Off-axis Integrated Cavity Output Spectroscopy for trace gas detection

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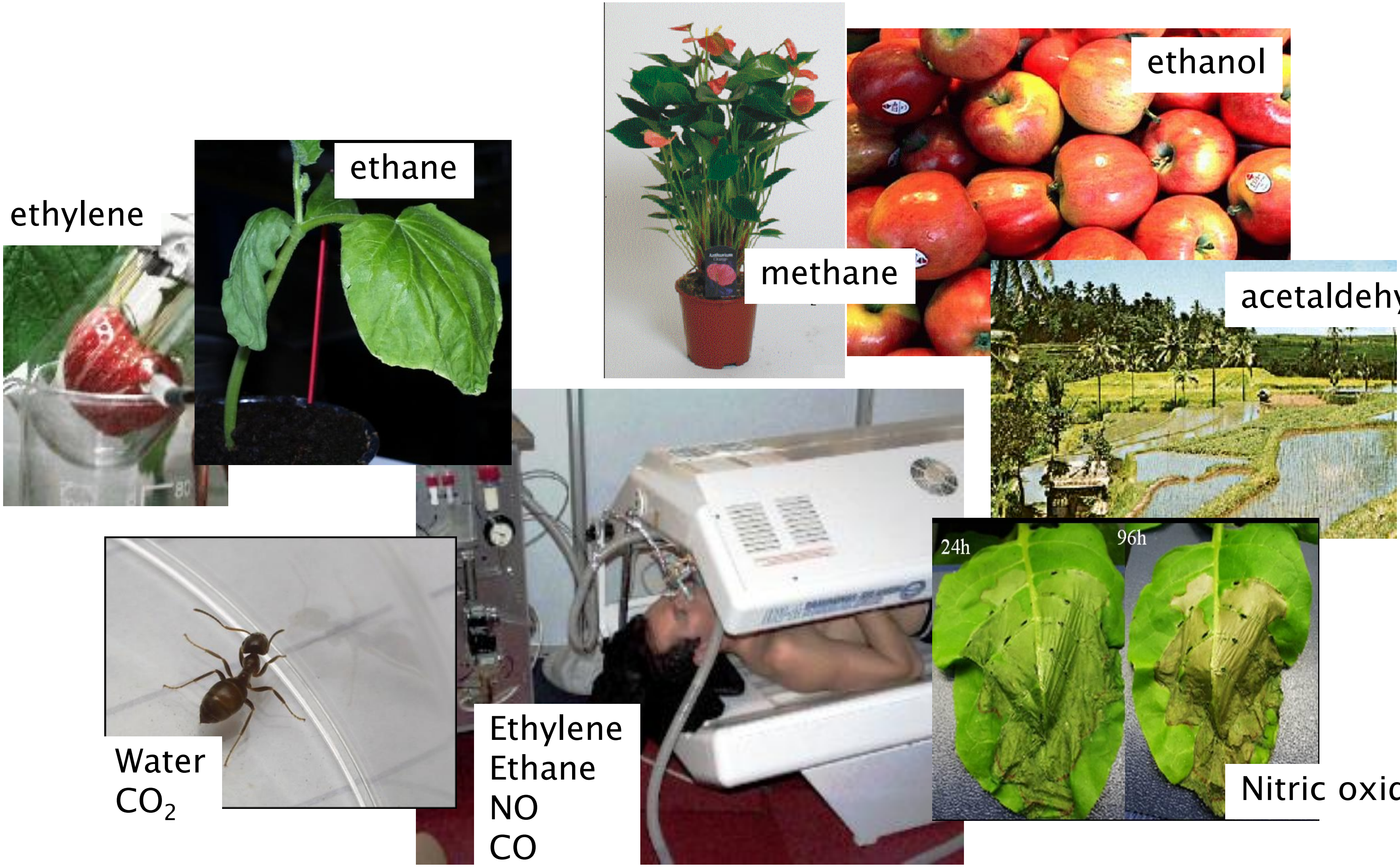
Life Science Trace Gas
Research Group

Motivation: Trace gas experiments



ethylene

ethane

methane

ethanol

acetaldehyde

Water
CO_2

Ethylene
Ethane
NO
CO
Acetone
HCN

Nitric oxide

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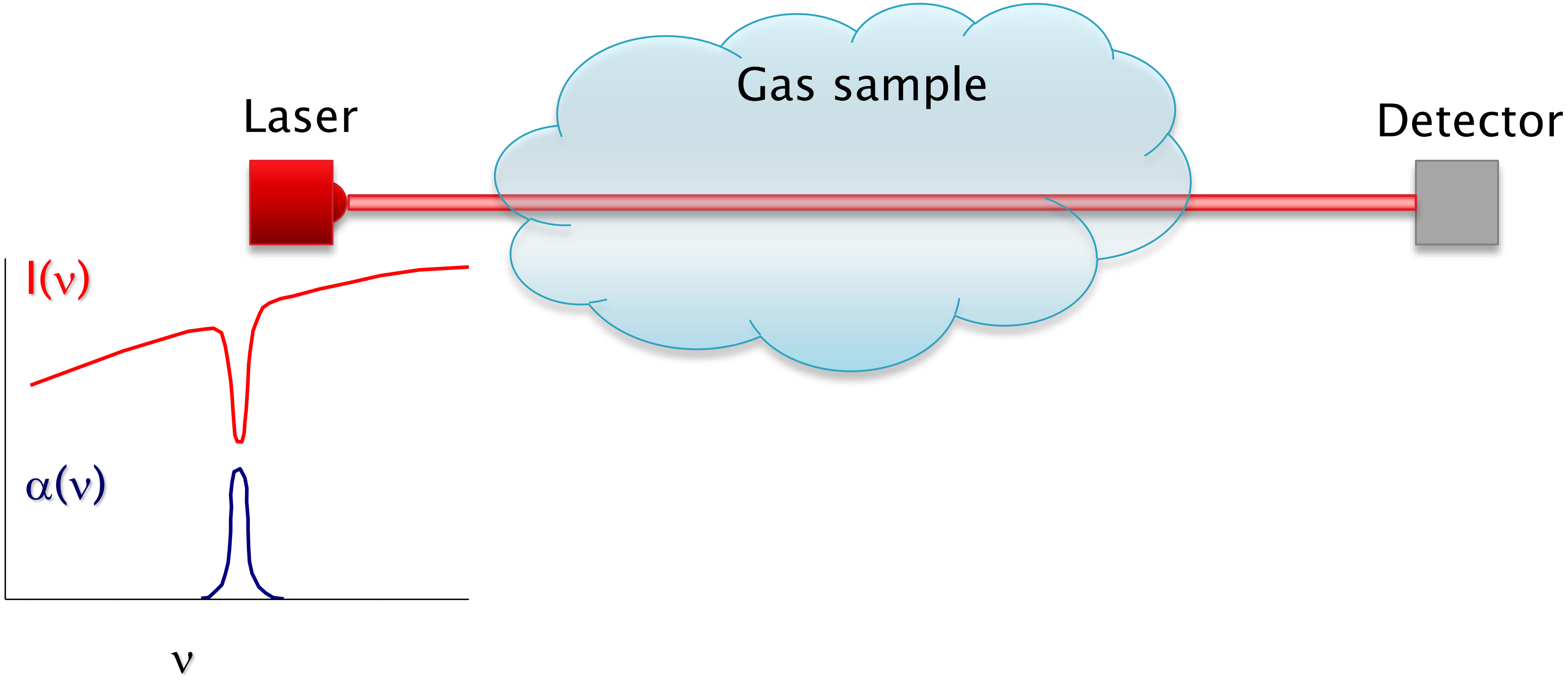
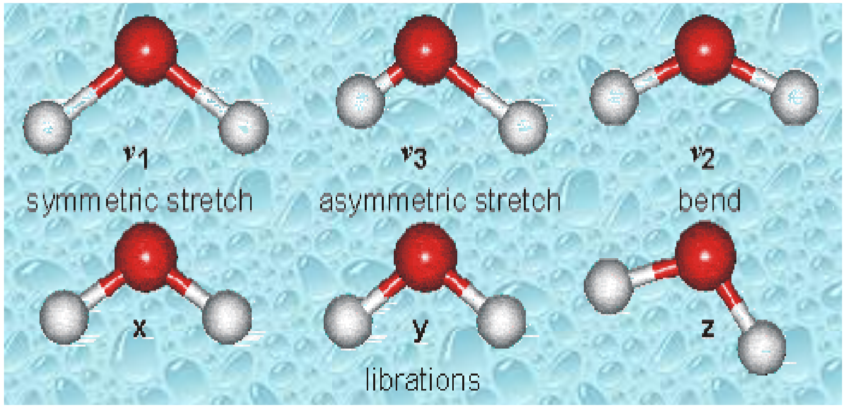
Laser spectroscopy on molecules





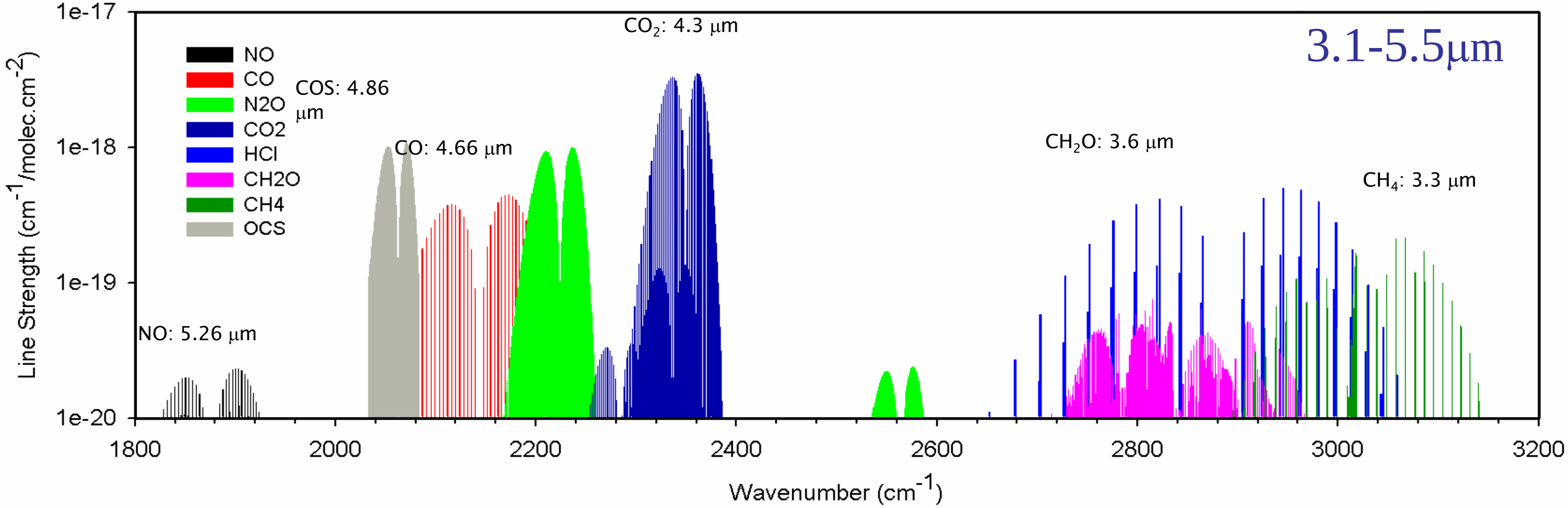
vibrations

Molecule with N atoms has 3N-6 vibrational normal modes

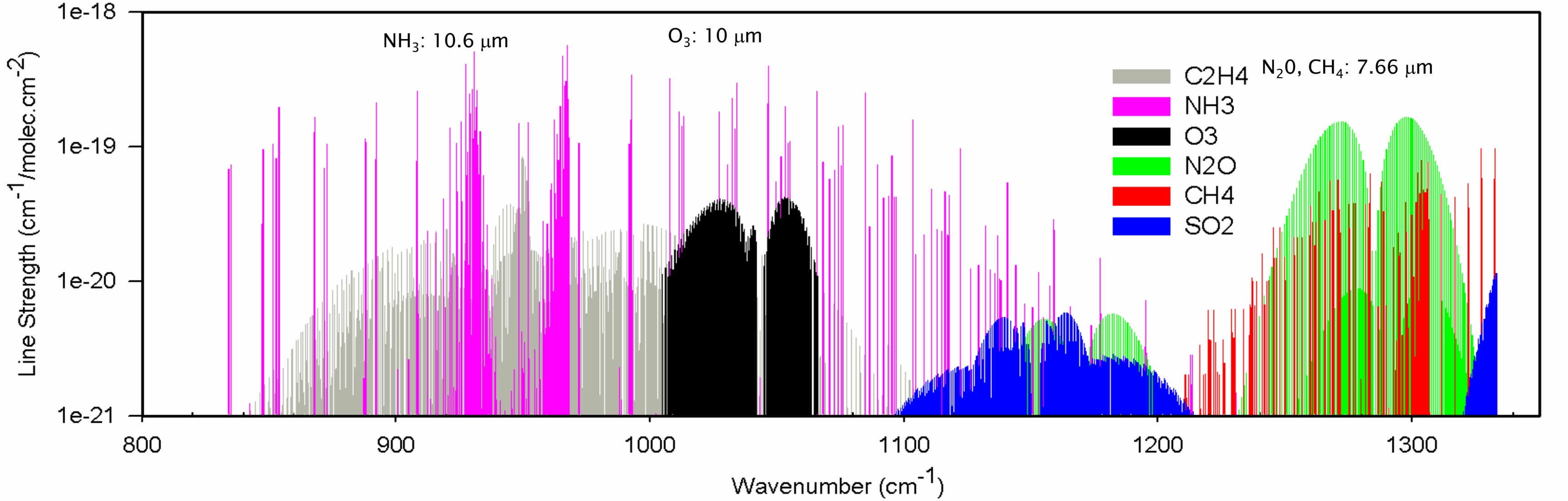
Rotations

Heavier atoms: Spectra become more compact and dense

Molecular spectral lines in the infrared



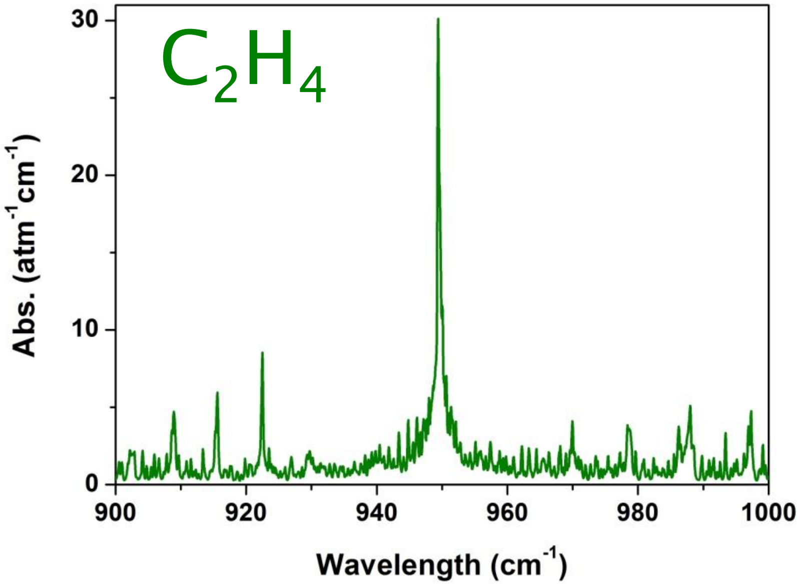
7.6-12.5 μm



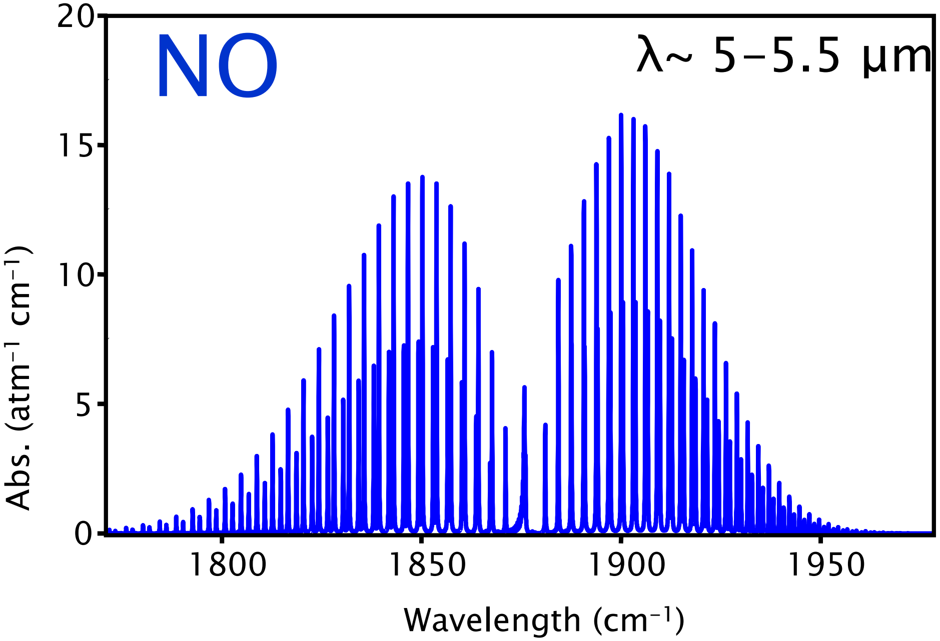
Frank Tittel et al.

Selectivity

λ~10–11 μm

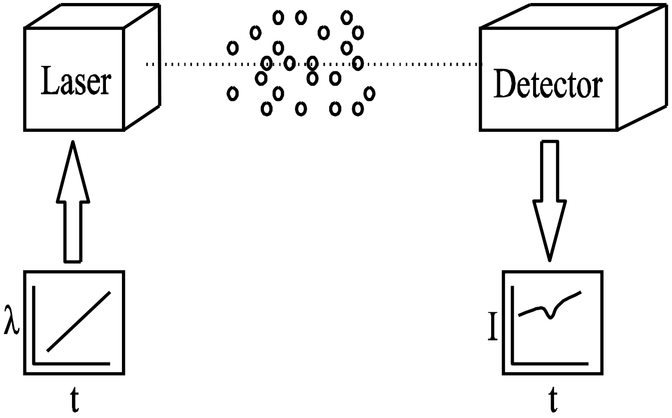


Each molecule has its own “fingerprint” absorption spectrum



Spectroscopy is very selective

Absorption



Lambert–Beer law:

Relates the absorbance α to a measurable quantity of relative change in intensity

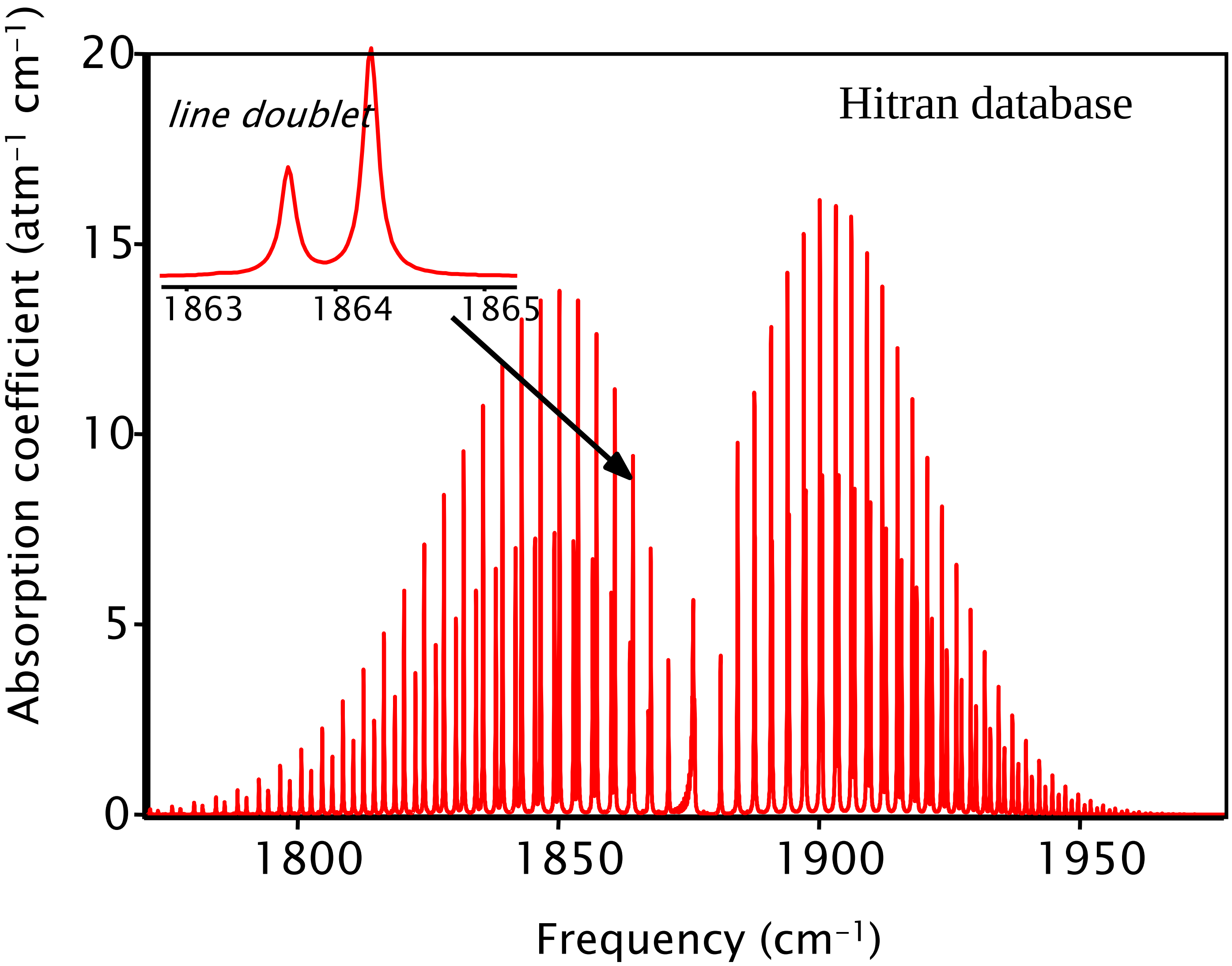
$$I_t = I_0 e^{-\alpha(\nu)} \quad or: \quad \alpha(\nu) = -\ln\left(\frac{I_t}{I_0}\right)$$

$$\alpha(\nu) = S \cdot g(\nu,\nu_0) \cdot n \cdot L \quad = \sigma \cdot n \cdot L$$

S	line strength connecting ground and exited states
$g(\nu,\nu_0)$	normalized line shape function (Gaussian, Lorentzian)
ν	frequency light source,
ν_0	line center frequency molecule
n	density of the molecules (molecules per unit volume).
L	effective optical path length

The product $\sigma(\nu)=S \cdot g$ has the dimension of [m^2] (or [cm^2])and may be viewed as a cross section for absorption of a photon

NO absorption spectrum



Example

$$I_t = I_0 e^{-\sigma n l} = I_0 e^{-\alpha}$$

Loschmidt number at 1 atmosphere and $0^{\circ}C \Rightarrow 2.686 \times 10^{25}$ (molecules/m^3)

σ : absorption crossection (cm^2)

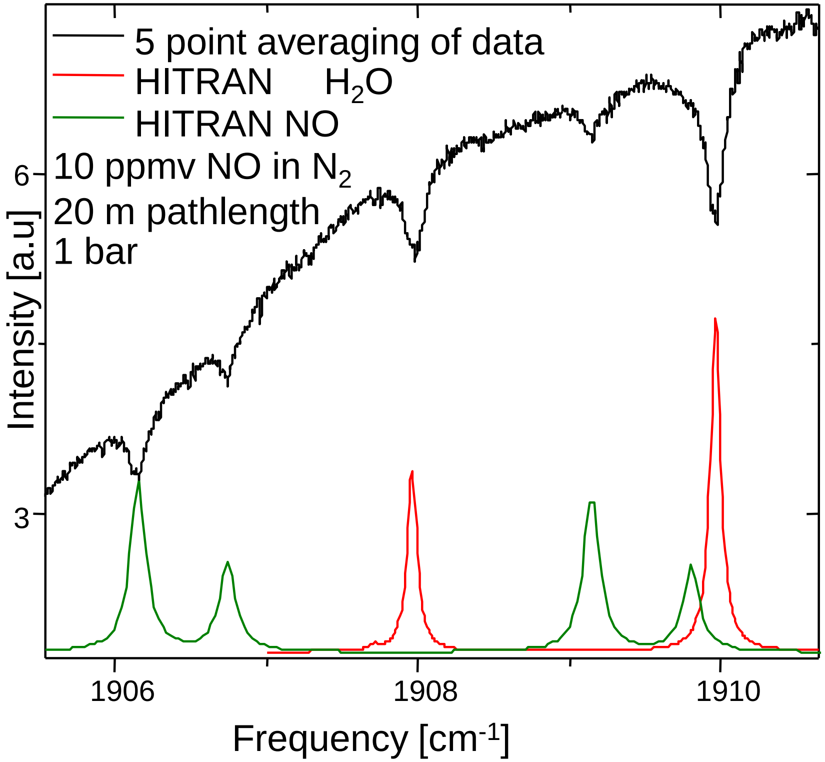
n = N (volume mixing ratio) x Loschmidts number ($2.686 \cdot 10^{19}$ molecules/cm^3)

1 ppmv is just detectable using 9 s integration

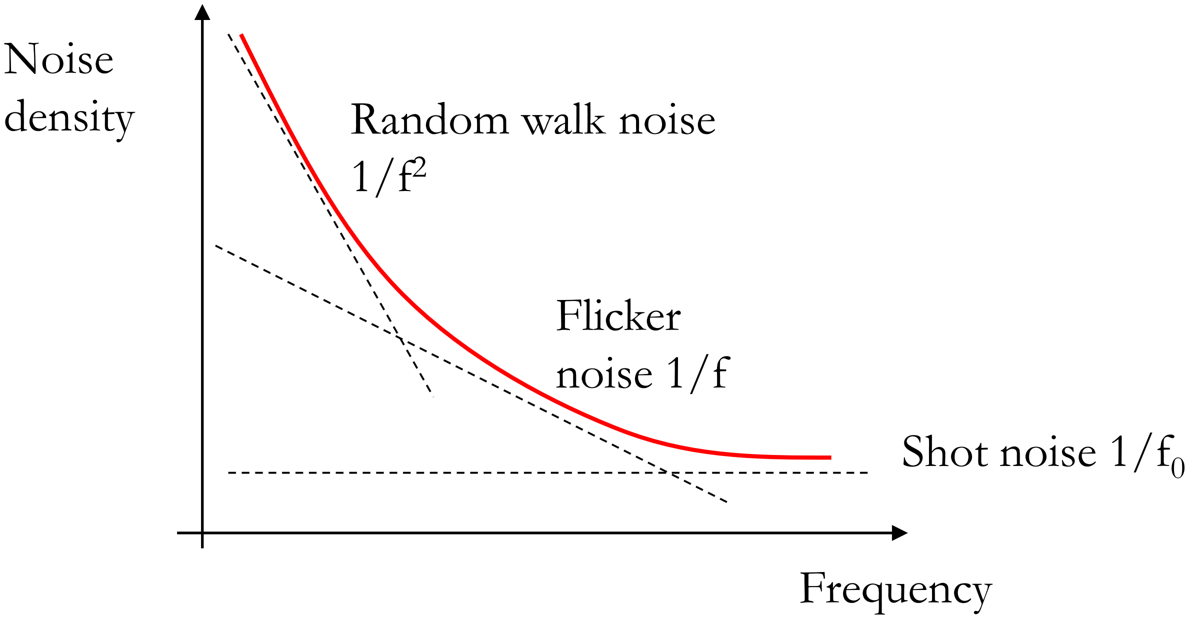
$\sigma = 4.4 \times 10^{-19}$ cm^2

$l = 2000$ cm

$\alpha_{min} = 0.024$ in 9 s



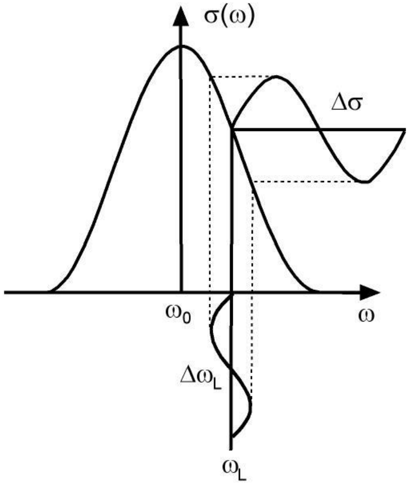
Noise

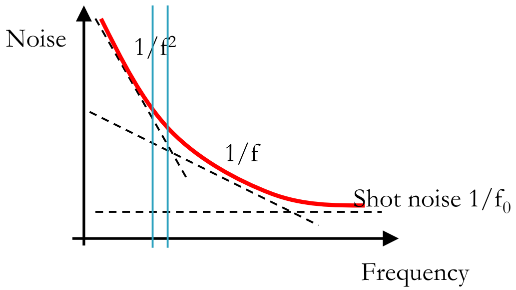


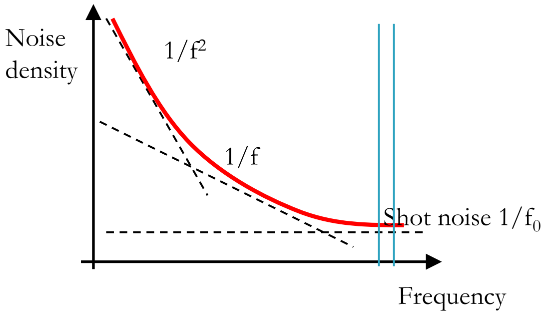
In most experiments technical noise sources, such as vibration of components in the lab, overwhelms the shot noise and degrades the sensitivity by many orders of magnitude

Improve sensitivity by modulation

- Modulate a parameter
  (e.g. laser wavelength, laser intensity)
- Use lock-in amplifier to isolate modulated signal
  from the noise
  (phase-sensitive detection- band pass filter)
- Zero baseline technique - measuring derivative
- Detection at high frequency,
  low 1/f noise → high signal-to-noise ratio





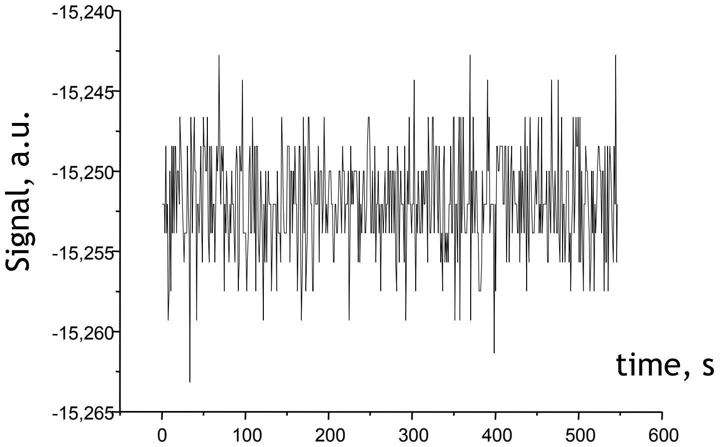


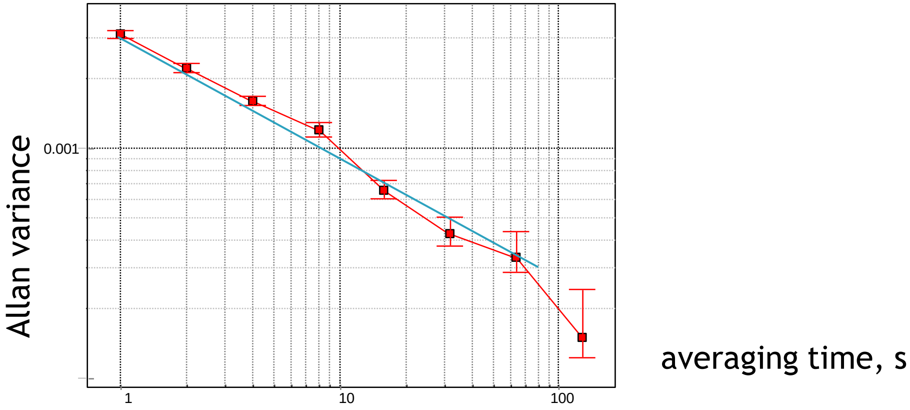
Allan variance to characterize the signal drift in laser spectroscopy

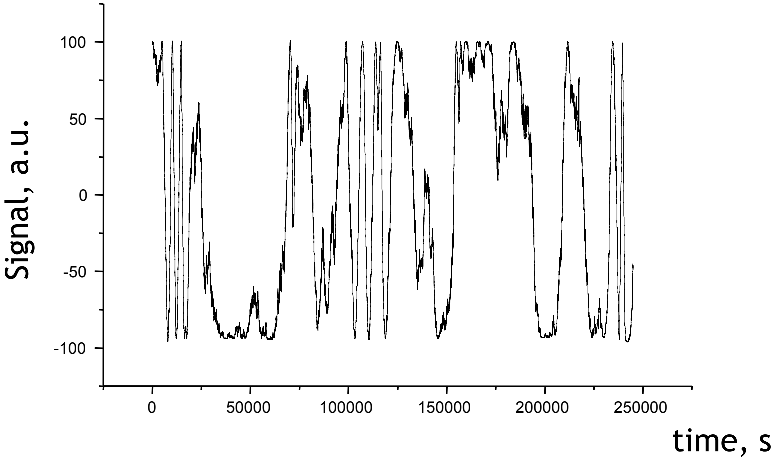
The Allan variance: known as two-sample variance

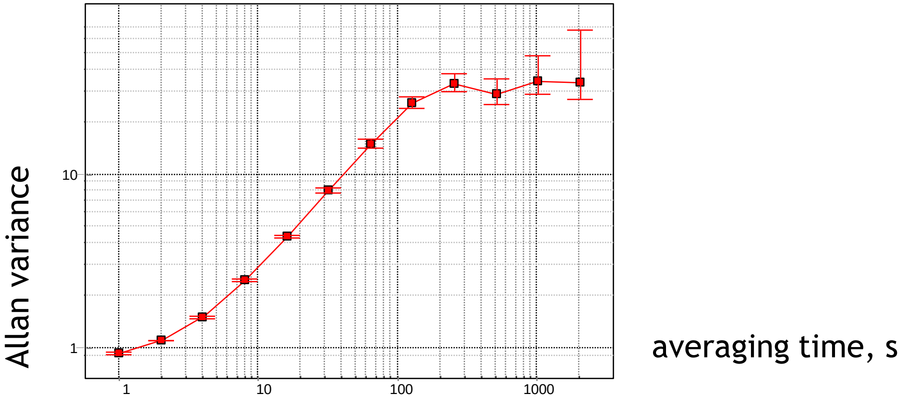
$$\sigma_y^2(\tau) = \frac{1}{2}\left\langle \left(\bar{y}_{n+1} - \bar{y}_n\right)^2 \right\rangle$$

is a measure of stability in clocks, oscillators, amplifiers,etc









P. Werle, Appl. Phys. B 102(2011) 313–329

How to compare complete detection systems?

Independent measuring time (sec)

½ second integration time gives an output bandwidth of 1 Hz

The SNR improves as the square root of the averaging time

For 9 s integration time gives factor $(18)^{1/2}$ SNR improvement

$$\text{Minimal detectable absorption (MDA)} \equiv \frac{(\alpha)_{\min}}{\sqrt{B}}$$

Minimal detectable absorption (MDA) = $\alpha_{\min} \text{x} (B)^{-1/2} = 0.024 \text{x} (18)^{1/2} = \boxed{1 \text{x} 10^{-1} \text{ Hz}^{-1/2}}$

Independent path length (sensitivity per cm)

Length = 2000 cm

Noise Equivalent Absorption Sensitivity

$$NEAS = \frac{MDA}{L} = \frac{(\alpha)_{\min}}{L\sqrt{B}}$$

NEAS =MDA/Length= $\boxed{5 \cdot 10^{-5} \text{ cm}^{-1} \text{ Hz}^{-1/2}}$

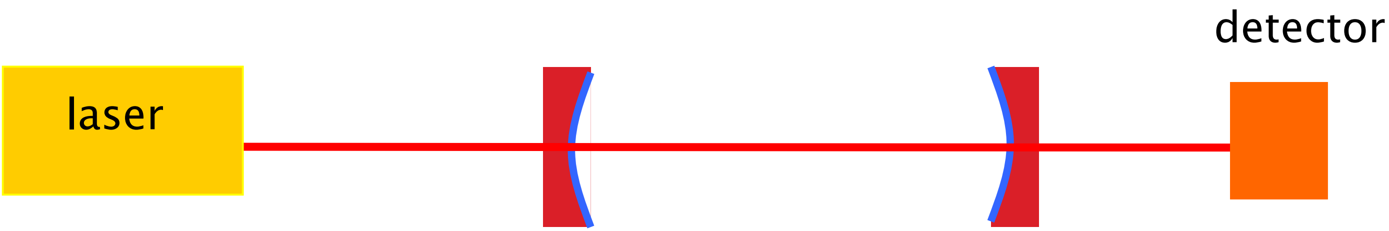
Methods for increasing sensitivity

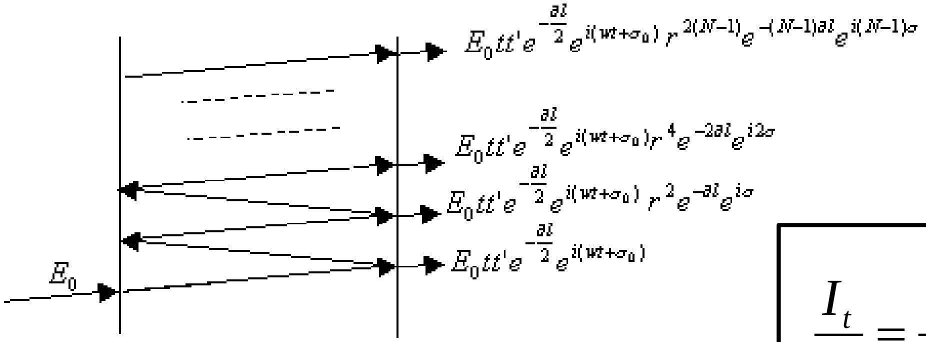
$$\alpha(\nu) = S \cdot g(\nu,\nu_0) \cdot n \cdot L \quad = \sigma \cdot n \cdot L$$

	Noise Equivalent Absorption Sensitivity ($\mathrm{cm^{-1}Hz^{-1/2}}$)
Direct absorption	10^{-5}
Wavelength modulation spectroscopy	10^{-8}
Cavity Ring Down Spectroscopy	10^{-11}
Integrated Cavity Output Spectroscopy	10^{-11}
Photoacoustic Spectroscopy	10^{-9}
Laser Induced Fluorescence	10^{-8}
NICE-OHMS	10^{-14}

Increasing effective path length: use optical cavities

interference of light within a Fabry-Perot cavity





$$\boxed{\frac{I_t}{I_0} = \frac{1}{1+F\sin^2(\delta/2)} \qquad \frac{I_r}{I_0} = \frac{F\sin^2(\delta/2)}{1+F\sin^2(\delta/2)}}$$

with $F = \dfrac{4R}{(1-R)^2}$ coefficient of Finesse

and δ phase of the light

Longitudinal modes cavity

$$\boxed{\frac{I_t}{I_0} = \frac{1}{1 + F\sin^2(\delta/2)}}$$

$$F = \frac{4R}{(1-R)^2}$$

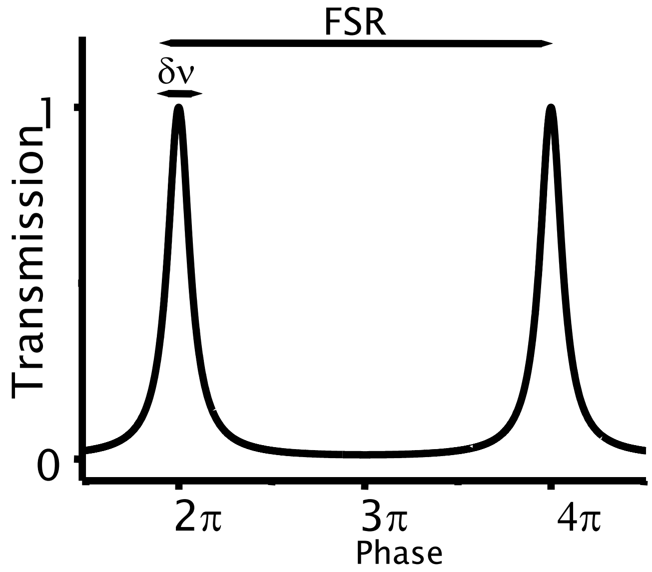
$$\delta = 4\pi\, n\, d \cos\Theta / \lambda$$

Maximum transmission at :

$\sin(\delta/2) = 0$ or $\delta = 2m\pi$

$\Delta\nu = \dfrac{c_0}{2nd}$ Free Spectral Range

$$\boxed{\text{Finesse } \Im = \frac{\Delta\nu}{\delta\nu} = \frac{\mathit{Free\ Spectral\ Range}}{\mathit{FWHM}} = \frac{\pi\sqrt{F}}{2}}$$



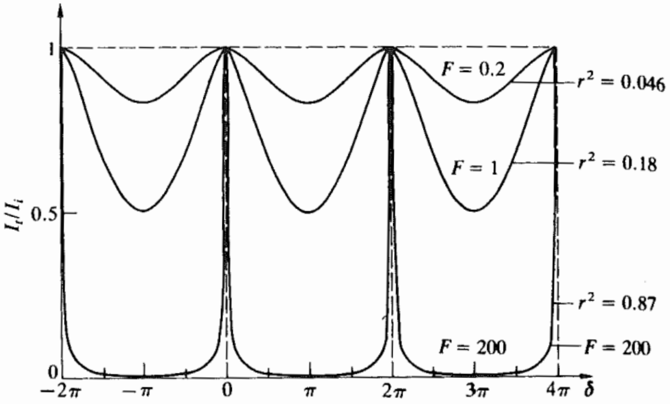
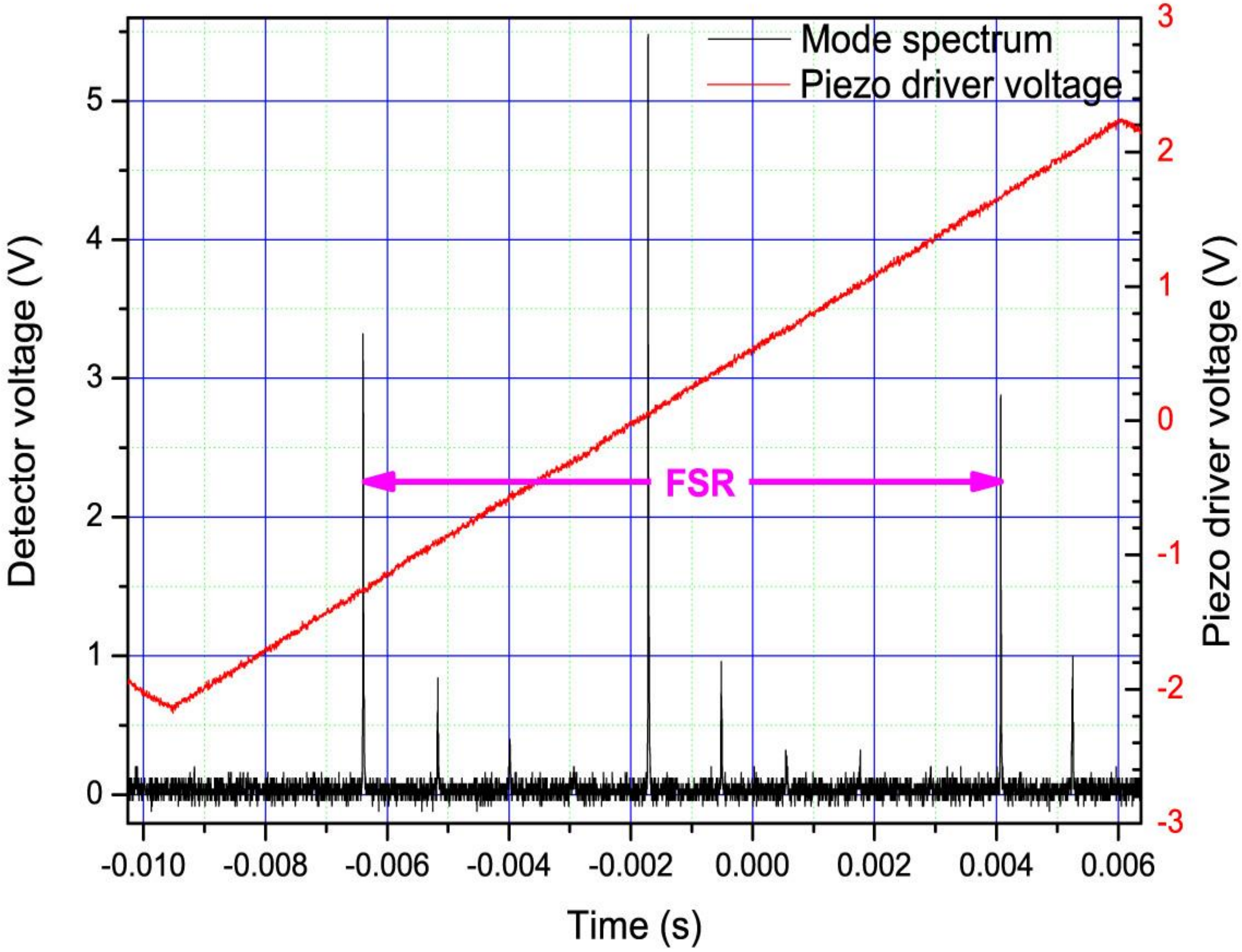


Figure 9.41 Airy function.

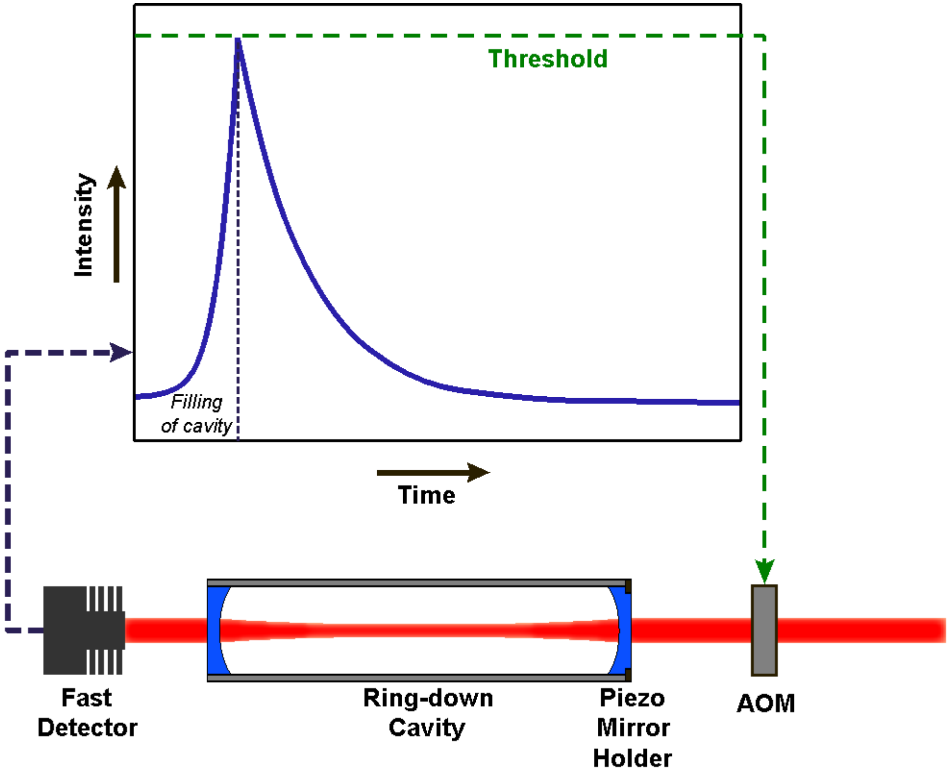
Specifications cavity

R=0.99963 => F=18480 FSR=250 MHz $\Delta\nu$ = 14 kHz



Cavity Ring Down Spectroscopy

$$\boxed{\frac{1}{\tau(\nu)} = \sigma(\nu) n c + \underbrace{\frac{c(1-R)}{L}}_{1/\tau_0}}$$



Effective path length:

$$\left.\begin{array}{r} l_{eff} = \dfrac{L}{1-R} \\[2ex] R{=}99.99\%,\ L{=}0.5\ \text{m} \end{array}\right\} \Rightarrow l_{eff} = 5\ \text{km}$$

- Power independent
- Result: absorption

Isolating n:

$$n = \frac{1}{\sigma(\nu)} \frac{1}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right)$$

Quantification of amount of substance in gas:
development of metrology standard

Needed: faster continuous scanning combined with sensitive detection

Which detection scheme?

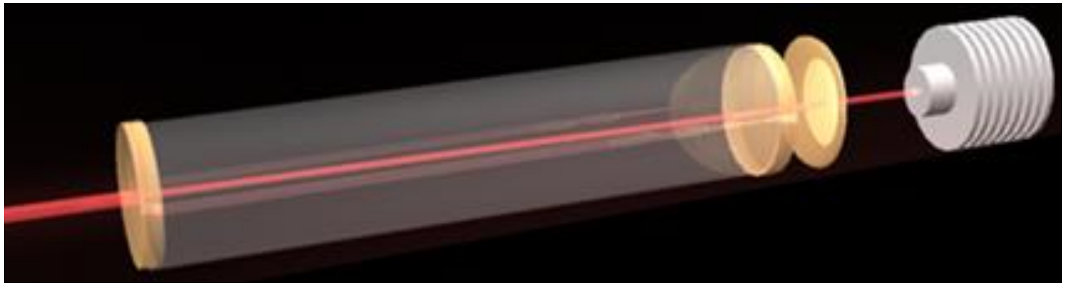
- CRD spectroscopy slow : 60 s to cross absorption line
- Use: Integrated Cavity Output Spectroscopy in its Off-Axis configuration (OA-ICOS)

Fast sampling approach:
Integrated Cavity Output Spectroscopy

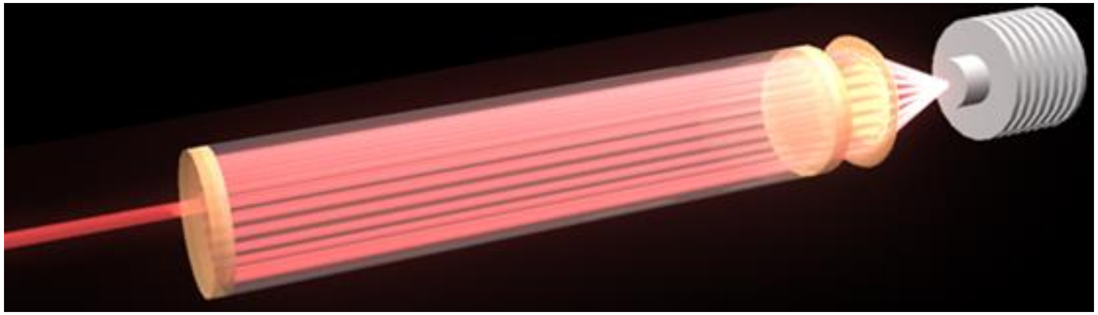
R=0.9998; Finesse=18480

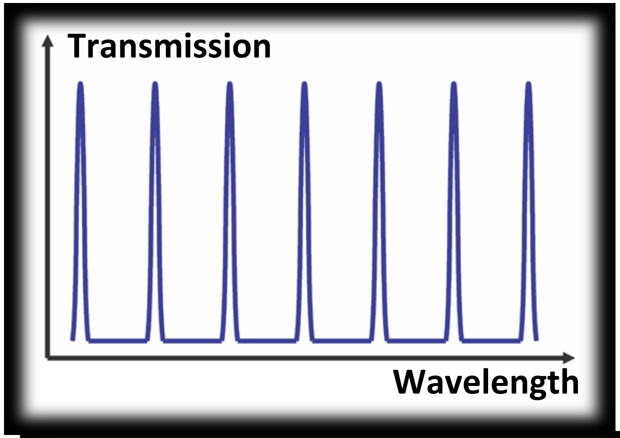
FSR=250 MHz $\Delta\nu$ = 14 kHz

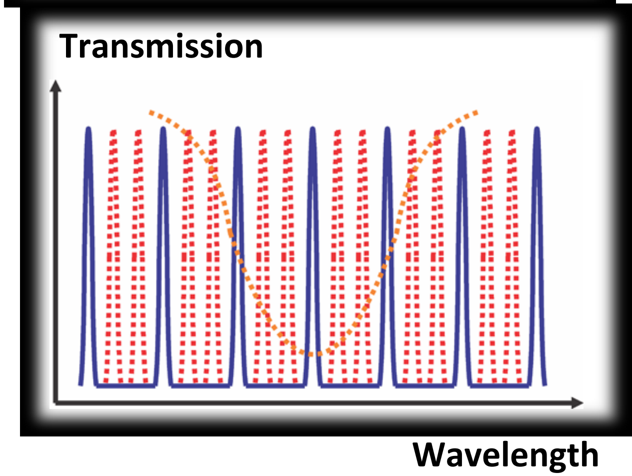
On-axis



Off-axis





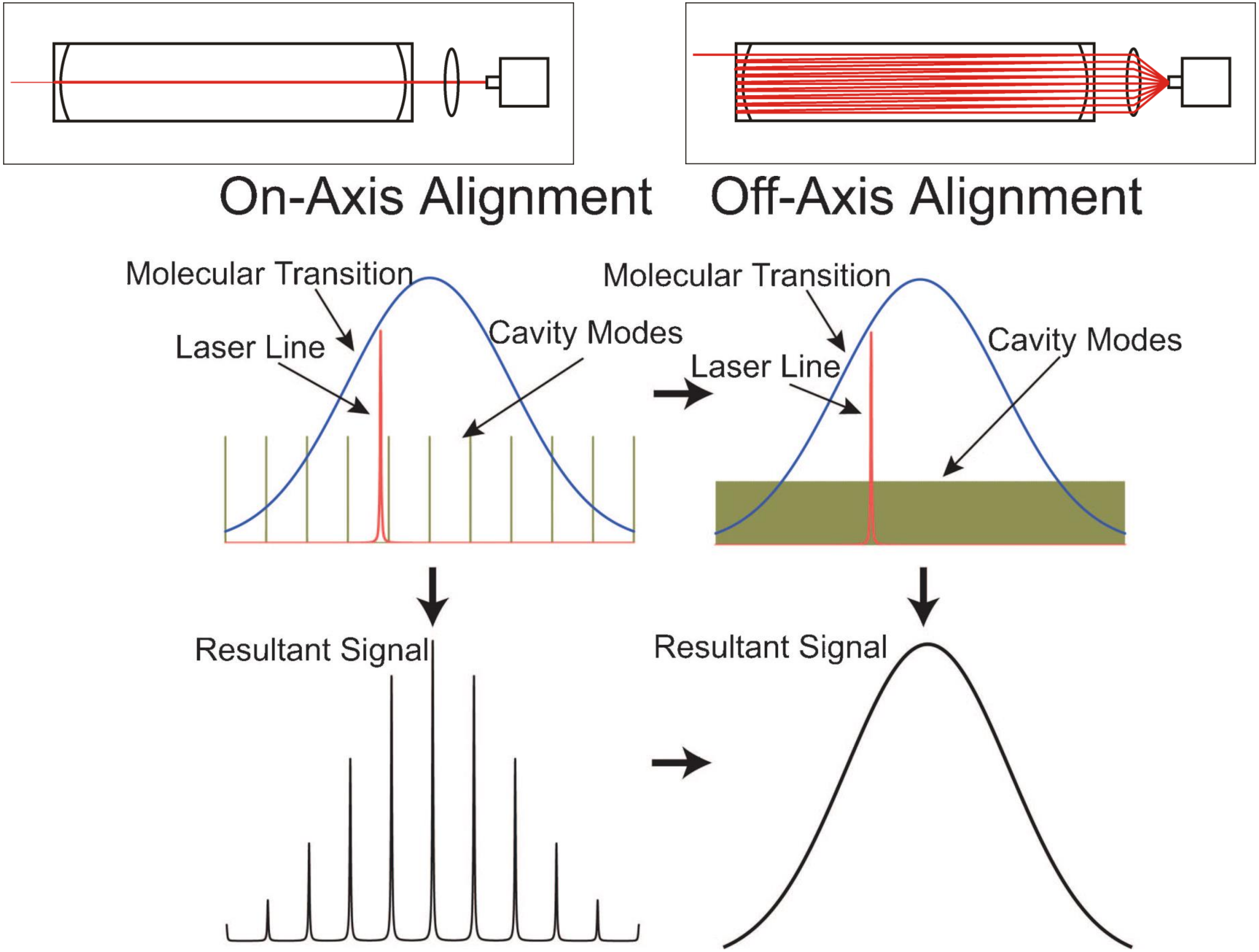


On-axis: Free Spectral Range

Off-axis: Multiple reflections before returning original position ➔ FSR collapses

- many cavity modes exist under molecular transition

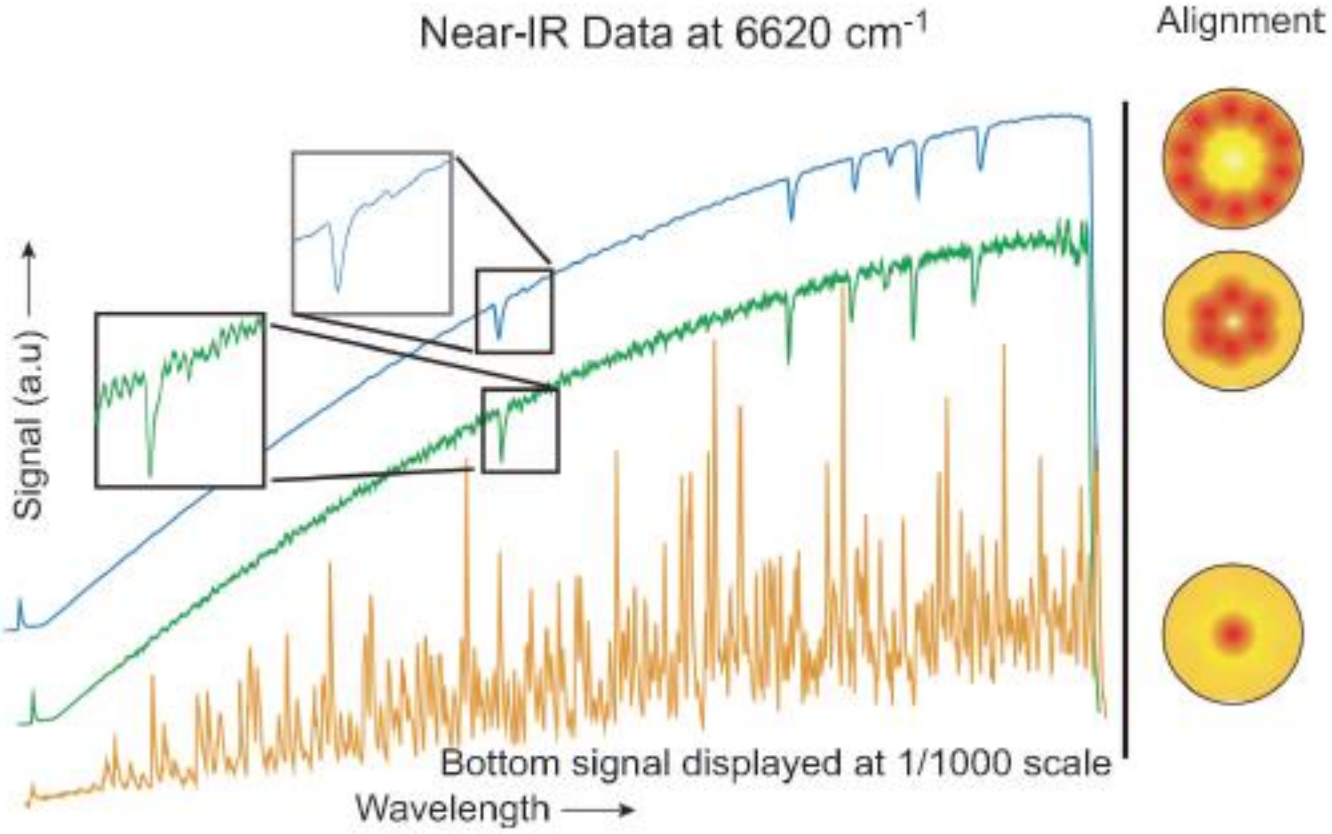
Integrated Cavity Output Spectroscopy



Engel et al., Applied Optics 45 (2006) 9221

Off-axis ICOS

Robust alignment at the cost of cavity throughput power



Engel et al., Applied Optics 45 (2006) 9221

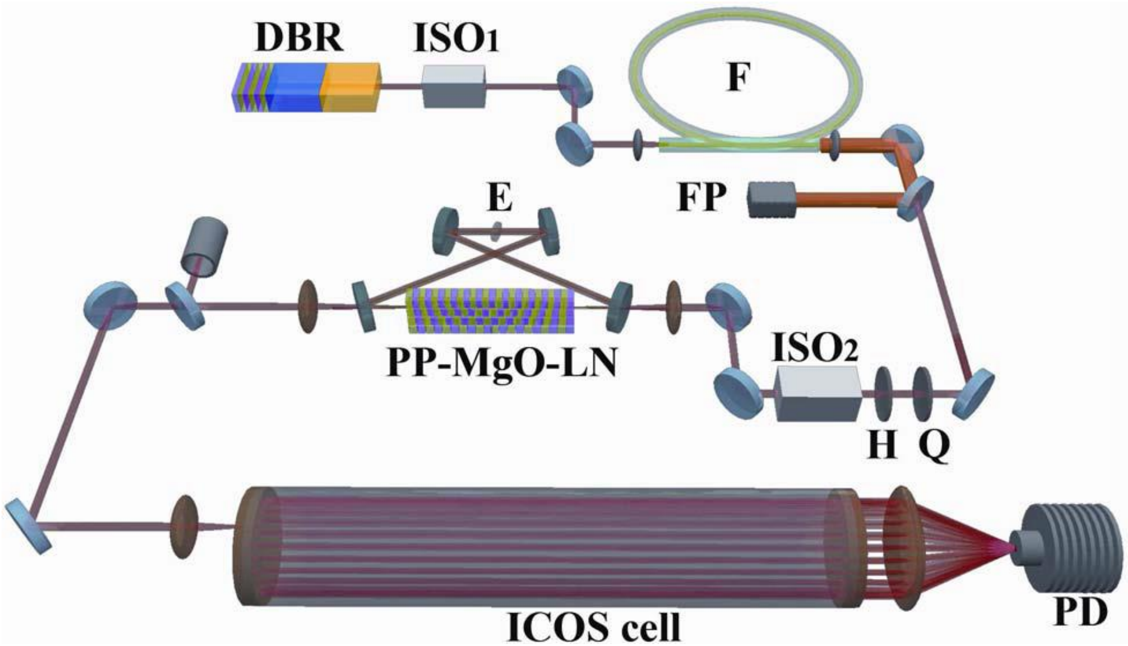
Detection with infrared Optical Parametric Oscillator

Singly-Resonant, cw OPO

Tuning range: 2.75-3.83 µm and 1.47-1.73 µm, 1 Watt

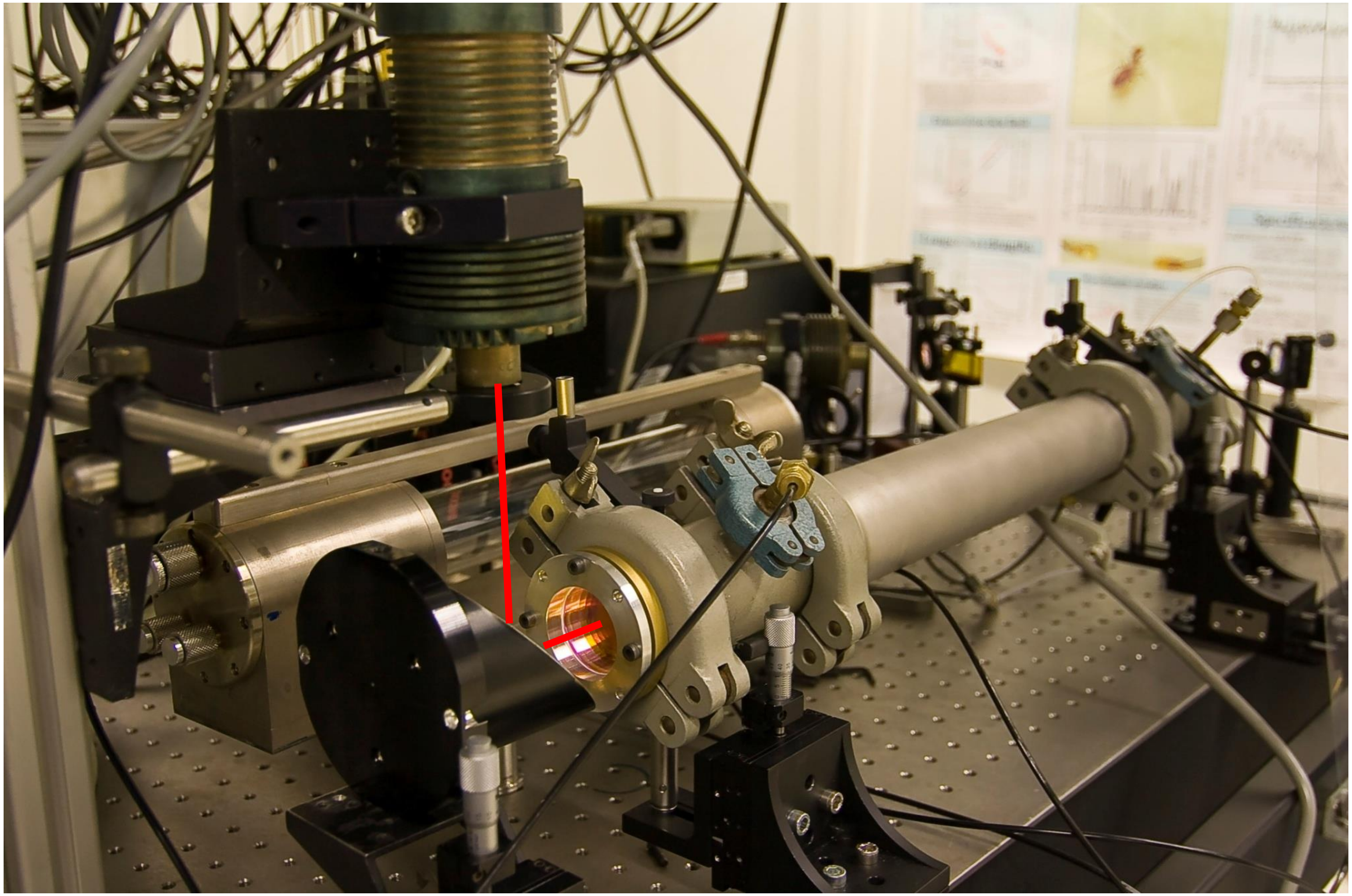
Pump system:

DBR diode laser: 80 mW, 1082 nm, 40 MHz linewidth,
Scan speed up to 100 THz/s; End-pumped fiber-amplifier: 25 W, 976 nm



Ngai et al., Appl. Phys. B, 85 (2006) 173–180

Experimental set-up

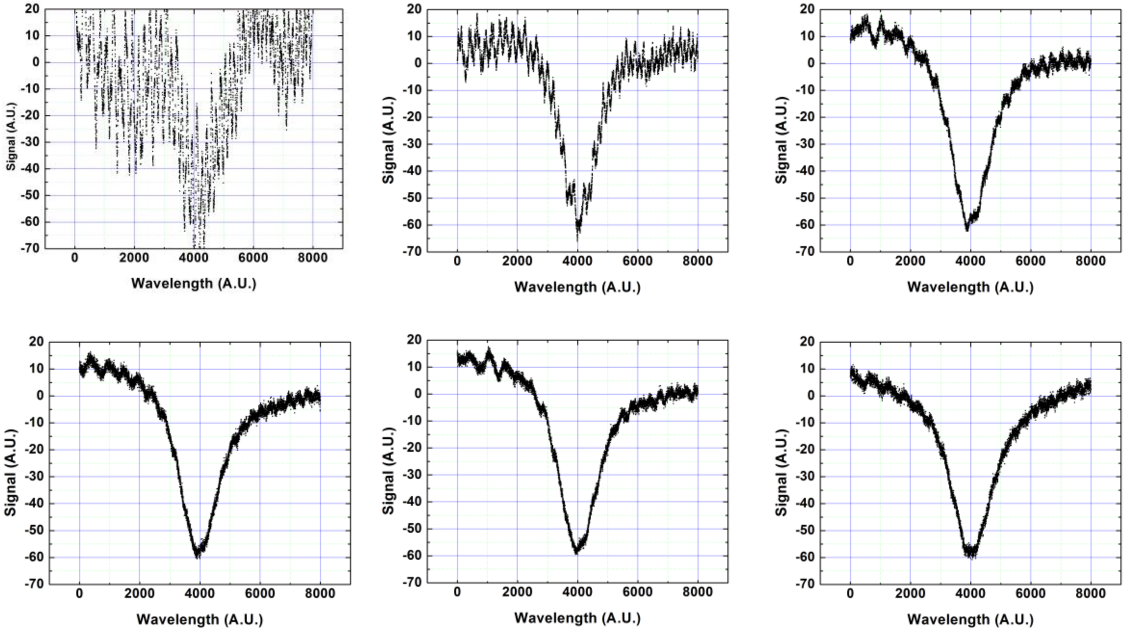


How is the S/N ratio changing with off-axis parameter?

20 ppbv C_2H_6 at 2997 cm^{-1}

2 inch mirrors
pressure 170 mbar
scanning rate 1 KHz

~0 mm 7 mm 14 mm



21 mm 28 mm 35 mm

1 ppbv of C_2H_6, at 2997 cm^{-1}, 250 mbar

1 inch mirrors

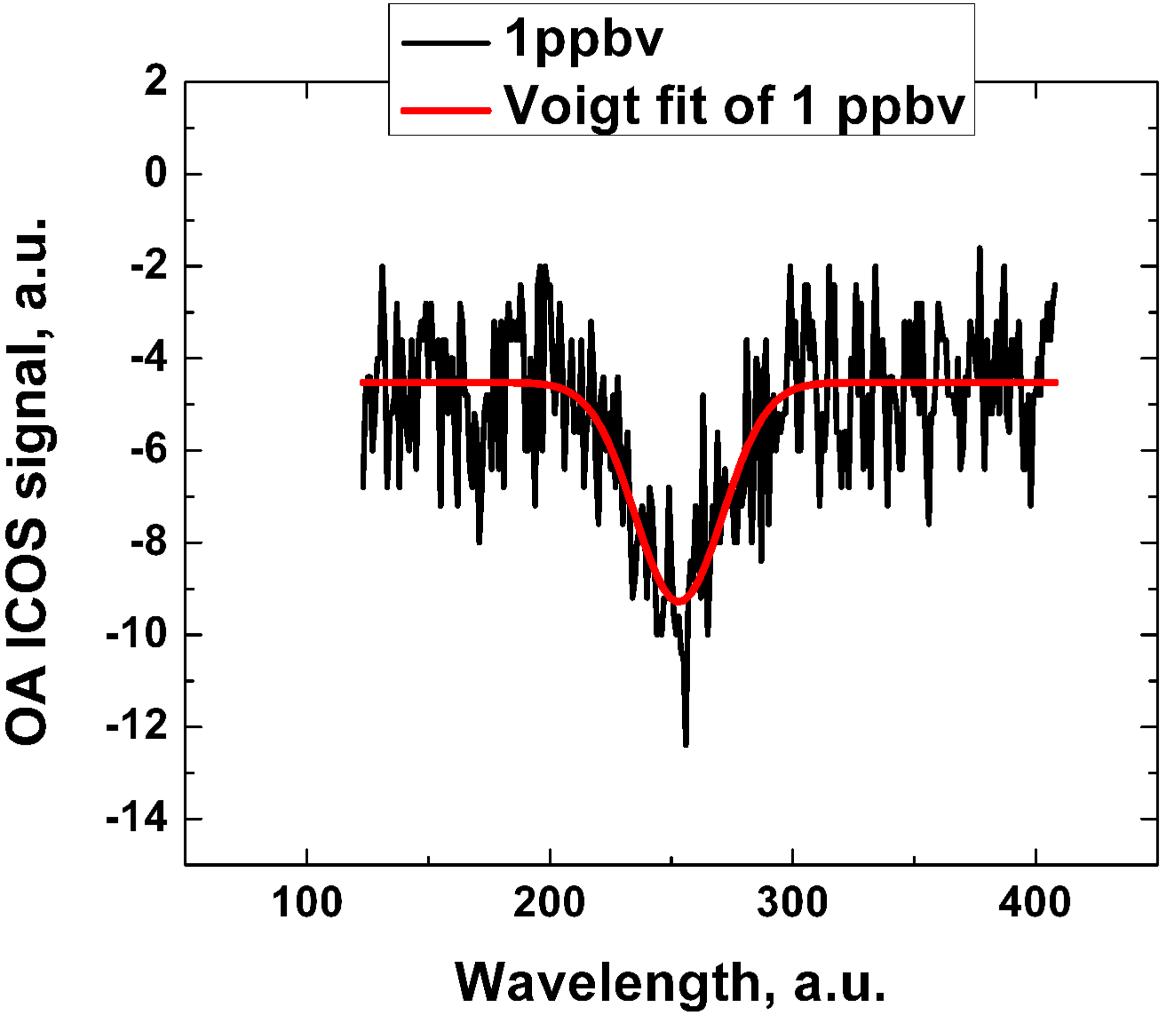
R=99.98%

P= 250 mW

100 Hz scanning rate

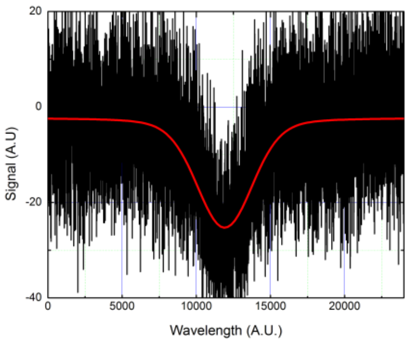
250 averages

2.5 s integration time

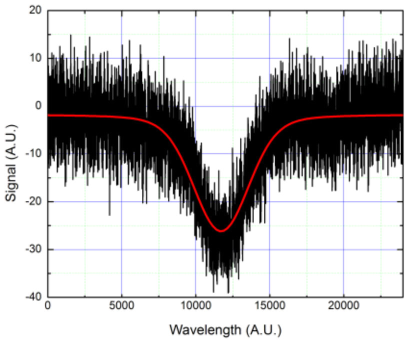


How is the S/N ratio with scan speed?

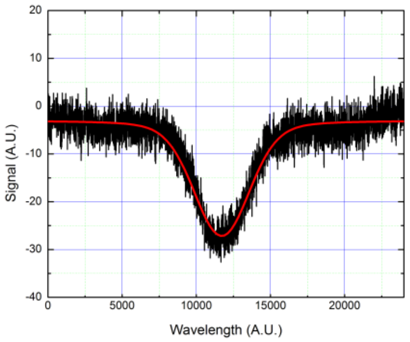
20 ppbv C_2H_6 2997cm^{-1}



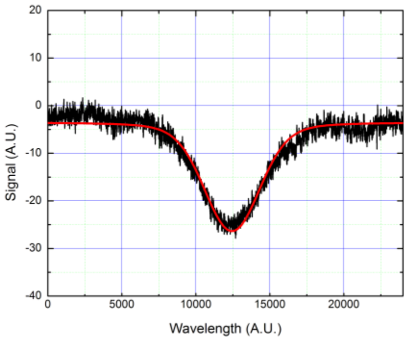
32 Hz



125 Hz



500 Hz



2000 Hz

20 mm off-axis

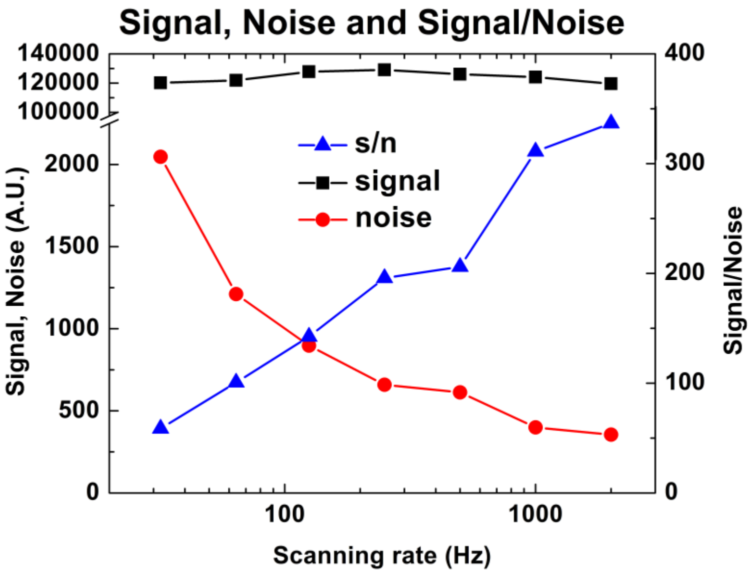
pressure 170 mbar
P = 500 mW

Fixed integration
time ~ 0.25 s

How is the S/N ratio with scan speed?

20 ppbv C_2H_6 2997cm^{-1}

20 mm off-axis



Noise-equivalent detection limit: 50 pptv in 0.25 s (1 kHz)

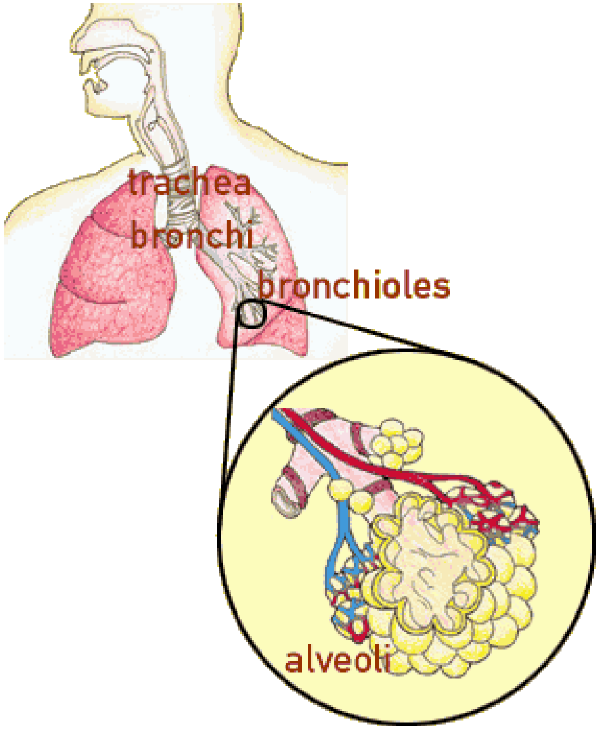
MDA =1.7x 10^{-6} Hz$^{-1/2}$
NEAS = 4.8 x 10^{-11} cm^{-1}Hz$^{-1/2}$

Arslanov et al, Opt. Lett. **35**, 3300 (2010)

Why fast detection?

Sampling from a single breath

Breath measurements



- Enormous potential, because of:
  - its inherent safety/minimum risk
  - non invasive, real-time
- Collection can be from neonates to very elderly or very ill patients

Source of exhaled gases

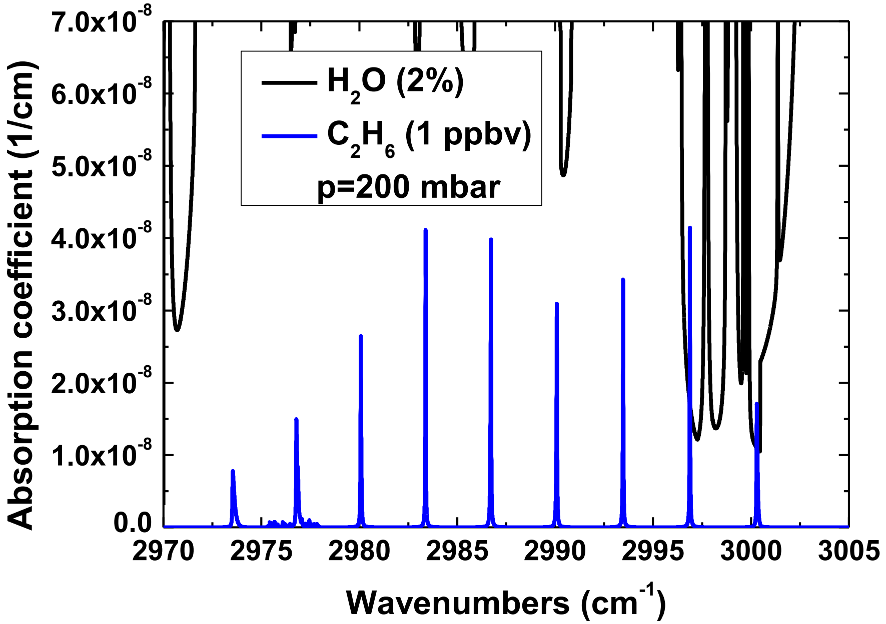
- from the blood via the alveolar-capillary junction in the lungs
- from mouth, nose, sinuses, airway and gastro-intestinal tract
- Exogenous origin: inspiration air, ingested foods and beverages, via the skin

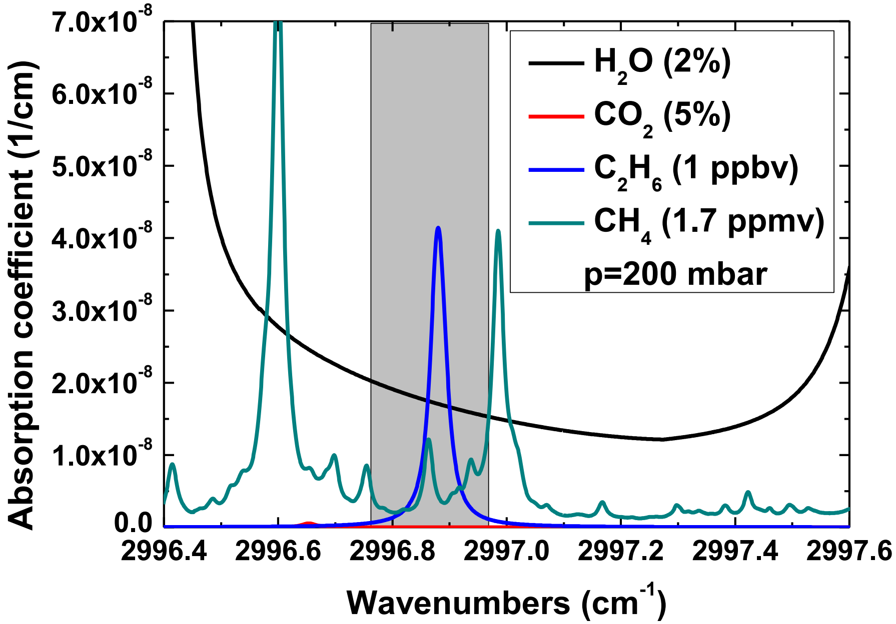
Concentration levels in breath

Concentration	Molecule
Percentage (%)	oxygen, water, CO_2
Parts-per-million (ppmv):	acetone, CO, methane, hydrogen
Parts-per-billion (~ ppbv):	formaldehyde, acetaldehyde, isoprene, pentane, ethane, ethylene, NO, carbon disulfide, methanol, ammonia, dimethylsulfide, etc.
Part per trillion (pptv, $1:10^{12}$)	unknown biomarkers

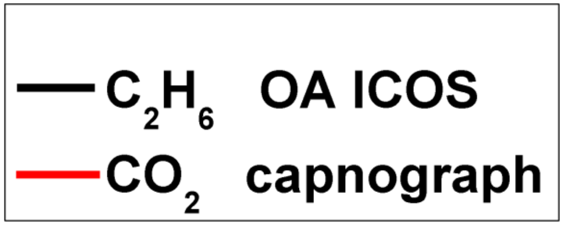
- There are about 1200 different gases in exhaled breath
- However composition and concentration gases varies per subject and condition

Breath sampling of ethane (C_2H_6)



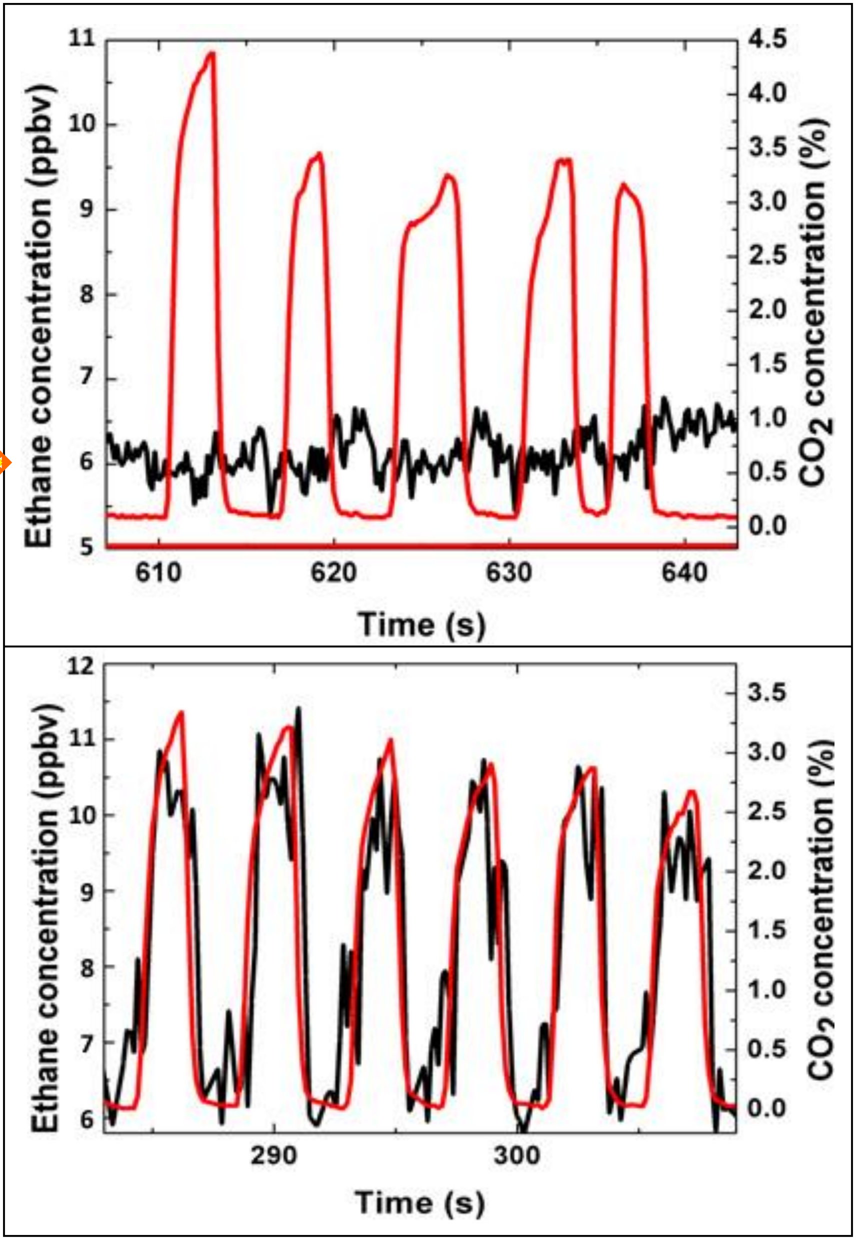


On-line breath sampling of ethane (C_2H_6)



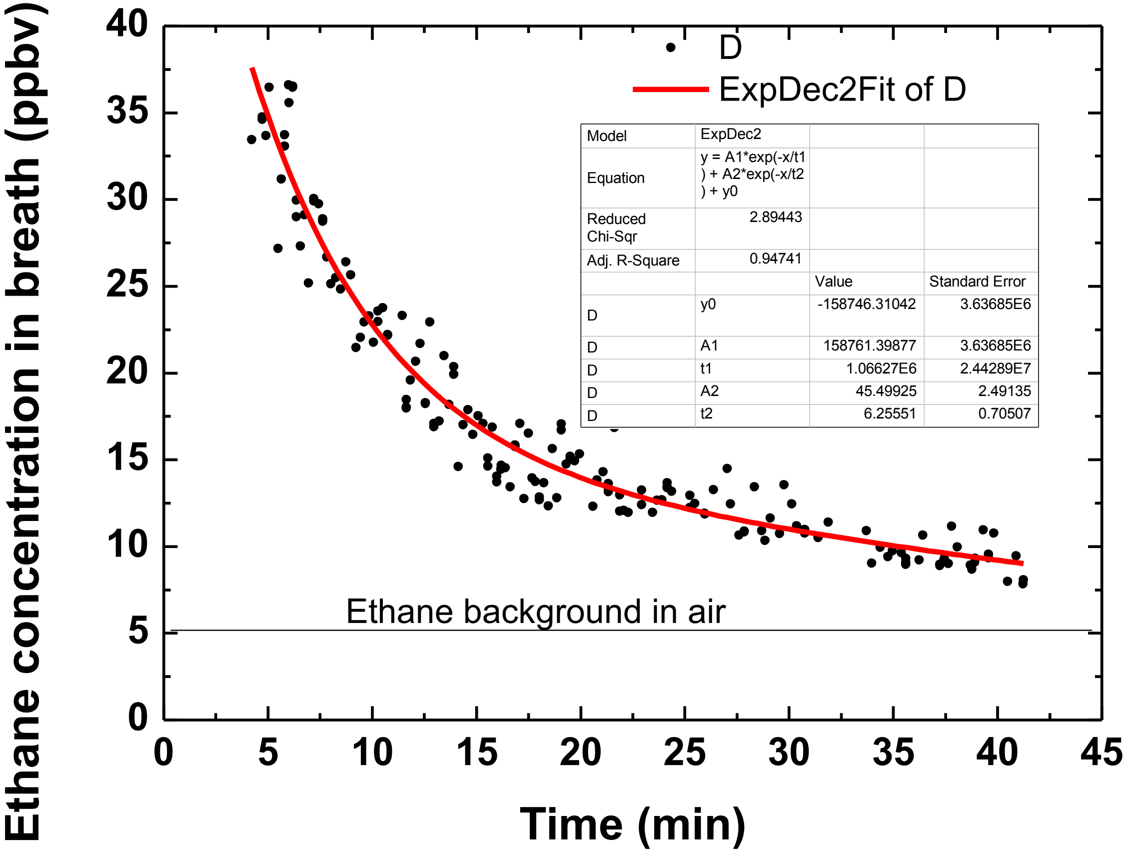
ethane background

elevated ethane level in a breath of smoker



On-line breath sampling of ethane (C_2H_6)

Long-term measurements,
wash out the blood and fat tissue



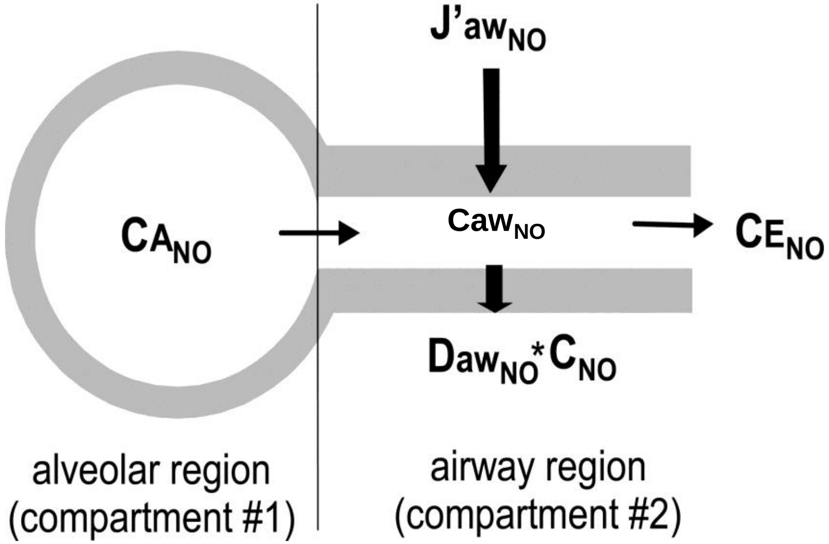
Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	2.89443		
Adj. R-Square	0.94741		
		Value	Standard Error
D	y0	-158746.31042	3.63685E6
D	A1	158761.39877	3.63685E6
D	t1	1.06627E6	2.44289E7
D	A2	45.49925	2.49135
D	t2	6.25551	0.70507

Approved clinical breath tests

- Ethanol: law enforcement
- CO test for neonatal jaundice
- H_2: gastro-intestinal tract
  (bacterial overgrowth, transit time)
- Taking substrate to exhale labeled $^{13}CO_2$
  - Urea: *Helicobacter pylori* infection stomach
  - Glucose: insulin resistance
  - Linoleic acid: fatty acid metabolism

- NO: asthma
  NO concentration indicates degree of inflammation (> 15 ppbv)
  - upper airway : 0.2 – 1 ppmv
  - lower airway : 1 – 10 ppbv
  - nasal cavities: 1 – 30 ppmv

How to measure NO?
Flow dependent, modeling NO exchange



3 parameters:

- steady-state alveolar concentration: **C_ANO** (ppb)
- mean airway tissue concentration of NO (wall concentration): **C_{AW}NO** (ppb)
- diffusing capacity in the airways: **D_{AW}NO** ($pl \cdot s^{-1} \cdot ppb^{-1}$)

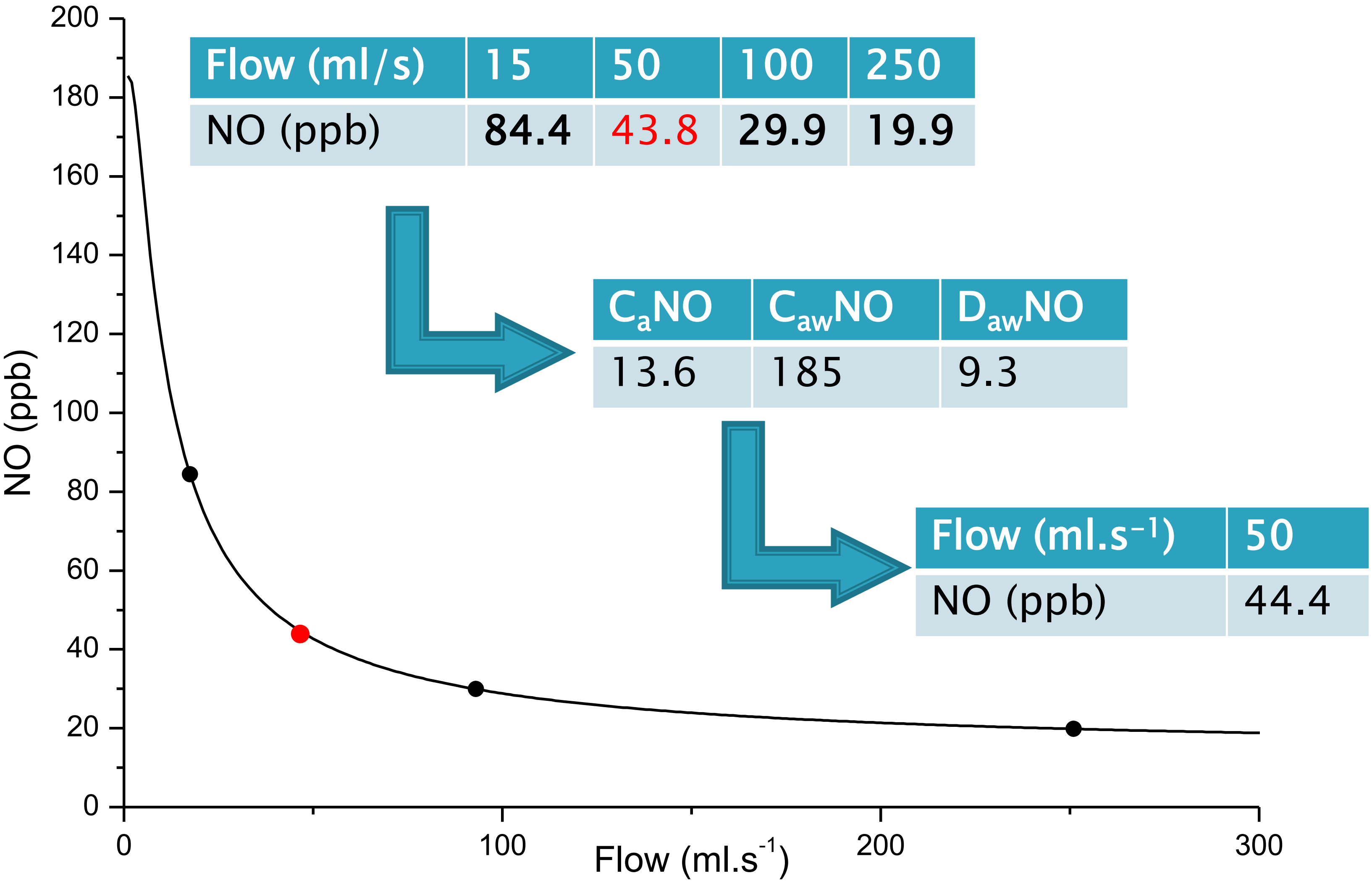
George et al. J Appl. Physiol. 96: 831–839 (2004)
Trumpet Model, J. Appl. Physiol. 102: 417–425 (2007)

Cristescu et al., J. of Breath Research 7 (2013) 017104

Flow dependency exhaled NO

Exhaled NO originates from various respiratory locations

Concentration is flow dependent

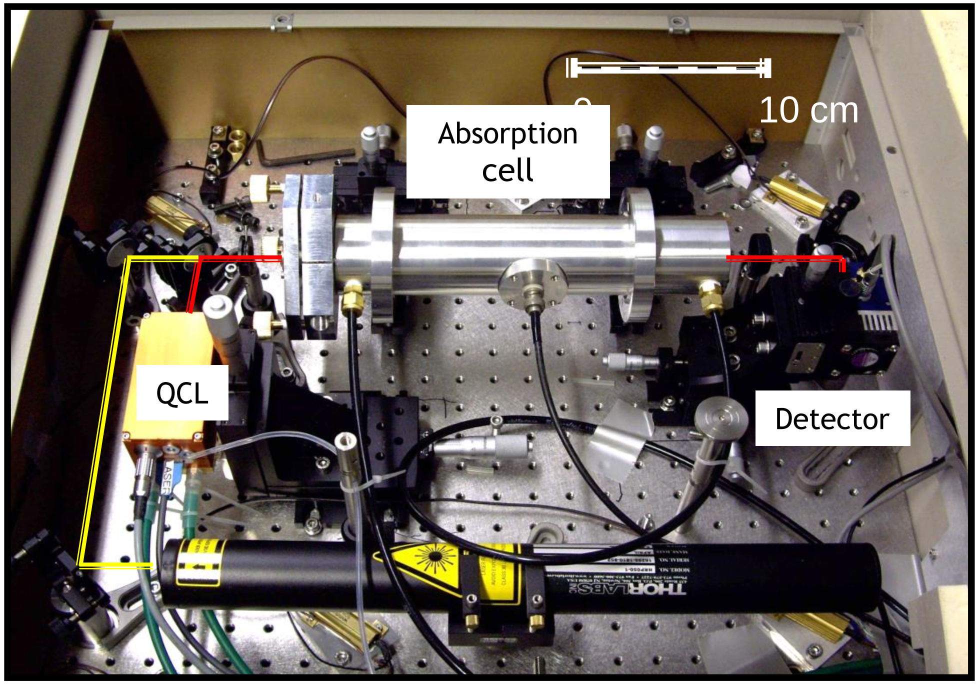


Flow (ml/s)	15	50	100	250
NO (ppb)	84.4	43.8	29.9	19.9

C_aNO	C_{aw}NO	D_{aw}NO
13.6	185	9.3

Flow (ml.s^{-1})	50
NO (ppb)	44.4

QCL-based detection of Nitric Oxide

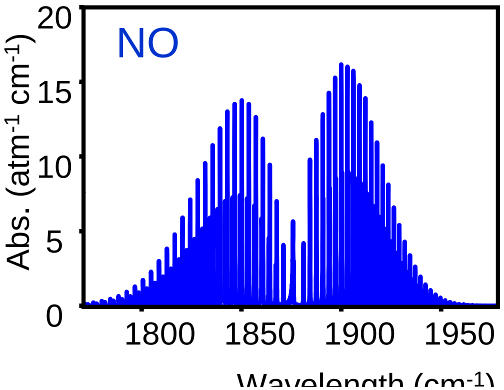


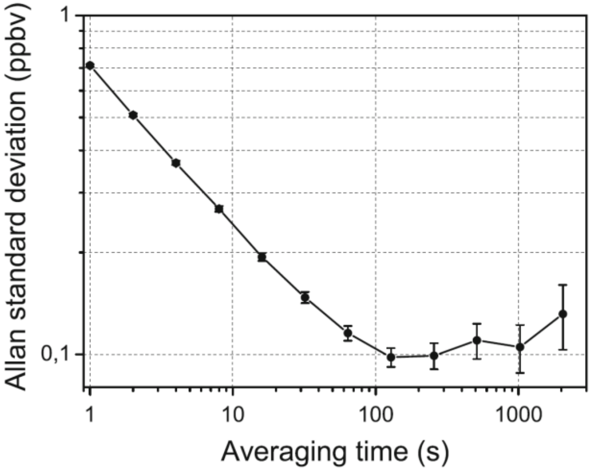
Source: TEC cw QCL @5.26 μm

Detector: 4 stage TEC, (HgCd)Te
$D^* = 3\cdot10^{11}\,\mathrm{cm\cdot Hz^{1/2}\cdot W^{-1}}$

Mirrors: R: 99.93 % @5.26 μm
effective path length 400 m

Marchenko et al., Appl. Phys. B 111 (2013) 359



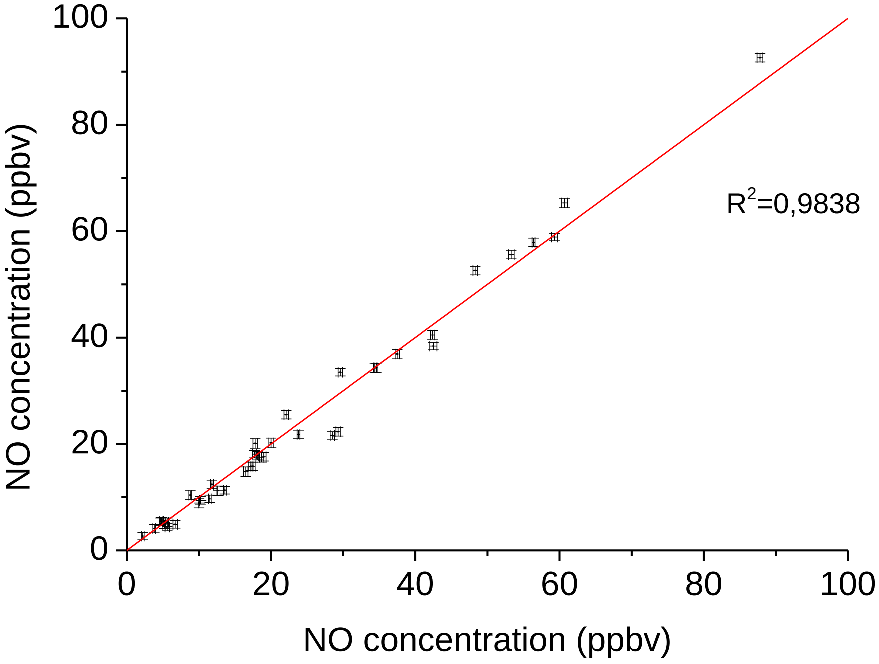


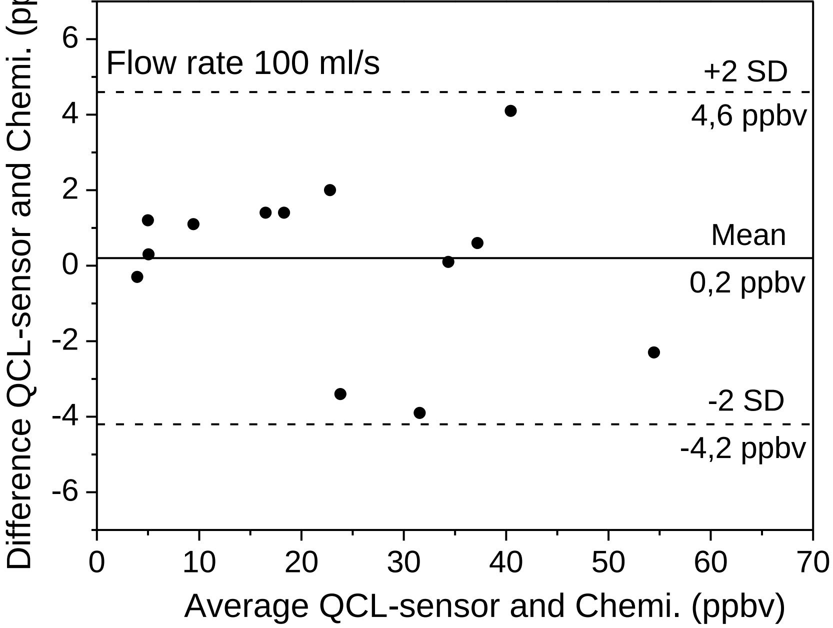
Detection limit: 0,7 ppbv in 1 s
Ultimate detection limit – 100 pptv
in 128 s averaging time

Comparison with chemiluminescence device

Chemiluminescence

Asthmatic children (5-15 year old)
Flows rates: 15, 50, 100, 300 ml/s



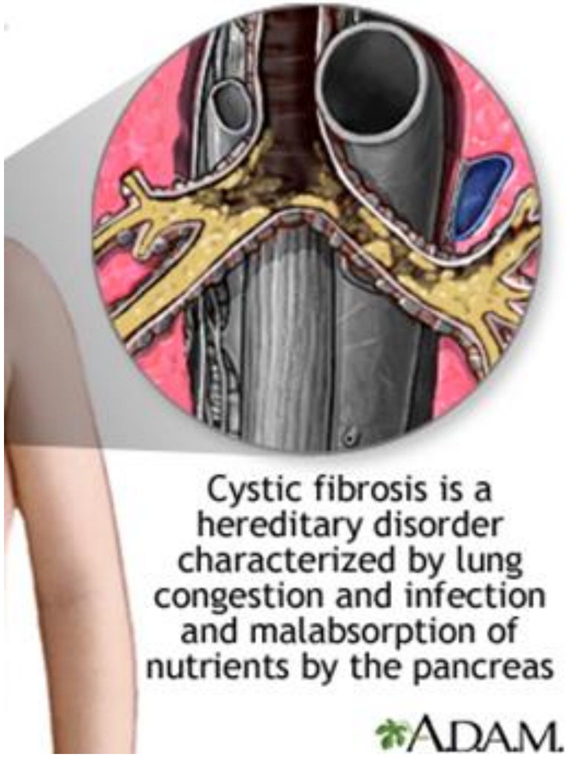


n=40

Bacterial lung infection

Cystic Fibrosis

- most common lethal genetic disease
  (1:4000 Caucasian children)



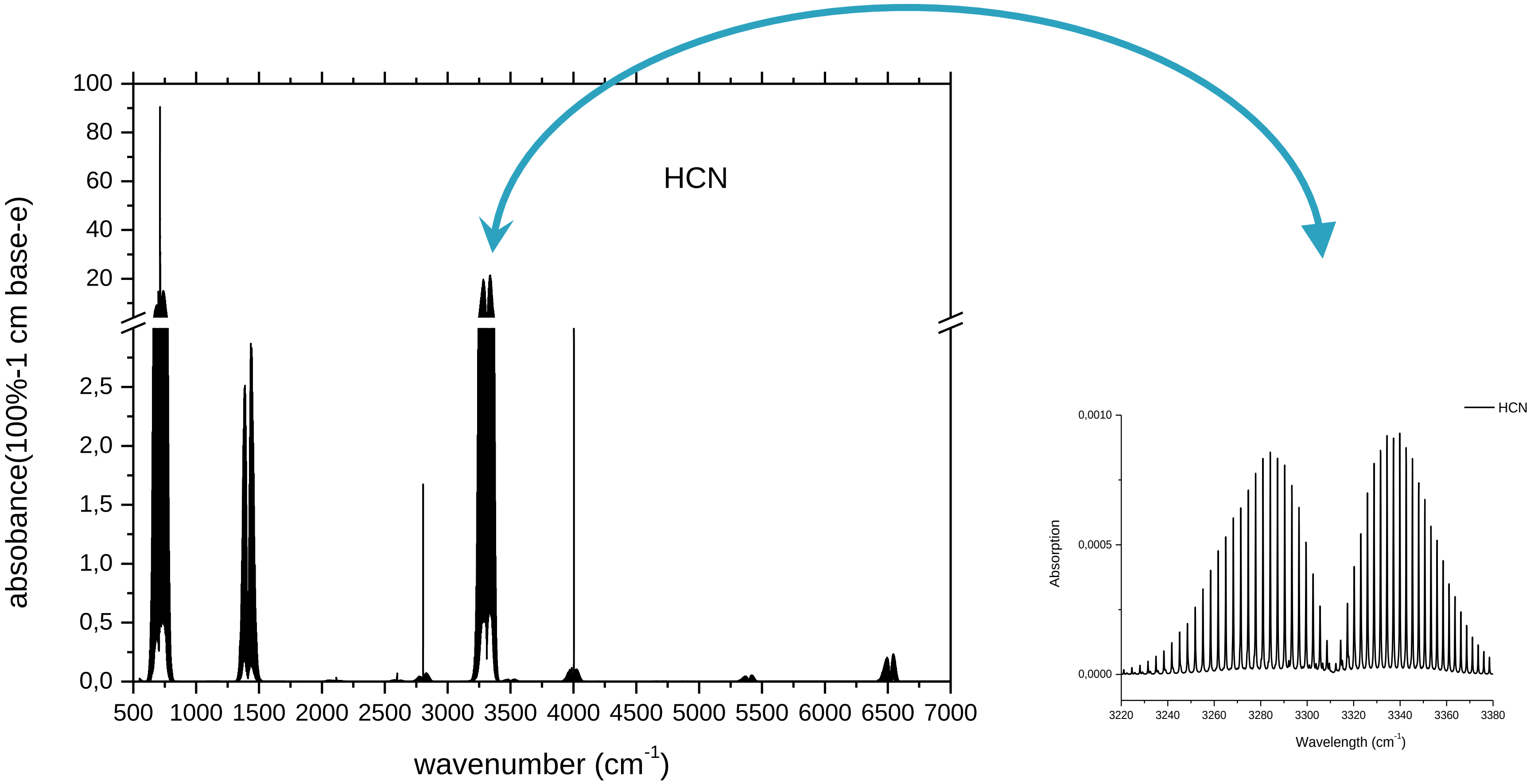
Cystic fibrosis is a hereditary disorder characterized by lung congestion and infection and malabsorption of nutrients by the pancreas

Bacteria: *Pseudomonas Aeruginosa*

- produce HCN
- most common infection in CF patients
- connection between *Pseudomonas* infection and irreversible lung function loss in Cystic Fibrosis
- Causes gradual decline in lung function parameters
- Best predictor for morbidity and mortality

Early recognition and treatment of respiratory infections are crucial for optimal prognosis of CF patients

Spectroscopic detection of Hydrogen Cyanide

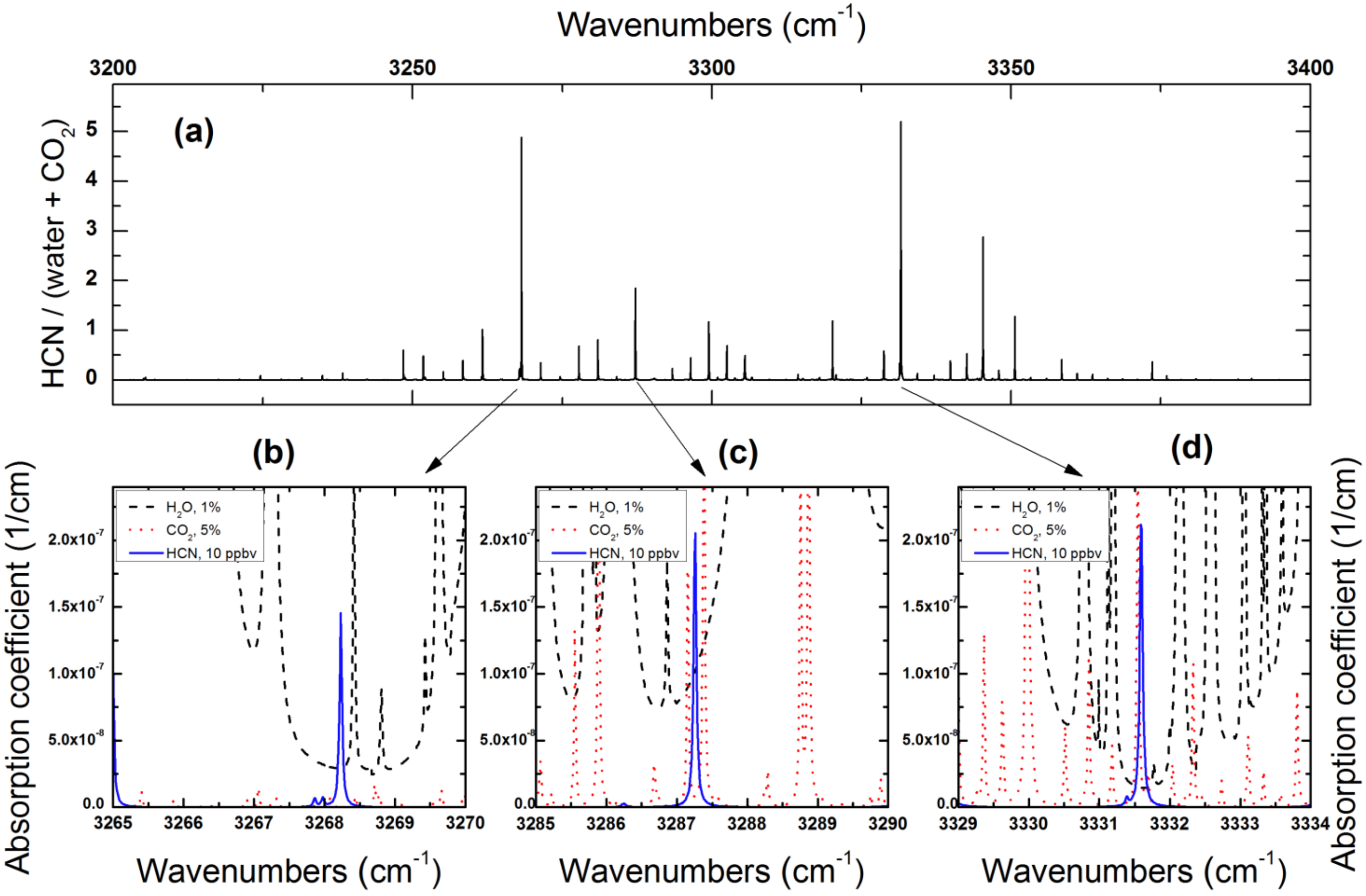


However: with biomedical applications:
high water and CO_2 content

With biomedical applications:
high water and CO_2 content

Ratio between
10 ppbv HCN
and
1% water + 5% CO_2

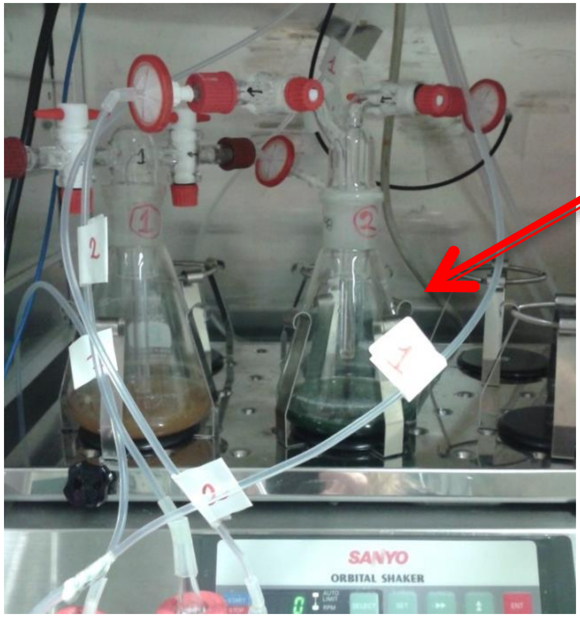
200 mbar



Detection limit:
0.4 ppbv HCN in 10 s (P8, v3 band) at 3287.25 cm^{-1}

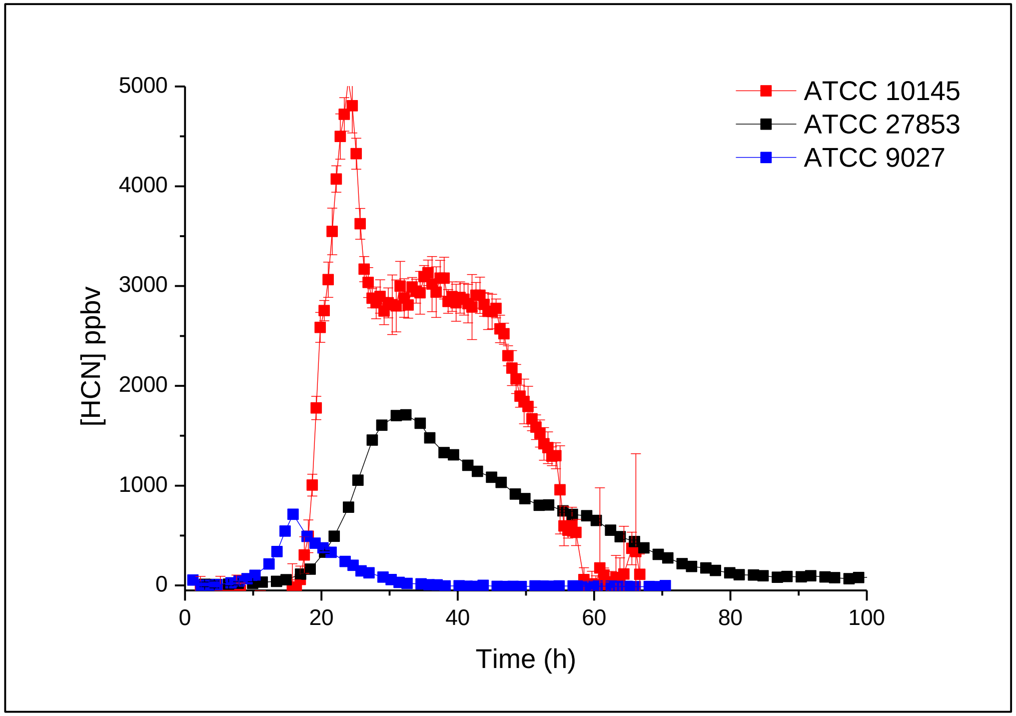
Arslanov et al., J. Biomedical Optics 18 (2013), 107002

Culture *Pseudomonas Aeruginosa*



Culture

Model reference strains



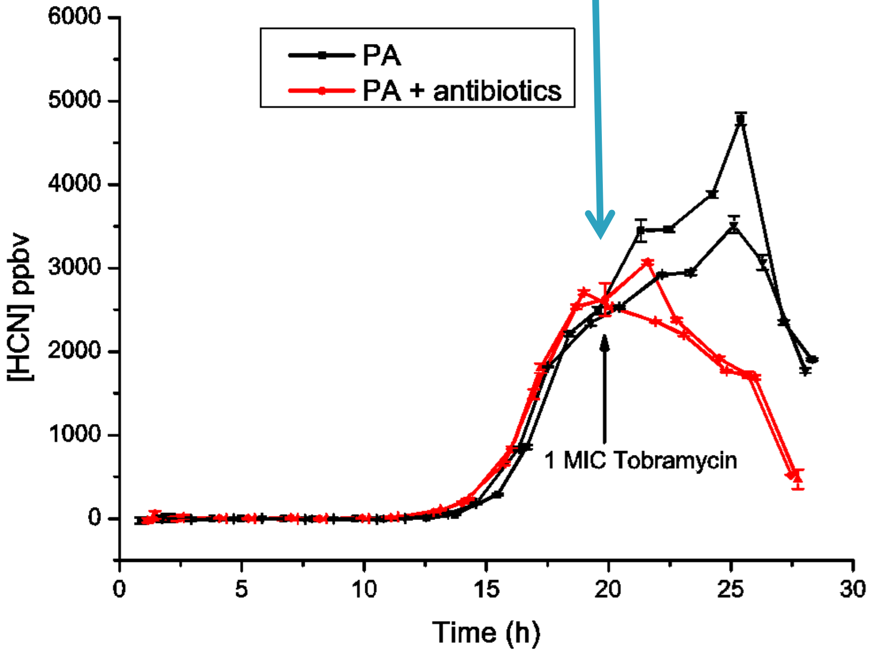
Treatment with antibiotics

Is this the right antibiotics for this specific culture?

Golden standard

- observe growth (over days)
- count colony forming units

- Time consuming
- Manpower consuming

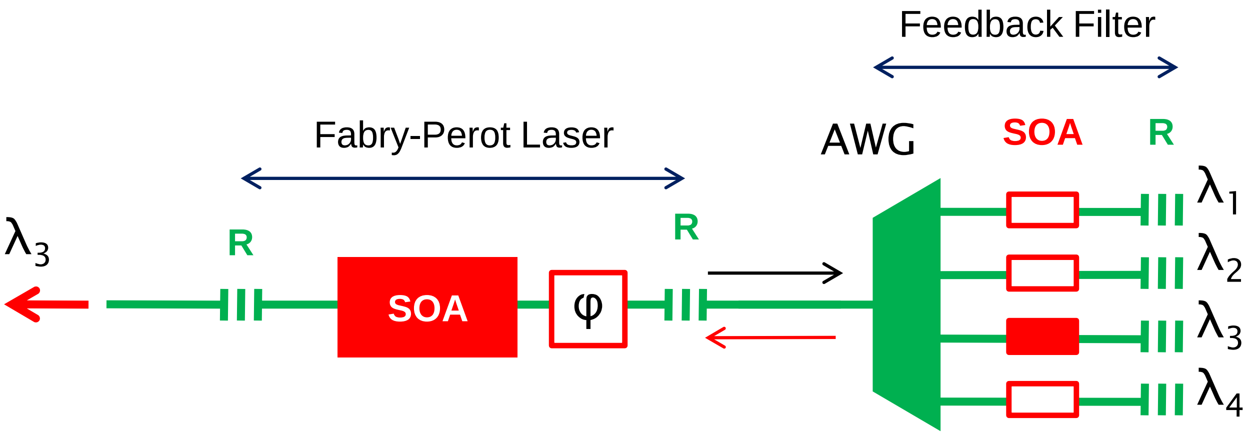


Immediate response

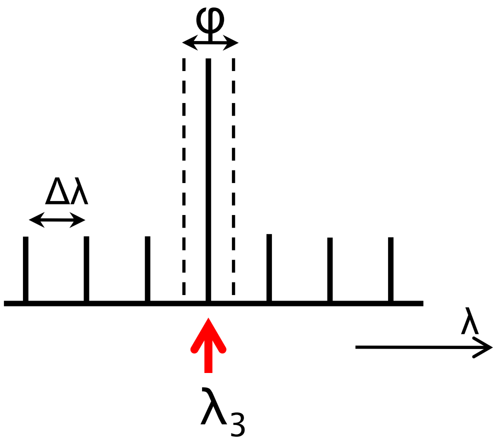
Addition of Tobramycin strongly reduces HCN production by *P. aeruginosa*

Clinical breath test study

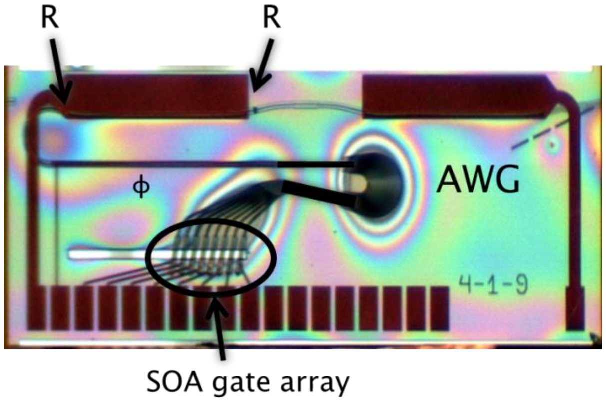
Using filtered feedback tunable laser at 1500–1600 nm

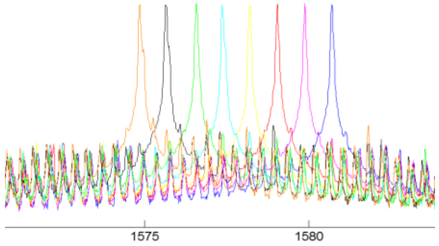


AWG: arrayed waveguide grating
SOA: semiconductor optical amplifier
$\Delta\lambda = 0.4$ nm (50 GHz ITU grid) → $L_{FP} = 822$ μm



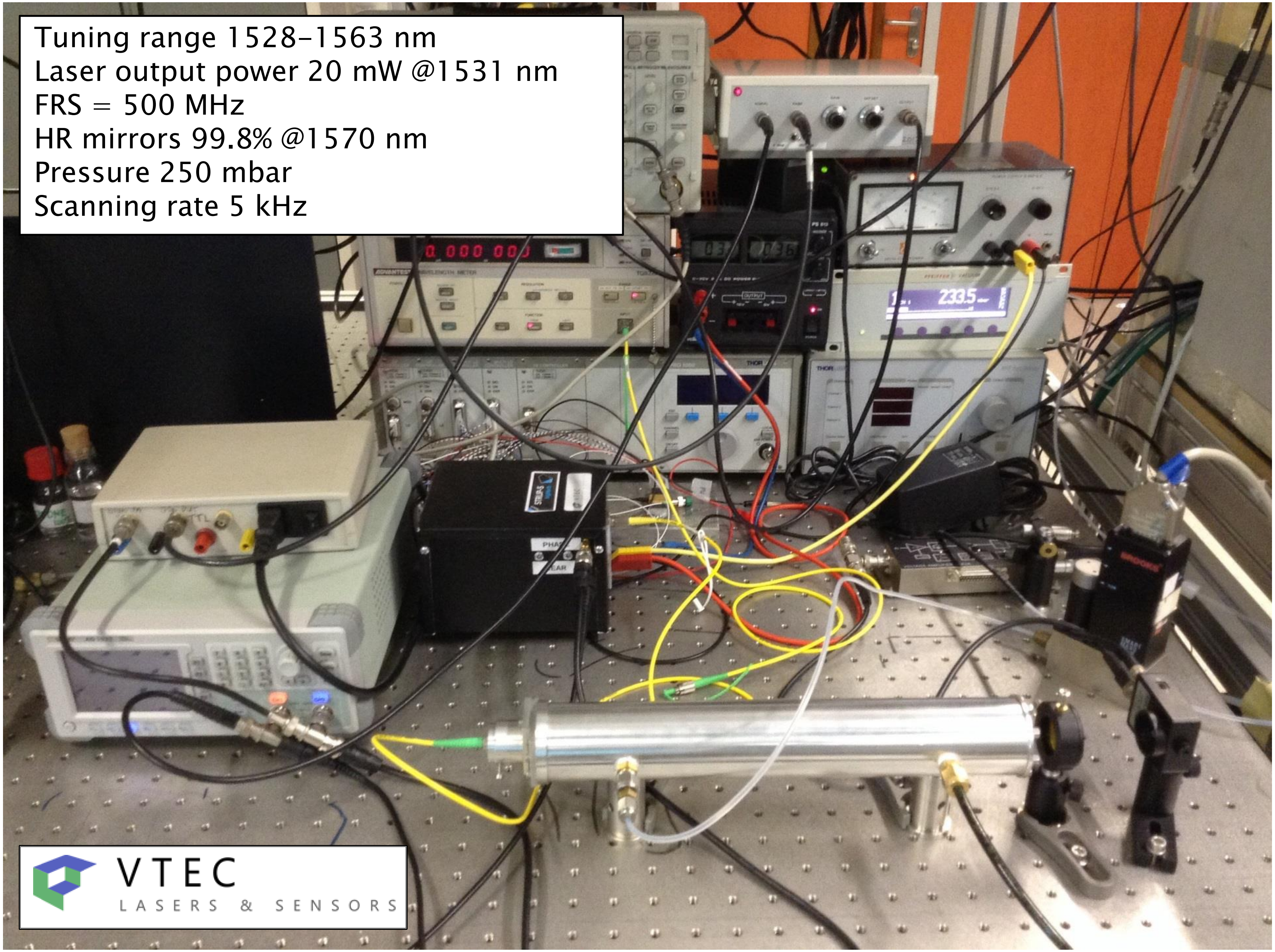
- Coarse tuning by SOA gate selection
- Fine tuning by in-cavity phase section





Docter et al., IEEE J. Sel. Top. Quan. Electron. **16** (2010) 1405

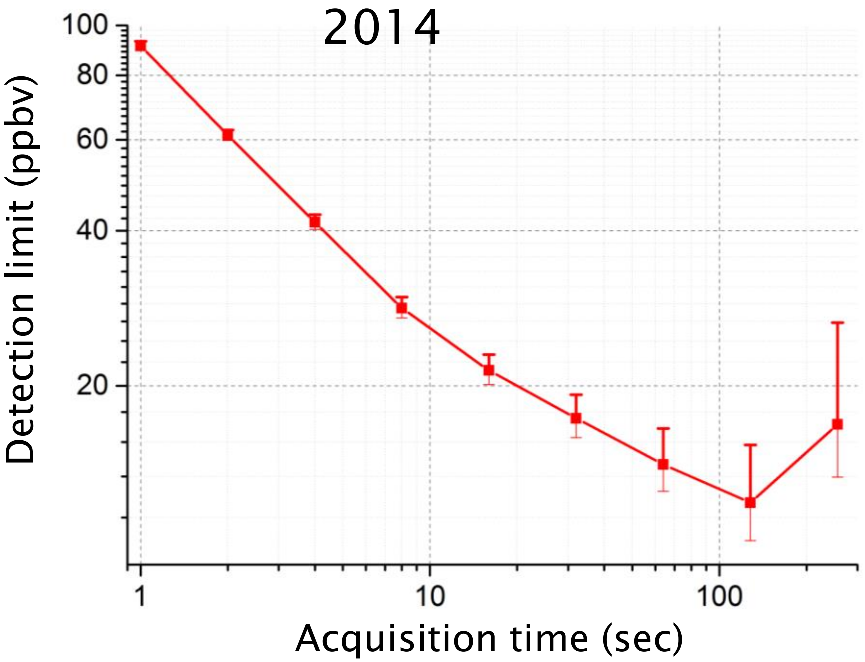
Test setup based on the laser from VTEC

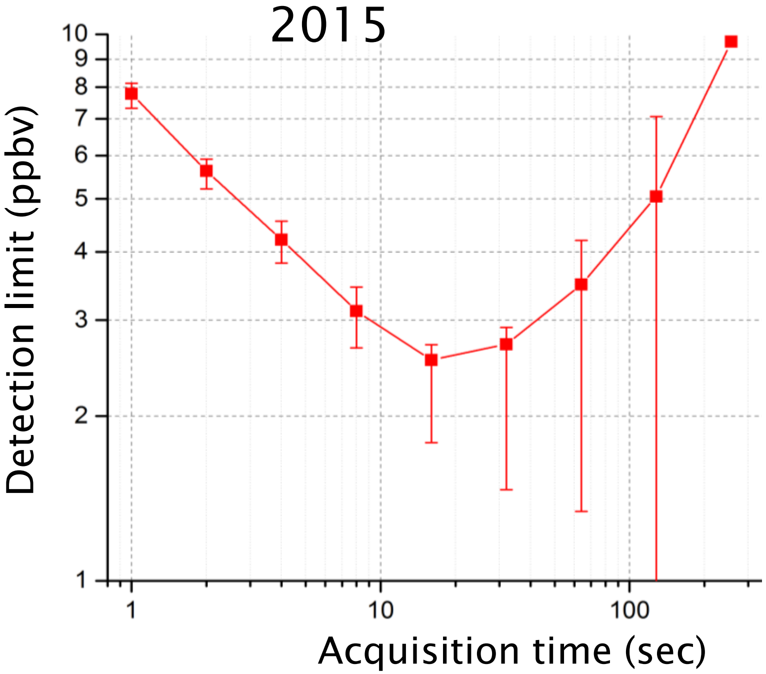


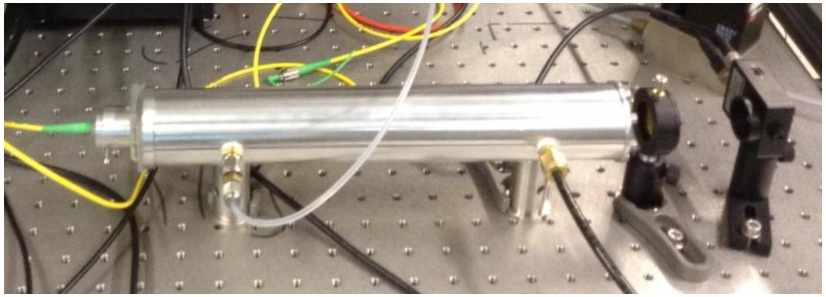
Tuning range 1528-1563 nm
Laser output power 20 mW @1531 nm
FRS = 500 MHz
HR mirrors 99.8% @1570 nm
Pressure 250 mbar
Scanning rate 5 kHz

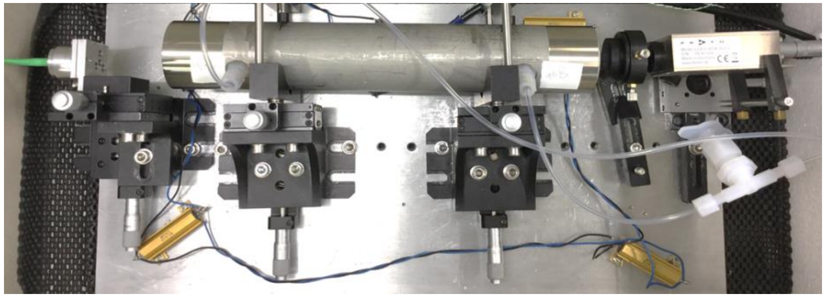
VTEC
LASERS & SENSORS

HCN detection limit









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Detectivity infrared detectors