# Cavity Enhanced Optical Feedback Assisted Quartz Enhanced Photo-Acoustic Spectroscopy with a 10.4 µm External-Cavity Quantum Cascade Laser

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## Introduction

The objective of this work is an extension of a recently developed method of double-resonance photo-acoustic spectroscopy (DR-PAS)[1,2] to the mid-IR spectral range with a commercially available External Cavity Quantum Cascade Laser (EC-QCL).

In DR PAS the optical power of the laser beam that is sent into a resonant photo-acoustic cell is enhanced by several orders of magnitude by optical resonance of a cavity built-up around the PAS cell. The method also provides a reliable mutual lock between the laser and the cavity as well as seamless scanning of the absorption spectrum within the entire tuning range of the laser.

In a feasibility demonstration with a low power (20 mW) telecom DFB laser[3] we achieved a significant increase of the sensitivity of photo-acoustic detection by building up the intracavity power nearly to 300 W. This resulted in a minimum detectable absorption loss (MDAL) of 3.2 × $10^{-10}$cm$^{-1}$/Hz $^{½}$, which is comparable with the sensitivity of other cavity enhanced methods.

This performance can be further enhanced in the mid-IR spectral range, which is now accessible with commercially available quantum cascade lasers (QCLs), especially broadly tunable EC-QCL would result in a sub- part-per-billion detection limit of multiple gases.

## EC-QCL Spectroscopic Source

A Daylight Solutions mid-IR External Cavity CW QCL with 72 mW peak power and a tuning range from 933 cm$^{-1}$ to 1006 cm$^{-1}$ (73 cm$^{-1}$) was used to study DR-quartz enhanced photoacoustic spectroscopy (QEPAS) of chemical trace gas species

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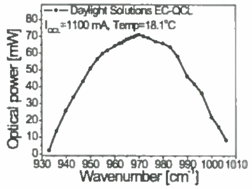
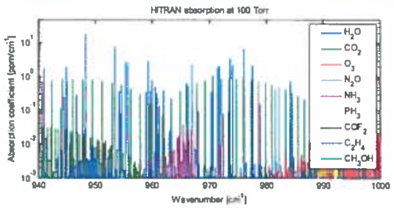


- Weak absorption of $H_2O$ and $CO_2$ – does not mask other species with lower concentrations
- Access to 7 important atmospheric molecules

## Atmospheric Absorptions in our EC-QCL range



## Molecules with strong Absorption within a 10.34 µm mid-IR EC-QCL Tuning Range

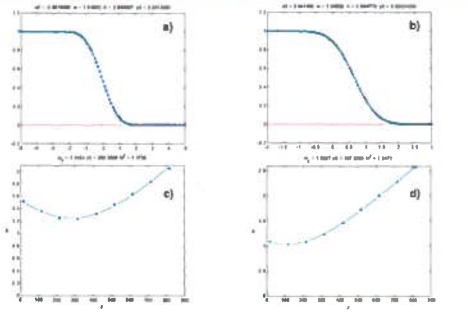
| Molecule | Concentration [ppm] | Absorption signal [ppm/cm] | Absorption [ppm/cm] per 1 ppm concentration |
|---|---|---|---|
| H_2O | 7750 | 18 | 0.00233 |
| CO_2 | 330 | 0.875 | 0.00265 |
| O_3 | 0.0266 | 0.0227 | 0.853 |
| N_2O | 0.32 | 0.00132 | 0.00412 |
| NH_3 | 0.001 | 0.0454 | 45.4 |
| PH_3 | 0.001 | 0.00432 | 4.32 |
| COF_2 | 0.001 | 0.000477 | 0.477 |
| C_2H_4 | 0.001 | 0.00821 | 8.21 |
| CH_3OH | 0.001 | 0.000804 | 0.804 |

## Experimental Challenges and their Solutions

- Availability of optical components in the mid-IR spectral range such as mirrors, wave plates, variable filters, isolators, even lenses is limited
  - Solution: For a proof of concept operate close to 10.6 µm where components for the $CO_2$ laser are commercially available
- Peak to peak wavelength excursion of high speed current modulation in current commercial models of EC-QCLs is much smaller than the pressure-broadened absorption line width. PZT modulation of the EC-QCL grating can be used only below 100 Hz

  Difficult to use wavelength modulation spectroscopy (WMS) with an EC-QCL
  - Solution: With a buildup-cavity a small wavelength modulation of the laser line results in large variation of the intra-cavity optical field intensity[2]. This makes an EC-QCL ideally suited for DR-QEPAS

## EC-QCL Characterization for Mode Matching

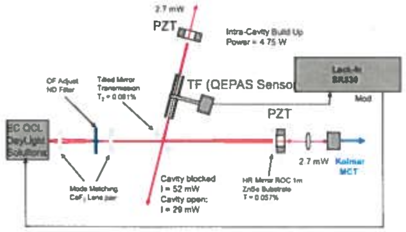


Top. EC-QCL beam profile at exit of device
a) – in horizontal and b) – in vertical directions obtained by moving blade method
Bottom. M² fits, c) - for horizontal, and d) – for vertical directions
Results:

| | | | |
|---|---|---|---|
| Horizontal direction: | $w_{0H}$ = 1.245; | $z_{w0H}$ = 284 mm, | $M^2_H$ = 1.17 |
| Vertical direction: | $w_{0V}$ = 1.031; | $z_{w0V}$ = 108 mm, | $M^2_V$ = 1.05 |

Excellent beam quality and small difference of the beam waist sizes permits to couple the EC-QCL beam into the built-up cavity with not < 80% efficiency and the strongest high order mode intensity not more than 5% assuming that the cavity mode size is in the middle between the two values for the H and V – directions

## Experimental Setup



QEPAS sensor responsivity was measured with a 1.39 µm 20mW DFB laser by comparison of a WMS signal and direct absorption for a distance of 91.4 cm.
The responsivity value of 11.3 V/(cm$^{-1}$•W) and the QEPAS sensor output voltage noise of 100 nV/√Hz correspond to a QEPAS sensor intrinsic detectivity of 8.9 × $10^{-9}$cm$^{-1}$•W/√Hz using non-optimum QEPAS resonator tubes which resulted in ~ 4 times lower than the best performance possible for a QEPAS sensor.

## Performance of DR QEPAS from $H_2O$ Measurements in Laboratory Air

With the cavity open to ambient laboratory air it was possible to sequentially lock the cavity to the cavity modes for an unlimited period of time and thus obtain an absorption spectrum of ambient air. It was not possible to scan the laser continuously due to some technical features of our setup. The signal from an atmospheric water line at 948.26 cm$^{-1}$ was equal to 7.1 mV, which agrees with our measured responsivity and intra-cavity power. The sensitivity of this measurement corresponds to 1.9 × $10^{-9}$cm$^{-1}$/√Hz and is equivalent to a $NH_3$ sensitivity of 0.05 ppt/√Hz.

## Results and Conclusions

- A DR-QEPAS $NH_3$ sensor prototype based on an EC-QCL operating in the 10.34 µm range was designed, built and tested
- With 52 mW of QCL output power, 4.75 W was achieved with a built-up cavity, which corresponds to a power enhancement of 91 times.
- A QEPAS sensitivity increase proportional to the power increase was achieved, which resulted in DR-QEPAS sensitivity of 1.9 × $10^{-9}$ cm$^{-1}$/√Hz.
- A sensitivity increase of ~4 times should be possible by optimization of the DR-QEPAS sensor.

## References

1. M. Selker, A. Riddle, B. Paldus, "System and Method for Gas Analysis Using Doubly Resonant Photo-Acoustic Spectroscopy", US Patent 7263871, 10/07/2005
2. A. Kachanov, S. Koulikov, "Method and Apparatus for the Photo-acoustic Identification and Quantification of Analyte Species in a Gaseous or Liquid Medium" US Patent Application 12/660,614, 03/02/2010
3. A. Kachanov, S Koulikov, A. Kosterev, and F.K. Tittel, "Ultra-Sensitive QEPAS in a power buildup cavity with a low-power diode laser, Poster presentation, MIRTHE Princeton Site Visit, 2009

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