# Raman instrument and application

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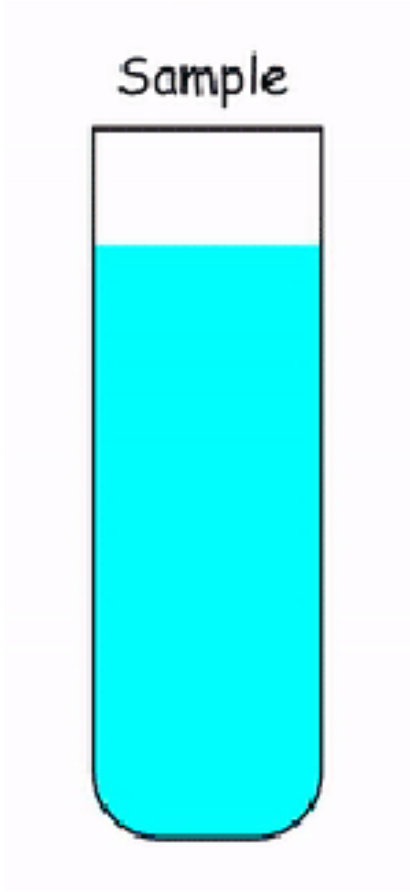
# When the light is illuminated to the sample…..
## *What happens?*



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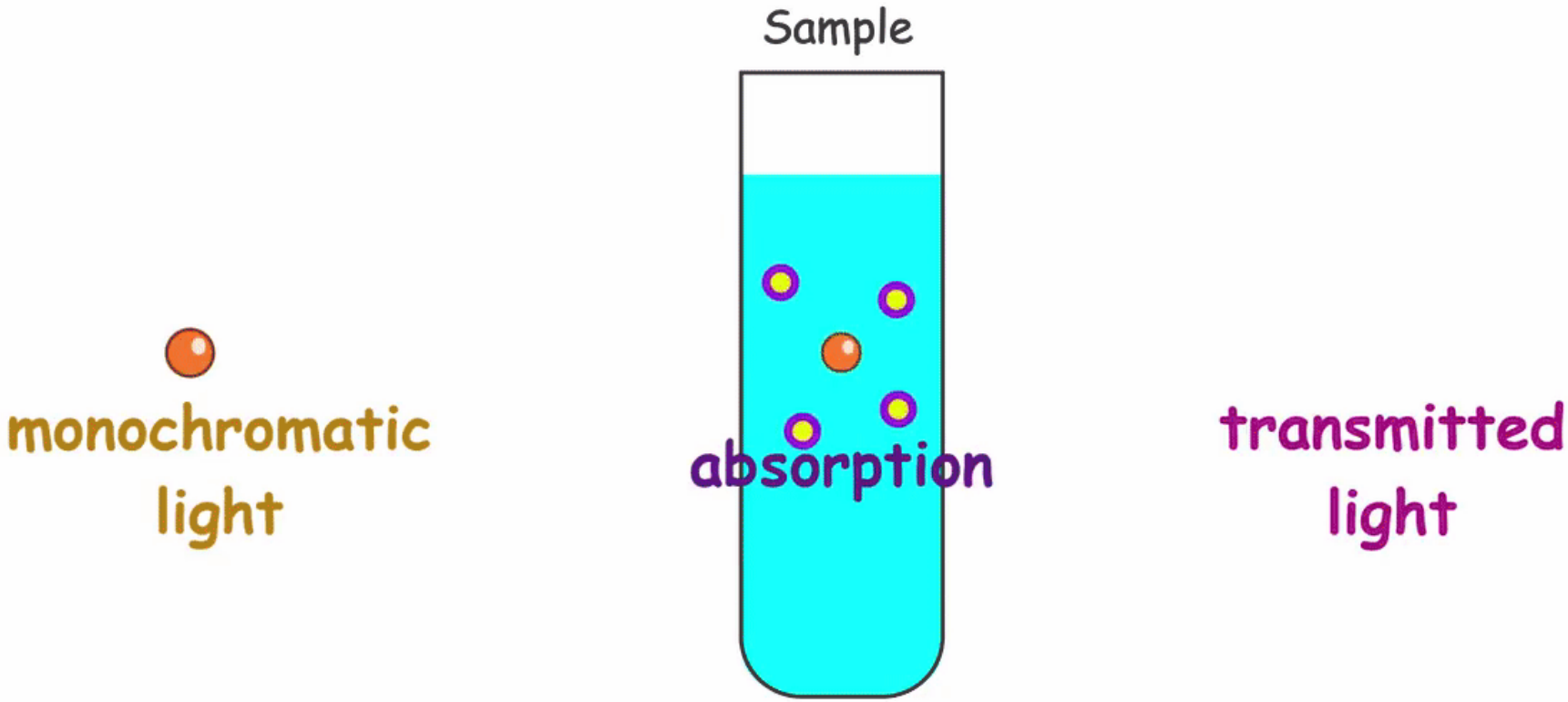
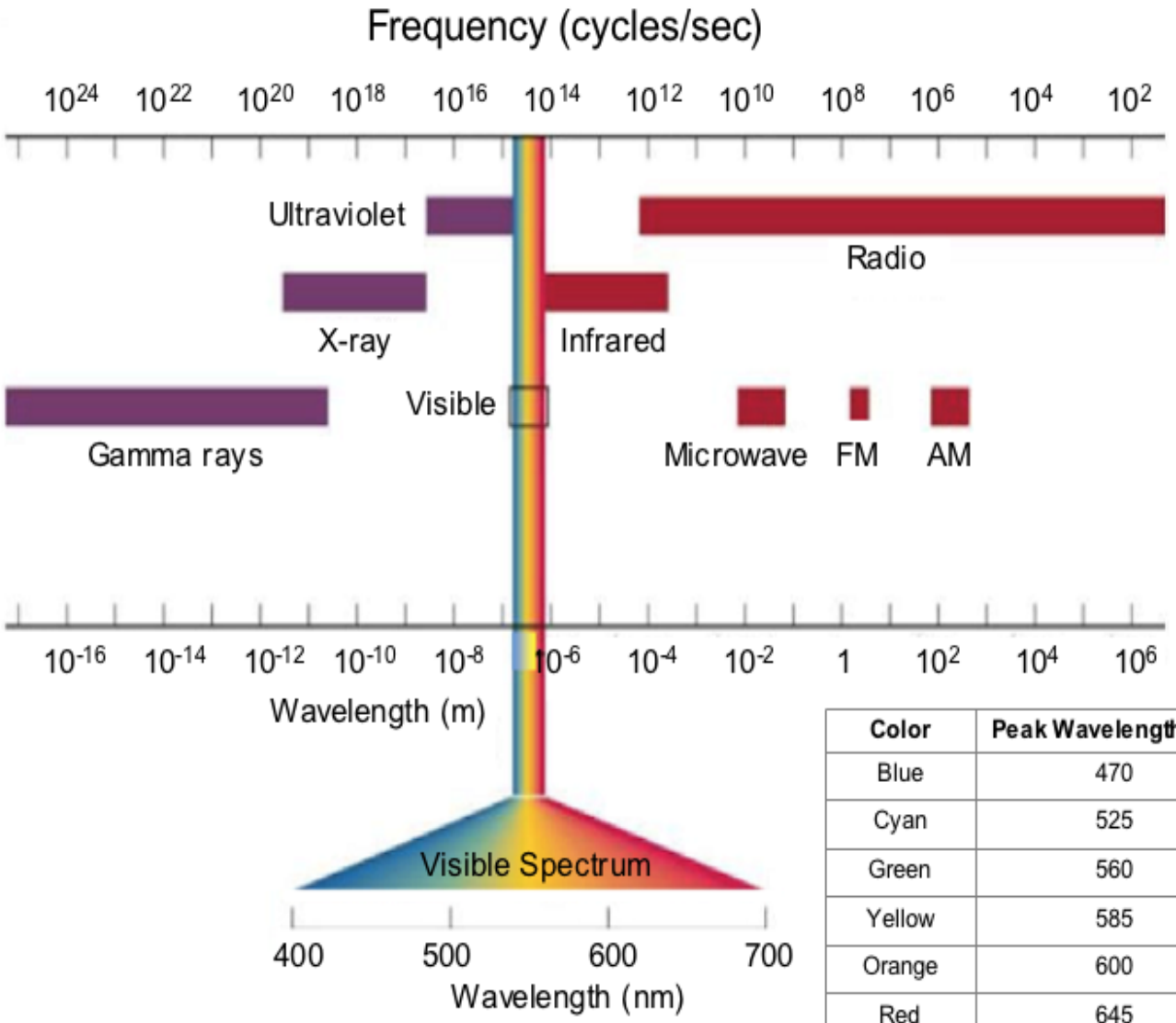



*Only for schematics & understanding*

https://studiousguy.com/raman-spectroscopy-uses/#Principle_of_Raman_Spectroscopy

# Spectroscopy
# “Light” – “Matter” interaction

# Spectroscopy techniques



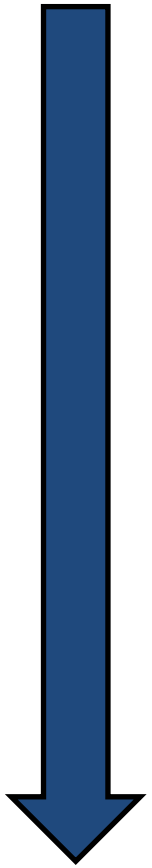

| Color | Peak Wavelength [nm] |
|---|---|
| Blue | 470 |
| Cyan | 525 |
| Green | 560 |
| Yellow | 585 |
| Orange | 600 |
| Red | 645 |
| Deep Red | 700 |

# Spectroscopy techniques

- X-ray fluorescence spectroscopy
  - Emission spectroscopy,
  - Studies electronic states
- UV/Vis spectroscopy
  - Absorption spectroscopy
  - Studies electronic states
- Fluorescence spectroscopy
  - Emission spectroscopy
  - Studies electronic states
- **Raman spectroscopy**
  - **Scattering spectroscopy**
  - **Studies vibrational states**
- **IR spectroscopy**
  - **Absorption (or reflection) spectroscopy**
  - **Studies vibrational states**
- Microwave spectroscopy
  - Absorption spectroscopy
  - Studies rotational states

**Vibrational spectroscopy**

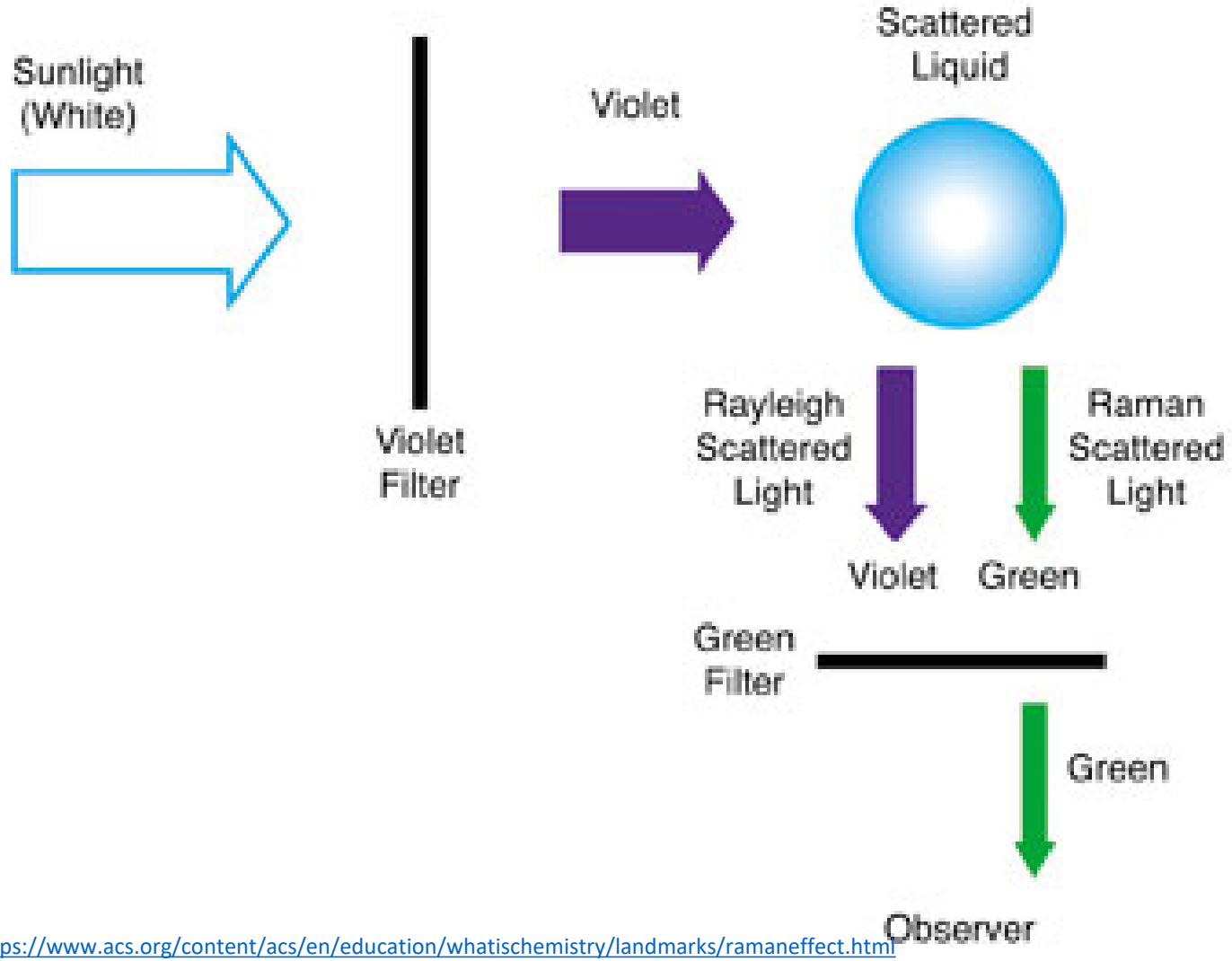
**High frequency, short wavelengths**



**Low frequency, long wavelengths**

# The Raman effect: History

- First experimental observation of the inelastic **scattering** light by **C. V. Raman** (Nobel prize, 1930) and K. S. Krishnan.
  (Light source: filtered beam of sunlight)




https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/ramaneffect.html

*Nature* **volume 121**, pages 501–502 (1928)

## A New Type of Secondary Radiation.

If we assume that the X-ray scattering of the 'unmodified' type observed by Prof. Compton corresponds to the normal or average state of the atoms and molecules, while the 'modified' scattering of altered wave-length corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and



*Nature* **volume 122**, pages 12–13 (1928)

: Benzene

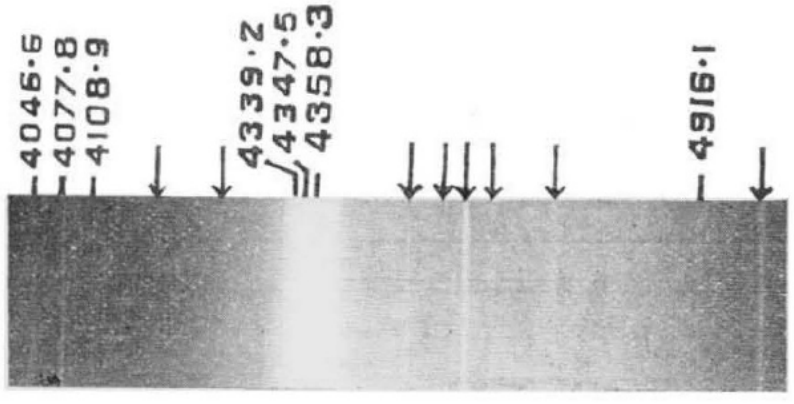



Fig. 1.



shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse radiation of the ordinary kind, having the same wave-length as the incident beam, is accompanied by a modified scattered radiation of degraded frequency.

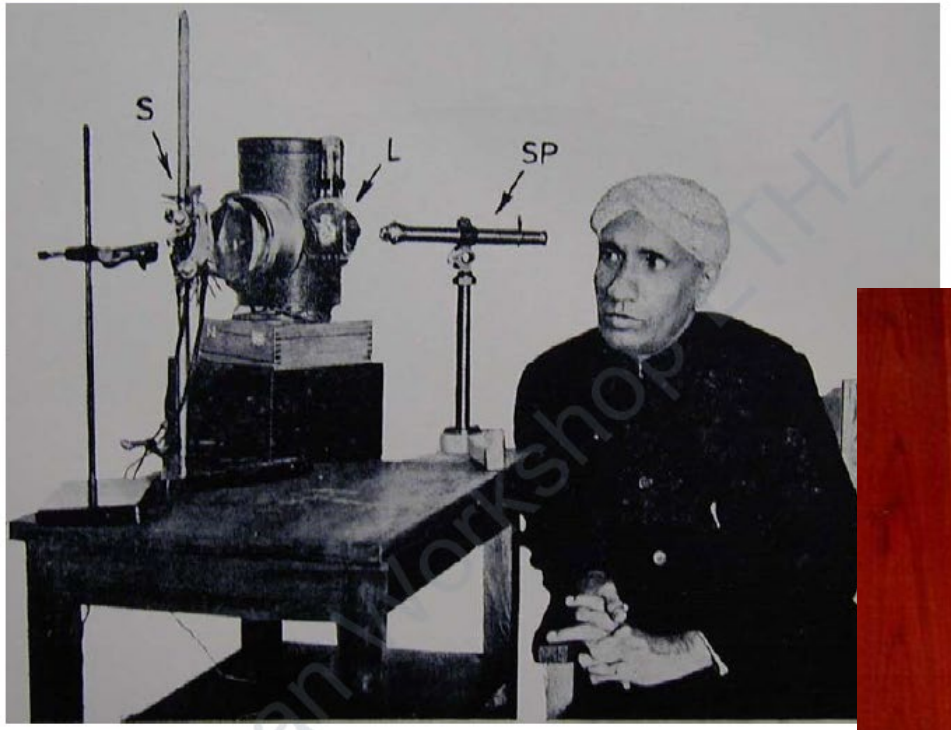
The new type of light scattering discovered by us naturally requires very powerful illumination for its observation. In our experiments, a beam of sunlight was converged successively by a telescope objective of 18 cm. aperture and 230 cm. focal length, and by a second lens of 5 cm. focal length. At the focus of the second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation *in vacuo*) or its dust-free vapour. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapour. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.

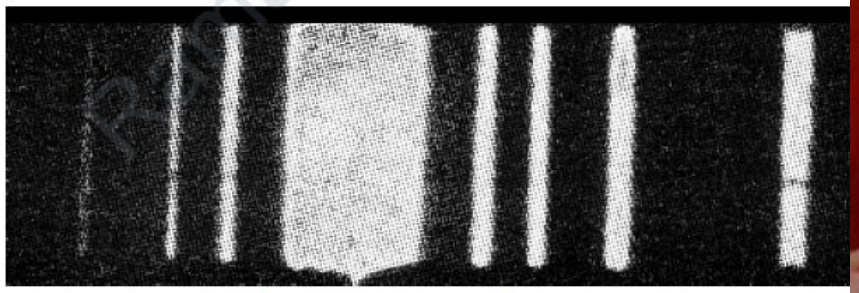
Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering and not a fluorescence is indicated in the first place by its feebleness in comparison with the ordinary scattering, and secondly by its polarisation, which is in many cases quite strong and comparable with the polarisation of the ordinary scattering. The investigation is naturally much more difficult in the case of gases and vapours, owing to the excessive feebleness of the effect. Nevertheless, when the vapour is of sufficient density, for example with ether or amylene, the modified scattering is readily demonstrable.

C. V. Raman.
K. S. Krishnan.

210 Bowbazar Street,
Calcutta, India,
Feb. 16.

# Discovery of the Raman Effect (1928; NPP 1930)



aS R S

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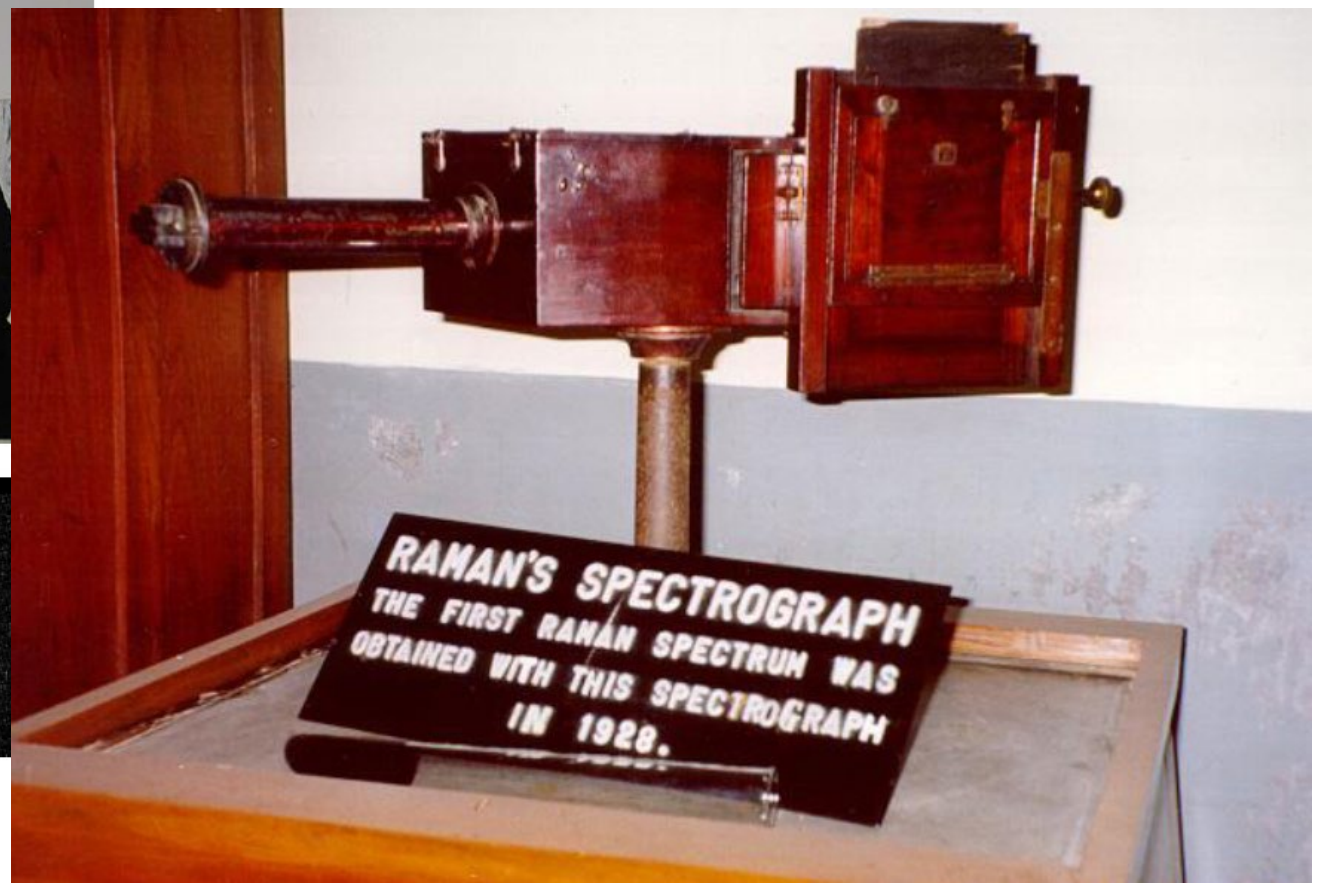


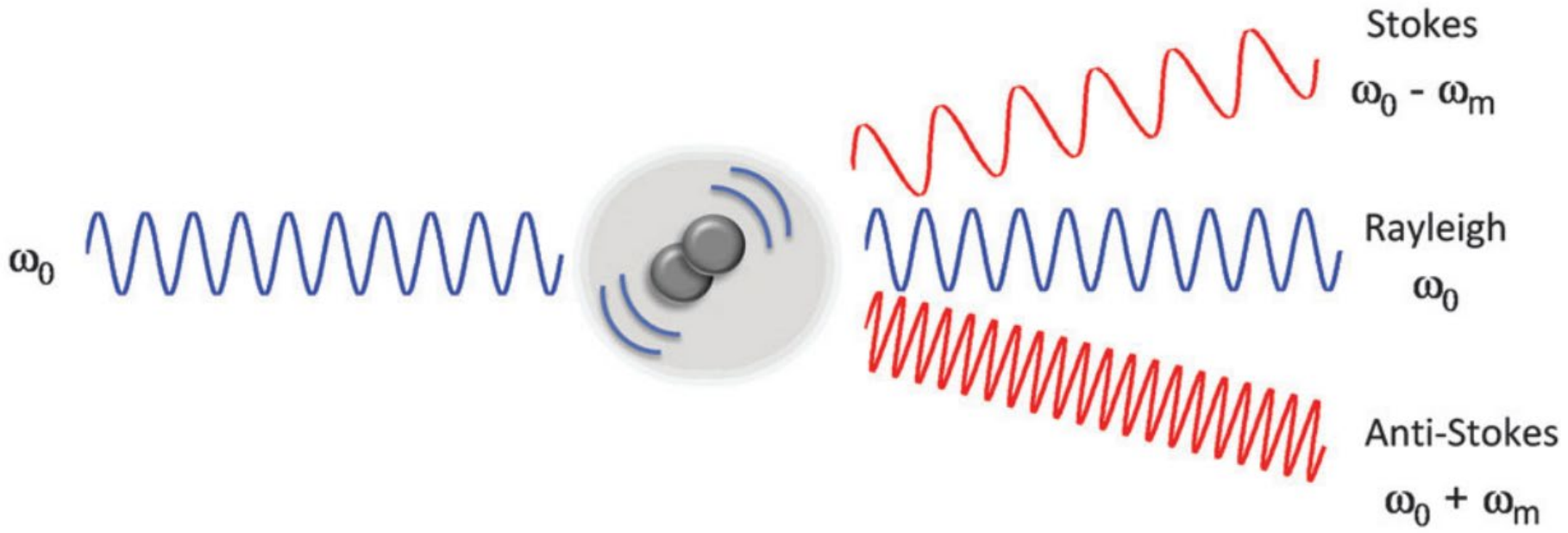
# Visual Guide to Raman Spectroscopy

# The Raman effect

Light interacting with matter can either be **elastically** or **inelastically** scattered.

- The ***elastic*** process (no energy is exchanged) is called **Rayleigh scattering**.

- The ***inelastic*** process (photon energy loss or gain) results in scattered light of different wavelength compared to the incident light : **Raman scattering**, **Brillouin scattering**



# What could be the origin of the Raman effect?

# Classical Description of the Raman Effect

**Incident electric field:**

$$E = E_0 \cdot \cos \omega_0 t \quad (1)$$

**Induced dipole moment:**

$$\mu = \alpha E \quad (2)$$

Induced Polarization

Polarizability

**(1) in (2):**

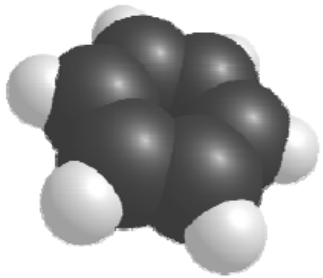
$$\mu = \alpha E_0 \cos \omega_0 t \quad (3)$$

**Oscillating molecule:**

$$q = q_0 \cdot \cos \omega_R t \quad (4)$$

**Expansion of α around q = 0:**

$$\alpha = \alpha(q) = \alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right)_0 q + \ldots \quad (5)$$



The classical theory of the Raman effect is based upon **polarizability** of molecules, which reflects how easy an electron cloud of a molecule can be distorted by an electric field (light)

# Raman Effect: Classical Description

**(5) in (3):**

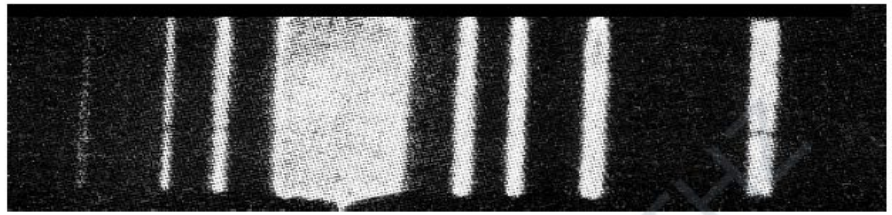
$$\mu = \left[\alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 \cos \omega_R t\right] E_0 \cdot \cos \omega_0 t \qquad (6)$$

**Applying trigonometric formula**

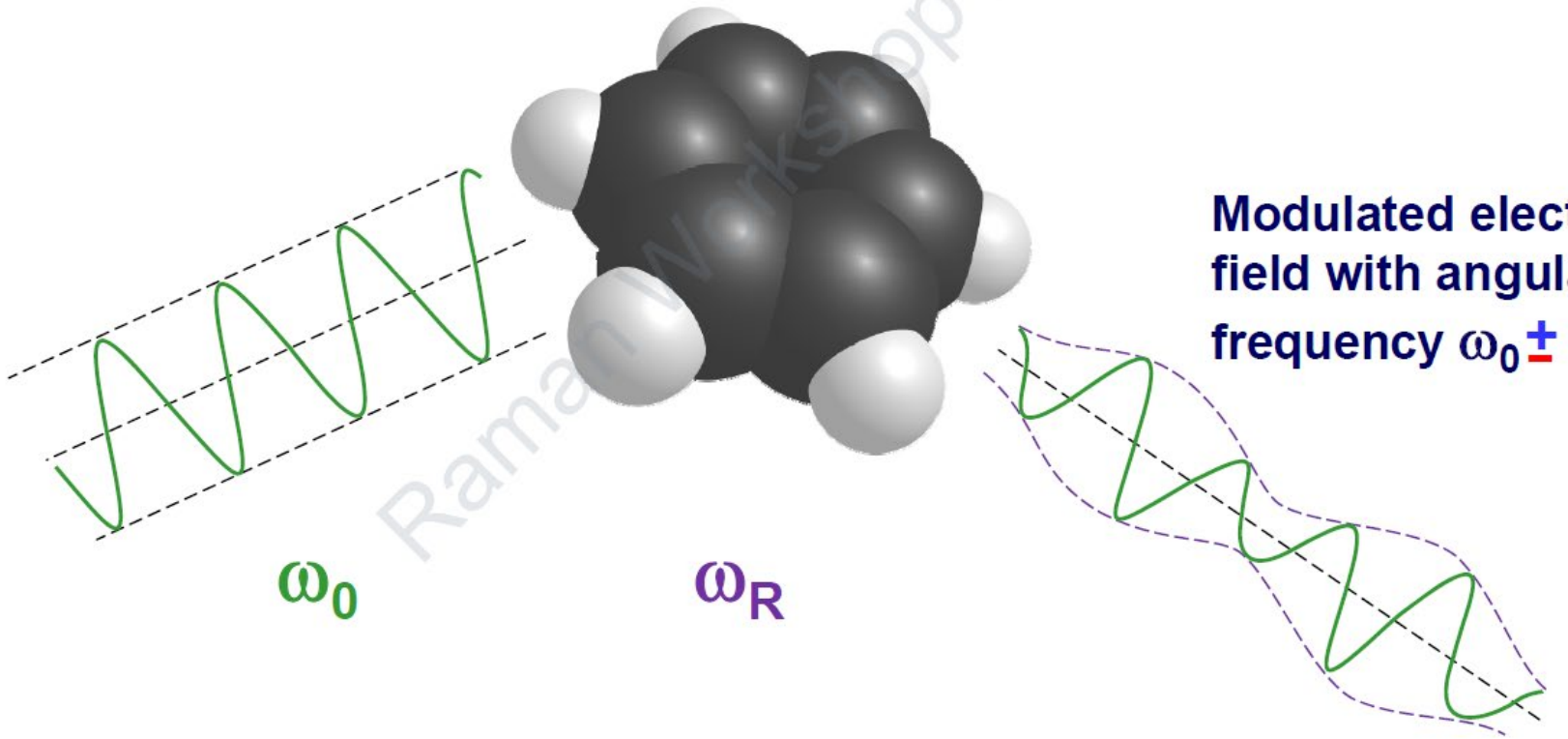
$$\mu = \underbrace{\alpha_0 E_0 \cos \omega_0 t}_{\text{Rayleigh scattering}} + \underbrace{\frac{1}{2}\left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \cos\left(\omega_0 - \omega_R\right) t}_{\text{Stokes Raman scattering}}$$

$$+ \underbrace{\frac{1}{2}\left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \cos\left(\omega_0 + \omega_R\right) t}_{\text{Anti-Stokes Raman scattering}} \qquad (7)$$

# Modulation of the incident electric field by vibrating molecule



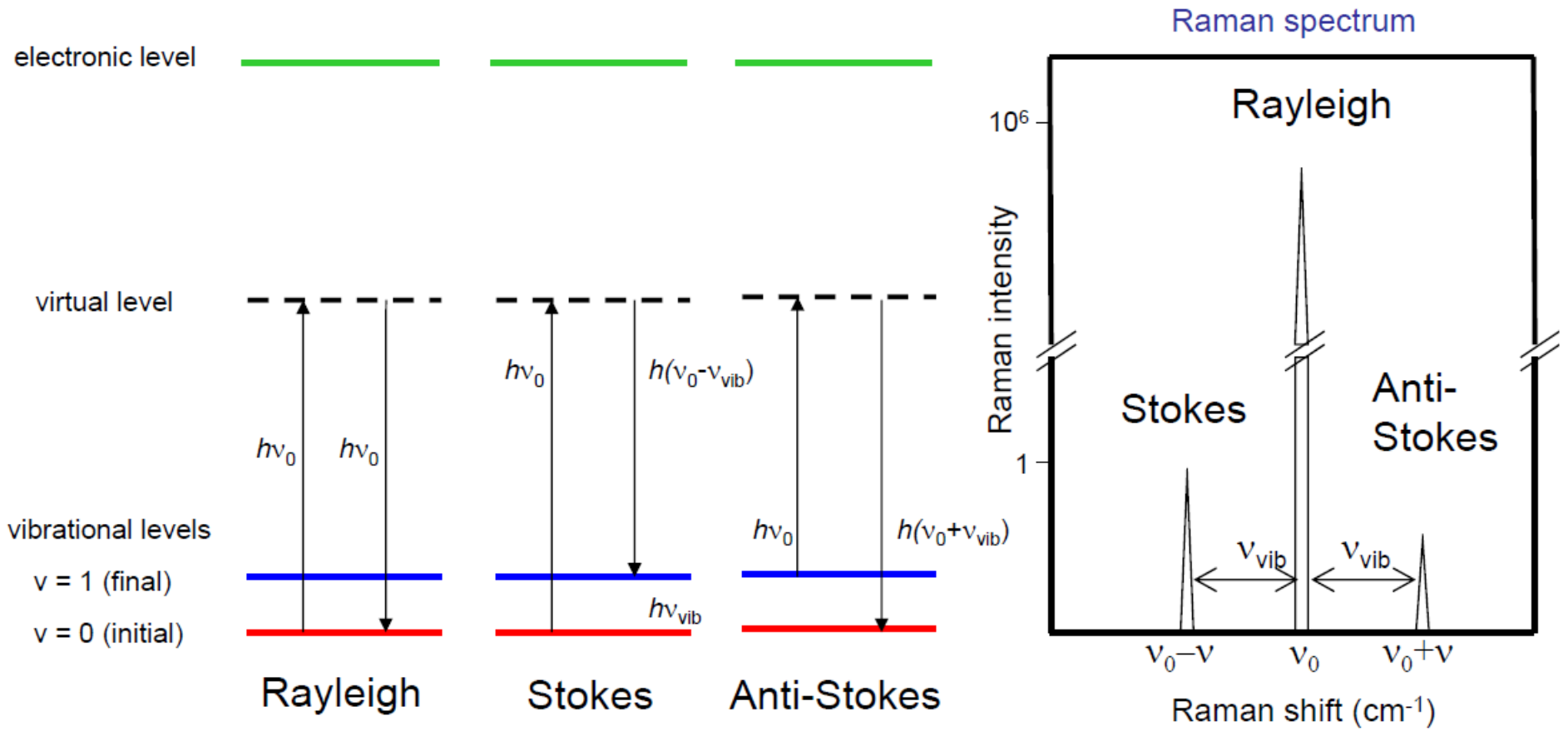
$\omega_0 + \omega_R$ $\omega_0$ $\omega_0 - \omega_R$



$\omega_0$ $\omega_R$

Modulated electric field with angular frequency $\omega_0 \pm \omega_R$

# Quantum mechanics approach




- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever $\nu_0$

# Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

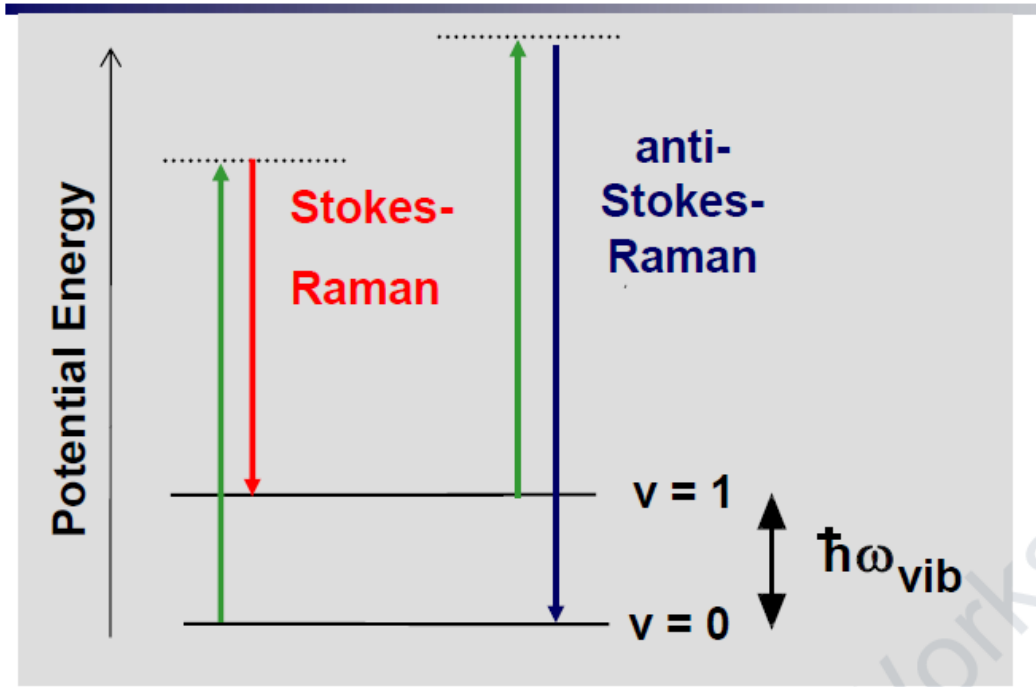
$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

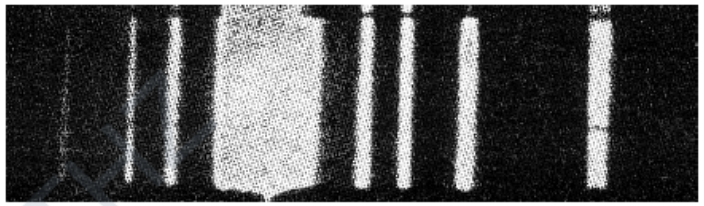
Stokes lines more intense than Anti-Stokes lines (factor 100)

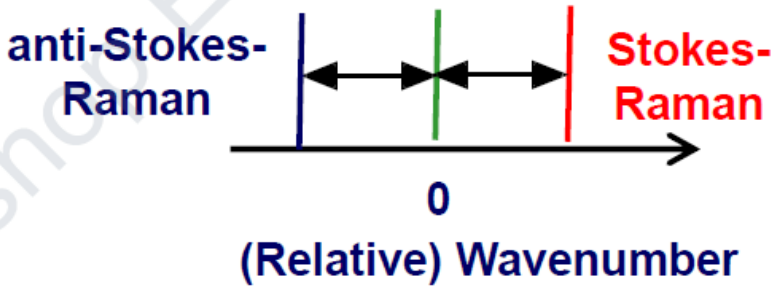
- Measure of Temperature:

$$\frac{I\,(\text{Anti-Stokes})}{I\,(\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

# Different Intensities for Stokes/anti-Stokes Scattering






Relative Intensities -> Boltzmann Factor

$$\frac{N(v=1)}{N(v=0)} = e^{-\Delta E/k_B T} = e^{-\hbar\omega_{vib}/k_B T}$$

**At room temperature:**

$$k_B T \approx 200\ cm^{-1} \text{ or } 1\ eV/40 = 25\ meV$$

**Helpful:** 500 nm = 20 000 $cm^{-1}$ ≈ 2.5 eV

**Examples:**

**S-S stretch**

$\approx 500\ cm^{-1}$

$e^{-500/200}$

$= e^{-5/2}$

$\approx 8\%$

**C-H stretch (aromatic)**

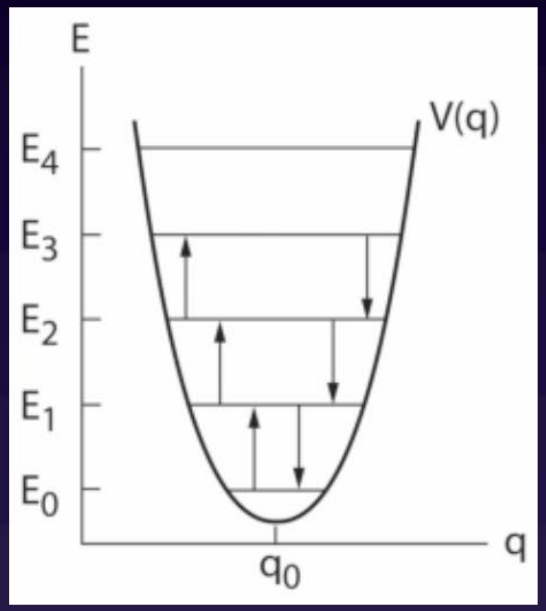
$\approx 3000\ cm^{-1}$

$e^{-3000/200}$

$= e^{-15}$

$\approx 3 \cdot 10^{-5}\ \%$

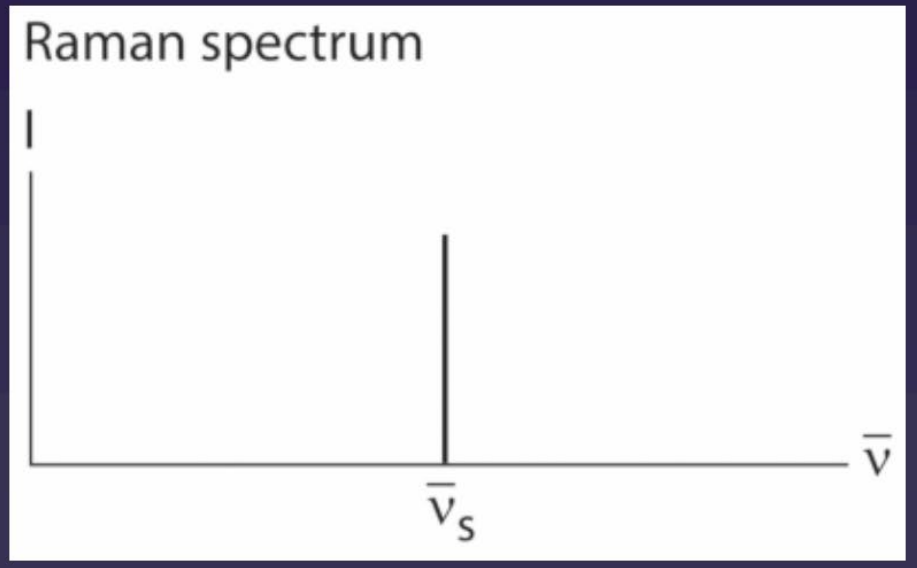
# Harmonic oscillator



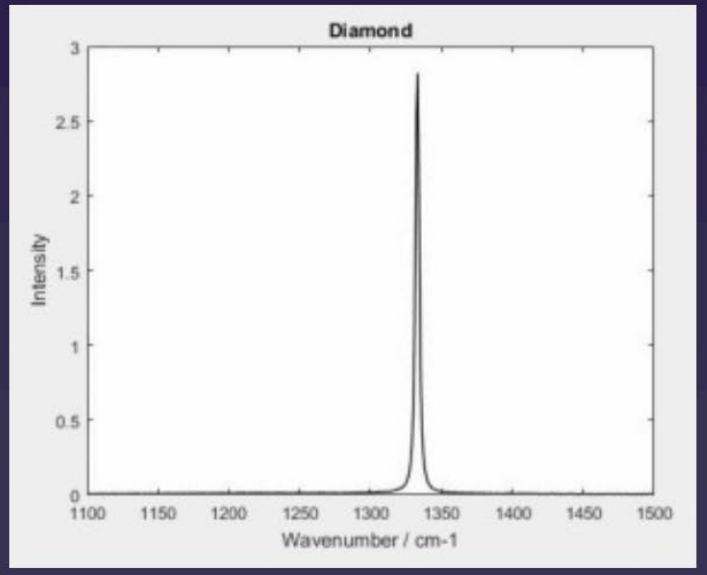

Energy: $E_n = (n + ½)\, h\, c\, \bar{\nu}$

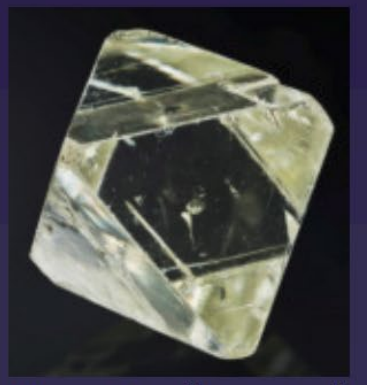
Selection rule: $\Delta n = \pm 1$

Energy of transition: $\Delta E = h\, c\, \bar{\nu}$



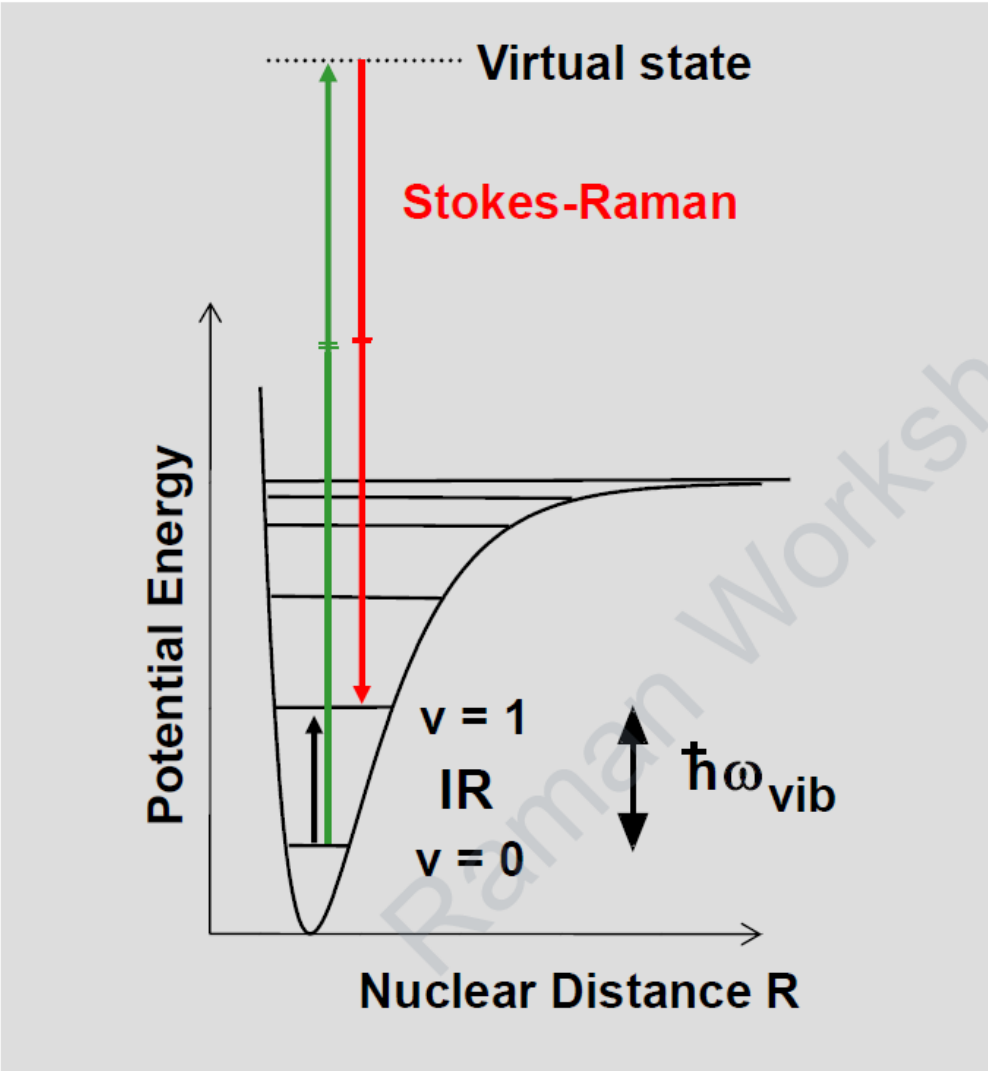

Raman (Stokes) spectrum of diamond ( $\bar{\nu}$ = 1331 $cm^{-1}$)

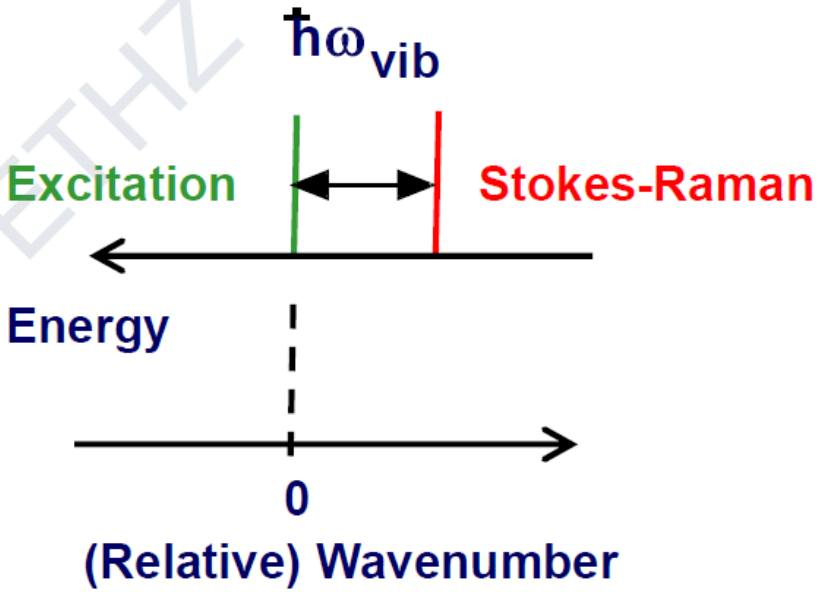


Premier diamond mine (1.86 ct)

# Energy Diagram ↔ Vibrational Spectrum



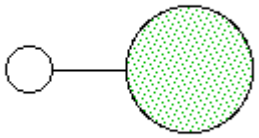



# Vibrations in Molecules

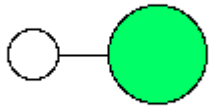
**Sym. Stretching**

**8086 $cm^{-1}$ = 1 eV**

**HCl** $\nu = 2991\ cm^{-1}$

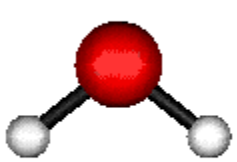


**HF** $\nu = 4139\ cm^{-1}$



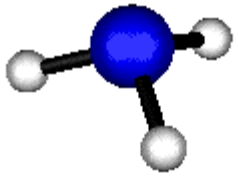
**Asym. Stretching** **Sym. Bending**

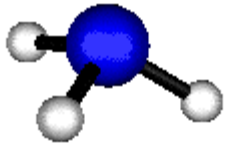
**$H_2O$** $\nu_1 = 3835\ cm^{-1}$ $\nu_3 = 3939\ cm^{-1}$ $\nu_2 = 1648\ cm^{-1}$

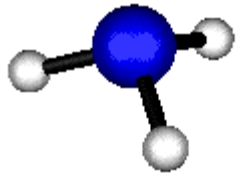


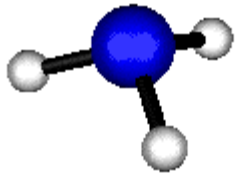
**Asym. Bending**

**$NH_3$** $\nu_1 = 3505.7\ cm^{-1}$ $\nu_3 = 3573.1\ cm^{-1}$ $\nu_2 = 1022\ cm^{-1}$ $\nu_4 = 1689.7\ cm^{-1}$

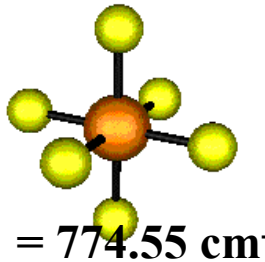


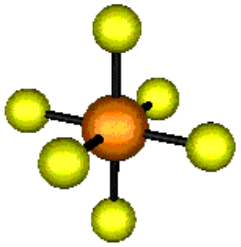


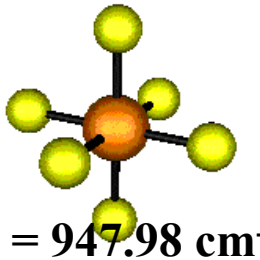


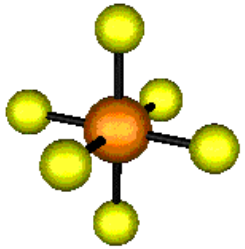


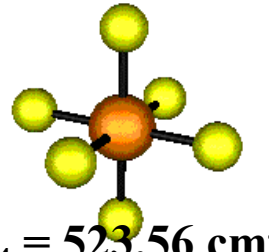
**$SF_6$** $\nu_5 = 643.35\ cm^{-1}$ $\nu_2 = 615.02\ cm^{-1}$ $\nu_6 = 348.08\ cm^{-1}$

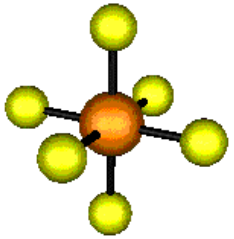










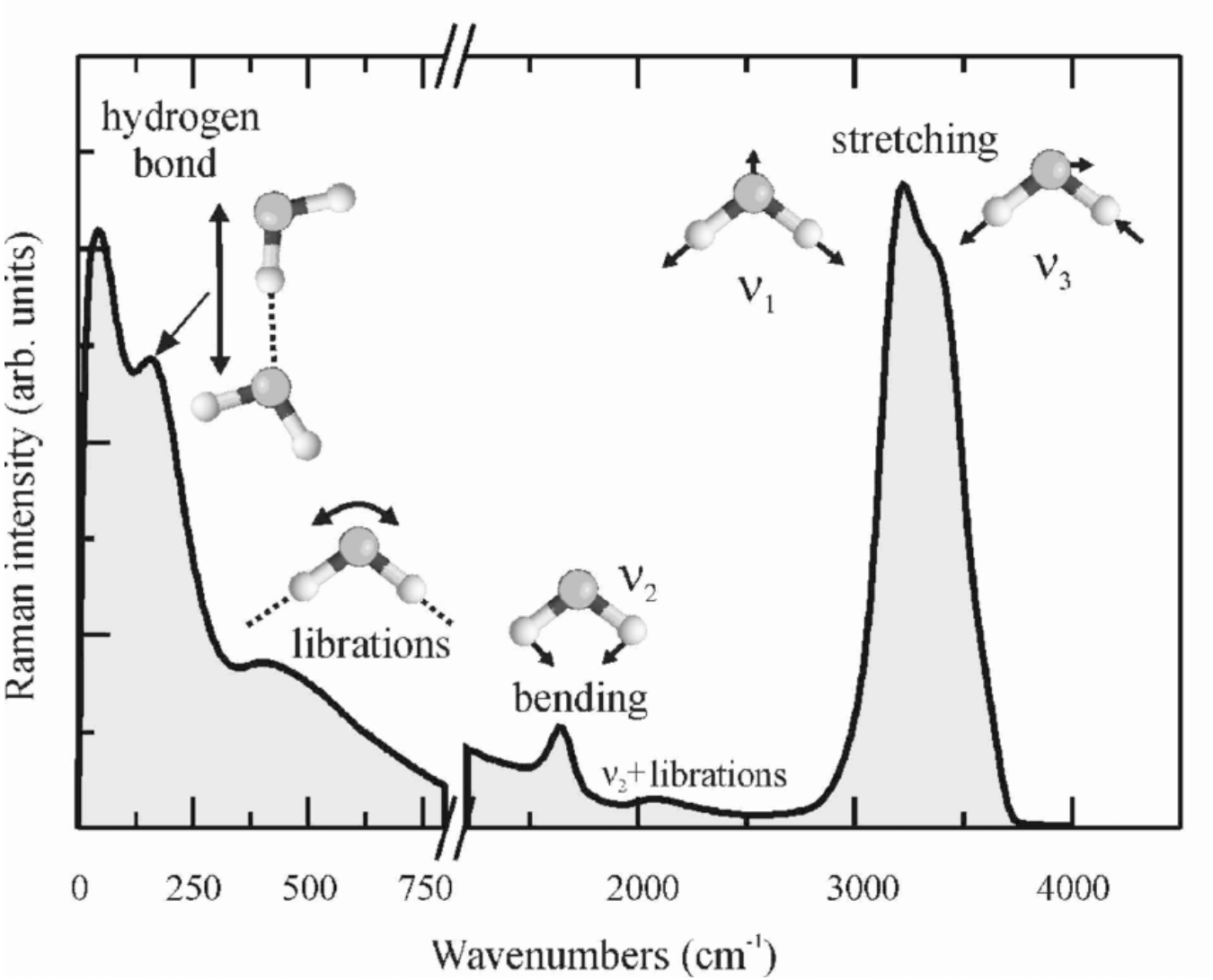


$\nu_1 = 774.55\ cm^{-1}$ $\nu_3 = 947.98\ cm^{-1}$ $\nu_4 = 523.56\ cm^{-1}$

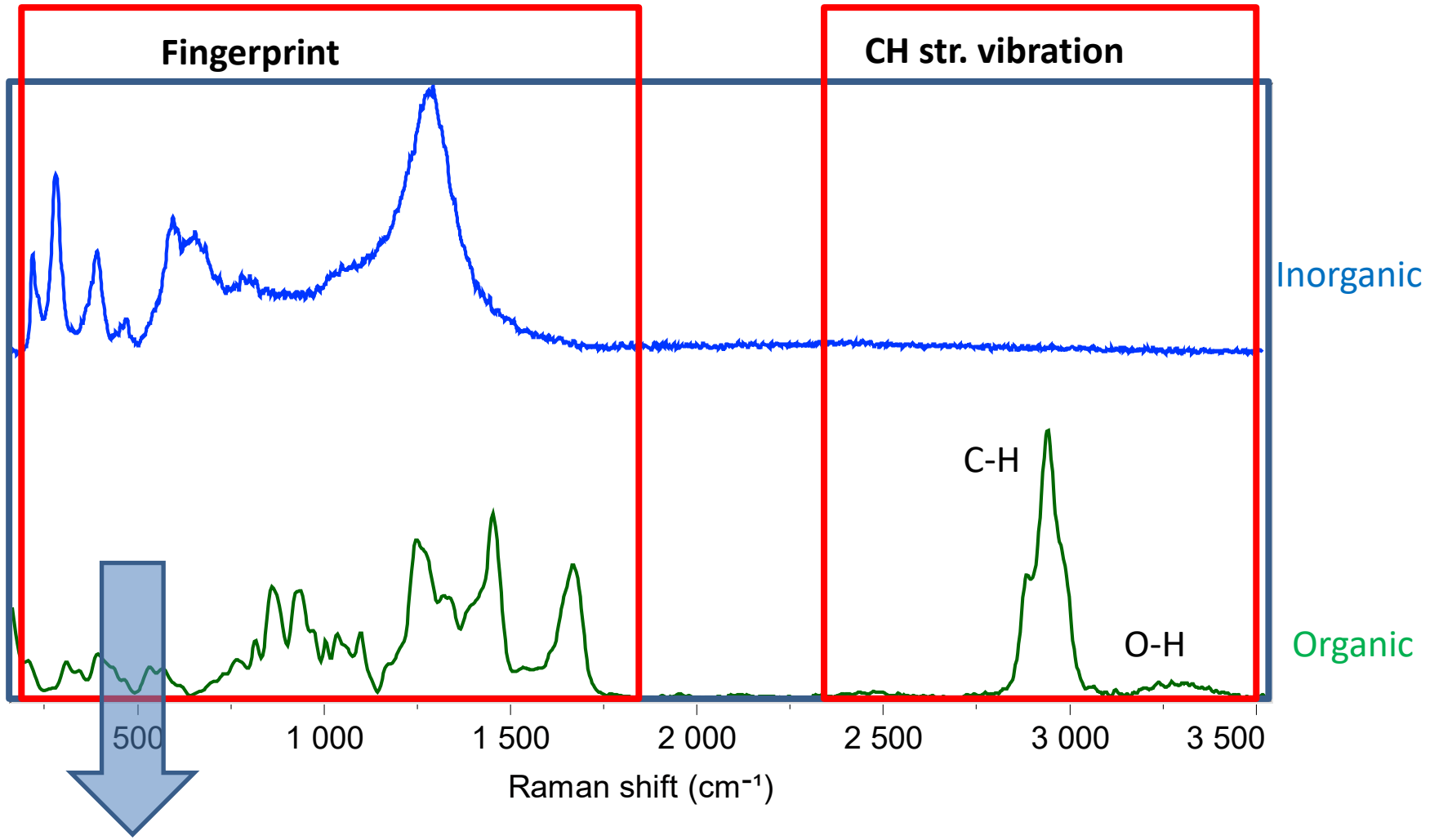
$H_2O$

**Asym. Stretching** **Sym. Bending**

$\nu_1 = 3835\ cm^{-1}$ $\nu_3 = 3939\ cm^{-1}$ $\nu_2 = 1648\ cm^{-1}$



# Characteristic frequencies for the vibrations

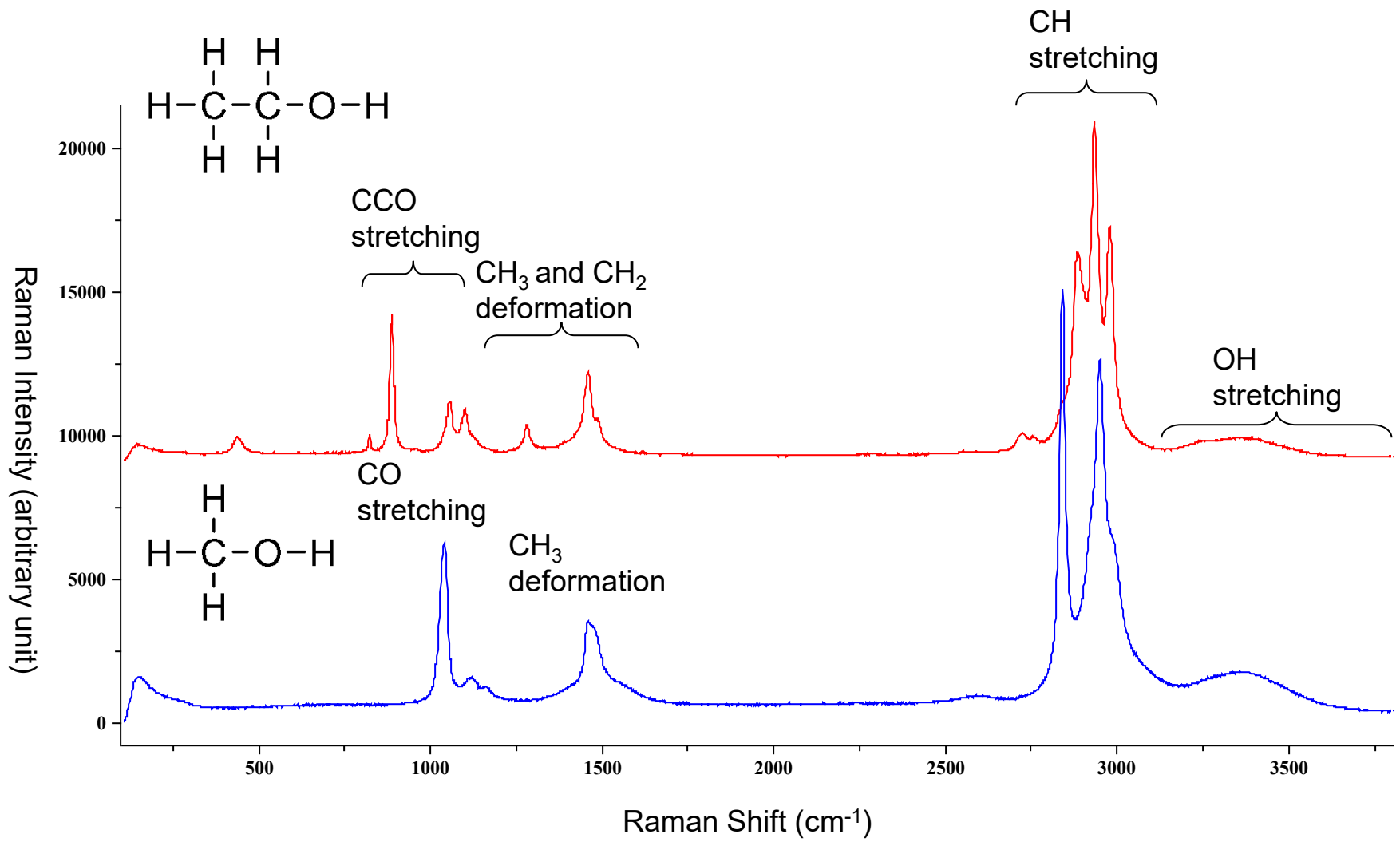



Vibrations which characterize different components

# Example

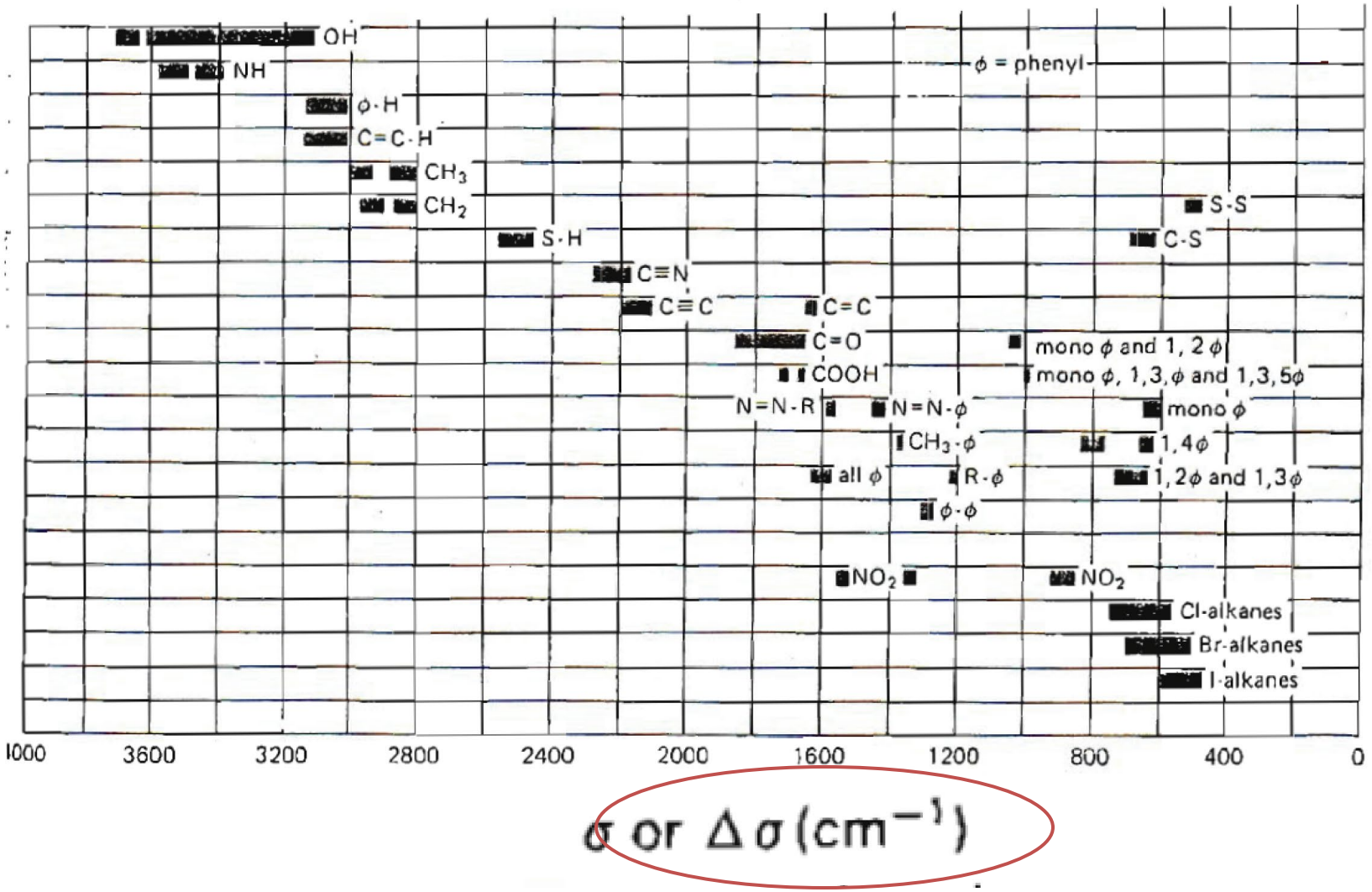
Significant identification of alcohols which differ just in one $CH_2$-group

**Methanol - $CH_3OH$ vs. Ethanol - $CH_3CH_2OH$**



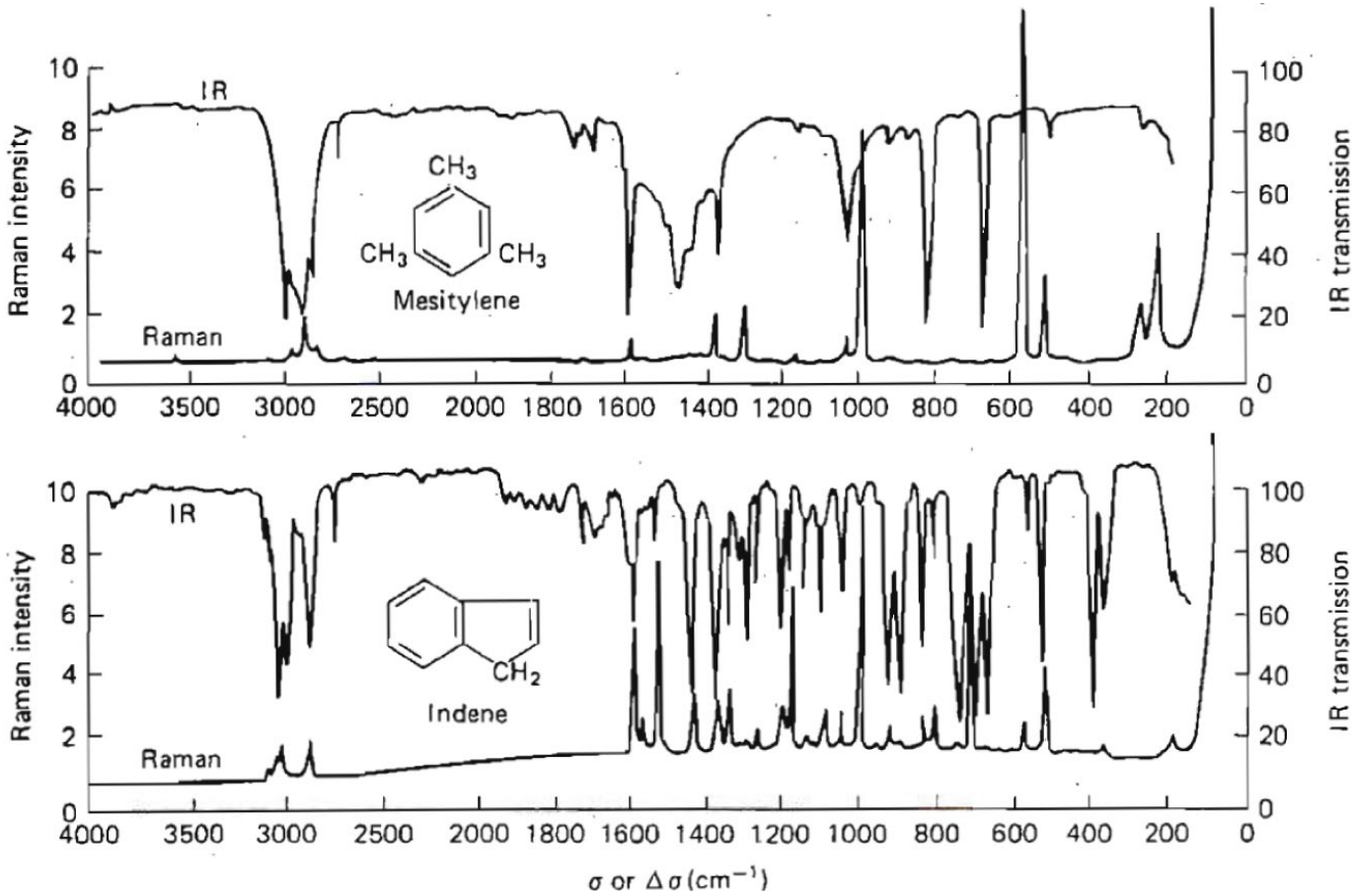
# Raman Spectroscopy: General

- Group assignments identify characteristic vibrational energy



# Raman Spectroscopy: General

- IR and Raman are both useful for Fingerprinting




- Symmetry dictates which are active in Raman and IR

# Raman vs IR Spectroscopy: General

- IR and Raman are both useful for Fingerprinting

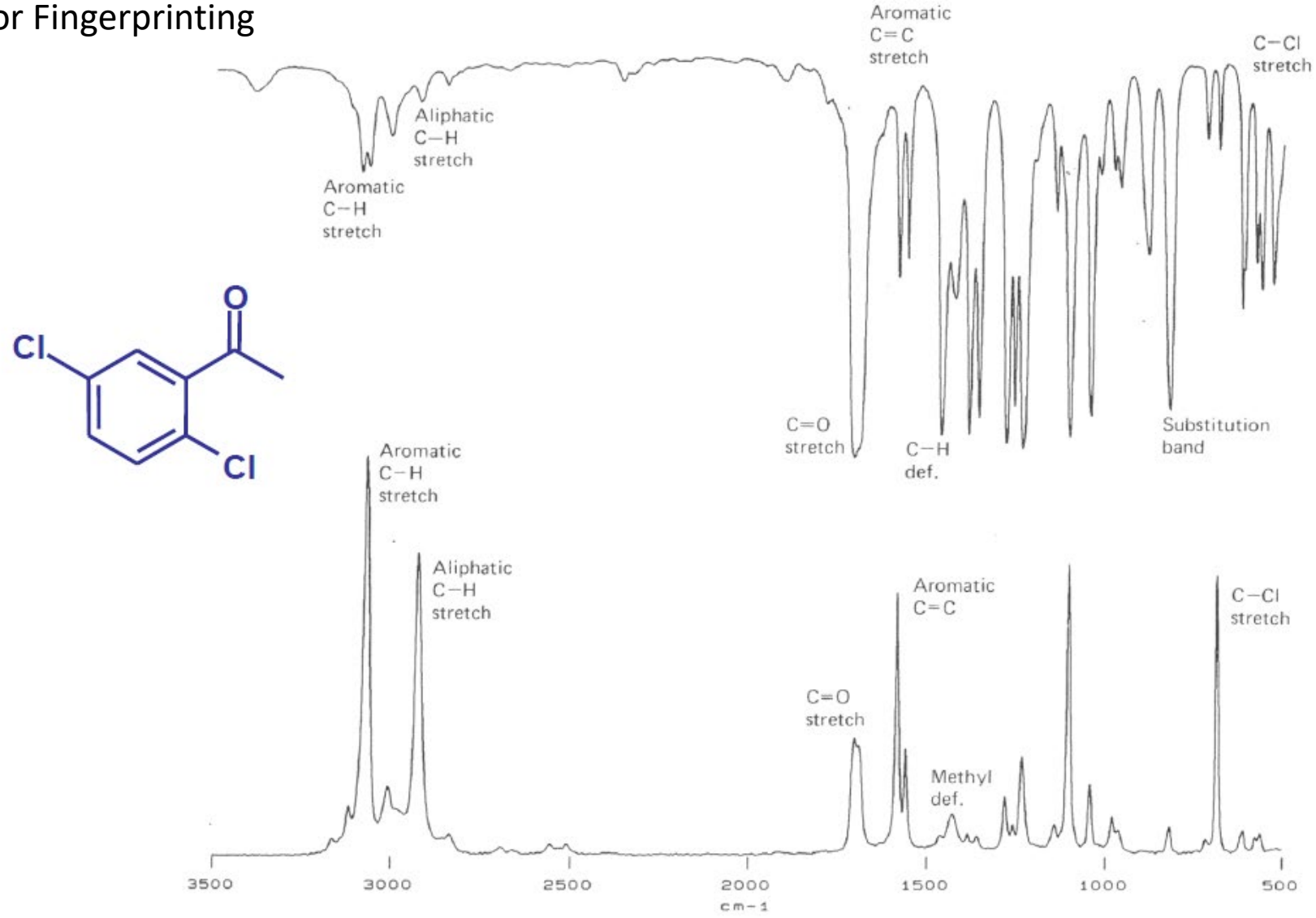



Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

- Symmetry dictates which are active in Raman and IR

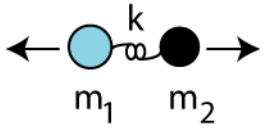
# Raman Spectroscopy: Classical Treatment

- Number of peaks related to degrees of freedom

  *DoF = 3N - 6 (bent) or 3N - 5 (linear) for N atoms*

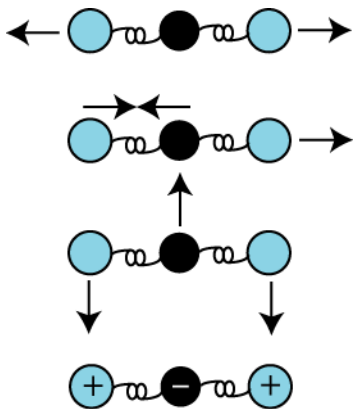
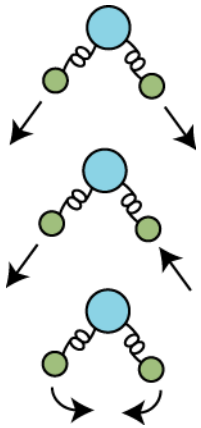
- Energy related to harmonic oscillator

$$\sigma \text{ or } \Delta\sigma = \frac{c}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$




- Selection rules related to symmetry

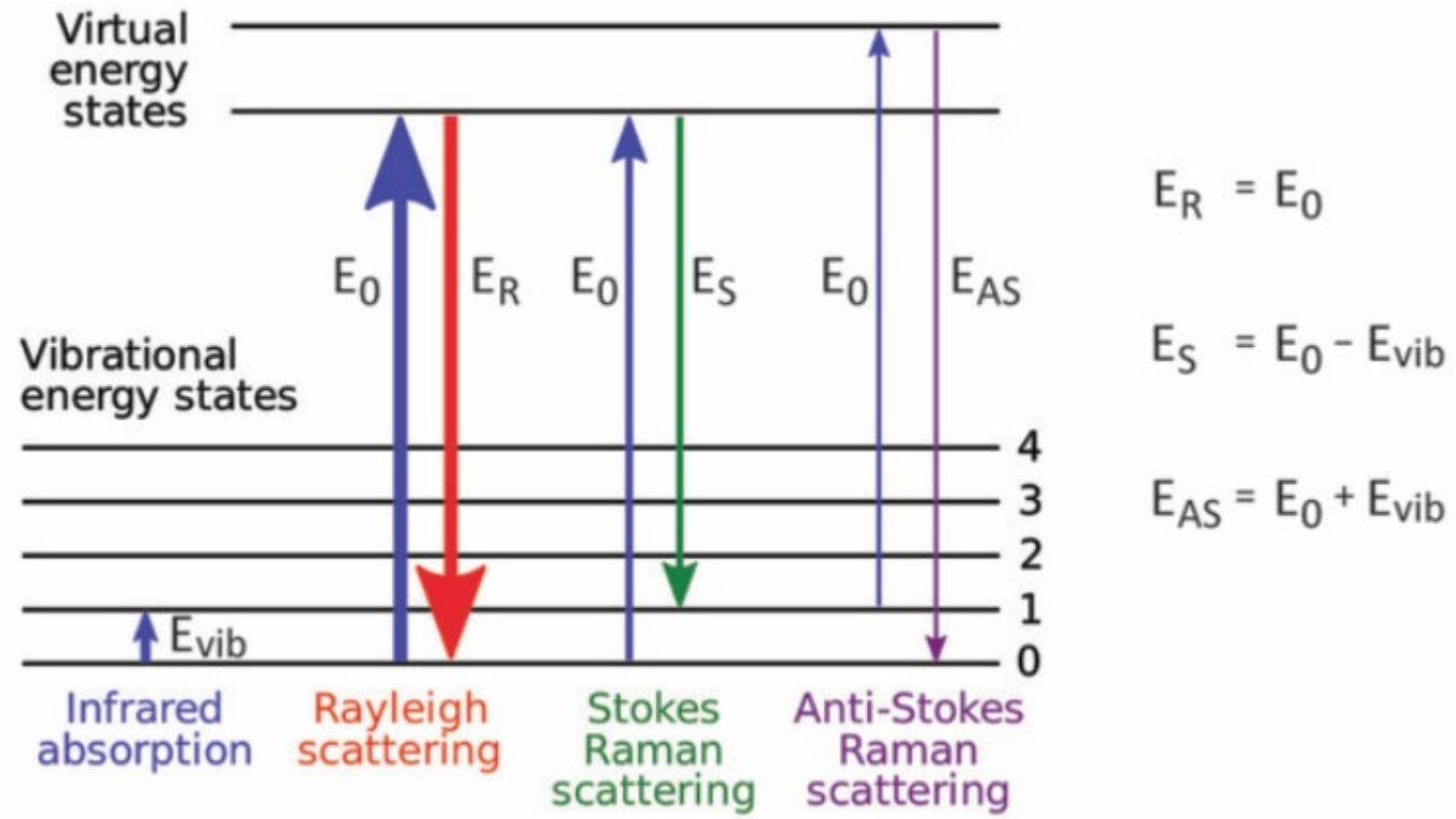
  *Rule of thumb: symmetric=Raman active, asymmetric=IR active*

| $CO_2$ | $H_2O$ |
|---|---|
|  Raman: 1335 $cm^{-1}$ <br> IR: 2349 $cm^{-1}$ <br> IR: 667 $cm^{-1}$ |  Raman + IR: 3657 $cm^{-1}$ <br> Raman + IR: 3756 $cm^{-1}$ <br> Raman + IR: 1594 $cm^{-1}$ |

# Introduction - Raman vs. IR

| | Raman | IR |
|---|---|---|
| Theoretical statements | It is due to the scattering of light by the vibrating molecules | It is the result of absorption of light by vibrating molecules |
| | The vibration is Raman active if it causes a change in polarisability | The vibration is IR active if there is a change in dipole moment during the vibration |
| | The molecule doesn't need to have a permanent dipole moment | The vibration concerned should have a change in dipole moment due to that vibration |
| Exp. statements | Water can be used as a solvent | Water cannot be used due to its intense absorption |
| | Sample preparation is not necessary<br>Sample can be almost in any state | Sample preparation is important<br>Gaseous samples can rarely be used |

# Energy transfer model

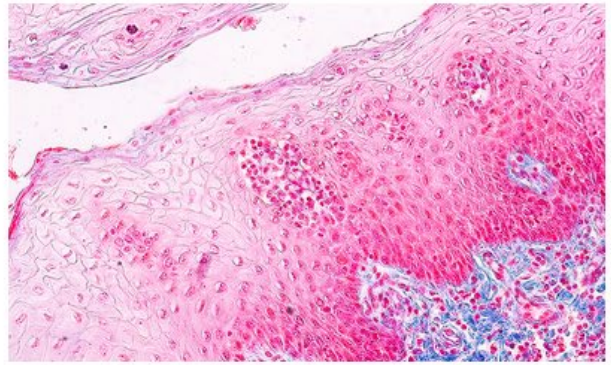



Inelastic processes:

- Gases, liquids: Excitation of *molecular vibrations, Rotation* $E_{vib} > E_{rot}$
- Crystals: Excitation of *lattice vibrations* (phonons)

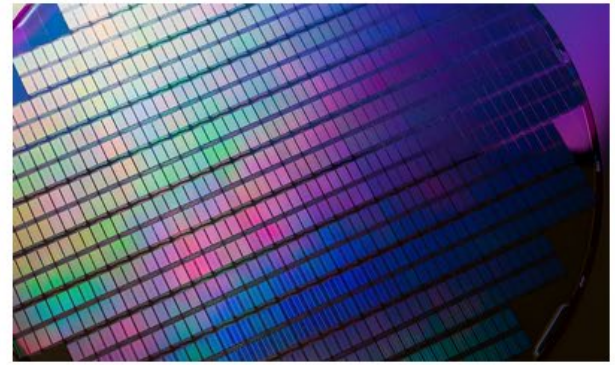
- Stokes spectrum = Energy map of vibrational states $E_{vib} = E_0 - E_s$
- Raman-spectroscopy is complementary to IR-spectroscopy

# *Application*



## Life sciences

- Life sciences home
- Cells
- Tissue
- Micro-organisms
- Plant biology



## Materials sciences

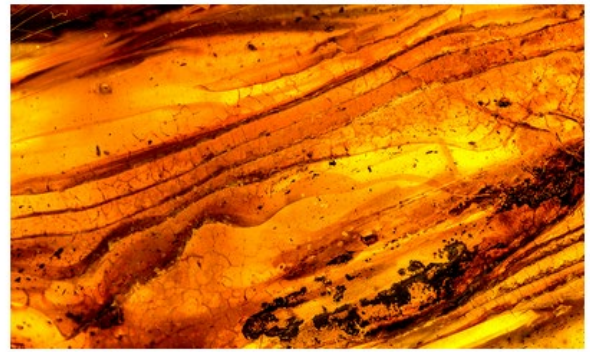
- Materials science home
- Carbon and nanotechnology
- Semiconductors
- Photovoltaics
- Battery technology

## Chemical Sciences

- Chemical sciences home
- Pharmaceuticals
- Polymers
- Chemicals
- Catalysis

## Analytical sciences

- Analytical sciences home
- Art and heritage
- Forensics
- Contamination



## Earth sciences

- Earth sciences home
- Geology
- Gemmology

# Advantages of Raman spectroscopy

- ‘See’ spectroscopy – you can measure it if you can see it
  - Visible lasers
  - Fluorescent label free
  - Adapted to common microscopy / optical components
- ‘Easy’ spectroscopy
  - Sharp and well resolved features spectral bands
  - Minimal sample preparation
  - Ambient and stress conditions
- High spatial resolution – lateral and axial (confocal)
  - 3D mapping
  - Through containers
- High chemical specificity and structural selectivity – crystallinity, orientation, hydration, polymorphism
- Good for aqueous solutions
- Non-destructive methods

# Raman Spectroscopy: Information

# *Why Raman?*

**Band Intensity**
- Polarizability of the chemical bond
- Orientation
- Detectability

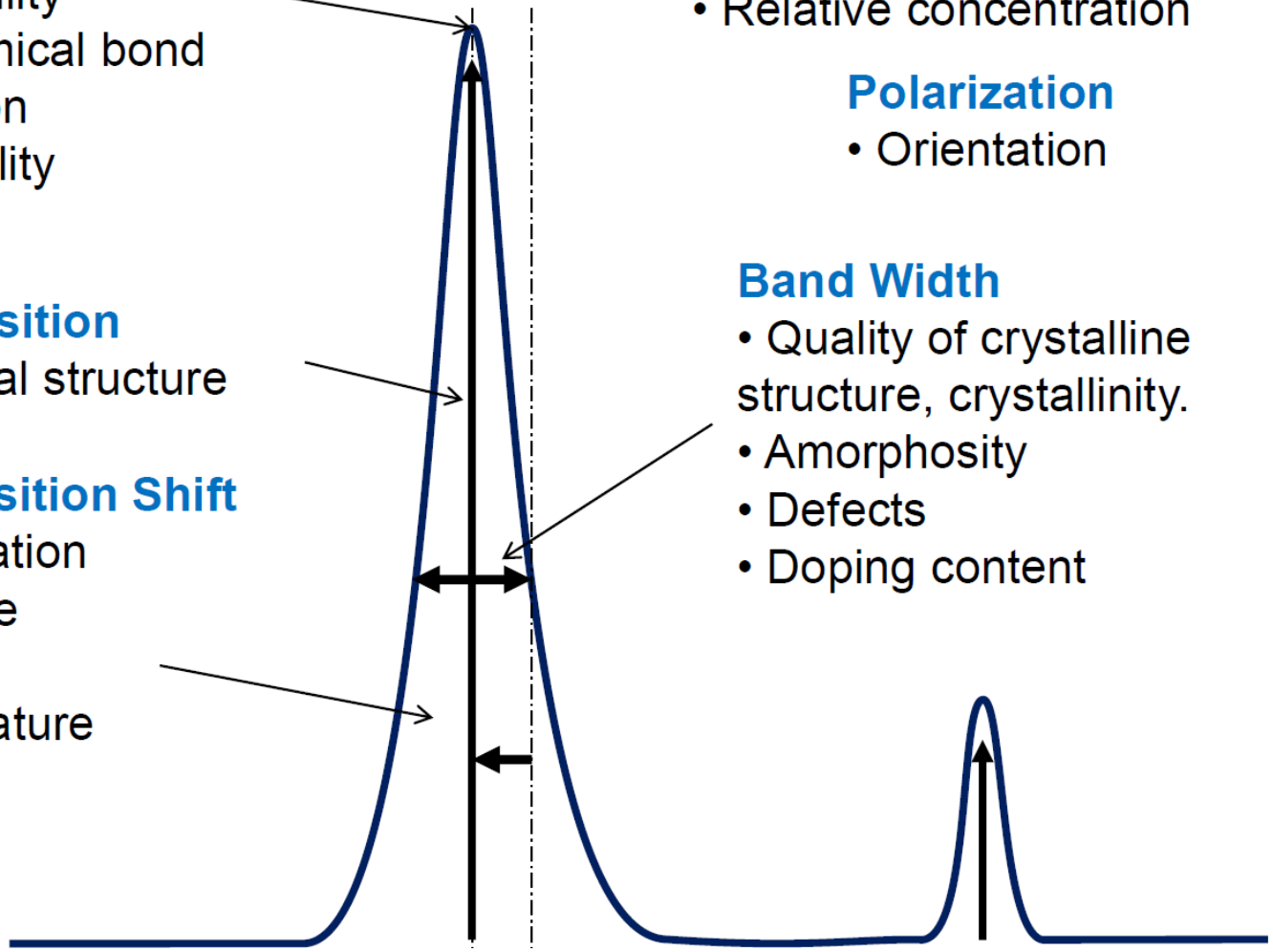
**Band Position**
- Chemical structure

**Band Position Shift**
- Deformation
- Pressure
- Stress
- Temperature

**Band Ratio**
- Relative concentration

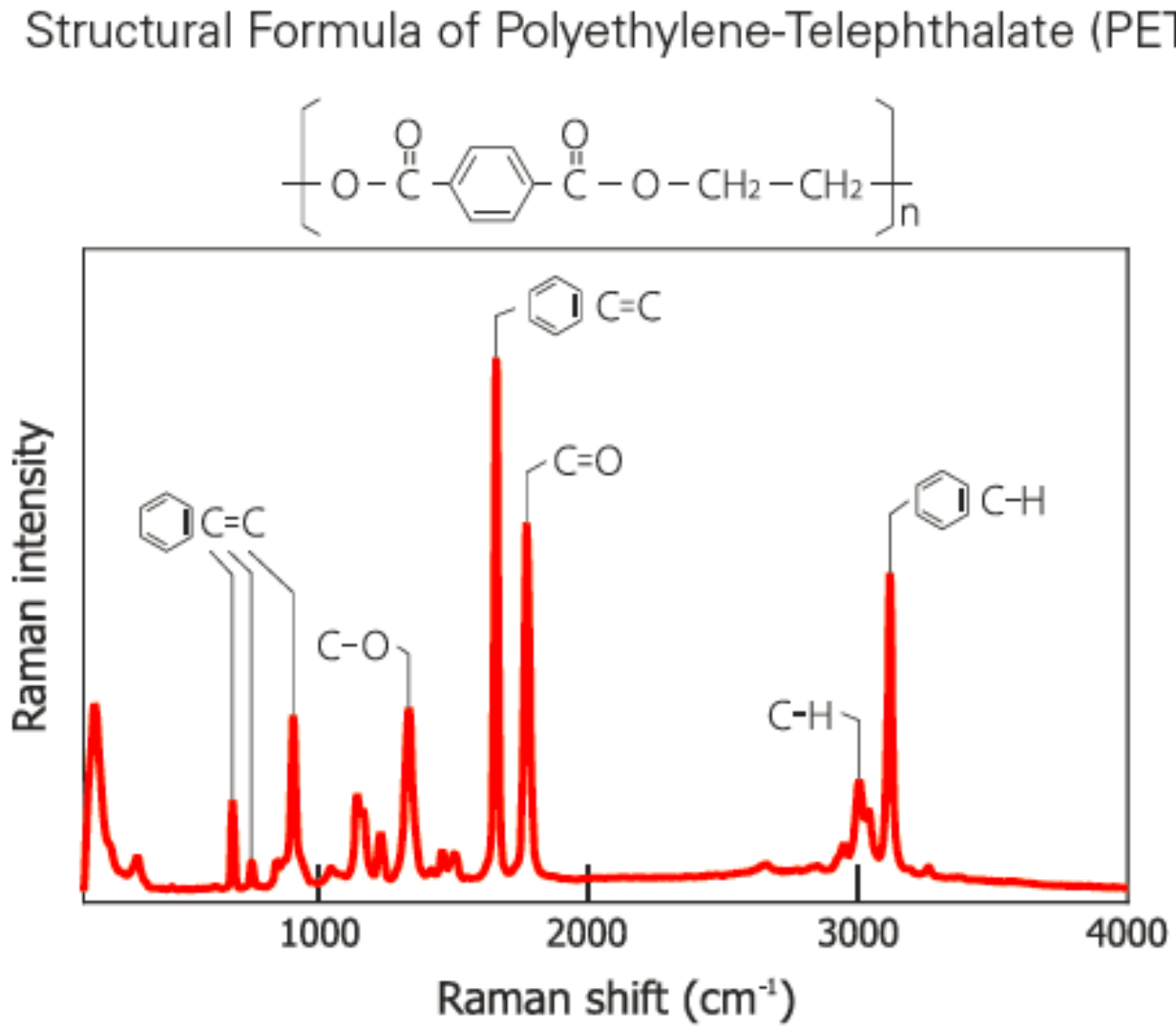
**Polarization**
- Orientation

**Band Width**
- Quality of crystalline structure, crystallinity.
- Amorphosity
- Defects
- Doping content

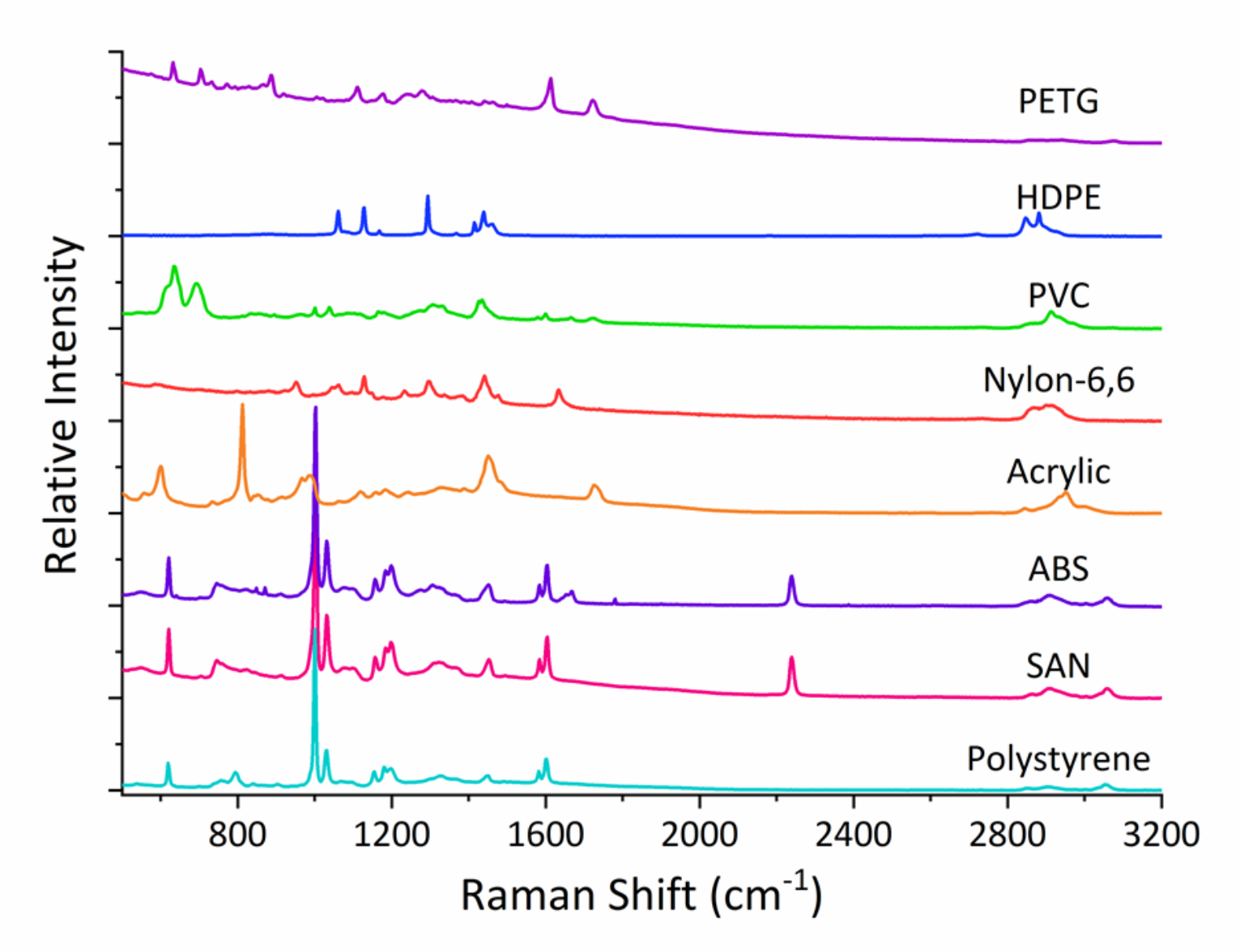


# Characteristic frequencies for the vibrations

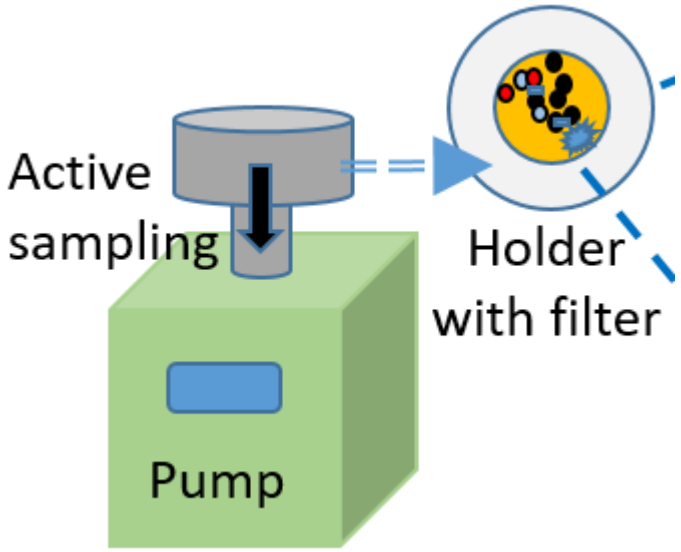
Polymers - PET

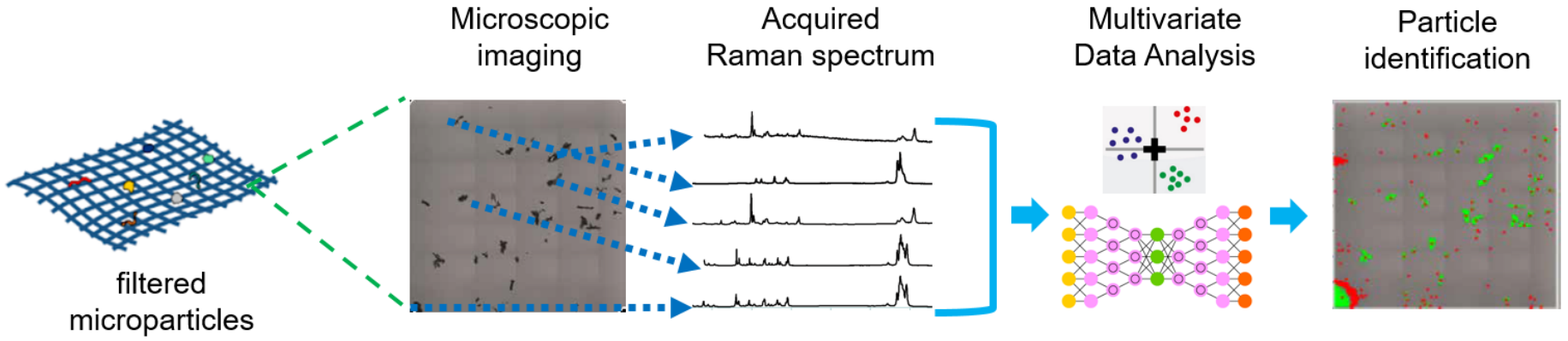


# Example of Raman spectra of polymers



# Particle identification with Raman spectroscopy

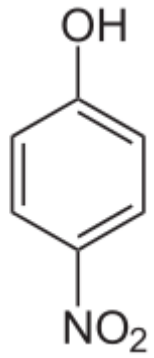


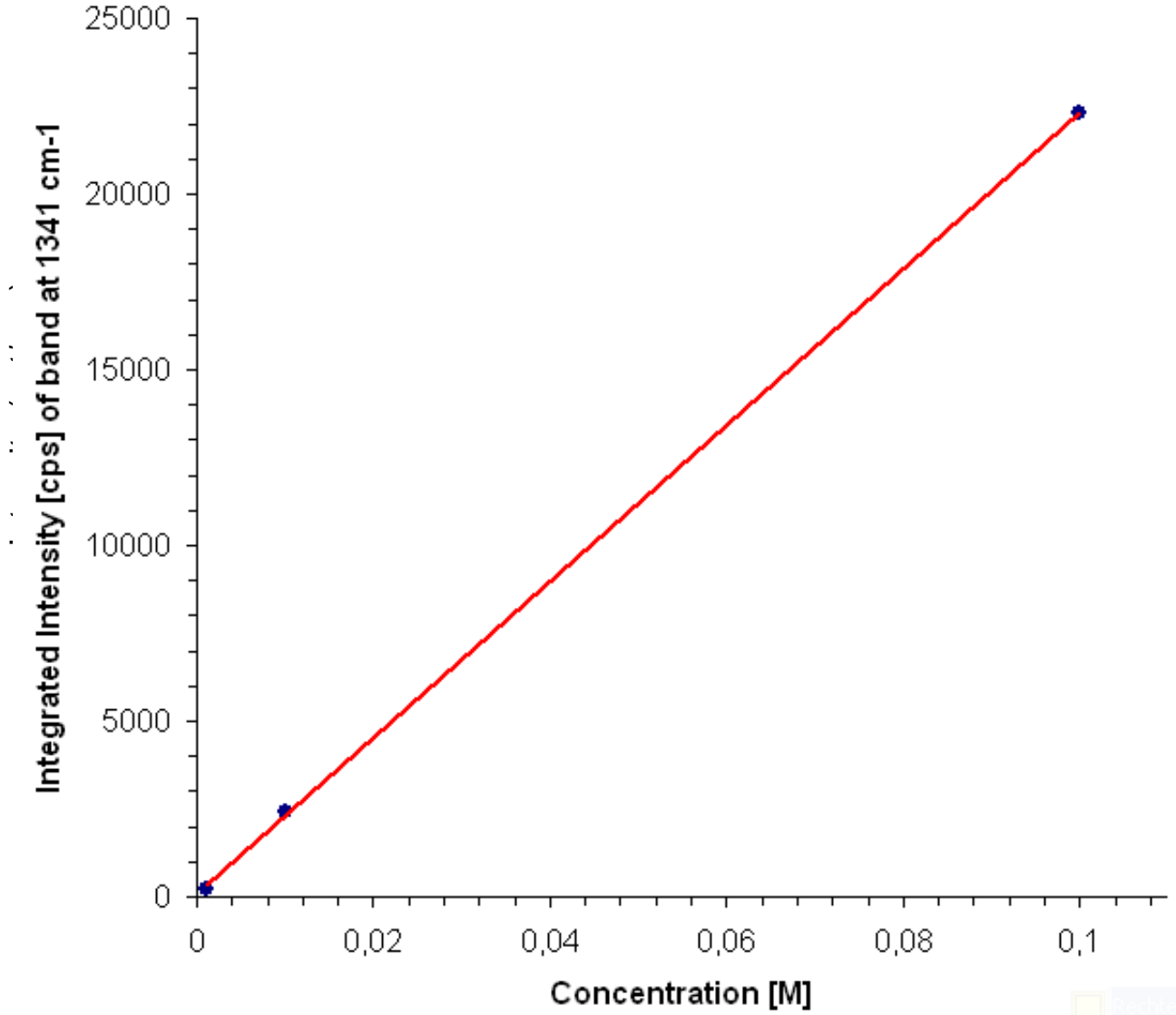




HORIBA
Scientific

# Intensity- concentration

4-Nitrophenol dissolved in $CH_2Cl_2$

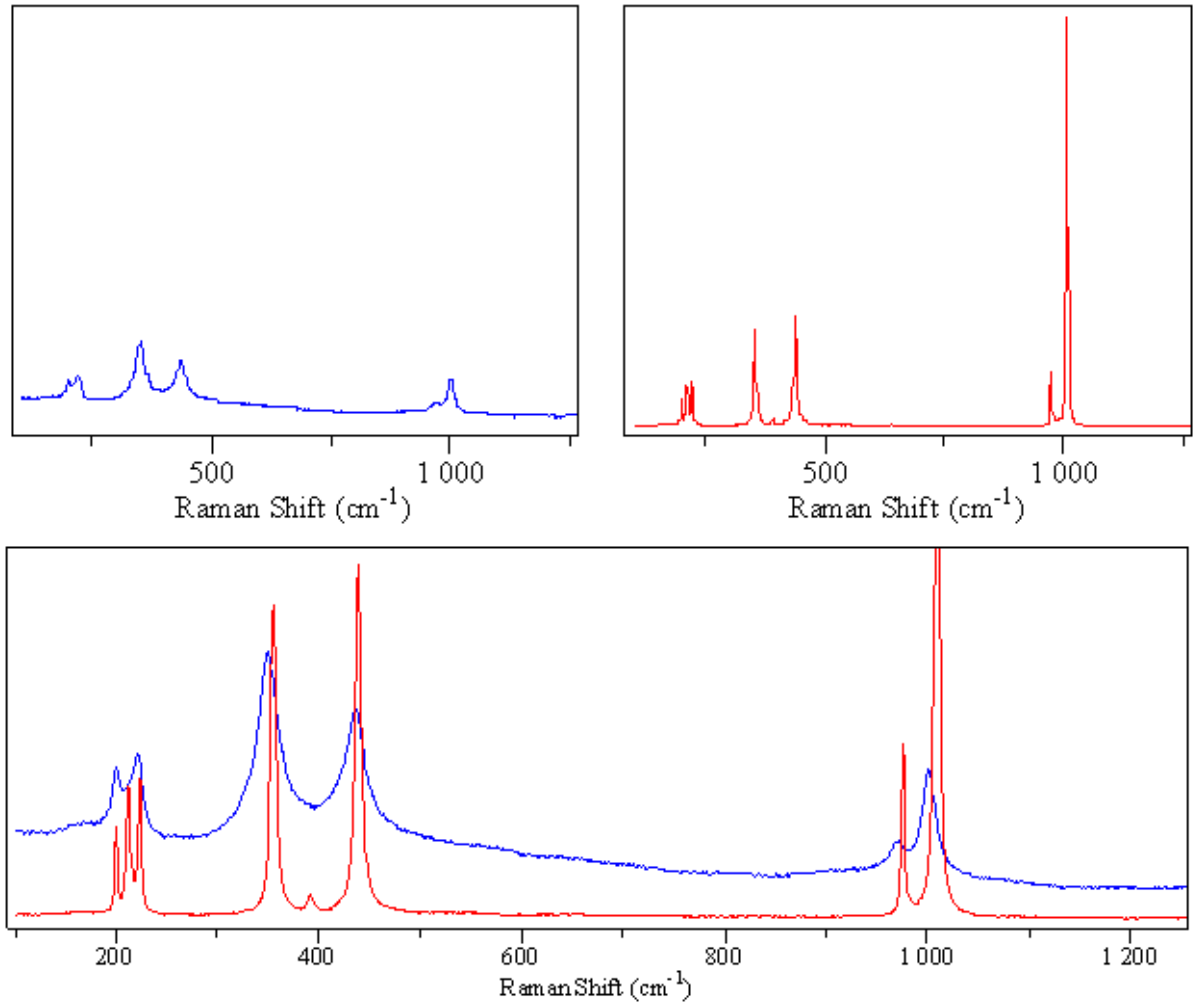


# Example : Zircon

- **Bandwidth – Crystallinity – Structural order/disorder**

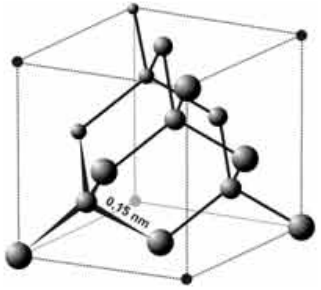
Raman spectra of zircon, showing typical amorphous (blue) and crystalline (red) spectra. (Broadness of peaks)

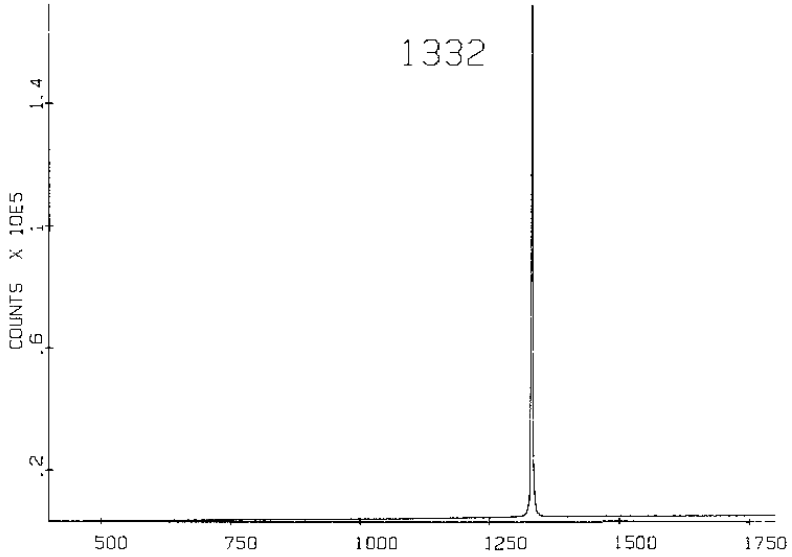


# Example

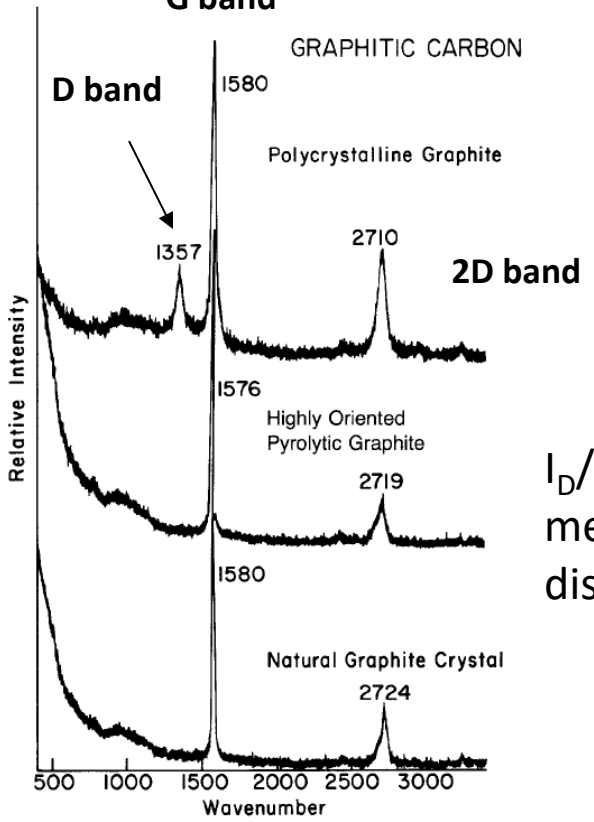
## Characteristic frequencies for the vibrations

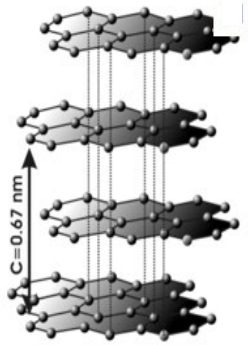
Diamond




Graphite

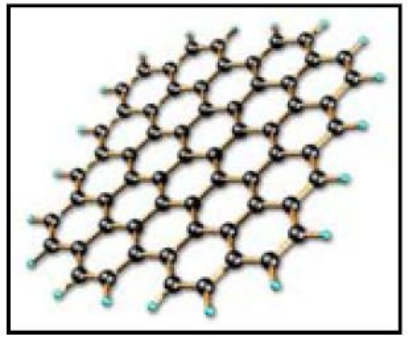


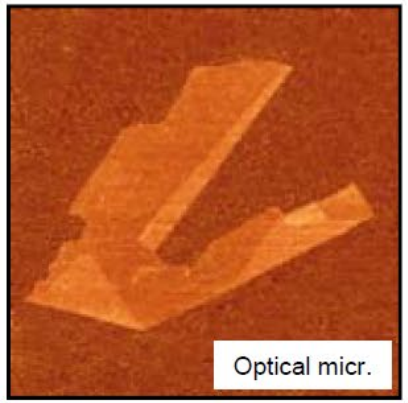



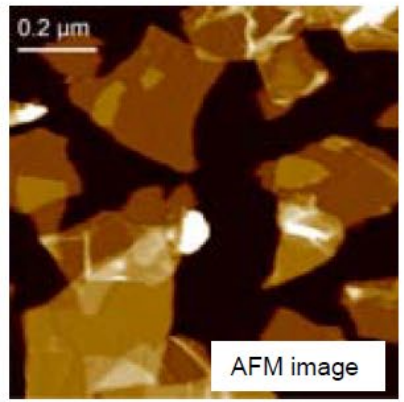

$I_D/I_G$ ratio is a measure of disorder

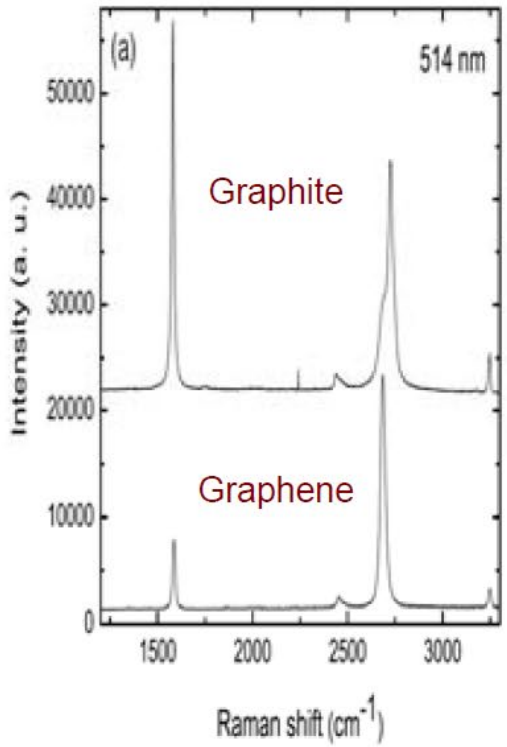
*From: « Characterisation of diamond films by Raman spectroscopy », D.S.Knight, W.B. White, J.Mater. Res. 4 (1989), 385-393.*

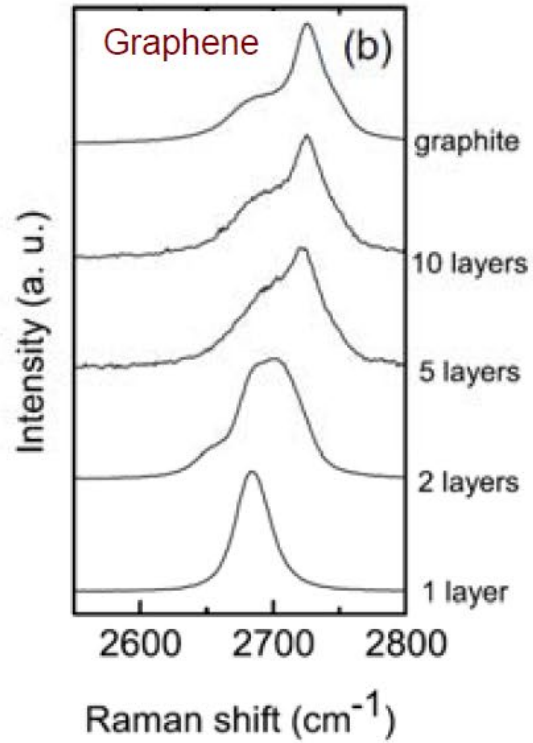
# Identification of single atomic layers of graphene

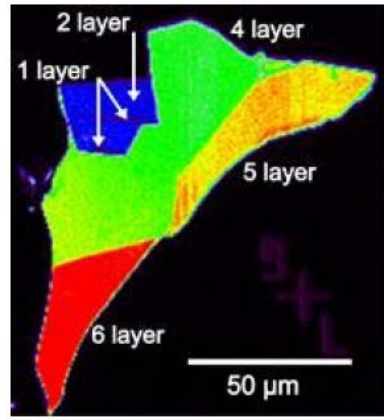




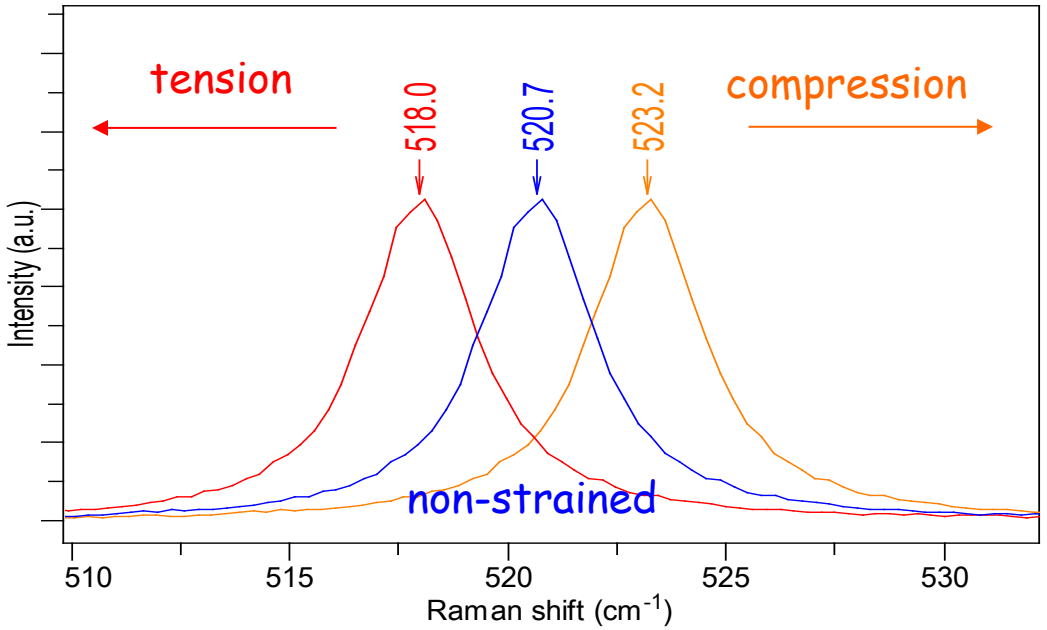




A. C. Ferrari, et al., Phys. Rev. Lett. 97, 187401 (2006)

# Raman probes-peaks

## Strain analysis

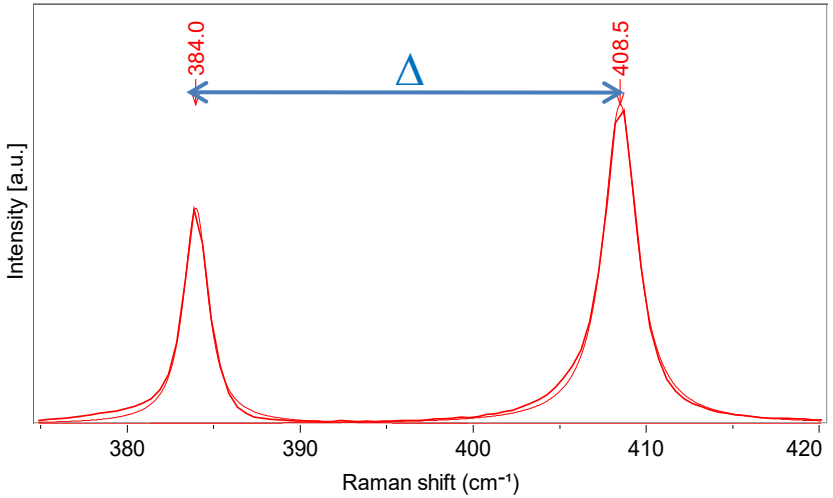
The peak position of a non-strained silicon crystal is at 520,7cm-1.
If a stress is applied to the structure (due to a defect, a coating, the lattice mismatch …),
the position peak shifts towards the low frequencies (tensile stress) or towards the high frequencies (compressive stress).

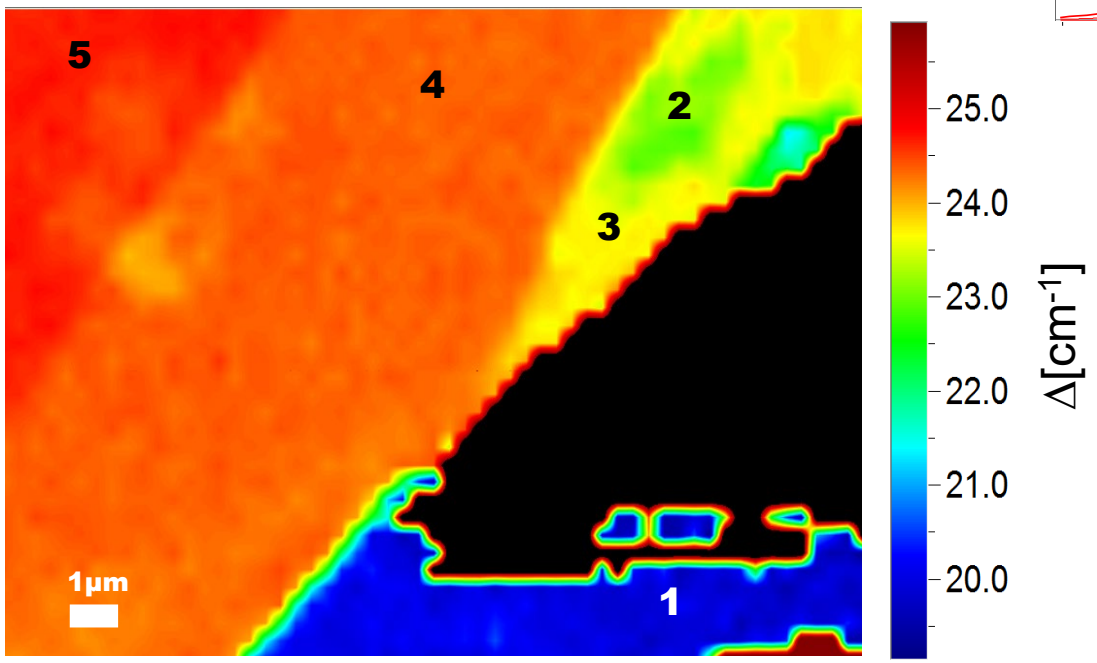


# Raman probes-peaks

## Number of layers

**The difference of 2 peak positions defines the number of layers of MoS2**



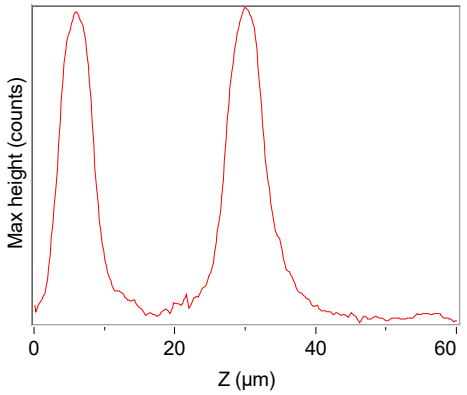



# Distribution of sample components - Multispectral analysis

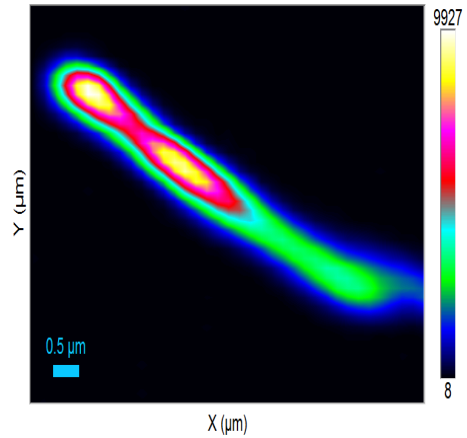
- Multispectral acquisition over 1 direction (X, Y or Z axis)
  - Profiles
- Multispectral acquisition over a plane
  - Maps or images
- Multispectral acquisition over a volume
  - 3D maps or images
- Multispectral acquisition over time or temperature
  - Kinetic profiles

# Distribution of sample components - Multispectral analysis

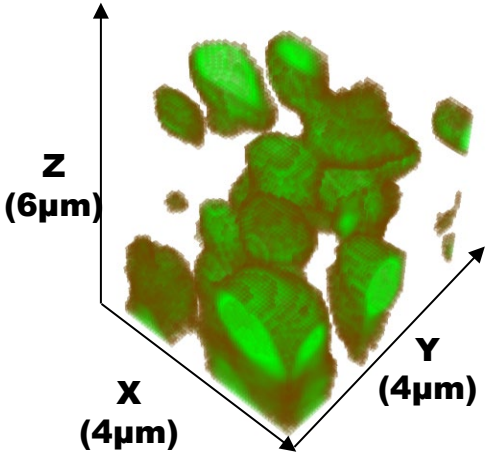
- **One direction profile (Z axis)**



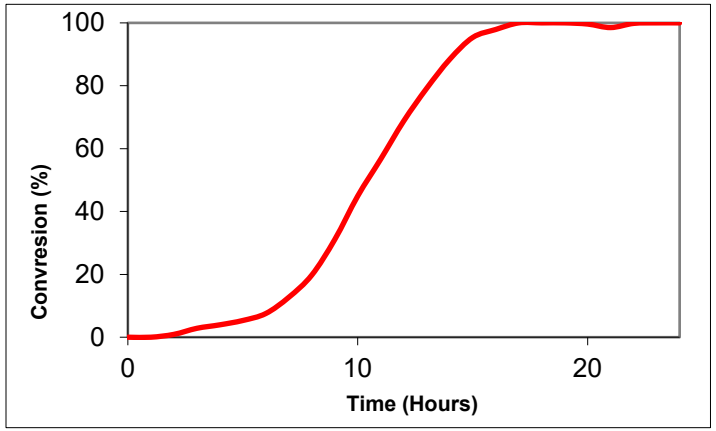

- **Plane (2D) maps**




- **Volume (3D) maps**

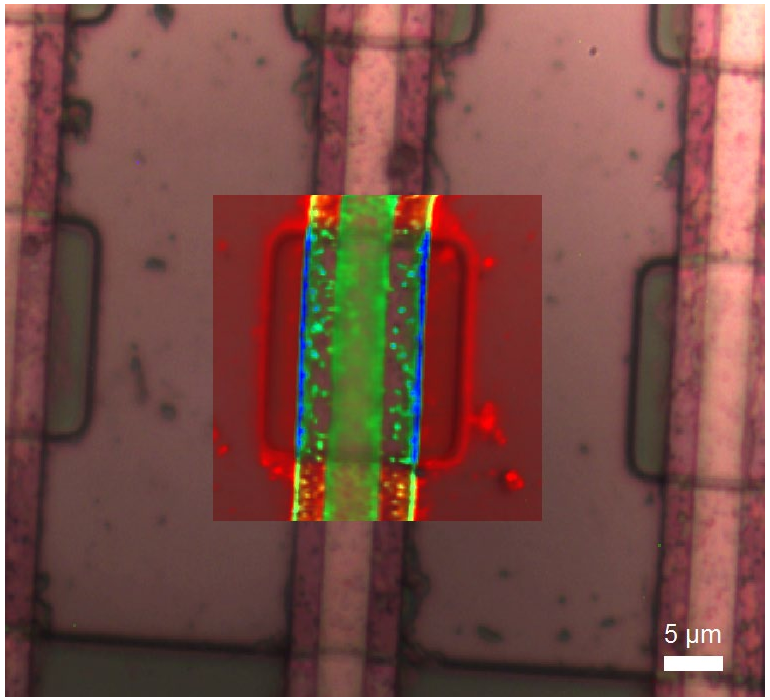


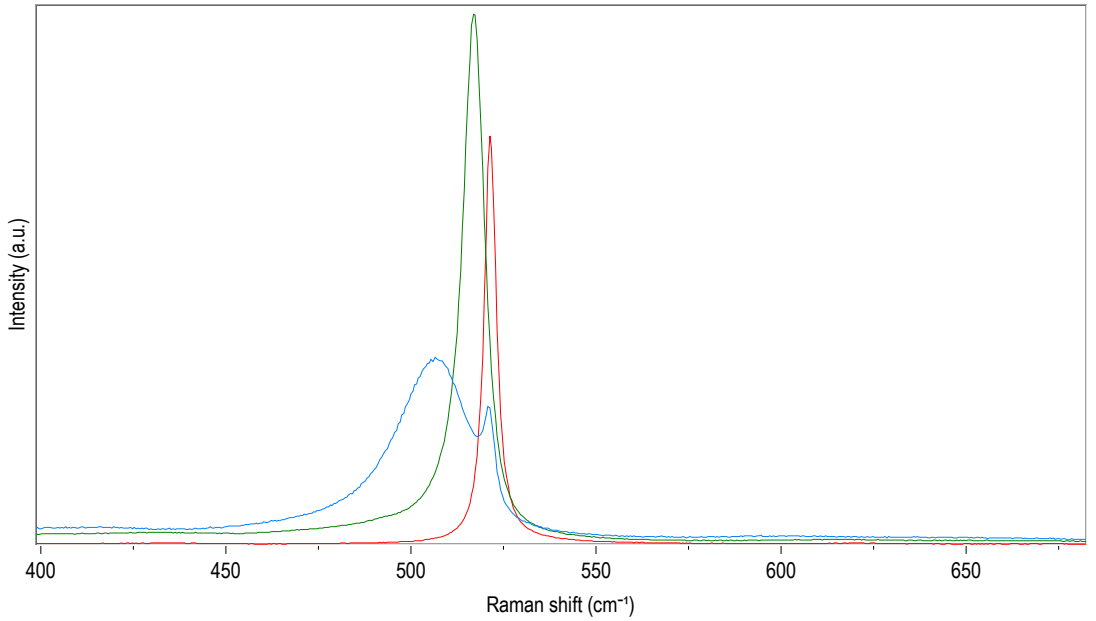

- **Kinetic profile**



# Distribution of sample components
# - Multispectral analysis

- Example of the Silicon with combined maps
  - Overlay of the chemical image with the video image

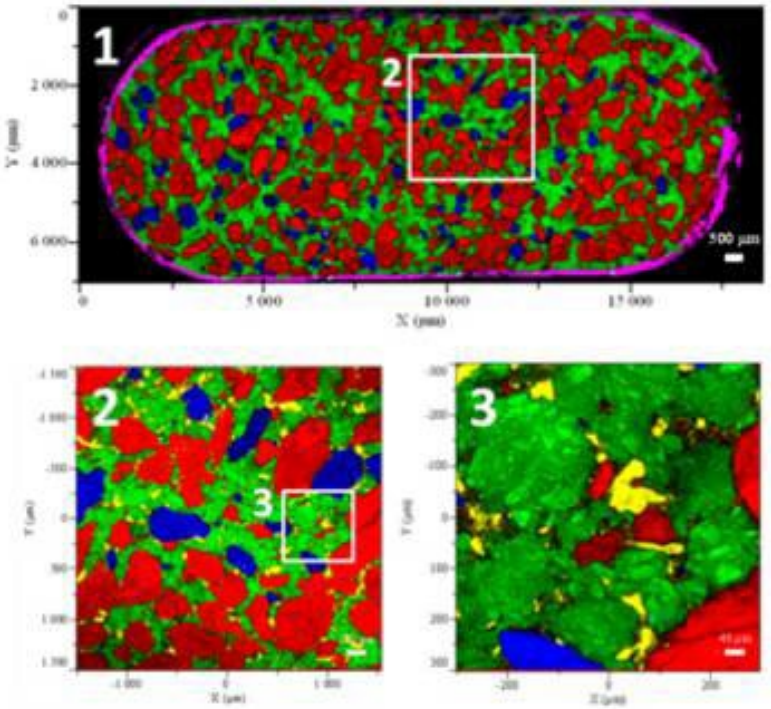


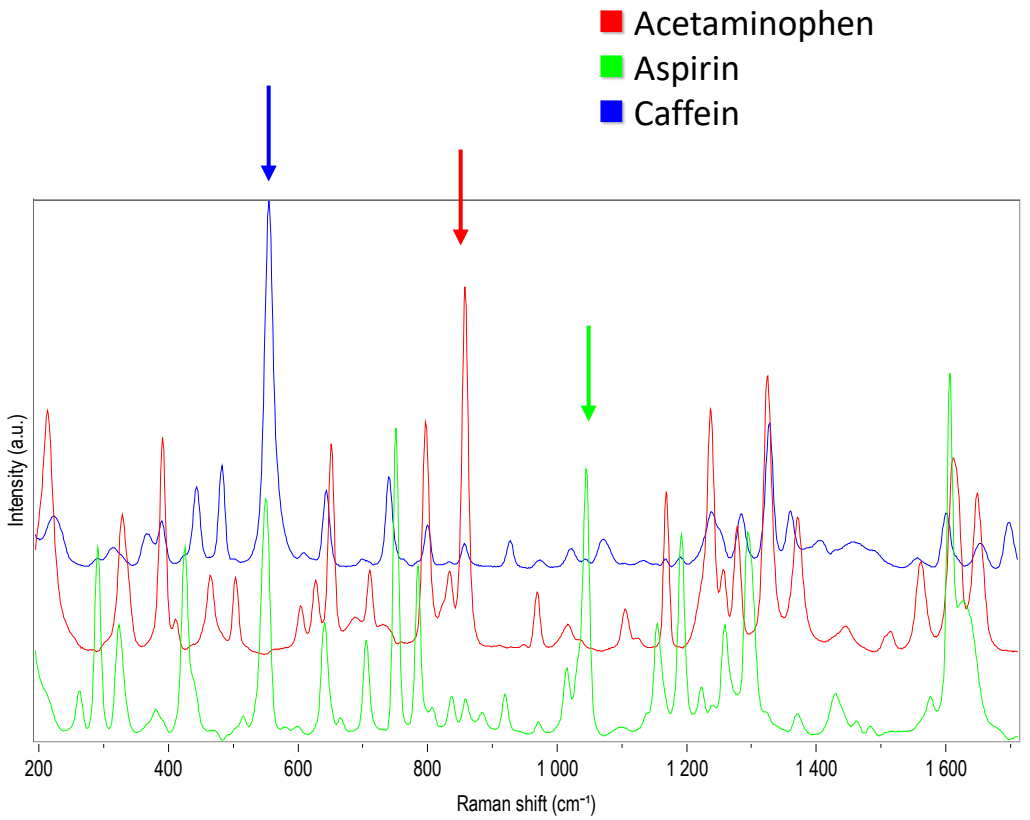




- Crystalline Si
- PolyCrystalline Si
- MicroCrystalline Si

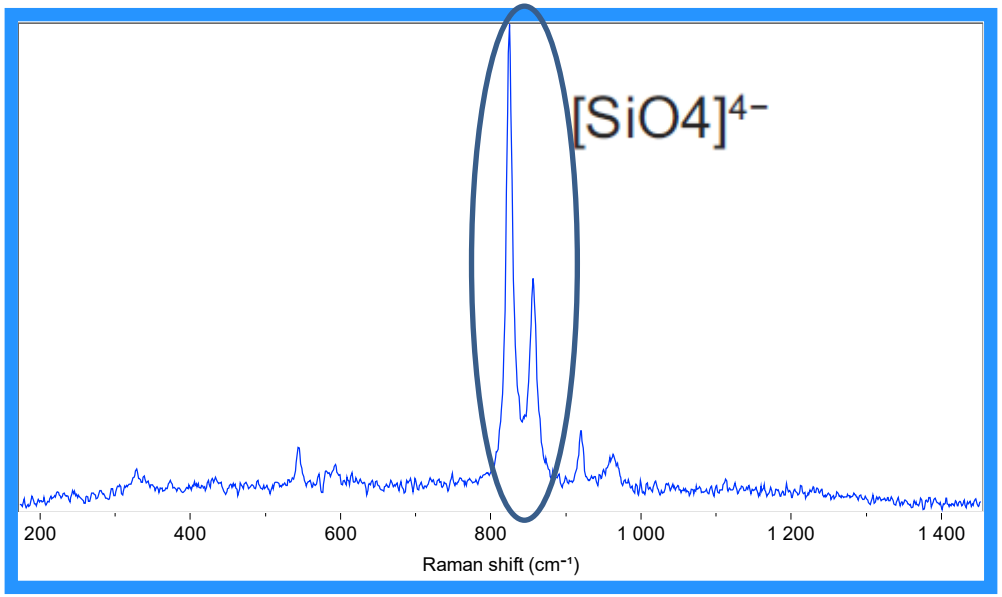
# Distribution of sample components (Pill)
# - Multispectral analysis

- Monitoring the **<u>Height/Area</u> of peaks** that can be assigned to a single compound



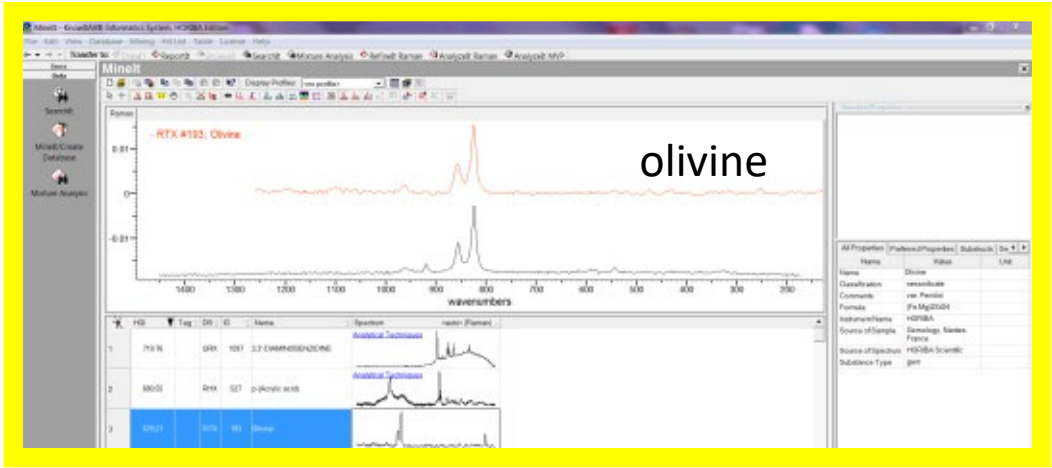
# Challenge/Issue: Databases




■ Databases can be used in order to directly identify the chemical compounds – should take into account the environment

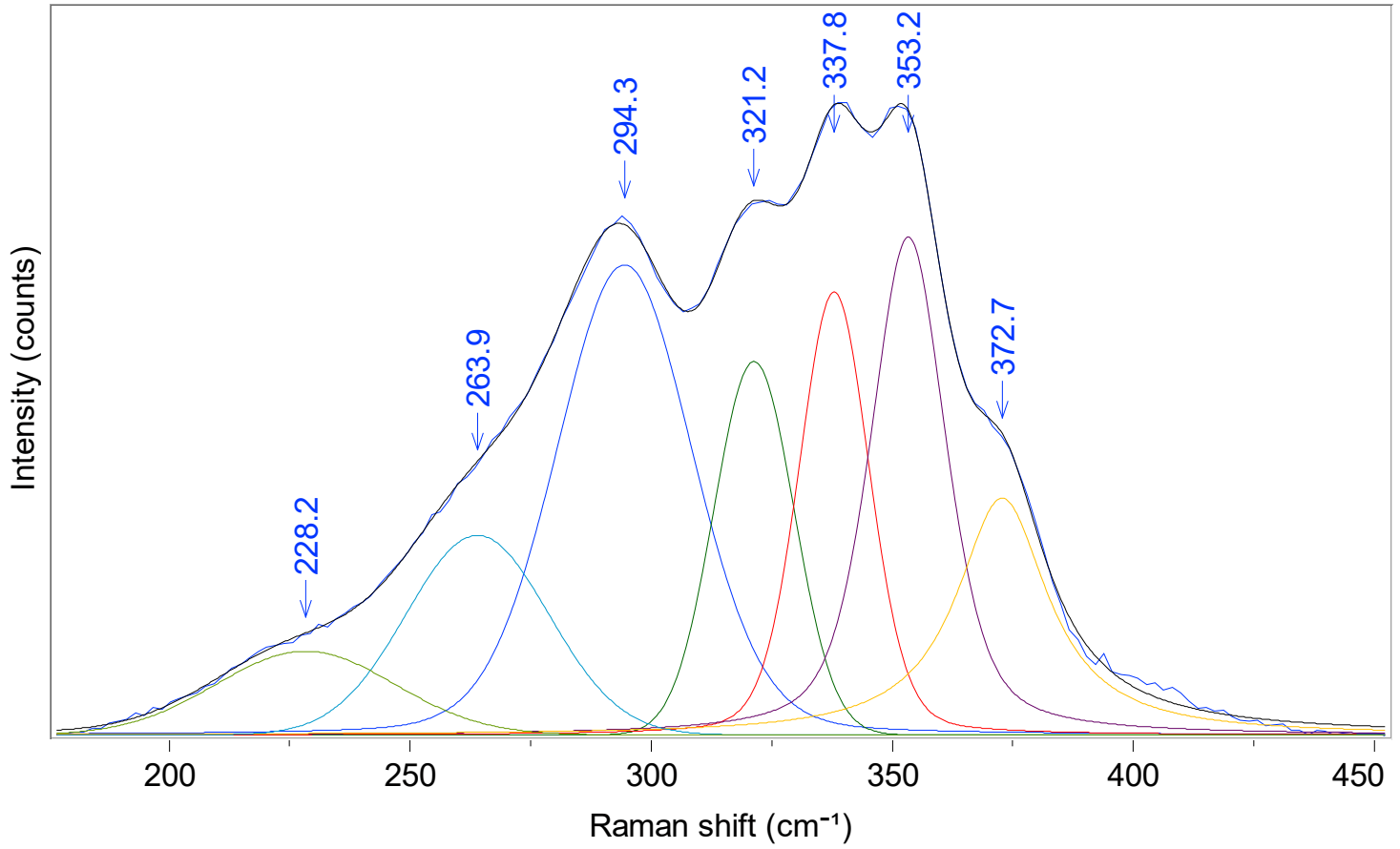
KIA Database search

■ Databases can be also used to analyze the vibrations (band – vibration assignment) :



# Challenge/ issues / AI tools

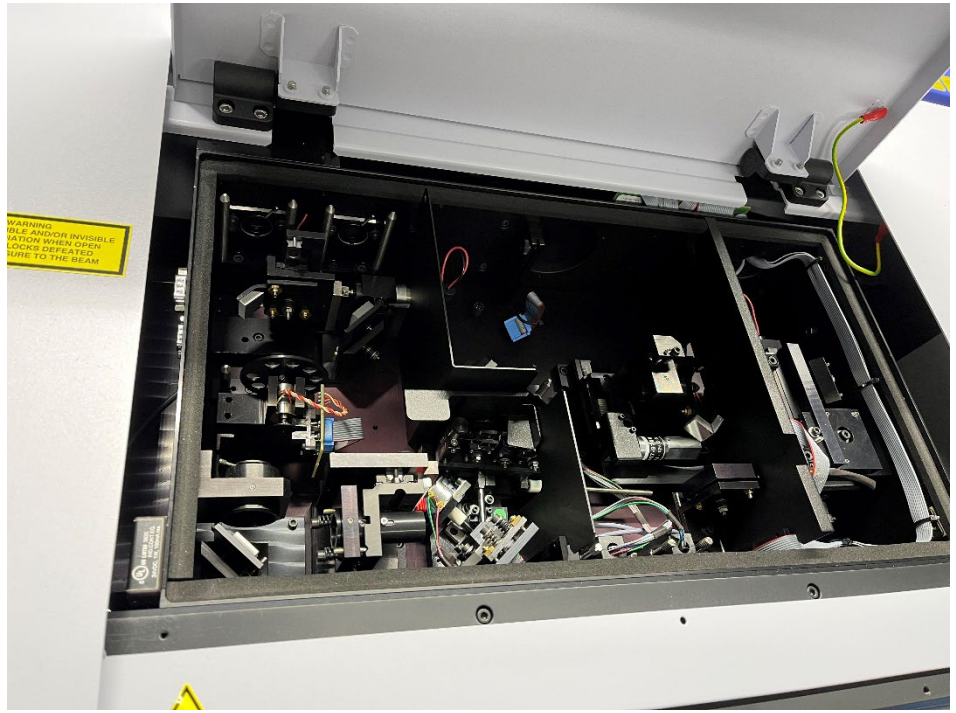
- Deconvolution
  - Choice in the peak shape type (gaussian, lorentzian, asymertric, etc…)
  - Possibility to fix / limit some parameters
  - A priori knowledge of the composition of the sample is recommended



# *Instrument & components*

# *Instrument & components - II*

## *Horiba*



## *Renishaw*

# Challenge to design a perfect Raman Instrument

**1 by $10^8$** photons is a **Raman photon**, rest of collected light is scattered Rayleigh light

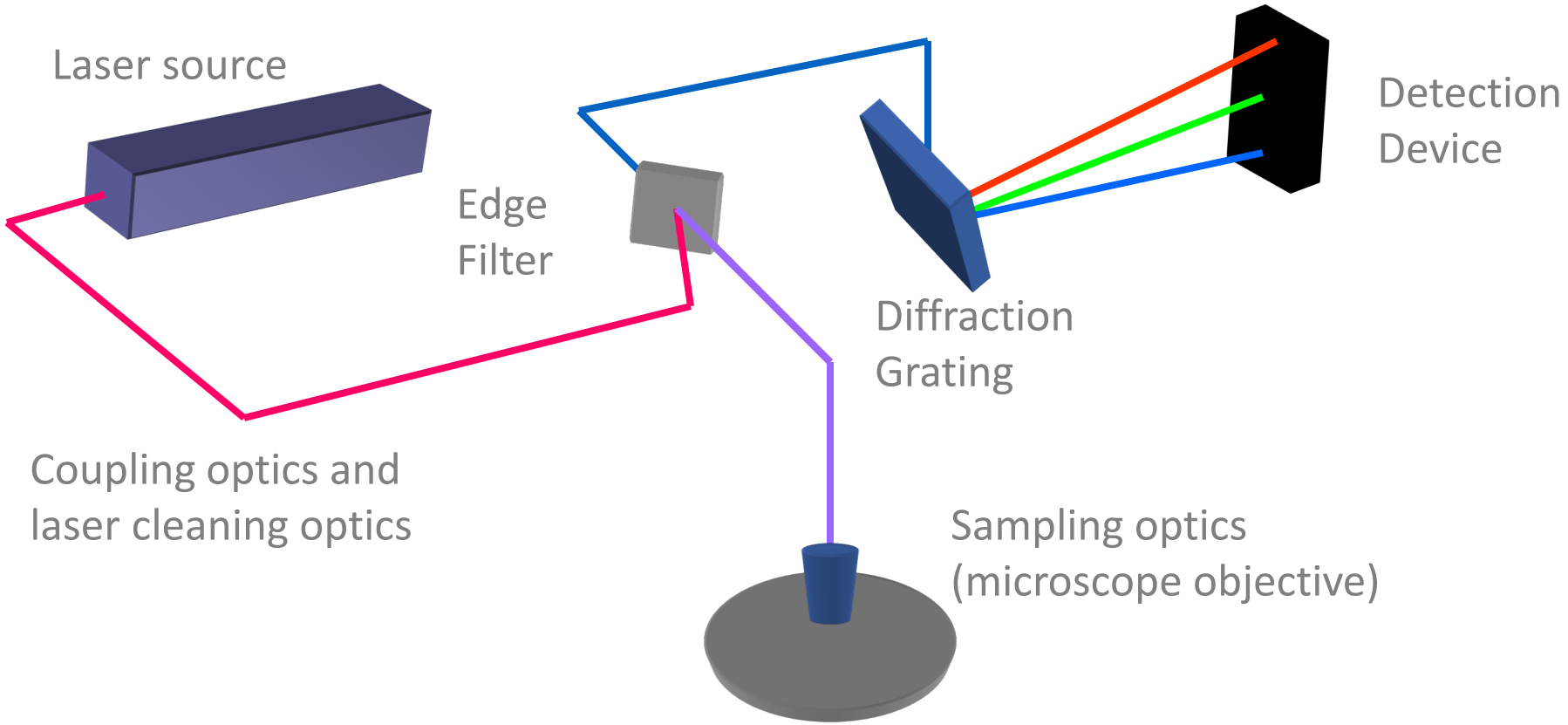
► **1st** challenge is **to get rid of this ‚stray light'**

Raman emission is very weak in numbers of photons

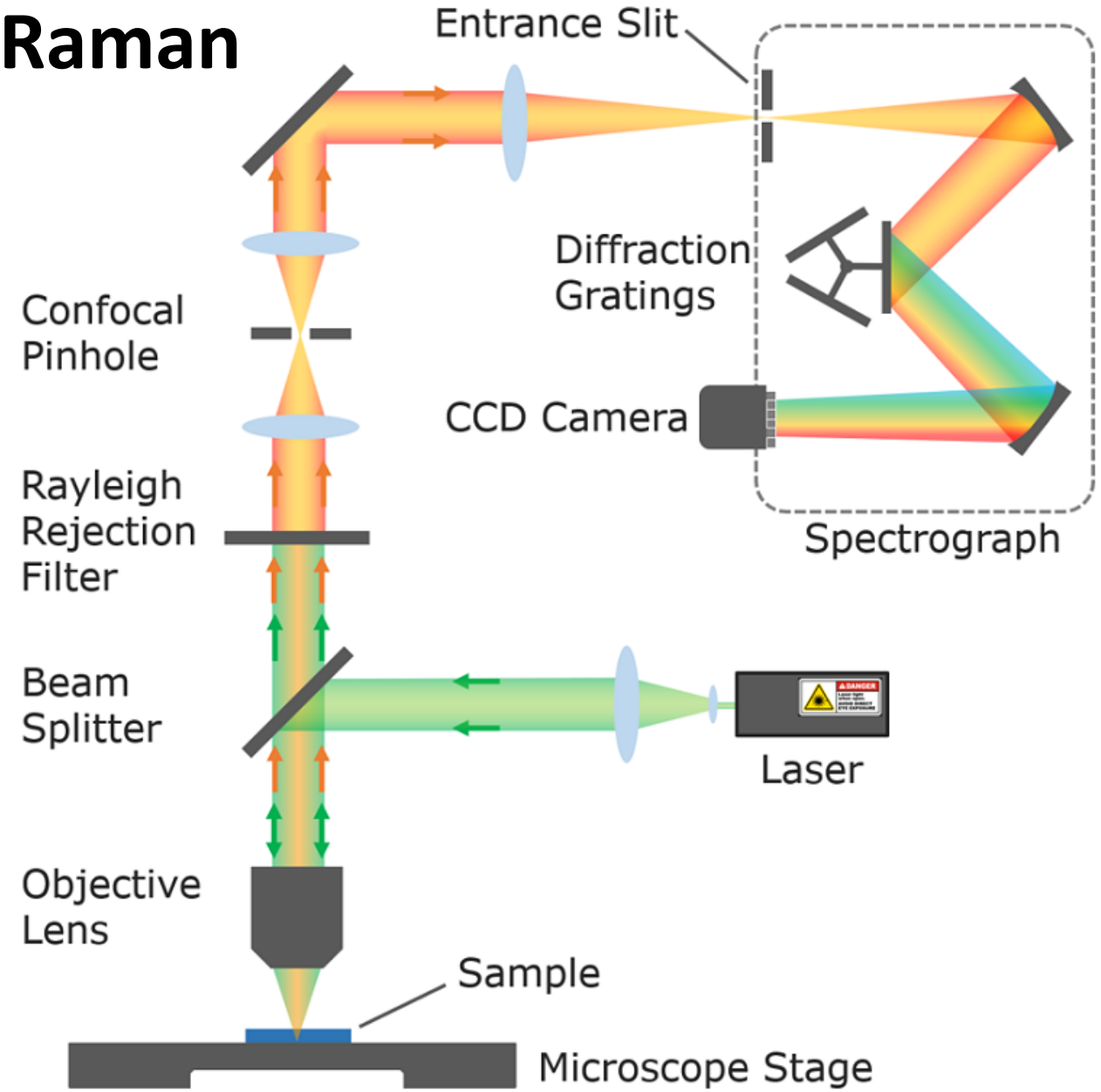
► **2nd** challenge is **to collect maximum of photons**

# Schematics of Raman spectrometer

A MicroRaman spectrometer typically consists in:



# Confocal Raman

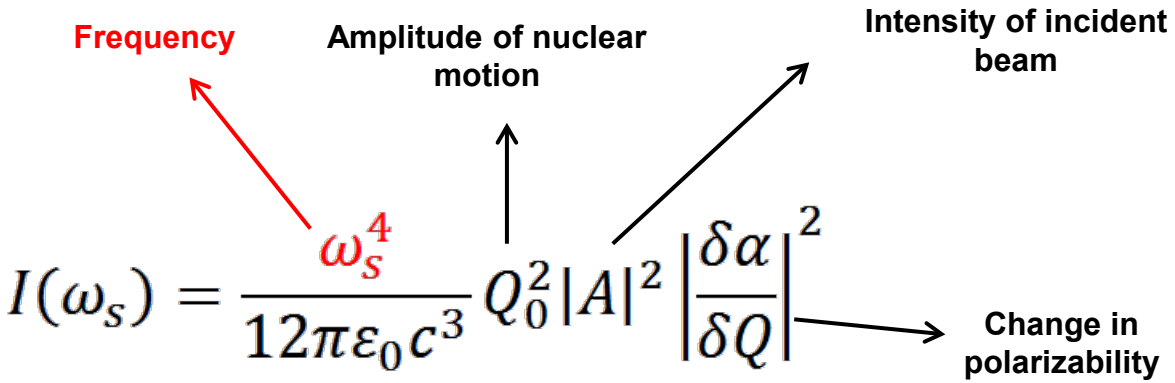



https://www.edinst.com/blog/what-is-confocal-raman-microscopy/

# Role of the laser

## Raman efficiency

- **Intensity of the Raman shifted light:**




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

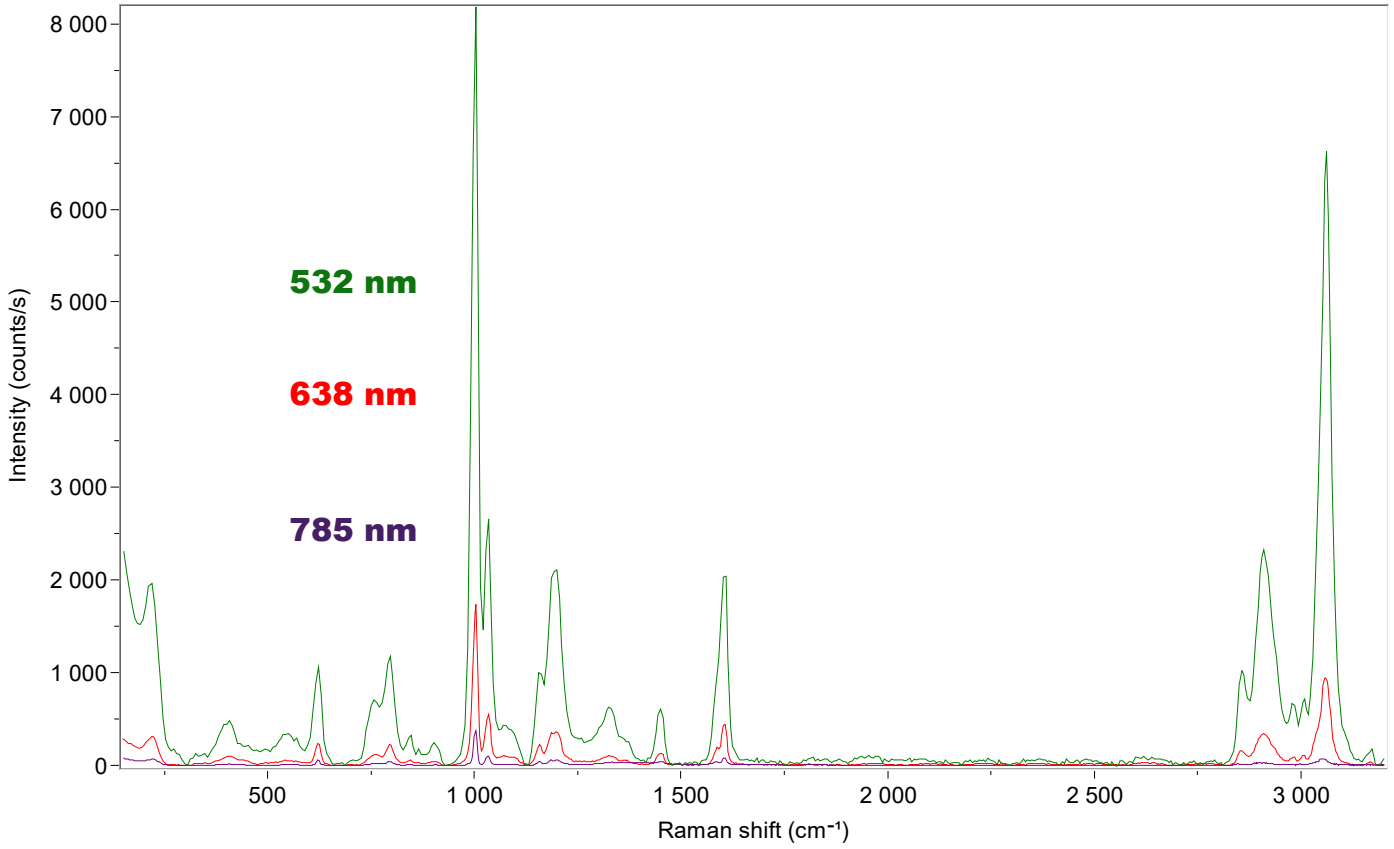
**The efficiency increases when going to shorter wavelengths**

# Role of the laser

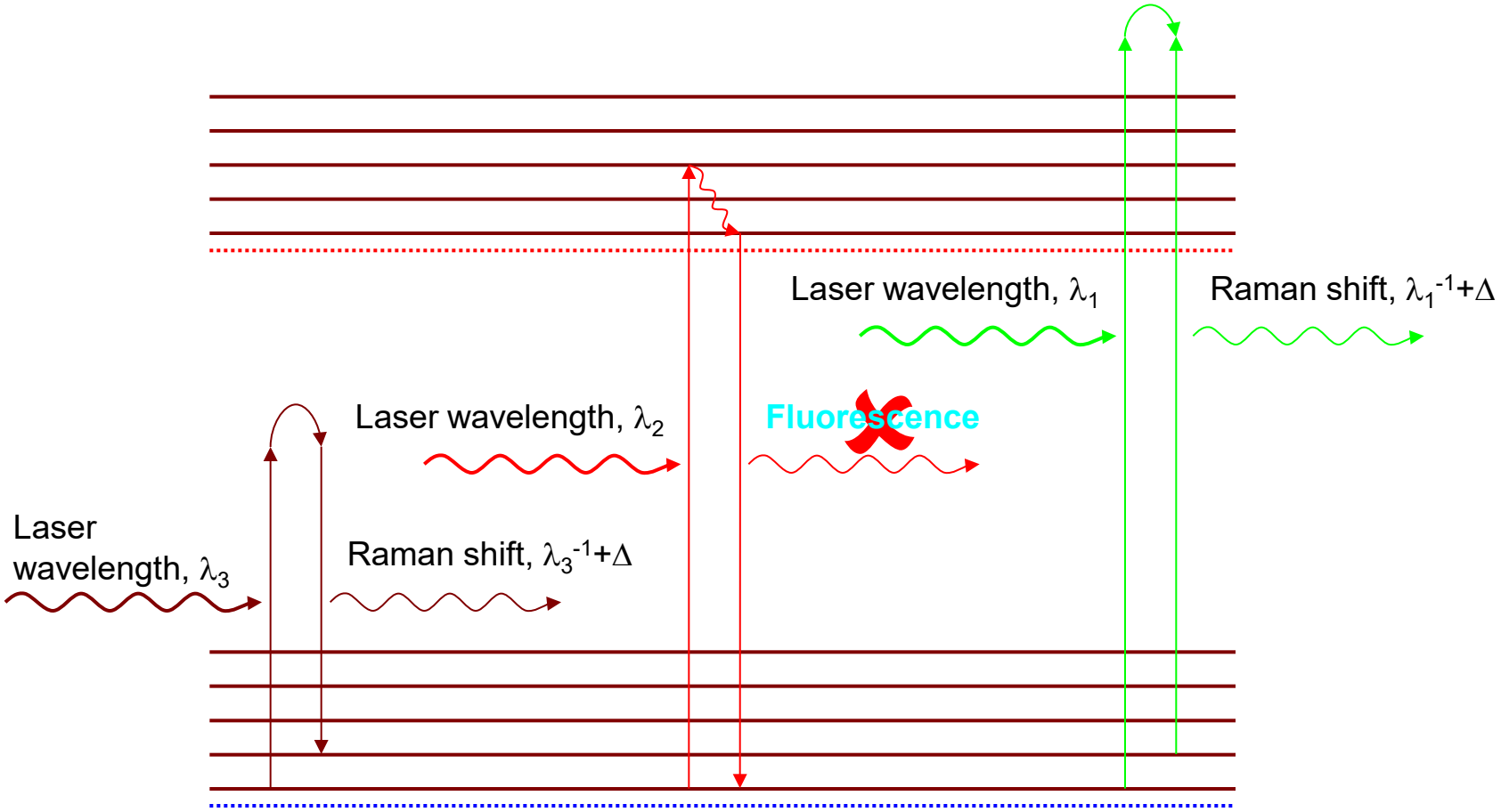
## Raman efficiency

- **Intensity of the Raman light:**

**Spectra (polystyrene) normalized for the acq. time, the laser power, the detector response**



# fluorescent : the enemy of Raman

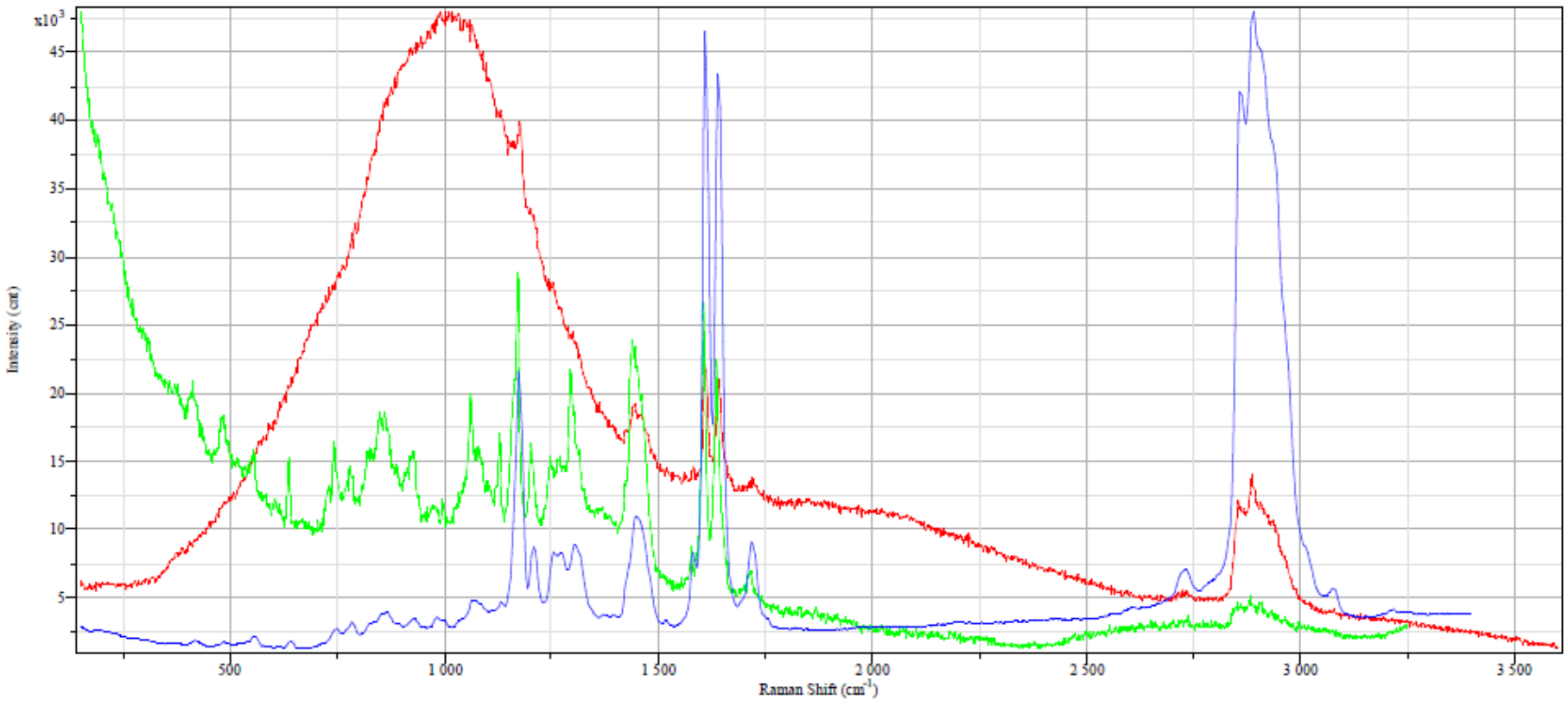



Laser wavelength: $\lambda_3 < \lambda_2 < \lambda_1$

# Commercial Hand cream

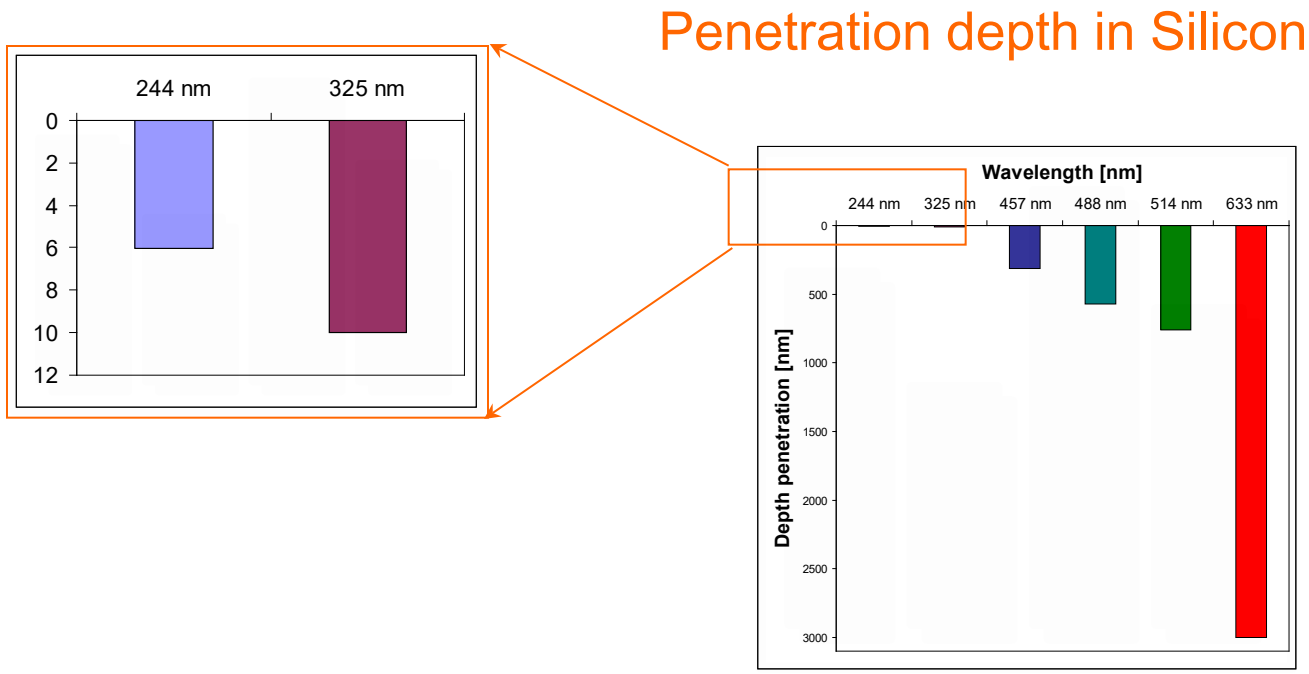
***Laser Excitation***

➔Reduction of Fluorescence



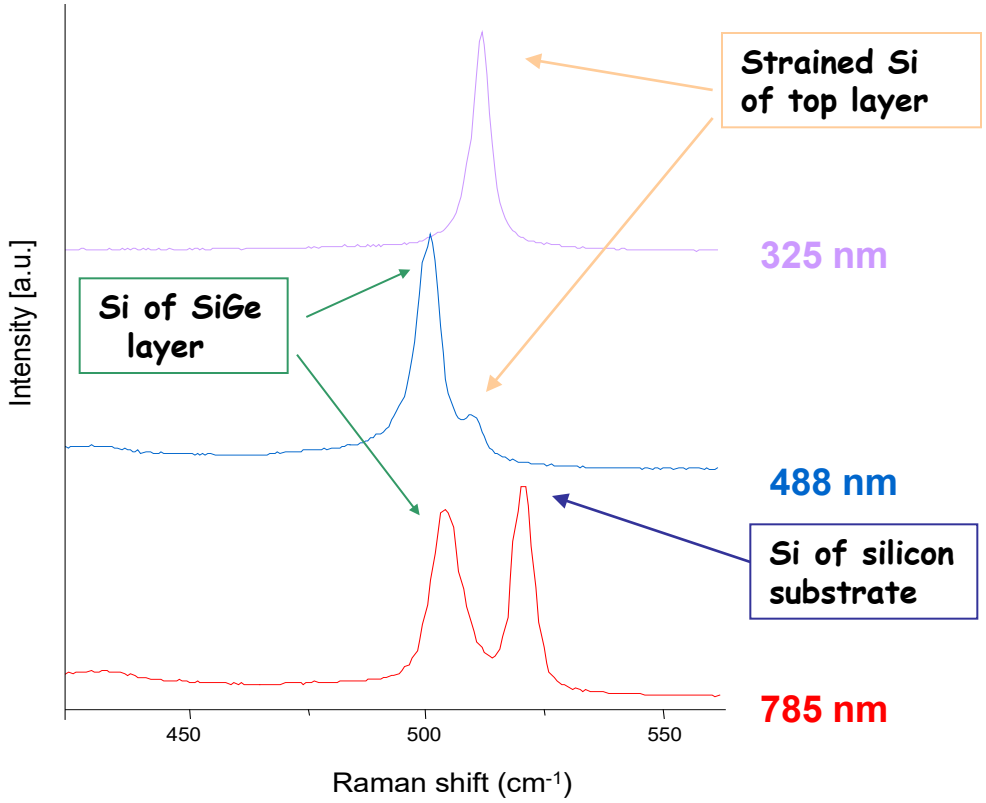

785 nm – 633 nm – 473 nm

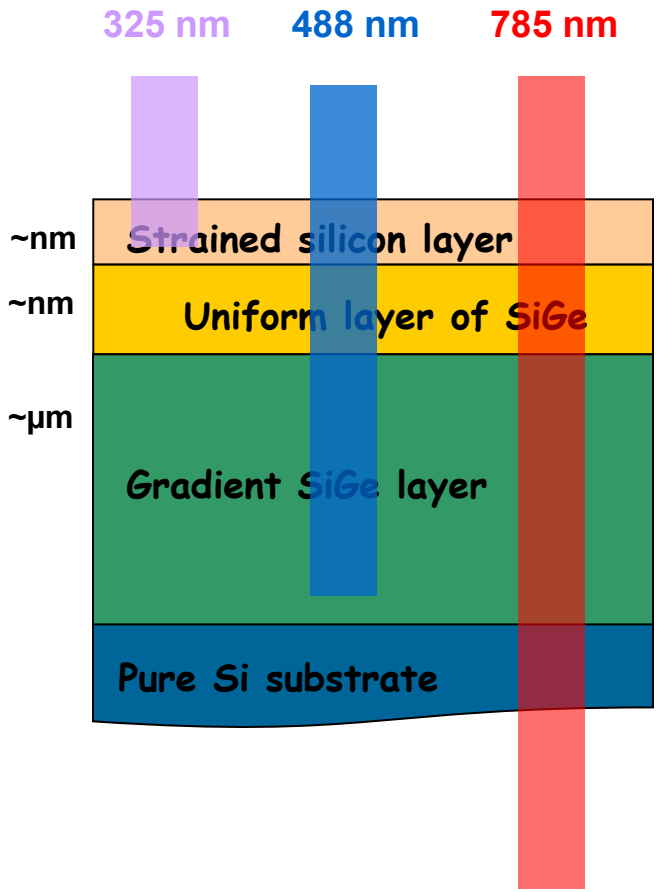
# Laser source: Penetration depth




- General: The larger the excitation wavelength, the deeper the penetration.
- The exact values depend on the materials. (absorption properties)

# Laser source: Penetration depth




- The higher the excitation wavelength, the deeper the penetration.

# Role of the laser (Wavelength dependence)

## Spot Size / spatial resolution

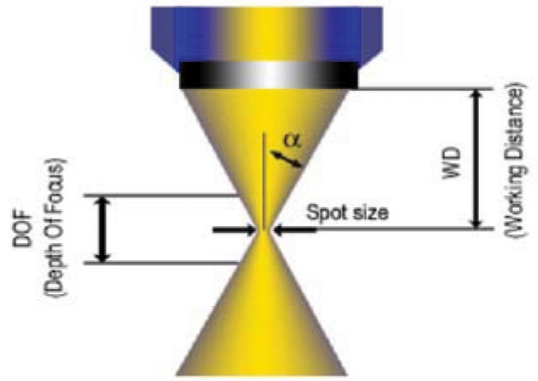
**Laser spot size D is defined by the Rayleigh criterion:**

excitation wavelength ($\lambda$)

$$D = 1{,}22\ \lambda / NA$$

objective numerical aperture (*NA*)

With NA=n sinα

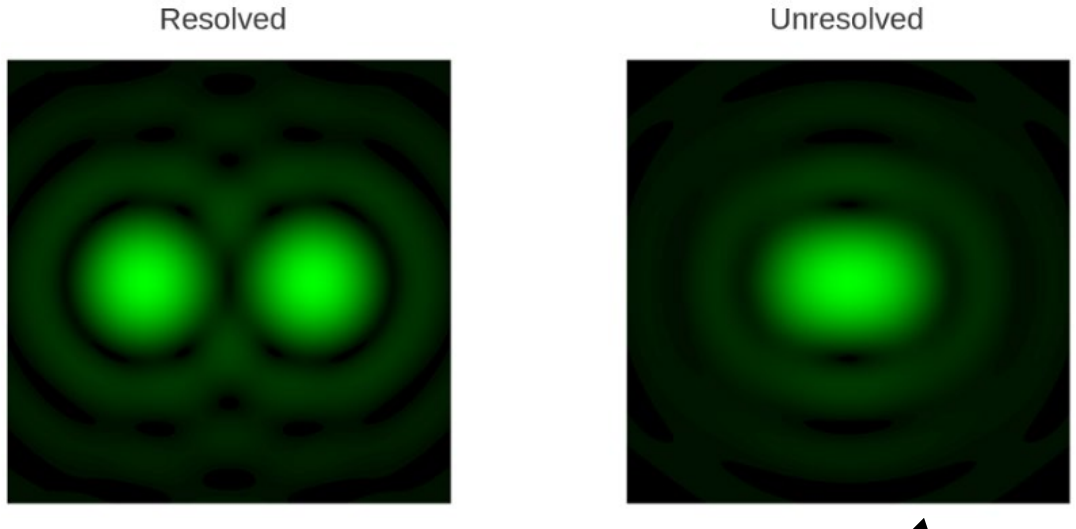



**The spatial resolution is roughly half of the laser spot size**

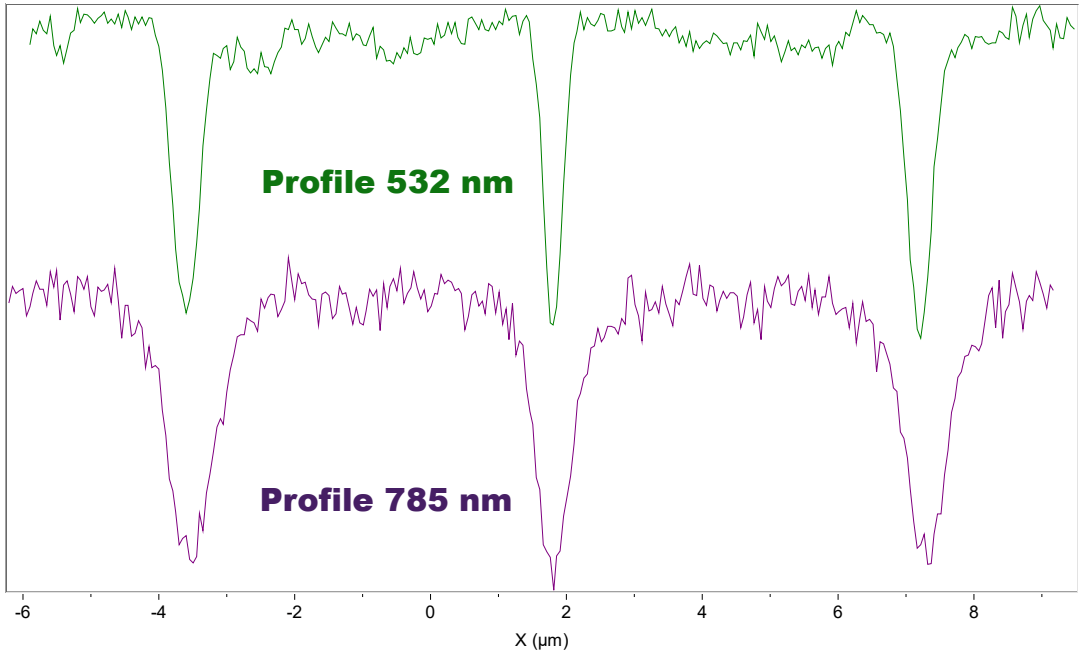
Rayleigh criterion enables the calculation of the dimension of the smallest object theoretically resoluble

**$\Delta d_{min}$ = 1.22 λ / 2 NA**

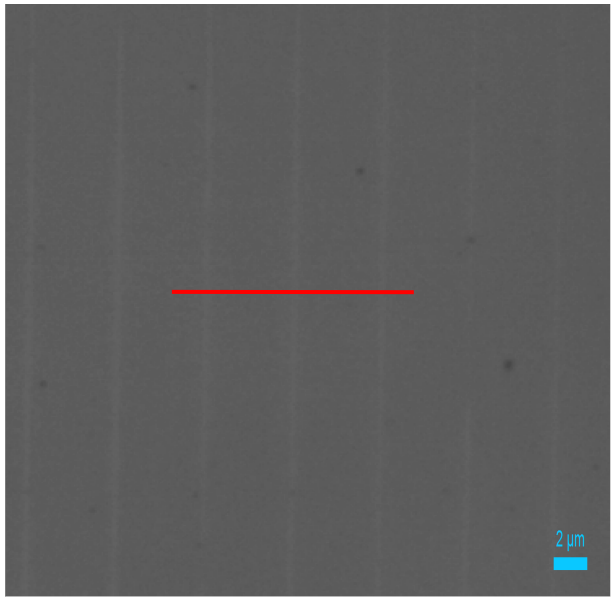
**= ultimate lateral resolution**



# Spatial resolution: wavelength dependence




**Profile along X axis**

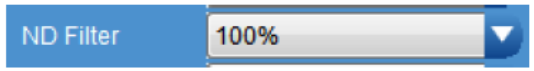



**FWHM 532 nm: 0.39 µm (average)**

**FWHM 785 nm: 0.73 µm (average)**

- **Use of patterned silicon: 100 nm wide gold covered stripes spaced every 5 µm (substrate: Si).**

# Filter



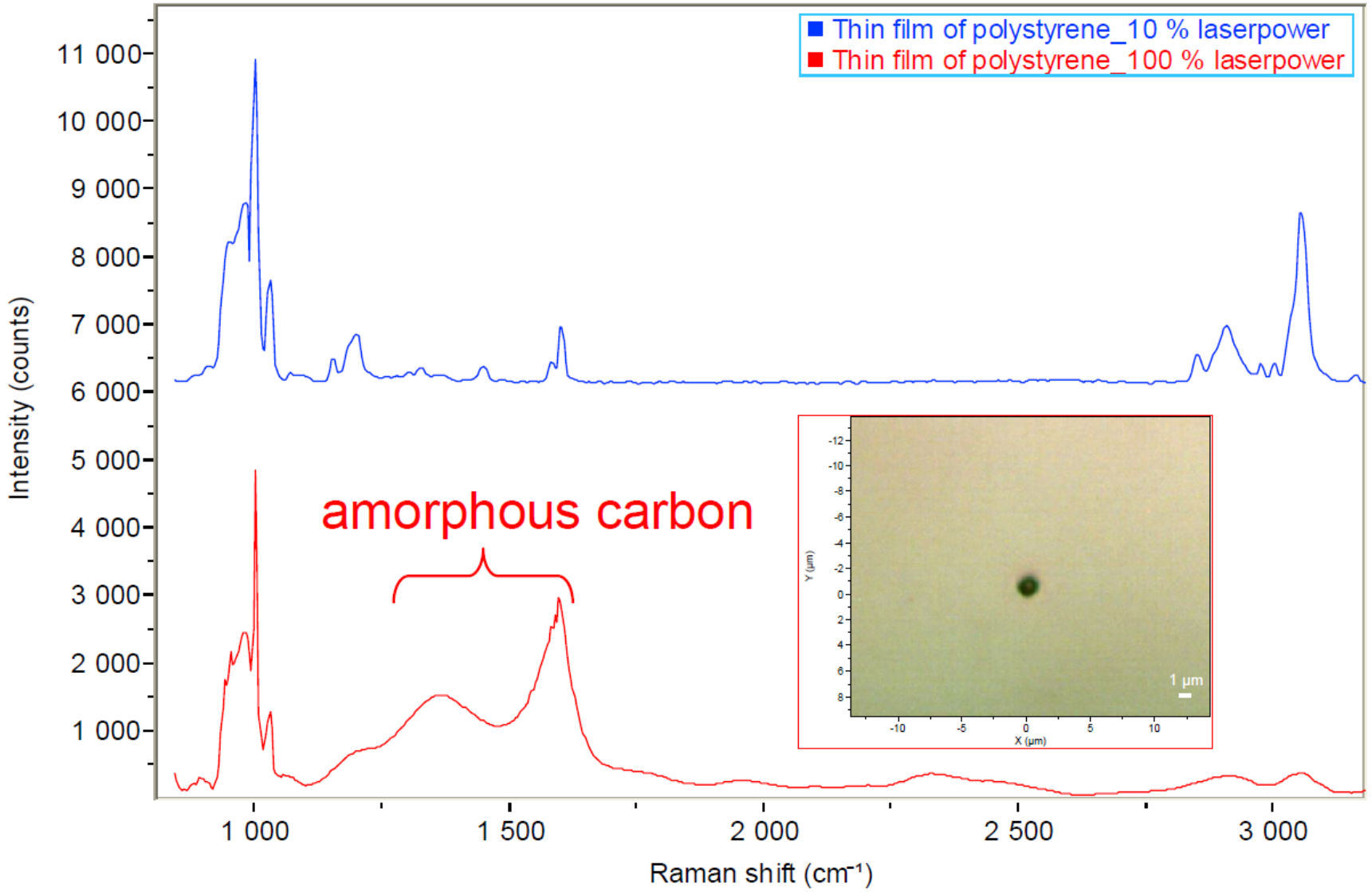

- Keep in mind: the usage of high numerical objective lenses causes a very small spot size of the laser which results in a high power density
- To avoid sample burning radiation power has to be adapted INDIVIDUALLY to the sample

| Laser wavelength: 473 nm<br>Laser power at sample: 25.5 mW | | | |
|---|---|---|---|
| Objective | N.A. | Laser spot size (µm) | **Radiation power ($kW/cm^2$)** |
| 100× | 0.90 | 0.64 | **~7900** |
| 50× | 0.75 | 0.77 | **~5400** |
| 10× | 0.25 | 2.31 | **~600** |

| Laser wavelength: 633 nm<br>Laser power at sample: 12.6 mW | | | |
|---|---|---|---|
| Objective | N.A. | Laser spot size (µm) | **Radiation power ($kW/cm^2$)** |
| 100× | 0.90 | 0.85 | **~2200** |
| 50× | 0.75 | 1.03 | **~1500** |
| 10× | 0.25 | 3.09 | **~200** |

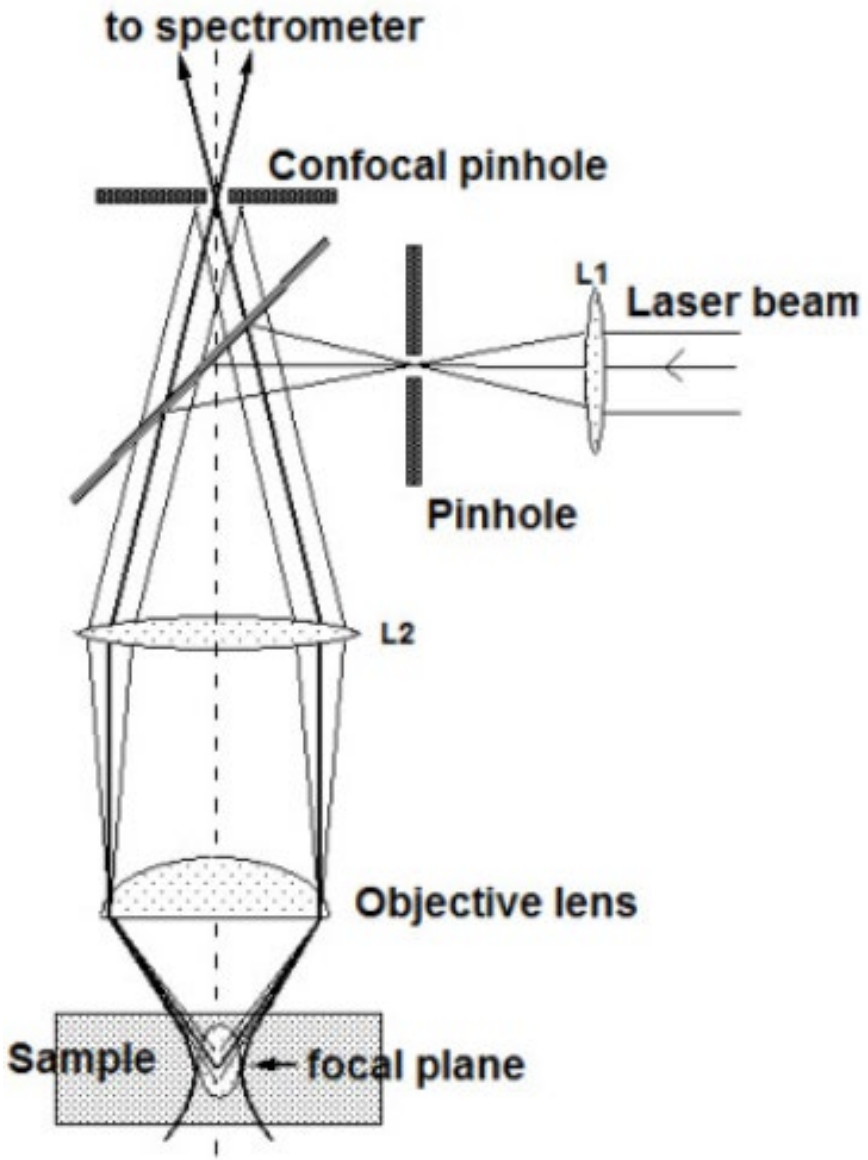
# Filter

ND Filter 100%



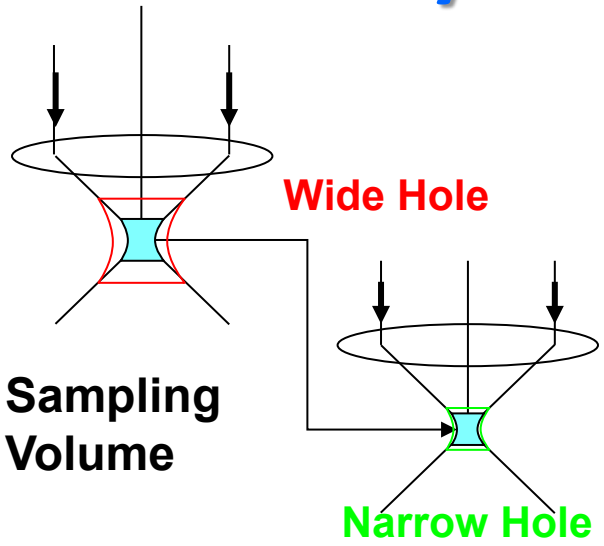
# Component : pin hole

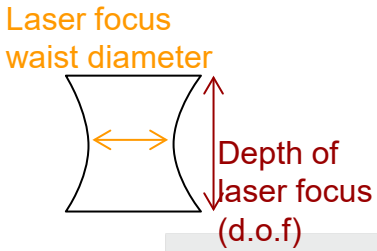
## : Confocality and spatial *Resolution*



# Component : pin hole

## : Confocality and spatial *Resolution*

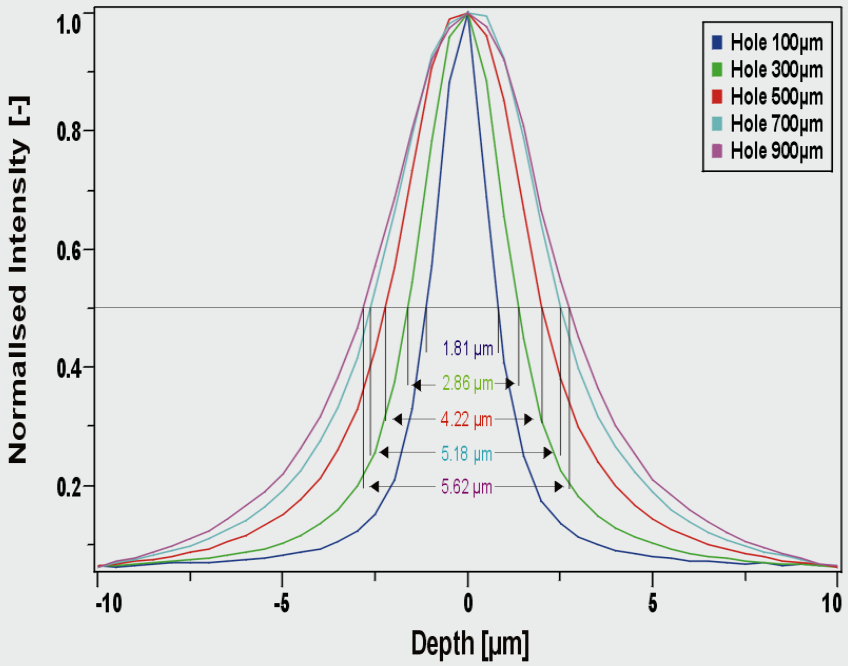



Narrow Hole:
Collecting Raman radiation that originates only from within a diffraction limited laser focal volume with a dimension of:

Focus waist diameter ~ 1.22 λ / NA
Depth of laser focus ~ 4 λ / $(NA)^2$

**Confocal z-scan against silicon with different hole apertures**
**$\lambda_{exc}$ = 633 nm**



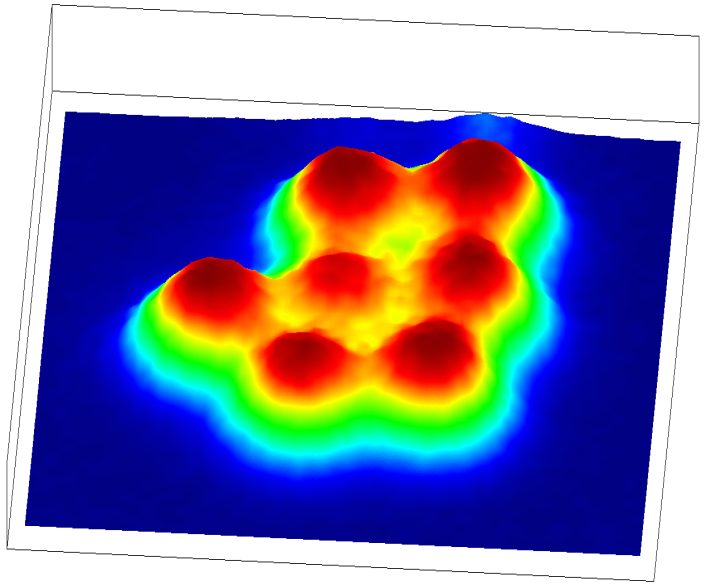
# Role of the confocal hole

## Confocal Hole

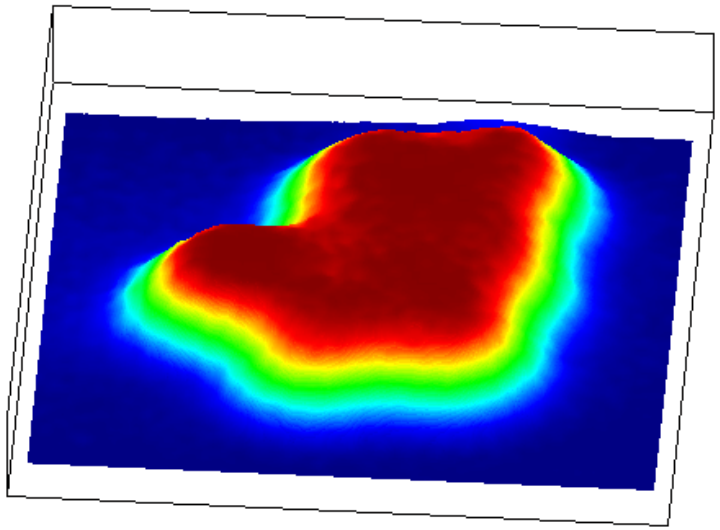
- **Increase the spatial resolution (X, Y and Z)**

**Measurement of 1µm polystyrene beads in confocal and non-confocal mode**

**Hole 100 µm (confocal)**

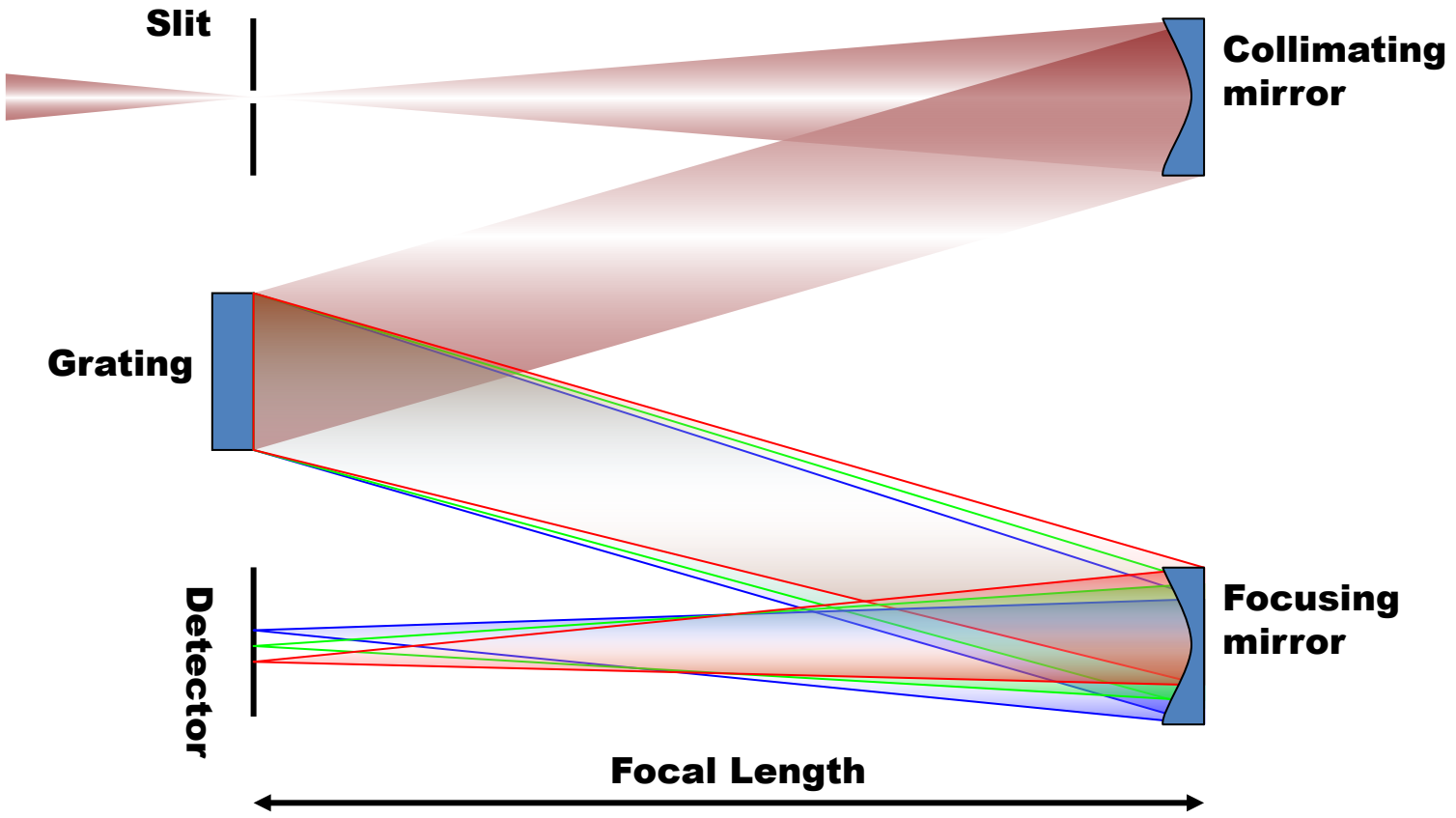


**Hole 500 µm (non confocal)**

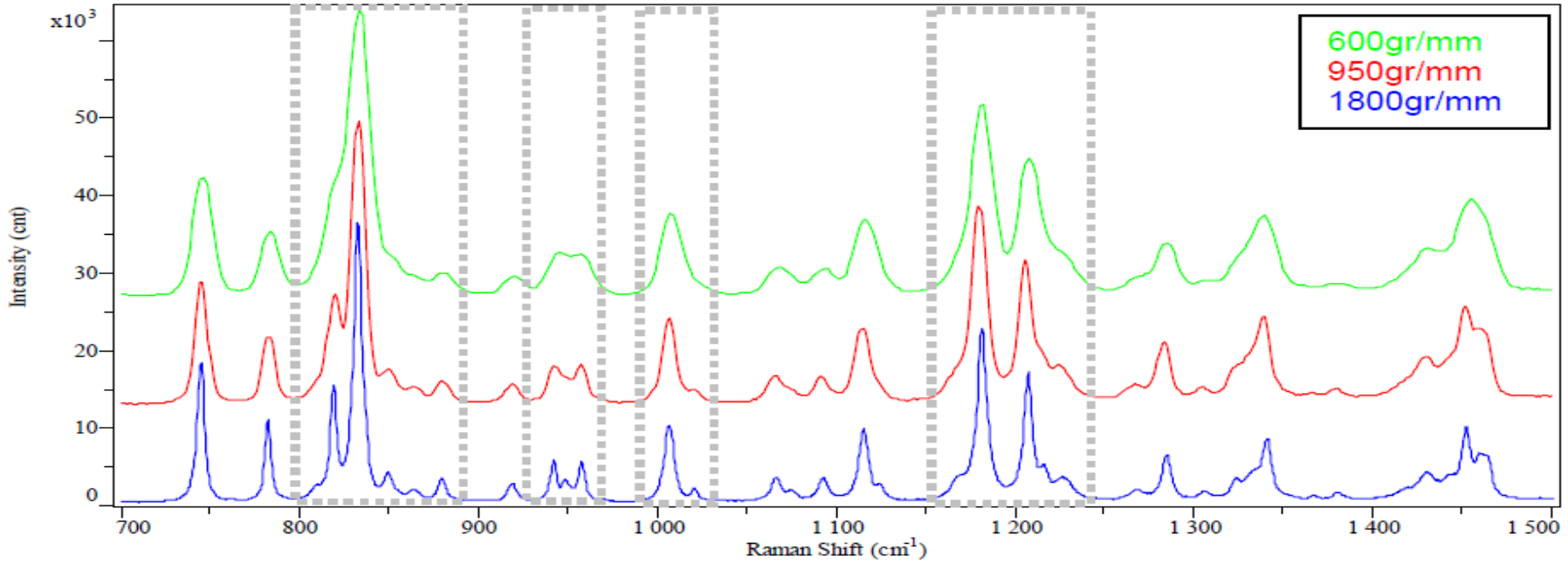


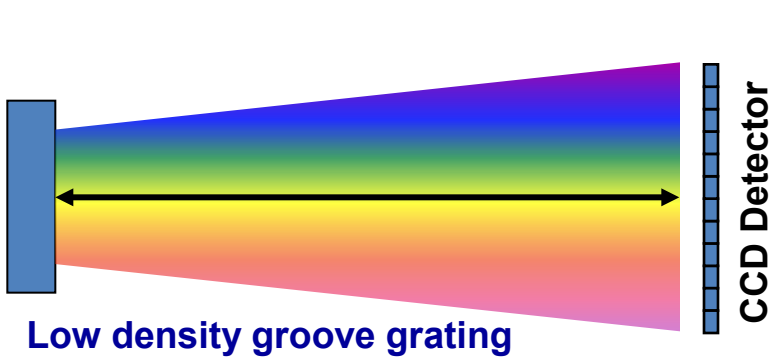
# Role of the spectrograph

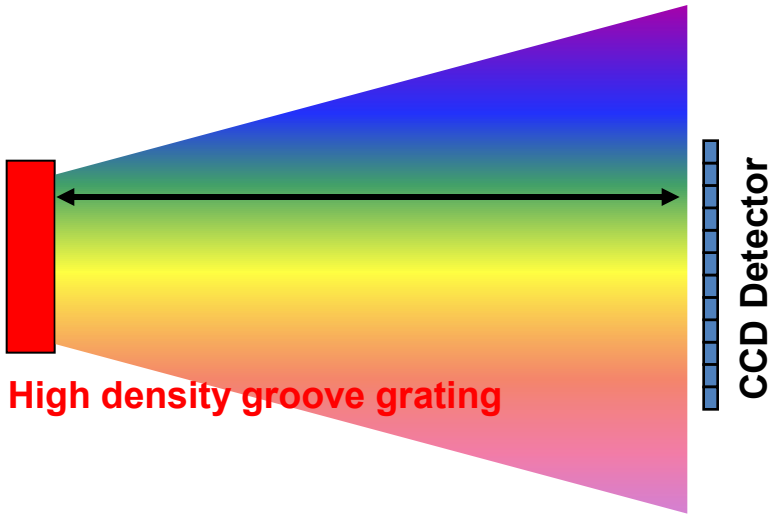
- **The spectrograph**



# Grating / groove density

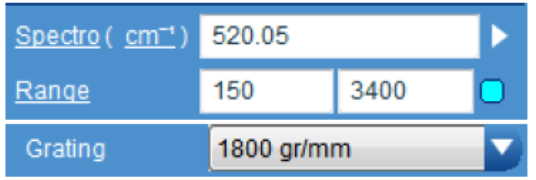


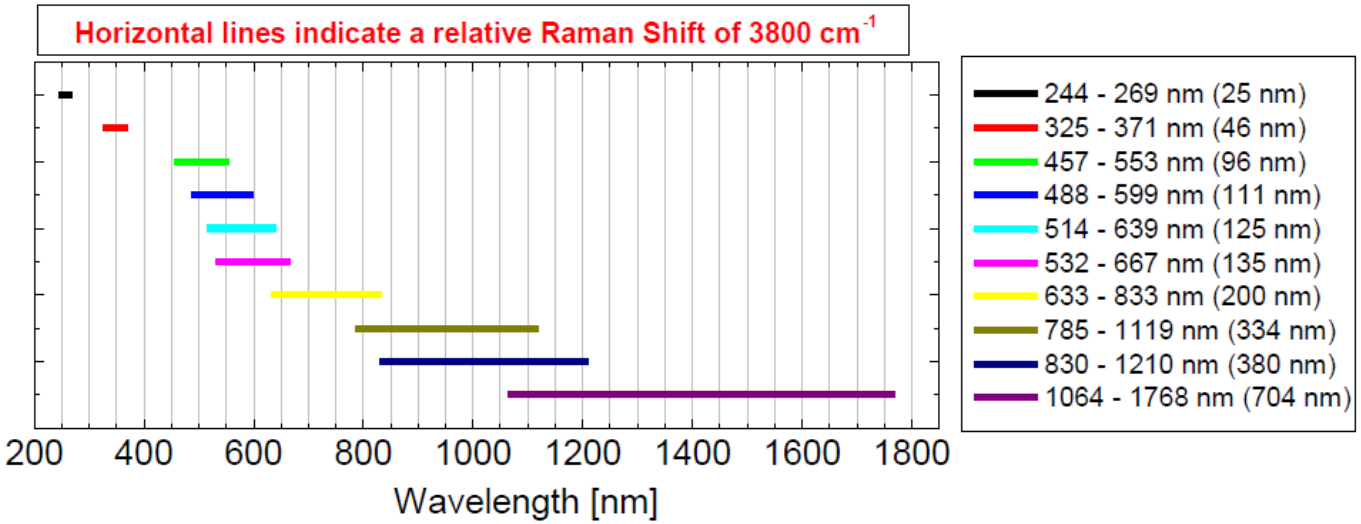




Same focal length
Same excitation wavelength

# Spectro & Grating

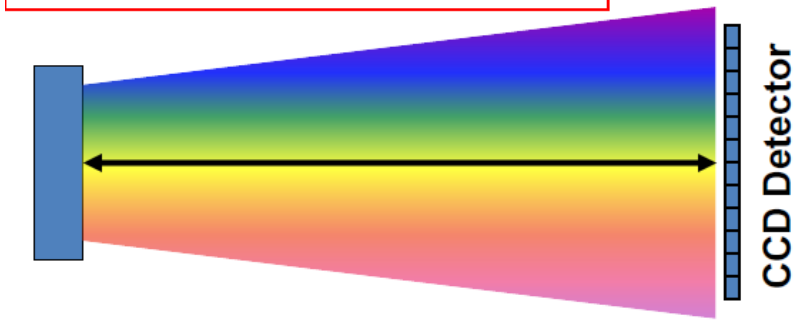



HORIBA Scientific

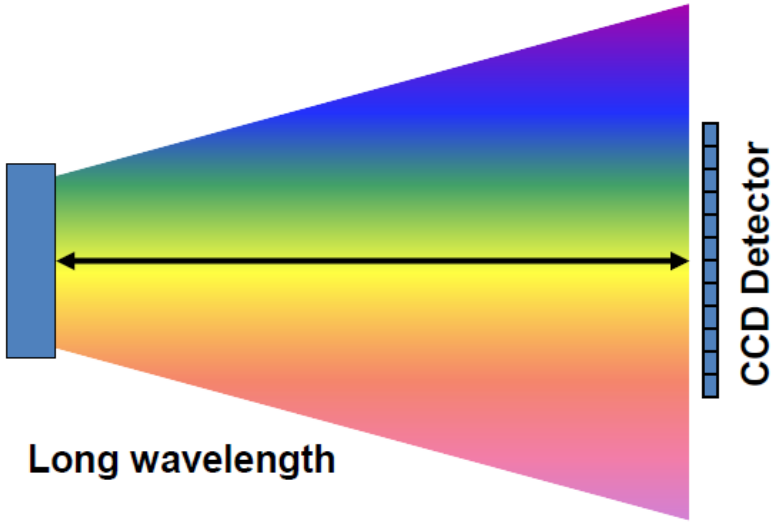



**Dispersion as a function of excitation wavelength**

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

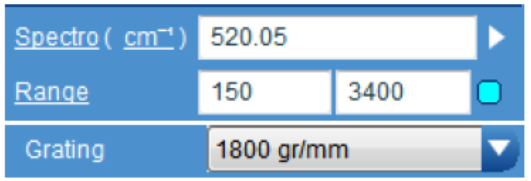



**Short wavelength**

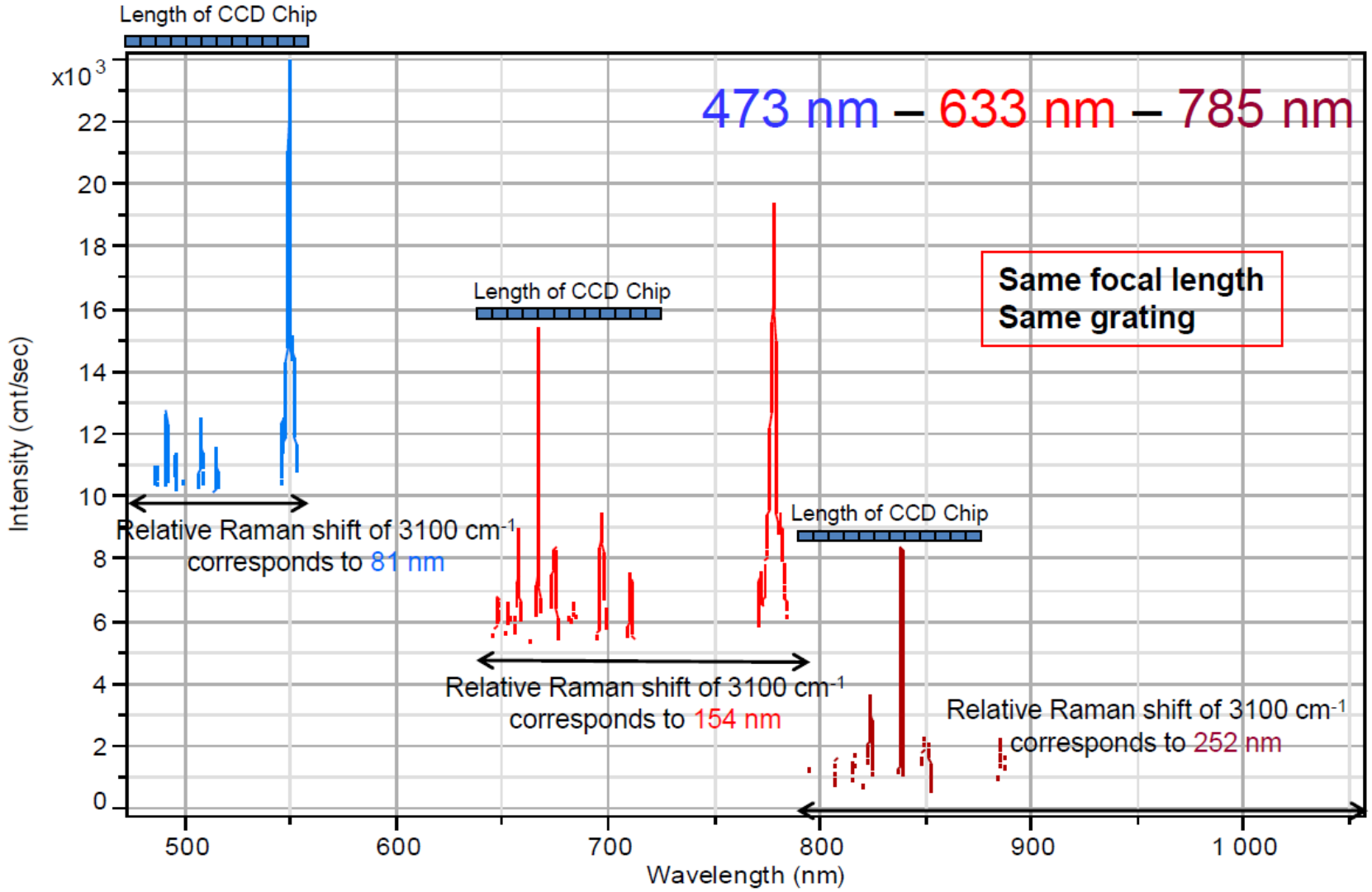



**Long wavelength**

# Spectro & Grating

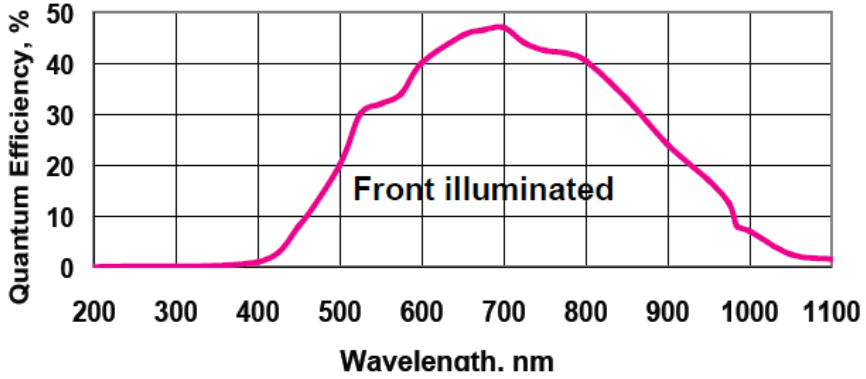


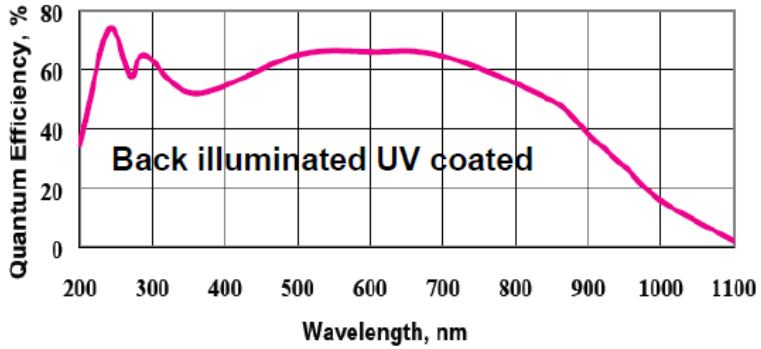

HORIBA Scientific

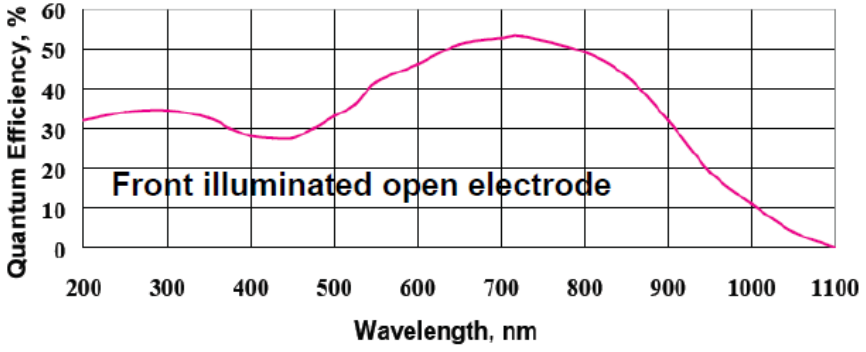


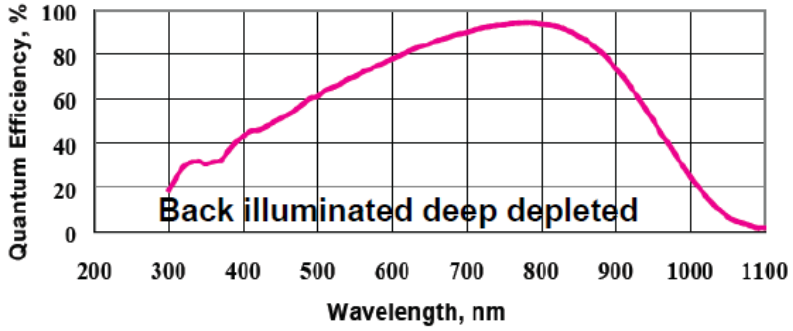
# Detector & Quantum Efficiency

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

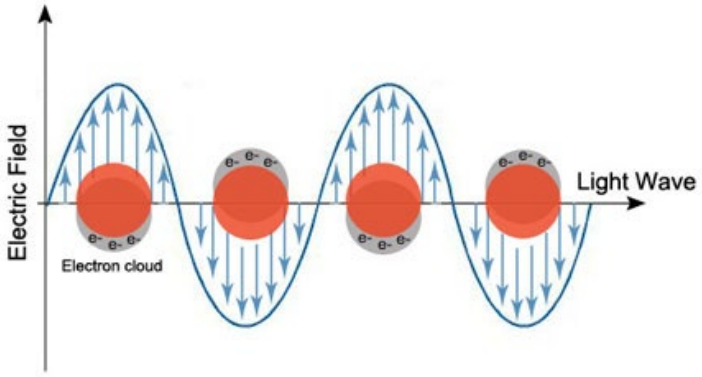


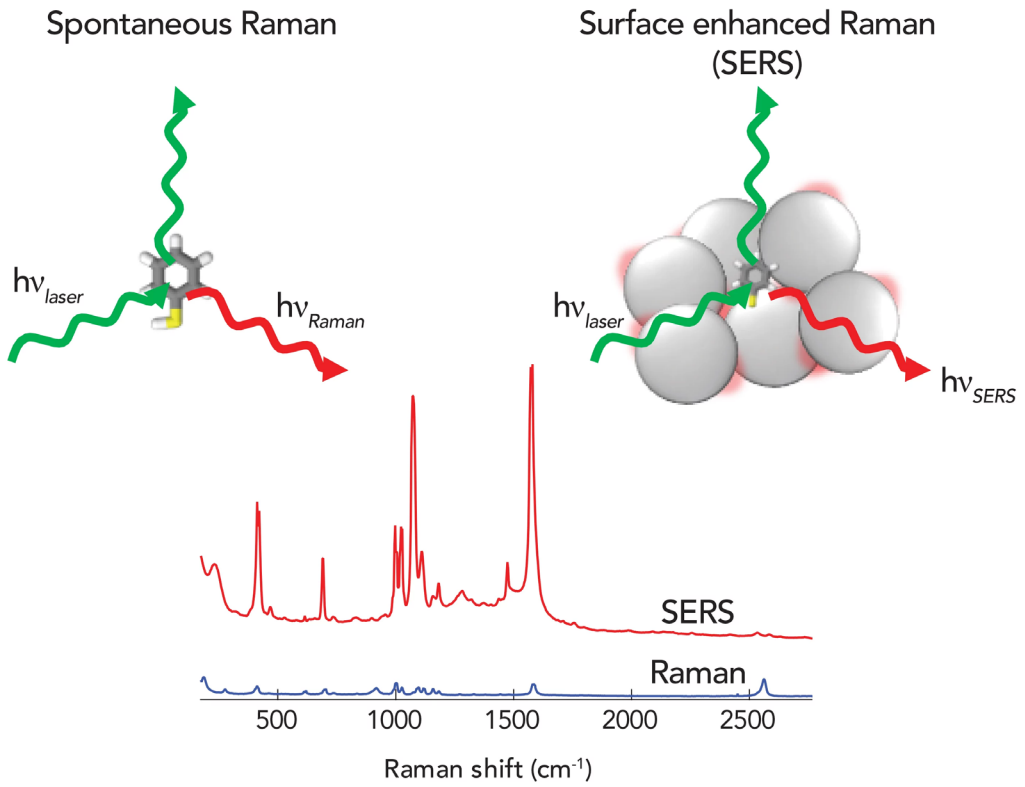



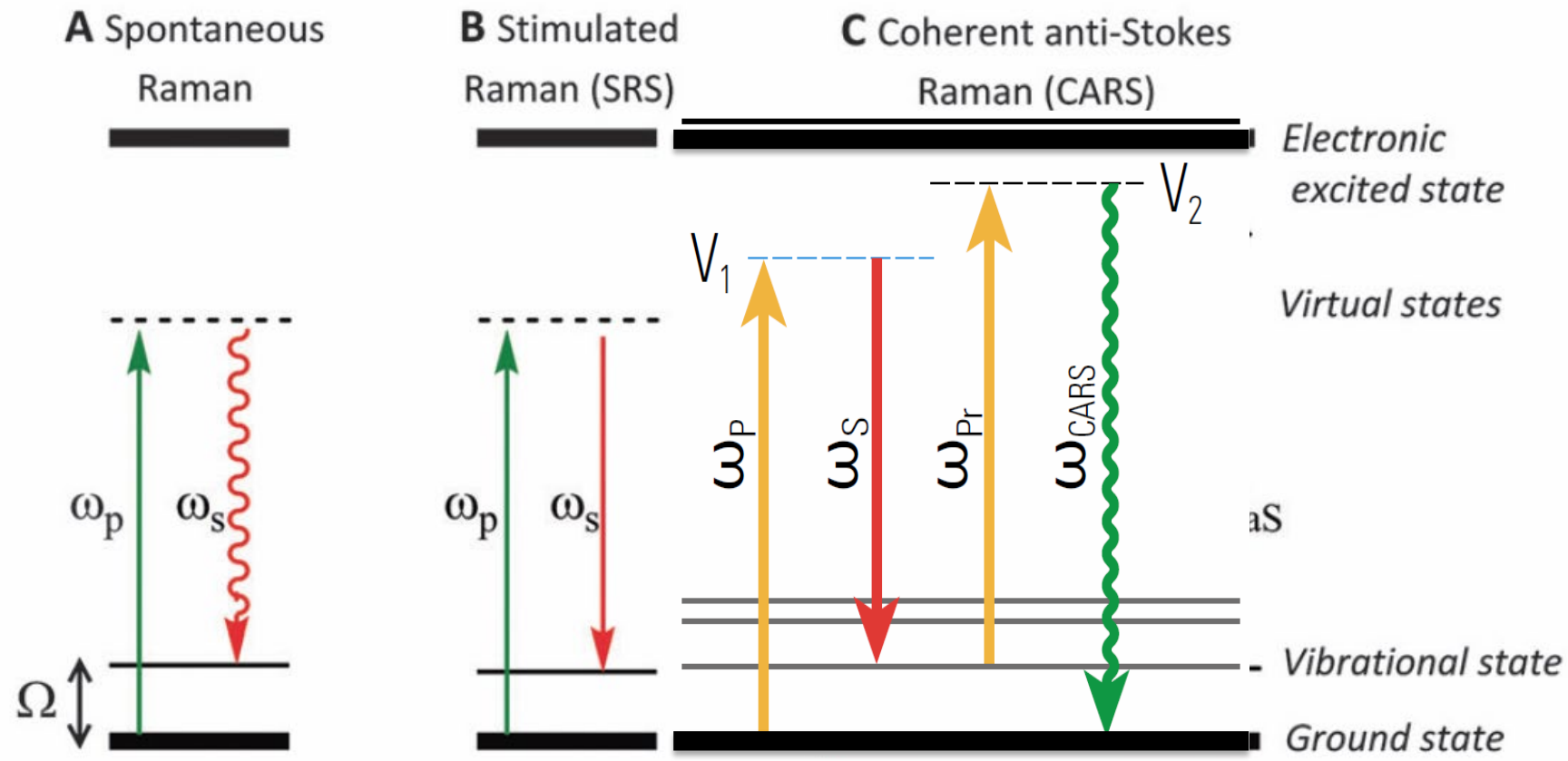
# On-going: Enhancing Raman signal



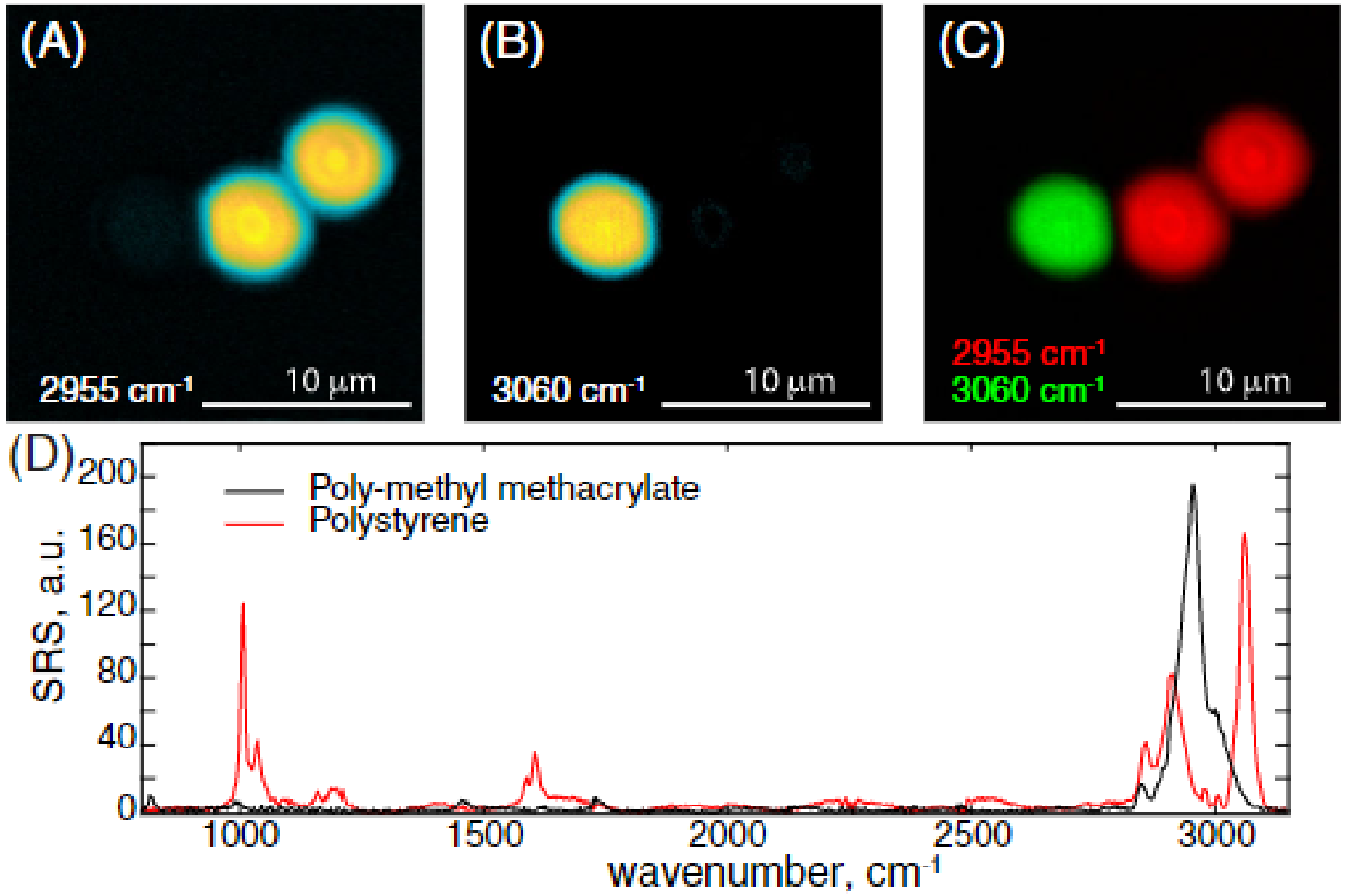

- SERS: Surface Enhanced Raman Scattering
- TERS: Tip-Enhanced Raman Scattering
- Gold, Silver, array., Plasmonics and etc.

# Microscopy
# : Spontaneous Raman, SRS, CARS



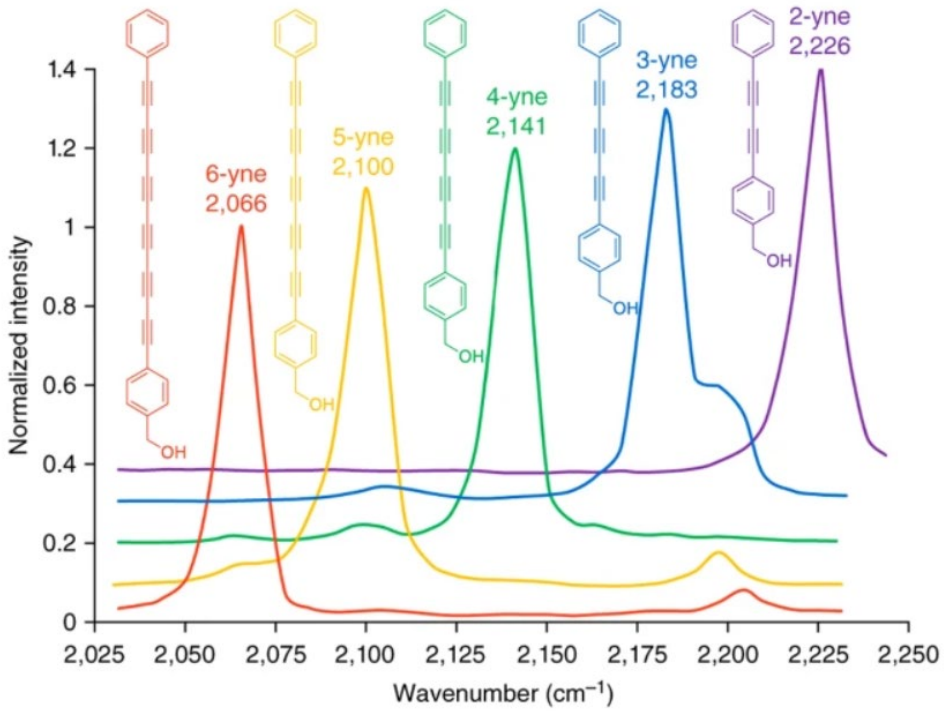
# Imaging – SRS / CARS

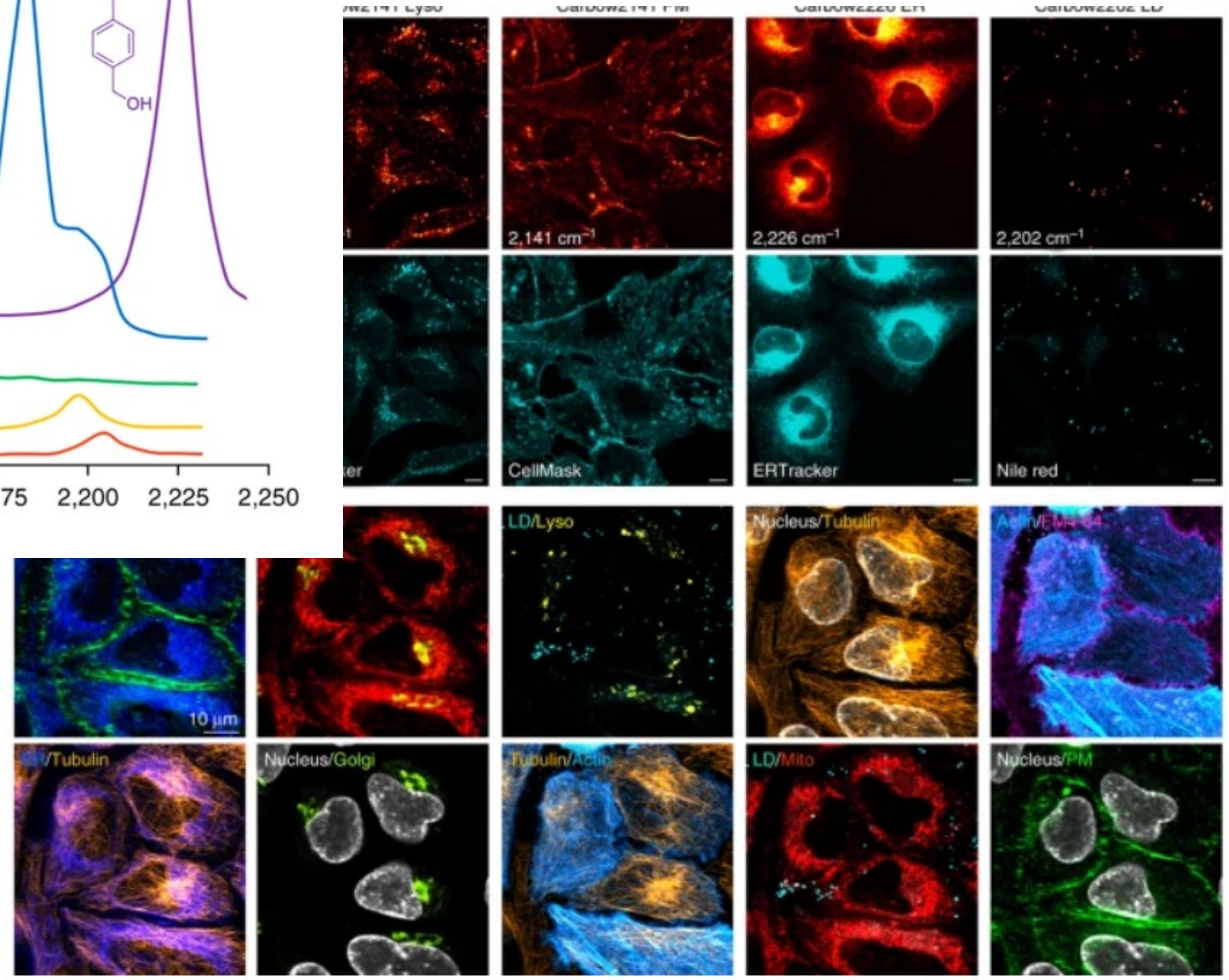
PS PMMA overlay




(A), (B) a cluster of three beads from a mixture of 5μm PMMA and PS beads. (C) Overlay of two SRS images acquired at resonance with PMMA (2955 cm−1, in red), and with PS (3060 cm−1,in green).

# On-going: Raman Tag for imaging

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# Summary & Comment

- Raman spectroscopy occurs as a result of a molecular vibration causing a "change in polarizability" of the molecule.

  - cf) IR: dipole moment change

- Raman microscope (spectroscopy) could utilize a lot and broadly of characteristic application including chemical imaging.
- To achieve the goal, it is important to understand the physics/optics and the components of Raman instrument.
- It would be good to consider not only experiment but also data (spectra) analysis and database library.

# References & Comments

**Sources**

- Horiba https://www.horiba.com/int/scientific/technologies/raman-imaging-and-spectroscopy/raman-spectroscopy/

- University of Washington : Raman tutorial

**Raman Workshop in ETH Zurich (2025)**

https://doctoral-school.ethz.ch/events/raman.html