Swiss Photonics workshop on Optical Gas Sensing

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Overview over optical gas sensing methods

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Outline

- Optical gas sensing: Brief introduction
- Raman spectroscopy
- Near-IR spectroscopy
- Mid-IR: molecular absorptions, laser sources, detection
- QCL and OPO- based QEPAS/cantilever measurements
- Isotope measurements in human breath
- Surgical smoke analysis
- First lead salt VECSEL studies on C_1-C_4 alkanes
- Mid-IR comb spectroscopy
- Conclusions and outlook

Key issues in gas sensing

Requirements	**Approach**
High sensitivity	Strong fundamental absorption lines: mid-IR for low concentrations, near-IR for higher concentrations feasible, ev. Raman for homonuclear molecules and high concentrations Sensitive detection scheme
Multi – component capability	Broad, continuous tuning range
High selectivity / specificity	Narrow laser linewidth, if selectivity is not an issue broadband sources, e.g. LEDs
In – situ monitoring	Room temperature operation Compact, robust set – up Easy or no sample preparation

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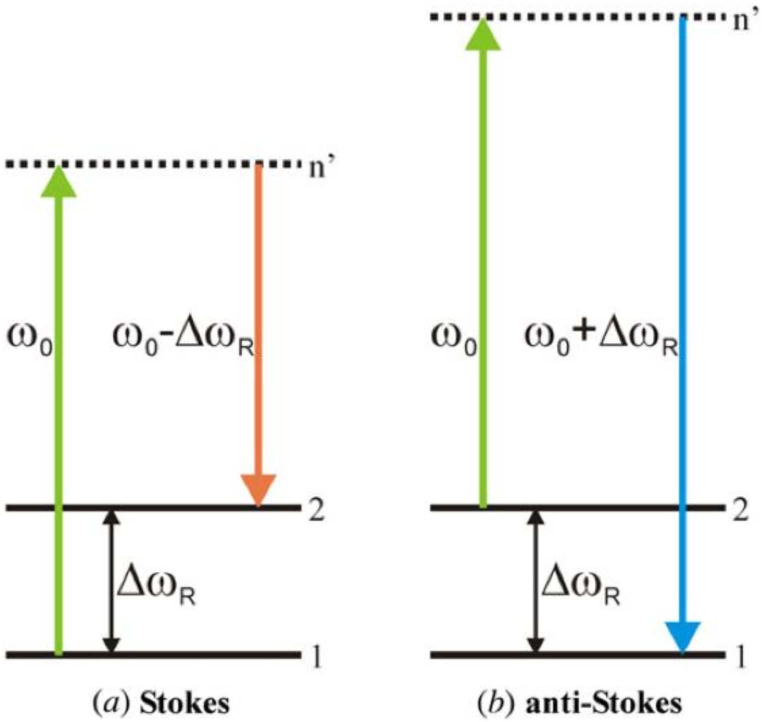
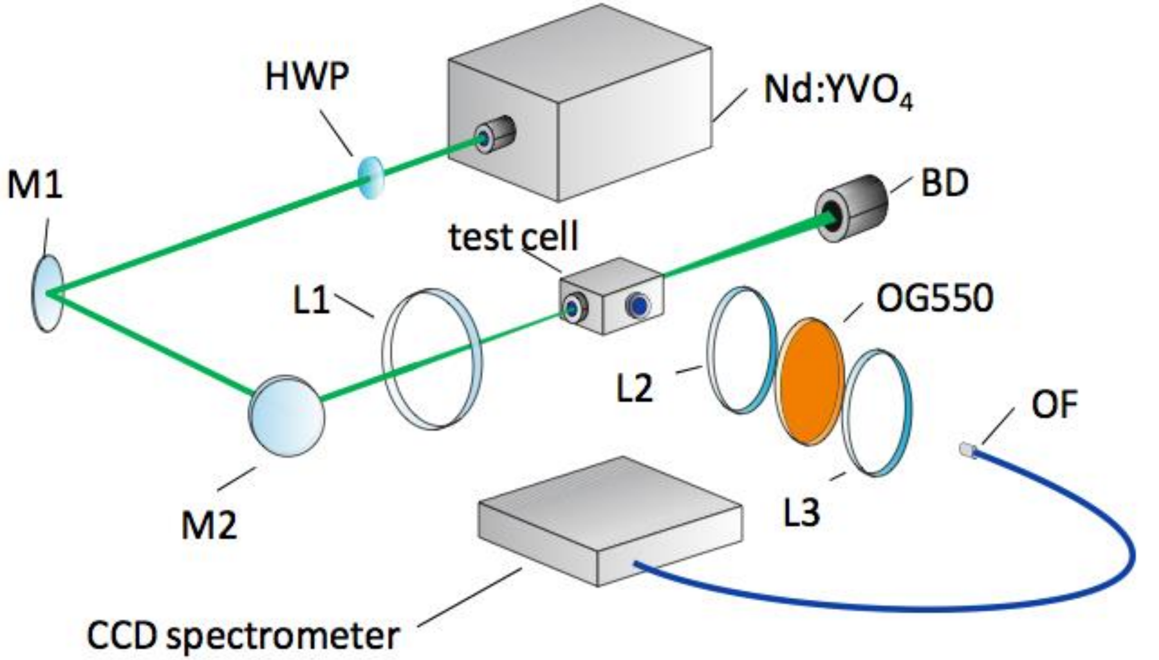
Raman spectroscopy for gas sensing





HWP: half wave plate; M: mirror; L: lens; BD: beam dump;
OF: optical fiber; OG550: optical filter

Excitation at one wavelength

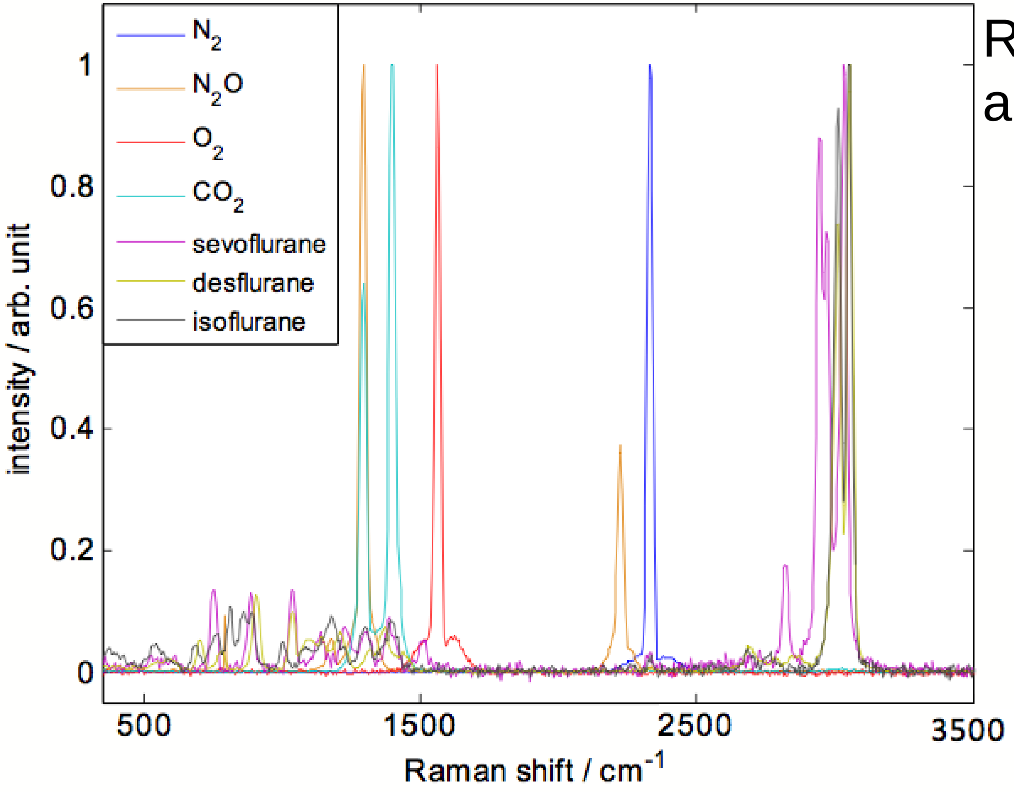
Frequency-doubled 8W-Nd:YVO$_4$ laser (no tunable laser required)

Raman scattering yields molecular specificity

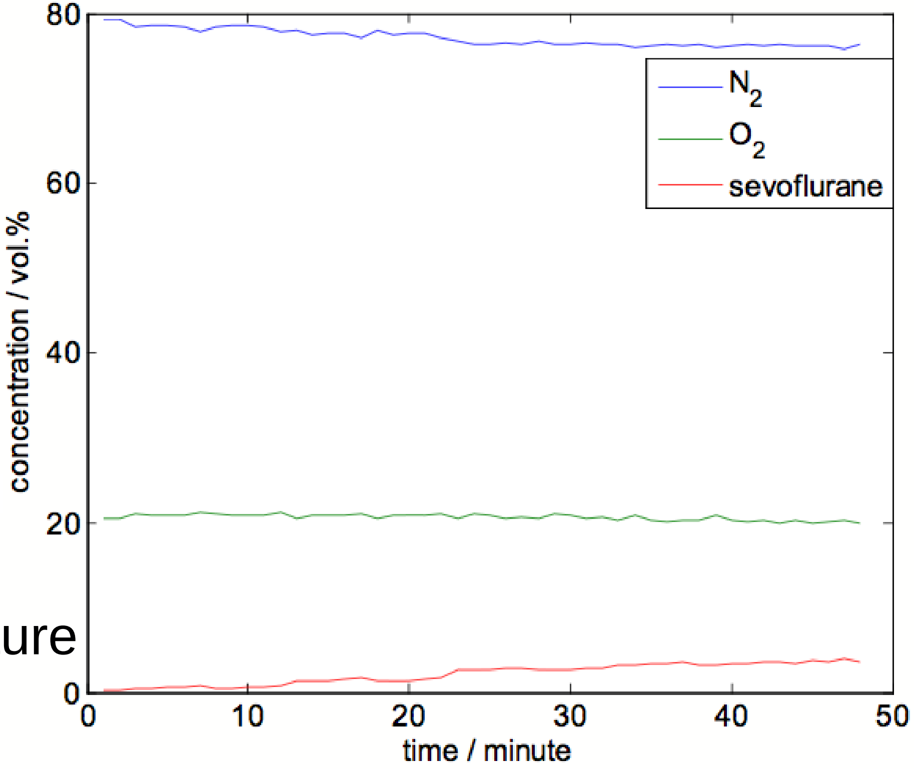
S. Schlüter et al.: Physics Procedia **39** (2012) 835 – 842

Raman spectroscopy

- also homonuclear molecules (like N_2, O_2)
- low sensitivity: % concentrations



Raman spectra of volatile anesthetic agents



Varying sevoflurane concentration in a mixture of N_2 and O_2 from 0.2 vol.% to 5.0 vol.%

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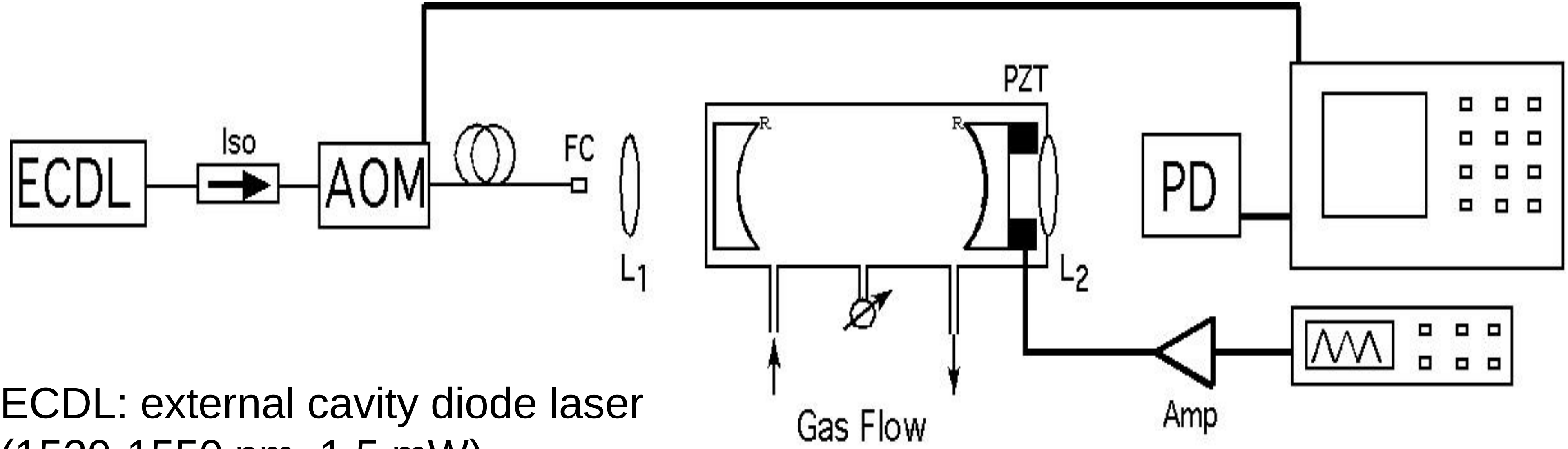
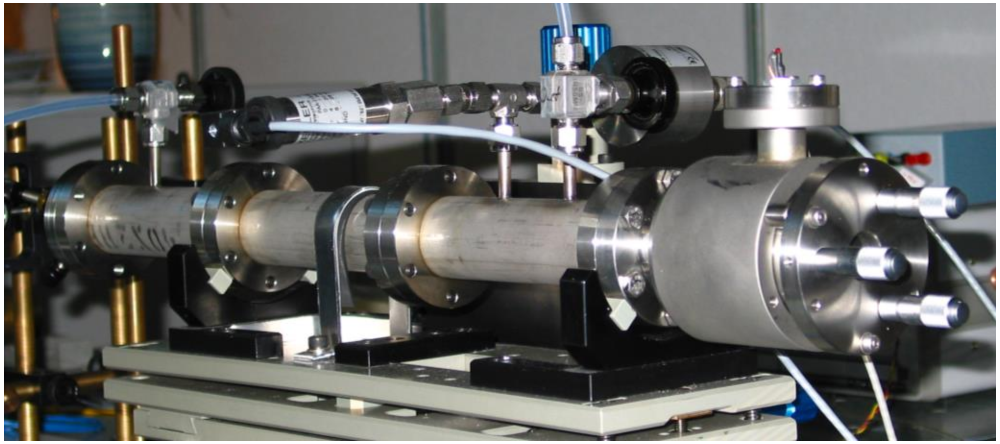
Near-IR diode laser cavity ringdown spectroscopy

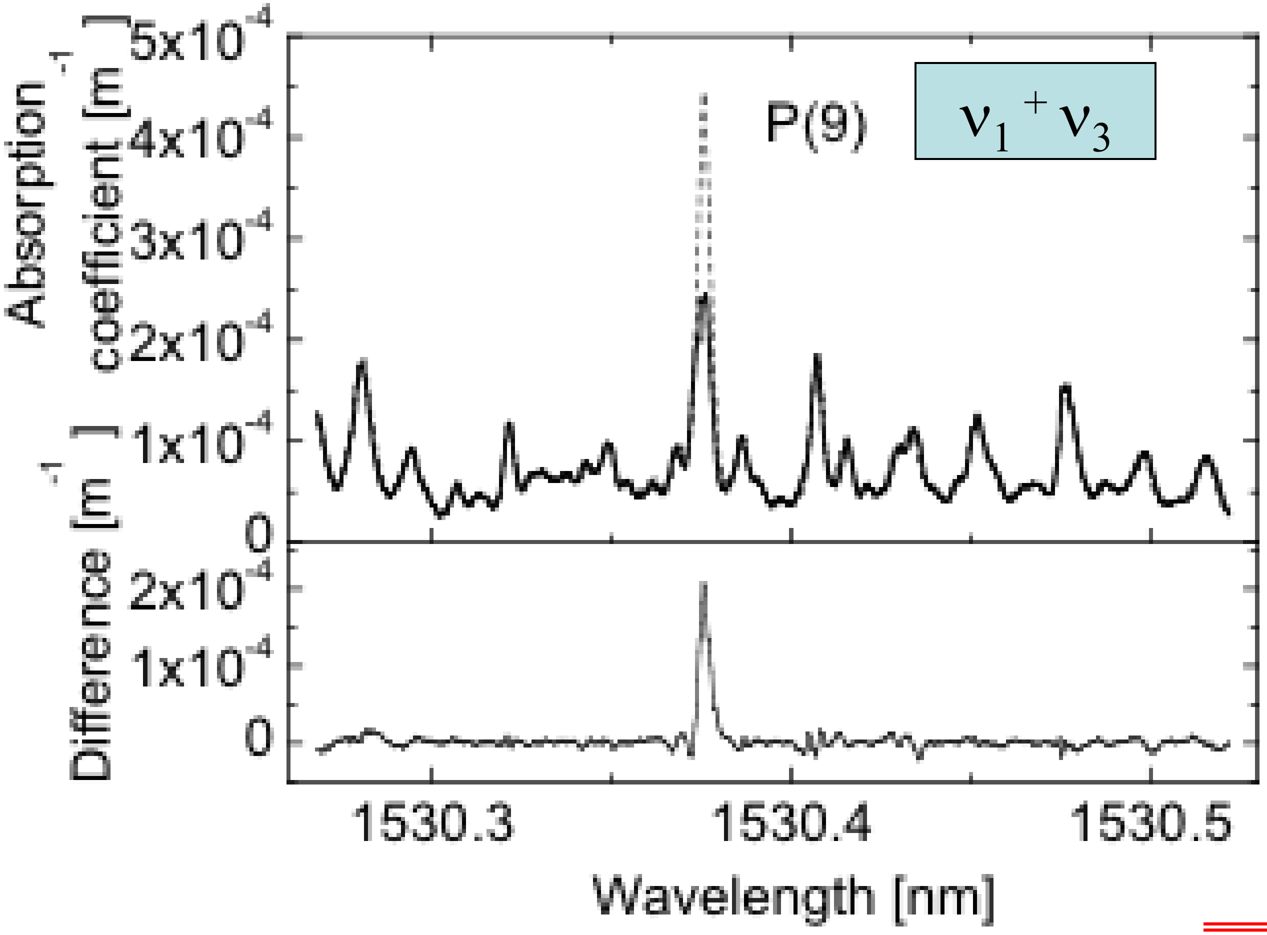


ECDL: external cavity diode laser
(1520-1550 nm, 1.5 mW)
ISO: optical isolator
AOM: Acousto-optic modulator
PD: photodiode

CTI project with ABB research center



NIR spectrum of C_2H_2 / C_2H_4 - mixture



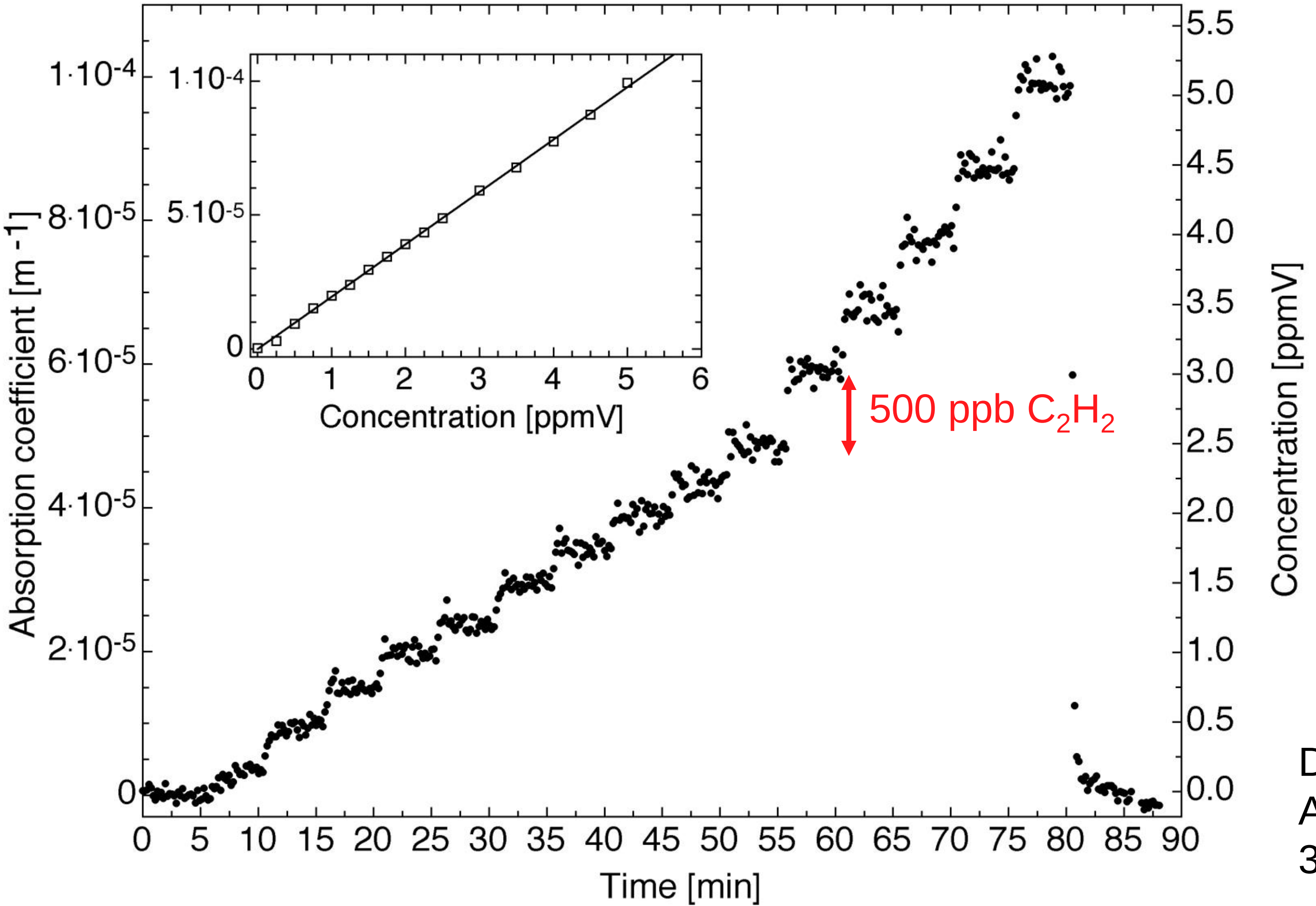
— Absorption spectrum of 99.95% ethylene (C_2H_4)

- - - - 10 ppm acetylene (C_2H_2) added to 99.95% C_2H_4

— residual

⟹ **Acetylene absorption line clearly detectable!**

Measurement of acetylene (C_2H_2) diluted in ethylene (C_2H_4



D. Vogler, et al.:
Appl. Phys. B **85**,
349 (2006)

LOD: 20 ppb C_2H_2 in synth. air, 4.5×10^{-8} cm^{-1} Hz$^{-1/2}$
160 ppb C_2H_2 in C_2H_4 flow

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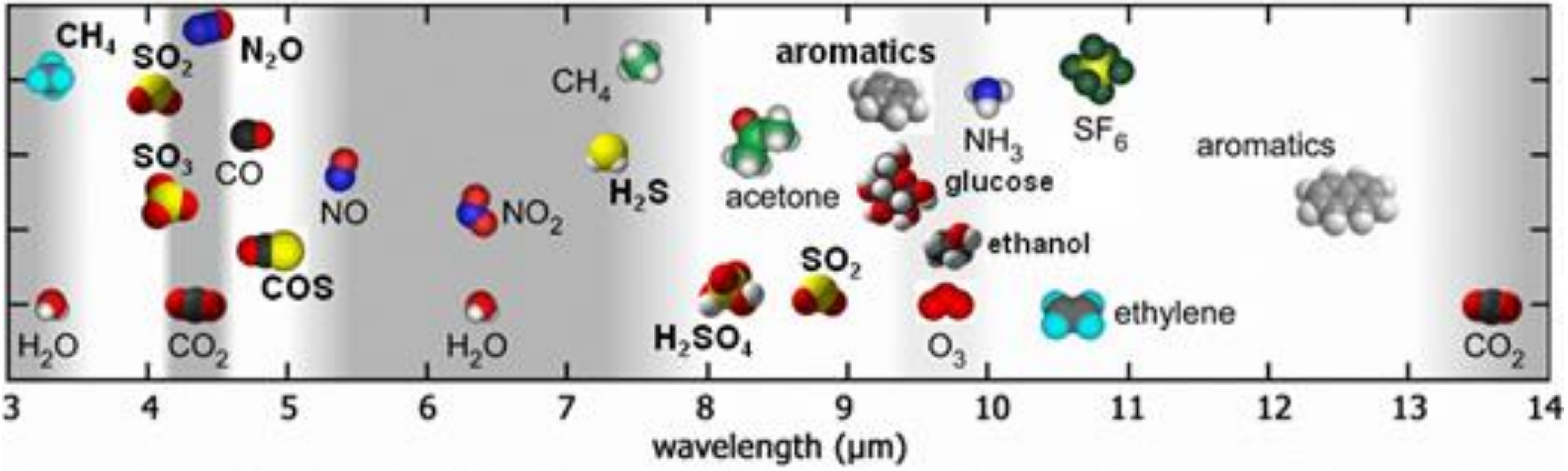
Molecular absorption in the mid-IR



From Daylight Solutions

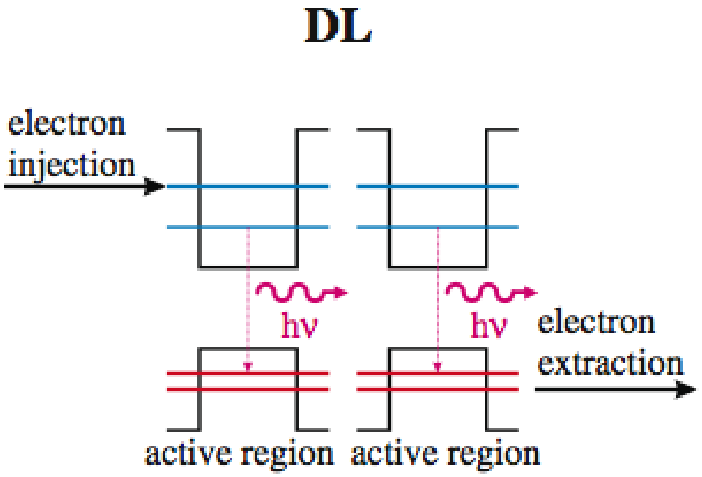
(Broadly) tunable narrow-band mid-IR lasers

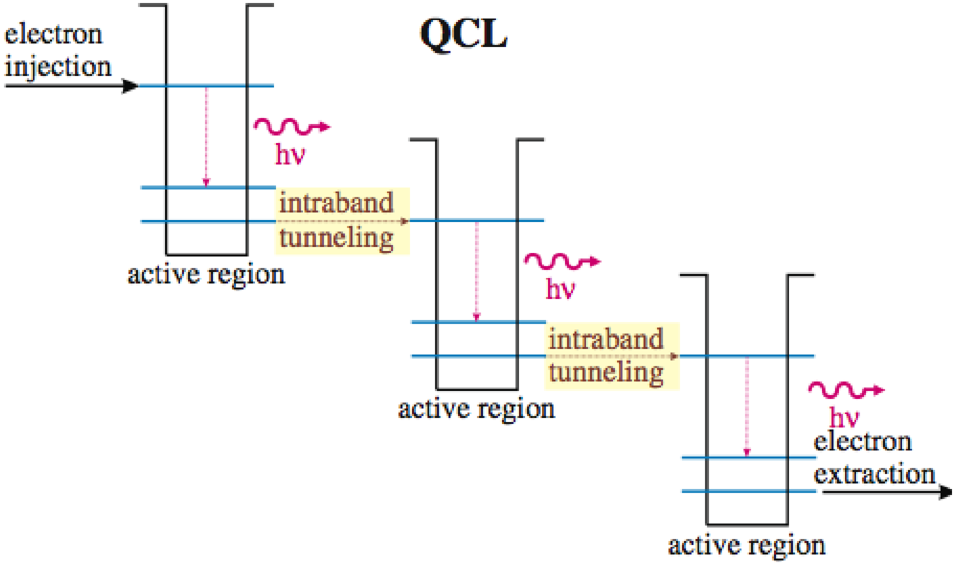
Laser	Wavelength [μm]	Tuning Characteristics	Power	Operation
CO_2	9 – 11	Only line tunable	Watts	RT operation
Sb-based ICL	3 – 5.3	Few nm	> 10 mW	RT operation
QCL	<4 – 12, THz	cm^{-1} to > 100 cm^{-1} per device	mW to W	LN_2/TE cooling, also RT
Lead-salt VECSEL	3 – 30	> 150 cm^{-1} (piezoel.)	< mW	Pulsed only TE cooling
DFG/OPO[a]	3 – 16	~ μm for specific setup	μW to mW Watts	RT operation

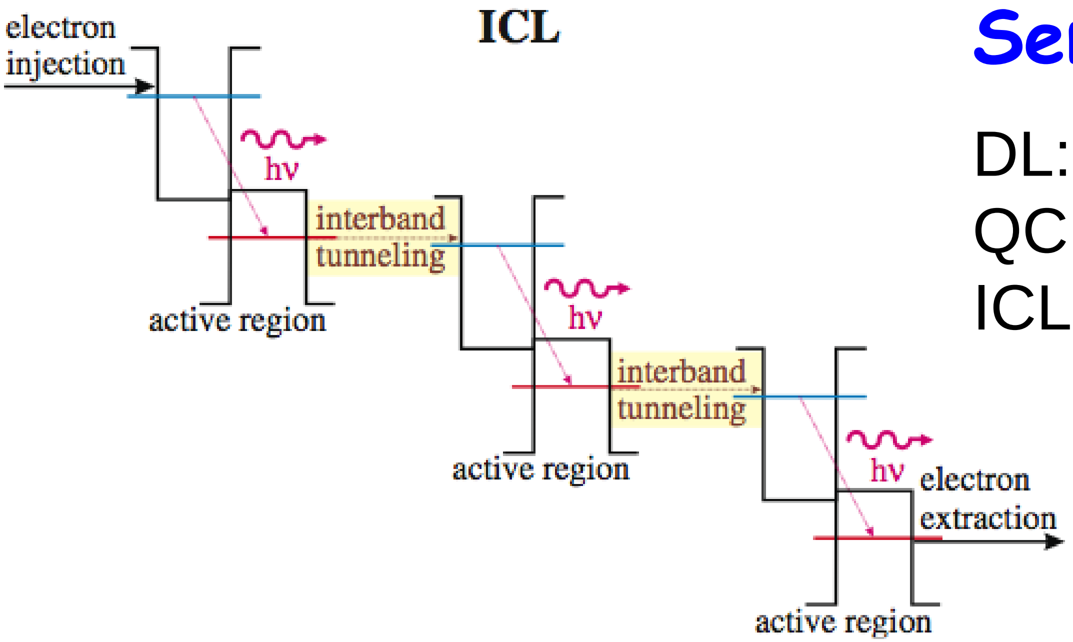
Ideal laser source does not exist yet

[a] DFG: difference frequency generation / OPO: optical parametric oscillator

Examples: PPLN (periodically poled lithium niobate, eventually with waveguide), $AgGaSe_2$, $LiInS_2$, $LiInSe_2$, etc. TE: thermoelectric cooling, RT: room temperature





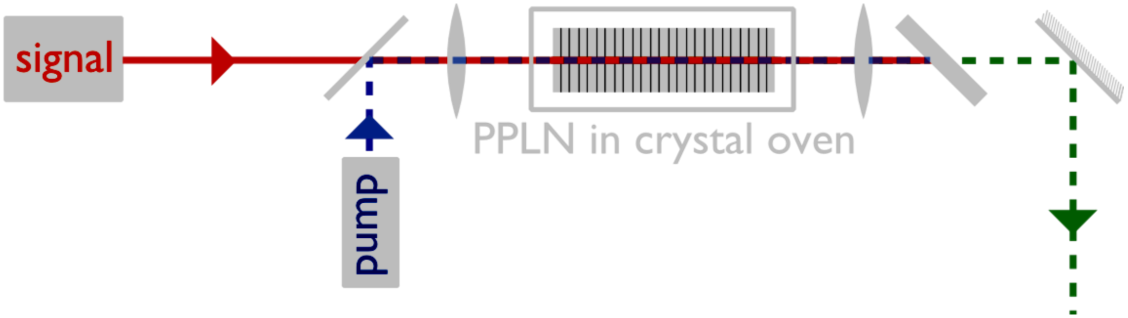


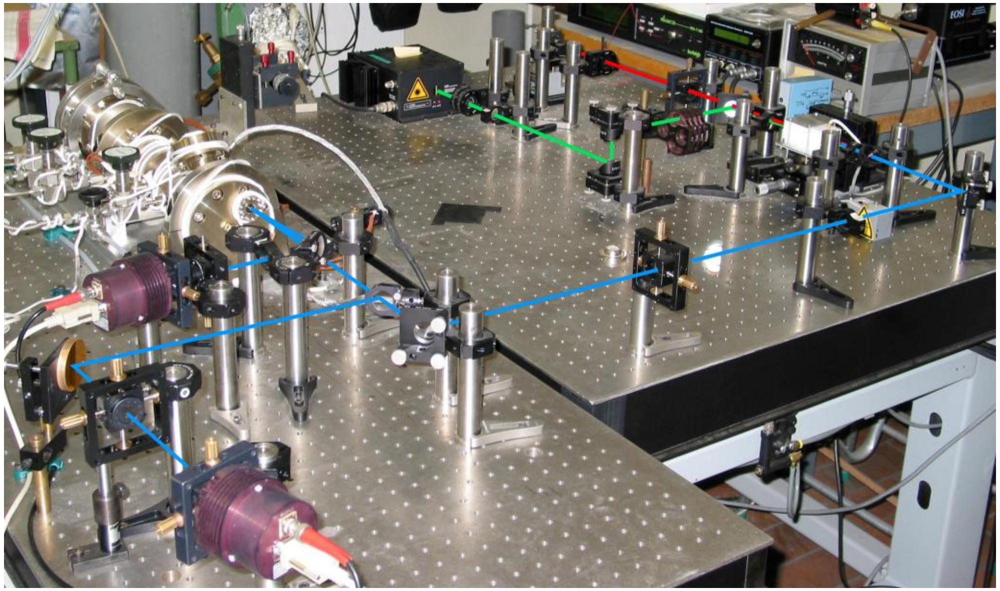
Semiconductor Lasers

DL: Diode Laser
QCL: Quantum Cascade Laser
ICL: Interband Cascade Laser

Tunable narrowband mid-infrared lasers

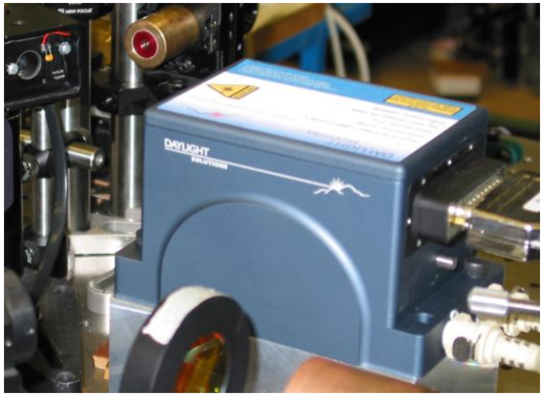
Difference frequency generation





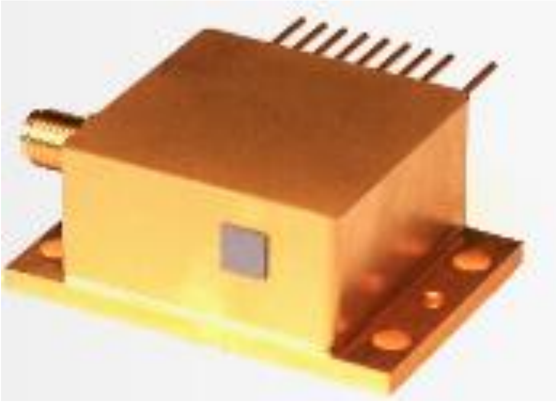
RT, 3-17 µm, broad tuning

Quantum cascade laser



TE, 4-12 µm, “broad” tuning, compact

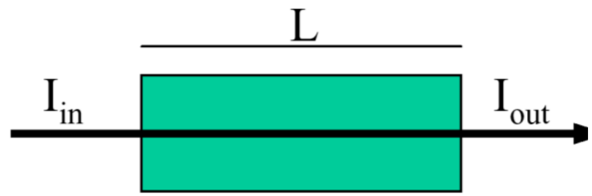
Diode-pumped VECSEL



TE, ≈ 3.4 µm, >150 cm^{-1} tuning, compact

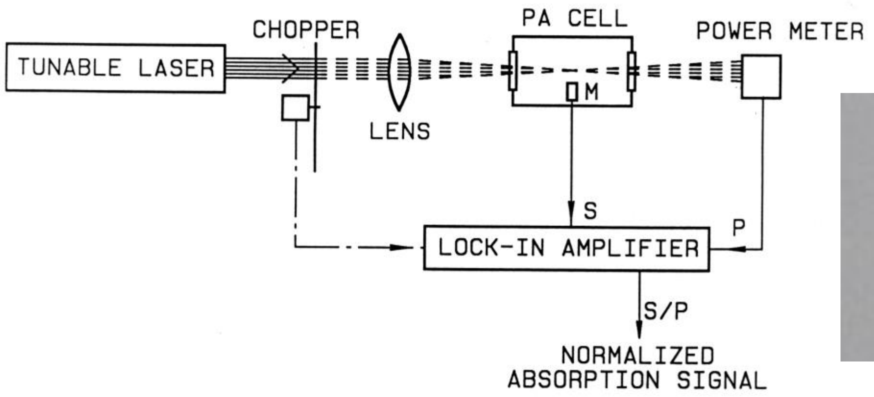
Absorption measurement: Detection schemes

Transmission



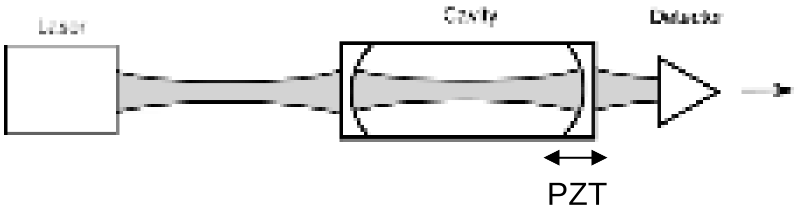
$$I_{out} = I_{in} \cdot \exp\{-\overbrace{N\,\sigma(\lambda)}^{\alpha(\lambda)}\,L\}$$

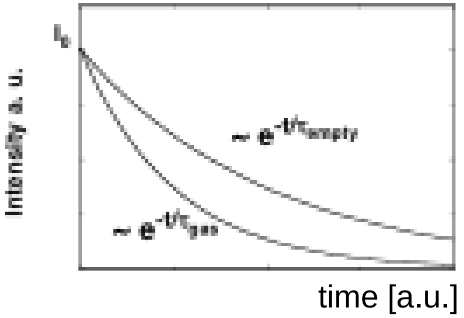
Photoacoustic



$$S(\lambda) = C\,P(\lambda)\,N_{tot}\,c_{gas}\,\sigma(\lambda)$$

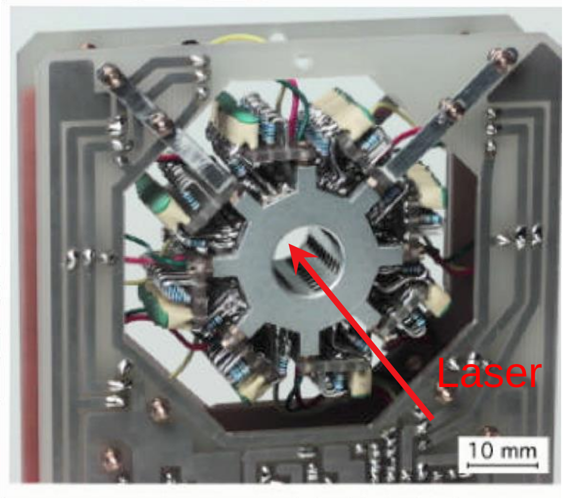
Cavity Ring-down



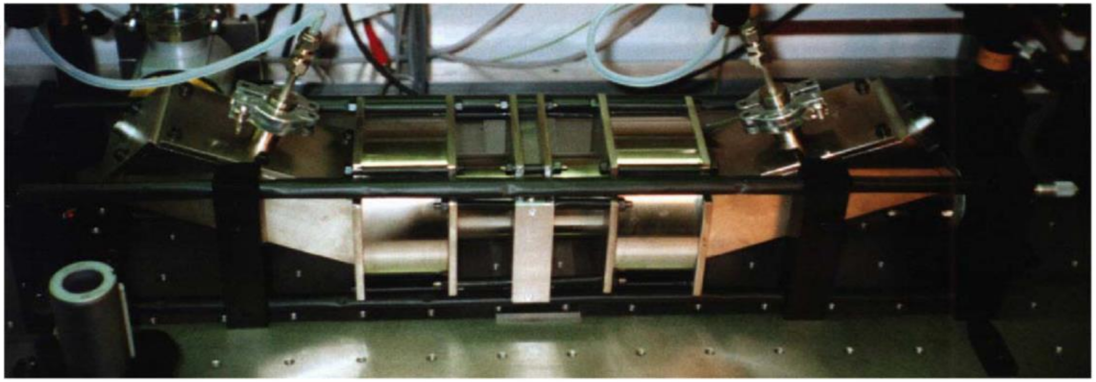


$$\alpha_{gas} = \frac{1}{c}\left(\frac{1}{\tau_{gas}} - \frac{1}{\tau_{empty}}\right)$$

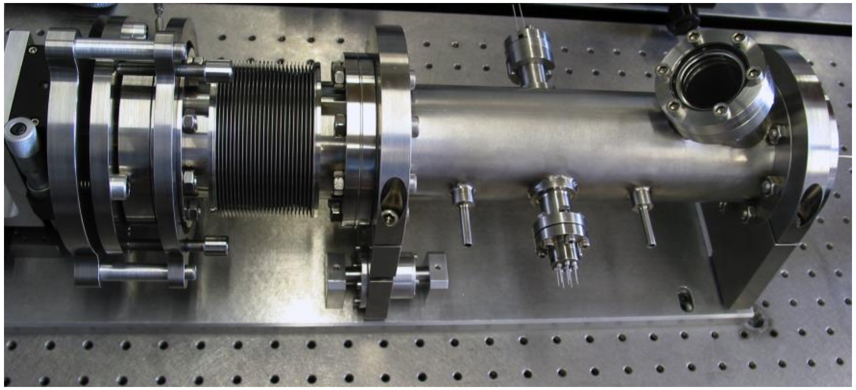
Various cell designs



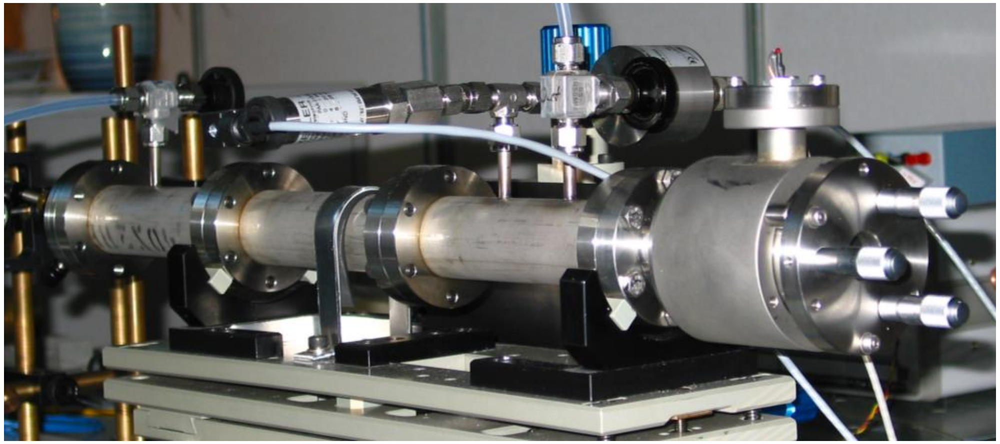
80-microphone photo-acoustic cell (A. Bohren)



18-pass resonant PA cell with 16 mics (M. Nägele)



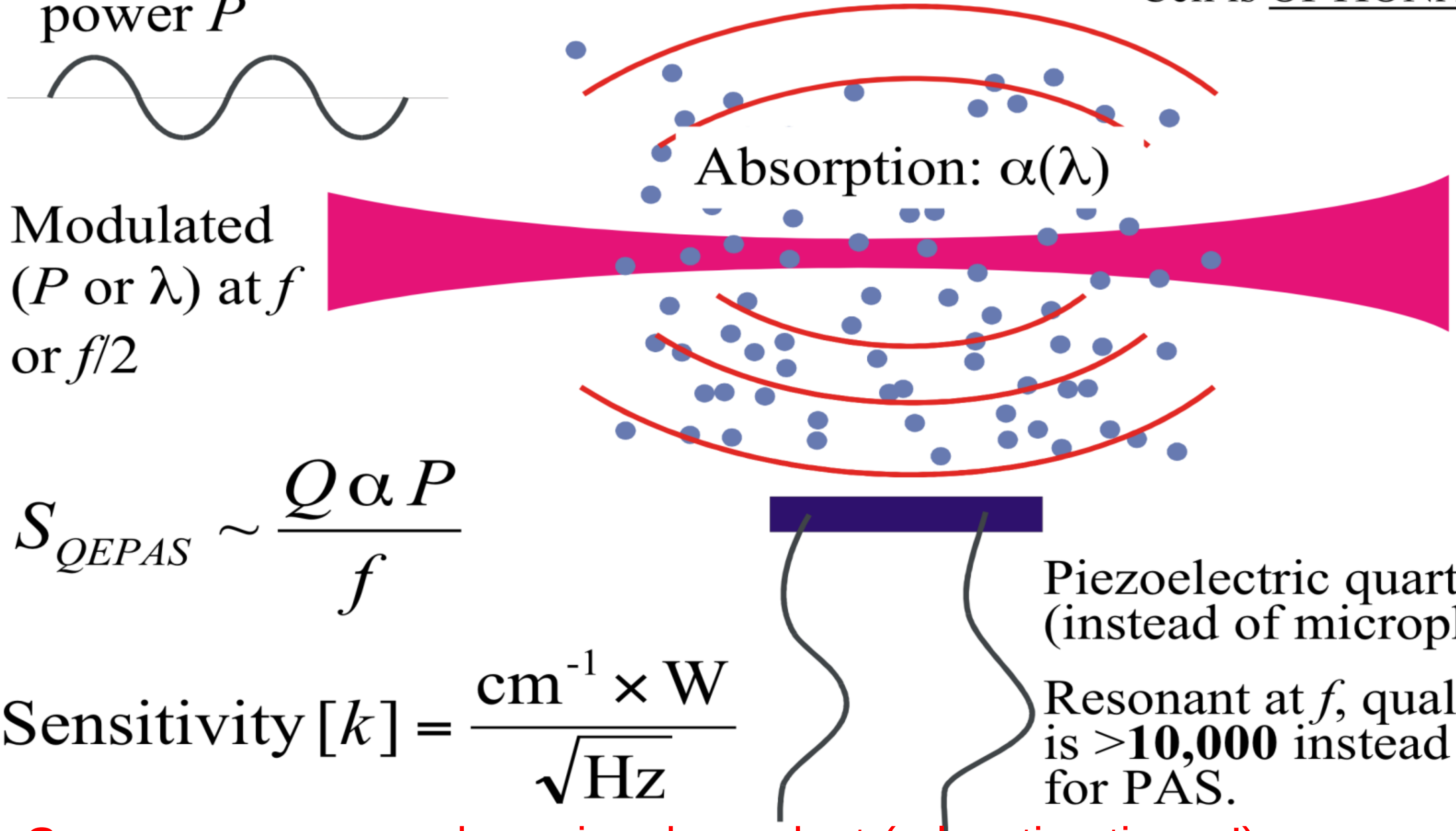
High-temperature multi-pass cell pathlength: 9 - 35 m (R. Bartlome)



Cavity-ringdown cell für NIR (D.Vogler)

Quartz-Enhanced Photoacoustic Spectroscopy (QEPAS)

- Resonant Cavity in L-PAS
- Cell is <u>OPTIONAL</u> in QEPAS.



Laser beam, power P

Absorption: $\alpha(\lambda)$

Modulated (P or λ) at f or $f/2$

Piezoelectric quartz crystal (instead of microphone)

Resonant at f, quality factor Q is >**10,000** instead of 20-200 for PAS.

$$S_{QEPAS} \sim \frac{Q\,\alpha\,P}{f}$$

$$\text{Sensitivity}\,[k] = \frac{\text{cm}^{-1} \times \text{W}}{\sqrt{\text{Hz}}}$$

S_{QEPAS}: pressure- and species-dependent (relaxation times !)

A. Kosterev et al, Optics Letters 27, 1902, 2002

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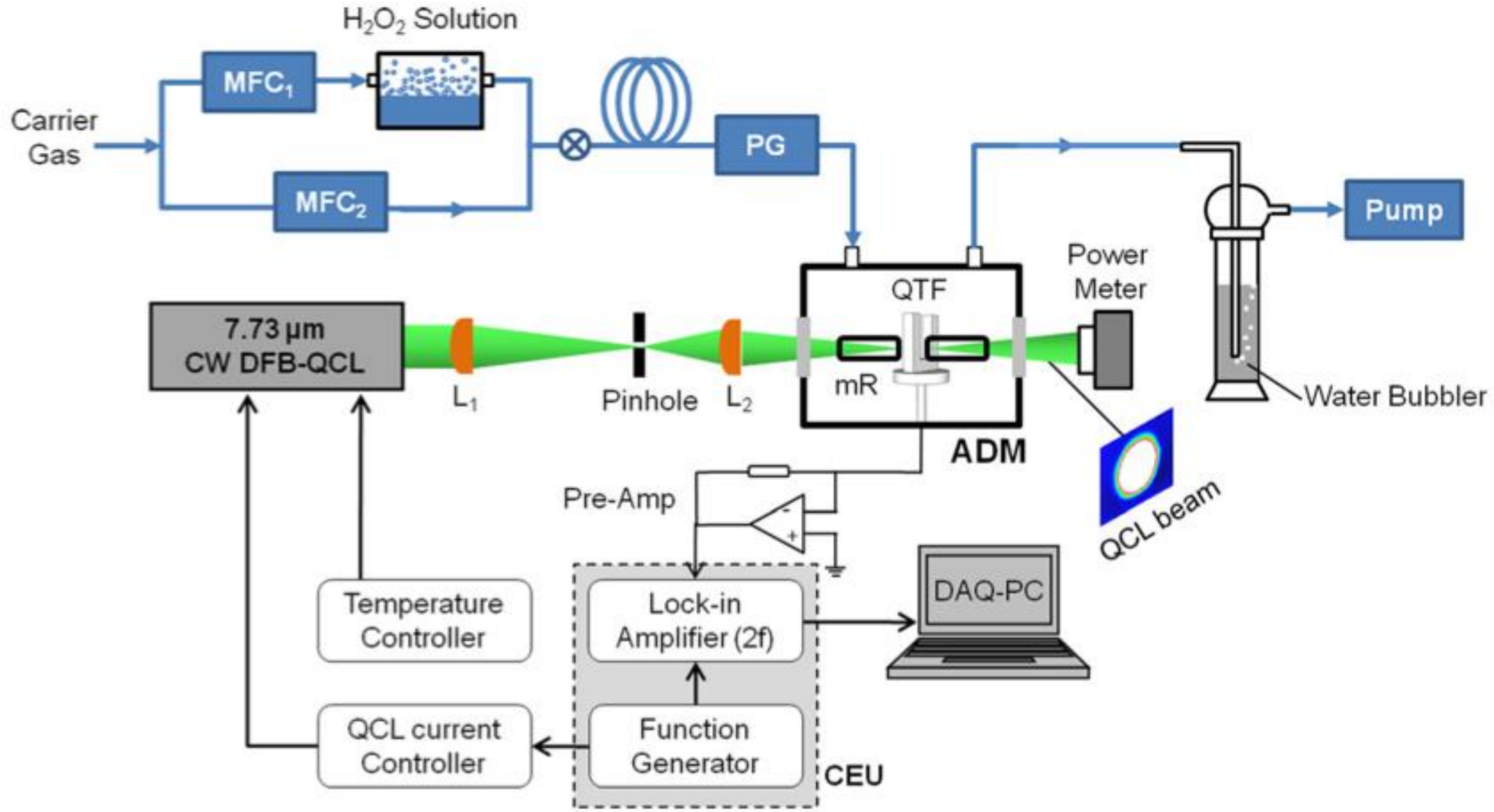
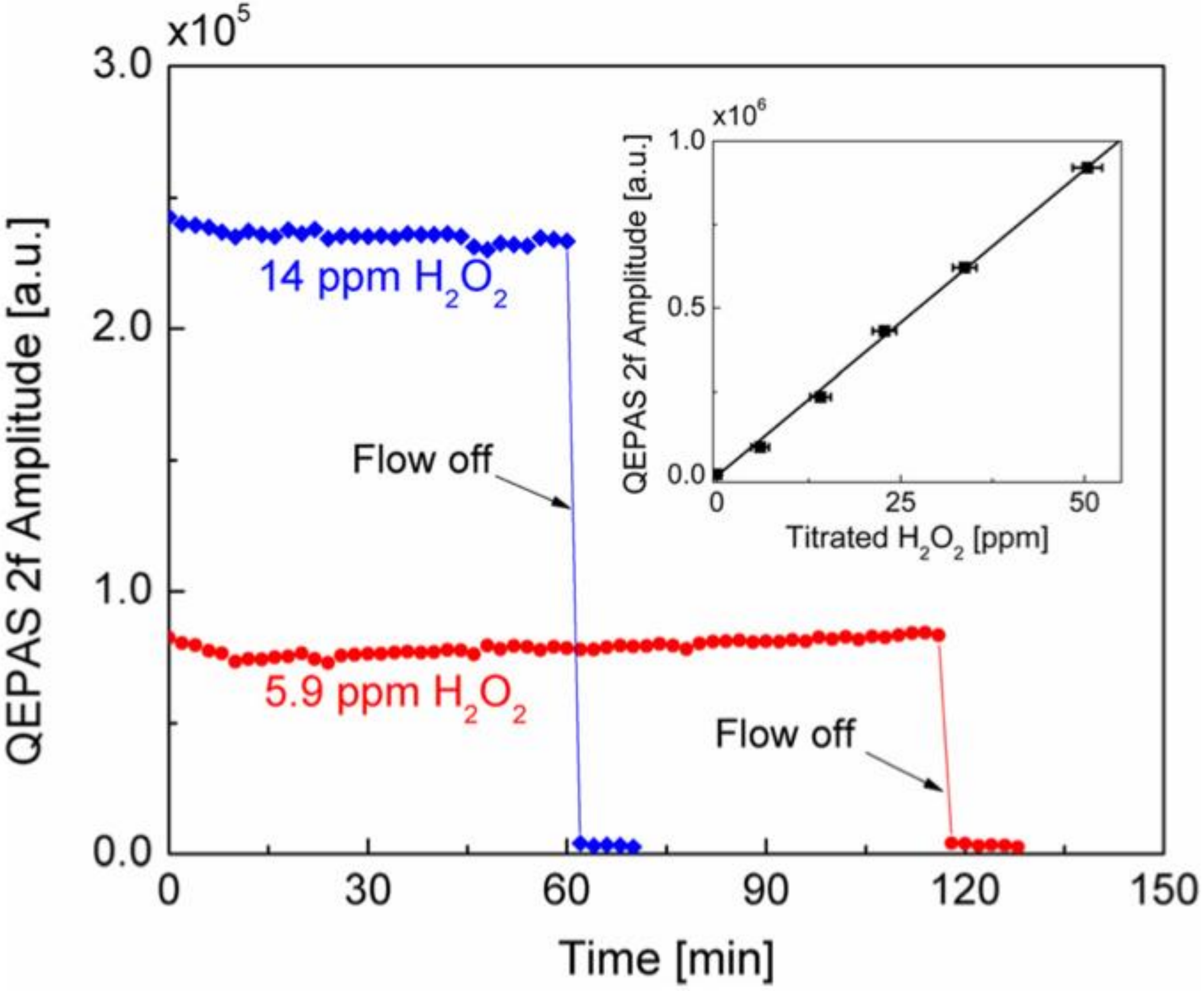
QCL-QEPAS setup for H_2O_2 detection



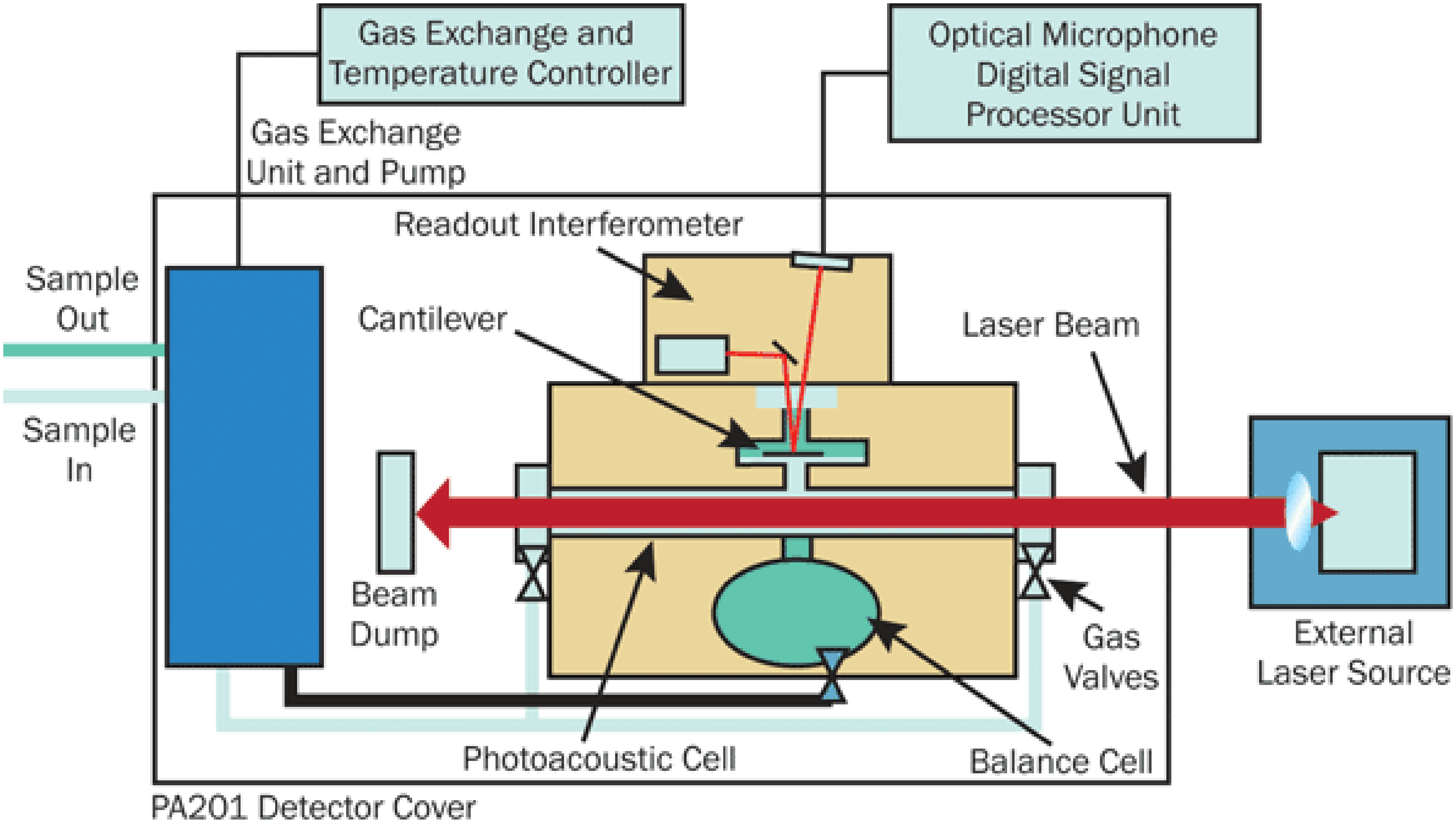
W. Ren et al.: Appl. Phys. Lett. **104**, 04117 (2014)



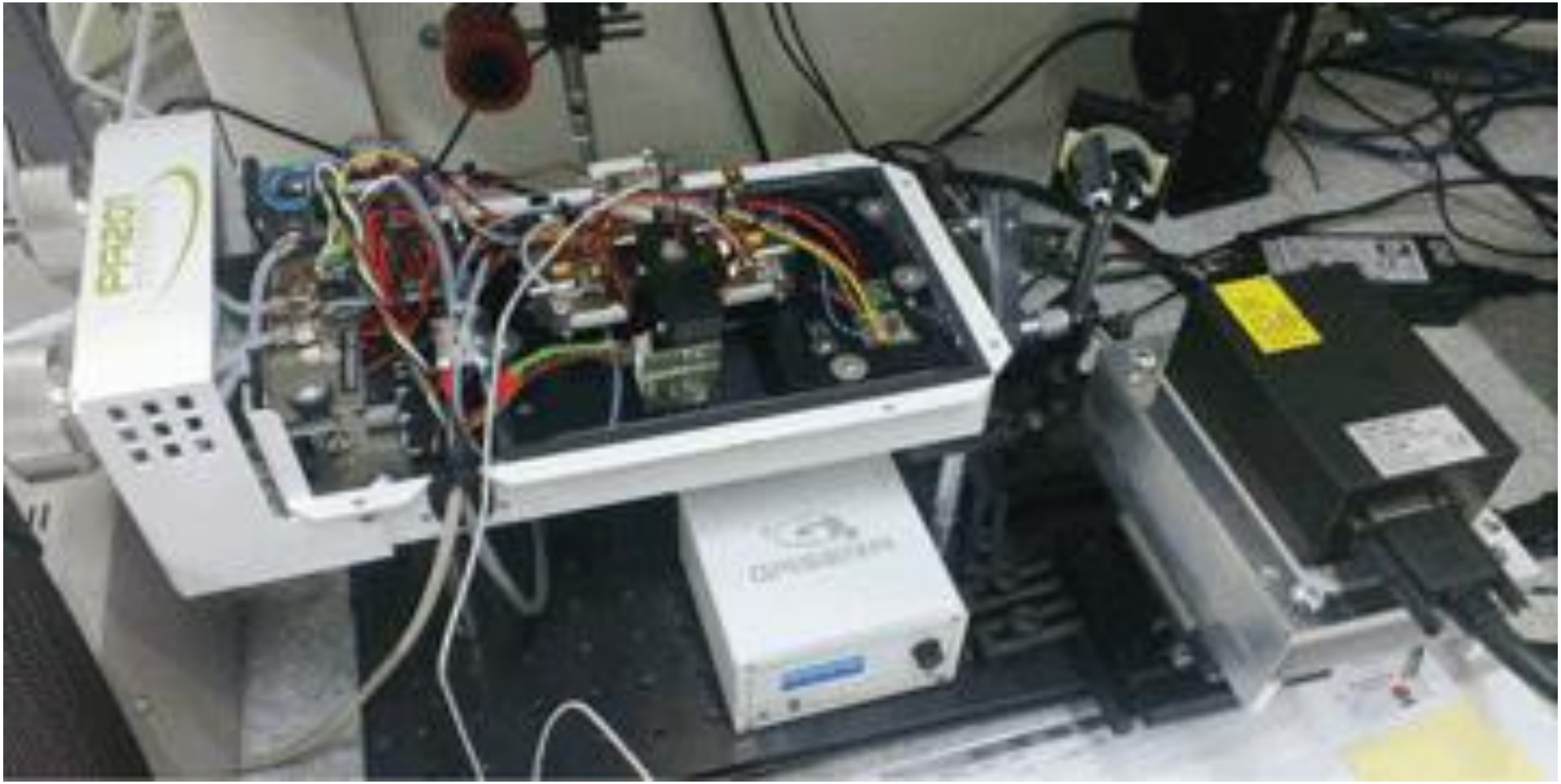
LOD: 12 ppb / 100 s

4.6×10^{-9} cm^{-1} W Hz$^{-1/2}$

OPO-based cantilever PAS



S. Sinialo (Gasera Ltd.) and H. Karlsson (Cobolt AB): Photonics Spectra (Dec 2014)

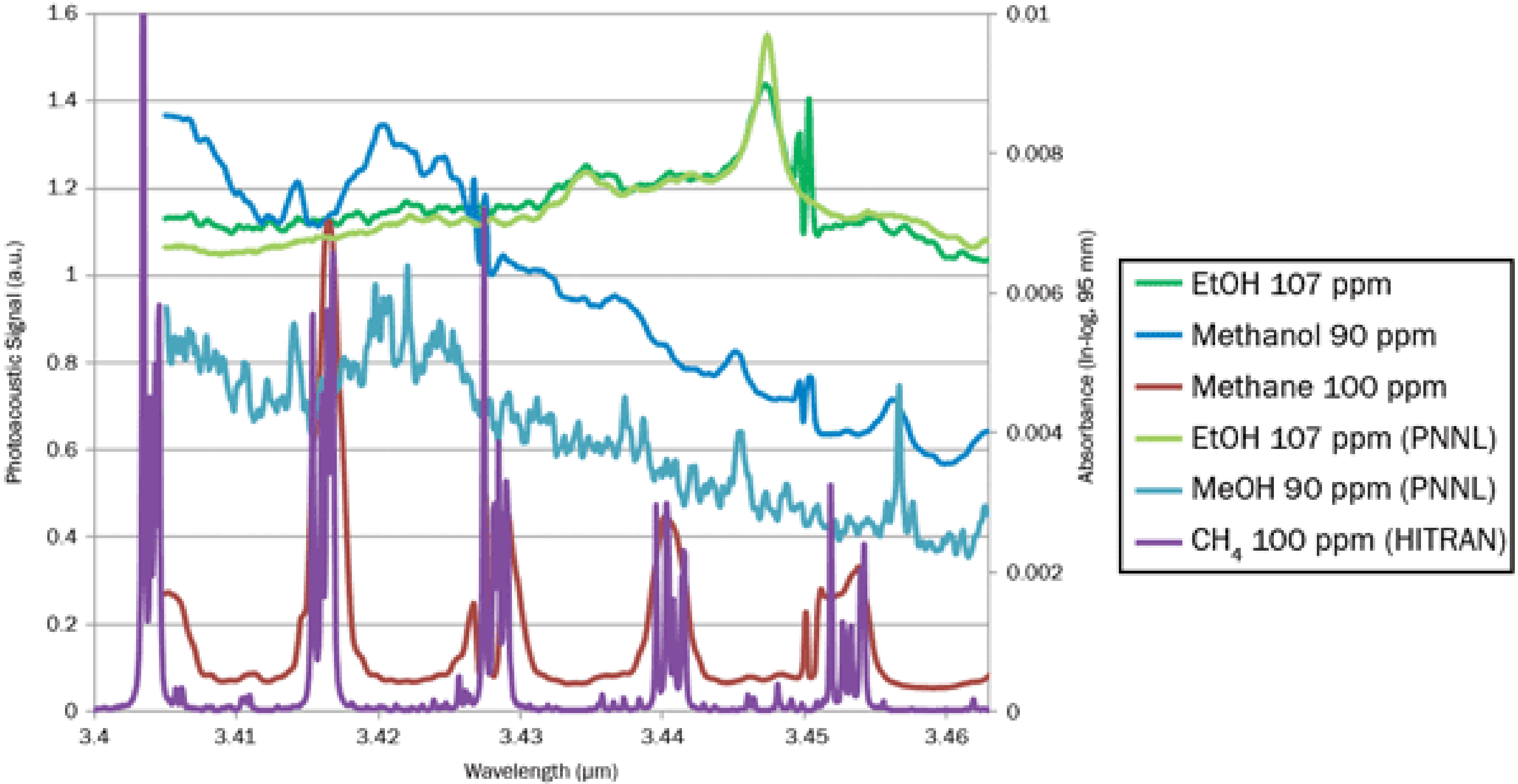


OPO: 3405-3463 nm, pulsed , 10 kHz, 4 ns, 5 μJ, av. power 110 mW, $\Delta\lambda = 1.3$ nm

Chopped at 135 Hz for PAS

Photonics Spectra (Dec 2014)

IR spectra of ethanol, methanol and methane



LOD (SNR=2, 1s): ethanol 7.7 ppb, methanol 11.4 ppb, methane 35 ppb

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Deuterated water (D_2O) as non-radioactive tracer

Why measure ? To determine:

- Total body water
- Energy expenditure
- Glucose synthesis rates
- Cholesterol synthesis rates

How to measure ?

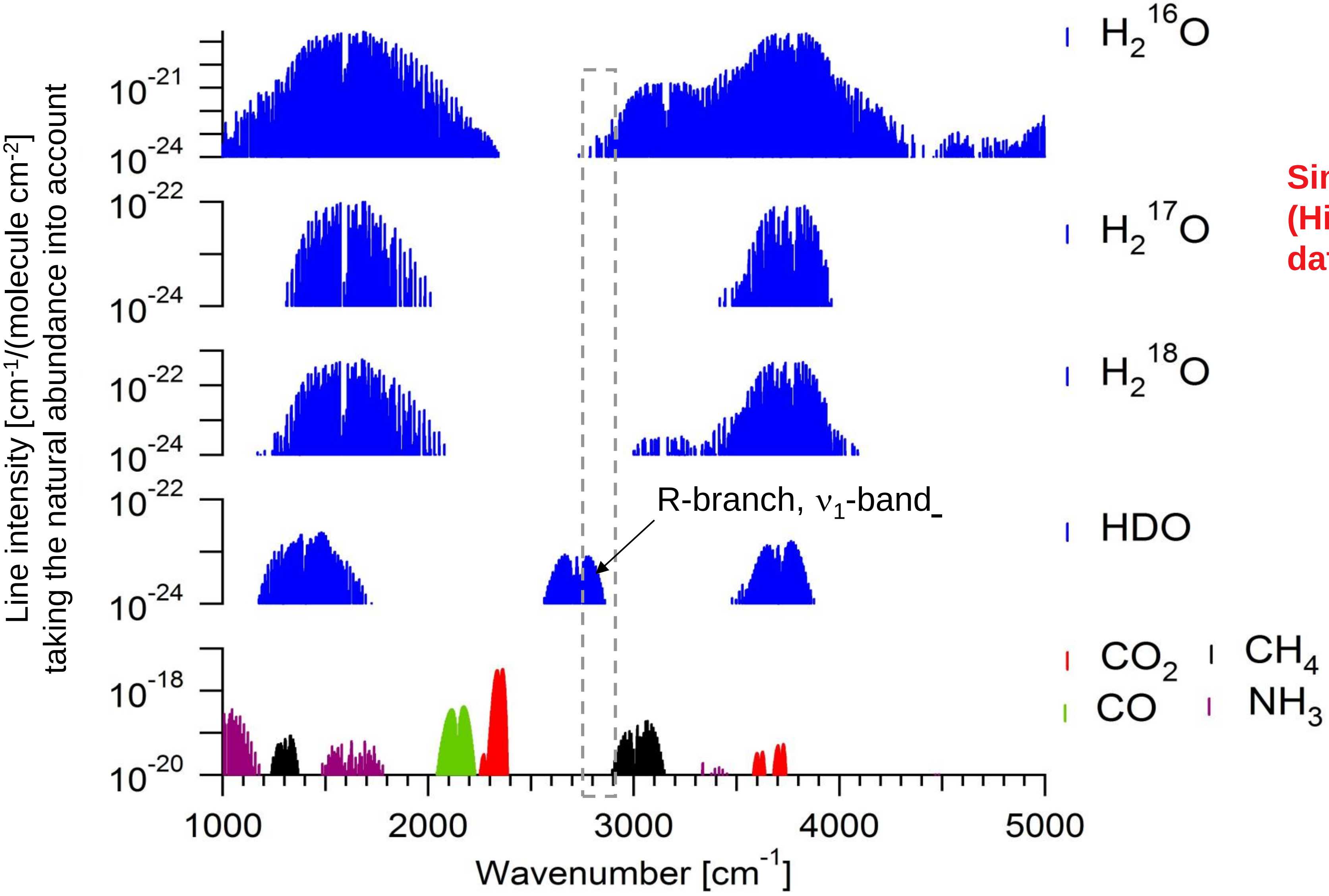
- Ingested D_2O mixes with water (H_2O) in the body → HDO

- HDO measurement in urine or saliva samples

Our approach:

Measure HDO directly in **breath** sample with laser spectroscopy

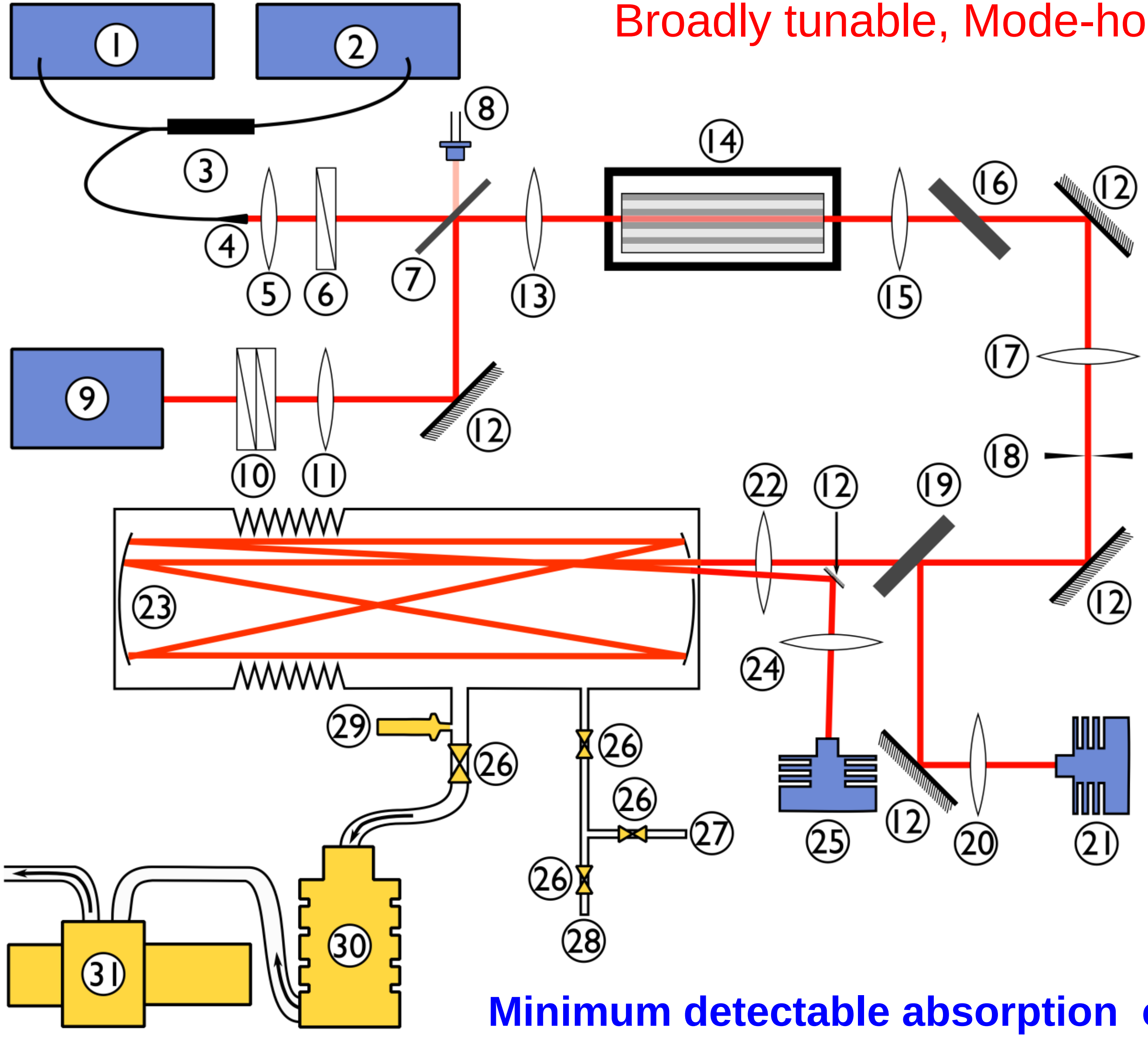
Analysis of human breath for biomarkers: D/H ratio



Simulation (Hitran database)

DFG spectrometer

Broadly tunable, Mode-hop free, Room temperature



1	ECDL, 1520-1600nm 5 mW CW
2	Wavemeter for ECDL
9	Nd:YAG, 1064.5 nm, 5 kHz, 6 ns, 300 mW av
14	PPLN, 5 cm, 8 periods
23	Heatable multipass cell up to 35 m
21/25	Detectors (VIGO)

Idler: 150 μW av.
2817 - 2920 cm^{-1} (29.5 μm)
2900 - 3144 cm^{-1} (29.9 μm)
Step size 0.002 cm^{-1}

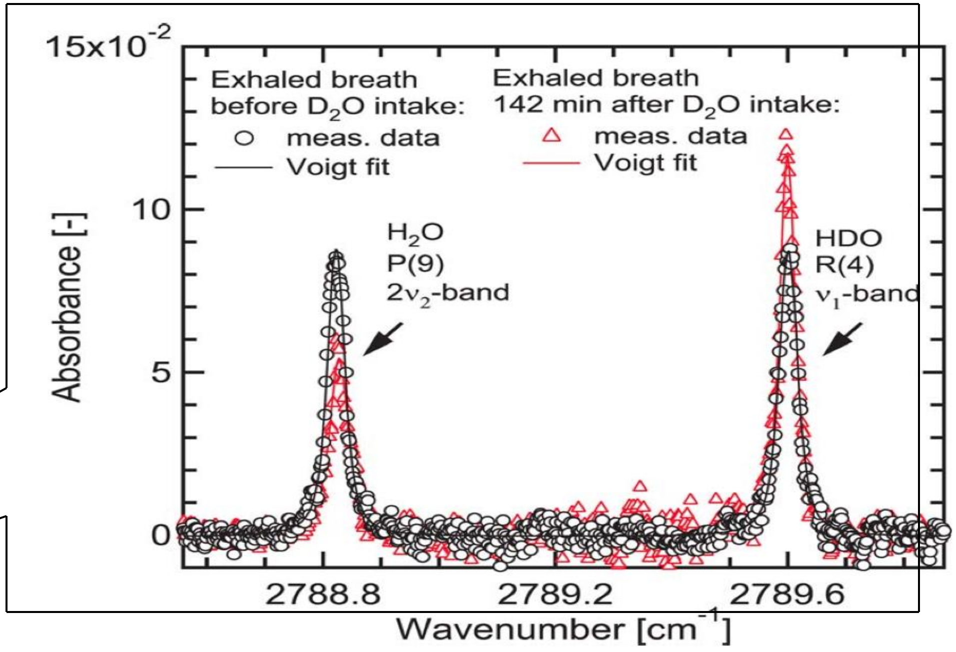
Minimum detectable absorption coefficient: 5×10^{-7} cm^{-1} $Hz^{-1/2}$

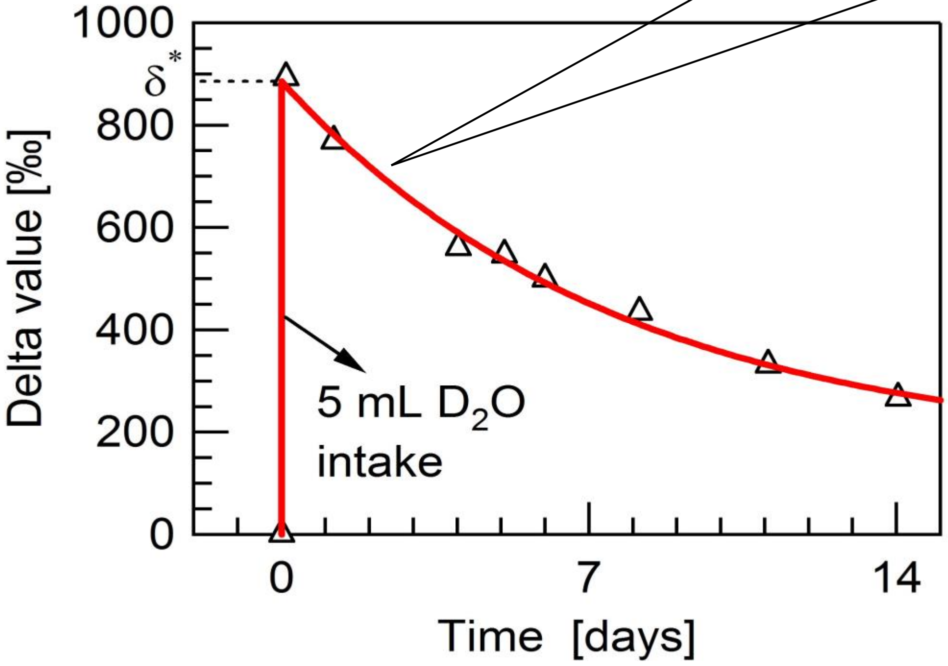
(few ppm for many compounds of interest)

Time-dependent measurements after heavy water intake

Delta value δD in ‰

$$\delta D = \left(\frac{D/H_{\text{sample}} - D/H_{\text{standard}}}{D/H_{\text{standard}}} \right) \times 1000$$





Half-life = 7.2 days

Total body water:

$$TBW = \frac{D_2O \text{ mass}}{\delta^* R_{\text{standard}}} = 38.2 \text{ kg}$$

$$= 53.1\ \%\ \text{of}\ 72\ \text{kg}$$

R. Bartlome et al.: *Opt. Lett.* **34**, 866 (2009)

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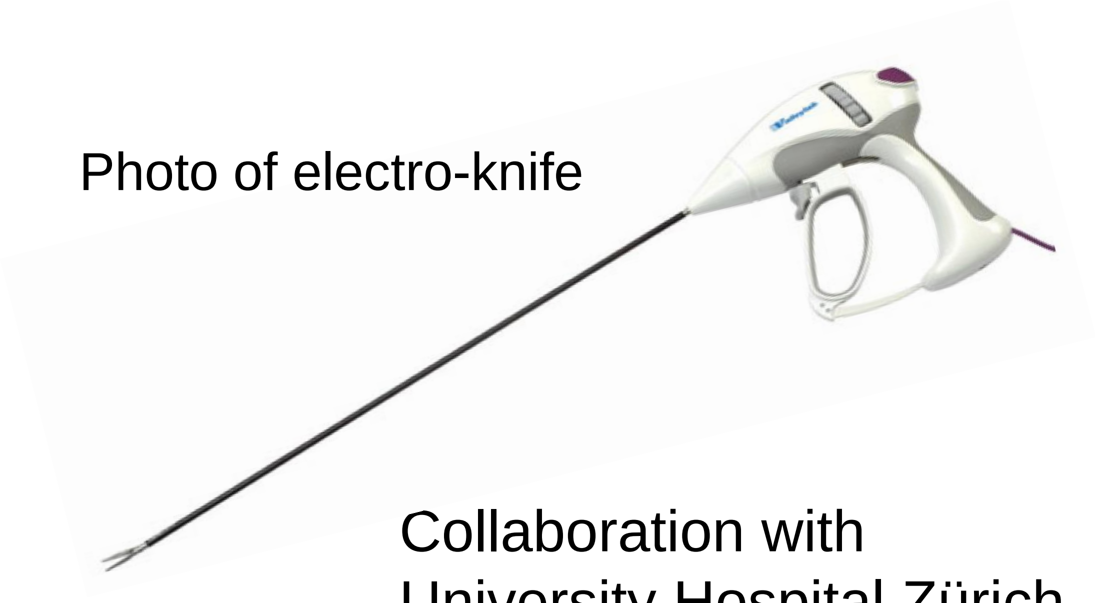
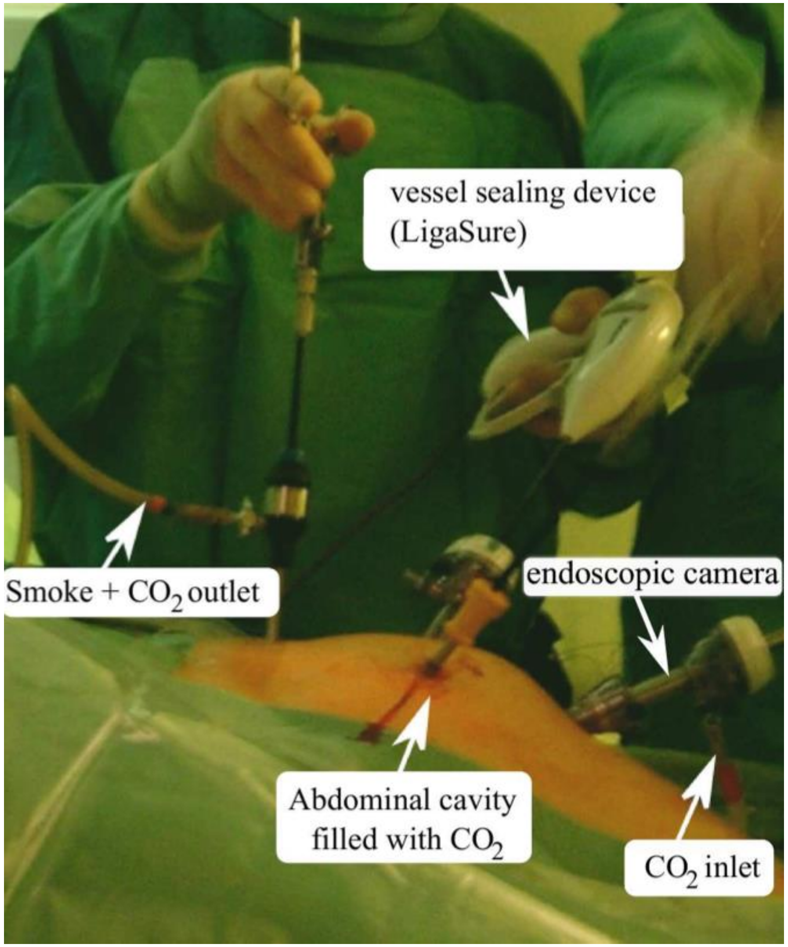
Surgical smoke : *in vivo* studies

Smoke produced during minimal-invasive surgery with electro-knives or lasers. Smoke samples are taken at the hospital, collected in Tedlar bags, followed by laser and FTIR spectroscopic analysis in our lab

Photo of electro-knife

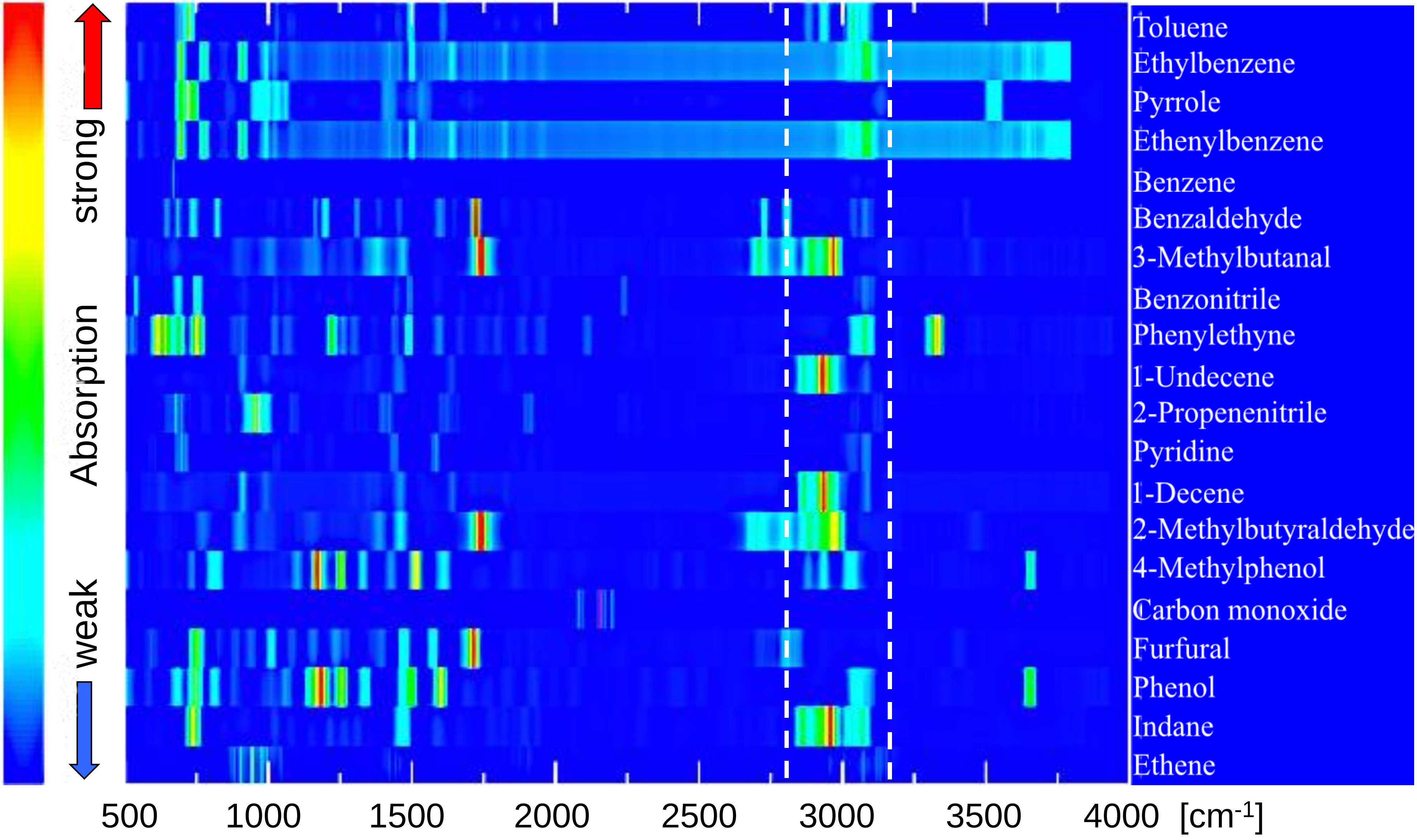


Collaboration with
University Hospital Zürich
(Dr. Dieter Hahnloser)



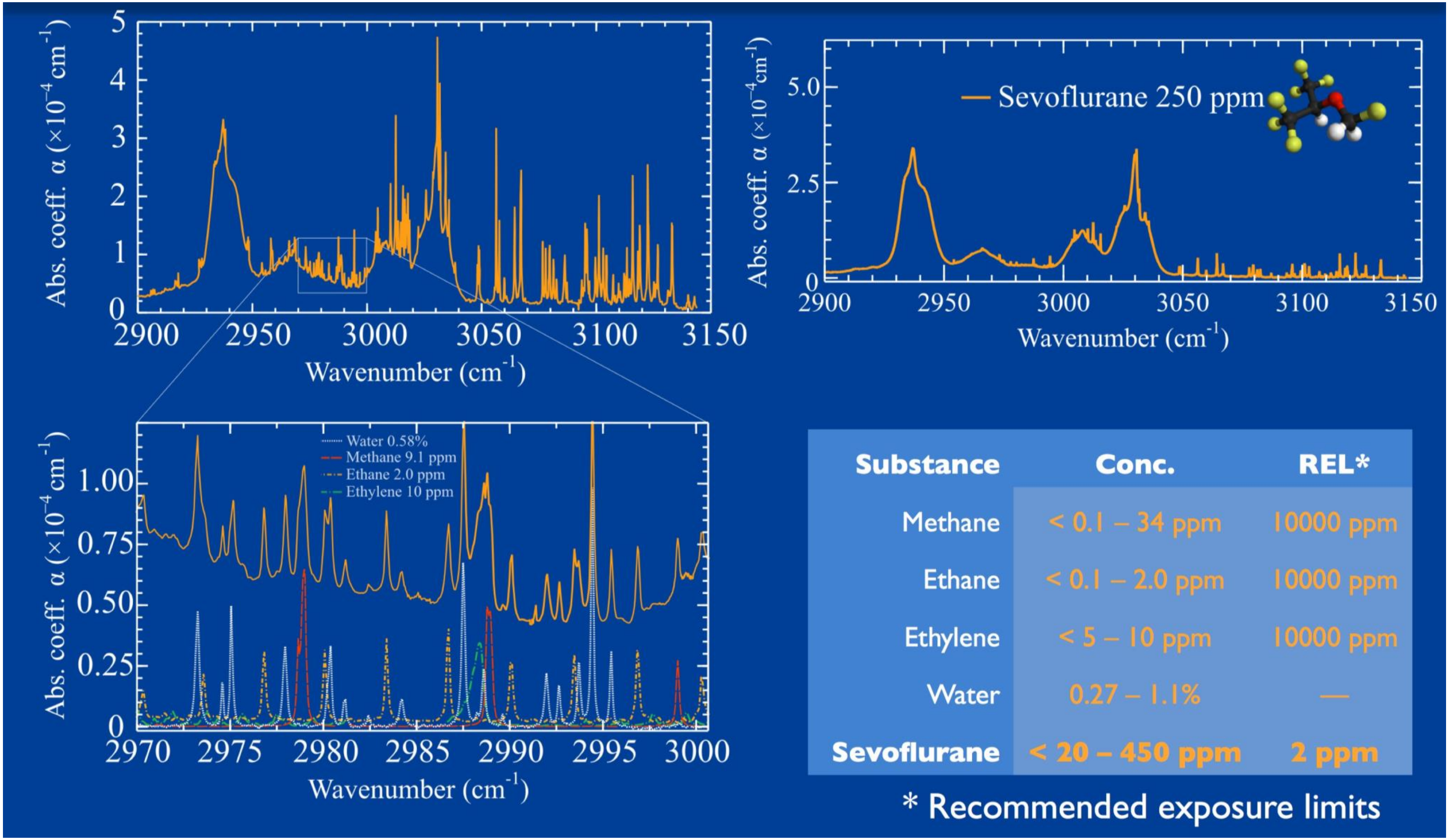
M. Gianella et al.: *Appl Phys. B* **109**, 485 (2012)
M. Gianella et al.: *Innov. Surgery* (20 June 2013)

Absorption ranges of species found in surgical smoke



Spectral analysisof surgical smoke

M. Gianella et al.: Appl. Spectr. **63**, 338-343 (2009)



Substance	Conc.	REL*
Methane	< 0.1 – 34 ppm	10000 ppm
Ethane	< 0.1 – 2.0 ppm	10000 ppm
Ethylene	< 5 – 10 ppm	10000 ppm
Water	0.27 – 1.1%	—
Sevoflurane	**< 20 – 450 ppm**	**2 ppm**

* Recommended exposure limits

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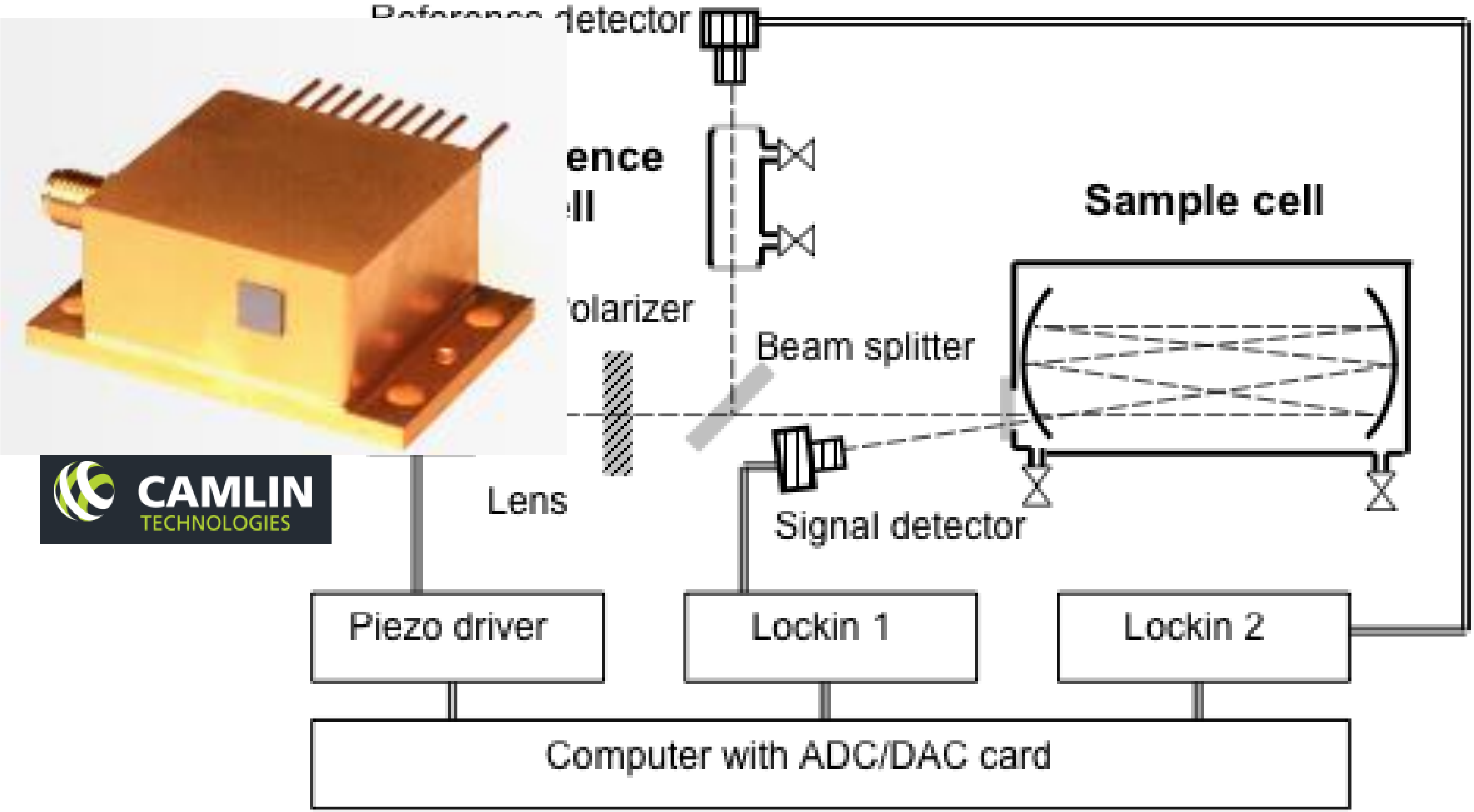
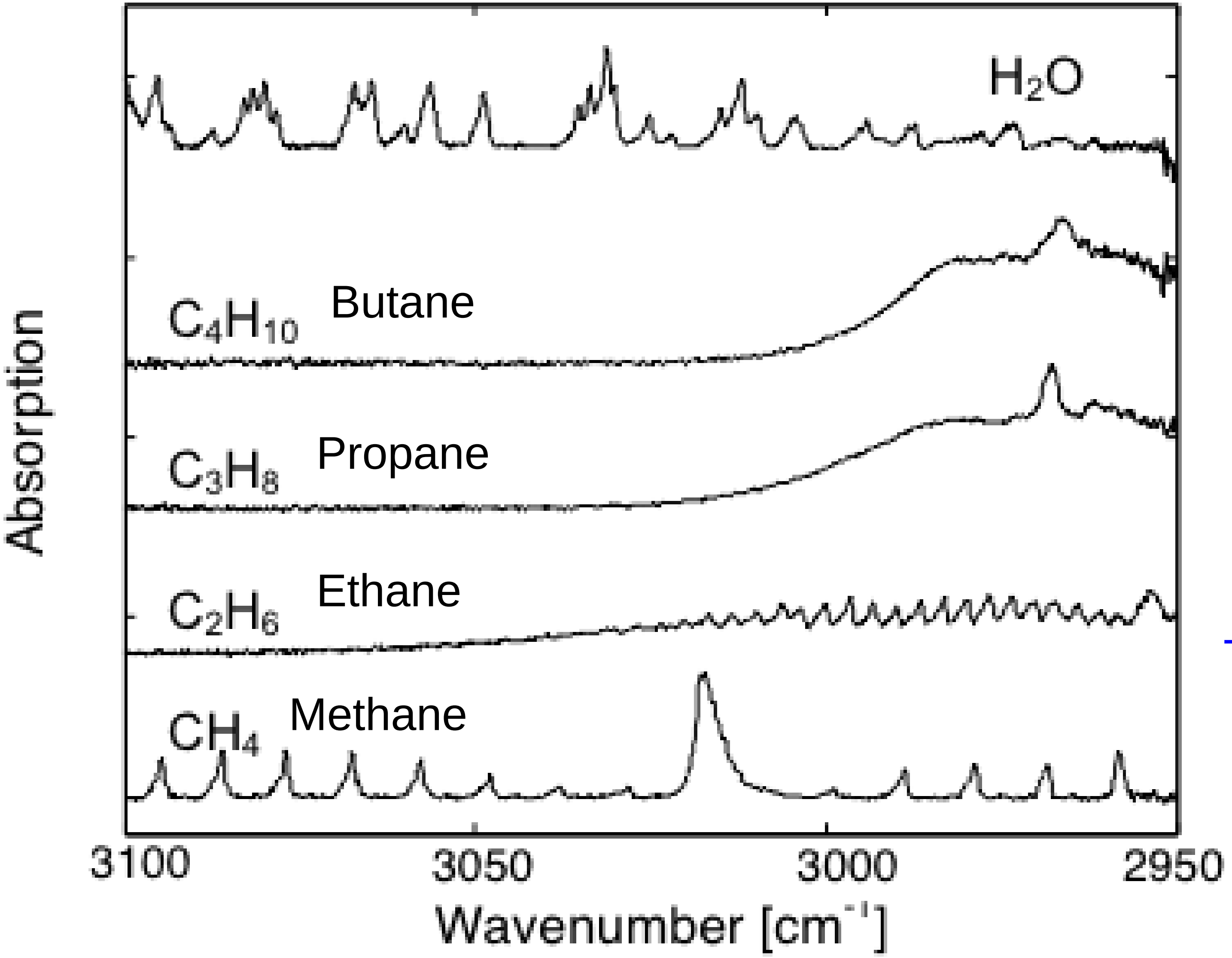
Experimental setup with VECSEL, sample and reference cell



Measured reference spectra of C_1 - C_4 alkanes



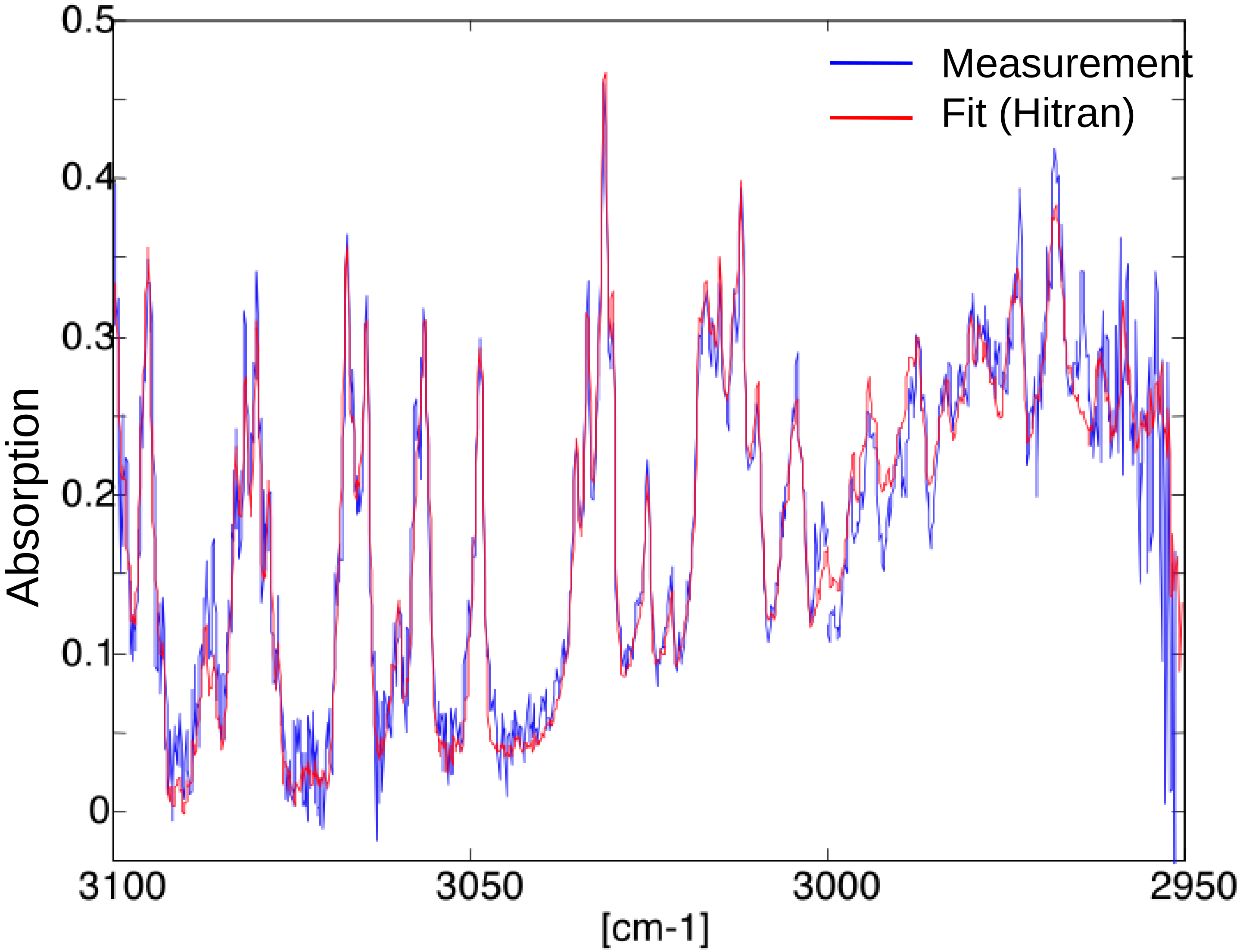
Individual gases buffered in N_2 at atm. pressure

averaged over 100 scans

Total acquisition Time: 200 s

Tuning by PZT voltage

Spectrum of mixture of C_1-C_3 alkanes and H_2O vapor



23 ppm methane
24 ppm ethane
20 ppm propane
1.7 %vv H_2O vapor
Buffer gas: N_2
atm. pressure

Measurement time
10 x 2 sec

Detection limit:
0.6 ppm

J. Rey et al.: Appl. Phys. B **117**, 935-030 (2014)

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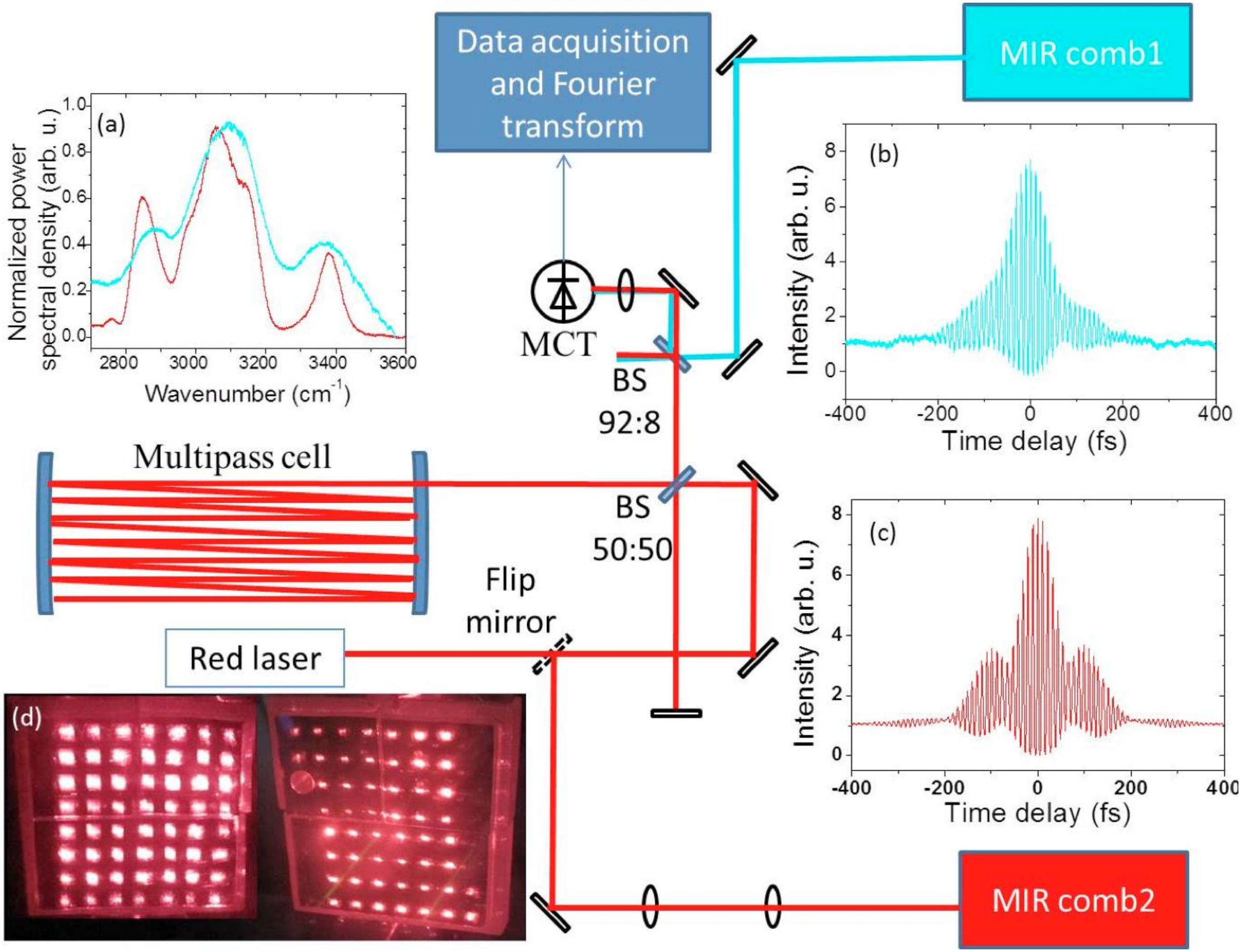
Mid-IR dual frequency comb spectroscopy



Combs based on
Er:fiber osc.
Rep rate: 250 MHz

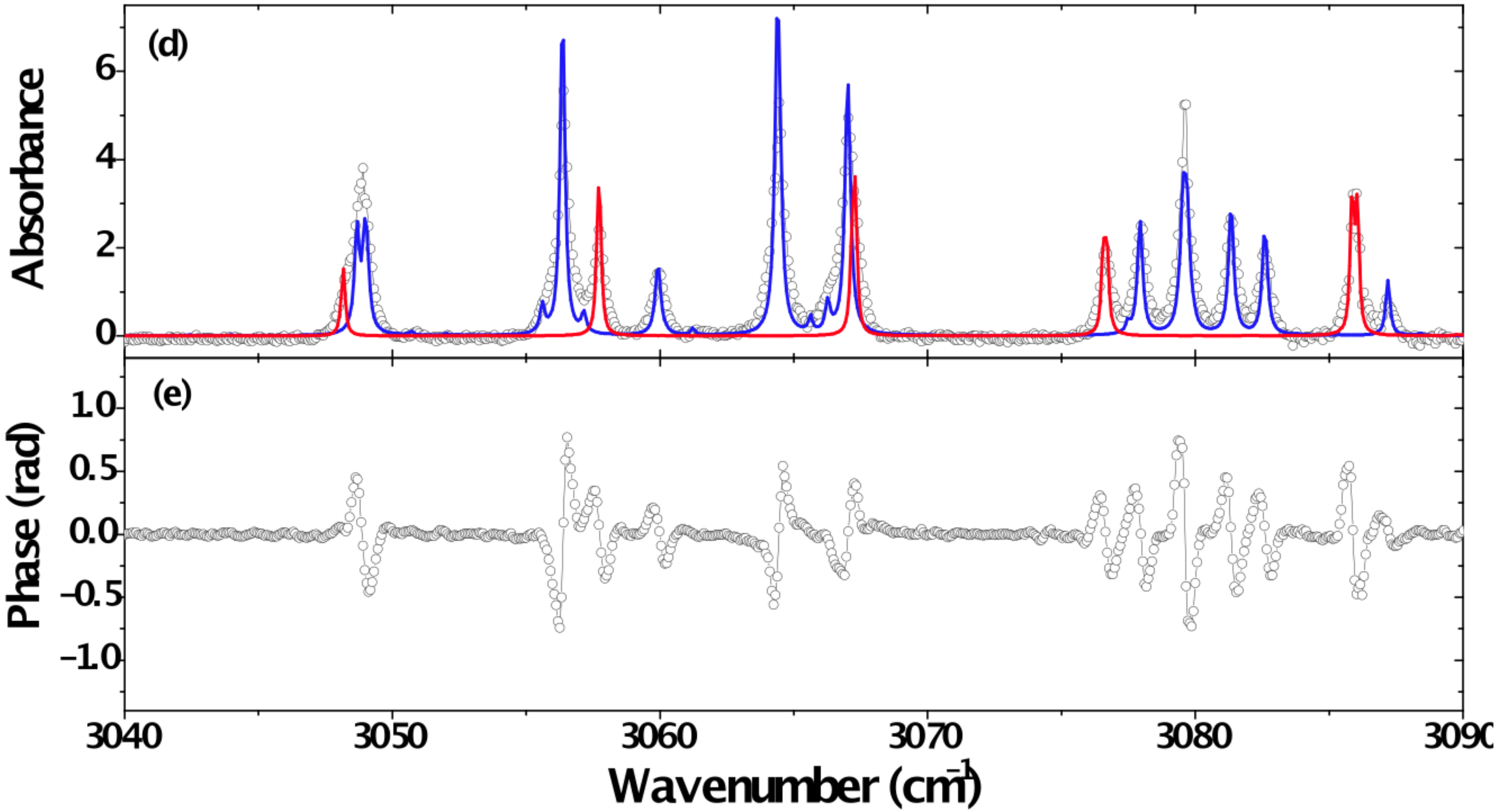
Comb1: 2.8-3.6 μm
120 mW, 80 fs

Comb2: 300 mW

Multipass cell:
580 m

F. Zhu et al.: Opt. Express (2015, to appear)

CH_4 and H_2O spectra of lab air



Comparison with HITRAN: 1.5 ppm CH_4, 1.3 % H_2O

LOD: 60 ppb CH_4 (80 ms, 580 m cell)

Conclusions

- Raman spectroscopy
  No tunable laser, only high conc., also homonuclear molecules

- Near-IR laser spectroscopy
  Low-cost diode laser, medium sensitivity

- Mid-IR Laser spectroscopy
  Strong molecular absorptions
  Broadly tunable laser sources: DFG, OPO, QCLs, new VECSELs

- QCL and OPO combined with QEPAS or cantilever PAS
  Miniaturization, measurements down to ppm-ppb level
  But only single gases, Interferences ? Gas pressure ?

- HDO in human breath: Isotope ratio measurements with DFG
  Enhanced deuterium content in breath for 1 month after ingestion of 5 mL D_2O, total body water

Conclusions and outlook

- DFG for **analysis** of surgical smoke

  Quantitative *in vivo* studies, identification of several gases (incl. anesthetic sevoflurane) at ppm level

- VECSEL analysis of C_1-C_4 alkanes

  ppm sensitivity, 10 scans à 2s = 20 s integration time

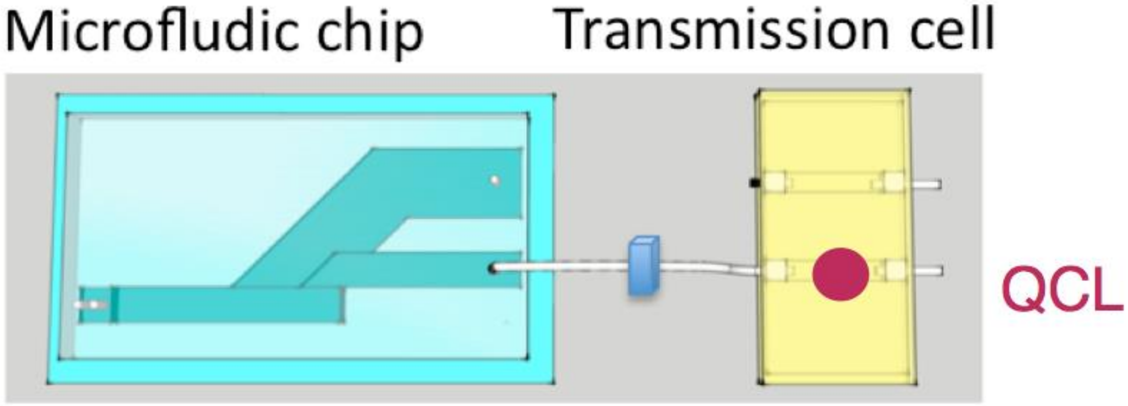
- Mid-IR frequency combs

  complex setup, sensitivity, analysis ?

→ **NO one-fits-all solution**

New lasers and detection schemes: smaller, cheaper, laser arrays

forensic applications



Quantitative detection
of cocaine in human saliva

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Thank you for your attention