C-PASS

Conference on Photonics
for Advanced Spectroscopy and Sensing

CONFERENCE ON PHOTONICS FOR ADVANCED SPECTROSCOPY AND SENSING

ENVIRONMENTAL AND BIO-MEDICAL APPLICATIONS SENSING, INDUSTRIAL PROCESS MONITORING AND AGRI-FOOD ANALYSIS

3 - 8 SEPTEMBER 2023 CASTELLANETA MARINA - ITALY

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1ST CONFERENCE ON PHOTONICS FOR ADVANCED SPECTROSCOPY AND SENSING

Book of Abstracts

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C-PASS is the first edition of the international conference series on **Photonics for Advanced Spectroscopy and Sensing,** held on **September 2023 in Castellaneta Marina, Italy**. It aims to bring together researchers from both industrial and academic research laboratories to stimulate new research initiatives in the fields of **integrated photonics, lasers, optical spectroscopy and sensing in the near- and mid-infrared spectral regions**.

Topics

- Gas and liquid sensing and spectroscopy
- Photoacoustic and photothermal gas sensing
- Integrated photonics for sensing and spectroscopy
- Sensor phenomenology, modeling and evaluation
- Emerging sensor technologies and applications
- Novel mid and near-IR sources for gas and liquid sensing
- Optical sensor systems: signals, processing and interfaces
- Optical sensors for agrifood analysis and industrial applications
- Environmental and bio-medical sensors, new instrumentation and methodology
- VOCs and particulate detection

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Sunday Sept. 3rd		Monday Sept. 4th		Tuesday Sept. 5th		Wednesday Sept. 6th		Thursday Sept. 7th		Friday Sept. 8th	
		Integrated Photonics		**Frequency Comb and Optical power build up approaches**		**Direct Absorption Spectroscopy**		**Spectroscopy for Atmoshperic Applications**		**Sensing for Bio, Food, and Petrochemical Applications**	
		09:00 - 09:15	Opening: **V. Spagnolo, M. Grande** and **W. Whelan Curtin**	09:00 - 09:30	**J. Faist** - Integrated optical frequency combs for mid-infrared spectroscopy	09:00 - 09:30	**S. Cristescu** - Optical absorption spectroscopy applied for trace gas sensing	09:00 - 09:30	**G. Wysocki**- Drone-assisted spectroscopic detection of trace-gas plumes – new technologies and emerging applications	09:10 - 09:30	**M. Wolff** - Photoacoustics analysis of methane isotopologues
		09:15 - 09:45	**M. Belkin** - Mid-infrared photonics integration on InP	09:30 - 09:50	**M. Marangoni** - High-speed dual-comb spectroscopy in the 8-12 um region	09:30 - 09:50	**P. De Natale** - Molecular detection with a sensitivity of parts per quadrillion	09:30 - 09:50	**M. Ghysels Dubois** - Around the "atmospheric world" under a balloon : a long-duration observation of the equatorial tropopause with the Pico-SDLA tunable diode laser spectrometers	09:30 - 09:50	**C. Cordero** - Challenges and Opportunities from Food Volatilomics: Sensing the Quality
		09:45 - 10:05	**I. Cristiani** - Photonic integrated circuits for laser frequency stabilisation	09:50 - 10:10	**K. Cossell** - Atmospheric measurements using open-path mid-infrared dual-comb spectroscopy	09:50 - 10:10	**J. Toivonen** - Fourier transform photoacoustic spectroscopy with broadband supercontinuum lasers	09:50 - 10:10	**W. Chen** - Cavity enhanced optical sensing of the atmosphere	09:50 - 10:10	**L. Dong** - Calibration-free Mid-infrared Exhaled Breath Sensor based on BF-QEPAS for Non-invasive Diagnosis
		10:05 - 10:25	**F. Francis** - Holographic metasurfaces for biophotonics and sensing applications	10:10 - 10:25	**M. Kotylar** - Optical Build up cavities for indirect spectroscopy fabricated using silicon processing technologies	10:10 - 10:25	**R. Krebbers** - Mid-infrared supercontinuum-based Fourier transform spectroscopy for multispecies open-path measurements	10:10 - 10:25	**B. Tuzson** - Recent advances in VOC analysis by mid-IR laser spectroscopy	10:10 - 10:25	**M. Olivieri** - H2 detection based on wavelength modulation and multipass absorption spectroscopy
		10:25 - 10:40	**J.H.M. Castro** - Control of Fano Spectral Profile based on a Silicon Nitride Photonic Crystal-Micro Ring Resonator structure	10:25 - 10:40	**S. Sam** - Bow-Tie Cavity for I-QEPAS for Isotope Analysis: Design and Optimization	10:25 - 10:40	**G. Menduni** - Quartz Enhanced Photoacoustic Spectroscopy and Light Induced Thermoelastic Spectroscopy for natural gas composition analysis	10:25 - 10:40	**D. Theiner** - Flexible molecular gas sensing platform in the terahertz domain	10:25 - 10:40	**H. Moser** - ATEX compliant, FPGA based three-channel quantum cascade laser sensor for sulfur species detection in petrochemical process streams
		10:40 - 11:00	**Coffee Break**	**10:40 - 11:00**	**Coffee Break**	**10:40 - 11:00**	**Coffee Break**	**10:40 - 11:00**	**Coffee Break**	**10:40 - 11:00**	**Coffee Break**
		Infrared Sources and Detectors		**Industrial Session**		**Photothermal Spectroscopy**		**Quartz-Enhanced Photoacoustic Spectroscopy**		**Spectroscopic Applications**	
		11:00 - 11:20	**P. Chevalier** - The quantum cascade laser pumped molecular laser: a widely tunable source from 100 GHz up to more than 3 THz	11:00 - 11:20	**M. Brandstetter** - Digital infrared spectroscopy: fast and flexible spectral and hyperspectral measurements	11:00 - 11:30	**P. Burgholzer** - Fundamental limits to spatial resolution in photothermal imaging	11:00 - 11:20	**Y. Ma** - Quartz-tuning-fork based Laser Spectroscopy for Trace Gas Detection	11:00 - 11:20	**A. Castrillo** - Comb-assisted frequency-stabilized cavity ring-down spectroscopy: application to ultra-sensitive detection of water vapour and beyond
		11:20 - 11:40	**Q. Wang** - Broadband Room-Temperature Mid-infrared Detection with Nanoparticles	11:20 - 11:35	**R. Aidam** - Neogly, QCL-based continuous glucose monitoring device	11:30 - 11:50	**M. Franko** - Recent Progress and Applications of Thermal Lens Spectrometry in Environmental and Bio-medical Sensing	11:20 - 11:35	**P. Patimisco** - Multi-QCL Quartz-Enhanced Photoacoustic Sensor for Environmental Monitoring	11:20 - 11:35	**I. Gazizov** - Improved Heterodyne Spectroradiometer: A Leap Towards Precise XCO2 Measurements
		11:40 - 11:55	**D. Pinto** - Long wavelength distributed feedback tapered quantum cascade lasers	11:35 - 11:50	**THORLABS - N. Reusch** - Gas Spectroscopy at Thorlabs – From Prisms to QEPAS	11:50 - 12:05	**K. Krzempek** - Photothermal gas detection using a miniaturized fiber Fabry-Perot cavity	11:35 - 11:50	**K. Kinjalk** - Highly Selective Toluene Detection using Quartz Enhanced Photoacoustic Spectroscopy at λ = 13.71 μm	11:35 - 11:50	**A. Walsh** - Evanescent wave quartz enhanced photoacoustic spectroscopy employing a side-polished fibre for methane sensing
		11:55 - 12:10	**M. Paparella** - Numerical and experimental analyses of optical coupling for GaSb diode lasers grown on Silicon substrate	11:50 - 12:05	**MCQ - G. Canuti** - All-in-one Gas mixer and pressure controlling system for spectroscopy	12:05 - 12:20	**J. Waclawek** - Compact Trace Gas Detection by Balanced-Detection ICAPS	11:50 - 12:05	**M. Ruizl** - QEPAS sensor for Surveying the Atmospheric Carbon Cycle	11:50 - 12:05	**G. V. B. Lukasievicz** - Photothermal Lens and Photothermal Mirror Techniques: Effects and Applications for Material Characterization
		12:10 - 12:25	**J. Fordyce** - Extended wavelength tuning of multi-section interband cascade lasers with slotted waveguides above 3 μm	12:05 - 12:20	**NANOPLUS - R. Weih** - Long Wavelength Cascade Laser Technology for Sensing Applications	12:20 - 12:35	**G. Malvicini** - Balanced – Interferometric Cavity Assisted Photothermal Spectroscopy with low – cost telecoms wavelength lasers for environmental and food analysis	12:05 - 12:20	**E. Kniazeva** - Ultra-compact QEPAS sensors for environmental detection of toxic gases and development of novel near-IR DFB laser diodes for photoacoustic spectroscopy	12:05 - 12:20	**G. Ricchiuti** - Photothermal Spectroscopy (PTS) of PMMA thin layer using micro-ring resonators (MRRs)
		12:25 - 12:40	**R. De Palo** - Surface Modification of Quartz-Tuning Forks for Light-Induced-Thermoelastic Spectroscopy	12:20 - 12:35	**ETG - F. Manassero** - TDL,ICL,QCL Qepas gas analyser	12:35 - 12:50	**Y. Zhang** - Controlling Spatial Resolution and Sensitivity in Nanoscale Chemical Imaging by Photothermal-Induced Resonance Spectroscopy	12:20 - 12:35	**G. Biagi** - Study of ammonia adsorption and desorption phenomena in a QEPAS sensor		
		12:45 - 14:30	**Lunch**	**12:45 - 14:30**	**Lunch**	**12:55 - 14:30**	**Lunch**	**12:40 - 14:30**	**Lunch**	**12:40 - 14:30**	**Lunch**
14.30 - 18.00	**PARTICIPANTS ARRIVAL FROM AIRPORTS**	**Hybrid Sources and Fibers**		**14.30-16.30**	**POSTER SESSION**	**Photoacoustic Spectroscopy**		**15.00-19.00**	**SOCIAL ACTIVITY VISIT TO MATERA**	**14-30 -19.00**	**PARTICIPANTS TRANSPORTATION TO AIRPORTS**
		14:30 - 14:50	**U. Willer** - Evanescent-field fiber sensors			14:30 - 14:50	**M. Sigrist** - Photoacoustic detection overview, from past to present				
		14:50 - 15:05	**P. Jaworsky** - Antiresonant Hollow-Core Fiber and Kagome Hollow-Core Fiber assisted Wavelength Modulation Spectroscopy of ethane in the mid-IR			14:50 - 15:10	**T. Rueck**- From Lab to Application – Digital Twins of Photoacoustic Gas Sensors				
		15:05 - 15:20	**A. Vorobev** - Graphene Electrodes on Silicon Nitride Devices for Near-Infrared Wavelength Tuning			15:10 - 15:30	**R. Li Voti** - Photoacoustic Characterization of Metal Nanoparticles Super-Aggregates				
		15:20 - 15:35	**G. Paikkath** - Photonic crystal hybrid lasers for intra-cavity Quartz Enhanced Photo-Acoustic Spectroscopy (QEPAS) and Photo-Thermal Spectroscopy (PTS)			15:30 - 15:45	**S. Borri** - A doubly-resonant cantilever-enhanced photoacoustic sensor for trace-gas detection				
		15:35 - 15:50	**A. Annunziato** - Optical Fiber Couplers Based on Indium Fluoride Optical Fibers			15:45 - 16:00	**J. Fekete** - Open photoacoustic cell for measurement of water vapor flux				
						16:00 - 16:15	**L.S. Li** - Multiscale photoacoustic tomography of genetically encoded photoswitchable proteins				
18.00-19.30	**WELCOME PARTY**										
19.30-21-00	**DINNER**	**19.30-21-00**	**DINNER**	**PIZZA DINNER**		**19.30-21-00**	**DINNER**	**SOCIAL DINNER**			

L.S. Li - Multiscale photoacoustic tomography of genetically encoded photoswitchable proteins

Integrated Photonics

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Mid-infrared photonics integration on InP

D. Burghart[1], K. Zhang[1], E. De Toma[1], G. Boehm[1], and M.A. Belkin[1]

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Short abstract: InP materials platform is highly suitable for mid-infrared photonic integration. We present measurements of mid-infrared losses and Kerr nonlinearities of InP-based dielectric waveguides, demonstrate functional mid-infrared photonic components, such as ring resonators and wavelength multiplexers, and report on their integration with multiple active devices on the same InP substrate.

Photonic integration can extend all the benefits of individual semiconductor devices to a wide variety of more complex applications. In the mid-infrared (mid-IR, λ≈3-15 μm), quantum cascade lasers (QCLs) based on InP have been established as versatile room-temperature semiconductor light source, due to their large spectral range of operation as well as their high output power. InP platform can also support passive dielectric waveguides with core/cladding refractive index contrast of up to ~0.6 and low optical losses across the entire mid-IR spectral range. As a result, the natural choice for a possible platform for the mid-IR photonic integrated circuits (PICs) would be the one based on InP. This talk will summarize our efforts towards the development of the first mid-IR PICs on InP, Fig. 1.

We will share the measurements of mid-IR optical loses in the InGaAs/InP and GaAsSb/InP waveguides and report the performance of more advanced passive mid-IR photonic components such as critically-coupled ring resonators with Q-factors over 10^5 and efficient wavelength multiplexers in this platform [1]. Measured mid-IR optical losses vary from as low as 0.2 dB/cm in the 5-6 μm wavelength range to over 5 dB/cm at wavelengths beyond 10 μm. We will also present measurement confirming high values of Kerr nonlinearity and low group velocity dispersion in the InGaAs/InP and GaAsSb/InP waveguides. Finally, we will discuss different approaches for integration of active photonic devices with the passive photonic components [2], including integration of multiple dissimilar active regions on the same InP substrate and present pulsed and continuous-wave operation of QCLs-based PICs at room temperature.

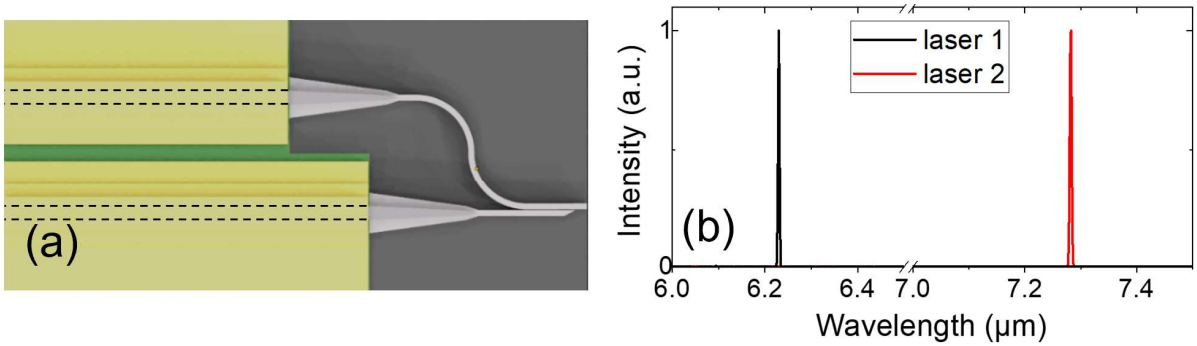

Fig. 1. (a) Microscope view of a mid-IR InP PIC made of two DFB QCLs adiabatically coupled to passive waveguides with their wavelength outputs multiplexed to a single passive waveguide. The PIC is being developed for spectroscopic sensing of NO_2 and SO_2 atmospheric pollutants. (b) Room temperature emission spectrum of the two lasers shown in (a) from a common passive waveguide output.

This work was supported by the EU Horizon 2020 PASSEPARTOUT project and by the German Research Foundation (DFG) grant number 463411319.

References

[1] K. Zhang, et al., "Mid-infrared microring resonators and optical waveguides on an InP platform," *Appl. Phys. Lett.* **120,** 061106 (2022).
[2] S. Jung, et al., "Homogeneous photonic integration of mid-infrared quantum cascade lasers with low-loss passive waveguides on an InP platform," *Optica* **6**, 1023-1030 (2019).

Photonic integrated circuits for laser frequency stabilisation

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Short abstract: Here we present frequency stabilization of semiconductor lasers, via integrated photonic circuits that might provide a credible route for the generation of sub- THz and THz radiation for applications in spectroscopy and 6G communications systems.

The exploitation of photonic integrated circuits (PIC) has marked a new route for the development of miniaturised devices enabling complex signal processing in the optical domain. [1] In particular, the capability to integrate multiple optical sources and control their emission frequency with a precision in the MHz range is set to boost frontier applications such as those related to THz wave generation via photomixing, 6G communication systems and basic science experiment settings [2].

In this work we present the design and experimental characterization of a fully-integrated frequency stabilizer based on silicon nitride on insulator (SiNOI) platform able to process and control up to 16 integrated lasers.

The stabilization concept is briefly schematized in Fig. 1a). Each laser signal is coupled into the SiNOI chip via a packaged optical fibre and is subsequently coded by on-chip thermo-optical modulator. The lasers are then sent to a shared high Q ring resonator exhibiting a 50 GHz free spectral range.

Each laser can be locked to a specific resonance of the ring by means of a closed loop configuration. A dedicated algorithm recovers the signal from each laser and converts any frequency drift in an electrical feedback signal that is sent to the driving optical circuitry devoted to the frequency tuning of the corresponding laser. The PIC architecture was designed in such a way as to eliminate any ambiguity that might come from the sign of frequency shift or power fluctuations of the laser under control

In the initial tests the stabilization circuits and algorithm have been evaluated over a period of 2 hours without external de-tuning. Results shows that the frequency has been stably mantained within ±50MHz.

The stabilization system has been then applied to the generation of an RF signal. Two lasers were simultaneously controlled via the integrated SiN chip : the signals, positioned at frequencies with a relative distance of 50 GHz (matching the FSR of the integrated wavelength meter ring resonator) were sent to a fast photodiode unit (65 GHz bandwidth) utilized to generate a 50 GHz beating signal (Fig. 1c) that showed a maximum deviation from the central frequency of ± 50 MHz over several hours. The developed chip promises to represent a crucial building block for the generation of stabilised sub THz and THz radiation through photomixing devices

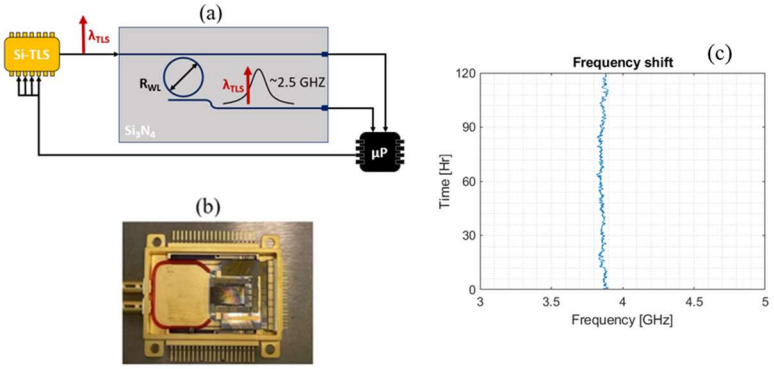

Fig. 1 Scheme of the *laser frequency stabilization set-up (a) through fully packaged Si_3N_4 PIC (b). the beating signal (50 GHz) RF mixed with a 46 GHz local oscillator to produce a 4 GHz signal revealed at the RF spectrum analyzer (c).*

References

[1] W. Shi, Y. Tian, A. Gervais, "Scaling capacity of fiber-optic transmission systems via silicon photonics", Nanophot. Vol.9, no.16 (2020).
[2] Moon SR, Han S, Yoo S, Park H, Lee WK, Lee JK, Park J, Yu K, Cho SH, Kim J. Demonstration of photonics-aided terahertz wireless transmission system with using silicon photonics circuit. Opt Express. 2020 Aug 3;28(16):23397-23408.

Holographic metasurfaces for biophotonics and sensing applications

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Short abstract: We present two holographic metasurface platforms, based on dielectric and plasmonic meta-atoms, for lab-on-chip imaging, sensing, and trapping applications.

Holographic metasurfaces are one of the most versatile platforms available for a burgeoning number of applications in photonics. The ability to control the scattering of light at a flat interface offers a large degree of freedom to design compact devices and materials with tailored responses to light [1]. From a technological point of view, metasurfaces are also perfectly aligned with most nano-photonics tools, which can easily create nano-features on virtually any type of substrates [2]. It is therefore not surprising that metasurfaces are increasingly employed for imaging and sensing applications in integrated devices. Here, we show that photonic metasurfaces are ideally suited for operation in a microfluidic environment, as they can be used to access specimens of interest with high spatial frequencies and proximity. These are two key desirable features of many bio-physics experiments, which are typically frustrated by the limited numerical aperture of the microscope objective used to access the sample [3].
Crucially, metasurfaces offer the possibility to conjugate a sensing function to imaging capabilities. Fig. 1a-d shows the capability of a holographic metasurface that produces an image which depends both on the wavelength of the light used and on the environment to which it is exposed [4]. Multiplexing information related to the refractive index of the surrounding medium is obtained by designing meta-atoms with resonant mode, with spectral features that shift when going from dry to wet. The metasurface operates in reflection, as it relies on a back-reflecting metallic layer. For some applications, a transmission configuration is desirable. For this purpose, we realized photonic metasurfaces based on zirconia. This material has the advantage of covering the full visible spectrum, being bio-compatible and extremely durable. To demonstrate the versatility of the platform, we designed an integrated microfluidic chip hosting a metalens that creates a tightly focused spot, which can be used to trap micrometric dielectric particles, in the visible range.

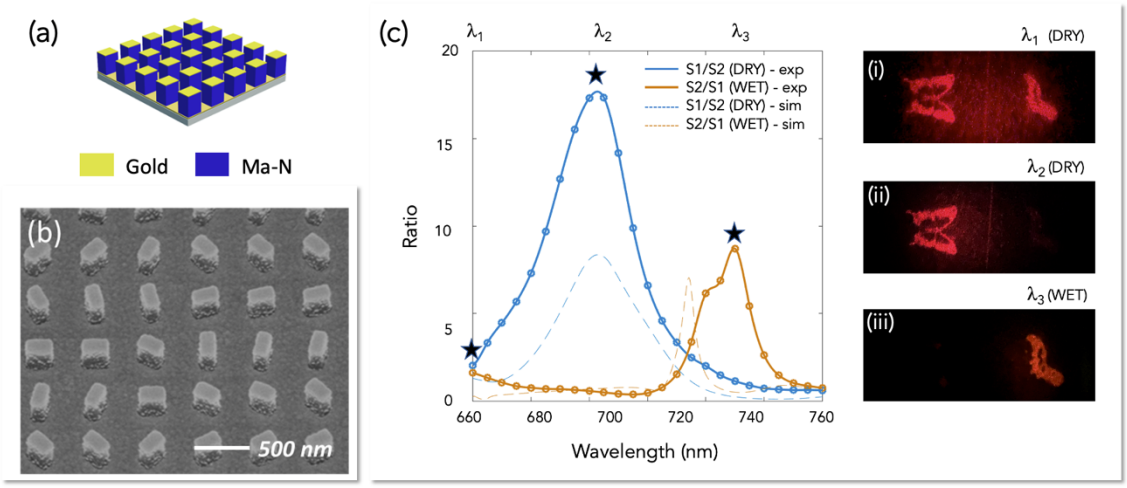

Fig. 1 (a) Sketch of the metasurface. (b) SEM of the meta-atoms. (c) Ratio of the metasurface efficiency in dry and wet conditions [(i)-(iii) are the holographic images produces at starred wavelengths].

We believe that metasurface technology has the potential to impact considerably the field of integrated sensing and imaging. Our results contribute positively to this effort.

References

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[2] Burch, James, and Andrea Di Falco. "Surface topology specific metasurface holograms." ACS Photonics **5**, 1762 (2018).
[3] Askari, M., Kirkpatrick, B.C., Čižmár, T. and Di Falco, A., "All-optical manipulation of photonic membranes". Opt. Express **29**, 14260 (2021).
[4] Yan, Libin, Jianling Xiao, Tomasz Plaskocinski, Mohammad Biabanifard, Saydulla Persheyev, Meisam Askari, and Andrea Di Falco. "Two-tier manipulation of holographic information." Optics Express **30**, 19145 (2022).

Control of Fano Spectral Profile based on a Silicon Nitride Photonic Crystal-Micro Ring Resonator structure

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** These authors contributed equally to this work: jesushernan.mendozacastro@poliba.it and artem.vorobev@poliba.it*

Short abstract: We realize a compact and tunable Si_3N_4 Fano resonator based on a Photonic Crystal (PhC) side coupled to a Micro Ring Resonator (MRR). The structure can support Fano lineshapes with high-Q factor (10^4), and asymmetry with both air and water top cladding.

Fano resonances possess sharp asymmetric line shape with steep-like profile and high Q-factor, and thereby can be used for high-contrast sensitive sensing [1]. Due to the sharp Fano line shape, a very slight perturbation in local environment can cause a detectible change in the extinction, transmission, or reflection spectrum by the significant enhancement of the interaction of light with the surrounding media. We propose a PhC-MRR Fano resonator (see Fig. 1.) where the spectral profile can be tuned from asymmetric resonances to symmetric Lorentzian lineshapes.

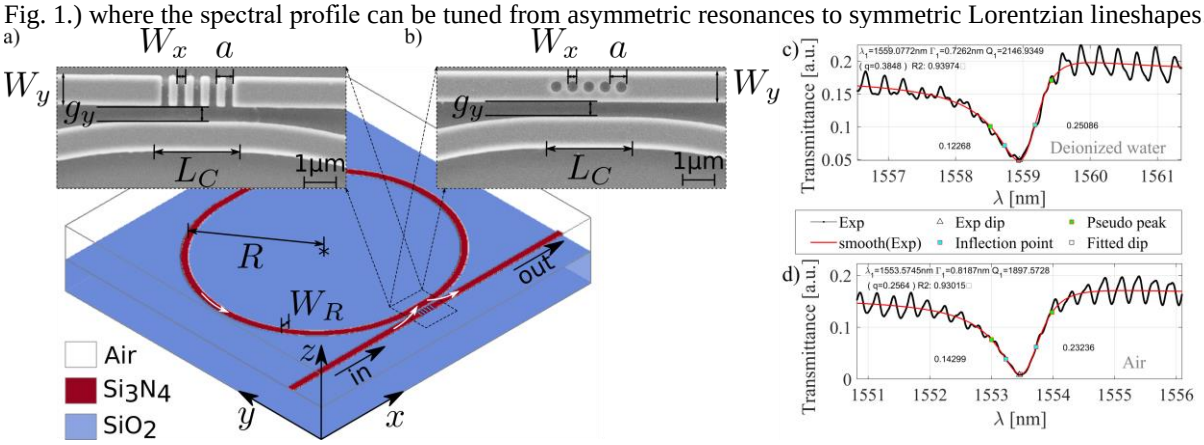

Fig. 1 (a) Schematic of the proposed PhC-MRR structure. The PhC integrate 5 rectangular or circular partially transmitting elements (PTE). The SEM image inset correspond to the coupling region of the fabricated device, where a= 550 nm (lattice period), W_x=200 nm and W_R= W_y=1100 nm. (b) Sketch and SEM image inset of the fabricated structure by PhC based air circles, where a=550 nm, W_x=300 nm, W_R= W_y=1100 nm. The coupling length in (a) and (b) is L_c=5a. The measured resonance of the proposed PhC-MRR for 5 rectangle PTEs and g_y=250 nm structure immersed on (c) Deionized water (DIW) and (d) air. Both shows experimental data in black and the fitted version in red. The adjusted parameters are shown upper left. The numbers next to the curve correspond to the calculated slopes based on dip, inflection, and pseudo peak points [2].

The fabricated devices, based on rectangles (Fig. 1(a)) and circles (Fig. 1(c)) shapes air-holes, were characterized when both air and DIW were considered as upper claddings. Fig.1 (c) and (d) exhibit an increment in the Fano asymmetry parameter q of ~1.55 times when a drop of DIW takes place. The asymmetric Fano-spectrum exhibited by our device would allow it to be use as a robust complex refractive index transducer for gas and liquid sensing due to the steeper resonances found [2–4]. Therefore, by engineering the coupling gap (g_y), the type (Circle or Rectangle) and the number of PTEs of the PhC-MRR structure is possible to achieve high Q-factor and q-asymmetry. In conclusion, a fully integrable, tunable, compact device compatible with many fabrication platforms and suitable for a refractive index sensor with improved limit of detection use [5], is presented.

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Infrared Sources and Detectors

The quantum cascade laser pumped molecular laser: a widely tunable source from 100 GHz up to more than 3 THz

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Short abstract: We demonstrate widely tunable THz emission at room temperature with potential for multi-milliwatts output power by pumping molecular gain media with a widely tunable quantum cascade laser. Laser operation is obtained with nitrous oxide, methyl fluoride and ammonia. We show how this laser is particularly relevant for molecular spectroscopy.

Generation of radiation in the terahertz frequency range (100 GHz to 10 THz) is a challenging problem. The lack of powerful and tunable sources in that frequency region can also limit the accuracy and resolution of spectroscopy techniques. In addition, the relevant part of molecules' rotational spectrum lies within that particular frequency region. While the ground state rotational spectrum of molecules is easily measured thanks to the large thermal population of lower rotational levels at room temperature, measuring the rotational spectrum of a molecule in the excited state can be much harder. Here we introduce the quantum cascade laser pumped molecular laser (QPML): a widely tunable source that can emit light between 100 GHz up to 10 THz and uses a widely tunable quantum cascade laser to pump ro-vibrational transitions. We first demonstrate the QPML concept using the nitrous oxide molecule[1], where more than 20 lines are measured between 300 GHz and 772 GHz. The concept was then further extended to the methyl fluoride[2] and ammonia[3] molecules. Compared to many existing THz sources, the QPML operates at room temperature, widely tunable and compact. We show that measuring the laser emission of a given molecule directly provides its rotational spectrum in the pumped excited state with +/-100 kHz accuracy. A derived system is presented that can further improve the accuracy of this technique. State of the art rotational spectroscopy of the nitrous oxide molecule has been obtained with this technique with the measurement of 20 lines, enabling recovery of the rotational spectrum with a +/- 5 kHz accuracy. Rotational constants were eventually recovered and a good agreement was found with existing work.

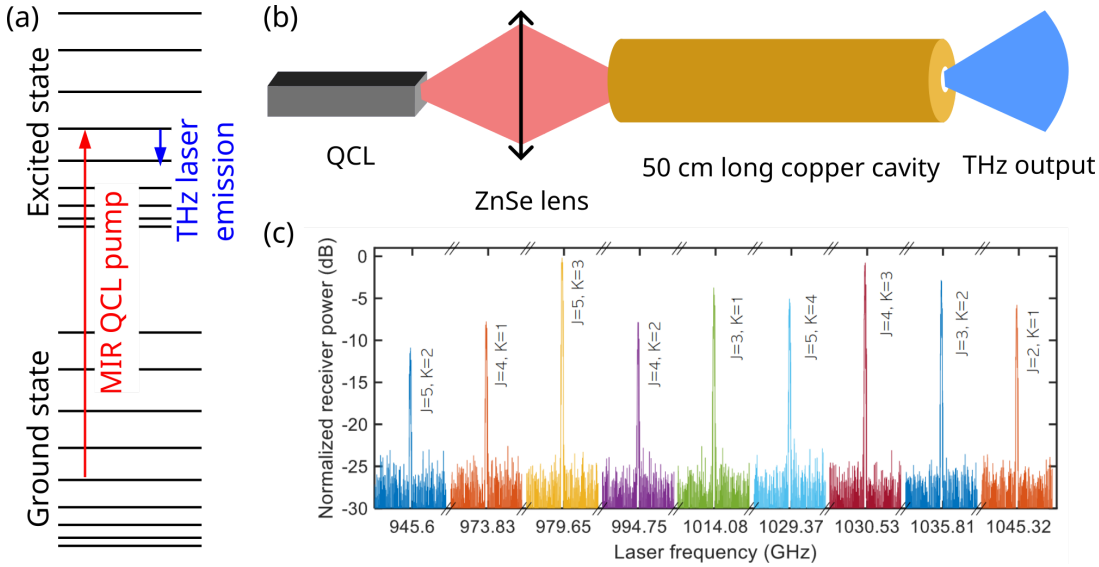

Fig. 1 (a) Energy level diagram showing the principle of the quantum cascade laser pumped molecular laser: light from a tunable QCL creates a population inversion between rotational levels in an excited vibrational state. (b) Basic schematic of the QPML principle. (c) Measured emission lines around 1 THz when using ammonia as the gain medium label as a function of the pumped transition quantum numbers.

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Broadband Room-Temperature Mid-infrared Detection with Nanoparticles

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Short abstract: By utilizing ratiometric luminescence, which can be modulated at MIR radiation under ambient conditions, a novel lanthanoid nanocrystal-based transducers for broadband mid-infrared (MIR) sensing is created. The high photostability and simplicity of processing provide opportunities for developing low-cost, scalable MIR imaging and spectroscopy techniques with unprecedented sensitivity.

MIR spectroscopy is widely used in life sciences, remote sensing, security, industrial imaging, and environmental monitoring. Despite significant attempts, the development of simple, low-cost, low-noise systems for MIR detection and imaging at room temperature remains a challenge. Converting MIR radiation to visible and near-infrared regions is an ideal approach, which can be easily detected and imaged with silicon photodetectors due to their high sensitivity, low cost, and CMOS compatible. Current MIR conversion technology is limited to nonlinear optics with bulky crystals[1] or resonant nanocavities[2], which suffer from low efficiency and phase match requirement.

Here, we report a transducers using lanthanide nanocrystals that realize broadband MIR detection under ambient conditions. The Nd doped $NaYF_4$ has two emission bands around 806 nm ($^4F_{5/2} \rightarrow {}^4I_{9/2}$) and 866 nm ($^4F_{3/2} \rightarrow {}^4I_{9/2}$), The 806 nm emission band is much weaker than that at 866 nm due to a nonradiative multiphonon-assisted depopulation process. Thanks to the ultralong luminescence lifetime of the metastable $^4F_{3/2}$ state, efficient MIR back-pumping from $^4F_{3/2}$ to higher energy levels ($^4F_{5/2}$, $^4F_{7/2}$) is possible. Consequently, the emission at 806 nm enhances drastically while that at 866 nm decrease significantly. With the improved sensitivity, stability, and fast response, we further performed proof-of-principle measurements for room-temperature MIR imaging using a low-cost CMOS camera. The broadband wavelength response ensures its application for MIR spectroscopy. The absorption spectra are recorded for gas mixture of CH_4, SO_2 and water from 1290 to 1670 cm^{-1} using lanthanide transducer.

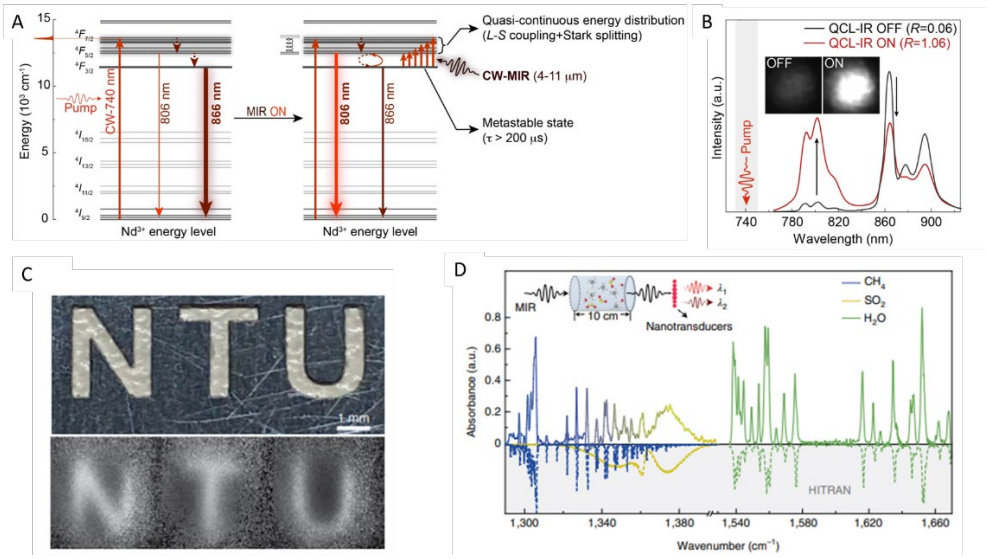

Fig. 1 (A) Working principle of broadband MIR sensing using Nd^{3+} nanotransducers. (B) Change in ratiometric luminescence nanotransducers with and without MIR radiation. (C) MIR imaging (7.3 μm) using lanthanide film captured by a CMOS camera. (D) Gas sensing for a mixture of CH_4, SO_2 and water using Nd nanotransducers. [3]

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Long wavelength distributed feedback tapered quantum cascade lasers

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Short abstract: We present an investigation on the electrical, optical, and spectral properties of distributed feedback tapered quantum cascade lasers emitting at 14-15 µm, based on the InAs/AlSb material system. Tapered lasers provide higher power outputs without degrading the beam quality. Devices with different taper angles were tested and compared with conventional ridge waveguide lasers.

Mid-infrared Quantum Cascade Lasers (QCLs) have drastically improved the quality of research and technology in many applications, such as free space communication, chemical sensing or imaging, and high-resolution spectroscopy. In some application, such as in photoacoustic and photothermal spectroscopy, high-power sources and good beam quality are two pre-requisites to achieve high performance. Within this context, tapered QCLs benefit from bigger active zone volume without degrading the quality of the fundamental transverse mode. The wider front facet further improves the quality of the beam along the slow axis, reducing its divergence angle [1].

In this work we present an investigation of tapered QCLs with taper angles ranging between 0° and 3°. The QCL was based on the InAs/AlSb material system emitting around 14-15 µm [2]. In this spectral range, BTEX compounds exhibit strong absorption, making such laser sources extremely interesting for environmental sensing applications. The presented devices feature an active zone composed of an InAs/AlSb superlattice sandwiched between undoped InAs spacers and highly-doped InAs cladding layers. The wafer grown by molecular beam epitaxy on an InAs substrate was processed into deep mesa ridge lasers using optical photolithography and wet chemical etching. Electron beam lithography and dry etching were employed to pattern Bragg gratings on top of the ridge waveguide. The periodicity of the grating was designed according to the Bragg law $\lambda_0 = 2n_{eff}\Lambda$, where Λ is the grating period, λ_0 is the vacuum wavelength at the gain peak and n_{eff} is the TM mode effective index obtained by simulation of the ridge waveguide. A grating periodicity of 2080 nm was used. A gold layer was deposited to provide electrical contact.
In Fig. 1(a) a scanning-electron microscope image of a straight device is shown. The devices were tested and compared in terms of electrical and optical properties, and in terms of spectral purity. Single-longitudinal mode operation was obtained, with a side-mode suppression ratio (SMSR) greater than 20 dB. In Fig. 1(b), emission spectra of a straight QCL, measured at different temperatures in CW operation, are portrayed.
In terms of optical properties, tapered device with higher taper angles provide a greater power output. An improvement of the slope efficiency is observed, which can be justified by the higher collection efficiency of the system towards higher taper angle devices. The larger front facet of tapered lasers reduces the divergence angle along the slow axis, allowing to collect more light. The far-field intensity profiles were measured in order to determine the beam divergence and estimate the devices brightness.

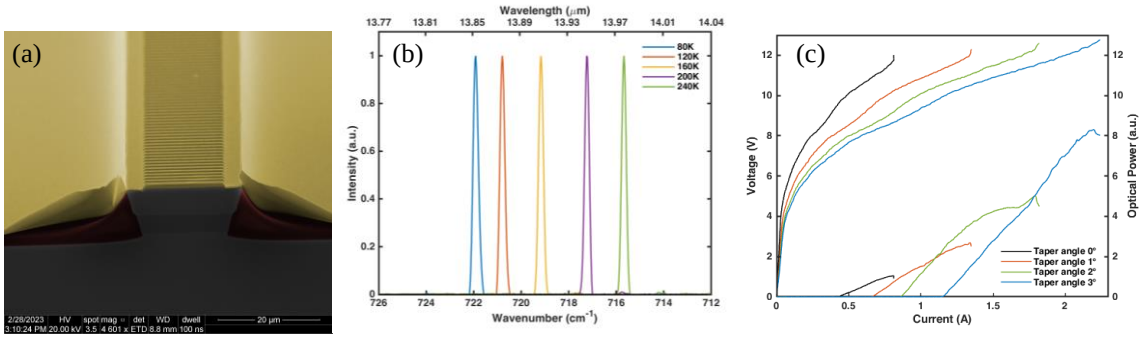

Fig. 1 (a) Scanning electron microscope image of the DFB-QCL. In yellow the gold layer, in brown the insulation layer and in dark grey the active zone of the device. (b) Representative straight DFB spectra, exhibiting single mode emission with a SMSR greater than 20 dB. The device was tested in CW operation at different temperatures. (c) Voltage-Light-Current curves for tapered devices, from 0° to 3° taper angles.

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Numerical and experimental analyses of optical coupling for GaSb diode lasers grown on Silicon substrate

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Short abstract: In this work, we model and experimentally demonstrate the optical coupling between a GaSb diode laser epitaxially grown on Silicon and butt-coupled to a silicon nitride waveguide. Coupling limits and approaches to mitigate them are also discussed.

The most mature technology enabling low-cost Photonic Integrated Circuits (PICs) is undoubtedly Silicon (Si) based platforms. The direct integration via epitaxy of III-V lasers on Si PICs will lead to low-cost, high integration density light sources on Si wafers. In this work, we study theoretically and experimentally the optical coupling between a 2.3 μm GaSb diode laser (DL) epitaxially grown on on-axis Si (001) [1], butt-coupled to SiN passive waveguides (WGs). Approaches to improve light transmission are also proposed.

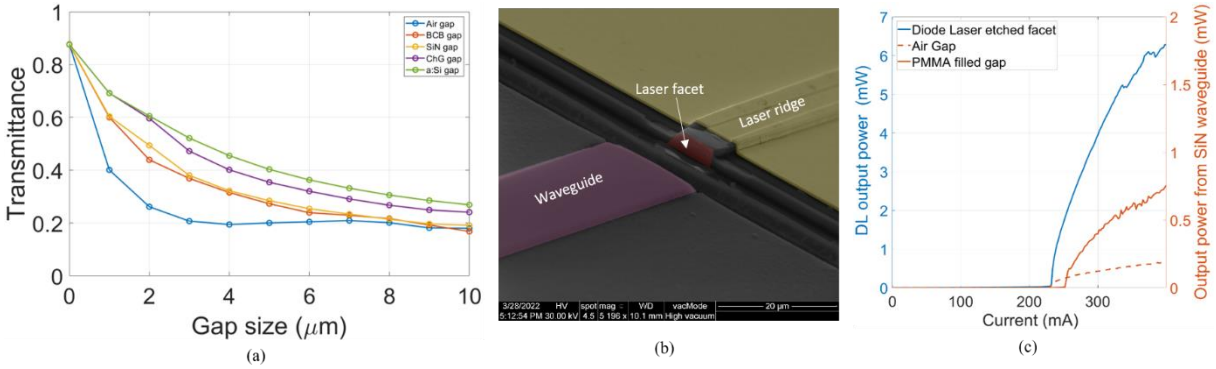

Fig. 1 (a) Numerical transmittance as function of gap sizes filled with different materials, for a SiN waveguide. (b) SEM details of the etch facet DL ridge and SiN waveguide in a butt coupling configuration. (c) Experimental L-I curves measured from a DL grown on Si butt-coupled to a SiN waveguide when the gap is air (red dashed curve) and filled with PMMA (red solid curve).

Definition of the cavity mirrors by etching the DL facets is mandatory for PICs with epitaxially grown lasers and this invariably results in an air gap separating the passive and active waveguides. Finite Difference Time Domain (FDTD) simulations of the coupling efficiency were first performed considering SiN passive waveguides clad by SiO_2 layers. Calculations show a drastic reduction of light coupling as the air gap increases (Fig.1 (a)). In order to experimentally prove the coupling, s-shape SiN WGs cladded by SiO_2 were patterned on Si substrate and recesses were defined to expose the Si substrate for the epitaxy. The DL heterostructures were grown by Molecular Beam Epitaxy and the facets were etched to achieve a butt-coupled configuration (Fig.1 (b)). The measurements confirm that light is coupled into the SiN WG (Fig.1 (c)) in agreement with the simulation results. Filling the gap with high-index materials is an approach for improving the transmission [2]. Polymers (e.g. PMMA) represent a straightforward option for filling the gap. The L-I curves (Fig.1 (c)) confirm the expected coupling improvement at the expense of a slight increase in the threshold current because of the lower facet reflectivity. Suppressing the gap by spin-coating polymers and patterning polymer-based WGs is another promising option. FDTD simulations show that high light transmission is expected in this configuration [2].

This work demonstrates the achievement of light coupling with DLs grown on a Si PIC and offers strategies to increase the coupling efficiency. This paves the way to fully monolithically integrated Si photonic chips for sensing applications.

Part of this work was supported by the French program on "Investments of the Future" (ANR-11-EQPX0016), the French ANR (ANR-19-CE24-0002) and the European Union (GA 780240 and 860808).

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Extended wavelength tuning of multi-section interband cascade lasers with slotted waveguides above 3 µm

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Short abstract: The design concept for Vernier tunable lasers will be employed on interband cascade laser architecture to extend the wavelength tuning range achievable in a multi-section device with slotted waveguides. This design involves four independently pumped stages that allow for quasi-continuous tuning over the emission range around 3.6 µm. Simulations and results are presented for the first implementation of this proof of concept design on Sb based materials.

Interband cascade lasers (ICLs) fabricated using Sb based III-V materials provide sources for the mid-infrared spectral range between 3 – 6 µm with low power consumption and efficient performance [1]. This spectral band is of particular interest to the detection of gasses involved in petrochemical processing, such as methane, ethane, and carbon dioxide since they have strong absorption in this range [2]. Correctly identifying a gas present in a sample requires single-mode emission and some tuning to match the absorption line, depending on the environmental conditions. Identifying multiple species is often done using multiplexing schemes with multiple lasers sources. Increasing the tuning range possible with one laser source allows for new possibilities in spectroscopic applications such as the ability to detect multiple gas species with one sensor.

Distributed feedback (DFB) ICLs are commercially available and used in these applications, but in order to offer a wider tuning range or to detect multiple gas species, multiple lasers are packaged together increasing costs and complexity. Other configurations that employ the Vernier tuning principle are seen in binary superimposed gratings (BSG), for example, that combine two DFB gratings and offer a wide tuning range but is not continuous [3]. An economical design alternative to the DFB has been recently demonstrated using a slotted waveguide on ICLs [4]. This allows a monolithic design frequently employed at telecommunications wavelengths using slotted waveguides in a Vernier tuning configuration; offering up to 50 nm at 1.5 µm of quasi-continuous tuning [5,6]. Meanwhile, external cavity ICLs achieve a tuning range of 150 nm at 3.2 µm and 300 nm at 3.8 µm due to the broad gain bandwidth of the ICL active medium [7,8]. Similar tuning ranges are expected to be within reach of slotted Vernier tuned ICLs, whose configuration is depicted below in Fig. 1. The geometry of the waveguide is simulated using FIMMWAVE to solve for dimensions that offer constructive/destructive interference at the wavelength of interest within the gain bandwidth supported by the material. Progress towards single-mode room temperature emission in continuous wave operation with ICLs will be presented.

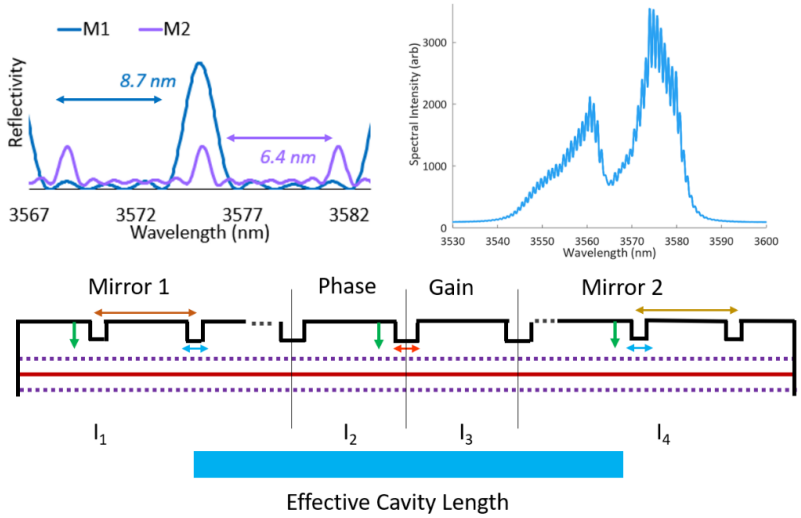

Fig. 1 *(Top Left)* Simulated reflectivity peaks from two different mirror patterns used to filter out a laser mode using the principle of Vernier Tuning. *(Top Right)* Spectral emission of FP ICLs fabricated on the material that will be used to develop the SVT ICLs, taken in pulsed mode at room temperature. *(Bottom)* Schematic of the SVT ICLs, complete with 4 sections independently pumped.

Acknowledgments: This project is part of the OPTAPHI Training Network and has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie agreement No. 860808 and the French program on "Investments for the Future" (ANR-11-EQPX-0016).

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Influence of incubation effect and repetition rate on multi-pulse fluence threshold for femtosecond-laser processing of quartz

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Short abstract: Ultra-fast pulsed laser machining is one of the most employed techniques for superficial texturing of solid materials. However, this method has rarely been used for micromachining of quartz, so in this work the multi-pulse fluence threshold and the incubation effect were investigated for quartz.

In this study, the influence of the incubation effect and the repetition rate on femtosecond-laser (fs-laser) processing of quartz was investigated. The multi-pulse ablation threshold of quartz was evaluated using 200 fs laser pulses at a wavelength of 1030 nm and at four different repetition rates, i.e., 0.06, 6, 60 and 200 kHz. Our results show a strong decrease in the multi-pulse ablation threshold with the number of pulses N, finding the role of incubation during the fs-laser ablation of quartz. Conversely, the influence of the repetition rate on incubation was negligible in the investigated frequency range. A saturation of the threshold fluence value is shown to occur at number of pulses N > 100 and well fitted by an exponential incubation model[1]. Using such model, we estimated the single-pulse ablation threshold value and the incubation coefficient for quartz.

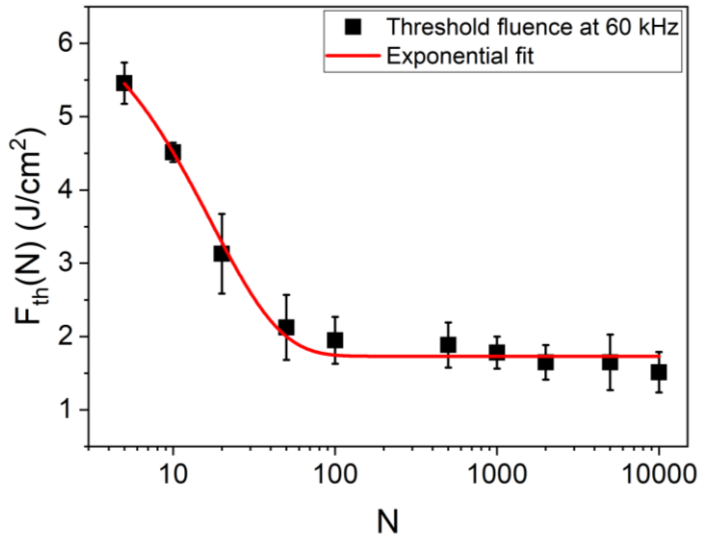

Figure 1. Multi-pulse fluence threshold Fth(N) as function of N at 60 kHz with the relative exponential fit

These data were then used to generate Laser-Induced-Period-Surface-Structures (LIPSS) on quartz surface which were found to enhance quartz hydrophilicity, decreasing the water contact angle (CA), from CA = 41° for pure quartz to 7° for LIPSS-textured quartz.

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Hybrid Sources and Fibers

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Evanescent-field fiber sensors

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Short abstract: The interaction of the evanescent field with the medium surrounding the fiber core can be used to set up compact sensing systems for gases or fluids. Different sensing devices, like etched fiber-bragg-grating sensors and waveguide based arrayed waveguide gratings for readout of wavelength shifts will be discussed.

Fiber optics are inherently advantageous for the setup of sensing devices: they are small in size, chemically robust and can for example be operated in environments with high magnetic fields or even in explosible regions. Conventional optical fibers are designed to guide light over large distances and thus prevent the interaction of the surrounding medium with the guided light due to their composition of core, cladding and coat.
However, interaction can be enabled by partially removing coat and cladding. Then, total internal reflection takes place at the interface between core and surrounding medium – changes in the outer medium then alter the guiding performance which can be caused by a change in refractive index or by absorption or a combination of both. In most cases, the signal is sensitive to changes in refractive index which can be caused by various substances or concentration changes in the surrounding environment. To achieve selectivity, the sensing region is often coated with special receptor molecules that enrich the species of interest close to the interface.
To enhance sensitivity, the change of the reflection characteristics of a fiber bragg grating (FBG) can be utilized instead of the change in transmission through a fiber. To setup a so-called etched-FBG or eFGB sensor, a fiber bragg grating is written into a standard single mode fiber close to the fiber tip with a femtosecond laser. Subsequently, the cladding is removed by wet etching. A second FBG written in the non-etched part is used as reference to account for and eliminate changes caused by temperature fluctuations.
Readout is commonly done by analysing the shift in bragg-wavelength caused by a change in refractive index. This can be done using a compact spectrometer, or with an arrayed waveguide grating (AWG) which can be processed as planar device. By design of the AWG, the covered spectral region and resolution is adapted to enable readout of the specific FBG-peaks and their shifts. Different sensing schemes will be discussed.

Antiresonant Hollow-Core Fiber and Kagome Hollow-Core Fiber assisted Wavelength Modulation Spectroscopy of ethane in the mid-IR

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Short abstract: In this work, we present the first direct comparison of mid-infrared Wavelength Modulation Spectroscopy-based detection of ethane at parts per billion by volume level using 1.3 m long absorption cells formed by an Antiresonant Hollow-Core Fiber and a Kagome Hollow-Core Fiber.

The rapid development of microstructured fiber technology, especially with regard to the design and fabrication of hollow-core fibers (HCFs), has significantly broadened the application area of optical fibers. The unique structure and light guidance properties of HCFs have made these fibers successfully used in laser-based spectroscopy of gases [1,2]. Since the HCF core is essentially empty, it can be easily and effectively filled with a target gas sample, and the gas-filled fiber can be used as a long, low-volume, versatile gas absorption cell within the sensor setup, providing alternative solution to commonly used multipass cells. To date, several types of different HCFs have been combined with various laser-based spectroscopic techniques, amongst which the Antiresonant Hollow-Core Fibers (ARHCFs) and Kagome HCFs have been shown to deliver the best performance in terms of low-loss guidance in the mid-infrared (mid-IR) spectral band and gas-filling capability [1,2]. However, direct comparison of both fibers in gas sensing has not been reported to date. In this work, we present for the first time a direct comparison of the application of both fibers in the mid-IR detection of ethane (C_2H_6) using the Wavelength Modulation Spectroscopy (WMS) technique. The 1.3 m long ARHCF and Kagome HCF used in the experiments had hollow cores with diameters of 84 µm and 116 µm, respectively. The input end-facets of the fibers were closed in specially designed chambers, which enabled their efficient gas-filling and light coupling into the HCFs. The C_2H_6 molecules were simultaneously excited inside the fibers using a custom built difference frequency generation source that emitted continuous wave radiation at 2996.88 cm^{-1}. During the measurements, ARHCF- and Kagome HCF-based absorption cells were filled with C_2H_6 with different concentrations and 2f WMS signal spectra for each fiber were recorded. The measurement results are depicted in Fig. 1.

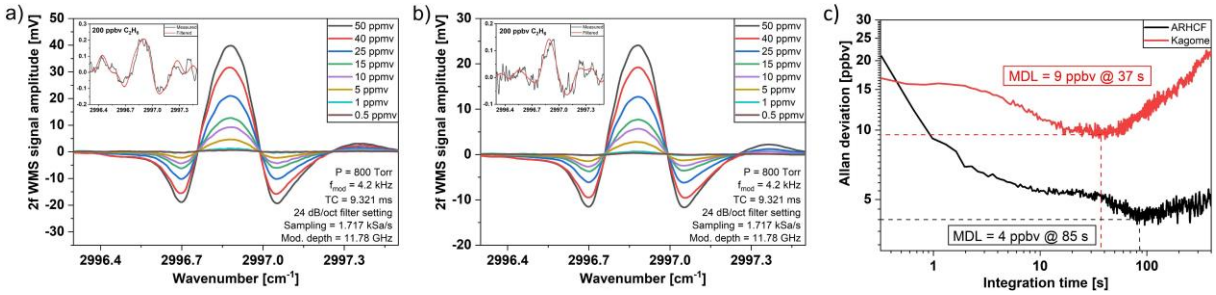

Fig. 1 Results of C_2H_6 detection in a 1.3 m ARHCF and a 1.3 m Kagome HCF. 2f WMS signal spectra registered for different concentrations of C_2H_6 within: (a) ARHCF, (b) Kagome HCF. (c) Allan deviation measured from the sensor's 2f noise amplitude recorded over a 60 min period of time while both fibers were filled with pure nitrogen.

The experiments showed that ARHCF delivers a minimum detection limit and stability more than two times better than Kagome HCF. This results from the multimode nature of the Kagome HCF [2], which leads to intermodal interference within the measurement path, manifesting itself as a parasitic modulation of the retrieved signal. Furthermore, the amplitude of the registered 2f WMS signals in the case of the Kagome HCF is reduced in contrast to that of the ARHCF. This is an effect of the sensitivity of the Kagome HCF to the refractive index change along its length induced by the presence of the measured gas and the increased pressure in its structure, leading to a modification of the guidance properties of this fiber.

Funding

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Graphene Electrodes on Silicon Nitride Devices for Near-Infrared Wavelength Tuning

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Short abstract: In this work, we present the integration of monolayer Graphene Electrodes (GE) in Silicon Nitride waveguides to achieve wavelength tuning in the Near-Infrared (NIR) range. The Electrolyte – monolayer Graphene – Waveguide (EGW) structure analysis and its fabrication process are presented.

Graphene, a semi-metallic 2D material with a zero-band gap with tunable and wideband optical properties, opens a new window into the field of near-infrared wavelength tuning. The tightly confined within the single graphene atomic layer free electrons create a very low density of states condition (especially when electron energy is close to the Dirac point). According to this property of graphene, the carrier density changes cause significant shifts in Fermi energy [1]. This action effects on the rate of interband transitions and therefore the optical constant. Therefore, its Fermi level can be tuned under external electric field, covering the range from NIR to THz wavelengths [1,2].

The integration of graphene electrodes with silicon nitride (Si_3N_4)-based devices is a promising way to improve tunability in the NIR range [3]. This choice is motivated by Si_3N_4 low optical losses (< 1 dB/cm), transparency over a wide wavelength range (400-2350 nm) and low thermo-optic coefficient (~2.45e-5 K^{-1} at 1.55 µm).

In this work, we analyse and experimentally characterise the Electrolyte Graphene Waveguide (EGW), in which the electrolyte is located above the GE as in Figure 1a, Si_3N_4-based Tunable Waveguides (TW) configurations (Figure 1b) and experimentally characterized (Figure 1c).

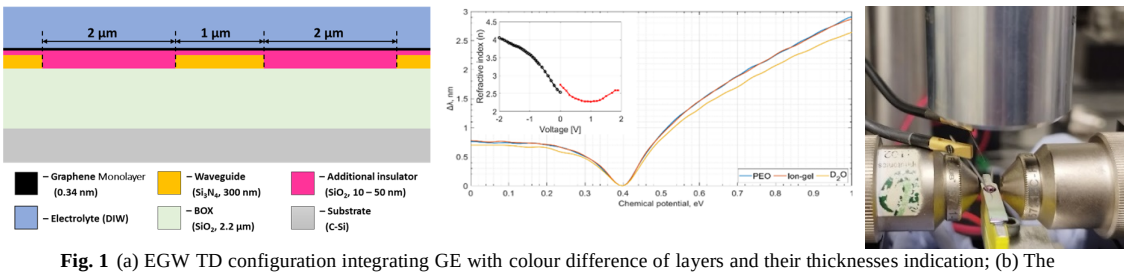

Fig. 1 (a) EGW TD configuration integrating GE with colour difference of layers and their thicknesses indication; (b) The $|\Delta\lambda|$ depends on the change in chemical potential for different electrolyte materials and measured dependance of the Graphene refractive index on the applied voltage (inset); (c) Fabricated Monolayer Graphene on Silicon Nitride Tunable Devices chip placed in the endfire setup..

The numerical results shows that it is possible to achieve a wavelength shift of several nanometers. An analysis of the experimental data on the additional insulator layer thicknesses (introduced to prevent potential carrier injections from the GE into the waveguide [3]) and their influence on tunable waveguides transmission is also carried out.

This work will help guide the design and fabrication of the wavelength tuning of graphene-based optical operating in the NIR. Presented TDs can be used in the implementation of high-precision tunable lasers with an external cavity.

We acknowledge the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 860808 (OPTAPHI).

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Photonic crystal hybrid lasers for intra-cavity Quartz enhanced Photo-acoustic spectroscopy (QEPAS) and Photo-thermal spectroscopy (PTS)

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Short abstract: This project deals with the design, fabrication and characterization of a photonic crystal(PhC) hybrid laser for intra-cavity QEPAS and PTS used for atmospheric sensing. To perform as an efficient excitation source for sensing, the laser has been optimized for its properties like single frequency, temperature stability, compactness, wavelength tunability and good output power.

Unmonitored anthropogenic activities leads to detereorating air quality due to toxic gases and volatile organic components like Benzene, Toluene, Ethylbenzene and Xylene(BTEX) with catastrophic effects on all life forms. Hence it is extremely important to monitor the air quality which creates a necessity to develop new compact photo-acoustic and photothermal sensors. The optical part of these sensors has an excitation source and probe source (in the case of PTS). The aim of this project is to develop an efficent excitation laser which meets the qualities like single frequency, temperature stability, wavlength tunability which increases the efficiency of these sensors.

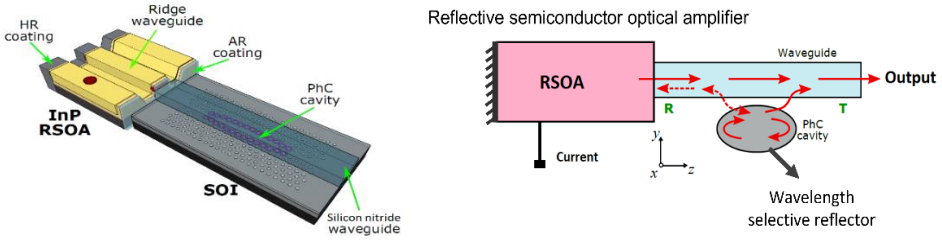

Fig 1 : 3D and 1D outer structure of the hybrid laser

The gain medium is electrically pumped to emit amplified spontaneous emission (ASE) which then travels through a silicon nitride (SiN) waveguide coupled to a 1-D PhC cavity to give a wavelenth selective feedback. The single frequency operation is associate with the wavelength selective 1-D photonic crystal reflector. Novel 1-D reflectors namely curved waveguide nanobeams were designed for high side mode suppression ratio (SMSR) and high Q factor to avoid mode hopping.

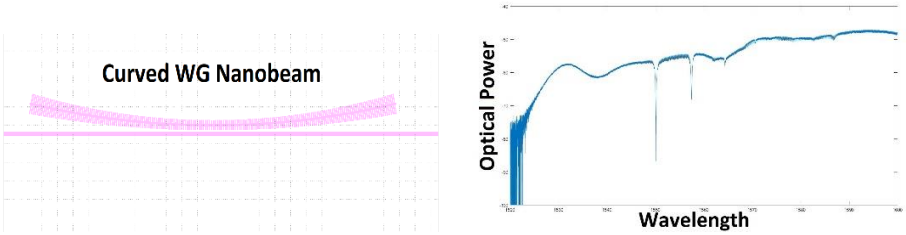

Fig 2 : Geometry and optical spectrum of curved WG nanobeams (High SMSR with just two resonances are observed)

Temperature stable operation (athermal) is achieved by freezing the net optical path length ($n \times L$) of the device by cladding the SiN waveguide which has a positive thermo optic coefficient (TOC) with SU8 polymer having a negative TOC. By adjusting the lengths of the respective SiN and SU8, the effects can be made to cancel each other in temperature ranges (0^0C to 10^0C). Without SU8 balcing, the Fabry-Perot fringe shift was observed to be 0.8 nm and with SU8 compensation it was reduced to 0.234 nm.
After optimizing each part of the laser, the next step would be to combine all parts for the lasing operation and then integrate the laser in QEPAS and PTS setups.

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Indium Fluoride Multimode Optical Fiber Coupler

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Short abstract: The design and the characterization of a novel 2×2 coupler, fabricated using indium fluoride optical fibers, is illustrated. The obtained results indicate that such fused optical fiber components can be manufactured and utilized in the Mid-infrared spectrum reaching low insertion losses and high transmission efficiency.

During the last years, Mid-infrared (Mid-IR) spectral range is attracting for its potential application in various areas, such as spectroscopy, chemical sensing, thermal imaging and light sources [1, 2]. In particular, the development of Mid-IR optical fiber lasers, operating in both continuous wave (CW) and pulsed regimes, is growing thank to the introduction of novel materials and dopants. However, the realization of compact, low cost and all-in fiber set-ups is still limited by the technological maturity of Mid-IR components, including couplers, combiners, splitters [3]. These components are typically made with soft glasses (e.g., chalcogenide or fluoride glasses), which exhibits optical transparency in Mid-IR wavelength range, and fabricated via fused biconical taper. The main drawbacks in the realization of chalcogenide/fluoride couplers, are the mechanical weakness, the need of accurate temperature/tension control and glass crystallization, which may result in considerable propagation losses [3]. Up to now, side-polished bonding and fused biconical tapering technique have been demonstrated for the fabrication of couplers based on ZBLAN fluoride optical fibers [2]. In terms of reliability and repeatability, the latter technique is considered to be superior to side-etching and side-polishing [4]. We report the fabrication of a novel 2×2 indium fluoride optical fiber coupler via Vytran® GPX-2400 glass processing system. Two identical pieces of IFG MM (0.30) 100/160 (Le Verre Fluoré, Bruz, France) optical fibers are cleaved through Vytran® LDC-400 cleaver. The optical fibers are inserted within a indium fluoride capillary (low refractive index) and clamped between two fiber holding blocks. By using a filament starting power $P_s = 12.2\ W$, the whole device is tapered down, reducing the initial diameter by six times. The measured capillary diameter in the waist region is $d_{cap,w} = 80\ \mu m$. In Fig. 1, the longitudinal view of the fabricated coupler, taken with Vytran® CCD camera, is reported. Moreover, Fig. 1 demonstrates absence of surface crystallizations. Fig. 2, taken with Dino-Lite camera, shows on the left, the graphite filament of the Vytran® while, on the right, the waist region of the coupler. The through port and cross port transmissions are experimentally characterized at the wavelength $\lambda = 1550\ nm$, measuring a coupling ratio of 85:15. The fabricated coupler pave the way to manufacturing high-quality fused devices and fill the gap in the Mid-IR applications [5].

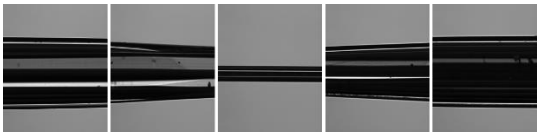

Fig. 1 Montage of optical micrographs, longitudinal view, of the 2×2 indium fluoride optical fiber coupler.

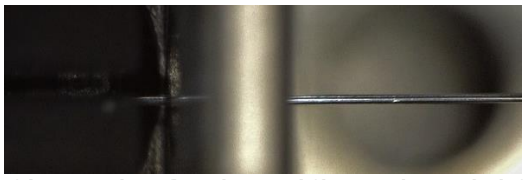

Fig. 2 On the right, the waist of the 2×2 indium fluoride optical fiber coupler; on the left, the graphite filament.

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Frequency Comb and Optical Power Build-up Approaches

Integrated optical frequency combs for mid-infrared spectroscopy

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ABSTRACT

Quantum cascade lasers have been shown to emit optical frequency combs with high optical power (1W) and excellent coherence. We will discuss the recent progress in this area, including the achievement of very short optical pulses (630fs) as well as the generation of highly controlled combs in ring lasers.

Constant progress in external cavity lasers as well as the recent demonstration of comb operation in quantum cascade lasers[1] has opened up new avenues for mid-infrared broadband optical spectroscopy. Indeed, dual comb spectroscopy with quantum cascade laser combs enables broadband measurements of chemicals with no moving parts. Recently, continuous tuning of these devices has enabled the measurement of very narrow absorption gas absorption lines (~100MHz) over a full bandwidth of 55cm^{-1} with an acquisition time of only 120ms[3], enabling their use for the study of chemical reactions and combustion analysis[4][5].

The quality of these dual-comb instruments depends greatly on the development of new QCL combs with high performances. We demonstrated a comb device delivering 1 watt of optical power over a bandwidth of more than 100cm^{-1} at 8μm wavelength[6].

Along with the engineering of widely broadband gain active regions, the possibility of achieving optical frequency combs is intimately related to the intersubband physics of the device and the presence of a very strong and broadband four wave mixing non-linear process that locks the modes together. The physics of the locking mechanism is very rich, and measurements of the phase relation between modes exhibiting a linear chirp of the optical frequency during one round trip of the cavity. Because this corresponds to phase that can be compensated using a grating-based stretcher compressor and further controlled by RF injection[7], quantum cascade laser based optical frequency comb generation allowed the generation of pulse as short as 630fs after compression. These results were verified using an upconversion technique with a sub-picosecond time resolution[8].

Another extremely promising avenue is the direct generation of optical solitons using ring quantum cascade lasers in which, by using a very low lateral loss waveguide, the symmetric counter-propagating modes undergo a spontaneous symmetry breaking and generate solitons[9]. We will discuss new results using RF injection in rings with very low backscattering.

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High-speed dual-comb spectroscopy in the 8-12 µm region

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Short abstract: We demonstrate dual-comb spectroscopy in the 8-12-µm range from two compact Erbium fiber combs at 250 MHz. A mode resolved spectrum acquired at Δf_{rep} = 1.6 kHz over a total time of 3·100 ms shows a promising figure of merit in excess of 10^7 $Hz^{0.5}$.

Dual-comb spectroscopy (DCS) has become a popular method for measuring gas absorption spectra over wide ranges with high temporal resolution [1]. The application of this technique to the mid-infrared region is essential for studying chemical kinetics in combustion environments, where strong absorption features are necessary to enhance the signal-to-noise ratio over a short measurement time due to the typically short absorption path length [2]. Recently, DCS has been demonstrated at full resolution in the water-free 8-12 µm absorption region, but this required a complex setup driven by self-referenced Chromium combs at a repetition frequency (f_{rep}) of only 80 MHz [3]. In this study, we demonstrate DCS between 8 and 12 µm using two compact Erbium fiber combs at a repetition frequency of 250 MHz, allowing for 10 times larger optical bandwidth to be observed without aliasing effects. Mid-infrared radiation is generated through difference-frequency-generation (DFG) between two phase-coherent pulse trains, one at 1.55 µm and the other around 1.85 µm [4]. The spectrometer was tested on an N_2O sample diluted in air, and the interferograms were phase-corrected through software using beat notes between the two combs and a pair of cw lasers [5]. A mode resolved spectrum was acquired over a total time of 3 x 100 ms, with a figure of merit computed to be ~2 x 10^7 $Hz^{0.5}$ [6].

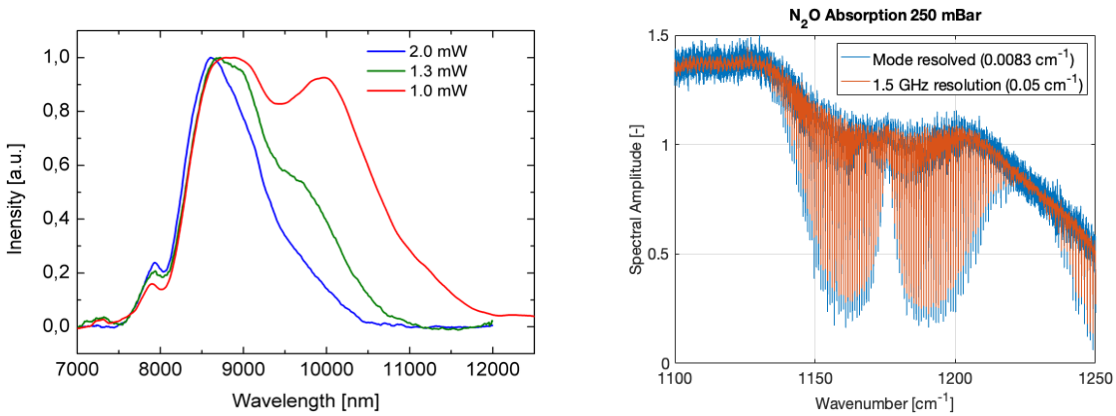

Fig. 1 (a) DFG spectra and optical power obtained upon slight frequency tuning of the signal pulses and adjustment of the phase-matching condition. (b) Comb-mode resolved N2O absorption spectrum with and without apodization

The spectrometer's performance is currently being evaluated by testing it at increasing values of Δf_{rep}, up to 10 kHz, within band-passed optical windows in the 8 to 12 µm range. The purpose of this testing is to determine the detection limit of various molecular compounds over measurement times of less than a millisecond, which is necessary for studying transient, non-repetitive phenomena in experiments related to combustion.

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Atmospheric measurements using open-path mid-infrared dual-comb spectroscopy

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Short abstract: We show results from a multi-month field deployment of an open-path mid-infrared dual-comb spectrometer operating in the 3-4 µm spectral region. This system measured methane, ethane, formaldehyde, N_2O, CO_2, and water isotopologues with 2-minute time resolution. We discuss applications of the data to climate change and air quality.

Open-path measurements of atmospheric gas species over km-scale path lengths are well suited to quantify emissions from sources like oil and gas, forest fires, and industry. Open-path dual-comb spectroscopy (DCS) combines high-resolution and broad spectral coverage with no instrument lineshape and near perfect frequency calibration. These features have enabled open-path DCS to provide accurate measurements of multiple trace gas species simultaneously in the near-infrared (NIR) across path lengths ranging from 100 m to several km. However, operation in the mid-infrared (MIR) spectral region can enable detection of more gas species. One important class of species are volatile organic compounds (VOCs), some of which are direct health hazards [1] and most of which are photochemically reactive and thus lead to increased ozone (O_3) production [2].

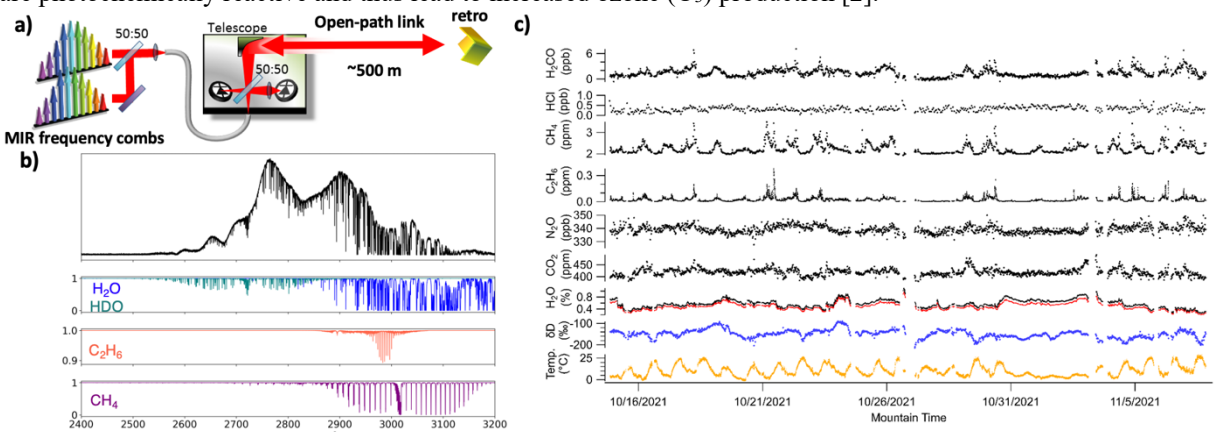

Fig. 1 Open-path MIR DCS. (a) Two MIR frequency combs are combined and coupled via fiber to a launch/receive telescope, which sends the light over a long open-air path to a retroreflector. The return light is detected with a photodetector at the telescope. (b) Example measured transmission spectrum and fit transmission spectra from several major species. (c) Time series of retrieval results over 3.5 weeks.

We have developed a robust MIR DCS system covering the 3-4 µm spectral region using difference frequency generation from NIR frequency combs [3]. We deployed this system at a field site in north-eastern Colorado for 4 months. This site is located in the Denver-Julesburg oil and gas basin and in an area with a large number of confined animal feeding operations, leading to a complex mixture of trace gas emissions. The system ran autonomously for much of this deployment with an uptime of >60 %. Fig. 1b) shows an example transmission spectrum measured at a 2-minute time resolution across a 475-m open-air path. Fig. 1c) shows the time series of retrieved trace gas concentrations for a 3.5-week time period. The data from these measurements show several interesting features. First, we see large variations in ethane (C_2H_6) that correlate strongly with methane (CH_4) variations, which is indicative of oil and gas CH_4 sources. By combining this data with separate ammonia (NH_3) measurements, we can attribute the observed CH_4 to the oil and gas and agricultural sectors. In addition, we observe formaldehyde (H_2CO), which is an important species for understanding O_3 formation [4]. We see H_2CO plumes that are correlated with C_2H_6, indicating oil and gas related sources of H_2CO (likely from combustion). We can also combine the H_2CO measurements with co-located nitrogen dioxide (NO_2) to show that O_3 formation is primarily VOC-limited in the fall to winter in this region.

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Optical Build up cavities for indirect spectroscopy fabricated using silicon processing technologies

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Short abstract: The sensitivity of spectroscopic techniques such as Quartz Enhanced Photoacoustic Spectroscopy and Photothermal Spectroscopy can be enhanced by using an optical build up cavity. Current approaches use large Fabry-Perot cavities that are many centimetres in length, which thus lack robustness. We are developing a compact Fabry-Perot cavity based on Distributed Bragg Reflectors and high contrast gratings fabricated on silicon.

The sensitivity of spectroscopic techniques such as Quartz Enhanced Photoacoustic Spectroscopy and Photothermal Spectroscopy can be enhanced by performing measurement inside a Fabry Perot cavity for the excitation laser as the intensity builds up and enhances the sensitivity by several orders of magnitude. Using an optical table-based experiment, a sensitivity of a few tens of ppt has been realised by Hayden et a. with excellent normalised noise equivalent absorption [1]. Crucially, the build-up of optical power requires efficient injection of the light into the cavity and delicate alignment, limiting intracavity enhancement to laboratory use and making the technique incompatible with portability.

We are developing a a compact Mid-IR Fabry-Perot cavity based on a millimetre-long resonator employing advanced silicon-based reflectors gratings and fabricated using semiconductor processing techniques, see figure 1. Laser diced silicon will be used to provide spacers that ensure that the mirrors are in near perfect alignment. The resulting FP cavity will be mechanically stable allowing deployment in a range of applications.

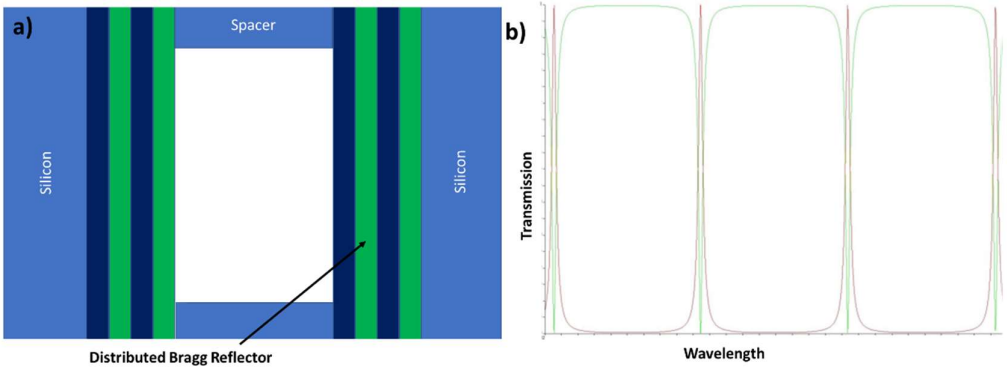

Fig. 1 Reflection and Transmission spectra of 2 pair SiN/Si FP structure with 1mm cavity

A number of different approaches will be followed, including metal mirrors, Distributed Bragg Reflectors and high contrast gratings. The first will be the realisation of a mid-IR Fabry-Perot based on a planar Fabry Perot cavity utilising Distributed Bragg Reflectors based on deposited Silicon nitride and polysilicon layers, see figure 1. In the final phase, one (or more) of the mirrors will be replaced by a high contrast grating [2,3] realised in a polysilicon layer on a silicon nitride lower cladding. The grating will be fabricated using electron beam lithography and dry etching.

Fabry Perot cavities fabricated using silicon processing techniques promises to provide robust low cost optical build up cavities for use in indirect spectroscopy, which will lead to enhanced performance and sensitivity.

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Bow-Tie Cavity for I-QEPAS for Isotope Analysis: Design and Optimization

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Short abstract: Space optic bow-tie cavity is implemented to enhance optical power at mid-infrared region. An acoustic detection module, a gas cell that contains microresonator tubes and custom quartz tuning fork, is placed at the cavity beam waist. As the gas is excited, the induced photoacoustic signal is read by the fork.

Although methods such as accelerator mass spectroscopy have been commonly used for isotope ratios analysis, the demand for high sensitivity, high speed, and compact system for on-field analysis has brought an intense interest to optical techniques of detection. Intracavity-Quartz-Enhanced Photoacoustic Spectroscopy (I-QEPAS) is chosen for this work. Since QEPAS can reach lowest detection limit, limited by the thermal noise of the quartz tuning fork [1], enhancing the intracavity power can improve significantly the signal (*Eq.1*) and therefore the sensitivity.

$$S \propto \Delta T \propto \frac{\epsilon(\upsilon) \cdot c_m \cdot P}{f_{mod} \cdot A \cdot \rho \cdot C_p} \qquad (Eq.1)$$

ΔT is photo-induced temperature change, $\epsilon(\upsilon)$ molar absorption coefficient, c_m molar concentration, P incident optical power, f_{mod} modulation frequency, A cross-section, ρ density, C_p heat capacity.

The standard two mirrors cavity can provide optical build-up with less complexity, but it has limitations when employed in spectroscopy including the need of an optical isolator at Mid-IR, and of a small focal point at fix position while tuning the cavity length to cover a wide range of the absorption line. To get rid of these limitations, for the proposed I-QEPAS, a bow-tie cavity composed by two curves and two flat mirrors with near-normal incident folding angle will be realized. Locking mechanism will be developed also to make the system compatible with 2f wavelength modulation to minimize the effect of coherent background noise [2]. The bow-tie cavity was primarily studied with ABCD matrix theory to get stability condition that depends on geometry parameter of the cavity. COMSOL simulation with Ray Optics module was done after and the result shows estimated maximum angle error tolerance (the different between the incident beam and the tilt angle of the mirrors) of single micro radian, and the and the beam waist change of larger than 100 um for 1 um error of the curve mirrors position along optical axis. With the estimated power enhancement factor of few hundreds, parts-per trillion detection limits can be reached [3].

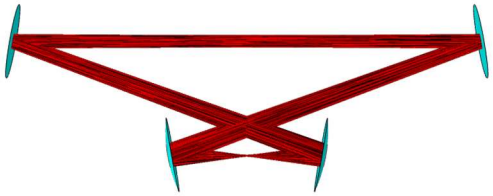

Fig. 1 Ray tracing simulation of ring cavity based on bow-tie configuration composed by 2 flat and 2 curve mirrors.

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Digital infrared spectroscopy: fast and flexible spectral and hyperspectral measurements

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Short abstract: A digital micromirror device is modified to enable fast (ms-regime) and flexible (freely programmable) NIR and MIR spectroscopy and hyperspectral imaging with sensitive single pixel detection. The multiplex advantage known from FTIR spectroscopy is exploited in the spectral and spatial domain. A broadband MIR supercontinuum laser serves as infrared source.

Infrared spectroscopy has developed strongly during the last two decades, driven by new infrared sources and new measurement concepts, such as photothermal approaches. Nevertheless, limitations remain for fast broadband spectroscopy and in particular for hyperspectral imaging. To overcome these limitations, we demonstrate a digital spectroscopy approach that exploits single-pixel detection for both spectroscopy (1D) and hyperspectral imaging (2D) microscopy in the MIR spectral range. The centrepiece of this approach is a spatial light modulator – a modified digital micromirror device (DMD) – that is applied to mask a spectrum or an image with a time-varying pattern. The intensity of the masked scene is then collectively focused on a single-pixel detector for synchronized intensity measurements, which allow for the reconstruction of the spectrum or hyperspectral image. Especially for the mid-IR spectral range, this concept brings decisive advantages:

- spectroscopy in the ms time regime
- image acquisition in the ms time regime
- application of an inexpensive single-pixel detector with excellent detectivity
- multiplex advantage – known from FTIR spectroscopy – in the spectral and spatial domain

We present NIR and MIR spectroscopy of gases, liquids and solids down to the sub-ms time regime [1,2], as well as diffraction limited 64×64 hyperspectral images that can be acquired and reconstructed in 450 ms and 162 ms per wavelength, respectively, which drastically improves the sample throughput in infrared chemical and biomedical imaging [3].

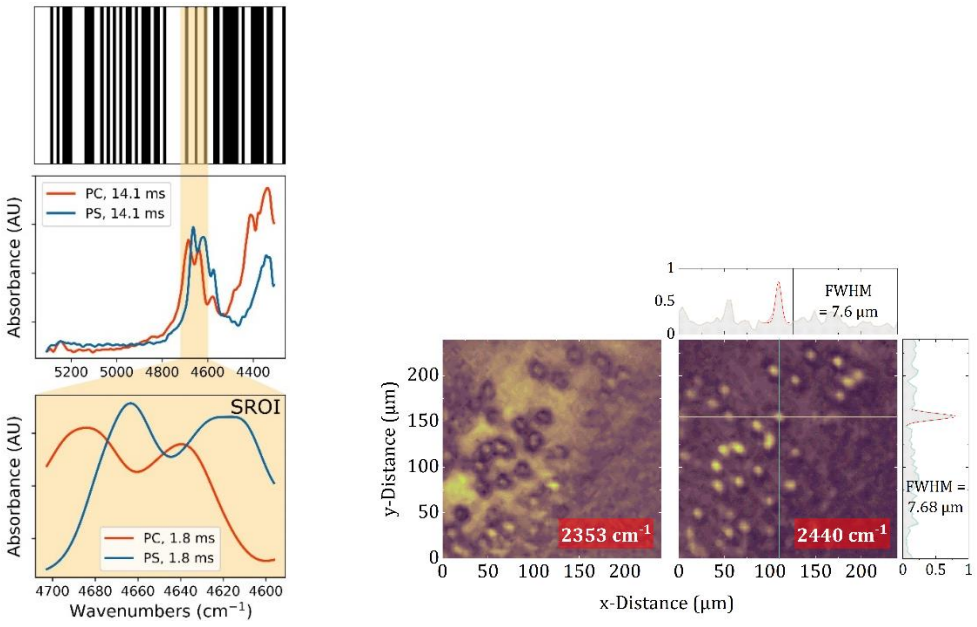

Fig. 1 Spectral coding via 1D barcode pattern structure displayed by a DMD allows flexible and fast spectroscopy, e.g. discrimination between polymers in 1.8ms measurement time (left); Hyperspectral single pixel imaging of red blood cells via 2D Hadamard pattern structures displayed by a DMD (right)

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Neogly, QCL-based continuous glucose monitoring device

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Short abstract: Introducing Neogly, a novel body-worn QCL-based non-invasive continuous glucose monitoring device. Developed under ISO 13485 regulation, it shows relevant glycemia predictions based on mid-infrared photoacoustic spectroscopy as well as AI-based algorithms fed by a numerical twin that covers the entire detection chain including device modeling and human skin properties.

Photoacoustic (PA) spectroscopy is among the most sensitive techniques for chemical emission monitoring, trace gas detection or biomolecule quantification [1]. In the mid-infrared, where many biomolecules of interest have their strongest absorption lines, this technique can take advantage of the high optical power and room temperature operation of quantum cascade lasers (QCL) [2]. However, this technique has never been used for continuous monitoring of a human body [3].

We recently developed such a device called Neogly. It has a compact footprint that enables autonomous, continuous, all-day glucose monitoring on the human body. This paper presents its design, manufacture and characterization according to the ISO 13485 regulation for medical devices, taking into account cost reduction – especially the manufacture of QCL based on standard CMOS tools [6] –, extreme integration and mass deployment. In this contribution, we present relevant details of the device. We conceived a novel PA-QCL core sensor using a proprietary physical model that accounts for viscous and thermal losses [4] and optical path optimization. We manufactured a dedicated compact electronics for laser driver, signal processing and communication modules. We programmed a custom Android application as user interface and communication platform with AWS cloud service. Finally, in order to feed our AI-based glycemia prediction algorithm, we created a numerical twin to assess numerous glycemia scenarios *in silico* and built a large database of synthetic PA glycemia measurements [5]. This tool makes relates physiology, physics, and real life conditions.

Already in the prototype stage, Neogly is demonstrating a new step in the dissemination of QCL technology, dedicated here to a societal challenge. We obtained preliminary results on diabetic and non-diabetic volunteers showing relevant non-invasive continuous glycemia prediction. Patients with type 1 diabetes are currently using the device in the frame of a clinical trial.

Fig. 1 Neogly, a novel device for non-invasive continuous glucose monitoring. The image shows the sensor connected to a portable battery and a handheld device with a user interface. Insert: Clarke Error Grid from data obtained with Neogly

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An Automatic All-In-One Digital Gas Mixer and Pressure Controller.

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Short abstract: The management of gas flow and pressure in vacuum conditions poses significant challenges. Manual skills and complex solutions are currently needed. To address this, we present GM Vacuum, an automatic all-in-one digital gas mixer and pressure controller that offers compactness, versatility, and precise control, revolutionizing the entire process.

Controlling gas flow and pressure in vacuum conditions presents considerable struggles, yet it is a crucial factor to ensure accurate and reproducible outcomes in various applications, including Gas Chromatography, Mass Spectrometry, and other analytical techniques. Achieving sufficient results has traditionally required bulky instrumentation and constant manual adjustments, leading nonetheless to inefficiencies, limitations in performance, and considerable time and space consumption.
To overcome these obstacles, we introduce GM Vacuum, an automatic all-in-one digital gas mixer and pressure controller. This innovative device integrates both functionalities into a single, compact unit, offering an efficient and versatile solution for automated gas generation and precise pressure control. GM Vacuum supplies a prominent level of compactness, ending the need for large-scale equipment and constant manual monitoring, thereby minimizing wasted resources.

Fig. 1 MCQ Instruments - GM Vacuum.

The device allows the creation of gas mixtures up to 600 ml/min and supplies automatic control of pressure in sample volumes up to 1L. With a rapid time-response of less than 10 seconds, it enables precise pressure control at different operating pressure values.
GM Vacuum is designed to accommodate various gas cell setups, offering unparalleled adaptability. Its advanced features and flexible configuration options ensure precise outcomes, tailored to meet specific requirements.
To assist in control and management, the device is equipped with PC software that supplies direct access to all parameters, simplifying every process without requiring specialized skills. The user-friendly interface enables easy control of essential actions with a few clicks. Furthermore, GM Vacuum offers easy integration into other systems, making it compatible with Profibus, Modbus, and Simulink through its USB connection. Additionally, a Python Library is provided to control the instrument via RS485, enhancing its versatility and adaptability.
Transportation and deployment of GM Vacuum are hassle-free due to its compact and lightweight design. It ensures swift and convenient setup in different locations, making it ideal for applications requiring mobility.

Long Wavelength Cascade Laser Technology for Sensing Applications

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Short abstract: Absorption spectroscopy in the mid- and long infrared region is a powerful technique with numerous industrial, environmental and medical applications. Over the last years continuous development of laser sources within this spectral range took place. The latest results in commercially available QC- and ICL-technology will be presented.

Since the first demonstration of continuous wave operation [1] Interband Cascade Lasers (ICLs) have shown tremendous improvement in their performance. Not only cw operation up to a temperature of more than 100°C has been shown [2] but also the capability of the interband cascade concept to operate to wavelengths beyond 13µm [3]. Recently we demonstrated another design improvement which focusses on the mitigation of intervalence band absorption [4]. This in turn led to a significant improvement of laser performance in the wavelength region around 6 µm [5]. A spectrum and LIV characteristics of an epi down mounted laser are shown in Figure 1. Furthermore, the latest results on QCLs, resonant cavity ICLEDs and long wavelength ICLEDs with emission um to 10.2µm will be shown.

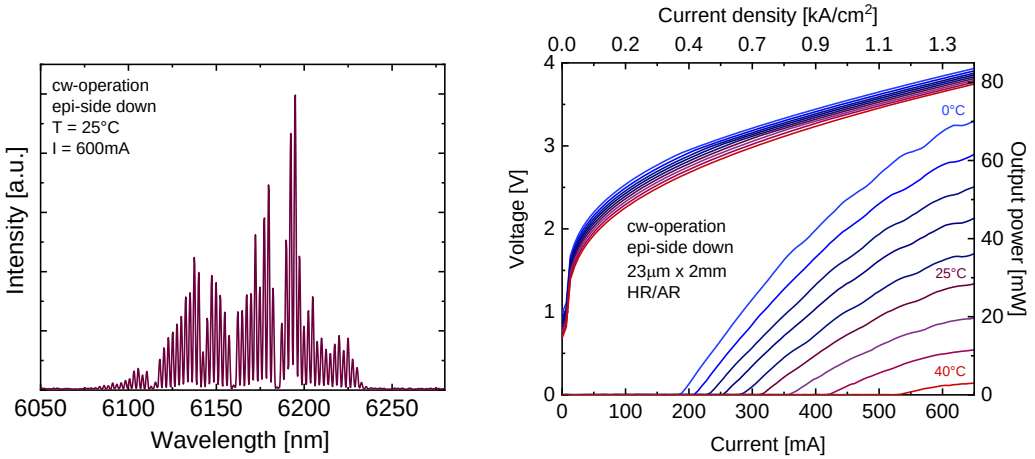

Fig. 1 Spectrum and LIV characteristics of an ICL operating beyond 6µm in cw.

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NH3 Monitoring in Livestock Farms with QEPAS TDL Technology

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Efficient in-line monitoring of gaseous ammonia (NH3) in livestock farms using QEPAS TDL technology with an automated pressure and temperature regulation system. Contributes to reducing NH3 emissions, a precursor to PM10, and enhances environmental management in these facilities.

The agricultural sector, especially livestock farming, plays a significant role in ammonia (NH3) emissions, which contribute to environmental degradation and air pollution. This study introduces a novel solution for addressing NH3 emissions in livestock farms through the implementation of Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) Tunable Diode Laser (TDL) technology. The QEPAS TDL system allows for real-time and accurate measurement of gaseous NH3 concentrations in bovine, ovine, swine, and poultry farms. To ensure optimal data collection conditions, an automated regulation system is integrated into the setup, controlling pressure and temperature variables. By continuously monitoring NH3 concentrations throughout the husbandry process, farmers can identify emission hotspots and implement targeted measures to reduce NH3 levels. This approach not only enhances environmental sustainability but also positively impacts animal welfare and overall farm productivity. Minimizing NH3 emissions also addresses the formation of PM10, a harmful air pollutant associated with respiratory and health issues. Consequently, improved air quality benefits both farm workers and livestock, promoting a healthier agricultural ecosystem. The user-friendly interface further simplifies data visualization and analysis, empowering farmers and farm managers to make informed decisions regarding NH3 management.

Fig. 1 ETG 8900 QEPAS.

As governments worldwide intensify their focus on environmental protection and sustainable practices, adopting effective NH3 management techniques becomes imperative for livestock farmers. The integration of QEPAS TDL technology with an automated regulation system offers a scalable and practical solution in line with global sustainability goals. In conclusion, this study underscores the importance of in-line monitoring and regulation of gaseous NH3 in livestock farms, facilitated by QEPAS TDL technology. By promoting environmentally responsible practices and supporting animal welfare, this innovative approach contributes to a greener and more sustainable future for livestock farming.

Direct Absorption Spectroscopy

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Optical absorption spectroscopy applied for trace gas sensing

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Short abstract: Optical absorption spectroscopy is a widely used method for gas detection. Mid-IR laser sources from narrowband to ultra-broadband supercontinuum light sources are combined with specific spectroscopic detection schemes. Applications are described for the single and multiple-species detection of gaseous pollutants in the atmosphere, wastewater treatment, fruit storage, breath analysis and plasma diagnostics.

A selection of several optical methods for gas detection applications over the last two decade of research will be presented. The choice is based on their maturity and high potential for applications outside the laboratory (e.g. in storage facilities, on a boat, aircraft and drone). A short historical overview and background on the laser sources will be shown in combination with various spectroscopic detection schemes we developed over the years, to achieve an optimal detection limit and selectivity. The common approach for optical absorption spectroscopy is the on-line, real-time analysis of single known molecule, sometimes two to three species at most at the same time. For this, high power (cw and pulsed) Quantum Cascade Lasers (QCL) operating at room temperature with power levels up to 1 Watt, and the related Interband Cascade Lasers (ICLs) are covering the mid-IR wavelength region from 3 to 24 μm. For the 2.5 to 5 μm wavelength region, high power, Periodically Poled Lithium Niobate Optical Parametric Oscillators (PPLN-OPO's) are available pumped by high power, near-infrared (fiber-) lasers with excellent spectroscopic properties (narrow linewidth, Gaussian beam profile, fast wavelength scanning). In the 'telecom' wavelength region, around 1.5 μm, semiconductor lasers have the advantage of the technical developments for the telecom industry, resulting in a small footprint, reliable tunability, low costs, long lifetime and low maintenance. Larger tuning ranges can be obtained by using these sources into external cavity setups. Applications will cover several Life Science fields from plant physiology, and microbiology to breath analysis during cardiac surgery [1].
Next to these, the broadband mid-IR light sources can provide the spectral coverage where most of the molecular species have their strongest absorption features (the "fingerprint" region). Based on these sources, one can develop spectroscopic systems capable of multi-species detection with high selectivity and sensitivity. The two main broadband mid-IR light sources that we corporate are supercontinuum sources and optical frequency combs.
Their output beam is spatially coherent, in contrary to the thermal sources, thus enabling long interaction lengths between light and the gas sample. Recently we have developed and reported different types of spectrometers [2] incorporated with these sources for different applications, such as detecting volatiles compounds in fruit storage facilities [3], environmental monitoring, wastewater treatment and study of plasma-based gas conversion [4].

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Molecular detection with a sensitivity of parts per quadrillion

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Short abstract: Saturated-absorption CAvity Ring-down (SCAR) spectroscopy is the only laser spectroscopy technique that achieves a sensitivity of 10^{-15} for $^{14}CO_2$ detection. This is disclosing, to compact and transportable laser spectroscopy set-ups, a wide range of applications in key areas.

Saturated-absorption cavity-ring-down spectroscopy (SCAR) has revolutionized molecular detection with its unprecedented sensitivity, detecting molecules at a few parts per quadrillion (ppq) [1,2,3]. Over the past ten years, the related technology has made great progress, since its first demonstration, taking to a portable instrument that can be deployed worldwide.

Fig. 1 Present SCAR spectrometer

One unique application of this technology is its ability to quantify an elusive molecule like $^{14}CO_2$, which constitutes only 10^{-12} of the total amount of carbon dioxide in the biosphere. Recently, SCAR instrumentation has been used to address specific problems in different areas of science and humanities, highlighting the versatility of this powerful technology. One notable application is its use in discriminating between biogenic and fossil content in materials and fuels [4], which can have significant implications for environmental and economic purposes. Additionally, SCAR has been utilized in radiological assessment of nuclear waste and decommissioning of nuclear power plants [5], providing a new approach to such significant problems. Another application involves ultra-sensitive dating of archaeological samples from a 4,500-year-old Sumerian site [6], shedding light on the history and development of human civilization.

The next frontier for SCAR technology is in the precise measurement of radiocarbon in atmospheric samples, which can provide important information about climate change and carbon cycle dynamics.

Furthermore, the nonlinear nature of SCAR spectroscopy has been exploited to record Lamb-dips of acetylene (the $(\nu 1 + \nu 3)$ R(1)e transition at 6561.0941 cm^{-1}). This has also extended the SCAR technique to a different molecule, in the telecom range, measuring on a buffer-gas-cooled molecular sample, at cryogenic temperature. Such combination of high precision and sensitivity has taken to a fractional uncertainty of 6×10^{-12}, improving the previous best result by one order of magnitude [7].

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Fourier transform photoacoustic spectroscopy with broadband supercontinuum lasers

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Short abstract: Broadband photoacoustic spectroscopy utilizing supercontinuum laser as a light source is presented. We apply Fourier transform to enable simultaneous broadband detection of hydrocarbons and nerve agent simulants. Further, we studied the effect of multi-pass configuration and light-source intensity noise to the detection performance.

Photoacoustic spectroscopy (PAS) is a unique gas sensing technique providing high sensitivity in small sample volumes and therefore widely used in single species detection [1]. Broadband operation required for multi-species detection can be realized by combining a light source with wide spectral coverage with a scanning Fourier transform spectrometer, which simultaneously generates a distinct modulation frequency for each wavenumber of the source. The resulting pressure waves at various frequencies are most accurately detected using an optically read cantilever microphone, which provides a wide frequency response with high sensitivity. This Fourier transform photoacoustic spectroscopy (FT-PAS) method with cantilever-enhanced pressure detection has recently been demonstrated using supercontinuum (SC) and optical frequency comb sources, instead of conventional thermal sources [2], for improved sensitivity and spectral resolution [3].

We utilize the spatial coherence of the SC source to enhance the sensitivity of FT-PAS using a miniature multi-pass arrangement. We used an external Herriott-type mirror configuration, which guides the light from a custom-built mid-infrared SC ten times through a miniature gas cell (95 mm long, 4 mm in diameter). We achieve a noise-equivalent detection limit of 11 ppb of methane in 40 s (eight scans). Moreover, we measure the C-H stretch bands of three hydrocarbons around 3000 cm^{-1} to demonstrate the system's ability to separate single species in complex gas mixtures. Fig. 1a shows the measured absorption spectrum of a gas mixture and the reference spectra of individual species, scaled according to a fitting routine. A simple least squares spectral fitting (residual shown in Fig. 1b) is able to extract the concentrations within the measurement uncertainty (Fig. 1c), which illustrates the suitability of SC-based FT-PAS for multi-species gas sensing.

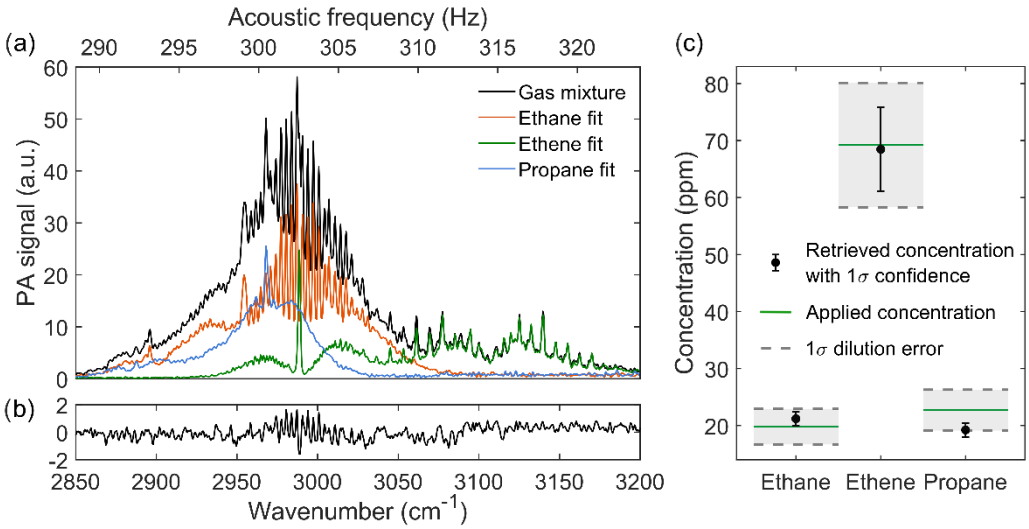

Fig. 1 (a) Measured photoacoustic spectra of C-H stretch bands of ethane, ethene and propane, separately (red, green and blue lines) and in a gas mixture (black line). Individual spectra, measured at concentrations differing from the concentrations in the mixture, are scaled linearly to fit the spectrum of the gas mixture. (b) Residual of the fit. (c) Concentrations retrieved from the spectral fitting compared to the applied concentrations.

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Mid-infrared supercontinuum-based Fourier transform spectroscopy for multispecies open-path measurements

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Short abstract: The emergence of broadband, spatially coherent mid-infrared supercontinuum sources enables novel opportunities in spectroscopy, especially in multispecies detection in the gas phase. Here we report our recent developments centred around detection of greenhouse gases, emission/leaks, and pollutants over open paths, demonstrating the detection of emissions in a turbulent, outdoor environment.

Ultra-broadband spectroscopy in the mid-infrared (MIR) wavelength range, where most molecular species have strong, distinct absorption features, has a great potential for gas sensing applications. Within the H2020 TRIAGE project, a MIR supercontinuum (SC) source and a compact, broadband spectrometer are being developed and applied for MIR spectroscopy [1]. MIR SC sources excel in their ability to provide broadband light together with a high spatial coherence. Using this unique combination of properties, we have recently demonstrated the potential of MIR SC sources in combination with a tailor-made Fourier Transform Spectrometer (FTS) and a multipass absorption cell for multispecies trace gas detection [2] next to measurements on gas conversions inside electric discharges [3]. Moreover, a novel application is to utilize the spatial coherence of the source to monitor outdoor gas concentrations over long integrated paths, in an open-path arrangement.

In open-path absorption spectroscopy, the light beam is guided through the area of interest, instead of sampling the gas in a cell. Therefore, it can be used for integrating concentrations over a path, which is useful for flux calculations of greenhouse gases in an area, or leak detection. Here, we present the results of open-path measurements of greenhouse gases (such as methane and carbon dioxide) and small hydrocarbons (such as ethanol) using a custom-built FTS with a MIR SC source from NKT Photonics (SuperK MIR). The entire system is transportable for outdoor measurements. The SC source has a total output power of ~450 mW and a spectral coverage of 1.4 – 4.1 μm. The beam of the SC source is sent over an open path to a cubic retroreflector and reflected to the FTS. Using the spatial coherence of the beam, optical path lengths of hundreds of meters can be achieved. The FTS [2] uses a balanced detection scheme to reduce the relative intensity noise of the SC source and can provide a spectral resolution up to 750 MHz (0.025 cm^{-1}).

As a demonstration of emission in an uncontrolled, turbulent outdoor environment, we evaporated liquid ethanol outside from an open box; the SC beam passed over this box 2 times (total path length 11 m). To track air turbulence, the sampling rate of the spectrometer was set to 2.5 Hz, yielding a spectral resolution of 30 GHz (1 cm^{-1}). In Fig. 1(a), a typical absorbance spectrum containing ethanol and water is shown with fitted simulated spectra (inverted) using the PNNL and HITRAN database. The retrieved concentrations of ethanol and water are shown in Fig. 1(b), which clearly shows how after one minute (indicated with the dashed line) liquid ethanol began to evaporate from the box. For ethanol, the single-shot precision was determined to be 33 ppm; the larger ethanol fluctuations demonstrate the dynamics of ethanol evaporation and wind turbulence. The retrieved water concentration remains very stable, demonstrating the ability to detect multiple gases without interference.

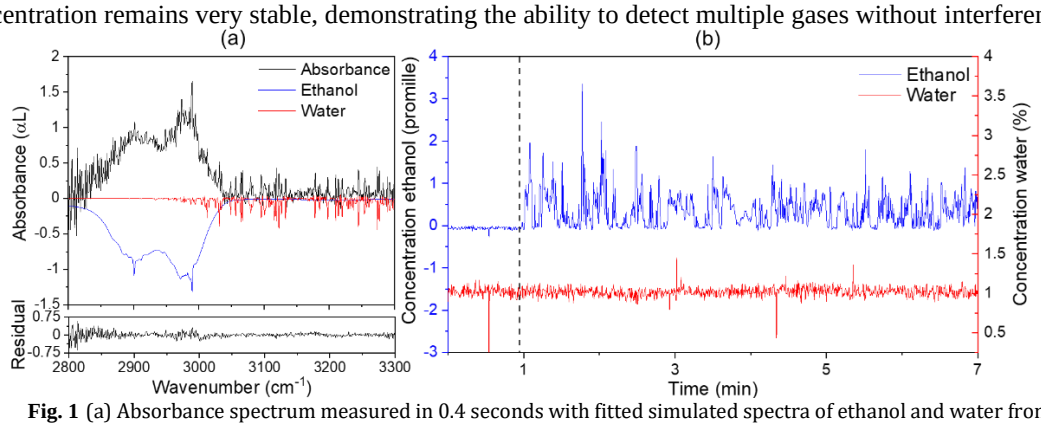

Fig. 1 (a) Absorbance spectrum measured in 0.4 seconds with fitted simulated spectra of ethanol and water from the PNNL and HITRAN database shown inverted, and (b) the retrieved ethanol and water concentrations at a sampling rate of 2.5 Hz. The evaporation of ethanol was introduced after 1 minute (indicated with a dashed line).

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Quartz Enhanced Photoacoustic Spectroscopy and Light Induced Thermoelastic Spectroscopy for natural gas composition analysis

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Short abstract: Petrochemical manufacturing processes brings significant risks during production, making rapid gas detection and response a life-safety necessity. Laser-based spectroscopic sensors are well suited for this application, providing high selectivity and sensitivity. We report on two optical techniques for natural gas composition analysis: quartz enhanced photoacoustic spectroscopy and light-induced thermo-elastic spectroscopy.

Hydrocarbons detection in natural gas (NG) could be a powerful tool to minimize the environmental impact of energy production for the petrochemical industry. NG is mainly composed of methane (C1) and ethane (C2), and thus their accurate detection would improve the forecasting efficiency during drilling operations. Among different gas sensing technologies, laser-based sensors provide high sensitivity and selectivity, and are suitable for real-time and in situ measurements.

In this work, we report on two laser-based sensors based on two optical techniques for the detection of hydrocarbons in NG-like mixtures, i.e., Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) and Light-Induced Thermoelastic Spectroscopy (LITES). Both developed sensors employ a quartz tuning fork (QTF) and an interband cascade laser emitting in the 3.3 μm wavelength range, where C1 and C2 exhibit strong absorption features. In QEPAS, the QTF is used as piezoelectric transducers to convert pressure waves generated via photoacoustic effect into an electrical signal [1]; in LITES the QTF is used as infrared photodetector exploiting the thermoelastic conversion induced by an optical absorption [2]. A standard QTF with a fundamental resonance frequency (f_0) of 32.7 kHz, coupled with two acoustic resonator tubes, was employed for QEPAS detection, while a custom T-shaped QTF with f_0 = 9.8 kHz was implemented in LITES sensor. Both techniques were combined with wavelength modulation approach with second harmonic detection. Two different methods were employed to retrieve C1 and C2 concentrations in NG-like mixtures: partial least square regression was employed to filter out energy relaxation dependence on gas matrix composition in QEPAS signals (left picture in Fig.1) with an accuracy > 95%; for LITES detection, an univariate analysis was used to determine C1 and C2 concentrations in mixtures (right picture in Fig.1), with an accuracy >98% [3].

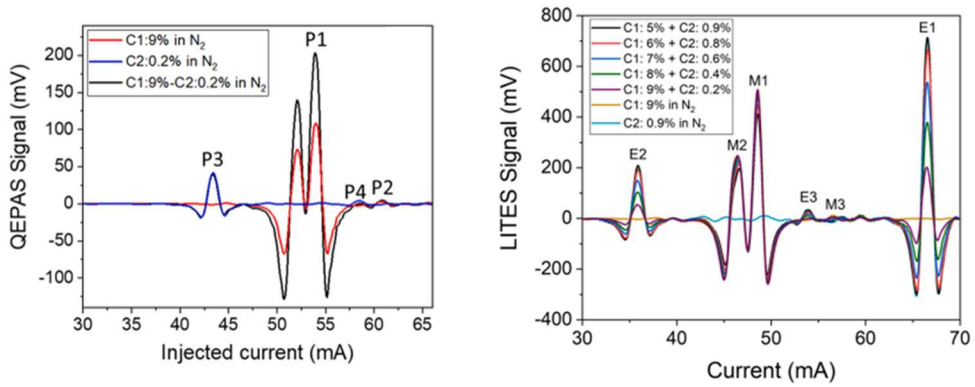

Fig. 1 (left) Comparison among QEPAS signals of C1-C2-N_2 mixtures containing 9% of C1 in N_2 (red curve), 0.2% of C2 in N2 (blue curve), and 9% of C1 and 0.2% of C2 in N2 (black curve) [2]; (right) Comparison among LITES signals of C1-C2-N_2 mixtures containing 9% of C1 in N_2 (gold curve), 0.2% of C2 in N_2 (azure curve), 5% of C1 and 0.9% of C2 (black curve), 6% of C1 and 0.8% of C2 (red curve), 7% of C1 and 0.0.6% of C2 (blue curve), 8% of C1 and 0.4% of C2 (green curve), 9% of C1 and 0.2% of C2 (purple curve), all in N_2 [3].

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Photothermal Spectroscopy

Fundamental limits to spatial resolution in photothermal imaging

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Short abstract: The spatial resolution limit in photothermal imaging is derived from the irreversibility of heat diffusion during propagation of the signals from the imaged subsurface structures to the sample surface. The temperature signals are converted into so-called virtual acoustic waves, which are their reversible counterparts and are used for image reconstruction.

In this work, we combine the different scientific fields of information theory, thermodynamics, regularization theory and non-destructive imaging, especially for photothermal imaging [1]. The goal is to get a better understanding of how information gaining for subsurface imaging works and how the spatial resolution limit can be overcome by using additional information. Here, the resolution limit in photothermal imaging is derived from the irreversibility of heat diffusion during propagation of the signals from the imaged subsurface structures to the sample surface, respectively. The temperature signals are converted into so-called virtual waves, which are their reversible counterparts and which can be used for image reconstruction by well-known ultrasound reconstruction methods. The conversion into virtual waves is an ill-posed inverse problem which needs regularization. The reason for that is the information loss during signal propagation to the sample surface, which turns out to be equal to the entropy production from heat diffusion. The spatial resolution from entropy production is equal to the diffraction limit -which is noise limited. Incorporating sparsity and non-negativity in iterative regularization methods gives a significant resolution enhancement, which is experimentally demonstrated by one-dimensional imaging of thin layers with varying depth or by three-dimensional imaging, either from a single detection plane or from three perpendicular detection planes on the surface of a sample cube (Fig. 1).

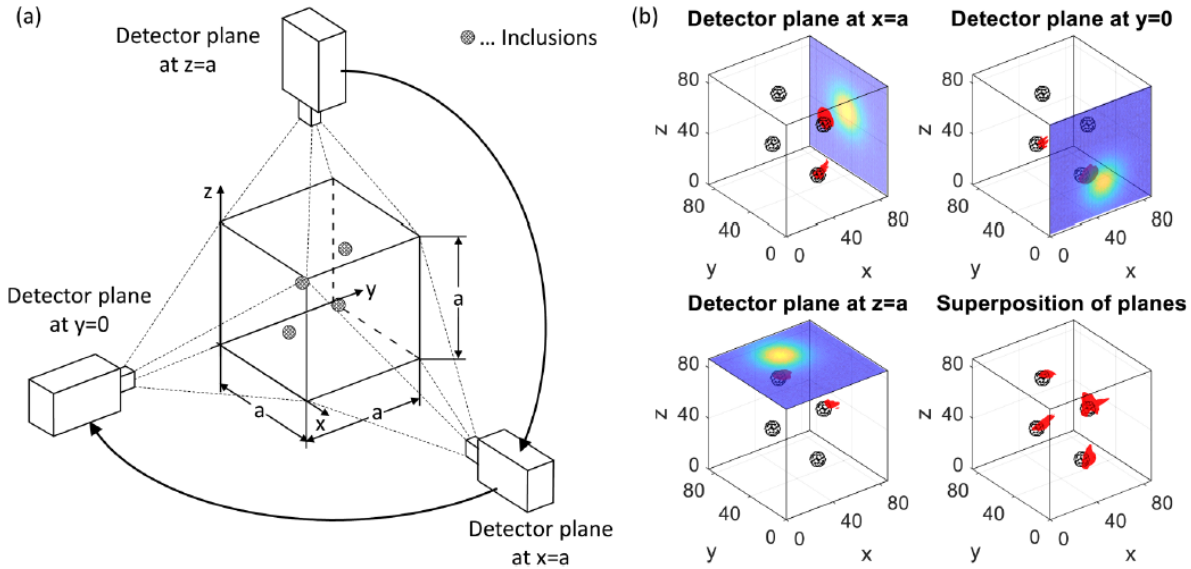

Fig. 1 (a) Experimental setup and detection planes of the thermographic measurements and (b) the isosurface illustration of the reconstructed internal heat sources obtained with reconstruction using sparsity and positivity for three different detector planes and a superposition of the single detector plane reconstructions [1]. The steel spheres had depths of 4.3 mm, 7.5 mm and 10.7 mm from the detection planes.

The virtual wave concept: the formal relationship between temperature field $T(\mathbf{r},t)$ and virtual wave field $T_{\mathrm{virt}}(\mathbf{r},t')$, for the same position vector $\mathbf{r}$ but different time scales t and t', is given by a Fredholm integral of the first kind:

$$T(\mathbf{r},t) = \int_{-\infty}^{\infty} K(t,t')\, T_{\mathrm{virt}}(\mathbf{r},t')\, \mathrm{d}t' \quad \text{with} \quad K(t,t') = \frac{c}{\sqrt{\pi\alpha t}}\, e^{-\frac{c^2(t')^2}{4\alpha t}} \quad \text{for} \quad t > 0. \qquad (1)$$

The thermal diffusivity α and the virtual speed of sound c are the characteristic parameters for heat and virtual wave propagation. While $T(\mathbf{r},t)$ obeys the heat equation, $T_{\mathrm{virt}}(\mathbf{r},t')$ fulfils the photoacoustic wave equation.

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Recent Progress and Applications of Thermal Lens Spectrometry in Environmental and Bio-medical Sensing

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Short abstract: Applications of TLS in environmental and bio-medical sensing, which include determination of iron species and ammonia by TLS and comparison to their microfluidic TLM detection are presented. Advantages of microfluidic FIA-TLM in terms of sensitivity and high sample throughput for determination of microcystin, Cr(VI) and HPV virus are discussed.

The versatility of thermal lens spectrometry (TLS) has been demonstrated by applications of this highly sensitive technique for determination of various analytes in variety of samples including environmental samples such as natural and wastewaters and phytoplankton as well as body fluids in biomedical diagnostics. In addition to high sensitivity, TLS offers a tool for small sample volume (< 1 μL) analysis and high sample throughput fast screening purposes. These advantages are particularly obvious when combining TLS with flow injection analysis (FIA) or microfluidic systems which however require a TLS microscope (TLM) as a detection tool [1-3].
This will be clearly demonstrated by a series of applications of TLS and TLM for determination of Fe(II) and Fe(III) in samples of surface waters where sample volumes of several 100 mL are easily collected and, for example, in samples of cloud water where available sample volumes are usually scarce for a series of intended analyses (microbiological assays, determination of organic and inorganic ions, etc..) and 1 μL size subsamples need to analysed. Another example is determination of ammonia in waters, which serves also as an intermediate in determination of biogenic amines.
High sample throughput capabilities of FIA-TLS and flow injection in microfluidic chips with TLM detection (μFIA-TLM) will be demonstrated for the case of Cr(VI), where colorimetric reaction with diphenylcarbazide (DPC) offers limits of detection of 0.07 μgL^{-1} and 0.6 μgL^{-1} were achieved for FIA-TLS and μFIA-TLM, respectively. In the case of μFIA-TLM sample throughputs of up to 20 samples/min. will be demonstrated, similar to results presented in Fig. 1, which provide higher LOD as compared to FIA-TLS primarily due to 200-times shorter optical interaction length in case of μFIA-TLM.

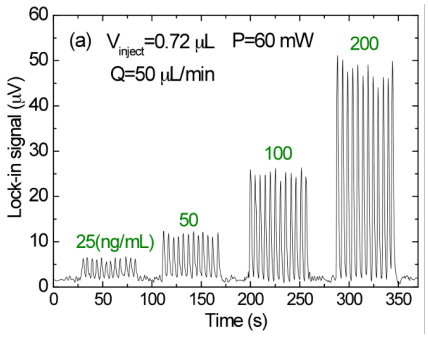

Fig. 1 Demonstration of high sample throughput for μFIA-TLM determination of Cr(VI) in a 50 μm deep microfluidic channel - replicate injections of 0.72 μL standard solutions with different concentrations of Cr(VI). 12 injections/min. at 50 μL/min carrier flow rate and 60 mW excitation laser power (514.5 nm).

As reviewed recently [3], microfluidic platforms in combination with immunoassays and enzymatic reactions enable significant reduction of reaction times in case of analysis relying on macromolecules such as antibodies and enzymes. Such platforms in combination with TLM detection enabled rapid and sensitive determination of neurotoxic substances such as microcystin arising from massive algal blooms, or biomarkers like NGAL (neutrophil gelatinase-associated lipocalin) - biomarker of acute kidney injury, and HPV virus antibodies in blood serum indicating infection with HPV as will be demonstrated, before presenting the conclusions of this paper.

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Photothermal gas detection using a miniaturized fiber Fabry-Perot cavity

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Abstract: We present a proof-of-concept experiment demonstrating the use of a miniaturized and robust fiber Fabry-Perot cavity for photothermal spectroscopic signal retrieval. The performance of the gas sensor was evaluated by measuring methane at 1651 nm, with a detection limit of 167 ppbv achieved for an integration time of 100 s.

Photothermal spectroscopy (PTS) is a powerful tool for selective and sensitive detection of gas molecules. In PTS, a *pump* laser with a wavelength that matches the absorption profile of the gas sample under test is used to excite the particles. Part of the absorbed light heats the gas, which locally modulates its pressure and refractive index (RI). As the modulation is directly correlated with the analyte concentration, detection of highly diluted samples requires using precise methods of extracting the spectroscopic signal from the RI shift. The best results are achieved using interferometric techniques, which utilize Fabry-Perot or Mach-Zehnder interferometers [1]. Sensitivity, long-term stability and repeatability in such sensors require specialized optical components and precise alignment, rarely achievable in out-of-lab conditions. Our results document the first attempt to utilize a robust, miniature, custom-built fiber Fabry-Perot cavity (FFPC) to extract the PTS signal. The FFPC is built by gluing two fiber mirrors (high reflectivity at 780 nm) into a glass ferule, forming a ~106 µm-long cavity with a Finesse of ~1370 (details on the FFPC design are given in [2]). A 80 kHz BW 780 nm laser beam was coupled into the cavity as presented in Fig. 1. The reflected beam was redirected using a PBS to a photodiode. The photodiode signal was used to lock the cavity to the *probe* laser (via a PID-controller and a PZT glued to the FFPC) and for monitoring the PTS-induced reflection signal modulation via a lock-in amplifier. The small footprint FFPC setup (dimensions 8 x 1.25 x 1.25 mm^3) was enclosed in a gas chamber, into which the gas samples were introduced. The proof of concept experiment used a 66 mW *pump* laser (beam focused in the center of the FFPC), which targeted methane gas (CH_4) at one of its near-IR transitions located at 1651 nm. When the gas molecules are excited with the *pump* laser in the FFPC, the resulting RI change causes a shift in the cavity optical pathlength, thus modulating the amplitude of the reflected beam. The *pump* laser's wavelength was modulated with a sinewave signal (1.1 kHz) and swept through the CH_4 absorption line using a 20 s sawtooth ramp applied to its current. Wavelength modulation spectroscopy technique was used to simplify the spectroscopic signal processing.

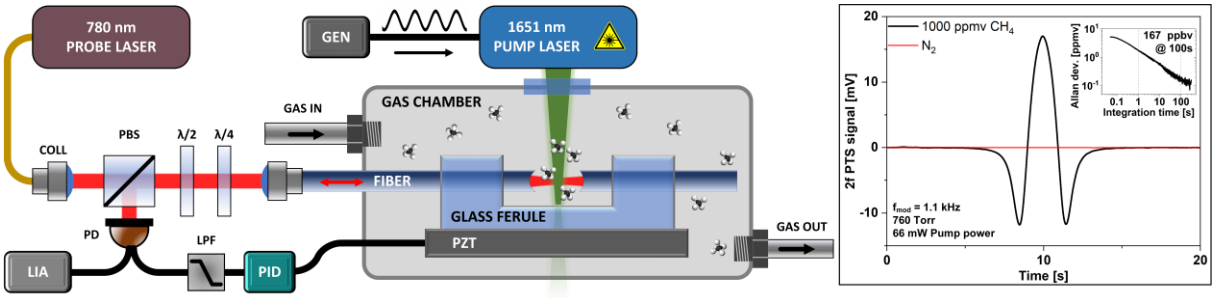

Fig. 1 Schematic of the sensor setup. The 2f PTS signal registered for 1000 ppmv CH_4 and the Allan deviation plot are shown on the right side. LIA – lock-in amplifier; COLL – collimator; PBS – polarization beam splitter; PD – photodiode; LPF – lowpass filter; PID – PID controller; PZT – PZT transducer; GEN – signal generator.

Based on noise measurements (N_2 in the gas chamber), the Allan deviation was calculated and plotted (inset in Fig. 1.). A minimum detection limit of 167 ppbv at an integration time of 100 s was achieved, which gives perspective for further improvement of this technique, e.g. by using higher Finesse FFPC's, or targeting stronger, mid-IR gas transitions.

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Compact Trace Gas Detection by Balanced-Detection ICAPS

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Short abstract: Compact gas detection employing balanced-detection ICAPS is reported. Balanced-detection was realized by using two identical cavities having a path length of only 1 mm. The system detected the reflectance of the individual interferometers, enabling sensor operation close to the fundamental limit of shot noise.

The miniaturization of sensitive as well as selective laser-based gas detectors is of big request among different fields of activity due to specific characteristics such as a fast sensor response or simply a small footprint. However, it still remains challenging. While methods based on direct absorption spectroscopy show a limited potential for miniaturization due to their dependence of sensitivity on the optical path length according to the Lambert-Beer law, indirect spectroscopic techniques of photothermal nature inherently exhibit high miniaturization potential. We have identified photothermal spectroscopy using a Fabry-Perot interferometer as transducer to be an excellent candidate for miniaturization of sensitive sensors due to its overall simplicity and the unique characteristics of this interferometer type emerging by the Finesse.

The implementation of a balanced detection scheme to our developed *Interferometric Cavity-Assisted Photothermal Spectroscopy* (ICAPS) method is a key improvement, which enhances the sensor's performance by efficient cancellation of noise. Within this scheme excess noise – i.e. probe laser noise as well as environmental noise, e.g. acoustic noise - can be removed with high efficiency. This is achieved by concurrently comparing the probe laser's intensity with and without the photo-thermal signal. Balanced-detection was realized by using two identical cavities having a path length of only 1 mm and a total sample gas volume of a few mm³ (see Fig. 1). The system used an all fiber-coupled probe laser configuration, which detected the reflectance of the individual interferometers, enabling sensor operation close to the fundamental limit of shot noise.

The metrological figures of merit were investigated by detection of different trace gases such as SO_2, CO and CO_2 using quantum cascade lasers and an interband cascade laser as powerful mid-infrared excitation sources. The induced refractive index changes were monitored by a near-infrared probe laser. The probe and excitation laser beams were arranged in transverse configuration, enabling the construction of simple and robust trace gas sensors. Selectivity was achieved by signal generation via wavelength modulation and detection at second harmonic (2*f*). For the targeted molecules a minimum detection limit down to the sub-ppbv level was achieved with a 1s integration time, corresponding to a normalized noise equivalent absorption of the order of 10^{-9} cm^{-1} W $Hz^{-1/2}$. Within the presentation, latest results regarding improvements in noise reduction performance and sensor robustness will be discussed.

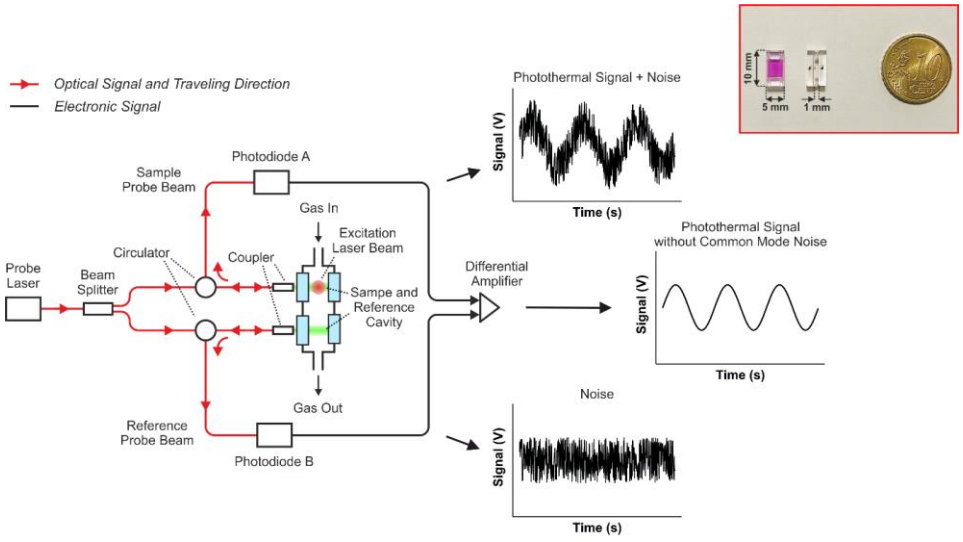

Fig. 1. Principle of balanced-detection ICAPS monitoring the interferometers reflectance [1]. Inset: Photograph of the employed interferometers having a mirror spacing of 1 mm.

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Balanced – Interferometric Cavity Assisted Photothermal Spectroscopy with low – cost telecoms wavelength lasers for environmental and food analysis

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Short abstract: Balanced - Interferometric Cavity Assisted Photo-thermal Spectroscopy (B-ICAPS) is a high sensitivity technique for gas analysis. The project makes use of custom Fabry-Perot interferometer coupled to a fibre array as miniaturized transducer for B-ICAPS, and of near-infrared excitation lasers to provide a low-cost technology keeping the competitive performance.

A Balanced - Interferometric Cavity Assisted Photo-thermal Spectroscopy (B-ICAPS) set-up (Fig.1) employs an excitation laser in the MID-IR that causes heating in the analyte gas on absorption, and a probe laser in the NIR to monitor the changes of the refractive index induced by the temperature change [1]. The optical sensor is composed of an interferometer, which is where the photo-induced effects are produced and the signal generated. The light that propagates inside the interferometer experiences a phase shift that is directly proportional to the refractive index change, therefore by detecting the light propagating through the cavity one can retrieve information regarding the change in refractive index. A Fabry-Pérot (FP) interferometer is the best optical element for monitoring the photo-induced changes in the gas sample, while a fibre array is a solution for a more compact sensor.

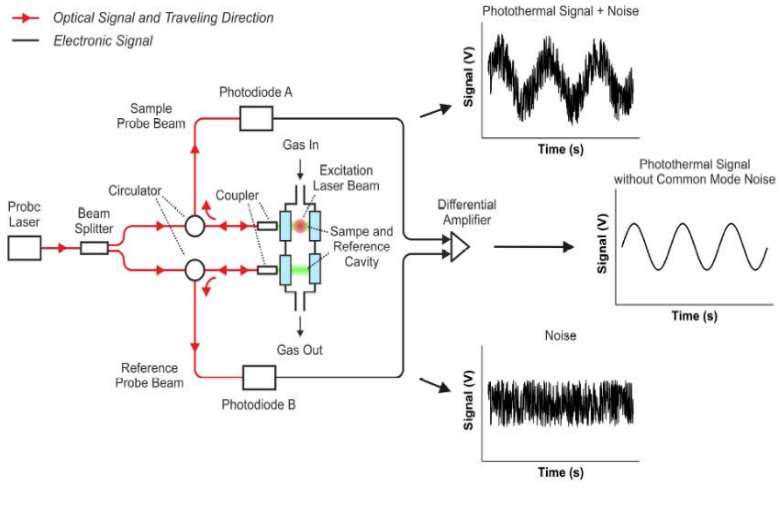

Fig. 1 Schematic of balanced-detection interferometric cavity-assisted Photothermal spectroscopy (B-ICAPS).

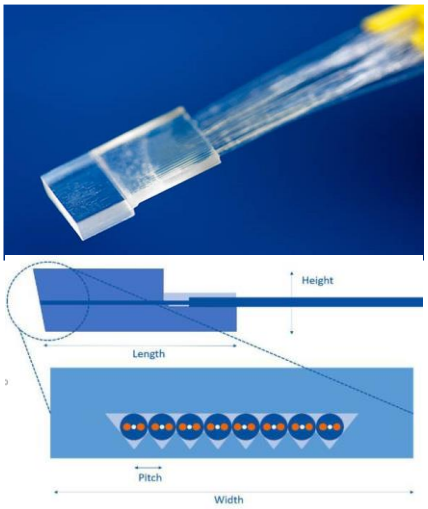

Fig. 2 Collimating fibre array: a) Picture; b) schematic b) schematic of 8-channel fibre array

The B-ICAPS detection scheme requires two identical FP interferometers with 1x0.5cm mirror area for sample and reference measurement to get rid of environmental noise and enable operations close to the limit of shot-noise. The main drawback of the current B-ICAPS scheme is the need of two separate FP cavities within the same gas cell. The two cavities have intrinsic production differences, therefore, to obtain identical resonances at the same wavelength they must be separately temperature-controlled, and this increase the complexity of the system. This is the reason why the new B-ICAPS system employs a collimating fiber array (Fig. 2a) instead of a standard single collimating lens: with a pitch of 250um, a width and height of 2.6mm and a length of 10mm (Fig.2b) it allows multiple beam paths with identical behavior, to be used for multiple synchronous measurements within the same FP cavity. Additional advantages of using the collimating fiber array are the smaller beam spot, 200um instead of 500um, that is more sensitive to photo-induced temperature changes of the gas, and the potential to directly attach it to the FP interferometer to make the system more rugged and stable, which is of crucial importance for such high-sensitive optical sensor.

The B-ICAPS system will employ very cost-effective telecoms laser technology that operate around 1.3 μm – 1.6 μm. Target gas analytes are nitric monoxide and methane, fundamental for environmental and food applications [2].

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Controlling Spatial Resolution and Sensitivity in Nanoscale Chemical Imaging by Photothermal-Induced Resonance Spectroscopy

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Short abstract: We introduce an analytical expression, modeling the photothermal expansion process and validating it with finite element simulations and AFM-IR experiments. These results enable experimentalists to achieve high signal intensity and high spatial resolution in AFM-IR experiments through selection of excitation laser parameters and accounting for material properties and sample geometries in both 2D and 3D chemical imaging.

Atomic force microscopy-infrared (AFM-IR) spectroscopy is an atomic force microscopy (AFM) based technique which combines nanoscale high-spatial resolution with the chemical analysis power of mid-infrared spectroscopy. The technique of AFM-IR relies on the detection of the pulsed wavelength tunable IR laser induced thermal expansion of the sample area underneath the AFM tip. However, the limitation on spatial resolution and sensitivity of the technique are not yet fully understood. In the analytical and numerical models of AFM-IR, we took into account laser heating, thermal and mechanical properties of materials and found good agreement with finite element simulations and AFM-IR experimental measurements with polymethyl methacrylate (PMMA) and polystyrene.

Building on our recently developed theoretical model of the AFM-IR signal, we now use a series of nanostructured polymer samples of mixed polymers with different features sizes and thicknesses to gain an understanding of how to control the spatial resolution and sensitivity in AFM-IR experiments. To achieve the goal, we make use of the advanced clean room technique to fabricate desired patterns on the chip, in addition, this technique allows us to precisely control the size, thickness and position of the features. As results, we have successfully fabricated three samples with 1 µm thick SU-8 covered by 100, 200 and 300 nm thick PMMA, respectively. The preliminary experimental results show clear chemical absorption spectra of two polymers and chemical images about designed patterns.

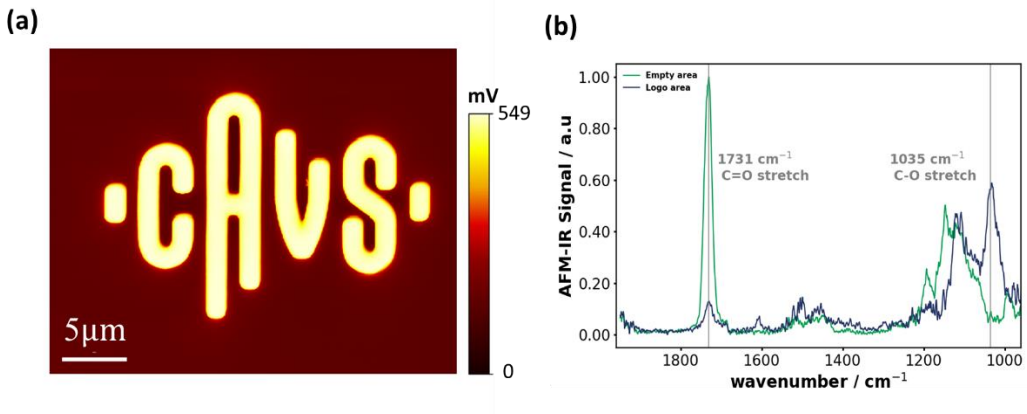

Fig. 1 (a) AFM-IR chemical map at 1035cm^{-1}. The bright logo part is designed by 1 µm thick SU-8 covered by 200nm PMMA, the empty area is designed only with 200nm thick PMMA. (b) AFM-IR spectra obtained on the position on the logo and empty area, respectively. The AFM-IR intensity is normalized at 1731cm^{-1}.

Photoacoustic Spectroscopy

Photoacoustic detection overview, from past to present

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Short abstract: Photoacoustic detection applied to trace gas sensing is overviewed. The continuing developments of new laser sources and novel PA detection schemes propel the applications further. Easiness of operation, high sensitivity down to sub-ppbv gas concentrations and high specificity enabling isotopic selectivity are outstanding properties of this non-zero background technique.

The sensing of chemical compounds is of utmost interest. Meaningful measurements require accurate, reliable and robust techniques. Numerous exciting instrumental developments are occurring in this field and are continuing to be made in the future. Optics-based sensors offer some distinct advantages over more conventional schemes such as easiness of operation, lack of sample preparation, often multi-component capability, high detection sensitivity and specificity. Generally, optical sensors include a light source (mostly lasers, but also LEDs), some kind of absorption cell (e.g. multipass or cavity-enhanced schemes) and some type of detection (optical, photoacoustic or else). Here we focus on photoacoustic detection and overview the development from past to present.

The discovery of photoacoustics dates back to 1880 [1]. The advent of lasers and the development of miniature electret microphones finally paved the way for versatile photoacoustic sensing tools.

This talk starts with a brief introduction into the principles of photoacoustics, followed by presenting the development of PA detection in gases from the beginning to today including new light sources, new PA schemes such as quartz-enhanced PA spectroscopy (QEPAS) or cantilever-enhanced PA spectroscopy (CEPAS). Actual examples of trace gas monitoring will be discussed.

An early example of a mobile, computer-controlled PA system employed two line-tunable CO_2 lasers ($^{12}CO_2$ and $^{13}CO_2$) and a resonant multipass PA cell for ambient air monitoring [2]. At the exit of a freeway tunnel ethene, ammonia and CO_2 were continuously recorded in real time during days by selectively tuning the CO_2 lasers sequentially to the most appropriate laser lines. A good correlation between the concentrations of the different pollutants with automatic traffic counts was found.

With time, new laser types like QCLs, ICLs or mid-IR LEDs became available and made sensing systems much more compact and portable. PA cell designs were improved and often miniaturized. An example is a 3D-printed PA gas cell equipped with a standard MEMS microphone. It was used for NO_2 detection in combination with a blue laser diode emitting at 450 nm [3]. An excellent detection limit of 33 pptv (1σ) was achieved.

QEPAS was introduced as a novel PA detection scheme in 2002 [4]. It uses a quartz tuning fork (QTF) as sensing element instead of the conventional PA cell and operates at the high QTF resonance frequency of typically 32.8 kHz with an unusual high Q-factor of ca. 20'000. However, the high resonance frequency requires special attention for multi-species detection. Most recent QEPAS developments include a novel customized clamp-type QTF which proves advantageous for lasers with poor beam quality while maintaining the high Q-factor of $> 10^4$ [5].

A further approach named CEPAS differs from both conventional PAS and QEPAS as it uses a cantilever as pressure sensor [6]. The movement of a thin silicon cantilever is measured interferometrically with a diode laser. Recently, CEPAS was also employed for multi-species detection using mid-IR supercontinuum-based Fourier-transform PAS with a multipass cell equipped with a cantilever microphone [7].

Since mid-IR LEDs are available as low-cost light sources they also find their role in gas sensing devices. Recently a novel non-dispersive sensing scheme involving differential mode excitation PAS was reported [8]. It represents a robust and simple setup and takes advantage of the nonlinear excitation of various acoustic modes in a cylindrical PA cell to provide a high selectivity. Without bandpass filter and only 40 μW of total light power entering the cell, a detection limit of 25 ppm m^{-1} for methane (1σ, 20s integration time) was obtained.

These and further examples demonstrate the high potential of PAS in its various configurations in trace gas sensing.

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From Lab to Application – Digital Twins of Photoacoustic Gas Sensors

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Short abstract: We present a holistic approach to fully analytically predict the photoacoustic signal during sensor operation. With such a Digital Twin of a photoacoustic gas sensor, cross-sensitivities to changes in temperature, pressure or composition of the gas sample can be drastically reduced without the need for prior sensor calibration.

The photoacoustic (PA) technique is a promising tool to develop low-cost and small-size, yet highly sensitive trace gas sensors. Hence, the number of publications dealing with the topic of PA gas sensors steadily increased within the last decade, however, this is not reflected in the number of sensors available on the market. One main reason for this mismatch is the complexity of the mechanisms behind PA signal generation, accompanied by intricate cross-sensitivities towards varying measurement conditions. Besides purely optical interference with other absorbing species within the sample, PA sensors are further sensitive to varying measurement conditions that affect the cascade of competing molecular collisions finally yielding PA energy release and the acoustic properties of the sample, respectively. As a consequence, resonant PA sensors that are based on high frequency modulation in the kHz range have hardly been used in real-life applications so far, where they must be able to handle highly fluctuating environments, e.g. the ratio of O_2, CO_2 and H_2O in breath analysis. Changes in composition may affect the PA signal by alteration of the relaxation efficiency $\epsilon_{\mathrm{relax}}$ while converting absorbed photon energy into sound energy. Therefore, the efficiency of relaxation must essentially be added to the formula that describes the PA sound pressure p_{PA} at half-length of an open-ended tube with radius r, and first-mode longitudinal acoustic resonance stimulation. Further, the acoustic mode is assumed to perfectly overlap with the monochromatic light with optical power P_0 and wavelength λ that is used to excite the analyte molecules with volume ratio N_i.

$$p_{\mathrm{PA}} = (\gamma - 1)\,\frac{Q}{\omega_{\mathrm{res}}}\,\sqrt{2}\,\frac{1}{\pi r^2}\,\frac{\mathrm{N_A}}{V_{\mathrm{mol}}}\,N_i\,\sigma_i(\lambda)\,P_0\,\epsilon_{\mathrm{relax}}$$

Herein, Q and ω_{res} are the quality and angular frequency of acoustic resonance, $\mathrm{N_A}$ is the Avogadro constant, V_{mol} is the molar volume and σ_i is the absorption cross-section. However, the whole complexity of PA signal generation is illustrated in Figure 1. Besides $\epsilon_{\mathrm{relax}}$, the composition of the sample $\sum \chi_i$ might also affect the heat capacity ratio γ as well as the acoustic properties of the sample. Further, $\epsilon_{\mathrm{relax}}$, γ and $\frac{Q}{\omega_{\mathrm{res}}}$ depend on the temperature T and the pressure p of the sample, and moreover, these system parameters mutually influence each other following a circular relation.

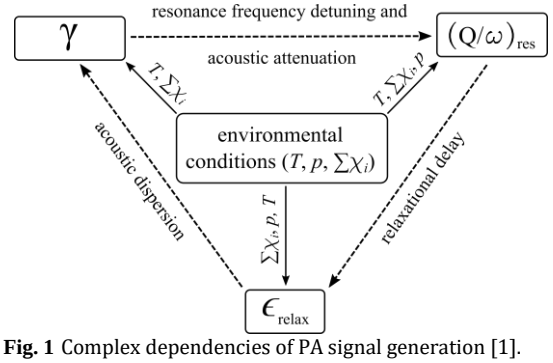

Fig. 1 Complex dependencies of PA signal generation [1].

We present our latest research findings, i.e. the implementation of an autonomous algorithm for modelling any relaxation cascade yielding $\epsilon_{\mathrm{relax}}$ [2], and further concepts, which in their entirety result in the implementation of a Digital Twin of photoacoustic gas sensors [3].

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Photoacoustic Characterization of Metal Nanoparticles Super-Aggregates

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Abstract. Photoacoustic spectroscopy revealed to be a robust and non-destructive technique for determining self-assembled nanostructures. The use of a straightforward approach based on photoacoustic detection allows to listen to both the absorption and scattering phenomena generated by nanoparticle suspensions. Photoacoustic results are compared with dynamic light scattering and local transmission electron microscopy measurements, allowing to obtain a well-defined interpretation of super-aggregates. This innovative morpho-optical approach opens new perspectives for advanced biomedical and structural applications.

Nanoparticles play a crucial role to tailor physico-chemical properties for improving performances of nanodevices and sensors in many fields of science and technology. Among others, metal-based nanoparticles (MNPs), whose average size falls in the range from units to hundreds of nanometres, show interesting optical and electrical properties that can be tuned by varying synthesis parameters. MNPs and corresponding covalent or non-covalent bioconjugates, obtained by interaction with drugs, enzymes, proteins, biomarkers, antibodies. The structural and morphological characterization of MNPs and bioconjugates is of fundamental interest to understand the interaction mechanism, where aggregation phenomena play an important role for understanding the controlled nanoparticle-drug interaction. Our attention recently oriented to MNPs functionalized by bifunctional organometallic thiols, containing Pt(II) centres and tributylphosphine ligands (among others trans,trans-4,4'-diethynyl (bistributylphosphine-Pt(II)thioacetyl) biphenyl, (Pt-DEBP)) to enhance solubility and with promising optoelectronic properties. The presence of two thiol terminal groups induces the interconnection into a superstructure network of MNPs [1,2]

A conventional strategy for characterizing large nanometric agglomerates of a selective self-assembly process involves different techniques, such as transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), dynamic light scattering (DLS), and others. However, as the size of the super-aggregate increases, it becomes difficult to understand the self-assembling growth of the nanoparticles. Although these techniques enable to determine the dimension of objects at micron- and nano-scale, none of them is intrinsically suited for gaining both spectroscopy and shape-size information. As an alternative, photoacoustic spectroscopy (PAS) provides quantitative information of the morpho-optical nature of the mesoscopic assemblies of the aggregates strictly correlated to their photonic and size-shape intrinsic properties [3]. The use of the photoacoustic detection approach allows to listen to both the absorption and scattering phenomena generated by nanoparticle suspensions [4,5]. Photoacoustic results were compared with dynamic light scattering and local transmission electron microscopy measurements, allowing to obtain a well-defined interpretation of super-aggregates. DLS measurements highlighted a broad population of nano-objects ranging from 10 to 200 nm. The PAS main results evidenced the presence of different super-aggregates with mean size 100 nm and 200 nm, whose mean filling factors are 50% and 30%, respectively. These morphological achievements are supported by local TEM imaging to evidence two similar size populations of nanoparticles self-assembled into nanostructured super-aggregates.

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A doubly-resonant cantilever-enhanced photoacoustic sensor for trace-gas detection

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Short abstract: Our most recent results on trace-gas detection with a novel cantilever-enhanced photoacoustic sensor are shown. The sensor is based on a doubly-resonant system, made of an acoustic and an optical resonator, and achieves a sensitivity below the ppt level on N_2O detection in the mid infrared.

The race towards compact and robust sensors able to detect extremely low concentrations of molecules in the air plays an important role in our modern society, impacting sectors such as energy production, environmental monitoring, transportation, agriculture, safety, and security. During the last decade, optical detection with ultra-high sensitivity, down to the part-per-quadrillion level, was demonstrated with cavity-ring down techniques [1]. An interesting alternative is represented by photoacoustic sensors based on quartz tuning forks and silicon cantilevers. These sensors present advantages in terms of costs and portability, and during last few years have shown great potential in achieving a sensitivity at the level of the techniques mentioned above, especially when combined with narrow-linewidth mid-infrared lasers and high-finesse optical cavities [2-4].

Here we report on our most recent measurements with a cantilever-enhanced photoacoustic sensor, in which the sensitivity is enhanced by a doubly-resonant - acoustic and optical - system. Our setup consist of a silicon MEMS cantilever as the acoustic transducer, whose displacement is measured with a balanced Michelson interferometer. The cantilever is mounted in a homemade photoacoustic cell, which also includes a high-Q-factor acoustic resonator placed inside a high-finesse optical resonator. This design, leveraging on a double standing wave effect, achieves a combined acoustic and optical amplification factor of several orders of magnitude compared to the standard configuration, thus strongly enhancing the final detection sensitivity. For our proof-of-principle demonstration of the technique, a mid-infrared quantum cascade laser at 4.5 μm is used, addressing N_2O rovibrational transitions.

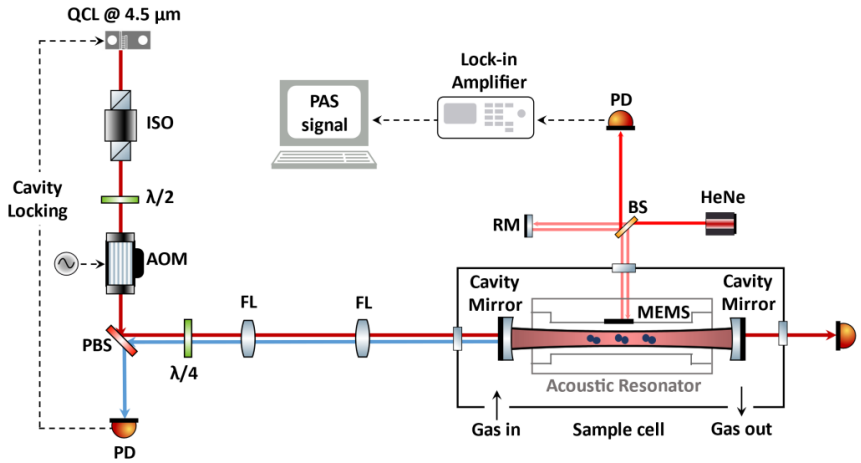

Fig. 1 Schematic representation of the setup. The building blocks are: the optical system (laser, mode-matching optics), the photoacoustic cell containing the MEMS transducer and the resonators, and the balanced Michelson interferometer.

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Open photoacoustic cell for measurement of water vapor flux

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Short abstract: Environmental monitoring requires high temporal resolution and sampling-free concentration measurements. We propose an open photoacoustic cell, capable of measuring atmospheric components under field conditions. The acoustic characterization of the cell was performed by numerical simulations and measurements in anechoic room. We applied the open cell in flux measurement successfully.

For most analytical instruments time resolution is critical to measure the exact variation of the analyte. Photoacoustic gas analysers are widespread nowadays and they have proven their applicability under various industrial conditions. We developed a fully open photoacoustic cell which is the slightly modified version of a previously introduced open cell based on the excitation of a combined acoustic mode of a cylindrical resonator [1].

The resonator is a 50 mm long cylindrical resonator with the diameter of 28 mm, resulting 12.5 kHz eigenfrequency of (0,2,1) eigenmode. The light source is a distributed feedback diode laser with a wavelength of 1371 nm where the absorption of water vapor is significant.

The cell acoustic characterization was done via computer simulations and also measurements in anechoic room. The results of the modelling were in good agreement with the measurements. We found that the threshold velocity is about 4 m/s.

The open cell was compared to a commercially available instrument (EC150 infrared gas analyzer, Campbell Sci. Ltd.) under field conditions. Eddy covariance flux measurement is a widely used technique to monitor the water vapor exchange between surface and the atmosphere [2]. For these measurements the monitoring of the wind speed is needed. To get proper flux values from the measurement data the maximization of the covariance $cov(w'\rho')$ is necessary, w' and ρ' is the fluctuation of the wind speed and water vapour density around their respective mean during an averaging period [2]. Using this method, we shifted one of the time series relative to the other one in both directions, scan by scan, until we found the maximum covariance. The open cell showed very similar results to the reference instrument by means of the covariance function shown in Figure 1.

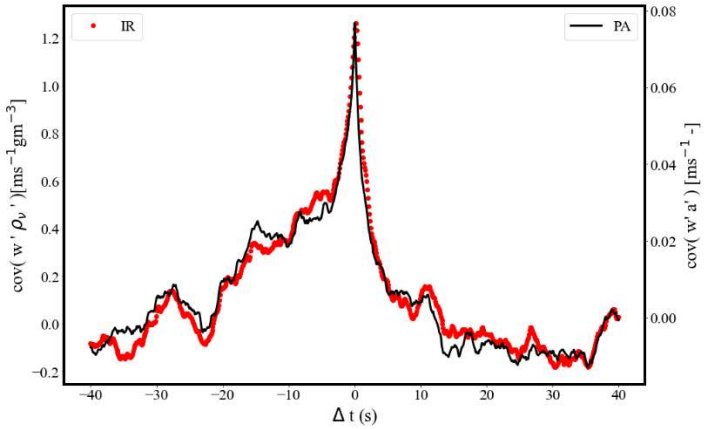

Fig. 1 Covarinace values of the infrared sensor (red dots) and the open cell (black line) as a function of timeshift (Δt), $(\rho_v{}')$ time series from the IR sensor, (a') time series from the open cell

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Multiscale photoacoustic tomography of genetically encoded photoswitchable proteins

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Short abstract: Here we describe a reversibly switchable nonfluorescent bacterial phytochrome for use in multiscale photoacoustic tomography (PAT) with the most red-shifted absorption among genetically encoded probes. We combined single-wavelength PAT with efficient photoswitching, which enhances detection sensitivity, increases penetration depth, and improves spatial resolution.

Taking advantage of various optical contrasts in biological tissues, optical imaging techniques have provided valuable information for biomedical studies at different length scales. However, strong optical scattering in tissue has led to substantial trade-off between the spatial resolution and penetration depth. Photoacoustic (PA) tomography (PAT), on the contrast, has overcome the depth and resolution limitations of pure optical imaging, by acoustically detecting the optical absorption contrast. PAT is inherently suited for molecular imaging, with a wealth of exogenous contrasts, such as organic dyes, nanoparticles, and fluorescent proteins. However, systematically-administered organic dyes and nanoparticles present challenges in effective targeting and clearing. Existing fluorescent proteins lack strong optical absorption at wavelengths beyond 750 nm, and thus are not suited for deep tissue imaging. In addition, all the above contrasts sufferer from the strong background signals generated by various endogenous biomolecules, especially hemoglobin, which typically have wideband absorption spectra and are much more abundant in tissue.

Given these limitations, we develop a new approach that combines deep-penetration PAT with a novel non-fluorescent bacteri-phytochrome BphP1, allowing high-resolution ultra-sensitive imaging of the genetically encoded biological process at depths.[1,2] By photoconverting between the red-light-absorption Pr state and the NIR-light-absorption Pfr state, BphP1 is a natural reversible switch in light perception. Capitalizing on the strong NIR absorption of BphP1 and its switching capability between two states, we demonstrate that this method can significantly enhance the detection sensitivity of PAT. Tens of mammalian cells can be detected at ~1 cm depth. We further demonstrate this high detection sensitivity by imaging the growth of BphP1-expressing cancer cells in deep tissue in vivo and monitoring the cancer metastasis. We also extended this method to PA microscopy, demonstrating substantially enhanced spatial resolution and image contrast on single bacteria, mammalian cells.

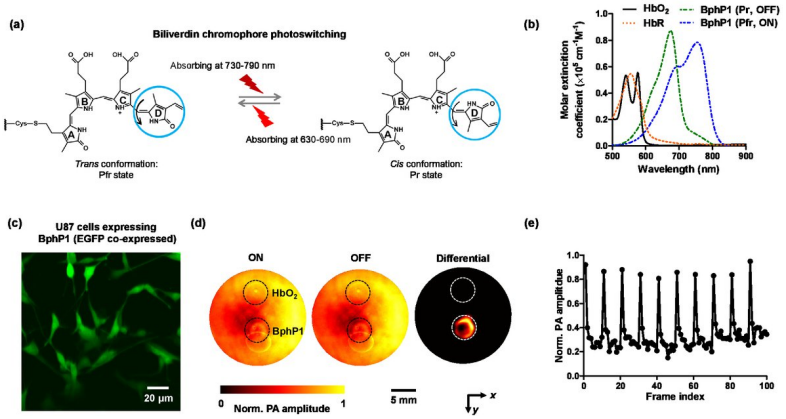

Fig. 1 Reversibly switchable BphP1 as a genetically-encoded photoacoustic imaging contrast. (a) Photoswitching of BphP1 from Pr state to Pfr state, and vice versa, with the NIR and far-red illumination. (b) Absorption spectra of oxy-hemoglobin, deoxy-hemoglobin, Pr and Pfr state BhpP1, showing the strong NIR absorption of BphP1. (c) U87 cells expressing BphP1, with EGFP co-expressed for fluorescence imaging. (d) The PA images of an optically scattering and absorbing phantom with BphP1-expressing U87 cells embedded at 10 mm. The ON and OFF state images do not show the tumor cells due to the strong background signal, and the differential image clearly reveals the tumor cell signals. (e) Reversibly switching BphP1-expressing U87 cells in scattering media.

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Spectroscopy for Atmospheric Applications

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Drone-assisted spectroscopic detection of trace-gas plumes – – new technologies and emerging applications

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Short abstract: Trace-gas plume detection and localization technologies based on drone-assisted, stand-off, open-path laser spectroscopic sensors will be presented. Recent progress and developments in the sensing technology area, as well as potential applications to variety of gases of atmospheric and industrial importance will be discussed.

Anthropogenic greenhouse gas emissions are often caused by localized sources and their quick detection, quantification, and spatial localization are of great importance to prevent excessive emissions. For detection of potent greenhouse gases of high industrial importance like methane, there are several widely accepted methods for detection of leaks that include portable extractive sensors, gas imaging cameras that support manual local detection, or larger area sensing technologies such as aircraft sensors, mobile gas labs, and satellite-based observations that have limited spatial resolution to detect localized leaks. Recently we demonstrated a promising set of techniques based on stand-off, open-path laser spectroscopic sensors with a capability of actively tracking a mobile retroreflector mounted on a drone (or any other vehicle) that enabled tomographic-like reconstruction of trace-gas plumes and enabled plume source location to within 1 m as well as estimation of emission rates within ± 30% error. Unlike other localization approaches reported in the literature utilizing drones equipped with point trace-gas sensors, the stand-off drone techniques are not restricted by the payload limits imposing constrains on sensor quality. In this talk, I will present drone-assisted stand-off spectroscopic detection of trace-gas plumes using two different spectroscopic techniques and two separate methodologies for stationary and drone-assisted methane plume reconstruction using inversion techniques to localize and estimate the flow rate of simulated methane leaks. The methodologies have been verified in a set of controlled laboratory and field experiments involving methane leak simulations. Recent progress and developments in the sensing technology area, as well as potential applications to variety of gases of atmospheric and industrial importance will be discussed.

Around the "atmospheric world" under a balloon : a long-duration observation of the equatorial tropopause with the Pico-SDLA tunable diode laser spectrometers

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Abstract for invited oral presentation

In the UTLS, water vapor is of particular importance because of its impact on the ozone stratospheric layer through chemical and radiative processes and its impact on the global radiative equilibrium, through the stratospheric water vapour feedback (Dessler, 2013; Dvortsov and Solomon, 2001; Riese et al., 2012; Solomon et al., 2010; Forster and Shine, 1999; Wang et al., 2017; Kirk-Davidoff et al., 1999). However, measuring stratospheric water vapor remains to date, a technical challenge.

Since the 90's, our team develops in-situ tunable diode laser spectrometers dedicated to the study of transport processes at the interface between the troposphere and the stratosphere (UTLS). Progresses in photonics have allowed to reliably probe water vapor, methane and carbon dioxide in such harsh environment. Recently, our Pico-SDLA instruments have been involved in the Stratéole-2 french-american project, to monitor continuously water vapor, methane and carbon dioxide in the equatorial tropopause region. In the frame of this project, three observation campaigns are scheduled: 2019-20, 2021-22 and 2025-26. In the frame of the first two campaigns, the instruments were flown under zero pressure balloons during 35 to 80 days, at an altitude between 18.5 and 20.5 km, thereby offering an original and unprecedented observational dataset. The measurements have allowed to observe the signature of large-scale circulation, atmospheric waves and deep convection on the lower stratospheric humidity.

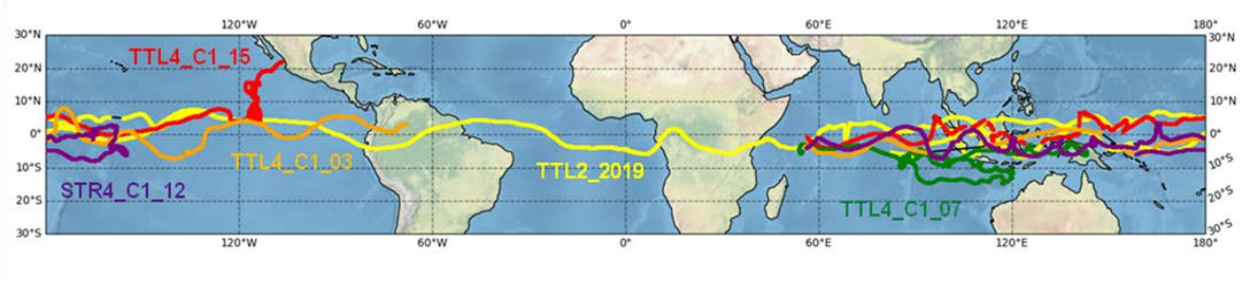

Figure 1: Trajectories of the balloons carrying the Pico-SDLA instruments during the first two campaigns of Stratéole-2.

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Cavity enhanced optical sensing of the atmosphere

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Short abstract: We overview our developments and applications of cavity-based spectroscopic instruments to optical sensing of trace gas and particulate matter (PM) in field intensive campaigns and in atmospheric simulation chambers.

Understanding the atmospheric chemistry is important for improving air quality (local/regional scale) and for providing reliable climate-change prediction (global scale). To test the degree of our understanding of the ongoing atmospheric chemistry, concentration profiles of key atmospheric species are measured in field campaigns in different environments (sea-side, remote forest, polar, rural, urban, ….) and are compared to the output of atmospheric models involving detailed chemical mechanism. Therefore, reliable concentration assessment of key atmospheric species (hydroxyl radicals OH, hydroperoxyl radicals HO_2, nitrate radicals NO_3, etc.) and their precursors (nitrous acid HONO, nitrogen dioxide NO_2, etc.) is essential. Real-time *in situ* monitoring of these species is challenging because of their high reactivity and ultralow concentrations in the range of pptv (parts per trillion by volume).

In gas sensing by Beer–Lambert-based absorption spectroscopy, the absorption intensity follows an exponential law with the optical absorption length, the use of long path absorption schemes is thus the essential way to improve the spectroscopic measurements sensitivity. Optical cavities bridge the gap between sensitivity and spatial scale, delivering long optical pathlengths in a small physical footprint and is widely used for high-sensitivity spectroscopy applications [1-2].

In this talk, we overview our developments and applications of cavity-based instruments [3] to optical sensing of trace gas and particulate matter (PM) in field intensive campaigns and in atmospheric simulation chambers.

Experimental details and preliminary spectroscopy results will be presented and discussed.

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Recent advances in VOC analysis by mid-IR laser spectroscopy

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Short abstract: Broadly tunable mid-IR laser sources (VECSEL and XT-QCL) open new exciting opportunities for the detection of volatile organic compounds. Real-time, fast, sensitive, and highly specific analysis of VOCs in human breath with compact instrumentation is demonstrated.

Volatile organic compounds (VOCs) are ubiquitous in our environment and everyday life. Hence, their selective and quantitative detection is of great interest in many industrial, environmental, forensic, and medical applications. In particular, breath analysis based on laser absorption spectroscopy as non-invasive analytical method has huge potential to be used for clinical diagnosis and therapeutic monitoring. Especially VOCs as biomarkers, associated with specific physiological and health conditions, represent a great clinical relevance.

As nearly all organic molecules, VOCs have intrinsically broad and congested absorption features, which make their quantification by mid-IR laser spectroscopy highly challenging. We address this by leveraging on recent advances in laser sources, such as the optically pumped, broadly tunable vertical-external-cavity surface-emitting laser (VECSEL) [1] accessing the 3 µm spectral region, known as the functional-group region, and on-chip QCL solutions with very large tuning (XT) [2] that can cover the full 4–10 µm range. While the VECSEL uses an external, movable top mirror mounted on a piezoelectric actuator to cover > 30 cm^{-1} and operates in pulsed mode, the XT-QCL provides cw-operation, fully electrical tuning, and high spectral resolution typical for DFB lasers. Using the Vernier effect, the XT-QCL emission frequency can be switched between six different single-mode lasing clusters, distributed over 40 cm^{-1}. This switching is achieved by current driving of integrated micro heaters located next to two distributed Bragg reflectors that form the laser cavity. Within each cluster, we apply an intermittent-continuous-wave (iCW) driving scheme [3, 4] to the laser for fast spectral scanning. Such devices are highly attractive because they allow high-resolution spectroscopy in several distinct channels. This is advantageous when several molecules have overlapping spectral features that may not be sufficiently distinguished within the tuning range of a single DFB-QCL.

In this work, we demonstrate the spectroscopic detection of VOCs, in particular of breath acetone [5], ethanol [6], and methanol using both types of lasers. Furthermore, we illustrate the capabilities of our approach for the detection of small oxygen-containing VOCs at amount fractions down to tens of ppb [7]. High-resolution spectral screening of various VOCs revealed significant fine structure in the ro-vibrational spectrum of molecules containing up to four carbon atoms (C4). Such distinct narrow features were also observed for larger molecules (~6 carbon atoms ~C6) with rigid molecular structure or high-order symmetry. This initiates a paradigm shift in the analysis of large organic molecules by laser spectroscopy. The broad measuring range, high spectral resolution, and the unique spectral fingerprints of many of the investigated VOCs assure excellent selectivity and large linearity range of the presented method. This enables multi-compound measurements and raises new opportunities for mid-IR laser-spectroscopic analysis of VOCs.

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Flexible molecular gas sensing platform in the terahertz domain

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Short abstract: We present a flexible platform for molecular sensing in the terahertz range combining an opto-electronic light source with a new generation of compact gas cells. Sensing is demonstrated by the measurement of various nitrious oxide (N_2O) transitions with a fast frequency sideband modulation technique.

The terahertz (THz) domain (0.3-10 THz) has been gaining attention due to the advancements in THz sources and detectors, and the abundance of molecules with large THz absorption cross-sections for environmental monitoring and medical diagnostics [1]. Practical applications rely on compact, rapid, and cost-effective gas sensing systems. Recently, substrate-integrated hollow waveguides (iHWGs) have been introduced as an alternative to standard bulky gas cells in the mid-infrared range [2]. These iHWGs offer an excellent volume-to-optical path length ratio, leading to an improved system sensitivity and maintain a robust device with a small footprint.
Here, we present the first implementation of iHWGs in a THz sensing system. Our recently introduced flexible opto-electronic THz source provides direct electronic control of the spectral content [3]. This is accomplished through the combination of electro-optic (EO) modulation for the generation of optical sidebands in the telecom range, and photomixing for difference frequency generation in the THz domain [3]. The versatility of the system is demonstrated by room temperature measurements of various rotational transitions of the greenhouse gas nitrous oxide (N_2O). Fig. 1(a) shows a schematic of the iHWG, a miniaturized gas cell consisting of a solid substrate with an integrated light-guiding channel and a sealing top plate with gas in- and outlet. In Fig. 1(b) an overview of the absorption coefficients α, extracted from several measurements at various N_2O lines, is presented and compared to the theoretical values calculated via the HITRAN database [4].

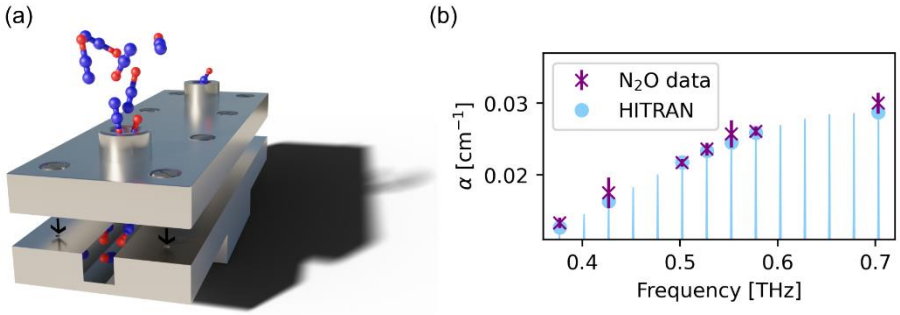

Fig. 1 (a) Sketch of an iHWG. (b) Summary of absorption coefficients α (purple) obtained from several transmission measurements of an iHWG filled with pure N_2O (N5.0 purity) at ~200 mbar and at 296 K. Comparison with the theoretical values (blue) determined with the HITRAN database [4] show good agreement.

The combination of iHWGs with a flexible THz source offers a highly versatile THz sensing platform that can be adapted to a variety of real-world gas sensing scenarios. This platform is capable of real-time control of the probing THz frequencies, which leads to substantially faster measurement times of ~1 min compared to other sensing methods. Furthermore, iHWGs provide an impressive volume-to-optical path length ratio of 10^4 and require only a small sample gas volume below 2 mL. Moreover, the integration into a solid substrate, guarantees unprecedented robustness and extended optical path lengths with meandering structures or more advanced concepts become possible [2]. This significantly increases the system's sensitivity, while maintaining a compact size and low production costs.

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Quartz-Enhanced Photoacoustic Spectroscopy

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Quartz-tuning-fork based Laser Spectroscopy for Trace Gas Detection

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Short abstract: Quartz-enhanced photoacoustic spectroscopy (QEPAS) and light-induced thermoelastic spectroscopy (LITES) are two quartz tuning fork based laser spectroscopy, which were invited in the year of 2002 and 2018, respectively. This presentation summarized the latest progress of our group in QEPAS and LITES based gas sensing.

Quartz tuning fork (QTF), a crystal component, is produced by photolithographic and chemical etching techniques. It is originally used to provide the clock rate in crystal watches, timers and electronic circuits. With a geometry of a U-shape, a QTF consists of two quartz fork tines and a hollow fork valley. Standard commercial QTFs possess a resonance frequency of 32.768 kHz and a Q-factor of ~10000 in a standard atmosphere pressure. The unique quadrupole structure of a QTF provides an excellent immunity to environment interference. Photoacoustic spectroscopy (PAS) is identified as an advanced technique for trace sensing. In traditional PAS, a microphone is used as an acoustic wave detector. A recent improvement of microphone-based PAS is quartz-enhanced photoacoustic spectroscopy (QEPAS) technique, which was first reported in 2002 [1]. This technique uses a low cost, commercially available mm sized piezoelectric QTF as an acoustic wave detector which possesses a high detection sensitivity and immunity to ambient acoustic noise. In QEPAS, a size limitation of the gas cell no longer exists and the cell volume can be reduced significantly, and even the gas cell can be optional [2]. However, QEPAS is a contact measurement technique, in which a QTF should be embed in a gas sample. This feature limits its application in many fields, such as combustion diagnosis, long distance measurement and remote sensing. In the year of 2018, a new technique of light-induced thermoelastic spectroscopy (LITES) was invented [3,4]. LITES is based on the light-thermo-elastic effect. In LITES, a QTF is used as a photothermal detector, and it can be placed far from the target gas. Therefore, LITES is a non-contact measurement method and can be used for remote and standoff gas detection. In this presentation, the latest research progress about QEPAS and LITES in our group will be discussed.

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Multi-QCL Quartz-Enhanced Photoacoustic Sensor for Environmental Monitoring

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Short abstract: Here we report on the realization and calibration of a Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) sensor using a three-wavelength source based on three beam-combined Quantum Cascade Lasers (QCLs) for detection of NO_2, SO_2 and NH_3 with detection limits below their natural abundance.

Recent developments in gas sensing technologies serve as valid and solid instrument for key-field applications as well as for human and environmental protection. The possibility to perform multi-gas detection is a crucial requirement for many real-world applications, such as environmental monitoring, safety and security, oil&gas and biomedical analysis. Moreover, sensing technologies must be able to offer real-time and in-situ operation as well as unambiguous identification and quantification of the gas samples constituents.

Optical techniques based on indirect absorption spectroscopy rely on the detection of non-radiative effects generated as consequence of the light absorption, i.e., photoacoustic or photothermal effect. Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) uses a tuning fork as a sound detector of the photoacoustic waves generated by the interaction between modulated laser light and gas molecules [1]. QEPAS technique can be coupled with any kind of laser source, with emission from ultraviolet to terahertz range. Moreover, the detection module of a QEPAS sensor is compact, lightweight and the influence of environmental noise on the detection sensitivity is strongly reduced. Therefore, in the recent years, QEPAS stated itself as one of the best techniques for in situ and real-time detection of trace gas concentrations [2].

In this work, we report on the realization and laboratory validation of a multi-QCL QEPAS sensor using a three-wavelength laser module. It contains three different QCLs with a single collimated beam output produced using dichroitic beam combiners in the module. A picture of the internal assembly of three QCLs with the mirror and the two spectral filters is reported in Fig. 1.

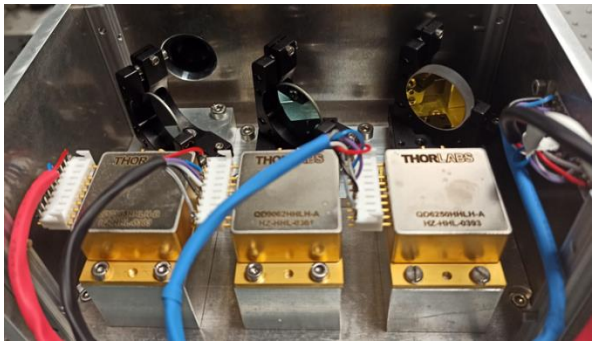

Fig. 1 Internal assembly of the three QCL mounted within the 3λ-QCL box.

The 3λ-QCL module was used as light source in a QEPAS sensor tested for detection of NO_2, SO_2 and NH_3, in sequence. Sensitivities of 19.99 mV/ppm, 19.39 mV/ppm and 73.99 mV/pp were reached for NO_2, SO_2 and NH_3 detection, respectively, with ultimate detection limits of 9 ppb, 9.3 ppb and 2.4 ppb, respectively, well below their typical natural abundance in air even when the signal integration time is as low as 0.1 s.

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Highly Selective Toluene Detection using Quartz Enhanced Photoacoustic Spectroscopy at λ = 13.71 µm

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Short abstract: We demonstrate a quartz-enhanced photoacoustic spectroscopy (QEPAS)-based sensor for detecting toluene, using a custom fabricated InAs-based quantum cascade laser operating at $13.71\ \mu m$. The sensing system is immune to spectral interferences from other gases in the BTEX group and achieved a minimum detection limit of $593\ ppb$ at $0.1s$.

Volatile organic compounds (VOCs) are among the many pollutants that enter the ambient air from anthropogenic and natural sources. Among all the VOCs, benzene, toluene, ethylbenzene, and xylene isomers (commonly called BTEX) are of utmost concern. The World Health Organization (WHO) has classified BTEX compounds as highly aggressive cancer-causing agents [1]. The severity of BTEX demands the development of highly efficient, low cost and rapid techniques for their identification and quantification.

BTEX exhibits strong absorption in the wavelength range of $13 - 15\ \mu m$ [2], which could be exploited to make highly sensitive and selective sensors. However, the lack of suitable sources beyond $12\ \mu m$ delayed the development of BTEX spectroscopy in this spectral domain. This work demonstrates a quartz-enhanced photoacoustic spectroscopy-based sensor for detecting toluene using a custom-built InAs-based QCL operating at $13.71\ \mu m$. The QEPAS detection module comprises a quartz tuning fork (QTF) and two resonator tubes. The fundamental flexural mode of the QTF has a resonance frequency of $f_0 = 12.457\ kHz$ and a quality factor $Q = 22{,}197$ at 200 Torr. A $2f$ wavelength modulation detection scheme is implemented by modulating the QCL current with a frequency of $f_0/2$, while slowly scanning the laser wavelength tuning range using a ramp signal [3]. The f_0 component of the QEPAS spectrophone signal output is acquired using a lock-in amplifier.

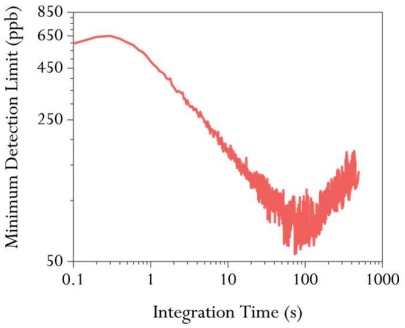

Fig. 1 Minimum detection limit as a the function of Integration time.

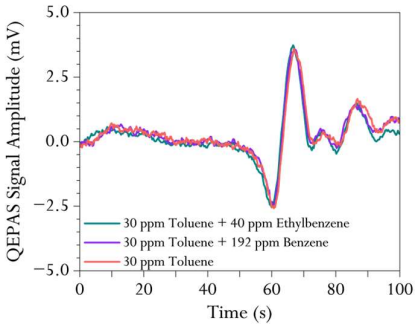

Fig. 2 Shape of QEPAS signal of toluene in different gas mixtures.

To determine the minimum detection limit of the sensor, a long-term noise level of the system is measured, followed by obtaining a calibration curve by varying the concentration of toluene from $0\ ppm\ to\ 150\ ppm$. The slope of the calibration curve is $0.12\ mV/ppm$. Using these results and the Allan deviation analysis, the minimum limit of detection of toluene is calculated to be $592\ ppb$ at $0.1s$ integration time, as shown in Figure 1. Furthermore, toluene, benzene, and ethylbenzene mixtures were studied to quantify the possible interferences on the sensor's performance. The study revealed no spectral interference from either benzene or ethylbenzene, as seen in Figure 2. The effect of xylene is not experimentally measured due to its unavailability; however, it is expected to behave like ethylbenzene as their absorption strengths are similar in this wavelength range [2].

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QEPAS sensor
for Surveying the Atmospheric Carbon Cycle

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Short abstract: We present the design and first results of a Photoacoustic Spectroscopy sensor to measure in-situ CO_2 concentration and its isotopic footprint, which will be improved with the implementation of Quartz Enhanced Photoacoustic Sensing (QEPAS). This feature will allow discerning between natural and anthropogenic CO_2 sources.

CO_2 is the largest greenhouse gas (GHG) contributor to human-caused global warming. Nowadays, different satellite-based and ground-based initiatives are operating with the main objective of globally monitoring atmospheric GHG concentrations and characterizing their sources and sinks [1]. In this sense, we are developing a ground-based system capable of generating a vertical characterization of atmospheric GHG with fine vertical resolution and supported by exhaustive measurements of surface concentrations. We address this challenge via the combination of optical spectroscopic techniques.

In this contribution we focus on the ground surface measurements of CO_2. The sensor being developed is based on the photoacoustic technique with a commercial acoustic detection module (Thorlabs ADM01) that comprises a Quartz Enhance acoustic detector (QEPAS) [2]. We aim to demonstrate a system working out-of-the-lab capable of CO_2 concentration measurements well in the sub-ppm range (we target 50 ppb), compact and cost-effective. Moreover, the system has been conceived to be able to obtain the isotopic concentration ($^{13}CO_2/^{12}CO_2$ ratio) with a target precision better than 0.1 ‰. For that purpose, we will use a quantum cascade laser (QCL) as optical excitation source tuned around 4.39 um, as this wavelength has been identified for CO_2 isotopologues measurements.

Currently the first sensor prototype operates in the near-infrared using an external cavity tunable laser (Pure Photonics PPCL700) and a custom made low Q acoustic detection module [3]. Figure 1 shows out first results for the characterization of the ambient laboratory air. The figure represent a water absorption feature identified at 6583.7 cm-1. It has been obtained using the external AM modulation input of the tunable laser set at the resonant frequency of the gas cell (1820 Hz) and first harmonic lock in detection (100 ms integration time). Given the absorbance of water vapor at this wavelength, these are promising results to achieve the target sensor specifications for CO_2 detection in the mid-infrared.

This is an ongoing development under the CarbonSurvey project (December 2022 - November 2024). We will present the sensor design and the laboratory results. By the end of the project, we will have the sensor prototype fully operational and calibrated at the Izaña Atmospheric center. Moreover, the sensing systems will be specifically designed for a straightforward in situ deployment in different areas of interest, providing full coverage of the most important blind spots existing today. This new generation of sensors could establish the necessary basis to guide decision-making policies in the green transition process ahead.

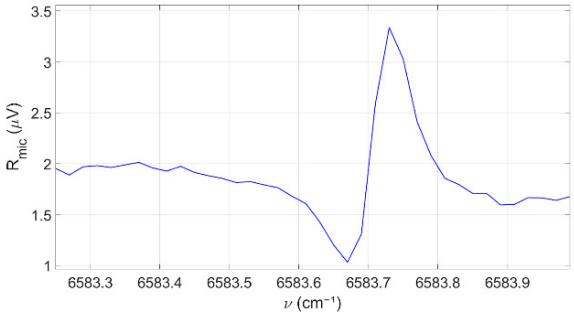

Fig. 1 PAS readout signal targeting a water absorption line

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Ultra-compact QEPAS sensors for environmental detection of toxic gases and development of novel near-IR DFB laser diodes for photoacoustic spectroscopy

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Abstract: The aim of this work is realising light ultra-compact QEPAS sensors for detection of toxic gases in atmosphere, implementing custom near-IR Distributed Feedback laser diodes (DFBs) (emitting at 2.4 um) with grating on the top of the ridge and having custom layer organisation.

Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) sensors for N_2O and CH_4 detection have been developed for potential drone monitoring to confirm the working ability of a compact, lightweight, and portable sensor head, implementing commercial laser source emitting at 7.840 µm [1]. The 2.3-2.5 µm spectral range is very attractive for gas sensing in the atmosphere since several gas species present strong absorption lines and it falls in a transparency window for standard air. Thereby we have focused our activities on the realization of custom near-IR Distributed Feedback (DFB) laser diodes with a novel structure for better DFB coupling. The realized laser sources will then be applied in the previously validated sensor heads for NH_3, CH_4 and HF detection.

Gas sensing. The objection of the work was to test the ability of given sensor head to work properly and to create 2 twin-sensors for CH_4 and NO_2 detection, in order to test the repeatability of QEPAS sensor and to investigate the possibility to detect both gases simultaneously. We used a custom T-shape QTF with a resonance frequency around 12 kHz and full characterisation of it was achieved. QEPAS signal acquisition for different concentration of Methane was performed and the linear behaviour of the sensor was confirmed. We performed a similar analysis N_2O detection. Bothe sensors were tested during 24 hours in laboratory conditions and minimum detection limits (MDLs) for 10 s integration time of 6.4 ppb (CH_4) and of 2 ppb (N_2O) were achieved.

Novel GaSb-based DFB laser diodes. We designed and realized custom DFB laser-diodes with a DFB grating on the top of the laser ridge. The active structure is based on InGaAsSb/AlGaAsSb quantum wells grown on GaSb substrate by molecular beam epitaxy. To increase the coupling factor between the guided optical mode and the grating, we have used thin AlGaAsSb upper cladding layers. 2D simulations of the laser properties according to different thickness of upper cladding and etching depth of the DFB structure were performed. DFB laser diodes with 0.5 µm thick upper cladding of and 0.2 µm top contact layer of were fabricated and fully evaluated. Threshold currents as low as 25 mA were achieved and the emitted power increases up to 9 mW. The devices exhibit single frequency operation without mode hopes, with a SMSRs of 25 dB on the whole tuning range (60 mA-300 mA), with a representative spectrum shown in Figure 1. Possibility to detect HF line at 4095.44 cm^{-1} using the developed device will be pursued.

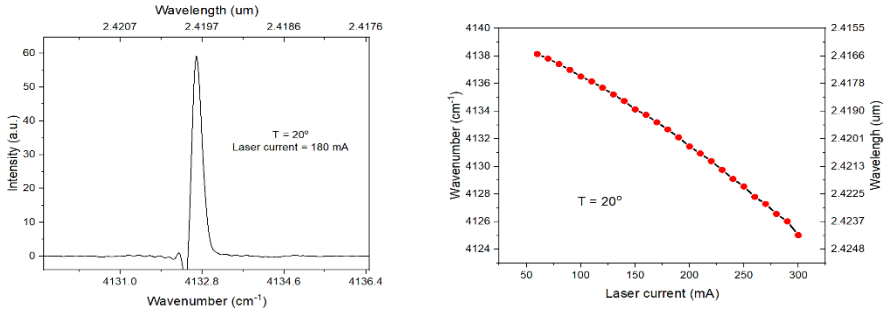

Figure 1. Left panel: optical spectrum of one of the realised device at T=20° and injected current of 180 mA. Right panel: laser emitted wavelength versus injected current at T=20°.

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Study of ammonia adsorption and desorption phenomena in a QEPAS sensor

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Short abstract: Ammonia monitoring is essential in agricultural and environmental applications. Sensor calibration remains a challenge due to the ammonia molecules strong tendency to be adsorbed and desorbed by surfaces. We measure the adsorption and desorption time in a thermoplastic polyurethane tube-based QEPAS sensor to predict the trend over time of the sensor signal.

Ammonia (NH_3) is commonly employed in several agriculture, food production and industrial processes. As a key component in fertilizers, it plays a vital role in promoting plant growth and increasing crop yields. Additionally, it is used as a refrigerant and a processing aid in food production, helping to preserve and enhance the quality of food products. This widespread use has raised concerns about its environmental and health impacts. Therefore, accurate and reliable NH_3 monitoring systems are essential to detect the concentration of this toxic gas. In recent years, quartz-enhanced photoacoustic spectroscopy (QEPAS) sensors have been extensively developed and optimized for NH_3 measurements, leading to several applications in various fields [1–3].
The challenge for these applications consists in facing the strong tendency of ammonia molecules to interact with surfaces, due to its strong dipole moment. Adsorption and desorption phenomena are influenced by several factors, including the properties of the surface (such as surface area, composition and roughness), the temperature and pressure of the environment. In this work, we report a QEPAS sensor based on a diode laser source targeting the NH_3 adsorption line at 1531.65nm (6528.90 cm^{-1}) with an injection current of 177.00 mA and optical power of 35.2 mW. A thermoplastic polyurethane (TPU) tube system is used to transport the gas from the gas cylinder to the detection module, which consists in a quartz tuning fork (QTF) coupled with two resonator tubes. A capacitive humidity and temperature sensor is integrated into the gas line to monitor the water vapour relative concentration and the gas temperature in real-time. While flowing a gas mixture containing ammonia through the sensor, the detected ammonia signal increases with time till a steady-state concentration is achieved. Conversely, when flushing nitrogen through the sensor, the signal decreases slowly. Both behaviours, shown in Fig.1, can be modelled considering the effect of adsorption and desorption phenomena of ammonia molecules interacting with the TPU tubes.

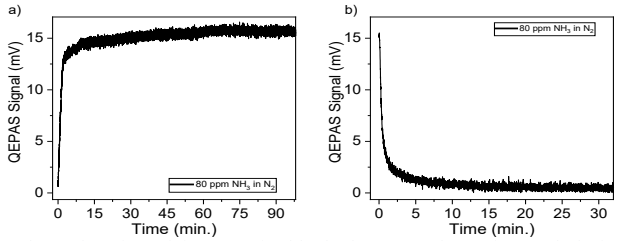

Fig. 1 QEPAS signal as a function of time acquired locked on NH_3 absorption peak during the adsorption(a) and the desorption process(b) at 400 Torr using a concentration of 80 ppm NH_3 in N_2.

In our experiment, we flushed mixtures containing different concentrations of ammonia through the QEPAS sensor to retrieve the gas-exchange time constant and the adsorption and desorption time constants. Then, the same gas mixture was flushed through the system by varying the tube length. Experimental data were fitted by using the model's equations. The results show that the gas exchange time constant is proportional to the tube length, while adsorption and desorption time constants of 28.11 min. and 6.09 min. were measured, respectively. Such parameters let us predict the trend over the time of the QEPAS signal of any ammonia concentration flowing through the sensor or, vice versa, to retrieve the unknown concentration of ammonia contained in a gas mixture flowing through the sensor, even if the steady-state condition has not been achieved yet.

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Sensing for Bio, Food, and Petrochemical Applications

PA spectrometer for methane isotopologues

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Short abstract: Certain applications require the determination of the isotopologic composition of hydrocarbons. The two main isotopologues of methane $^{12}CH_4$ and $^{13}CH_4$, for instance, are important for climate and planetary research as well as for natural gas exploration. We present a photoacoustic analyzer for methane isotopologues and first measurements results.

We developed an isotope-selective analyzer for methane based on photoacoustic spectroscopy. A spectrally tunable interband cascade laser emitting in the range of the Q-branches of the fundamental molecular vibration of the two main isotopologues, $^{12}CH_4$ and $^{13}CH_4$, serves as radiation source [1]. The optimum center wavelength of the laser has been determined using a mathematical algorithm [2].

The analyzer integrates a cylindrically symmetrical sample cell. The photoacoustic signal is measured by an analog microphone [3]. As an example, Figure 1 shows the phase-sensitively detected microphone signal as function of the average laser current (i.e. emission wavelength of the laser) for 25% $^{12}CH_4$ with three different $^{13}CH_4$ concentrations in nitrogen (296 K, 1013 hPa).

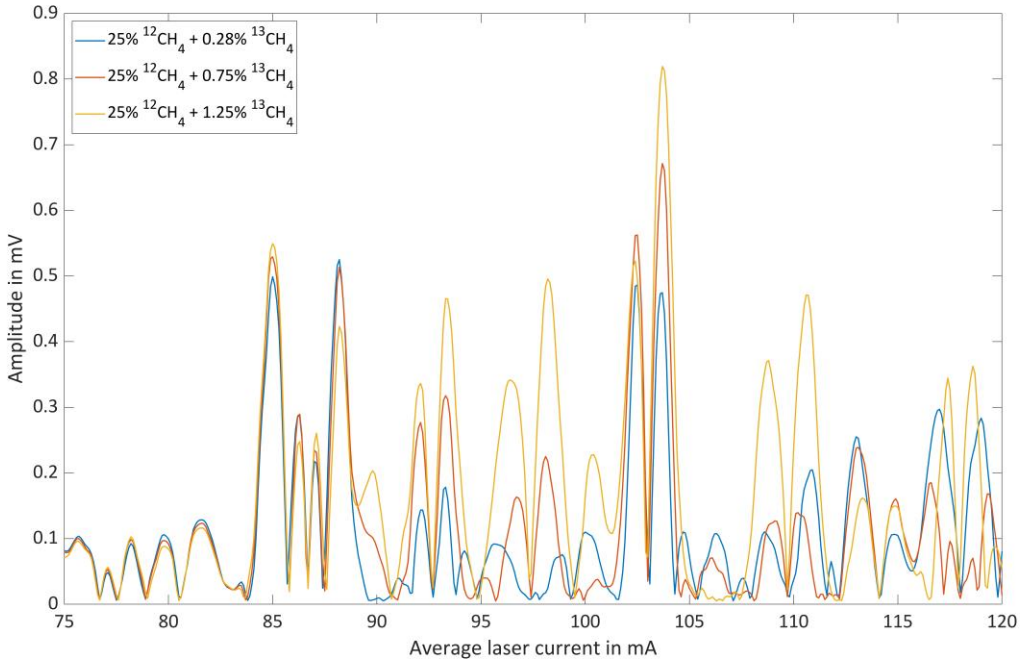

Fig. 1 Photoacoustic signal as function of the average laser current for 25% $^{12}CH_4$ with three different $^{13}CH_4$ concentrations in nitrogen.

In our presentation we will also report results of a cross-validation and the error for predicting unknown concentrations.

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Challenges and Opportunities from Food *Volatilomics*: Sensing the Quality

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Short abstract: The food Volatilome encrypts high-level information on product's Quality (authenticity, identity, sensory pleasantness etc.). High-resolution profiling and fingerprinting by multidimensional analytical techniques give access to this information while opening intriguing opportunities for sensing. The question is: Are sensing technologies ready for Artificial Intelligence smelling?

Since their introduction, high-resolution separations techniques based on chromatography helped scientists to unrevealing Nature's complexity facilitating highly-informative screenings, supporting markers discovery in *omics* applications and offering many opportunities to implement system biology-like strategies for investigation, the so-called *integrationist* approach [1]. More recently, in the field of food *volatilomics*, comprehensive two-dimensional gas chromatography (GC×GC), has demonstrated its potentials boosting the research in many directions all intercepting the concept of Quality. Patterns of volatiles can be used as product's unique fingerprint for *identitation* [2], benchmarking, spoilage detection, and aroma blueprinting above all.

The contribution discusses the challenging task of marker discovery by multidimensional platforms and effective data processing workflows [3]. In particular, the key-role of Artificial Intelligence (AI) algorithms for computer vision (i.e., "*…a field of AI that enables computers and systems to derive meaningful information from digital images…*" [4]) and smelling (e.g., *AI smelling machine* [5]) is discussed and proof-of-evidence on the feasibility and effectiveness of such "comprehensive" approaches presented through the authors research experience on high-quality food products (hazelnuts and extra-virgin live oil).

A strategy capable to answer many questions about product qualities (*e.g.*, sensory quality, freshness, authenticity, presence of sensory defects etc.) with a single measure realized by combining many analytical dimensions (*e.g.*, sample preparation, separation, multiple detection, olfactometry, etc.) can be simplified and realized with an array of specialized sensors? Is that possible to intercept the trajectory of Quality by early detection of key-volatiles patterns along the supply chain? Are we all ready to be challenged by Nature's complexity?

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Calibration-free Mid-infrared Exhaled Breath Sensor based on BF-QEPAS for Non-invasive Diagnosis

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Short abstract: We demonstrate a calibration-free mid-infrared (MIR) exhaled breath sensor for real-time ammonia measurements at ppb-level, which can be used for the non-invasive diagnosis of liver and kidney diseases. The ammonia content exhaled by 8 healthy volunteers is recorded and the real-time measurement results are analyzed.

The advancement of science and technology has led to the emergence of an increasing number of non-invasive screening techniques. These techniques were developed to compensate for the shortcomings of conventional diagnostic procedures and serve as an essential foundation for the prevention, diagnosis, treatment, and evaluation of the prognosis of diseases, such as the use of photoacoustic technology to determine the levels of sugar in human blood, the diagnosis of human intestinal malabsorption diseases utilizing Raman spectroscopy, the measurement of human exhaled ammonia by quartz-enhanced photoacoustic spectroscopy (QEPAS) for screening of liver and kidney diseases [1], and the measurement of blood alcohol levels through the skin by gas-phase biosensors. All of these things point to non-intrusive screening techniques, which are the future of clinical diagnosis.

Breath analysis, compared with blood analysis, can enable real-time non-invasive diagnostics through the quantification of exhaled biomarkers [2]. Here, we demonstrate a calibration-free mid-infrared (MIR) exhaled breath sensor for real-time ammonia measurements at ppb-level, as shown in Fig. 1, which can be used for the non-invasive diagnosis of liver and kidney diseases [3]. The exhaled breath sensor employs a 10.359-μm MIR quantum cascade laser (QCL) to target a strong NH_3 absorption line and adopts the beat-frequency quartz-enhanced photoacoustic technique (BF-QEPAS) to remove the requirements of the calibration process and wavelength locking in the conventional QEPAS technique. By studying the adsorption-desorption effect and optimizing the modulation depth and modulation frequency of the sensor system, a detection limit of 9.5 ppb is achieved at an integration time of 3 ms. The ammonia content exhaled by eight healthy volunteers is recorded, and the real-time measurement results are analyzed. Compared with conventional QEPAS sensors, the proposed BF-QEPAS-based sensor offers higher sensitivity and a faster response time, as well as no need for calibration and wavelength locking.

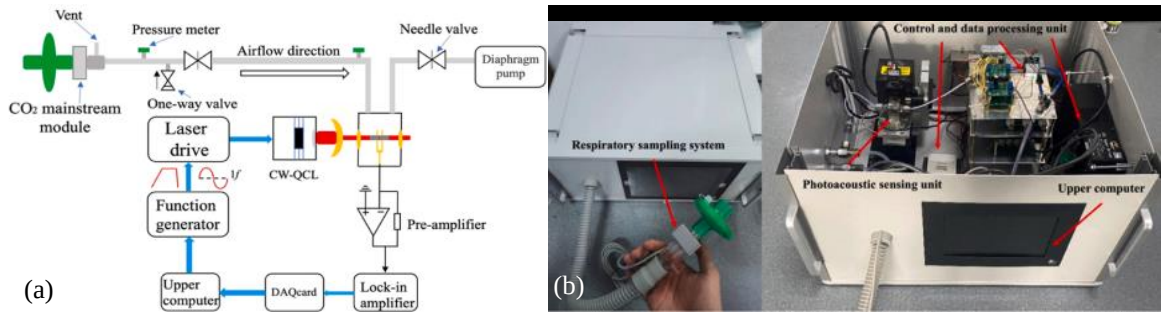

Fig. 1 (a) Schematic of human exhaled ammonia sensor based on BF-QEPAS; (b) prototype photos of human exhaled ammonia sensor based on BF-QEPAS

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H_2 detection based on wavelength modulation and multipass absorption spectroscopy

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Short abstract: In this work wavelength modulation and multipass absorption spectroscopy are employed to detect H_2 line located at 2.12 μm. The sensor applicability for measuring H_2 in N_2-based mixtures was tested by detecting H_2 absorption spectrum using both a commercial photodetector and a quartz tuning fork.

The problem of climate change and its link to energy production prompted most countries to the development of new sources of clean and renewable energy. Among them, hydrogen (H_2) has the advantages of being clean, pollution-free, abundant, easy storable and can be directly converted into thermal, mechanical, and electrical energy. Moreover, H_2 is considered as an alternative to the use of fossil fuels in the transportation sector and is largely employed in many industrial settings such as refiners, steel, and chemical industry [1]. However, H_2 is a flammable and explosive gas. Thereby, the development of sensors capable of real-time and continuous monitoring of H_2 is one of the main challenges. In recent years, various H_2 sensing methods have been employed, such as electrochemical sensors, resistance-based sensor, and mechanical sensors [2]. Optical sensors represent an effective solution, providing both high sensitivity and high selectivity through laser excitation of gas absorption transitions in the infrared range. In particular, Tunable Diode Laser Spectroscopy (TDLAS) is employed as sensing technique for many applications, such as environmental monitoring or industrial processes [3]. However, when dealing with H_2 direct absorption-based detection, a serious limit is represented by the weak H_2 absorption, whose spectrum is limited to vibrational bands of low-intensity quadrupole transitions. Thus, increasing the optical pathlength can help in detecting such a weak absorber. In this work, 2f wavelength modulation and multipass absorption spectroscopy are combined to target the strongest H_2 absorption line located at 2.12 μm with an absorption coefficient of $4.56*10^{-6}$ cm^{-1} at atmospheric pressure [4]. Fig. 1 shows a schematic of the experimental apparatus employed. A DFB diode laser, having emission wavelength resonant with the H_2 absorption transition, and a 10.13 m HERRIOT multi-pass cell were employed in the experimental setup. The generated signal was detected by a photodetector (PD) and demodulated by a lock-amplifier to detect the 2f component. The sensor applicability for measuring H_2 in nitrogen-based mixtures was tested. The PD was subsequently replaced by a quartz tuning fork (QTF) employed in Light-Induced Thermoelastic spectroscopy configuration. QTFs were proved as a low-cost and highly sensitive alternative to PDs, providing an increase of the signal to noise ratio. In both configurations, the sensor applicability for measuring H_2 in nitrogen-based mixtures was tested with sensitivity levels in the ppm range.

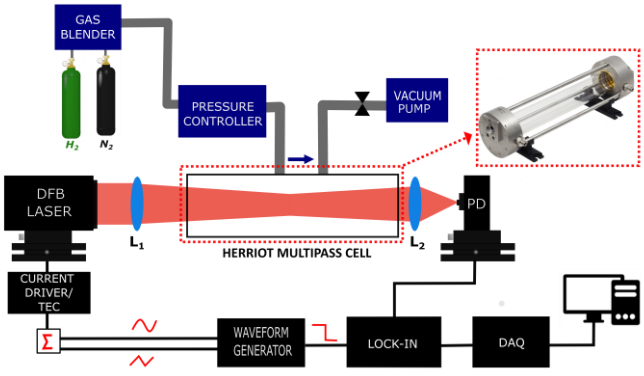

Fig. 1 Schematic of the experimental apparatus.

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ATEX compliant, FPGA based three-channel quantum cascade laser sensor for sulfur species detection in petrochemical process streams

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Short abstract: An FPGA based three-channel QCL sensor prototype is installed in an industry rack and equipped with the required safety infrastructure allowing a certified operation under ATEX/IECEx regulations for hazardous and explosive environments.

The sensitive and selective detection of gaseous sulfur species with the emphasis on hydrogen sulfide (H_2S), carbonyl sulfide (COS) and methyl mercaptan (CH_3SH) down to sub-ppmv concentration levels plays a crucial role across a wide range of petrochemical applications [1], [2].

In this work a previously developed triple distributed feedback (DFB) quantum cascade laser (QCL) based sulfur species sensor using a 8.0 µm source for H_2S, a 7.5µm source for CH_3SH and a 4.9 µm source for COS detection based on wavelength modulation spectroscopy (WMS) with modulation frequency multiplexing [3] is optically revised and equipped with a field-programmable gate array (FPGA) hardware.

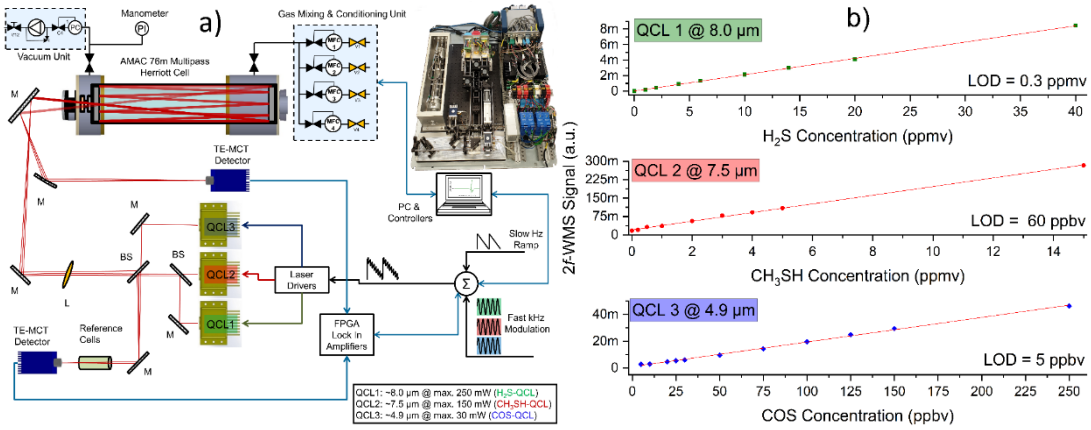

Figure 1: a) Optical and peripheral layout. b) N_2 calibration results.

The laser radiation of the individual QCLs is co-aligned and focused with a plano-convex lens (f=500 mm). The resulting modulation frequency multiplexed laser beam is split into a reference and signal path before being coupled into an astigmatic 76 m Herriott multipass cell (AMAC76-LW, *Aerodyne Inc.*) and subsequently focused onto optically immersed, thermoelectrically cooled MCT detectors (PVI-4TE-12, *Vigo Systems*). The reference path is equipped with methane (CH_4), H_2S and carbon monoxide (CO) reference gas cells for accurate wavelength calibration and laser drift compensation. The detector signals are digitized, de-glitched and demodulated at the individual modulation frequencies and further processed using a self-developed multi-channel filtering and lock-in amplifier chain implemented in FPGA hardware (NI 7856R, *National Instruments*). The resulting spectra are subjected to a normalization and modulation index compensation method based on the zero-, second-, and fourth-order harmonics of WMS.

In order to meet with on-site safety regulations, the QCL sensor prototype is installed in an industry rack and equipped with the required safety infrastructure allowing a certified operation under ATEX/IECEx regulations for hazardous and explosive environments.

Quantitative measurements were performed using calibration gas mixtures in nitrogen (N_2), methane (CH_4) and propene (C_3H_6) matrices in order to investigate the sensitivity and linear response of sensor system. The corresponding limits of detection (LOD) were assessed according to DIN 32645 and resulted in ~0.3 ppmv for H_2S, ~60 ppbv for CH_3SH and ~5 ppbv for COS respectively.

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Spectroscopic Applications

Comb-assisted frequency-stabilized cavity ring-down spectroscopy: application to ultra-sensitive detection of water vapour and beyond

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Short abstract: The talk will cover the description of a comb-assisted cavity ring-down spectrometer developed for water vapor detection. The possibility of determine SI-traceable H_2O concentrations in N_2, at the ppb level with a sub-percent uncertainty, will be discussed. Applications of the technique to other molecular targets will be also presented.

The need for higher-purity processing gases in the semiconductor and optoelectronic industry is continually leading to more stringent specifications for a variety of speciality gases. This demand, in turn, is pushing the detection capability of analytical instrumentation to finer levels. One of the most critical impurities is water vapor, being the most difficult to be removed. As polar molecule, it is adsorbed on surfaces and then desorbed into any gas flow, thus affecting industrial processes significantly. Even at trace levels, it influences electrical and chemical properties of materials, impacting on the quality and performances of semiconductor devices. Despite the huge difficulty in removing water vapor from gas distribution systems, admitted mole fraction levels are becoming increasingly low, being, in some cases, as low as the part-per-billion (ppb).
In the framework of the European project PROMETH2O (Metrology for trace water in ultra-pure process gases, https://www.prometh2o.eu/), we will present here the results of trace water vapor measurements by means a comb-assisted frequency-stabilized cavity ring-down spectrometer (CA-FSCRDS), operating at the wavelength of 1.4 μm. The spectrometer is an upgraded version of that described in [1], the main novelty being the use of a Booster Optical Amplifier (BOA) to increase the optical power injected into the high-finesse cavity [2]. It is based on a high-Q optical resonator showing an empty-cavity ring-down time of about 130 μs. The characterization of the spectrometer revealed a minimum detectable absorption coefficient of 9×10^{-12} cm^{-1} and a noise equivalent absorption of 3×10^{-11} $cm^{-1}/\sqrt{Hz}$. With the spectrometer operating at 7170.277881 cm^{-1}, namely in coincidence with the $2_{2,1}\leftarrow3_{2,2}$ transition of the $\nu_1+\nu_3$ $H_2{}^{16}O$ vibrational band, we demonstrated the measurement of water vapor mole fractions down to 395 ppb, with a statistical uncertainty of 2 ppb, and a SI-traceable combined uncertainty (k=1) as low as 4 ppb [3]. Preliminary results of a comparison with a calibrated commercial CRDS trace water analyser (from Tiger Optics, LLC), traceable to the humidity standards of the Istituto Nazionale di Ricerca Metrologica (INRIM), will be also presented.
The achieved sensitivity and accuracy levels allowed for the use of the CA-FSCRDS technique in other intriguing applications such as Lamb-dip spectroscopy of acetylene [2, 4], and Doppler-limited spectroscopy of HD [5, 6]. In this respect, the most recent results will be briefly discussed.

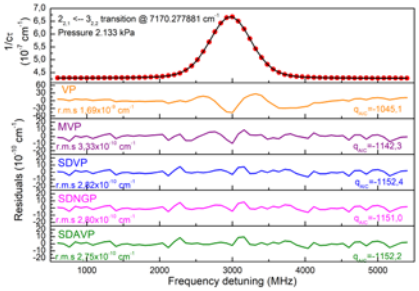

Fig. 1 Upper plot: example of trace water detection in a nitrogen flow. Lower plots: residuals of line fitting by means of different semiclassical line shape models.

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Improved Heterodyne Spectroradiometer: A Leap Towards Precise XCO_2 Measurements

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Short abstract: We introduce an improved Multichannel Laser Heterodyne Spectroradiometer (MLHS) for near-infrared greenhouse gas detection, offering high spectral resolution, compact design, and cost-effectiveness. MLHS provides column measurements and vertical profiling of CO_2, alongside Doppler wind measurements, showing promising results when compared with established networks.

Recent developments around instrumental control of carbon balance are aimed at, but not limited to, highly accurate evaluation of sources and sinks of major greenhouse gases (GHG) by natural landscapes, cities, industrial and agricultural objects. Direct assimilation of monitoring data by atmospheric models is complicated because CO_2 is a well-mixed gas whose mixing ratio varies only by a few percent. Nowadays, there is significant progress in the development of instruments based on commercial telecom components to make GHG measurements accessible [1].

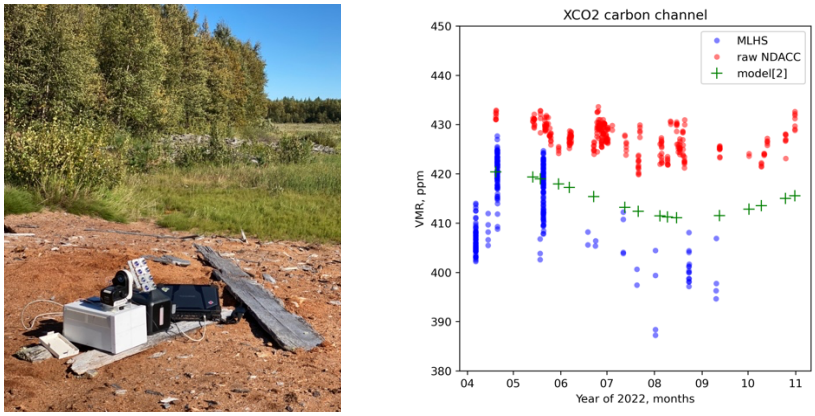

Fig. 1 Previous MLHS instrument performing measurements; preliminary results of 2022 campaign.

We present the Multichannel Laser Heterodyne Spectroradiometer (MLHS) for exploring the Earth's atmosphere in the near-infrared range, addressing the lack of coverage for greenhouse gases in existing measurement networks. High spectral resolution ($\lambda/\delta\lambda \sim 10^7$) of solar occultation heterodyne spectroscopy enables us to study the structure and dynamics of the atmosphere while maintaining a compact and low-cost design.

Following the 2022 measurement campaign with a Fourier-spectrometer station for XCO_2 and XCH_4 (Fig. 1), we identified key limitations of the prototype. By improving thermal stability, optimizing optical scheme, and applying accurate sensors for atmospheric parameters, we are developing the next generation of MLHS. In our opinion, heterodyne spectroradiometers do demonstrate promising results in greenhouse gas measurements, showcasing a potential as an effective, low-cost solution for expanding existing measurement networks to enhance our understanding of the Earth's atmosphere.

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Evanescent wave quartz enhanced photoacoustic spectroscopy employing a side-polished fibre for methane sensing

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Short abstract: Quartz-enhanced photoacoustic spectroscopy (QEPAS) employs a quartz tuning fork to detect photoacoustic signals, for sensitive trace gas detection. To circumvent the need for free-space optics, we present an evanescent wave approach within a QEPAS set-up using a side-polished fibre. Methane detection in the IR in the parts-per-thousand range is presented.

Quartz enhanced photoacoustic spectroscopy employs a quartz tuning fork as a resonant acoustic transducer, detecting weak acoustic signals generated by light absorption of a target gas. QEPAS enables sensitive trace gas detection. Methane, for example, was detected recently with QEPAS at 28 ppbv in an integration time of 0.1 s using only a very small sample volume, ~7 cm^3 [1]. The majority of QEPAS configurations presently require free space optics for gas excitation, which are susceptible to misalignment and reduce the technique's suitability to harsh environments. To circumvent the need for free-space optics, evanescent wave (EW) approaches have been developed, where optical fibres are placed between the quartz tuning fork (QTF) tines. To enable the exposure of the EW, tapered fibres, where the cladding thickness is reduced to a few microns thickness using a flame, are being used. Acetylene mixing ratios as low as 13 ppmv have been reported by using tapered fibres in combination with QEPAS [2]. A disadvantage of this approach is that tapered fibres are susceptible to fracture. A more robust arrangement is to use a side-polished fibre, where access to the EW field is generated through grinding and polishing of the cladding on one side. Here, we present the first integration of a side polished fibre in a QEPAS sensor. The set-up does not require any free space optics, thereby increasing robustness and suitability to harsh environments, while at the same time maintaining the advantages of the QEPAS technique.

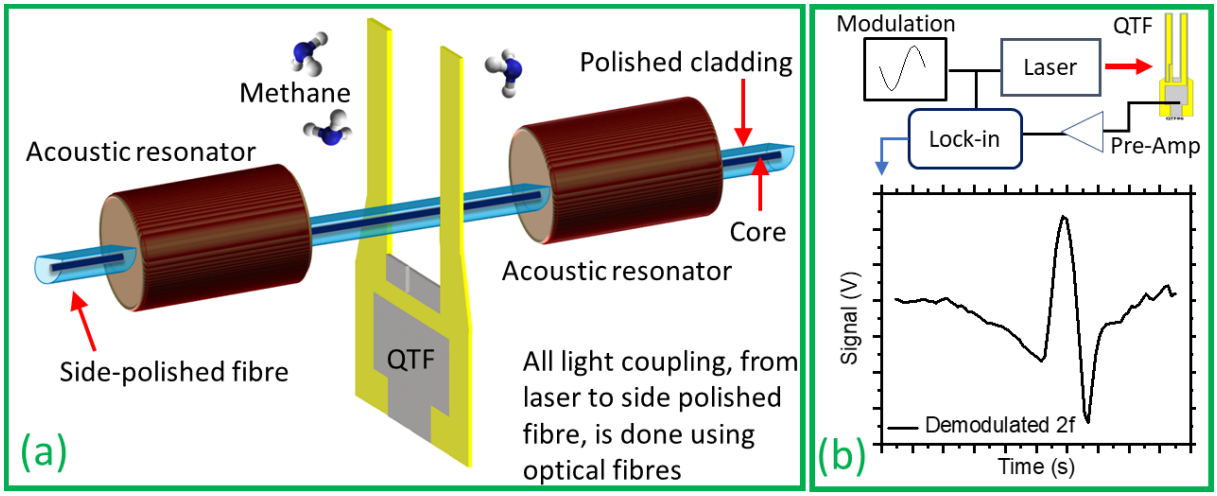

Figure 1 (a) Schematic of sample chamber components. (b) QEPAS electrical configuration and 2f demodulated spectrum of methane measured using a side polished fibre.

In this EW-QEPAS study we use methane (an important greenhouse gas and flammable atmospheric pollutant) as target gas for first proof-of-principle detection experiments. The set-up contains a pigtailed discrete mode laser diode (Eblana EP1654) with an output power of ~7 mW to excite the methane at 1653.7 nm. The laser power is amplified to ~80 mW using a boaster optical amplifier (Thorlabs BOA1084P) and connected to the sample chamber using an optical fibre vacuum feedthrough. The side-polished fibre (Phoenix Photonics, SPF-S-SM-2) located in the sample chamber is cleaved on one side to allow the polished section of the fibre to pass through the acoustic resonators and QTF of the QEPAS acoustic detection module (Thorlabs, ADM01), Figure 1(a). Sample measurements of methane in nitrogen, at ratios of parts-per-thousand (by volume), will be presented, Figure 1(b).

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Photothermal Lens and Photothermal Mirror Techniques: Effects and Applications for Material Characterization

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Short abstract: Applications of photothermal lens and photothermal mirror methods and the advances in their theoretical description are presented. The advances comprise investigating the effects of radiation forces, generation and detection of pressure transients and thermoelastic waves, description of sample–fluid heat coupling effect, and characterization of liquid samples using mid-infrared excitation.

The mode-mismatched dual-beam photothermal lens (PTL) and photothermal mirror (PTM) have been widely applied in the characterization of solid, liquid, and gas samples due to their remote, sensitive, and non-destructive characteristics. The PTL and PTM techniques detect a broad range of phenomena arising from the interaction of tightly focused laser beams and matter at different time scales. A pulsed or continuous laser beam may induce a thermal perturbation and momentum transfer from the light to the sample in these techniques. The effect is probed by monitoring the probe beam phase shift caused by the surface expansion of the heated area, the photoelastic effects, and the spatial distribution of the refractive index within the sample and in the fluid surrounding it. The transient signal is monitored at the far-field detector by analyzing the wavefront distortion of the probe beam. Thermal, optical, and mechanical properties can be quantitatively determined for solids, liquids, and gas. The applications involve material characterization of optical glasses, polymers, metals, alloys, semiconductors, fuels, and dyes. Here we show applications of PTL and PTM methods under continuous or pulsed Gaussian laser excitations and the advances in their theoretical description over the past few years. The advances comprise investigating the effects of radiation forces in liquids [1,2], generation and detection of pressure transients in liquids [3,4] and thermoelastic waves in metals [5], analytical description of sample–fluid heat coupling effect in photothermal techniques [6,7], and recent PTL results using mid-infrared (mid-IR) excitation for characterization of liquid samples.

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Photothermal Spectroscopy (PTS) of PMMA thin layer using micro-ring resonators (MRRs)

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Short abstract: We present one of the first demonstrations of on-chip Photo-Thermal Spectroscopy. We use Si_3N_4 micro-ring resonators (MRRs) coated with a thin-film of PMMA, as sensitive devices, and a dual-beam transversal configuration. We use a tunable probe laser emitting in the NIR and as an excitation source, we use an External Cavity Quantum Cascade Laser (EC-QCL).

In this work, we report on a compact photothermal sensor that relies on integrated optics. In particular, micro ring resonator-based sensors, fabricated from complementary metal-oxide-semiconductor (CMOS) compatible materials, such as silicon (Si) and silicon nitride (Si_3N_4), have gained growing interest due to their high sensitivity, small footprint and low fabrication costs [1]. In this work, we combine the MRR as a transducer for a pump-probe PTS measurement of Polymethylmethlyacrylate (PMMA). A 200 nm PMMA layer is spin-coated on top of the 33 µm radius MRR with four rectangular partially transmitting elements (PTE) in the gap region, engineered to achieve high Q-factor (Fig. 1a). PMMA absorption peak is positioned at $\tilde{\nu} \sim 1730$ cm^{-1}. In PTS, modulated light absorption by the analyte under investigation is photoinduced by a periodic modulation of the sample's temperature and in turn of its refractive index. Photothermal phenomenon is directly proportional to the optical power of the excitation source and for this reason it takes advantage of the recent development of powerful mid-IR laser sources.

In our setup we use a tunable NIR laser to tune the MRR at the inflection point of a picked resonance within the transmission spectrum, aiming for maximized shift sensitivity, and an EC-QCL that emits between 1560-1770 cm^{-1}, covering the spectral region in which the polymer absorbs. The MIR source is focused on top of the waveguide via a reflective microscope objective such that the beam spot-size (~ 20 µm) is collected only on top of the ring. PTS enables to gain a qualitative spectral information of the target analyte by sweeping the pump laser in pulsed mode on the chip and recording the lock-in amplifier (LIA) demodulated signal using the pulse rate as a reference trigger.

The PTS signal has been optimized in terms of pulse frequency and pulse width in order to maximize the resulting PTS signal at the absorption peak of PMMA. By normalizing the PTS signal by the optical power of the excitation laser, recorded via an MCT detector, the normalized PMMA PTS spectrum is recorded and is reported in Fig. 1b.

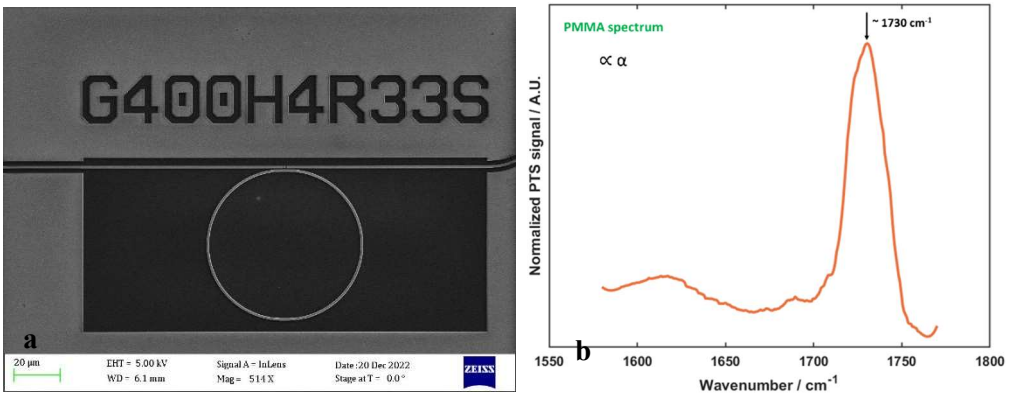

Fig. 1a Scanning Electron Microscope (SEM) image of the MRR used for the PTS experiment – **b** Normalized PTS signal of PMMA.

Moreover, as the PT signal is inversely proportional to the volume of interaction between the probe and pump laser, this sensing scheme holds great promises for realizing miniaturized and highly sensitive sensors.[2]

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Poster Session

Enhanced non-destructive chirality sensing: a single photon approach

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A high sensitivity optical birefringence sensor based on a heralded photon source is presented, calibrated and stability-tested. The single photon nature of the proposed sensor finds its application both to fragile biological samples as a tool for chiral molecules detection, and in optical metrology when low intensities are required.

Chirality in nature can be found at every scale, ranging from elementary particles up to galaxies. A chiral object is a structure that is non-superimposable with its own mirror image. At the molecular scale, where chirality manifests itself with the formation of enantiomers, chiral structures interaction with light results to be polarisation-dependent (a phenomenon known in literature as *optical activity*). High sensitivity optical techniques result therefore well suited to be among the best performing techniques for chirality sensing.
A first way optical activity may present itself is through dichroism, i.e a polarisation dependency of the imaginary part of the refractive index, macroscopically resulting in a polarisation-dependent absorption. The optical activity may as well affect the real part of the refractive index (representing the velocity of propagation of light through the medium), in which case is referred to as *birefringence*.
Optical rotatory dispersion (ORD) is an optical technique that senses chiral objects via their birefringence [1]. When a linearly polarized light (LPL), that can be seen as composed of equal amount of left (LCP) and right circular polarized (RCP) light, impinges on the sample, the LCP and RCP components are de-phased since propagate at different velocities inside the sample (circular birefringence). The induced RCP-LCP dephasing can be measured outside the sample as a rotation in the linear polarization of an angle $\boldsymbol{\theta}$, which results to be

$$\boldsymbol{\theta} = \frac{\boldsymbol{\pi}\, \boldsymbol{l}}{\boldsymbol{\lambda}} (\boldsymbol{n_{LC}} - \boldsymbol{n_{RC}})$$

Where $\boldsymbol{l}$ is the length of the sample, $\boldsymbol{\lambda}$ the test laser beam wavelength and ($\boldsymbol{n_{LC}}$ - $\boldsymbol{n_{RC}}$) the optical circular birefringence. Since such birefringence is usually as weak as one part on 10^6 the most common way to improve the detection limit relies either on employing high-power lasers to enhance Signal-to-Noise Ratio (SNR) or on increasing the optical pathlength inside the sample, for example by means of optical cavities. Unfortunately for biological samples, where the high source intensities may trigger undesired reactions, the laser power must be kept as low as possible to avoid sample degradation, especially for long acquisition times. The same holds true in metrological applications, where high-power sources may cause system perturbation. These applicative needs inspired the development of quantum metrological techniques specifically tailored for birefringent detection at low source power (down to the single photon level).
In this panorama, we proposed a highly stable, high performing twin photon source quantum-enhanced sensor capable to detect a linear polarisation rotation as low as in the μrad range, taking advantage of the high stability offered by coincidence counting together with the dual arm configuration. Being designed and implemented to operate in the telecom range, the devised sensor represents an innovative step towards fibre-cabled portable twin-photon source-based quantum enhanced metrology devices meant to offer ultra-high precision measurements of chemical or biological samples out of a laboratory-controlled environment. Moreover, it has shown to be capable to achieve an optical activity detection limit (*OADL*) per unit length as low as

$$\frac{\boldsymbol{\lambda\sigma}}{\boldsymbol{\pi}} = \boldsymbol{8.9 \times 10^{-13}\ m}$$

while integrating over 2.7×10^6 coincidence events. The aforementioned limit results to be comparable within an order of magnitude with the results reported in [2] for a sample experiencing a 100μm-long birefringent path, but operating in single photon regime and for wavelengths in the telecom range, more suitable for future fibre-coupled implementations.

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A compact MEMS based photoacoustic sensor for trace-gas detection

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Short abstract: We describe the development and the first characterization of a compact trace-gas sensor based on innovative Micro electro-mechanical systems (MEMS) structure photoacoustic spectroscopy. The sensor was characterized in order to find the optimal operating parameters (pressure, molecule absorption line and laser modulated frequency). N_2O was selected as test molecule.

Highly sensitive trace gas detection instruments are required in many fields of applications (i.e. biological, environmental, industrial, fundamental physics and medical ones) [1-4]. In principle, large different spectroscopic and non-spectroscopic methods could be used. In particular, a wide range of spectroscopy techniques are based on absorption of infrared (IR) radiation.

During the last two decades, photoacoustic spectroscopy (PAS) started to attract more and more attention both scientific community and industry. In recent years, several sensors based on quartz-enhanced photo-acoustic spectroscopy (QEPAS) have been developed, allowing for more compact dimensions and showing higher sensitivity levels, with great potentiality for environmental monitoring [5]. Even higher sensitivities can be reached with a different technique, called Cantilever-Enhanced Photoacoustic Spectroscopy (CEPAS) [6-7], which makes use of a small thin cantilever for photoacoustic signal detection. The design of the cantilever unit and the reading of its tiny oscillations induced by the gas pressure wave are the key elements determining the sensor sensitivity [8], so the opto-mechanical interactions and the fabrication methods of cantilevers have a fundamental role to improve sensor performance [8,9]. Indeed, we take advantages of Micro electro-mechanical systems (MEMS) realization techniques for the realization of our "microphones".

In order to enhance the optomechanical response of such sensors, we designed different silicon structures. We simulated mechanical response by using a Finite Element Modelling (FEM) software. In our setup, like in the CEPAS technique, the detection of moving elements is performed by using an interferometric technique [10].

We tested such structures in the Mid Infrared by using a quantum cascade laser as source for N_2O detection.

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Light Induced Thermo-Elastic Spectroscopy aided with a dual-band all-silica Antiresonant Hollow-Core Fiber

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Short abstract: In this work, we present Light Induced Thermo-Elastic Spectroscopy (LITES) of carbon dioxide and nitrous oxide at 4985.9 cm^{-1} and 2188.2 cm^{-1}, respectively utilizing a self-made, all-silica, dual-band Antiresonant Hollow-Core Fiber-based gas absorption cell.

Laser-based gas detection has been known as a powerful and highly efficient tool for targeting molecular fingerprints of various gaseous substances. However, a vast majority of laser-based sensors suffer from high complexity due to the use of multiple optical components and expensive photodetectors. To address this issue, we propose to combine two techniques: utilization of low-volume Antiresonant Hollow-Core Fiber (ARHCF) based gas absorption cells and a quartz tunning fork (QTF) as a broadand detector via the Light Induced Thermo-Elastic Spectroscopy (LITES) [1]. In LITES, the QTF is employed as photodetector via excitation by a local heating of its structure due to absorption of a sinusoidally modulated laser beam. With light focused on the quartz, the material starts to heat up in the focal spot, and, via a thermoelastic effect, its structure in this area temporarily deforms. If the modulation frequency matches the QTF resonance frequency, the modulated thermal expansion of the material causes vibrations of the QTF, which leads to the generation of a measurable piezoelectric signal. The spectroscopic signal is encoded in the amplitude of the laser beam passing through a gas sample, before it is focused on the QTF. The schematic of the developed sensor is shown in Fig. 1(a). The gas absorption cell was based on a 1 m long ARHCF, which enabled low-loss transmission of light in the near- and mid-IR. The QTF used was a standard resonator with an in vacuum resonance frequency of 32.768 kHz. To employ the QTF as a light detector, the aluminum shielding tube was removed. As a result, the resonance frequency of the QTF shifts slightly to 32.756 kHz. The sensor was aimed on detection of CO_2 and N_2O, which were excited at 4985.9 cm^{-1} and 2188.2 cm^{-1} wavelengths, respectively. The spectroscopic signal readout was based on the Wavelength Modulation Spectroscopy technique with 2nd harmonic detection, where two lasers were sinewave modulated at the frequency equal to the half of the resonance frequency of the QTF. Thanks to the unique configuration, the sensor reached Noise Equivalent Absorption coefficients of 8.6×10^{-7} cm^{-1} and 1.7×10^{-6} cm^{-1} for N_2O and CO_2, respectively. The results shown in Figs. 1(b) and 1(c) are at a level comparable to those achievable in similar LITES systems [1]. We expect that this result can be increased with further optimization of the QTF electronics, exploitation of custom QTFs optimized for LITES, and optimized ARHCF structure.

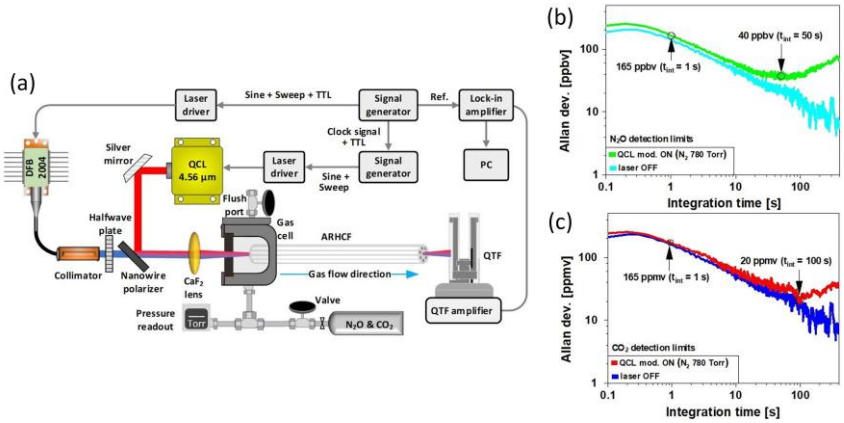

Fig. 1 (a) Schematic of the sensor setup. Allan deviation plots calculated from the noise retrieved with pure nitrogen flowing through the ARHCF-based gas absorption cell: (b) detection limit for N_2O, (c) detection limit for CO_2.

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Rugged and sensitive optical detection of NO via Interferometric Cavity-Assisted Photothermal Spectroscopy

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Short abstract: We report on the detection of NO by Interferometric Cavity-Assisted Photothermal Spectroscopy (ICAPS) in combination with a DFB-QCL emitting at 1900 cm^{-1} as excitation source. The transduction scheme is realized by combining a probe diode laser and a Fabry-Perot interferometer, embedded in a compact air-tight gas cell. A NNEA of $3.3 \cdot 10^{-6}$ $Wcm^{-1}Hz^{-1/2}$ was achieved corresponding to a LOD of 2.5 ppm.

Photothermal Spectroscopy (PTS) is an indirect technique that measures thermal effects on a gas sample induced by modulated photon absorption and molecular non-radiative relaxation. The periodically absorbed energy is released in the form of heat, producing a local gas expansion. In Interferometric Cavity-Assisted Photothermal Spectroscopy (ICAPS) a Fabry-Perot Interferometer (FPI) and a probe laser are used as optical transducer for refractive index variations, induced by gas thermal expansion [1]. The high miniaturization capabilities of FPIs make this technique extremely attractive for rugged gas sensing.

A DFB-QCL emitting at 1900 cm^{-1} was used to target the R(6.5) absorption line of NO and to induce the gas thermal expansion. The QCL wavelength was scanned across the absorption line and 2f wavelength modulation spectroscopy (2f-WMS) approach was used as detection scheme. A telecom diode laser was coupled to the FPI and the reflected intensity was collected on a photodetector (APD). The highest sensitivity is achieved when the probe wavelength is tuned to an inflection point of the interferometric fringe. Nevertheless, the tracking of the inflection point might be difficult without any prior information on the interferometric fringe shape, which varies with incident optical power of the probe laser. We implemented a locking routine, based on wavelength modulation of the probe diode laser, exploiting the correspondence of the 2f-zero locking with the inflection point. Two separate lock-in amplifiers (LIAs) demodulated the APD signal: one retrieved the photothermal signal (or 2*f*-ICAPS signal), while the other was used as part of the servo loop to lock the probe wavelength to the inflection point. This ensured stable and efficient detection of photothermal effects, avoiding drifts of the sensor. A schematic of the experimental setup is presented in Fig. 1(a).

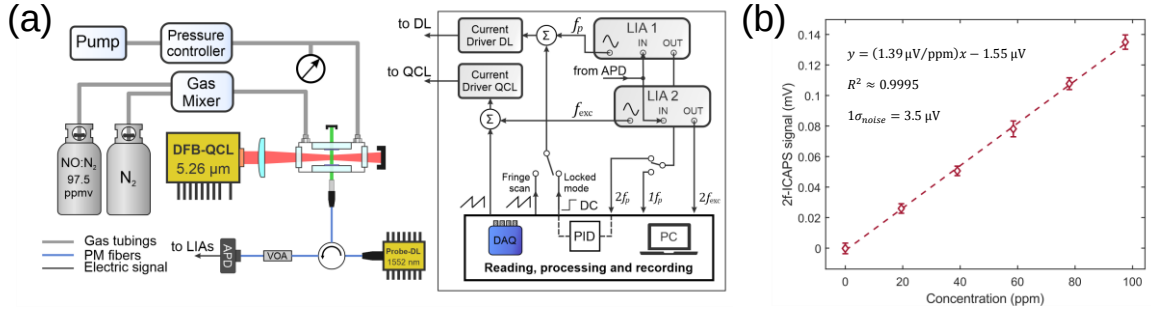

Fig. 1 (a) Schematic of the experimental setup. Amplified photodetector (APD), Lock-in Amplifier (LIA), Variable Optical Attenuator (VOA). (b) Calibration curve of the sensor obtained as linear fitting of the experimental data (diamonds).

The sensor was calibrated spanning a range of concentration between 0 and 97.5 ppmv of NO in N2, by diluting the standard concentration of 97.5 ppmv $NO:N_2$ with pure nitrogen. The calibration curve, presented in Fig. 1(b), was obtained by linear fitting of the signal peak value for different concentrations. An excellent linearity of the response was obtained, as proven by the coefficient of determination of the calibration curve ($R^2 \approx 0.9995$). From the sensor's noise (measured in absence of the analyte) and sensitivity (slope of the calibration curve), a noise equivalent concentration (NEC) of 2.5 ppm was achieved with 1 sec time constant. This value corresponds to a normalized noise equivalent absorption of $3.3 \cdot 10^{-6}$ $Wcm^{-1}Hz^{-1/2}$, with an optical power 30 mW and a bandwidth of 78 mHz.

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Elliptical-tube based quartz-enhanced photoacoustic spectroscopy

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Short abstract: We propose an elliptical-tube off-beam quartz-enhanced photoacoustic spectroscopy method, in which an elliptical tube is employed as an acoustic resonator to match the stripe-like beam emitted from a high-power multimode laser diode (MLD), resulting in a ~3 times higher signal-to-noise ratio (SNR) gain factor compared with the circular resonator.

Trace gas sensing based on photoacoustic spectroscopy (PAS) is widely used in many fields [1]. Multimode laser diodes (MLDs) are small-sized, inexpensive and high-power laser sources, which are available from both single emitters and diode arrays at power output levels ranging from tens of milliwatts to hundreds of Watts. Combination of MLDs and QEPAS has the potential to realize a compact, cost-effective and highly sensitive gas sensor, since the detection sensitivity of QEPAS is proportional to its optical excitation power [2]. In this letter, we reported elliptical-tube off-beam QEPAS (EO-QEPAS), which is proposed for MLDs as excitation laser sources in QEPAS. An elliptical resonator is designed to work together with the stripe-like beam emitted from a MLD and is assembled with a QTF in the off-beam configurations as an acoustic detection module (ADM).

The structure of designed ADM is shown in Fig. 1 (a). A standard QTF is placed on the outside of a 3D-printed elliptical resonator to probe acoustic vibration energy via a slit. The sound pressure distribution inside the ADM was subsequently simulated using COMSOL Multiphysics software. With the parameters of the ADM fixed, the sound pressure distribution inside the ADM is close to the one-dimensional longitudinal acoustic model, as shown in Fig.1(b). Figure 1(c) plots the values of the sound pressure along the center axis of the elliptical resonator for the different resonator lengths. When L = 5.5 mm close to the half-wavelength of the sound waves, the simplest standing wave forms, whose only antinode is located in the middle of the elliptical resonator. When L = 10.5 mm close to a wavelength, the standing wave with two antinodes forms. A M-shape sound pressure distribution is observed. Compared with L = 5.5 mm, the higher values of the sound pressure can be obtained, as the node of the sound pressure is located in middle of the resonator and the slit does not act as an energy relief hole. The curves for L = 6.5 mm, 7.5 mm, 8.5 mm, 9.5 mm are the transition zone between half and a wavelength of the sound waves. The maximum sound pressure in the middle of the resonator can be reached when L = 9.5 mm.

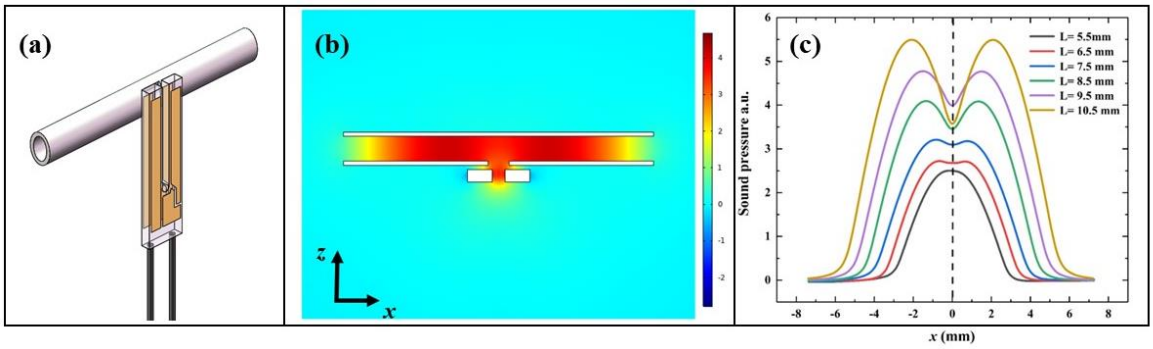

Fig. 1 (a)Schematic diagram of an ADM in EO-QEPAS. (b) Sound pressure distribution simulated by COMSOL Multiphysics software. (c) Simulated sound pressures along the center axis of the resonator.

To assess the performance of EO-QEPAS, the measurement results employing a bare QTF, a circular-tube off-beam QEPAS system (CO-QEPAS) and the EO-QEPAS system were obtained by flushing the certified 1-ppm NO_2:N_2 gas mixture into the ADM. The bare QTF has a large background noise due to the prong gap limit of the QTF. The background noise in the EO-QEPAS system is significantly reduced.The EO-QEPAS system has a SNR gain factor of ~19 compared to the bare QTF, while the CO-QEPAS system only has a SNR gain factor of ~6.

In conclusion, Although the signal amplitude can be significantly enhanced through the increase of the optical power in QEPAS, the growing part of the signal amplitude is usually balanced out by the noise that grows more due to the mismatch between the traditional resonator and beam shape. The elliptical resonator is proposed specifically for a strip-shaped laser beam, which allows to fully utilize the optical power with a low noise output.

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Ppb-level photothermal nitric oxide detection using a mode-locked laser and self-heterodyne harmonic amplification

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Abstract: We present a unique method for extracting the photothermal signal by exciting the gas molecules inside the cavity of a mode-locked laser. The induced refractive index modulation is translated into a shift in its pulse repetition frequency. A 9.6 ppbv limit-of-detection for nitric oxide was achieved with 136 s averaging.

Photothermal spectroscopy (PTS) is a method that is used for selective and sensitive detection of gas molecules. In PTS, a *pump* laser with a wavelength that matches the absorption profile of the gas sample under test is used to excite the particles. As a part of the absorbed light heats the gas via nonradiative energy transfer, local modulation of the pressure and refractive index (RI) of the gas are observed. In PTS, detection of low gas concentrations requires the use of precise methods to extract the spectroscopic signal from the induced RI shift. Most published configurations relied on the use of Fabry-Perot or Mach-Zehnder interferometers [1]. However, sensitivity, long-term stability, and repeatability in such sensors requires specialized optical components, complex apparatus, and precise alignment, rarely achievable in out-of-lab conditions. We propose a unique method for probing the PTS signal, which exploits features of mode-locked (ML) lasers and a technique developed by us, which allows for non-complex multiplication of the registered spectroscopic signal - self-heterodyne harmonic amplification (SHHA). The sensor setup is shown in Fig. 1, along with an Allan deviation plot presenting the sensor performance.

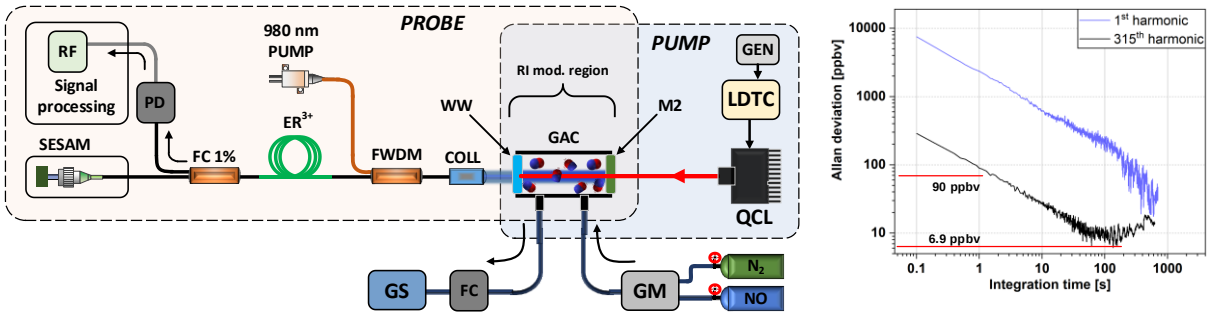

Fig. 1 Experimental setup. SESAM – semiconductor saturable absorber mirror, RF – RF spectrum analyzer, PD – photodiode, FC –coupler, Er^{3+} - active fiber, FWDM - wavelength division multiplexer, COLL – fiber collimator, WW – wedged window, M – mirror, M2 – CaF_2 HR coated window, GAC – 20 cm long gas absorption cell, GM – gas mixer, FC – flow controller, GS - gas scrubber. QCL – mid-IR pump laser, LDTC – laser controller, GEN – signal generator.

The sensor comprises a home-built SESAM-based ML fiber laser operating at 1.55 µm, a 20 cm gas absorption cell (GAC) integrated into its linear cavity, and a 120 mW, 5.26 µm quantum cascade laser (QCL) that excites the nitric oxide (NO) molecules inside the cell. The QCL beam is co-linearly aligned with the ML laser oscillating beam in the GAC, therefore, the photothermal effect modulates the refractive index (RI) of the gas sample, inducing a change in the ML's cavity optical pathlength and, as a result, the pulse repetition frequency. This encodes the amplitude of the PTS signal directly into frequency deviations of the ML's beatnotes. To simplify signal extraction, the QCL's wavelength is modulated with a sinewave signal (f_0 = 300 Hz) and swept through the NO absorption line, if necessary. An RF signal analyzer with a custom application demodulates the electrical signal from the photodiode (PD) at a chosen beatnote frequency to monitor the pulse repetition frequency. The self-heterodyne harmonic amplification technique employed in this sensor allows for further multiplication of the observed frequency deviation by demodulating the signal at higher beatnotes of the ML laser, which are clearly observable in its RF spectrum. Based on the Allan deviation plot, the sensor reached a detection limit equal to 6.9 ppbv for a 136 s integration time.

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Recent developments on QEPAS sensor using a radial resonator for mid-infrared measurements

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Short abstract: We present recent developments on a photoacoustic gas detector employing a custom quartz tuning fork and an acoustic radial resonator. A prototype was fabricated and characterised with a telecom laser diode and quantum cascade lasers, demonstrating state-of-the-art sensitivity while facilitating optical alignment compared to traditional configurations.

Quartz enhanced photoacoustic spectroscopy (QEPAS) is an optical method for trace gas measurements down to a few parts per billion. A QEPAS detector is composed of a quartz tuning fork (QTF) [1] associated to acoustic resonators to enhance the overall sensitivity. The traditional configuration of these resonators is called "on-beam", in which two tubes, usually presenting a sub-mm diameter, are placed around the QTF and used at their first acoustic longitudinal resonance (Fig. 1a). This configuration typically enables a tenfold sensitivity enhancement compared to the QTF alone, to reach a state-of-the-art normalised noise equivalent absorption (NNEA) of ~1.10^{-9} $cm^{-1}.Hz^{-1/2}$ [2]. However, the fact that the laser beam has to pass through these narrow tubes without touching their walls is a major drawback, as it considerably complicates optical alignment, even more so in the mid-infrared region or with spatially extended optical sources.
To circumvent this drawback we presented the first radial acoustic resonator used in quartz enhanced photoacoustic spectroscopy (QEPAS) exhibiting a NNEA of 3.9 10^{-9} $cm^{-1}.Hz^{-1/2}$ [3]. Compared to the "on-beam" configuration, laser beam alignment is facilitated as the beam should be focused in a larger 2x2 mm^2 area.

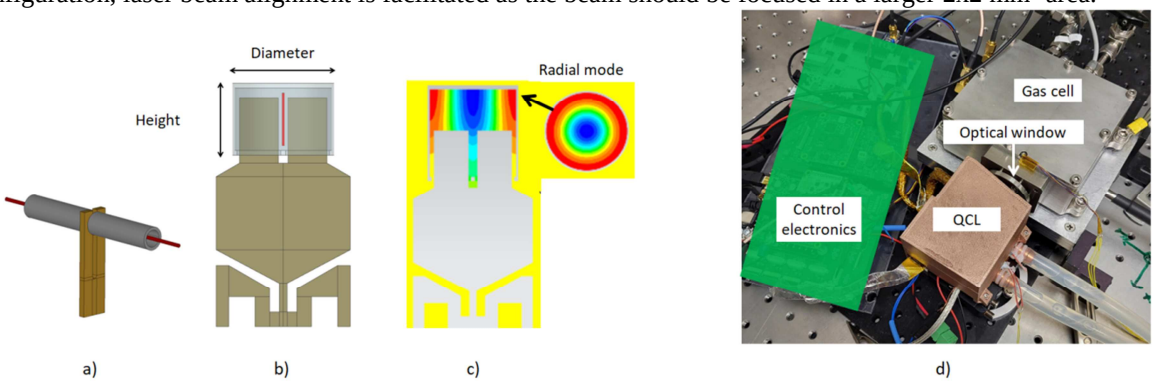

Fig. 1 (a) Classic on-beam configuration with a watch tuning fork. (b) New configuration using in-plane configuration with a radial resonator. (c) Acoustic simulation of the radial mode. (d) Experimental setup for photoacoustic measurements using a quantum cascade laser array.

We present an improvement of this configuration allowing a near tenfold increase in sensitivity to reach 5.10^{-10} $cm^{-1}.Hz^{-1/2}$ and to further facilitate optical alignment. The laser beam was placed in an "in-plane" configuration (Fig. 1b) to increase the optic-acoustic overlap and a gold mirror was placed in the back of the acoustic radial resonator. The coupling between our custom QTF and the radial resonator was carefully studied through finite element simulations in order to optimise the sensitivity (Fig. 1c).
This new configuration was implemented (Fig. 1d) and tested by using either a telecom laser diode targeting C_2H_2 at 6490.05 cm^{-1} or a quantum cascade laser array, mainly used to target NH_3 at 1049 cm^{-1}.
We will present the optimisation of our sensor through simulations and the obtained experimental results (NNEA, background, stability...).
Afterwards, a second design was made using large input/output laser windows to allow the use of two quantum cascade lasers arrays covering the spectral band from 8 to 10 μm. This prototype has been fully integrated and will be characterised during the next months.

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FPGA implementation of closed-loop detection method for quartz enhanced photoacoustic spectroscopy

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Short abstract: A new signal processing method implementing a closed-loop oscillation of a quartz tuning fork and a differential measurement has been developed on FPGA for fast and precise QEPAS measurements. This paper presents the implementation of this new processing method on FPGA and experimental validations.

Quartz enhanced photoacoustic spectroscopy (QEPAS) makes use of a quartz tuning fork (QTF), i.e. a resonant detector, usually presenting a frequency of a few kHz and quality factors of a few thousands or tens of thousands [1]. The traditional detection scheme in QEPAS consists in measuring the QTF resonance frequency and modulating the laser at half of the resonant frequency, and then the signal is recovered through lock-in detection. However, this method presents drawbacks. First, the frequency variation of the QTF resonance, due to temperature or gas parameters, can induce a signal drift as the laser modulation is not updated fast enough. Second, the measurement time can be a few seconds since one has to wait for the total relation of the QTF which is a multiple of the quality factor over the frequency. In order to overcome these drawbacks, we presented a new detection method [2]. As shown in figure 1, it consists of an oscillator circuit tracking the tuning fork resonance, with an extra phase-shifted output used to modulate the laser current. The laser beam passes in between the tuning fork prongs, generating a photoacoustic signal at the QTF frequency. A phase quadrature is set between the resonator piezoelectric actuation force from the oscillator circuit and the photoacoustic actuation force from the laser beam. This induces a shift of the oscillator frequency that is proportional to the photoacoustic force and, thus, to the gas concentration. This frequency shift is instantaneous, allowing fast measurements.

The new detection method has recently been implemented on FPGA as shown in Figure 1. A Direct Digital Synthesis (DDS) based oscillator has been developed to control the tuning fork excitation and the laser modulation. Synchronous detection and PID control are then performed by the FPGA's microprocessor using DDS's trigger signals. The PID system has been tuned with Ziegler-Nichols method. Moreover, a Python interface has been developed to control the DDS and monitor real-time data on FPGA.

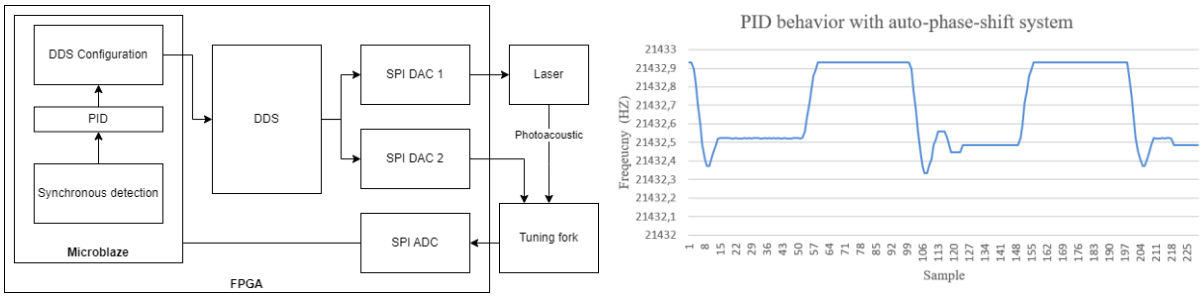

Fig. 1 Left: Schematic of the QEPAS active detection method on FPGA. Right: Differential measurements.

Experimental validation has been performed. First, we validated each block separately, then we performed measurements in a traditional open-loop detection scheme and found a similar signal-to-noise ratio as the one obtained with a commercial instrument leading to a NNEA of 2.10^{-8} W.cm^{-1}.Hz$^{-1/2}$. Then, we tested the closed-loop detection. We found optimal phase shifts values, that were later applied to the laser modulation sequentially as shown in Figure 1 (Right). At each phase shift, the PID stabilizes its command at the resonant frequency, then, the differential frequency is computed. Following this method, the FPGA revealed an NNEA of 1.10^{-6} W.cm^{-1}.Hz$^{-1/2}$, which is lower than expected compared to a reference instrument (HF2LI). This could be explained by a low quantization step size from the ADC (12 bits). Current works are ongoing with a 20 bits ADC and an improved synchronous detection.

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Design and Fabrication of Directional Coupler Based Wavelength Combiner for Multi Gas Sensing Applications

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Short abstract: We propose an on-chip 2x1 duplexer based directional coupler, bound with micro laser sources, enabling the simultaneous measurement of multiple gases. The simulation results show coupling efficiency of about 95% for the target wavelengths for ammonia and methane in line with preliminary experimental results.

Real-time, low-cost, detection and measurement of gas and liquid concentrations is important for both understanding and monitoring a variety of gas phenomena from industrial processes to environmental change. Various types of gas sensors are available in the market, still the sensing of multiple pollutants and the data analysis quality is often not promising. Quartz enhanced photoacoustic spectroscopy (QEPAS) is an alternative technique [1], utilizing a quartz tuning fork (QTF) for the highly sensitive detection of trace gases. To achieve the simultaneous detection of multiple gases in real-time, it is preferable to utilize an optical wavelength combiner to exploit the target wavelengths at the same time. The target wavelengths equal to 1530 nm and 1653.7 nm corresponds to the unique optical absorption characteristics of the ammonia and methane gases, respectively. In this regard, we introduce a 2x1 optical on-chip duplexer based on a directional coupler for multi-gas sensing to improve the speed and accuracy of gas detection by allowing for simultaneous measurement of multiple gases using a on-chip bound micro laser sources [2]. By quickly switching the lasers, the duplexer allows for the detection of different gases with high temporal resolution. In addition, the use of a duplexer in multi-gas sensing can also reduce the complexity and cost of the sensor system. Instead of using multiple systems of detectors for each gas of interest, an on-chip laser and QEPAS system can be used with the duplexer to detect multiple gases in real-time.

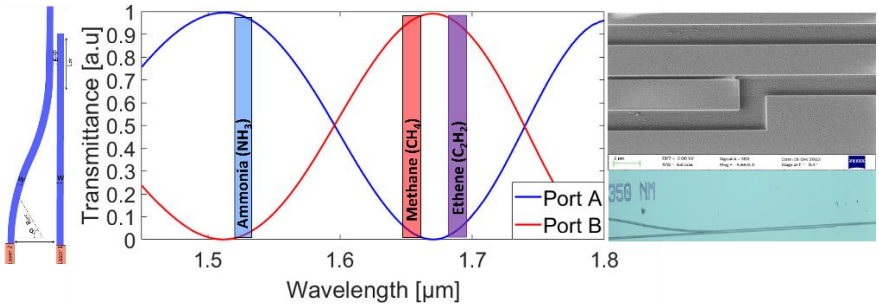

Fig. 1 Fig. 1 (a) Schematic diagram of design parameters of directional coupler (DC) -based wavelength duplexer. (b) Numerical results of output power transmittance of the designed DC duplexer with respect to a range of wavelength launching at Port A and Port B. (c) Microscopy image (bottom) and a SEM detail of the fabricated duplexer (top).

The performance of the proposed duplexer has been optimized using the beam propagation method (BPM), the schematic of the computational cell is shown in Fig 1. (a). Fig.1(b) shows the simulated transmittance spectra, for input Port A and B with an optical power coupling efficiency equal to 95% and 97 % for the wavelength equal to 1530 nm and 1653.7 nm respectively. It is interesting to see the chance of including Ethene gas at 1684 nm having optical power coupling efficiency of 97 %.

The proposed device was fabricated using CMOS compatible method and the microscopy and SEM images are depicted in Fig.1(c). The integrated, compact, and lightweight device could be exploited in sensors mounted on drones for real-time monitoring and large spatial convergence. This novel platform may constitute a breakthrough by filling the gap between lower-cost sensors, with inferior performance, and highly sensitive micro sensing device.

Acknowledgment

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Investigation on a 4-µm emitting laser based on a fluoroindate fiber doped with praseodymium

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Short abstract: A novel continuous-wave laser based on fluoroindate fibers, doped with praseodymium, is investigated. The laser is designed to emit at 4 µm when pumped at 1500 nm wavelength. Several simulations are performed by varying the laser cavity length, the output mirror reflectivity and the pump power, obtaining promising efficiency and low pump power threshold.

The development of fiber lasers emitting in the middle infrared (Mid-IR) range have attracted much research interest in the last years, thanks to a feasible number of applications, including earth pollution monitoring, agrifood, communications, chemical spectroscopy, industrial and medical applications [1-2]. Recent studies have been focused on improving fiber lasers performances, with the aim of optimizing their efficiency, maximum power output, and wavelength tunability [1-5]. Different glasses can be exploited in the Mid-IR, depending on the desired wavelength operation range. Chalcogenide, tellurite, and fluoride ones are among the most promising. The suitable host glass choice depends on the peculiar application, also considering that there is a slight dependence of the employed rare-earth dopant emission with the hosting glass structure. Erbium, holmium, thulium, dysprosium, neodymium, europium, and praseodymium are the mainly employed activating ions, since they show a good solubility in the aforesaid materials [1-5]. In this work, a novel continuous wave laser, based on a fluoroindate fiber double cladding 2-D, by Le Verre Fluoré (see the on line catalogue), doped with praseodymium with the concentration $N_{Pr} = 1.6 \times 10^{26}\ ions/m^3$ is designed.

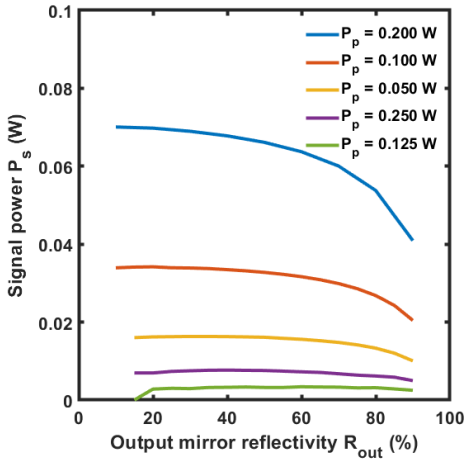

Fig. 1 Signal power P_s as a function of the output mirror reflectivity R_{out} for different input powers P_p, fiber length $L_{fiber} = 0.4\ m$, $N_{Pr} = 1.6 \times 10^{26}\ ions/m^3$, input mirror reflectivity $R_{in} = 95$ %.

Fig. 1 shows the output power P_s as a function of the output mirror reflectivity R_{out} for different input powers P_p, fiber length $L_{fiber} = 0.4\ m$, $N_{Pr} = 1.6 \times 10^{26}\ ions/m^3$, input mirror reflectivity $R_{in} = 95$ %. The output power P_s is maximized for an output mirror reflectivity R_{out} between $R_{out} = 15\%$ and $R_{out} = 50\%$. Preliminary simulations show a potential good efficiency $\eta \approx 25\%$ and low threshold input power, about $P_{th} = 0.02\ W$. Further investigations could lead to better performances. The interest of this investigation also lies in considering available on market fiber for the laser design.

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Fabrication of Mid-IR Tapered Devices Using Fluoride and Chalcogenide Optical Fibers

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Short abstract: The fabrication of tapered optical fibers and combiners using resistive filament fusion splicer with fluoroindate and selenide glasses is illustrated, providing a practical framework for the development of mid-infrared devices.

Optical fiber tapers are a highly adaptable device that can be utilized in a wide plethora of applications [1]-[3]. These applications include fiber optic sensing of temperature, external refractive index, pressure or chemical compounds, as well as optical communication for purposes such as coupling, mode filtering, or mode matching. The tapers can also be used for imaging to either magnify or demagnify an image. In addition, pump combiners can be employed to reach the power threshold for lasing in rare earth doped optical fibers. Lastly, the photonic lantern is a device that needs the tapering and can be used for astrophotonics application. The tapers are generally fabricated by stretching and heating the optical fiber to gradually reduce its diameter while considering the adiabaticity criteria to avoid high losses [4]. This paper illustrates the manufacturing process of fused optical fiber devices based on indium fluoride (also known as fluoroindate) and selenide optical fibers, since the current state of fused optical fiber devices for mid-infrared applications is not advanced enough to enable widespread commercial use. Even though some research papers detailing the successful production and testing of soft-glass optical fiber devices are reported in literature, additional work is necessary [5]. The authors use a fusion filament splicer to manufacture fused biconical tapers, fabricating a seven-input optical fiber combiner and a single optical fiber taper for each kind of considered glass. In particular, the fluoroindate optical fibers and low refractive index fluoroindate capillaries have been provided by Le Verre Fluoré (Bruz, France); the selenide optical fibers and the low refractive index selenide capillaries have been provided by SelenOptics (Rennes, France). The set dimensions are: down taper length L_1= 20 mm, waist length L_2 = 20 mm, up taper length L_3 = 20 mm. The waist diameter for the combiners is d_{cw} = 110 µm (tapered down to 20% of the initial capillary diameter), the waist diameter for the optical fibers is d_{fw} = 35 µm (tapered down from an initial diameter d_{fi} = 100 µm). The start filament power for fluoroindate step-index optical fiber is P_1 = 10.4W; for selenide optical fiber is P_2 = 7.7W; for fluoroindate 7×1optical fiber combiner is P_3 = 12.0W; for selenide 7×1optical fiber combiner is P_4 = 8.4W. In Fig. 1, a series of microscopic images taken with a CCD camera is reported; the distance between two consecutive images (each 800 µm long) is about L_4 = 6 mm.

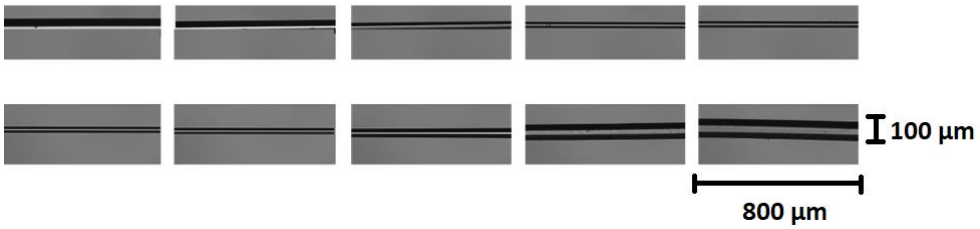

Fig. 1 Series of microscopic images of fluoroindate step-index optical fiber taper taken with CCD camera.

The fluoroindate optical fiber taper has been measured at wavelength λ = 1.55 µm, employing an SLED optical source. It shows an insertion loss IL < 1.0 dB, demonstrating the feasibility to obtain high quality fused optical fiber devices with low losses. The devices show low insertion losses and no surface crystallizations. This is an important step towards reliable fabrication, particularly for fluoroindate optical fibers which necessitate a higher level of accuracy than selenide optical fibers.

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The Impact of Spectral Peak Deformations on Near-Infrared Wavelength Modulated Photoacoustic Hydrocarbon Sensors

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Short abstract: We present the impact of water and pressure induced signal alterations on a wavelength modulated near-infrared photoacoustic methane and ethane sensor. With a Fourier Transform based simulation of the excited spectral region the measured signal characteristics can be modeled showing good agreement and thus increases the reliability of the sensor.

Measurement devices based on photoacoustic spectroscopy (PAS) are susceptible to acoustic, relaxational, and spectral influences. Overlapping absorption spectra of the individual components in the sample or peak deformations due to pressure broadening result in signal alterations [1,2]. If amplitude modulation (AM) of the light source is applied, the effect of overlapping absorption characteristics on the measured PAS signal is linear, i.e. a 10% offset on the stimulated peak yields a 10% signal increase. With wavelength modulated (WM) PAS for on-peak detection, however, the frequency spectrum of the generated sound wave is altered by distortions of the excited peak, yielding signal losses. In order to quantify those losses, we introduce a simulation tool based on Fast-Fourier-Transform (FFT) analysis of overlapping spectra in WM PAS. Fig. **1** illustrates the schematic of the simulation process applied in order to model the measured signal alterations. In plot (1) species A indicates the analyte of interest (black solid line) and B the interfering molecule, which exhibits overlapping absorption characteristics (blue dashed line). The sum spectrum (2) of the measurement matrix is displayed by the black dash dotted line. Scanning the stimulated spectral region (3) of the sum spectrum, as indicated by the red sinusoidal waveform with modulation frequency f_{mod}, results in a periodic, time-dependent WM signal (4). Preforming a FFT on the simulated WM signal yields the frequency spectrum (5). At twice the modulation frequency of the light source, the spectrum shows a distinct peak, whose amplitude is a quantity comparable to the measured PAS amplitude. By normalizing the FFT amplitude and the PAS amplitude those parameters may be compared to one another (6). As this analysis only accounts for spectral influences, a full compensation of potential PA cross-sensitivities requires additional consideration of relaxation effects and acoustic phenomena.

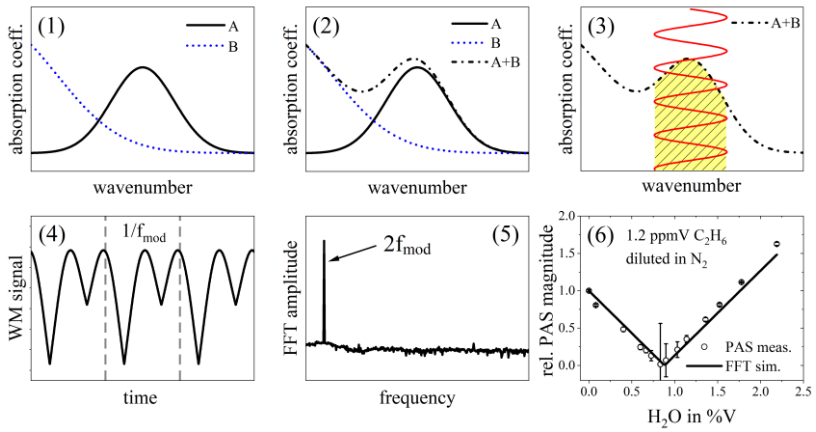

Fig. 1 Schematic representation of the workflow of the FFT based simulation. First, the individual spectra are acquired (1), then the sum spectrum (A+B) is generated (2), which is scanned by the WM modulated light source (3). This generates a time dependent WM signal (4). The amplitude of the FFT of the WM signal (5) can be compared with the measured PAS amplitude (6).

Plot (6) in Fig. **1** shows the normalized results of the FFT simulation (black solid line) in comparison to the measured PAS amplitude (black circles) for C_2H_6 detection, scanning the spectral region from 2973.39 to 2973.73 cm^{-1}. While the C_2H_6 concentration was kept constant at 1.2 parts-per-million (ppmV) the humidity content was increased.

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Design of an FPGA Digital Lock-In Amplifier for QEPAS Applications

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Short abstract: A digital lock-in amplifier dedicated to QEPAS applications has been designed, based on a low-cost FPGA device. Dual-phase detection is used for measurement of both phase and magnitude of the QEPAS signal. The CORDIC algorithm has been extensively exploited for generating the sinusoidal reference signal and for efficient phase detection.

In Quartz-Enhanced Photo-Acoustic Spectroscopy, synchronous detection techniques are always employed for full exploitation of the resonance properties of the QTF. Thus, one of the key electronic building blocks of a QEPAS sensor is the lock-in amplifier (LIA), which demodulates the second harmonic component of the signal generated by the QTF in a classic 2f detection scheme. A digital implementation of the LIA offers several advantages over an analog counterpart, such as, for instance, robustness and performance repeatability against temperature fluctuations and ageing [1]. Moreover, generation of the sine wave reference in the digital domain is much more effective in terms of distortion, if a sufficiently high number of bits is used to represent the signals, and electronic noise and drifts cannot affect the generated reference. Last, high-order low pass filters can be easily designed and optimized in the digital domain, once again insensitive to parameter fluctuations which plague analog implementations. We propose a dual-phase, FPGA-based LIA in which the CORDIC (COordinate Rotation DIgital Computer) algorithm [2] is extensively exploited to perform different tasks. First, CORDIC is used to generate the digital samples of the sinusoidal reference with the desired accuracy. The algorithm computes the sine and cosine of a given angle by applying a number of discrete rotations to a vector with initial y component equal to zero. The main advantage of this kind of algorithm is that, if these partial rotations are suitably chosen, only simple shift and add operations are required and implementing them in an FPGA is simple and cost effective. In our case, we have also exploited the following property of CORDIC: if a given value is assigned to the initial x-component of the vector to be rotated, the final result of the application of the algorithm is the product of the sine or cosine of the desired angle and this given value. As a result, a phase accumulator is used to generate the reference signal (the sine and the cosine waves at the desired frequency) by means of the CORDIC algorithm and the multiplication of the reference with the QTF signal is automatically executed by assigning the samples of this signal to the initial amplitude of the x-component of the rotating vector. In this way, the need of hardware multipliers is avoided, resulting in the remarkable saving of FPGA resources and, as a consequence, making possible LIA implementation on a low-cost FPGA.

A detailed study has been carried out to identify the most effective configuration for the narrow-band low-pass filter of the LIA. Comparative evaluation of different solutions in terms of needed FPGA resources and selectivity performance results in the final filter configuration, based on the cascade of a shaping filter followed by an IIR and a symmetric FIR filter. The shaping filter is employed to improve the IIR performance, sharpening the transition band of the resulting filter. Another filtering stage, composed by a second order linear recursive filter followed by an IIR 6^{th} order type II Chebyshev filter has been also added in the path of the QTF signal, to reduce the in-band quantization error and improve the signal-to-noise ratio.

For the LIA implementation, a Cyclone IV FPGA from Intel, with 22k logic elements, 66 18x18 bits embedded multipliers and 4 PLLs. The circuit generates by means of the CORDIC alghoritm also the sine wave modulation signal for the laser in the QEPAS sensor. The resolution of the reference frequency for the LIA is 11.6 mHz and a 32-bit phase accumulator has been used. The accuracy of the reference sine wave is dominated by the precision of the master clock, since the intrinsic accuracy of the CORDIC algorithm is very high: the standard deviation of the error of the generated signals is of the order of 10^{-10}. The input signal from the QTF preamplifier is sampled at 232kS/s, with a 14-bit resolution. The number of FPGA logic elements employed for the LIA core is about 18.5k. The circuit has been used in a real QEPAS sensor for detection of H_2O vapor and CO_2 and has been demonstrated to be fully functional.

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Mobile Breath Acetone Sensor based on UV-LED Photoacoustic Spectroscopy

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Short abstract: A mobile photoacoustic sensor for determining the breath acetone in the ppbV-range is presented. Based on low-cost components, this sensor is targeting a future mainstream market application e.g. in the private healthcare or lifestyle sector.

The anaerobic threshold (AT) (also known as upper lactate threshold (LT2)) describes the maximum workload intensity an athlete can achieve while maintaining a balance between the formation and breakdown of lactate. While training at an intensity close to this level, the endurance capacity is supposed to enhance. Therefore, low-cost devices determining the anaerobic threshold are attractive to both competitive and hobby athletes. Acetone concentration in exhaled breath has been found to reach a maximum at the aerobic threshold [1]. Thus, monitoring the acetone level during an intensity increase, the anaerobic threshold can be determined. Besides, breath acetone is recognized as a biomarker for monitoring ketogenic diets. Therefore, measuring the acetone level helps people in overcoming obesity [2] or children suffering epileptic seizures [3].

We present a mobile breath acetone sensor based on amplitude modulated photoacoustic spectroscopy (AM-PAS). Using a LED light source (1) and a MEMS-microphone (2) as a detector together with a 3D-printed measuring cell (3), we realized a sensitive gas sensor only consisting of low-cost elements. Electronics, i.e. LED driver, lock-in amplifier, frequency generator, and power supplies are implemented as printed circuit boards. The modulation frequency is determined by an acoustic resonance monitoring system (4) [4]. Verification measurements with ProtonTRansfer-TimeOfFlight-MassSpectrometry (PTR-TOF-MS) verified a high sensitivity resulting in a minimum detection limit (3σ) of 72 ppbV with 10 s integration time and averaging over 200 values at 5 Hz sampling rate (see **Fig. 1**).

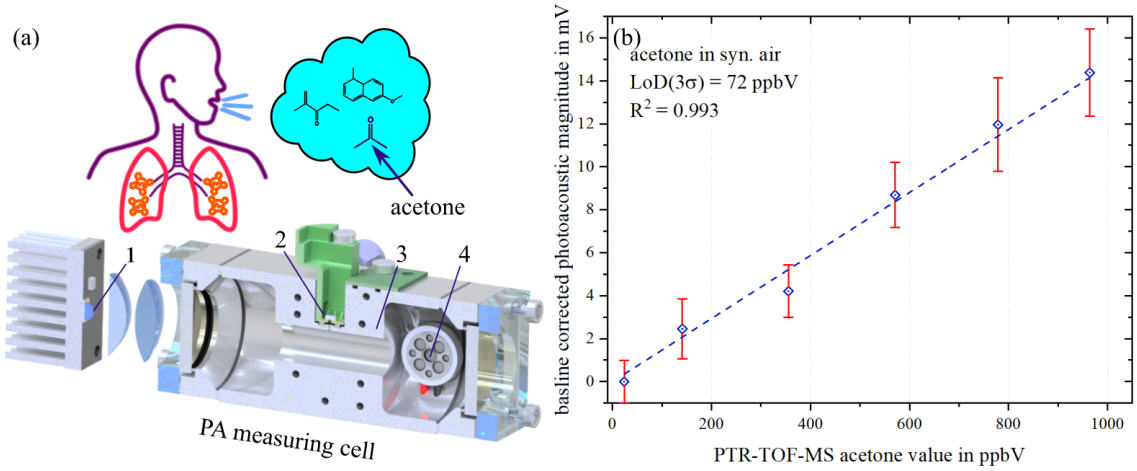

Fig. 1 Photoacoustic measurement of acetone in the ppbV range. In (a) the idea of measuring alveolar acetone is illustrated. The 3D-printed measuring cell (3) features inter alia a speaker for determining the resonance frequency (4), a MEMS microphone (2) close to the resonator center, and a high-power UV-LED (1). (b) presents a characterization measurement of acetone diluted in synthetic air. The measurement points are verified by an in-line measurement with PTR-TOF-MS.

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Mobile Nitrogen Dioxide Monitoring in Ambient Air with Photoacoustic Spectroscopy

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Short abstract: A mobile measurement station for photoacoustic detection of NO_2 in ambient air was developed. Standalone devices were replaced by printed circuit board solutions, a chemiluminescence reference sensor, a gas system suited for easily accessible calibration and a digital twin for cross-sensitivity compensation were implemented.

Nitrogen dioxide (NO_2) in ambient air is largely generated by anthropogenic combustion processes in transportation and energy generation. The NO_2 produced in this way poses a risk to respiratory health due to its high oxidative reactivity [1], which is why an EU directive has set a limit of 40 µg/m^3 as an annual average [2]. As an established standard measuring device, chemiluminescence based detectors (CLDs) are bulky and expensive, which has so far limited the spatial resolution of NO_2 monitoring. Photoacoustic spectroscopy (PAS) has been demonstrated to be a valid alternative method [3].

We transferred the thoroughly studied laboratory setup for PAS NO_2 detection into a mobile measurement station. The left part of Fig. 1 schematically shows the infrastructure inside the station: In addition to the PAS setup, a CLD was implemented for verification purposes. Two parallel gas lines can be operated to either analyze ambient air or calibrate the sensors. Both lines lead through a glass container at a high flow rate, from which the sensors extract their sample gas individually. Only one mode of operation can be chosen by the 3/2-way valves at a time. While the blue fiber coupled laser and the resonant photoacoustic cell (PAC) were copied from the laboratory, all standalone devices were separated and replaced by a PYNQ Z2 Linux based FPGA development platform with analog frontends. All control and readout operations are performed on the PYNQ, i.e. switching between calibration and ambient monitoring, acquiring the resonance parameters of the PAC, and sampling and filtering the microphone signal by an integrated lock-in amplifier.

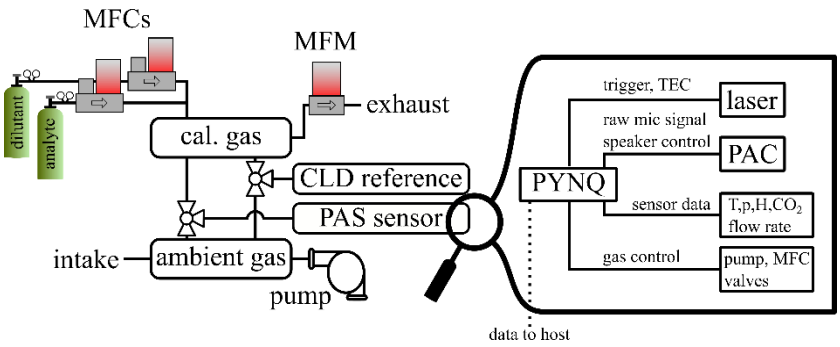

Fig. 1 Schematic of the measurement station with two gas lines for calibration and ambient analysis, respectively. Parallel to the PAS sensor a CLD reference is used. The PAS sensors functionality is based on the PYNQ Z2 board controlling the parameters and analyzing the sensor data.

PAS measurements in an environment such as ambient air, which is subject to changes in e.g. temperature, pressure and humidity are susceptible to influences that do not originate from variations in NO_2 concentration. Therefore, secondary sensors monitor ambient parameters, and a digital twin system is implemented to compensate all relevant cross-sensitivities, i.e. towards H_2O, CO_2, temperature, and pressure.

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Compensation of composition variation induced sensitivity changes in gas phase photoacoustics

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Short abstract: We suggest a calibration and concentration calculation procedure and prove that it can be used to determine the analyte's concentration with relative accuracy of about one percent, even when the composition of the measured gas varies drastically.

Photoacoustic (PA) concentration measurement technique for measurements in gas matrices with stable composition was proven to yield percentage-level accuracy in concentration measurements decades ago [1]. These results triggered a gradual increase in the use of the PA technique in various applications, including exhaled breath analysis [2], industrial process monitoring and control [3,4], environmental monitoring [5] etc. After the successful introduction of the PA method for measurements under stable gas composition, the next leap is to use it for applications in which the concentration of the main components of the measured gas varies. However, due to the complex nature of PA signal generation, the method is notoriously sensitive to gas composition variations through several effects. Whenever there is a concentration variation of the main components of the gas matrix, variations of the PA system's sensitivity (S) caused by changes in the physical properties of the measured analyte must be considered. The most important physical parameters which affect the PA system's sensitivity are the heat capacity ratio and the sound speed. Their effects are summarized graphically with the help of Figure 1.

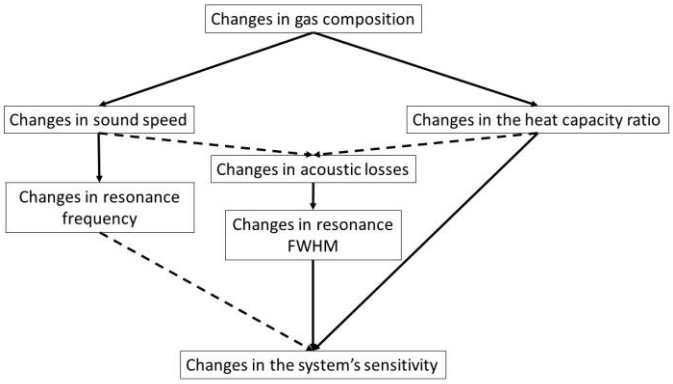

Fig. 1 Graphical representation of the cascade of changes induced by gas composition variations leading to the composition dependency of the sensitivity of a PA system. Dependencies that can be calculated with simple mathematical formulas or can be determined via measurements only are represented by solid and dashed arrows, respectively.

A novel calibration and concentration calculation method is proposed to keep the relative accuracy of the PA measurements in the few percentages range even in case of large-scale composition variations resulting in drastic changes in the acoustic and thermal properties of the measured gas. The proposed method has two components: the first one is a series of specifically planned calibrations which separates the impacts of resonance frequency and heat capacity variations, while the second one is a concentration calculation process. The method rigorously compensates for the frequency and heat capacity dependence of *S* as well as for the dependence of the FWHM of the resonance curve of the PA cell on the thermal and acoustic properties of the measured gas and has a general applicability.

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Two-dimensional IR correlation spectroscopy for characterizing mineral and organic-matter bands in humic substances and soil fractions

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Short abstract: Methods for humic substances and soil fractions using homospectral and heterospectral two-dimensional correlation spectroscopy (2D-COS) is proposed for accurate band estimation and identification, especially for soil organic matter, which exhibits weak bands compared to mineral-matrix bands.

Two-dimensional correlation spectroscopy (2D-COS) techniques offer improvement with respect to traditional spectroscopic methods by transforming 1D spectra into 2D correlation maps and help identifying correlations between individual bands. 2D-COS simplifies the spectra of samples with many overlapping bands and increases the spectral resolution. This is essential for soil organic matter (SOM) with relatively weak IR bands as compared to mineral-matrix bands. An IR method using 2D-COS for soil-fraction spectra is proposed for more accurate estimation and identification of bands, in particular for SOM. 2D-COS spectra of soil fractions of sod-podzolic and chernozem soils obtained using different fractionation and filtration options and IR modalities (attenuated total reflection [ATR], diffuse-reflectance [DRIFT], and photoacoustic FTIR [FTIR-PAS]) were recorded and compared with the spectra for humic substances. Samples for contrasting formation conditions and different land use (native steppe, shelterbelt, fallow, and arable land for chernozems) and samples of sections of genetic horizons were used. Homospectral 2D-COS (self-correlation of a set of spectra for changing conditions) and heterospectral 2D-COS (building a 2D map using two sets of data to be compared, Fig. 1) were used.

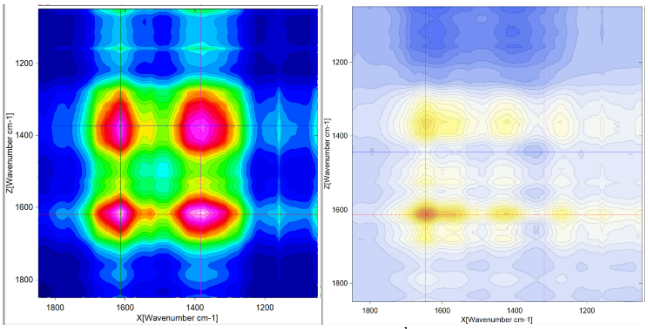

Fig. 1 DRIFT heterospectral 2D-COS of chernozem in 1900–1100 cm^{-1} range, native steppe, the main variable (X) and permanent fallow, correlated (Z); synchronous (left) and asynchronous (right) maps color scale: blue (no correlation), pink (most correlated) for synchronous, and from blue (negative) to orange (positive) through white (no correlation) for asynchronous maps. All bands in the steppe–fallow pair are pronounced: 1650, 1570, 1510, 1430, 1270, 1190 cm^{-1}.

For sod-podzolic and chernozem soils, synchronous 2D-COS maps of size fractions show a positive correlation in 4000–3600 (hydrogen bonds), 1700–1150, and 1100–200 cm^{-1} (quartz) ranges, Fig. 1. Asynchronous 2D-COS maps show differences at 3700–3600, 3000–2800, 1700–1400, 1250–1050, 800, and 500 cm^{-1}. The bands in the 3700–3600 cm^{-1} range belong to hydrogen bonds and indicate an increase in the proportion of silicate and quartz not bound to SOM or bound to adsorbed water in small fractions. This is consistent with increased intensity for adsorbed-water band at 1640 cm^{-1}. The bands at 1070, 797, and 505 cm^{-1} belong to crystalline quartz, and their proportion increases with the fraction size. The most important is the manifestation of peaks at 1562, 1444, 1251, and 1158 cm^{-1} with no significant contribution from inorganic matrix and due to carboxylate groups, aromatic compounds, and Amide III band. The intensity of these correlation bands is significant for the discrimination of size fractions. 2D-COS reveals bands of functional groups of the surface of soil particles, organic components, in particular a larger number of aliphatic component bands of SOM, as well as adsorbed water species, including the long-wavelength region, where the dominance of the mineral components hinders the use of either SOM extraction or destructive treatments (annealing or chemolysis). 2D-COS with granulometric methods for separating soil fractions showed that the range of 20 μm – 1 mm is informative and can be used for a detailed soil analysis. Aliphatic compounds seem to accumulate more in large fractions of native steppe compared to fallow.

The proposed approach for sod-podzolic and chernozem soils provides an extra data set for identifying SOM components with high reliability. The methodology of 2D-COS IR experiments will be expanded to submicrometer fractions and extracts of SOM.

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Uncertainty in Measurement by Thermal-Lens Spectrometry

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Short abstract: The concept of uncertainty in thermal-lens measurements was tested for most common "implementation–task" combinations of thermal lensing, including finely dispersed solutions, solvents, and supramolecular chemical systems; the uncertainty budget was calculated and compared with statistical treatment by accuracy/precision concept. The differences in uncertainty for various thermal-lens problems are discussed.

Applied studies by photothermal spectroscopy (PTS) are focused on biomedical sciences and biophotonics, materials sciences, and chemical and Earth sciences [1]. The possibilities of photothermal methods in all these areas are based on five main parameter groups, namely: (1) high measurement sensitivity; (2) simultaneous non-destructive assessment of optical and thermophysical parameters of the test object; (3) broad spectral range, from UV to IR; (4) high spatial resolution with microscopic implementation; and (5) a broad selection of objects, including those with complex composition. These features result in increasingly growing number of samples and applications, and the test objects have very complex chemical composition and structure, including nanomaterials, molecular and supramolecular ensembles, dynamically changing samples, and living systems. For basic research and practical applications, the methods of investigation and analysis should provide high accuracy and at the same time also high precision of measurement. For PTS, taking into account its sensitivity and spatial resolution, these parameters become particularly crucial.

However, another specific problem of PTS is that it is based on the interconnection of two groups of phenomena: light absorption and heat transfer, which both contribute to the signal. From the viewpoint of detection and versatility, this greatly increases the sensitivity and number of practical tasks. However, from the viewpoint of accuracy, it makes the problem of metrological support very complex and sophisticated. Moreover, the concepts of accuracy and precision for systematic and random errors, respectively, based on statistical treatment of existing data only, may result in incorrect interpretation and, thus, wrong decisions for such complex methods as PTS.

Therefore, PTS needs the metrological support based on the demands of the state-of-the-art concept of traceability and uncertainty in measurement (ISO 17.020: 5725 series standards and ISO/IEC Guide 98 series) and corresponding experiment design. In this study, to the best of our knowledge, we test the concept of uncertainty in photothermal measurements for the first time. As a photothermal method, we selected thermal-lens spectrometry (TLS), since it is used for determination of light-absorption (and concentration) as well as thermophysical parameters of test materials. TLS offers reliable and flexible instrumentation and data treatment schemes and is used for the largest variety of samples among all the photothermal methods.

For most common "instrumental implementation–applied task" combinations of thermal lensing, including transient and steady-state thermal-lens measurements of finely dispersed solutions, solvents with various thermooptical properties, and supramolecular chemical systems, we calculated the uncertainty budget and compared the results and predictions with statistical treatment by the accuracy/precision concept [2].

It was found that for tasks in large-scale applications (analytical concentration or absorbance measurements), there is an increase in the number of factors in the uncertainty budget, with an increased number of A-type (statistical) factors and a high overall accuracy class. To the contrary, for complex characterization of dispersed systems (size and thermophysical parameters), B-type factors (a priori, preset/known parameters) start to play a more important part. Uncertainty concept provides a more reliable prediction of the measurement accuracy compared to purely statistical treatment for instrument errors and solvent parameters. Under the tested conditions, thermal-lens spectrometry was used for determination of thermophysical parameters of nanomaterials including nanofluids and graphene oxide. Thermal lensing can reveal fine absorbance changes due to supramolecular interactions between planar organic compounds (π–π interaction) and planar compounds with metal complexes (π–d interaction).

These findings can be extended to other PTS methods and neighboring techniques like transmission photometry and photoacoustics with commercially produced instruments. Assessment of uncertainty in measurement can assure more correct selection of the techniques and provide more reliable and traceable data.

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Signal-to-Noise Ratio analysis of a transimpedance preamplifier for the readout of a quartz tuning fork in a QEPAS sensor

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Short abstract: This work presents a study of the Signal-to-Noise Ratio (SNR) of a transimpedance amplifier for the readout of a quartz tuning fork in a Quartz Enhanced Photoacoustic Spectroscopy sensor. The influence of a lock-in amplifier and feedback resistor on the SNR are analyzed and discussed.

Quartz Enhanced Photoacoustic Spectroscopy (QEPAS) is an indirect absorption technique largely employed for trace gas detection. With its high selectivity and sensitivity, it is suitable for many gas sensing applications, such as environmental monitoring, industrial process control, as well as medical diagnosis and detection of toxic gases or the explosives.

The core of any QEPAS sensor is composed by a Quartz Tuning Fork (QTF) as sensitive element. Thus, the ultimate performances of a QEPAS sensor are strictly related to the analog electronic front-end circuitry used for the QTF signal readout. Different analog preamplifier configurations can be employed; among them, a transimpedance amplifier (TIA) with a 10 MΩ feedback resistor represents the state-of-the-art solution for the design of the signal conditioning chain of a QTF [1-3]. Additionally, a Lock-In Amplifier (LIA) is usually employed to extract the desired signal harmonic and get rid of the unwanted noise, thus maximizing the overall SNR. The time constant of the LIA low-pass filter plays an important role in the determination of either the SNR or the signal acquisition time [2]: a long time constant increases the SNR, with the disadvantage to lengthen the acquisition time. Therefore, in real-time applications, the time constant of the lock-in filter must be properly chosen as a trade-off between the sensitivity and the desired signal acquisition time.

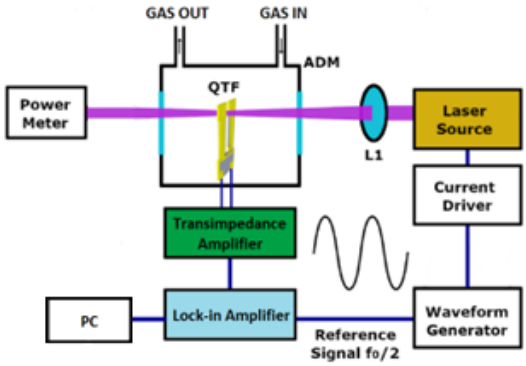

Fig. 1 Experimental apparatus of a QEPAS experiment. ADM – Acoustic Detection Module, QTF – Quartz Tuning Fork, L1– lens, PC – Personal Computer.

In this work, general guidelines to properly choose the feedback resistor of the TIA and the LIA time constant, with the aim of maximizing the SNR and optimizing the signal acquisition time are defined. To compare the main noise contributions at the output of the transimpedance amplifier, a mathematical model was developed using MATLAB software. Finally, experimental measurements employing a standard QTF at atmospheric pressure were performed to validate the theoretical model, with the experimental set-up shown in Fig. 1.

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Benzene detection using Quartz-Enhanced PhotoAcoustic Spectroscopy

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Short abstract: The detection of Volatile Organic Compounds (VOCs) such as benzene has emerged as mandatory requirement in several applications, such as breath analysis. In this work, the development of a QEPAS sensor for benzene detection using a custom laser source with emission wavelength at 14.8 µm is presented.

The selective detection and analysis of VOCs provides key information for different purposes ranging from the toxicological analysis of indoor/outdoor environments to the investigation of biological processes. One important field of application is breath analysis, which has emerged as a promising technique for early and non-invasive diagnosis of different diseases as some cancer types, diabetes, and respiratory problems. Commonly found VOCs, especially in indoor environments, are Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX group). These are well known to be toxic, mutagenic and/or carcinogenic. Benzene levels in air can be elevated by emissions from burning coal and oil, gasoline service stations, and motor vehicle exhaust [1].

Benzene detection with optical spectroscopy techniques is challenging since it has weak absorption features in the molecule fingerprint region (mid-infrared), where others interferents are present. Instead, benzene has strong absorption in far-infrared region, where optical detectors are characterized by low responsivities due to their wavelength dependency. Quartz-Enhanced PhotoAcoustic Spectroscopy (QEPAS) technique takes advantage of a quartz tuning fork (QTF), whose response is wavelength independent, employed as a sharply resonant acoustic transducer to detect weak photoacoustic excitation. The QTF is typically coupled with two millimetric resonator tubes, used to enhance the photoacoustic wave intensity. The QTF and the tubes compose the QEPAS spectrophone [2]. In this work, a QEPAS based sensor was developed to detect benzene (C_6H_6) molecules by targeting absorption features located at 673.98 cm^{-1} (14.8 µm).

The employed light source for C_6H_6 detection is a custom Quantum Cascade Laser (QCL) with central emission at 14.8 µm. The laser operates in continuous wave regime in a temperature range from −10°C to 10°C. For the benzene detection, the working temperature has been set to -5°C using a water-cooling system. The output optical power at 750 mA is 3.8 mW. The QEPAS spectrophone consisted of a custom T-shaped QTF with fundamental resonance frequency of f_0 = 12458 Hz and quality factor Q of ~14000 at an operating pressure of 500 Torr. The latter was selected being the one providing the highest QEPAS peak signal is 500 Torr. 2f-wavelength modulation (WM) detection was employed modulating the laser current with a sinusoidal dither at $f_0/2$ and acquiring the f_0-component of the QEPAS signal using a lock-in amplifier with a time constant of 100 ms. A slow ramp is also applied to the laser current driver to scan across the selected absorption feature. Starting from a certified mixture of 100 ppm of benzene in nitrogen (N_2), several dilutions in dry N_2 using a gas mixer were generated to calibrate the sensor and evaluate its response, as shown in Fig.1 a). The best linear fit was imposed to the experimental data, as shown in Fig.1 b) and a sensitivity of 8.9 mV/ppm was extracted with R^2= 0.9999.

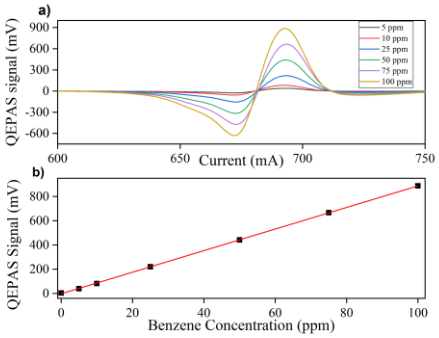

Fig. 1 a) QEPAS spectral scans at different benzene concentrations**.** b) Peak values extracted from QEPAS spectral scan plotted as a function of the benzene concentration (black squares) and corresponding best linear fit (red line).

With a 1σ noise of 0.15 mV, a minimum detection limit of 17 ppb was estimated with a signal integration time of 0.1 s. For a lock-in integration time of 30 seconds a minimum detection limit as low as 1.7 ppb was achieved. In future works QEPAS-based sensors could be suitable for the analysis of breath samples.

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Light-Induced Thermoelastic Spectroscopy – based sensor for CO detection

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Short abstract: Carbon monoxide (CO) detection plays a key role in environmental monitoring, safety, and industrial process control applications. In this work it is reported about a compact, rugged, and portable CO sensor box based on Light-Induced Thermoelastic Spectroscopy (LITES).

Carbon monoxide (CO) is a colourless, tasteless, odourless, non-irritant, highly flammable, and toxic gas. It is mainly produced by incomplete combustion of carbonaceous fuels, such as oil, natural gas, coal, et cetera. For these reasons, CO is a major pollutant and harmful gas; hence, the development of fast-responsive, compact, rugged, and portable sensors based on selective and sensitive techniques is highly desirable for environmental monitoring, safety, and industrial process control applications, among others. In this work, it is reported about a compact CO sensor box based on the Light-Induced Thermoelastic Spectroscopy (LITES) detection scheme, shown in Fig. 1. In LITES, a quartz tuning fork (QTF) is used as a light detector in place of a conventional photodetector in the conventional Tunable Diode Laser Absorption Spectroscopy (TDLAS) configuration. Modulated laser light is absorbed within a gas cell containing the target gas, then it is focused on one of the QTF's clamped ends. Here, light absorption induces a local temperature gradient, generating a local strain field, hence a piezoelectric charge deposition [1]. The spectral responsivity of QTFs employed as light detectors has been proven to be comparable to that of commercially available photodetectors, while displaying a flat behaviour throughout the entire infrared spectral range [2].

Recently, a CO sensor box based on the Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS) technique has been demonstrated [3]. While maintaining the same characteristics in terms of compactness, portability and ruggedness, the sensor's optical core unit, i.e., the sensor head, has been properly modified to fit an 18 cm long gas cell in it, thus separating the QTF from the gas sample matrix. With respect to QEPAS, this peculiarity of the LITES technique offers three main advantages: i) being the resonator separated by the gas sample, QTF's performances are no more affected by aggressive chemicals eventually composing the sample gas matrix and it can be exploited for non-contact sensing; ii) signal dependence on the relaxation rates of the target molecule in a fluctuating matrix is avoided, hence the sensor calibration is free from non-spectral cross-correlations [4]; iii) detection limit in the ppb scale is achieved with a sensing architecture and footprint almost identical with respect to the previously demonstrated CO QEPAS sensor.

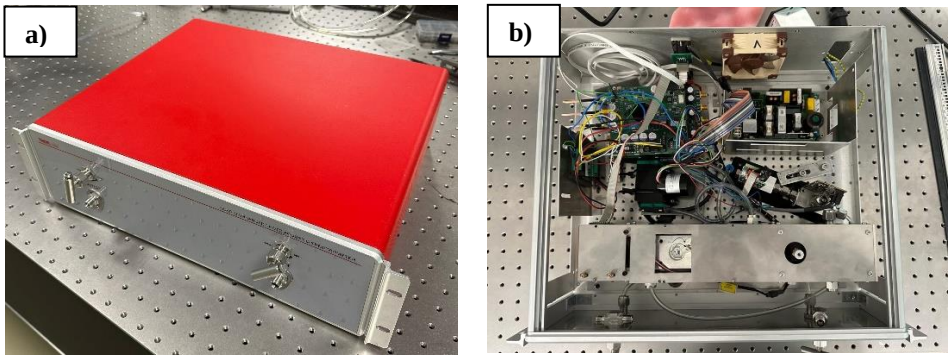

Fig. 1 Picture of the **a)** outer and the **b)** inner view of the 19-inches, 3-units sized CO LITES-based sensor box. Length x Width x Height: 36 x 48.2 x 13.3 cm, 10 kg weight.

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NO-NO_2 Simultaneous Detection Exploiting Two Different and Independent Resonance Modes of a Custom Quartz Tuning Fork

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Short Abstract: In this work, a dual-gas quartz-enhanced photo-acoustic spectroscopy sensor, employing acoustic resonators at both anti-nodes and two quantum cascade lasers, has been demonstrated. This spectroscopic configuration has been tested to analyze in real-time and in continuous flow the chemical reaction 3 NO_2 + H_2O → NO + 2 HNO_3.

Simultaneous detection and quantification of different trace gases is an important topic in many applications, such as environmental and atmospheric monitoring, chemical reaction and industrial process control, oil&gas and food industry and breath analysis. The requirement of simultaneity is a mandatory, for example, for self-calibrating sensors, for instantaneous determination of isotope concentration ratios and for the analysis of non-repeatable events.

Quartz-Enhanced Photo-Acoustic Spectroscopy (QEPAS) has proved to be a reliable technique for trace gas detection, allowing real-time and *in situ* measurements with high sensitivity and selectivity [1]. QEPAS employs a Quartz Tuning Fork (QTF) to detect weak sound waves generated by the gas molecules absorbing < 40 kHz modulated laser light. The laser light is focused between the QTF prongs at one of the anti-node points of the selected resonance mode and is further modulated at the resonance frequency (or one of its sub-harmonics) of the selected mode. When the fundamental flexural mode has a resonance frequency < 4 kHz, the first overtone mode becomes also accessible for QEPAS operation. The first overtone mode has one anti-node on the top of the prong, coincident with the fundamental mode one, and one anti-node close to the middle of the prong. Therefore, a frequency-modulated multiplexing scheme for simultaneous dual-gas detection can be realized by focusing two laser sources, each at one anti-node [2].

A dual-gas QEPAS sensor capable of simultaneous detection of nitrogen mono-oxide (NO) and nitrogen di-oxide (NO_2) is here presented (Fig. 1a). For the first time, two quantum cascade lasers have been employed to excite independently and simultaneously both the fundamental and the first overtone flexural mode of the QTF, respectively. The Laser #1 has an emission wavelength targeting the NO absorption line located at 1900.075 cm^{-1}, while the Laser #2 has an emission wavelength targeting an NO_2 absorption line located at 1601.77 cm^{-1}. Acoustic resonators were applied to each anti-node to enhance the acoustic waves amplitude. A detection sensitivity of about 300 ppb at 100 ms integration time was achieved for NO detection. The sensing performance allowed the monitoring in time of the chemical reaction in continuous flow of a concentration of 3000 ppm of NO_2 in nitrogen (N_2) with water vapor, giving NO and nitric acid (HNO_3) as reaction products (Fig. 1b) [3].

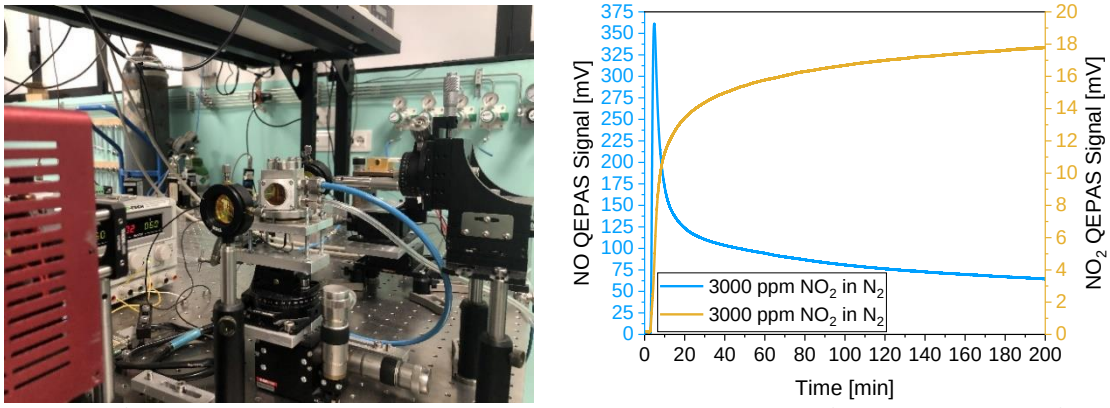

Fig. 1 a) Detail of the developed optical setup. b) NO-NO_2 simultaneous detection with 3000 ppm of NO_2 in N_2 at a pressure of 450 Torr.

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Mid-Infrared Quartz-Enhanced Photoacoustic Sensor for ppb-Level CO Detection in a SF_6 Gas Matrix Exploiting a T-Grooved Quartz Tuning Fork

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Short abstract: This program develops a QEPAS sensor for CO detection in SF_6 with minimum detection limit of 90 ppb. A custom T-shaped quartz tuning fork was designed to maximize CO photoacoustic response in SF_6. And a mid-infrared QCL with a central wavelength at 4.61 um was employed as the excitation source.

In the power grid, the gas insulation equipment is filled with insulating gas SF_6. When different faults occur in the equipment, different SF_6 decomposition substances will be produced. Among these decomposition products, CO can be used as an indicator gas to identify low-temperature overheating insulation defects in GIS equipment. When the CO concentration is within 20 ppm, it means that the GIS is working in a safe state [1]. from 2002, QEPAS sensors have been realized and more than 30 different analytes have been detected by using various wavelength laser sources, spanning from UV-visible to terahertz range, in most cases with ultimate detection limits in parts-per-billion range [2]. In QEPAS, 32.7 kHz commercial quartz tuning forks (QTF) act as spectrometers for signal sensing, but CO has a relatively slow vibration-to-translational (V-T) energy-transfer rate, which leads to a weak QEPAS signal output when a 32.7 kHz commercial QTF is employed. In all sensors reported in the literature, trace analyte was detected in N_2 or air matrix. When the gas matrix changes, damping should be considered. The main energy dissipation mechanism occurring in a vibrating prong is the damping by the surrounding fluid [3]. Because the QEPAS signal is proportional to the QTF quality factor, the ultimate sensor sensitivity will be dependent on the matrix composition. For gas matrices composed by molecules with heavy molecular weight, such as the SF_6, matrix, the drop of the QTFs' quality factor due to damping effects may strongly affect the sensor performances.

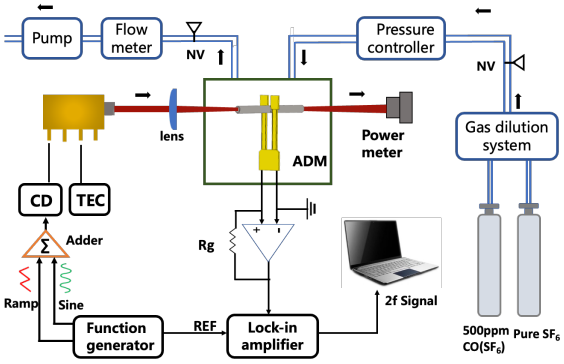

Fig. 1 Schematic of the CO QEPAS sensor.

In this program, a custom T-shape QTF with grooves carved on the prong surface was designed with a resonance frequency of 8 kHz, 4 times lower than the standard QTF, and a quality factor of ~11,000 in air, at atmospheric pressure. By means of this QTF, the QEPAS technique was applied to the measurement of CO in the SF_6, environment. A mid-infrared DFB-QCL laser with a center wavelength of 4.61 um was chosen as the light source to excite the CO molecules. Finally, a minimum detection limit of 90 ppb at 1 s of integration time was achieved, corresponding to a NNEA of 1.8×10^{-7} W·cm·Hz$^{-1/2}$. A sensor response time of ~3 min was measured when the gas flow rate is 60 sccm. The overall performances match the requirements for real-time monitoring of GIS discharge, offering a compact and reliable alternative to the bulky instruments currently employed to accomplish the task.

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Tunable SiN-based devices integrating Graphene electrodes

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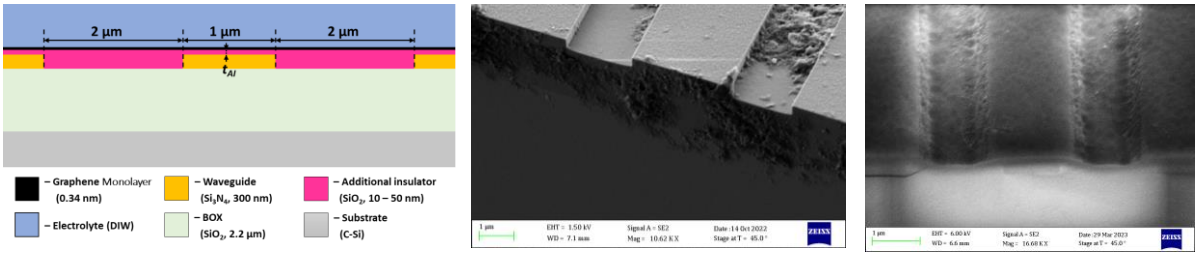
Short abstract: In this work, we present tunable Silicon Nitride waveguides exploiting graphene electrodes (GE), working in the Near-Infrared (NIR) range. In particular, we focus on the analysis of the fabrication of the additional insulator layer.

Graphene, a semi-metallic 2D material with a zero-band gap with tunable and wideband optical properties, opens a new window into the field of near-infrared wavelength tuning. The tight confinement of free electrons, within the single graphene atomic layer, creates a very low density of states condition (especially when electron energy is close to the Dirac point). According to this property of graphene, the carrier density changes cause significant shifts in Fermi energy [1]. This action effects on the rate of interband transitions and, hence, on the optical graphene optical properties. In turn, its Fermi level can be tuned under external electric field, covering the range from NIR to THz wavelengths [1–3].
The integration of the silicon nitride (Si_3N_4)-based waveguides (Figure 1a) and graphene electrodes (GE) opens a way for the realization of NIR tunable devices [4]. However, the direct transfer of graphene on to the Si_3N_4 layer is not satisfactory due to potential carrier injections from the GE and high level of absorption [3]. To prevent these effects, and additional SiO_2 insulator (AI) placed on the waveguide can be used.
In this work, we analyse and experimentally characterise the planarized additional layer of the Electrolyte Graphene Waveguide (EGW) configuration (in which the electrolyte is located above the GE as in Figure 1a).



(a) **(b)** **(c)**

Fig. 1 (a) EGW TD configuration integrating GE with the indication of the different layers and their thicknesses (b) SiN patterned device cross-section; (c) One-etching-step planarization result after SiO_2 deposition on the SiN device.

The thickness of the additional insulator layer (t_{AI}, which measured from the top of the Si_3N_4 waveguide) has a great influence on the operation of the EGW TW. When t_{AI} is small (< 10 nm) – it is not possible to prevent potential carrier injections from the GE into the waveguide. The opposite case (> 90 nm) causes a weak electrostatic bond, which is expressed in high applied voltages (from -40 V to 40 V) [3].
For the successful graphene transferring process a planarized surface is needed (to avoid GE cracks). The 300 nm deep trenches (Fig 1(b)) in the Si_3N_4 layer should be fully filled by insulator material (SiO_2). At the same time t_{AI} should be in the range between 10 and 90 nm. In this regard, the additional insulator layer growing and planarization were analysed (Fig 1(c)).
This work will help guide the fabrication of the optical devices with graphene-based wavelength tuning in the NIR.

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Integrated waveguide coupled Si_3N_4 Photonic Crystal Nanobeam Cavity for refractive index sensing

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Short abstract: We realize a compact and flexible Si_3N_4 resonator based on a Photonic Crystal Nanobeam (PhCN) cavity constituted by elliptical nano-pillars. Engineering the side-coupled waveguide, the structure exhibits high-Q factor (10^4), enhanced Extinction Ratio (~2x) and higher level of transmission(~1dB) with respect to a straight waveguide. Experiments for liquid sensing will be considered.

Fully integrable ultra-high-Q resonators can create a paradigm shift for label free sensing applications based on refractive index (RI). Therefore, decreasing the losses in the waveguide and coupling region of a waveguide-coupled resonator is required. By tailoring the directional coupler excitation to a resonator, is possible to achieve lower loss single mode-coupling compared to straight bus waveguide directional coupler [1–3]. Therefore, we study the enhancement features for a waveguide coupled high-Q PhCN based on elliptically shaped nanopillars. The sketch of the PhCN cavity and the fabricated device, considered in this work, are shown in Fig. 1(a) and (b), respectively. Fig. 1(a), shows three different cross sections of the PhCN resonator immersed in different analyte refractive index (n_A) that can vary from 1 (gases-like) to 1.45 (SiO_2-like). The vertical widths $(W_y(i))$ of the dielectric pillars are quadratically modulated ($W_y(i) = W_y(0) + i^2(W_y(i_{max})-W_y(0))/i_{max}^2$), from the center to both sides where i increases from 0 to i_{max} (see Fig. 1(a)-left). By means of 3D-FDTD simulations [3], the geometrical parameters of the pillars are set to maximize the Q-factor. In the other hand, the bus waveguide is bent to optimize the excitation mechanism of the modes supported by the structure.

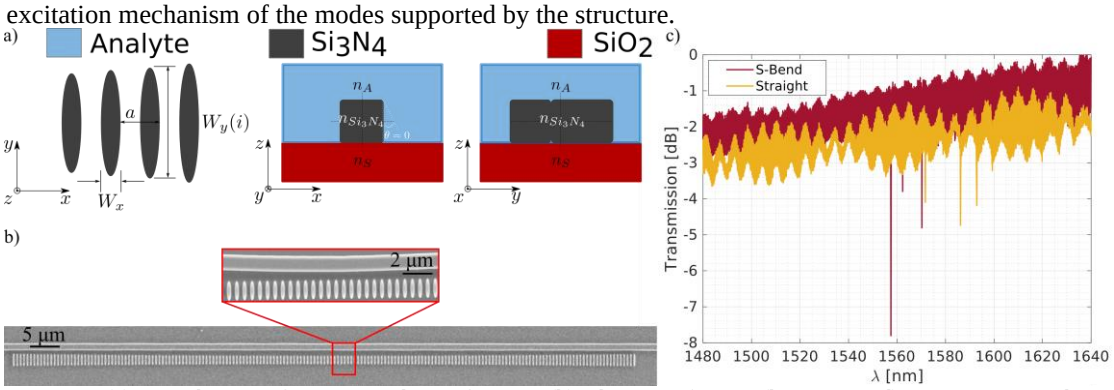

Fig. 1 (a) Lateral views of a segment shape of picture (b) where a = 516 nm (lattice period), W_x = 328 nm and W_y parabolically modulated from $W_y(0)$ =2.8a in the centre to $W_y(92)$ = 4.0a on either side. (b) SEM image of proposed PhCN side-coupled to a straight waveguide (top view). The inset, shows a zoomed image of the PhCN based on elliptical pillars. (c) Experimental transmission spectra of two fabricated devices as in (b) with a straight (dark yellow) and S-Bend (dark red) waveguide side-coupling configuration.

The proposed device exhibits calculated Q-factors (fundamental mode) upper than 10^6 for a broad range (~100nm) of elliptical nanopillar configurations. In contrast, Fig. 1(c) shows the experimental measurements of the proposed device in both side-coupling configuration: straight and S-bend. The experimental Q-factors are in the range of (1.0-2.3) 10^4, in line with the measurements reported in the same type of cavities [4]. Besides, the enhanced transmission level (~1dB) and the Extinction Ratio (~2x) can highly impact the sensitivity and the limit of detection of the proposed device as a refractive index sensor for label free sensing applications. Moreover, the novel High-Q 1D PhCN design, based on elliptical nanopillars, is compact in size (~100·10 µm^2) and resilient against fabrication errors (+/-40 nm). We acknowledge the European Union's Horizon 2020 MSC project OPTAPHI (grant No. 860808) and the CINECA award under the ISCRA initiative, for the availability of high-performance computing resources and support (project METAFORE).

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Photoacoustic Spectroscopy SF_6 Decomposition Sensors for an Electric Power System

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Short abstract: A sensitive photoacoustic multicomponent gas sensor for the online monitoring of the SF_6 decompositions was developed for an electric power system. The minimum detection limits of 440 ppb, 90 ppb and 115 ppb were achieved for CO, H_2S and SO_2 in SF_6 buffer gas.

High voltage gas insulated apparatus such as the gas insulated switchgears (GIS) and the gas insulated lines (GIL) have been widely used in power transmission and distribution systems around the world. Due to the high dielectric strength, chemically inactive and environmentally acceptable property, sulfur hexafluoride (SF_6) was widely chosen as the preferred dielectric gas for electrical insulation or interruption purposes in electric power systems. However, GIS/GIL failures occur from time to time from manufacturing defects. Health monitoring of gas insulated apparatus is critical to improve the reliability and to reduce the life cycle cost. Among the various methods for the monitoring, optical sensing developed fast in recent years due to their highly sensitive and anti-electromagnetic interference characteristic. Therefore, a sensitive photoacoustic multicomponent gas sensor for the online monitoring of the SF_6 decompositions in an electric power system was developed. An on-line ppb-level SF_6 decomposition detection gas sensor was developed via a 303 nm solid state laser and two near-IR diode lasers for an electric power system. The minimum detection limits of 440 ppb, 90 ppb and 115 ppb were achieved for CO, H_2S and SO_2 in SF_6 buffer gas by means of a time division multiplexing (TDM) method.

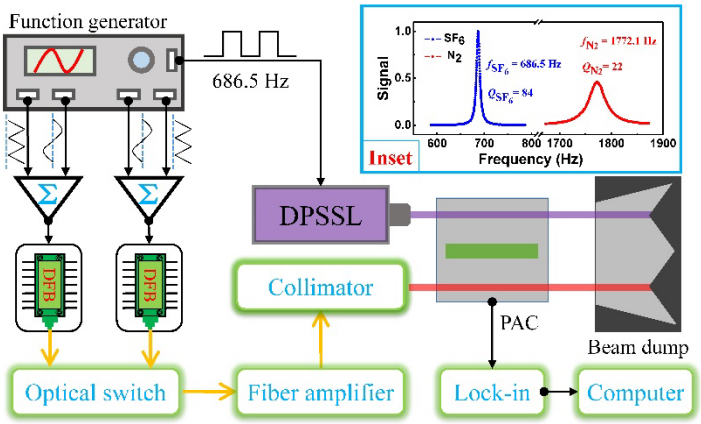

Fig. 1 Schematic of the online multicomponent gas monitoring system for SF_6 decompositions based on two NIR DFB lasers, an UV diode-pumped solid-state laser (DPSSL), a 1.5 W fiber amplifier, and a dual-channel photoacoustic cell (PAC). Inset: Resonance frequency response curves of the PAC in SF_6 (blue) and N_2 (red) buffer gases.

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Semi Photonic Integration of Quartz Enhanced Photoacoustic Spectroscopy for Greenhouse Gas Detection in Agriculture

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Short abstract: Greenhouse gas emissions from agricultural activities contribute significantly to climate change. Therefore, the development of portable and robust sensing technologies for greenhouse gas detection in harsh environments is needed. We present the application of photonic integration (PI) to Quartz Enhanced Photoacoustic Spectroscopy (QEPAS) for greenhouse gas monitoring in agriculture settings.

QEPAS uses a quartz tuning fork to detect the acoustic waves generated by the absorption of light by a target gas [1]. It is a sensitive and selective spectroscopic technique for trace gas sensing. Most QEPAS configurations presently require free-space optics for gas excitation, which must be carefully aligned to achieve maximum sensitivity, and consequently are sensitive to external vibrations, making field measurements difficult due to the high risk of misalignment. Photonic integration is the process of combining multiple photonic components onto a single chip to create a high-performance optical system [2]. For the PI of laser gas analysers (LGA), such as QEPAS sensors, the target gas is detected using evanescent waves. PI of LGAs offers the distinct advantage of removing free-space optics, increasing sensor robustness and mobility, and reducing instrument footprint. While concurrently, keeping the same selectivity, comparable sensitivity, and the real-time monitoring capabilities of their free-space counterparts. A PI-QEPAS is a proficient sensor for monitoring greenhouse gas emissions in harsh agricultural environments, facilitating the implementation of sustainable agricultural practices and environmental management strategies.

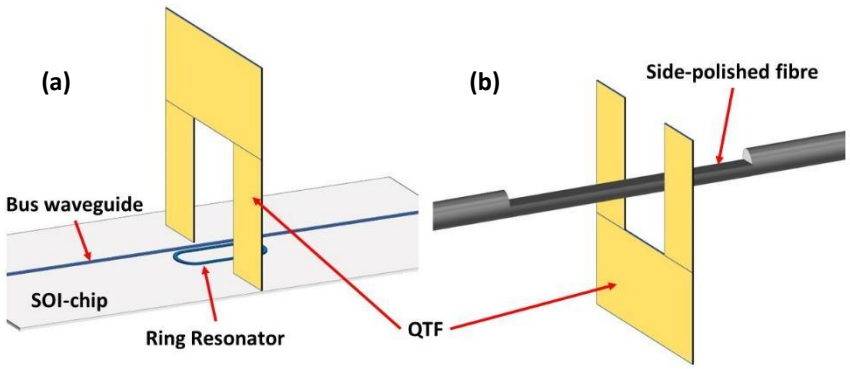

Fig. 1 Semi PI-QEPAS concepts. (a) An SOI-based technique, with an optical resonator placed between prongs of the QTF and light coupled with a laser source through a bus waveguide. (b) Evanescent wave excitation of the target gas using a side-polished fibre. Both configurations do not consist of any free-space optics, addressing misalignment issues.

We will present Semi-PI QEPAS sensing for methane (CH_4) monitoring, (a) by the power build-up of the excitation wave using an optical ring resonator and (b) by EW excitation of the gas using a side-polished fibre passing through the tines of a QTF [3]. All light coupling from the laser source to between the QTF prongs will be delivered via bus waveguides or through optic fibre, with no free space optical components.

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Room-temperature operation of single mode GaSb-based interband cascade DFB lasers at 6.17 µm

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Short abstract: Application ready GaSb-based distributed feedback (DFB) interband cascade lasers with emission wavelength around 6.17 µm are presented. The epi-down mounted device is operated in continuous wave mode at room temperature. The optimized epitaxial design is based on reducing resonant intersubband absorption in the valence band and rebalancing internally generated carriers.

In the mid-infrared range, the absorption strength of several industrially relevant analytes is particularly high. Because interband cascade lasers (ICLs) are able to emit over a wide range in the mid-infrared and have rather low power consumption [1], they are important building blocks for mobile and compact sensor systems for use in applications ranging from environmental analysis and process monitoring to biomedical diagnostics. While the performance sweet spot ICLs is between 3 and 4 µm, the upper wavelength limit has recently been pushed further [2,3]. In the case GaSb based ICLs, the longest continuous-wave (cw) emission wavelength reported so far is 5.2 µm [4] and 6.8 µm in the case of pulsed broad area devices [5].

In this work, we present a GaSb-based DFB ICL with emission wavelengths around 6175 nm based on an optimized layer design. In the active region the thickness of the GaInSb layer in the W-QW was adjusted to 3.5 nm to reduce the intersubband absorption in the valence band [2]. To balance the internally generated carriers, a Si-doping of 1×10^{18} cm^{-3} in the 3 InAs layers of the e-injector was used. The 9 active stages are surrounded by 760nm thick GaSb separate confinement layers and 2 µm (top) and 3.5 µm (bottom) InAs/AlSb cladding layers. The fabricated laser is dry chemically etched through the active region and utilizes a lateral metal grating to achieve longitudinal mode selection. The laser is coated with an HR metal coating at the back facet and a thin Al_2O_3 layer at the front facet. In Fig. 1 (a) the electro-optical characteristics of an epi-down mounted device (8 µm wide; 1 mm long) in cw operation at room temperature is shown. The emission spectrum at 6178 nm and the spectral tuning behavior are plotted in Fig. 1 (b), (c).

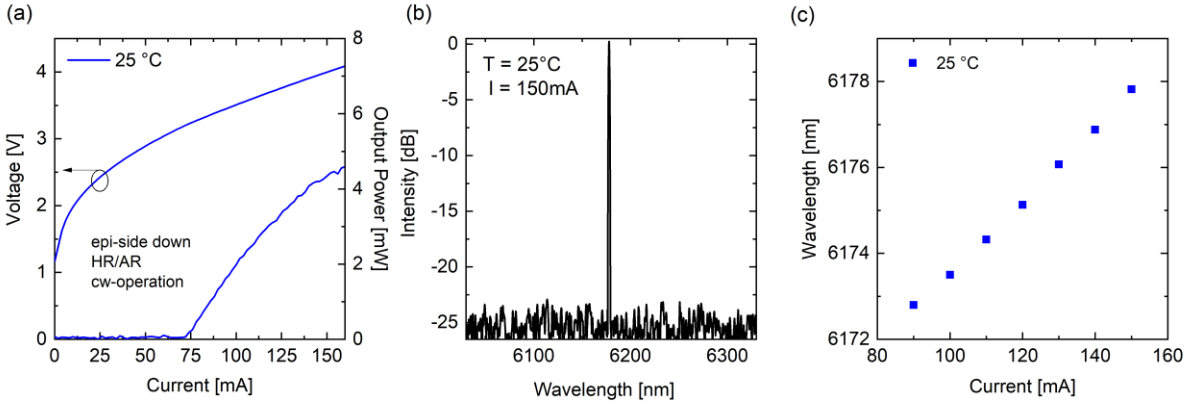

Fig. 1 (a) Light-current-voltage curves of a 8µm x 1mm epi-down mounted DFB-ICL in continuous wave mode. (b) Emission spectrum of the DFB-ICL at 25 °C and 150 mA with a side mode suppression ratio of more than 20 dB. (c) The spectral tuning shows mode hop free behaviour and a current tuning coefficient of 0.09 nm/mA is ectracted.

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Innovative QCLs for PhotoAcoustic Spectroscopy

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MIRSENSE, S.A.

Abstract

Laser spectroscopy gas detection is one of the reference techniques for gas sensing combining high selectivity and sensitivity, high accuracy, and low response time, while requiring low. Mirsense has been working for more than 8 years now for a wider adoption of this technology into practical applications. We present in the following our latest innovations designed to become the building blocks for many spectroscopic systems.

Fist, a plug and play electronic driving board for QCL pulsed operation will be presented. Pulsed operation allows to dramatically reduce the QCL electrical consumption, while offering additional knobs for wavelength modulation, such as modulated below-threshold inter-pulse currents. Current up to several amperes delivered in a few nanoseconds, a key feature to limit wavelength emission broadening.

Second, the latest performances of antimonide QCL emitting in the 10-20µm wavelength range will be presented. These new lasing emission bands enable for example the detection of BTEX molecules in the mid-IR range, leading to outstanding sensitivities and selectivity for trace gas detection.

Third, a new multi-wavelength QCL source for large molecules spectroscopy has been prototyped. The source can drive 2 multiplexers with 15 channels, allowing the simultaneous use of two lasers for DIAL operations and up to 30 lasers total for sequential use. The combined lasers spectral coverage can therefore be greater that 60cm^{-1} using temperature scans to cover the spectral distance between two lasers. The proximity electronics also favor an easy integration, limiting the input power supply to 5V and allowing a simple SPI connection for the source control.

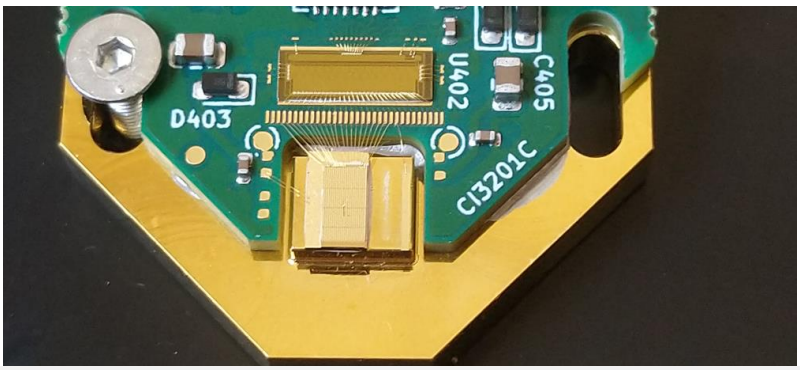

Figure 1 – A photo of the multi-wavelength QCL prototype developped by Mirsense. A wide spectral coverage for broad molecules spectroscopy is achieved, and full control over the power/wavelength emission pattern of the underlying single QCLs is possible for the integrators.

Development of a broadband cavity-enhanced absorption spectrometer for simultaneous measurements of NO_2 and particulate matter (PM)

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Short abstract: A novel instrument based on broadband cavity enhanced absorption spectroscopy (BBCEAS) has been developed using a supercontinuum broadband light source, which showcases its ability in simultaneous measurements of NO_2 concentration and the extinction of particulate matter (PM).

Simultaneous measurements of atmospheric gaseous compounds and particulate matter (PM) can largely advance our understanding on climate−atmosphere chemistry and gas−particle heterogeneous interactions and be of great interest for air quality monitoring [1]. Taking NO_2 and PM as the target species, herein, a novel spectroscopic instrument of broadband cavity-enhanced absorption spectroscopy (BBCEAS) using a supercontinuum (SC) broadband light source has been developed for simultaneous measurements of the NO_2 concentration and PM extinction, which can present a high correlation ($r \sim 0.7- 0.96$) in polluted environments [2].

Side-by-side intercomparison was carried out with reference NOx analyzer for NO_2 and OPC-N2 particle counter for particulate matter, which shows a good linear correlation with $r^2 > 0.90$. Measurement limits (1σ) of the developed instrument were experimentally determined to be 230 pptv in 40 s for NO_2 and 1.24 Mm^{-1} for the PM extinction in 15 s, respectively.

This work provides a promising method in simultaneously monitoring atmospheric gaseous compounds and particulate matter, which would further advance our understanding on gas-particle heterogeneous interactions in the context of climate change and air quality.

Experimental details and the preliminary results will be discussed and presented [3].

Acknowledgments

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