Quantum Cascade Laser Sources: Recent Advances and Applications

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OUTLINE

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- Motivation: Wide Range of Gas Sensing Applications
- Key Characteristics of QC Lasers: October 2009
- Selected Applications of Trace Gas Detection
  - NH_3 Detection for Environmental and Health Applications
  - Nitric Oxide Detection
- Future Directions and Outlook
  - Fiber coupled CW EC-QCL Nitric Oxide Detection System
  - Detection of Broadband Molecular Absorbers
  - Development of QC Laser Arrays
  - Ultra-compact QCL based Analyzers
  - 33

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Wide Range of Trace Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (e.g. fire detection)
  - Automobile, Truck, Aircraft and Marine Emissions
- **Rural Emission Measurements**
  - Agriculture & Forestry, Livestock
- **Environmental Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Nuclear Safeguards, Pharmaceutical, Metals Processing, Food & Beverage Industries
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Applications in Health and the Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

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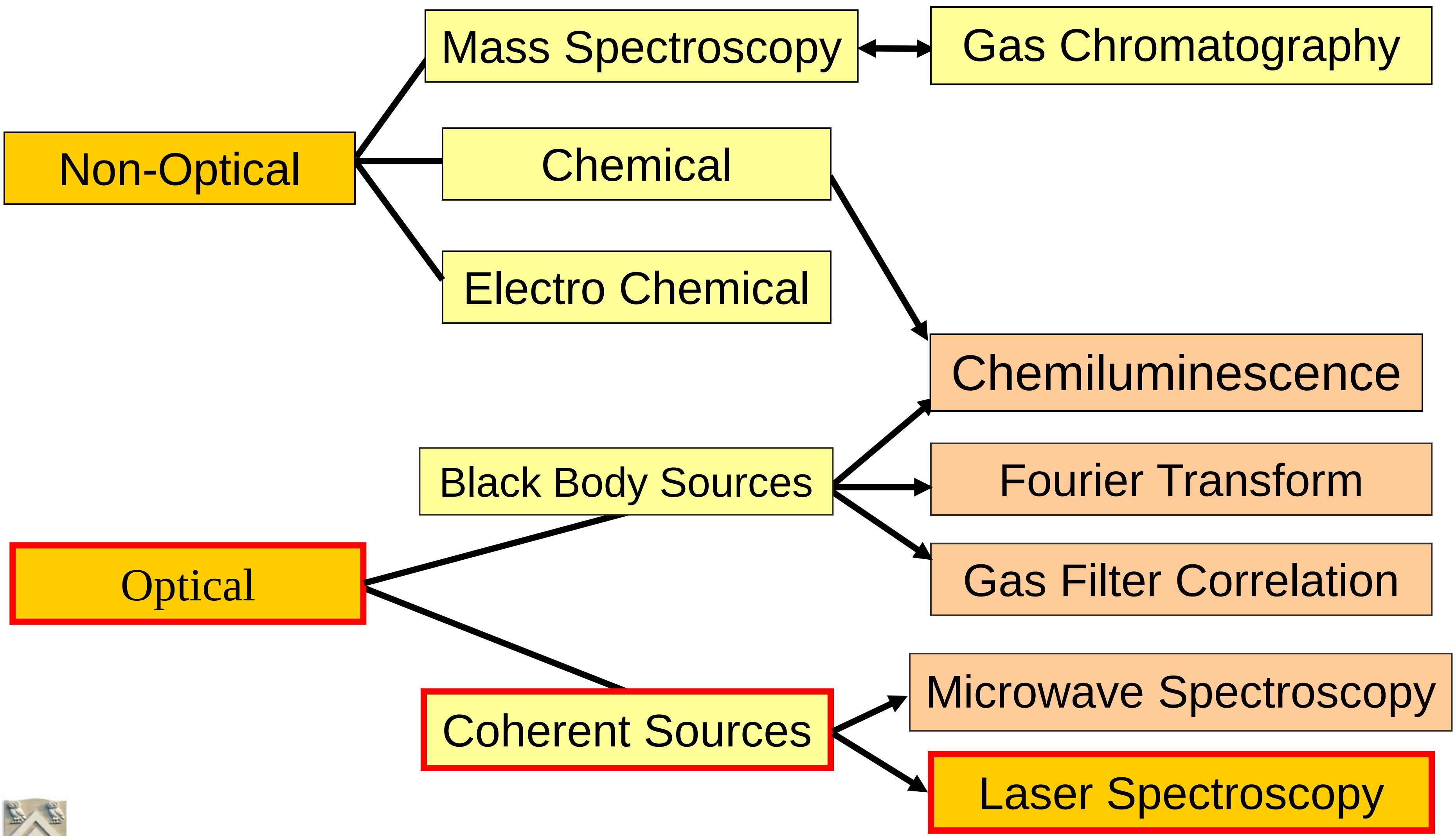
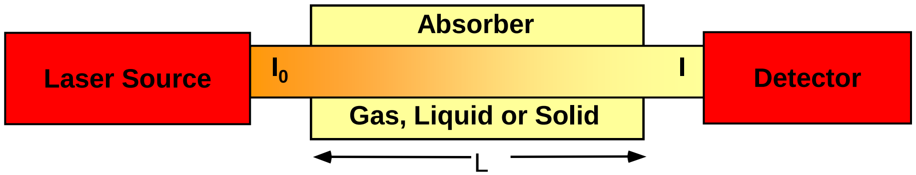
Existing Methods for Trace Gas Detection



Basics of Optical Trace Gas Analyzers

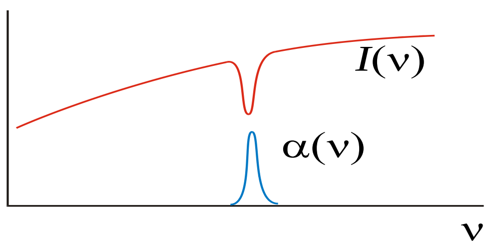


Beer-Lambert's Law of Linear Absorption

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

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

ν - frequency [cm^{-1}]; P_a- partial pressure [atm]



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

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 spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

Key Requirements: Sensitivity, specificity, rapid data acquisition and multi-species detection

Optimum Molecular Absorbing Transition

- NIR Overtone or Combination Bands
- **MIR Fundamental Absorption Bands**

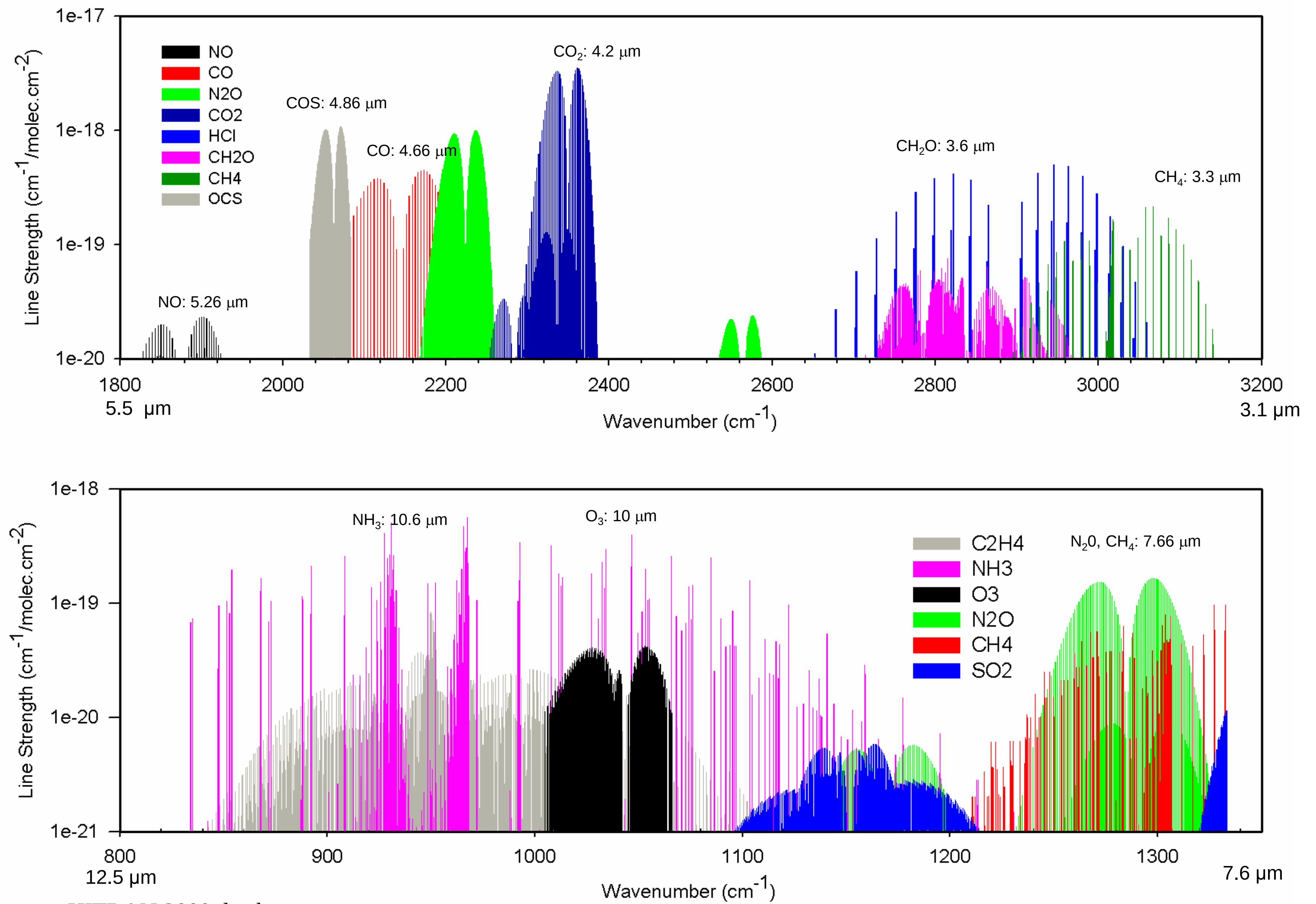
Long Optical Pathlengths

- Multipass Absorption Cell White, Herriott)
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector); Standoff and Remote Detection
- Fiberoptic evanescent wave Spectroscopy

Spectroscopic Detection Schemes

- Wavelength or Frequency Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy (PAS or QEPAS
- Laser Induced Breakdown Spectroscopy

Molecular Absorption Spectra within the two Mid-IR Atmospheric Windows



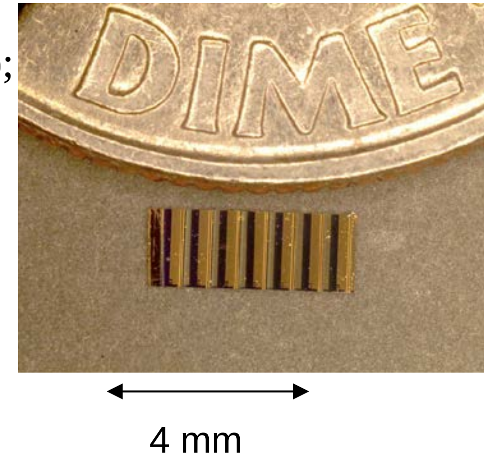
Source: HITRAN 2000 database

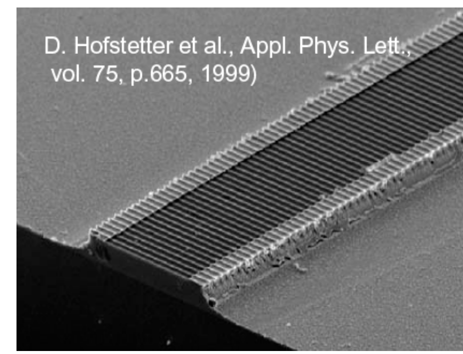
Mid-IR Source Requirements for Laser Spectroscopy

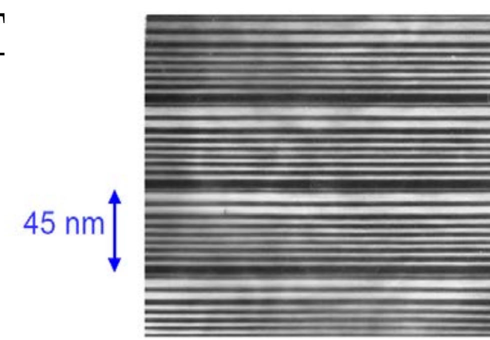
REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Optimum Wavelength, Power
Selectivity (Spectral Resolution)	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelength
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	No Consumables
Field deployable	Compact & Robust

Key Characteristics of mid-IR QCL and ICL Sources-2009

- **Band – structure engineered devices**
  (Emission wavelength is determined by layer thickness – MBE or MOCVD); mid-infrared QCLs operate from 3 to 24 µm (AlInAs/GaInAs)
- Compact, reliable, stable, long lifetime, and commercial availability
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength
- **Broad spectral tuning range in the mid-IR**
  (4-24 µm for QCLs and 3-5 µm for ICLs and GaSb diodes)
  - 1.5 cm^{-1} using injection current control for DFB devices
  - 10-20 cm^{-1} using temperature control for DFB devices
  - > 430 cm^{-1} using an external grating element and FP chips with heterogeneous cascade active region design; also QCL DFB r array
- **Narrow spectral linewidth**
  - CW: 0.1 - 3 MHz & <10Khz with frequency stabilization (0.0004 cm^{-1})
  - Pulsed: ~ 300 MHz
- **High pulsed and cw powers of QCLs and ICLs at TEC/RT temperatures**
  - Pulsed and CW powers of ~ 1.5 W; high temperature operation ~300K
  - >50 mW, TEC CW DFB @ 5 and 10 µm
  - > 600 mW (CW FP) @ RT; wall plug efficiency of ~15 % at 4.6µm;







Quantum Cascade (QC), Interband (IC) and GaSb Laser Availability in October 2009

- Commercial Sources
  - Adtech, CA
  - Alpes Lasers, Switzerland & Germany
  - Alcatel-Thales, France
  - Corning, NY
  - Hamamatsu, Japan
  - Physical Sciences, Inc (Maxion Technologies, Inc
  - Nanoplus, Germany

- Research Groups
  - Harvard University
  - Fraunhofer-IAF, Freiburg, Germany
  - NASA-JPL, Pasadena, CA
  - Naval Research Laboratories, Washington, DC
  - Northwestern University, Evanston, IL
  - Princeton University (MIRTHE), NJ
  - State University of New York
  - Technical University, Zuerich, CH
  - University of Montpelier, France
  - UK: Sheffield

Recent Applications of QCL based Trace Gas Sensors

Motivation for NH_3 Detection

- Monitoring of gas separation processes
- Detection of ammonium-nitrate explosives
- Spacecraft related gas monitoring
- Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver diseases)

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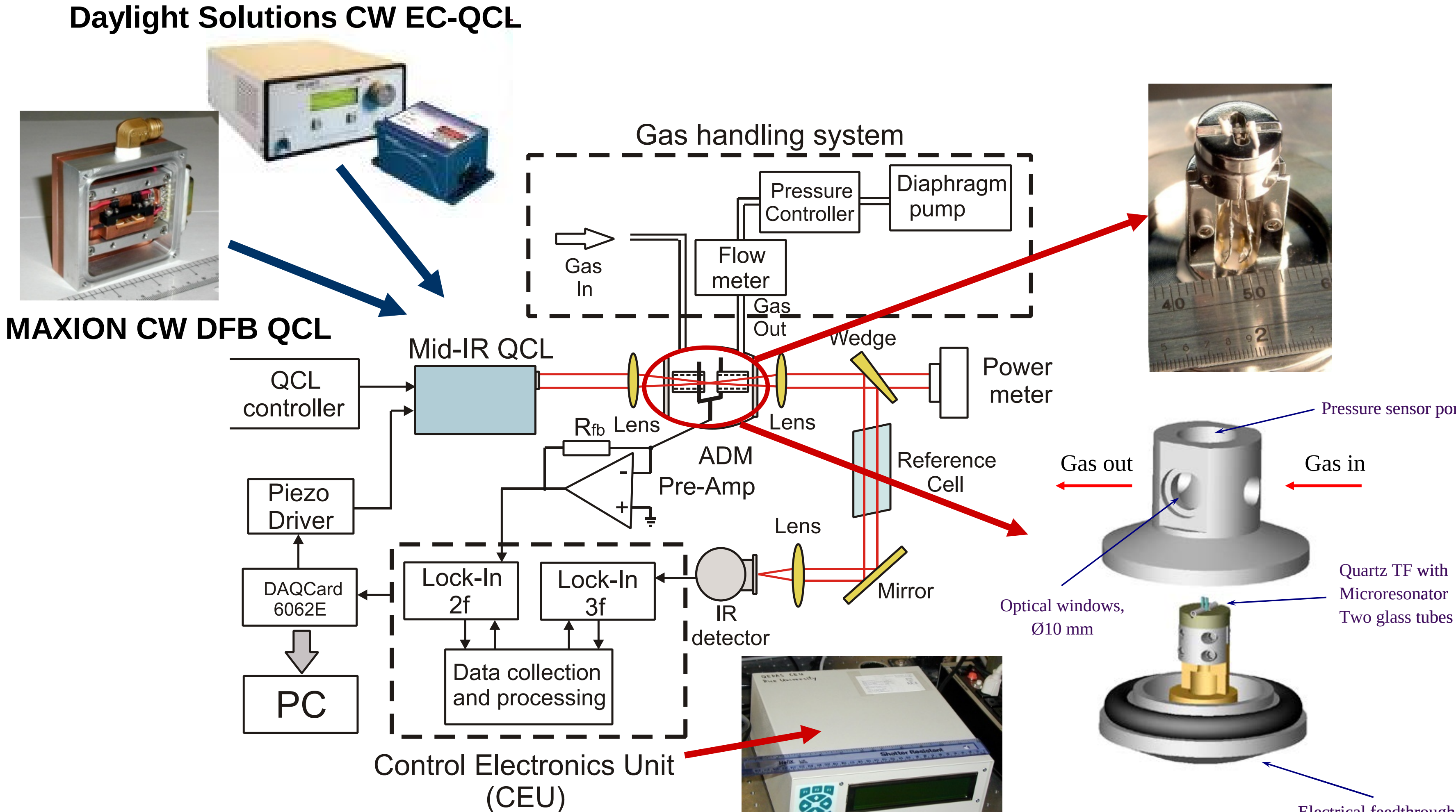
Mid-IR QEPAS based NH_3 Gas Sensor Architecture



Noise–equivalent concentration (NEC) is 6 ppb for a1s time constant and 20mW excitation power at 1046.4 cm^{-1} (110 Torr)

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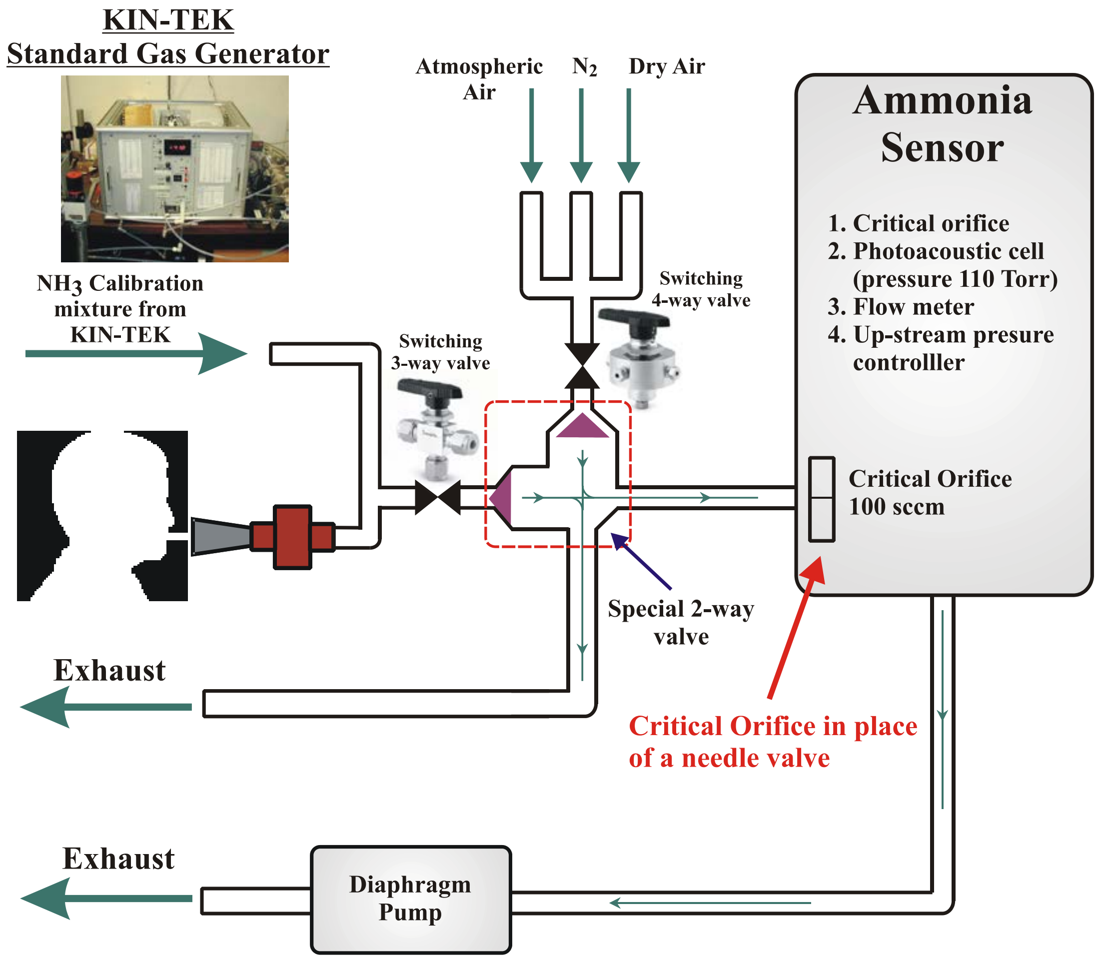
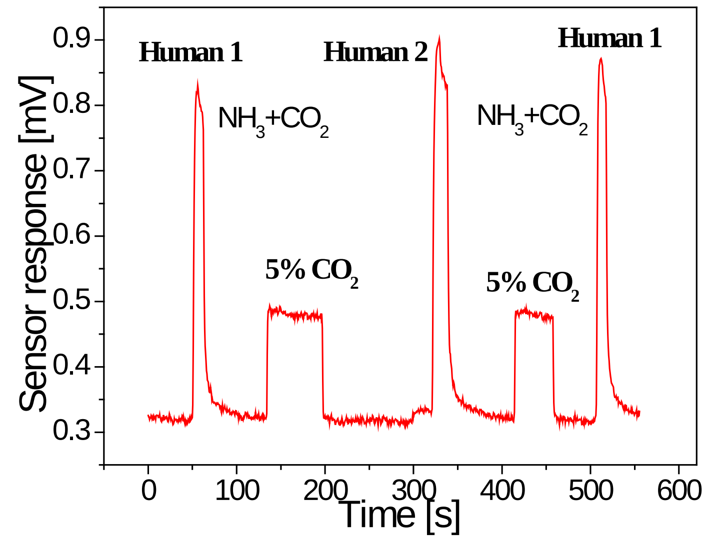
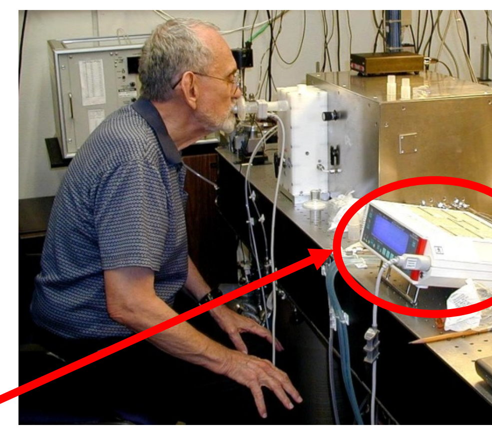
Real-time Breath Monitor Interface







- Controlled flow
- Continuous control of mouth pressure
- Continuous monitoring of CO_2 concentration (capnograph) and its use in QEPAS data processing

T.Risby: 12:00 Sept.7 & Poster

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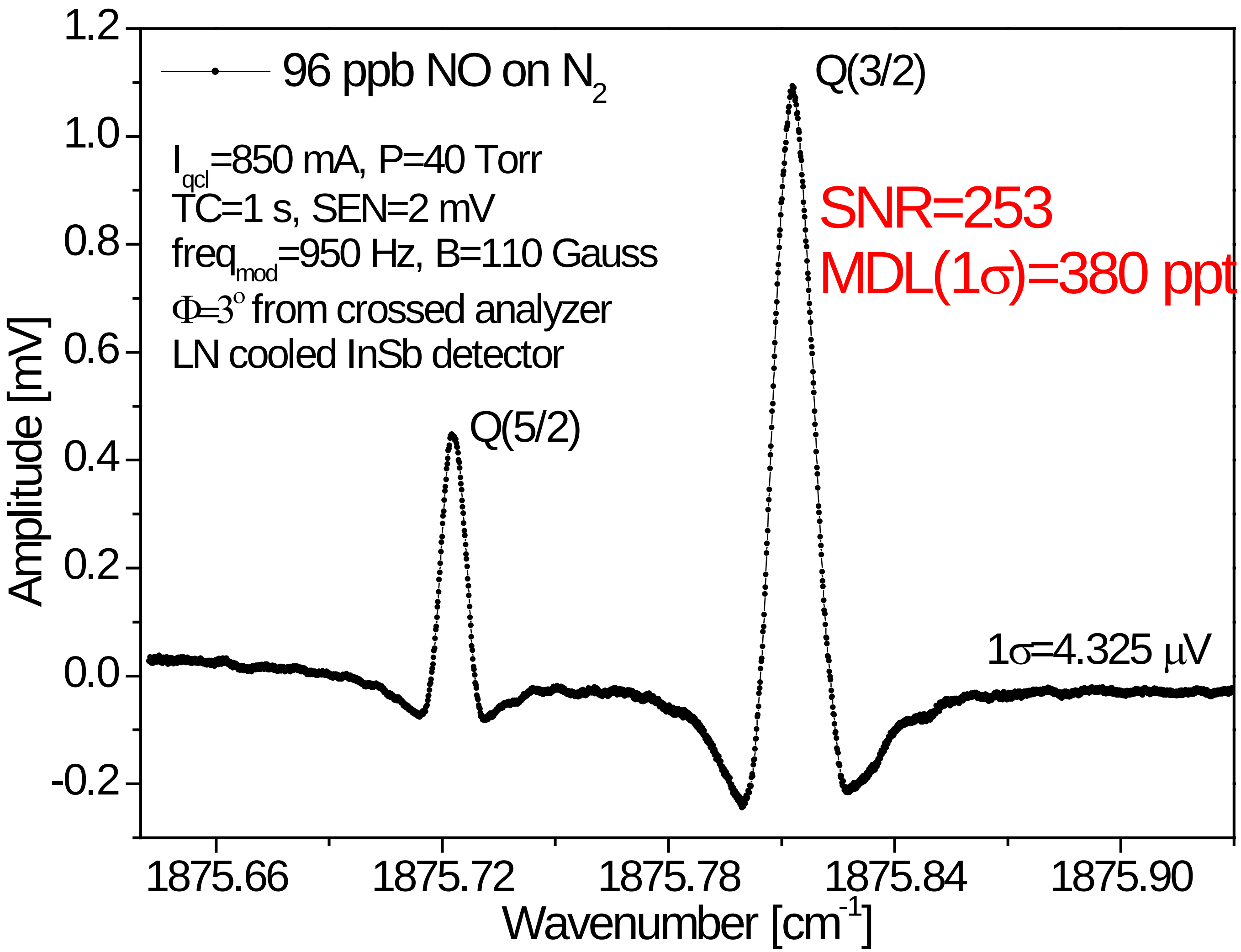
Motivation for Nitric Oxide Detection

- Environmental pollutant
  - Product of fossil fuel combustion process (automobile and power plant emissions)
  - Precursor of smog and acid rain

Faraday Rotation Spectroscopy of Nitric Oxide



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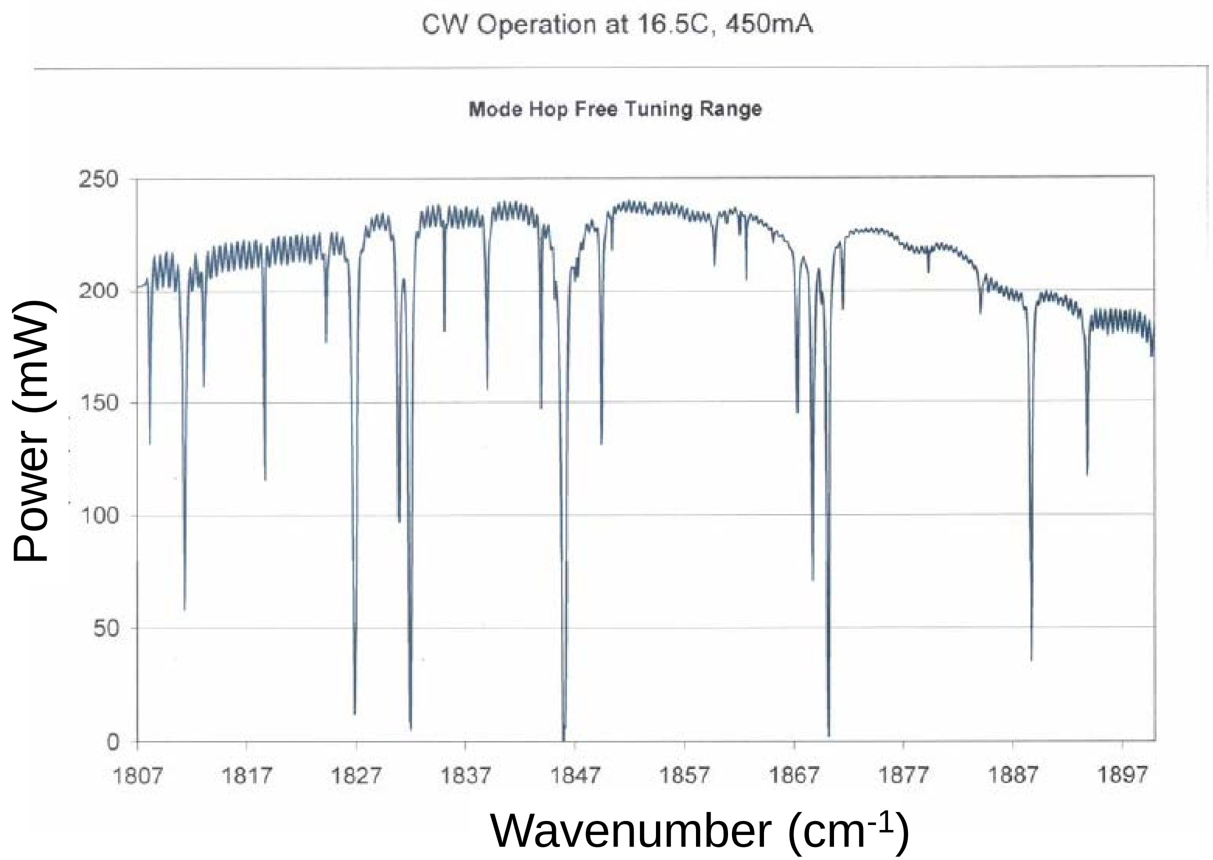
Future Directions and Outlook of Chemical Trace Gas Sensing Technology

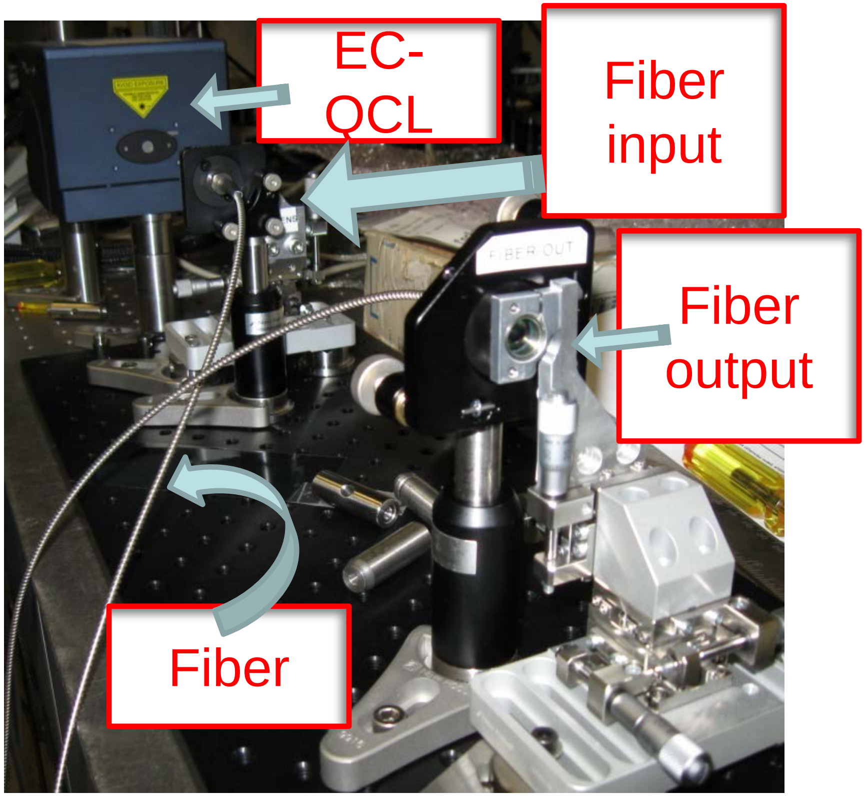
High power fiber-coupled QCL for NO detection



- LASER SOURCE EC-QCL (Daylight Solutions, Inc)
  - Tuning range 5.13-5.67 µm
  - Maximum tuning Rate 38 nm/sec
  - Highest optical power: ~250 mW
  - TE cooling, RT operation

Collaboration with: V. Spagnolo
Politecnico Bari and CNR-LIT[3]

Fiber coupled QCL and QEPAS detection system



- High coupling efficiency of laser output to fiber
- Beam size matching to QEPAS after collimation
- Aspheric lenses for both coupling and re-collimating.
- 86% coupling efficiency

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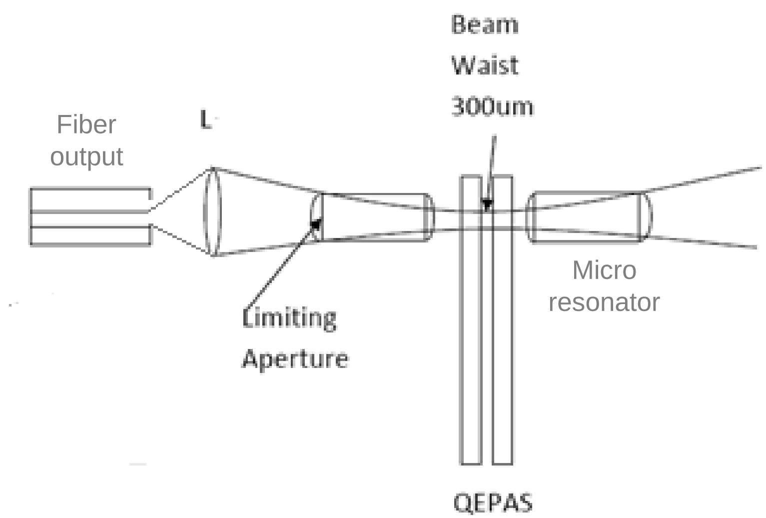
Material: $AsSe_3$,
- 22 μm core diameter
- Single mode operation
- FC-PC termination
- AR Coated.



Collaboration with :V. Spagnolo, Politecnico Bari and CNR-LIT[3]

Monitoring of Broadband Absorbers

- Freon 125 (C_2HF_5)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals, e.g. chemical warfare agents
- Acetone (CH_3COCH_3)
  - Recognized biomarker for diabetes
- TATP (Acetone Peroxide, $C_6H_{12}O_4$)
  - Highly Explosive
- Uranium Hexafluoride (UF_6)

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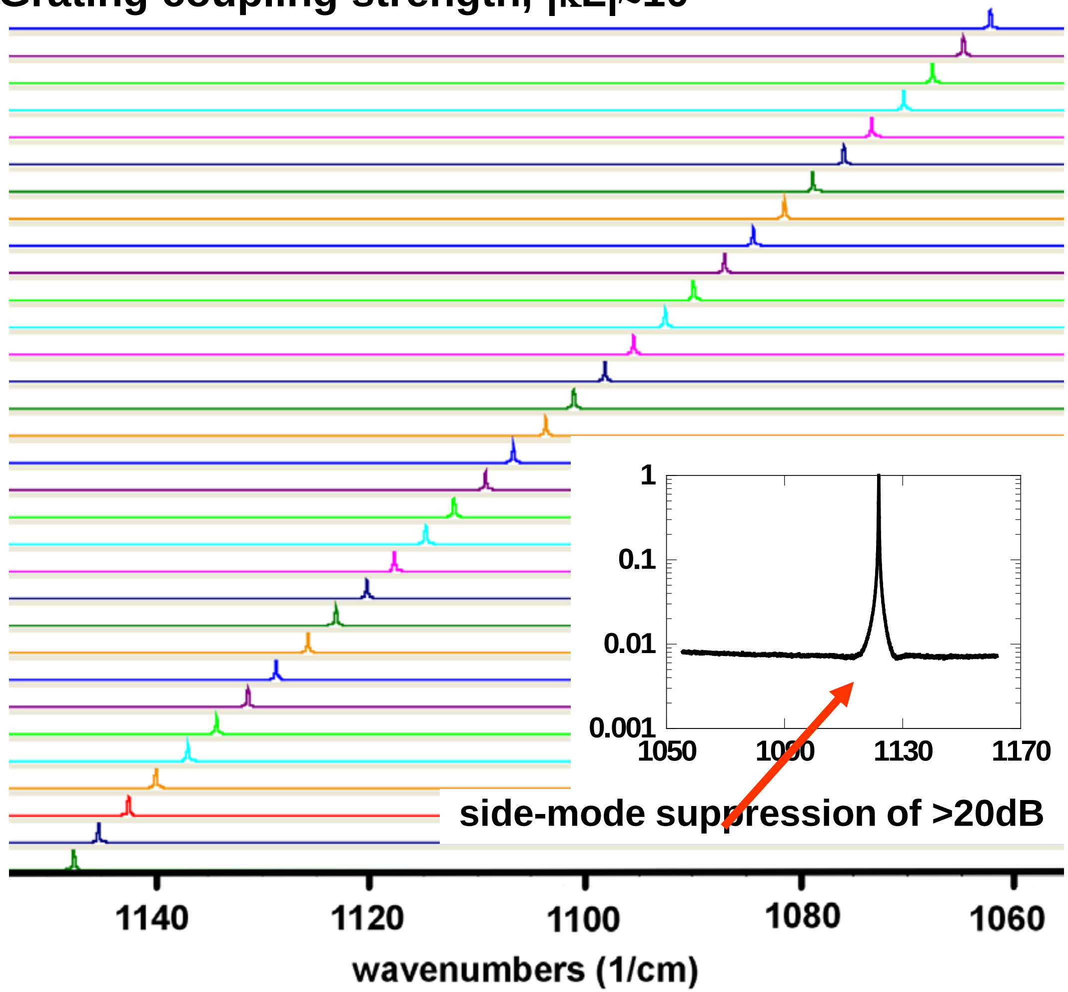
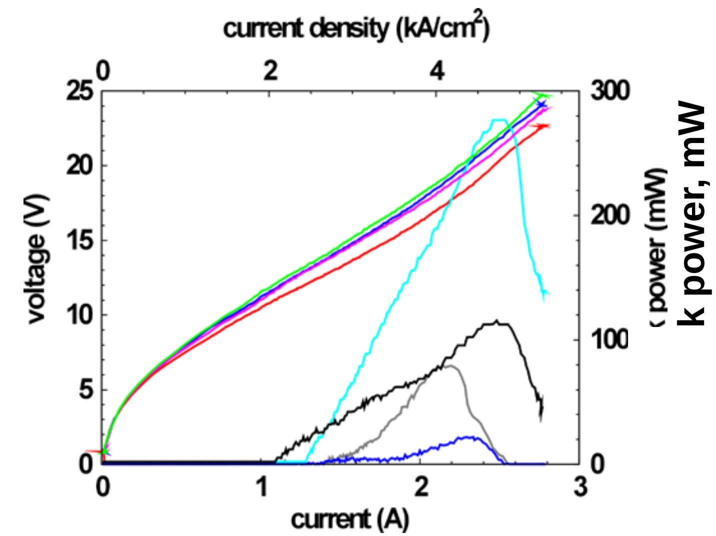
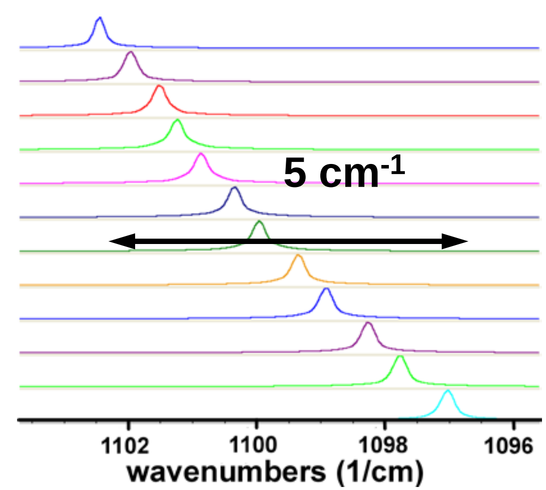
DFB QCL array performance

Emission spectrum of a DFB-QCL array
Pulsed operation (80kHz, 50ns) at room temperature
Grating coupling strength, |κL|≈10



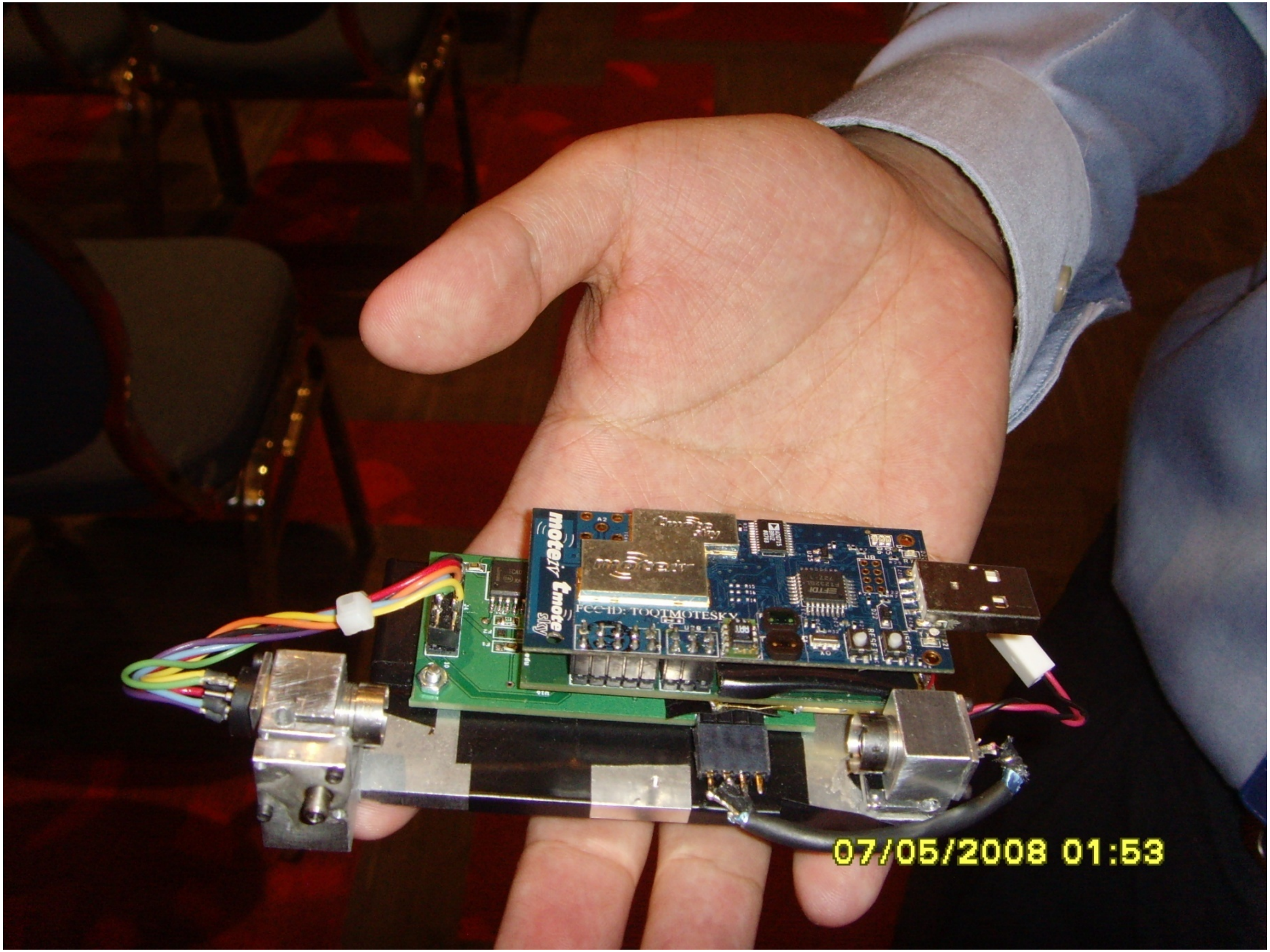




Temperature tuning by DC current

Lee, Belkin, et al., APL 2007

Ultra-compact Diode Laser based Trace Gas Sensor



Summary & Future Directions of Laser based Gas Sensor Technology

- **Semiconductor Laser based Trace Gas Sensors**
  - Compact, tunable, and robust
  - High sensitivity ($<10^{-4}$) and selectivity (3 to 500 MHz)
  - Capable of fast data acquisition and analysis
  - Detected 14 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, H_2S, H_2CO, SO_2, C_2H_5OH, C_2HF_5 ,TATP and several isotopic species of C, O, N and H.
- **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality – NH_3, H_2CO, NO, isotopic ratio measurements of CO_2 and CH_4, fire and post fire detection; quantification of engine exhausts)
  - Industrial process control and chemical analysis (NO, NH_3, H_2O, and H_2S)
  - Medical & biomedical non-invasive diagnostics (NH_3, NO, N_2O and CH_3COCH_3)
  - Ultra-compact, low cost, robust sensors (CO and CO_2)
- **Future Directions and Collaborations**
  - Improvements of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR intersubband and interband quantum cascade lasers
  - Further development of spectraphone technology
  - New applications enabled by novel broadly wavelength tunable quantum cascade lasers based on heterogeneous EC-QCL (i.e sensitive concentration measurements of broadband absorbers, in particular HCs, UF_6 and multi-species detection)
  - Development of optically gas sensor networks based on QEPAS and LAS

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