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QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at 8.4 μm.

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OUTLINE:

- Motivation: Wide Range of Chemical Sensing Applications
- Widely Tunable Mid-IR QCL Sensor Platform
- External Cavity Quantum Cascade Lasers
  - Quartz Enhanced L-PAS (Freon 125, acetone)
  - Nitric Oxide
- Summary and Future Directions

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Boston, MA
USA

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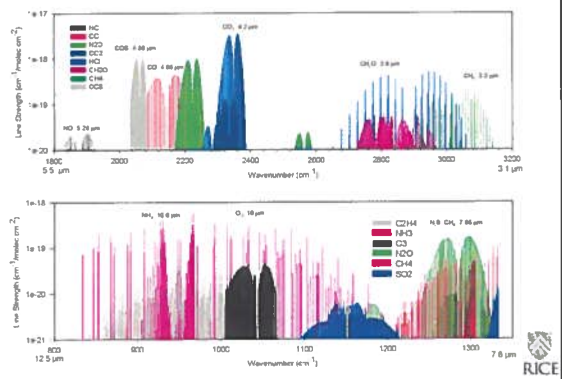
9-12, 2007

HITRAN Simulation of Absorption Spectra



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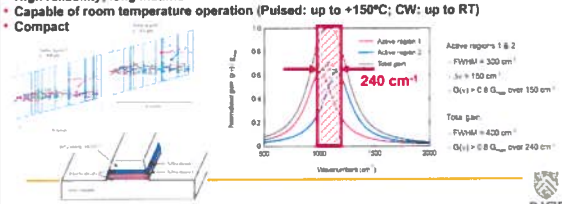
Mid-IR Source Requirements for Laser Spectroscopy

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 Wavelengths
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 – 24μm)
- 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^{-1} temperature tuning, ~2cm^{-1} current tuning) or external cavity (>200 cm^{-1} tunability → pulsed mode)
- High reliability, long lifetime
- Capable of room temperature operation (Pulsed: up to +150°C; CW: up to RT)
- Compact



R. Maulini, A. Mohan, M. Giovannini, J. Faist, E. Gini Appl. Phys. Lett. 88, 201113 (2006)

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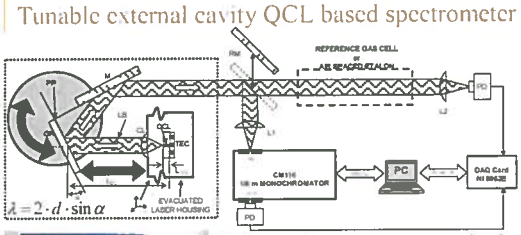
Tunable external cavity QCL based spectrometer



- High resolution mode-hop free wavelength tuning
  - PZT controlled EC-length
  - PZT controlled grating angle
  - QCL current control
- Motorized course grating angle tuning
- Vacuum tight QCL enclosure with build-in 3D lens positioner (TEC laser cooling + chilled water cooling)

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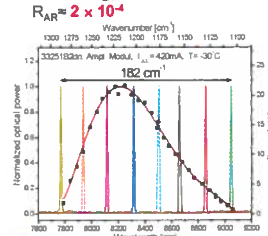
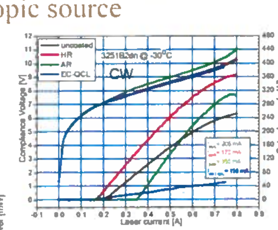
Performance of a 8.4 μm EC-QCL spectroscopic source

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

AR coating:
$R_{AR} \approx$ **2 x 10^{-4}**





Tunability **182 cm^{-1}**
@8.4 μm (7.77μm - 9.05μm)
15.3 % of the center wavelength

G. Wysocki, R. F. Curl, F. K. Tittel, F. Capasso, L. Diehl, M. Troccoli, R. Maulini, J. Faist, manuscript in preparation 2007

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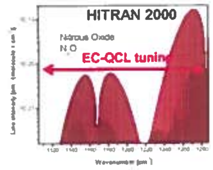
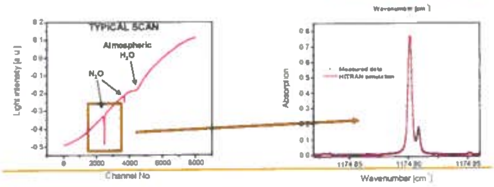
High resolution spectroscopy with a 8.4µm EC-QCL

- Mode hop free scan of up to ~1.25 cm^{-1} with a resolution <0.001cm^{-1} (30MHz) can be performed anywhere within the tuning range





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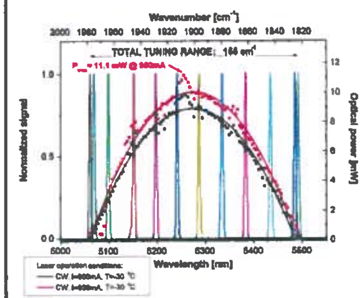
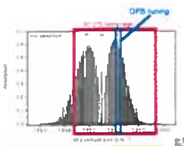
Wide Wavelength Tuning of a 5.2µm EC-QCL



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



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

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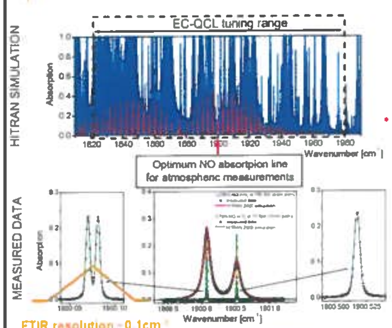
High resolution spectroscopy with a 5.2µm EC-QCL



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

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

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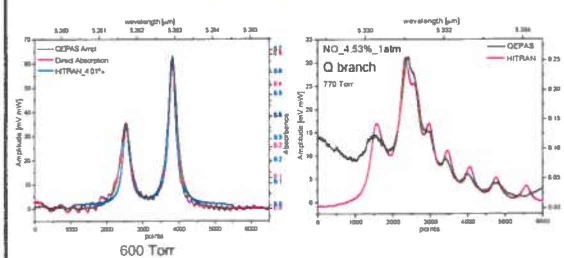
NO measurements with 5.2µm CW EC-QCL using QFT as a chopper



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Motivation for Monitoring Freon 125 and acetone

- Freon 125 (C_2HF_5)
  - Refrigerant (leak detection)
  - Safe simulant for toxic chemicals e.g. chemical warfare agents
- Acetone (CH_3COCH_3)
  - Recognized biomarker for diabetes

BOTH MOLECULES HAVE BROADBAND UNRESOLVABLE ABSORPTION FEATURES !!!

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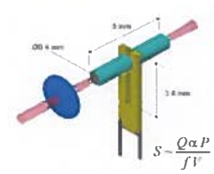
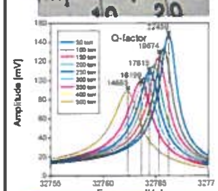
QEPAS sensor





- Miniature size, 0.3 mm³ detection volume
- Dimensions in mm: length = 3.8, gap size = 0.3, thickness = 0.3, width = 0.58
- Piezo-active material
- Signal currents ≈ pA
- Intrinsically high Q factor, ~10,000 at ambient pressure; Q_{vacuum} ~ 125,000

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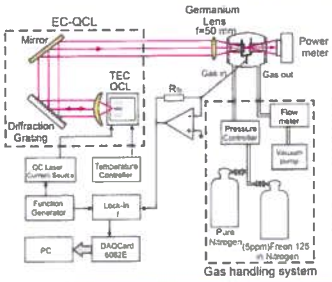
8.4 µm RT CW EC-QCL based QEPAS trace gas sensor



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
- Does not require an IR photodetector

R. Lewicki, G. Wysocki, A.A. Kosterev, F. K. Tittel „QEPAS based detection of broadband absorbing molecules using a widely tunable, cw quantum cascade laser at 8.4 µm", Optics Express, Vol. 15, No. 12, June 2007

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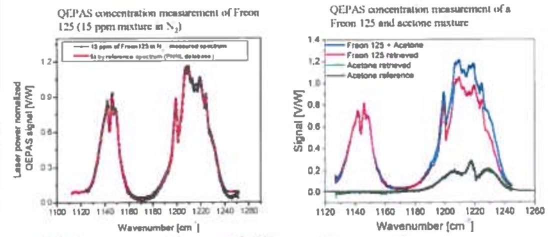
Spectroscopy of Broadband Absorbers with Widely Tunable EC-QCL at λ = 8.4 µm



- Minimum detection limit (1σ) of ~ 3 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

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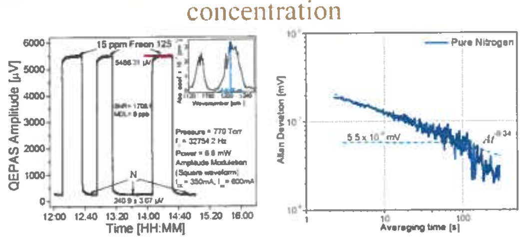
Single point measurements of Freon 125 concentration



$NNEA = 7.92 \cdot 10^{-9} (cm^{-1} \cdot W / \sqrt{Hz})$

For t = 100s NEC = 0.1ppb

Minimum detection limit (1σ) : ~ 9 ppb in 1 sec

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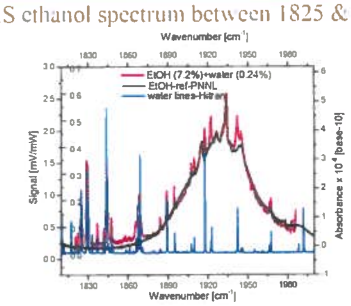
QEPAS ethanol spectrum between 1825 & 1980 cm⁻¹



Reference spectrum from the PNNL spectral database (black line).
Sharp features on the ethanol spectrum correspond to the water absorption lines.
Blue line depicts water absorption spectrum simulated using HITRAN database.

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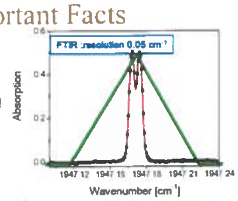
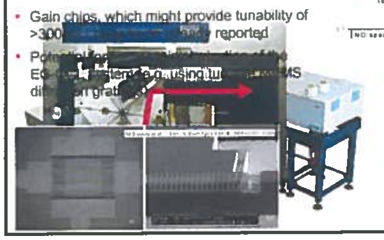
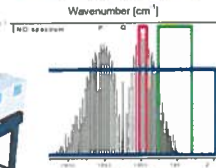
EC-QCL - Important Facts

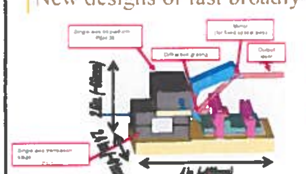
- Laser spectroscopy provides superior resolution compared to other techniques e.g. FTIR
- Single mode operation of the laser is required for high resolution spectroscopy
- Wavelength tunability of single mode (DFB) mid-IR semiconductor lasers is ~10cm⁻¹
- Gain chips, which might provide tunability of >300 [illegible] reported
- Po[illegible] E[illegible] e.g. using [illegible] MS di[illegible] grat[illegible]



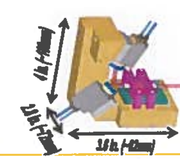




New designs of fast broadly tunable EC-QCLs (2007)



- Optical configuration based on the previous EC-QCLs
- Fast tuning capabilities:
  - Broadband tuning up to 1KHz
  - High resolution mode-hop free tuning up to 400Hz



- New optical configuration
- Fast tuning capabilities:
  - Broadband tuning up to 6 KHz
  - High resolution mode-hop free tuning up to 6 KHz

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Summary & Future Directions of mid-IR Sensor Technology

- Widely tunable, continuous wave and thermoelectrically cooled EC-QCL operating at 8.4μm and 5.2 μm were developed
- Trace gas detection of two broadband absorbing molecules were demonstrated
- Mode-hop free wavelength tuning enables high resolution (<0.001cm-1) 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 with output optical power up to 50 mW was demonstrated for 8.4 μm QC laser
- Future design of EC-QCL will focus on increasing of the scanning speed which now is limited by the mechanical resonances of the EC-QCL construction.
- 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