Development of Optical Trace Gas monitoring Technology for NASA Human Space Flight

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OUTLINE

HABITATION 2006

- Motivation: Gas sensing applications
- Quartz Enhanced Laser-PAS
- Selected Applications of QE-PAS
  - NH3 Detection with 1.5 μm RT cw DFB Diode Laser
  - H2CO Detection with 3.5 μm CW DFB Interband Cascade Laser
- Tunable mid-IR laser sources
  - External Cavity QCL design
  - High resolution spectroscopy of NO using EC-QCL
- Summary and future directions

Motivation: Gas Sensing Applications

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes (eg. early fire sensing)
  - Automobile and Aircraft Emissions
- **Rural Emission Measurements**
  - Agriculture and Animal Facilities
- **Environmental Monitoring**
  - Atmospheric Chemistry (e.g. ecosystems and airborne)
  - Volcanic Emissions
- **Chemical Analysis and Industrial Process Control**
  - Chemical, Pharmaceutical, Food & Semiconductor Industry
- **Spacecraft and Planetary Surface Monitoring**
  - Crew Health Maintenance & Human Life Support Program
- **Medical Diagnostics** (eg. breath analysis)
- **Biohazard and Toxic Chemical Detection**
- **Homeland Security**
- **Fundamental Science and Photochemistry**

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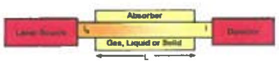
Fundamentals of Laser Absorption Spectroscopy

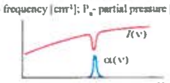


Beer-Lambert's Law of Linear Absorption

$I(\nu) = I_0\, e^{-\alpha(\nu)\, P_a\, L}$

$\alpha(\nu)$ - absorption coefficient [$cm^{-1}\ atm^{-1}$]; L – path length [cm]

ν - frequency [cm^{-1}]; P_a - partial pressure [atm]



$\alpha(\nu) = C\ S(T)\ g(\nu - \nu_0)$

C - total number of molecules of absorbing gas/atm/cm³ [$molecule\ cm^{-3}\cdot atm^{-1}$]

S – molecular line intensity [$cm\cdot molecule^{-1}$]

$g(\nu - \nu_0)$ – normalized spectral lineshape function [cm], (Gaussian, Lorentzian, Voigt)

Optimum Molecular Absorbing Transition
- Overtone or Combination Bands (NIR)
- Fundamental Absorption Bands (MID-IR)

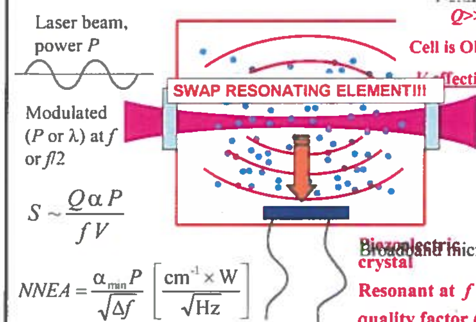
Long Optical Pathlengths
- Multipass Absorption Cell
- Cavity Enhanced, Cavity Ringdown & Intracavity Spectroscopy
- Open Path Monitoring (with retro-reflector)
- Evanescent Field Monitoring (fibers & waveguides)

Spectroscopic Detection Schemes
- Frequency or Wavelength Modulation
- Balanced Detection
- Zero-air Subtraction
- **Photoacoustic Spectroscopy**

From conventional PAS to QEPAS

Laser beam, power P

Modulated (P or λ) at f or $f/2$



Cavity resonant Q>>1000

Cell is OPTIONAL!

Effective volume

Broadband microphone / Piezoelectric crystal

Resonant at f

quality factor Q

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

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

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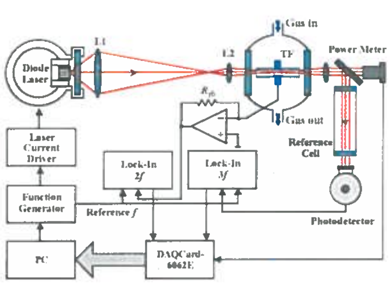
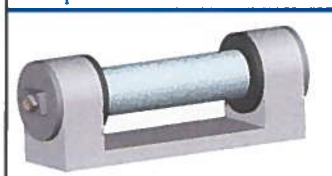
Diode laser based Quartz-Enhanced Photoacoustic Spectrometer

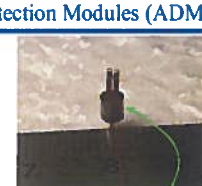


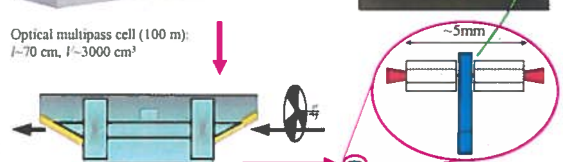
A. Kosterev et al. Appl. Phys. B 80, 133 (2005)

Comparative Size of Absorbance Detection Modules (ADM)



Optical multipass cell (100 m): l~70 cm, V~3000 cm³

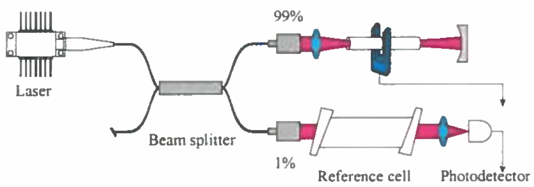




Resonant photoacoustic cell (1000 Hz): l~60 cm, V~50 cm³

QEPAS ADM: l~0.5 cm, V~0.05 cm³

Near-IR QEPAS Gas Sensor



Diode laser is wavelength modulated at half the resonant frequency of the TF, signal is detected at the TF resonant frequency – 2*f* modulation spectroscopy

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NASA Target Gas Opportunity Matrix

Molecule	Detection Limit (ppb)	QEPAS detectable?	
		1.3-1.7 µm	2-5 µm
Formaldehyde	10	No	X
Acetaldehyde	20	Experiments required	
Ammonia	100	X	X
Carbon monoxide	1000	Probably not	X
Hydrogen cyanide	100	X	X
Carbon dioxide	<2%	X	X
Nitrogen dioxide	100	Probably not	X
HF	100	Experiments required	
Acrolein (2-Propenal)	5	Unlikely	
Water vapor	10-90%	X	X

X – Demonstrated

X – Highly expected based on the existing technology level

X – Expected with the technology advance

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QEPAS Performance for 10 Trace Gas Species (Dec'05)

Molecule (Host)	Frequency, cm^{-1}	Pressure, Torr	NNEA, $cm^{-1}W/Hz^{1/2}$	Power, mW	NEC (τ=1s), ppmv
H_2O (N_2)**	7181.17	60	2.1×10^{-9}	5.8	0.18
HCN (air: 50% hum) **	6539.11	60	$< 2.6\times10^{-9}$	50	0.1
C_2H_2 ((N_2)**	6529.17	75	$\sim2.5\times10^{-9}$	~40	0.06
NH_3 (N_2)*	6528.76	60	5.4×10^{-9}	38	0.50
CO_2 (exhaled air)	6514.25	90	1.0×10^{-8}	5.2	890
CO_2 (N_2) ***	4990.00	300	1.5×10^{-7}	4.6	130
CH_2O (N_2) *	2832.48	100	1.1×10^{-8}	4.6	0.28
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

* - Improved microresonator

** - Improved microresonator and double optical pass through QTF

*** - Without microresonator

NNEA – normalized noise equivalent absorption coefficient.

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

For comparison: conventional PAS 2.2×10^{-9} $cm^{-1}W/\sqrt{Hz}$ (1,800 Hz) for NH_3*

* M. E. Webber, M. Pushkarsky and C. K. N Patel, Appl. Opt. 42, 2119-2126 (2003)

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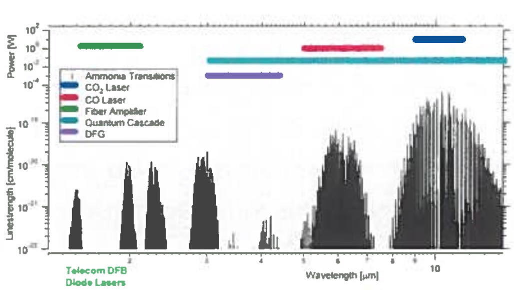
Motivation for NH_3 Detection

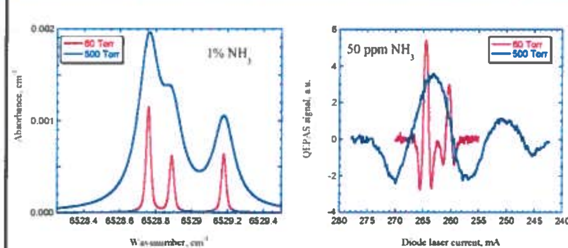
- Spacecraft related gas monitoring
- Monitoring NH_3 concentrations in the exhaust stream of NO_x removal systems based on selective catalytic reduction (SCR) techniques
- Semiconductor process monitoring & control
- Monitoring of industrial refrigeration facilities
- Pollutant gas monitoring
- Atmospheric chemistry
- Medical diagnostics (kidney & liver dysfunctions)

Infrared NH_3 Absorption Spectra



M. Webber et al. 2003, Pranalytica

Ammonia Detection using a 1.53 µm Telecom Diode Laser

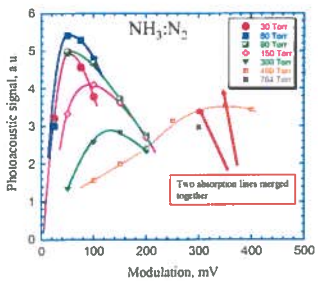


Spectral simulations based on data from Webber et al., APPLIED OPTICS 40, 2031-2042 (2001)]

QEPAS spectra at different pressures of NH_3:N_2 gas mixture; t=0.3s, 38 mW diode laser excitation power at 6529 cm^{-1}

Applied Optics 43, 6213-6217, 2004

Pressure Dependence of QEPAS Sensitivity



- Peak optical absorption varies with pressure
- Q-factor decreases at higher pressure
- V-T relaxation is faster at higher pressure
- Acoustic resonator enhancement factor changes with pressure

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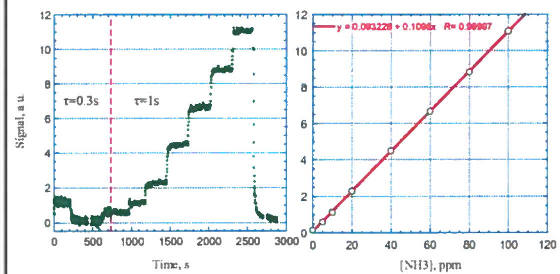
Calibration and Linearity of QEPAS based NH_3 Sensor



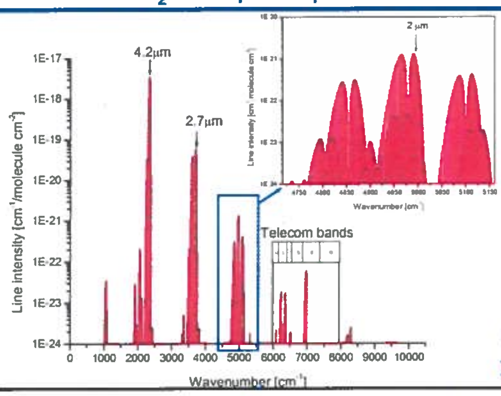
Noise-equivalent (1s) concentration (NEC), for τ=1s time constant is 0.65 ppmv for 38 mW excitation power

90 last points of each step averaged

(Traditional PAS* – 2.2×10⁻⁹ cm⁻¹W/√Hz)
*Webber et al., APPLIED OPTICS 42, 2119, 2003

To Date Noise-equivalent Absorption (NEA) Coefficient k=5.4×10⁻⁹ cm⁻¹W/Hz$^{1/2}$

CO_2 absorption spectrum



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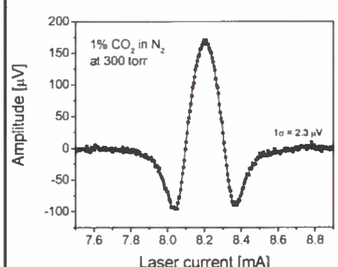
CO_2 detection limit



- SNR : ~74 (~135 ppm of CO_2)
- Laser power: ~ 4.6 mW
- Lock-in time constant: 1 s
- Peak absorption coefficient: ~ 1.4×10⁻³ cm⁻¹
- Normalized noise equivalent sensitivity for CO_2 in dry N_2:

$$NES = 1.54\times10^{-7}\,cm^{-1}W/\sqrt{Hz}$$

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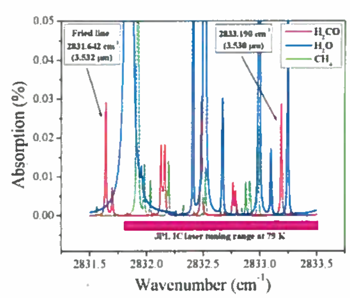
Motivation for Precision Monitoring of H_2CO

- Pollutant due to incomplete fuel combustion processes
- Potential trace contaminant in industrial manufactured products
- Precursor to atmospheric O_3 production
- Medically important gas

HITRAN Based Simulation of a H_2CO-H_2O-CH_4 Spectrum in Tuning Range of a 3.53μm IC Laser



- H_2CO : 10 ppb
- H_2O : 3%
- CH_4 : 2 ppm
- Optical path: 100 m
- Total pressure: 30 Torr

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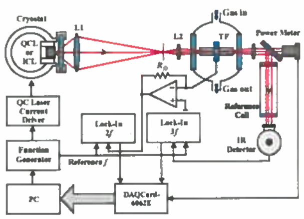
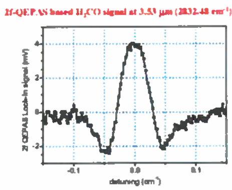
QCL based Quartz-Enhanced Photoacoustic Sensor





- $[H_2CO]$: 13.27 ppm
- QEPAS NNEA Sensitivity:
  1.1×10^{-8} cm^{-1} W/√Hz;
  NEC (τ=1s): 0.28 ppmv (5 mW)

For comparison:
QEPAS Sensitivity for NH_3 :
5.4×10^{-9} cm^{-1}W/ √ Hz
NEC (τ=1s): 0.50 ppmv (38 mW)

M. Horstjann et al., Applied Physics B 79, 799, 2004

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Merits of QE Laser-PAS based Trace Gas Detection

- High sensitivity (ppm to ppb gas concentration levels) and excellent dynamic range
- Immunity to ambient and flow acoustic noise, laser noise and etalon effects, which allows applications that involve harsh operating environments
- Required sample volume is very small. The volume is ultimately limited by the gap size between the TF prongs, which is < 1 mm³ for the presently used QTF.
- No spectrally selective elements are required
- Applicable over a wide range of pressures, including atmospheric pressure
- Sensitive to phase shift introduced by vibrational to translational (V-T) relaxation processes and hence the potential of concentration measurements of spectrally interfering species
- Ultra-compact, rugged and low cost compared to LAS that requires a multipass absorption cell and infrared detector(s)
- Potential for optically multiplexed concentration measurements

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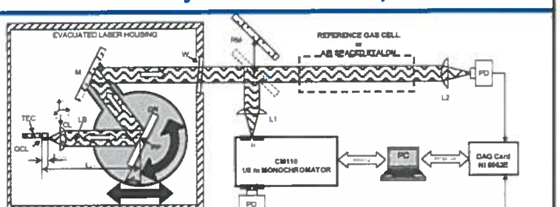
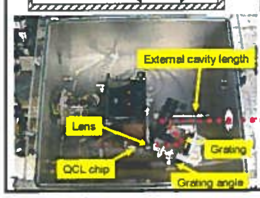
External Cavity QCL Based Spectrometer

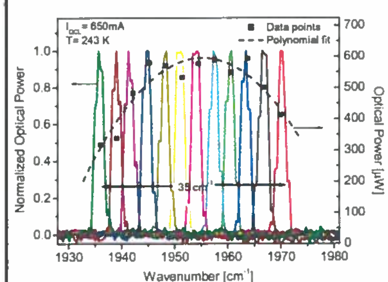




- PZT controlled EC-length
- PZT controlled grating angle
- Optimization of cavity alignment performed by means of lens positioning using electrically controlled 3D translation stage

G. Wysocki et al. Applied Physics B, 81, p 769 (2005)

Wide Wavelength Tuning with Diffraction Grating



- Coarse wavelength tuning is performed by varying diffraction grating angle
- Due to residual reflection at the QCL output facet a mode hop free tuning across the available bandwidth is not possible

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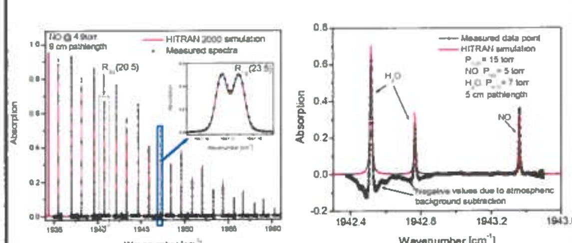
Mid-IR NO Absorption Spectra Acquired with a Tunable TEC QCL



Summary and Future Directions

- **QEPAS based Trace Gas Sensors**
  - Ultra compact (~ 0.2 mm³), robust & low cost sensors based on QEPAS
  - QEPAS is immune to ambient noise. The measured noise level coincides with the thermal noise of the QTF
  - Best to date demonstrated QEPAS sensitivity is 2.1 x 10^{-9} cm^{-1}W/√Hz for H_2O:N_2
  - QEPAS exhibits a low 1/f noise level, allowing data averaging for more than 3 hours
  - Detected 14 trace gases to date: NH_3, CH_4, N_2O, CO_2, CO, NO, H_2O, COS, HCN, C_2H_4, C_2H_2, C_2H_5OH, SO_2, H_2CO and several isotopic species of C, O, N & H
  - Sensitive to phase shift introduced by V-T relaxation dynamics
  - Potential for spectrally interfering species concentration measurements
- **Applications in Trace Gas Detection**
  - Environmental & Spacecraft Monitoring (NH_3, CO, CH_4, C_2H_4, N_2O, CO_2 and H_2CO)
  - Medical Diagnostics (NO, CO, COS, CO_2, NH_3, C_2H_4)
  - Industrial process control and chemical analysis (NO, NH_3, H_2O)
- **Future Directions and Collaborations**
  - QEPAS based applications using novel thermoelectrically cooled cw and broadly wavelength tunable quantum and interband cascade lasers
  - Investigate QTFs with lower resonant frequencies
  - Investigate amplitude modulation QEPAS potential and limitations
  - New target gases, in particular VOCs and HCs
  - Development of optically multiplexed gas sensor networks based on QEPAS