Introduction
History of Raman

istory of Raman Scattering

In 1928, C. V. Raman discovers that small changes occur the frequency of a small portion of th light scattered by molecules.

The changes reflect the vibrational properties of the molecule.

C.V. Raman was awarded the **Nobel Prize in Physics in 1930** for his discovery.

Sir Chandrasekhara Venkata Raman

C. V. Raman, K. S. Krishnan, *Proc. Roy. Soc. London*, **1929,** *122,* 23.

volution of Raman System

2010

2000

1990

1980

1970

1960

Transmission Measurements for Bulk

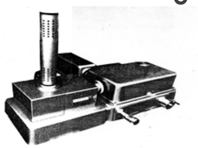
Ultra Fast Raman Mapping

DuoScan – mapping without XY stage

Holographic notch filters were demonstrated to provide superior laser rejection

Triple Spectrographs with MCD's introduced by Dilor, JY, and Spex (now HORIBA Scientific).

JY Double -Concave Holographic Gratings



1966 – 1st laser based Raman

Huge systems in early years with long acquisition time

VBGs-Ultra low frequency

ParticleFinder - Particle Analysis

First AFM/TERS Raman Microscope Combination

Dilor (now HORIBA Scientific) and Renishaw introduce first successful benchtop systems

CCD detectors

1976- MOLE™ by Lirinord (now HORIBA Scientific) 1st commercial Micro-Raman

First commercial Holo gratings

1957-Cary 81 1st "easy-to-use" Analytic Instrument

aman papers vs other techniques

	Nature	Science	Royal Chemistry Society	Journal of Applied Physics	journal Pharmaceutical review	Earth and planetary science	total
NMR	39 800	354 000	221 000	594 000	519 000	1 200	**1 729 000**
Raman	12 400	159 000	119 000	596 000	188 000	1 360	**1 075 760**
XRD	5 860	166 000	171 000	171 000	79 600	3 610	**597 070**
FTIR	3 080	141 000	101 000	150 000	127 000	1 310	**523 390**
XPS	3 290	86 800	84 100	108 000	71 300	78	**353 568**
SIMS	152	5 310	419	8 110	1 370	70	**15 431**
CLSM	903	5 720	3 340	1 850	2 330	38	**14 181**

Raman spectroscopy is extremely versatile!

mparison of FTIR and Raman Spectroscopy

- Advantages of Raman over FTIR:
  - Avoids many interferences from solvents, cells and sample preparation methods
  - Better selectivity, peaks tend to be narrow
  - Depolarization studies possible, enhanced effects in some cases
  - Can detect IR-inactive vibrational modes
- Advantages of FTIR over Raman:
  - Raman can suffer from laser-induced fluorescence and degradation
  - Raman lines are weaker, the Rayleigh line is also present
  - Raman instruments are generally more costly
  - Spectra are spread over many um in the IR but are compressed into several nm (20-50 nm) in the Raman
- Final conclusion – they are complementary techniques!

man Spectroscopy: Informations

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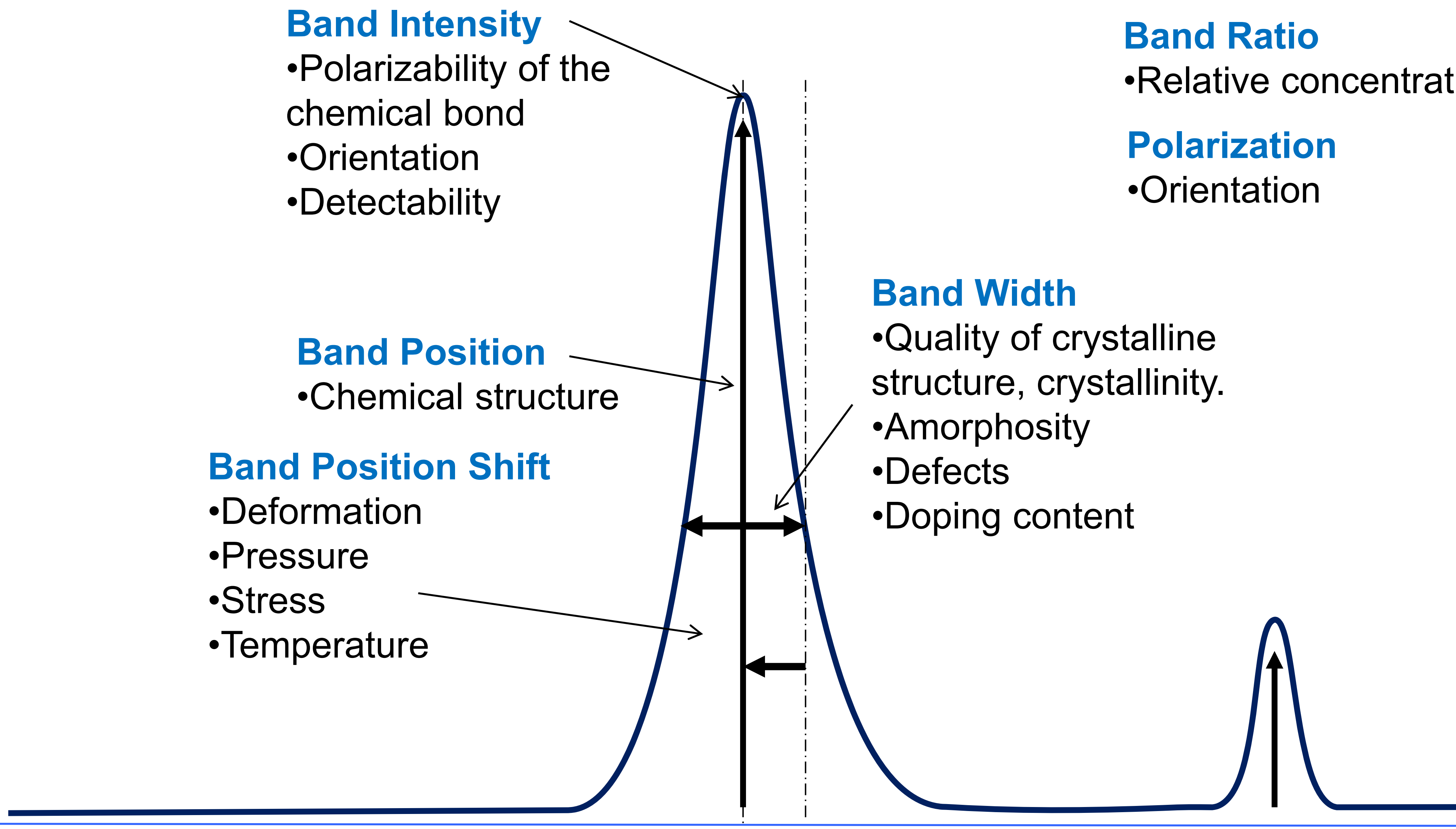
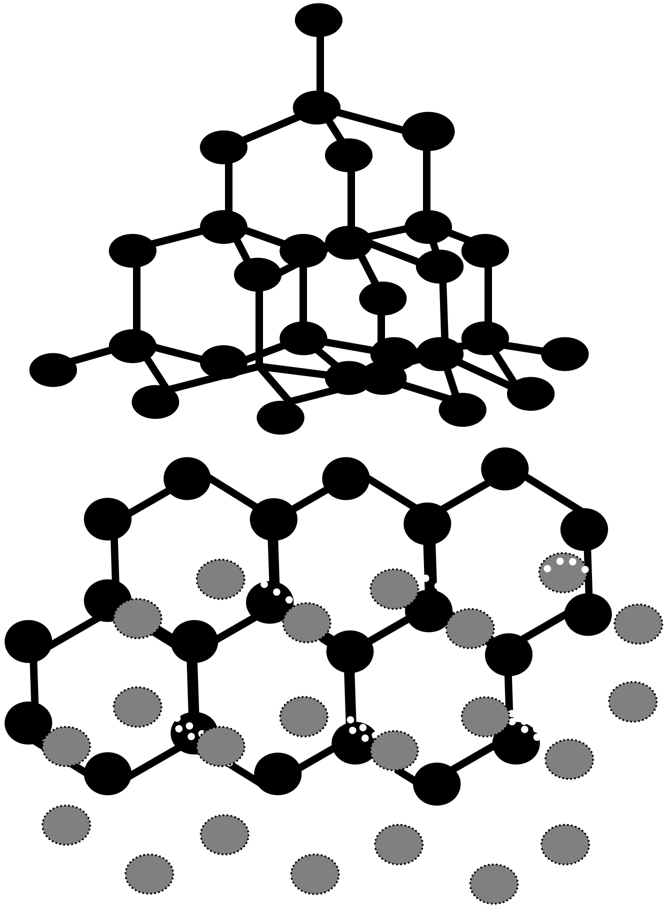
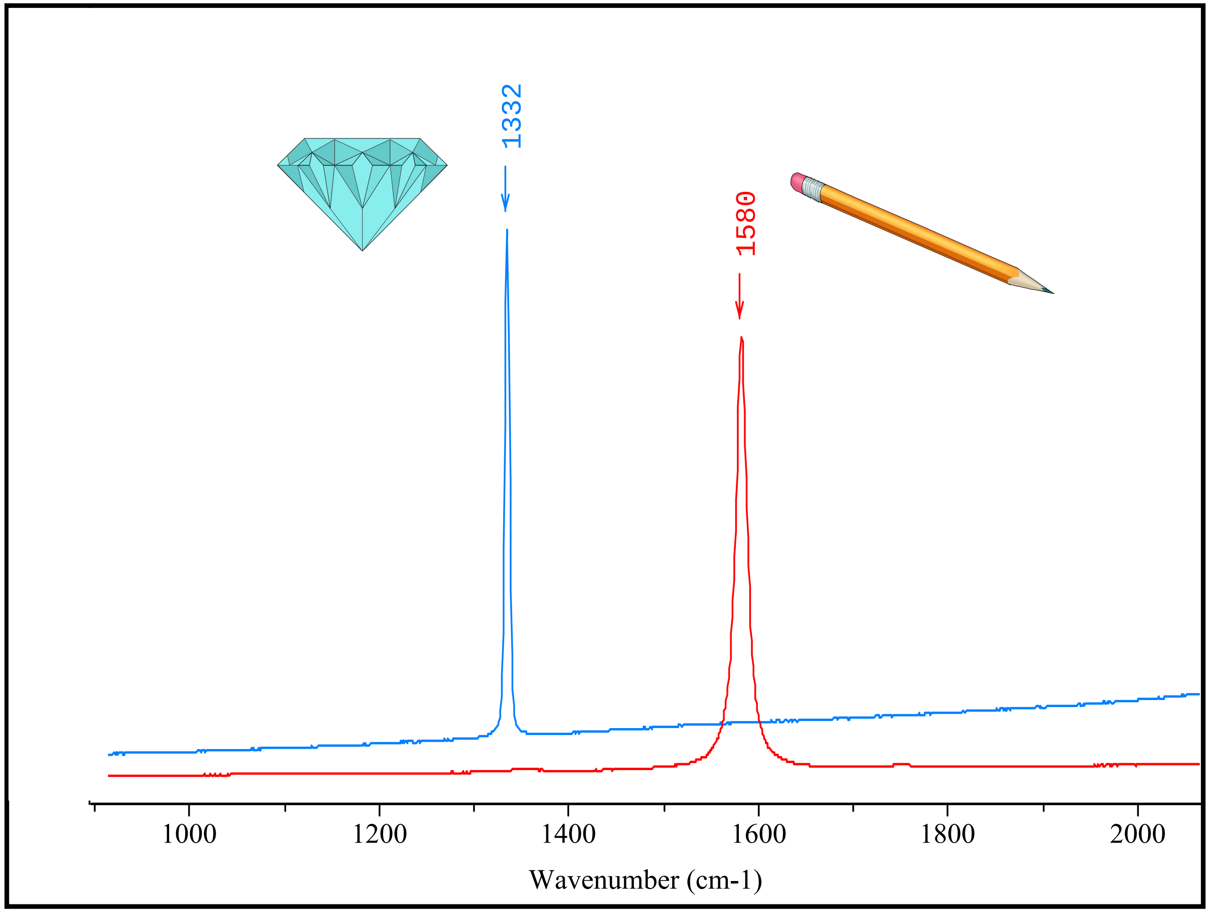


arbon Allotrope

Raman spectrum is unique for material.

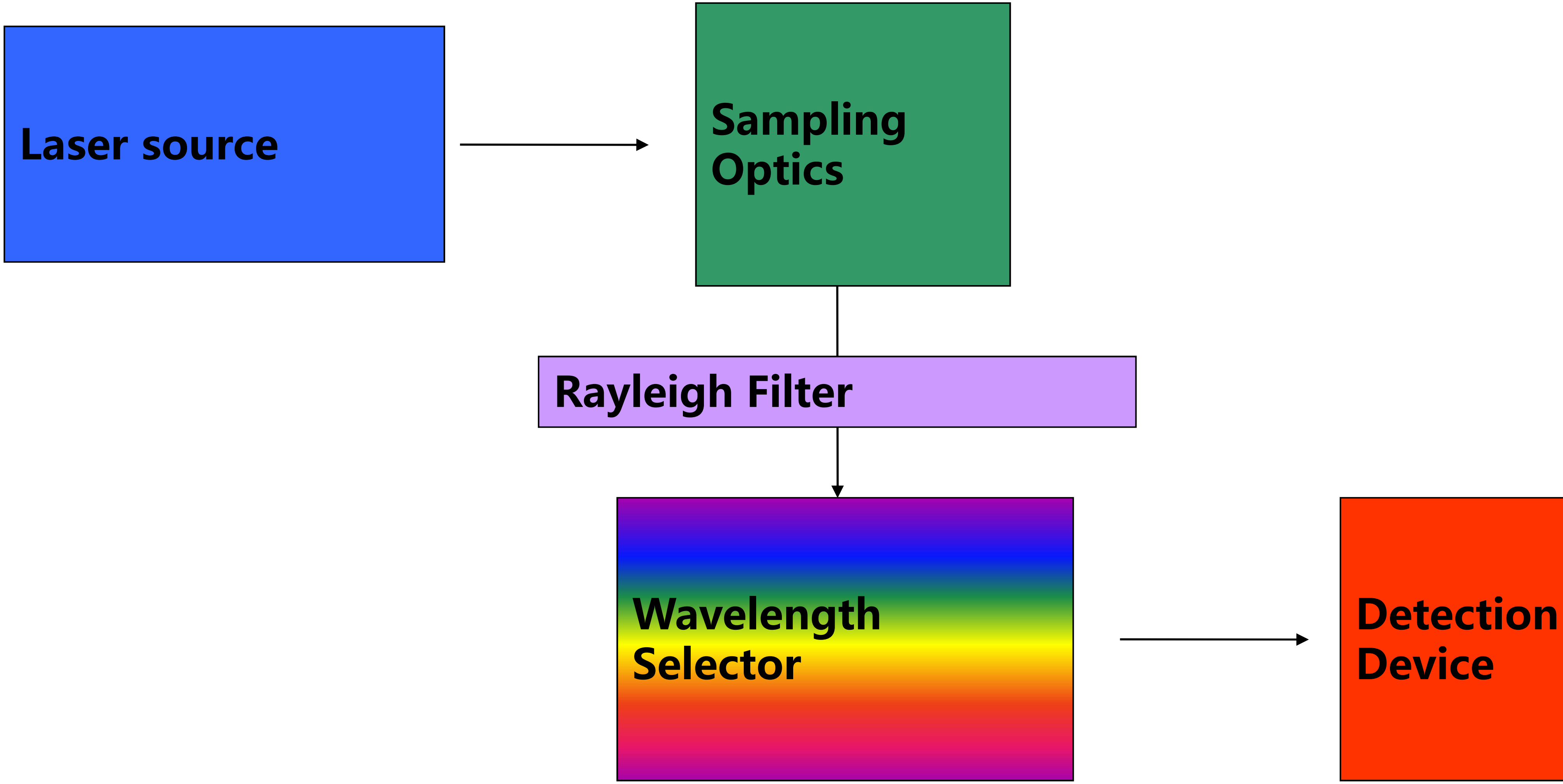


Diamond & Graphite



Basic Components of Raman system

aman Spectrometer



Laser source

Which laser shall I choose?

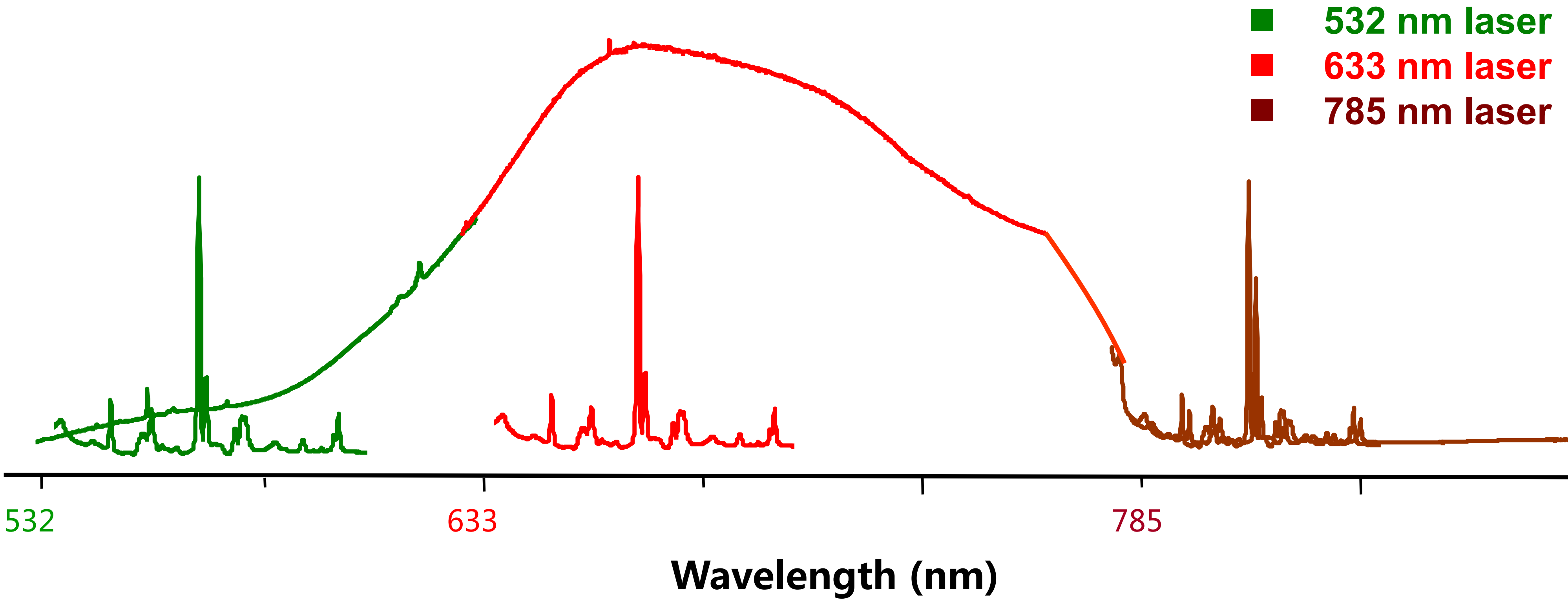
The relationship of the signal intensity with laser wavelength:

$$I_{Raman} \propto 1/\lambda^4$$

Choose short wavelength laser for each sample ?

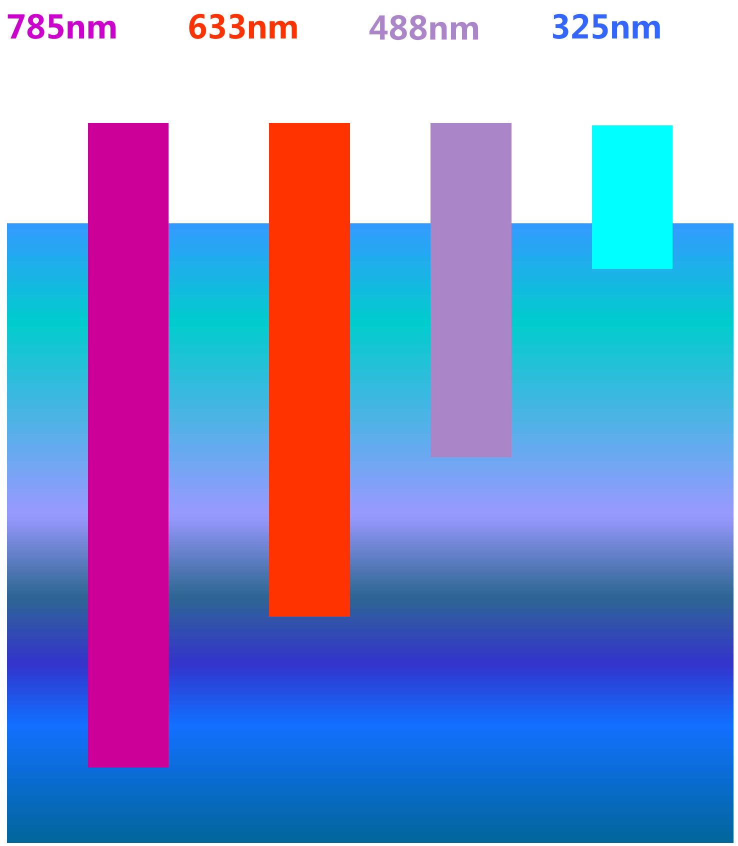
Theoretically YES. However, considering instrument response, green is the most common laser.

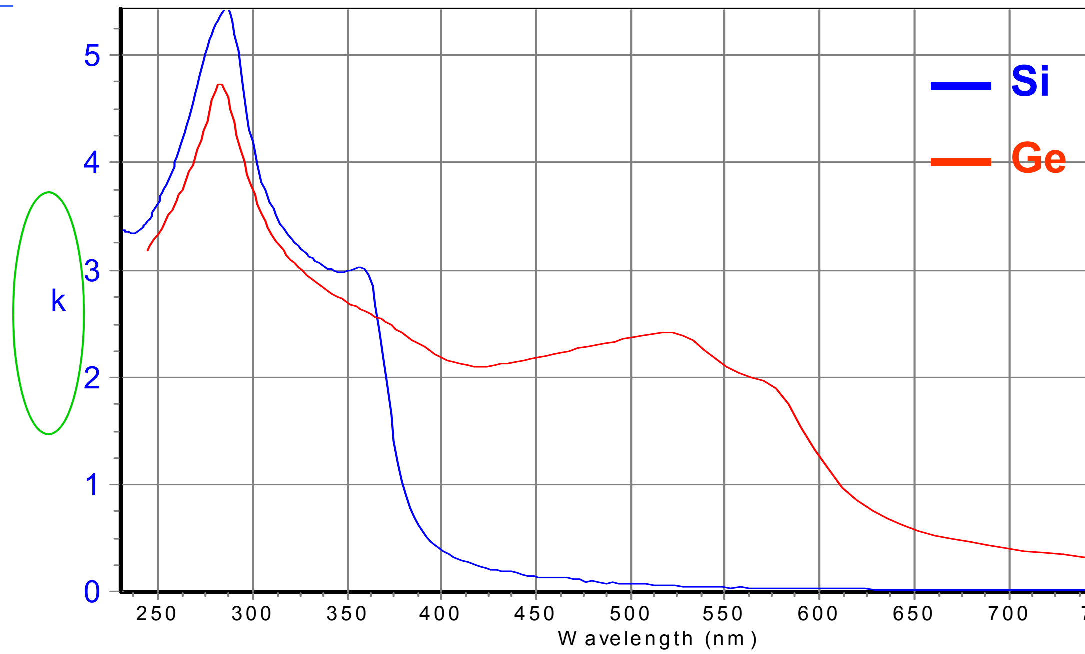
void Fluorescence Influence



Fluorescence emission will stay with the same wavelength (nm).
Raman will stay with the same wavenumber(cm^{-1}).

fo from Different Depths





$$D_p = \frac{1}{\alpha} = \frac{\lambda}{4\pi k}$$

D_p-penetration depth

K-extinction coefficient

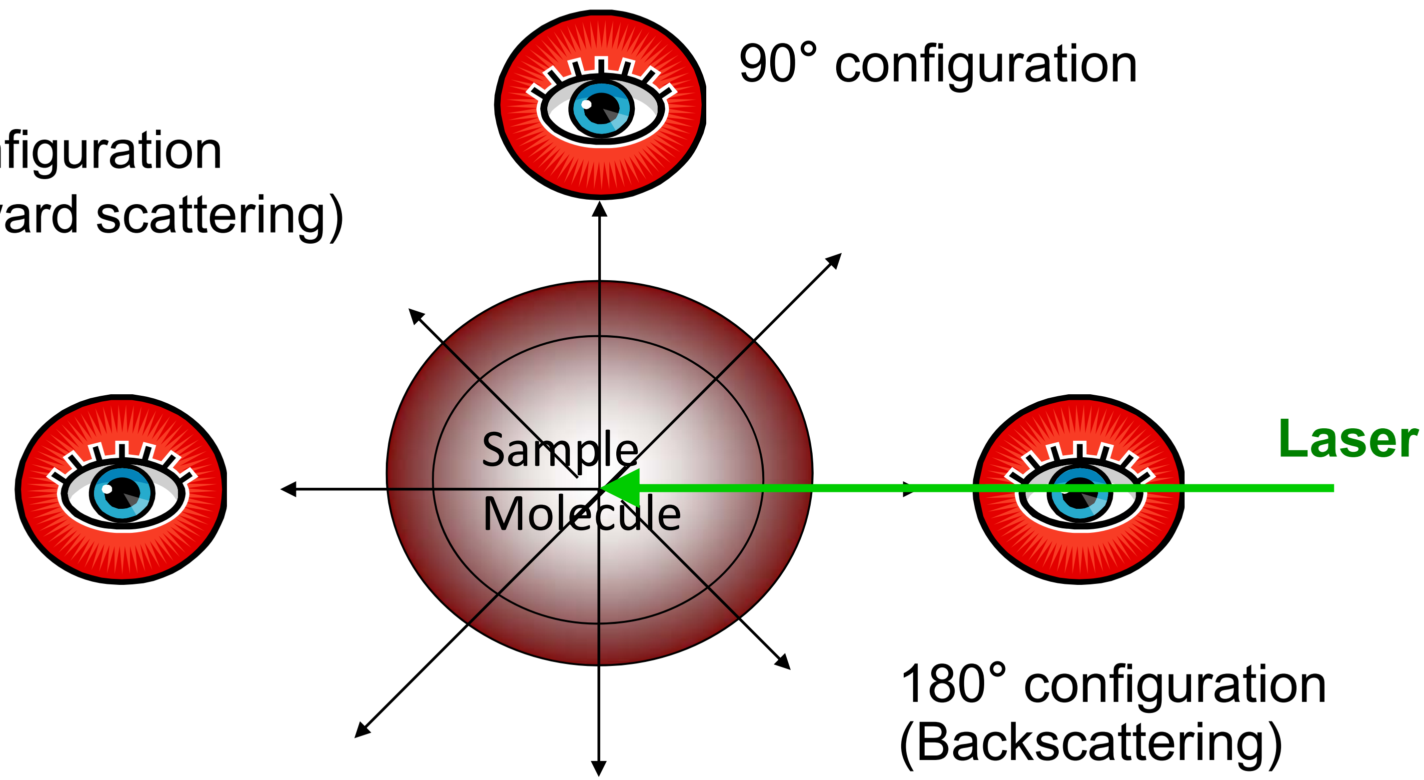
hy so many laser choices

1. To avoid fluorescence interference
2. To avoid black body interference
3. To probe at different depths
4. To benefit from Resonance

Sampling optics / Microscope

ampling Geometry

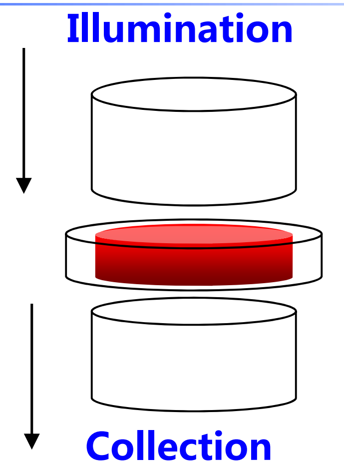
- Theoretically, Raman scattering can be observed from any angle. Practically and historically, three angles were favored; 0°, 90° and 180°.



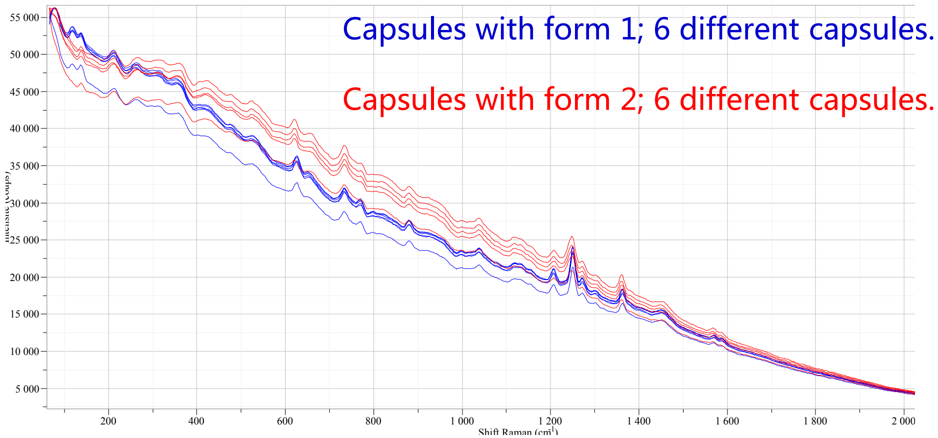
° Collection = Forward scattering

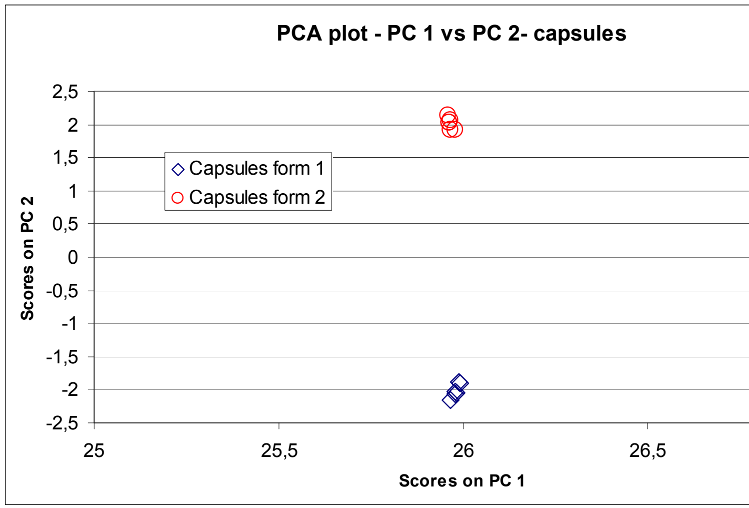
Transmission Raman (forward scattering)

- No spatial resolution
- Volume measurement
- No information about component distribution
- **Good statistical representation of the whole sample**



e.g. Transmission Raman of Capsules

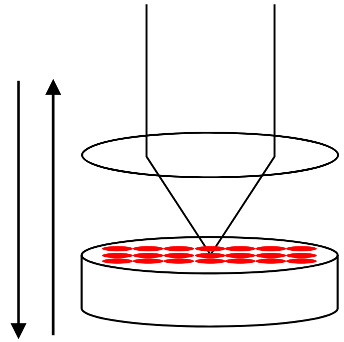




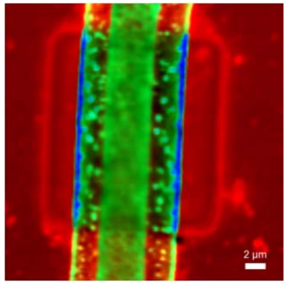
80 °Collection = back-scattering

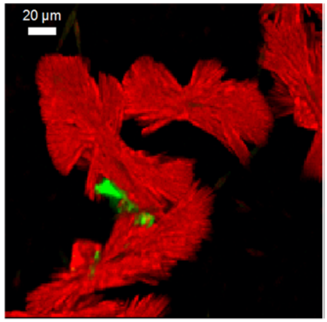
Raman Microspectroscopy (back-scattering)

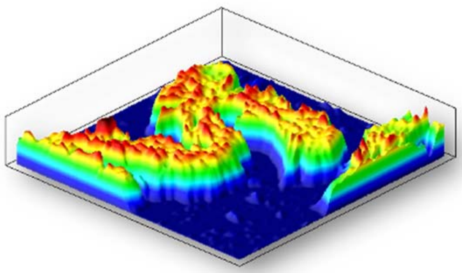
Illumination Collection

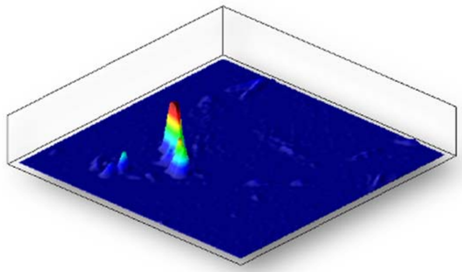


- Surface measurement
- Measurements of distribution of different components possible (Rama
  mapping)
- High spatial resolution
- **As a whole, good statistical representation of the <u>surface (limited</u>** **<u>by the penetration depth)</u>**

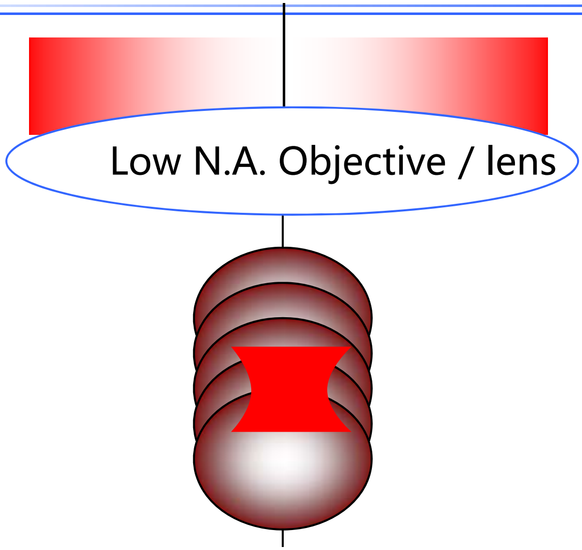


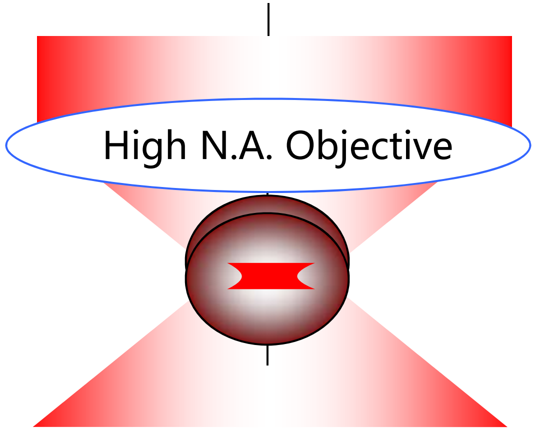




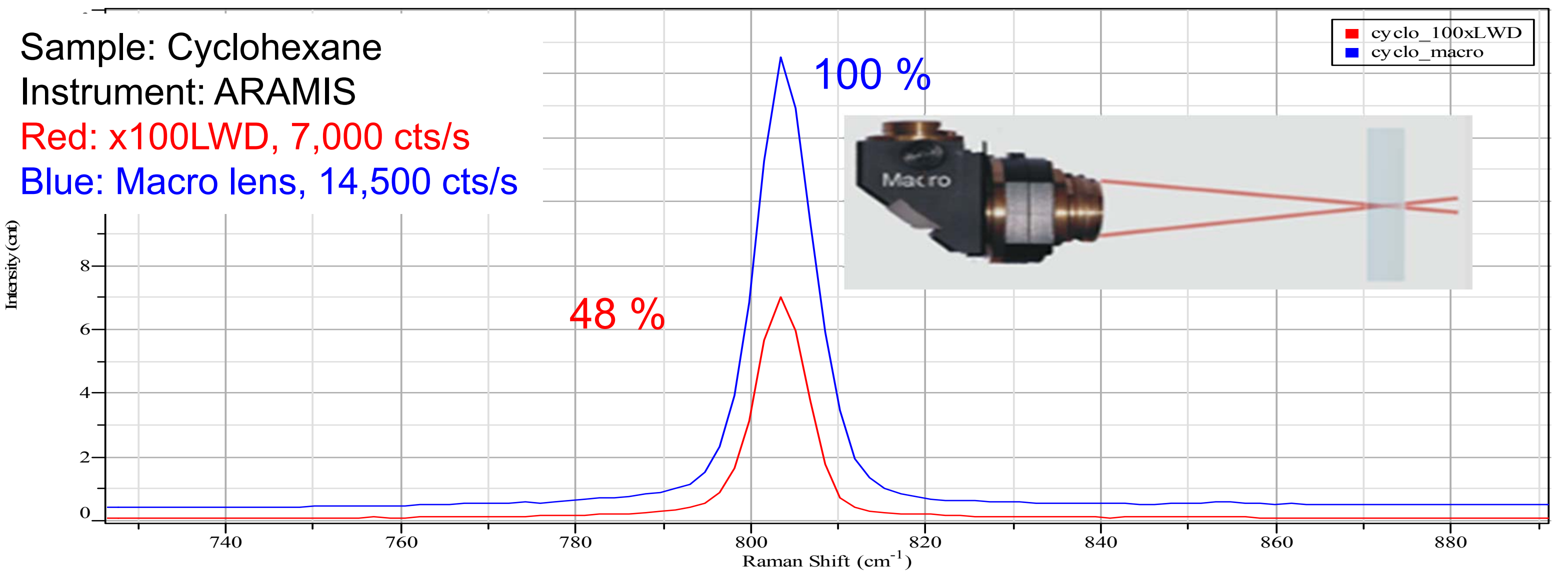


ranparent Sample





For **transparent samples,** low N.A. lens enables
- Large sampling volume → **increases sensitivity**

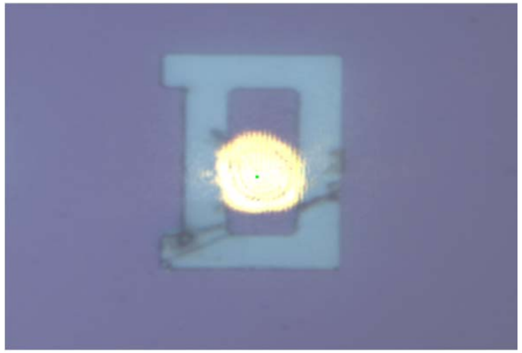


chromatic objective

HORIBA Scientific
Mirror based design :

We observe the sample image and the laser spot on the same plan.

Lens based design :



Optimized on sample image

Optimized on laser spot

The positioning of the measurement point is t
in X and Y, and almost impossible in Z.

PERFECT TOOL FOR UV-RAMAN MEASUREMENTS
Unique design from HORIBA!

Confocality

rue Confocal Microscope

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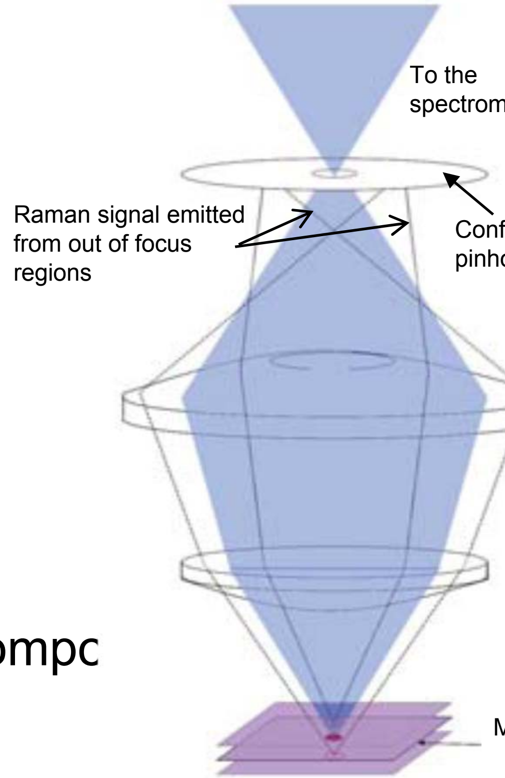
Advantages of confocal Raman:

- ✓ Tremendous improvement of axial resolution (~2 µm)
- ✓ Better lateral resolution (<1µm)
- ✓ Efficient reduction of fluorescence interference



Applications:

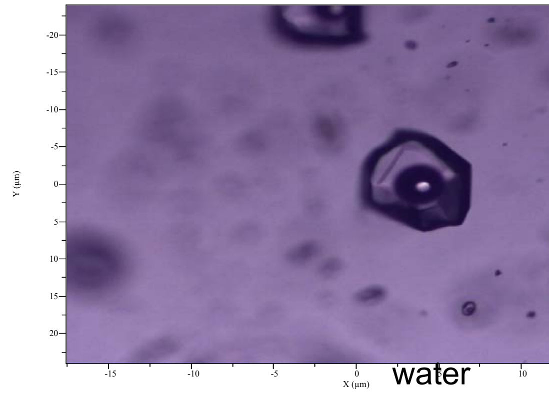
- Minute samples quantities – micron and sub-micron particles
- Thin films and multilayer samples
- Inclusions in matrices
- IMAGING : phases and components distribution (copolymers, compo

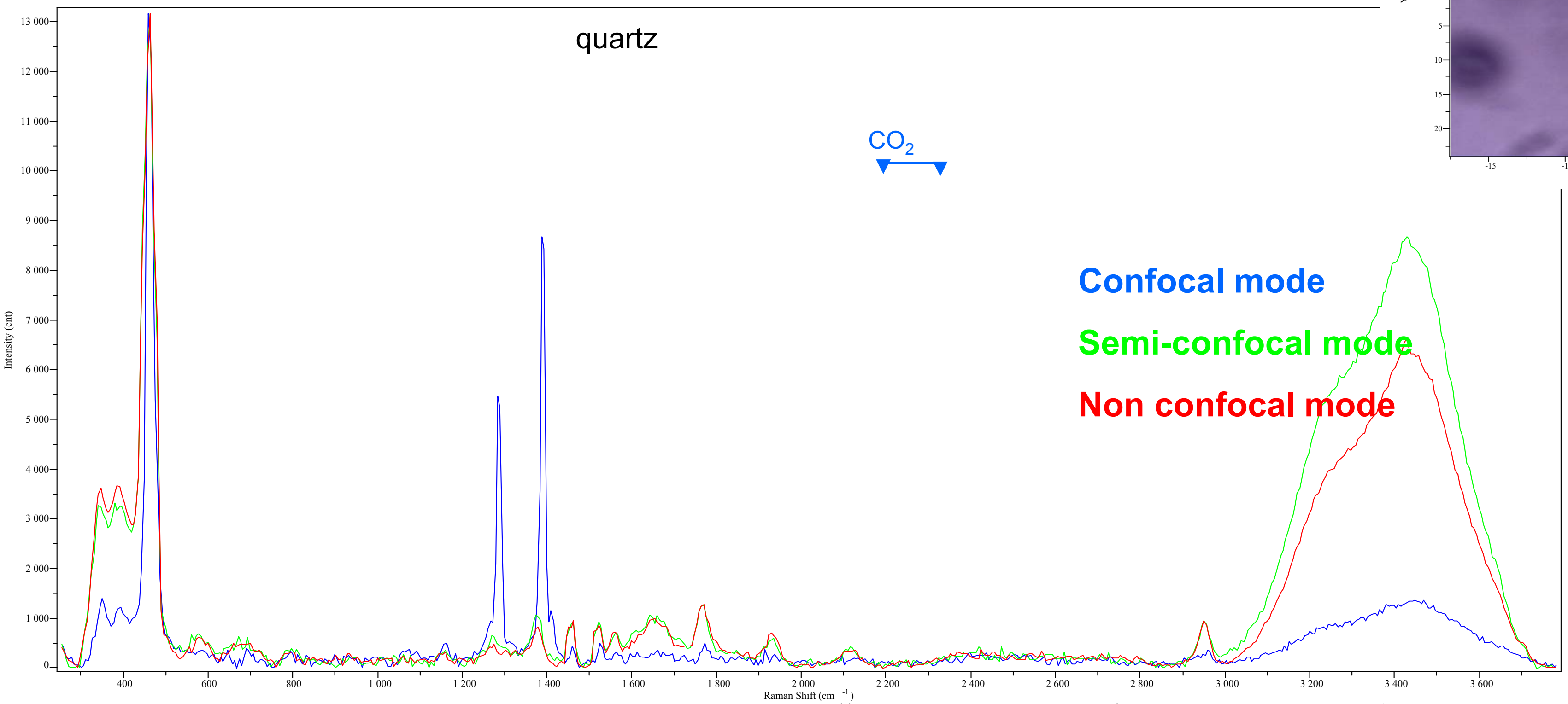
The confocal pinhole acts as an adjustable spatial filter allowing a precise selection of the analyzed volume.

Only LabRAM HR evolution has a continuously adjustable pinhole

nfocality for fluid inclusions

Fluid inclusion image: quartz matrix, water and CO2 inclusion





All spectra are normalized according to the quartz peak

The semi-confocal and the confocal modes enable to get less interference from the matrix signal (quartz) and improve the signal for each fluid: water in semi-confocal mode, CO_2 gas in confocal mod

gh lateral Resolution=diffraction limit

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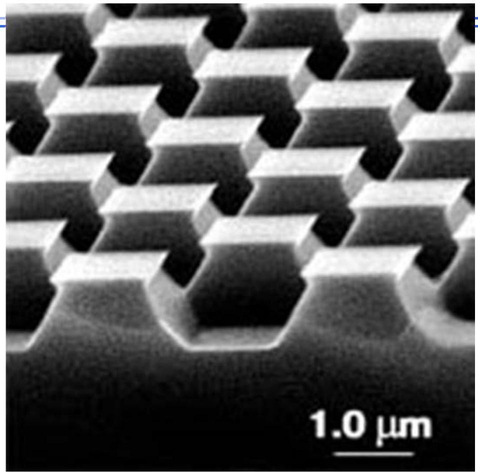
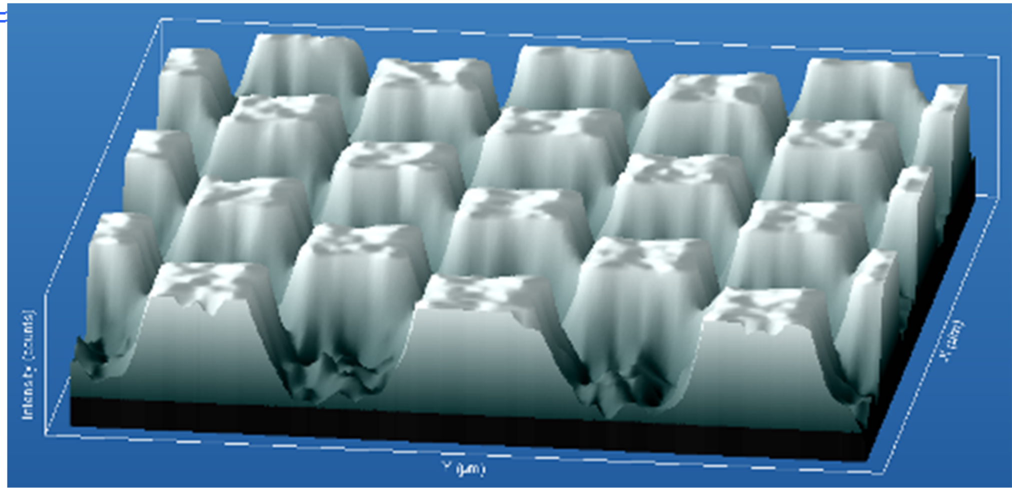
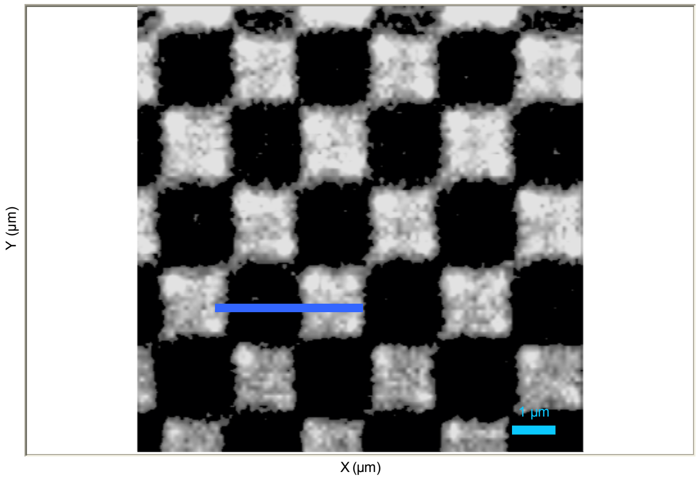
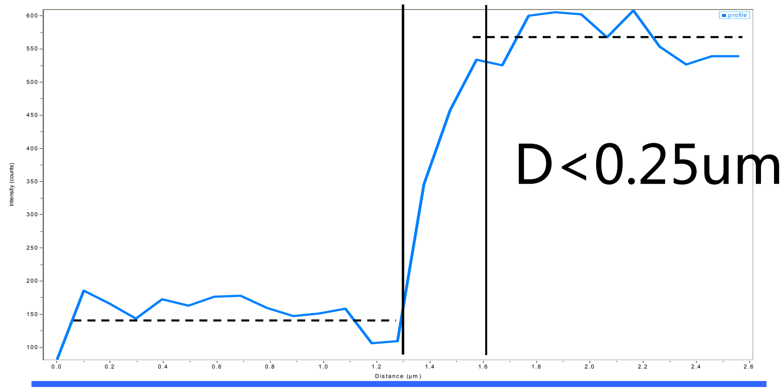


TGX calibration grating
Mikromasch



Measurement time 240s, 10201 points, 24 ms/points, 0.1um step
633nm , 100X/0.9, swift



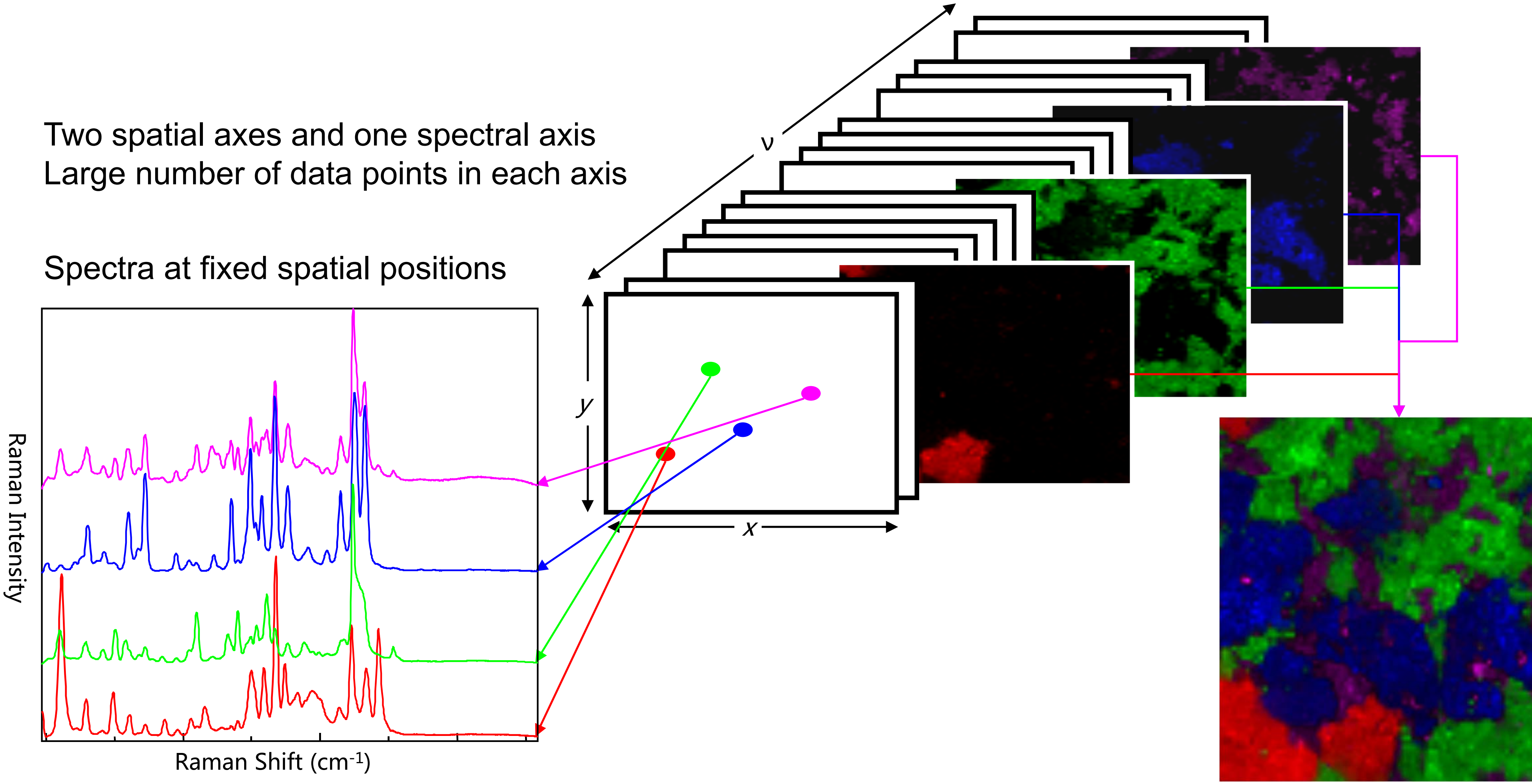


Raman imaging

hat is Raman mapping?

Two spatial axes and one spectral axis
Large number of data points in each axis

Spectra at fixed spatial positions

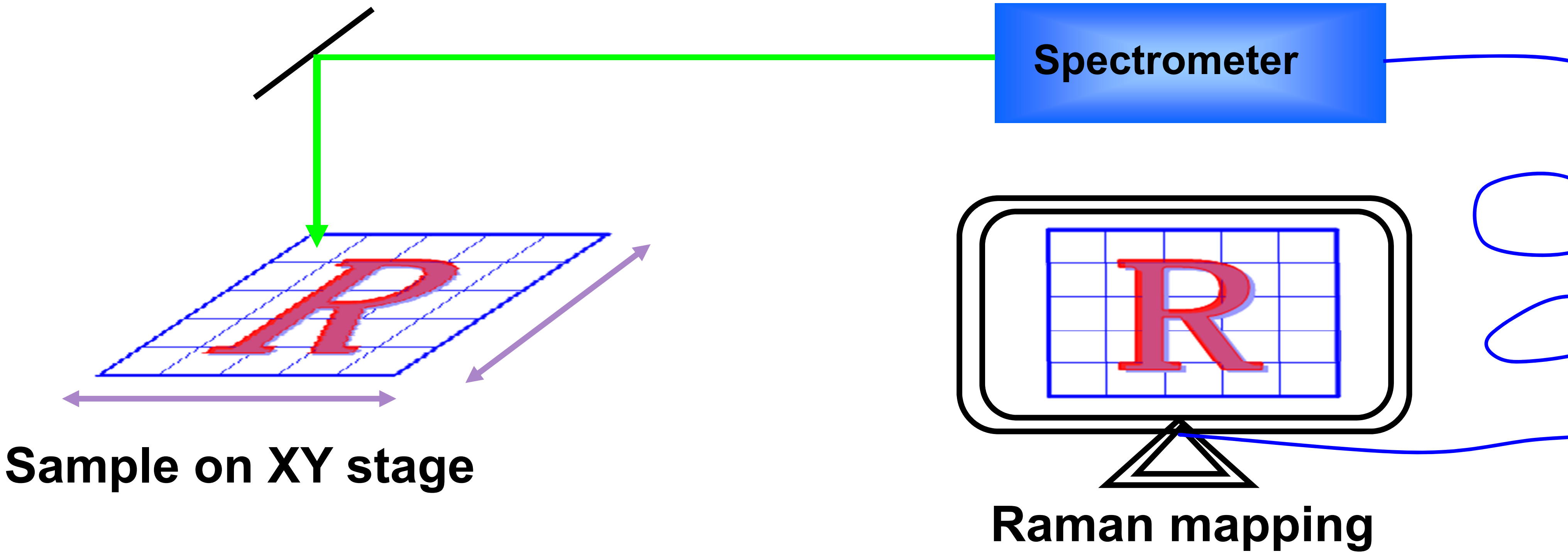


Images at fixed spectral pos

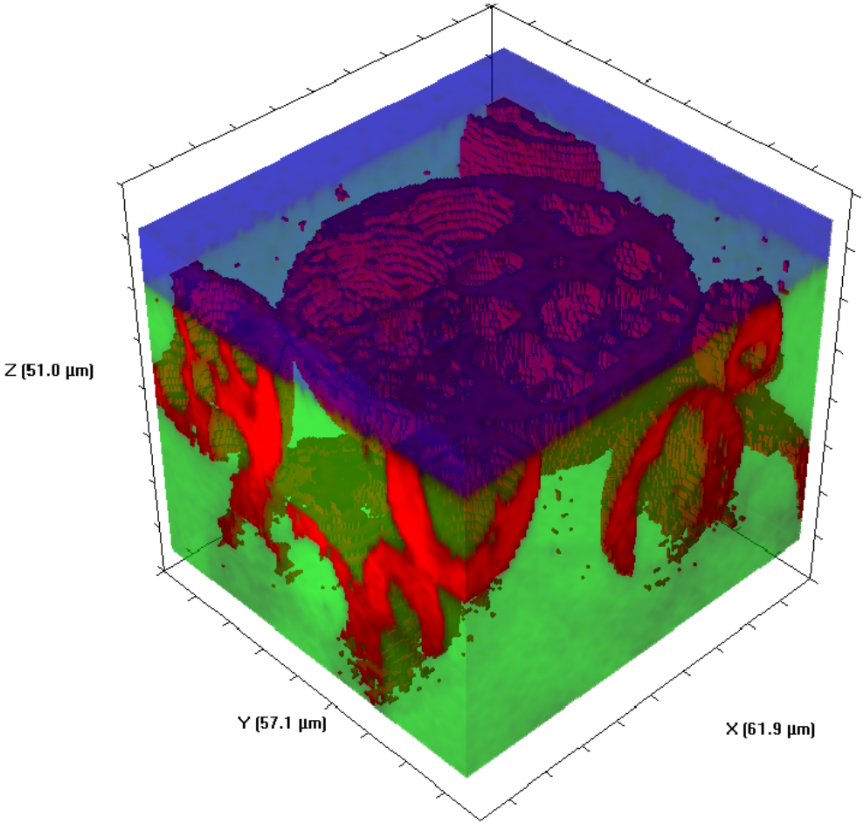
ow to make Raman Mapping?

For each point, the Raman spectrum is acquired.

The data cube is then analyzed with Raman band information (e.g. band position, bar width, band shift, etc.)



3D Imaging



Description:

XYZ volume map of expanded polymer bead in matrix.

System:	LabRAM HR
Laser:	660 nm
Grating:	300 gr/mm
Objective:	x100
Acq. Time:	0.8 s x 1
Step X:	1 µm
Step Y:	1 µm
Step Z:	1 µm
No. pixels:	186,992 (62X x 58Y x 52Z)

- Bead
- Matrix
- Oil (Immersion objective)

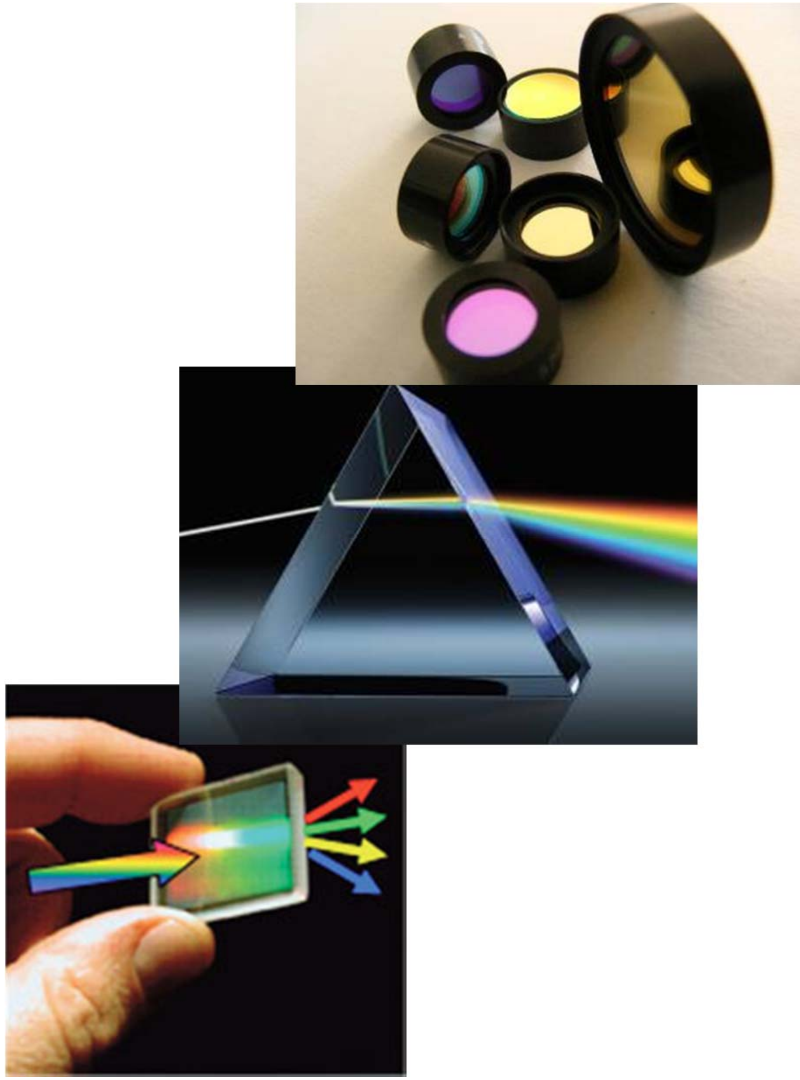
Filters

avelength Selector

Rayleigh is 10^9~10^{12} higher than Raman

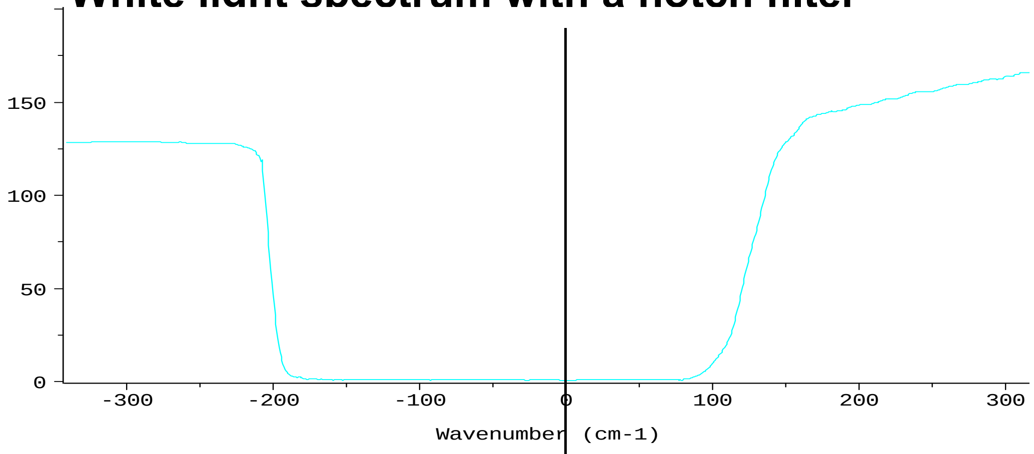
Method to filtrate Rayleigh:

- Filter
  - Edge
  - Notch
  - VBG
- Monochromator-Dispersive Raman
  - Dispersion by Prism
  - Dispersion by Grating
- Michelson Interferometer – FT-Raman

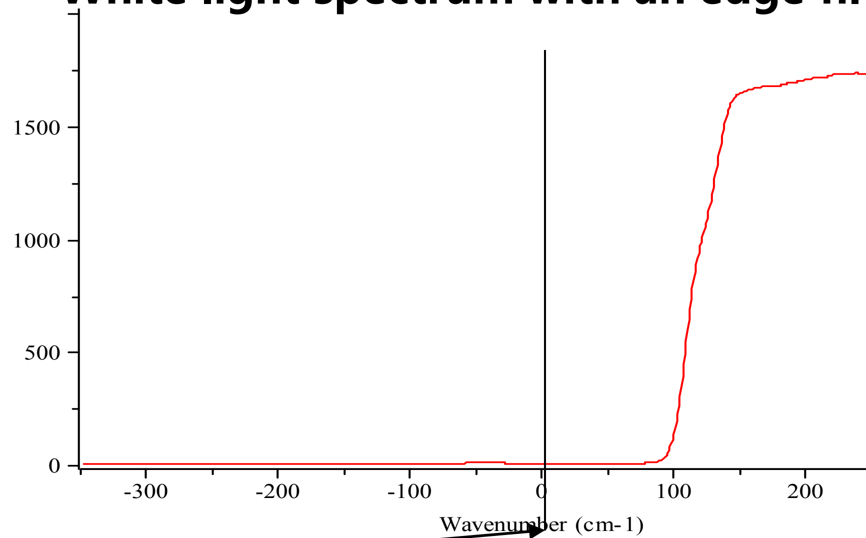


otch filter & edge filters

White light spectrum with a notch filter



White light spectrum with an edge fil



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 use dielectric edge filter due to good cut-off and no aging, but An Stokes-Raman is not obtainable.
Notch dielectric filters are available but their cut-off is not as good as holographic Notch filters.

ltra Low Frequency Applications

Examples

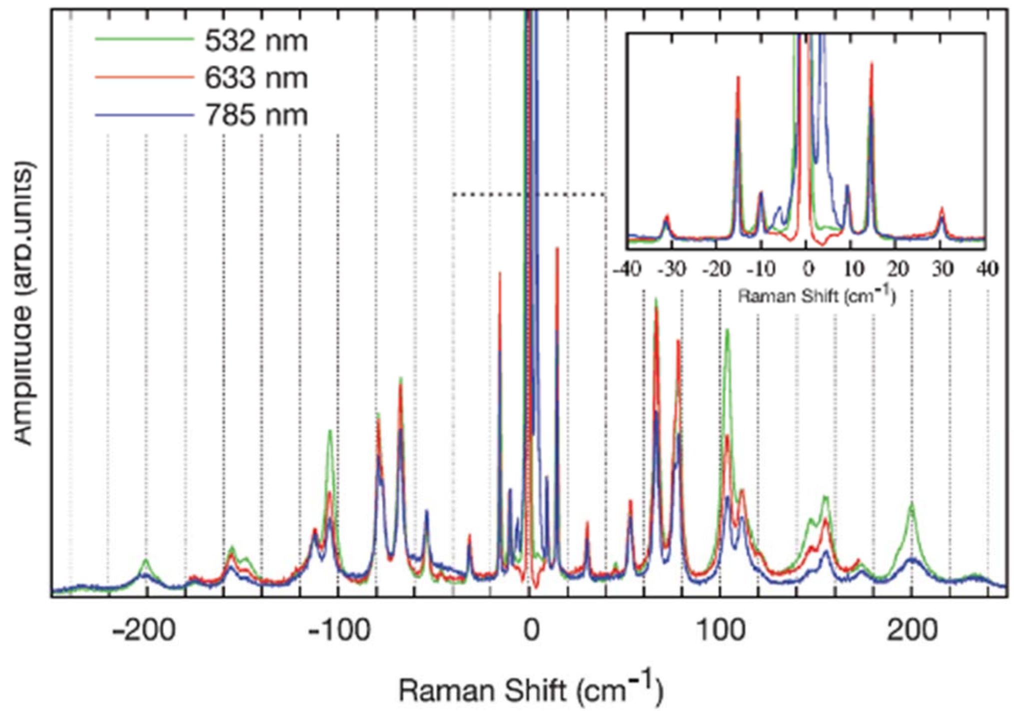
- ULF bands of protein molecule.
- "Boson peak" in amorphous glasses to study the liquid-glass transition.
- ULF vibration modes in minerals and organic materials, such as sulfur and L-Cystine.
- Radial breathing mode of carbon nanotubes and quantum dots.
- Shear mode of graphene.
- Relaxation modes in liquids, binary mixtures and solutions.
- Acoustic modes

tration with Volume Bragg Gratings BGs)

Ultra low frequency detection by VBGS:

- Down to 10 cm^{-1}
- Both stokes and anti-stokes
- Easy to make ULF on single stage spectrometers.

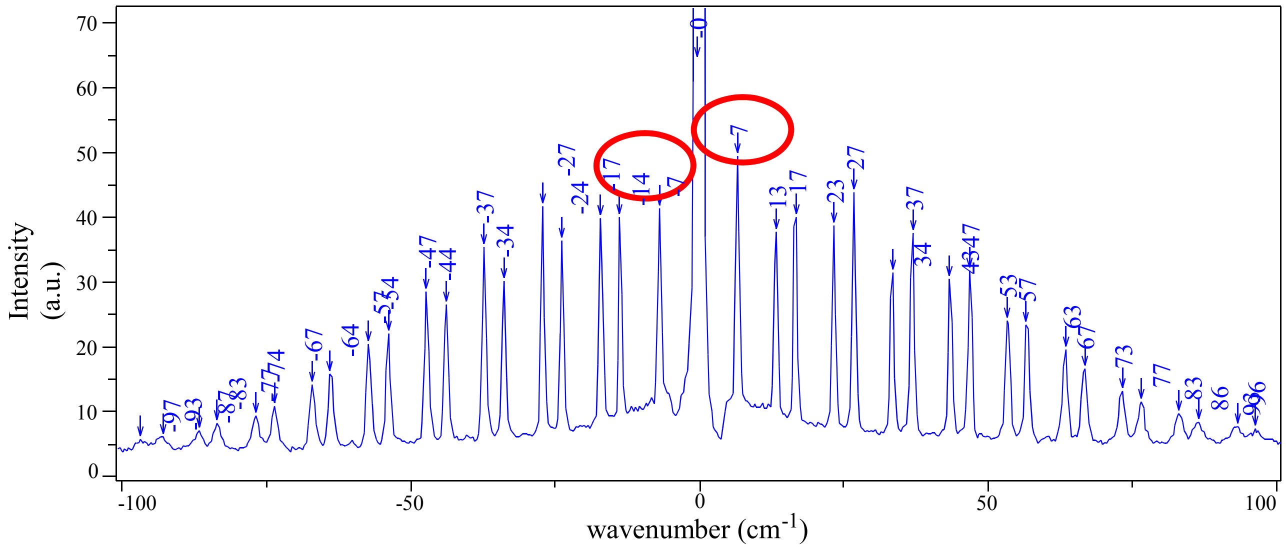
- **VBGs filters replace substractive monochromator filtering**

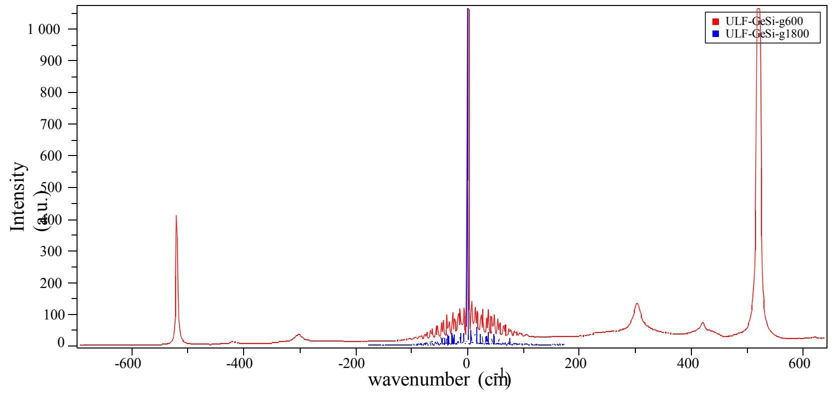


ULF Raman measurements of L-Cystine at 532, 633, and 785 nm wavelengths. Stokes and Anti-Stokes bands at 9 cm^{-1} are clearly resolved at all wavelengths.

ULF Results

SiGe superlattice spectrum @ 633 nm





Red: grating 600 - Blue: grating 1800

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

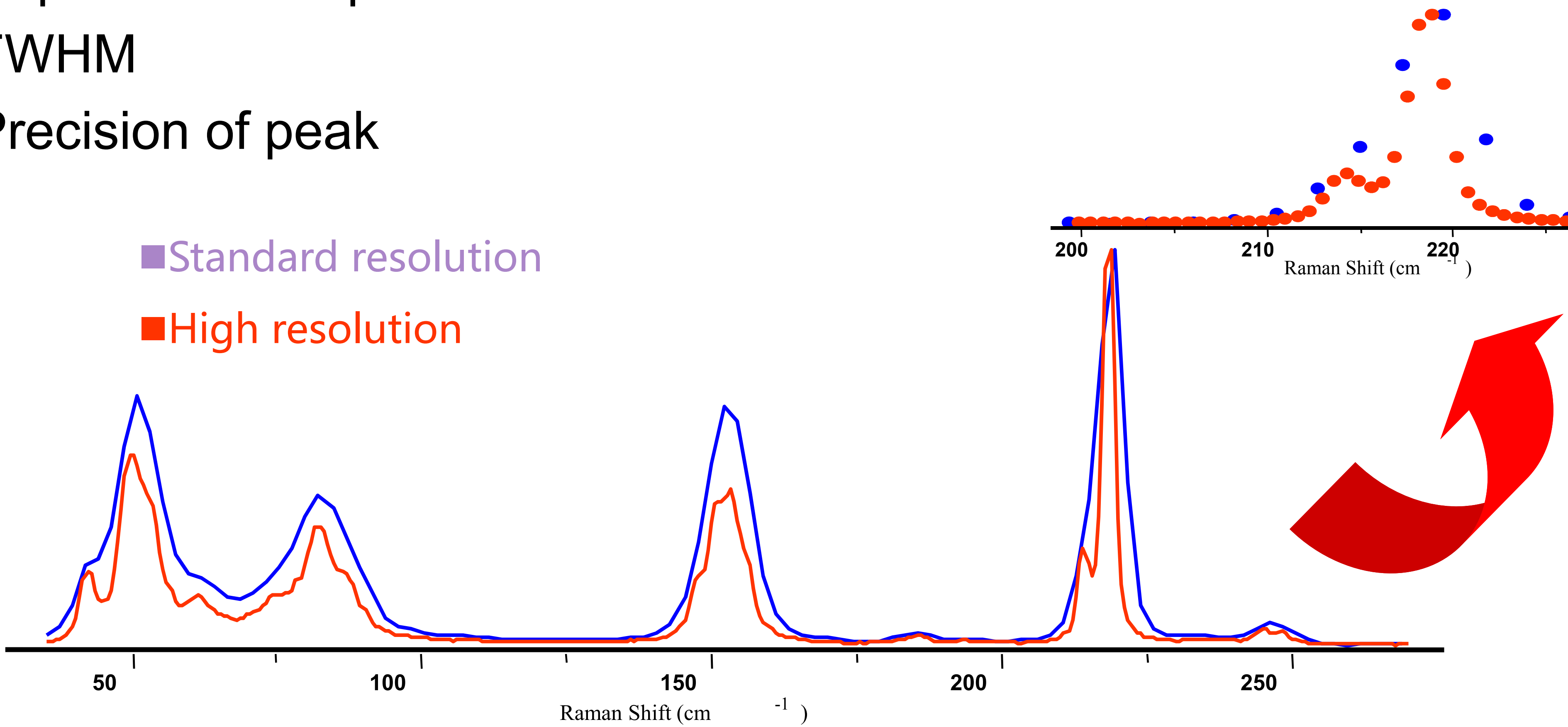
Key points/Lock-out specs

- Preserves high throughput advantage of single stage spectrographs (favoring sensitivity, mapping speed…)
  - 3 BNF on the Raman path have a transmission >70% @ 633 nm
  - In comparison, standard edge filter has a transmission of about 95%
- Allows measurements down to 10 cm^{-1} (sometimes less depending on λexc & sample reflectivity/scattering efficiency)
- Stokes and anti-stokes features measured simultaneously
- Allows to measure the entire Raman/PL range

Spectrometers

Spectral Resolution

- Separation of 2 peaks
- FWHM
- Precision of peak



hy is high resolution required?

The Stress of Si can be characterized by the peak

In this case, the max shift is 0.5 cm^{-1} which requires a HIGH SPECT RESOLUT

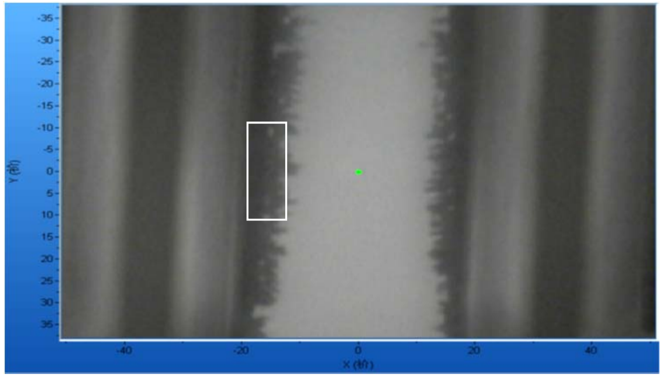
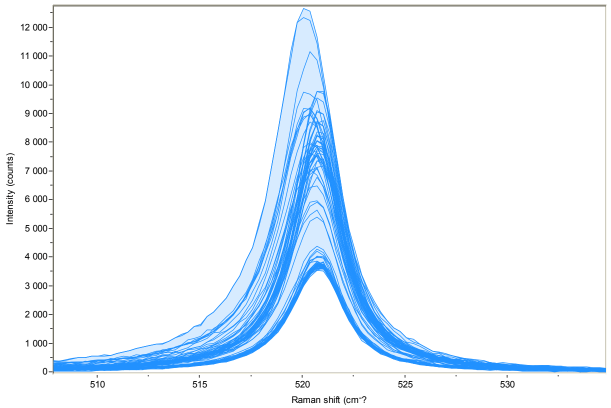
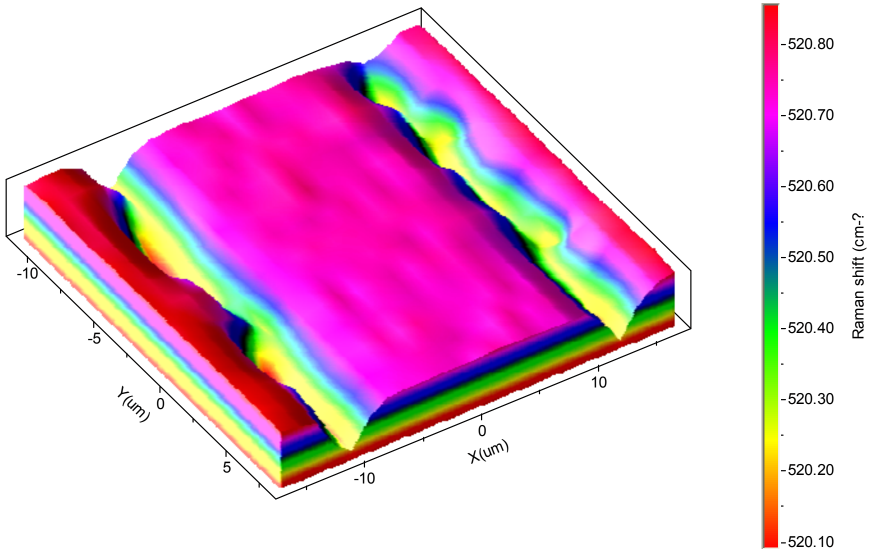


Image of Si chip



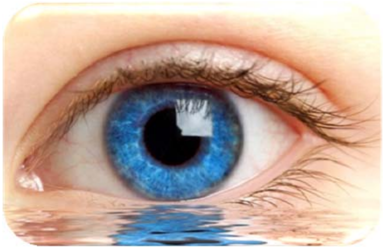
Raman spectra



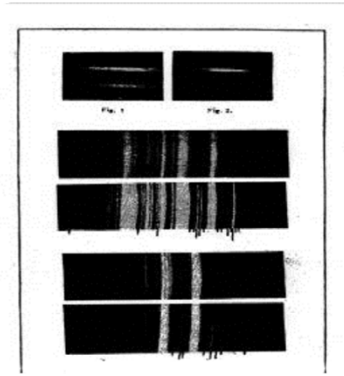
Distribution of Si stress from Raman mapping

Detection

aman Detection Device History



Human Eyes



Photosensitive Plate

PMT

CCD

Choice of a Multi Channel Detector

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The choice of a multi channel detector depends on:

- Spectral range (UV, Vis, NIR)
- Spectral resolution (pixel size)
- Sensitivity (QE of front vs. back illuminated detectors)
- Raman or Luminescence (etaloning in back illuminated cameras)
- Long or short integration time (TE versus LN_2 cooling)

LabSpec 6

Spectroscopy Suite

owerful!

- Spectrum database searching*
  - Chemical identification within seconds
- Multivariate Analysis (MVA)*
  - Obtain results, fast
- ParticleFinder*
  - Automated particle location and characterization
- 3D Surface and Volume display*
  - Full display capabilities for 2D and 3D data
- MultiWell high throughput screening*
  - Fast analysis of well plates and microtitre plates

power

* Optional modules

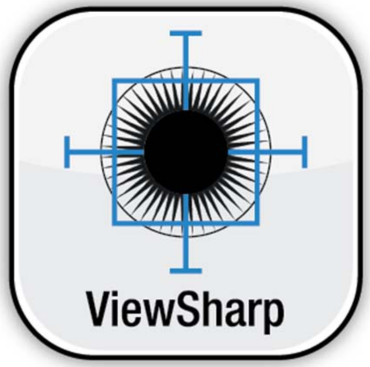
Ease of Use

LabSpec6: EasyNav package

“Easily navigate through high power microscopic images in an easy and sharp manner and acquire sharp Raman images”

+

+



EasyNavTM package is more than just tracking!

NavMap™

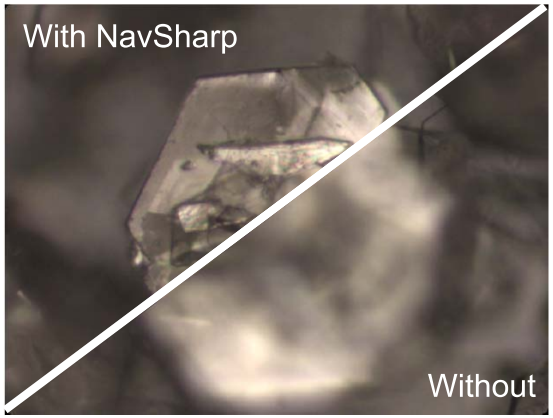
NavMap™=Navigation Map

• takes low mag image of sample
• instantly know where you are on your sample
• easier to navigate, click & pan directly on the low mag NavMap image, no need for joystick anymore for enhanced user experience

NavSharp™

NavSharp™ =Sharp Navigation

• real time tracking of the focus based on video image competes with Renishaw LiveTrack, but much faster



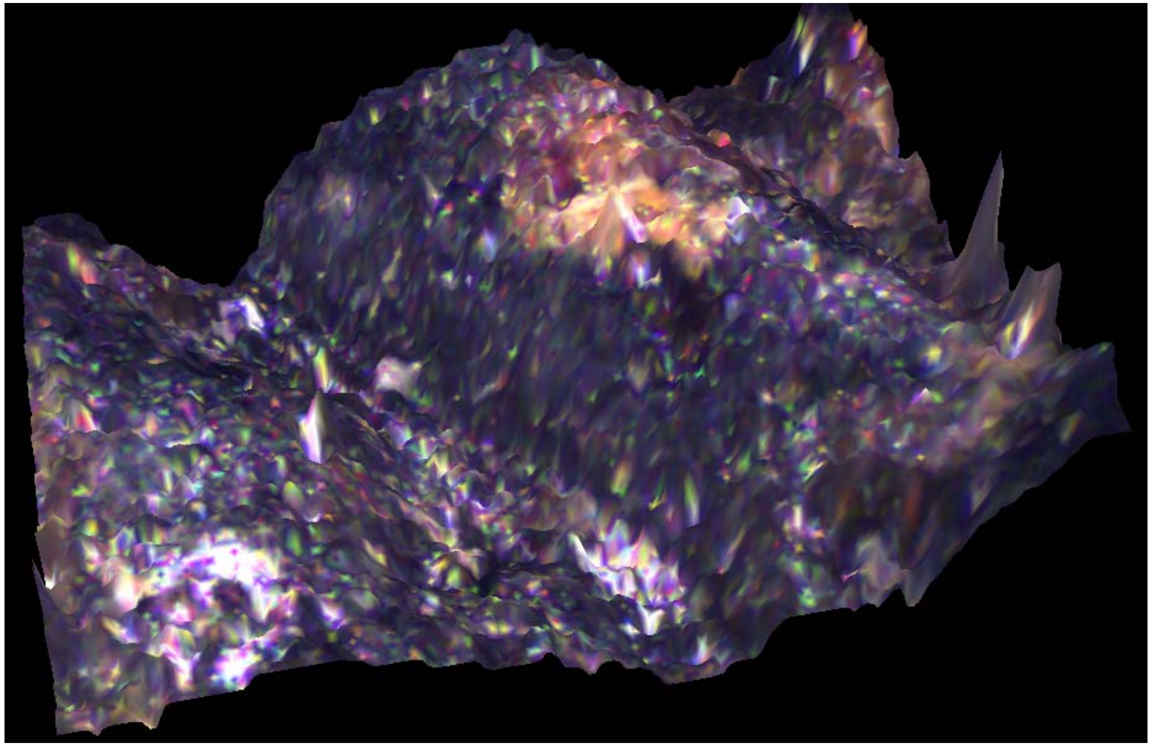
ViewSharp™

ViewSharp™=Viewing Sharply

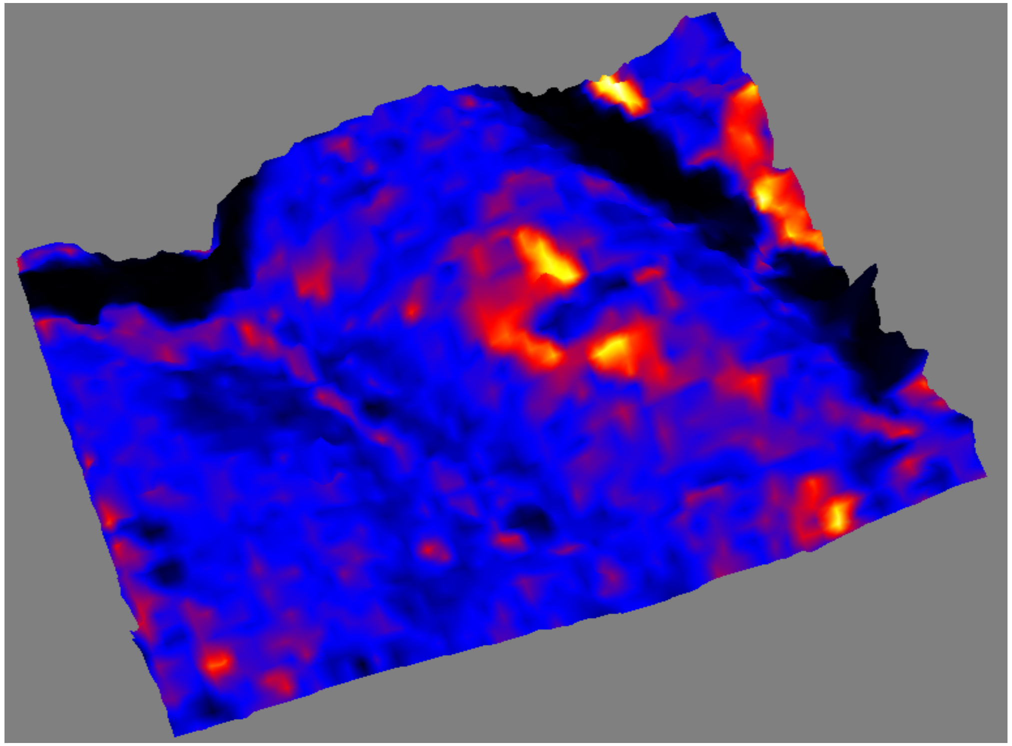
• another add-on compared to LiveTrack; builds the complete image in focus
• gives an instant 3D topography of the sample
• much faster than autofocus of laser at each point
• 0.2µm XYZ resolution with 100X image

ViewSharp example

3D – image of Rutile



3D - Raman image

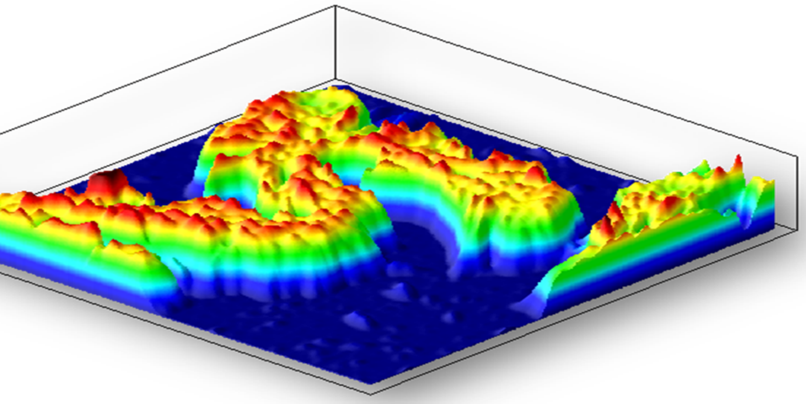


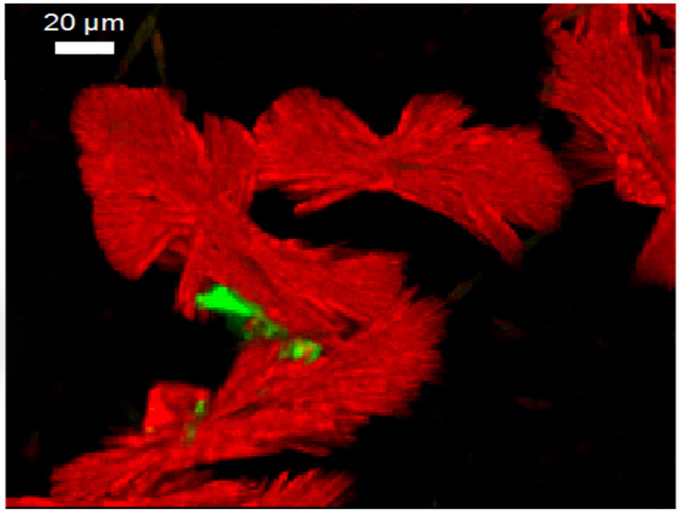
Imaging and Display

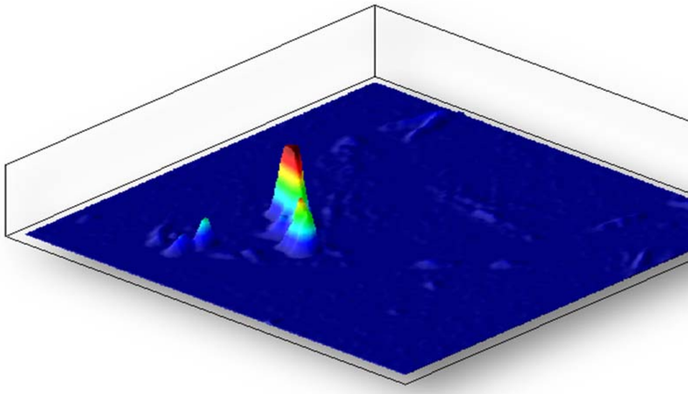
Image processing

2D and 3D image display modes

Sodium sulfide crystal forms







3D Surface/volume display

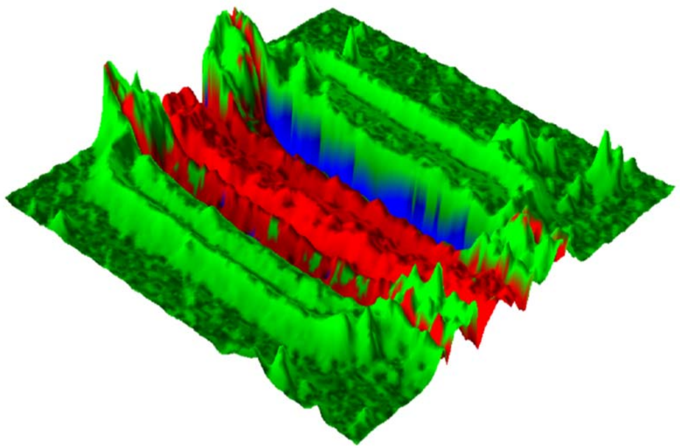
Advanced display module for

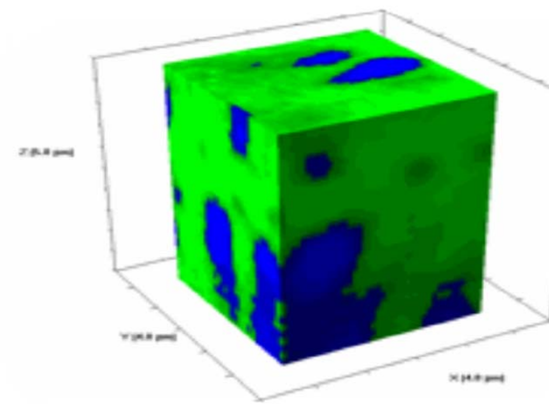
- 2D images as 3D surfaces
- 3D volumes

Full display control

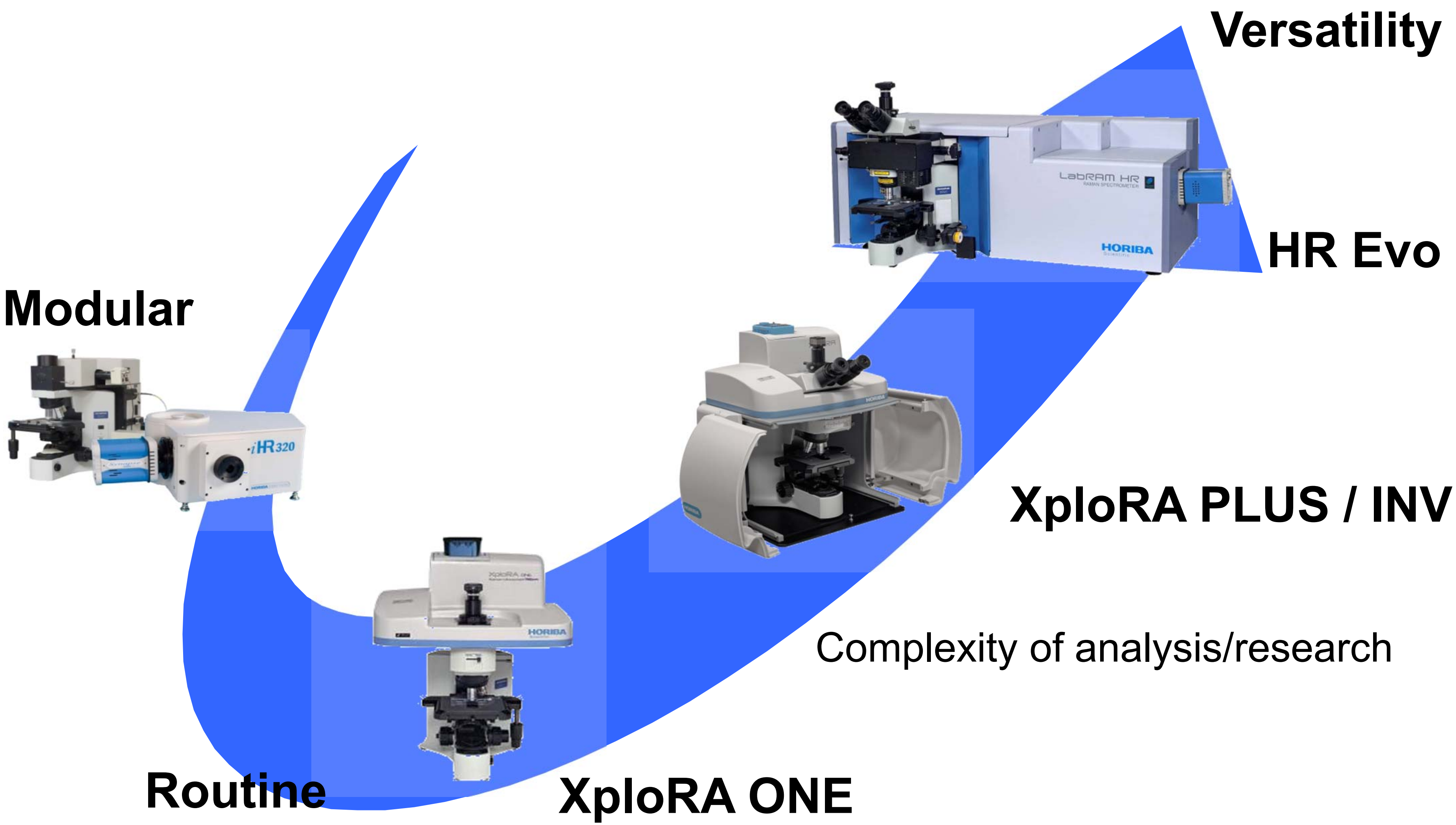
Lighting | rotation | transparency | slicing

OPTION





HORIBA Scientific
ONE Raman solution for everyONE



Thank you

Omoshiro-okashiku

Joy and Fun

감사합니다

Cảm ơn

ありがとうございました

Dziękuję

धन्यवाद

Grazie

Merci

谢谢

நன்ற

ขอบคุณครับ

Obrigado

Σας ευχαριστούμε

Tack ska ni ha

شُكْرا

Большое спасибо

Danke

Gracias