Current and Emerging Laser Sensors for Greenhouse Gas Detection and Monitoring

Presented by:

Mickey B. Frish
Physical Sciences Inc.
20 New England Business Center
Andover, MA 01810
frish@psicorp.com

MIRTHE Workshop on Air Monitoring in Energy Extraction
August 9, 2013

Princeton University
Princeton, NJ
Outline

- Needs and Applications for GHG Sensing
- Descriptions of Current Laser Sensing Technologies for CH₄ and CO₂
  - Near-IR vs Mid-IR
- Future applications for Mid-IR ICL/QCL Sensors
  - Laser and detector technology development needs
NEEDS AND APPLICATIONS
• **Good science demands good data**
  - Accurate, reliable widespread sensors
  - Skilled people to operate sensors and interpret data

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**Methane Concentrations at New York Botanic Garden Station**

![Graph showing methane concentrations over time](image)


**Is this an errant sensor or the real effect of Mother Nature??**
Anthropogenic CH$_4$ – Natural Gas

- **US natural gas system:**
  - Gathering
    - >493,000 active natural-gas wells (90% use fracking) across 31 states in the U.S. in 2009
  - Transmission
    - ~250,000 miles of pipeline, ~1700 transmission stations, ~17,000 compressors.
  - Distribution
    - 500-1000 gate stations, ~132,000 surface metering and pressure regulation sites, >1,000,000 miles pipeline, >61,000,000 end-user customer meters.
    - Maintaining the security and integrity of this system is a continual *legally-regulated* process of searching for, locating, and repairing leaks.
Elevated methane concentrations on Boston streets measured by vehicle-mounted mobile near-IR laser-based Cavity Ringdown Spectrometer.

-- Attributed to leaky pipelines --

“American consumers are paying billions of dollars for natural gas that never reaches their homes, but instead leaks from aging distribution pipelines, contributing to climate change, threatening public health, and sometimes causing explosions.”

| Total U.S. Unaccounted for Gas from Natural Gas Systems from 2000-2011<sup>a</sup> | 2.6 trillion cubic feet of natural gas |
| Total U.S. Reported Emissions from Natural Gas Distribution Systems from 2010 - 2011<sup>b</sup> | Equivalent to releasing 56.2 million metric tons of CO<sub>2</sub> |
| Significant Incidents on U.S. Natural Gas Distribution Systems from 2002-2012<sup>c</sup> | 796 incidents / 116 fatalities / 465 injuries / $810,677,757 in property damage |


- But how much atmospheric methane anthropogenic vs biogenic?

**Sensors and science are needed!**
**Anthropogenic CO₂ – Fossil Fuel Combustion**

*Calculated* fossil fuel CO₂ emissions all sectors – power production, industrial, mobile, residential, commercial, and cement

Project Vulcan, K. Gurney, Purdue University, 2002.

- Not illustrated: CO₂ pipelines
  - 3900 miles existing CO₂ pipelines support enhanced oil recovery (EOR)
  - Network emerging (~120,000 miles by 2050) to support carbon capture and sequestration (CCS)
Tools for Detecting GHG Sources

- **Reliable, cost-effective tools are needed to:**
  - Monitor and map (spatially and temporally) sources of escaping CH$_4$ and CO$_2$
  - Provide sufficient sensitivity and resolution to distinguish local GHG sources from ambient
  - Provide fast health and safety danger alerts

- **Current and emerging tools include:**
  - Permanent or mobile/aerial trace gas detectors
  - Permanent open-path sensors for fenceline monitoring
  - Sensor networks for mapping ~ km$^2$ areas and measuring fluxes at surfaces and sub-surface downholes
    - Future networks will comprise ~100s – 1000s of inexpensive continuously-operated spatially and temporally correlated sensors
CURRENT LASER-BASED SENSORS
Tunable Diode Laser Absorption Spectroscopy (TDLAS)

TDLAS is an *active* optical method for detecting and quantifying one or more analyte gases mixed with other gases.

**Competitive Features**
- *Selective*; generally insensitive to cross-species interference
- *Sensitive*; sub-ppm detection of many gas species
- *Fast*; sub-second response time
- *Configurable*; point, open-path, or standoff sensor
- *Non-contact*; only the probe beam need interact with the analyte

Accepted as rugged, reliable, accurate commercial industrial sensors and analyzers
- *Thousands currently in use*
- Emerging high-volume market opportunities (process control, environmental monitoring) demand: *reduced cost, simplicity, autonomy, reliability, and accuracy*
TDLAS Technology Niche

- **Near-IR** TDLAS now fulfills many GHG sensor needs
  - *Near-IR is suitable and preferable for sensing many simple molecules*
  - *Sensors utilize proven robust electronics platforms*
    - Reliable laser sources
    - High precision
    - Very low power consumption (< 1 W)
    - Compact
    - Minimal maintenance
    - Acceptable cost; ~$10,000 per sensor unit

- **Mid-IR** interband cascade lasers (ICLs) and quantum cascade lasers (QCLs) enhance sensitivity over short paths
  - *Enables miniaturization and detection of trace pollutants and complex molecules*

- Mass-produced chip-scale TDLAS sensors may enable future wide-area deployment of sensor networks

- Mid-IR Challenges:
  - Low-noise uncooled mid-IR detectors
  - Laser cost, power consumption, wavelength diversity, availability, reliability
### Practical TDLAS Detection Limits for Some Gases

| ppm-m |
|------------------|------------------|------------------|------------------|
| **Near-IR (<2.2 μm)** | **2 to 3 μm** | **4 to 8 μm** |
| **Gas** | **300 K 1 atm** | **Gas** | **300 K 1 atm** | **flames** | **300 K 1 atm** | **flames** |
| HF | 0.2 | HCN | 1.0 |
| H₂S | 20.0 | CO | 40.0 | 0.02 | 0.7 | 0.0001 | 0.005 |
| NH₃ | 5.0 | CO₂ | 1.0 |
| H₂O | 1.0 | NO | 30.0 | 0.6 | 3 | 0.03 | 0.2 |
| CH₄ | 1.0 | NO₂ | 0.2 |
| HCl | 0.15 | O₂ | 50.0 |
| H₂CO | 5.0 | C₂H₂ | 0.2 |

- Mid-IR laser sources spanning wavelengths from 3 -12 μm, enable sub-ppm-m detection of many complex hydrocarbons, TICS, and chemical agents
- **Optical methods** provide long optical path lengths to sense trace concentrations (~ ppbs)
  - Open-path
  - Multi-pass Herriot cell
  - Resonant cavities
    - Intra-cavity Optical Spectroscopy (ICOS)
    - Cavity Ringdown Spectroscopy (CRDS)
    - Solid-state nanoresonators
Extractive:
Localizing leaks in pipeline components such as valves and fittings.

Point:
Permanent installation at surface and subsurface or downhole sites.

Open Path:
Continuous and permanent pipeline health and safety monitoring.

In-situ:
Monitoring and controlling CO₂ separation processes.

Standoff:
Surveying pipelines or surface areas from walking, mobile, and aerial platforms.
Absorption Spectroscopy Fundamentals

- Gas molecules absorb light at specific colors ("absorption lines")

**Beer-Lambert law**

\[ I_\nu = I_{\nu o} \exp \left[ S(T) \ g(\nu - \nu_o) \ N \ell \right] \]

where:

- \( \nu \) = optical frequency (= c/l)
- \( \nu_o \) = line center frequency
- \( g(\nu) \) = lineshape function
- \( \ell \) = path length
- \( N \) = absorbing species number density
- \( S(T) \) = temperature dependent linestrength
- \( I_{\nu o} \) = unattenuated laser intensity
- \( I_\nu \) = laser intensity with absorption
- \( \Delta I \) = change in intensity (= \( I_{\nu o} - I_\nu \))
- \( c \) = speed of light
- \( \lambda \) = wavelength of light

**Absorbance**

\[ \text{Absorbance} = -\ell \ln \left( \frac{I_\nu}{I_{\nu o}} \right) \approx \frac{\Delta I}{I_{\nu o}} \text{ (with small } \Delta I) \]

**CH}_4 Spectrum**

- Mid-IR fundamental
- Near-IR overtone

**200x linestrength advantage is the mid-IR appeal**

(when deployed judiciously)
TDLAS System Components

- A frequency agile (i.e. tunable) laser beam transits an analyte gas sample
- Laser wavelength scans repeatedly across absorption line unique to analyte gas
- Received signal processed to deduce analyte concentration
- Laser sources
  - SWIR – Distributed Feedback (DFB) laser or
  - SWIR – Vertical Cavity Surface Emitting Laser (VCSEL)
  - MWIR – Interband Cascade Lasers
  - LWIR – Quantum Cascade Laser
Portable Standoff near-IR TDLAS for Natural Gas Leak Survey

- Like a flashlight, laser beam illuminates a surface
- Senses analyte gas between transceiver and illuminated surface
  - **Standoff range ~100 ft with handheld transceiver**
- Scanning laser beam across plume results in rapidly changing analyte gas measurement
- Can detect hazardous gas levels through windows for emergencies and responder safety
- ~2000 RMLDs in use for natural gas leak surveying; CO₂ version in demonstration
Other Standoff Configurations

**Manned Aerial**
Commercial Pipeline Leak Survey Service

Mini-UAV
Lab prototype – for mapping landfill CH$_4$ emissions

D. Picciaia et al., *Proceedings Sardinia 2011, Thirteenth International Waste Management and Landfill Symposium*

**Portable Extractive**
New commercial product

**Mobile**
Robust High-Precision Ambient CO$_2$ Sensor

- Near-IR (2.0 µm) – ICOS design (~60m optical pathlength)
- Measures CO$_2$ mole fraction in dry air to 1:3000 with 1 minute averaging
- Applications:
  - Monitoring CO$_2$ sources, sinks, and transport
  - Sequestration site monitoring and leak detection
Peaks occur at night when winds are calm, mixing is minimized and CO₂ from plant respiration builds up.
- Near-IR
- Continuous operation
  - No adjustment, calibration, or zeroing
- Diurnal variations correlate with point sensor measurements
- Leaking CO$_2$ yields statistically distinct signature
Pipeline Monitors

- Permanent alarms to detect and mitigate small to potentially explosive leaks
  - Near-IR
  - Wireless
  - Solar-powered
  - Real-time alarm notification
  - Easy installation & alignment

- Currently in demonstration
  - 600' ft path
  - Months of maintenance-free operation
Methane Open Path Data

METHANE CONCENTRATION MEASURED

- Concentration
- 100 per. Mov. Avg. (Concentration)

July 2013
EMERGING MID-IR SENSORS
FuelFinder™

- Intended for locating leakage of refined petroleum products from buried distribution pipelines
  - Primarily gasoline

- Man-portable mid-IR backscatter TDLAS
  - Wavelength ~3 µm

- Capitalizes on recent advances in Interband Cascade Lasers (ICLs) that operate at room temperature

- Senses volatile complex hydrocarbon vapors
• For airborne (UAV and balloon) \( \text{CO}_2 \) measurements
  - *A precise instrument rugged enough for the field and economical enough for widespread use by monitoring networks.*

• Requirements:
  - 1 ppmv precision @ ~0.1 Hz
  - < 100 gm
  - Battery power
  - Deployable in an unconditioned payload

• Solution:
  - Absorption spectroscopy using room-temperature mid-IR LED integrated with a miniaturized control and signal processing system
Vision – Chip-scale Mass-Produced TDLAS Integrated-Optic Sensors and Networks

- Laser source, photodetector, and optical gas sampling element integrated on a miniature monolithic platform
  - Each envisioned device senses one chemical;
    - Several devices working in tandem sense several chemicals
  - Novel gas sensing elements use solid-state optical waveguides
- Fabricated using established production techniques
  - Complete assembly with electronics in cell-phone style package
  - Cost ~ few $100’s when produced in quantities of hundreds of thousands or more
  - Similar to proven commercial near-IR telecom products

Application – Distributed Sensor Networks

- Each sensor detects one of a choice of several chemicals
- All sensors communicate wirelessly with a central processor
- Network provides wide area coverage and improves average sensitivity compared to individual sensors
Cost Challenges

- **Mickey’s Mantra:**
  - “TDLAS is not much more complex than compact disk players”
  - “The smallest and lowest cost currently-available TDLAS sensors fit in a smoke-alarm type package weighing about three pounds”
  - “Yet TDLAS sensors cost >$10,000 per unit,
    - Despite laser chip costs that could be ~$50 -$100 each if designed for low-power spectrometry and produced in many tens of thousands

- **Cost drivers**
  - Laser packages intended for telecommunications industry produced in relatively low volumes @$1000 each
  - Bulk optical components
  - Discrete component electronics

- **Impact**
  - *TDLAS today is too expensive, bulky, and power-hungry to deploy practically in distributed sensor networks*
Technical Challenges

- **Practical** devices require improved power efficiency, specifically for laser and detector thermal control
  - Solutions:
    - Harness laser waste heat efficiently
    - Design for uncooled detectors
      - Smaller is better

- Detection goals require:
  - Mid-IR lasers
  - High-Q resonant sensing elements
  - Simple optical coupling between sensor element, laser source, and detector
TDLAS Laser Sources vs. Needs

Near-IR example

- **Distributed FeedBack (DFB) Laser**
  - 14-pin butterfly package with integral thermo-electric cooler
  - ~10 mW output power
  - Optically-isolated fiber optic output
  - ~700 – 2300 nm

- **Vertical Cavity Surface Emitting Laser (VCSEL)**
  - TO-8 package with integral thermo-electric cooler
  - ~0.4 mW output power
  - Fiber-coupling optional (w/reduced power)

- **Monolithic spectrometers need:**
  - μW's of laser power
  - Stable, but not necessarily sub-ambient, laser temperature

**COTS Lasers are Overkill**

Need: Near and Mid-IR Lasers designed for widely-deployed gas sensing applications
Novel Packaging to Meet the Challenges

- Eliminate thermo-electric cooler (TEC)
  - *Heat, don’t cool*
  - *Proven in near-IR benchtop configuration*

- Eliminate microlenses and optical isolator
  - *Enabled by monolithic integrated platform*

- Simplify Electronics
  - *Reduce to ASIC*
Summary

- Near-IR laser sensors for natural gas leak detection are established widely-accepted commercial technologies
  - One of the largest laser-based gas sensing applications
  - CO$_2$ sensors are available using similar sensor platforms

- Widely-deployed sensors for “ubiquitous monitoring” will benefit from mid-IR integrated optics
  - Requires laser sources designed for gas sensing application
  - Cost per laser <$100 in mass production
  - Developing these sources is the challenge to the MIRTHE community