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Portable Laser Based Mid-IR Gas Sensors: Development and Real-World Applications

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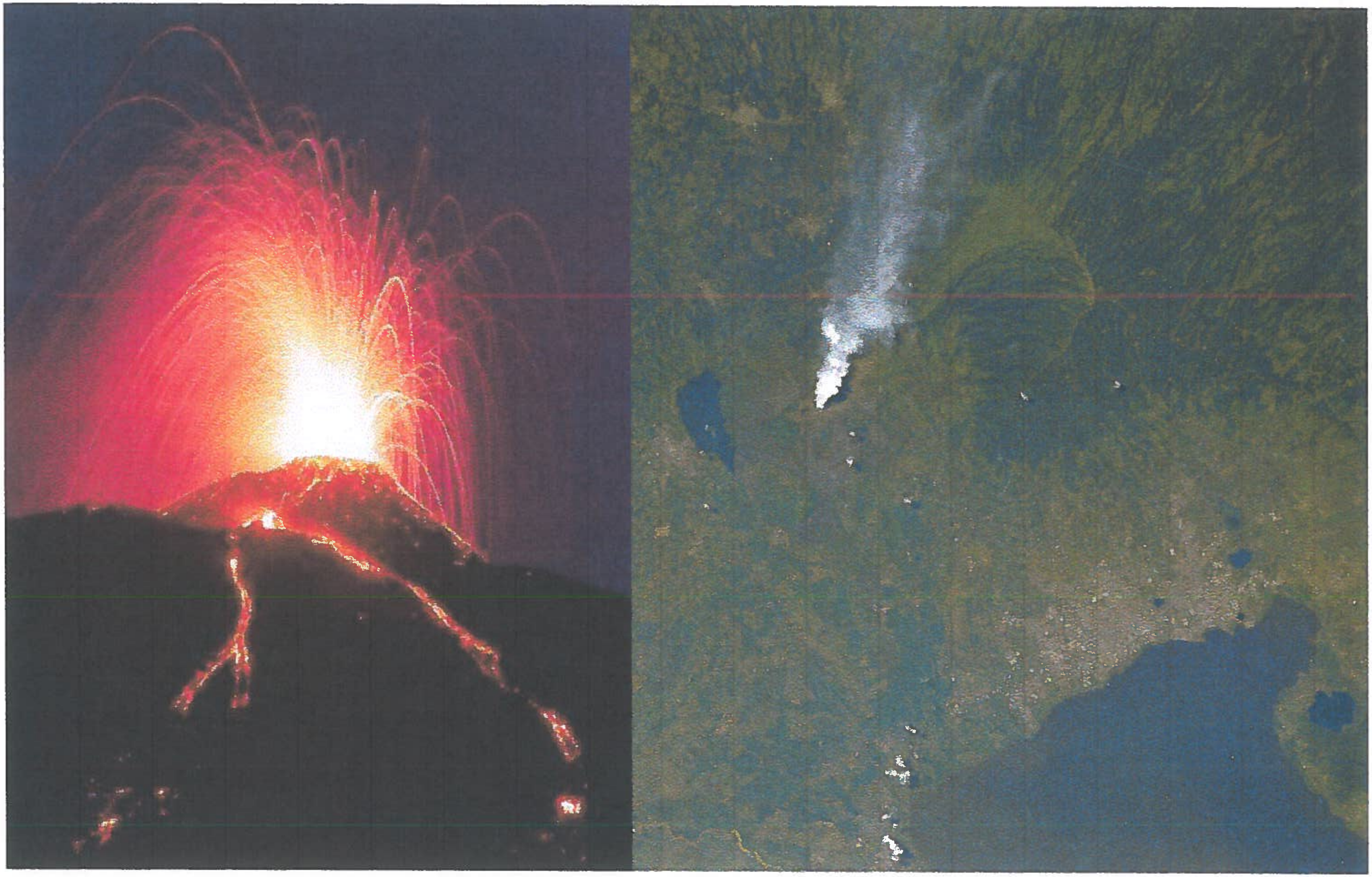
2001 Annual Meeting of the American Chemical Society, Chicago, Illinois
"The World According to Process Analytical Chemistry"
Thursday, August 30, 2001

Extensive Ground and Airborne Studies

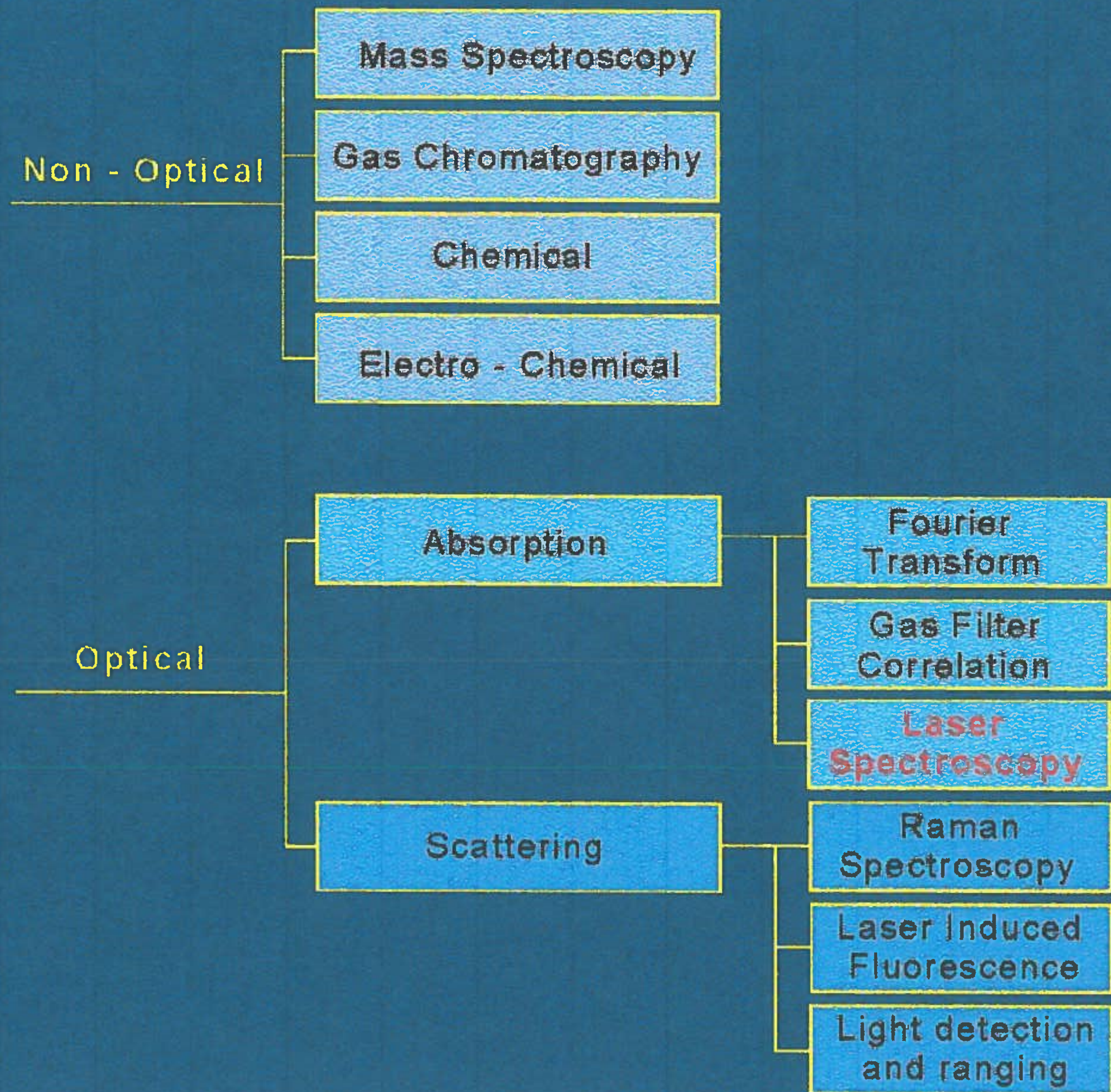
Volcanic Gas Emission Studies



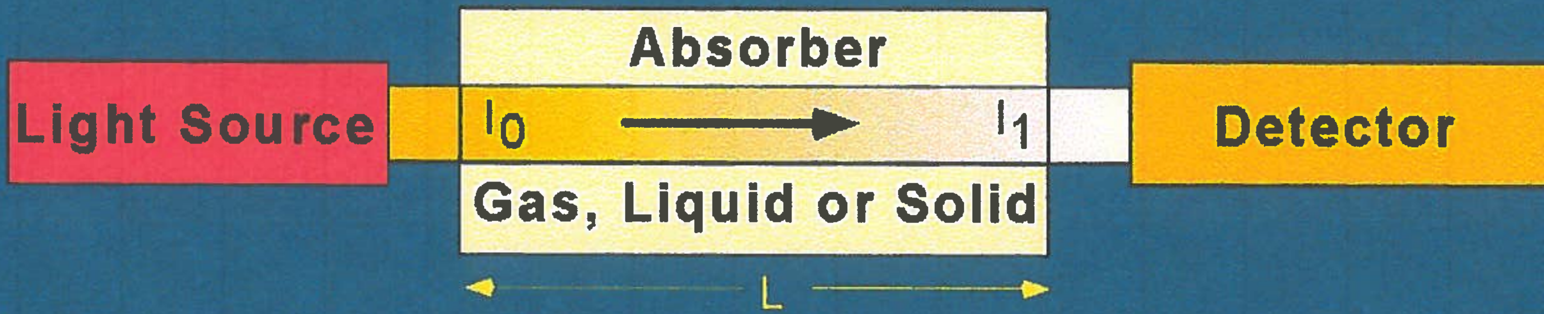
Wish List for Trace Gas Detectors

- Compact, rugged and portable
- Sensitive
- Selective
- Wide dynamic range
- Multiple-species detection
- Real-time
- Room-temperature operation
- No consumables
- Auto-calibration
- Some applications: High-precision

Gas Detection Technologies



Direct Absorption Spectroscopy



Beer's Law:

$$I(v) = I_0(v) \cdot e^{-\alpha(v) \cdot L}$$

with

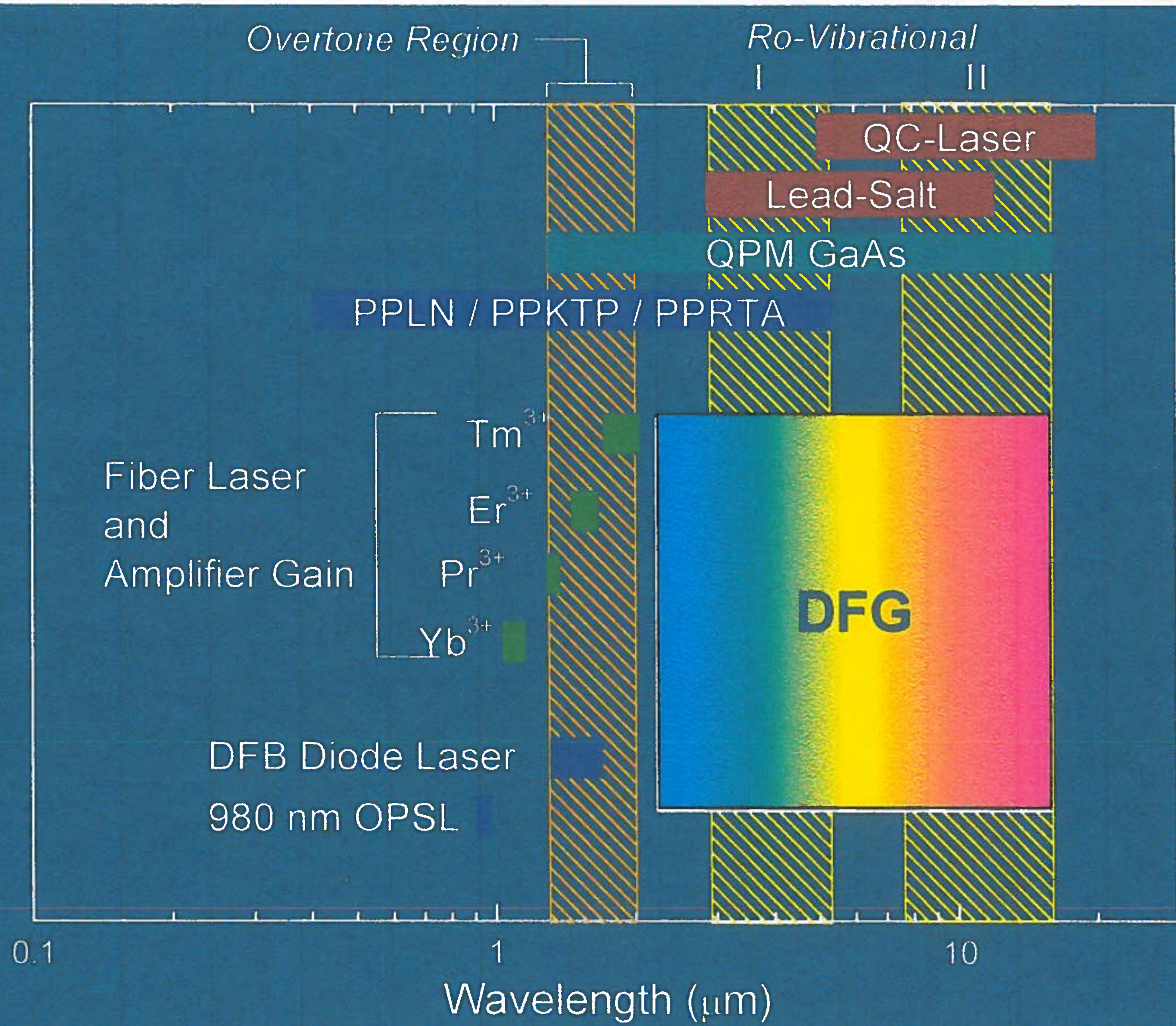
$$OD = -\alpha(v) \cdot L$$

Molecular Concentration:

$$C = \frac{OD_{peak} \cdot \gamma_L \cdot \pi}{S \cdot L \cdot p} \cdot \frac{T}{N_L}$$

OD_{peak} denotes the peak optical density; γ_L, Lorentzian HWHM; S, linestrength; L, optical path length; p, pressure; T, temperature; N_L, Loschmidts' number

Laser Sources and Wavelength Coverage



Sensitivity Enhancement Techniques

- Long Absorption Pathlength

  Non-resonant:
  - Multi-Pass Cell
  - Open Path with Retro-Reflector

  Resonant:
  - Cavity Enhanced
  - Cavity Ring-Down

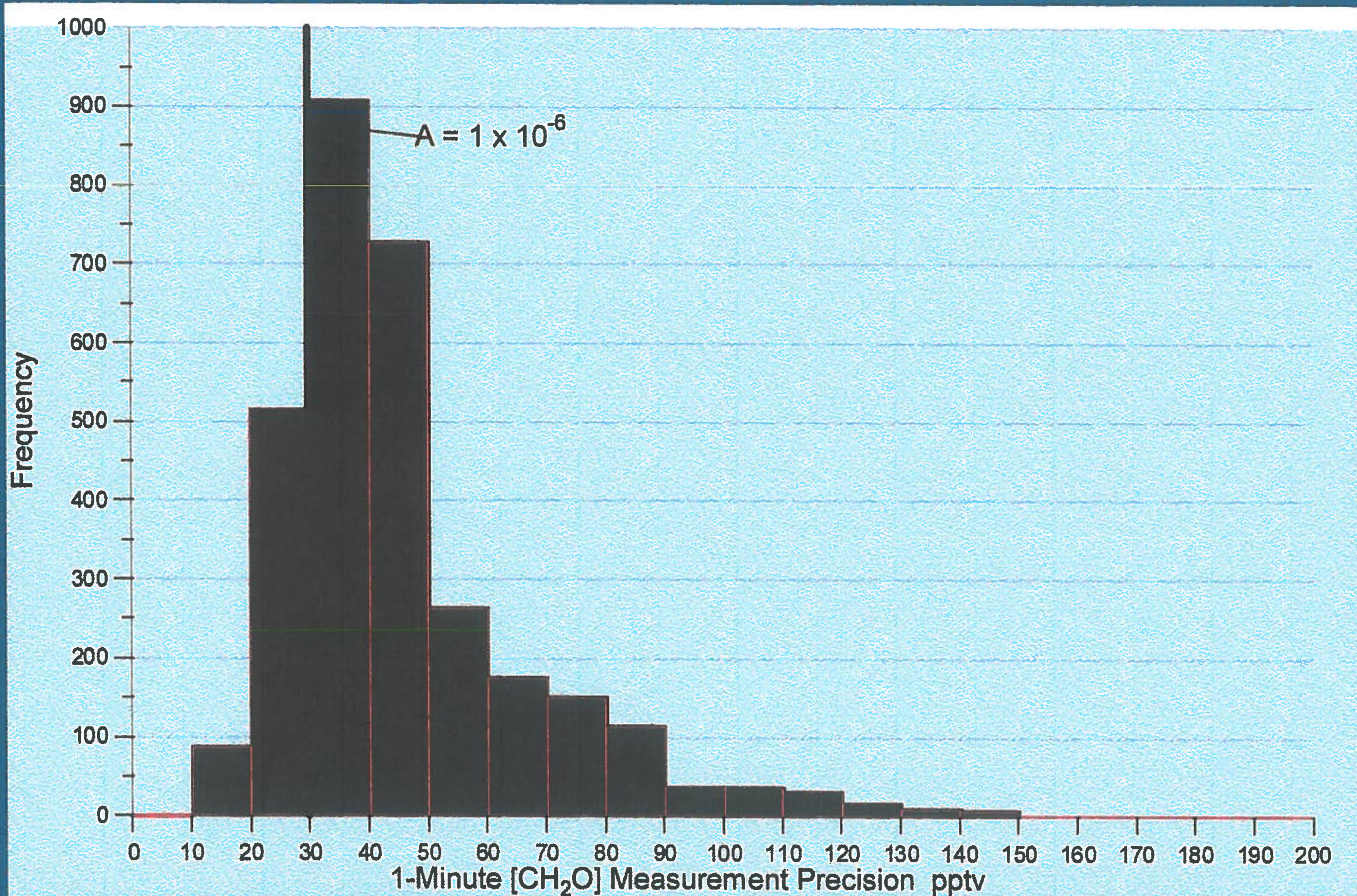
- Mid-IR Detection Schemes
  - Direct Absorption Spectroscopy
  - Derivative Spectroscopy: FM / WM / TTFM
  - Photo-acoustic / Photo-thermal Spectroscopy
  - Balanced Detection: Hobbs / Dual-beam

  In Addition: Zero-Air Subtraction

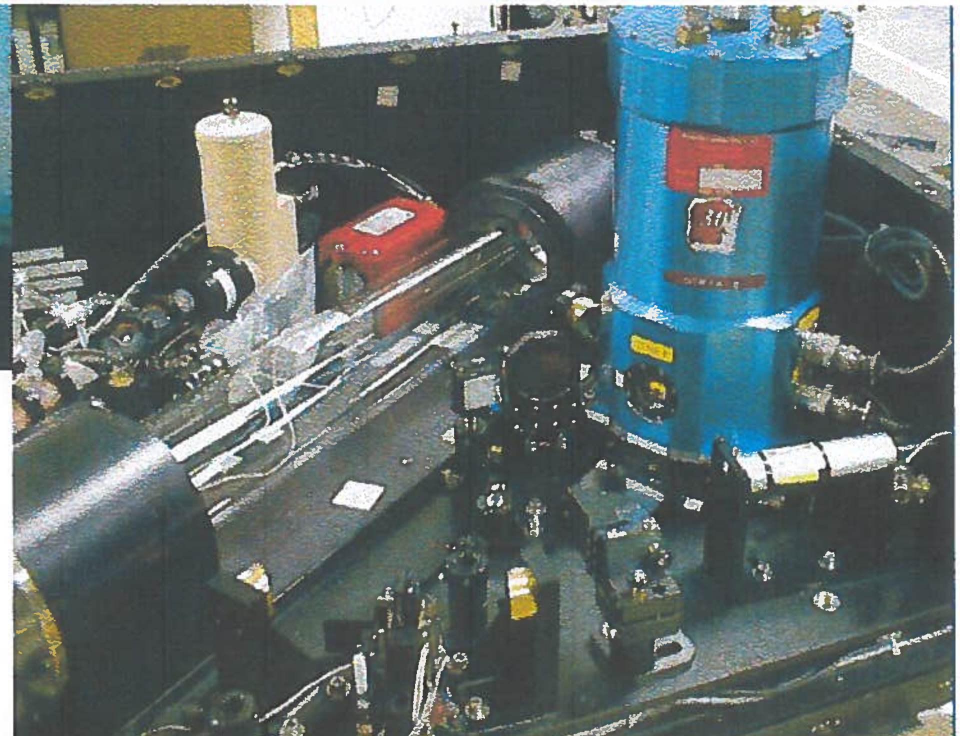
⇒ Match technique(s) to application considering:

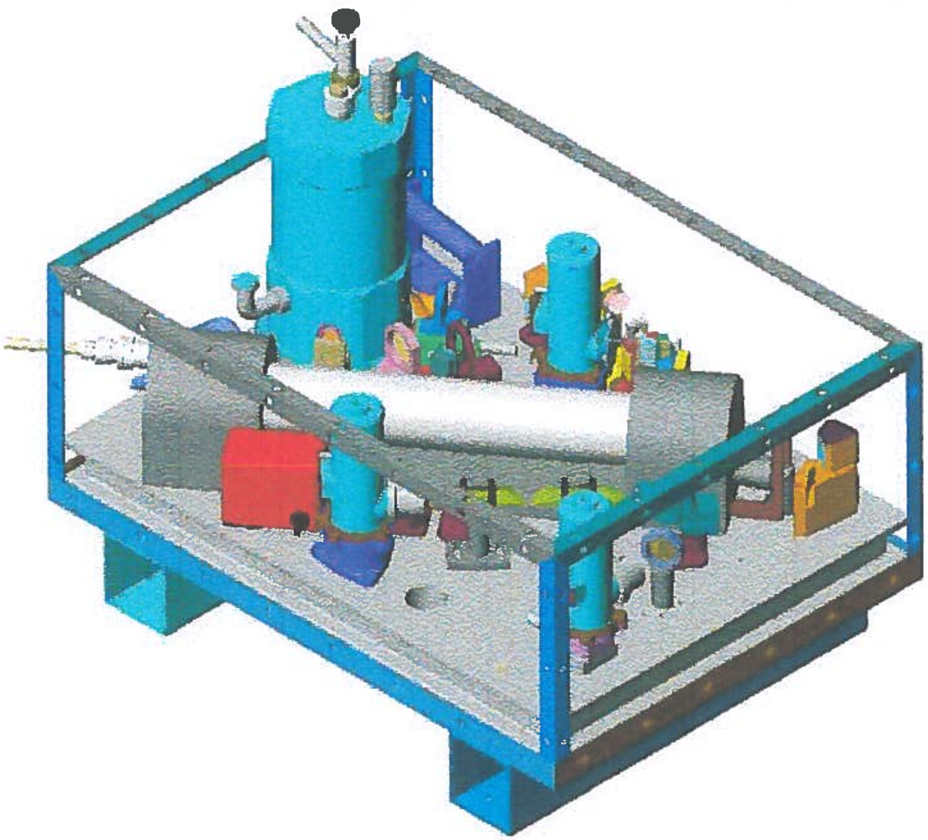
Sensitivity, Dynamic Range, Vibration, Complexity, Gas Composition, Inherent Cross-Sensitivities, etc.

Airborne CH_2O Measurement Precision (1σ) For Entire TOPSE Campaign (N_{total} = 3286 pts)

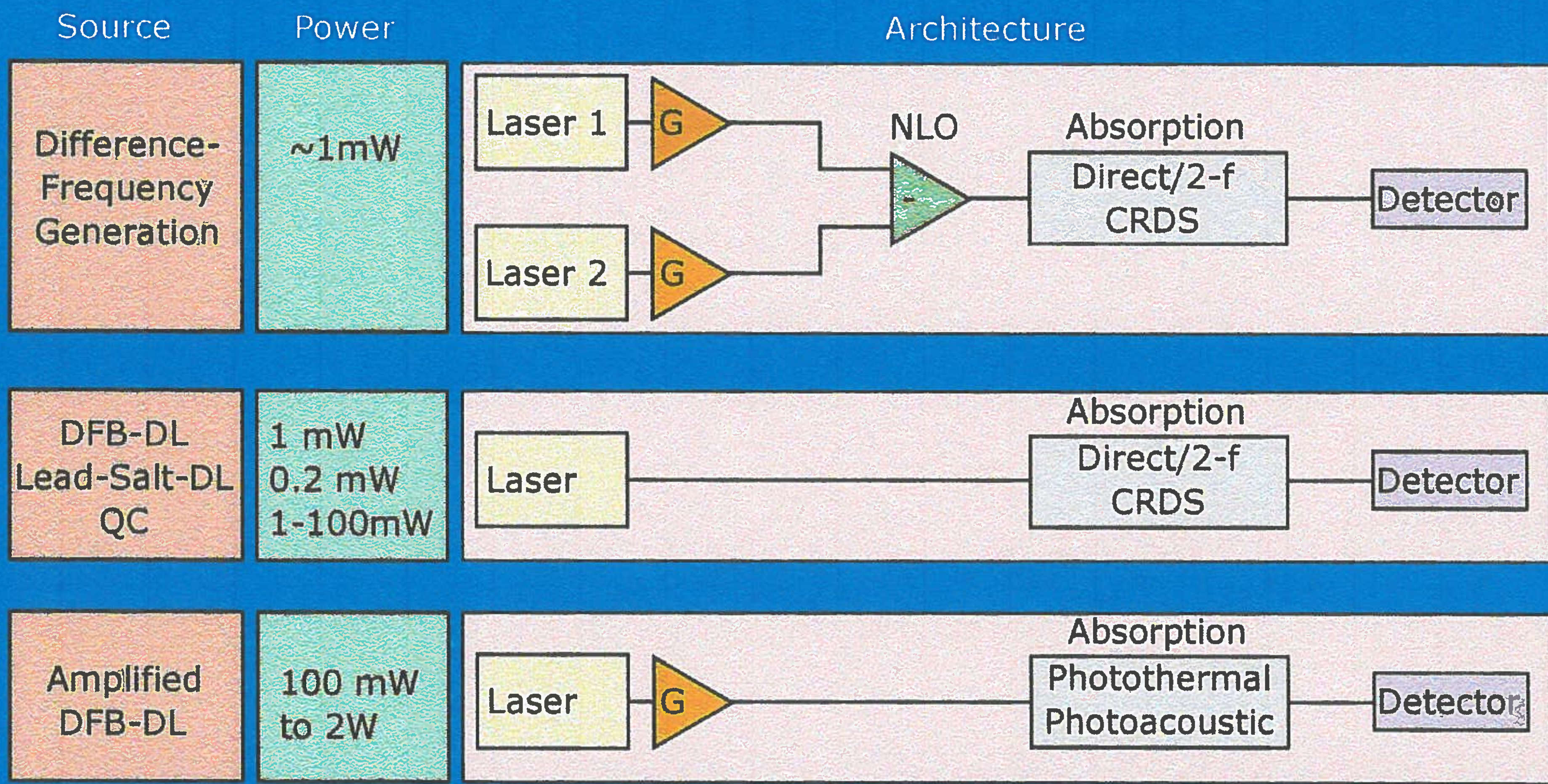


NCAR Dual Channel Airborne Laser System





Overview of sources, optical power and detection enhancing techniques



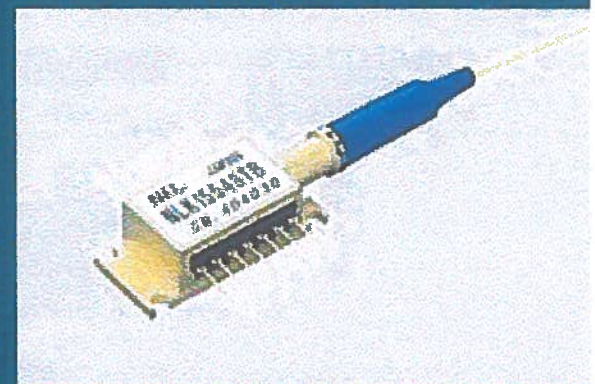
DL: Diode Laser / QC: Quantum Cascade Laser / DFB-DL: Distributed Feedback Diode Laser
G: Gain Block; Fiber Amplifier / NLO: Non-linear optical frequency mixing
CRDS: Cavity Ring-Down Spectroscopy / 2-f: Wavelength modulation spectroscopy

Diode Lasers, DFG and Molecules

Diode Lasers:

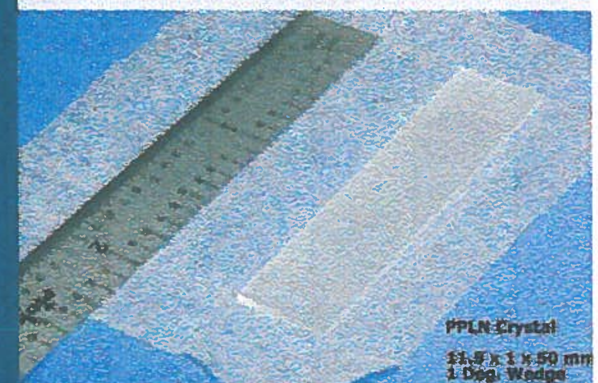
Desirable characteristics for spectroscopy

- Stable/reproducible frequency, easy to modulate
- Narrow linewidth (<MHz)
- Low RIN –165 dB $Hz^{-1/2}$
- Room temperature operation
- Compact and rugged (MTBF=10 - 100 years)



DFG: Difference Frequency Generation

- NIR diode lasers can be shifted into the spectroscopically important 3-5 μm region



Molecules:

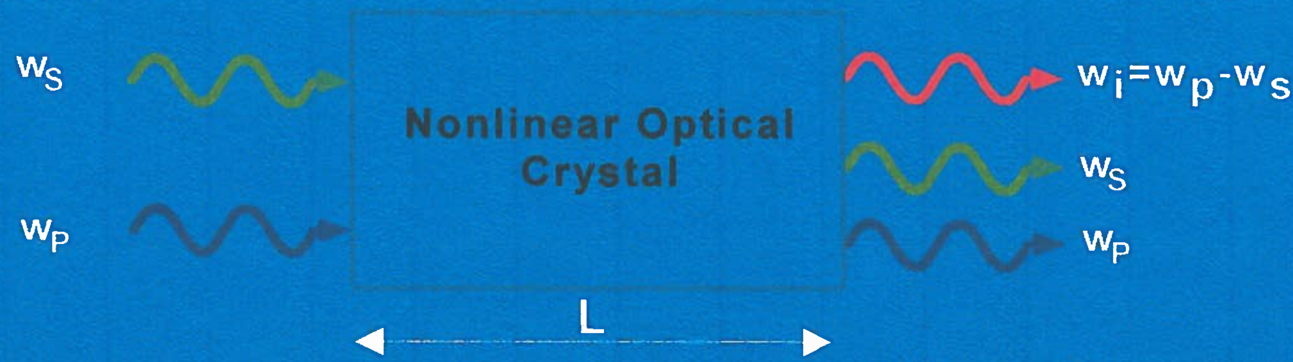
Strongest absorption in the spectroscopic 'fingerprint' 2-20 μm region

- Detected to date: 13 species including CH_4, H_2O, N_2O, NO_2, NO, NH_3, H_2CO, CO, CO_2, HCl, CH_3OH, SO_2, C_6H_6

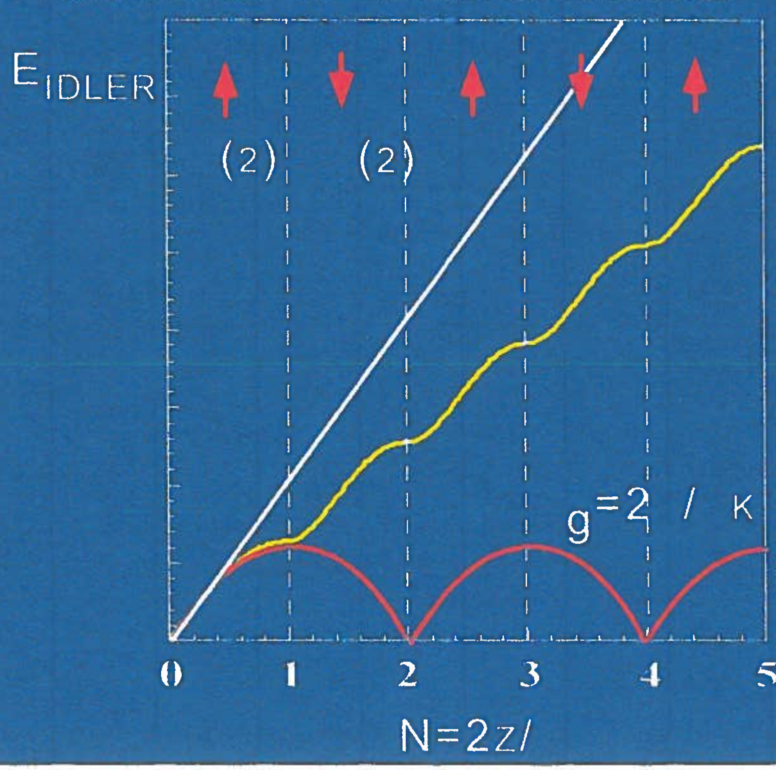
Fiber Optic Amplifiers

Dopant	Emission λ(nm)	Pump λ (nm)	Transition	Slope Efficiency (%)
Nd	900 - 950 1050 - 1100	810	3 - 4 level	50
Yb	970 - 1160	915 / 975	3 - 4 level	90
Er	1520 - 1590	980 / 1480	3 level	60
Pr	1280 - 1340	980-1030	4 level	14
Er/Yb	1520 - 1590	975 1010-1100	3 level	45
Tm	1600 - 2100	810 / 1600	3 level	36 / 70

Difference Frequency Generation



Quasi-Phase Matching:



Power: $P = C \cdot P_{pump} \cdot P_{signal} \cdot L$

> 1 mW with 0.46 W x 1.25 W pump and 5 cm long PPLN

- Pump beam quality is retained
- Largest d_{eff} (4.5 x of B.F. $LiNbO_3$)
- QPM: Any frequency mixing within crystal transparency (PPLN: 0.4–5 μm)

Unique Advantages of DFG

- High-power and narrow-linewidth
- **Spatial beam characteristics**
- Flexibility and tuning coverage
- Self-compensation of temperature induced drifts
- All optical telecommunication components

Superior, compact tunable laser source from 2.3-4.6 μm

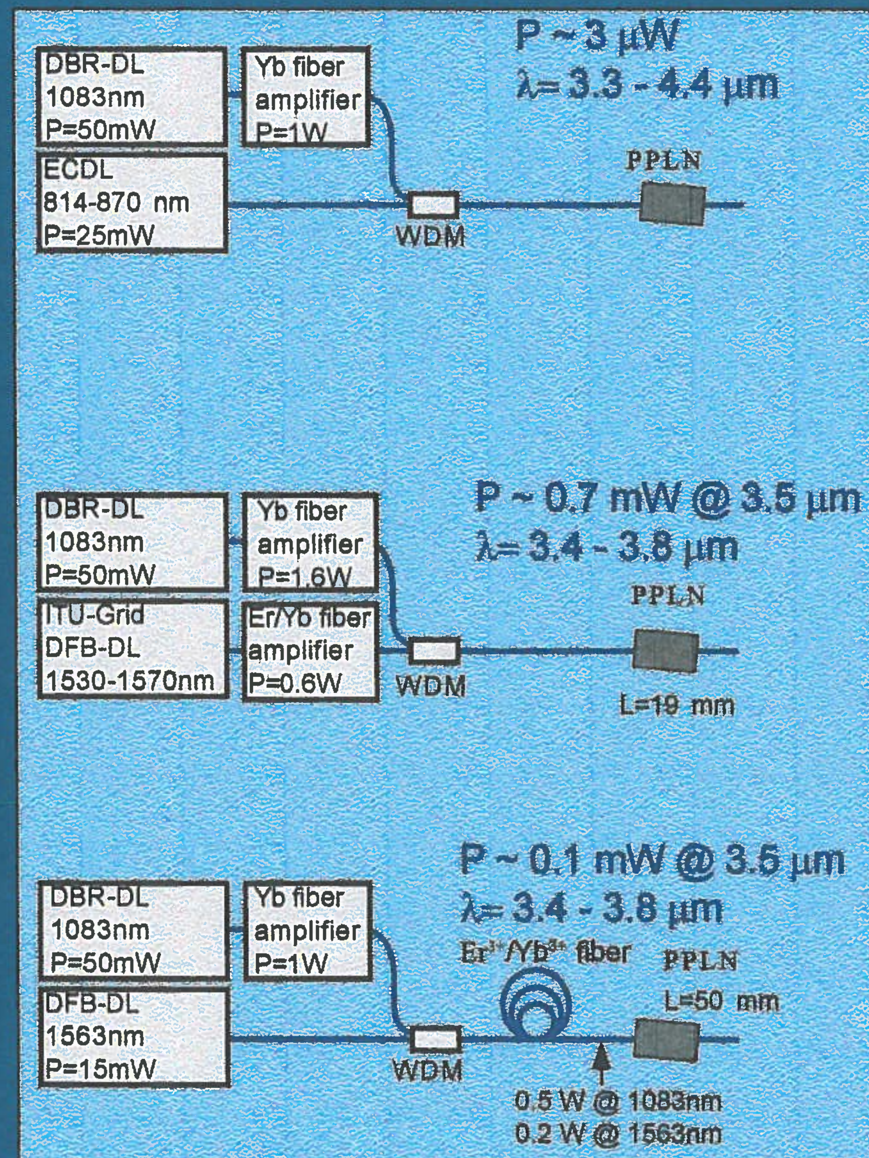
Two DFG Based Gas Sensing Approaches

Multi-species detection:

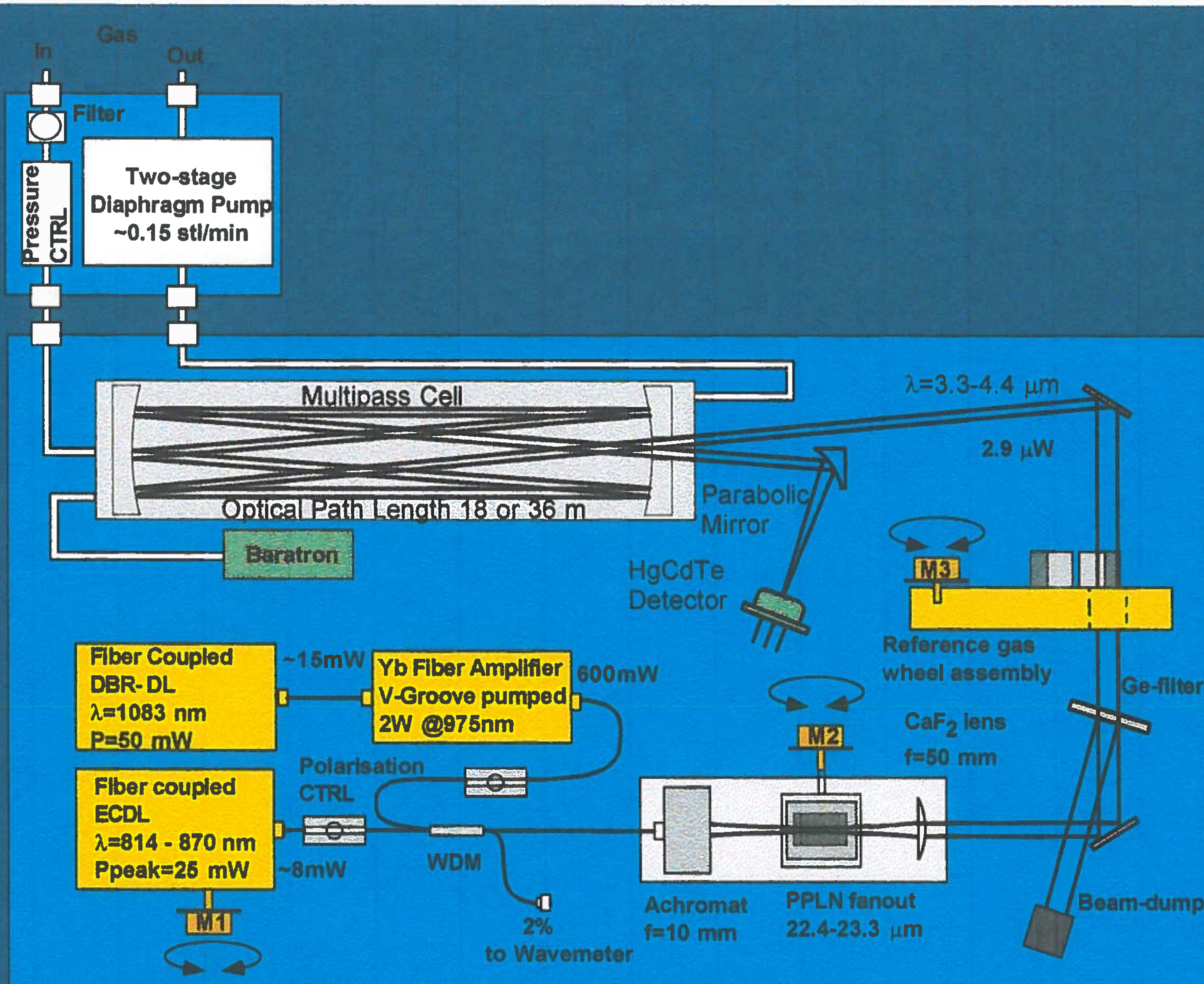
- widely tunable:3.3-4.4μm
- moderate DFG power
- good sensitivity

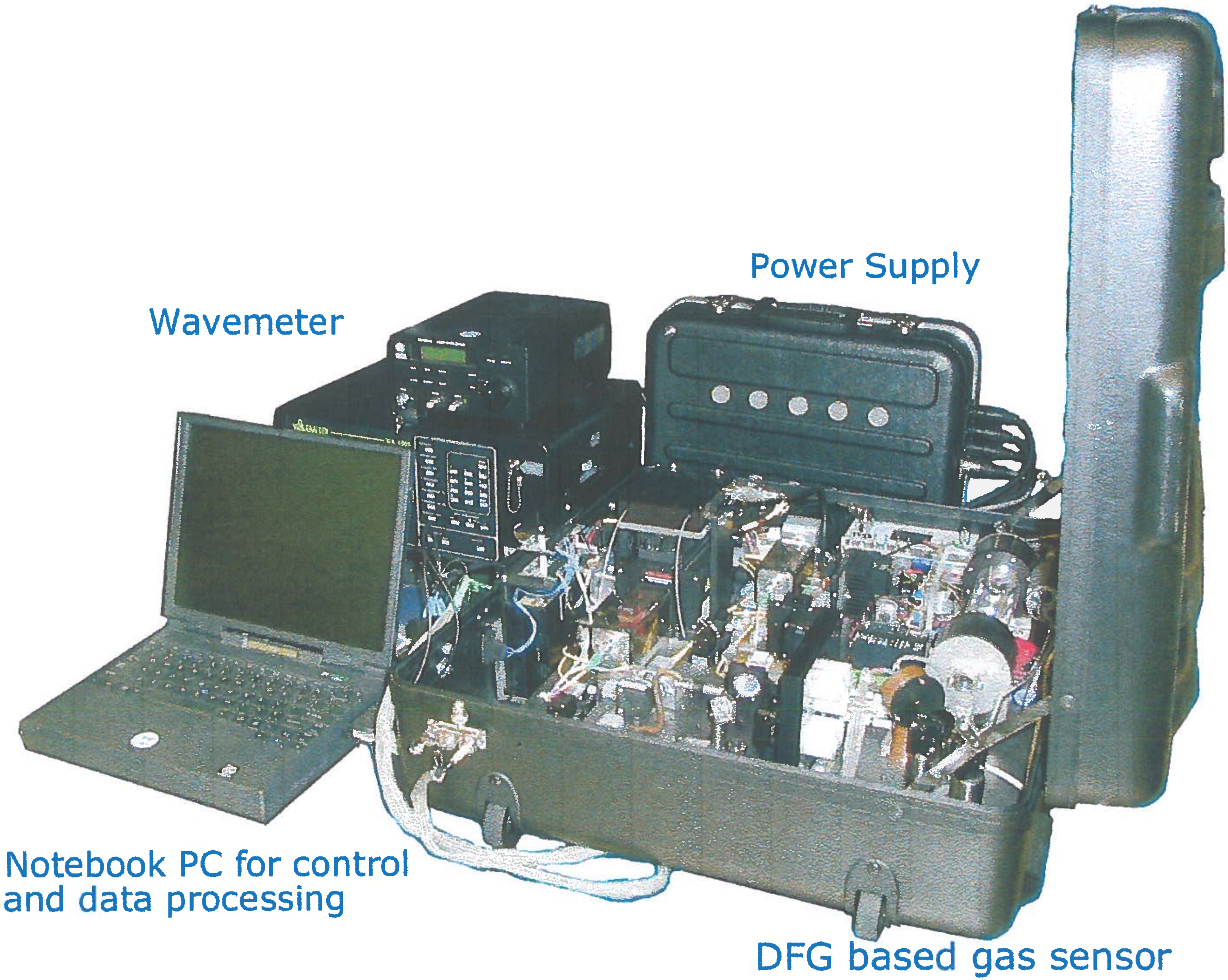
Single-species detection:

- ITU-diode laser selection
- high DFG power
- high sensitivity

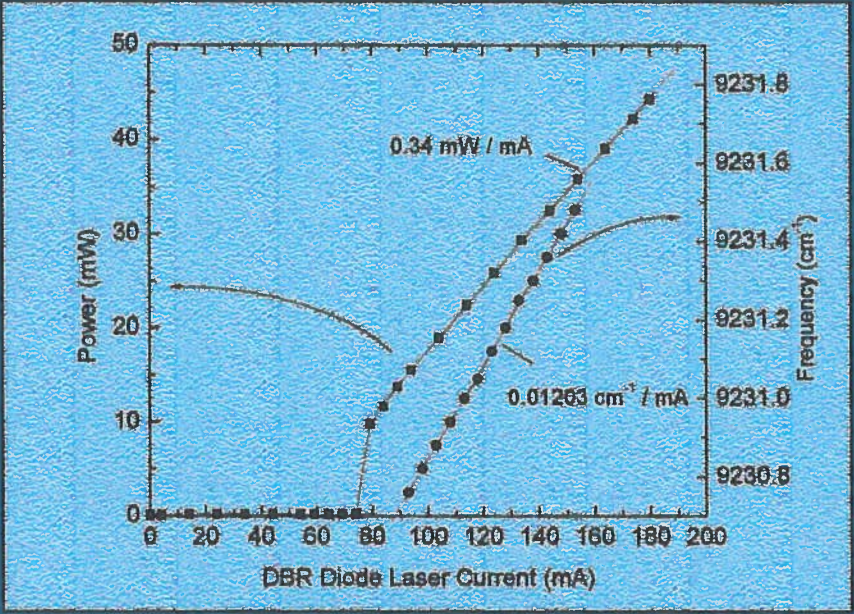


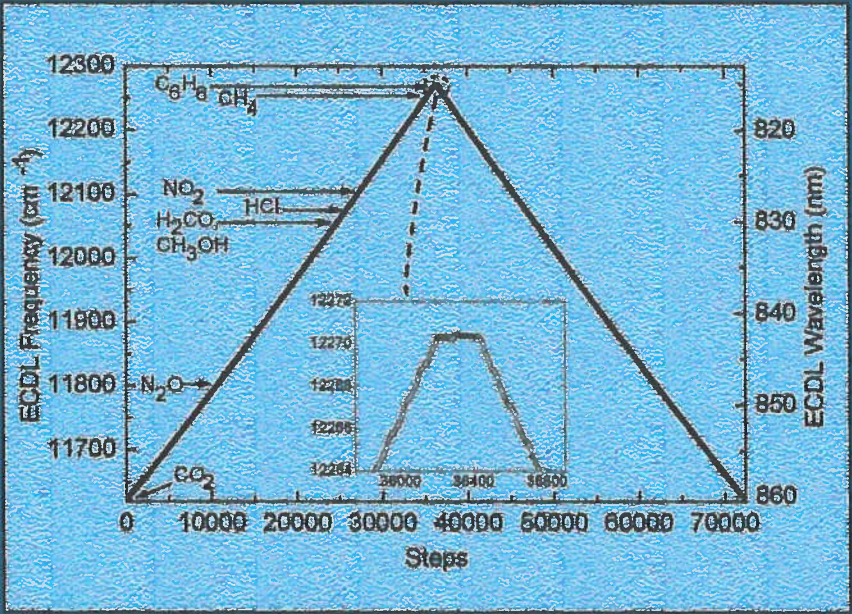
Schematic of Tunable DFG Based Gas Sensor

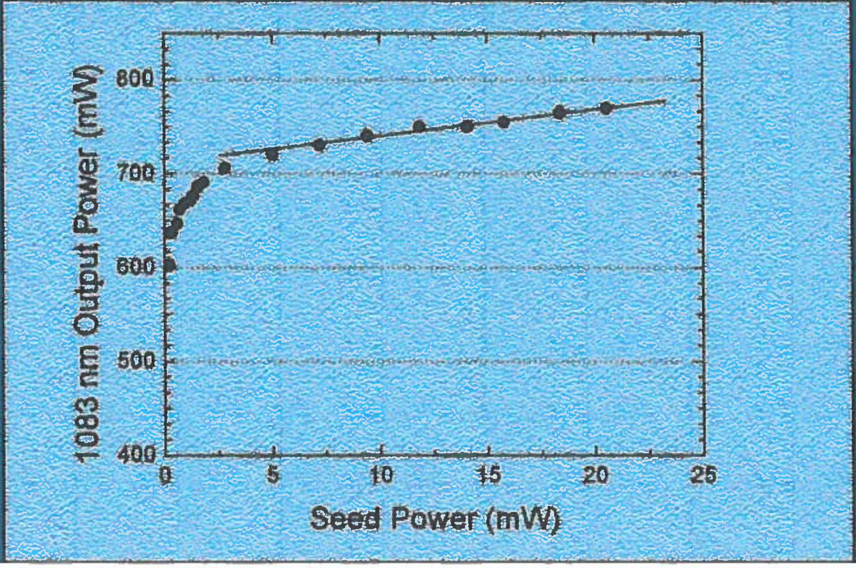


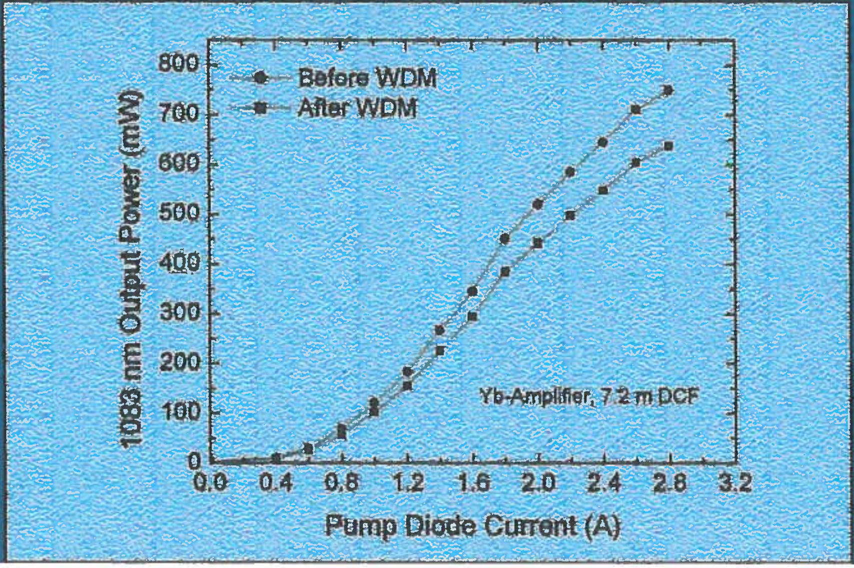

Wavemeter
Power Supply
Notebook PC for control
and data processing
DFG based gas sensor

Characteristics of Diode Lasers and Yb Fiber Amplifier

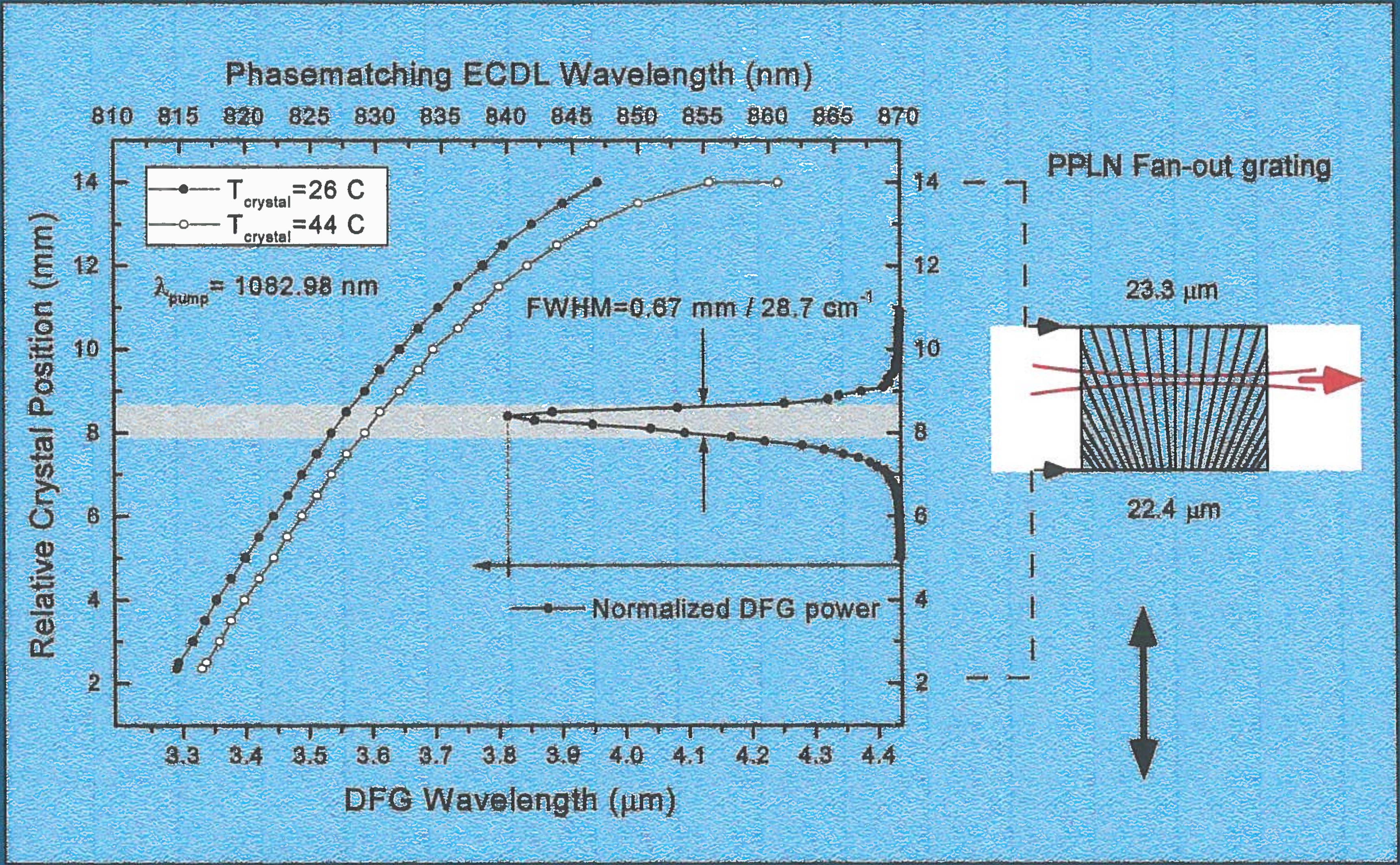




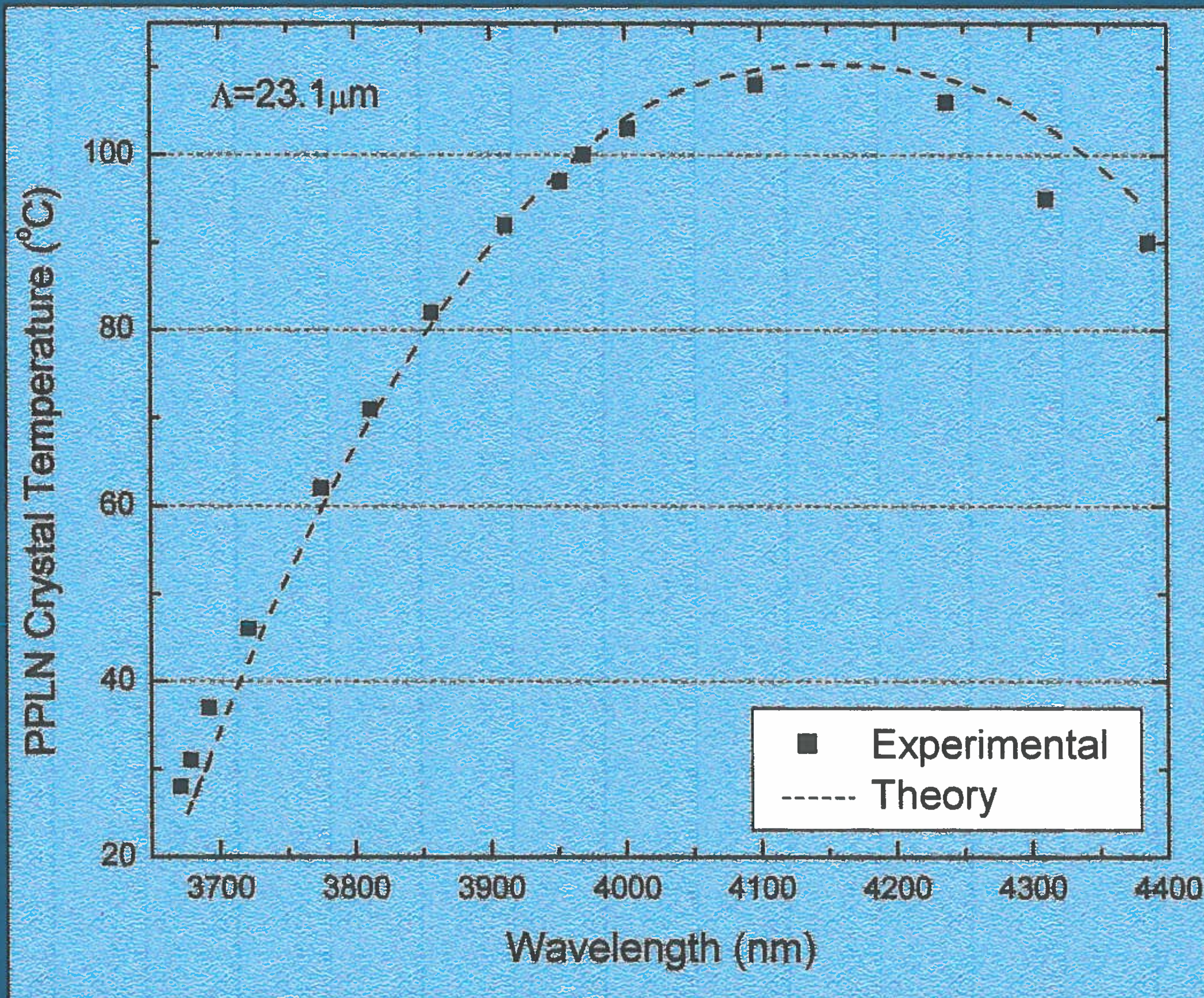




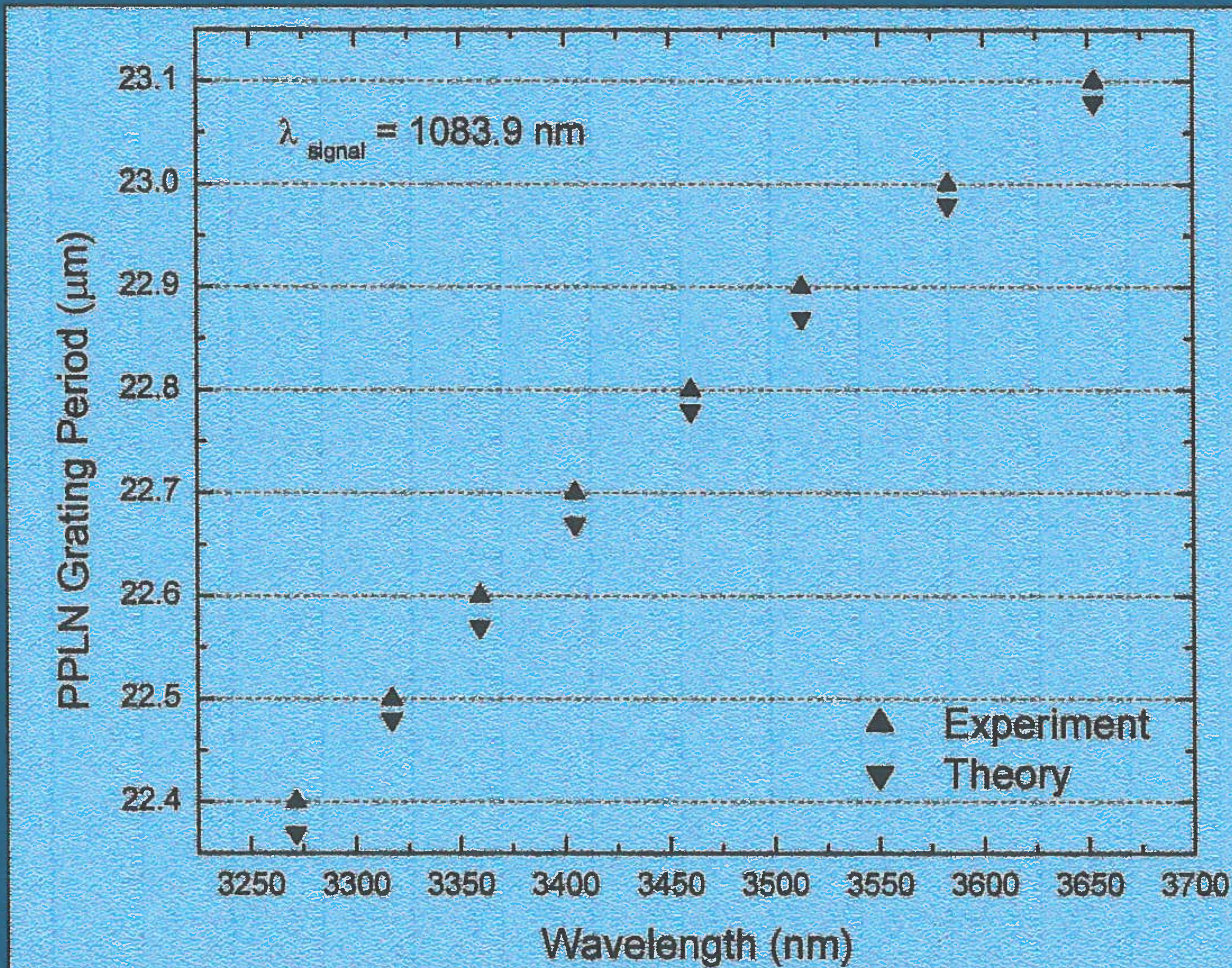
PPLN QPM Approaches III



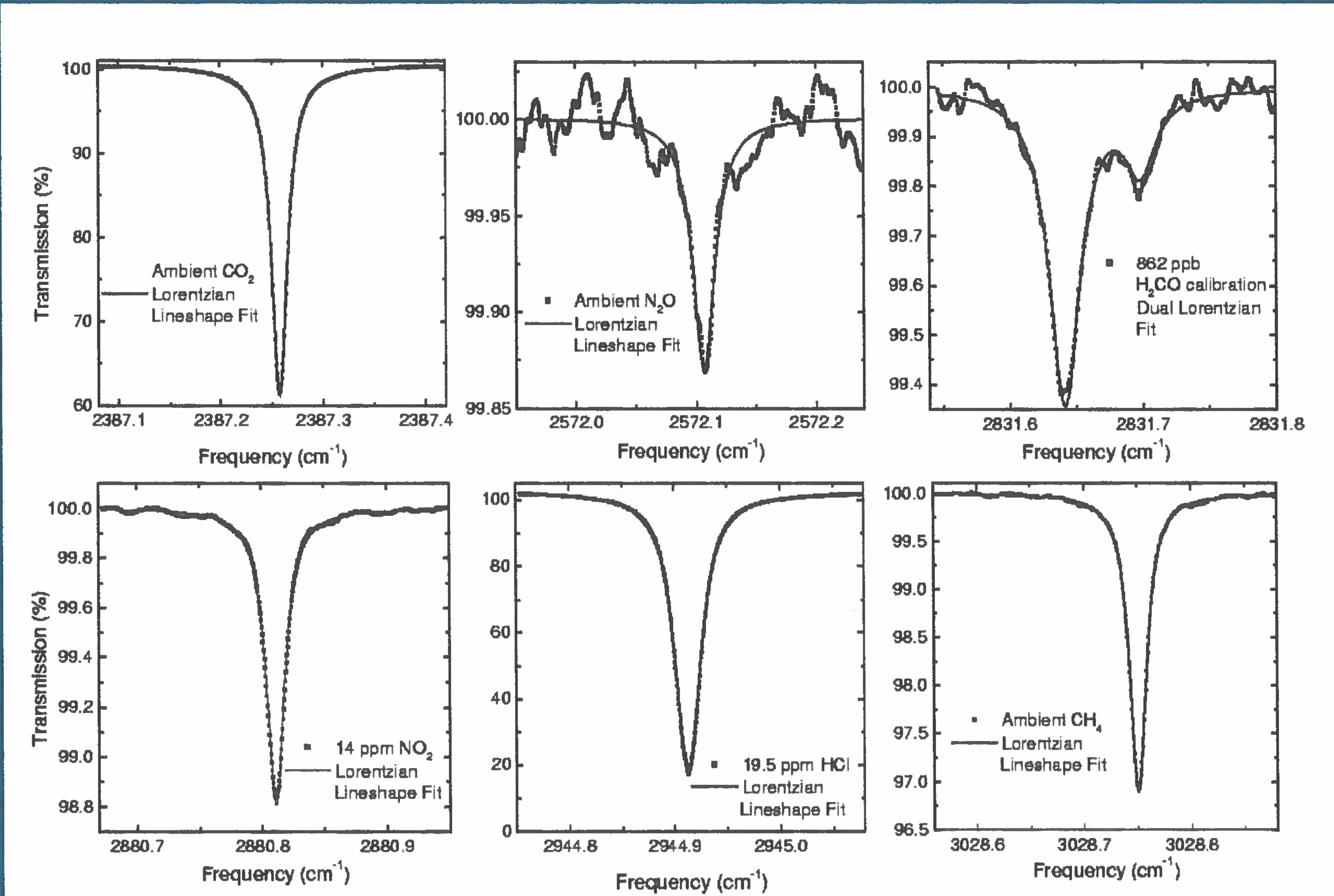
PPLN QPM Approaches I



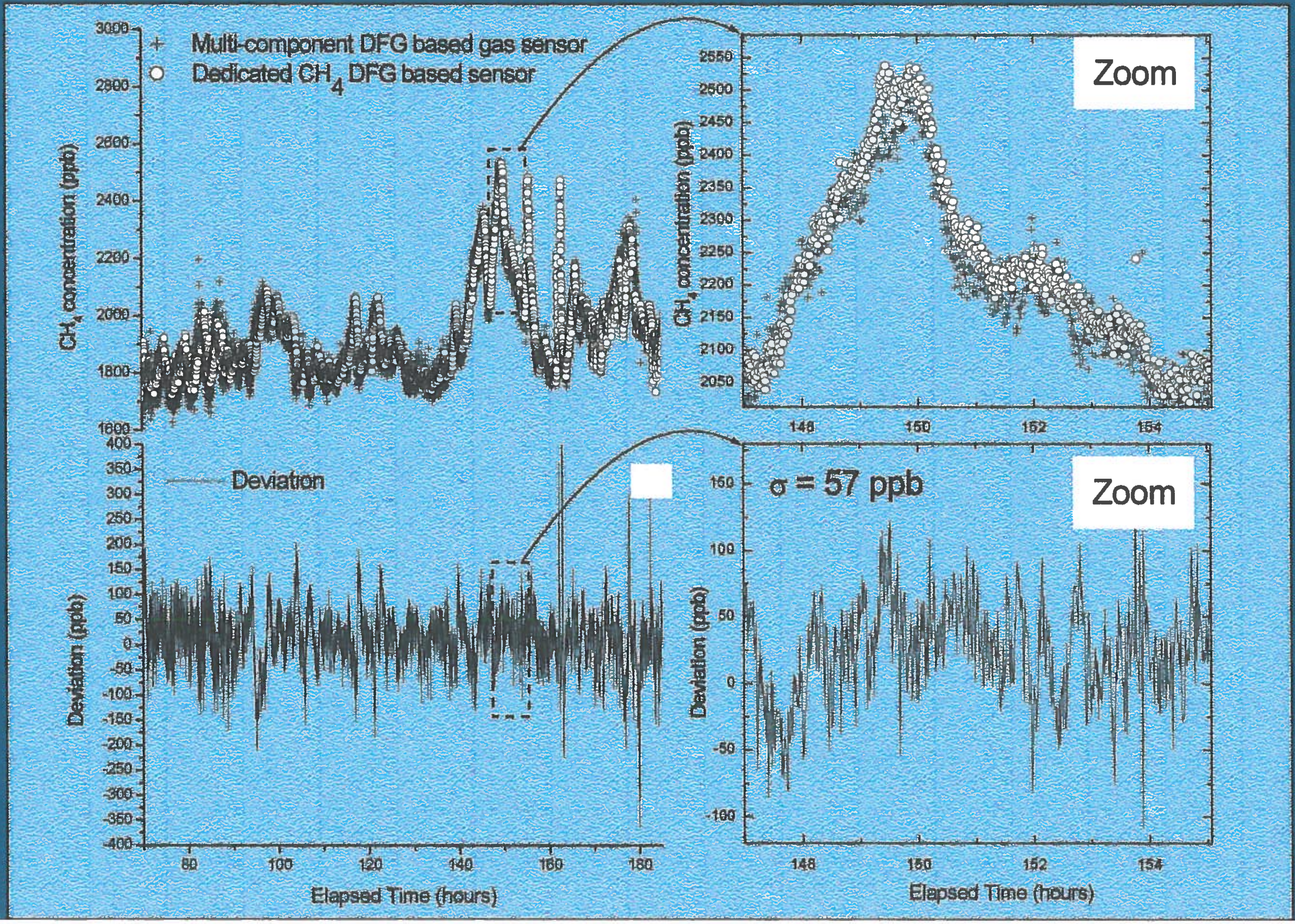
PPLN QPM Approaches II



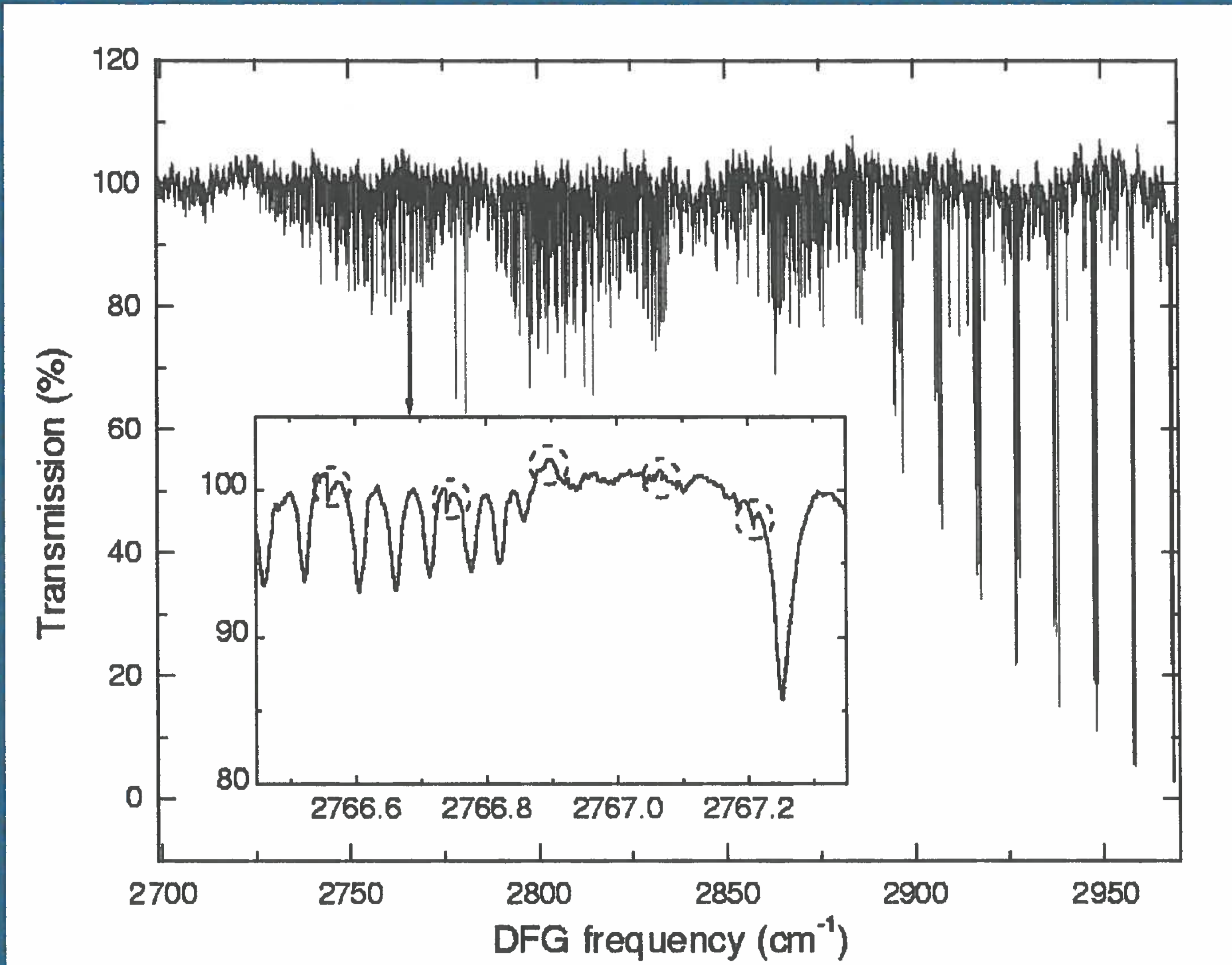
Individual Spectra of CO_2, N_2O, H_2CO, NO_2, HCl, CH_4



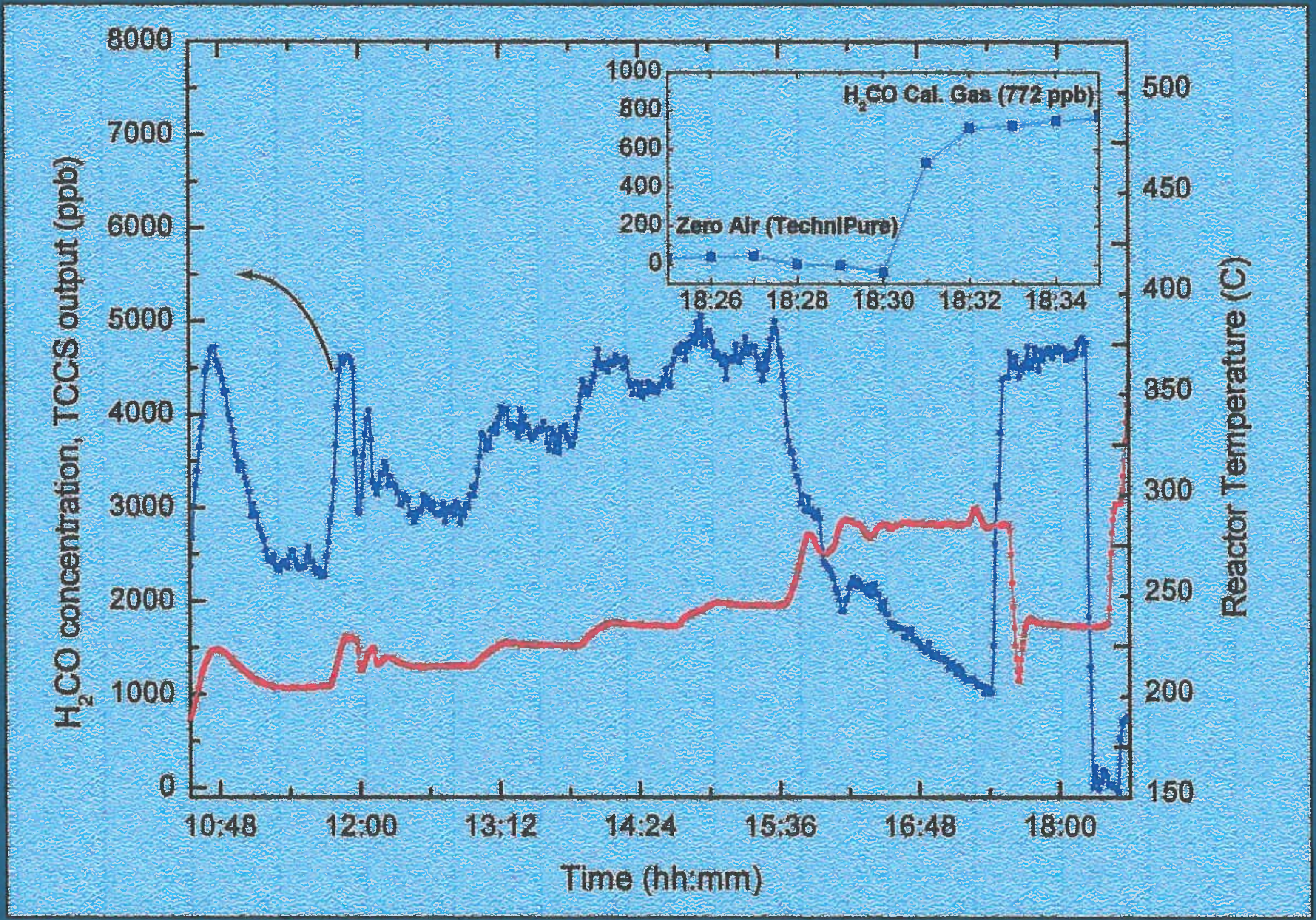
Intercomparison of Two DFG Sensors



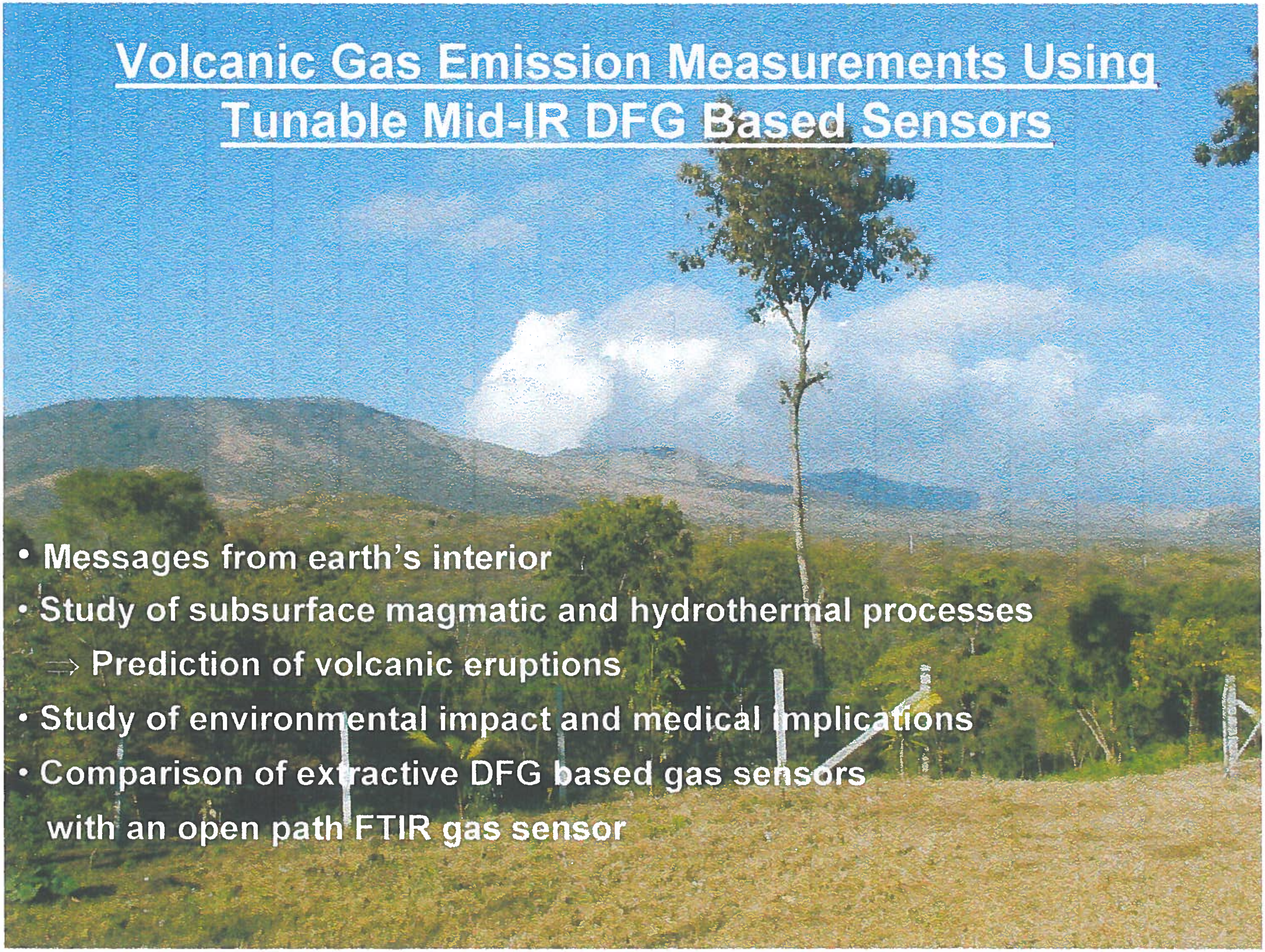
Continuous Absorption Spectra of Formaldehyde and Methane Over 270 cm^{-1}



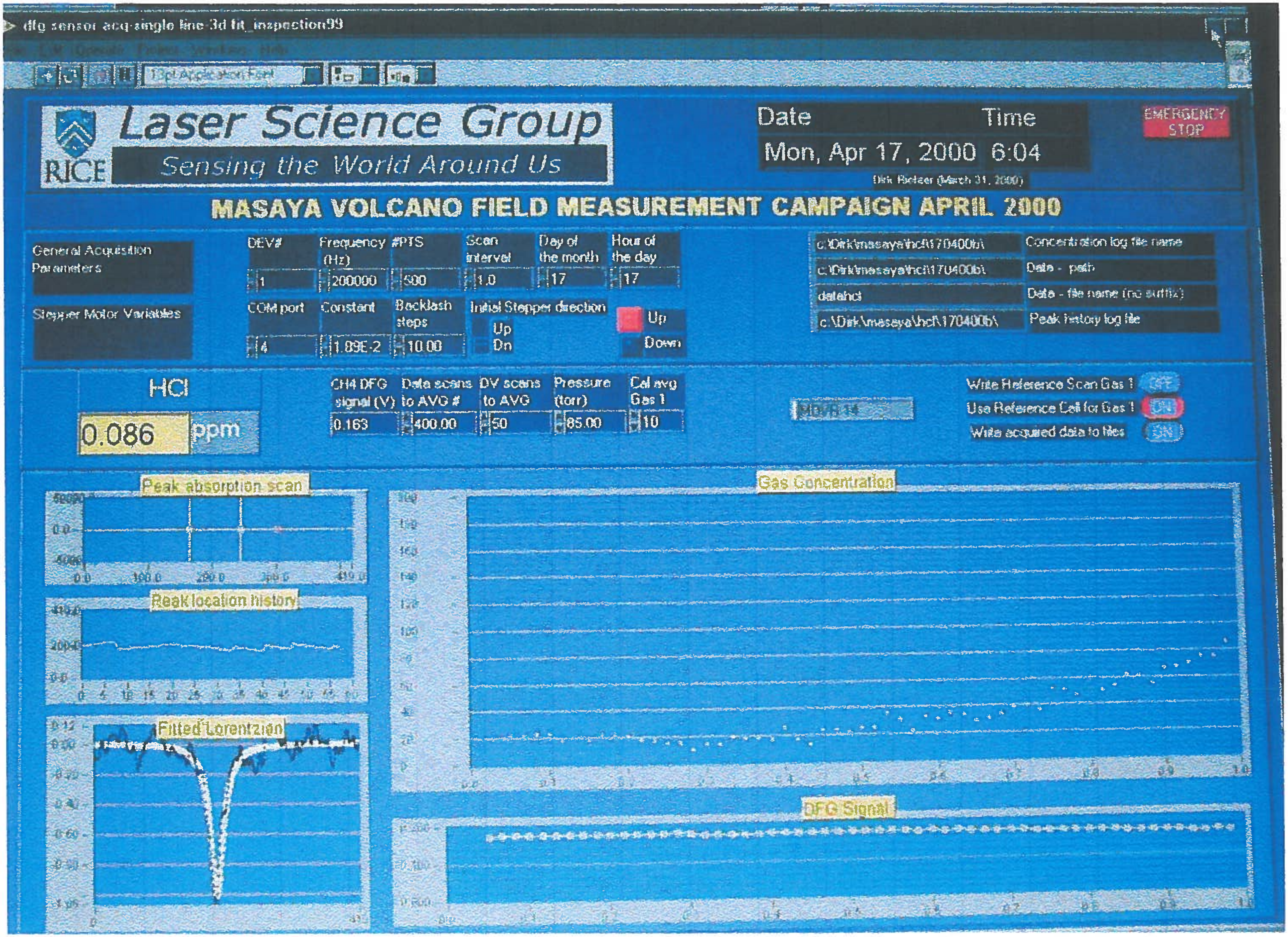
H_2CO Concentration in NASA TCCS



Volcanic Gas Emission Measurements Using Tunable Mid-IR DFG Based Sensors



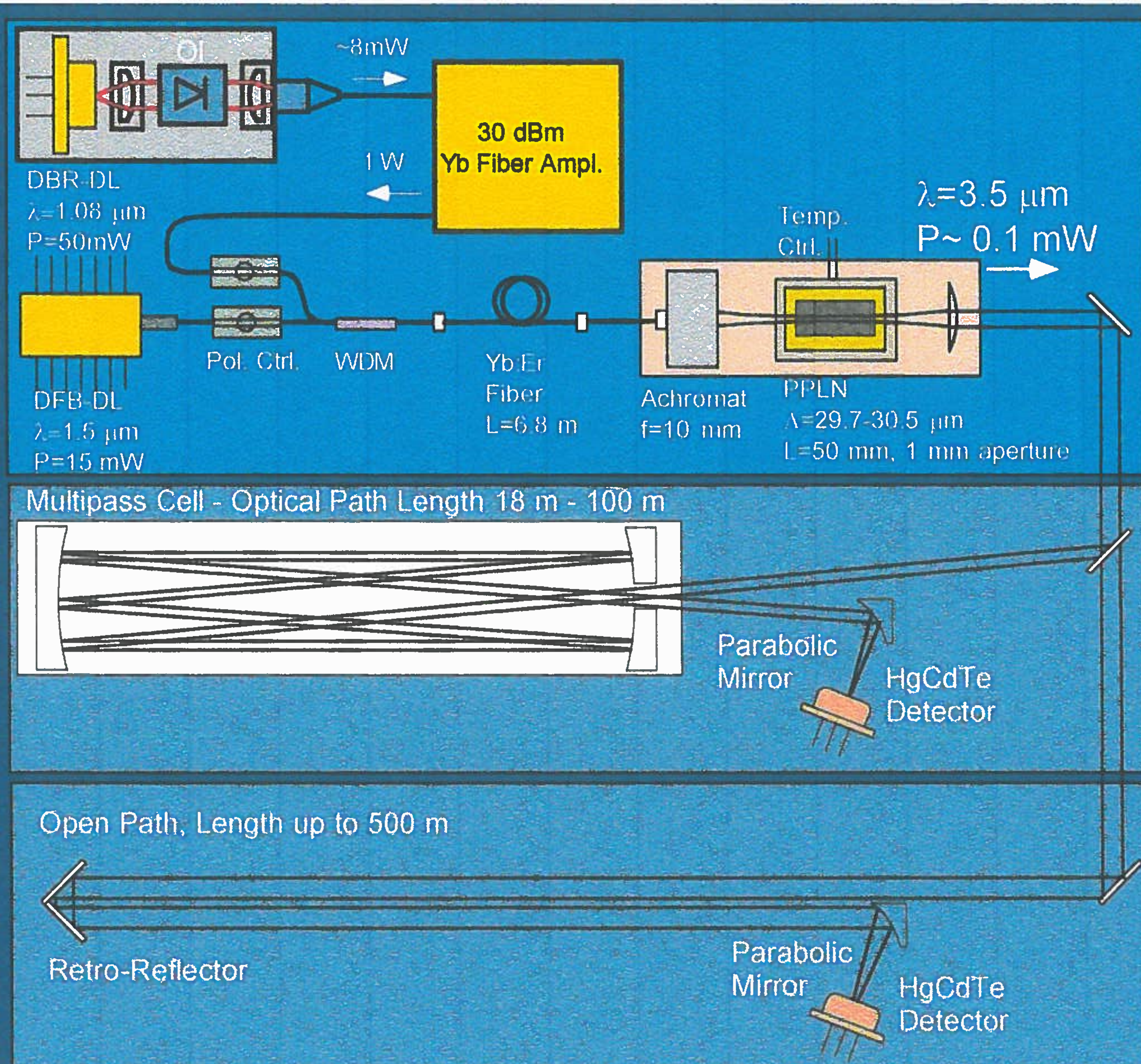
- Messages from earth's interior
- Study of subsurface magmatic and hydrothermal processes
  ⇒ Prediction of volcanic eruptions
- Study of environmental impact and medical implications
- Comparison of extractive DFG based gas sensors with an open path FTIR gas sensor

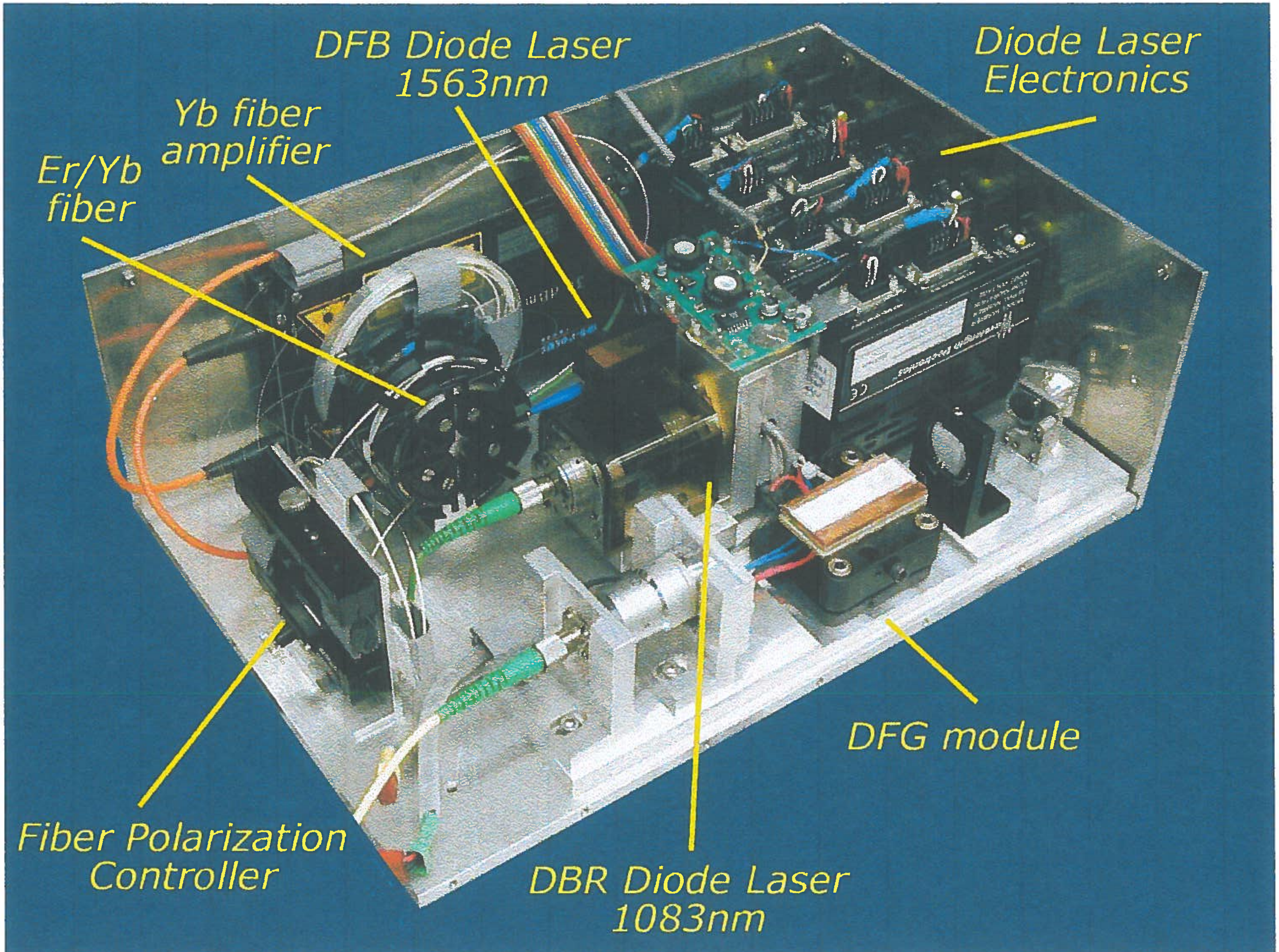

dfg sensor acq-single line-3d fit_inspection99
Laser Science Group
Sensing the World Around Us
RICE
Date
Time
Mon, Apr 17, 2000
6:04
EMERGENCY STOP
MASAYA VOLCANO FIELD MEASUREMENT CAMPAIGN APRIL 2000
General Acquisition Parameters
Stepper Motor Variables
DEV#
Frequency (Hz)
#PTS
Scan interval
Day of the month
Hour of the day
1
200000
500
1.0
17
17
COM port
Constant
Backlash steps
Initial Stepper direction
4
1.89E-2
10.00
Up
Dn
Up
Down
Concentration log file name
Data - path
Data - file name (no suffix)
Peak history log file
HCl
0.086
ppm
CH4 DFG signal (V)
Data scans to AVG #
DV scans to AVG
Pressure (torr)
Cal avg Gas 1
0.163
400.00
50
85.00
10
Write Reference Scan Gas 1
Use Reference Cell for Gas 1
Write acquired data to files
Peak absorption scan
Peak location history
Fitted Lorentzian
Gas Concentration
DFG Signal

Summary: DFG vs FTIR

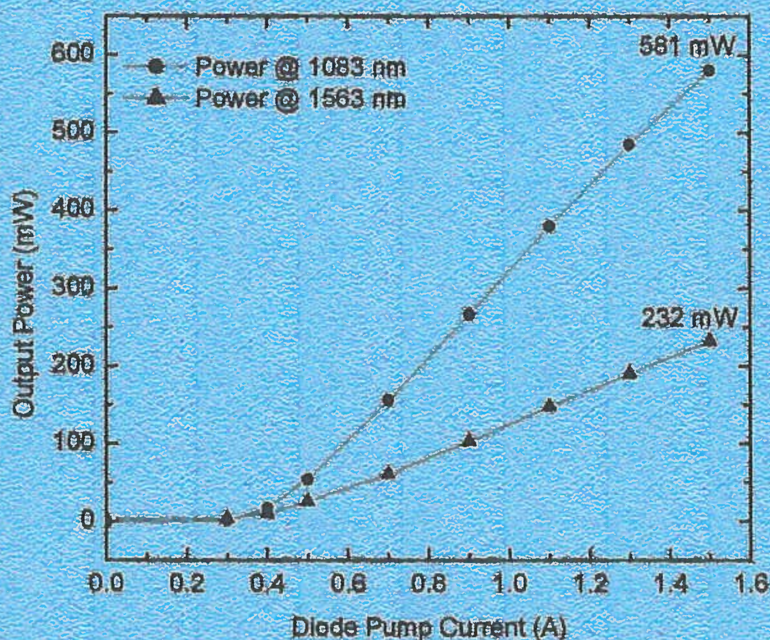
Gas Species	DFG Center Frequency (cm^{-1})	DFG Measured Concentrations (Min - Max) (ppm)	Field Sensitivity (MDC)	
			DFG	FTIR (mean)
CH_4	3028.751	1.85 - 2.05	32 ppb	419 ppb
CO_2	2388.640	374 - 567	3 ppm	30 ppm
H_2O	2649.348	18000 - 21200	670 ppm	710 ppm
HCl	2843.624	MDC - 0.175	15 ppb	15 ppb
SO_2	2505.239	MDC - 22.65	3 ppm (@ 4μm)	200 ppb

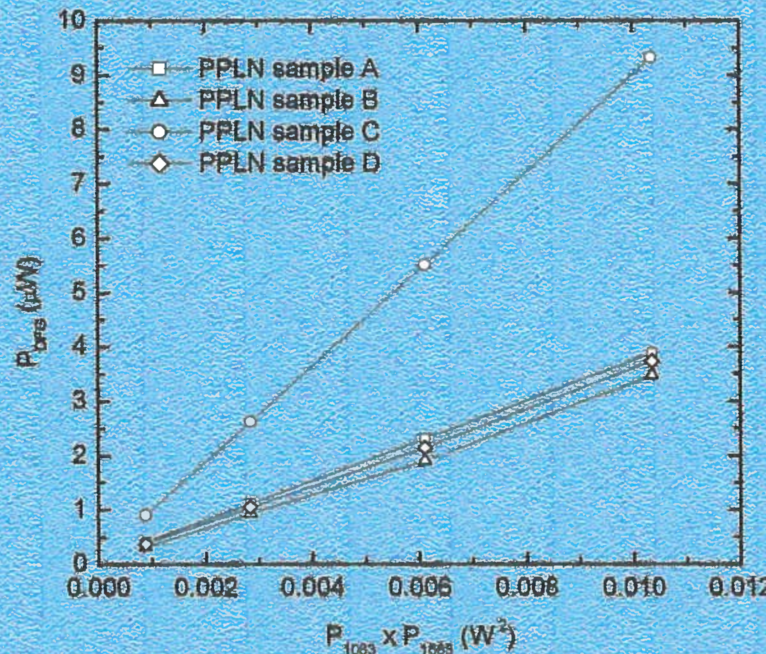
Novel Modular Designs




DFB Diode Laser
1563nm
Diode Laser
Electronics
Yb fiber
amplifier
Er/Yb
fiber
DFG module
Fiber Polarization
Controller
DBR Diode Laser
1083nm

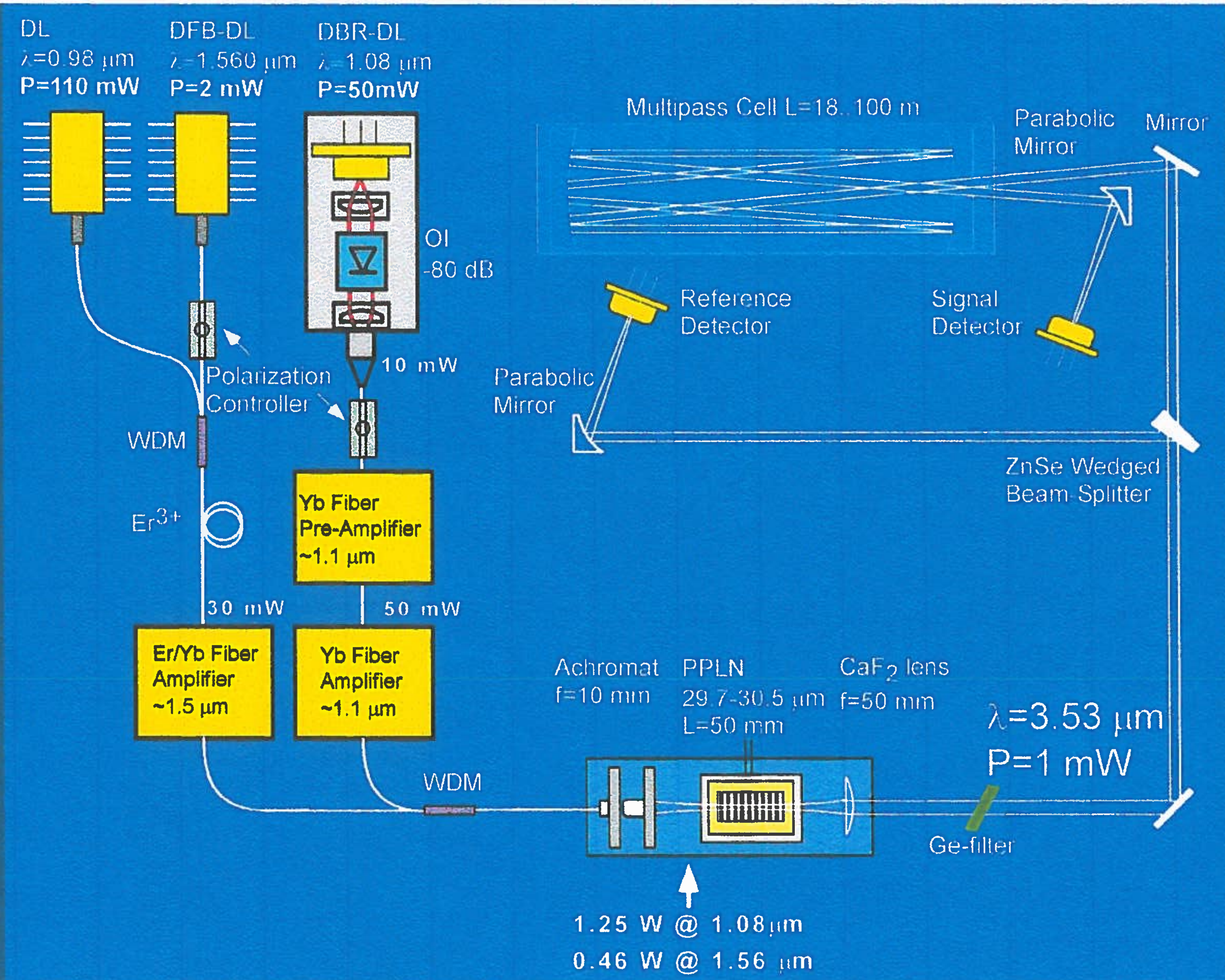
Performance Characteristics



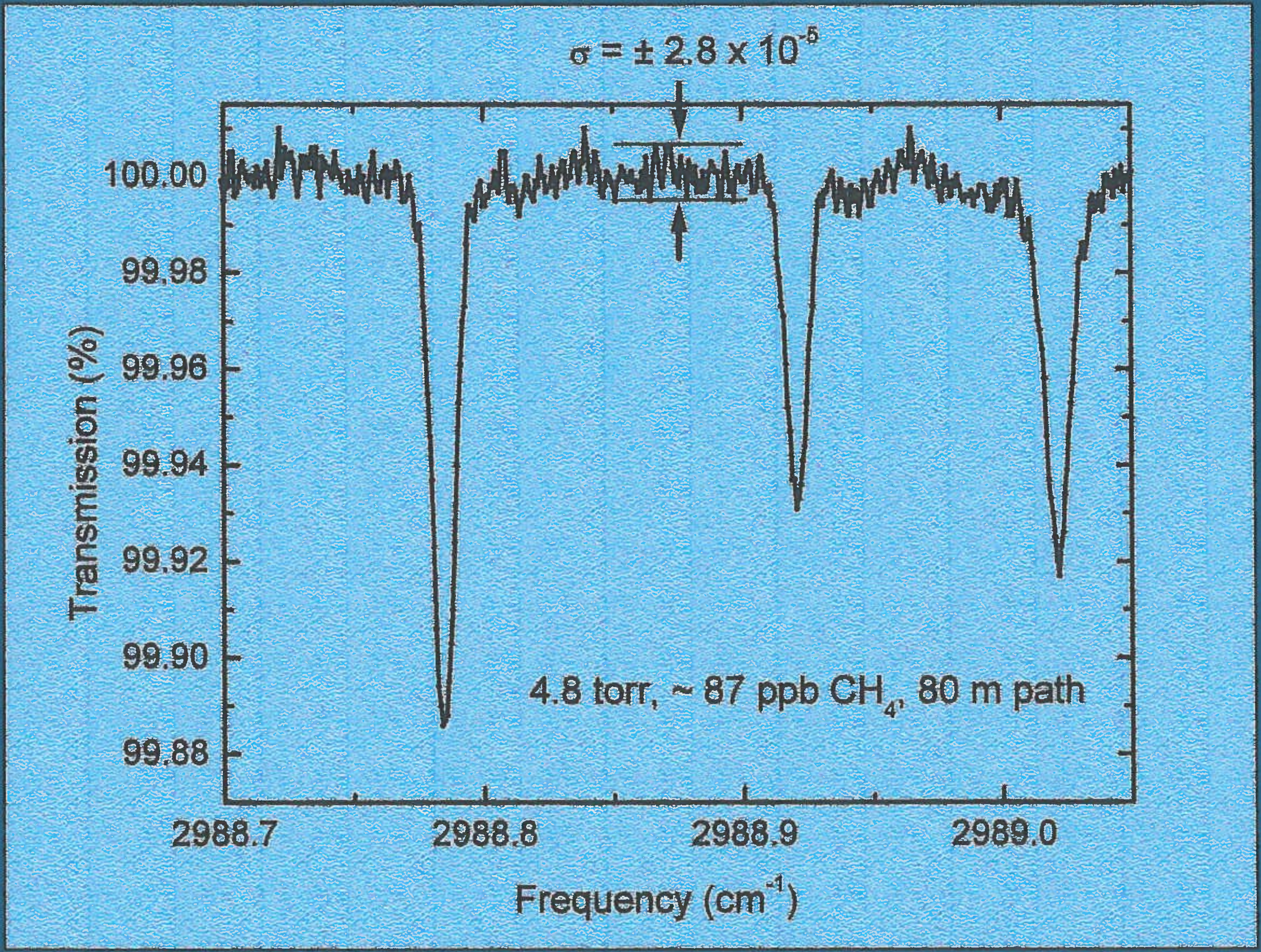


PPLN Sample	A	B	C	D
Thickness (mm)	0.5	1	1	0.5
Length (mm)	19	19	50	20.5
Conversion Efficiency ($\mu W \times W^{-2} \times cm^{-1}$)	199	174	181	176

High–Power Dual Beam DFG Spectrometer



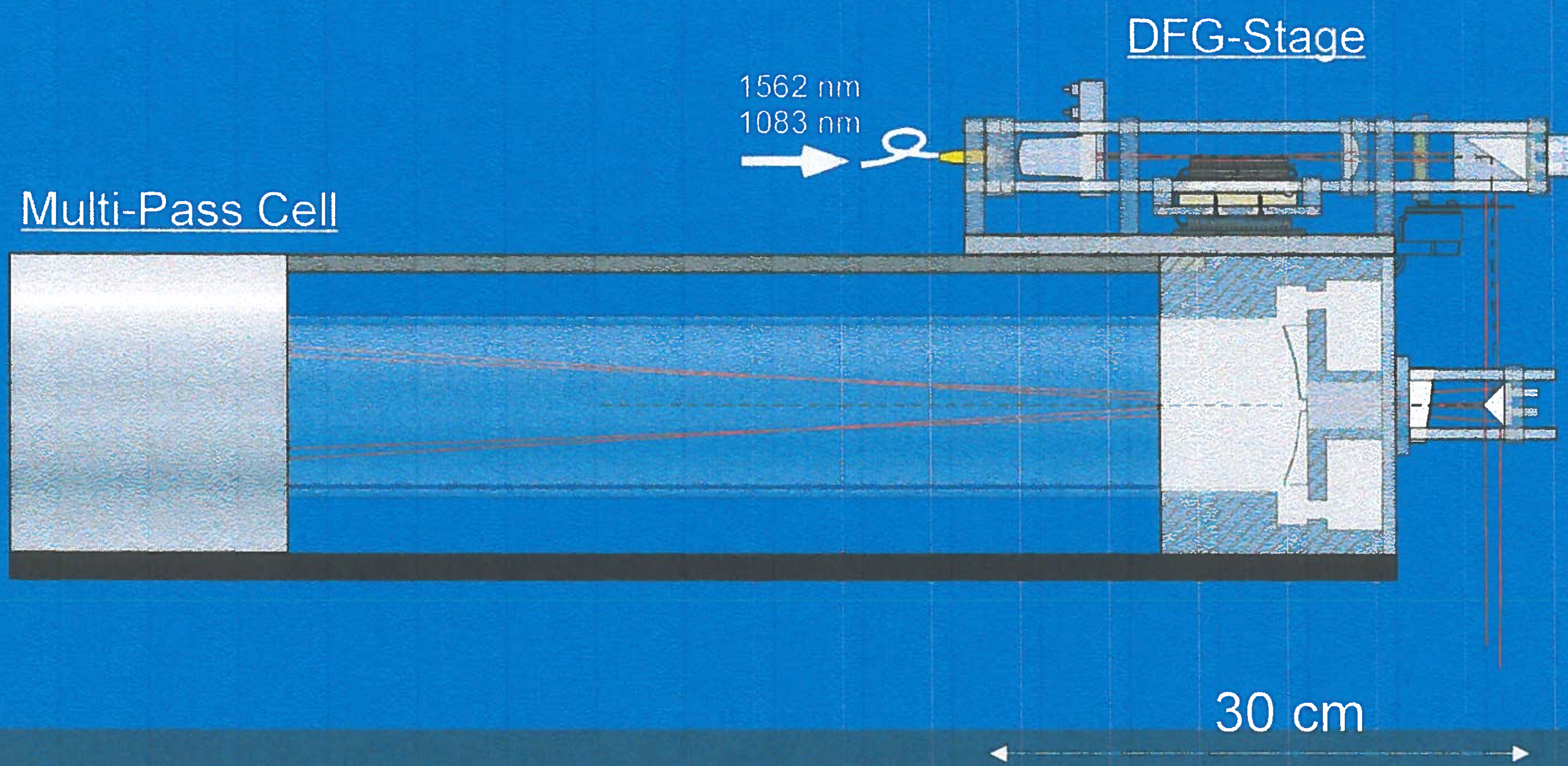
Dual Beam Spectroscopy of Methane at 3.3 μm



Design Status in 2000/2001

Device Characteristics	Unit	Past	Projected
SPECIES DETECTED		11+	1..3 (per diode pair)
MINIMAL DETECTABLE ABSORBANCE		$2x10^{-4}$ - $2.8x10^{-5}$	$5x10^{-7}$
DFG POWER	μW	3 – 1100	1400
SPECTRAL RESOLUTION	MHz	40 .. < 2	< 0.1 (0.000003 cm^{-1})
RESPONSE TIME	sec	1..30	1..30
LONG-TERM OPERATION	days	7+	Continuous / 24h Airborne
DYNAMIC RANGE	ppb	$10^1..10^5$	$10^{-2}..10^5$
SIZE (Source)	ft^3	0.3..3	0.06 (laptop size)
LIFETIME	years	>10	>20
VIBRATION SENSITIVE		no (tested up to 25G)	TBD
MAINTENANCE REQUIRED		none	none

Current NCAR Developments: Airborne High-Power DFG Based Trace Gas Sensor



Current Development Highlights: "Plug-and-Pray" to "Plug-and-Play"

- Fiber Laser Seed Source
  - **60 ppb** (16 MHz) absolute frequency stability over 24 hours
  - **No** pump diode laser dependency ($\Delta\lambda$, ΔI)
  - <100 kHz linewidth (free-running)
- DFB Diode Laser Seed Source
  - **173 ppb** (33 MHz) absolute frequency stability over 24 hours
  - **100 Hz** frequency tuning accuracy (over 12 GHz | 0.4 cm^{-1})
  - <2 MHz linewidth (free-running)
- DFG Module
  - Rugged, close-coupling design
  - Clean, predictable near Gaussian spatial mid-IR beam
  - ~0.0003% / h power stability (~1/1000 of Fiber Amplifier Stability)
  - Self-compensating temperature induced drift (Residual<5.6 MHz/h)