Recent Advances and Applications of Semiconductor Laser based Gas Sensor Technology

RICE

Florence FLAIR - 2007

Sept 2-7, 2007

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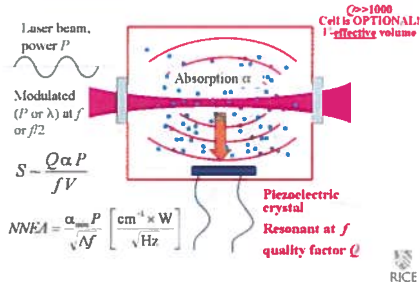
Wide Range of Trace Gas Sensing Applications

- 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

Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)

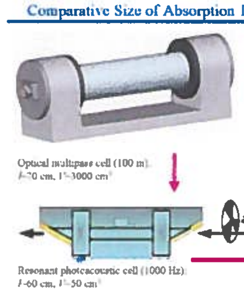


$$S \sim \frac{Q \alpha P}{f V}$$

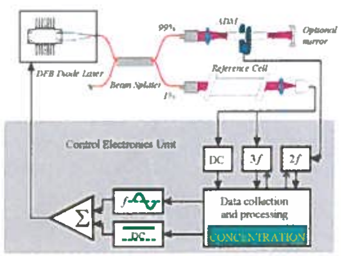
$$NNEA = \frac{\alpha_{min} P}{\sqrt{\Delta f}} \left[\frac{cm^{-1} \times W}{\sqrt{Hz}}\right]$$

Comparative Size of Absorption Detection Modules (ADM)

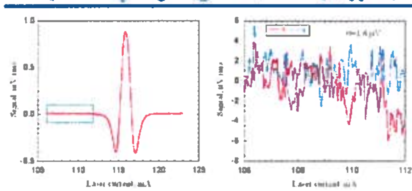
- Resonant frequency f = 32.8 kHz
- Intrinsically high Q factor: Q_{vacuum} ~ 125 000, Q_{air} ~10 000 for ambient conditions
- Piezoelectric: requires no transducer
- Miniature size
- Mass produced for watches & clocks → low cost



QEPAS based Gas Sensor Architecture



QEPAS H_2O signal @ 7306.75 cm⁻¹ (48 ppmv)

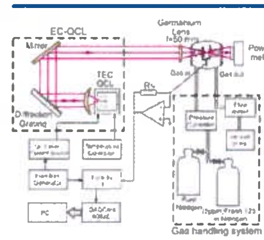


Laser power in the cell: 9.5 mW   Time constant: 1s, SNR~530

Peak absorbance: 4.8×10⁻⁵ cm⁻¹ (HITRAN)

→ NNEA=1.9×10⁻⁹ cm⁻¹W/(Hz)$^{1/2}$; NEC=90 ppbv

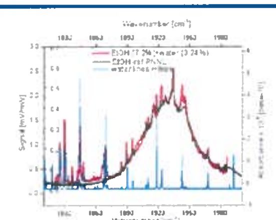
QCL based Quartz-Enhanced Photoacoustic Gas Sensor



QEPAS characteristics:

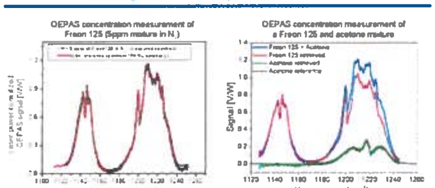
- High sensitivity (ppm to ppb)
- Excellent dynamic range
- Immune to environmental noise
- Ultra-small sample volume (< 1 mm³)
- Sensitivity is limited by the fundamental thermal TF noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

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)

Spectroscopy of Freon 125 (C_2HF_5) and CH_3COCH_3 with Widely Tunable 8.4 µm CW EC-QCL



* 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 broad band absorbers

QEPAS Performance for 13 Trace Gas Species (Sept '07)

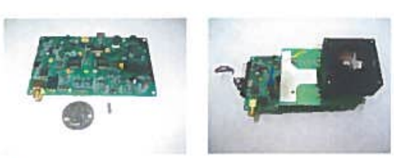
Molecule (Host)	Frequency, cm⁻¹	Pressure, Torr	NNEA, cm⁻¹W/Hz^{½}	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7306.75	60	1.9×10⁻⁹	9.5	0.09
HCN (air: 50% RH)*	6539.11	60	<4.3×10⁻⁹	50	0.16
C_2H_2 (N_2)**	6529.17	75	~2.5×10⁻⁹	~40	0.03
NH_3 (N_2)*	6528.76	575	3.1×10⁻⁹	60	0.06
CH_4 (N_2)*	6057.09	950	2.9×10⁻⁸	13.7	2.1
CO_2 (breath ~100% RH)	6361.25	50	1.6×10⁻⁸	26	40
H_2S (N_2)*	6357.63	780	5.6×10⁻⁹	45	0.13
CO_2 (N_2+1.5% H_2O)*	4991.26	50	1.4×10⁻⁸	4.4	18
CH_2O (N_2:75% RH)*	2804.90	75	8.7×10⁻⁹	7.2	0.12
CO (N_2)	2196.66	50	5.3×10⁻⁷	13	0.5
CO (propylene)	2196.66	50	7.4×10⁻⁸	6.5	0.14
N_2O (air+5%SF_6)	2195.63	50	1.5×10⁻⁸	19	0.007
C_2H_5OH (N_2)**	1934.2	770	2.2×10⁻⁷	10	90
C_2HF_5 (N_2)***	1208.62	770	7.8×10⁻⁹	6.6	0.009
NH_3 (N_2)*	1046.39	110	1.6×10⁻⁸	20	0.006

* Improved microresonator
** Improved microresonator and double optical pass through ADM
*** With amplitude modulation and metal microresonator

NNEA – normalized noise equivalent absorption coefficient.
NEC – noise equivalent concentration for available laser power and τ=1s time constant.

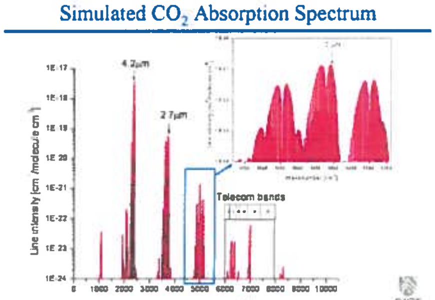
For comparison: conventional PAS 2.2 (2.6)×10⁻⁹ cm⁻¹W/√Hz (1,000, 10,000 Hz) for NH_3

Miniature QEPAS CO_2 sensor (λ=2µm) v2.0 boards



- Small size
- Relatively low cost
- High efficiency switching power supplies
- PWM Peltier cooler driver
- 0.2W control system power consumption
- Projected sensitivity* to CO_2: 110 ppm with 1sec. lock-in TC
- Over 10³ improvement in sensitivity @4.2µm

Simulated CO_2 Absorption Spectrum



Summary and Future Directions

- Near and Mid-Infrared Semiconductor Laser based Trace Gas Sensors
  - Compact, robust sensor technology based on multipass cell absorption, cavity enhanced and quartz enhanced photoacoustic spectroscopy (QEPAS)
  - High sensitivity (<10⁻⁴) and selectivity (3 to 500 MHz)
  - Fast data acquisition and analysis
  - Detected 13 trace gases to date: NH_3, CH_4, H_2S, N_2O, CO_2, CO, NO, H_2O, COS, C_2H_4, SO_2, C_2H_5OH, C_2HF_5 and isotopic species of C, O, N and H
- New Applications of Trace Gas Detection
  - Distributed sensor networks for environmental monitoring (NH_3, CO, CH_4, C_2H_4, N_2O, CO_2 and H_2CO)
  - Inexpensive and sensitive sensors for industrial process control and chemical analysis (HCN, NO, NH_3, H_2O)
  - Wearable sensors for medical & biomedical diagnostics (NO, CO, COS, CO_2, NH_3, C_2H_6)
  - Sensor network technologies for law enforcement and homeland security
- Future Directions and Collaborations
  - Further improvements of the existing sensor technologies using novel, thermoelectrically cooled, cw, high power mid-IR interband and intersubband quantum cascade lasers and QEPAS
  - New applications enabled by novel widely tunable quantum cascade lasers (especially sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs)
  - Development of optically multiplexed gas sensor networks based on QEPAS