Emerging Pollution and Atmospheric Trace Gas Detection: Concepts and Environmental Applications

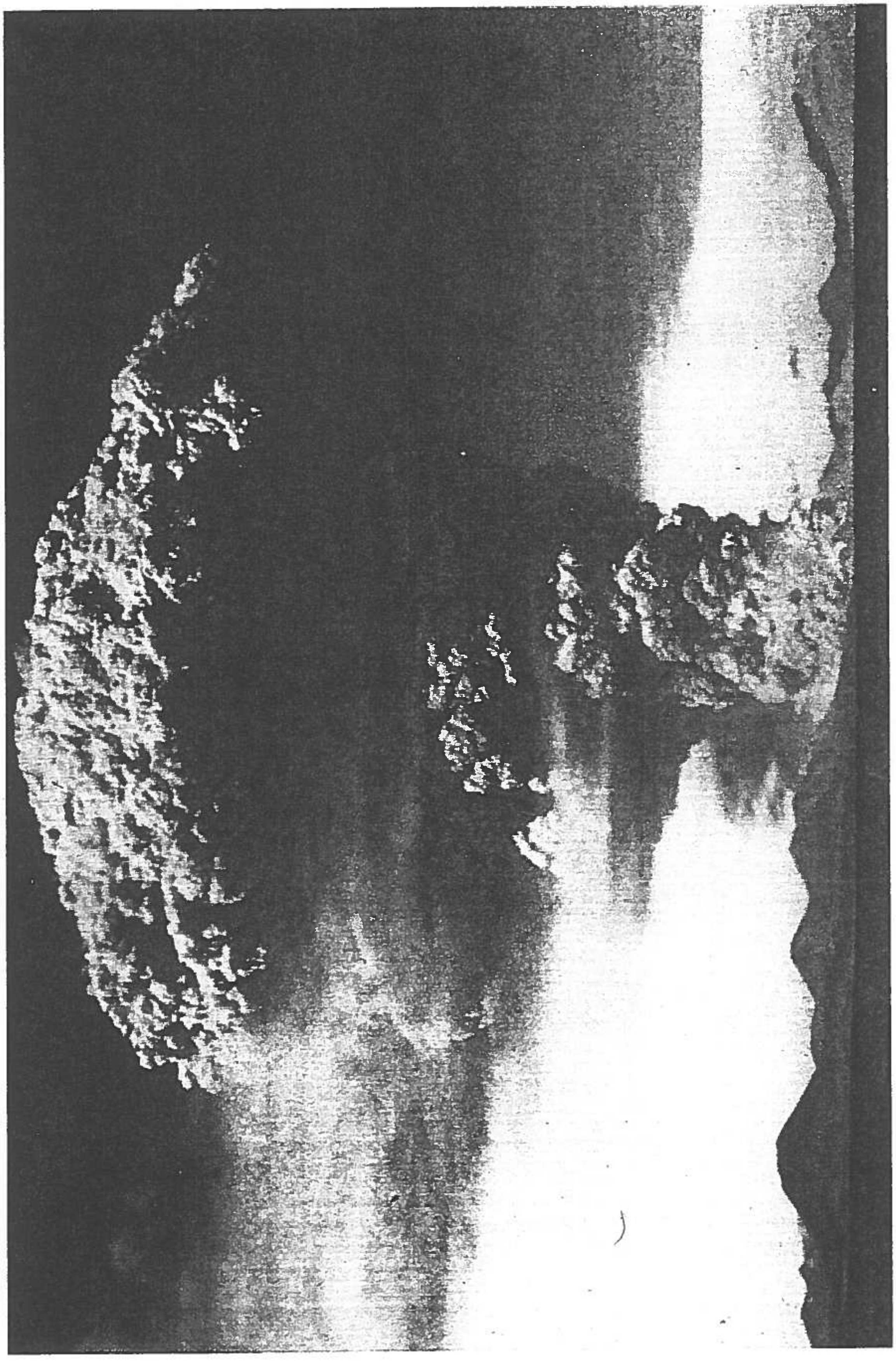
Frank K. Tittel
Electrical & Computer Engineering Department
Rice University
Houston, Texas

Outline

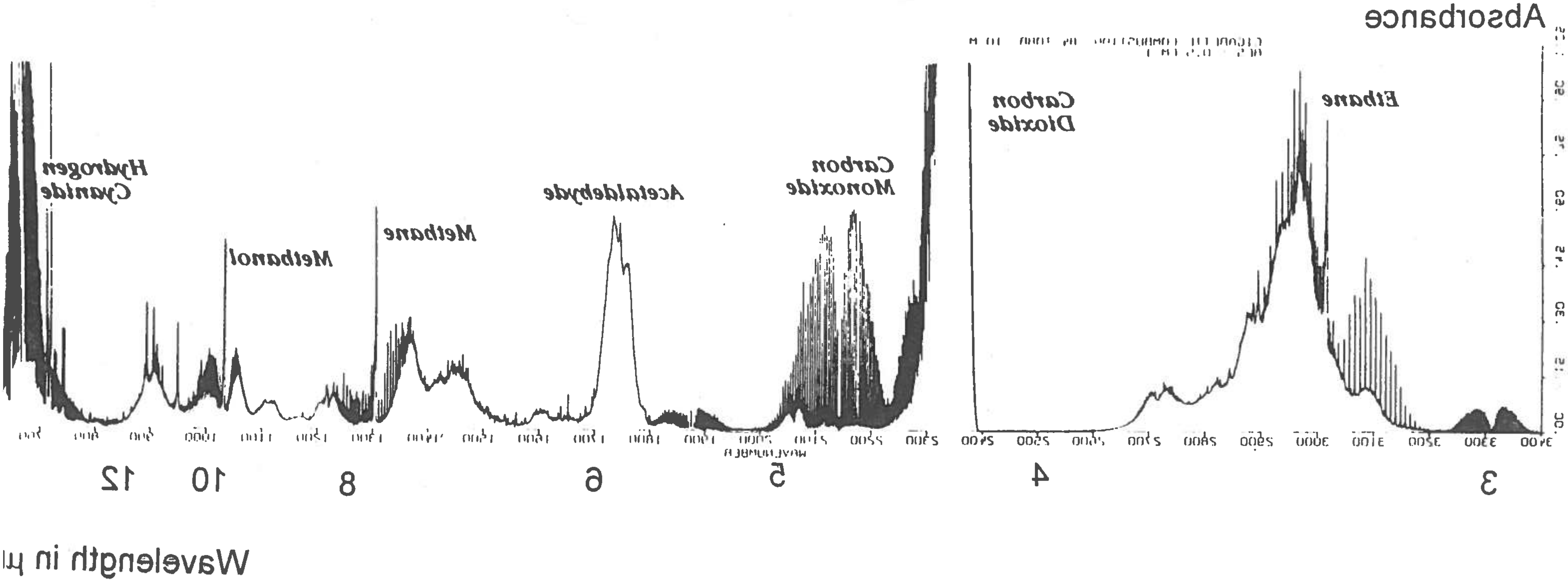
* Motivation, Design, and Technology Issues
* Performance Characteristics of Compact IR Sensors
* Detection of Pollutants and Trace Gas Species
* Outlook and Summary

Applications of Trace Gas Detection

* Urban Emission Measurements
  - Industrial Plants
  - Combustion Sources
  - Automobile
  - Waste Dumps
* Rural Emission Measurements
  - Agriculture
  - Forest Fires
* Environmental Monitoring
  - Atmospheric Chemistry
  - Volcanic Emissions
* Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Life Support
* Chemical Analysis and Process Control
  - Semiconductor Industry
* Medical Applications
* Aircraft Identification



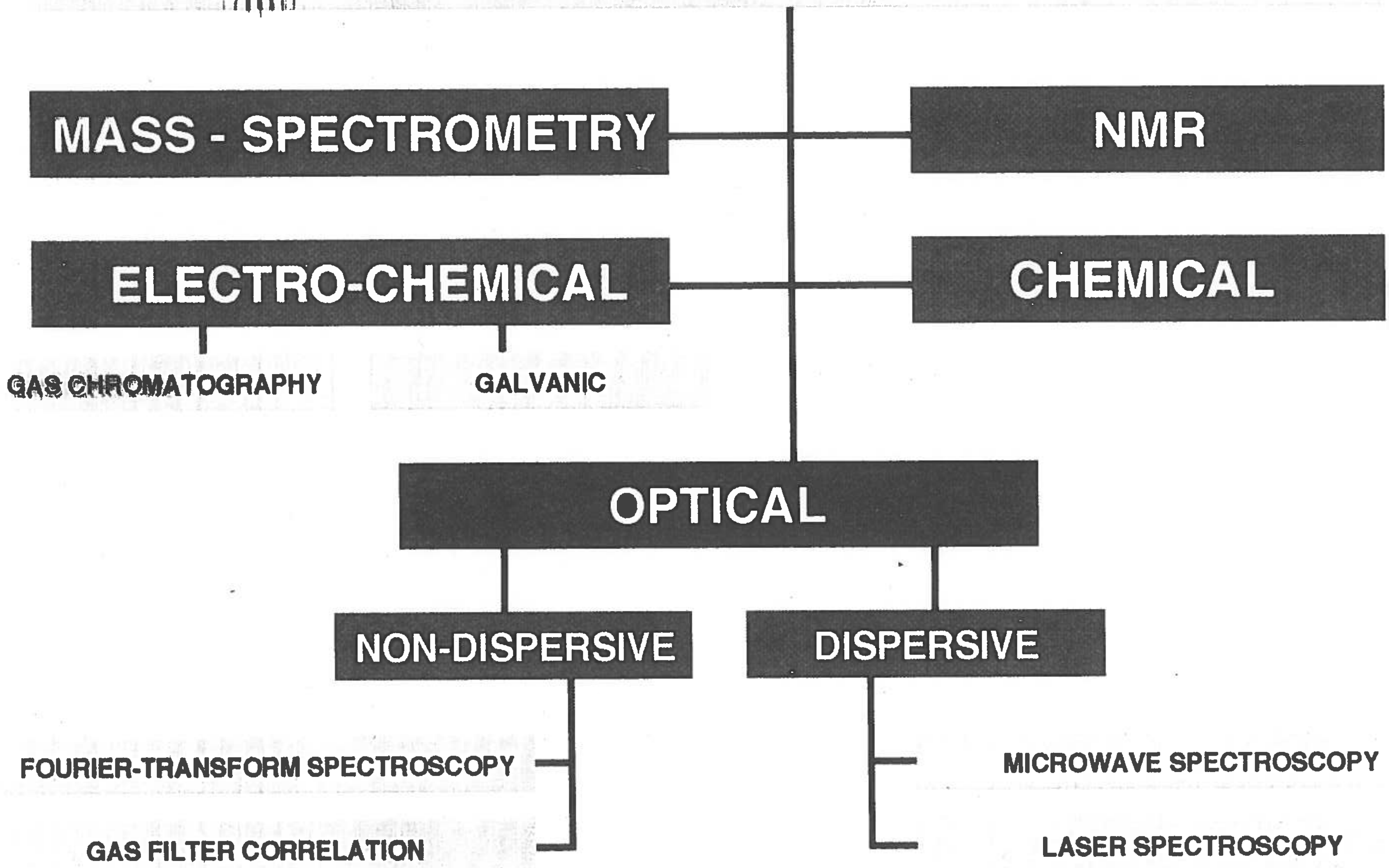
Spectrum of Cigarette Smoke



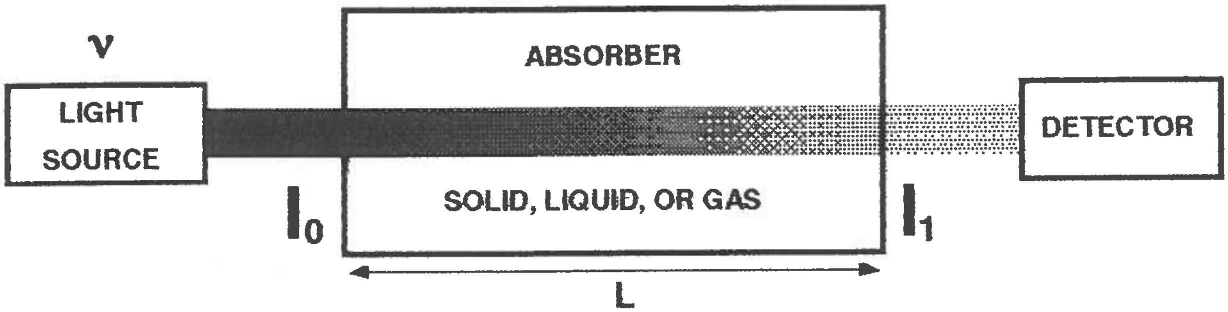
Fraunhofer Institut Physikalische Meßtechnik IPM

taken from: Nicolet Analytical Instruments Guid

EXISTING METHODS FOR TRACE GAS DETECTION



SPECTROSCOPIC DETECTION



BEER'S LAW

$$I_1 = I_0 \cdot e^{-\alpha(\nu) \cdot L}$$

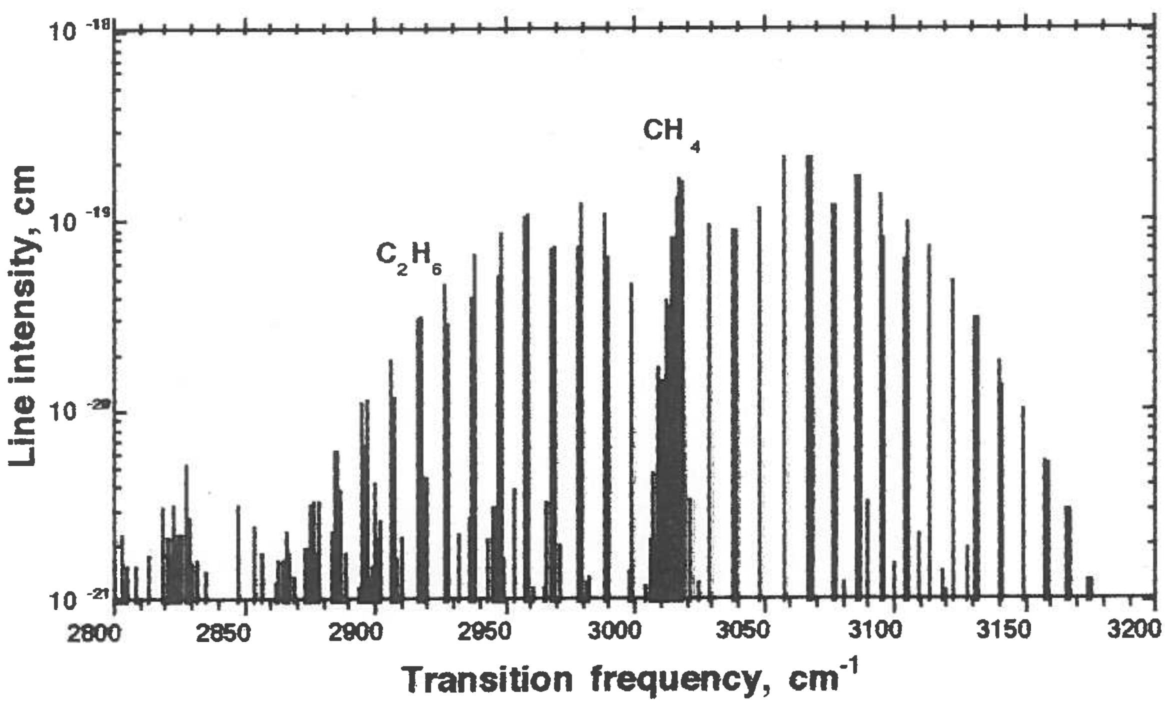
$\alpha(\nu)$ - absorption coefficient (cm^{-1}), L - path length (cm), ν - frequency (cm^{-1})

MOLECULAR ABSORPTION COEFFICIENT

$$\alpha(\nu) = C \cdot \frac{S}{\Delta\nu} \cdot g(\nu)$$

C - gas concentration (cm^{-3}), S - line intensity (cm), $\Delta\nu$ - linewidth (cm^{-1}),

$g(\nu)$ - numerical line profile: Gaussian, Voigt, or Lorentzian



Tunable CW IR Coherent Sources

- **Solid State Lasers**
  Color center lasers, tunable (1-4 μm), low temperatures

- **Lead Salt Diode Lasers**
  Tunable (3-30 μm), each diode ~100 cm^{-1}
  Undesirable discontinuities, low temperature needed

- **CO and CO_2 Sideband Lasers**

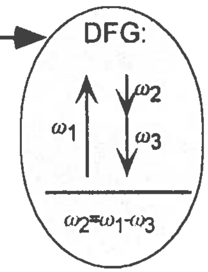
- **Optical Parametric Oscillators (OPO)**
  Tunable 2-14 μm ($LiNbO_3$, KTP, BBO, $AgGaS_2$, $AgGaSe_2$, $ZnGeP_2$), Pulsed and CW

- **Tunable III-V Semiconductor Diode Lasers**
  Single Frequency: InGaAs/AlGaAs 620 nm-2.1 μm;
  GaSb based lasers 2-6 μm;
  DFB quantum cascade lasers (3-17 μm) pulsed at RT

- **Difference Frequency Generation (DFG)**
  Tunable & RT: QPM & BPM $LiNbO_3$ (2-5.3 μm);
  $AgGaS_2$ (3-9 μm); $AgGaSe_2$ (>8-20 μm);
  GaSe (7-18 μm); GaAs (2-16 μm)

Enabling DFG Technologies

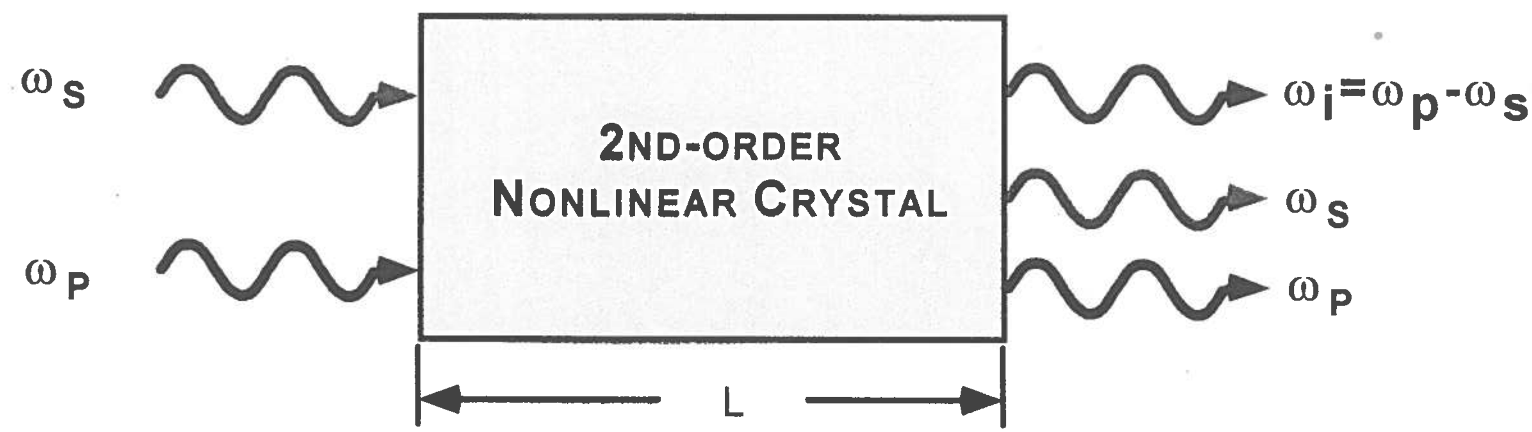
Single Frequency Diode Lasers	- DBR / DFB Diode Laser 1064 nm, 1083 nm and 1560 nm
Power Amplification and Fiber Delivery	- Yb and Yb/Er Doped Fiber Amplifiers - Wavelength Division Multiplexer (WDM)
Nonlinear Optical Materials	Periodically Poled Lithium Niobate (PPLN); GaAs [Future]
High Sensitivity Absorption Spectroscopy	-Multipass Cell or Open Path -Utilizing Lambert Beers Law: $I = I_o \cdot e^{-\alpha L}$
Quasi Room-Temperature Mid Infrared Detectors	- TE cooled HgCdTe / InAs - NEP ~5pW/$\sqrt{Hz}$
Real Time Data Acquisition / Analysis	- A/D card / Laptop - LabVIEW Software - μ–processor and DSP



Features of DFG Sensor

- Compact
- High Sensitivity
- High Selectivity
- Wavelength Tunable
- Fast Data Acquisition and Analysis
- Room Temperature
- Lightweight
- Robust
- Power Efficient
- No Consumables

Difference Frequency Generation

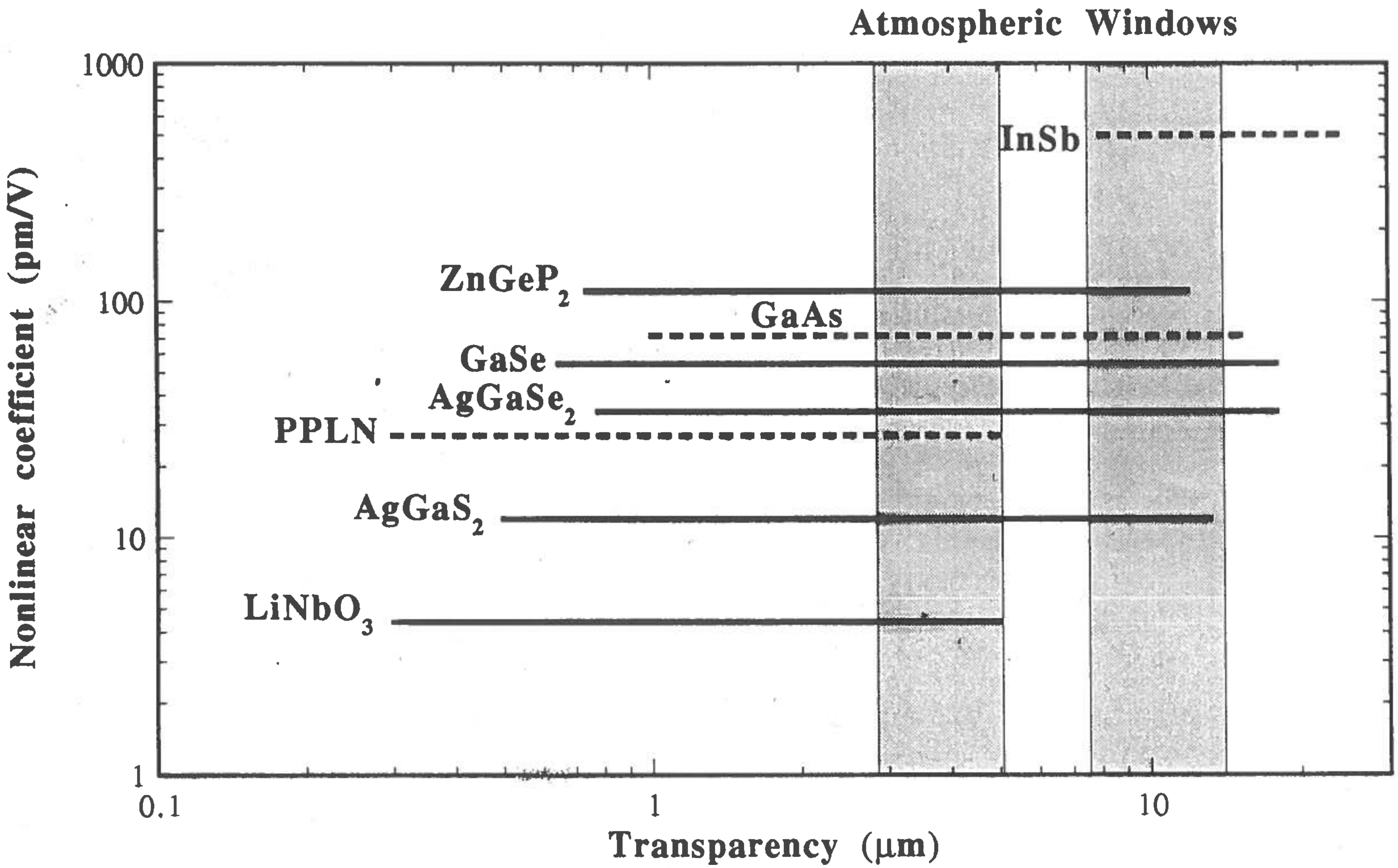


Power: $P = C \cdot P_{PUMP} \cdot P_{SIGNAL} \cdot L$

Example for PPLN at 3.5 μm

$C \sim 350\ \mu W / cm \cdot W^2$
1.6 μW for 40 and 60 mW pump LDs

Characteristics of Mid-IR Nonlinear Optical Crystals



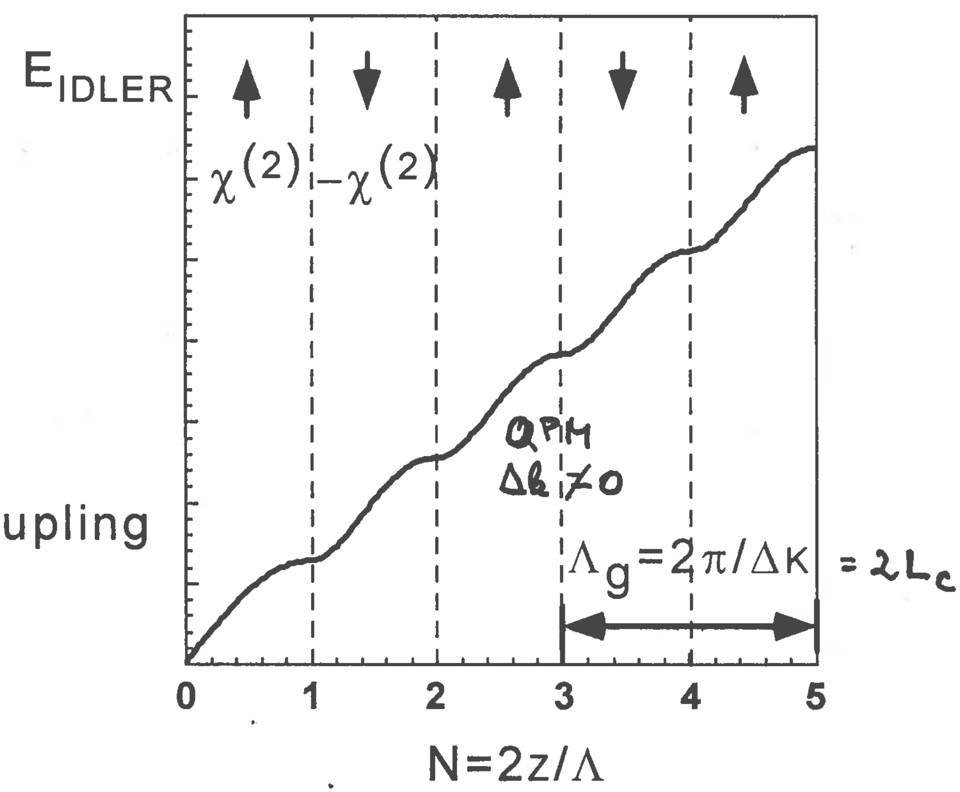
Quasi Phasematching (QPM): Alternative to Birefringent Phasematching

Not Phasematched:

- $n_{idler} \neq n_{pump}, n_{signal}$
- π phase slip every L_c

Quasi Phasematched:

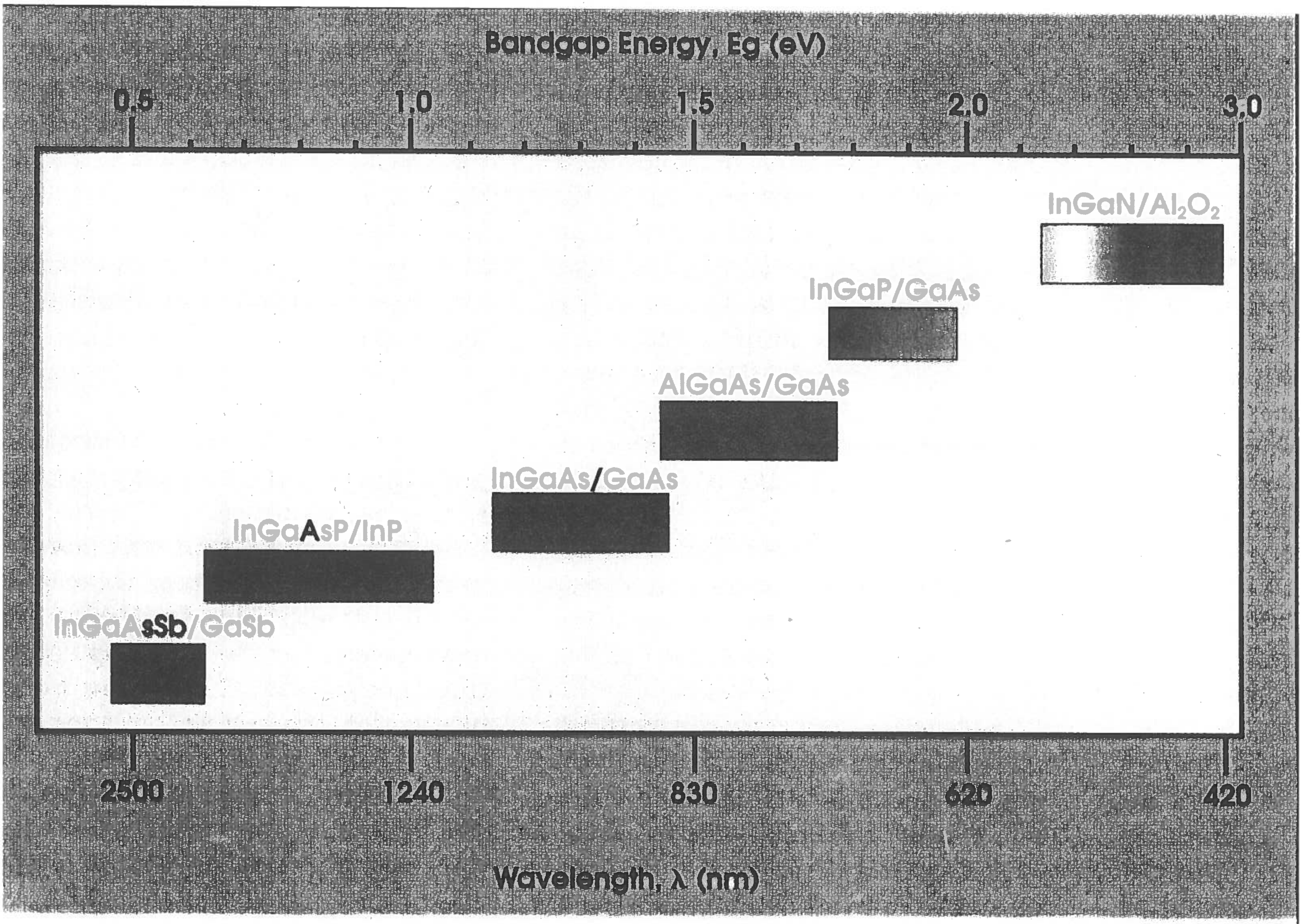
- $n_{idler} \neq n_{pump}, n_{signal}$
- π phase slip every L_c
- change sign of nonlinear coupling every L_c $(-\chi^{(2)} = |\chi^{(2)}| e^{\pm i\pi})$



- Any nonlinear optical interaction may be phasematched, no walk-off
- Highest effective nonlinear coefficient, for DFG: d_{33} = 27 pm / V
  c.f. $LiNbO_3$ = 5.95 pm / V , KTP = 4.2 pm / V

Advantages of Diode Laser Pump Sources

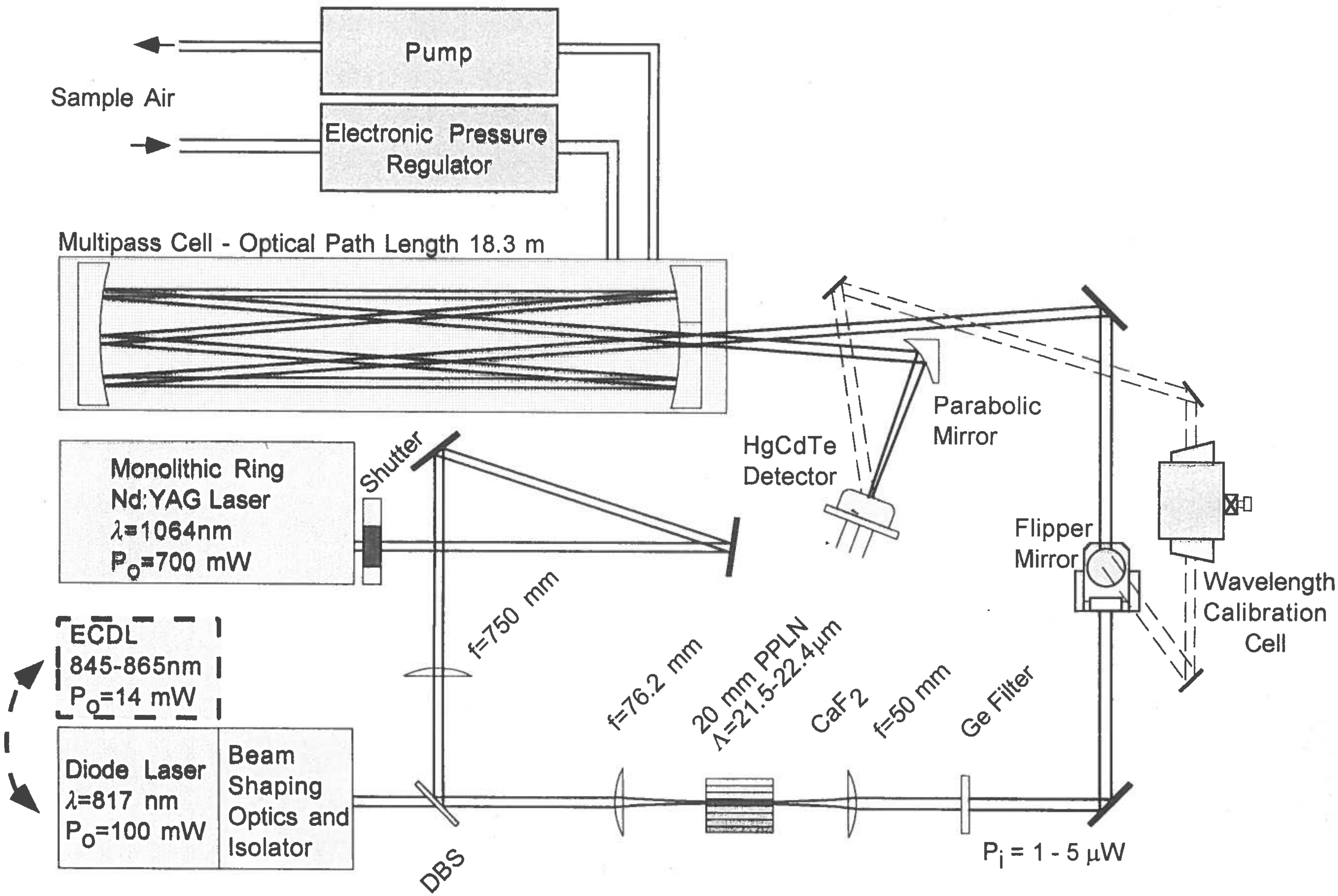
* Broad wavelength coverage (630 nm to 2 μm, with gaps)
  - Tunability (0.3 nm/°C, or 2 MHz/μA typical)
  - High efficiency ($\eta_{elec} \geq 30\%$, 0.1-1 W/A)
  - FP, DBR, DFB, ECDL, VCSEL
* CW single-mode power (1 to 500 mW)
  - With amplification: ≥ 1 W (MOPA, Fiber)
* Narrow linewidth (≤ 15 MHz)
* Amplitude and frequency stability
* Direct frequency modulation (f ≤ 0.1 GHz, 10 GHz range)
* Room temperature or TE cooled operation
* Convenient Fiber Pigtailing
* Reliability (≥ 10,000 hrs.), small size, and low cost


Bandgap Energy, Eg (eV)
0.5
1.0
1.5
2.0
3.0
InGaN/Al2O2
InGaP/GaAs
AlGaAs/GaAs
InGaAs/GaAs
InGaAsP/InP
InGaAsSb/GaSb
2500
1240
830
620
420
Wavelength, λ (nm)

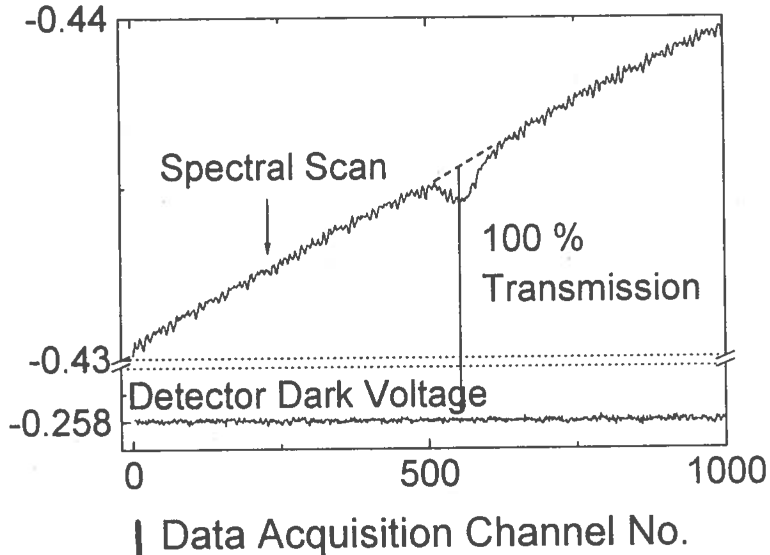
Basic CW DFG Architectures

* Fixed High Power Diode or Solid State Laser and Tunable Diode Laser
* Two Diode Lasers
  - Diode amplified
* Fiber Coupled and Amplified
  - Single, dual cascade or multiple channels
* Hybrid DFG Systems
  - Cavity enhanced

CW DFG Gas Sensor using PPLN

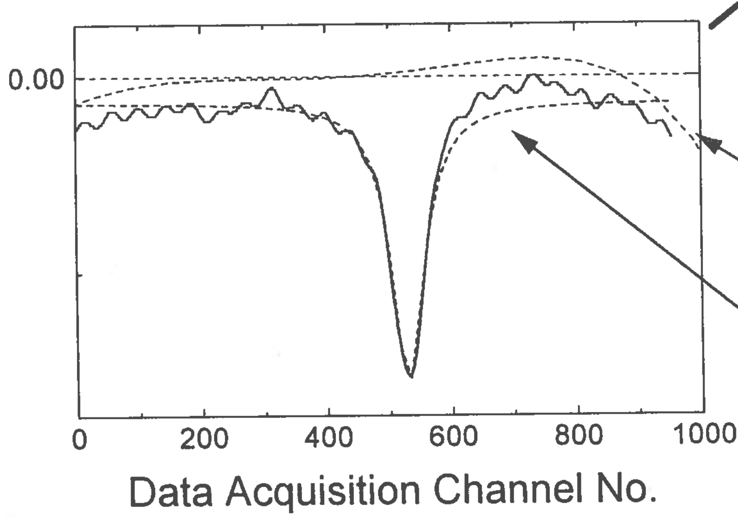


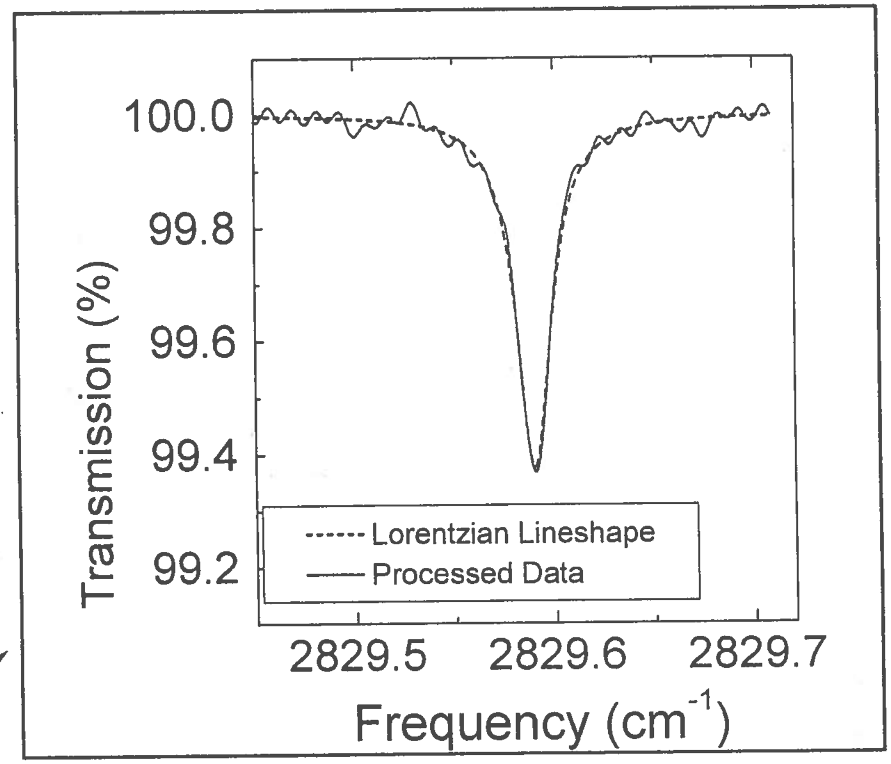
Direct Absorption Spectroscopy: Analysis



-Low-Pass Filtering

-Baseline Slope Removed



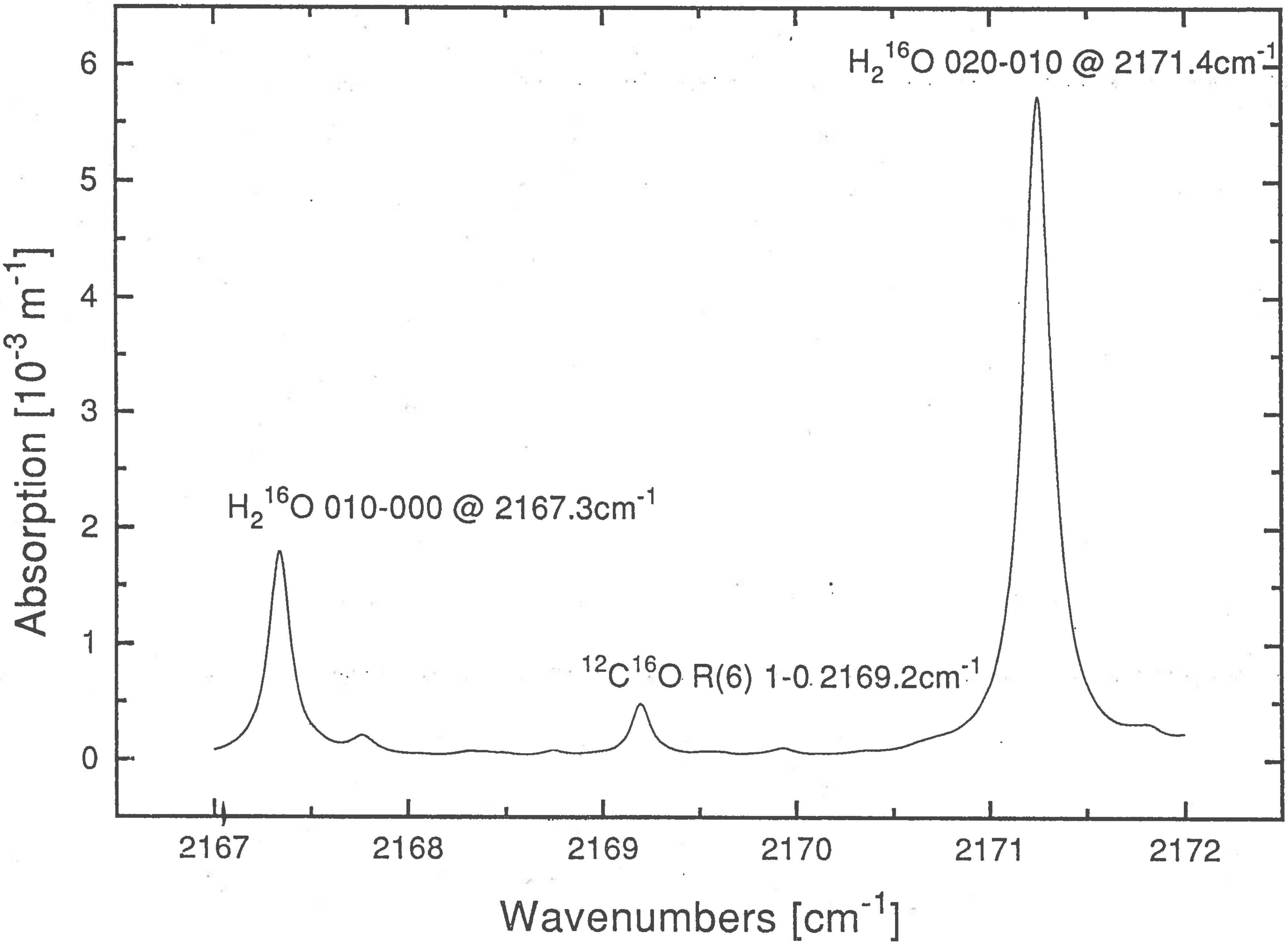


Baseline Estimation

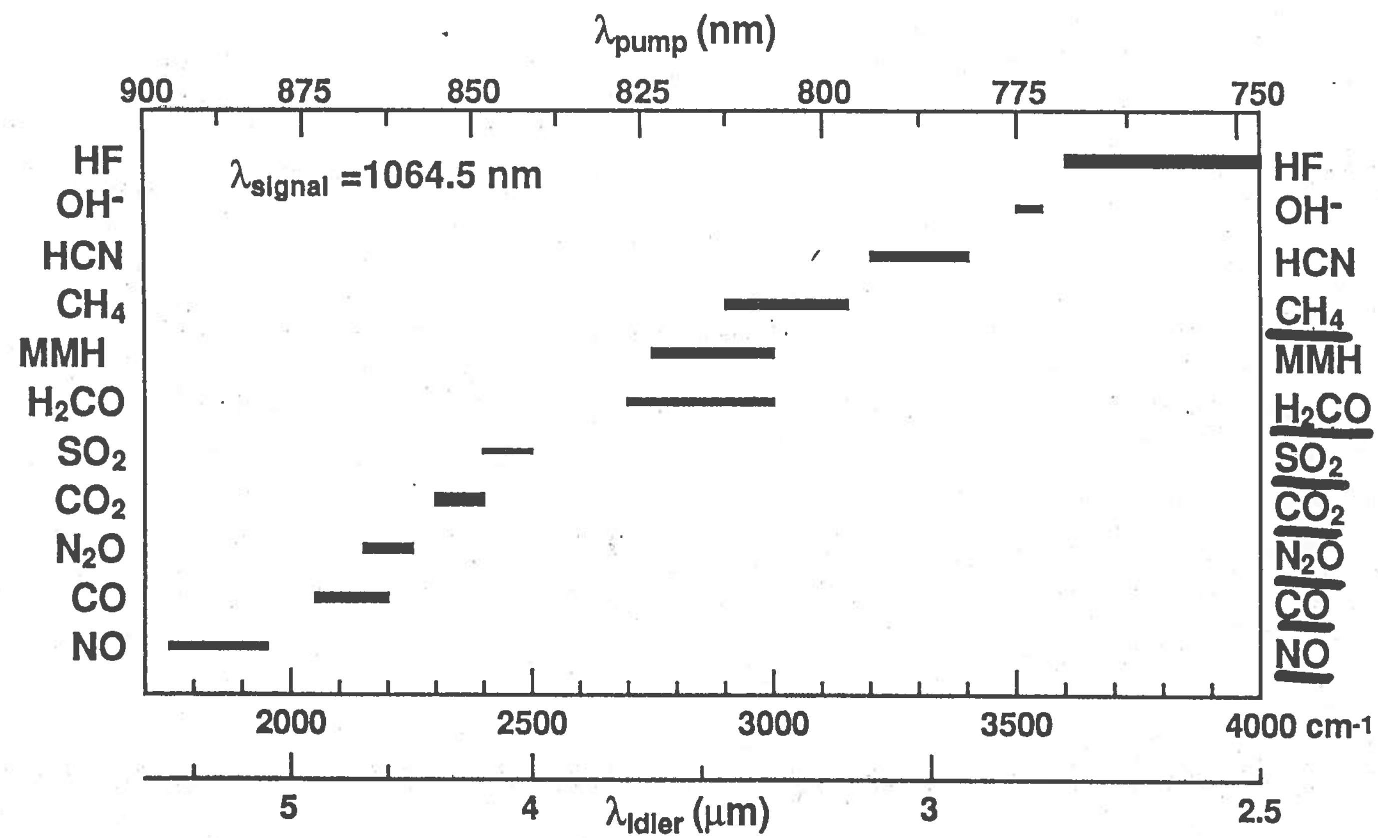
$$= ao + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + a_5 x^5$$

$$= \frac{1}{2\pi} \frac{\gamma}{(w - w_o)^2 + (\gamma/2)^2}$$

Absorption Spectrum of Air ~4.6μm

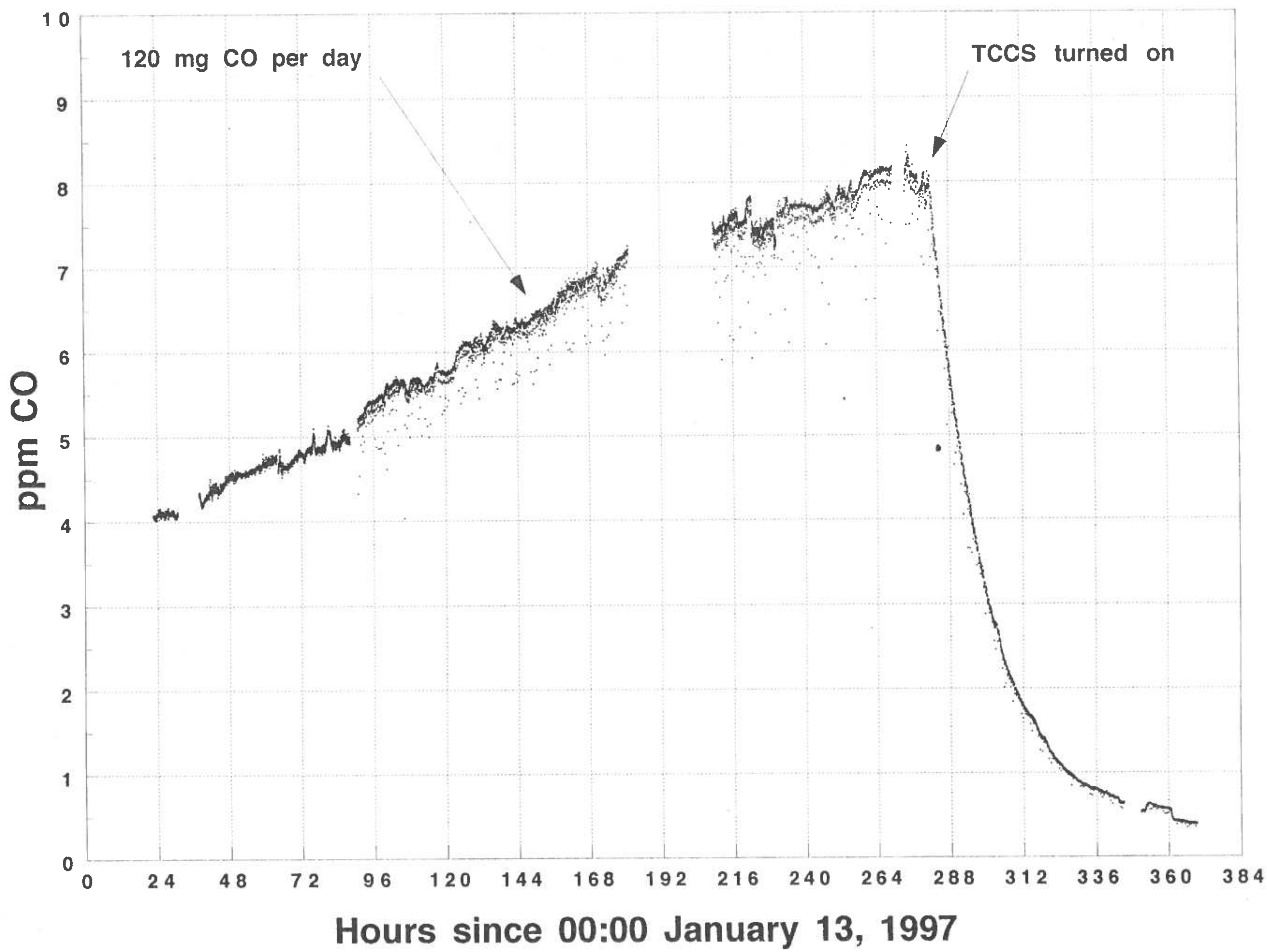


MID-INFRARED WAVELENGTH COVERAGE BY DIFFERENCE-FREQUENCY MIXING IN PPLN

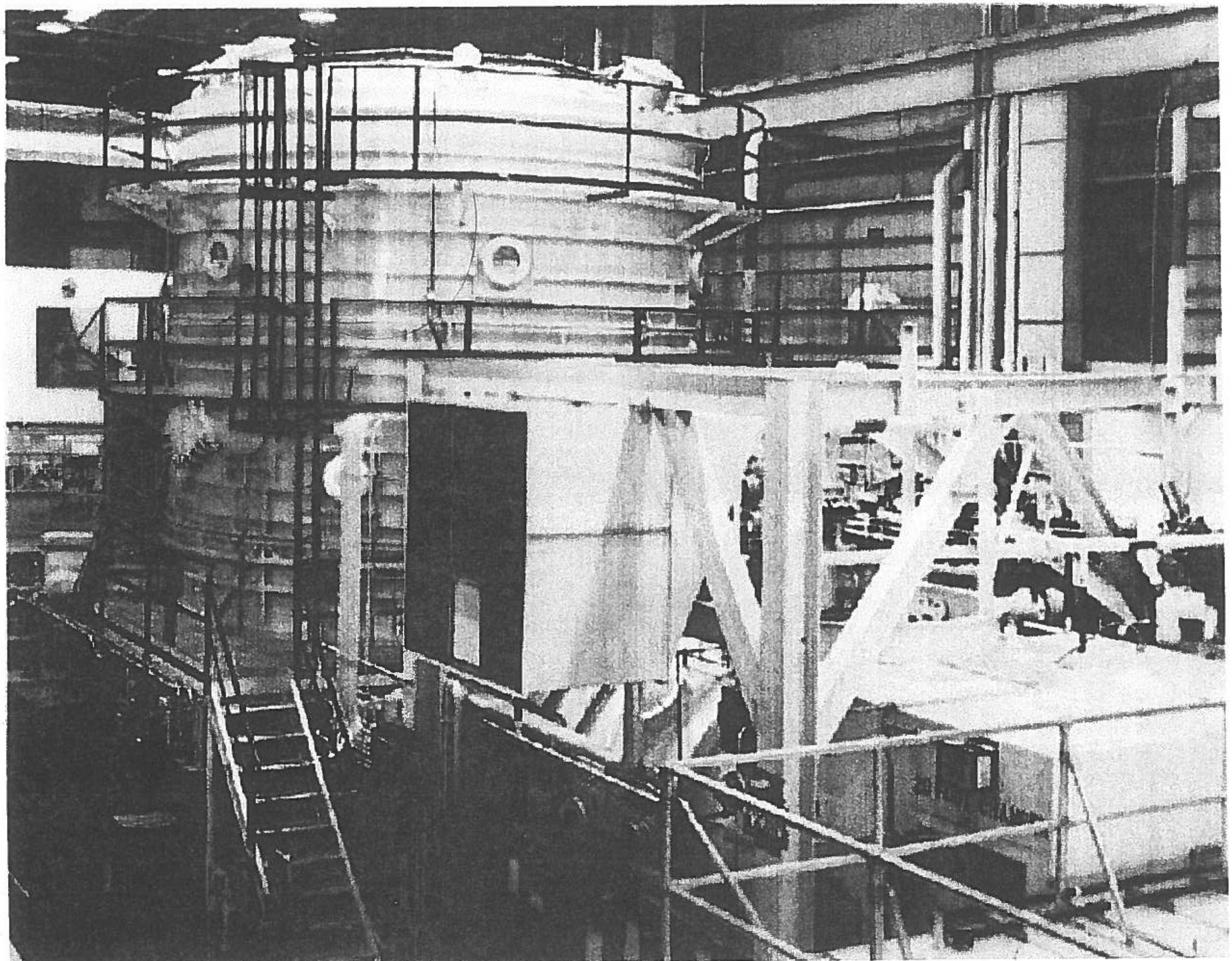



RICE IN SPACE
RICE

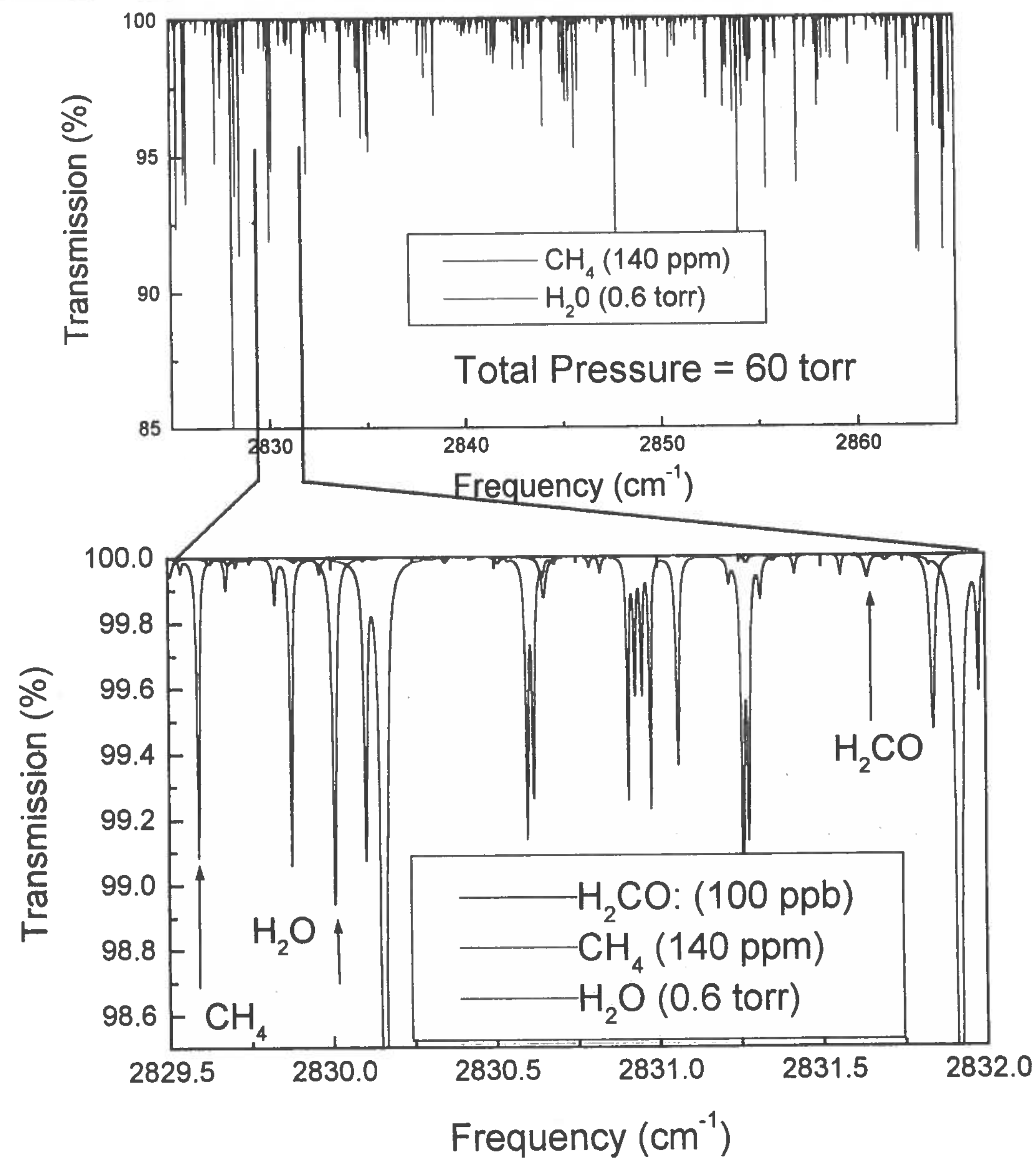
Carbon Monoxide in Chamber Air During EHTI Phase 2A Test at NASA JSC



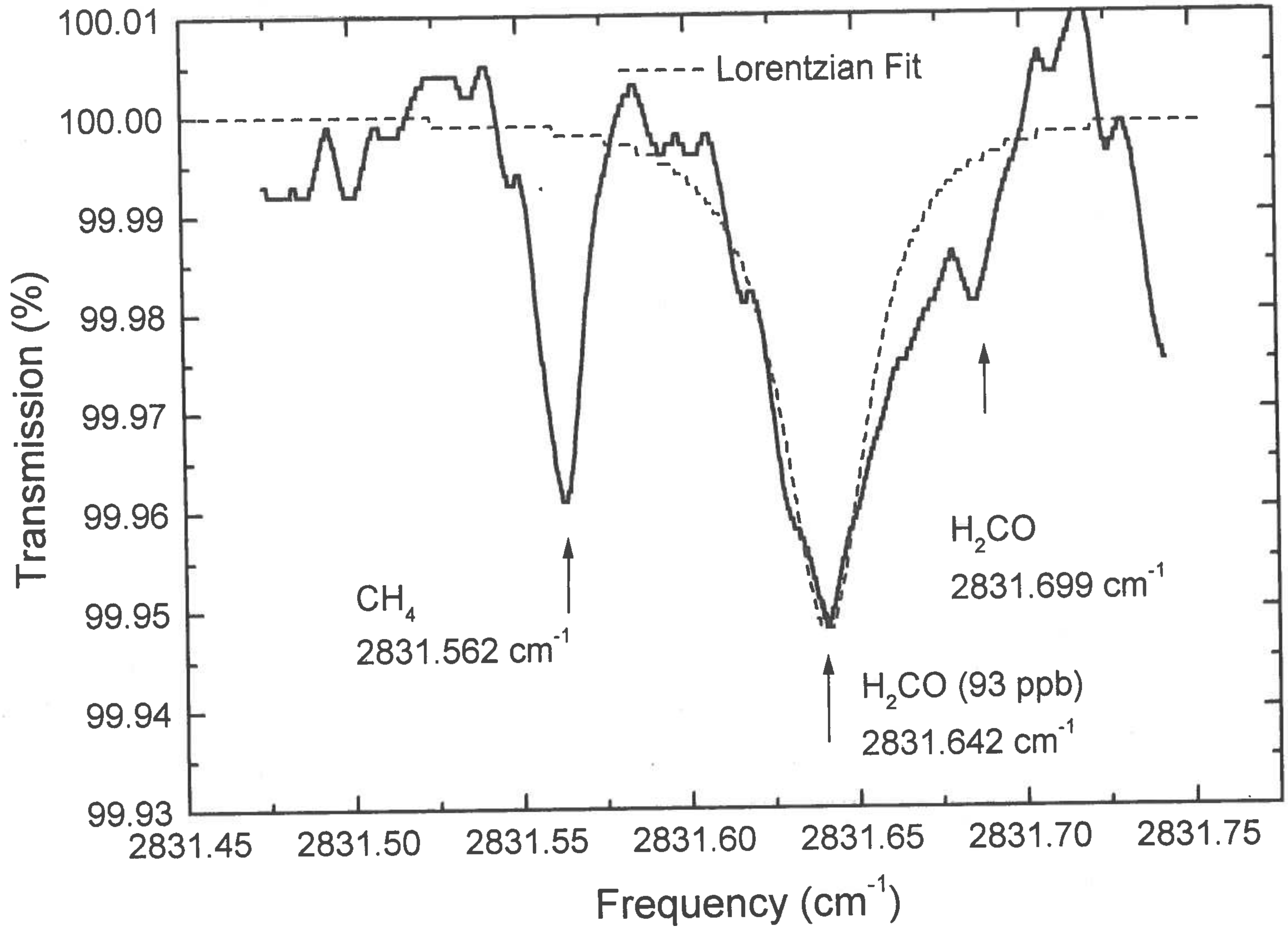
NASA Man-Rated 20 Foot Chamber



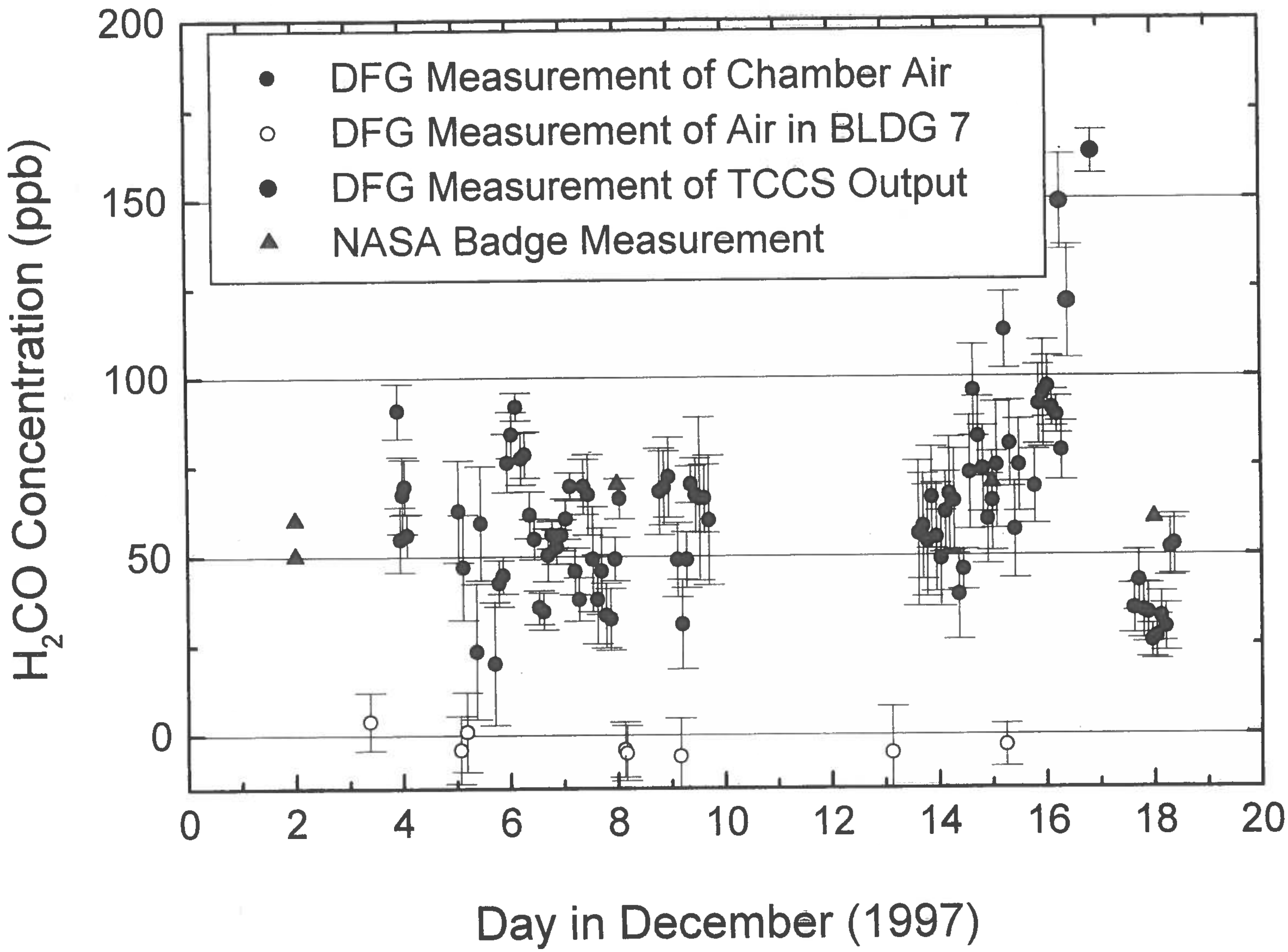
Spectroscopic Environment Encountered for H_2CO Monitoring in the NASA Lunar-Mars Life Support Chamber



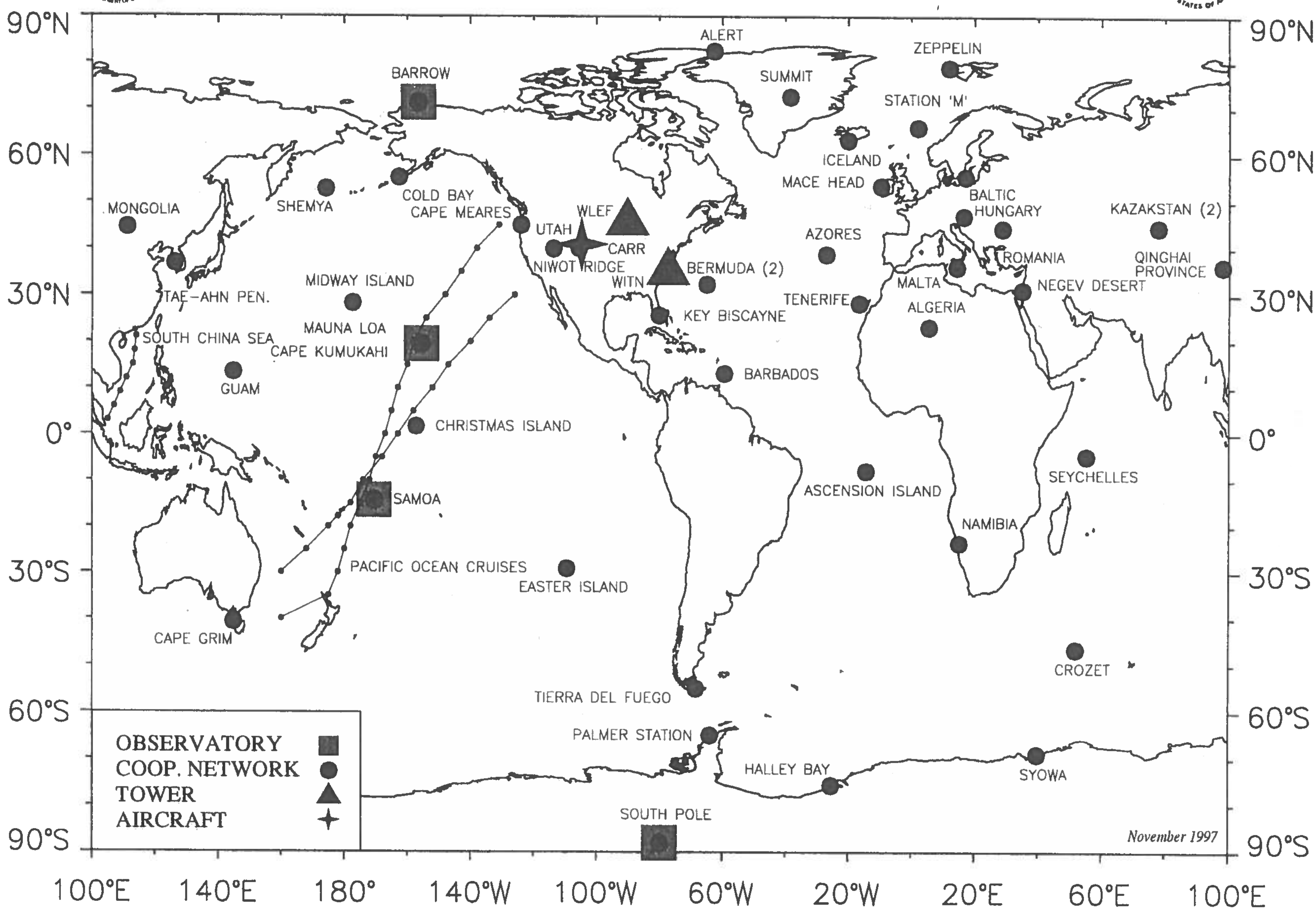
H_2CO Spectrum of Lunar-Mars Life Support Chamber Air



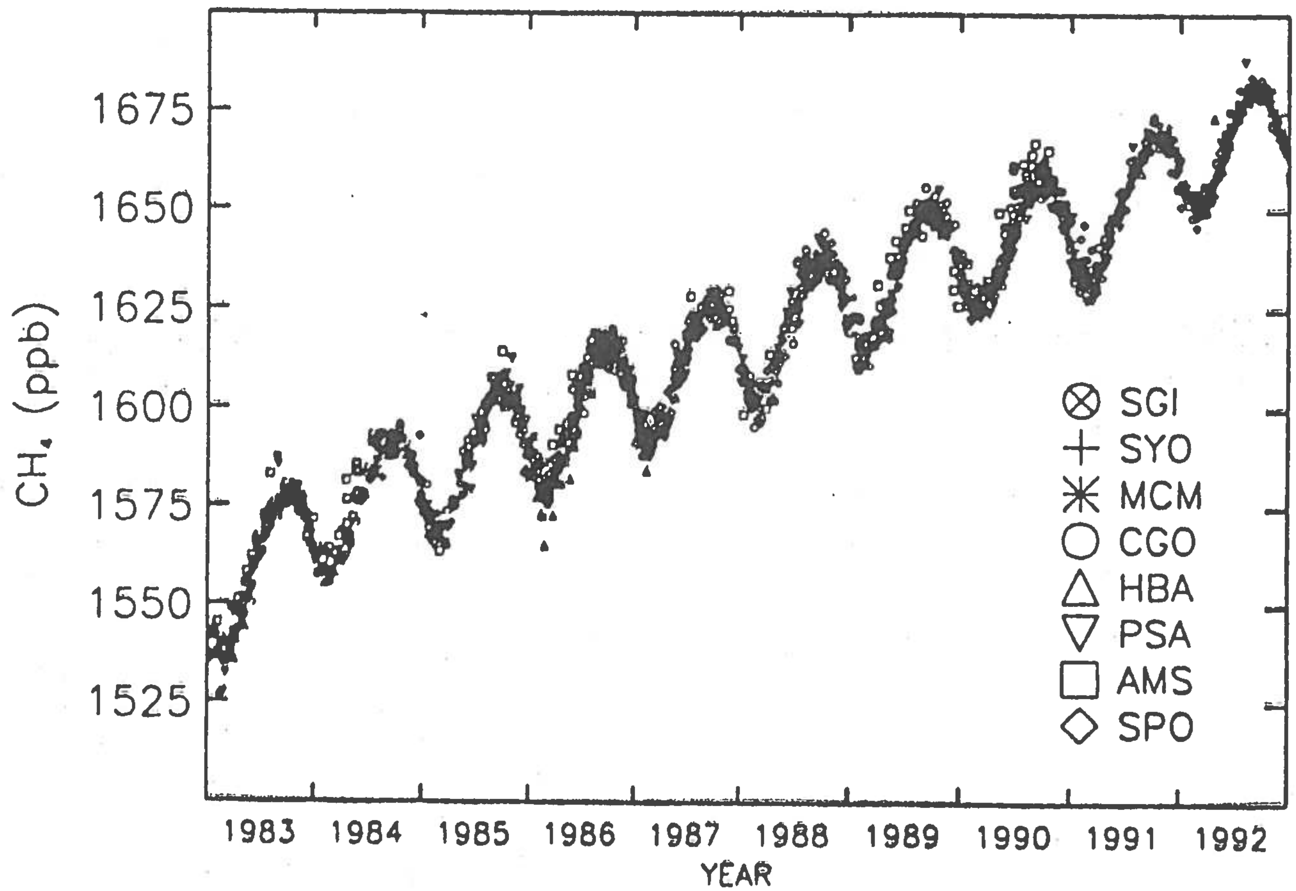
H_2CO Concentration Measurements
NASA-Lunar Mars Life Support Test-Phase III



NOAA CMDL Carbon Cycle Group Measurement Programs

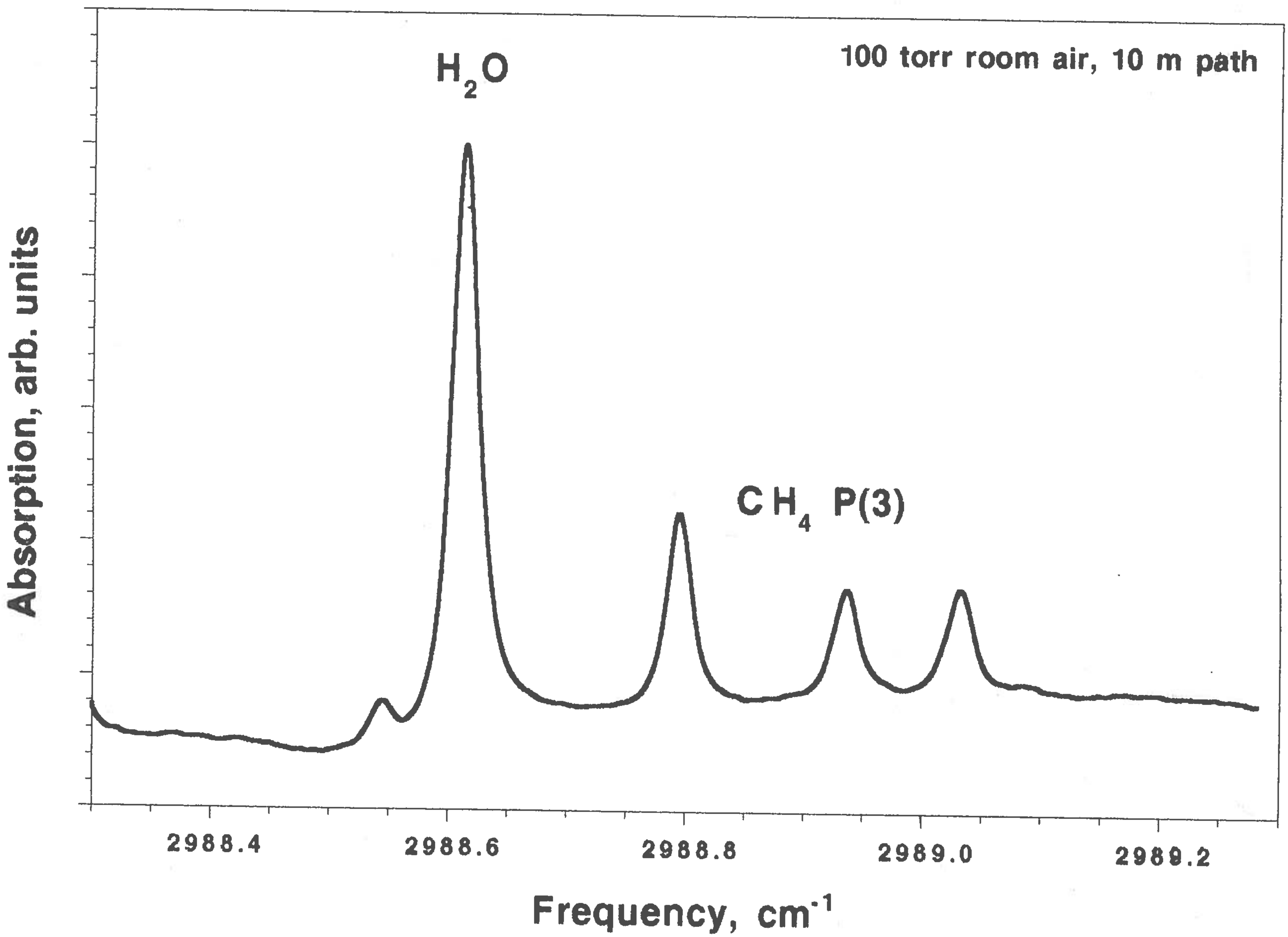


The NOAA CMDL Carbon Cycle Group maintains 4 measurement programs. In situ measurements are made at the CMDL baseline observatories: Barrow, Alaska; Mauna Loa, Hawaii; Tutuila, American Samoa; and South Pole, Antarctica. The cooperative air sampling network includes 48 fixed sites and 3 commercial vessels. Measurements from very tall towers and aircraft began in 1992. Presently, atmospheric carbon dioxide, methane, carbon monoxide, hydrogen, nitrous oxide, sulfur hexafluoride, and the stable isotopes of carbon dioxide are measured. Dr. Pieter Tans, Carbon Cycle Group, Boulder, Colorado, (303) 497-6678. ptans@cmdl.noaa.gov.

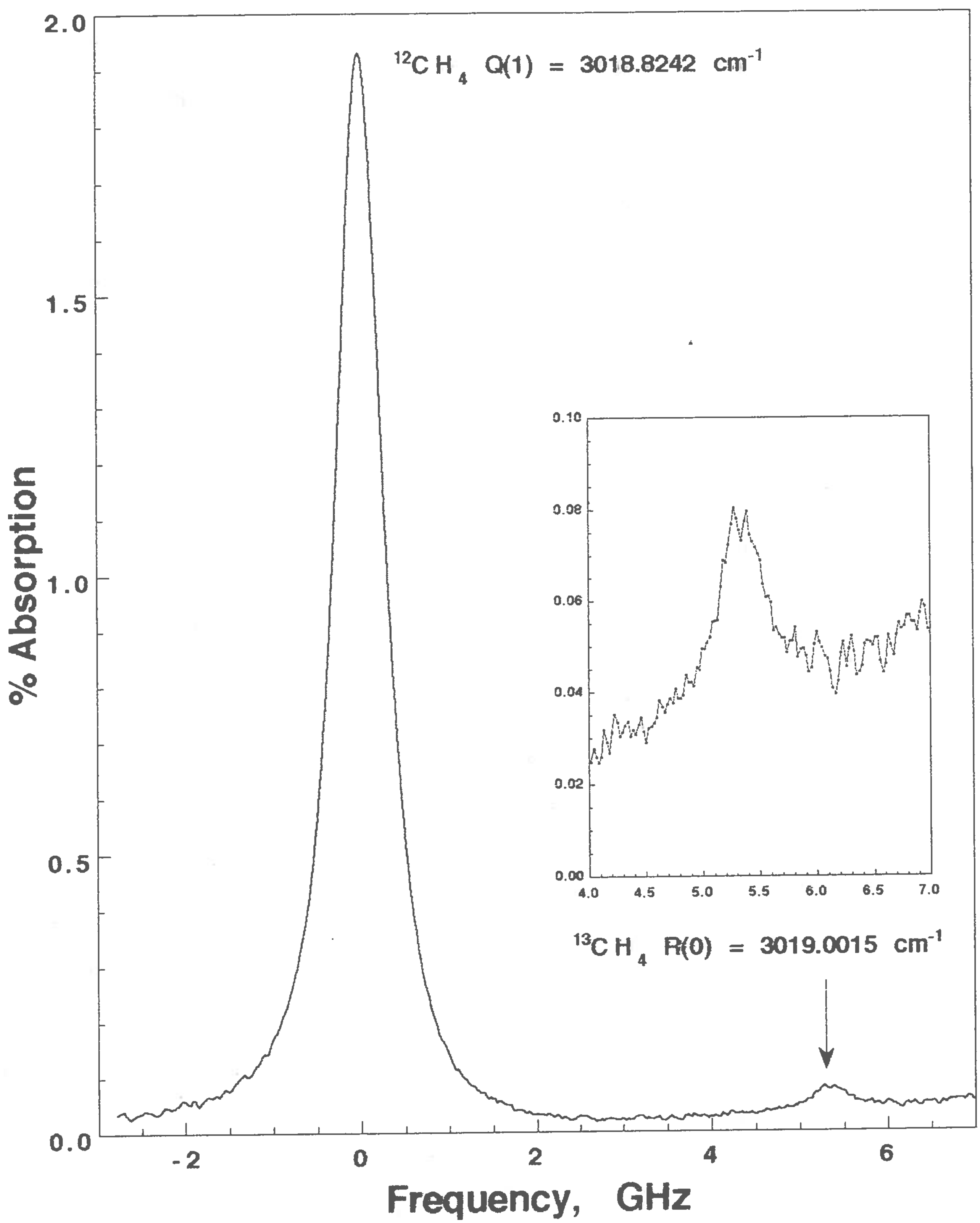


Comparison of methane mixing ratios determined from eight sites (SPO, MCM, AMS, SGI, SYO, PSA, HBA, and CGO) in the latitude band 30°-90°S. Only those samples believed to be representative of background conditions are shown.

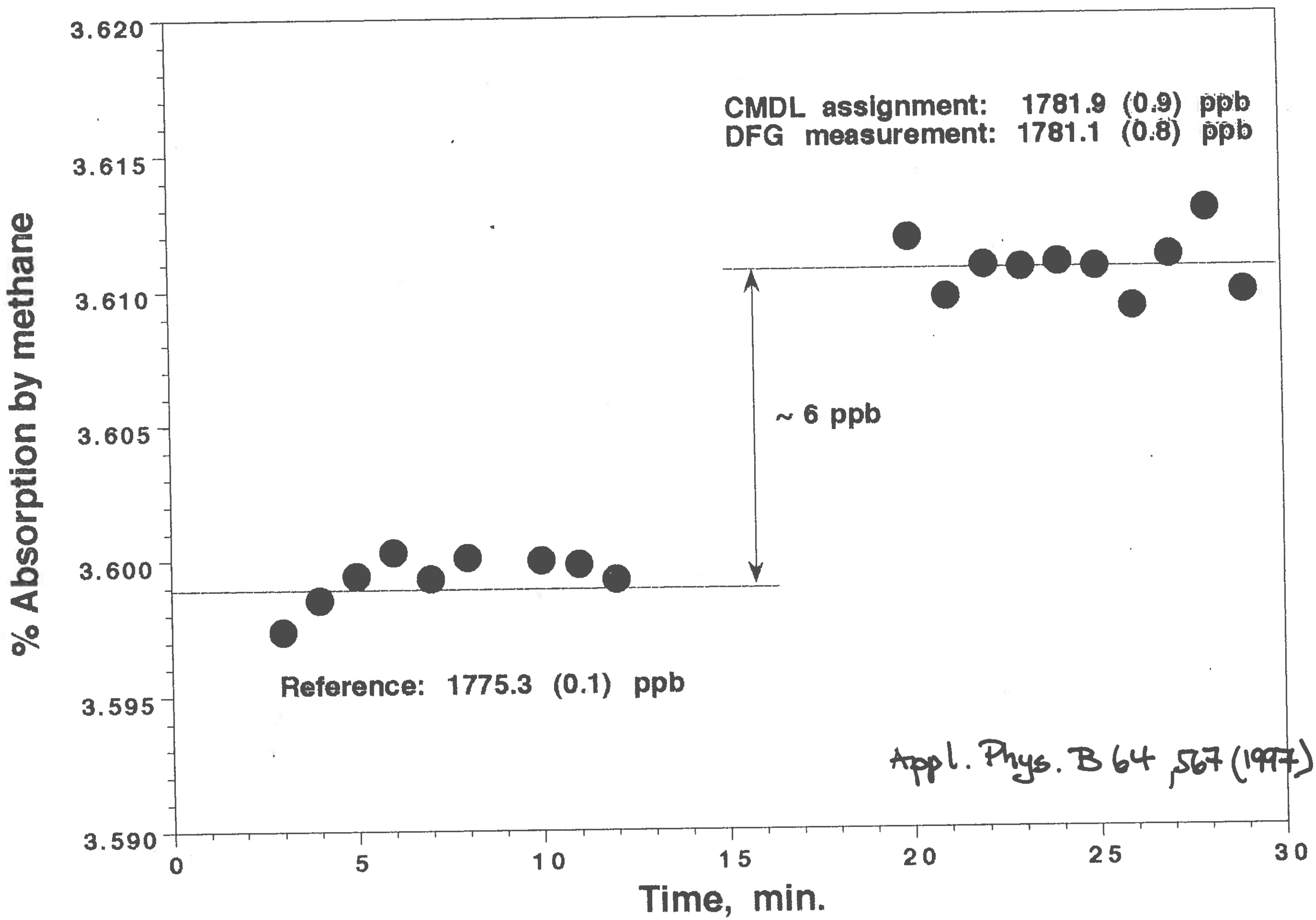
DIRECT ABSORPTION SPECTRUM OF AIR AT 3.4 μm



$^{13}C/^{12}C$ RATIO MEASUREMENT IN ATMOSPHERIC METHANE



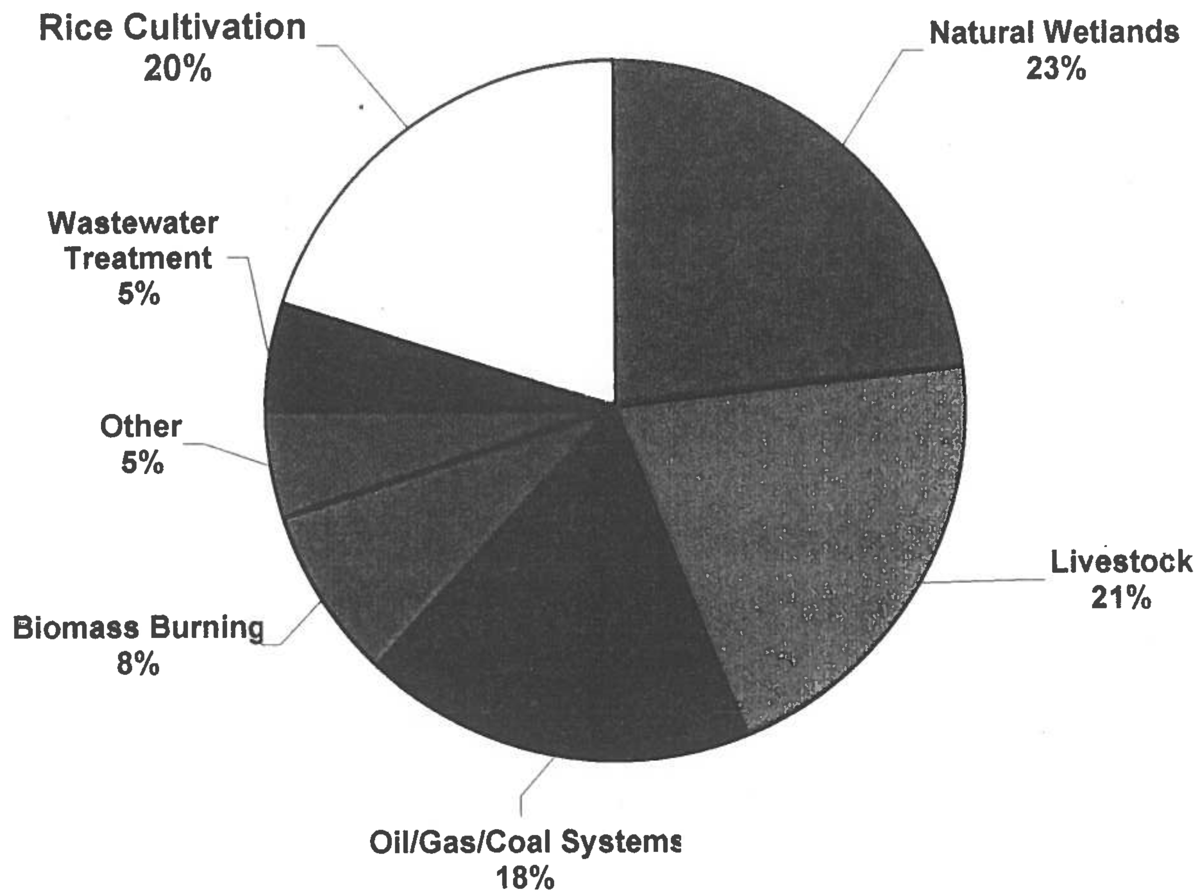
BLIND TEST



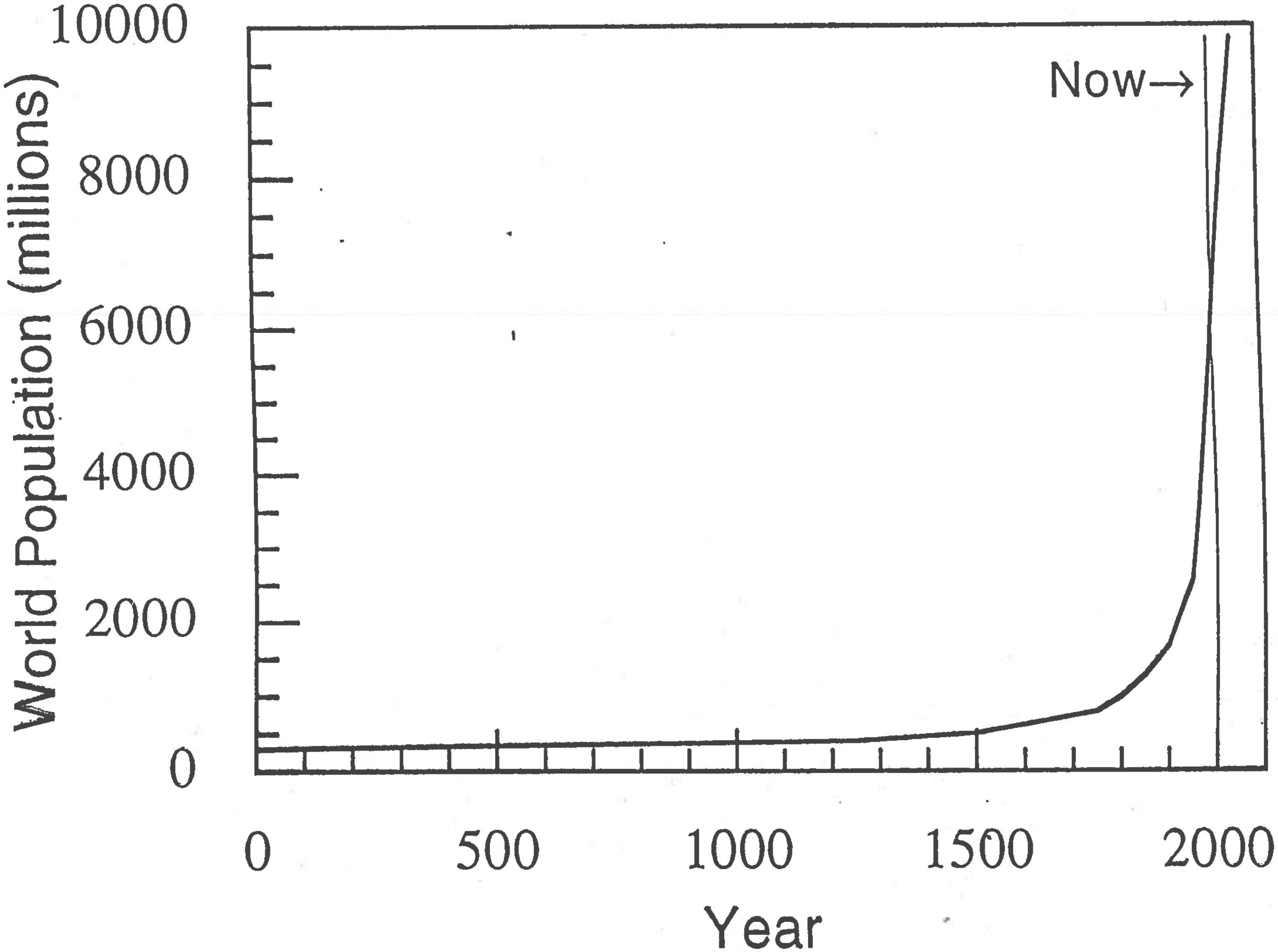
CMDL assignment: 1781.9 (0.9) ppb
DFG measurement: 1781.1 (0.8) ppb
~ 6 ppb
Reference: 1775.3 (0.1) ppb
% Absorption by methane
3.620
3.615
3.610
3.605
3.600
3.595
3.590
0
5
10
15
20
25
30
Time, min.
Appl. Phys. B 64, 567 (1997)

Monitoring Methane in Rice - Based Agroecosystem

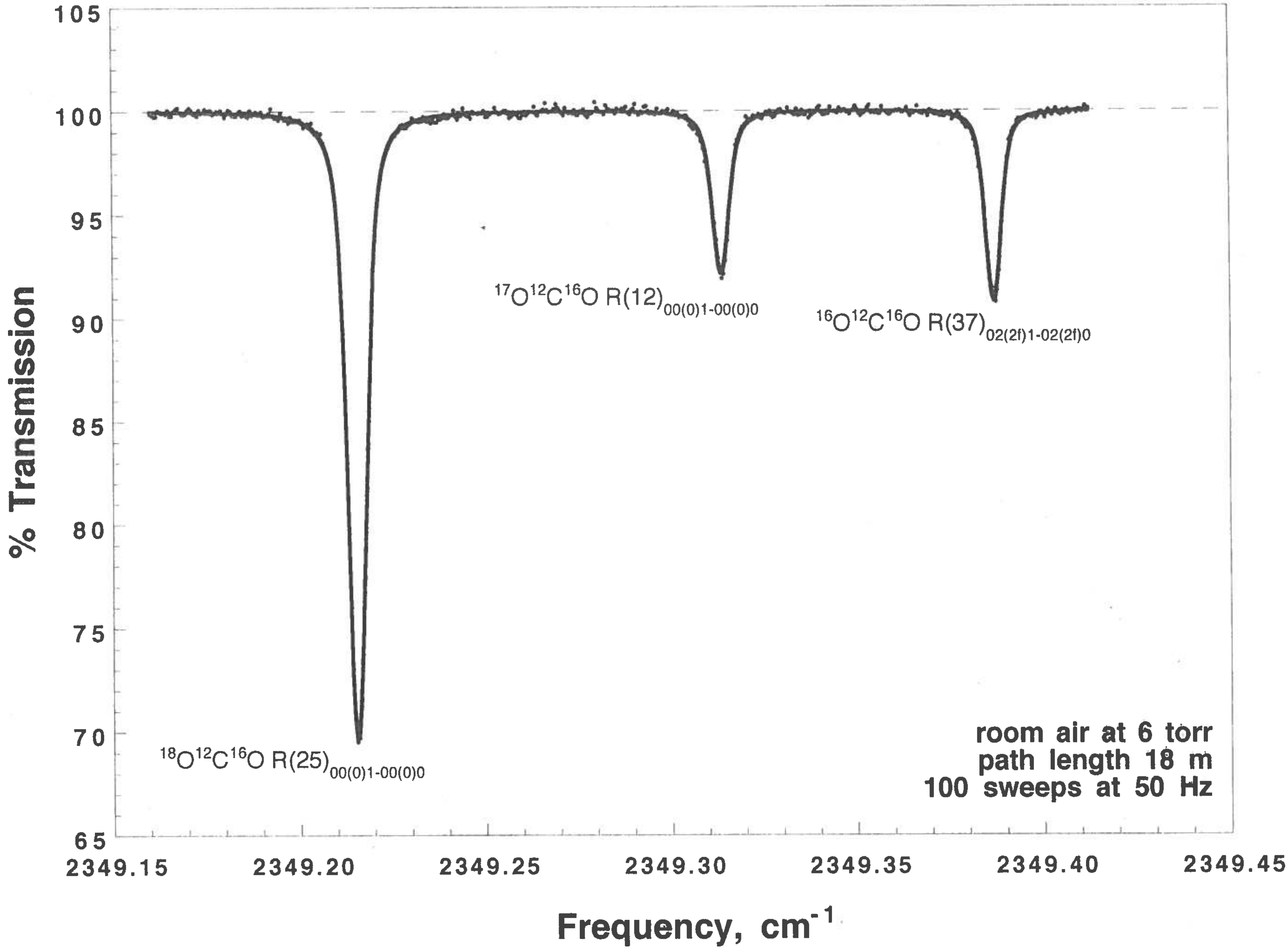
Sources of Methane Emission



Long-Term World Population Trends (1950-2025)



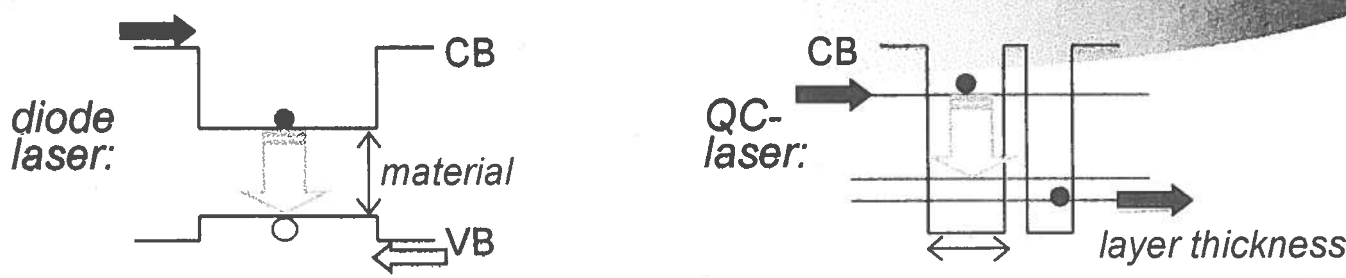
Measurements of the $^{16}O/^{17}O/^{18}O$ isotopic ratio in atmospheric carbon dioxide



Desired Improvements

* More IR DFG Power
  - Balanced Detection
* Less Optical Pump Power
  - Waveguide DFG Structure
* Fiber Coupled Pump Sources
  - Fiber Amplifiers
* More Wavelength Coverage
  - Resonantly Enhanced $\chi^{(2)}$
* Cavity Enhanced DFG Spectroscopy
* Faster Data Processing
* Smaller Size
* Lower Cost

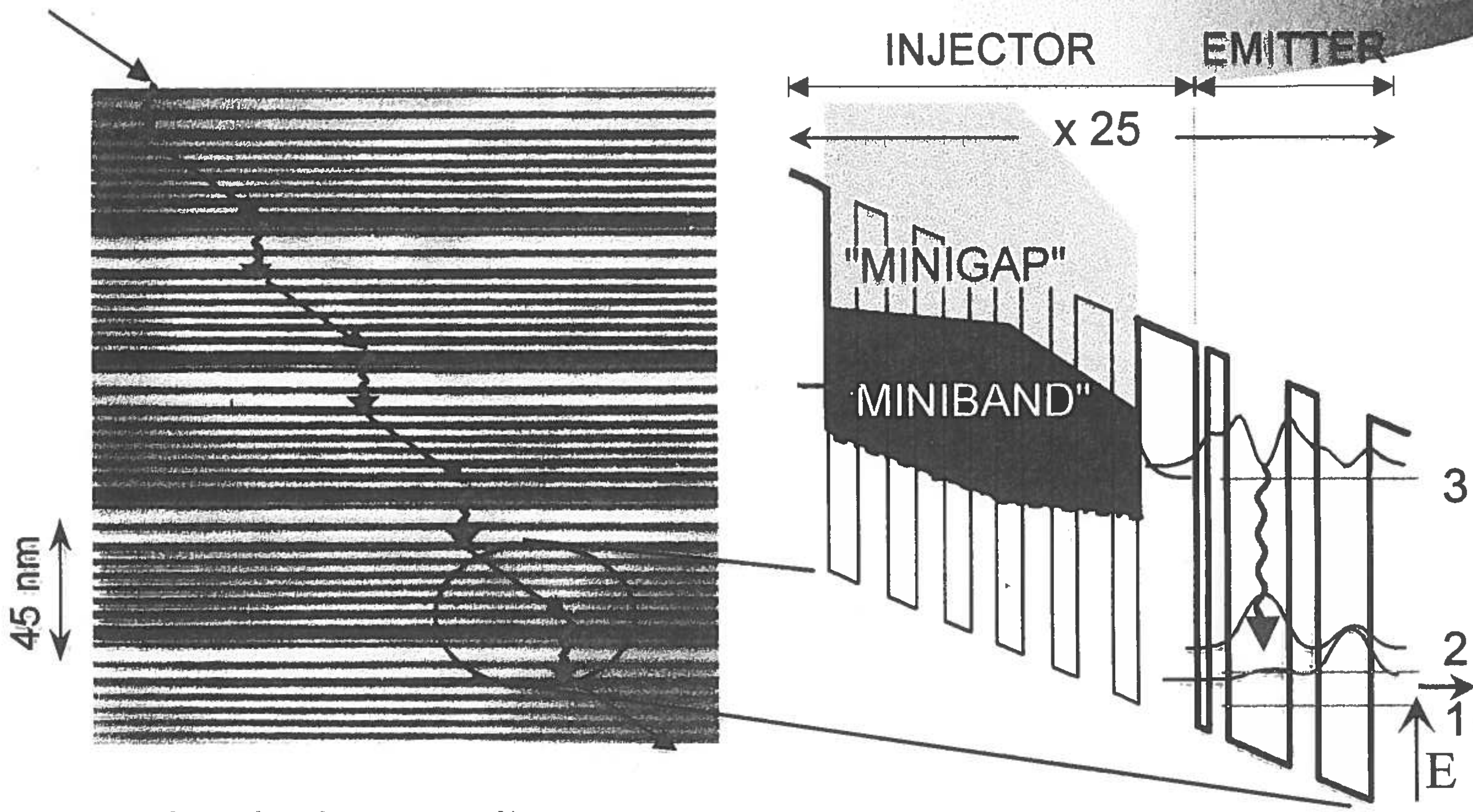
unipolar quantum-cascade (QC) laser



- *"materials by design": band structure engineering and MBE*
  population inversion, matrix elements, scattering times, and transport are *designed* for optimum performance
- tailor wavelength throughout mid-IR via thickness control:
  » **3 - 17 μm**
- N laser photons per injected electron through cascading:
  » **very high power: 0.5 - 1 W**
- wide range of sensor applications:
  » **environmental, automotive, medical, military, ...**

Lucent Technologies
Bell Labs Innovations

state-of-the-art room temperature $\lambda = 5\mu m$ QC-laser

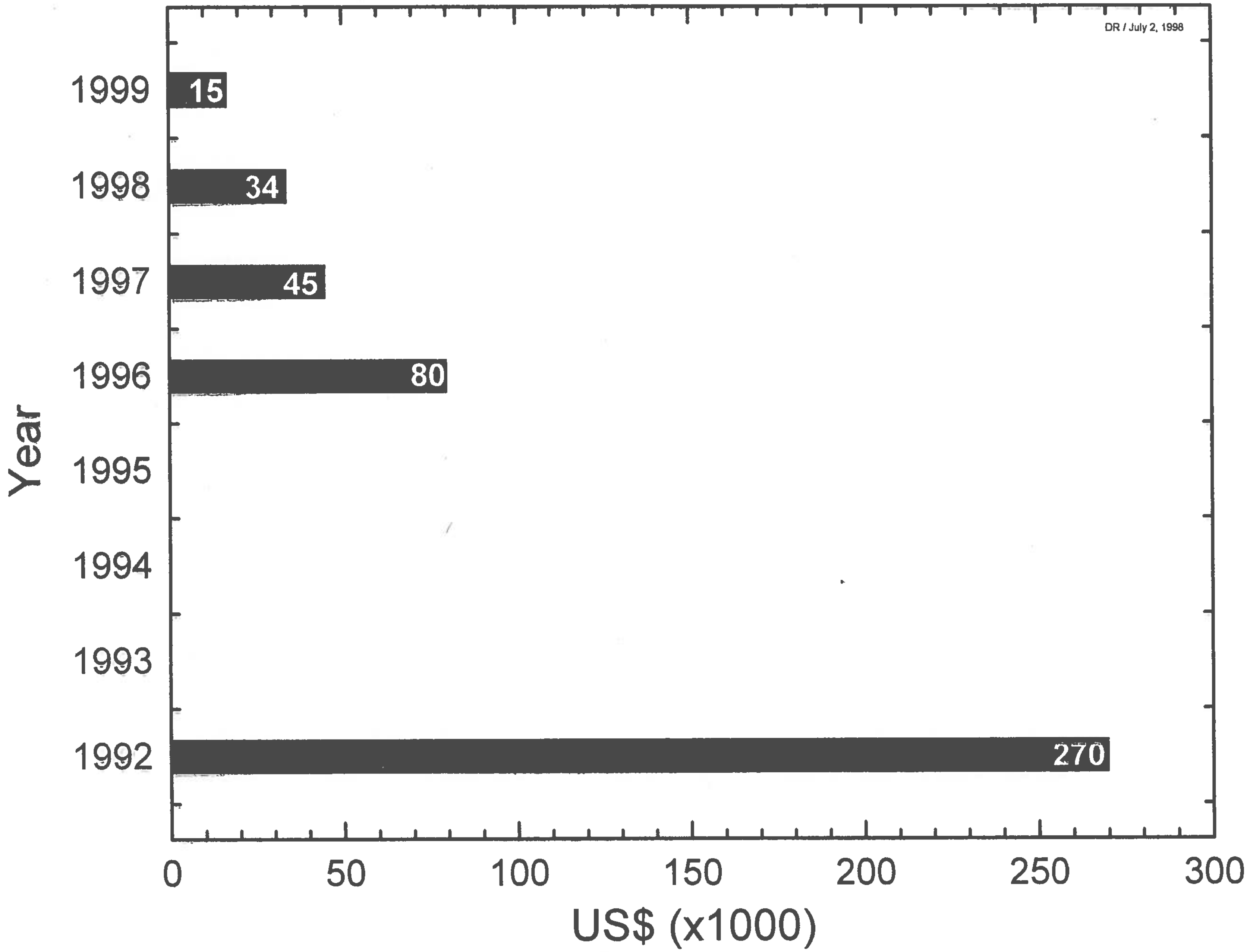


molecular beam epitaxy

STATUS OF DFG-BASED GAS SENSORS

Device Characteristics	Unit	1998	1999 projected
SPECIES DETECTED		8	11
MINIMUM DETECTABLE ABSORBANCE		1×10^{-4}	5×10^{-5}..1×10^{-5}
SELECTIVITY	MHz	50	30
RESPONSE TIME	sec	1..10	0.1..10
LONG-TERM STABILITY	%	1	1
DYNAMIC RANGE	ppb	10^{1}..10^{4}	10^{1}..10^{4}
SIZE	ft^3	0.75	0.5
WEIGHT	lbs	<50	<20
LIFETIME OF DIODE LASER	hrs	10,000	>100,000
MAINTENANCE REQUIRED		none	none
VIBRATION SENSITIVE		yes	no

Cost Evolution: 1992 - 1999



Summary

* Diode Laser Based Trace Gas Sensor
  - Compact, tunable, robust
  - High sensitivity and resolution
    Current limits: ~10^{-4} absorption
  - Fast DATA acquisition and analysis

* Applications in Trace Gas Detection
  - CO and H_2CO : NASA-JSC
  - CH_4 : NOAA and NASA
  - NO and CO : Baylor College of Medicine

* Future Outlook
  - Fiber-coupled (alignment insensitive)
  - Fiber amplifiers
  - Cavity enhanced spectroscopy
  - Longer mid-IR wavelengths

Robert F. Curl

Frank K. Tittel

David G. Lancaster

Dirk Richter

http://www.ruf.rice.edu/~lasersci/

Acknowledgments

L. Goldberg (NRL)

M. Fejer (Stanford)

L. Hollberg (NIST)

J. Graf (NASA)

K. Petrov (Gemfire)

R.F. Curl

D. Lancaster

D. Richter

Y. Morimoto

C. Babich

J. Klattenhoff

A. Kosterev

R. Weidner

National Aeronautics and Space Administration (NASA)

Texas Advanced Technology Program

Welch Foundation