European Double Doctorate Training Network

Photothermal Spectroscopy (PTS) of PMMA thin layer using micro-ring resonators (MRRs)

Optical Sensing using Advanced Photo-Induced Effects

OPTAPHI

An EU Marie Skłodowska-Curie ITN

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C-PASS 2023

OPTAPHI has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 860808

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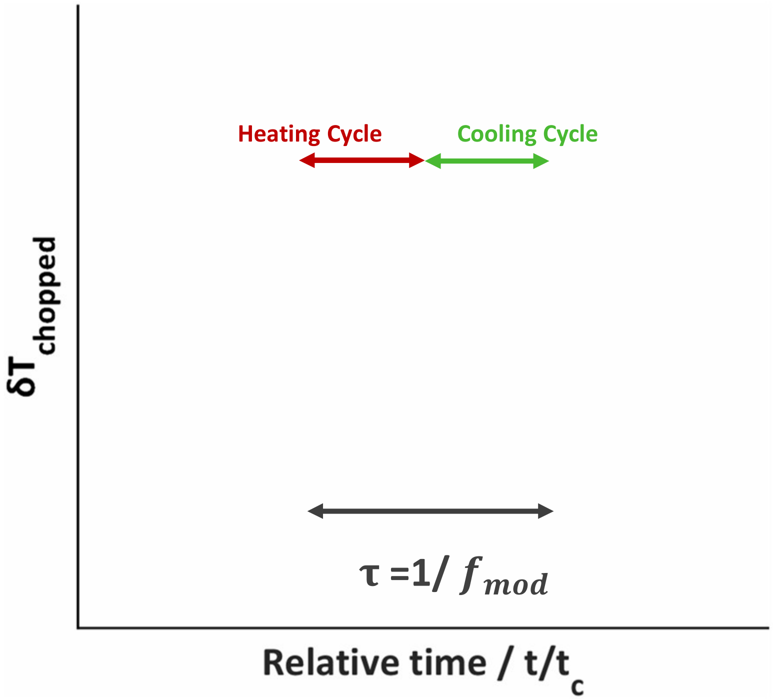
Photothermal Spectroscopy principle

- Mid-IR spectroscopy
  ν = 4000 – 400 cm-1
  λ = 2.5 – 25 µm
- Quantitative and qualitative information of molecular species
- Label-free & non-destructive



PHOTOTHERMAL SPECTROSCOPY

Temperature and refractive index (Photothermal)

$$\text{Signal} \propto \Delta T = \frac{P(\tilde{\nu})\,\alpha(\tilde{\nu})\,d}{\rho C_P V f_{mod}}$$

$$\Delta T \propto \Delta n$$

P ... Optical power
A ... Beam cross section area
$\alpha(\tilde{\nu})$......Absorption coefficient
d...........Optical pathlength
f_{mod} ... Modulation Frequency
c_P ... Heat Capacity
ρ ... Density
V......Volume

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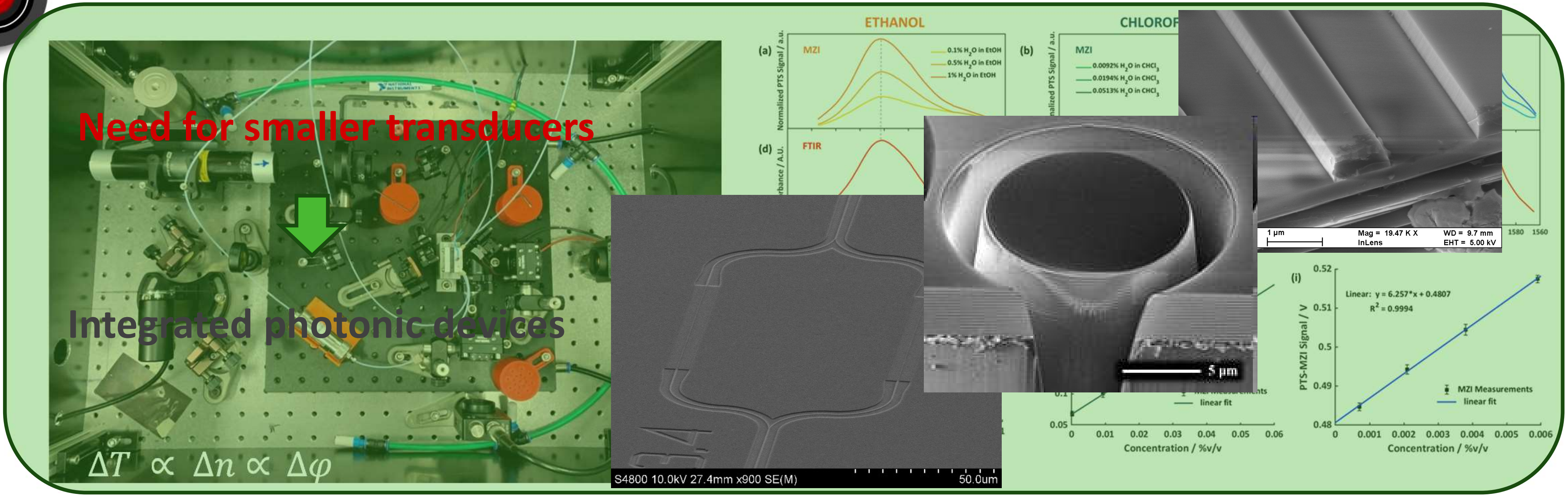
Free-space Photothermal Spectroscopy Mach-Zehnder Interferometer (PTS-MZI)[2]



PTS enables for sensor miniaturization[1]: $\text{Signal} \propto \Delta T = \dfrac{\mathbf{P}(\tilde{\nu})\ \alpha(\tilde{\nu})\ d}{\rho\ C_P\ V\ f_{mod}}$

- Decrease test sample volume and of reagents/solvents/waste
- Shorten the duration of the analysis
- Different conditions of heat transfer
- Smaller optical pathlengths **d**

1. Bialkowski, S.E.Photothermal Spectroscopy Methods forChemical Analysis; John Wiley &Sons, 1996.
2. Ricchiuti, G.; Dabrowska, A.; Pinto, D.; Ramer, G.; Lendl, B. Dual-Beam Photothermal Spectroscopy Employing a Mach–Zehnder Interferometer and an External Cavity Quantum Cascade Laser for Detection of Water Traces in Organic Solvents. Anal. Chem. 2022, 94 (47), 16353–16360. https://doi.org/10.1021/acs.analchem.2c03303.

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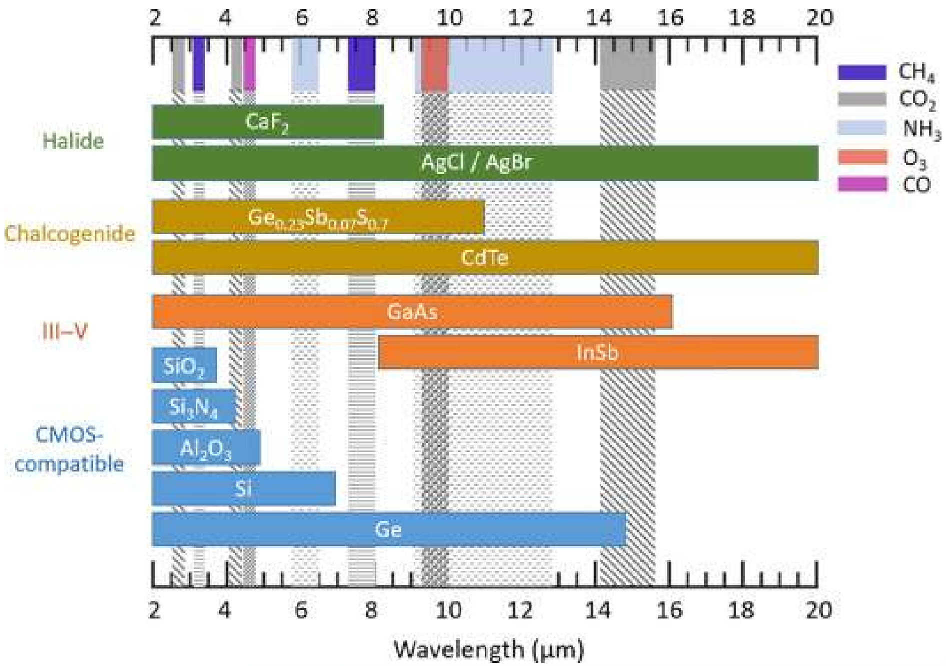
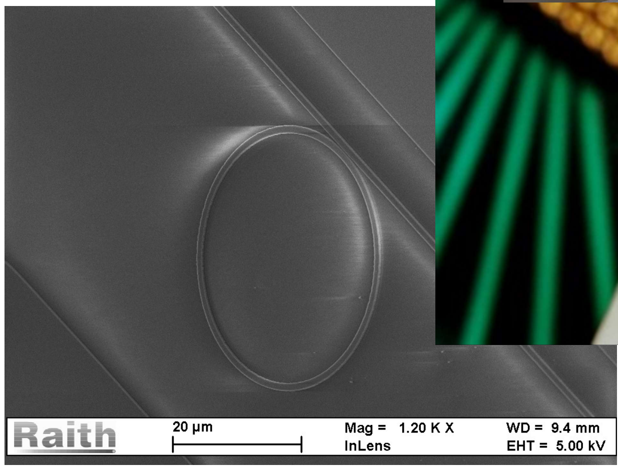
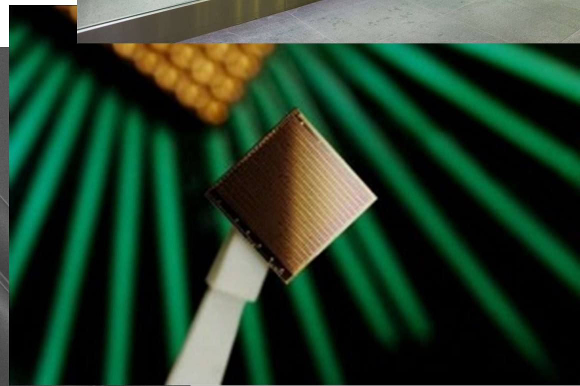
Photonic Integrated Circuits (PICs)

Integrated circuit are widely used for:
- Data communications
- Sensing
- Industrial applications
- Biomedical applications



Main features:
- Low cost
- Compact and light
- Low power consumption
- High efficiency
- High speed
- Low thermal issues
- Large integration capacity





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The sensitive device: micro-ring resonators (MRRs)

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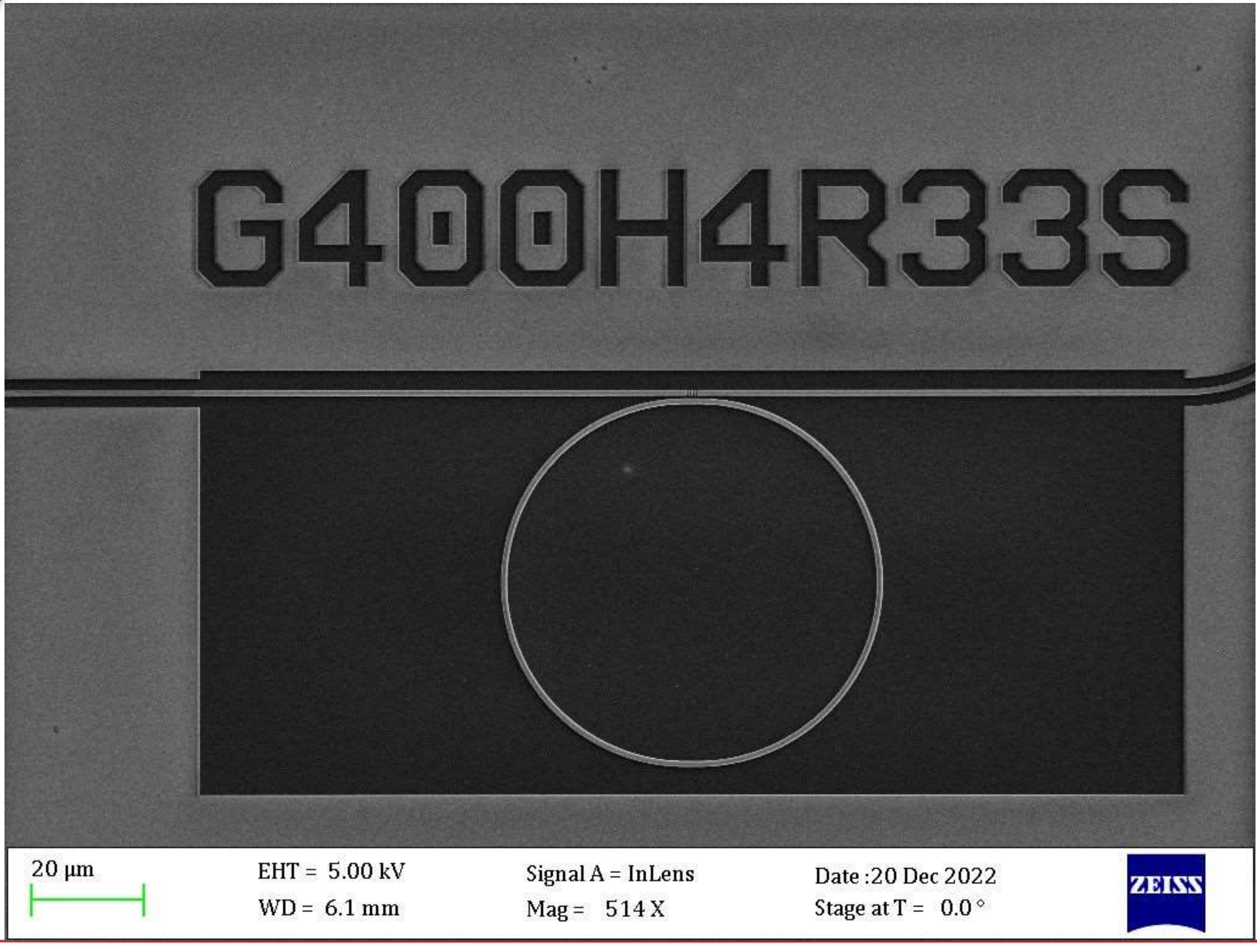

The sensitive device is a MRR made in Si_3N_4 (n ~ 2)

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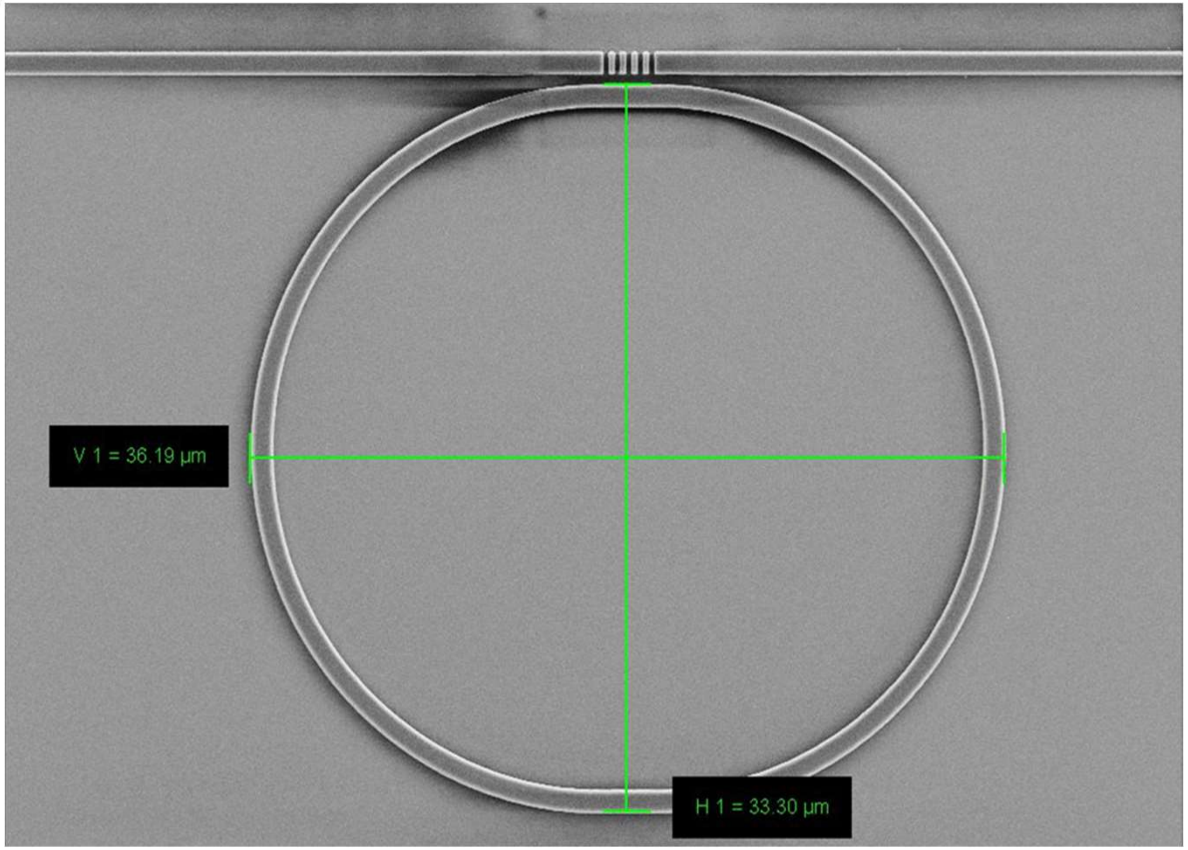

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The used rings have a radius of 16 or 33 µm

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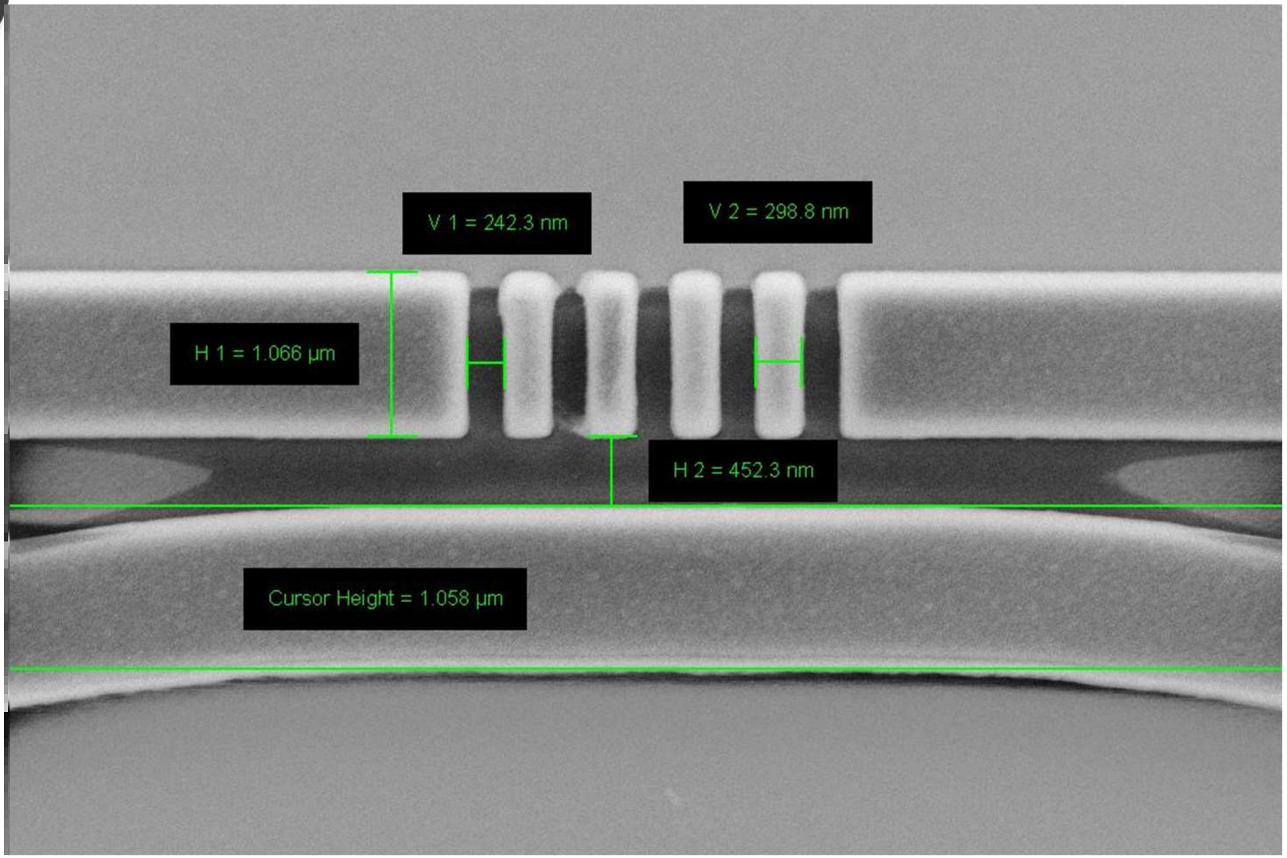

The sensitive device is a MRR made in Si_3N_4 (n ~ 2)

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MRR partially transmitting elements (PTE) in the gap region have been engineered to achieve high Q-factor and sharp asymmetric Fano resonances

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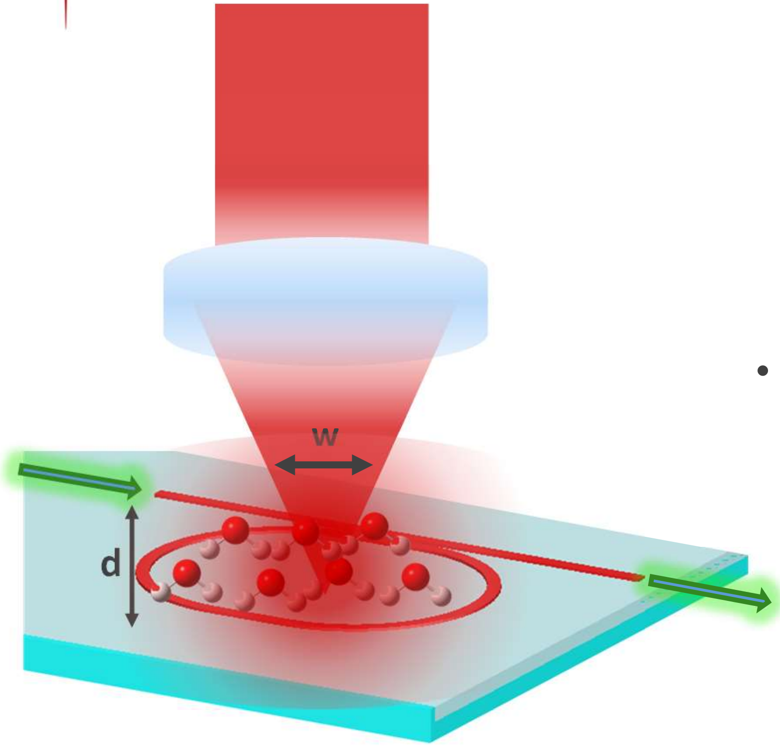


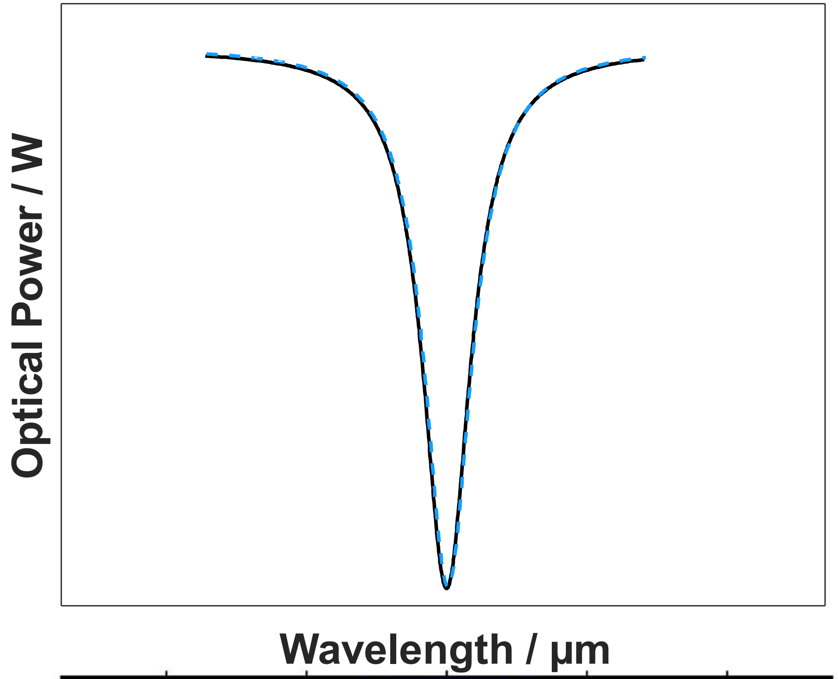
Refractive index and Temperature sensor

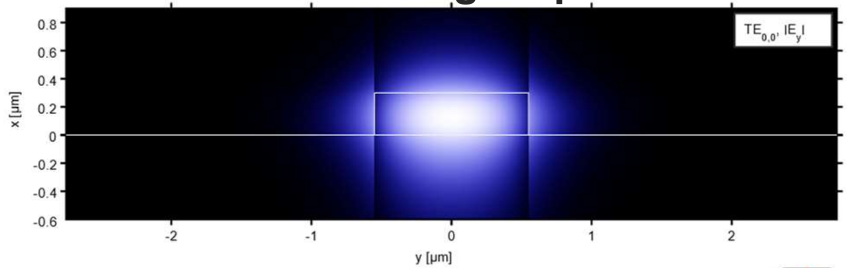
- n_{eff} change due to the change of n_{clad} in the waveguide

$$\Delta\lambda_{Res} \propto \Delta n_{eff}$$

- T change photoinduced by an excitation source, introduce a n_{eff} change related to the $\frac{dn}{dT}$ of the materials

$$\Delta\lambda_{Res} \propto \Delta T \propto \Delta n_{eff}$$





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The analyte: Polymethylmethacrylate (PMMA), n_{clad}

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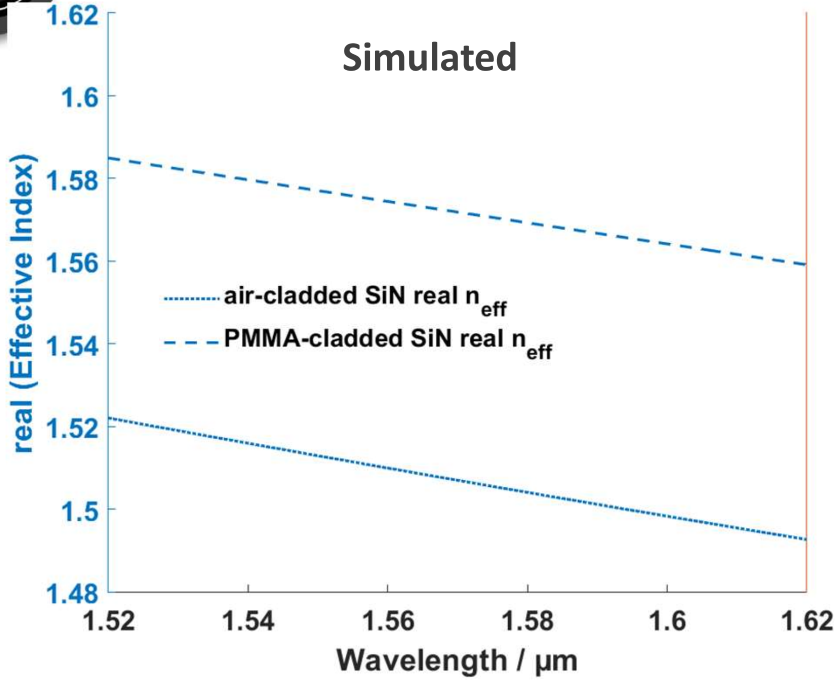
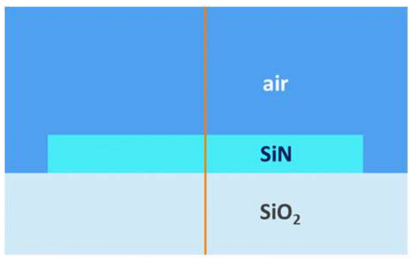
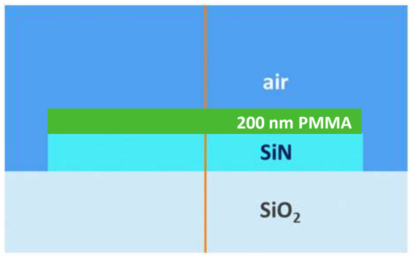
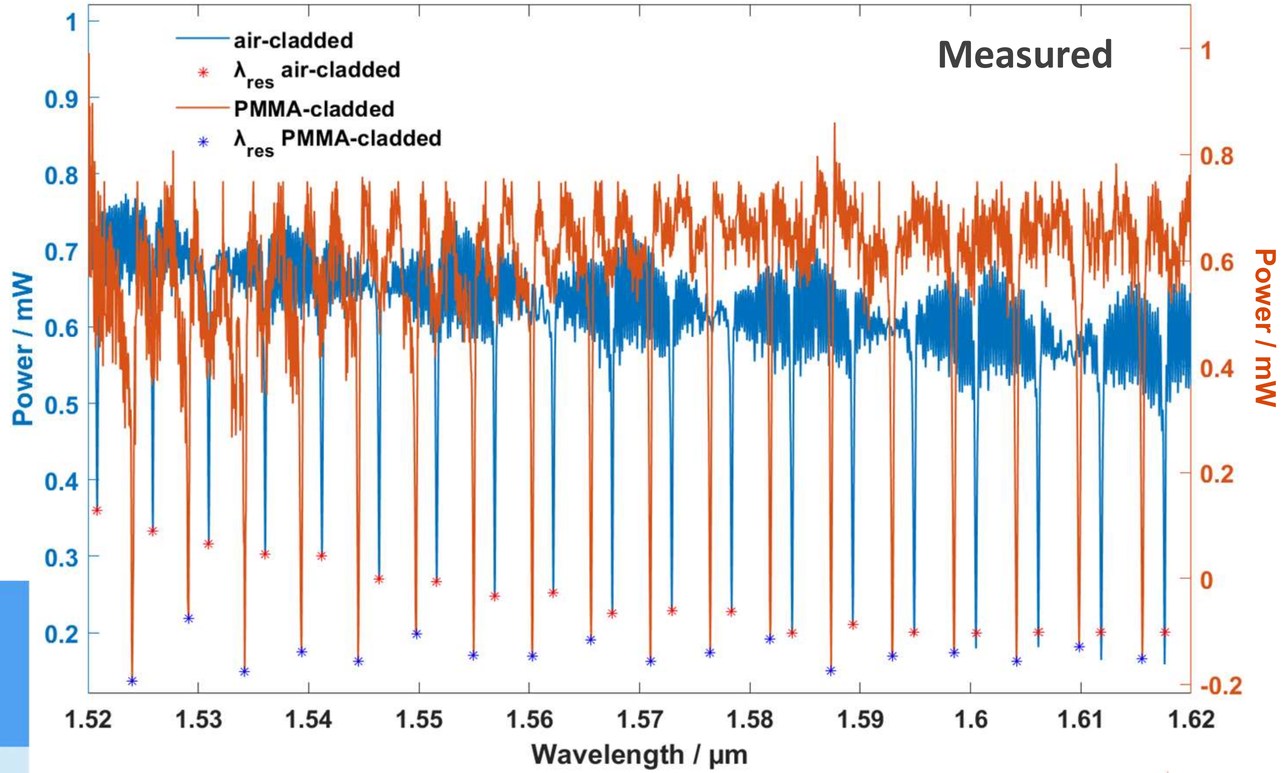






Ring: G400H4R33S T holder: 20℃



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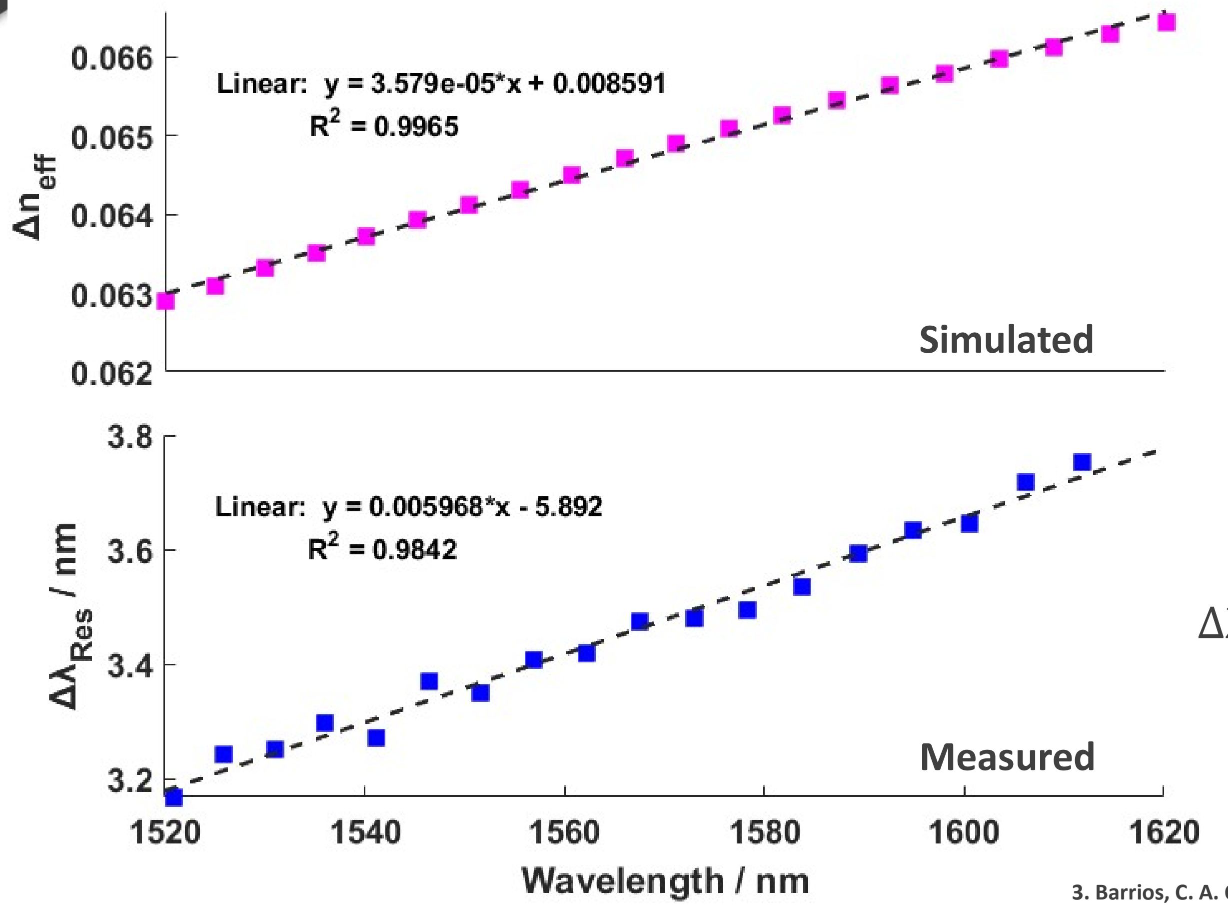

$$\Delta n_{clad}(@1550\ nm) \sim 0.48\ \text{RIU}$$

$$\Delta n_{eff} \sim 0.064$$

$$\Delta\lambda_{Res} \sim \boxed{\mathbf{3.35\ nm}} + \text{m} \cdot FSR$$

Calculated[3]

$$\Delta\lambda_{Res} = -\Delta n_{eff} \frac{2\pi}{\lambda_{Res,0}} \cdot \left(\frac{2\pi n_g(\lambda_{Res,0})}{\lambda_{Res,0}{}^2}\right)^{-1}$$

$$\Delta\lambda_{Res} = \boxed{\mathbf{3.1\ nm}}$$

3. Barrios, C. A. Optical Slot-Waveguide Based Biochemical Sensors. Sensors 2009, 9 (6), 4751–4765. https://doi.org/10.3390/s90604751

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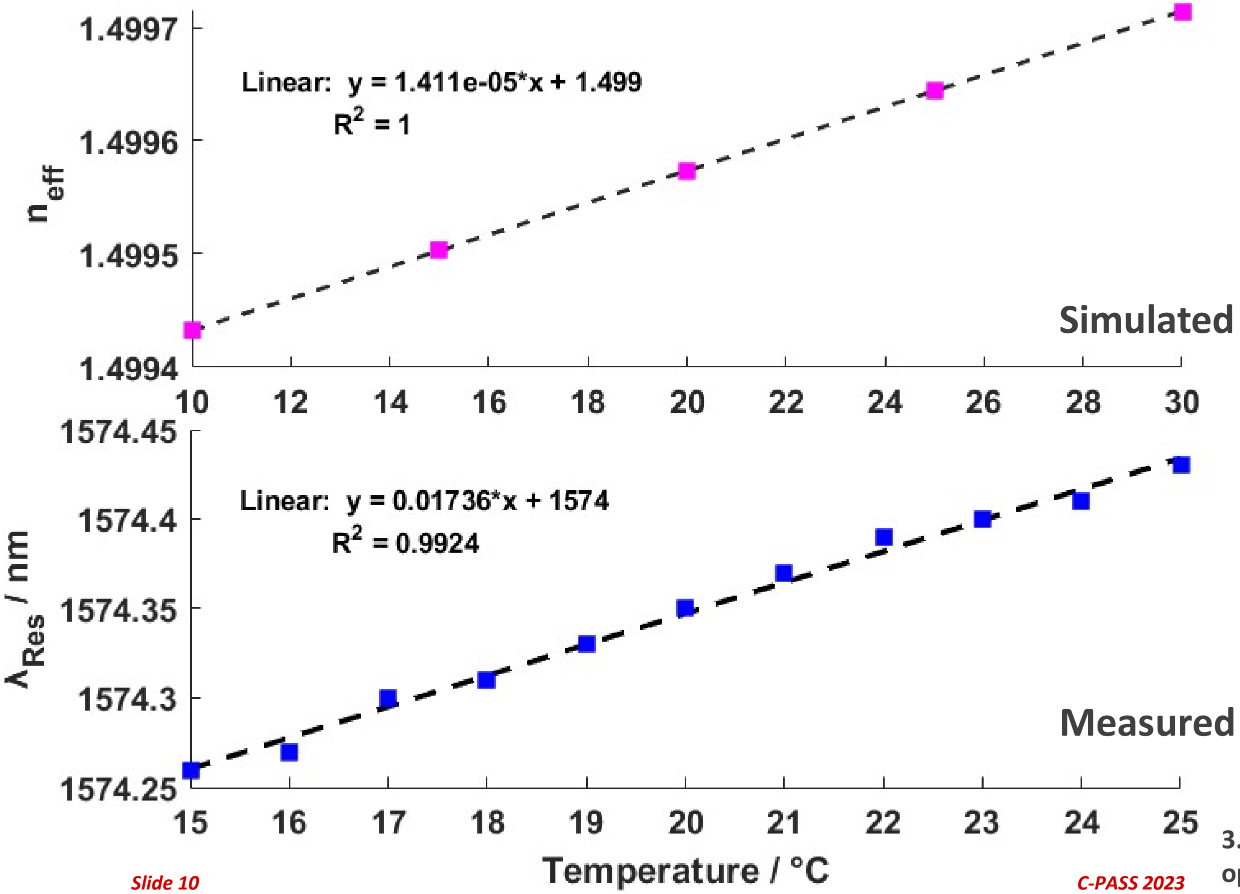
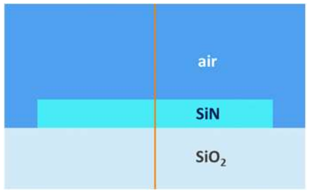
The thermo-optical effect of SiN, dn/dT





SiN TOC= 2.1e-5 [RIU/° C]

$$\Delta T_{SiN} \sim +1\,°C$$

$$\frac{\Delta n_{eff}}{\Delta T} \sim 1.411e-5$$

$$\frac{\Delta \lambda_{Res}}{\Delta T} \sim \mathbf{17\ pm}$$

Calculated[3]

$$\frac{\Delta \lambda_{Res}}{\Delta T} = \left(\frac{\Delta n_{eff}}{\Delta T} + n_{eff}\alpha_{TH}\right) \cdot \frac{\lambda_{Res}}{n_{eff}}$$

$$\frac{\Delta \lambda_{Res}}{\Delta T} = \mathbf{18\ pm}$$

3. Rabus, D. G. Integrated Ring Resonators: The Compendium; Springer series in optical sciences; Springer: Berlin Heidelberg, 2007

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The experimental setup

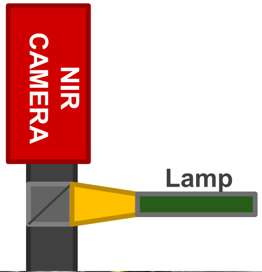
G400H4R33S spin-coated with ~ 200 nm PMMA

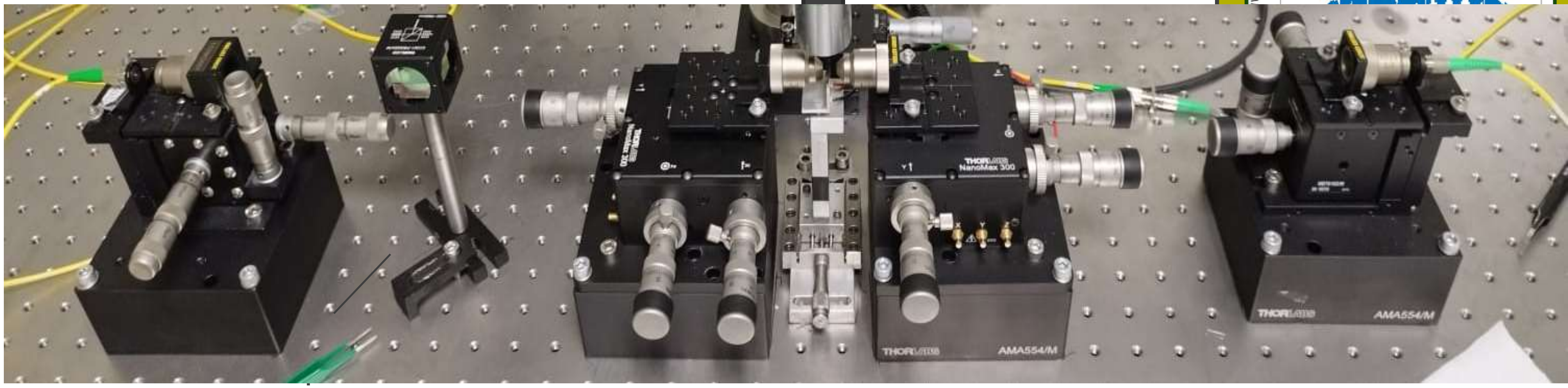
$$Q = \frac{\nu_0}{FWHM} \sim 8900$$

Sample holder T = 20 °C
FP effect → fringes

Picked resonance @1593.444 nm
Inflection Point @1593.530 nm

Humidity level ~ 48-49%





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The experimental setup

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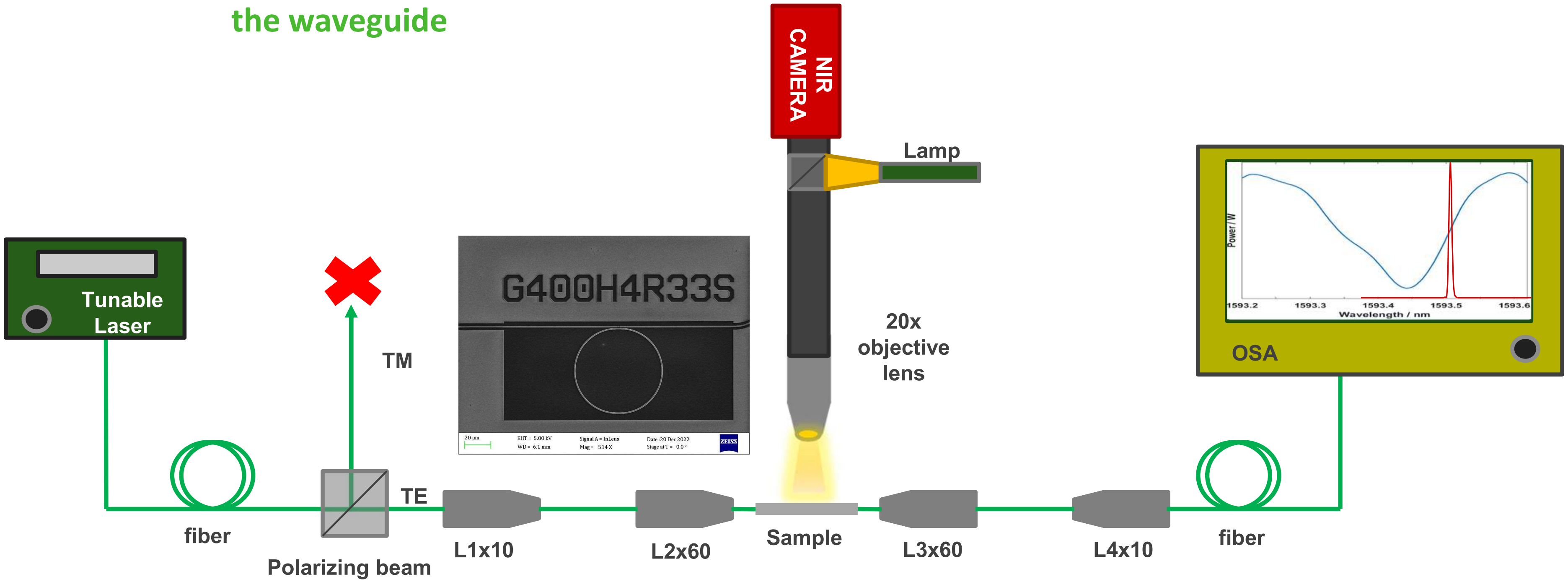
End-Fire setup is used to edge-couple the **probe laser (TLS – Yenista Optics) tunable laser (1500-1630 nm)** onto the waveguide



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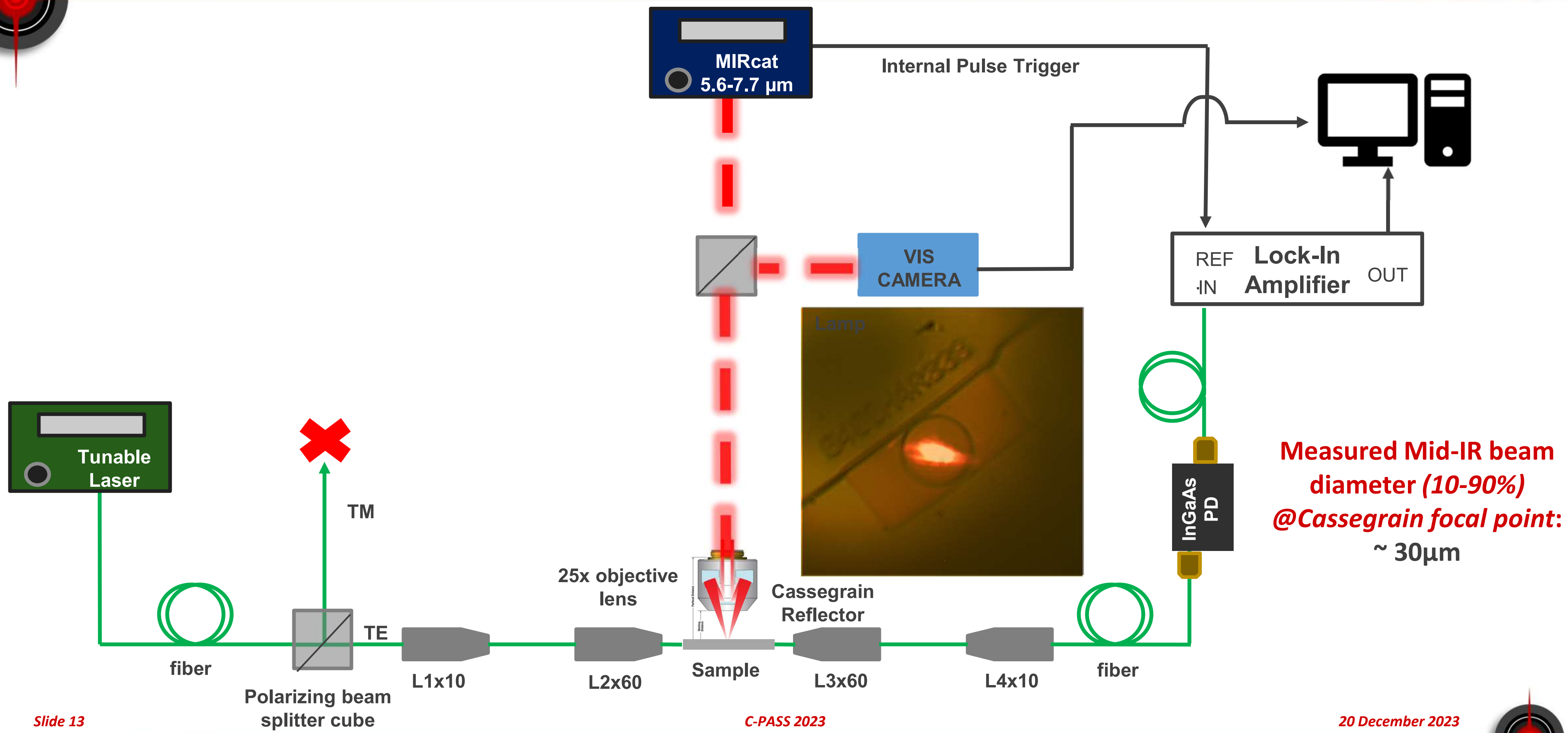

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Results: optimal operational conditions

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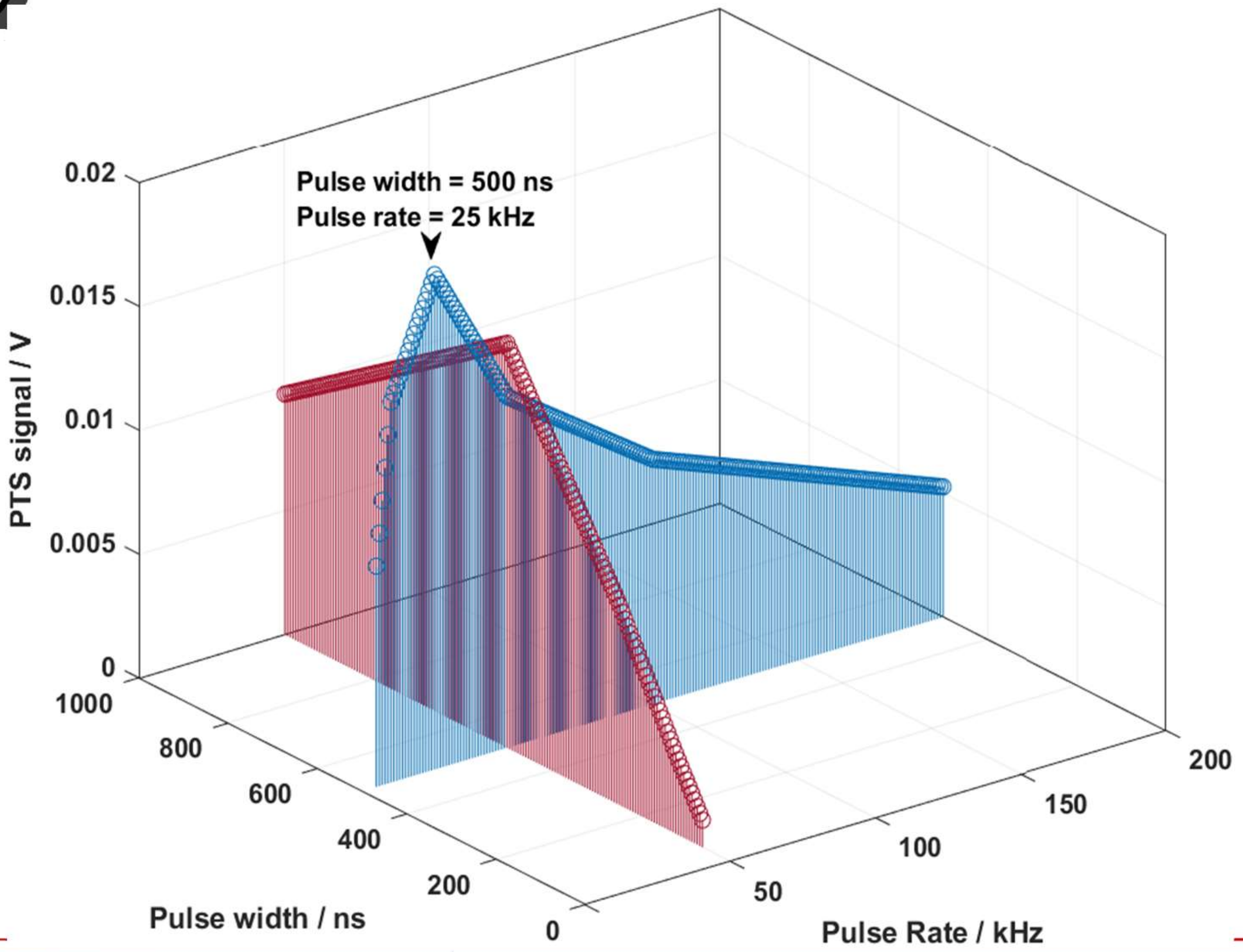

The LIA demodulated signal is maximized using:

- Pulse width= 500 ns
- Pulse rate= 25 kHz
- Duty cycle = 1.25%

- EC-QCL forward sweep scan mode= 5 cm^{-1}/step
- LIA time constant τ= 100 ms
- EC-QCL operational current= 750 mA

NO COOLING IS NEEDED FOR THE LASER HEAD IN THE PULSED MODE !

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The thermo-optical effect of SiN+PMMA, dn/dT

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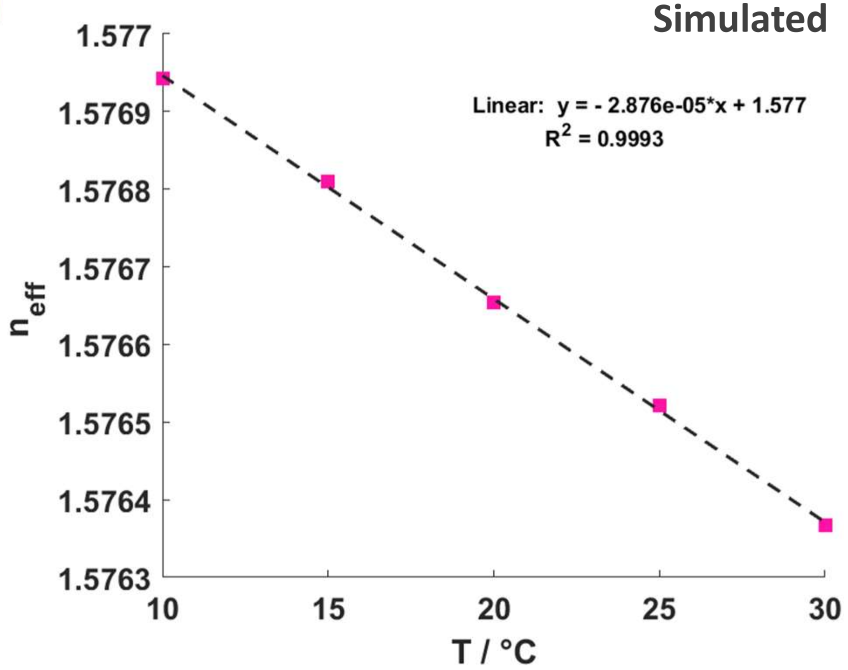
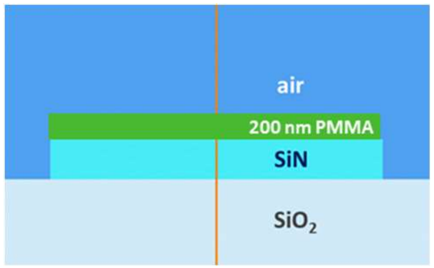
PMMA TOC= -1.3e-4 [RIU/° C]

Simulated





$$\Delta T_{SiN\ +\ PMMA} \sim +1\,°C$$

$$\frac{\Delta n_{eff}}{\Delta T} \sim -2.876e-5$$

Calculated[3]

$$\frac{\Delta\lambda_{Res}}{\Delta T} = \left(\frac{\Delta n_{eff}}{\Delta T} + n_{eff}\alpha_{TH}\right) \cdot \frac{\lambda_{Res}}{n_{eff}}$$

$$\frac{\Delta\lambda_{Res}}{\Delta T} = -25\ pm$$

3. Rabus, D. G. Integrated Ring Resonators: The Compendium; Springer series in optical sciences; Springer: Berlin Heidelberg, 2007

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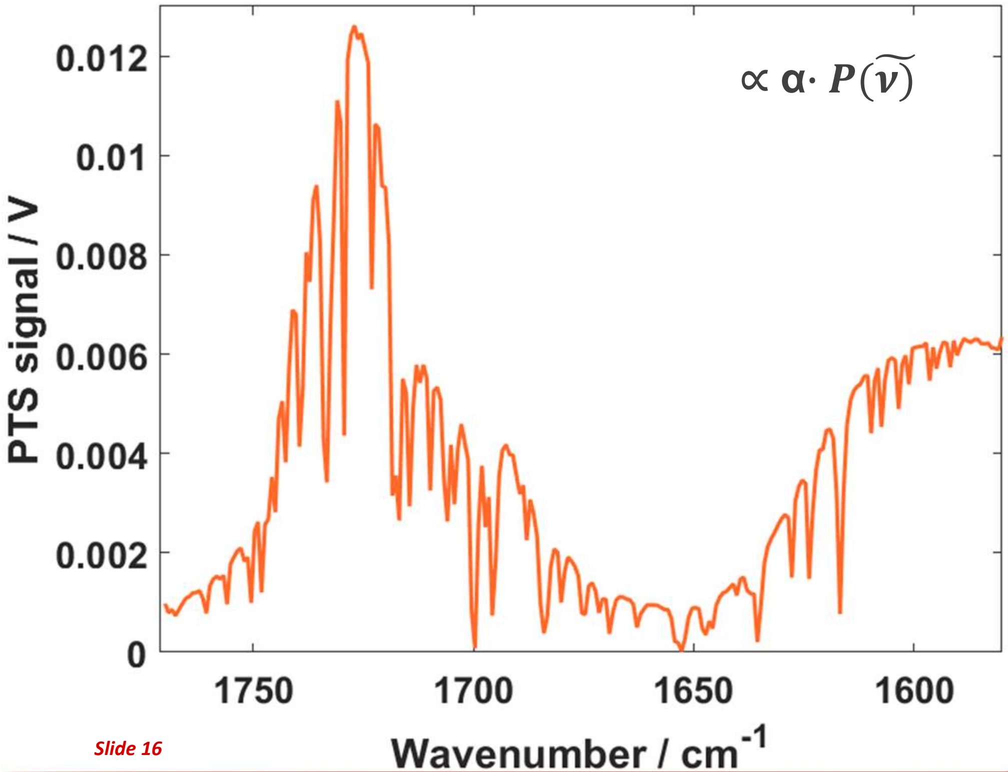
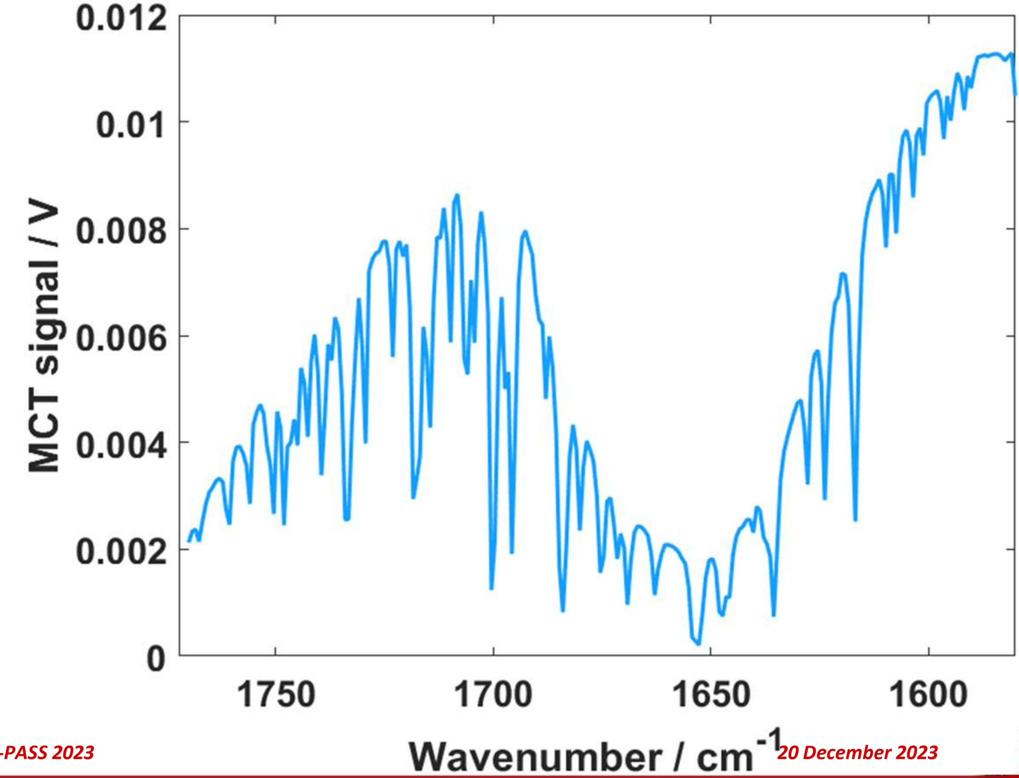
Results: 200 nm PMMA spectrum

The LIA demodulated PTS signal is acquired by scanning the MIRcat between 1580-1770 wavenumbers on top of the PMMA coated sample



The excitation laser optical power $P(\widetilde{\nu})$ has been recorded by means of an MCT detector between 1580-1770 wavenumbers (no interaction with the sample!)



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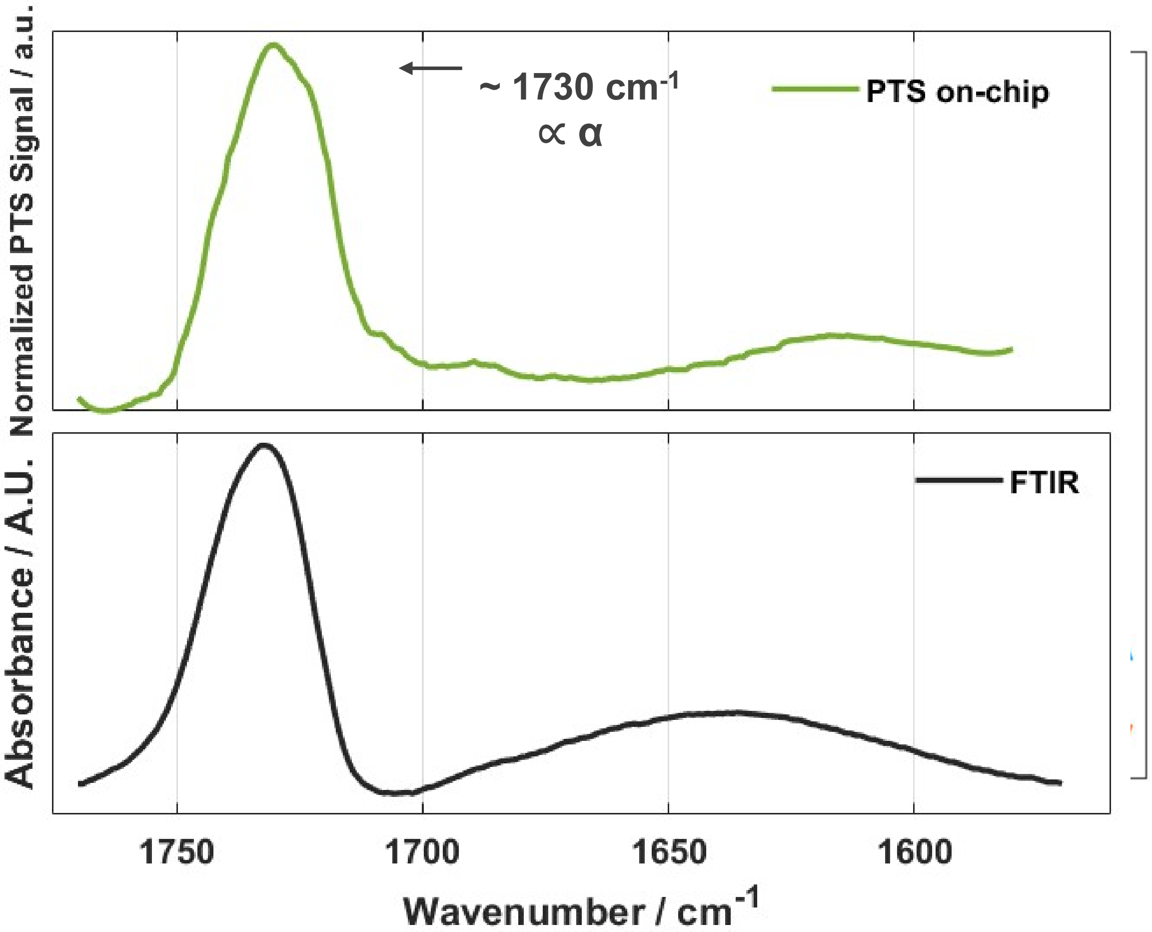
Results: 200 nm PMMA spectrum

The **LIA demodulated signal** is normalized by the **excitation laser optical power** $P(\widetilde{\nu})$ to retrieve only the analytical information of the target analyte

A Savitzky–Golay filter has been used to remove water vapor contribution

Similar qualitative results have been obtained using a MRR with half the radius



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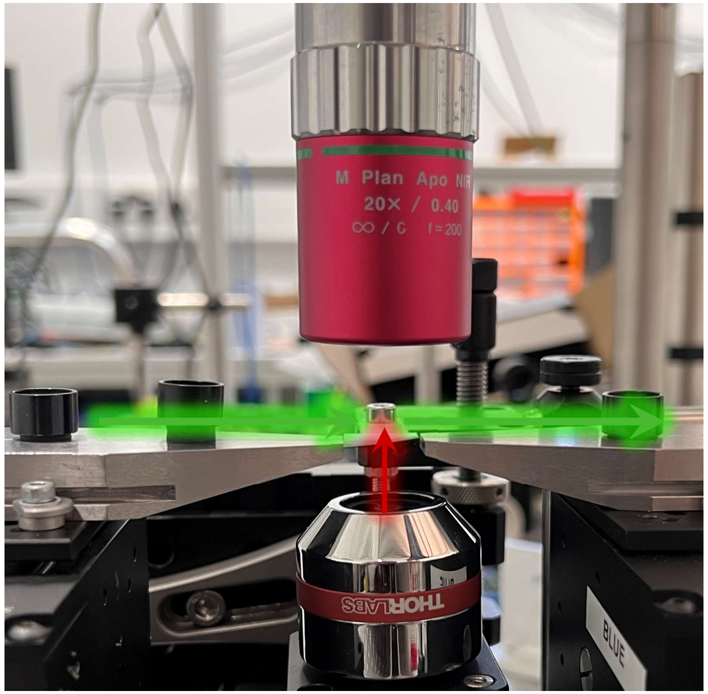
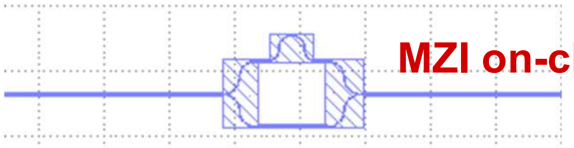
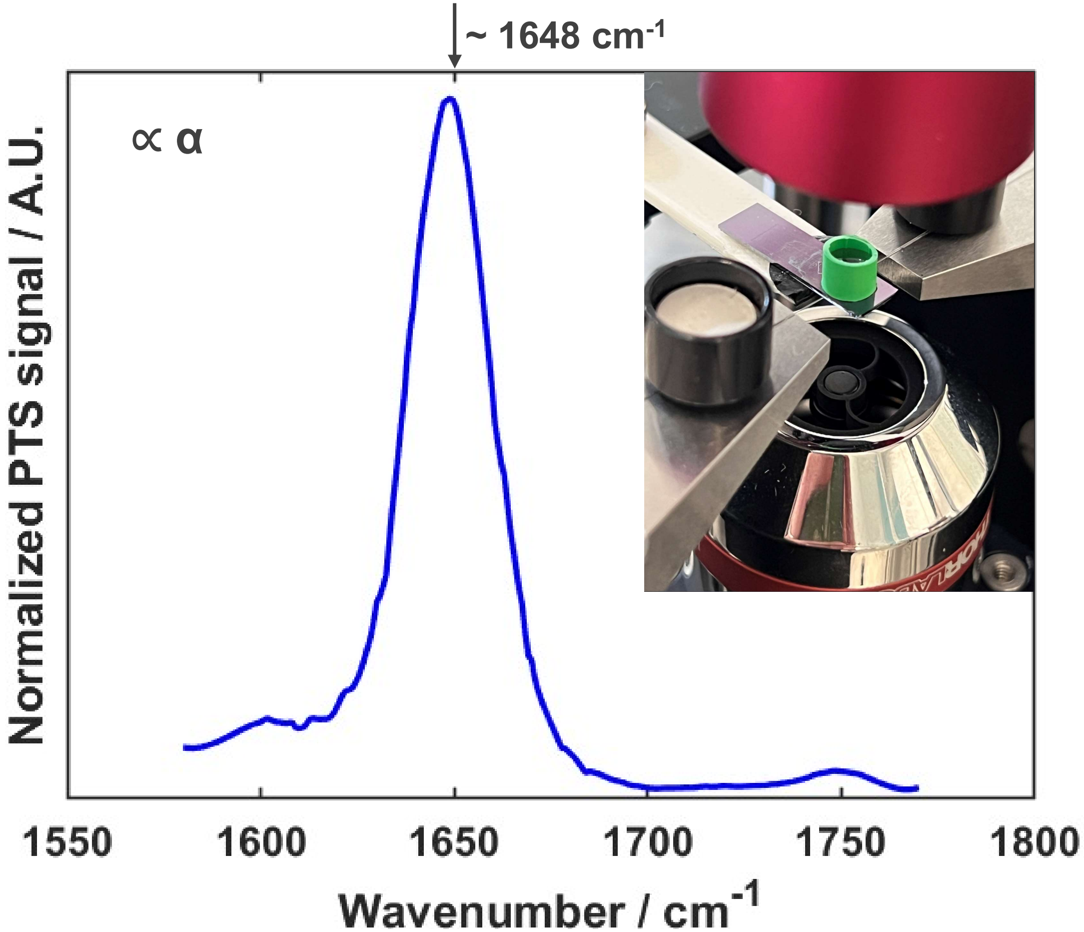
Current developments & future works





MZI on-chip



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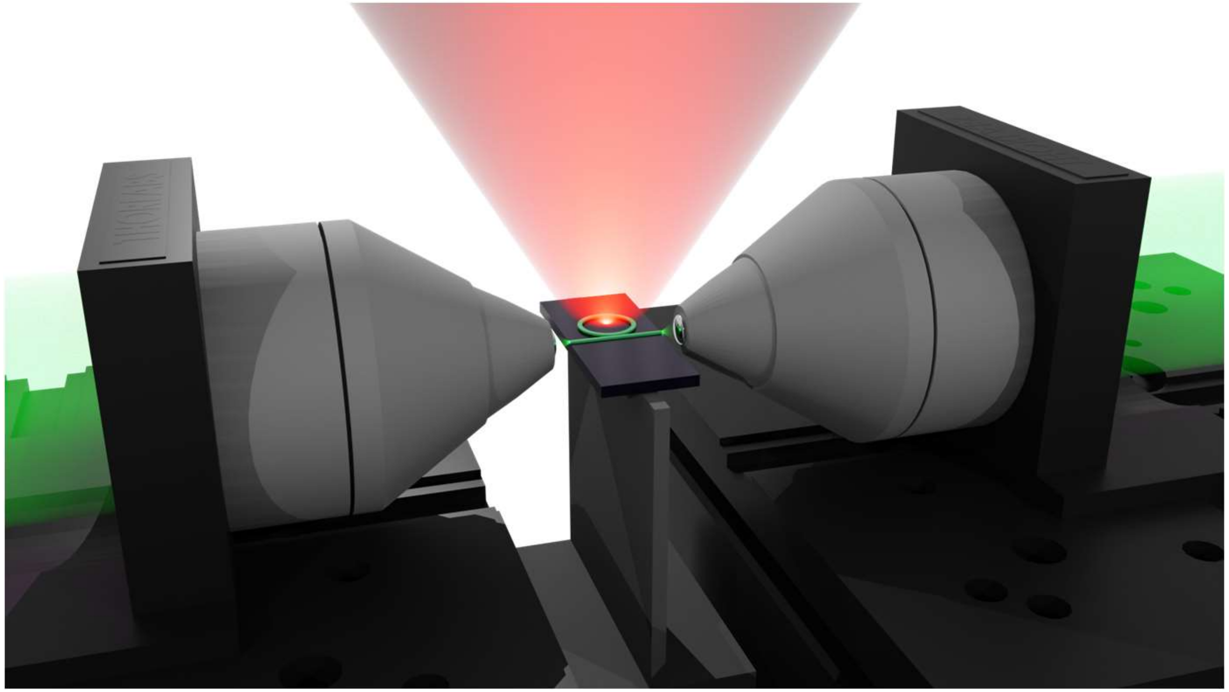
Conclusions

- **A first demonstration of PTS on-chip using an EC-QCL has been given for targeting PMMA absorption feature**

- **Qualitative spectra are in excellent agreement with reference method**

- **Preliminary first demonstration of PTS on-chip for liquid samples has been shown**
    - **Attractive solution especially for proteins detection where small pathlengths are needed to probe in aqueous solutions**



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Greetings

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THANK YOU ALL!

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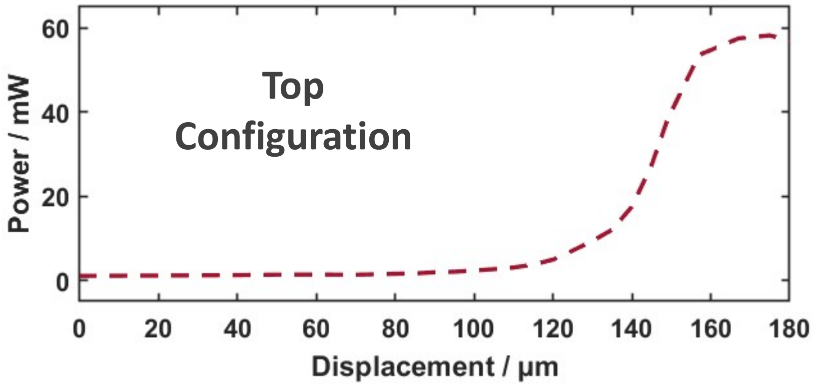
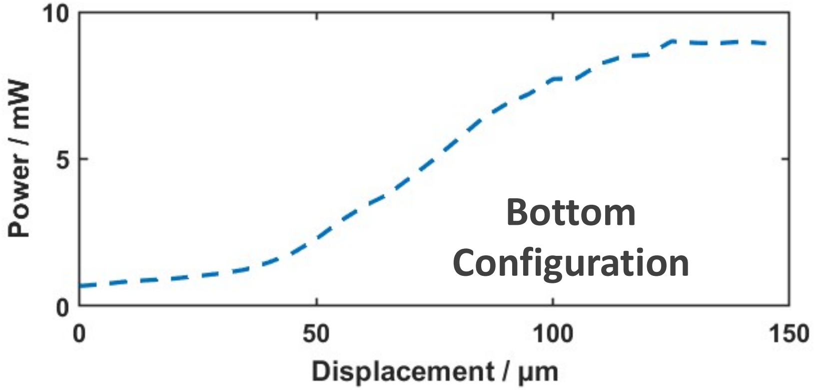
Recent results: bottom excitation using a Cassegrain Reflector





CONS:

- ***LESS Mid-IR OPTICAL POWER AVAILABLE***
- ***BEAM SPOT SIZE LARGER IN COMPARISON WITH TOP EXCITATION CONFIGURATION***

Beam Properties	
Spatial Mode	TEM_{00} (nominal)
Pointing Stability	MIRcat-QT: < 2 mrad (centroid change)
	MIRcat-1xxx: < 2mrad per 100 cm-1 of tuning (centroid change)
Beam Waist	< 2.5 mm ($1/e^2$ intensity radius, typical value, varies with λ)
	30 to 50 cm from output port (typical value, varies with λ)
Beam Divergence	< 4 mrad (full angle, $1/e^2$ intensity width, varies with λ, measured at with λ = 4 µm)
Linear	>100:1, vertically polarized, perpendicular to laser base

Mid-IR beam diameter *(10-90%)* *@Cassegrain focal point*:

~ 30µm (Top excitation)

~ 50 µm (Bottom excitation)

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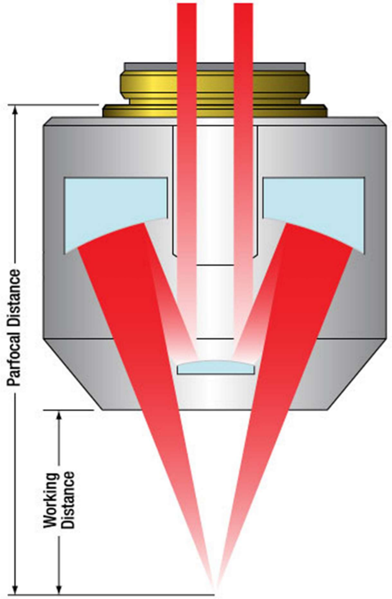

Item #		LMM15X-P01	LMM25X-P01	LMM40X-P01
Mirror Coating		Protected Silver (R_{avg} > 97% Over 450 nm - 2 µm; R_{avg} > 95% Over 2 µm - 20 µm)		
Magnification[a]		15X	25X	40X
Numerical Aperture		0.3	0.4	0.5
Focal Length		13.3 mm	8 mm	5.0 mm
Parfocal Distance[b]		63.3 mm	45.0 mm	30.0 mm
Back Focal Length		Infinity	Infinity	Infinity
Design Tube Lens Focal Length[c]		200 mm	200 mm	200 mm
Entrance Pupil Diameter[d]		8.0 mm	6.4 mm	5.1 mm
Working Distance[b]		23.8 mm	12.5 mm	7.8 mm
Field of View		1.2 mm	0.7 mm	0.5 mm
Resolution[e]		1.1 µm	0.8 µm	0.7 µm
Obscuration[f]	Secondary Mirror Only	22%	22%	18%
	Mirror and Spider Vanes	26%	26%	24%
Transmitted Wavefront Error		<λ/14 RMS at 450 nm		
Damage Threshold	Pulsed	1.0 J/cm^2 (1064 nm, 10 ns, 10 Hz, Ø0.230 mm)		
Objective Threading		36 (RMS)		
RMS Thread Depth		4.7 mm	4.5 mm	4.7 mm

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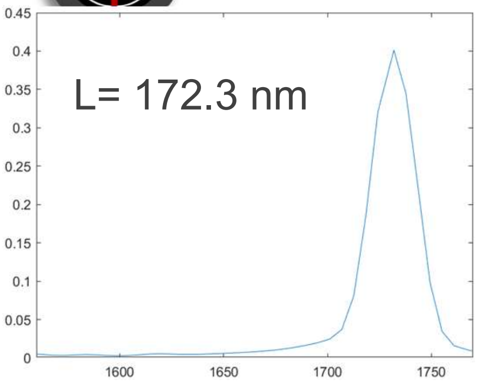

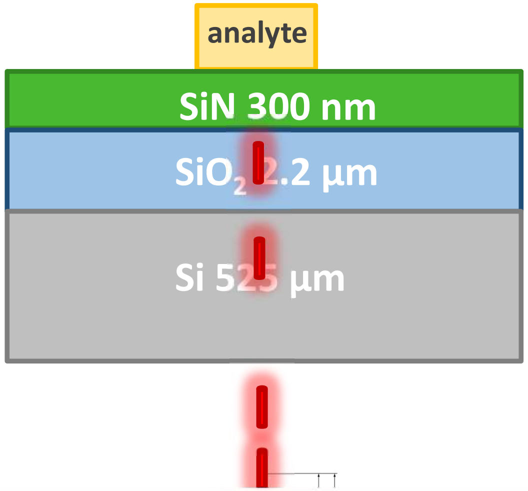

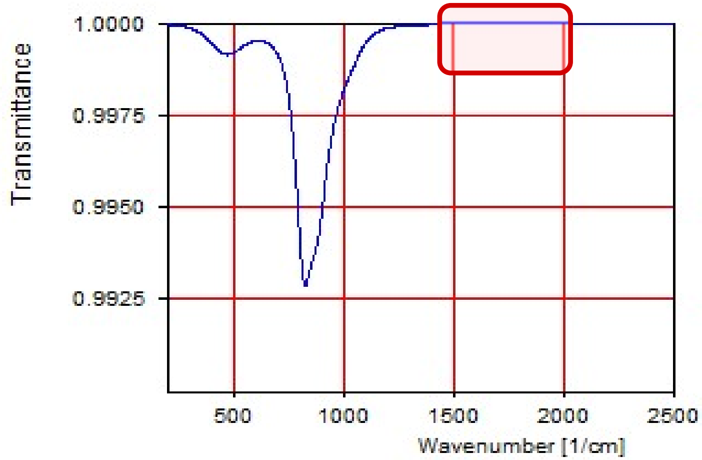

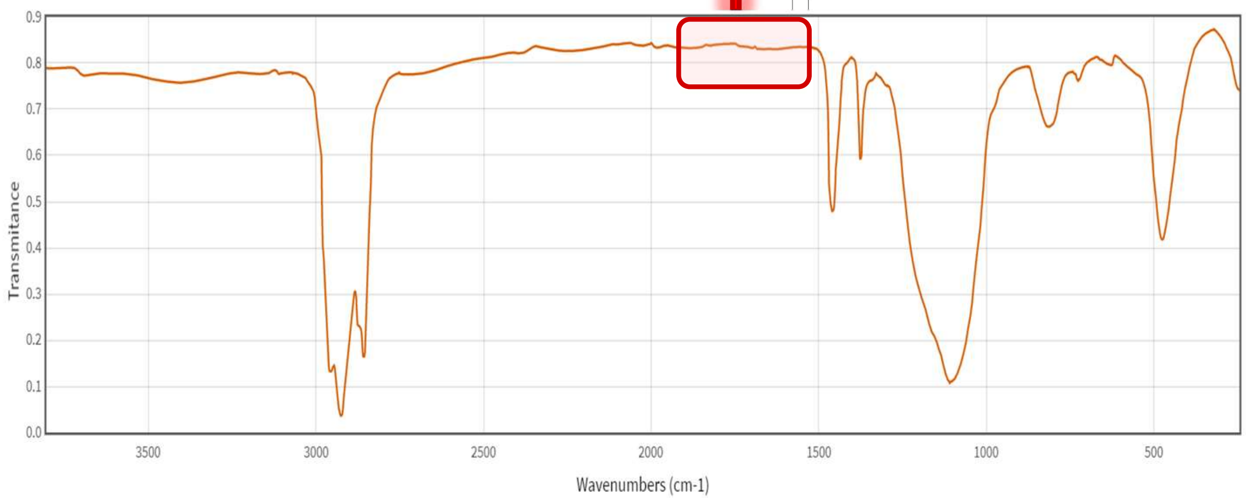

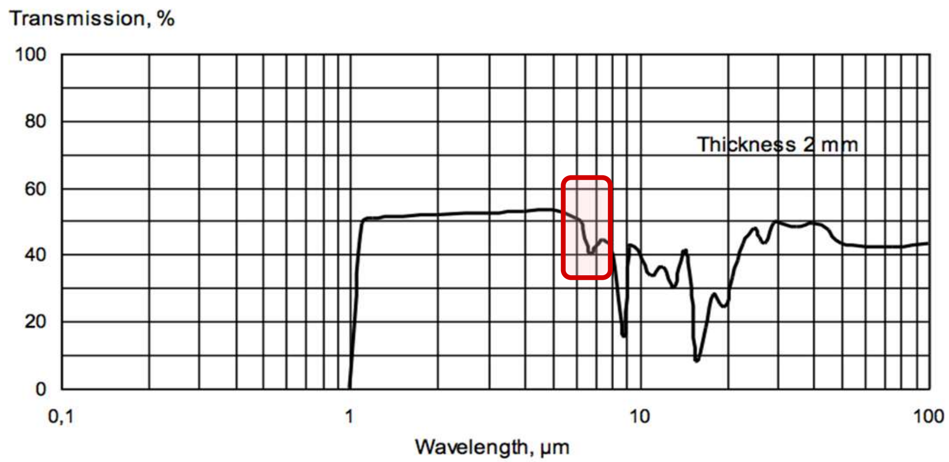

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