SWISS PHOTONICS

Zurich University of Applied Sciences

zh aw School of Engineering

From THz to X-ray - Inventing the Future

Progress in NIR spectroscopy and its industrial applications

ETH, 31.03.2016

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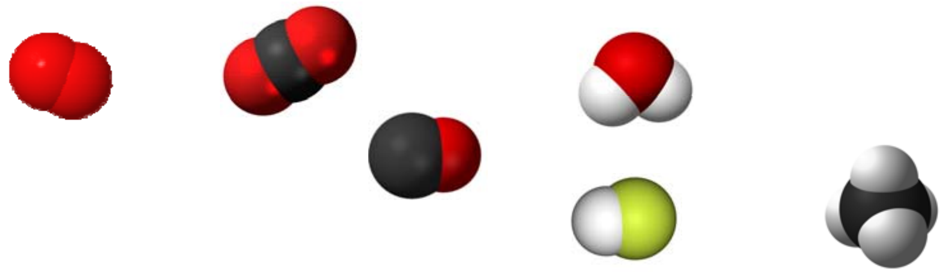
Outline



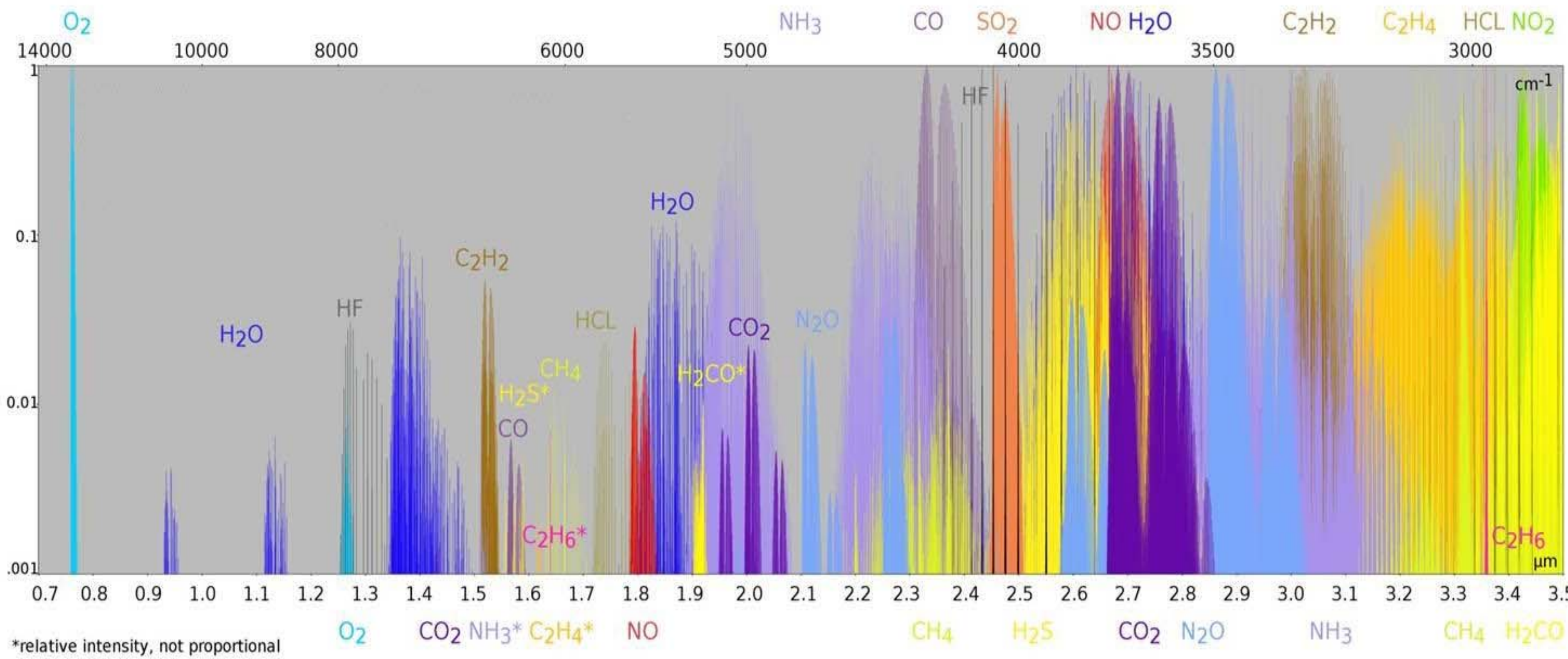
- NIR spectroscopy for gas sensing
- Tunable Diode Laser Absorption Spectroscopy theory and practice
- New sensititvity enhancement strategies
- Tunable Diode Laser Absorption Spectroscopy in industry
- Outlook

http://www.spectrasensors.com

Courtesy of Mettler-Toledo

Spectroscopy in the NIR

Gas sensing in the NIR:



http://www.nanoplus.com

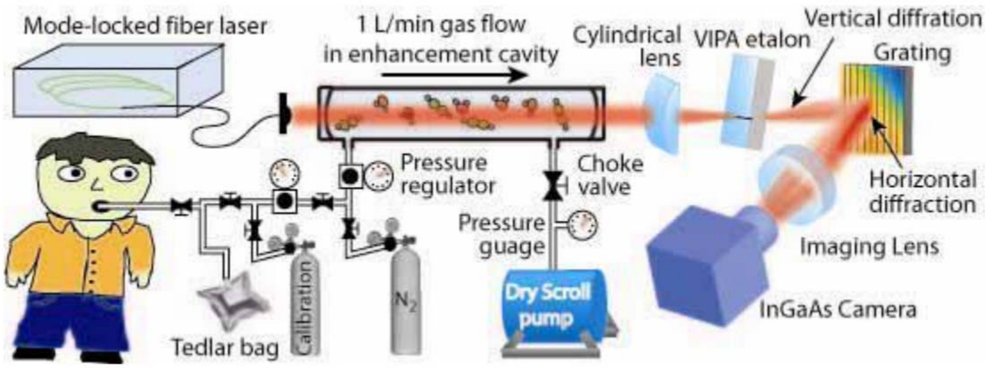
Why Gas Sensing?

Typical applications (NIR,MIR):

- **Industrial**: process control, combustion, safety
  O_2, CO, CO_2, H_2O, H_2S, HCl, HF, …
- **Environmental**: air pollution, atmosphere research, detection of toxic gases
  NOx, CH_4, CO, CO_2, H_2O, …
- **Diagnostic**: breath analysis, biomedicine
  O_2, CO, CO_2, …

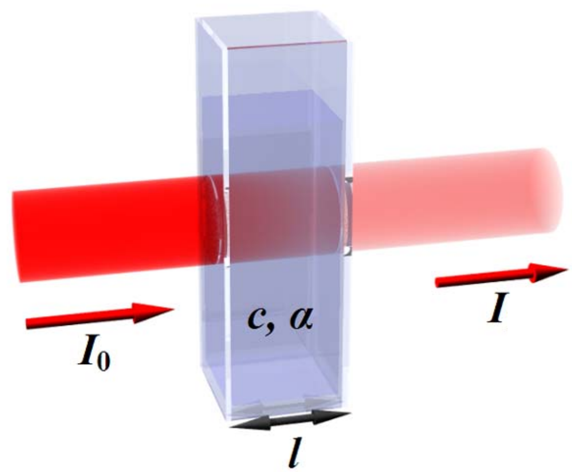
Courtesy of Mettler-Toledo

https://es.licor.com/env/products/gas_analysis/LI-7700/



M.J. Thorpe *et al.*, Opt. Express (2008), 16, 2387–2397

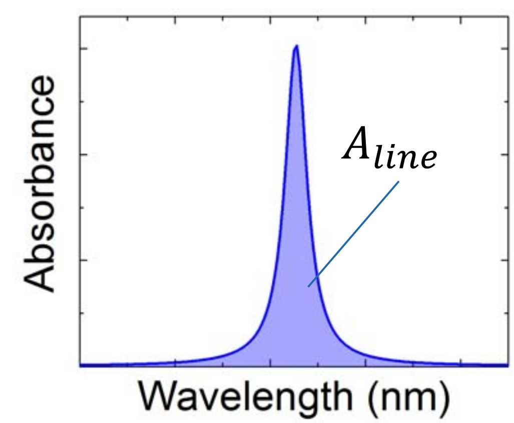
Tunable Diode Laser Absorption Spectroscopy



Beer-Lambert law: $I(\nu) = I_0(\nu) \cdot e^{-A(\nu)}$

Absorbance $A(\nu) = S_T \cdot \mathrm{g}(\nu - \nu_0) \cdot N \cdot l$

I: Intensity after passing through the gas
I_0: Intensity of the incident light
S_T: Line strength
g: Normalized line shape
N: Molecular concentration
l: Optical path length



Line Area $A_{line} = \int_{-\infty}^{+\infty} A(\nu)\, d\,\nu = S_T \cdot N \cdot l$

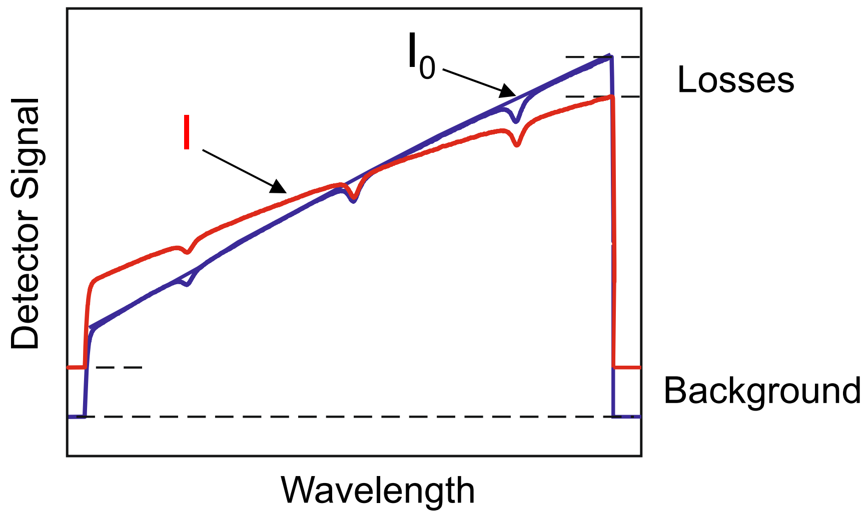
Direct Absorption Spectroscopy in Practice

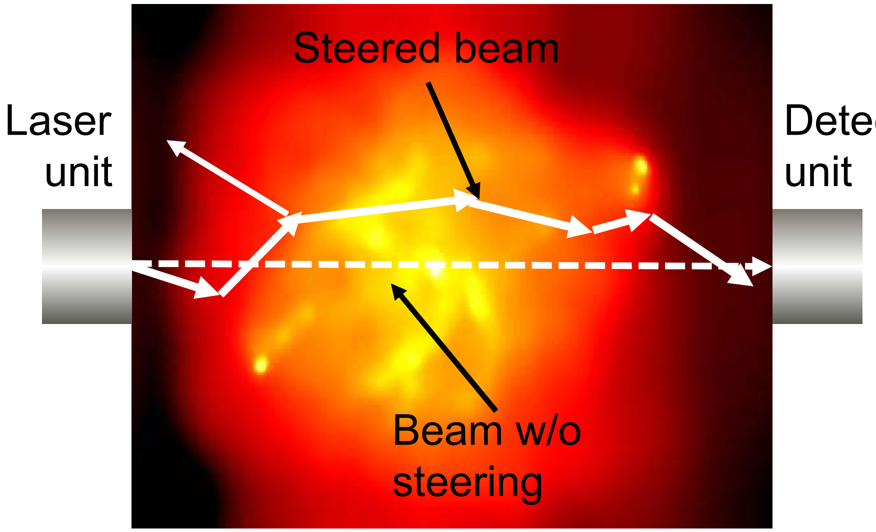
Absorption profile depends on:

- temperature
- pressure
- matrix (broadening effects)

Undesired effects:

- Interferometric effects
- Instrumental drift
- Scattering/absorption from dust
- Beam steering
- Background light





Direct Absorption Spectroscopy in Practice: Interferometric Effects

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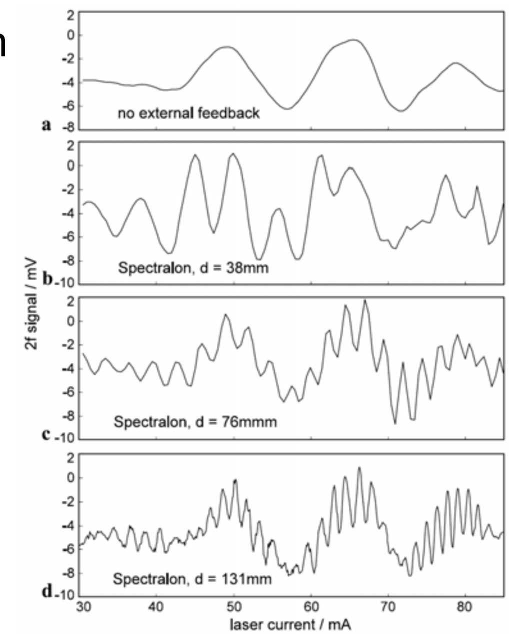
Causes:

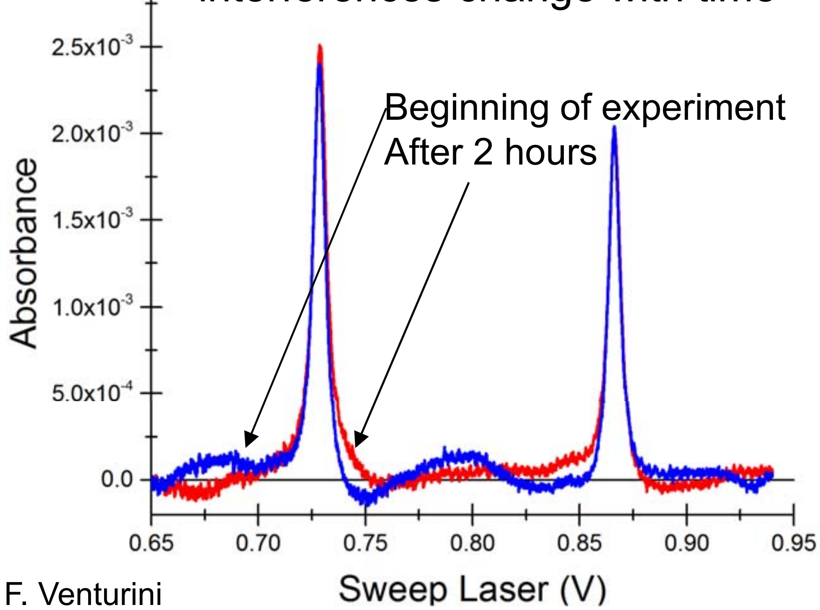
- Fabry Perot etalons
- Self-mixing
- Diffuse reflection (dust, dirt)

DFB laser @ 1686 nm with feedback from a diffuse reflector (Spectralon™)



D. Masiyano et al., Appl Phys B (2009)

VCSEL @ 760nm, O_2 measurement: Fabry Perot and self mixing interferences change with time



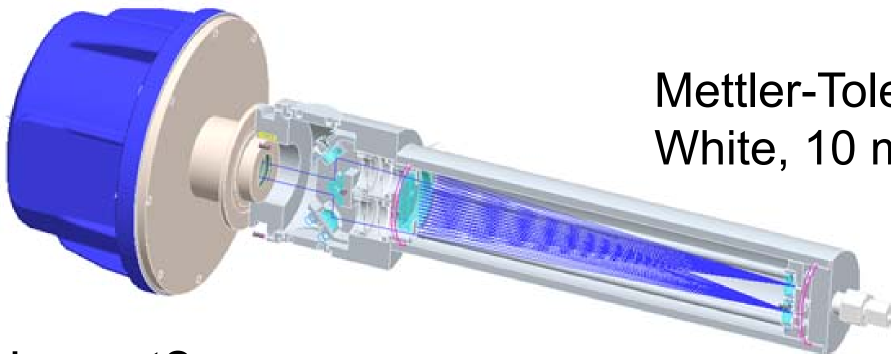
Common strategies:

- Wedging, AR coating
- Balance detection
- Filtering
- Mechanical modulation
- Optical isolator

Strategies for Improvement of Sensitivity

- Trade off between required sensitivity and system complexity and operational costs

- Current industrial solutions: multipass cells (Herriott, White, circular …)



Mettler-Toledo
White, 10 m

Courtesy of Mettler-Toledo

Neo Monitors
Herriott cell, 11.4 m

http://www.norskanalyse.no/

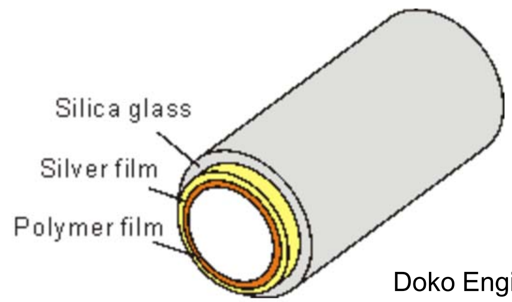
- What is next?
    - Hollow core fibers
    - GASMAS
    - CRDS
    - Frequency comb
    - ….

Courtesy of Mettler-Toledo

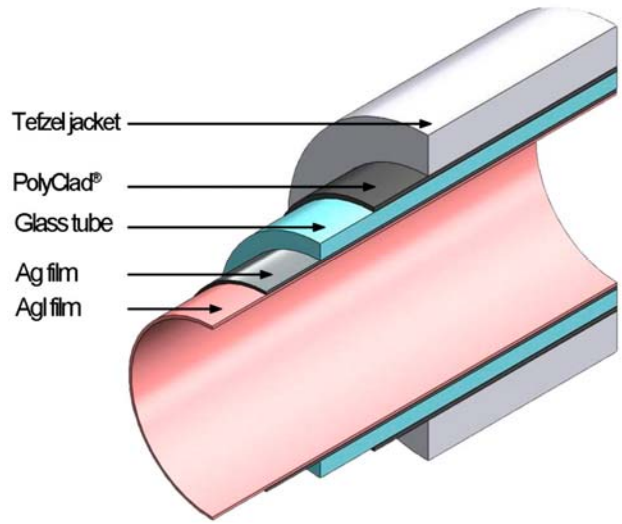
Hollow Core Fibers

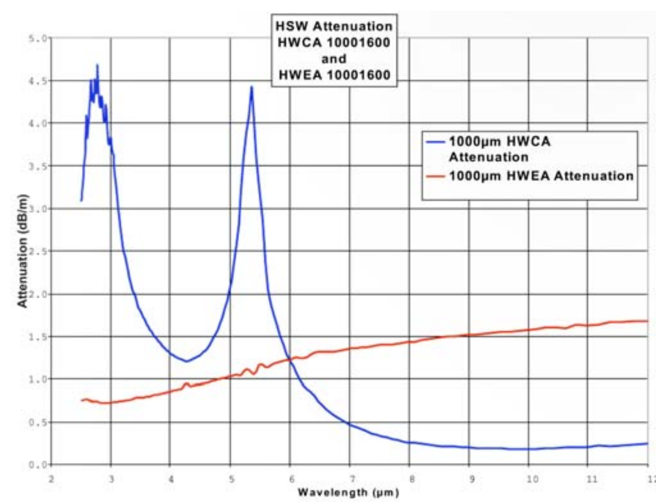
Advantages:

- Coiling enables long optical path length with small physical dimensions
- Low sampling volume



Doko Engineering, www.do-ko.jp





www.polymicro.com

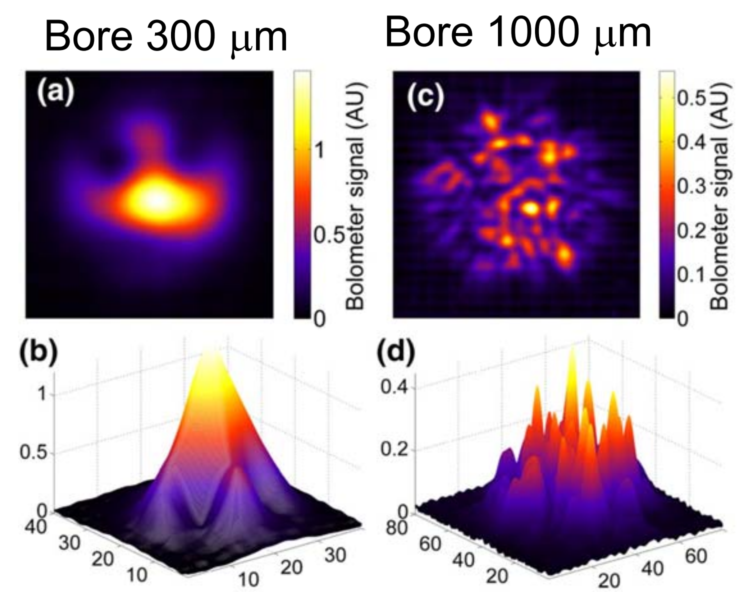
Challenges:

- Interferences
- Bending losses
- Gas exchange times

Hollow Core Fibers

Losses:

- Losses depend on bore radius $\sim \frac{1}{r^3}$
- Losses depend on bend radius $\sim \frac{1}{R}$



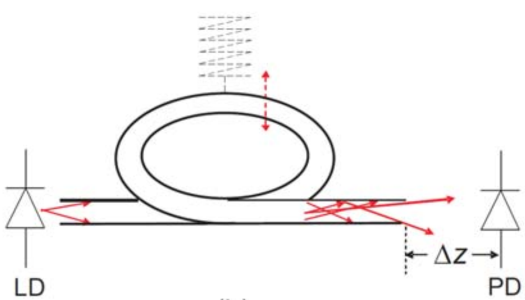
D. Francis *et al.*, Appl. Phys. B (2015) 119:75–86

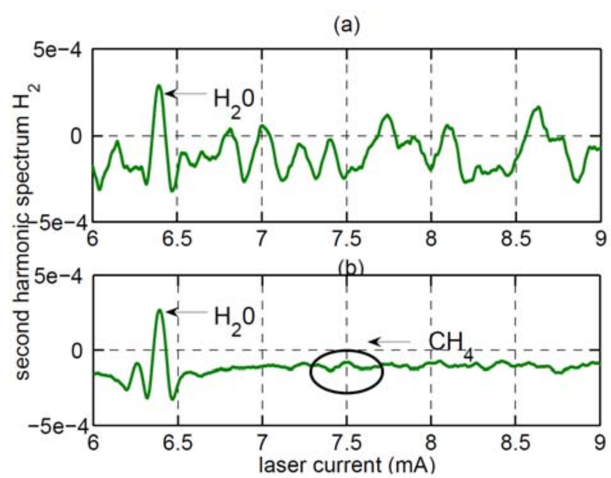
Strategies against interferences

→ Selection of dimensions

→ Suppression through vibrations

→ Post processing (filtering)





Laser @ 2.365 µm
3m fiber filled with air

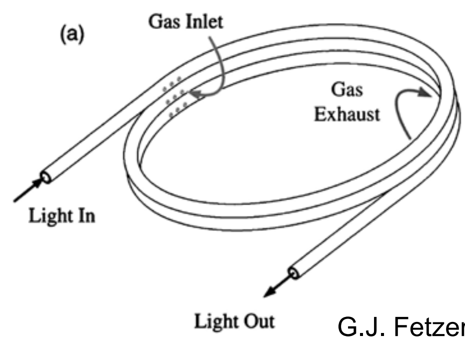
J. Chen, PhD Thesis (2010)

Hollow Core Fibers

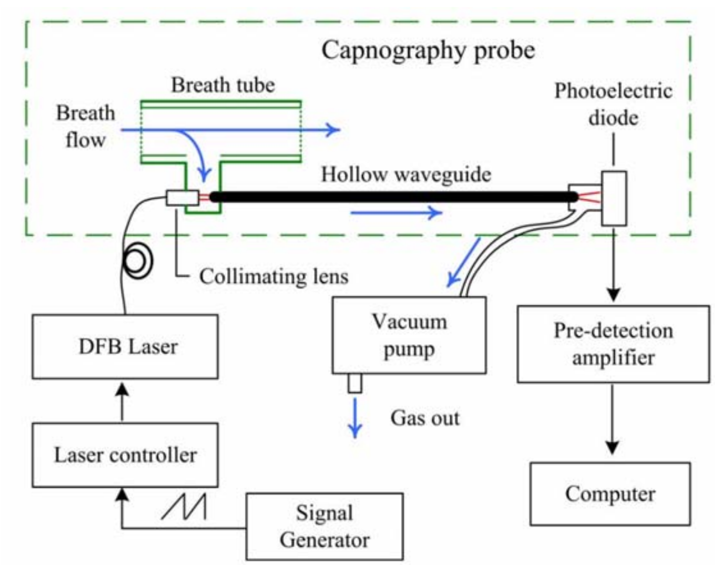
Strategies to improve response time:

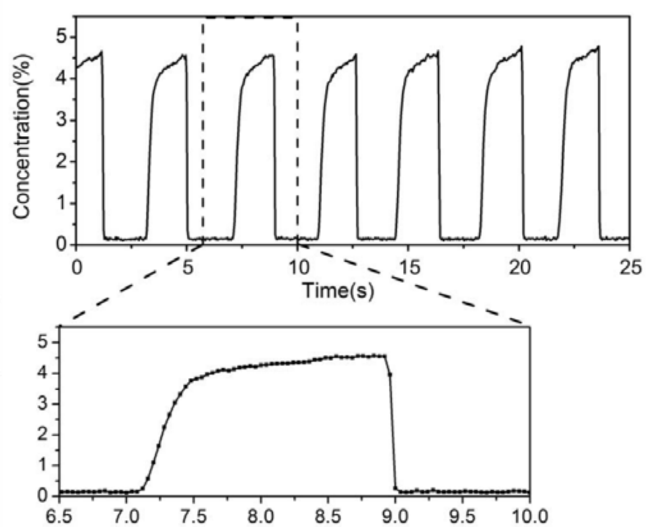
→ Gas inlet (e.g. holes)

→ Differential pressure



G.J. Fetzer, Applied Optics 41 (2002)





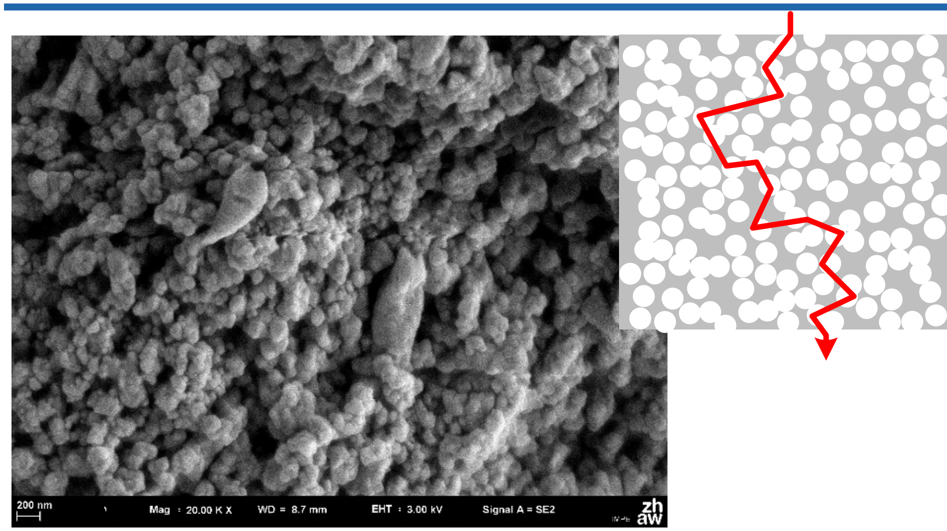
Breath analysis of CO_2

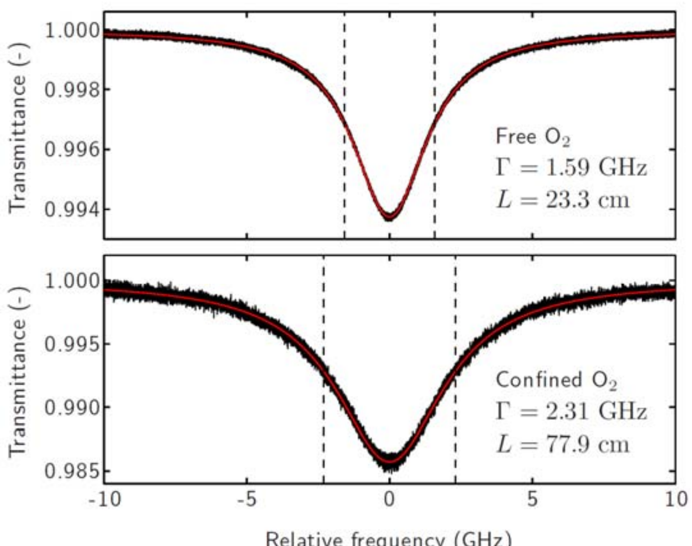
Laser 2.04 µm, 12 cm fiber

Pump: 5 mL/s @ 50 Hz

B.Xiong *et al.*,COL 13 (11) 111201 (2015)

Gas in Scattering Media Absorption Spectroscopy (GASMAS)





T. Svensson, Appl. Phys. Lett. **96**, 021107 (2010)

- Porous media is used as random miniature multipass gas cells

Advantages:

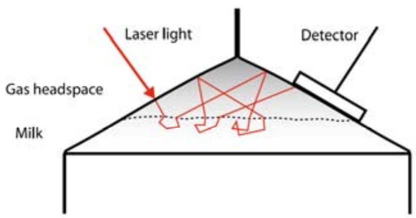
- Very long optical path length with minimal physical dimensions
- Low sampling volume

Challenges:

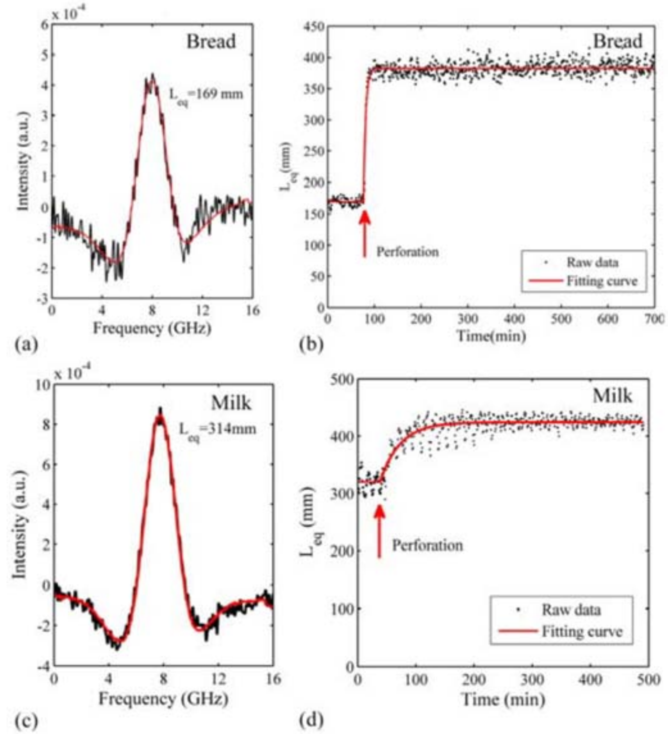
- Effective path length is not known →measurement by TOF or by reference gas $L_{eq} = L_{ref} \frac{A_{abs}}{A_{ref}}$
- Random interferences → Mechanical modulation

GASMAS Applications

- Food monitoring



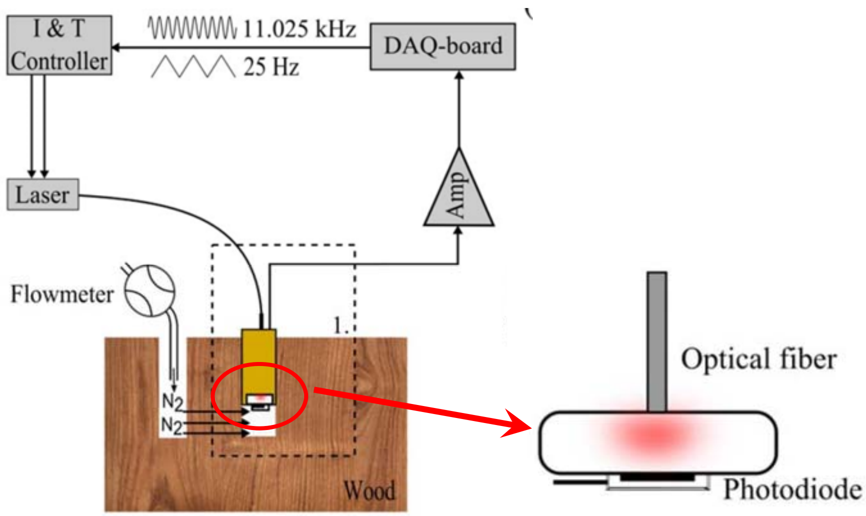
L_{eq} determined from second gas of known concentration, e.g. H_2O vapour

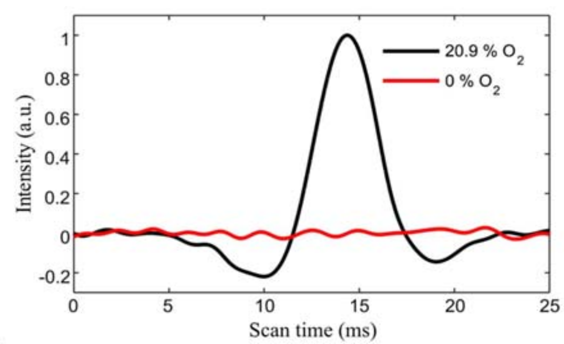


M. Lewander *et al.*, Appl Phys B, 93 619–625 (2008)

S. Svanberg *et al.*, Optics Express 24 (2016)

- Gas diffusion (N_2) measurement in wood





SNR ~ 60

Larsson *et al.*, Applied Optics, 54, 9772 V (2015)

Tunable Diode Laser Absorption Spectroscopy in Industry

ABB

Servomex

Siemens

GE

Neo Monitors

Mettler-Toledo

Sick

Ametek

Yokogawa

Endress+Hauser

…and many more!

Tunable Diode Laser Absorption Spectroscopy in Industry

Growth presence in industrial applications due to:

Performance:

- Sensitivity due to strong absorption lines in NIR/MIR
- Selectivity thanks to narrow laser linewidth
- Fast response times (1s), real-time, continuous measurement
- Multi component capability

Costs:

- Easy maintenance
- Low installation costs
- In-situ, easy integration

Examples of Industrial Installations

In-line and **cross-stack**:

- Direct measurement on
- Harsh envitronment, temperature, dust

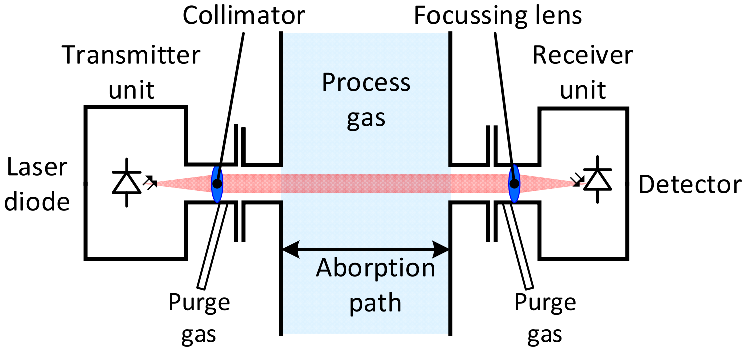
Extractive:

- Sample is extracted by a sampling-system, treated and sent to analyzing system

In-line

Courtesy of Mettler-Toledo

Cross-stack



Tunable Diode Laser Absorption Spectroscopy in Industry

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Process & Safety	Combustion	Storage & Transportation	Environment

- Production (e.g. vi… chloride monom…)
- Flare
- Inerting & Blanketing

- Aggressive environment
- high T (up to 600°C)
- wide P range (mbar to 25bar)
- background gases
- dust

Conclusions and Outlook

Conclusions

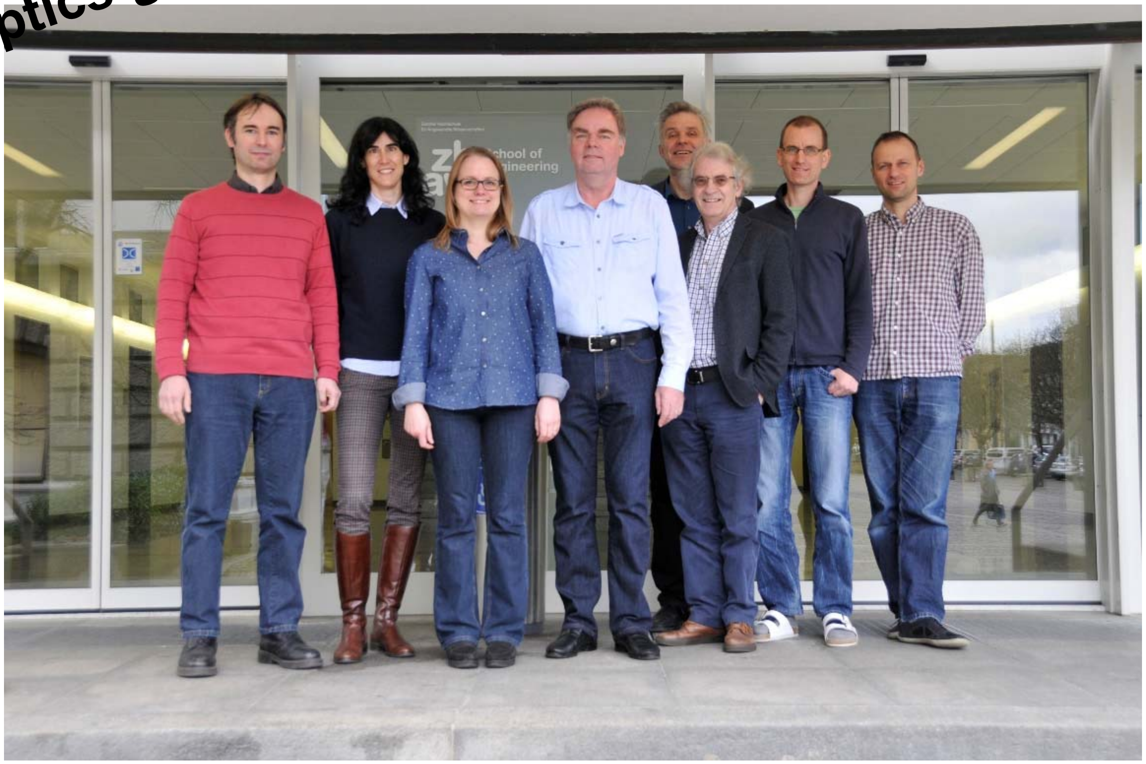
- Tunable Diode Laser Absorption Spectroscopy is a sensitive and robust gas sensing technique
- This method has already a significant market share for industrial applications
- Potential of becoming leading technique

Outlook: What is next?

- Increase sensitivity towards trace sensors
- Compact and easy to install to reduce or eliminate the sampling line and the product and drain volumes
- Possibly expansion to MIR (laser sources, detectors)
- *Laser with broad tuning range for multiparameter detection*

Thank you!

Applied optics group



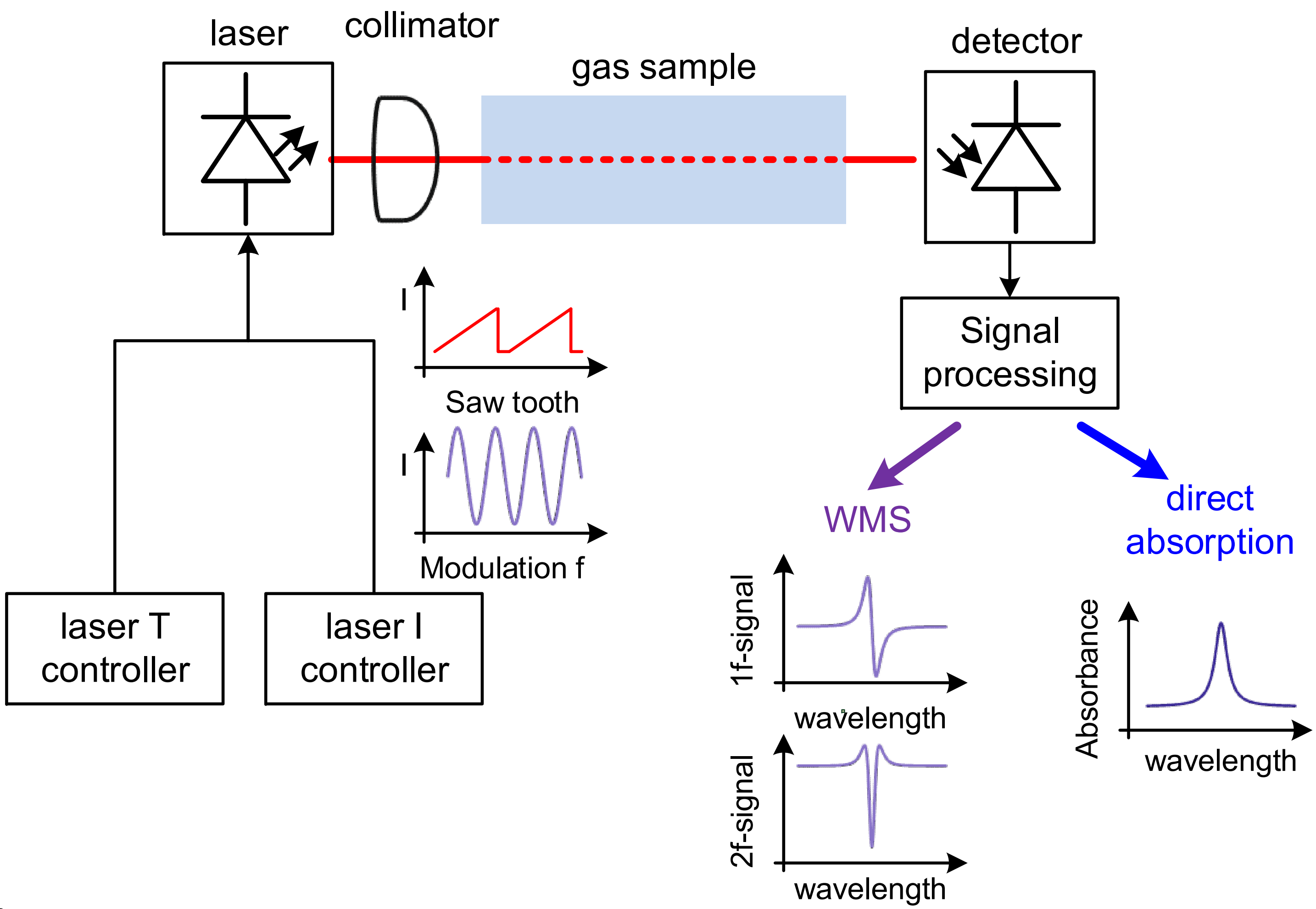
Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

CTI-Project Nr. 17176.1 PFNM.NM

IAMP Institute of Applied Mathematics and Physics

Tunable Diode Laser Absorption Spectroscopy

Schematic sensor setup:



Gas in scattering media absorption spectroscopy (GASMAS)

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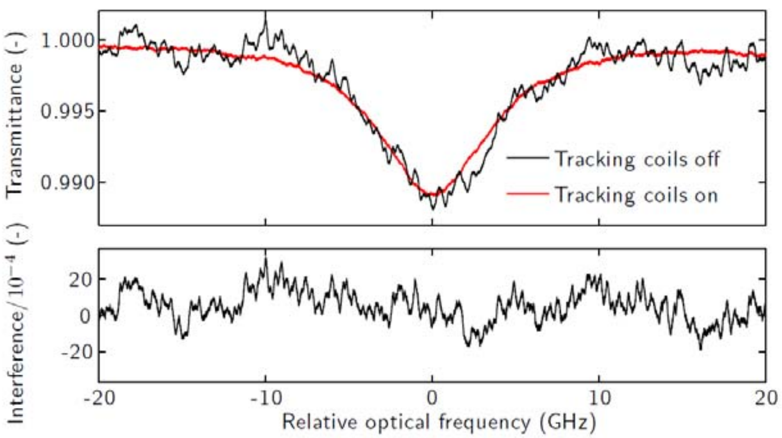
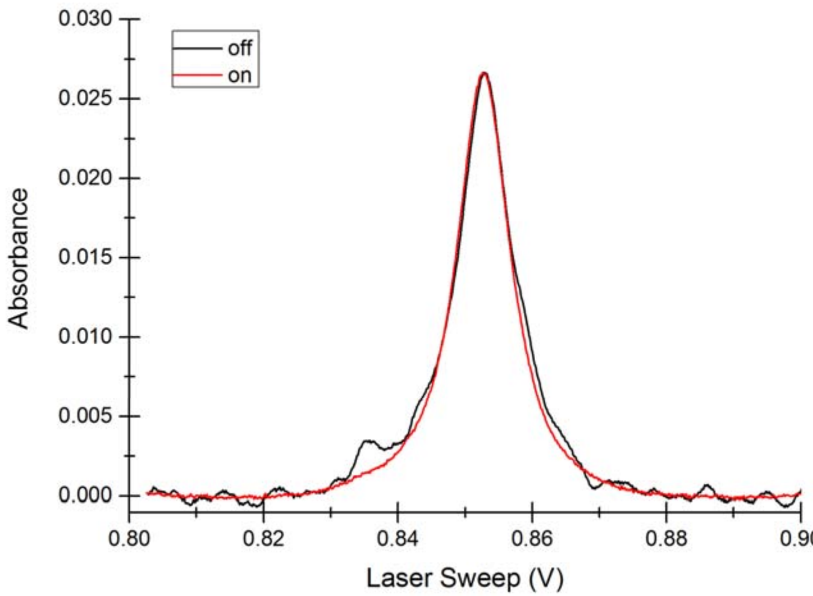
- Mechanical modulation for interference suppression:



T. Svensson *et al.*, Optics Express (2010) 16460

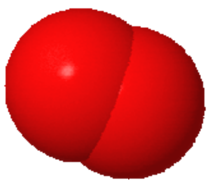
Water vapour @ 936 nm, measurement in alumina, L_{eff} = 1 m (6 mm thick sample)



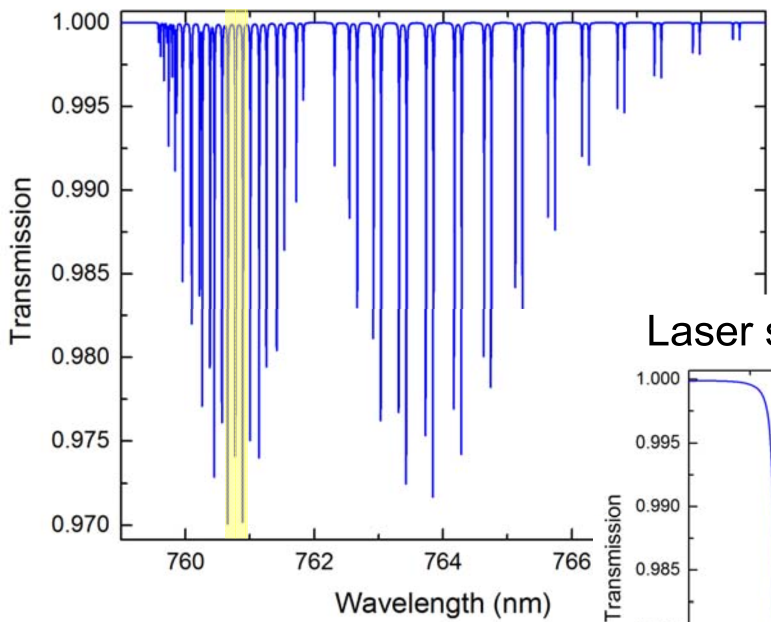
O_2 @760 nm, measurement in ZrO_2, L_{eff} = 5.6 m (7.5 mm thick sample)

Direct Absorption Spectroscopy

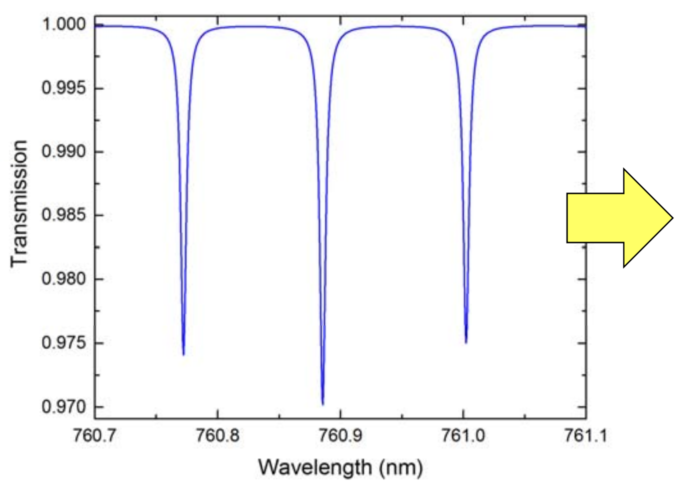
Example: Oxygen



Oxygen absorption spectrum



Laser scan over selected lines



Determine absorbance