Tunable Mid-IR External Cavity Quantum Cascade Laser based Spectroscopic Sensor for Acetone Detection

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OUTLINE

Optics East 2007
Boston, MA
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- Motivation: Wide Range of Chemical Sensing
- New mid-IR EC QCL laser technology
- Selected Applications to Trace Gas Detection in Medical Diagnostics and Homeland Security
  - Detection of acetone
- Future Directions and Conclusions

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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**

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DLS Widely Tunable Mid-IR Pulsed EC QCL

Introduced in 2006

Room Temperature—No Cryogenic Cooling

Center Wavelengths: 4.5 μm, 5.5 μm, 8.5 μm, 9.5 μm, 10.5 μm

Tuning Range: >10%

Average Power (CW): 1 mW–10 mW

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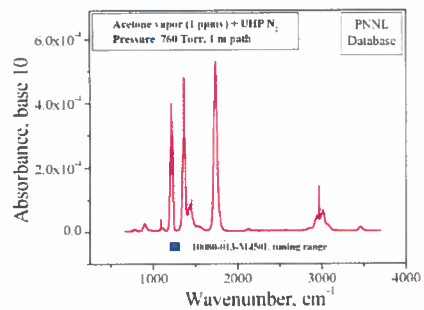
Simulated Acetone Spectrum



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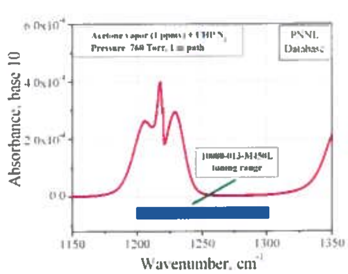
Simulated acetone spectrum in tuning range of pulsed DLS EC-QCL



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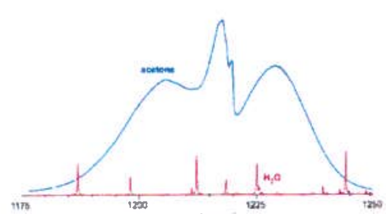
Comparison of acetone spectrum at 8.2 μm with H2O interferences



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EC-QCL Absorption Platform

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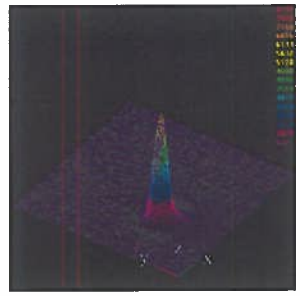
3D beam profile of DLS pulsed EC-QCL



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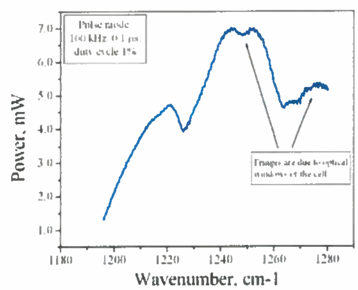
EC-QCL Output Power



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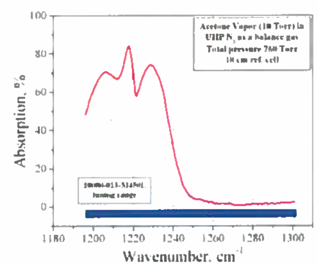
Measured Acetone Absorption Spectrum



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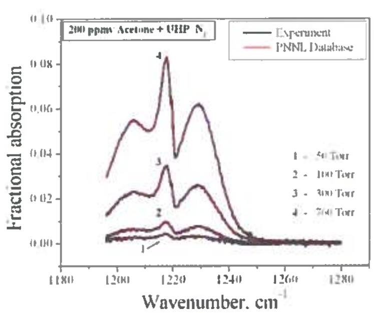
Experimental spectra of acetone at different pressures with fitting curves



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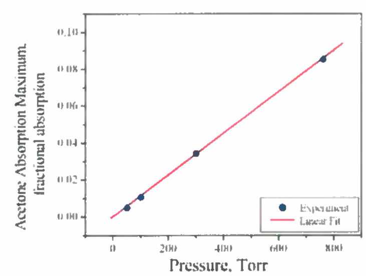
Linear characteristics of the acetone absorption amplitude with pressure



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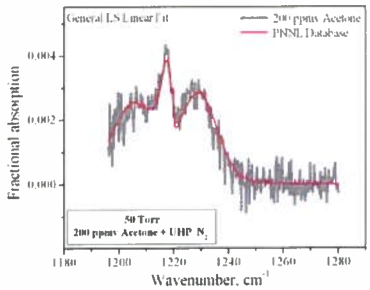
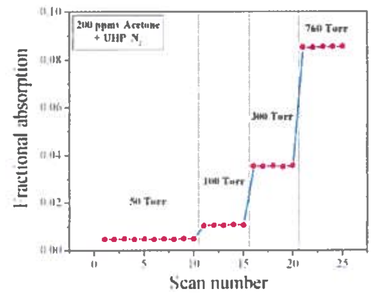
Acetone absorption spectrum at a gas mixture pressure of 50 Torr



Acetone absorption measurements at 4 different pressures



Development of a breath acetone monitor by DLS and JHU

- Measurement of ketosis
- Goal: To detect breath acetone at concentrations 10 ppb with a response time of 0.1 seconds. Portable device to allow breath analysis to be performed in a variety of situations.
- Direct absorption spectroscopy
  - Quantum cascade laser
  - Pathlength 12 meters
  - Atmospheric pressure
  - Scan about 70 cm^{-1}

Advantages of breath tests

- Breath can be analyzed non-invasively from spontaneously breathing human subjects (neonate to the elderly), laboratory animals (from mice to horses), or from intubated patients (in ORs or ICUs).
- Breath can be sampled in the clinic, the home, the field, at the patient bedside, or in the physician's office by nurses, technicians, physicians and by the patient themselves.
- Breath analysis can be used:- for nutritional studies, for exercise studies, to detect disease, to stage disease, to monitor therapy or to monitor treatment

History of breath analysis

- Presence of water vapor in breath has been used for centuries to establish life.
- Classical medicine has used subjective impressions of the odors of urine, breath, *etc* to "diagnose" disease.
- Lavoisier first detected carbon dioxide in breath in 1784.
- Earliest modern publications on breath analysis date from late 1960s - early 1970s and mirror the development of modern analytical chemistry particularly gas chromatography and mass spectrometry

Breath is an instantaneous product of the following sources

- Molecules originating from inspiratory air (current or historical exposure)
- Molecules that are directly or indirectly derived from foods and beverages
- Molecules produced by normal and abnormal physiologies may originate from cells or tissues throughout the body.

Breath biomarkers in humans

as many as 400 different molecules in breath, many with defined biochemical pathways:

compound	concentration	physiological basis
acetaldehyde	ppb	ethanol metabolism
acetone	ppm	decarboxylation of acetoacetate
ammonia	ppb	protein metabolism
carbon dioxide	%	product of respiration
carbon disulfide	ppb	gut bacteria
carbon monoxide	ppm	production catalyzed by *heme oxygenase*
carbonyl sulfide	ppb	gut bacteria
ethane	ppb	lipid peroxidation
ethanol	ppb	gut bacteria
ethylene	ppb	lipid peroxidation
hydrocarbons	ppb	lipid peroxidation/metabolism
hydrogen	ppm	gut bacteria
isoprene	ppb	cholesterol biosynthesis
methane	ppm	gut bacteria
methanethiol	ppb	methionine metabolism
methanol	ppb	metabolism of fruit
methylamine	ppb	protein metabolism
nitric oxide	ppb	production catalyzed by *nitric oxide synthase*
oxygen	%	required for normal respiration
pentane	ppb	lipid peroxidation
water	%	product of respiration

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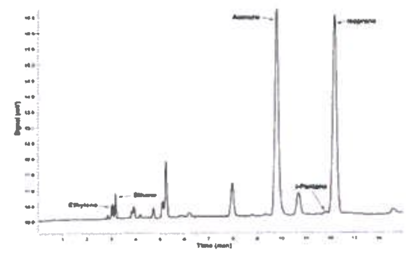
Normal human breath profile



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Method for breath collection or breath sampling is as important as the method of analysis

- Breath molecules originate from tissues and cells throughout the organism including oral/nasal cavities
- Breath components will change during the breath cycle (mouth, nose, sinuses, airway, alveolar etc)
- Breath composition will change with breathing physiology

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Single breath sampling

- Control flow
- Control mouth pressure monitor pressure continuously
- Monitor the concentration of carbon dioxide continuously

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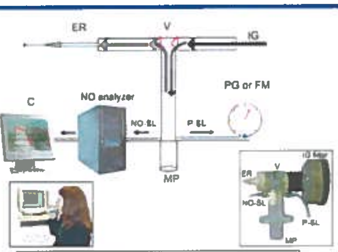
A real time breath NO monitor



ATS/ERS (*Am J Respir Crit Care Med* 171:912-930, 2005)

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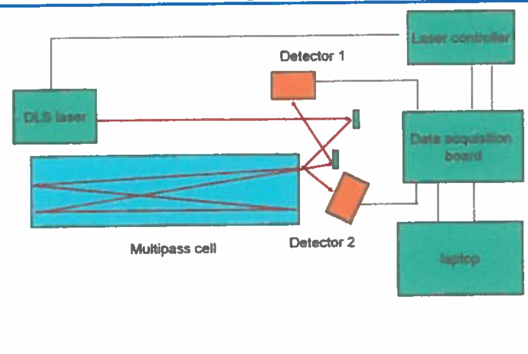
Human Acetone Levels

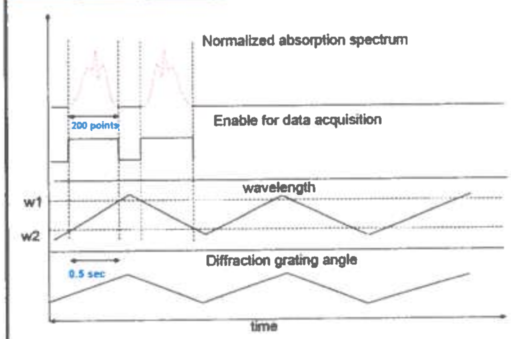
Physical State	Blood Acetone Concentration	Breath Acetone Concentration	
	(mg/liter)	(µg/liter)	(ppm)
Healthy	0.84[4]	1.16[5] to 1.3[6]	0.5
3-Day Fasted	46.5[7]	64.6*	27*
Ketoacidotic	290[7]	403*	170*
	424[5]	589*	248*
Diabetic**			2 to 5[8]

*calculated using 720:1 blood to breath acetone ratio
**insulin dependent, adequately controlled diabetic

Basic design of system

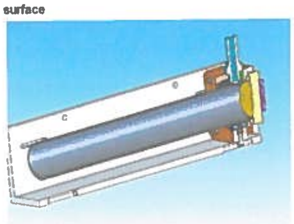


Data acquisition

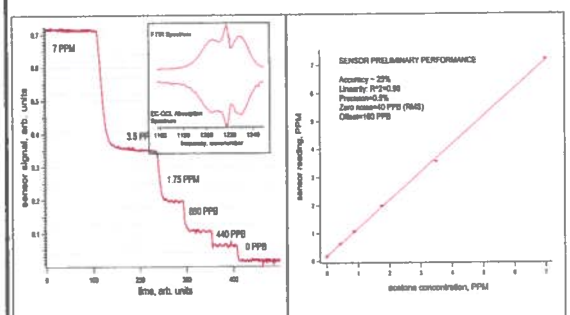


Absorption cell design

- Etalon free components
- Single part tip/tilt flange
- Simple cylindrical outer surface for heating
- Mirror may be removed and mounted back with no alignment
- No extra volume, no hidden volume
- Inlet port next to mirror surface
- Vacuum compatible

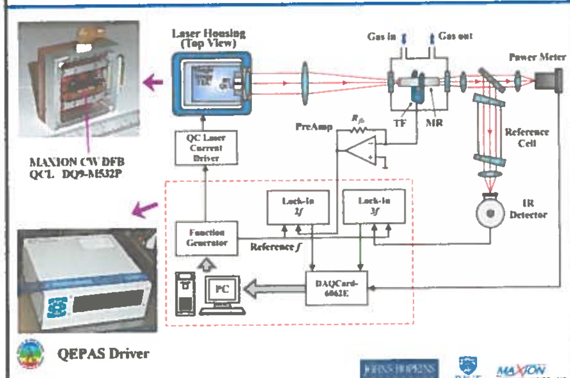


Preliminary acetone data



New DLS widely tunable cw EC-QCL

Mid-IR QEPAS based NH_3 Gas Sensor Architecture



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Conclusions

- Clinical breath analysis will only be successful if physicians, physiologists, analytical chemists, laser spectroscopists, solid state physicists collaborate.
- MIRTHE is unique in that all the above experts are involved.
- Finally MIRTHE's success will rely on you students who will be trained to talk across disciplines.

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