Sensitive Detection of NO and SO_2 using a Quantum Cascade Laser based QEPAS sensor

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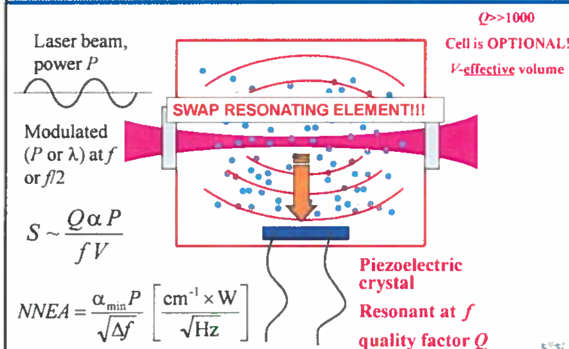
From Conventional PAS to QEPAS



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

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

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
- 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
- Photofragmentation of nitro-based explosives (TNT)

Quartz Tuning Fork as a Resonant Microphone

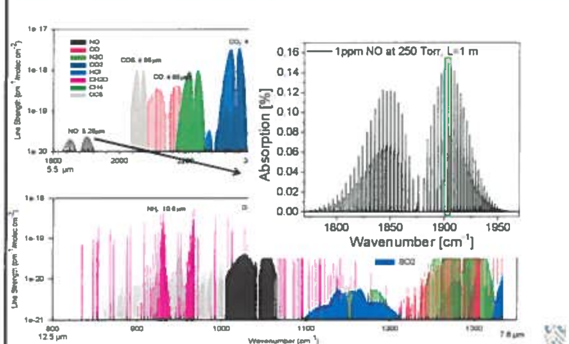
Unique properties

- 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 (~10^6) – 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

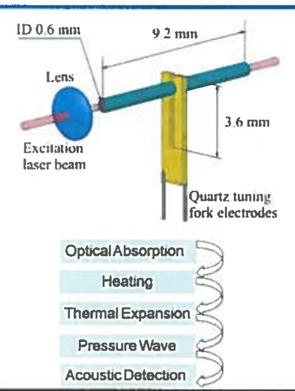
- Resonant frequency ~32.8 kHz
- Force constant ~26800 N/m
- Electromechanical coefficient ~7×10^{-6} C/m

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



Source: HITRAN 2000 database

QEPAS Technique: QTF and Micro-resonator



Micro-resonator (mR) tubes

- Must be close to QTF, but must not touch the QTF (25-50 μm gaps).
- Optimum inner diameter: 0.6 mm
- Optimum micro-resonator tubes must be ~ 4.4 mm long (~λ/4<l<λ/2 for sound at 32.8 kHz)
- **Maximum 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^3)
- 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_BT 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

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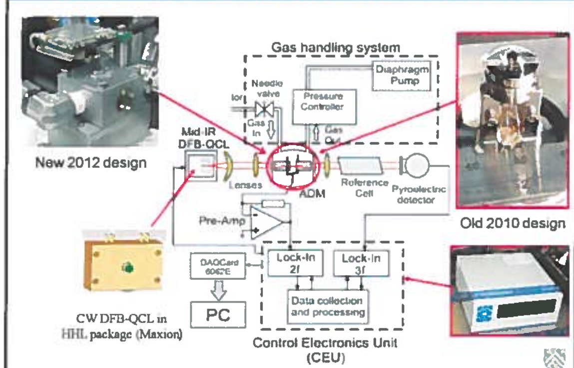
QCL based WMS QEPAS NO Gas Sensor



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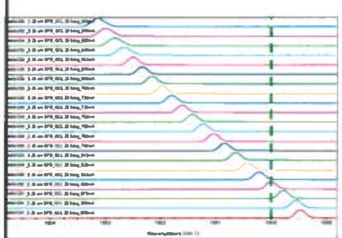
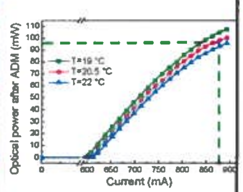
Performance of a 5.26 µm CW HHL TEC DFB-QCL



Single frequency QCL radiation recorded with FTIR for different laser current values at a QCL temperature of 20.5ºC



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

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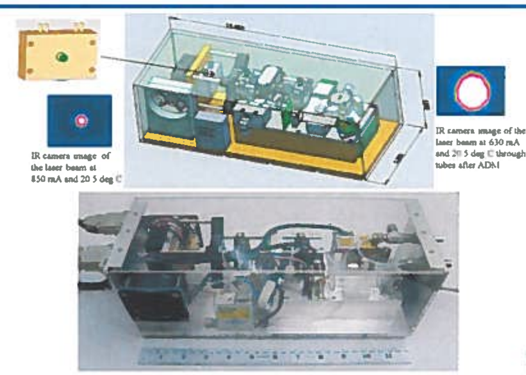
CW TEC DFB QCL based QEPAS Sensor Platform



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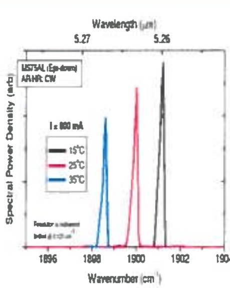
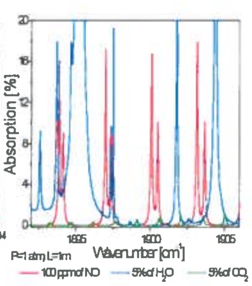
Emission spectra of a 1900cm^{-1} TEC CW DFB QCL and HITRAN Simulated spectra





Output power: 117 mW @ 25 C

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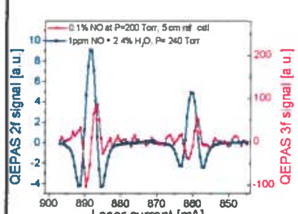
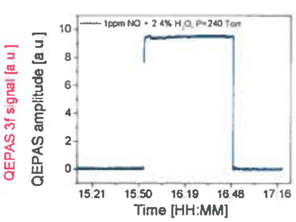
Performance of 2012 CW DFB-QCL based NO Sensor Platform



2f QEPAS signal (navy) and reference 3f signal (red) when laser was tuned across **1900.08 cm^{-1}** line



2f QEPAS signal amplitude for 1 ppm NO when laser was locked to the **1900.08 cm^{-1}** line

Minimum detectable NO concentration is:

~3 ppbv (1σ; 1 s time resolution)

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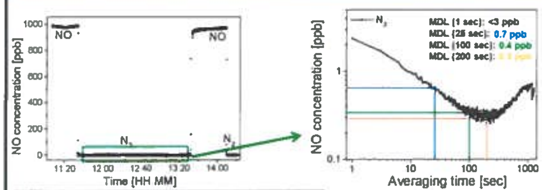
Long Term Stability of QEPAS based NO Sensor



2012 QEPAS Mid-IR sensor technology

2010 QEPAS Mid-IR sensor technology for medical breath sensing Hellertown, PA)

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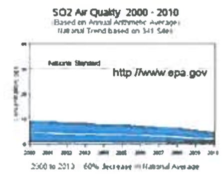
Motivation for Sulfur Dioxide Detection

- Prominent air pollutant
- Annual SO_2 concentrations range from ~ 1 - 6 ppb
- SO_2 is emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In atmosphere, SO_2 converts to sulfuric acid and is a primary contributor to acid rain
- SO_2 reacts to form sulfate aerosols
- SO_2 exposure affects lungs and causes breathing difficulties



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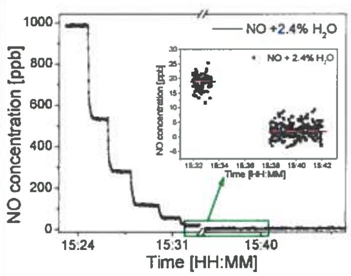
Dilution of a 1000 ppb NO Reference Concentration



Set NO [ppb]	Measured NO [ppb]
1000	985
500	530
250	278
100	115
50	56
20	18

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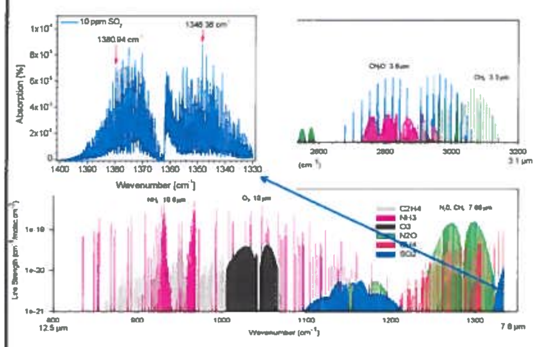
Molecular Absorption Spectra within two Mid-IR Atmospheric Windows



Source: HITRAN 2000 database

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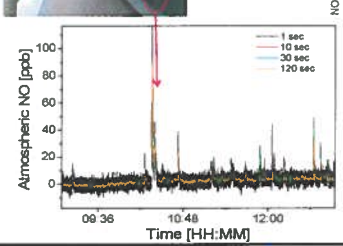
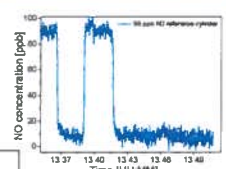
Preliminary Atmospheric Nitric Oxide Measurements





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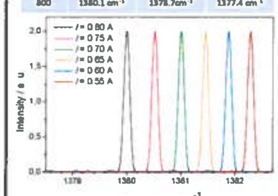
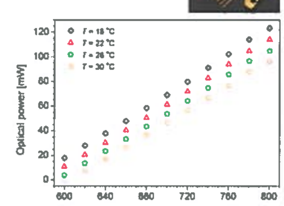
Performance of a 7.24 μm CW HHL TEC DFB-QCL

Current (mA)	T = 20 °C	T = 30 °C	T = 40 °C
550	1382.3 cm⁻¹	1381.1 cm⁻¹	- - -
600	1381.9 cm⁻¹	1380.7 cm⁻¹	1379.4 cm⁻¹
650	1381.5 cm⁻¹	1380.2 cm⁻¹	1378.9 cm⁻¹
700	1381.0 cm⁻¹	1379.8 cm⁻¹	1378.4 cm⁻¹
750	1380.6 cm⁻¹	1379.3 cm⁻¹	1377.9 cm⁻¹
800	1380.1 cm⁻¹	1378.7cm⁻¹	1377.4 cm⁻¹



An example of single frequency DFB-QCL radiation for different laser current values at a QCL temperature of 20 °C



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

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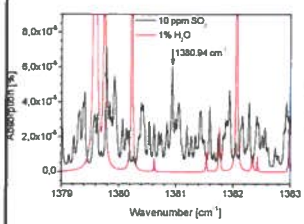
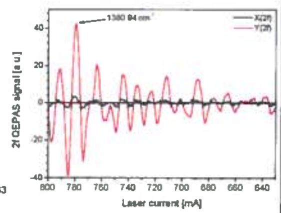
SO_2 Line Selection for a 7.24 μm CW RT DFB-QCL



Simulated HITRAN absorption spectra of 10 ppm SO_2 and 1% water vapor (P=100 Torr, T=296 K, L=1cm).



QEPAS spectrum of 10 ppm SO_2 at P=100 Torr for 7.24 μm CW RT DFB-QCL operating at 20.5 °C.

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QEPAS Performance for 17 Trace Gas Species (May 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 [illegible]	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	4.6×10 [illegible]	50	0.16
C_2H_2 (N_2)*	6523.88	720	4.1×10 [illegible]	57	0.03
NH_3 (N_2)*	6528.76	575	3.1×10 [illegible]	60	0.06
C_2H_4 (N_2)*	6177.07	715	5.4×10 [illegible]	15	1.7
CH_4 (N_2+1.2% H_2O)*	6057.09	760	3.7×10 [illegible]	16	0.24
CO_2 (breath ~50% RH)	6361.25	150	8.2×10 [illegible]	45	40
H_2S (N_2)*	6357.63	780	5.6×10 [illegible]	45	5
HCl (N_2 dry)	5739.26	760	5.2×10 [illegible]	15	0.7
CO_2 (N_2+1.5% H_2O) *	4991.26	50	1.4×10 [illegible]	4.4	18
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10 [illegible]	7.2	0.12
CO (N_2 +2.2% H_2O)*	2176.28	100	1.4×10 [illegible]	71	0.002
N_2O (air+5%SF_6)	2195.63	50	1.5×10 [illegible]	19	0.007
NO (N_2+H_2O)	1900.07	250	7.5×10 [illegible]	100	0.003
C_2H_5OH (N_2)**	1934.2	770	2.2×10 [illegible]	10	90
SO_2 (N_2 +2.4% H_2O)*	1380.94	100	2.0×10 [illegible]	40	0.1
C_2HF_5 (N_2)***	1208.62	770	7.8×10 [illegible]	6.6	0.009
NH_3 (N_2)*	1046.39	110	1.6×10 [illegible]	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 [illegible] $cm^{-1}W/\sqrt{Hz}$ (1,800; 10,300 Hz) for NH_3*,(**)

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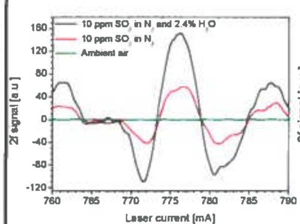
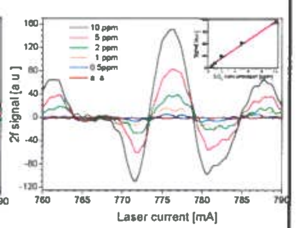
2f Wavelength Modulation QEPAS Results for SO_2



2f QEPAS signal for dry SO_2 gas (red) and moisturized with 2.4% H_2O (black) when laser was tuned across 1380.9 cm^{-1} line.



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)

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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 of **3 ppbv** was achieved at a gas pressure **of 240 Torr** and sampling time of 1 sec.
- A 1σ minimum detection limit 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}**.
- After adding water vapor to analyzed SO_2 mixture more than 3 times improvement in detected signal was observed.
- Laser spectroscopy with a mid-infrared, room temperature, continuous wave, high performance DFB QCL is a promising analytical approach for real time atmospheric measurements and breath analysis.
- Future tasks for the SO_2 will include line locking for long term measurements as well as using a high power QCL (>200 mW) operating at strongest SO_2 absorption line at 1348 cm^{-1}.
- Compact, robust semsitive and selective QCL based QEPAS sensor technology offers a promising future to perform real-time environmental, biomedical and industrial emission measurements.

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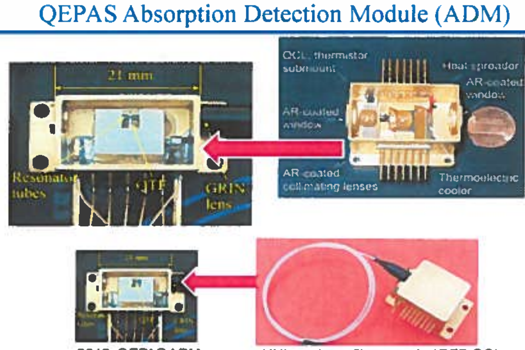
Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module (ADM)



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)