European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

1ST TRAINING SCHOOL

Universitat de Barcelona, Spain, 13 - 15 June 2013

Action Start date: 01/07/2012 - **Action End date**: 30/06/2016

2012 - 2013 (*Ongoing Action*)

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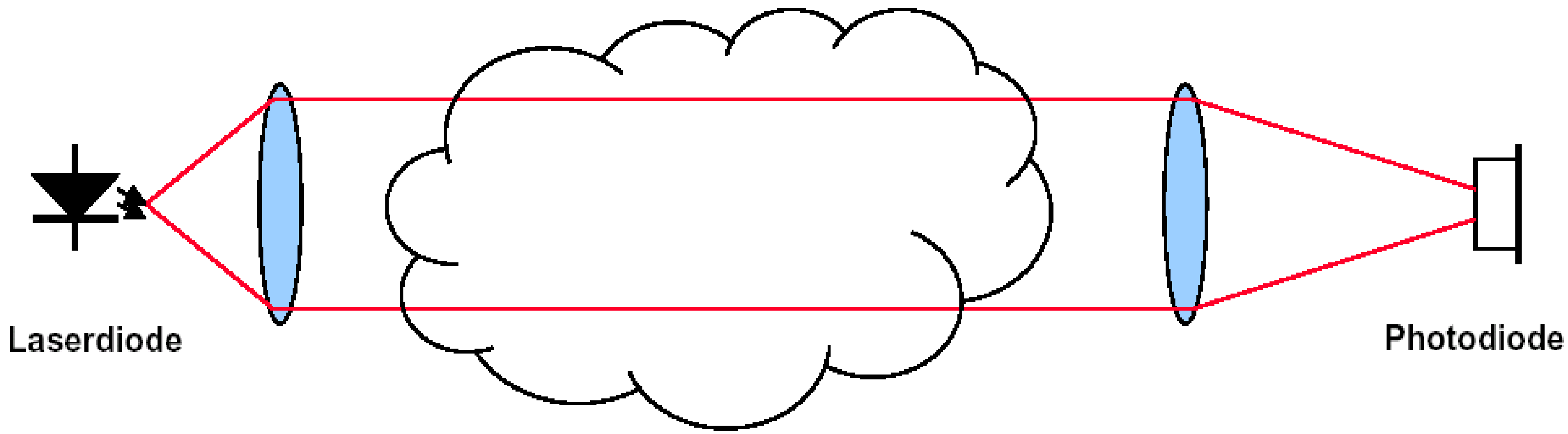
Germany

Optical Gas Detection Methods

Absorption spectroscopy

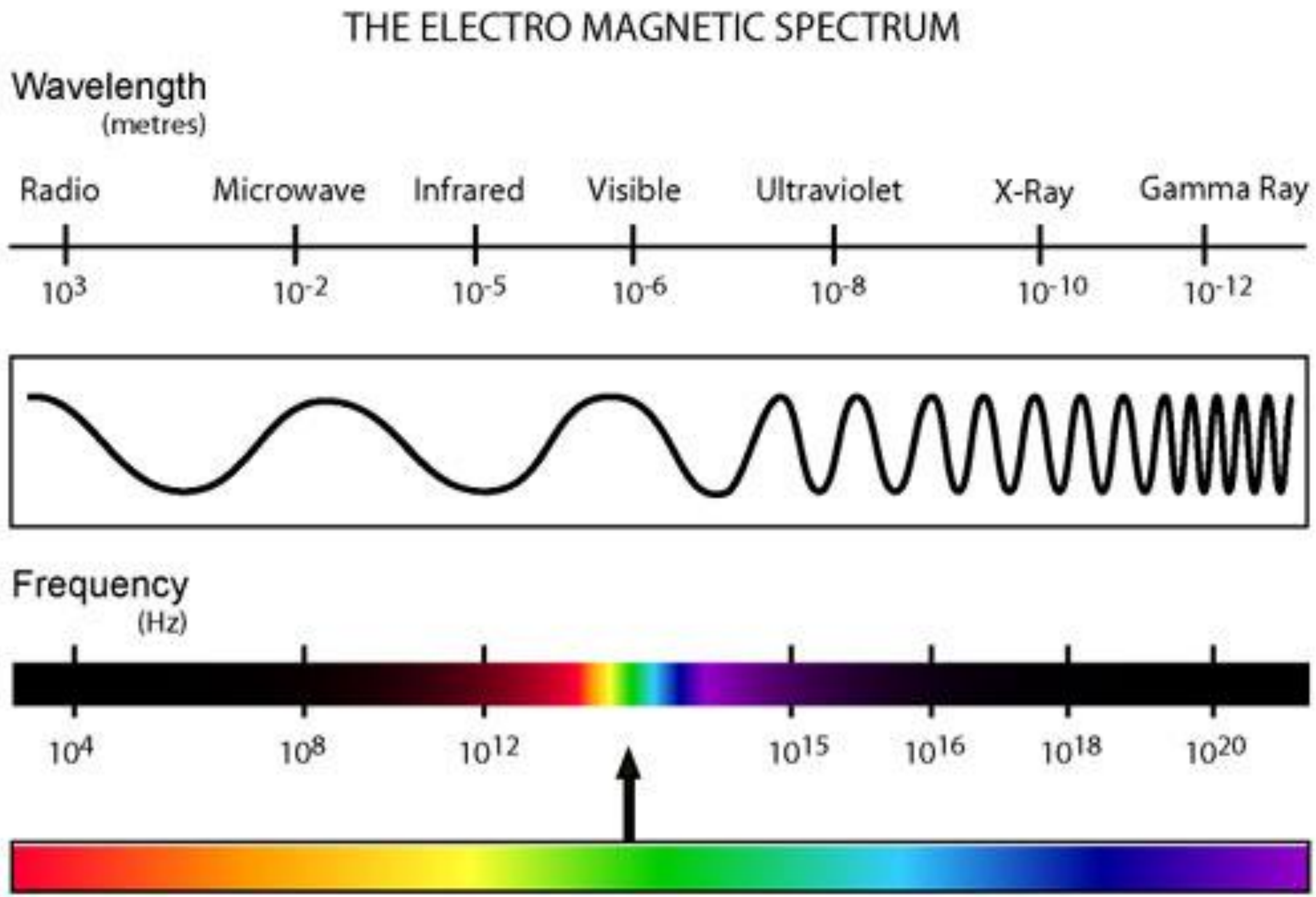
- Molecule specific absorption of electromagnetic radiation at characteristic wavelengths



Measurement principle

Transmission Measurement

Absorption spectroscopy



Source: scheeline.scs.illinois.edu

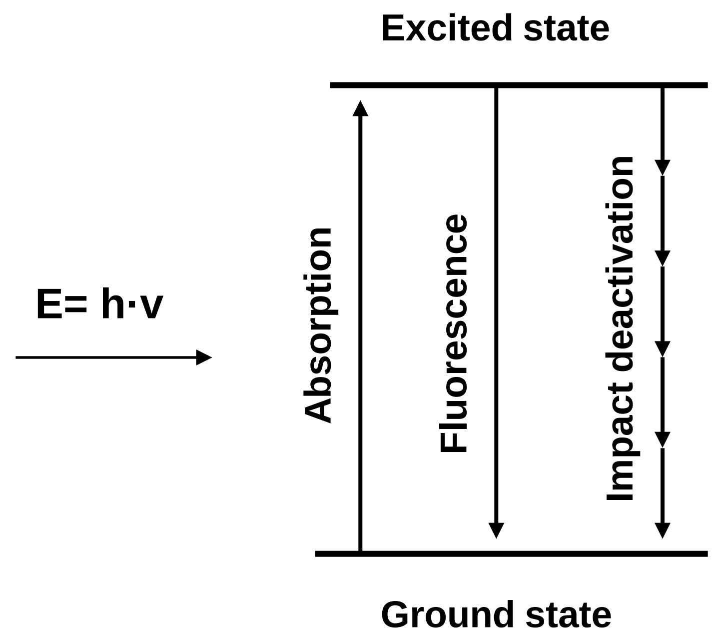
Absorption spectroscopy

- Absorption spectroscopy
  - UV / VIS
  - IR
  - Terahertz
  - Microwave range

  - IR based sensors are most relevant for air pollution measurements

Absorption of electromagnetic radiation

- **Two – Level System**
- Absorption of photons
- Transition ground state → excited state
- Absorption for E_1-E_2=h·v
- Relaxation caused by
  - Fluorescence
  - Mechanical deactivation
- UV/VIS: electronic transitions
  - Interaction of light with valence electrons
- IR: Rotation and vibration transitions
  - Interaction of light with dipole moments of molecules

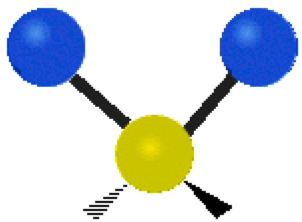


Absorption of electromagnetic radiation

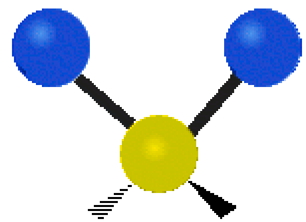
- Molecules can fall back radiant or nonradiant from the excited state E_2 to the ground state E_1 – absorbed light quantum will be reemitted
- Radiative recombination is used by fluorescence spectroscopy
- IR spectroscopy is using the amount of energy which is transformed from kinetic energy by inelastic impacts
  The transformation of the energy difference $(E_1\text{-}E_2) = h \cdot n$ in translation energy results in a higher velocity of the colliding molecules
- Increase of velocity equivalent with increase of gas temperature
- Increase of temperature leads to thermo elastic expansion of the sample and therefore to an increase of pressure

Oscillation and Rotation spectra

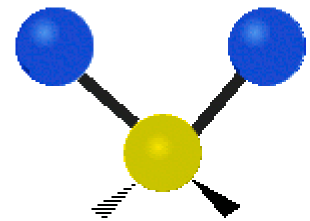
Symmetrical stretching



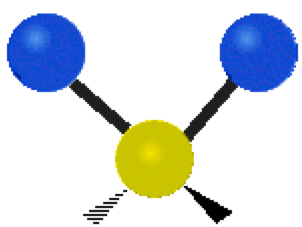
Asymmetrical stretching



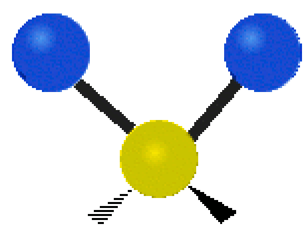
Scissoring



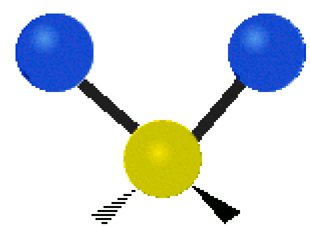
Rocking



Wagging

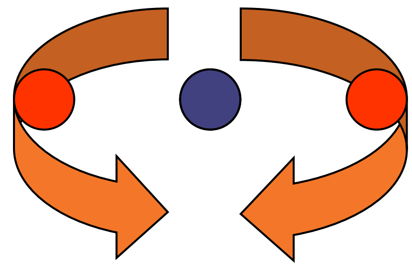


Twisting



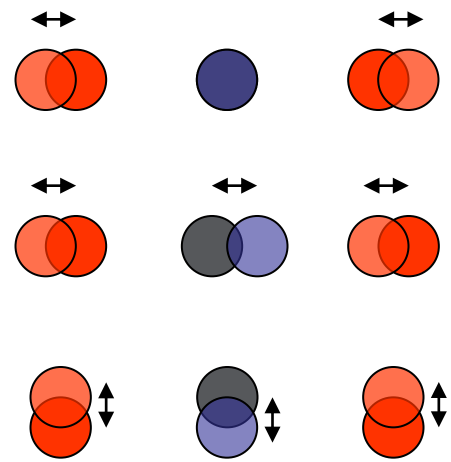
Oscillation and Rotation spectra

- **Oscillation and rotation modes (e.g. CO_2)**
- Rotation modes



	1/cm	µm
Rotation modes	0,7	

- Oscillation modes
  - Symmetric stretching
  - Asymmetric stretching
  - Bending vibration



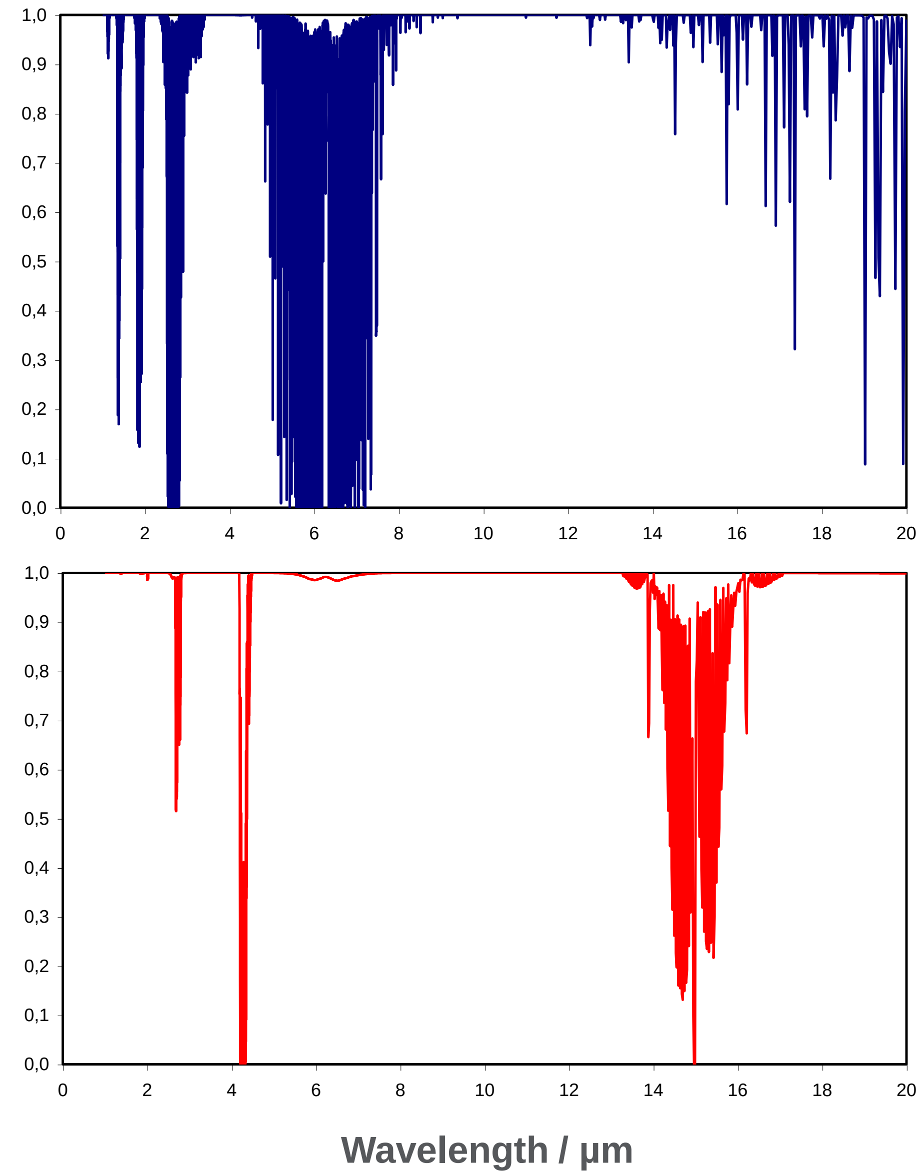
	1/cm	µm
Symmetric stretching	~~1388~~	~~7,2~~
Asymmetric stretching	2349	4,26
Bending vibration	667	14,99

Absorption of electromagnetic radiation

- Absorbed energy in sample (Lambert-Beer Law)
  - $I_{abs} = I_0 \cdot (1 – \exp (- \alpha \cdot L))$
    - With I_0 as irradiated intensity and L as sample length
- Absorption coefficient α of transition E_1 to E_2
  - $\alpha = \sigma \cdot (N_1 - N_2)$
    - With σ as absorption cross section, N_1 and N_2 as occupation densities of the ground state E_1 and the excited state E_2

IR absorption of gases

- **IR spectra of gases**
- **HITRAN spectra of**
  H_2O (0,7 Vol%)
  CO_2 (1000 ppm) from 1-20 µm
- “Atmospheric window”
- NDIR:
  - CH_4, CO_2: 3 – 5 µm
  - Others: 8 – 12 µm



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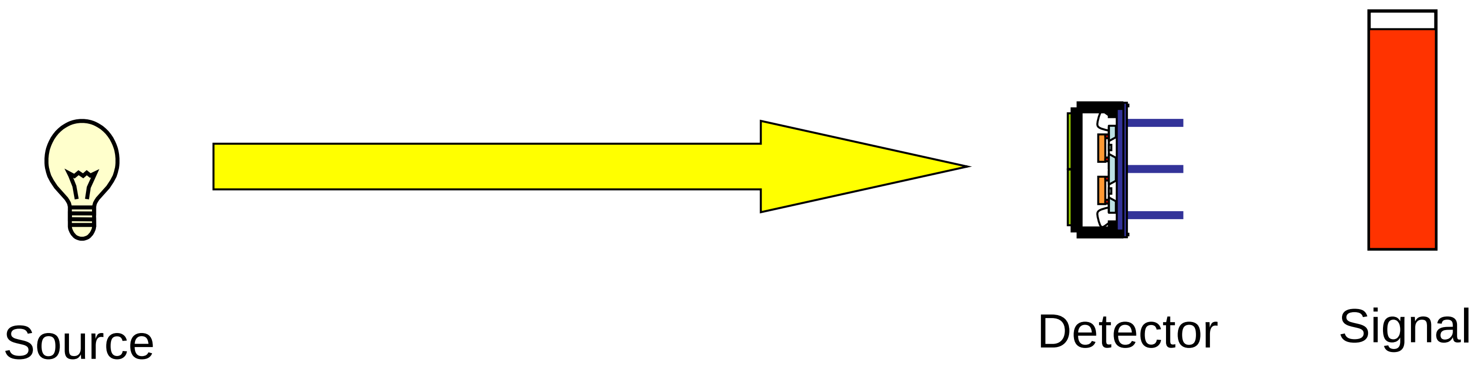
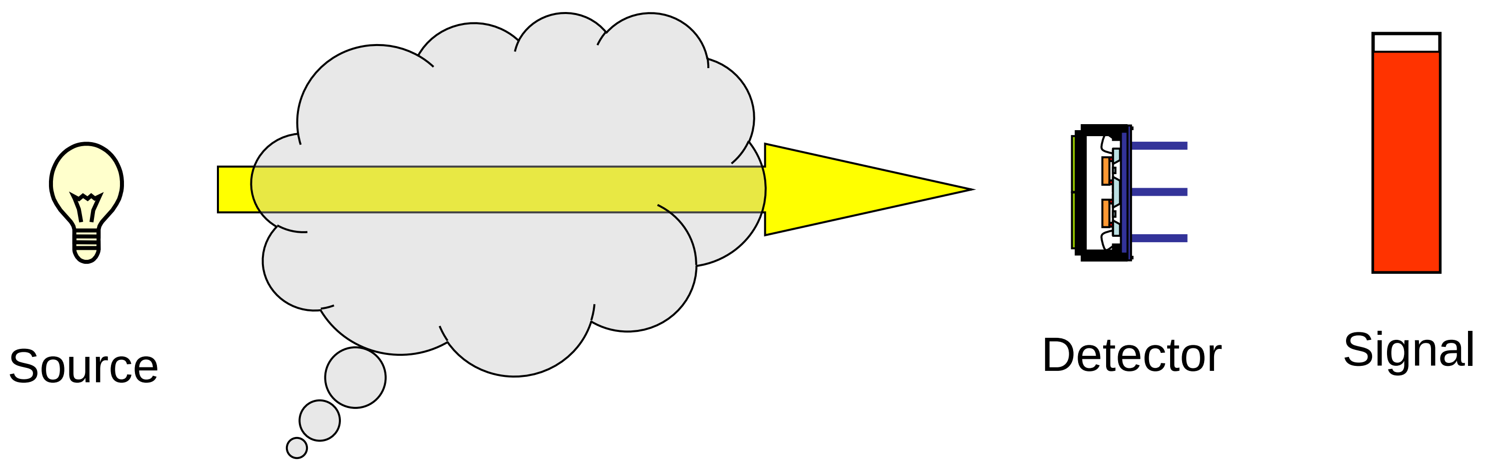
Measuring principle of NDIR systems

- Measuring principle
- IR-Radiation is emitted by the source
- Detector measures the IR-Radiation



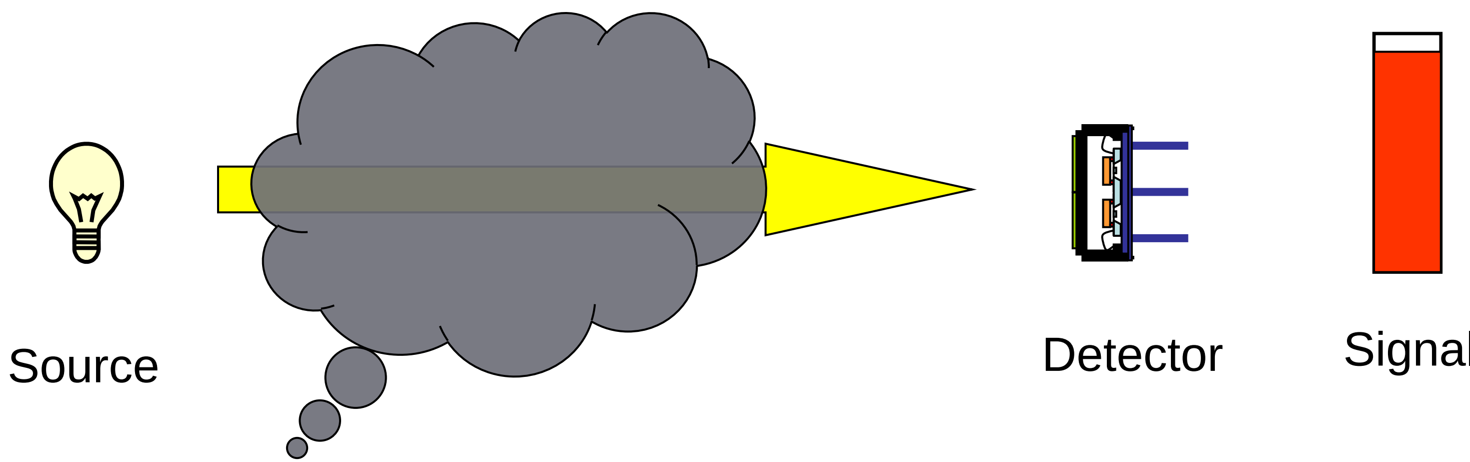
Measuring principle of NDIR systems

- Measuring principle
- Radiation is emitted by the source
- Detector measures the IR-radiation
- Gas is absorbing IR-radiation



Measuring principle of NDIR systems

- Higher gas concentration results in a stronger absorption
- Lambert-Beer law $I_{abs} = I_0 \cdot \exp(-c \cdot \varepsilon \cdot L)$

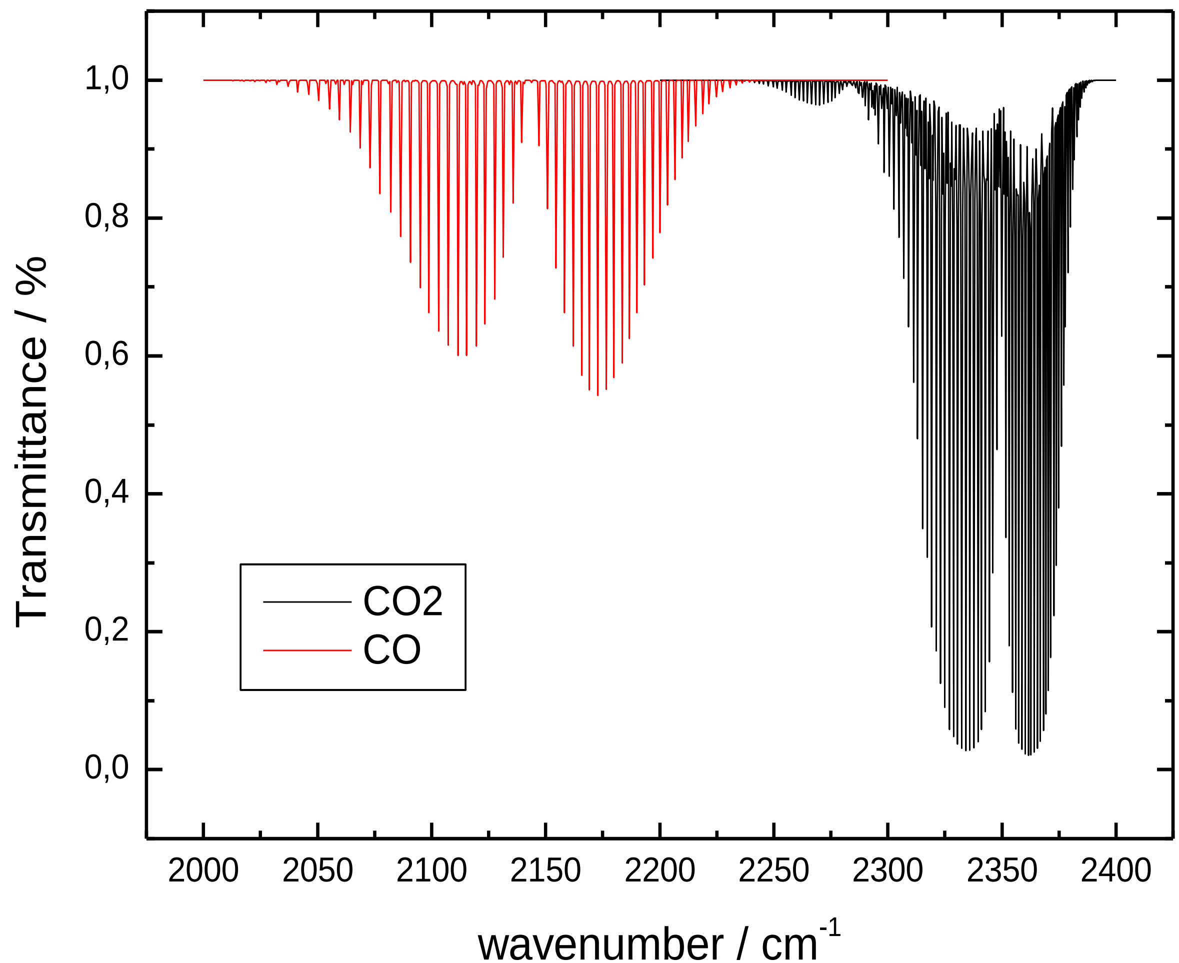


Measuring principle of NDIR systems

- **Selectivity**
- Simulation
  10 ppm CO / CO_2
- Absorption way 1 m
- Pressure 1 bar
- Temperature 296 K

HITRAN calculations of CO and CO_2 transmittance

optical path 1m, pressure 1 atm, partial pressures 0.0001 atm, temperature 296K

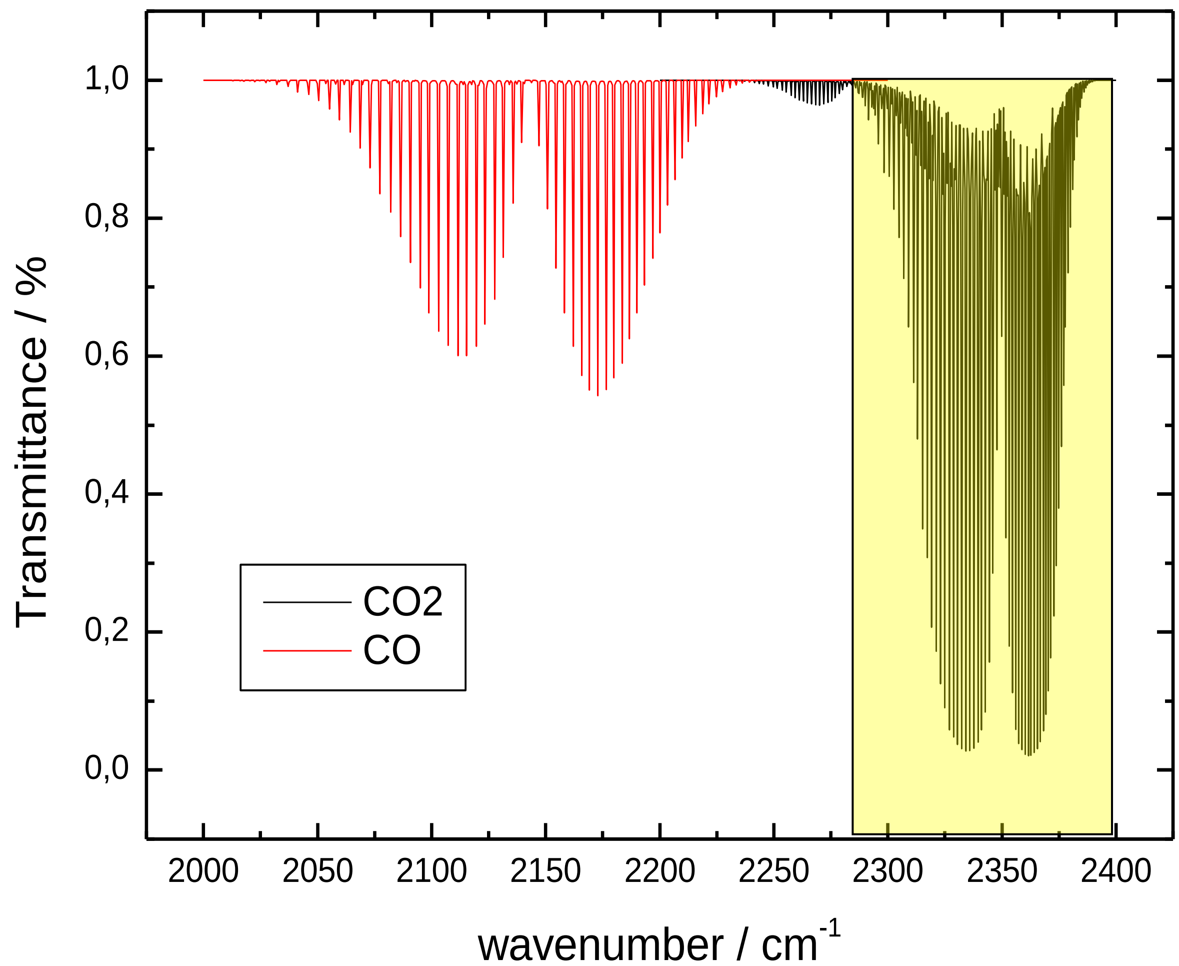


Measuring principle of NDIR systems

- **Selectivity**
- Simulation
  10 ppm CO / CO_2
- Path length 1 m
- Pressure 1 bar
- Temperature 296 K
- Filter at 4,1 – 4,4 µm

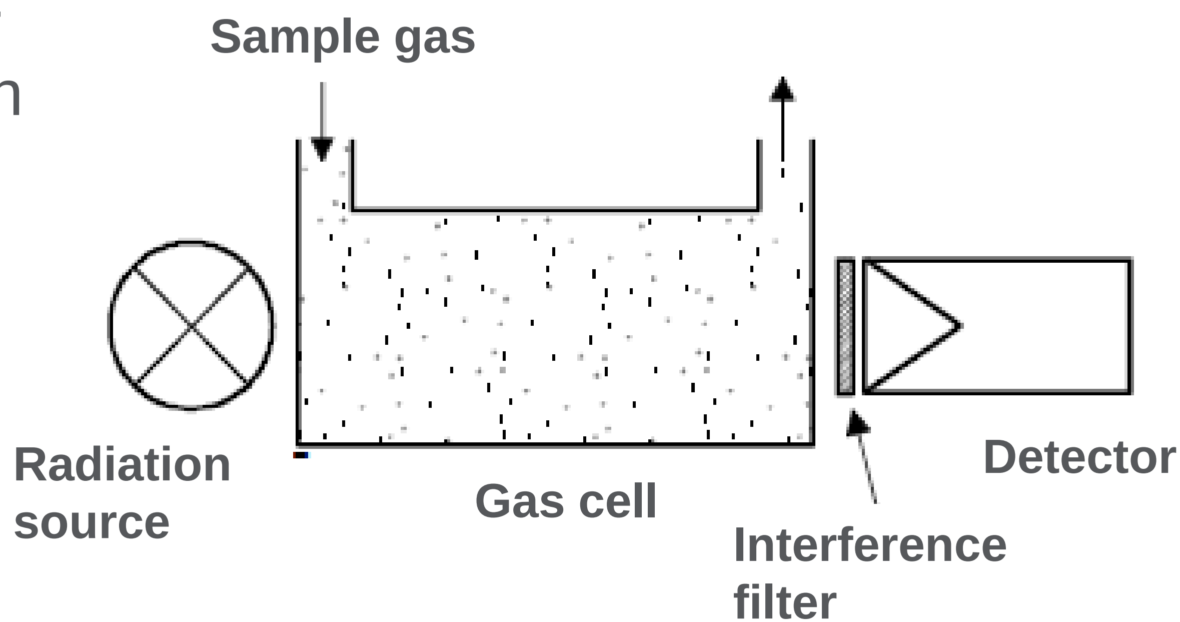
HITRAN calculations of CO and CO_2 transmittance

optical path 1m, pressure 1 atm, partial pressures 0.0001 atm, temperature 296K



Measuring system setup

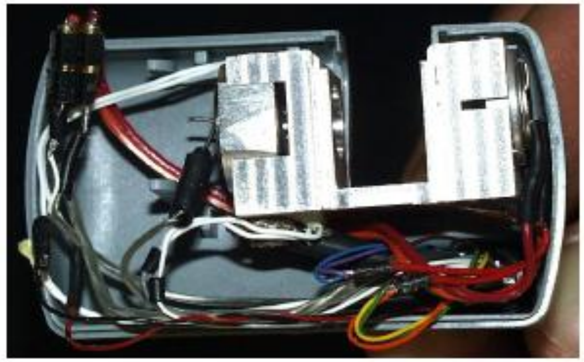
- **Single channel sensor**
- Radiation source
- Gas measurement cell
- Interference filter for wavelength selection
- Radiation detector

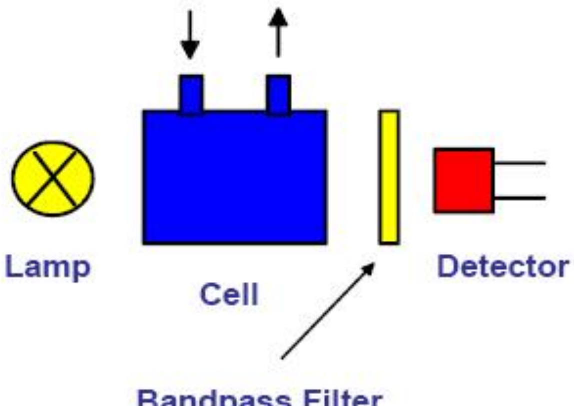


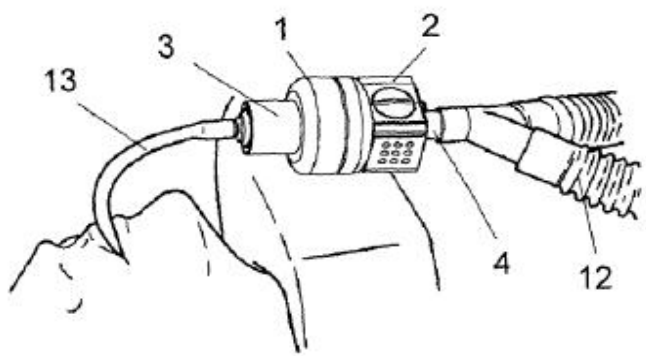
Measuring system setup

Single Channel Sensor

- \+ low weight, low production costs
- \+ no moving parts
- \- Prone to concentration drifts (dirt, lamp ageing)
- \- frequent zeroing required (U_{bright})

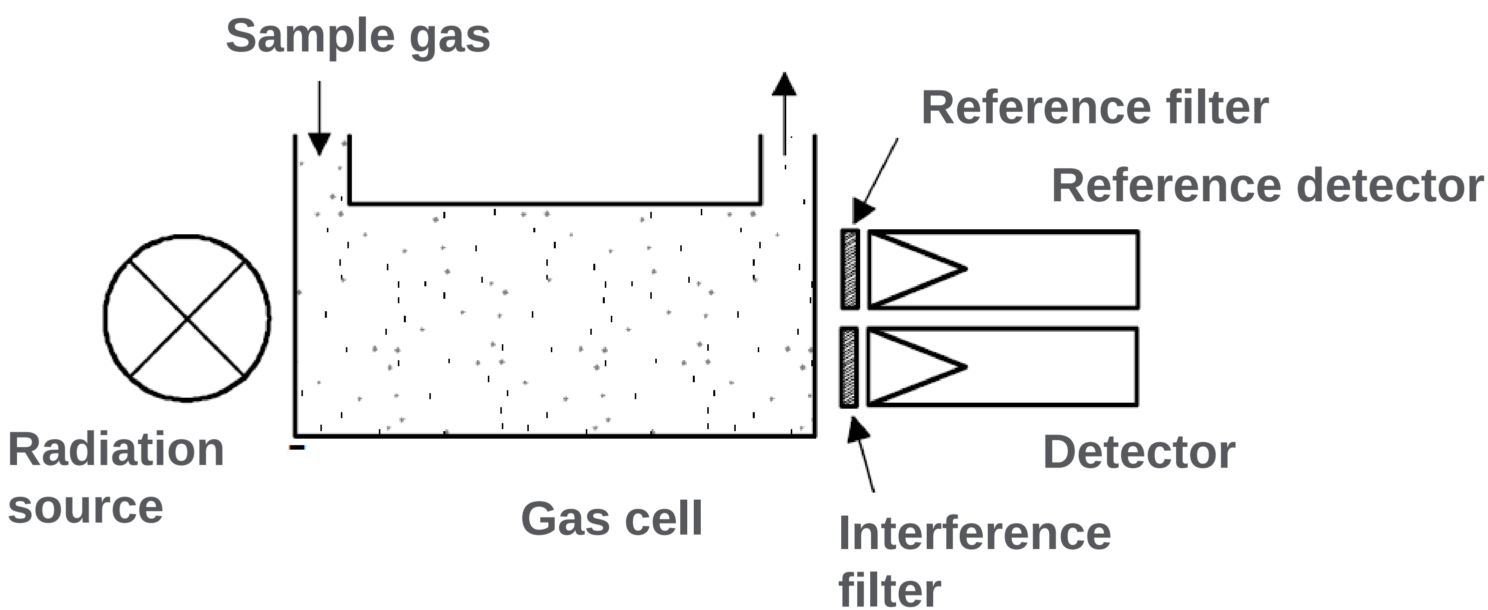






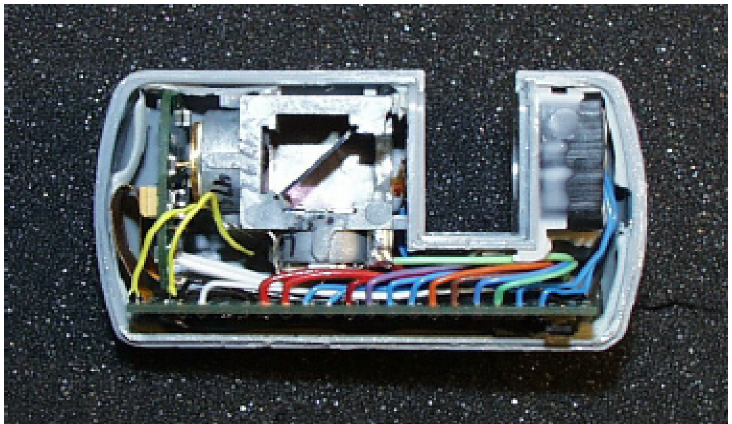
Measuring system setup

- **Sensor with reference channel**
- Radiation source
- Gas measurement cell
- Two interference filter for wavelength selection

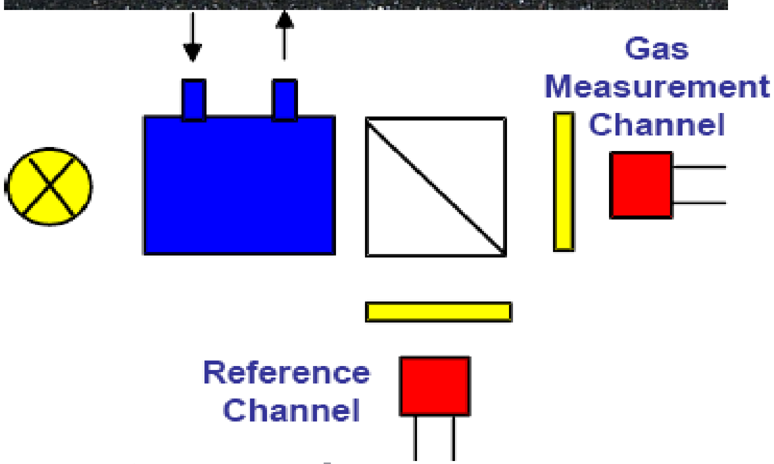


Measuring system setup

CO_2 Sensor for Intensive Care



additional optical channel:
continuous measurement of I_0

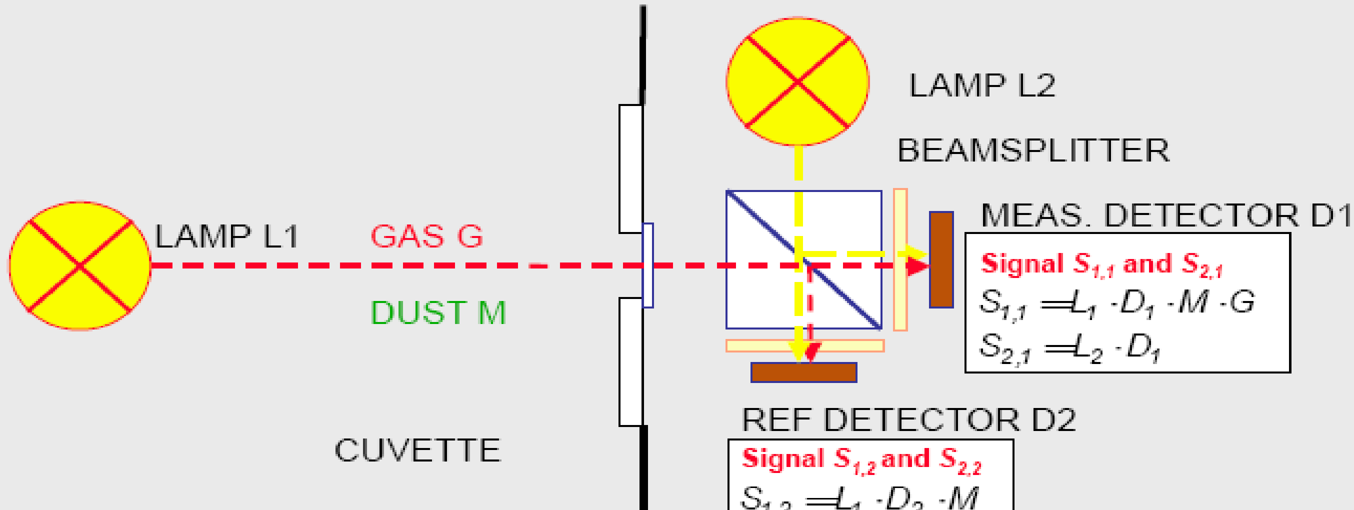


- \+ low drifting
- \+ collinear setup (beam splitter)
- \+ no moving parts
- \- detector adjustment (temperature behaviour, ageing)
- \- only one measurement channel (CO_2)

Measurement Wavelength: 4.3µm

Measuring system setup

POLYTRON IR
DOUBLE COMPENSATION



Signal $S_{1,1}$ and $S_{2,1}$

$$S_{1,1} = L_1 \cdot D_1 \cdot M \cdot G$$
$$S_{2,1} = L_2 \cdot D_1$$

Signal $S_{1,2}$ and $S_{2,2}$

$$S_{1,2} = L_1 \cdot D_2 \cdot M$$
$$S_{2,2} = L_2 \cdot D_2$$

$$S_1 = \frac{S_{1,1}}{S_{1,2}} = \frac{L_1 \cdot D_1 \cdot M \cdot G}{L_1 \cdot D_2 \cdot M} = \frac{D_1}{D_2} \cdot G$$

$$S_2 = \frac{S_{2,1}}{S_{2,2}} = \frac{L_2 \cdot D_1}{L_2 \cdot D_2} = \frac{D_1}{D_2}$$

THUS:

$$S = \frac{S_1}{S_2} = G$$

Signal depending only on *G* (Gas)

Signal not depending on *L*, *D* and *M*

Application examples

Infrared Carbon Dioxide Sensor for Automotive Applications

Dr.- Ing. Michael Arndt

Sensor Development
Robert Bosch GmbH

Email: Michael.Arndt@de.bosch.com

Automotive Electronics

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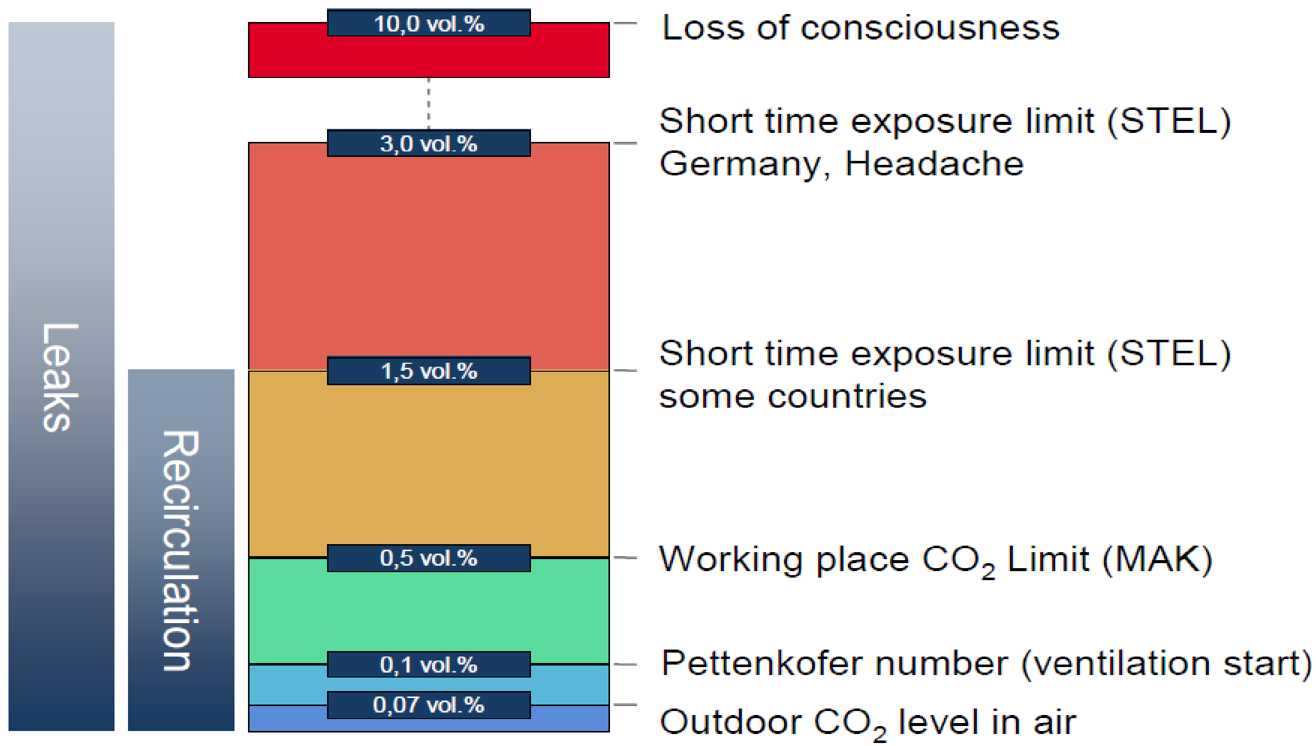
Application examples

Infrared Carbon Dioxide Sensor for Automotive Applications

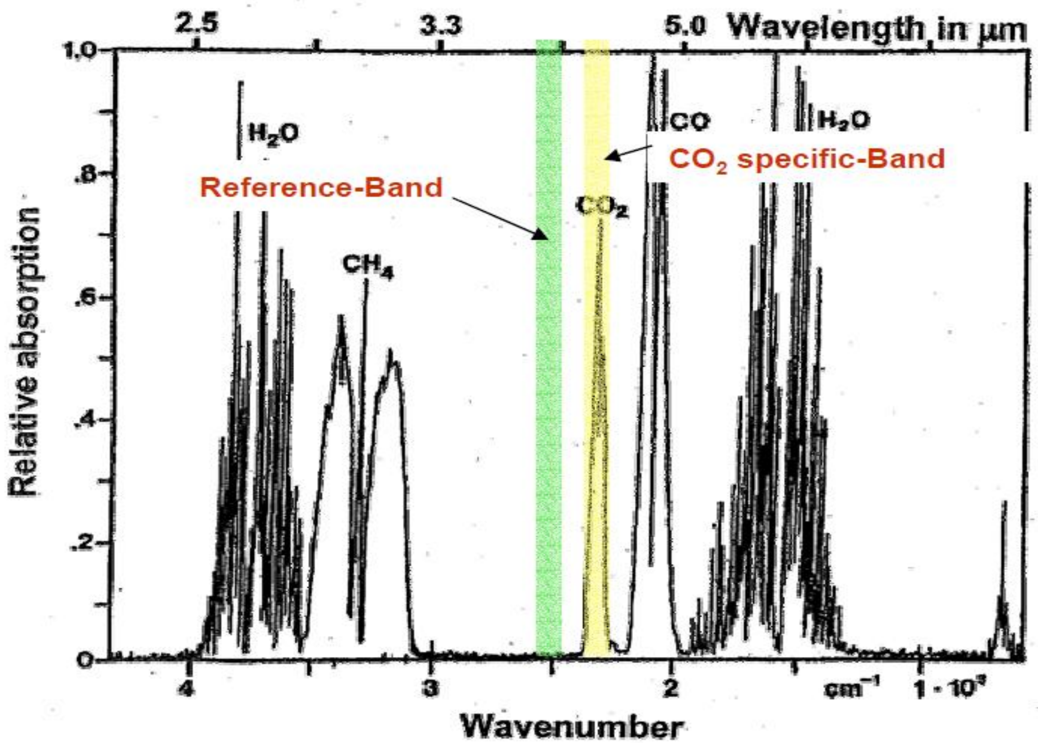
Carbon Dioxide in Cars



Application examples

Infrared Carbon Dioxide Sensor for Automotive Applications

Spectroscopic Gas-Measurement



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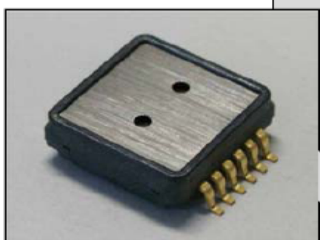
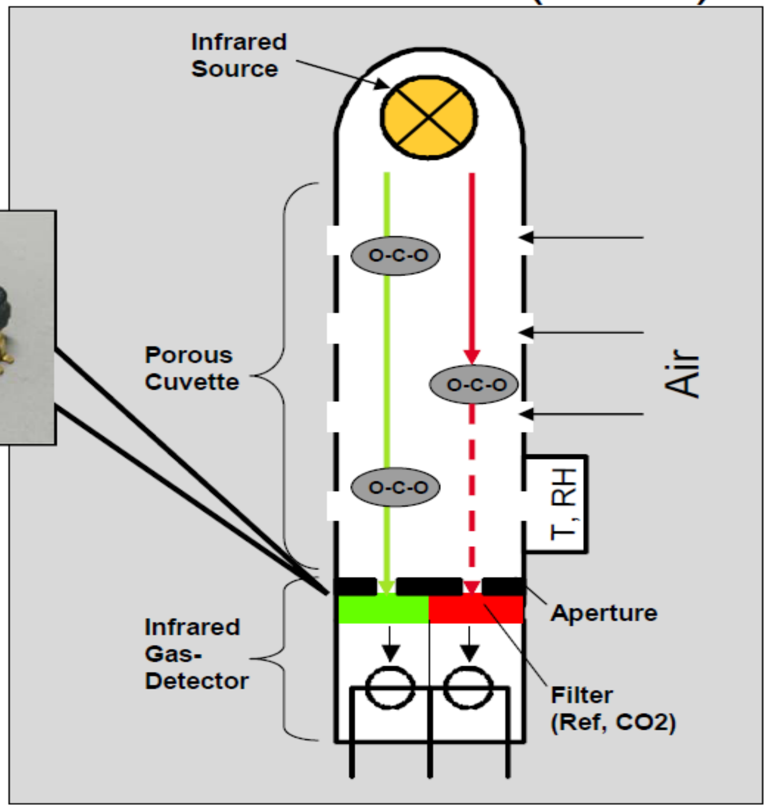
Application examples

Infrared Carbon Dioxide Sensor for Automotive Applications

Climate Control Sensor (CCS)



Bosch
IR-gasdetector

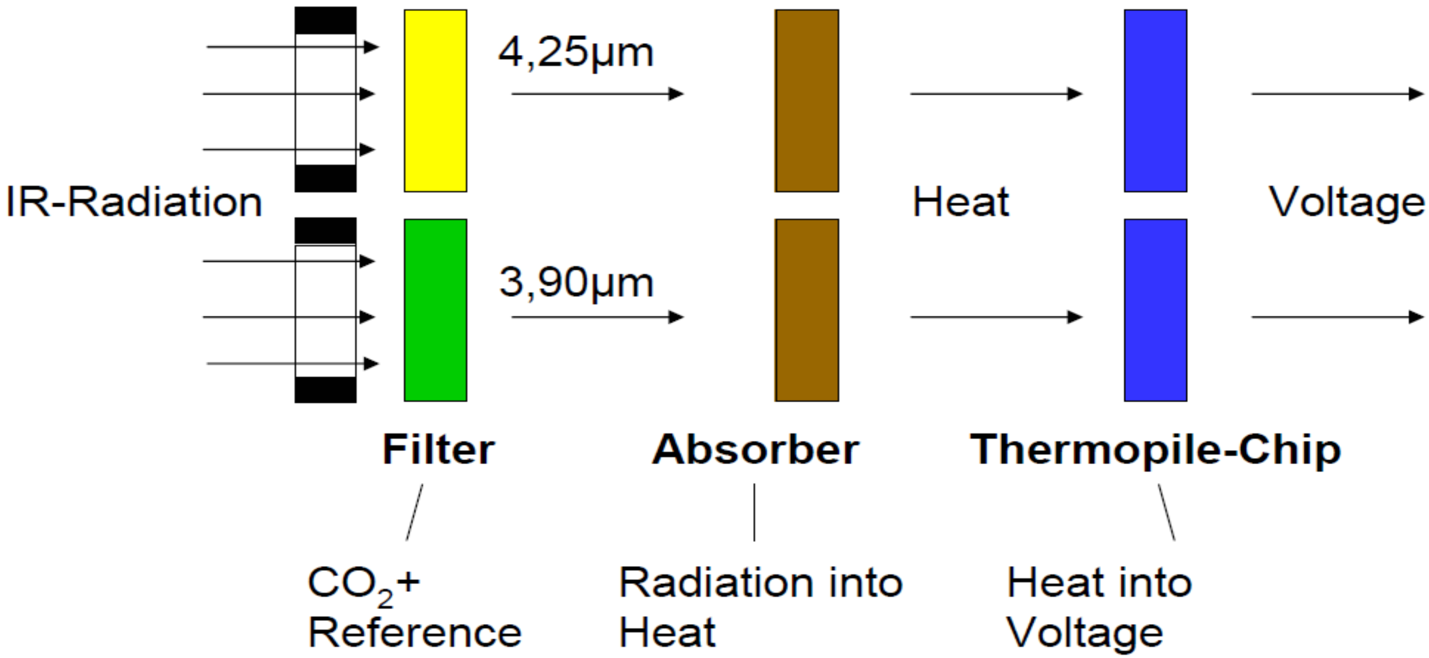


Range: 0..3 vol.%
Resolution: <0.02 vol.%
Interface: digital or analog

Application examples

Infrared Carbon Dioxide Sensor for Automotive Applications

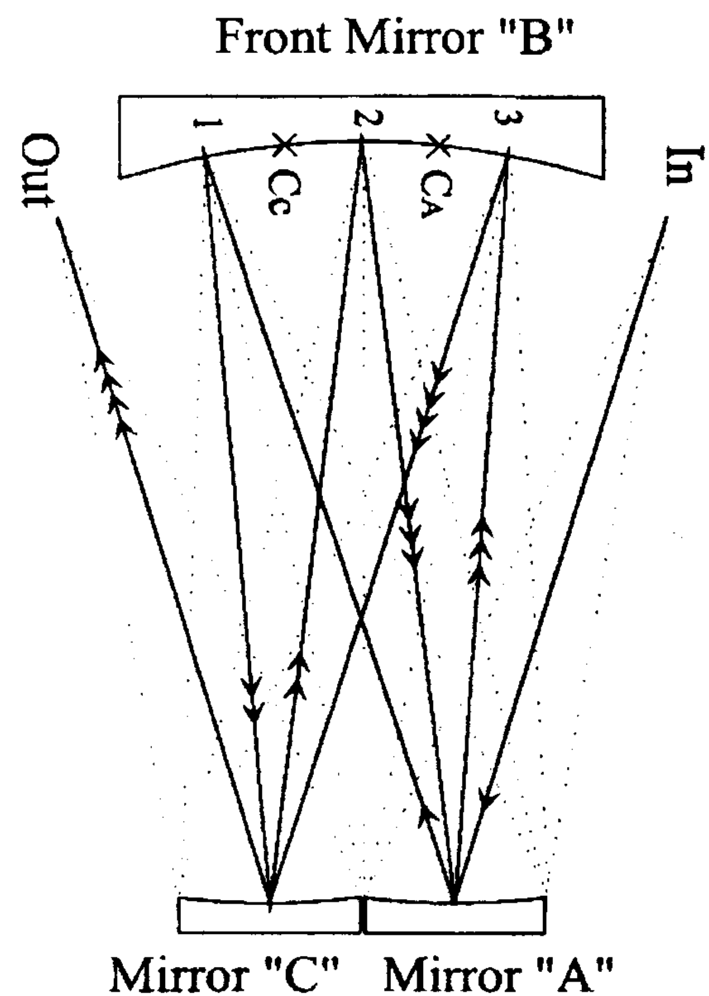
Bosch Infrared Gasdetector



Long path cell

- **White cell (= optical long path cell)**
- John White 1942
- Multiple reflections
- Three spherical mirrors with identical radius of curvature
- Good transmission
- Uncritical alignment

J.-F. Doussin, R. Dominique, C. Patrick: Multiple-pass cell for very-long-path infrared spectrometry, Applied Optics, Vol.38, No.19, 1999



White cell – functional principle

- Multiple reflections
- Three spherical mirrors with identic radius of curvature
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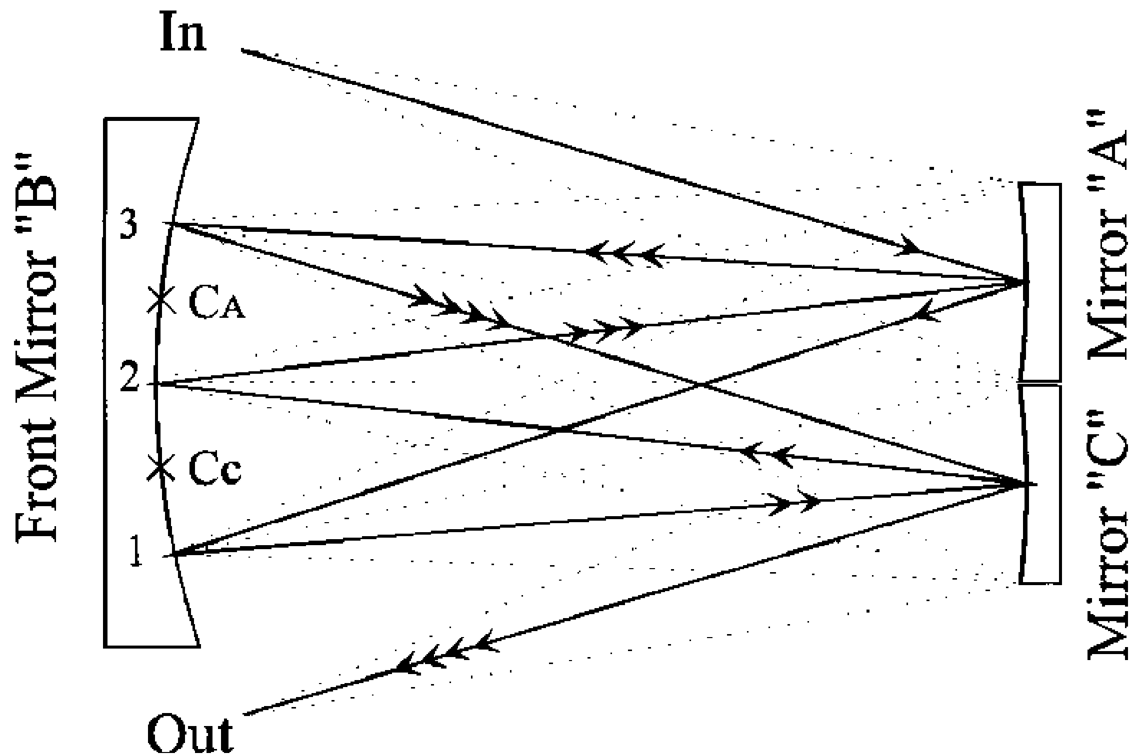

Source: Jean-Franc¸ ois Doussin, Ritz Dominique, Carlier Patrick, *Multiple-pass cell for very-long-path infrared spectrometry, 1999 Optical Society of America*

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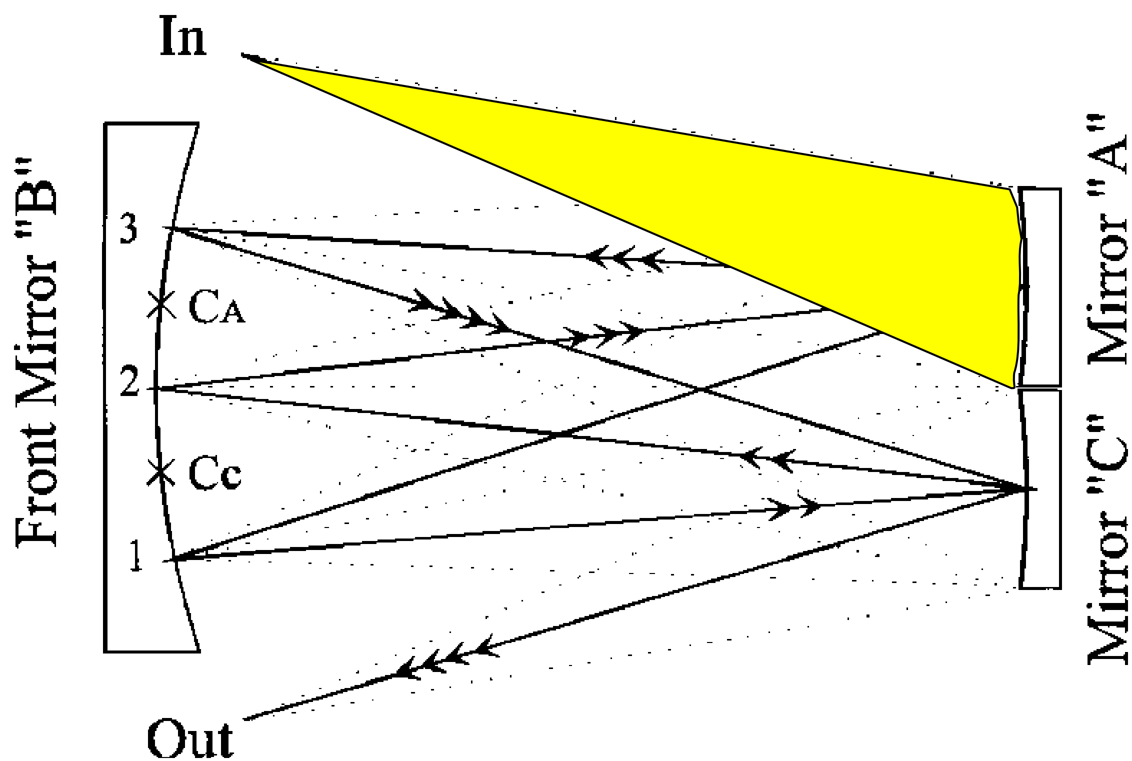

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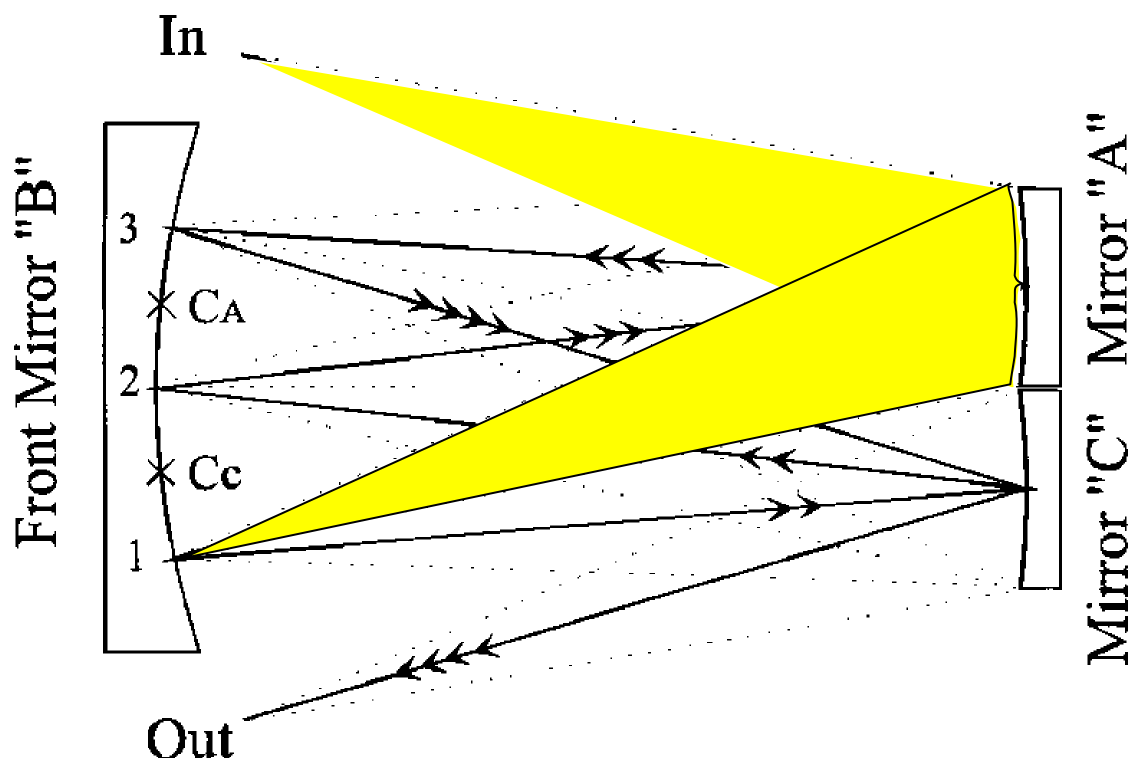

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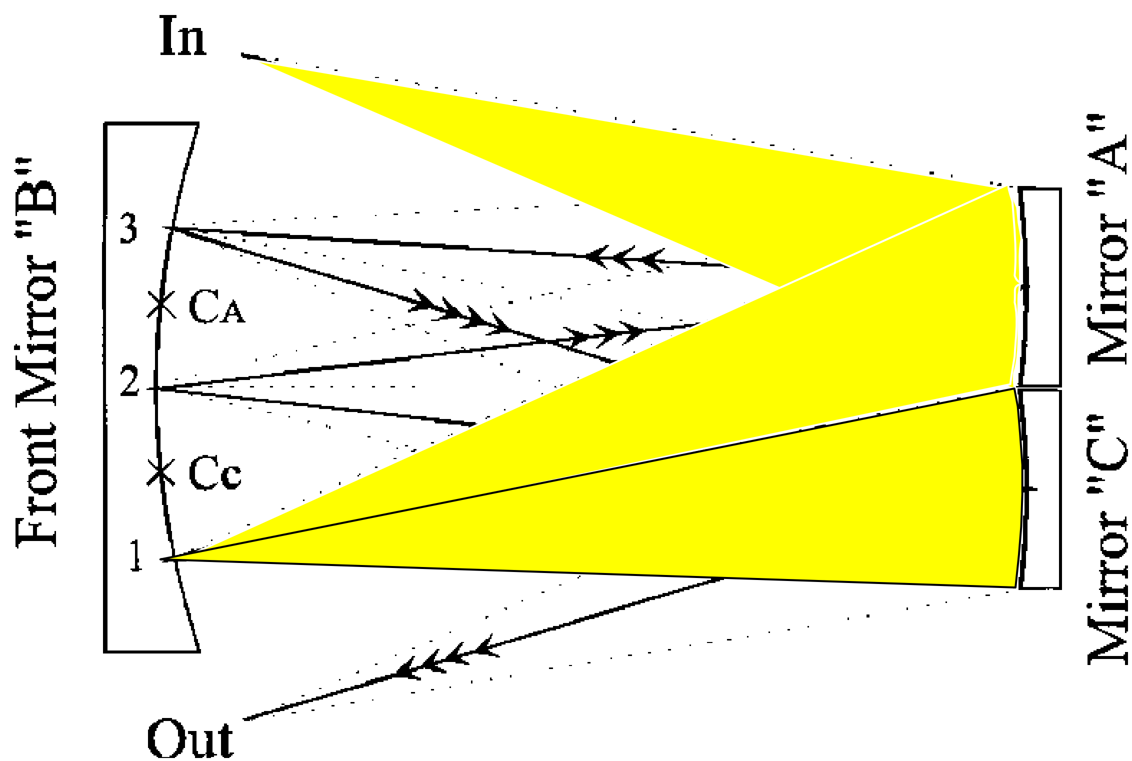

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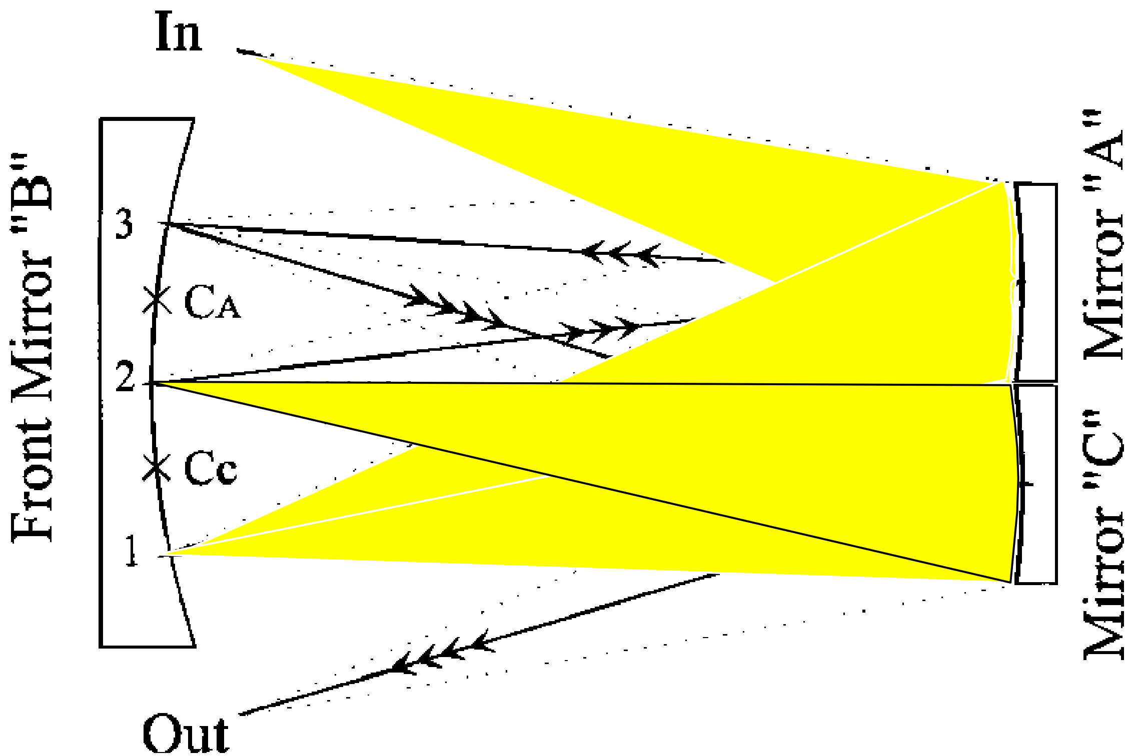

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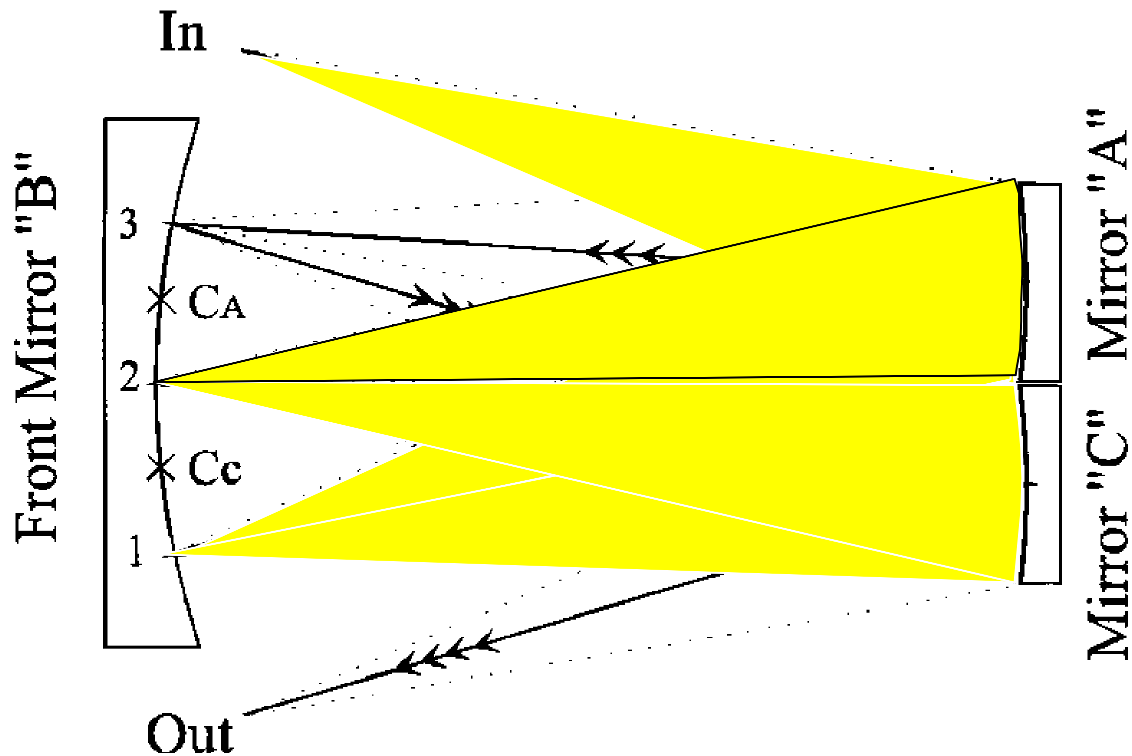

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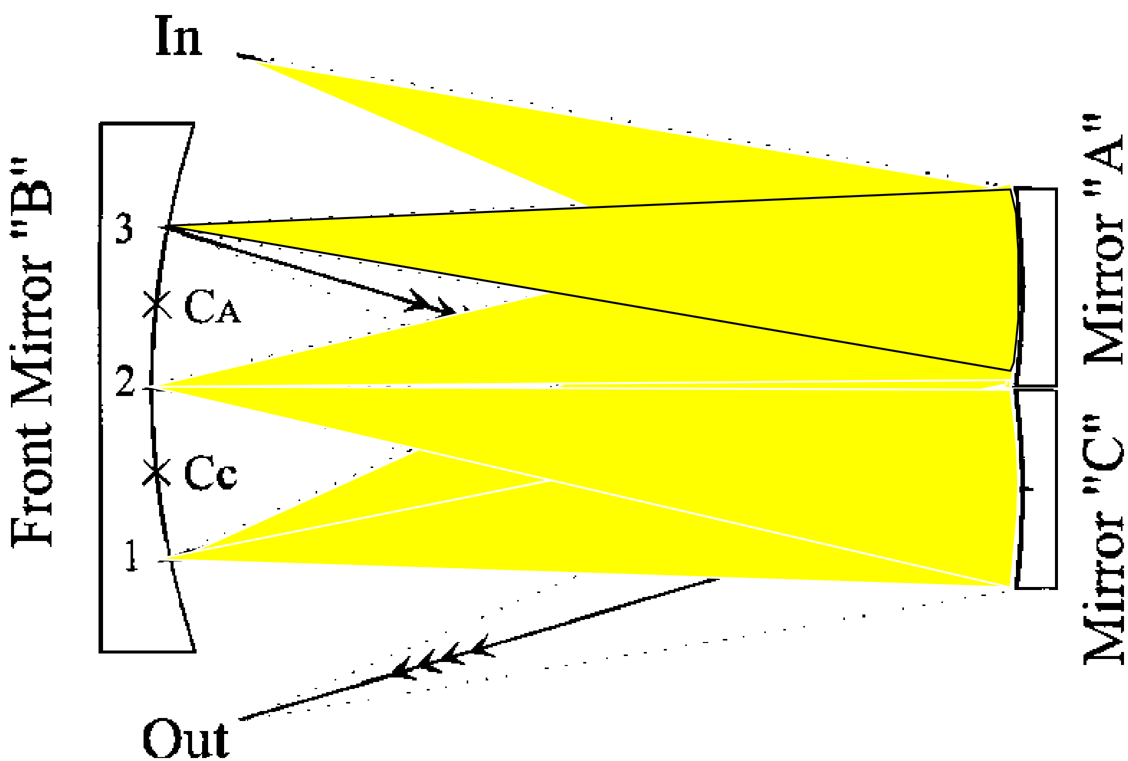

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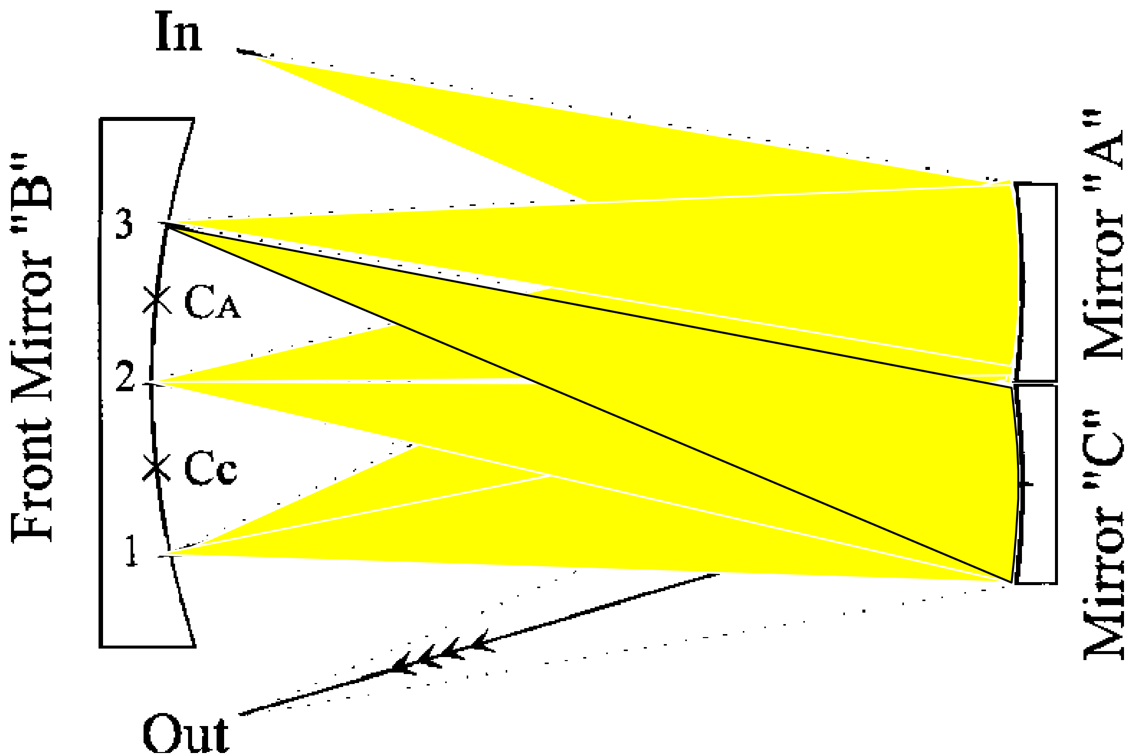

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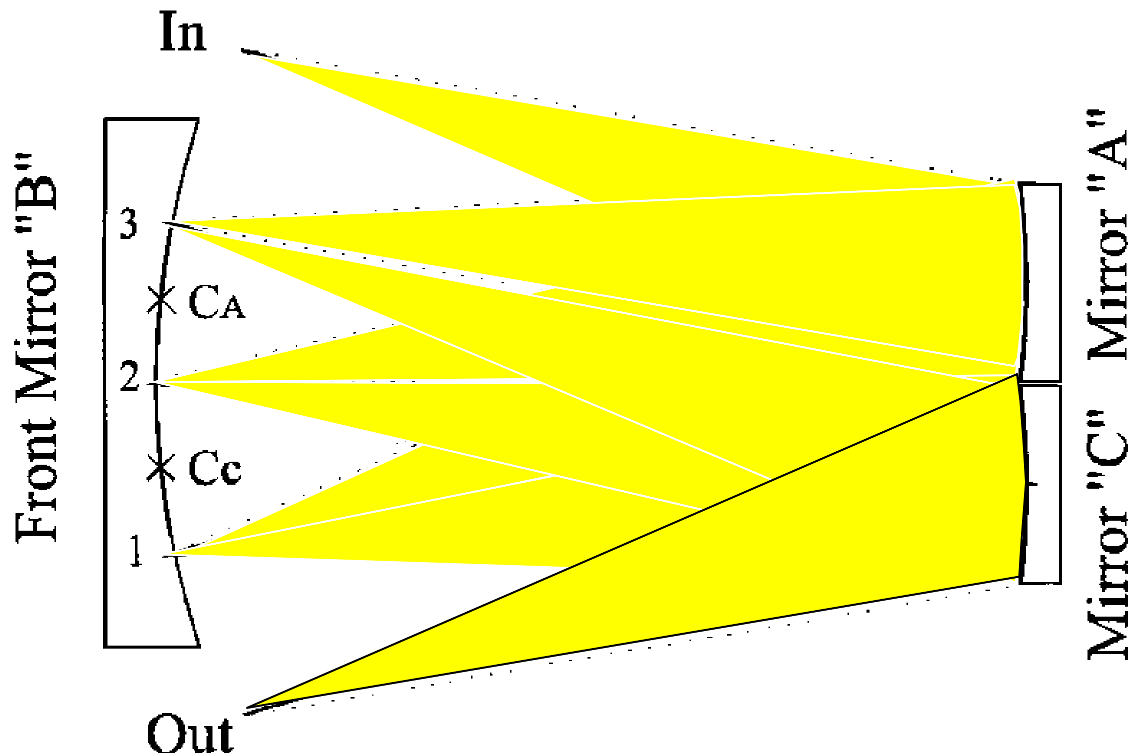

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Photo-acoustics

- First description by Alexander Graham Bell 1880
- Energy supply with short flashes of light
  - → Temperature variation
  - → Pressure variation
  - → Measurement with a microphone

Photo-acoustical gas measurement

- **Photo-acoustical spectroscopy (PAS)**
- PAS uses the energy which is transformed into kinetic energy by inelastic impacts
- The transformation of the energy difference $(E_1\text{-}E_2) = h \cdot \nu$ in translation energy results in a higher velocity of the colliding molecules
- Increase of velocity equivalent with increase of gas temperature
- Increase of temperature leads to thermo elastic expansion of the sample and therefore to an increase of pressure

Photo-acoustical gas measurement

- Increase of velocity is equivalent with increase of gas temperature T
- For a sample which is approximately an ideal gas:

$$p \cdot V = n \cdot k \cdot T$$

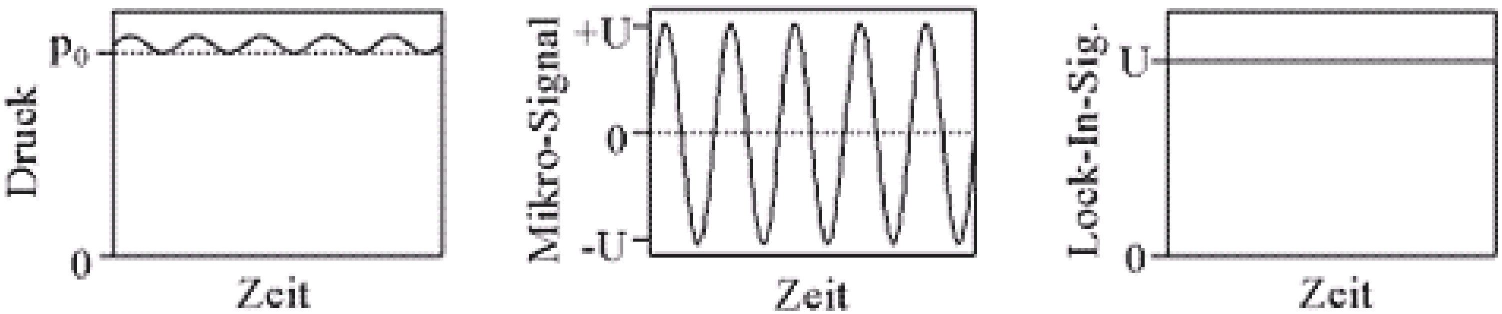
with p being the pressure, n the number of particles and k the Boltzmann constant

- An increase of temperature leads with constant volume V (and density) to an increase of pressure p
  → thermo elastic expansion

Photo-acoustical gas measurement

- An interruption of irradiation leads due to the diffusion of the molecules to a heat dissipation over the measurement cell
  → Pressure reduction to initial value
- Modulated irradiation results in a small periodic variation of pressure (typically 10^{-2} to 10^{-1} Pa) with the same frequency as the modulation of the radiation source
  – the photo-acoustic signal
- Detection of this acoustic wave with a microphone eliminates the background (atmospheric pressure) because only pressure variations are detected
- Microphone signal yields a a constant offset-free signal

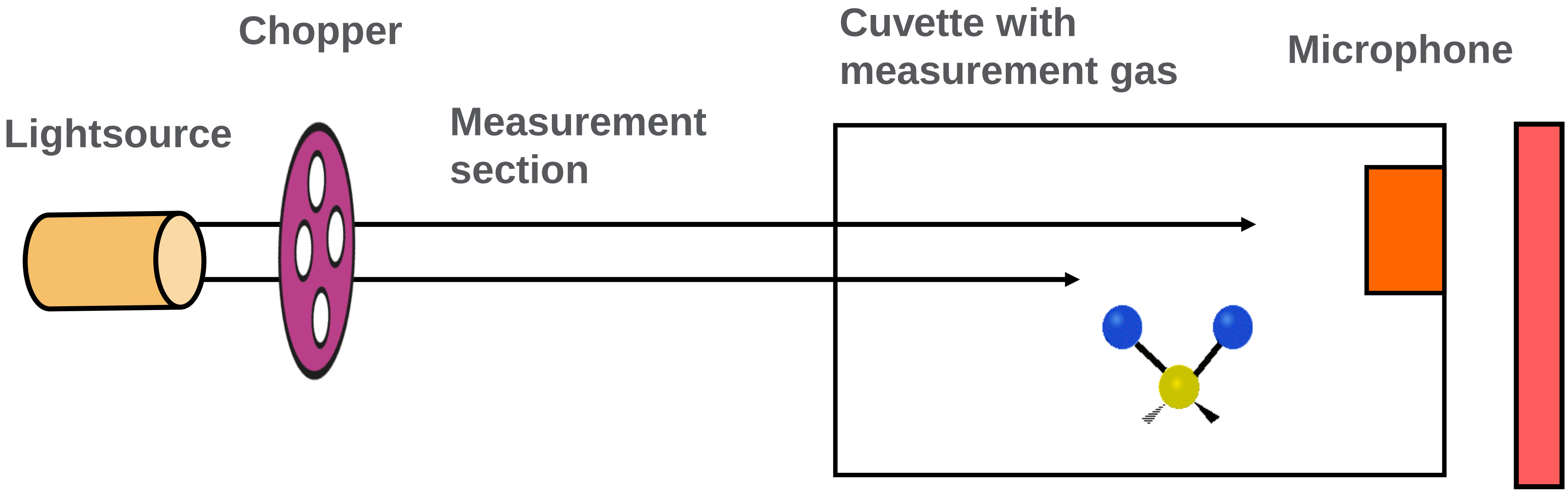
Photo-acoustical gas measurement



Time course of the harmonic pressure variation in the measurement cell, the microphone voltage and the lock-in signal

Photo-acoustical gas measurement

- Resonant excitation with alternating light
- Often used with laser light sources
- Partially use acoustic resonators



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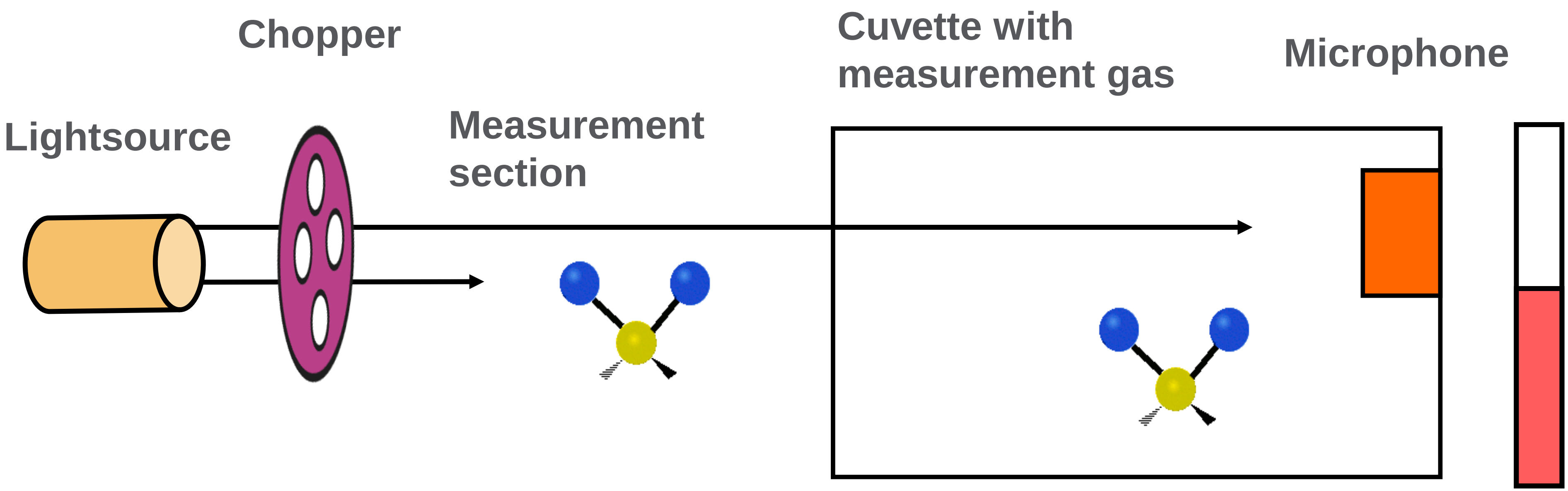
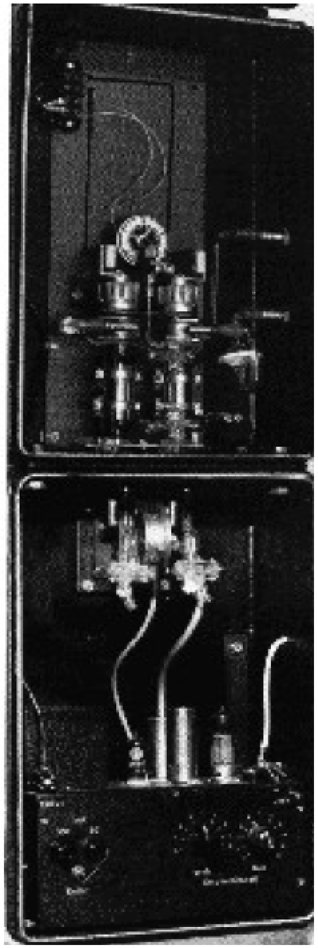


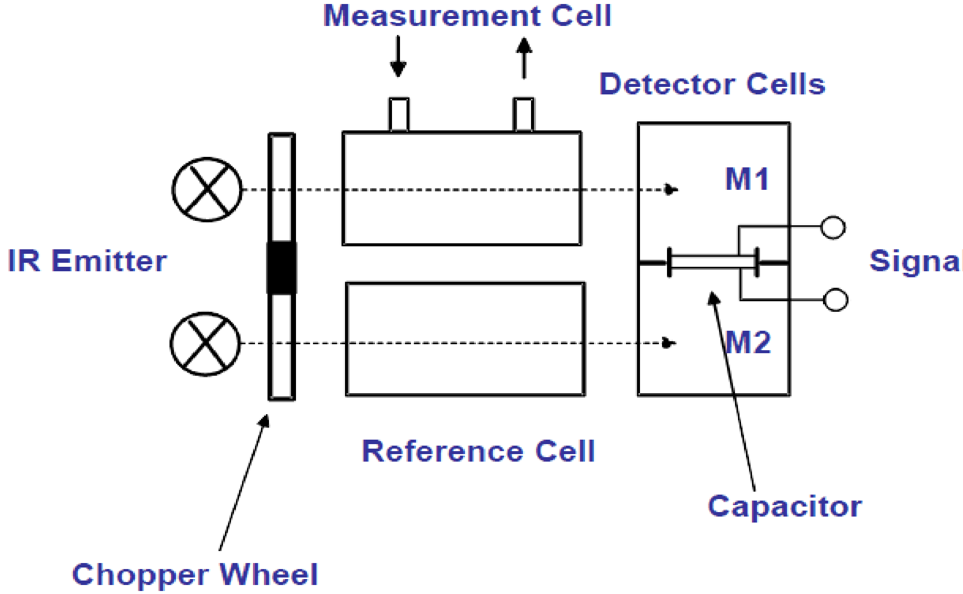
Photo-acoustical gas measurement



URAS (Ultrarot-Absorptionsschreiber)

Lehrer, Luft (1938)

acoustooptic / optopneumatic
Detector (target gas as a positive filter)

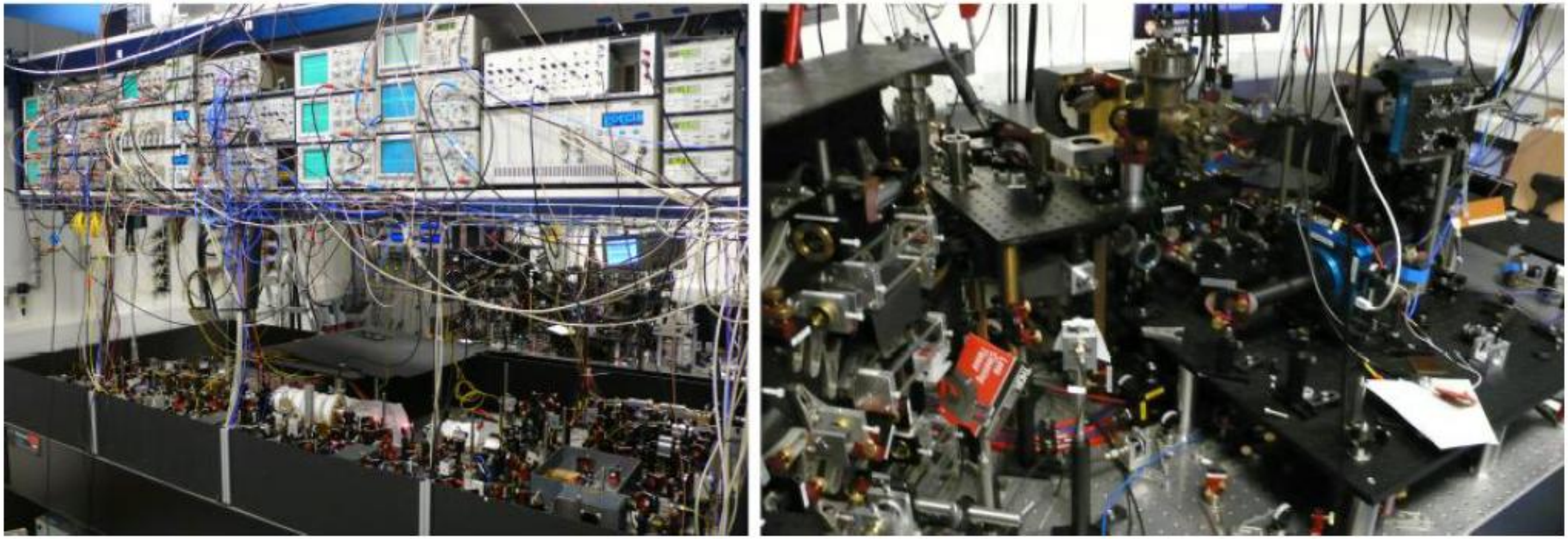


Δp = 0.1µbar, Δx = 1nm, ΔC = 0.016pF
Full scale values: N_2O, CO_2: 100ppm
Hydrocarbons, CO: 500ppm

Laser spectroscopy

- Measurement principle
- Single Mode Laser
- Wavelength adjustment
- Direct spectroscopy
- Open Path system
- Multireflexion cell
- Derivative spectroscopy
- Cavity-Ring-Down

Laser spectroscopy

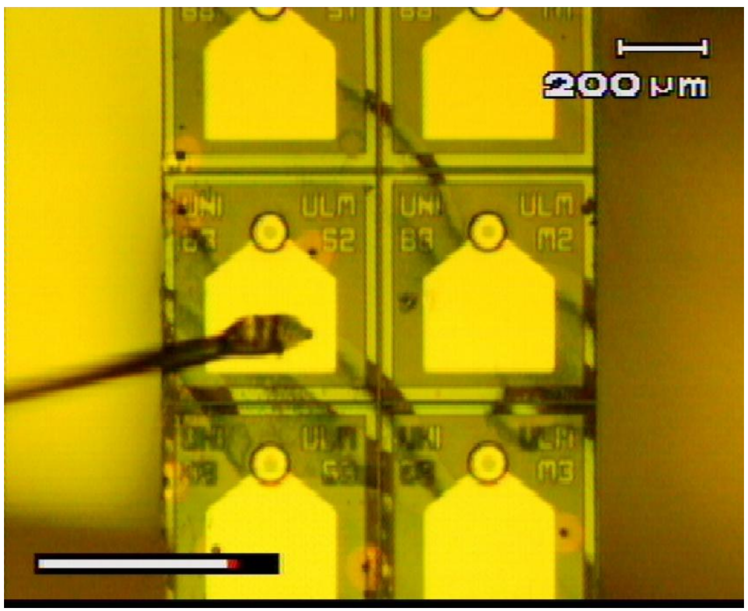


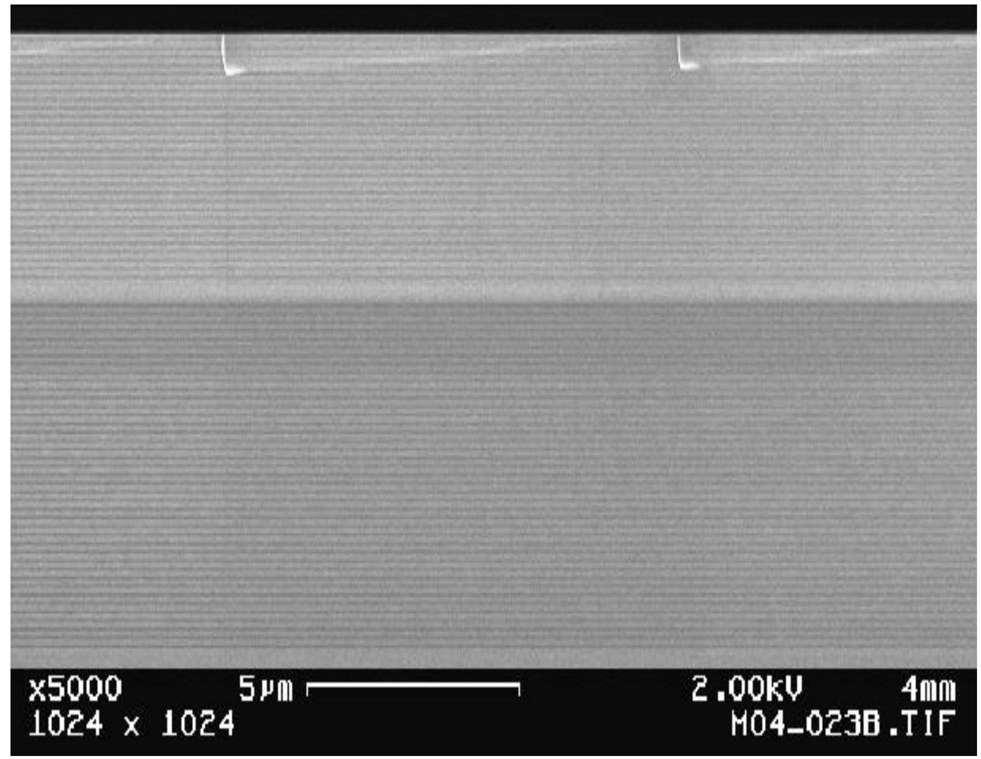
Laser spectroscopy in basic research (University Cambridge)

Laser spectroscopy

Wavelength stabilisation of a laser

- **Laser as selective light source**
- **Requirement for laser diodes:**
- Single Mode: Only one wavelength
- Suitable Wavelength
- Wavelength adjustable

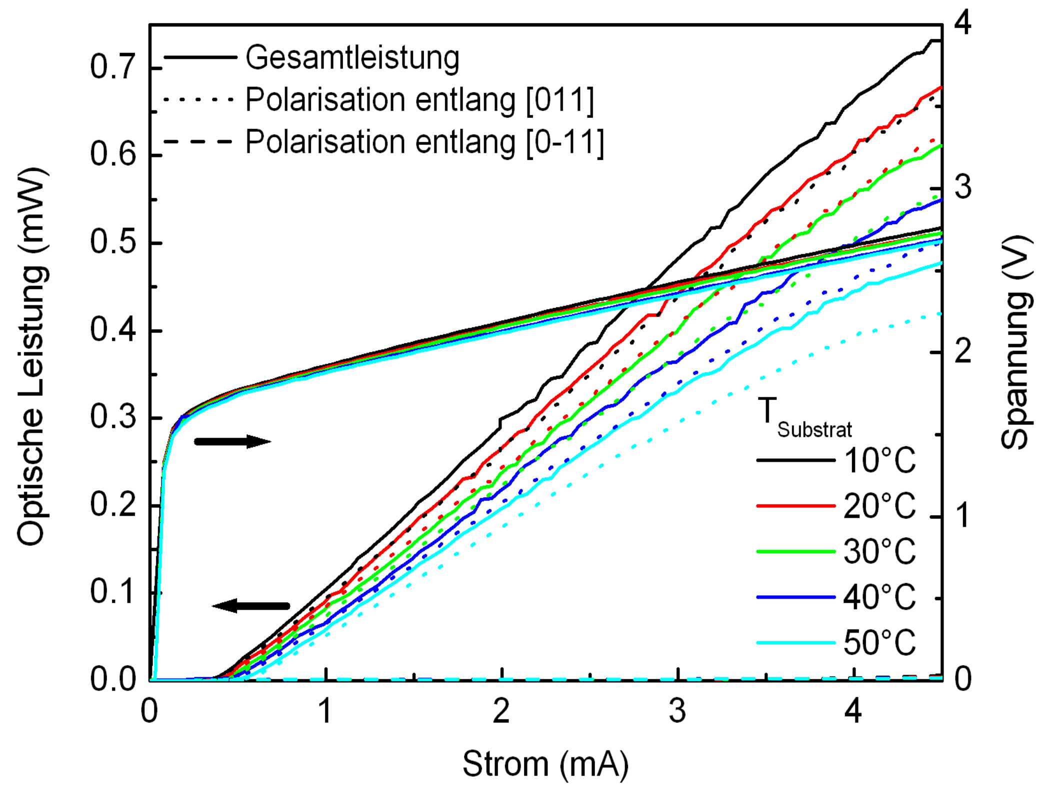




Surface-emitting laser diodes (VCSEL)

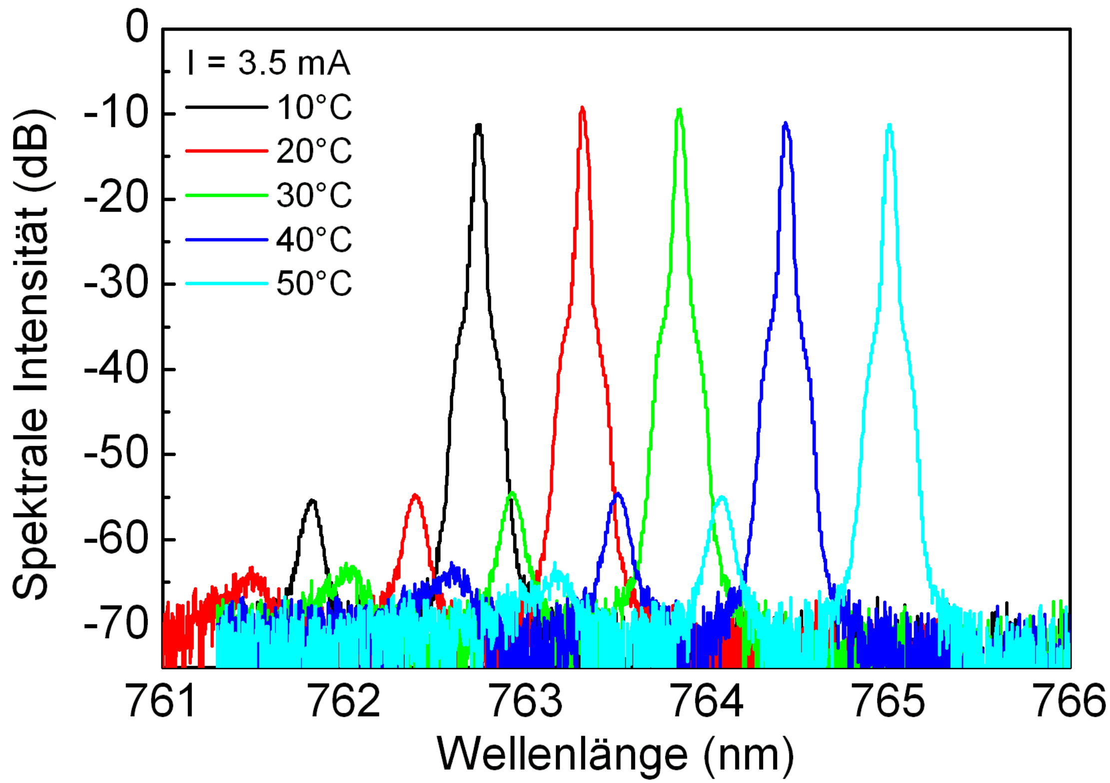
Laser spectroscopy

- **Laser characterization**
- Investigations regarding to electrical behavior and radiation power
- Voltage-Current characteristic
- Optical power as a function of current



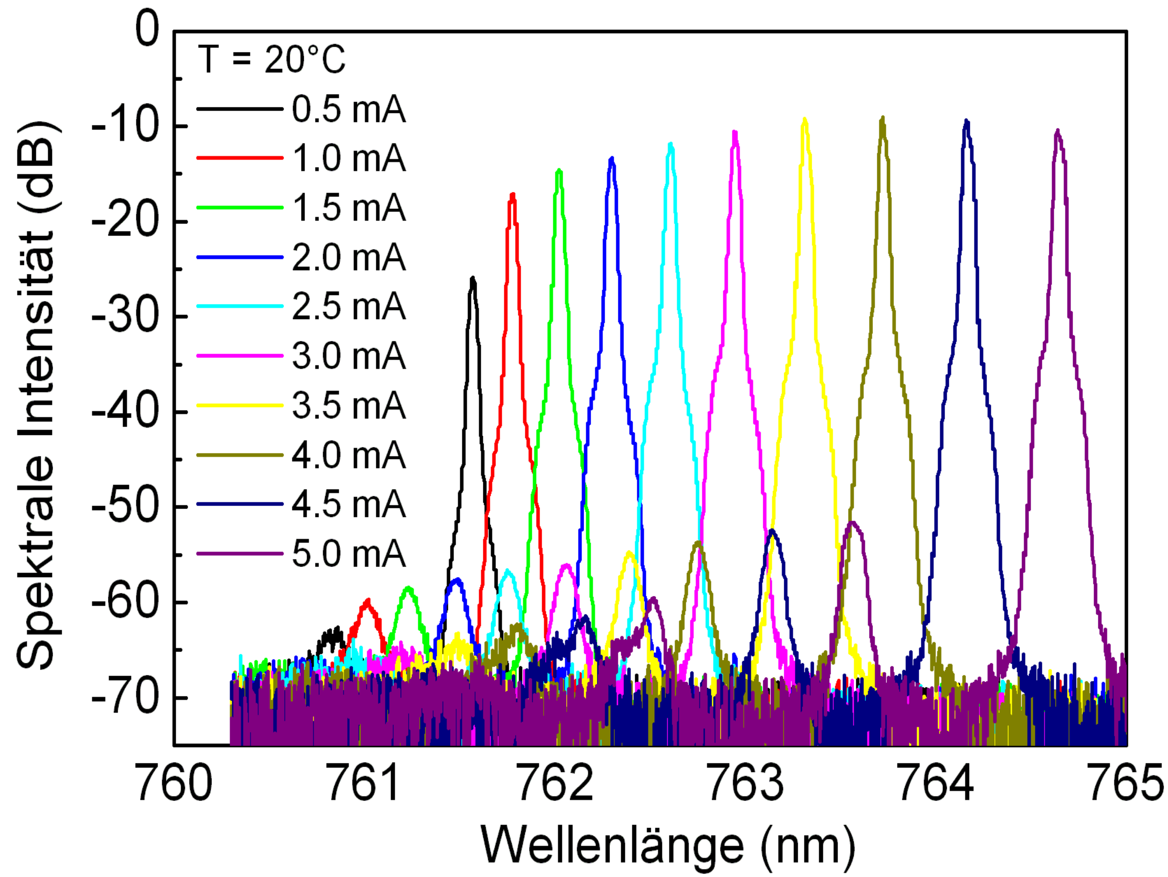
Laser spectroscopy

- **Laser characterization**
- Adjustment regarding to laser substrate temperature



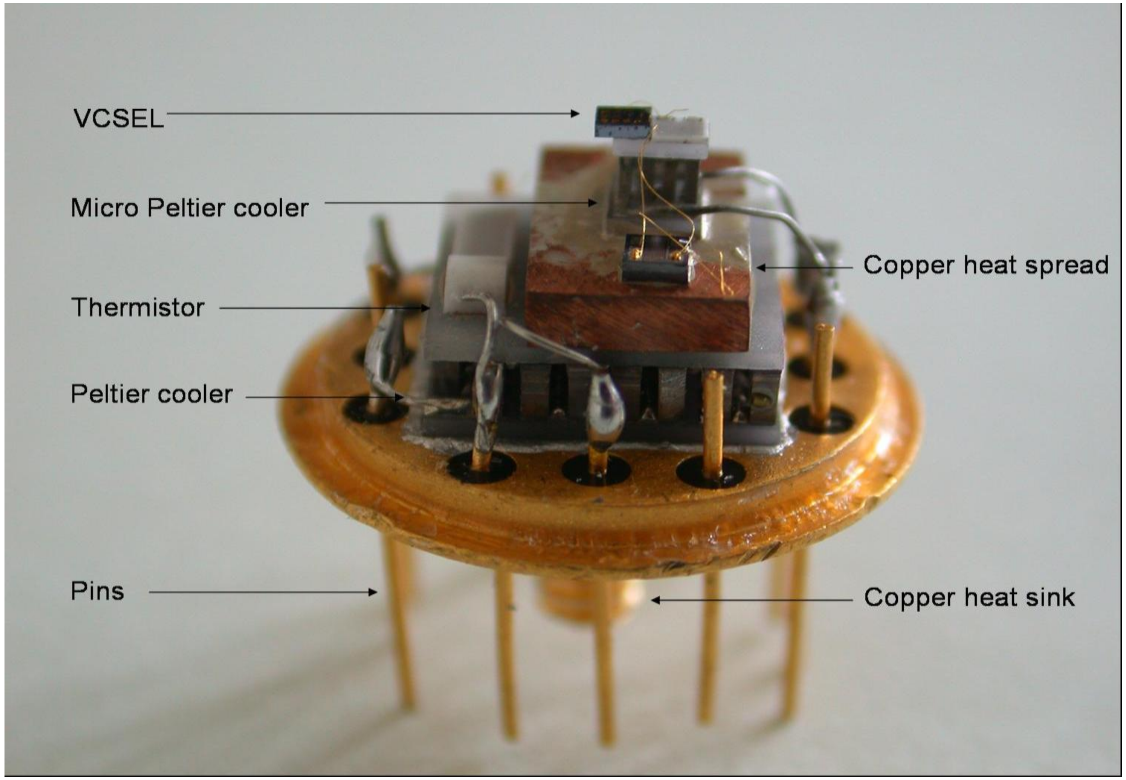
Laser spectroscopy

- **Laser characterization**
- Adjustment regarding to the laser current
- Record of spectra with different currents ($T_{substrate}$=20°C)
- Up to 3mA laser current few secondary modes
- Adjustment rate: 0,0625 nm/mA

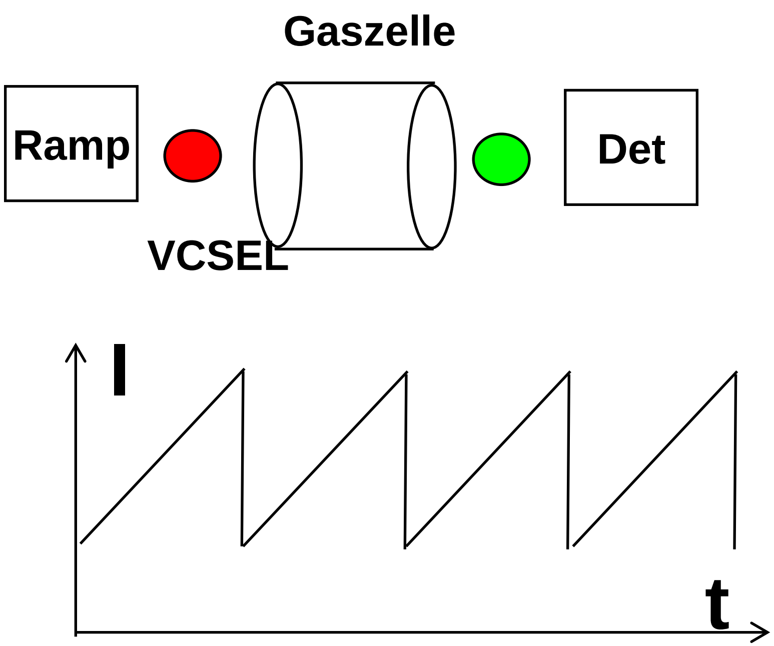


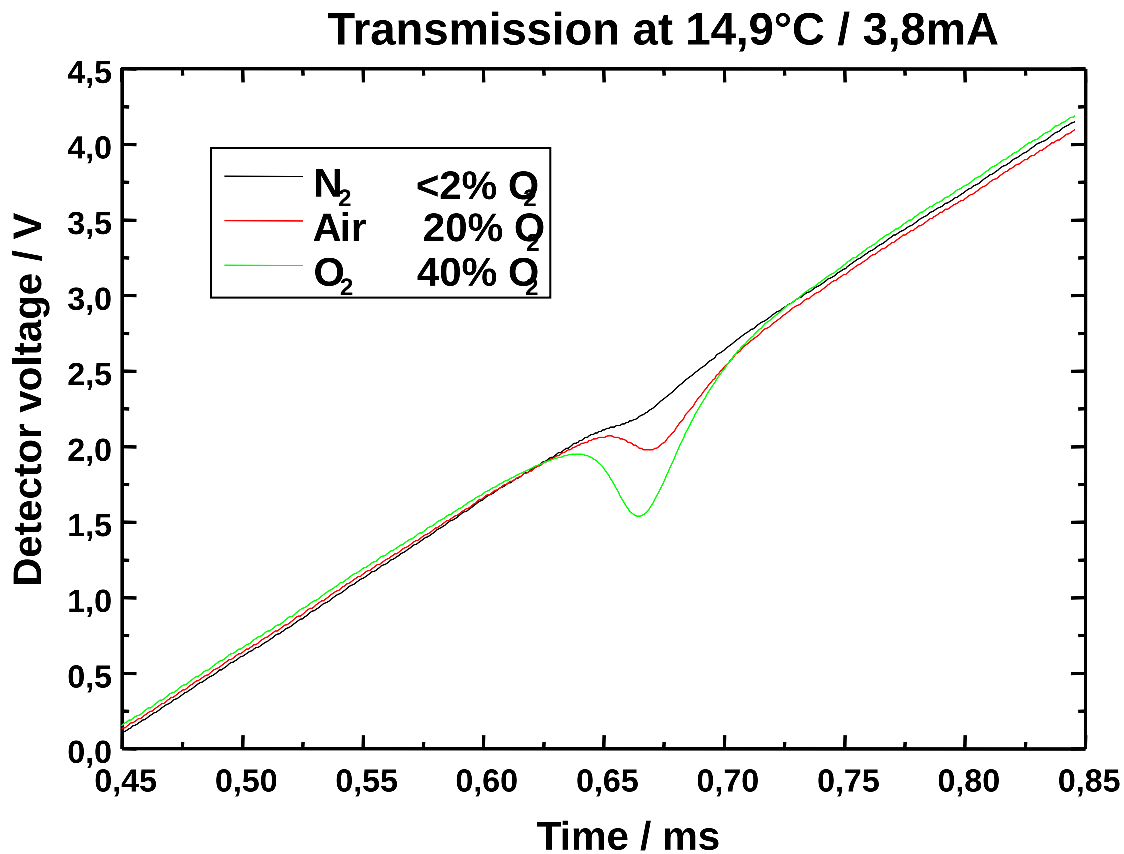
Wavelenght stabilization of a laser

- **762 nm VCSEL on a two-step Peltier cooler**
- With this setup temperature differences of more than 130K could be achieved. With a temperature tuning coefficients of 0,055nm/K this corresponds to a modehop-free tuning range of more than 7nm.



Wavelenght stabilization of a laser





- On base current modulated saw tooth pulse with a frequency of 1100Hz, standard pressure , 298K

Cavity-Ring-Down Spectroscopy

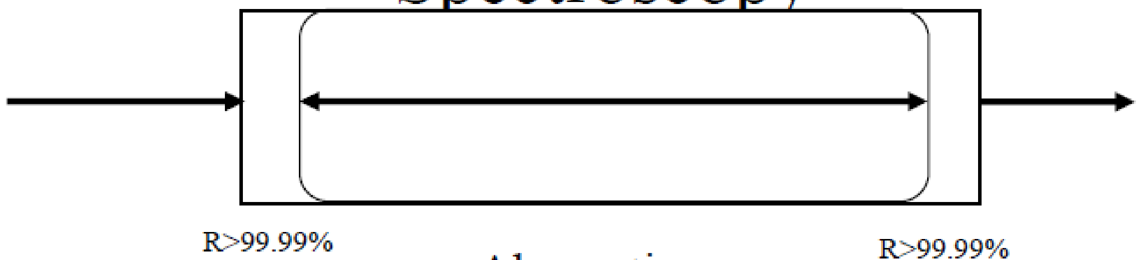
Ring Down Cavity Spectroscopy Technique

First Developed by O'Keefe and Deacon
Rev. Sci. Instr. 59, 2544 (1988)
Theory: Romanini and Lehmann
J. Chem. Phys. 99, 6287 (1993)

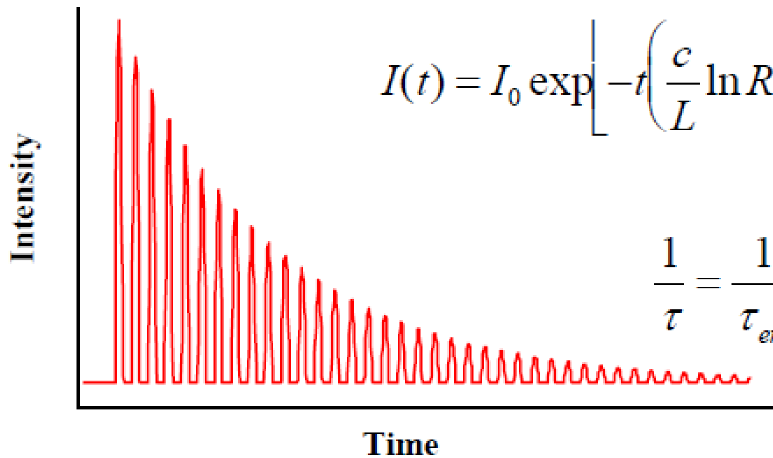
- Use a passive optical cavity formed from two high reflective mirrors (T~1-100 ppm)
- Excite cavity with a pulsed laser to 'fill' with photons
- Detect exponential decay of light intensity inside resonator
- Decay rate reflects:
  - Loss due to mirrors (slowly changing with wavelengths)
  - Absorption of gas between mirrors

Cavity-Ring-Down Spectroscopy

Cavity Ring-Down Absorption Spectroscopy



Absorption



$$I(t) = I_0 \exp\left[-t\left(\frac{c}{L}\ln R + c\cdot\sigma(\lambda)\cdot N\right)\right]$$

$$L_{eff} = L/(1-R)$$

$$\frac{1}{\tau} = \frac{1}{\tau_{em}} + N\cdot\sigma\cdot c$$

Where:
- c : speed of light
- L : length of cavity
- R : mirror reflectivity
- σ : absorption cross section
- N : number density
- L_{eff}: effective pathlength

History of FTIR spectroscopy

- About 1800: F.W. Herschel discovers infrared radiation
- 1891: Development of the Michelson-Interferometer (“ether experiment”)
- ~1900: Rayleigh: Calculation of the spectrum from an interferogram with Fourier transformation
- 1911: Rubens and Wood: First type of FT spectroscopy (two-plate quartz interferometer, long wave IR, but: calculation effort too big)
- 1953: Fellgett discovers multiplex advantage over grating spectrometer
- 1956: first long wave IR spectrum with Michelson-Interferometer
- 1964: First commercial FTIR spectrometer (Research and Industrial Instruments Company)
- 1965: Development of Fast Fourier Transformation algorithm (Cooley and Tukey) →significantly lower calculation effort

Albert Abraham Michelson

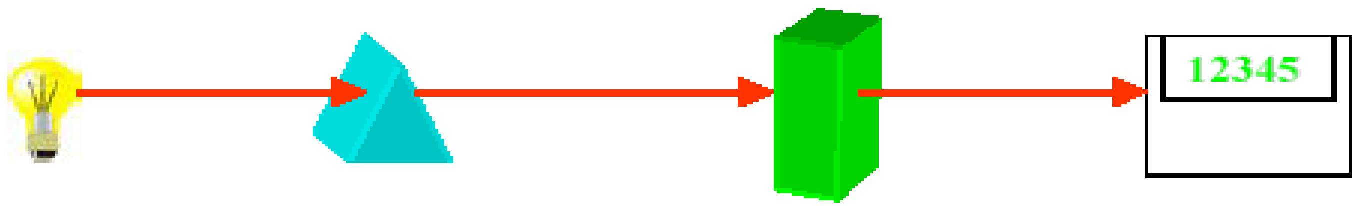
John William Strutt, Lord Rayleigh

- **Today widely used and established method**
  Well known manufacturer: Bruker, ThermoScientific

FTIR spectroscopy –measurement principle

Conventional IR Spectroskopy:

IR source → Monochromator → Probe → Detector → Signal processing

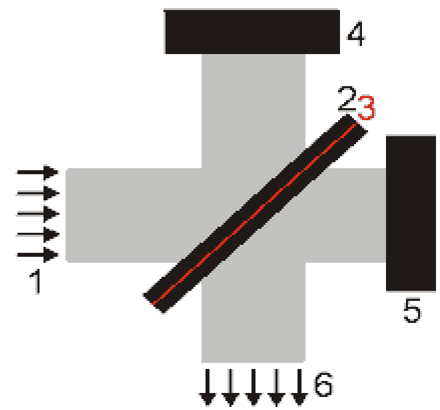


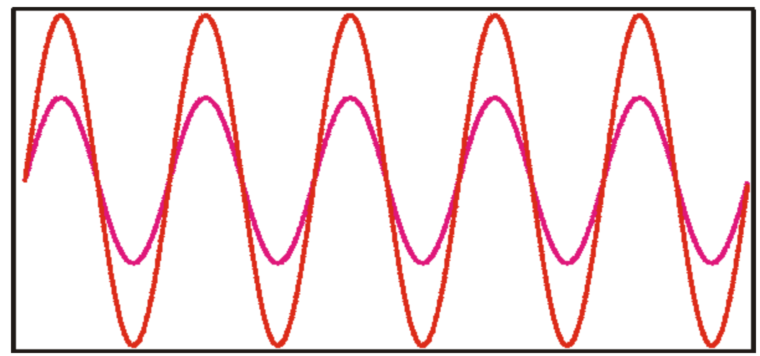
Fourier Transformation IR (FTIR) Spectroskopy:

IR source → Interferometer → Probe → Detector → Signal processing

FTIR spectroscopy - Interferometer

- **Functionality of an interferometer**
- Light wave is divided in two parts
- Two Waves run through paths with different length
  → phase shift
  → constructive or deconstructive interference





Schematic setup of a Michelson interferometer and resulting interferogram

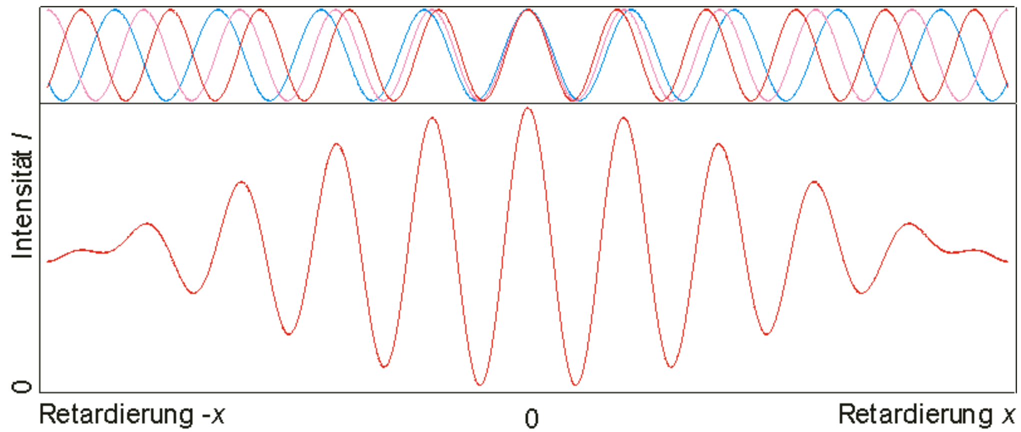
FTIR spectroscopy - Interferometer

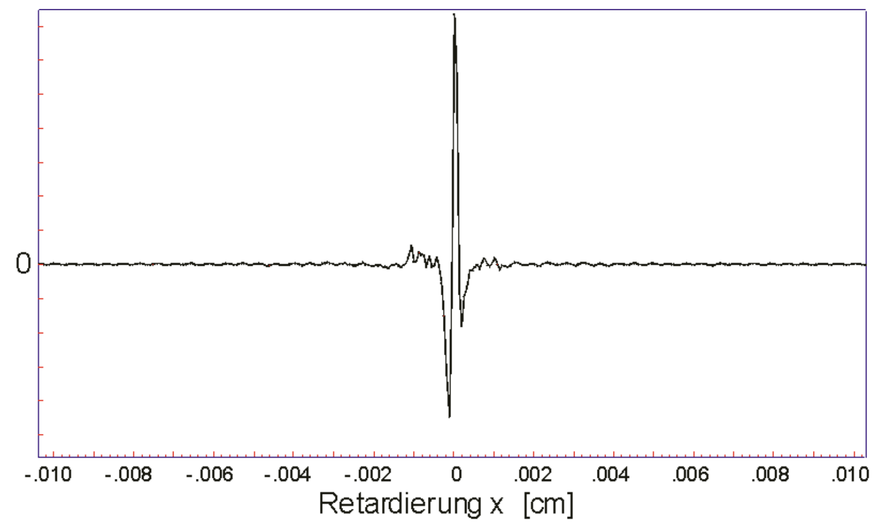
- **Polychromatic interference**
- Spectrometer process the light of many wave lengths
  $\rightarrow$ interference by every wave length
  $\rightarrow$ superposition
- Intensity at detector as function of the mirror way x

$$I(x) = \int_B I(\tilde{v})\cos(2\pi\tilde{v}x)d\tilde{v}$$

$$\tilde{v} = Wellenzahl$$

$$B = Bandbreite$$





FTIR spectroscopy - FFT

Monochromatic Interference: constructive *n·λ* **and destructive** *(2n+1) ·λ/2*

$$I(x) = I_0\left(1 + \cos\left(2\pi \nu x\right)\right)$$ **Interferogramm**

Continuos Spectrum: $-\infty \leq \nu \leq \infty$

$$I(x) = \int_0^\infty I(\nu)\cos(2\pi \nu x)d\nu$$ **Interferogramm**

$$I(\upsilon) = \int_0^\infty I(x)\cos(2\pi \upsilon x)dx$$ **Spectrum**

Fourier transformation of interferogramm of place- I(x) or time-domain I(t) into frequency-domain I(v) results inb spectrum of the substance

Only for limited intervals possible

FTIR spectroscopy - FFT

Continuous Fourier Transformation

$$\hat{x}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} x(t) e^{-\mathrm{i}\omega t} d\,t \qquad x(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \hat{x}(\omega) e^{\mathrm{i}\omega t} d\,\omega$$

Discreet Fourier Transformation

$$\hat{x}_k = \sum_{n=0}^{N-1} x_n e^{-\mathrm{i}2\pi \frac{kn}{N}} \qquad x_n = \frac{1}{N} \sum_{k=0}^{N-1} \hat{x}_k e^{\mathrm{i}2\pi \frac{kn}{N}}$$

=> Sampling theorem should not be infringed

Fast Fourier Transformation

Fast Fourier Transformation (FFT) is an algorithm for fast calculation of the values of a discreet Fourier Transformation (DFT)

FTIR spectroscopy - FFT

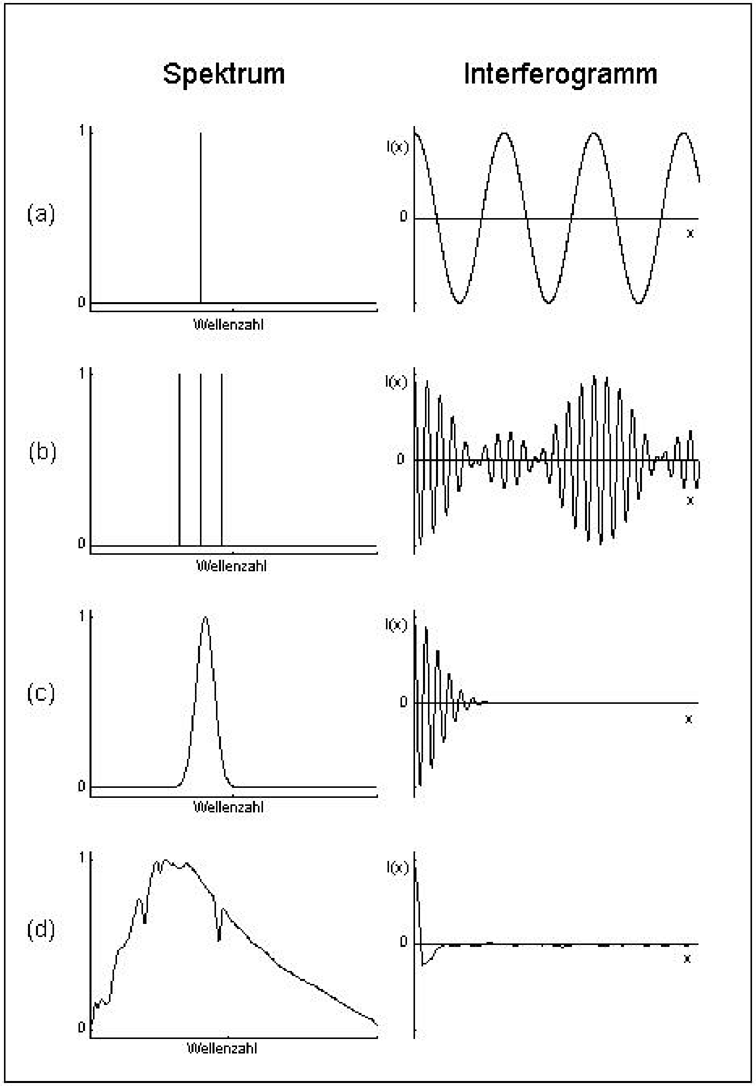
Interferogramms of different spectra

a- monochromatic wave

b- three monochromatic waves

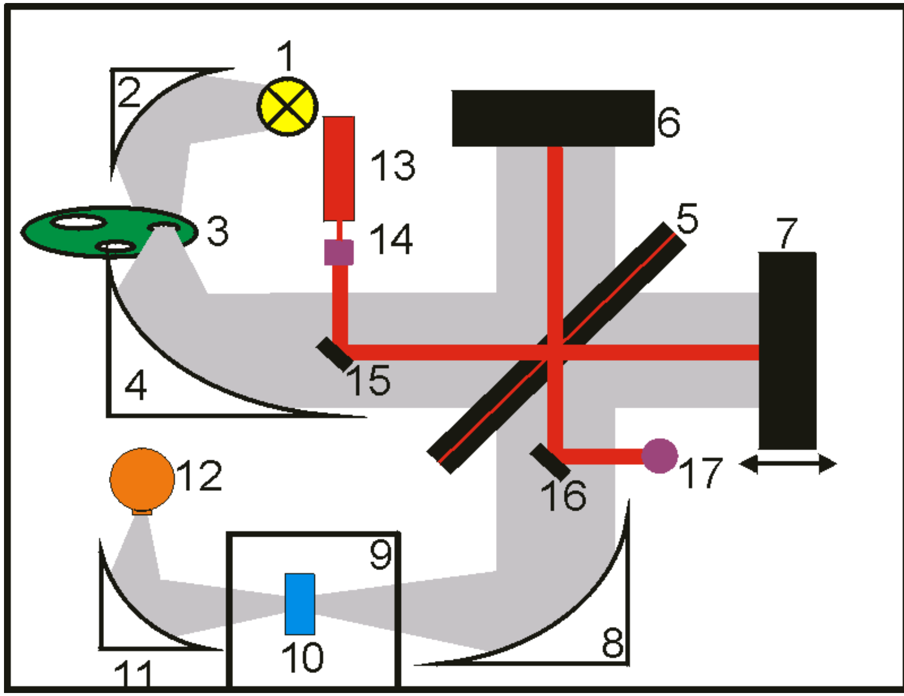
c- continuos spectra

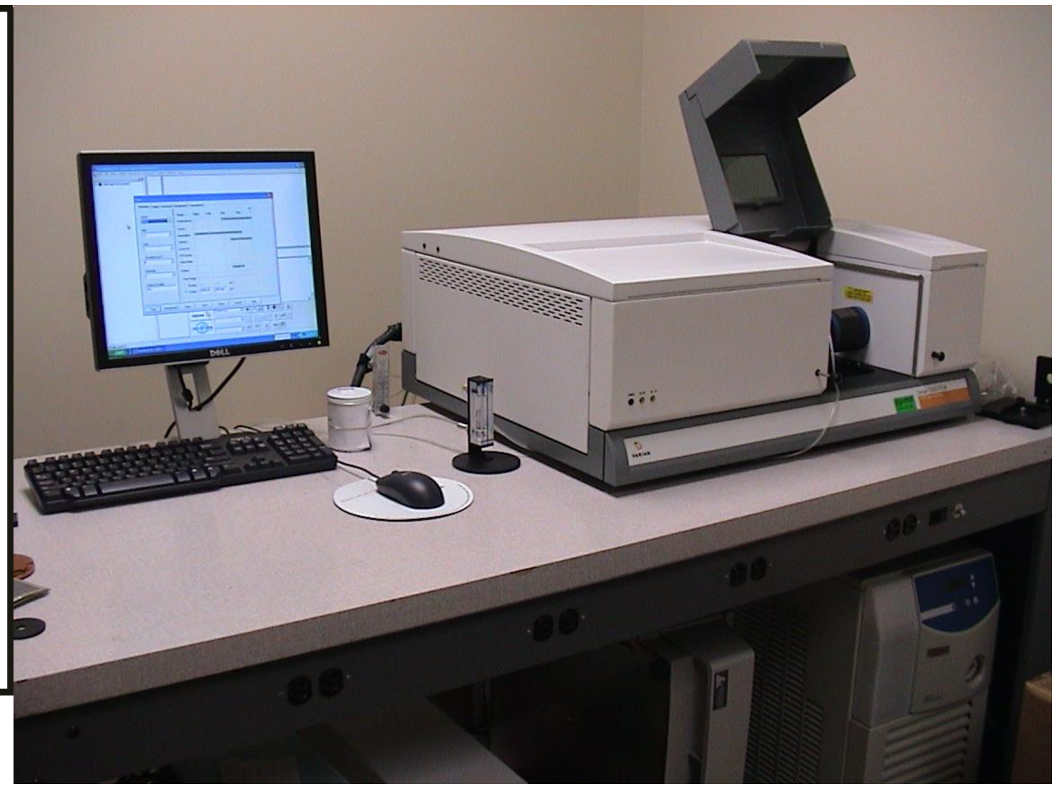
d- broadband emitter



FTIR spectroscopy - Practice

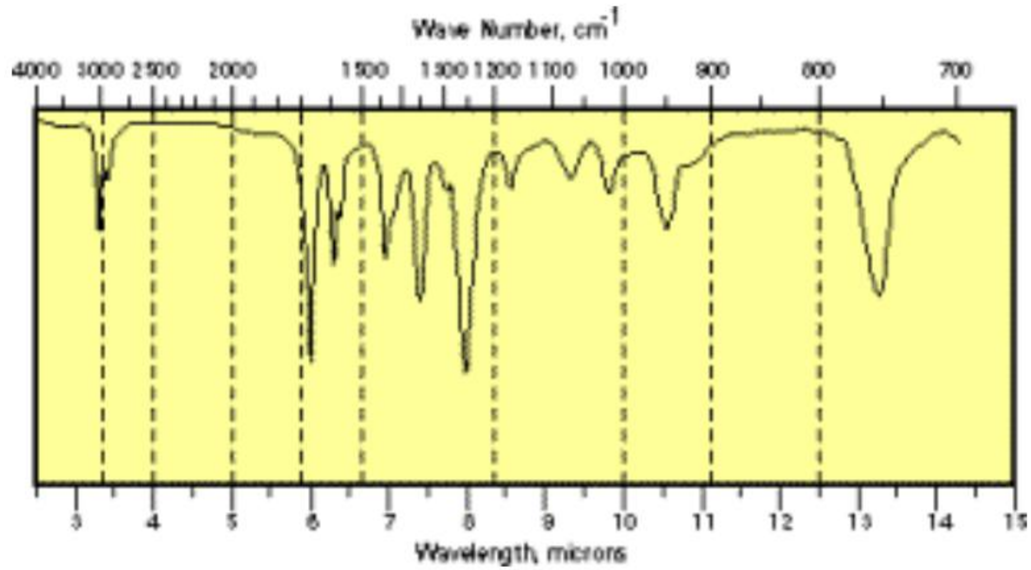
Setup of an FTIR spectrometer





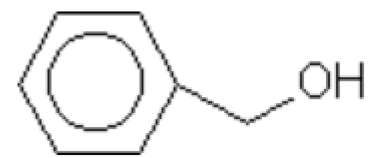
FTIR spectroscopy - Application

- **Assignment of the signals**
- Molecular formula: C_7H_8O
  → How looks the belonging molecular structure?



- Interpretation:
- 3400-3200 cm^{-1}: strong Peak → OH
- 3100 cm^{-1}: weak peak → unsaturated CH
- 2900 cm^{-1}: weak peak → saturated CH
- 2200 cm^{-1}: no unsymmetric triple bond
- 1720 cm^{-1}: no C=O group

Answer:



FTIR spectroscopy – Microspectroscopy

Advantages due to MOEMS technology

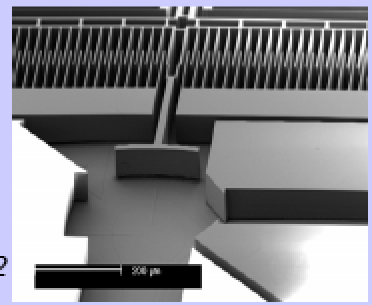
Replacement of the macroscopic mirror and its drive with an oscillating micro-mirror.

- Increased reliability and ruggedness.
- System miniaturization.
- Cost reduction.
- Ultra-rapid scan capability. Acquisition time of 0.2 ms for a single scan.

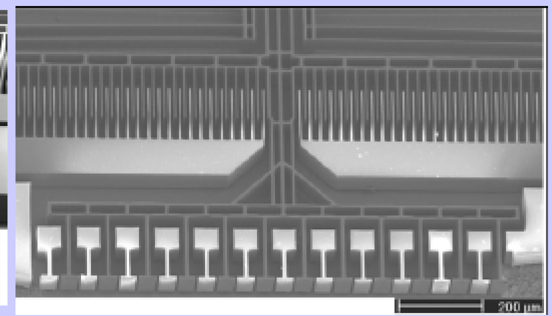
Example of MEMS based FTS:

a) Translatory mirror, b) Lamellar grating booth with in-plane-comb drive

Quelle:
O. Manzardo, Ph.D. Thesis, Neuchatel, 2002



a)



b)

Fraunhofer

QUALITY MANAGEMENT Certificate

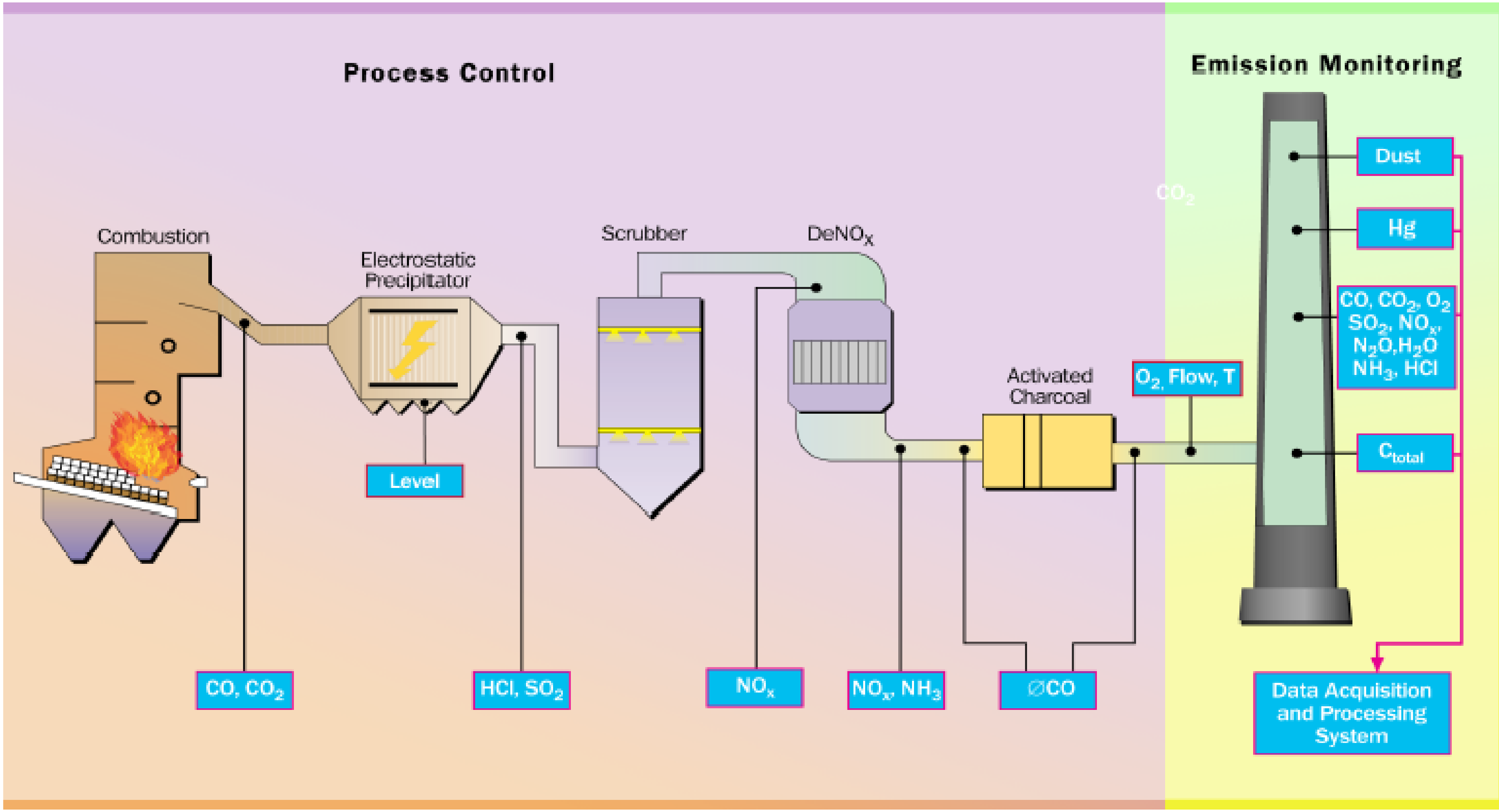
Fraunhofer Institut Photonische Mikrosysteme IPMS

CARINTHIAN TECH RESEARCH

thilo.sandner@ipms.fraunhofer.de

Spectrometer Workshop
Jena, 2008-03-13

Application example



Thank you for your attention