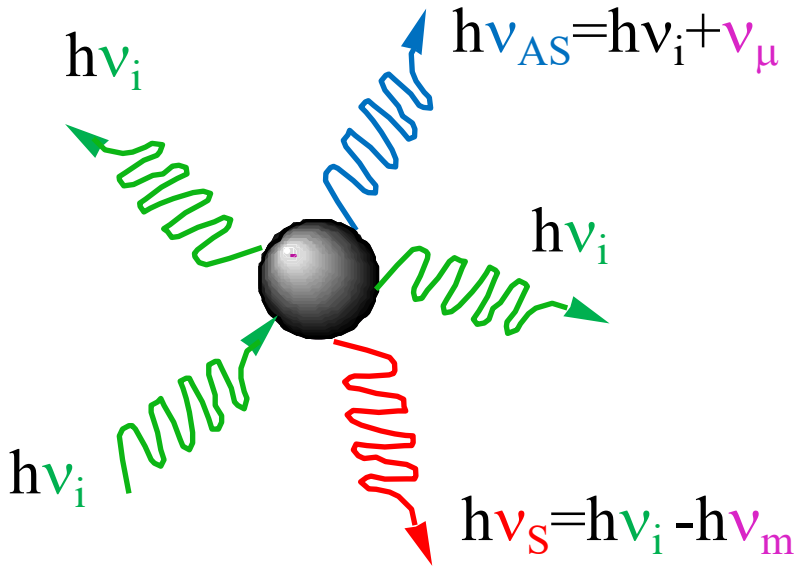
Raman Scattering

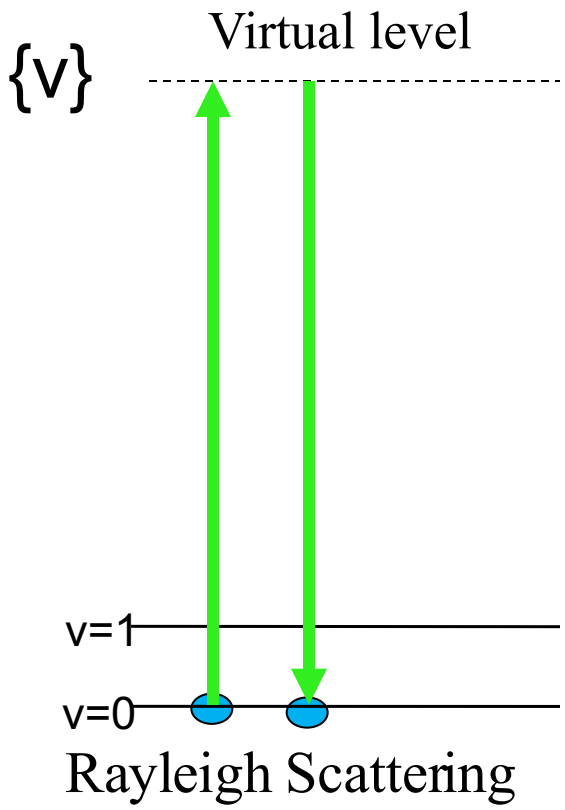
$$h\nu_i \neq h\nu_m \quad \text{or} \quad \langle \Psi_f | \hat{\mu} | \Psi_i \rangle = 0$$

Rayleigh Scattering:
(elastic)

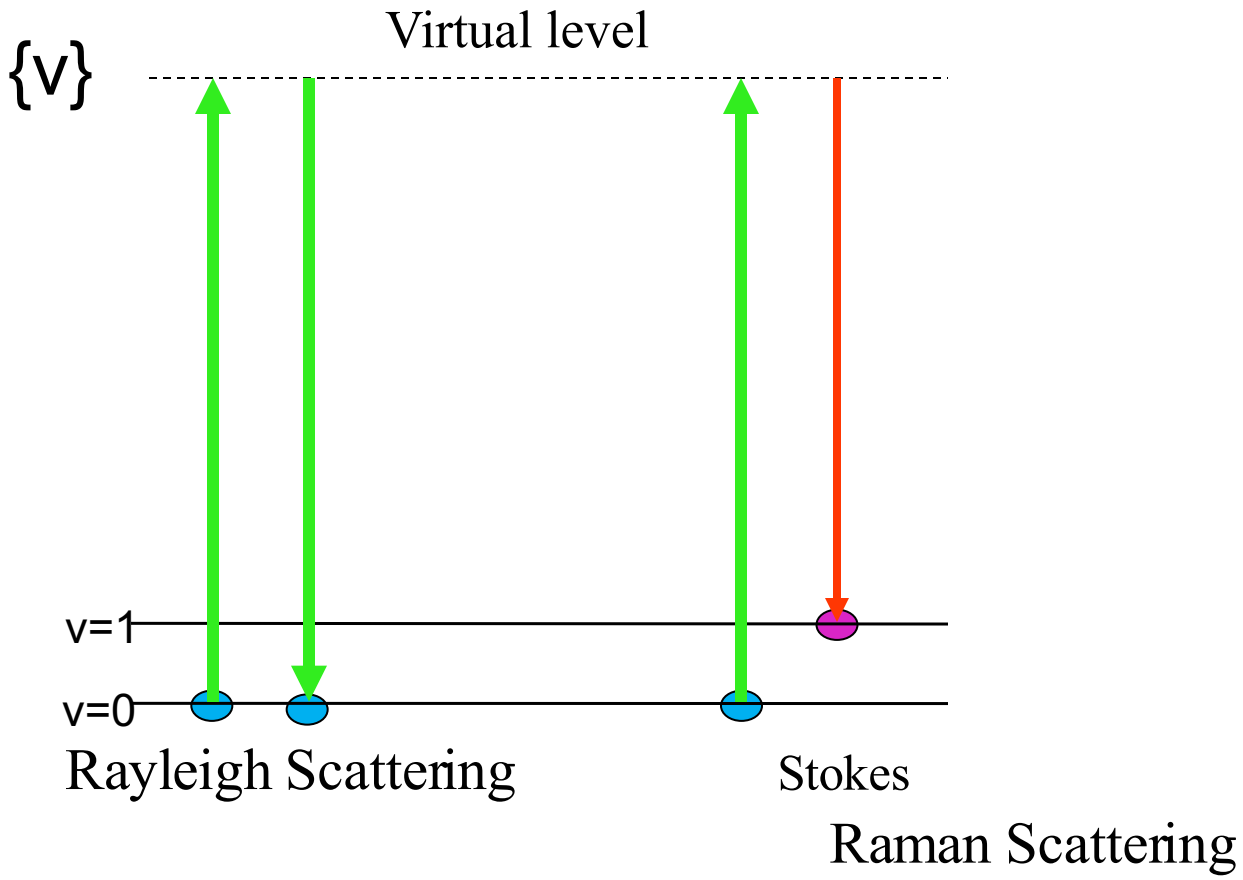
Raman scattering:
(inelastic)



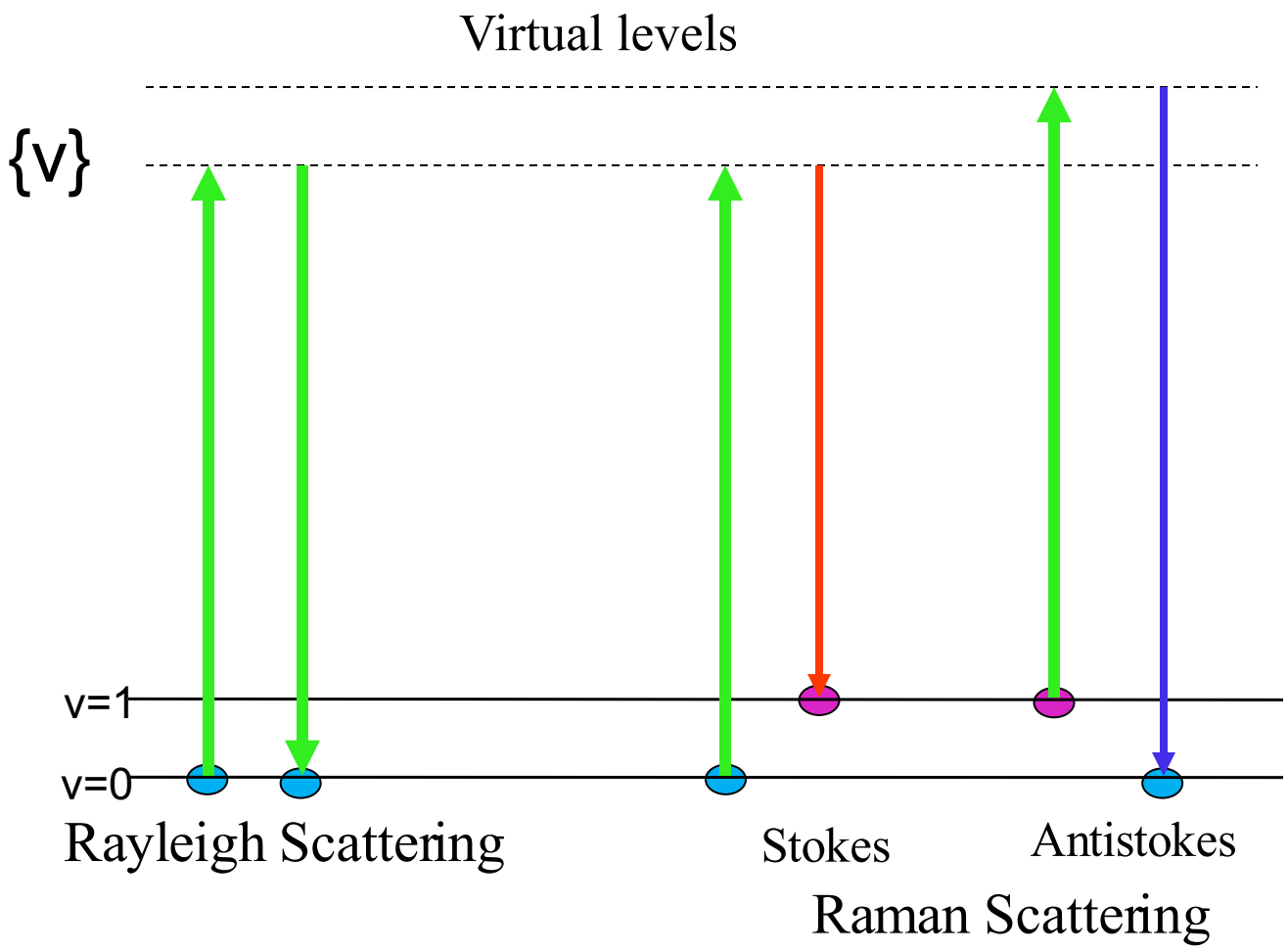
Rayleigh and Raman Scattering



Rayleigh and Raman Scattering



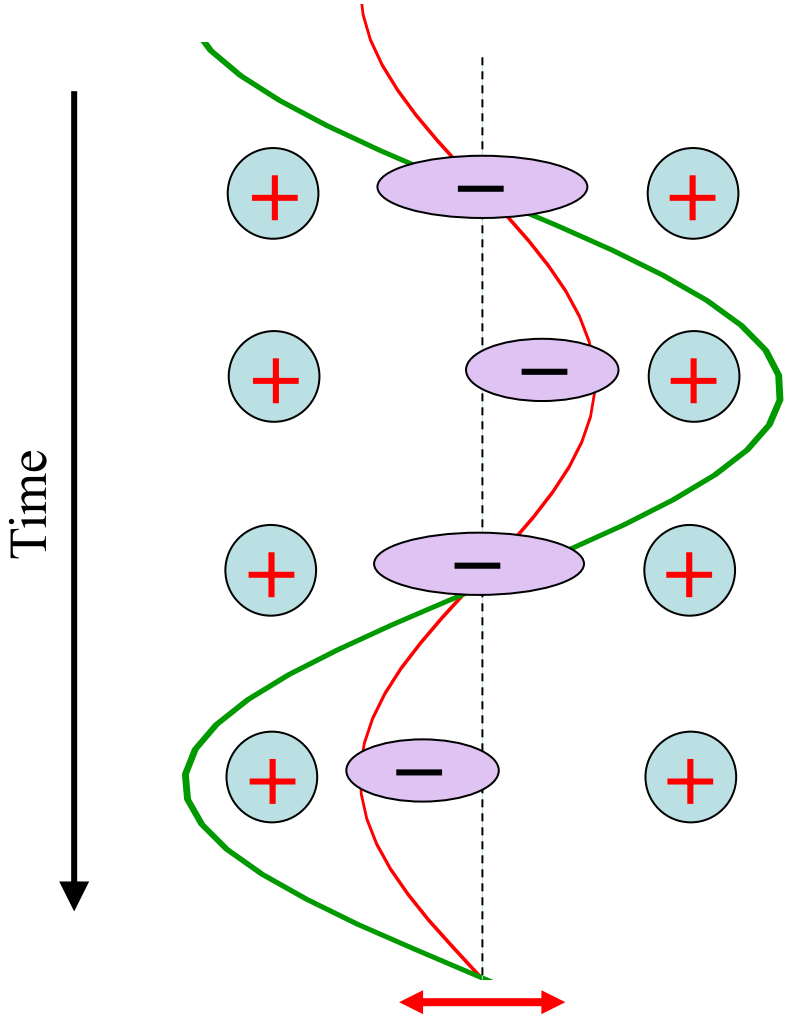
Rayleigh and Raman Scattering



Spontaneous RS light goes in all directions

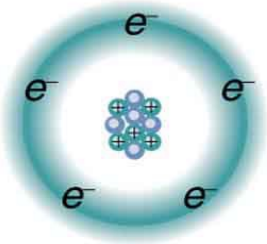
Spontaneous Raman Scattering

$\omega_p >> \omega_{vib}$ stretched



Induced Polarization:

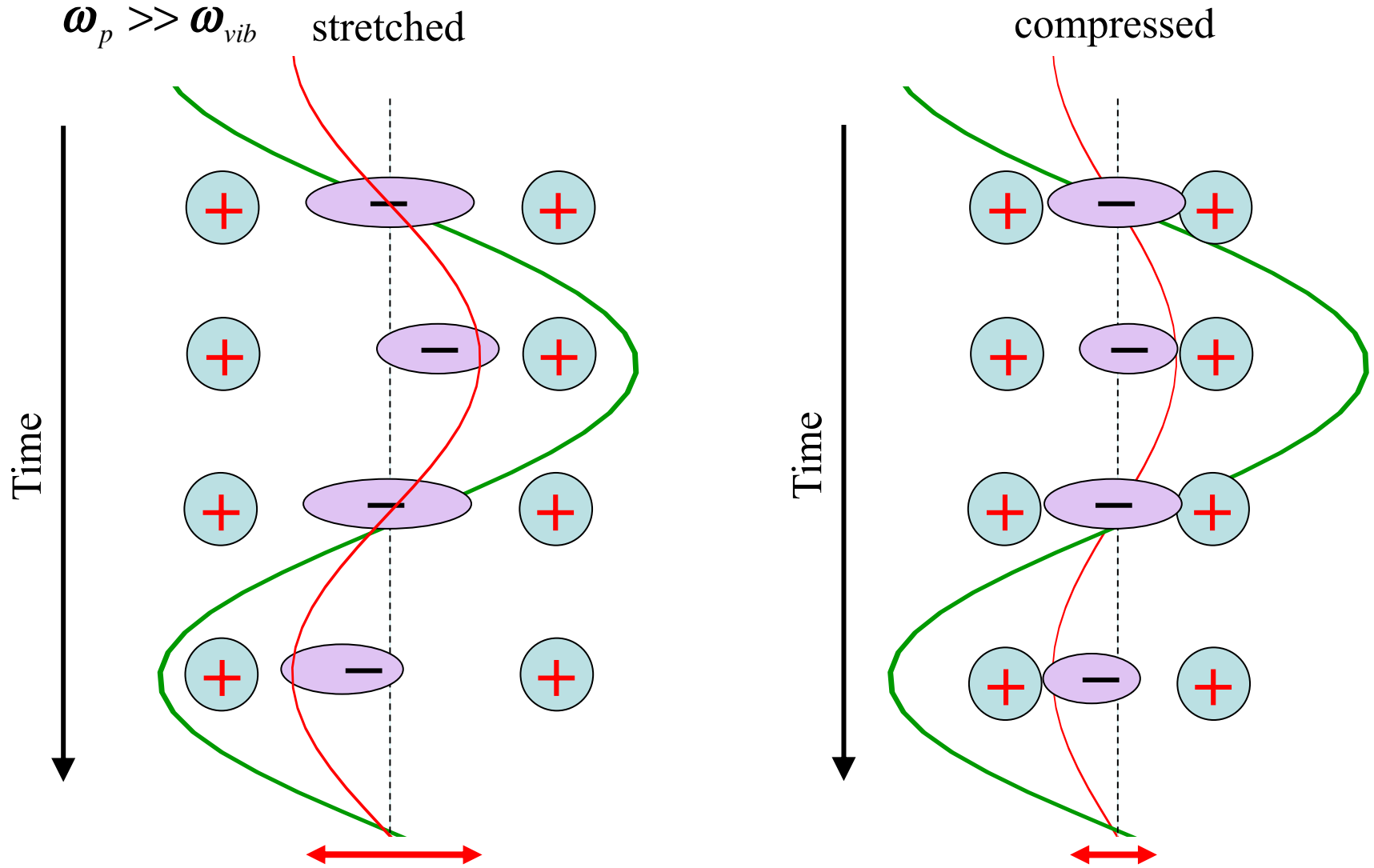
$$\vec{P}(\vec{E}) = \sum \boldsymbol{\mu}_i(\vec{E}) \simeq \sum \boldsymbol{\varsigma}_i \cdot \vec{E}$$



Polarizability is a measure of how much the electronic cloud can be changed by an external electric field.

Spontaneous Raman Scattering

$\omega_p >> \omega_{vib}$



$$P(E_p) = \chi(R) \cdot E_p = \chi_0 \cdot R_0 (1 + \delta \cdot \sin \omega_{vib} t) \cdot E_0 \sin(\omega_p t)$$

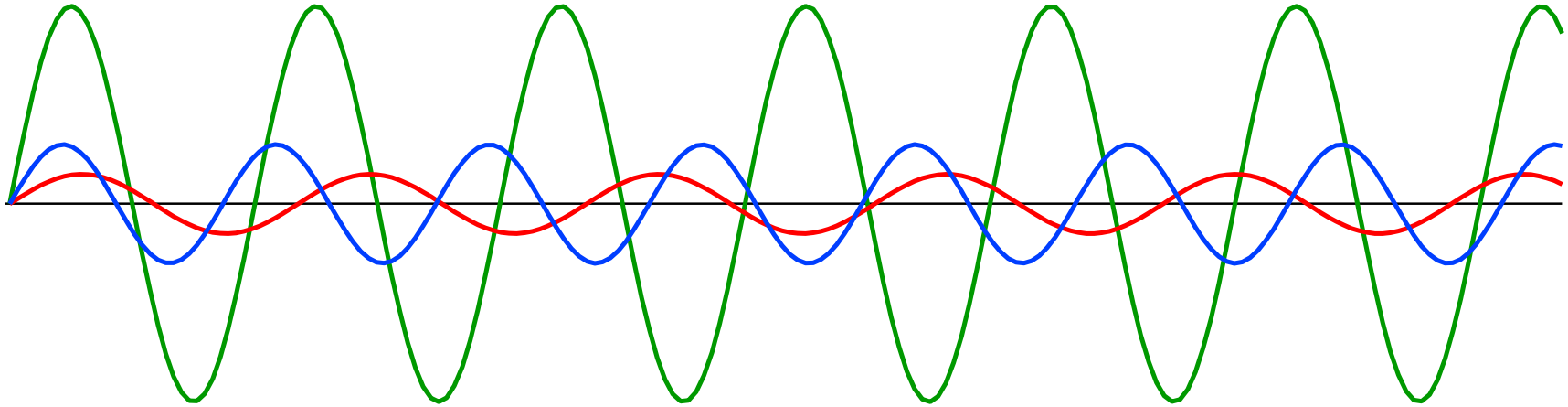
Spontaneous Raman Scattering

$$P(E_p) = \chi(R) \cdot E_p = \chi_0 \cdot R_0 (1 + \delta \cdot \sin \omega_{vib} t) \cdot E_0 \sin(\omega_p t)$$

$$E_{ind}(t) \propto P(E_p(t)) \propto (1 + \delta \cdot \sin \omega_{vib} t) \cdot E_0 \sin(\omega_p t)$$

$$E_\Sigma = E_p + E_{ind} = \alpha \cdot E_0 \sin(\omega_p t) + \beta \cdot \sin \omega_{vib} t \cdot E_0 \sin(\omega_p t)$$

$$E_\Sigma(t) = \alpha \cdot E_0 \sin(\omega_p t) + 1/2 \cdot \beta \cdot [\cos((\omega_p - \omega_{vib})t) - \cos((\omega_p + \omega_{vib})t)]$$



$$\omega_P; \quad \omega_S = \omega_P - \omega_{vib}; \quad \omega_{AS} = \omega_P + \omega_{vib}$$

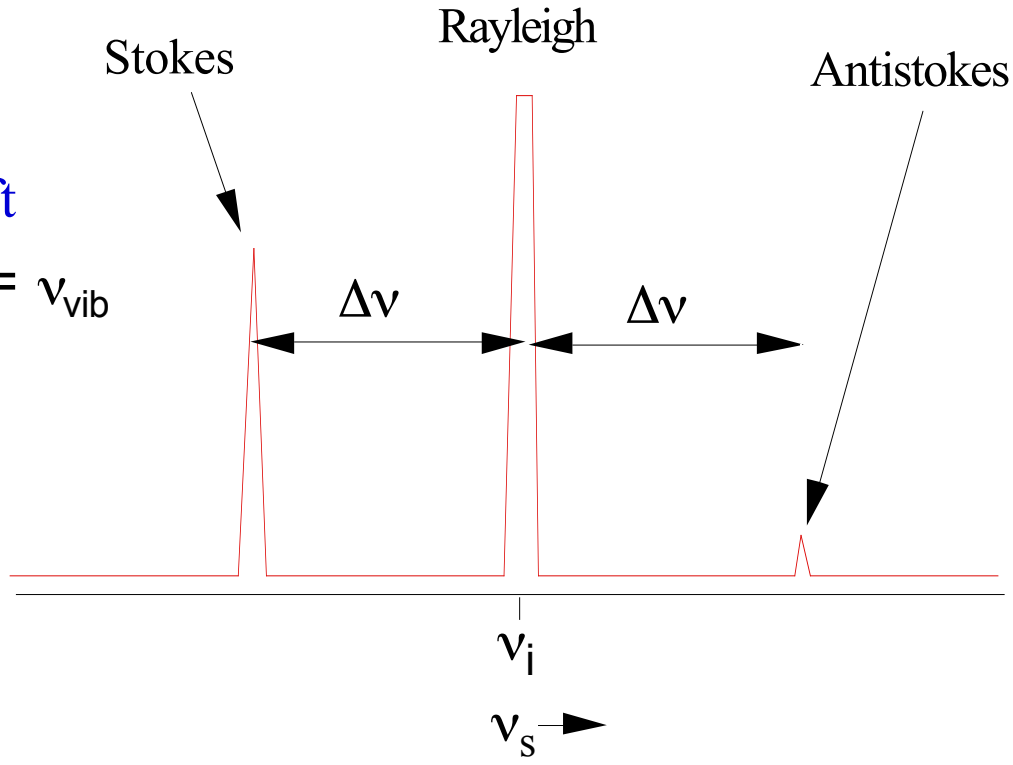
Raman scattering last as long as the duration of the pump light !

Spontaneous Raman Scattering

Raman Shift

$\Delta\nu = |\nu_i - \nu_s| = \nu_{vib}$

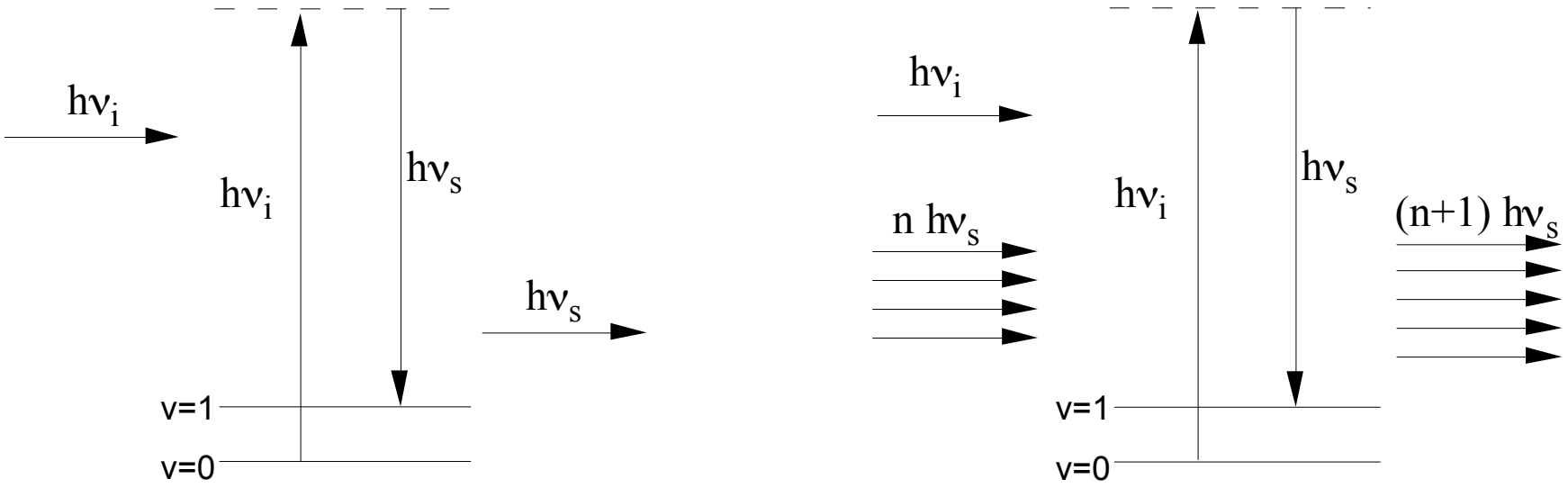
$\Delta\nu(H_2) = 4155.2$



$$I_{rsc} \propto I_{pump} \cdot \frac{\nu_p^4}{(\nu_{el}^2 - \nu_p^2)^2} N; \quad (\nu_{el} - \nu_p) >> \nu_{vib}.$$

$$\frac{I_{AS}}{I_S} = \left(\frac{\nu_{AS}}{\nu_S}\right)^4 \exp\left(-\frac{h\nu_{vib}}{kT}\right)$$

Stimulated Raman Scattering (SRS)



SRS produces coherent light!

$$I_{SRS} \propto I_{RS} \cdot l \propto I_p \cdot l.$$

$$I_{SRS} = I_p(1-\exp(-n \cdot l \cdot \boldsymbol{\sigma}_{RS})). \simeq I_p \cdot n \cdot l \cdot \boldsymbol{\sigma}_{RS}.$$

SRS cross-section

Process	Cross-Section of	σ (cm^2)
absorption	UV	10^{-18}
absorption	IR	10^{-21}
scattering	Rayleigh	10^{-26}
scattering	Raman	10^{-29}

- Raman transitions are generally much weaker
- RS signal appears only, if there are Raman-active vibrations =>
  Background-free ($\neq \nu_p$) technique.
- Pump light can be discriminated by dispersive elements (diffraction grating)
  or (for spontaneous RS) by angle.

SRS cross-section

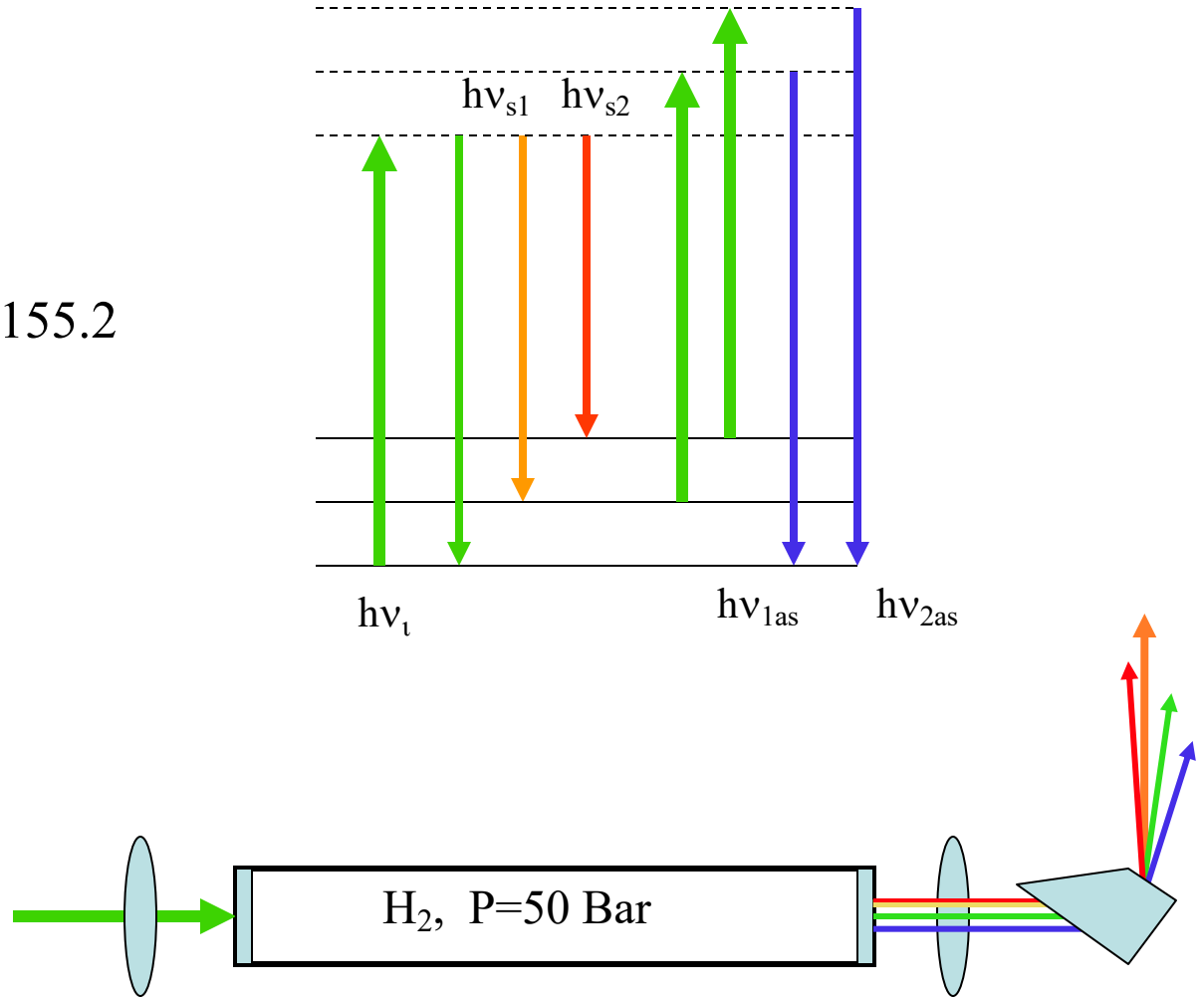
$$I_{rsc} \propto I_{pump} \cdot \frac{\nu_p^4}{(\nu_{el}^2 - \nu_p^2)^2} \propto \frac{1}{\lambda^4}.$$

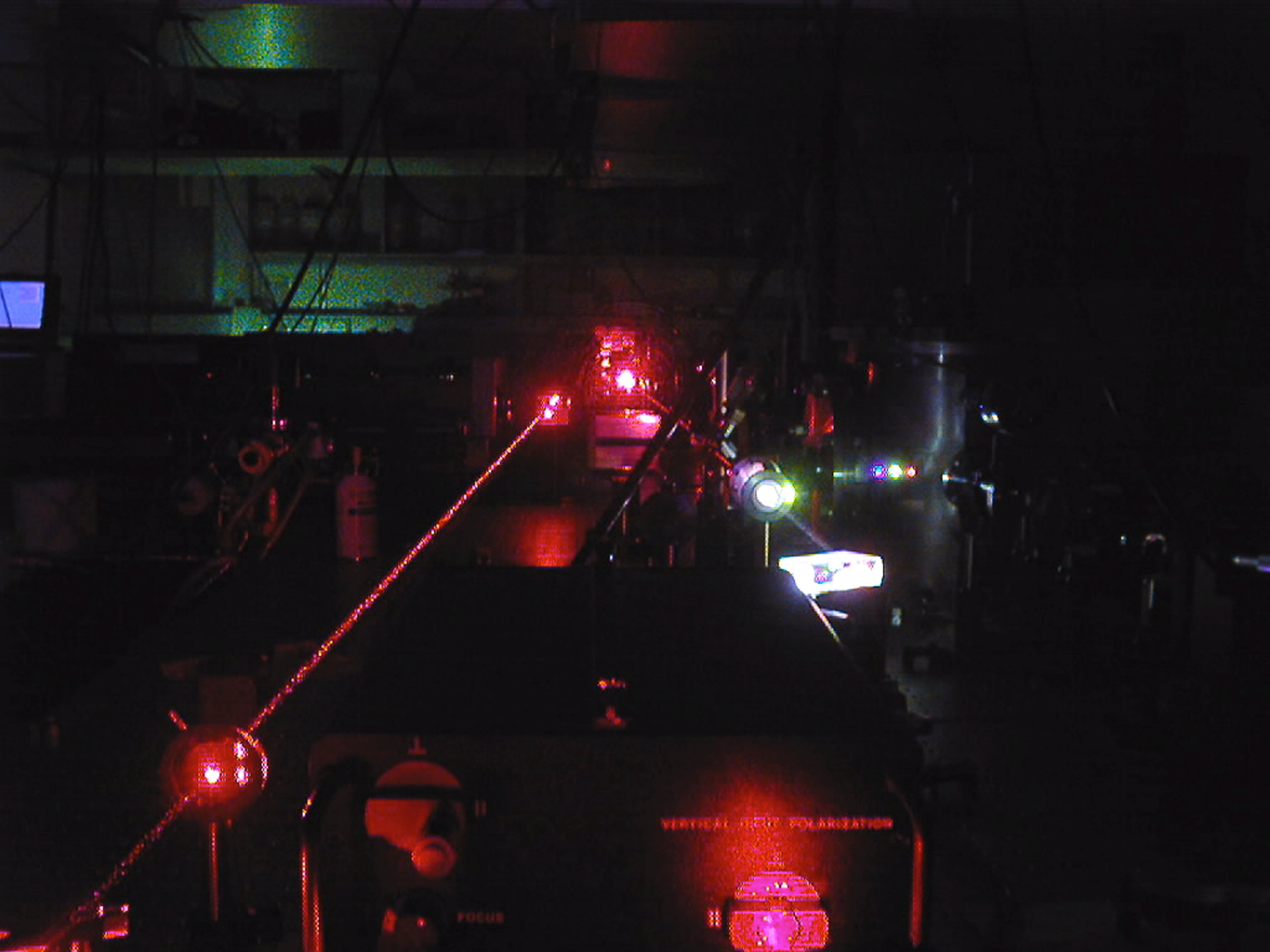
λ_{ex} (nm)	σ (x 10^{-28} cm^2)
532.0	0.66
435.7	1.66
368.9	3.76
355.0	4.36
319.9	7.56
282.4	13.06

Pump laser wavelength should be close to the band origin of electronic transition

SRS for light wavelength conversion

$\Delta\nu(H_2)= 4155.2$




VERTICAL ZERO POLARIZATION
FOCUS

Raman Spectroscopy

1923 – Inelastic light scattering is predicted by A. Smekel

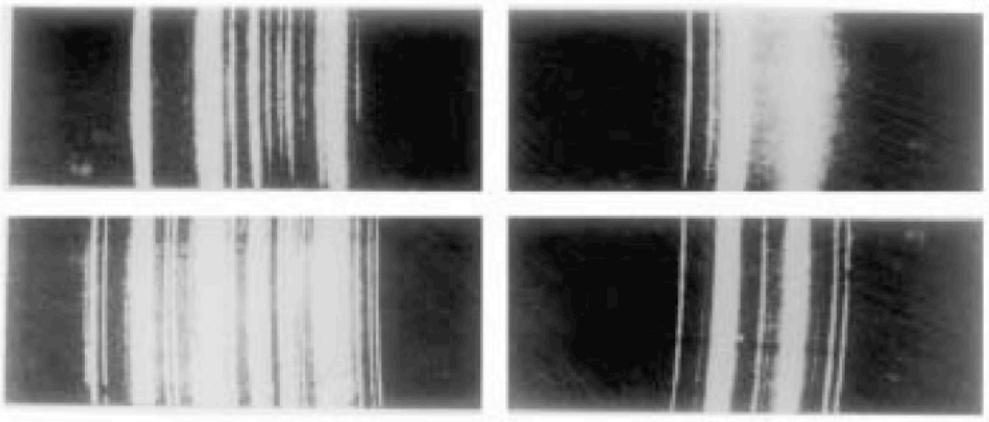
1928 – Landsberg and Mandelstam see unexpected frequency shifts in scattering from quartz

1928 – C.V. Raman and K.S. Krishnan see “feeble fluorescence” from neat solvents

First Raman Spectra:

Filtered Hg arc lamp spectrum:

C_6H_6 Scattering



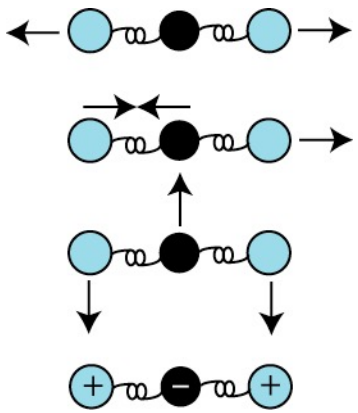
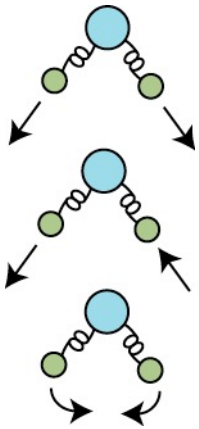
Raman Spectroscopy: selection rules

General: molecular polarizability must change during the molecular vibration

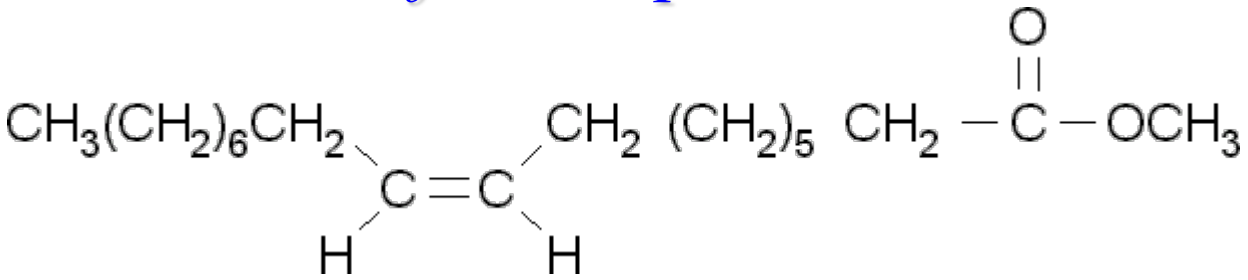
- symmetric vibrations: strong Raman, no IR;
- asymmetric vibrations: weak Raman, strong in IR.
- bending vibrational modes: weak Raman, strong in IR
- For a molecule with centre of inversion ($\vec{r} \rightarrow -\vec{r}$):

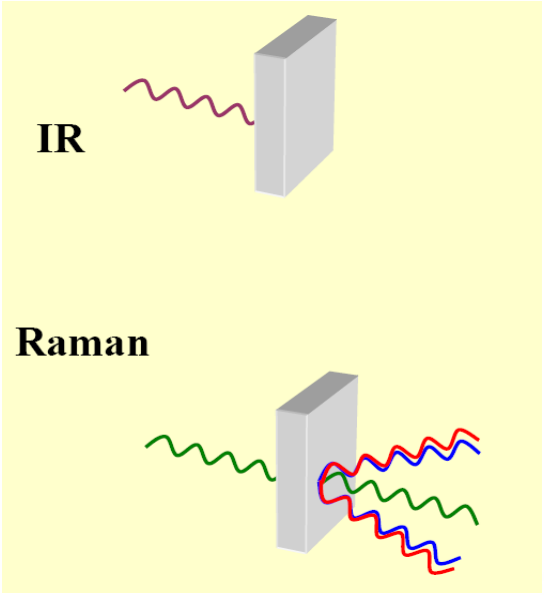
  Alternative: either **RS** (for sym) or **IR** (asym)
- For non-centrosymmetric molecules (e.g., biomolecules):

  Both RS and IR are active for all vibrations.

CO_2	H_2O
 Raman: 1335 cm^{-1} IR: 2349 cm^{-1} IR: 667 cm^{-1}	 S. Raman + W. IR: 3657 cm^{-1} W. Raman + S. IR: 3756 cm^{-1} W. Raman + S. IR: 1594 cm^{-1}

Raman vs Infrared Spectra





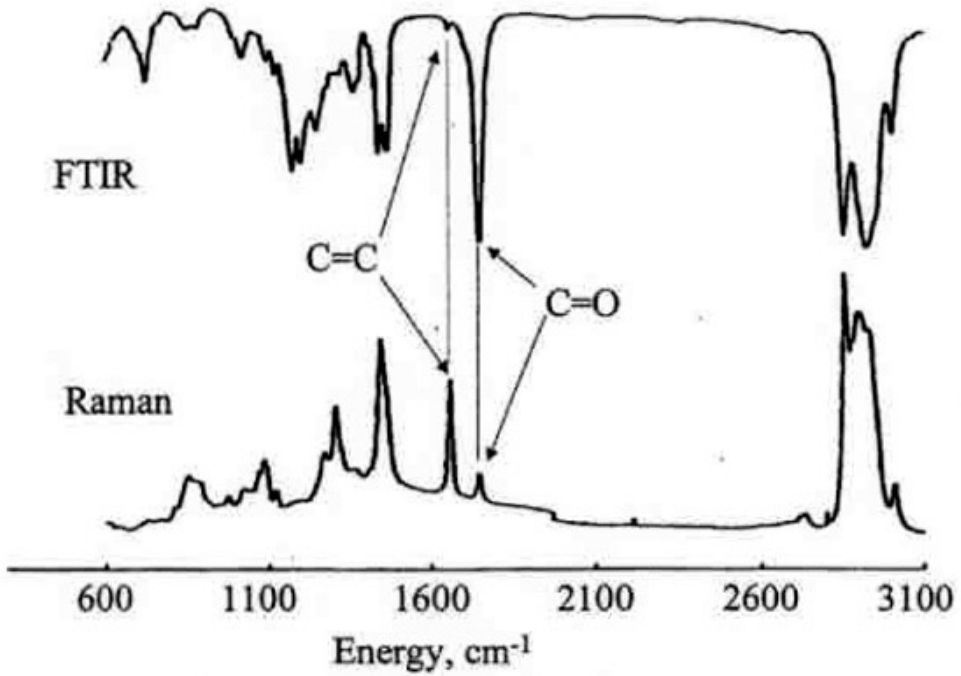


Figure 2.2. FTIR (upper) transmission and Raman scattering (lower) of oleic acid methyl ester.

Raman Spectroscopy vs IR absorption

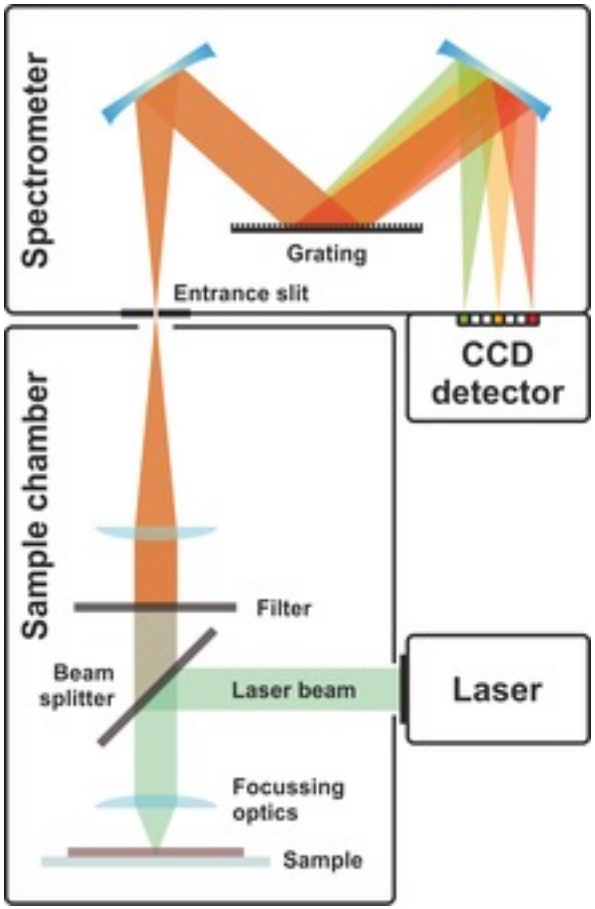
+

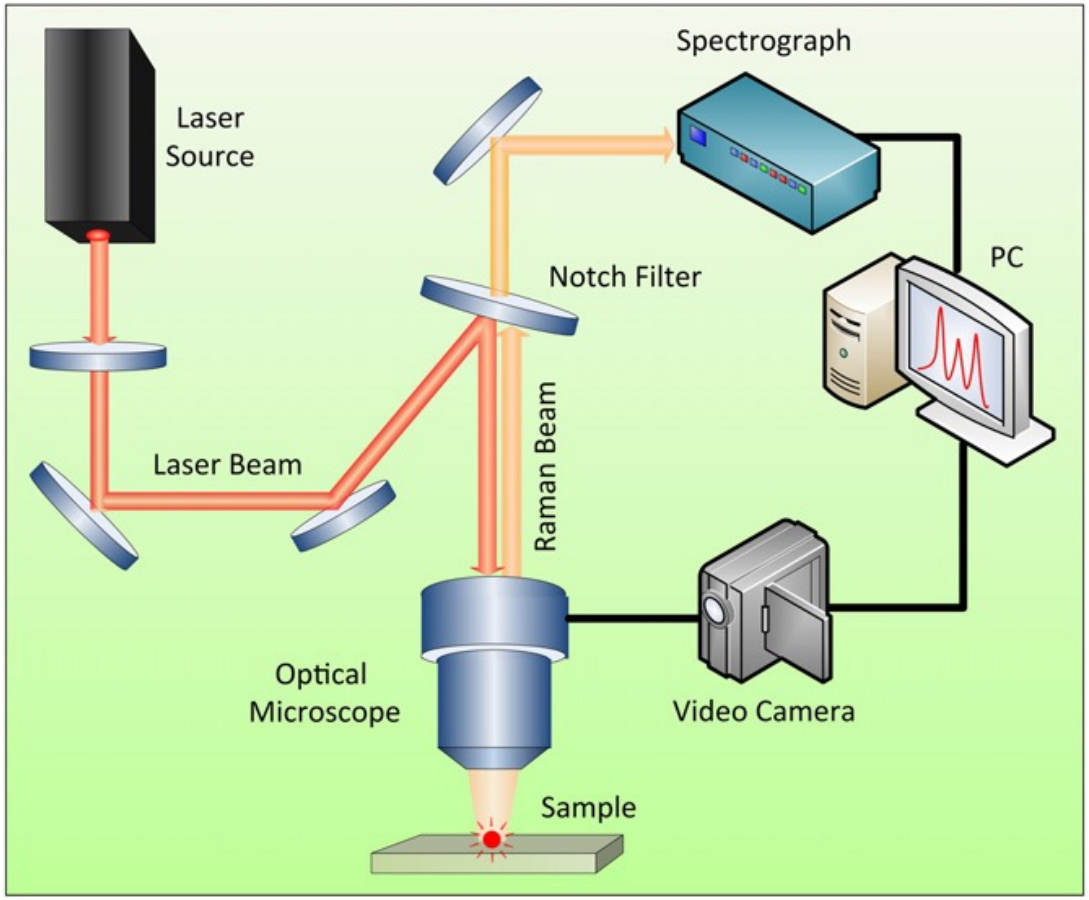
Monitors ALL Raman-active vibrations at once;
Fast, => fits well for 2D/3D space-resolved Raman microscopy;
Monitors vibrations that are not IR-active; complementary to IR absorption;
(e.g., diamond, graphite, graphene);
Background free;
Does NOT require a tunable (laser) light source;
Does not require IR light source;
Can work with polar solvents;
Compatible with solid, surface, liquid and gas-phase samples.

—

Much much lower sensitivity
Insensitive to IR active vibrations in centrosymmetric molecules;
More difficult to determine absolute concentrations

Raman Spectrometers





Raman Spectroscopy: PMT vs CCD

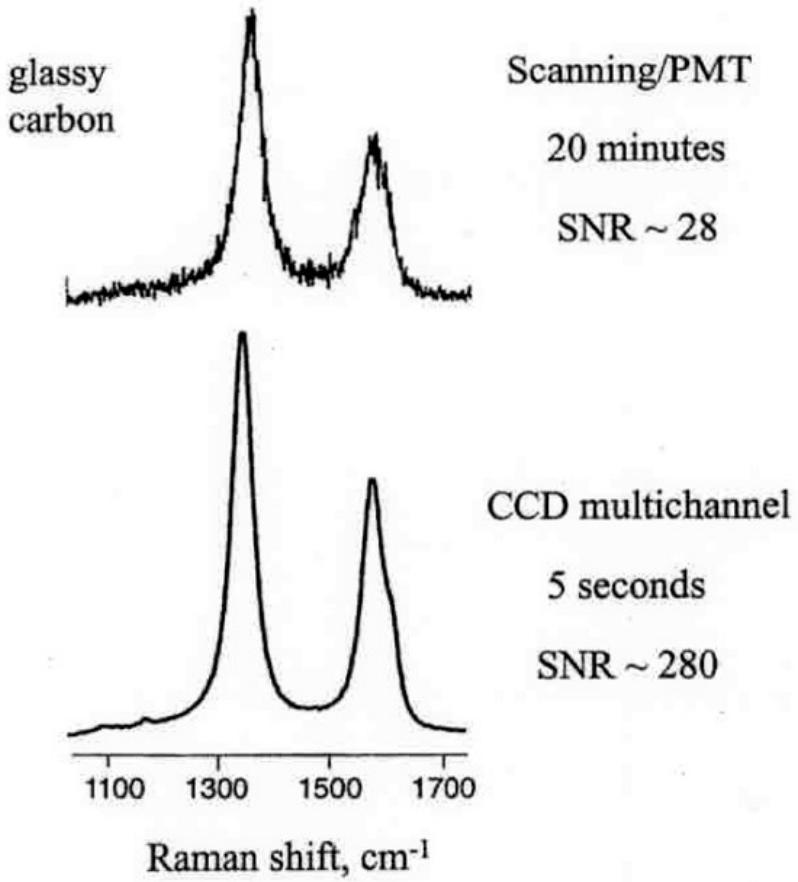
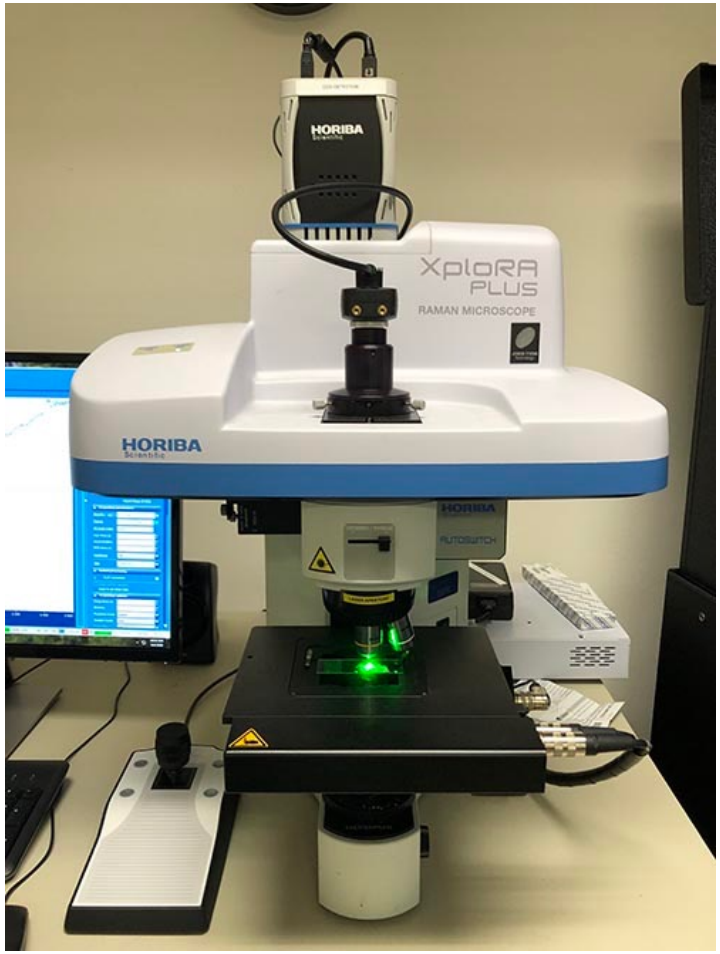


Figure 1.6. Spectra of solid glassy carbon obtained with a state-of-the-art spectrometer in 1985 (Spex 1403 double monochromator with photon counting PMT) and a multichannel/CCD spectrometer of 1996 (Chromex 250 spectrograph, back thinned silicon CCD); 514.5 nm laser at 50 mW in both cases; measurement times and signal/noise ratios (SNR) as shown.

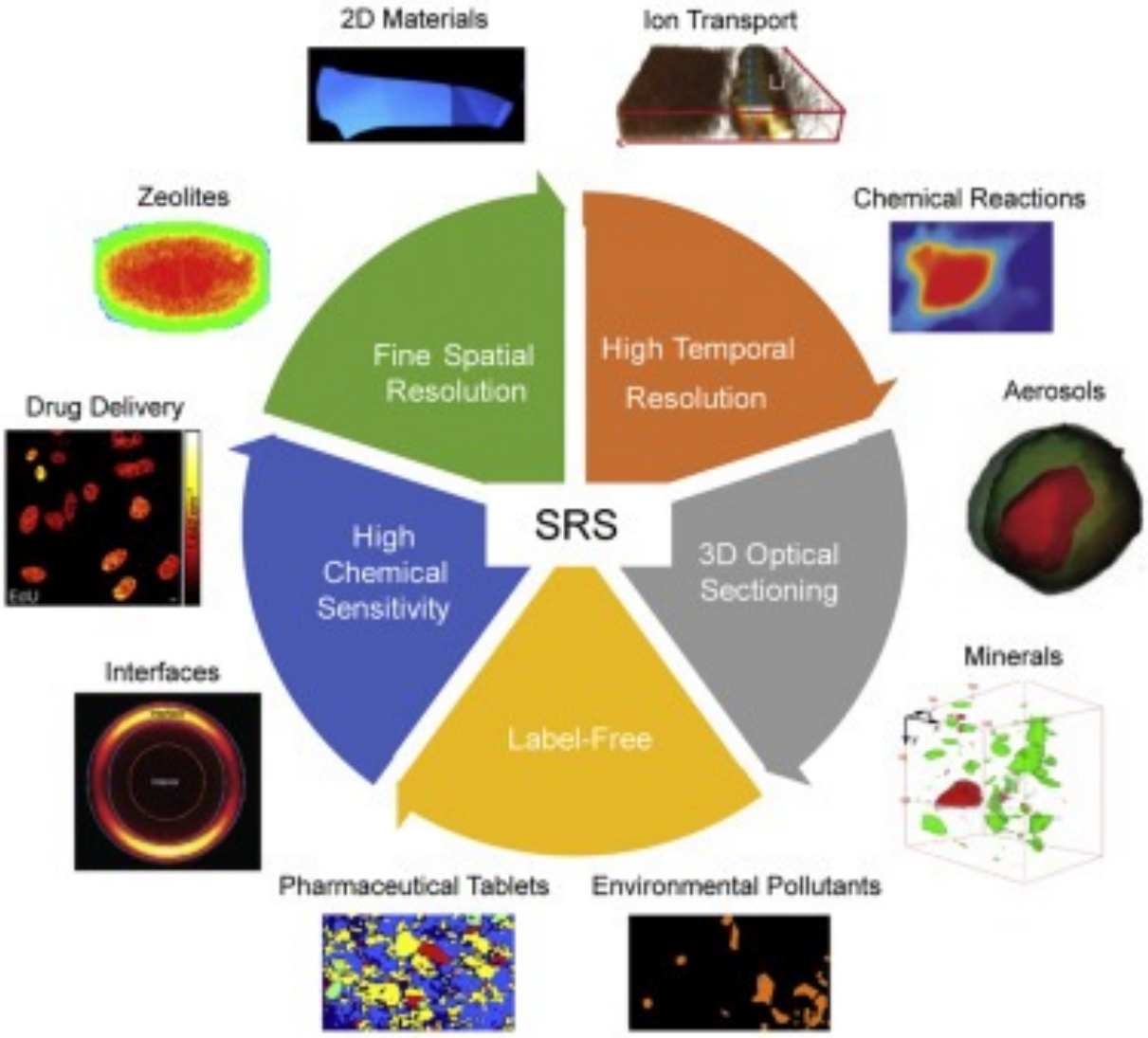
Raman Spectrometers

Compact for express analysis

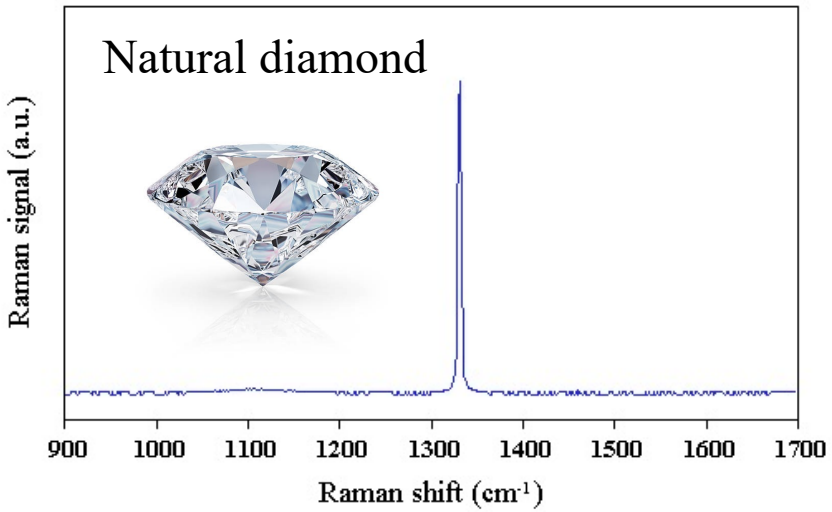


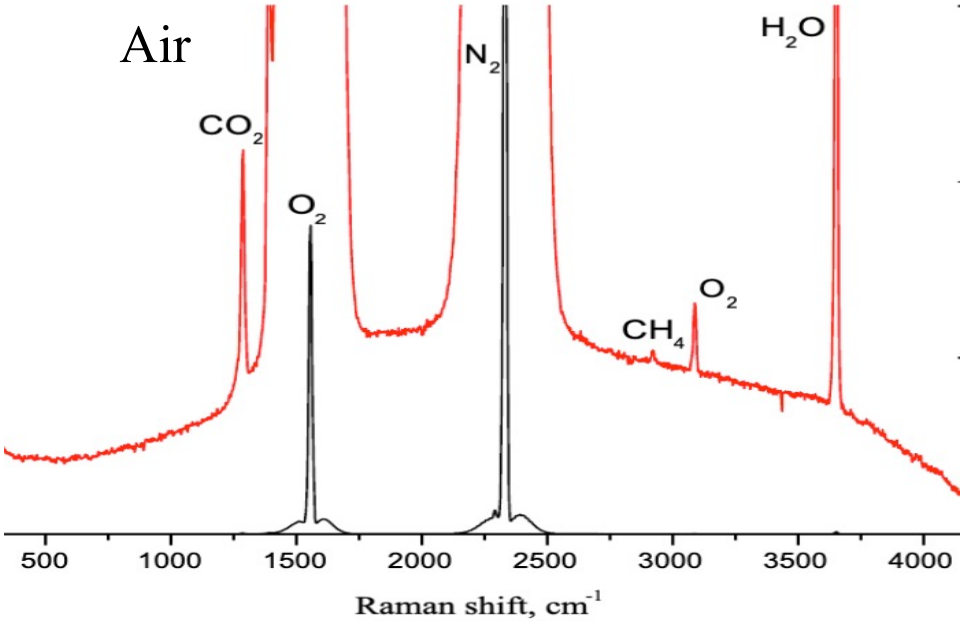
Scanning for Raman microscopy

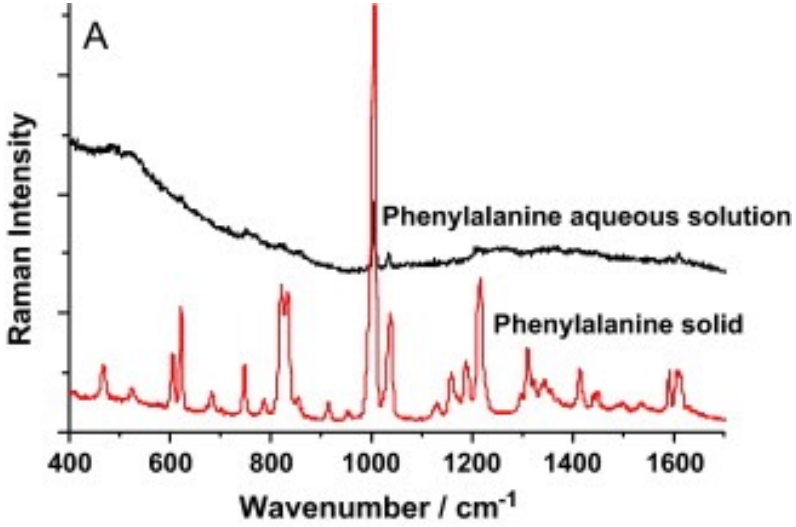
Raman Spectroscopy applications

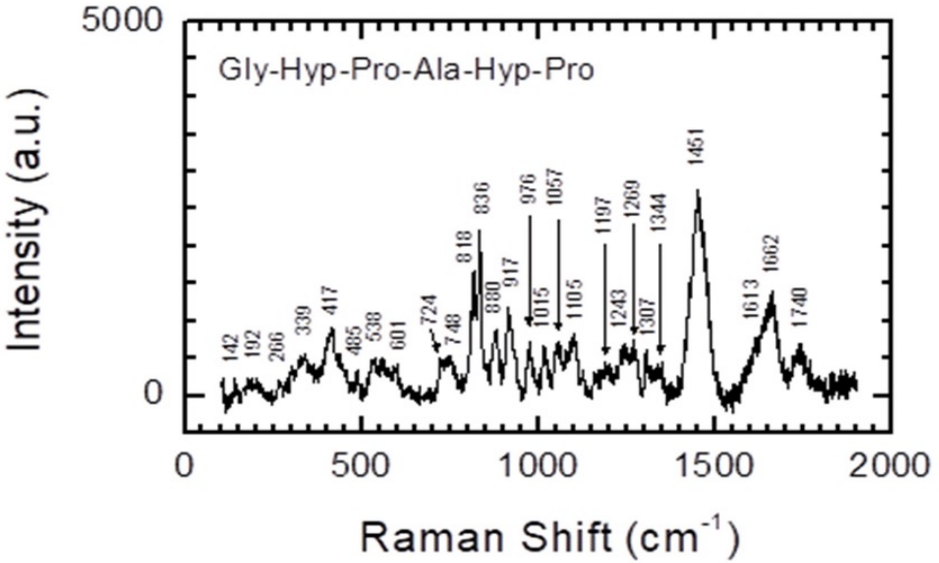


Raman Microscopy applications









Raman Spectroscopy applications

Natural pearl or fake?

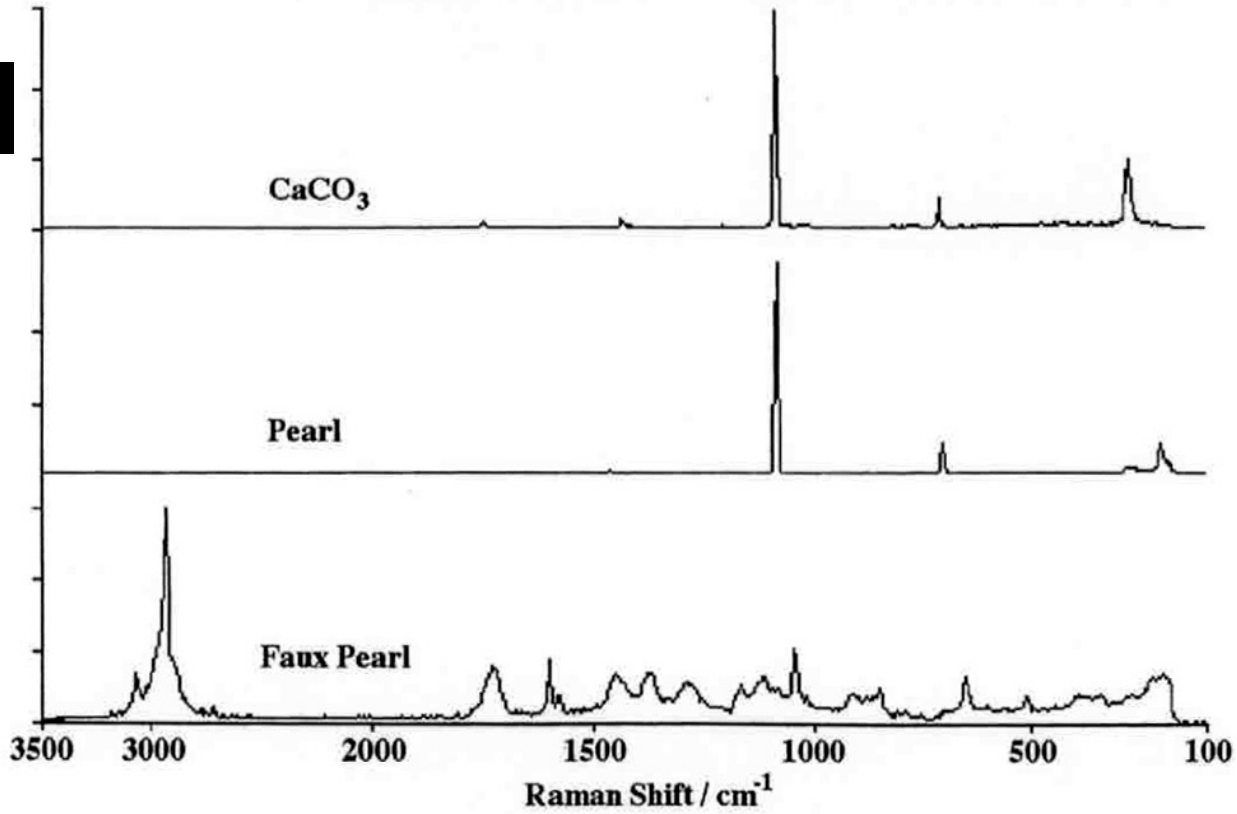
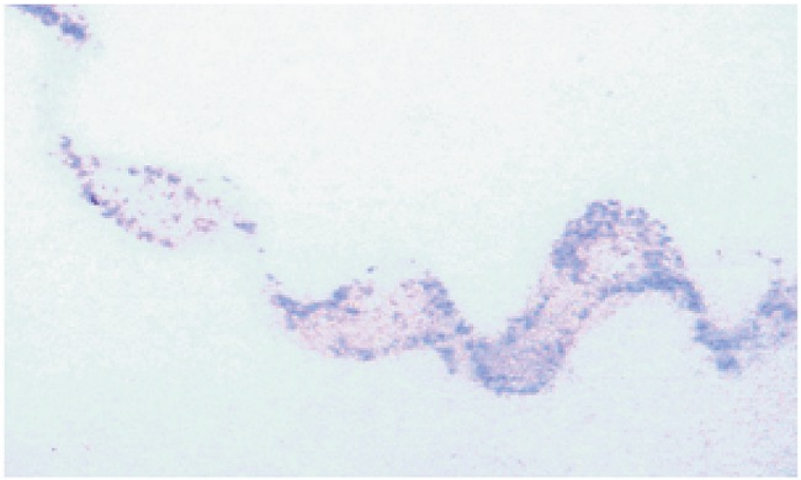


Figure 3 The Raman spectra of calcium carbonate (top), natural pearl (middle), and faux pearl (bottom). (Adapted with permission from Ref. 9.)

The Vinland Map: Genuine or Forged?

Thought to be a 15th century European map of the world (found in America)

Debates and study since 1957 till 2018



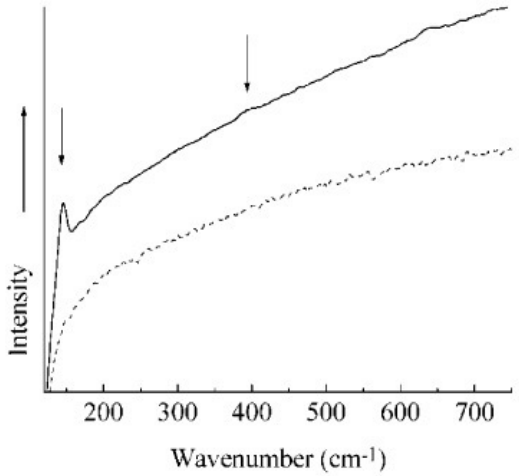


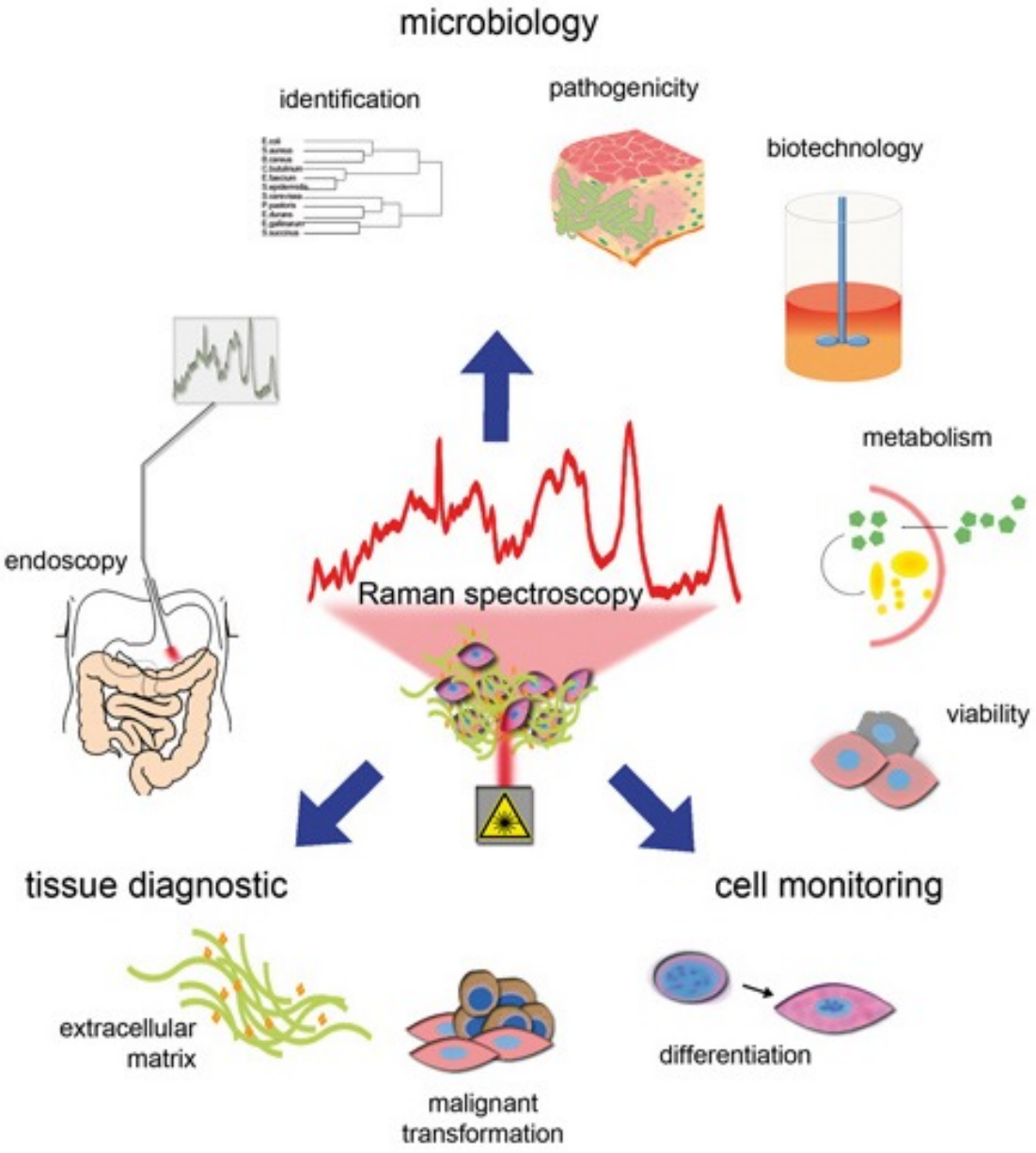
Figure 5. Anatase and plain parchment from the Vinland Map; solid line, anatase in yellow line; dotted line, plain parchment.

Anatase - mineral form of titanium dioxide (TiO_2)

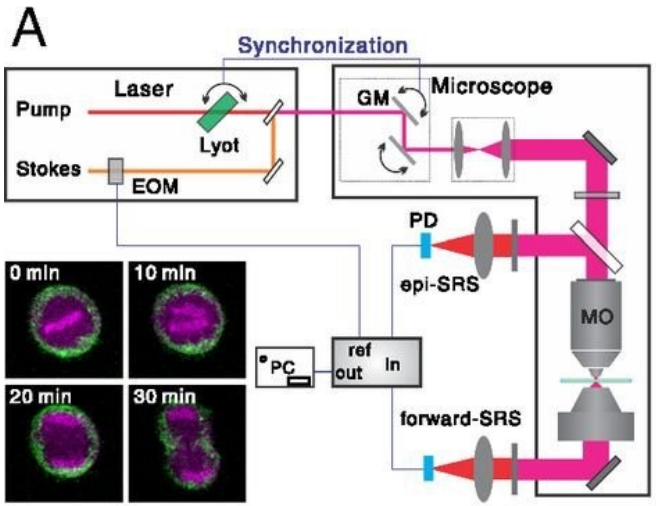
CONCLUSIONS

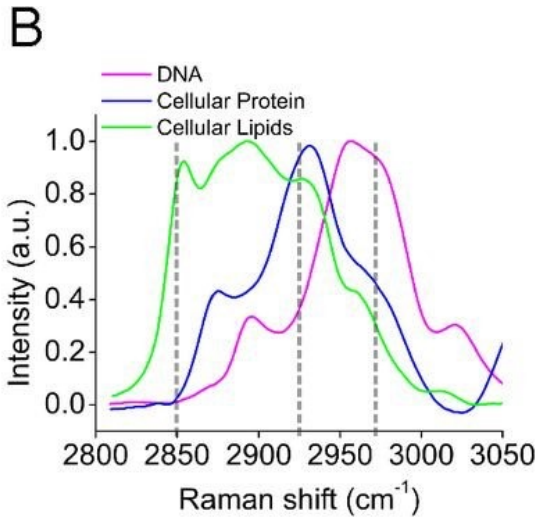
The use of Raman microprobe spectrometry has conclusively identified the materials used in the construction of two significant historical documents, the Vinland Map and the Tartar Relation. Although the inks used for the Tartar Relation are entirely appropriate for the period of its construction, one of those used to draw the Vinland Map is not. The presence of a yellow line containing anatase, closely associated with a stable carbon ink, indicates that the VM is a modern forgery.

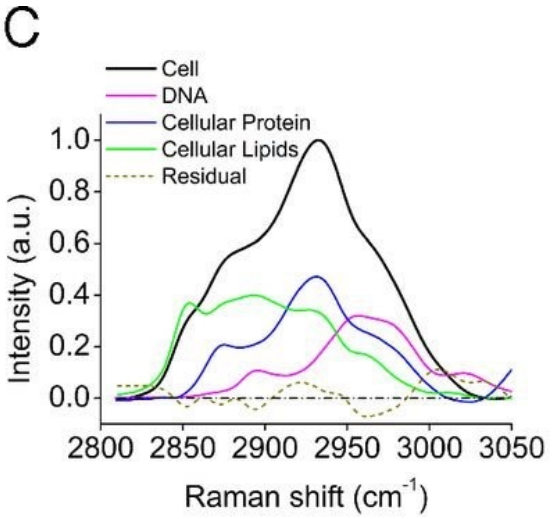
Raman Spectroscopy bio applications

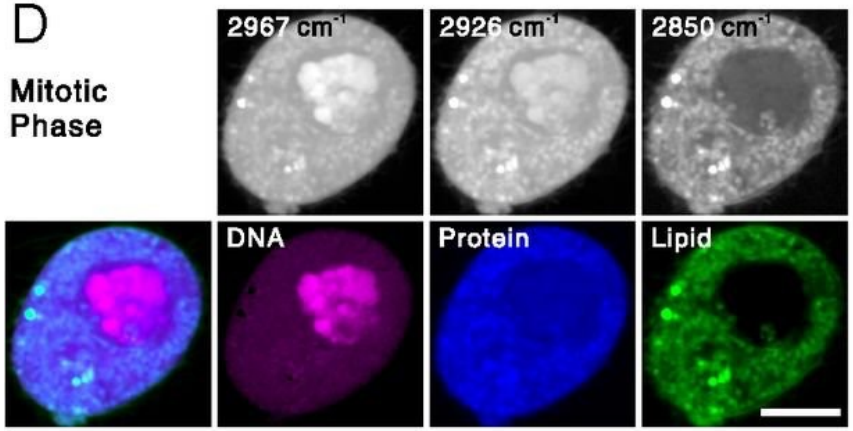


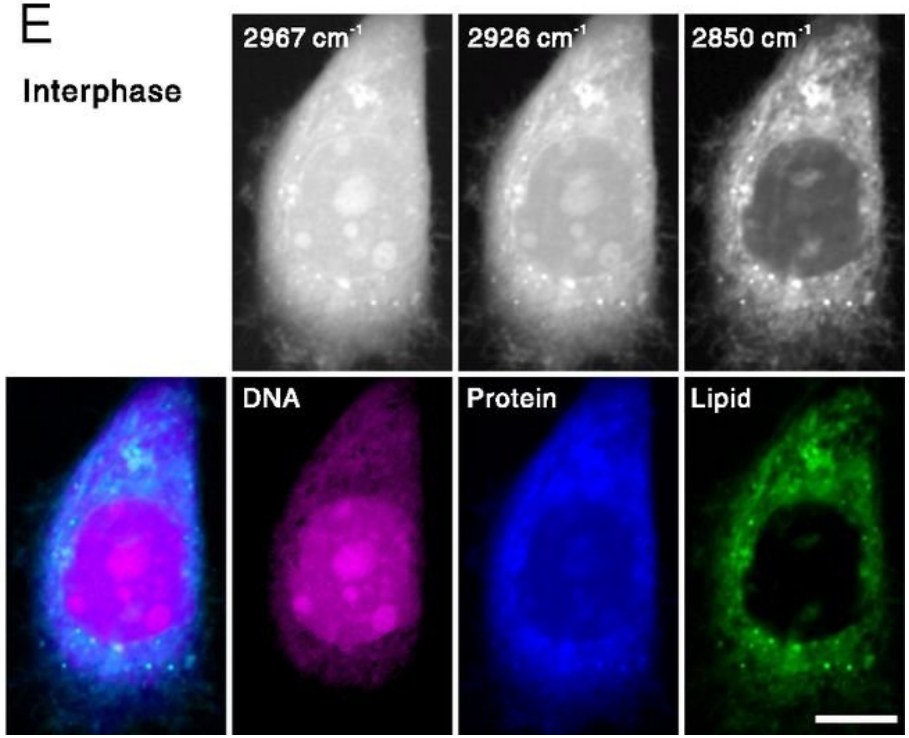
Raman Spectroscopy applications

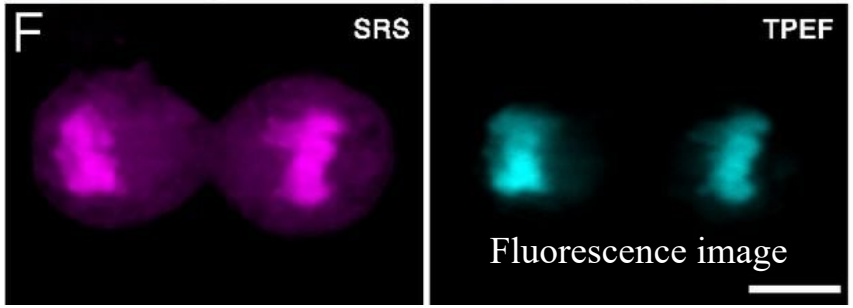












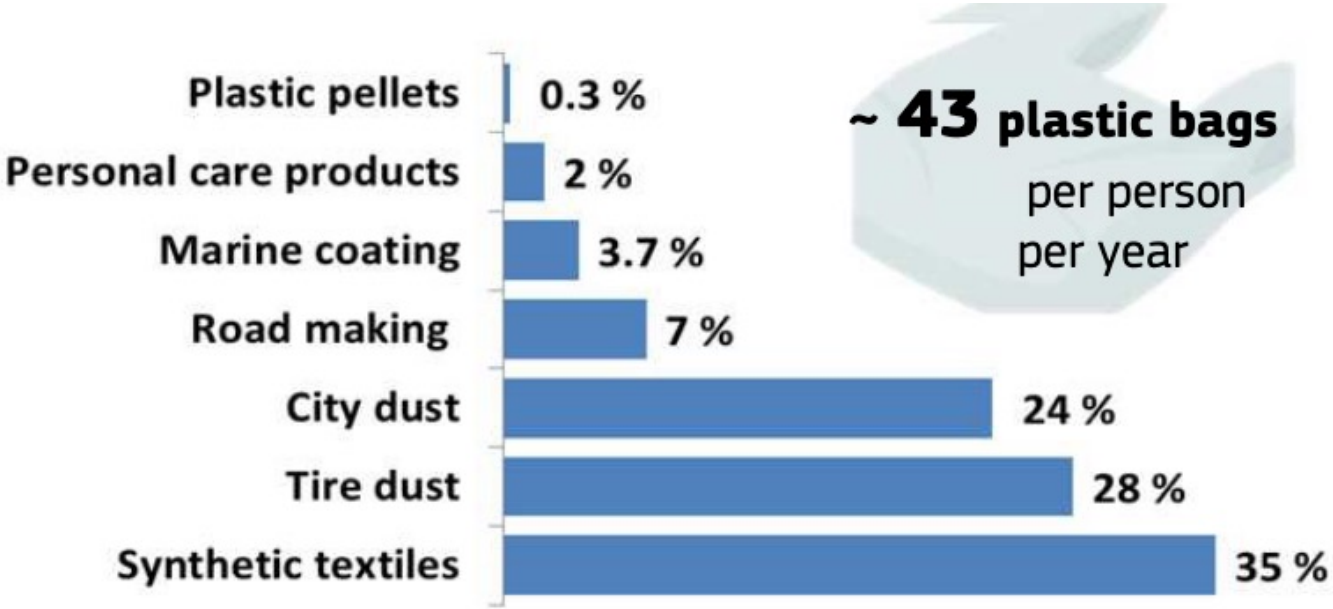
Micro- & Nano-plastics

Annual production of plastics: 300 mln tons

Plastic particles of 0.1 μm to 5000 μm

Sources: natural/intentional fragmentation of plastics

PE, PP, PET, PBS, PCL, PVC, PES, PVA, AcC,….

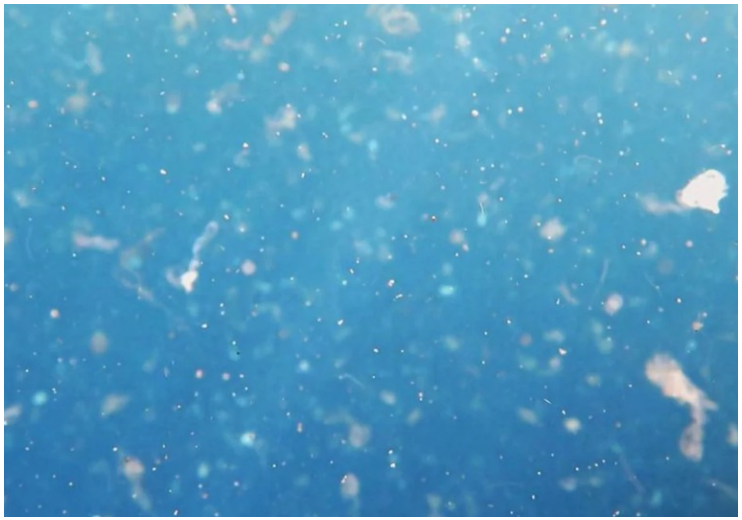


Micro- & Nano-plastics

Long-living pollutants: natural degradation of some microplastics takes 100s of years.

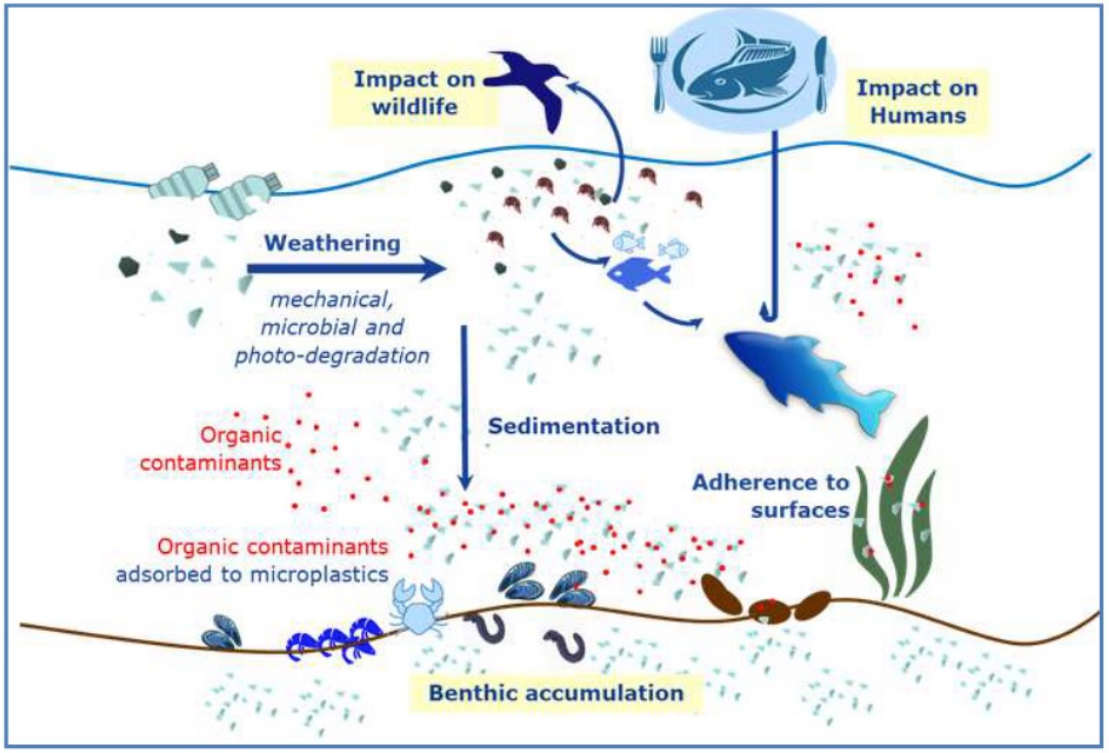
MP are difficult to filter and to collect;
Plastics are dumped to oceans with waste.

Accummulated in ocean.



How do they come to our body?

- With food (plastic packaging, bottles);
- With water (overcome filtering and purifications);
- From food via sea cycle



Health hazards

Due to small size and chemical resistance M/NPplastics penetrate to blood; from blood to heart and even to brain.

Bacteria and viruses have high affinity to plastics:
MPs serve as their long-distance transport to our body.

Annual intake: 70-100'000 particles per year, accummulations.

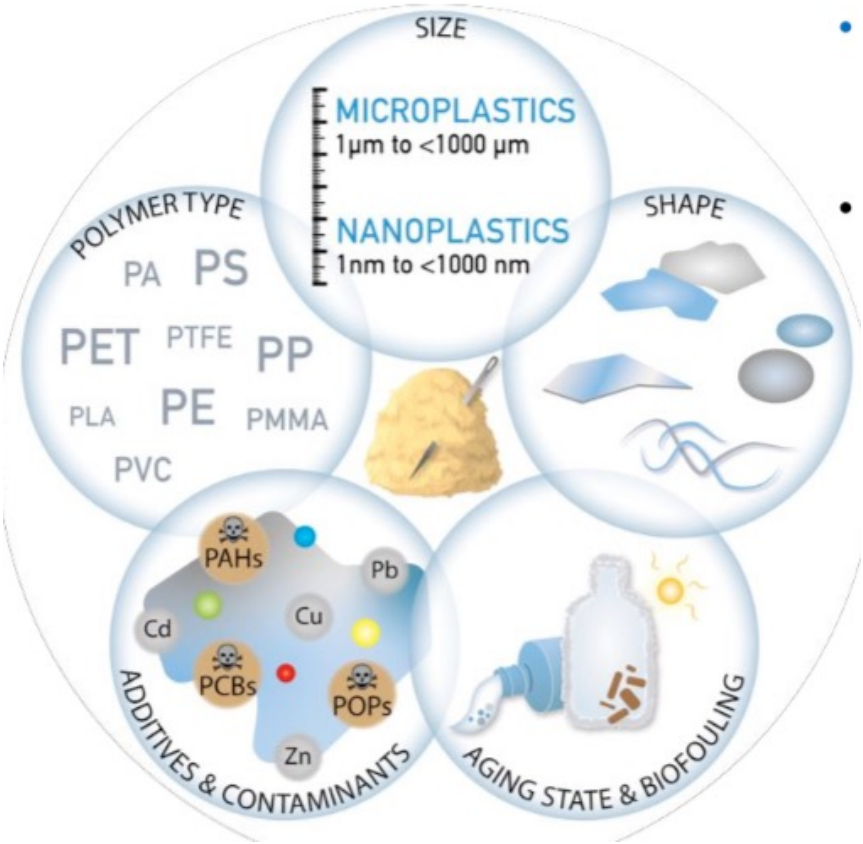
Potential health problems:

- Oxidative stress
- DNA damage
- Cancer
- Autoimmune response

Need to be detected, identified and quantified

Micro- & Nanoplastics: Complex Analytes

- Broad size range (10^5)
- Different types of polymers
- Different shapes
- Various additives and contaminants
- Different aging state

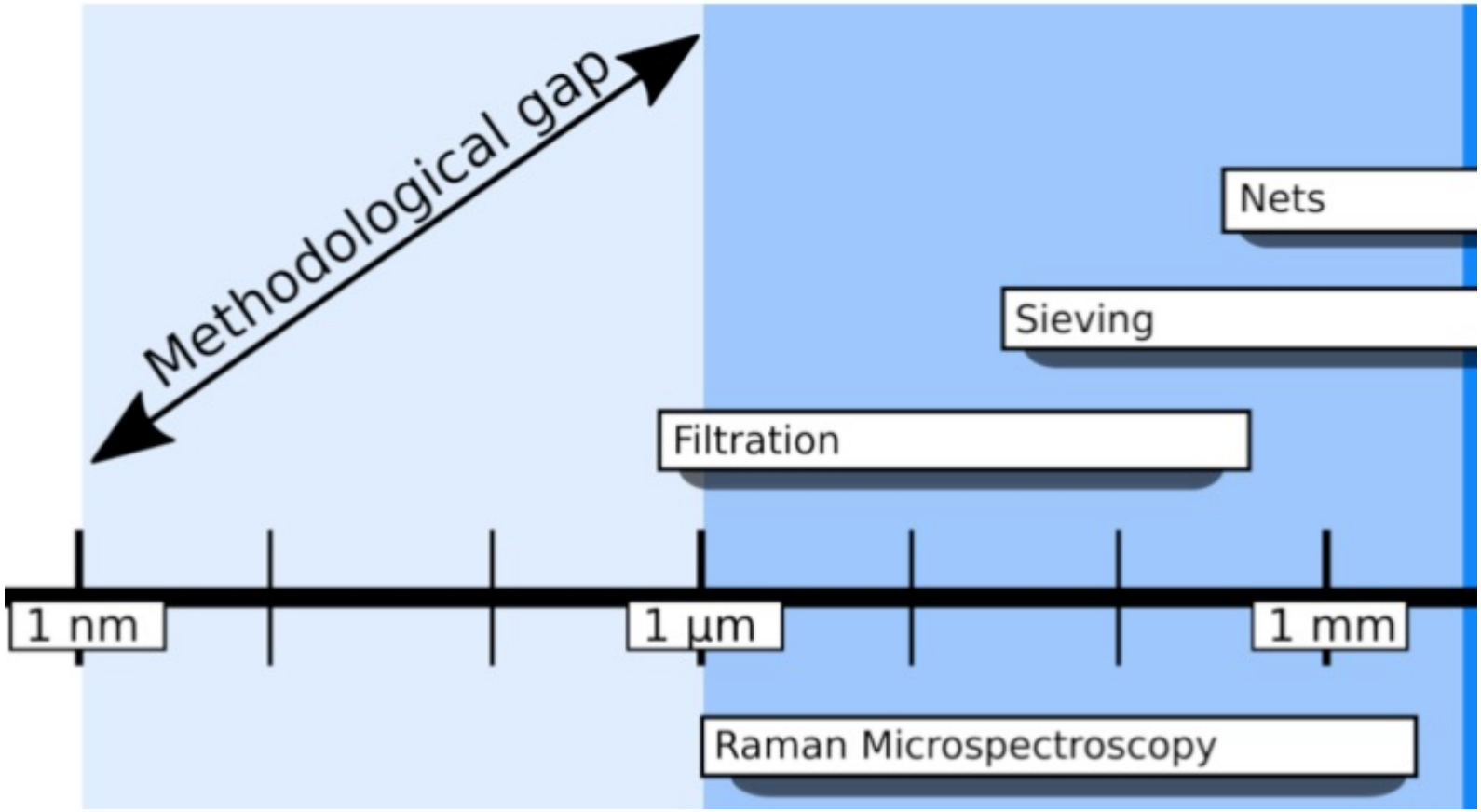


Multi dimensional output data:

- Types of plastic
- Concentration for each type
- Size distribution

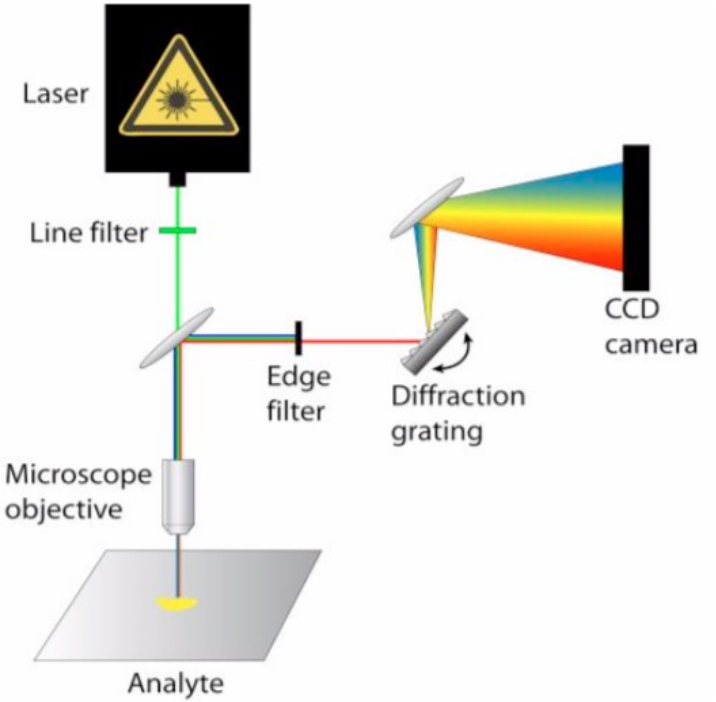
Relatively new and Extremely complex practical problem yet to be developed.

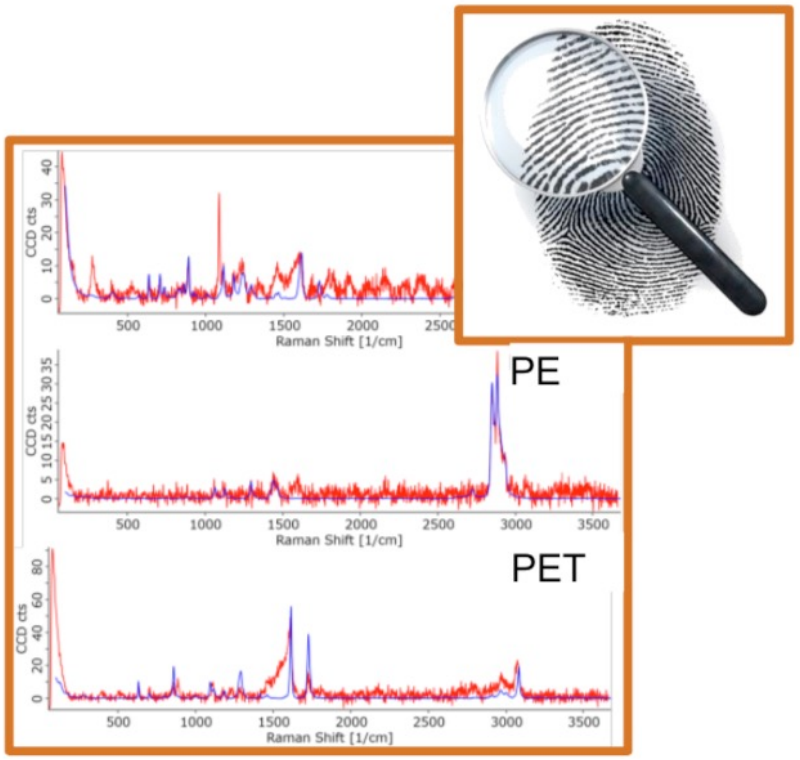
Analysis of Nanoplastics: Analytical Challenge



Physical separation provides limited size characterization

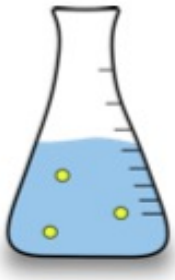
Scanning Raman Micro-spectroscopy (RM)

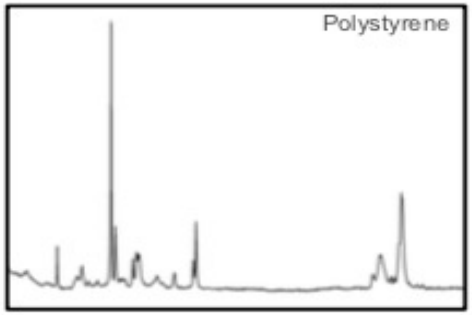


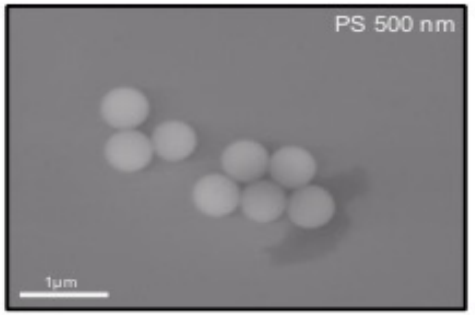


- Non-contact and non-destructive analysis
- No or little interference of water
- Chemical analysis at the µm-level
- 2D & 3D Raman imaging

Scanning Raman Micro-spectroscopy (RM)







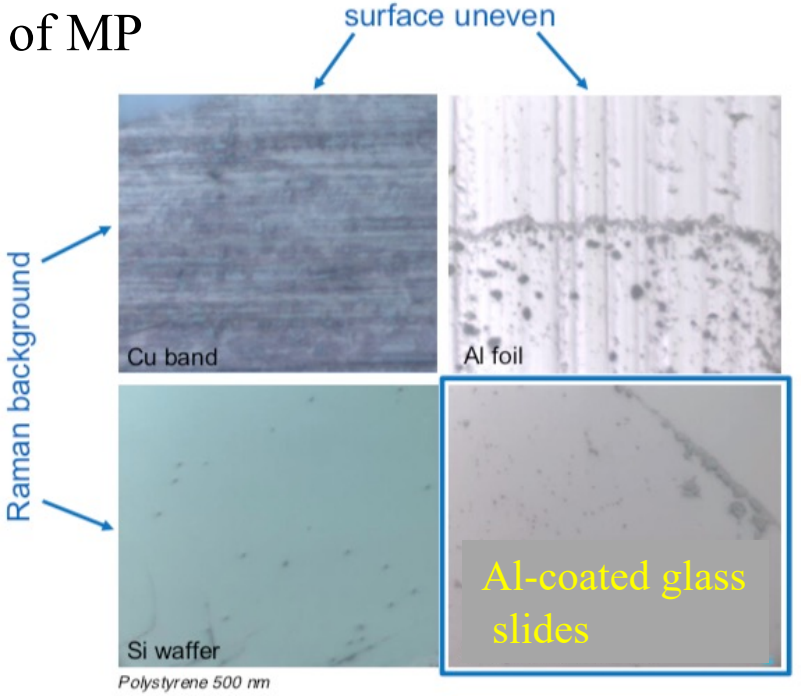
Sample → **Raman** → **SEM**

- Removing impurities,
- Selective digestion of proteins, lipids, etc.,
- Centrifuge and multistage filtering to a desired max size of particles.
- Keep track of quantity.

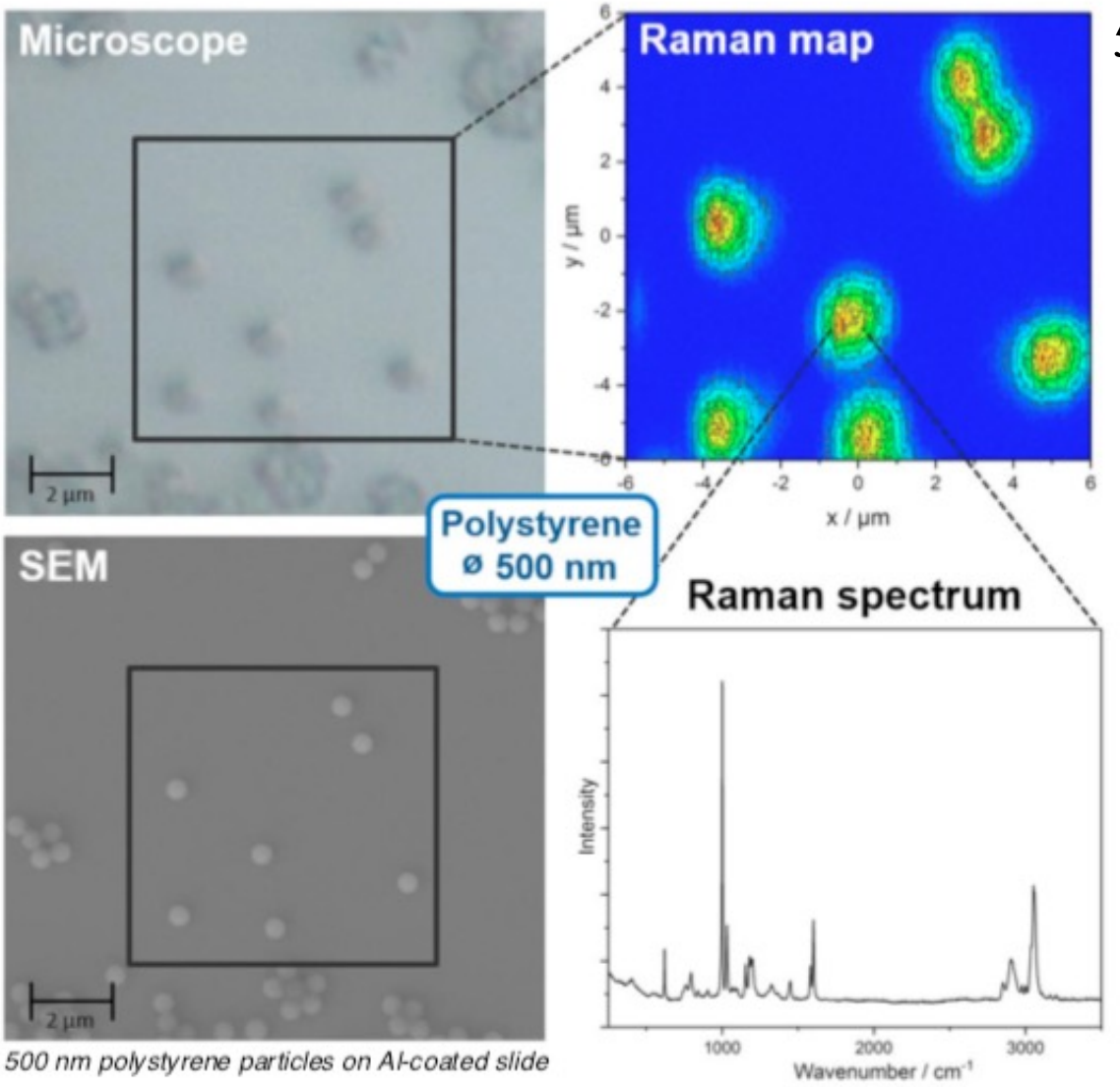
➢ Difficult to get a golden MP-free standards.

Chemical identity, Number of MP

Size and shape



RM-based Analysis of Particles ~1 μm



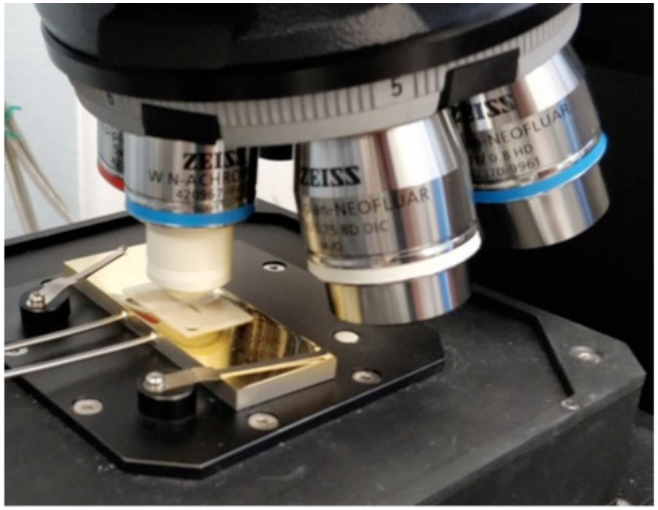
500 nm polystyrene particles on Al-coated slide

50 nm scan step

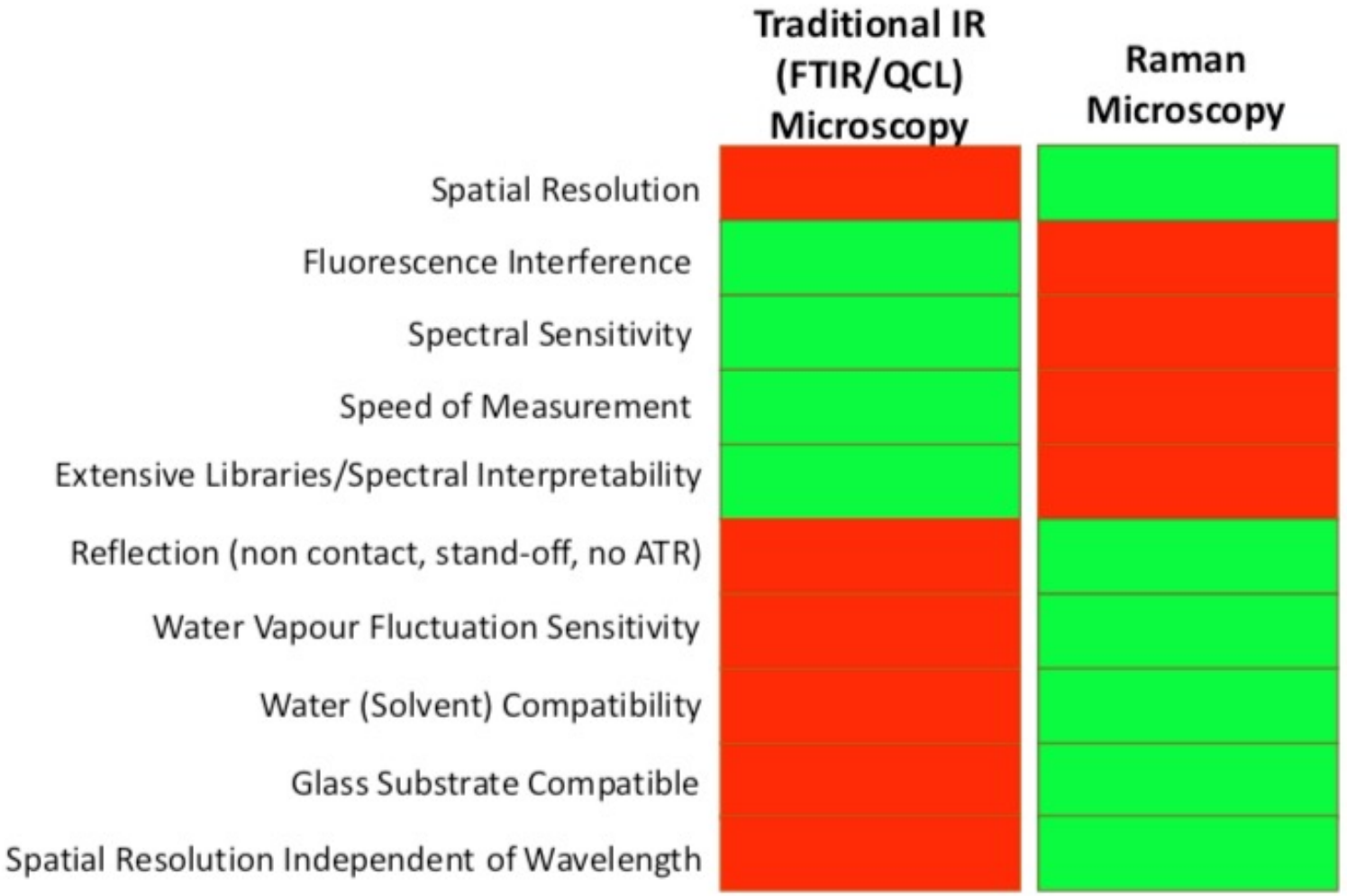
$$2w_0 = 2.44\frac{\lambda \cdot F}{D}$$

λ= **532** nm

R=$w_0 \simeq$0.7 μm

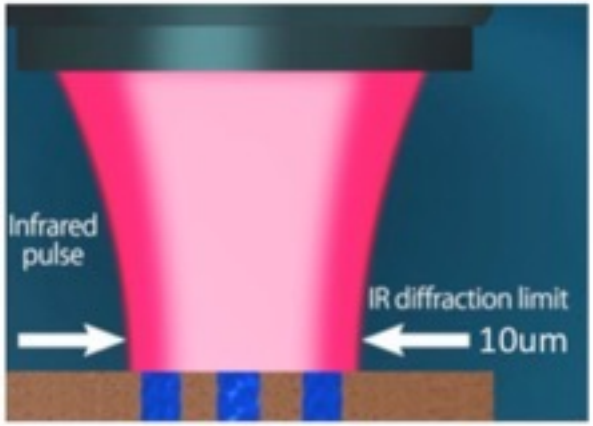


IR absorption or Raman microscopy?

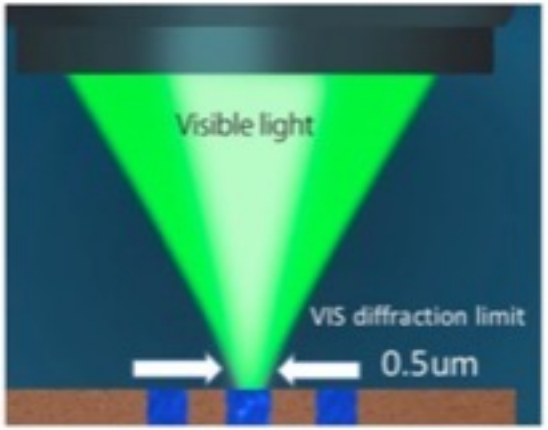


How to combine the benefits of both approaches ?

Optical Photothermal IR Spectroscopy (O-PTIR)



Beam of a pulsed **IR** laser is focused.

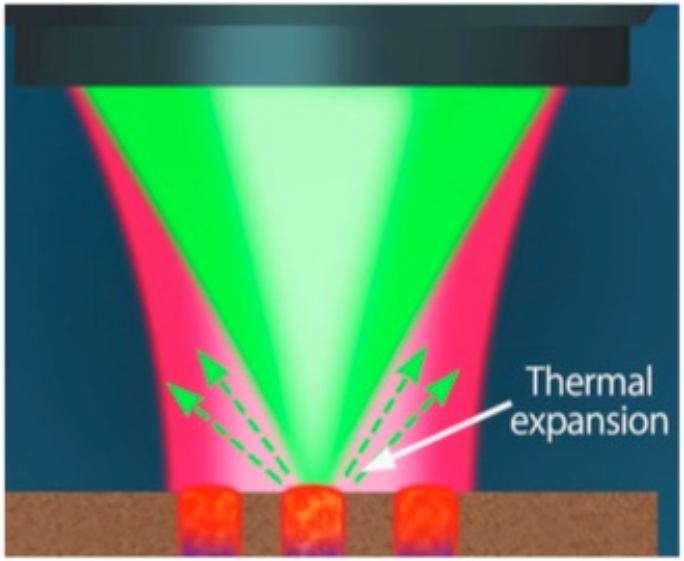


Laser beam in **visible** is focused colinearly with IR

IR absorption causes local temporal heating, which leads to change of refractive index => change in scatter of visible light.

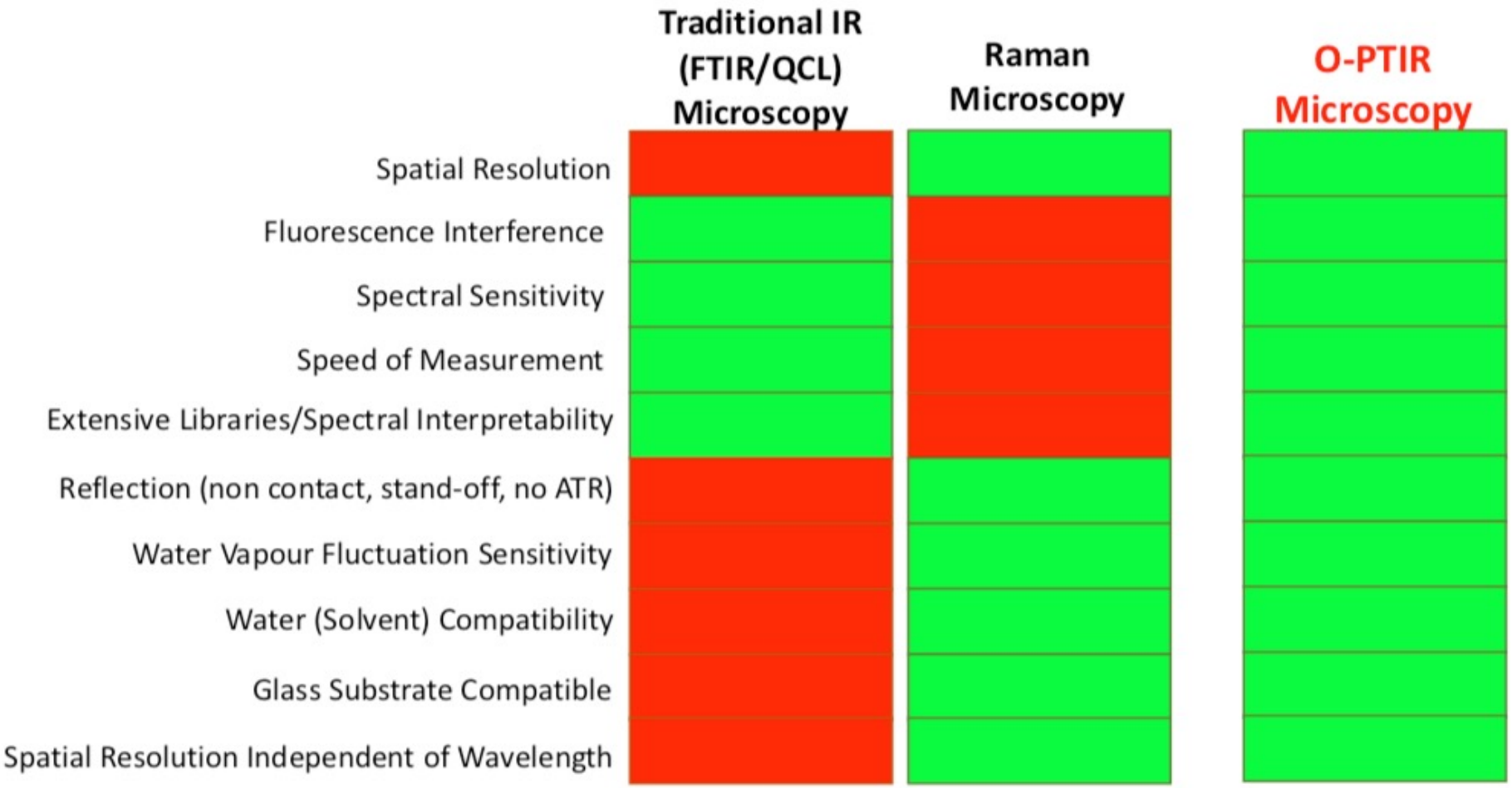
Spectrum is detected by detecting visible, while scanning IR.

IR absorption, but only in the ≃0.7 μm focal arear of **visible**

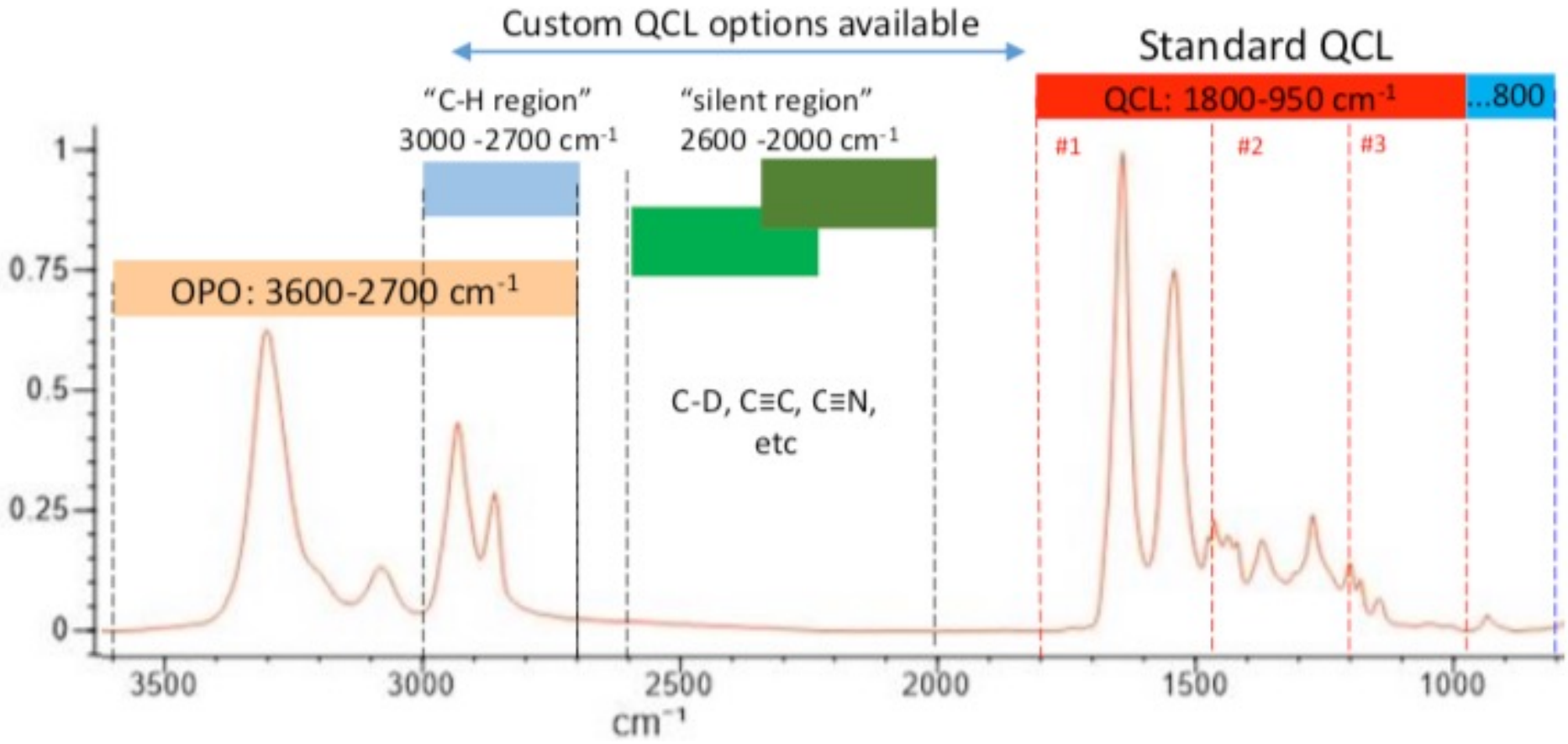


Sensitivity of IR with resolution of Raman

IR absorption and Raman vs O-PTIR microscopy



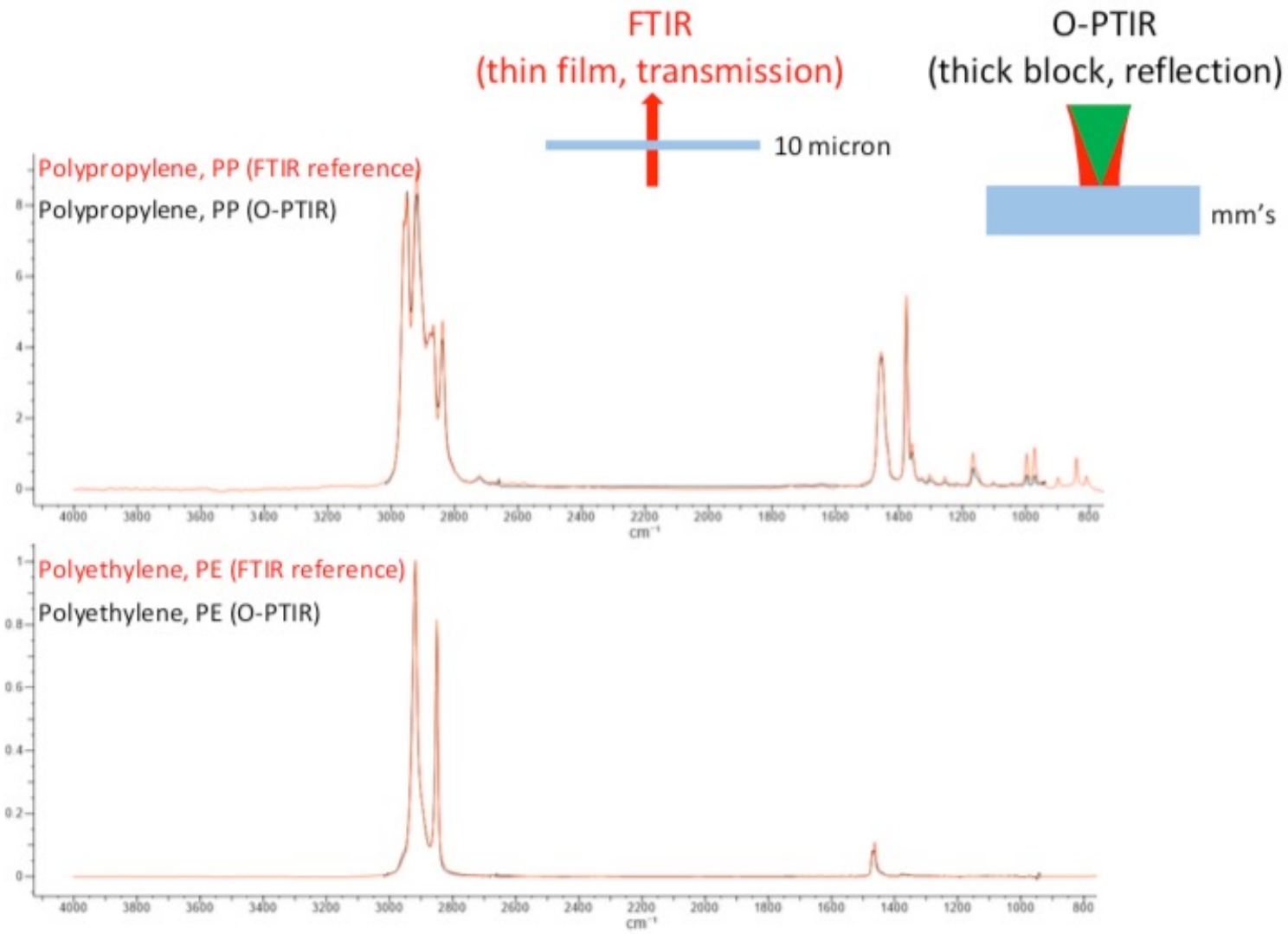
Tunable IR laser sources



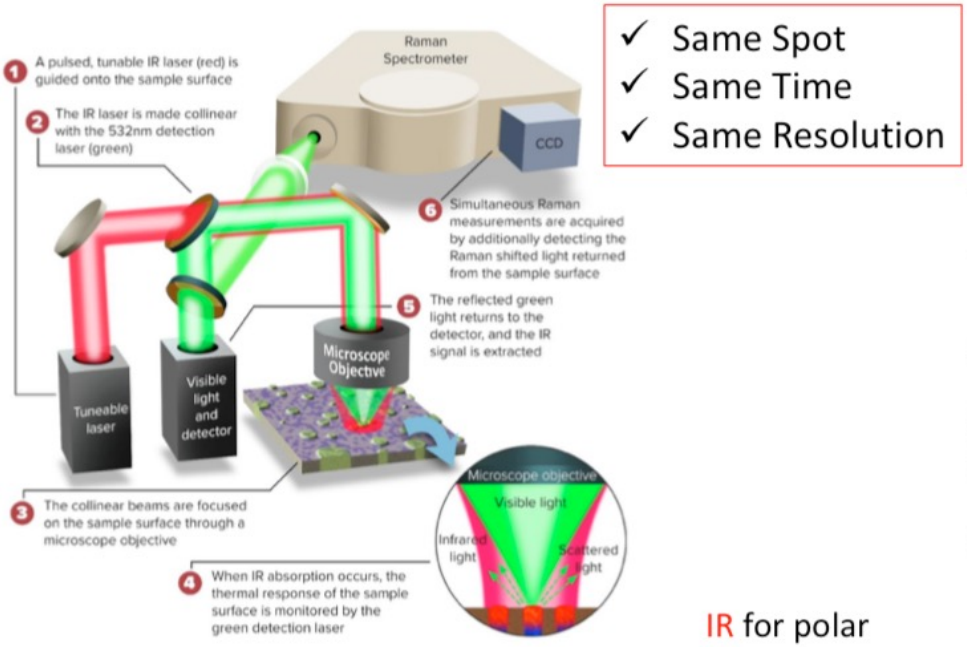
IR OPO – bulky, energy inefficient, require maintance.

QCL – a semiconductor-based, compact, but limited tunability range for each specific type.

Use of IR spectral data bases



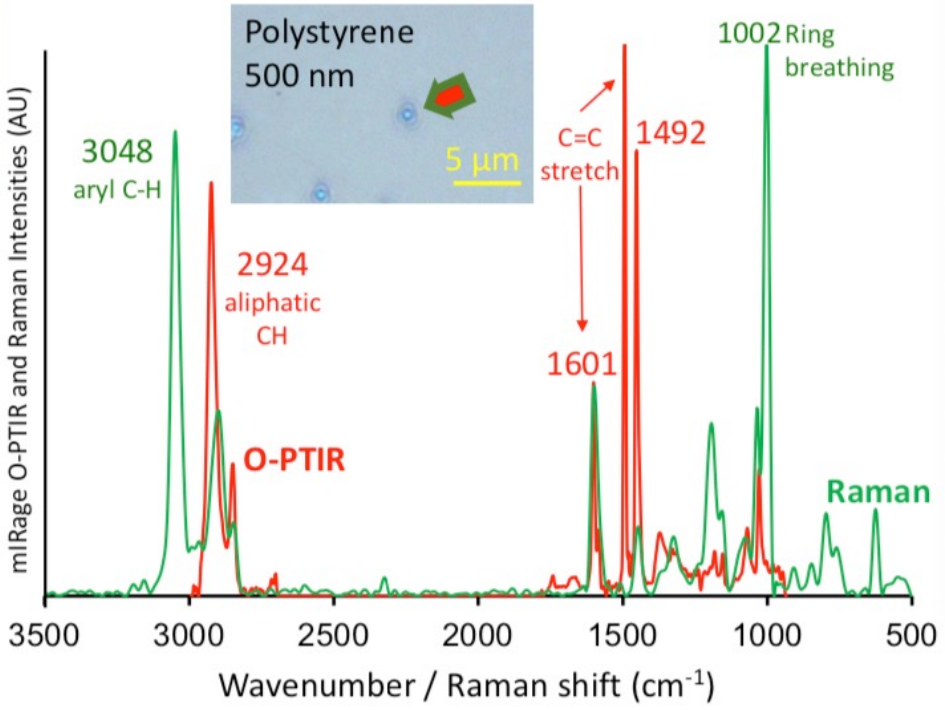
Simultaneous IR and Raman microscopy with <1 μm resolution



- ✓ Same Spot
- ✓ Same Time
- ✓ Same Resolution

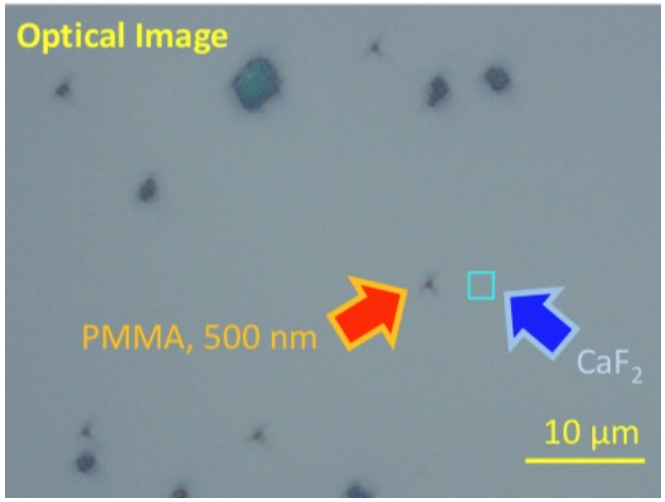
IR for polar

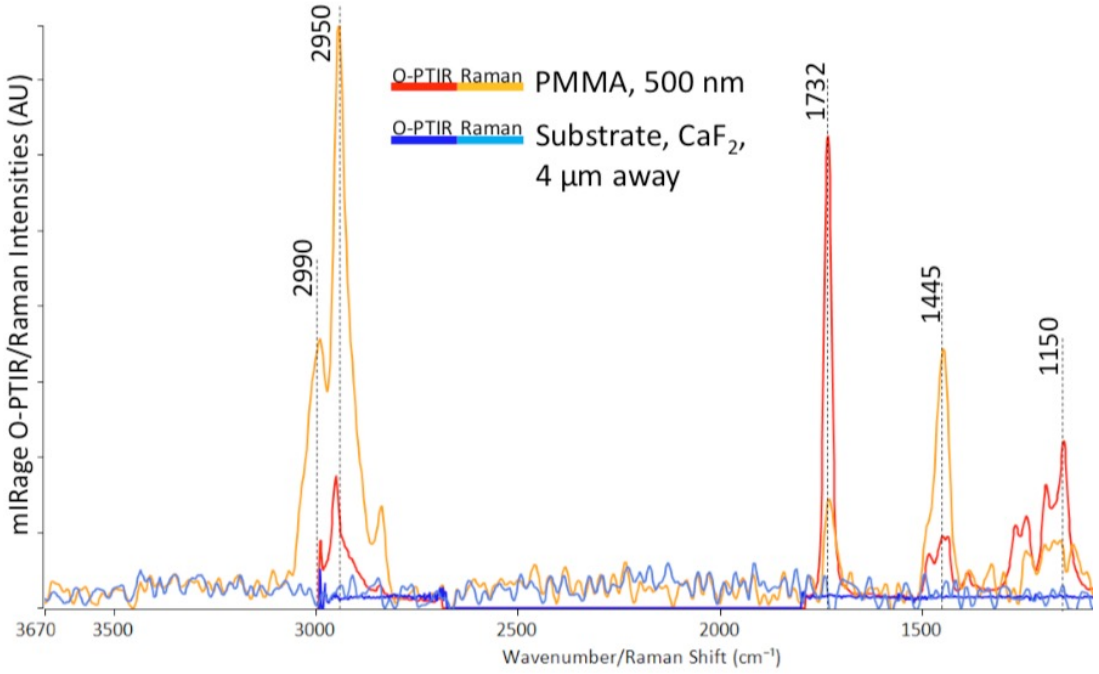
Raman for non-polar



IR + Raman microscopy

- ➢ Locate and make a 2D digital map of beads;
- ✓ Pre-program X-Y scan to stop at the locations of suspected MP beads;
- ✓ Point microscope one by one to this locations
- ➢ At each location scan IR to get O-PTIR and Raman spectra





IR + Raman microscopy

- Search in thew available databases of IR and Raman for the best hit