Advanced Measurement Concepts for Mid-infrared Semiconductor Laser based Trace Gas Sensor Technologies: Opportunities & Challenges

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New Laser Based Trace Gas Sensor Technology
- Novel Multipass Gas Absorption Cells & Electronics
- Quartz Enhanced Photoacoustic Spectroscopy

Examples of nine Mid-infrared Trace Gas Species
- C$_2$H$_6$, NH$_3$, NO, CO, SO$_2$, CH$_4$, N$_2$O, H$_2$O$_2$ & C$_3$H$_6$O

Future Directions of Laser Based Trace Gas Sensor Technologies and Conclusions

Research support by NSF ERC MIRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation, and Sentinel Photonics Inc. via an EPA Phase 1 SBIR sub-award is acknowledged
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 (e.g isotopologues, climate modeling,…)
  - Volcanic Emissions

- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Pharmaceutical, Metals Processing, Food & Beverage Industries, Nuclear Technology & Safeguards

- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Life Support

- **Applications in Medical Diagnostics and the Life Sciences**

- **Technologies for Law Enforcement, Defense and Security**

- **Fundamental Science and Photochemistry**
“Curiosity” Landed on Mars on August 6, 2012
Laser based Trace Gas Sensing Techniques

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (Mid-IR)

- **Long Optical Pathlength**
  - Multipass Absorption Cell (White, Herriot, Chernin, Sentinel Photonics/Aeris Technologies)
  - 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 & Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
Demonstration of CH4 Sensor Performance

- Develop of Prototype Package in Year 1
- Develop of 2nd Generation Sensor System Year 2
- Develop Pre-Production Package
HITRAN Simulated Mid-Infrared Molecular Absorption Spectra

Source: HITRAN 2012 database
## 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 pptv)</td>
<td>Optimum Wavelength, Power</td>
</tr>
<tr>
<td>Selectivity (Spectral Resolution)</td>
<td>Stable Single Mode Operation and Narrow Linewidth</td>
</tr>
<tr>
<td>Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers</td>
<td>Mode Hop-free Wavelength Tunability</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>High wall plug efficiency, no cryogenics or cooling water</td>
</tr>
<tr>
<td>Field deployable in harsh environments</td>
<td>Compact &amp; Robust</td>
</tr>
</tbody>
</table>
Key Characteristics of Mid-IR QCL & ICL Sources – Sept. 2014

- **Band – structure engineered devices**
  Emission wavelength is determined by layer thickness – MBE or MOCVD; Type I QCLs operate in the 3 to 24 µm spectral region; Type II and GaSb based ICLs can cover the 3 to 6 µm spectral range.
  - Compact, reliable, stable, long lifetime, and commercial availability
  - Fabry-Perot (FP), single mode (DFB) and multi-wavelength devices

- **Wide spectral tuning ranges in the mid-IR**
  - 1.5 cm⁻¹ using injection current control for DFB devices
  - 10-20 cm⁻¹ using temperature control for DFB devices
  - ~100 cm⁻¹ using current and temperature control for QCL DFB Array
  - ~ 525 cm⁻¹ (22% of c.w.) using an external grating element and FP chips with heterogeneous cascade active region design; also QCL DFB Array

- **Narrow spectral linewidths**
  - 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**
  - Room temperature pulsed power of > 30 W with 44% wall plug efficiency
  - CW powers of ~ 5 W with 23% wall plug efficiency at 293 ºK
  - > 600 mW CW DFB @ 285 ºK; wall plug efficiency 23% at 4.6 µm
Motivation for Mid-infrared $\text{C}_2\text{H}_6$ Detection

- **Applications in medical breath analysis**
  - Asthma
  - Schizophrenia
  - Lung cancer
  - Vitamin E deficiency

- **Applications in atmospheric chemistry and climate R & D**
  - Fossil fuel and biofuel consumption
  - Biomass burning
  - Vegetation/soil
  - Natural gas loss

HITRAN absorption spectra of $\text{C}_2\text{H}_6$, $\text{CH}_4$, and $\text{H}_2\text{O}$

C$_2$H$_6$ Detection with a 3.36 µm CW DFB LD using a Novel Compact Multipass Absorption Gas Cell and Control Electronics


2f WMS signal for a C$_2$H$_6$ line at 2976.8 cm$^{-1}$ at 200 Torr

Minimum detectable C$_2$H$_6$ concentration: ~740 pptv (1σ; 1 s time resolution)

MGC dimensions: **17 x 6.5 x 5.5 (cm)**

Distance between the MGC mirrors: 12.5 cm
This figure shows the result of a sequence of four fracking injections obtained by directional drilling, which creates horizontal production in target stratum.

A proposed DOE-ARPA-E CH4 detection project at 3.327 µm will start in 2015 at a well platform of 10 m x 10 m with a 1 m spatial resolution.
Oil in Water Detection

- Produced water
  - legislation: < 15 ppm
- Injection water
  - Economic reasons
    target value: < 5 ppm or lower
Motivation for NH$_3$ Detection

- Medical diagnostics
  - Kidney disease
  - Liver failure and Cirrhosis
  - Brain Cells dysfunction
  - Drowsiness and Coma

- Atmospheric chemistry

- Pollutant gases monitoring

- Monitoring NH$_3$ concentrations in the exhaust stream of NO$_x$ removal systems based on selective catalytic reduction (SCR) techniques associated with electric power plants

- Spacecraft related trace gas monitoring
Conventional Photoacoustic Spectroscopy (PAS)

Laser beam, power \( P \)

Modulated \((P \text{ or } \lambda) \) at \( f \) or \( f/2 \)

\[
S \sim \frac{Q \alpha P}{f V}
\]

\[
NNEA = \frac{\alpha_{\min} P}{\sqrt{\Delta f}} \left[ \frac{\text{cm}^{-1} \times W}{\sqrt{\text{Hz}}} \right]
\]
NH₃ Measurements based on an EC-QCL PAS Sensor System

Schematic of a Daylight Solutions 10.36 µm CW TEC EC-QCL based PAS NH₃ Sensor.

Diurnal profile of atmospheric NH₃ levels in Houston, TX.

Comparison between NH₃ and particle number concentration time series from July 19 to July 31 2012.

NH₃ sensor deployed at the UH Moody Tower rooftop monitoring site.
Unexpected Remote Detection of NH₃ based on PAS

A chemical incident occurred at ~ 6 a.m. after two trucks collided on I-59. Both trucks caught fire. [www.chron.com]

Estimated hourly NH₃ emission from the Houston Ship Channel area is about 0.25 ton. Mellqvist et al., (2007) Final Report, HARC Project H-53.
Remote Detection of Sporadic NH$_3$ Emissions from the Parish Electric Power Plant, TX

The Parish electric power plant is located near the Brazos River in Fort Bend County, Texas (~27 miles SW from downtown Houston)
<table>
<thead>
<tr>
<th>Species/parameter</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>Daylight Solutions External Cavity Quantum Cascade Laser (Photo-acoustic Spectroscopy)</td>
</tr>
<tr>
<td>CO</td>
<td>Thermo Electron Corp. 48C Trace Level CO Analyzer (Gas Filter Correlation)</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>Thermo Electron Corp. 43C Trace Level SO$_2$ Analyzer (Pulsed Fluorescence)</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>Thermo Electron Corp. 42C Trace Level NO-NO$_2$-NO$_x$ Analyzer (Chemiluminescence)</td>
</tr>
<tr>
<td>NO$_y$</td>
<td>Thermo Electron Corp. 42C-Y NO$_y$ Analyzer (Molybdenum Converter)</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)</td>
</tr>
<tr>
<td>HCl</td>
<td>Mist Chamber coupled to Ion Chromatography (Dionex, Model CD20-1)</td>
</tr>
<tr>
<td>VOC$_s$</td>
<td>IONICON Analytik Proton Transfer Reaction Mass Spectrometer and TCEQ Automated Gas Chromatograph</td>
</tr>
<tr>
<td>PBL height</td>
<td>Vaisala Ceilometer CL31 with updated firmware to work with Vaisala Boundary Layer View software</td>
</tr>
<tr>
<td>Temperature</td>
<td>Campbell Scientific HMP45C Platinum Resistance Thermometer</td>
</tr>
<tr>
<td>Wind speed</td>
<td>Campbell Scientific 05103 R. M. Young Wind Monitor</td>
</tr>
<tr>
<td>Wind direction</td>
<td>Campbell Scientific 05103 R. M. Young Wind Monitor</td>
</tr>
</tbody>
</table>
- Emission events from specified point sources (i.e., industrial facilities)
- Estimated NH₃ emissions from cows (1.3 tons/day)
- Estimated NH₃ emissions from soil and vegetation (0.15 tons/day)
- EPA PMF (biogenic: 74.1%; light duty vehicles: 12.1%; natural gas/industry: 9.4%; heavy duty vehicles: 4.4%)
- Livestock might account for approximately 66.4% of total NH₃ emissions
- Increased contribution from industry (→ 18.9%)
From Conventional PAS to Quartz Enhanced PAS (QEPAS)

- Laser beam, power $P$
- Modulated ($P$ or $\lambda$) at $f$ or $f/2$

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

$NNEA = \frac{\alpha_{\text{min}} P}{\sqrt{\Delta f}} \left[ \frac{\text{cm}^{-1} \times \text{W}}{\sqrt{\text{Hz}}} \right]$
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 (~$10^6$) – linear from thermal noise to breakdown deformation
  - 300K noise: $x \sim 10^{-11}$ cm
  - Breakdown: $x \sim 10^{-2}$ cm
- Wide temperature range: from 1.6K to ~700K

Acoustic Micro-resonator (µR) Tubes

- Optimum inner diameter: 0.6 mm; µR-QTF gap is 25-50 µm
- Optimum mR tubes must be ~ 4.4 mm long (~$\lambda/4 < l < \lambda/2$ for sound at 32.8 kHz)
- SNR of QTF with µR tubes: $\times 30$ (depending on gas composition and pressure)
Simulated HITRAN high resolution spectra @ 130 Torr indicating two NH₃ absorption lines of interest. No overlap between NH₃ and CO₂ absorption lines was observed for the selected 967.35 cm⁻¹ NH₃ absorption line in the ν₂ R-band.
QEPAS based NH$_3$ Gas Sensor Architecture

- Loccioni breath sampler
- CW TEC DFB QCL in HHL package (Hamamatsu)
- Gas handling system
  - Diaphragm Pump
  - Pressure Controller & Flow Meter
- Gas in
- Gas out
- Quartz TF with Microresonator
- Two glass tubes
- Optical windows, Ø10 mm
- Pressure sensor port
- Electrical feedthrough

Control Electronics Unit (CEU)
- DAQCard 6062E
- Pre-Amp
- Lock-In 2f
- Lock-In 3f
- Data collection and processing
- PC

CW TEC DFB QCL in HHL package (Hamamatsu)
Real-time Exhaled Human NH$_3$ Breath Measurements

Successful testing of a 2nd generation breath ammonia monitor installed in a clinical environment. (Johns Hopkins, Baltimore, MD and St. Luke’s Hospital, Bethlehem, PA)

Minimum detectable concentration of NH$_3$ is: 
~ 6 ppbv at 967.35 cm$^{-1}$ (1$\sigma$; 1 s time resolution)
Motivation for Nitric Oxide Detection

• **NO in medicine and biology**
  - Important signaling molecule in physiological processes in humans and mammals (1998 Nobel Prize in Physiology/Medicine)
  - Treatment of asthma, chronic obstructive pulmonary disease (COPD) & lung rejection

• **Environmental pollutant gas monitoring**
  - Ozone depletion
  - Precursor of smog and acid rain
  - $\text{NO}_x$ monitoring from automobile exhaust and power plant emissions

• **Atmospheric Chemistry**
Molecular Absorption Spectra within two Mid-IR Atmospheric Windows and NO absorption @ 5.26µm

Source: HITRAN 2012 database
Emission Spectra of a $1900\text{cm}^{-1}$ TEC DFB QCL and HITRAN simulated spectra of NO, H$_2$O & CO$_2$

Output power: 117 mW @ 25 C

Thorlabs/Maxion
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 20.5°C.

CW DFB-QCL optical power and current tuning at three different temperatures.
CW TEC DFB QCL based QEPAS NO Gas Sensor

Schematic of a DFB-QCL based Gas Sensor.
PcL – plano-convex lens, Ph – pinhole,
QTF – quartz tuning fork, mR – microresonator,
RC- reference cell, P-elec D – pyro electric detector

Compact Prototype NO Sensor
(September 2012)
Performance of CW DFB-QCL based WMS QEPAS NO Sensor Platform

2f QEPAS signal (navy) and reference 3f signal (red) when DFB-QCL was tuned across 1900.08 cm\(^{-1}\) NO line.

Minimum detectable NO concentration is:
~ 3 ppbv (1\(\sigma\); 1 s time resolution)
QCL based TDLAS Sensor for Detection of NO Emission from Cancer Cells

Schematic drawing of the sensor setup

Dependence of the TDLAS sensor signal from biological samples on the gas flow (black squares). The inset shows spectra corresponding to the data points.

M. Koehring et al, Appl. Phys B, May 2014
Motivation for Carbon Monoxide Detection

- **CO in Medical Diagnostics**
  - Hypertension and abnormality in heme metabolism

- **Public Health**
  - Extremely dangerous to human life even at a low concentrations. CO must be monitored at low concentration levels (<35 ppm).

- **Atmospheric Chemistry**
  - Incomplete combustion of natural gas, fossil fuel and other carbon containing fuels.
  - Impact on atmospheric chemistry through its reaction with hydroxyl (OH) for troposphere ozone formation and changing the concentration levels of greenhouse gases (e.g. CH₄).
Performance of a 4.61 μm high power CW TEC DFB QCL

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

Estimated max wall-plug efficiency (WPE) is ~ 7% at 1.25A QCL drive-current.
CW DFB-QCL based CO QEPAS Sensor Results

Dilution of a 5 ppm CO reference gas mixture when the CW DFB-QCL is locked to the 2169.2 cm\(^{-1}\) R6 CO line.

Minimum detectable CO concentration is:

\(~ 2 \text{ ppbv} \) (1\(\sigma\); 1 s time resolution)

P. Stefanski et al., Appl. Phys. B., June 3, 2014 (online)
Motivation for Sulfur Dioxide Detection

- **SO₂ exposure affects lungs and causes breathing difficulties, bronchitis, cardiovascular disease**
- Currently, reported annual average atmospheric SO₂ concentrations range from ~1 - 6 ppb
- Prominent air pollutant
- Emitted from coal fired power plants (~73%) and other industrial facilities (~20%)
- In the atmosphere SO₂ converts to sulfuric acid → primary contributors to acid rain
- SO₂ reacts to form sulfate aerosols
- Primary SO₂ exposure for 1 hour is 75 ppb

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

Minimum detectable SO₂ concentration is: ~100 ppbv (1σ; 1 s time resolution)
QEPAS based CH$_4$ and N$_2$O Gas Sensor

Motivation for CH$_4$ and N$_2$O Detection

- Medical Diagnostics
  - Nausea, blurred vision, vomiting
- Prominent greenhouse gases
- Sources: wetlands, leakage from natural gas systems, fossil fuel production and agriculture

Detection Limit (1$\sigma$) with a 1-sec averaging time
Methane (CH$_4$) (1275.04 cm$^{-1}$) 13 ppbv
Nitrous Oxide (N$_2$O) (1275.5 cm$^{-1}$) 6 ppbv
N$_2$O concentration in the ambient laboratory air: 331 ppbv

Measurements performed with a DFB-QCL based QEPAS Sensor installed in the Aerodyne Mobile Laboratory (Sept 7, 2013)

Atascocita Landfill, Humble, TX 77396

CH$_4$ Perimeter Measurements

A to B: 3.5 miles
B to C: 1.5 miles
A to C: 2.2 miles

A: 29.9599° North, 95.2334° West
B: 29.9364° North, 95.2508° West
C: 29.9547° North, 95.2462° West (Landfill)

Motivation of $\text{H}_2\text{O}_2$ Detection

- Oxidative capacity of atmosphere and balance of $\text{HO}_x$;
- Acid rain formation & In-cloud oxidation of $\text{S(IV)}$ to $\text{S(VI)}$;
- Active agent in decontamination and sterilization systems;
- $\text{H}_2\text{O}_2$ in breath is a biomarker of oxidative stress;
- $\text{H}_2\text{O}_2$ concentration levels in Houston have not been reported despite of atmospheric conditions, such as high humidity, high solar radiation levels, and the presence of the petrochemical industry.
QEPAS based Hydrogen Peroxide (H₂O₂) Sensor System

Schematic of QCL based QEPAS sensor:
ADM – acoustic detection module; CEU – control electronics unit; PC – personal computer.

H₂O₂ Exposure limit is set at 1 ppmv by OSHA

Simulated spectra (HITRAN) of H₂O₂ at 296 K and 130 Torr, along with atmospheric interfering molecules of CH₄ and N₂O; two target wavelengths at 1294.1 and 1294.9 cm⁻¹ are shown.

### QEPAS Performance for Trace Gas Species (September 2014)

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, cm⁻¹</th>
<th>Pressure, Torr</th>
<th>NNEA, cm⁻¹ W/Hz⁻¹</th>
<th>Power, mW</th>
<th>NEC (τ=1s), ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃ (air)</td>
<td>35087.70</td>
<td>700</td>
<td>3.0×10⁻⁸</td>
<td>0.8</td>
<td>1.27</td>
</tr>
<tr>
<td>O₂ (N₂)</td>
<td>13099.30</td>
<td>158</td>
<td>4.74×10⁻⁷</td>
<td>1228</td>
<td>13</td>
</tr>
<tr>
<td>C₂H₂ (N₂)*</td>
<td>6523.88</td>
<td>720</td>
<td>4.1×10⁻⁹</td>
<td>57</td>
<td>0.03</td>
</tr>
<tr>
<td>NH₃ (N₂)*</td>
<td>6528.76</td>
<td>575</td>
<td>3.1×10⁻⁹</td>
<td>60</td>
<td>0.06</td>
</tr>
<tr>
<td>C₂H₄ (N₂)*</td>
<td>6177.07</td>
<td>715</td>
<td>5.4×10⁻⁹</td>
<td>15</td>
<td>1.7</td>
</tr>
<tr>
<td>CH₄ (N₂+1.2% H₂O)*</td>
<td>6057.09</td>
<td>760</td>
<td>3.7×10⁻⁹</td>
<td>16</td>
<td>0.24</td>
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<tr>
<td>N₂H₄</td>
<td>6470.00</td>
<td>700</td>
<td>4.1×10⁻⁹</td>
<td>16</td>
<td>1</td>
</tr>
<tr>
<td>H₂S (N₂)*</td>
<td>6357.63</td>
<td>780</td>
<td>5.6×10⁻⁹</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>HCl (N₂ dry)</td>
<td>5739.26</td>
<td>760</td>
<td>5.2×10⁻⁸</td>
<td>15</td>
<td>0.7</td>
</tr>
<tr>
<td>CO₂ (N₂+1.5% H₂O) *</td>
<td>4991.26</td>
<td>50</td>
<td>1.4×10⁻⁸</td>
<td>4.4</td>
<td>18</td>
</tr>
<tr>
<td>CH₂O (N₂:75% 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 (N₂ +2.2% H₂O)</td>
<td>2176.28</td>
<td>100</td>
<td>1.4×10⁻⁷</td>
<td>71</td>
<td>0.002</td>
</tr>
<tr>
<td>CO (propylene)</td>
<td>2196.66</td>
<td>50</td>
<td>7.4×10⁻⁸</td>
<td>6.5</td>
<td>0.14</td>
</tr>
<tr>
<td>N₂O (air+5%SF₆)</td>
<td>2195.63</td>
<td>50</td>
<td>1.5×10⁻⁸</td>
<td>19</td>
<td>0.007</td>
</tr>
<tr>
<td>C₂H₅OH (N₂)**</td>
<td>1934.2</td>
<td>770</td>
<td>2.2×10⁻⁷</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>NO (N₂+H₂O)</td>
<td>1900.07</td>
<td>250</td>
<td>7.5×10⁻⁹</td>
<td>100</td>
<td>0.003</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>1295.6</td>
<td>150</td>
<td>4.6×10⁻⁹</td>
<td>100</td>
<td>12</td>
</tr>
<tr>
<td>C₂HF₅ (N₂)**</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>NH₃ (N₂)*</td>
<td>1046.39</td>
<td>110</td>
<td>1.6×10⁻⁸</td>
<td>20</td>
<td>0.006</td>
</tr>
<tr>
<td>SF₆</td>
<td>948.62</td>
<td>75</td>
<td>2.7×10⁻¹⁰</td>
<td>18</td>
<td>5×10⁻⁵ (50 ppt)</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 ×10⁻⁹ cm⁻¹ W/√Hz for NH₃
Use of Canines in non-invasive & sensitive Cancer Detection

- **Bladder Cancer**
  - Urine
  - Sensitivity 73%
  - Specificity 56-92%

- **Ovarian cancer**
  - Carcinoma Tissue
  - Sensitivity 100%, Specificity 98%
  - Blood
  - Specificity 100%, Sensitivity 95%

- **Lung Cancer**
  - Breath
  - Sensitivity 99%
  - Specificity 99%

- **Breast Cancer**
  - Breath
  - Sensitivity 88%
  - Specificity 98%

- **Prostate Cancer**
  - Urine
  - Sensitivity 99%

- **Melanoma**
  - Skin VOCs
  - Potential!

- **Colorectal cancer**
  - Breath 91% Specificity 99%
  - Stool 97% Specificity 99%

Breath 2014, Torun, Prof. T. Jezierski et al., Institute of Genetics and Animal Breeding, PAS
Advantages & Disadvantages of Canines in Cancer Detection

**Advantages**
- Non-invasive, safe and easy sample collecting
- Relatively easy training and interpretation of dogs’ indications
- Odor samples can be tested several times
- Extremely high detection sensitivity and specificity
- Potential of VOCs are useful in search, rescue and emergency applications

**Disadvantages**
- To-date a “black-box technology”
- It is a method based on earning a reward, which becomes unreliable after ~4 years
- Variation of sensitivity and specificity
- Re-training of dogs is not effective

Breath 2014, Torun, Prof. T. Jezierski et al., Institute of Genetics and Animal Breeding, PAS
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$_2$O
- Responsivity depends on the speed of sound and molecular energy transfer processes
- Cross sensitivity issues
Future Directions and Outlook

• New target analytes: formaldehyde (CH$_2$O), ethylene (C$_2$H$_4$), ozone (O$_3$) and nitrate (NO$_3$)

• Ultra-compact, low cost, robust sensors (e.g. CH$_4$, NO, CO…)

• QCL based ultra-portable atmospheric carbon isotope monitor for $^{12}$CH$_4$ & $^{13}$CH$_4$

• Monitoring of broadband absorbers: acetone (C$_3$H$_6$O): MDL of 1.5 ppm with a 7mW ICL & AM, or 20ppb with a 100mW QCL @ 8.23µm; benzene (C$_6$H$_6$)…

• Optical power build-up cavity designs (I-QEPAS)

• THz QEPAS based sensors

• Development of trace gas sensor networks
Potential Integration of a CW DFB-QCL and QEPAS Absorption Detection Module

Why is THz based Trace Gas Sensing useful?

Several gas species such as HF, OH, HCN, HCl, HBr, NH₃, H₂O₂, H₂S, H₂O & explosives (in the vapor phase) show strong absorption bands in the THz spectral range.

Mainly rotational levels are involved in THz absorption processes and rotational-translational (R-T) relaxation rates are up to three order of magnitude faster with respect to vibrational-translational (V-T) in the mid-infrared.

QEPAS signal strongly depends on the energy relaxation rates due to the possibility to operate at low pressure, & thereby taking advantages of the typically very high QTF Q-factors.
Why have QEPAS sensors not been developed in the THz spectral range so far?

Standard QTFs have a very small volume (~0.3×0.3×3 mm³)

In QEPAS sensor systems, it is critical to avoid laser illumination of the QTF, since the radiation blocked by the QTF prongs results in an undesirable non-zero background as well as a shifting fringe-like interference pattern.

The standard QTF prong separation of 330 µm is comparable with the THz wavelength which prevents the use of a QEPAS sensor architecture in the THz range unless we use large sized QTFs.
Custom fabricated QTFs scaled in Dimensions (~7 & 3 times larger) with respect to a standard QTF

Standard photolithographic techniques were used to etch the custom QTF, starting from a z-cut quartz wafer. Chromium/gold contacts were deposited on both sides of the custom QTF.

Currently verification that the larger QTFs behave similar to a “standard” QTF in terms of vibrational modes and Q factor is in progress.
THz QCL Sources via Nonlinear Optics

Use intra-cavity DFG in mid-IR QCLs

\[ W(\omega_{\text{THz}}) \propto |\chi^{(2)}|^2 W(\omega_1)W(\omega_2) \times l_{\text{eff}}^2 \]

**THz QCL source based on intra-cavity DFG**

- Same fabrication/user operation as regular QCLs
- Room temperature operation
- Broadband THz tuning


IQCLSW 2014, Policore, Italy: M.A. Belkin et al, UT Austin, USA

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**Monolithic tuners: 0.58 THz of tuning** – Jung *et. al.*, *Nature Comm.* **5**, 4267 (2014)
THz QEPAS Sensor System for Methanol (CH$_3$OH) Detection

Legend

**PM** – parabolic mirror
**QTF** – quartz tuning fork
**C** – power combiner
**LM** - low-frequency modulation (ramp)
**HM** - high-frequency modulation
**CEU** - control electronics unit
THz QEPAS Performance in Locked Mode and Long-term Stability

Stepwise methanol concentration measurements

- **Lock-in $\tau = 100$ ms**

N2

NEC = 7 ppm (@ a laser power of 40 $\mu$W & a 4sec lock-in constant)

Absorption coefficient normalized to detection bandwidth and optical power:

$NNEA = 2.0 \times 10^{-10} \ \text{cm}^{-1}\text{W(Hz)}^{-1/2}$

Proposed Intracavity-QEPAS (I-QEPAS) Sensor System

- RT CW DFB QCL, $\lambda = 4.33$ microns
- Low noise current driver $\rightarrow$ narrow QC laser linewidth $\sim 1$ MHz
- Bow-tie cavity $\rightarrow$ 4 high reflectivity mirrors, R=99.9%
- Electronic Control Loop + PZT driver lock of cavity resonant frequency to QCL frequency

Comparison of I-QEPAS with Other Trace Gas Sensing Techniques

Cylindrical Multi-pass Trace Gas Absorption Cell

- No movable parts
- Toroidal design corrects optical aberrations
- Flexibility for alignment
- High path-to-volume ratio

Shoe-box size instrumentation

Small and portable

L. Emmenegger et al, IQCLSW 2014, Policore, Italy
NO$_2$ Sensitivity Test at Jungfraujoch (3850m asl), Switzerland

L. Emmenegger et al, IQCLSW 2014, Policore, Italy
Isotopic Ratio Measurements of $\delta^{18}$O (‰) & $\delta^{13}$C (‰) performed at the Jungfraujoch (3850m asl), Switzerland

Allan-Werle variance plot

L. Emmenegger et al, IQCLSW 2014, Policore, Italy
Development of robust, compact, sensitive, selective mid-infrared trace gas sensor technology based on room temperature, continuous wave DFB laser diodes and high performance QCLs for environmental monitoring and medical diagnostics.

Interband cascade and quantum cascade lasers were used in TDLAS, PAS and QEPAS based sensor platforms.

Eight target trace gas species were detected with a 1 sec sampling time:

- C₂H₆: ~3.36 µm, detection sensitivity of 740 pptv using TDLAS
- NH₃: ~10.4 µm, detection sensitivity of ~1 ppbv (200 sec averaging time)
- NO: ~5.26 µm, detection limit of 3 ppbv
- CO: ~4.61 µm, minimum detection limit of 2 ppbv
- SO₂: ~7.24 µm, detection limit of 100 ppbv
- CH₄ and N₂O: ~7.28 µm, detection limits of 13 and 6 ppbv, respectively
- H₂O₂: ~7.73 µm, detection limit of 75 ppb

New target analytes: CH₂O and C₂H₆O