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

COST Action TD1105

4th International Workshop *EuNetAir* on

Innovations and Challenges for Air Quality Control Sensors

FFG - Austrian Research Promotion Agency | Austrian COST Association

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CONCEPTS FOR MOBILE SENSING OF INORGANIC NITROGENOUS POLLUTANTS IN EXHAUSTS AND THE ATMOSPHERE

CARINTHIAN TECH RESEARCH

ASSIC
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Inorganic Nitrogenous Pollutants

- **NO**
- **NO_2**
- N_2O
- NH_3
- …

- chemically reactive
- respiratory irritants / toxins
- environmentally problematic
  low-level ozone, environmental acidification …
- politically exploited

Anthropogenic Sources: virtually any high-temperature combustion processes that relies on air as one reaction component
industrial furnaces, heaters, all types of combustion engines …

… and worsening, as lean combustion reduces CO_2 emissions at the cost of increasing NO_x levels

→ reliable & fast metrology tools needed

Analytics - State of the Art vs. Demand

- **Chemi-Luminescence Detection (CLD)** | NO, NO_2
- **non-dispersive UV/VIS** | NO, NO_2
  typically using analyte-specific ED light sources
- **high-resolution FT-IR** | NO, NO_2, N_2O, NH_3 & more
  typically using long-path gas cells
- electrochemical **sensors** | NO_x
  commercial devices for motor / combustion control,
  lots of research going on

current need for …

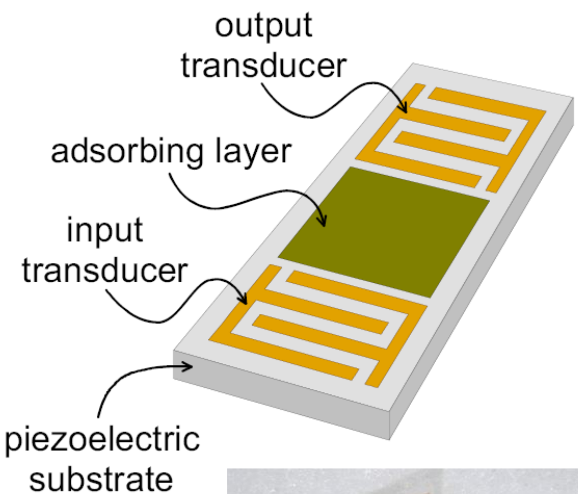
→ mobile devices (sensors)

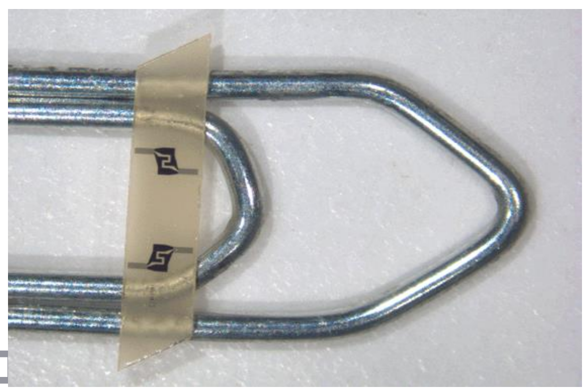
→ full & direct speciation

→ wider / customised dynamic ranges

Strategic Approach I – Chemical SAW Sensors

– *fundamental concept*:
electrochemical sensor layer (metal oxide nano-layers), coupled to a surface-sensitive surface acoustic wave transducer for signal generation and transduction

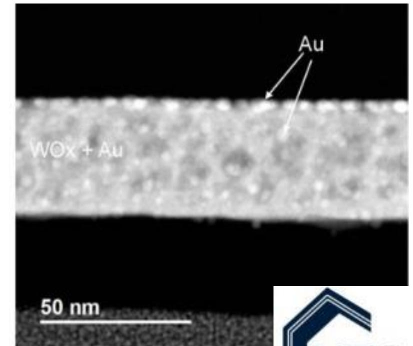


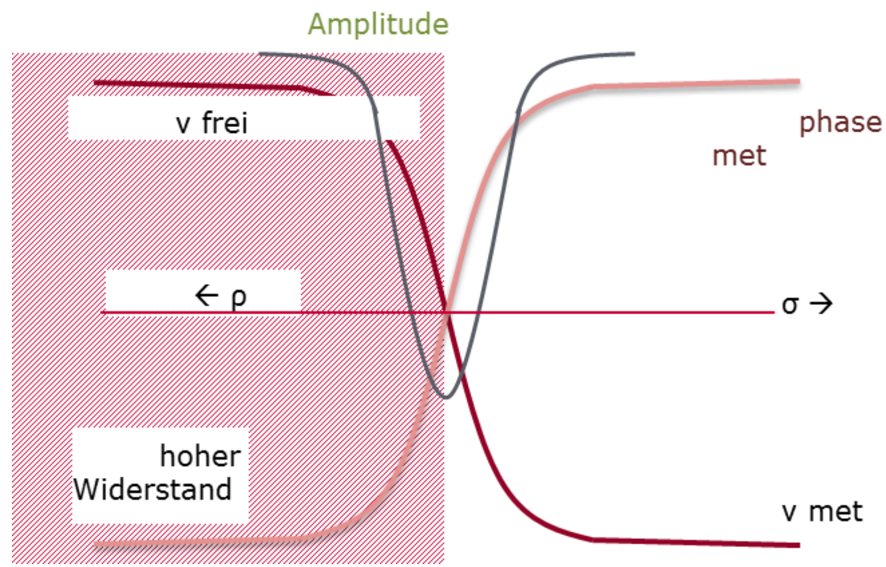


– integrated temperature sensing & compensation
– compatible with mass-accumulating or catalytic layers
– multiplexing possible
– suitable for temperatures up to 650°C
– wirelessly & fully passively interrogable (2.4 GHz band)

SAW NO_x Sensor

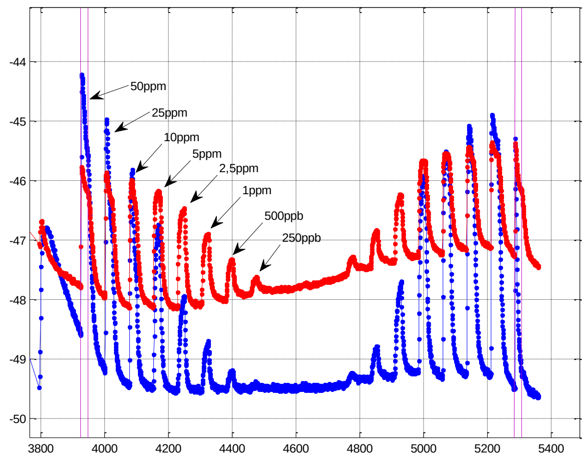
- *SAW operated in electro-acoustics mode*
  - very high sensitivity to resistance changes in the functional layers (Au:WO_3 nano-layers)
    over a limited range
  - analytical range tuneable by layer / transducer matching
    LoDs down to ppb range feasible
  - convenient range and/or analyte expansion in array form
  - evaluation of amplitude or phase data



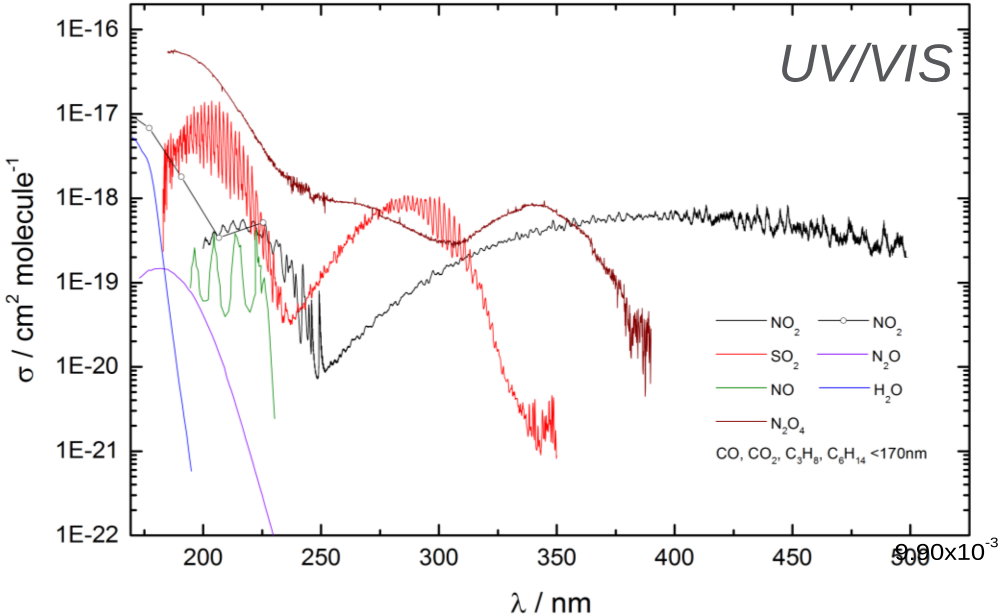


SAW NO_x Sensor - Results

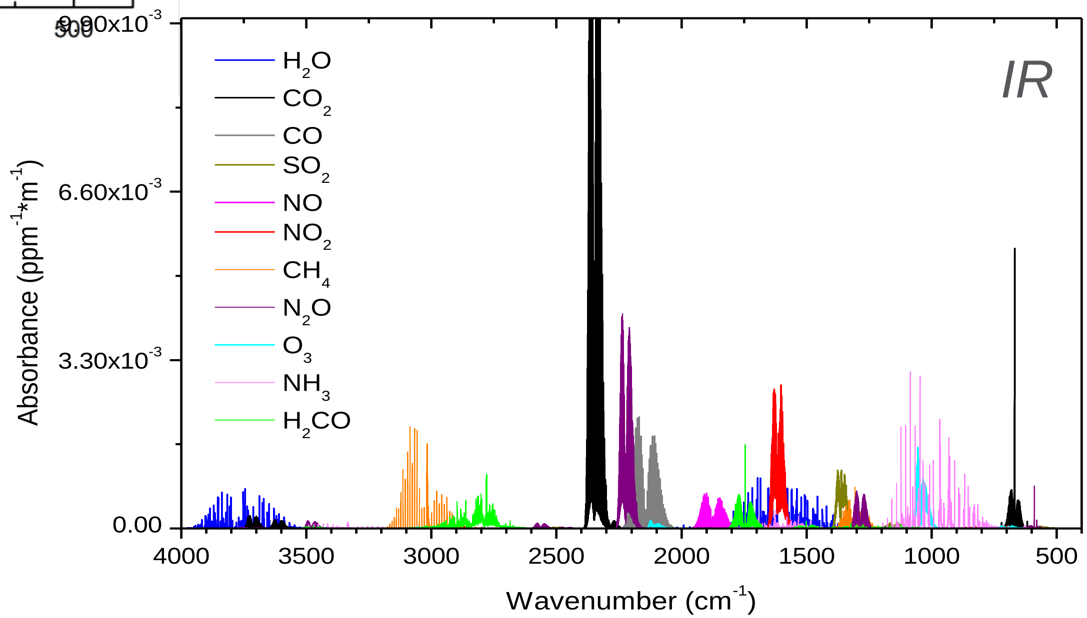
- ✓ principle works, both in the lab and in the field
- ✓ differentiation NO / NO_2
- ✓ *in-situ* measurements of untreated combustion gases possible
- – cross-sensitivities remain an issue
- – response times are a little high
- – under certain conditions, exhaust gas composition can saturates the layers, rendering the sensor blind to analyte changes



Strategic Approach II – Spectroscopic Sensors



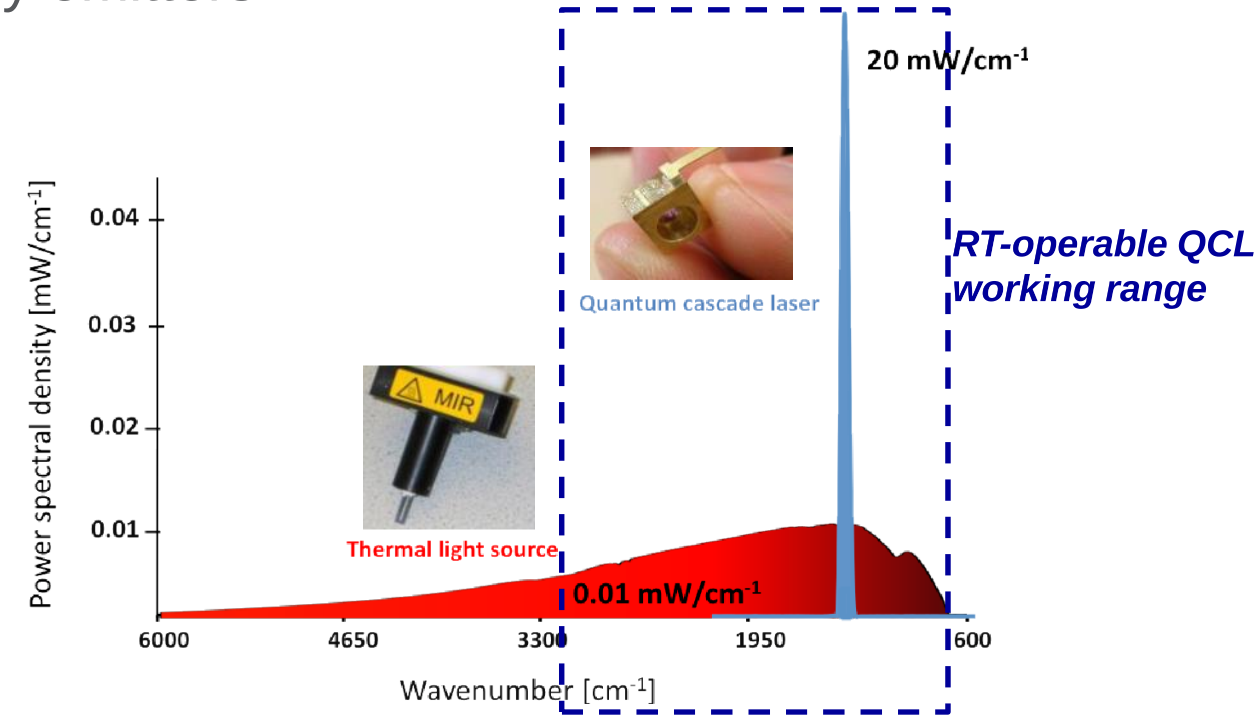
- direct probing of analytes
- differentiation possible
- wide sensitivity ranges
- cross-sensitivities easier to detect and compensate



- LoD design by optics design
- no aging / poisoning of layers
- response times limited only by exchange time of sample volumes

Integration Approach: mid-IR QCL Devices

– spectral power density of QCLs up to 10^5 times higher than blackbody emitters



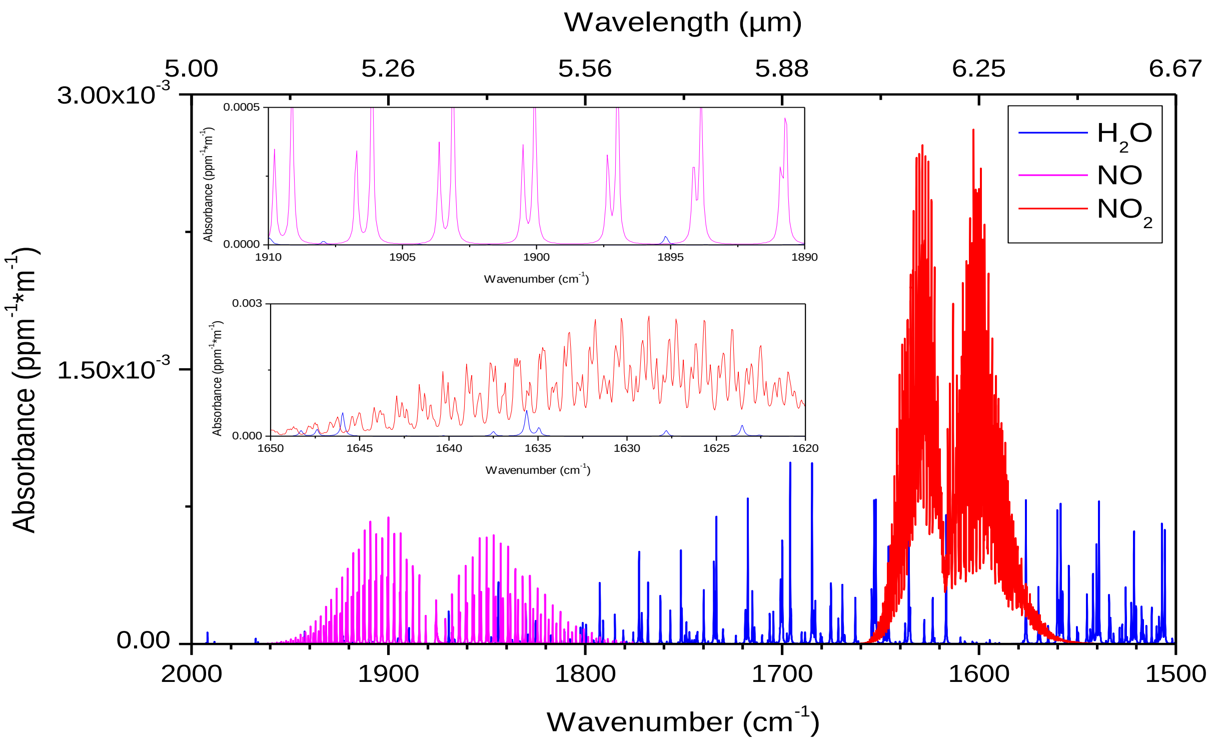
– enables longer absorption pathlengths | lower LoDs | better SNR

– narrow emission wavelengths; wavelength-tuneable options available

– compatible with wider range of detection principles

mid-IR Absorption Spectroscopy of NO_x-es

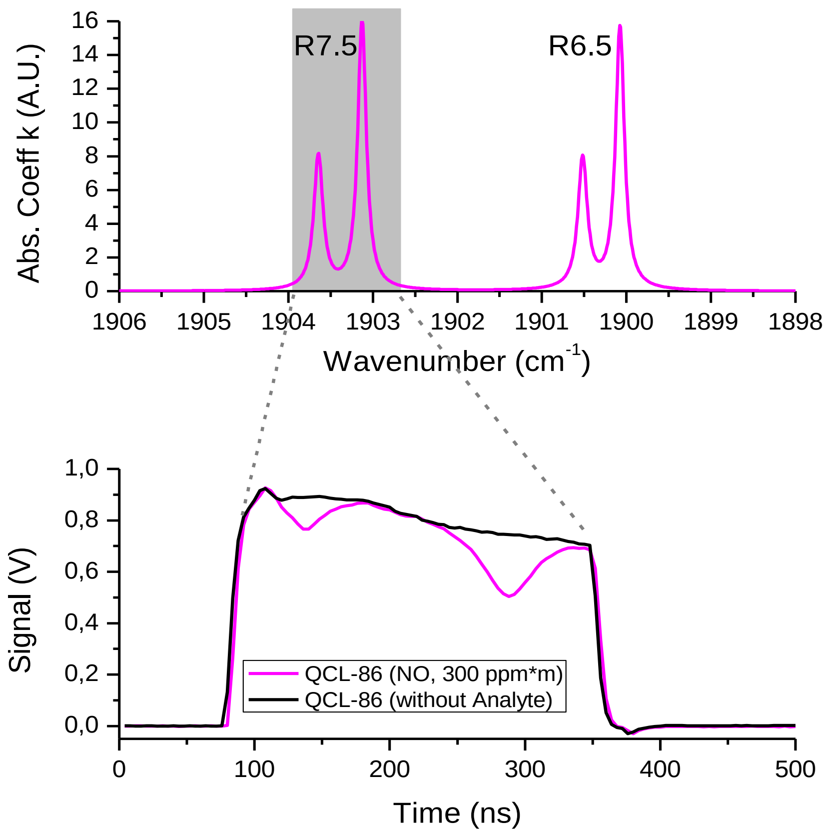
- wealth of narrow gas absorption lines
- non-dispersive IR sensors cannot resolve spectral overlaps, high-resolution spectroscopy can

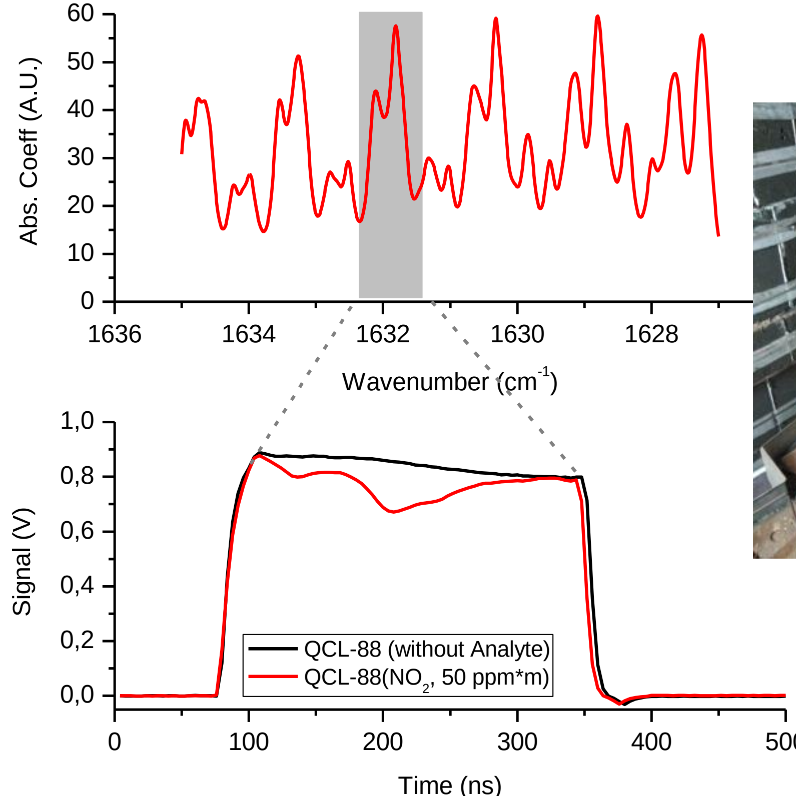


→ full-range HR-FTIR → narrow-range **QCL spectroscopy**

EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Example: DFB-QCL NO_x Sensing





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C. Reidl-Leuthner, Appl. Spectrosc. 2013

- pulsed chirping-mode QCL operation scans across band
  Alternative: external cavity QCL with scanning mirror

DFB-QCL Gas Sensing

- ✓ scanning across absorption bands enables integrated background compensation
- ✓ careful wavelength selection enables highly selective, independent measurement of different species
- – classical “molehill on mountain” problem of absorption spectroscopy
- – QCLs are (still | very) expensive
  in particular tuneable varieties
- – rapid detectors & detector electronics required
- – sample temperatures influence the quantification
- – **detection sensitivity** directly dependent on interaction pathlength
  i.e. high sensitivity requires long pathlengths

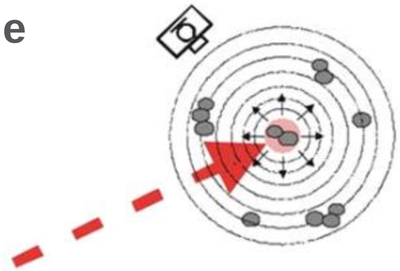
→ *option 1*: tune the photonics – analyte interactions

→ *option 2*: change the detection principle

Alternative Detection Concept: QEPAS
(Quartz-Enhanced Photo-Acoustics)

Photoacoustics Principle

Modulated Laser Beam
↓
Local Absorption
↓
Local Heating
↓
Thermal Expansion
↓
Pressure Wave
↓
Detection by Microphone



$$S = k\frac{\alpha c P Q}{f A}$$

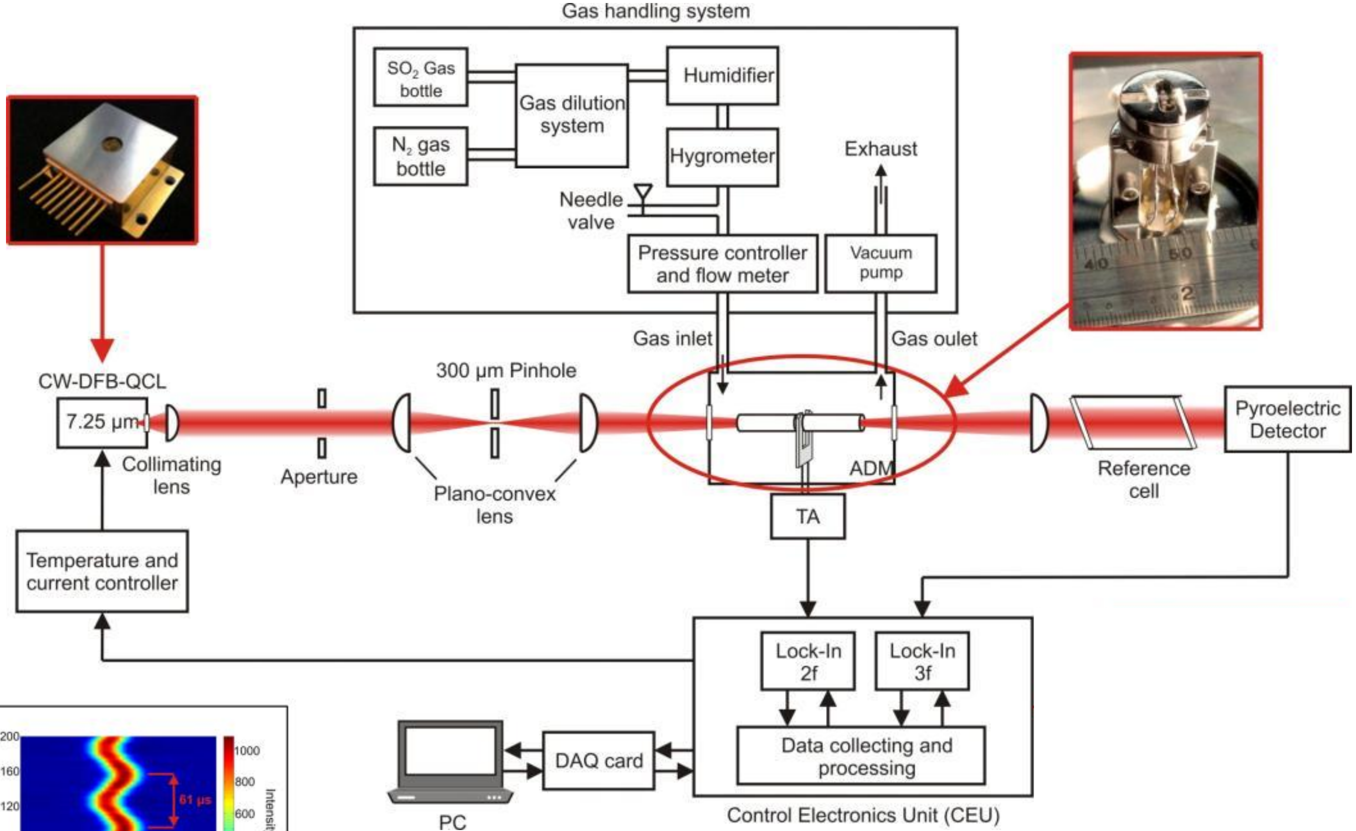
S	Photoacoustic signal (N/m²)
k	System constant microphone transfer function etc.
α	Absorption coefficient (L/(mol·cm))
c	Concentration (mol/L)
P	Optical power (W | kg·m²/s³)
Q	Quality factor
f	PA sound frequency (s⁻¹)
A	Resonator cross-section (m²)

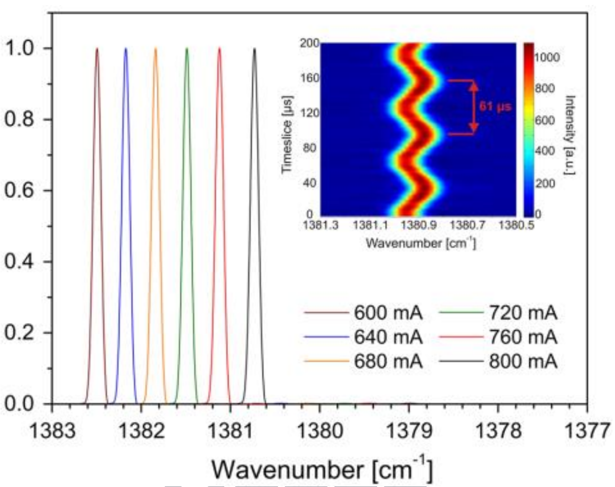
→ **detection sensitivity does not rely on long interaction pathlengths**

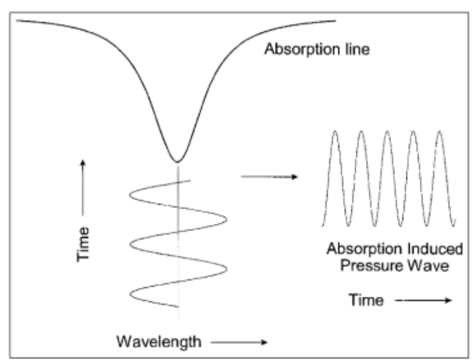
***optimising performance*: quartz tuning fork to increase quality factor Q**

- Quality factors of $10^4 – 10^5$
- reduced sensitivity towards disturbances by external acoustic sources
- high dynamic range ($\sim 10^6$)
- low cost: ~ 0.30 €

QEPAS Gas Sensing Layout (Laboratory)







J.P. Waclawek, Appl. Phys. B 2014

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