Emerging Trace Gas Detection Techniques: Concepts and Real World Applications

Frank K. Tittel
Rice University
Houston, USA

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

OUTLINE

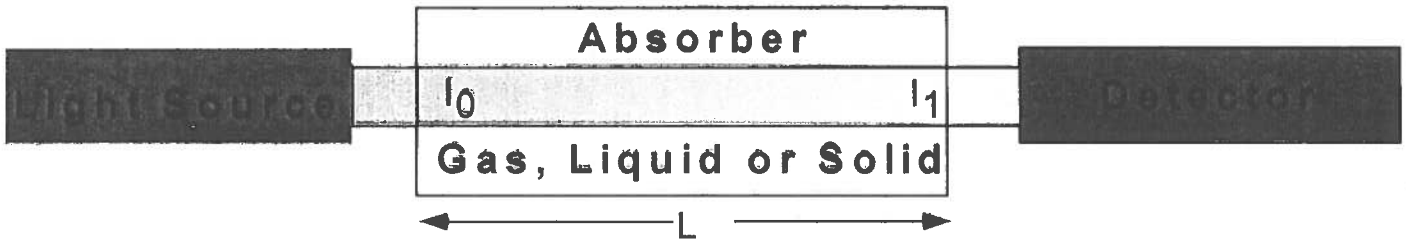
- Motivation, Design, and Technology Issues
- Infrared Diode Laser Based Gas Sensors
- Performance Characteristics of Compact IR Sensors
- Selected Applications of Trace Gas Detection
- Outlook and Summary

Applications of Trace Gas Detection

- Urban and Industrial Emission Measurements
  - Industrial Plants
  - Combustion Sources
  - Automobile
- Rural Emission Measurements
  - Agriculture
- Environment Monitoring
  - Atmospheric Chemistry
  - Volcanic Emissions
- Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Life Support
- Chemical Analysis and Process Control
  - Semiconductor Industry
- Medical Applications

RICE

Absorption Spectroscopy



Beer's Law

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

$\alpha(\nu)$-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 - absorption line strength (cm), $\Delta\nu$ – linewidth (cm^{-1})

g (ν) - line shape function: Gaussian, Voigt, or Lorentzian profile

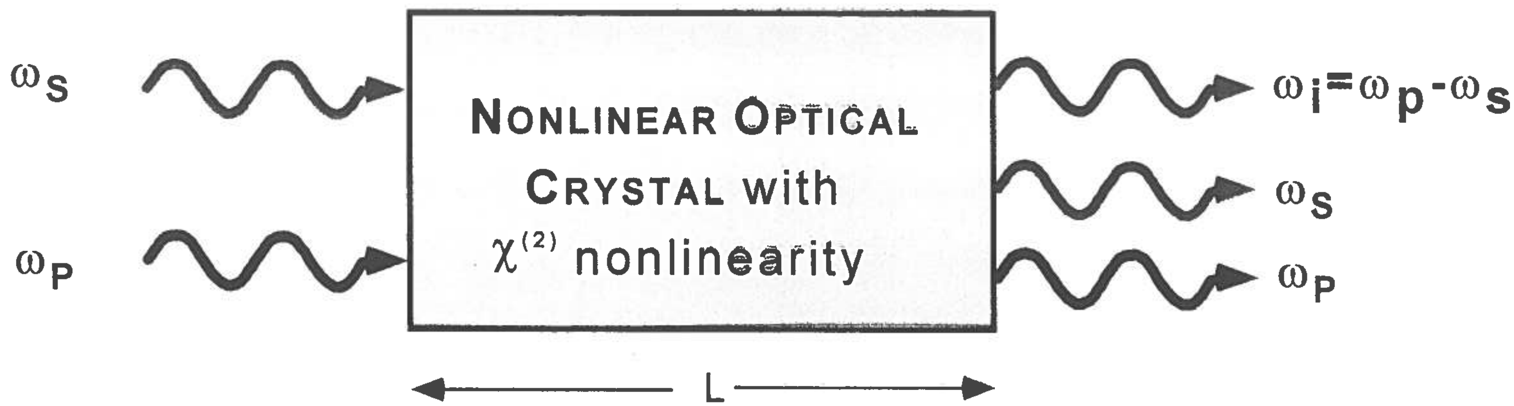
RICE

Diode Laser Based Trace Gas Detection Methods

- Overtone Laser Spectroscopy
- Tunable Infrared Diode Laser Absorption Spectroscopy
  - Lead salt diode lasers
  - Mid-infrared diode lasers
  - Quantum Cascade - DFB lasers
- DFG Based Laser Spectroscopy
  - Optical frequency conversion of two diode lasers in a NLO material

RICE

Difference Frequency Generation



MID-IR POWER: $P_i \sim C \cdot P_{PUMP} \cdot P_{SIGNAL} \cdot L\, h(\zeta,\mu)$

$C = (\omega_i/n_i)^3 d^2_{eff}$, $\mu = k_s/k_p$, $\zeta = L/b$

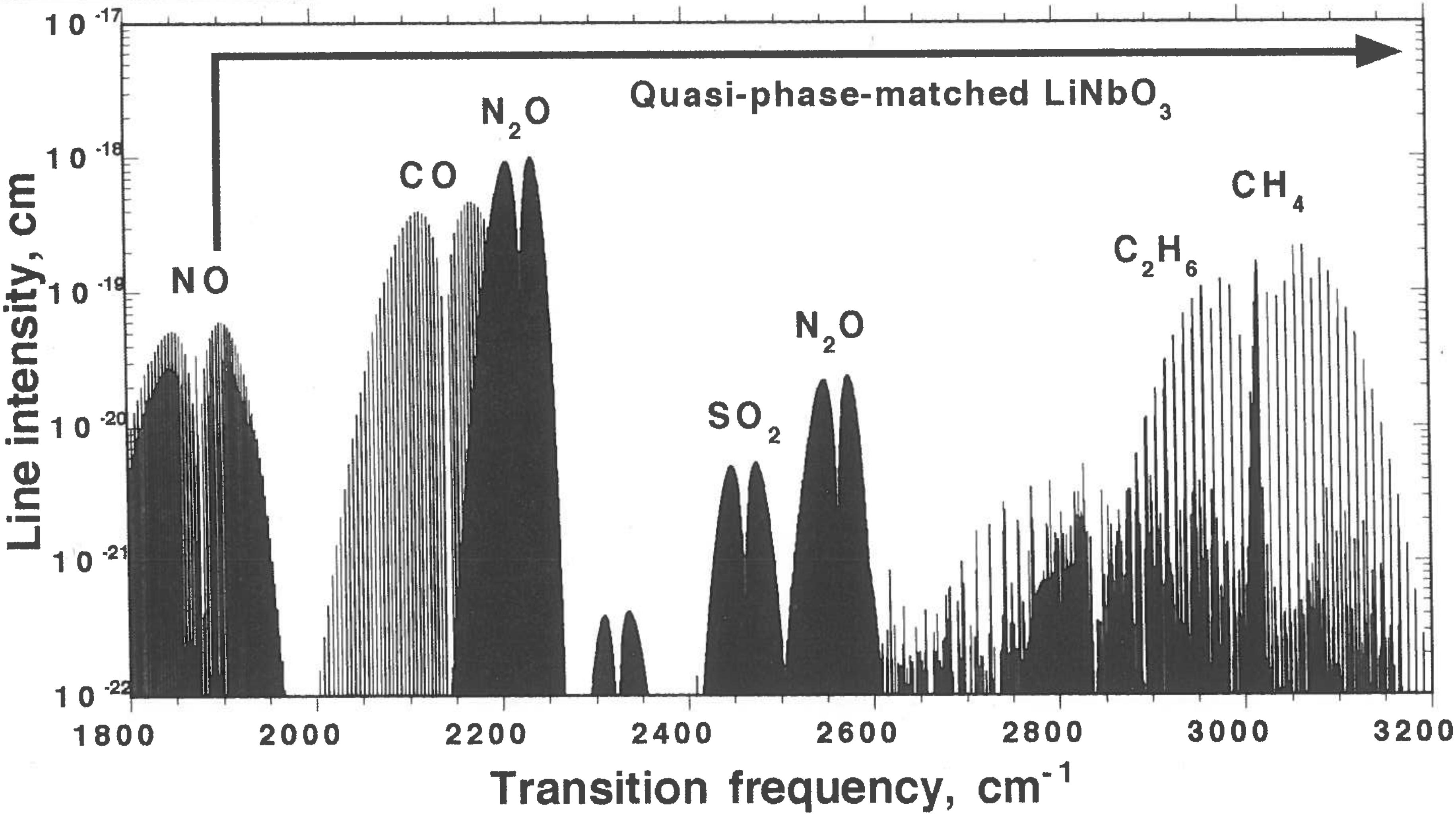
EXAMPLE: FOR PPLN AT 3.5 μM

$C \sim 450\ \mu W / cm \cdot W^2$

~3 μW for 6mW and 540mW LD pump sources

RICE

SURVEY ABSORPTION SPECTRA OF SOME ATMOSPHERIC TRACE GASES

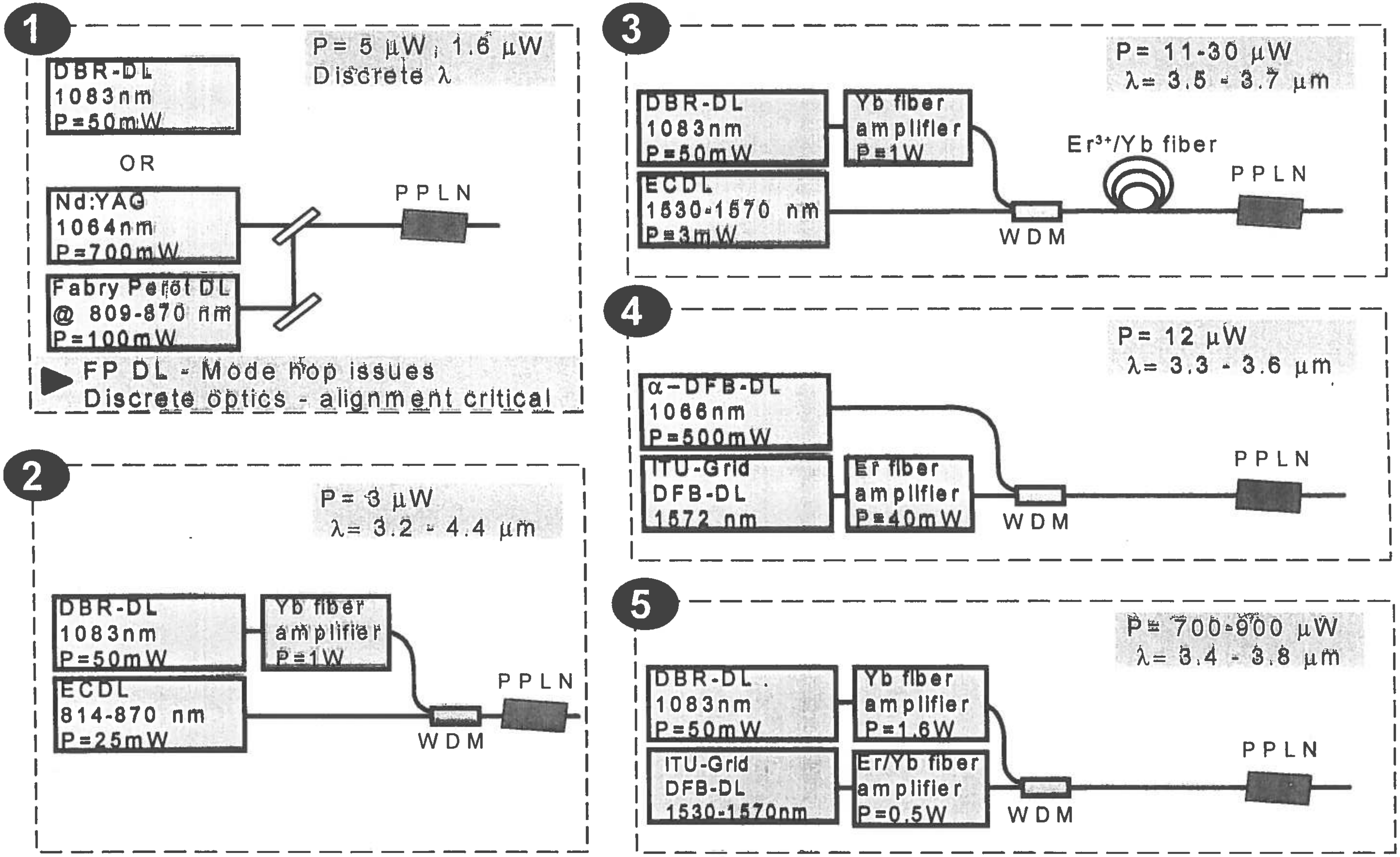


Design Features of CW DFG Sensor

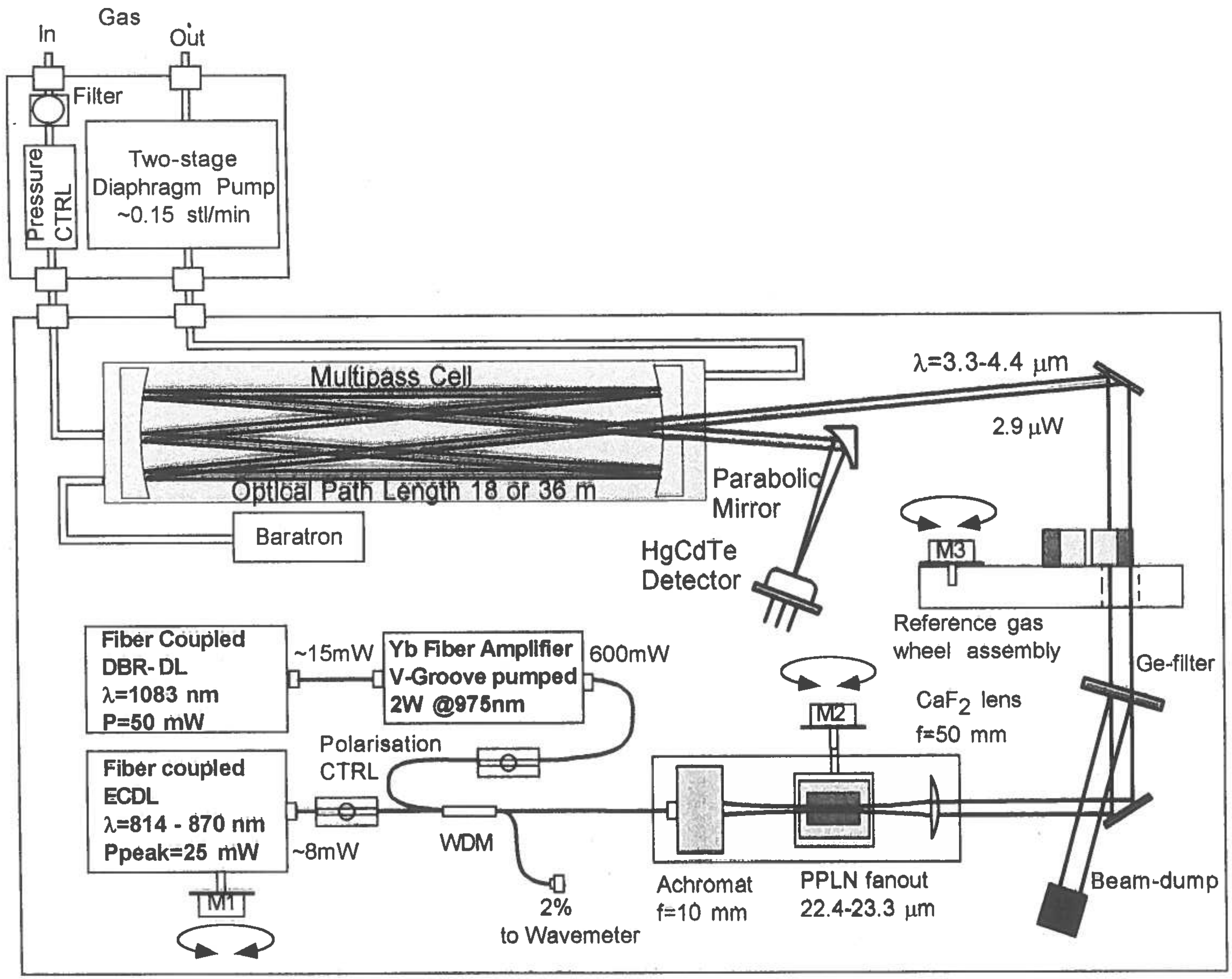
- Adequate Mid-infrared DFG Power
- High Sensitivity (ppb concentrations)
- High Selectivity (<30 MHz)
- Wavelength Tunable
- Single and Multiple Trace Gas Species
- Fast Data Acquisition and Analysis
- Room Temperature
- Non-invasive, Point or Remote Monitoring
- Compact, Lightweight and Robust
- Power Efficient
- No Consumables , Low Maintenance and Cost Effective

RICE

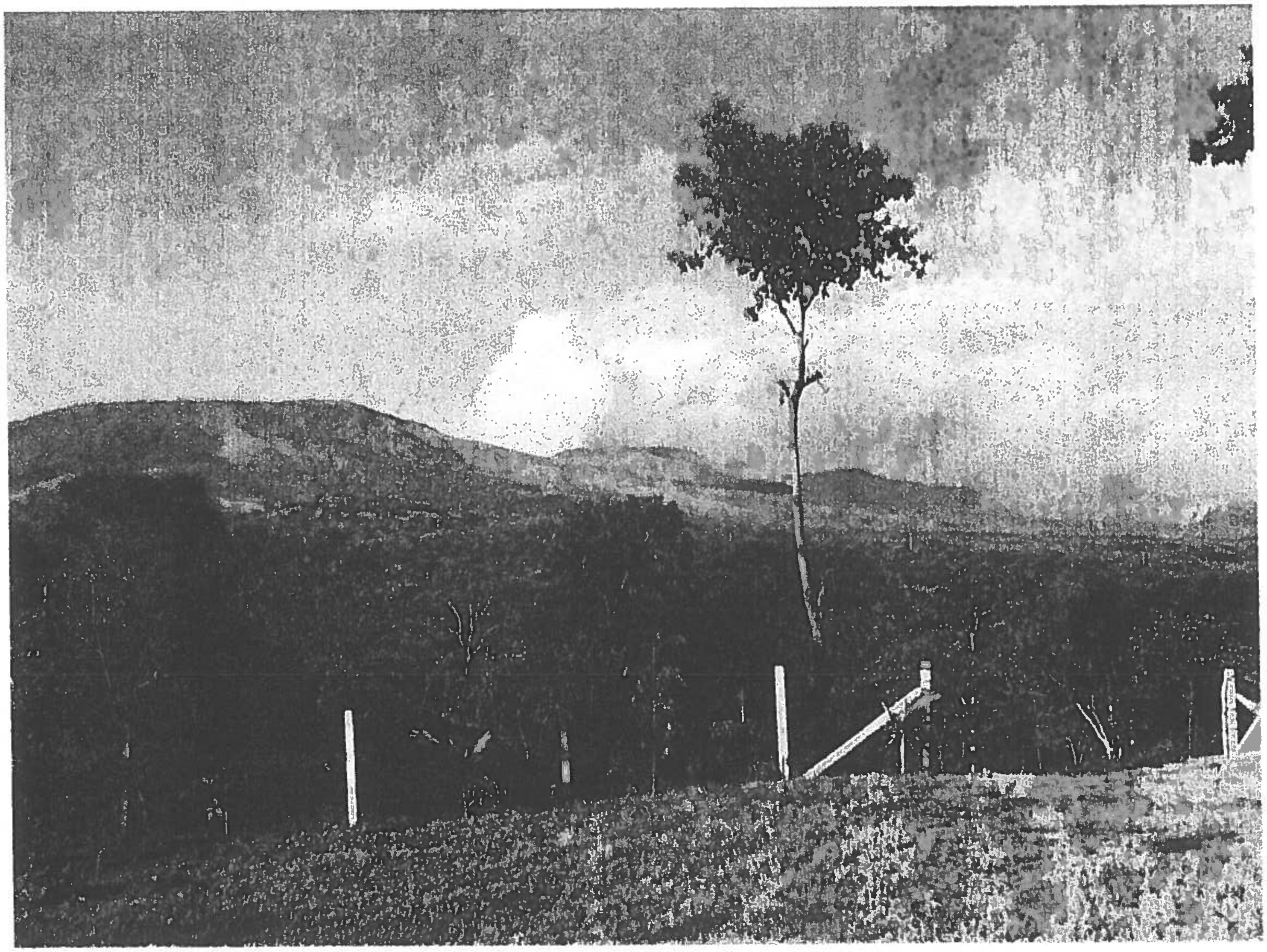
DFG Pump Source Combinations



Schematic of DFG multi-component gas sensor

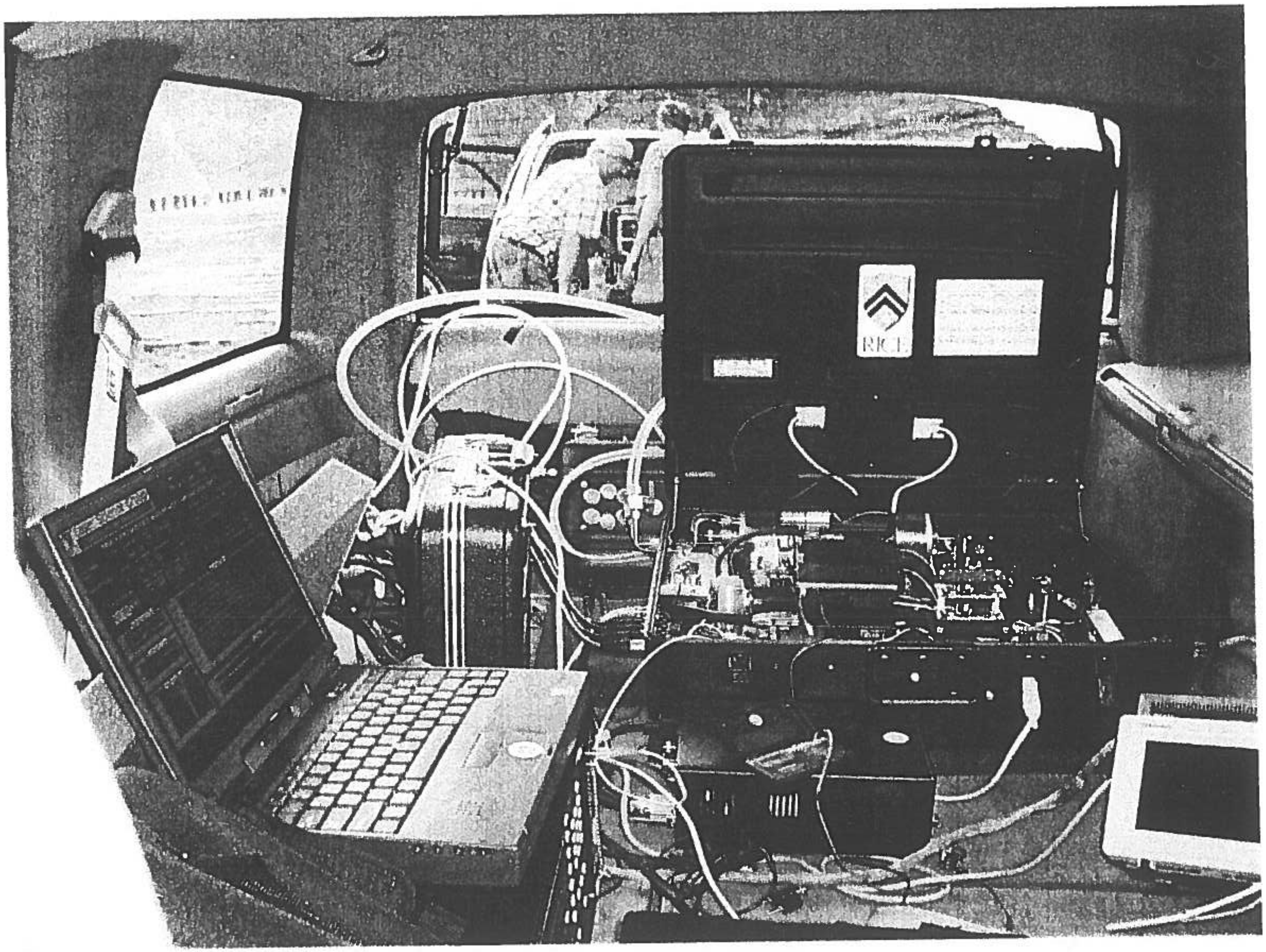


Masaya Volcano Emissions Campaign April 2000



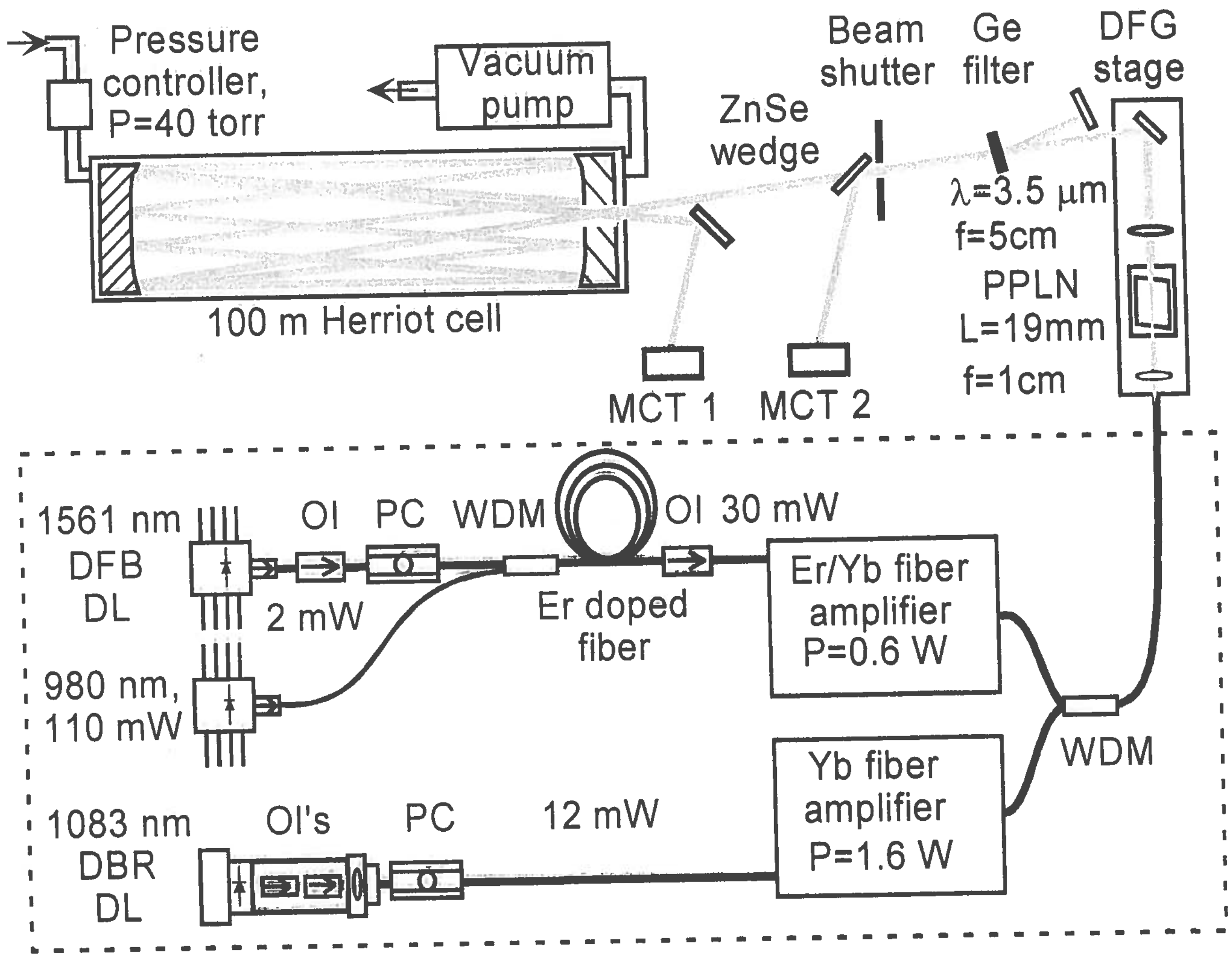
RICE

Masaya Volcano Emissions Campaign April 2000

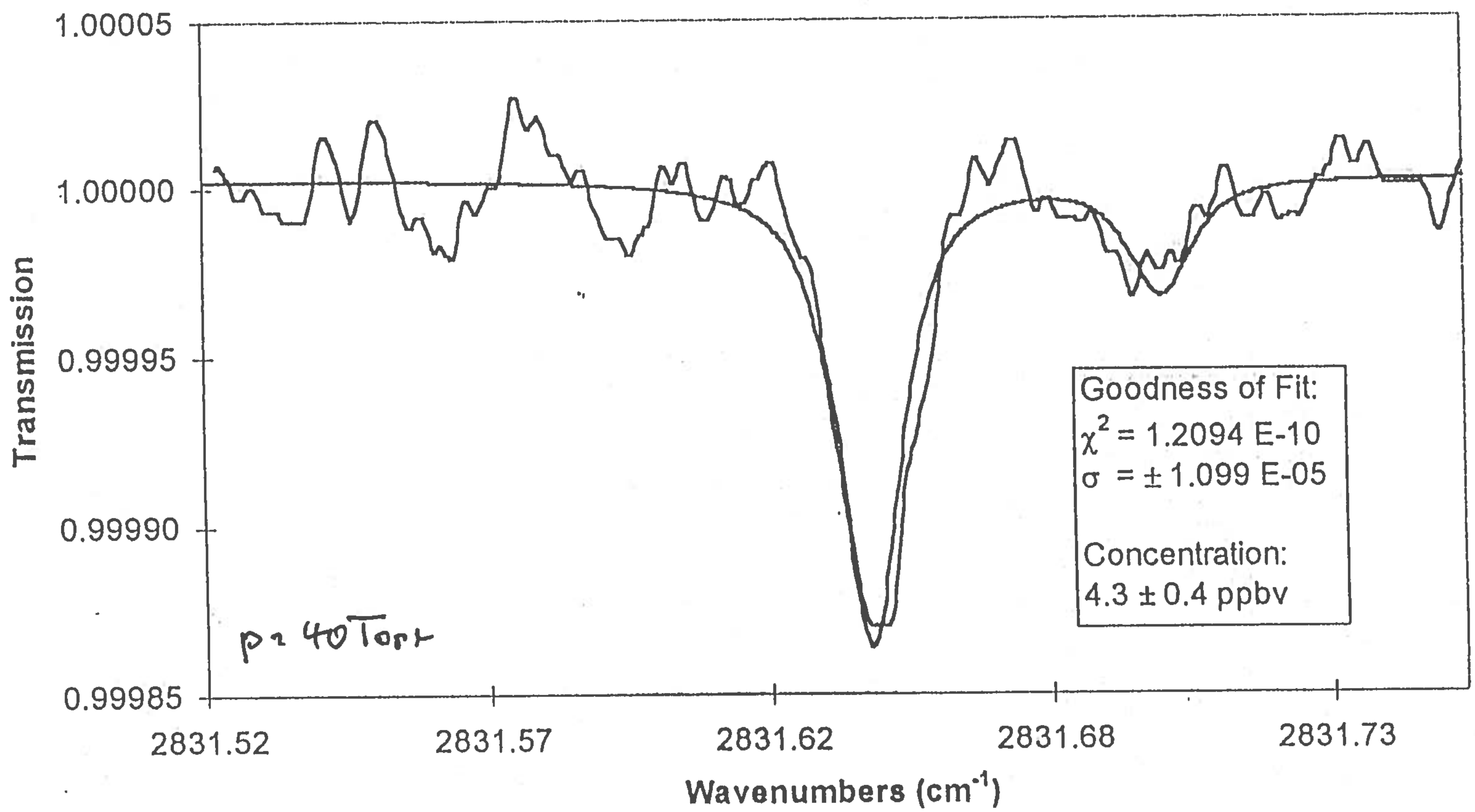


RICE

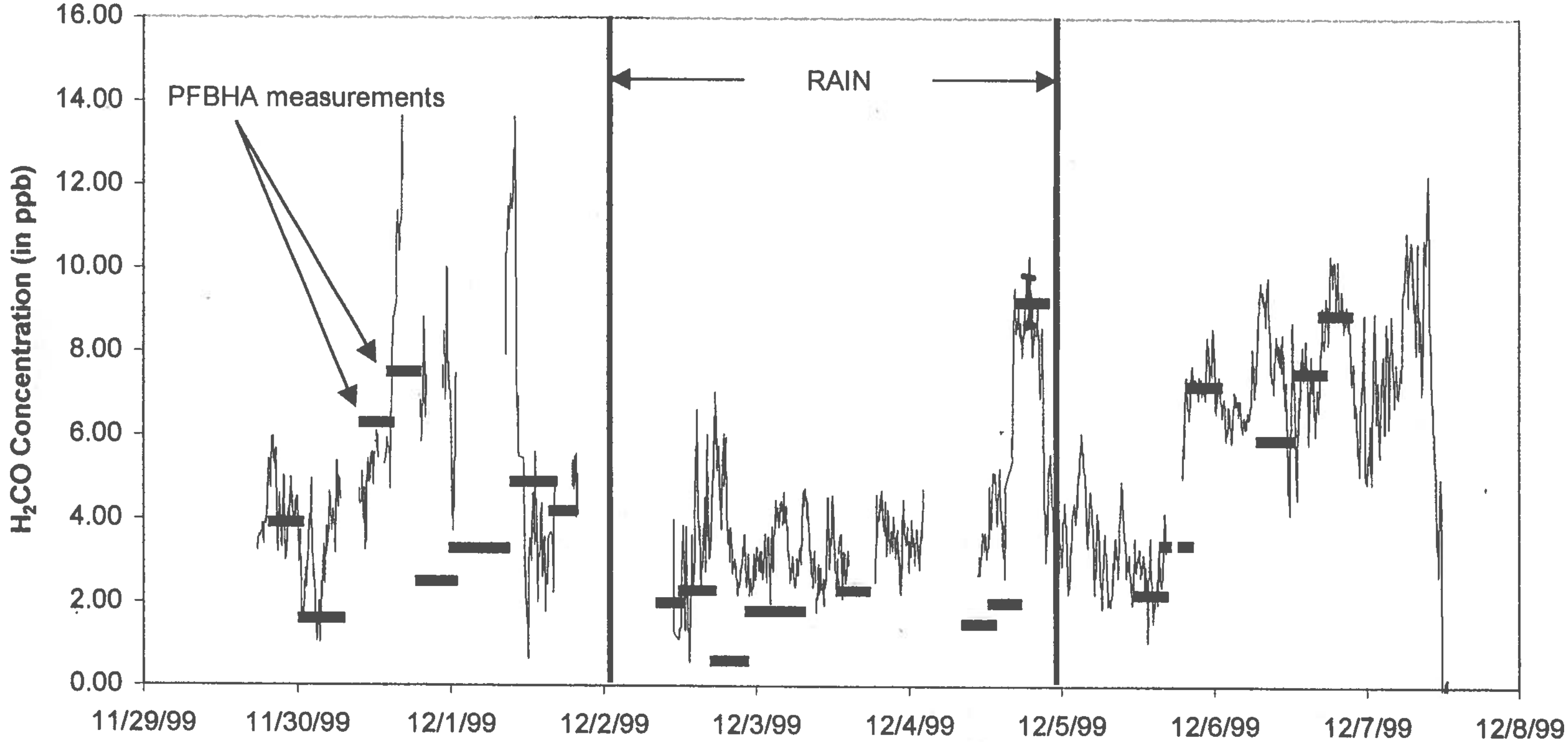
DFG Spectroscopic Source at 3.53 μm



H_2CO Detection in Ambient Air at 3.53 μm



9 Day H_2CO Detection at 3.53 μm in Houston

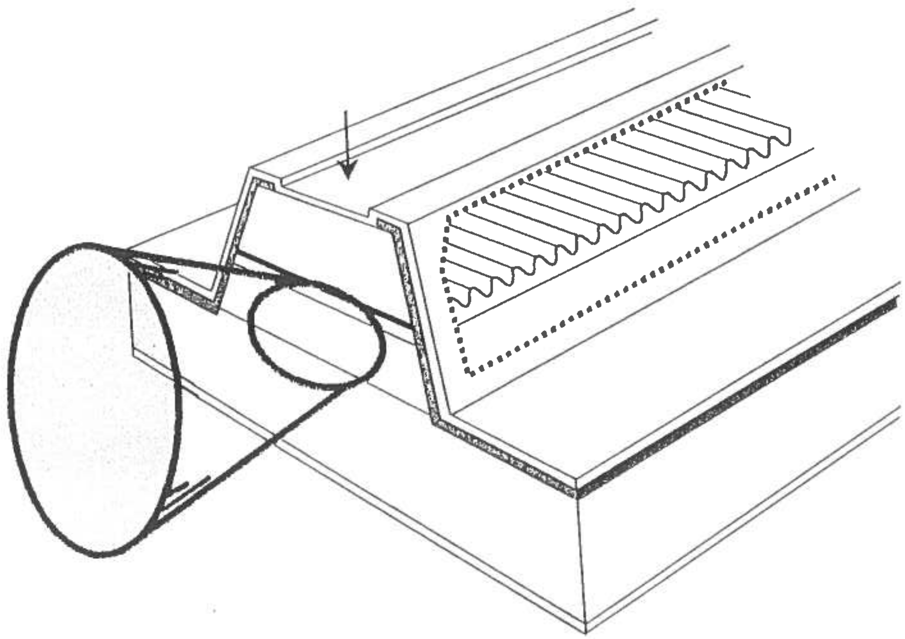


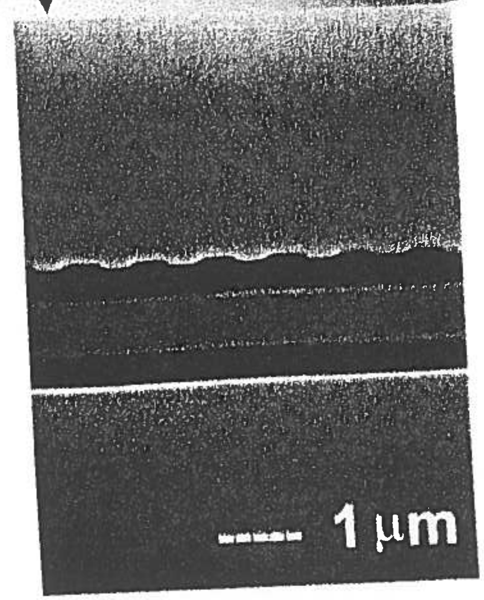
Key Characteristics of Quantum Cascade Lasers

- Laser wavelengths cover entire range from 3.4 to 17μm determined by layer thickness of same material
- Intrinsically high power lasers (determined by number of stages)
  - CW: 0.2W @ 80 °K, ~100 mW single frequency
  - Pulsed: 0.5W peak at room temperature, ~15 mW avg. @ 300 °K
- High Spectral purity (single mode)
- Wavelength tuning by current or temperature scanning
- High reliability: low failure rate, long lifetime, robust operation and extremely reproducible emission wavelengths

RICE

QC - distributed feedback laser

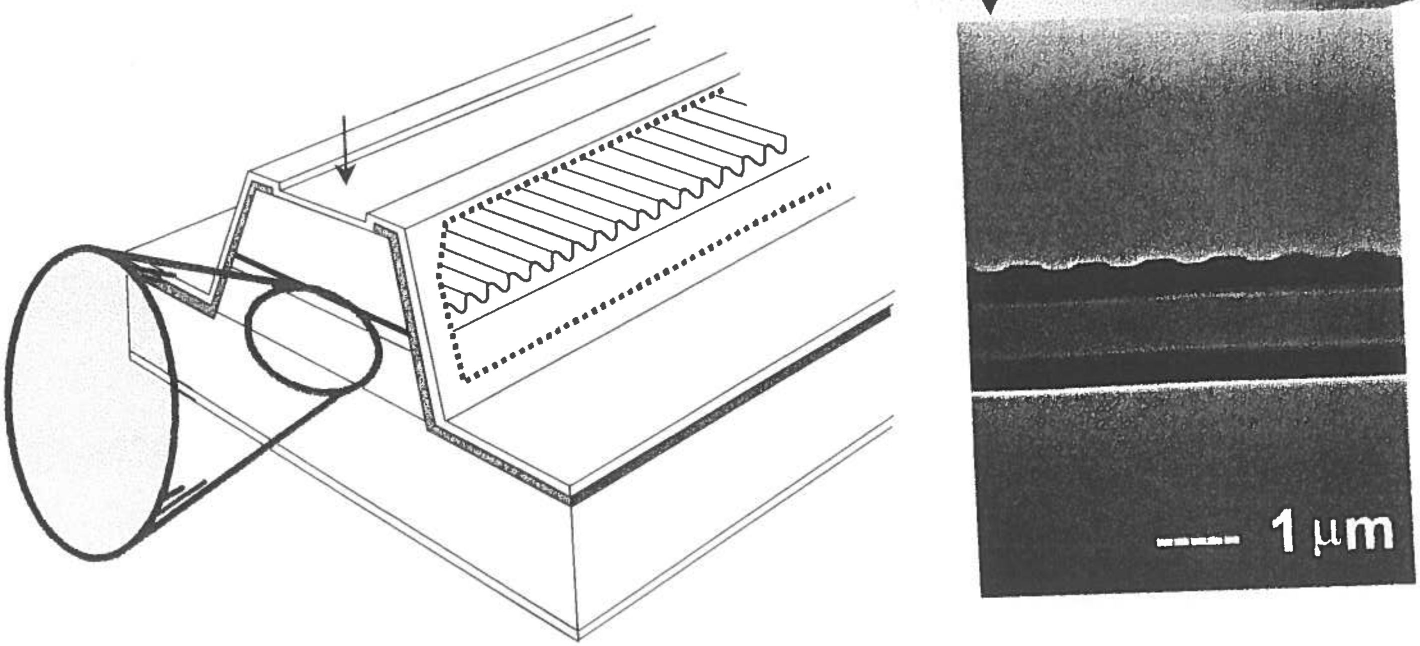




grating selects single-mode, tunable by temperature

$$\lambda_{em} = 2\, n(T)\, \Lambda_{grat}$$

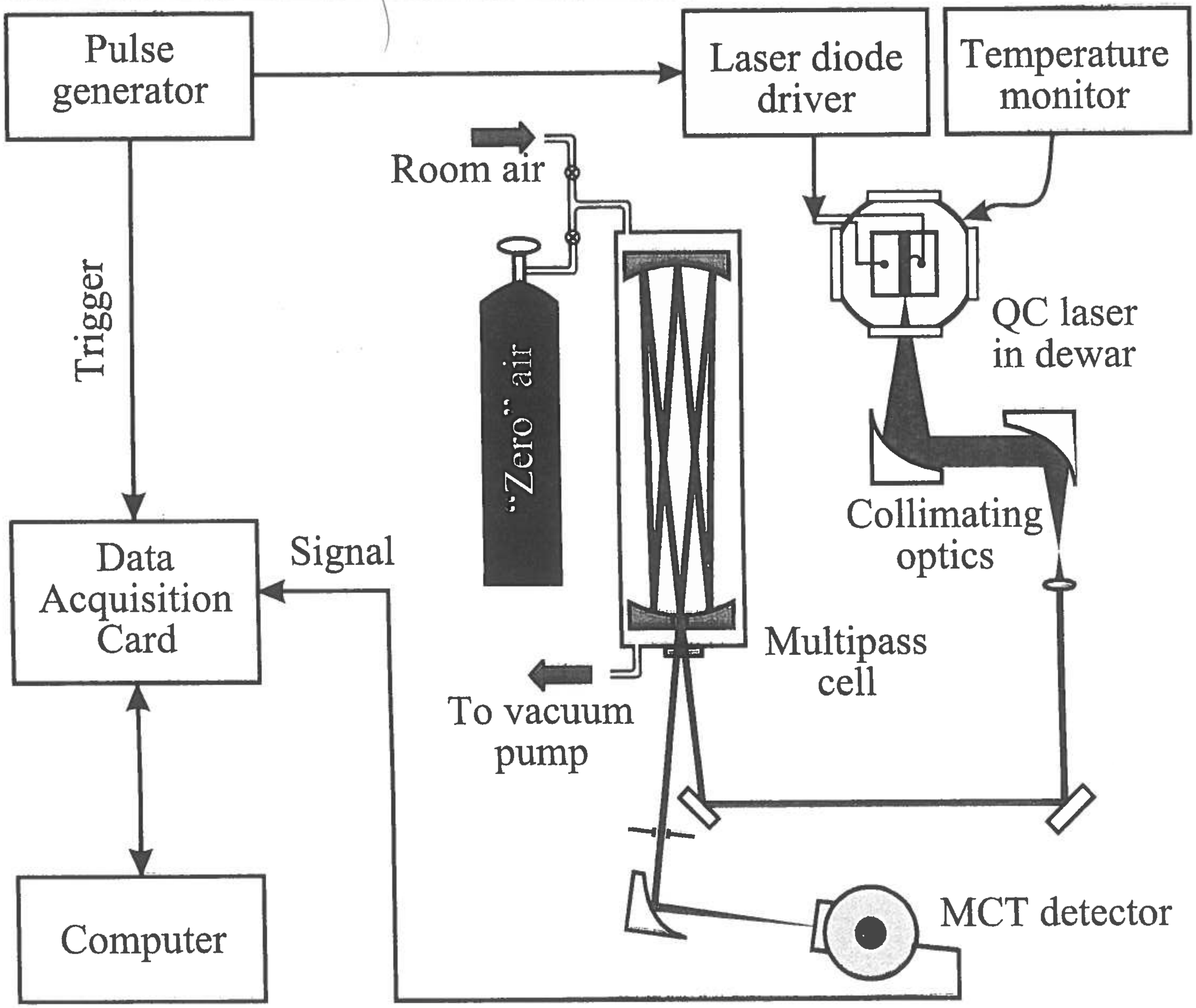
QC - distributed feedback laser



grating selects single-mode, tunable by temperature

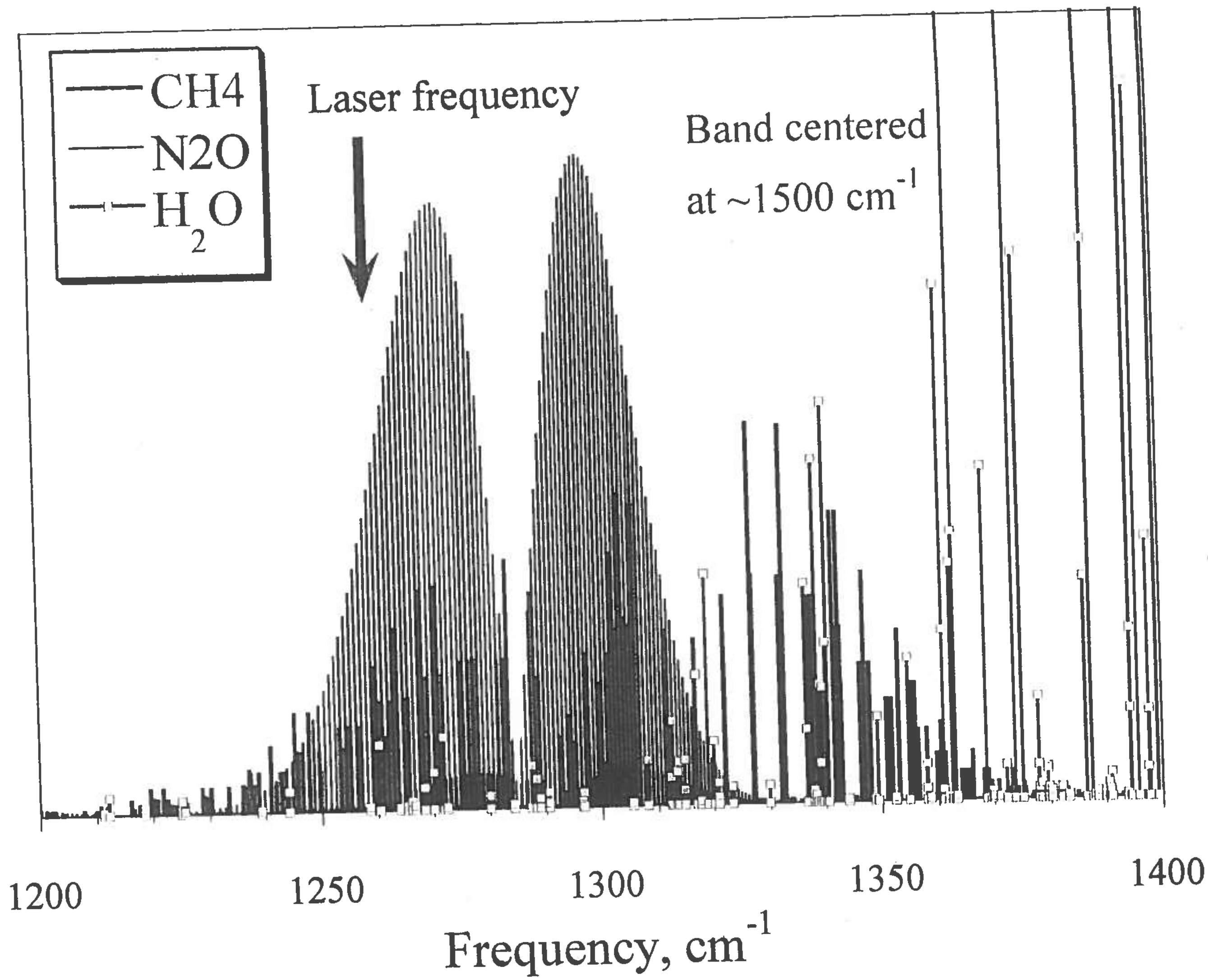
$$\lambda_{em} = 2\, n(T)\, \Lambda_{grat}$$

Trace Gas Detection with a Multipass Cell



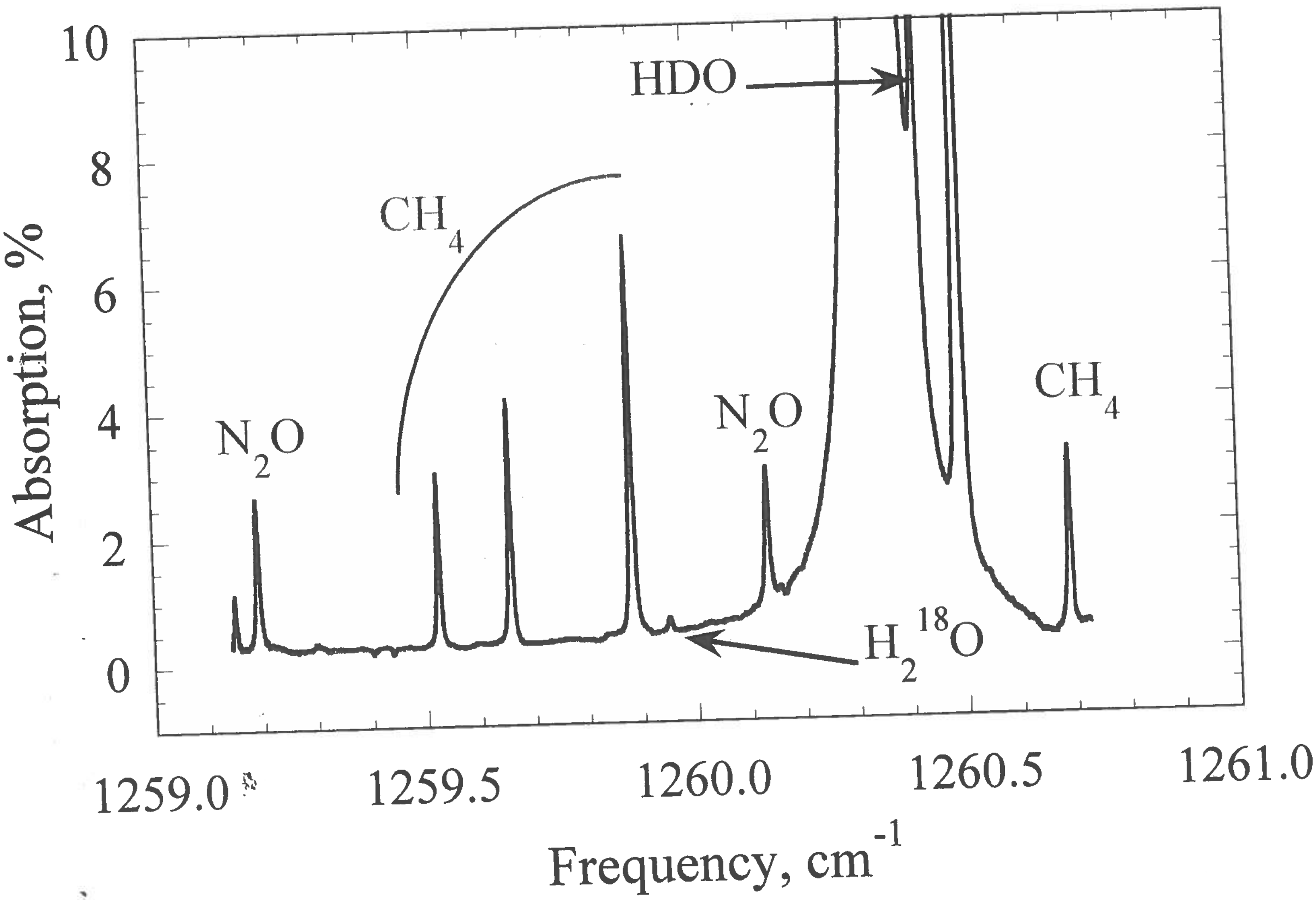
RICE

CH_4, H_2O and N_2O Absorption Spectra



RICE

Absorption Spectrum of Room Air



RICE

Summary

- Diode Laser Based Trace Gas Sensors
  - Compact, tunable, robust (alignment insensitive)
  - High sensitivity ($<3 \cdot 10^{-5}$) and selectivity (<60 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: CH_4, H_2CO, NO_2, N_2O, HCl, CO_2 CO, NO, H_2O, SO_2, isotopic species of $^{12,13}C$, $^{16,17,18}O$, $^{35,37}Cl$
- Current Applications in Trace Gas Detection
  - H_2CO and CO: NASA-JSC, NCAR and EPA
  - CH_4: NOAA, NASA-JPL, and gas industry
- Future Directions
  - New DFG pump lasers:Fiber and tunable DBR diode lasers
  - Cavity enhanced spectroscopy
  - Longer mid-IR wavelengths(5-16 microns) with orientation patterned GaAs
  - Medical Diagnostics: CO, NO, CO_2 and NH_3

RICE