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Spectroscopic Applications of Quantum Cascade Lasers

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OUTLINE

PQE
2000
Snowbird,
UT

- Motivation and Background
- Design of QC-DFB Laser Spectrometers
- Real World Applications
- Outlook and Summary

Wide Range of Gas Sensor Applications

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

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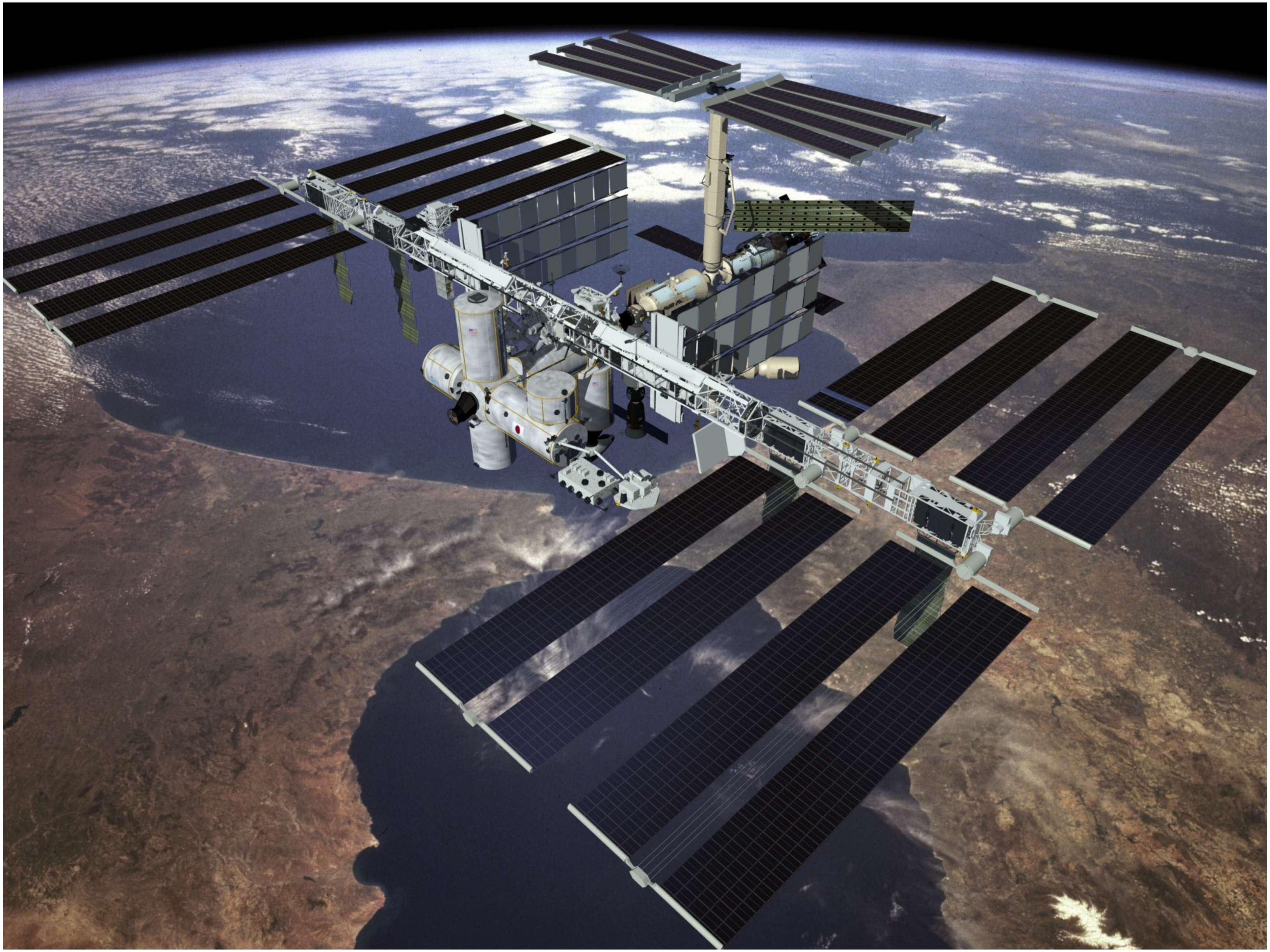
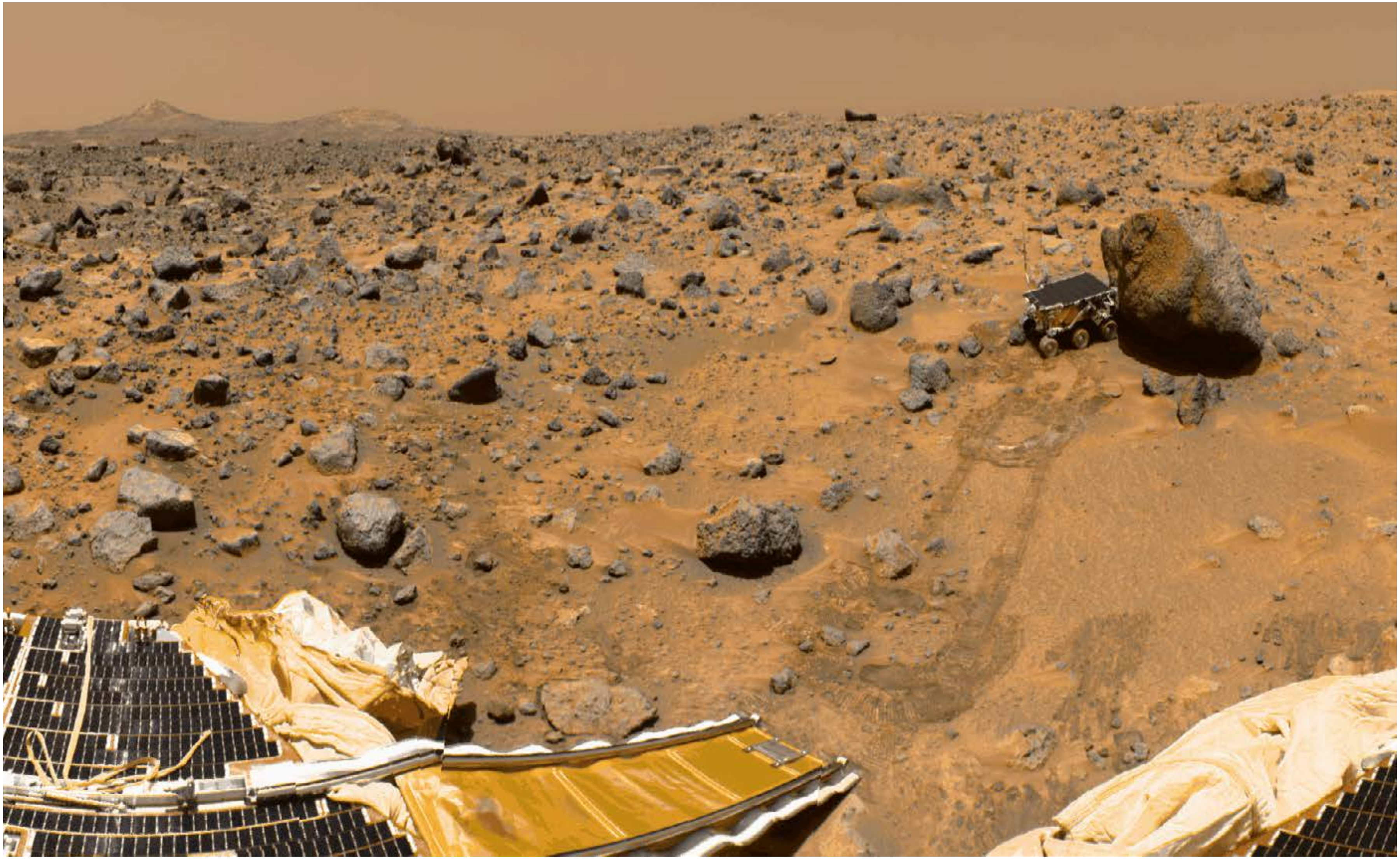
Vulcano, Italy

Stromboli, Italy

International Space Station



Mars NASA Pathfinder Climate Monitoring



Air Composition

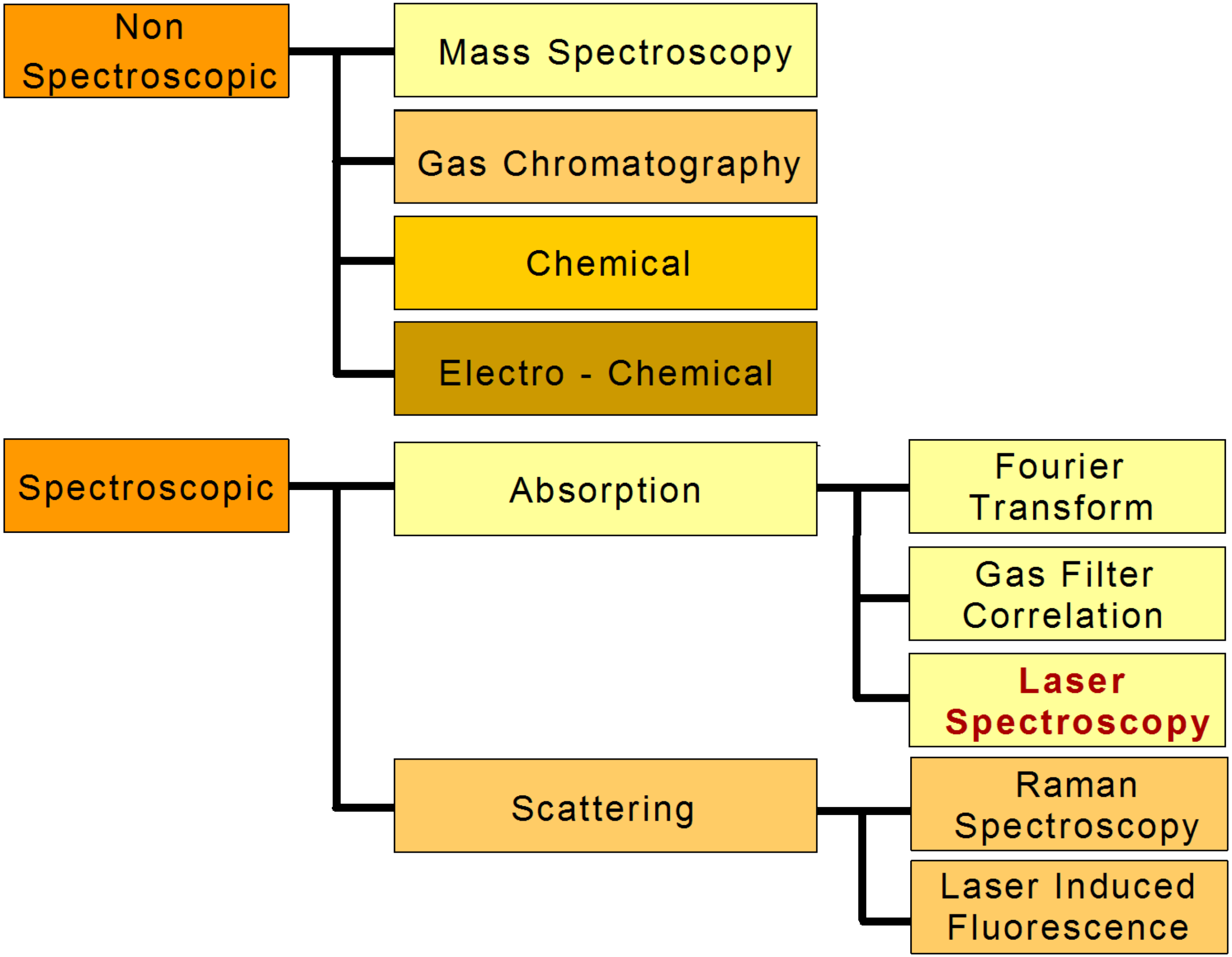
Main Components

- Nitrogen 78%
- Oxygen 21%
- Water 0.8%
- CO_2 0.03 %

Trace Components

- Methane 1.7 ppm
- CO 0.4 ppm
- N_2O 0.3 ppm
- O_3 0.03 ppm
- …

Existing Techniques for Trace Gas Detection



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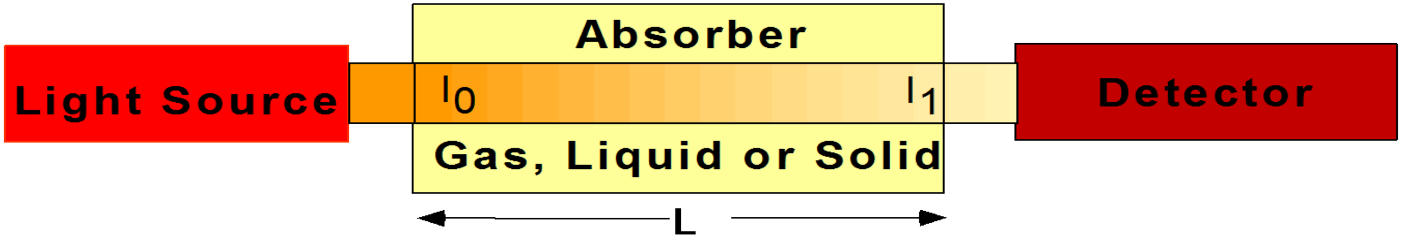
Absorption Spectroscopy



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

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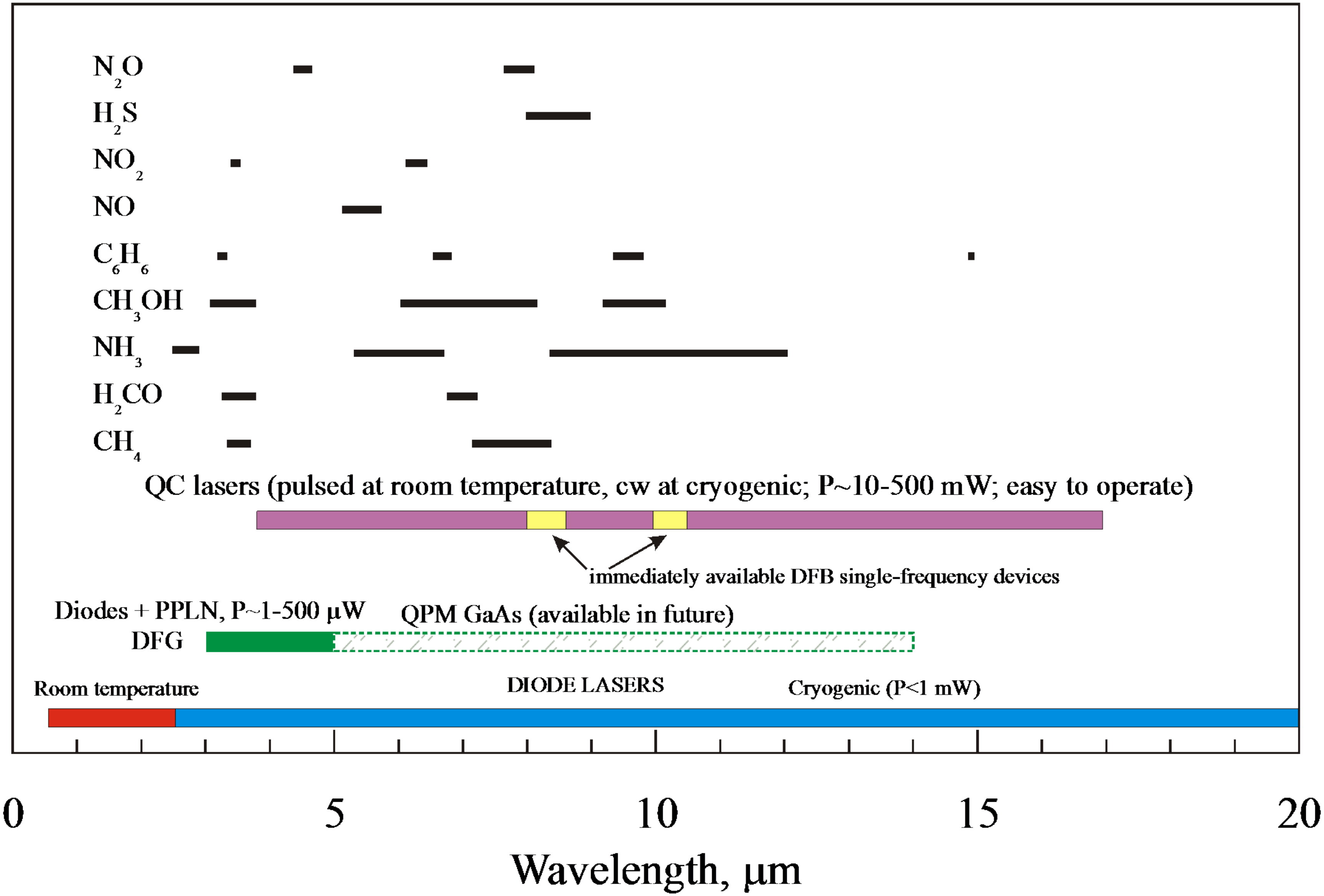
Spectral Coverage by Diode/QC Lasers



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

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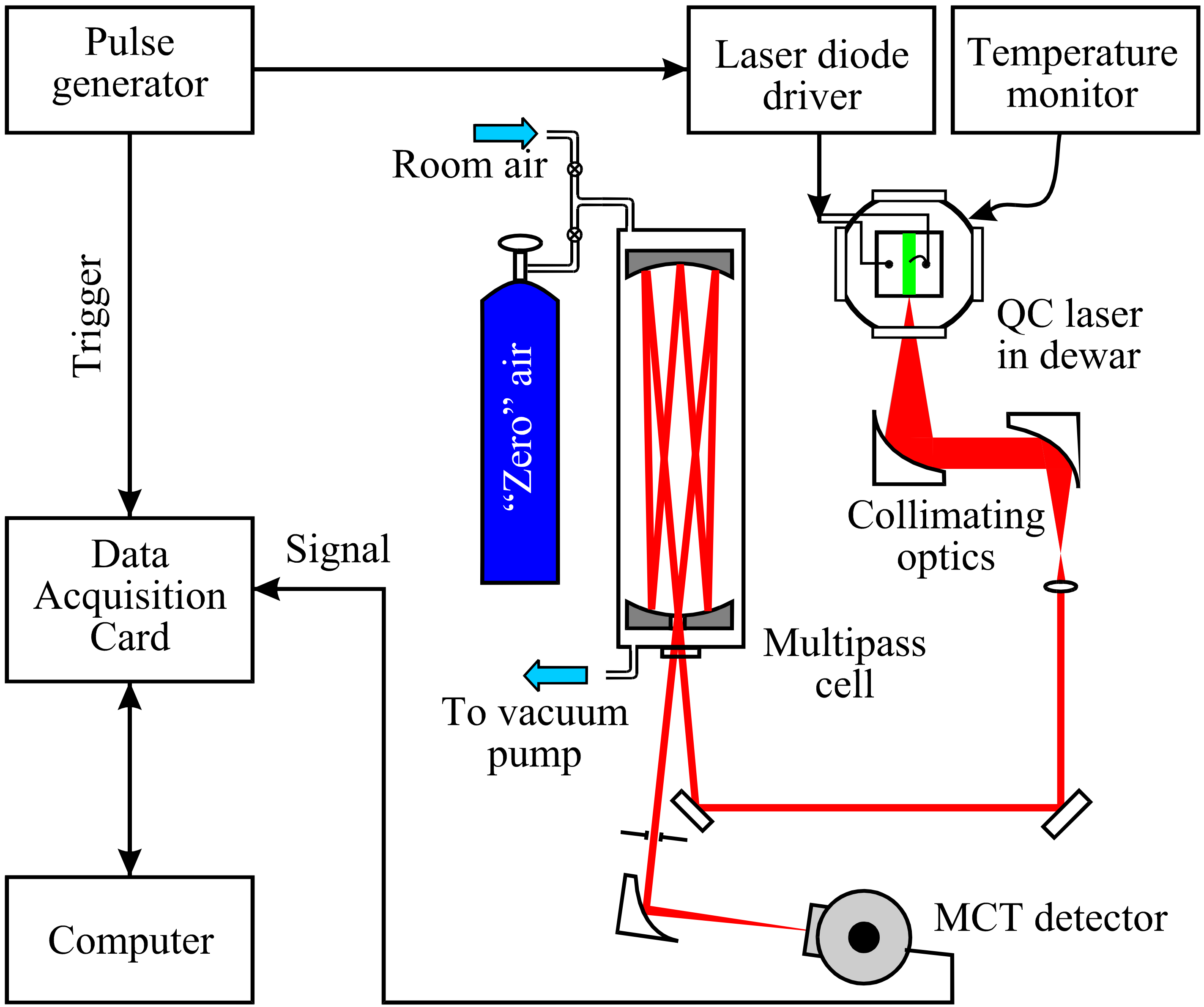
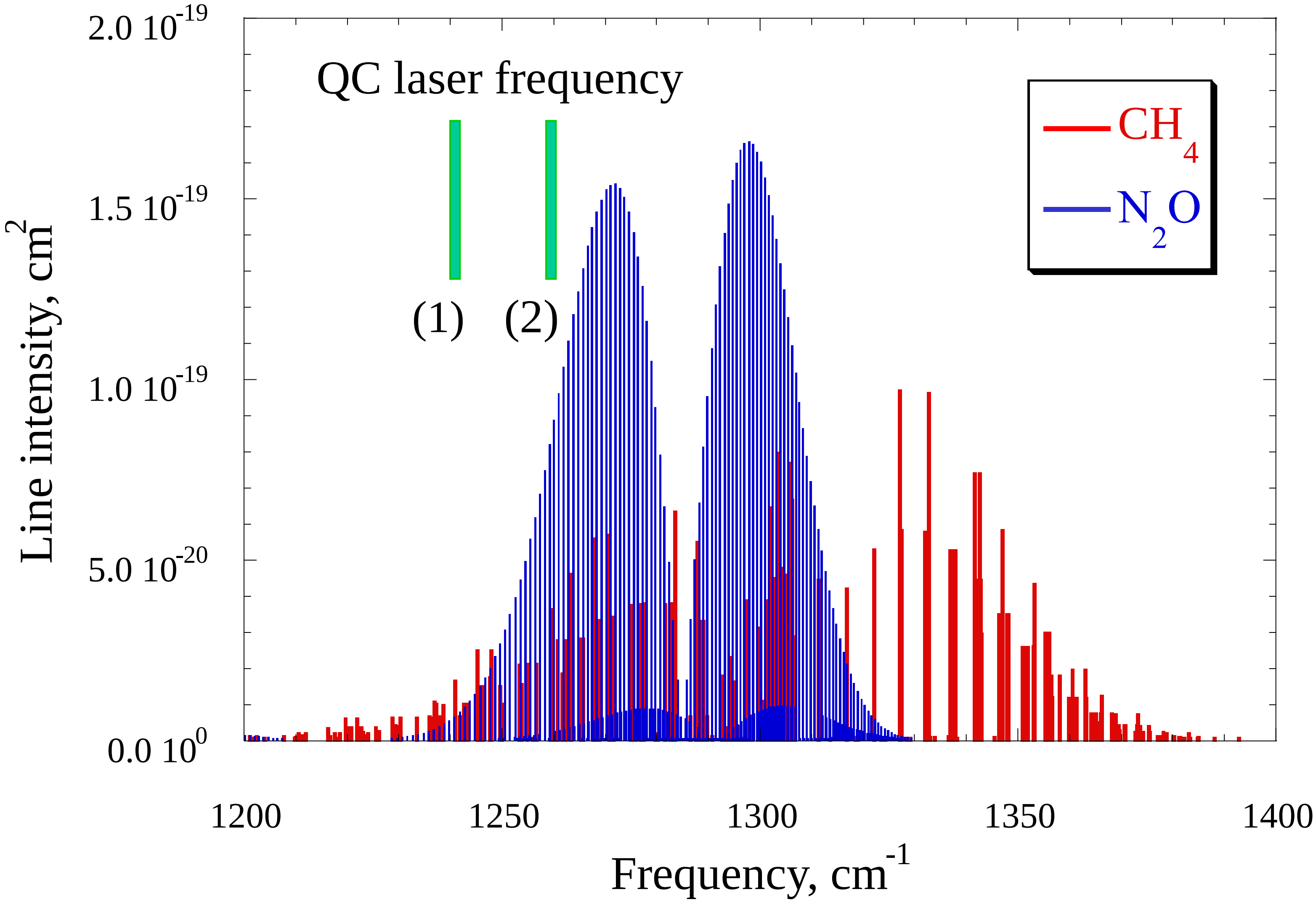
Trace Gas Detection with a Multipass Cell



Motivation for CH_4 Detection

- Contributor to global warming
- Important in tropospheric and stratospheric chemistry
- Emitted by microorganisms
- Can leak from gas pipelines

CH_4 and N_2O Absorption Spectra



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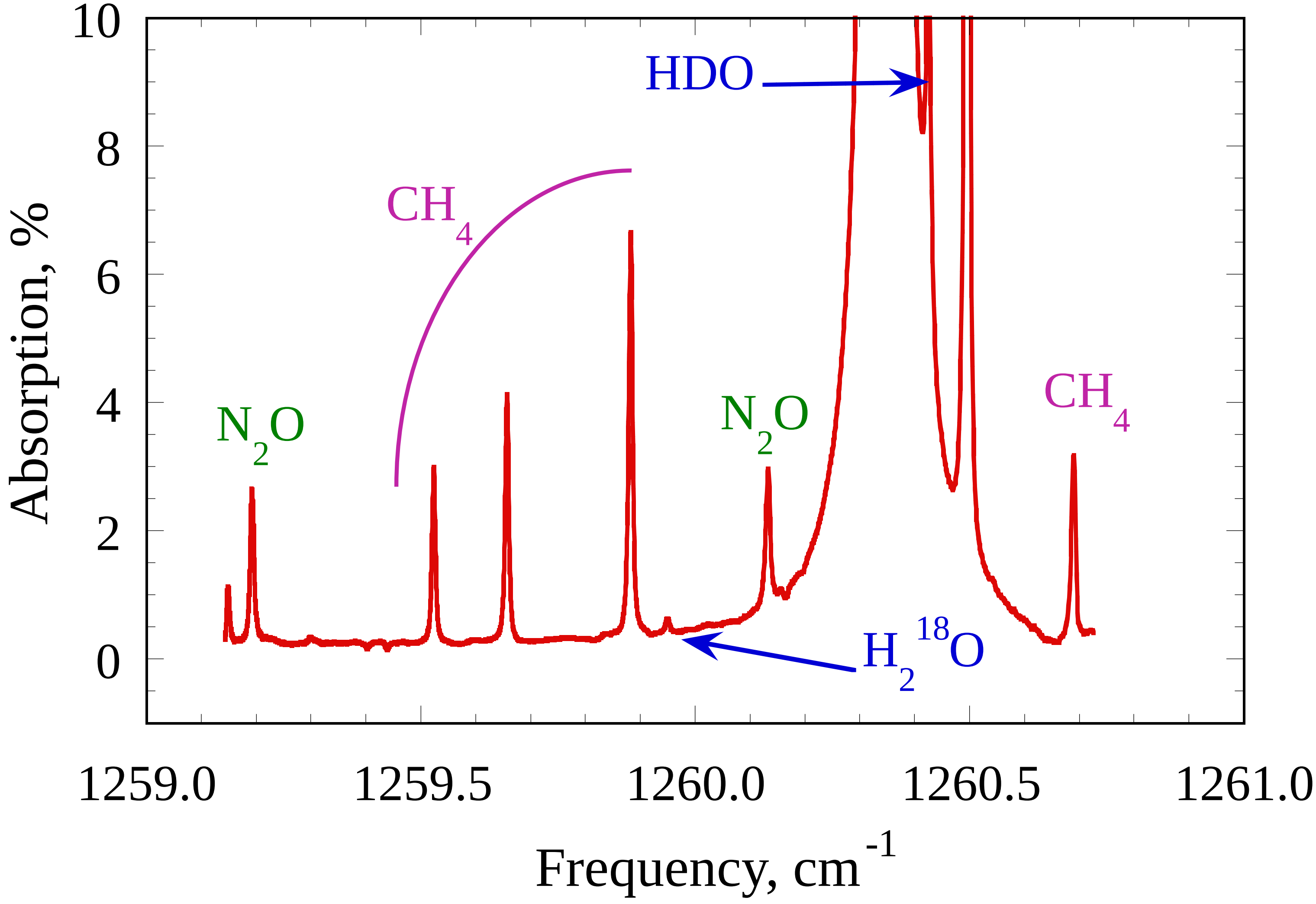
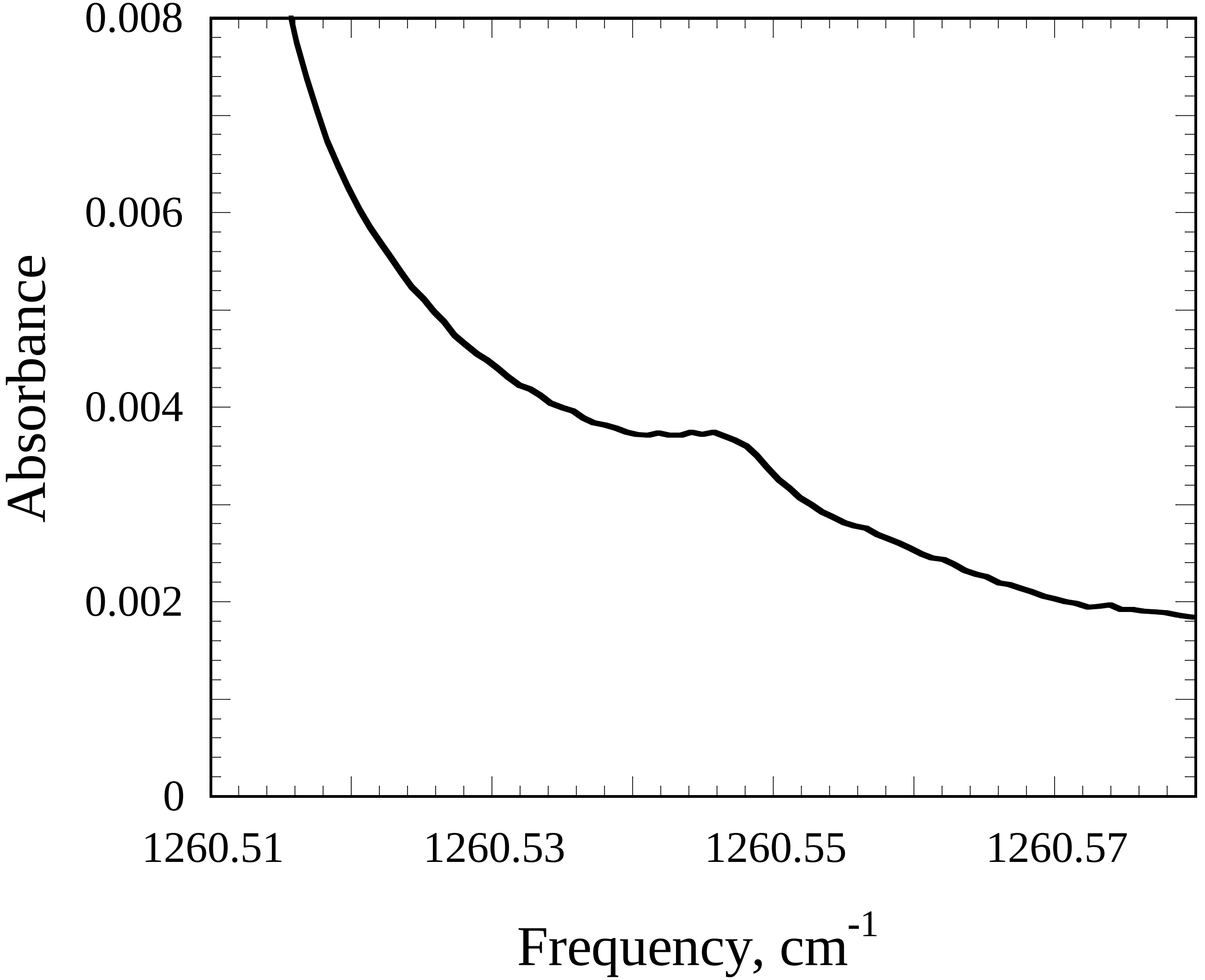
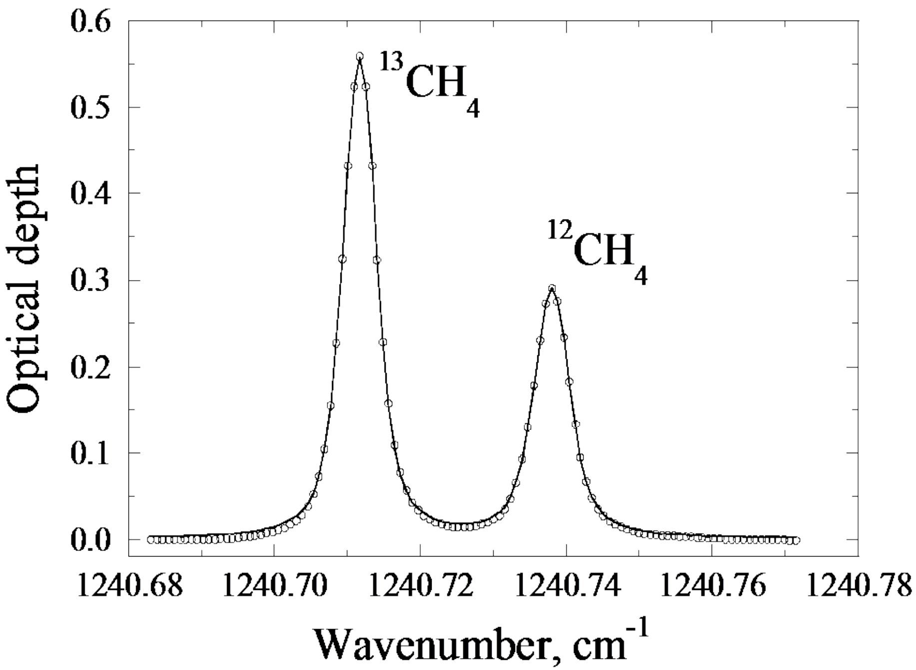
Absorption Spectrum of Room Air

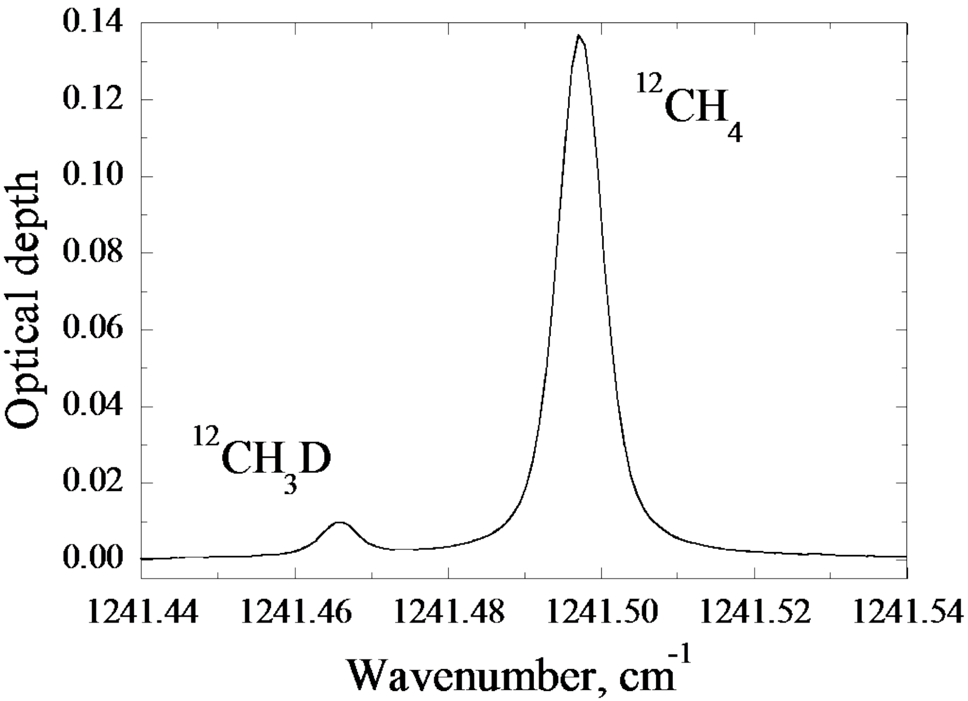


$^{13}CH_4$ Absorption Line at 1260.5 cm^{-1} on the Shoulder of H_2O line



Isotopic Composition of CH_4





Pressure: 16.9 Torr   Pathlength: 43 cm

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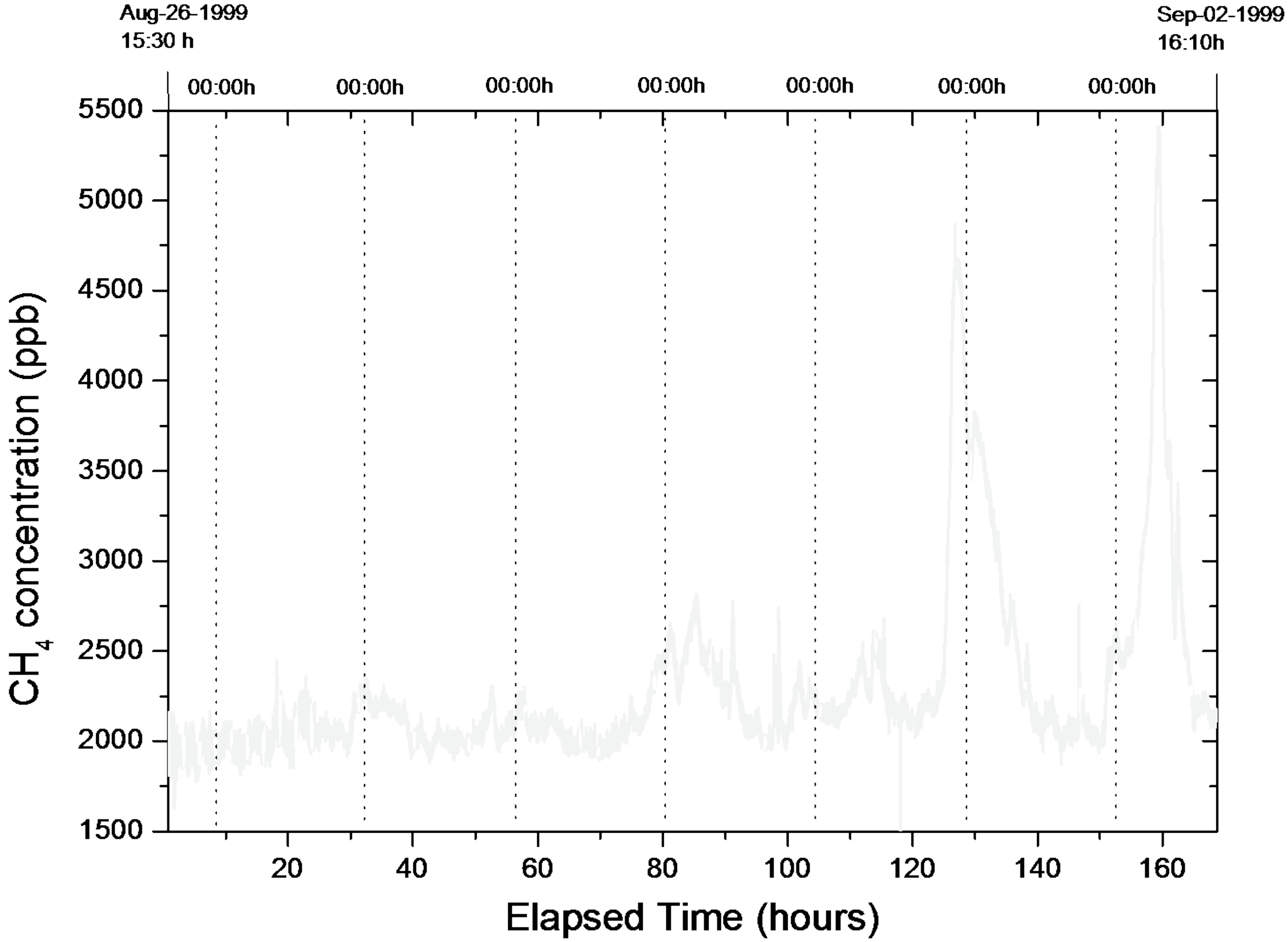
Continuous Detection of Ambient CH_4 for a 7 Day Period



Laser-Based CH_4 Detection Reported to Date

- First overtone
  - band: $2\nu_3$
    line intensity: ~ $1.33\cdot10^{-21}$ cm
    source: diode laser at 1.66 μm (Uehara and Tai, 1992)
    sensitivity: 600 $ppb\cdot m\cdot Hz^{-1/2}$
- Fundamental
  - band: ν_3 (CH asymmetric stretch)
    line intensity: ~ $2.13\cdot10^{-19}$ cm
    source: diode laser at 3.2 μm DFG (Rice, 1995)
    sensitivity: 12 $ppb\cdot m\cdot Hz^{-1/2}$; 4 ppb $\cdot m\cdot Hz^{-1/2}$ (Rice, 1999)
  - band: ν_4 (CH bend)
    line intensity: ~ $0.97\cdot10^{-19}$ cm
    source: lead-salt diode laser at 7.8 μm (Webster et al, 1994)
    sensitivity: 14 $ppb\cdot m\cdot Hz^{-1/2}$; 5 $ppb.m.Hz^{-1/2}$ (Rice,1999)

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Measured Emission from Rice Paddies of Different Countries

Country	Total Area of Rice Paddies (10^{10} m^2)	Percent of World Rice Area	Total Rice Grain Yield (000 t)	Percent of World Rice Grain	Annual CH_4 Emissions (Tg)	Percent of Average CH_4 World Emission
China	32.2	21.8	174,704	36.8	13-17	37.6
India	42.23	28.6	92,422	19.5	2.4-6	10.5
Japan	2.31	1.6	13,421	2.8	0.02-1.04	1.3
Thailand	11.7	7.9	19,241	4.1	0.47-8.77	11.6
Philippines	3.5	2.4	8,919	1.9	0.31-0.70	1.4
USA	1.0	0.7	6,388	1.3	0.04-0.47	0.6
Total	92.94	63.0	315,095	66.5	16-34	63.0
World Total	147.5	100	473,489	100	25-54	100

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Monitoring Methane in Rice - Based Agroecosystem

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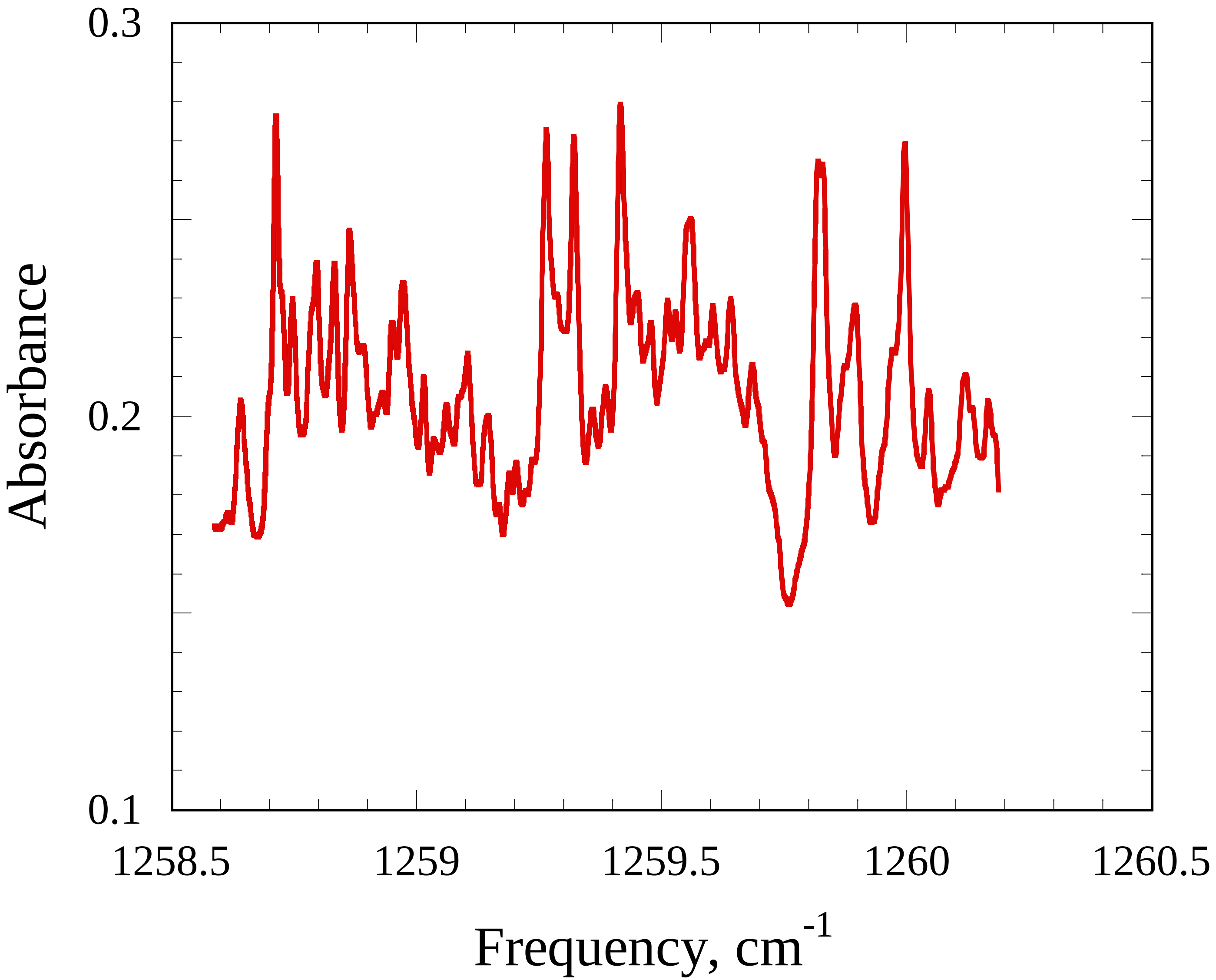
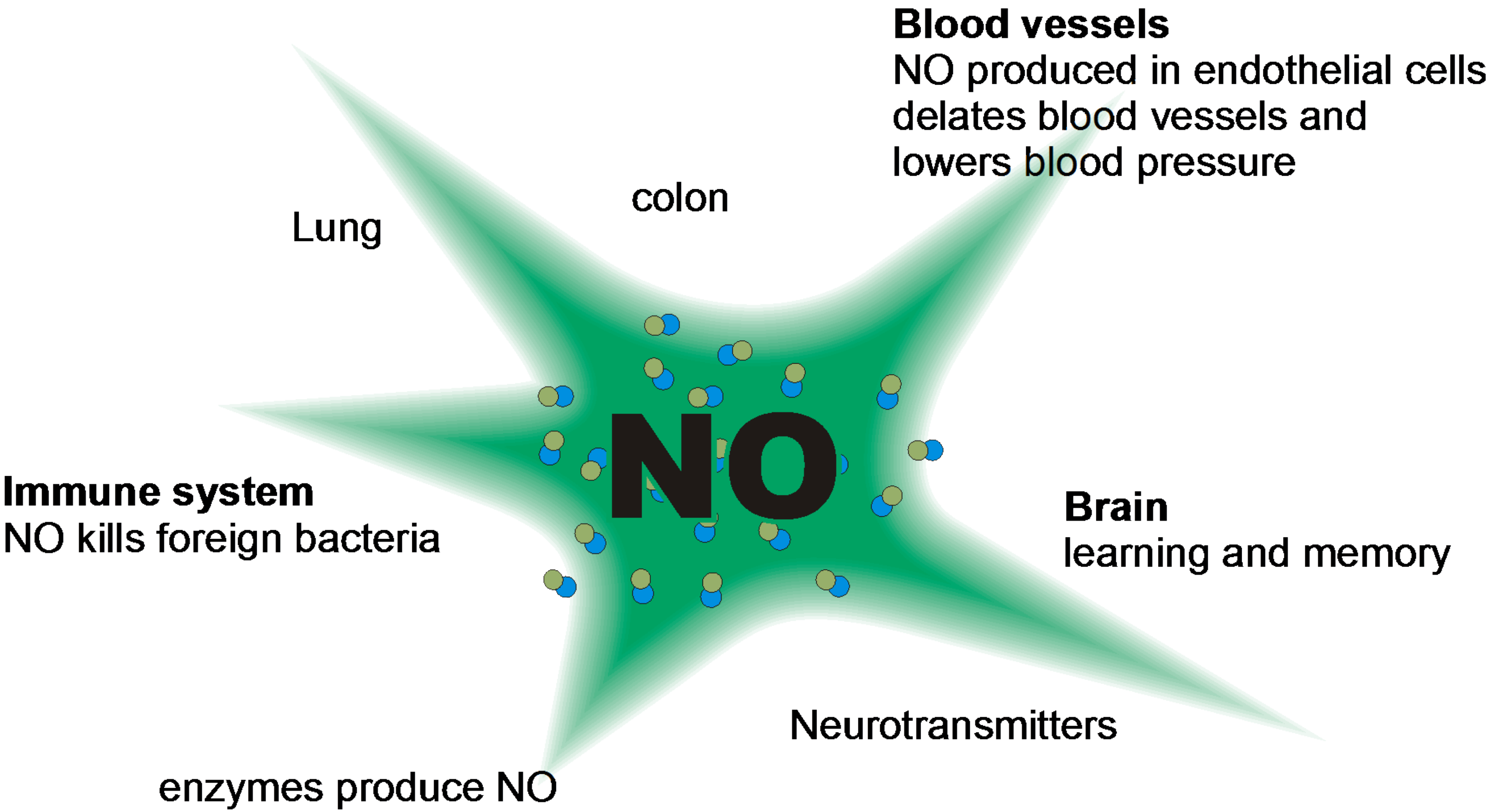
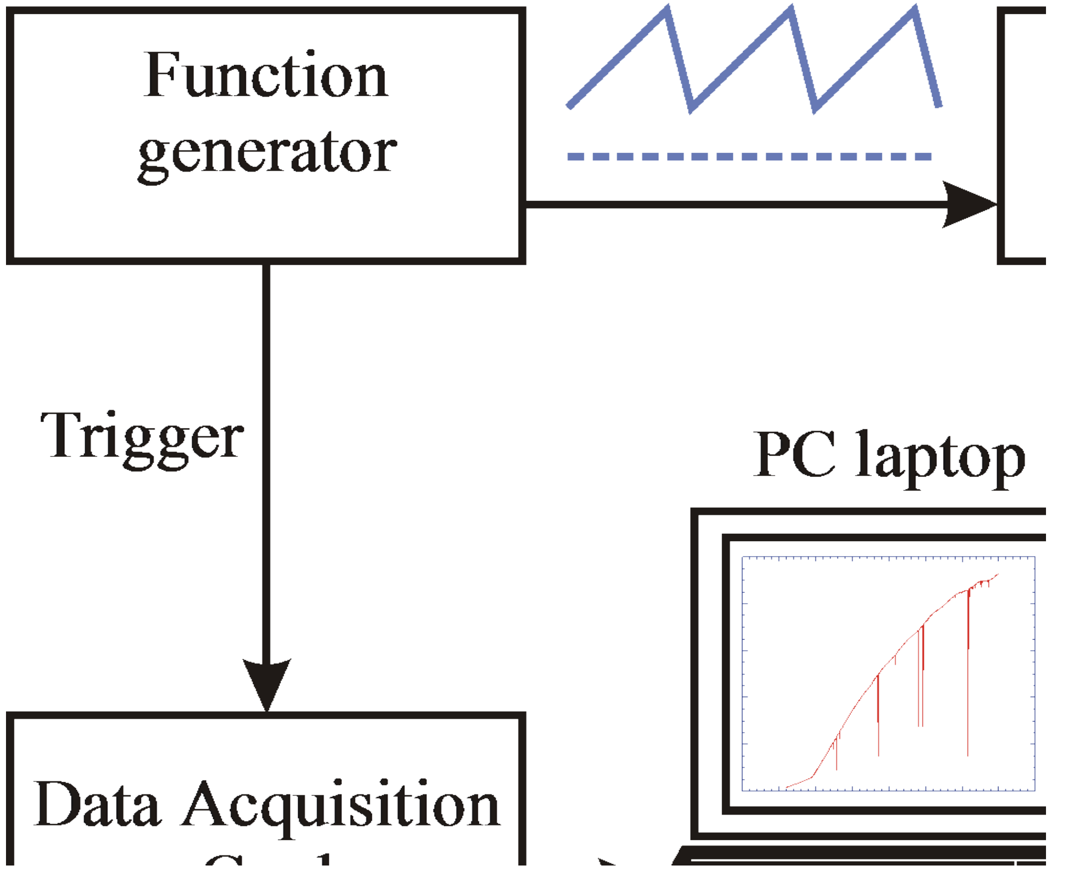
Ethanol Absorption Spectrum at 1259.5 cm^{-1}



Nitric Oxide: Various Human Functions

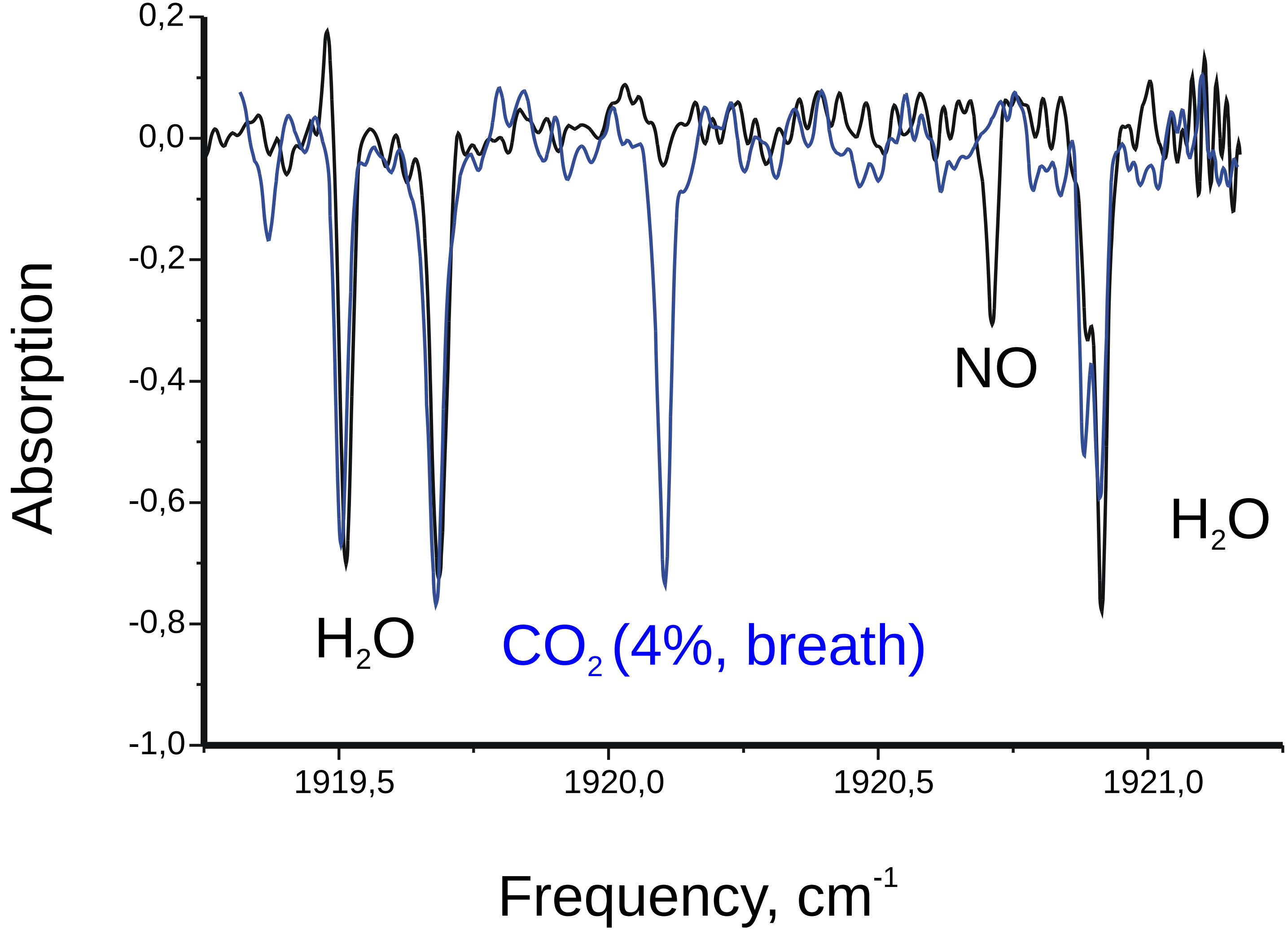


Cavity Enhanced QC Laser Spectroscopy



$$\frac{\langle I_{out} \rangle}{I_{in}} \approx \frac{T^2}{2(T+\alpha L)}; \quad T=(1-R)<<1; \ \alpha L<<1$$

Cavity Enhanced Spectroscopy of CO_2, H_2O and NO at 5.2 μm



Summary

- QC-DFB Laser Based Trace Gas Sensors
  - Compact, tunable, robust
  - High sensitivity ($<10^{-4}$) and selectivity (<50 MHz)
  - Fast data acquisition and analysis
  - Detected trace gases: CH_4, N_2O, H_2O, NO, CO_2 at 5.2 and 8 μm
  - Isotopic Compositions
- Current Applications in Trace Gas Detection
  - CH_4: NOAA, NASA-JPL, and gas industry
- Future Directions
  - More efficient suppression of optical interference fringes
  - Pulsed quasi room temperature operations
  - Detection of complex molecules
  - Cavity enhanced spectroscopy
  - Medical Diagnostics: NO, CO, CO_2 and NH_3

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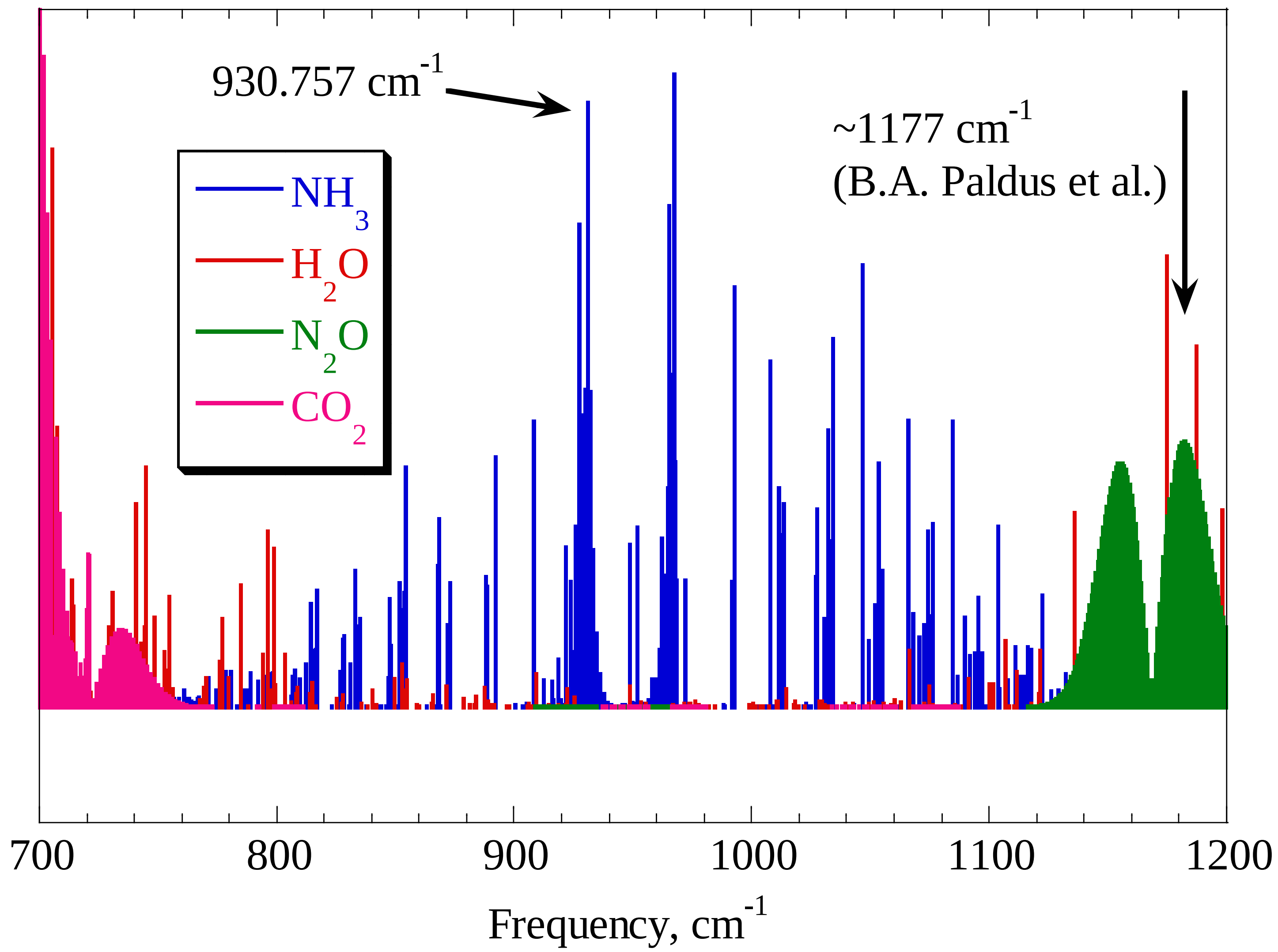
Strategy for NH_3 Concentration Measurements

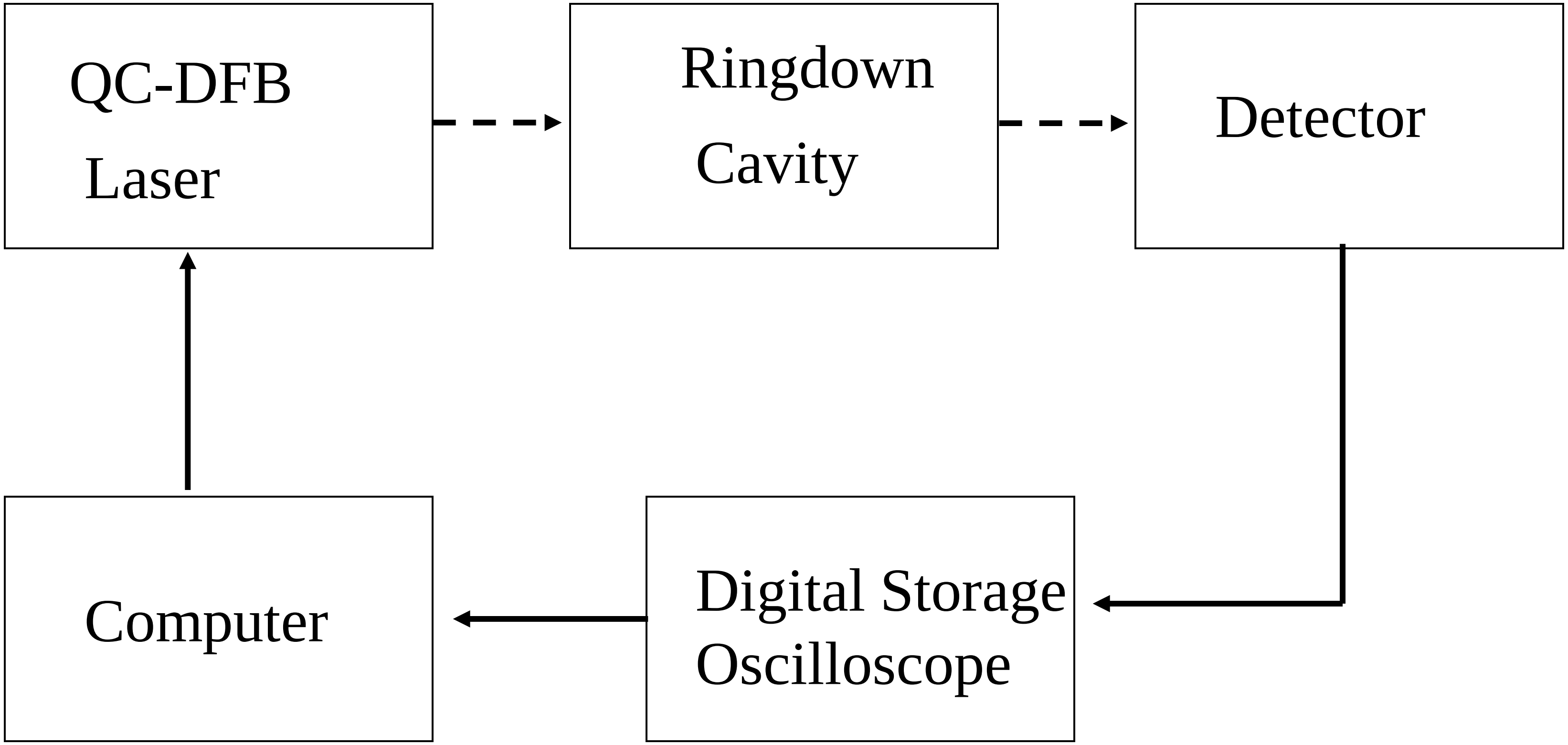


Worldwide Megadirty Megacities

	Population, m		Sulphur dioxide	Particulate matter	Lead	Carbon monoxide	Nitrogen dioxide	Ozone
	1990, ext.	2000, proj.						
Bangkok	7.16	10.26	○	●	▨	○	○	○
Beijing	9.74	11.47	●	●	○	-	○	▨
Bombay	11.13	15.43	○	●	○	○	○	-
Buenos Aires	11.58	13.05	-	▨	○	-	-	-
Cairo	9.08	11.77	-	●	●	▨	-	-
Calcutta	11.83	15.94	○	●	○	-	○	-
Delhi	8.62	12.77	○	●	○	○	○	-
Jakarta	9.42	13.23	○	●	▨	▨	○	▨
Karachi	7.67	11.57	○	●	●	-	-	-
London	10.57	10.79	○	○	○	▨	○	○
Los Angeles	10.47	10.91	○	▨	○	▨	▨	●
Manila	8.40	11.48	○	●	▨	-	-	-
Mexico City	19.37	24.44	●	●	▨	●	▨	●
Moscow	9.39	10.11	-	▨	○	▨	▨	-
New York	15.65	16.10	○	○	○	▨	○	▨
Rio de Janeiro	11.12	13.00	▨	▨	○	○	-	-
Sao Paolo	18.42	23.60	○	▨	○	▨	▨	●
Seoul	11.33	12.97	●	●	○	○	○	○
Shanghai	13.30	14.69	▨	●	-	-	-	-
Tokyo	20.52	21.32	○	○	-	○	○	●

Source: United Nations ● High pollution ▨ Moderate to heavy pollution ○ Low pollution - No data available

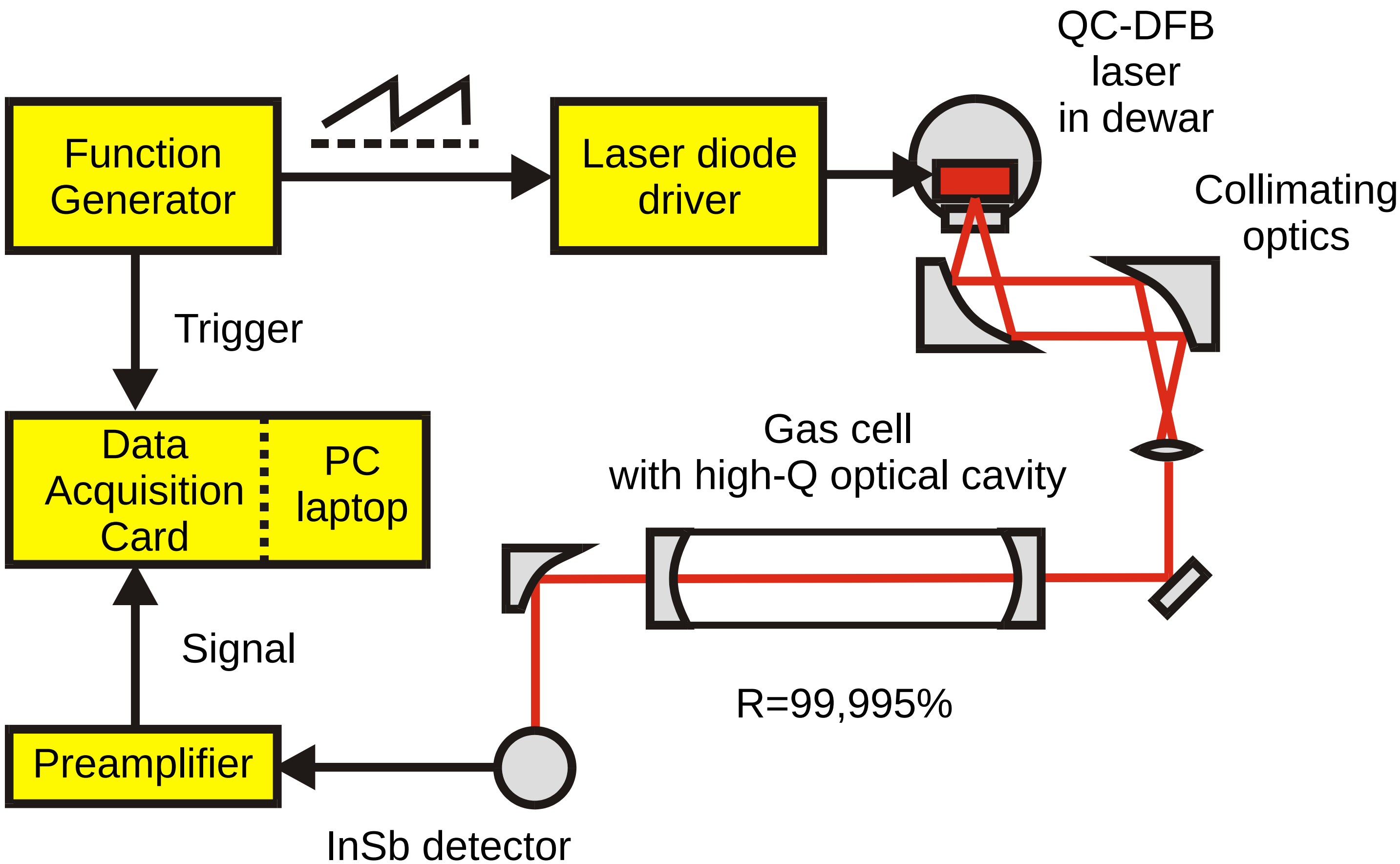
CRLAS Principle



$$I(t) = I_0 \exp\left[-\frac{t\,(1 - R) + A}{t_r/2}\right]$$

$$A = t_r/2(1/\tau - 1/\tau_o)$$

Cavity Enhanced QC-Laser Spectroscopy

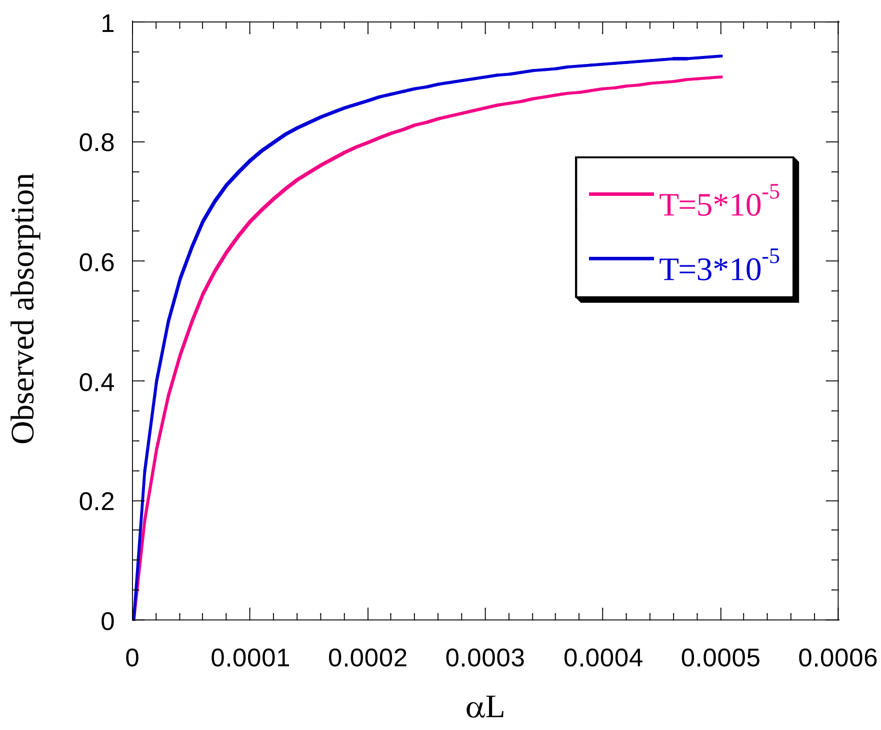


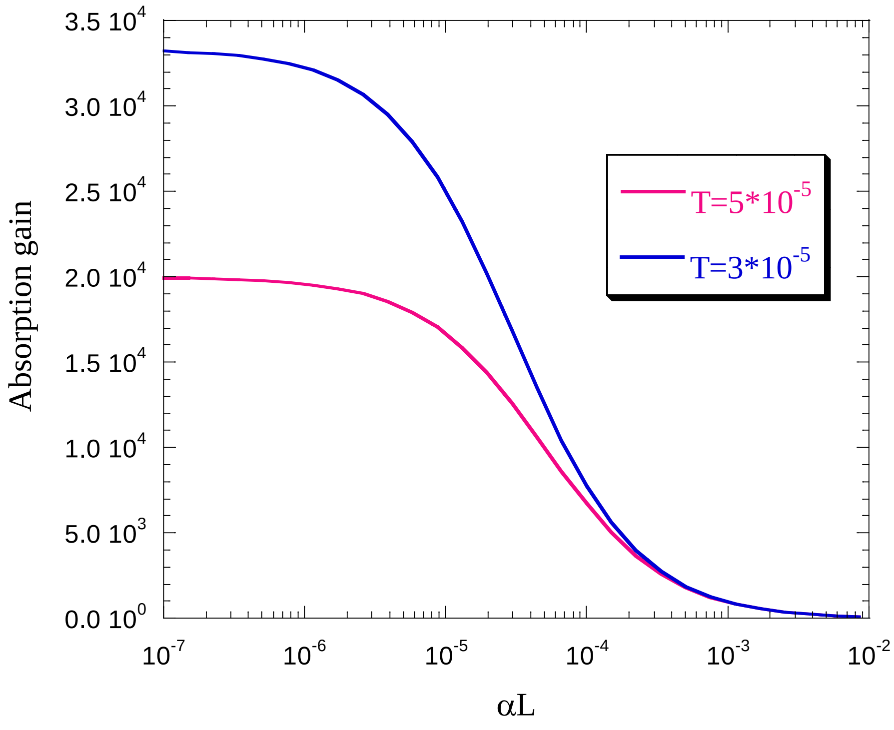
$$\alpha = \frac{1}{L}\left\{1-\frac{\left[-(1-R)+\sqrt{(1-R)^2+4RT_n}\right]^2}{\sqrt{4R^2T_n}}\right\}$$

Cavity Enhanced Absorption

Observed absorption : $A_{obs} = \dfrac{I_{empty} - I_{sample}}{I_{empty}} = \dfrac{\alpha L}{T + \alpha L}$

Absorption gain : $g = \dfrac{A_{obs}}{\alpha L} = \dfrac{1}{T + \alpha L}; \quad g \approx \dfrac{1}{T}$ if $\alpha L << T$

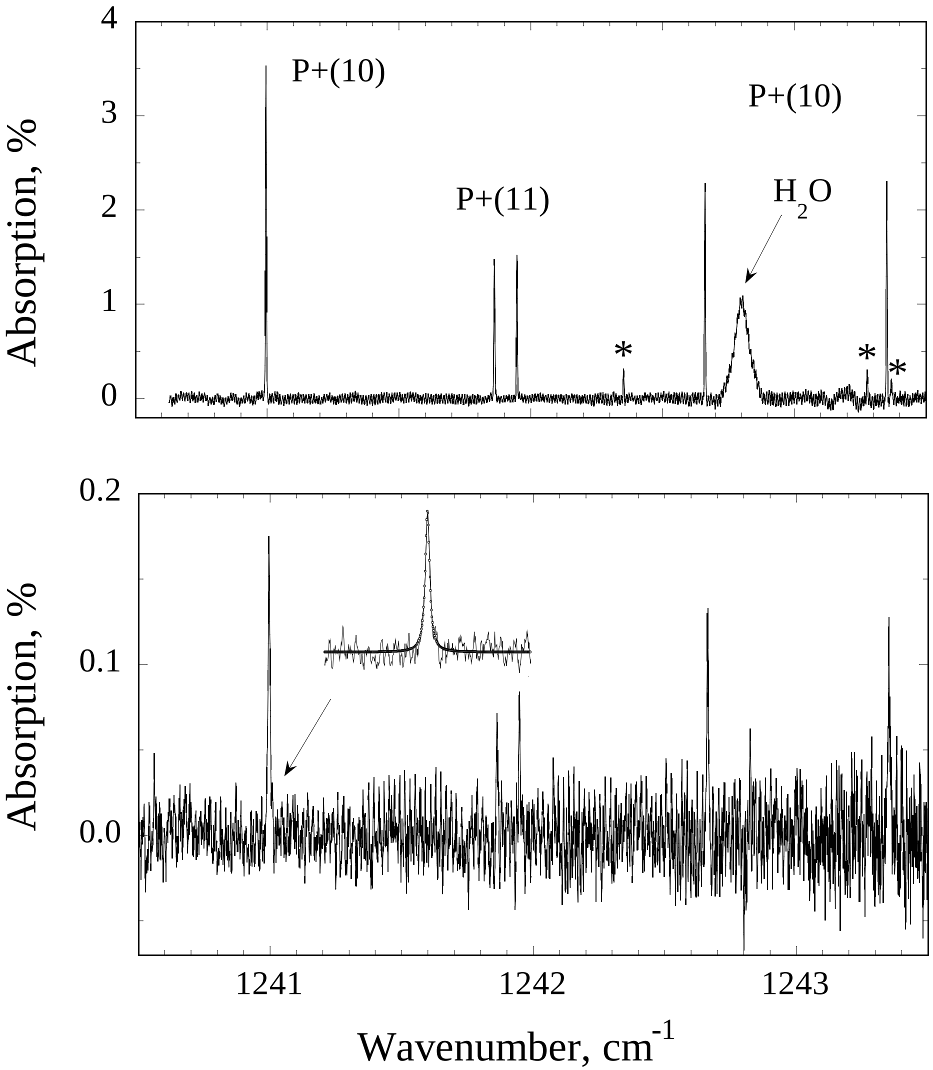




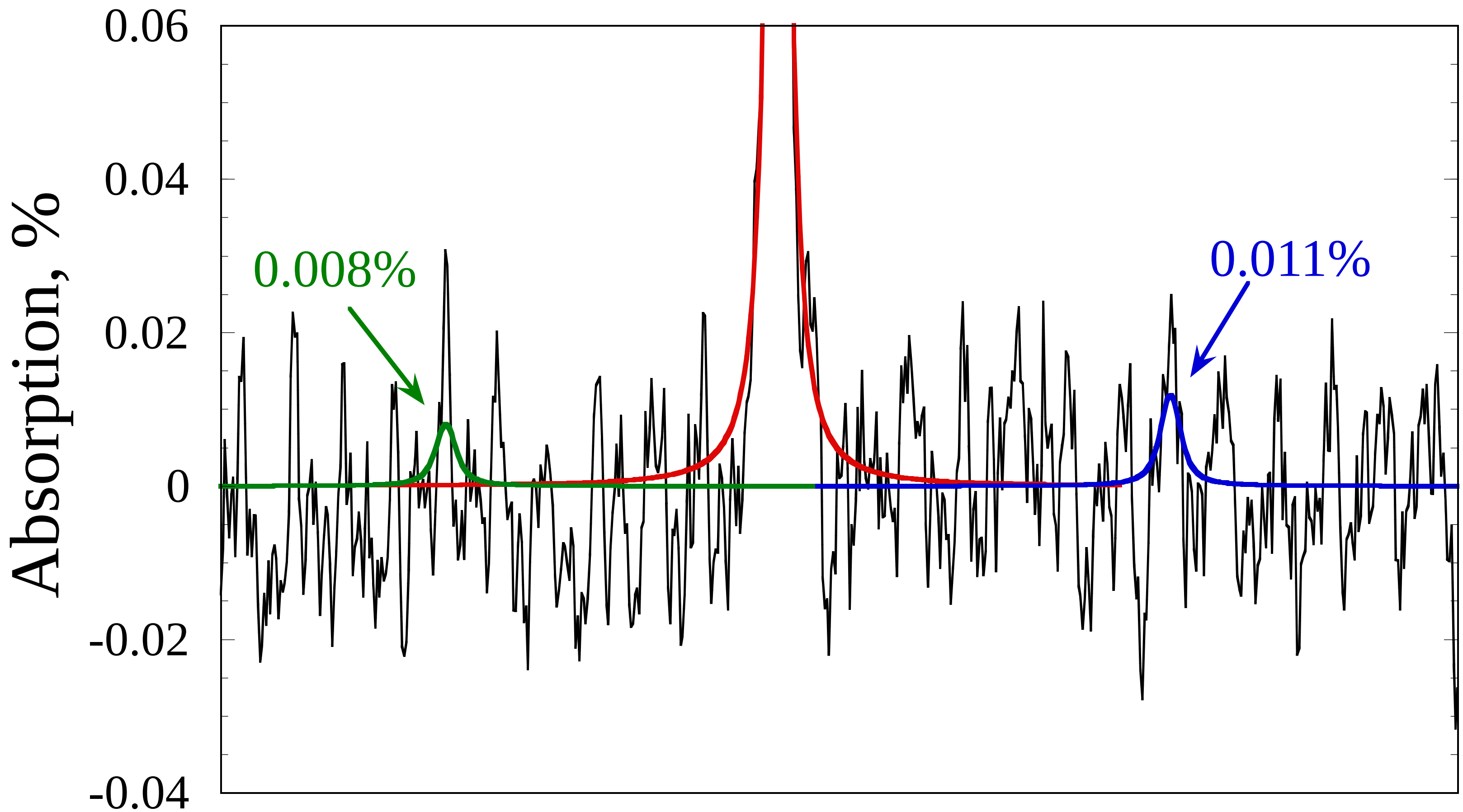
Detection of CH_4 Near 1241 cm^{-1}

6.5 mTorr,
pure CH_4

16 ppm of CH_4
in 50 Torr of air



Estimate of Detection Sensitivity



Simulated false “lines” are always ♎ 0.01%

❾The detection limit for absorption is 10^{-4}

Summary and Future Outlook

- A cw QC-DFB laser based gas sensor at 8 μm was designed and tested for methane and nitrous oxide detection
- A detection limit of 10^{-4} for absorption was obtained
- Isotopic composition measurements were demonstrated

Future development

- More efficient suppression of optical interference fringes
- Detection of more complex organic molecules
- Room-temperature operation

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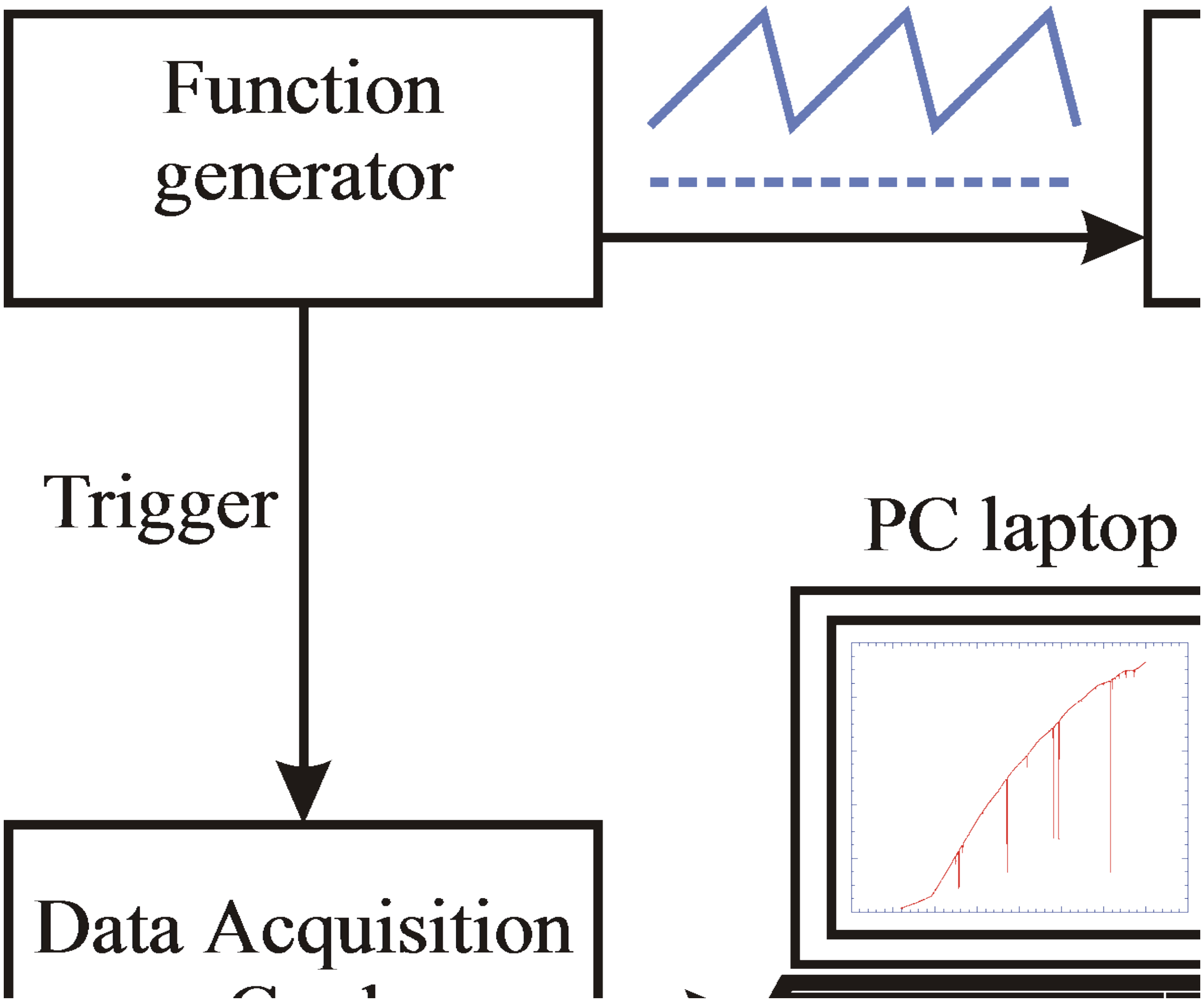
Cavity Enhanced QC Laser Spectroscopy



HITRAN Simulated NO Absorption Spectrum