



Dual-gas quartz-enhanced photoacoustic spectroscopy sensor exploiting two fiber-combined interband cascade lasers

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ABSTRACT

In this work, a novel indium fluoride glass 2-input-1-output fiber combiner was designed and fabricated to combine two Interband Cascade Laser (ICL) sources emitting in the mid-infrared wavelength range. To test the combiner performance, a dual-gas quartz-enhanced photoacoustic spectroscopy sensor was demonstrated for the detection of carbon dioxide (CO₂) and nitric oxide (NO), employing two fiber-coupled ICLs having central emission wavelengths of 4,234 nm and 5,263 nm, respectively. The laser beams were coupled via the fiber combiner and then focused into a commercial acoustic detection module equipped with an input fiber-port, thus resulting in a plug-and-play sensing system. Tens of ppm-level detection limits at 3 σ are achieved for both pollutants with a lock-in integration time (τ) of 0.1 s. Finally, an Allan-Werle analysis demonstrated the stability of the sensor, allowing the achievement of detection limit of 13 ppm and 4 ppm at $\tau = 10$ s for CO₂ and NO, respectively.

1. Introduction

InfraRed (IR) laser-based sensors for trace gas detection have emerged as a powerful tool in various application fields, such as environmental monitoring of polluting agents, industrial and manufacturing processes control, and diagnostic solutions for human health care [1–4]. These sensing systems leverage the unique properties of light-matter interactions to detect the presence and quantify the concentrations of specific gas molecules with high sensitivity and high selectivity [5]. Fiber-based systems play a key role in the development of innovative trace gas sensors, enabling the efficient and versatile delivery of the beam from the laser source to the sensing volume, overcoming the limitations of free-space systems [6–9]. The main advantages of implementing fibers in optical sensing include: (i) manageability – fibers are flexible and can be positioned in compact and complex arrangements, allowing for the integration of optical sensors in a wide range of environments [10]; (ii) efficiency – fibers can minimize optical losses, resulting in higher power available for sensing and thus improving the

signal-to-noise ratio in the detection [11]; and (iii) stability – guided propagation of light in fibers provides enhanced stability and immunity to environmental interferences, thus improving the reliability of the gas sensing apparatus [12]. A novel development in laser-based gas sensors is the coupling of Interband Cascade Lasers (ICLs) sources, operating in the mid-IR region, with optical fibers [13,14]. This spectral region, typically defined as the wavelength range from 2.5 to 25 μm [15], is particularly interesting for gas sensing due to the presence of fundamental roto-vibrational transitions of many molecules [16]. Since silica optical fibers are not suitable to guide light with low-loss in the mid-IR wavelength range, different materials have been explored as beam delivery systems for ICLs. In recent years, Indium Fluoride Glasses (IFGs) fibers proved to be an optimal solution, since they are characterized by both low Fresnel losses and wide transmission window, from visible up to approximately 5.3 μm [17,18]. Although several laser sources have already been employed with IFG fibers [19–22], the development of fiber combiners represents a further step towards the realization of multi-gas sensors, allowing the simultaneous coupling of different laser

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sources. Indeed, this could improve the capabilities and versatility of the sensing system, enabling the integration of multiple lasers onto a single sensing platform with the aim of targeting different gas species sequentially or even simultaneously [23] and, at the same time, reducing the sensing system footprint [24].

Quartz-Enhanced Photo-Acoustic Spectroscopy (QEPAS) is a highly sensitive technique that has been widely adopted for trace gas sensing [25–29]. QEPAS is an evolution of the Photo-Acoustic Spectroscopy (PAS), relying on the photoacoustic effect for the detection, *i.e.*, the generation of acoustic waves by the target gas molecules absorbing modulated laser light and relaxing energy via non-radiative processes [30–33]. While PAS exploits microphones to detect pressure waves, in QEPAS a Quartz Tuning Fork (QTF) is employed as acoustic transducer. The QTF is coupled with resonator tubes and housed within a stainless-steel chamber, composing the Acoustic Detection Module (ADM). In QEPAS sensors, the laser beam, having an emission wavelength resonant with one (or more) optical transitions of the target gas molecules, passes through the two resonator tubes aligned with one of the vibrational antinodes of the QTF, generating acoustic waves impacting the internal surfaces of the prongs. These pressure waves put the prongs in motion, generating an electric signal due to the direct

piezo-electric effect of quartz [34–36]. The electric signal is directly proportional to the concentration of the target molecules that generate the pressure waves.

In this work, we present a compact and rugged dual-gas QEPAS sensor employing two fiber-coupled mid-IR ICLs combined with a novel developed IFG fiber combiner. The two selected lasers, having a central emission wavelength of 4,234 nm and 5,263 nm, allowed the detection of carbon dioxide (CO₂) and nitric oxide (NO), respectively, representing two of the most crucial molecules in the environmental pollution processes and for diagnostic solutions in human health care [37,38].

2. Dual-Gas QEPAS Sensor

Fig. 1a shows a schematic of the employed experimental setup, while Fig. 1b depicts a photo of the fabricated fiber combiner connected to the fiber port of the ADM.

Two different Interband Cascade Lasers (ICLs), emitting at 4,234 nm (ICL #1 in Fig. 1a) and 5,263 nm (ICL #2 in Fig. 1a) were exploited to target the CO₂ absorption feature located at 2,361.46 cm⁻¹ and the NO absorption feature located at 1,900.08 cm⁻¹, respectively [39]. The ICL #1 (model 3858/25–19 from Nanoplus GmbH) injection current was

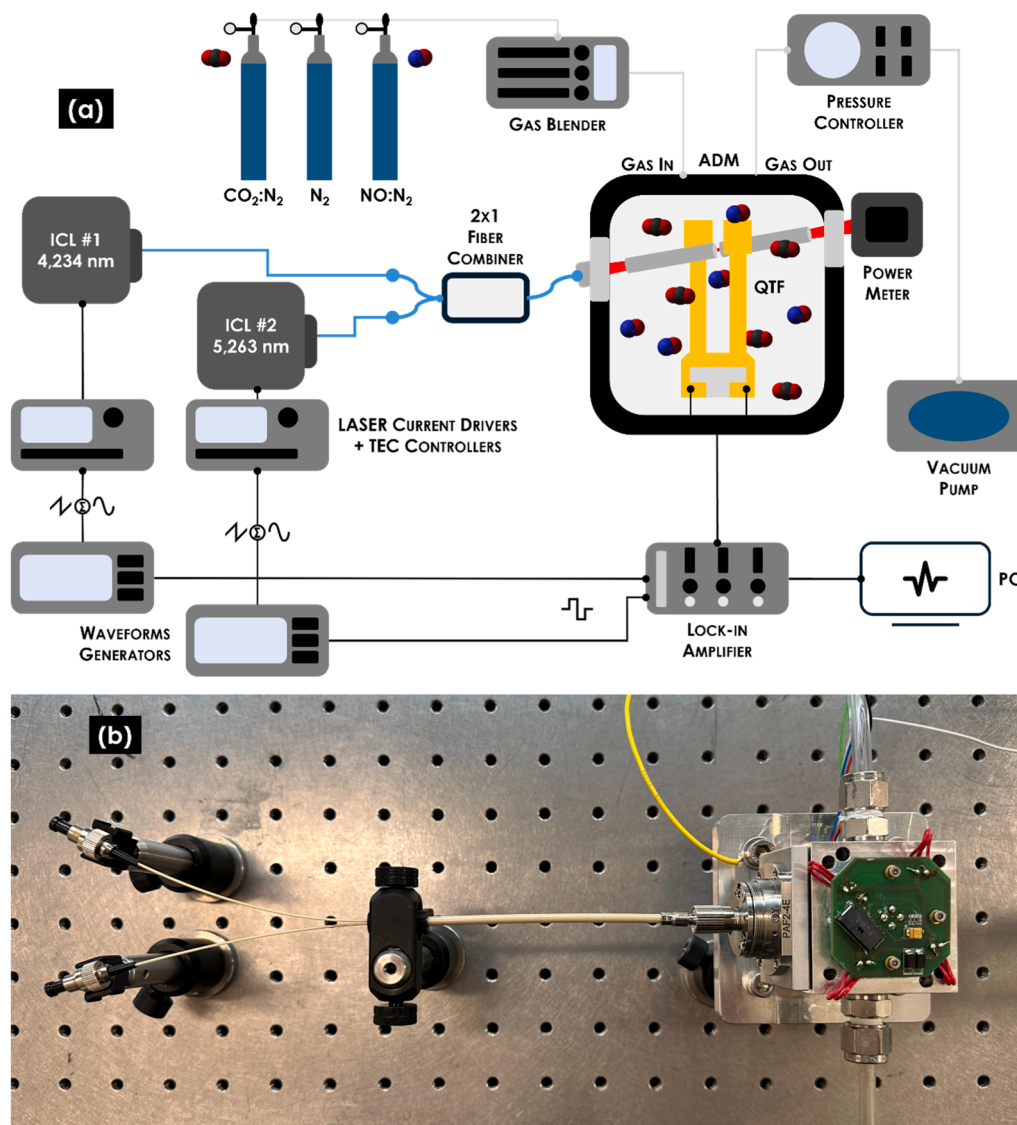


Fig. 1. (a) Schematic of the experimental setup. ICL – Interband Cascade Laser, TEC – Thermo-Electric Cooler, ADM – Acoustic Detection Module, QTF – Quartz Tuning Fork, PC – Personal Computer; (b) Photo of the custom-made 2-input-1-output fiber combiner (center-left) coupled with the ADM through its input fiber port (right).

modulated by applying a sinusoidal wave having an amplitude of 15.5 mVpp and its tuning range was scanned by superimposing a sawtooth wave having an amplitude of 50 mVpp and a frequency of 5 mHz. Likewise, the ICL #2 (model 3468/04–28 from Nanoplus GmbH) injection current was modulated by an 8 mVpp sinewave voltage added to a sawtooth wave with an amplitude of 60 mVpp and a frequency of 5 mHz. The operating temperatures of ICL #1 and ICL #2 were set to 10 °C and to 20 °C, respectively. The collimated beam of each laser was coupled into the FC/APC input connector of an Indium Fluoride Glass (IFG) fiber via a focusing lens. To mitigate etalon effects, the lens and the connector were slightly tilted and mounted into a lens tube directly UV glued (model NOA61) to the laser collimating lens (model 390036IR3, with a focal length of 4 mm and a NA of 0.56), as reported by Zifarelli *et al.* in Ref. [13]. The fabricated fiber combiner, described in the next section, allowed delivering the beam of the two fiber-coupled lasers to the fiber port (PAF2–4E from Thorlabs GmbH [40]) mounted on a commercial ADM (ADM01 from Thorlabs GmbH [41]). The fiber port, equipped with an aspheric lens having a focal length of 4 mm and an AR coating in the 2 – 5 μm range, is used to focus the light inside the ADM and between the two prongs of the QTF by passing through the resonator tubes without hitting them. Thus, the delivery of the laser beams to the input of the ADM in the reported work is fully made with optical fibers, and the beam was aligned using the five-axis translation stage of the fiber port. A mass flow-meter and pressure controller (MC3S-D from Alicat Scientific, Inc.) was employed to set and maintain a constant working pressure of the gas mixture inside the ADM, with the aid of a vacuum pump. A 3-input-channel gas mixer (GB-103 from MCQ Instruments) controlled the gas flow and enabled the generation of different gas mixtures. The developed QEPAS sensor operates at a working pressure of 300 Torr and with a total gas flow rate of 50 SCCM which resulted in the optimal working conditions. The ADM encloses the spectrophone, which consists of a T-shaped QTF acoustically coupled to a pair of metallic acoustic resonator tubes to enhance signal detection [42]. The “T” region of the QTF is 2 mm-thick and 2.4 mm-long, with prongs 1.4 mm-thick and 9.4 mm-long. Instead, the crystal width is 0.25 mm. The resonator tubes have an inner diameter of 1.6 mm and each are 12.4 mm-long [41,42]. At 300 Torr, a resonance frequency (f_r) of 12,439.55 Hz and a quality factor over 15,000 were measured. In this work, the QEPAS measurements were carried out exploiting a wavelength modulation technique along with a 2 f detection scheme: a sinewave having a frequency of $f_r/2$, generated by a waveform generator (33500B from Keysight Technologies, Inc.), was continuously applied to the ICL current driver (ITC4002QCL from Thorlabs GmbH) while the electrical signal generated by the QTF was demodulated by the lock-in amplifier (MFLI 500 kHz from Zurich Instruments Ltd.) at f_r . For all measurements, the lock-in integration time (τ) was set to 0.1 s and the sampling time was set to 3 \bullet τ .

3. IFG Fiber Combiner

An optical fiber combiner was realized for both coupling mid-IR laser sources and QEPAS sensing with the two selected ICLs presented in the previous section. Customized IFG optical fibers with core diameter $d_{co} = 25 \mu\text{m}$ and cladding diameter $d_{cl} = 100 \mu\text{m}$ were fabricated by Le Verre Fluoré (Bruz, France) and their measured attenuation α is reported in Fig. 2.

The IFG optical fiber segments were cleaved with a diamond blade employing an automatic cleaver based on tension-and-scribe process. The combiner fabrication process is sketched in Fig. 3.

Firstly, as shown in Fig. 3a, the IFG optical fiber segments were inserted in a custom low-refractive index IFG tube with external diameter (d_{cap}) of 550 μm . The global structure, consisting of both optical fibers and the tube, was secured in the fiber holding blocks of the glass processing system, *i.e.*, Vytran GPX-2400, with an applied pre-tension. By means of heating and pulling technique, effectively addressing the well-known thermo-mechanical issues associated with fluoride glasses, a

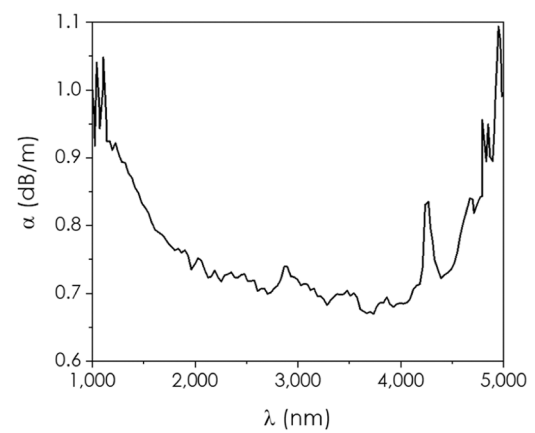


Fig. 2. Measured attenuation α , expressed in dB/m, of the IFG optical fibers employed for the combiner fabrication.

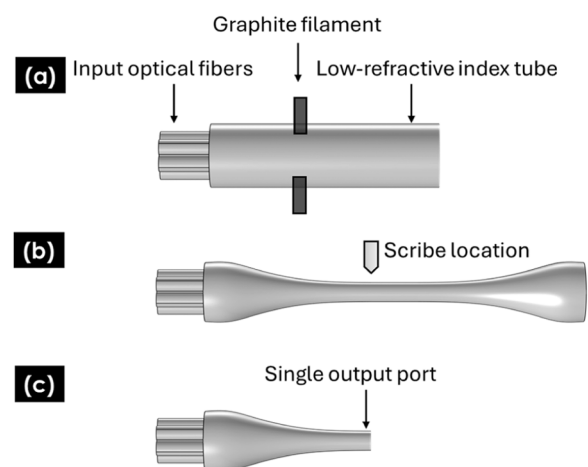


Fig. 3. Sketch of the optical fiber combiner fabrication. (a) Optical fibers inserted in a low-refractive index tube; (b) Fused bi-conical taper obtained via stretching and heating technique; (c) Cleaving of the fused bi-conical taper in the waist region.

fused bi-conical taper was obtained, as depicted in Fig. 3b [43,44]. Fig. 4 depicts a microscope image during the combiner fabrication, showing the tube containing the IFG optical fibers being drawn.

As the filament is heated, the pulling speed provided by the movement of the right fiber-holding block is greater than the feeding rate of the left fiber-holding block. This results in a reduction in diameter, as evident in Fig. 4, when comparing the non-tapered left side with the right side undergoing the drawing process. A gradual and controlled

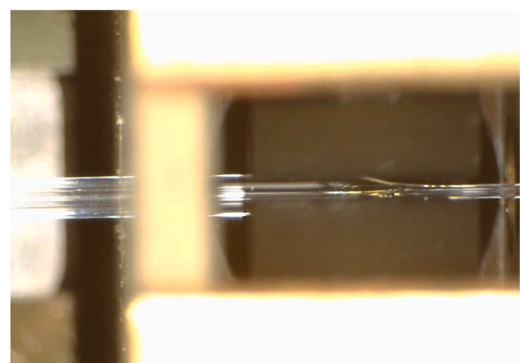


Fig. 4. Drawing of the tube containing IFG optical fibers.

down-taper transition was implemented to adhere to the adiabatic criterion, minimizing transition losses by preventing mode coupling with higher-order modes and ensuring efficient light propagation [45]. For fluoride glass processing, it is crucial to maintain stable operation during the thermal process at a temperature near the glass transition temperature (T_g) of 275 °C to prevent crystal formation [43]. This was possible by operating the commercial graphite filament of Vytran GPX-2400 with a start filament power of 12.1 W. A constant argon flow rate of 0.35 L/min inside the graphite filament is used to mitigate potential issues with air impurities or humidity. This is important, as the presence of crystallization, evident as a grainy appearance on the outer surface of the device, can lead to high insertion loss [46]. To assist the collapse of air holes and achieve a homogeneous cross-section, a pump with negative pressure was attached to one end of the tube [47]. The obtained bi-conical taper was then cleaved in the waist region, *i.e.* the narrowest point, as illustrated in Fig. 3c. This constitutes the single output port of the device. The combiner diameter in the waist region (d_w) is approximately equal to 140 μm , ensuring that the two beams at different wavelengths are spatially close, thus allowing proper alignment of the guided light at different wavelengths between the QTF prongs. The fabricated combiner was then coated and equipped with standard FC/APC connectors to (i) ensure high durability; (ii) facilitate the connection with the sources; and (iii) minimize back-reflection. The final fabricated device is reported in Fig. 1b and has a total length of 23 cm.

The measured Insertion Losses (ILs) of the fabricated 2×1 optical fiber combiner at three representative wavelengths in the mid-IR spectral range are reported in Table 1. It was verified that the device is symmetric, *i.e.*, the insertion losses do not depend on the employed input port.

These values include the coupling losses due to the connection from the ICL to the input optical fiber of the combiner and the attenuation of the employed optical fibers [18]. Both the coupling losses and the attenuation are larger at $\lambda_2 = 5,263$ nm than at the other tested wavelengths. These factors can partially explain the higher measured insertion loss at $\lambda_2 = 5,263$ nm. The device used in this work was also tested a year after its fabrication and displayed negligible signs of aging, confirming the ILs reported in Table 1.

The fabricated optical fiber combiner based on indium fluoride glass can operate at any wavelength, up to about 5,500 nm. It is worthwhile mentioning that the proposed approach is easily scalable to a higher number of input optical fibers, enabling multi-gas detection by adopting a single combiner with multiple input ports and additional lasers. An alternative solution could involve using 2×1 IFG optical fiber couplers, potentially in a cascaded configuration. For instance, the cascade of two fused couplers could merge light from three lasers emitting different wavelengths into a single common port.

For measurements requiring the combining of sources emitting at wavelengths longer than 5500 nm, other glasses, *e.g.* chalcogenide-based, could be considered. To date, the only commercially available mid-IR compatible combiners are produced by IRflex Corporation, utilizing arsenic sulfide optical fibers and supporting operation up to approximately 6,500 nm [48]. In this case, due to the high refractive index $n \sim 2.4$ of arsenic sulfide glass, the best theoretical transmission is only 69 % if no anti-reflection coatings are considered.

Table 1
Measured ILs of the IFG fiber combiner for three representative wavelengths.

λ (nm)	IL (dB)
3345	1.2
4234	1.1
5263	2.2

4. QEPAS Results and Discussion

The QEPAS sensor was calibrated turning sequentially ICL #1 for the detection of carbon dioxide (CO_2) and ICL #2 for the detection of nitric oxide (NO). At the output of the fiber combiner, optical power of 0.17 mW and of 0.08 mW were measured for the CO_2 and NO calibration, respectively. For both gases, QEPAS spectral scans were acquired at each concentration dilution step and representative spectra for both CO_2 and NO are shown in Fig. 5a and Fig. 5b, respectively.

No interference fringes are observed, confirming that the focused beam dimensions, achieved through the PAF2-4E fiber port lens, allowed the laser light to pass through the QTF and resonator tubes without hitting them. The tuning range of the ICL #2 allowed targeting the NO absorption features both at 1,900.08 cm^{-1} and at 1,900.52 cm^{-1} (P3 in Fig. 5b) [39]. The P1 and P2 values were retrieved and plotted as a function of the target gas concentration and the results as well as the linear best fitting curves are shown in Fig. 6.

The linear fit returned an R^2 of 0.998 and 0.9994 for the calibration of CO_2 and NO, respectively, demonstrating the linearity of the sensor. The Minimum Detection Limit (MDL) for each gas was calculated as the concentration providing a Signal-to-Noise Ratio (SNR) equal to 3. The noise level was evaluated as the standard deviation of the QEPAS signal when the emission wavelength of the laser was tuned out of any absorption feature. The sensitivities (*i.e.*, the slope of the linear fits), the noise levels, and the calculated MDLs at 3σ are reported in Table 2.

At $\tau = 0.1$ s, both MDLs are in the tens of ppm range and the realized sensor allows the monitoring of the carbon dioxide level in atmosphere [49]. Furthermore, it was experimentally verified that there are no electric interference and matrix effects between the two QEPAS signals, since no changes in the CO_2 signal, at a fixed concentration, were observed when NO traces were added in the nitrogen-based gas matrix, while the ICL #2 had been tuned far from the NO absorption features, and vice versa [50]. Finally, the Allan-Werle standard deviation analysis was employed to verify the stability of the sensor and evaluate the MDLs at different integration time [51]. For this measurement, pure nitrogen was flowing in the ADM and both lasers were tuned at an emission wavelength far from any absorption features, and the modulation was provided either to ICL #1 or to ICL #2. The results are shown in Fig. 7a and Fig. 7b.

In both cases, a similar trend was observed up to $\tau = 10$ s: the noise level slightly increases at short integration time and after a τ of 0.4 s follows a $1/\sqrt{\tau}$ -like trend, as expected in a detection limited by the thermal noise of the QTF [52,53]. At τ greater than 10 s, the two curves differ. While the trend in Fig. 7b confirms a detection limited by white noise sources, mechanical instabilities in the coupling system of ICL #1 and the optical fiber cause an increase of the standard deviation. Since this difference is evident at long integration time, the developed sensor allows quasi real-time detection of both gases and the calculated MDLs at a lock-in integration time of 10 s are reported in Table 2. The CO_2 detection limits change from 31 ppm at $\tau = 0.1$ s down to 13 ppm, and from 13 ppm down to 4 ppm for the NO detection, at an integration time of 10 s.

5. Conclusions

In this work, we report on the development of a dual-gas QEPAS sensor for the detection of CO_2 and NO exploiting two fiber-coupled ICL sources combined with a novel optical fiber combiner based on IFG, whose output port was directly connected to the fiber port of an ADM. The sensor was calibrated for both gases and the linearity and the interference-free of the responses were verified. Finally, an Allan-Werle analysis was carried out to assess the stability of the sensor. Although mechanical instabilities in the ICL-fiber coupling system arising at long integration time, the developed sensor allowed CO_2 MDLs of 31 ppm at 0.1 s of integration time and of 13 ppm at $\tau = 10$ s. The NO detection is limited by the thermal noise of the sensitive element, reaching MDLs of

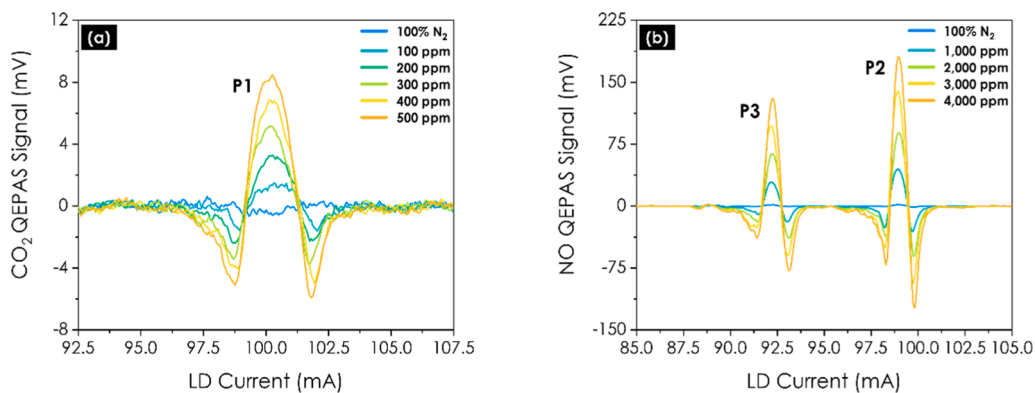


Fig. 5. Representative 2f-QEPAS spectra for (a) CO₂ concentrations from 100 ppm to 500 ppm and (b) NO concentrations from 1,000 ppm to 4,000 ppm. In both cases, the spectra measured for pure N₂ is also shown.

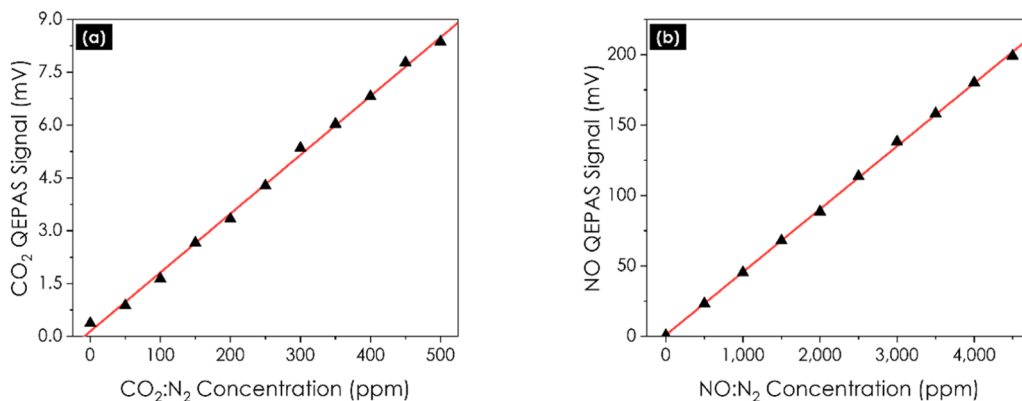


Fig. 6. QEPAS signals peak values as a function of the target gas concentration values (black triangles) and corresponding linear fit (red solid line) for (a) CO₂ and for (b) NO.

Table 2

Summary of the sensing performances of the dual-gas QEPAS sensor.

	CO ₂	NO
Sensitivity	16.7 μV/ppm	44.6 μV/ppm
Noise Level	171 μV	186 μV
MDL @ 0.1 s	31 ppm	13 ppm
MDL @ 10 s	13 ppm	4 ppm

13 ppm at 0.1 s of integration time and of 4 ppm at $\tau = 10$ s. The developed dual-gas QEPAS sensor represents an innovative sensing system for the detection of multiple gases with strong absorption

features in the mid-IR spectral range and proves, in addition, high sensitivity and stability, well-suited characteristics for practical, portable and field-deployable gas sensing application scenarios. The fiber coupling of mid-IR sources will be further optimized to fully exploit the optical power of lasers, thus making the proposed sensor comparable to sensing system employing free-space light sources in terms of MDL.

Author contributions

Luigi Melchiorre and Francesco Anelli equally contributed to this work.

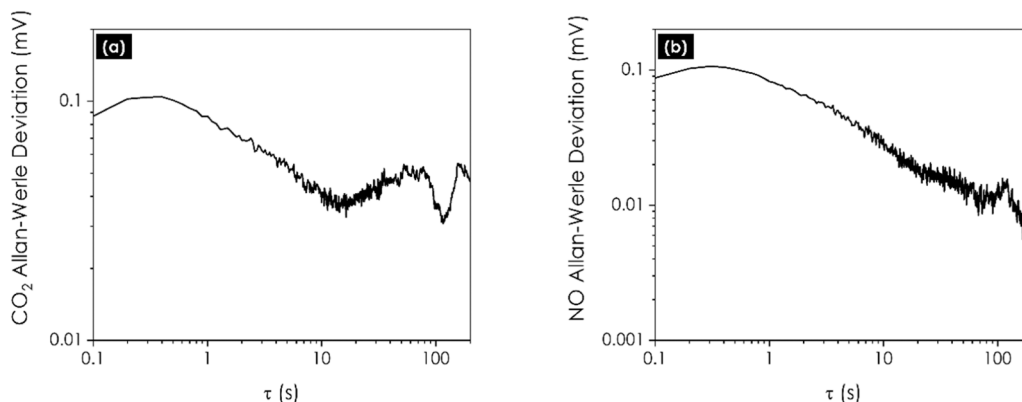


Fig. 7. Results of the Allan-Werle standard deviation analysis for the detection of (a) CO₂ with ICL #1 and (b) NO with ICL #2.

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CRediT authorship contribution statement

Angelo Sampaolo: Writing – review & editing, Supervision, Conceptualization. **Giovanni Magno:** Writing – review & editing, Supervision, Conceptualization. **Solenn Cozic:** Supervision, Formal analysis, Conceptualization. **Laurine Bodin:** Validation, Investigation. **Luigi Melchiorre:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Vincenzo Spagnolo:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Francesco Prudeniano:** Writing – review & editing, Methodology, Funding acquisition, Conceptualization. **Andrea Annunziato:** Investigation, Conceptualization. **Giansergio Menduni:** Writing – original draft, Supervision, Formal analysis, Conceptualization. **Francesco Anelli:** Writing – original draft, Investigation, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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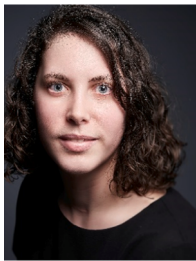
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