QCL-Based Sensors for Chemical Kinetic Applications

Presented by:

OSA Laser Systems Technical Group

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OSA Laser Systems Technical Group

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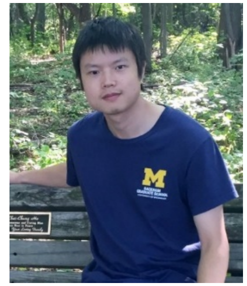

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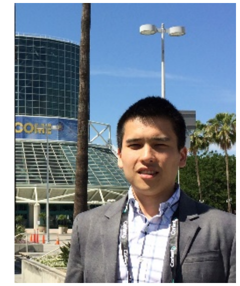

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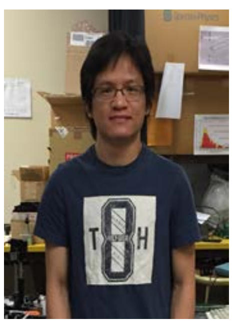

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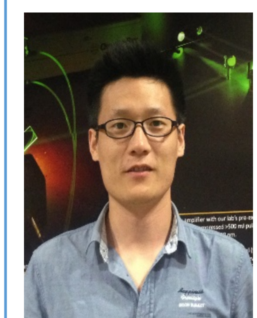

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Laser Systems Technical Group

Laser Systems (PL)

This group encompasses novel laser system development for a broad range of scientific, industrial, medical, remote sensing and other directed-energy applications. The group addresses technical issues concerning sources that cover the full spectral range, including: ultraviolet, visible, infrared, terahertz and microwave. Strong overlap with other technical groups that study and develop laser techniques and technologies brings together researchers and engineers to produce sources with unique performance, such as high-power, ultra-short pulses and high coherence.

On-Demand Laser Systems Webinars

You can watch any of the following webinar presentations, which were hosted by the OSA Laser Systems Technical Group, on-demand.

- From Semiconductor Nanolasers to Photonic Integrated Circuits
- III-Nitride Nanowire Light-Emitting Diodes Grown by Molecular Beam Epitaxy
- InAs/GaSb Mid-Wave Cascaded Superlattice Light Emitting Diodes

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Announcements

Upcoming Applied Optics Feature Issue

The Laser Systems Technical Group will be organizing a feature issue of ***Applied Optics*** on near- to mid-IR (1-13 μm) III-V semiconductor lasers.

This special issue will focus on recent advances in the field of III-V semiconductor lasers emitting in the near- to mid-infrared spectral regions, with particular emphasis on devices that emit radiation with wavelengths between 1 and 13 μm.

Submissions for this feature issue will be accepted from 1 May2017 until 1 June 2017.

Learn more >>

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OSA Laser Systems Technical Group

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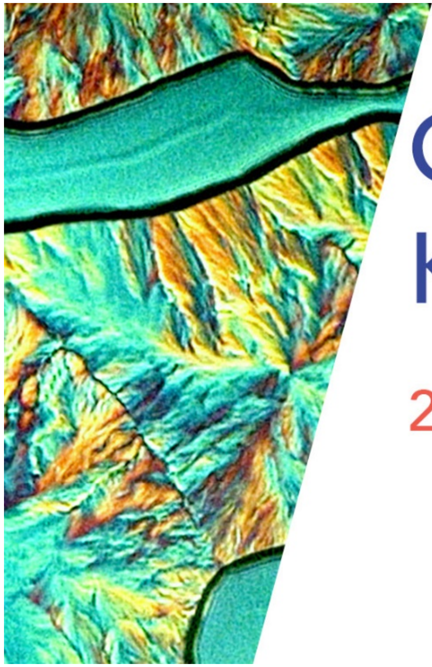
- LinkedIn site (global reach)
- Announce new activities
- Promote interactions
- Complement the OSA Technical Group Member List

Welcome to Today’s webinar!

OSA Laser Systems Technical Group



QCL-Based Sensors for Chemical Kinetic Applicaitons Webinar

29 November 2018 • 10:00 EST

OSA Laser Systems Technical Group

Aamir Farooq
Associate Professor, KAUST

QCL-Based Sensors
for Chemical Kinetic Applications

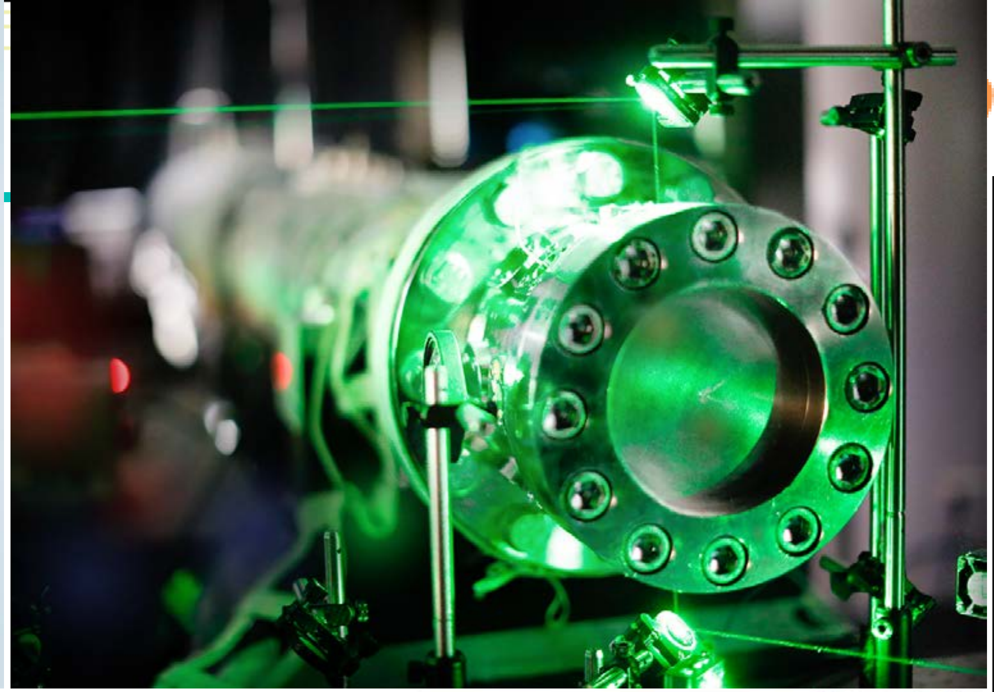
Laser Systems Technical Group
Optical Society of America (OSA)
Nov 29, 2018

Aamir Farooq

Mechanical Engineering Program

Clean Combustion Center (CCRC)

King Abdullah University of Science and Technology (KAUST)



Chemical Kinetics and Laser Sensors Laboratory

Principal Investigator: *Prof. Aamir Farooq*

Clean Combustion Research Center (CCRC)

King Abdullah University of Science and Technology

Talk Outline

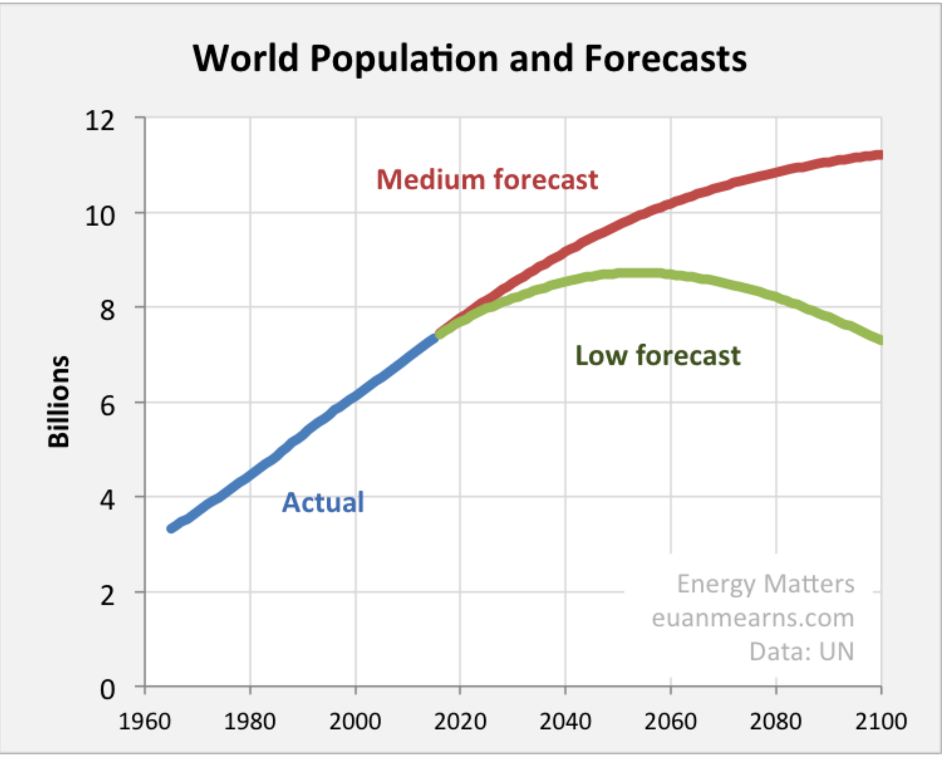
- Motivation for chemical kinetic studies

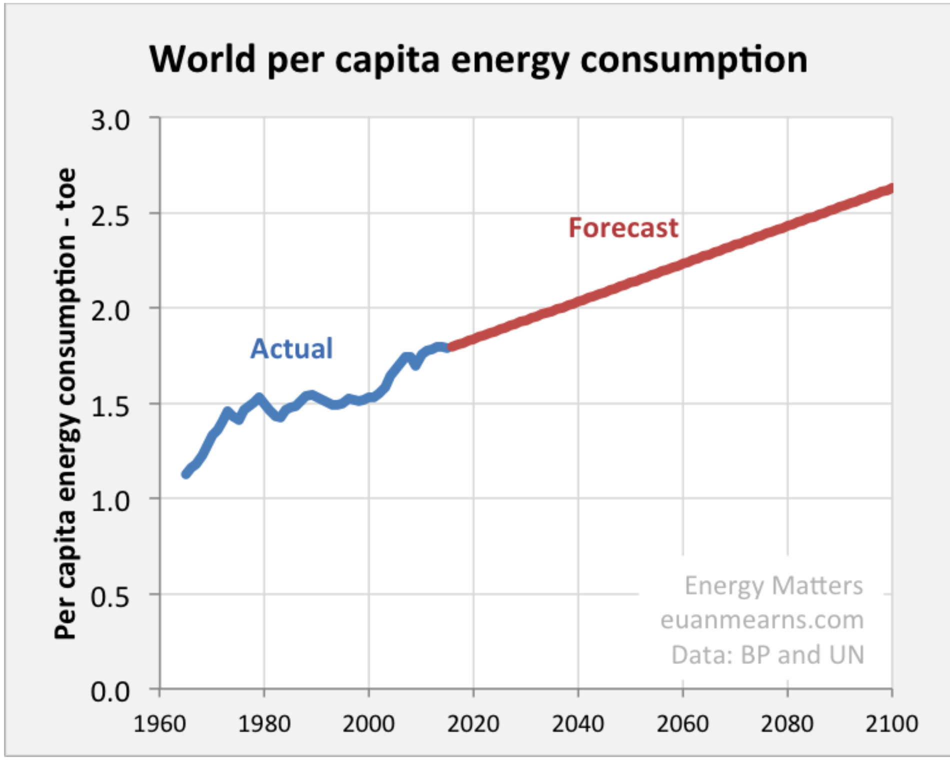
- Measurement challenges

- Case studies:
  1. Chirped-laser sensor for temperature
  2. Chirped-laser and cavity-enhanced sensor for CO
  3. Comb-assisted spectroscopy of N_2O

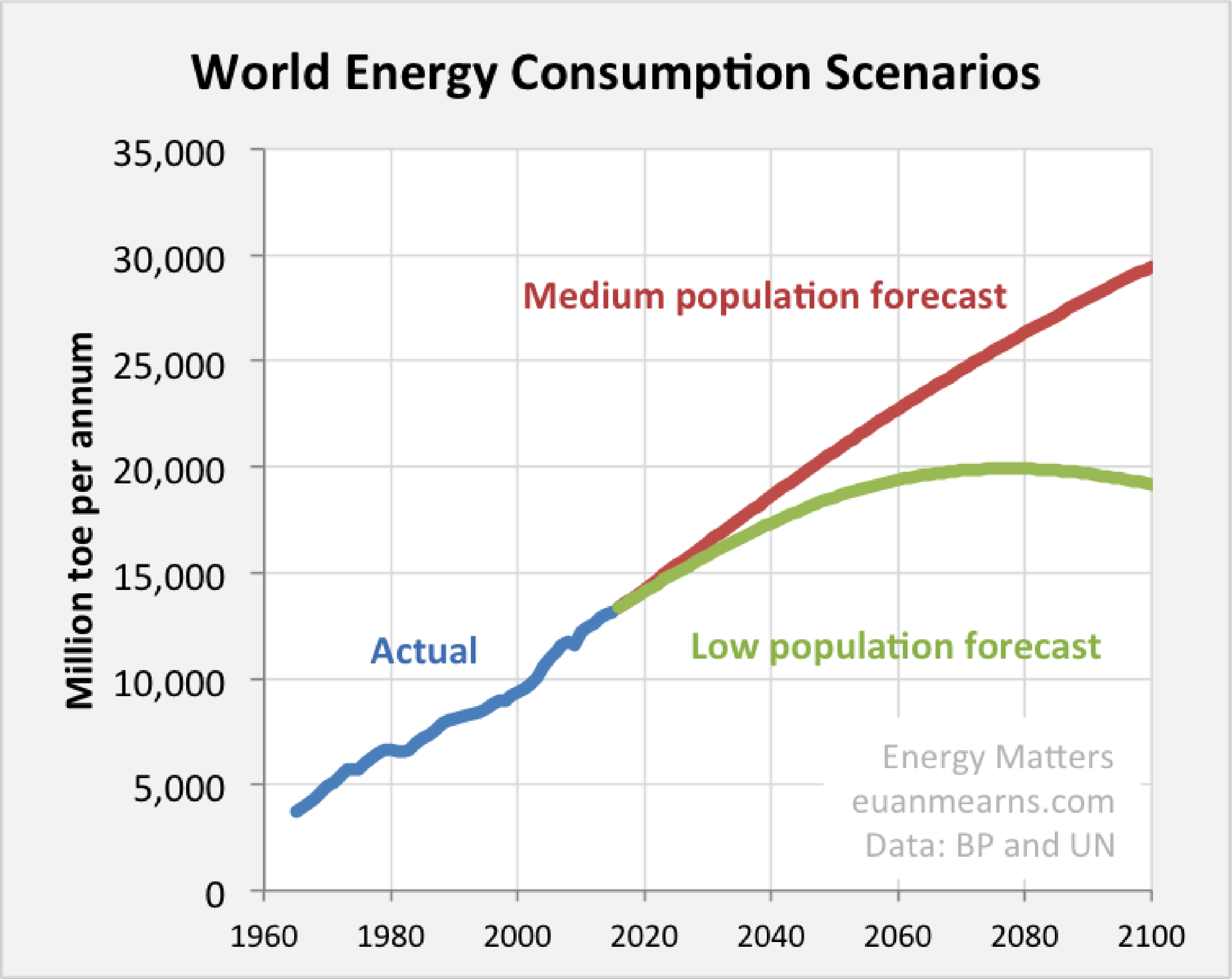
Growth in Population

- Predictions and forecasts are always tricky…
- It is important to take a long-term view





Growth in Energy Consumption



- 50% increase by 2050
- 2x increase by 2080

GHG Emission?

What we need for power sector?

Filling this need requires a portfolio of technology

Wind, solar, nuclear, combustion

What we need for transport sector?

- Electric vehicles
- Hybrid vehicles
- Combustion vehicles

Liquid fuels (surely) for:

- ➢ Airplanes
- ➢ Marine
- ➢ Heavy transport / trucks

US DoE Prediction

- ICEs will dominate ground transportation for decades
- Achieving GHG emission goals will require:
  - Fuels that enable more efficient engine design
  - Low-carbon biofuels and lower carbon petroleum fuels
- Developing new fuels and new engines together – co-optimization

Future Energy Challenges

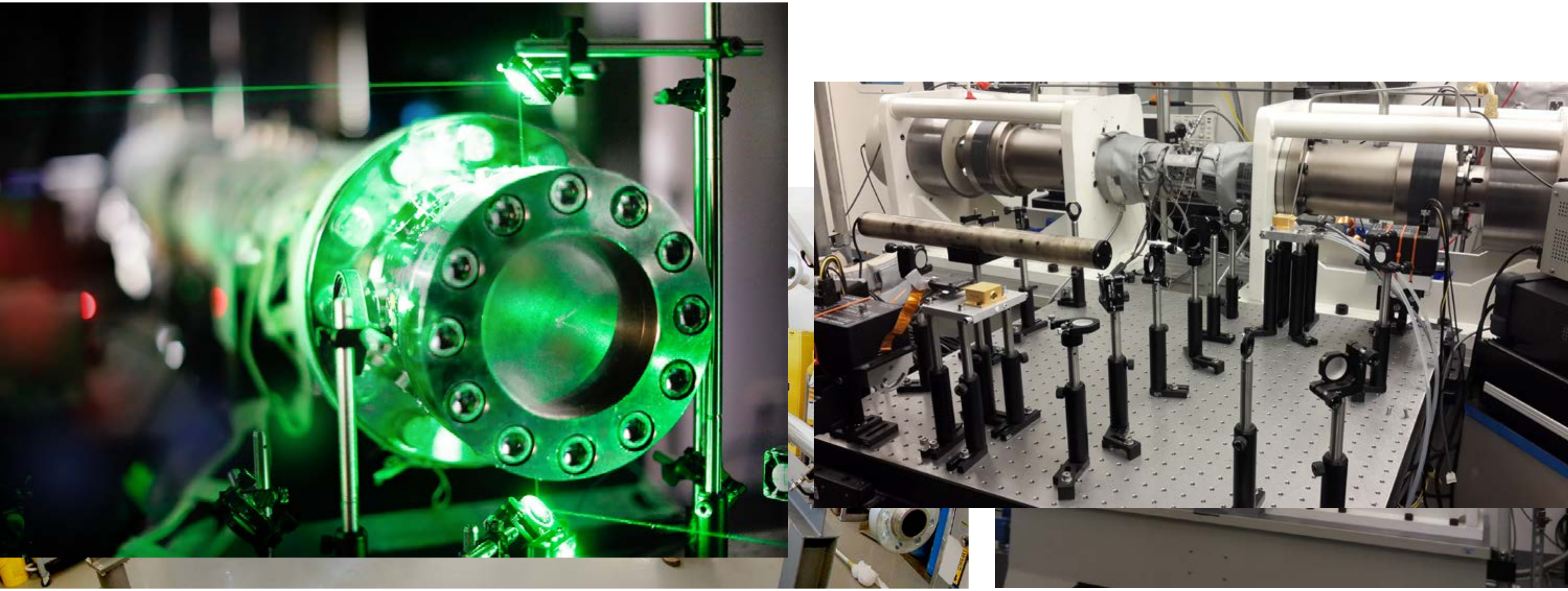
- GHG emissions, pollution and NOx
- Extremely high-pressure combustion
- Low-temperature combustion
- Gasoline, diesel, jet, bio and synthetic fuel modeling
- Soot and PAH production
- HCCI / PCCI engine modeling
- Reduced mechanisms / CFD modeling
- Aerosol physics, heterogeneous chemistry

All problems require a better understanding of

Fundamental Fuel Chemical Kinetics
Enabled by Shock Tubes, RCM, and Laser Diagnostics

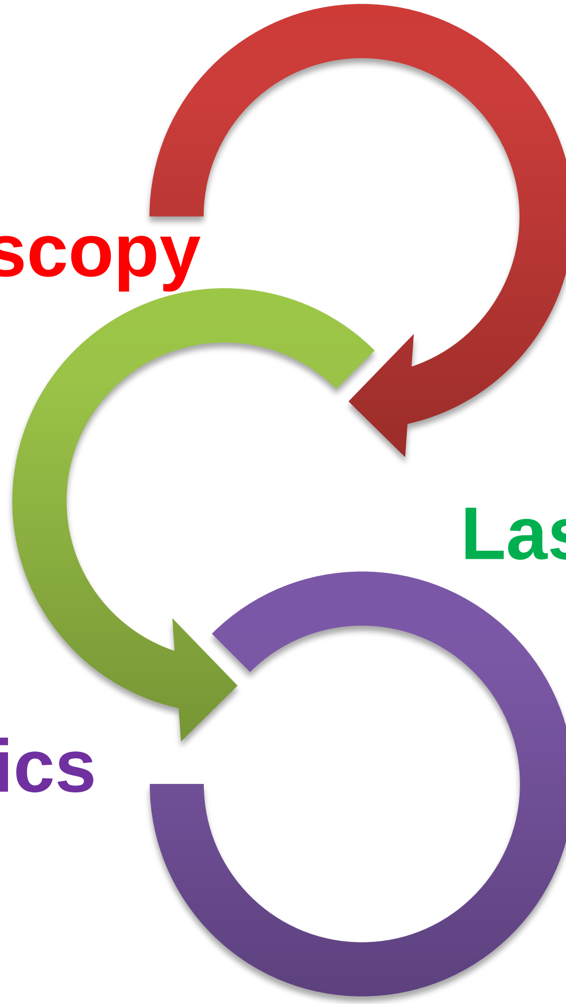
Chemical Kinetics in ST and RCM

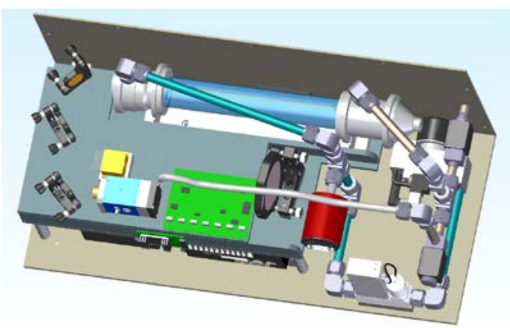
- ❑ ST and RCM are 'ideal reactors' to study fuel chemistry
  - ➢ Coupled with laser diagnostics, these reactors can be used to study fundamental reaction kinetics
  - ➢ Laser sensors must be developed to address specific chemical kinetic questions

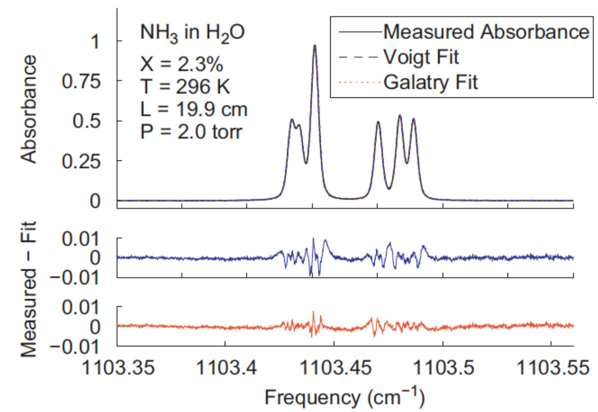


Spectroscopy to Kinetics…

Precision spectroscopy

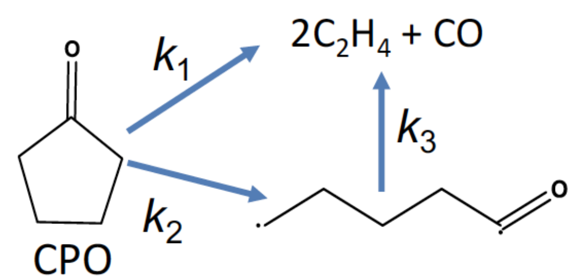






Laser sensors

Chemical kinetics



Talk Outline

- Motivation for chemical kinetic studies
- **Measurement challenges**
- Case studies:
  1. Chirped-laser sensor for temperature
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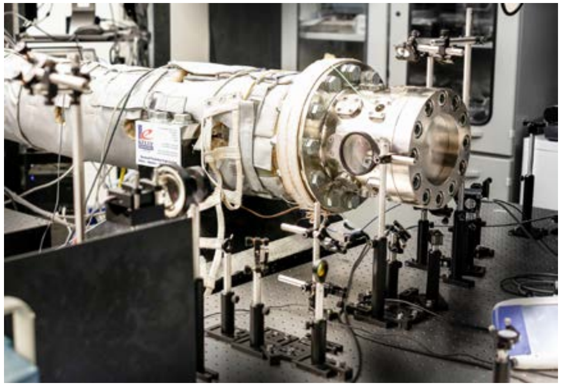
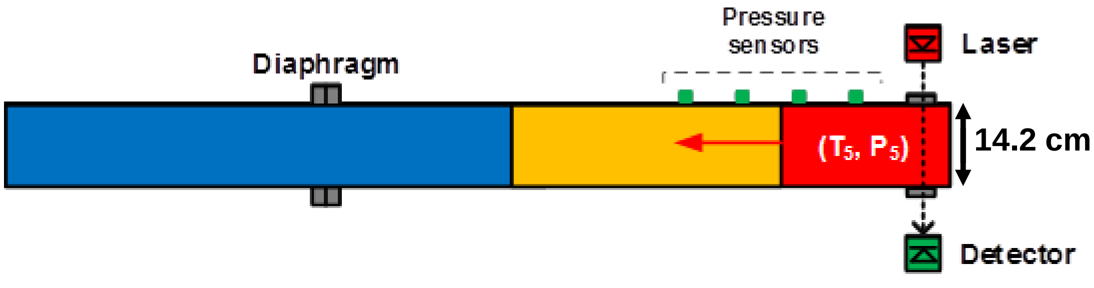
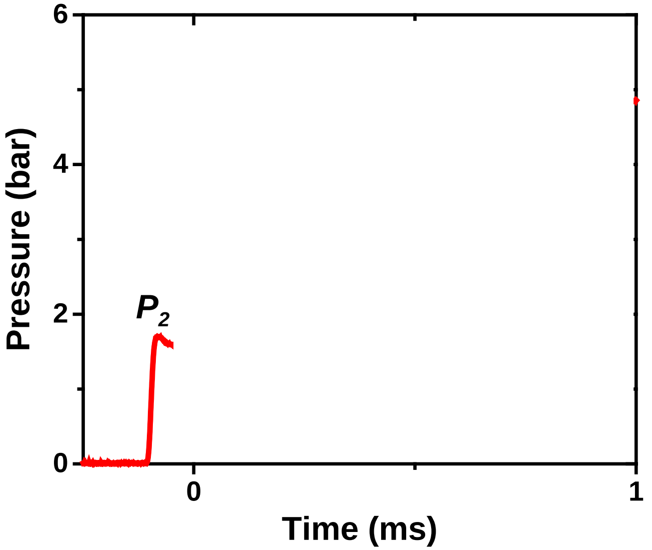
Shock Tube Facility

- Heating/pressurizing gases through shock wave.
- T_5/P_5 determined from shock wave velocity measurement (1-D normal shock relations).
- Conditions: T_5 = 700 – 3000 K, P_5 = 1 – 100 bar
- Test times: 100 μs to 10 ms

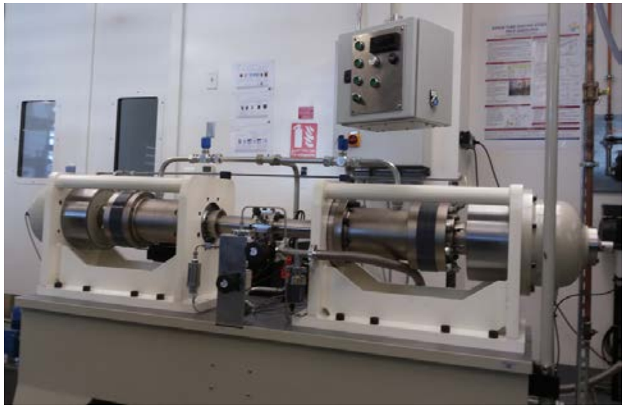




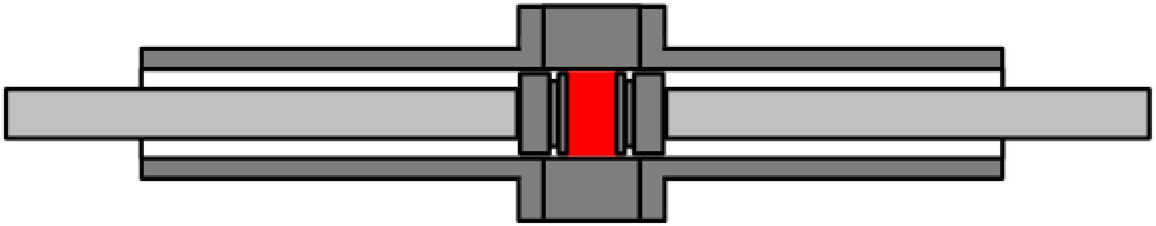


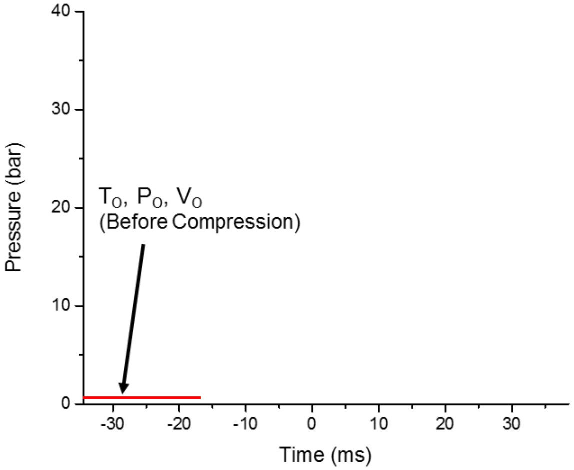
Rapid Compression Machine Facility

- Piston compression raises temperature
- Conditions: T_C = 600 – 950 K, P_C = 10 – 40 bar
- T_C determined from isentropic relations
- Test times: 1 – 200 ms



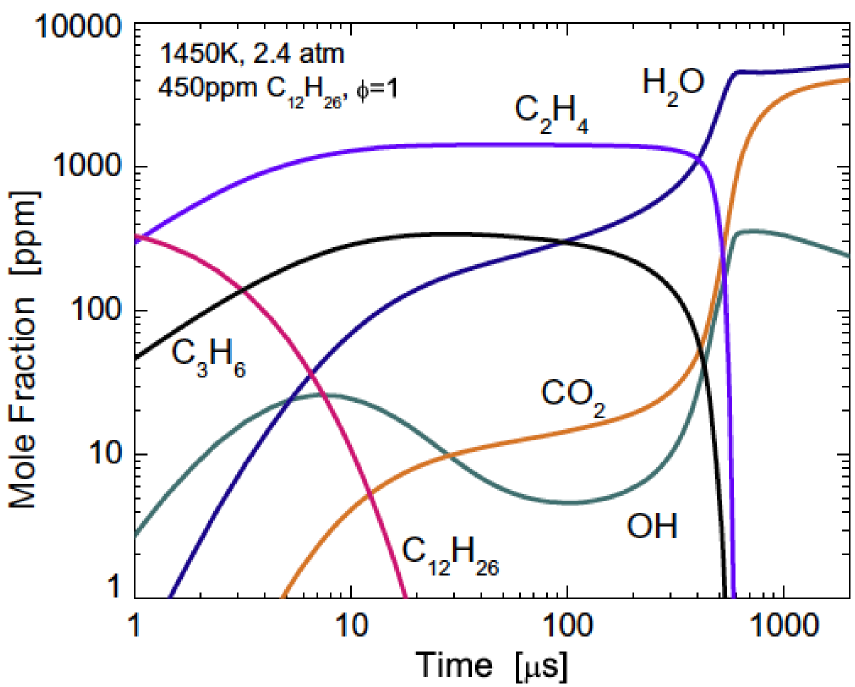
End of Compression

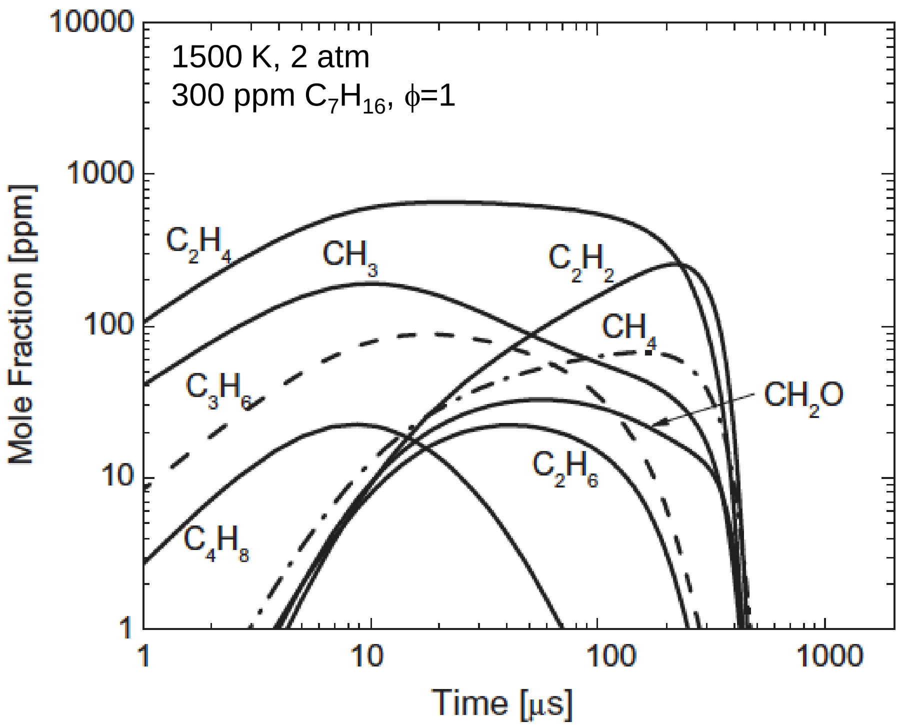




Many species, time scales, trace amounts, …

- Chemical systems are very complex with many species
- Time scales vary several orders
- Concentrations vary over several orders
- <u>Sensing challenges</u>: spectral interference, time resolution, trace detection, multiple wavelengths, optical access, beam steering, thermal emission, scattering, window fouling, etc.





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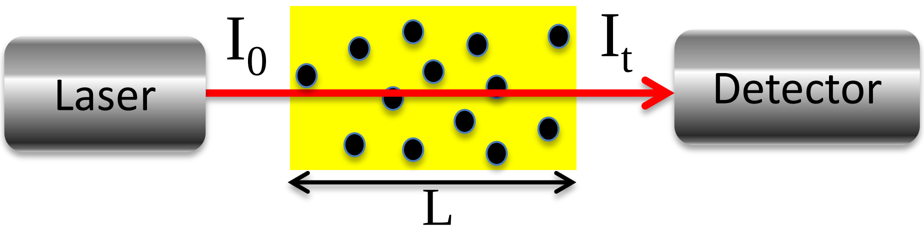
Absorption Spectroscopy

- <u>Absorption</u>: non-intrusive, time-resolved, line-of-sight measurement

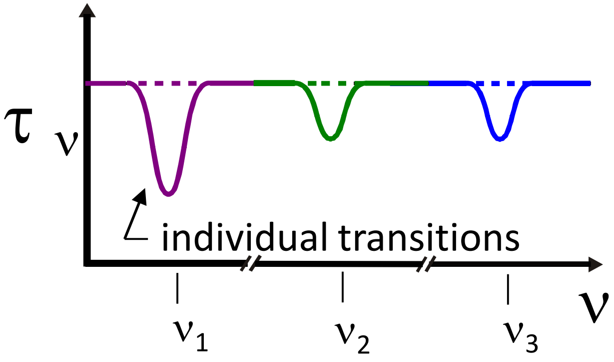
- Beer-Lambert relation:

$$\tau_\nu \equiv \frac{I_t}{I_o} = \exp(-k_\nu \cdot L)$$



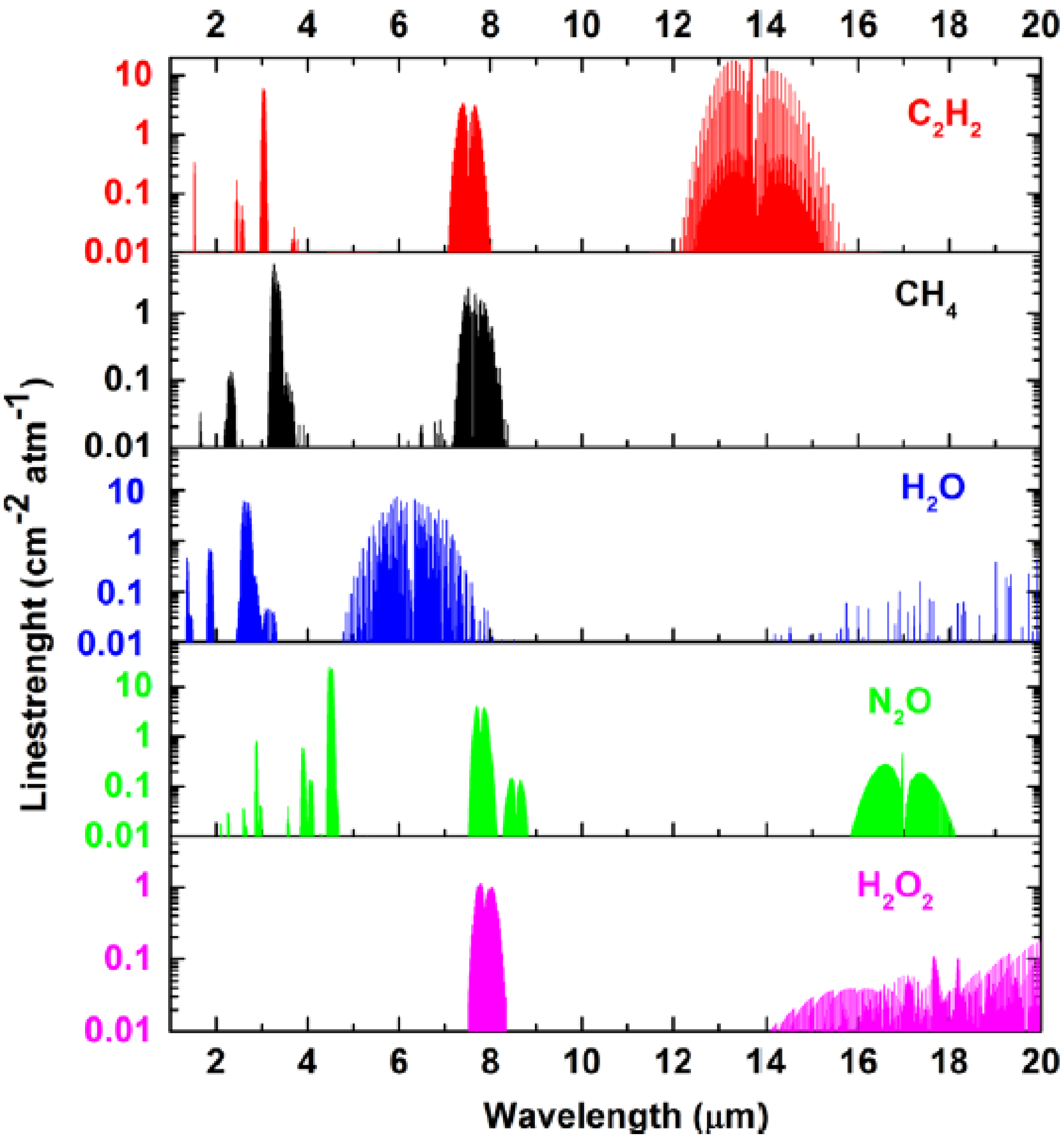
- Spectral absorption coefficient

$$k_\nu = S(T)\cdot\Phi(T,P,\chi_i)\cdot\chi_i\cdot P$$



- Quantitative determination of:
  - **Species concentration (C_i or χ_i)**
  - **Temperature, pressure**
  - **Velocity, mass flux**

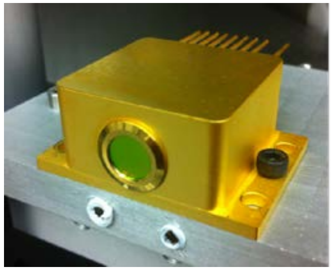
Mid-IR Wavelength Region



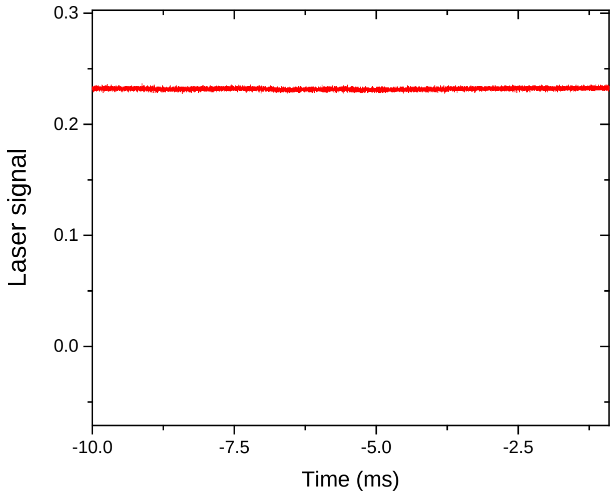
Mid-IR region provides greater sensitivity and selectivity.

Wavelength Agility of QCLs

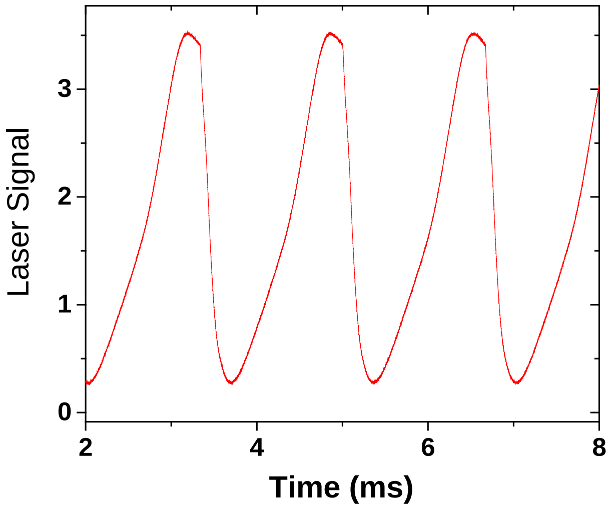
- DFB-QCLs can be used in three modes



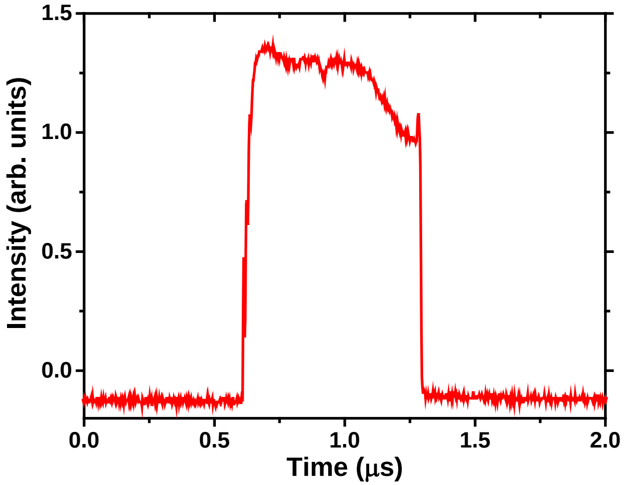
cw - Fixed Wavelength



cw – Scanned Wavelength



Pulsed – Down-chirp



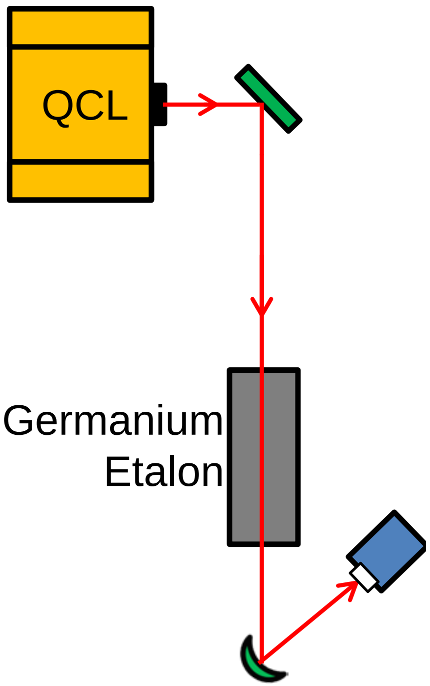
Line-width < 0.0001 cm^{-1}
Wavelength scan rate = 0

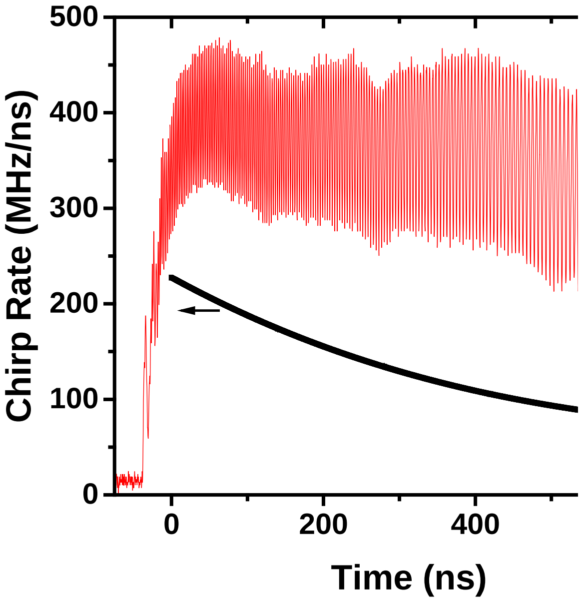
< 0.001 cm^{-1}
~ 0.1 $cm^{-1}/\mu s$

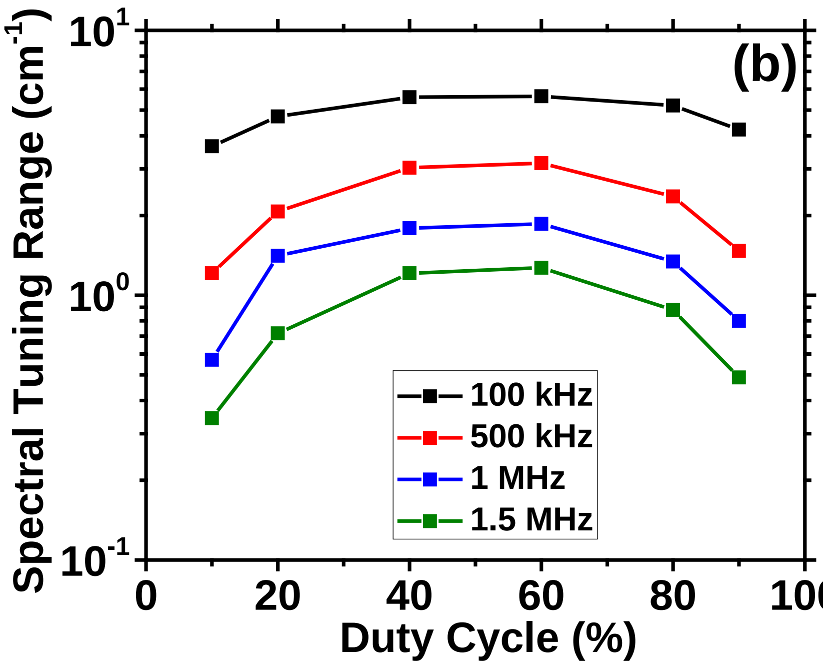
> 0.01 cm^{-1}
~ 5 $cm^{-1}/\mu s$

Down-chirp Characterization

- Germanium etalon used to convert time domain to wavelength domain.





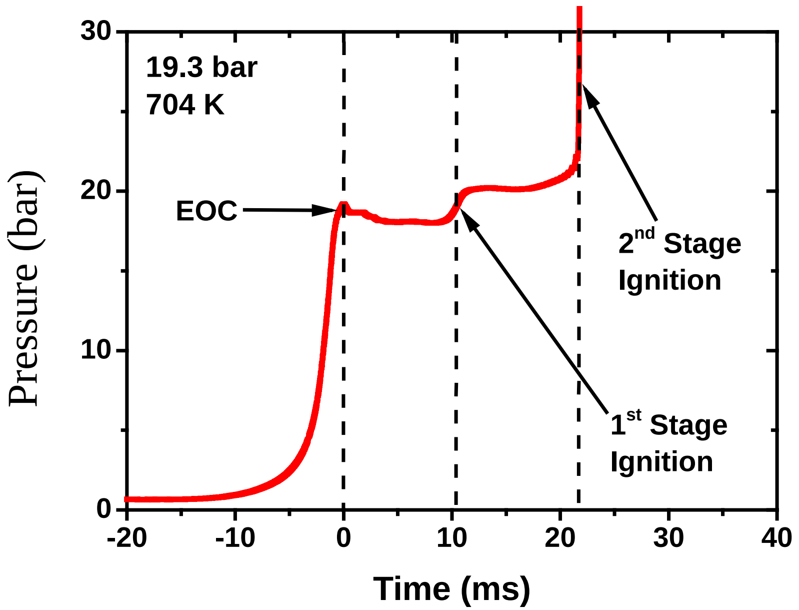


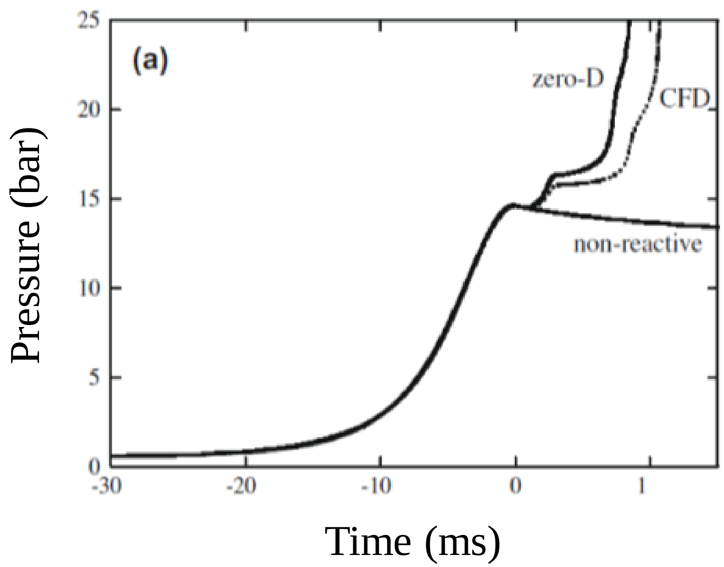
- Intra-pulse down-chirp results in rapid and broad spectral wavelength tuning
- Laser line-width directly proportional to the chirp rate

R. Chrystie, E. Nasir, A. Farooq, *Optics Letters 39* 6620 – 6623

Temperature Measurement in RCMs

- ❑ Central core gas is assumed adiabatic because of creviced pistons
- ❑ Heat loss is modeled as an isentropic expansion
- ❑ In two-stage ignition, first-stage heat release causes heat loss characteristics to deviate from non-reactive case





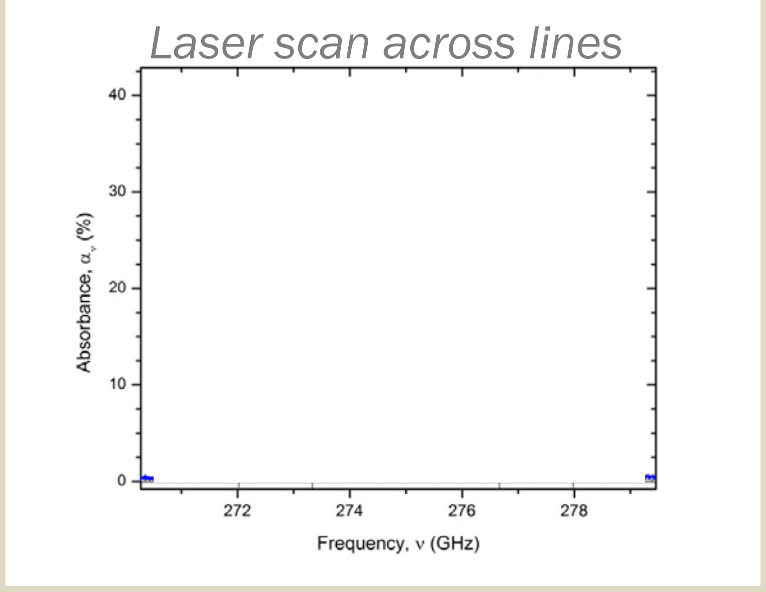
- ❑ Temperature measurements needed to understand the limitation of zero-D modelling and build multi-zone heat transfer models

Two-line Thermometry

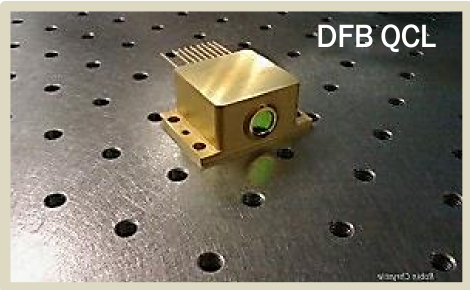
- Ratio of two absorption lines: a calibration-free T-sensing method

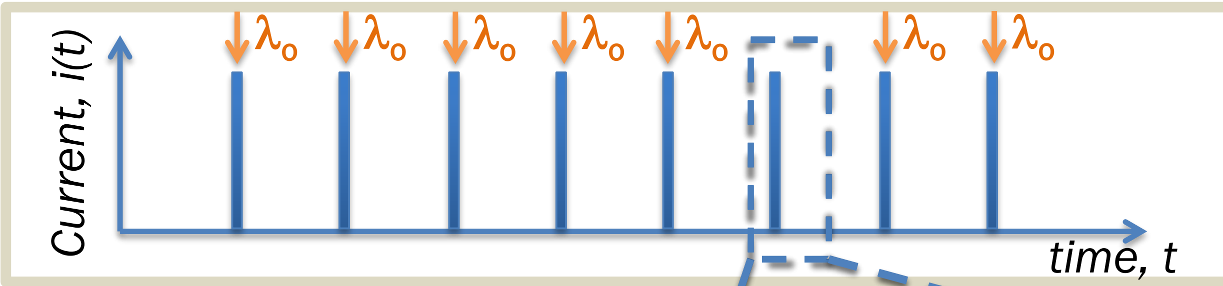
$$T = \frac{hc/k(E_2'' - E_1'')}{\ln R + \ln(S_2(T_0)/S_1(T_0)) + (hc/k)(E_2'' - E_1'')/T_0} \qquad R = \frac{Area1}{Area2}$$

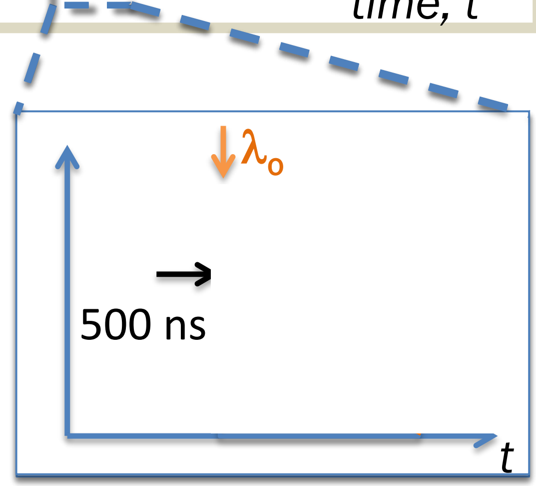
- Laser scan by current-modulation is generally slow (~ few kHz)

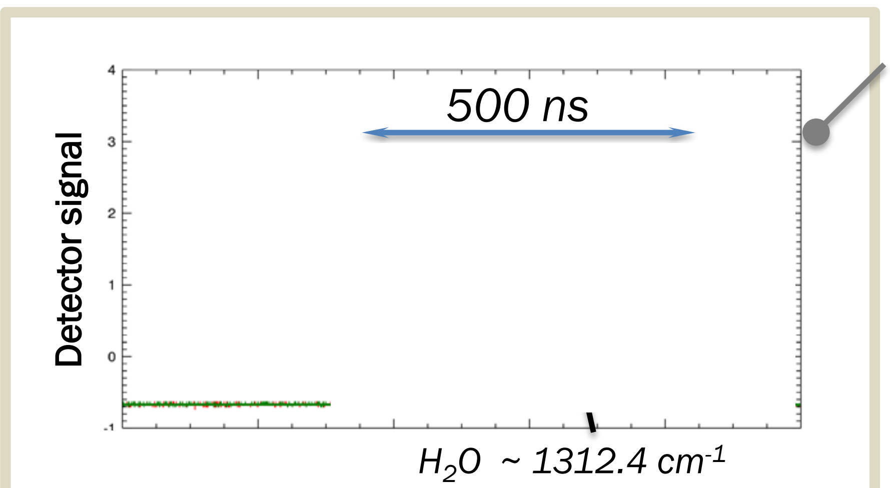


Chirped-QCL Temperature Sensor









Transmission Trace

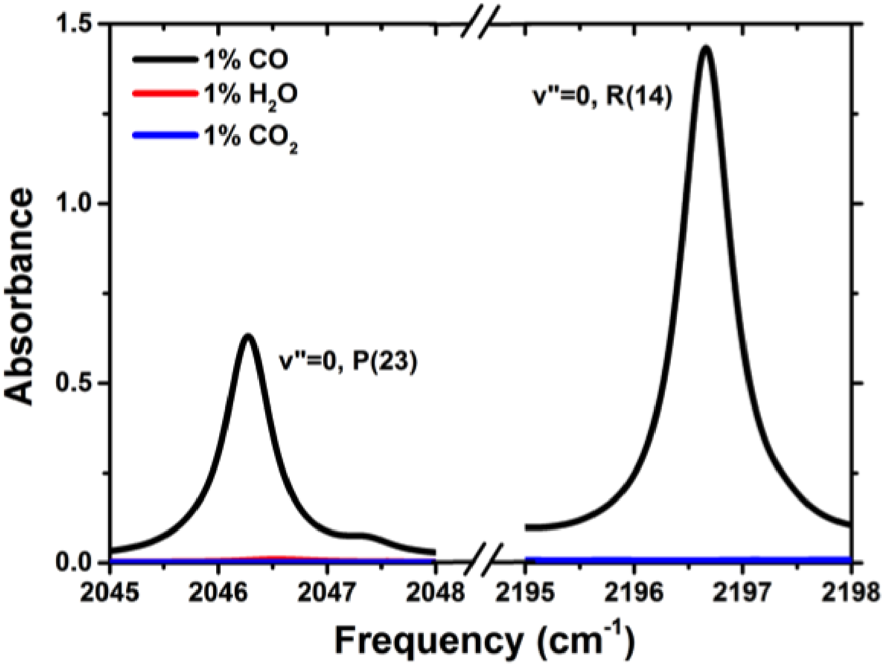
Temperature measurements every 500 ns

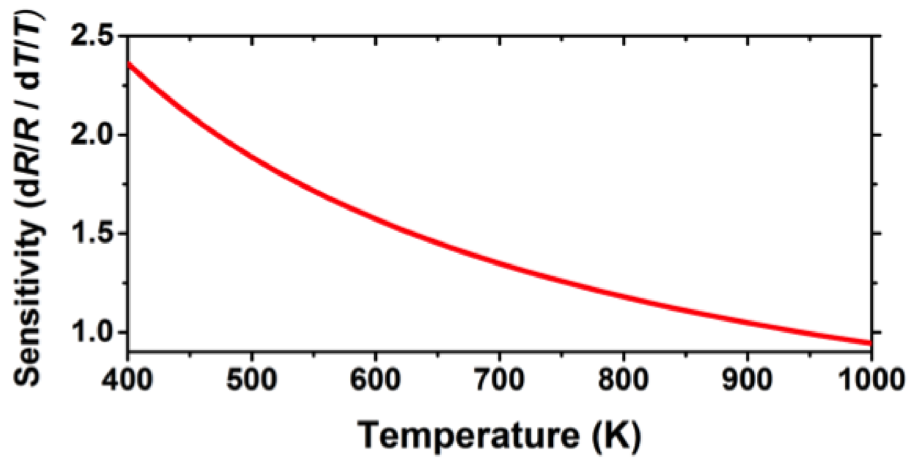
R. Chrystie, E. Nasir, A. Farooq, *Optics Letters 39* 6620 – 6623

Temperature Measurement using CO

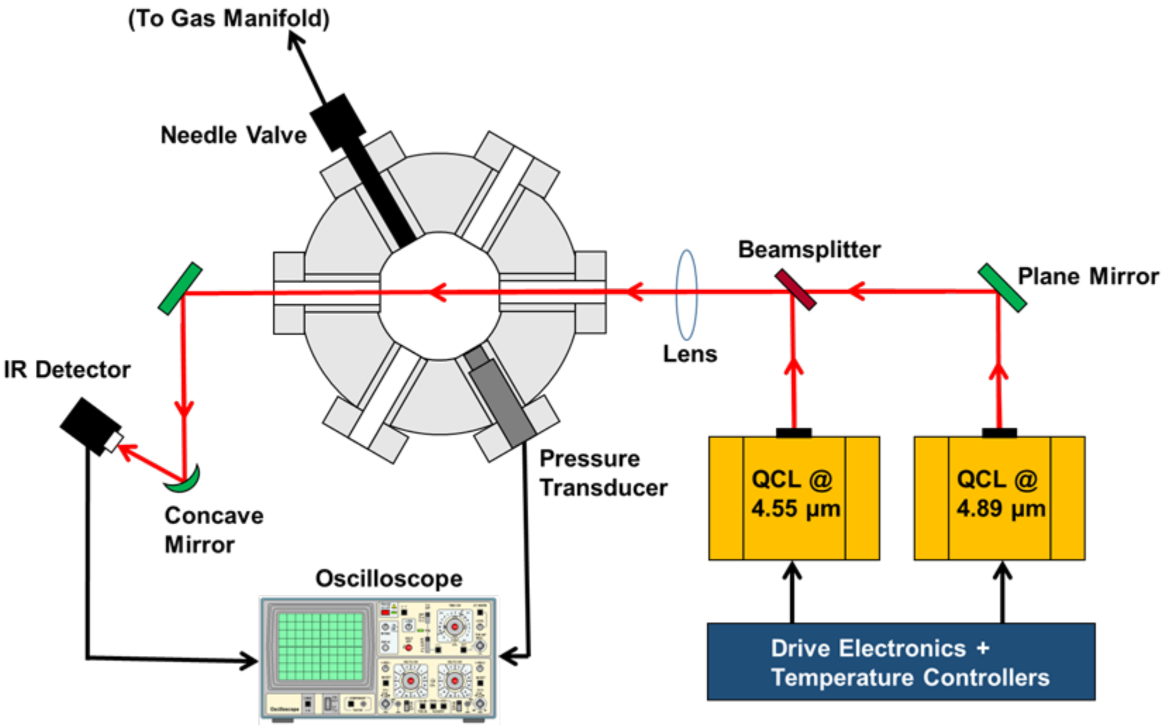
- Two CO lines: 2046.28 cm^{-1} (4.89 μm) and 2196.66 cm^{-1} (4.55 μm):
  - Fundamental band lines for high absorbance.

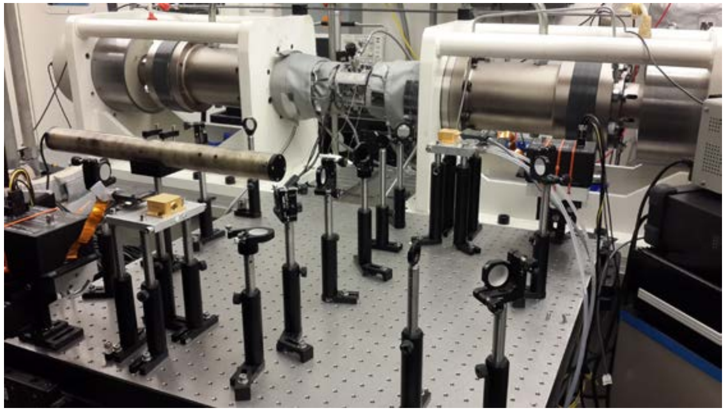
HITRAN Simulation
***P* = 10 bar, *T* = 700 K, *L* = 50.8 mm**





Optical Schematic

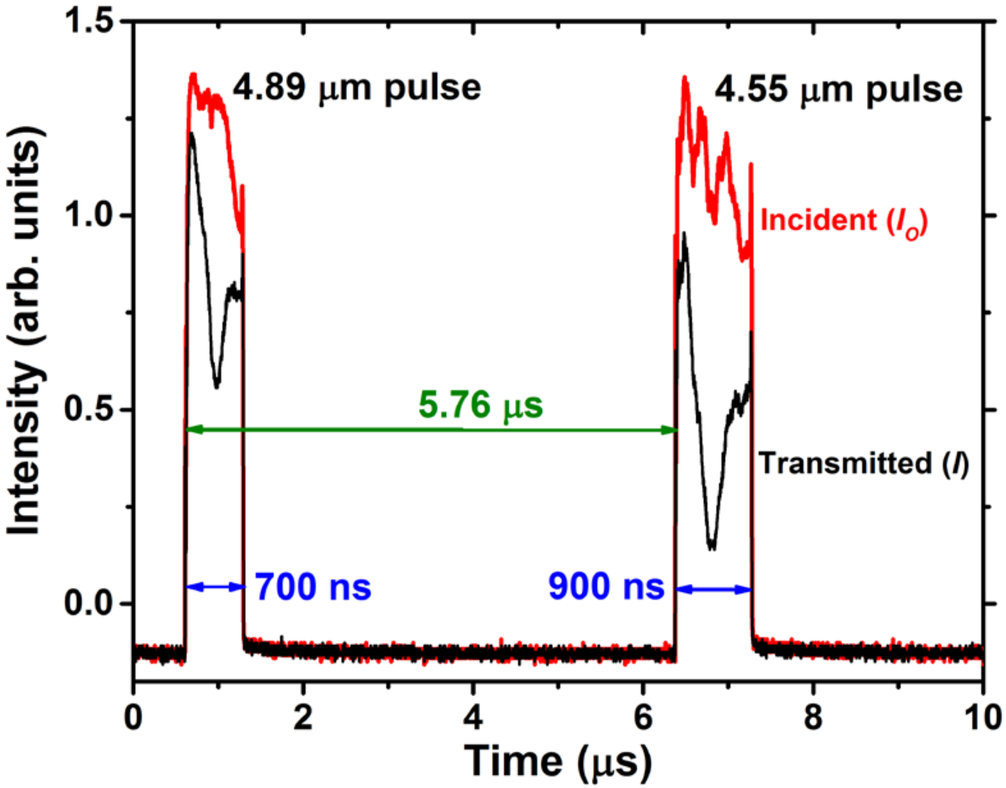




- ❑ Two QCLs aligned on a collinear path through the RCM
- ❑ MCT AC-coupled detector used at 500 MHz bandwidth

Laser Time Multiplexing

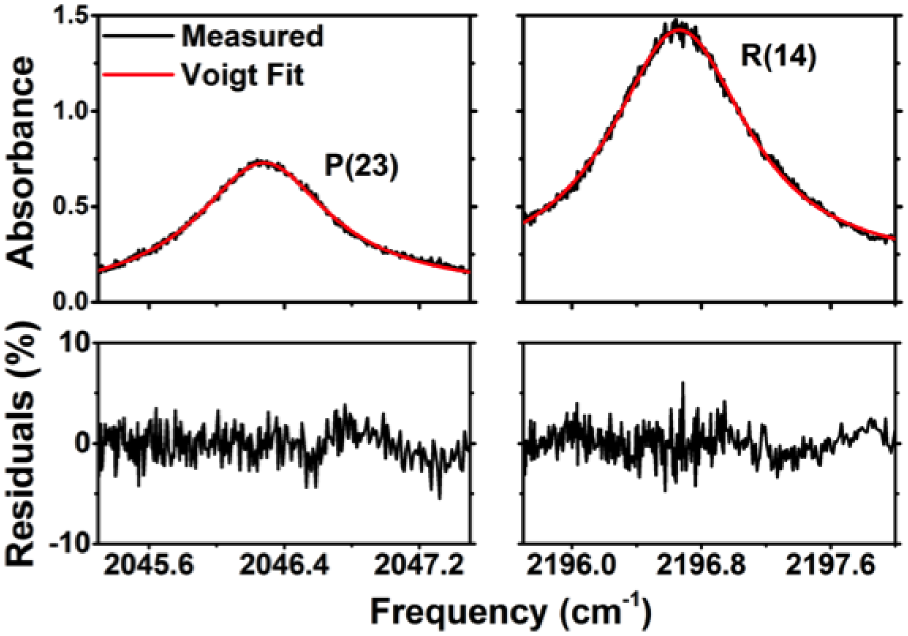
- Both lasers were pulsed at 100 kHz (**10 μs** time period) at a fixed time delay.

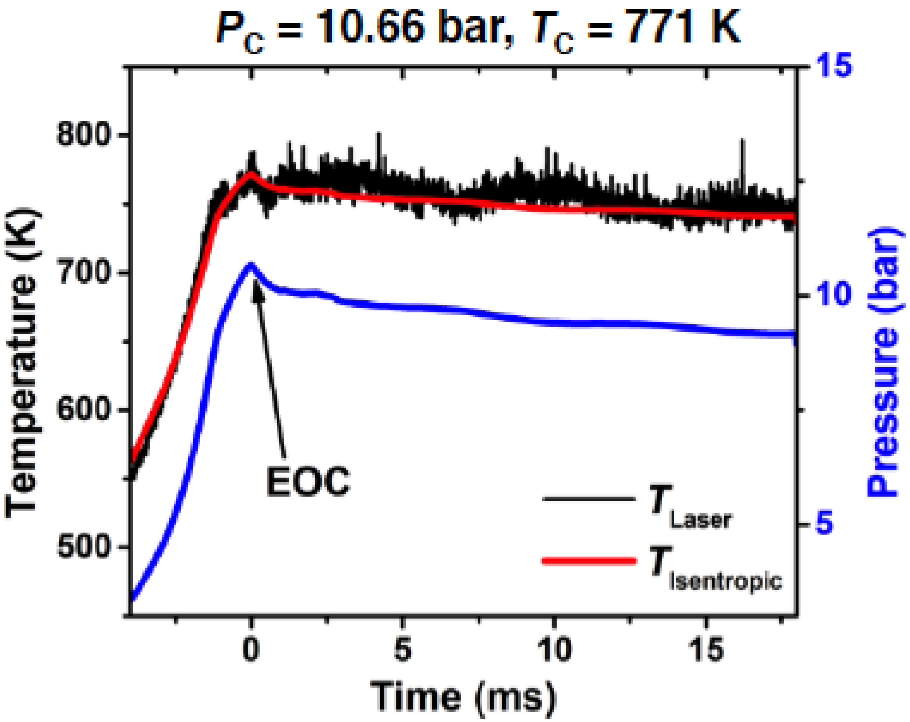


- Both laser pulses provide the same wavelength tuning range ($\Delta\nu \sim 2.8\ cm^{-1}$).

Measured spectra: $CO-N_2$ Experiments

- The sensor was initially tested on 1% $CO-N_2$ non-reactive mixtures
- CO line-shapes fit to a Voigt profile

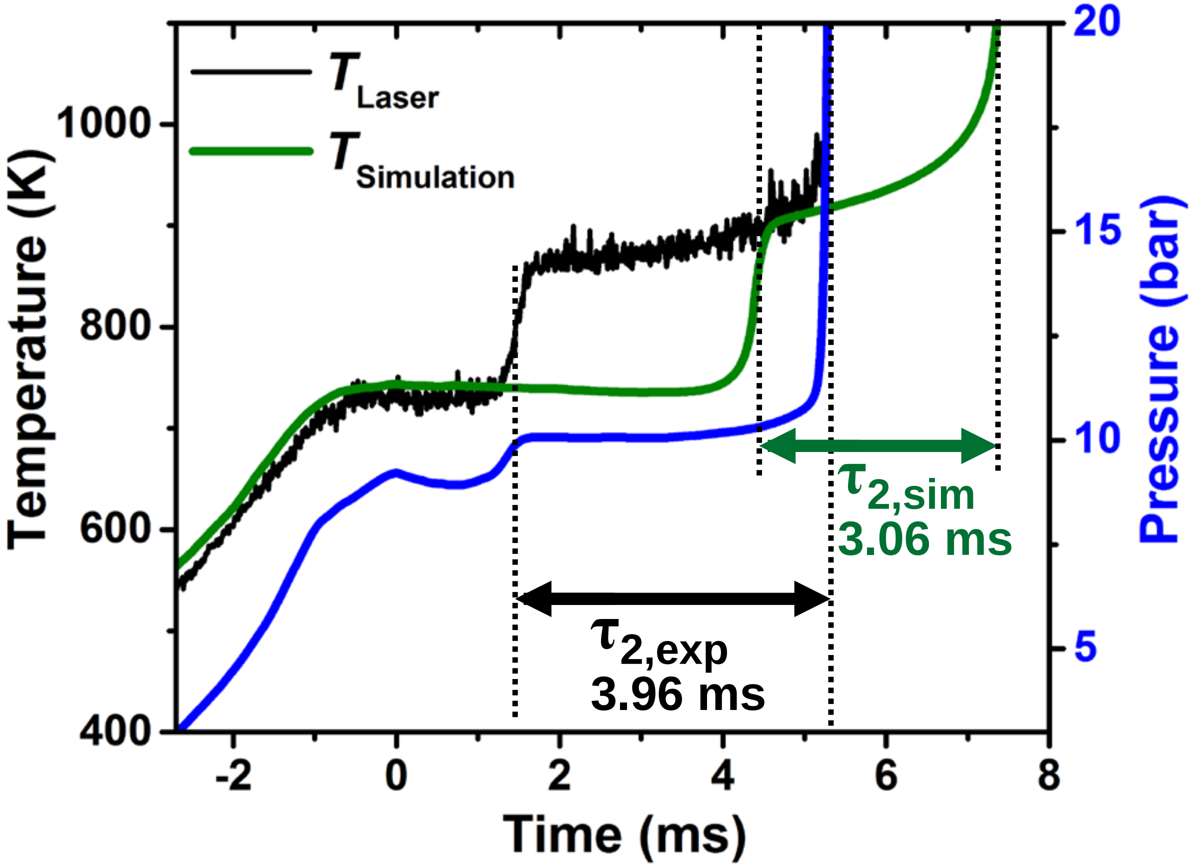




- Measured temperature agreed with isentropic calculation

Nasir & Farooq, *Proc. Combust. Inst.* 36 (2017)

Temperature Results: n-Pentane Oxidation



$\Delta T_{exp} < \Delta T_{sim}$

$\tau_{2,exp} > \tau_{2,sim}$

- **Intra-pulse down-chirp → Rapid, calibration-free temperature sensing**
- **First ever determination of temperature rise during 1st stage ignition**

Nasir & Farooq, *Proc. Combust. Inst.* 36 (2017)

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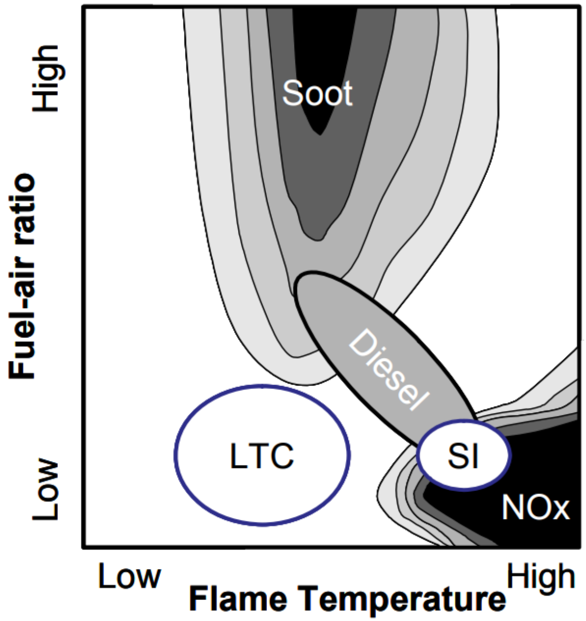
- Measurement challenges

- Case studies:
  1. Chirped-laser sensor for temperature
  2. **Chirped-laser and cavity-enhanced sensor for CO**
  3. Comb-assisted spectroscopy of N_2O

Investigation of LTHR Chemistry

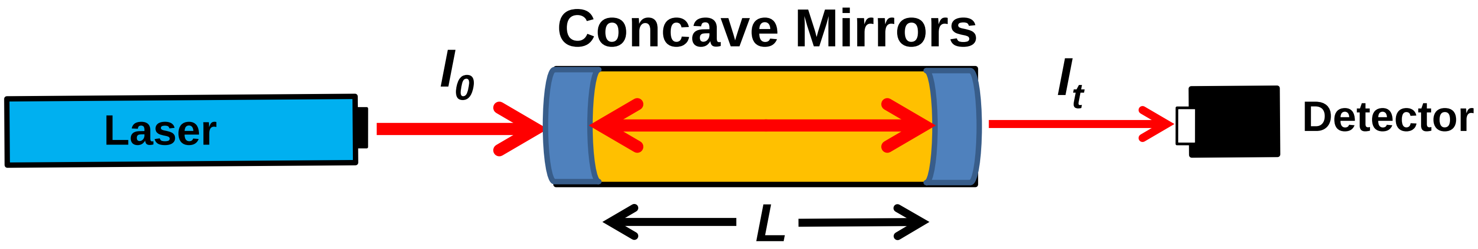
- ❑ Low-temperature heat release (LTHR) is very important for
  - o Controlling HRR in HCCI-like engines
  - o Reducing end-gas temperature in DISI engines



- ❑ Investigation of LTHR chemistry should be done in dilute fuel conditions to suppress large temperature changes
- ❑ Highly sensitive diagnostics are needed for LTHR studies in rapid compression machines (RCMs)

Cavity-Enhanced Detection of CO

- Develop a *pulsed* cavity enhanced (CEAS) diagnostic for RCM for increased sensitivity

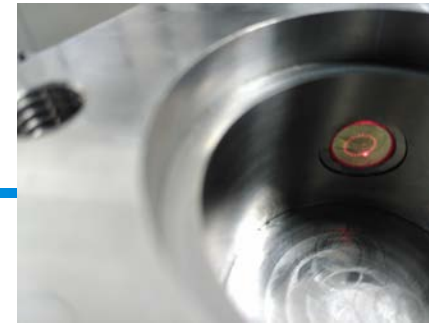


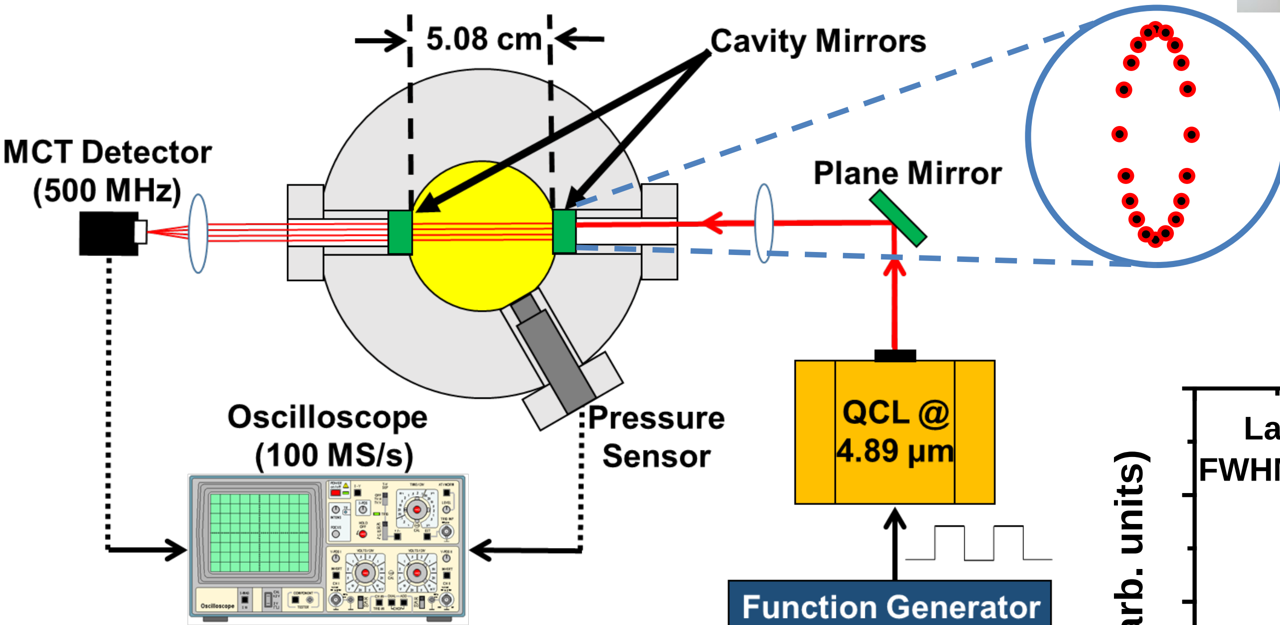
$$A_{CEAS} = \ln (I_0 / I_t) \rightarrow \quad A_{SP} = -\ln\left(1 - \frac{e^{A_{CEAS}} - 1}{G}\right)$$

$$G = \frac{1}{1-R}$$

- Utilize intra-pulse down-chirp of pulsed QCLs for cavity noise suppression
- Measure CO formation during 1st stage oxidation experiments in RCMs

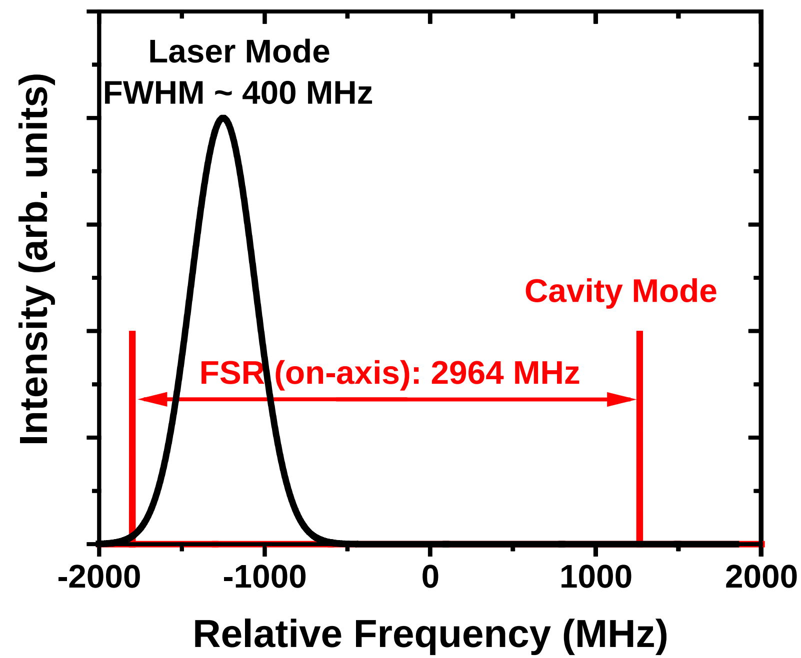
Optical Scheme: Off-axis CEAS





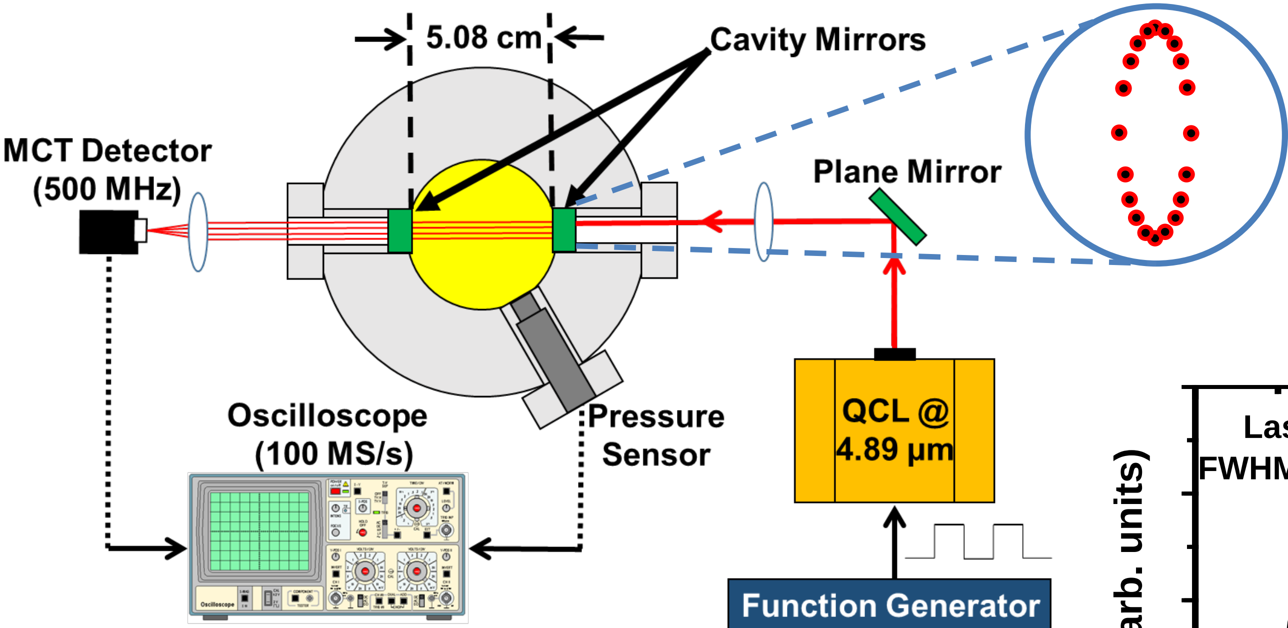
$$FSR_{eff} = \frac{c}{2nL_{eff}}$$

$$L_{eff} = L * (\# \text{ of spots})$$



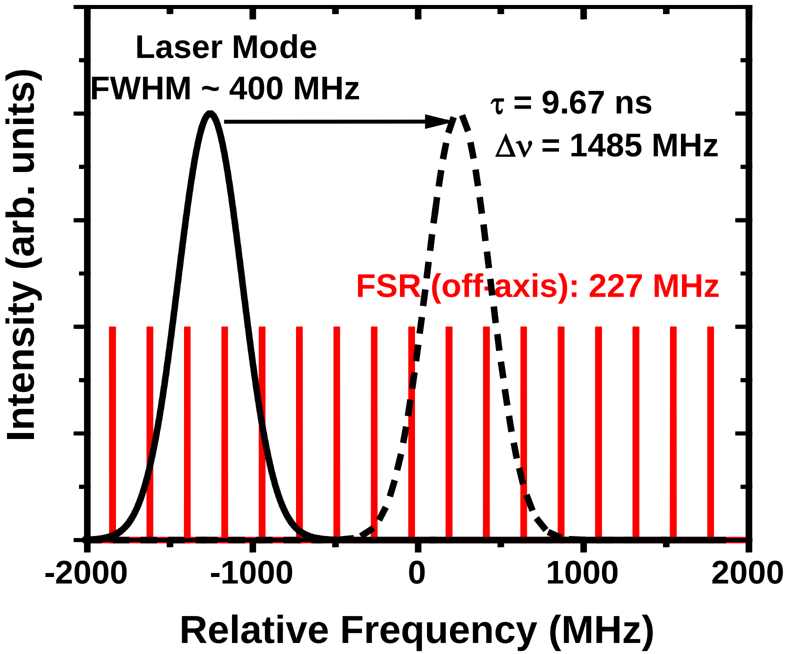
Optical Scheme: Off-axis CEAS

100 kHz pulse repetition rate



$$FSR_{eff} = \frac{c}{2nL_{eff}}$$

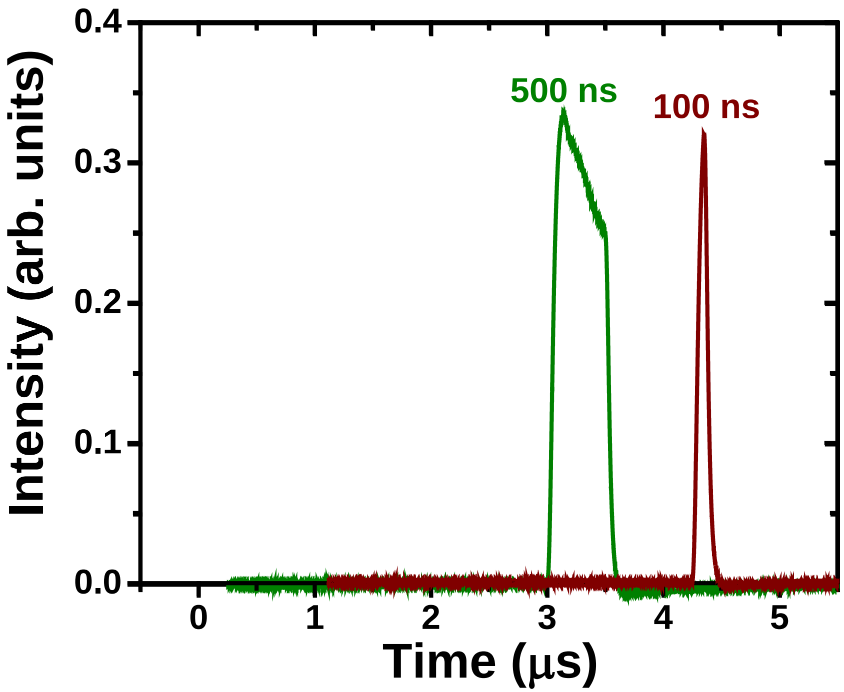
$$L_{eff} = L \text{ x } (\# \text{ of spots})$$

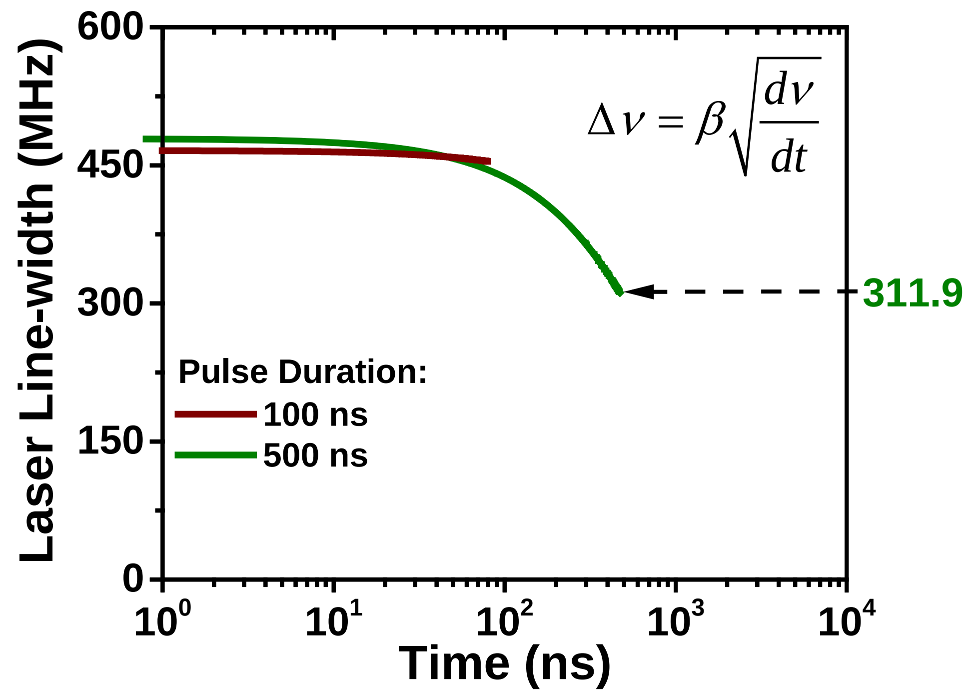


1. Off-axis alignment reduces cavity FSR
2. Frequency down-chirp provides further coupling

Pulse width, chirp rate, line-width

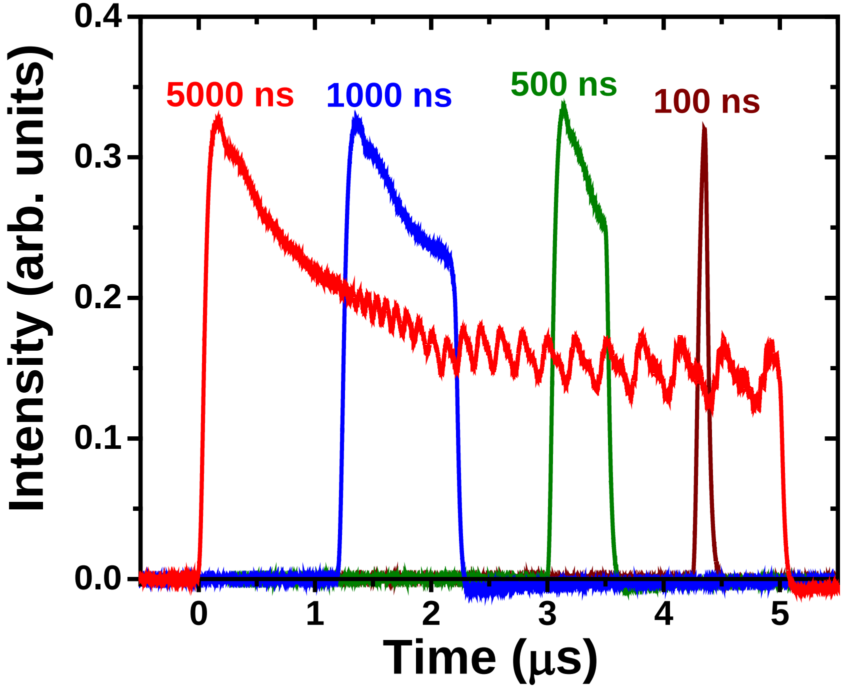
- QCL near 4.89 µm used at 100 kHz pulse repetition rate
- Spectral down-chirp / line-width varies with pulse duration

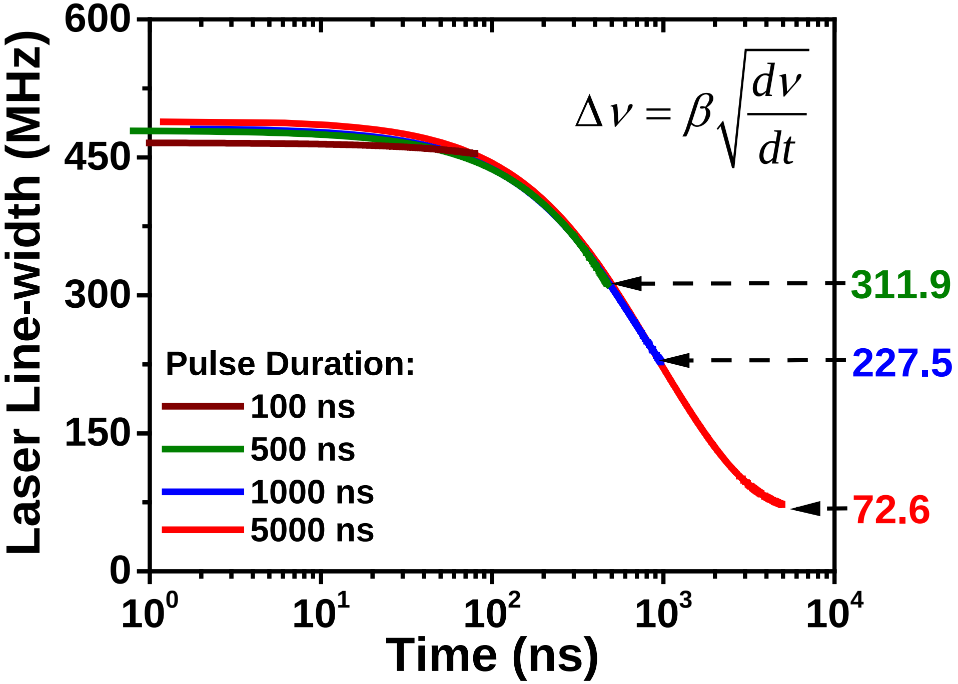




Pulse width, chirp rate, line-width

- QCL from Alpes Lasers at 4.89 µm used in pulsed mode:
  - o 100 kHz pulse repetition rate **(10 µs time resolution)**
- Spectral down-chirp rate varies with pulse duration.

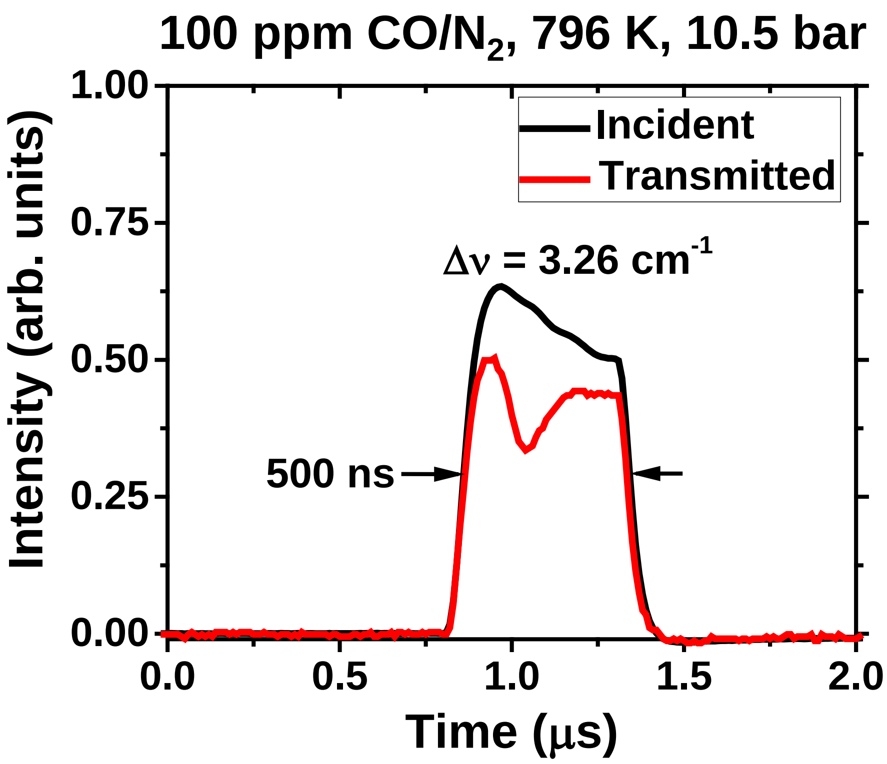


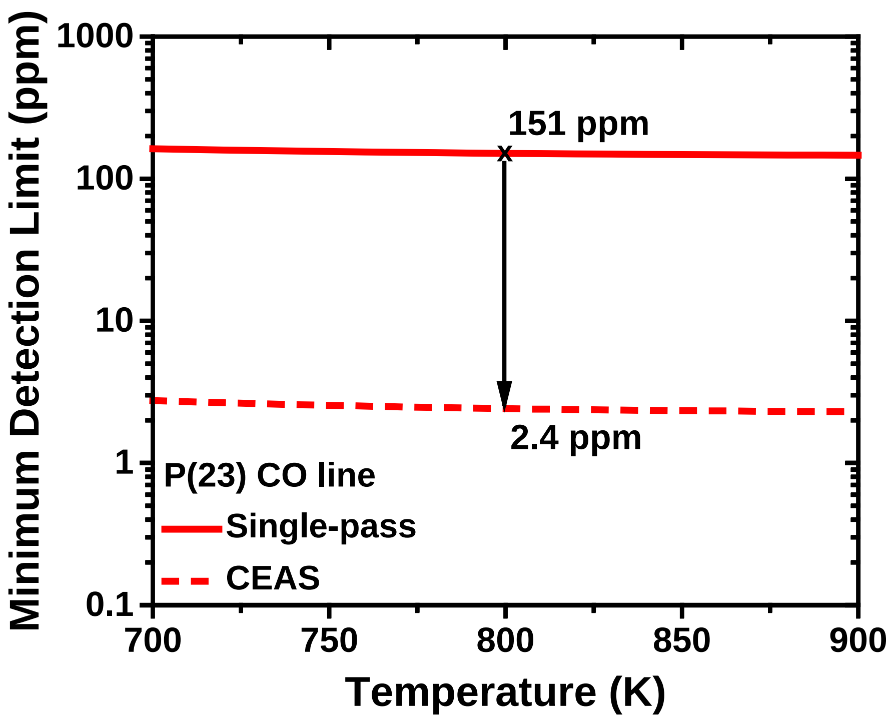


- 500 ns pulse duration was selected for RCM experiments

Gain Calibration and Detection Limit

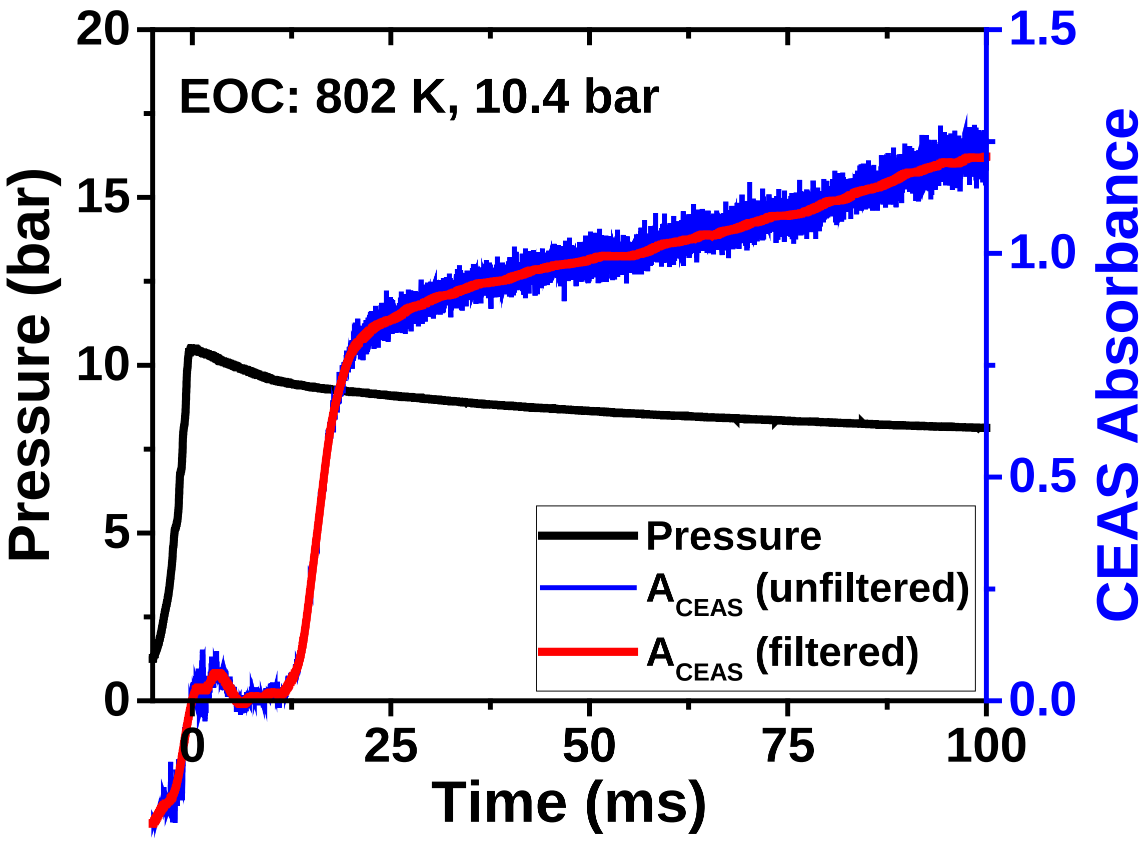
- ❑ High reflectivity mirrors centered at 4.89 µm.
- ❑ Manufacturer specs: R = 99.5% ± 0.2% → Gain factor: 200 ± 95
- ❑ Gain measured using known CO/N_2 mixtures.
- ❑ We found R = **99.25% ± 0.04%** → Gain factor: **133 ± 8**





CO Measurement in Fuel Oxidation

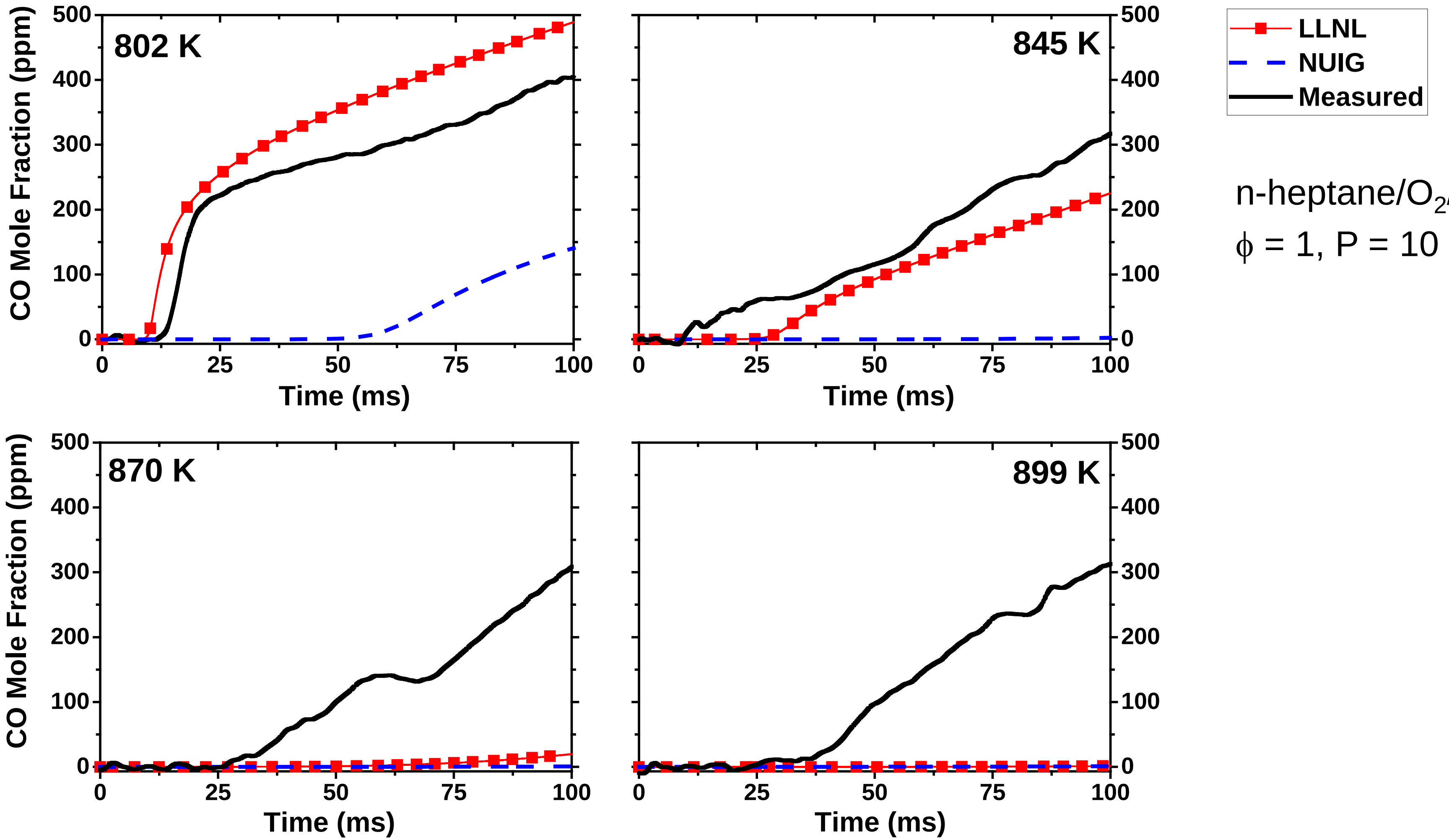
- Heat release suppressed with diluted fuel/air mixtures
- Peak CEAS absorbance used for CO mole-fraction history



Mixture:
0.2% n-heptane
4.4% O_2
95.4% N_2

Nasir & Farooq, *Optics Express* 26 (2018)

CO Measurements Compared with Models



n-heptane/O_2/N_2

ϕ = 1, P = 10 bar

- **Intra-pulse down-chirp + OA-CEAS → Highly sensitive, time-resolved measurements**

Talk Outline

- Motivation for chemical kinetic studies

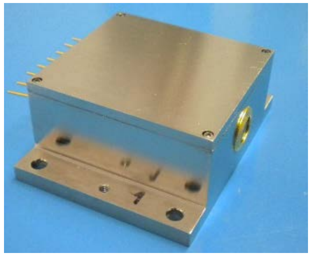
- Measurement challenges

- Case studies:
  1. Chirped-laser sensor for temperature
  2. Chirped-laser and cavity-enhanced sensor for CO
  3. **Comb-assisted spectroscopy of N_2O**

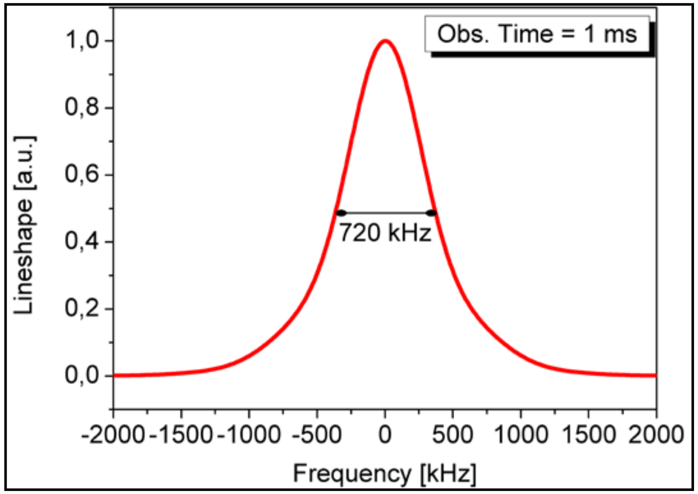
     (in collaboration with Prof. Marangoni @ POLIMI)

DFB QCL vs EC-QCL

DFB-QCLs



- Narrow linewidth (~ 1 MHz)
- Fast tunability (MHz bandwidth)
- Narrow tunability range (1-2 cm^{-1})
- Low ouptut power (a few mW)

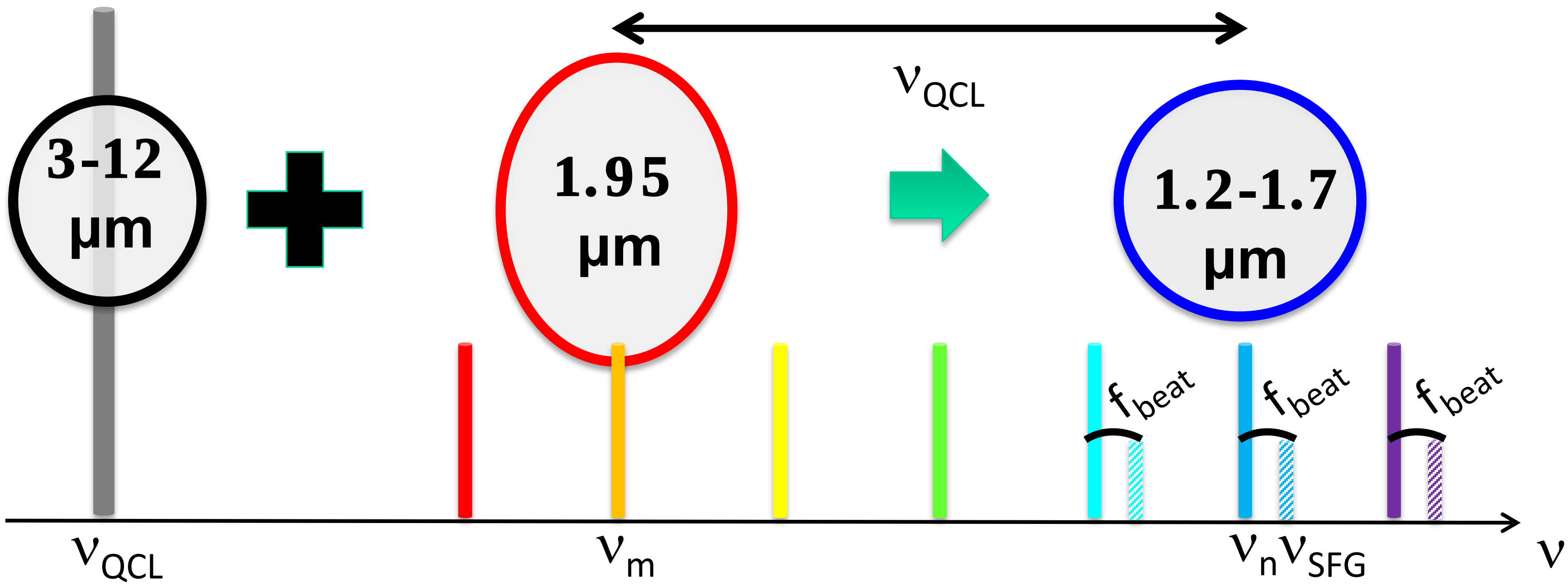


EC-QCLs

- Ultrabroad tuning range (> 100 cm^{-1})
- High output power (> 100 mW)
- Almost full MIR coverage

THEY SUFFER FROM A BROAD EMISSION LINEWIDTH and FREQUENCY JITTER!

Sum-Frequency Generation Referencing



Starting point: $\nu_m = f_{ceo} + mf_{rep}$; $\nu_n = f_{ceo} + nf_{rep}$; ν_{QCL}

SFG: $\nu_{SFG} = \nu_{QCL} + \nu_m = \nu_{QCL} + f_{ceo} + mf_{rep}$

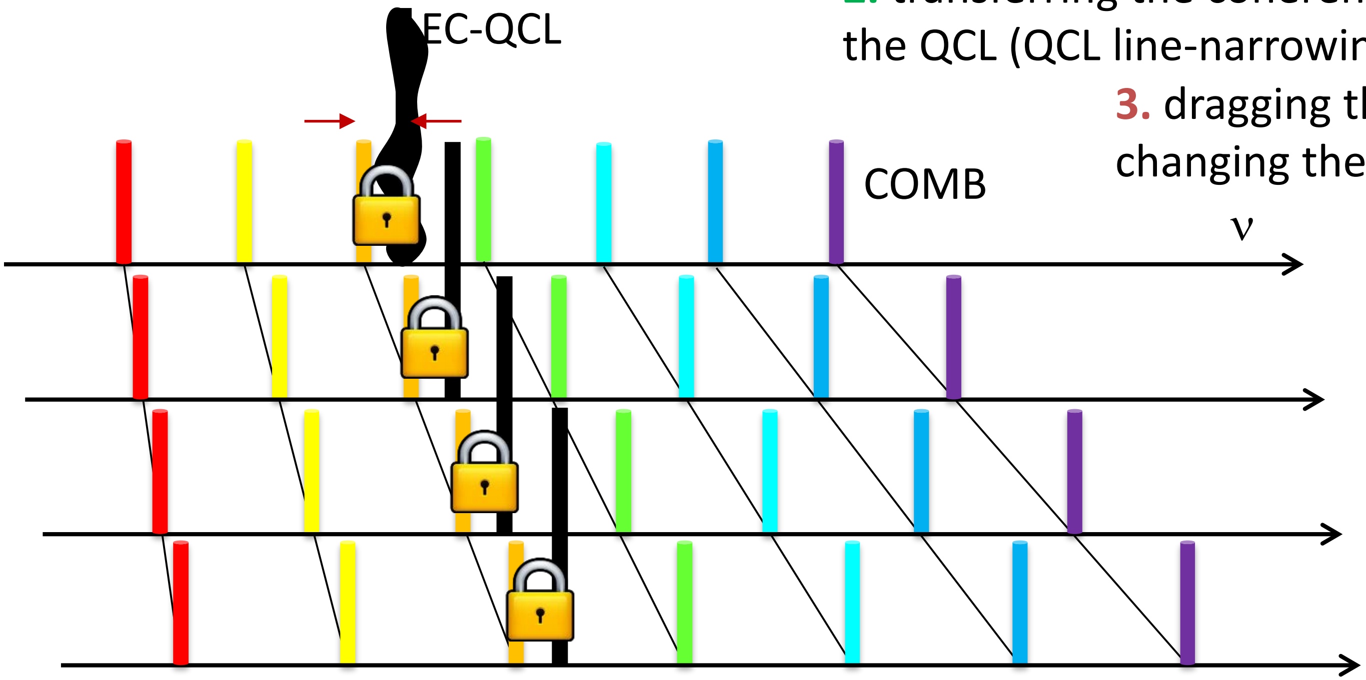
Referencing: $f_{beat} = |\nu_{SFG} - \nu_n| = |\nu_{QCL} - (n-m)f_{rep}|$

Phase-locking of EC-QCL to a Frequency Comb

1. fixing the comb-QCL frequency offset

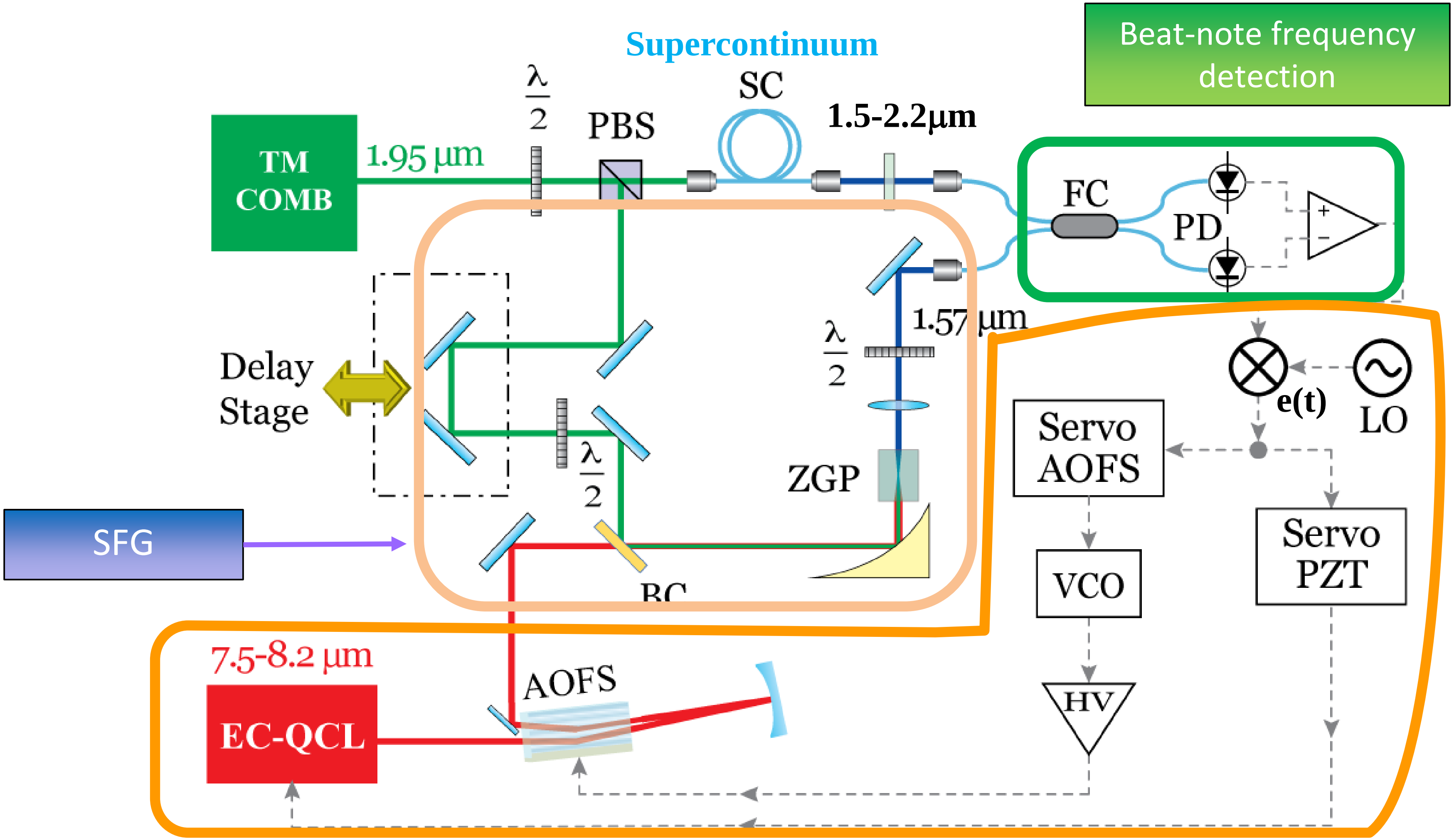
2. transferring the coherence of the comb to the QCL (QCL line-narrowing)

3. dragging the QCL frequency by changing the comb spacing



Objective: To perform, **for the first time with EC-QCLs**, precision spectroscopy with a comb-defined frequency axis

Experimental Setup

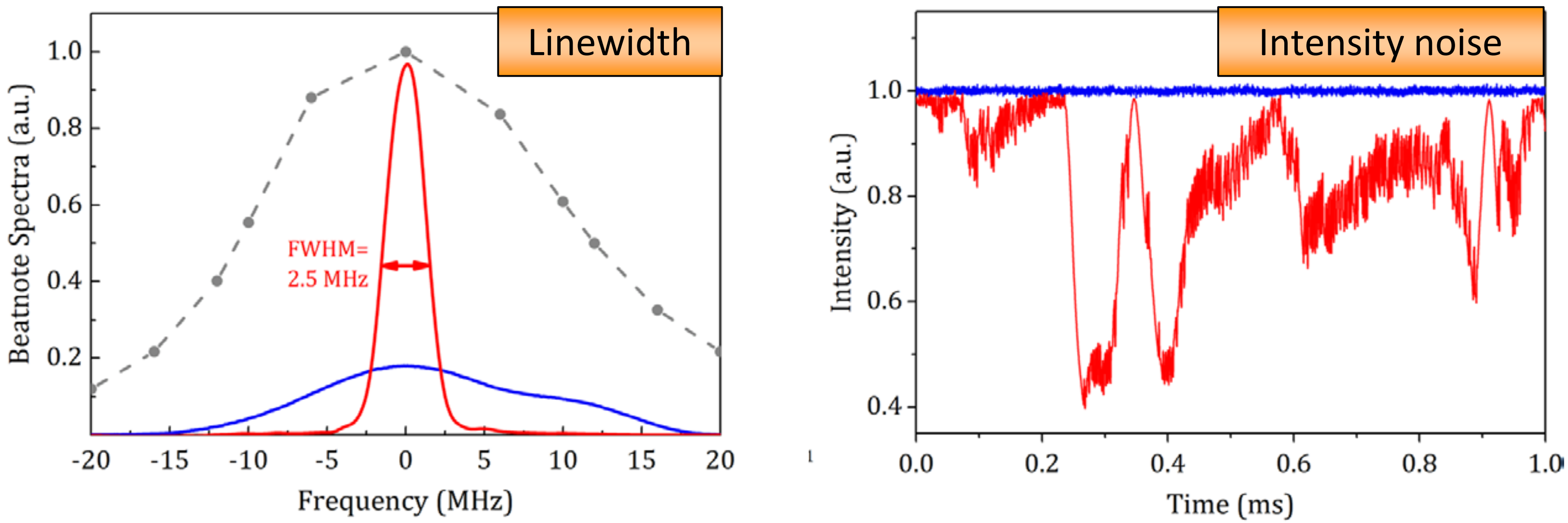


Feedback to the EC-QCL:

- via PZT;
- via AOFS

Lamperti et al., *Scientific Reports* 8 (2018)

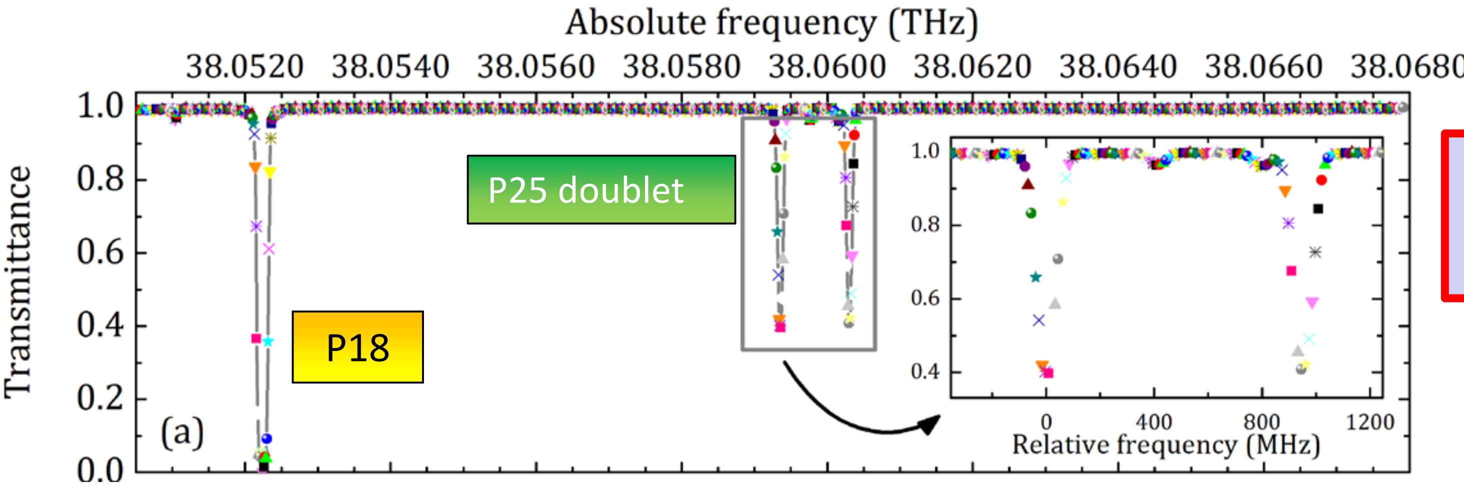
Frequency Locking of EC-QCL



SLOW LOCKING, via piezo modulation of the EC-QCL

FAST LOCKING, via external acousto-optic modulation

Comb-calibrated Absorption Spectra

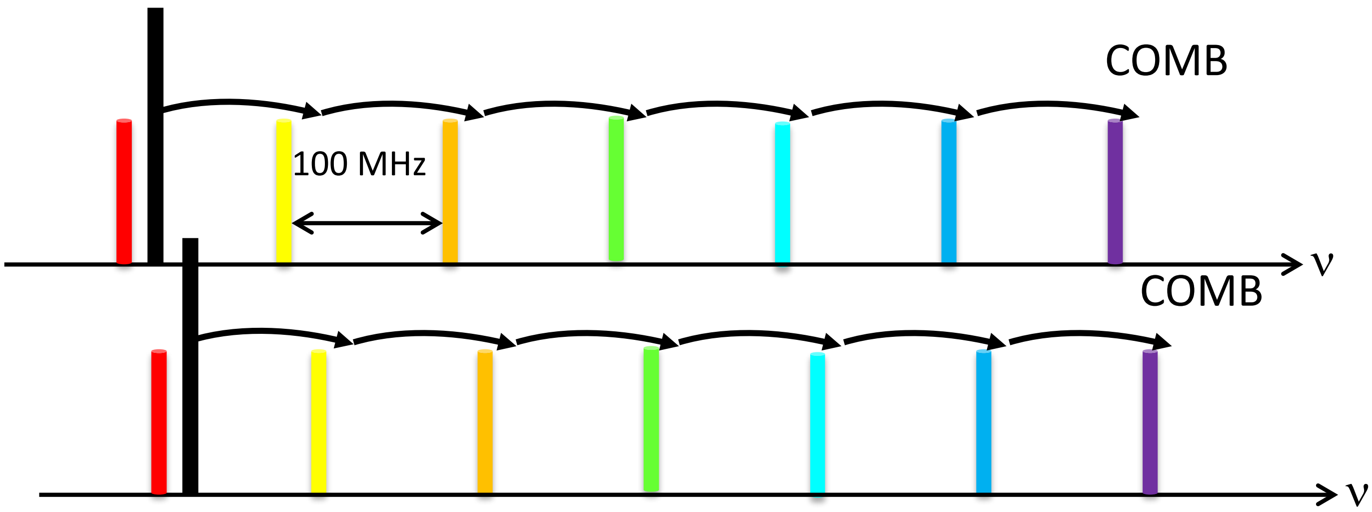


Gas sample: N_2O
Pressure: 0.025 mbar
Cell length: 66 cm

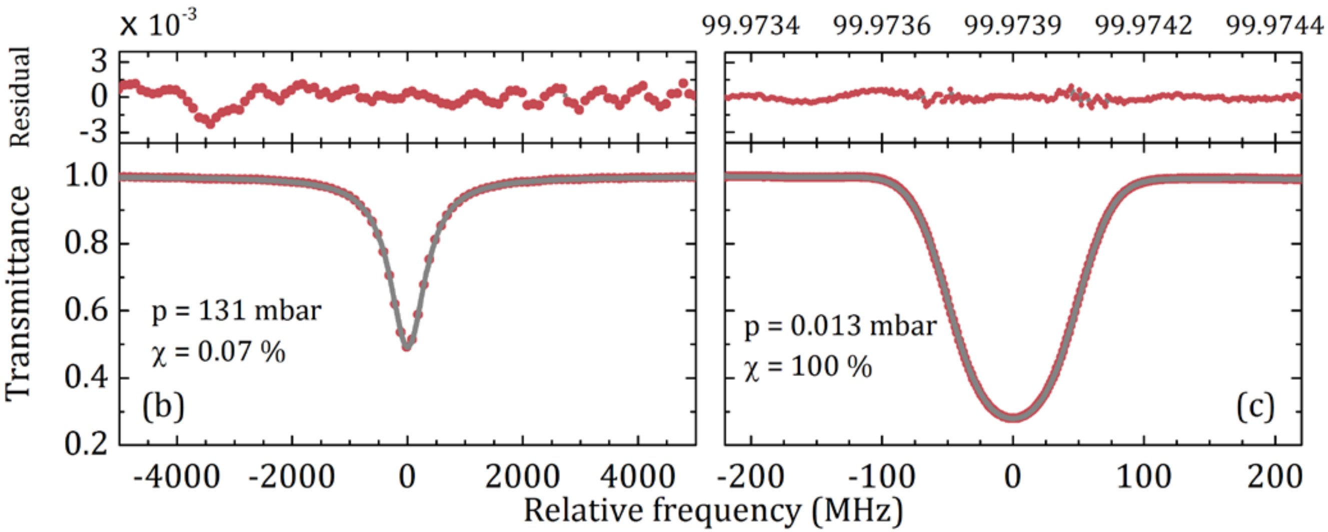
First ever demonstration with an EC-QCL

Stepped scan

+ Interleaving



Precision Spectroscopy of P(18) Line



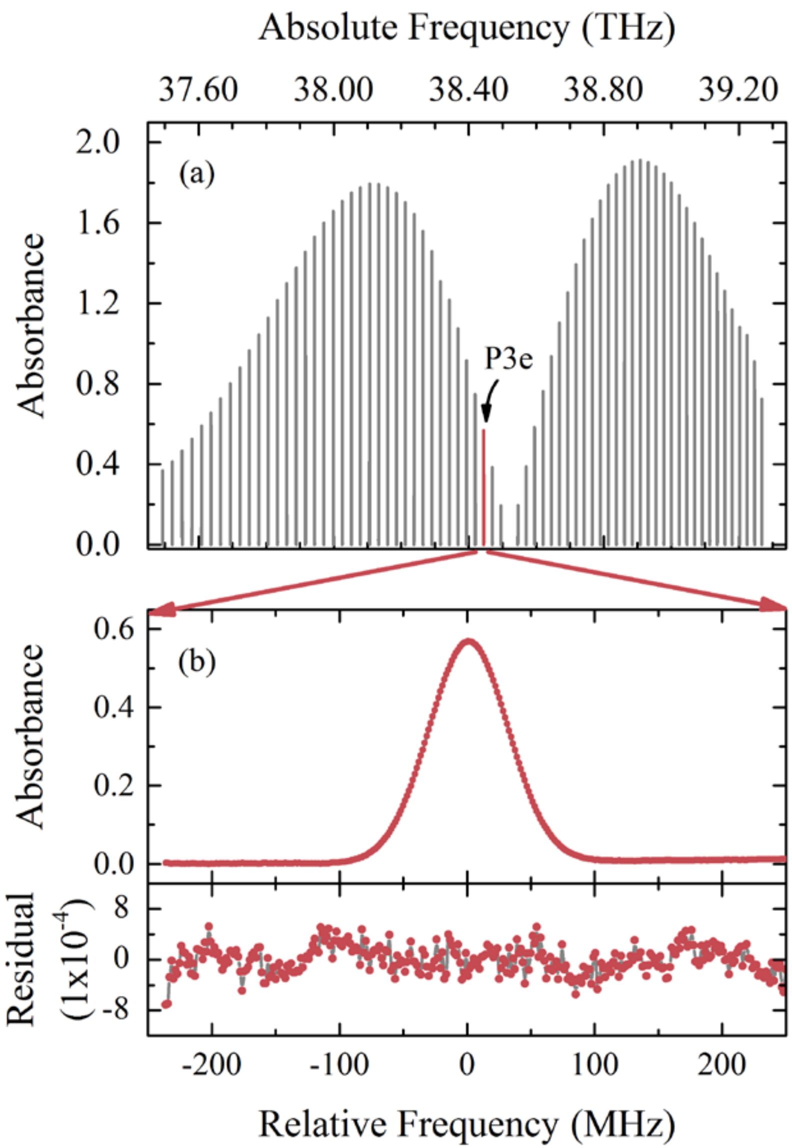
High pressure + dilution
Stepped scan: 100 MHz spacing
Voigt fitting
SNR ~ 1000
Line centre reproducibility ~ 500 kHz

Low pressure + pure sample
f_{rep}-tuning scan: 1.5 MHz spacing
Gaussian fitting
SNR ~ 1000
Line centre reproducibility ~ 47 kHz

NEARLY FLAT RESIDUALS

Alsaif et al., *JQSRT* 211 (2018)

Precision Spectroscopy of ν_1 band of N_2O



Fully automated setup:

- Linelist upload from HITRAN
- EC-QCL tuning to the 1st line
- Comb locking of the EC-QCL
- Rep-rate scanning
- Spectral profile acquisition
- EC-QCL tuning to the 2nd line...

Uncertainty budget

Uncertainty source	Type A (kHz)	Type B (kHz)
Experimental reproducibility	10-170	
Laser line shape asymmetry		60
Pressure leakage		2
Pressure reading		0.5
Frequency scale uncertainty		0.5
Total uncertainty	62-180 kHz	

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