Absorption Spectroscopy with Quantum Cascade Lasers

Frank K. Tittel
Rice University
Houston, USA

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

- 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

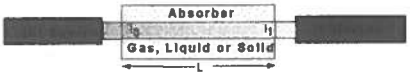
Wide Range of Gas Sensor Applications

- Urban and Industrial Emission Measurements
  - Industrial Plants
  - Combustion Sources
  - Automobile
- 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

Air Composition

Main Components		Trace Components	
• Nitrogen	78%	• Methane	1.7 ppm
• Oxygen	21%	• CO	0.4 ppm
• Water	0.8%	• N_2O	0.3 ppm
• CO_2	0.03 %	• O_3	0.03 ppm
		• ...	

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})

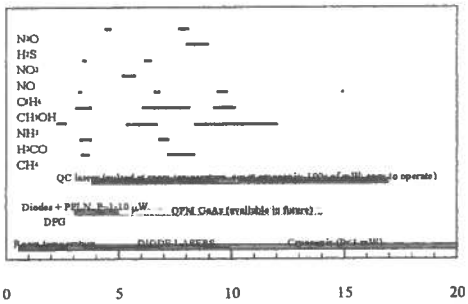
Molecular Absorption Coefficient

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

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

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

Spectral Coverage by Diode/QC Lasers

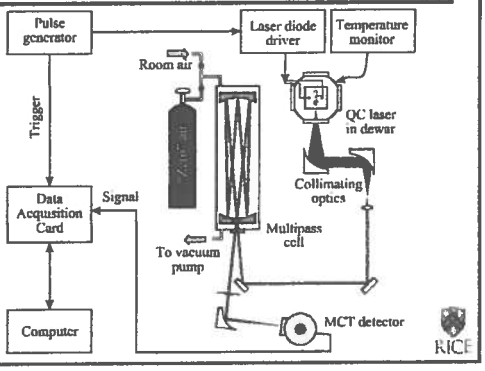


Key Characteristics of Quantum Cascade Lasers

- 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

photos /

Trace Gas Detection with a Multipass Cell



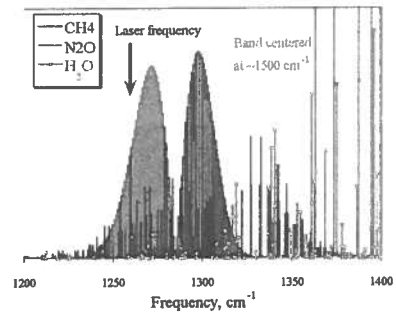
RICE

Motivation for CH_4 and N_2O Detection

- Contribution to global warming
- Important in tropospheric and stratospheric chemistry
- Emitted by agricultural sources
- CH_4 leaks from gas pipelines

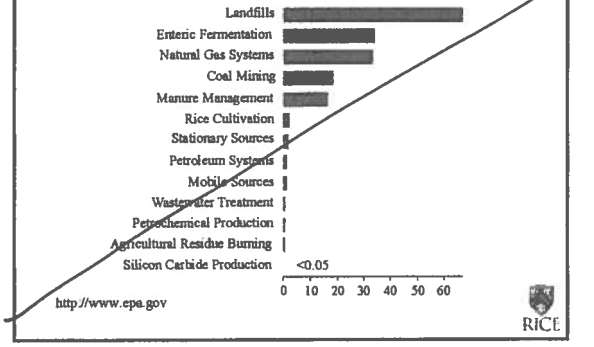
RICE

CH_4, H_2O and N_2O Absorption Spectra



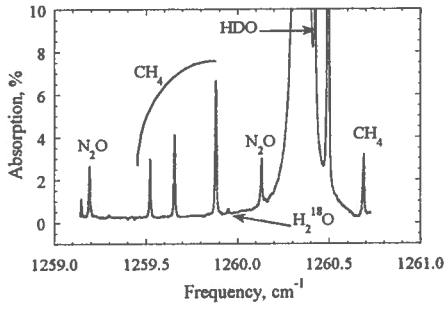
RICE

Sources of atmospheric CH_4



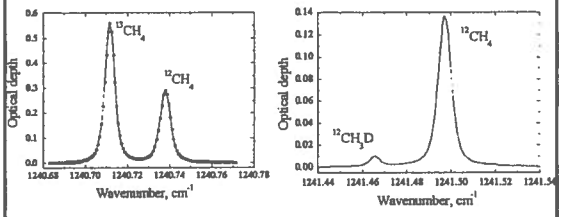
RICE

Absorption Spectrum of Room Air



RICE

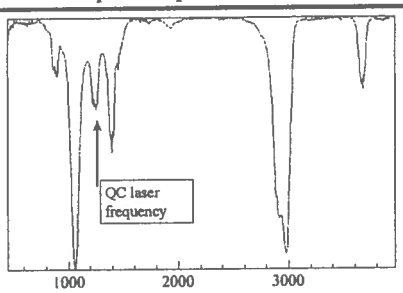
Isotopic Composition of CH_4



Pressure: 16.9 Torr Pathlength: 43 cm

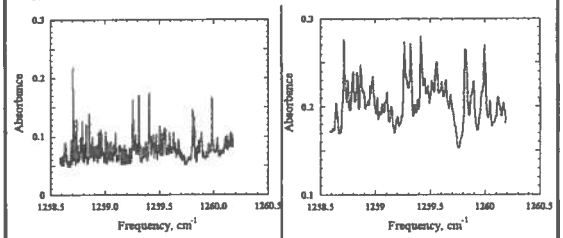
RICE

IR Absorption Spectrum of Ethanol



RICE

High-resolution IR Ethanol Spectrum



Pure ethanol vapor

P=1 Torr

Ethanol vapor +air

P_{eth}=1 Torr, P=36.6 Torr

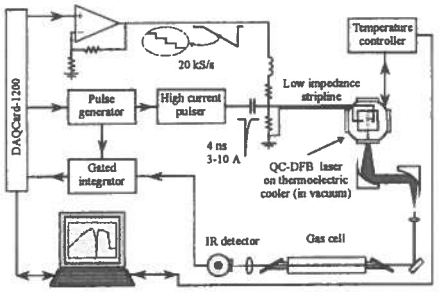
RICE

Pulsed Operation of a QC-DFB Laser

ADVANTAGES	DISADVANTAGES
♦ Laser can be operated at near-room temperature	♦ Broader linewidth (~400 MHz)
♦ Easy temperature handling	♦ Less average power
♦ No consumables (liquid N_2)	♦ More sophisticated electronics for driving QC laser and data acquisition
♦ Compact	

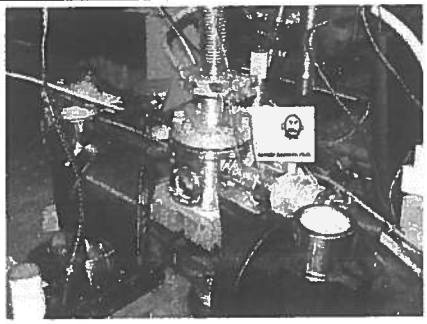
RICE

Pulsed QC-DFB Spectrometer



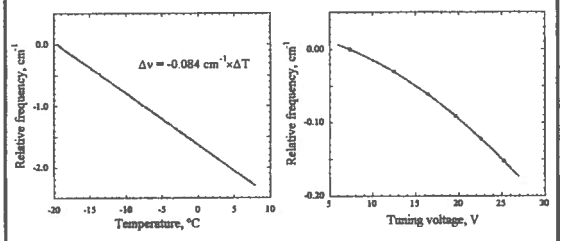
RICE

Pulsed QC Laser Housing

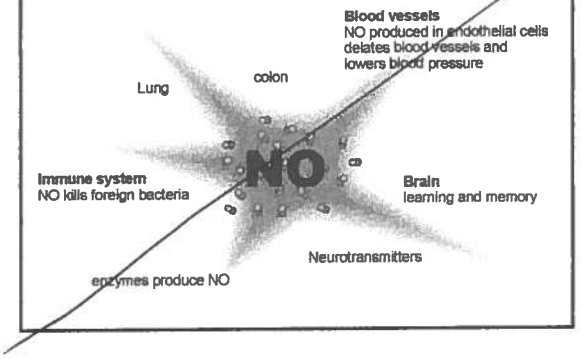


RICE

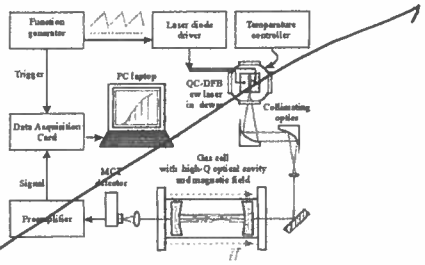
Tuning of the Pulsed QC-DFB Laser



Nitric Oxide: Various Human Functions

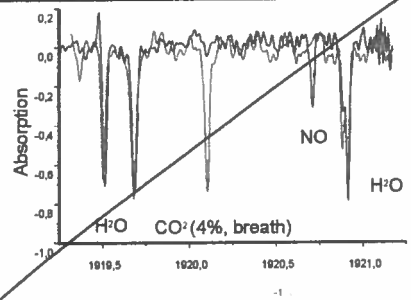


Cavity Enhanced QC Laser Spectroscopy



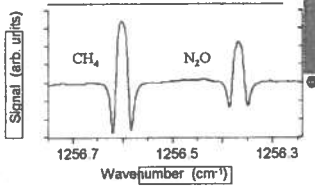
$$\frac{\langle I_{out}\rangle}{I_{in}} \approx \frac{T^2}{2(T+\alpha L)};\quad T=(1-R)\ll 1;\ \alpha L \ll 1$$

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



High sensitivity detection of stratospheric CH_4 and N_2O by wavelength modulation spectroscopy

Collaboration with:
Christopher Webster et al.
JPL, NASA, Caltech, CA



- LN2 cooled, continuous wave QC-DFB lasers (single-mode and tunable) at λ ≈ 8.0 μm
- reliable detection over 8 hours of measurement time
- detection limit: ~ 2ppbv

Summary

- QC-DFB Laser Based Trace Gas Sensors
  - Compact, tunable, CW or pulsed, 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, NH_3, and C_2H_5OH
  - Isotopic Compositions
- Current Applications in Trace Gas Detection
  - CH_4: NOAA, NASA-JPL, and gas industry
  - NH_3: NASA-JSC, semiconductor industry, combustion diagnostics
- 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

RICE

20