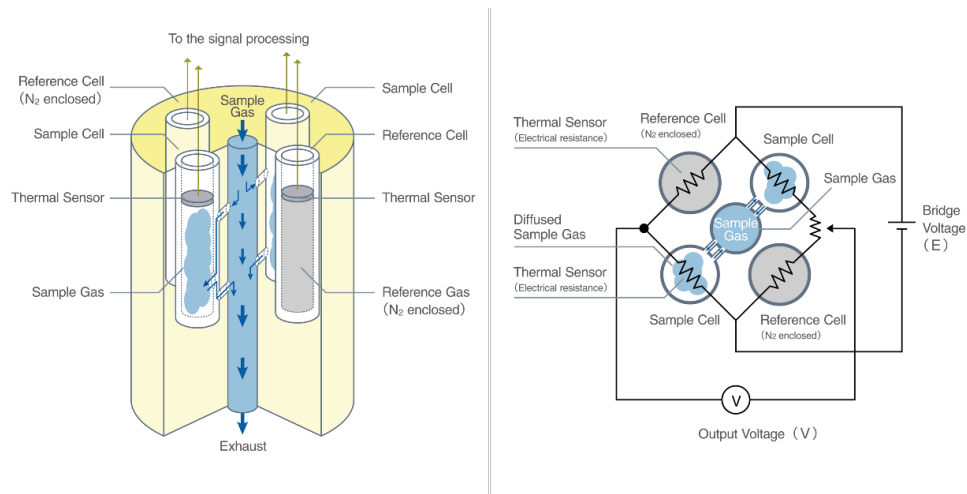


Figure 1.6. Basic structure and working principle (bridge circuit) of a gas analyzer using a TCD [68].

While TCDs may lack the sensitivity of other detection methods, their simplicity, stability, and universal response make them valuable for specific applications, particularly where high concentrations must be measured or where the non-destructive nature of the measurement is critical.

The operating principle involves measuring the heat transfer from a heated element to the surrounding gas. The detector typically consists of heated elements (often thermistors or resistance wires) placed in both sample and reference chambers [69]. These elements are maintained at constant temperature through a feedback circuit, with the power required for temperature maintenance depending on the thermal conductivity of the surrounding gas. As the gas composition changes, the power requirement changes proportionally, providing a measure of gas concentration.

The theoretical foundation rests on the kinetic theory of gases, which relates thermal conductivity to molecular properties such as mass, size, and structure [70]. Lighter molecules generally exhibit higher thermal conductivities due to their higher molecular velocities. This explains why hydrogen, with thermal conductivity approximately seven times that of air, is particularly easy to detect using TCDs. Conversely, heavier molecules like carbon dioxide (CO₂) have lower thermal conductivities, about 0.6 times that of air, also making them readily detectable against an air background [71].

The sensor response can be expressed through the heat transfer equation [72]:

$$Q = \frac{k \cdot A \cdot \Delta T}{d}, \quad (1.3)$$

Equation 1.3. Thermal-conductivity-detector response equation.

where Q is the heat transfer rate, k is the thermal conductivity of the gas, A is the surface area of the heated element, ΔT is the temperature difference between the element and the gas, and d is the characteristic dimension of the heat transfer path. By maintaining constant temperature (and thus constant Q), changes in k directly indicate changes in gas composition.

TCDs offer several unique advantages since they provide universal response to all gases, as every gas has a characteristic thermal conductivity. Furthermore, the measurement is completely non-destructive, as gas molecules are neither consumed nor altered, making TCDs ideal for continuous monitoring or as detectors in gas chromatography [73]. Long-term stability is excellent, as there are no chemical reactions or surface effects to cause drift and the sensors can detect high gas concentrations up to 100%, unlike many methods that saturate at lower levels. Simple, robust construction with no moving parts or consumable components ensures reliable operation with minimal maintenance.

However, TCDs also have significant limitations that restrict their application space. For example, sensitivity is relatively poor compared to other methods, typically limited to ppm to percent levels rather than parts-per-billion (ppb) detection [74]. The non-selective response means TCDs cannot distinguish between different gases in mixtures without prior separation. Performance is sensitive to flow rate and pressure variations, requiring careful control in precision applications. Although the power consumption is lower than in catalytic sensors, it still limits battery operation. Finally, the dynamic range for a given configuration is limited, often requiring range switching for wide concentration variations.

Acoustic wave gas sensors, like those shown in Figure 1.7, represent a category of devices that detect gases through their effects on acoustic wave propagation.

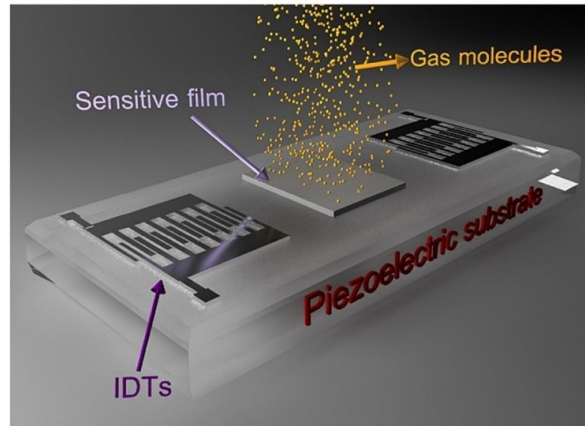


Figure 1.7. Surface-acoustic-wave-based H_2S gas sensors incorporating sensitive layers of single-walled carbon nanotubes decorated with Cu nanoparticles [75].

This class includes surface acoustic wave (SAW), bulk acoustic wave, and quartz crystal microbalance (QCM) sensors [76]. These devices exploit the extreme sensitivity of acoustic resonators to mass changes, enabling detection of trace quantities of adsorbed gas molecules.

The basic principle involves generating acoustic waves in a piezoelectric substrate and monitoring changes in wave propagation characteristics, *i.e.* frequency, amplitude, or phase, caused by gas interaction [77]. In SAW sensors, interdigitated transducers on a piezoelectric substrate generate surface waves that propagate along the crystal surface. A chemically selective coating in the wave path absorbs target gas molecules, adding mass that decreases wave velocity and shifts the oscillation frequency. The frequency shift Δf relates to the mass change Δm through [78]:

$$\Delta f = -\frac{K \cdot f_0^2 \cdot \Delta m}{A}, \quad (1.4)$$

Equation 1.4. Frequency shift in a surface-acoustic-wave sensor.

where K is a constant depending on substrate properties, f_0 is the unperturbed frequency, and A is the active sensor area. This quadratic dependence on frequency explains why acoustic sensors typically operate at high frequencies (MHz to GHz) to maximize sensitivity.

QCM sensors use bulk acoustic waves resonating through the thickness of a quartz crystal disc [79]. Electrodes on opposite faces excite thickness-shear mode vibrations,

with the resonance frequency determined by the crystal thickness and mass loading. The Sauerbrey equation describes the frequency–mass relationship for rigid films [80]:

$$\Delta f = -\frac{2 \cdot f_0^2 \cdot \Delta m}{A \cdot \sqrt{\rho_q \cdot \mu_q}}, \quad (1.5)$$

Equation 1.5. Frequency–mass relationship in a quartz-crystal-microbalance sensor.

where ρ_q and μ_q are the density and shear modulus of quartz, respectively. This exceptional mass sensitivity, capable of detecting nanogram-level changes, makes QCM sensors valuable for trace gas detection when combined with appropriate selective coatings.

Acoustic sensors offer unique advantages that make them attractive for certain applications. Indeed, they achieve extremely high sensitivity to mass changes, enabling sub-ppb detection with appropriate coatings [81]. Operation at room temperature with low power consumption (typically milliwatts) suits battery-powered applications. The digital frequency output is inherently immune to amplitude noise and easily interfaced to digital systems. Potential for wireless and passive operation through SAW transponder configurations enables deployment in hazardous or inaccessible locations [82]. Finally, multiple parameters such as frequency, amplitude, and phase can be extracted from a single measurement, providing additional information about gas properties or coating behavior.

However, acoustic sensors require selective coatings, representing both their greatest strength and most significant weakness. Coating development requires extensive optimization, and no truly universal coating exists [83]. Furthermore, environmental factors, particularly temperature, pressure, and humidity, strongly affect acoustic properties and can overwhelm gas responses without careful compensation. Coating saturation limits dynamic range, as absorbed molecules eventually fill available binding sites. The complexity of coating development and optimization increases development time and cost. Finally, mechanical vibrations and acoustic noise can interfere with measurements, particularly in industrial environments.

Each presented non-optical gas sensing approach excels in specific applications but faces fundamental constraints that prevent universal adoption.

Cross-sensitivity represents perhaps the most pervasive challenge across non-optical sensors. Apart from carefully designed electrochemical sensors, most non-optical methods respond to multiple gases, complicating identification in real-world environments where gas mixtures are the norm [84]. This limitation has driven development of sensor arrays and pattern recognition algorithms [85], but these solutions increase system complexity and cost while still struggling with unexpected interferences.

Environmental sensitivity plagues all non-optical sensors to varying degrees. For example, temperature affects reaction kinetics in electrochemical sensors, surface chemistry in SMO sensors, and acoustic properties in SAW devices [86]. Humidity influences electrolyte concentration, surface reactions, and acoustic wave propagation [87], and pressure variations further affect gas diffusion rates and thermal conductivity [88]. While compensation schemes can address known environmental effects, they add complexity and may not account for all conditions encountered in field deployment.

Long-term stability remains a persistent issue, manifesting differently across sensor types. Indeed, electrochemical sensors face finite lifetimes from electrolyte loss and electrode degradation [89]. SMO sensors experience baseline drift from surface restructuring and contamination [90], while catalytic sensors suffer catalyst poisoning and activity loss [91]. Even relatively stable TCDs can experience drift due to heating element aging [92]. This instability necessitates frequent calibration and eventual replacement, increasing operational costs and limiting deployment in remote locations.

Despite these limitations, non-optical sensors continue to dominate many markets due to compelling practical advantages. Low cost enables widespread deployment for basic safety monitoring. Simple operation requires minimal training for end users. Proven reliability in specific applications provides confidence for safety-critical uses. Existing infrastructure and regulations favor continued use of established technologies [93]. These factors explain why non-optical sensors remain the workhorses of gas detection even as optical methods offer superior technical performance.

1.2. Optical Gas Sensing

Optical sensors exploit the interaction between electromagnetic radiation and gas molecules, typically through absorption, emission, or scattering processes governed by precise selection rules and molecular spectroscopy principles [94]. These interactions provide highly specific “fingerprints” for different gas species, offering the potential for unambiguous identification and quantification even in complex mixtures [95].

The key advantages of optical sensing stem from its non-invasive nature. Indeed, this characteristic eliminates many degradation mechanisms that plague non-optical sensors, potentially enabling long-term stable operation with minimal maintenance [96]. Furthermore, the spectroscopic signatures of molecules are fundamental properties determined by their structure, providing an absolute reference that does not drift over time [97].

The interaction between electromagnetic radiation and gas molecules forms the foundation of optical gas sensing. When photons encounter molecules, several processes can occur: (i) absorption, where photons are absorbed and molecules transition to higher energy states; (ii) emission, where excited molecules release photons and return to lower energy states; and (iii) scattering, where photons change direction or energy through interaction with molecules [98]. For gas sensing, absorption spectroscopy dominates due to its straightforward implementation and quantitative nature [99].

As shown in Figure 1.8, molecular energy levels are quantized according to quantum mechanics, with distinct levels corresponding to electronic, vibrational, and rotational states [100].

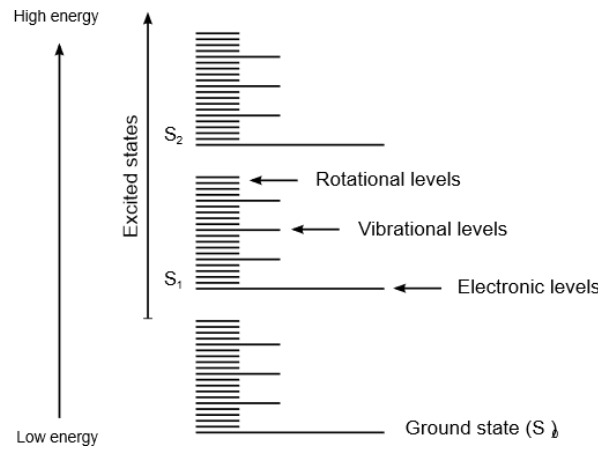


Figure 1.8. A diagram representing singlet energy levels in a molecule to help explain the concept of electronic, rotational, and vibrational energy-levels [101].

The energy differences between these levels determine which photon wavelengths can be absorbed. Electronic transitions typically require ultraviolet (UV) or visible photons, vibrational transitions occur in the infrared (IR) range, and pure rotational transitions appear in the far-IR and microwave regions. Most practical gas sensors operate in the near- and mid-IR where rotational–vibrational transitions provide strong, characteristic absorption features [102].

The specificity of optical gas sensing arises from the unique energy level structure of each molecule, determined by its atomic composition [61].

The Beer–Lambert law provides the quantitative foundation for absorption-based gas sensing, relating the intensity of transmitted light to the properties of the absorbing medium [103]:

$$I(\lambda) = I_0(\lambda) \cdot e^{-\alpha(\lambda) \cdot c \cdot L}, \quad (1.6)$$

Equation 1.6. Beer–Lambert law.

where $I(\lambda)$ is the transmitted intensity at wavelength λ , $I_0(\lambda)$ is the incident intensity, $\alpha(\lambda)$ is the wavelength-dependent absorption coefficient, c is the gas concentration, and L is the optical path length. This exponential relationship has deep implications for sensor design. In conditions of small absorption (*i.e.*, $\alpha(\lambda) \cdot c \cdot L \ll 1$), the Beer–Lambert law linearly correlates transmitted and incident intensity, simplifying gas quantification.

Overlapping spectral features from different absorbing species in gas mixtures could complicate the correlation between $I(\lambda)$ and the specific gas target, thus requiring either sophisticated spectral analysis or selection of interference-free wavelengths.

For this reason, the choice of wavelength region profoundly impacts the sensor architecture and the detection strategy. Figure 1.9 illustrates the electromagnetic spectrum, highlighting various properties across the range of frequencies and wavelengths [104]. Ozaki and colleagues defined the near-IR region as the 1–3 μm wavelength range. The near-IR region offers mature laser and detector technology adapted from telecommunications, though absorption strengths are relatively weak as they arise from overtone and combination bands [105].

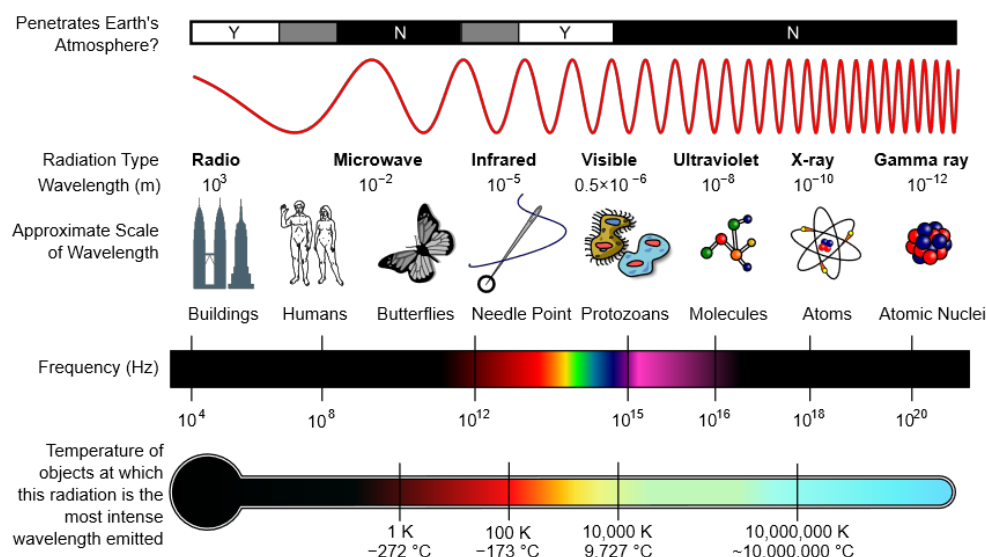


Figure 1.9. A diagram of the electromagnetic spectrum, showing various properties across the range of frequencies and wavelengths [104].

By contrast, the mid-IR region (3–20 μm) accesses fundamental vibrational transitions with high absorption strengths, enabling higher sensitivity but requiring specialized sources and detectors [105], [106]. The optimal choice depends on application requirements, with near-IR favored for its technological maturity and mid-IR chosen when ultimate sensitivity is crucial.

TDLAS has emerged as one of the most successful and widely deployed optical gas sensing techniques [23]. By combining the narrow linewidth and wavelength tunability

of semiconductor lasers with several detection schemes, TDLAS can achieve remarkable sensitivity and selectivity in a relatively simple implementation.

In TDLAS, a laser beam passes through a gas sample, and a photodetector measures the transmitted intensity. By scanning the laser wavelength across a molecular absorption line and measuring the intensity reduction, the integrated absorbance provides a direct measure of gas concentration. The narrow laser linewidth (typically less than 1 MHz compared to GHz-wide molecular lines at atmospheric pressure) enables resolution of individual absorption features, providing excellent selectivity even in the presence of interfering species [107].

The high performance of TDLAS arises from the laser source's ability to concentrate high optical power in a narrow spectral bandwidth, thus allowing both high resolution in the detection of absorption features and high signal-to-noise ratio (SNR) since the detector noise can be considered negligible [108]. Typical optical sources are distributed-feedback (DFB) and distributed-Bragg-reflector (DBR) lasers, offering single-mode operation with mode-hop-free tuning over several nanometers [109]. Wavelength tuning is achieved by adjusting temperature (coarse, ≈ 0.1 nm/K) or injection current (fine, ≈ 0.01 nm/mA).

Direct absorption spectroscopy, while conceptually straightforward, often lacks the sensitivity required for trace gas detection. Shot noise in the detector, arising from the large direct-current (DC) light level, limits the minimum detectable absorption in practical systems. This limitation motivated the development of modulation techniques that shift the measurement to higher frequencies where detector noise is reduced [110]. Wavelength modulation spectroscopy (WMS) has become the dominant approach in commercial TDLAS systems [111].

In WMS, a high-frequency sine wave (tens of kHz) is superimposed on a low-frequency ramp signal (a few Hz), and this double-modulated waveform is used to drive the laser injection current [112]. Lock-in detection at harmonics of the modulation frequency effectively suppresses $1/f$ noise and laser intensity fluctuations. The second harmonic ($2f$) detection scheme has proven particularly effective, as the $2f$ signal shape approximates the second derivative of the absorption line profile,

providing a zero baseline for non-absorbing spectral regions and natural discrimination against broadband absorption [113].

The WMS description is based on an intensity representation of an optical wave, so that only the absorption of the sample is considered, and dispersion effects due to the sample can be neglected. The description is based on the instantaneous laser frequency:

$$\nu(t) = \nu_0 + \Delta\nu \cdot \cos(\omega \cdot t), \quad (1.7)$$

Equation 1.7. Instantaneous laser frequency expression.

where ν_0 is the optical carrier frequency and $\omega = 2\pi f$ is the modulation angular frequency due to the laser injection current modulated at the same angular frequency. In addition to frequency modulation, the current waveform applied to the laser source produces a sinusoidal modulation of the laser intensity and is given by:

$$I(t) = I_0 + \Delta I \cdot \cos(\omega \cdot t). \quad (1.8)$$

Equation 1.8. Modulated laser intensity expression.

The amplitude ΔI of the sinusoidal intensity modulation is determined by the slope of the laser power versus the current characteristics, which is assumed constant across a wavelength scan. The instantaneous laser frequency interacts with the absorption feature. Expanding the absorption coefficient $\alpha(\nu(t))$ for a small $\Delta\nu$:

$$\begin{aligned} \alpha(\nu(t)) = & \alpha_0 + \left. \frac{\partial \alpha}{\partial \nu} \right|_{\nu=\nu_0} \cdot \Delta\nu \cdot \cos(\omega \cdot t) + \frac{1}{2} \cdot \left. \frac{\partial^2 \alpha}{\partial \nu^2} \right|_{\nu=\nu_0} \cdot (\Delta\nu)^2 \cdot \\ & \cos^2(\omega \cdot t) + \dots, \end{aligned} \quad (1.9)$$

Equation 1.9. Absorption coefficient expansion.

where α_0 can be considered to be the background absorption contribution. The laser is modulated both in intensity and in wavelength simultaneously. Thus, assuming a small absorption I_{abs} , from the Beer–Lambert law we have:

$$\begin{aligned} I_{abs}(t) = & [I_0 + \Delta I \cdot \cos(\omega \cdot t)] \cdot [1 - L \cdot \left(\alpha_0 + \left. \frac{\partial \alpha}{\partial \nu} \right|_{\nu=\nu_0} \cdot \Delta\nu \cdot \right. \\ & \left. \cos(\omega \cdot t) + \frac{1}{2} \cdot \left. \frac{\partial^2 \alpha}{\partial \nu^2} \right|_{\nu=\nu_0} \cdot (\Delta\nu)^2 \cdot \cos^2(\omega \cdot t) \right)], \end{aligned} \quad (1.10)$$

Equation 1.10. Modulated laser intensity expression in small-absorption conditions.

where L is the effective length over which the absorption takes place to produce an acoustic wave detectable by the QTF (in other words, L is comparable with the thickness t_0 of the QTF). Hence, the 1ω -signal, $S_{1\omega}$, is given by:

$$S_{1\omega} = L \cdot \Delta I \cdot \alpha_0 - L \cdot \left. \frac{\partial \alpha}{\partial \nu} \right|_{\nu=\nu_0} \cdot \Delta \nu, \quad (1.11)$$

Equation 1.11. $S_{1\omega}$ expression.

and the 2ω -signal, $S_{2\omega}$, is given by:

$$S_{2\omega} = -L \cdot \Delta I \cdot \left. \frac{\partial \alpha}{\partial \nu} \right|_{\nu=\nu_0} \cdot \Delta \nu + \frac{I_0}{2} \cdot \left. \frac{\partial^2 \alpha}{\partial \nu^2} \right|_{\nu=\nu_0} \cdot (\Delta \nu)^2, \quad (1.12)$$

Equation 1.12. $S_{2\omega}$ expression.

This result shows that the background absorption contributes to the $S_{1\omega}$, whereas it does not contribute to $S_{2\omega}$. If we assume that the absorption coefficient has a pure Lorentzian lineshape, $S_{1\omega}$ has a pure first derivative line-shape with a constant background; $S_{2\omega}$ consists of two terms: the first term, arising from a residual amplitude modulation is proportional to the first derivative, whereas the second is the second-derivative expression arising from the laser wavelength modulation. Hence, $S_{2\omega}$ is not a pure second derivative of the Lorentzian lineshape but is distorted by a contribution originating from the residual amplitude modulation. This distortion does not affect the peak position of $S_{2\omega}$ since the first derivative of the Lorentzian lineshape vanishes when $\nu = \nu_0$ [114].

TDLAS offers numerous advantages that have motivated its commercial success, such as:

- the exceptional sensitivity and selectivity enable detection of trace gases in complex mixtures without prior separation [115];
- fast response, limited only by gas transport to the measurement region, allows real-time monitoring of dynamic processes [116];
- absolute concentration measurements based on spectroscopic parameters eliminate the need for calibration gases in many applications [117];
- wide dynamic range spanning six or more orders of magnitude accommodates everything from trace contamination to process control [118];

- immunity to sensor poisoning or degradation, as the measurement is purely optical, ensures long-term stability [119].

However, the main challenge for real-world deployment of TDLAS is the cost of laser sources and detection electronics, remaining relatively high compared to non-optical sensors. Furthermore, mechanical vibrations and temperature fluctuations can introduce noise through etalon fringes formed by partial reflections in the optical path and, if the free spectral range is comparable to molecular linewidths, it can be difficult to distinguish from true absorption signals [120].

While TDLAS provides excellent sensitivity for many applications, detecting extremely low gas concentrations requires further enhancement of the interaction path between light and gas molecules, as highlighted in Equation 1.6. Multipass- and cavity-based absorption spectroscopy techniques achieve this by forcing light to interact multiple times with gas molecules in a compact volume either in an absorption cell [121] or in optical resonators [122]. These methods push detection limits to extraordinary levels, enabling measurements that would be impossible with single-pass techniques.

This dramatic enhancement in sensitivity comes at the cost of increased complexity in optical alignment, device control and signal processing [123], [124].

As an alternative to direct absorption techniques, PAS offers a fundamentally different approach to optical gas sensing by detecting acoustic waves generated through light absorption [125]. This indirect detection method is based on the photoacoustic effect, occurring when modulated light is absorbed by target molecules, causing periodic heating and cooling of the gas. This temperature modulation creates pressure waves at the modulation frequency that can be detected by acoustic transducers, such as sensitive microphones [126].

The theoretical framework for photoacoustic generation reveals the factors that influence sensitivity. For weak absorptions, the pressure amplitude p is given by [127]:

$$p = \frac{(\gamma-1) \cdot P_0 \cdot \alpha \cdot C}{V_{CELL} \cdot f \cdot \tau}, \quad (1.13)$$

Equation 1.13. Pressure amplitude expression within photoacoustic generation.

where γ is the heat capacity ratio, P_0 is the laser power, V_{CELL} is the cell volume, f is the modulation frequency, and τ is the thermal relaxation time. This relationship highlights key design considerations: maximizing laser power and minimizing cell volume directly improve sensitivity, while the frequency dependence requires optimization based on gas properties, acoustic resonances and performance of the sound detector.

Traditional photoacoustic cells, such as those shown in Figure 1.10, employ resonant acoustic cavities to amplify the photoacoustic signal.

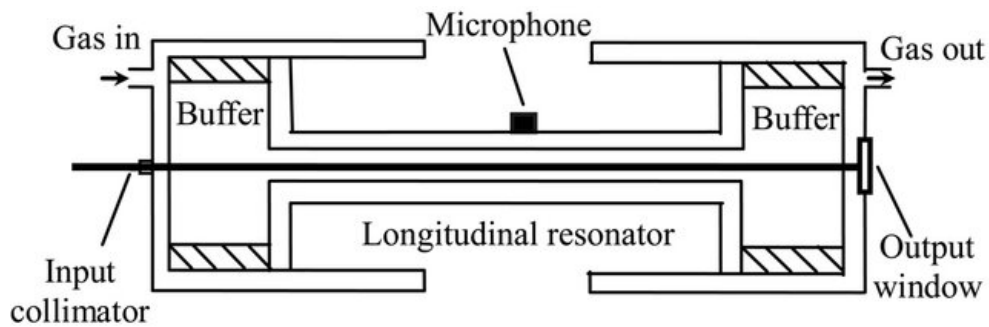


Figure 1.10. Conventional structure of a photoacoustic cell [128].

By matching the light modulation frequency to an acoustic resonance of the cell, signal enhancement factors of 100 or more can be achieved [129]. Common configurations include cylindrical resonators supporting longitudinal modes, Helmholtz resonators with high quality factors (Q s) at low frequencies, and differential designs that suppress external acoustic noise by measuring the pressure difference between illuminated and dark regions [130].

The choice of acoustic transducer critically impacts performance. Commercial electret microphones offer good sensitivity at low cost but suffer from $1/f$ noise at low frequencies. Micro-electromechanical systems (MEMS) microphones provide smaller size and better reproducibility but typically with reduced sensitivity due to their higher operating frequencies [131]. For ultimate performance, optical microphones based on interferometry or membrane deflection can achieve shot-noise-limited detection, though at substantially increased complexity [132].

Photoacoustic spectroscopy offers several compelling advantages: the signal amplitude scales directly with laser power, encouraging the use of high-power sources

without concern for detector saturation that would occur in transmission measurements. Since the technique is based on the measurement of the absorption effect on gas molecules, the detection mechanism is wavelength-independent, *i.e.* the same acoustic detector works across the entire optical spectrum, from UV to far-IR. The technique is inherently suited to miniaturization, as sensitivity improves with decreasing cell volume (Equation 1.13) [133].

However, photoacoustic detection also faces unique challenges. For example, acoustic noise from the environment can overwhelm weak photoacoustic signals, requiring careful acoustic isolation or noise cancellation techniques. Furthermore, the need for gas-phase relaxation to convert absorbed energy to heat makes some molecules difficult to detect, such as those with slow vibrational–translational (V–T) relaxation times (τ) [134].

A fundamental vibration is activated when a molecule in its ground state absorbs a quantum of energy. The molecule can be deactivated by emitting a photon or colliding with surrounding molecules. Since the radiative lifetime for infrared radiation is long (usually between 10^{-1} and 10^{-3} s), this mechanism can be neglected. Thus, the molecule mainly loses vibrational energy through collisions with its nearest neighbors. Landau and colleagues proposed a theoretical model to describe a collinear collision between a vibrating molecule and a non-vibrating one [135]. The model is based on the elementary kinetic theory, in which molecules are treated as hard spheres with a finite collision diameter. It supposes a v ($1 \rightarrow 0$) transfer when a molecule in the $v = 1$ state collides with another molecule in the $v = 0$ state. All other non-excited molecules are supposed to be in the state $v = 0$ and a Boltzmann distribution is assumed to rule the population between two levels. With these assumptions, the relaxation time τ is introduced, which is proportional to the inverse of the number of collisions suffered by one molecule per second. Since the collision rate is proportional to the number of molecules in a given volume, and hence to the gas pressure P , τ is inversely dependent on P . Thus, the relaxation time is expressed as the inverse of the product between a rate constant k and P . In other words, τ represents the V–T relaxation time, *i.e.*, the time required to transfer the vibrational energy of the excited molecule into kinetic energy (translation) of the surrounding ones. These V–T energy transfer processes

result in a heat production rate. Population-based analyses are widely adopted. The molecular density N_{tot} of the absorbing gas is modeled by a two-level system, consisting of a vibrational ground state having molecule density N and an excited state with molecule density N' . In the approximation that $N' \ll N$, the rate equation for N' is given by:

$$\frac{dN'}{dt} = N \cdot \sigma \cdot \Psi - \frac{N'}{\tau}, \quad (1.14)$$

Equation 1.14. Rate equation for excited-state molecule density.

where Ψ and σ denote the photon flux and the absorption cross-section, respectively. Radiative relaxation time and stimulated emission from the excited state have both been neglected. For a harmonic modulation at frequency f of the photon flux $\Psi = \Psi_0(1 + e^{i2\pi ft})$, periodic heating occurs in the sample, generating pressure waves. The frequency-dependent QEPAS signal generated at the modulation frequency f will be given by:

$$S = K \cdot Q(P) \cdot P_L \cdot I_{2f}(P) \cdot \epsilon(f, \tau(P)) = \frac{K \cdot Q(P) \cdot P_L \cdot I_{2f}(P)}{\sqrt{1 + [2\pi \cdot f \cdot \tau(P)]^2}}, \quad (1.15)$$

Equation 1.15. Frequency-dependent QEPAS signal expression.

where K is a sensor constant, $Q(P)$ is the QTF quality factor and P_L is the laser power, $I_{2f}(P)$ is the peak intensity of the second-derivative of the absorption line as simulated using the HITRAN database (as usually obtained when operates in wavelength-modulation and 2f-detection [136]) and $\epsilon(f, \tau(P))$ is the radiation-to-sound conversion efficiency, given by:

$$\epsilon(f, \tau(P)) = \frac{1}{\sqrt{1 + [2\pi \cdot f \cdot \tau(P)]^2}}, \quad (1.16)$$

Equation 1.16. Radiation-to-sound conversion efficiency.

where τ can be expressed as:

$$\tau = \frac{1}{K \cdot P}. \quad (1.17)$$

Equation 1.17. Relaxation time expression.

For instantaneous relaxation, i.e. $2\pi \cdot f \cdot \tau \ll 1$, $\epsilon = 1$ and the QEPAS signal is independent of the modulation frequency [137].

Recent developments have dramatically improved photoacoustic performance. Cantilever-enhanced photoacoustic spectroscopy replaces traditional microphones with micro-cantilevers, achieving exceptional sensitivity through interferometric readout of cantilever deflection [138]. Differential Helmholtz resonators provide common-mode rejection of external acoustic noise [139]. Furthermore, light-emitting diode (LED)-based photoacoustic sensors demonstrate that inexpensive, broadband sources can achieve useful sensitivity when combined with appropriate acoustic-enhancing elements [140]. Finally, as described in the following section, quartz-enhanced photoacoustic spectroscopy uses quartz tuning forks as acoustic transducers, combining the advantages of photoacoustic detection with the exceptional properties of quartz resonators.

Each optical gas sensing method represents a different trade-off between sensitivity, complexity, and practical constraints. Understanding these trade-offs is crucial for selecting appropriate techniques for specific applications and for identifying opportunities where new approaches might offer advantages. Figure 1.11 shows a comparison in terms of normalized noise-equivalent absorption (NNEA) for different categories of gas detection techniques, as a function of optical path length [114].

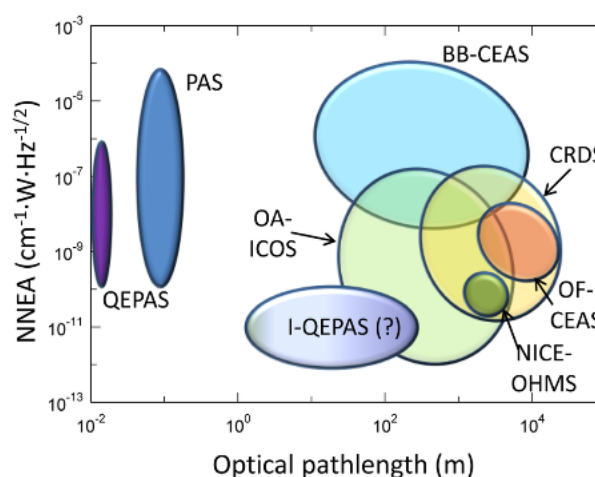


Figure 1.11. Normalized noise-equivalent absorption for categories of gas detection techniques as a function of optical path length. BB-CEAS, broadband cavity-enhanced spectroscopy; CRDS, cavity ring-down spectroscopy; OA-ICOS, off-axis integrated cavity output spectroscopy; OF-CEAS, optical feedback cavity-enhanced absorption spectroscopy; NICE-OHMS, noise-immune cavity-enhanced optical heterodyne spectroscopy; PAS, photoacoustic spectroscopy; QEPAS, quartz-enhanced photoacoustic spectroscopy; I-QEPAS, intracavity quartz-enhanced photoacoustic spectroscopy [114].

Direct absorption spectroscopy techniques, such as the ones shown in Figure 1.11—BB-CEAS (broadband cavity-enhanced spectroscopy), CRDS (cavity ring-down spectroscopy), OA-ICOS (off-axis integrated cavity output spectroscopy), OF-CEAS (optical feedback cavity-enhanced absorption spectroscopy), and NICE-OHMS (noise-immune cavity-enhanced optical heterodyne spectroscopy)—provide the simplest implementation but suffers from limited sensitivity due to noise on the large, transmitted light signal. Its straightforward nature makes it suitable for high concentration measurements or when extreme sensitivity is not required. The ability to use broadband sources for simultaneous multi-species detection represents a distinctive advantage, particularly in process monitoring applications [141].

TDLAS employing wavelength modulation achieves significantly improved sensitivity through noise suppression and derivative detection. The technique has matured to the point where commercial instruments operate reliably in industrial environments. The main limitations remain cost and the need for wavelength-specific lasers for each target gas. As laser prices continue to fall and wavelength coverage expands, TDLAS will likely penetrate new markets currently dominated by non-optical sensors [142].

Cavity-enhanced techniques push sensitivity to extreme levels, enabling detection limits unmatched by other methods. CRDS provides the ultimate in sensitivity and absolute accuracy [124], while ICOS offers a practical compromise with reduced complexity [143]. These techniques excel in research applications and specialized monitoring where their high cost and complexity are justified by performance requirements. Ongoing efforts to simplify cavity-based sensors may eventually bring their extraordinary capabilities to broader markets [144].

Photoacoustic spectroscopy occupies a unique place by eliminating optical detection entirely. The wavelength independence makes it particularly attractive for mid-IR sensing where detectors are expensive and noisy. The acoustic detection principle also enables novel configurations that are unfeasible with transmission-based methods. As will be shown in the following section, combining photoacoustic principles with quartz tuning fork transducers has created particularly powerful sensing approaches [145].

Furthermore, the development of integrated photonic platforms promises to miniaturize bulky optical systems onto chips, potentially achieving the cost reductions necessary for widespread deployment [146].

Hybrid approaches that combine multiple techniques demonstrate advantages beyond what any single method can achieve. Cavity-enhanced photoacoustic spectroscopy multiplies the sensitivity gains of both approaches [147]. Dual-comb spectroscopy enables broadband, high-resolution measurements without mechanical scanning [148]. Photothermal spectroscopy measures refractive index changes from gas heating, by combining absorption and interferometric detection principles [149]. These innovative combinations suggest that the boundaries between traditional categories are becoming less relevant as researchers creatively merge different physical principles.

Each advance has addressed specific limitations of previous non-optical methods while introducing new challenges. The next section examines how quartz tuning forks have enabled particularly creative approaches that combine mechanical, optical, and acoustic phenomena in novel ways.

1.3. Quartz Tuning Fork-Based Optical Configurations

The integration of quartz tuning forks (Figure 1.12) as acoustic transducers and optical detectors in gas sensing represents one of the most innovative developments in modern gas-sensing technology [114].

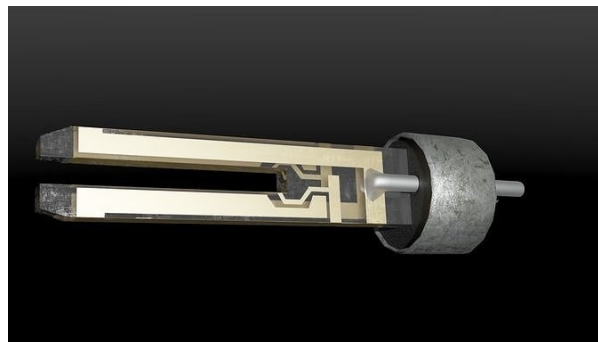


Figure 1.12. Three-dimensional model of a quartz tuning fork [150].

This section examines two groundbreaking techniques—QEPAS and LITES—that exploit the exceptional properties of quartz resonators to achieve high sensitivity in remarkably compact configurations [151], [152].

The story of QTF-based sensing begins with recognizing that these humble components, mass-produced by the billions for timing applications, possess remarkable properties that make them ideal for gas detection [153], [154]. Their journey from use in wristwatches to sophisticated gas sensors exemplifies how creative thinking can transform commonplace technologies into powerful scientific instruments.

QTFs have been manufactured for decades as frequency standards in electronic devices, with the ubiquitous 32.768 kHz (2^{15} Hz) watch crystal representing one of humanity's most precisely manufactured mechanical devices [155]. Their adoption in gas sensing exploits several extraordinary properties that arise from the combination of quartz material characteristics and optimized mechanical design.

The operational principle relies on the piezoelectric properties of crystalline quartz, where mechanical stress generates electrical charge and vice versa [156]. This bidirectional coupling enables QTFs to function simultaneously as acoustic transducers, eliminating the need for external readout mechanisms. When the prongs vibrate in their fundamental flexural mode, alternating charges appear on electrodes deposited on the prong surfaces, and the resulting electrical signal can be analyzed to retrieve the gas concentration.

As derived from the Euler–Bernoulli model, the resonance frequency f_0 of a QTF is determined by the prong dimensions and material properties according to [157]:

$$f_0 = \frac{\lambda_n^2}{4\pi} \cdot \frac{t}{L^2} \cdot \sqrt{\frac{E}{\rho}}, \quad (1.18)$$

Equation 1.18. Resonance frequency of a quartz tuning fork as a function of prong dimensions and material properties.

where λ_n is a mode-dependent constant (approximately 1.875 for the fundamental flexural mode), t is the prong thickness, L is the prong length, E is Young's modulus, and ρ is the material density. The standard 32.768 kHz frequency was chosen for convenient binary frequency division in digital circuits [158], but this frequency fortuitously provides excellent characteristics for gas sensing applications.

Along with the resonance frequency, the quality factor represents another key parameter in sensing applications. Defined as the ratio of energy stored to energy

dissipated per oscillation cycle, Q determines both the frequency selectivity and the noise performance of the resonator [159]. It is given by:

$$Q = \frac{f_0}{\Delta f_{FWHM}}, \quad (1.19)$$

Equation 1.19. Mathematical expression of the QTF quality factor.

where f_0 and Δf_{FWHM} are the resonance frequency and the full-width at half-maximum (FWHM) of the resonance profile, respectively. At atmospheric pressure, commercial 32.768 kHz QTFs achieve Q s of 10,000–15,000, limited primarily by air damping. This high Q value provides narrow resonance bandwidth (typically 3–5 Hz), enabling efficient accumulation of acoustic energy and excellent rejection of noise.

Temperature stability represents another key advantage of QTFs. Commercial devices use AT-cut quartz oriented to minimize temperature coefficients near room temperature. Typical frequency drift is less than 10 ppm/°C, significantly better than that of silicon MEMS resonators, which may drift 30–50 ppm/°C [160]. This stability, originally required for accurate timekeeping, proves invaluable for gas sensing where temperature fluctuations could otherwise cause unacceptable baseline drift.

However, the resonance frequency and geometrical dimensions of commercial QTFs were optimized for timing applications rather than for gas sensing.

The invention of QEPAS in 2002 by Kosterev and colleagues marked a paradigm shift in photoacoustic gas sensing [151]. By replacing traditional microphones with commercial QTFs as acoustic transducers, QEPAS achieved sensitivity comparable to that of conventional photoacoustic spectroscopy, despite its dramatically smaller dimensions [161]. This breakthrough arose from recognizing that the narrow bandwidth and high Q of QTFs—often viewed as limitations—could be turned into advantages through appropriate system design [162].

In the basic QEPAS configuration, a modulated laser beam is directed between the QTF prongs, with the laser modulation frequency precisely matched to the QTF resonance. When gas molecules absorb the modulated light, they undergo periodic heating and cooling at the modulation frequency, generating acoustic waves [163]. These acoustic waves impinge on the QTF prongs, exciting mechanical vibrations that

generate a piezoelectric signal proportional to the acoustic pressure—and thus to the gas concentration [164].

The QEPAS signal S can be expressed as [165]:

$$S \propto P \cdot \alpha \cdot Q \cdot \varepsilon, \quad (1.20)$$

Equation 1.20. Expression of the quartz-enhanced photoacoustic spectroscopy signal.

where P is the laser optical power, α is the gas absorption coefficient, Q is the QTF's quality factor, and ε is the gas radiation-to-sound conversion efficiency. α is also equal to:

$$\alpha = N_{tot} \cdot \sigma \cdot c, \quad (1.21)$$

Equation 1.21. Expression of the gas absorption coefficient.

where N_{tot} is the total number of molecules per unit volume, σ is the absorption cross section of the optical transition, and c is the target gas concentration.

The spatial constraints of directing a laser beam between the prongs of a commercial 32.768 kHz QTF, separated by only 300 μm , require careful optical design [166]. The beam must be focused to a waist smaller than the prong gap while maintaining sufficient depth of focus to avoid clipping. Typical implementations employ beam waists of 50–150 μm , achievable using simple lens systems.

QEPAS detection is intrinsically immune to environmental acoustic noise because of the sharp resonance properties of the quartz resonator employed. Indeed, the narrow bandwidth of the QTF—typically 3–5 Hz at atmospheric pressure—acts as an extremely selective acoustic filter [167]. Environmental noise, even when present at the QTF resonance frequency, rarely maintains the phase coherence required for resonant excitation. Furthermore, the differential nature of the QTF's antisymmetric mode provides common-mode rejection of uniform pressure fluctuations. These properties enable QEPAS operation in acoustically noisy environments that would overwhelm conventional photoacoustic sensors.

An acoustic resonator system is also coupled with the QTF for QEPAS sensing to enhance the detection sensitivity to weak acoustic pressure signals. The acoustic resonator typically consists of an open-ended, rigid circular tube with negligible wall thickness. When a sound wave generated by a source located near one end of the

resonator propagates through the tube, multiple reflections from the open ends can constructively interfere with the incident wave. This interaction creates a standing-wave pattern in which specific points along the resonator appear stationary. If the resonator tube diameter is much smaller than the sound wavelength, the excited sound field varies only along the resonator length, resulting in a one-dimensional acoustic field. Therefore, the resonator tube can be regarded as a one-dimensional acoustic resonator. In this approximation, a nearly complete reflection of a dominant mode sound wave occurs at the open end of the resonator. Therefore, the standing-wave antinodes correspond approximately to the open ends of the resonator. In practice, however, the antinode of a standing sound wave in an open-ended resonator is located slightly outside the end point, at a distance known as the open-end correction (OEC). The OEC arises from the interaction between the air inside and outside the resonator. The mismatch between the one-dimensional acoustic field inside the tube and the three-dimensional field radiated outside causes the external air to oscillate in phase with the internal field. Consequently, the pressure antinode appears slightly beyond the tube end [168].

While commercial 32.768 kHz QTFs enabled the initial development of QEPAS, their dimensions were optimized for timekeeping rather than gas sensing. This recognition motivated the development of custom QTFs specifically designed for QEPAS applications, exploring different frequencies, dimensions, and geometries to enhance sensitivity and relax implementation constraints [169].

Lower frequency QTFs offer several potential advantages. Indeed, since the acoustic wavelength scales inversely with frequency, lower-frequency QTFs allow the use of larger resonator tubes, thereby relaxing optical alignment tolerances. The increased oscillation period provides more time for acoustic energy accumulation, potentially improving sensitivity for gases with slow V–T relaxation, as shown in Equation 1.17. Custom QTFs operating at frequencies from 2.8 kHz to 30 kHz have been demonstrated, with prong lengths up to 20 mm, enabling exploitation of both fundamental and overtone modes for simultaneous dual-gas detection [170].

Together with the scaling of QTF dimensions, recent innovations in prong geometry have been adopted. A non-uniform prong thickness along the prong axis led to the

development of T-shaped prongs, as shown in Figure 1.13, where additional mass is added to the free end, altering the stress-field distribution.

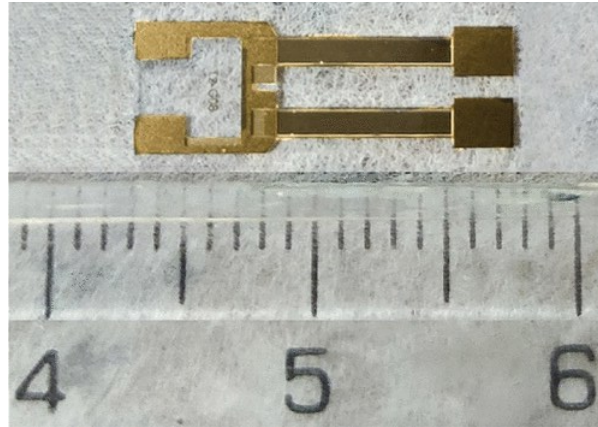


Figure 1.13. T-shaped QTF [171].

When the prongs of a tuning fork vibrate at a resonance mode frequency, the stress produced along each prong induces local polarization in the quartz, generating surface charges. These charges are collected by electrodes appropriately deposited along the prongs. The polarization depends on the stress field through the piezoelectric tensor of quartz. An increase in the stress amplitude leads to a proportional increase in the piezoelectrically induced charge and, consequently, in the QTF current signal. The stress field is mainly localized at the junction between the prong base and the QTF support, extending partially into the support region. When a QTF is used in a QEPAS sensor, the laser beam is focused between the QTF prongs, not far from the prong top, and it can be treated as the acoustic source for the prong deformation. In other words, a prong deformation results from a stress field induced by pressure waves hitting close to the prongs top. Simulations show that the T-shaped geometry provides a more favorable stress-field distribution along the inner prong surfaces—where the generated charges are collected—thereby enhancing QEPAS signal generation. A decrease in the resonance frequency of the fundamental mode is also predicted [172].

The invention of LITES in 2018 by Ma and colleagues marked a fundamentally different approach to QTF-based gas sensing [173]. In this spectroscopic technique, QTFs replace the photodetectors used in TDLAS, exploiting the thermoelastic

response generated in the quartz resonator when it is illuminated by modulated light partially absorbed by the target gas.

The LITES signal can be expressed as [174]:

$$S_{LITES} \propto P \cdot \alpha(\nu) \cdot L, \quad (1.22)$$

Equation 1.22. Expression of the light-induced thermoelastic spectroscopy signal.

where P is the laser optical power, $\alpha(\nu)$ is the gas absorption coefficient at the laser emission frequency ν , and L is the optical path length. Since the LITES signal scales with the absorption path length, the technique can benefit from multipass cells to enhance sensitivity.

The QTF used in LITES experiments is made of α -quartz with a Z-cut orientation, slightly rotated ($\approx 2^\circ$) around the X-axis. This material exhibits high transparency throughout most of the near-IR range due to its large bandgap (≈ 6.3 eV), although its optical absorption strongly depends on wavelength.

As shown in Figure 1.14, in the near-IR region ($\approx 1\text{--}3.5$ μm), quartz shows extremely low absorption and transmits over 90% of the incident light.

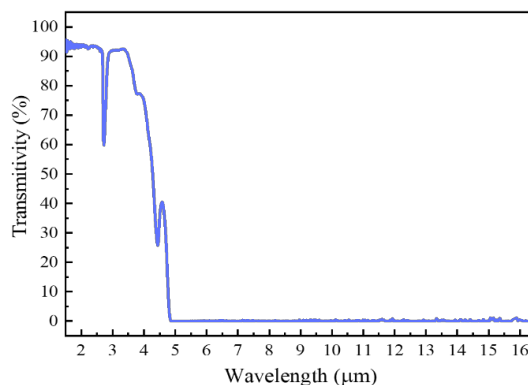


Figure 1.14. Optical absorbance of quartz from the near-IR to the mid-IR region.

As the wavelength increases to around 3.5–4.8 μm , the transmittance gradually decreases, and beyond ≈ 4.8 μm , quartz becomes highly absorbing due to fundamental vibrational transitions of Si–O bonds. Thus, in the mid-IR region (up to ≈ 10 μm), most of the absorbed optical energy is converted into localized heating within a shallow surface layer of the QTF.

Absorption of the modulated laser light produces periodic temperature variations (ΔT) in the illuminated region. These thermal oscillations lead to thermoelastic expansion and contraction of the quartz, generating a mechanical stress field. When the modulation frequency matches the mechanical resonance frequency (f_0) of the QTF, the resulting stress drives the prongs into resonant vibration. The oscillatory motion is transduced into an electrical signal *via* the piezoelectric effect of quartz, which constitutes the basis of the LITES signal. Finite element method (FEM) simulations performed in *COMSOL Multiphysics* confirm that the temperature field induced by a focused laser beam strongly depends on the illumination position along the prongs. The maximum thermoelastic coupling occurs when the laser is focused near the base of the prongs—where the strain energy density of the resonant mode is highest. Under this condition, even a small periodic heating leads to a significant mechanical response. Figure 1.15 shows the spectral dependence of responsivity for the T-shaped QTF, together with the best-performing and broadband Thorlabs GmbH photodetector (model PDA10CF), and three broadband Vigo infrared photodetectors, as specified in the manufacturers' datasheets. The PDA10CF operates only within a narrow spectral range, whereas the Vigo detectors require three separate designs (PVI-4, PVI-6, and PVI-10.6, where the final digits denote the optimal operating wavelength) to cover the entire mid-infrared range. However, as the spectral bandwidth increases, the responsivity correspondingly decreases.

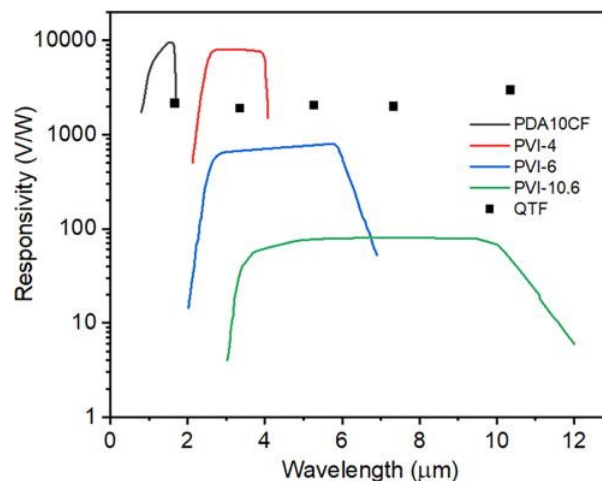


Figure 1.15. Responsivity (solid lines) as a function of wavelength for three models of photovoltaic Vigo HgCdTe detectors—PVI-4 (red), PVI-6 (blue), and PVI-10.6 (green)—and

for the Thorlabs PDA10CF InGaAs amplified photodetector (black), as provided by the manufacturers. Responsivity of the T-shaped QTF, when employed as a photodetector, is represented by black squares [174].

The T-shaped QTF photodetector covers the entire infrared spectral range with a nearly flat spectral response, as predicted by the theoretical model described earlier, providing an excellent compromise between broadband operation and high responsivity [174].

Furthermore, the possibility of separating the optical absorption path from the detection chamber in LITES provides remarkable flexibility. The light–gas interaction path can be optimized independently either for long path length or efficient gas exchange. Conversely, the QTF can be positioned in a controlled environment, isolated from corrosive or contaminating gases, and operated under low-pressure conditions to enhance sensitivity [175].

The spatial response of the quartz tuning fork was mapped by focusing the modulated laser beam on different regions of the prongs. The measurements revealed that the maximum signal amplitude was obtained when the laser spot was positioned near the base of a prong, close to its junction with the stem. This region corresponds to the area of highest strain in the fundamental flexural mode of the QTF. This observation confirmed that the detected signal originates from thermoelastic excitation of the resonant mode, rather than from direct optical absorption or photocarrier generation [175].

The dependence of the signal on the surrounding pressure was also investigated. As the pressure was reduced from atmospheric conditions (≈ 760 Torr) to about 5 Torr, the mechanical quality factor of the QTF increased significantly, resulting in a notable enhancement of the LITES signal. Under these low-pressure conditions, the SNR improved by nearly a factor of four compared to operation at atmospheric pressure, indicating that reduced viscous damping allows for greater mechanical energy accumulation within the resonator.

A comparison between the QTF acting as a thermoelastic photodetector and a commercial amplified photodetector was also performed under identical experimental conditions. The results demonstrated that, when properly aligned and operated at reduced pressure, the QTF provided a SNR approximately six times higher than that of the conventional detector. Additionally, the LITES signal was found to scale linearly

with the incident optical power, as well as with the magnitude of the strain field associated with the resonant mode, in agreement with theoretical expectations.

Overall, the results demonstrate that a quartz tuning fork can function as a highly sensitive and broadband photothermal detector. Optimal performance is achieved when the excitation occurs in the region of maximum strain and when mechanical losses are minimized through operation at reduced pressure.

While QEPAS and LITES both employ QTFs as transducers, their fundamental detection mechanisms lead to distinct advantages and optimal application domains. Understanding these differences is crucial for selecting the appropriate technique for specific sensing challenges and for identifying opportunities for further innovation.

QEPAS detects sound waves generated *via* photoacoustic effect in the gas phase, providing several inherent advantages. The signal generation occurs exactly where absorption takes place, eliminating concerns about beam alignment stability or power fluctuations after the absorption region. The technique is inherently wavelength-independent—the same QTF responds equally well to acoustic waves generated by UV, visible, or infrared absorption. Finally, the small dimensions of the quartz resonator enable detection that is immune to environmental noise [176].

The primary limitations of QEPAS stem from the acoustic generation and propagation requirements. The technique requires efficient conversion of absorbed optical energy to acoustic waves, which depends on molecular relaxation processes that vary dramatically between gases [177]. Furthermore, the target molecule relaxation depends on the remaining components in the mixture, thus requiring not trivial signal analysis [178], [179]. Finally, sensitivity enhancement can be achieved by exploiting high-power laser sources, which can be difficult to realize in the mid-IR spectral range [180].

LITES separates the optical absorption path from the detection chamber, providing complementary advantages. The explicit path length dependence enables sensitivity improvements through multipass cells. Furthermore, the non-contact nature eliminates concerns about corrosive gases, particulates, or condensation that could affect the piezoelectric detector. Finally, the high and flat spectral responsivity of QTF when

employed as photodetector in LITES enables optical gas sensing with laser sources emitting in a wide spectral range [181].

Both techniques benefit from the exceptional properties of QTFs:

- high Q factors enabling narrow-band detection and noise rejection;
- piezoelectric readout eliminating complex detection electronics;
- millimeter-scale dimensions of the detector enabling extreme miniaturization;
- excellent long-term stability from crystalline quartz properties.

The choice between QEPAS and LITES depends on specific application requirements including gas properties, environmental conditions, and performance targets.

1.4. Integrated Photonic Approaches for Gas Sensing

The emergence of PICs for gas sensing marks the convergence of two breakthrough technologies: the outstanding sensitivity of optical spectroscopy and the manufacturing scalability of integrated circuits [182].

This final section examines how miniaturization and integration can overcome the size, cost, and complexity barriers that have historically restricted optical gas sensors to laboratory or specialized applications [183]. By confining light in micro- and nanoscale waveguides on chip-scale platforms, PICs promise to deliver laboratory-grade performance in mass-producible devices suitable for ubiquitous deployment [184].

The drive toward photonic integration in gas sensing parallels the transformation that electronic integrated circuits brought to computing and telecommunications [185]. Just as the transition from discrete transistors to integrated circuits enabled the digital revolution, the integration of optical components on photonic chips could democratize access to sophisticated physico-chemical sensing capabilities [186]. However, this transition faces unique challenges stemming from the fundamental physics of light–matter interactions and the need to maintain sufficient optical path lengths for measurable absorption in microscale devices [187].

The realization of fully integrated gas sensors requires the inclusion, on the same chip, of an optical source, a propagation path where light–gas interaction occurs, and a detector.

The foundation of any photonic integrated sensor lies in its material platform, which determines key properties such as transparency window, optical confinement, integration density, and compatibility with active components [188].

The data in Figure 1.16 enable photonic designers to select appropriate passive material platforms across different regions of the mid-IR spectrum.

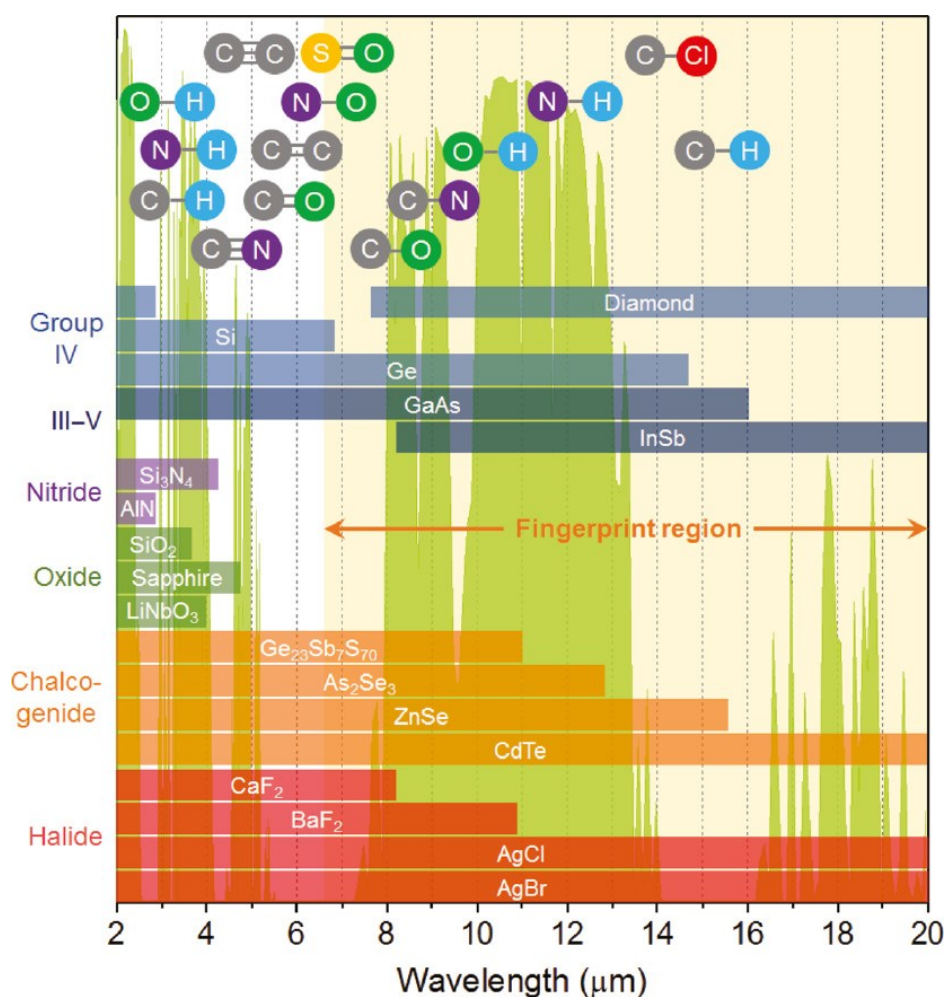


Figure 1.16. The mid-IR spectral regime. The bars represent the optical transparency windows (where material attenuation is < 1 dB/cm) of various materials; the top panel depicts the spectral locations of the primary absorption bands of different chemical bonds; and the background shows the infrared atmospheric transmission spectrum [189].

For wavelengths shorter than 3.5 μm , standard silicon-on-insulator (SOI) or silicon nitride (Si_3N_4 or SiN) on silica (SiO_2) can be used, as the silicon dioxide cladding remains optically transparent in this regime. At longer wavelengths, strong optical absorption in silicon dioxide compromises the optical performance of single-mode SOI strip waveguides [189].

Unlike electronic circuits, where silicon dominates almost exclusively, photonic integration relies on a variety of materials, each offering distinct advantages and limitations for gas sensing applications [190].

Silicon photonics has emerged as the leading platform due to its compatibility with complementary metal–oxide–semiconductor (CMOS) manufacturing infrastructure. The SOI platform, adopted from advanced CMOS technology, provides high-quality single-crystal silicon layers on insulating substrates, ideal for low-loss waveguide fabrication [191]. The high refractive index contrast between silicon ($n \approx 3.5$) and silicon dioxide ($n \approx 1.45$) enables tight optical confinement, allowing waveguide bend radii below 5 μm and dense integration of optical components [192].

The maturity of silicon processing enables sophisticated device fabrication with nanometer precision. Electron-beam lithography can define features below 100 nm, while deep-UV photolithography provides cost-effective manufacturing for features above 200 nm [193]. Advanced etching techniques create smooth sidewalls essential for low-loss waveguides. Most importantly, the existing ecosystem of foundries, design tools, and packaging technologies accelerates development and reduces costs through shared infrastructure.

As shown in Figure 1.17, for gas sensing applications, SOI offers transparency from 1.1 μm to approximately 3.6 μm , covering important near-IR absorption bands of many gases, as illustrated in Figure 1.16 [194].

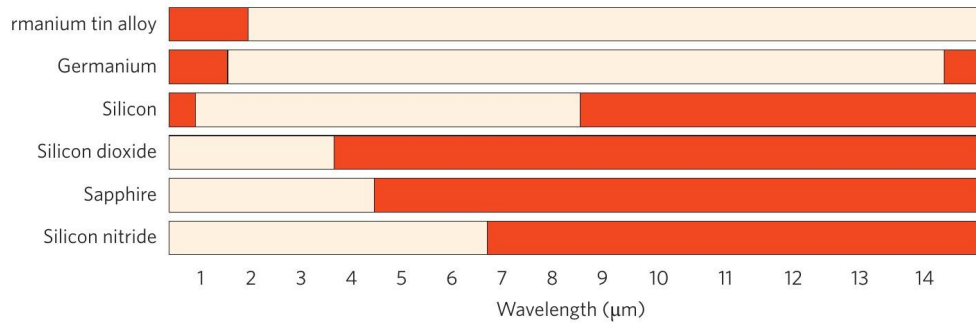


Figure 1.17. Infrared wavelength range over which waveguide propagation loss is less than 2 dB/cm. The white areas represent optical transparency; the red areas signify high loss [146].

Indium phosphide (InP) platforms, such as indium gallium arsenide (InGaAs) on InP or aluminum indium arsenide (InAlAs) on InP, offer the unique advantage of monolithic integration of active and passive components [195]. As a direct-bandgap semiconductor, InP enables efficient light emission and detection at wavelengths from 1.2 to 2 μm , with quantum cascade structures extending operation to the mid-IR [196]. This capability allows complete sensor systems—including tunable lasers, modulators, waveguides, and detectors—to be fabricated on a single chip without complex assembly.

However, the InP-on-InGaAs platform faces several limitations compared with the SOI platform, particularly near the boundary of the near-IR region (*i.e.*, 3 μm). The lower index contrast (*i.e.*, ≈ 0.3) requires larger device dimensions, limiting integration density. Material costs are substantially higher, and processing infrastructure is less developed. Propagation losses, particularly at longer wavelengths, exceed those achievable in silicon or silicon nitride [197]. Despite these challenges, InP remains attractive for applications requiring integrated sources and detectors.

Silicon nitride-on-insulator (SiNOI) has emerged as a versatile platform for passive photonic circuits, offering exceptional performance in applications where active components are provided externally [198]. With propagation losses below 0.1 dB/cm from visible through near-IR wavelengths, Si_3N_4 enables high- Q resonators and long propagation paths impossible in other integrated platforms [199]. The moderate index contrast between silicon nitride and silica in their near-IR transparency region (≈ 0.6)

provides a balance between confinement and coupling efficiency, facilitating fiber interfaces and reducing sensitivity to fabrication variations.

The amorphous nature of deposited Si_3N_4 films offers both advantages and challenges. Unlike crystalline materials, there are no grain boundaries or crystallographic defects to cause scattering. Furthermore, the lack of two-photon absorption at telecommunications wavelengths enables high-power operation [200]. However, the deposition process must be carefully controlled to minimize absorption from hydrogen incorporation and stress-induced cracking in thick films required for optimal confinement.

Recent developments in silicon nitride technology have pushed the boundaries, realizing ultra-low-loss waveguides with propagation losses below 0.001 dB/cm, approaching the theoretical limits imposed by material absorption [201]. Thick silicon nitride platforms (> 700 nm) enable engineered dispersion for non-linear optics, including supercontinuum generation and frequency comb synthesis [202], [203]. These capabilities open new possibilities for broadband spectroscopy on chip-scale platforms.

The integration of light sources at wavelengths matching molecular absorption features is a critical step toward fully integrated on-chip optical sensing. This challenge has driven extensive research into on-chip lasers, with different approaches suited to different wavelength ranges and application requirements. However, the indirect bandgap of silicon precludes efficient light emission, necessitating hybrid integration with III–V semiconductors or external laser sources. Recent advances in heterogeneous integration, as shown in Figure 1.18—where III–V gain materials are bonded to processed silicon photonic circuits—have demonstrated impressive results, achieving on-chip lasers with performance comparable to discrete devices [204].

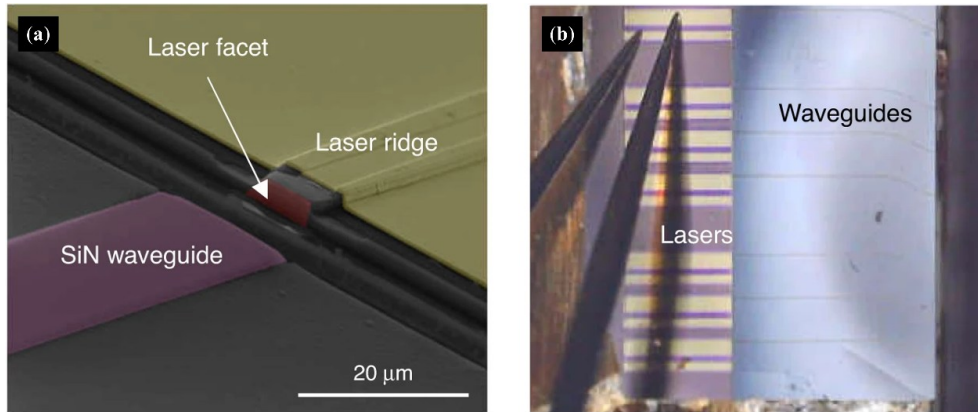


Figure 1.18. (a) Scanning electron microscope image showing a laser ridge with its etched facet and a passive waveguide. (b) Picture of a laser bar equipped with silicon nitride waveguides ready to be tested on the probe station [205].

In Figure 1.18, growth and device fabrication challenges arising from the template architecture were overcome to demonstrate more than 10 mW output power in continuous-wave operation at room temperature. In addition, approximately 10% of the light was coupled into the SiN waveguides, in good agreement with theoretical calculations for this butt-coupling configuration.

For near-IR sensing, the heterogeneous integration of III–V gain materials with silicon photonics has proven highly successful. By bonding thin III–V layers to processed silicon circuits, the advantages of both materials are combined since silicon provides low-loss passive circuits and high-density integration, while III–V materials provide efficient gain [206]. Recent demonstrations have achieved threshold currents below 10 mA, output powers exceeding 100 mW, and linewidths below 100 kHz, matching the performance of discrete lasers [207].

The key to successful heterogeneous integration lies in the bonding process and interface engineering. Direct wafer bonding using plasma activation creates void-free interfaces with negligible optical loss [208]. Adhesive bonding using polymers or spin-on glasses provides more tolerance to surface topology but may introduce additional loss [205]. Advanced designs employ tapered mode converters to efficiently transfer light between III–V and silicon waveguides, achieving coupling efficiencies exceeding 90% [209].

Mid-IR integrated sources present greater challenges but offer access to fundamental molecular vibrations with absorption strengths orders of magnitude stronger than near-IR overtones. Quantum cascade lasers (QCLs) based on InP have achieved room-temperature operation from 3–12 μm in edge-emitting configurations [210]. Recent work on integrating QCLs with passive photonic circuits shows promise, though thermal management and mode matching remain challenging [211].

Alternative approaches to mid-IR generation leverage non-linear optics in materials with broad transparency, exploiting the well-established expertise in chip fabrication developed for the telecommunication range. For example, difference frequency generation using two near-IR pumps can produce tunable mid-IR output [212]. Furthermore, optical parametric oscillators based on micro-resonators have demonstrated broad wavelength coverage with modest pump requirements [213]. Finally, supercontinuum generation in highly non-linear waveguides creates broadband sources suitable for simultaneous multi-species detection [214].

The central challenge in miniaturized gas sensors lies in maintaining sufficient optical path length for measurable absorption despite chip-scale dimensions. Various strategies have been developed to enhance light–gas interaction within the constraints of photonic integration, each with distinct advantages and trade-offs.

Evanescent-field sensing represents the most straightforward approach, exploiting the exponentially decaying optical field extending beyond the waveguide core [215], as shown in Figure 1.19.

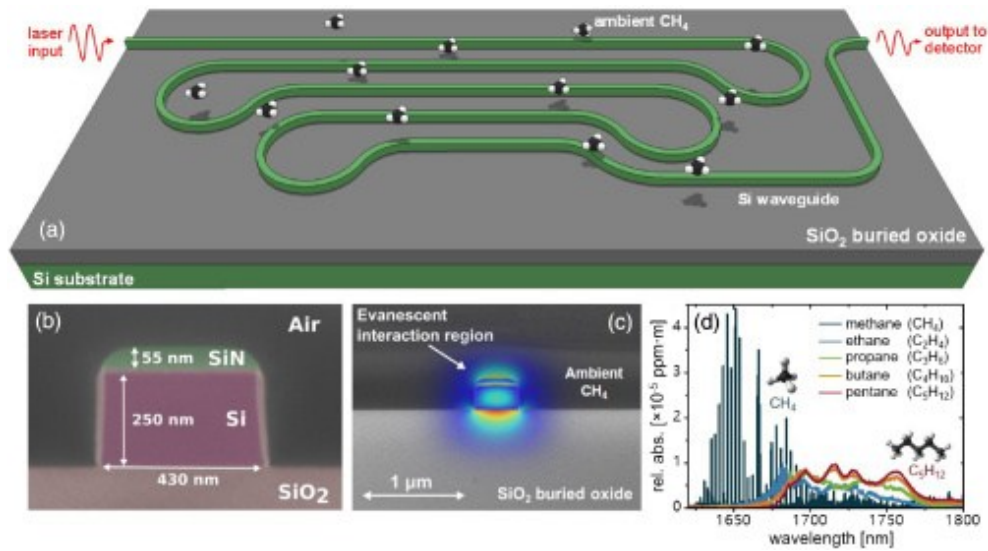


Figure 1.19. (a) Schematic representation of a silicon photonic waveguide absorption spectrometer. The evanescent field of the guided mode in a 10 cm SOI waveguide probes ambient CH₄ via IR-TDLAS. The “paperclip” geometry provides a spatially efficient configuration, occupying merely 16 mm². (b) False-color cross section of the silicon waveguide. The dimensions are chosen to operate near the cut-off frequency, enhancing the modal overlap with ambient air. (c) E_y field profile of the waveguide’s fundamental transverse-magnetic mode, optimized for large overlap. (d) Absorption spectra retrieved from the HITRAN and PNNL databases, showing low spectral crosstalk between the selected transition and other common natural gas constituents [216].

By optimizing waveguide dimensions to maximize the evanescent field while maintaining single-mode operation, a significant fraction of the optical power can interact with the surrounding gas [216].

Strip waveguides in SOI can place up to 20–30% of the optical mode in the gas cladding, though this comes at the cost of increased propagation loss from surface roughness scattering [216], [217].

In slot waveguides, the guided field propagates in narrow air gaps between high-index rails [218], thus enhancing the light–gas interaction. The discontinuity of the electric field at the dielectric interface enhances the field intensity in the low-index slot, with values exceeding 10× those of conventional strip waveguides. However, the fabrication of narrow slots (typically 50–200 nm) requires advanced lithography, and scattering losses increase rapidly with decreasing slot width [219]. To address these challenges, a nanophotonic waveguide for methane (CH₄) detection at 3270.4 nm was

developed, achieving a limit of detection of 0.3 ppm—over two orders of magnitude lower than the state of the art in on-chip spectroscopy—as shown in Figure 1.20 [220].

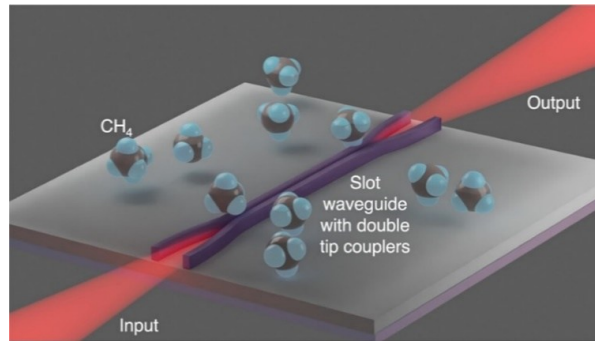


Figure 1.20. Layout of the sensor chip including double-tip couplers. The chip has a footprint of 1 cm^2 and features 1.15 cm -long straight waveguides terminated by $50\text{ }\mu\text{m}$ -long couplers [220].

This result was achieved using a Si slot waveguide designed to maximize the light–analyte interaction, while special double-tip fork couplers at the waveguide facets suppressed spurious etalon fringes.

Subwavelength grating waveguides represent an innovative approach that effectively creates a metamaterial with engineered refractive index [221]. By creating periodic variations of different materials in the waveguide with periods much smaller than the optical wavelength, the structure behaves as a homogeneous medium with properties determined by the fill factor. When one of the materials is replaced with air, these structures can achieve high field overlap with the gas while maintaining low loss, though they require precise fabrication to avoid Bragg reflections [222]. The improvement over strip-waveguide structures results from an increased interaction of the mode field with the surrounding air and a higher group index that can be tuned by adjusting the subwavelength grating period, as shown in Figure 1.21 [223].

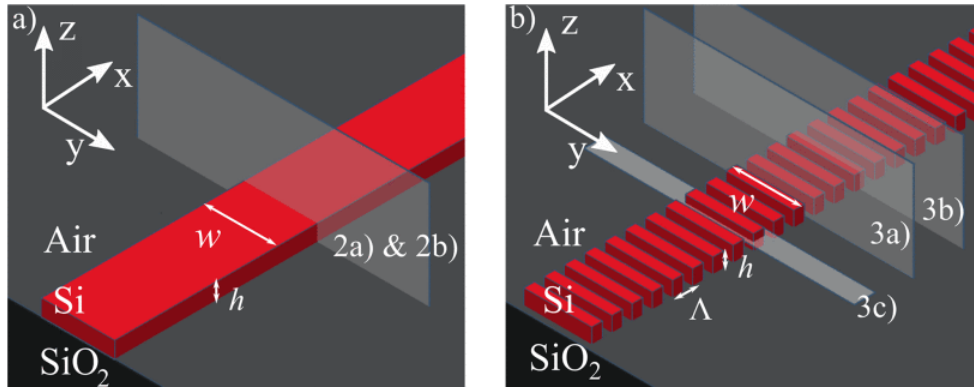


Figure 1.21. Three-dimensional representation of (a) a strip waveguide and (b) a subwavelength-grating waveguide. The shaded transverse planes indicate the positions of the field monitors for the calculated field distributions [223].

Suspended membrane waveguides maximize gas interaction by removing the substrate beneath the waveguide, allowing gas access from all sides [224]. The complete immersion of the waveguide in the analyte provides nearly 100% overlap between the optical mode and the gas. However, mechanical fragility limits the length of suspended sections, and the fabrication process is complex, requiring sacrificial layers and careful release procedures to avoid stiction [225].

Photonic crystal waveguides introduce another degree of freedom by creating engineered photonic bandgaps that confine light through distributed Bragg reflection rather than total internal reflection [226]. Slow-light effects near the band edge can enhance light–matter interaction by increasing the effective path length. Line defects in photonic crystals can guide light while maintaining high field overlap with infiltrated gases. The challenge lies in the precise fabrication required and the sensitivity to disorder that can localize light and increase losses [227].

Optical resonators provide a powerful method for enhancing sensitivity by effectively increasing the interaction length through multiple passes. In the context of photonic integration, micro-resonators offer high quality factors in microscopic footprints, with precise dimensional control enabling reproducible performance difficult to achieve with bulk optics.

Micro-ring resonators have become the workhorse of integrated photonic sensors due to their simple geometry, small footprint, and versatile functionality [228]. A

waveguide bent into a closed loop supports whispering-gallery modes that circulate around the ring perimeter. When coupled to a bus waveguide, the ring acts as a wavelength-selective filter, with free spectral range determined by the optical path length and finesse defined by the quality factor [229]. Figure 1.22 shows a photothermal, waveguide-based sensor capable of measuring the optical absorption spectrum of a thin film in contact with the chip, enabling determination of the polymer absorption spectrum [230].

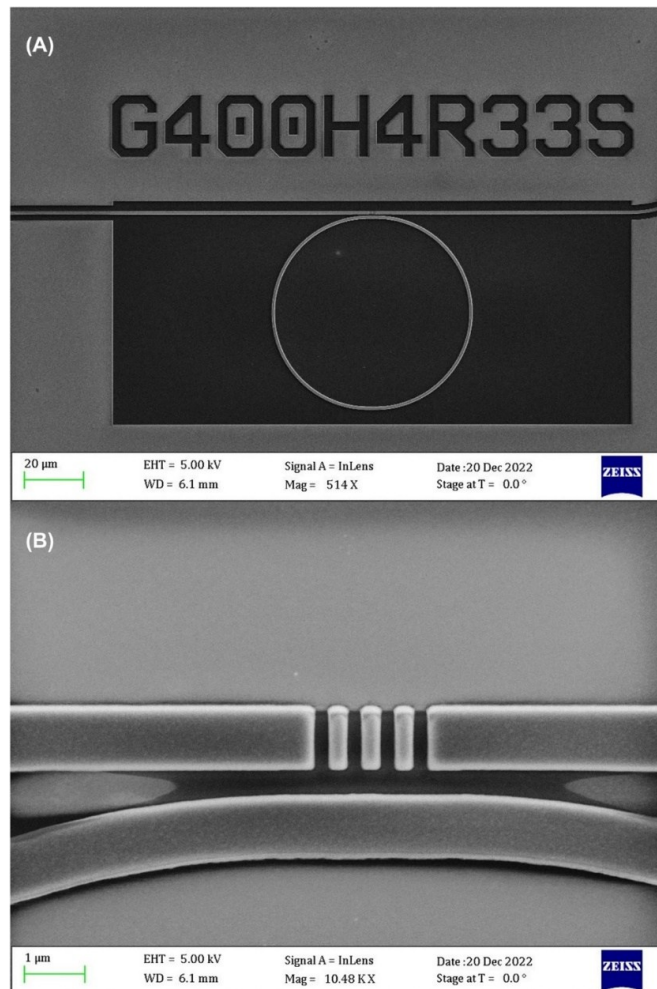


Figure 1.22. SEM images of a micro-ring resonator [230].

For gas sensing applications, micro-ring resonators typically operate in the under-coupled regime, where intrinsic losses dominate over coupling losses. This ensures that gas absorption constitutes the primary loss mechanism, maximizing sensitivity.

By monitoring the transmission at the steepest slope of a resonance, minute absorption changes translate into measurable intensity variations. The sensitivity scales with the quality factor Q , motivating the development of ultra-high- Q resonators [231].

Recent advances have pushed micro-ring Q factors above 10^7 in silicon photonics, though practical gas sensors typically operate with Q factors of 10^4 – 10^6 to balance sensitivity with dynamic range and environmental stability [232]. Achieving high Q requires minimizing all sources of loss—sidewall-roughness scattering, substrate leakage, and material absorption. Advanced fabrication, such as oxidation smoothing or reflow techniques, can reduce roughness to near-atomic scales. The interaction between the resonator mode and the surrounding gas can be further enhanced using the aforementioned waveguide structures [233].

In silicon photonic integrated circuits, efficient on-chip photodetection requires materials with a direct bandgap, since silicon is transparent in the 1.3–1.6 μm telecommunications window and cannot absorb light effectively. As an example, Figure 1.23 shows the coupling of photonic waveguides to integrated detectors using three-dimensional inverse-taper structures.

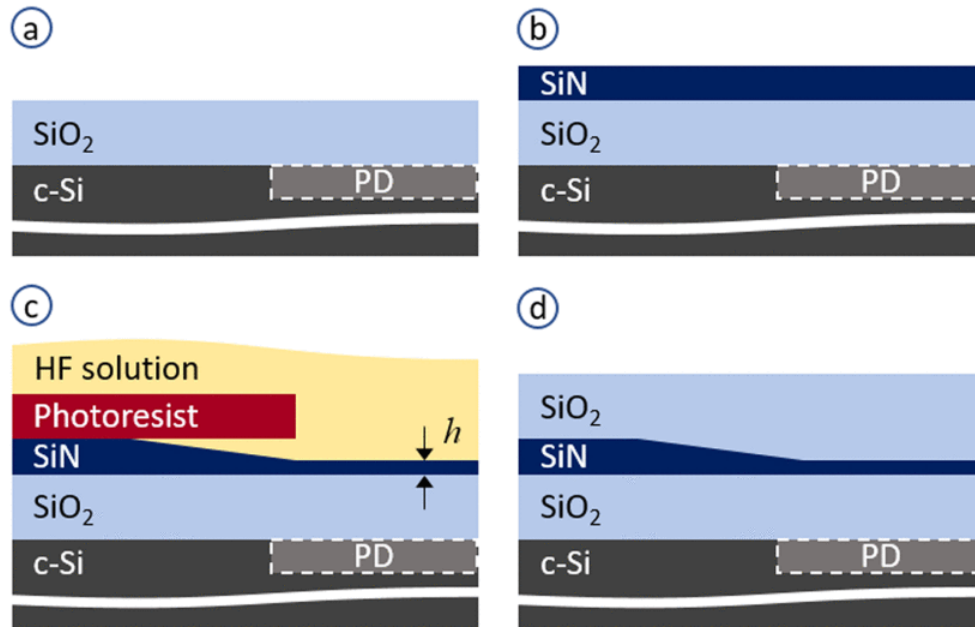


Figure 1.23. Schematic of the fabrication process to realize wedge profiles in photonic waveguides. (a) The Si substrate, in which the photodetector devices are already realized, is covered by a thick SiO₂ cladding. (b) Deposition of the waveguiding SiN film follows. (c) The

photoresist-patterned SiN film is etched in a buffered HF solution to realize a wedge profile. The thickness h of the etched SiN film is controlled via the etch duration. (d) The three-dimensional PIC layer is covered by an SiO₂ top cladding [234].

Compound semiconductors such as InGaAs and InP are therefore introduced to enable optical-to-electrical conversion within the same chip platform. Heterogeneous integration, where thin III–V epitaxial layers are bonded directly onto silicon substrates, has emerged as the most reliable approach to realize such detectors. This technique enables waveguide-integrated InGaAs photodiodes that combine high responsivity and wide electrical bandwidth with CMOS-compatible processing. Devices produced by this method routinely achieve quantum efficiencies above 90% and bandwidths exceeding 40 GHz, comparable to those of discrete InGaAs detectors. Evanescently coupled geometries are often employed to ensure efficient optical coupling between the silicon waveguide and the III–V absorbing layer, reducing reflection losses and optimizing mode overlap. Although monolithic growth of InGaAs on silicon has been explored, the large lattice mismatch introduces dislocations and interfacial defects that limit performance. For this reason, hybrid and heterogeneous integration remain the dominant strategies for implementing high-speed, low-noise on-chip photodetectors. These architectures combine the optical efficiency of III–V materials with the scalability and integration density of silicon photonics, providing a practical route toward fully integrated transceivers for data-communication and sensing applications [235].

The realization of integrated gas sensors requires careful attention to system-level design beyond the photonic components themselves. The transition from laboratory demonstrations to commercial products often encounters challenges in packaging, gas handling, thermal management, and system integration that can negate the advantages of photonic integration if not properly addressed. There are several critical areas that need to be considered carefully before moving to integrated sources and, ultimately, to fully integrated, on-chip sensors.

Optical packaging must provide stable, low-loss coupling between optical fibers and on-chip waveguides while maintaining gas access to the sensing region [236]. Edge coupling through polished or etched facets offers broadband operation and polarization flexibility but requires precise alignment with tolerances below 1 μm . Anti-reflection

coatings are essential to minimize back-reflections that can destabilize laser sources or create interference fringes [237].

Grating couplers provide an attractive alternative for wafer-scale testing and packaging, allowing vertical coupling that simplifies assembly [238]. However, their wavelength and polarization dependence limits spectroscopic applications unless carefully designed. Recent advances in apodized and focusing grating couplers have achieved coupling efficiencies exceeding 90% with 3 dB bandwidths over 100 nm, though this still falls short of the broadband operation possible with edge coupling [239].

Gas handling in miniaturized sensors presents unique challenges and opportunities. The small active volumes—typically nanoliters to microliters—enable rapid response times but require careful flow control to ensure representative sampling [240]. Microfluidic channels integrated with photonic circuits create defined gas cells with controlled flow patterns, exemplified in Figure 1.24 [241].

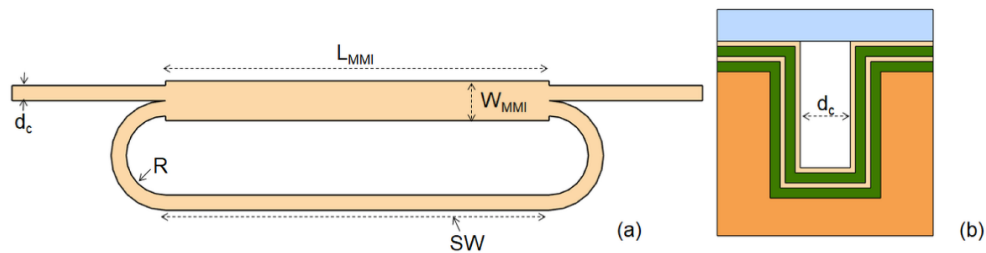


Figure 1.24. (a) Schematic layout of a planar optofluidic ring resonator based on an *h*-ARROW. (b) Schematic cross section of the *h*-ARROW structure [241].

The laminar flow regime in microscale channels can be exploited for flow-cytometry-like measurements of individual gas packets [242].

Temperature control and thermal management become critical in integrated sensors where multiple heat-dissipating components share a small chip. Thermoelectric coolers integrated with the photonic chip can maintain stable temperatures, essential for wavelength-stable laser operation and drift-free measurements [243]. Thermal isolation structures, such as suspended platforms or deep trenches, can separate temperature-sensitive components from heat sources [244].

Electronic integration leverages the CMOS compatibility of silicon photonics to create sophisticated control and readout circuits alongside optical components [245]. Transimpedance amplifiers convert photodetector currents to voltages with noise levels approaching theoretical limits. Digital signal processors implement lock-in detection, wavelength scanning, and spectroscopic fitting algorithms. Furthermore, application-specific integrated circuits (ASICs) can provide complete sensor control in millimeter-scale packages [246].

Power management becomes crucial for battery-operated or energy-harvesting applications. While photonic components could consume negligible power, the associated electronics, temperature control, and potentially integrated light sources can dominate power budgets. Duty-cycling strategies that activate sensors only when needed can extend battery life. Energy harvesting from ambient light, vibration, or temperature gradients could enable truly autonomous sensors [247].

Photonic integrated gas sensors are beginning to transition from research demonstrations to practical applications, driven by compelling advantages in specific markets where traditional sensors fall short.

Industrial process control represents an immediate opportunity where the value of improved sensitivity and stability justifies higher initial costs. Integrated sensors can monitor traces of contaminants in semiconductor manufacturing, detect leaks in chemical plants, or optimize combustion in power generation [248]. The small size enables *in situ* measurements at multiple points, providing spatial resolution impossible with centralized analyzers.

Environmental monitoring could be transformed by networks of integrated sensors providing unprecedented spatial and temporal resolution [249]. Air quality monitoring in urban areas requires sensors at every street corner—a deployment scale only possible with low-cost, mass-produced devices. Integration with wireless communications and cloud analytics enables real-time pollution mapping and source identification. The same technology could monitor greenhouse gases for climate research or detect fugitive emissions from industrial facilities [250].

Medical diagnostics through breath analysis represents a particularly exciting frontier. Human breath contains hundreds of VOCs that serve as biomarkers for various

diseases [251]. Integrated sensors capable of detecting multiple compounds simultaneously could enable non-invasive diagnosis of conditions ranging from diabetes to lung cancer. Point-of-care devices that provide immediate results could transform healthcare delivery, particularly in resource-limited settings [252].

Consumer applications, while requiring the lowest costs, could represent the largest market if technical and economic barriers are overcome. Personal air quality monitors integrated into smartphones or wearables could help individuals avoid pollution exposure [7]. Smart home systems could monitor indoor air quality and automatically adjust ventilation. Automotive sensors could optimize engine performance while monitoring cabin air quality [253].

Looking ahead, several technological trends are poised to shape the evolution of integrated gas sensors. Heterogeneous integration will become increasingly sophisticated, potentially combining multiple material platforms in three-dimensional architectures [254]. For example, III–V lasers, silicon photonic circuits, and CMOS electronics could be stacked vertically with through-silicon vias providing interconnections, as shown in Figure 1.25 [255], [256], [257].

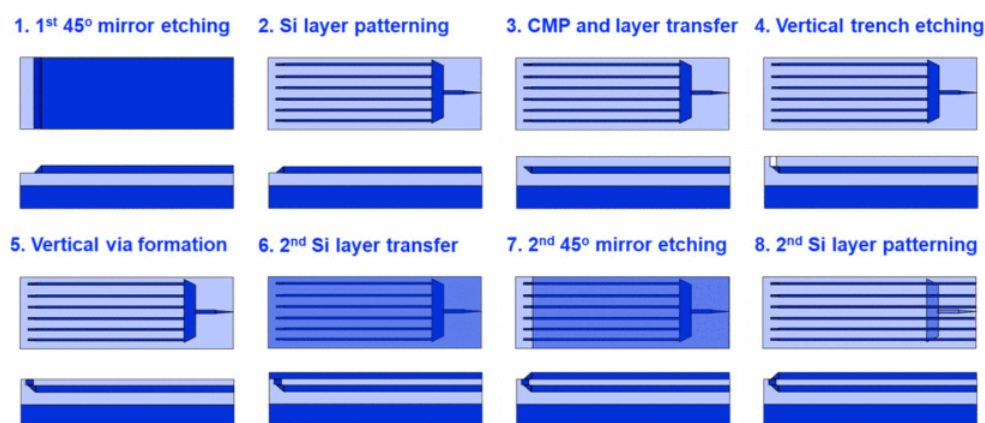


Figure 1.25. Fabrication process flow of a U-shaped vertical coupler [255].

In addition, the device described above in Figure 1.23 was developed by tapering the waveguide vertically using an engineered wet-chemical etching process.

Mid-IR photonic platforms will mature, by providing access to fundamental molecular vibrations with orders of magnitude stronger absorption than near-IR overtones [258]. Materials such as silicon–germanium, suspended silicon, and chalcogenide glasses

will enable integrated sensors operating beyond 5 μm wavelength. The challenge lies in achieving a comparable level of maturity in sources, detectors, and passive components to that of the near-IR domain.

Standardization efforts will accelerate development and adoption by enabling component reuse and foundry access. Process design kits (PDKs) specifically for gas sensing components will allow designers to focus on system-level innovation rather than device optimization [259]. Shared multi-project wafer runs will reduce prototyping costs, enabling small companies and research groups to access advanced fabrication.

The convergence of multiple technological advances with growing market demand creates a compelling vision for the future of gas sensing. Integrated photonic sensors could become as ubiquitous as temperature sensors today, fundamentally changing how we monitor and understand our chemical environment. From networks of environmental monitors providing real-time pollution data to medical devices detecting disease before symptoms appear, the applications seem limited only by imagination.

This examination of gas sensing techniques reveals a field in dynamic evolution—driven by increasingly demanding applications and enabled by advances across multiple scientific and engineering disciplines. From the mature foundation of non-optical sensors to cutting-edge developments in photonic integration, each approach offers unique capabilities while facing distinct challenges that define its optimal domain of application.

CHAPTER 2

2. Near-IR Beat-Frequency QEPAS for Rapid Multi-Gas Detection

The evolution of QEPAS has witnessed significant advances in recent years, with the development of beat-frequency (BF) QEPAS (BF-QEPAS) representing a paradigm shift in the approach to simultaneous gas concentration measurement and QTF resonance characterization [163]. Conventional QEPAS has demonstrated exceptional sensitivity and selectivity for trace gas detection, but faces inherent limitations when applied to rapidly varying sensing scenarios [260]. Indeed, the need for periodic QTF characterization, due to potential drift in resonance parameters under changing environmental conditions, has motivated the development of alternative approaches capable of overcoming this fundamental limitation while preserving the exceptional analytical performance that characterizes QEPAS.

The significance of developing advanced QEPAS methodologies extends beyond purely technical considerations, encompassing critical applications in environmental monitoring, industrial process control, and energy infrastructure management where the measurement of detector performance and the simultaneous detection of multiple hydrocarbon species provide essential information for source identification, leak characterization, and compositional analysis [261]. Natural gas systems, in particular, present complex analytical challenges as they typically contain both methane and ethane in varying ratios that serve as fingerprints for distinguishing between different sources and assessing leak severity [262]. Traditional detection methods often necessitate separate measurement systems for each target species, resulting in

increased complexity, cost, and measurement time, limiting their applicability in field deployments [263].

The global importance of accurate methane and ethane monitoring has intensified dramatically in recent decades, driven by increasing recognition of their roles in climate change, industrial safety, and energy resource management [264], [265], [266]. According to the latest Global Methane Budget, methane emissions now total approximately 575 million metric tons per year (2010–2019 average), significantly higher than earlier estimates, with natural gas leaks representing a substantial contribution to these emissions [267], [268]. The ability to rapidly distinguish between thermogenic sources (containing both methane and ethane) and biogenic sources (predominantly methane) has become crucial for atmospheric research and environmental policy development [269], [270].

This chapter presents the BF-QEPAS technique, beginning with a detailed theoretical analysis of the underlying physical principles and progressing through extensive experimental implementation for simultaneous methane and ethane detection in the near-IR spectral region. The investigation addresses both the fundamental aspects of BF-QEPAS signal generation and the practical considerations for optimizing system performance in real-world sensing applications, with particular emphasis on the trade-offs among measurement speed, sensitivity, and the extraction of QTF resonance parameters from complex spectroscopic signatures.

2.1. Beat-Frequency Technique

The BF approach applied to QEPAS represents a fundamental departure from conventional QTF-based sensing methods, introducing a signal processing framework that enables simultaneous extraction of gas concentration and resonance parameters through analysis of transient response characteristics [163].

The theoretical foundation of BF-QEPAS rests upon the dynamic response characteristics of the QTF when subjected to photoacoustic excitation slightly detuned from its resonance frequency. Figure 2.1 depicts a side-by-side comparison of conventional QEPAS and BF-QEPAS techniques, illustrating the steady-state and transient responses of the QTF, respectively [163].

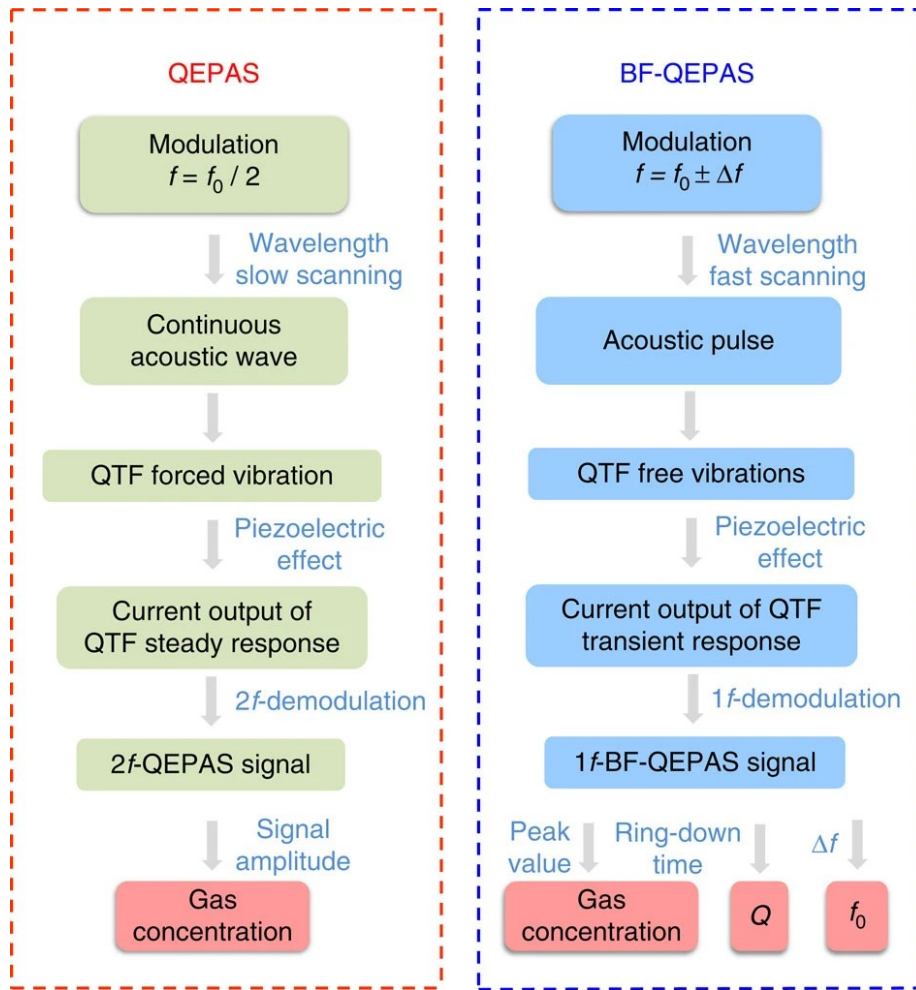


Figure 2.1. A side-by-side comparison of conventional QEPAS and BF-QEPAS techniques [163].

In contrast to conventional QEPAS, the laser modulation frequency f in BF-QEPAS is intentionally detuned from the QTF resonance frequency f_0 . The laser wavelength is rapidly scanned at a rate comparable to or faster than the QTF response time. By analyzing the beat signal generated between the laser modulation frequency and the QTF resonance frequency, a BF-QEPAS sensor can determine the target gas concentration, the QTF resonance frequency, and the Q -factor in a single measurement.

Moreover, in conventional QEPAS, a continuous acoustic wave causes forced vibrations of the QTF. The transient response of the QTF is typically neglected, and

only the steady-state behavior is considered, since the long averaging times (> 300 ms) effectively average the transient response to zero. In BF-QEPAS, an acoustic pulse induced by target-gas absorption is generated through rapid wavelength scanning ($> 30 \text{ cm}^{-1} \cdot \text{s}^{-1}$), causing the QTF prongs to vibrate for a short duration. Subsequently, the QTF prongs freely vibrate at their resonance frequency once the acoustic pulse has terminated. The vibration energy is dissipated through both extrinsic and intrinsic QTF loss mechanisms, governed by the quality factor. The QTF signal is demodulated at the laser modulation frequency f . When the averaging time is short enough (< 100 ms) to provide a sufficient system detection bandwidth, a BF signal with an exponential decay envelope is generated from the QTF transient response. The concentration of the trace gas, the resonance frequency, and the Q -factor of the QTF can be obtained by measuring the peak amplitude, the BF frequency offset (Δf), and the decay time (τ) of the BF-QEPAS signal, respectively.

The QTF can be accurately described by the Butterworth–Van Dyke equivalent circuit model, which represents the mechanical resonance through a motional branch composed of a series resistor–inductor–capacitor (RLC) circuit, and a parallel capacitance C_0 accounting for the electrodes.

According to this model, the electrical behavior of the QTF follows Ohm's law for the motional branch:

$$U(t) = R_m \cdot \frac{dq}{dt} + L_m \cdot \frac{d^2q}{dt^2} + \frac{q}{C_m}. \quad (2.1)$$

Equation 2.1. Ohm's law applied to the motional branch of the QTF Butterworth–Van Dyke equivalent circuit, where R_m , L_m , and C_m represent, the mechanical losses, effective mass, and stiffness of the resonator, respectively.

Here, R_m accounts for the energy losses—mainly due to acoustic and viscous damping—while L_m corresponds to the effective mass of the resonator, and C_m is related to its elastic stiffness.

The total admittance of the QTF can therefore be expressed as:

$$Y(\omega) = i \cdot \omega \cdot C_0 + \frac{1}{R_m + i \cdot \omega \cdot L_m + \frac{1}{i \cdot \omega \cdot C_m}}. \quad (2.2)$$

Equation 2.2. Total admittance of the QTF derived from the Butterworth–Van Dyke model, including the motional RLC branch in parallel with the static capacitance C_0 due to the electrodes.

This model provides a purely electrical representation of the QTF dynamics—without invoking Newton’s law of motion—and is widely used in the theoretical and numerical description of QEPAS systems [114].

The mathematical description of the BF-QEPAS signal can then be formulated as the convolution of the photoacoustic excitation function with the impulse response of the QTF.

In the BF spectroscopic technique, the laser tuning range is scanned using a custom waveform composed of a fast-rising ramp followed by a stationary level [271]. In contrast to the continuous acoustic-wave excitation employed in conventional QEPAS, the rapid wavelength transitions of the absorption function in BF-QEPAS generate a photoacoustic pulse within the gas mixture, as illustrated in Figure 2.1.

The response of the QTF to such a pulsed photoacoustic excitation can be described by the impulse response function of an underdamped harmonic oscillator ($Q > 1/2$):

$$h(t) = a \cdot e^{-\frac{t}{\tau}} \cdot \sin(2 \cdot \pi \cdot f_d \cdot t + \varphi) \cdot u(t). \quad (2.3)$$

Equation 2.3. Impulse response function describing the quartz tuning fork response to a transient photoacoustic excitation.

Here, a is the maximum amplitude of the response, $\tau = (2 \cdot Q)/\omega_r$ is the decay time constant, $f_d = f_0(1 - 1/(4 \cdot Q^2))^{1/2}$ is the damped oscillation frequency, and $u(t)$ is the unit step function. For high- Q resonators, typical of QEPAS applications ($Q > 10,000$ at atmospheric pressure), the damped frequency is approximately equal to the resonance frequency, *i.e.*, $f_d \approx f_0$.

The extraction of quantitative information from BF-QEPAS signals requires fitting functions that accurately reproduce the temporal evolution of the acquired waveforms, while capturing the essential physics of the beat-frequency process.

The most commonly employed fitting function for a single absorption line is expressed as:

$$f_{fit}(t) = A \cdot e^{-\frac{t}{\tau}} \cdot \sin(2 \cdot \pi \cdot \Delta f_{fit} \cdot t + \varphi_0) + offset. \quad (2.4)$$

Equation 2.4. Mathematical expression of the most widely used fitting function for single absorption lines.

In this equation, A represents the signal amplitude, τ is the exponential decay time constant, Δf_{fit} is the fitted beat frequency, φ_0 is the initial phase, and *offset* accounts for any DC component in the signal. It is noteworthy that the amplitude A in Equation 2.4 depends on the magnitude of the generated acoustic wave and, consequently, on the gas concentration.

The quality factor and resonance frequency of the QTF can be extracted from the fitted parameters using the following relationships:

$$Q_{BF} = \pi \cdot f_0 \cdot \tau, \quad (2.5)$$

Equation 2.5. Expression for the retrieved QTF quality factor.

and:

$$f_0 = f_{MOD} \pm \Delta f_{fit}. \quad (2.6)$$

Equation 2.6. Expression for the retrieved QTF resonance frequency.

The sign in Equation 2.6 depends on whether the modulation frequency lies above or below the resonance frequency, as defined in the experimental configuration.

For gas mixtures with multiple components exhibiting overlapping spectral features, or for species with complex multi-line absorption profiles such as ethane (C_2H_6) in the investigated spectral range, the simple single-exponential model of Equation 2.4 may become inadequate. In these cases, multi-component fitting models are employed:

$$f_{fit}(t) = \sum_i A_i \cdot e^{-\frac{t}{\tau_i}} \cdot \sin(2 \cdot \pi \cdot \Delta f_i \cdot t + \varphi_i) + offset. \quad (2.7)$$

Equation 2.7. Mathematical expression of the fitting function accounting for multiple absorption lines.

This approach allows decomposition of complex beat signals into their individual components, corresponding to different absorption features, and accurately models the linear superposition of multiple contributions.

In conventional QEPAS-based sensors, the amplitude of the $2f$ component is generally lower than that of the fundamental ($1f$) signal [163]. However, the $2f$ harmonic is often preferred for detection because its peak position coincides with the center of the target absorption line.

In the BF-QEPAS technique, by contrast, the signals corresponding to the first, second, and third harmonics share the same waveform shape. The optimal harmonic component must therefore be determined experimentally for each configuration.

The successful implementation of BF-QEPAS requires careful optimization of several experimental parameters to maximize both the information content and the reliability of the extracted data. Along with the modulation amplitude and the operating pressure—parameters also optimized in conventional QEPAS—the choice of the detuning frequency (Δf) and the wavelength scan rate plays a critical role in determining the signal amplitude and, consequently, the accuracy of parameter extraction.

Figure 2.2 shows the dependence of the BF-QEPAS signal amplitude on the laser modulation frequency [271].

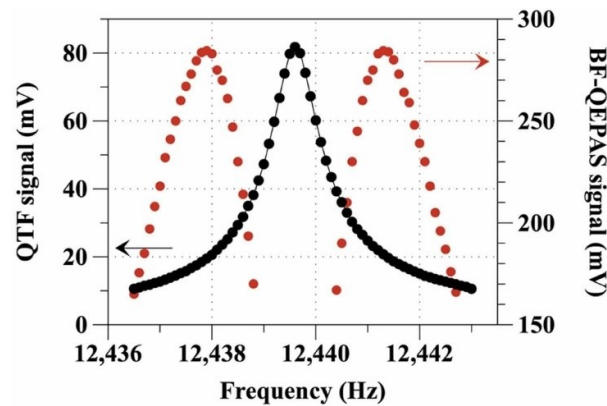


Figure 2.2. Red dots: BF-QEPAS peak signal for a gas mixture containing 250 ppm of NO in standard air as a function of the laser modulation frequency at 400 Torr. Black dots: Resonance curve at 400 Torr measured by electrically exciting the QTF [271].

Two factors determine the amplitude of the BF-QEPAS signals. The first factor is the response of the QTF to the acoustic wave generated at the laser modulation frequency. The QTF is more efficiently excited when the laser modulation frequency f approaches its resonance frequency f_0 . The second factor is the value of the BF, Δf . A small Δf results in a longer interval between two consecutive constructive interferences (*i.e.*, a longer beat period). As this interval increases, a larger portion of the QTF's vibrational energy is dissipated before the next excitation pulse. These two mechanisms act together to define the modulation frequency that maximizes the BF-QEPAS signal. As

an example, the BF-QEPAS signal measured at different nitric oxide (NO) concentrations is reported in Figure 2.3.

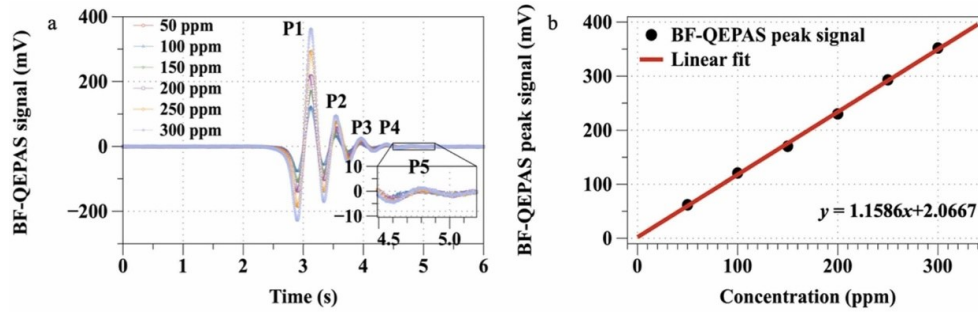


Figure 2.3. (a) QEPAS spectral scans measured for different NO concentrations in standard air. (b) QEPAS peak amplitudes plotted as a function of NO concentration (black dots). The red solid line represents the best linear fit of the experimental data [271].

The calibration curve in Figure 2.3(b) was obtained by extracting the value of the first positive peak (labeled as P1 in Figure 2.3(a)) for each NO concentration. These values were then plotted as a function of the NO concentration, as shown in Figure 2.3(b). For each NO concentration, the five positive peaks (P1–P5 in Figure 2.3(a)) can be used to determine both the resonance frequency and the quality factor of the QTF. The time intervals between the five peaks were used to calculate the inverse of the beat frequency Δf . The QTF resonance frequency was then retrieved as $f_0 = f + \Delta f = 12,439.6$ Hz. An exponential fit ($e^{-t/\tau}$) of the five peaks was applied to estimate the QTF decay time constant (τ) and, consequently, its quality factor.

The wavelength scanning strategy also requires careful optimization for BF-QEPAS applications. Traditional QEPAS implementations employ slow triangular or sinusoidal wavelength scans to achieve steady-state conditions at each spectral position, but BF-QEPAS benefits from fast staircase ramp profiles to reduce measurement time.

Therefore, the rise time of the staircase ramp represents another critical parameter influencing the transient response characteristics, as shown in Figure 2.4.

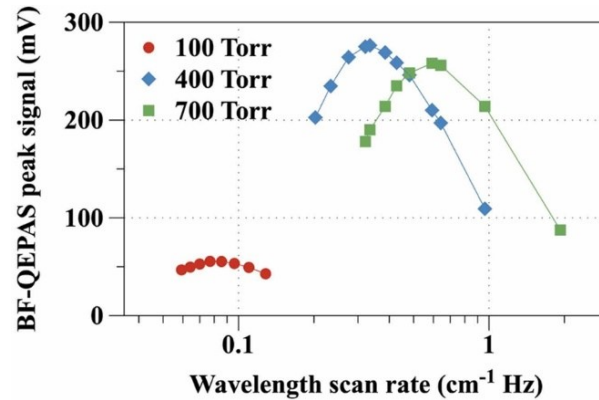


Figure 2.4. BF-QEPAS peak signal as a function of the wavelength scan rate, measured at 100 Torr (red dots), 400 Torr (blue diamonds), and 700 Torr (green squares) for a gas mixture containing 250 ppm of NO in standard air [271].

As shown in Figure 2.4, for each investigated pressure, the BF-QEPAS signal exhibits a similar dependence on the wavelength scan rate, characterized by a well-defined maximum corresponding to optimal excitation conditions. Owing to the pressure dependence of the quality factor, the QTF accumulation time decreases with increasing pressure. Consequently, a slower scan rate must be used at higher pressures to optimize the BF-QEPAS signal.

The BF-QEPAS approach offers several distinct advantages over conventional QEPAS, making it particularly attractive for multi-gas sensing applications, as demonstrated by the QEPAS signal in Figure 2.5 and the BF-QEPAS signal in Figure 2.4 [271].

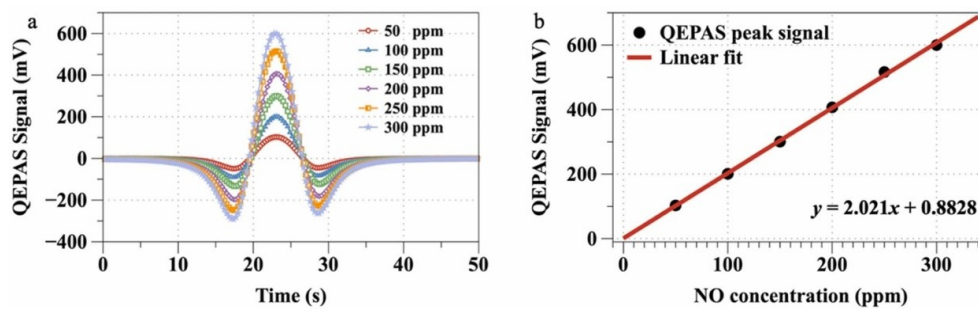


Figure 2.5. (a) QEPAS spectral scans measured for different NO concentrations in standard air. (b) QEPAS peak amplitudes plotted as a function of NO concentration (black dots). The red solid line represents the best linear fit of the experimental data [271].

After the parameter optimization phase, both techniques were compared at 400 Torr using gas mixtures containing 50–300 ppm of NO diluted in standard air for calibration

[271]. The strongest NO absorption line, located at 1900.07 cm^{-1} , was considered in this comparison. Figure 2.5 shows the QEPAS scans for different NO concentrations. For each spectral scan, peak values were extracted and plotted as a function of the NO concentration. A detection sensitivity of 2.02 mV/ppm was obtained from the slope of the linear fit of the data points. The noise level was determined by flushing standard air through the acoustic detection module and acquiring the 1σ standard deviation of the signal, with the laser wavelength fixed at the NO absorption line (triangular ramp disabled). The measured QEPAS noise was 0.18 mV , corresponding to a minimum detection limit (MDL) of 90 ppb and a NNEA value of $5.9 \times 10^{-9}\text{ cm}^{-1} \cdot \text{W} \cdot \text{Hz}^{-1/2}$. For the BF-QEPAS configuration, the slope of the linear fit of the data points yields a sensitivity of 1.16 mV/ppm . As in the QEPAS case, the BF-QEPAS noise was measured by flushing standard air through the module and acquiring the σ standard deviation of the signal, with the laser emission fixed at the NO absorption line. The measured noise level was 0.21 mV , corresponding to an MDL of 180 ppb and an NNEA value of $2.5 \times 10^{-9}\text{ cm}^{-1} \cdot \text{W} \cdot \text{Hz}^{-1/2}$.

The most significant advantage is the substantial reduction in measurement time, with complete information retrieved in seconds rather than minutes. This improvement arises from the elimination of steady-state settling requirements, since the transient nature of beat signals enables the extraction of multiple parameters during wavelength transitions.

The simultaneous extraction of gas concentration and QTF resonance parameters is another major advantage, eliminating the need for separate characterization procedures and enabling real-time validation of measurement accuracy. This capability is particularly valuable in field deployment scenarios where environmental variations might affect the QTF properties and compromise measurement reliability in conventional systems.

Nonetheless, BF-QEPAS also entails several limitations that must be carefully considered in practical implementations. The complexity of signal processing represents a significant challenge, requiring fitting algorithms and real-time data processing. The parameter extraction is also more sensitive to noise and signal

artifacts, since the fitting algorithms must accurately resolve multiple parameters from limited data sets.

2.2. Near-IR Methane/Ethane BF-QEPAS Sensor

This section presents the practical implementation of beat-frequency QEPAS for the simultaneous detection of methane (C1) and ethane (C2), serving as a compelling demonstration of the BF-QEPAS capabilities for multi-gas sensing applications [272]. The selection of methane and ethane as target analytes is motivated by their critical importance in natural gas composition analysis, environmental monitoring, and industrial leak detection, where the ability to rapidly determine the concentration ratios of these species provides essential information for source identification and characterization [262].

Figure 2.6 presents the experimental setup employed for the comparative study between conventional QEPAS and BF-QEPAS techniques.

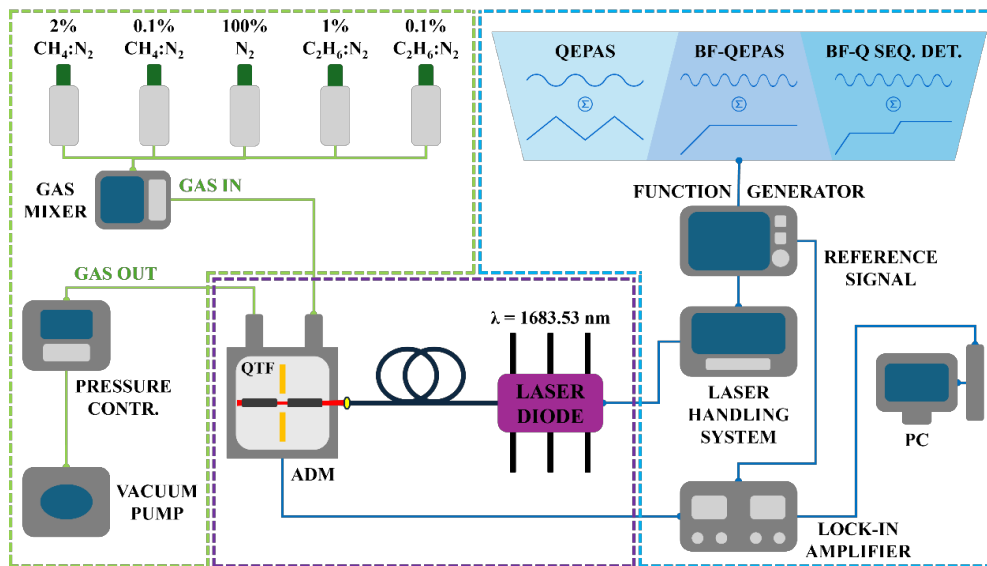


Figure 2.6. Experimental setup used for the comparative study between conventional QEPAS and BF-QEPAS techniques.

The system architecture consists of three main subsystems: the gas handling system for precise mixture preparation, the optical detection module incorporating the laser source and acoustic detection components, and the electronic signal processing unit for modulation generation and data acquisition.

The gas handling system, shown in the dashed green section of Figure 2.6, incorporates five certified gas cylinders containing 2% CH₄ in nitrogen (N₂), 0.1% CH₄ in N₂, 1% C₂H₆ in N₂, 0.1% C₂H₆ in N₂, and pure N₂ used for target gas dilution. These cylinders are connected through a precision gas blender (MCQ Instruments, GB6000) that allows the preparation of accurate gas mixtures across the 0–1% concentration range for both target species. The system maintains a controlled flow rate of 50 standard cubic centimeters per minute (SCCM) through the acoustic detection module (ADM), while the pressure is regulated at 750 Torr using a precision pressure controller (Alicat Scientific, MC Series).

The optical system employs a DFB laser diode (Eblana Photonics Ltd., EP1684-0-DM-B06-FA) operating at a central wavelength of 1683.53 nm. This wavelength was specifically selected for its ability to address the absorption features of both target gases through wavelength tuning at a fixed operating temperature of 15 °C. The laser delivers up to 8 mW of continuous-wave power in single-frequency operation and exhibits mode-hop-free tuning over a range sufficient to simultaneously probe the methane six-line cluster centered at 5938.12 cm⁻¹ and the ethane absorption band at 5937.3 cm⁻¹ [273], [274].

The laser output is coupled through a fiber collimator (OZ Optics Ltd., LPC Series) and precisely aligned to the ADM (Thorlabs GmbH, ADM01), which houses a custom T-shaped QTF with optimized geometry for enhanced acoustic coupling [52].

The fundamental spectroscopic differences between C1 and C2 in the near-IR region create distinct challenges for unified sensing approaches. These differences must be carefully considered when designing dual-gas BF-QEPAS systems.

Figure 2.7 shows the absorption spectrum of ethane in the targeted wavelength region at atmospheric pressure. For comparison, the absorption spectrum of methane is also reported in a different spectral range, highlighting the higher spectral complexity of C₂H₆ [275].

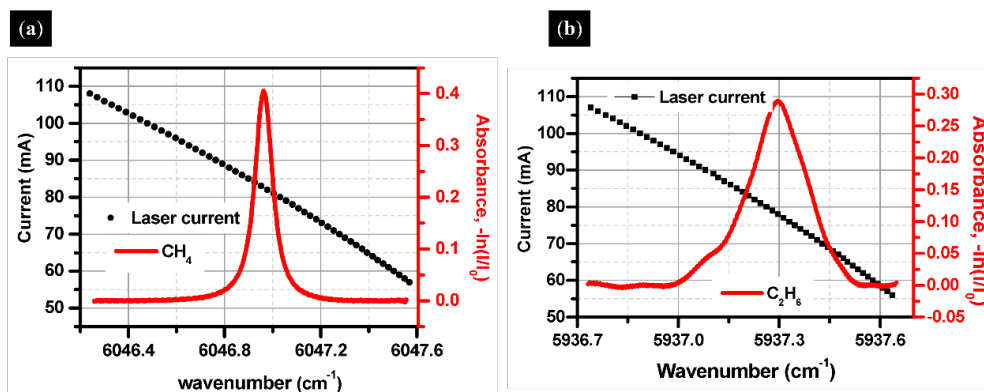


Figure 2.7. (a) Absorption spectrum of methane near 6046.95 cm^{-1} . The left axis shows the laser current versus laser frequency, and the right axis shows the absorbance of the methane line. (b) Absorption spectrum of ethane near 5937.3 cm^{-1} . The left axis shows the laser current versus laser frequency, and the right axis shows the absorbance of ethane over the tuning wavelength range [275].

Methane exhibits well-resolved absorption lines with relatively narrow linewidths and high peak absorption cross-sections in the targeted spectral region. The six-line cluster centered at 5938.12 cm^{-1} arises from the carbon-hydrogen stretching $2\nu_3$ overtone transitions [42].

The narrow linewidth of individual methane transitions (typically $0.1\text{--}0.2 \text{ cm}^{-1}$ at atmospheric pressure) produces well-defined Voigt-like absorption features that yield clear, interpretable BF-QEPAS signals, as previously reported [276]. The strong absorption cross section of the targeted feature ($6.18 \times 10^{-22} \text{ cm}^2/\text{molecule}$ at 5938.1 cm^{-1} [273]) ensures adequate signal-to-noise ratios even at ppm concentration levels.

In contrast, ethane exhibits a more complex spectroscopic signature composed of multiple overlapping features centered at 5937.3 cm^{-1} , together with weaker sidebands that form a broadband absorption profile [274]. The ethane spectrum in this region arises from combinations of C–H stretching overtone vibrations, producing a dense manifold of transitions that are not individually resolved.

As shown in Figure 2.7, the integrated absorption strength of ethane is comparable to that of methane despite its broadband character. However, the distributed intensity among multiple overlapping features reduces the peak absorption cross section of each individual transition. This spectroscopic characteristic has profound implications for BF-QEPAS signal analysis, as discussed in subsequent sections.

The ADM employed in this investigation houses a custom T-shaped QTF coupled with a dual-tube resonator system, as described in Chapter 1, and its electrical characterization is shown in Figure 2.8.

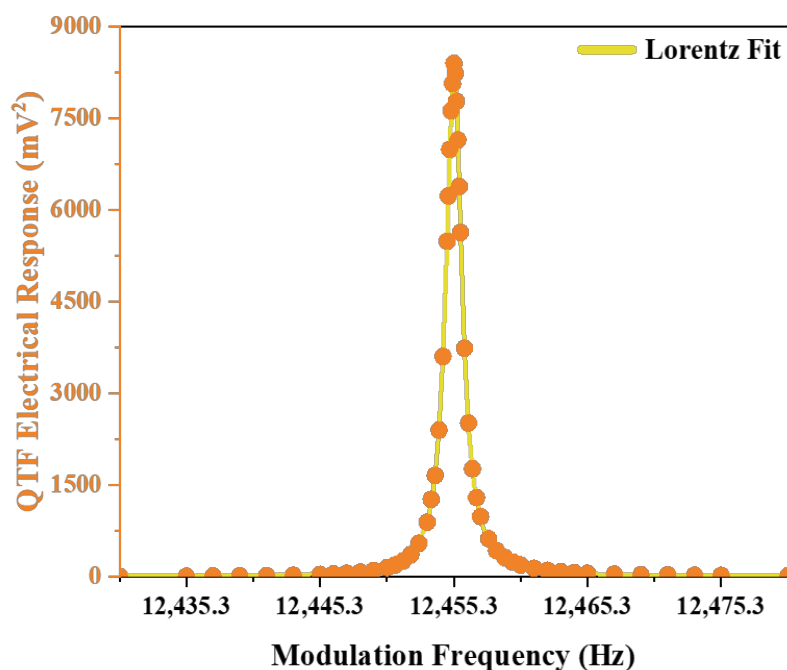


Figure 2.8. Electrical characterization of the QTF. The solid yellow line represents the best Lorentzian fit.

From the Lorentzian fit (solid yellow curve in Figure 2.8) of the experimental data (orange points), a resonance frequency of 12,455.31 Hz and a quality factor of approximately 8770 were obtained at an operating pressure of 750 Torr.

The implementation of BF-QEPAS requires careful optimization of modulation and wavelength scanning parameters to maximize the information content of the acquired signals while maintaining adequate signal-to-noise ratio. The system design illustrated in Figure 2.6 incorporates three distinct operating modes to allow a comprehensive comparison between the conventional and beat-frequency approaches.

For conventional QEPAS measurements, wavelength modulation is achieved by applying a sinusoidal waveform at half the QTF resonance frequency ($f_{MOD} = f_0/2 =$

6227.63 Hz) to the laser injection current. The modulation amplitude is 80 mV peak-to-peak (pp), corresponding to conditions optimized for WMS-2 f detection. Wavelength scanning employs a triangular ramp at 5 mHz with sufficient amplitude to traverse the entire spectral region containing both methane and ethane absorption features. The slow scanning rate ensures steady-state conditions at each wavelength, allowing accurate quantitative analysis but requiring measurement times of about 200 s for complete dual-gas characterization.

BF-QEPAS signal optimization requires a fundamentally different approach, specifically developed for transient signal analysis. Figure 2.9 illustrates the optimization of the modulation frequency and scan rate for methane detection.

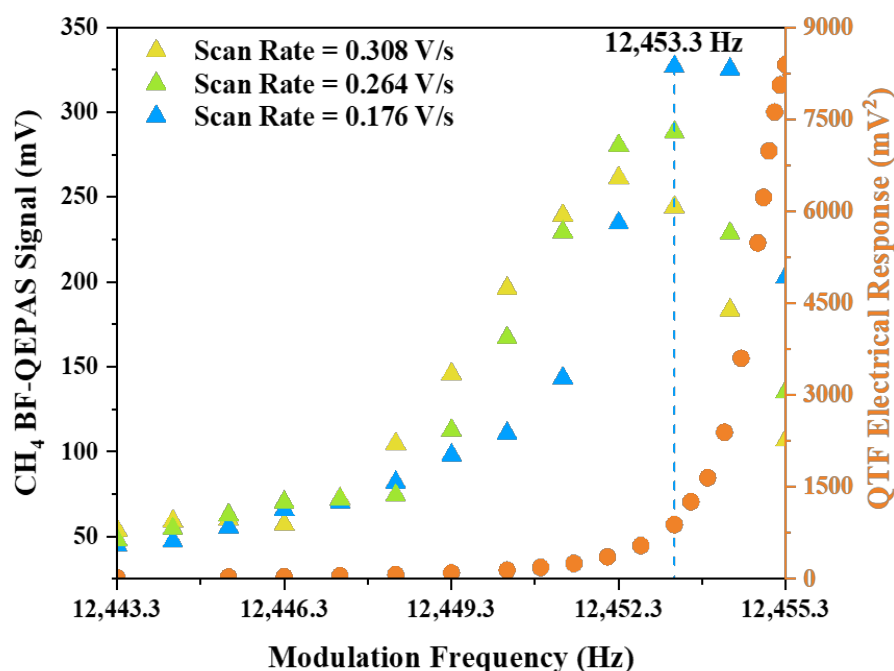


Figure 2.9. CH₄ BF-QEPAS peak signal as a function of the modulation frequency. Orange dots correspond to values obtained from the QTF electrical characterization; yellow, green, and blue triangles represent CI BF-QEPAS measurements at progressively lower scan rates.

Due to the symmetry of the results, only the measurements at frequencies lower than the QTF resonance frequency are reported. Similar trends in the CH₄ BF-QEPAS signals were observed across different scan rates. As previously reported in the

literature, an optimal detuning frequency can be identified at each scan rate investigated. The peak shifts slightly toward higher detuning frequencies for faster scan rates—*i.e.*, faster scans of the absorption feature—because of the need for a higher beat frequency in the detection to prevent signal loss in the slow demodulated response.

An optimal detuning of $\Delta f = 2$ Hz at a scan rate of 0.176 V/s provides adequate signal amplitude while ensuring sufficient temporal resolution for accurate parameter extraction within practical measurement timeframes.

A similar optimization was performed for ethane detection, yielding the same optimal detuning and a scan rate of 0.192 V/s, reflecting the differences between the C1 and C2 absorption features.

Systematic calibration studies were conducted for both conventional QEPAS and BF-QEPAS techniques using certified gas standards diluted in nitrogen carrier gas. The calibration protocols encompassed a concentration range from 0.02% to 1% for both methane and ethane, providing comprehensive characterization of sensor linearity and sensitivity across analytically relevant levels.

Figure 2.10(a) presents the $2f$ -QEPAS spectra acquired for different methane-in-nitrogen mixtures, showing the characteristic second-derivative absorption profiles with background-free baselines.

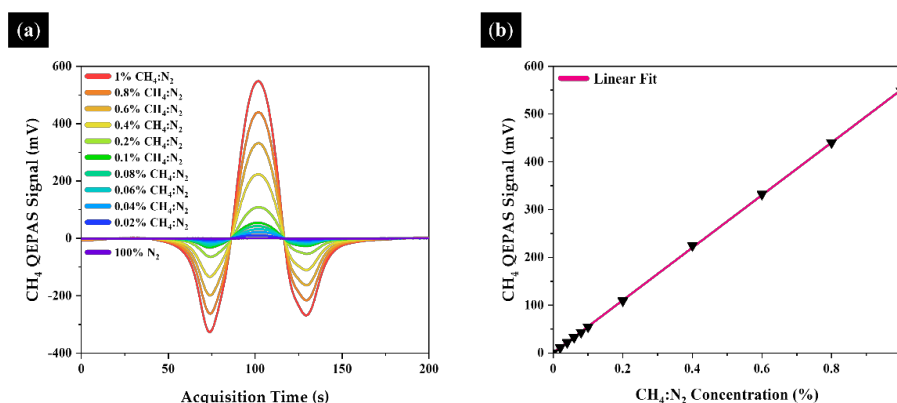


Figure 2.10. (a) CH_4 $2f$ -QEPAS spectra acquired for different methane-in-nitrogen concentrations. (b) Methane calibration data in the QEPAS configuration. The solid pink line represents the best linear fit of the experimental data.

The methane calibration data shown in Figure 2.10(b) demonstrate excellent linearity, with a sensitivity of 549.89 ± 1.56 mV/% and a correlation coefficient (R^2) exceeding 0.9999. This high degree of linearity validates the quantitative accuracy of the QEPAS approach and confirms the absence of significant non-linear effects such as saturation or power broadening under the experimental conditions employed.

The ethane calibration results, presented in Figure 2.11, show similar linearity despite the more complex spectral structure.

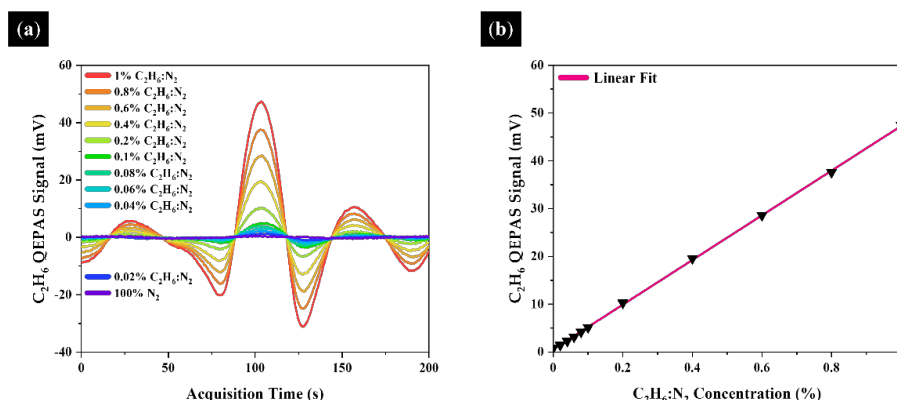


Figure 2.11. (a) C_2H_6 2f-QEPAS spectra acquired for different ethane-in-nitrogen concentrations. (b) Ethane calibration data in the QEPAS configuration. The solid pink line represents the best linear fit of the experimental data.

The acquired QEPAS spectra highlight the broadband absorption feature of ethane. Using the maximum signal obtained at each concentration, the calibration curve shown in Figure 2.11(b) was derived. The sensitivity of 46.85 ± 0.22 mV/% is approximately 12 times lower than that observed for methane, reflecting the differences in absorption cross-sections and spectral structure between the two gases. The correlation coefficient remains high ($R^2 > 0.999$), confirming the quantitative reliability of ethane measurements.

The noise level of the system was determined by analyzing the standard deviation of the signal with pure N_2 flowing through the ADM. Considering a 1σ noise level of 0.09 mV and the retrieved sensitivities, the MDLs (for $SNR = 1$) were calculated to be 1.7 ppm for CH_4 and 20 ppm for C_2H_6 , with an integration time of 100 ms.

Figure 2.12 shows the corresponding BF-QEPAS calibration data for methane, highlighting the characteristic damped oscillatory signals that contain both concentration and QTF parameter information.

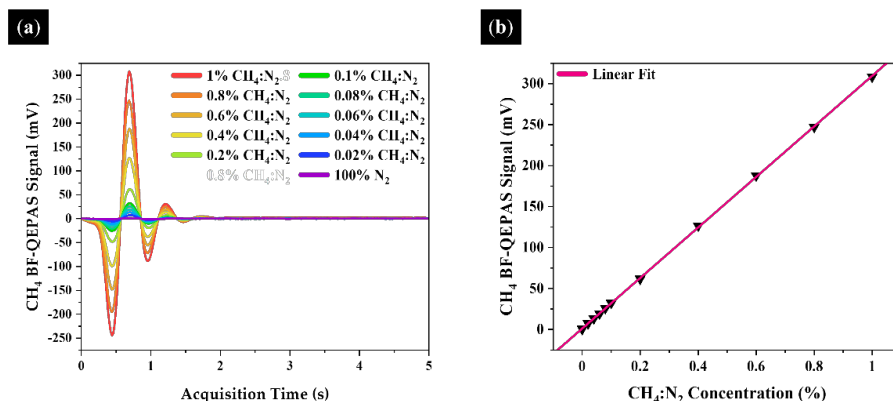


Figure 2.12. (a) CH_4 1f-BF-QEPAS spectra acquired for different methane-in-nitrogen concentrations. (b) Methane calibration data in the BF-QEPAS configuration.

The signal amplitudes show a clear dependence on methane concentration, with beat frequencies of approximately 2 Hz.

The peak signal values were extracted to obtain the BF-QEPAS calibration shown in Figure 2.12(b). This curve yields a C1 sensitivity of $308.38 \pm 1 \text{ mV}/\%$ ($R^2 > 0.999$), representing a reduction of approximately 44% compared to conventional QEPAS.

Figure 2.13 presents the BF-QEPAS calibration results for ethane, showing the more complex signal structure that arises from the broadband absorption profile.

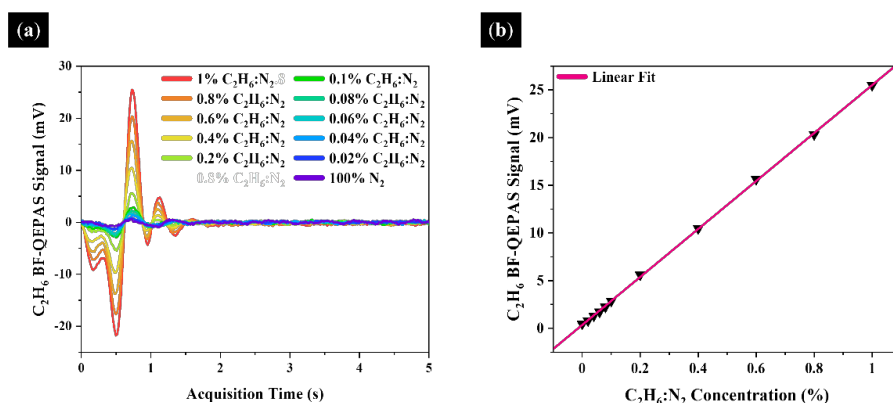


Figure 2.13. (a) C_2H_6 1f-BF-QEPAS spectra acquired for different ethane-in-nitrogen concentrations. (b) Ethane calibration data in the BF-QEPAS configuration.

The overlapping absorption features create composite beat signals that exhibit irregular oscillation patterns, particularly at higher concentrations where weaker absorption sidebands contribute to the overall signal structure.

The ethane BF-QEPAS calibration (Figure 2.13(b)) yields a sensitivity of 25.16 ± 0.12 mV/%, representing a reduction of approximately 46% compared to conventional QEPAS. The correlation coefficient remains high ($R^2 > 0.999$) when using peak signal amplitudes for calibration, confirming that quantitative ethane detection is achievable despite the complex signal structure.

The BF-QEPAS system showed higher noise levels of 0.16 mV with a 5.097 ms integration time, resulting in MDLs of 5 ppm for methane and 62 ppm for ethane.

While these detection limits represent degradation factors of approximately threefold for both gases compared to conventional QEPAS, the twentyfold reduction in integration time more than compensates for this sensitivity loss in applications requiring rapid measurements.

The extraction of QTF resonance parameters from BF-QEPAS signals represents one of the most significant advantages of the beat-frequency approach, enabling real-time system characterization and measurement validation.

For methane detection, the well-resolved absorption features produce clean beat signals that can be accurately modeled using the single-exponential decay function described by Equation 2.4. Figure 2.14 illustrates representative fitting results for methane BF-QEPAS signals for a 1% CH₄:N₂ mixture, demonstrating excellent agreement between experimental data and fitted curves, with correlation coefficients typically exceeding 0.98.

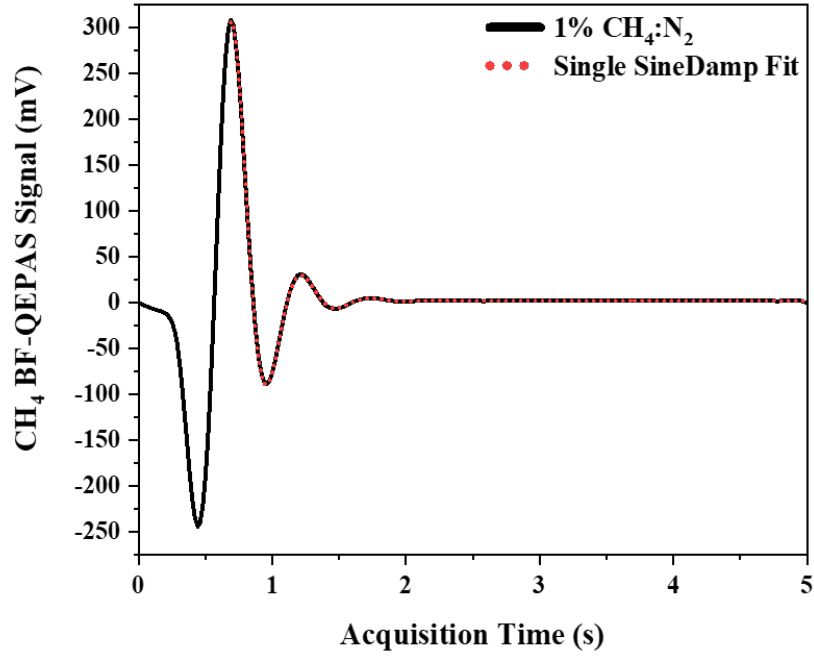


Figure 2.14. BF-QEPAS signal for a 1% $\text{CH}_4:\text{N}_2$ mixture. The red dotted line represents the best single damped-sine fit.

Using the fitting function employed in Figure 2.14, the extracted QTF resonance frequencies and quality factors are presented in Figure 2.15 as functions of methane concentration.

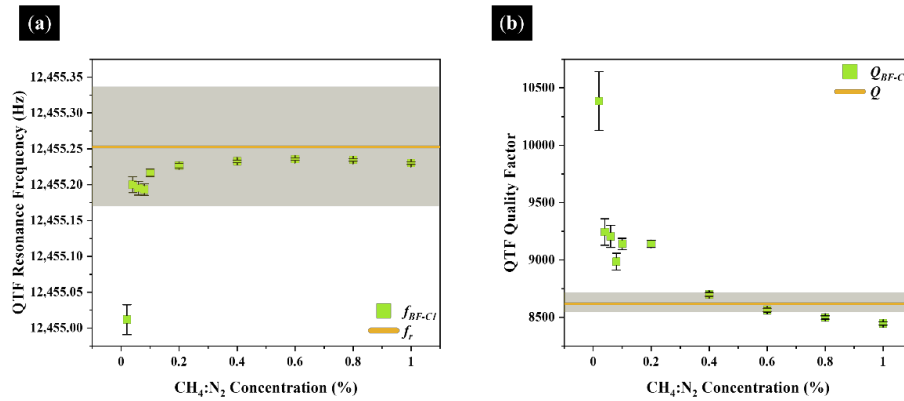


Figure 2.15. Retrieved QTF resonance frequencies and quality factors from the analysis of methane BF-QEPAS signals at different $\text{CH}_4:\text{N}_2$ concentrations.

The extracted resonance frequencies show excellent agreement with independently measured values, with average relative errors of approximately 4.42 ppm across the entire concentration range. The extracted quality factors show similar accuracy, with average relative errors of 4.8% and good stability at higher concentrations where the signal-to-noise ratio is optimal.

The accuracy of parameter extraction improves systematically with increasing methane concentration due to the enhanced SNR, which facilitates more precise fitting. At concentrations above 0.4%, the extracted parameters stabilize within $\pm 1\%$ of the reference values, demonstrating the reliability of the BF-QEPAS approach for parameter monitoring in practical sensing applications.

The analysis of ethane BF-QEPAS signals presents significantly greater challenges due to the complex absorption structure that creates composite beat signals. Figure 2.13(a) shows representative ethane BF-QEPAS signals at different concentrations, revealing the irregular oscillation patterns that arise from multiple overlapping absorption features.

Attempts to fit the ethane signals using single-exponential decay models yield poor correlation coefficients ($R^2 \approx 0.94$ for high-concentration signals), indicating that the simple decay model cannot adequately describe the composite beat-signal structure. The complex absorption spectrum results in the overlap of multiple damped sinewaves corresponding to different spectral features, producing patterns that complicate parameter extraction.

Improved fitting can be achieved using multi-component decay models according to Equation 2.7, as demonstrated in Figure 2.16.

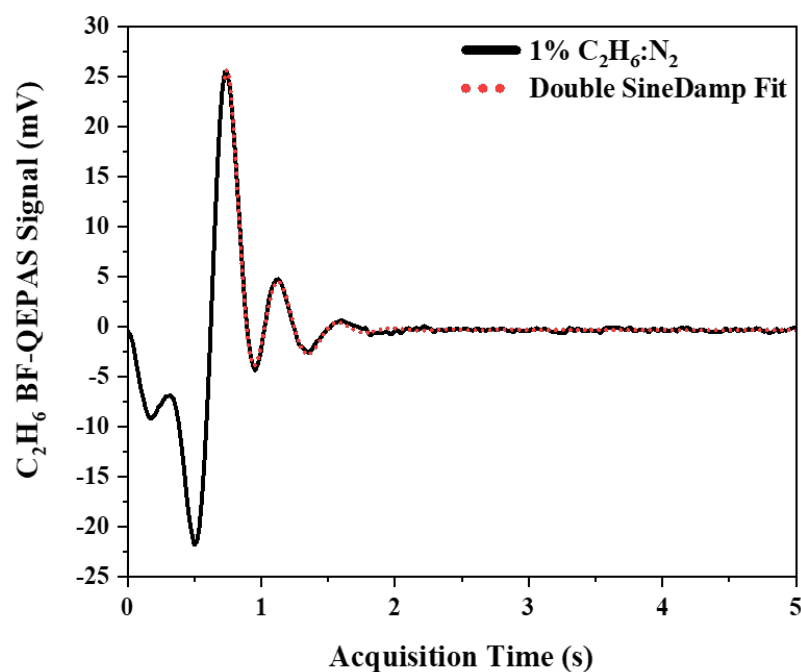


Figure 2.16. BF-QEPAS signal for a 1% $C_2H_6:N_2$ mixture. The red dotted line represents the best double damped-sine fit.

The two-component model provides significantly better correlation coefficients ($R^2 > 0.99$) for high-concentration ethane signals, enabling the extraction of parameters associated with the dominant absorption features.

The extracted parameters from ethane signals show much greater variability and poorer agreement with reference values, as illustrated in Figure 2.17.

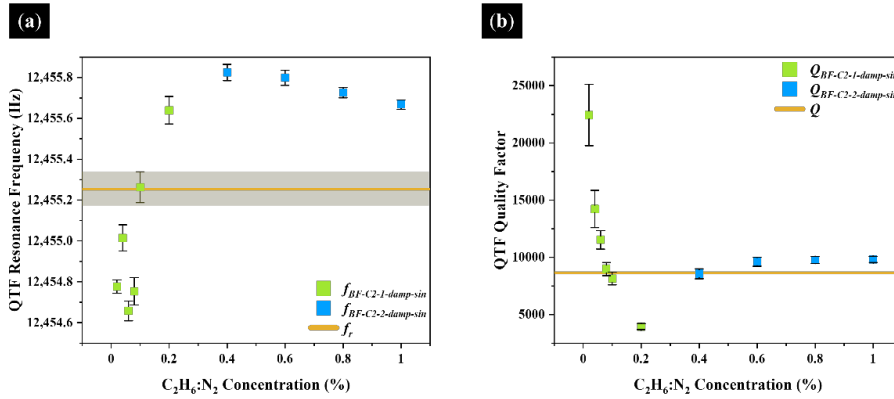


Figure 2.17. Retrieved QTF resonance frequencies and quality factors from the analysis of ethane BF-QEPAS signals at different $C_2H_6:N_2$ concentrations.

The high scatter in both frequency and quality factor determinations confirms that ethane BF-QEPAS signals are not suitable for reliable QTF parameter extraction under typical experimental conditions.

Therefore, the comparison between the results in Figure 2.15 and Figure 2.17 indicates that only the analysis of the C1 BF-QEPAS signal can reliably retrieve both f_0 and Q . Since both hydrocarbons are typically present in the mixture [270], [277], the methane signal can be analyzed to determine both the resonance frequency and the quality factor, thereby validating the measurement, while the BF signals of C1 and C2 provide the corresponding gas concentrations. However, applying multi-component damped-sine models within BF-QEPAS signal analysis could enable the effective treatment of multi-peak analytes such as ethane.

The sequential detection capabilities of the BF-QEPAS system represent one of its most practical advantages for multi-gas sensing applications. The measurement protocol employs a double-staircase ramp configuration that allocates dedicated time intervals for analyzing each gas while maintaining rapid overall measurement times, as illustrated in the inset of Figure 2.6.

Figure 2.18 presents comparative results for sequential detection of methane and ethane using both conventional QEPAS and BF-QEPAS approaches.

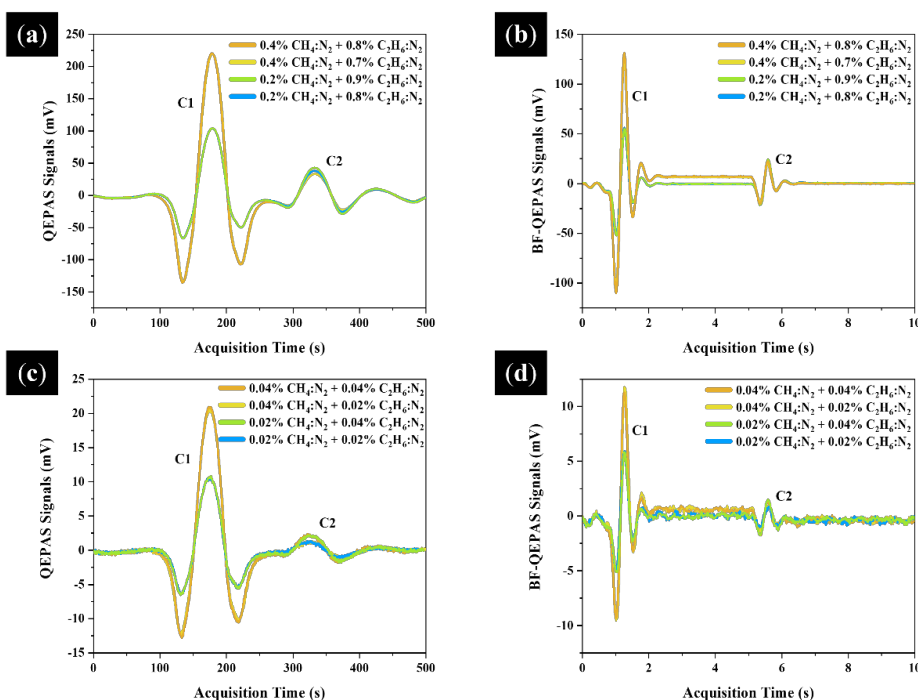


Figure 2.18. Sequential detection of methane and ethane. (a) QEPAS configuration for $\text{CH}_4:\text{N}_2$ concentrations above 0.1% and $\text{C}_2\text{H}_6:\text{N}_2$ concentrations near this value. (b) BF-QEPAS configuration under the same conditions. (c) QEPAS configuration for both $\text{CH}_4:\text{N}_2$ and $\text{C}_2\text{H}_6:\text{N}_2$ concentrations below 0.05%. (d) BF-QEPAS configuration under the same low-concentration conditions.

Eight representative gas mixtures with varying concentrations of both species are analyzed to demonstrate the quantitative accuracy and measurement precision achievable with each technique.

The conventional QEPAS measurements require approximately 500 s to complete the dual-gas analysis, with slow wavelength scanning necessary to achieve steady-state conditions at each spectral position. Despite the extended measurement time, the technique provides excellent quantitative accuracy with average relative errors of approximately 2.3% for concentration measurements.

The BF-QEPAS approach completes the same dual-gas analysis in ≈ 10 s, representing a 50-fold improvement in measurement speed. The quantitative accuracy yielded average relative errors of 3.2% for high-concentration measurements (Figure 2.18(b)) and 5.7% for samples approaching the detection limits (Figure 2.18(d)). The slightly

reduced accuracy compared to conventional QEPAS is attributed to the shorter signal integration times and the lower MDL achieved in BF-QEPAS.

The comprehensive comparison between conventional QEPAS and BF-QEPAS for methane and ethane detection reveals complementary strengths and limitations that suggest optimal application domains for each technique. Table 2.1 summarizes the key performance metrics obtained from the reported experimental study.

Table 2.1. Summary of key performance metrics obtained from the comparative study of QEPAS and BF-QEPAS techniques.

Parameter	QEPAS (CH₄)	QEPAS (C₂H₆)	BF-QEPAS (CH₄)	BF-QEPAS (C₂H₆)
Sensitivity (mV/%)	549.89 ± 1.56	46.85 ± 0.22	308.38 ± 1	25.16 ± 0.12
MDL (ppm, 1 σ)	1.7	20	5	62
Integration time (ms)	100	100	5.097	5.097
Linearity (R ²)	> 0.9999	> 0.999	> 0.999	> 0.999
Measurement time (s)	≈ 200	≈ 200	< 5	< 5
Parameter extraction	No	No	Yes	Limited

Conventional QEPAS provides superior sensitivity and detection limits for both target gases, making it the preferred choice for applications requiring ultimate analytical performance or trace-level detection capabilities. The technique is also simpler to implement and analyze, requiring only standard lock-in amplification and basic signal-processing procedures.

BF-QEPAS offers dramatically improved measurement speed with acceptable sensitivity for many practical applications. The ability to simultaneously extract QTF parameters provides valuable system validation and compensation capabilities that enhance measurement reliability in challenging environments.

The two techniques can be considered complementary, and alternating between QEPAS and BF-QEPAS measurements could provide *quasi*-real-time system validation.

The gas-specific performance trends reveal important practical considerations for multi-gas sensing implementation. C1 detection is straightforward with both techniques due to the favorable spectroscopic properties of its target absorption lines. Conversely, C2 detection is more challenging for both approaches but remains quantitatively accurate, although parameter extraction is not reliable with BF-QEPAS due to its complex absorption structure.

The reported study represents the first attempt to detect complex molecules using the BF-QEPAS approach. The high performance achieved and the complex nature of BF-QEPAS signals, particularly for gases with broadband absorption profiles, motivate the application of advanced signal-processing techniques designed to extract maximum information from the acquired waveforms.

Wavelet-based analysis techniques have shown promise for decomposing complex signals into constituent components [278]. The time-frequency localization properties of wavelets make them particularly suitable for analyzing signals with time-varying frequency content, as occurs in BF-QEPAS measurements during wavelength scanning.

Machine-learning approaches, including neural networks and support vector machines, can potentially identify specific gas species based on characteristic beat-signal signatures, even in the presence of spectral interference or complex absorption structures. However, such approaches require extensive training datasets and may lack the transparency needed for quantitative analytical applications [279].

Several future developments of the BF-QEPAS sensor have been identified based on the experimental results and analysis presented in this chapter. These developments address both fundamental limitations of the current approach and practical considerations for field deployment.

Advanced spectrophone designs optimized specifically for detecting acoustic pulses represent a promising direction for further development. The integration of multiple

spectrophones with different resonance frequencies could enable simultaneous multi-frequency measurements with enhanced information content.

The demonstrated methane/ethane BF-QEPAS sensor represents a significant advance toward practical multi-gas sensing systems capable of addressing the demanding requirements of industrial, environmental, and scientific applications. The technique's combination of rapid measurement capabilities, real-time parameter extraction, and quantitative accuracy provides a compelling foundation for next-generation optical gas sensing platforms. While challenges remain in optimizing performance for gases with complex absorption structures, the fundamental principles demonstrated in this work provide clear pathways for addressing these limitations through continued technological development and innovation.

CHAPTER 3

3. Mid-IR Fiber Combiner System for Optical Sensing

The design of beam delivery systems in optical gas sensors represents a crucial step toward achieving robust and stable detection. For this reason, the integration of optical fibers constitutes a fundamental advance in trace gas sensing, enabling efficient delivery of laser radiation to the sensing region while maintaining the exceptional beam quality required for high-sensitivity spectroscopic measurements [280]. This chapter explores the implementation of mid-IR fiber-based beam delivery systems, with particular emphasis on the development of novel fiber combiner architectures that enable multi-gas detection capabilities. The convergence of advanced waveguide theory, specialized mid-IR transparent materials, and innovative coupling strategies has created new paradigms for optical gas sensing that overcome many limitations of free-space optical systems, while also introducing unique challenges that must be carefully addressed through systematic design approaches [281].

The transition from free-space to guided-wave optical systems in gas sensing applications is motivated by several compelling advantages. Optical fibers provide mechanical flexibility that enables remote sensing configurations, eliminating the need for precise optical alignment—especially in harsh environments—and enabling deployment in otherwise inaccessible locations [282]. The inherent mechanical stability of fiber-coupled systems reduces noise associated with mechanical vibrations that plague free-space optical paths. Furthermore, the development of specialized mid-IR transmitting fibers has extended these advantages into the molecular fingerprint

region, where fundamental vibrational transitions provide absorption strengths orders of magnitude greater than the overtone and combination bands accessible in the near-IR [283].

However, the implementation of fiber-based beam-delivery systems in the mid-IR presents unique challenges that distinguish it from well-established telecommunications fibers operating at shorter wavelengths. The limited transparency of conventional silica fibers beyond 2.5 μm necessitates the use of alternative materials such as fluoride glasses, chalcogenides, and crystalline compounds, each presenting distinct trade-offs in terms of transmission window, mechanical properties, and environmental stability [284]. Moreover, coupling mid-IR laser sources requires careful consideration of mode matching, numerical-aperture compatibility, and Fresnel reflection losses, which become increasingly significant due to the high refractive index characteristic of mid-IR transmitting materials [285].

This chapter addresses these challenges through an examination of optical waveguide principles as applied to gas sensing, followed by the detailed implementation and characterization of a dual-gas sensing system based on a novel indium fluoride glass (IFG) fiber combiner.

3.1. Optical Waveguides for Beam Delivery in Gas Sensing

The theoretical foundation of optical waveguides for gas sensing applications rests upon the electromagnetic theory of guided-wave propagation, which defines the fundamental limits and opportunities for beam delivery in spectroscopic systems [258].

The extension of fiber optics to the mid-IR spectral region introduces several fundamental considerations that significantly impact beam delivery for gas sensing applications. Material absorption becomes the dominant loss mechanism, as multiphonon absorption edges associated with lattice vibrations in glass networks typically limit transmission at longer wavelengths [286]. For silica-based fibers, the fundamental Si–O vibrational modes create strong absorption beyond approximately 2.5 μm , necessitating alternative glass compositions for mid-IR applications. This constraint of well-established silica fibers has driven the development of fluoride,

chalcogenide, and other glass systems, each offering distinct transmission windows and mechanical characteristics [287].

Fluoride glass fibers, particularly those based on the ZBLAN ($\text{ZrF}_4\text{--BaF}_2\text{--LaF}_3\text{--AlF}_3\text{--NaF}$) composition, have emerged as a practical solution for extending fiber transmission to approximately $4.5\text{ }\mu\text{m}$ [288]. The lower phonon energies associated with the heavier fluoride ions compared to oxygen in silica shift the multiphonon absorption edge, creating a transmission window—illustrated in Figure 1.16—that encompasses important molecular absorption features of gases such as CO_2 ($\approx 4.26\text{ }\mu\text{m}$), CO ($\approx 4.67\text{ }\mu\text{m}$), and various hydrocarbons, as shown in Figure 3.1.

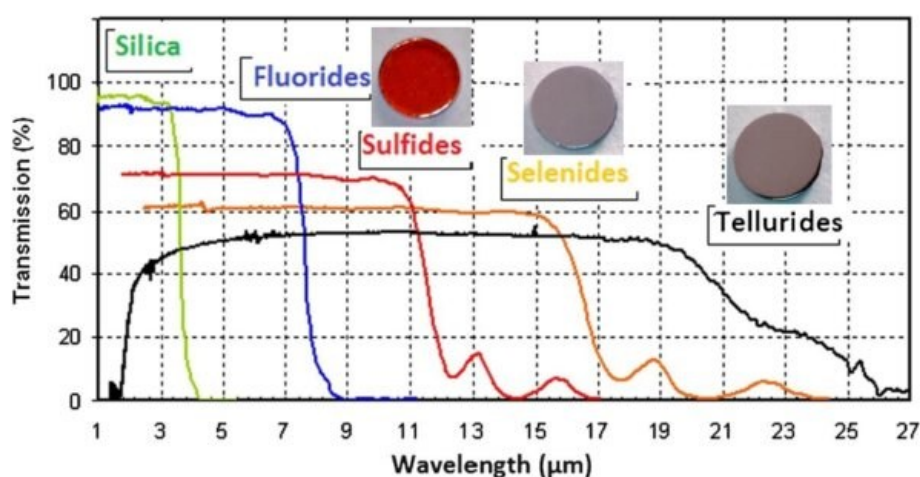


Figure 3.1. Transmission windows of silica, fluoride, and chalcogenide glasses [289].

However, fluoride glasses present unique challenges, including hygroscopic behavior, lower mechanical strength compared to silica, and susceptibility to crystallization during fiber drawing, which must be carefully managed through controlled processing conditions [290].

The development of indium fluoride (InF_3)-based glasses represents a further evolution in mid-IR fiber technology, extending useful transmission to approximately $5.5\text{ }\mu\text{m}$ while maintaining reasonable mechanical properties and environmental stability [291]. The $\text{InF}_3\text{--GaF}_3\text{--ZnF}_2\text{--BaF}_2\text{--SrF}_2\text{--NaF}$ glass system, optimized for fiber drawing and long-term stability, exhibits minimum optical losses below 0.1 dB/m in the $2\text{--}5\text{ }\mu\text{m}$ range when processed under controlled-atmosphere conditions to

minimize hydroxyl-ion contamination [292]. These properties make InF_3 fibers particularly suitable for accessing the strong NO absorption features near $5.26\ \mu\text{m}$, as well as other important atmospheric and industrial gases in the extended mid-IR region [293].

For applications requiring transmission beyond the limits of fluoride glasses, chalcogenide compositions based on sulfur, selenium, and tellurium provide transparency extending to $10\text{--}12\ \mu\text{m}$ or beyond [294]. The covalent bonding in these glasses results in lower phonon energies compared to ionic fluoride glasses, though at the expense of increased refractive indices (typically 2–3) that complicate coupling and create significant Fresnel reflection losses at interfaces. Chalcogenide fibers exhibit strong non-linear optical effects that enable wavelength conversion but can also lead to unwanted spectral broadening at high power levels [295].

The modal characteristics of mid-IR fibers differ from their visible and near-IR counterparts due to both wavelength scaling effects and the properties of mid-IR transmitting materials. The mode-field diameter (MFD) of the fundamental mode scales approximately linearly with wavelength for a given V -parameter, resulting in larger mode areas that can ease coupling tolerances but may also increase bend sensitivity, as shown in Figure 3.2.

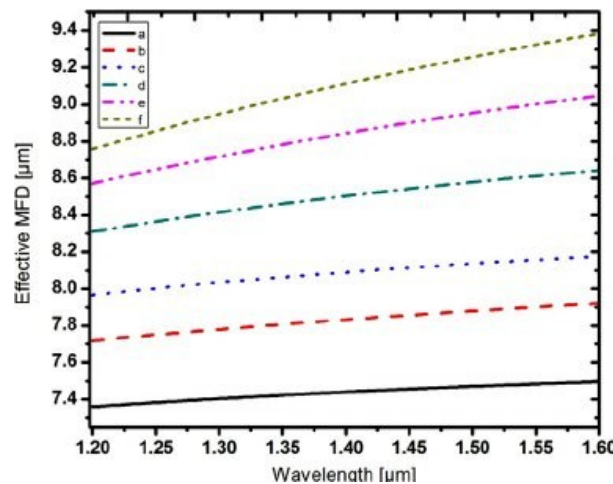


Figure 3.2. Mode-field diameter versus wavelength for varying numbers of claddings [296].

Figure 3.2 shows that the MFD increases with wavelength, indicating that the optical fiber can operate over a wider range of normalized frequencies while maintaining single-mode behavior [296].

For single-mode operation at mid-IR wavelengths, core diameters typically range from 10–20 μm for fluoride fibers to 50–200 μm for chalcogenide fibers, depending on the specific index contrast and operating wavelength [297].

The development of hollow-core fibers (HCFs) represents a paradigm shift in beam delivery for gas sensing, as these structures guide light primarily through air rather than solid glass, thereby circumventing material absorption limitations and enabling low-loss transmission across broad spectral regions [298]. Photonic bandgap fibers achieve guidance through periodic microstructure that creates forbidden frequency bands for transverse propagation, while anti-resonant fibers rely on coherent reflection from thin glass membranes surrounding a hollow core. For gas sensing applications, hollow-core fibers offer the additional advantage of allowing gas to fill the core region, creating distributed interaction lengths that can enhance sensitivity compared to single-pass cells [299].

The high refractive indices of many mid-IR transmitting materials create substantial Fresnel reflection losses at fiber interfaces. For a fiber with refractive index n in air ($n_{\text{air}} = 1$), the power reflection coefficient at normal incidence is:

$$R = \left(\frac{n-1}{n+1} \right)^2. \quad (3.1)$$

Equation 3.1. Power reflection coefficient at normal incidence.

For chalcogenide fibers with $n \approx 2.4$, this results in approximately 17% power loss per interface without anti-reflection coatings, compared to only 3.5% for silica fibers ($n \approx 1.46$ at 1.55 μm). This consideration becomes particularly important in fiber-coupled gas-sensing systems, where multiple interfaces may be present, necessitating the development of broadband anti-reflection coatings optimized for mid-IR wavelengths [300].

Beyond simple point-to-point beam delivery, the development of fiber combiners and splitters enables more sophisticated sensing architectures. The evanescent-field coupling between adjacent fiber cores provides the basis for constructing wavelength-

flattened power combiners using the fused biconical taper (FBT) technique [301], [302].

A fused coupler consists of two parallel optical fibers that are twisted, stretched, and fused together so that their cores are brought into close proximity, as shown in Figure 3.3.

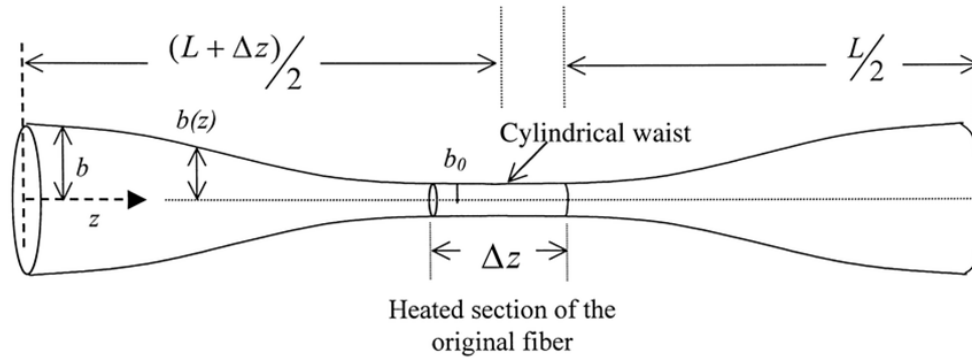


Figure 3.3. Schematic of an exponential taper profile formed by heating a fiber of radius b over a fixed length z and pulling it through a distance L [303].

This configuration forms the coupling region, whose length determines the power transfer ratio between the two fibers. During fabrication, light is launched into one input port while the output powers are continuously monitored. Once the desired coupling ratio is achieved, the automated pulling process is stopped. The resulting device is a single fused structure containing two closely spaced cores, produced through the FBT process.

While single-mode fibers provide optimal beam quality for spectroscopic applications, their small core sizes and strict numerical aperture requirements can limit coupling efficiency from divergent mid-IR sources. Multimode fibers with core diameters of 100–400 μm can achieve higher coupling efficiencies but suffer from modal dispersion and speckle effects that may impact measurement stability. The use of few-mode fibers or mode-filtering techniques represents a compromise approach that maintains reasonable coupling efficiency while preserving adequate beam quality for sensing applications [304].

Recent advances in fiber-based beam shaping have introduced new possibilities for optimizing light delivery in gas sensors. Tapered fibers can provide mode size

conversion between different fiber types or create expanded beam waists for improved coupling to gas cells, as shown in Figure 3.4.

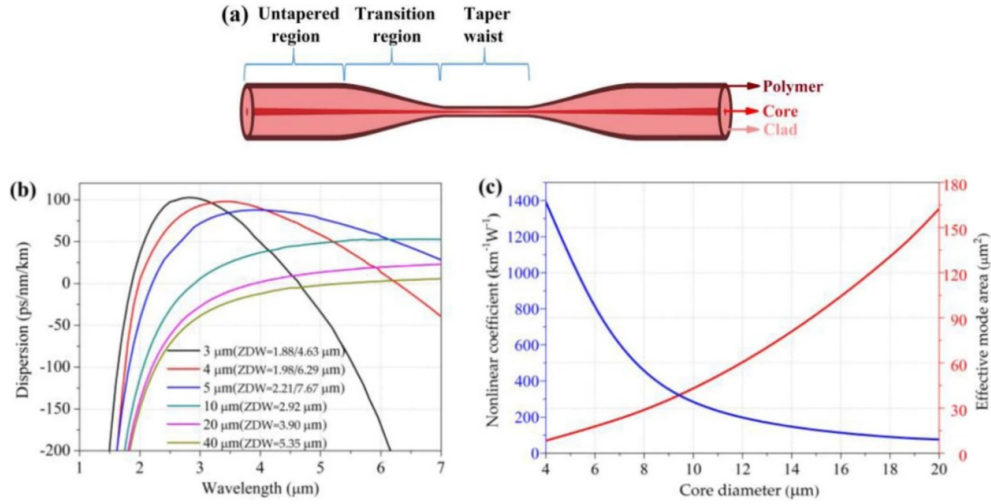


Figure 3.4. (a) Schematic of a typical chalcogenide tapered fiber (adapted with permission from [305], copyright The Optical Society). (b) Dispersion. (c) Non-linear coefficient, and effective mode area of a chalcogenide fiber with As_2Se_3 core and As_2S_3 cladding as a function of the core diameter [306].

The adiabatic taper condition, which ensures low-loss mode evolution, requires that the taper angle $\Omega(z)$ must satisfy:

$$\Omega(z) \ll \frac{\lambda}{(2 \cdot \pi \cdot n \cdot r)}, \quad (3.2)$$

Equation 3.2. Adiabatic taper condition.

where r is the local fiber radius. For better visualization and understanding, Figure 3.5 shows how the taper angle is defined.

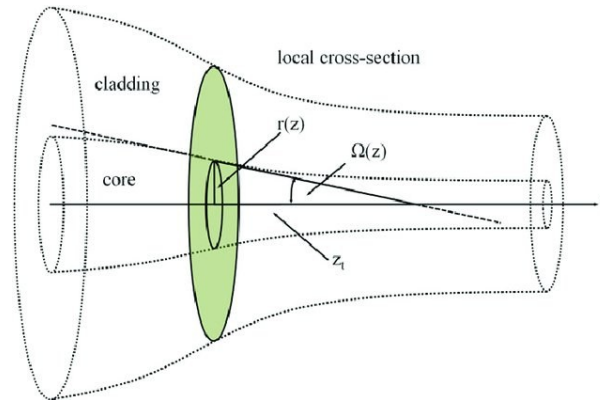


Figure 3.5. Schematic of a fiber taper, showing the local taper angle $\Omega(z)$ [307].

This condition becomes increasingly stringent at longer wavelengths, requiring longer taper lengths for mid-IR applications. Conversely, the larger mode sizes at mid-IR wavelengths can facilitate certain applications such as evanescent wave sensing, where the penetration depth of the evanescent field scales with wavelength [308].

The integration of multiple laser sources through fiber combiners enables simultaneous multi-gas detection, significantly enhancing the analytical capabilities of optical sensors [309], [310]. The theoretical basis for fiber combining relies on the orthogonality of modes in the output fiber, with power coupling coefficients determined by the overlap integrals between input and output modes. For wavelength-independent combining, the coupling ratio depends primarily on the geometric configuration of the fused region rather than material dispersion, enabling broadband operation suitable for multi-wavelength sensing systems [311].

The integration of optical fibers with QEPAS introduces unique considerations for beam delivery system design. The small gap between QTF prongs requires precise mode control to avoid clipping while maximizing the optical power delivered to the gas sample [312]. Fiber-coupled systems provide inherent beam quality and pointing stability that is particularly advantageous for QEPAS, where mechanical vibrations can couple into the acoustic signal. Near-IR fiber-coupled QEPAS sensors for sequential detection of CH_4 and C_2H_6 in air [276], as well as systems for exhaled ammonia (NH_3) monitoring employing an erbium-doped fiber amplifier [313], together with configurations embedding an optical system within a sealed metallic cylinder containing an aspheric micro-lens to couple a single-mode interband cascade laser to

an indium fluoride glass fiber [280], represent just a few examples of the technological developments that have paved the way for the present work.

3.2. Mid-IR NO/CO₂ QEPAS Sensor

The practical implementation of the principles discussed in the previous section is demonstrated through the development of a dual-gas QEPAS sensor for simultaneous detection of carbon dioxide and nitric oxide, obtained through a single beam delivery system with alternating laser sources, using a novel IFG fiber-combiner. This system represents a significant advance in fiber-integrated gas sensing technology, combining the exceptional sensitivity of QEPAS with the flexibility and stability advantages of all-fiber beam delivery and the coupling of multiple sources in the mid-IR spectral region [314]. The selection of CO₂ and NO as target gases is motivated by their critical importance in environmental monitoring, industrial process control, and biomedical diagnostics, where simultaneous detection can provide valuable insights into combustion efficiency, atmospheric chemistry, and metabolic processes [315].

Figure 3.6 illustrates the experimental configuration of the dual-gas QEPAS sensor.

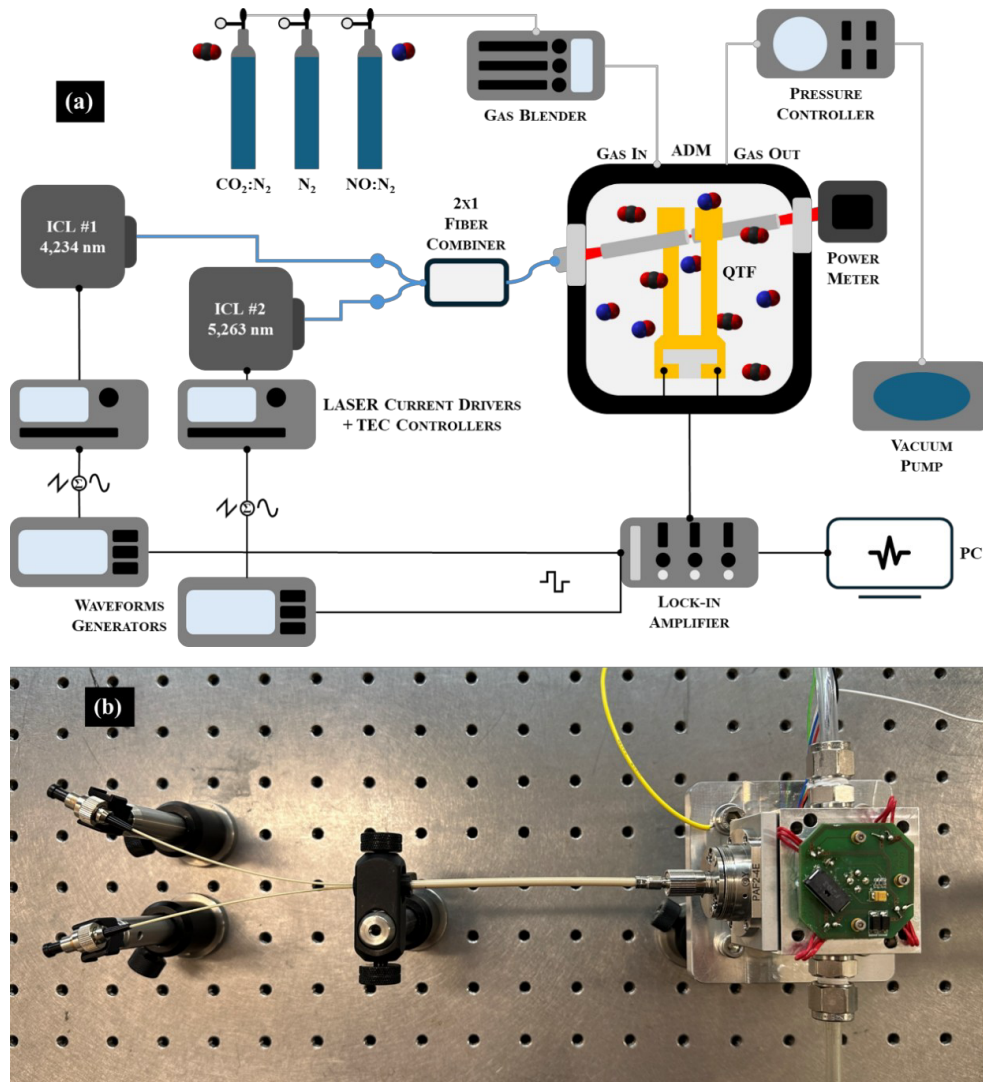


Figure 3.6. (a) Schematic of the experimental setup. ICL, interband cascade laser; TEC, thermoelectric cooler; ADM, acoustic detection module; QTF, quartz tuning fork; PC, personal computer. (b) Photograph of the custom-made 2-input-1-output fiber-combiner (center-left) coupled with the ADM through its input fiber port (right) [314].

As shown in Figure 3.6(a), the sensor architecture employs two interband cascade lasers (ICLs). ICL #1, emitting at a central wavelength of 4.234 μm , accesses the ν_3 asymmetric stretching mode of CO₂ at 2361.46 cm^{-1} ($3.54 \times 10^{-18}\text{ cm/molecule}$), while ICL #2, emitting at a central wavelength of 5.263 μm , targets the fundamental R-branch transition of NO at 1900.08 cm^{-1} ($2.32 \times 10^{-20}\text{ cm/molecule}$) [316]. The choice of ICLs for this application leverages their unique advantages for mid-IR gas sensing, including room-temperature continuous-wave operation, narrow linewidth emission

suitable for high-resolution spectroscopy, and wall-plug efficiencies exceeding 15% that enable battery-powered portable systems [317]. The photograph in Figure 3.6(b) shows the actual implementation of the fiber combiner connected to the acoustic detection module through its fiber port, demonstrating the compact nature of the all-fiber beam delivery system.

The development of the IFG fiber combiner represents a crucial enabling technology for this multi-gas sensing system. The fabrication process, adapted from established techniques for silica fiber devices but modified to accommodate the unique properties of fluoride glasses, begins with the preparation of custom IFG optical fibers with a core diameter of 25 μm and an outer (cladding) diameter of 100 μm . Figure 3.7 presents the measured attenuation spectrum of these fibers, fabricated by Le Verre Fluoré (Bruz, France), demonstrating excellent transmission characteristics throughout the 2–5 μm spectral range.

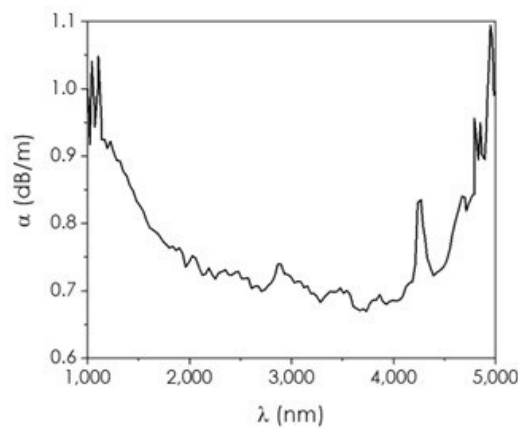


Figure 3.7. Measured attenuation α , expressed in dB/m, of the IFG optical fibers employed for the combiner fabrication [314].

As evident from the attenuation curve, the fibers exhibit losses below 0.5 dB/m across most of the transmission window, with a gradual increase toward longer wavelengths due to the approaching multiphonon absorption edge. At the specific operating wavelengths of 4.234 μm and 5.263 μm , the attenuation is approximately 0.3 dB/m and 0.8 dB/m, respectively. The slightly higher attenuation at 5.263 μm reflects the fundamental limit imposed by the InF_3 -based glass system but remains sufficiently low

for practical sensor implementation, especially considering the relatively short fiber lengths ($\ll 1$ m) employed in the sensing system [318].

The fiber combiner fabrication employs a carefully controlled fused biconical taper technique using a modified glass processing station. The process, illustrated schematically in Figure 3.8, consists of three main steps.

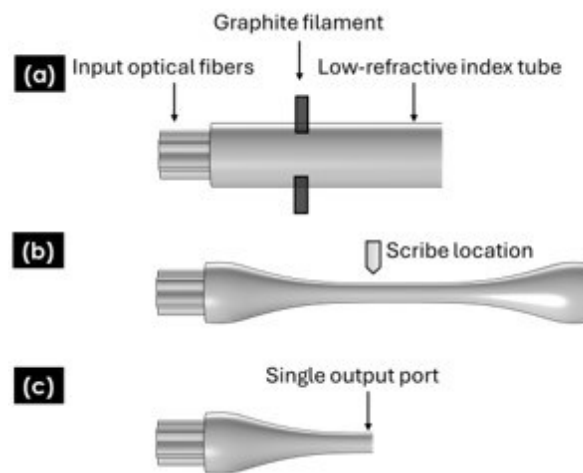


Figure 3.8. Sketch of the optical fiber combiner fabrication. (a) Optical fibers inserted into a low-refractive-index tube. (b) A fused biconical taper obtained via stretching and heating. (c) Cleaving of the fused biconical taper in the waist region [314].

As shown in Figure 3.8(a), two IFG fiber segments are first inserted into a custom low-refractive-index fluoride glass tube with outer diameter of 550 μm , creating a confined geometry that facilitates controlled mode coupling during the tapering process. Figure 3.8(b) depicts the stretching and heating phase, where the fiber assembly undergoes controlled elongation while being heated, resulting in a fused biconical taper structure. Finally, as indicated in Figure 3.8(c), the taper is cleaved at the waist region to create the 2 $\times$ 1 combiner configuration with a single output port.

The critical challenge in processing fluoride glasses lies in their propensity for crystallization when heated above the glass transition temperature ($T_g \approx 275$ $^{\circ}\text{C}$), which would create severe scattering losses. To address this issue, the heating profile is precisely controlled using a graphite filament at an initial power of 12.1 W, with argon at a flow rate of 0.35 L/min to prevent atmospheric moisture ingress and suppress crystallization [319].

Figure 3.9 shows a microscope image captured during the actual fabrication process, revealing the tube containing the IFG optical fibers undergoing the drawing procedure.

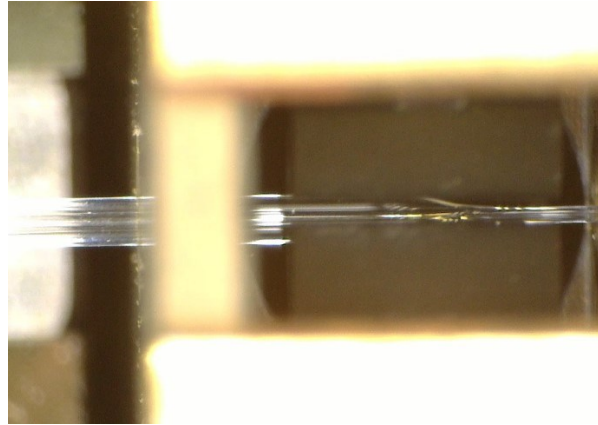


Figure 3.9. Drawing of the tube containing the IFG optical fibers [314].

The image clearly demonstrates the diameter reduction from the non-tapered region on the left to the drawn section on the right, illustrating the gradual transition that ensures adiabatic mode evolution. During the tapering process, the fiber assembly is drawn while simultaneously heating the central region, with the pulling speed and feeding rate optimized to achieve a waist diameter of approximately 140 μm while maintaining the structural integrity of both fiber cores within the supporting tube. The final device, with a total length of 23 cm including FC/APC connectors, exhibits insertion loss values of 1.1 dB at 4.234 μm and 2.2 dB at 5.263 μm , demonstrating excellent performance for mid-IR applications [320].

The integration of the fiber combiner with the QEPAS detection system requires careful consideration of beam delivery into the acoustic detection module. The commercial ADM employed in this work incorporates a T-shaped quartz tuning fork with prong dimensions optimized for operation at 12.44 kHz, providing a quality factor exceeding 15,000 at 300 Torr. The QTF is acoustically coupled to a pair of metallic resonator tubes with an inner diameter of 1.6 mm and length of 12.4 mm each, designed to create organ-pipe acoustic resonances that enhance the photoacoustic signal by concentrating sound waves at the QTF [172].

The critical alignment between the focused laser beam and the QTF-resonator assembly is achieved using a fiber-coupled aspheric lens system (Thorlabs GmbH,

PAF2-4E), with a focal length of 4 mm and an anti-reflection coating optimized for the 2–5 μm range, mounted on the inlet window of the ADM. This configuration focuses the combined beam from the fiber combiner to a waist of approximately 120 μm positioned at the center of the gap between the QTF prongs, ensuring efficient acoustic generation while avoiding clipping and spurious reflections from the resonator tubes.

The spectroscopic performance of the dual-gas sensor is characterized through systematic calibration measurements using certified gas mixtures. For CO_2 detection, the ICL #1 injection current is modulated with a 15.5 mVpp sinusoidal waveform at half the QTF resonance frequency ($f_{\text{MOD}} = 6.22 \text{ kHz}$), creating wavelength modulation that generates the $2f$ photoacoustic signal. A slow sawtooth scan (50 mVpp, 5 mHz) is superimposed, enabling acquisition of full absorption profiles for spectroscopic analysis. The operating temperature of 10 $^\circ\text{C}$ provides optimal mode stability and an output power of 0.17 mW after fiber coupling [321].

Similar operating parameters are used for NO detection using ICL #2, with a modulation amplitude of 8 mVpp and a scan amplitude of 60 mVpp at 20 $^\circ\text{C}$. The lower output power of 0.08 mW after fiber coupling reflects the increased coupling losses associated with the larger beam divergence and the higher fiber attenuation.

Figure 3.10 presents representative $2f$ -QEPAS spectra obtained at different concentrations of the target gases.

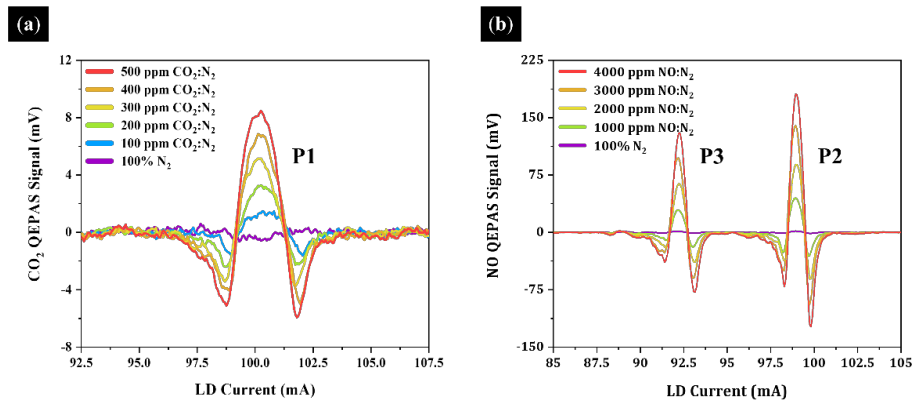


Figure 3.10. Representative $2f$ -QEPAS spectra for (a) CO_2 concentrations from 100 to 500 ppm and (b) NO concentrations from 1000 to 4000 ppm. In both cases, the spectra measured for pure N_2 are also shown [314].

The CO₂ spectra shown in Figure 3.10(a) were acquired for concentrations ranging from 100 to 500 ppm in a nitrogen matrix, with the baseline spectrum for pure N₂ included for reference. The signal resembles the characteristic second-derivative of an absorption peak, with the P1 amplitude increasing linearly with concentration. The NO spectra displayed in Figure 3.10(b), covering concentrations from 1000 to 4000 ppm, reveal the presence of two absorption features labeled P2 and P3, corresponding to transitions at 1900.08 cm⁻¹ and 1900.52 cm⁻¹, respectively. The tuning range of ICL #2 is sufficient to capture both features, though the P2 transition is selected for quantitative analysis due to its stronger absorption coefficient.

The lock-in amplifier, configured with an integration time constant of 0.1 s and 24 dB/octave filter roll-off, demodulates the QTF signal at the resonance frequency to extract the $2f$ component proportional to gas concentration. No interference fringes are observed in the recorded spectra, confirming that the fiber-coupled beam successfully traverses the QTF-resonator assembly without spurious reflections that could compromise measurement stability. This absence of optical interference validates both the quality of the fiber combiner and the effectiveness of the anti-reflection-coated fiber port in minimizing back-reflections [322].

Calibration curves constructed from dilution series measurements, shown in Figure 3.11, demonstrate excellent linearity over the investigated concentration ranges.

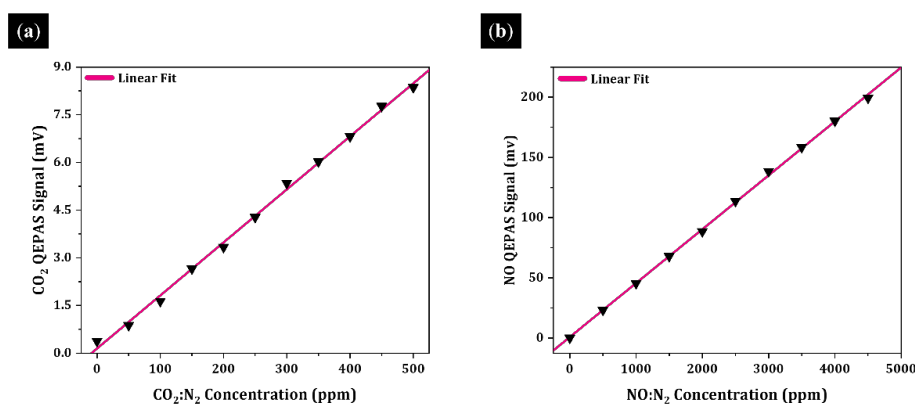


Figure 3.11. QEPAS signal peak values as a function of target gas concentration (black triangles) and corresponding linear fits (red solid lines) for (a) CO₂ and (b) NO [314].

For CO₂, measurements spanning 100–500 ppm yield a linear correlation coefficient $R^2 = 0.998$, with sensitivity of 16.7 $\mu\text{V/ppm}$ and noise level of 171 μV , resulting in an

MDL of 31 ppm at 0.1 s integration time and in an NNEA of $4.39 \times 10^{-7} \text{ W cm}^{-1} \text{ Hz}^{-1/2}$. The NO calibration, covering 1000–4000 ppm, achieves $R^2 = 0.9994$ with a sensitivity of $44.6 \mu\text{V/ppm}$ and a noise level of $186 \mu\text{V}$, corresponding to an MDL of 13 ppm and to an NNEA of $4.65 \times 10^{-9} \text{ W cm}^{-1} \text{ Hz}^{-1/2}$. These detection limits, while modest compared to some free-space QEPAS implementations, represent excellent performance for a fully fiber-integrated system operating with sub-milliwatt optical powers [323].

The absence of spectroscopic interference between the two detection channels is experimentally verified by monitoring the CO_2 signal while introducing varying concentrations of NO into the gas mixture, and vice versa, with the non-target laser tuned off its corresponding absorption line. This spectroscopic selectivity, combined with the inherent selectivity of QEPAS to the target absorption wavelength, enables reliable multi-gas detection without the need for gas separation or complex chemometric analysis [179].

The long-term stability of the fiber-coupled sensor is evaluated through Allan–Werle deviation analysis, which reveals the optimal integration time and identifies the dominant noise sources limiting detection performance. The results of this analysis are shown in Figure 3.12.

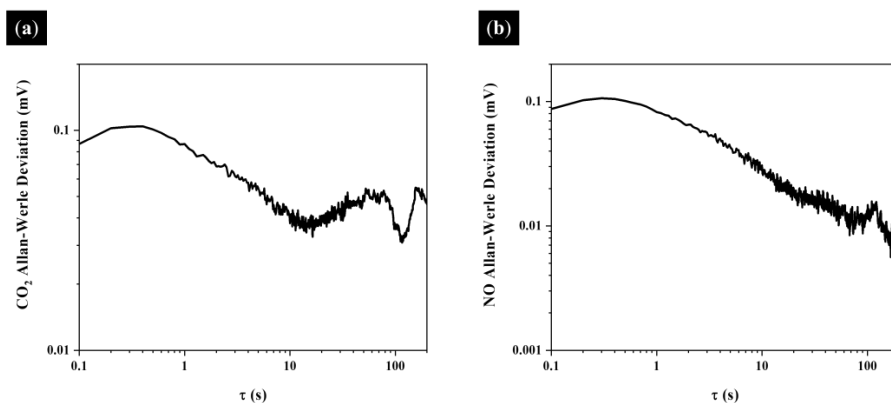


Figure 3.12. Results of the Allan–Werle standard deviation analysis for the detection of (a) CO_2 with ICL #1 and (b) NO with ICL #2 [314].

For short integration times, both detection systems exhibit Allan deviation values that increase slightly up to 0.4 s. As shown in Figure 3.12(a), between 0.4 s and 10 s, the CO_2 and NO responses maintain the expected $\tau^{-1/2}$ scaling, indicating continued white-

noise limitation. However, the CO₂ case shows deviation from ideal behavior beyond 10 s integration time, attributed to mechanical instabilities in the ICL–fiber coupling that introduce pointing variations affecting the coupling efficiency [324].

The optimal integration time of 10 s for both systems yields improved detection limits of 13 ppm for CO₂ and 4 ppm for NO, representing 2.4× and 3.3× improvements, respectively, compared to the 0.1 s integration time. These performance metrics demonstrate that the fiber-coupled system can achieve detection sensitivities suitable for many practical applications, including atmospheric monitoring where CO₂ levels typically exceed 400 ppm and industrial emission monitoring where NO concentrations often range from tens to thousands of ppm [325].

The successful demonstration of this dual-gas QEPAS sensor validates several important design principles for fiber-integrated mid-IR gas sensing systems. First, the low insertion loss achieved by the IFG fiber combiner (1.1–2.2 dB) confirms that efficient wavelength-independent power combining is feasible in fluoride glass systems despite their challenging processing requirements. The symmetric behavior of the combiner, verified by interchanging the input ports, indicates uniform mode coupling in the fused region and suggests that the fabrication process is sufficiently controlled for reproducible device manufacturing [326].

Second, the stability advantages of fiber-coupled beam delivery are clearly demonstrated by the absence of interference fringes and the white noise-limited performance at short integration times. The mechanical isolation provided by the flexible fiber link effectively decouples the laser sources from the acoustic detector, preventing vibration-induced noise that often limits the performance of free-space QEPAS systems. This advantage becomes particularly important for field-deployable sensors subject to mechanical disturbances [327].

The power limitations imposed by fiber coupling losses and the relatively low output powers of current ICLs represent the primary constraint on detection sensitivity. With typical fiber coupling efficiencies of 30–50% for mid-IR lasers and additional losses in the combiner and delivery fiber, the optical power reaching the QTF is reduced by approximately an order of magnitude compared to free-space coupling. Future improvements in ICL output power and fiber coupling techniques, such as the use of

tapered fibers or optimized lens systems, could significantly enhance detection limits while maintaining the advantages of fiber integration [328].

The wavelength scalability of the IFG fiber combiner design is particularly noteworthy, as the device can theoretically operate across the entire 2–5.5 μm transmission window of indium fluoride glass. This capability enables the targeting of numerous molecular species with absorption features within this spectral region. The modular nature of the fiber-coupled architecture and the possibility to increase the number of input ports facilitate rapid reconfiguration for different target gases simply by adding multiple laser sources, without requiring realignment of the detection system [329].

Looking toward practical implementation, the demonstrated sensor architecture is well-suited for integration into industrial process monitoring systems where the fiber-coupled design enables remote placement of sensitive laser sources away from harsh environments. The multiplexing capability inherent in the fiber combiner approach could be extended to three or more laser sources through cascaded combiners, enabling comprehensive multi-gas analysis with a single detector. For atmospheric monitoring applications, the addition of a multipass cell between the fiber output and QTF could enhance sensitivity by increasing the effective absorption path length while maintaining the stability advantages of fiber beam delivery [330].

The development of this dual-gas QEPAS sensor represents a significant step toward practical, field-deployable mid-IR spectroscopic instruments that combine high sensitivity with robust operation. While the current detection limits do not match the ultimate sensitivity achievable with optimized free-space systems, the demonstrated performance is sufficient for many real-world applications where reliability, stability, and ease of deployment are paramount. As mid-IR laser and fiber technologies continue to advance, the fundamental architecture validated in this work provides a platform for next-generation optical gas sensors that can address increasingly demanding analytical challenges in environmental monitoring, industrial process control, and biomedical diagnostics [331].

CHAPTER 4

4. Semi-Integrated QEPAS and LITES Sensing Platforms

The evolution toward miniaturized, integrated optical gas-sensing systems represents a fundamental paradigm shift in trace-gas detection, driven by demand for compact, portable, highly sensitive devices capable of real-time environmental monitoring in challenging conditions [332]. The growing need for distributed sensor networks—monitoring air quality, industrial emissions, and environmental parameters over wide areas—has intensified efforts to develop platforms that combine the sensitivity of optical spectroscopy with the robustness and manufacturability needed for large-scale deployment [233], [333].

Traditional gas sensing approaches, while offering excellent analytical performance in controlled laboratory environments, often suffer from significant limitations when deployed in real-world scenarios. Free-space optical systems, despite superior sensitivity and selectivity, suffer from mechanical instabilities and are susceptible to environmental perturbations that compromise accuracy and long-term reliability [332].

The integration of photonic components with piezoelectric resonators offers unprecedented opportunities to address these fundamental limitations by creating hybrid sensing platforms that leverage the advantages of both optical spectroscopy and mechanical-to-electrical transduction [233]. These semi-integrated architectures are a crucial intermediate step toward fully integrated photonic gas sensors, addressing chip-scale implementation challenges while preserving high-sensitivity optical detection and the exceptional mechanical properties of quartz transducers [334].

Developing semi-integrated platforms is especially compelling because they can exploit multiple detection mechanisms within a single, compact architecture. Implementing QEPAS and/or LITES within a unified platform provides complementary capabilities that enhance reliability, enable cross-validation, and can improve gas identification through multimodal analysis [335]. This capability is a significant advance over single-method detection, allowing researchers to exploit each technique's strengths while mitigating their individual limitations.

For this first semi-integration of QEPAS and LITES, the SiNOI platform was selected for several compelling technical advantages [336]. Si_3N_4 exhibits a broad transparency window from ≈ 400 nm to $8\text{ }\mu\text{m}$, encompassing absorption features of many gases across the visible, near-IR, and mid-IR [337]. This transparency, combined with the material's high refractive index ($n_{\text{SiN}} \approx 2$), enables compact, strongly confining waveguides while remaining compatible with established semiconductor processes.

The properties of Si_3N_4 are well suited to sensing applications requiring long-term stability and environmental robustness. It exhibits excellent thermal stability, with low thermal-expansion coefficients well matched to silicon-oxide substrates, ensuring stable operation over wide temperatures without significant wavelength drift or coupling-efficiency variations [189]. Additionally, silicon nitride is chemically inert and resistant to environmental degradation, making it suitable for deployment in harsh industrial and environmental monitoring applications where sensors may be exposed to corrosive gases or extreme operating conditions [338].

The optical properties of Si_3N_4 enable waveguides with propagation losses as low as 0.1 dB/cm in optimized processes, ensuring efficient power delivery to sensing regions while minimizing background absorption that could interfere with gas-specific signals [198]. The high index contrast between Si_3N_4 ($n_{\text{SiN}} \approx 2$) and typical claddings (air, $n \approx 1$; SiO_2 , $n \approx 1.45$) enables tight confinement and compact device geometries readily integrated with control electronics and packaging [339].

The compatibility of Si_3N_4 with CMOS manufacturing processes represents a crucial advantage for scaling semi-integrated sensing platforms to high-volume production. It can be deposited and patterned using standard techniques—chemical vapor deposition

(CVD), photolithography, and reactive-ion etching—leveraging existing fabrication infrastructure and process optimizations from telecom and computing [340].

The development of semi-integrated sensing architectures addresses several critical challenges that have historically limited the deployment of optical gas sensors in practical applications. The elimination of bulk optical components such as lenses, mirrors, and laser beam splitters not only reduces system complexity and cost but also dramatically improves mechanical stability and reduces sensitivity to environmental perturbations such as vibration, thermal drift, and atmospheric turbulence [216]. The compact footprint unlocked by photonic integration facilitates the development of portable and even wearable sensing devices, opening new application domains in personal exposure monitoring, mobile environmental assessment, and distributed sensor networks [341].

Furthermore, the potential for integrating multiple wavelengths and detection schemes on a single photonic chip creates opportunities for comprehensive multi-gas analysis capabilities that would be impractical to achieve using discrete optical components [342]. This multiplexing capability is particularly valuable for applications requiring simultaneous monitoring of multiple gas species, such as industrial process control, combustion optimization, and comprehensive environmental monitoring programs.

The semi-integrated approach also provides a practical pathway for transitioning from laboratory-based research systems to field-deployable sensing platforms. By remaining compatible with standard fiber-optic coupling and packaging while incorporating integrated photonics, these hybrids bridge the gap between the performance of free-space optics and the robustness required in real-world sensing [343].

This chapter investigates semi-integrated platforms that combine Si_3N_4 optical waveguides with QTF-based detection, demonstrating both QEPAS and LITES within a unified architecture.

4.1. Strip Waveguides

The implementation of strip Si_3N_4 waveguides (WGs) for QTF-based gas-sensing represents a complex multidisciplinary challenge requiring careful integration of

optical design, mechanical engineering, materials science, and fabrication-process optimization [344]. Unlike traditional free-space optical systems, integrated waveguide platforms must incorporate all necessary functionalities—including beam shaping, coupling optimization, and environmental protection—within the stringent constraints imposed by planar fabrication processes and material compatibility requirements [200].

For rectangular waveguide geometries with Si_3N_4 cores surrounded by air or SiO_2 cladding, as shown in Figure 4.1, the modal characteristics are primarily set by waveguide width, height, and the refractive-index contrast between the core ($n \approx 2$) and the claddings (air, $n \approx 1$; SiO_2 , $n \approx 1.45$) [345].

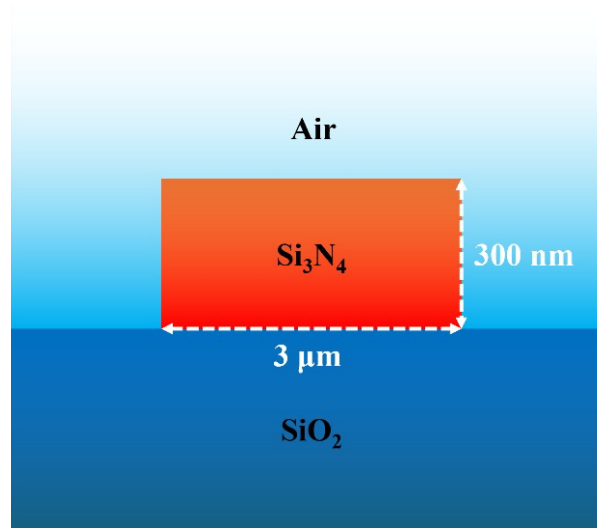


Figure 4.1. Cross-sectional schematic of the air-clad Si_3N_4 optical waveguide structure [342].

The waveguide dimensions must be optimized to achieve single-mode operation at the design wavelength while maximizing the fraction of optical power that extends into the surrounding medium as an evanescent field, thereby enhancing the interaction between guided light and target gas molecules [172]. It is possible to modify the Beer–Lambert law to account for this field portion by introducing a power-confinement factor (PCF):

$$P_{OUT} = P_{IN} \cdot e^{-\alpha_{INT} \cdot L - PCF \cdot \alpha_{GAS} \cdot C \cdot L}, \quad (4.1)$$

Equation 4.1. Beer–Lambert law for waveguides.

where P_{OUT} is the output optical power, P_{IN} is the input power, L the interaction path length, PCF the power-confinement factor, c the target gas concentration, α_{INT} the intrinsic guiding losses, and α_{GAS} the gas absorption coefficient.

This optimization represents a fundamental step, since stronger optical confinement generally reduces the coupling efficiency to external elements, while weaker confinement may lead to excessive propagation losses, multimode operation, or increased sensitivity to fabrication tolerances [346].

Numerical simulations employing FEMs and mode-solver algorithms (Figure 4.2) show that, at $\lambda = 1.392 \mu\text{m}$, waveguide cross-sections of $3 \mu\text{m}$ width and 300 nm height provide an optimal balance—single-mode operation, low propagation losses, and sufficient evanescent-field strength for efficient coupling to the QTF [171].

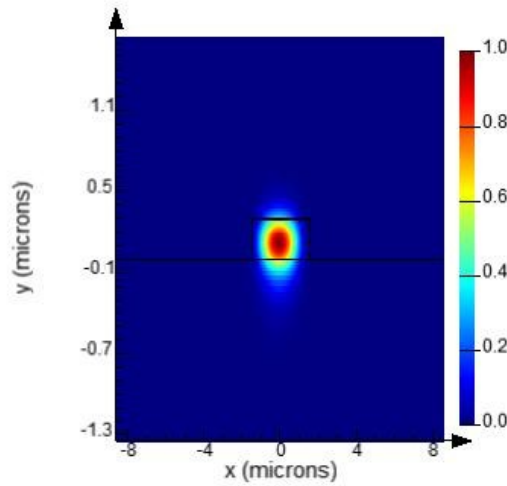


Figure 4.2. Simulated electric-field amplitude with superimposed waveguide outline, showing a well-confined TE mode.

These dimensions ensure the fundamental transverse-electric (TE) mode is well confined in the core while maintaining significant field overlap with the surrounding air-filled regions ($\approx 10\%$) where gas molecules are present.

The experimental implementation of the semi-integrated platform is shown schematically in Figure 4.3, which presents the complete configuration used for both QEPAS and LITES.

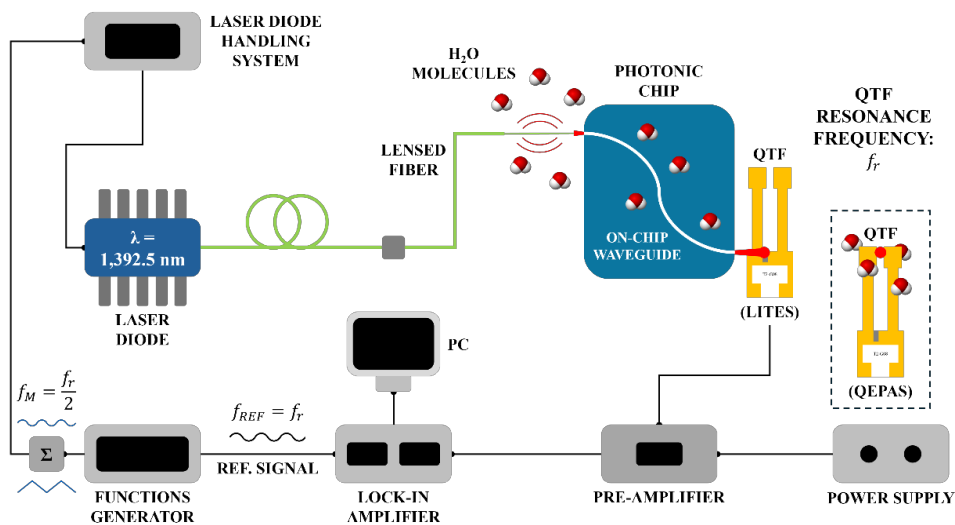


Figure 4.3. Schematic of the experimental setup for QEPAS and LITES. The QTF position relative to the waveguide output spot (red dot) differentiates between LITES and QEPAS configurations (dashed box) [342].

The laser source is a DFB diode operating at 1392.5 nm, selected to target the water-vapor (H_2O) absorption transition at 7181.16 cm^{-1} . This transition was chosen because the absorption is strong enough at realistic atmospheric H_2O levels, the wavelength is compatible with mature telecommunications-grade lasers and detectors, and the line is well isolated from interfering atmospheric absorptions that could complicate analysis [273]. The laser provides a maximum continuous-wave output power of approximately 4 mW with single-frequency operation and a linewidth of less than 1 MHz, suitable for high-resolution spectroscopic applications.

The laser output is coupled to the Si₃N₄ waveguide *via* a customized tapered lensed fiber (Highpak Solutions, Suffolk, UK) that delivers a $\approx 2.5\text{ }\mu\text{m}$ spot at the fiber tip. This coupling approach represents a practical compromise between coupling efficiency and mechanical simplicity, as it eliminates the need for complex free-space optical systems while providing adequate power delivery for sensing applications. The measured coupling efficiency from the lensed fiber to the Si₃N₄ waveguide is $\approx 30\%$, primarily limited by MFD mismatch; together with on-chip propagation and output-coupling losses, this yields $\approx 300\text{ }\mu\text{W}$ available at the waveguide output port [347].

The waveguide cross-section is shown in Figure 4.1. The chip is fabricated on a SiNOI platform with a 300 nm-thick Si_3N_4 layer deposited on a 525 μm -thick silicon carrier wafer. The underlying silicon substrate is thermally oxidized to form a 2.2 μm -thick SiO_2 buffer layer that provides optical isolation and prevents substrate-leakage losses that would otherwise compromise waveguide performance [178].

Figure 4.4(a) and Figure 4.4(b) show more details of the photonic chip, incorporating several features optimized for QTF coupling and sensing.

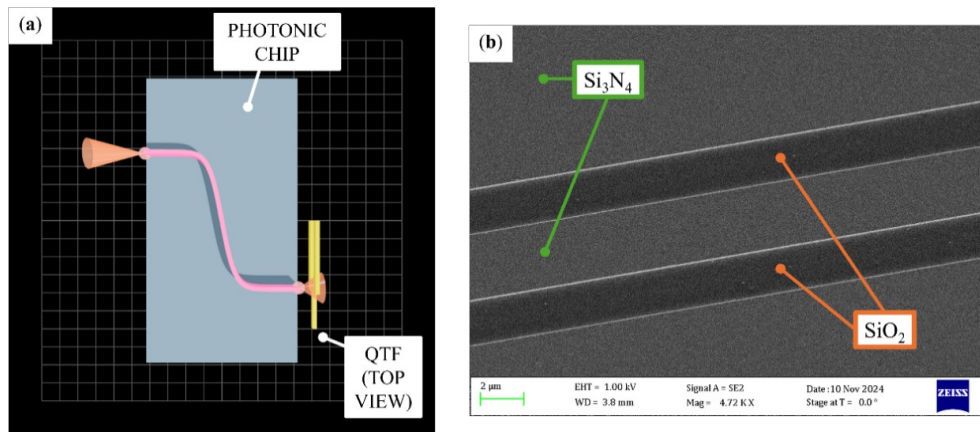


Figure 4.4. Waveguide details. (a) Not-to-scale three-dimensional rendering of the on-chip waveguide topology. (b) SEM image of the Si_3N_4 waveguide geometry at 4720 $\times$ magnification (green arrows indicate Si_3N_4 layer; orange arrows indicate SiO_2 one) [342].

As shown in Figure 4.4(a), the waveguide geometry incorporates an S-shaped bend configuration that serves multiple critical functions within the sensing architecture. First, the curved geometry prevents scattered light from the input coupling region from directly illuminating the QTF, thereby reducing background signals that could interfere with the weak absorption-induced signals being measured. Second, the S-bend provides adequate physical separation between the input fiber coupling region and the QTF interaction region, allowing independent optimization of both coupling efficiency and sensing performance. Third, the gentle curvature of the S-bend (designed with bend radii exceeding 100 μm) ensures low-loss optical transmission while providing the necessary spatial separation for practical device assembly [348].

Figure 4.4(b) presents detailed scanning electron microscopy (SEM) images of the fabricated waveguide structures, clearly revealing the uniform cross-sectional geometry achieved through optimized fabrication processes, with no visible

fabrication artifacts. The SEM images, acquired at 4720 $\times$ magnification, show the Si₃N₄ waveguide core surrounded by SiO₂ cladding layers, with sidewall roughness below 2 nm root-mean-square (RMS) to minimize scattering losses [330].

The main steps of a conventional silicon-nitride waveguide fabrication process are shown in Figure 4.5 and described below.

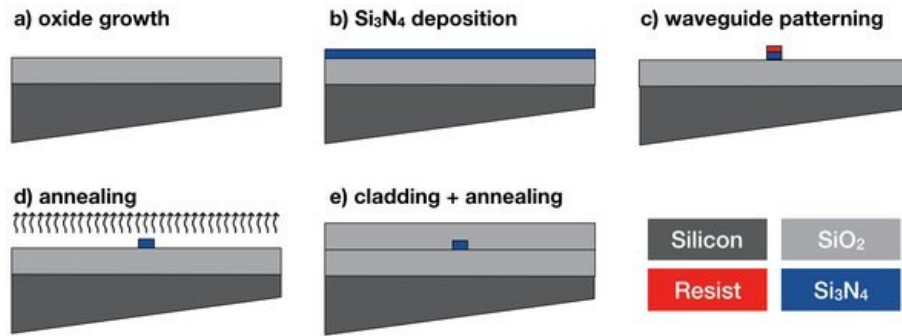


Figure 4.5. Conventional fabrication process of silicon-nitride waveguides. (a) Growth of the thermal bottom oxide layer. (b) Si₃N₄ deposition by LPCVD, with multiple cycles used to relax film stress for thicker layers. (c) Waveguide patterning. (d) Annealing of Si₃N₄ to remove excess hydrogen. (e) Deposition of the cladding SiO₂ cladding by LPCVD—typically low-temperature oxide (LTO), though high-temperature oxide (HTO) or tetraethyl orthosilicate oxide (TEOS) may also be used—followed by final annealing to densify the cladding and remove residual hydrogen [349].

The fabrication process begins with the preparation of high-quality silicon substrates followed by thermal oxidation to create the SiO₂ underlayer. Low-pressure (LP) chemical vapor deposition (LPCVD) of stoichiometric Si₃N₄ is performed at ≈ 800 °C using dichlorosilane (SiH₂Cl₂) and ammonia precursors. The deposition conditions are carefully optimized to minimize hydrogen incorporation and internal stress while achieving the target film thickness of 300 nm with uniformity better than $\pm 3\%$ across the wafer [350].

Photolithographic patterning employs advanced deep-UV lithography with i-line exposure ($\lambda = 365$ nm) to define waveguide patterns with sub-micrometer resolution. The photoresist system is optimized for high-contrast, vertical sidewall profiles, and the development process is carefully controlled to achieve the smooth sidewall morphology necessary for low scattering losses. Dry etching by inductively coupled plasma with fluorine-based chemistry (SF₆/CHF₃ mixture) provides highly anisotropic

profiles and precise depth control, ensuring complete removal of Si_3N_4 in the cladding regions while maintaining the target height within $\pm 5\%$ [205].

Post-fabrication processing includes thermal annealing at 1100°C in nitrogen ambient to reduce interface trap density and improve the optical quality of the waveguide structures. This annealing step also helps to relieve residual stress in the Si_3N_4 films and optimize the refractive index profile. A thin protective SiO_2 capping layer can then be deposited to ensure environmental protection and create symmetric cladding conditions that improve modal characteristics and reduce polarization sensitivity [351].

The final chip preparation involves precision dicing using diamond blade saws to create individual devices with high-quality optical facets suitable for fiber coupling. The facets are then polished with progressively finer abrasives to reach surface roughness below 1 nm RMS , minimizing coupling losses and back-reflections that could affect sensitive absorption measurements [352].

The optical characterization of the fabricated waveguides reveals several important performance metrics that directly impact sensing capabilities. Propagation-loss measurements using the Fabry–Perot resonance method—accounting for coupling and facet reflectivity—yield $\approx 4\text{ dB/cm}$ at $1.55\text{ }\mu\text{m}$ [341], [353]. While these losses are higher than those in state-of-the-art, telecommunications-optimized Si_3N_4 platforms (which reach $< 0.1\text{ dB/cm}$), they represent excellent performance for sensing-optimized geometries that prioritize evanescent-field accessibility over minimum loss [354].

The measured output power at the waveguide termination is $\approx 300\text{ }\mu\text{W}$, reduced by the input-coupling efficiency (limited by MFD mismatch between the lensed fiber and waveguide), propagation losses, and facet-reflectivity losses. Theoretical estimates based on the measured coupling efficiency ($\approx 30\%$), propagation losses (4 dB/cm over a 2.3 cm length), and Fresnel reflectivity at the air– Si_3N_4 interfaces ($\approx 11.1\%$) predict an output power of $\approx 1.35\text{ mW}$, indicating additional unaccounted loss mechanisms contributing to the observed discrepancy [355].

This $\approx 6.53\text{ dB}$ discrepancy between the predicted and measured output power can be attributed to several factors commonly encountered in practical photonic systems.

MFD mismatch between the lensed fiber and the fundamental SiN WG mode is a significant source of coupling loss, particularly given the larger WG core compared to the lensed-fiber spot size. Small fabrication imperfections—including sidewall roughness, slight dimensional variations, and minor material inhomogeneities—contribute to scattering losses that are difficult to predict theoretically. Additionally, parasitic reflections within the waveguide structure, particularly at interfaces between different materials or at geometric discontinuities, can create standing wave patterns that redistribute optical power and reduce the effective transmission efficiency [356]. These coupling-efficiency limitations present key opportunities for future optimization. Implementing mode adapters and spot-size converters at the waveguide input can significantly improve coupling efficiency by better matching the mode-field diameter between the fiber and the waveguide. Advanced coupling structures—such as grating couplers or three-dimensional coupling elements fabricated *via* direct-laser-writing or micromolding techniques—can potentially achieve higher efficiencies while relaxing alignment tolerances [357].

The QTF used in this work is a custom-designed, T-shaped, low-frequency model (T2-G08) featuring grooved prong surfaces that optimize stress distribution and enhance electromechanical conversion efficiency [358]. Figure 4.6 presents the QTF electrical response, showing the squared-voltage output (mV^2) as a function of excitation frequency (Hz).

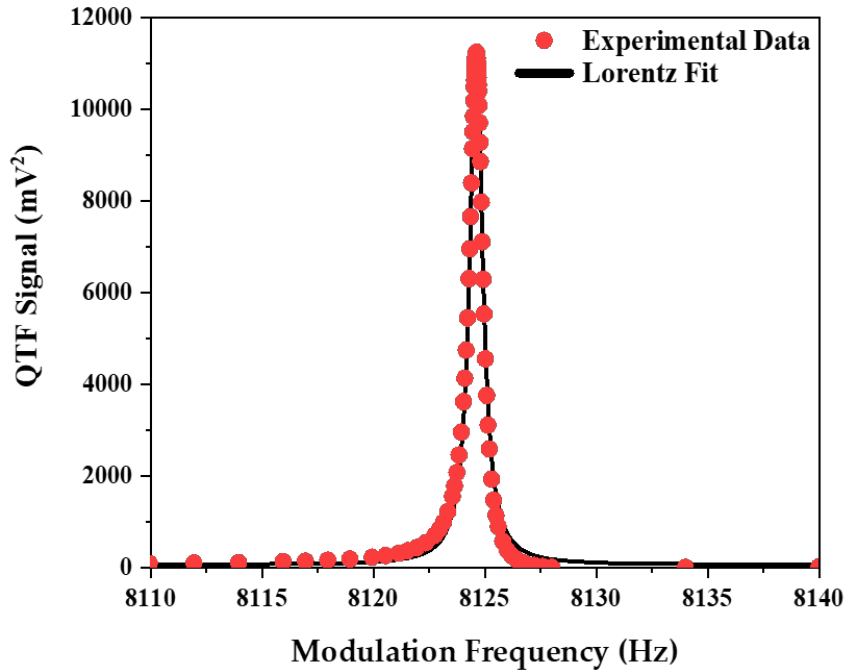


Figure 4.6. Electrical characterization of the QTF measured under atmospheric pressure conditions. Red dots: experimental data; black line: Lorentzian fit [342].

The resonance curve, fitted with a Lorentzian function, shows a sharp peak at 8124.61 Hz with FWHM ≈ 0.71 Hz, yielding a quality factor of $\approx 11,000$ at atmospheric pressure.

The resonance properties of the QTF can be significantly affected by the presence of nearby objects, altering the boundary conditions and thus creating additional damping mechanisms [178]. To characterize these effects systematically, the QTF resonance frequency and quality factor are monitored as a function of the distance between the QTF and the photonic chip. Figure 4.7 illustrates the experimental configuration used for this proximity study, showing four distinct positions (labeled A, B, C, and D) at which measurements are performed [359].

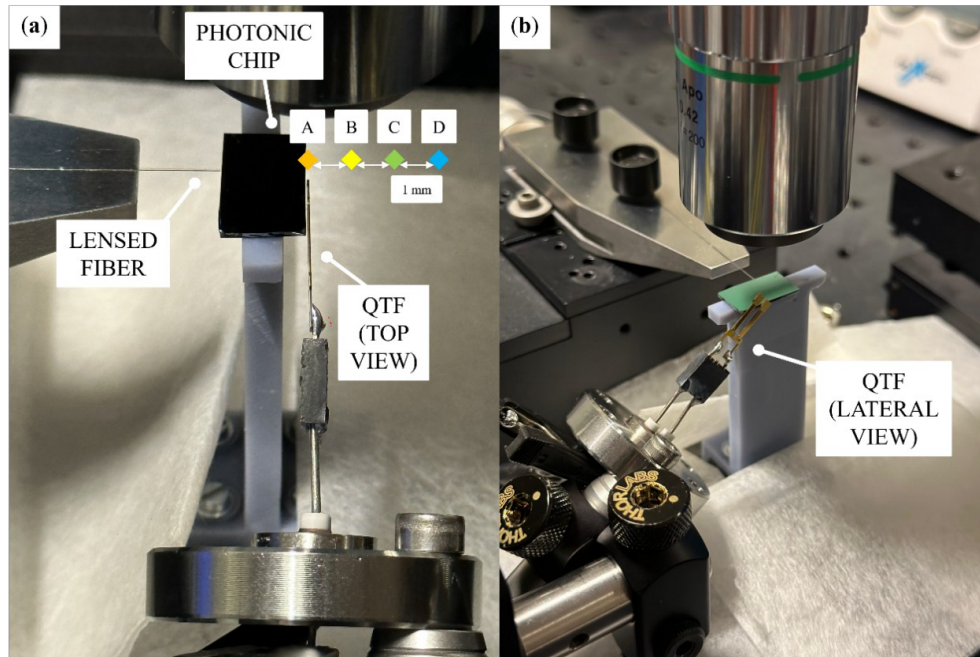


Figure 4.7. Photographs of the semi-integrated sensing system. (a) The lensed optical fiber (left) couples laser light into the on-chip waveguide (center), while the QTF (right) serves as the detector. (b) Lateral view of the same semi-integrated sensing system [342].

Position A represents the closest proximity configuration, with the QTF positioned within tens of micrometers from the waveguide output facet. This configuration is set using precision translation stages with micrometer resolution, guided by real-time monitoring through a short-wave infrared (SWIR) camera equipped with a 20 $\times$ objective. Positions B, C, and D correspond to separations of 1 mm, 2 mm, and 3 mm, respectively, enabling systematic investigation of proximity effects on both QTF resonance and sensing performance [360].

The proximity study shows that the QTF resonance properties remain remarkably stable across the investigated range, with no detectable changes in resonance frequency or quality factor. This stability indicates that the boundary conditions are not significantly perturbed by the presence of the photonic chip, suggesting that the sensing performance will be primarily determined by the optical coupling efficiency rather than by mechanical coupling variations [361].

The laser-diode temperature and injection current are controlled by a commercial driver (CLD1010, Thorlabs GmbH) providing temperature stability better than ± 0.1

°C and current stability better than ± 0.1 % over the measurement duration. This level of stability is essential for maintaining consistent optical power delivery and wavelength accuracy throughout the spectroscopic measurements [362].

WMS is employed to enhance sensitivity and suppress noise. The laser injection current is sinusoidally modulated at half the QTF resonance frequency ($f_{MOD} = 4062.305$ Hz), producing wavelength modulation that generates $2f$ signals at the QTF resonance when gas absorption occurs. The modulation amplitude is optimized to maximize SNR while avoiding under- or over-modulation effects that could distort line shapes or introduce harmonic artifacts [363].

Superimposed on the high-frequency modulation is a slow triangular scan that sweeps the laser wavelength across the target absorption line. The scan amplitude and frequency are optimized to capture the complete absorption profile while maintaining adequate temporal resolution for real-time monitoring applications. The scan parameters used are a 0.2 cm^{-1} amplitude and 5 mHz frequency, providing complete spectral coverage of the water vapor transition at 7181.16 cm^{-1} [364].

The QTF current response is converted to voltage using a transimpedance amplifier. The amplified signal is then processed using a digital lock-in amplifier that demodulates the signal at the QTF resonance frequency. The lock-in amplifier is configured with an integration time constant of 100 ms and a roll-off of 24 dB/octave to optimize the trade-off between measurement speed and noise rejection [280].

The sensing performance of the semi-integrated platform is evaluated *via* systematic H₂O absorption measurements using both QEPAS and LITES, alternating between techniques by moving the QTF as shown in Figure 4.8. The measurements are performed at room temperature (approximately 20 °C) and atmospheric pressure (760 Torr) [365].

Figure 4.8 presents representative spectral measurements obtained using both QEPAS and LITES techniques at different QTF positions.

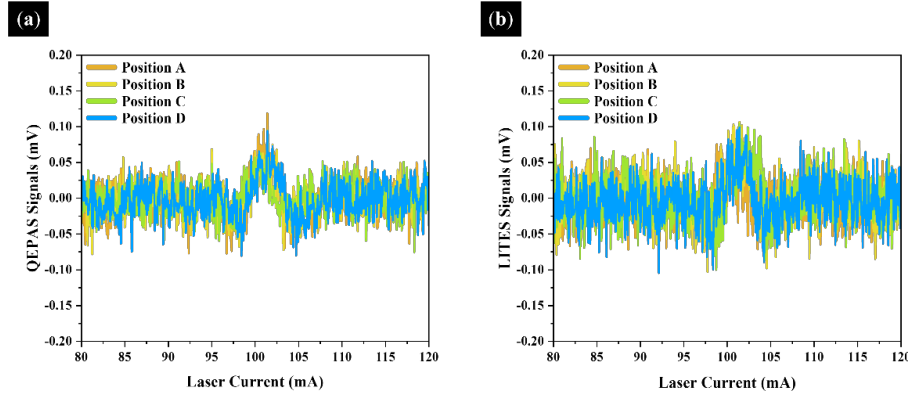


Figure 4.8. 2f-WMS spectra over the laser tuning range at four different QTF positions for (a) QEPAS and (b) LITES measurements. Position A represents the closest distance between the QTF and waveguide output, with subsequent positions (B, C, and D) spaced at 1 mm increments [342].

The spectral data in Figure 4.8 clearly demonstrate H₂O absorption with characteristic second-harmonic line shapes, confirming proper WMS operation.

The noisy second harmonic signals are fitted using theoretical models that account for the wavelength modulation parameters, the molecular absorption line parameters (obtained from the HITRAN spectroscopic database), and the instrumental response characteristics [238]. The resulting second-derivative Voigt fitting function is implemented in Python 3.11 as:

$$V_{2f-fit}(x) = -a \cdot \frac{d^2}{dx^2} \cdot [V(x - x_0, \sigma, \gamma)] + y_0, \quad (4.2)$$

Equation 4.2. Second derivative Voigt fitting function.

where a is the amplitude scaling factor; x_0 is the position of the peak in the scan; σ is the Gaussian width parameter; γ is the Lorentzian width parameter; and y_0 is the baseline offset. The leading minus sign accounts for the lock-in detection phase.

The fitting procedure enables accurate determination of peak signal amplitudes even in the presence of baseline drift, noise, and potential interference from weak absorption features.

Figure 4.9 presents representative fitted spectra for both QEPAS and LITES measurements at Position A, along with the raw experimental data showing the laser current dependence of the measured signals.

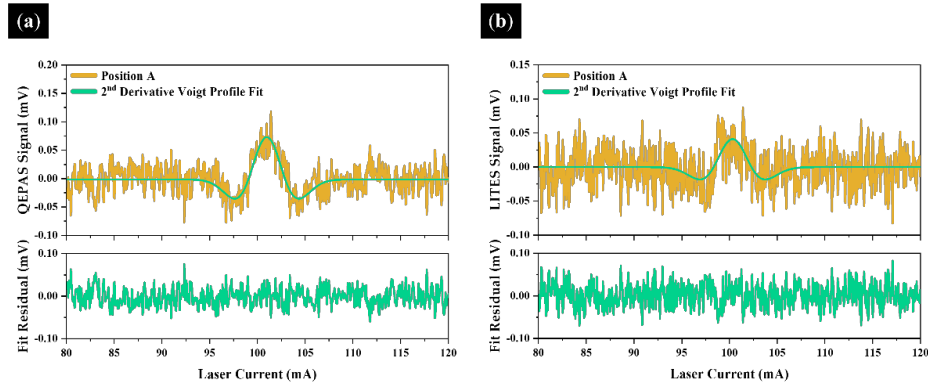


Figure 4.9. Second-derivative Voigt fits for (a) QEPAS and (b) LITES at QTF Position A. Green: fitted Voigt profiles; orange: experimental data. Lower panels show the fit residuals [342].

The excellent agreement between the fitted curves and experimental data shown in Figure 4.8 confirms the model validity and the accuracy of the extracted parameters. The fitting residuals, typically less than 2% of the peak signal amplitude, indicate that systematic errors are minimal and that the measurement uncertainties are dominated by random noise sources rather than systematic biases [239].

The noise levels for both techniques at different positions are summarized in Table 4.1, providing a quantitative comparison of measurement precision.

Table 4.1. Noise levels for both QEPAS and LITES techniques at different QTF positions (A through D) [342].

Technique	QTF Position			
	A	B	C	D
QEPAS	0.023 mV	0.019 mV	0.022 mV	0.019 mV
LITES	0.026 mV	0.027 mV	0.026 mV	0.028 mV

The noise levels, measured as the standard deviation of the baseline signal away from the absorption feature, range from 0.019 to 0.028 mV for both techniques, with slight variations depending on position and measurement conditions. These noise levels are primarily determined by the electronic noise of the detection system, mechanical vibrations, and acoustic interference from the laboratory environment [240].

The SNRs calculated from the peak signal amplitudes and noise levels are presented in Table 4.2, providing the key performance metrics for comparing the two sensing approaches.

Table 4.2. SNRs calculated using peak values extracted from fitted signals for both QEPAS and LITES techniques at different QTF positions (A through D) [342].

Technique	QTF Position			
	A	B	C	D
QEPAS	3.2	2.7	1.9	2.9
LITES	1.6	2.8	2.5	2.0

The results demonstrate that both techniques achieve comparable detection performance, with QEPAS showing slightly superior performance at the closest proximity (Position A) and LITES showing optimal performance at intermediate separation (Position B), despite the short interaction length in LITES and the highly divergent laser output in both techniques [242].

Based on the measured SNRs and the 1.6% H₂O used [273], MDLs can be calculated for both techniques. The QEPAS measurements yield an MDL of approximately 0.5%, while LITES achieves an MDL of approximately 0.6%. While these detection limits are modest compared to optimized free-space implementations, they represent significant achievements for semi-integrated platforms and demonstrate the feasibility of chip-scale sensing using QTF transducers.

Potential improvements in sensitivity may be achieved by optimizing the light–gas interaction length, reducing optical losses in the Si₃N₄ platform, and improving the optical coupling efficiency to the QTF. Further enhancements are expected from increased optical power on chip, improved beam shaping to reduce divergence, and the use of optimized QTF geometries and resonant enhancement schemes.

The demonstrated semi-integrated QEPAS/LITES platform using strip Si₃N₄ waveguides represents a significant step toward practical chip-scale gas-sensing systems. While current performance levels are not suitable for many environmental monitoring applications, the numerous identified optimization opportunities suggest

that substantial improvements in sensitivity, selectivity, and functionality can be achieved through continued research and development efforts.

4.2. Subwavelength Waveguides

The evolution toward enhanced light–gas interaction in chip-scale sensing platforms has motivated the investigation of subwavelength waveguide (SWG) structures as a solution for sensitivity enhancement while preserving integration advantages. These photonic structures exploit engineered periodicity at dimensions significantly smaller than the operating wavelength to create metamaterial-like properties that dramatically improve gas detection capabilities compared to conventional strip waveguide architectures [221].

Subwavelength periodic structures, such as the one shown in Figure 4.10, are arrangements of different materials with a pitch small enough to suppress diffraction effects arising from their periodicity.

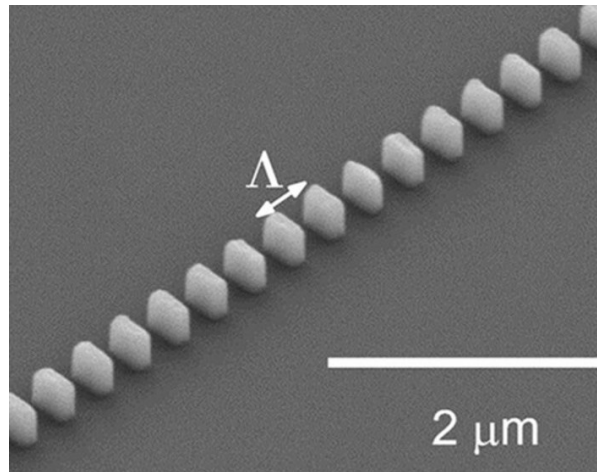


Figure 4.10. SEM image of a SWG waveguide having a width of 300 nm, a pitch of 300 nm, and a duty cycle of 33%. Propagation losses were measured to be ≈ 3.0 dB/cm at $\lambda = 1.5 \mu\text{m}$ [366].

Consider the periodic waveguide structure shown in Figure 4.11 which consists of rectangles of refractive index n_1 spaced at a pitch Λ at the boundary of two media with refractive indices n_2 (superstrate/upper cladding) and n_3 (substrate/lower cladding).

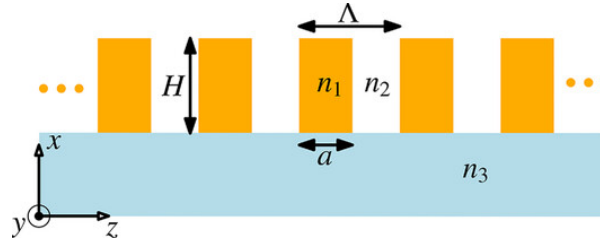


Figure 4.11. Schematic of a z -periodic dielectric waveguide, with n_1 , n_2 , and n_3 being the refractive indices of the core, cladding, and substrate materials (typically $n_1 > n_2, n_3$). In general description, two types of structures are considered: crosswise structures where light travels along the x or y direction, and lengthwise structures where light travels along the z direction [366].

The duty cycle of the structure is a/Λ and the height of the core layer is H . Many applications of subwavelength structures use the SOI waveguide platform, where the waveguide core material is silicon, $n_1 \approx 3.5$, the bottom cladding is silicon oxide, $n_3 \approx 1.45$, and the upper cladding is silicon oxide, a polymer, or air, so that $n_2 \approx 1$. This results in subwavelength pitches of the order of $\Lambda \approx 300$ nm for a free-space wavelength $\lambda \approx 1.55$ μm .

The periodic structure shown in Figure 4.11 can generally operate in the following regimes, depending on the ratio between the structure's pitch (Λ) and the free-space wavelength (λ): (i) diffraction ($\Lambda > \lambda$, *i.e.*, comparable to or smaller than the wavelength), where the incoming beam is scattered in different orders; (ii) Bragg reflection ($\Lambda \approx \lambda$), where the incoming beam is reflected backwards; and (iii) subwavelength ($\Lambda \ll \lambda$), where diffraction due to periodicity is suppressed.

When light travels through the structure shown in Figure 4.11 in the z direction, it is index-guided laterally (x direction). Such a structure behaves as a periodic segmented waveguide, so a convenient description of its behavior can be obtained using the Bloch–Floquet formalism [227]. Since this structure is periodic only in the longitudinal z direction, but not in the transversal x and y directions, supercell methods are not appropriate for the numerical analysis, and optimized numerical tools should be utilized. Light propagating in a segmented waveguide adapts to the periodicity as Bloch–Floquet modes of the periodic structure, with a mechanism that is formally similar to electron propagation in periodic crystals. Propagation of a Bloch mode through a z -periodic waveguide can be expressed as:

$$E(x, z + \Lambda) = E_B(x, z) \cdot e^{-\gamma_B \Lambda}, \quad (4.3)$$

Equation 4.3. Bloch–Floquet propagation formalism.

where $E_B(x, z)$ is the Bloch mode field distribution within a single period and γ_B is its complex propagation constant. In general:

$$\gamma_B = \alpha_B + ik_B = \alpha_B + i \left(\frac{2\pi}{\lambda} \right) \cdot n_B, \quad (4.4)$$

Equation 4.4. Complex propagation constant mathematical expression.

where α_B and k_B are the attenuation and propagations constants and n_B is the effective index of the Bloch mode.

For a given pitch, Λ , the behavior of a periodic waveguide is highly dependent on operating frequency (ω), or equivalently the free-space wavelength (λ). Figure 4.12(a) shows a schematic k – ω diagram of a periodic waveguide.

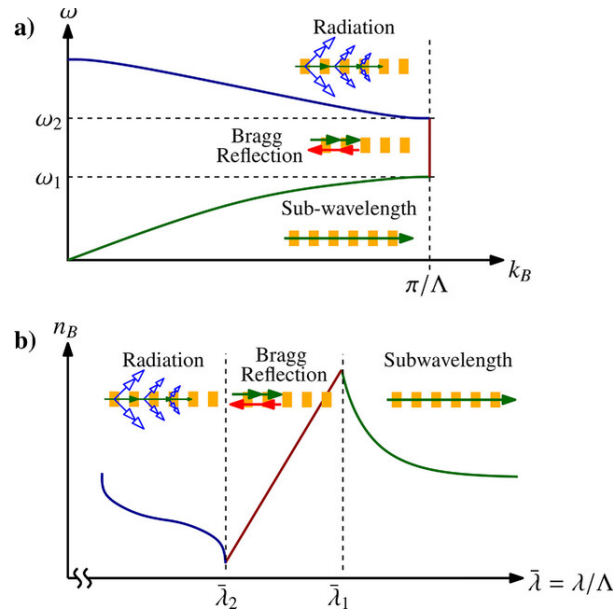


Figure 4.12. (a) Schematic dispersion diagram in the first Brillouin zone of a periodic waveguide with lengthwise propagation (along the z axis). (b) An equivalent representation of the Bloch mode effective index (n_B) of the periodic waveguide as a function of the wavelength-to-pitch ratio λ/Λ . Higher order diffraction and reflection bands are not shown [366].

For low frequencies ($\omega < \omega_1$), the propagation constant (k_B) grows monotonically, indicating that the periodic waveguide behaves as a conventional waveguide.

Propagation through a periodic waveguide in this subwavelength regime is illustrated in Figure 4.13(a).

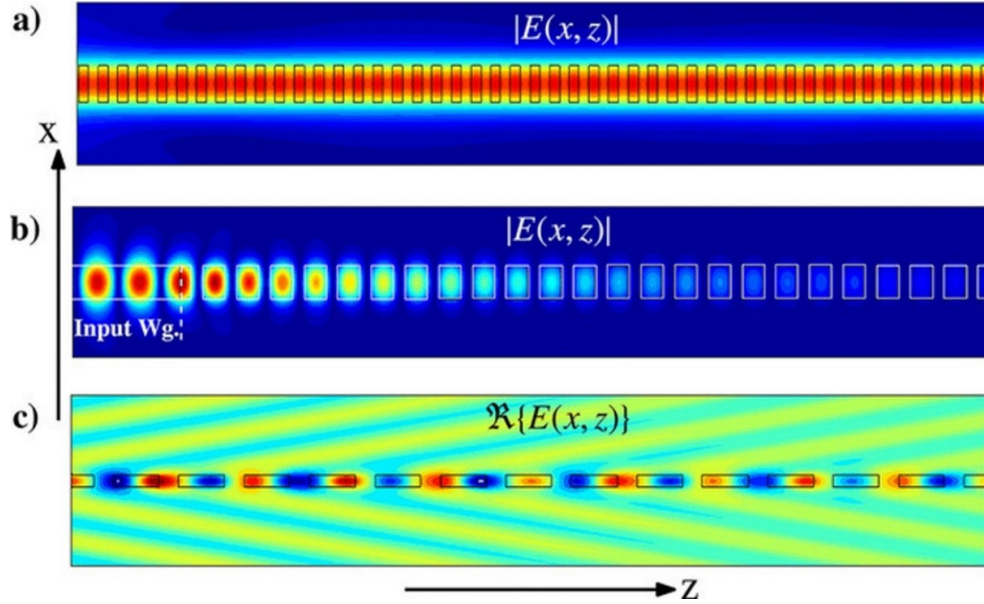


Figure 4.13. Propagation of light through a periodic waveguide with symmetric vertical structure (i.e., $n_{\text{substrate}} = n_{\text{cladding}}$). (a) In the subwavelength regime ($\lambda \gg \Lambda$) the structure behaves as a conventional dielectric waveguide. (b) In the bandgap light is reflected back into the uniform (non-segmented) input waveguide forming a standing wave pattern, whereas it is gradually attenuated in the periodic waveguide. (c) For wavelengths comparable to the pitch of the structure, light is radiated out of the waveguide. Only the $k = -1$ diffraction order is propagating in this figure [366].

In the frequency range corresponding to the photonic bandgap ($\omega_1 < \omega < \omega_2$), light cannot propagate through the structure and Bragg reflection occurs (Figure 4.13(b)). In this regime k_B is constant:

$$k_B^{\text{Bragg}} = \frac{\pi}{\Lambda}. \quad (4.5)$$

Equation 4.5. Propagation constant mathematical expression in photonic bandgap regime.

Above the first bandgap, the Bloch–Floquet mode becomes leaky and light is partially radiated out of the waveguide, as shown in Figure 4.13(c).

For some applications, it is useful to re-plot the k – ω diagram of Figure 4.12(a) as the effective index of the Bloch–Floquet mode, n_B , versus the wavelength-to-pitch ratio (λ/Λ). This results in the graph shown in Figure 4.12(b). In the deep subwavelength

regime, when $\lambda \gg \Lambda$, n_B is virtually flat. As the bandgap is approached, n_B increases, and then closely follows the linear relation:

$$k_B^{Bragg} \approx \frac{\lambda}{2\Lambda}. \quad (4.6)$$

Equation 4.6. Propagation constant mathematical expression in deep subwavelength regime.

within the bandgap. Although this linear behavior has been rigorously proven only for a two-layer periodic stratified structure [367], most periodic waveguides of practical interest exhibit this approximately linear response within the bandgap. For lower values of λ/Λ light is diffracted out of the waveguide. Although not shown here for simplicity, it should be noticed that higher order reflection and diffraction bands appear alternately for decreasing values of λ/Λ .

The subwavelength regime is reached when the ratio of wavelength and pitch is high enough for the effective index of the Bloch–Floquet mode to drop below the Bragg threshold:

$$n_B < \frac{\lambda}{2\Lambda}. \quad (4.7)$$

Equation 4.7. Effective index of the Bloch–Floquet mode for subwavelength regime.

Reflection and diffraction effects are then suppressed and the structure operates in the subwavelength regime. Light propagates through the SWG strongly suppressed diffraction/reflection, despite the longitudinal discontinuities, as shown in Figure 4.13(a).

Figure 4.14 shows a geometric schematic of the SiNOI, unbent SWG and conventional strip devices tested in our experiments. The photonic chip has $8 \times 15 \text{ mm}^2$ dimensions and integrates different copies of the structures for redundancy.

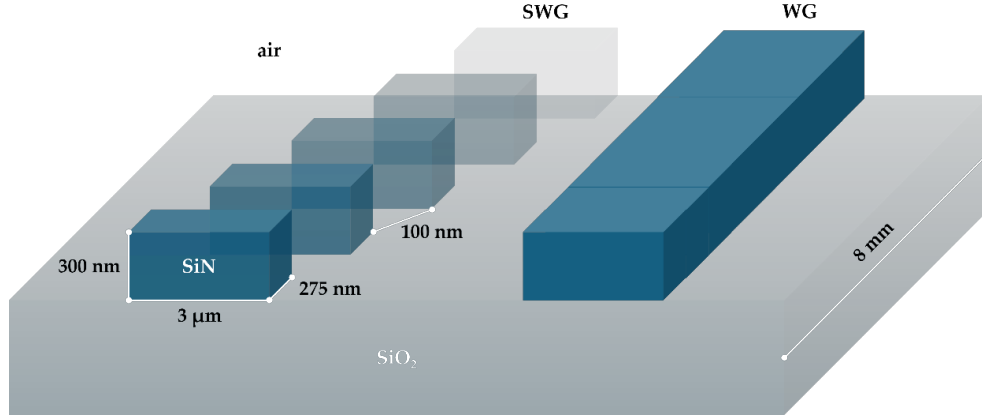


Figure 4.14. Schematic representation of the SWG and conventional strip WG device designs.

The critical advantage for gas sensing applications lies in the PCF enhancement (Equation 4.1) achievable through SWG design. Unlike conventional strip waveguides where gas interaction occurs only through evanescent field penetration ($PCF \approx 10\%$, as discussed before), SWG structures enable direct field overlap with gas molecules in the air-filled segments (*i.e.*, $PCF \approx 100\%$ within the air-filled segments). For a structure with total length L comprising solid segments of length L_1 and air segments of length L_2 (*i.e.*, $L = L_1 + L_2$), the effective power confinement factor (PCF_{eff}) becomes:

$$PCF_{eff} = PCF_{solid} \cdot \frac{L_1}{L} + PCF_{air} \cdot \frac{L_2}{L}. \quad (4.8)$$

Equation 4.8. Mathematical expression of effective PCF [366].

This relationship reveals that even modest air fill factors (L_2/L) can provide substantial sensitivity enhancement compared to strip waveguide architectures [229].

The experimental investigation used the same setup shown in Figure 4.3 and SWG devices incorporating 18,000 individual unit cells distributed over an 8 mm total device length. As shown in Figure 4.14, each unit cell consisted of a 275 nm silicon nitride block followed by a 100 nm air gap, yielding a total pitch $\Lambda = 375$ nm. This period was specifically chosen to ensure subwavelength operation at $\lambda = 1.392$ μm (*i.e.*, $\lambda/\Lambda \gg 1$), avoiding diffractive losses [231].

The waveguide cross-section incorporated a 3 μm width and 300 nm height, dimensions optimized for single-mode operation at 1.392 μm while maximizing evanescent field strength, as already reported in the previous paragraph (see Figure 4.1

and Figure 4.2). The air-clad design eliminated dielectric cladding layers that would otherwise impede gas access, ensuring maximum sensitivity to environmental gas concentrations. The total air-filled length $L_2 = 1.8$ mm represents 22.5% of the total device length, limited by both fabrication and propagation constraints.

The optical characterization revealed the fundamental trade-off between sensitivity enhancement and propagation losses inherent in SWG design.

The MDL of a spectroscopic waveguide sensor depends primarily on waveguide properties (length L , power confinement factor or PCF, propagation loss α_{INT} , coupling efficiency E), on laser properties (input power P_{IN}), on detector properties (noise equivalent power or NEP), and on gas ones (absorption coefficient α_{GAS}). Analytical expression for MDL dependence on the above quantities can be derived from Beer–Lambert law:

$$MDL = \frac{-\ln\left[1 - \frac{NEP}{P_{IN} \cdot E^2 \cdot e^{-\alpha_{INT} \cdot L}}\right]}{PCF \cdot \alpha_{GAS} \cdot L}. \quad (4.9)$$

Equation 4.9. MDL of a waveguide sensor [220].

In our experiment, propagation losses of 8.59 dB/cm for SWG devices were retrieved using indirect power measurements, and represented a $2.35\times$ increase (calculated as the ratio between $Losses_{SWG}$ and $Losses_{WG}$) compared to reference strip WG (3.65 dB/cm) measured using the same approach, corresponding to intrinsic loss coefficients α_{INT} of 1.98 cm^{-1} and 0.84 cm^{-1} , respectively [368].

The increased losses in SWG devices arise from several physical mechanisms. Scattering from the numerous silicon nitride–air interfaces dominates due to inevitable sidewall roughness and dimensional variations at nanoscale feature sizes. Additionally, mode coupling losses to radiation modes occur at each interface, particularly where fabrication imperfections create deviations from the ideal periodic structure [369].

Despite the loss penalty, the SWG design achieved a dramatic enhancement in effective power confinement factor to $PCF_{eff} = 30.25\%$, calculated according to Equation 4.8 with measured air fill factor $L_2/L = 22.5\%$. This represents a $3.03\times$ improvement (calculated as the ratio between PCF_{SWG} and PCF_{WG}) compared to the

reference strip waveguide PCF $\approx 10\%$, resulting in a favorable sensitivity-to-loss ratio (SLR) of $3.03/2.35 = 1.29$ [215].

The achievement of $SLR > 1$ represents a critical milestone, demonstrating that practical sensing benefits can be realized despite increased propagation losses. This favorable ratio aligns well with theoretical predictions and comparable experimental demonstrations reported in the literature and shown in Equation 4.8 [226].

Due to the enhancement in terms of light–gas interaction pathlength, the spectroscopic performance evaluation employed LITES technique targeting the water vapor absorption transition at 7181.16 cm^{-1} under controlled environmental conditions (*i.e.*, a water vapor concentration of 1.6% [273]) with the custom T-shaped QTF ($f_0 = 8124.11 \text{ Hz}$, $Q > 10,000$) as photo-thermo-elastic transducer. Figure 4.15 shows the H_2O 2f-LITES signals obtained exploiting the SWG device (namely SWWG in the Figure 4.15 legend) and the conventional strip WG (namely BWG in the Figure 4.15 legend), employed as a reference, as a function of the laser driver current.

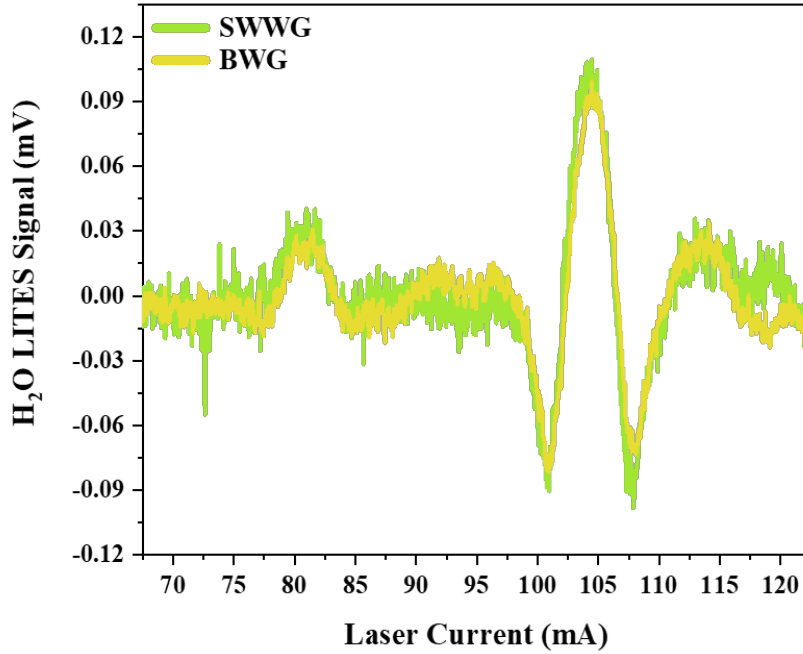


Figure 4.15. $2f$ -LITES signals related to H_2O sensing exploiting SWG (namely SWWG, green) and strip WG (namely BWG, yellow).

The measured peak signal amplitudes demonstrated the enhanced sensitivity of SWG devices, achieving peak amplitudes comparable to the reference strip waveguide devices.

SNR analysis revealed values of 19 for SWG devices compared to 16 for strip WG devices under the operating conditions. The higher SNR for the strip WG relative to Section 4.1 is attributable to the shorter device length (lower α_{INT}) and the unbent geometry, which avoids curvature losses. Noise characterization indicated comparable performance ($6.76 \mu V$ vs. $6.87 \mu V$) between device types, suggesting that electronic noise sources dominate over optical scattering or other structure-related effects [341].

The experimental validation confirms theoretical predictions regarding SWG performance while identifying specific areas for optimization. The measured sensitivity enhancement factor of 3.03, previously calculated in SLR determination, agrees well with calculated effective power confinement factor improvements,

validating the effective medium theory framework for subwavelength structure design [370].

Although the absolute signal amplitudes obtained with SWG and strip waveguides are comparable for the relatively short device lengths investigated, a more meaningful performance metric is provided by the SLR. Despite the higher propagation losses exhibited by SWG devices, the enhanced light–gas interaction enabled by the subwavelength structure results in a net sensitivity gain, yielding an SLR greater than unity. This indicates that, per unit propagation length, the sensitivity enhancement provided by SWG structures outweighs the associated loss penalty, making them intrinsically more efficient sensing elements than conventional strip waveguides, even under length-constrained conditions.

The primary limitation identified is the relatively small air fill factor (22.5%) imposed by fabrication and mechanical stability requirements for silicon nitride segments.

The propagation loss penalty ($2.35\times$) represents another optimization target. Advanced fabrication techniques, including improved lithographic processes and post-fabrication smoothing treatments, could potentially reduce interface scattering while maintaining the fundamental sensitivity advantages. The development of aperiodic or graded structures might also suppress coherent reflections, potentially responsible for interference fringes [350].

System-level improvements could provide substantial performance gains beyond waveguide optimization alone. Integration of mode adapters and spot-size converters could improve coupling efficiency by 3–6 dB, while on-chip power monitors and temperature sensors could enable real-time compensation for environmental variations [360].

The successful demonstration of SWG-based gas sensing establishes a foundation for integration within advanced photonic sensing platforms. The compatibility with standard silicon nitride processing enables incorporation into complex circuits featuring multiple sensing elements, on-chip references, and integrated calibration features [233].

The combination of SWG enhancement with the LITES technique represents a particularly promising approach, as the path-length dependence of LITES naturally complements the extended effective interaction lengths achievable with subwavelength structures. This synergy could enable multiplicative sensitivity improvements when both techniques are optimally combined [174].

Looking toward practical deployment, the demonstrated $SLR = 1.29$ provides confidence that SWG structures can contribute meaningfully to integrated sensor performance. However, realizing the full potential requires addressing fabrication challenges, optimizing air fill factors, and developing sophisticated signal processing techniques to extract gas-specific signals from complex spectral signatures [371].

The investigation of MEMS-integrated detection elements represents another promising direction for system-level optimization. Micro-fabricated resonators integrated directly on photonic chips could improve mechanical coupling while reducing packaging complexity, enabling array-based sensing configurations that leverage the enhanced sensitivity of SWG structures [358].

Future research directions include exploration of non-linear optical effects in SWG structures, which could enable new sensing modalities beyond simple absorption spectroscopy. The enhanced field confinement and engineered dispersion properties might facilitate efficient wavelength conversion or stimulated scattering processes that provide complementary information about gas composition [298].

The successful implementation of subwavelength waveguide technology represents a significant advance toward realizing high-performance integrated photonic gas sensors. By demonstrating favorable sensitivity-to-loss ratios through sophisticated nanophotonic engineering, this work establishes SWG structures as valuable components for next-generation optical sensing platforms.

The demonstrated semi-integrated sensing platform offers several significant advantages compared to traditional free-space optical systems. The elimination of bulk optical components dramatically improves mechanical stability and reduces sensitivity to environmental perturbations such as vibration, thermal fluctuations, and air currents that commonly affect free-space beam propagation. The compact chip-scale format enables portable instrument development and facilitates integration with electronic

control systems and wireless communication modules for distributed sensing applications [247].

The ability to operate both QEPAS and LITES detection modes using the same hardware platform provides valuable redundancy and the potential for enhanced measurement reliability through cross-validation of results. The different physical mechanisms underlying each technique mean that they may respond differently to certain types of interference or environmental variations, allowing more robust operation through algorithmic combination of the two measurement techniques [248].

The compatibility of the Si_3N_4 platform with CMOS fabrication processes creates opportunities for mass production and cost reduction through established semiconductor manufacturing infrastructure. The potential for integrating multiple wavelengths and sensing schemes on single chips opens pathways for comprehensive multi-gas analysis capabilities that would be difficult to achieve using discrete optical components [249].

However, the current implementation also reveals several limitations that represent opportunities for future optimization. The coupling efficiency between the lensed fiber and the waveguide, currently limited to approximately 30%, significantly reduces the optical power available for sensing applications. Advanced coupling structures such as three-dimensional adiabatic couplers, spot-size converters, or integrated lens systems could potentially improve coupling efficiencies to 80% or higher, directly translating to improved detection limits [250].

The choice of H_2O as the target analyte, while convenient for proof-of-principle demonstrations, represents a relatively strong absorber that may not fully reveal the ultimate sensitivity limitations of the platform. Future evaluations using weaker absorption lines or trace-level concentrations of environmentally important gases such as methane, carbon dioxide, or nitrogen dioxide would provide more stringent tests of the sensing capabilities [251].

The current QTF positioning and alignment procedures, while adequate for laboratory demonstrations, would benefit from automated assembly and precision packaging techniques for practical sensor deployment. The development of standardized packaging approaches that maintain optimal geometric relationships while providing

environmental protection and long-term stability represents an important engineering challenge for commercial implementation [252].

Several promising directions for future development can enhance the performance and broaden the application scope of semi-integrated sensing platforms. The integration of on-chip laser sources, particularly through heterogeneous integration techniques that combine III–V semiconductor gain materials with Si_3N_4 passive circuits, could eliminate fiber coupling losses while enabling more compact and robust sensor architectures [7]. Recent advances in heterogeneous integration have demonstrated high-performance lasers with output powers exceeding 100 mW and linewidths suitable for high-resolution spectroscopy, suggesting that fully integrated sensing platforms may soon become feasible.

Advanced waveguide designs incorporating slow-light structures, resonant cavities, or multipass configurations could significantly enhance the effective optical path length and thus improve detection sensitivity. Slot waveguides that concentrate optical fields in air-filled regions could enhance the light–gas interaction while maintaining compatibility with established fabrication processes [253]. Photonic crystal waveguides operating near the band edge could exploit slow-light propagation to increase interaction times, though these approaches typically require more complex fabrication and may introduce additional loss mechanisms.

The development of custom QTFs optimized specifically for photonic integration represents another promising avenue for performance enhancement. QTFs with integrated optical coupling structures, enhanced surface areas for acoustic interaction, or novel geometries optimized for specific sensing applications could provide significant sensitivity improvements over commercial devices originally designed for timing applications [254].

The extension of the platform to mid-IR wavelengths, where many gas species exhibit stronger fundamental vibrational absorptions, could provide orders of magnitude sensitivity improvements. While this extension would require development of mid-IR compatible waveguide materials and laser sources, the potential for accessing absorption strengths 100–1000 times stronger than near-IR overtones could justify the additional complexity [372].

CONCLUSION

This thesis investigates advanced photonic strategies for gas sensing, outlining a coherent progression from conceptual innovation to semi-integrated implementation. The research journey has bridged the long-standing gap between the analytical performance of laboratory systems and the practical requirements of compact, deployable instruments. Through the systematic development of beat-frequency (BF) quartz-enhanced photoacoustic spectroscopy (QEPAS), mid-infrared (mid-IR) fiber-integrated architectures, and semi-integrated silicon nitride-on-insulator platforms, this work has established a unified framework for the photonic integration of opto-acoustic and opto-thermo-elastic sensing.

The main scientific contributions can be summarized as follows.

- The development of the BF-QEPAS technique demonstrated that advanced modulation and signal processing strategies can drastically improve measurement speed (up to fiftyfold compared to conventional full-scan QEPAS) while enabling *quasi*-simultaneous multi-gas detection and *in situ* monitoring of sensor parameters;
- The implementation of mid-IR fiber combiner systems validated the feasibility of all-fiber architectures in the molecular fingerprint region, achieving detection limits down to a few ppm for carbon dioxide (CO₂) and nitric oxide (NO). These results confirm that alignment-free, vibration-tolerant sensing systems can be realized through optimized fluoride glass components;
- The demonstration of semi-integrated photonic platforms combining silicon nitride (Si₃N₄) waveguides with quartz tuning fork detectors established a practical pathway toward chip-scale sensors. The dual implementation of QEPAS and light-induced thermoelastic spectroscopy (LITES) within a

common architecture provided complementary detection capabilities, improving robustness and measurement reliability;

- The exploration of subwavelength waveguide (SWG) architectures in Section 4.2 provided an advanced platform to investigate light–matter interactions beyond conventional optical confinement. By engineering the geometry at the nanoscale, it was possible to enhance the evanescent field overlap with the surrounding gas and to control modal propagation losses with unprecedented precision. Experimental validation of water vapor (H_2O) detection using SWG and conventional strip waveguide devices demonstrated the potential of photonic-crystal-like structures to tune both sensitivity and selectivity. This study highlights how subwavelength engineering can act as an enabling technology for future generations of fully integrated opto–acoustic and opto–thermo–elastic sensors, combining the sensitivity of free-space systems with the robustness of on-chip devices.

Beyond these experimental achievements, the thesis contributes conceptually to the broader goal of photonic integration for ubiquitous chemical monitoring. The explored approaches show that compact optical sensors can achieve sufficient sensitivities for real-world applications in environmental monitoring, industrial safety, and process control. Importantly, the architectures described are compatible with mature semiconductor fabrication processes, enabling scalable and cost-effective production. This technological compatibility marks an essential step toward the democratization of high-performance optical gas sensing.

From a technology transfer perspective, the sensing architectures developed in this thesis are particularly well suited for industrial adoption. The emphasis on fiber-based and photonic integrated solutions directly addresses key industrial requirements, including mechanical robustness, reduced alignment sensitivity, long-term stability, and compatibility with automated manufacturing processes. These features make the proposed platforms attractive for applications such as industrial process monitoring, emissions control, leak detection, and safety systems, where reliability and maintainability are as critical as sensitivity.

To provide a direct overview of the sensing capabilities demonstrated throughout this thesis, Table 4.3 summarizes the key experimental results obtained for the investigated gas species, including the achieved minimum detection limits (MDLs), employed sensing techniques, integration times, and reference chapters.

Table 4.3. Summary of the MDLs achieved for the investigated gas species using different sensing techniques throughout this thesis, together with the corresponding integration times and reference chapters. C₂H₆, ethane; CH₄, methane; ppm, parts-per-million.

Molecule	MDL	Technique	Integration Time	Ref. Chapter
C ₂ H ₆	20 ppm (1 σ)	QEPAS	100 ms	Section 2.2
C ₂ H ₆	62 ppm (1 σ)	BF-QEPAS	5.097 ms	Section 2.2
CH ₄	1.7 ppm (1 σ)	QEPAS	100 ms	Section 2.2
CH ₄	5 ppm (1 σ)	BF-QEPAS	5.097 ms	Section 2.2
CO ₂	31 ppm (3 σ)	QEPAS	100 ms	Section 3.2
CO ₂	13 ppm (3 σ)	QEPAS	10 s	Section 3.2
NO	13 ppm (1 σ)	QEPAS	100 ms	Section 3.2
NO	4 ppm (1 σ)	QEPAS	10 s	Section 3.2
H ₂ O	0.5% (1 σ)	QEPAS	100 ms	Section 4.1
H ₂ O	0.6% (1 σ)	LITES	100 ms	Section 4.1

The achieved detection limits for the investigated gas species enable a wide range of application fields, including natural gas leak detection, environmental monitoring and process control, emissions and biomedical diagnostics, and atmospheric sensing and calibration. The results reported in Table 4.3 reflect a coherent progression from low to higher levels of photonic integration, moving from free-space QEPAS systems to fiber-integrated and semi-integrated photonic platforms. This progression highlights the feasibility of maintaining competitive detection performance while increasing compactness, robustness, and integration density.

Several challenges remain for future research. Improving coupling efficiency between light sources and integrated waveguides, currently limited to $\approx 30\%$, is crucial for

further sensitivity enhancement. Extending integration to the long mid-IR range will require new material platforms with lower optical loss and tailored dispersion. The realization of on-chip light sources through heterogeneous integration could eliminate external coupling entirely, paving the way for fully self-contained sensing systems.

Looking ahead, the convergence of photonic integration with micro-electromechanical systems (MEMS), microfluidics, and artificial intelligence is expected to open new frontiers in chemical sensing. Machine learning algorithms could analyze multimodal data to identify complex gas mixtures; microfluidic structures could provide precise gas handling and preconcentration; and advanced packaging could enable stable operation in harsh environments.

In summary, this work has demonstrated that photonic integration can resolve the traditional trade-off between sensitivity, compactness, and deployability that has long limited optical gas sensing. By establishing design principles and validating integrated architectures, this research lays the groundwork for a new generation of optical sensors—ones that are scalable, intelligent, and pervasive. As society's demand for environmental awareness and industrial safety continues to grow, the technologies explored in this thesis offer both immediate impact and a clear roadmap toward a future where high-performance photonic gas sensors become as widespread and indispensable as their electronic counterparts.

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