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Raman Spectroscopy

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Raman Basics & Technique

September 2020

Outline

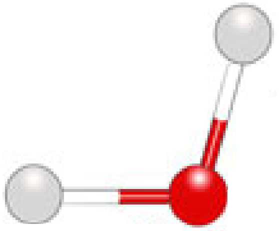
- Principles of Raman effect in a nutshell
- What information does Raman give?

- Instrument Parameters I
  - Laser
  - Filter / Attenuator
  - Collecting lens
  - Rayleigh Filter
  - Confocal Aperture
  - Slit
  - Spectrometer & Grating
  - Detector & Quantum Efficiency
  - Correction of Instrument Function

Stokes Raman Effect

O—H $\xrightarrow{\text{light}}$ O—H

Molecule in vibrational ground state

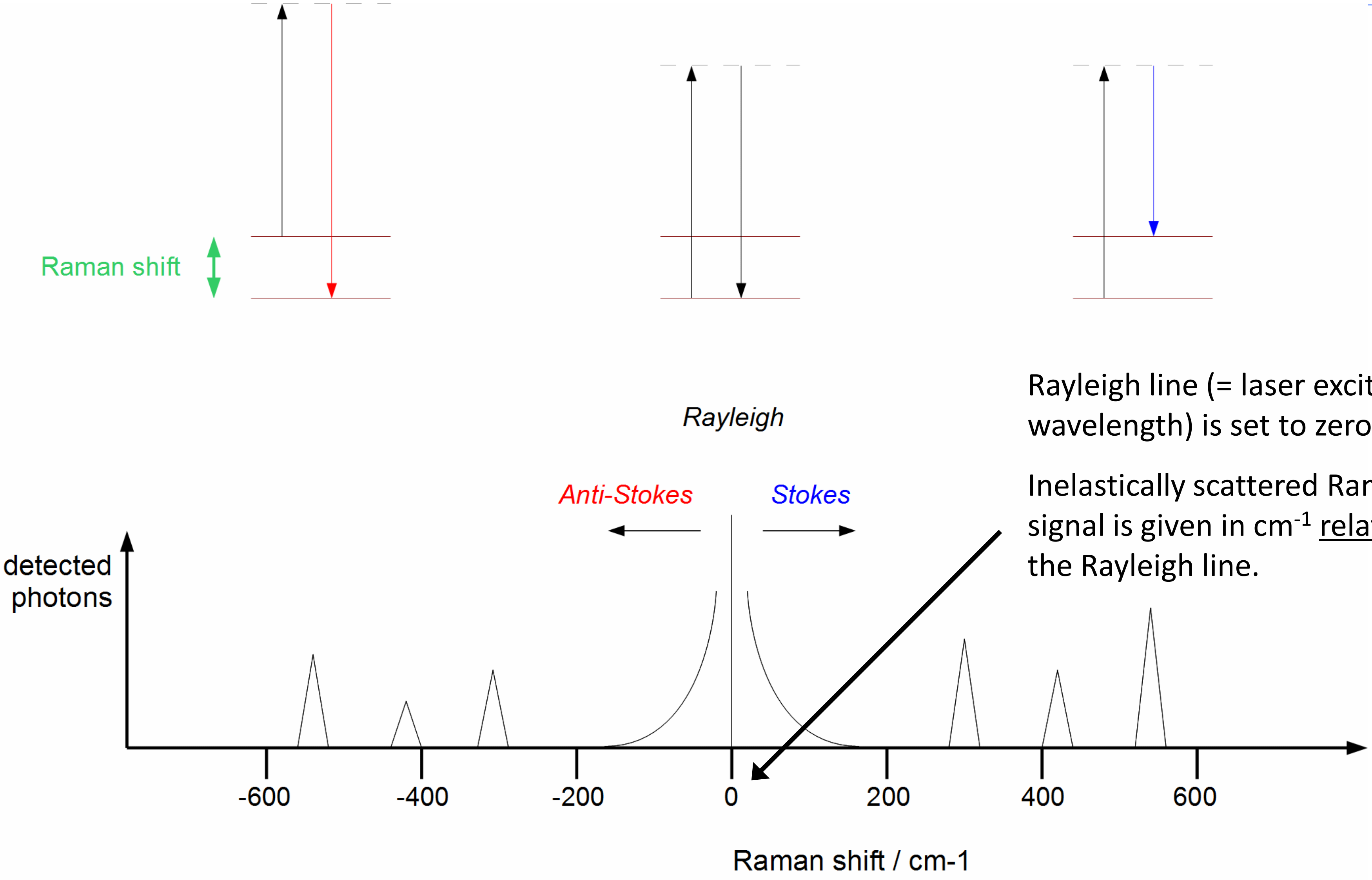


Light interacting with molecules causing several effects at the same time:

1) There are molecules which remain unchanged → Rayleigh Scattering (elastic scattering)

2) There are molecules which are promoted to a higher vibrational energy state → Raman scattering (inelastic scattering). The energy required to do this is taken from the incident light. The light loses energy changing wavelength / colour → Stokes Raman effect

Raman Spectrum



Rayleigh line (= laser excitation wavelength) is set to zero.

Inelastically scattered Raman signal is given in cm^{-1} relative to the Rayleigh line.

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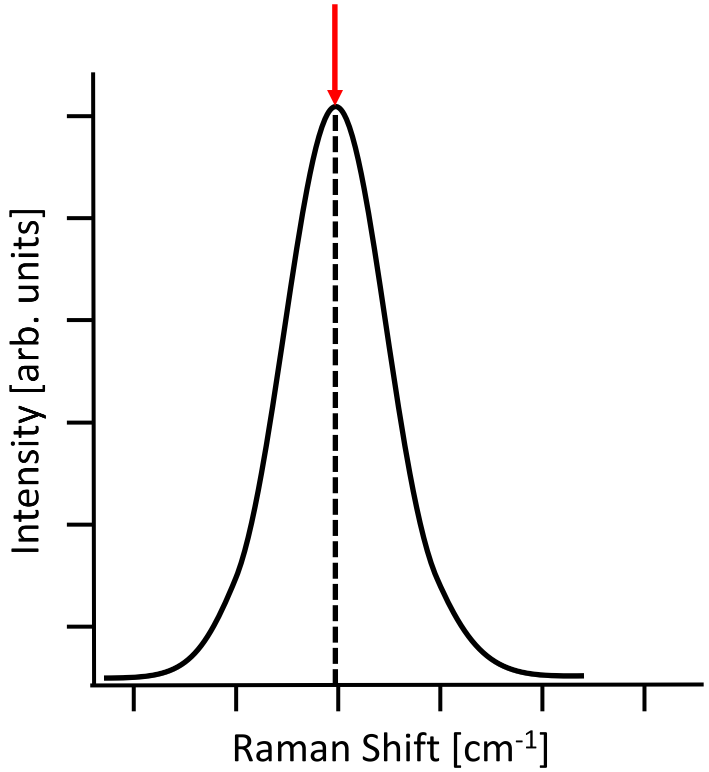
Raman Information

- Chemical Identity
- Crystal Phases (Polymorphism)

Peak Position

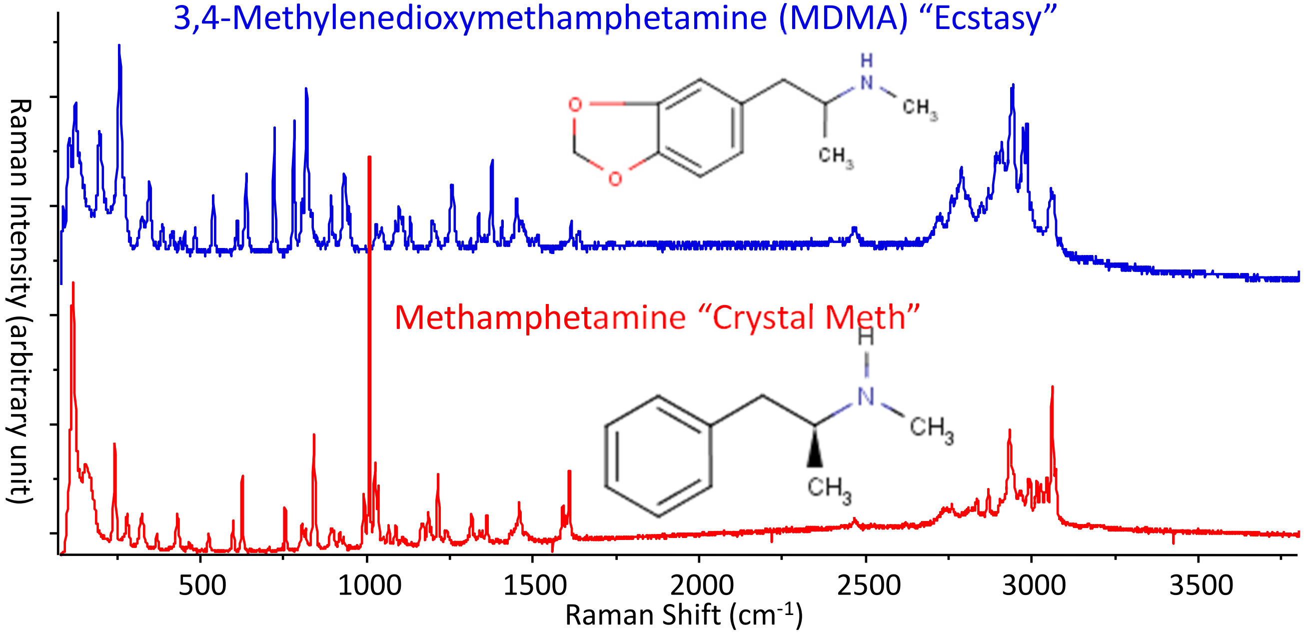


Raman Information

- Chemical Identity
- Crystal Phases (Polymorphism)

Peak Position

Chemical Identification of Similar Structures

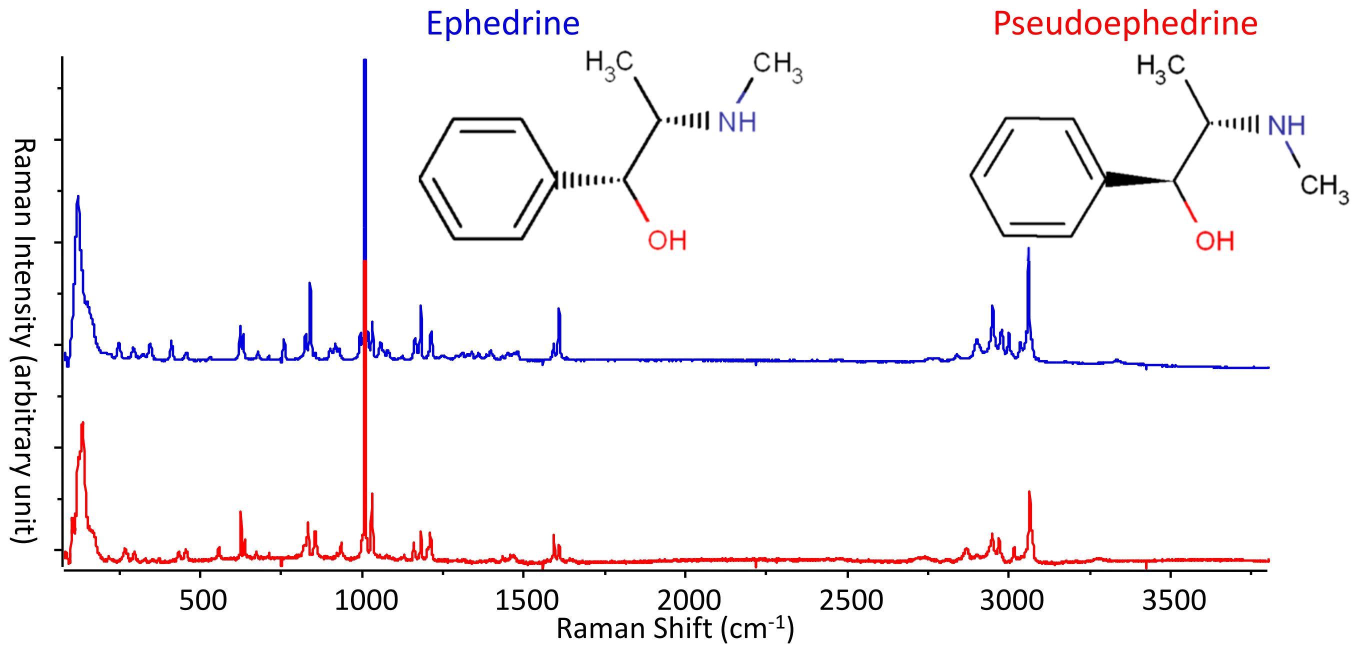


Raman Information

- Chemical Identity
- Crystal Phases (Polymorphism)

Peak Position

Chemical Identification of Diastereomeres

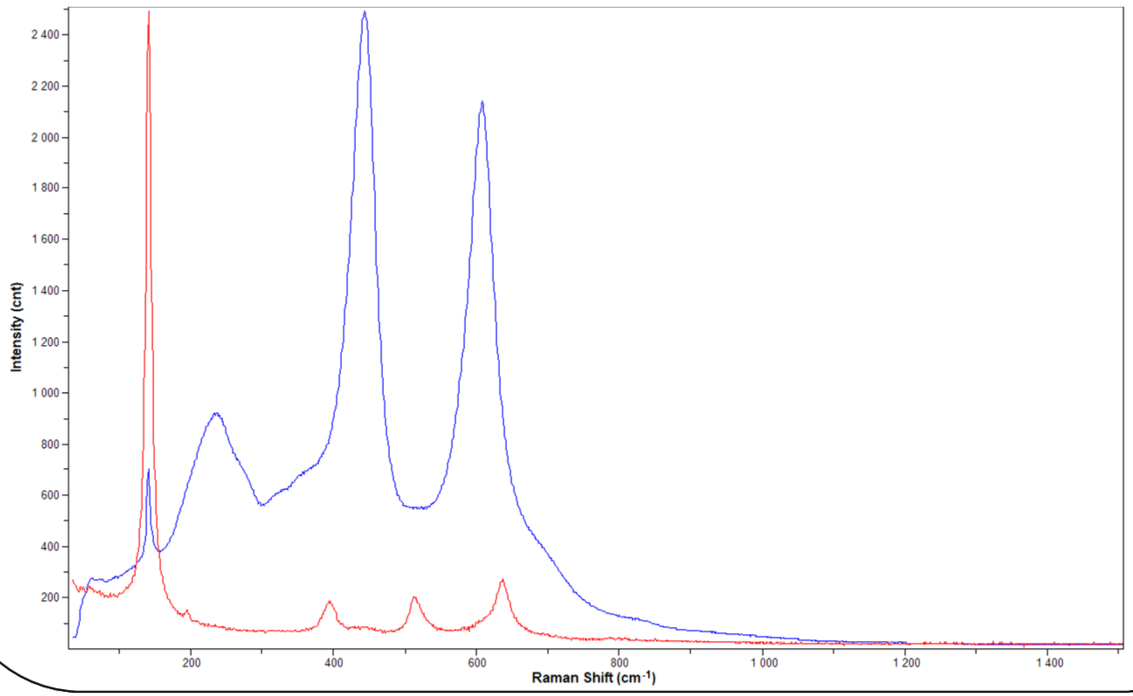


Raman Information

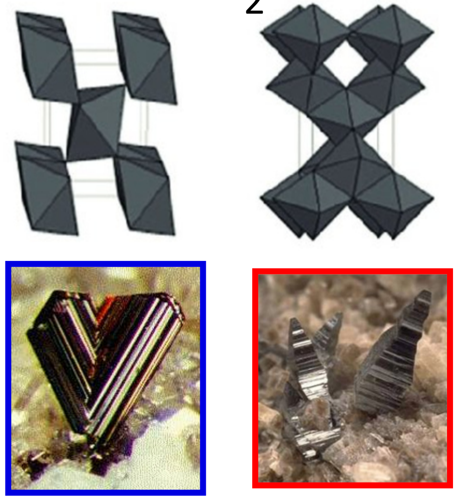
- Chemical Identity
- Crystal Phases (Polymorphism)

← Peak Position

Chemical Identification of Polymorphs



TiO_2



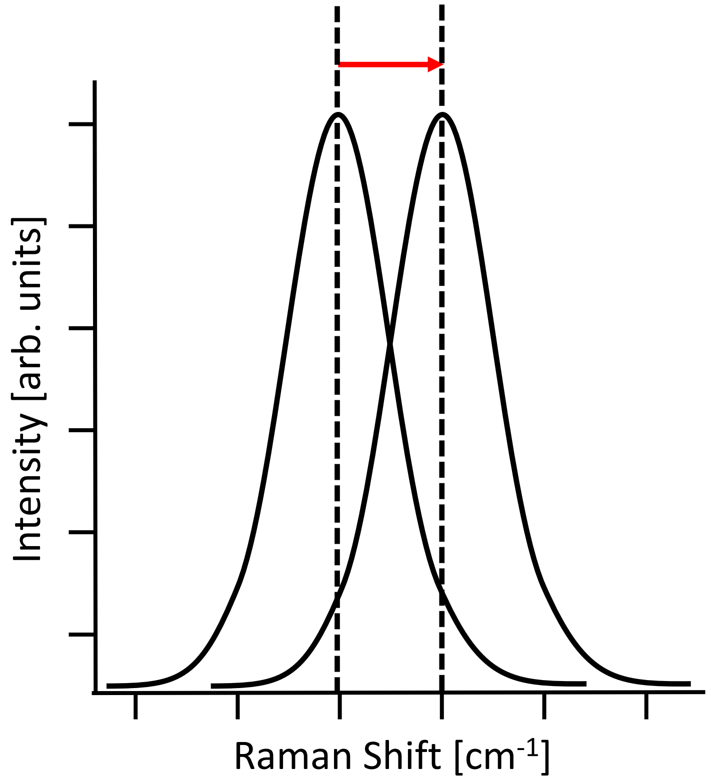
Rutile   Anatase

- Identical chemical composition
- Different crystalline structure

Raman Information

- Strain, Stresses
- Temperature

← Peak Shift

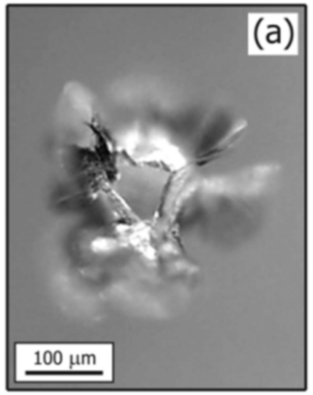


Raman Information

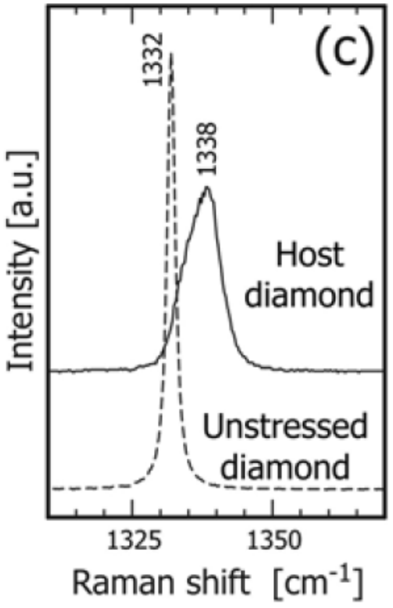
- Strain, Stresses
- Temperature

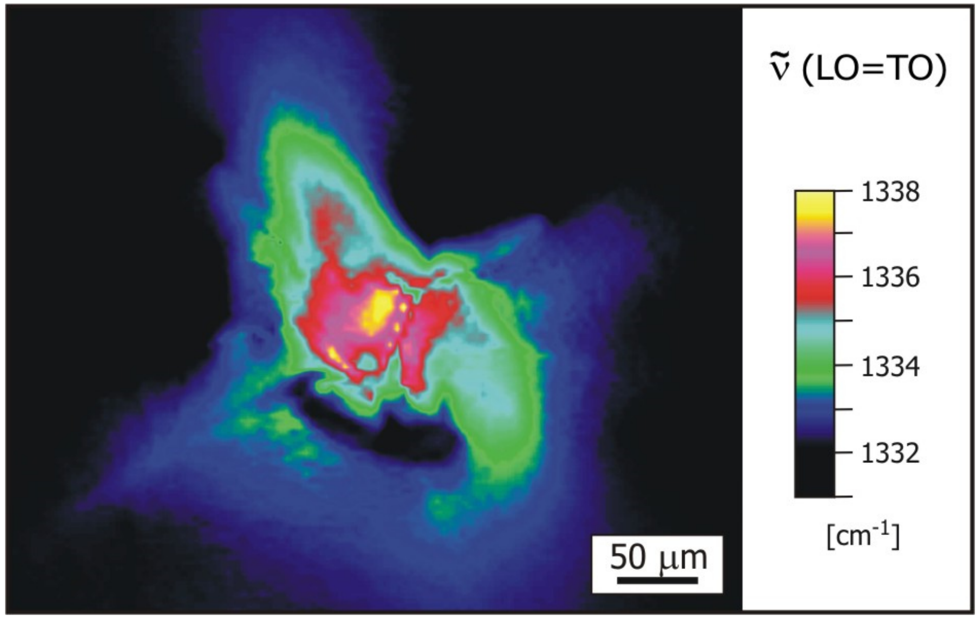
← Peak Shift

Associated pressures mapped around diamond inclusion



Strain induced up-shift of diamond band indicate pressures up to 2.7 GPa

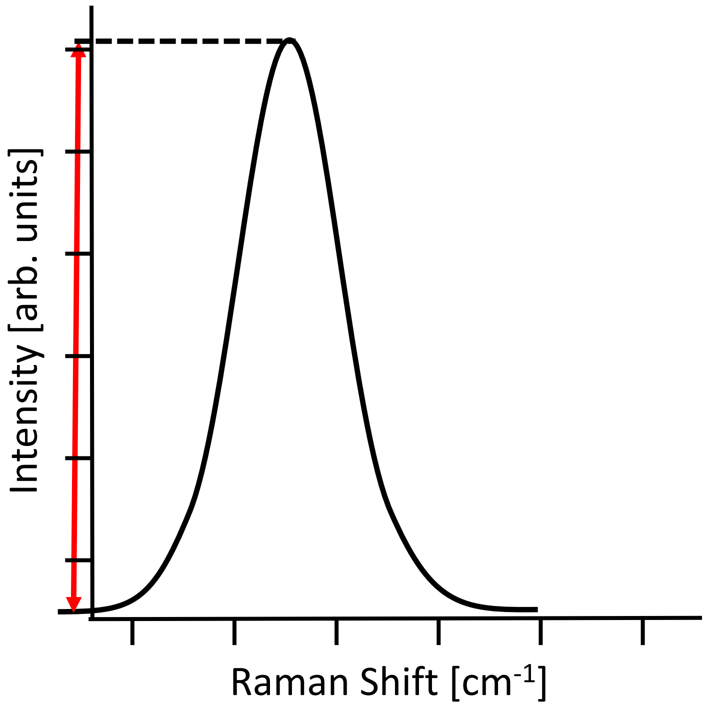




Nasdala, L., Harris, J.W., Hofmeister, W., Micro-spectroscopy of diamond. Asia Oceania Geosciences Society, 4th Annual Meeting, 2007.
Nasdala, L., Raman barometry of mineral inclusions in diamond crystals. Mitt. Österr. Miner. Ges. 149 (2004)

Raman Information

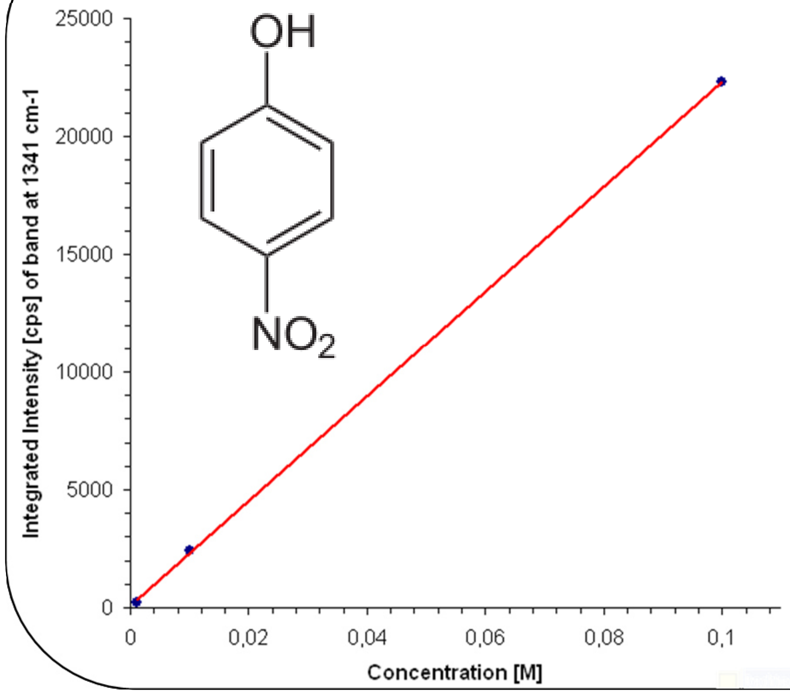
- Concentration ⟵ Peak Intensity

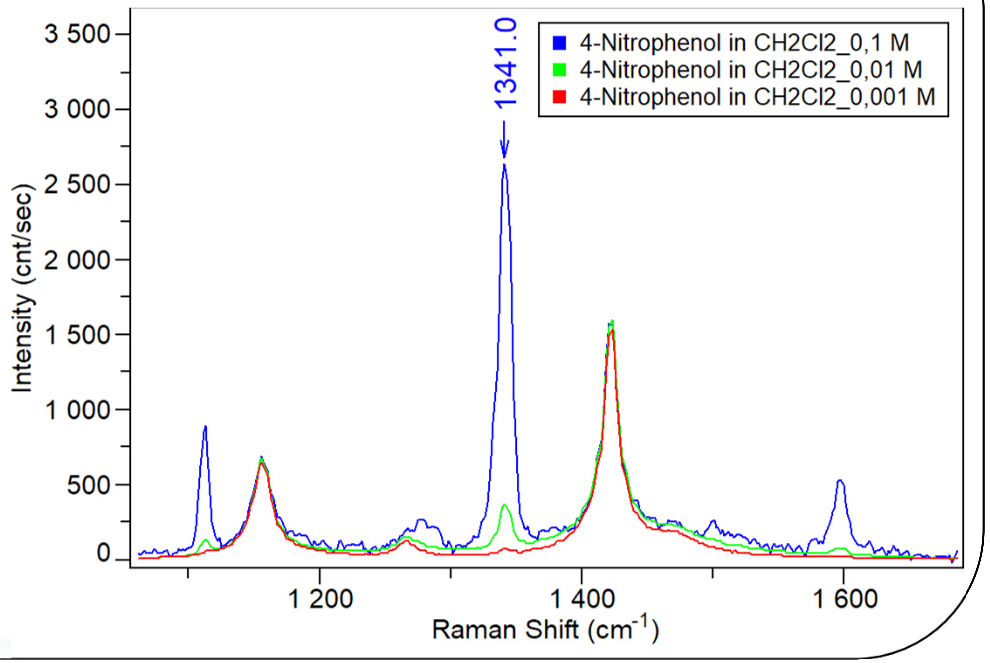


Raman Information

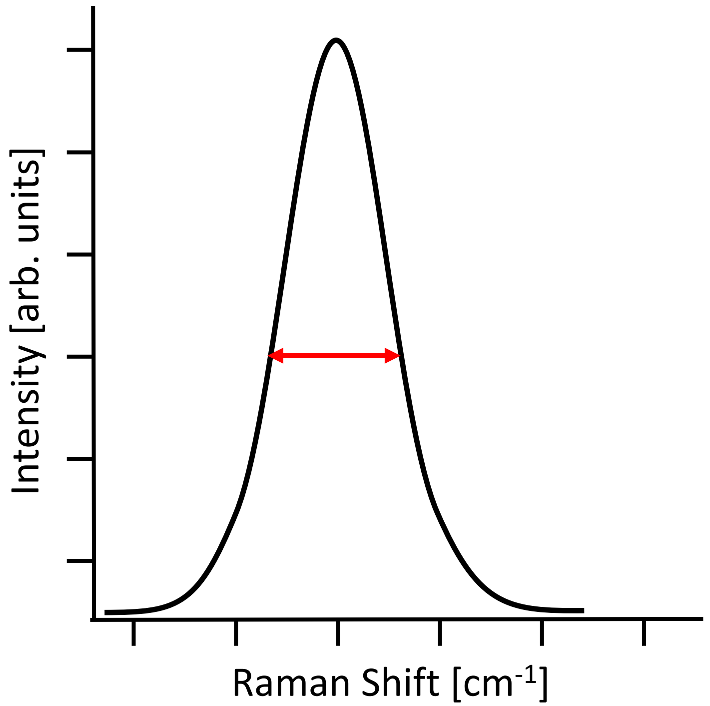
- Concentration ⟵ Peak Intensity

4-Nitrophenol dissolved in Dichlormethane CH_2Cl_2





Raman Information



- Structural Order/Disorder
- Crystallinity

Peak Width

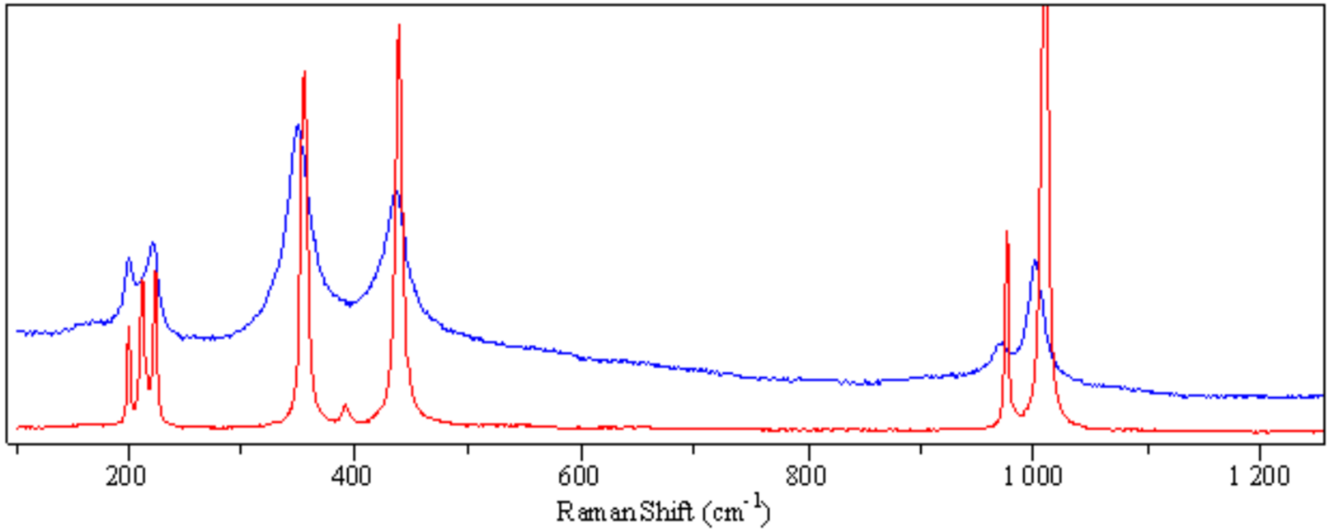
Raman Information

Raman Information

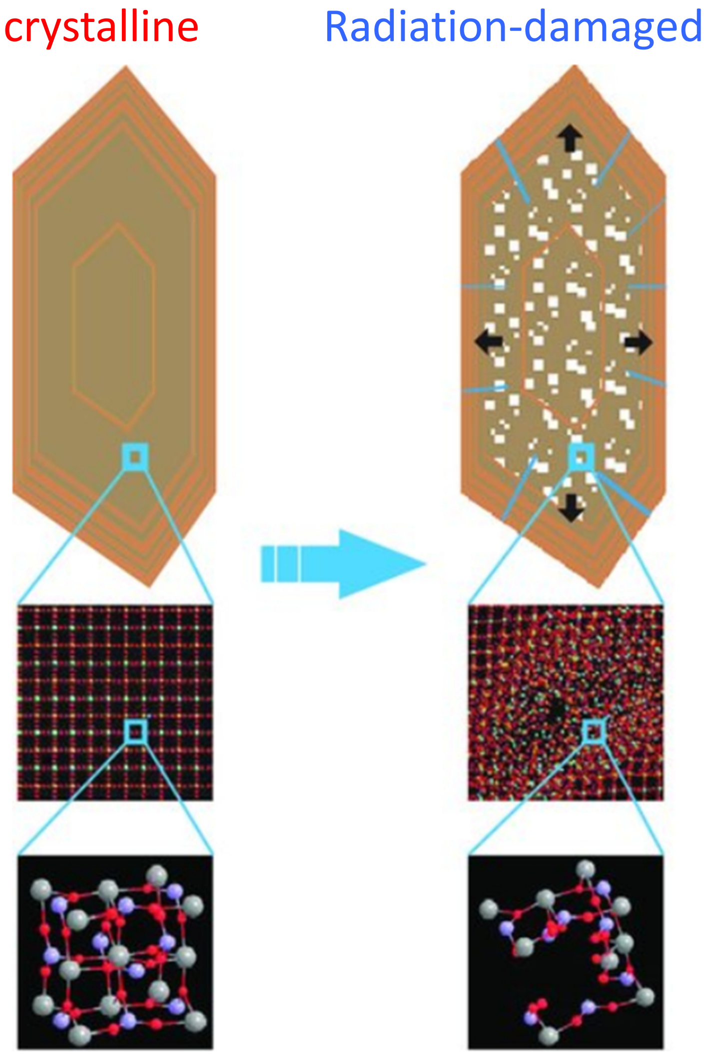
- Structural Order / Disorder
- Crystallinity

← Peak Width

Spectra of crystalline and radiation-damaged zircon



Radiation-damaged zircon (blue)
crystalline zircon (red)



Xu et al. (2012): Reverse age zonation of zircon formed by metamictisation and hydrothermal fluid leaching; Lithos 150:256-267

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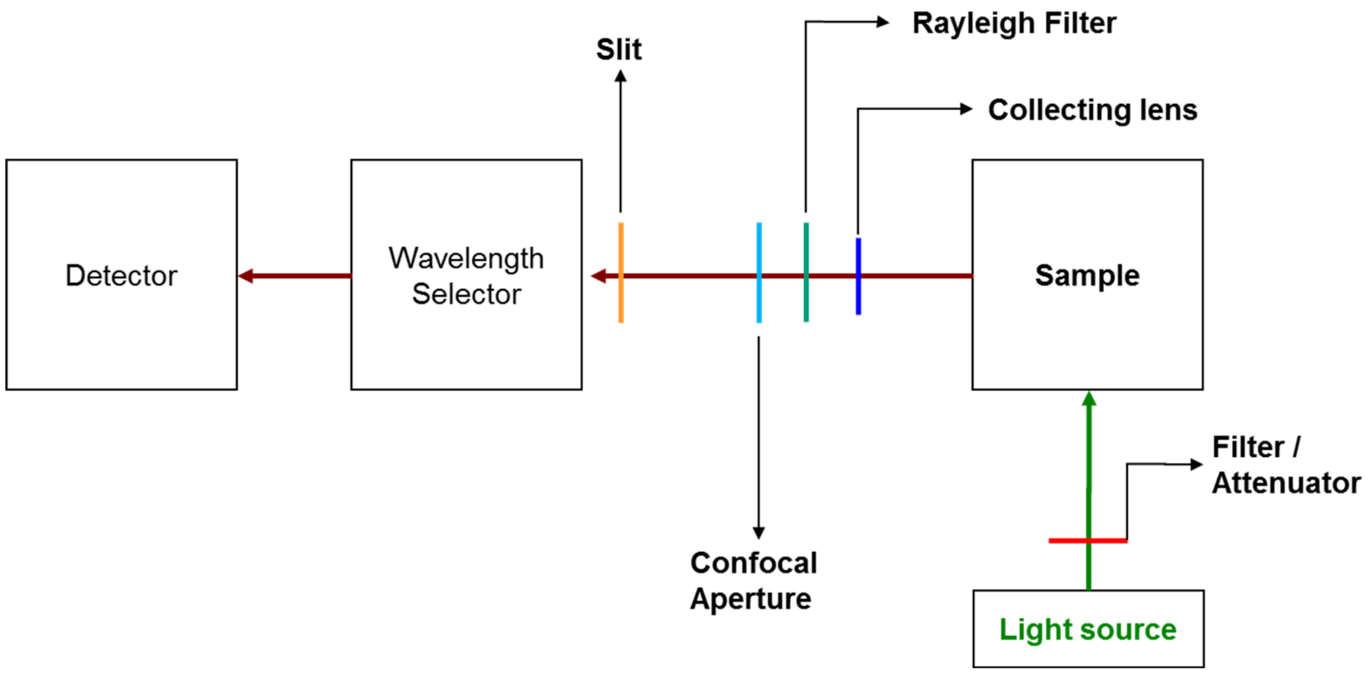
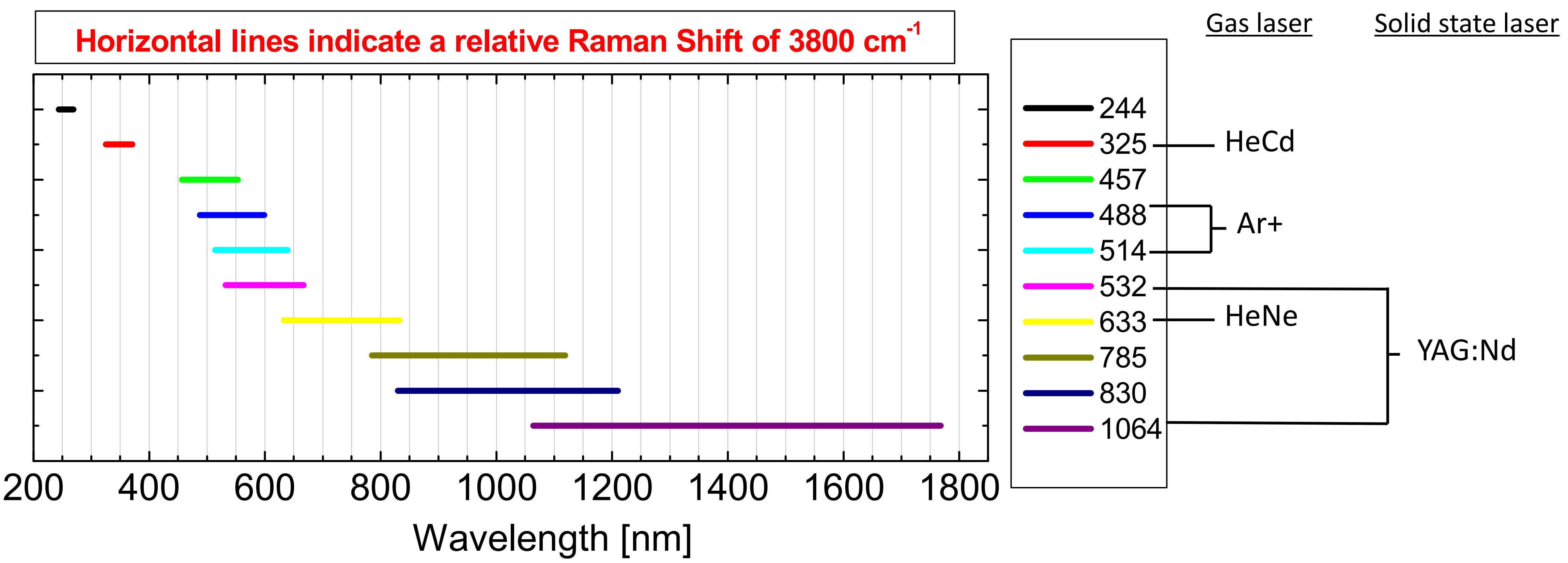


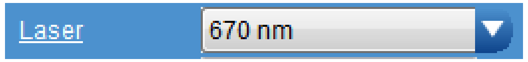
Laser source

Laser 670 nm

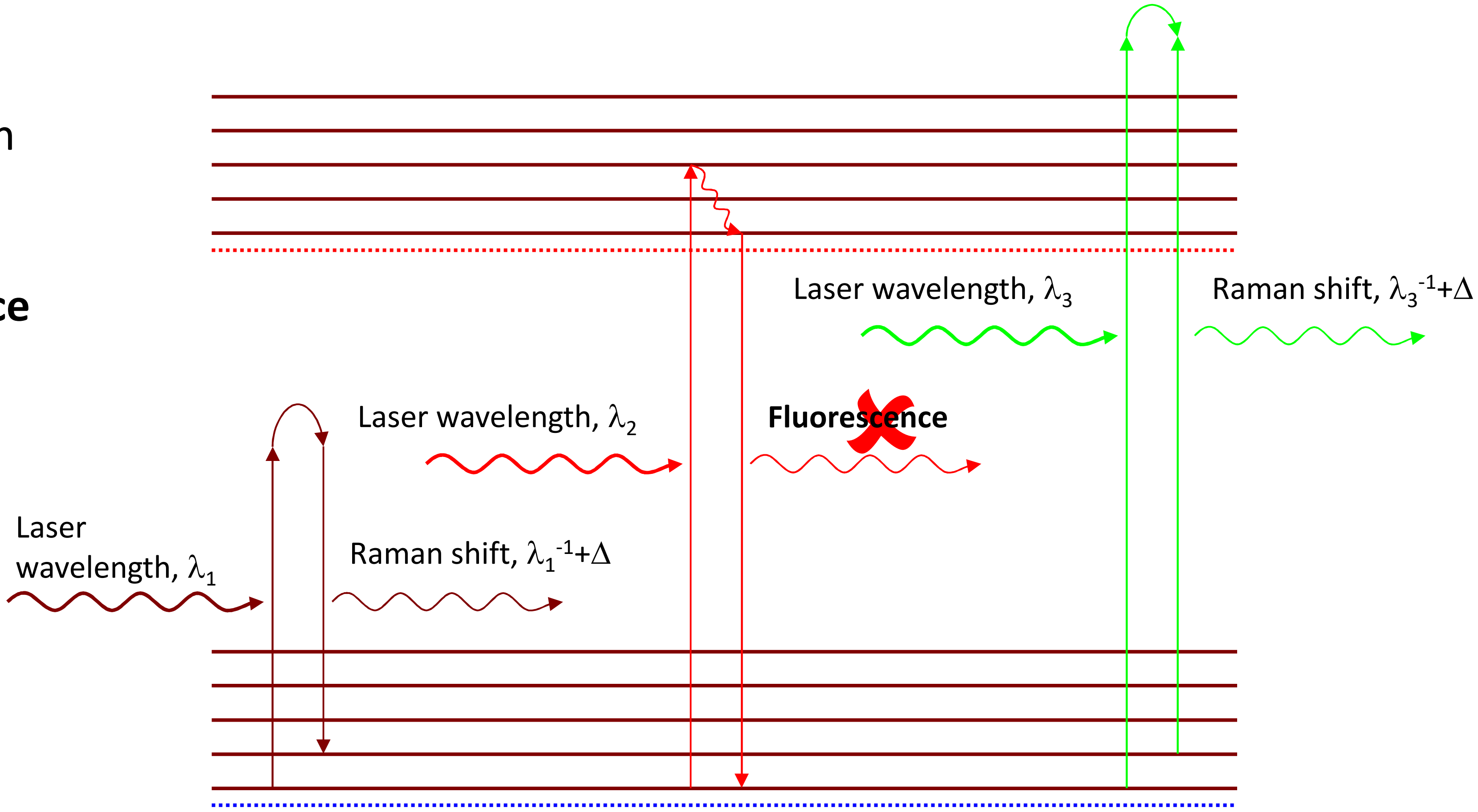


Possible wavelengths are 227, 244, 257, 325, 364, 413, 442, 457, 473, 488, 514, 532, 633, 647, 660, 785, 830, 1064 nm.

Laser source



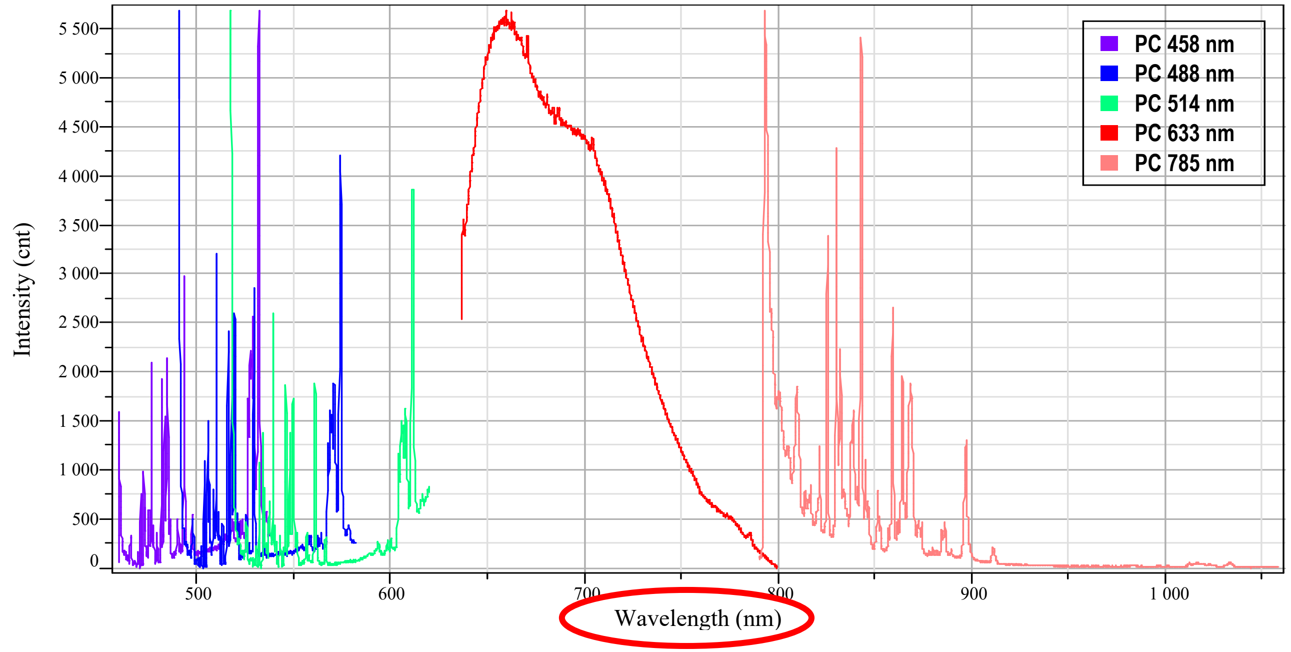
The most important reason for changing the excitation wavelength is to **avoid luminescence/fluorescence**



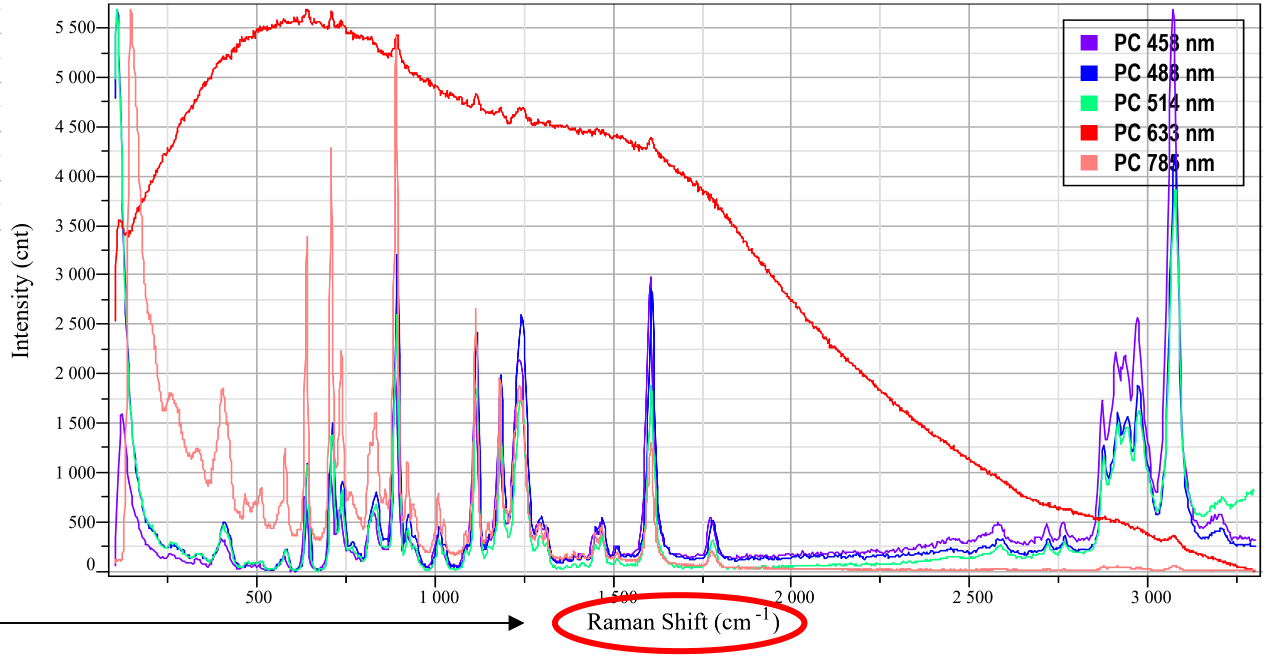
Laser wavelength: $\lambda_1 < \lambda_2 < \lambda_3$

Laser source

Laser 670 nm



Polycarbonat spectra at different excitation wavelengths



Fluorescence is wavelength dependent

Ordinary Raman is wavelength independent

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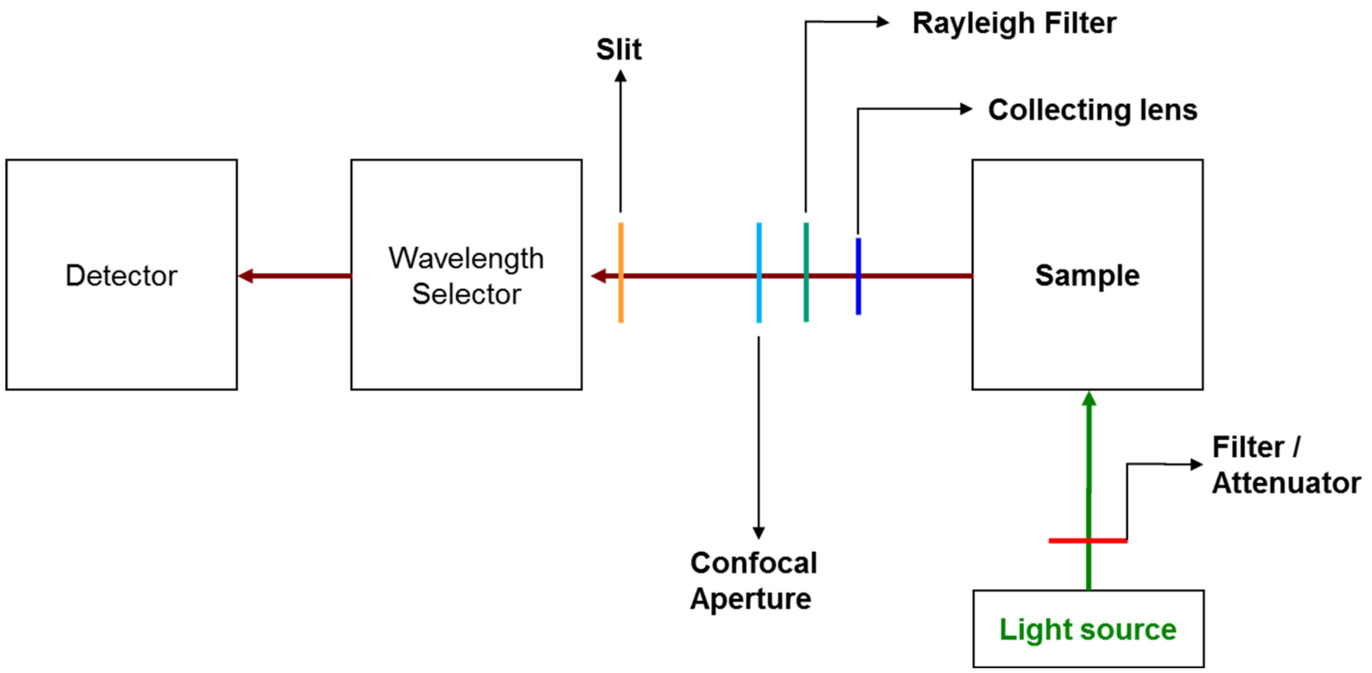
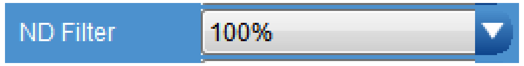


Filter



- Keep in mind: the usage of high numerical objective lenses causes a very small spot size of the laser which results in a high power density
- To avoid sample burning radiation power has to be adapted INDIVIDUALLY to the sample

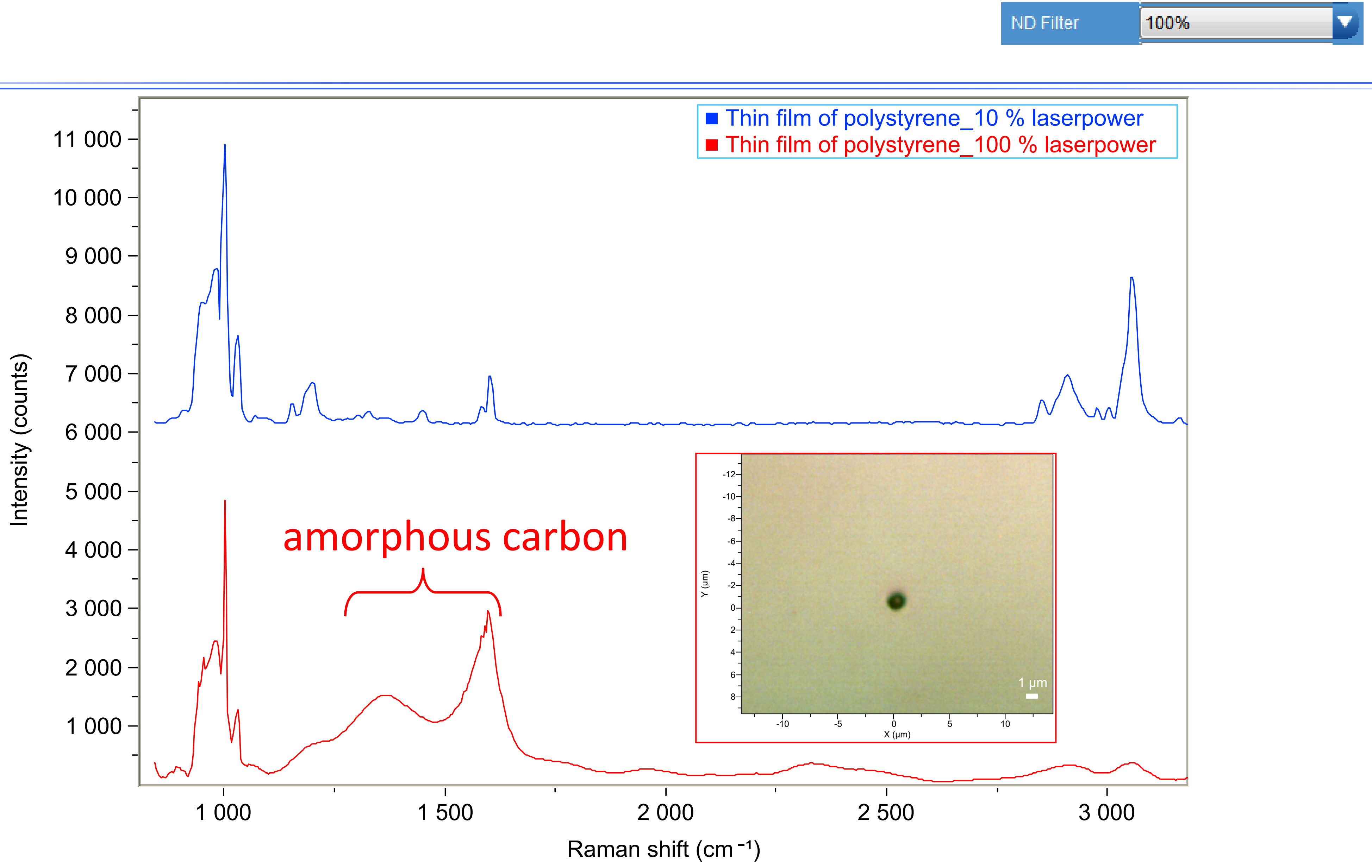
Laser wavelength: 473 nm
Laser power at sample: 25.5 mW

Objective	N.A.	Laser spot size (µm)	**Radiation power (kW/cm²)**
100×	0.90	0.64	**~7900**
50×	0.75	0.77	**~5400**
10×	0.25	2.31	**~600**

Laser wavelength: 633 nm
Laser power at sample: 12.6 mW

Objective	N.A.	Laser spot size (µm)	**Radiation power (kW/cm²)**
100×	0.90	0.85	**~2200**
50×	0.75	1.03	**~1500**
10×	0.25	3.09	**~200**

Filter

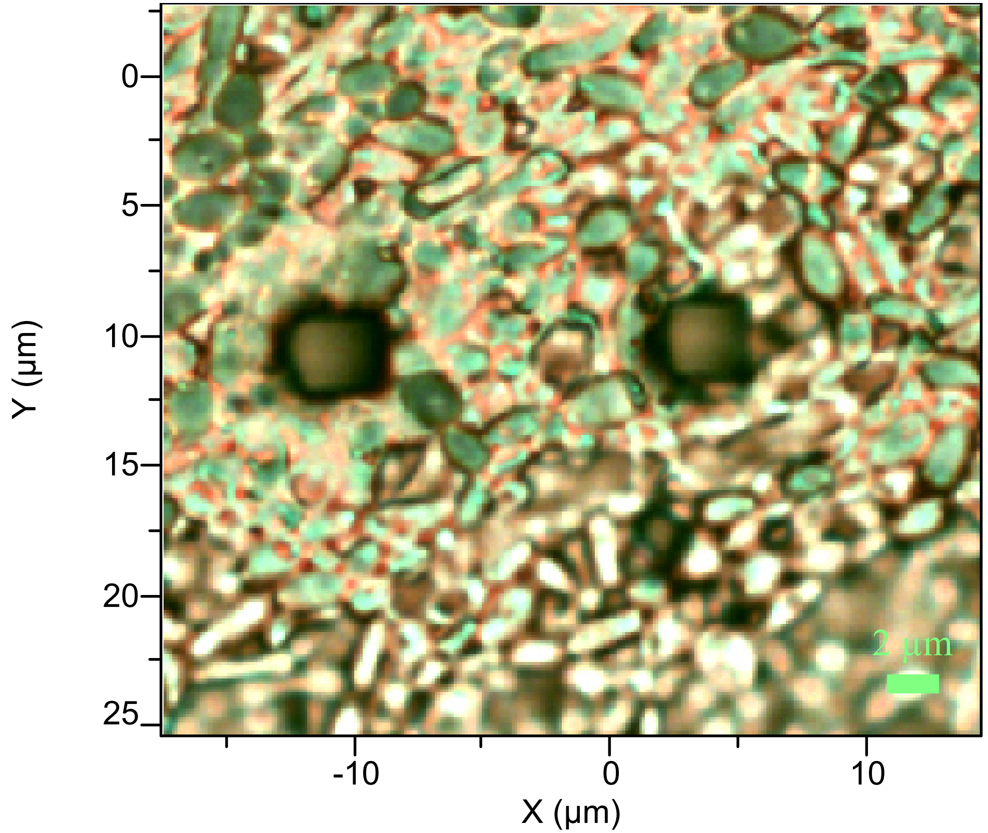


ND Filter
100%
Thin film of polystyrene_10 % laserpower
Thin film of polystyrene_100 % laserpower
amorphous carbon
Intensity (counts)
11 000
10 000
9 000
8 000
7 000
6 000
5 000
4 000
3 000
2 000
1 000
1 000
1 500
2 000
2 500
3 000
Raman shift (cm⁻¹)
Y (µm)
X (µm)
1 µm

Filter

ND Filter 100%

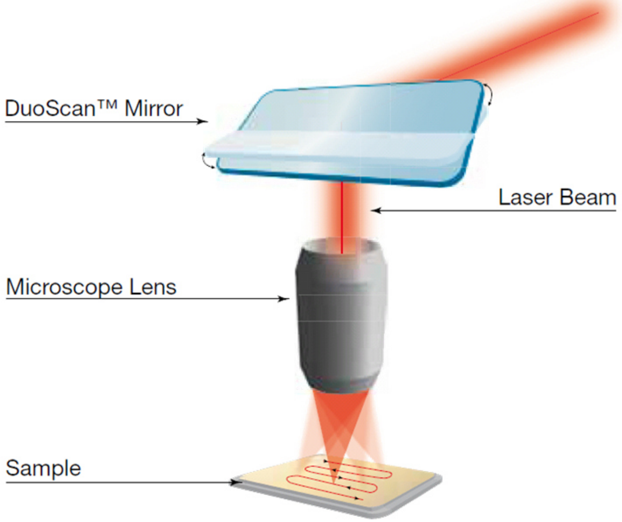
Candida Tropicalis after laser radiation with too much power



Excitation: 473 nm

Laser power > 1 % (0.16 mW)

DuoScan



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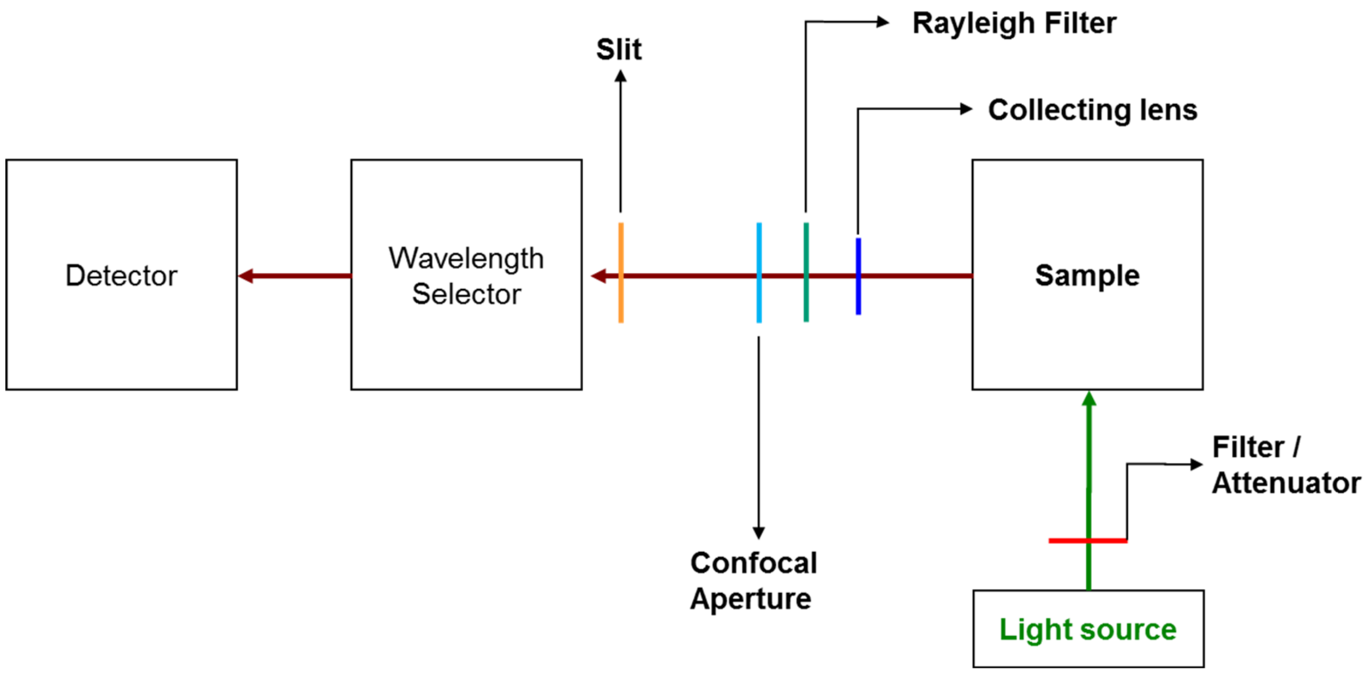
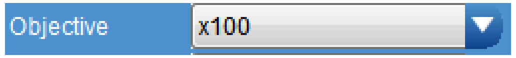
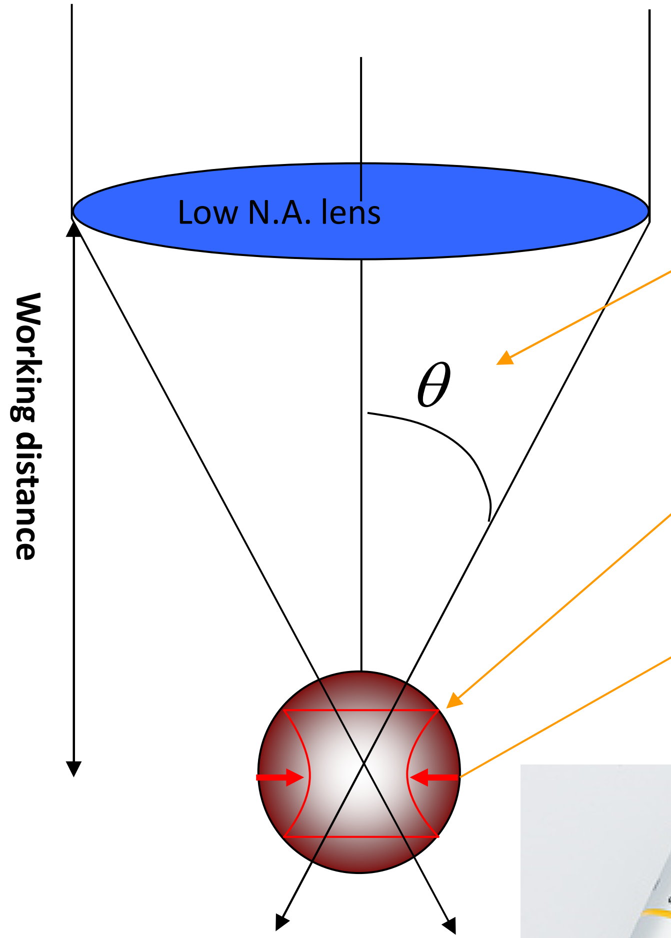


Collecting lens

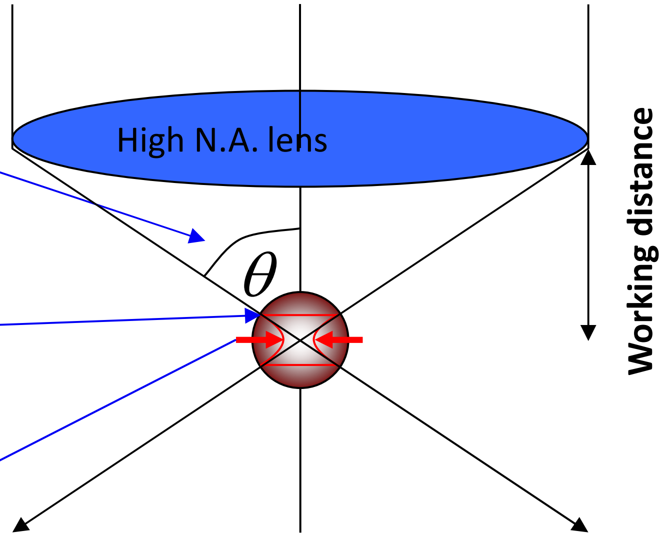




Collection solid angle
Large for high N.A. lens
Small for low N.A. lens

Sampling volume
Small for high N.A. lens
Large for low N.A. lens

Laser spot size
Small for high N.A. lens
Large for low N.A. lens

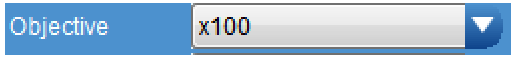


NA = n · sin (Θ)

n: refraction index

Θ: aperture angle

Collecting lens

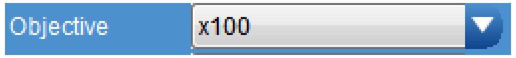






Objective	N.A.	Working distance [mm]
x100	0.90	0.21
x50	0.75	0.38
x10	0.25	10.6
x100 LWD	0.80	3.4
x50 LWD	0.50	10.6

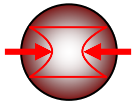
Collecting lens



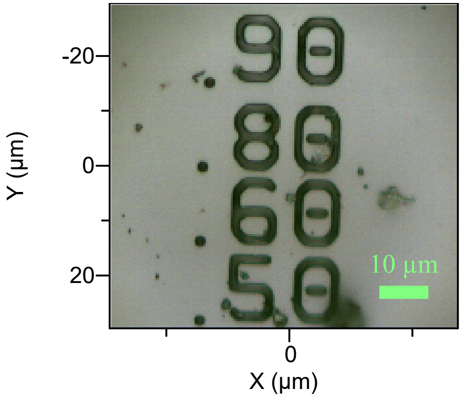
A distinction between opaque and transparent samples must be made

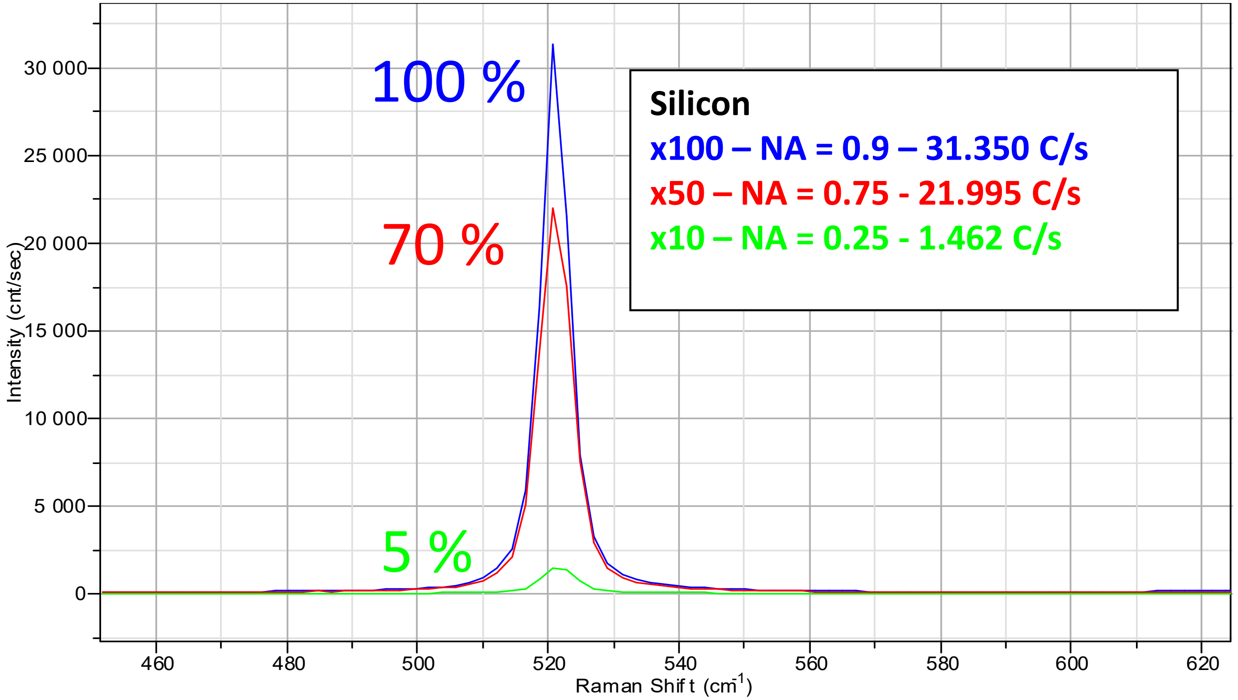
For opaque samples, high N.A. lenses work better because there is almost no penetration of the laser into the sample. High N.A. lenses enable:

- High laser power density (mW/µm^3) → **increases sensitivity**
- Wide collection solid angle → **increases sensitivity**

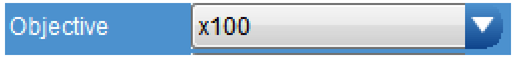


Example for an opaque sample: Silicon wafer





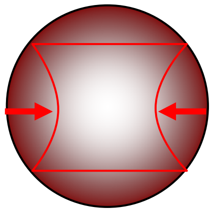
Collecting lens

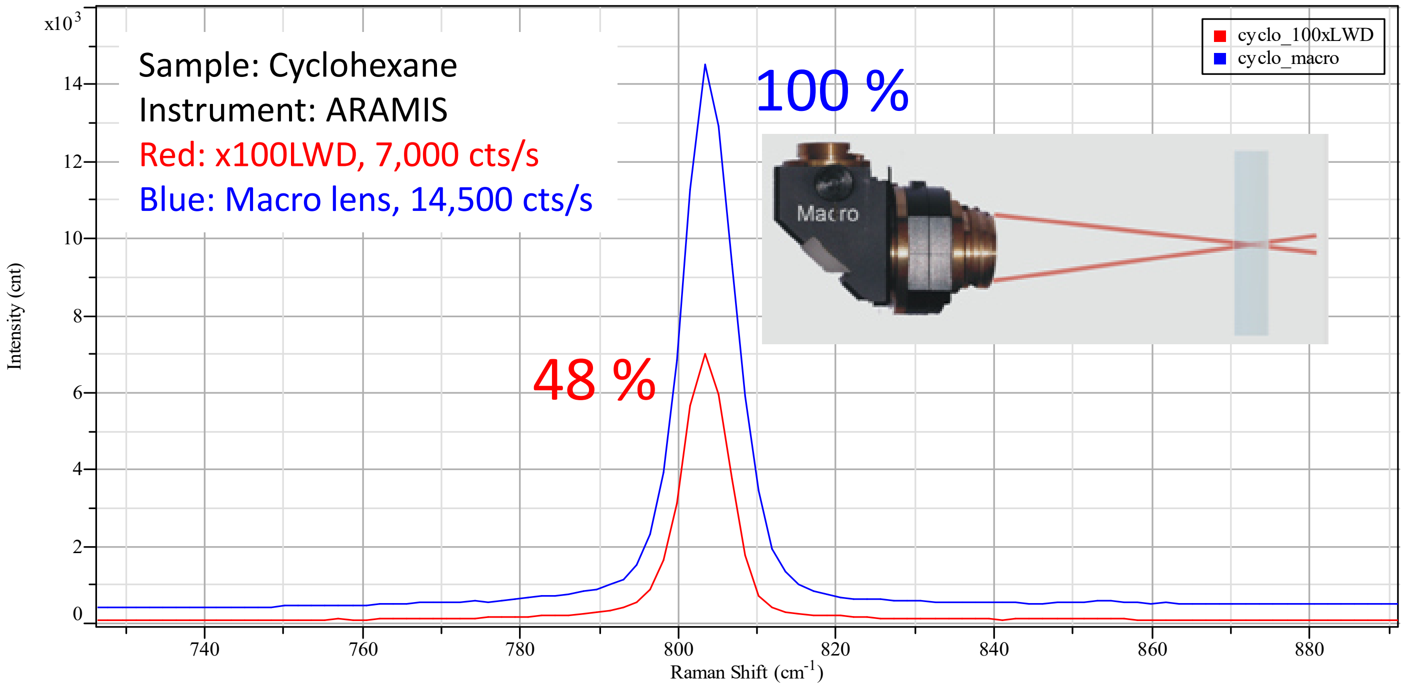


A distinction between opaque and transparent samples must be made

For transparent samples, low N.A. lenses work better because of increased penetration depth of the laser into the sample. Low N.A. lenses enable:

- Large sampling volume → **increases sensitivity**





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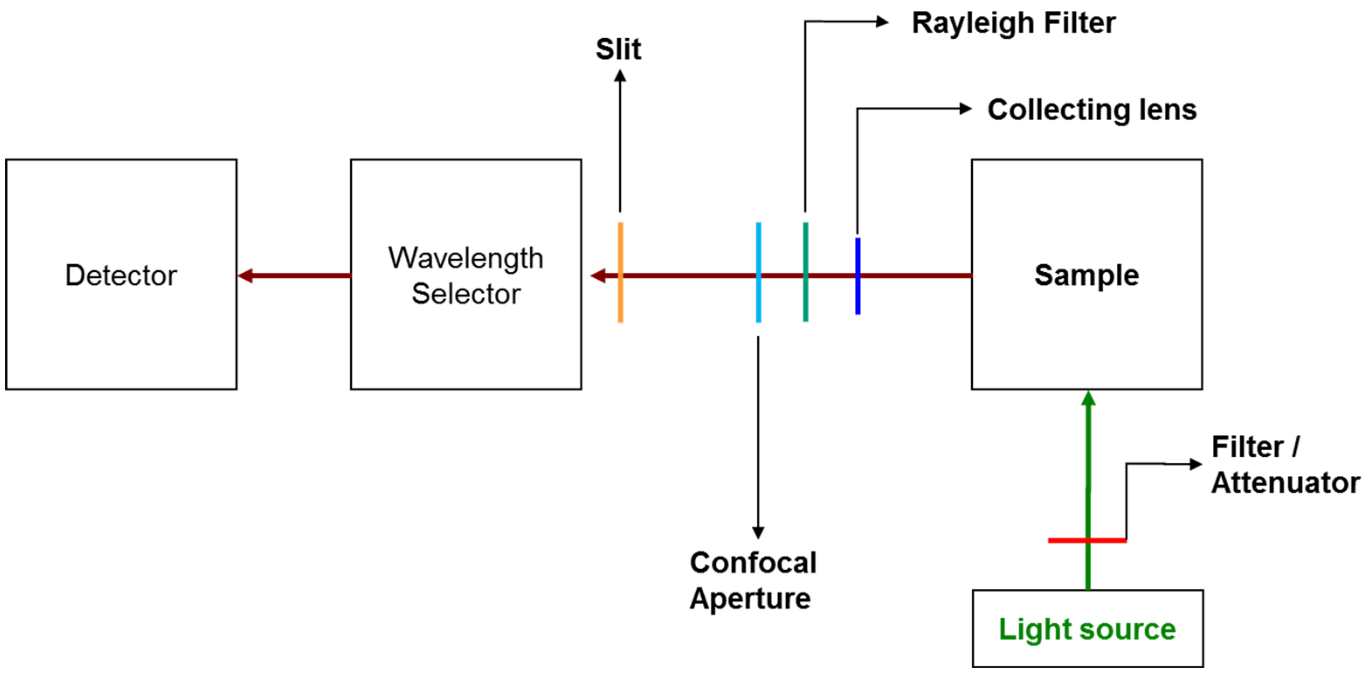
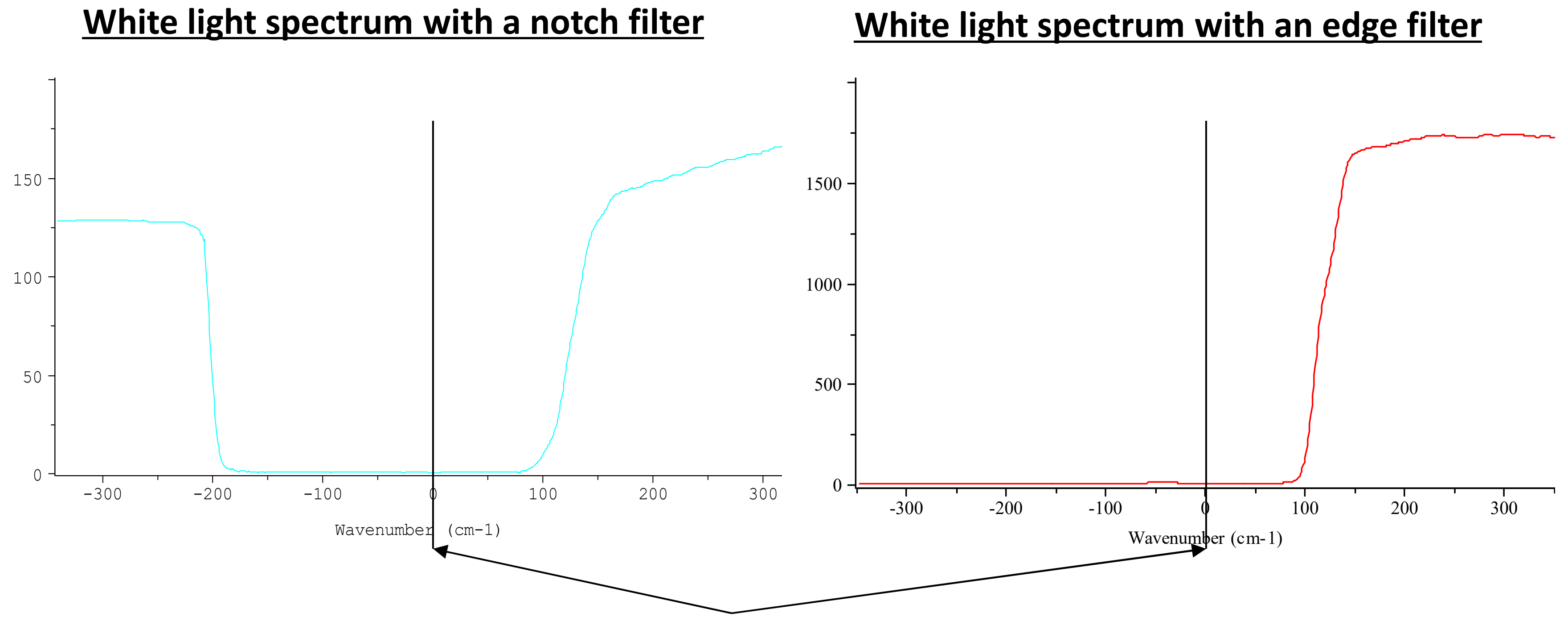


Rayleigh Filter



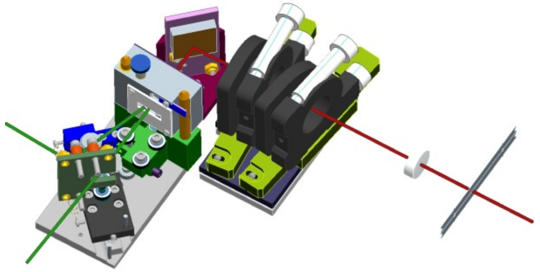
Zero Raman shift → Excitation laser position

- A finite life time
- Stokes and Anti-Stokes Raman

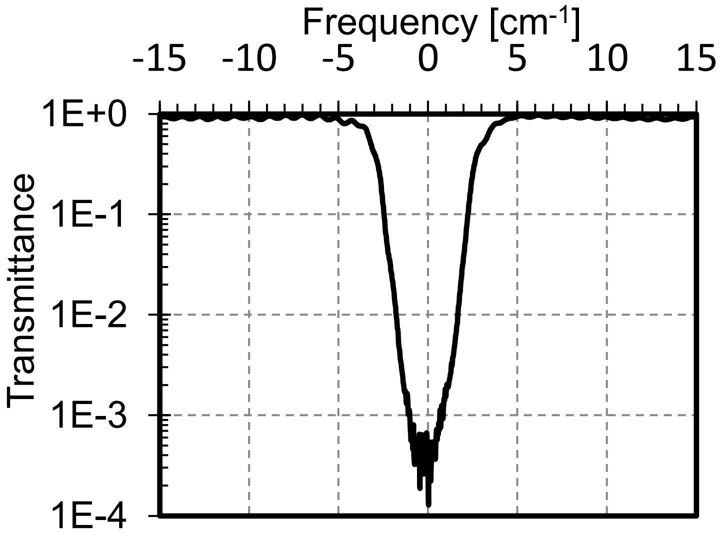
- A virtually infinite life time
- Stokes Raman only

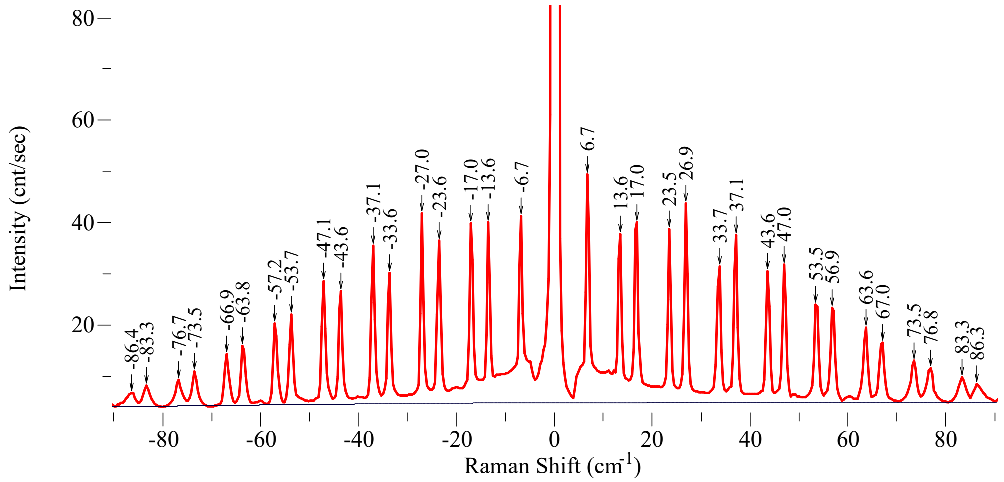
There is a cost advantages to the edge filter due to no aging, but Anti-Stokes-Raman is not obtainable

Rayleigh Filter



ULF (Ultra Low Frequency)





Ultra-Lattice of GeSi

data courtesy of :
P. H. Tan, State Key Laboratory for SL and Microstr., Institute of Semiconductors, Beijing, P. R. China
K. Brunner, University Wurzburg, Germany

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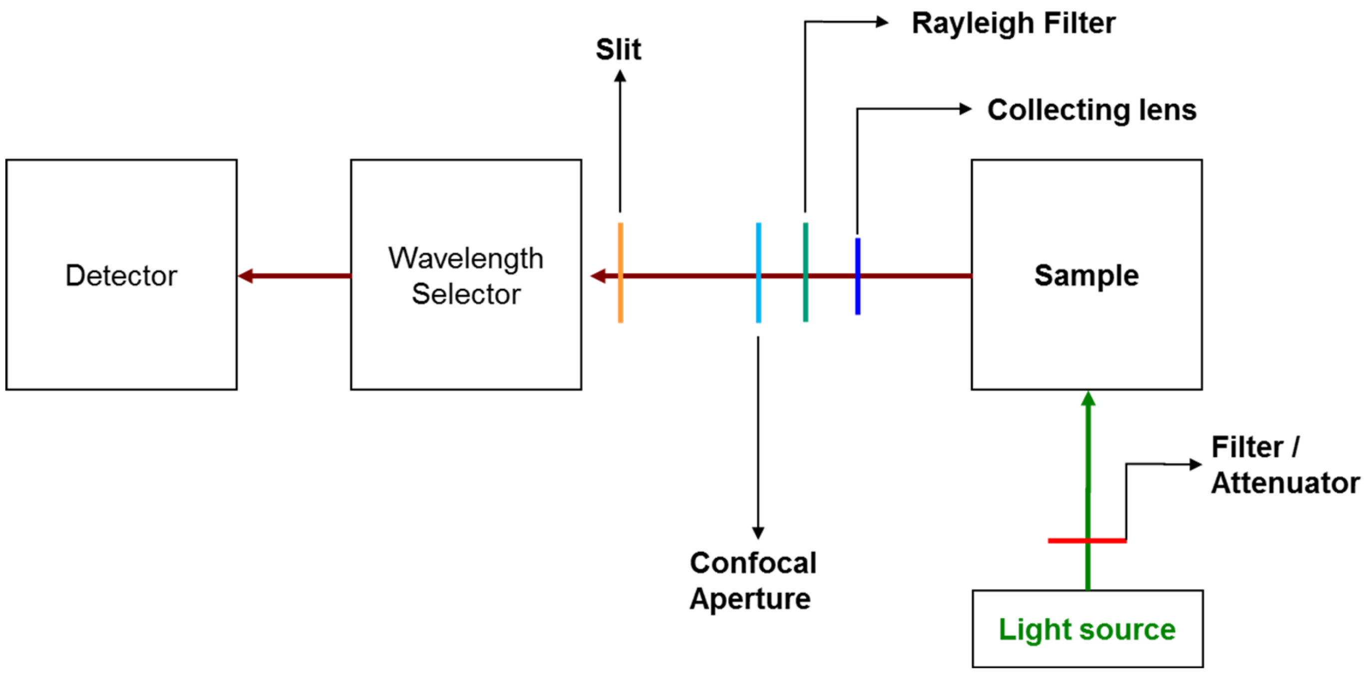
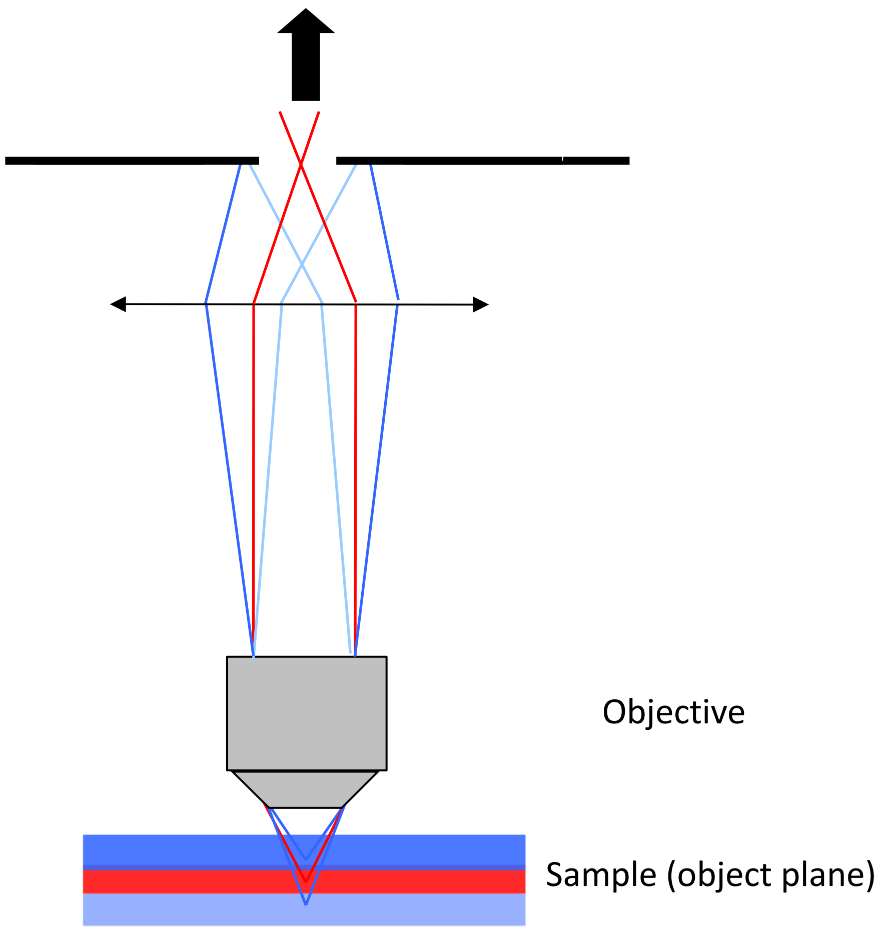
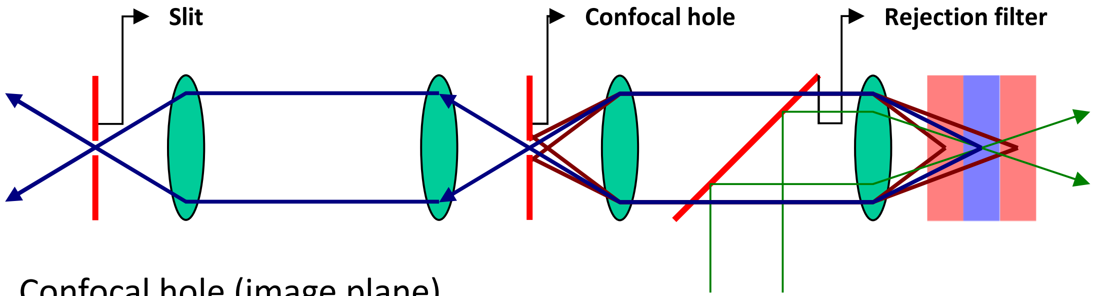


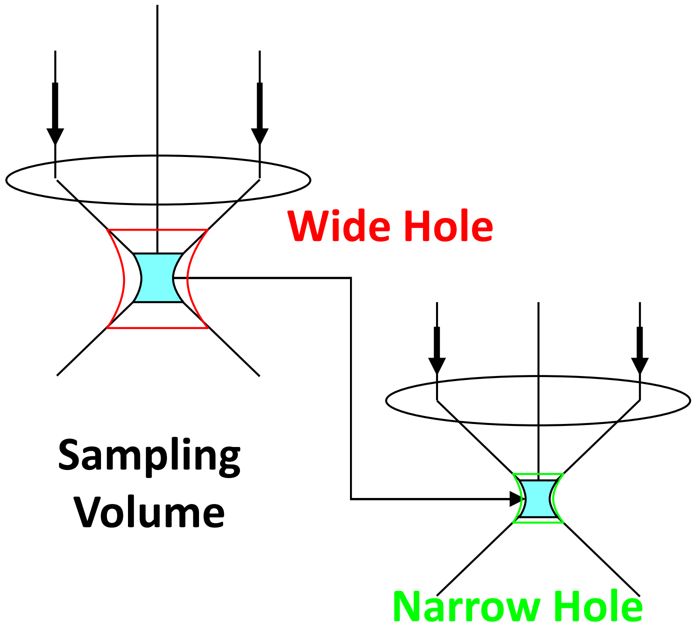
Confocal Aperture

Hole 1000



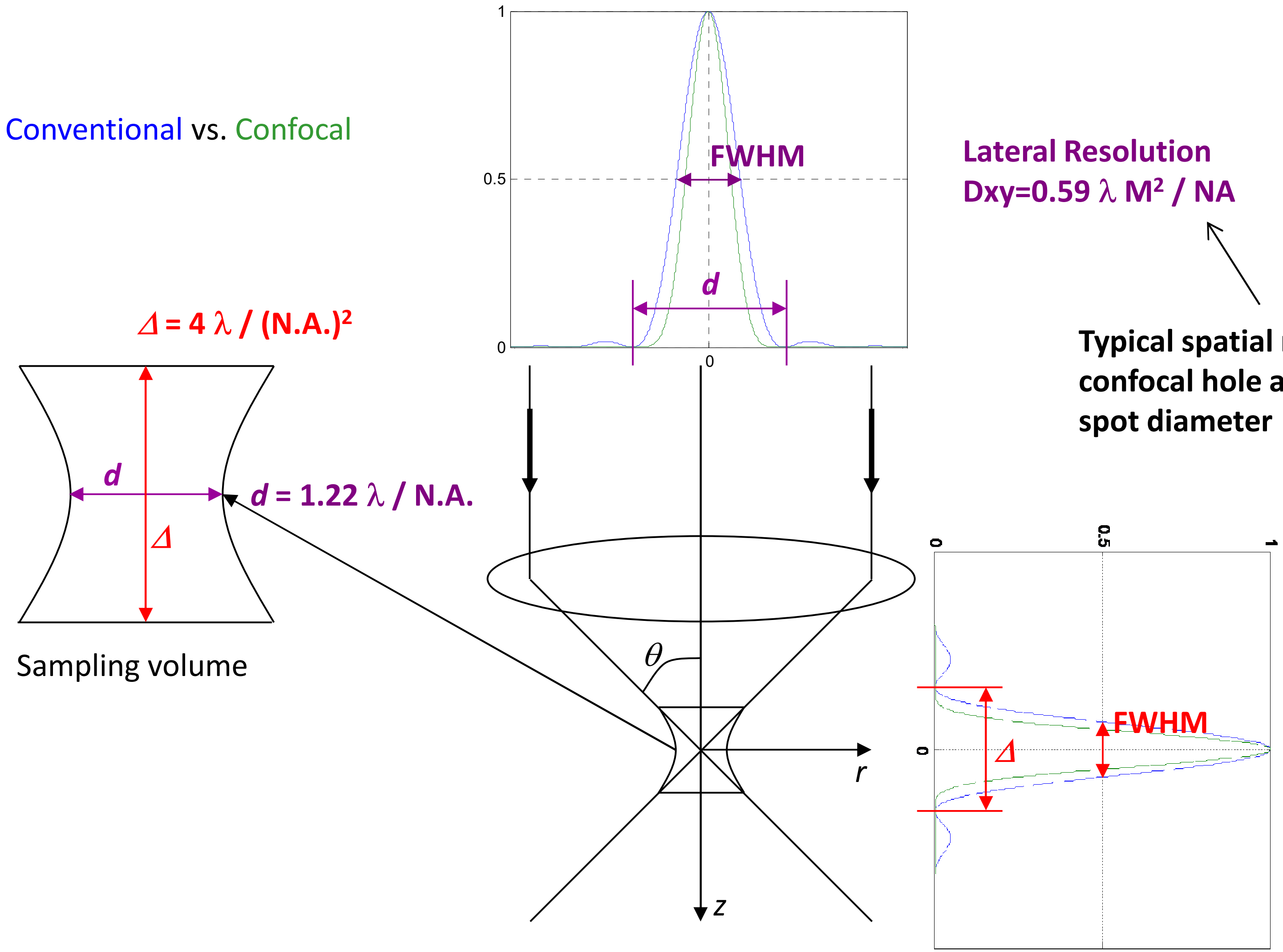


Confocal hole (image plane)



Confocal Aperture

Hole 1000



Lateral Resolution
Dxy=0.59 λ M² / NA

Typical spatial resolution, if the confocal hole aperture fits with the spot diameter

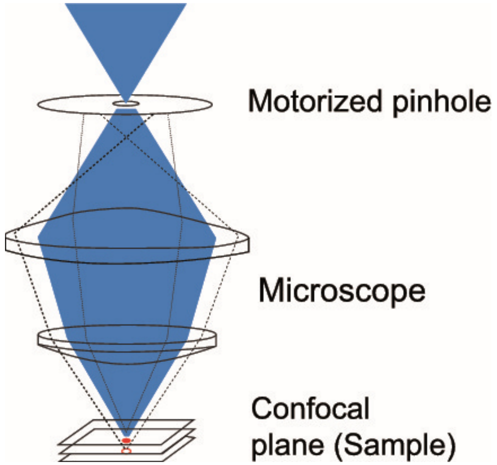
$$D_Z = \frac{0.88\lambda M^2}{n - \sqrt{n^2 - NA^2}}$$

Confocal Aperture

Theoretical limits in spatial resolution

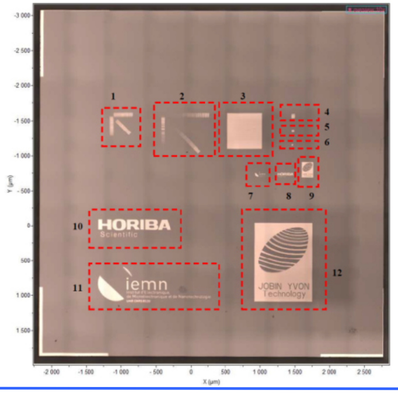
	D_{xy} (µm)	D_z (µm)
473	0,3	0,9
532	0,4	1,0
633	0,5	1,2
785	0,6	1,5

With 100x/0,9 objective, in air, and M^2=1.1

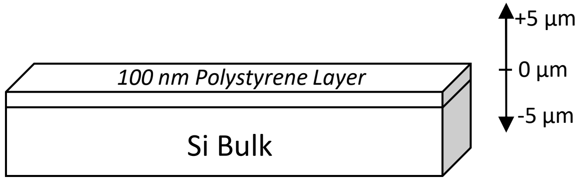


Experimental determined limits in spatial resolution done with 532 nm laser & x100 dry air objective

For lateral resolution: sample from IEMN laboratory 40 nm gold on Si 1:1:1

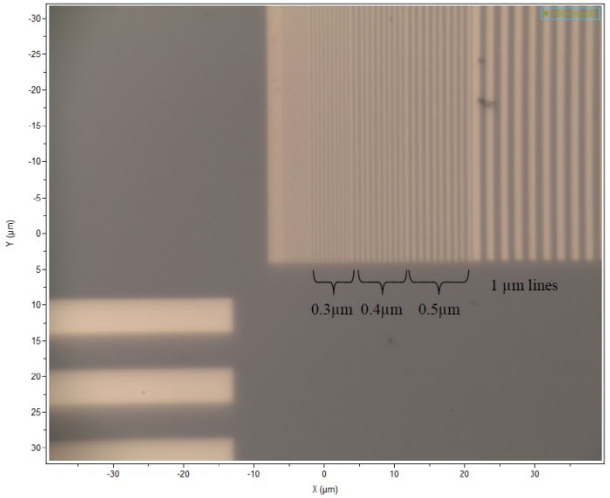


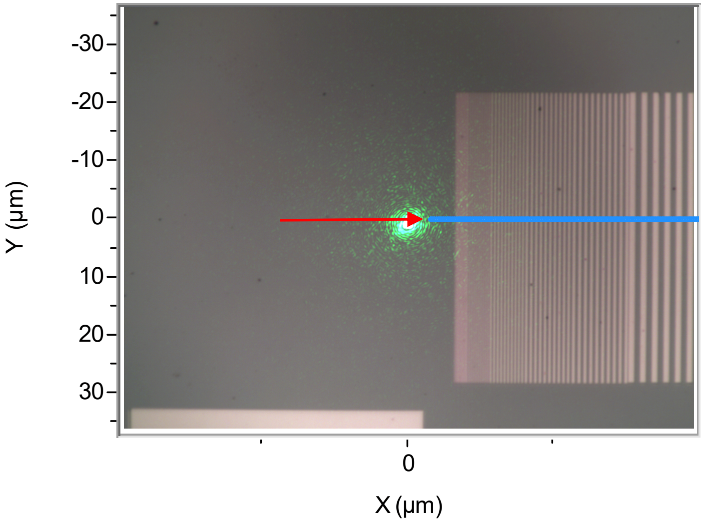
For axial resolution: 100 nm PS layer on Si 1:1:1



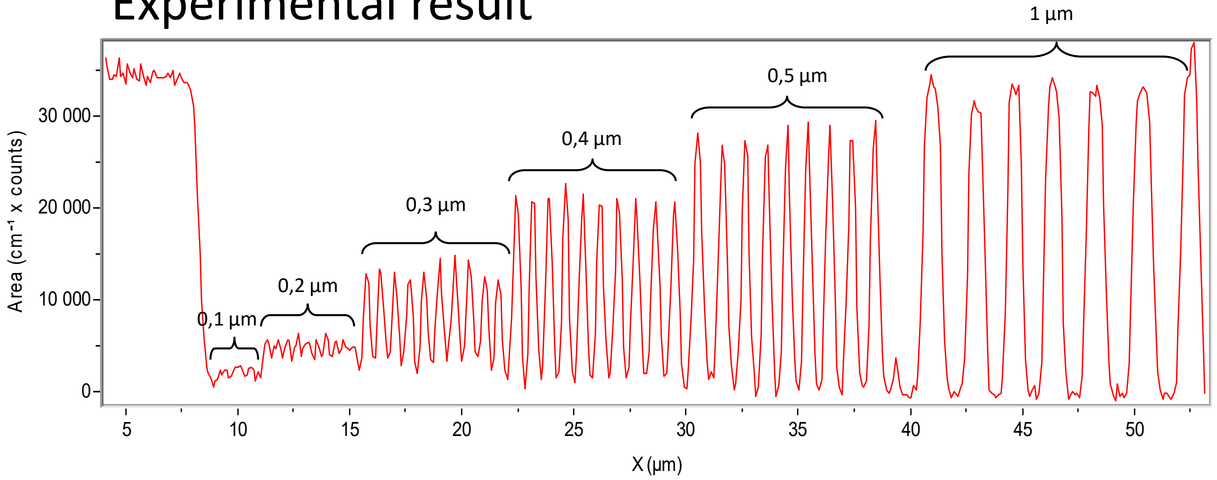
Confocal Aperture

Lateral resolution:
Line scan over gold pattern (40 nm height) with varying distance





Experimental result

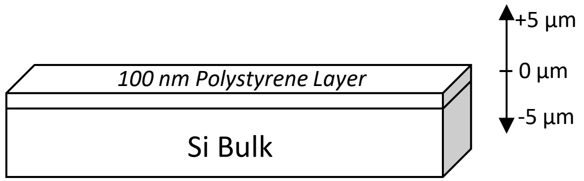


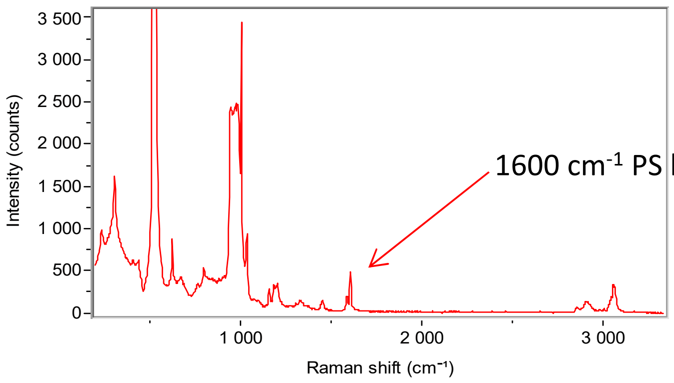
Theory	D_{xy} (µm)	D_z (µm)
473	0,3	0,9
532	0,4	1,0
633	0,5	1,2
785	0,6	1,5

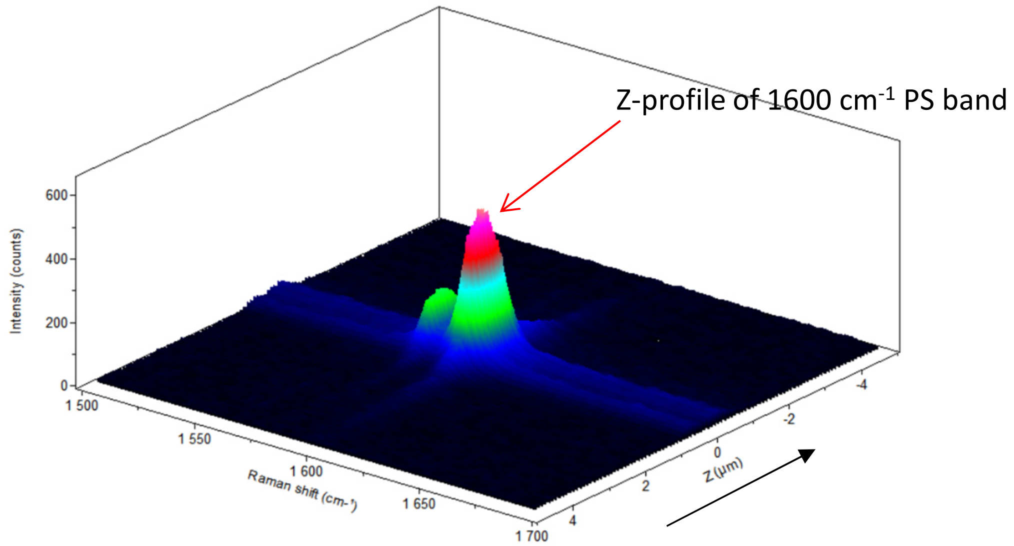
Confocal Aperture

Hole 1000

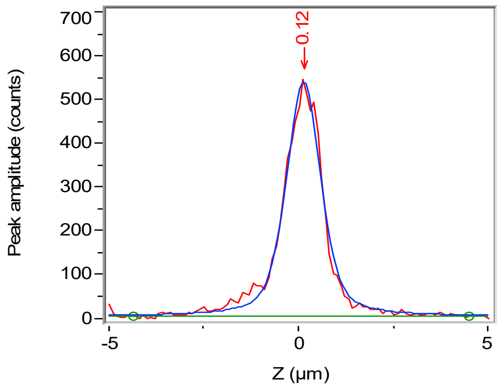
Axial resolution: z-scan through a 100 nm thick Polystyrene layer







Experimental result: Fit of z-profile of 1600 cm^{-1} PS band

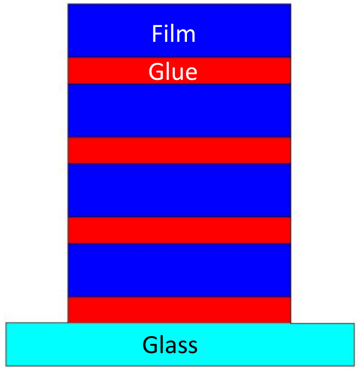


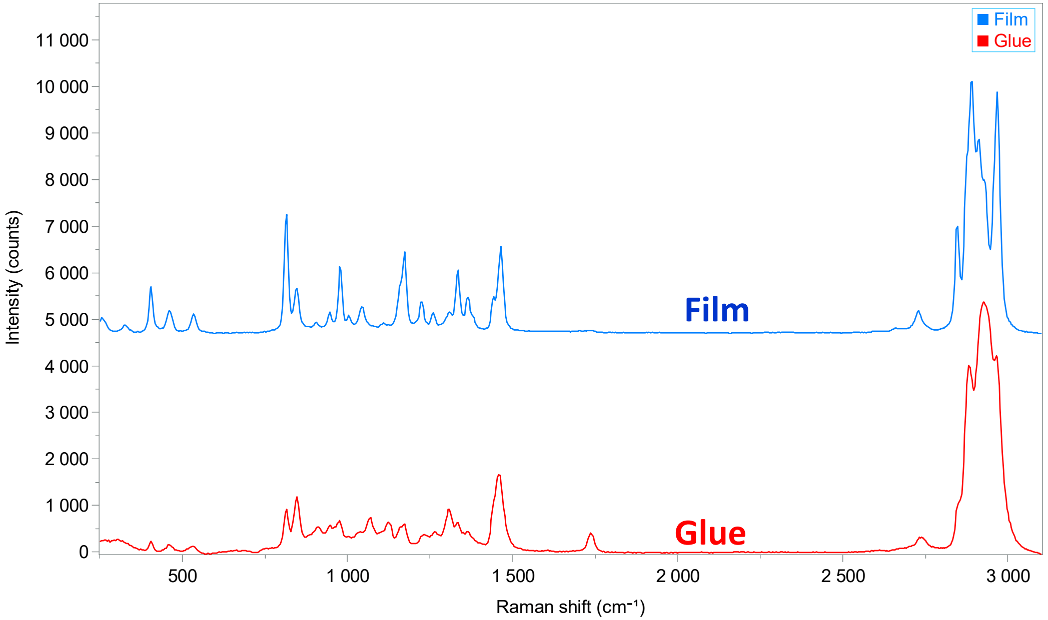
Peakposition	Amplitude	Gauß-Lorenz	FWHM	Area
0,12	537,62	0,56	1,05	701,58

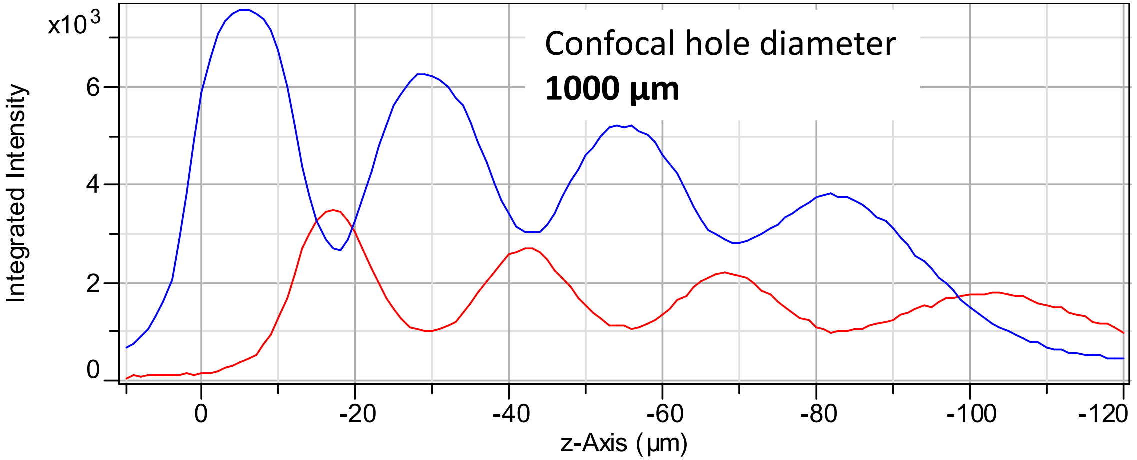
Theory	D_{xy} (µm)	D_z (µm)
473	**0,3**	**0,9**
532	**0,4**	**1,0**
633	**0,5**	**1,2**
785	**0,6**	**1,5**

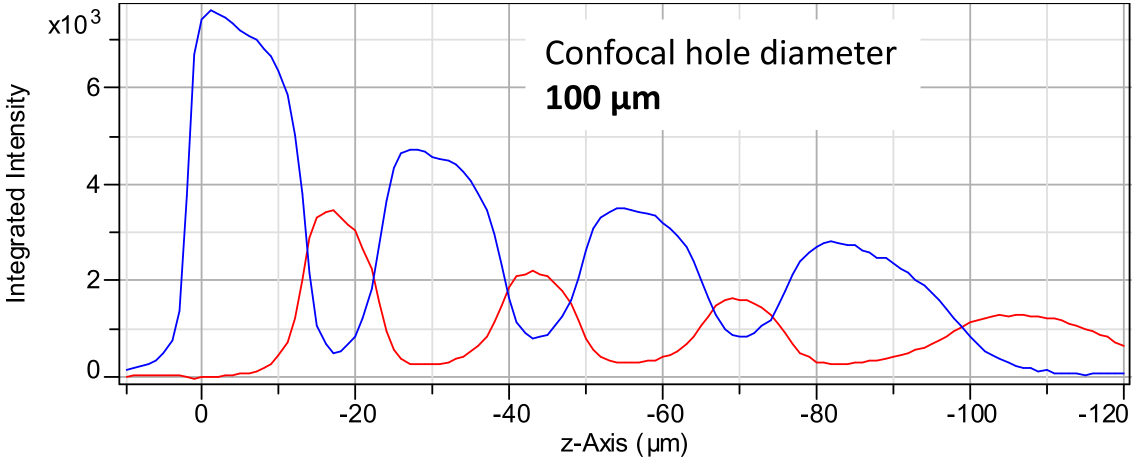
Confocal Aperture

Z-scan of multi layered polymer

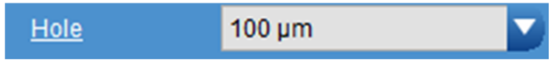








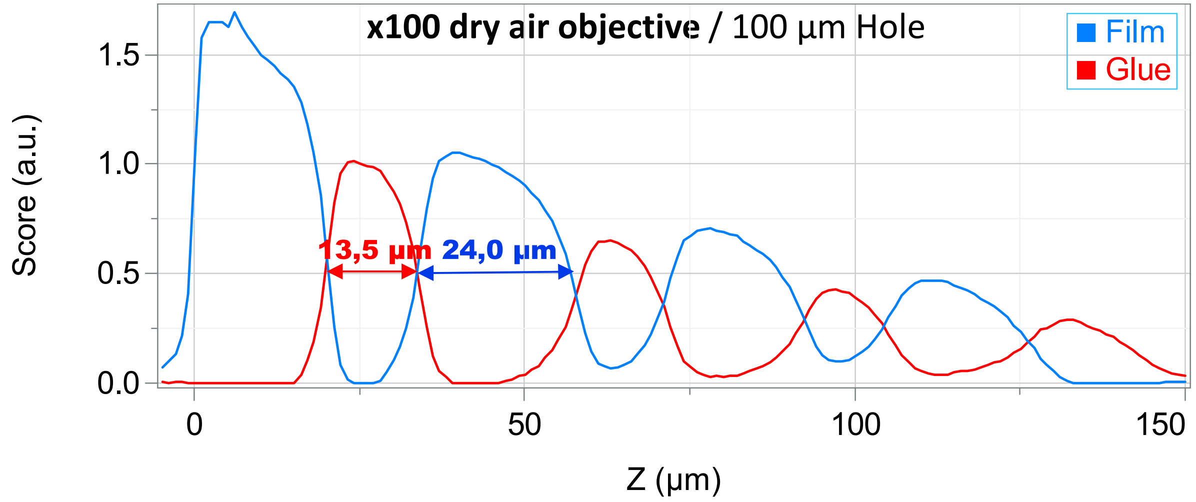
The narrow hole improves axial resolution.

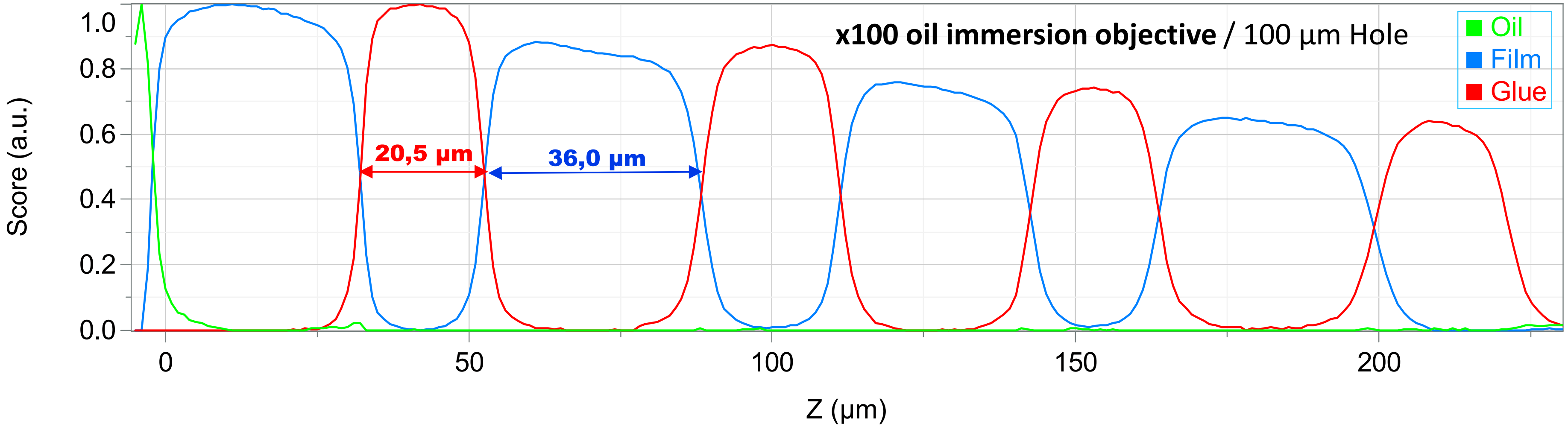


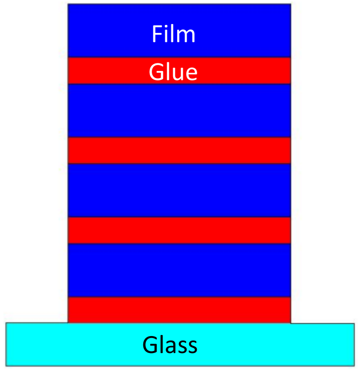
Confocal Aperture

Confocal z-scan x100 dry air objective versus x100 oil immersion objective

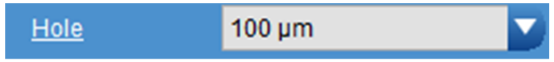
The oil immersion objective improves axial resolution remarkably in comparison with the x100 dry air objective





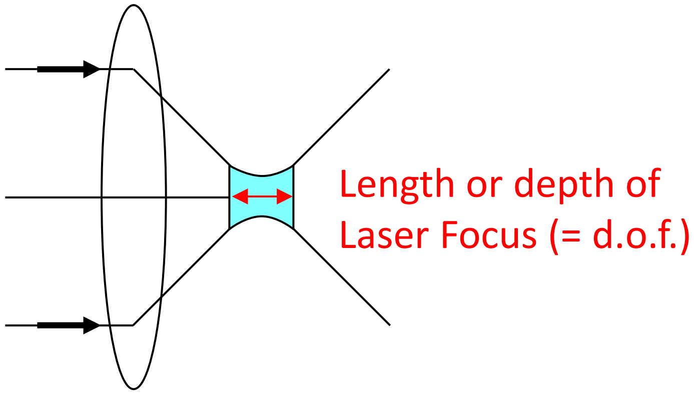


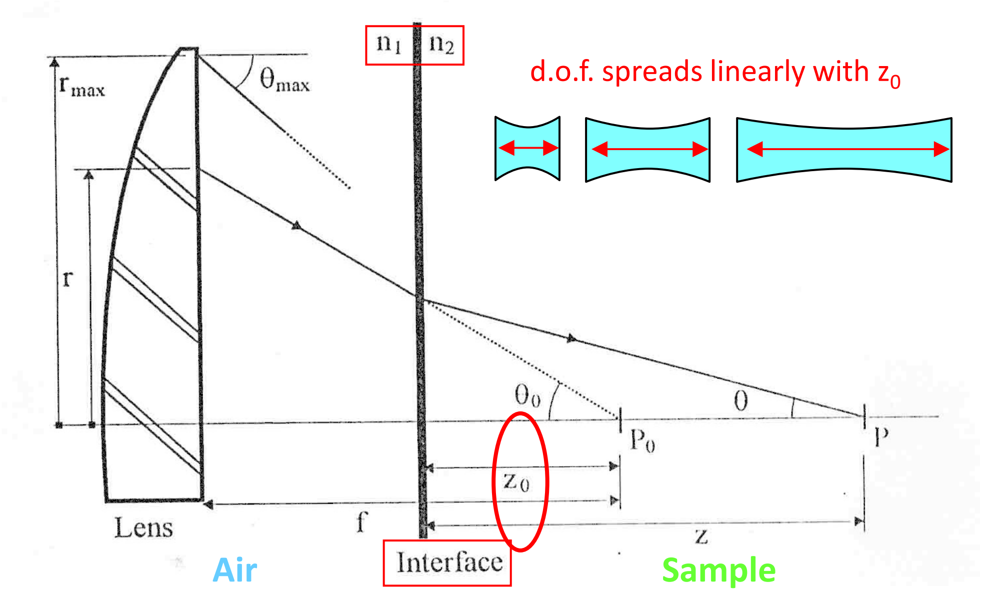
Confocal Aperture



In absence of refraction ($n_1 = n_2$) all rays are focused at point P_0, which is related to the nominal focal distance z_0 (= corresponding to the value on the micrometer scale of microscope).

But refraction ($n_1 \neq n_2$) causes:
Rays to be focused deeper into the sample at point P which lies a distance z below the sample/air interface, the actual point of focus z doesn't correspond with the nominal focal point z_0 anymore.
The length of focus (or depth of focus = d.o.f) increases linearly with z_0, means the length of laser focus spreads with increasing depth: d.o.f = $k \cdot z_0$





Data and figures from
Modeling and Measuring the Effect of Refraction on the Depth Resolution of Confocal Raman microscopy
Neil. J. Everall, Applied Spectroscopy, Vol. 54, 6, 2000

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- Principles of Raman effect in a nutshell
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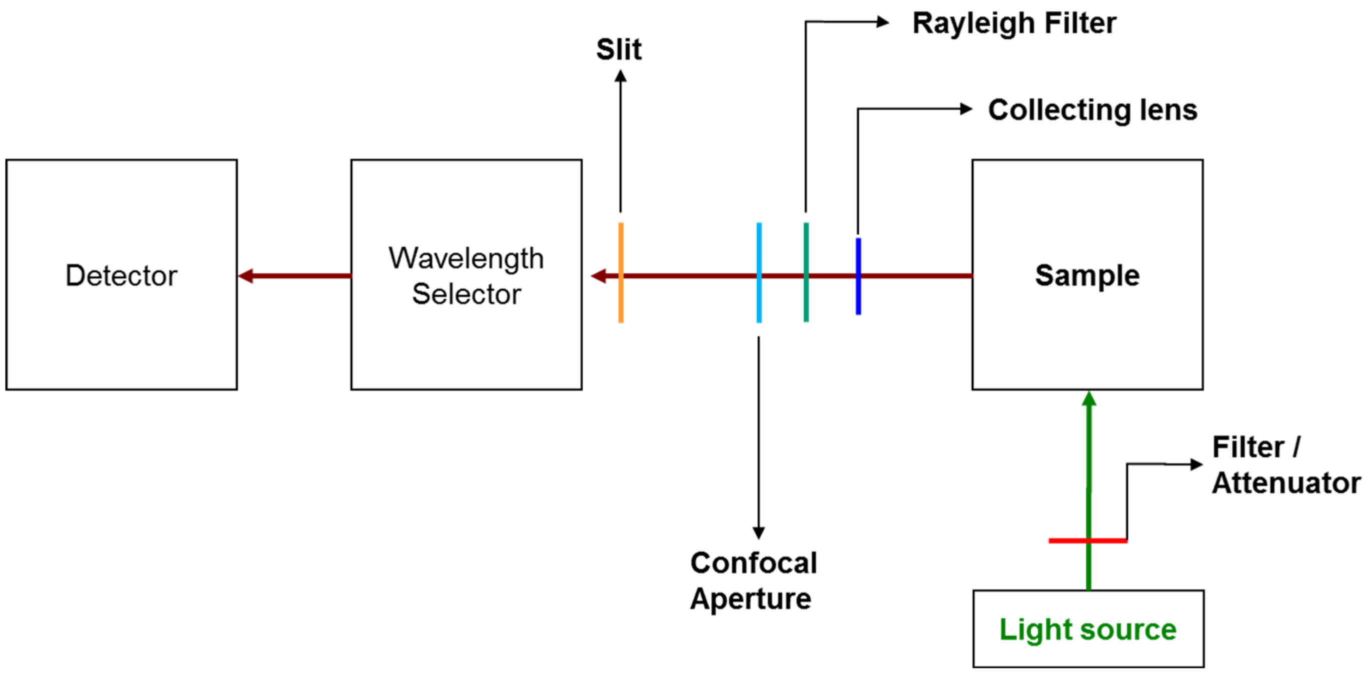
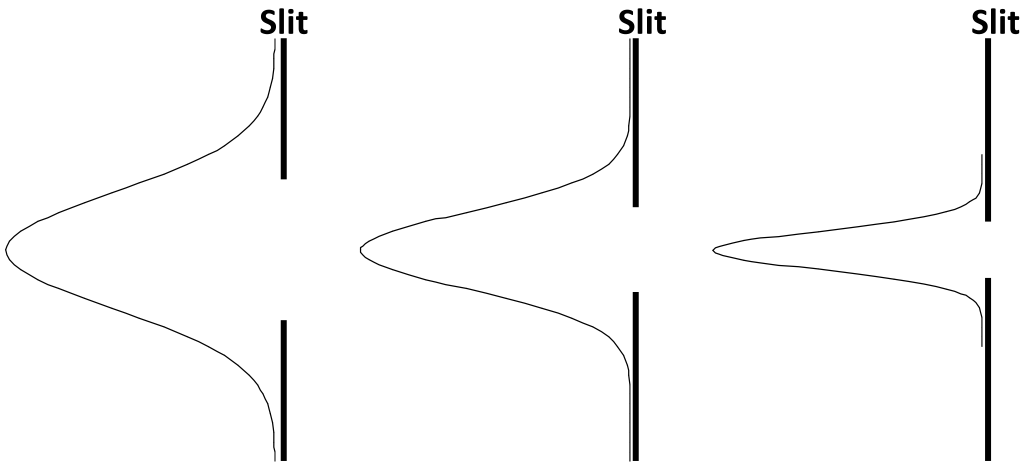
  - Rayleigh Filter
  - Confocal Aperture
  - Slit
  - Spectrometer & Grating
  - Detector & Quantum Efficiency
  - Correction of Instrument Function



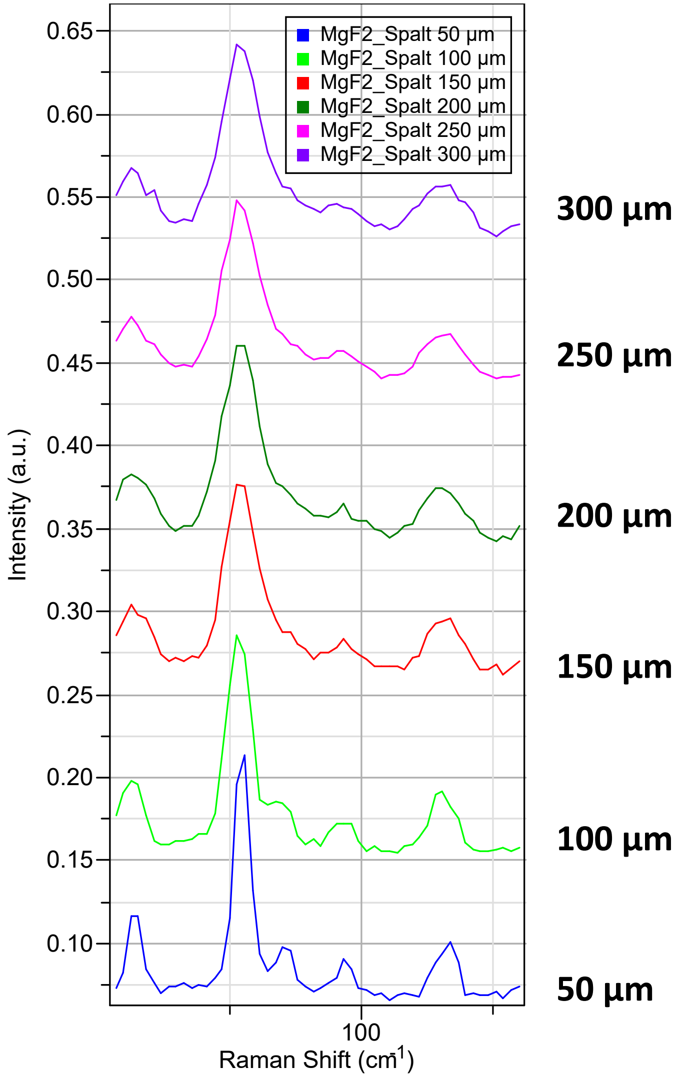
Slit

Slit 100



One of the parameters that determines the spectral resolution is the entrance slit width. The narrower the slit, the narrower the FWHM (full width at half maximum), and the higher the spectral resolution.

When recording a line with a natural width smaller than the monochromator's resolution, the measured width will reflect the spectrograph's resolution.



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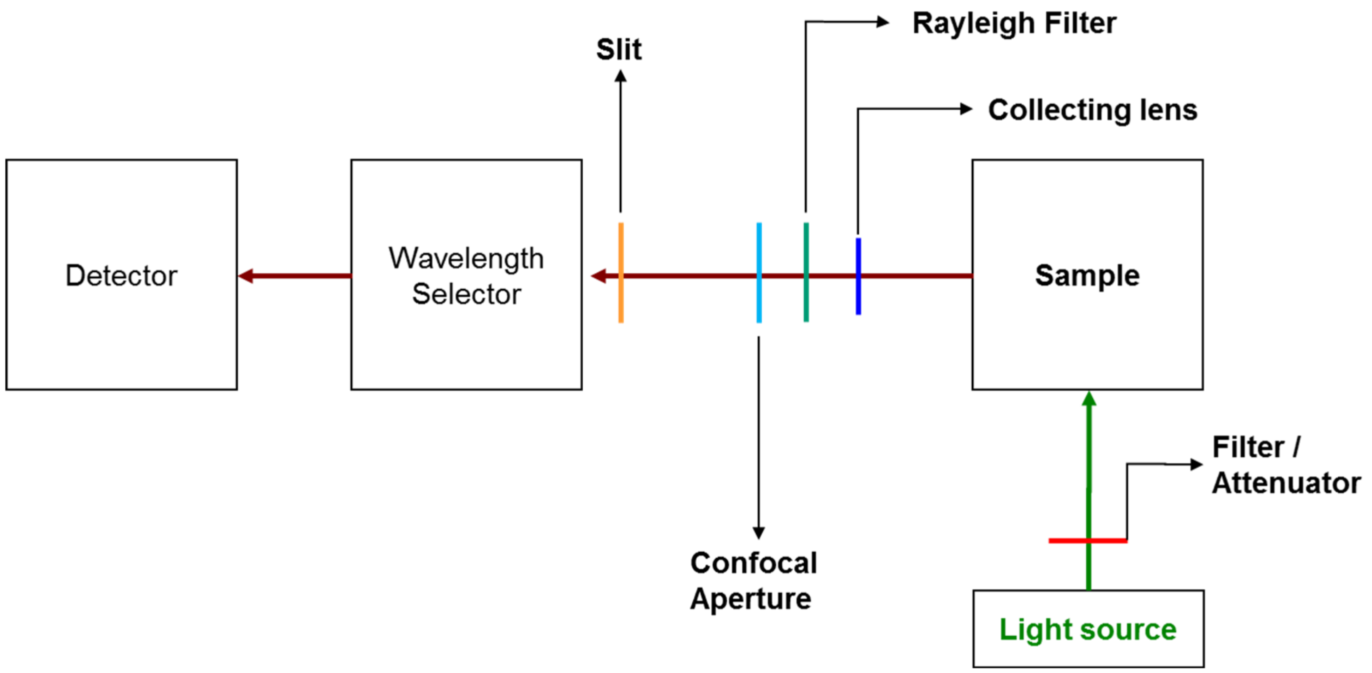
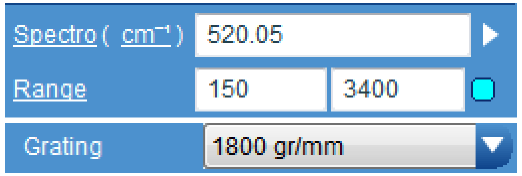
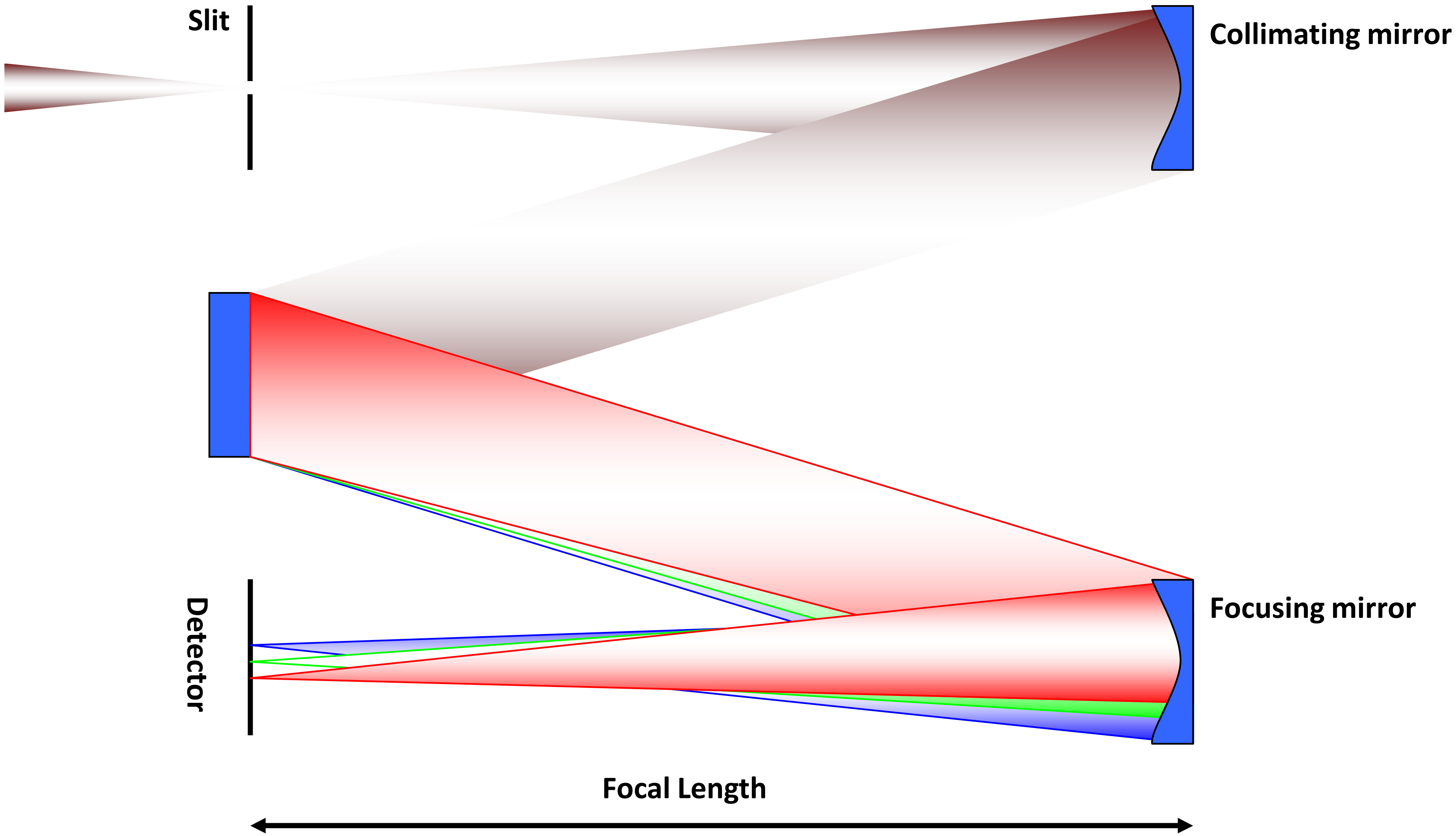


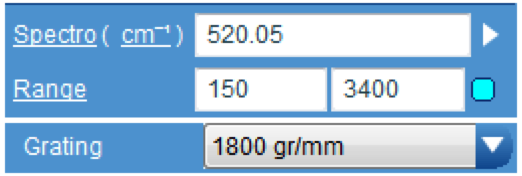
Spectrometer & Grating



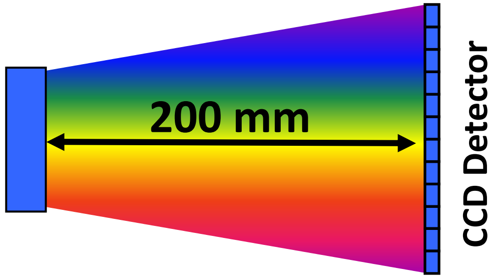


Schematic diagram of a Czerny-Turner spectrograph

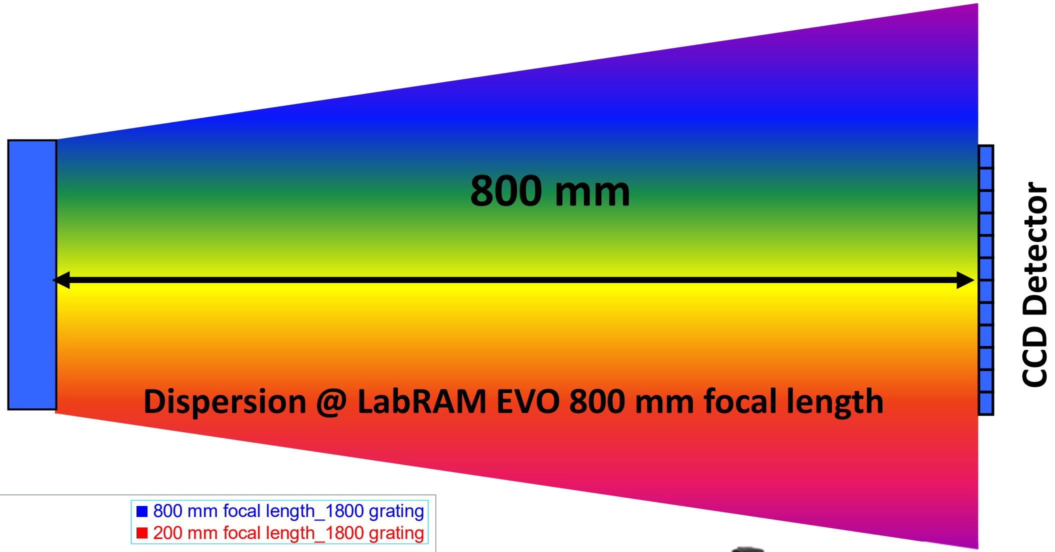
Spectrometer & Grating



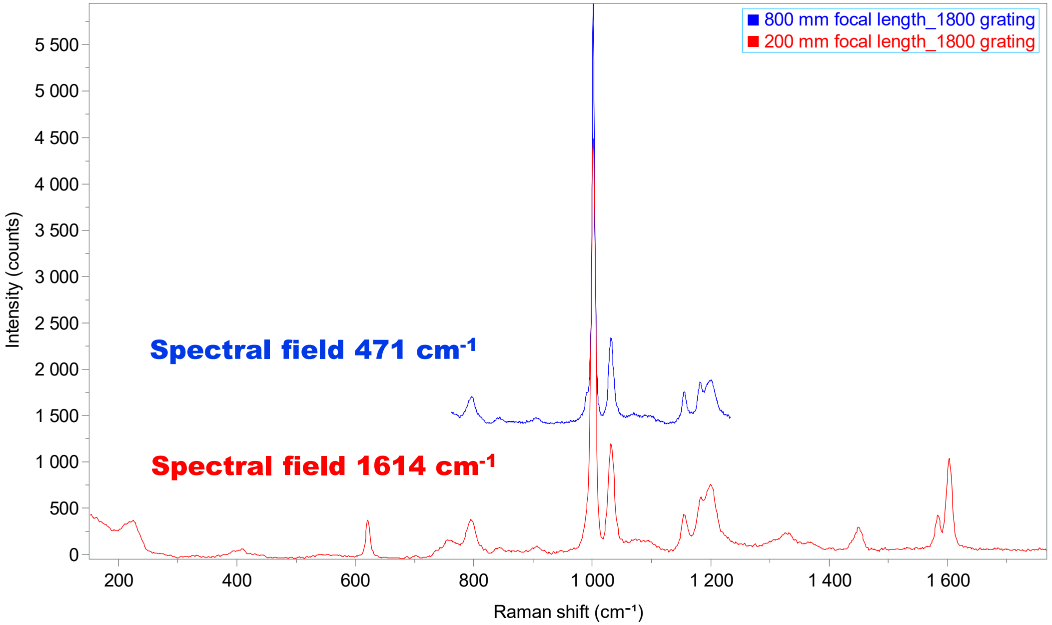
- Different focal length
- Same grating
- Same excitation wavelength



Dispersion @ XploRA 200 mm focal length

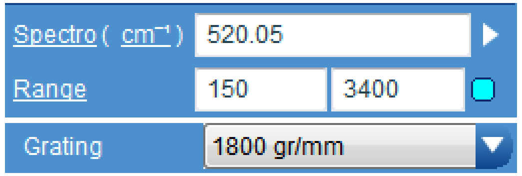


200 mm focal length

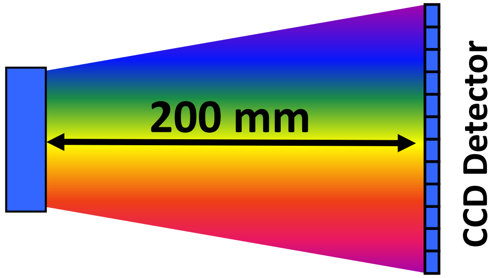


800 mm focal length

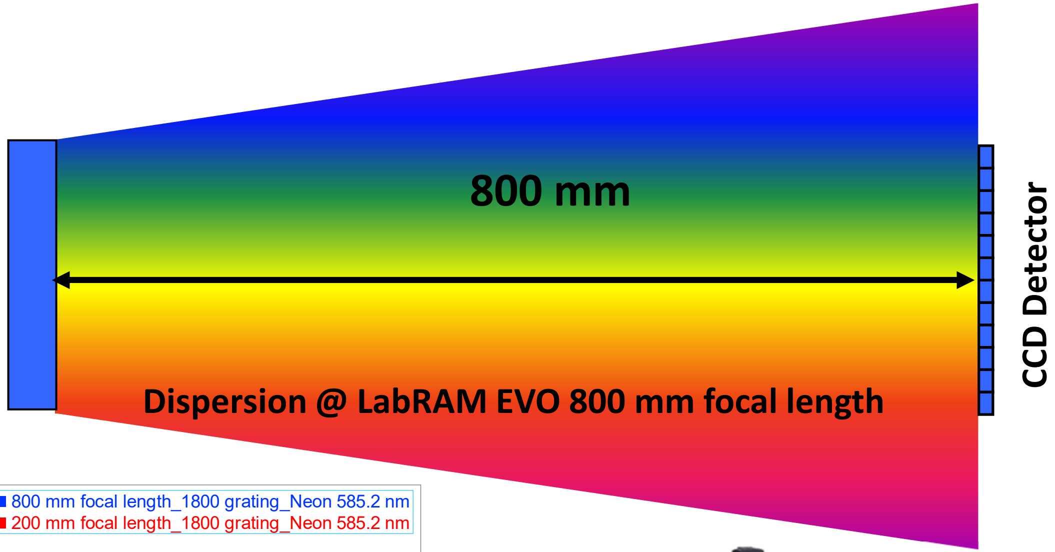
Spectrometer & Grating



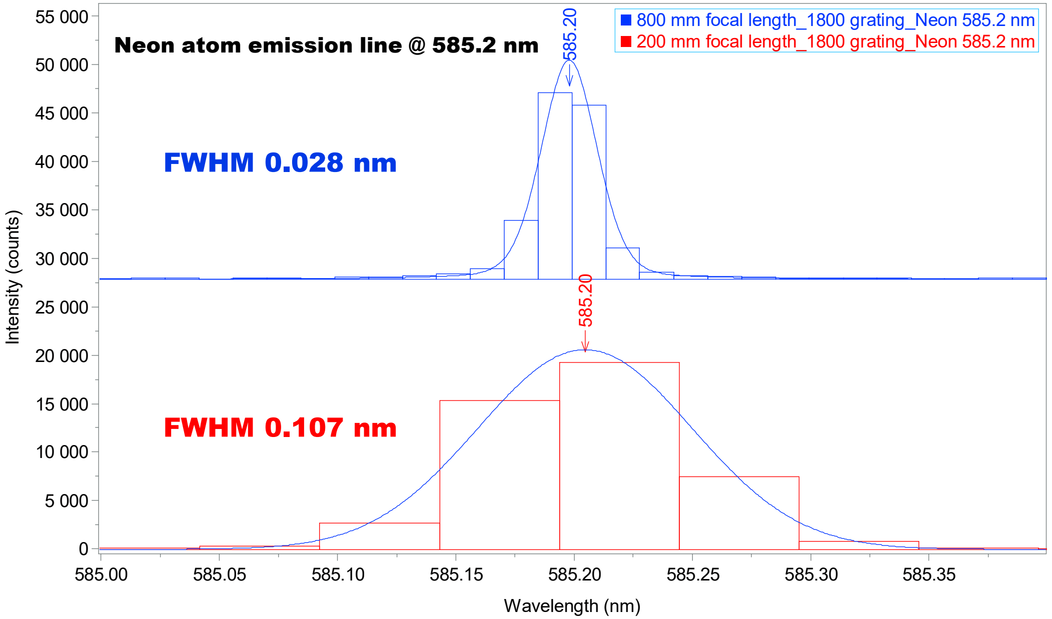
- **Different focal length**
- **Same grating**
- **Same excitation wavelength**



Dispersion @ XploRA 200 mm focal length

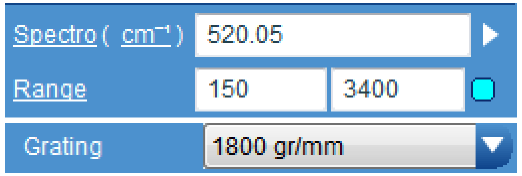


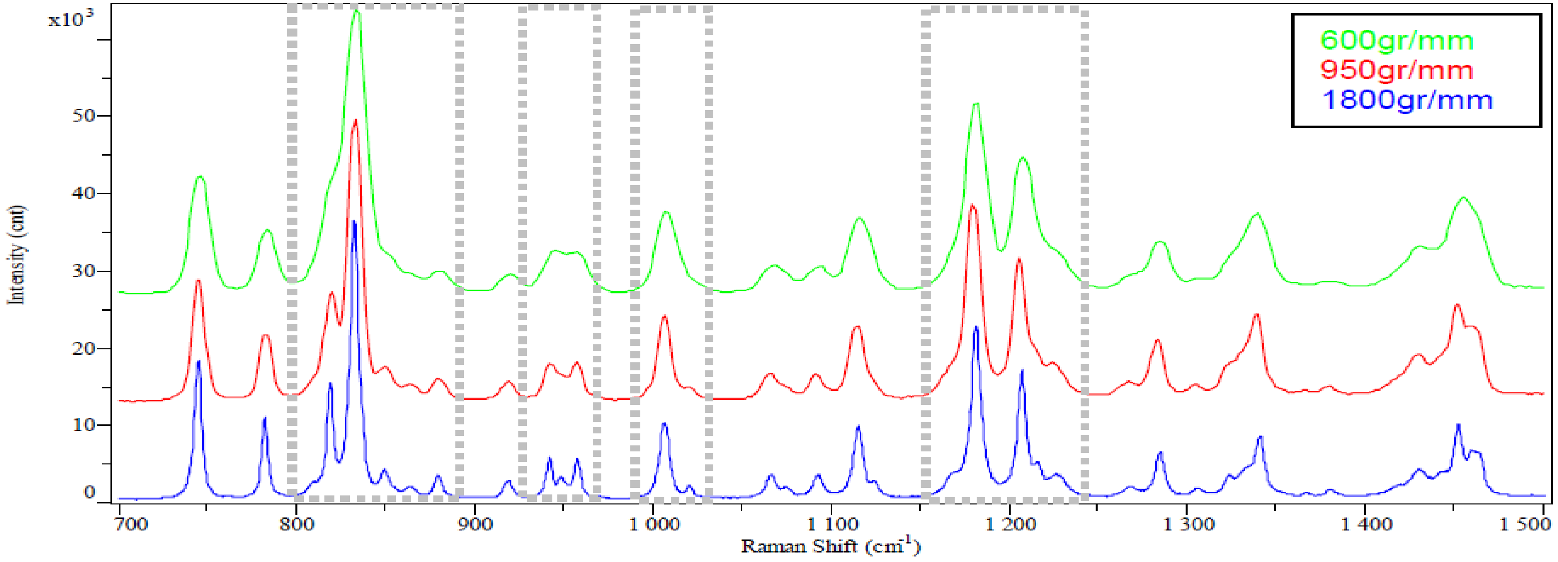
200 mm focal length



800 mm focal length

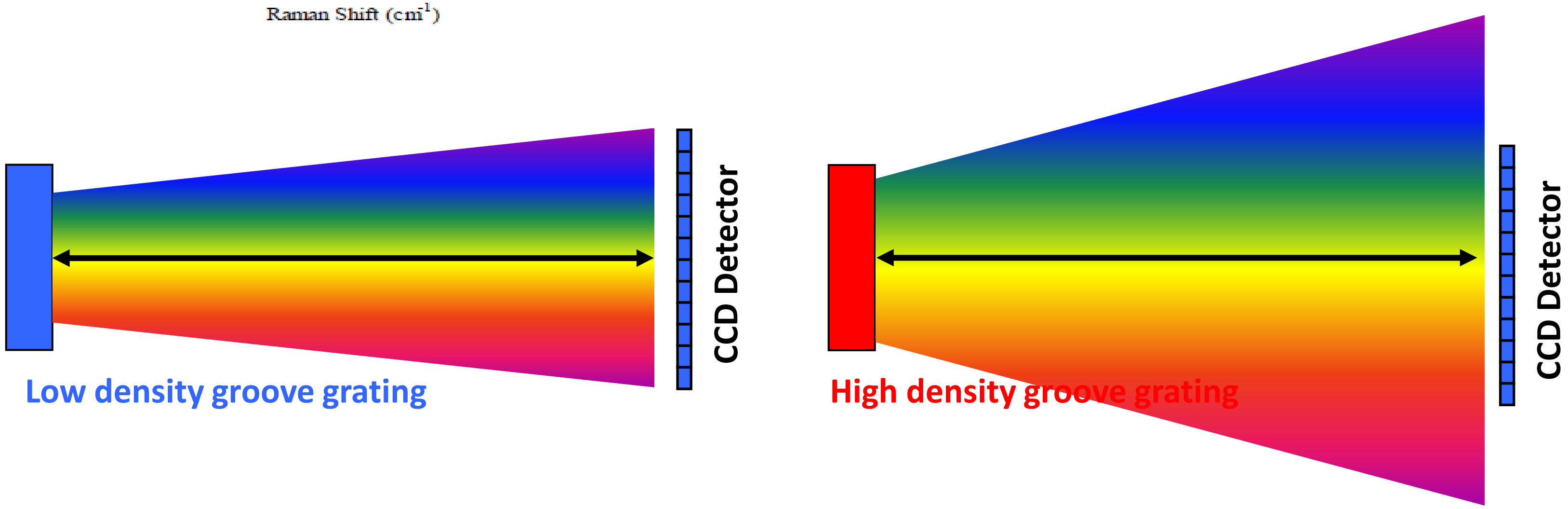
Spectrometer & Grating



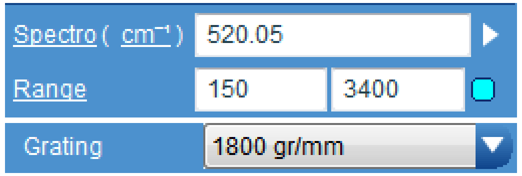


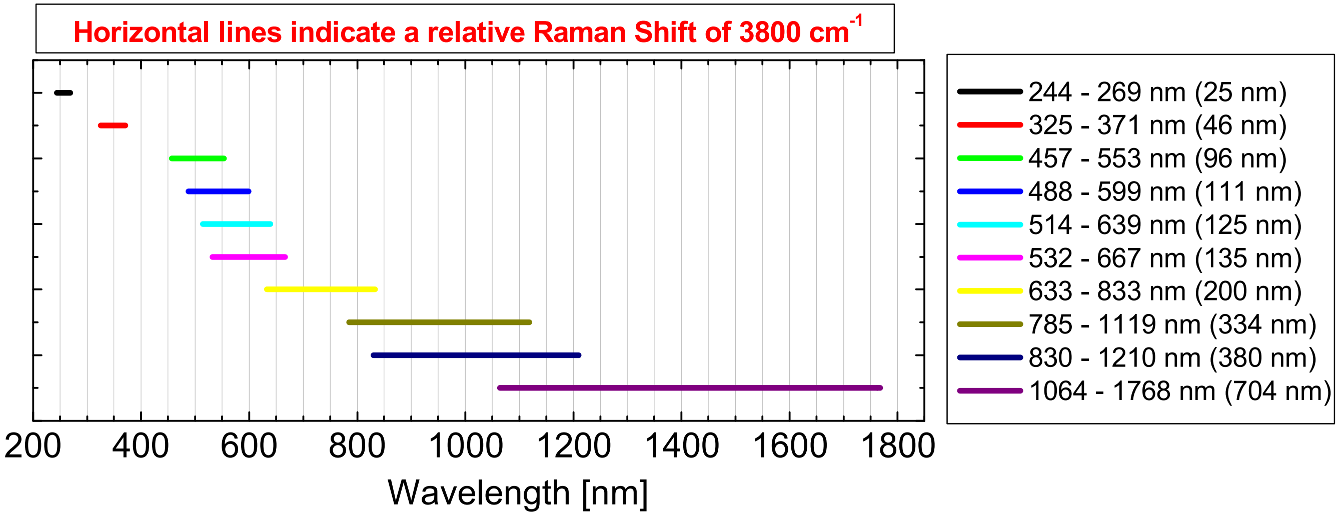
Dispersion as a function of groove density

- **<u>Different grating</u>**
- **Same focal length**
- **Same excitation wavelength**



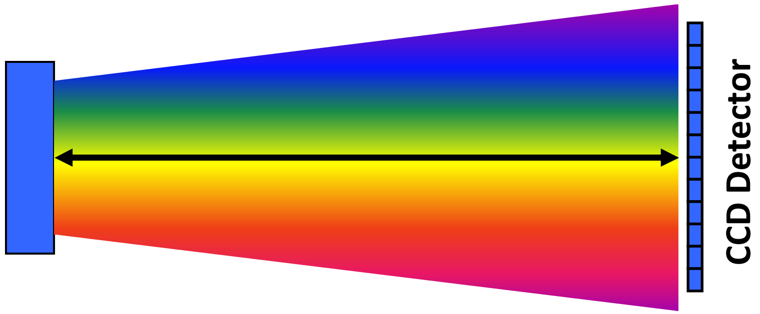
Spectrometer & Grating



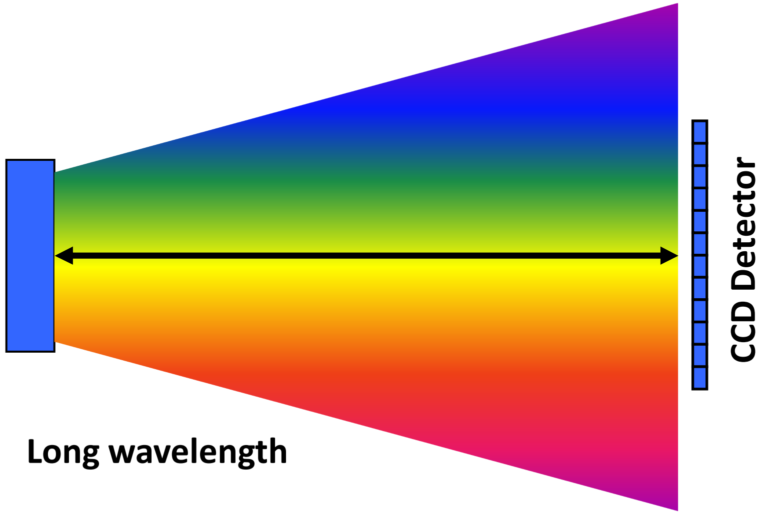


Dispersion as a function of excitation wavelength

- **<u>Different excitation wavelength</u>**
- **Same grating**
- **Same focal length**

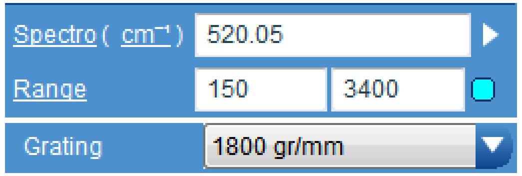


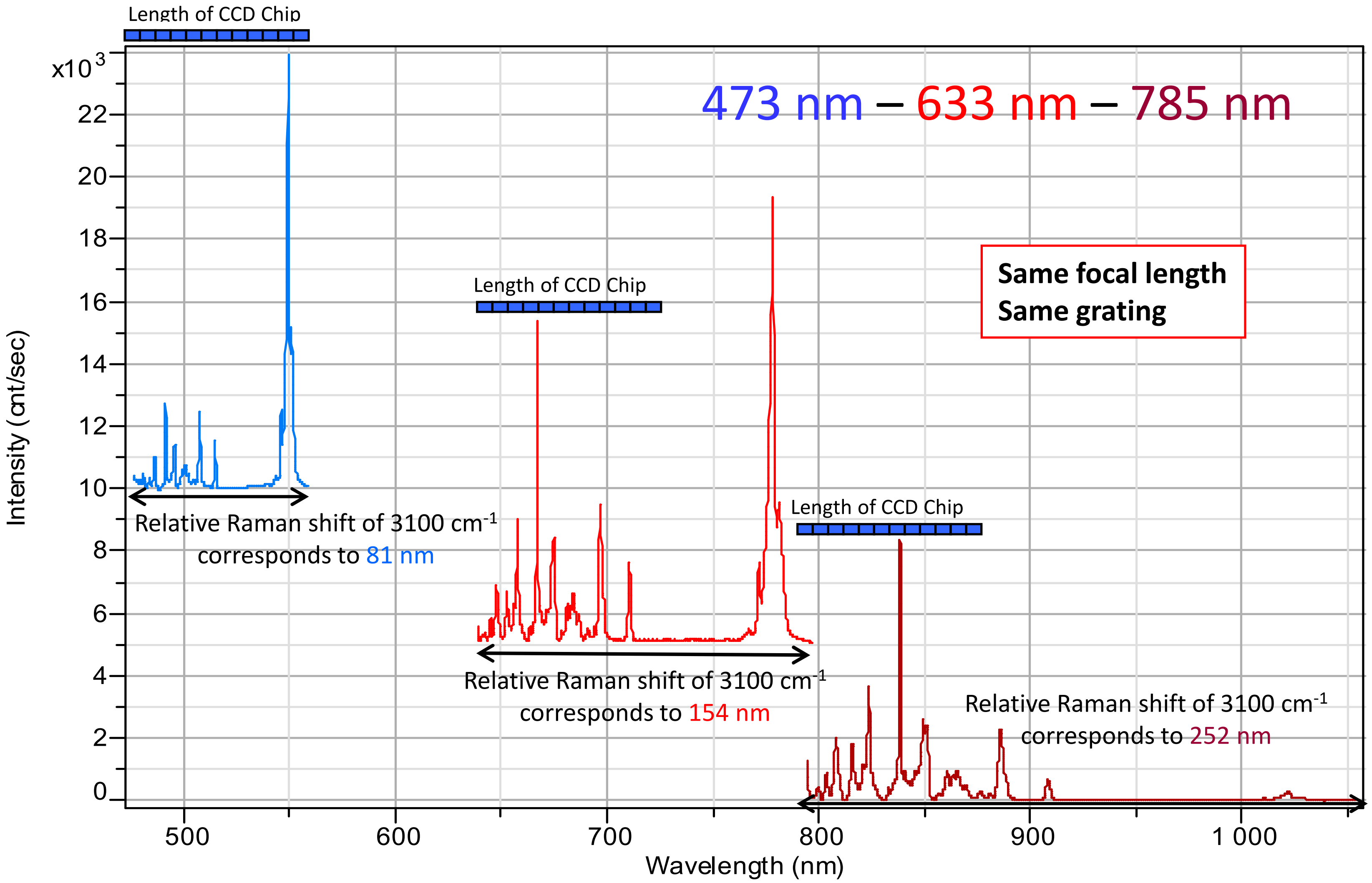
Short wavelength



Long wavelength

Spectrometer & Grating





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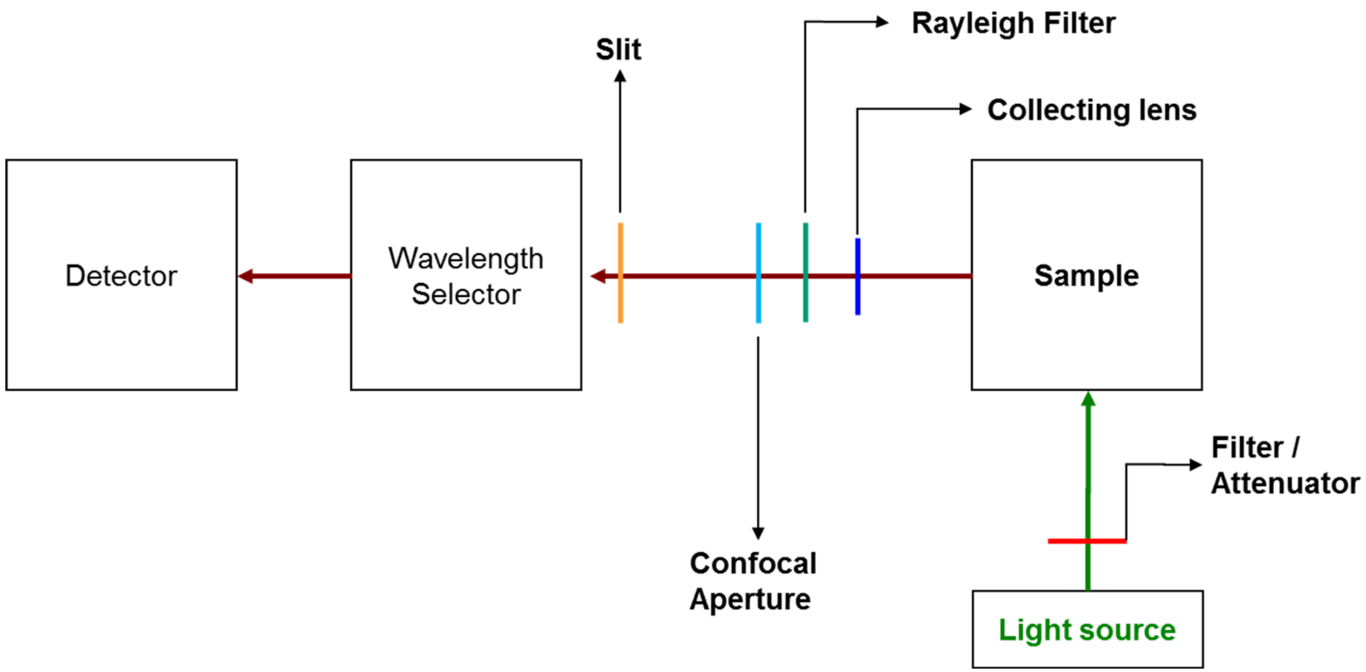
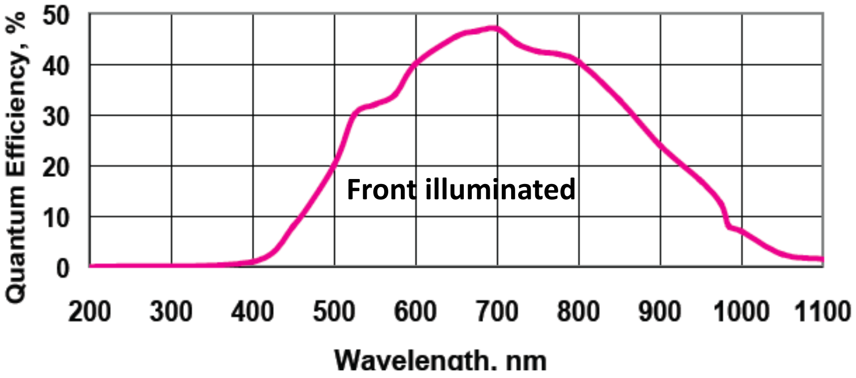
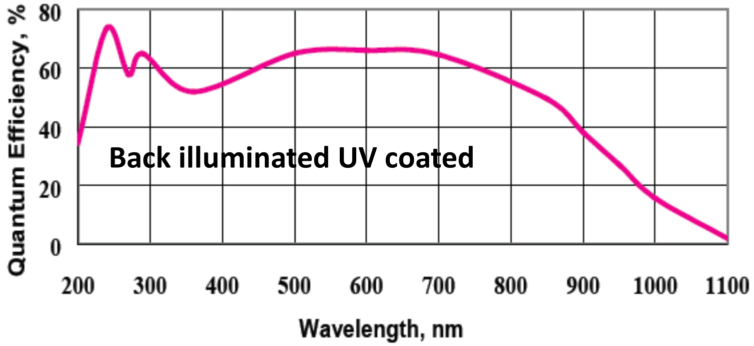
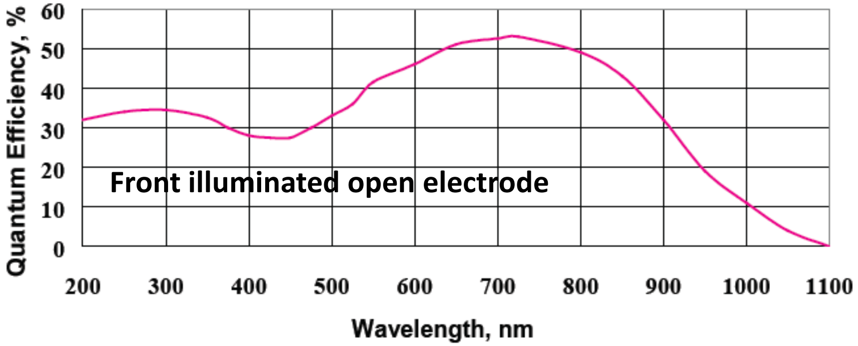


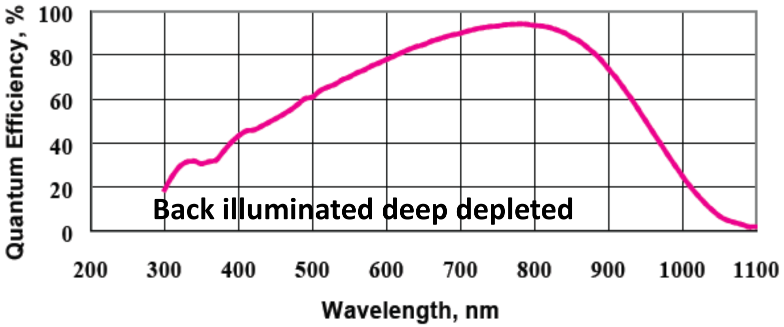
Detector & Quantum Efficiency

Comparison of different detectors concerning quantum efficiency between 200 – 1100 nm

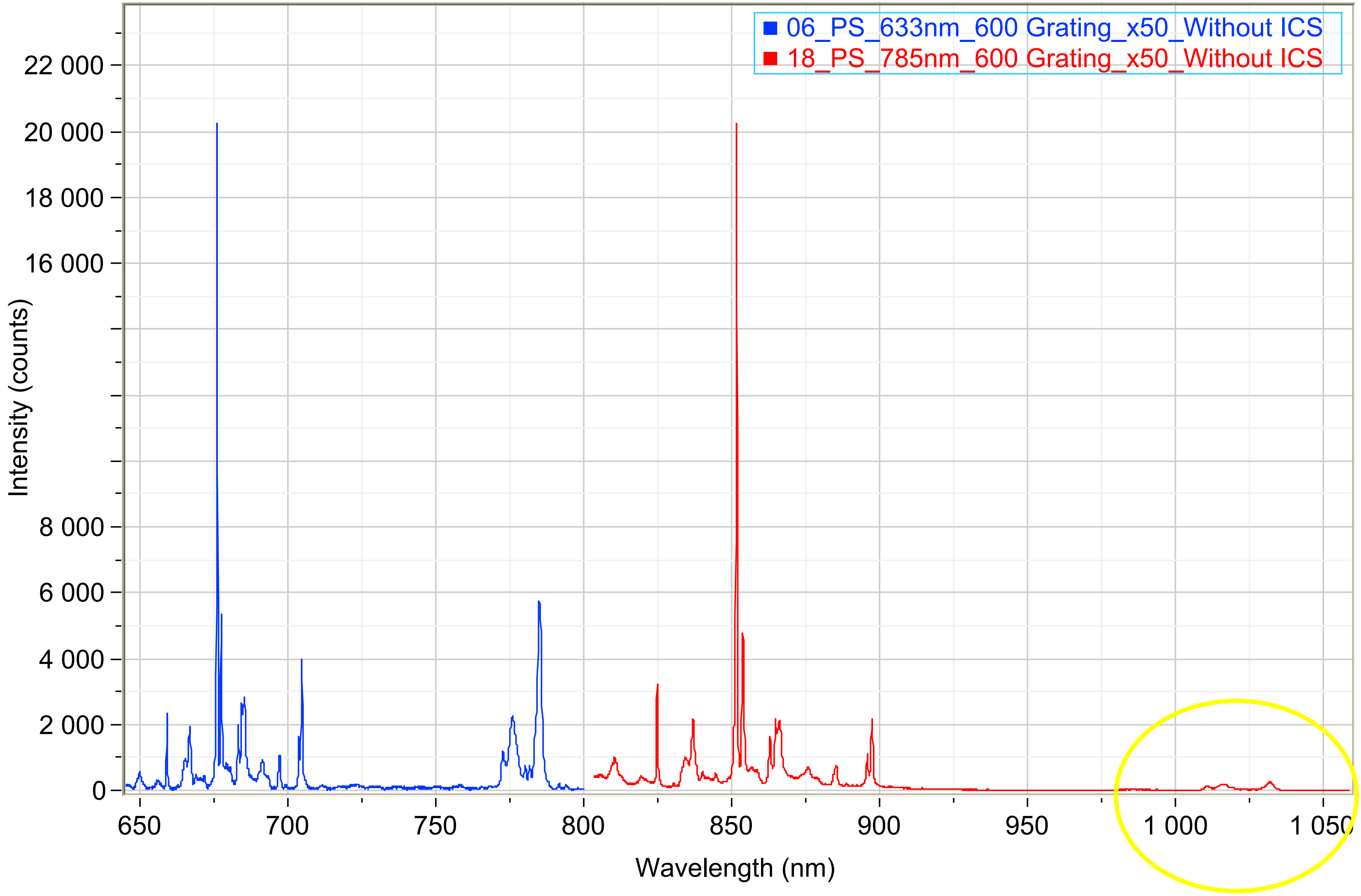








Detector & Quantum Efficiency



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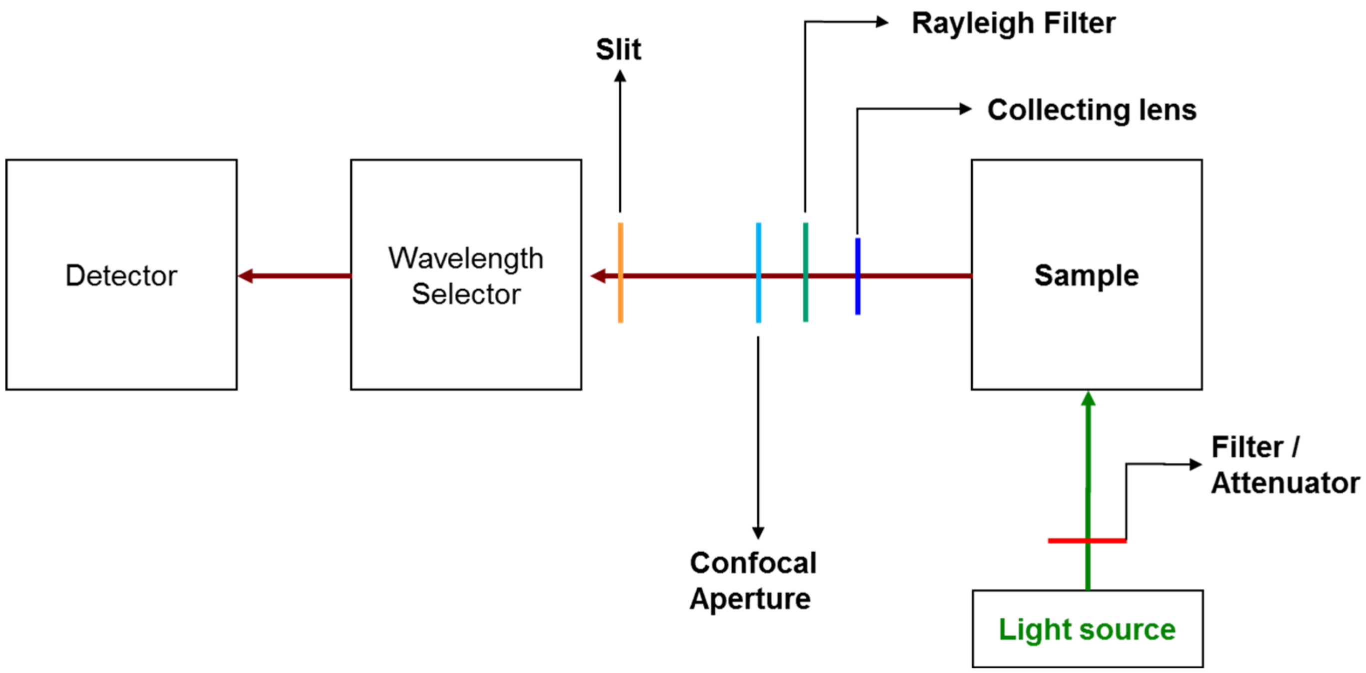

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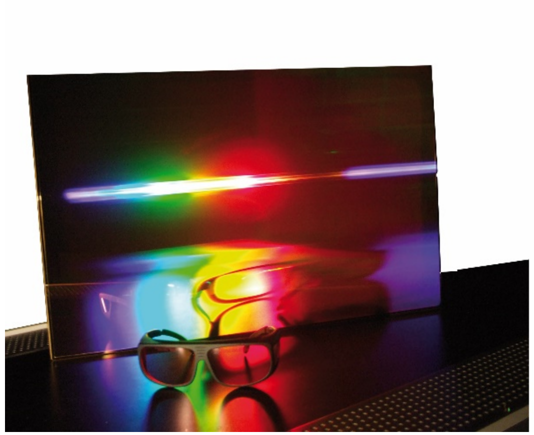
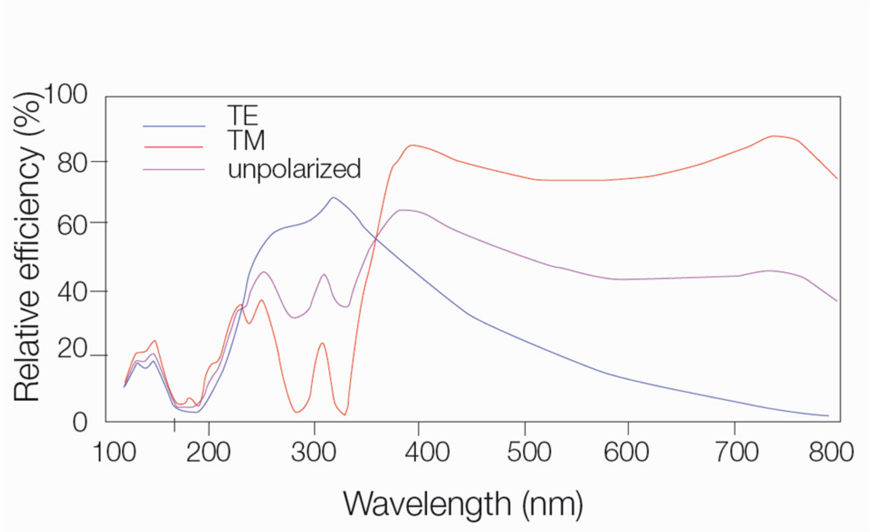
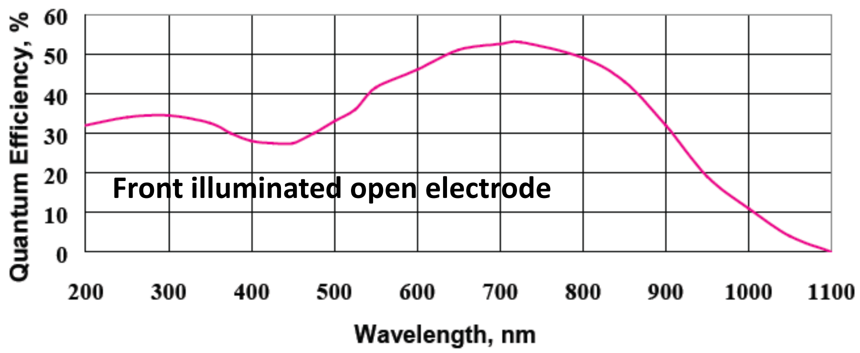


Reflectivity of the gratings vary with the wavelength as well as the transmission capability of lenses.

All this together (detector, gratings, mirrors, lenses) are generating a wavelength depended instrument function.





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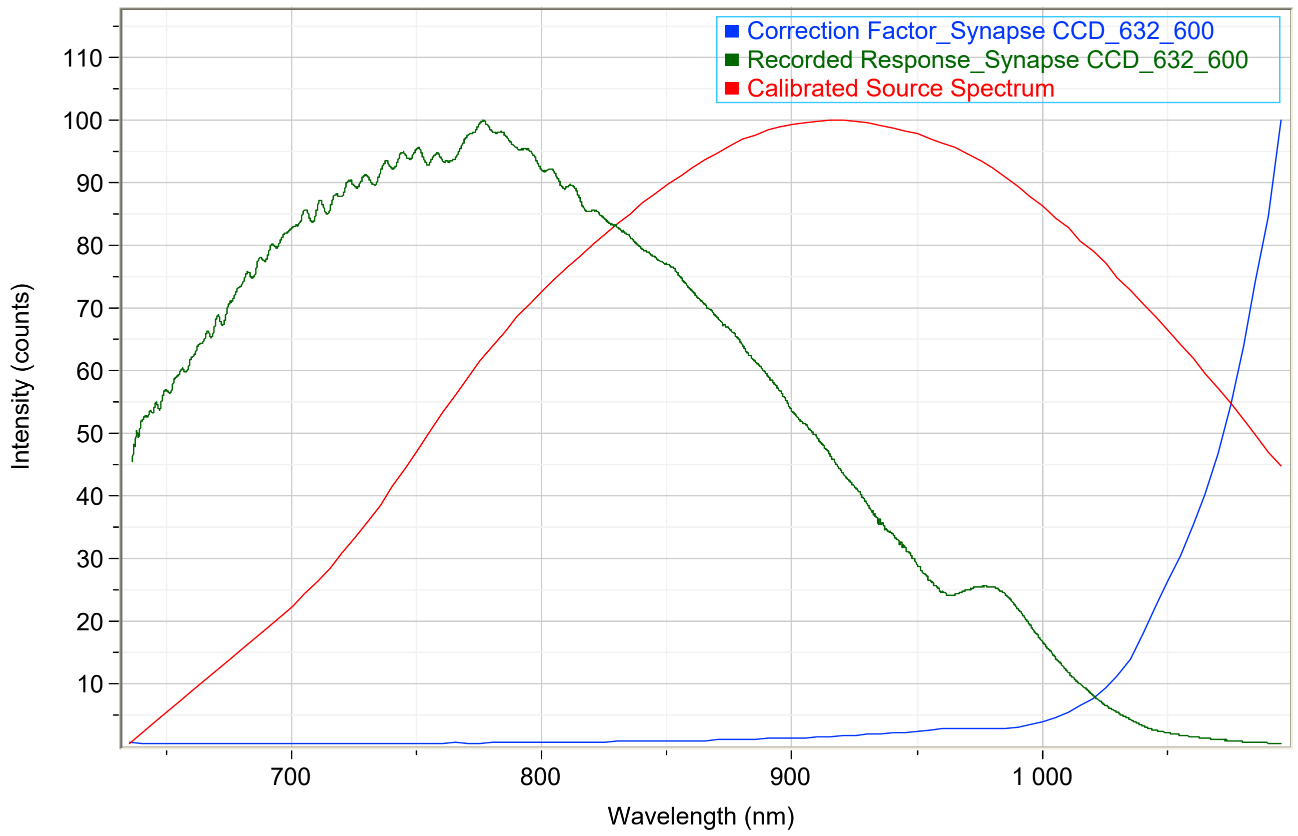

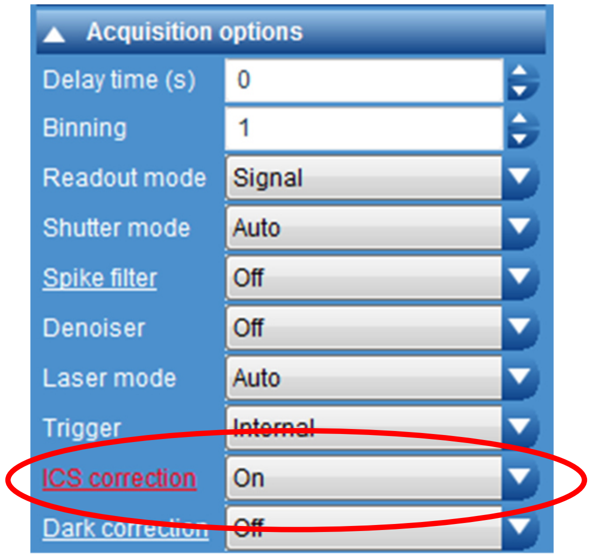

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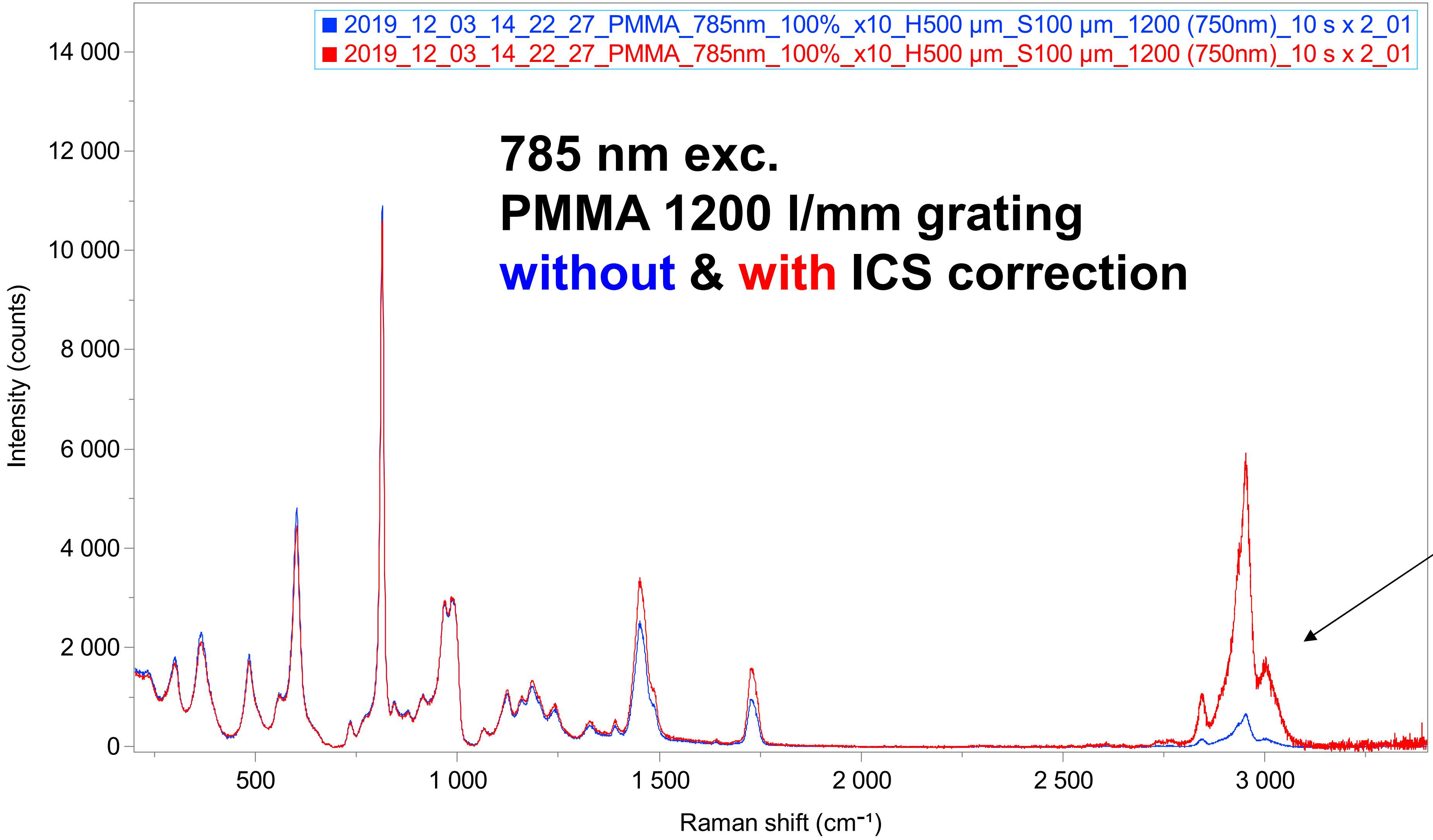
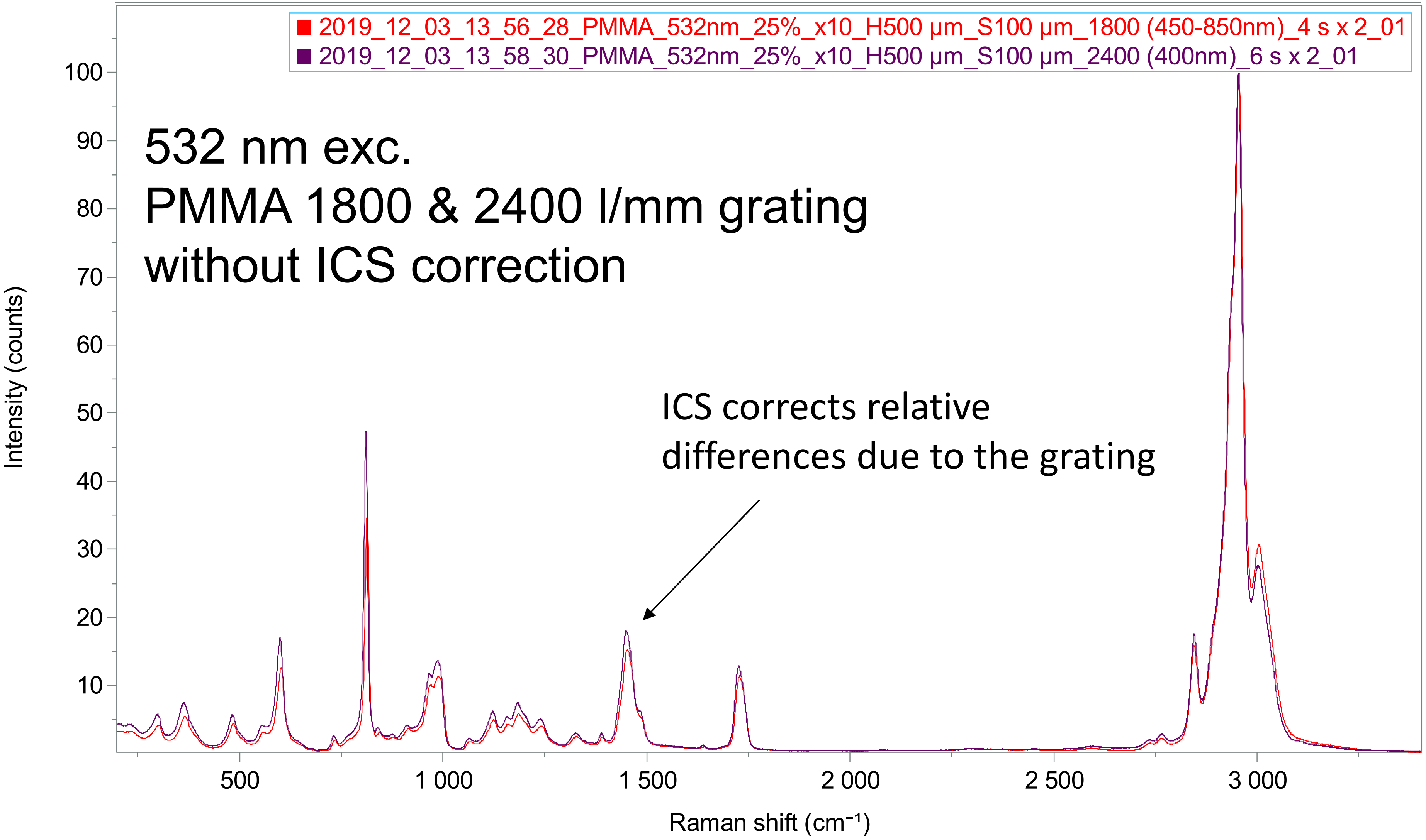


Please consider: Correction of instrument function is a prerequisite for comparison of spectra and / or relative band intensities acquired with different conditions

ICS corrects detector quantum efficiency

Correction of Instrument Function



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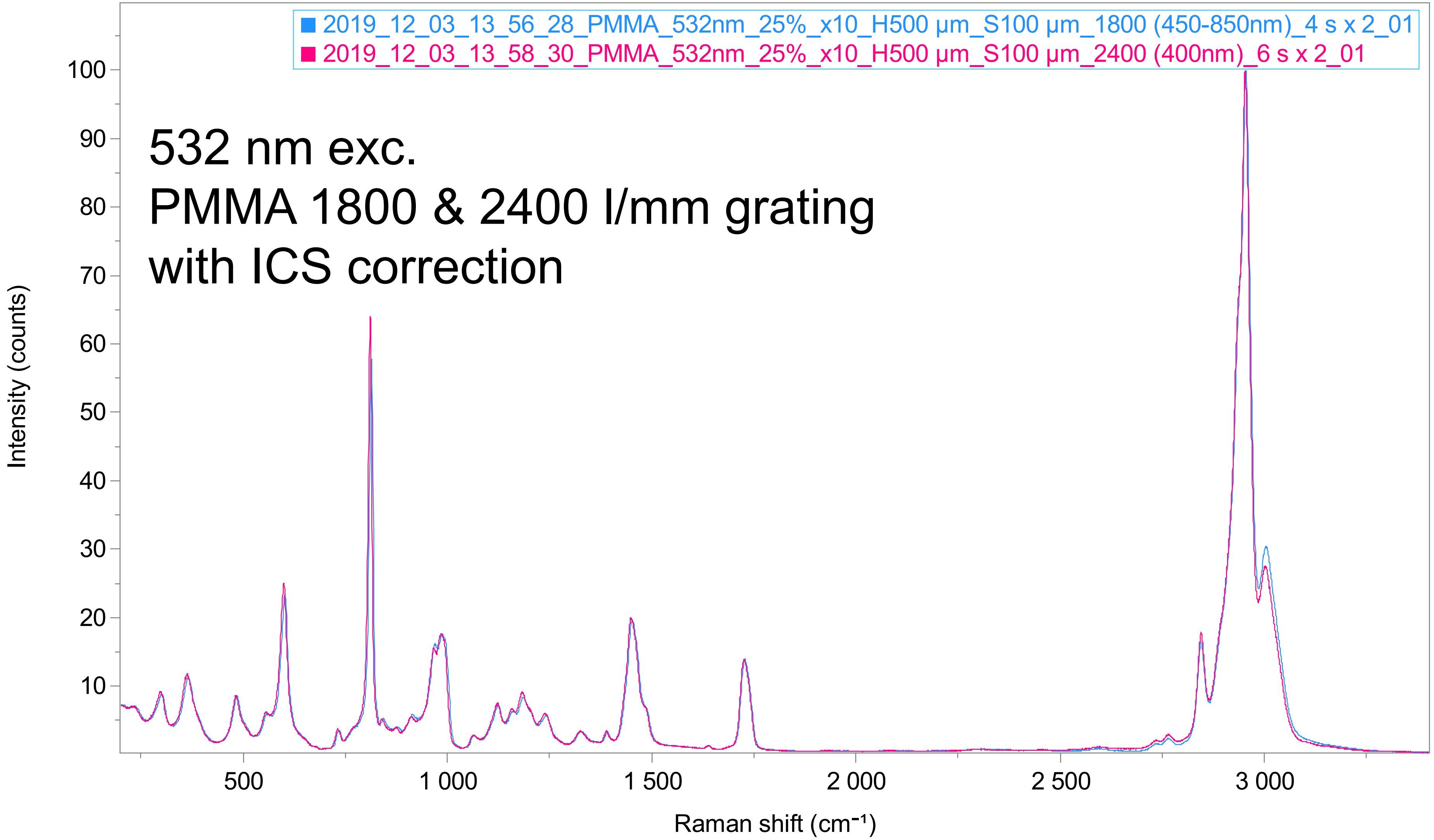
Correction of Instrument Function



Please consider: Correction of instrument function is a prerequisite for comparison of spectra and / or relative band intensities acquired with different conditions

Thank you

Omoshiro-okashiku
Joy and Fun

Thank you

감사합니다

Cảm ơn

ありがとうございました

Dzi ę kuj ę

धन्यवाद

Grazie

Merci

谢谢

நன்றி

ขอบคุณครับ

Obrigado

Σας ευχαριστούμε

Tack ska ni ha

شُكْرا

Большое спасибо

Danke

Gracias