Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

Institut für Meteorologie und Klimaforschung

Angewandte Spektroskopie mit Halbleiterlasern

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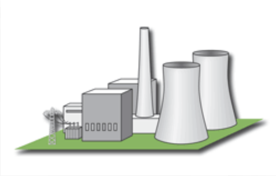
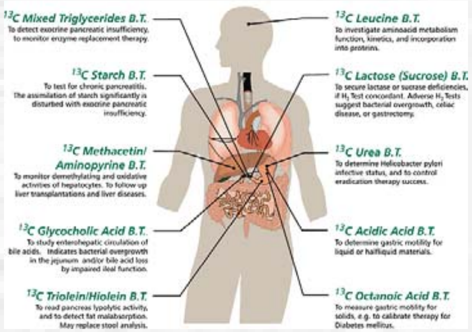
Sitzung 17. April 2007 – Vertilas GmbH, München

Applications for laser-optical Sensors



- Industrial Process Control & Emission Monitoring
- **Plasma Diagnostics, Combustion Diagnostics, High Purity Gases**
- Biomedical Isotopical Diagnostics
- Environmental Research

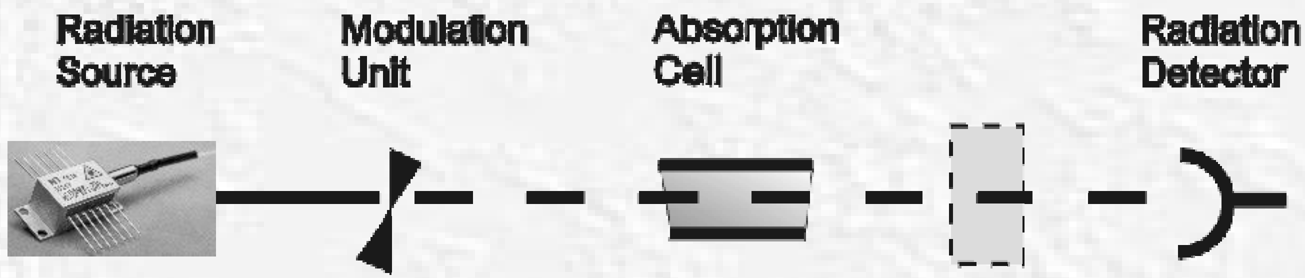


from **Biosphere/Atmosphere** fluxes ....

... to the **upper Troposphere**

and **lower Stratosphere**

Optical Gas Analysis



Laser-
Spectrometer

Specifity !

Gasfilter-
Korrelator

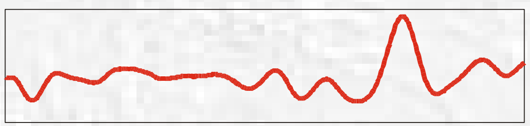
Monochromator
Interferometer
DOAS, FTIR

Opto-pneumatic
Detector NDIR
(Lehrer-Luft)

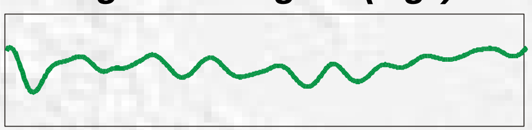
insert selective element

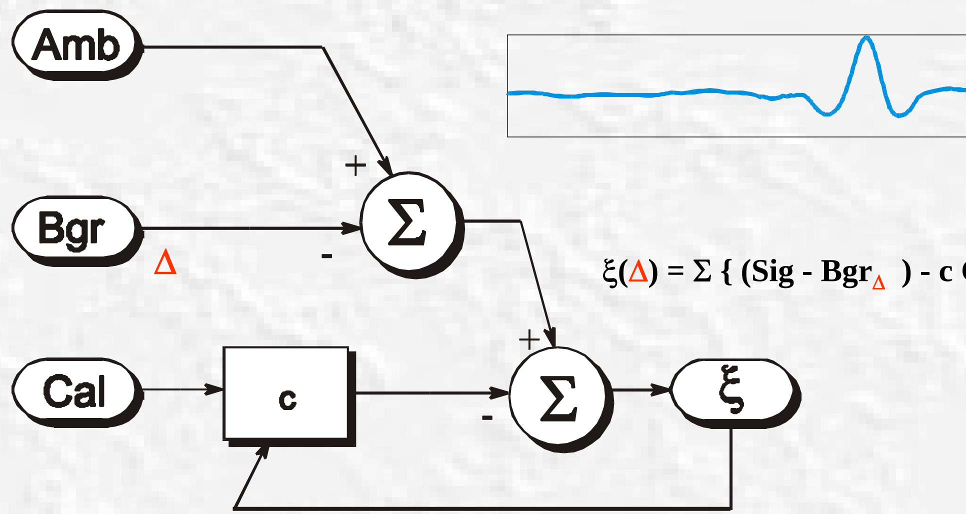
Signal Processing

Measurement Signal (Amb)



Background Signal (Bgr)



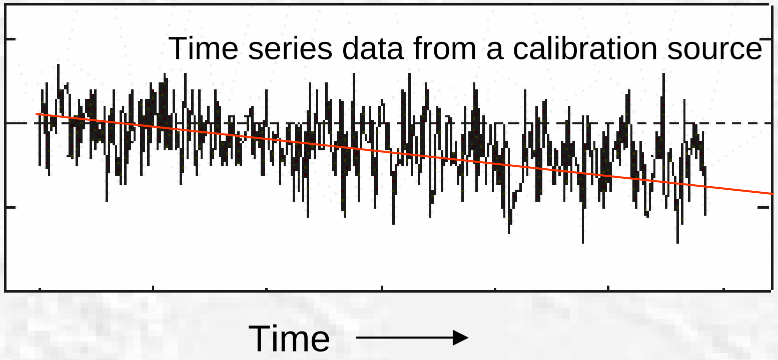


Amb - Bgr

$$\xi(\Delta) = \Sigma \{ (Sig - Bgr_{\Delta}) - c\ Cal \}^2$$

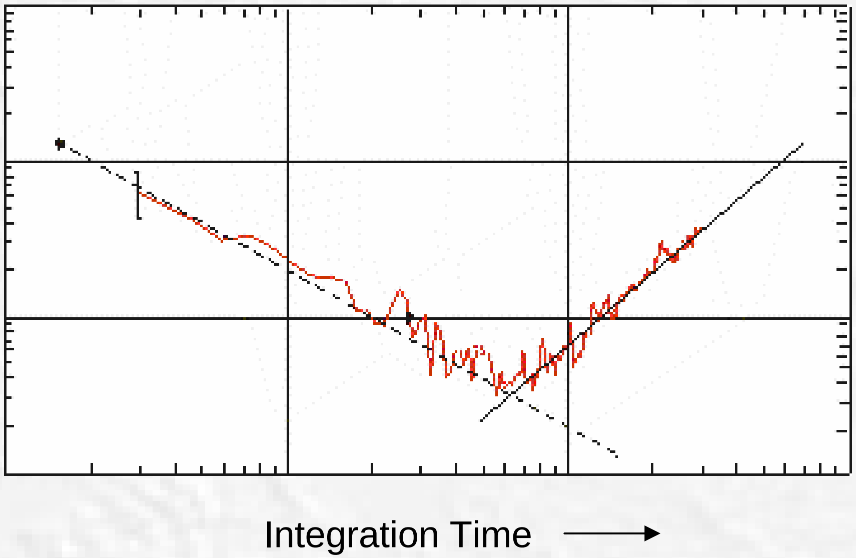
*P. Werle, P. Mazzingh, F. D´Amato, M. De Rosa, K. Maurer, F. Slemr, "**Signal Processing and Calibration Procedures for in-situ Diode-Laser Absorption Spectroscopy**", Spectrochimica Acta A - Review 60, 1685-1705 (2004) (for paper click here)*

System Stability and Allan Variance



$$\sigma_A^{\ 2}(\tau) = \frac{1}{2m} \cdot \sum_{s=1}^{m} \left(A_{s+1}(\tau) - A_s(\tau) \right)^2$$

$$A_s(\tau) = \frac{1}{k} \cdot \sum_{l=1}^{k} x_{(s-1)k+l} \quad , \quad s = 1..m$$



How long can we average data ?

Werle et al. „The limits of signal averaging", Appl. Phys. B 57, 131-139 (1993)
(for Paper click here)

Minimum of Allan Plot defines maximum integration time (= detection limit !) for signal averaging

Methane Budget of the Earth's Atmosphere

Problem :

Large uncertainties in surface sources

Solution :

Flux density measurements using eddy correlation, which is the only direct method

Requirements :

very fast and precise methane sensors

"A major limitation to research on surface exchange and flux measurements is the lack of sensitive, reliable, and fast-response chemical species sensors that can be used for eddy-correlation flux measurement. Therefore, we recommend that continued effort and resources be expended in developing chemical species sensors with the responsiveness and sensitivity required for direct eddy-correlation flux measurements." (Global Tropospheric Chemistry Workshop, 1989)

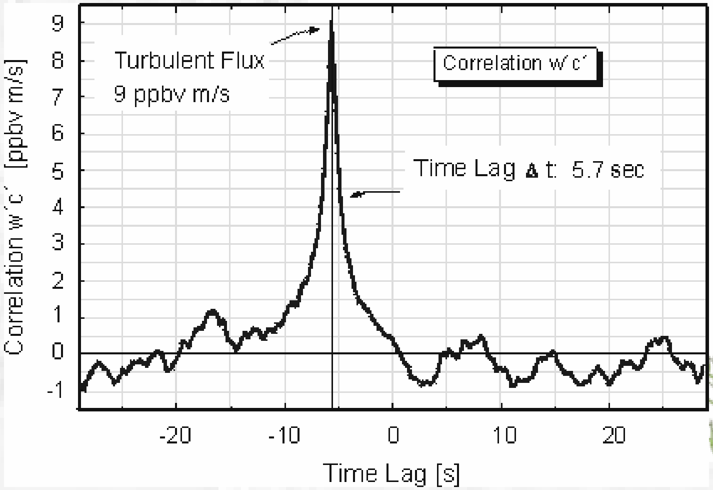
Item	Production [Tg C/Year]	
Natural sources		
marshes	120	(100-200)
termites	20	(10-50)
oceans	10	(5-20)
Anthropogenic sources		
coal and gas mining	100	(70-120)
rice cultivation	60	(20-100)
animals	80	(65-100)
waste treatment	80	(60-100)
biomass burning	40	(20-80)
Sinks		
reaction with OH	430	(350-510)
deposition	30	(15-45)
Atmospheric increase	37	(34-40)

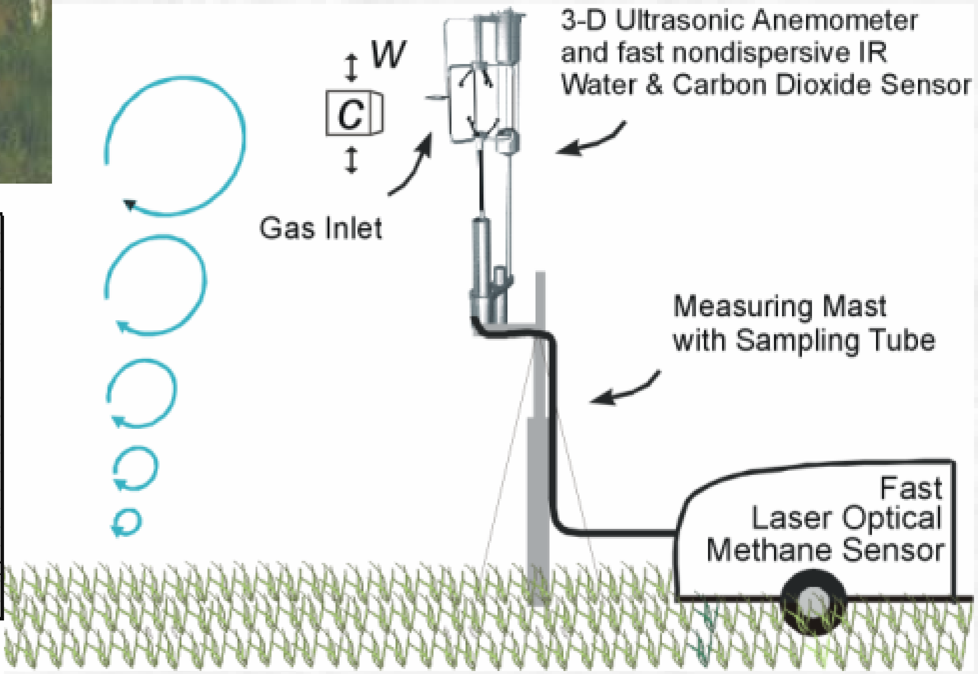
(shaded) surface sources

after: Graedel, T.E., P.J. Crutzen, 1994: Chemie der Atmosphäre - Bedeutung für Klima und Umwelt, Spektrum akademischer Verlag, Heidelberg.

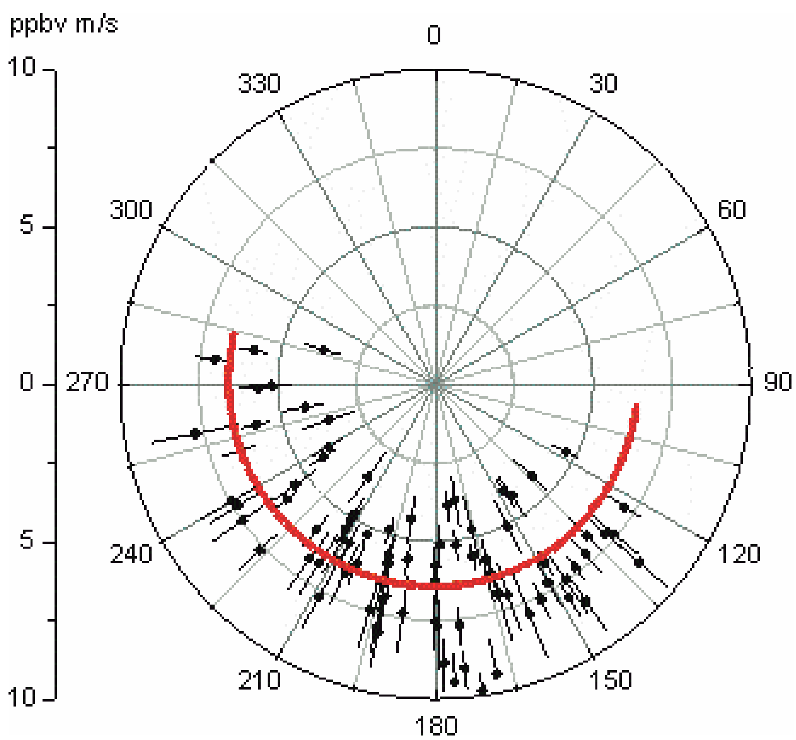
Micrometeorological Measurements of Methane Fluxes

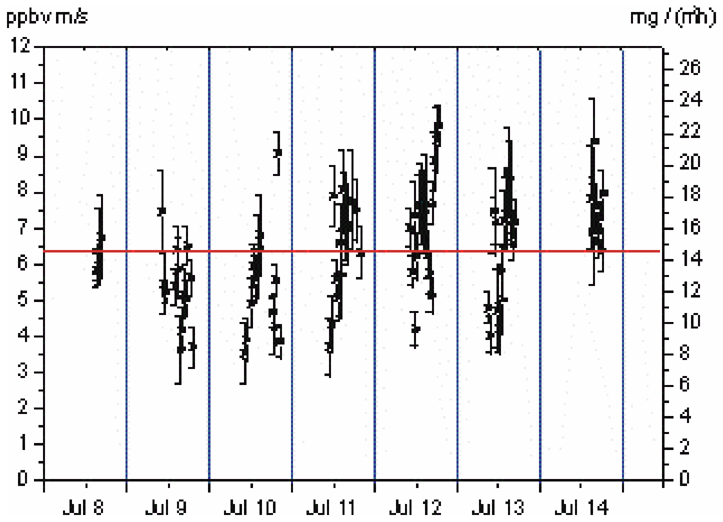
based on the Eddy Correlation Technique have been conducted together with closed chamber measurements in Italian rice paddy fields.





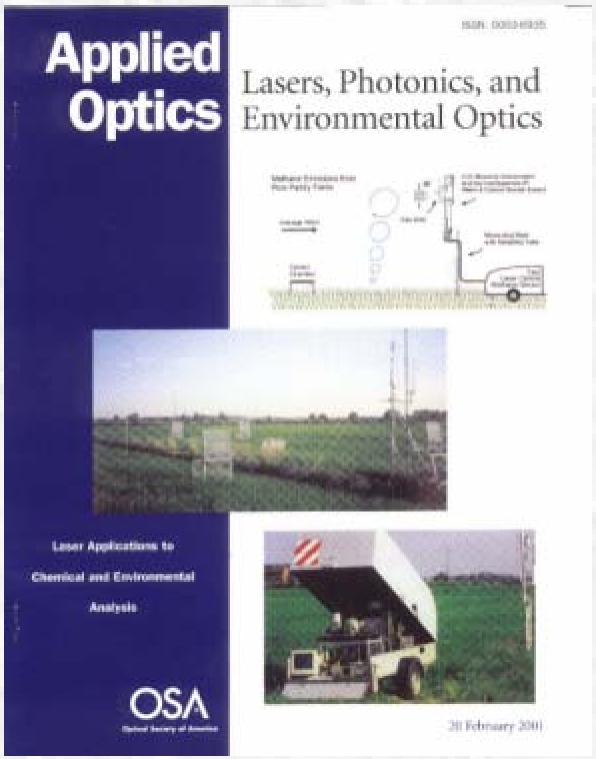
Mean daytime flux ...





Mean Daytime Flux : 6,35 ppbv m/s

details are published ....



- Werle and Kormann, Appl. Opt. **40**, 846-858 (2001)

Airborne in-situ measurements ...

are a useful tool for calibration and validation of remote sensing instruments for atmospheric research

the fast response of TDLS allows detection of fine structures also when operating at the cruise speed of jet aircrafts

achieved scientific results indicates further area to be investigated by the next generation of airborne or satellite remote sensors

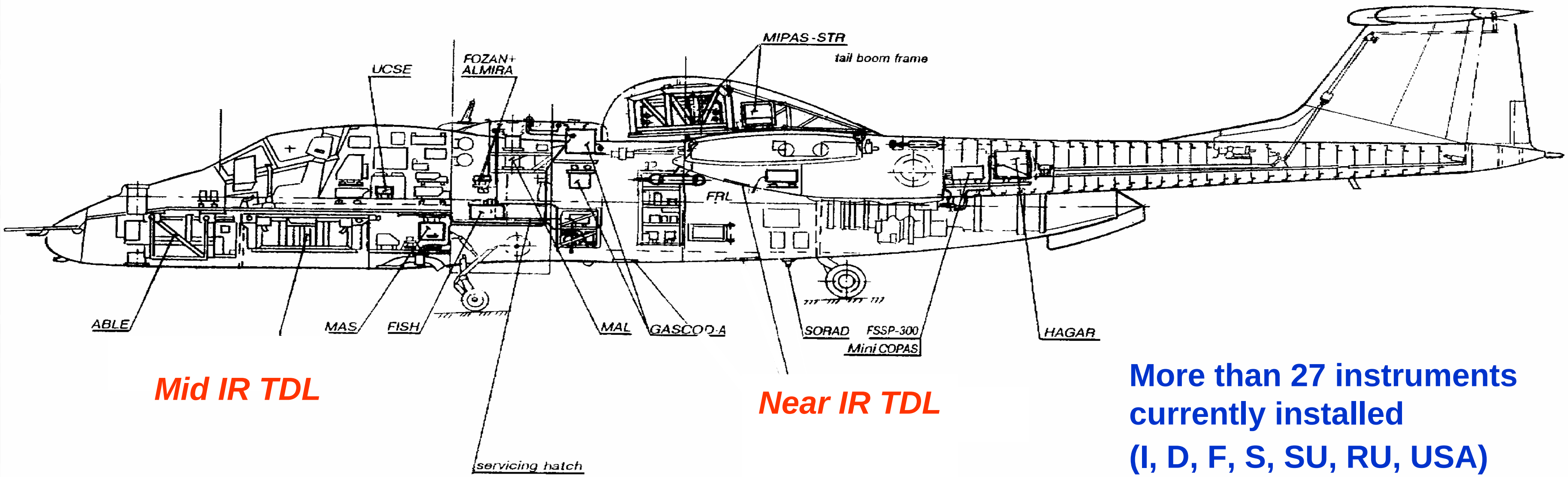
- study of ultra-thin clouds (UTTC, PSC)
- small scale effects leading to mixing phenomena very important in homogeneous and heterogeneous chemistry (tropical convection, polar vortex filaments)

Stratospheric Research Aircraft




Aircraft	**WB-57**	**ER-2**	**M-55**	**Proteus**
Make	EEC	Lockheed	Myasishchev	Scaled Composites
Operated by	NASA	NASA	Geophysica EEIG	Angel Technol. Corp.
Birth	1944 (B57)	1955 (U2)	1988	1998
Flight parameters				
Altitude (m)	18000	21300	21830	18600 (22000 design)
Range (km)	4600	4100	4500	5500
Cruise Speed (m/s)	210	210	210	120
Payload (kg)	2700	1000	1500	3200
Duration (h)	6 h 30’	6 h 30’	5 h 40’	20

Instruments on M55 Geophysica



More than 27 instruments currently installed (I, D, F, S, SU, RU, USA)

INOA instruments :

Mid-Infrared TDL for HNO_3/H_2O or N_2O/CO

Near-Infrared TDL for CH_4 and CO_2

The TDLS on the Geophysica are part of a complete payload system including *in situ* and remote sensing instruments, particle analysis etc...

⇒ **This is necessary to achieve valuable scientific results**

Cryogenically Operated Laser Diode (COLD)

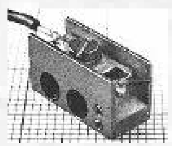
Laser sources:

single mode FP lead salt TDL

λ = 5.8 μm for HNO_3 and H_2O

λ = 4.6 μm for N_2O and CO

Multipass cell:



astigmatic Herriott cell

absorption path 36 m

low volume (0.3 *l*)

Detectors:

HgCdTe, LN_2 cooled (signal)

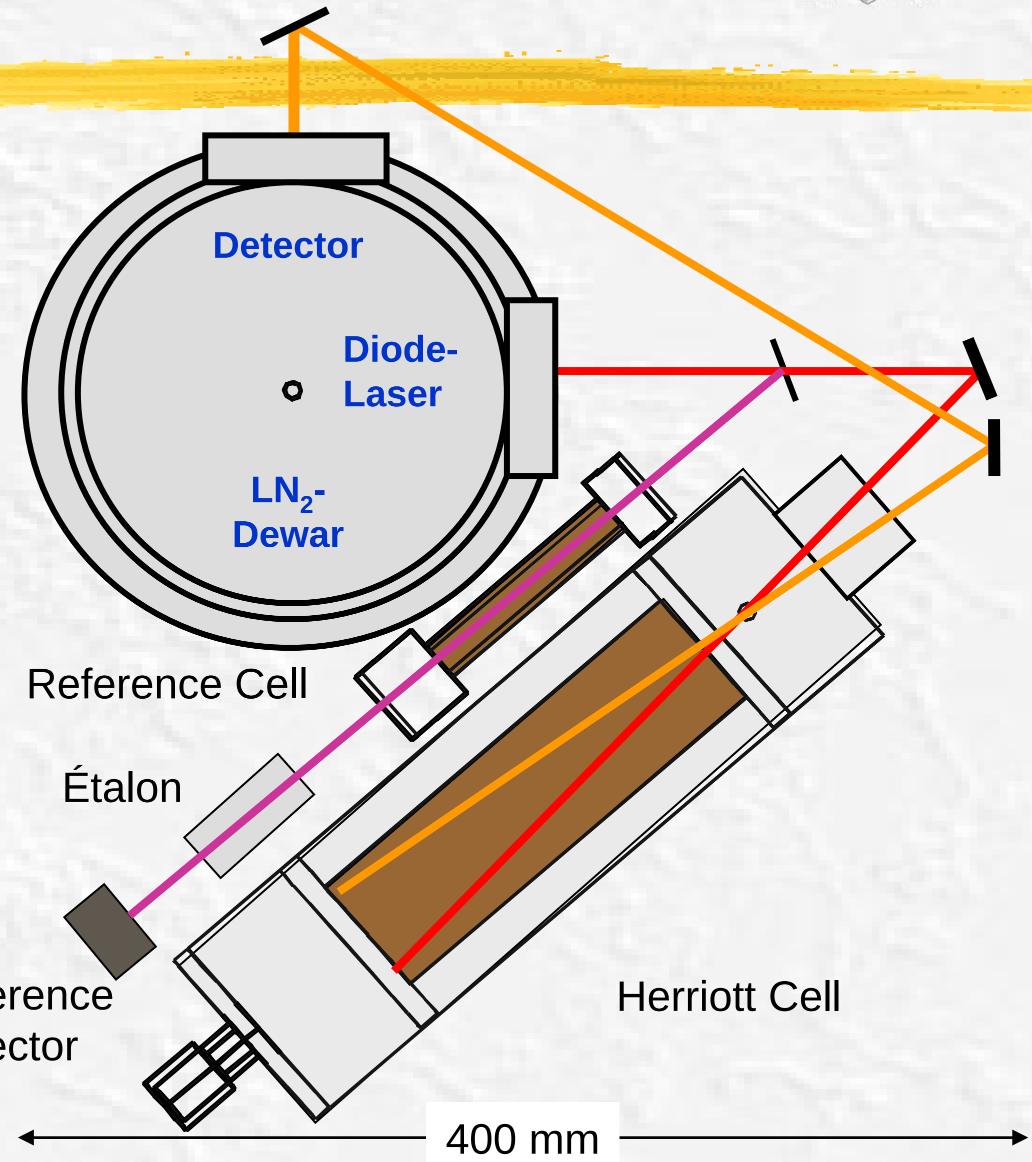
InSb, TE cooled (reference)

Optomechanical design:

Pressurised box (LN_2)

Temperature stabilisation

Compact



COLD – Data Processing

Acquisition

- direct absorption with fast sweep integration
- sample rate 5 MS/s @ 12 bit resolution
- 1000 points spectra acquired @ 2 kHz
- up to 64,000 averaged scans
- equivalent resolution up to 28 bit (2.6 10^8)
- interleaved acquisition of reference spectra

Data processing

- FFT filtering and/or fringe subtraction
- lineshape fitting of the averaged spectra
- number density retrieved from HITRAN
- concentration calculated as f(T, P)

Achieved performance

Absorption sensitivity

$< 10^{-5}$ in laboratory tests

$\approx 10^{-4}$ during flights

Ultimate sensitivity is due to fringes, not to detection technique

Measurements campaigns

The instruments up to now were used in 5 measurement campaigns

Campaign	*Aim*	*Base*	*Date*	*TDL*
APE-THESEO [1,2]	**Tropics**	**Mahe**	**March 1999**	**HNO_3 & H_2O**
ENVISAT Test & Val [1,3]	**Mid-Latitude**	**Forlì**	**July 2002**	**N_2O**
ENVISAT Validation [1,3]	**Mid-Latitude**	**Forlì**	**October 2002**	**N_2O**
EUPLEX [2]	**Arctic**	**Kiruna**	**February 2003**	**N_2O**
TROCCINOX [2]	**Tropics**	**Araçatuba**	**February 2005**	**CO**
SCOUT [2]	**Tropics**	**Darwin**	**December 2005**	**N_2O & CO**
AMMA [2,3]	**Tropics**	**Niamey**	**August 2006**	**N_2O & CO**

In the 35 scientific flights already performed (+ transfer and test flights) the COLD TDL experienced only 5 failures (1 aircraft fuse; 4 software crashes)

Acknowledgements for funding the campaigns:
[1] *Italian Space Agency;* [2] *European Commission;* [3] *European Space Agency*

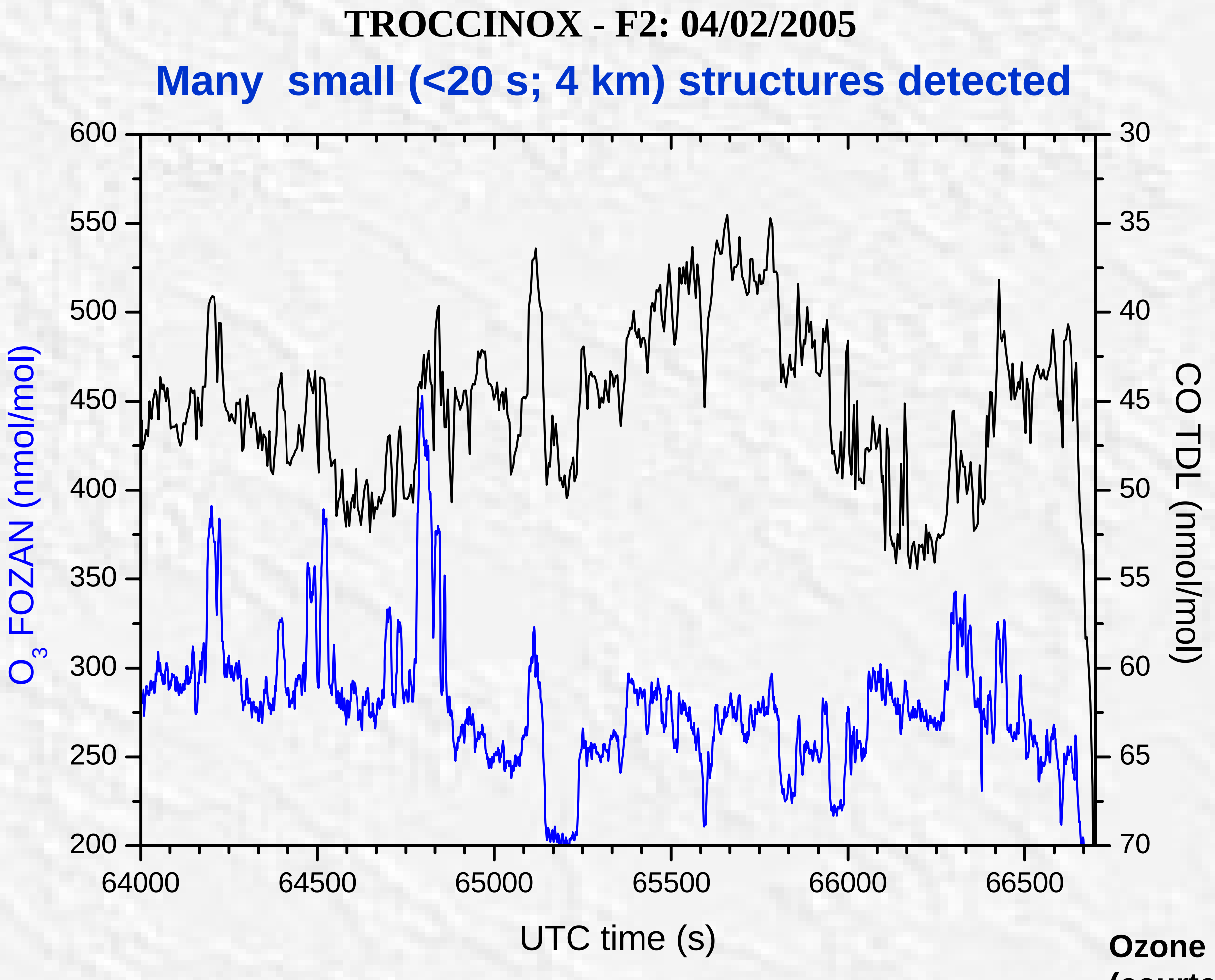
Airborne Measurements

TROCCINOX - Tropical Convection Cirrus and Nitrogen Oxides Experiment

Araçatuba (Brazil), January-February 2005

COLD TDL measuring gas phase N_2O and CO

Anticorrelation of CO with stratospheric ozone

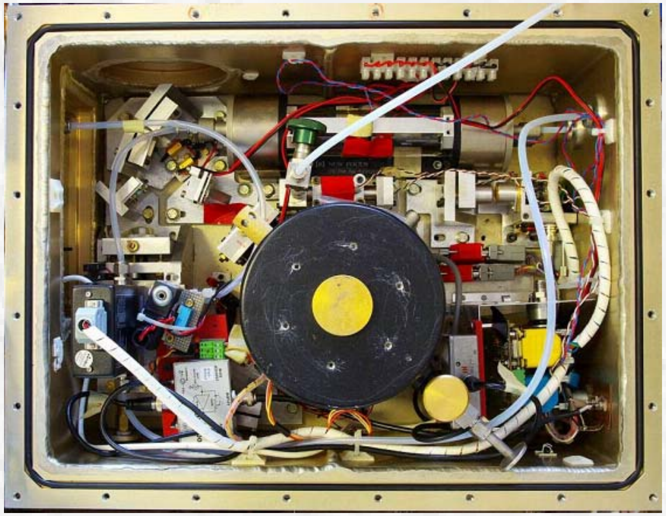


Ozone measured by FOZAN
(courtesy of Fabrizio Ravegnani)

COLD after several campaigns

Learned from campaigns

Liquid nitrogen is not a problem
Actually sometimes it is an advantage



in case of power failure
⇒ the laser remains cool

in case of high humidity on ground
⇒ keeps the whole optics dry
⇒ used for flushing the cell

Reliability was found quite high

⇒ No laser failures during campaigns, just replacements for different targets
⇒ The same set of mirrors still in use after 6 years and 5 campaigns!
⇒ Alignment found very stable (no realignment required in campaigns).

Main problems were: multimode emission from some lasers
communication failure with the laser controller

Missions and future developments

- Increasingly-sophisticated scientific questions addressed by *in situ* payloads (aircraft, balloon) has increased demand for higher precision, higher accuracy measurements of tracers and water
- Aircraft platforms need duplication with differing techniques for continuous intercomparison (TDL, QCL, CRD, DFG, ...)

- fast systems for airborne eddy correlation measurements
- in-situ measurements of reactive species in open multipass cells
- airborne measurements of water isotopes ...

Measurement challenges at low optical densities

How

can we improve

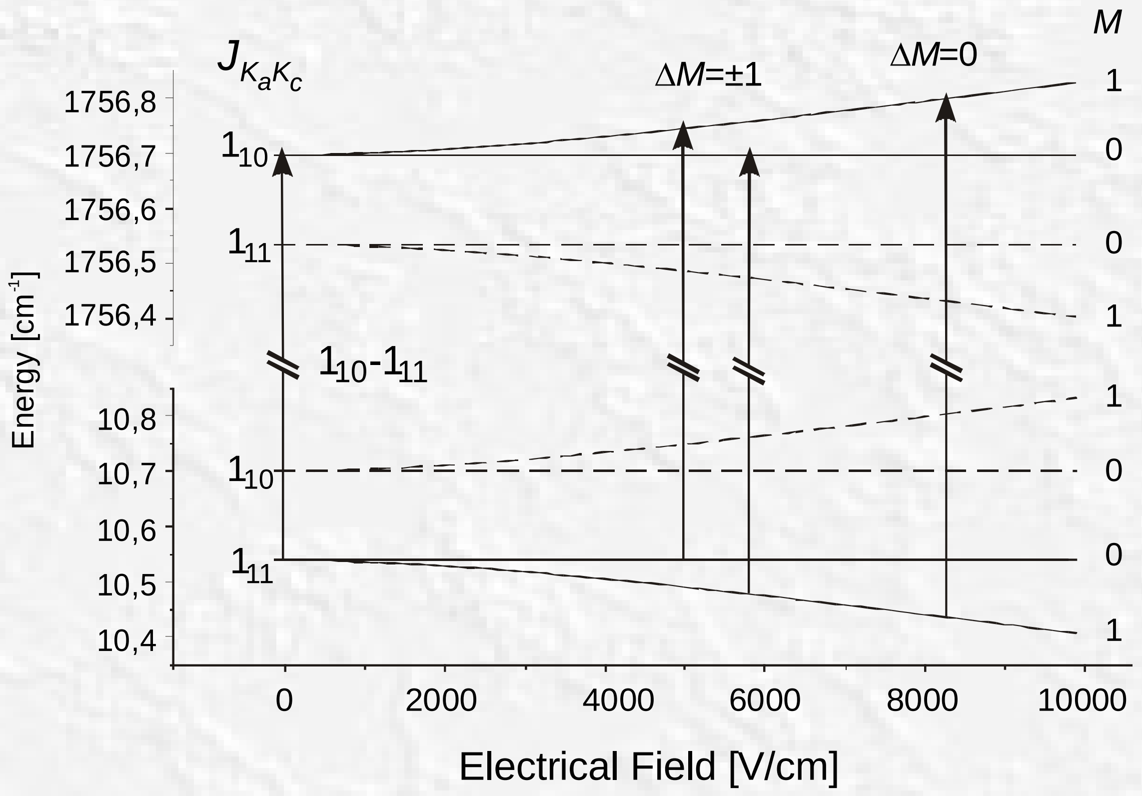
the system stability,

the detection limits

and overall system performance ?

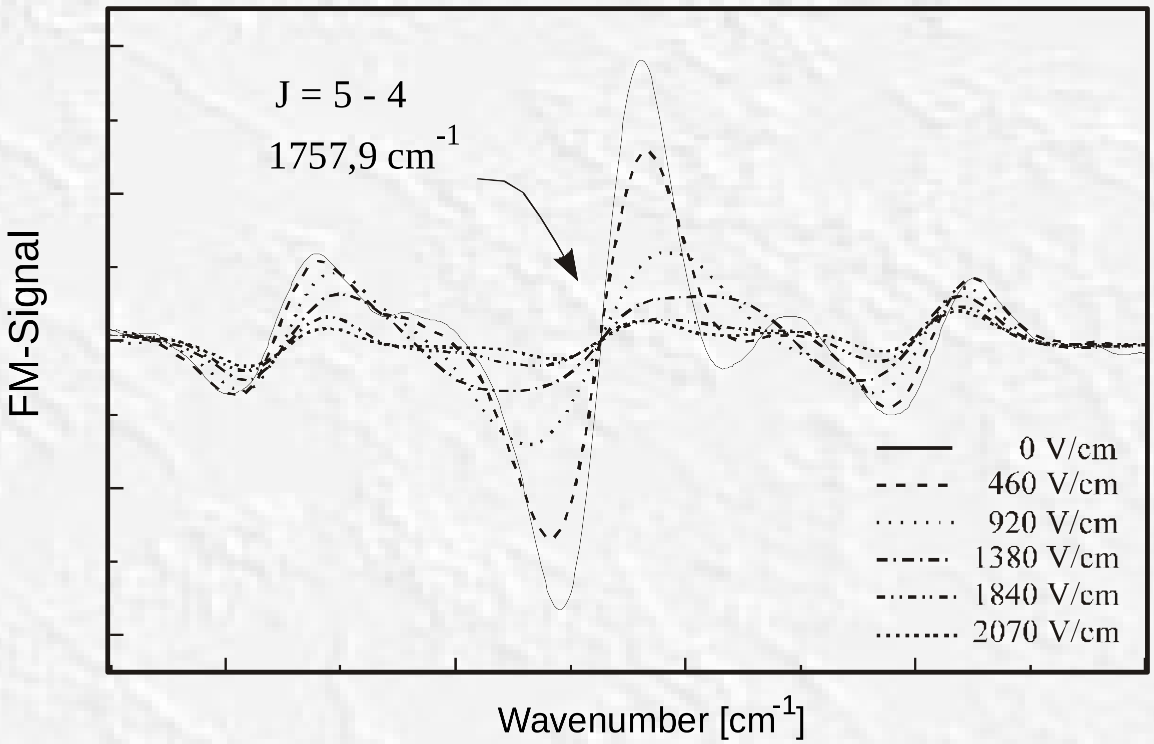
Concept : Sample Modulation - Stark Effekt

a periodic modulation of sample energy levels ...

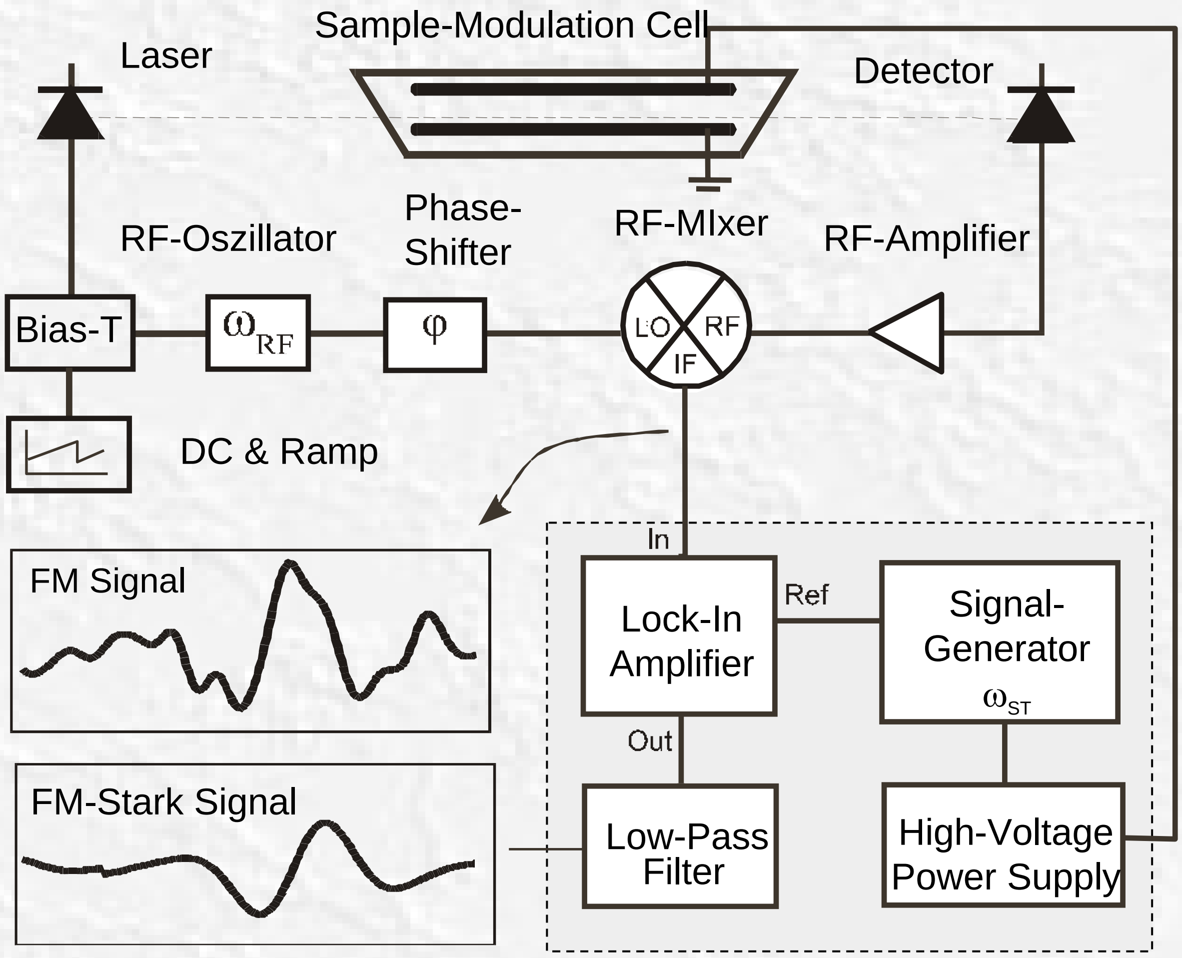


Background Suppression

… influences signal from sample only – background is not affected

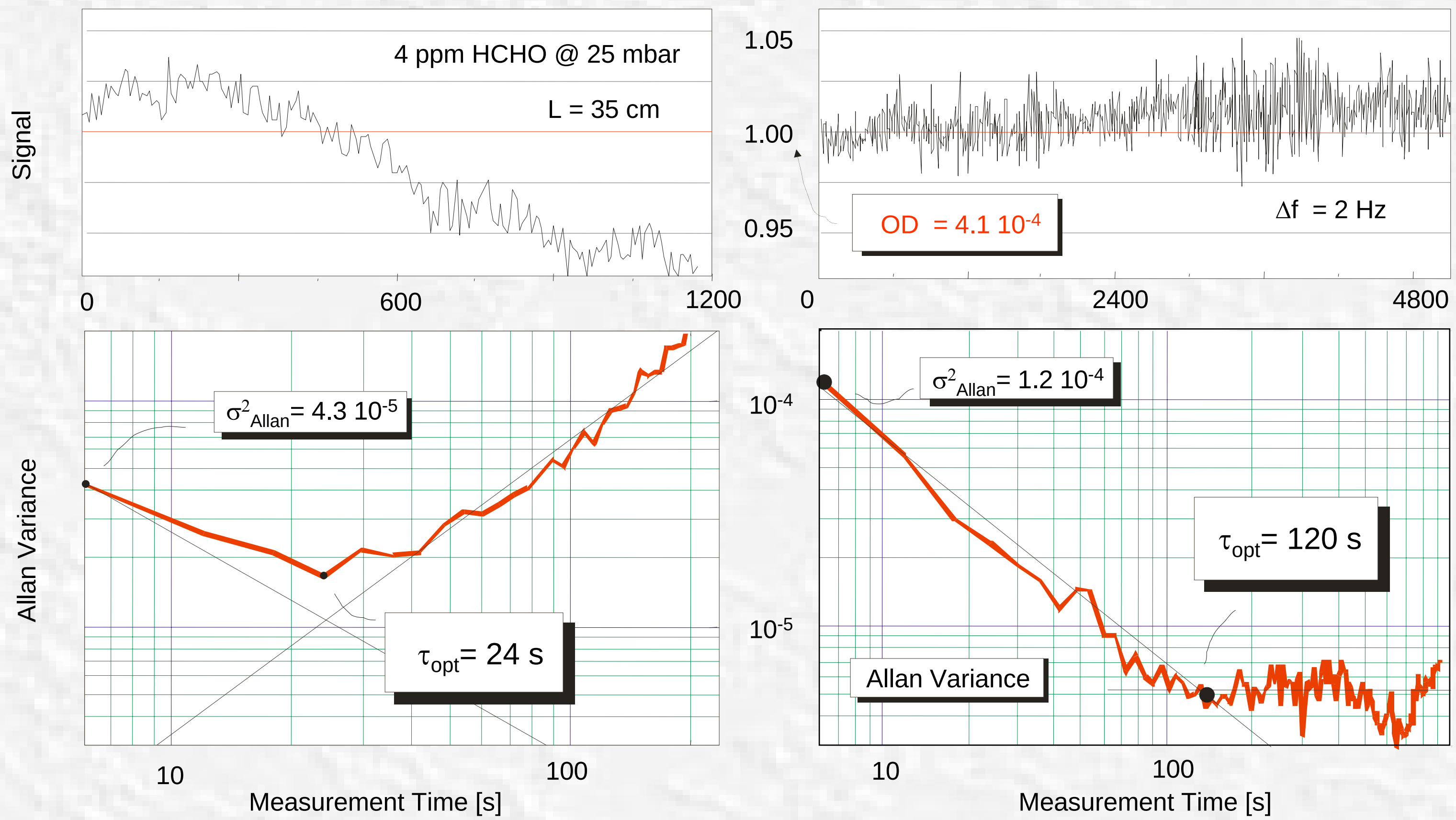


A Laser – Sample Double Modulation Setup



a promising approach ...

no sample modulation | sample modulation



Thank you !