Mid-Infrared Laser based Gas Sensor Technologies for Environmental Monitoring, Medical Diagnostics, Industrial and Security Applications

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- New Laser Based Trace Gas Sensor Technology
  - Novel Multi-pass Absorption Cell & Electronics
  - Quartz Enhanced Photoacoustic Spectroscopy
- Examples of Mid-Infrared Sensor Architectures
  - C_3H_6, NH_3, NO, CO, and SO_2
  - Future Directions of Laser Based Gas Sensor Technology and Conclusions

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. measurement of isotopes)
  - 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 Medical Diagnostics and the Life Sciences
- Technologies for Law Enforcement, Defense and Security
- Fundamental Science and Photochemistry

Laser based Trace Gas Sensing Techniques

- Optimum Molecular Absorbing Transition
- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)
- Long Optical Pathlength
- Multi-pass Absorption Cell (White, Herriot, Chernin)
- Cavity Enhanced and Cavity Ringdown Spectroscopy
- Open Path Monitoring (with retro-reflector), Standoff and Remote Detection
- Fiber-optic Diode Laser Wave Spectroscopy
- Spectroscopic Detection Schemes
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic & Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

Other spectroscopic methods

- Faraday Rotation Spectroscopy (limited to paramagnetic chemical species)
- Differential Optical Design Spectroscopy (DODIS)
- Noise Immune Cavity Enhanced-Optical Heterodyne Molecular Spectroscopy (NICE-OHMS)
- Frequency Comb Spectroscopy
- Laser Induced Breakdown Spectroscopy (LIBS)

Mid-IR Source Requirements for Laser Spectroscopy

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<th>REQUIREMENTS</th>
<th>IR LASER SOURCE</th>
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<td>Field deployable in harsh environments</td>
<td>Compact, Robust, Packaging, Low Noise</td>
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Key Characteristics of Mid-IR QCL & ICL Sources – Oct 2012

- **Band - structure engineered devices**
  - Emission wavelength is determined by layer thickness - MBE or MOCVD. Type II QCLs operate in the 3 to 25 μm spectral region.
  - Type I and GaSb based ICLs can cover the 3 to 6 μm spectral range.
  - Compact, reliable, stable, long lifetime, and commercial availability.
  - Faraday-Pert (FP), single mode (DFB) and multi-wavelength devices.

- **Wide spectral tuning range in the mid-IR**
  - > 5 μm: using injection current control for DFB devices
  - 80-200 cm⁻¹ using temperature control for DFB devices
  - 152 cm⁻¹ (20% of c.w.) using an external, passing-current and FP-chip with heterogeneously cascadic active region design, also QCL DFB Array

- **Narrow spectral linewidths**
  - 50 MHz for 1.39 μm DFB with frequency stabilization (h-0.0004 cm⁻¹)

- **High-pulsed and CW powers of QCLs at TEC/CRT**
  - Room temperature pulsed power > 30 W with 20% wall plug efficiency and CW power > 1 W with 20% wall plug efficiency
  - > 7 W, TEC CW DFB at 6 μm
  - > 50 mW (CW/PP) @ 6 μm, wall plug efficiency of ~17% at 4.5 μm.

Improvements and New Capabilities of QCLs and ICLs

- **Optimum wavelengths (3 to 20 μm) and power (10 mW to >1 W)** at room temperature (>15 °C and < 20 °C) with state-of-the-art fabrication/processing methods based on MBE and MOCVD, good wall plug efficiency and lifetime (>20,000 hours) for detection sensitivities from 5 ppm with low electrical power budget.
- **Stable single TEM00 transverse and axial mode, CW and pulsed operation of mid-infrared laser sources (narrow linewidth of ~300 MHz to < 1 kHz)**
- **Mode hop-free ultra-broad wavelength tunability for detection of beam absorbers and multiple absorption lines based on external cavity or mid-infrared semiconductor arrays**
- **High beam quality for directionality and/or cavity mode matching, implementation of innovative collimation concepts**
- **Fast data acquisition based on fast time response**
- **Compact, robust, readily, commercially available and affordable in order to be field deployable in harsh operating environments (temperature, pressure, etc.)**

Motivation for Mid-infrared C₂H₅ Detection

- Atmospheric chemistry and climate
  - Fossil fuel and biofuel consumption,
  - Biomass burning,
  - Vegetation/soil,
  - Natural gas leak
- Oil and gas prospecting
  - Application in medical breath analysis (a non-invasive test to identify and monitor different diseases)
  - Asthma
  - Schizophrenia
  - Lung cancer
  - Leukemia
  - Vitamin E deficiency

![HITRAN absorption spectra of C₂H₅, CCl₃, and H₂O](image)

C₂H₅ Detection with a 3.35 μm DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics

- Minimum detectable C₂H₅ concentration is ~120 ppbv (2σ: 1 s time resolution)

![Schematic diagram of C₂H₅ gas sensor using a compact 2-pass multipass absorption cell and control electronics](image)

Motivation for NH₃ Detection

- Monitoring of gas separation processes
- Detection of ammonium-nitrate explosives
- Spacecraft related gas monitoring
- Monitoring NH₃ concentrations in the exhaust stream of NOₓ 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)

Conventional PAS

- Laser beam, power $P$
- Modulated ($P$ or $λ$) at $f$
- $S \approx \frac{Q α P}{fV}$
- $NNEA = \frac{\alpha_{max} P}{\sqrt{M}} \frac{1}{\sqrt{Hz}}$

![Diagram of conventional PAS](image)
Atmospheric NH₃ Measurements using an EC-QCL PAS Sensor

Schematic of a Dantoni Solutions CRW-10 34 μm TEC EC-QCL based PAS NH₃ Sensor

Sporadic increased NH₃ concentration levels related to emissions by the Parish electric power plant, TX

The Parish electric power plant is located near the Bracon River in Fort Bend County, Texas (-27 miles SW of downtown Houston)

From Conventional PAS to QEPAS

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 (-10⁹) - Sine from thermal noise to breakdown deformation
- 300 K noise: 10⁻¹¹ cm
- Breakdown: 10⁻⁸ cm
- Wide temperature range from 1.6 K to ~700 K

Acoustic Micro-resonator (μR) tubes
- Optimum inner diameter 0.6 mm, μR-QTF gap is 25-50 μm
- Optimum μR tubes must be -4.4 mm long (-3/4 of G/2), for sound at 32.8 kHz
- SNR of QTF with μR tubes ~30 (depending on gas composition and pressure)

NH₃ Detection due to a Fire resulting from a Truck Collision

Estimated locally NH₃ emissions from the Houston Ship Channel area is about 67.5 tons. Multiple particles loaded with NH₃ related salts were caught by the [www.chrm.org]

QEPAS based NH₃ Gas Sensor Architecture
**Real-time exhaled human NH₃ Breath Measurements**

- Acute pressure (black), CO₂ (red), and NH₃ (blue) profiles of a single breath exhalation lasting 480 s.
- Successful testing of a 2nd generation breath ammonia sensor (in a clinical environment) (Johns Hopkins, Baltimore, MD) and St. Luke's Hospital, Bethlehem, PA.
- Minimum detectable concentration of NH₃ is ~6 ppbv at 407.25 cm⁻¹ (1σ; 1 s time resolution).

**Motivation for Nitric Oxide Detection**

- Atmospheric Chemistry
- Environmental pollutant gas monitoring
  - NOₓ 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

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

- Emission spectra of a 1900 cm⁻¹ TEC CW DFB QCL and HITRAN Simulated spectra
- Output power: 117 mW @ 23°C

**QCL based WMS QEPAS NO Gas Sensor Platform**

- Schematic of a QCL-QEPAS based Gas Sensor
- Compact Prototype NO Sensor (September 2012)

**Performance of 2012 CW DFB-QCL based WMS QEPAS NO Sensor Platform**

- 2F QEPAS signal (sawtooth) and reference 3F signal (narrow) when laser was tuned across 1900.00 cm⁻¹ (1σ)
- 2F QEPAS signal amplitude for 95 ppbv NO when laser was locked on the 1900.00 cm⁻¹ line
- Minimum detectable NO concentration is: ~3 ppbv (1σ; 1 s time resolution)
Motivation for Carbon Monoxide Detection

- 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 tropospheric ozone formation and changing the level of greenhouse gases (e.g., CH₃).

- Public Health
  - Extremely dangerous to human life even at a low concentrations. Therefore CO must be carefully monitored at low concentration levels.
  - CO in medicine and biology
    - Hypertension, neurodegenerations, heart failure and inflammation have been linked to abnormality in CO metabolism and function.

Performance of a NWU 4.6 μm high power CW TEC DFB QCL

![Graph showing the performance of a NWU 4.6 μm high power CW TEC DFB QCL.](Image)

CW DFB-QCL based CO QEPAS Sensor Results

![Images and graphs showing CW DFB-QCL based CO QEPAS Sensor Results.](Images)

Minimum detectable CO concentration is: ~2 ppmv (1σ: 1 x time resolution)

Motivation for Sulfur Dioxide Detection

- Premature air pollutant
- Emitted from coal fired power plants (~72%) and other industrial facilities (~28%)
- In atmosphere SO₂ reacts to sulfate acid
- Primary contributor to acid rain
- SO₂ reacts to form sulfate aerosols
- Premix SO₂ exposure for 1 hour ~71 ppb
- SO₂ exposure affects lungs and causes breathing difficulties
- Currently reported annual average atmospheric SO₂ concentrations range from ~1 - 6 ppb

![Images and graphs showing CW DFB-QCL based SO₂ QEPAS Results.](Images)

Close-up of a NWU 4.6 μm high power CW TEC DFB QCL

- CW DFB-QCL based SO₂ QEPAS Results

Optimum NH₃ Line Selection for a 10.34 μm CW TEC DFB QCL

![Images and graphs showing Optimum NH₃ Line Selection for a 10.34 μm CW TEC DFB QCL.](Images)

- 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 967.53 cm⁻¹ NH₃ absorption line in the α R band.

- Absorption x 10⁻³ [m⁻¹]

QEPAS Based TATP Detection

- QEPAS Based TATP Detection

- DIEHL

- JLU Clausthal
Potential Integration of a CW DFB- QCL and QEPAS Absorption Detection Module

Summary and Outlook

- Laser spectroscopy with a mid-infrared, room temperature, continuous wave, DFB laser diode and high performance DFB-QCL is a promising analytical approach for real time atmospheric measurements and breath analysis.
- Six infrared semiconductor lasers from Nippon Laser, Daylight Solutions, Maxscan Technologies (FST), Hamamatsu, Northwestern University and AdtechOptics were used recently (2011-2012) by means of TDLAS, PAS and QEPAS.
- Seven target trace gas species were detected with a 1 sec sampling time:
  - CO at $0.1-0.3$ ppm with a detection sensitivity of 100 ppb using TDLAS
  - NO at $0.6$ ppm with a detection sensitivity of $\pm$ 1 ppm (200 sec averaging time).
  - NO at $0.3$ ppm with a detection limit of 1 ppb.
  - SO$_2$ at $0.2$ ppm with a detection limit of 1 ppb.
  - CH$_4$ at $0.2$ ppm with a detection limit of 2 ppb.
  - CH$_4$ and CH$_3$ with $0.2$ ppm sensitivity and detection limits of 20 and 7 ppb, respectively.
- New target analytes such as OCS, CH$_2$O, HONO, H$_2$O$_2$, C$_2$H$_4$, C$_3$H$_6$, and C$_6$H$_6$
- Monitoring of broadband absorbers: acetone and UF$_6$
- Compact, robust sensitive and selective single frequency, mid-infrared sensor technology is capable of performing precise and accurate concentration measurements of trace gases relevant in environmental, biomedical, industrial monitoring and national security.

Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm$^3$ to $\sim$2cm$^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 noise, half energy in the TF symmetric mode
- Absence of low-frequency noise: SNR scales as $\sqrt{t}$ up to $\sim$3 hours as experimentally verified
- QEPAS: some challenges
  - Cost of Spectrophone assembly
  - Sensitivity scales with laser power
  - Effect of H$_2$O
  - Responsivity depends on the speed of sound and molecular energy transfer processes
  - Cross sensitivity issues

Long Term Stability of QEPAS based Sensor for NO Concentration Measurements in Exhaled Breath

Future Directions and Outlook

- New target analytes such as OCS, CH$_2$O, HONO, H$_2$O$_2$, C$_2$H$_4$, C$_3$H$_6$, and C$_6$H$_6$
- Ultra-compact, low cost, robust sensors (e.g., C$_2$H$_2$, NO, CO…...)
- Monitoring of broadband absorbers: acetone, TATP acetone peroxide, UF$_6$
- Optical power build-up cavity designs
- Development of trace gas sensor networks