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SMR 1302 - 21

WINTER SCHOOL ON LASER SPECTROSCOPY AND APPLICATIONS

19 February - 2 March 2001

Novel Laser Sources for Applied Spectroscopy

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These are preliminary lecture notes, intended only for distribution to participants.

Introduction

Requirements for high resolution spectroscopy:

- tunability around the wavelength of interest
- amplitude and frequency stability
- narrow linewidth emission spectrum

⇓

Sources based on frequency mixing:

Difference Frequency Generation (DFG)	Second Harmonic Generation (SHG)
periodically poled $LiNbO_3$ (PP-LN) ⇓ CO_2 ro-vibrational spectroscopy @ 4.25 μm	periodically poled $KTiOPO_4$ (PP-KTP) ⇓ I_2 electronic spectroscopy @ 541 nm

Introductory definitions

Lambert-Beer's law: $P = P_0 e^{-\alpha L}$

small absorptions ($\alpha L \ll 1$) ⇨ $\frac{\Delta P}{P_0} \simeq \alpha L$

Sensitivity definition: $(\alpha L)_{min}$ or, if (1) holds, $(\Delta P/P_0)_{min}$. α_{min} (1/cm) is sometimes given as a figure of sensitivity because it is independent of the absorption pathlength, L.

Maximum sensitivity ⇨ only intrinsic quantum fluctuations (shot noise)

At the shot noise limit: $\alpha L = \sqrt{\frac{2eB}{\eta P_0}}$

where
B = detection bandwidth
e = electron charge
η = photodetector responsivity
P_0 = incident radiation power

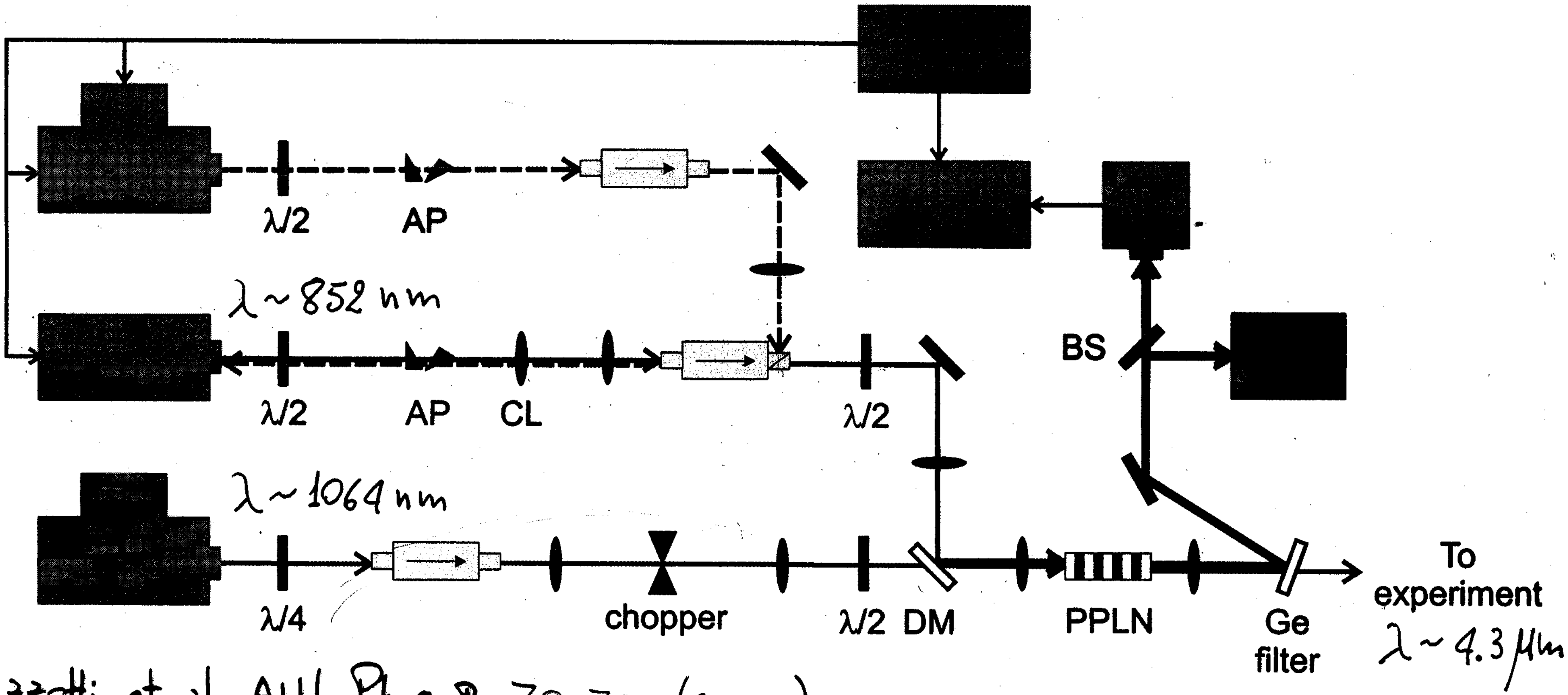
example:
$\alpha L \approx 10^{-8}$ @ P_0 = 1 mW, 1-s averaging, $\eta \cong 0.8$ A/W (λ = 1.064 μm)

but, in general, technical noises are dominant

Two ways to lower the detectability threshold of gases

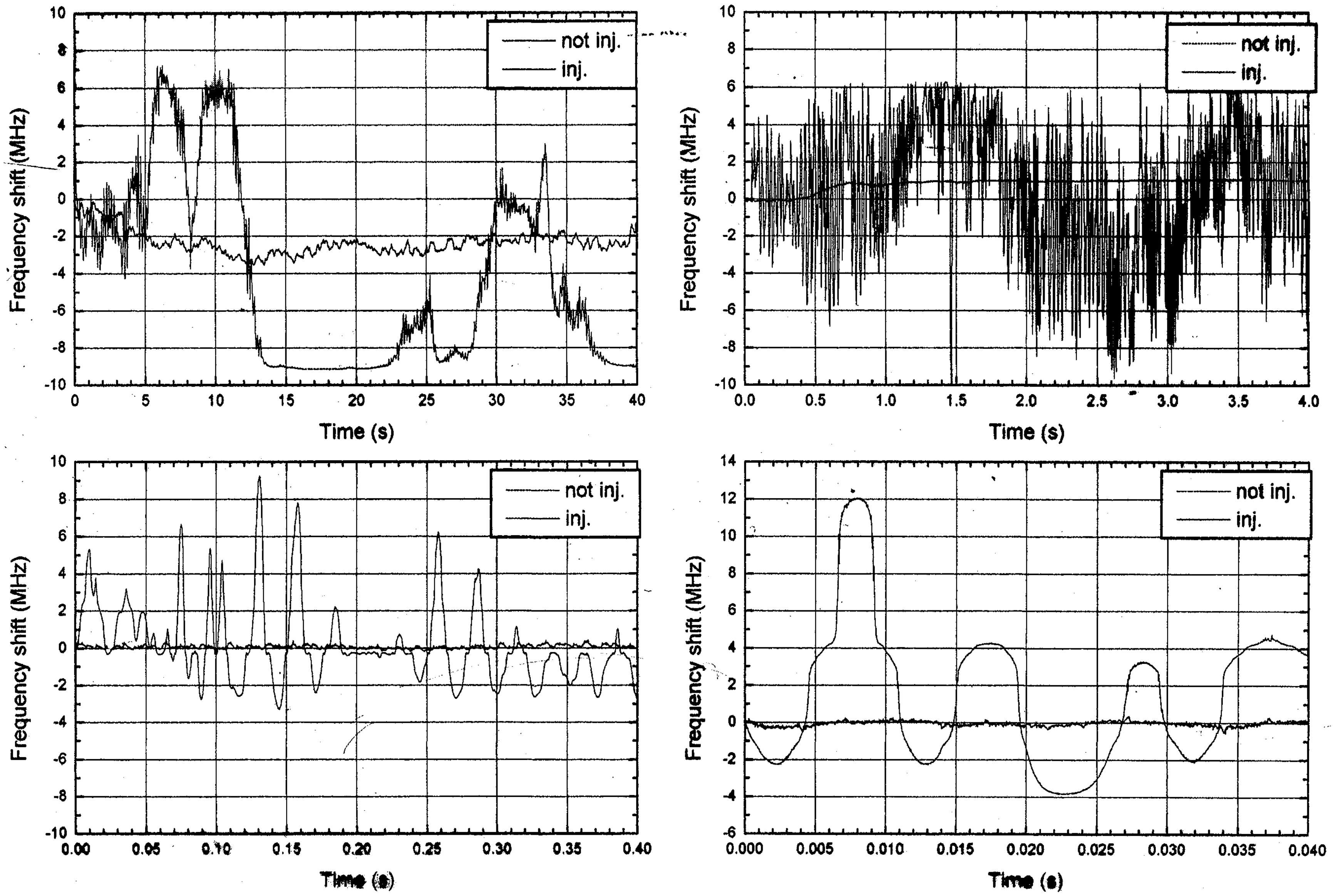
Decreasing noise	➪	different spectroscopic techniques to reduce excess noise squeezing
Increasing signal	➪	increasing absorption pathlength,L (multiple pass cells, high finesse cavities) increasing α, using sources resonant with fundamental vibrations

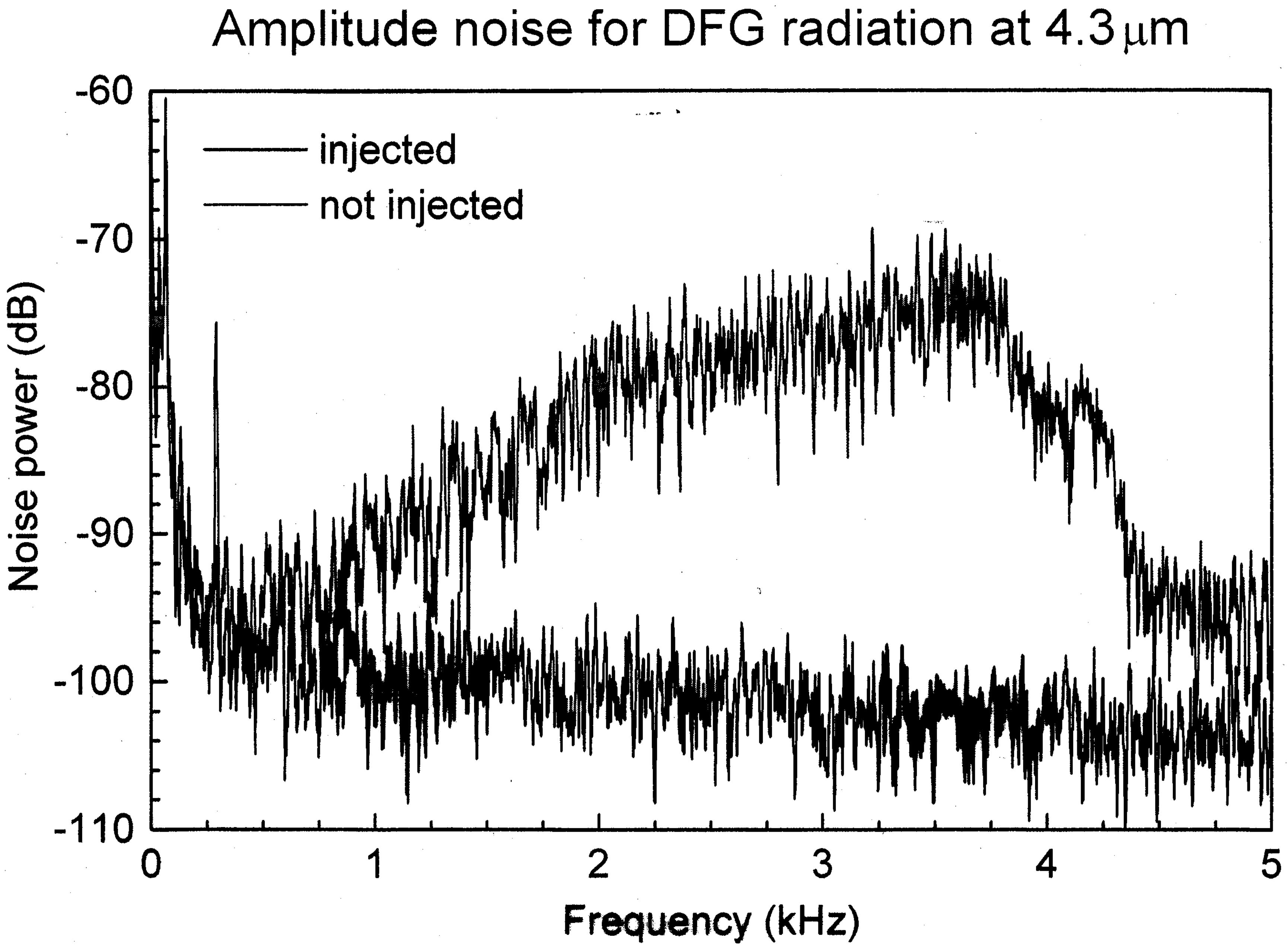
DFG set-up at INOA

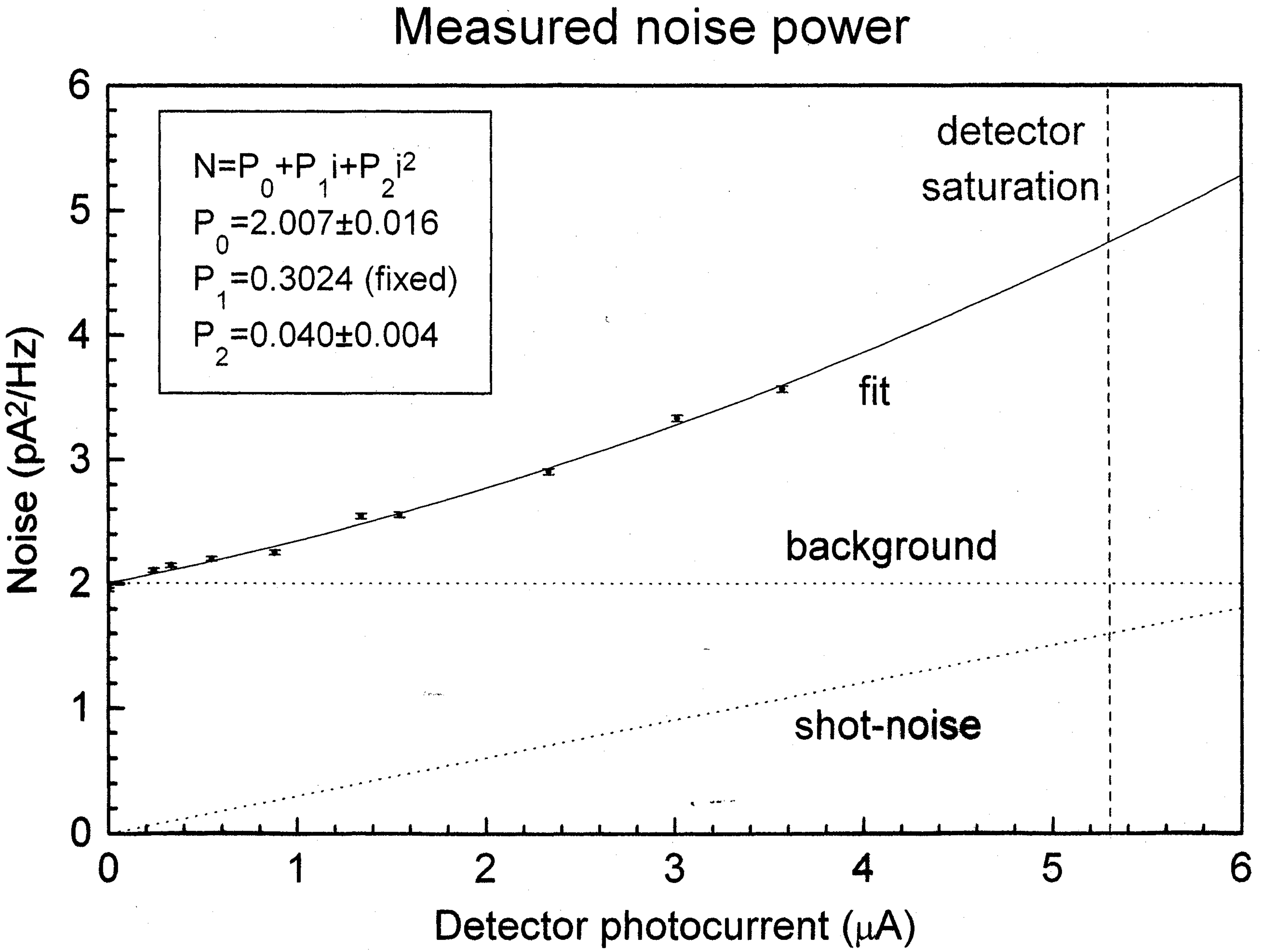


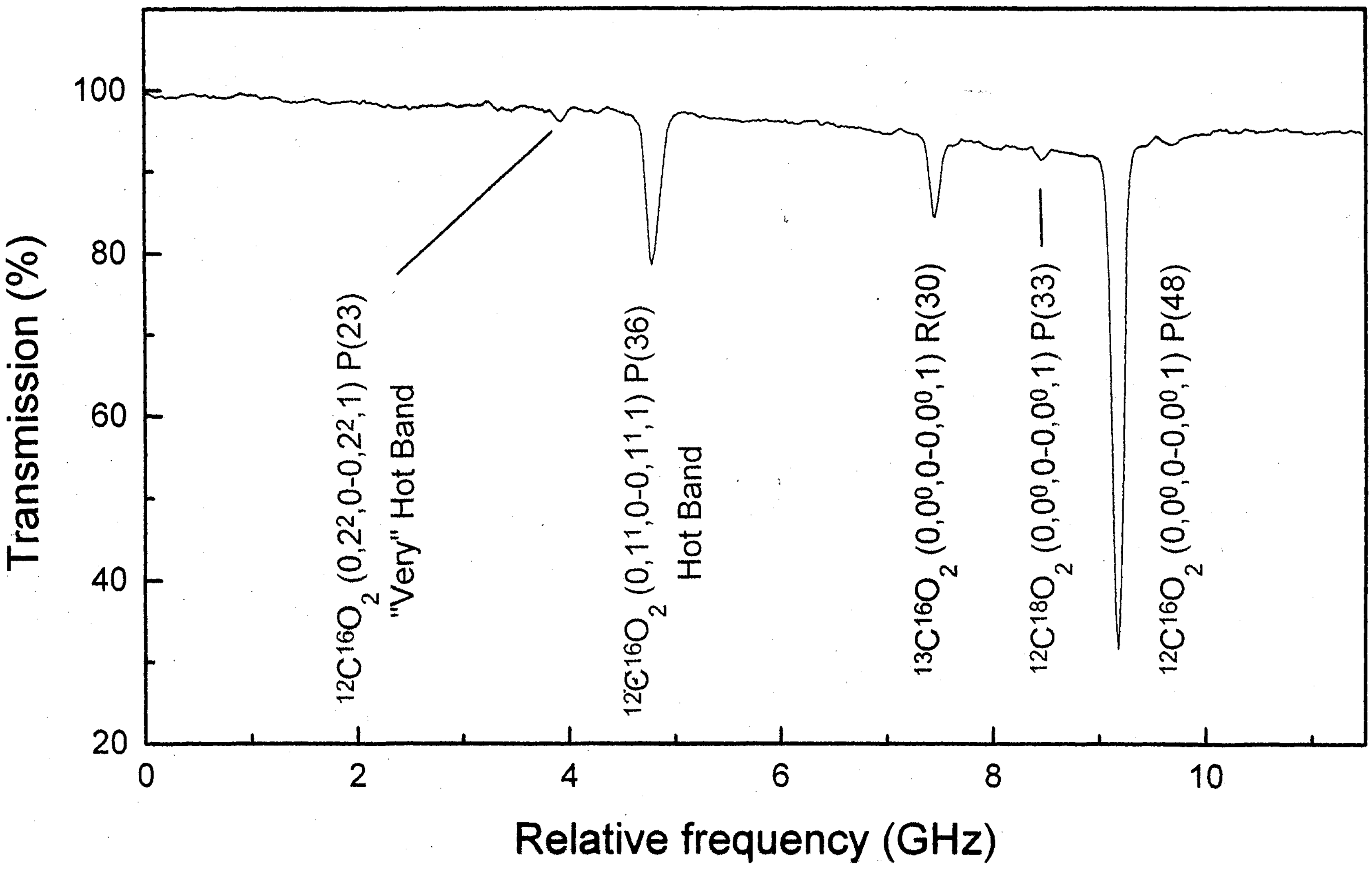
Mazzotti et al., Appl. Phys. B 70, 747 (2000)
Mazzotti et al., OSA - TOPS, Vol. 31, 122 (2000)

Slave DL injected/not injected frequency noise




Amplitude noise for DFG radiation at 4.3 μm
injected
not injected
Noise power (dB)
-60
-70
-80
-90
-100
-110
0
1
2
3
4
5
Frequency (kHz)

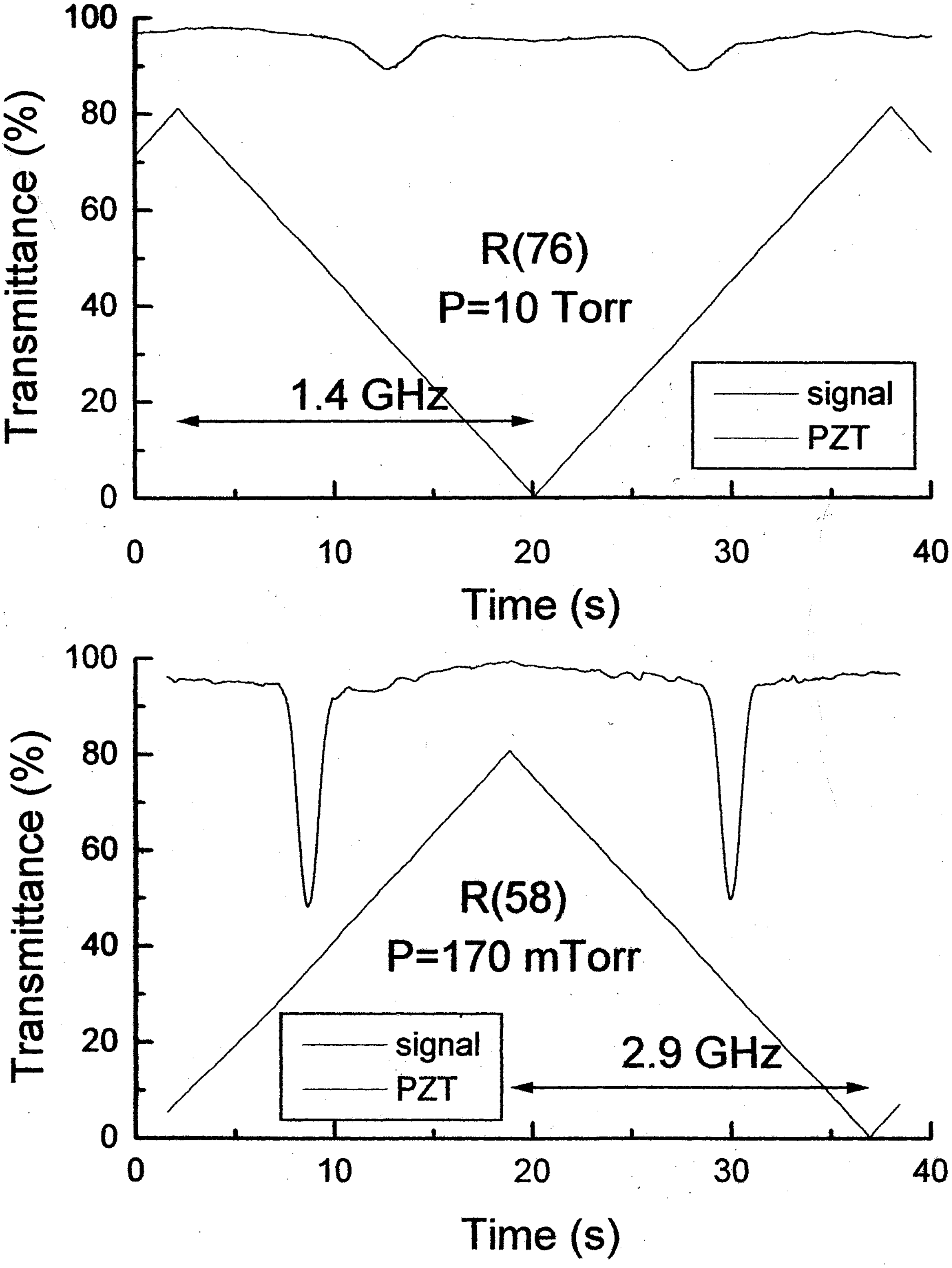

Measured noise power
N=P_0+P_1i+$P_2$$i^2$
P_0=2.007±0.016
P_1=0.3024 (fixed)
P_2=0.040±0.004
detector
saturation
fit
background
shot-noise
Noise (pA^2/Hz)
Detector photocurrent (μA)
0
1
2
3
4
5
6
0
1
2
3
4
5
6



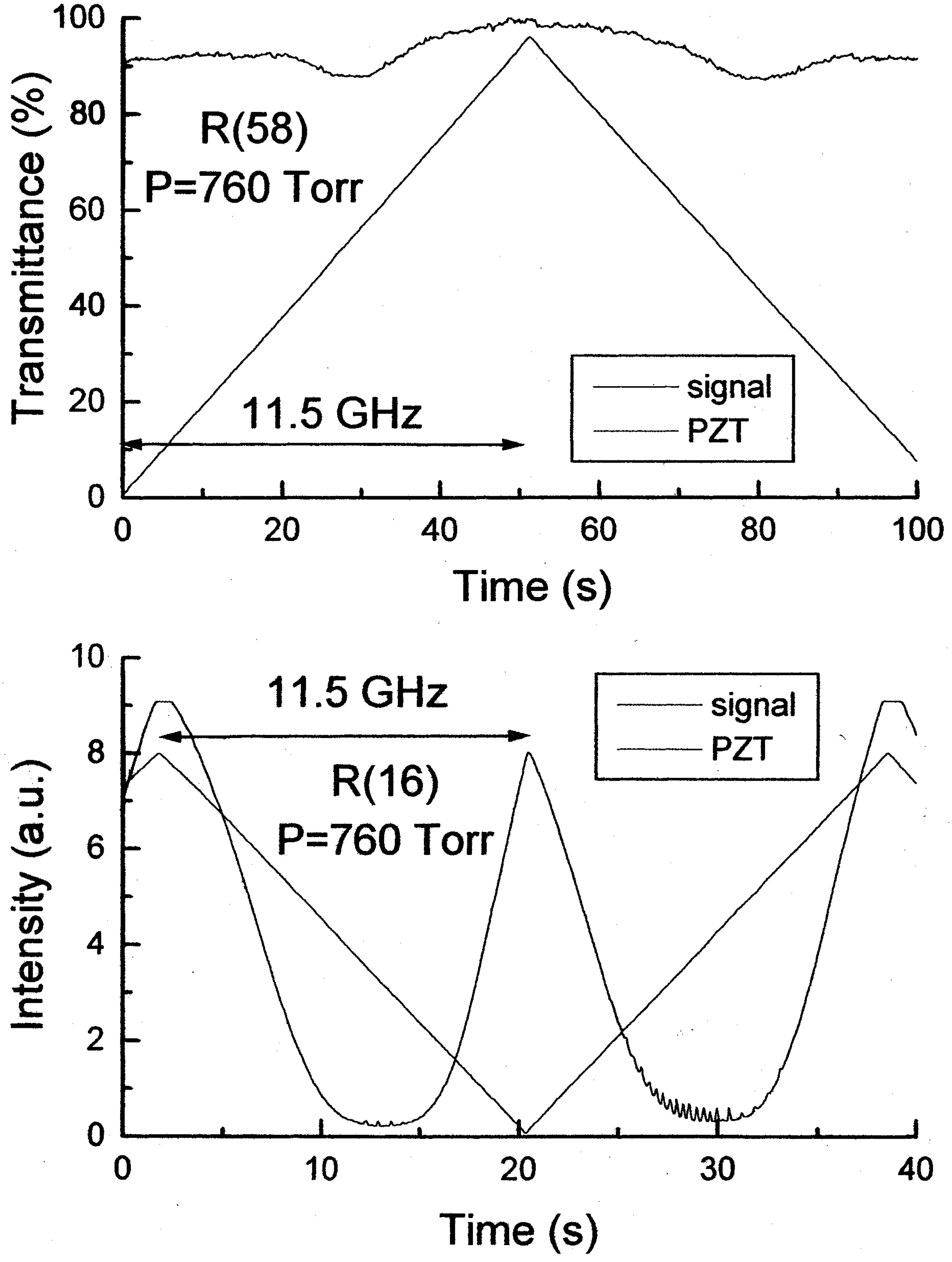
CO$_2$ Spectroscopy around 4.339 μm

Pathlength=4 mm, Pressure=2.5 Torr

Pure CO_2
(0,0,0-0,0,1) absorption lines (L=21 cm)



Atmospheric CO_2 (0,0,0-0,0,1) absorption lines (L=27 cm)



Saturation intensity

- We have generated 10 μW of IR radiation at 4.3 μm in a single pass scheme.

$$\Downarrow$$

- Might one achieve saturation of the strongest lines of this fundamental vibrational band of CO_2 with such a low power

???

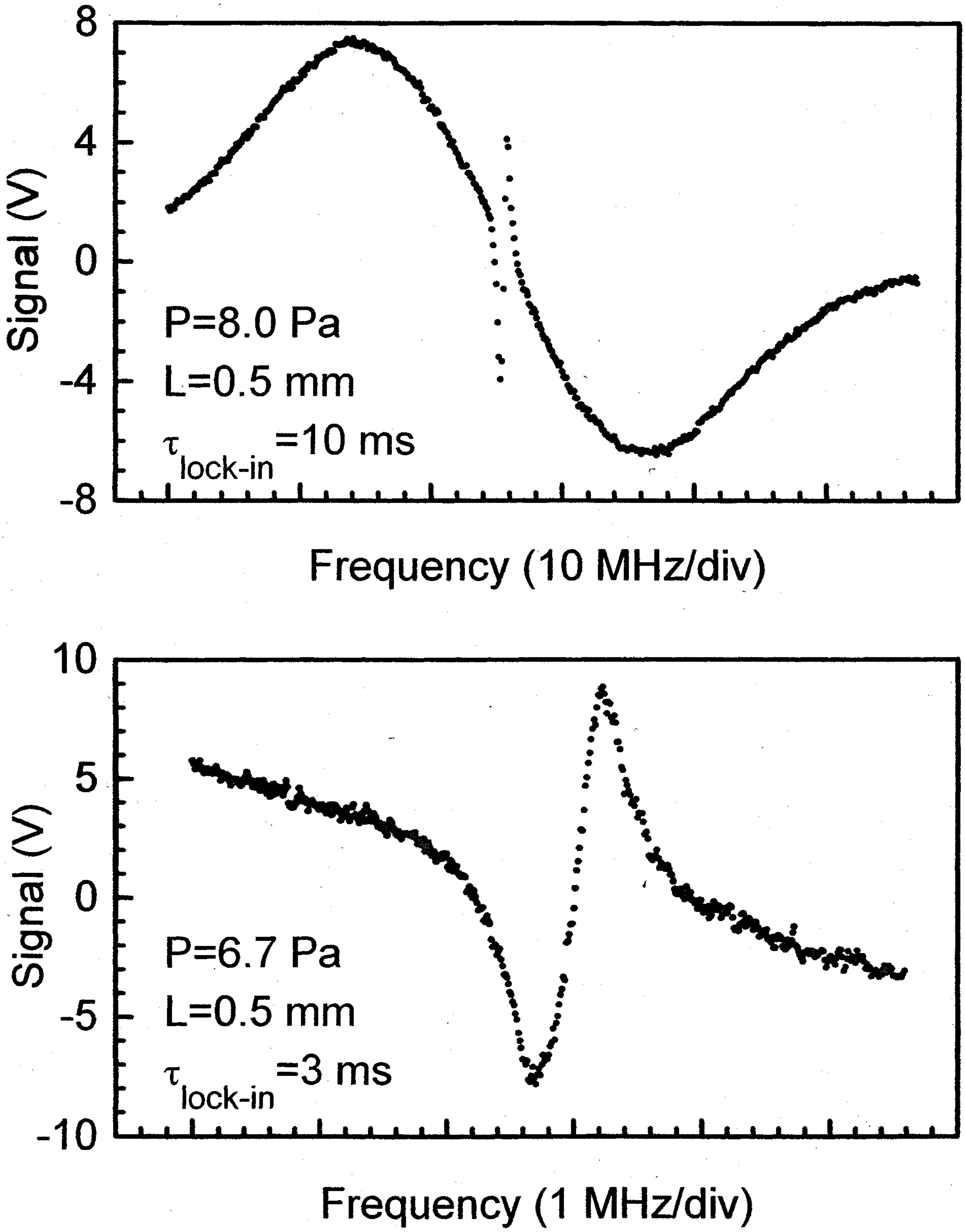
- The expression for saturation intensity is: $I_S = \frac{c\varepsilon_0}{2}\left(\frac{h\gamma}{\mu}\right)^2$

  and for:

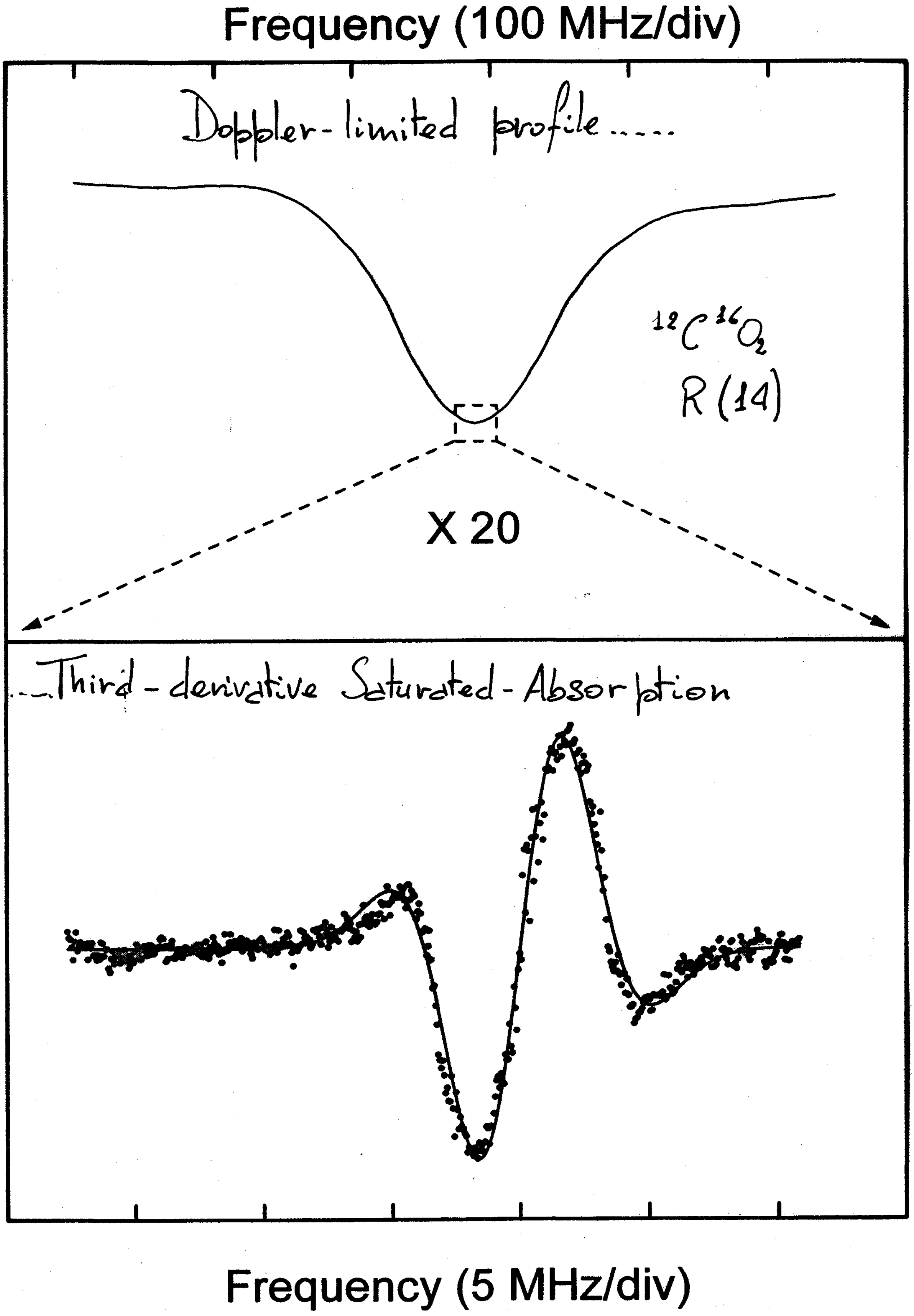
  - γ=2 **MHz**, (FWHM)
  - **μ=7.69x10^{-31} C·m,**
  - P=10 μW,
  - w=25 μm,

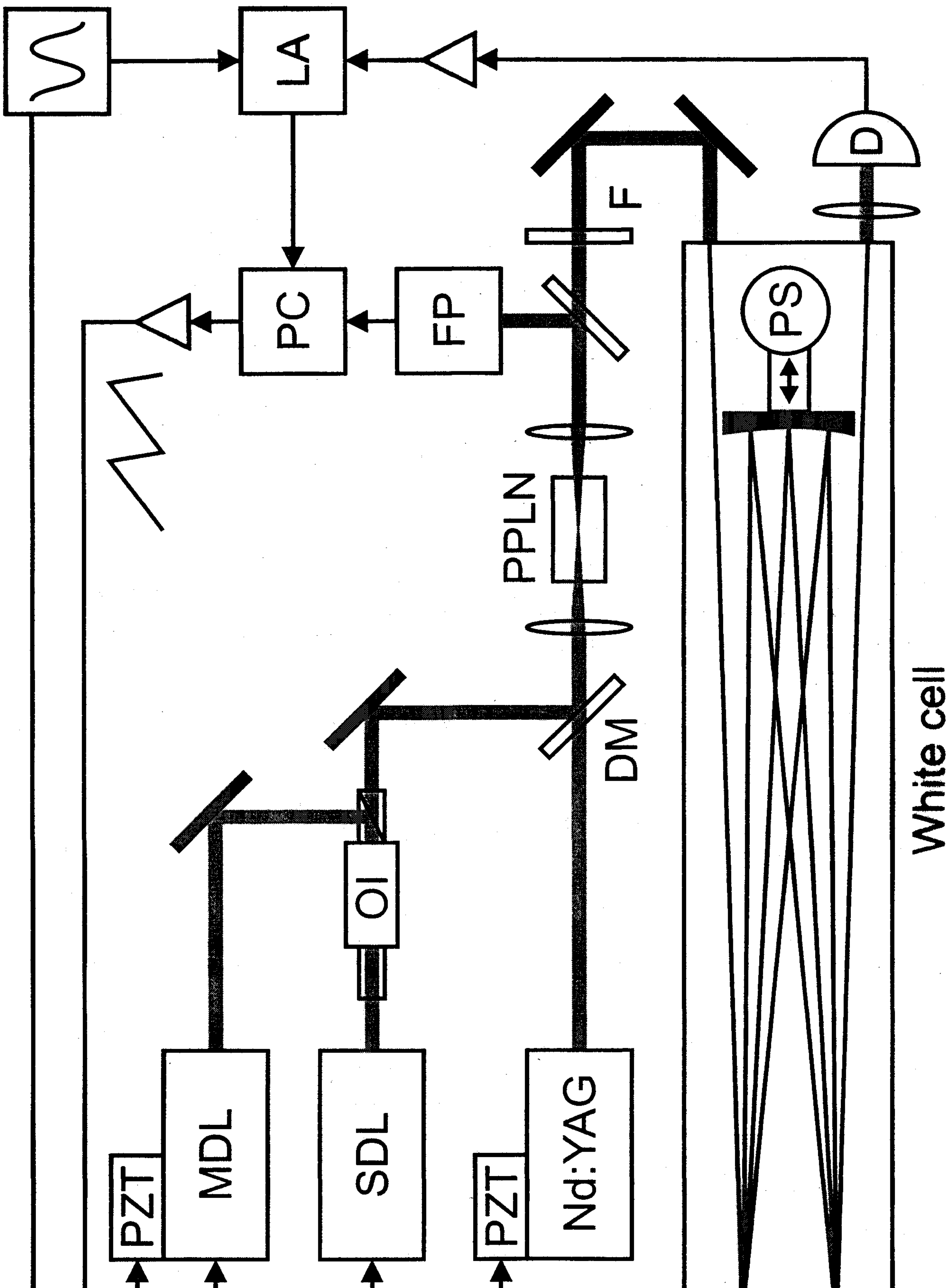
  we get: $I \approx I_S$

Saturated-absorption dips of CO_2 R(14) line recorded in first derivative

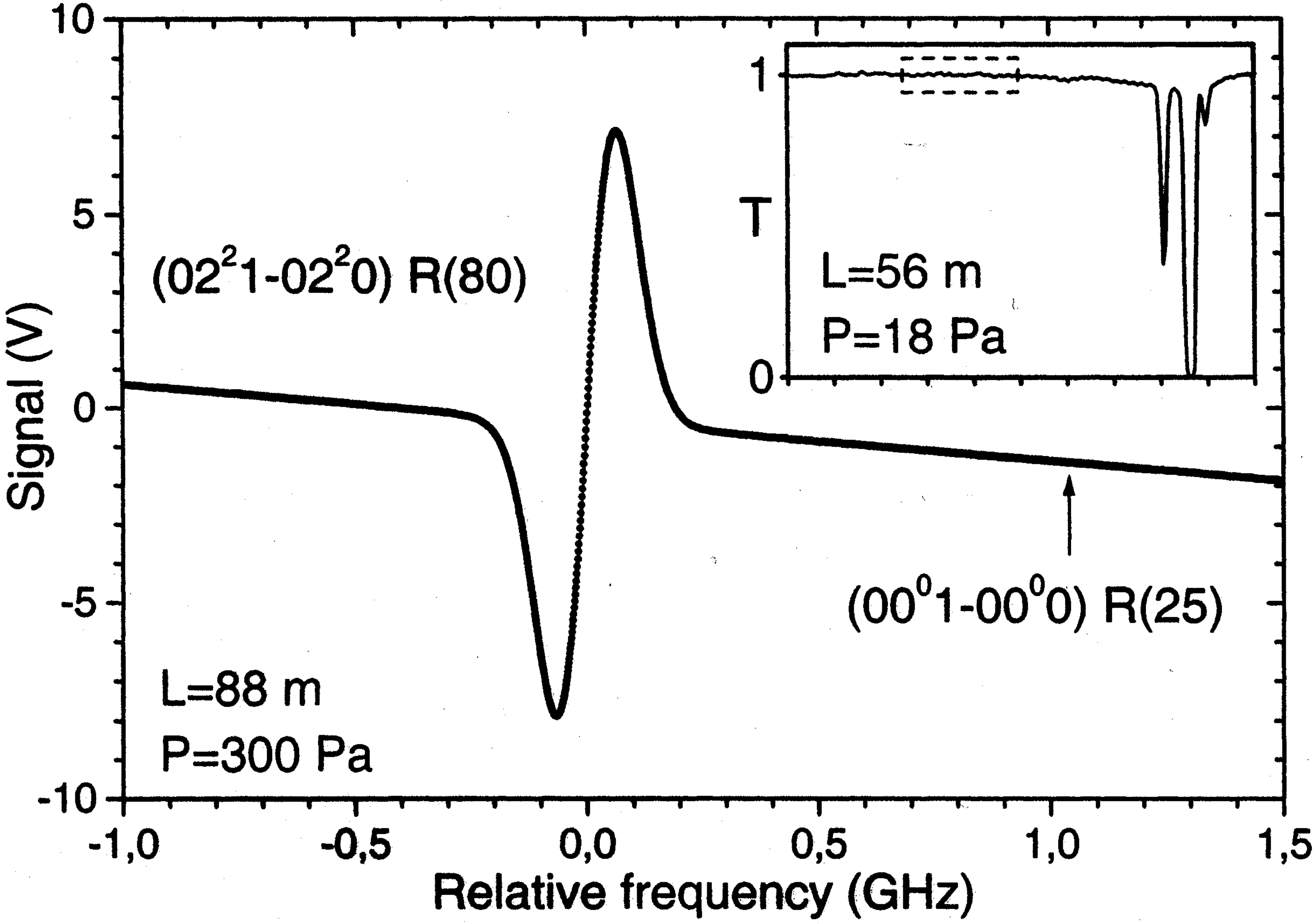


D. Mazzotti, P. De Natale, G. Giusfredi, C. Fort, J. Mitchell, L. Hollberg,
Opt. Letters 25, 350 (2000)

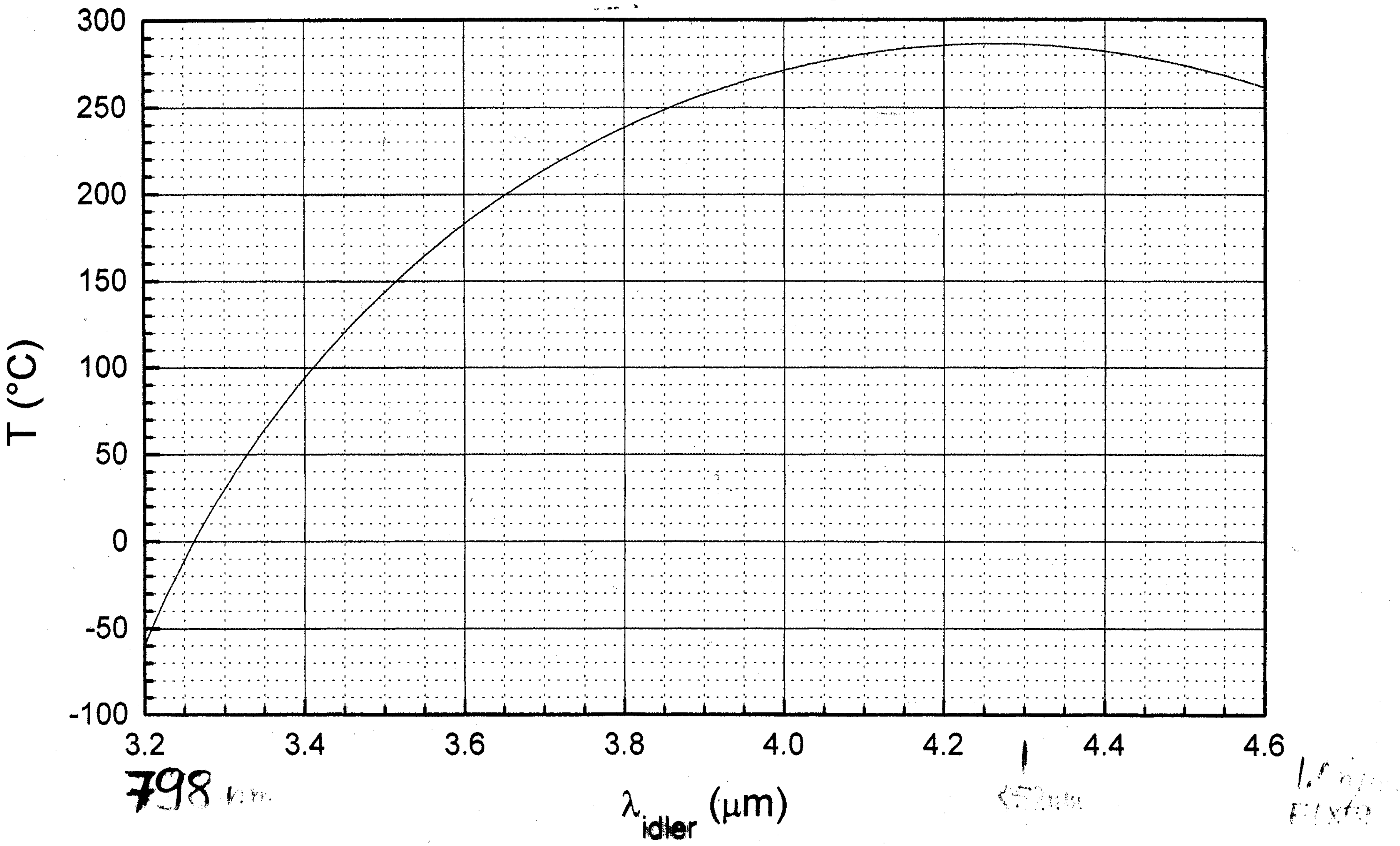



LA
PC
FP
F
D
PS
PPLN
DM
OI
MDL
SDL
Nd:YAG
PZT
PZT
White cell

Test of the Spin-Statistics Theorem ($\beta^2/2<1.7\times10^{-11}$)



Quasi-Phase-Matching tuning curve for Periodically Poled LiNbO$_3$ (Λ=22.0 μm)



MOLECULAR SPECTROSCOPY

WHY MOVE TO LONGER λ?

- Linestrength CO_2 5 orders of magnitude 1.6 -> 4.3 μm
- Metrology

CO_2 IR transition	$2\nu_1+2\nu_2+\nu_3$ P(8)	$\nu_1+2\nu_2+\nu_3$ R(24)	ν_3 R(16)
λ (μm)	1.577	2.002	4.235
S (cm/molecule)	$1.2\ 10^{-23}$	$1.0\ 10^{-21}$	$3.5\ 10^{-18}$
Sensitivity ($Hz^{-1/2}$)	$7\ 10^{-8}$	$7\ 10^{-7}$	$4\ 10^{-7}$ ($2\ 10^{-7}$)
Sens. (ppb m $Hz^{-1/2}$)	1000	100	0.01 (0.005)
Reference	[1]	[1]	[2]

LINE

APPARATUS

M.D.A.

[1] G. Modugno, C. Corsi, M. Gabrysch, F. Marin, M. Inguscio, *Appl. Phys. B 67, 289 (1998).*

[2] D. Mazzotti, P. De Natale, G. Giusfredi, C. Fort, J. Mitchell, L. Hollberg, *to be published.*

Available Tunable Coherent Sources at $\lambda > 2\ \mu m$

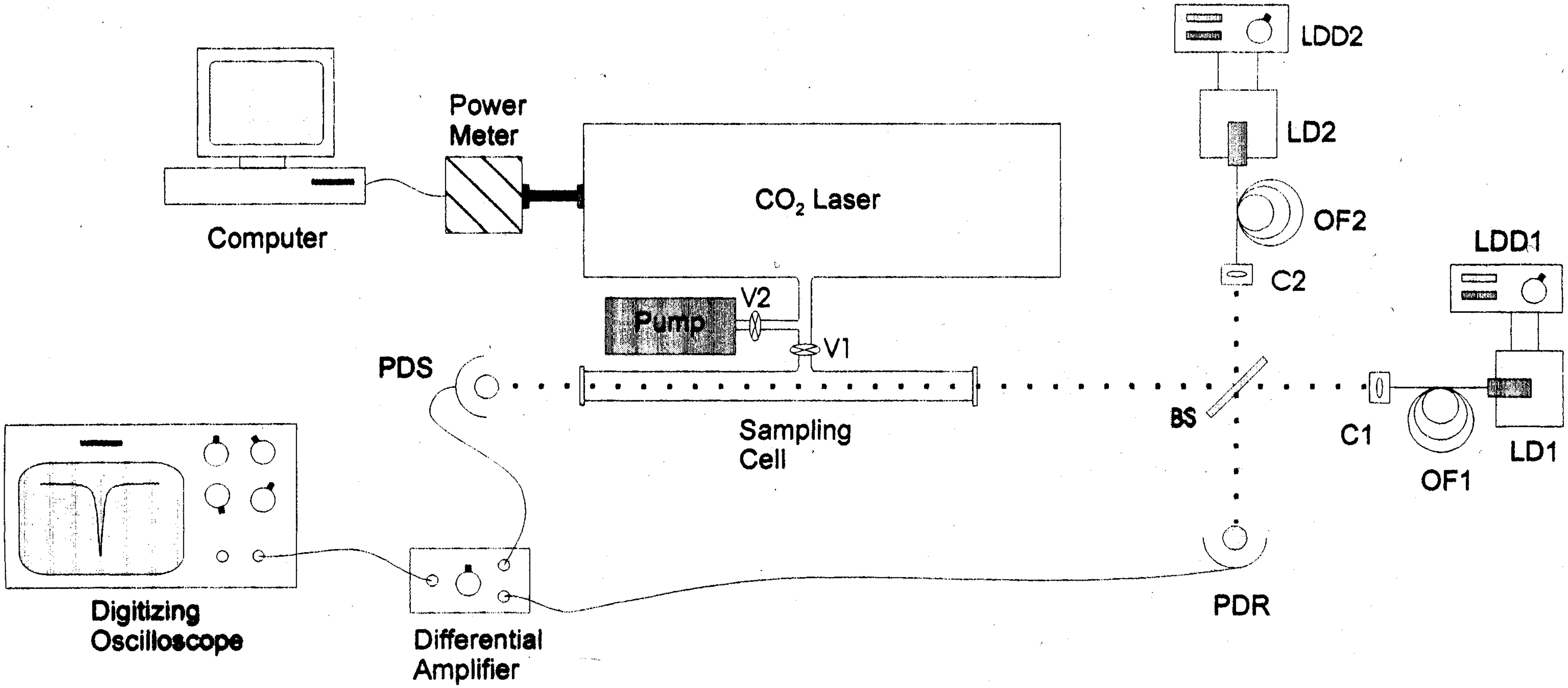
- Lead-salt diodes ⇒ multimode operation, low power, cryogenic operation required

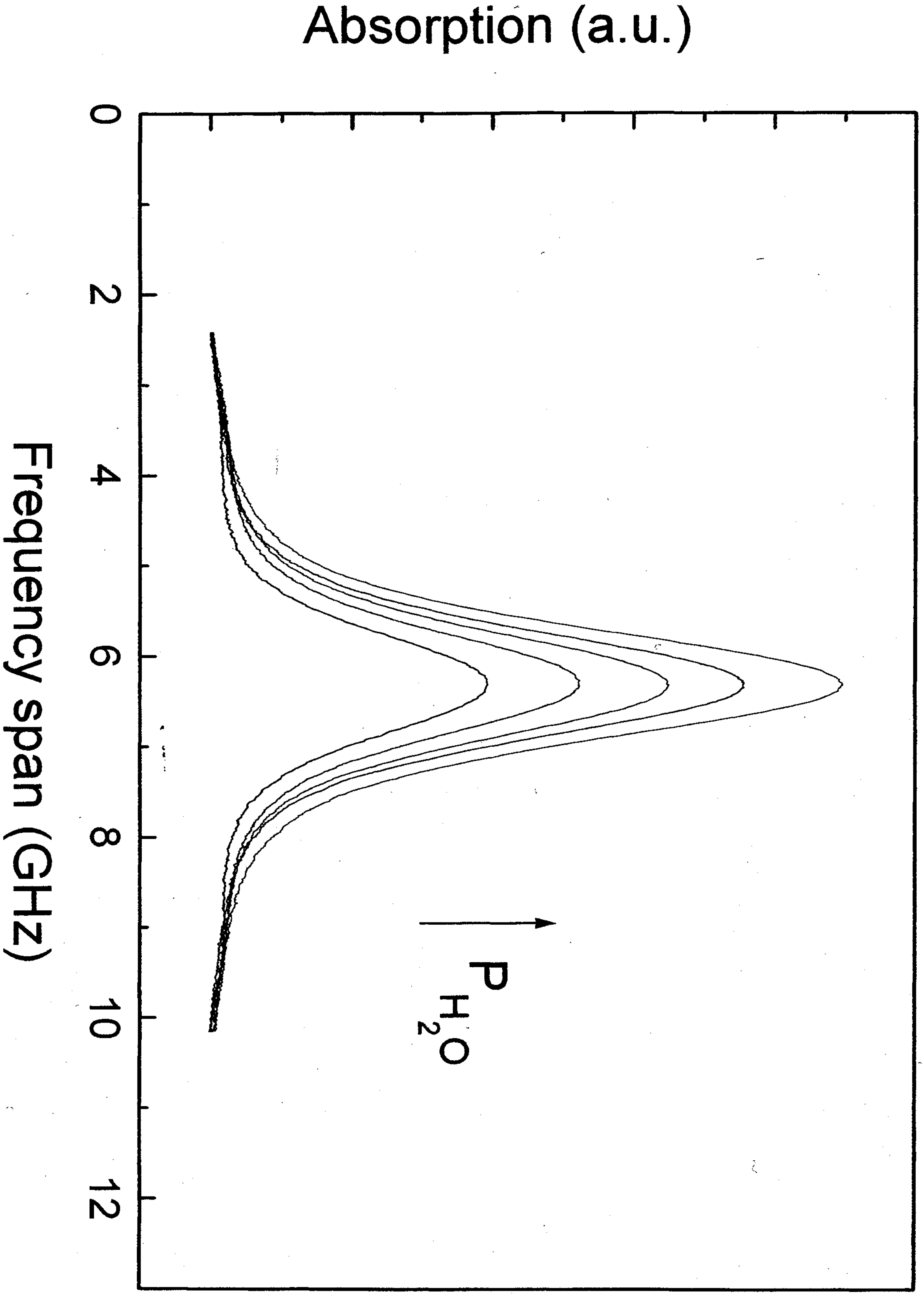
- Quantum cascade lasers ⇒ single-mode, high power, cryogenic operation required

- Non-linear optical devices pumped by diodes and diode-pumped solid-state lasers

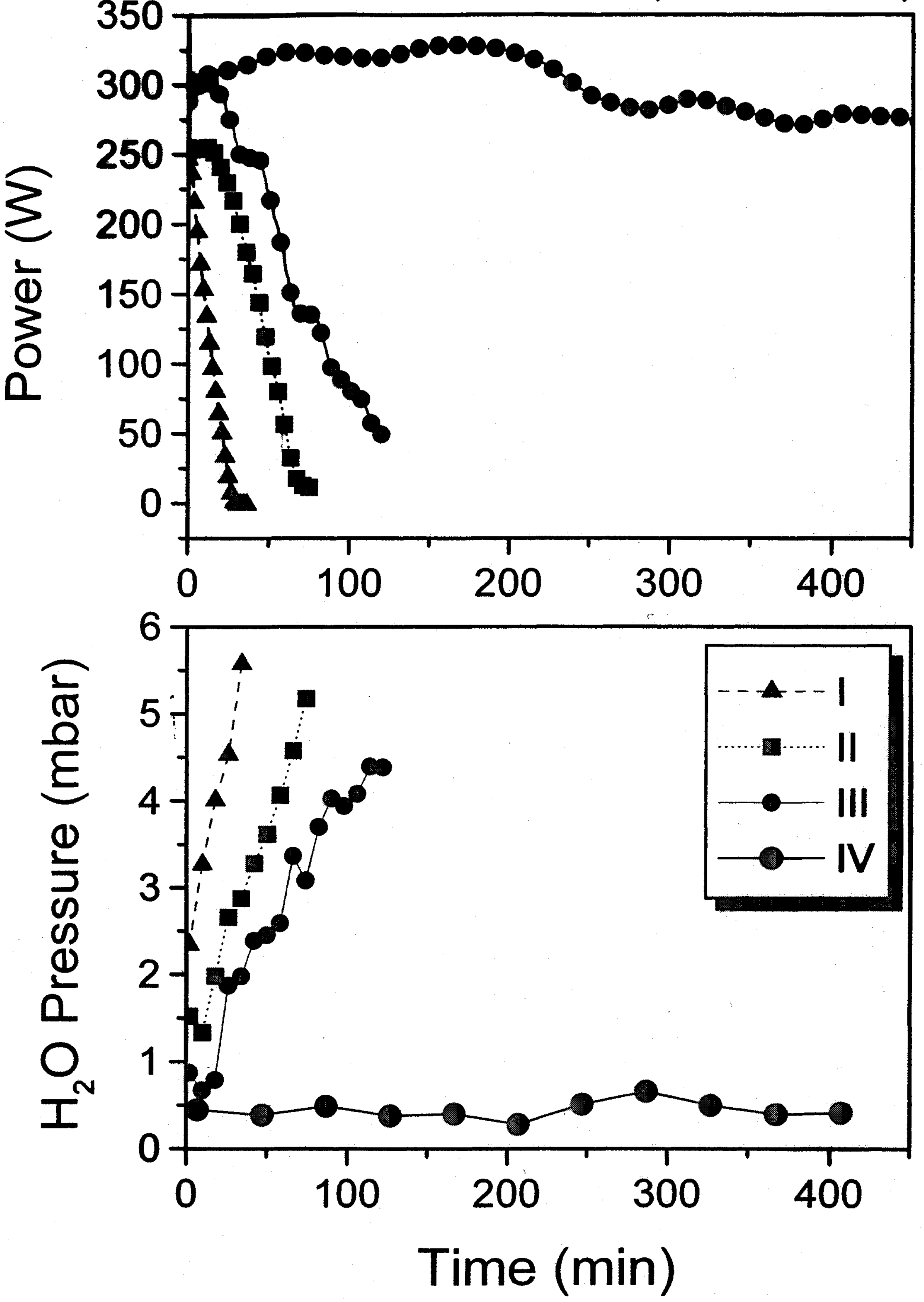
Difference Frequency Generation (DFG)

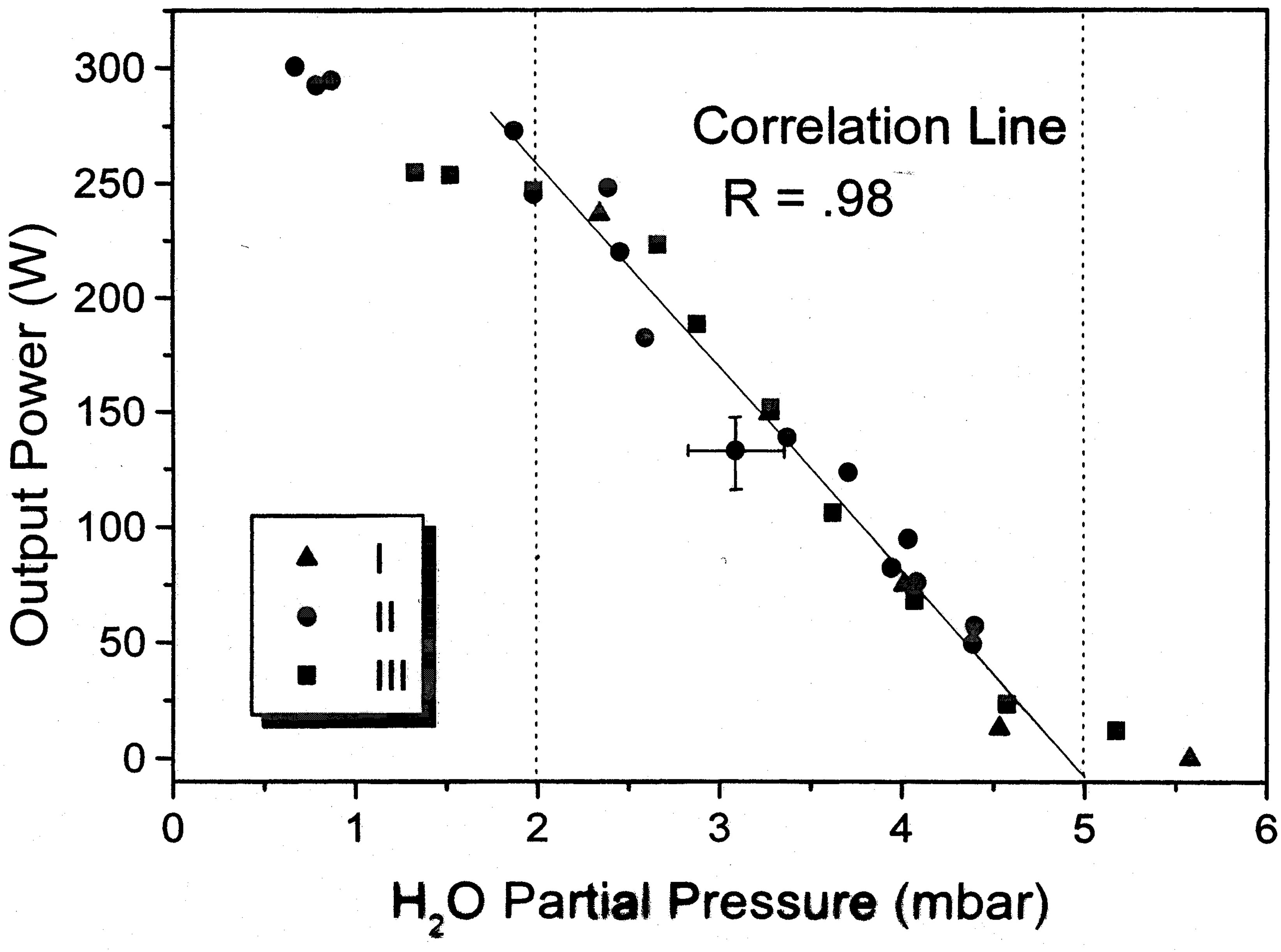
Optical Parametric Oscillation (OPO)


LDD2
Computer
Power Meter
CO_2 Laser
LD2
OF2
LDD1
C2
Pump
V2
V1
PDS
Sampling Cell
BS
C1
LD1
OF1
Digitizing Oscilloscope
Differential Amplifier
PDR


Absorption (a.u.)
Frequency span (GHz)
0
2
4
6
8
10
12
P_{H_2O}

L. LORINI, P. DE NATALE, A. LAPUCCI, IEEE J. OF QUANTUM ELECT., 34, 949-954 (1998)




Correlation Line
R = .98
Output Power (W)
300
250
200
150
100
50
0
H$_2$O Partial Pressure (mbar)
0
1
2
3
4
5
6
▲ I
● II
■ III

DESIRABLE FEATURES

- **Real time and continuous monitoring**
- Remote operation
- Sensitivity
- Discrimination among different molecules ⇒ Resolution

Trade off

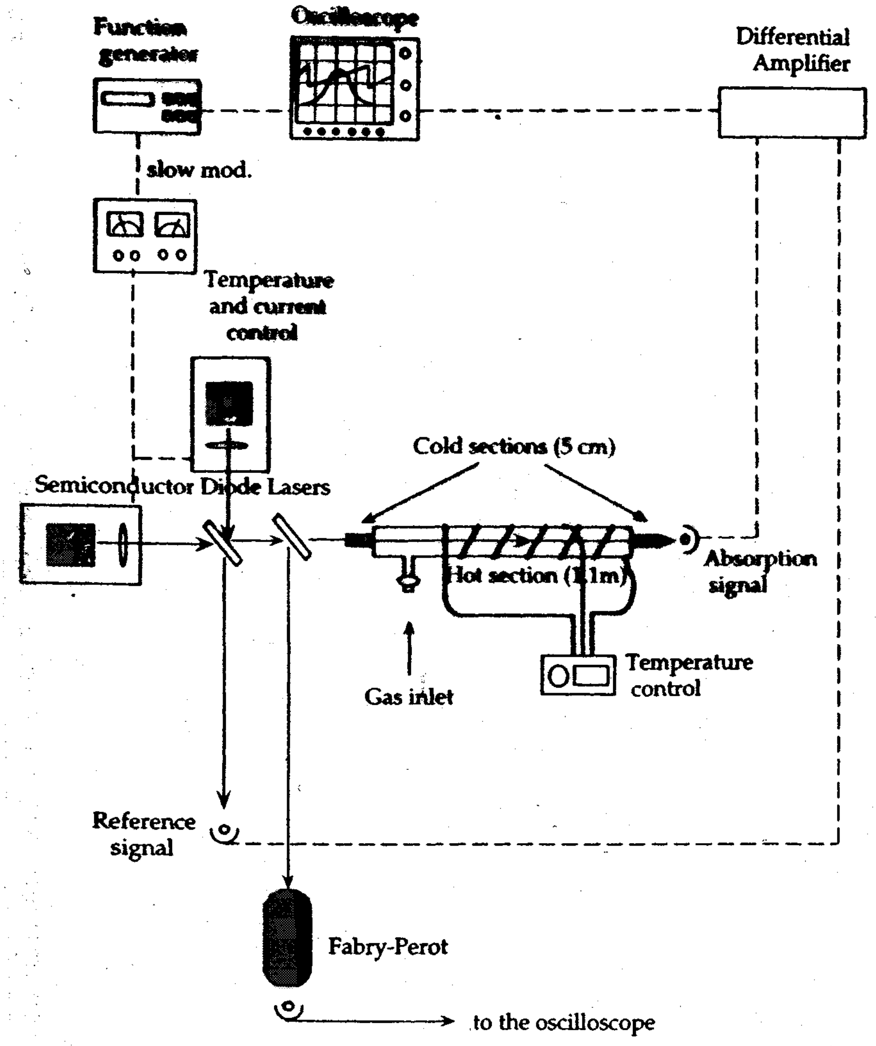
- Simultaneous detection of different species
- Field instrument ⇒ Low energy consumption, small size, low weight
- Low cost
- Ruggedness
- Accuracy

non puoi fotografare un paesaggio con un microscopio!

⬇

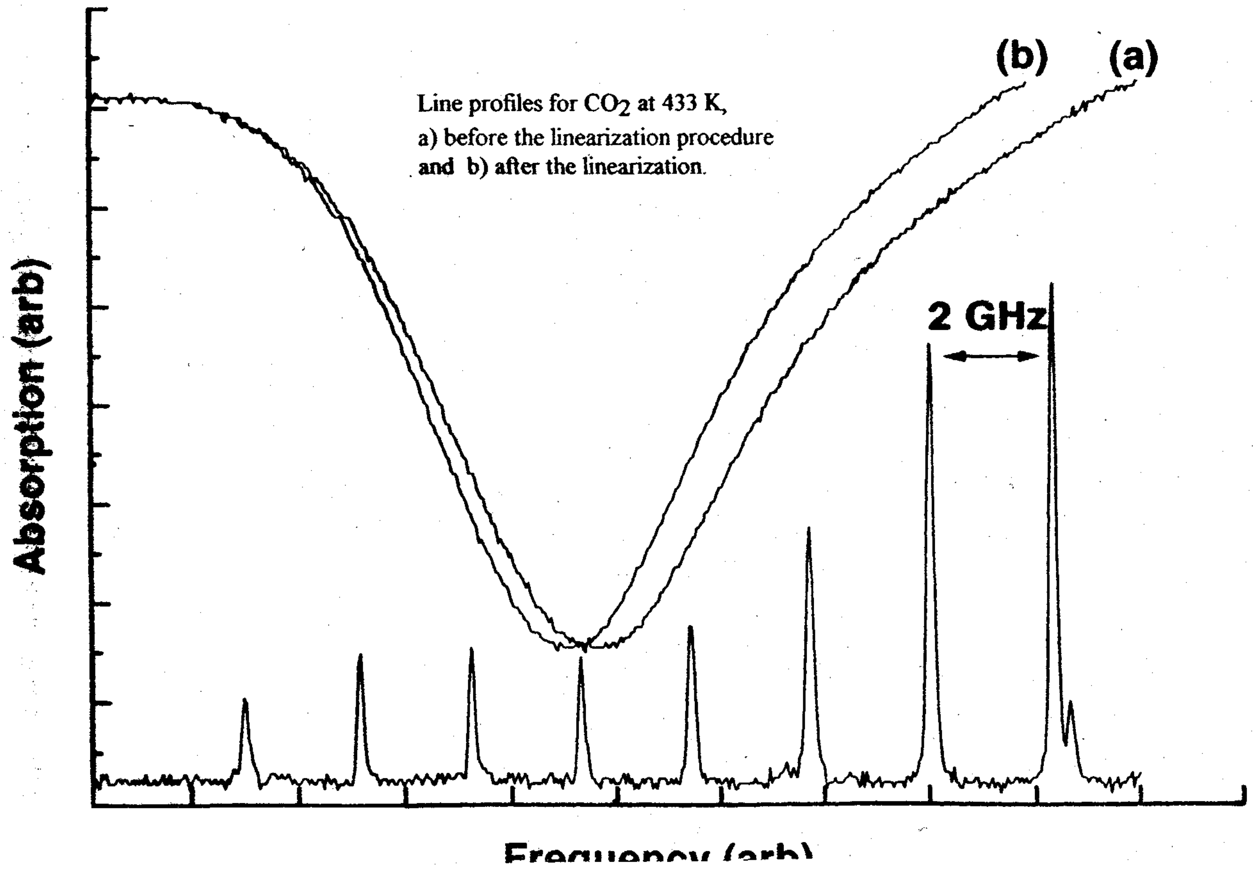
Solution...

Semiconductor Laser Diodes



Gianfrani, Gabrysch,
Corsi, De Natale

App. Opt. 36, 9481 (1997)



Line profiles for CO_2 at 433 K,
a) before the linearization procedure
and b) after the linearization.

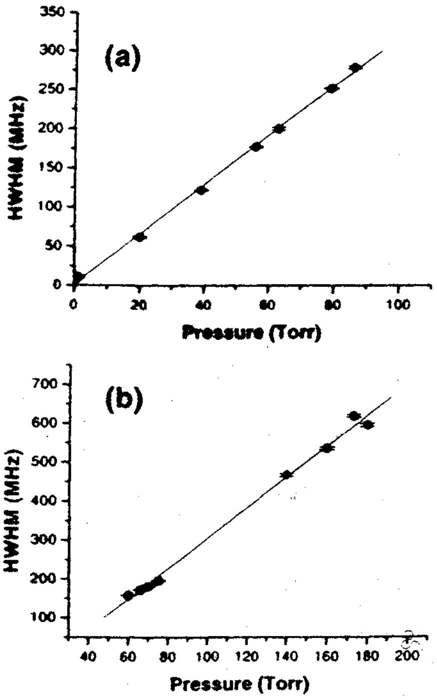


Fig. 2. Measured Lorentzian half-widths (HWHM) versus pressure for (a) pure CO_2 and (b) a fixed pressure of CO_2 (50 Torr) broadened by H_2O. Error bars are shown relative to the pressure uncertainty, and the error on the ordinate is within the point size.

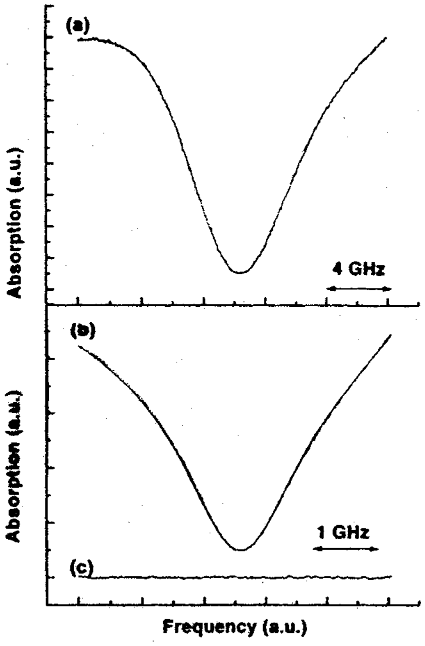


Fig. 5. Experimental absorption profiles at 433 K for (a) the (1, 0, 1)–(0, 0, 0) $2_{1,2}$–$3_{1,3}$ line of H_2O (P = 110 Torr) and (b) the (3, 0^0, 1)–(0, 0^0, 0) $P(16)$ line of CO_2 (P = 148 Torr). The solid curve is the fit, and the residuals are plotted in (c).

TABLE I

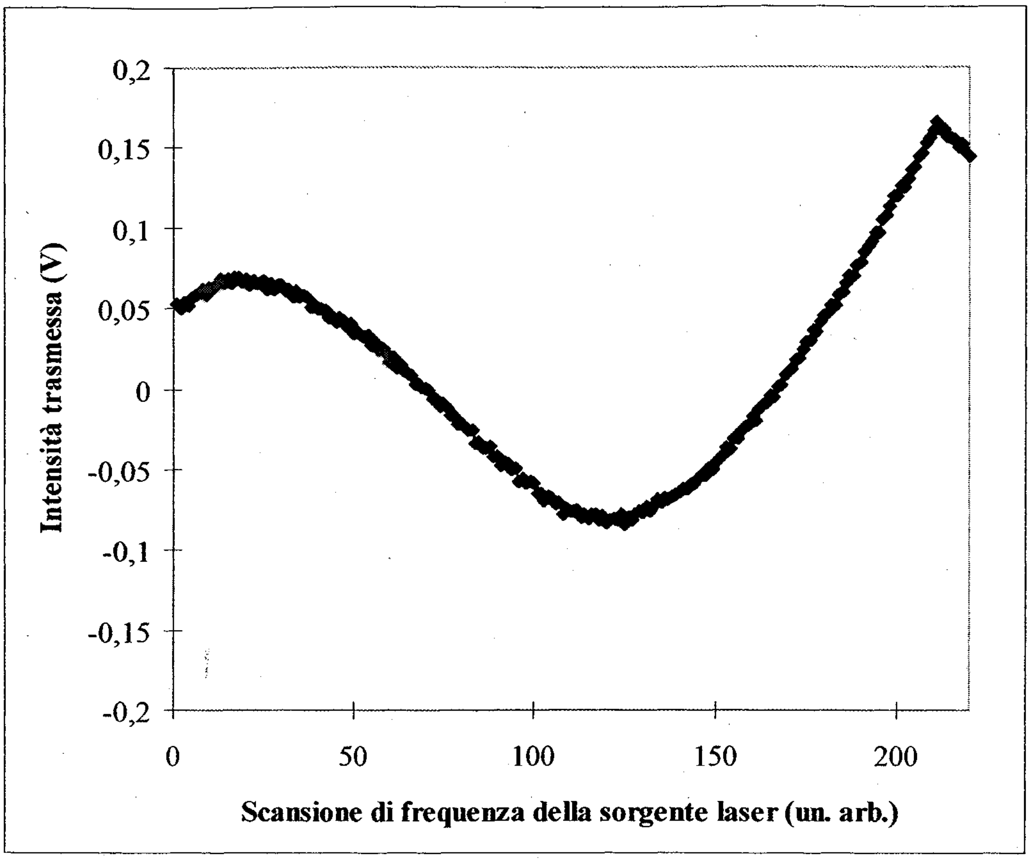
Comparison among broadening coefficients for the H_2O and CO_2 lines at a temperature T = 433 K. The meaning of the symbols is explained in the text.

	Present Data	**from Literature**
Broadening coefficients for H_2O (1, 0, 1) - (0, 0, 0) $2_{1,2}$ - $3_{1,3}$ line (MHz/Torr)	$\gamma_{H2O} = 28.2 \pm 0.6$ $\gamma^{CO2} = 6.0 \pm 0.4$	$\gamma_{H2O} = 13 \pm 1^{(a)}$ $\gamma^{CO2} = 4.3 \pm 0.4^{(b)}$
Broadening coefficients for CO_2 (3, 0^0,1)-(0, 0^0,0) P(16) line (MHz/Torr)	$\gamma_{CO2} = 3.2 \pm 0.1$ $\gamma^{H2O} = 4.0 \pm 0.1$	$\gamma_{CO2} = 3.2 \pm 0.3^{(c)}$

(a) Average of the twelve data in Tab. 4 from Ref. [10]. The exponent giving the temperature dependence is taken from Ref. [11].

(b) Average of the twelve data in Tab. 2 from Ref. [9].

(c) From Ref.6. The temperature coefficient n is from Hitran96 database (n=0.7)

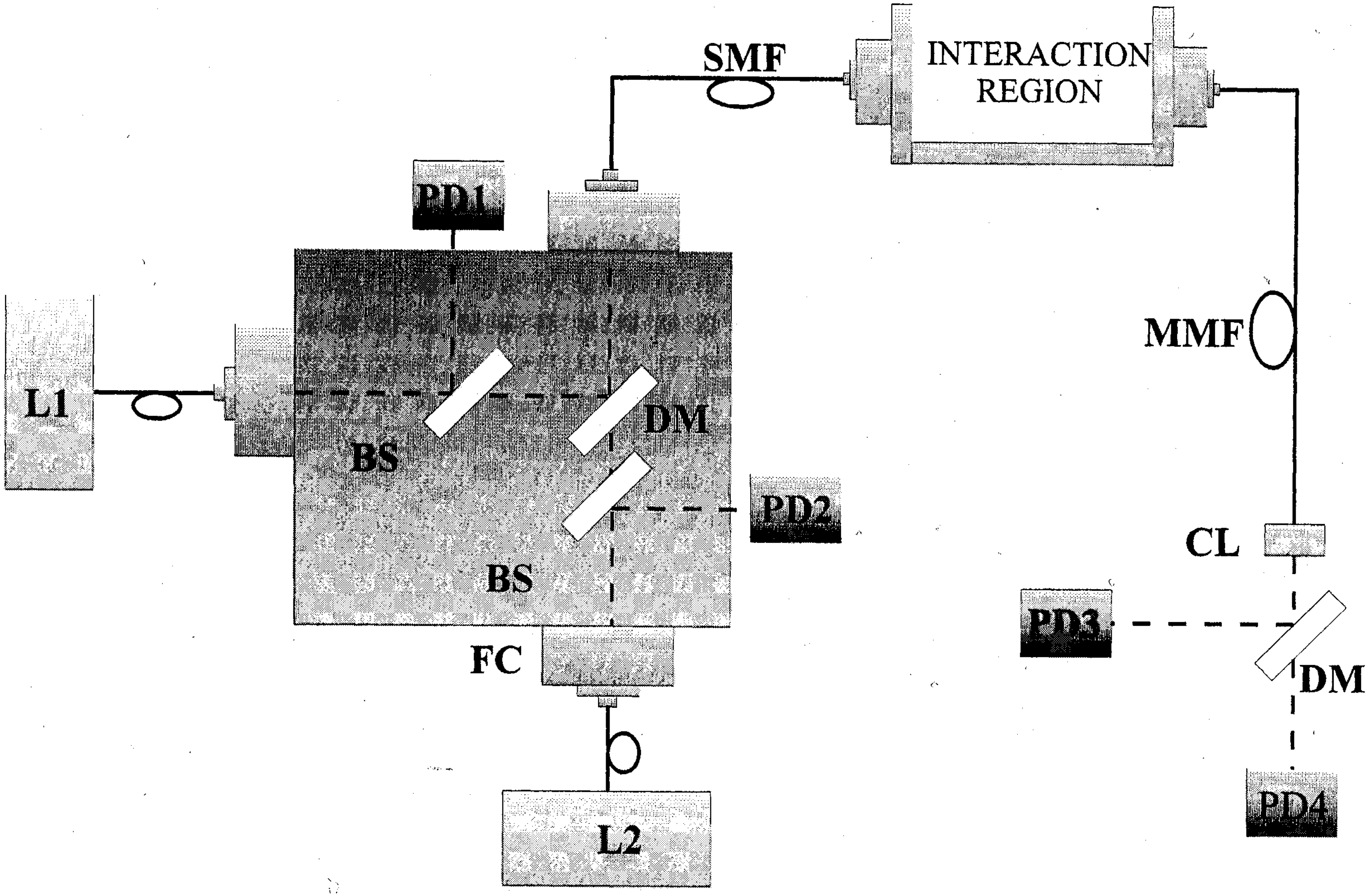


riga H_2O $(1,0,1)-(0,0,0)$ $2_{1,2}-3_{1,3}$

$\lambda \simeq 1.392\ \mu m$

schema "open path"

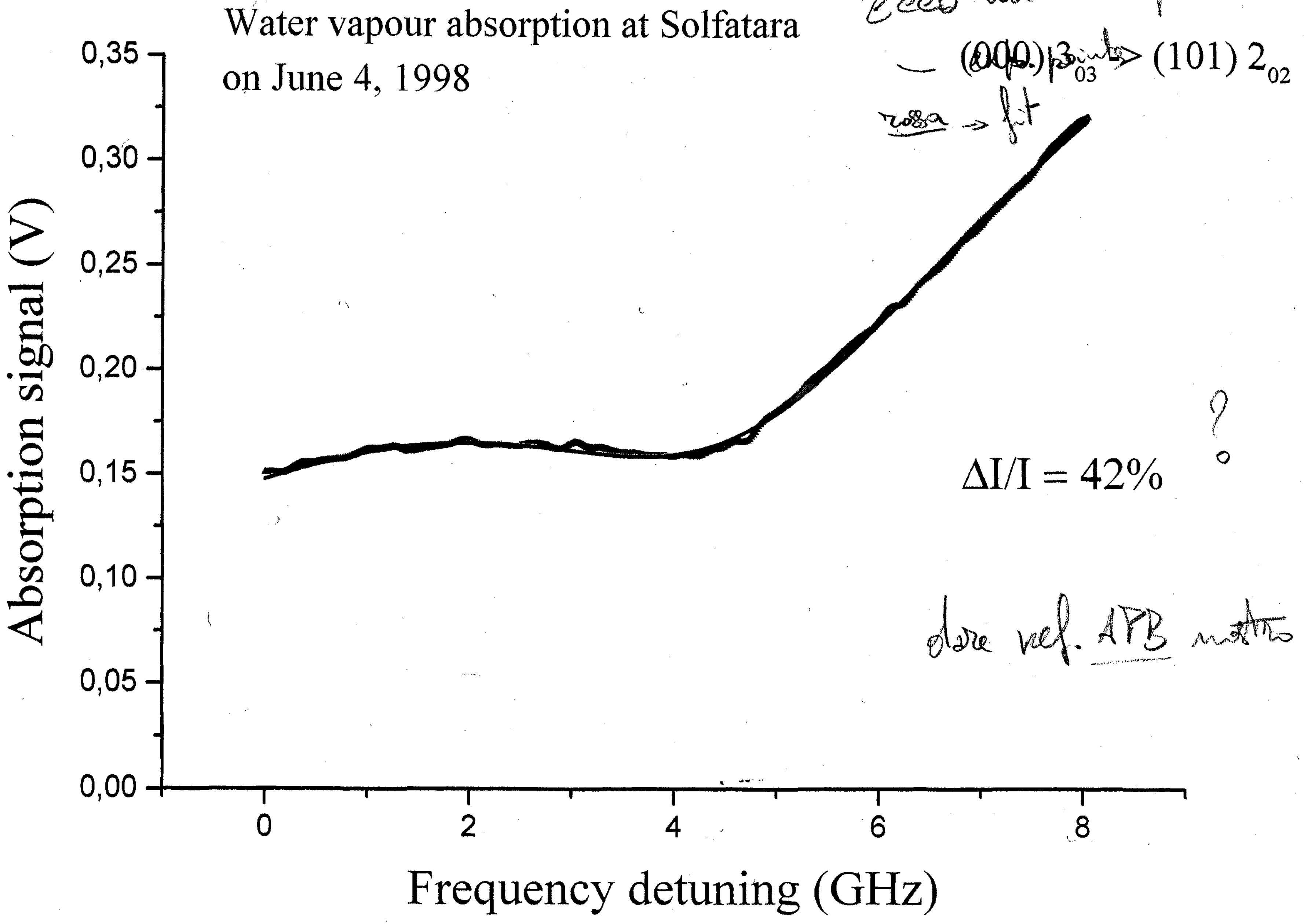
P. De Natale et al., in "Applications of Photonic Technology", SPIE Vol. 3491, 783-787 (1998)



L= laser; PD=photodiode; FC= input/output fiber port; BS= beam-splitter; DM= dichroic mirror SMF= single mode fiber; MMF= multimode fiber; CL= collimating lens

L. Gianfrani, P. De Natale, G. De Natale, Appl. Phys. B 70, 467-470 (2000)

Ecco un esempio di registrazione



exp. punti

rossa → fit

?

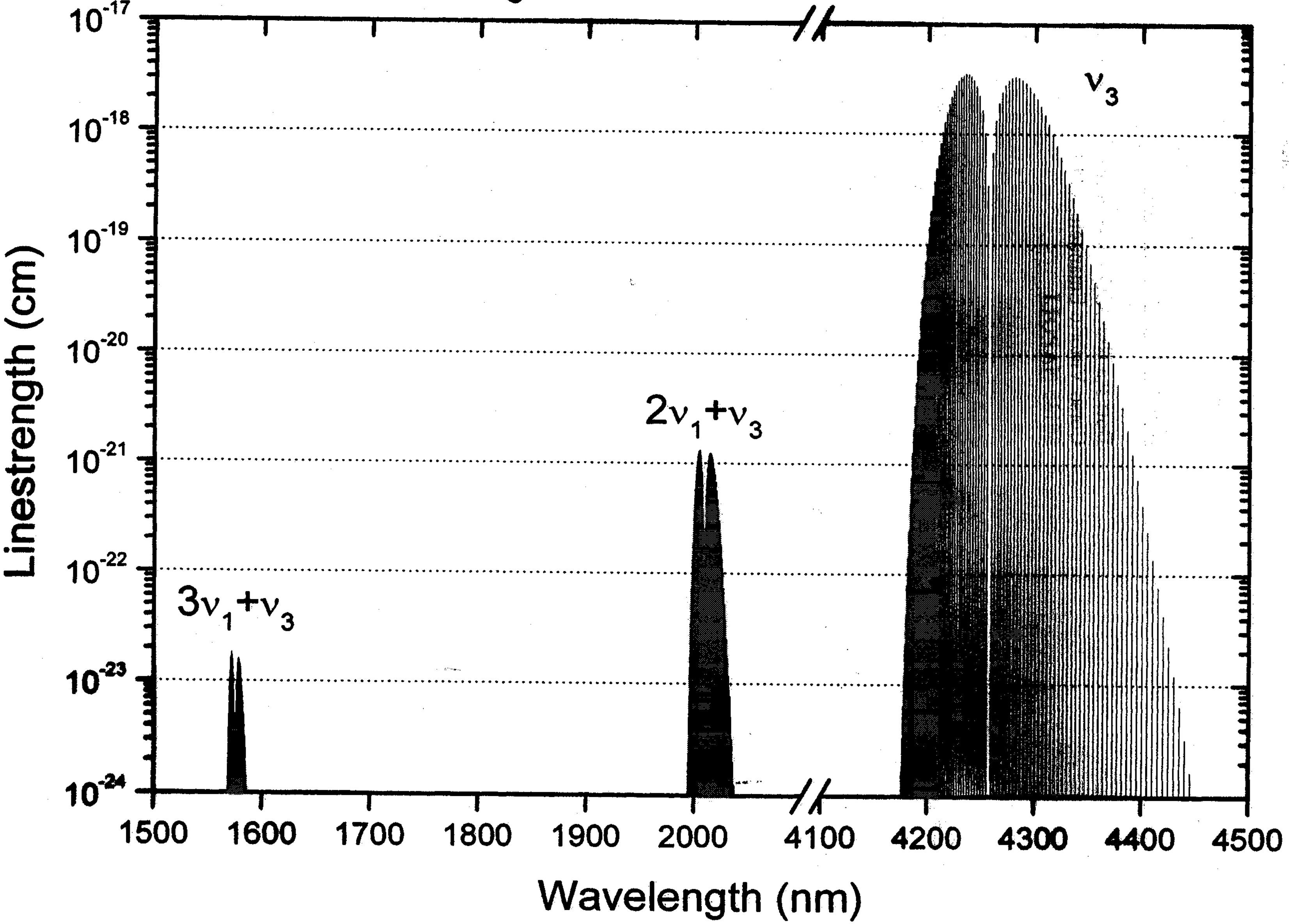
dare ref. APB nostro

How to go beyond, thus increasing the Sensitivity?

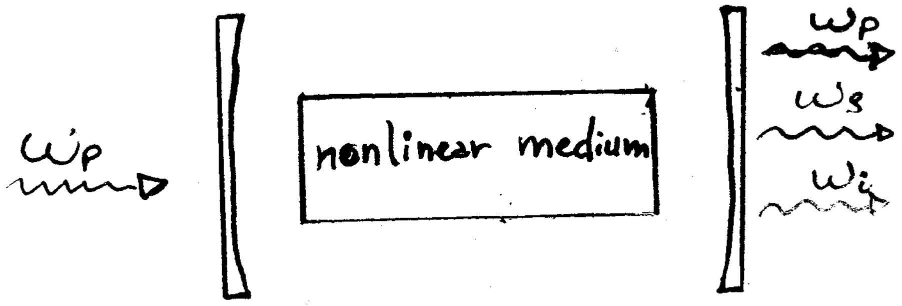
Still laser diodes!

At the border of the available spectral range we find ≈ 2 μm wavelength room-temperature operated laser diodes

$^{12}CO_2$


10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
10^{-22}
10^{-23}
10^{-24}
Linestrength (cm)
ν_3
$2\nu_1+\nu_3$
$3\nu_1+\nu_3$
1500
1600
1700
1800
1900
2000
4100
4200
4300
4400
4500
Wavelength (nm)

OPTICAL PARAMETRIC OSCILLATOR



Energy conservation: $\omega_p = \omega_s + \omega_i$

Momentum conservation: $\bar{k}_p = \bar{k}_s + \bar{k}_i$

→ change of refractive index

- Doubly Resonant Oscillator (DRO)
- Singly Resonant Oscillator (SRO)

Widely-tunable parametric oscillator for high-resolution spectroscopy

K. Schneider, P. Kramper, P. de Natale[a]*, S. Schiller, J. Mlynek, and M. Inguscio*[b]
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Tel.: +49-7531-883842, Fax: -+49-7531-883072
e-mail: Klaus.Schneider@uni-konstanz.de

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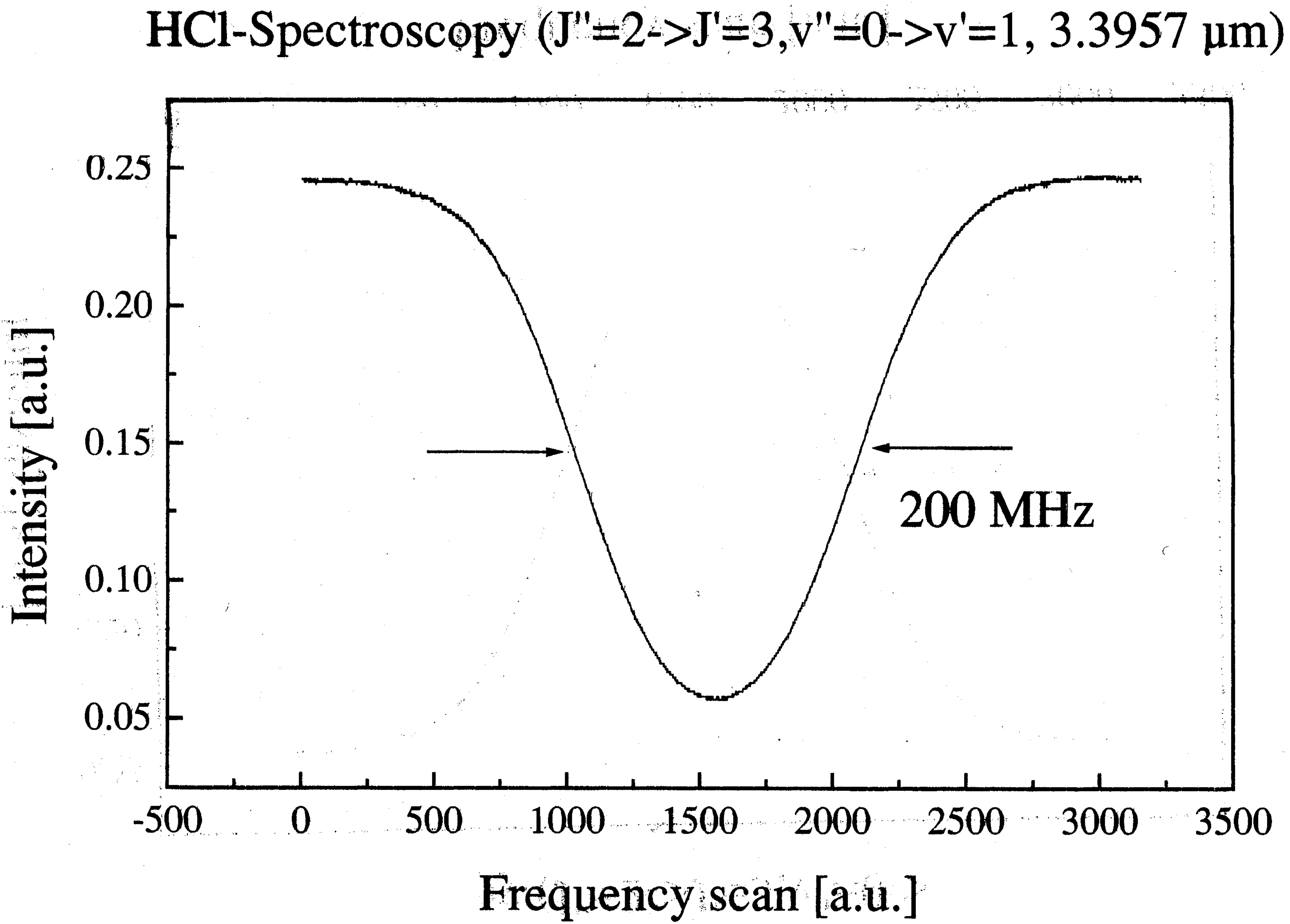
[b]*present address: LENS, Largo E. Fermi, 2, 50125 Firenze, Italy*

We report a continuous-wave, single-frequency parametric oscillator for the 1.45-4 µm range with high conversion efficiency and good long term stability. Spectroscopic measurements on HCl were possible, due to the excellent spectral properties of our device.

Presented at
CLEO/IQEC '98
S. Francisco, U.S.A.


HCl-Spectroscopy (J''=2->J'=3,v''=0->v'=1, 3.3957 µm)
Intensity [a.u.]
0.25
0.20
0.15
0.10
0.05
200 MHz
-500
0
500
1000
1500
2000
2500
3000
3500
Frequency scan [a.u.]

K. Schneider et al.:
Widely-tunable parametric oscillator for high-resolution spectroscopy

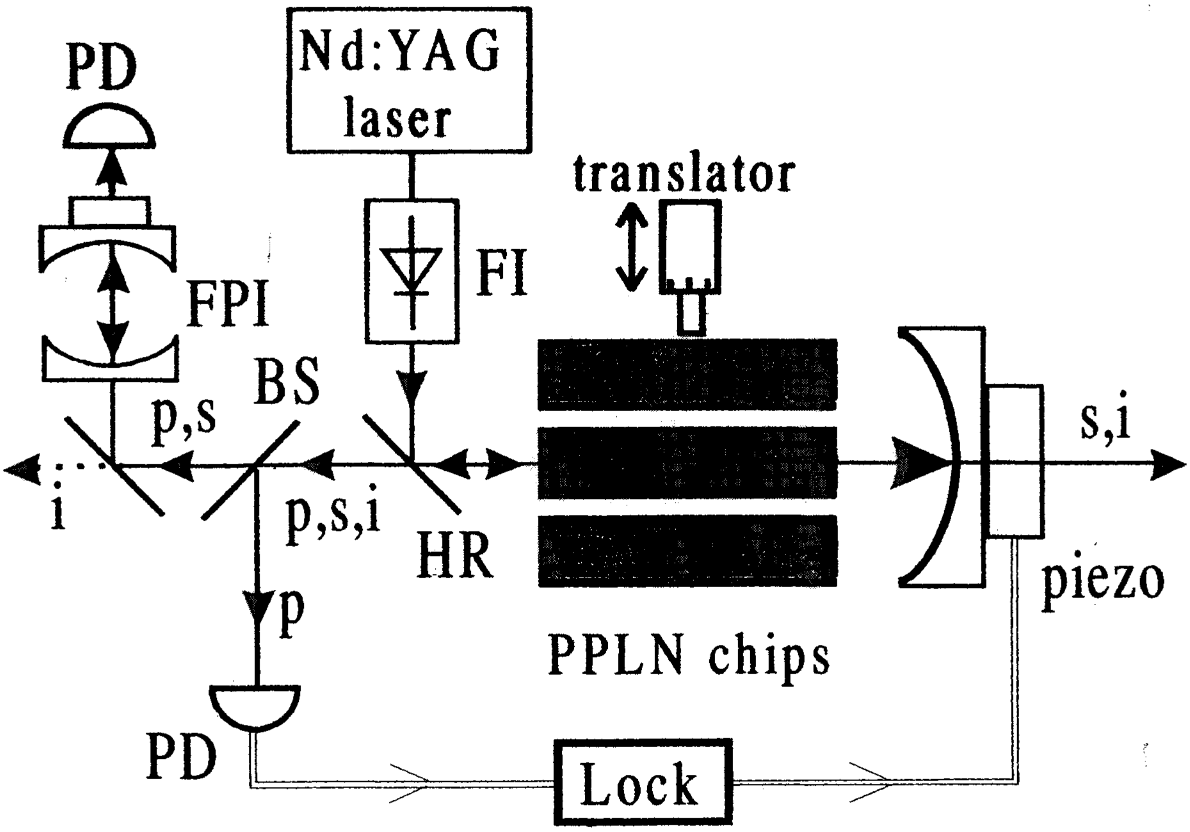


Figure 1

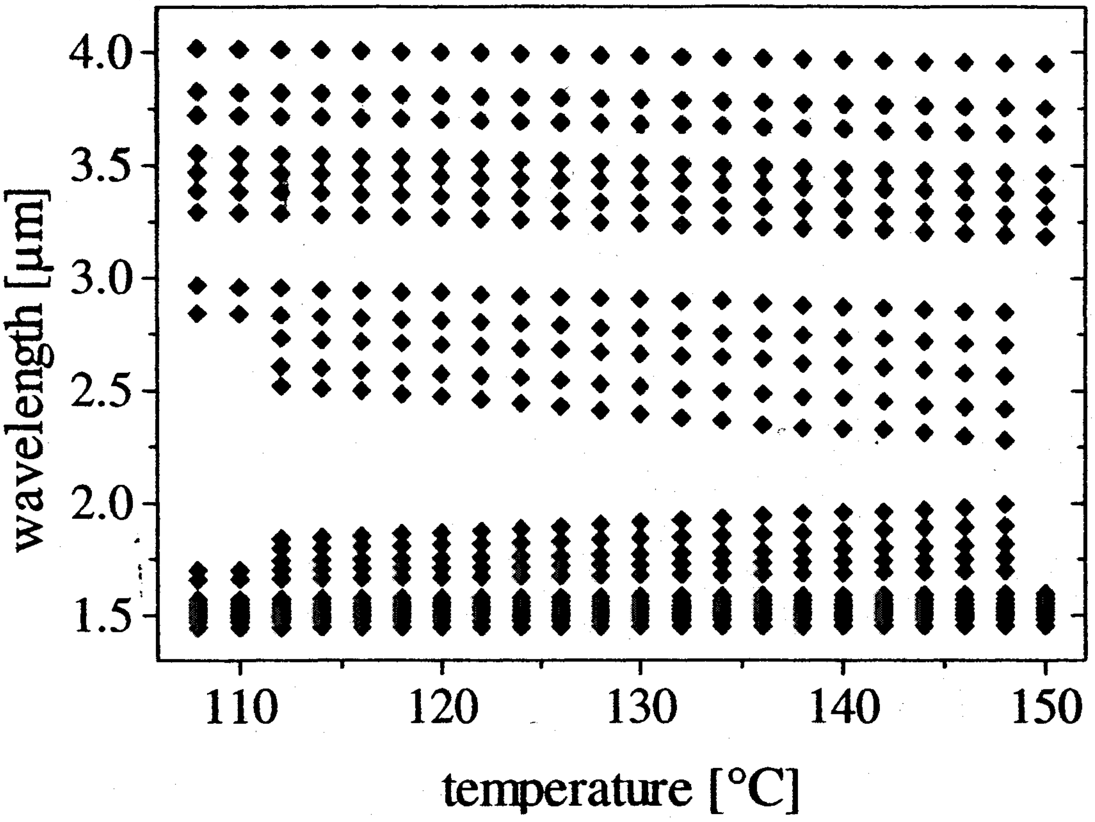

4.0
3.5
3.0
2.5
2.0
1.5
wavelength [µm]
110
120
130
140
150
temperature [°C]

Figure 2

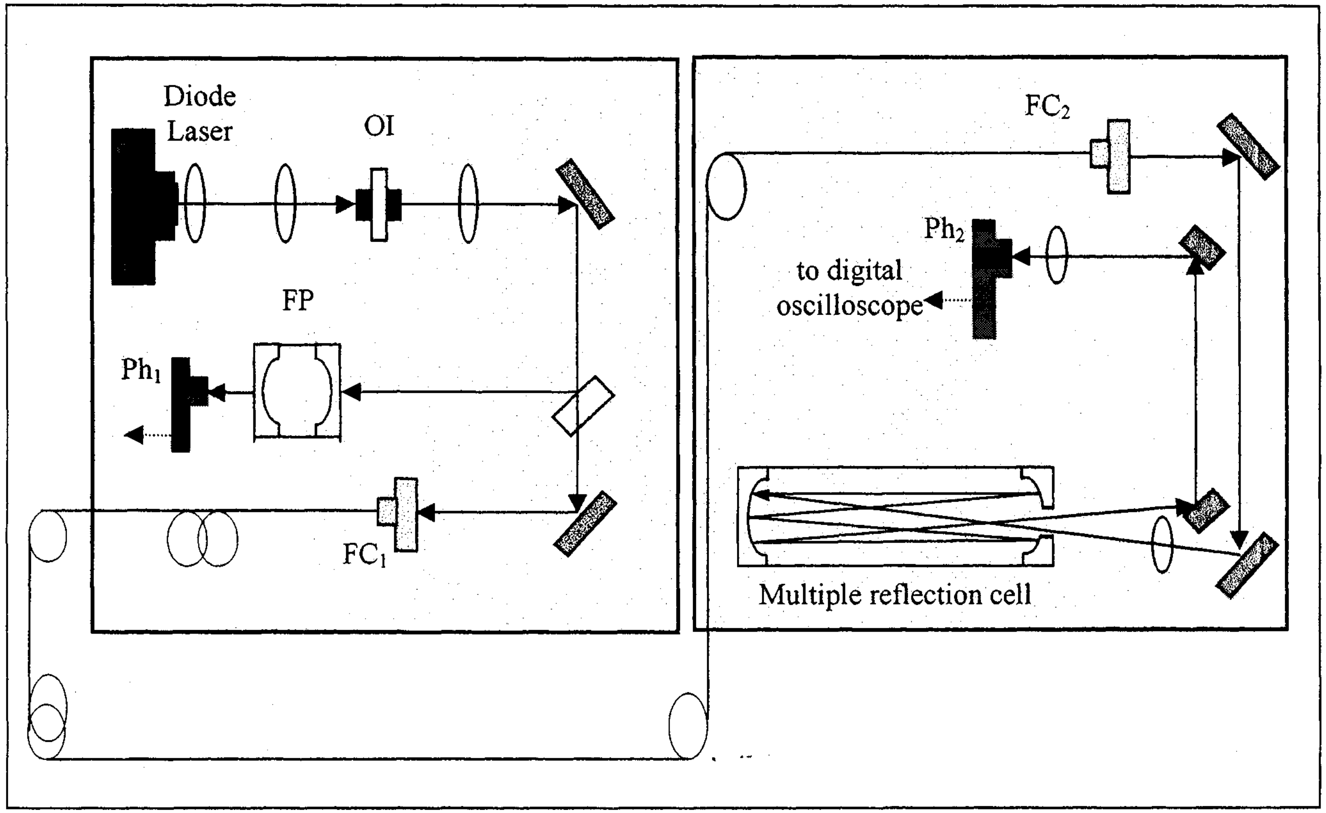
ADVANTAGES OF A (DISTRIBUTED FEEDBACK SEMICONDUCTOR) LASER-BASED SPECTROMETER

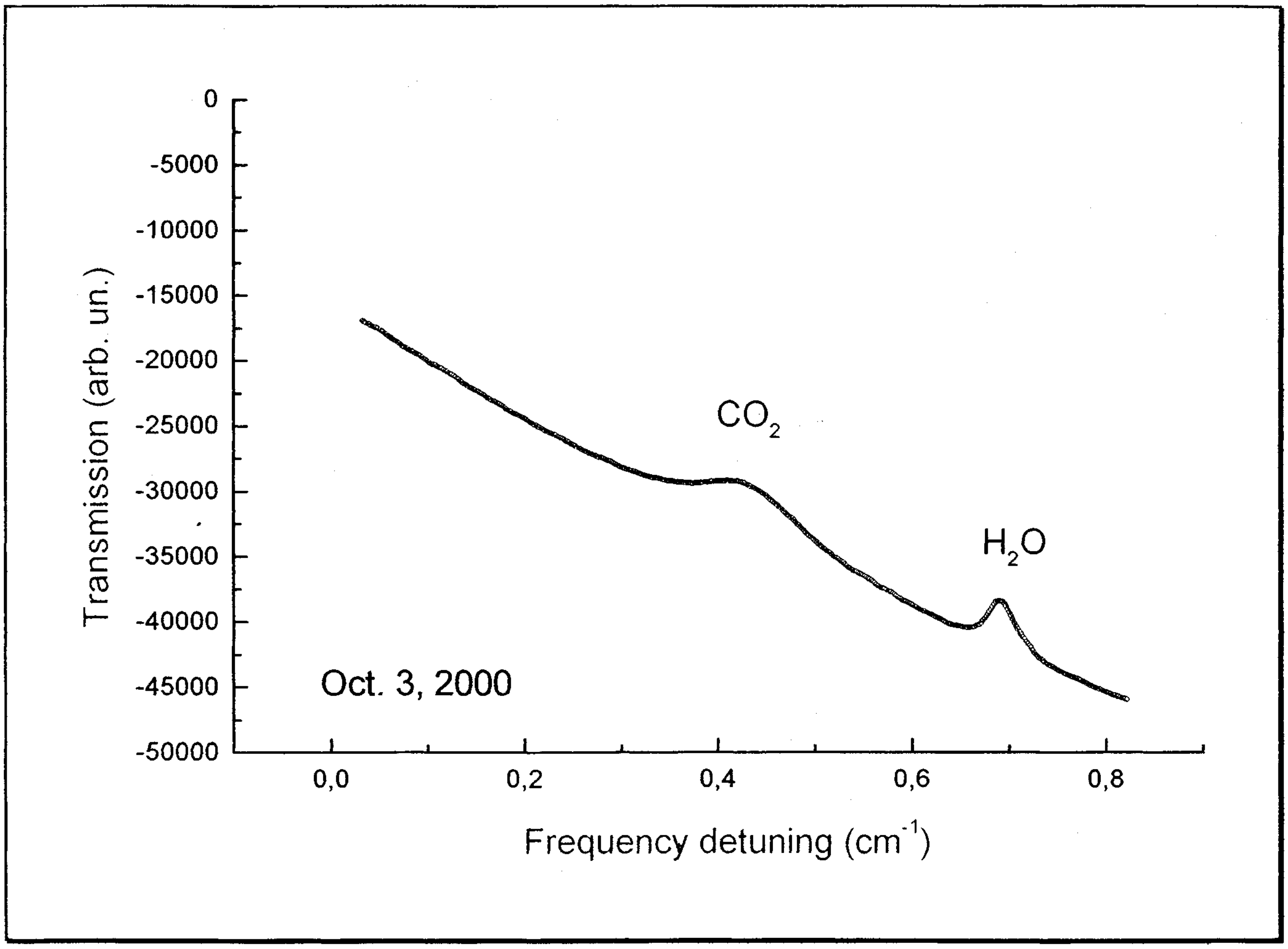
- Very high molecular selectivity.
- Single mode, tunable source.
- Very compact, battery operated laser.
- Remote operation with fibers.
- Multiplexed operation.
- Short acquisition times (tens of ms) → High precision measurements.

Next Step....

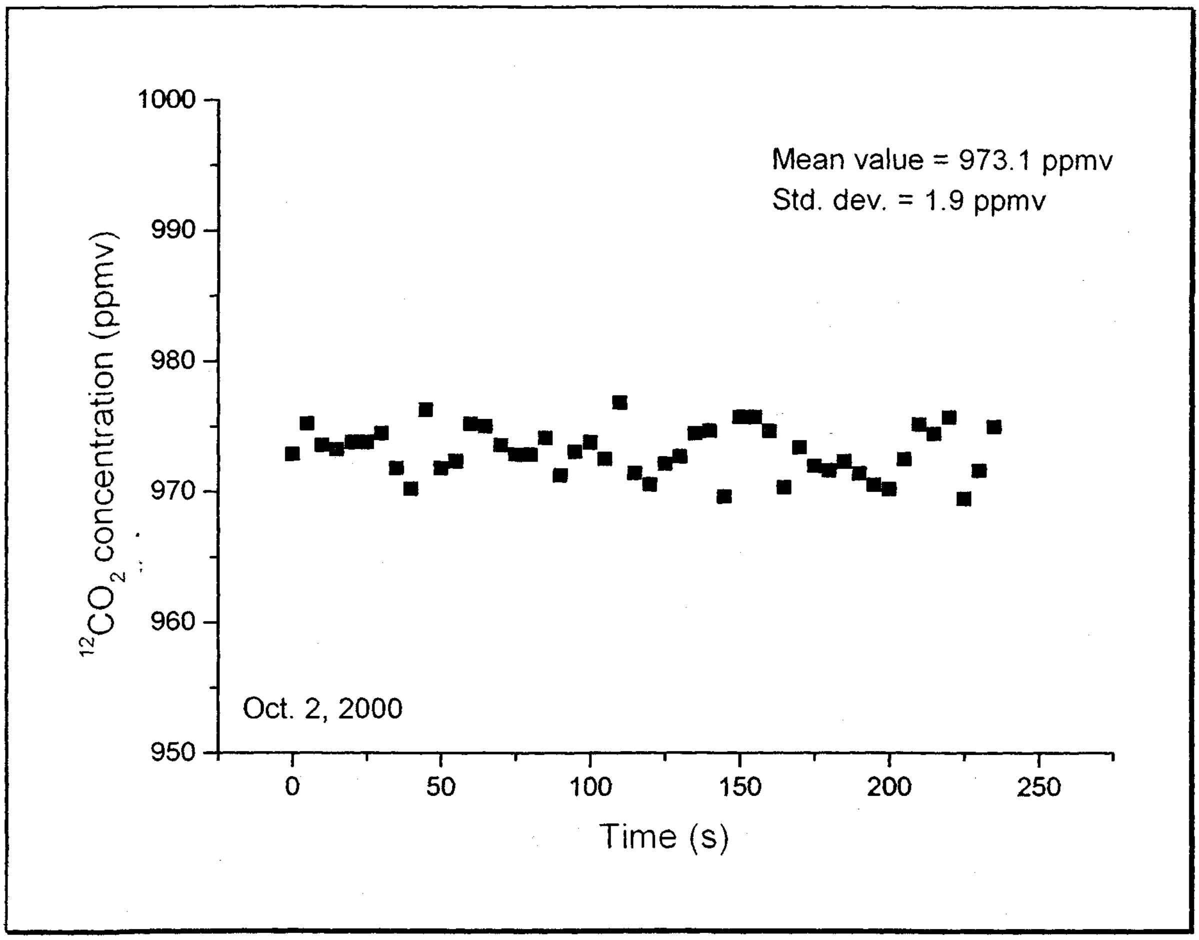
- GaAs waveguided QPM non-linear devices
- Transparency range up to $\lambda \simeq 12\,\mu m$
- Strong non-linearity, strongly guiding ($P_{in} \gtrsim 200\,mW$, $P_{out} \gtrsim 1\,mW$, single pass)
- Possible integration with semiconductor diode lasers.

SCHEMA DELLO SPETTROMETRO



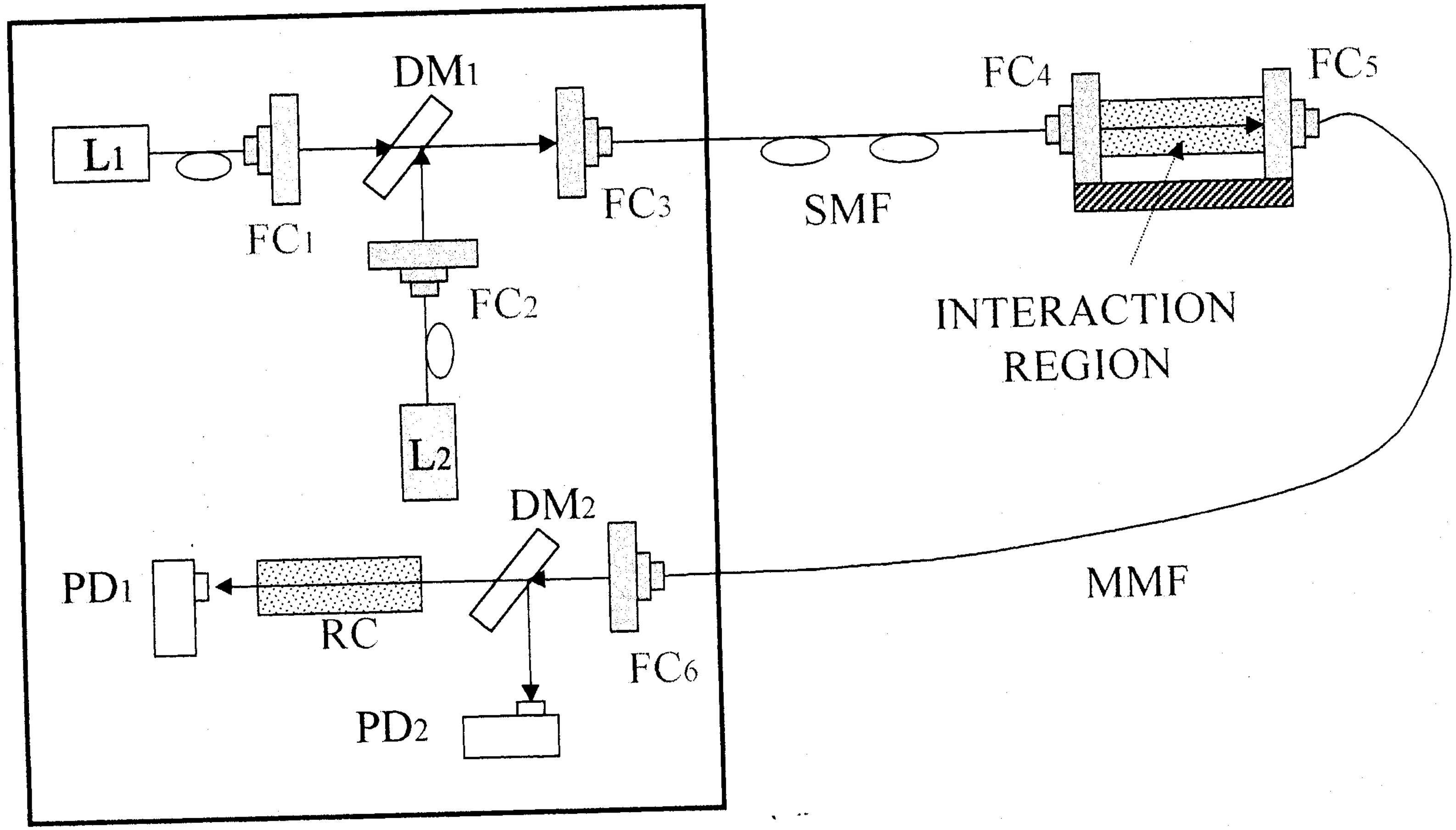


Accuratezza ≈ 1 %



⬇

Riproducibilità nel breve termine ≈ 2 ‰


L_1
FC_1
DM_1
FC_2
L_2
FC_3
SMF
FC_4
FC_5
INTERACTION REGION
MMF
DM_2
FC_6
PD_1
RC
PD_2