Spawning the Atmosphere Measurements Workshop, Bern, 22.1.2014

Tracking the signature of stable CO_2 isotopes by quantum cascade laser spectroscopy

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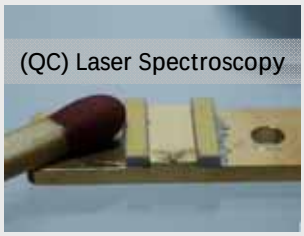
Materials Science & Technology

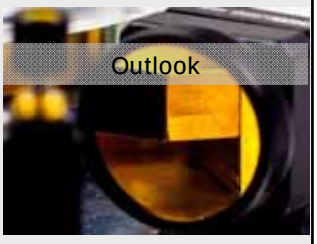
Outline

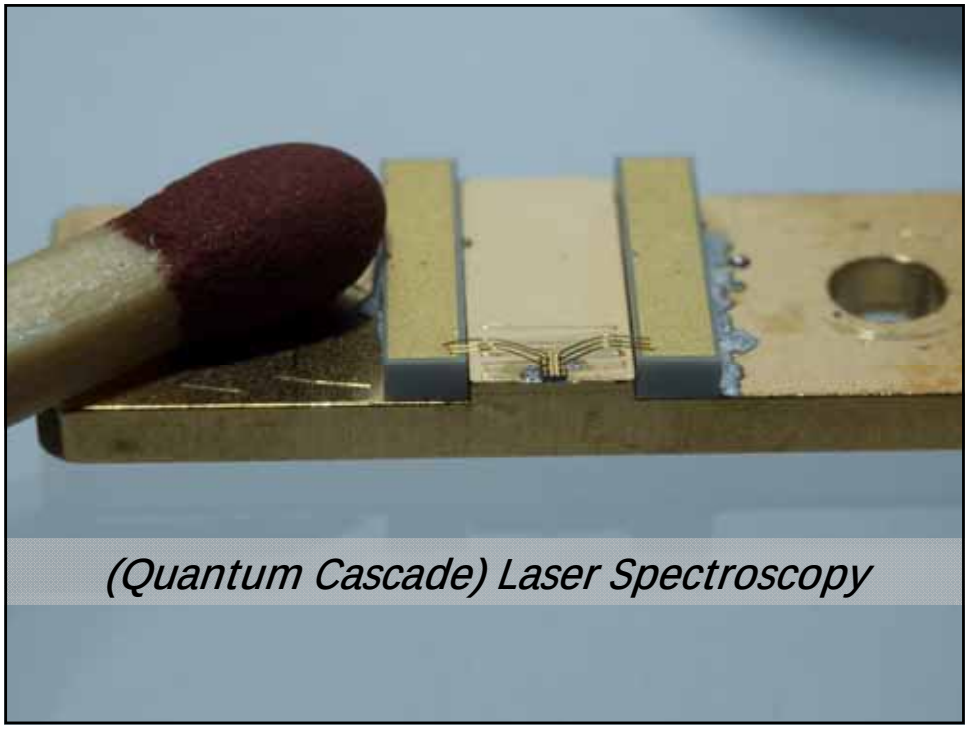
1 (QC) Laser Spectroscopy



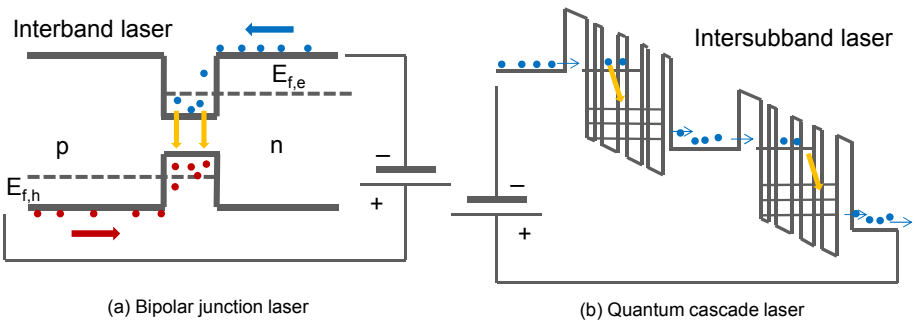
2 Measurements / Results

3 Outlook





Intersubband lasers can be tailored by the thickness of layers



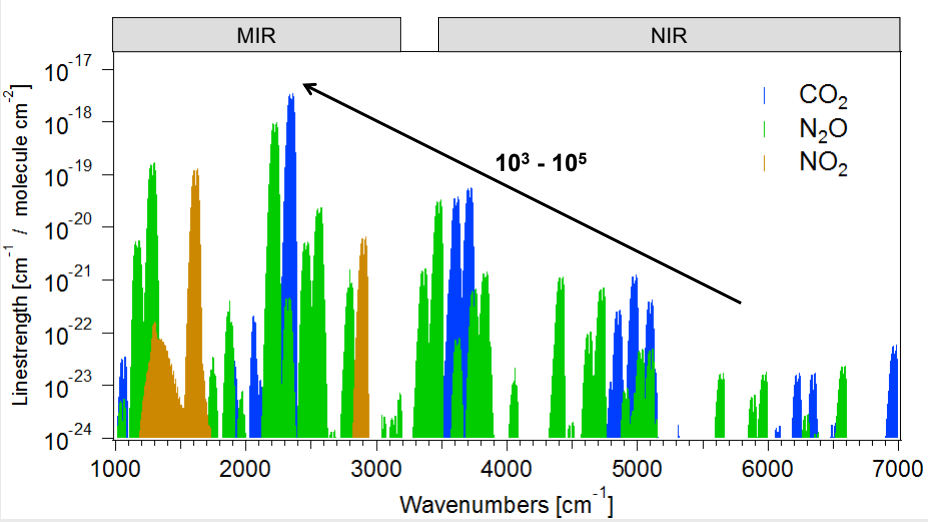
(a) Bipolar junction laser

(b) Quantum cascade laser

UV to NIR

MIR to THz

Absorption line strength are stronger in the MIR compared to the NIR

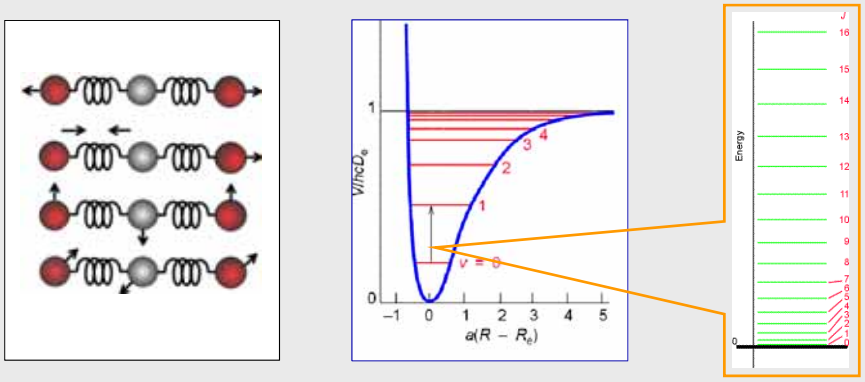


Ro-vibrational transitions for qualitative and quantitative detection

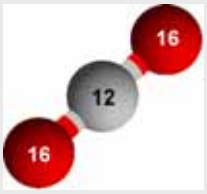
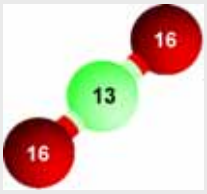
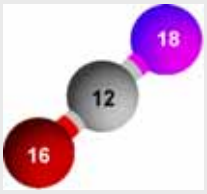
CO_2 molecule in the infrared

Vibrational states

Rotational states



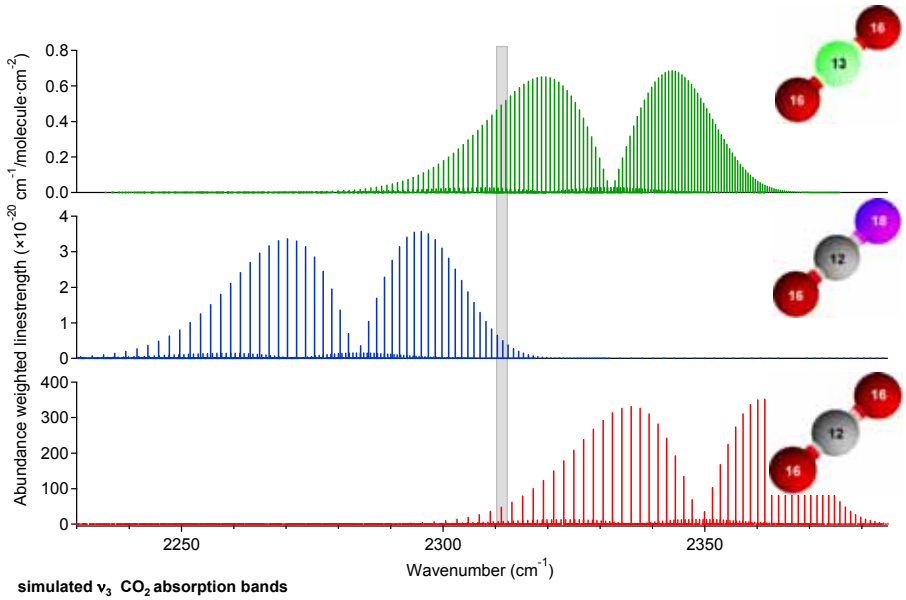
stable CO_2 isotopologues

626	636	628
		
0.98	0.01	0.003

natural abundance

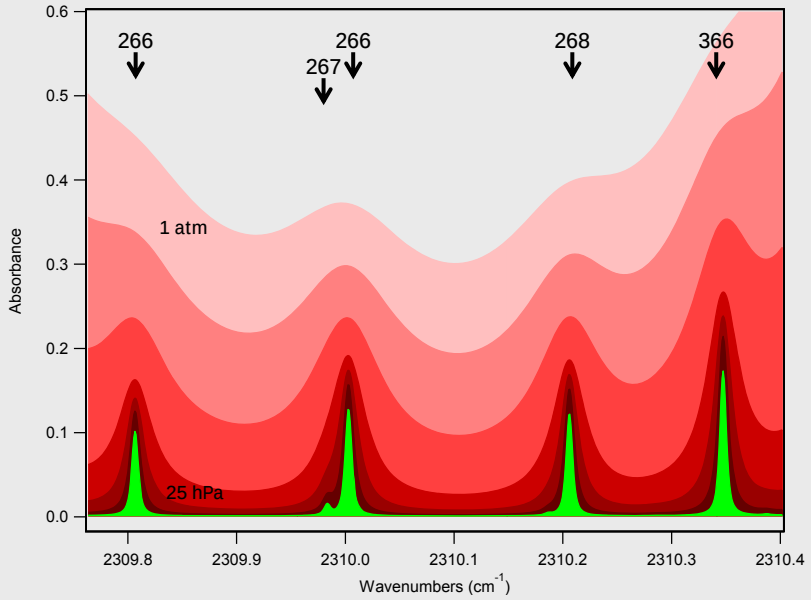
$$\delta^{13}C = \left(\frac{\alpha_{13,s} / \alpha_{12,s}}{\alpha_{13,ref} / \alpha_{12,ref}} - 1 \right) \cdot 1000‰$$

The energy of the molecular transitions depends on the mass of the atoms

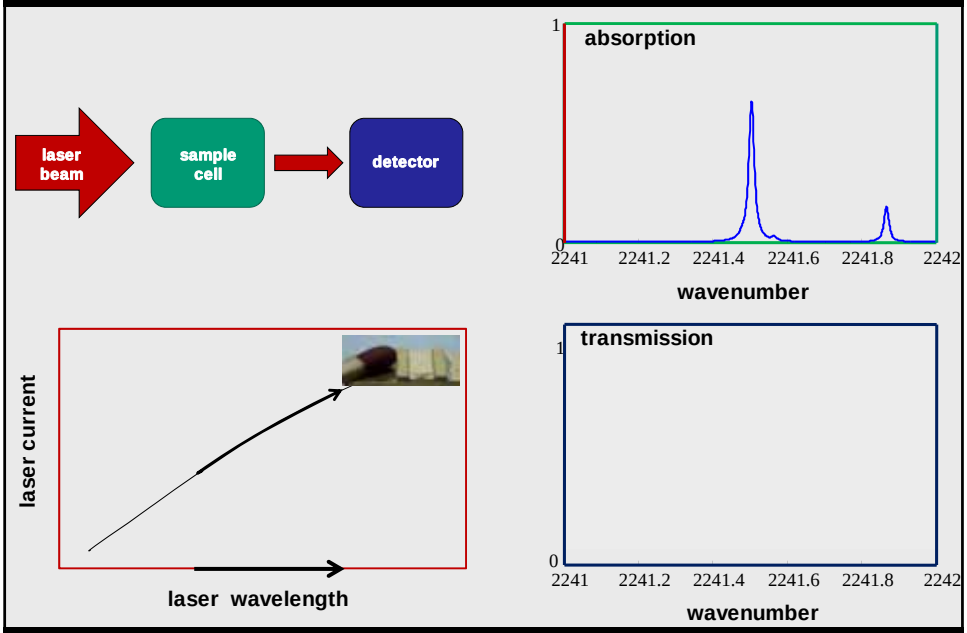


simulated ν_3 CO_2 absorption bands

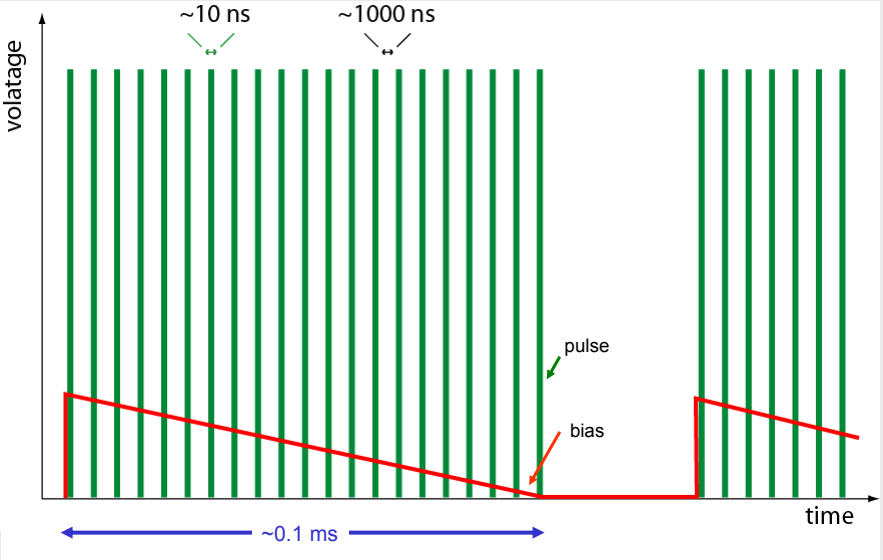
Broadening of the absorption lines changes with pressure



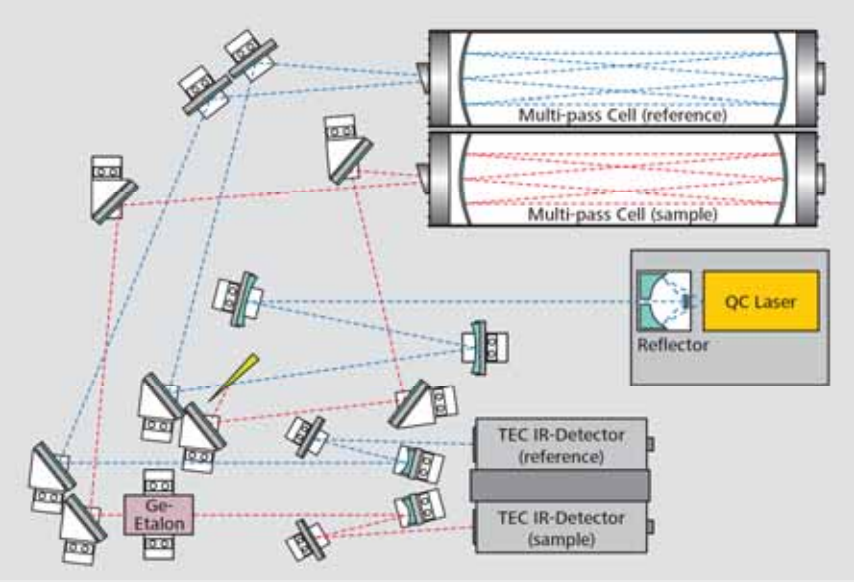
Direct absorption spectroscopy is based on a simple concept



When only pulsed lasers are available...

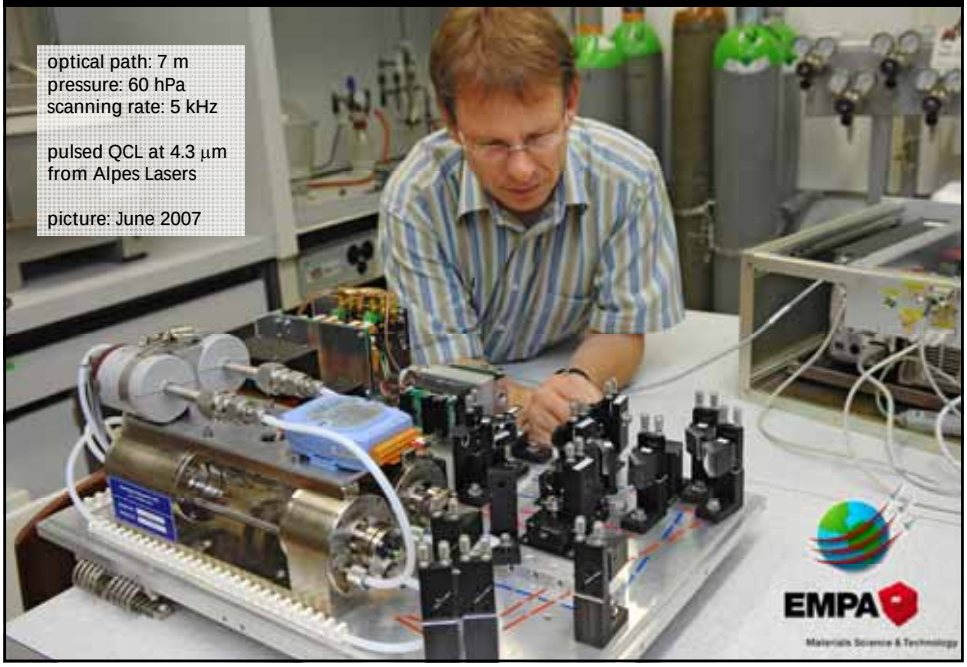


Optical layout for CO_2 isotopologues: spectral ratio method for best precision

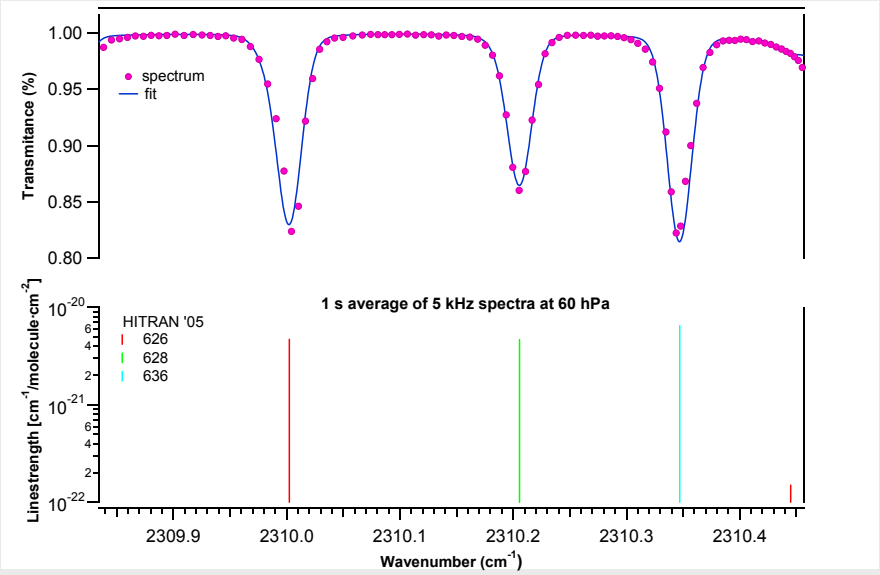


Tuzson et al. Appl. Phys. B (2008)

Setup of the optics

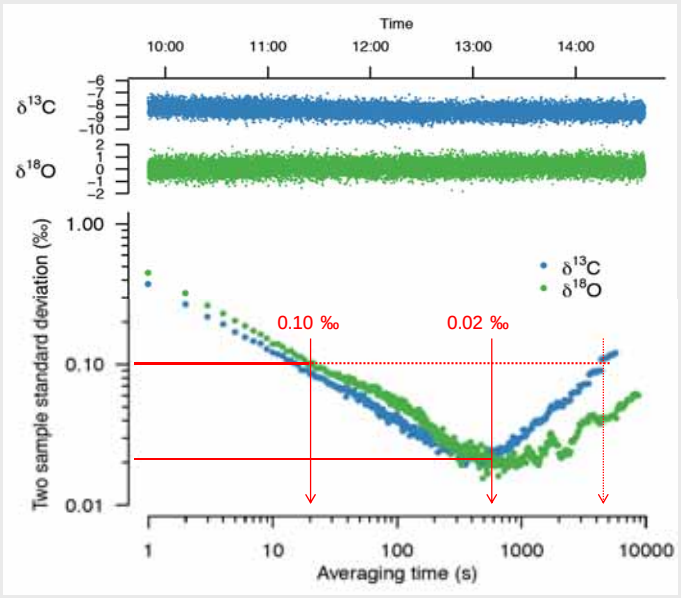


CO_2 Spectrum: measurement (dots) and simulation (line)



Tuzson et al. Appl. Phys. B (2008)

Measurement precision and stability as shown by the Allan Variance Plot



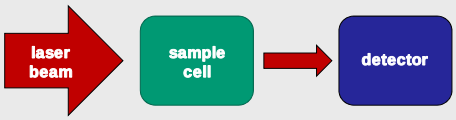
year	1σ min	Ref.
2006	0.16 ‰	Infr. T.
2009	0.05 ‰	APB
2013	0.02 ‰	ACP

Sturm et al., ACP (2013)

Logarithmic dependence between the transmission of light and the number of absorbing molecules (Beer–Lambert law)

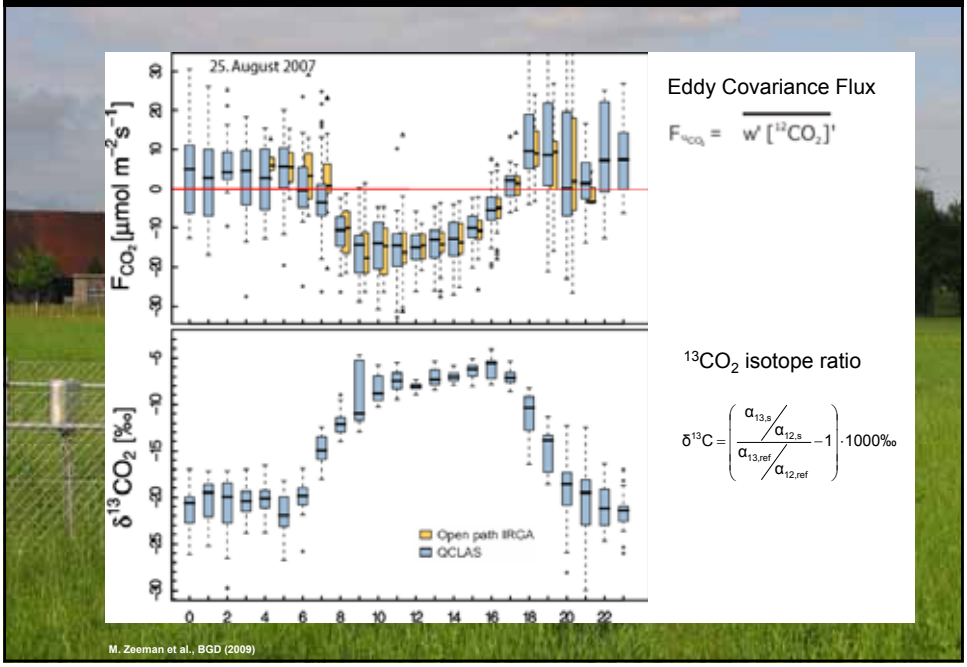
$$I(\nu) = I_0(\nu) \cdot e^{-\alpha(\nu) LPC}$$

$$\alpha(\nu) = N \cdot S(T) \cdot g(\nu, \nu_0, T, P)$$



I: Light Intensity
ν: wavelength
LPC: pathlength, pressure, concentration
α: absorption coeff.
N: number of molecules
S: line strength

First field measurements using continuous QCLAS in Chamau



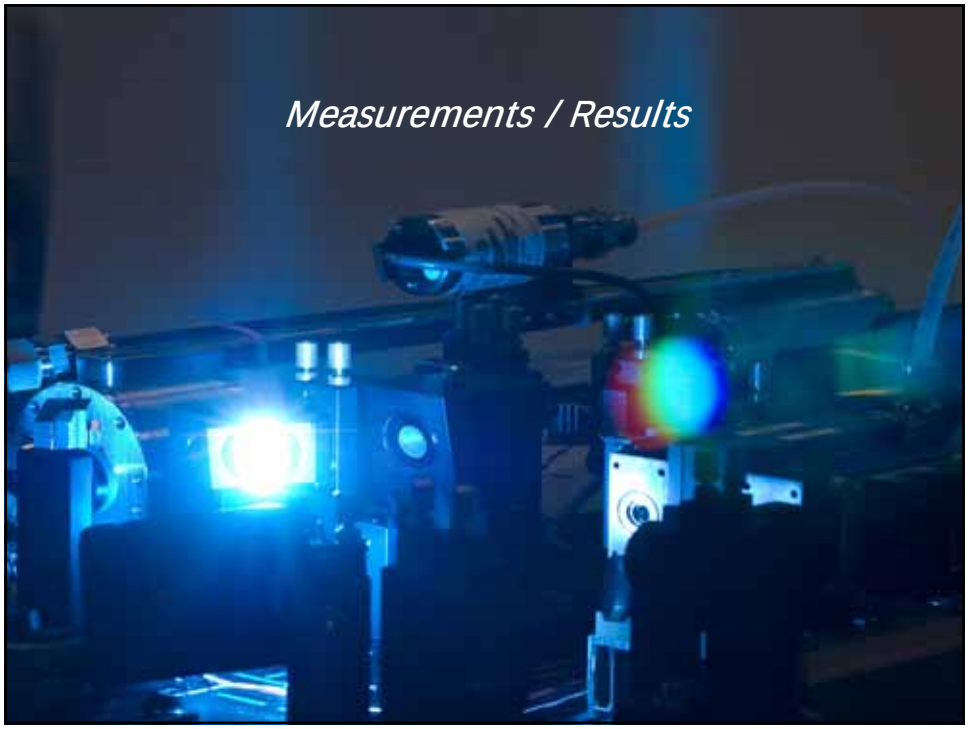
M. Zeeman et al., BGD (2009)

Eddy Covariance Flux

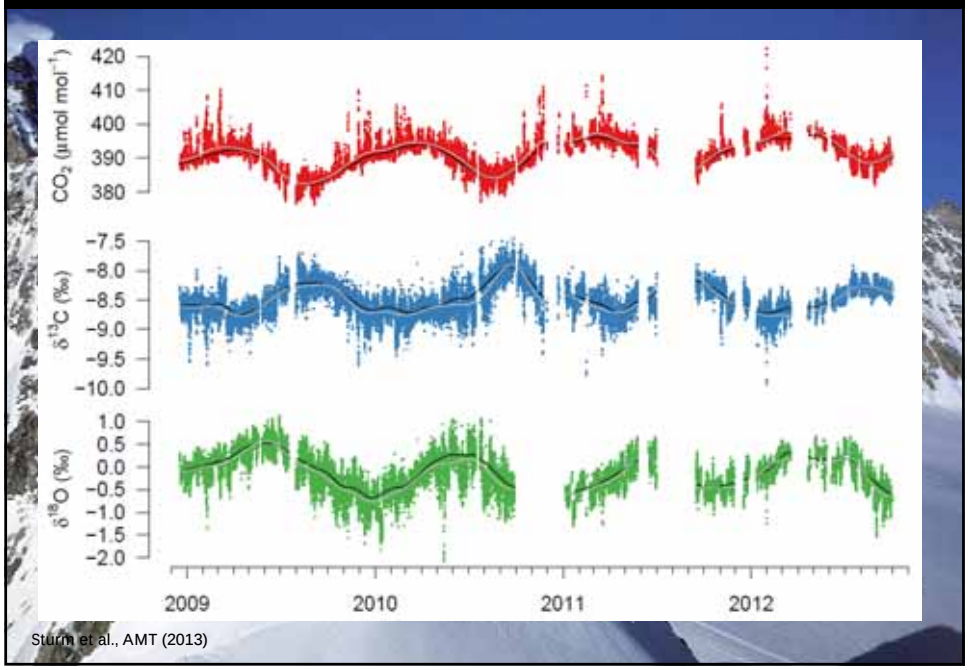
$$F_{^{13}CO_2} = \overline{w' [^{13}CO_2]'}$$

$^{13}CO_2$ isotope ratio

$$\delta^{13}C = \left(\frac{\alpha_{13,s} / \alpha_{12,s}}{\alpha_{13,ref} / \alpha_{12,ref}} - 1 \right) \cdot 1000‰$$

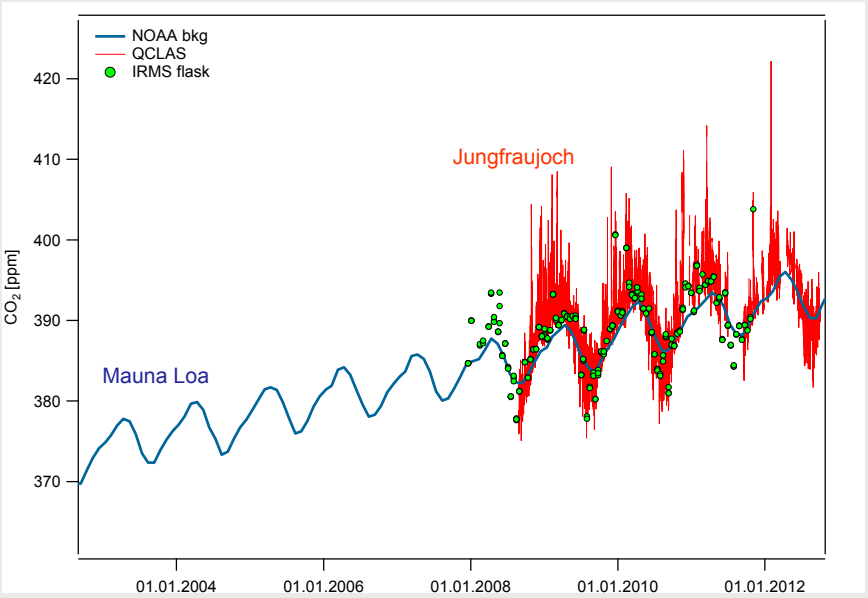


CO_2 concentration and isotopic signature at Jungfraujoch

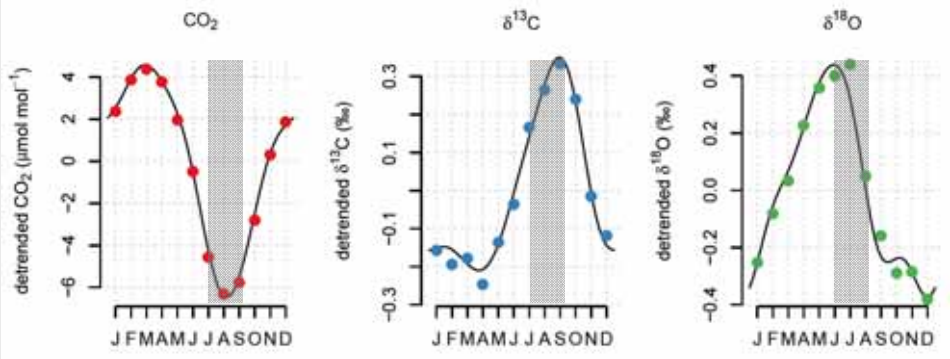


Sturm et al., AMT (2013)

Putting time series into perspective



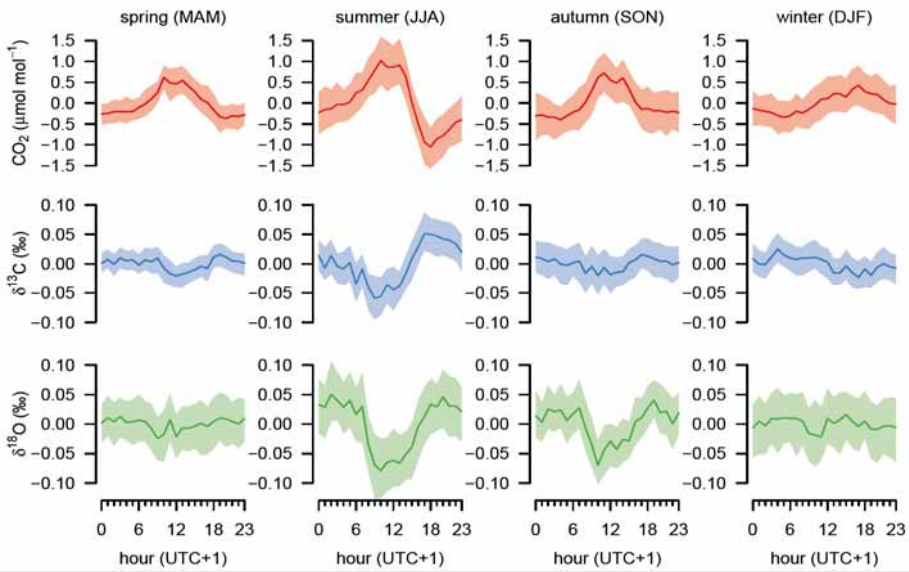
Saisonal trends of CO_2, $\delta^{13}C$ und $\delta^{18}O$



Mean seasonal cycles from detrended and monthly bin-averaged data (points) and the annual harmonic part of the smoothed curve fit (lines).

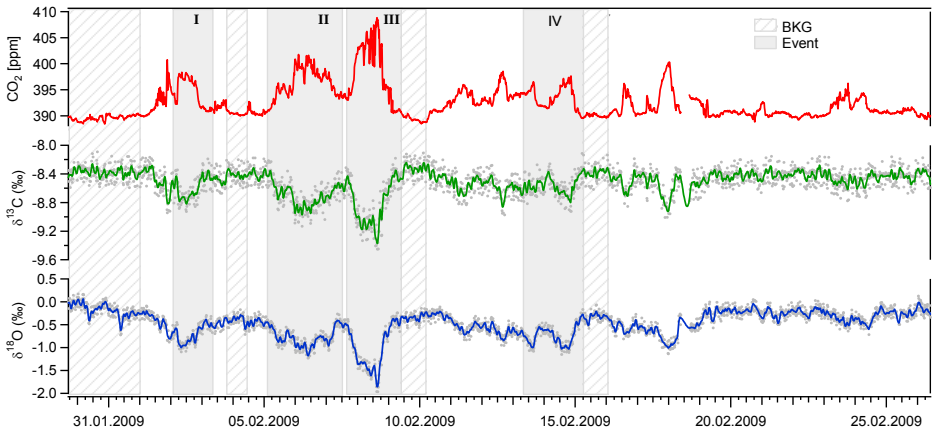
Sturm et al., AMT (2013)

Mean diurnal cycles



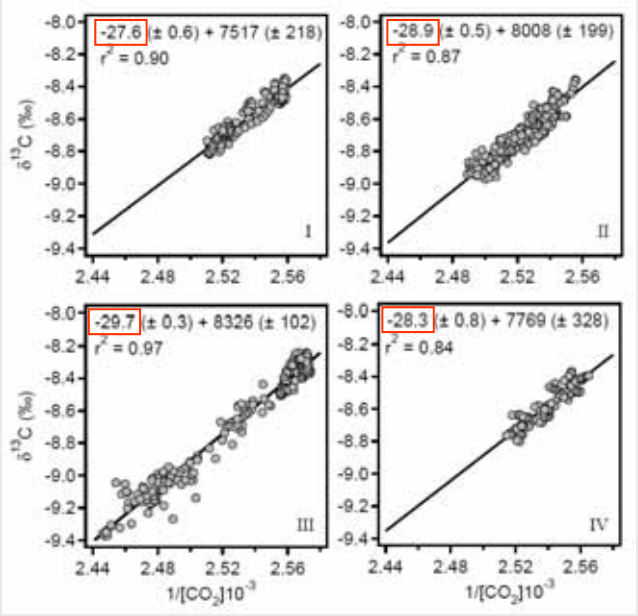
difference to the daily mean with 95% confidence interval of hourly mean from bootstrap resampling

Signature of winter pollution events

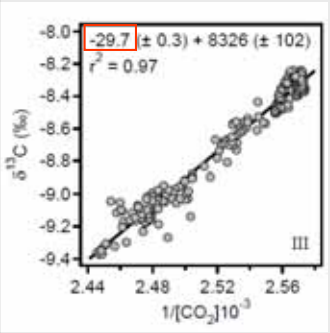


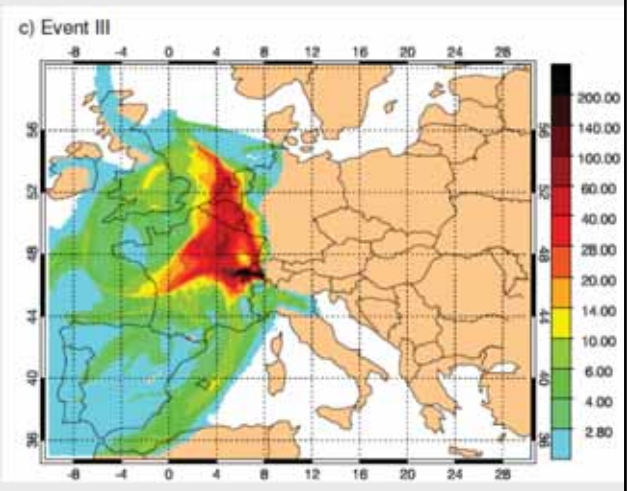
Tuzson et al., ACP (2011)

Isotopic signature of $\delta^{13}C$ based on Keeling plots



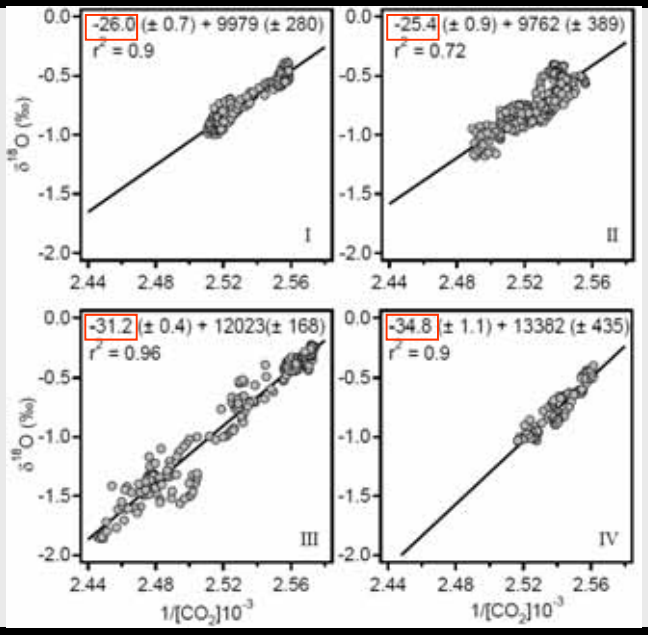
$\delta^{13}C$-CO_2 in pollution event from the NW



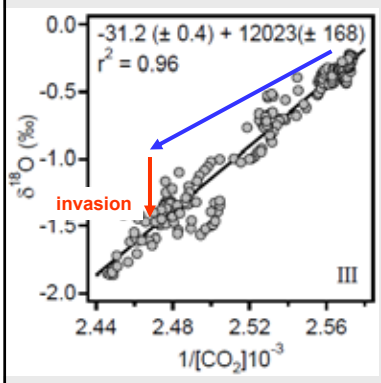


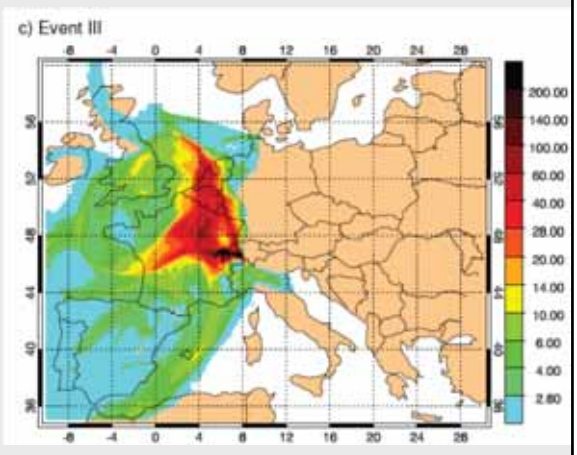
Tuzson et al., ACP (2011)

Isotopic signature of $\delta^{18}O\text{-}CO_2$ based on Keeling plots



$\delta^{18}O\text{-}CO_2$ in pollution event from the NW



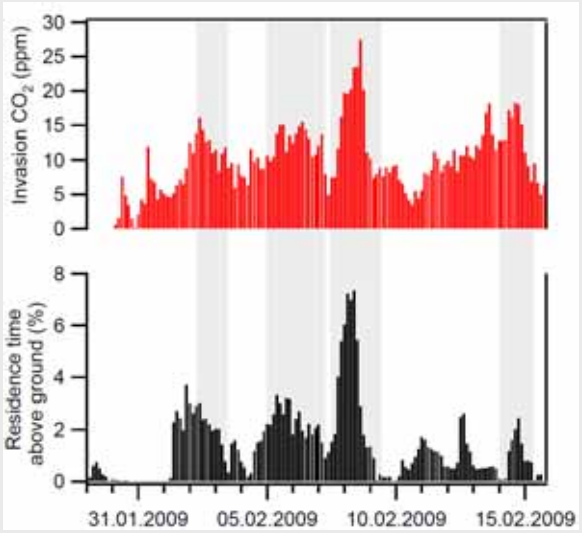


Tuzson et al., ACP (2011)

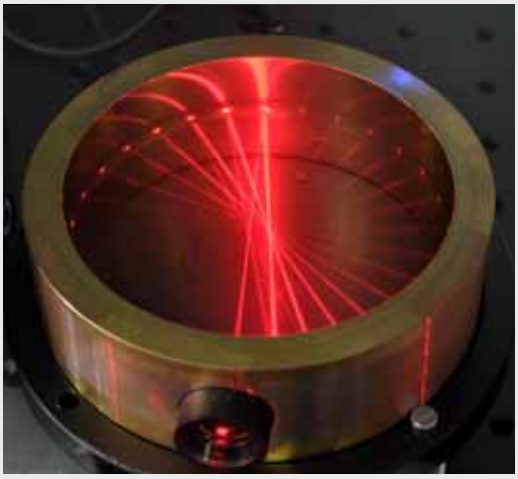
Estimated CO_2 from invasion compared to residence time near ground

$[CO_2]_m = [CO_2]_{bkg} + [CO_2]_p$

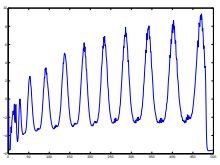
$\delta^{18}O_m\ [CO_2]_m = \delta^{18}O_{bkg}\ [CO_2]_{bkg} + \delta^{18}O_p\ [CO_2]_p + \delta^{18}O_{inv}\ [CO_2]_{inv}$



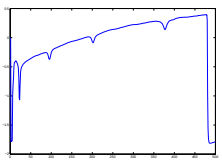
Toroidal gas cell



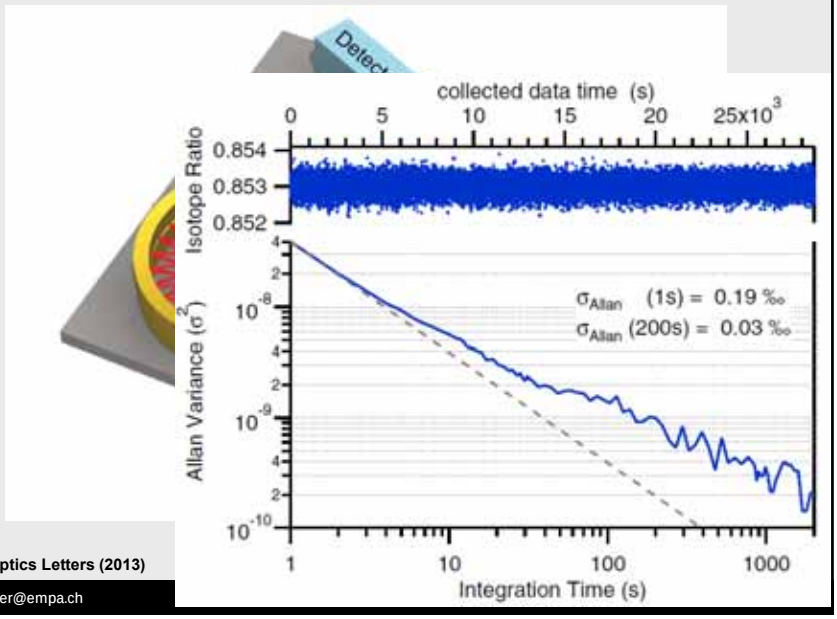
-> optical interference



with absorption mask
(patent pending)



Simplified optics for high-precision measurements



Tuzson et al., Optics Letters (2013)

Current optical platform

Summary

1	2	3
(QC) Laser Spectroscopy	Measurements / Results	Outlook
MIR most sensitive (isotopes) selective powerful direct absorption	high time resolution yearly and daily trends analysis of single events	instruments will improve combine measurements with transport models

Acknowledgements

Empa
- Béla Tuzson
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