Infrared Technologies for Environmental Sensing: Present and Future Opportunities and Challenges

F.K. Tittel, R.F. Curl, L. Dong, J. Doay, A.A. Kusterer, R. Lewicki, and D. Thomay
Rice Quantum Institute, Rice University, Houston, TX, USA
http://rice.rice.edu/lasers/

• Motivation: Chemical Sensing Applications
• Fundamentals of Laser Absorption Spectroscopy
• New Laser Sensing Technologies (QEPAS)
• Selected Applications of Trace Gas Detection
• Quantum Enhanced Photonic Spectroscopy (QEPS)
• NH3 Detection for Environmental Applications
• Nitric Oxide Detection (LAS & Faraday Rotation Spectroscopy)
• Monitoring of Broadband Absorbers
• Future Directions of Laser based Gas Sensor Technology

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

Greenhouse Gases and Climate Change

• Carbon credit and carbon trading
• Need to measure and locate all sources and sinks
• Must be in real time and continuous
• Multiple greenhouse gases
• Carbon dioxide
• Methane
• Nitrous oxide

Existing Methods for Trace Gas Detection

Mass Spectroscopy → Gas Chromatography

Non-Optical

Desorption Electric Chemical

Electro Chemical

Chemiluminescence

Optical

Black body Sources

Fourier Transform

Coherent Sources

MIDR Analyzer

Microwave Spectroscopy

Laser Spectroscopy

Basics of Optical Trace Gas Analyzers

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

Optimum Molecular Absorption Transition
• NIR Overtones or Combination Bands
• MIR Fundamental Absorption Bands

Long Optical Pathlengths
• Multiple Absorption Cell (2D or 4D, Horn)
• Grating Enhanced, Grating Ringdown & Transient Spectroscopy
• Open Path Monitoring (with remote
  reference), Transflective and Remote Detection
• First-principle evanescent wave Spectroscopy

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows
### 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 Line Width</td>
</tr>
<tr>
<td>Multi-gas Components, Multiple</td>
<td>Tunable Wavelength</td>
</tr>
<tr>
<td>Absorption Lines and Broadband</td>
<td></td>
</tr>
<tr>
<td>Absorbers</td>
<td></td>
</tr>
<tr>
<td>Directionality or Cavity Mode</td>
<td>Beam Quality</td>
</tr>
<tr>
<td>Matching</td>
<td></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 QCL and ICL Sources - Nov 2009

- **Bead - structure engineered devices**
  - Optimal wavelength is tunable. Laser wafers - MBE or MOVCD
  - mid-infrared QCLs ranging from 3 to 25 μm (AlGaAs/AlGaAs/AlAs)
- **Compact, reliable, stable, long lifetime, and commercial availability**
- **Safety-friendly (SF), single mode (SM) and multi-mode wavelengths**
- **Broad spectral range in the mid-IR**
  - 4 μm (QCLs at 3-4 μm) and 3 μm (AlGaAs/AlAs)
  - 1.5 μm (QCLs at 1.5 μm)
  - 1.5 μm (QCLs at 1.5 μm)
- **Narrow spectral linewidth**
  - 2 μm (2 μm with frequency stabilization (QCL 2 μm))
  - Pulsed = 300 MHz
- **High pulsed and CW powers of QCLs at TEC/RT**
  - Pulsed and CW powers of 24 W and 3 W respectively; high temperature operation >300°C
  - >200 mW (RT) CW DFB @ 5 μm
  - >500 mW (RT) CW DFB @ 1 μm
- **Wall plug efficiency of >17% at 4 μm**

### Quantum Cascade (QC), Interband (IC) and GaSb Laser

**Availability in November 2009**

- **Commercial Sources**
  - Adtech, CA
  - Alpes Lasers, Switzerland & Germany
  - Alcatel-Thales, France
  - Hamamatsu, USA & Japan
  - Maxion Technologies, Inc (Physical Sciences, Inc), MO
  - Nanotune, Germany
  - Pranalytica, CA
- **Research Groups**
  - Harvard University
  - Fraunhofer-JF, Freiburg, Germany
  - NASA-JPL, Pasadena, CA
  - Naval Research Laboratories, Washington, DC
  - Northeastern University, Evanston, IL
  - Princeton University (MPRTH), NJ
  - State University of New York
  - Technical University, Zurich, CH
  - University of Montpelier, France
  - UK: Sheffield

### Quartz Enhanced Photoacoustic Spectroscopy

- **From conventional PAS to QEPAS**
  - **Laser beam, power P**
  - **Modulated (P or λ) at f or f/2**
  - **S ∝ 2αP**
  - **fV**
  - **NNEA = α_{max}P \frac{1}{\sqrt{2f}}**
  - **Effective volume**
  - **Swap Resonating Element**
  - **Cell is OPTIONAL!**
  - **Resonant at f**
  - **Quality factor Q**

### Quartz Tuning Fork as a Resonant Microphone

- **Unique properties**
  - Extremely low thermal noise: Q~10,000 at 1 Hz
  - Q~100,000 in vacuum
  - Low sensitivity to external sound
  - Large dynamic range - linear from thermal noise to breakdown deformation
  - 300 K noise: α=10^{-8} W
  - Breakdown: α=10^{-3} W
  - Wide temperature range from 1.56K (superfluid helium) to ~700K
  - Low cost (~$1)
- **Other parameters**
  - Resonant frequency ~32.8 kHz
  - Force constant ~26000 nN
  - Electromechanical coefficient ~7×10^-4
  - Cm
QEPAS spectrophone

- Micro-resonator tubes
  - Must be close to QTF but not touch TF (30-50 mm gaps)
  - Optimum inner diameter 6.41 mm (10% lower signal with 0.6 mm diameter tubes)
  - Each micro-resonator tube 3-mm long (~22 for sound at 32.8 kHz)
  - Gain: ±10 to ±20

Windows
- Must be tilted to prevent reflected light from entering micro-resonator tubes
- Exact positioning is not important, to the best of our current knowledge

Typical QTF Resonance Curves

- Air, 750 Torr Q=13,270
- Vacuum Q=33,500

Frequency, Hz

What about QEPAS Modeling?


Also: S. L. Frebough, F. Reigam, & E. A. Tresser, "Modelling the Response of Photoacoustic Gas Sensors", Cornell Conf, Boston, MA, Oct 10-12, 2009

Alignment-free QEPAS Absorption Detection Module

Comparative Sizes of QEPAS & PAS ADMs

Optical multipass cell (100 m): l=70 cm, P=3000 cm²

Resonant photoacoustic cell (1 kHz): l=40 cm, L=50 cm³

QEPAS spectrophone: l=1 cm, L=0.05 cm³
Merits of QEPAS based Trace Gas Detection

- Very small sensing module and the sample volume (a few mm³)
- Optical detector is not required
- Wide dynamic range
- 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: \( A_T^2 \) energy in the TF symmetric mode, directly observed
- Absence of low-frequency noise: SNR scales as \( 1/\tau \), up to \( \tau = 3 \) hours experimentally verified

QEPAS: some challenges

- Responsivity depends on the speed of sound and molecular energy transfer processes
- Sensitivity scales with laser power

WM QEPAS signal for H₂O line @ 7306.75 cm⁻¹, 48 ppbv

Laser power in cell: 9.5 mW; Time constant: \( 1 \mu s \); SNR=550
Peak absorbance: \( 4 \times 10^{-4} \) cm⁻¹ (HITRAN); RHs thermal background
= NNEA=1.9x10⁻⁹ W/(Hz)⁰.⁵; NEC=90 ppbv

Line locking based on 3f detection

Principal Architecture of a QEPAS Gas Sensor

QEPAS Performance for 13 Trace Gas Species (Nov. '09)

Long-term Averaging: H₂S, Allan Variance Analysis

For component concentrations: \( r = 95\% \) (3σ) \( 90\% \) (2σ) \( 68\% \) (1σ)
NCE/TP/NCs = 0.8/0.5/0.3