Recent Advances in Mid-infrared Semiconductor Laser based Trace Gas Sensor Technologies

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http://ecc.rice.edu/lasersci/

- Motivation: Chemical Sensing Applications
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sensing Technologies (QEPAS)
- Selected Applications of Trace Gas Detection
  - NH$_3$ and NO Detection for Environmental Monitoring & Medical Diagnostics
  - Monitoring of Broadband Absorbers
- Future Directions of 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, 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 Biomedical and the Life Sciences**

- **Technologies for Law Enforcement and National Security**

- **Fundamental Science and Photochemistry**
### Mid-IR Source Requirements for Laser Spectroscopy

<table>
<thead>
<tr>
<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (% to ppt)</td>
<td>Optimum Wavelength, Power</td>
</tr>
<tr>
<td>Selectivity (Spectral Resolution)</td>
<td>Single Mode Operation and Narrow Linewidth</td>
</tr>
<tr>
<td>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</td>
<td>Tunable Wavelength</td>
</tr>
<tr>
<td>Directionality or Cavity Mode Matching</td>
<td>Beam Quality</td>
</tr>
<tr>
<td>Rapid Data Acquisition</td>
<td>Fast Time Response</td>
</tr>
<tr>
<td>Room Temperature Operation</td>
<td>No Consumables</td>
</tr>
<tr>
<td>Field deployable</td>
<td>Compact &amp; Robust</td>
</tr>
</tbody>
</table>
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, Chernin)
  - Cavity Ringdown and Cavity Enhanced Spectroscopy
  - Open Path Monitoring (with & without 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)
Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

Source: HITRAN 2000 database
Key Characteristics of mid-IR QCL and ICL Sources - May 2010

- **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 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 at TEC/RT temperatures**
  - Pulsed and CW powers of 34 W and 3 W respectively; high temperature operation ~300K
  - >280 mW, TEC CW DFB @ 5 µm
  - > 600 mW (CW FP) @ RT; wall plug efficiency of ~17 % at 4.6 µm;
Quantum Cascade (QC), Interband (IC) and GaSb Laser Commercial and Research Activity in May 2010

• **Commercial Sources**
  - Adtech, CA
  - Alpes Lasers, Switzerland & Germany
  - Alcatel-Thales, France
  - Cascade Technologies, UK
  - Corning, NY
  - Hamamatsu, USA & Japan
  - Maxion Technologies, Inc MD (Physical Sciences, Inc)
  - Nanoplus, Germany
  - Pranalytica, CA

• **Research Groups**
  - Harvard University
  - Fraunhofer-IAF & IPM, Freiburg, Germany
  - Institute of Electron Technology, Warsaw, Poland
  - NASA-JPL, Pasadena, CA
  - Naval Research Laboratories, Washington, DC
  - Northwestern University, Evanston, IL
  - Princeton University (MIRTHE), NJ
  - Shanghai Institute of Microsystem and Information Technology, China
  - Sheffield University, UK
  - State University of New York
  - Technical University, Zuerich, CH
  - University of Montpelier, France
  - University of Vienna, Austria
Quartz Enhanced Photoacoustic Spectroscopy
From conventional PAS to QEPAS

Laser beam, power $P$

Modulated ($P$ or $\lambda$) at $f$ or $f/2$

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

$NNEA = \frac{\alpha_{\text{min}} P}{\sqrt{\Delta f}} \left[ \frac{\text{cm}^{-1} \times W}{\sqrt{\text{Hz}}} \right]$
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 ($\sim 10^6$) – linear from thermal noise to breakdown deformation
  - 300K noise: $x \sim 10^{-11}$ cm
  - Breakdown: $x \sim 10^{-2}$ cm
- Wide temperature range: from 1.56K (superfluid helium) to ~700K
- Low cost (<$1$

Other parameters
- Resonant frequency $\sim 32.8$ kHz
- Force constant $\sim 26800$ N/m
- Electromechanical coefficient $\sim 7 \times 1$ C/m
Typical QTF Resonance Curves

\[ Q = \frac{f_0}{\Delta f_{\sqrt{2}}} \]

- **Air, 760 Torr**: \( Q = 13270 \)
- **Vacuum**: \( Q = 93500 \)

Frequency, Hz

TF current, nA
What about QEPAS Modeling?


Also: S. L. Firebaugh, F. Roignant & E.A. Terray, “Modelling the Response of Photoacoustic Gas Sensors”; Comsol Conf, Boston, MA; Oct 8-10, 2009
Principal Architecture of a QEPAS Gas Sensor
Signal-to-noise ratio as a function of pressures for different tube sizes and bare QTF.

Q factor and frequency of the QTF as a function of pressure for different tube lengths and diameters.
**QEPAS spectrophone**

**Micro-resonator (mR) tubes**
- Must be close to QTF but *not* touch QTF (25-50 μm gaps).
- Optimum inner diameter 0.6 mm
- Optimum micro-resonator tubes are 4.4 mm long (≈λ/4 < l < λ/2 for sound at 32.8 kHz)
- **Maximum SNR of QTF with mR tubes:** ×30 (depending gas composition and pressure)
Acoustic and quartz resonators - interaction

When acoustic and QTF resonances coincide, the measured $Q$ is significantly reduced.
Alignment-free QEPAS Absorption Detection Module

[Image: A photograph of a QEPAS module with labels for Resonator tubes, QTF, and GRIN lens. The module has a label indicating 21 mm.]
Off-beam QEPAS based Gas Sensor

Source: K. Liu, X. Gao (AIoFM), W. Chen (ULCO), A. Kosterev et al. (Rice)
Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm$^3$)
- Extremely low dissipative losses
- Optical detector is not required
- Wide dynamic range
- Frequency and spatial selectivity of acoustic signals
- Rugged transducer – quartz monocystal; 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

- Responsivity depends on the speed of sound and molecular energy transfer processes
- Sensitivity scales with laser power
- Effect of H$_2$O
- Cross sensitivity issues
# QEPAS Performance for 15 Trace Gas Species (May ‘10)

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, cm(^{-1})</th>
<th>Pressure, Torr</th>
<th>NNEA, cm(^{-1})W/Hz(^{\propto})</th>
<th>Power, mW</th>
<th>NEC (τ=1s), ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O (N(_2))**</td>
<td>7306.75</td>
<td>60</td>
<td>1.9×10(^{-9})</td>
<td>9.5</td>
<td>0.09</td>
</tr>
<tr>
<td>HCN (air: 50% RH)*</td>
<td>6539.11</td>
<td>60</td>
<td>4.6×10(^{-9})</td>
<td>50</td>
<td>0.16</td>
</tr>
<tr>
<td>C(_2)H(_2) (N(_2))*</td>
<td>6523.88</td>
<td>720</td>
<td>4.1×10(^{-9})</td>
<td>57</td>
<td>0.03</td>
</tr>
<tr>
<td>NH(_3) (N(_2))*</td>
<td>6528.76</td>
<td>575</td>
<td>3.1×10(^{-9})</td>
<td>60</td>
<td>0.06</td>
</tr>
<tr>
<td>C(_2)H(_4) (N(_2))*</td>
<td>6177.07</td>
<td>715</td>
<td>5.4×10(^{-9})</td>
<td>15</td>
<td>1.7</td>
</tr>
<tr>
<td>CH(_4) (N(_2)+1.2% H(_2)O)*</td>
<td>6057.09</td>
<td>760</td>
<td>3.7×10(^{-9})</td>
<td>16</td>
<td>0.24</td>
</tr>
<tr>
<td>CO(_2) (breath ~50% RH)</td>
<td>6361.25</td>
<td>150</td>
<td>8.2×10(^{-9})</td>
<td>45</td>
<td>40</td>
</tr>
<tr>
<td>H(_2)S (N(_2))*</td>
<td>6357.63</td>
<td>780</td>
<td>5.6×10(^{-9})</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>HCl (N(_2) dry)</td>
<td>5739.26</td>
<td>760</td>
<td>5.2×10(^{-9})</td>
<td>15</td>
<td>0.7</td>
</tr>
<tr>
<td>CO(_2) (N(_2)+1.5% H(_2)O) *</td>
<td>4991.26</td>
<td>50</td>
<td>1.4×10(^{-9})</td>
<td>4.4</td>
<td>18</td>
</tr>
<tr>
<td>CH(_2)O (N(_2):75% RH)*</td>
<td>2804.90</td>
<td>75</td>
<td>8.7×10(^{-9})</td>
<td>7.2</td>
<td>0.12</td>
</tr>
<tr>
<td>CO (N(_2))</td>
<td>2196.66</td>
<td>50</td>
<td>5.3×10(^{-9})</td>
<td>13</td>
<td>0.5</td>
</tr>
<tr>
<td>CO (propylene)</td>
<td>2196.66</td>
<td>50</td>
<td>7.4×10(^{-9})</td>
<td>6.5</td>
<td>0.14</td>
</tr>
<tr>
<td>N(_2)O (air+5%SF(_6))</td>
<td>2195.63</td>
<td>50</td>
<td>1.5×10(^{-8})</td>
<td>19</td>
<td>0.007</td>
</tr>
<tr>
<td>NO (N(_2)+H(_2)O)</td>
<td>1900.07</td>
<td>250</td>
<td>7.5×10(^{-9})</td>
<td>100</td>
<td>0.003</td>
</tr>
<tr>
<td>C(_2)H(_5)OH (N(_2))**</td>
<td>1934.2</td>
<td>770</td>
<td>2.2×10(^{-9})</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>C(_2)H(_6)F(_5) (N(_2))***</td>
<td>1208.62</td>
<td>770</td>
<td>7.8×10(^{-9})</td>
<td>6.6</td>
<td>0.009</td>
</tr>
<tr>
<td>NH(_3) (N(_2))*</td>
<td>1046.39</td>
<td>110</td>
<td>1.6×10(^{-8})</td>
<td>20</td>
<td>0.006</td>
</tr>
</tbody>
</table>

* - 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/√Hz (1,800; 10,300 Hz) for NH\(_3\)*, (**)  

Recent Applications of mid-infrared Laser 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)
Mid-IR EC-QCL based AM-PAS Sensor for atmospheric NH$_3$ Detection

Gas handling system
- Gas Cylinder
- Vacuum pump
- Flow meter
- Needle Valve
- Pressure Controller
- Gas In
- Gas Out

Tunable QCL controller
- Piezo Driver
- DAQCard 6062E
- PC

EC-QCL
- Mech. Chopper
- Function Generator
- Lock-In Amplifier
- Pocket Lock-In

Photo-Acoustic Cell
- Mirror
- Reference Cell
- Pyroelectric Detector

A ring differential resonance
Photo-Acoustic Cell:
1. acoustic resonator,
2. microphone,
3. gas input and output,
4. window
Tuning range of a Daylight Solutions CW TEC 10.34 μm EC-QCL and HITRAN simulated spectra at 200Torr
Preliminary NH$_3$ Data after Sensor Installation on the 100 m high Moody Tower Roof (UH campus)

Moody Tower at the UH campus, Houston, TX

Ammonia sensor and electronics installed on Moody Tower roof.

Diurnal trend of NH$_3$ concentration by using acquired data for a period of 16 days (Feb. 12 – Mar. 1, 2010)
## Important Biomedical Species

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Biological/Pathology Indication</th>
<th>Center wavelength [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>C₅H₁₂</td>
<td>Inflammatory diseases, transplant rejection</td>
<td>6.8</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>Lipid peroxidation and oxidation stress, lung cancer (low ppbv range)</td>
<td>6.8</td>
</tr>
<tr>
<td>Carbon Dioxide isotope ratio</td>
<td>^1³CΟ₂/^1²CΟ₂</td>
<td>Helicobacter pylori infection (peptic ulcers, gastric cancer)</td>
<td>4.4</td>
</tr>
<tr>
<td>Carbonyl Sulfide</td>
<td>COS</td>
<td>Liver disease, acute rejection in lung transplant recipients (10-500 ppbv)</td>
<td>4.8</td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>CS₂</td>
<td>Disulfiram treatment for alcoholism</td>
<td>6.5</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>Liver and renal diseases, exercise physiology</td>
<td>10.3</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>CH₂O</td>
<td>Cancerous tumors (400-1500 ppbv)</td>
<td>5.7</td>
</tr>
<tr>
<td>Nitric Oxide</td>
<td>NO</td>
<td>Nitric oxide synthase activity, inflammatory and immune responses (e.g. asthma) and vascular smooth muscle response (6-100 ppb)</td>
<td>5.3</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>H₂O₂</td>
<td>Airway inflammation, oxidative stress (1-5 ppbv)</td>
<td>7.9</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>Smoking response, lipid peroxidation, CO poisoning, vascular smooth muscle response</td>
<td>4.7</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C₂H₄</td>
<td>Oxidative stress, cancer</td>
<td>10.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>Ketosis, diabetes mellitus</td>
<td>7.3</td>
</tr>
</tbody>
</table>
Advantages of using CW DFB-QCL in the sensor architecture:
- Small laser package -> system compactness,
- DFB-QCL room temperature operation,
- Performing WM spectroscopy at optimum modulation depth,
- Baseline reduction with 2f WM.
Real-time Breath Monitor Interface

- Controlled flow
- Continuous control of mouth pressure
- Continuous monitoring of CO₂ concentration (capnograph) and its use in QEPAS data processing
Line selection for HAMAMATSU CW DFB QCL

Single mode QCL radiation recorded with FTIR for different laser current values at laser temperature of 18°C.

HITRAN simulated spectra @ 130 Torr indicating two NH₃ absorption lines of interest.
QEPAS based breath analyzer using a DFB-QCL
Motivation for Nitric Oxide Detection

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - $\text{NO}_x$ monitoring from automobile exhaust and power plant emissions
  - Precursor of smog and acid rain
- Industrial process control
  - Formation of oxynitride gates in CMOS Devices
- 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)
High power fiber-coupled QCL for NO detection

- **Mid-IR EC-QCL (DLS)**
  - Wavelength tuning range:
    5.26-5.53 μm (1807-1900 cm⁻¹)
  - MHF spectral range 5% of center wavelength:
    5.4 μm; (1846 cm⁻¹)
  - Maximum tuning Rate 38 nm/sec
  - Highest optical power: ~250 mW
  - TE cooling, RT operation

Collaboration with:
V. Spagnolo
Politecnico Bari and CNR-LIT³
NO absorption line selection

0.05% NO in N\textsubscript{2} at 1 atm

- Selected NO line 1900.08 cm\textsuperscript{-1}
- High resolution mode-hop-free tuning is possible
- Laser Power: \textasciitilde170 mW
CW MHF QCL based QEPAS NO sensor

3 ppm NO in N₂ and H₂O at 250 Torr after background subtraction

Signal to noise >200

- Lowest detectable concentration < 15ppb
Emission spectra of the Maxion 1900 cm\(^{-1}\) CW DFB TEC QCL and HITRAN simulated spectra
CW vs. Pulsed: Allan Variance for Measured NO

- Narrow Line width
  - Improved specificity
  - Greater absorption
  - Improved accuracy

- Higher Power
  - TE-cooled detectors
  - Longer path lengths

- But, can be more susceptible to optical fringes
- TE-Cooled Detector (VIGO)

- Variance vs. integration time shows
  - the limits of averaging

- NO line at 1900 cm\(^{-1}\) measured
- CW and pulsed, same laser

- Concentration noise, sdev @ 1 Hz
  - CW: 0.1 ppb
  - Pulsed: 0.5 ppb

Source: M. Zahniser, et. al. Aerodyne, FACSS 2009
Future Directions and Outlook of Chemical Trace Gas Sensing Technology
Monitoring of Broadband Absorbers

- Freon 125 (C₂HF₅)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals, e.g. chemical warfare agents
- Acetone (CH₃COCH₃)
  - Recognized biomarker for diabetes
- TATP (Acetone Peroxide, C₆H₁₂O₄)
  - Highly Explosive
- Uranium Hexafluoride (UF₆)
- Hydrazine (N₂H₄)
UF₆ Mid-Infrared Absorption Bands

Absorption spectrum of gas mixture under investigation and observed spectral features identification.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>( v, \text{ cm}^{-1} )</th>
<th>( \sigma, \text{ cm}^{-1}/\text{atm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2v_3+v_6 )</td>
<td>1386±2</td>
<td>0.0018</td>
</tr>
<tr>
<td>( v_1+v_2+v_6 )</td>
<td>1341</td>
<td>0.0088</td>
</tr>
<tr>
<td>( v_1+v_3 )</td>
<td>1290.9±0.5</td>
<td>0.72</td>
</tr>
<tr>
<td>( 2v_2+v_6 )</td>
<td>1211±2</td>
<td>0.0007</td>
</tr>
<tr>
<td>( v_3+v_3 )</td>
<td>1156.9±0.5</td>
<td>0.82</td>
</tr>
<tr>
<td>( v_3+2v_6 )</td>
<td>905±2</td>
<td>0.0035</td>
</tr>
<tr>
<td>( v_1+v_4 )</td>
<td>852.8±0.5</td>
<td>0.12</td>
</tr>
<tr>
<td>( v_3+v_5 )</td>
<td>821</td>
<td>0.33</td>
</tr>
<tr>
<td>( v_3 )</td>
<td>625</td>
<td>350</td>
</tr>
</tbody>
</table>


A. Nadezhdinskii et al, GPI, Moscow, March 2008

Also: G. Baldaccini et al., Nuovo Cimento 8, 203, 1986
HR coated CW 7.74 μm FP-QCL in EC-configuration @ -30°C

FTIR spectra for 2mm cavity length 7.74 μm FP-QCL (A758BHB2 I) in external cavity

Resistance @ RT is $R = 650\Omega$

Threshold with grating $I_{th} = 301.5\, mA$

Threshold without grating $I_{th} = 350\, mA$
Simulant molecules for UF$_6$

Single mode spectral frequency tuning range of the tested FP-QCLs cover the $\nu_1 + \nu_3$ UF$_6$ combination band centered at $\sim$1291 cm$^{-1}$ and several methane (CH$_4$) and acetylene (C$_2$H$_2$) absorption lines.

Experimental spectrum of absorption cross-section $\sigma$ of the analyzed uranium hexafluoride sample (circles) as well as the obtained model spectra of $^{238}$UF$_6$ (solid line) and 235UF6 (dotted line) [1].

HITRAN simulation for 100 ppm of CH$_4$ and C$_2$H$_2$ concentrations. Spectra were simulated at a 100 Torr pressure and 1 meter pathlength.

Ethane absorption spectrum

Abs. coefficient, cm$^{-1}$/ppb

Frequency, cm$^{-1}$

$4 \times 10^{-8}$ cm$^{-1}$
Proposed QEPAS-OPBC Sensor Configuration

DFB diode laser

High reflectivity dielectric mirrors

Photodiode

PZT

QTF

Feedback electronics

Circulating power = Source power / (1-R)

Very conservatively, ×100

Alex Kachanov  Skymoon Research. R & D
QEPAS MDAL Comparison with CRDS, ICOS & TDLAS

Minimum Detectable Absorption Loss (MDAL) [cm$^{-1}$/Hz] can be used for comparison of different techniques:

- Cavity Ring Down Spectroscopy (CRDS): \( \sim 3 \times 10^{-11} \)
- Integrated Output Spectroscopy (ICOS): \( \sim 3 \times 10^{-11} \)
- Multipass Gas Cell based TDLAS: \( \sim 2 \times 10^{-11} \)

- QEPAS (Sept 2009) MDAL (DFB 100mW): \( 1.9 \times 10^{-8} \)
- QEPAS-OPBC MDAL (DFB 20 mW): \( 3.2 \times 10^{-10} \)
- QEPAS-OPBC + micro-resonator (estimated): \( \sim 7 \times 10^{-12} \)

QEPAS-OPBC can be as sensitive as CRDS, ICOS and TDLAS and retain most of the performance merits of QEPAS.
Laboratory air spectrum with OPBC-QEPAS system

Bandwidth = 2.6 Hz; NEA = $6.7 \times 10^{-10} \text{ cm}^{-1}/\sqrt{\text{Hz}}$

An absorption coefficient $[10^{-6} \text{ cm}^{-1}]

Wavelength [nm]

$k_x$, $k_y$, HITRAN

RICE
The proposed QEPAS based $\text{N}_2\text{H}_4$ sensor would use a thermoelectrically cooled CW, DFB, QCL operating at \(~957$ cm\(^{-1}\) (10.5$\mu$m) with an output power of 100 mW. At this wavelength and assuming a noise equivalent absorption coefficient of \(~5.10^{-9}$ cm\(^{-1}\) W/$\sqrt{\text{Hz}}$, and a $\text{N}_2\text{H}_4$ absorption of \(~7.10^{-6}$ cm\(^{-1}\)/ppm at 1 atm, the estimated detection sensitivity will be \(~7$ ppbV for a 1 Hz bandwidth. 
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: NH₃, CH₄, N₂O, CO₂, CO, NO, H₂O, COS, C₂H₄, H₂S, H₂CO, SO₂, C₂H₅OH, C₂HF₅, TATP and several isotopic species of C, O, N and H.

- **New Applications of Trace Gas Detection**
  - Environmental Monitoring (urban quality – NH₃, H₂CO, NO, isotopic ratio measurements of CO₂ and CH₄, fire and post fire detection; quantification of engine exhausts)
  - Industrial process control and chemical analysis (NO, NH₃, H₂O, and H₂S)
  - Medical & biomedical non-invasive diagnostics (NH₃, NO, N₂O, and CH₃COCH₃)
  - Ultra-compact, low cost, robust sensors (CO and CO₂)

- **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 spectrophone 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, UF₆ and multi-species detection)
  - Development of optically gas sensor networks based on QEPAS and LAS
Optimum NO$_2$ transition for FRS experiment

$4_{41} < -4_{40}$ at 1613.245 cm$^{-1}$, $3_{30} < -3_{31}$ at 1614.813 cm$^{-1}$ or $2_{21} < -2_{20}$ at 1615.929 cm$^{-1}$
Tuning range of a Daylight Solutions CW 6.19 μm NO₂ EC-QCL (21062-MHF-012)