Recollections of Tycho Jaeger (1972-1980)

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

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Outline:
- Motivation: Chemical Sensing Applications
- Fundamentals of Laser Absorption Spectroscopy
- New Laser Sensing Technologies (QEPAS)
- Selected Applications of Trace Gas Detection
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
  - 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

Sensitivity Enhancement Techniques for Laser Spectroscopy

- Optimum Molecular Absorbing Transition
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (MID-IR)
- Long Optical Pathlength
  - Multipass Absorption Cell (White, Herriot, Chemia)
  - Cavity Ringdown and Cavity Enhanced Spectroscopy
  - Open Path Monitoring (with & without retro-reflector): Standoff and Remote Detection
  - Fiber optic Evanescent Wave Spectroscopy
- Spectroscopic Detection Schemes
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Phasoracoustic Spectroscopy
  - Laser Induced Breakdown Spectroscopy (LIBS)

Molecular Absorption Spectra within two Mid-IR Atmospheric Windows

<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>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>
Quartz Enhanced Photoacoustic Spectroscopy

First Report of PAS in 1880

Alexander Graham Bell’s "photophone" used a voice coil to modulate a mirror which transmitted sunlight to a receiver containing a selenium resistor.

Mature, Sept. 23, 1880, pp. 500-503

Resonant Photoacoustic Spectroscopy

Quartz Tuning Fork as a Resonant Microphone

Unique properties
- Extremely low internal losses:
  - Q=10,000 at 1 am
  - Q=100,000 in vacuum
- Acoustic quadrupole geometry
- Low sensitivity to external sound
- Large dynamic range (~10^5) - linear from thermal noise to breakdown deformation
- 300K noise: ~10^{-11} cm
- Breakdown: ~10^4 cm
- Wide temperature range: from 1.56K (superfluid helium) to ~700K
- Low cost (~$1)

Other parameters
- Resonant frequency: ~32.8 kHz
- Force constant: ~26000 N/m
- Electromechanical coefficient: ~7·10^{-4} C/N

QEPAS spectrophone

- Micro-resonator (mR) tubes
  - Must be close to QTF but not touch QTF (25-50 μm gap)
  - Optimum inner diameter 0.6 mm
  - Optimum micro-resonator tubes are 4.4 mm long (~λ/4<λ/2 for sound at 32.8 kHz)
  - Maximum SNR of QTF with mR tubes: ~30 (depending on gas composition and pressure)
Alignment-free QEPAS Absorption Detection Module

Merits of QEPAS based Trace Gas Detection

- Very small sensing module and sample volume (a few mm³)
- 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 $k_B T$ energy in the TF symmetric mode
- Absence of low-frequency noise: SNR scales as $V_i$, up to $r$=3 hours as experimentally verified
- QEPAS: some challenges
  - Responsivity depends on the speed of sound and molecular energy transfer processes
  - Sensitivity scales with laser power
  - Effect of $H_2O$
  - Cross-sensitivity issues

Recent Applications of mid-infrared Laser based Trace Gas Sensors

NIR QEPAS based multi-species sensor system

QEPAS Performance for 15 Trace Gas Species (May '10)

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)
Mid-IR EC-QCL based AM-PAS Sensor for atmospheric NH₃ Detection

Preliminary NH₃ Data after Sensor Installation on the 100 m high Moody Tower Roof (UH campus)

QEPAS and PAS based NH₃ measurements with a 10.34μm DLS EC-QCL spectroscopic source

Important Biomedical Species

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Biological/Pathology Indication</th>
<th>Cancer wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paracetamol</td>
<td>C₇H₉NO₂</td>
<td>Liver damage (inflammation, oxidative stress)</td>
<td>15.9 μm</td>
</tr>
<tr>
<td>Formalin</td>
<td>CH₂O</td>
<td>Cancerous tumors (100-1000 μm)</td>
<td>2.7 μm</td>
</tr>
<tr>
<td>Malic acid</td>
<td>MD</td>
<td>Nucleic acid synthesis activity, inflammatory and immune responses (HPO-400 μm)</td>
<td>8.3 μm</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>H₂O₂</td>
<td>Airway inflammation, oxidative stress (1-4 μm)</td>
<td>7.8 μm</td>
</tr>
<tr>
<td>Porphyrins</td>
<td>C₈H₈N₄S</td>
<td>Bacterial growth (100-1000 μm)</td>
<td>6.7 μm</td>
</tr>
<tr>
<td>Bilirubin</td>
<td>CH₁₃NO₂</td>
<td>Oxidative stress, cancer</td>
<td>10.8 μm</td>
</tr>
</tbody>
</table>

QEPAS based NH₃ Gas Sensor Architecture

Real-time Breath Monitor Interface

Advantages of using CW DBS-QCL in the sensor architecture:
- Small laser package — system compactness,
- DBS-QCL room temperature operation,
- Performing SM spectroscopy at optimum modulation depth,
- Sensitive detection with 21 W/H.
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 (TNT)

Motivation for Nitric Oxide Detection in Beijing 2008

- 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
- 40cm–effective optical pathlength
- Routine/Real-time Extinction Rates ×10⁻⁴
- 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 cavity-loss free tuning using Germanium modulation at 50th harmonic)

Faraday Rotation Spectroscopy of Nitric Oxide

- 98 ppb NO on H2
- L = 5 m, P = 40 Torr
- TD = 1 s, SNR = 2 mL
- SNR = 200 Hz, SNR=1000 Gauss
- Q=0 from crossed analyzer
- LN cooled InGa detector
- 1σ=4.355 μV

Ethane absorption spectrum

- 4×10⁴ cm⁻¹

Future Directions and Outlook of Chemical Trace Gas Sensing Technology
**Proposed QEPAS-OPBC Sensor Configuration**

DFB diode laser  
High reflectivity dielectric mirrors  
Photodiode  

PZT  
QTF  

Feedback electronics

Circulating power = Source power / (1-R)  
Very conservatively, ×100

**QEPAS MDAL Comparison with CRDS, ICOS & TDLAS**

Minimum Detectable Absorption Loss (MDAL) [cm⁻¹/νHz] can be used for comparison of different techniques:

- Cavity Ring Down Spectroscopy (CRDS): ~ 3 × 10⁻⁹
- Integrated Output Spectroscopy (ICOS): ~ 3 × 10⁻⁹
- Multipass Gas Cell based TDLAS: ~ 2 × 10⁻⁹

- QEPAS (Sept 2009) MDAL (DFB 100 mW): 1.9 × 10⁻⁸  
- QEPAS-OPBC MDAL (DFB 30 mW): 3.2 × 10⁻¹⁰  
- QEPAS-OPBC + micro-resonator (estimated): ~ 7 × 10⁻¹²

QEPAS-OPBC can be as sensitive as CRDS, ICOS and TDLAS and retain most of the performance merits of QEPAS.

**Laboratory air spectrum with OPBC-QEPAS system**

**Principle of resonant optothermoacoustic detection (ROTADE) sensor operation**

- Modulated power source (such as a laser beam)
- Energy transfer (diffusion or thermal conductivity)
- Thermal expansion and resonant vibration
- Mechanical stress
- Electric response

**Near infrared QTF and ROTADE images**

- Transmitted Power: Tuning Fork Signal
- Tuning Fork Signal

**Wireless Sensor Networks for Trace Gas Sensing**

- Advantages?
  - Spatial resolution  
  - Measure fluxes  
  - Detect spikes before diffusion  
- What is needed?
  - Ultra low power  
  - Fast duty cycling capability  
  - Low cost, Replicable  
  - Ultra miniature  
  - Autonomy (no consumables; auto.  
    processing; auto. start)

To Internet via Base Station
Ultra-compact Diode Laser based Trace Gas Sensor

Key Characteristics of mid-IR QCL and ICL Sources - May 2010

- Band-structure engineered devices
- Mid-IR wavelength is determined by laser design
- MBE or MOCVD
- End infrared QCL emitter from 3.4 to 31 μm (Δλ/λ~0.2)
- Compact, reliable, stable, long lifetime, and commercial availability
- Fast (μs): single-mode QCL and multi-wavelength devices
- Spectral tunability range in the mid-IR
- EC-QCLs for QCLs and 2-3 μm for LASE-QCL-based laser
- 1.5 cm⁻¹ using injection current control for DFB devices
- 10-20 cm⁻¹ using temperature control for DFB devices
- >400 cm⁻¹ using an external cavity design and FP rings with heterogeneously broadened active region design
- Narrow spectral linewidth
- CW: 0.1 - 3 MHz, Δλ/λ~0.2 with frequency stabilization (0.0004 cm⁻¹)
- Pulsed: ~200 MHz
- High output and CW powers of QCLs at TEC/RT operation
- Pulsed and CW powers of 15 W and 3 W respectively, high temperature operation ~>700K
- >200 mW (CW) and 1 W (1545 nm)
- >200 mW (CW) and 1 W (1545 nm)

Tunable external cavity QCL based spectrometer

- Fine wavelength tuning
- PZT controlled EC-length
- PZT controlled grating angle
- QCL current control
- Monodetector coarse grating angle tuning
- Vacuum light QCL enclosure with built-in 2D lens positioner (TEC laser cooling + optional chilled water cooling)

Wide Wavelength Tuning of a 5.3μm EC-QCL

- Coarse wavelength tuning of 150 cm⁻¹ is performed by varying diffraction grating angle
- Power output is ~50 mW
- Access to Q(3)/Q transition of NO at 1075 cm⁻¹ for LMR spectroscopy

From conventional PAS to QEPAS

- Laser beam, power P
- Modulated (P or L) at f or f2
- SWAP RESONATING ELEMENT
- Standing wave
- NNEA = αP / √(hf)
- Resonant at f quality factor Q
- Bias (bias)