Mid-Infrared Semiconductor Laser Based Trace Gas Sensor Technologies: Recent Advances and Applications

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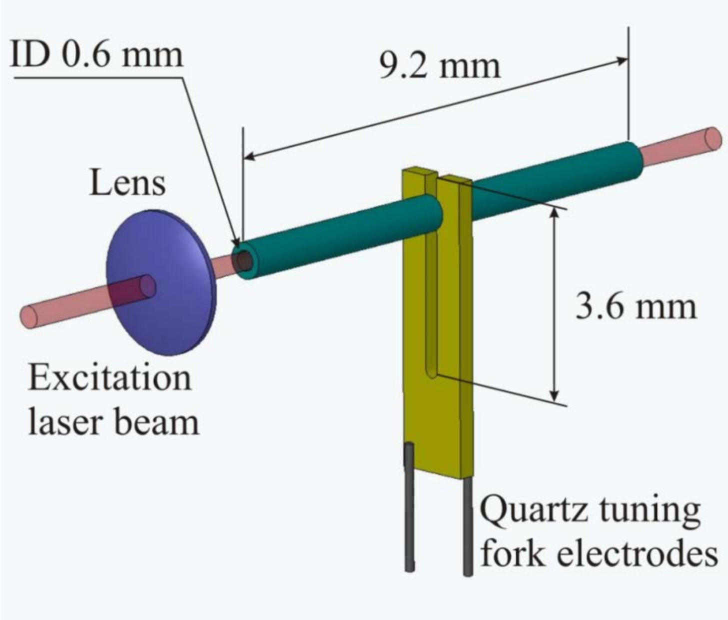
Introduction

Recent advances in the development of sensors based on infrared semiconductor lasers has led to a wide range of trace gas sensing applications, such as urban, industrial and rural emission measurements, environmental monitoring, chemical analysis and industrial process control as well as applications in biomedical, medical diagnostics and the life sciences [see: **www.ece.rice.edu/lasersci**].

The development of compact trace gas sensors, in particular based on quantum cascade and interband cascade lasers permit the targeting of strong fundamental rotational-vibrational transitions in the mid-infrared. Two laser based sensor technologies, Quartz-Enhanced Photo-Acoustic Spectroscopy (QEPAS) and TDLAS based on an a innovative, compact multi-pass absorption cell will be described. Four examples of recent mid-infrared sensor architectures, which include **NO, SO_2, NH_3 and C_2H_6** have under gone detailed performance evaluation.

The future direction of our research includes improved and novel sensor architectures as well as detection of additional atmospheric trace gases, such as **CH_4, N_2O, HONO and H_2O_2**

Quartz Tuning Fork as a Resonant Microphone for QEPAS



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 ($\sim10^6$) – linear from thermal noise to breakdown deformation
  - 300K noise: $x\sim10^{-11}$ cm
  - Breakdown: $x\sim10^{-2}$ cm
- Wide temperature range: from 1.6K to ~700K

Acoustic Micro-resonator (mR) tubes

- Optimum inner diameter:0.6 mm; mR-QTF gap is 25-50 µm
- Optimum mR tubes must be ~ 4.4 mm long ($\sim\lambda/4<l<\lambda/2$ for sound at 32.8 kHz)
- SNR of QTF with mR tubes: ×30 (depending on gas composition and pressure)

Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm^3 to ~$2cm^2$)
- Extremely low dissipative losses
- Optical detector is not required
- Wide dynamic range
- Frequency and spatial selectivity of acoustic signals
- Rugged transducer – quartz monocrystal; can operate in a wide range of pressures and temperatures
- Immune to environmental acoustic noise, sensitivity is limited by the fundamental thermal TF noise: $k_B T$ energy in the TF symmetric mode
- Absence of low-frequency noise: SNR scales as $\sqrt{t}$, up to t=3 hours as experimentally verified

QEPAS: some challenges

- Cost of spectrophone assembly
- Sensitivity scales with laser power
- Effect of H_2O
- Responsivity depends on the speed of sound and molecular energy transfer processes
- Cross sensitivity issues

Mid-IR QEPAS Performance for 8 Trace Gas Species (Sept 2012)

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	4.6×10^{-9}	50	0.16
C_2H_2 (N_2)*	6523.88	720	4.1×10^{-9}	57	0.03
NH_3 (N_2)*	6528.76	575	3.1×10^{-9}	60	0.06
C_2H_4 (N_2)*	6177.07	715	5.4×10^{-9}	15	1.7
CH_4 (N_2+1.2% H_2O)*	6057.09	760	3.7×10^{-9}	16	0.24
CO_2 (breath ~50% RH)	6361.25	150	8.2×10^{-9}	45	40
H_2S (N_2)*	6357.63	780	5.6×10^{-9}	45	5
HCl (N_2 dry)	5739.26	760	5.2×10^{-8}	15	0.7
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 +2.2% H_2O)*	2176.28	100	1.4×10^{-7}	71	0.002
N_2O (air+5%SF_6)	2195.63	50	1.5×10^{-8}	19	0.007
NO (N_2+H_2O)	1900.07	250	7.5×10^{-9}	100	0.003
C_2H_5OH (N_2)**	1934.2	770	2.2×10^{-7}	10	90
SO_2 (N_2 +2.4% H_2O)*	1380.94	100	2.0×10^{-8}	40	0.1
C_2HF_5 (N_2)***	1208.62	770	7.8×10^{-9}	6.6	0.009
NH_3 (N_2)*	1046.39	110	1.6×10^{-8}	20	0.006

* - 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, 18 dB/oct filter slope.

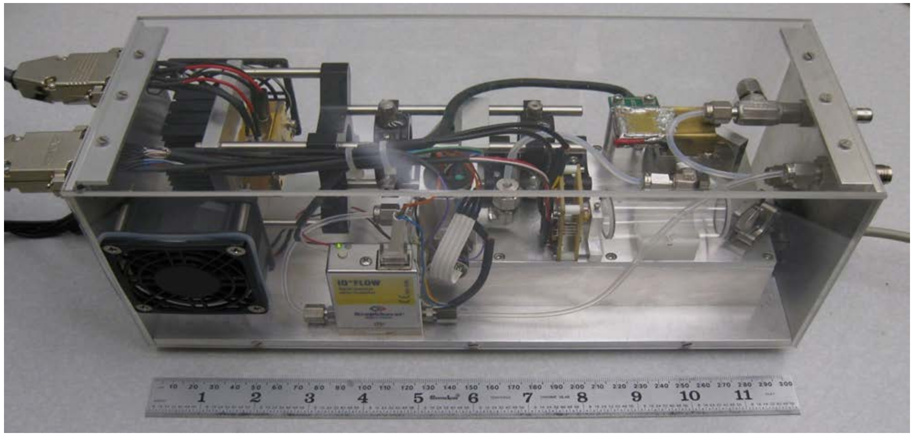
For comparison: conventional PAS 2.2 (2.6)×10^{-9} $cm^{-1}W/\sqrt{Hz}$ (1,800; 10,300 Hz) for NH_3*, (**)

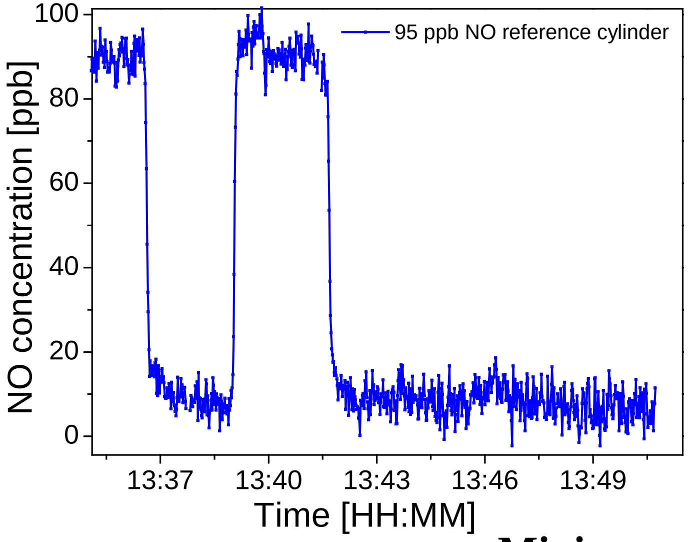
* M. E. Webber et al, Appl. Opt. 42, 2119-2126 (2003); ** J. S. Pilgrim et al, SAE Intl. ICES 2007-01-3152

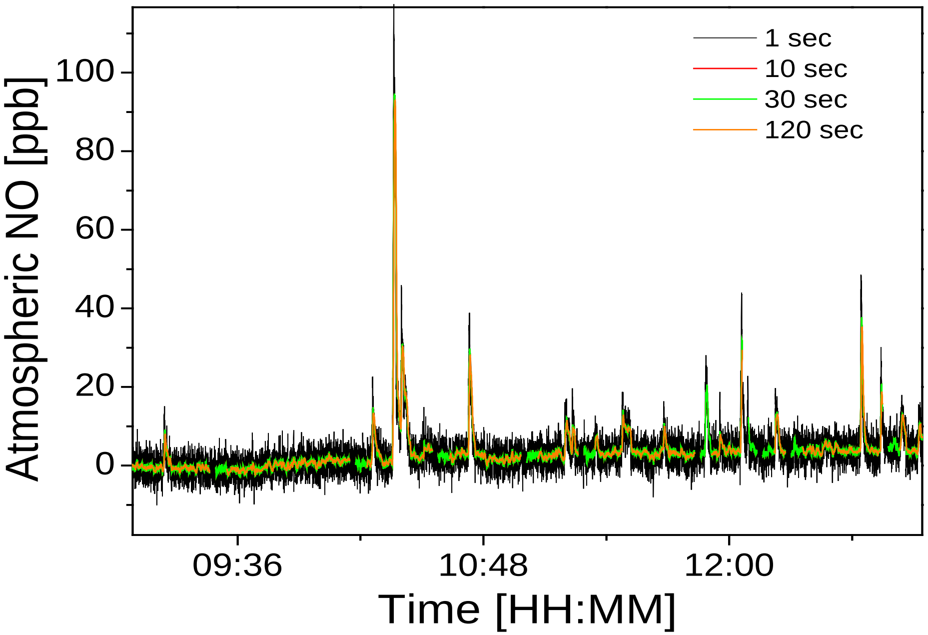
CW TEC DFB QCL based QEPAS NO Sensor Platform

Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NO_X monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control and analysis
- NO in medicine and biology
  - Important signaling molecule in physiological processes in humans and mammals (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, COPD, acute lung rejection







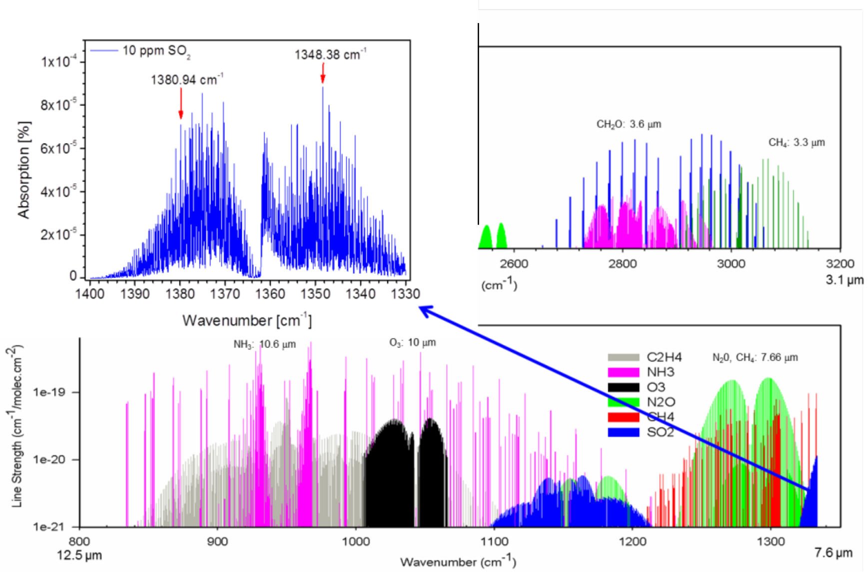
Minimum detectable NO concentration is:

~ 3 ppbv (1σ; 1 s time resolution)

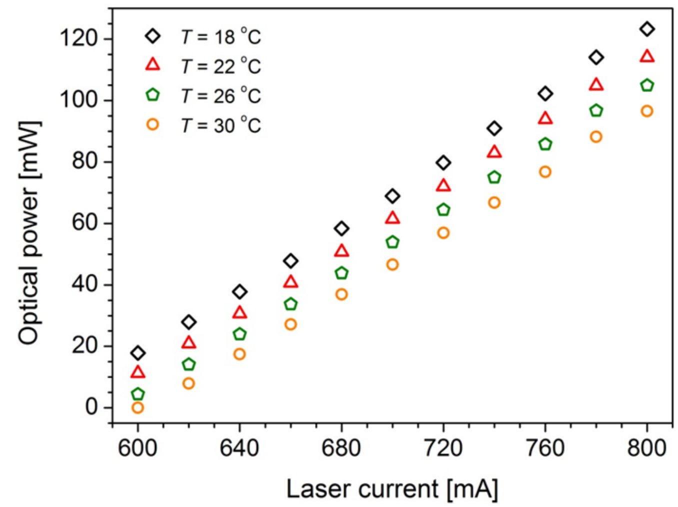
Mid-Infrared QEPAS Based SO_2 Detection

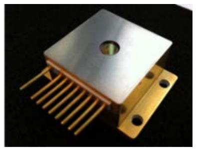
Motivation for Sulfur Dioxide Detection

- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere SO_2 converts to sulfuric acid ➔ primary contributors to acid rain
- SO_2 reacts to form sulfate aerosols
- Primary SO_2 exposure for 1 hour is 75 ppb
- SO_2 exposure affects lungs and causes breathing difficulties
- Currently, reported annual average SO_2 concentrations range from ~ 1 - 6 ppb

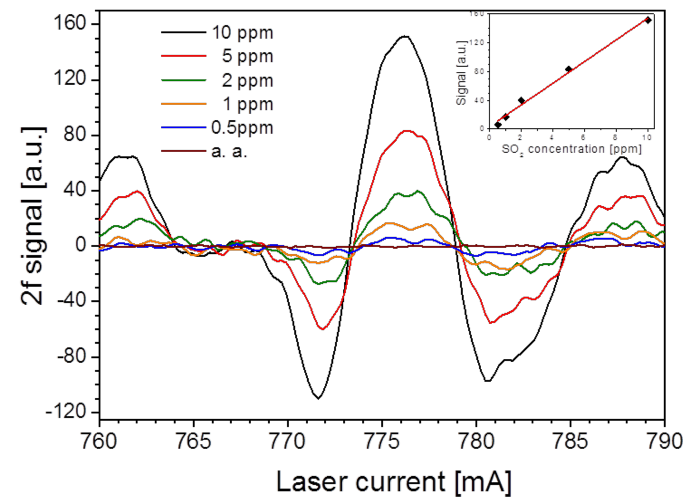


Molecular Absorption Spectra within two Mid-IR Atmospheric Windows





CW DFB-QCL optical power and current tuning at three different operating temperatures.

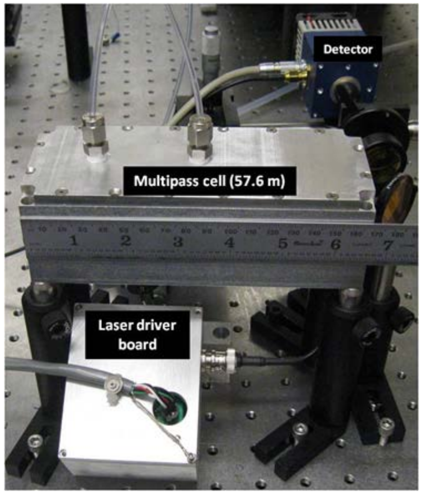


2f QEPAS signals for different SO_2 concentrations when laser was tuned across **1380.9 cm^{-1}** line.

Minimum detectable SO_2 concentration is:

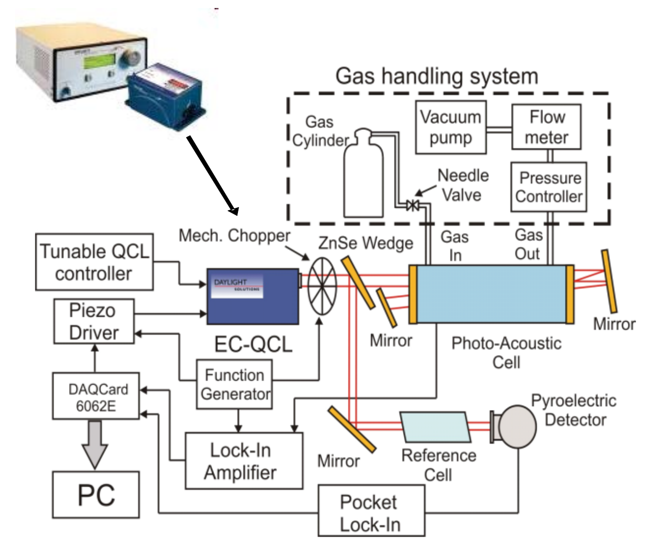
~ 100 ppbv (1σ; 1 s time resolution)

Mid-Infrared ppbV Detection of NH_3(10.36µm) and C_2H_6(3.36µm)

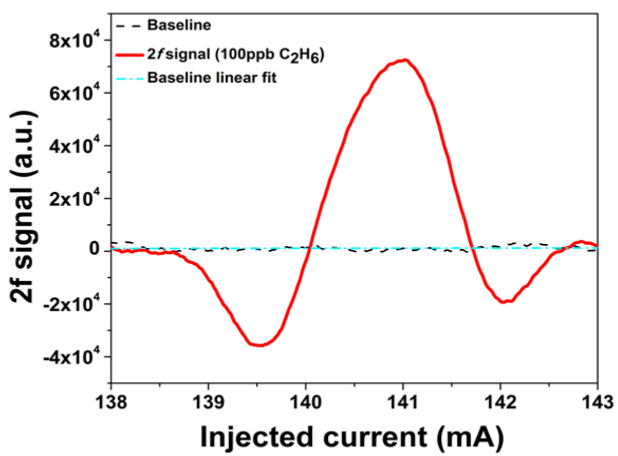


Innovative long path, small volume multipass gas cell:57.6m with 459 passes

MGC dimensions: **17** x **6.5** x **5.5** (cm)
Distance between the MGC mirrors: 12.5 cm

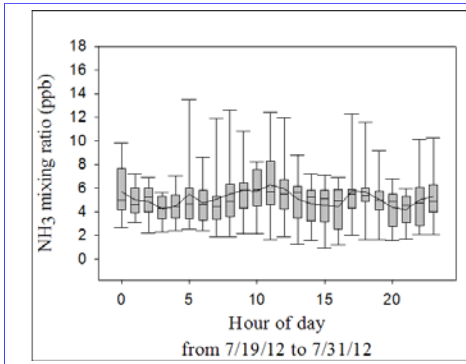


10. 36µm EC-QCL based AM-PAS Sensor Platform for Atmospheric NH_3 Detection

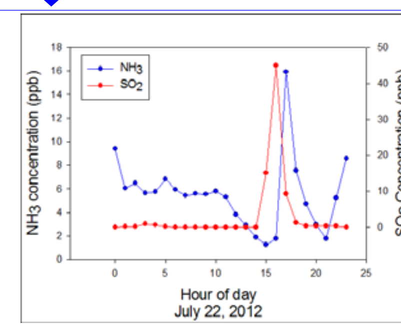


2f WMS signal for a C_2H_6 line at **2976.8 cm^{-1}** (3.36µm) at 200 Torr

Minimum detectable C_2H_6 concentration is:
~ 130 pptv (1σ; 1 s time resolution)

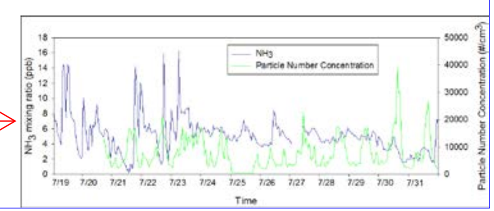


Diurnal profile of atmospheric NH_3 levels

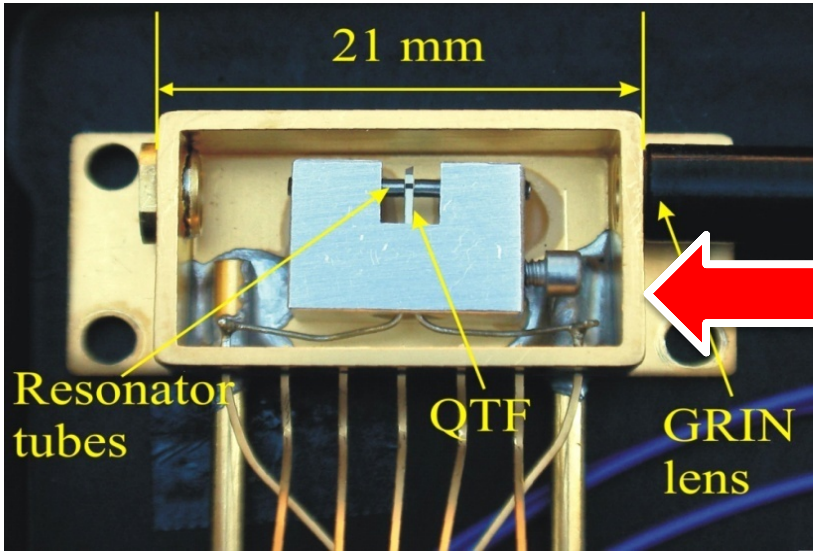


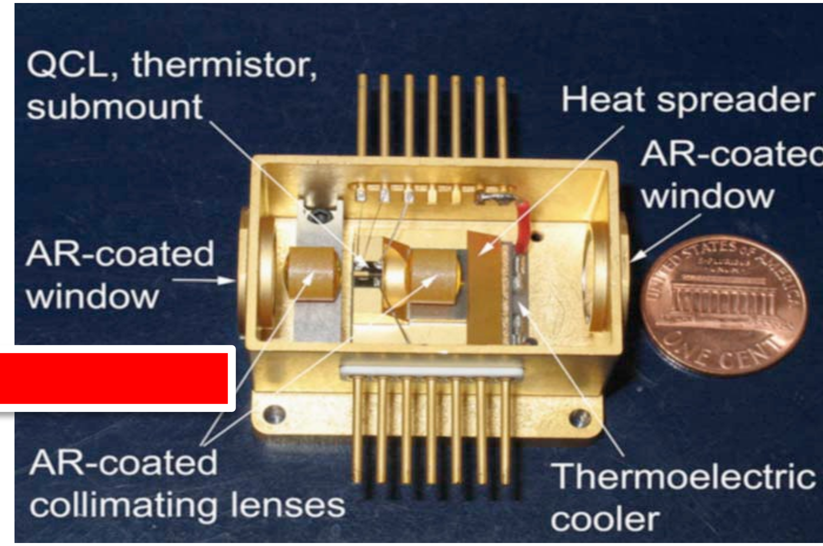
Correlation between NH_3 and SO_2

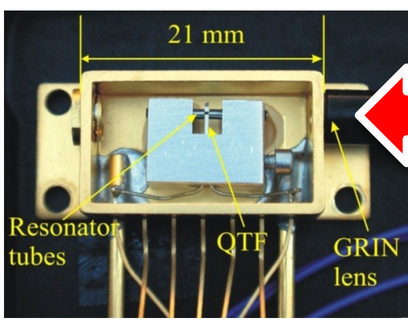
Comparison between NH_3 and particle number concentration time series 7/19/12-7/31/12



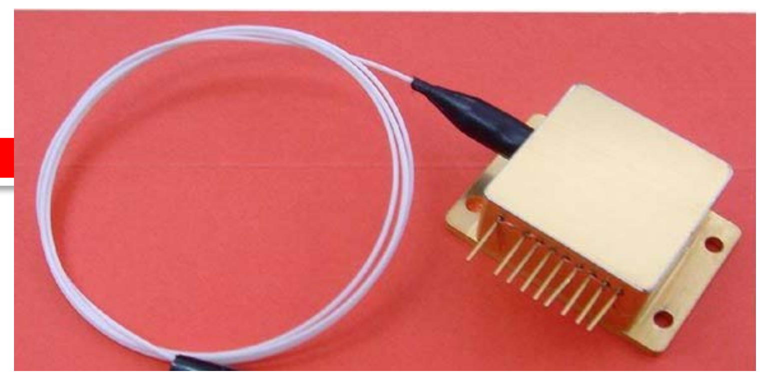
Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module (ADM)







2012 QEPAS ADM



HHL package fiber coupled DFB-QCL

A. Lyakh, et al “1.6 W high wall plug efficiency, continuous-wave room temperature quantum cascade laser emitting at 4.6 μm” Appl. Phys. Lett. **92**, 111110 (2008)

Summary and Outlook

- A 5.26 µm and 7.24 µm CW TEC HHL packaged DFB-QCL based QEPAS sensor for **NO** and **SO_2** detection was demonstrated.
- For interference free **NO** absorption line located at **1900.08 cm^{-1}** a 1σ minimum detection limit (MDL) of **3 ppbv** was achieved at a gas pressure of 240 Torr and sampling time of 1 sec.
- A 1σ MDL of **100 ppbv** was achieved at a gas pressure of 100 Torr and sampling time of 1 sec for a **SO_2** absorption line at **1380.94 cm^{-1}**.
- Addition of water vapor to NO and SO_2 trace gas mixture results in an improved QEPAS signal of > 100 and 3 times, respectively.
- An AM-PAS technique was employed to monitor NH_3 with a 65 mW, 10.34 µm CW TEC EC-QCL. MDL obtained for an absorption line at **965.35 cm^{-1}** was ~**0.7 ppbv** for a 300 sec averaging time.
- For an interference free C_2H_6 absorption line located at **2976.8 cm^{-1}** a MDL of **130 pptv** with a 1 second lock-in amplifier time constant was achieved using a novel multi-pass gas absorption cell .
- Next objective will be CH_4 and N_2O detection with a high power 7.23 µm CW TEC HHL packaged DFB-QCL based QEPAS sensor platform.
- Compact, robust sensitive and selective mid-IR based QEPAS sensor technology permits sensitive, selective, real-time environmental, biomedical and industrial emission measurements