Development of Advanced Mid-infrared Laser Based Gas Sensor Technology

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- Motivation and Technology Issues
- Infrared Diode and QC Laser-based Gas Sensors
- Performance Characteristics of mid-IR Sensors
  - Novel photoacoustic spectroscopy (PAS)
- Selected applications of trace gas detection
  - Fire emission gases

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May 2002

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Project Administrative Summary

- **Prime contract:**
- **Technical POC: John Hines, Fundamental Biology Program**
- **Period of Performance: 1/1/03 – 12/31/05**
- **Deliverables:**
  - Annual reports (due 10/31 each year)
  - Final report 12/31/05
- **Current Funding: $600,000 through 12/31/05 ($300,000 / JPL, $300,000 / Rice)**
- **Funding Agency: NASA**

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Project Technical Summary

- Overall Project Goal:
  To develop and demonstrate advanced gas sensor technology in the spectroscopically important 3 to 4.4 micron spectral region based on Type 2 QCL absorption and photoacoustic spectroscopy (PAS)

- Individual team responsibilities:
  - **Rice** - sensor architectures and performance, novel PAS *detection technique, and monitoring of potential fire* emission gases
  - **JPL** - development and characterization of Type 2 quantum cascade and Sb III-V based diode lasers

Wide Range of Gas Sensor Applications

- Urban and Industrial Emission Measurements
  - Industrial Plants - Fenceline perimeter monitoring
  - Combustion Diagnostics
  - Automobile
- Rural Emission Measurements
  - *Agriculture*
- Environmental Monitoring
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Spacecraft and Planetary Surface Monitoring**
  - **Crew Health Maintenance & Life Support**
  - **Fire Emission gas detection**
- Diagnostic and Industrial Process Control
  - Petrochemical and Semiconductor Industry
- Medical Diagnostics

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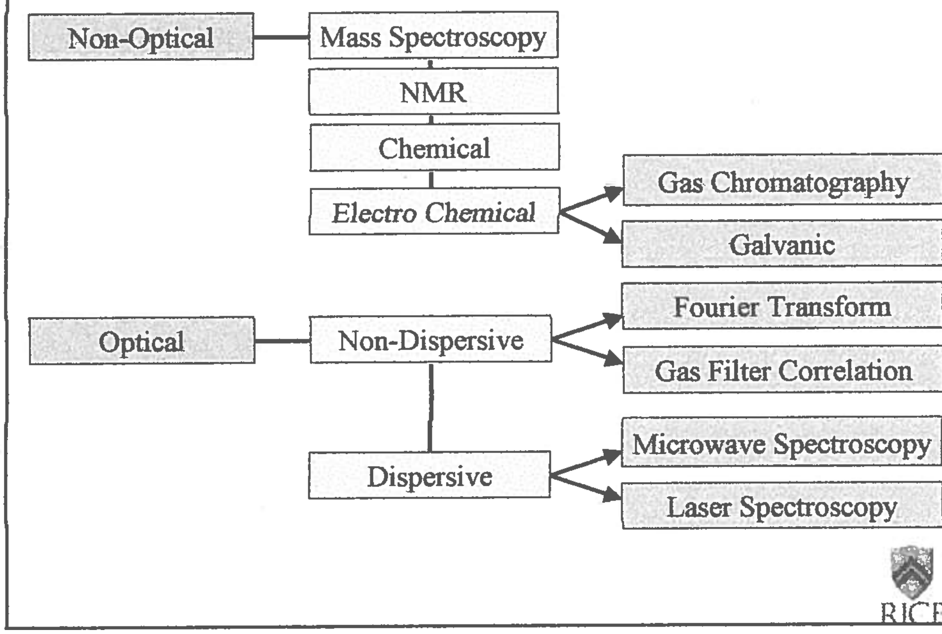
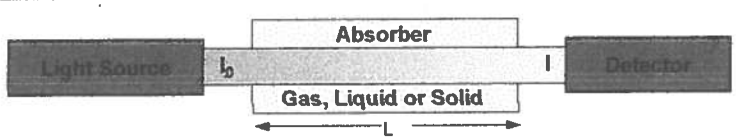
Existing Methods for Trace Gas Detection



Absorption Spectroscopy



Beer's Law

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

$\alpha(\nu)$ - absorption coefficient [cm^{-1} atm^{-1}]; L – path length [cm]
ν - frequency [cm^{-1}]; P_a- partial pressure [atm]

Molecular Absorption Coefficient

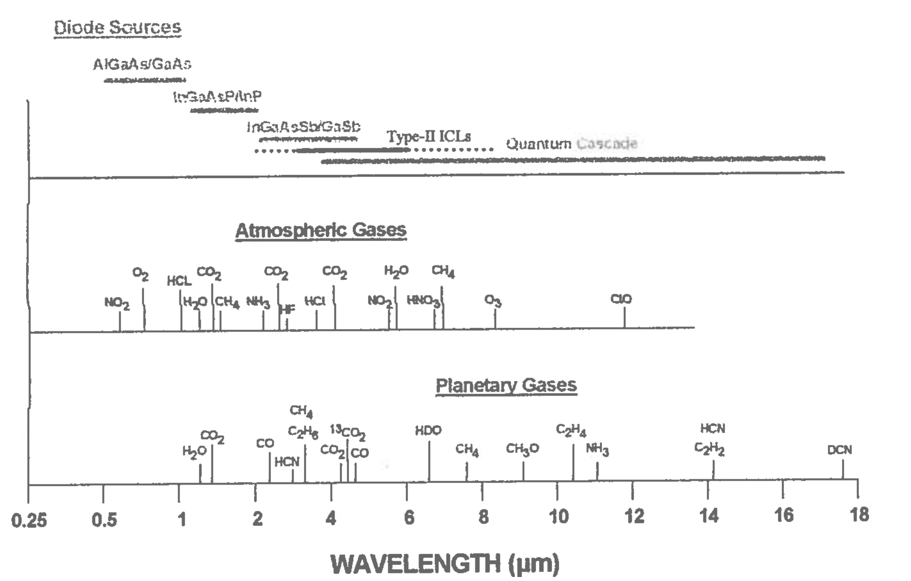
$$\alpha(\nu)=C\cdot S\cdot g(\nu-\nu_0)$$

C - total number of molecules of absorbing gas/atm/cm^3 [molecule$\cdot cm^{-3} \cdot atm^{-1}$]
S - molecular line intensity [cm $\cdot$molecule^{-1}]
$g(\nu - \nu_0)$ - normalized lineshape function [cm],(Gaussian, Lorentzian, Voigt)

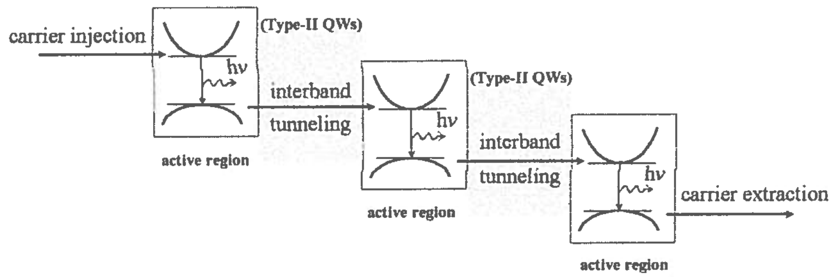
IR Source Requirements for Spectroscopy

REQUIREMENTS	SOURCE
• Sensitivity	• Power
• Specificity	• Line Width
• Multi-gas Components	• Tunable
• Directionality	• Beam Quality
• Rapid Data Acquisition	• Response

Laser Diode Operating Ranges & Absorption Lines of Gases



Type-II Interband Cascade Lasers

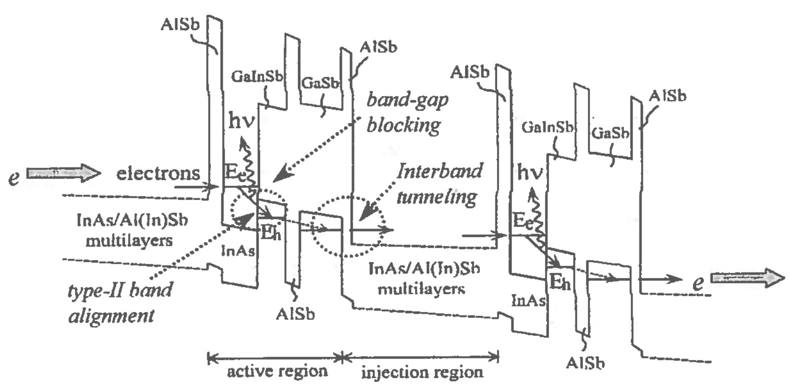


- retaining advantage of cascade, but circumventing phonon scattering in intraband QCLs
- suppressing Auger recombination through band-structure engineering
- wide wavelength tailoring range (2 – 6 microns)
- uniform injection of carriers over every cascade stage
- good confinement on carriers

⇒ **low threshold current, high efficiency, high output power**

Rui Q. Yang

Type-II Interband Cascade Design Example



Nearly lattice-matched InAs/GaSb/AlSb system with natural type-II broken-gap alignment

- band-gap blocking feature ⇒ excellent carrier confinement with significant flexibility
- less mature material system compared to GaAs- and InP-based systems

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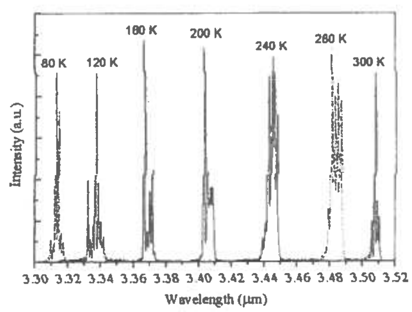
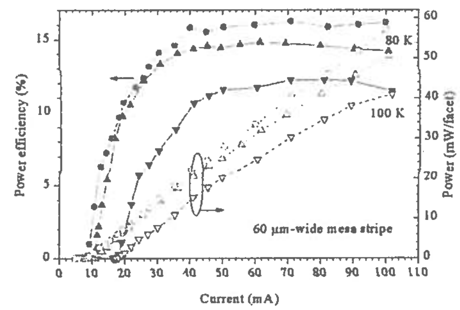
Recent Interband Cascade Laser Results

(Yang, Bradshaw, Bruno, Pham, & Wortman at ARO Quantum Cascade Laser Workshop , Oct. 9, 2001, Arlington, VA)

- 18 cascade stages, epi-side-up mounting onto Cu, uncoated facets
- operated up to 300 K in pulsed & 150 K in cw
- low threshold current density (~11 A/cm^2 80 K)
  ⇒ suppression of various loss mechanisms
- record-high wall-plug efficiency (>16% in cw)
  <DEQE>~333% (18.5% per stage) in cw at 80 K

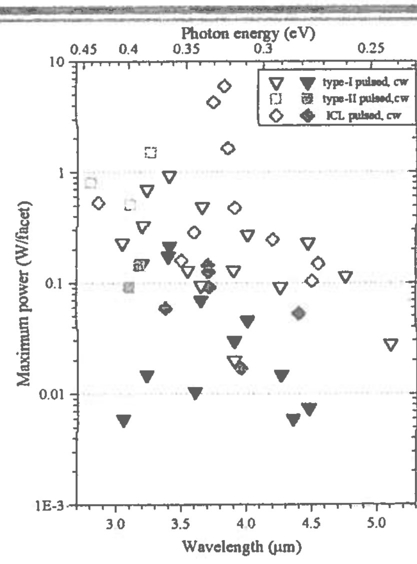


Room-temperature IC laser



Record-high power efficiency

Research Status of III-V Sb-based Interband Diode Lasers

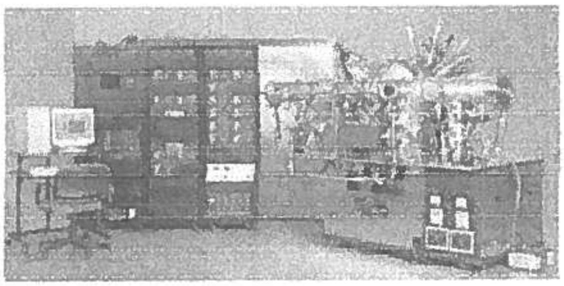


Record-high peak power (~6W/facet) demonstrated by ICL

New Molecular Beam Epitaxy System for JPL

This machine will **improve JPL's competitive position** by attracting talent and enabling new science and improved instruments in

- Mid-IR (2-9 µm) infrared lasers
- Long-wavelength infrared detectors
- Thermo-photovoltaic devices
- Passive *millimeter wave imagers*



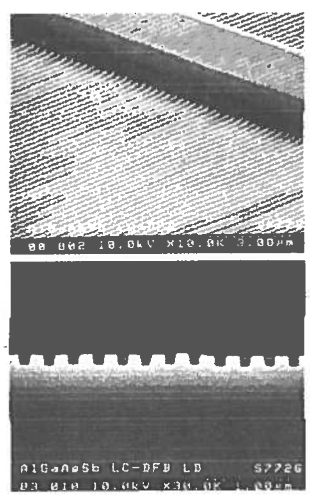
Applied Epi Modular GEN III System
(4-Inch MBE for Sb-Based Heterostructures)

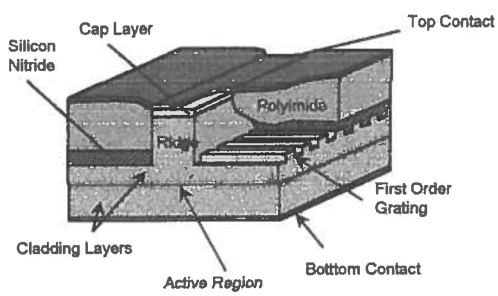
Having:

- Orders of magnitude improvement in sensitivity
- Potentially big science payoffs!
- Myriad of NASA & JPL applications

Single-Mode DFB Laser Fabrication

- *Laterally coupled* distributed feedback laser structure – avoids need for crystal regrowth on top of gratings.





- Successfully developed electron-beam lithography and dry etch processes for fabricating distributed feedback laser gratings very close to waveguide ridges.

Design Features of Laser Based Gas Sensors

- Adequate Mid-infrared Power
- High Sensitivity (ppb concentrations)
- High Selectivity (<30 MHz)
- Wavelength Tunable (Single or Multiple Trace Gases)
- 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

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Molecules Detected with Type 1 QC Lasers at Rice

Molecule	Wavelength and method
$^{12}CH_4$ and $^{13}CH_4$, N_2O, H_2O and HDO	8 μm, CW and pulsed, ambient air, 100 m pathlength, Voigt fit and linear regression analysis
C_2H_5OH	8 μm, CW, 100 m pathlength, linear regression analysis
NO	5.2 μm, CW, ICOS and CRDS
NH_3	10 μm, pulsed, 1 m pathlength
CO	4.6 μm, pulsed, ambient air, 1 m pathlength, reference channel
CO_2	15.5 μm, pulsed, ambient air, 1 m pathlength

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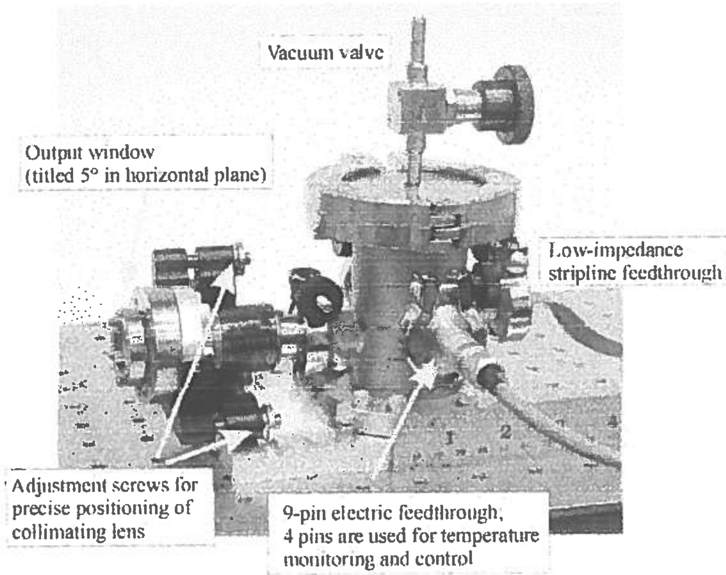
TE Cooled Pulsed QC Laser Assembly



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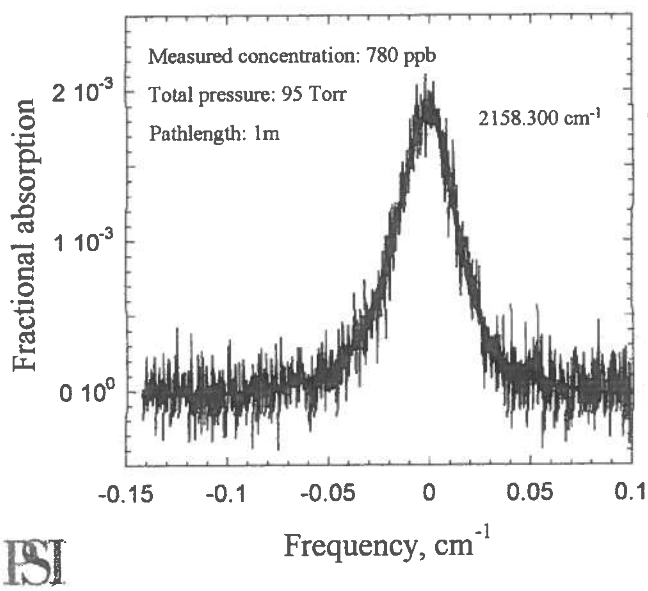
CO Absorption: Ambient Air Sample



Two IR detectors

Sensitivity ~10 ppb

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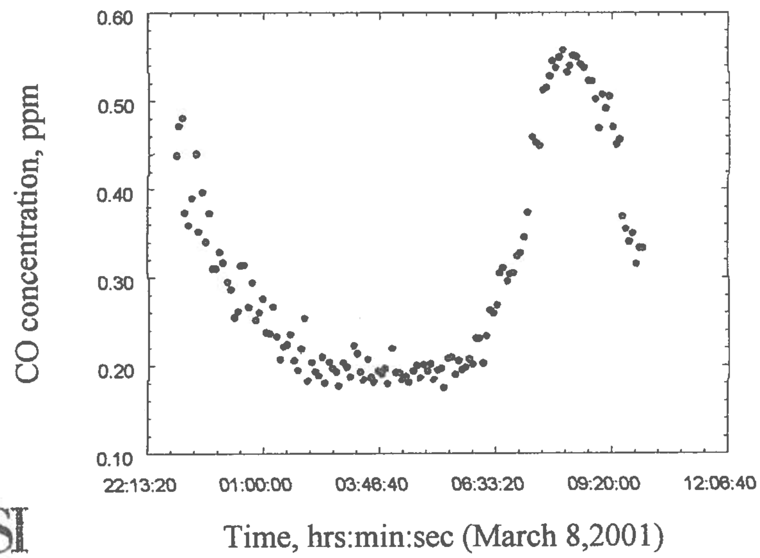
CO Concentration Measurements



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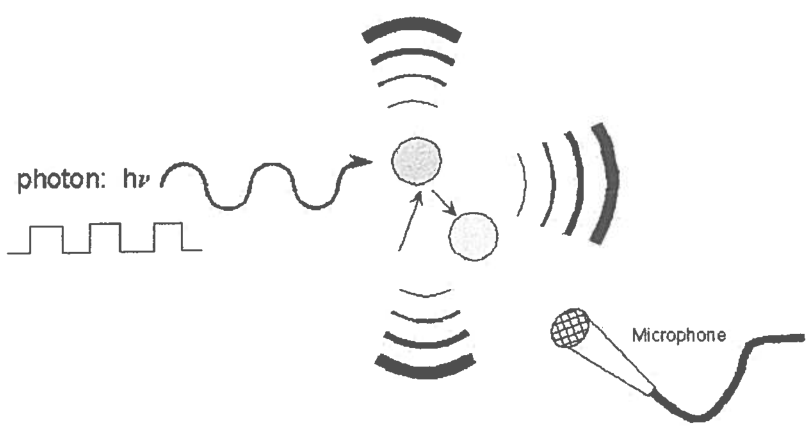
Principle of Photoacoustic Spectroscopy



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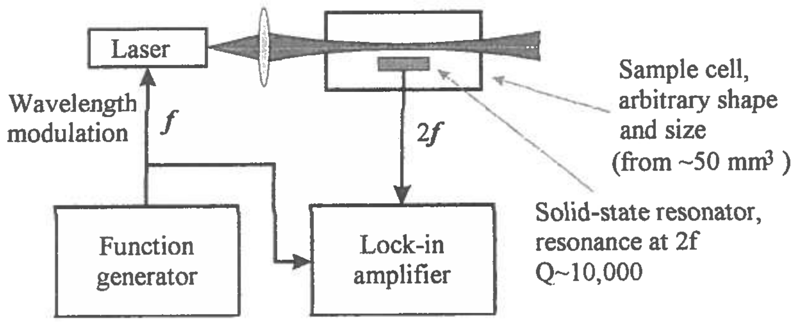
Schematic of PAS with a solid state resonator



Detection Limit of Some Fire Gases

Species	Wavenumber (cm^{-1})	Wavelength (μm)	Line S 10^{-20}/cm/mol	Toxicity,pmm	Detection Limit, ppbv
HF	4030	2.44		2000	
HCN	1460			140	
HCl	2925	3.42	100	150	0.005
CH_2O	2780	3.6		250	
C_2H_4O	1764	5.7	-	20,000	-
NH_3	1720	5.9	12	9,000	0.1
NO	1900	5.2	18	100	0.03
CO_2	2299	4.35	0.33	150,000	-
CO	2190,2151	4.65, 4.9	18.9	3,500	0.1

Rice Statement of Work

- Year One
  - Refine Target Gas List
  - Feasibility demonstration of photoacoustic spectroscopy with a solid state resonator
- Year Two
  - Evaluate type 2 QC lasers for monitoring of fire emission gases
- Year Three
  - Demonstration of a single frequency type 2 QC laser-based gas sensor
  - Field studies with gas sensor

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JPL Statement of Work

- Year One
  - Development of type 2 QC lasers
  - Characterization and performance studies
- Year Two
  - Development of Sb III-V based diode lasers.
  - Characterization and performance studies
- Year Three
  - Optimization of type 2 QC and Sb laser devices
  - Novel device fabrication techniques, etc..

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