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Trends and Innovation of Infrared Semiconductor Laser based Chemical Sensing Technologies

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OUTLINE

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Goslar

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- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sources and Sensing Technologies
- Selected Applications of Trace Gas Detection
  - Quartz Enhanced L-PAS (NH3, Freon 125, acetone & TATP)
  - Nitric Oxide Detection (Faraday Rotation Spectroscopy, Remote Sensing and Cavity Enhanced Spectroscopy)
- Future Directions and Conclusions

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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 Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

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Sensitivity Enhancement Techniques for Laser Spectroscopy

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriot)
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector): Standoff and Remote Detection
  - Fiberoptic Evanescent Wave Spectroscopy
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic Spectroscopy
  - Laser Induced Breakdown Spectroscopy (LIBS)

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Key Characteristics of mid-IR QCLs and ICL Sources-2008

- **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)

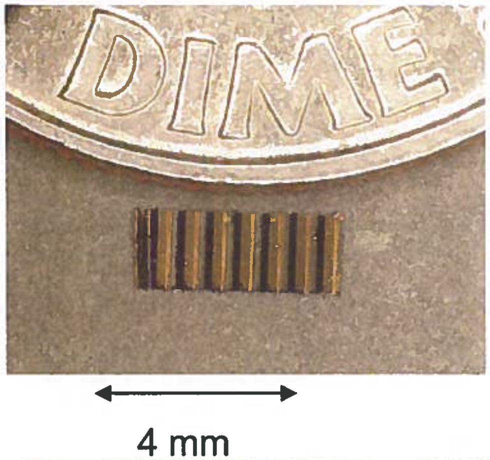
- Compact, reliable, stable, long lifetime, and commercial availability

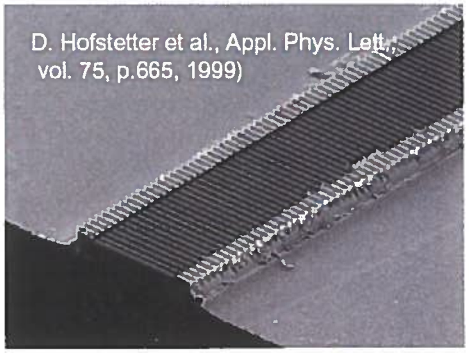
- Fabry-Perot (FP), single mode (DFB) and multi-wavelength

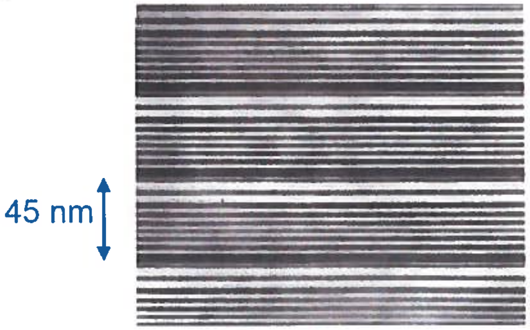
- **Spectral tuning range in the mid-IR**
  (4-24 µm for QCLs and 3-5 µm for ICLs)
  - 1.5 cm^{-1} using injection current control
  - 10-20 cm^{-1} using temperature control
  - > 200 cm^{-1} using an external grating element and heterogeneous cascade active region design; also QC laser array (Harvard)

- **Narrow spectral linewidth**
  - CW: 0.1 - 3 MHz & <10Khz with frequency stabilization (0.0004 cm^{-1})
  - Pulsed: ~ 300 MHz (chirp from heating)

- **High pulsed and cw powers of QCLs and ICLs at TEC/RT temperatures**
  - Pulsed and CW powers of ~ 1.5 W; high temperature operation ~300 K
  - >50 mW, TEC CW DFB @ 5 and 10 µm
  - > 600 mW (CW FP) @ RT; wall plug efficiency of ~15.% at 4.6µm;
  - Princeton, Northwestern, Harvard, ETH, NRL, FI-IAF, UMBC,
  - commercialization by Adtech Optics, Pranalytica, Alpes, DLS, Alcatel Thales, Nanoplus, Laser Components, Maxion, Corning, Hammamatsu

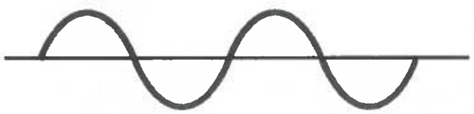






From conventional PAS to QEPAS

Laser beam, power P



Modulated (P or λ) at f or $f/2$

$$S \sim \frac{Q \alpha P}{f V}$$

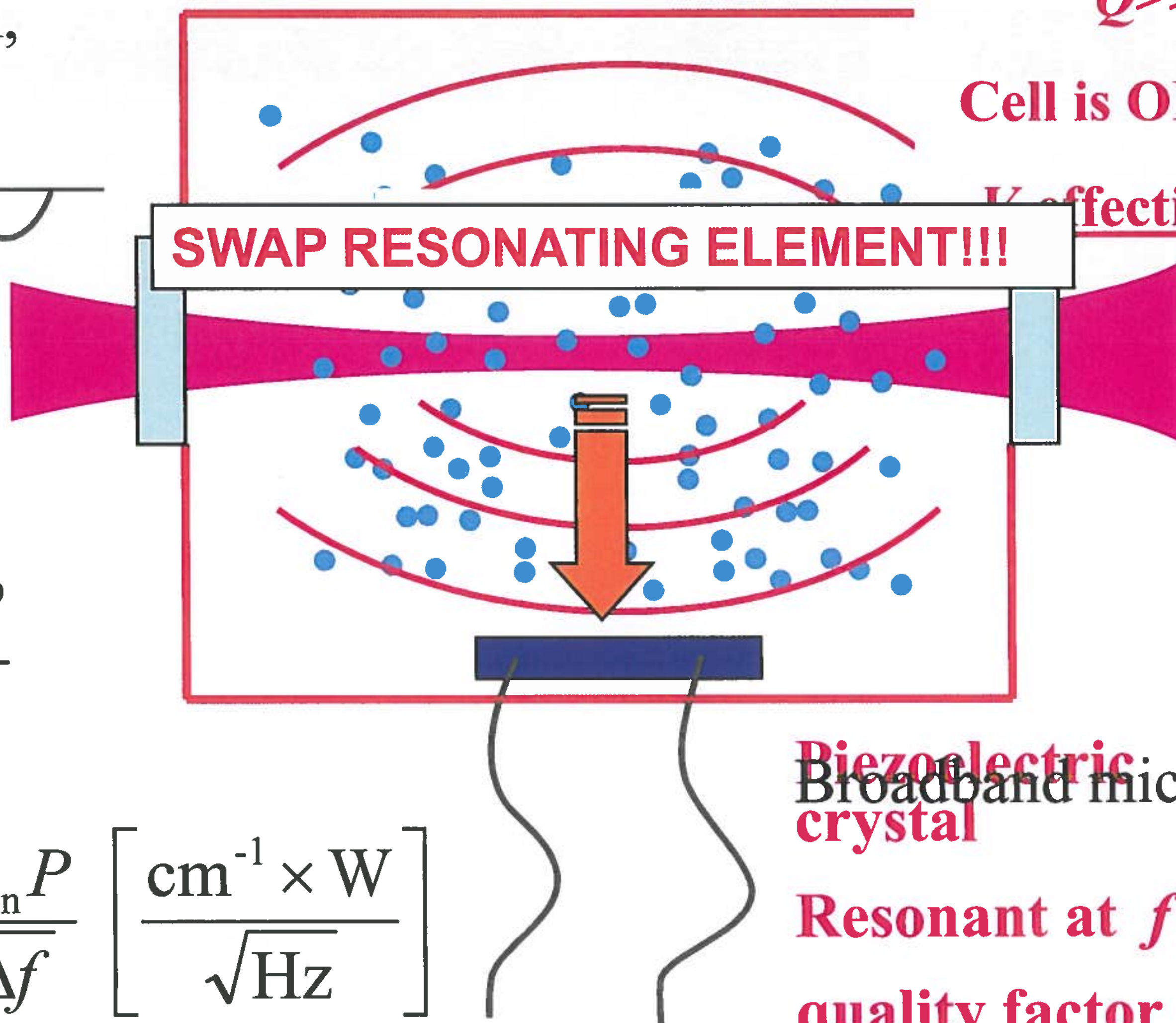
$$NNEA = \frac{\alpha_{min} P}{\sqrt{\Delta f}} \left[\frac{cm^{-1} \times W}{\sqrt{Hz}} \right]$$

Cavity resonant

Q>>1000

Cell is OPTIONAL!

V effective volume



Broadband microphone

Piezoelectric crystal

Resonant at f

quality factor Q

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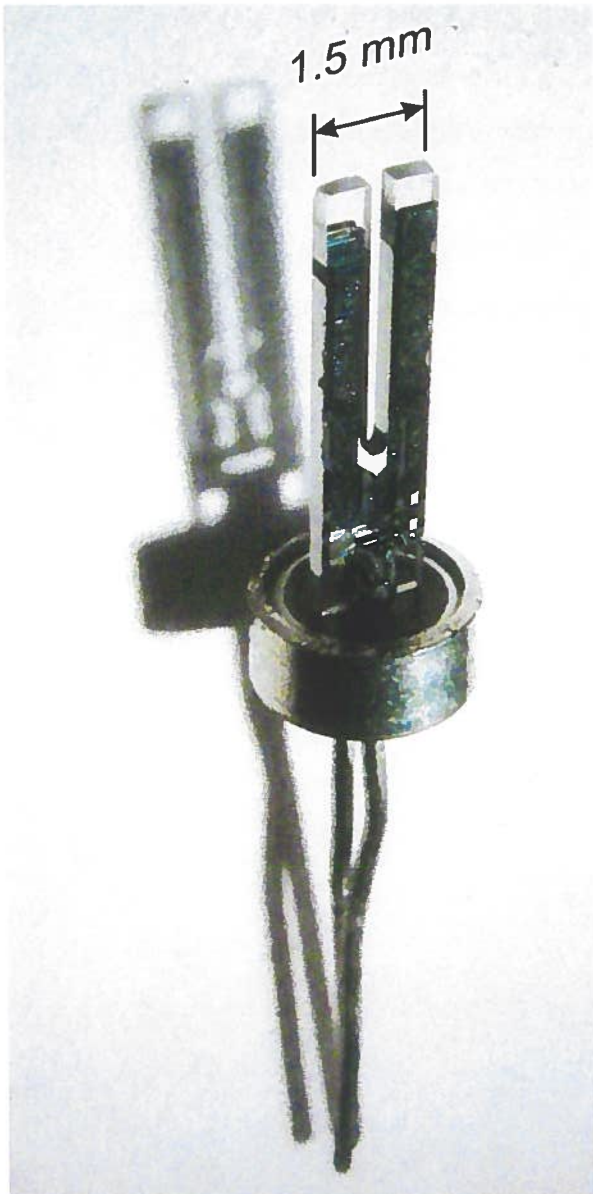
Quartz Tuning Fork as a Resonant Microphone



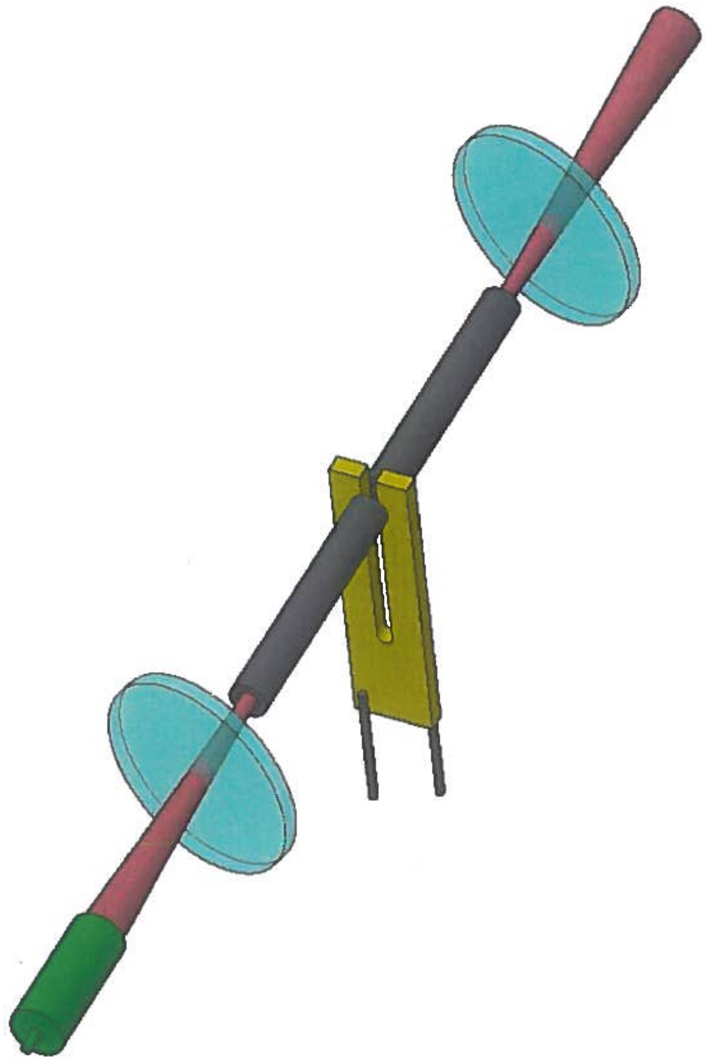
Unique properties

- Extremely low internal losses:
  - Q~10 000 at 1 atm
  - Q~100 000 in vacuum
- Acoustic quadrupole geometry
  - Low sensitivity to external sound
- Large dynamic range – linear from thermal noise to breakdown deformation
  - 300K noise: x~10^{-11} cm
  - Breakdown: x~10^{-2} cm
- Wide temperature range: from 1.56K (superfluid helium) to ~700K
- Low cost (<$1)

Other parameters

- Resonant frequency ~32.8 kHz
- Force constant ~26800 N/m
- Electromechanical coefficient ~7×10^{-6} C/m

Absorption Detection Module for QEPAS Gas Sensor



Microresonator tubes

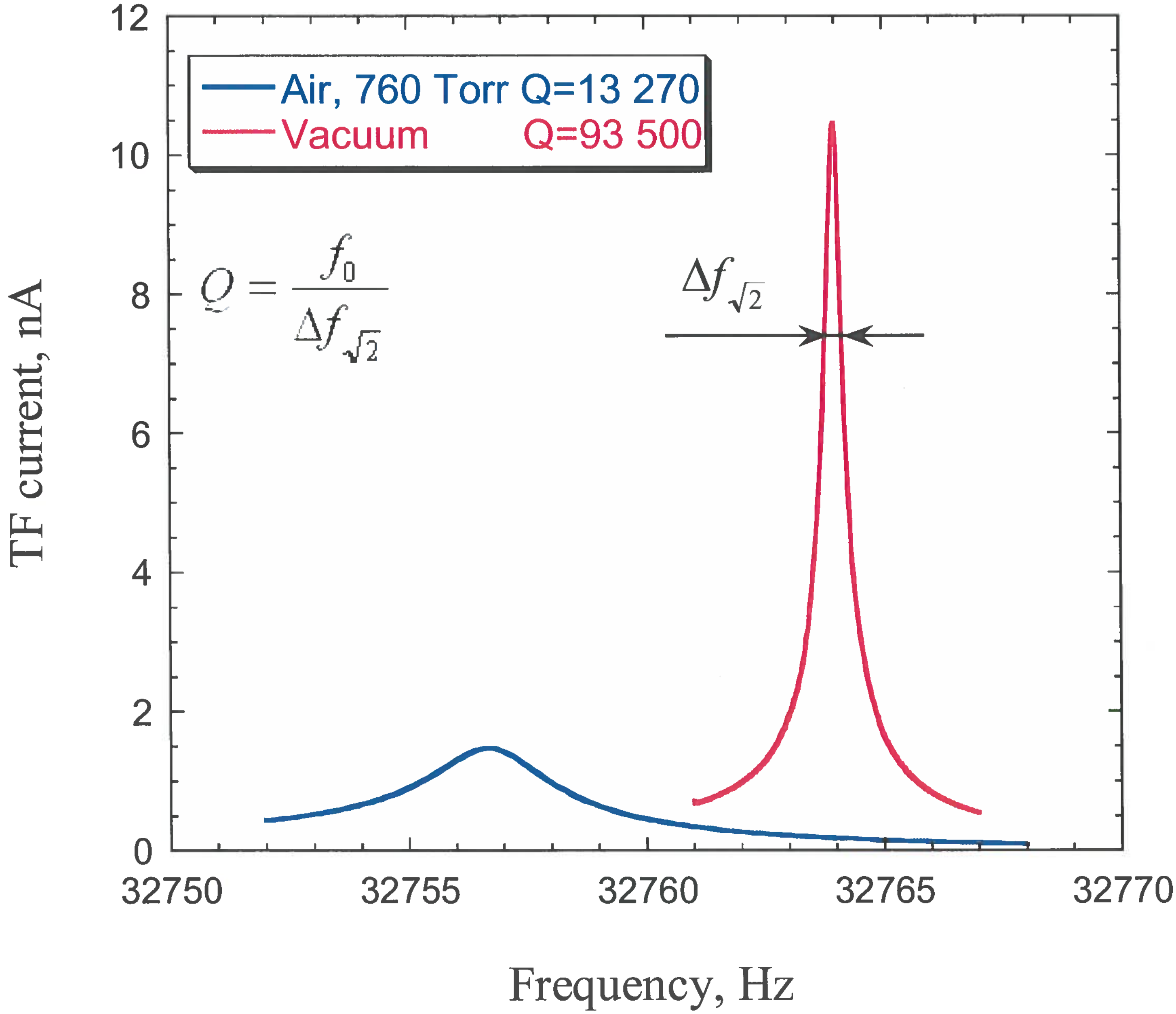
- Must be close to the QTF but not touching TF (i.e. 30-50 μm gaps).
- Inner diameter 0.41 mm; 10% lower signal with 0.6 mm diameter tubes.
- Each tube ~5mm long (~λ/2 for sound at 32.8 kHz) ?

Gain: ×10 to ×20

Windows

- Must be tilted to prevent the reflected light from entering the microresonator tubes.
- Exact positioning is not critical

Typical QTF Resonance Curves



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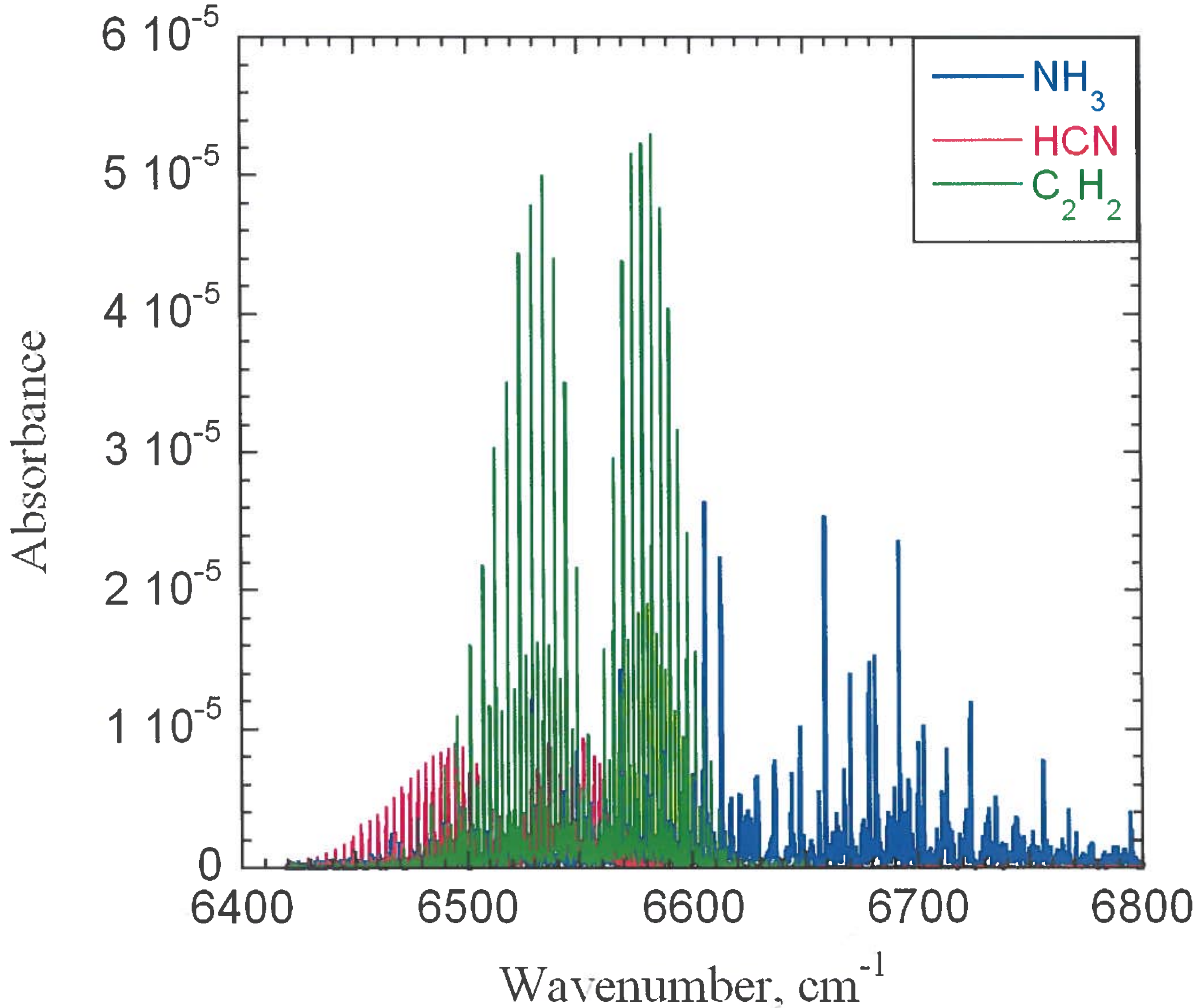
Merits of QEPAS based Trace Gas Detection

- Ultra-compact; small sample volume - $<1 mm^3$
- Rugged and low cost transducer – quartz monocrystal
- High immunity to environmental acoustic noise
- Sensitivity is limited by the fundamental thermal TF noise – $k_B T$ energy in the TF symmetric mode, directly observed
- White noise spectrum – SNR scaling as $\sqrt{t}$ up to t=3 hours was observed
- High Sensitivity (ppm to sub ppb) and excellent dynamic range
- Applicable over a wide range of pressures
- Temperature, pressure and humidity insensitive

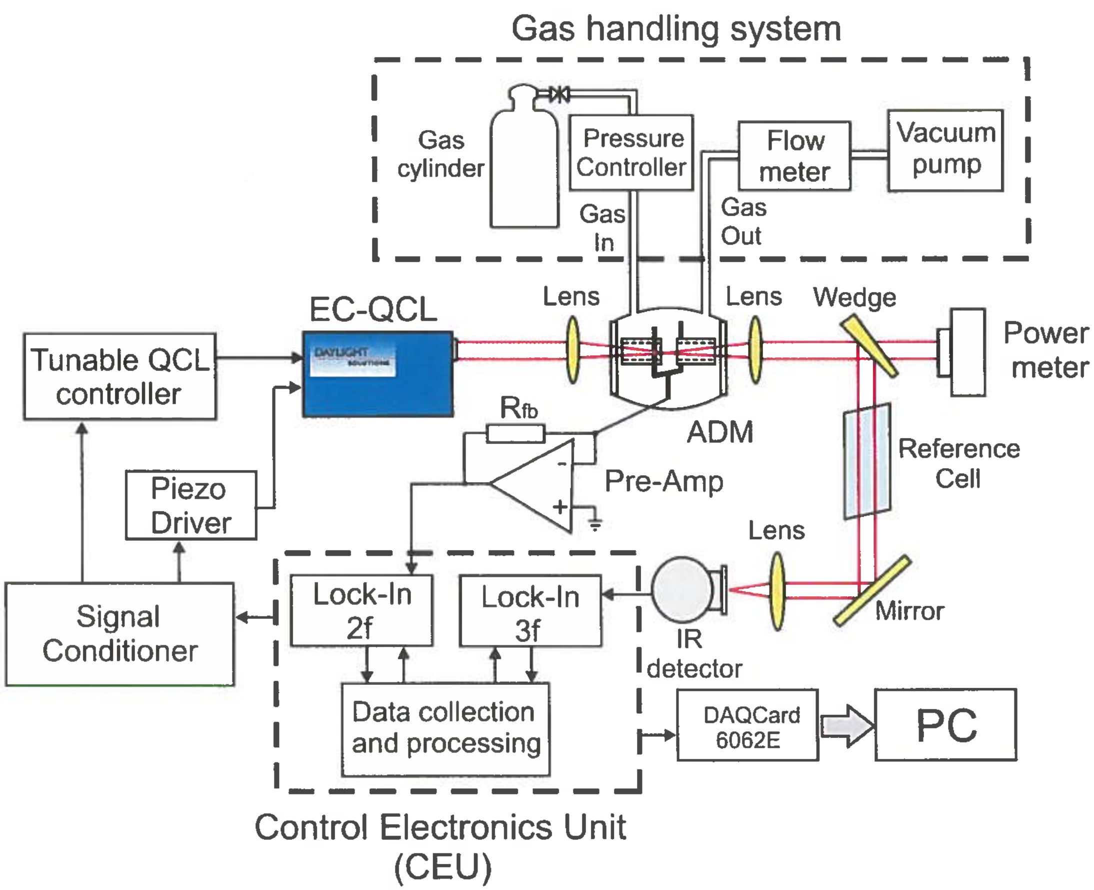
Overlapping NIR absorption bands



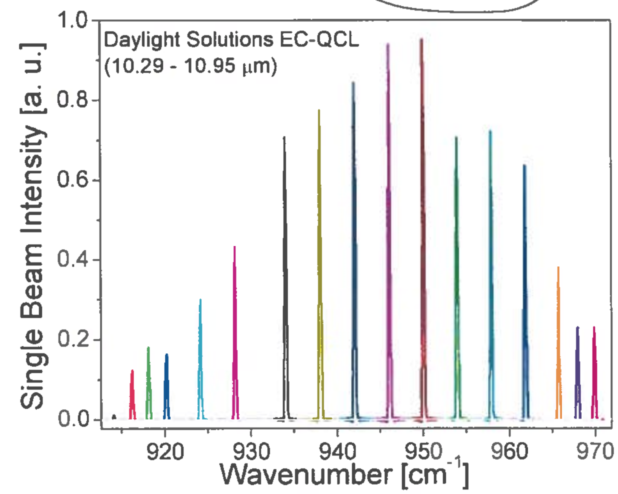
Data Comm
5μm (AK)

~~DLS... Array~~

DLS EC-QCL based QEPAS Sensor

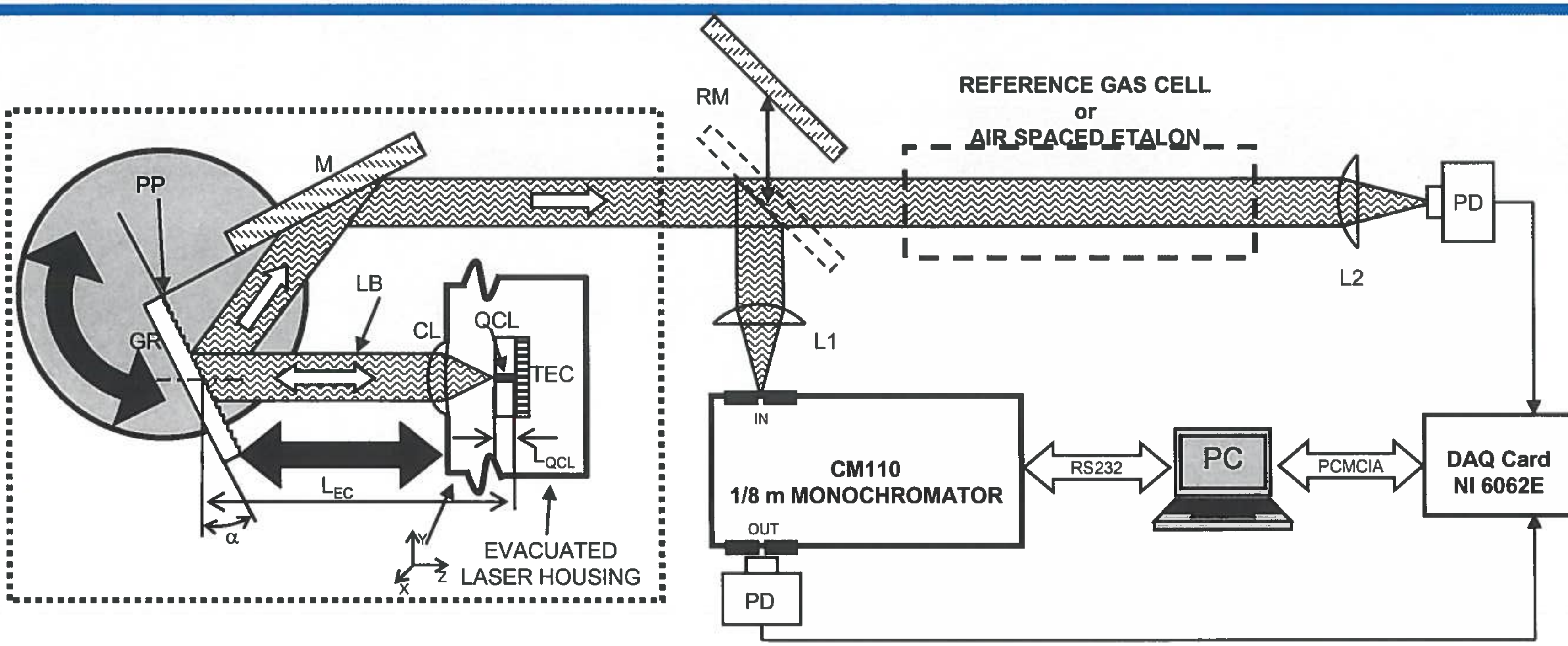


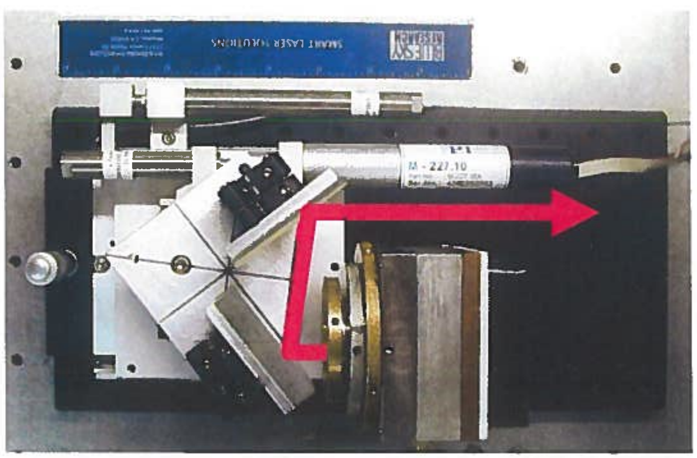
↓ NH_3 free CO_2, H_2O



54 cm^{-1}
944 cm^{-1}
10.6 μm
34 mW.

Tunable external cavity QCL based spectrometer





- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + optional chilled water cooling)

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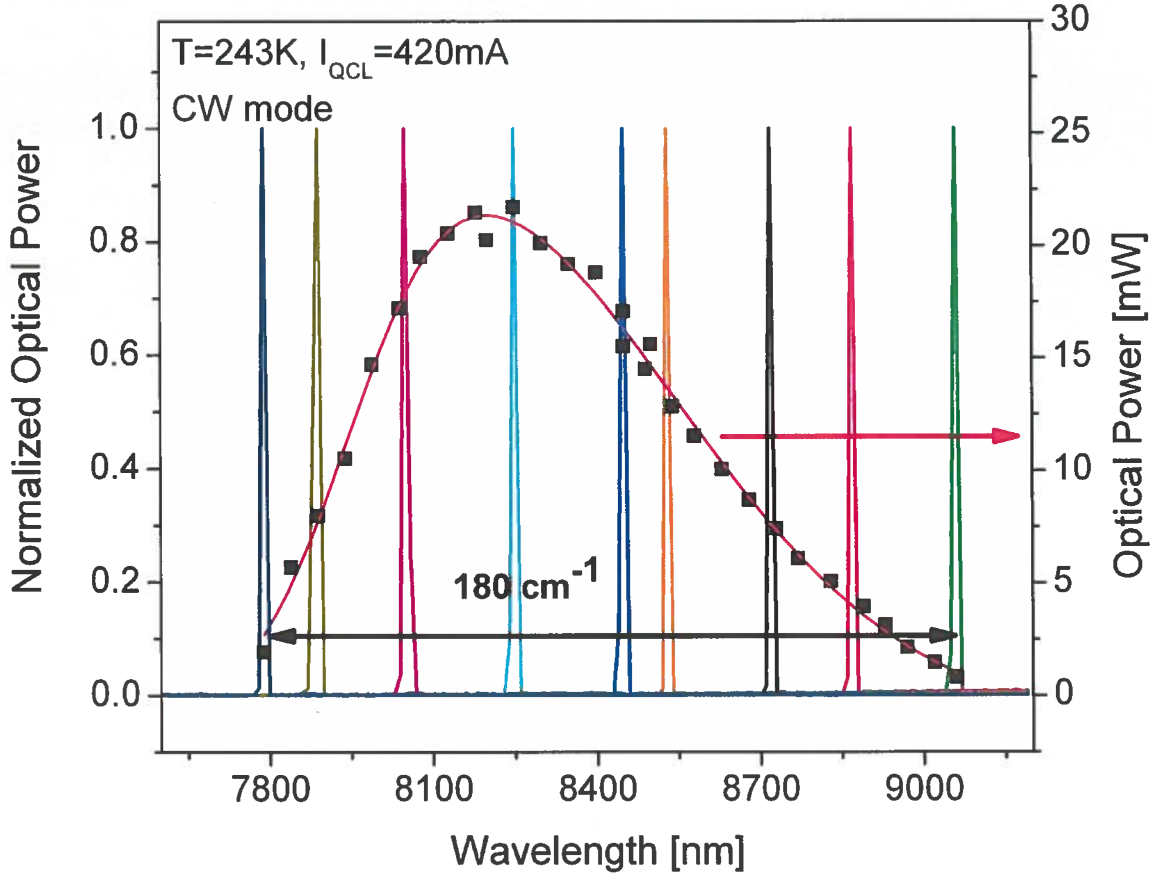
Performance of 8.4 μm cw EC-QCL Spectroscopic Source



Tunability **182 cm^{-1}** @8.4 μm;(1100 to 1280 cm^{-1}); λ_c=15%

AR coating:
$R_{AR} \approx$ **2 × 10^{-4}**

$P_{EC\text{-}opt}$: ~ **50 mW @ -30 C, ; also 103 mW @ 8.3 μm & -25 C; ~700mA; 2007 QCL technology**

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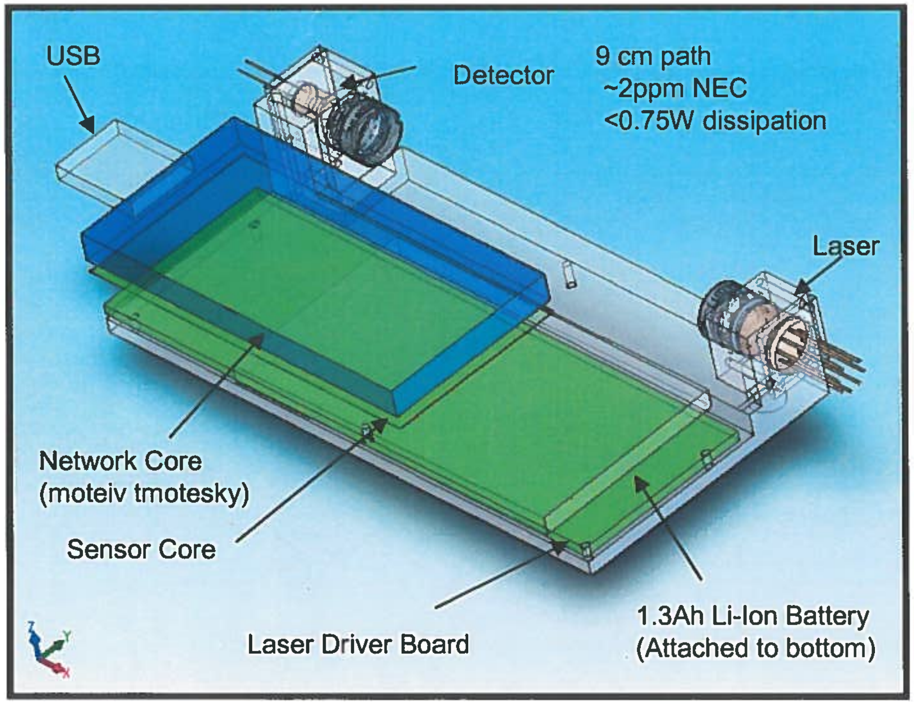
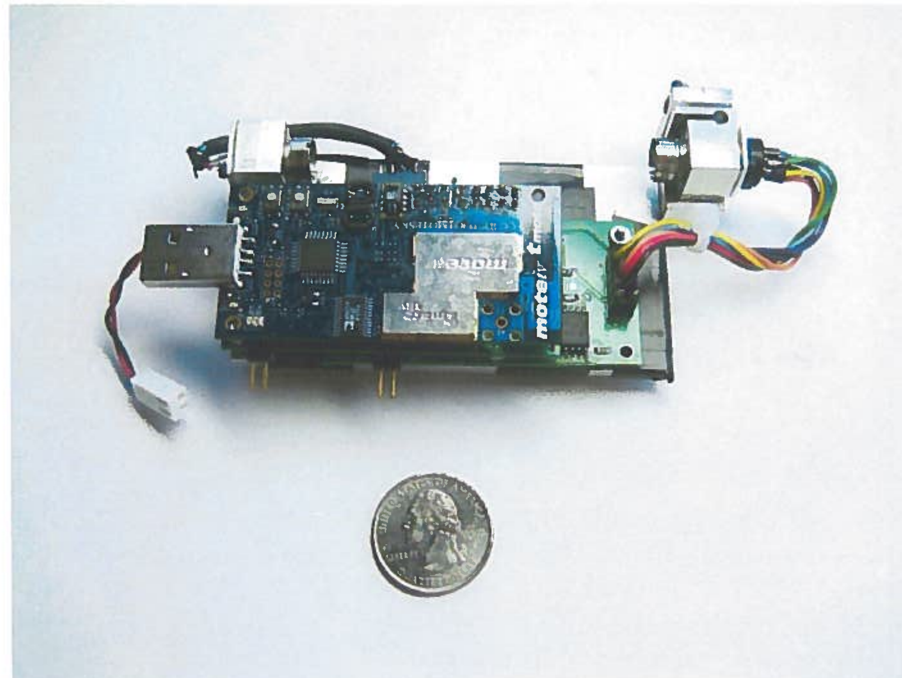
PHOTONS v4.0 - 2.7μm CO2 Direct Absorption Based Sensor





- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- 0.2W control system power consumption
- Detection sensitivity of CO_2 1 ppm with 1sec. lock-in time constant
- Over 100x improvement in sensitivity is possible @ 4.2μm

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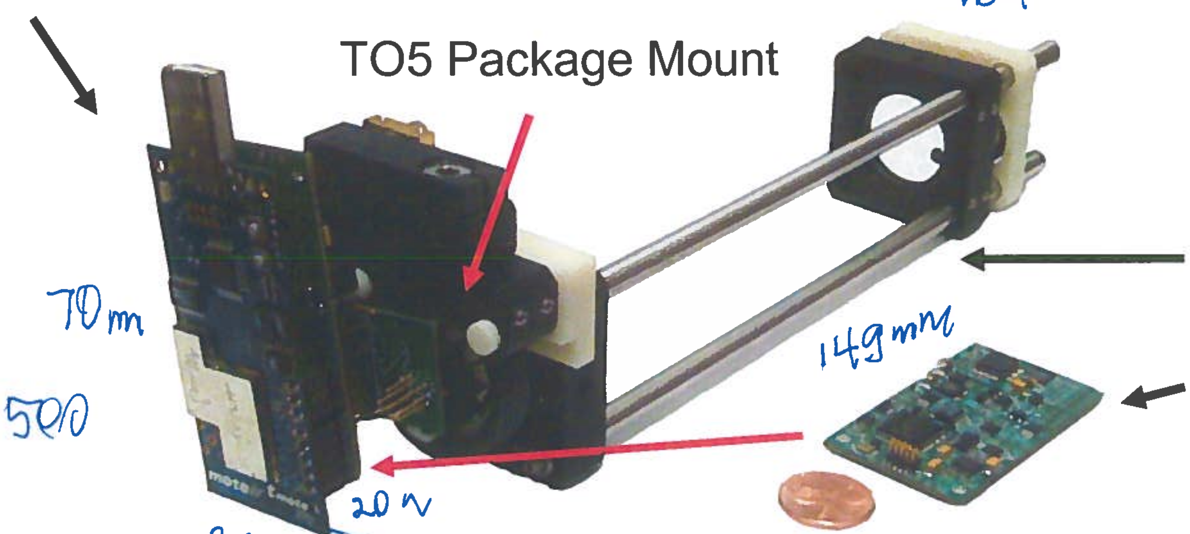
Custom Multipass Cell based TDLAS Platform

- Designed for TO5 Packaged Lasers with Integrated TEC
- Wavelength modulation capability (scan, 1f, or 2f)
- Quadrature lock-in amplifier
- Low noise current driver
- TEC driver, 0.001 °C stability
- Battery Powered



ULM ~ 0.75mW/ $400

TDLAS with a 763nm VCSEL measuring O_2