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Recent Advances and Applications of Semiconductor Laser based Gas Sensor Technology

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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, 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 Industries
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support
- **Applications in Medicine and Life Sciences**
- **Technologies for Law Enforcement and National Security**
- **Fundamental Science and Photochemistry**

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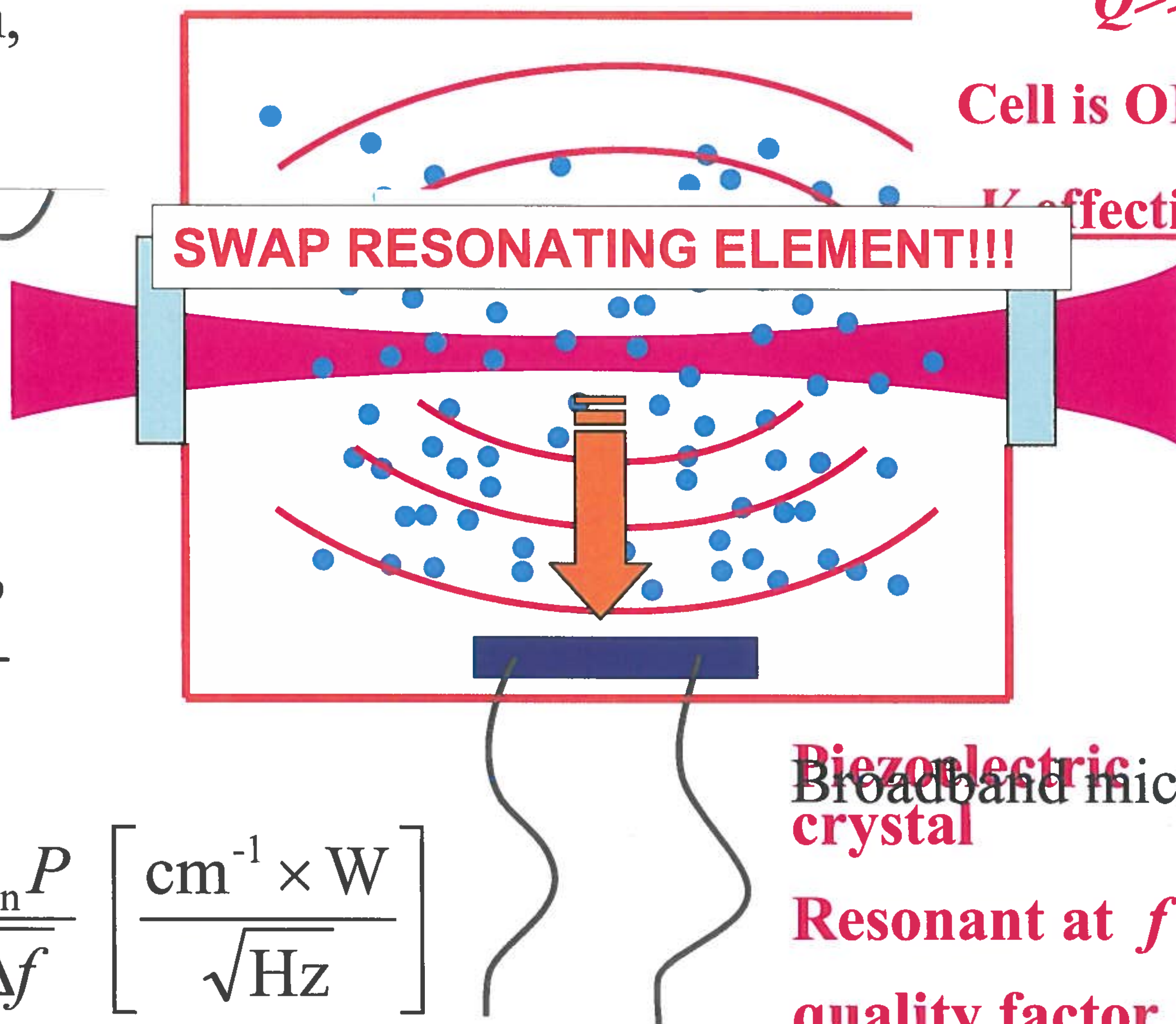
From conventional PAS to QEPAS

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

Piezoelectric crystal

Broadband microphone

Resonant at f

quality factor Q

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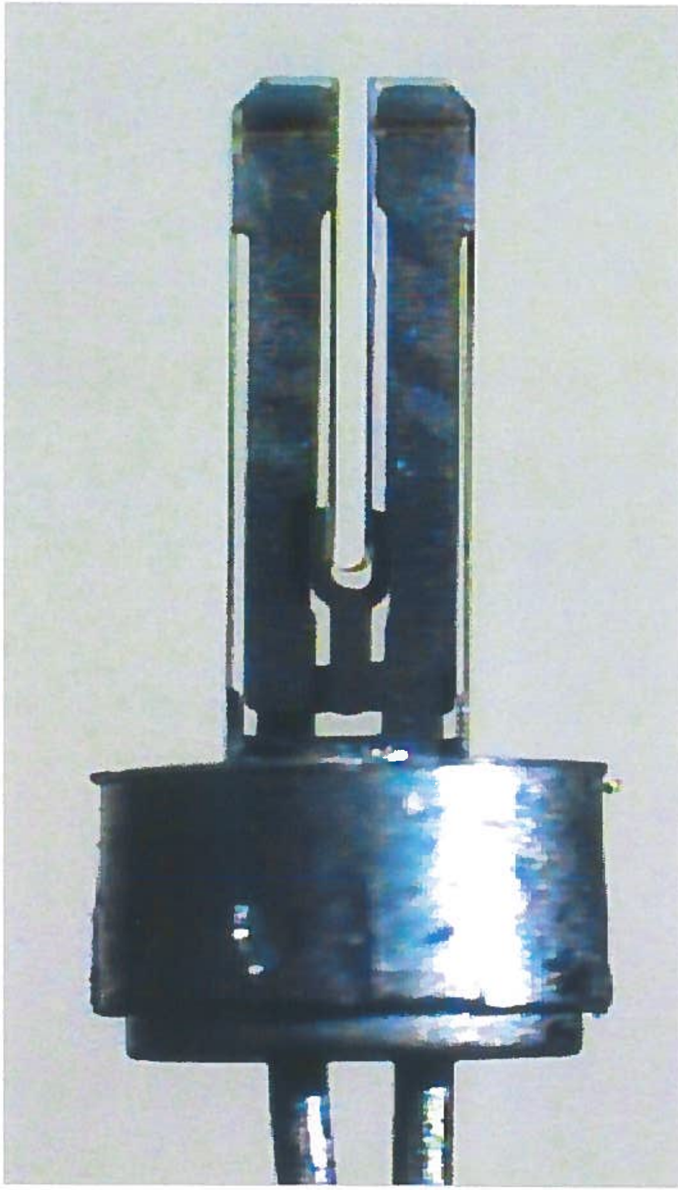
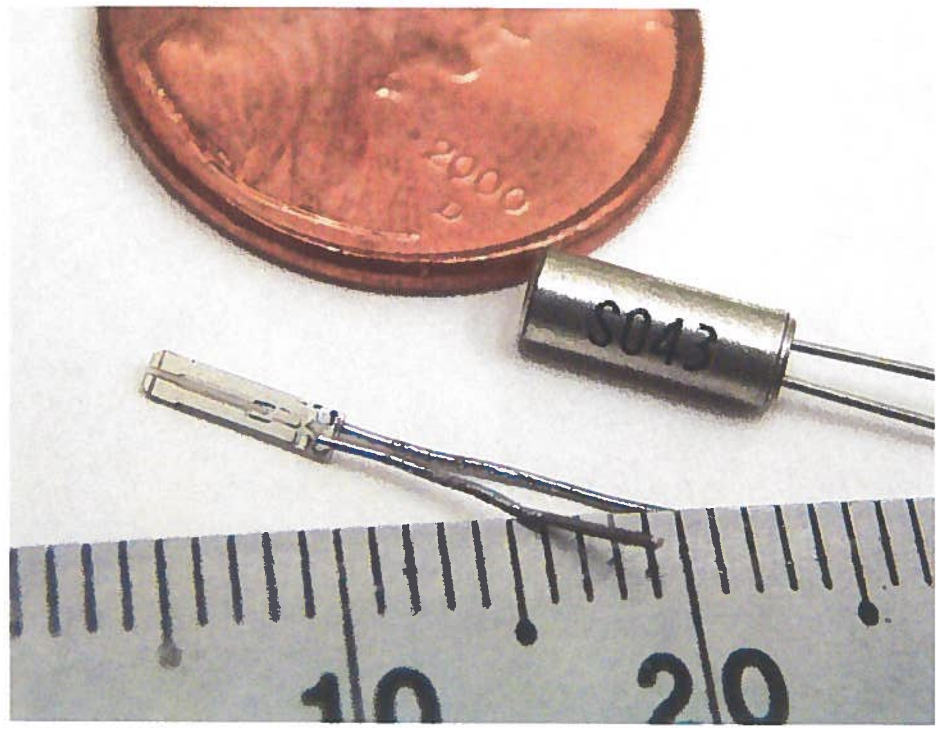
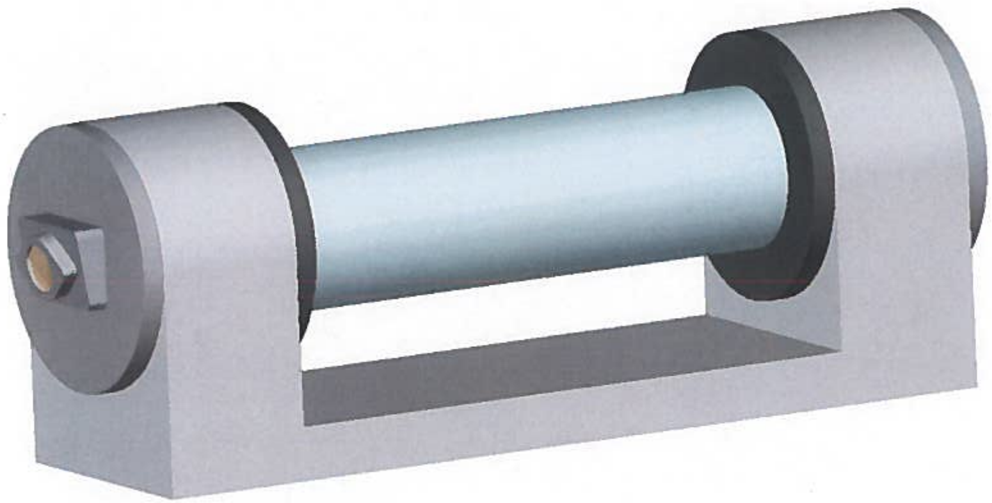
Quartz tuning fork (TF) as a resonant microphone



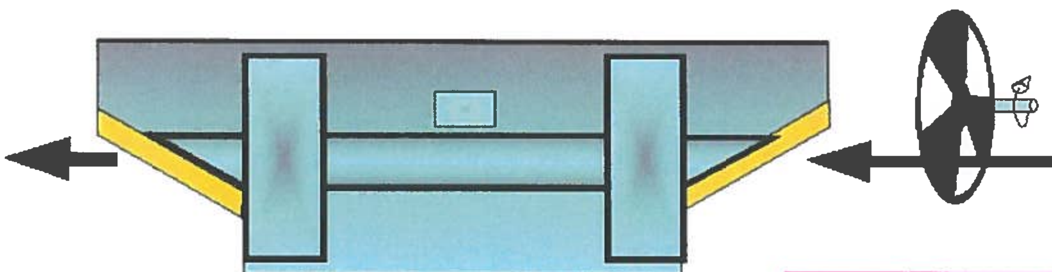
- Resonant frequency f=32.8 kHz
- Intrinsically high Q factor: Q_{vacuum} ~ 125 000, Q_{air}~10 000 at ambient conditions;
- Piezoelectric: requires no transducer
- Miniature size
- Mass produced for clocks – low cost



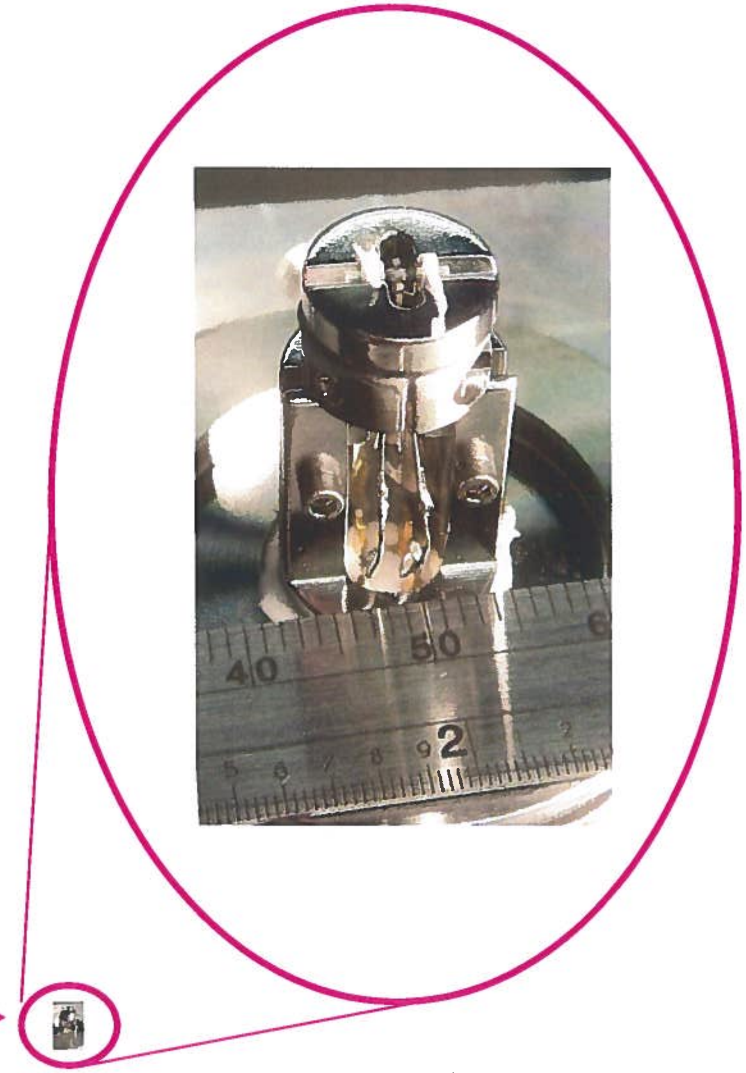
Comparative Size of Absorbance Detection Modules (ADM)



Optical multipass cell (100 m):
l~70 cm, *V*~3000 cm^3

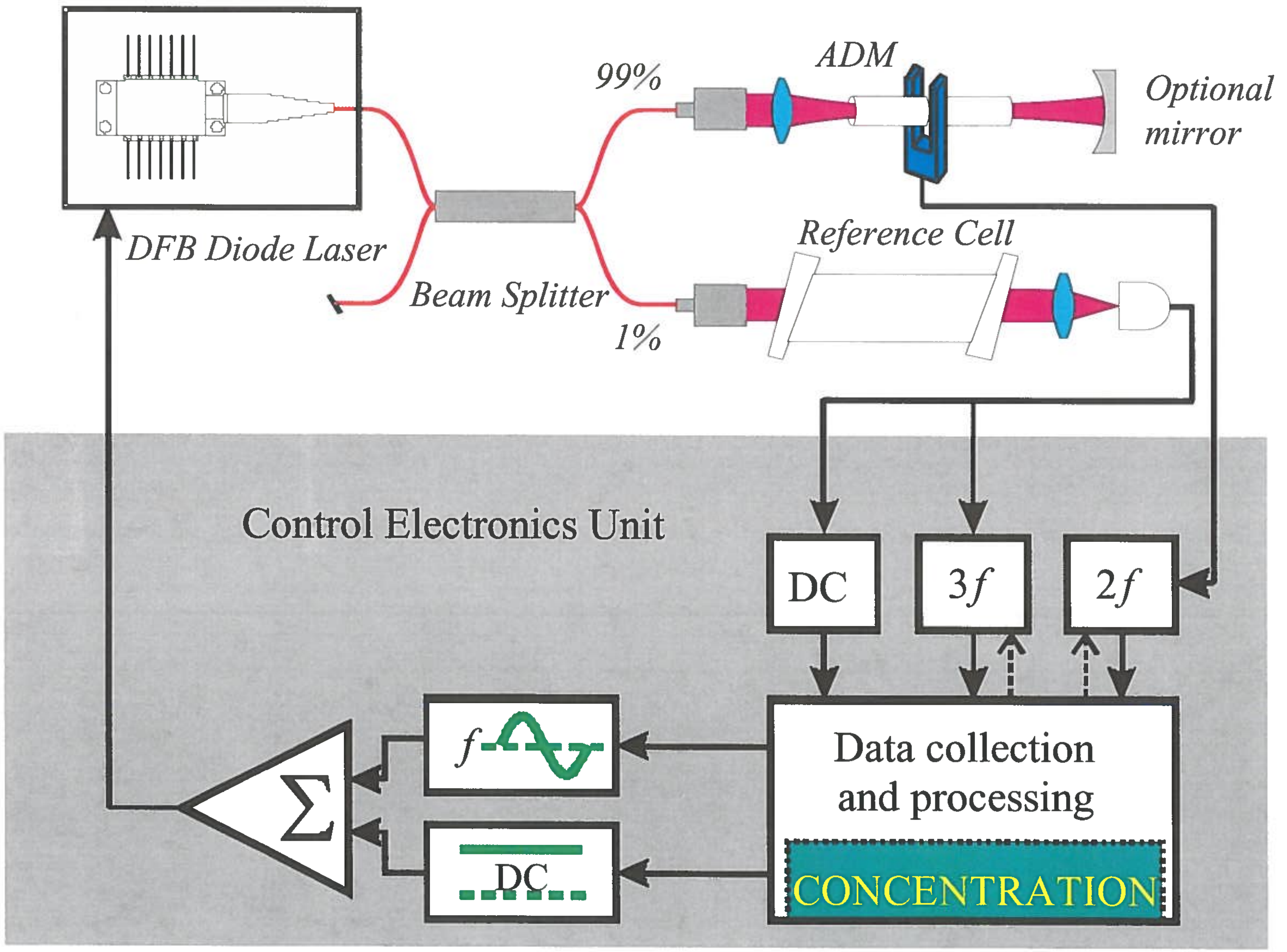


Resonant photoacoustic cell (1000 Hz):
l~60 cm, *V*~50 cm^3

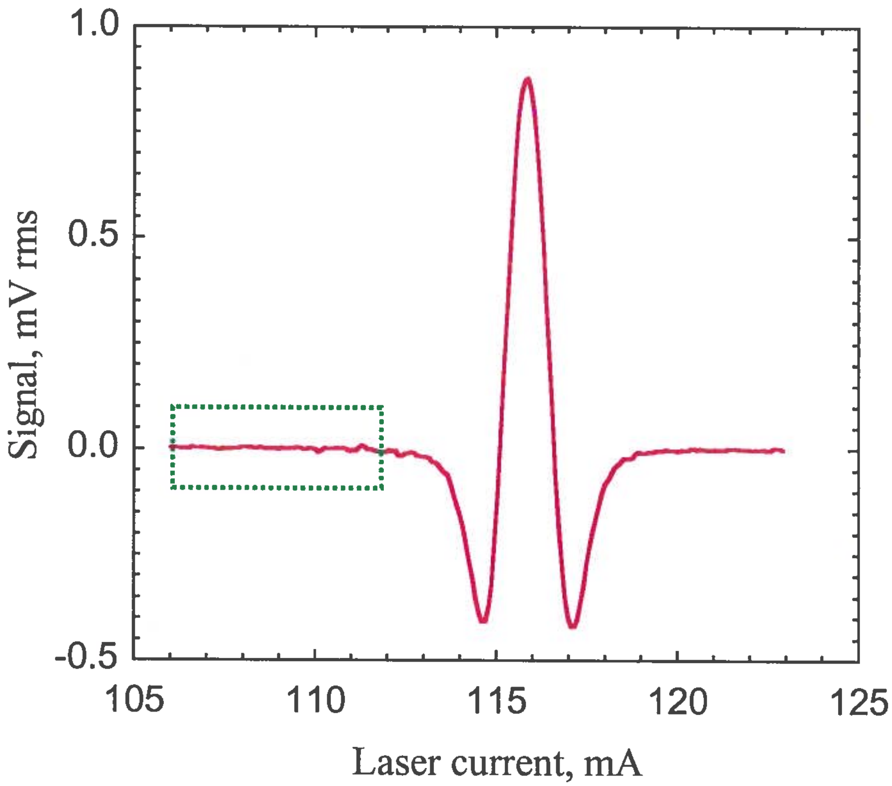


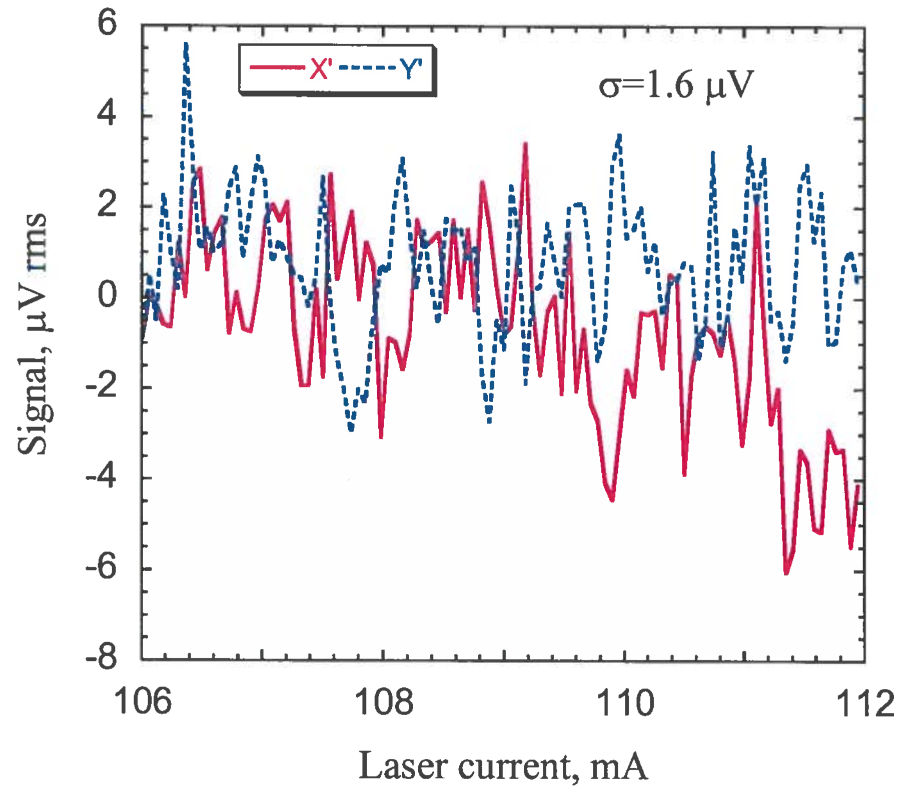
QEPAS spectrophone:
l~1 cm, *V*~0.05 cm^3

QEPAS based Gas Sensor Architecture



QEPAS signal: 7306.75 cm^{-1} H_2O line, 48 ppmv



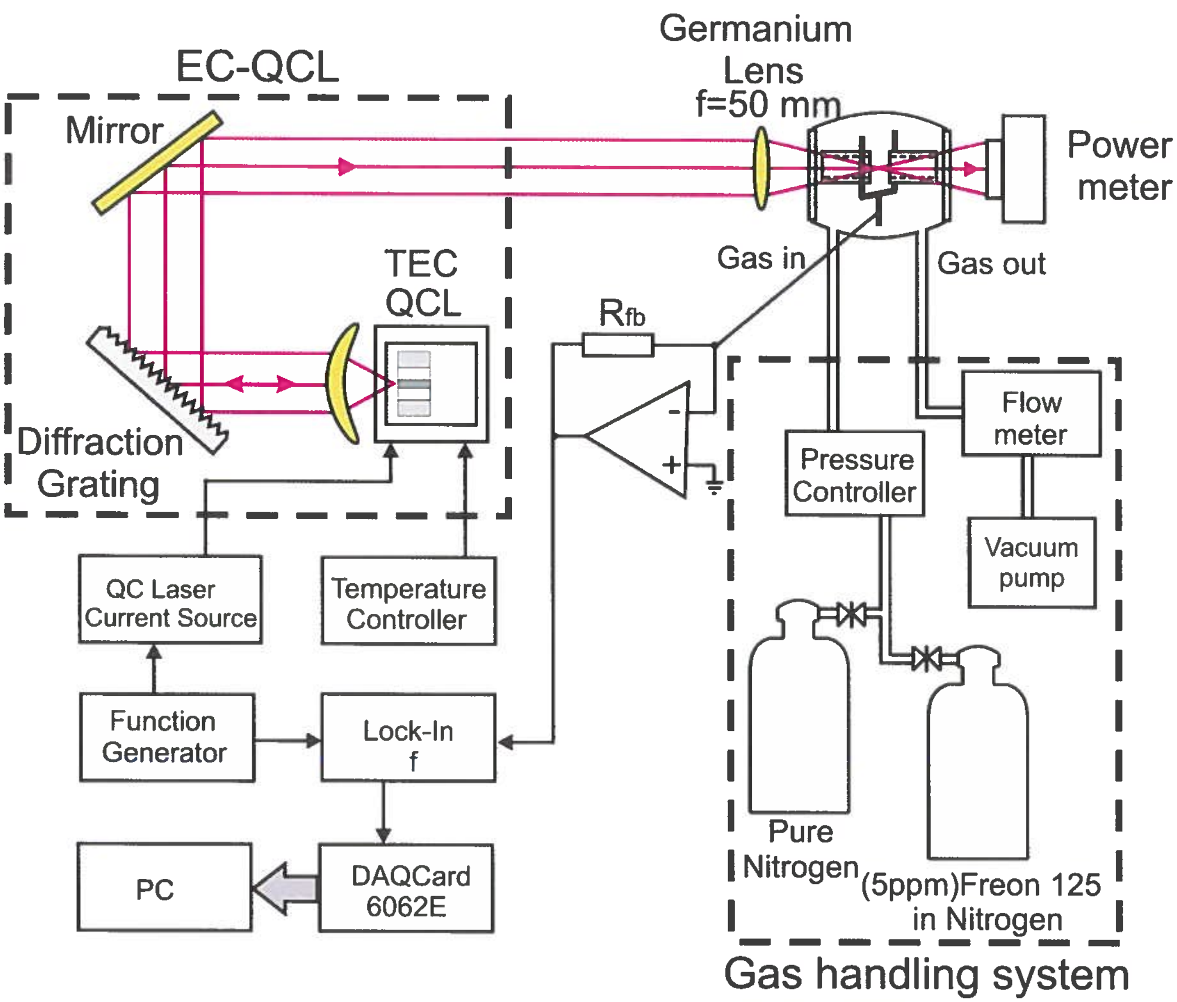


Laser power in the cell: 9.5 mW   Time constant: 1s, SNR=550

Peak absorbance: 4.8×10^{-5} cm^{-1} (HITRAN)

⇒ **NNEA=1.9×10^{-9} cm^{-1}W/(Hz)$^{1/2}$; NEC=90 ppbv**

QCL based Quartz-Enhanced Photoacoustic Gas Sensor



QEPAS characteristics:

- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume (< 1 mm^3)
- Sensitivity is limited by the fundamental thermal TF noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

R. Lewicki, G. Wysocki, A.A. Kosterev, F. K. Tittel „QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at 8.5 μm", Optics Express 15, 7357-7366, 2007

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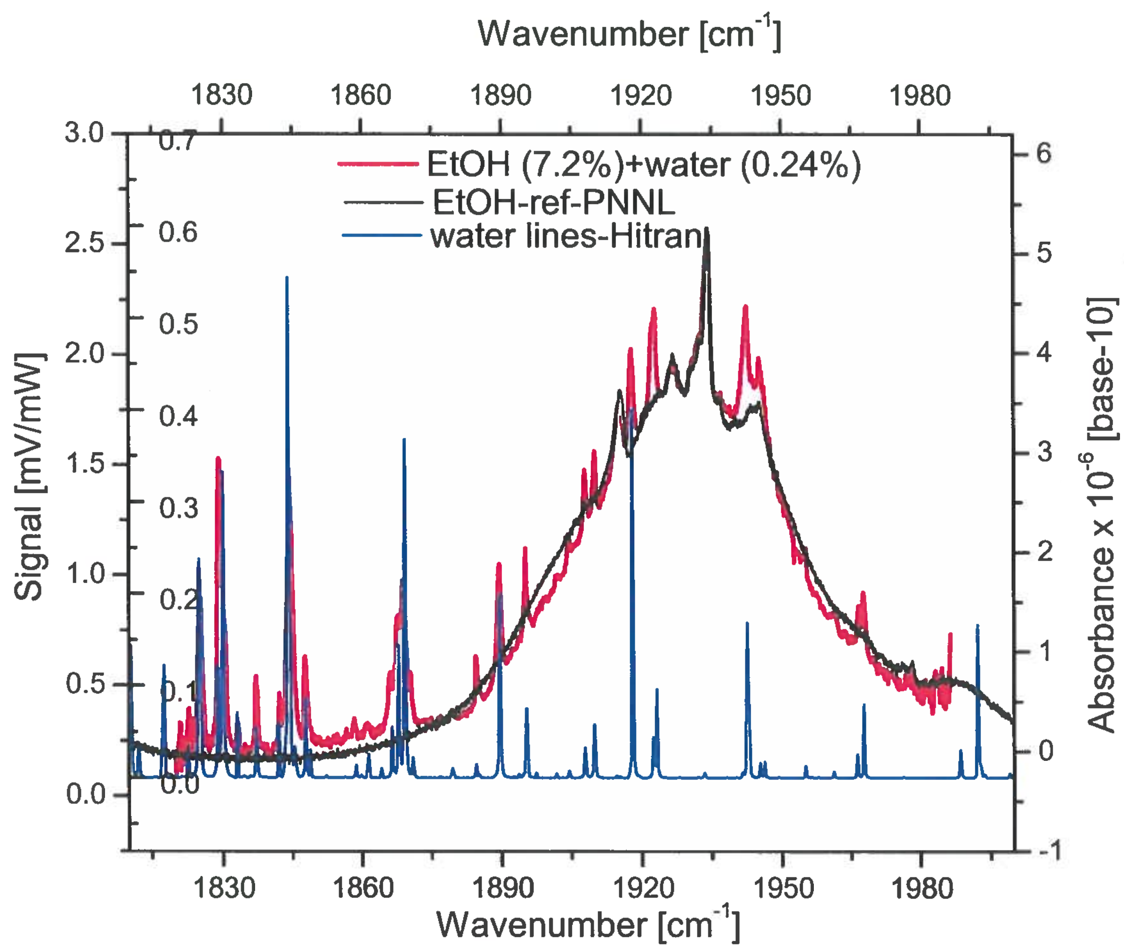
QEPAS Ethanol Spectrum between 1825 & 1980 cm^{-1}



Reference spectrum from the PNNL spectral database (red line). Sharp features on the ethanol spectrum correspond to the atmospheric water absorption lines (blue line depicts water absorption spectrum simulated using HITRAN database)

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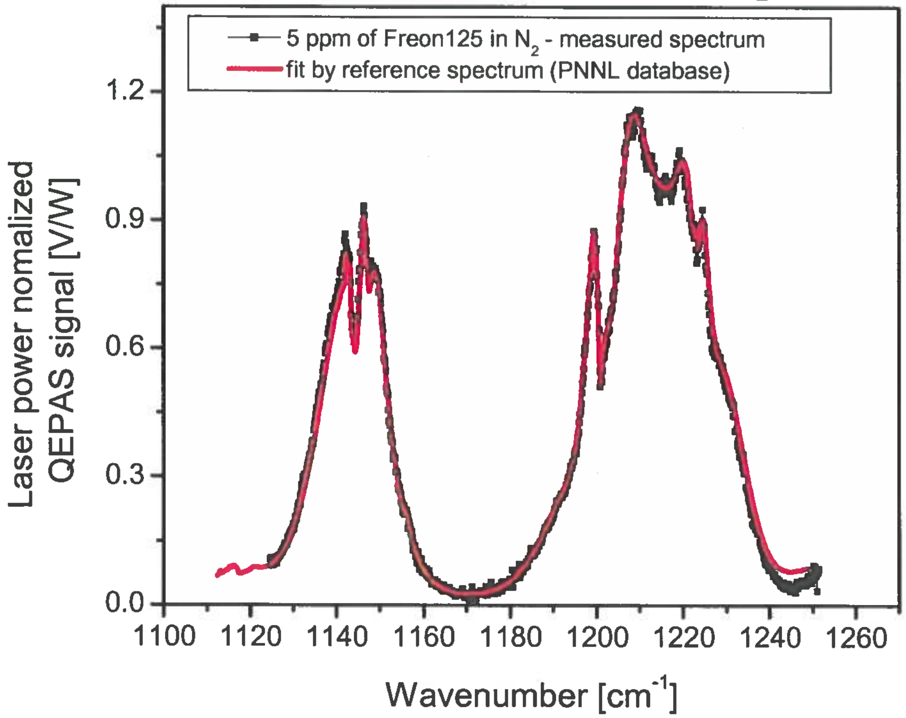
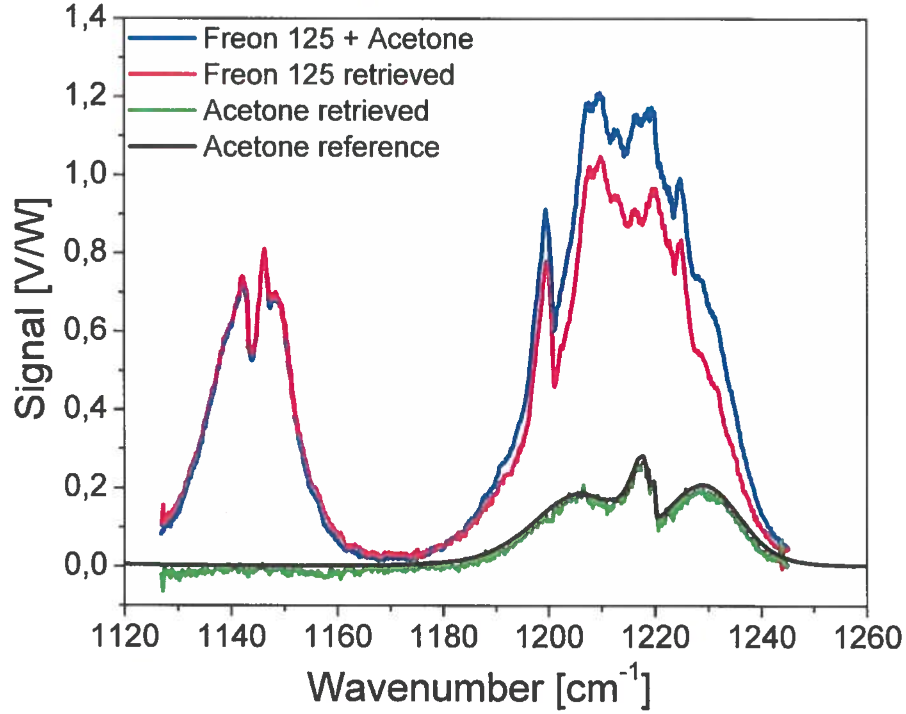
Spectroscopy of Freon 125 (C_2HF_5) and CH_3COCH_3 with Widely Tunable 8.4 μm CW EC-QCL

QEPAS concentration measurement of Freon 125 (5ppm mixture in N_2)



QEPAS concentration measurement of a Freon 125 and acetone mixture



- Minimum detection limit (1σ) of **~4.5 ppb** was obtained for Freon 125 with an average laser power of 6.6 mW

- Wide tunability enables excellent molecular selectivity for broad band absorbers

R. Lewicki et al Optics Express 15, 7357, 2007

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QEPAS Performance for 11 Trace Gas Species (Sept '07)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{½}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10^{-9}	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	$< 4.3\times10^{-9}$	50	0.16
C_2H_2 (N_2)**	6529.17	75	$\sim 2.5\times10^{-9}$	~ 40	0.06
NH_3 (N_2)*	6528.76	60	5.4×10^{-9}	38	0.50
CH_4 (N_2)*	6057.09	950	2.9×10^{-8}	13.7	2.1
CO_2	6361.25	90	1.6×10^{-8}	26	410
CO_2 (N_2+1.5% H2O) *	4991.26	50	1.4×10^{-8}	4.4	18
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10^{-9}	7.2	0.12
CO (N_2)	2196.66	50	5.3×10^{-7}	13	0.5
CO (propylene)	2196.66	50	7.4×10^{-8}	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007
C_2H_5OH **	1934.2	770	2.2×10^{-7}	10	90
C_2HF_5 (Freon 125)***	1208.62	770	2.6×10^{-9}	6.6	0.003

* - Improved microresonator
** - Improved microresonator and double optical pass through ADM
*** - With amplitude modulation and metal microresonator

NNEA – normalized noise equivalent absorption coefficient.
NEC – noise equivalent concentration for available laser power and τ=1s time constant.

For comparison: conventional PAS 2.2×10^{-9} $cm^{-1}W/\sqrt{Hz}$ (1,800 Hz) for NH_3*

* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003)

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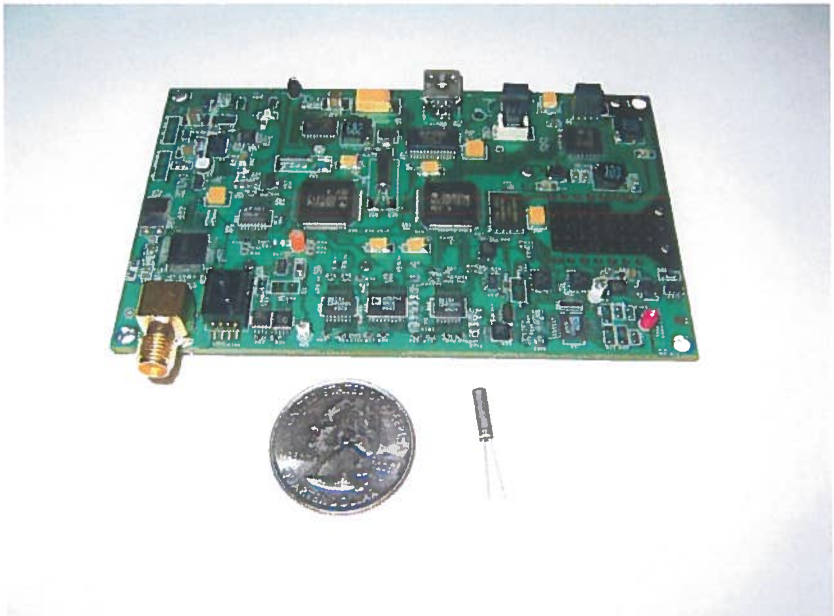
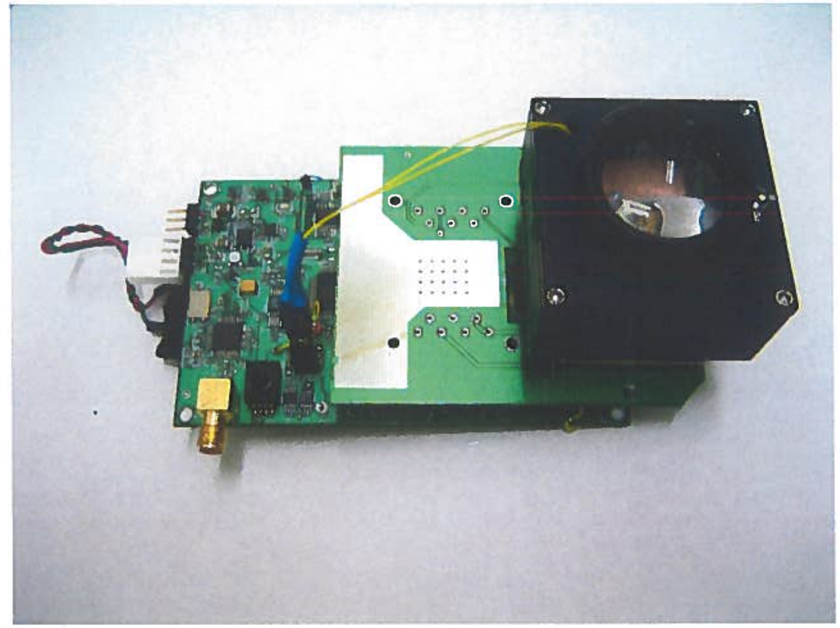
Miniature QEPAS CO_2 sensor (λ=2μm) v2.0 boards

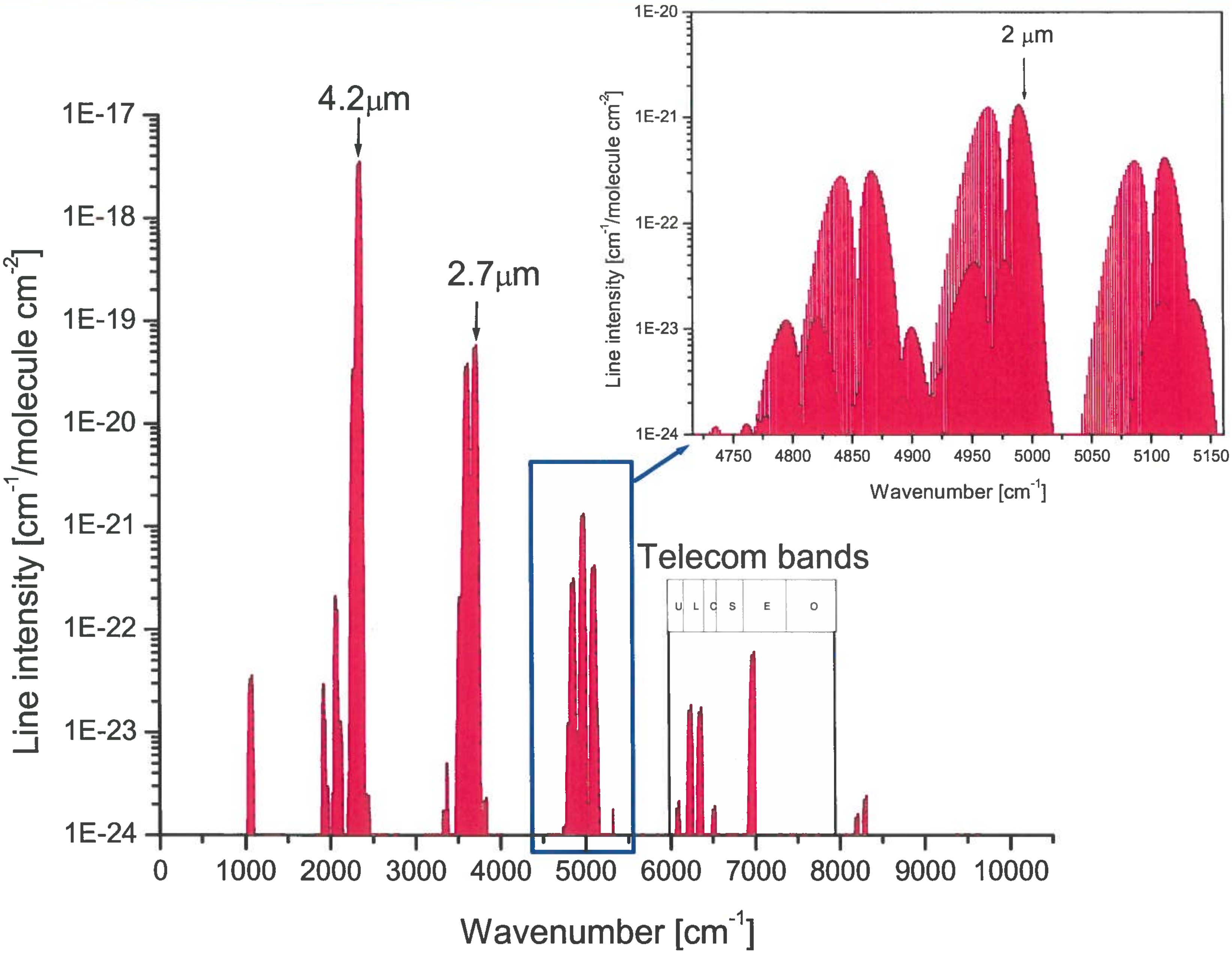




- 0.2W control system power consumption
- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- Projected sensitivity* to CO_2 110 ppm with 1sec. lock-in TC
- Over 10^3 improvement in sensitivity @4.2μm

*G. Wysocki, A. A. Kosterev, and F. K. Tittel "Influence of Molecular Relaxation Dynamics on Quartz-Enhanced Photoacoustic Detection of CO_2 at λ = 2 μm", Applied Physics B 85, 301-306 (2006)

Simulated CO_2 Absorption Spectrum



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Summary

- Development of widely tunable, continuous wave and thermoelectrically cooled EC-QCLs is of importance for laser spectroscopy applications
- Quantum cascade lasers are excellent spectroscopic sources on account of their wavelength tunability, high output power and robustness
- Wide wavelength tuning capability along with a true mode-hop free wavelength tuning was demonstrated using a novel tracking system of coupled cavity modes
- The feasibility of performing high resolution spectroscopic measurements of small and large molecular trace gas species with cw TEC EC-QCL based sensor systems was demonstrated
- Present EC-QCL based sensor designs demonstrate excellent suitability for spectroscopic trace gas concentration measurements using wavelength and amplitude modulation techniques that offer high sensitivity and precision even with relatively slow scanning speeds.
- There is still room for significant improvements of our EC-QCL sensor design

TF based spectrophone