Recent Advances in Infrared Semiconductor based Chemical sensing Technologies

F.K. Tittel, L. Dong, A.A. Kosterev, R. Lewicki and D. Thomazy
Rice Quantum Institute, Rice University, Houston, TX, USA
http://ece.rice.edu/lasersci/

• Motivation: Wide Range of Trace Gas Sensing
• Key Characteristics of QC Lasers: Oct. 2009
• Quartz enhanced Photoacoustic Spectroscopy
• Selected Applications of Trace Gas Detection
  ▪ NH$_3$ Detection for Environmental and Medical Applications
  ▪ Nitric Oxide detection
• Future Directions and Outlook
  ▪ Development of Semiconductor Laser Arrays
  ▪ Monitoring of broadband absorbers (Detection of UF$_6$)
  ▪ Optical Power Built-up Cavity (OPBC) for QEPAS Sensor

Work supported by NSF, NASA, DoE and the Robert Welch Foundation
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 Health and the Life Sciences
- Technologies for Law Enforcement and National Security
- Fundamental Science and Photochemistry
Existing Methods for Trace Gas Detection

Non-Optical

Mass Spectroscopy

Chemical

Gas Chromatography

Electro Chemical

Chemiluminescence

Black Body Sources

Fourier Transform

Gas Filter Correlation

Optical

Coherent Sources

Microwave Spectroscopy

Laser Spectroscopy
Basics of Optical Trace Gas Analyzers

**Beer-Lambert’s Law of Linear Absorption**

\[ I(\nu) = I_0 e^{-\alpha(\nu) P_a L} \]

- \( \alpha(\nu) \) - absorption coefficient [cm\(^{-1}\) atm\(^{-1}\)]; L - path length [cm]
- \( \nu \) - frequency [cm\(^{-1}\)]; \( P_a \) - partial pressure [atm]

\[ \alpha(\nu) = C \cdot S(T) \cdot g(\nu - \nu_0) \]

- \( C \) - total number of molecules of absorbing gas/atm/cm\(^3\) [molecule/cm\(^3\) · atm\(^1\)]
- \( S \) - molecular line intensity [cm · molecule\(^{-1}\)]
- \( g(\nu - \nu_0) \) - normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

**Key Requirements:** Sensitivity, specificity, rapid data acquisition and multi-species detection

**Optimum Molecular Absorbing Transition**
- NIR Overtone or Combination Bands
- MIR Fundamental Absorption Bands

**Long Optical Pathlengths**
- Multipass Absorption Cell White, Herriott)
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector); Standoff and Remote Detection
- Fiberoptic evanescent wave Spectroscopy

**Spectroscopic Detection Schemes**
- Wavelength or Frequency Modulation
- Balanced Detection
- Zero-air Subtraction
- Photoacoustic Spectroscopy (PAS or QEPAS)
- Laser Induced Breakdown Spectroscopy
Molecular Absorption Spectra within the two Mid-IR Atmospheric Windows

Source: HITRAN 2000 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 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>
Key Characteristics of mid-IR QCLs and ICL Sources-2009

- **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 r 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 and ICLs at TEC/RT temperatures**
  - Pulsed and CW powers of ~ 1.5 W; high temperature operation ~300K
  - >50 mW, TEC CW DFB @ 5 and 10 μm
  - > 600 mW (CW FP) @ RT; wall plug efficiency of ~15 % at 4.6μm;
Quantum Cascade (QC), Interband (IC) and GaSb Laser Availability in Oct. 2009

- **Commercial Sources**
  - Adtech, CA
  - Alpes Lasers, Switzerland & Germany
  - Alcatel-Thales, France
  - Corning, NY
  - Hamamatsu, Japan
  - Physical Sciences, Inc (Maxion Technologies, Inc),
  - Nanoplus, Wuerzburg, Germany

- **Research Groups**
  - Harvard University
  - Fraunhofer-IAF, Freiburg, Germany
  - NASA-JPL, Pasadena, CA
  - Naval Research Laboratories, Washington, DC
  - Northwestern University, Evanston, IL
  - Princeton University (MIRTHE), NJ
  - Sheffield, UK
  - State University of New York
  - Technical University, Zuerich, CH
  - University of Montpelier, France
Quartz Enhanced
Photoacoustic Spectroscopy
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 – 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 ~32.8 kHz
- Force constant ~26800 N/m
- Electromechanical coefficient ~$7 \times 10^{-6}$ C/m
QEPAS spectraphone

Microresonator tubes

- Must be close to the QTF but not touching it (30-50 mm gaps).
- Inner diameter 0.41 mm; 10% lower signal with 0.6 mm diameter tubes.
- Each piece ~5mm long (~1/2 for sound at 32.8 kHz)

Gain: ×10 to ×20

Windows

- Must be tilted to prevent the reflected light from going back into the microresonator.
- Exact positioning is not important, to the best of our current knowledge.
Comparative Sizes of QEPAS & PAS ADMs

Optical multipass cell (100 m):
$l \sim 70 \text{ cm}$, $V \sim 3000 \text{ cm}^3$

Resonant photoacoustic cell (1000 Hz):
$l \sim 60 \text{ cm}$, $V \sim 50 \text{ cm}^3$

QEPAS spectrophone:
$l \sim 1 \text{ cm}$, $V \sim 0.05 \text{ cm}^3$
Alignment-free QEPAS Absorption Detection Module
Recent Applications of QCL 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)
### Important Biomedical Target Gases in Exhaled Human Breath

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Biological/Pathology Indication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>$CH_3(CH_2)_3CH_3$</td>
<td>Lipid peroxidation, oxidative stress associated with inflammatory diseases, immune responses, transplant rejection, breast and lung cancer</td>
</tr>
<tr>
<td>Ethane</td>
<td>$C_2H_6$</td>
<td>Lipid peroxidation and oxidative stress</td>
</tr>
<tr>
<td>Carbon Dioxide isotope ratio</td>
<td>$^{13}CO_2 / ^{12}CO_2$</td>
<td>Marker for Helicobacter pylori infection, Gastrointestinal and hepatic function</td>
</tr>
<tr>
<td>Carbonyl Sulfide</td>
<td>COS</td>
<td>Liver disease &amp; acute rejection in lung transplant recipients (10-500 ppb)</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>CS$_2$</td>
<td>Schizophrenia</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>Hepatic encephalopathy, liver and renal diseases, fasting response</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>Cancerous tumors, breast cancer (400-1500 ppb)</td>
</tr>
<tr>
<td>Nitric Oxide</td>
<td>NO</td>
<td>Inflammatory and immune responses (e.g., asthma) and vascular smooth muscle response (6-100 ppb)</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>$H_2O_2$</td>
<td>Airway Inflammation, Oxidative stress (1-5 ppb)</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>Smoking response, CO poisoning, vascular smooth muscle response, platelet aggregation (400-3000 ppb)</td>
</tr>
<tr>
<td>Ethylene</td>
<td>$H_2C=CH_2$</td>
<td>Oxidative stress, cancer</td>
</tr>
<tr>
<td>Acetone</td>
<td>$CH_3COCH_3$</td>
<td>Fasting response, diabetes mellitus response, ketosis</td>
</tr>
</tbody>
</table>
Noise-equivalent concentration (NEC) is 6 ppb for a 1s time constant and 20mW excitation power at 1046.4 cm\(^{-1}\) (110 Torr)
- Controlled flow
- Continuous control of mouth pressure
- Continuous monitoring of CO$_2$ concentration (capnograph) and its use in QEPAS data processing

T.Risby: 12:00 Sept.7 & Poster
Wavenumber dependance of CW RT DFB QCL output power

NH₃ absorption line of interest (967.35 cm⁻¹) 2009 Hamamatsu 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)
Motivation for Nitric Oxide Detection

- Environmental pollutant
  - Product of fossil fuel combustion process (automobile and power plant emissions)
  - Precursor of smog and acid rain
EC-QCL Based Faraday Rotation Spectrometer

- EC-QCL Operating at 5.3μm – NO Fundamental Band
- 44cm effective optical pathlength
- Rochon Polarizer Extinction Ratio <10⁻⁵
- Not sensitive to water interference
- Sensitivity Not Limited by Interference Fringes
- Gas Cell Volume (~ 250ml)
- Easy and Robust Optical Alignment
- Continuous NO Monitoring (Absorption Line Locking enabled with mode-hop free tuning using Zeeman Modulation at 3rd harmonic)
Faraday Rotation Spectroscopy of Nitric Oxide

- 96 ppb NO on N₂
- $I_{\text{cd}}=850$ mA, $P=40$ Torr
- $T_C=1$ s, $\text{SEN}=2$ mV
- $\text{freq}_{\text{mod}}=950$ Hz, $B=110$ Gauss
- $\Phi=3^\circ$ from crossed analyzer
- LN cooled InSb detector

SNR=253
MDL(1σ)=380 ppt

1σ=4.325 μV
Future Directions and Outlook of Chemical Trace Gas Sensing Technology
High power fiber-coupled QCL for NO detection

- LASER SOURCE EC-QCL (Daylight Solutions, Inc)
  - Tuning range 5.13-5.67 μm
  - Maximum tuning Rate 38 nm/sec
  - Highest optical power: ~250 mW
  - TE cooling, RT operation

Collaboration with: V. Spagnolo
Politecnico Bari and CNR-LIT³
Fiber coupled QCL and QEPAS detection system

- High coupling efficiency of laser output to fiber
- Beam size matching to QEPAS after collimation
- Aspheric lenses for both coupling and re-collimating.
- 86% coupling efficiency

FIBER
Material: AsSe$_3$.
- 22 µm core diameter
- Single mode operation
- FC-PC termination
- AR Coated.

Collaboration with: V. Spagnolo, Politecnico Bari and CNR-LIT$^3$
Monitoring of Broadband Absorbers

- Freon 125 ($C_2HF_5$)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals, e.g. chemical warfare agents
- Acetone ($CH_3COCH_3$)
  - Recognized biomarker for diabetes
- TATP (Acetone Peroxide, $C_6H_{12}O_4$)
  - Highly Explosive
- Uranium Hexafluoride ($UF_6$)
Absorption spectrum of gas mixture under investigation and observed spectral features identification.


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

Also: G. Baldaccini et al., Nuovo Cimento 8, 203, 1986
QEPAS MDAL comparison with CRDS, ICOS & TDLAS

Minimum Detectable Absorption Loss (MDAL) $[\text{cm}^{-1}/\sqrt{\text{Hz}}]$ 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 + μresonator (estimated): $\sim 7 \times 10^{-12}$

QEPAS-OPBC can be as sensitive as CRDS, ICOS and TDLAS as well as retain most of the merits of QEPAS
DFB QCL array performance

Emission spectrum of a DFB-QCL array
Pulsed operation (80kHz, 50ns) at room temperature
Grating coupling strength, |\(\kappa L|\approx10\)

Side-mode suppression of >20dB

Temperature tuning by DC current

Lee, Belkin, et al., APL 2007
Ultra-compact Diode Laser based Trace Gas Sensor
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 near and mid-IR intersubband and interband quantum cascade lasers
  - Further development of spectraphone 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
Merits of QEPAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Low sensitivity to environmental acoustic noise
- Significant reduction of sample volume (< 1 mm³)
- Applicable over a wide range of pressures
- Rugged transducer-quartz monocystal, which can operate in a wide range of pressures and temperatures and is humidity insensitive
- Ultra-compact, rugged and low cost detection module (compared to other laser based sensor architectures)
## QEPAS Performance for 13 Trace Gas Species (Sept. ‘09)

<table>
<thead>
<tr>
<th>Molecule (Host)</th>
<th>Frequency, cm(^{-1})</th>
<th>Pressure, Torr</th>
<th>NNEA, cm(^{-1})W/Hz(^{0.5})</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\times10(^{-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>&lt;4.3\times10(^{-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\times10(^{-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\times10(^{-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\times10(^{-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\times10(^{-9})</td>
<td>16</td>
<td>0.24</td>
</tr>
<tr>
<td>CO(_2) (breath ~100% RH)</td>
<td>6361.25</td>
<td>150</td>
<td>8.2\times10(^{-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\times10(^{-9})</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>CO(_2) (N(_2)+1.5% H(_2)O)*</td>
<td>4991.26</td>
<td>50</td>
<td>1.4\times10(^{-8})</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\times10(^{-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\times10(^{-7})</td>
<td>13</td>
<td>0.5</td>
</tr>
<tr>
<td>CO (propylene)</td>
<td>2196.66</td>
<td>50</td>
<td>7.4\times10(^{-8})</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\times10(^{-8})</td>
<td>19</td>
<td>0.007</td>
</tr>
<tr>
<td>C(_2)H(_2)OH (N(_2))**</td>
<td>1934.2</td>
<td>770</td>
<td>2.2\times10(^{-7})</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>C(_2)HF(_5) (N(_2))***</td>
<td>1208.62</td>
<td>770</td>
<td>7.8\times10(^{-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\times10(^{-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)\times10\(^{-9}\) cm\(^{-1}\)W/√Hz (1,800; 10,300 Hz) for NH\(_3\)*. (**)

5.3 μm QCL based QEPAS Gas Sensor for NO detection

External Amplitude Modulation:

- QTF is used as a mechanical chopper at $f \approx 32\text{kHz}$
- No chirp associated with the laser current modulation
- High resolution mode-hop-free tuning is possible
High resolution EC-QCL based NO Spectrum

4.2% NO in N₂ at 600 Torr

- HITRAN 2005 (600 Torr, path: 1 cm)
- HITRAN 2005 (5 Torr, path: 1 cm)
- QEPAS measurement

Normalized QEPAS Amplitude [mV/mW]

Absorbance (base 10)

Wavenumber [cm⁻¹]