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WINTER COLLEGE ON
SPECTROSCOPY AND APPLICATIONS

(8 - 26 February 1999)

"Remote Detection of Volcanic Emissions Using Diode Lasers"

presented by:

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Winter College on Spectroscopy and Applications

Livio Gianfrani

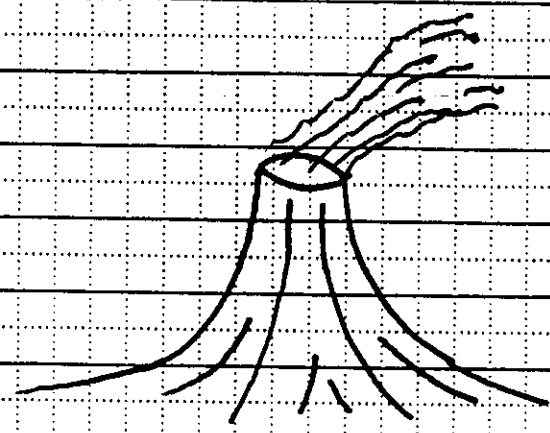
lecture 1

"Remote detection of volcanic emissions using diode lasers"

Contents of the 1st lecture

- The importance of monitoring volcanic gaseous emissions.
- Brief overview of commonly used remote sensing techniques.
- [illegible]
- An example of a diode laser based spectrometer: operation at Solfatara Volcano, Napoli.
- Future challenges.

Volcanic gas



"Volcanic gas is a telegram from the earth's interior"
Matsuo, Japan 1975.

It originates from volatile components dissolved in magma.

Volcanos may have open conduits* (Stromboli and Mt. Etna) or closed conduits+ (Vulcano and Mt. Vesuvio)

* Plume is produced by direct degassing of the magma.

+ Low emission takes place in a variety of fumaroles.

Constituents

Volcanic gas consists mostly of H_2O; other major species are: CO_2, SO_2, H_2S and HCl.

Minor constituents are: H_2, HF, CH_4, CO, S_2, N_2, Ne.

The relative proportions depends on the nature of magma.

Many processes may cause temporal variation in chemical composition:

- changes in temperature and/or pressure of the magma;
- changes in degassing rate of the magma;
- chemical reactions between the gas flow and surrounding materials during the ascent toward the surface.

Predicting volcanic activity

So far, a number of observations evidencing changes in chemical compositions of volcanic gas prior to eruptions have been reported.

Examples:

- Pinatubo volcano, the Philippines, 1991: anomalous change in SO_2 flux.
- Mt. Etna: SO_2 flux changes from 1000 t/day (low state of activity) to 5000 - 25000 t/day during eruptions.
- Asama volcano, Japan:
  SO_2 flux < 300 t/day during calm stage
  SO_2 flux ≥ 500 t/day before and during eruptions

Monitoring of volcanic gas

It is important to monitor the chemical composition in order to predict volcanic eruptions.

It is also of considerable interest to estimate the contribution of volcanic emissions to the global atmospheric budgets.

Gas chromatography : not suitable since gas samples must be collected.

Solution :

Remote sensing techniques

Main indicators :

SO_2 or CO_2 fluxes

CO_2/H_2O CO_2/SO_2 HCl/SO_2 ratios

Remote Sensing techniques

Classified as:

Active
a source (laser or lamp) of radiation is used.

Passive
solar, sky or black-body radiations are used.

Methods	Principle of operation	Active	Passive	Source
DOAS	absorption	x	x	Lamp or sky
COSPEC	absorption		x	Sky
DIAL	back scattering and absorption	x		Pulsed laser
FTIR	dispersion	x	x	Lamp or black-body radiation
TDLAS	absorption	x		Diode lasers

COSPEC

This is the most widely used technique to monitor volcanic plumes. It is generally configured to measure SO_2 concentration. UV diffuse sky radiation is employed. If wind velocity is measured, it provides SO_2 fluxes.

Large errors come from:
- uncertainty in windspeed
- scattering effects

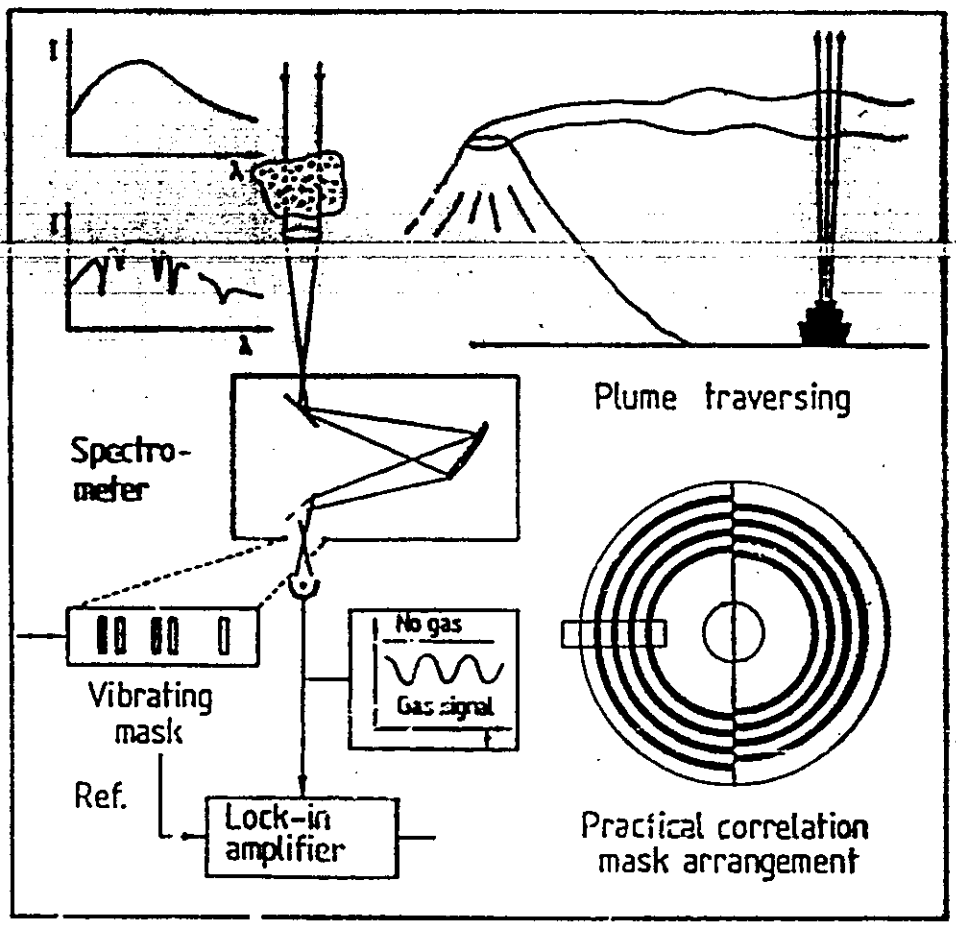
It is suitable for measurements from ground base, shipborne or airborne platforms.

DOAS

When using the passive scheme, it is limited by the Fraunhofer lines.

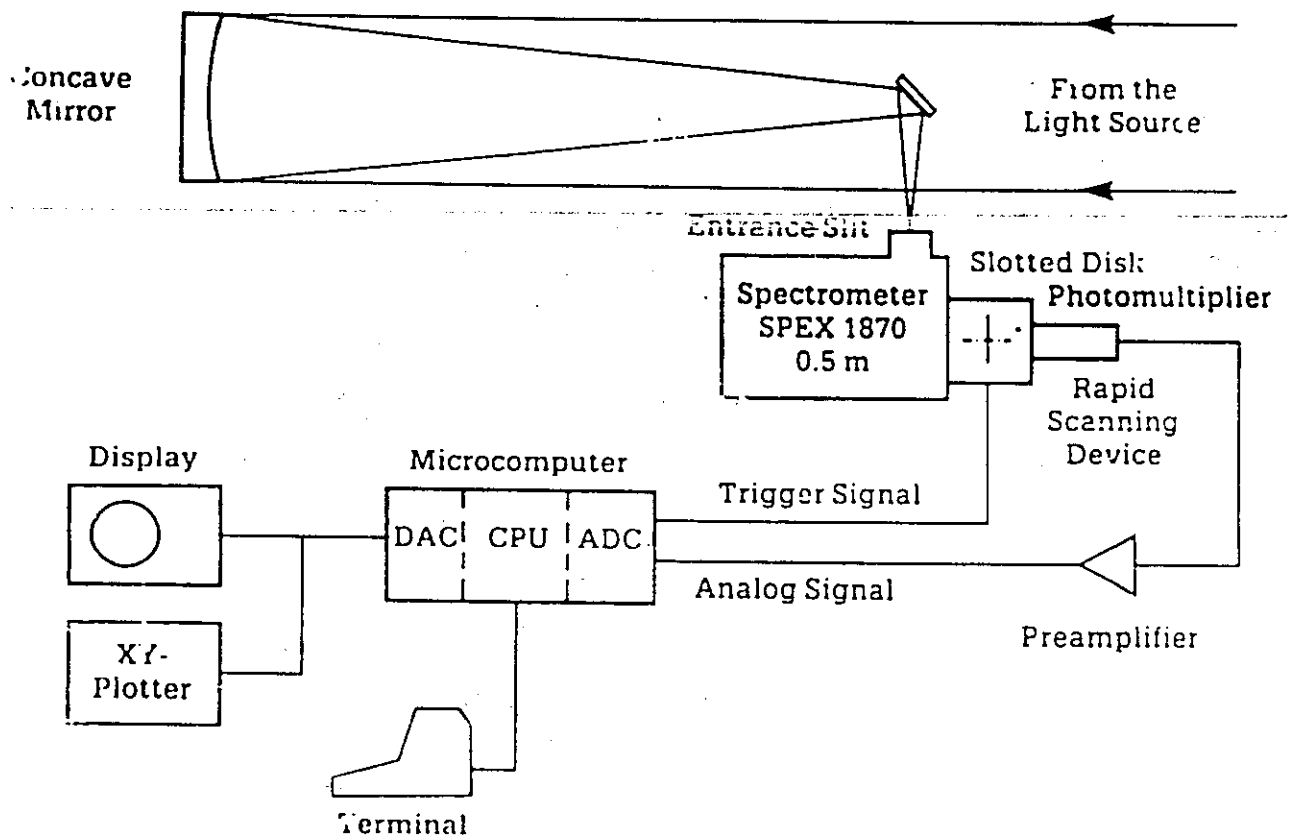
In both cases: low resolution

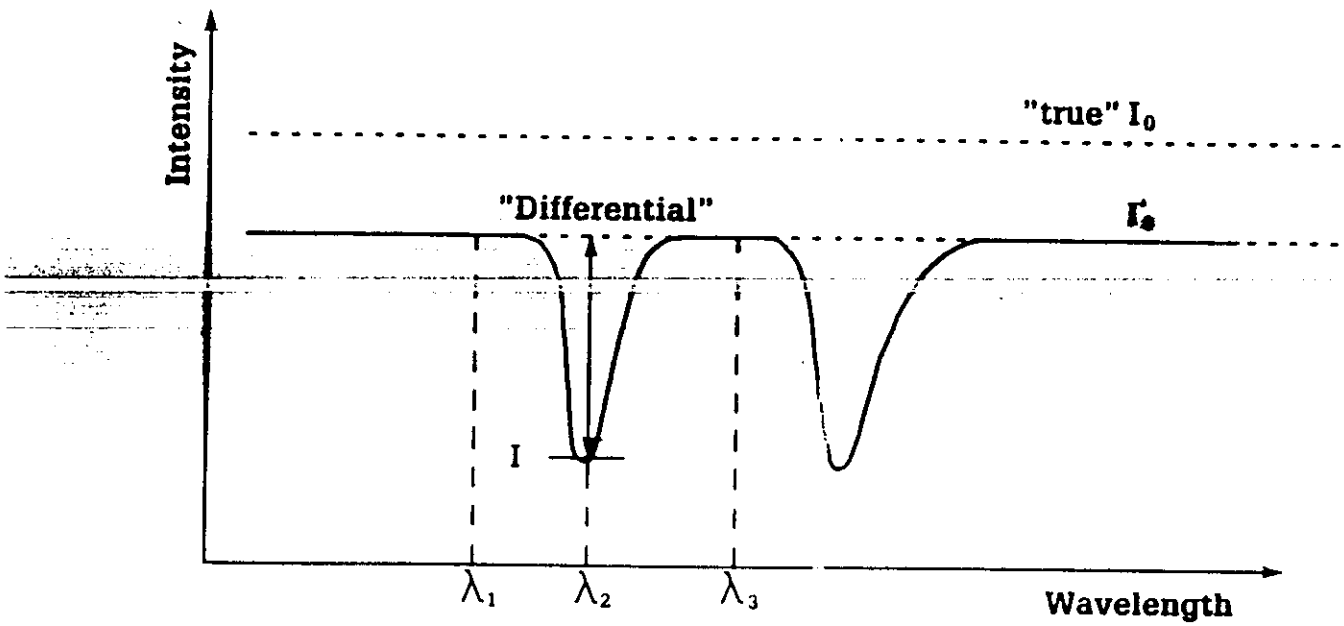
COSPEC



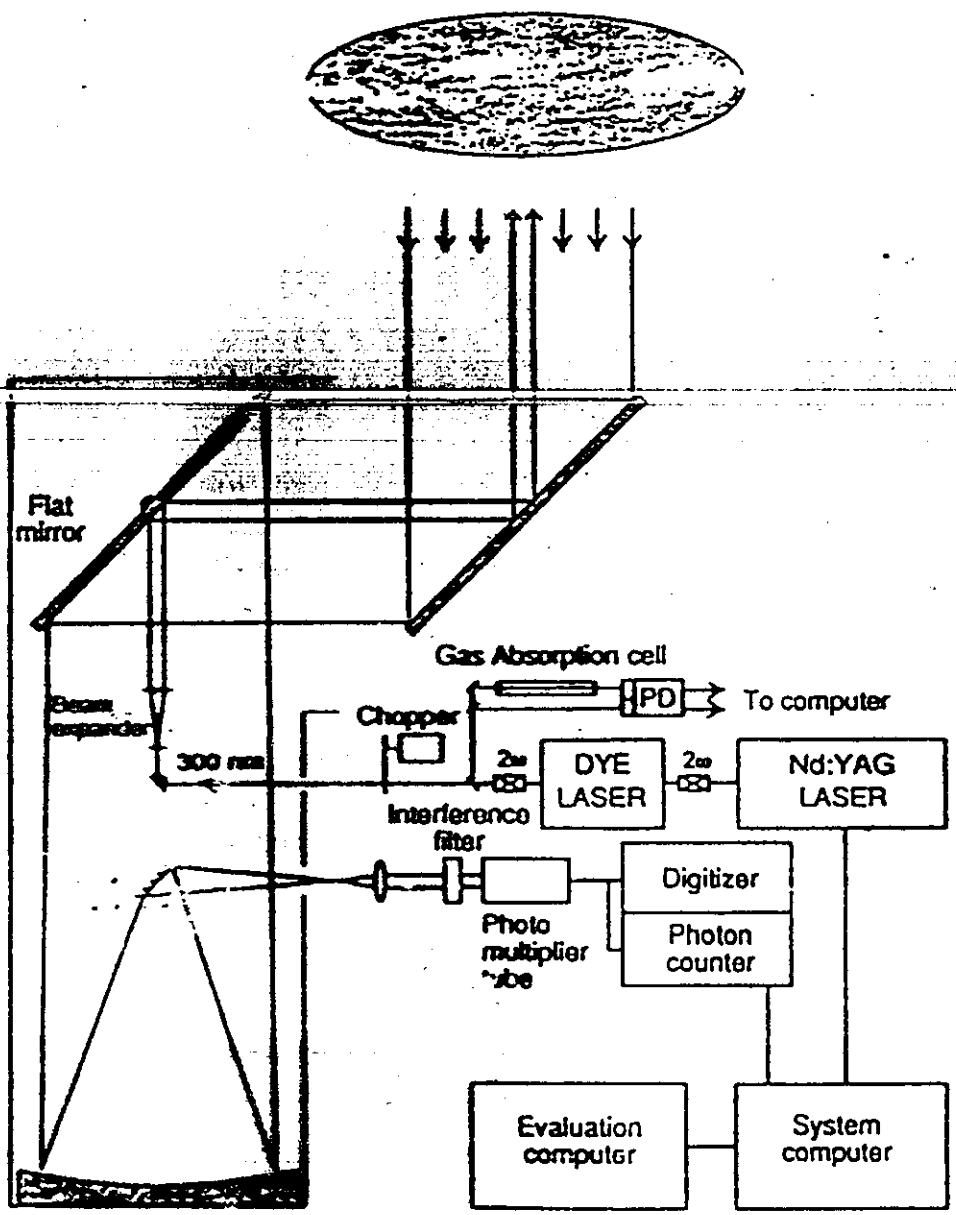
P. Weibring et al.: Appl. Phys. B67, 419 (1998)

DOAS


Concave Mirror
From the Light Source
Entrance Slit
Spectrometer SPEX 1870 0.5 m
Slotted Disk
Photomultiplier
Rapid Scanning Device
Display
Microcomputer
DAC
CPU
ADC
Trigger Signal
Analog Signal
Preamplifier
XY-Plotter
Terminal


Intensity
"true" I_0
"Differential"
I_0
I
λ_1
λ_2
λ_3
Wavelength

LIDAR



P. Weibring et al.: Appl. Phys. B 67, 419 (1998)

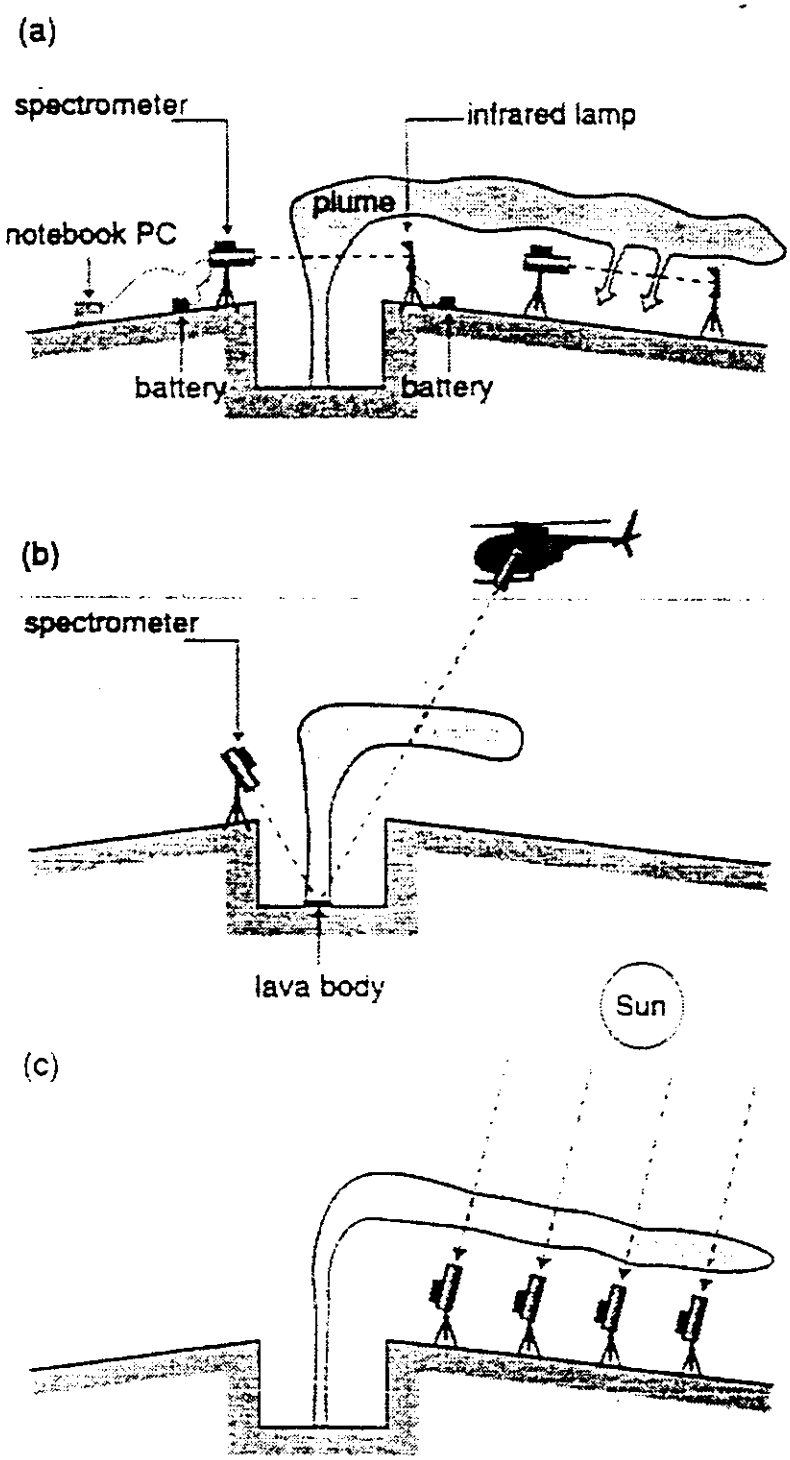
FTIR

Main advantage: possibility to measure several gases of interest.

Some gases, such as H_2S, cannot be detected because their absorption bands are overlapped with H_2O or CO_2 bands.

Fluxes cannot be measured.

Measurements of HCl/SO_2 and HCl/CO_2 ratios have been reported.



C. Oppenheimer et al.: Appl. Phys. B 67, 505 (1998)

TDLAS

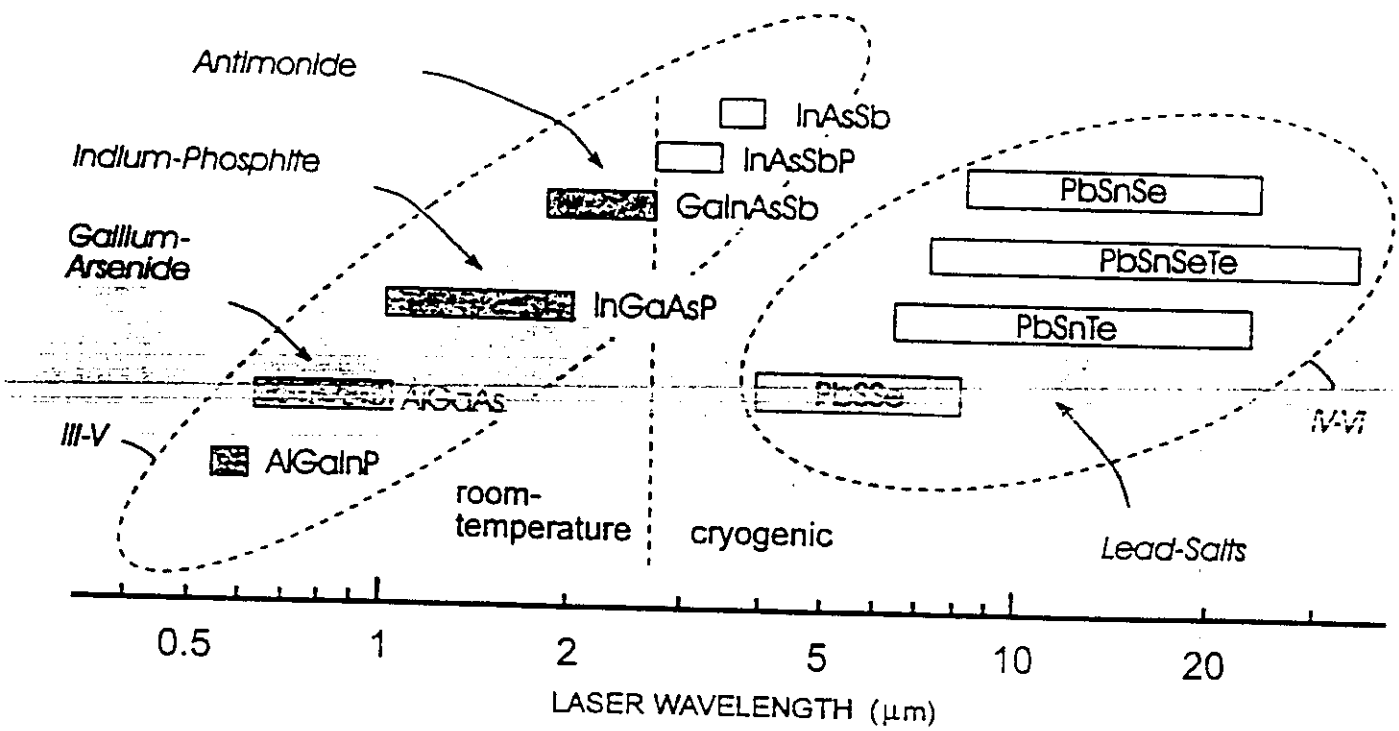
Using diode lasers in the spectral window 1 ÷ 2 μm, remote operation is possible.

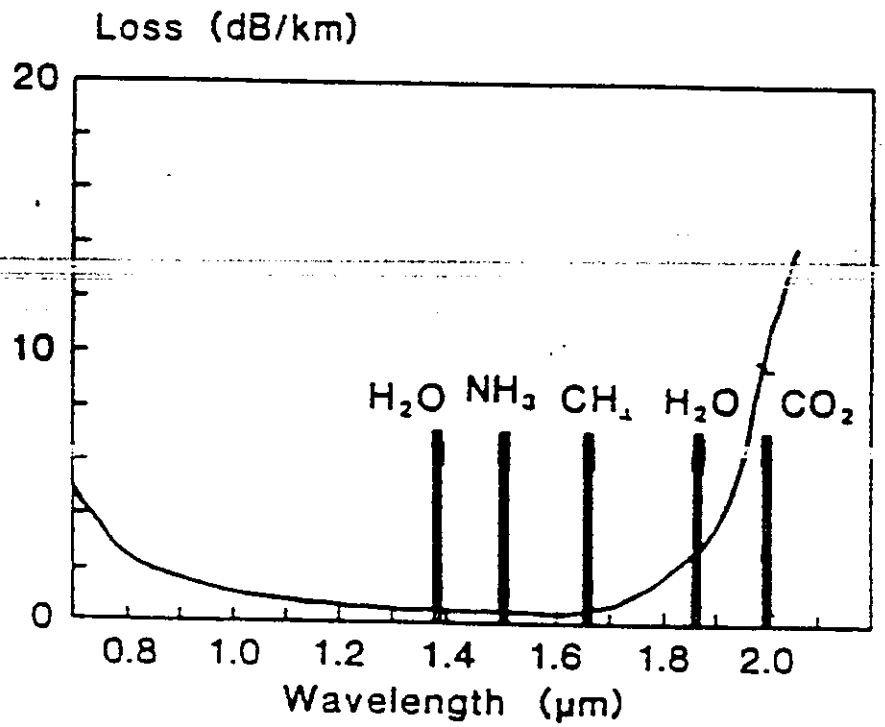
A diode laser based spectrameter has very low electric power consuption. This enables continuous gas monitoring over very long times using batteries and solar panels.

Absorption features are observed with very high resolution ⇒ high selectivity.

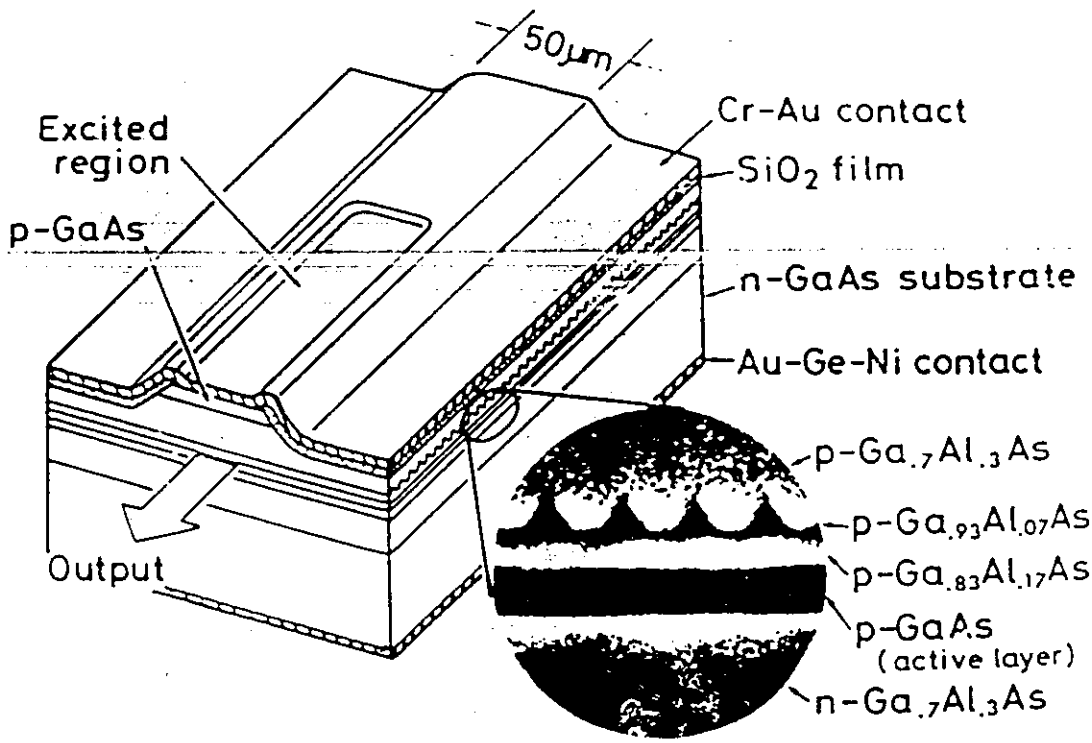
This kind of spectrometer is very compact and easy to use.

In the near-IR molecular absorptions are due to overtone or combination vibrational bands which in many cases have low intensities.


Antimonide
Indium-Phosphite
Gallium-Arsenide
III-V
InAsSb
InAsSbP
GaInAsSb
InGaAsP
AlGaAs
AlGaInP
PbSnSe
PbSnSeTe
PbSnTe
PbSSe
IV-VI
Lead-Salts
room-temperature
cryogenic
0.5
1
2
5
10
20
LASER WAVELENGTH (μm)


Loss (dB/km)
20
10
0
H_2O NH_3 CH_4 H_2O CO_2
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Wavelength (μm)

DFB diode laser



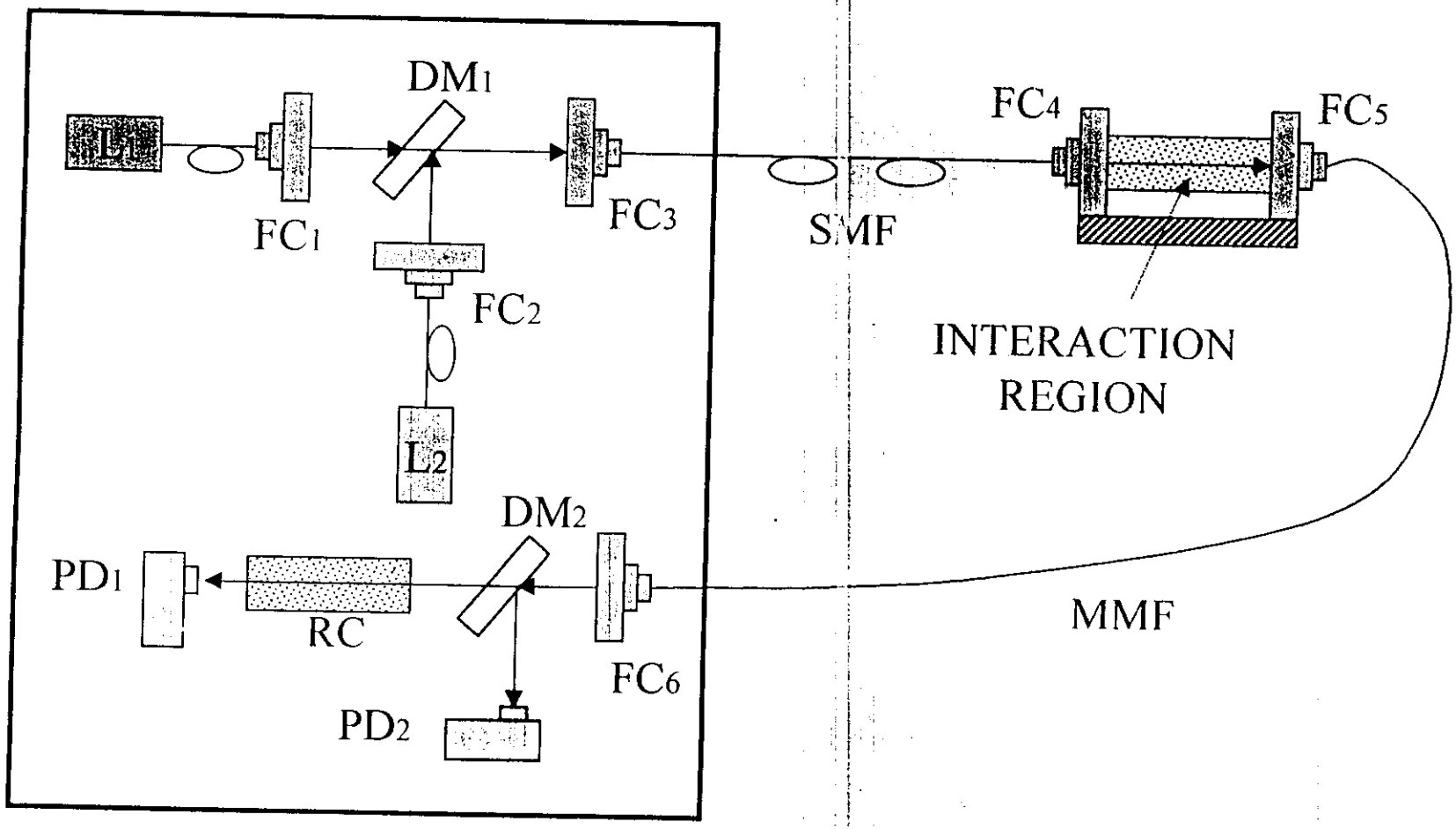
Commercially available DFB diode lasers

Wavelength (μm)	Detectable gas
.761	O_2
.812	H_2O
1.3213	HF
1.3925	H_2O
1.3964	H_2O
1.5125	OH
1.5401	NH_3
1.5650	H_2S
1.5747	H_2S
1.5787	CO_2, CO
1.6537	CH_4
1.7944	HCl
1.9508	HBr
2.0000	CO_2
2.0040	CO_2

DFB source at 1.393 μm

Model: SU1393-CF-I-FC

I_{th}	70 mA @ 23 °C
P	1 mW @ 100 mA and 23 °C
λ	1.39218 μm @ 23 °C
SMSR	>30 dB
Δλ/ΔT	0.84 Å/°C
Δλ/ΔI	0.063 Å/mA
Tuning range	1.3910 μm @10 °C 1.3940 μm @45 °C


DM1
L1
FC1
FC3
FC2
L2
SMF
FC4
FC5
INTERACTION
REGION
DM2
PD1
RC
FC6
PD2
MMF

The Solfatara volcano, at Campi Flegrei, Napoli

Temperature (°C)	H_2O (%)	CO_2 (%)	H_2S (%)
160	85-95	15-5	1

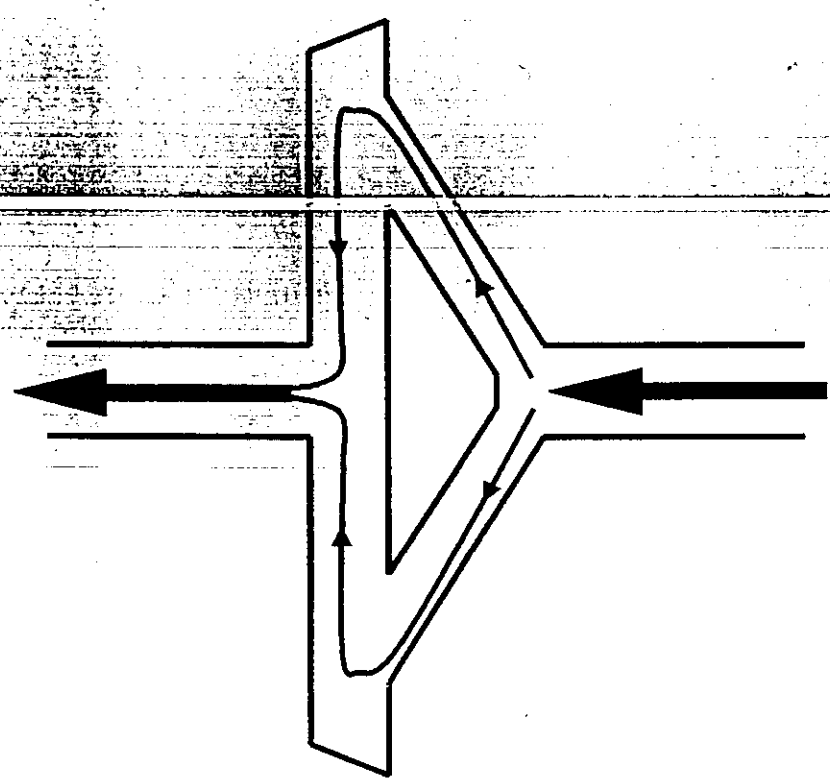
Interaction region

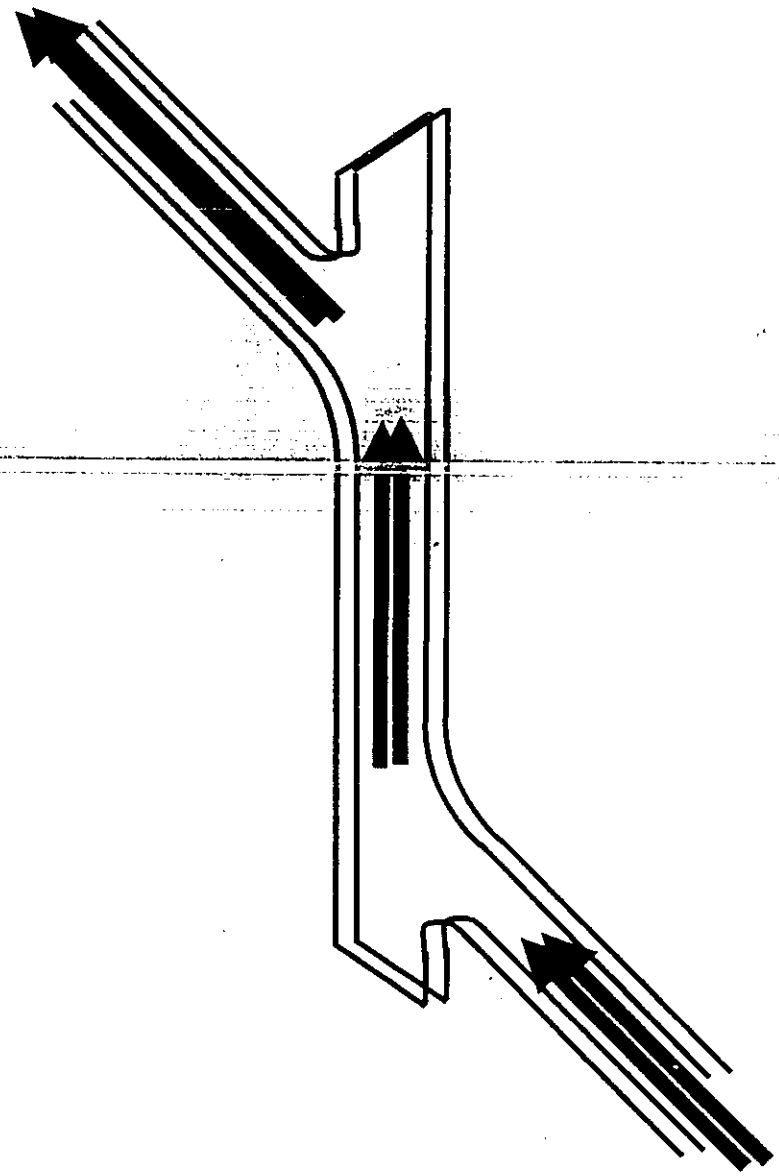
Open-path configuration

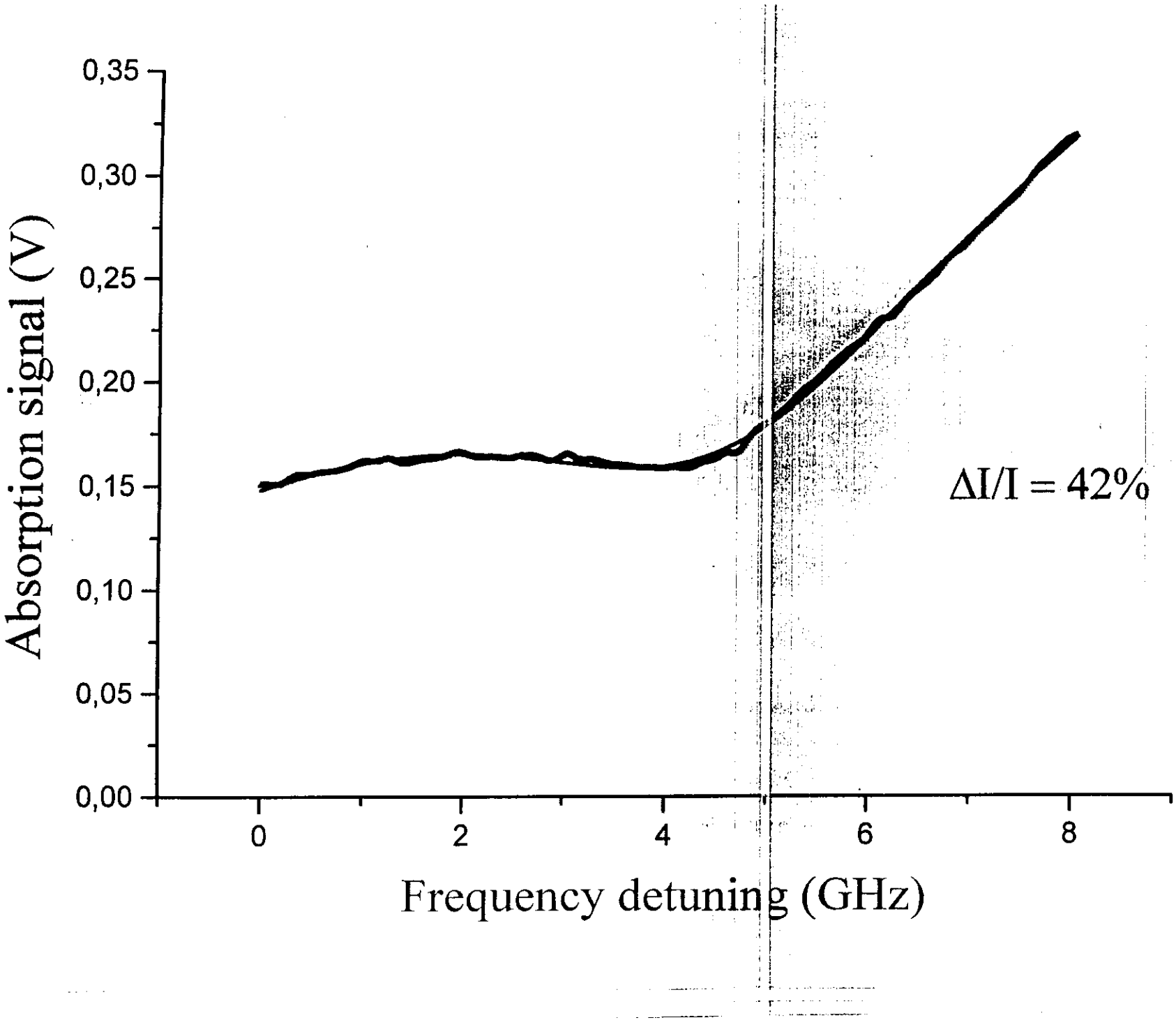
- very easy
- influence of the environment

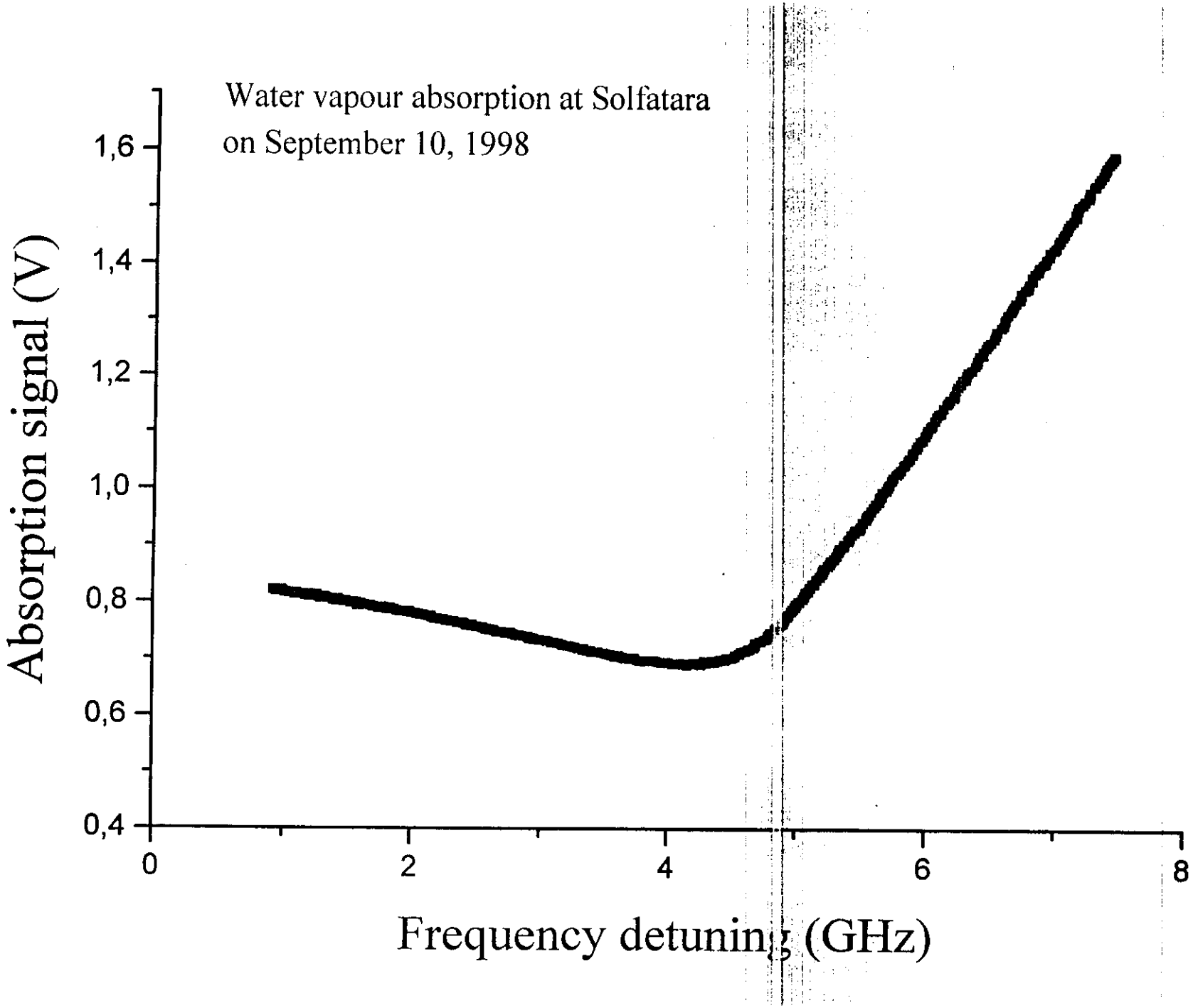
Confined configuration (using a sample cell where the volcanic gas flows)

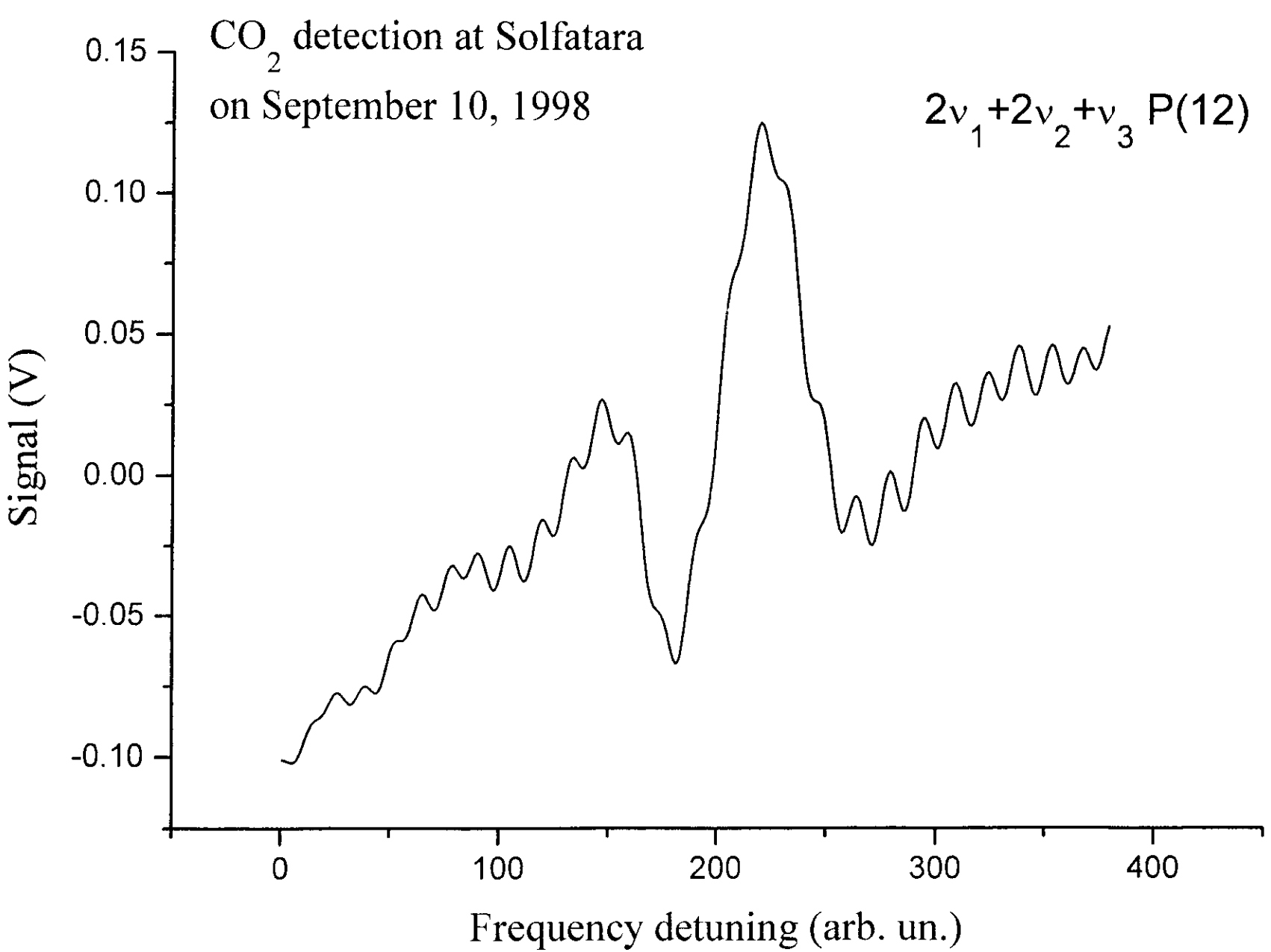
- well defined interaction region
- no contact between the volcanic gas and the collimation optics of the fiber bench.
- condensation of H_2O and sulphur must be avoided.



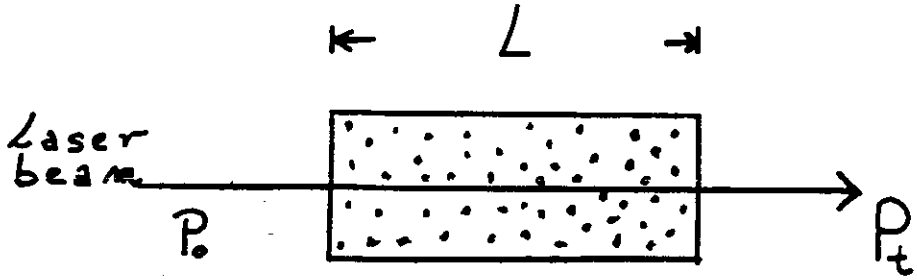



0,35
0,30
0,25
0,20
0,15
0,10
0,05
0,00
Absorption signal (V)
0
2
4
6
8
Frequency detuning (GHz)
ΔI/I = 42%


Water vapour absorption at Solfatara
on September 10, 1998
Absorption signal (V)
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0
2
4
6
8
Frequency detuning (GHz)


CO_2 detection at Solfatara
on September 10, 1998
$2\nu_1+2\nu_2+\nu_3$ P(12)
Signal (V)
0.15
0.10
0.05
0.00
-0.05
-0.10
0
100
200
300
400
Frequency detuning (arb. un.)

Laser absorption and Beer-Lambert law



$$I_t(\tilde{\nu}) = I_0 \exp\left[-K(\tilde{\nu}) N L\right]$$

$K(\tilde{\nu})$ absorption cross section in units of cm^2/mol

N concentration of the absorbing species in units of mol/cm^3

Absorption lineshapes

The spectral lines have a nonzero width and a definite lineshape which depends on the relative importance of each of several broadening mechanisms:

natural line broadening

Doppler broadening

collisional broadening

$$K(\tilde{\nu}) = S\, g(\tilde{\nu} - \tilde{\nu}_0)$$

$K(\tilde{\nu})$: line-strength; $g(\tilde{\nu} - \tilde{\nu}_0)$: shape function

$$S = \int_{-\infty}^{+\infty} K(\tilde{\nu})\, d\tilde{\nu} \quad \text{in } \frac{\text{cm}}{\text{mol}}$$

$$K(\tilde{\nu}_0) = \frac{S}{\pi \gamma_m}$$ for a Lorentzian lineshape

$$K(\tilde{\nu}_0) = \frac{S}{\gamma_D} \sqrt{\frac{\ln 2}{\pi}}$$ for a gaussian lineshape

It is important to point out that

$K(\tilde{\nu}_0)$ depends on p, T of the gas sample

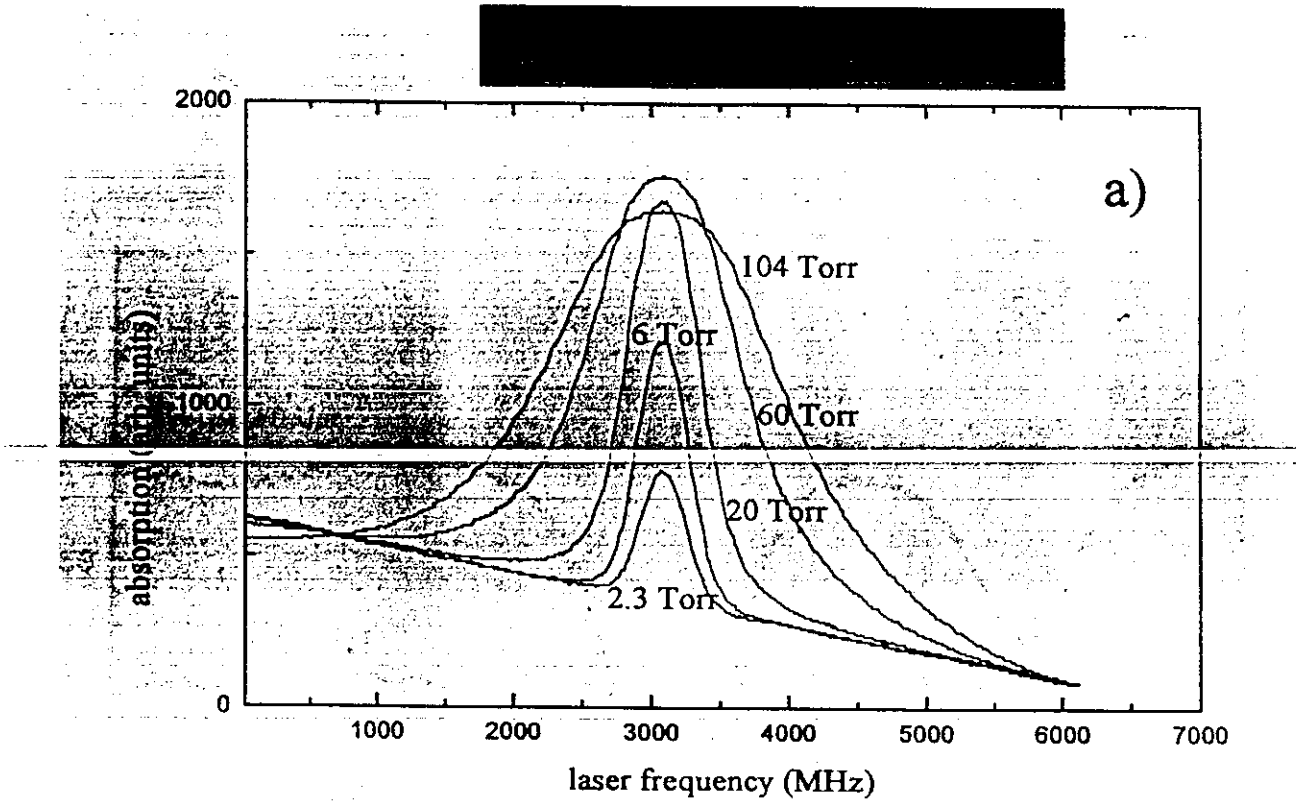
S depends on T

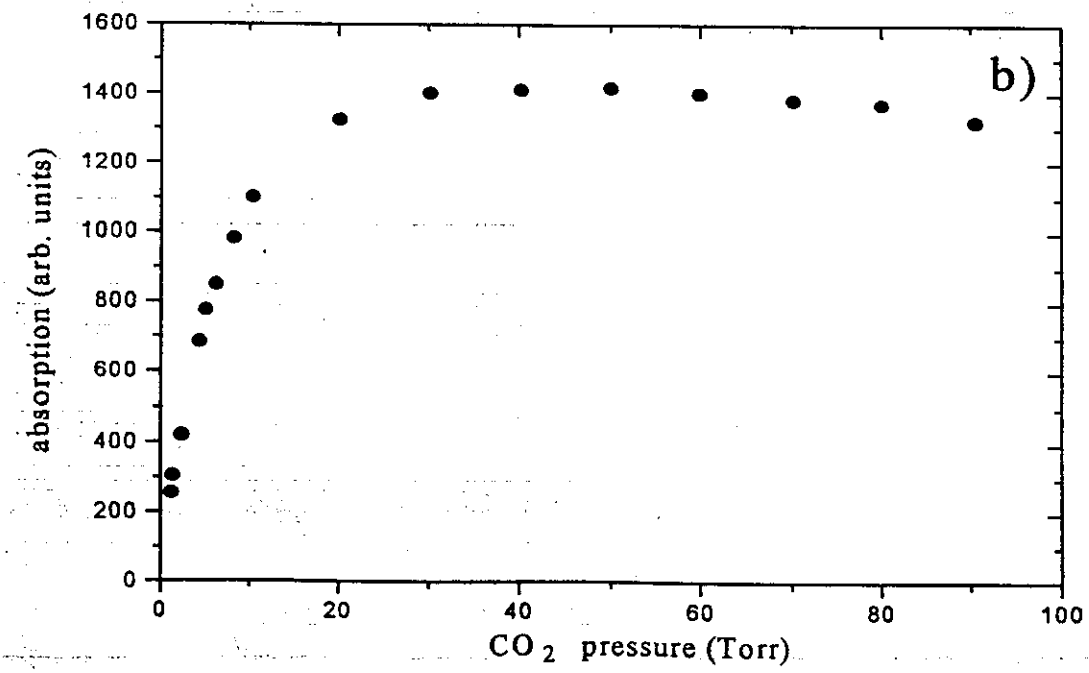
For a linear molecule:

$$S(T_0) = S(T)\,\frac{T}{T_0}\,\exp\left[1.439\,E''\,\frac{T_0 - T}{T_0 T}\right]$$

not including induced emission term.

The dependence on T is due to the fact that S is proportional to the fractional population.


a)
104 Torr
6 Torr
60 Torr
20 Torr
2.3 Torr
absorption (arb. units)
2000
1000
0
1000
2000
3000
4000
5000
6000
7000
laser frequency (MHz)


b)
absorption (arb. units)
1600
1400
1200
1000
800
600
400
200
0
0
20
40
60
80
100
CO 2 pressure (Torr)

Retrieval methods

- H_2O $\nu_1 + \nu_2$ band $3_{03} \rightarrow 2_{02}$

$\sigma_0(T_0) = 1.46\,(4)\ 10^{-20}\ cm^2/mol$

$\Downarrow$

$\bar{\sigma}_0(T)$ $T \simeq 160\ °C$ in a low pressure regime

$\Downarrow$

$$\sigma_0(T,P) = \bar{\sigma}_0(T_0)\,\frac{\gamma_D}{\gamma}\,\frac{1}{\sqrt{\pi \ln 2}} =$$

$$= 6.8\,(2)\ 10^{-22}\ cm^2/mol$$

from the Beer-Lambert law

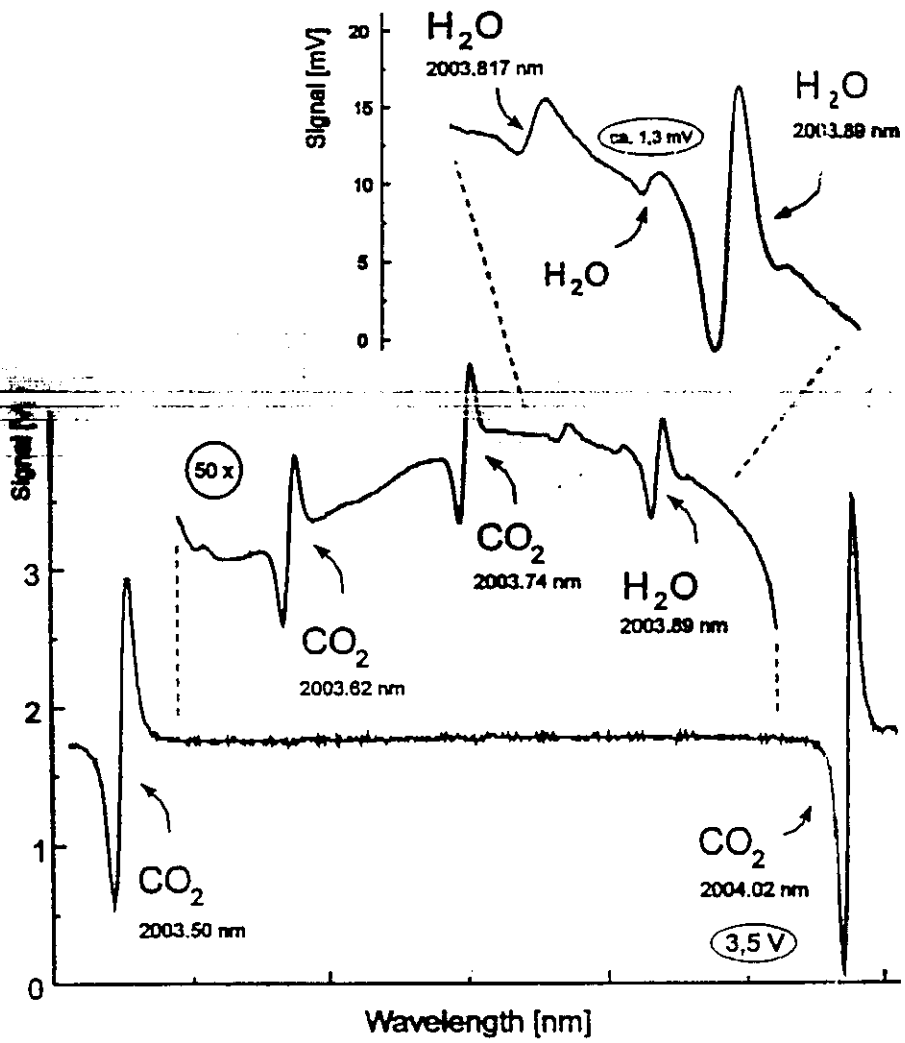
$$N = -\frac{1}{\bar{\sigma}_0(T,P)\,L}\,\ln\frac{P_t(\tilde{\nu}_0)}{P_0(\tilde{\nu}_0)}$$

- CO_2

$$P_{flow} = P_{r.c.}\,\frac{A_f}{A_t}\cdot\frac{\sigma_t}{\sigma_f}\cdot d$$

Campaigns at Solfatara

Date	Measured H_2O pressure (Torr)	Measured CO_2 pressure (Torr)	Ratio
June 4, 98	1770 (60)	-	-
Sept. 10, 98	2100 (7C)	220 (4C)	0.105



P. Werle et al.: Appl. Phys. B 67, 307 (1998)

In the case of direct absorption measurements for both molecules we can measure H_2O and CO_2 partial pressures from the linewidths of the absorption profiles.

L_1 HWHM for H_2O line

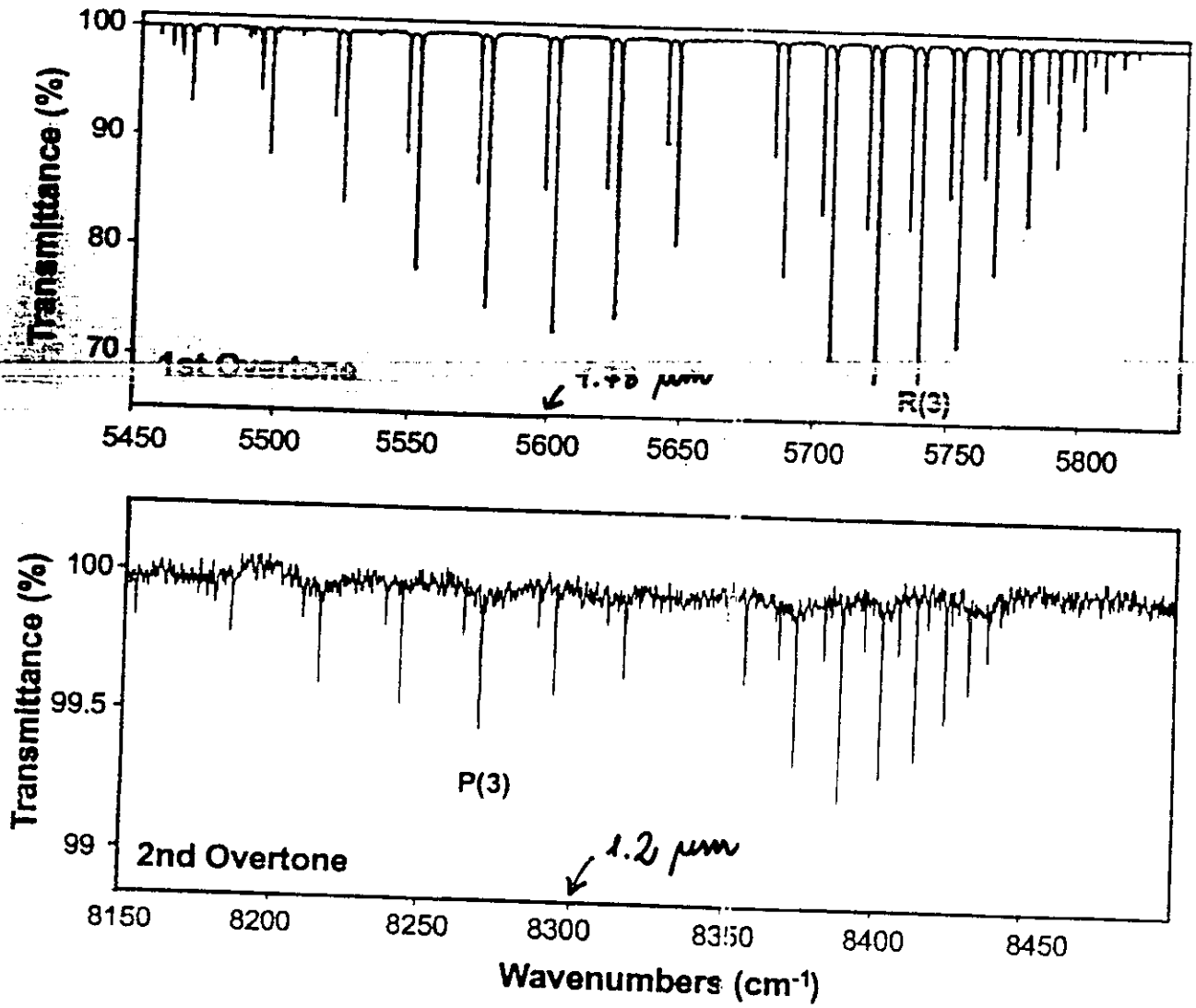
L_2 HWHM for CO_2 line

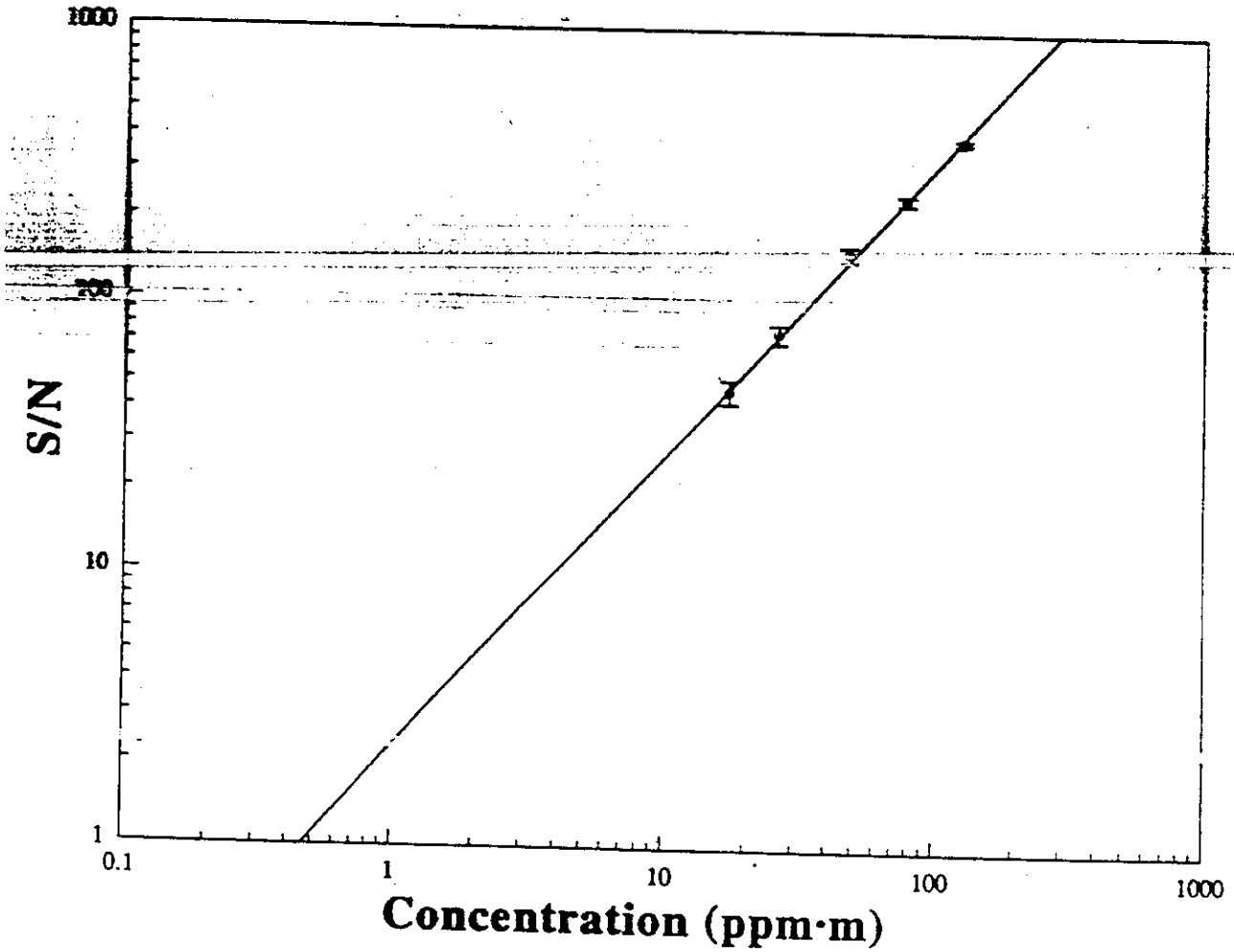
$$L_1 = \gamma_{H_2O}^{H_2O} P_{H_2O} + \gamma_{H_2O}^{CO_2} P_{CO_2}$$

$$L_2 = \gamma_{CO_2}^{H_2O} P_{H_2O} + \gamma_{CO_2}^{CO_2} P_{CO_2}$$

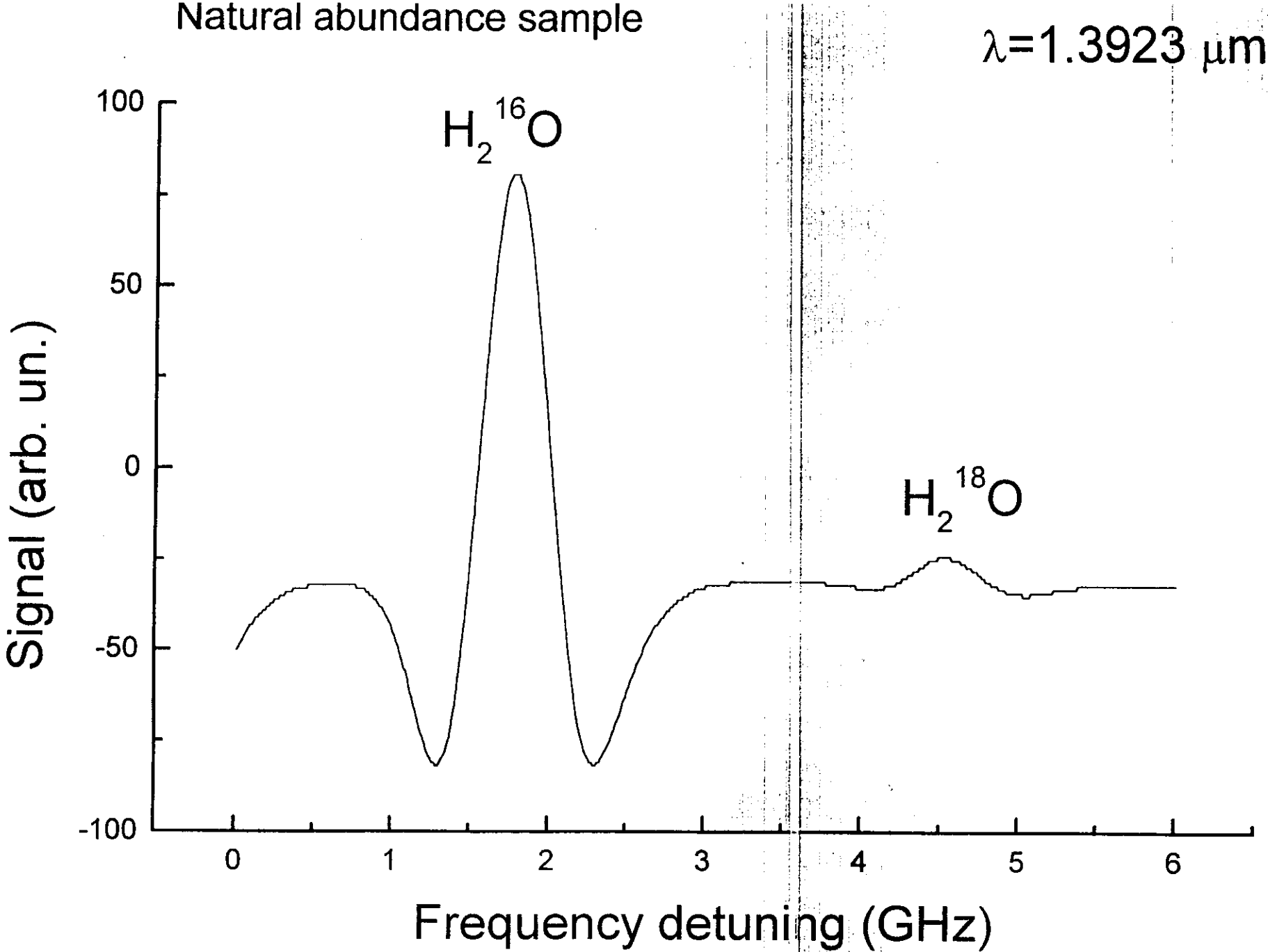
L Gianfrani et al. Appl. Opt. 36, 9481 (1997)

HCl


Transmittance (%)
100
90
80
70
1st Overtone
1.75 μm
R(3)
5450
5500
5550
5600
5650
5700
5750
5800
Transmittance (%)
100
99.5
99
P(3)
2nd Overtone
1.2 μm
8150
8200
8250
8300
8350
8400
8450
Wavenumbers (cm-1)



C. Corsi et al.: Appl. Phys. B68, 267 (1999)


Natural abundance sample
λ=1.3923 μm
H2 16O
H2 18O
Signal (arb. un.)
100
50
0
-50
-100
0
1
2
3
4
5
6
Frequency detuning (GHz)

Useful references

K. Natsu et al.: Geochem. J. 27, 361, 1993

H. Edner et al.: J. Geophys. Res. 99, 18827, 1994

L. Gianfrani et al.: Appl. Opt. 36, 9481, 1997

P. Weibring et al.: Appl. Phys. B67, 419, 1998

C. Oppenheimer et al.: Appl. Phys. B67, 505, 1998

P. De Natale et al.: SPIE, volume 3491, 783, 1998

L. Gianfrani et al.: Opt. Lett., submitted.

Summary

Diode laser absorption spectroscopy can be efficiently used to measure the concentration of several molecular species in a volcanic gas. Remote operation is possible thanks to optical fibers.

Real time, higly selective and continuous monitoring can be performed, even in a very hostile environment such as that found inside or close to a crater.

Useful references

K. Notsu et al.: Geochem. J. 27, 361, 1993

H. Edner et al.: J. Geophys. Res. 99, 18827, 1994

L. Gianfrani et al.: Appl. Opt. 36, 9481, 1997

P. Weibring et al.: Appl. Phys. B67, 419, 1998

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APPLICATIONS of PHOTONIC TECHNOLOGY 3

Closing the Gap between Theory, Development, and Application

SPIE Volume 3491

Gas concentration measurements with DFB lasers to monitor volcanic activity

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Keywords: Optical measurements, gas sensors; Remote sensing, surveillance

Abstract
We report construction and operation of a multiplexed laser spectrometer, based on fiber coupled Distributed Feed-Back (DFB) semiconductor diode lasers, for monitoring concentration of gases emitted from volcanoes. The main problems related to this particular application, as well as the way of operation of the apparatus are discussed. The first experimental data, recorded at the test site of Solfatara volcano, Naples, Italy are reported. To our knowledge, this is the first design of a small, low power consuming laser spectrometer for geochemical applications.

Introduction
Quantitative data on the time evolution of the chemical composition of the gaseous emissions from a volcanic area may be related to the state of activity of the volcano. Therefore, continuos monitoring systems, which are able to work in remote areas and during periods of intense activity, are required. With this in mind, a laser based sensor, which can be remotely operated using optical fibers, has been developed. This sensor relies on highly selective laser radiation absorption of overtone transitions for the gases of interest in the 1.3-1.6 μm spectral range. It allows continuous monitoring of water vapour, carbon dioxide and, possibly, hydrogen sulphide and carbon monoxide in gaseous flows as, for instance, the natural fumaroles.

Experimental apparatus
A sketch of the experimental set-up is reported in Fig.1.
The sources are two Distributed Feed-Back (DFB) diode lasers emitting, respectively, at a center wavelength of 1578 nm and 1393 nm. Both have about 4 nm tunability around the center emission wavelength and have a linewidth of about 10 MHz. They are tuned into resonance with, respectively, the (0, 0, 0)-(3, 0, 1) vibro-rotational band of CO_2 and the (0, 0, 0)-(1, 0, 1) band of H_2O. The Doppler linewidth of these lines is about 600 MHz (FWHM), to which further broadening due to atmospheric pressure operation must be added [1].
The fiber coupled DFB lasers are connected to two collimating input ports, mounted on a 5x4 cm miniature breadboard. On this breadboard are also fixed two small beamsplitters (BS), taking 7% radiation power from each beam, and then directed onto two InGaAs detectors (PD1, PD2), with a 10 kHz bandwidth, the electric signals being used for common mode noise rejection. The two transmitted beams are coupled co-propagating by a dichroic beam-splitter and re-launched into a single-mode fiber by an

optical output port also fixed on the breadboard. After 30 meters of propagation inside the single-mode fiber, the two-colours beam is again collimated in air, to cross the interaction region, which is geometrically defined by two stainless steel optical ports. These ports are screwed onto a stainless steel block and can be translated, one with respect to the other.

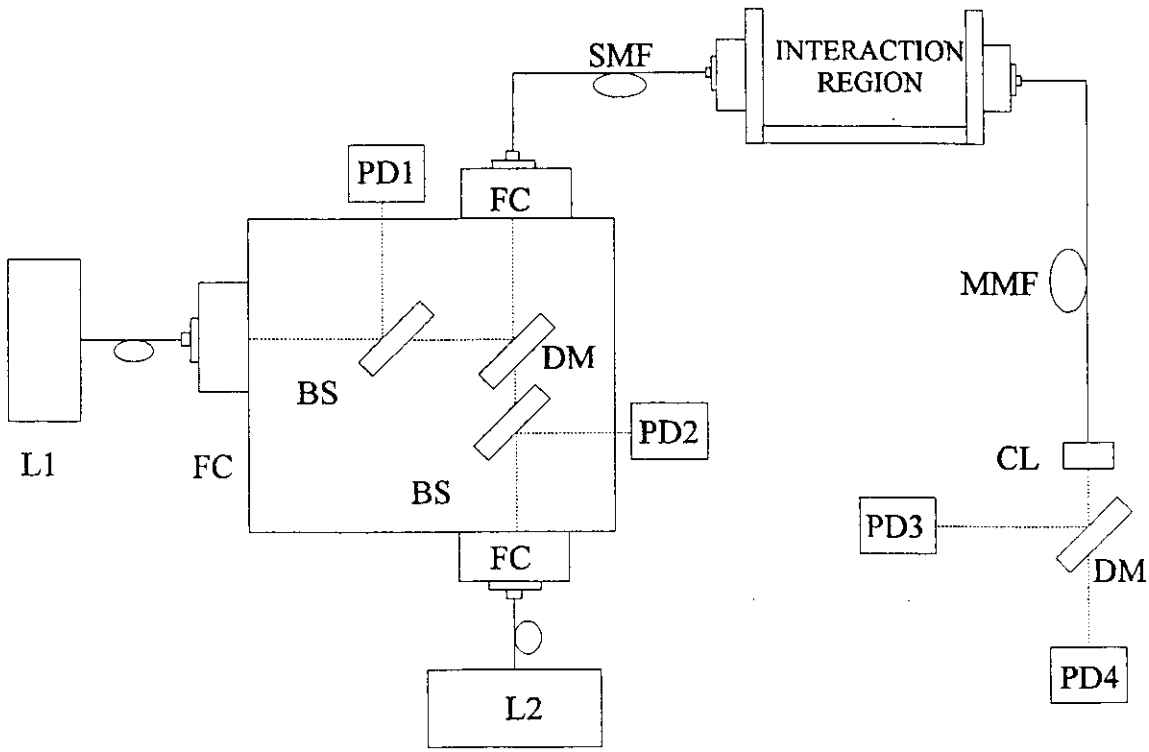

Fig. 1. Schematic diagram of the diode lasers based sensor for remote detection of H_2O and CO_2. L=laser; PD=photodiode; FC=input/output fiber port; BS=beam-splitter; DM=dichroic mirror; SMF=single-mode fiber; MMF=multi-mode fiber; CL=collimating lens.

Thus, the absorption path-length can be changed between 20 and 30 cm. The output fiber is a multimode fiber, with a core diameter of 63 μm and 0.27 NA (numerical aperture), to reduce launch losses. Indeed, as will be discussed below, the two-colour beam interacts with a hot jet of gas, with a consequent degradation of the beam quality, which becomes less critical for fiber launch when a multimode core is used.

The 30 meters long multimode fiber takes the radiation back to the rest of the apparatus. The collimated output from the multimode fiber is finally wavelength selected by a dichroic mirror and detected onto two InGaAs detectors (PD3 and PD4). Interference effects, due to the fact that a large number of modes can, in principle, be supported by the multimode fiber, do not significantly degrade the absorption signals. Total losses of the system, from the laser fiber output to the collimated output from the multimode fiber, are similar for the two wavelengths and amount to about 8 dB, including the 0.3 dB loss due to the beamsplitter. Most of the losses (more than 5 dB) occur in the interaction region, even in absence of flow, due to the critical operation of collimating and re-launching radiation in a second fiber after a beam-path of more than 20 cm.

Experimental results and conclusions

The sensor has been tested at Solfatara volcano, Pozzuoli, near Naples, in Italy.

The collimated radiation interacts with a jet of hot gas from the ground, at a temperature of about 160 °C. The gas contains a large quantity of water vapour (about 80%), about 20% of CO_2 and trace amounts of many other components, like CO and H_2S. The gas composition puts enormous problems to any optical system, for many reasons. First of all, water vapour easily condensates wherever temperature decreases below 100 °C, not only forming fog on the optics, but also large amounts of liquid phase water. Moreover, simultaneous presence of sulphur and water takes to efficient formation of sulphuric acid on any device around the fumarolic emissions. Besides this difficult chemical-physical framework, it must be taken into account that small sized rock particles may be ejected by the fast fumarolic flows. It is therefore evident that very stringent requirements must apply to all the experimental set-up.

Remote operation with optical fibers is the only way to leave all the instrumentation at a safe distance. Kevlar coating of the fibers has demonstrated to be very resistant to chemical offences, enhanced by the high temperature of the ground, up to about 70-80 °C, where fibers lie.

One of the most difficult problems to solve was the design of the gas-radiation interaction region. Two different approaches can be basically used. One is an open-path configuration, in which the gas freely flows through the interaction region, without any special constraint. The main drawback of this choice is that the measurements would strongly depend on external atmospheric conditions. Also, when the stainless steel block with the two fiber ports is held just inside the fumarolic flow, a drastic decrease of the device lifetime can be easily forecasted, due to the very extreme conditions. The other approach consists in constraining part of the flow into a tube, which terminates with a cell, equipped with two transparent windows. The cell fits the interaction region between the two ports.

A recording of a water vapour line, with an open-path scheme and the apparatus close to a moderately flowing emission, is shown in Fig. 2.

The line scan is performed by current tuning of the laser. This allows scans as wide as 15 GHz to be performed with short scan time of the order, typically, of a few milliseconds. Such wide scans are required to fully record the very broad absorption profiles.

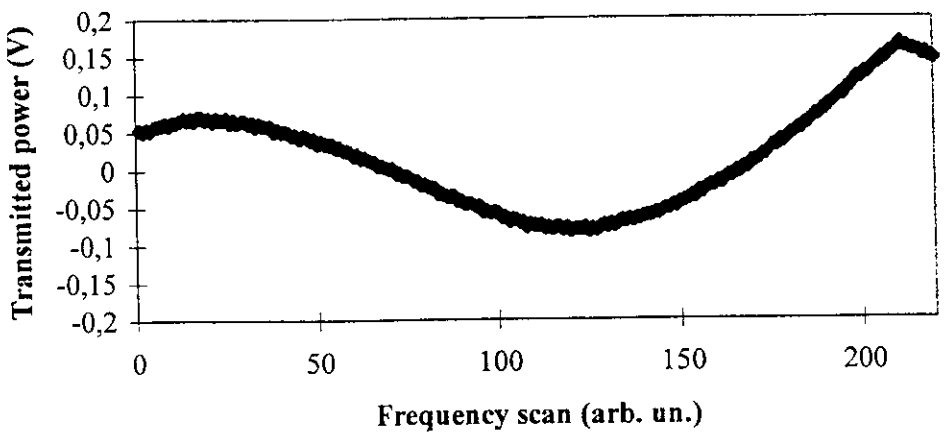

Fig. 2. Example of water vapour detection in a moderately flowing emission at Solfatara volcano, using an open path scheme.

This is mostly due to the pressure broadening because of the strong cross-section of water vapour [1]. The effect of linear modulation of the laser current on the transmitted intensity baseline can be seen even if a dual beam scheme has been used.

Choosing a properly working design for a constrained flow has been very hard. An all-glass tube and cell design demonstrated quite convenient, due to the excellent chemical properties of the glass, the easy of cleaning from condensed substances, the resistance to temperature changes, the possibility to easily solder the transparent windows on the cell, without any special holder. A very difficult task was the choice of a design which does not decrease too much the flow temperature. In particular, the flow temperature inside the cell must be greater than 130 °C. Indeed, below about 130 °C and 100 °C the condensation of sulphur compounds and water vapour, respectively, occurs. In this case, the propagation of the laser beams is not allowed.

In Fig.3 is shown a water vapour line recorded in the presence of a strong flow inside a glass cell operating with an external heating, to maintain windows temperature always above 130°C. The flow reached the cell after a 1.2 meters path inside a dewar glass tube, made with two concentric tubes, the inner one being separated by the external one, and soldered at the extremes. This allows to minimize thermal losses of the flow.

Even if all these preliminary tests of the apparatus were performed using a portable generator, the final goal is to build a spectrometer able to operate for as long time as possible without resorting to line supplied power. In this respect, diode lasers are ideal, due to the extremely low power requirements. A battery operated system, with possible solar panel integration, could be built, with continuous operation of several weeks. On the other side, heating the cell is very power consuming. Therefore, we have recently built and successfully tested a cell which allows spectrometer operation without any external heating nor thermal insulation. In this case, the windows of the cell were efficiently kept above 130 °C using the fumarolic emission as heating agent.

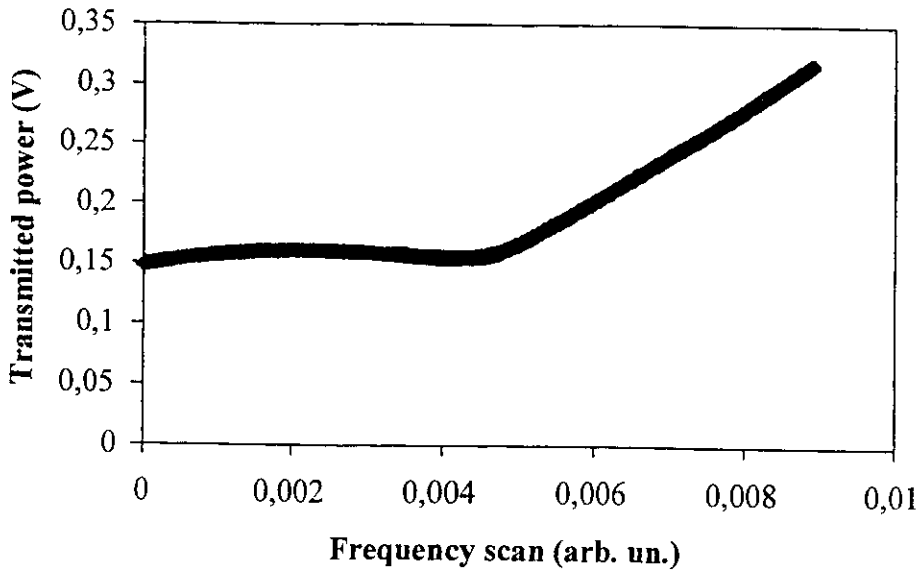

Fig. 3. Water vapour absorption in the presence of gaseous emissions strongly flowing inside the sample cell, at Solfatara volcano.

In conclusion, we have built a new kind of laser based spectrometer, able to operate in extreme environments and for simultaneous detection of different molecular species, with extremely reduced power requirements. The apparatus has been successfully tested for several months at Solfatara volcano, near Naples, paying special attention to materials' resistance and durability and to the design of the interaction region.
Some preliminary recordings for water vapour lines have been shown. At present, we are working on the calibration of the apparatus in order to provide an accurate concentration measurement for H_2O and CO_2. Also, we are going to use wavelength modulation techniques to improve the signal-to-noise ratio for weaker lines, eventually belonging to less abundant species, as is the case of $^{13}CO_2$ or $C^{18}O^{16}O$.

References

[1] Gianfrani L., Gabrysch M., Corsi C., De Natale P., "Detection of H_2O and CO_2 using DFB lasers: measurement of broadening coefficients and assessment of the accuracy levels for volcanic monitoring" Applied Optics, **36,** 9481-9486 (1997).

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