

## Highly sensitive and rugged gas optical detection via interferometric cavity- assisted photothermal spectroscopy

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Daide Pinto

daide.pinto@tuwien.ac.at



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# Outline

1. Motivation – Gas sensing
2. Laser spectroscopy for gas sensing: ICAPS
3. Experimental Setup & Results
4. Conclusion & Outlook

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## 1. Industrial Process Control

Detection of leaks

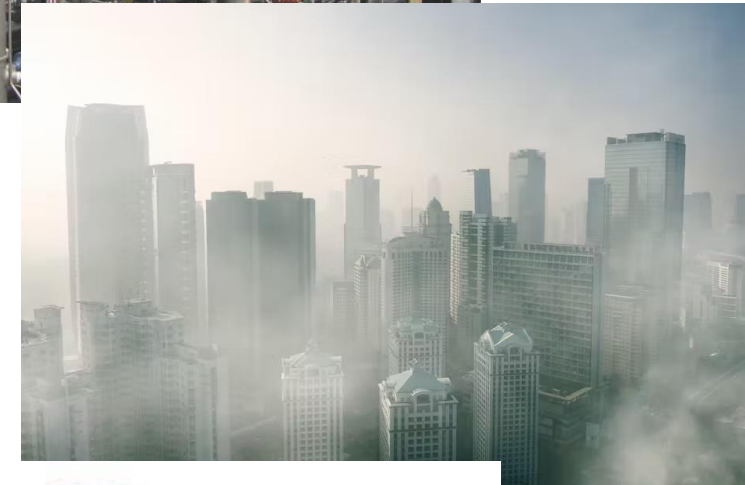
In-line/on-line monitoring



## 2. Environmental Monitoring

Greenhouse gases monitoring

Detection of toxic gases and pollutant



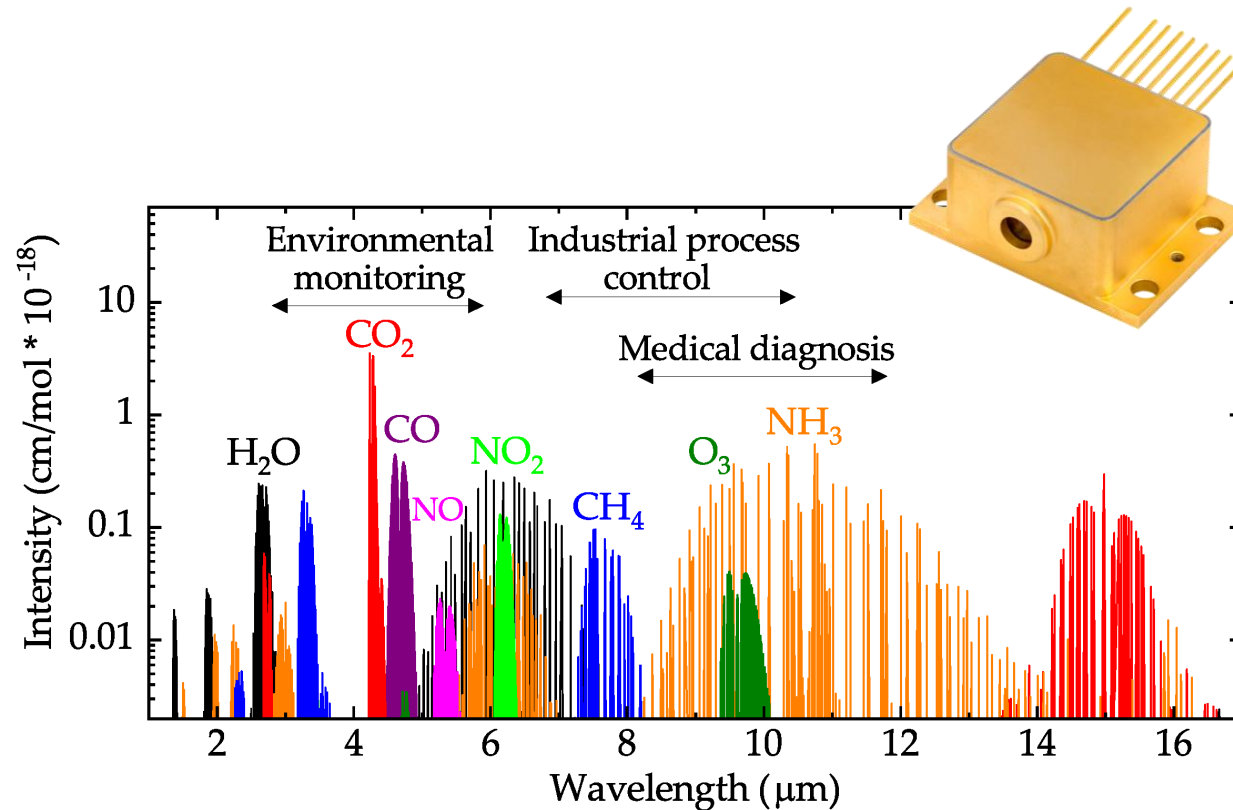
## 3. Health and Life Science

Breath analysis for early-stage disease detection



## Why laser spectroscopy?

- High selectivity:  
roto-vibrational absorption lines  
can be targeted selectively to  
avoid cross-talking
- High sensitivity:  
many approaches are capable to  
achieve sub-ppb detection limits
- High speed measurement
- No sample treatment needed

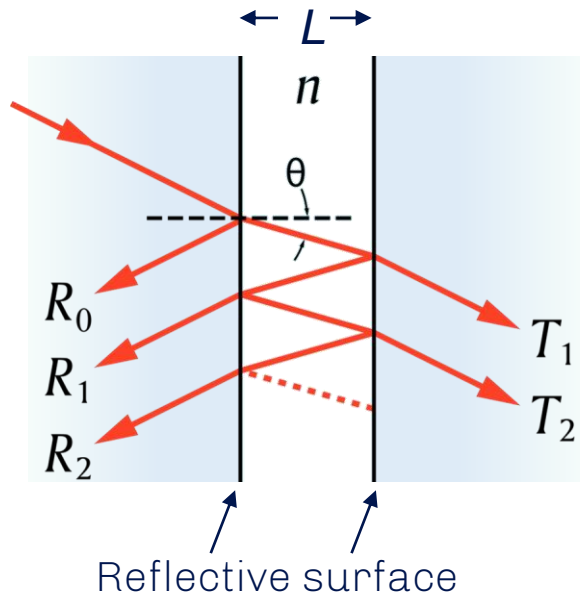


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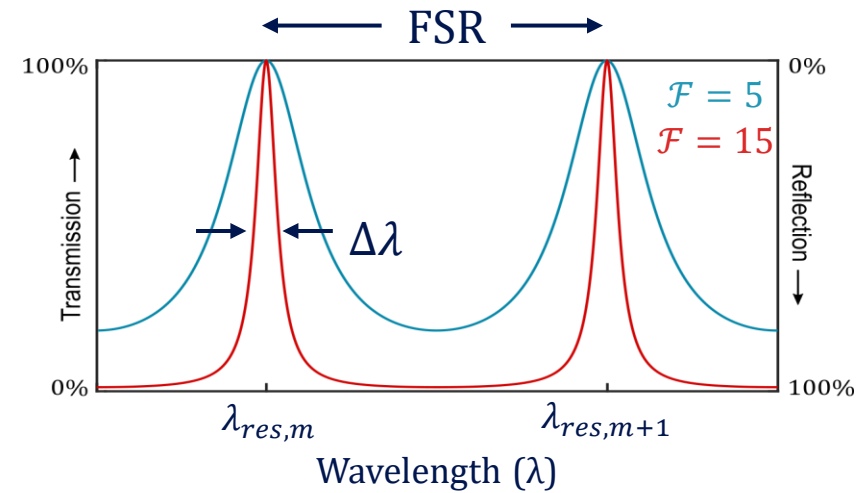
Direct absorption – TDLAS

Indirect absorption – PAS, PTS



$$\mathcal{F} := \frac{\text{FSR}}{\Delta\lambda} = \frac{\pi\sqrt{R}}{1-R}$$

## Interferometer Transfer Function

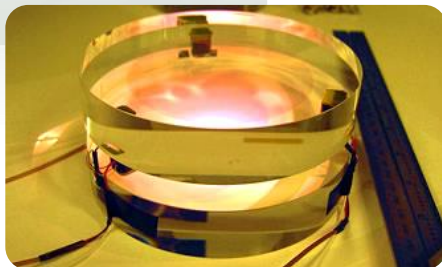
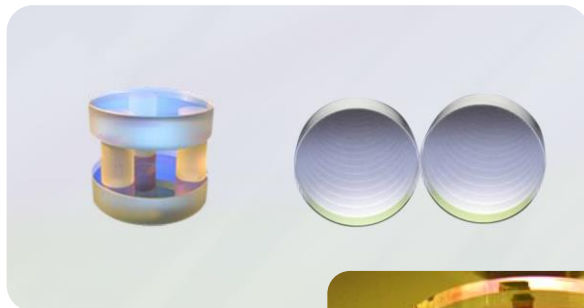


Reflected intensity:

$$I_R = I_0 \frac{4R \sin^2(\varphi)}{(1-R)^2 + 4R \sin^2(\varphi)}$$

$$m\lambda_{res,m} = 2nL \cos \theta$$

- $I_R$  ..... Reflected intensity
- $I_0$  ..... Incident intensity
- $R$  ..... Mirror reflectivity
- $\lambda_{res}$  ..... Resonance wavelength
- $n$  ..... Medium refractive index
- $m$  ..... Integer number

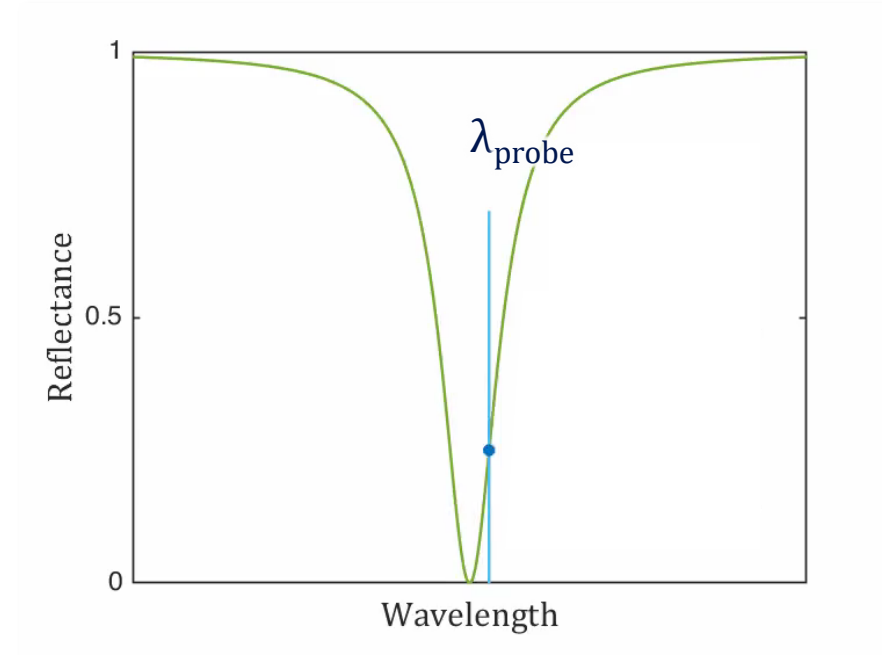
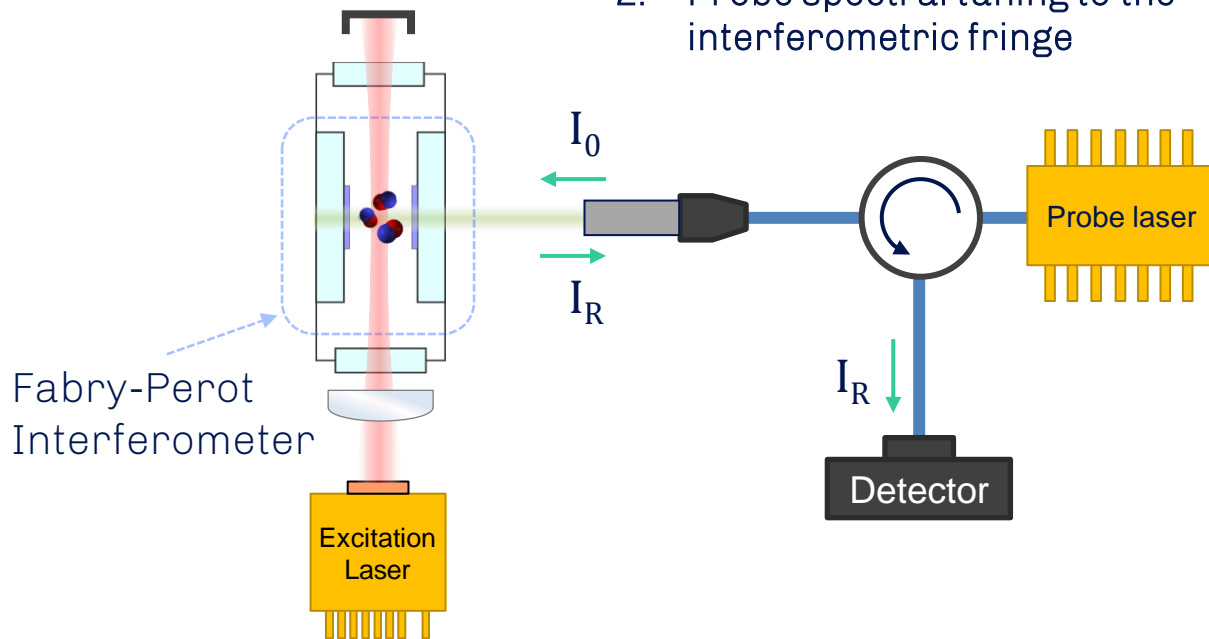




## ICAPS principle

Fundamental conditions:

1. Spatial overlap of probe and excitation beams
2. Probe spectral tuning to the interferometric fringe



On the side-fringe (inflection point):

1.

$\delta n$

Transduced linearly as

$\delta I_R$

2.

The higher the Finesse, the higher will be the sensitivity towards photothermal effect

Clausius-Mossotti approximation: 
$$\delta n = -\frac{n_0 - 1}{T_{abs}} \delta T$$

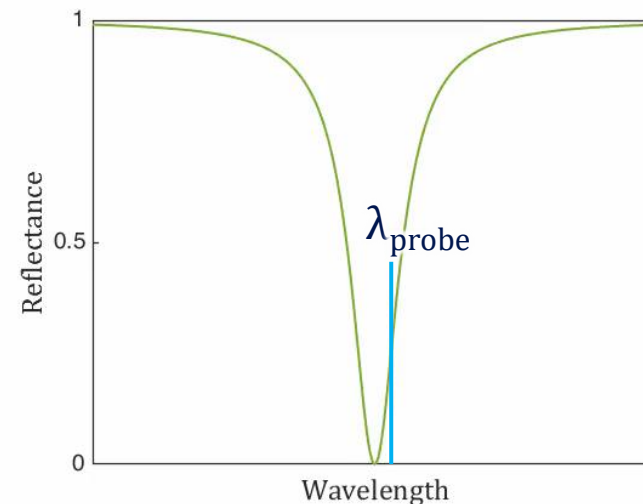
[1] D. Pinto, J.P. Waclawek, S. Lindner, H. Moser, G. Ricchiuti, B. Lendl, Wavelength modulated diode probe laser for an interferometric cavity-assisted photothermal spectroscopy gas sensor, Sensors and Actuators B: Chemical. 377 (2023) 133061. doi:10.1016/j.snb.2022.133061.

- In real-case scenarios, many parameters affect the interferometer stability:

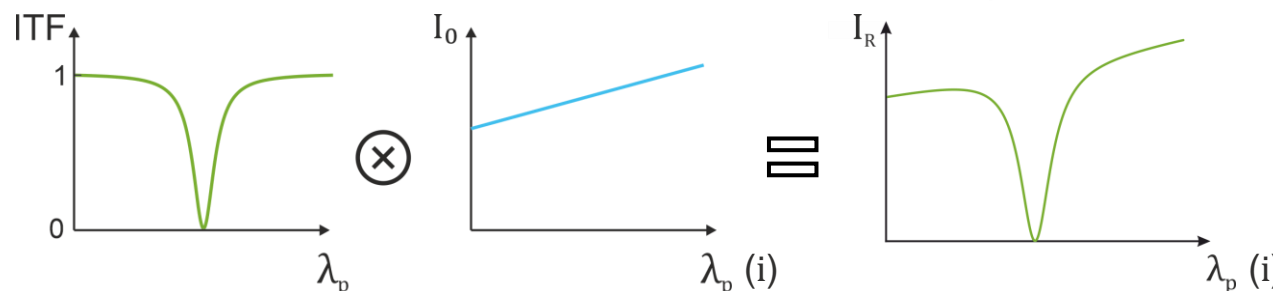
- Temperature
- Pressure
- Gas composition



Affect the refractive index

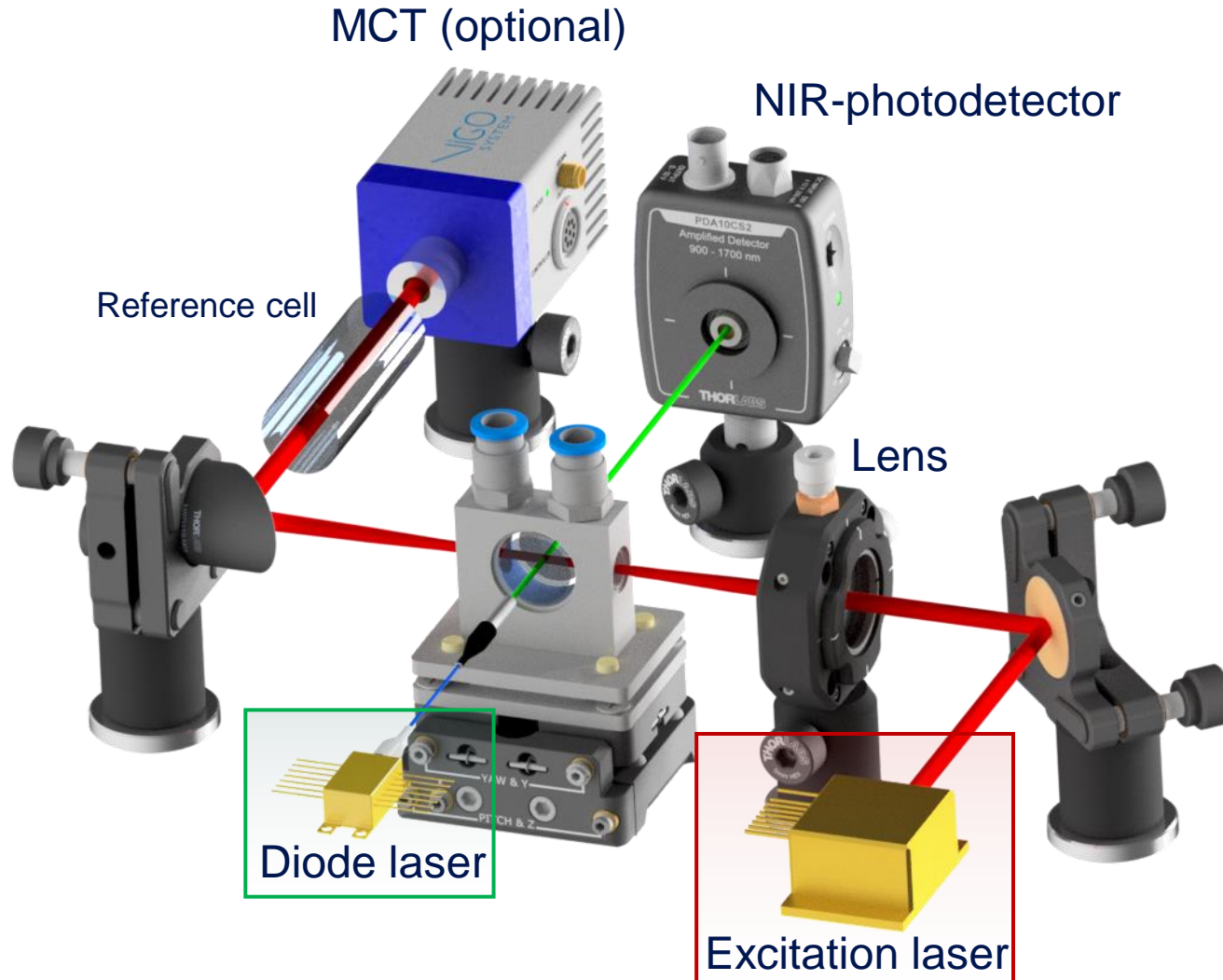


- ! Probe laser must be locked to the inflection point to compensate for drifts
- Diode lasers are capable of fast wavelength tuning by acting on the bias current. However, also the emitted optical intensity ( $I_0$ ) changes as a function of the current!



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### Excitation laser:

- CW-DFB-QCL @ 5.26  $\mu\text{m}$  ( $1900\text{ cm}^{-1}$ )
- Optical Power 30 mW

### Probe diode laser:

- CW-DFB-DL telecom @ 1552 nm

### NIR detector

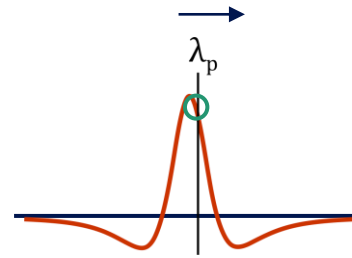
Shift in detection from MID-IR to NIR, where photodetectors are cheaper and perform better.

## 2f zero-crossing locking

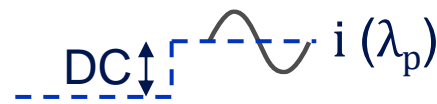
Current dithering of probe



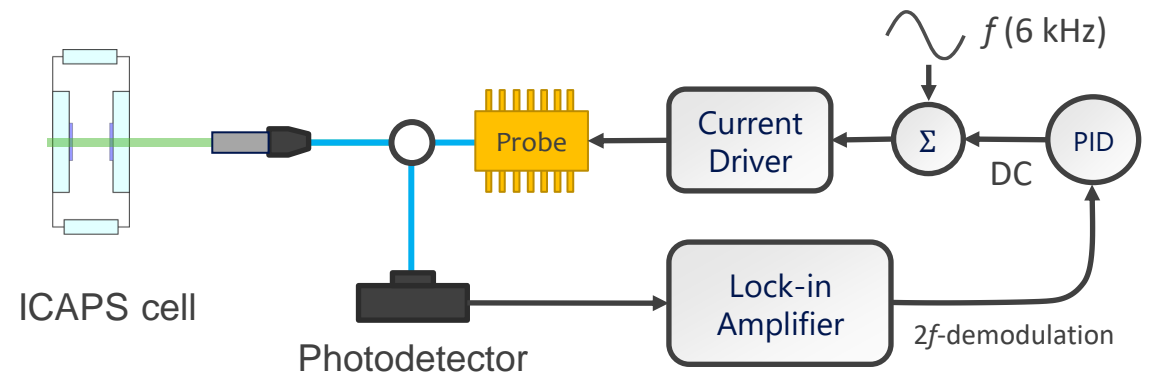
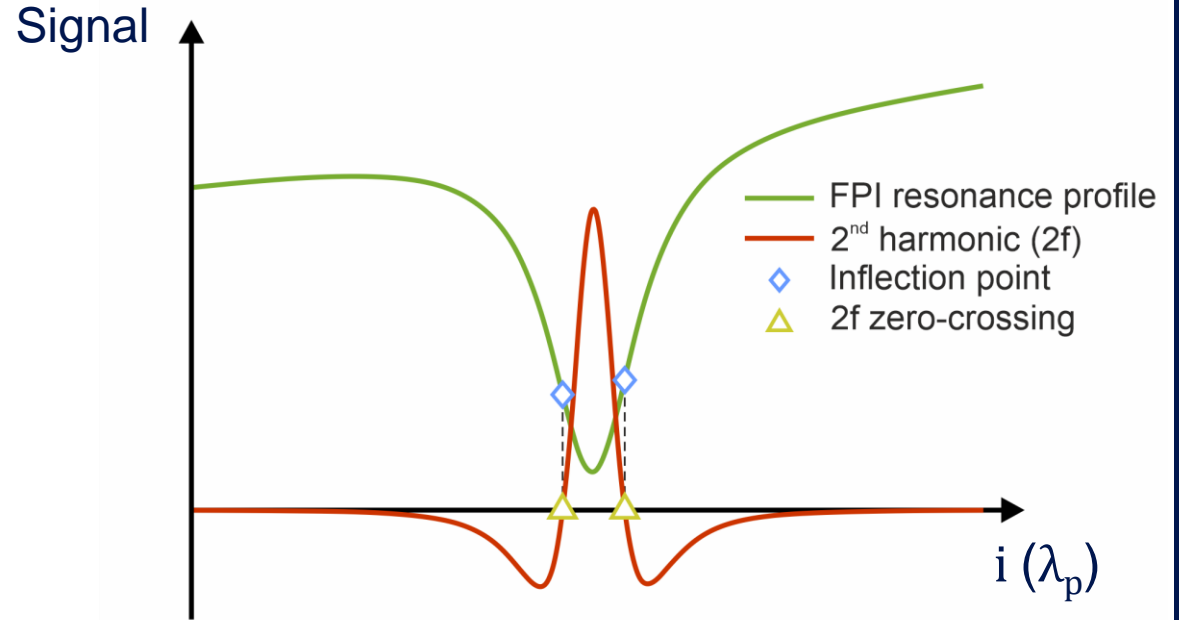
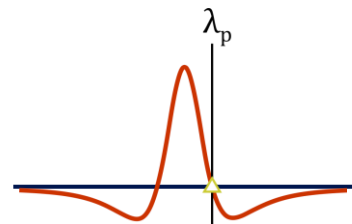
2<sup>nd</sup> harmonic signal used as error signal

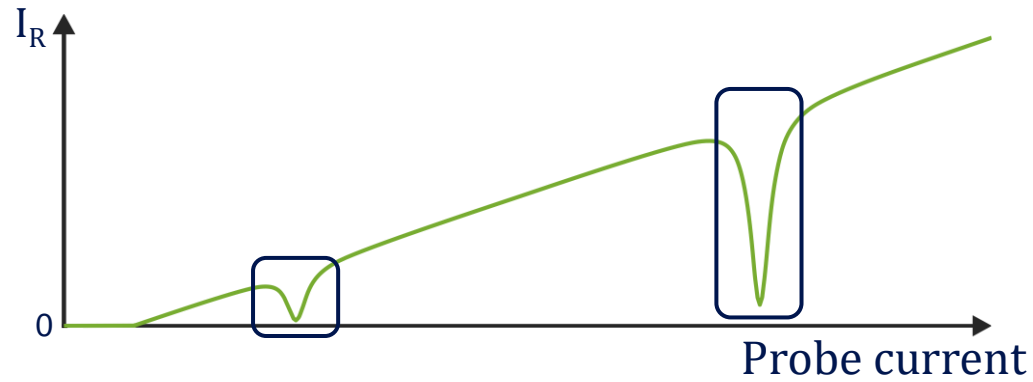


PID controller acts on probe DC current



2<sup>nd</sup> harmonic signal kept to zero-crossing

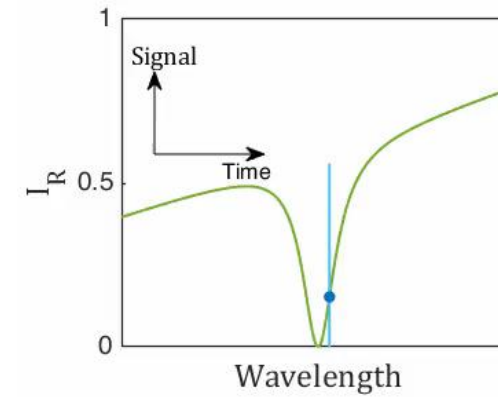




System sensitivity depends upon:

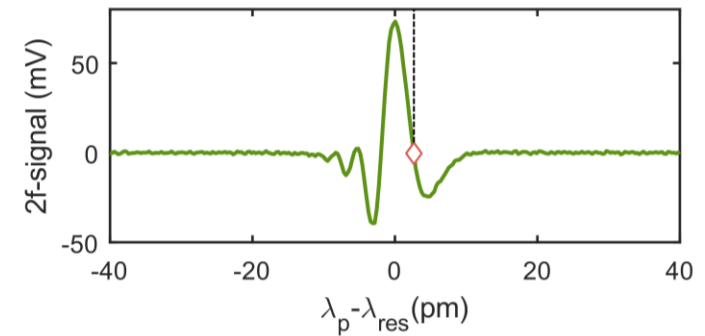
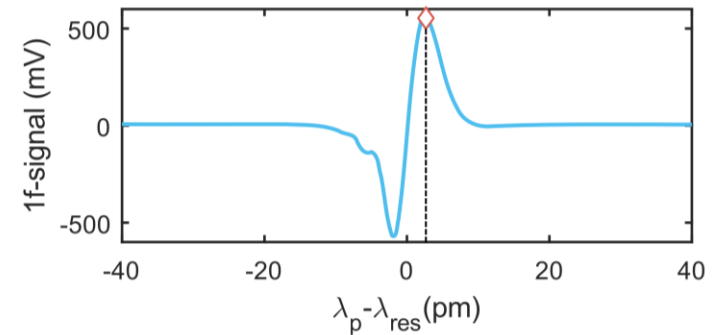
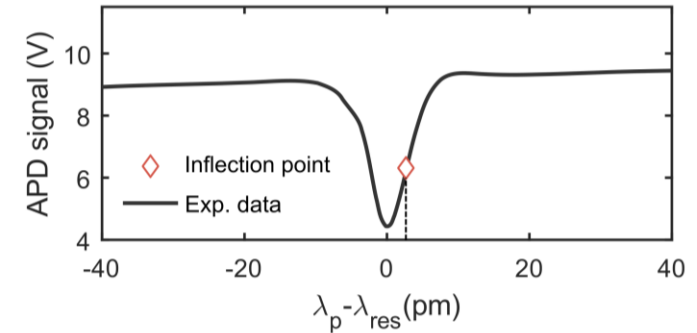
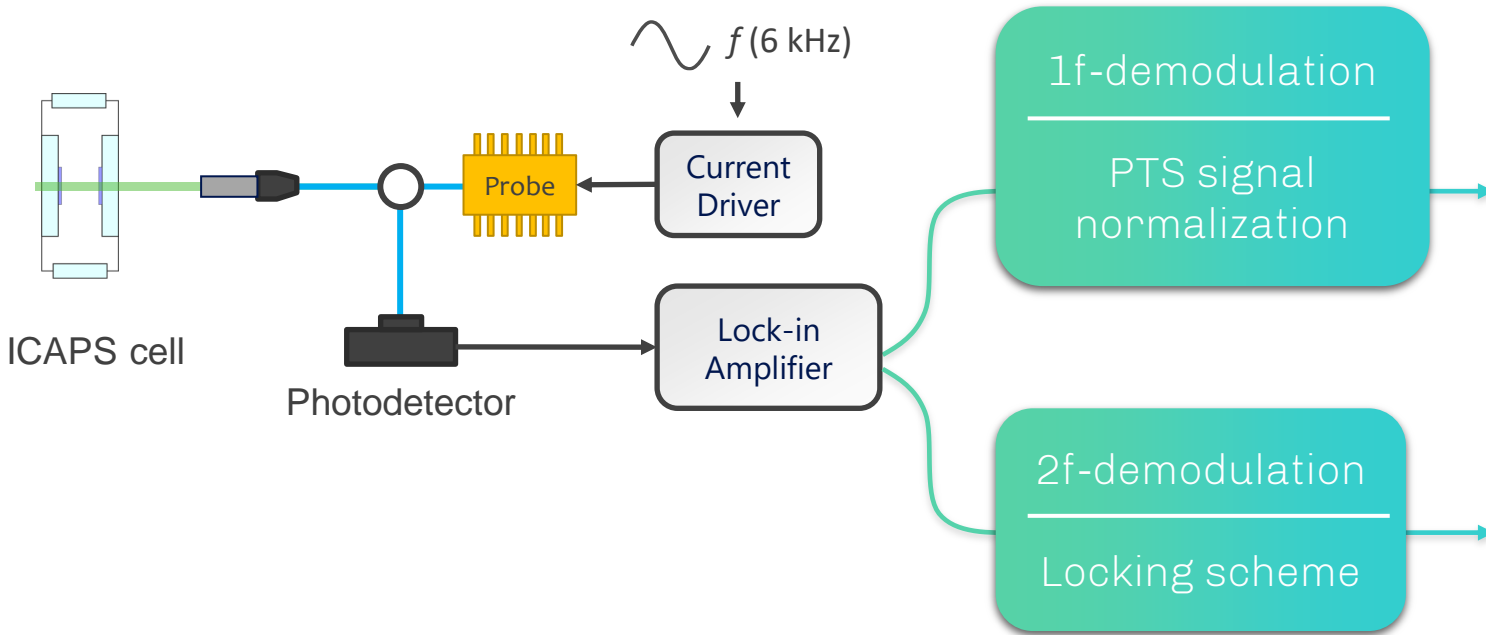
1. incident intensity
2. interferometric fringe quality

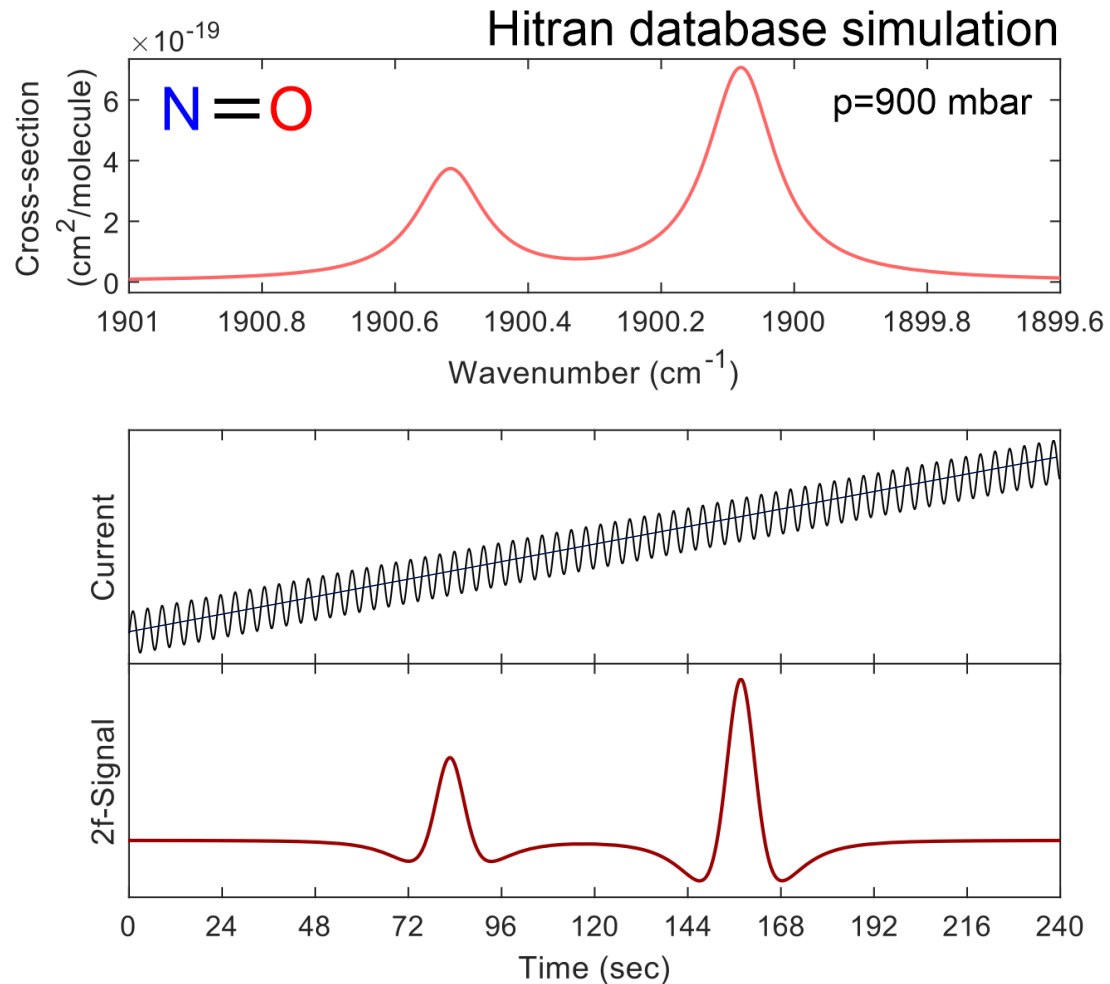
- ! Probe wavelength is modulated for locking purposes



Real-time investigation of the interferometer

## Summary of the probe line





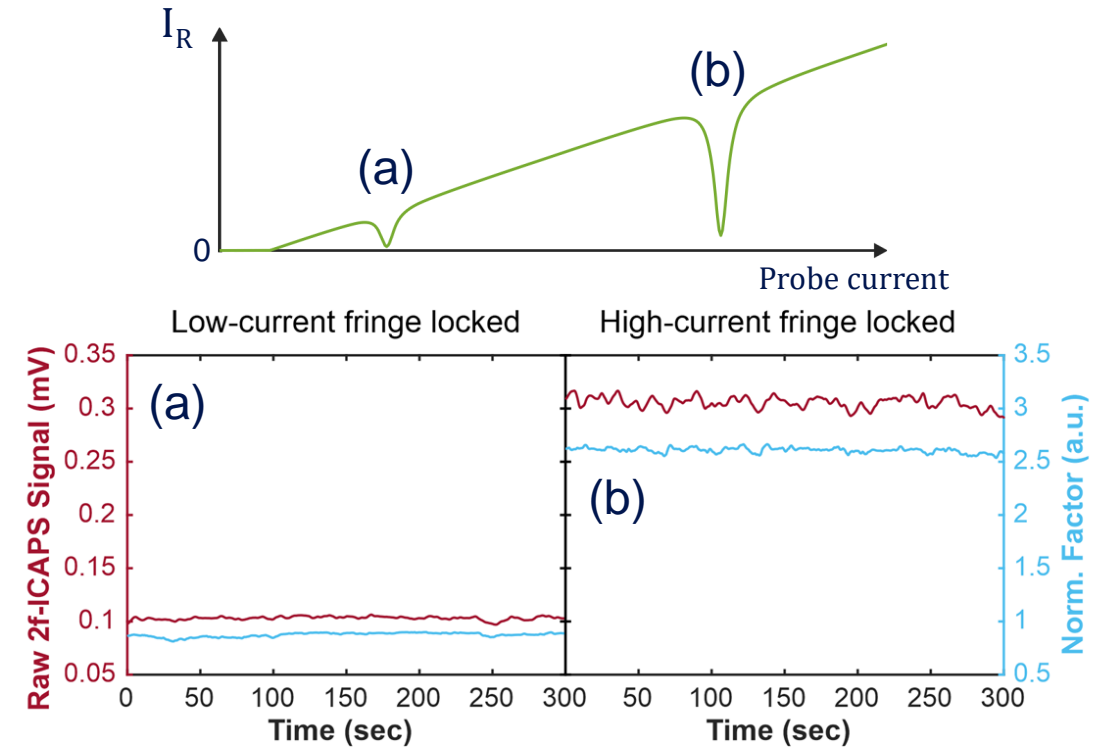
QCL current is modulated with a sine wave ( $f_{exc}$ ) and scanned across the analyte absorption line

The signal is demodulated at the 2<sup>nd</sup> harmonic ( $2f_{exc}$ )

- ✓ Background free technique
- ✓ Peak value stores the analytical information

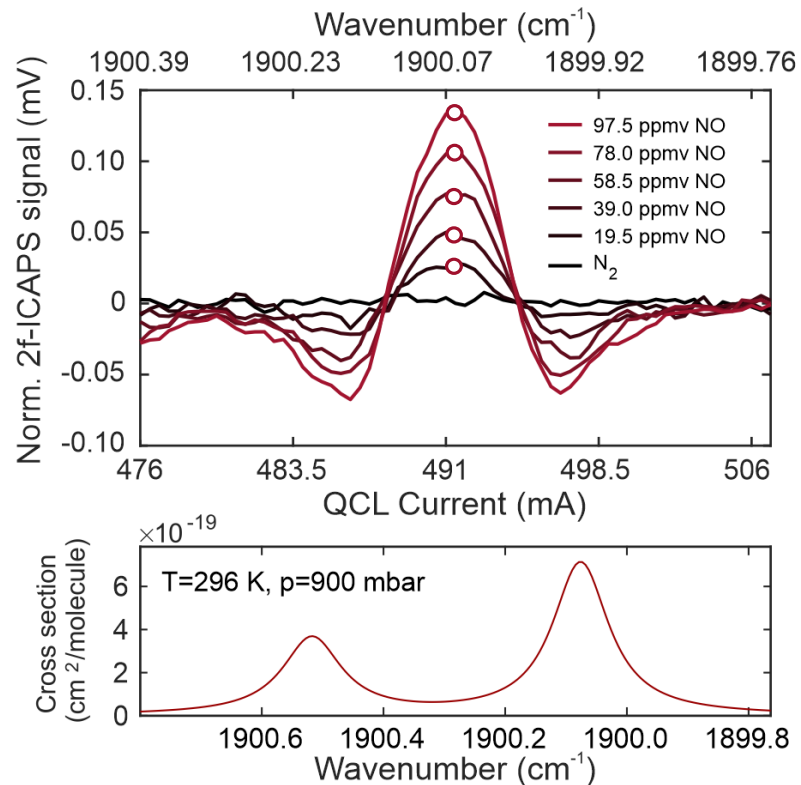


1. A constant PTS signal was generated (97.5 ppm of NO/N<sub>2</sub>)
2. The PTS signal was transduced at low-current and high-current fringes
3. The PTS signal is normalized to the probe 1f-demodulated signal (ratio of red and blue curves)
4. Normalized signal doesn't depend upon:
  - Interferometer quality (aging)
  - Varying optical intensity



— Photothermal signal  
 — Normalization factor } Ratio only depends upon gas concentration

## Spectral Scan



- ✓ Excellent linearity ( $R^2 = 0.999$ ) in the whole concentration range

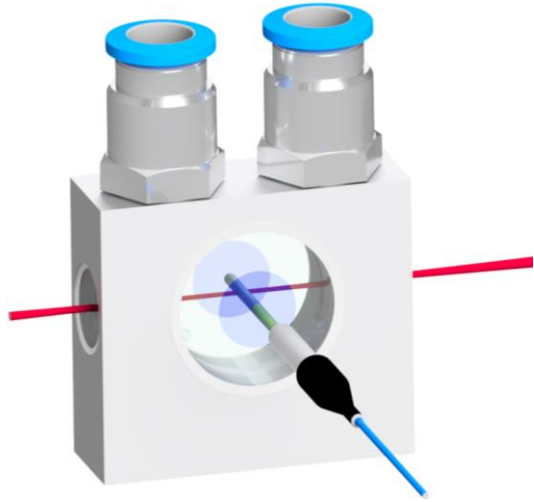
- ✓  $NEC = \frac{1\sigma_{noise}}{\text{sensitivity}} \approx 2 \text{ ppm}$

- ✓  $NNEA = \frac{P\alpha_{min}}{\sqrt{\Delta f}} \sim 3 \cdot 10^{-6} \text{ W cm}^{-1} \text{ Hz}^{-\frac{1}{2}}$   
( $\alpha_{min} \approx 3 \cdot 10^{-5} \text{ cm}^{-1}$ )

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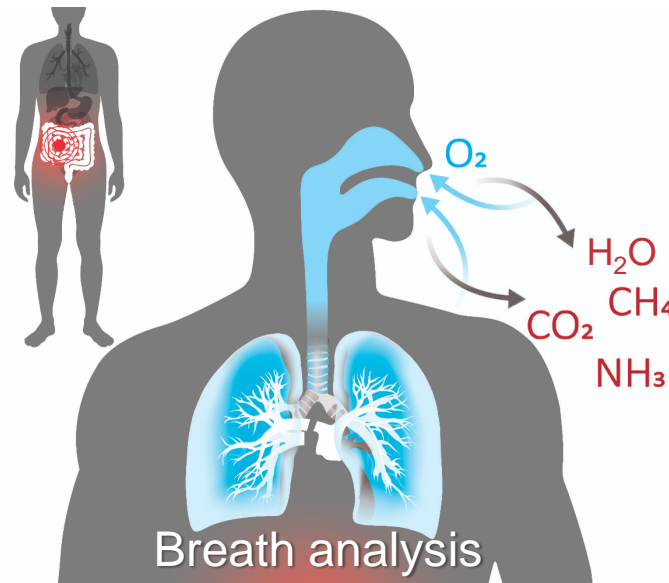
## Advantages over other techniques



- ✓ Reduced sensing volume: design of portable and rugged sensors
- ✓ Modulation frequency can be freely tuned: fundamental for slow relaxing gases
- ✓ Open for many applications!



Sensing on drone applications

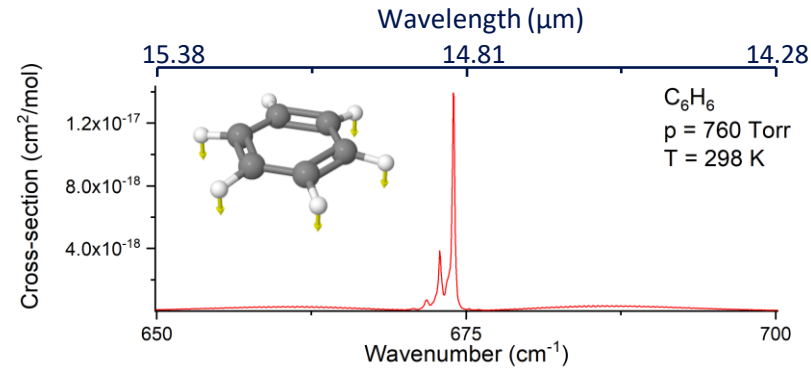
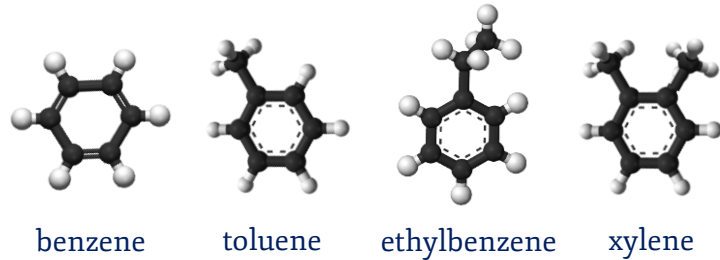


Breath analysis



Industrial & environmental monitoring

- Long-wavelength QCLs for BTEX detection



Optical Sensing using  
Advanced Photo-Induced Effects

**PTAPHI**

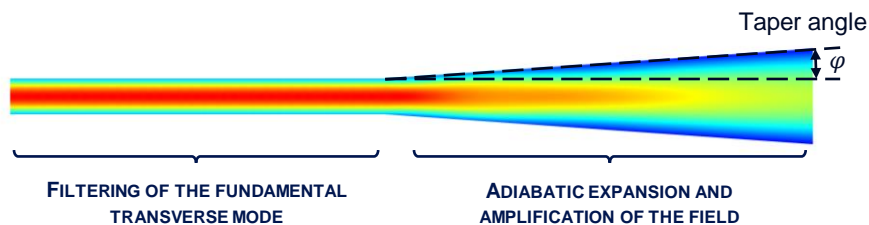
A European Double Doctorate Training Network

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- Tapered QCLs for improved optical power output

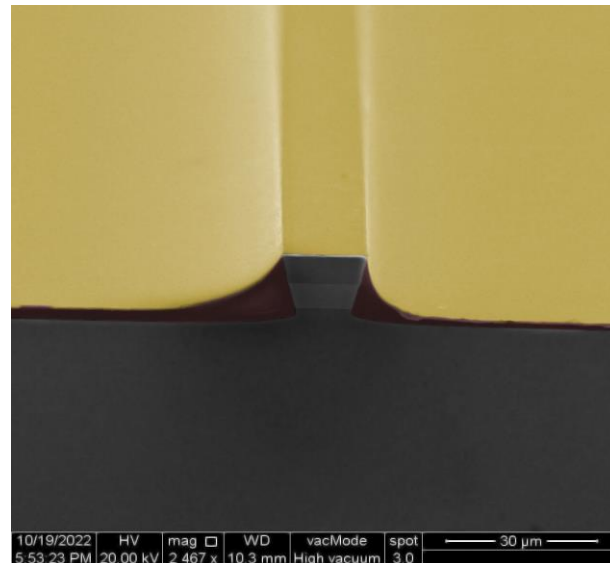
$$PTS \text{ signal} \propto \frac{P_{exc} \alpha}{fV}$$



POSTER 12430-90

Tapered quantum cascade lasers in the long-wavelength mid-infrared region

Mercoledì, Febbraio 1 • 18:00 - 20:00  
Moscone Center, Level 2 West



# Thank you for your attention



Special thanks to the ones contributing to this work:

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- Stefan Lindner
- Giovanna Ricchiuti
- Bernhard Lendl

And the CAVS and Nanomir Groups



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