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Mid-infrared laser based trace gas sensor technologies: recent advances and applications-I

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GE Global Research

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Outline

- Introduction
- CH_4 absorption line selection and ICL characterization
- Sensor system configuration
- Performance optimization and assessment
- Laboratory stationary measurements
- Field tests at a commercial natural gas storage facility
- Summary

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Compact Methane Sensor System based on a novel Multipass Gas Cell and a 3.3 µm CW, TEC, DFB Interband Cascade Laser

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Photonics West 2016

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Mid–infrared interband and quantum cascade laser based trace gas sensor technologies: recent advances and applications

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Austria

July 12-17, 2015

- Novel Laser-Based Trace Gas Sensor Technology
  - Mid-IR TDLAS based on a Novel Multipass Gas Cell Design
  - Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)
- Examples of four Mid-infrared Trace Gas Species
  - CH_4, C_2H_6, H_2CO and H_2S
- Future Directions of QEPAS-Based Trace Gas Sensor Technologies and Conclusions
  - I (Intra-cavity) – QEPAS
  - New custom QTFs

Research support by NSF ERC MIRTHE, NSF-ANR NexCILAS, the Robert Welch Foundation, and Sentinel Photonics Inc. via an EPA Phase 2 SBIR & sub-awards ARPA-E is acknowledged

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 isotopologues, climate modeling,...)
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Petrochemical, Semiconductor, Pharmaceutical, Metals Processing, Food & Beverage Industries, Nuclear Technology & Safeguards
- **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**

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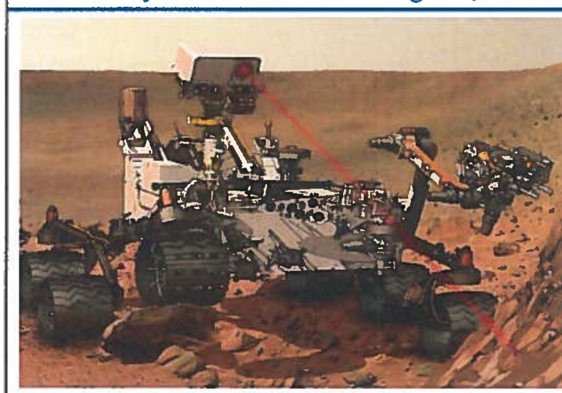
"Curiosity" Landed on Mars on August 6, 2012



Laser-Based Trace Gas Sensing Techniques

- **Optimum Molecular Absorbing Transition**
  - Overtone or Combination Bands (NIR)
  - Fundamental Absorption Bands (Mid-IR)
- **Long Optical Pathlength**
  - Multipass Absorption Gas Cell (e.g., White, Herriot, Chernin, Aeris Technologies, and Circular Cylindrical Multipass Cell
  - Cavity Enhanced and Cavity Ringdown Spectroscopy
  - Open Path Monitoring (with retro-reflector or back scattering from topographic target): Standoff and Remote Detection
  - Fiberoptic & Wave-guide Evanescent Wave Spectroscopy
- **Spectroscopic Detection Schemes**
  - Frequency or Wavelength Modulation
  - Balanced Detection
  - Zero-air Subtraction
  - Photoacoustic & Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

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Other Spectroscopic Methods

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

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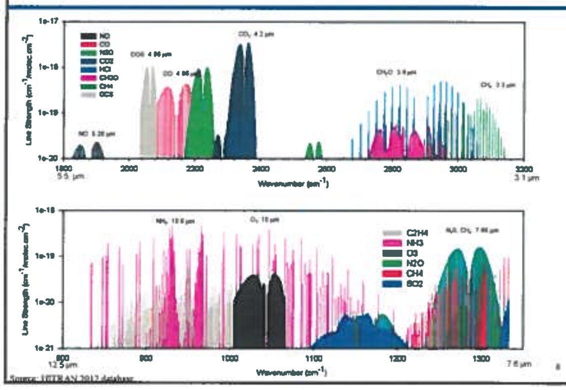
HITRAN Simulated Mid-Infrared Molecular Absorption Spectra



Source: HITRAN 2012 database

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Mid-IR Source Requirements for Laser Spectroscopy

REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to pptv)	Optimum Wavelength and Power
Selectivity (Spectral Resolution) or Specificity	Stable Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines, and Broadband Absorbers	Mode Hop-Free Wavelength Tunability
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response Time
Room Temperature Operation	High Wall Plug Efficiency, No Cryogenics or Cooling Water
Field Deployable in Harsh Environments	Compact and Robust

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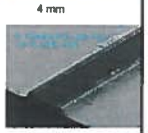
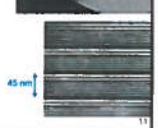
Key Characteristics of Mid-IR QCL & ICL Sources – July 2015

- **Band – structure engineered devices**
  Emission wavelength is determined by layer thickness – MBE or MOCVD; QCLs operate in the 3 to 24 µm spectral region and ICLs can cover the 3 to 6 µm spectral range.
  - Compact, reliable, stable, long lived, and commercially available
  - Fabry-Perot (FP), single mode (DFB) and multi-wavelength devices
- **Wide spectral tuning ranges in the mid-IR**
  - 1.5 cm^{-1} using injection current control for DFB devices
  - 10-20 cm^{-1} using temperature control for DFB devices
  - ~100 cm^{-1} using current and temperature control for QCLs DFB Array
  - ~ 525 cm^{-1} (22% of c.w.) using an external grating element and FP chips with heterogeneous cascade active region design, also QCL DFB array & Optical Frequency Combs (OFCs) > 100 to <450 cm^{-1} with kHz to sub-kHz resolution and a comb spacing of > 10 GHz
- **Narrow spectral linewidths**
  - CW: 0.1 - 3 MHz & <10kHz with frequency stabilization
  - Pulsed: ~ 300 MHz
- **High pulsed and CW powers of QCLs at TEC/RT temperatures**
  - Room temperature pulsed peak power of ~203 W with 10% wall plug efficiency
  - CW powers of ~ 5 W with 23% wall plug efficiency at 293 K
  - > 600 mW CW DFB at TEC/RT, wall plug efficiency 23% at 4.6 µm

4 mm





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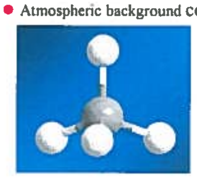
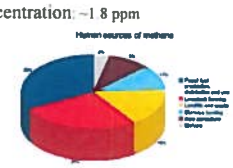
Introduction

Methane is one of the major atmospheric greenhouse gases contributing to global warming and climate change.

- Global warming potential (GWP) of 25 compared to GWP of 1 for CO_2 for a 100-year period)
- Short lifetime in the atmosphere (~12 yrs) compared to CO_2 and N_2O
- Atmospheric background concentration: ~1.8 ppm





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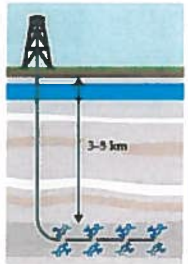
Typical Oil & Gas Production Site near Houston, TX



The result of a sequence of four fracking injections obtained by directional drilling which creates horizontal production in the target stratum is depicted in a figure published in Physics Today 2016.

A DOE-ARPA-E funded methane detection project at 3.33 µm was started in 2015 at various Texas located wellpad sites (typically,10-30 m x10 m with a 1 m spatial resolution.) was started in 2015

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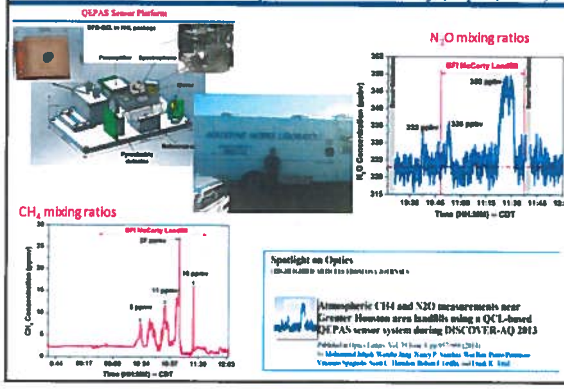
CH_4 and N_2O Measurements performed with a DFB-QCL based QEPAS Sensor installed in the Aerodyne Mobile Laboratory (Sept 7, 2013)



Comparison of proposed Rice CH_4 Sensor System and current commercially available CH_4 Sensor Platforms

	Rice	Picarro	ABB-LGR I	ABB-LGR II	Aerodyne
Opt. Path length and method	MIR TDLAS: ~ 9 m	NIR CRDS: >2000m	NIR OA-ICOS: > 1000m	NIR OA-ICOS: > 2000m	MIR TDLAS: 70-100 m
Sensitivity/sec	< 5-10 ppb	1-2 ppb	5 ppb	2 ppb	<1 ppb
Accuracy (drift)	2 ppb stabilized	2 ppb	20 ppb, temp. stabilized	2 ppb	2 ppb
Cell Volume, cc	60	30	500	2000	2000
Pump Size (10 sec flush time)	~ 1 lpm	~ 0.5 lpm	~ 11 lpm	~ 45 lpm	~ 45 lpm
Cavity Mirror Reflectance	98.5%-99%	>99.99%	>99.99%	>99.99%	>99.99%
Power Consumption	2-20 W	200 W	70 W	200 W	400 W
Weight	~ 2-4 kg	~ 20 kg	~ 15 kg	~ 40 kg	~ 40 kg
Cost	~ 20-25K USD	~ 40-50K USD	~ 25K USD	~ 40K USD	~ 100K USD

US Department of Energy Advanced Research Project Agency – Energy (ARPA-E), Methane Observation Networks with Innovative Technology to obtain Reductions (MONITOR)

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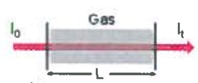
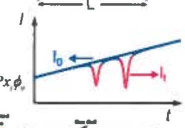
Spectroscopy Fundamentals

Beer's Law: $\frac{I_t}{I_o} = \exp(-k_v L)$



where: I_t is transmitted light intensity
I_0 is incident light intensity
k_v is absorption coefficient
L is optical path

$k_v = S(T) P x_i \phi_v$



Multipass Gas Cell:

The minimum detection limit can be improved by increasing the effective optical path without increasing the physical length

3D Rice LSG simulation of a multipass cell Based on RLSG custom software (L=100mm R=100mm D=15mm)

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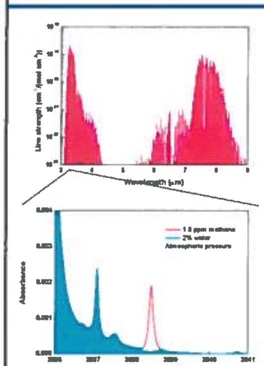
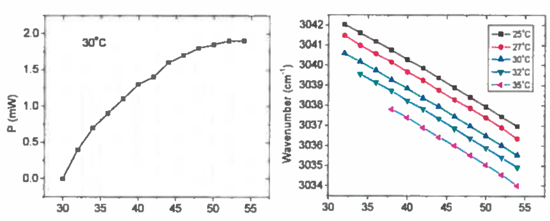
CH_4 Absorption Line Selection



- The fundamental ν_1 and ν_3 CH_4 bands are located at ~7.7 µm and ~3.3 µm, respectively
- A high detection sensitivity for methane measurements using quantum cascade lasers (QCLs) at 7.7 µm was previously reported
- Compact, TEC, CW, DFB ICLs emitting at 3-4 µm wavelengths became recently commercially available
- An interference-free CH_4 absorption line located at 3038.5 cm^{-1} was selected as the optimum target absorption line
- The 3.3µm CH_4 absorption line can be used at atmospheric pressure

ICL Characterization & Performance Evaluation

Nanoplus ICL, 3.291 µm center-wavelength



Performance evaluation for a 3.291-µm CW RT ICL at different operating temperatures and injection currents. (a) ICL output power response curves; (b) Emission wavenumber curves.

Current turning rate: -0.232308 cm^{-1}/mA ; Temperature turning rate: -0.23994 cm^{-1}/°C

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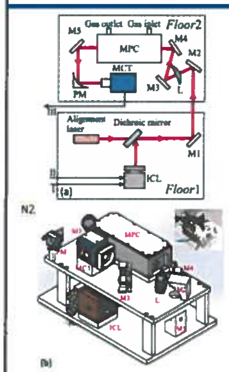
Schematic of Trace Gas Sensor System



- Laser source (Nanoplus)
  - Current: 42 mA
  - Temperature: 30 °C
  - Power: 1.5 mW
- Multipass gas cell (Sentinel Photonics/Aeris Technologies, Inc)
  - 54.6 meter, 435-passes, sealed
  - Sampling volume: 220 mL
  - Dimensions: 16.9 x 6.6 x 5.3 cm^3
- Sensor system platform
  - Two-floor design with folded optical path
  - Low power consumption: 6 W
  - Dimensions: 32 x 20 x 17 cm^3

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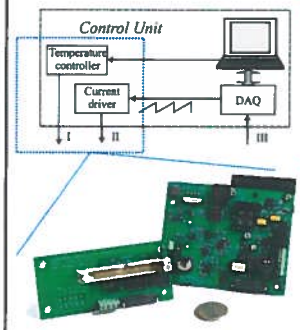
Electronics Controller for Sensor System



- Control unit
  - Laptop+NI DAQ+OEM laser driver
  - Direct absorption spectroscopy
  - DAQ: acquiring data & scanning the ICL wavelength
- OEM laser driver for ICL
  - Neo Monitors, Oslo, Norway
  - Size: 10 x 8 cm^2
  - Low noise characteristic: ≤ 1 nA/√Hz
  - On-board TEC driver: ±3 A, 15 V
  - Single voltage power supply 12-24V

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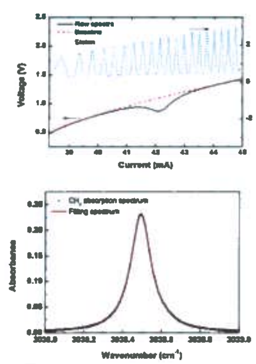
Data Processing for CH_4 Detection



A 4-step algorithm for CH_4 detection

- 150 spectra were averaged
- Baseline of the spectral scan was fitted and eliminated
- Linearized using fringe spacing of a germanium etalon
- Lorentzian line shape fitting to retrieve concentration information

Interference-free absorption line of CH_4 at 3038.5 cm^{-1} obtained from laboratory air at atmospheric pressure together with a fitted baseline and a transmission signal from a germanium etalon.

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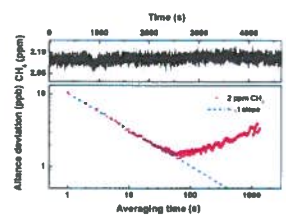
Allan-Werle Deviation Analysis



Allan-Werle deviation plot was acquired in a time period of ~1.5 hours using a certified 2 ppm CH_4 cylinder with a 1 Hz sampling rate

1-s measurement precision is σ=10.53 ppb
60-s measurement precision is σ=1.43 ppb

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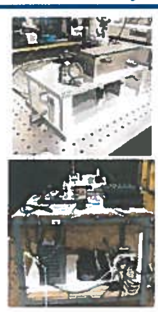
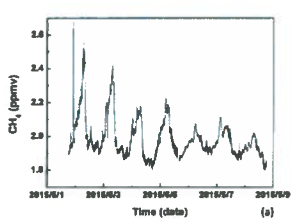
Stationary Laboratory Measurements





CH_4 concentrations measured over a 7-day period in ambient air on the Rice University campus during spring 2015.

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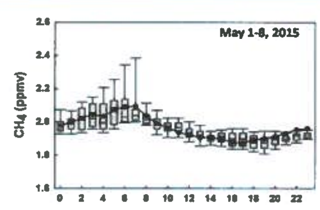
Laboratory Stationary Measurements



Diurnal variations of CH_4 mixing ratio. Bottom whisker, bottom box line, top box line and top whisker indicate the 5th, 25th, 75th and 95th percentile, respectively. Line inside the boxes and continuous solid line represent the hourly median and mean of the data respectively

The diurnal profile of the methane concentration shows an increase in concentration during the early morning with a subsequent gradual decrease after ~8:00 CDT to its typical background level of ~1.87 ppm in the Greater Houston area.

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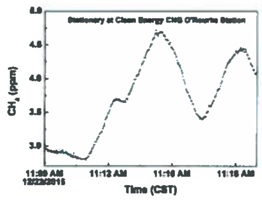
Mobile field Tests: December 2015



CH_4 concentrations measured for a sampling period of ~ 10 minutes at a Clean Energy CNG O'Rourke Station in Houston, TX.

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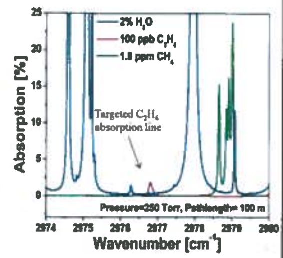
Motivation for Mid-infrared C_2H_6 Detection

- **Application in medical breath analysis**
  - Asthma
  - Schizophrenia
  - Lung cancer
  - Vitamin E deficiency
- **Atmospheric chemistry and climate**
  - Fossil fuel and biofuel consumption
  - Biomass burning
  - Vegetation/soil
  - Natural gas loss



HITRAN absorption spectra of C_2H_6, CH_4, and H_2O

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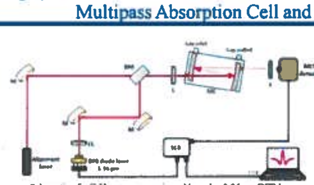
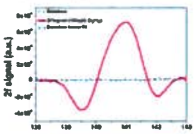
C_2H_6 Detection with a 3.36 μm CW DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics



Schematic of a C_2H_6 gas sensor using a Nanoplus 3.36 μm DFB laser diode. M – mirror, CL – collimating lens, DM – dichroic mirror, MC – multipass cell, L – lens, SCB – sensor control board.

Innovative long path, small volume multipass gas cell: **57.6 m with 459 passe**



2f WMS signal for a C_2H_6 line at 2976.8 cm^{-1} at 200 Torr

Minimum detectable C_2H_6 concentration: ~ 740 pptv (1σ; 1 s time resolution)

MGC dimensions: **17 x 6.5 x 5.5 (cm)**
Distance between the MGC mirrors: 12.5 cm

Summary and Conclusions

- A 3.291 μm CW room-temperature ICL based absorption sensor was developed for methane detection using a 54.6 m optical path length multipass gas cell.
- A two-floor mechanical design with a folded optical path resulted in a sensor system dimension of 32 x 20 x 17 cm^3
- Good electrical power management resulted in a low power consumption of the CH_4 sensor system: 6 W.
- A MDL of 10.5 ppb for CH_4 with a 1 sec integration time was achieved.
- Laboratory measurements and mobile-mode operation tests were conducted and results demonstrate the suitability of the sensor system to generate spatial distributions of CH_4 in urban areas and oil and gas production sites.

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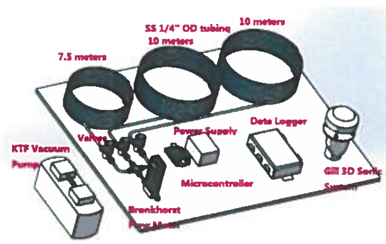
Summary, Conclusions and Future Developments

- Development of robust, compact, sensitive, selective mid-IR trace gas sensor technology based on RT, CW high performance DFB ICLs & QCLs for detection of explosives and TICs as well as environmental monitoring and medical diagnostics.
- Interband cascade and quantum cascade lasers were used in QEPAS and TDLAS based sensor platforms
- Performance evaluation of seven target trace gas species were reported. The minimum detection limit (MDL) with a 1 sec sampling time were :
  - C_2H_6: MDL of 24 ppbv at ~3.36 μm; CH_4: MDL of 13 ppbv at ~7.28 μm; N_2O: MDL of 6 ppbv at ~7.28 μm.
- I-QEPAS demonstration with a power enhancement factor of 240 providing a corresponding increase in detection sensitivity
  - CO_2: for the P(42) absorption line located at ~ 4.33 μm (2311.105 cm^{-1}), a MDL of 300 pptv at 50mbar was achieved for a 20 sec integration time.
- Development of "active" I-QEPAS system for CO and NO detection in the few ppt range
- Development of Trace Gas Sensors for the monitoring of broadband absorbers: acetone(C_3H_6O), propane (C_3H_8), benzene (C_6H_6)
- Development of Mid-IR Electrically pumped Interband Cascade Optical Frequency Combs (OFCs) with JPL, Pasadena, CA, NRL, Washington, and the U. of Bari (Italy).

Portable three Line Methane Sampling System for Laboratory and Field Use



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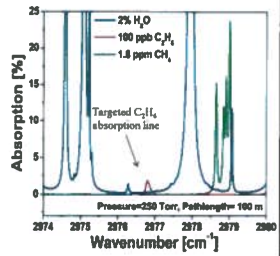
Motivation for Mid-infrared C_2H_6 Detection

- **Application in medical breath analysis**
  - Asthma
  - Schizophrenia
  - Lung cancer
  - Vitamin E deficiency
- **Atmospheric chemistry and climate**
  - Fossil fuel and biofuel consumption
  - Biomass burning
  - Vegetation/soil
  - Natural gas loss



HITRAN absorption spectra of C_2H_6, CH_4, and H_2O

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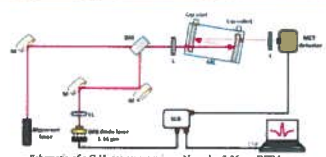
C_2H_6 Detection with a 3.36 µm CW DFB LD using a Novel Compact Multipass Absorption Cell and Control Electronics



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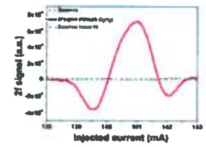
Innovative long path, small volume multipass gas cell: **57.6 m with 459 passes**



2f WMS signal for a C_2H_6 line at 2976.8 cm^{-1} at 200 Torr

Minimum detectable C_2H_6 concentration: ~740 pptv (1σ; 1 s time resolution)

MGC dimensions: **17 x 6.5 x 5.5 (cm)**
Distance between the MGC mirrors: 12.5 cm

Hydrogen Peroxide (H_2O_2)

- Strong oxidant species in the atmosphere
- Associated with the formation of acid rain and atmospheric aerosols
- Employed in the synthesis of multiple chemical products & as bleaching agent in the pulp and paper industry
- Used for decontamination and sterilization of medical and pharmaceutical facilities
- Biomarker of lung and respiratory system diseases in exhaled breath

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Vapor-Phase Hydrogen Peroxide (VPHP)

- VPHP is used for:
  - Decontamination of health-care and pharmaceutical facilities
  - Sterilization of medical equipment and packing materials in the food industry
- VPHP units: gas-phase H_2O_2 generated from concentrated liquid H_2O_2 solutions
- H_2O_2 concentrations between 200-1200 ppm are produced in the gas-phase and maintained for ~10 min
- After decontamination procedures, ambient H_2O_2 concentrations need to be monitored

Source: Bioquell UK Ltd

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Techniques for Detection of H_2O_2

- **Wet-chemistry methods based on fluorescence spectroscopy, colorimetric analysis and chemiluminescence**
  - Transfer from the gas to a liquid phase required for subsequent analysis
  - Interference from other species and formation of sampling artifacts
- **Mid-IR laser-based spectroscopy**
  - Direct detection in the gas-phase
  - Real-time detection
  - High sensitivity and specificity

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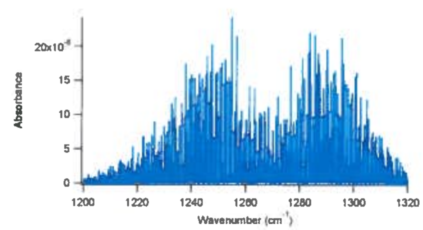
H_2O_2 Absorption in the Mid-IR Region



Fundamental ν_6 H_2O_2 band located at ~7.5-8.3 µm

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