QUANTUM CASCADE LASER BASED TRACE GAS SENSORS

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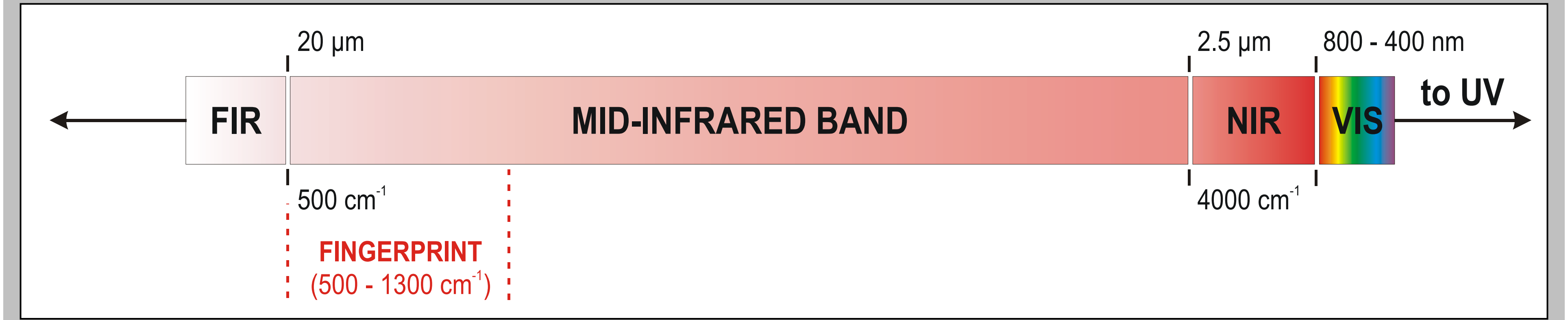
Why Mid-IR Technology for Trace Gas Sensing?



- ✓ Analytes absorb with unique molecular signatures
- ✓ Selectivity inherently based on wavelength
- ✓ Single-mode, tunable QCLs promise sensitivity and miniaturization
- ✓ Can be used for simultaneous quantitative monitoring of different analytes in air for environmental detection, process monitoring, biomarkers in breath, etc.

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Outline

Quantum Cascade Laser Based Trace Gas Sensors

EC-QCL HWG Multianalyte Detection

Wavelength Selection by Cavity Length Variation

EC = external cavity, HWG = hollow waveguide, QCL = quantum cascade laser

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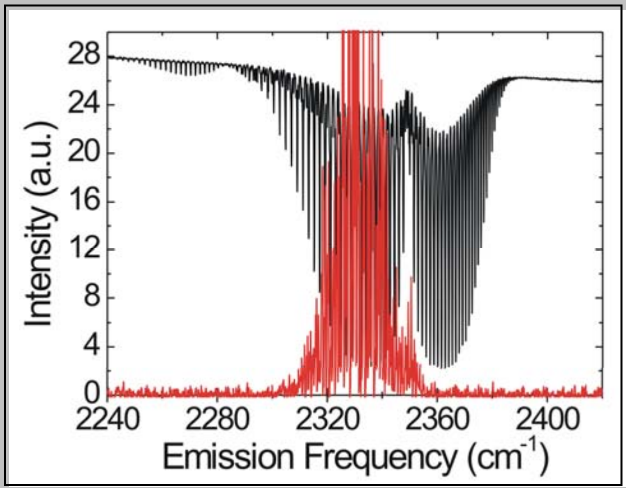
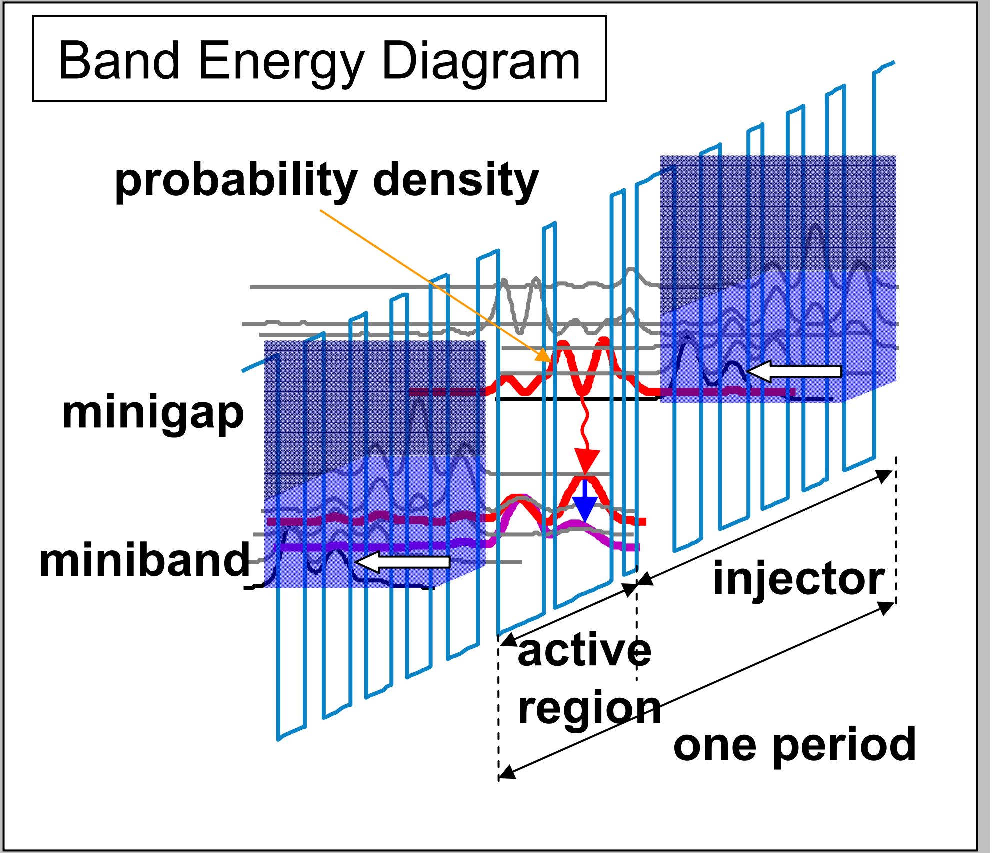
Quantum Cascade Lasers (QCL) for Trace Gas Sensing

Fundamentals

Intersubband transitions between quantized conduction band states

- **Injector**: Supplies electrons
- **Active region**: Design of energy levels 3 and 2 to achieve:
  - light amplification
  - desired laser frequency $\nu=(E_3-E_2)/h$





Young, C. *et. al*., Sensors and Actuators B: Chemical, 140(1), pp. 24-28.

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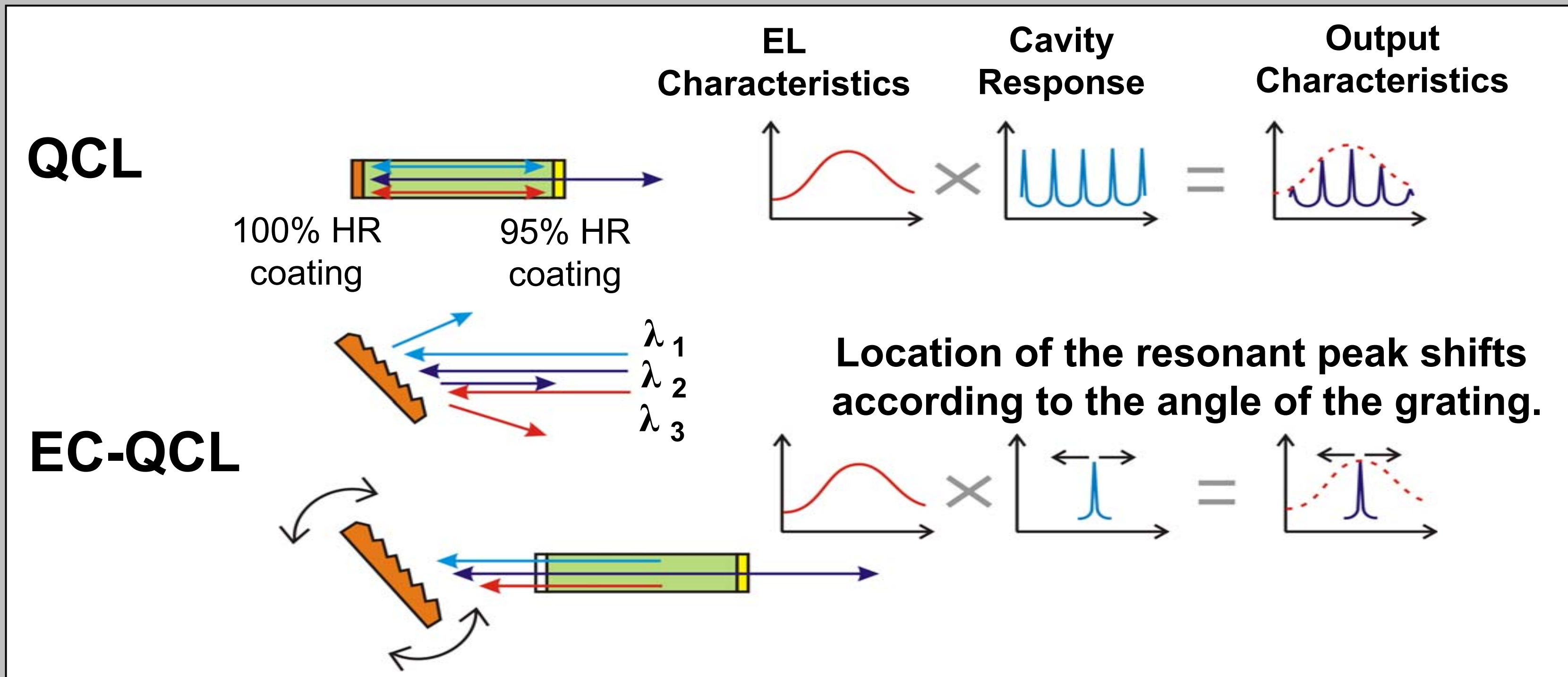
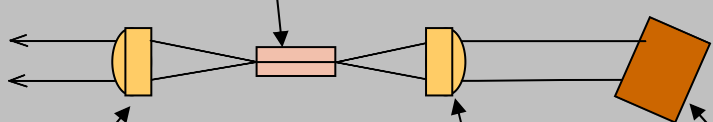
Widely Tunable EC-QCLs for Spectroscopic Applications

Fundamental Principles



Scheme Courtesy of Daylight Solutions, Inc.



- QCL tuning options: current or temperature (few cm^{-1}), external cavity
- EC provides ~ +/- 5% cm^{-1} tuning range of the central emission frequency

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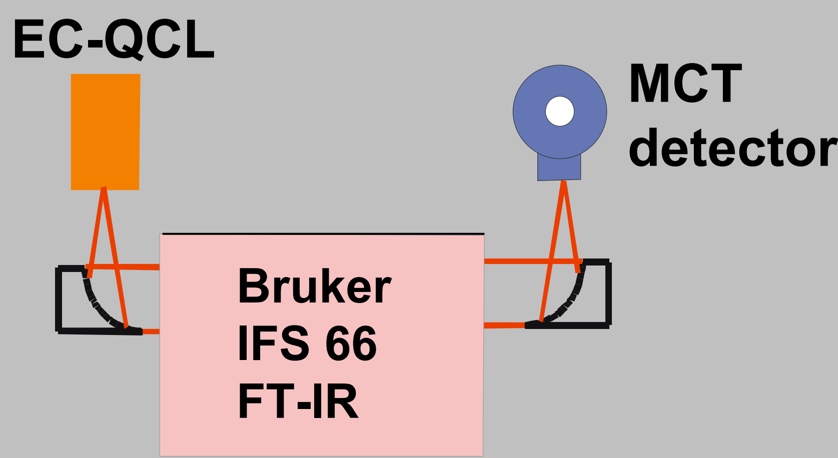
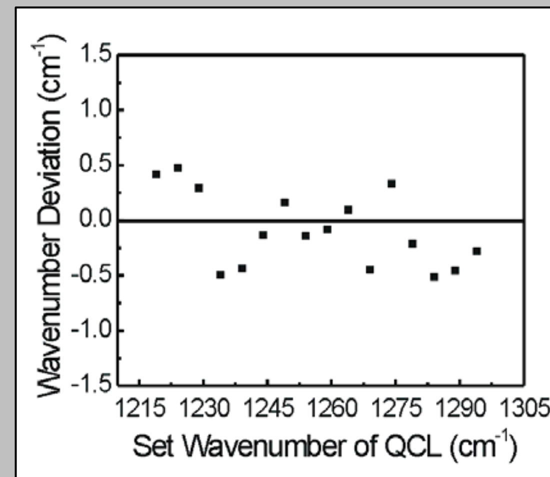
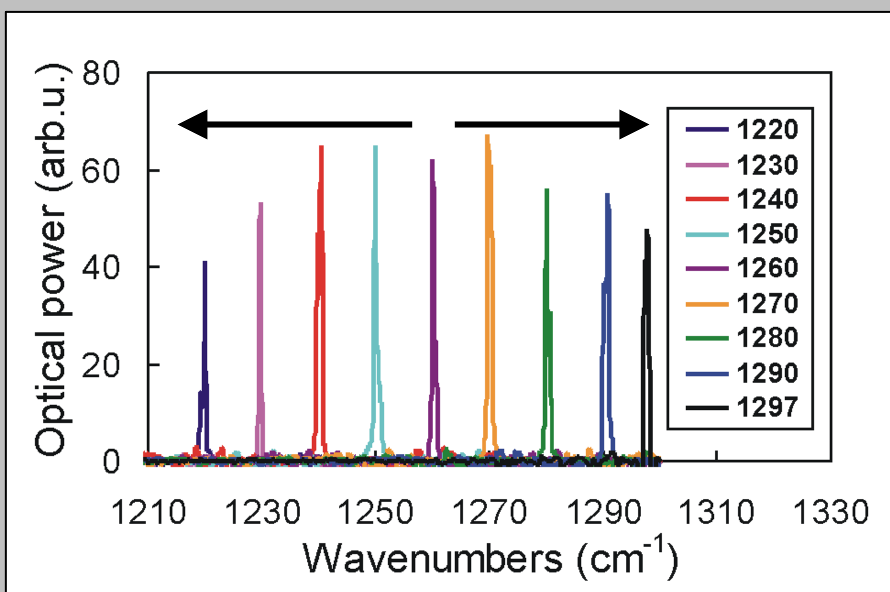
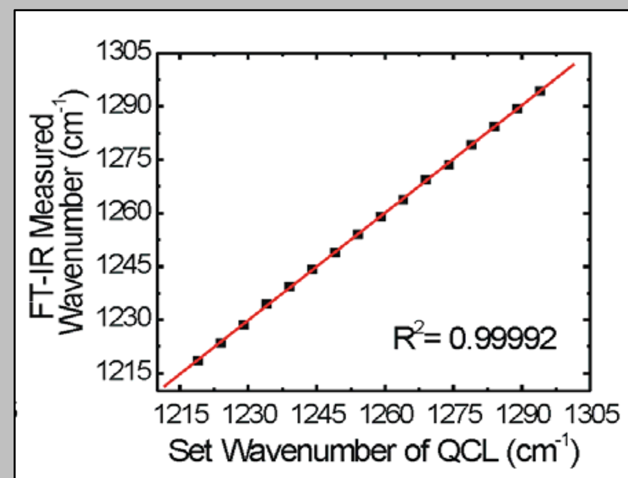
EC-QCL Emission Characterization

Central emission frequency of 1258 cm^{-1}









Operating Conditions: Temp: 0 C, Pulse Width: 0.50 μsec, Frequency: 100.0 kHz, Duty Cycle: 5%, I: 1500 mA

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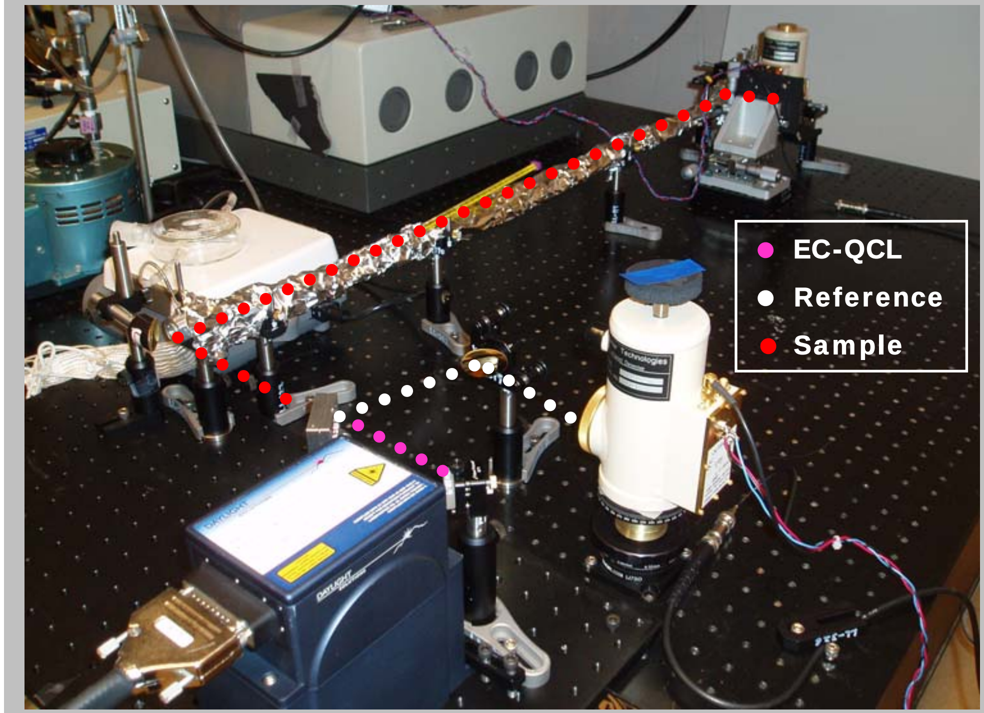
EC-QCL Trace Gas Sensor Experimental Setup

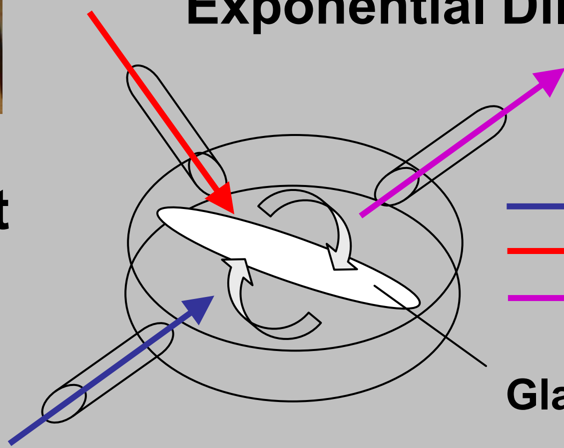
Individual analytes measured



Exponential dilution performed for three analytes to derive limit of detection (LOD):

- Ethyl chloride at 1287.25 cm^{-1}
- Dichloromethane at 1262 cm^{-1}
- Trichloromethane at 1220 cm^{-1}

Exponential Dilution Flask



$$C = C_0 e^{-\alpha t}$$

Where

C = final concentration

$\mathbf{C_0}$ = initial concentration

α = flowrate/vol of EDF

t = time elapsed between initial absorption and signal regeneration

Lovelock, J., Anal. Chem. 33, 163 (1961); Charlton, C., et. al., Appl. Phys. Lett. 86, 194102 (2005); Young, C.., et. al., Sens. Act. B. (2009)

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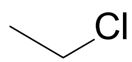
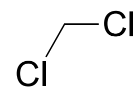
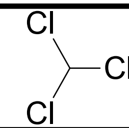
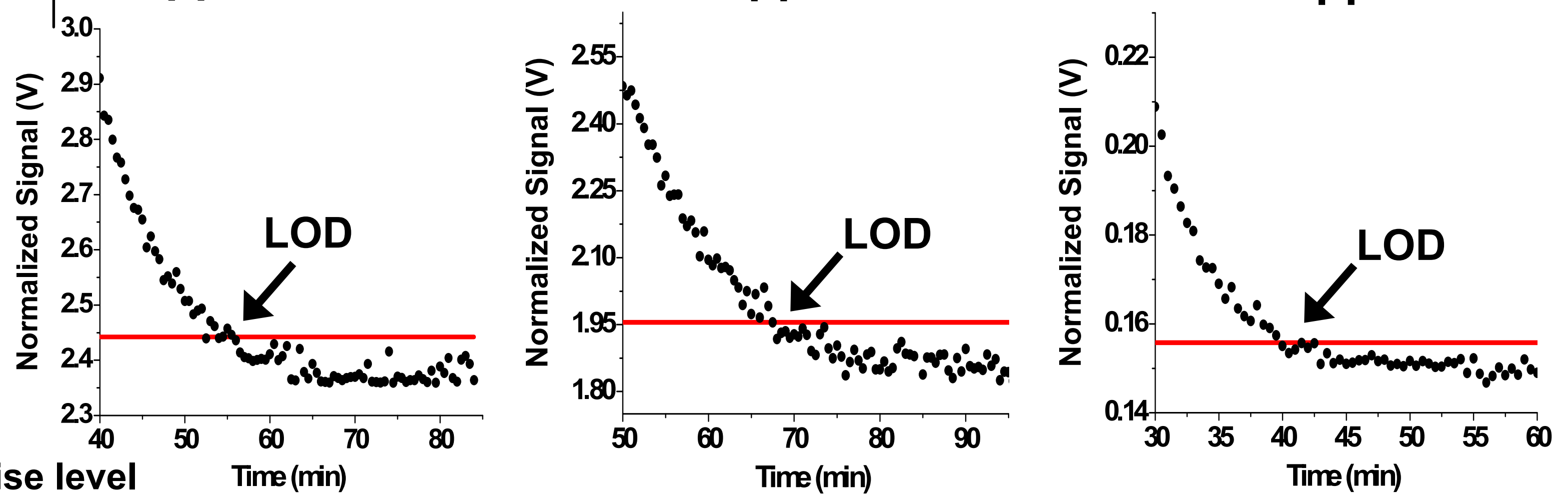
Univariate Results

EC-QCL precisely tuned to the Q-branch of CH_2 wag vibrational mode for each analyte

Analyte	Ethyl Chloride	Dichloromethane	Trichloromethane
Chemical Structure			
Assignment	υ_7	υ_9	υ_4
LOD	**13 ppb**	**7 ppm**	**11 ppb**
Variance	**5 ppb**	**5 ppm**	**15 ppb**



= noise level

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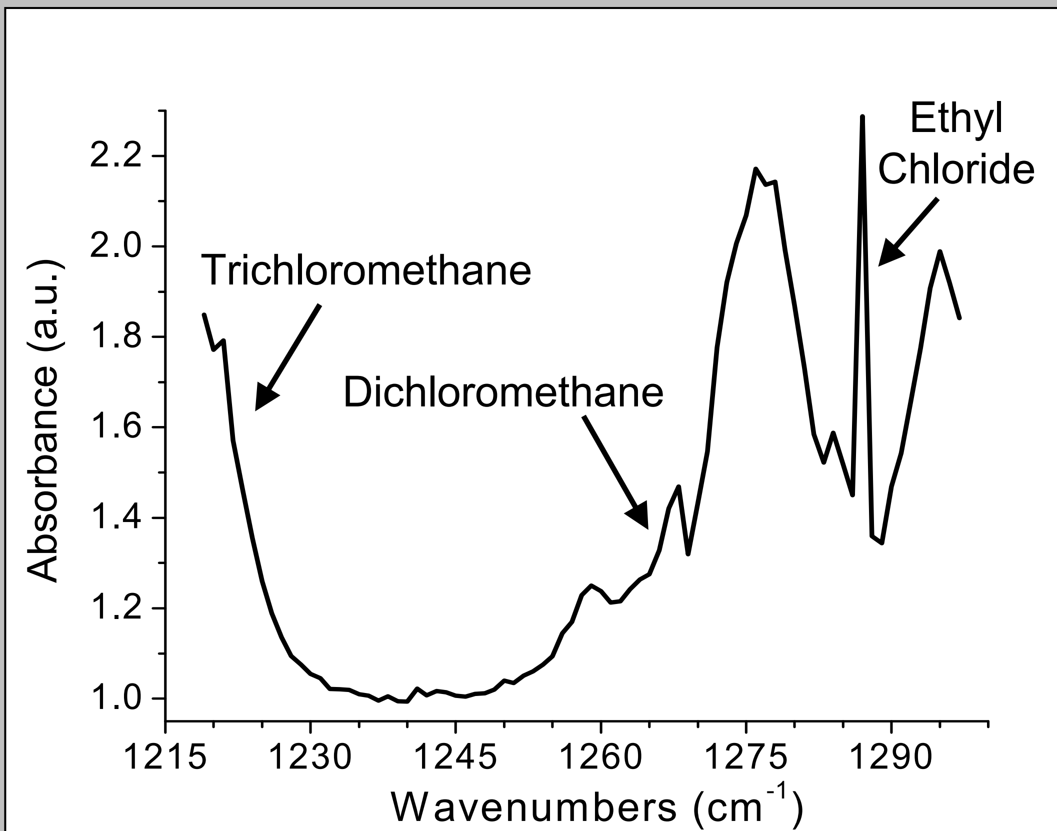
Quantitative Measurement of An Analyte in Mixture

Partial Least Squares (PLS) model based on 11 training set mixtures

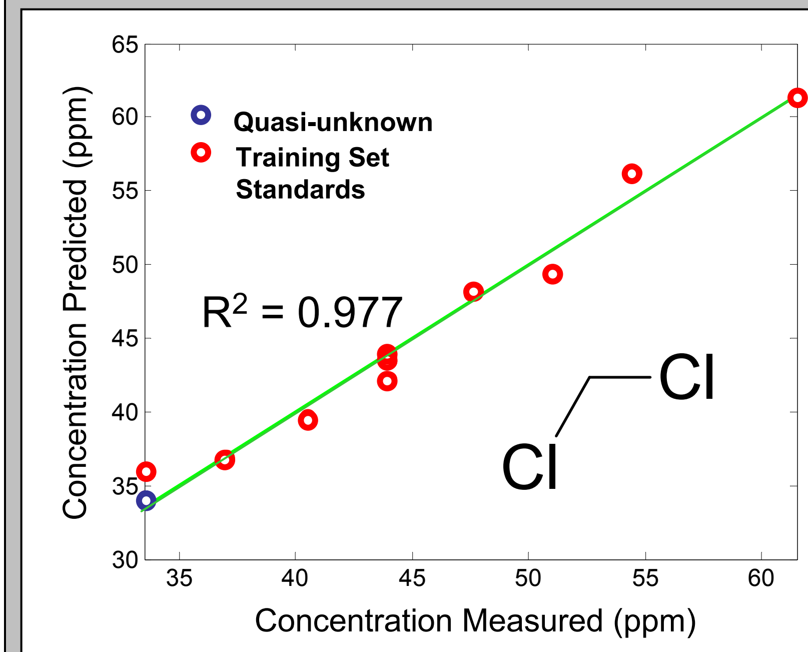
EC-QCL HWG gas spectrum,

1 cm^{-1} resolution



PLS Model Validation

(MATLAB (Mathworks ©)



Cross Validation, 7 Latent Variables

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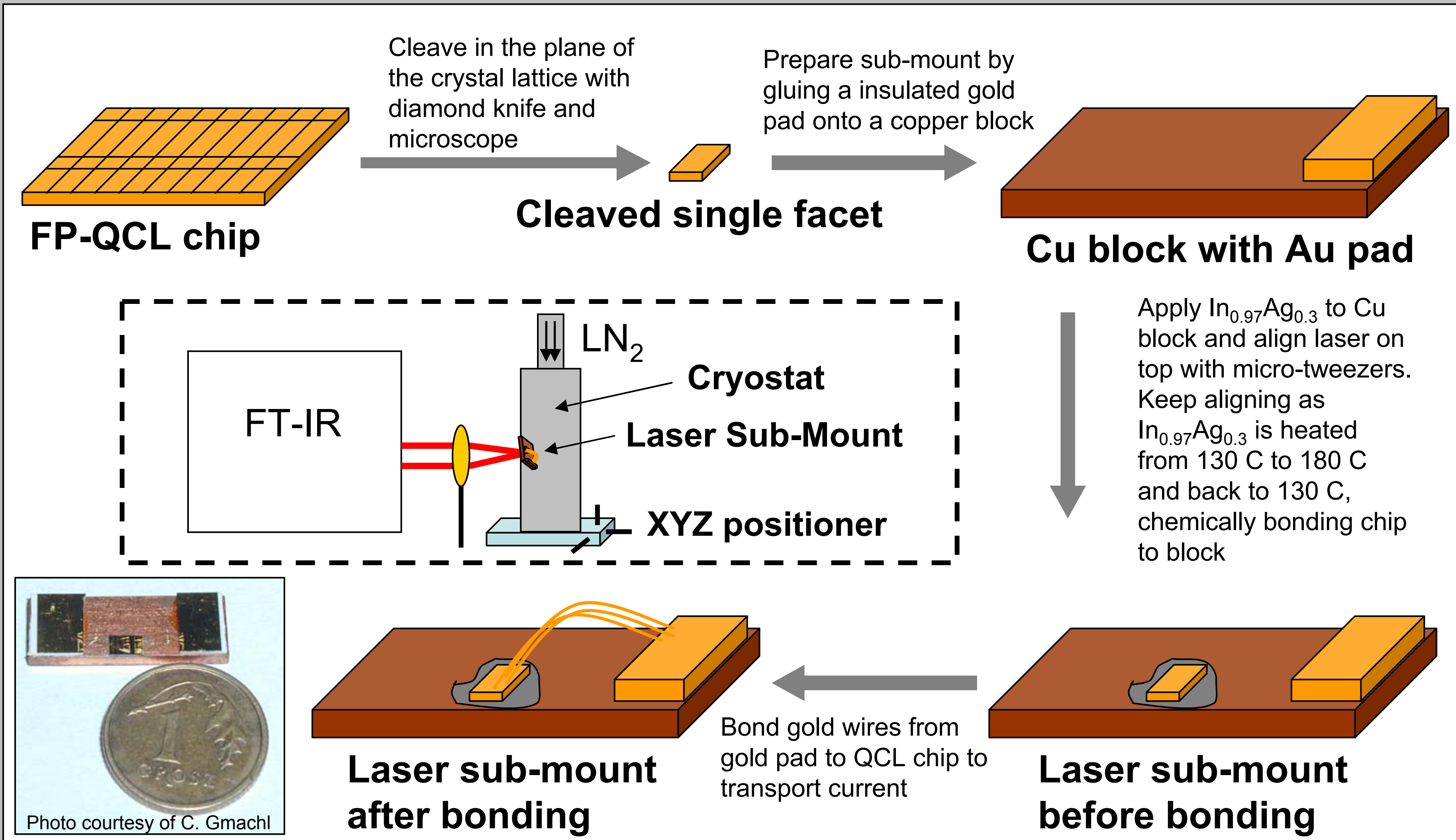
Mounting and Measuring the QCL

Collaboration with Mid-Infrared Photonics Group, MIRTHE, Princeton University



Young, C. *et. al*., Applied Physics Letters, 94(9), pp. 091109.

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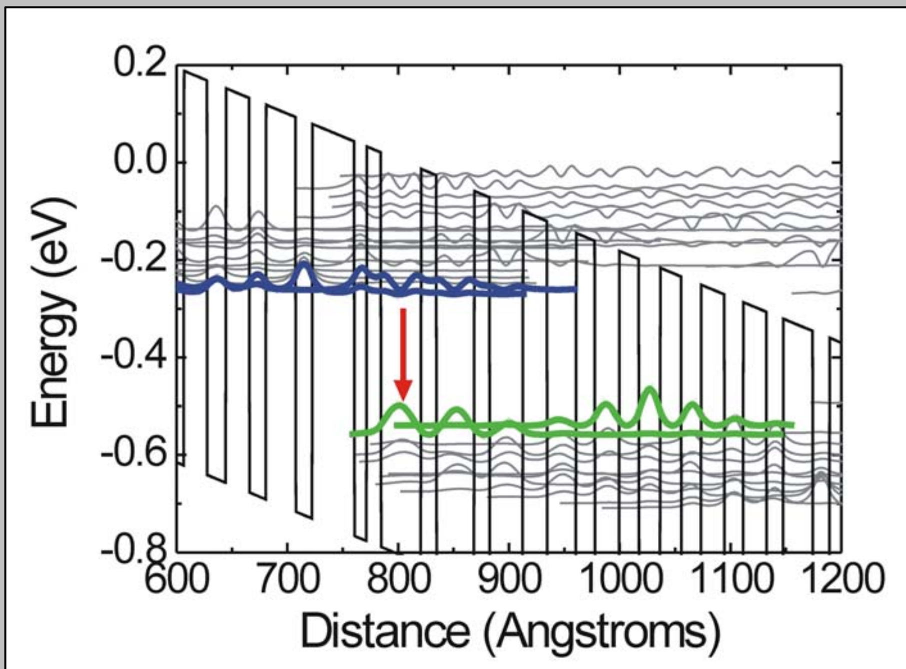
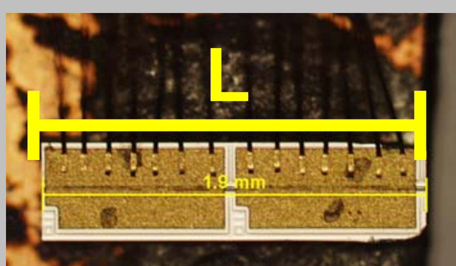
QCL Emission Tuning by Δ Cavity Length

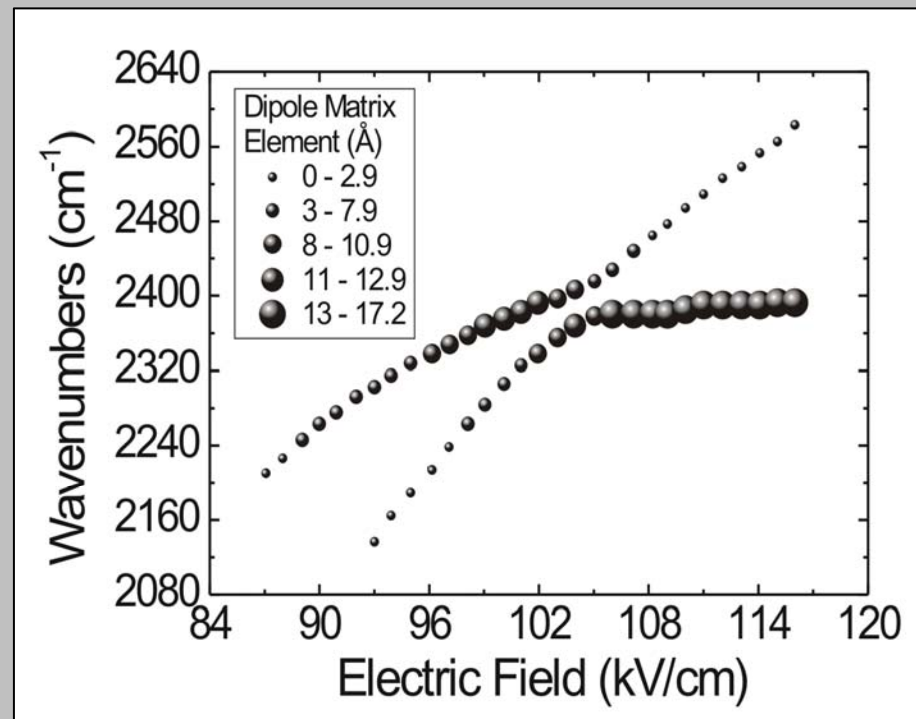
Theoretical

QCL Band Energy Diagram





Theoretical Calculations



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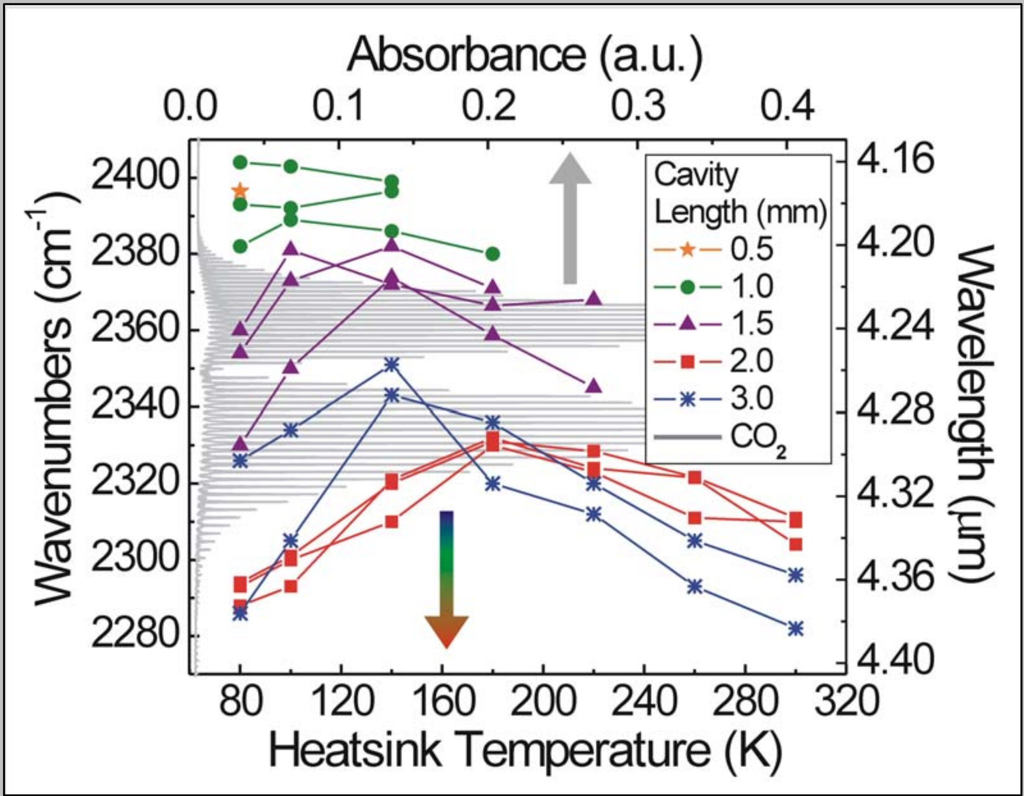
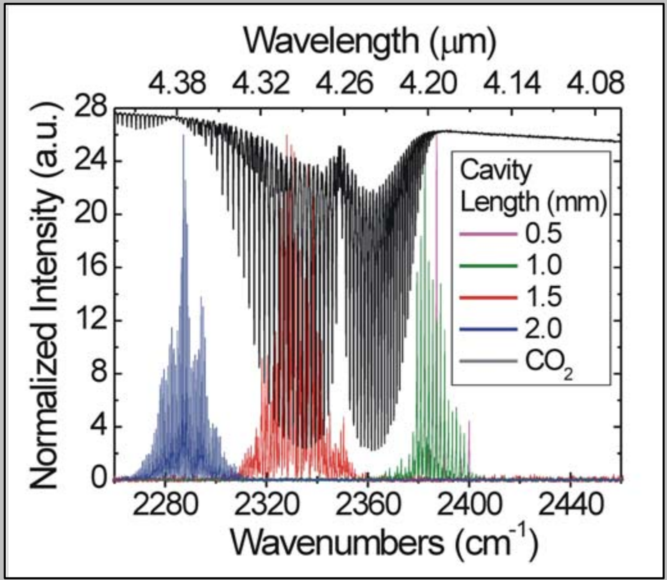
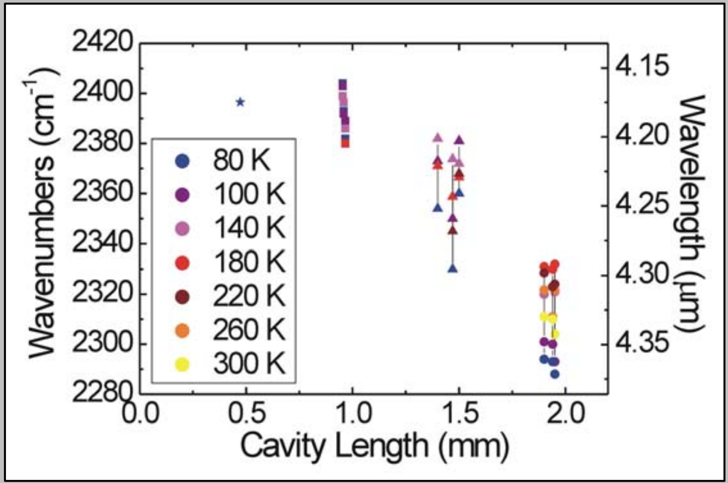
Towards Precise Overlap of QCL and Analyte Absorption





Frequency emission shifts with respect to cavity length due to changes in *n* and $\vec{E}$



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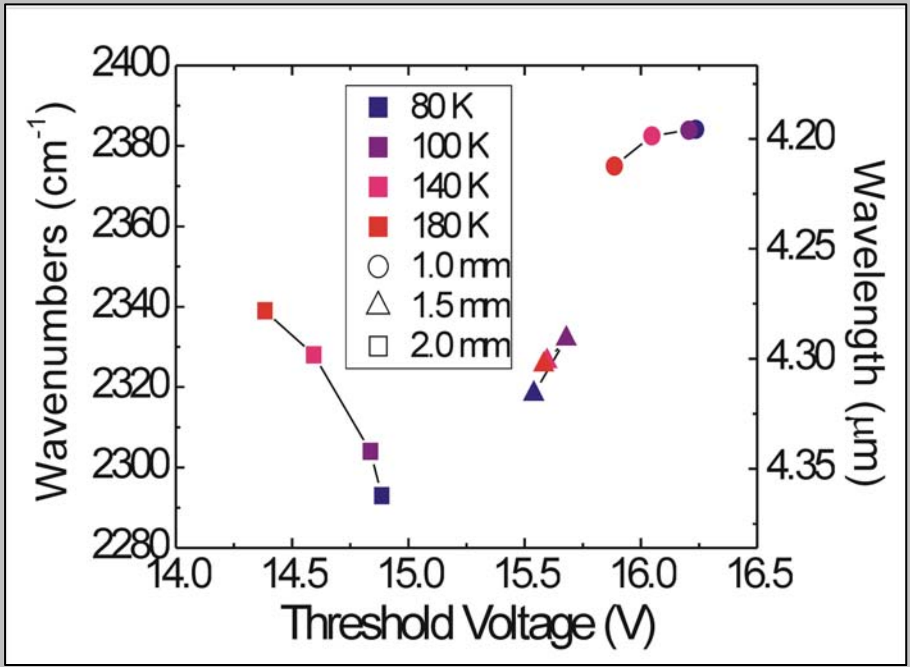
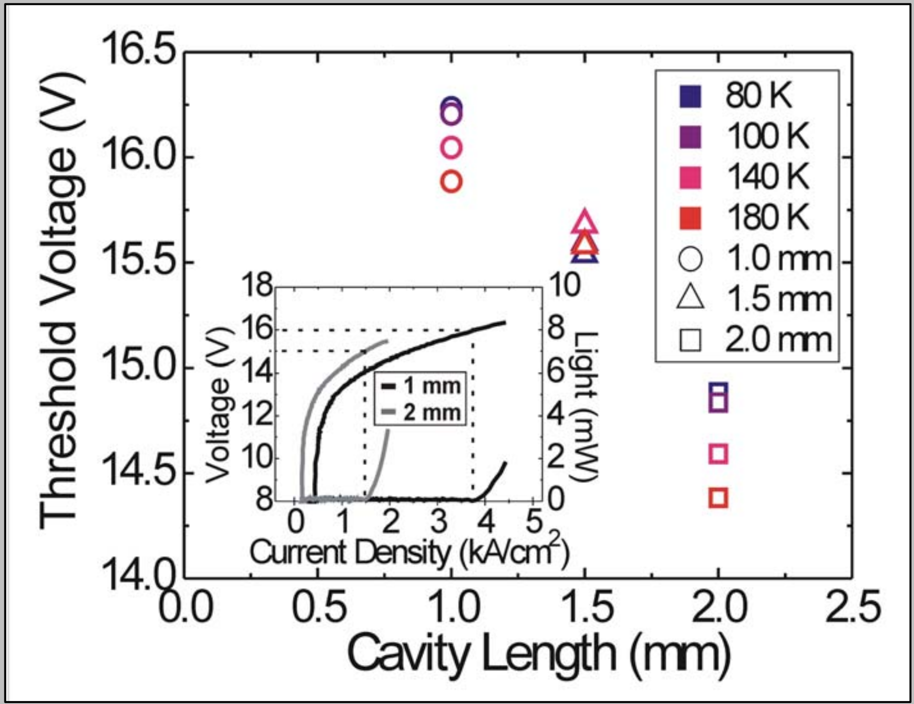
Cavity Length Dependence: Δ E_{field} Causes Δ λ_{em}

Experimental Results Confirm Theoretical Calculations

Emission Frequency Vs. V_{th}



V_{th} Vs. Cavity Length



Shorter cavity length:

- Increase in E_{field} (V_{th})
- Increase in λ_{em}

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Acknowledgments

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- Adtech Optics, Inc. for providing a507BH QCL

Questions?