Laser based Chemical Sensor Technology: Recent Advances and Applications

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- Motivation: Wide Range of Chemical Sensing
- Fundamentals of Laser Absorption Spectroscopy
- New laser sources and sensing technologies
- Selected Applications of Trace Gas Detection
  - Detection of formaldehyde and nitric oxide
  - Volcanic gas emission studies
  - Quartz Enhanced Photacoustic Spectroscopy (QEPS)
- Future Directions 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, 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 Industries
- Spacecraft and Planetary Surface Monitoring
  - Crew Health Maintenance & Life Support
  - Applications in Medicine and Life Sciences
  - Technologies for Law Enforcement and National Security
- Fundamental Science and Photochemistry

International Space Station

Worldwide Megadirty Mega Cities

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Megacity Air Pollution: Houston, TX

Trace Gas Monitoring in a Petrochemical Plant

University of Szeged, Hungary
Fundamentals of Laser Absorption Spectroscopy

Requirements:
- Sensitivity
- Selectivity
- Multi-gas Capabilities
- Speed of Data Acquisition

Optimized Molecular Absorption Transition
- Combination Bands (NIR)
- Fundamental Absorption Bands (1000-2000 nm)

Laser Optical Parameters
- Multigas Absorber
- Cavity Enhanced, Cavity Ringdown
- Transmittance Spectroscopy
- Open Path Monitoring (with retroreflectors)
- Porous Metal Masking (Heterodyne measurement)

Spectroscopic Detection Schemes
- Frequency Modulation
- Phase Modulation
- Raman Detection
- Photodissociation Spectroscopy

Simulated CO₂ Absorption Spectrum

Existing Methods for Trace Gas Detection

- Non-Optical
  - Mass Spectroscopy
  - Gas Chromatography
  - Electro-Chemical
  - Chemiluminescence

- Optical
  - Non-Dispersive
    - Fourier Transform
    - Gas Filter Correlation
  - Dispersive
    - Microwave Spectroscopy
    - Laser Spectroscopy
IR Laser Sources and Wavelength Coverage

Quantum Cascade Laser: Basic Facts

- Semiconductor lasers (III-V materials)
- Multiple quantum-well heterostructure
- Intersubband transitions
- Band-structure engineering (emission wavelength defined by the layer thickness – MBE, MOVD etc.)
- Independent of material energy bandgap
- Cascading (each electron creates N laser photons)
- Number of periods N determines laser power
- High reliability, long lifetime
- Compact

43 nm

Key Characteristics of Mid-IR QCLs and ICLs

- Laser wavelengths cover the entire Mid-IR range from 3 to 24 μm
- High power (>500 mW cw, >5W peak for pulsed)
- High spectral purity - single frequency with DFB structure or external cavity
- Continuous tuning by temperature (~10 cm⁻¹) or current (~1 cm⁻¹) or external cavity (>200 cm⁻¹ in pulsed mode)
- High reliability: low failure rate, long lifetime and robust
- Capable of room temperature operation
  - Pulsed: up to +150ºC
  - CW: up to RT

Wavelength Coverage of IR Detectors

Motivation for Monitoring of H₂CO

- Toxic pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products (e.g., resins, foam)
- Atmospheric H₂CO is a key hydrocarbon oxidation product which leads to the photochemical generation of ozone and release of hydrogen radicals
- Medically important gas

H₂CO Detection in Ambient Air at 3.53 μm

Transmission

concentration (8.49 ± 0.57) ppbv

goodness of fit

\[ \chi^2 = 3.4272 \times 10^{-10} \]

\[ a = 1.852 \times 10^{-5} \]
DFG and ICL based H₂CO Sensor for studying Urban Air Pollution

Detection of Formaldehyde

No significant difference in line intensity between the vibrational band v₃ (C=O stretch) at 5.7 μm and bands v₂ and v₁ (C-H stretches) at 3.6 μm

Accessible with QCLs  Accessible with ICLs

TexAQS II Field Campaign Summer 2006

- To study ozone formation and transport, a coordinated field study was conducted in August and September 2006 in Houston
- 5 aircraft, two ground chemistry sites, ~20 periphery and meteorological sites
- Participation by ~300 scientists from academia, national laboratories, industry and government

Moody Tower, UH Campus

Dual CW ICL Based Trace Gas Sensor for TexAQS '06

Measurement technique:
- Two CW DFB ICLs
- 100 m Herriott multipass cell
- Both laser beams co-aligned with a 50/50 beam splitter
- Two optical channels and two detectors:
  - Signal
  - Reference (coast line locking)
- Wavelength modulation (20)
- Phase sensitive detection at two different modulation frequencies (lock-in amplifiers, 2 for each channel)
- Concentration measurement by linear least squares fitting of the pre-acquired reference spectrum (calibration mixture) to the sample spectrum

- Automatic self-calibration
- Automatic LN₂ refilling system
- Remote operation

Sensor Performance – Two Channel Detection

H₂CO concentration (ppb) versus Wind Direction

Mean H₂CO concentration versus wind direction at sampling site (tons in ppb)

Major ethylene sources in Harris County

Dilution with UHP N₂

Dilution with 100ppb C₄H₄ in N₂

- Linear response of the sensor
- No cross-talk between channels
- C₄H₄ sensitivity: ~150 ppb (1σ) in 1 sec
- H₂CO sensitivity: ~3.5 ppb (1σ) in 1 sec
NO as a Biomarker

- NO is biochemically involved in most tissues and physiological processes in the human body
- NO excretion increases in exhaled breath in lung diseases such as:
  - Asthma
  - Chronic Obstructive Pulmonary Disease
  - Acute lung rejection
  - Acute respiratory distress syndrome
  - Pneumonia (useful for intubated patients)

Why is Breath so Useful?

- Breath can be analyzed non-invasively from spontaneously breathing human subjects (neonate to the elderly), laboratory animals (from mice to horses), or from intubated patients (in ORs or ICUs).
- Breath can be sampled in the clinic, the home, the field, at the patient bedside, or in the physician’s office by nurses, technicians, physicians and by the patient themselves.
- Breath analysis can be used for nutritional studies, exercise studies, to detect disease, stage disease, to monitor therapy or to monitor treatment.

Dogs Can Smell Cancer

Innovative Cancer Therapeutics (March 2006)

Diagnostic Accuracy of Canine Scent Detection in Early-and Late-Stage Lung and Breast Cancers

By smelling breath samples, dogs detected breast and lung cancer patients with accuracies of 88% and 93%, respectively.

The evidence is clear - gas phase molecules are uniquely associated with cancer. We need sensors that can detect these biomarkers.

Chronic Obstructive Pulmonary Disease

- Chronic obstructive pulmonary disease (COPD)
- Accumulation of inflammatory products in the small airway lumen and wall
- Alveolar NO
  - Reflects peripheral lung inflammation and the response to anti-inflammatory treatment
  - Not affected by smoking or inhaled corticosteroids
Curcumin Pilot Study

- Curcumin (Turmeric)
  - Polyphenol (diferuloylmethane)
  - Anti-inflammatory and anti-oxidant
- Hypothesis: Curcumin reduces indices of inflammation in individuals with severe COPD

Breath Biomarkers in Humans

As many as 400 different molecules in breath, many with well defined biochemical pathways

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
<th>Physiological basis/Pathology indication</th>
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</thead>
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<td>Lactate</td>
<td>ppm</td>
<td>Metabolic disorders, diabetes</td>
</tr>
<tr>
<td>Acetone</td>
<td>ppm</td>
<td>Glucose metabolism, type 1 and type 2 diabetes</td>
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<tr>
<td>Lactate</td>
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<tr>
<td>Acetone</td>
<td>ppm</td>
<td>Glucose metabolism, type 1 and type 2 diabetes</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>ppm</td>
<td>Inflammation, cardiovascular disease</td>
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<tr>
<td>Carbon dioxide</td>
<td>ppm</td>
<td>Respiratory disorders, lung diseases</td>
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<td>Oxygen</td>
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<td>Carbon monoxide</td>
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<td>Nitrogen dioxide</td>
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</tr>
<tr>
<td>Sulfur dioxide</td>
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<td>Respiratory disorders, lung diseases</td>
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</table>

Laser-based ICOS Nitric Oxide Sensor

- Online NO concentration measurements at 30Hz.
- Comparison of ICOS and commercial chemiluminescence sensor (shaded - solid line)
- NO-NO concentrations (ppm)
- Time (sec) averaged

Simulated NO Absorption Spectrum

- Q-branch (absorbance for LMR spectroscopy) ~187 cm⁻¹
- Why is it difficult to obtain a DPB-QCL at 187 cm⁻¹?
  - Absorption lines in the P and R branches are stronger and therefore more suitable for most LAS applications
  - Fabrication process of a DPB is costly
  - Q-branch is very narrow which additionally requires a higher precision in DPB fabrication

Volcanological Applications

- CO₂, the most abundant component of volcanic gases after H₂O
- d¹³C is a sensitive tracer of magmatic vs. hydrothermal or groundwater contributions to volcanic gases
- Monitoring d¹³C can be used in eruption forecasting and volcanic hazard assessment
**CO₂ Absorption Line Selection Criteria**

- Three strategies:
  - Similar strong absorption of ¹²CO₂ and ¹³CO₂ lines
  - Very sensitive to temperature variations
  - Similar transition lower energies
    - Requires a dual path length approach to compensate for the large difference in concentration between major and minor isotopic species or
    - Can be realized if different vibrational transitions are selected for the two isotopes (4.35 μm for ¹²CO₂ and 2.76 μm for ¹³CO₂)

- For the first 2 strategies both absorption lines must lie in a laser frequency scan window
- Avoid presence of other interfering atmospheric trace gas species

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Widely Tunable, CW, TEC Quantum Cascade Lasers

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**High resolution CO₂ absorption spectrum at 2311 cm⁻¹**

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**Tunable external cavity QCL based spectrometer, 2006**

- Fine wavelength tuning
- PZT controlled EC-length
- PZT controlled grating angle
- QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + chilled water cooling)

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**Mid-IR NO Absorption Spectra acquired with a Tunable TEC QCL**

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**Wide Wavelength Tuning of a 5.3μm EC-QCL**

- Coarse wavelength tuning of 185 cm⁻¹ is performed by varying diffraction grating angle
- Access to Q(3,3) transition of NO at 1875.8 cm⁻¹ for LMR spectroscopy

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High resolution spectroscopy with a 5.3μm EC-QCL

- Mode hop free scan of up to 80cm⁻¹ with a resolution <0.001cm⁻¹ (30MHz) can be performed anywhere within the tuning range.

Performance of a 8.4 μm EC-QCL spectroscopic source

- Broader wavelength tunability
- Faster tuning speed
- All Solid state designs
  - MEMS
  - All electrical tuning (in collaboration with QC-L research groups)
  - Tunable Distributed Bragg Reflectors (DBR)
    (carrier-induced refractive index tuning)
  - Electronically tunable extraordinary transmission gratings (tunable mirrors and filters) (work presently carried out at Princeton)

First Report of PAS in 1880

- Alexander Graham Bell's "phonograph" used a voice coil to modulate a mirror which transmitted sunlight to a receiver containing a selenium resistor.
  - Nature, Sept. 23, 1886, pp. 500-503
From conventional PAS to QEPAS

Laser beam, power $P$

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

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

$N_{NEA} = \frac{\alpha P}{V}$ [cm$^3$/W/$\sqrt{\text{Hz}}$]

Quartz tuning fork (TF) as a resonant microphone

- Resonant frequency 8-32 kHz
- Excessively high Q factor: $Q_{\text{ultrasonic}}$ ~ 125 000, $Q_{\text{acoustic}}$ ~ 10 000 in ambient conditions
- Piezoelectric, requires no transducer
- Miniature size
- Mass produced for clocks – low cost

Quartz Tuning Fork based Spectrophone

Quartz Tuning Fork based Spectrophone

0.4 mm

3.8 mm

Equivalent Electrical Circuit of a Quartz TF

\[ \omega_0 = \frac{1}{\sqrt{LC}} \]

\[ Q = \frac{L}{R} \sqrt{\frac{C}{L}} \]

\[ \sqrt{\frac{1}{\omega_0^2}} = \frac{4kT}{R} \]

Typical QTF Resonance Curves

- Air, 760 Torr $Q_{\text{air}}$ = 13 270
- Vacuum $Q_{\text{vacuum}}$ = 95 500

Frequency, Hz

TF current, mA
Comparative Size of Absorbance Detection Modules (ADM)

- Optical multipass cell (100 m)
  - i<30 cm, f<3000 cm²
- Resonant photoacoustic cell (1000 Hz)
  - i<40 cm, f<50 cm²
- QEPAS specrophone
  - i<1 cm, f<0.05 cm²

Motivation for NH₃ Detection

- Monitoring of gas separation processes
- 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 dysfunctions)

Simulated Infrared NH₃ Absorption Spectra

QEPAS based Gas Sensor Architecture

NH₃ Measurements at an Oklahoma State University Research Feedyard

2ν3 Absorption Band of CH₄ (HITRAN)
Motivation for Monitoring of Freon 125 and acetone

- Freon 125 (C₂F₅H₆)
- Refrigerant (leak detection)
- Safe simulant for toxic chemicals e.g. chemical warfare agents
- Acetone (CH₃COCH₃)
- Recognized biomarker for diabetes

ICL based Quartz-Enhanced Photoacoustic Gas Sensor

Spectroscopy of Broadband Absorbers with Widely Tunable EC-QCL at λ = 8.4 μm

- Minimum detection limit (1σ) of ~4.5 ppb was obtained for Freon 125 with an average laser power of 6.6 mW
- Wide tunability enables excellent molecular selectivity for broadband absorbers

QEPAS ethanol spectrum between 1825 & 1980 cm⁻¹

Reference spectrum from the PNNL spectral database (red line). Sharp features on the ethanol spectrum correspond to the atmospheric water absorption lines (blue line depicts water absorption spectrum simulated using HITRAN database)

Merits of QEPAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immune to environmental noise - acoustic quadrupole
- Ultrasensitive sample volume (<1 mm³)
- Applicable over a wide range of temperatures and pressures, including atmospheric pressure
- Sensitivity is limited by the fundamental thermal TF noise: kₜF energy in the symmetric mode is directly observed
- Rugged and low cost compared to other spectroscopic techniques that require infrared detector(s)
- Sensitive to phase shift introduced by V-T relaxation processes – additional selectivity
- Potential for trace gas sensor networks

QEPAS Performance for 11 Trace Gas Species (June'07)

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<th>Molecule</th>
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For comparison: conventional PAS 1.5×10⁻² cm⁻¹/Hz⁻¹/Hz at 1.800 Hz for NH₃.

Future of Chemical Trace Gas Sensing

Existing Environmental Trace Gas Networks

- Fluxnet (pictured) (Oak Ridge National Laboratory)
  - http://www.fluxnet.org
- Carbon tracker (National Oceanic and Atmospheric Administration)
  - http://www.carbontracker.noaa.gov
- National Ecological Observatory Network (NEON) (National Science Foundation)
- Rely on sparse data (due to cost/size of sensors) or satellite data
- Deploy with other types of sensors (e.g., wind)

$H_2CO$ concentration (ppb) versus Wind Direction

Wireless Sensor Networks for Gas Sensing

- Each point called "mote"
- Advantages?
  - Spatial resolution
  - Measure fluxes
  - What is needed?
  - Low power
  - Low cost
  - Ultra miniature
  - Replicable
  - Autonomy

To internet via Base-station

Miniature QEPAS $CO_2$ sensor ($\lambda=2um$) v2.0 boards

Summary & Future Directions of mid-IR Sensor Technology

- Semiconductor Laser based Trace Gas Sensors
  - Compact, tuneable, and robust
  - High sensitivity (<10$^{-14}$) and selectivity (3 to 500 MHz)
  - Fast data acquisition and analysis
- Detector 1 kHz gain in data: $NO$, $CO$, $CH_4$, $C_2H_6$, $C_2H_4$, $H_2O$, $CO_2$, $N_2O$, $SO_2$, $NO_2$, $HS$, $NH_3$, and several isotopic species of $C$, $O$, $N$ and $H$
- New Applications of Trace Gas Detection
  - Distributed sensor networks for Environmental monitoring ($NO$, $CO$, $CH_4$, $C_2H_6$, $C_2H_4$, $H_2O$)
  - Sensing and diagnostic sensors for industrial process control and chemical analysis (HCN, NO, NH$_3$, H$_2$O)
  - Wearable sensors for Medical & Biomedical Diagnostics (NO, CO, COS, CO$_2$, $NH_3$, $C_2H_4$)
  - Hard-field sensors and sensor network technologies for Law Enforcement and Homeland Security
- Future Directions and Collaborations
  - Improvements of the existing sensing technologies using novel, thermoelectrically cooled, cw, high power, and broadly wavelength tunable mid-IR interband and intersubband quantum cascade lasers
  - New applications enabled by novel broadly wavelength tunable quantum cascade lasers (especially sensitive concentration measurements of broadband absorbers, in particular VOCs and HCN)
  - Development of optically multiplexed gas sensor networks based on QEPAS
FT-IR survey absorption spectrum of benzene vapor (C₆H₆)

![Atmospheric absorption spectrum](image1)

Wave number (cm⁻¹)

500  750  1000  1250  1500  1750  2000  2250  2500

Proposed H₂¹⁸O/ H₂¹⁶O Isotopic Ratiometer Scheme

![Isotopic Ratiometer Scheme](image2)