

# Acetylene measurement using quantum cascade lasers at 14µm

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# Gas analyzers

Tunable laser spectroscopy  
(TLS)



Gas chromatography  
(GC)



Non dispersive infrared  
spectroscopy (NDIR)



Trace gas detection  
Process gas production  
Purity control  
Air quality monitoring

Fouier Transform  
Infrared Spectroscopy  
(FTIR)

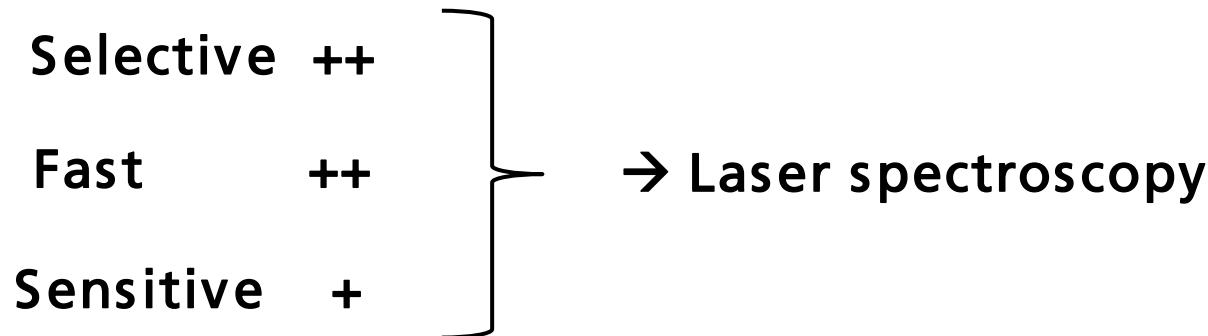


Electrochemical  
cell (EC)

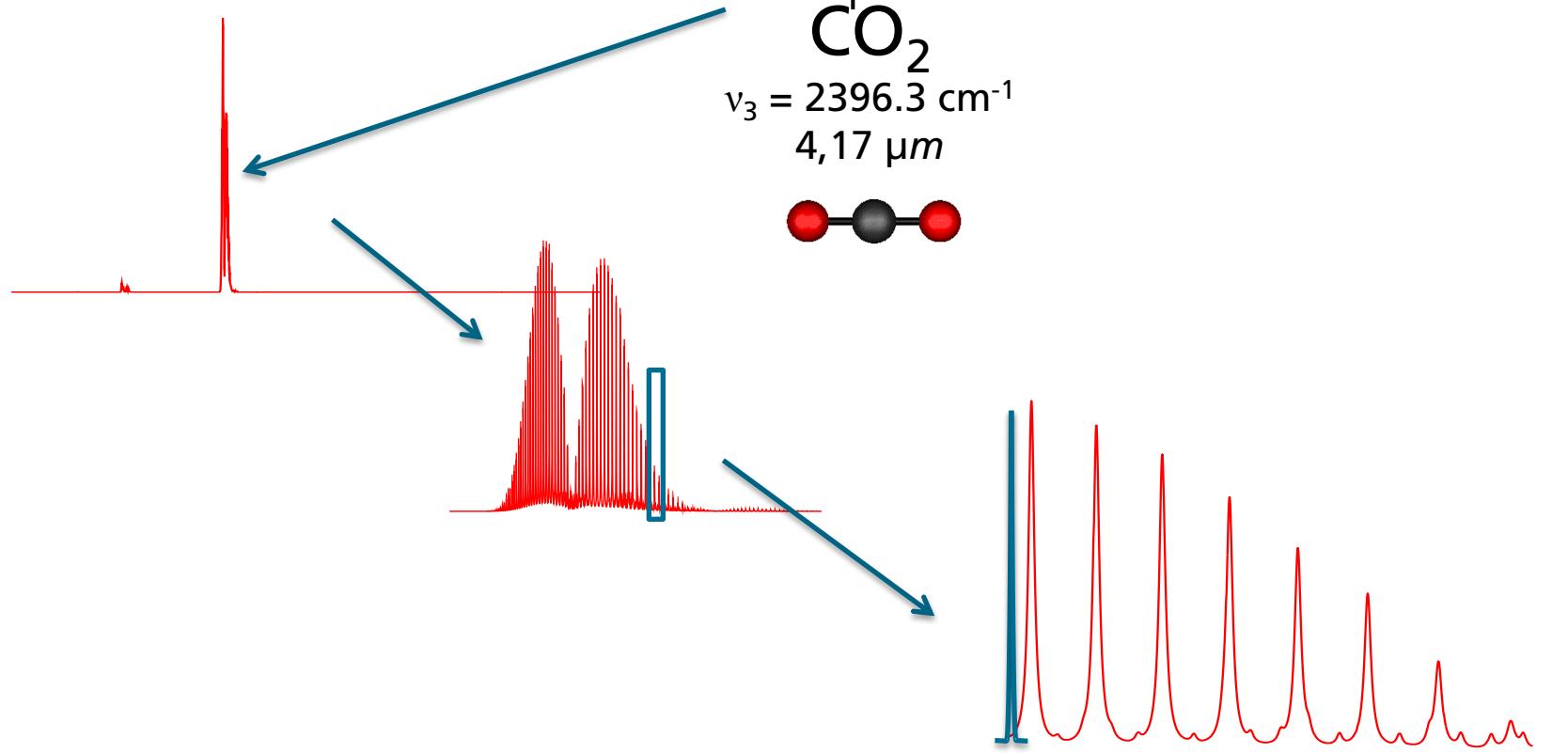
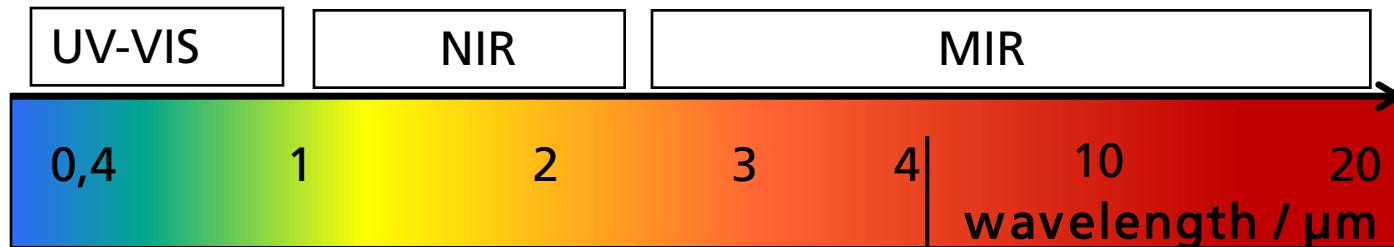
# Motivation

Joint project: QUIP

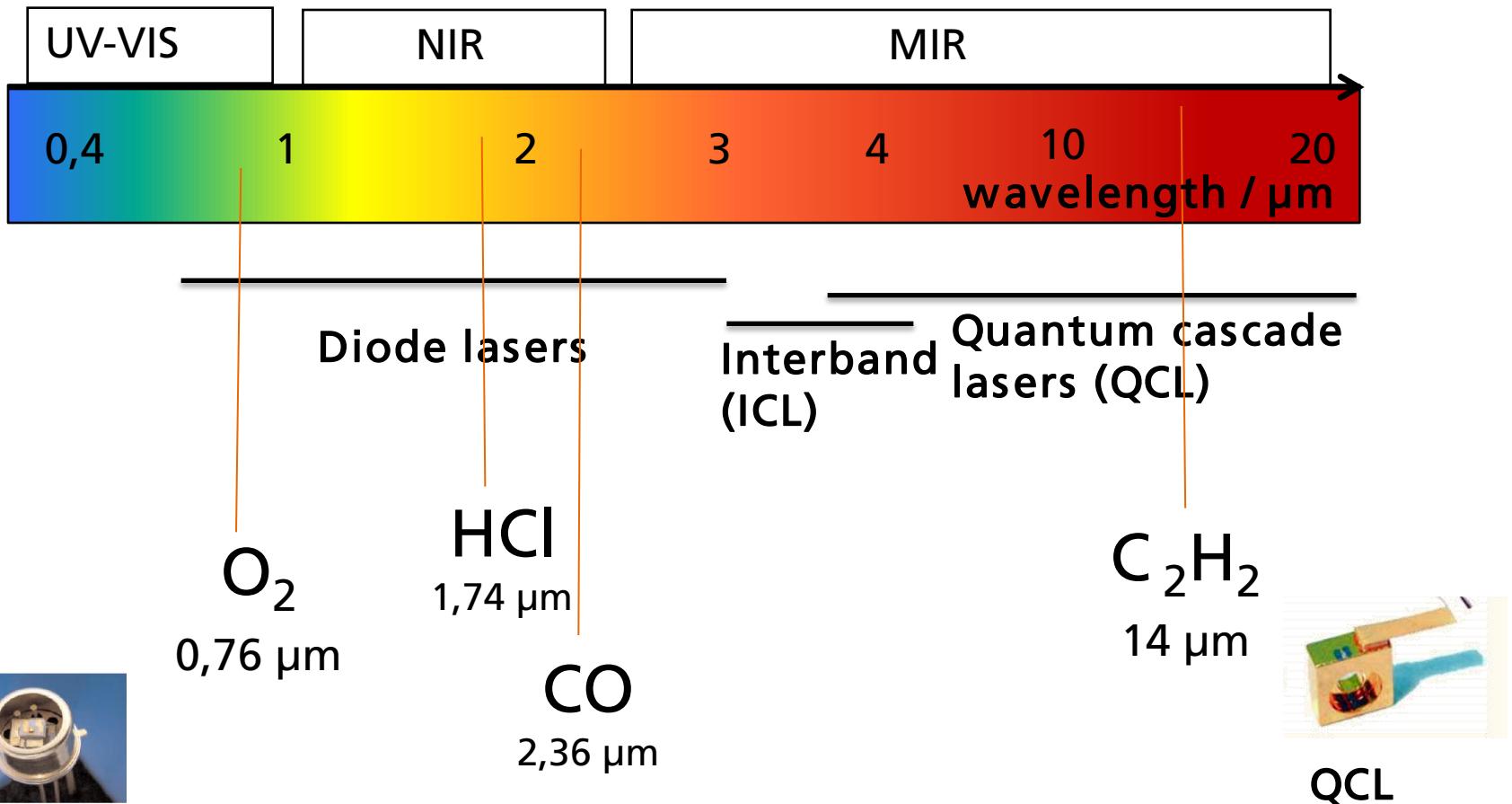
Gas analyzer development for  
acetylene trace detection  
within seconds in a complex  
gas matrix



# Laser spectroscopy

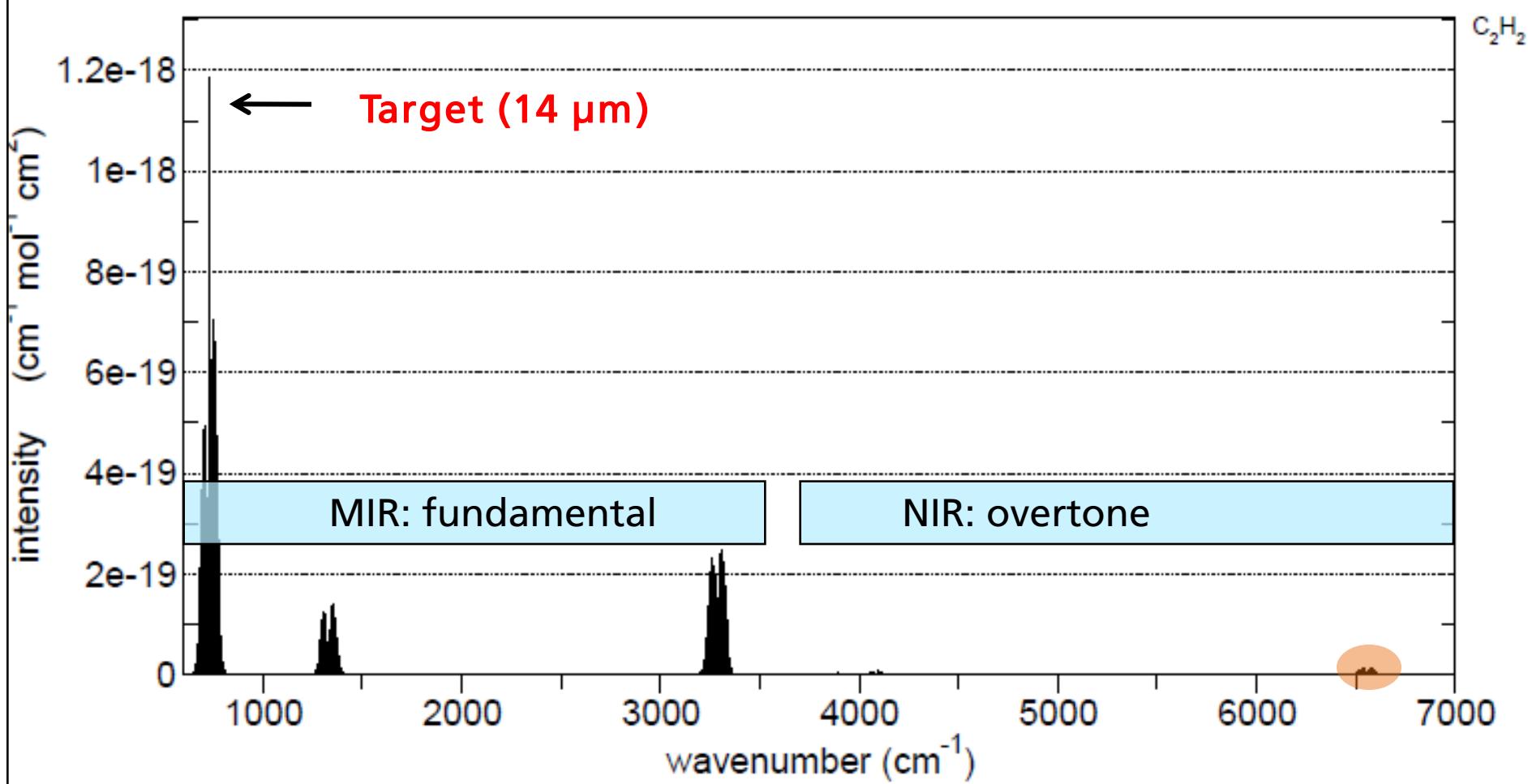


# Gases and laser

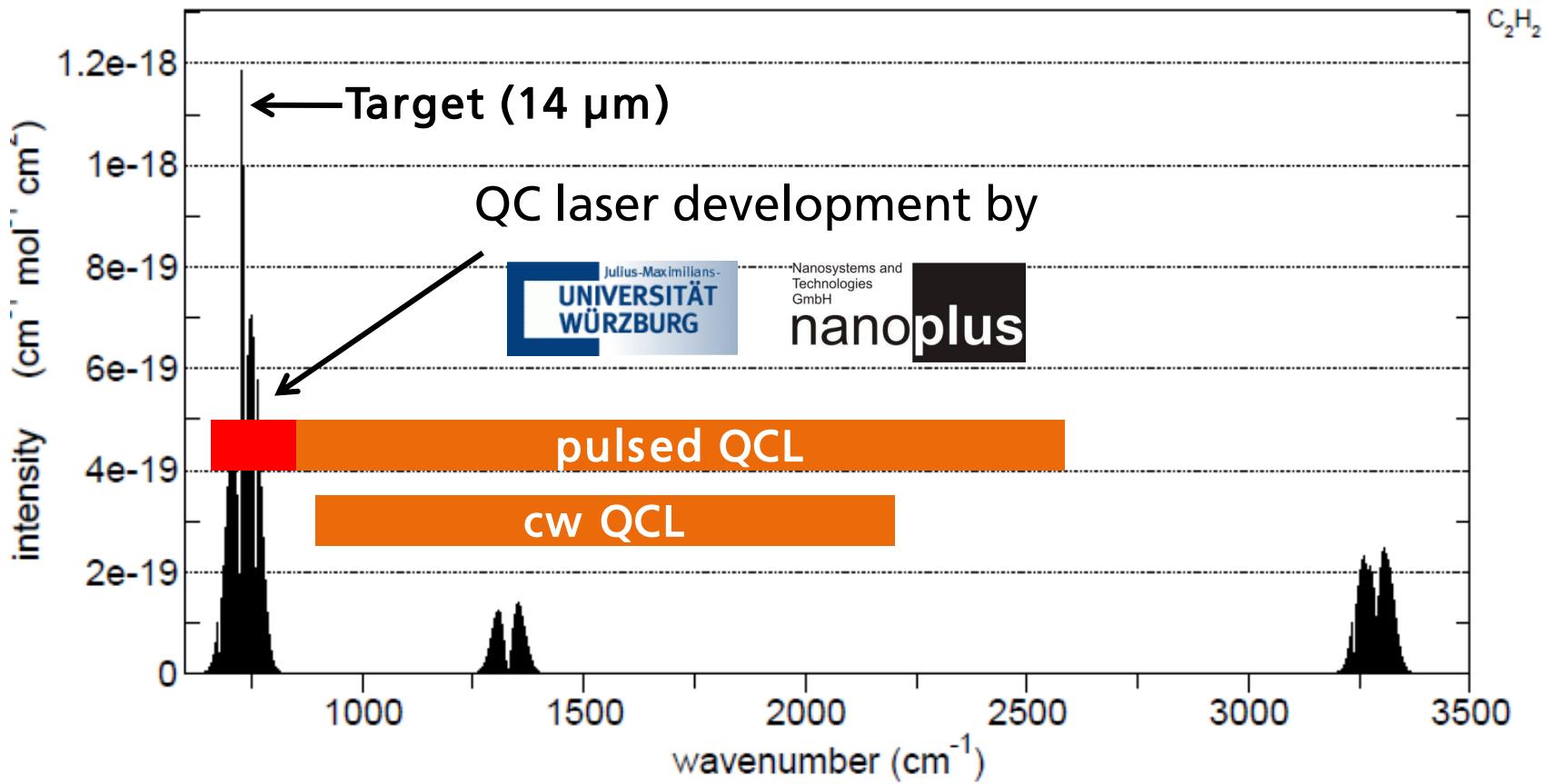


VCSEL

# Acetylene absorption lines



# Acetylene absorption lines

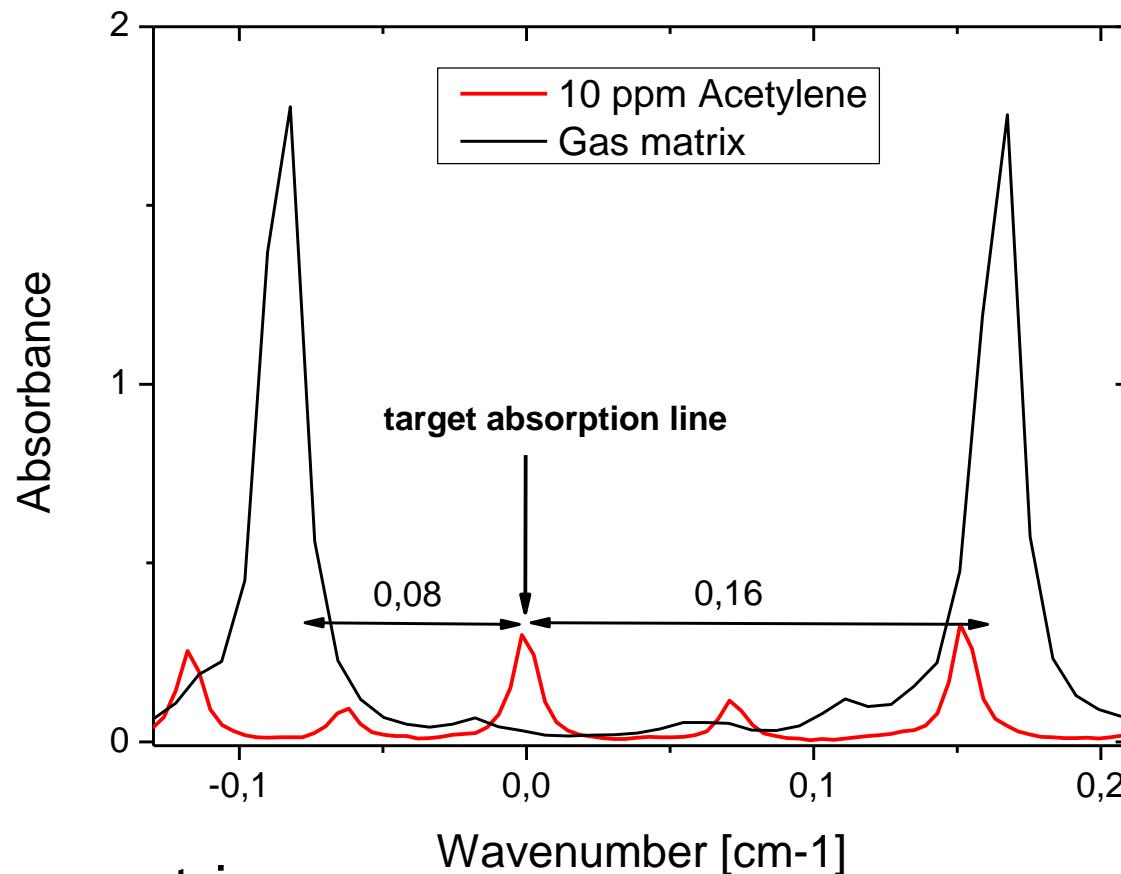


# Spectral measurement window

Selection of the absorption line

No Hitran data available

→ FTIR spectra of acetylene and the gas matrix

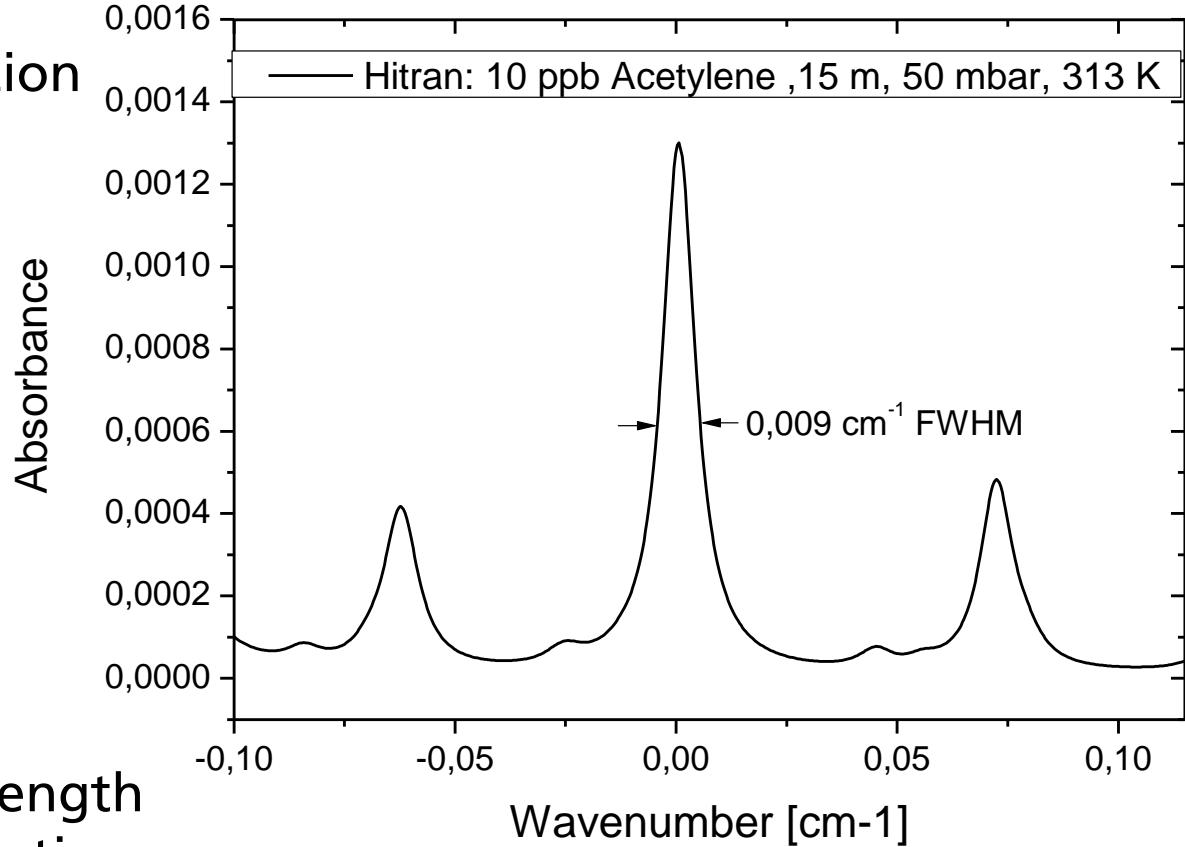


Strong and complex gas matrix  
→ 50 mbar

# Objectives

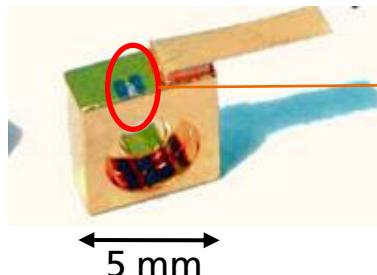
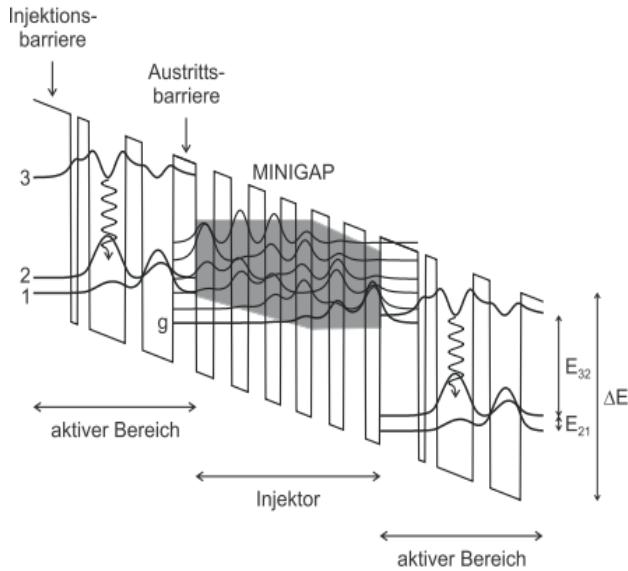
Requirement: detection limit of 10 ppb C<sub>2</sub>H<sub>2</sub>

Hitran simulation



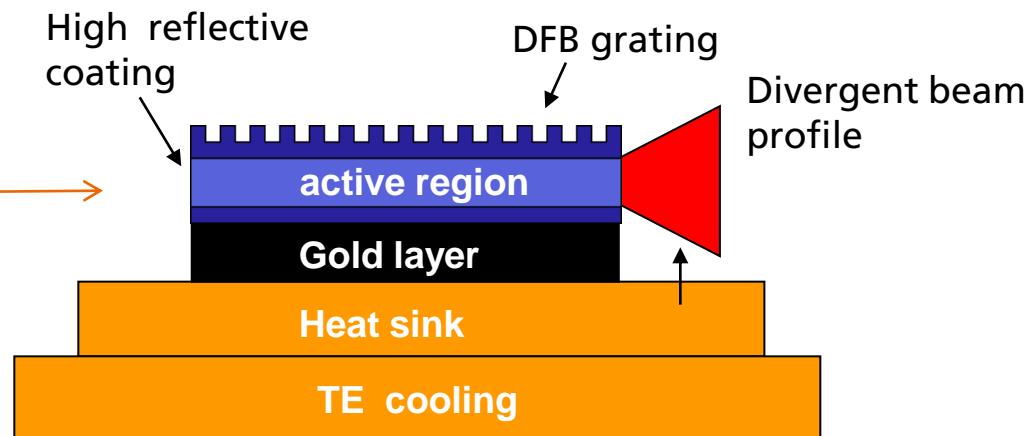
- long optical path length
- High spectral resolution
- High transmission resolution

# Quanten cascade laser (QCL)



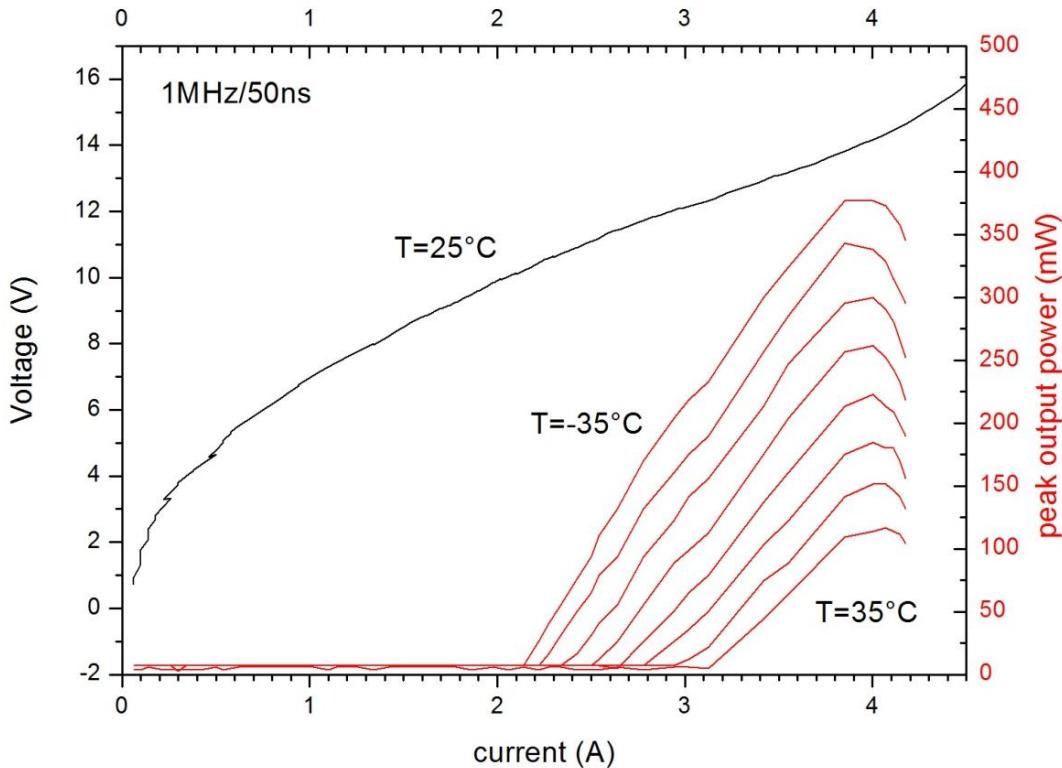
Energy level diagram in the conductive band

Multi layer system grown molecular beam epitaxy



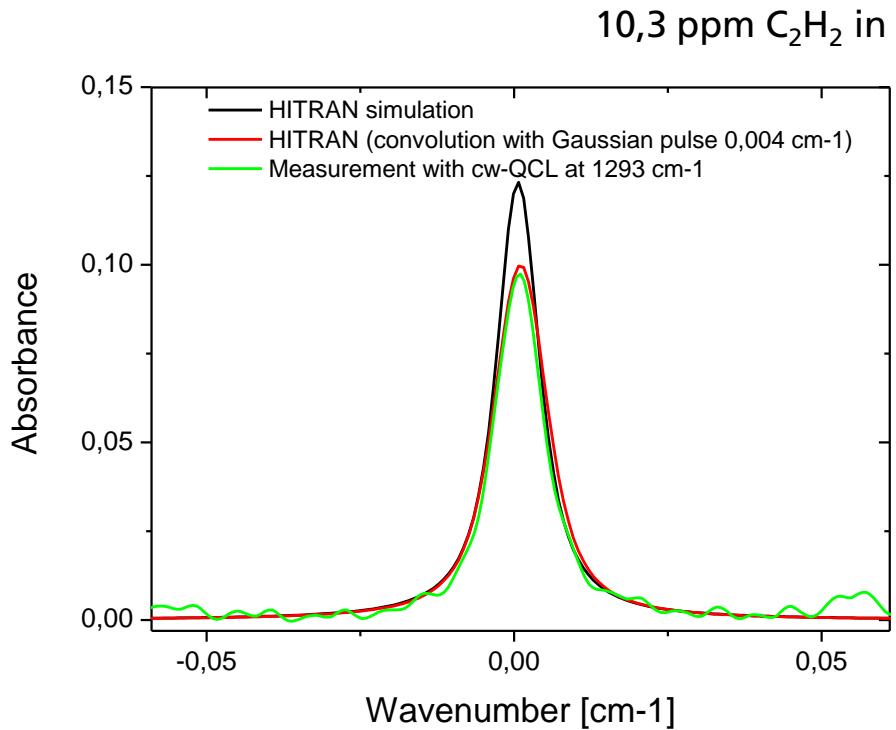
# Quantum cascade laser

- emission center at  $14\text{ }\mu\text{m}$
- DFB QCL
- for pulsed operation
- max. 350 mW peak power
- 5 % duty cycle



# Spectral line width

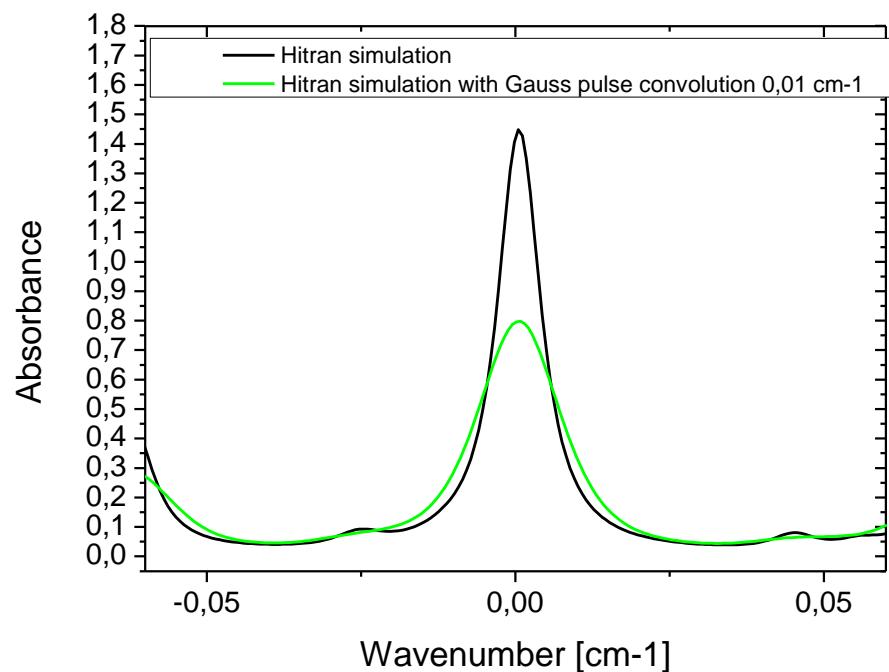
cw- QC laser (7  $\mu\text{m}$ )



Weak line intensity  
Narrow spectral line width  
High average power

VS.

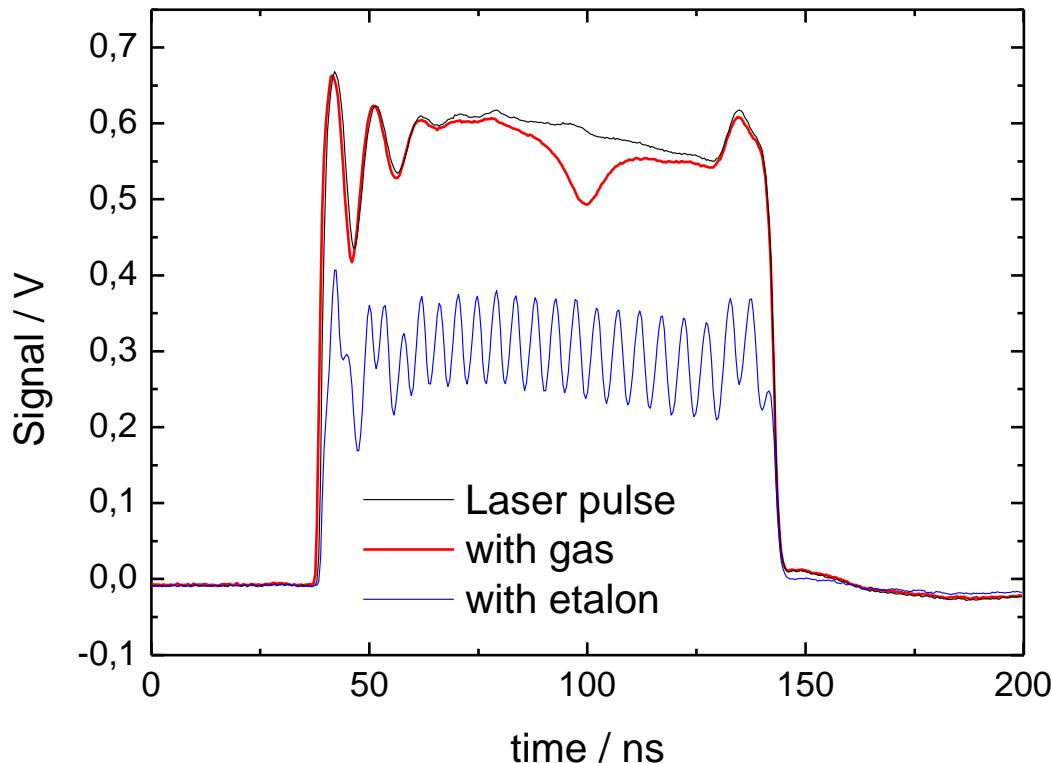
pulsed QC laser (14  $\mu\text{m}$ )



strong line intensity  
"broad" spectral pulse width  
Weak average power

# Intra pulse method

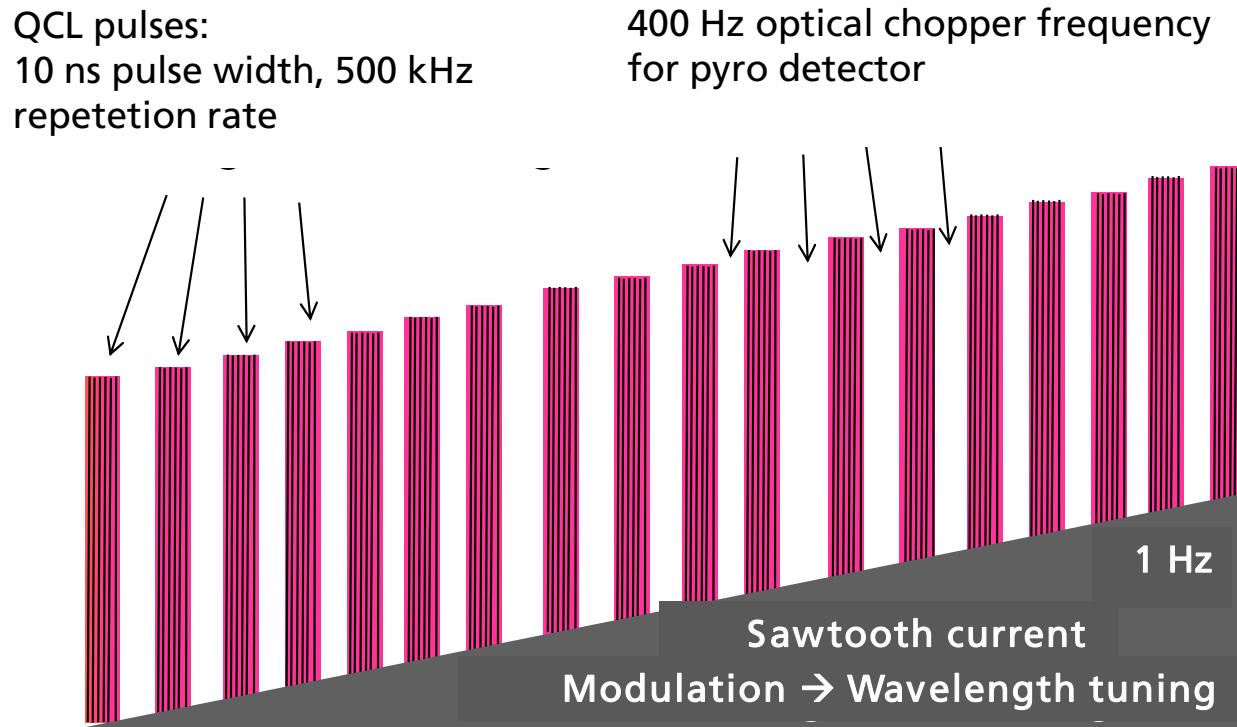
- Spectral tuning during laser pulse by heating with laser current → chirp
- Measurement of the absorbtion line during the pulse
- Detection of the signal is only with broadband electronics (>100 MHz) → expensive and complex data accquisition



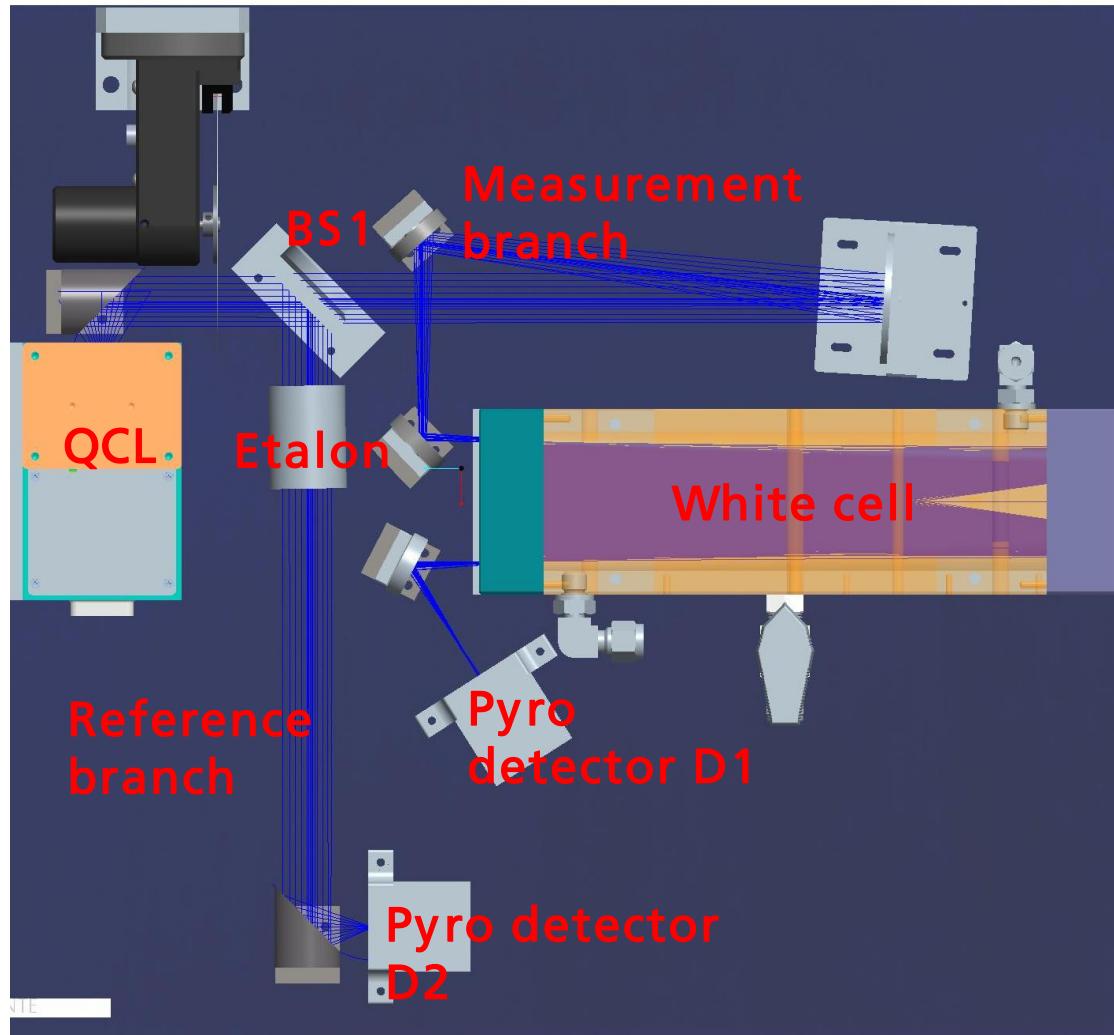
→ No TE cooled MCTs for 14 µm as standard product available  
→ Pyro detector !

# Interpulse method with pyro detector

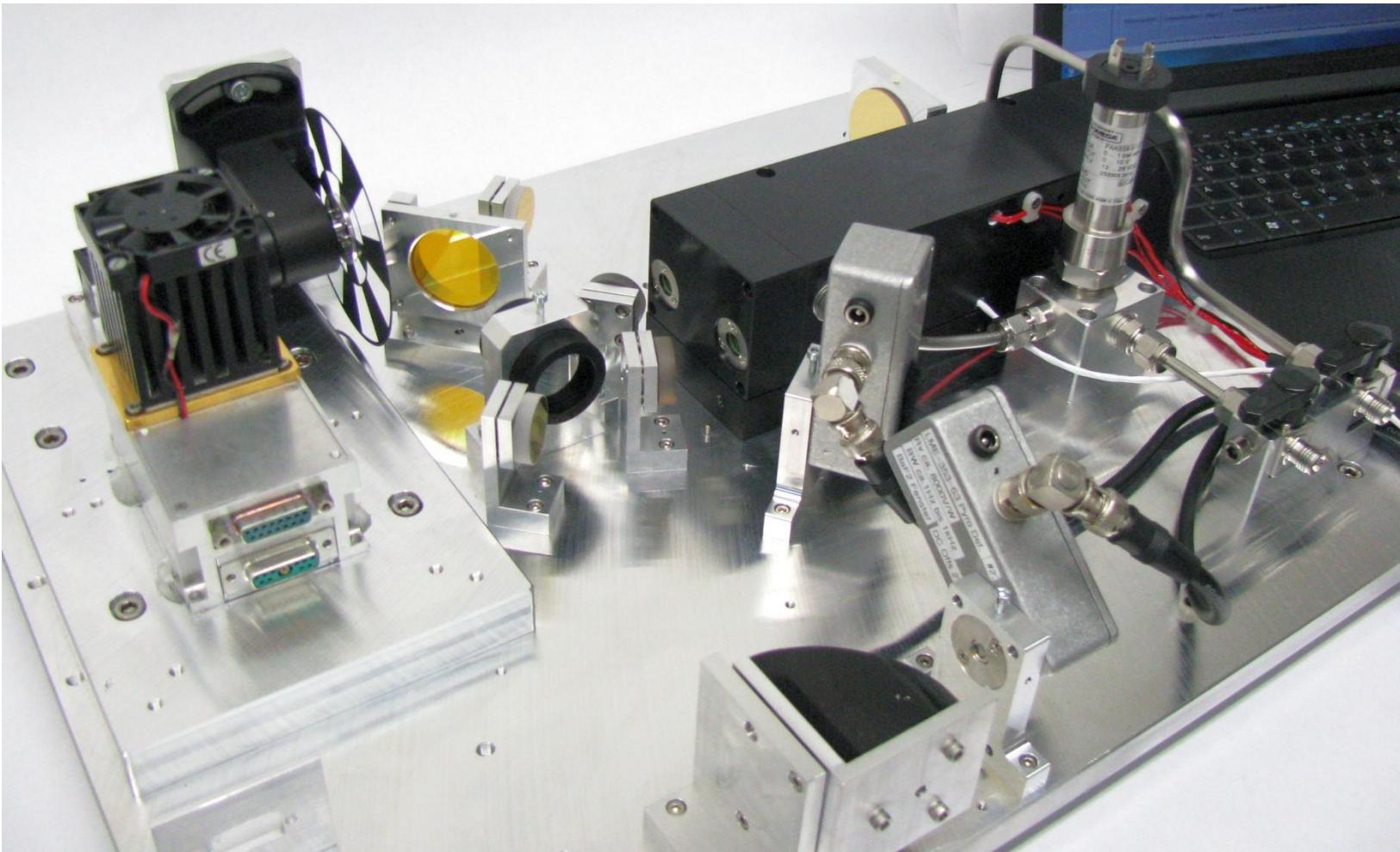
- Spectral resolution independent of electronic bandwidth
- Short laser pulses → narrow spectral pulse width
- Wavelength tuning by a sub threshold current ramp



# QC-Laser spectrometer



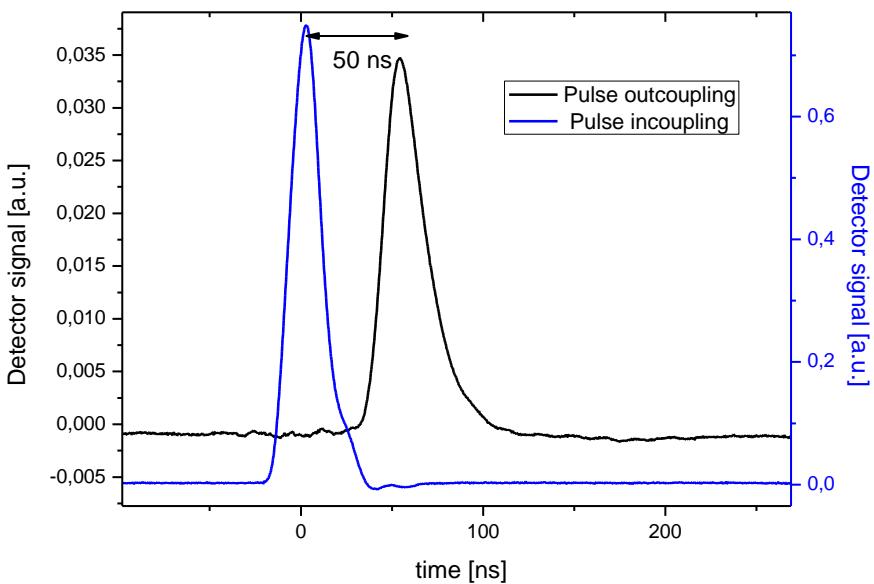
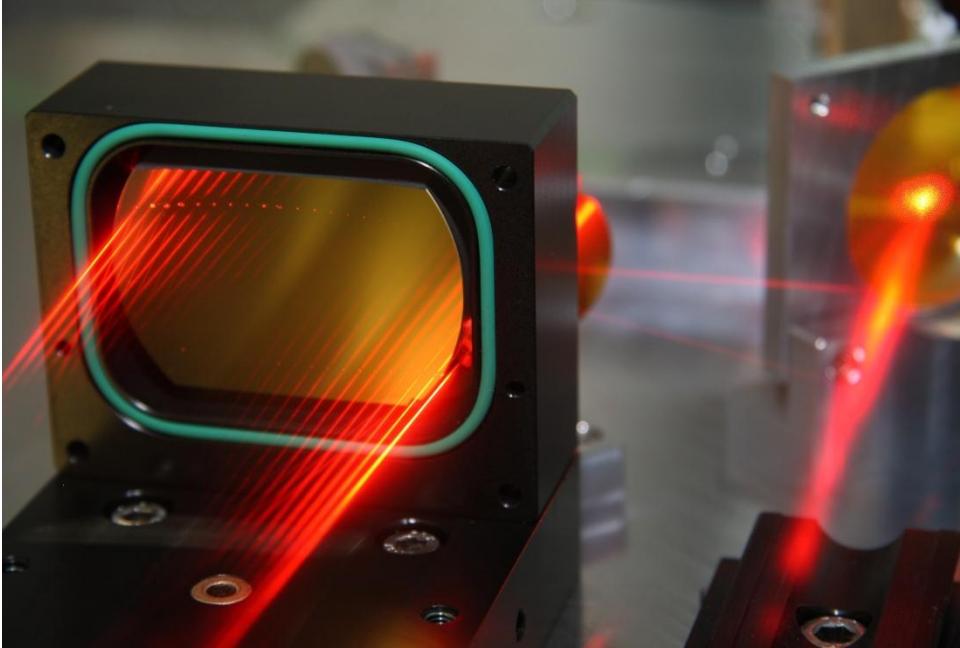
# Setup



Foot print 400 x 300 mm for 19" rack

# White cell

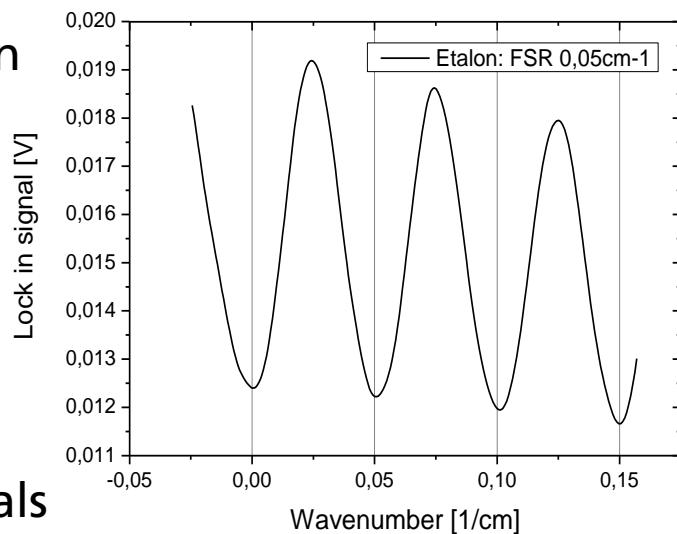
- 76 reflections
- 15 m optical path length
- 320 ml



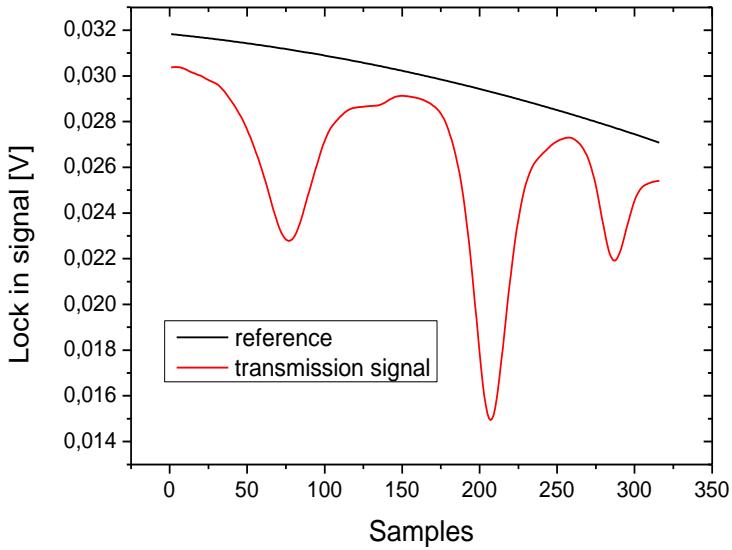
Measurement of time delay  
→ Optical way

# Measurement of C<sub>2</sub>H<sub>2</sub> in N<sub>2</sub>

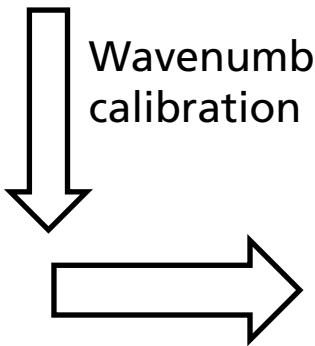
Etalon



Raw signals

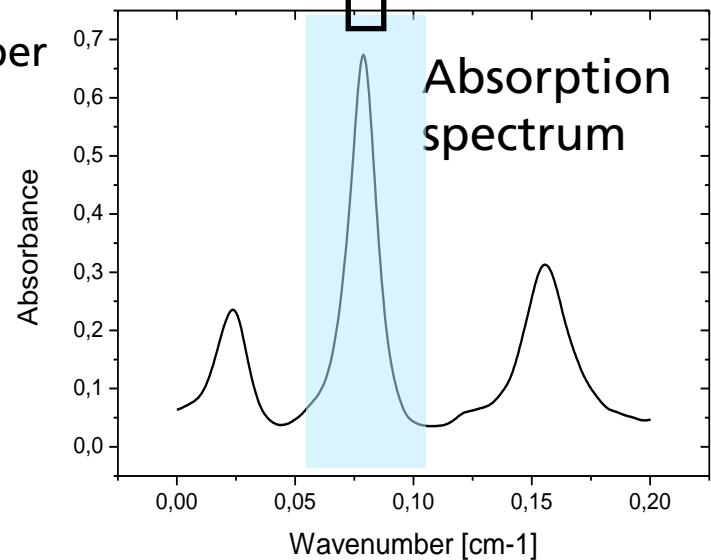


Wavenumber calibration



Concentration  
10,3 ppm C<sub>2</sub>H<sub>2</sub>

Integration &  
calibration



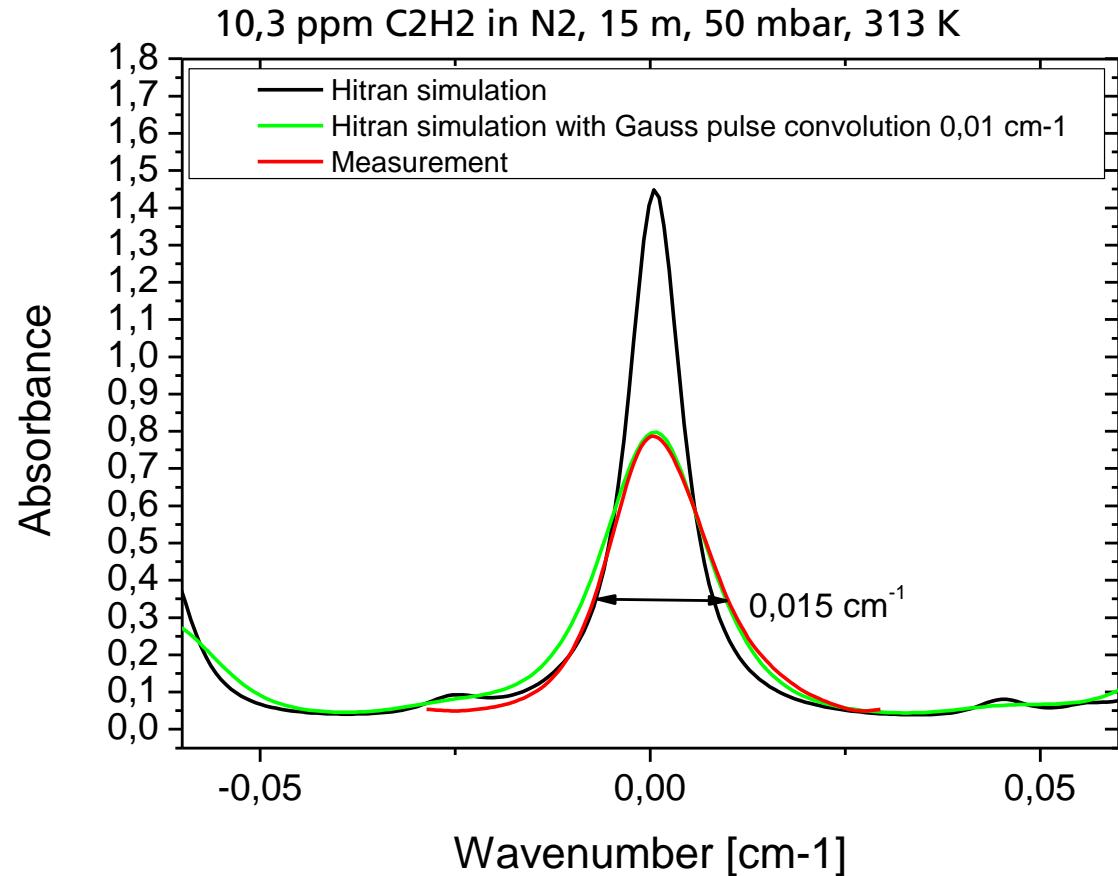
# Spectral resolution

spectrometer resolution checked by gas absorption line

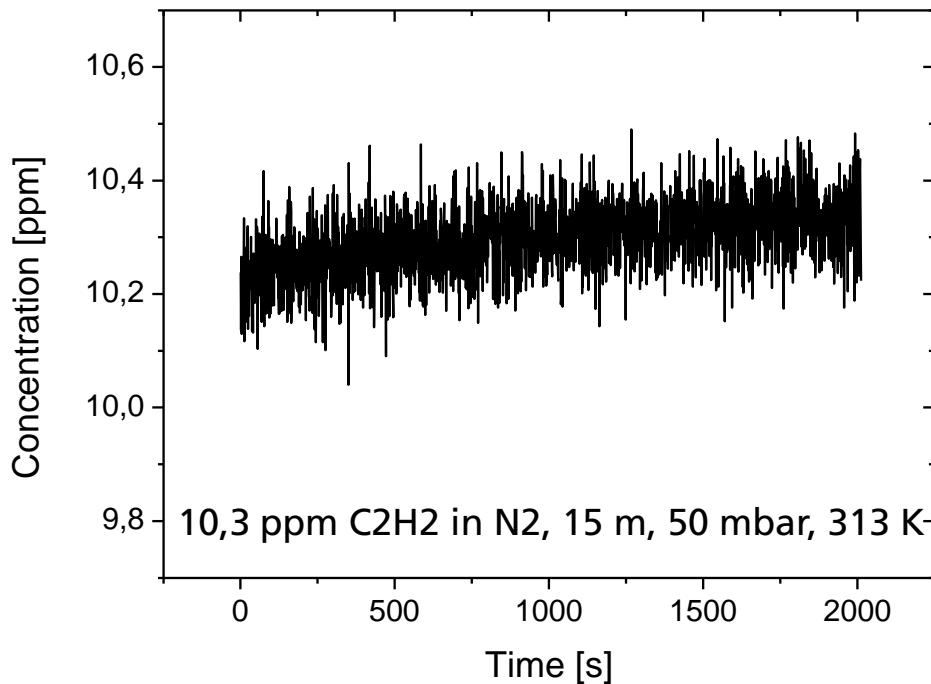
0.015 cm<sup>-1</sup> FWHM of measured absorption line

→ Convolution of the Hitran simulation with Gaussian pulse shape

→ Spectral system resolution: 0.01 cm<sup>-1</sup>



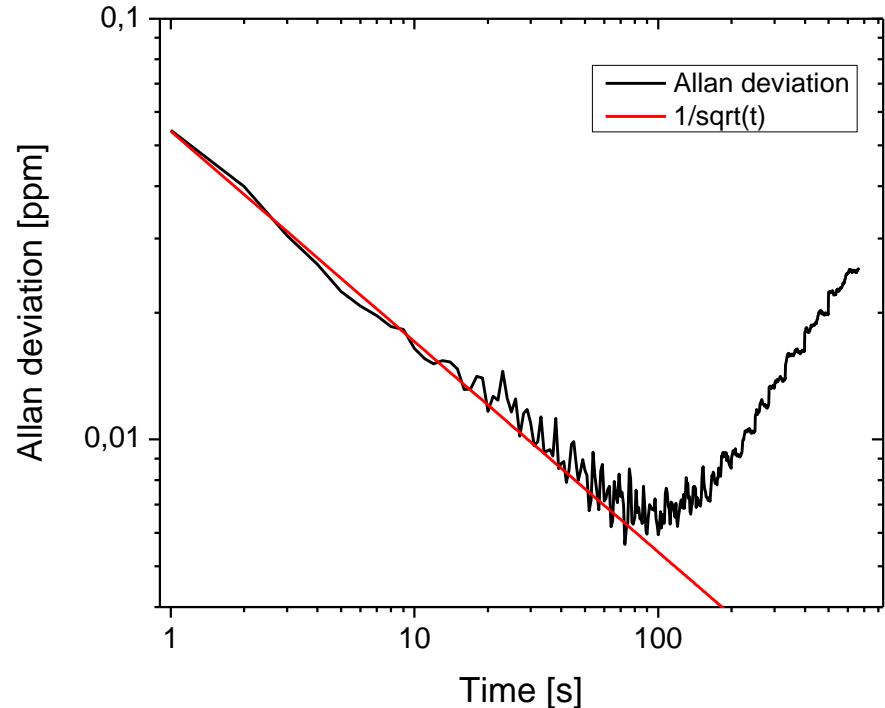
# Estimation of detection limit



**Noise equivalent concentration (NEC,  $1\sigma$ )**  
1 s : 55 ppb  
20 s: 10 ppb

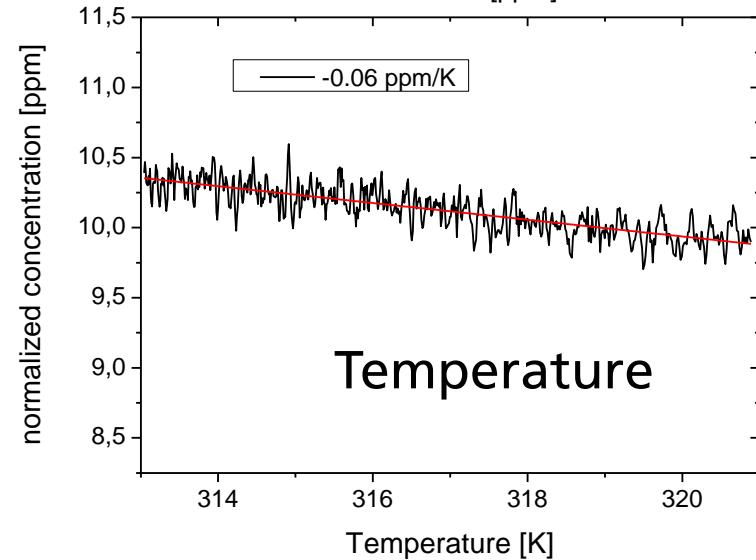
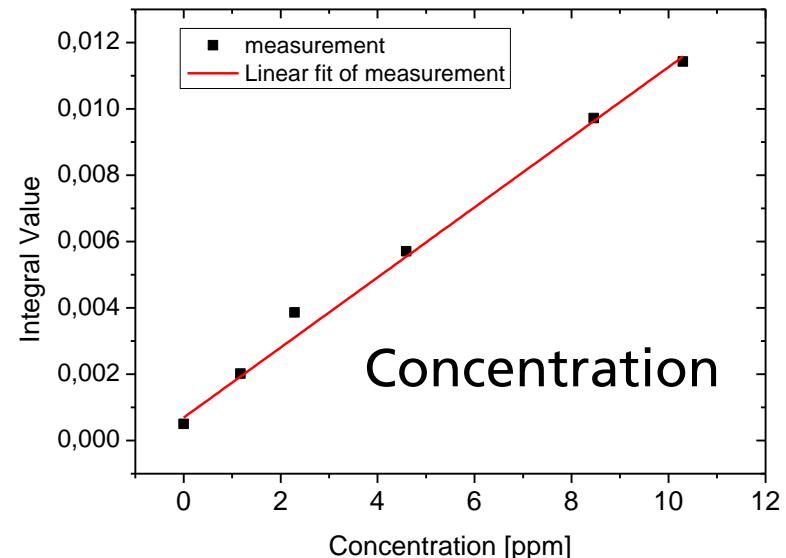
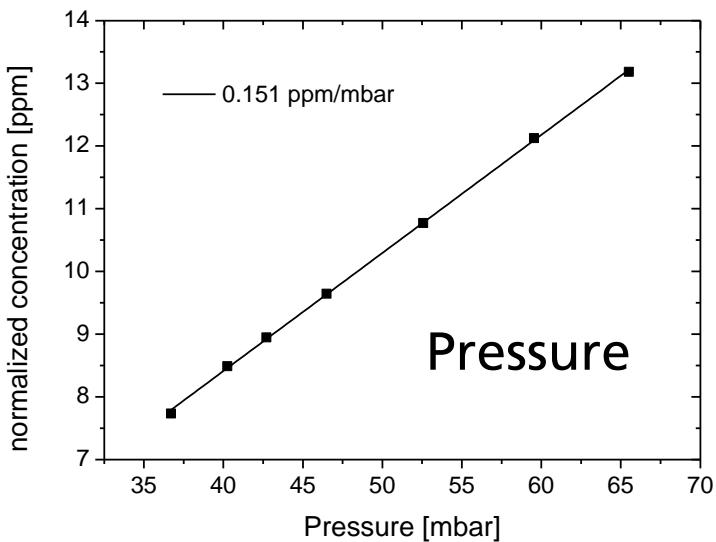
30 min measurement of 10,3 ppm testgas concentration

→ Calculating Allan standard deviation

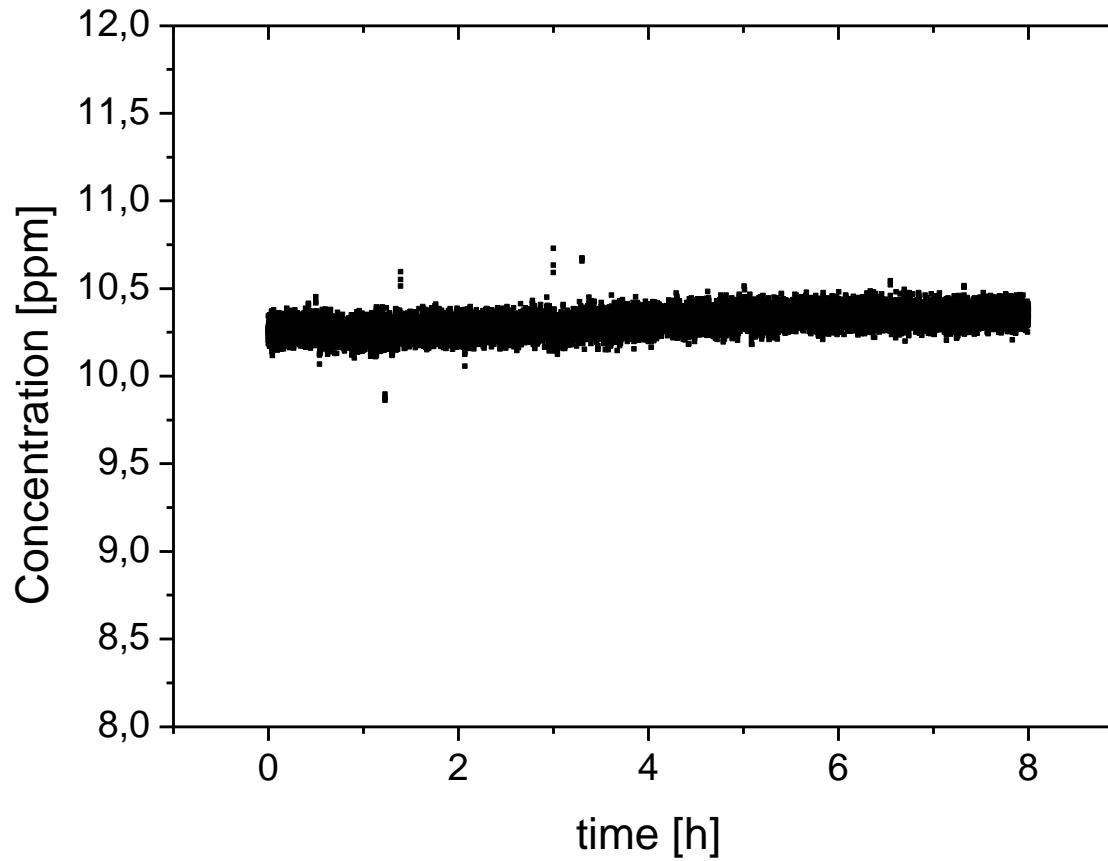


# System calibration

## Linear calibration functions

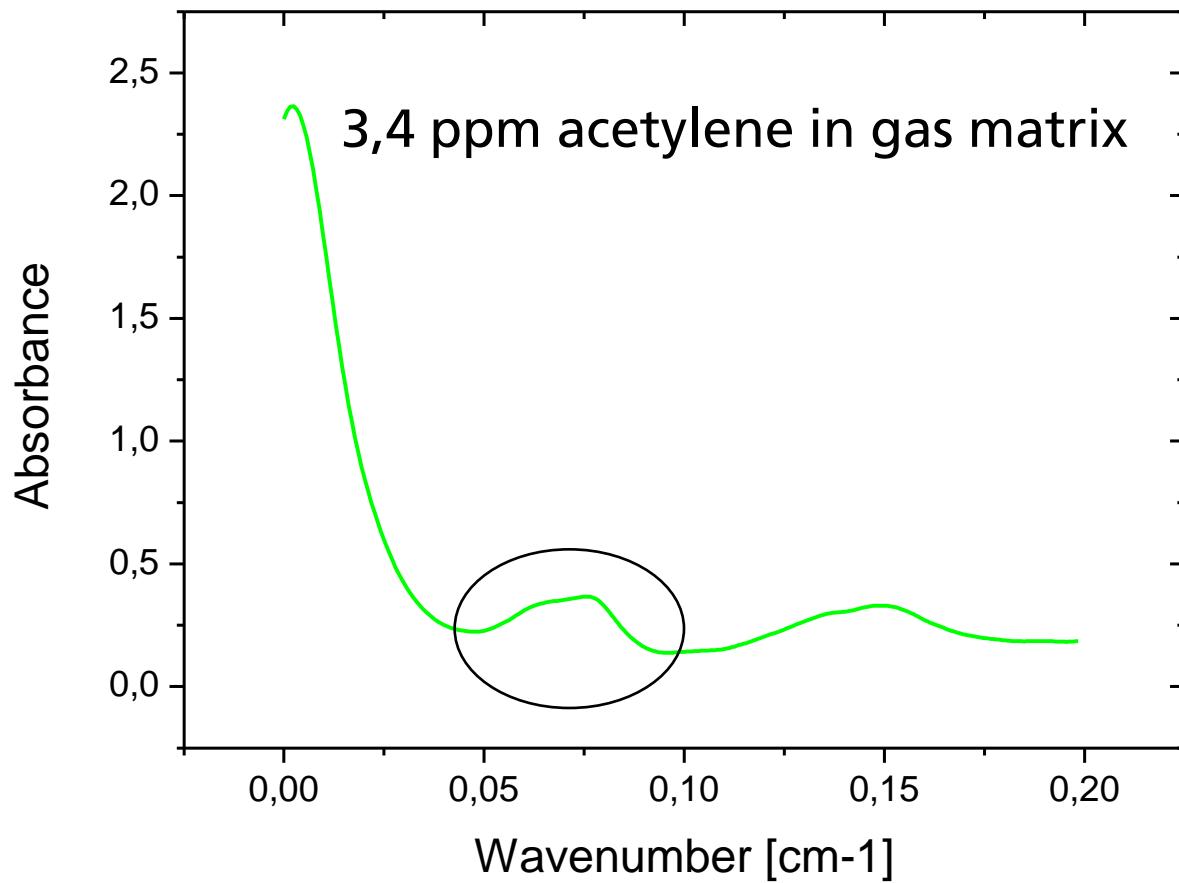


# Long term measurement



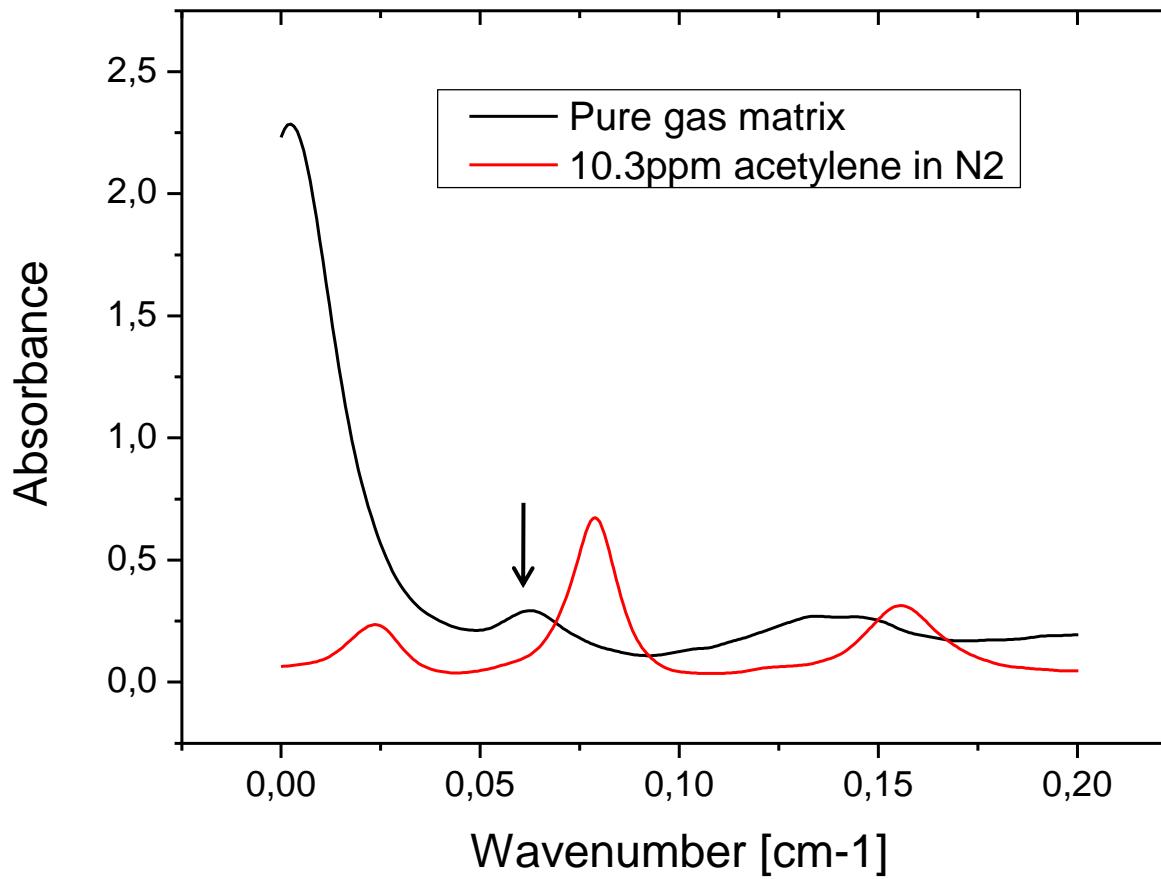
→ High drift stability < 0.05 ppb/h

# Gas matrix control: gas mixture



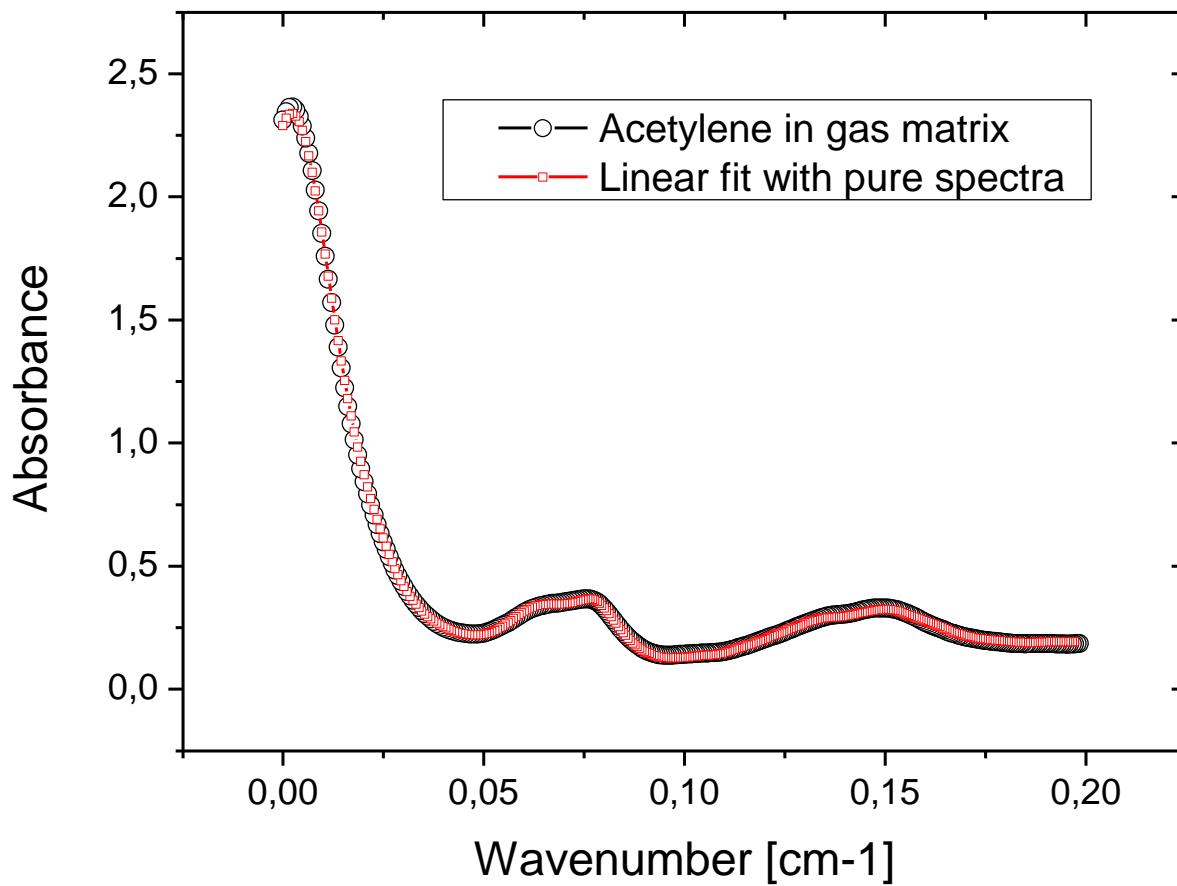
absorption lines are not well separated → linear combination

# Gas matrix control: pure spectra



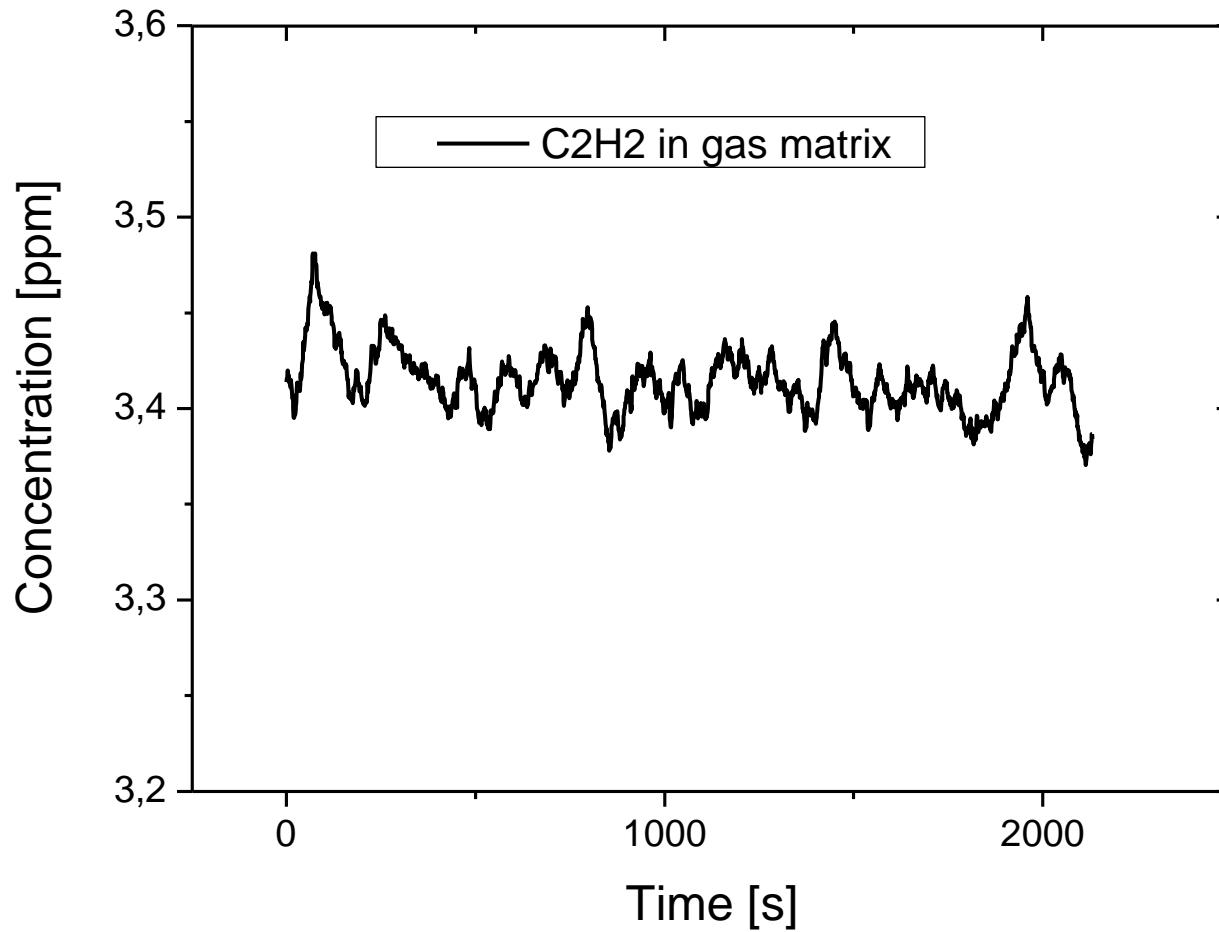
Low C<sub>2</sub>H<sub>2</sub> conc. → the target absorption line disappears

# Gas matrix control: linear spectra fit



Linear spectra fit → 3.41 ppm acetylene

# Gas matrix control: measuring

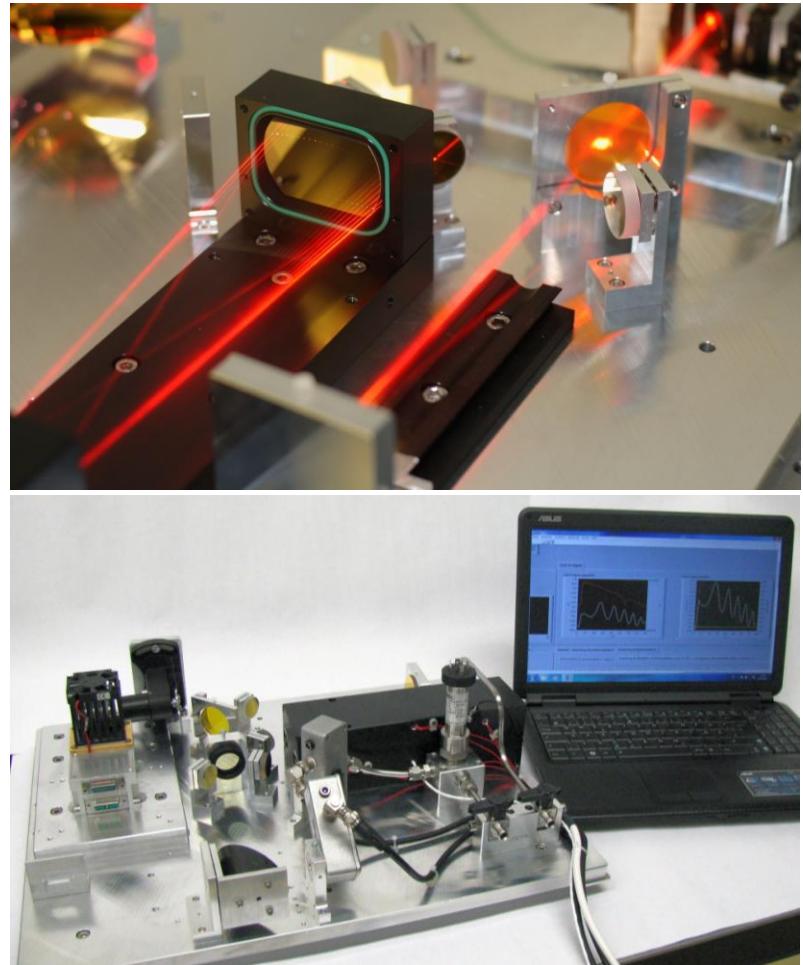


→ NEC (10 s): 16 ppb

# Conclusion

Laser spectrometers features

- High resolution of  $0,01\text{ cm}^{-1}$
- NEC of 10 ppb in 20 s
- Simple to calibrate and long drift stability
- Gas matrix control with linear spectra fit works
  - NEC of 16 ppb in 10s





# **Thank you for your attention!**

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