

### Widely Tunable, High Power, Mode-hop Free, CW External Cavity Quantum Cascade Lasers at 5.3 & 8.5µm

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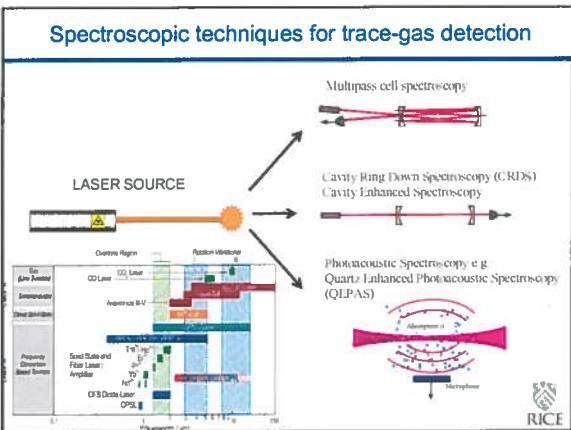
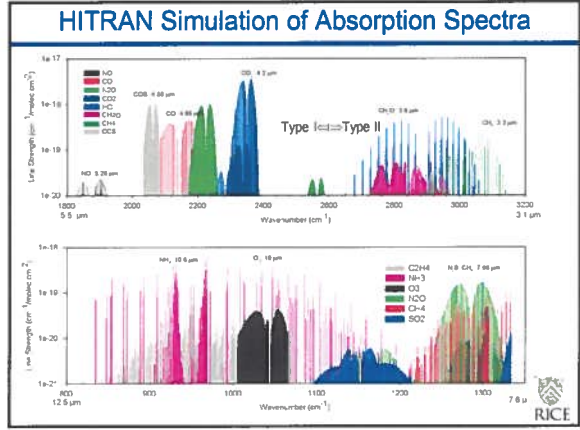
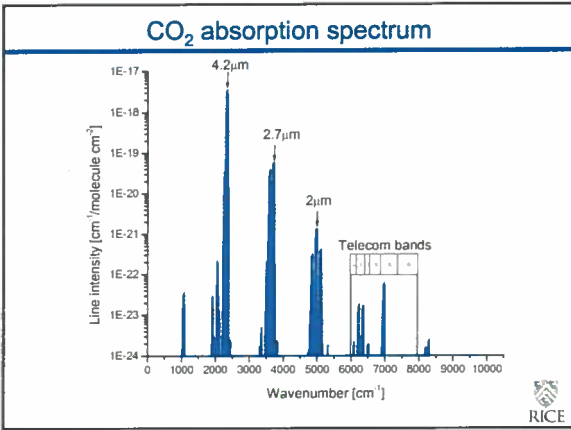
**OUTLINE:**

- Motivation: Tunable mid-infrared lasers
- External Cavity Quantum Cascade Lasers
  - CW, RT EC-QCL at  $\lambda = 5.3\mu\text{m}$ 
    - Performance characteristics
    - Spectroscopic measurements
  - High power, CW, RT EC-QCL at  $\lambda = 8.5\mu\text{m}$ 
    - Performance characteristics
    - Spectroscopic measurements
- Summary and Future Directions

Financial Support by:

### 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**


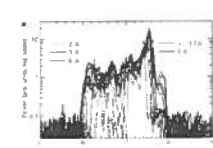



### Mid-IR Source Requirements for Laser Spectroscopy

REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Wavelength, Power
Selectivity (Spectral Resolution)	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelength
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	No Consumables
Field deployable	Compact & Robust

### Quantum Cascade Laser: Basic Facts

- Semiconductor lasers (III-V materials)
- Multiple-quantum-well heterostructure
- Intersubband transitions (emission wavelength defined by band-structure engineering and independent of material energy bandgap)
- Laser wavelengths cover the Mid-IR range (~3 – 24 $\mu$ m)
- High quantum efficiency (Cascading: 1 electron = N photons)
- High laser power (>500 mW cw, >5W peak for pulsed)
- High spectral purity - single frequency with DFB structure (~10 cm<sup>-1</sup> tunability) or external cavity (>200 cm<sup>-1</sup> tunability → pulsed mode)
- High reliability, long lifetime
- Capable of room temperature operation (Pulsed: up to +150°C; CW: up to RT)
- Compact


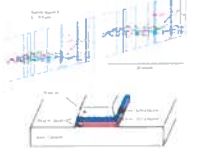




C. Grisch et al. Nature, v. 445, 883 (2002)

Hochstetler et al. Appl. Phys. Lett. vol. 75, p. 654, 1999

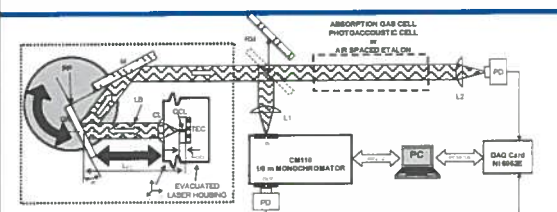
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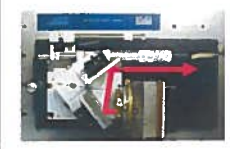



R. Maulini, M. Minetti, M. Geronzi, J. Faust, E. Ott, Appl. Phys. Lett. 88, 2911 (2006)

### Tunable external cavity QCL based spectrometer, 2006

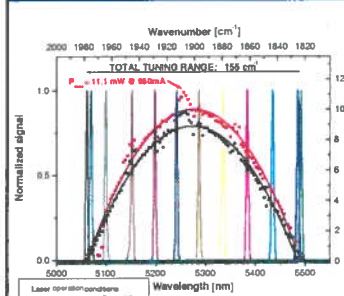


- Fine wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized coarse grating angle tuning
- Vacuum tight QCL enclosure with built-in 3D lens positioner (TEC laser cooling + chilled water cooling)

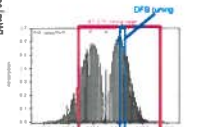


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### Wide Wavelength Tuning of a 5.3 $\mu$ m EC-QCL



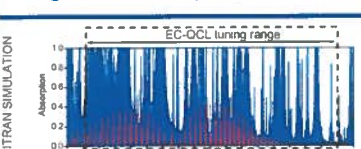
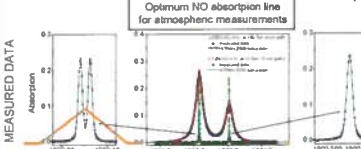
- Coarse wavelength tuning of 155 cm<sup>-1</sup> is performed by varying diffraction grating angle
- Max. CW power ~11mW
- Access to Q(3/2) transition of NO at 1875.8 cm<sup>-1</sup> for LMR spectroscopy



G. Wysocki, R. F. Curl, F. K. Tittel, R. Maulini, J. Faust, manuscript in preparation 2007

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### High resolution spectroscopy with a 5.3 $\mu$ m EC-QCL

- Mode hop free scan of up to ~2cm<sup>-1</sup> with a resolution <0.001cm<sup>-1</sup> (30MHz) can be performed anywhere within the tuning range

FTIR resolution ~0.1cm<sup>-1</sup>

G. Wysocki, R. F. Curl, F. K. Tittel, R. Maulini, J. Faust, manuscript in preparation 2007

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### Breath Biomarkers in Humans

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


Compound	Concentration	Physiological basis/Pathology Indication
Acetaldehyde	ppb	Ethanol metabolism
Acetone	ppm	Decarboxylation of acetoacetyl, diabetes, protein metabolism, liver and renal disease
Ammonia	ppb	Gut bacteria, schizophrenia
Carbon dioxide	%	Product of respiration, Helicobacter pylori
Carbon disulfide	ppb	Gut bacteria, schizophrenia
Carbon monoxide	ppm	Production catalyzed by heme oxygenase
Carbonyl sulfide	ppb	Gut bacteria, liver disease
Ethane	ppb	Lipid peroxidation and oxidative stress
Ethanol	ppb	Gut bacteria
Ethylene	ppb	Lipid peroxidation, oxidative stress, cancer
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, oxidative stress
Water	%	Product of respiration


Torrence Risby, Johns Hopkins University

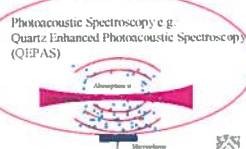
## QCLs for Absorption Spectroscopy

**QCLs, ICLs:**

- Pulsed (DFB - RT)**
  - Easily achievable RT operation
  - High peak power
  - Lower etalon effects
  - Broadened laser linewidth (chirp)
  - Limited applicability due to pulsed operation
- CW (DFB - LN and RT)**
  - Superior laser linewidth (high spectroscopic selectivity)
  - LN cooling
  - Limited availability for RT operation (usually with low optical power)
- CW (EC - LN and RT)**
  - Wide frequency tuning range
  - Still under development
  - Limited availability

**Multipass cell spectroscopy**  


**Cavity Ring Down Spectroscopy (CRDS) / Cavity Enhanced Spectroscopy**  


**Photoacoustic Spectroscopy e.g. Quartz Enhanced Photoacoustic Spectroscopy (QEPAS)**  


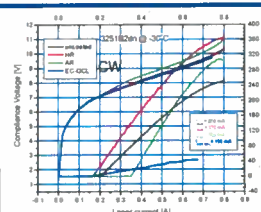
DFB - Distributed Feedback  
 LN - Liquid Nitrogen Temperature  
 LN - Liquid Nitrogen temperature  
 EC - External Cavity configuration

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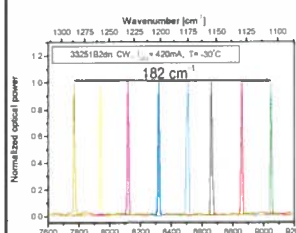
## EC-QCL emitting at $\lambda = 8.5 \mu\text{m}$

$P_{\text{EC-opt}}$  up to **50 mW (cw)**

AR coating:  
 $R_{\text{AR}} = 2 \times 10^{-4}$



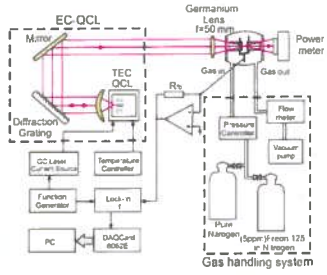
**Tunability  $182 \text{ cm}^{-1}$**   
 @  $8.4 \mu\text{m}$  ( $7.77 \mu\text{m} - 9.05 \mu\text{m}$ )  
 15.3 % of the center wavelength



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## 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 ( $< 1 \text{ mm}^3$ )
- Sensitivity is limited by the fundamental thermal TF noise
- Compact, rugged and low cost
- Potential for trace gas sensor networks

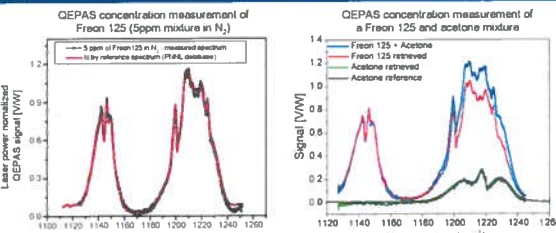
R. Lewicki, G. Wysocki, A.A. Kostarev, F. K. Tittel, QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at  $8.5 \mu\text{m}$ , submitted to Optics Express, April 2007

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## Motivation for Monitoring of Freon 125 and acetone

- Freon 125 ( $\text{C}_2\text{HF}_5$ )
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals e.g. chemical warfare agents
- Acetone ( $\text{CH}_3\text{COCH}_3$ )
  - Recognized biomarker for diabetes

## Spectroscopy of Broadband Absorbers with Widely Tunable EC-QCL at $\lambda = 8.5 \mu\text{m}$



**Minimum detection limit ( $1\sigma$ ) of  $\sim 4.5 \text{ ppb}$  was obtained for Freon 125 with an average laser power of 6.6 mW**

**Wide tunability enables excellent molecular selectivity for broad band absorbers**

R. Lewicki, G. Wysocki, A.A. Kostarev, F. K. Tittel, QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at  $8.5 \mu\text{m}$ , submitted to Optics Express, April 2007

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## EC-QCL in Laser Spectroscopy

REQUIREMENTS	IR LASER SOURCE
Sensitivity (% to ppt)	Power
Selectivity	Single Mode Operation and Narrow Linewidth
Multi-gas Components, Multiple Absorption Lines and Broadband Absorbers	Tunable Wavelength
Directionality or Cavity Mode Matching	Beam Quality
Rapid Data Acquisition	Fast Time Response
Room Temperature Operation	No Consumables
Field deployable	Compact & Robust

## Summary & Future Directions

- Widely tunable, continuous wave and thermoelectrically cooled EC-QCLs operating at 5.3 $\mu\text{m}$  and 8.5 $\mu\text{m}$  were demonstrated
- Mode-hop free wavelength tuning enables high resolution (<math>0.001\text{cm}^{-1}</math>) spectroscopic applications
- PZT actuated mode tracking system allows employing gain chips operating at both shorter and longer wavelengths without modification of its mechanical construction (chips with lower efficiency AR coatings can be used)
- Wavelength tunability up to 15% of the center wavelength was demonstrated
- Output optical power up to 50 mW
- The main limitations in the scanning speed (limited by the mechanical resonances of the EC-QCL construction), which will be addressed in future EC-QCL designs.
- The novel broadly wavelength tunable quantum cascade lasers enable new applications in laser based trace gas sensing
  - Sensitive concentration measurements of broadband absorbers, in particular VOCs and HCs
  - Multi-species detection

