

# Product Characterisation

## Vibrational Spectroscopy (Infrared and Raman)

### Lecture 2

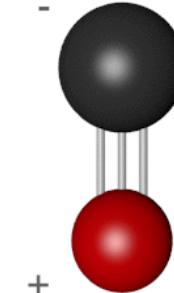
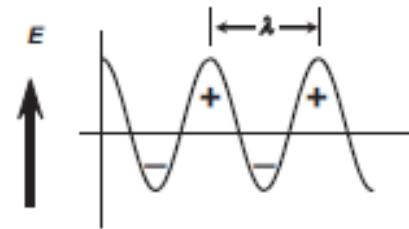
Prof. Sergei Kazarian,  
BONE 440, s.kazarian@imperial.ac.uk

# Vibrational Spectroscopy

- Brief summary of last lecture
- Applications of Infrared spectroscopy
- FTIR spectroscopic imaging
- Raman spectroscopy:
  - Fundamentals
  - Applications to polymeric materials and pharmaceutical samples
  - SERS, TERS and nano-imaging

# Brief summary Lecture 1: Infrared selection rules

$$\frac{\partial \mu}{\partial r} \neq 0 \quad \text{Infrared active}$$

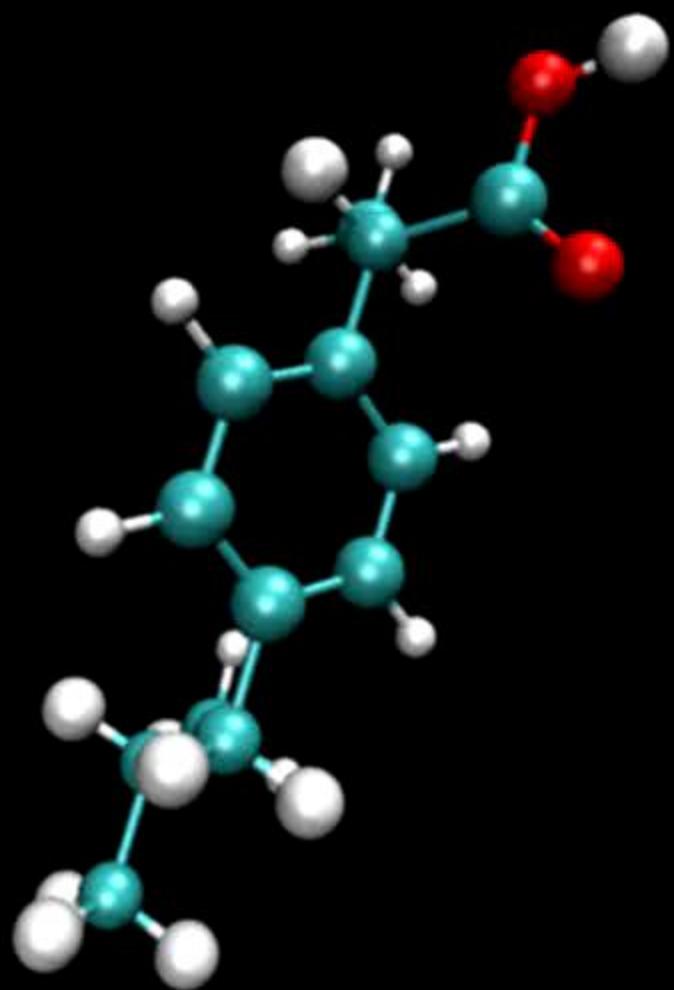


$\mu$  is a dipole moment,  $\mu = q \times r$ ,  $q$  is charge and  $r$  is distance (e.g. bond length).

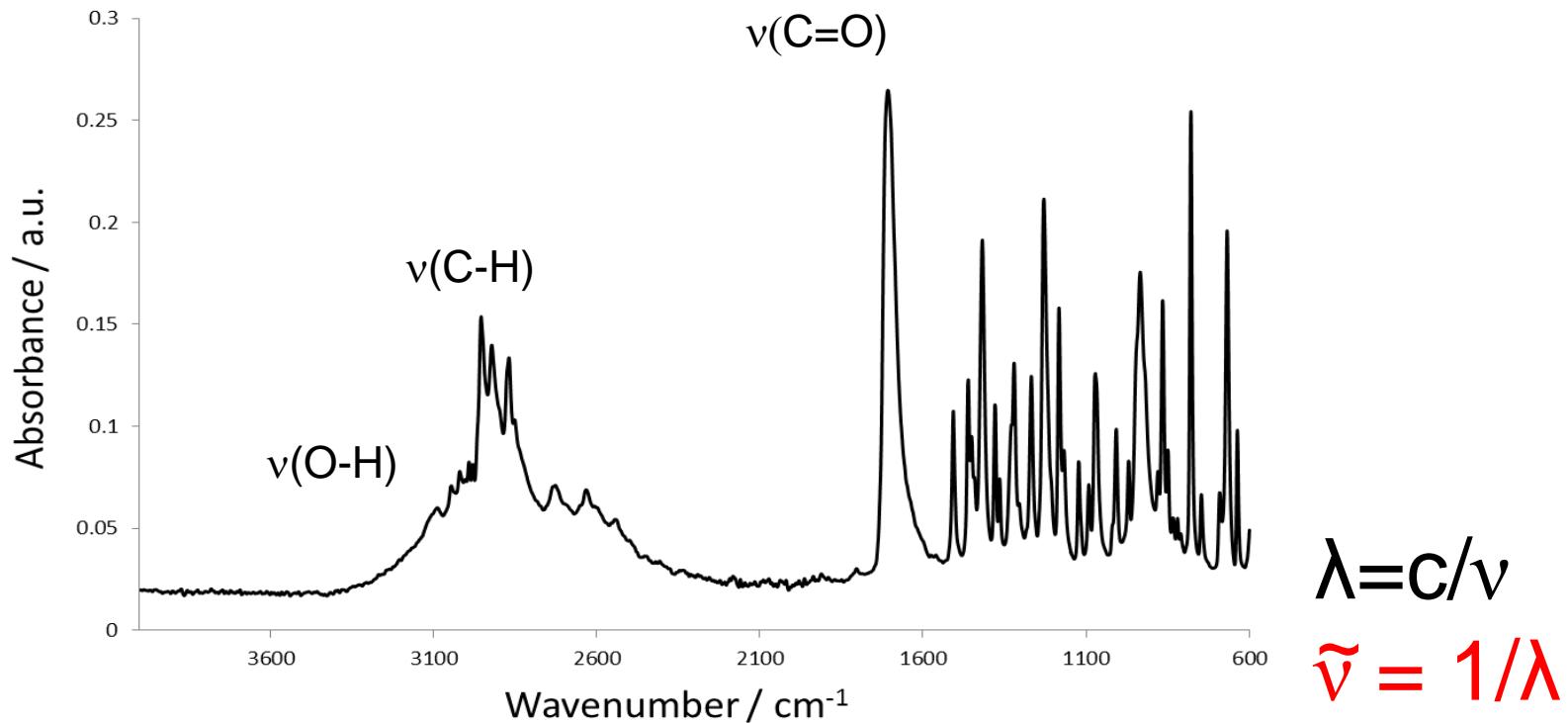
Why do  $\text{CO}_2$  and other molecules absorb infrared radiation and show infrared absorption spectrum?

$3N - 6$  for non-linear molecules

$3N - 5$  vibrational modes for linear molecules, such as  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ...



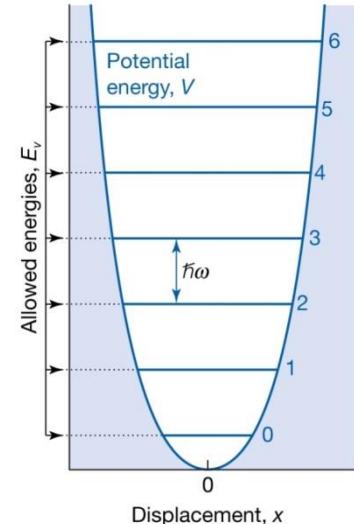
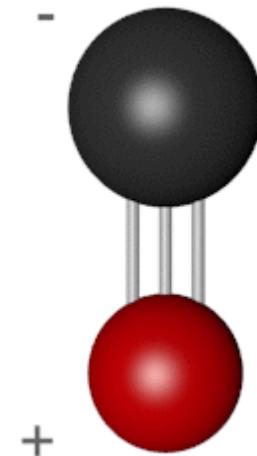
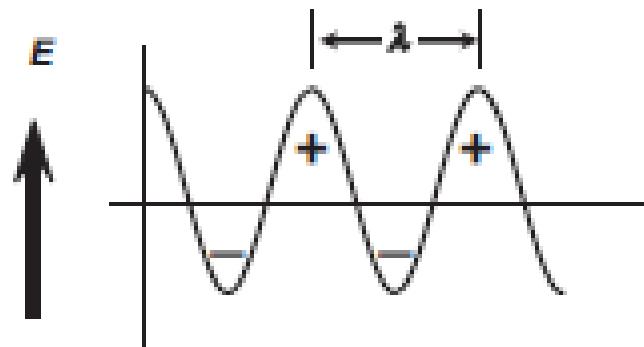
# Number of vibrations and infrared spectrum of ibuprofen



Spectrum is a representation of what electromagnetic radiation is absorbed or emitted by the sample

Infrared spectrum of ibuprofen tablet measured with a diamond ATR accessory

# Change of dipole moment during molecular vibration



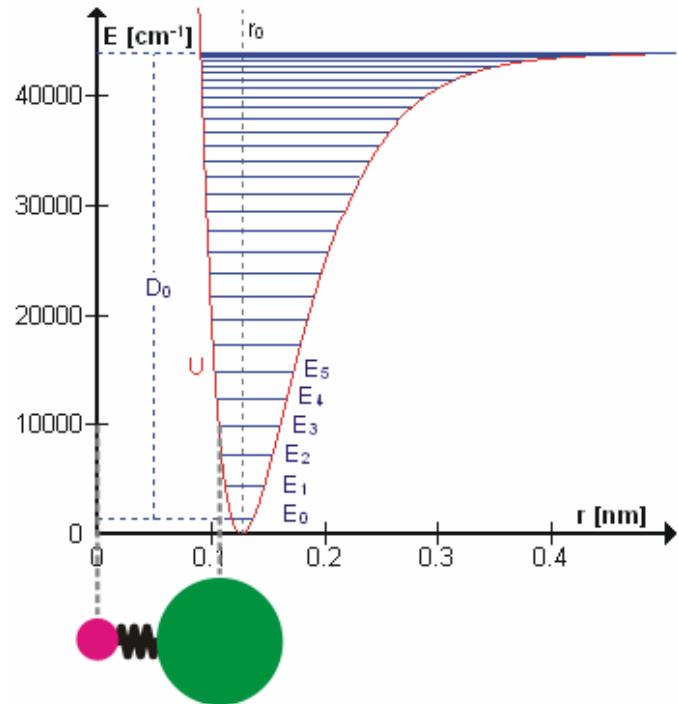
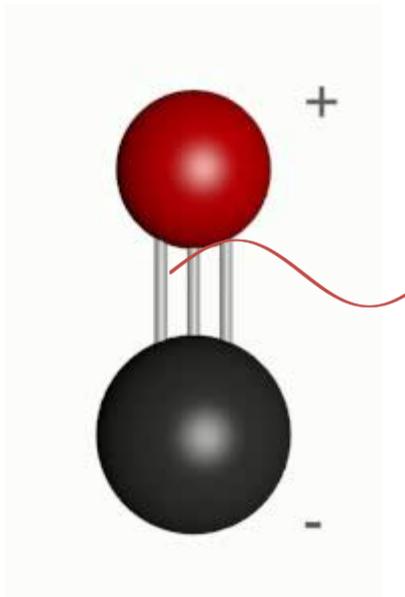
$$\frac{\partial \mu}{\partial r} \neq 0$$

$\Delta V = \pm 1$   
(for harmonic oscillator)

$$\lambda = c/v$$

$$\tilde{\nu} = 1/\lambda$$

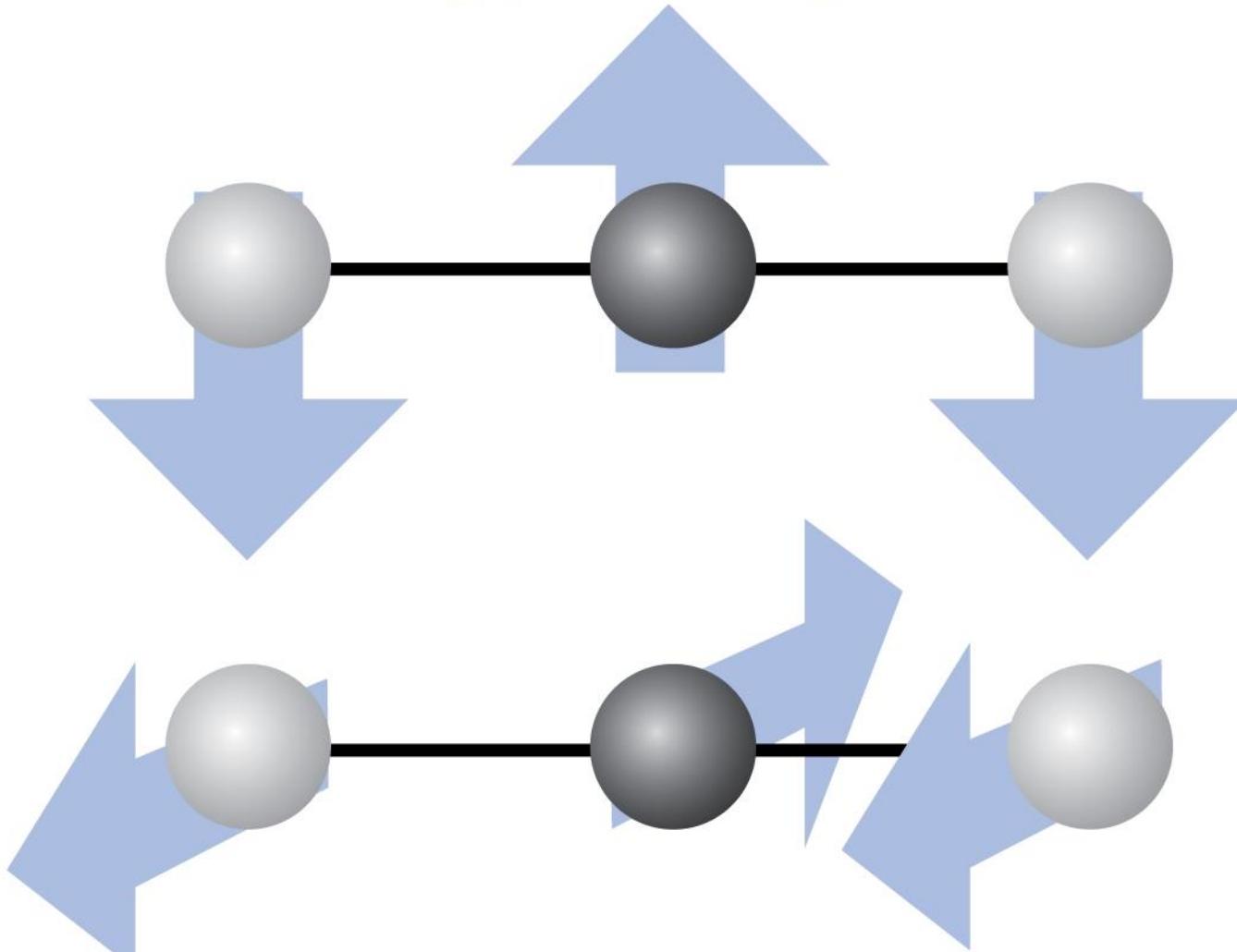
# Change of dipole moment during molecular vibration



- Photon of correct frequency interacts with changing electric field of vibrating molecule
- Amplitude of vibration changes but vibrational frequency does not
- Vibrational amplitude is quantised

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{\kappa}{\mu}} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

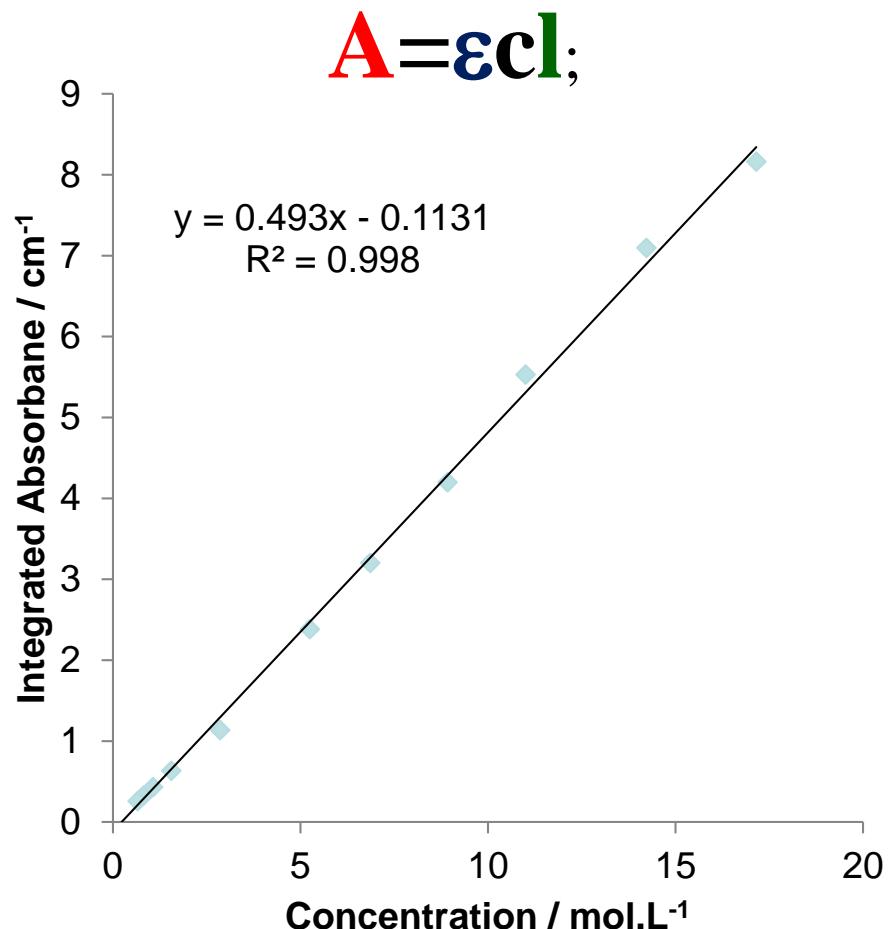
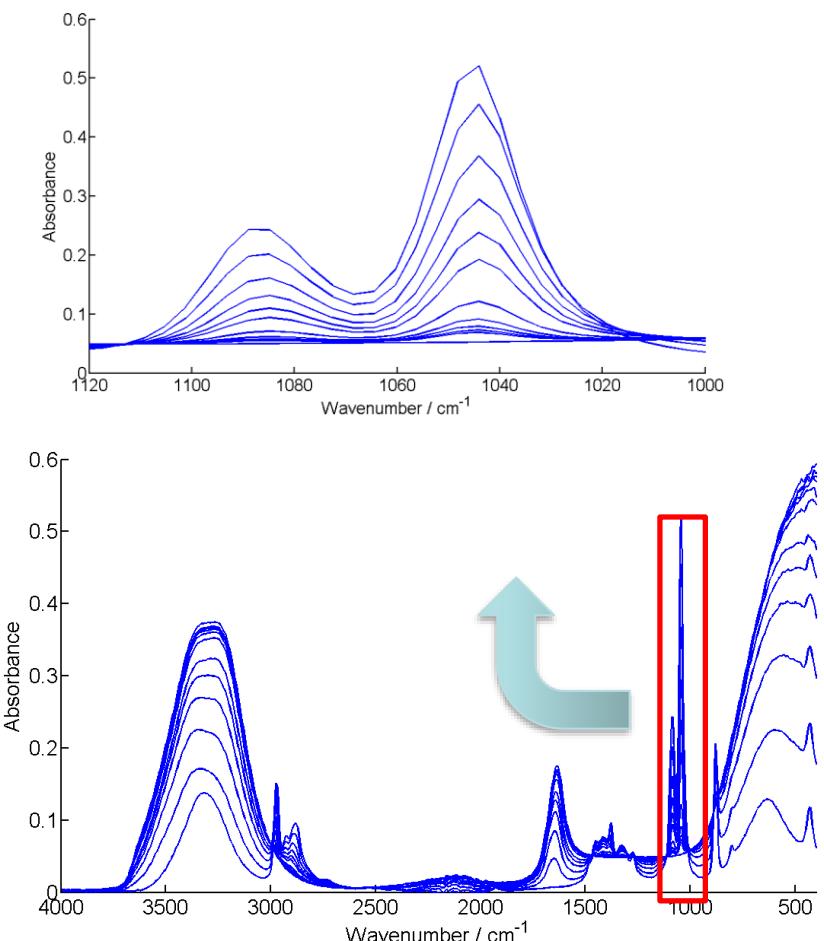
# Bending modes of carbon dioxide molecule $\nu_2$ (667 cm<sup>-1</sup>)



**Degenerate vibrations (in this case double degenerate)**

# Beer-Lambert Law

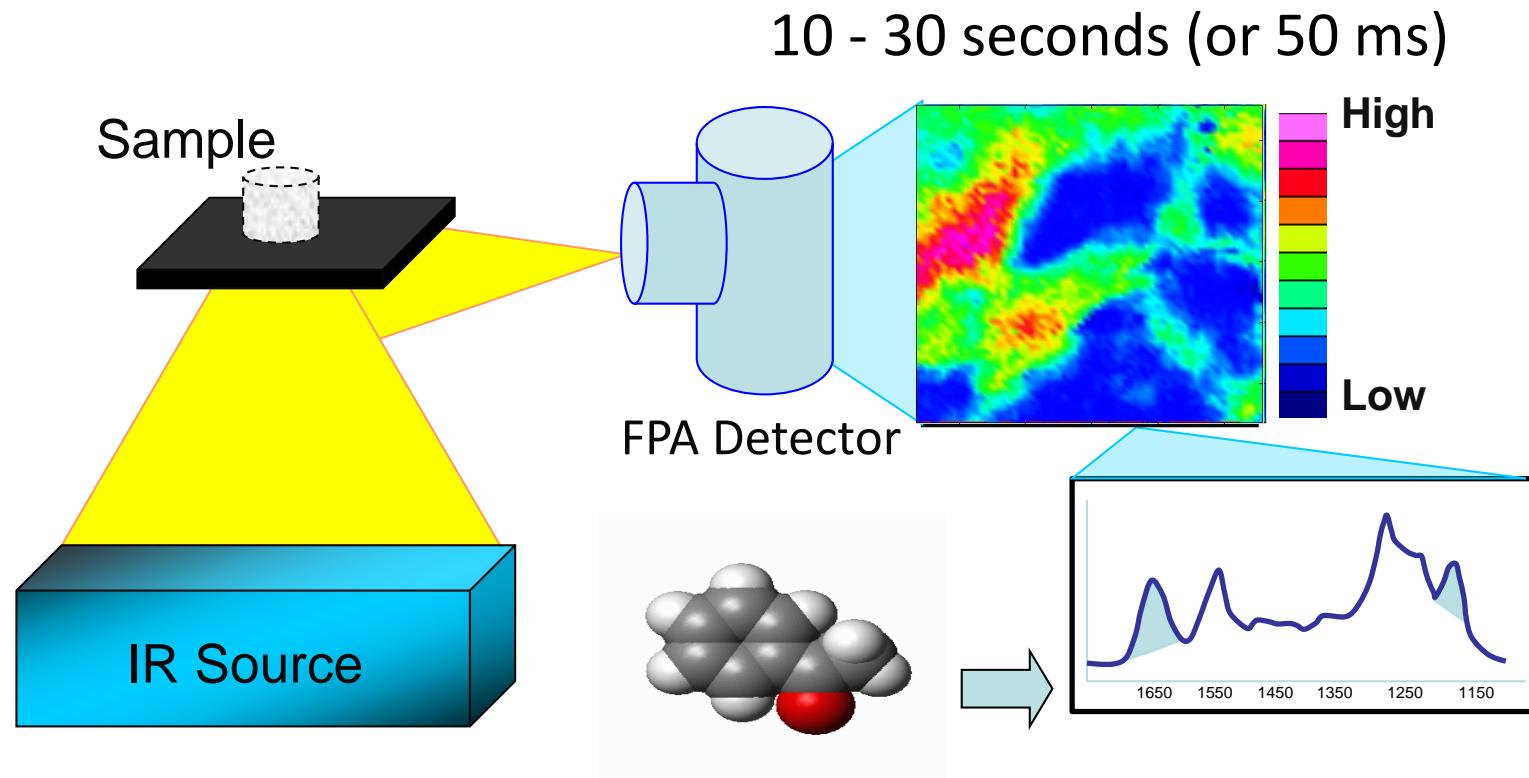
## Ethanol – water solutions



Spectra measured during demonstration: starting with pure water, ethanol was gradually added into the solution. Left: you may see that absorbance of water bands decrease while absorbance of ethanol bands increase. Right: plot of absorbance of ethanol band as a function of concentration of ethanol in solution resulted in a straight line.

# Chemical imaging with IR spectroscopy

Chemical photography: one image is worth a thousand spectra

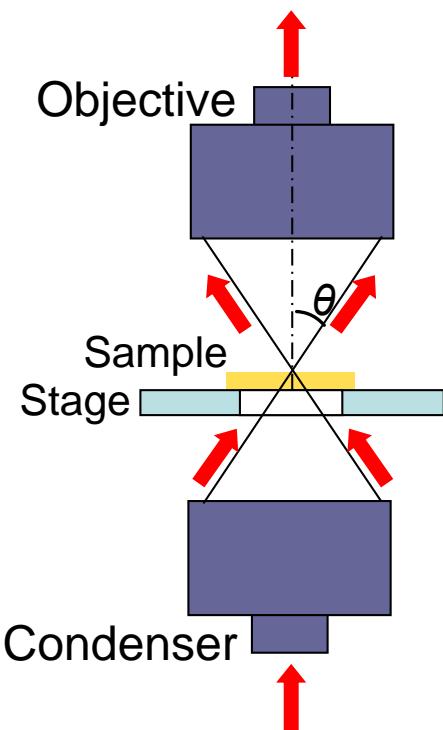


Combining FTIR spectrometer with an infrared array detector  
(64 x 64 or 128 x 128 pixels)

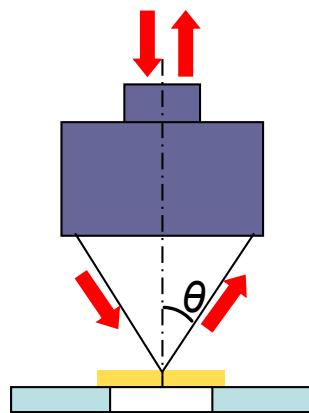
The FPA has a pixel size of 40  $\mu\text{m}$ , spectral range 5000 - 950  $\text{cm}^{-1}$  and can be used also in the near IR by substituting the Ge window with a BaF<sub>2</sub> window

# Common infrared microscopy sampling techniques

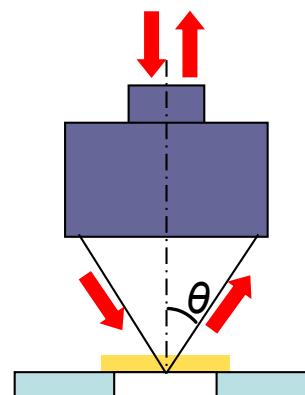
Transmission



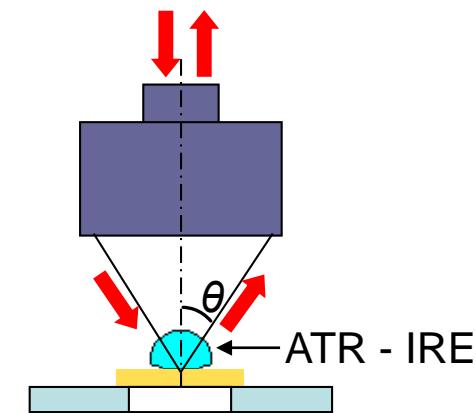
Reflectance



Absorption/  
Reflectance



Micro - ATR



Sample thickness:  
10 – 20  $\mu\text{m}$

Sample thickness:  
NA

Sample thickness:  
5 - 10  $\mu\text{m}$

Sample thickness:  
NA

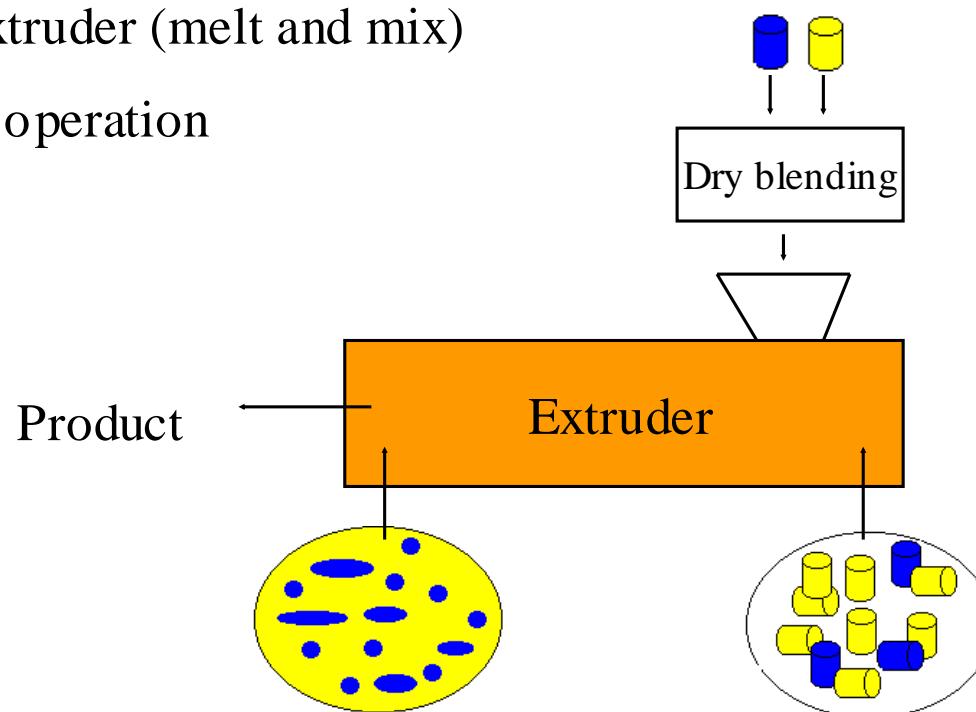
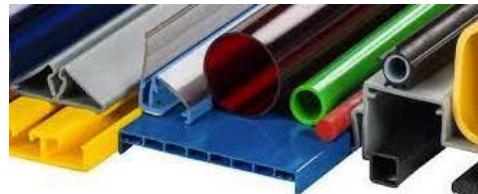
# FTIR Imaging of Heterogeneous Materials and Products

- It is possible to engineer new materials by blending or mixing.
- The quality of the product in almost all polymer processes depends in part on how well the material was mixed.
- Better understanding of mixing process helps to optimise its conditions and increase the quality of the final product

# Mixing Polystyrene and Polyethylene: an example of first applications of FTIR imaging

## What is the blender or mixer?

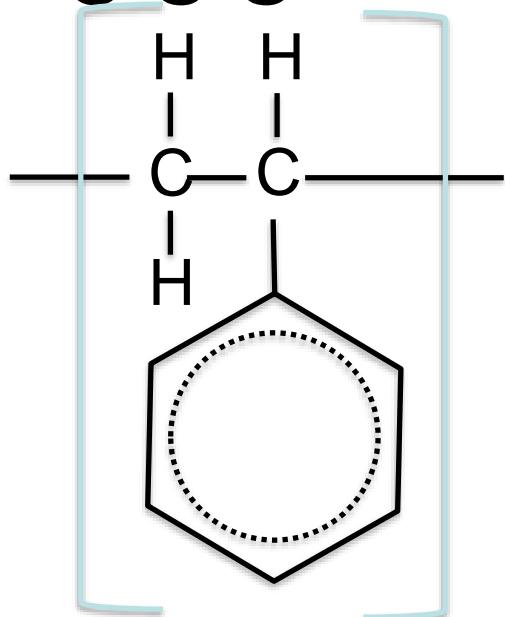
- Twin-screw Extruder (melt and mix)
- Continuous operation



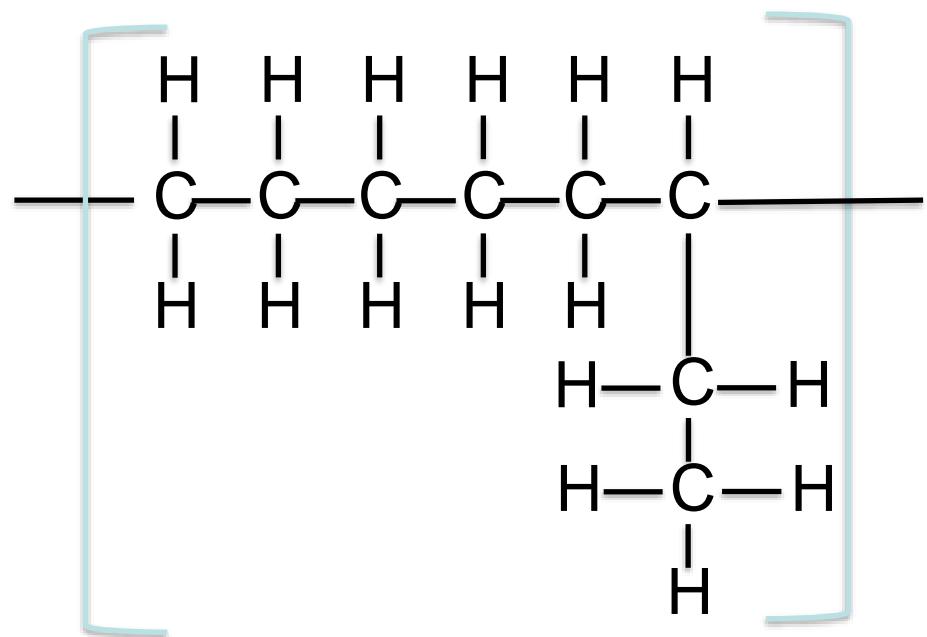
# Tri-block copolymer (SEBS) compatibilizer for PS/LDPE polymer blends

-S-S-S-S-S-EB-EB-EB-EB-EB-S-S-S-

S-S-S-



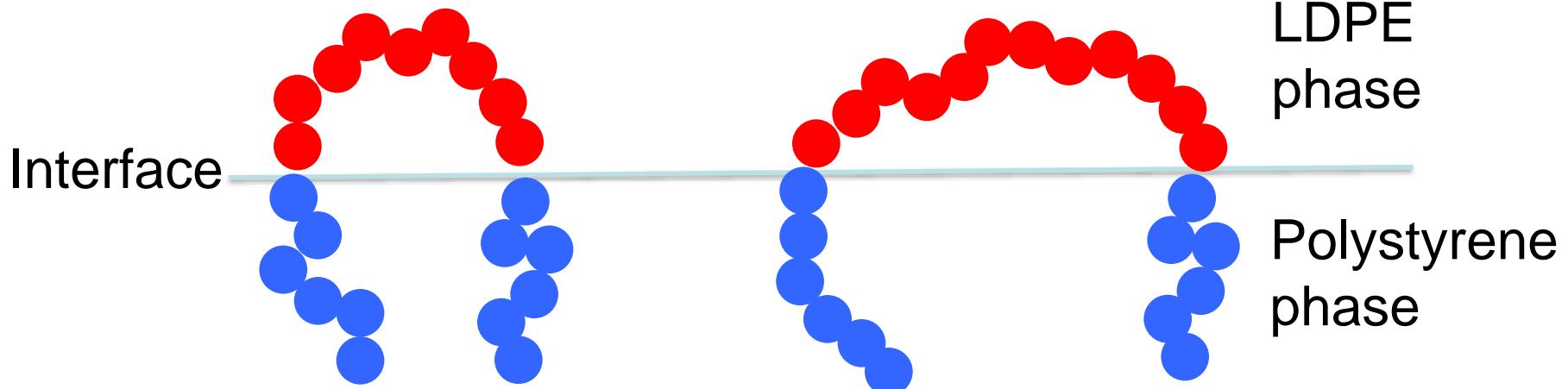
Polystyrene  
(PS)



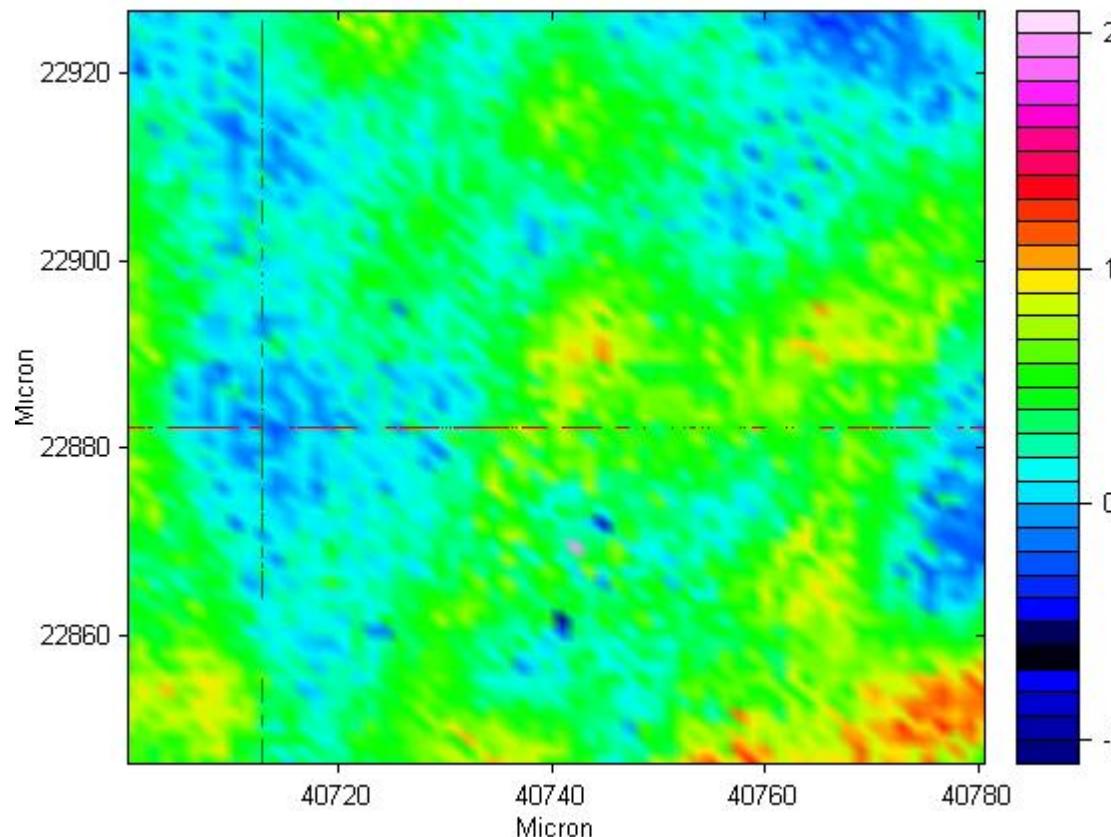
Poly(ethylene-butylene)  
(PEB)

# How does it work?

- Works as a surfactant (emulsifying effect)
  - Reduces interfacial tension (enhancing interfacial adhesion)
  - Stabilises morphology
- S-S-S-S-S-S-EB-EB-EB-EB-EB-EB-S-S-S-S-S-



# FTIR Imaging of PS/LDPE blend - 5% of compatibilizer



FTIR image was obtained by plotting absorbance of a spectral band of polystyrene as a function of all 4096 pixels in FPA array detector

# Polymer blends used in friction bearing PA/PTFE



## Interesting Properties:

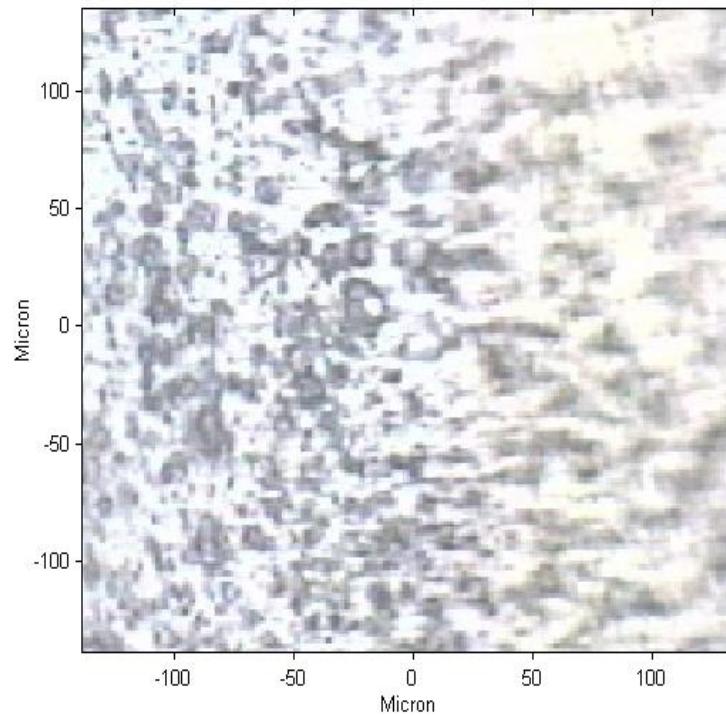
- low frictional resistance, lubricant-, wear- and maintenance-free bearings and hinges;
- combination of **PTFE** (excellent gliding properties, but expensive and hard to process) and **PA** (easy to process, strong, tough, resilient, resistant to oils, solvents, alkali).
- Compounding both materials means trying to combine fire and water!

## Easy to analyze:

- Strong IR and Raman spectra (easy to distinguish)

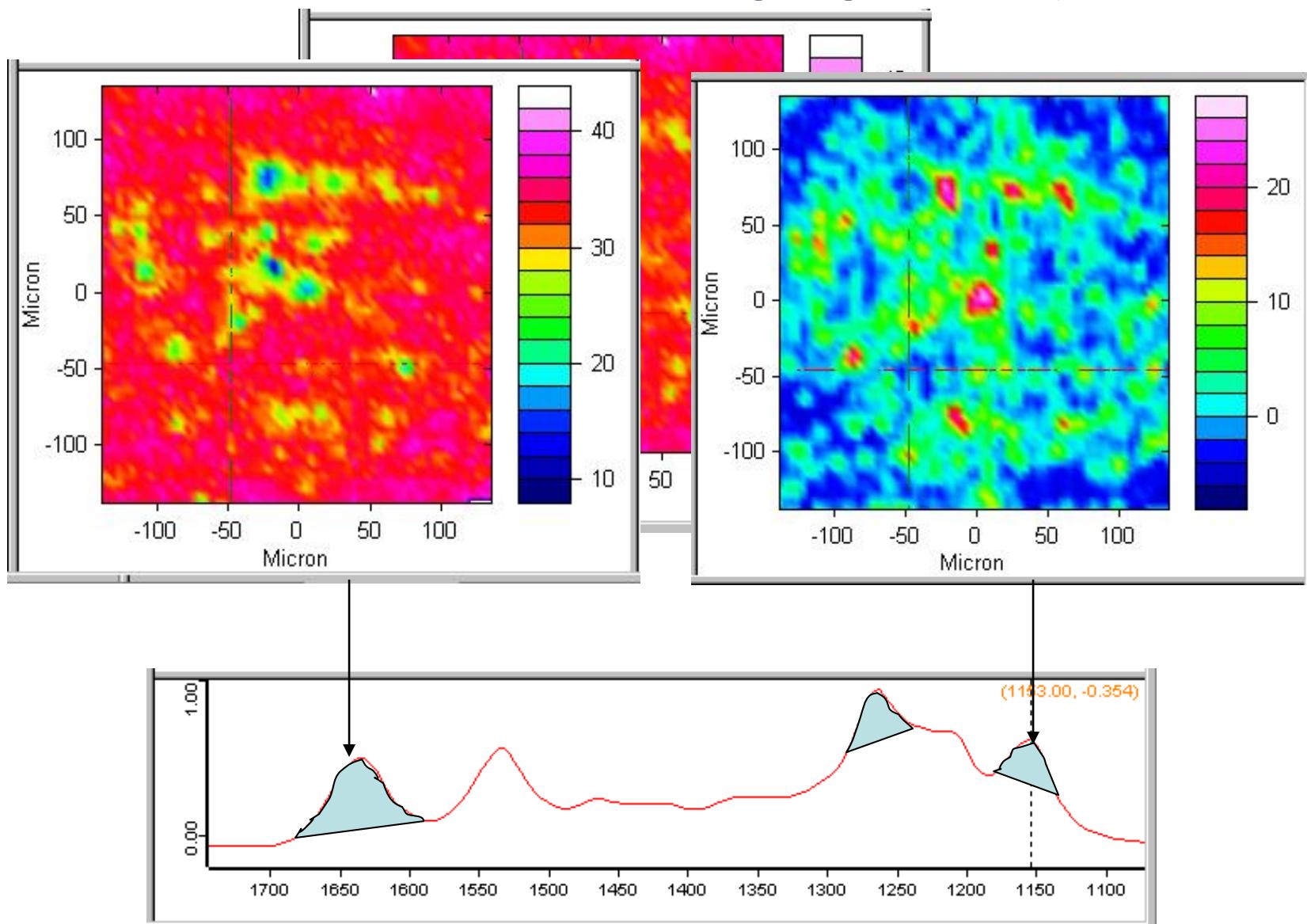
# Polymer blend used in friction bearing

80% PA, 18% PTFE, 2% Silicon Oil



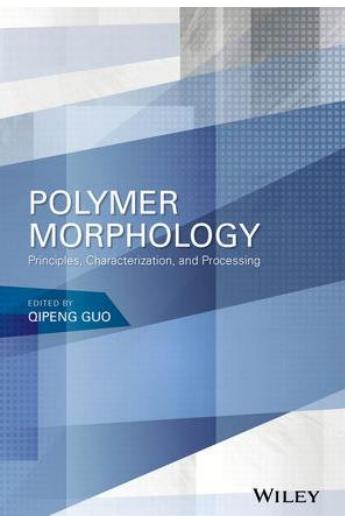
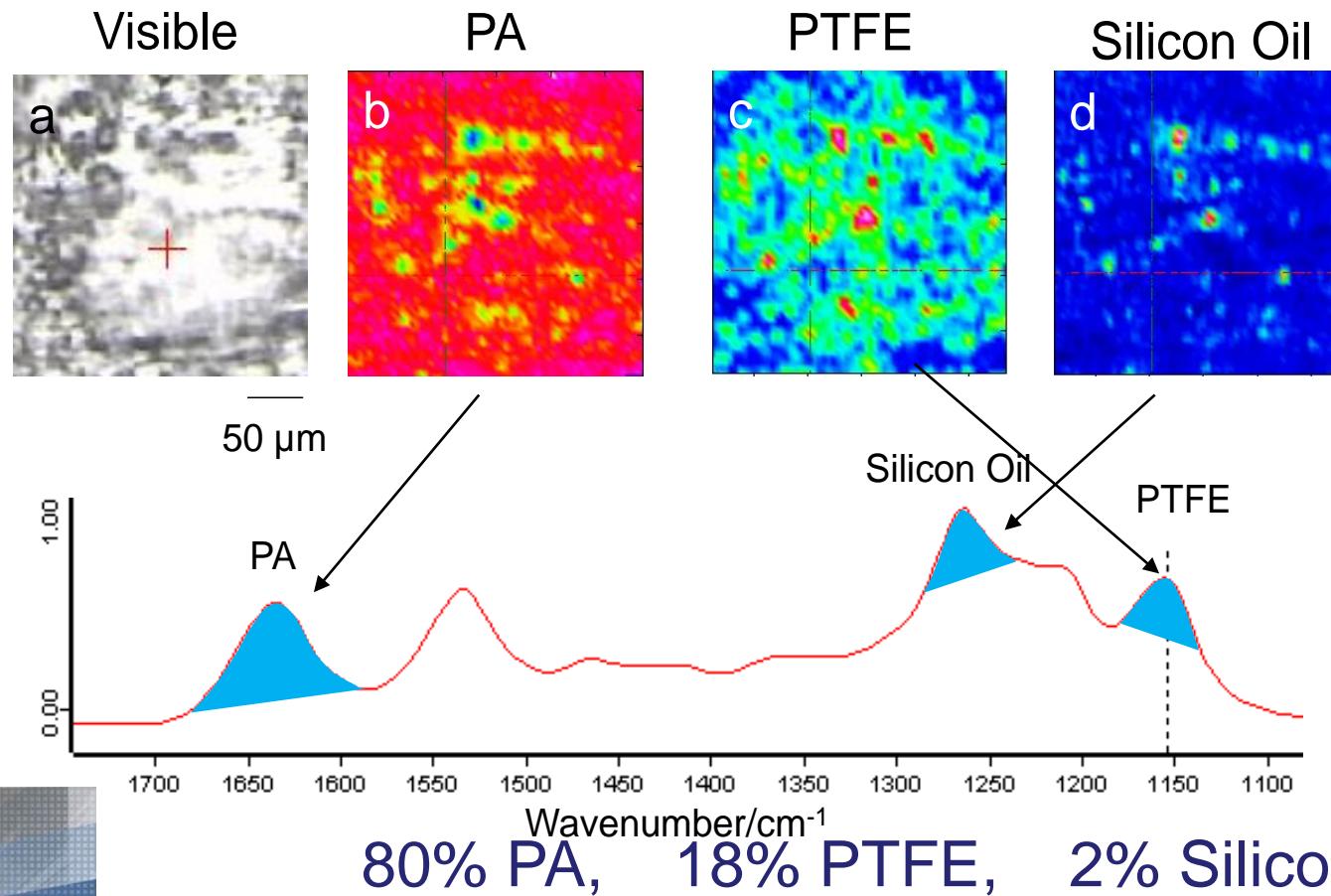
**Optical image**

# Transmission FT-IR imaging of polymer blend



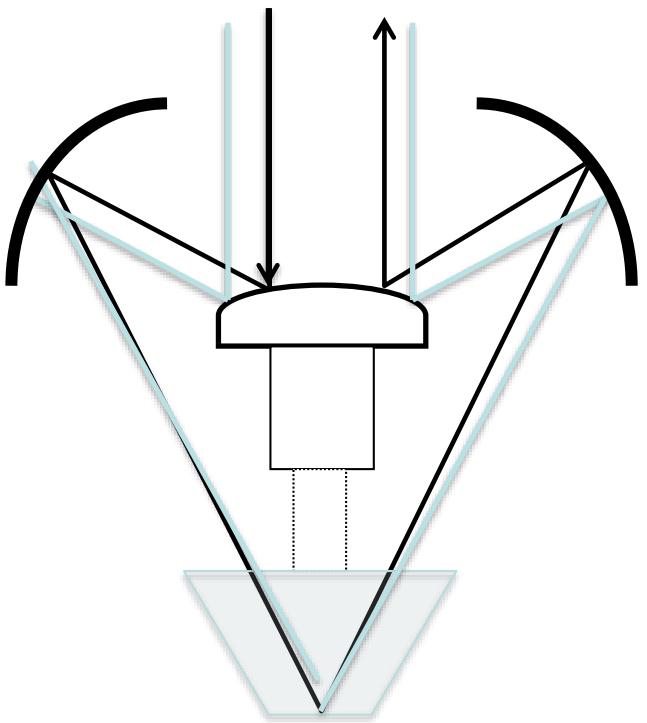
FTIR image was obtained in transmission by plotting absorbance of a spectral band of PTFE (right) and polyamide (left) as a function of all 4096 pixels in FPA array detector

# Transmission FT-IR imaging of polymer blend



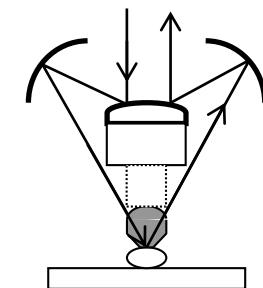
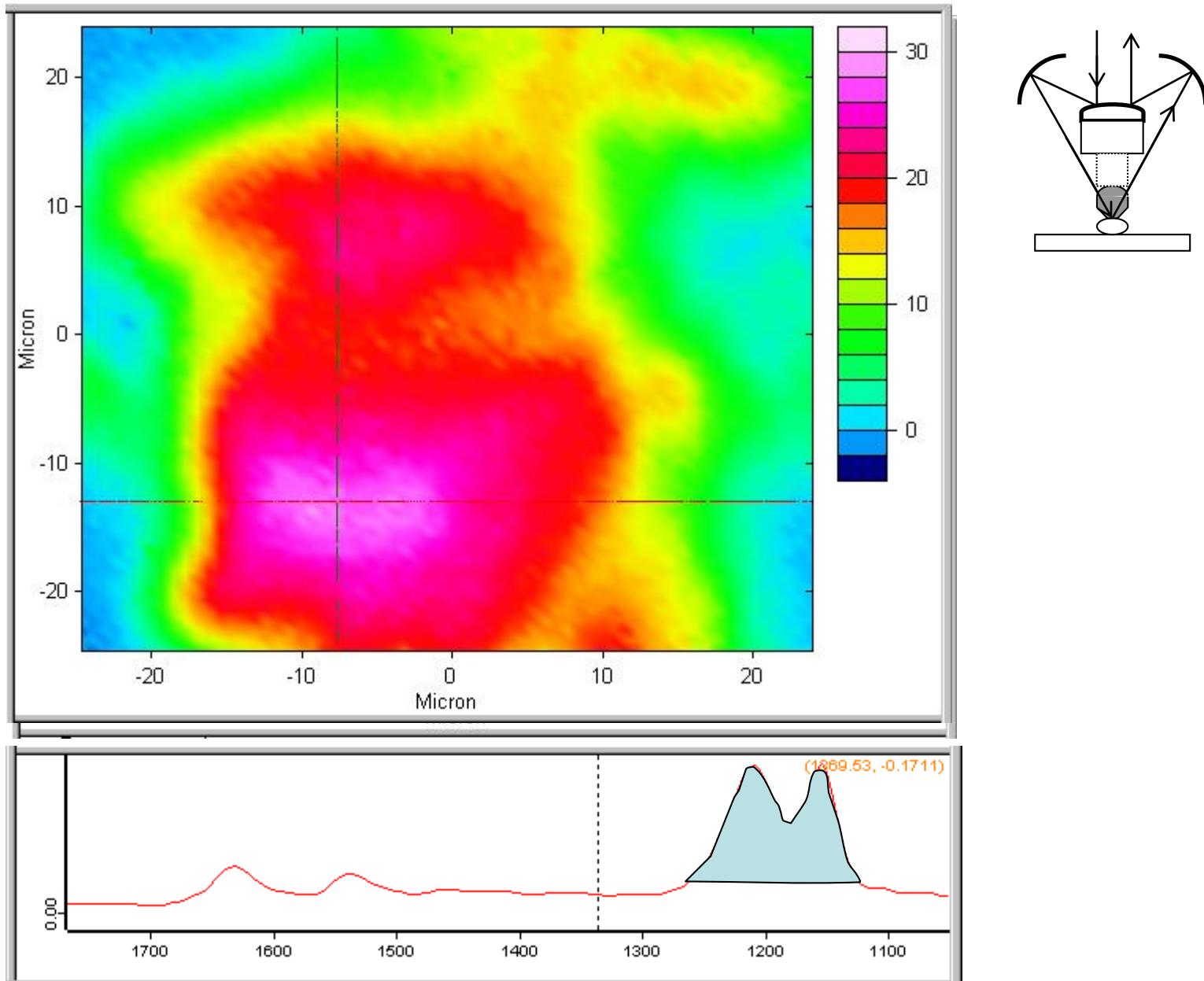
**Polymer Morphology:**  
Principles, Characterization, and Processing  
Ed. Qipeng Guo (2016)

# A Closer Look with micro ATR-IR Imaging

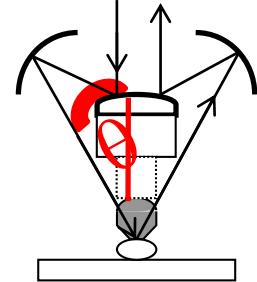


As IR is form of light,  
microscope optics can be  
made

# Closer look with micro-ATR imaging



# Rayleigh Criterion



An **Airy disk** is the central bright circular region of the pattern produced by light diffracted when passing through a small circular aperture.

$$r = \frac{1.22\lambda}{2NA}$$

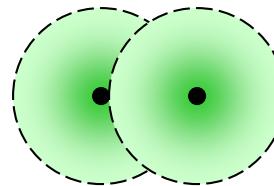
$\lambda$  is wavelength of light

Not resolved



$$NA = n \sin \theta$$

Just resolved

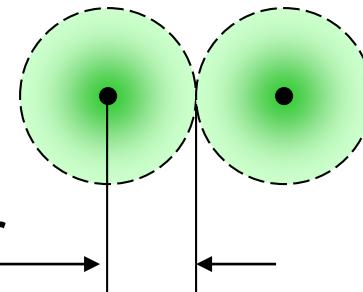


NA: Numerical Aperture

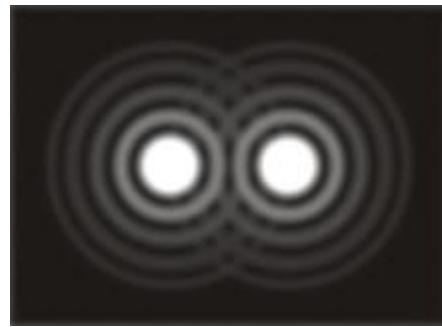
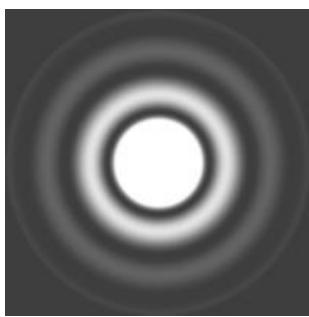
n is refractive index of the medium between objective and the sample.

Higher NA leads to high spatial resolution

Resolved

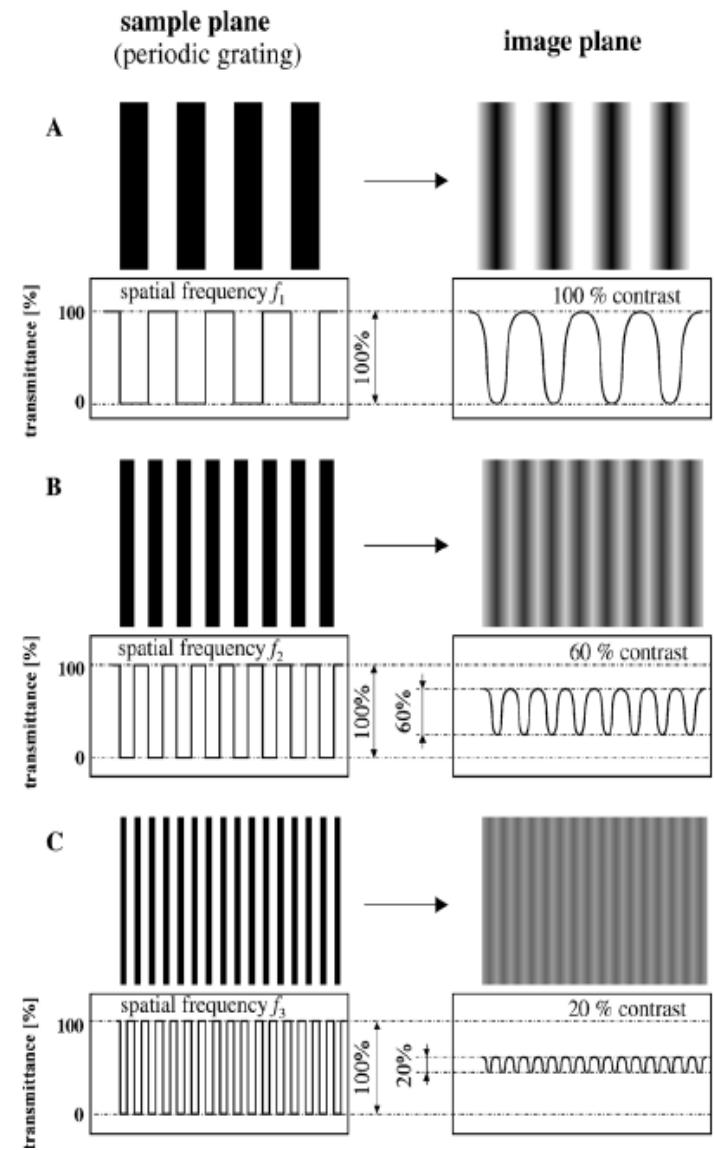
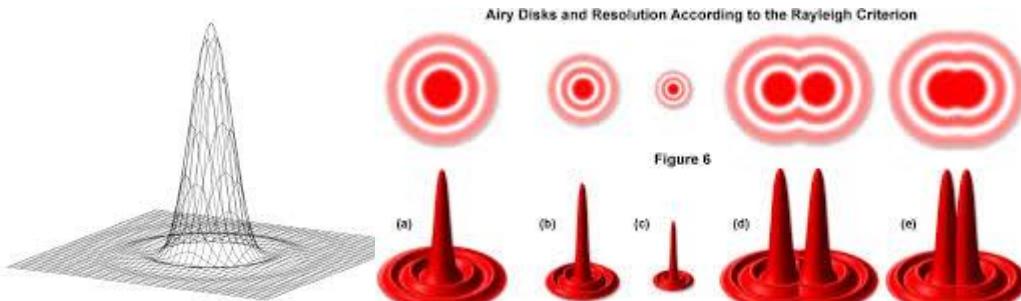


# Airy disk and Rayleigh criterion

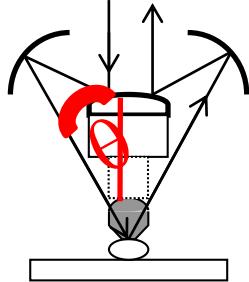


Airy disk is a diffraction pattern

$$r = \frac{1.22\lambda}{2NA}$$



# Micro-ATR FTIR imaging



Germanium ATR objective can be used with an IR microscope.

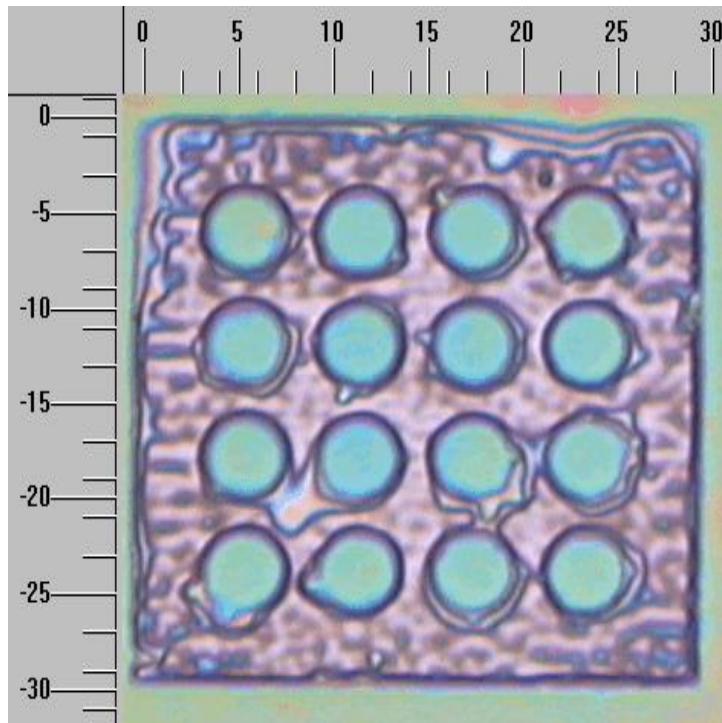


Provides small field of view ( $50 \times 50 \mu\text{m}^2$ ) with very high spatial resolution because of increased NA of objective due to high refractive index of Ge (n=4)

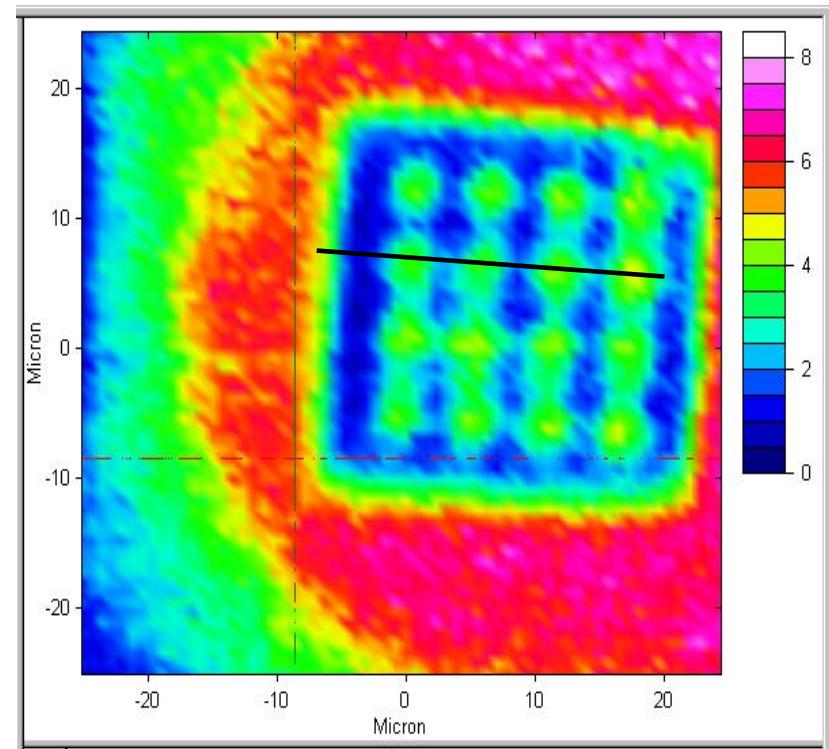
$$r = \frac{1.22\lambda}{2NA}$$

$$NA = n \sin \theta$$

# Enhanced spatial resolution can be achieved with ATR crystal

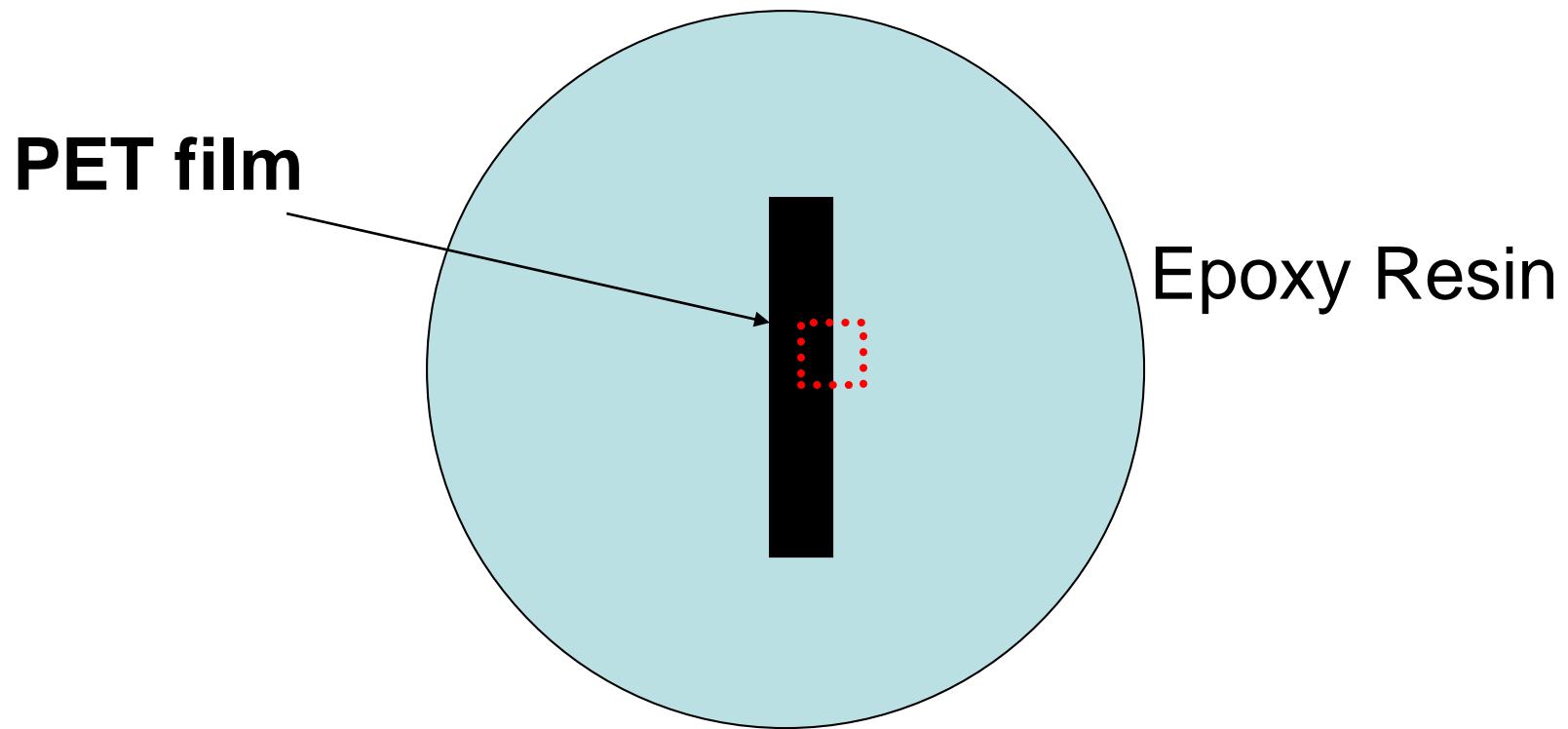


Visible image of a silicon wafer  
coated with pattern of PMMA film



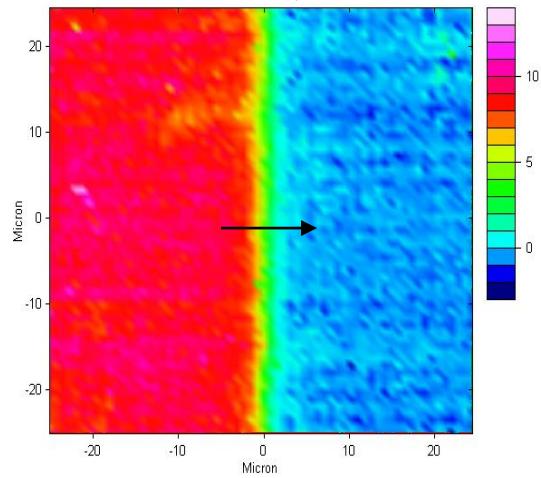
FTIR image of the same grid,  
based on absorbance of the  $\nu(\text{C}=\text{O})$   
band at  $1723 \text{ cm}^{-1}$

Sample of PET/epoxy laminate:  
a representative of real samples where  
refractive indices are not too different

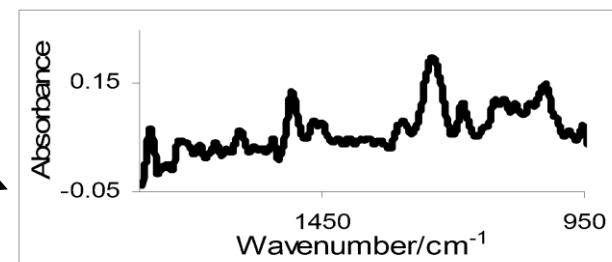
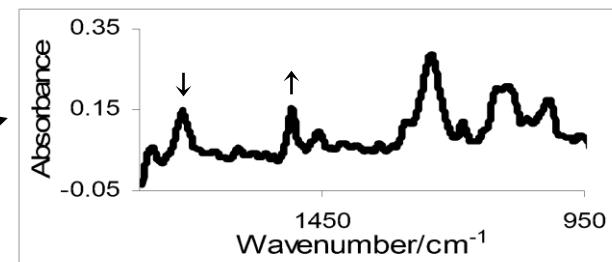
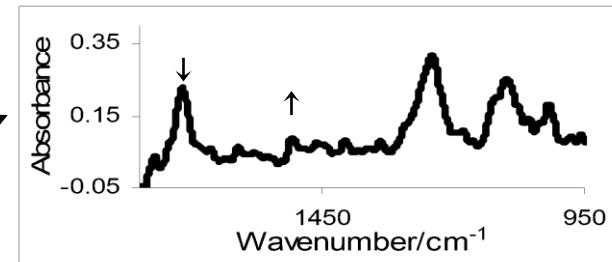
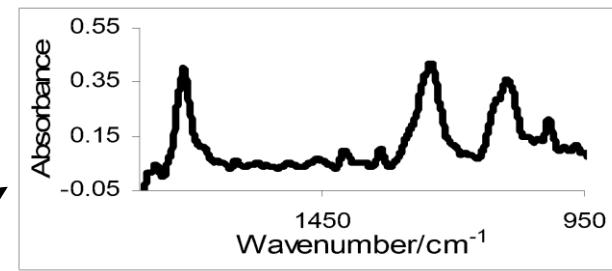
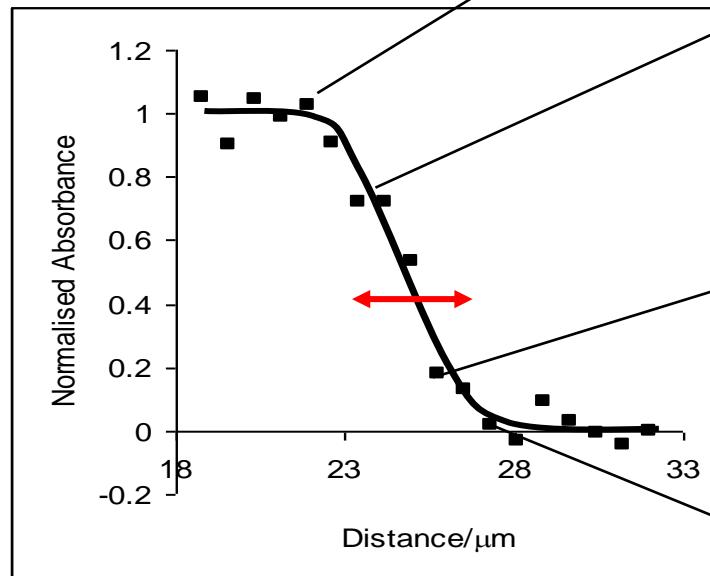


# FTIR image of the interface of PET/epoxy laminate

50 x 50  $\mu\text{m}^2$



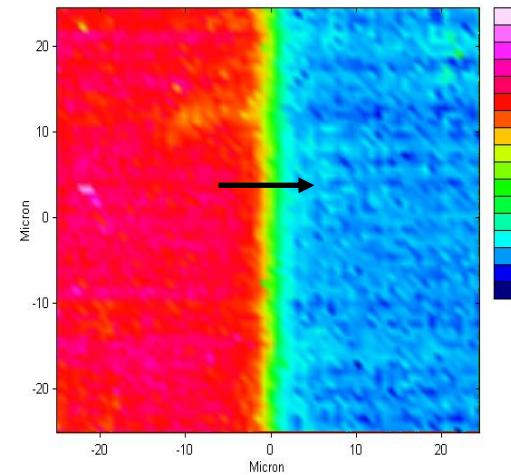
4  $\mu\text{m}$



# Enhanced spatial resolution with micro ATR Imaging

- the test in previous slide provided the value of achieved spatial resolution
- the value ca.  $4 \text{ } \mu\text{m}$  at ca.  $1600 \text{ cm}^{-1}$  ( $\lambda = 6 \text{ } \mu\text{m}$ )
- spatial resolution is assessed by measurement of real sample
- via 5-95% absorbance profile

$$r = \frac{1.22\lambda}{2NA}$$



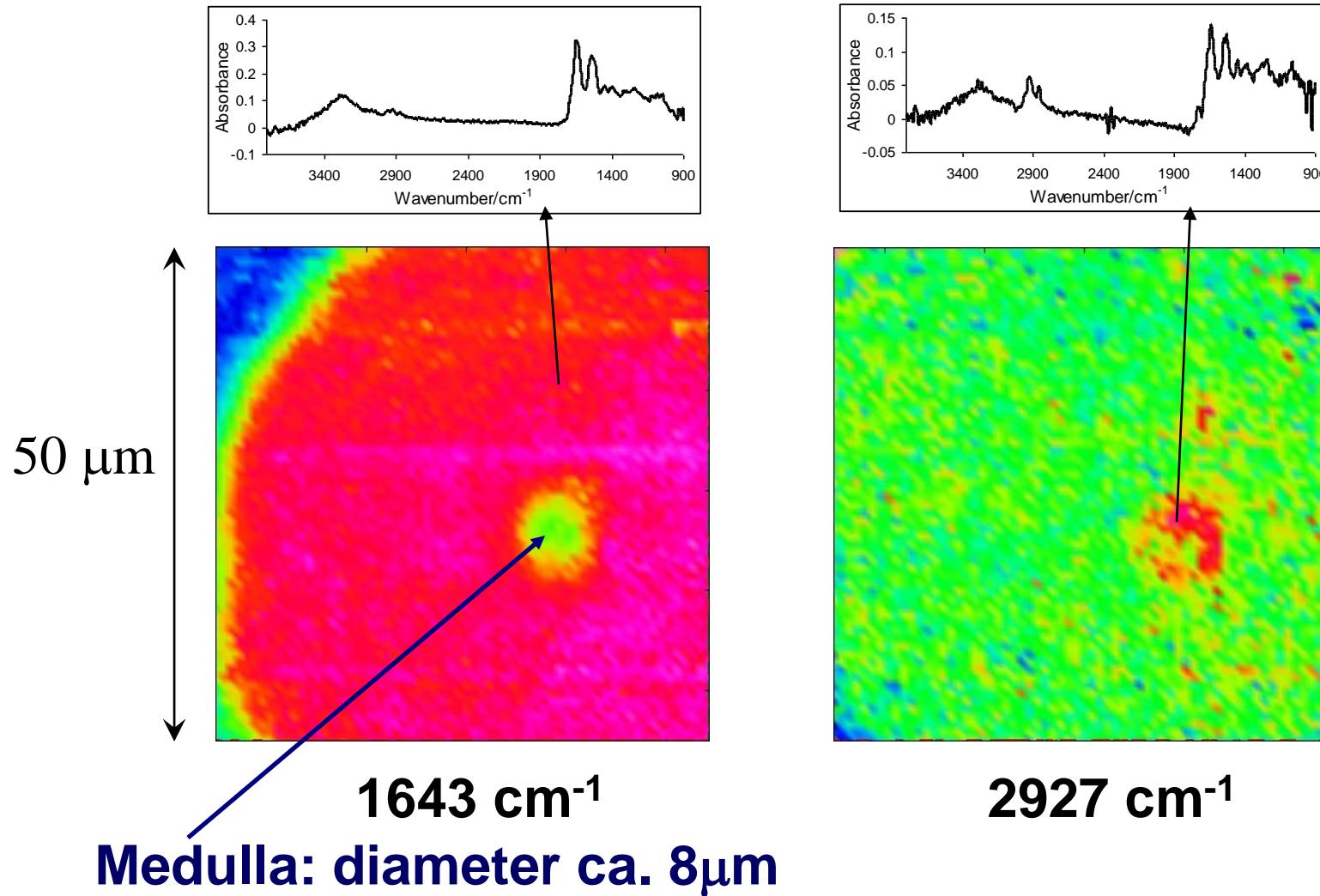
# Visible image of the cross-session of hair



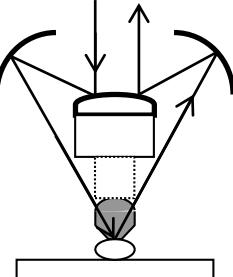
← →

**140 µm**

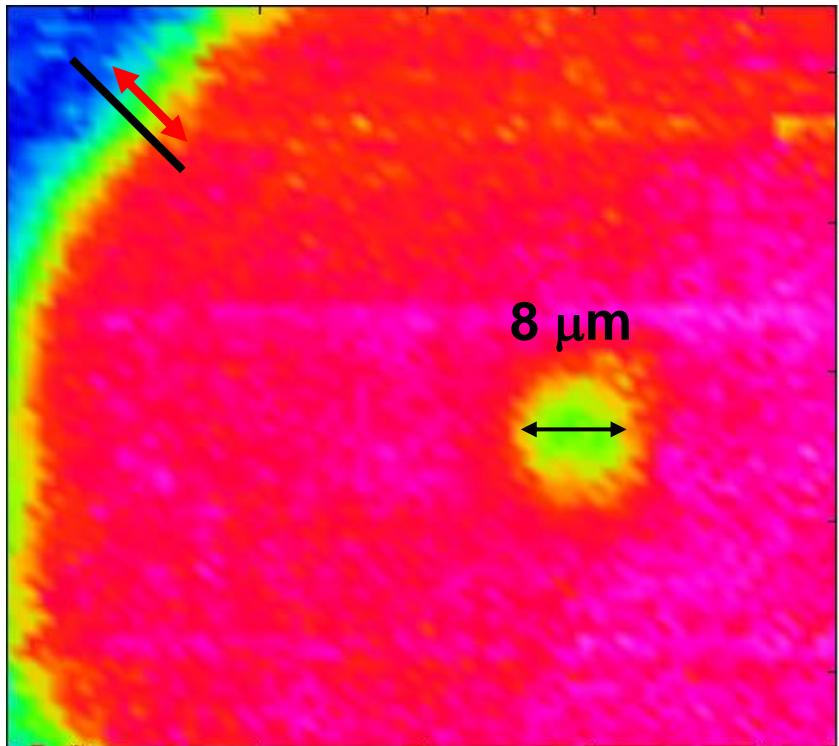
# Imaging of Human Hair Without Synchrotron



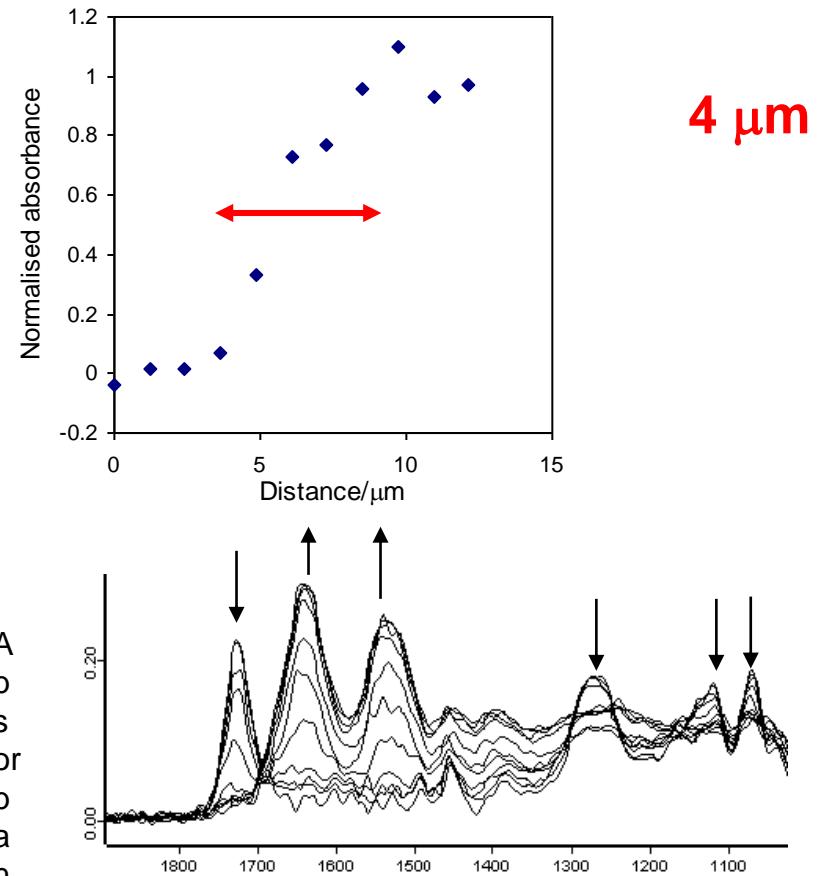
# Micro ATR-FTIR imaging of hair: imaging without a synchrotron



10  $\mu\text{m}$

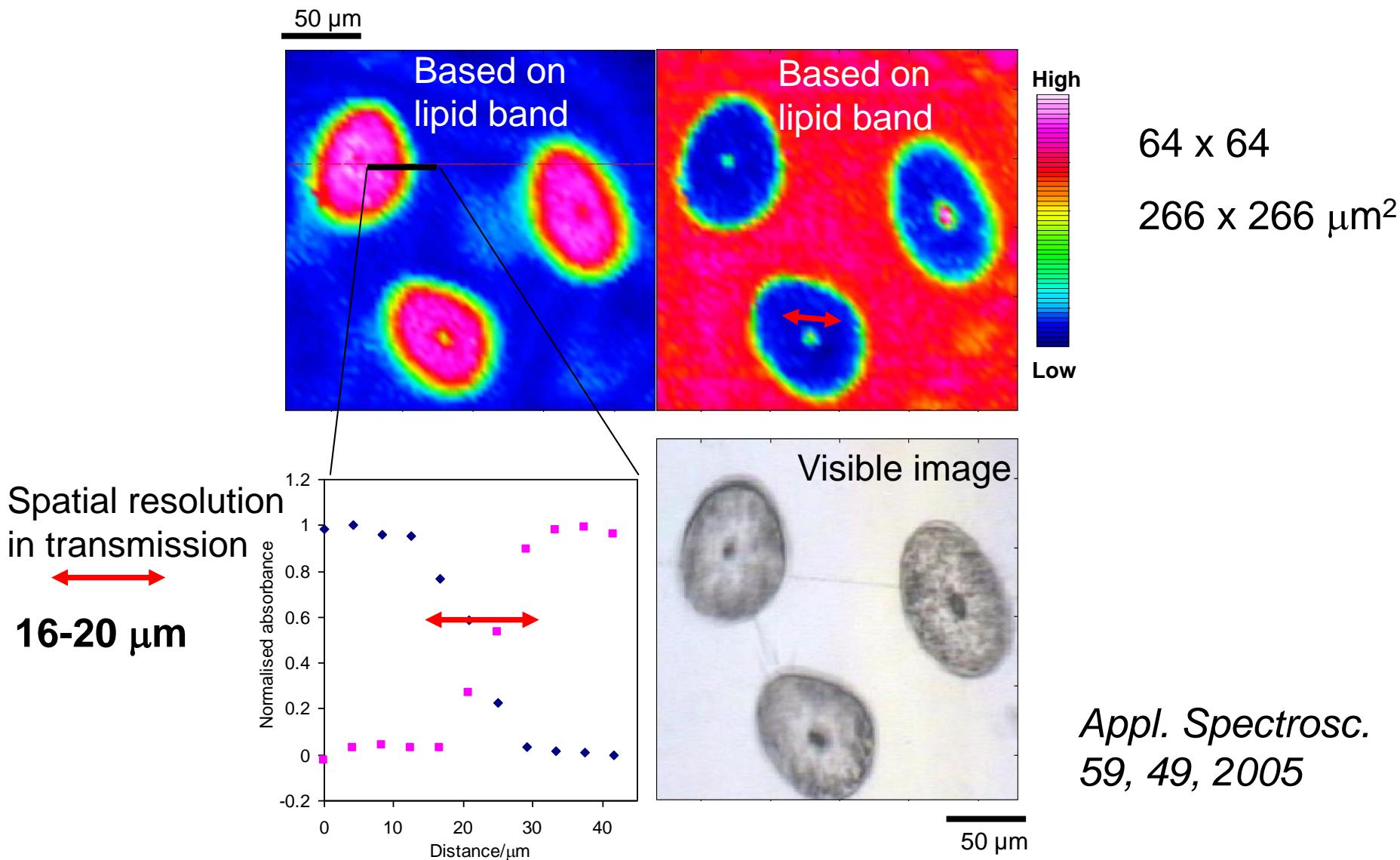


Chemical information (via spectra) from  
the very central part of human hair can be  
obtained with Micro ATR imaging

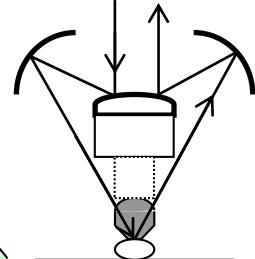


# Transmission FTIR imaging of hair

Although medulla is clearly visible in transmission, spectra from medulla will contain information from the surrounding areas because the spatial resolution ca. 20  $\mu\text{m}$



# Breaking the diffraction limit



$$r = \frac{1.22\lambda}{2NA}$$

50  $\mu\text{m}$

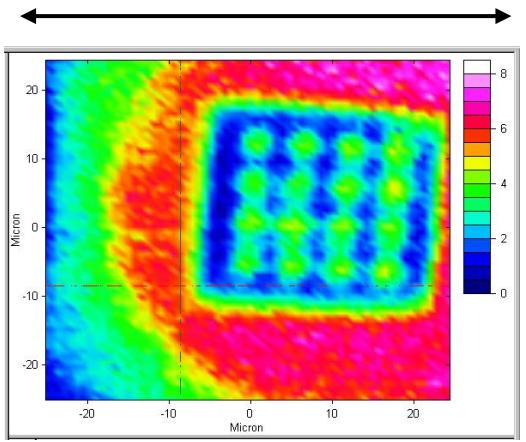


Image obtained with the band at  $\lambda = 6 \mu\text{m}$

$$NA = n \sin \theta$$

$n$  is the refractive index  
(for Ge  $n = 4$ )

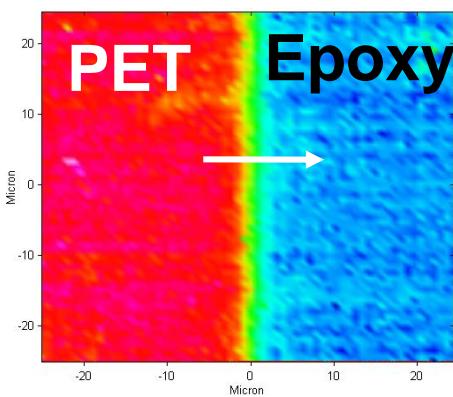
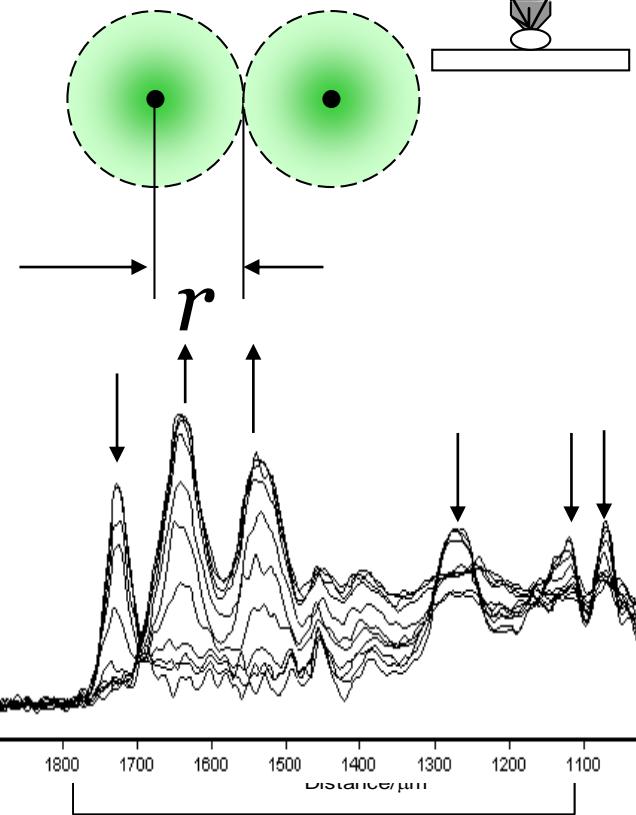


Image of the interface

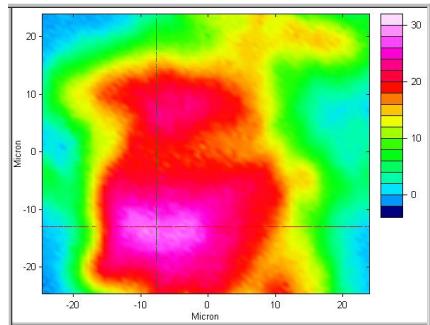


Absorbance profile for the band at  $\lambda = 6 \mu\text{m}$

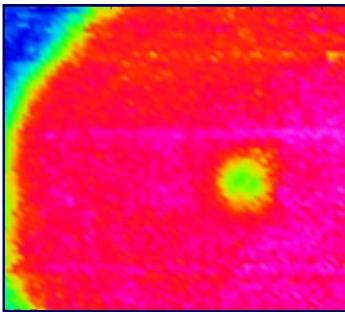
Spatial resolution  $2-4 \mu\text{m}$  has been achieved which is beyond the diffraction limit of IR light in air  
Spectra are different within a distance of less than 1  $\mu\text{m}$

# ATR imaging with enhanced resolution

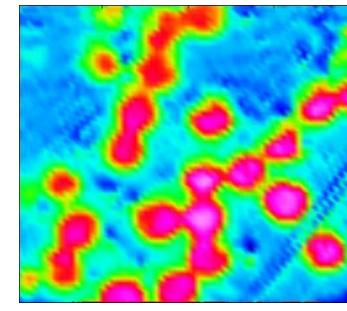
## Broad range of applications



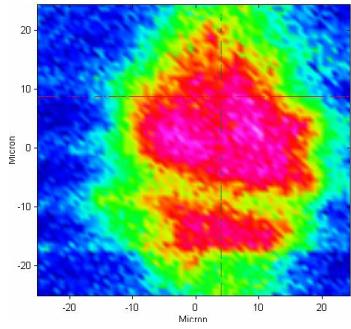
Polymer blends



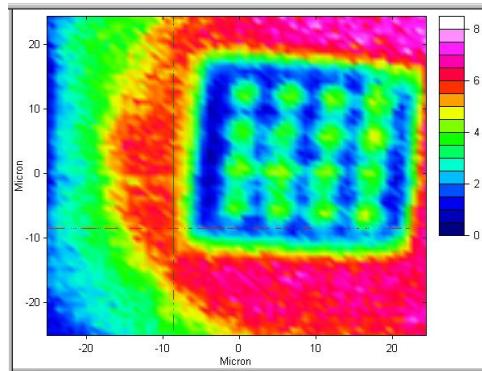
Imaging of hair  
without synchrotron



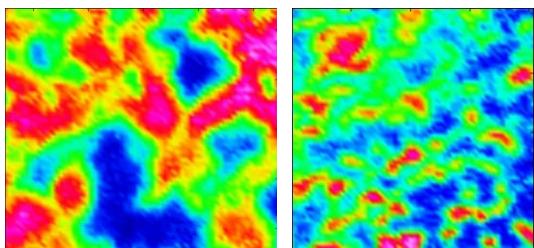
Fibres in  
polymer matrix



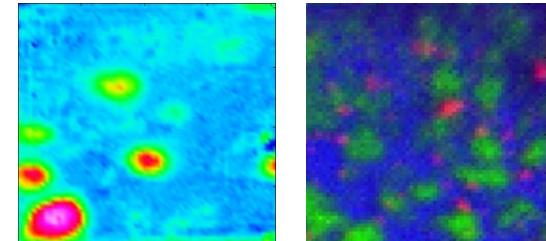
Skin surface



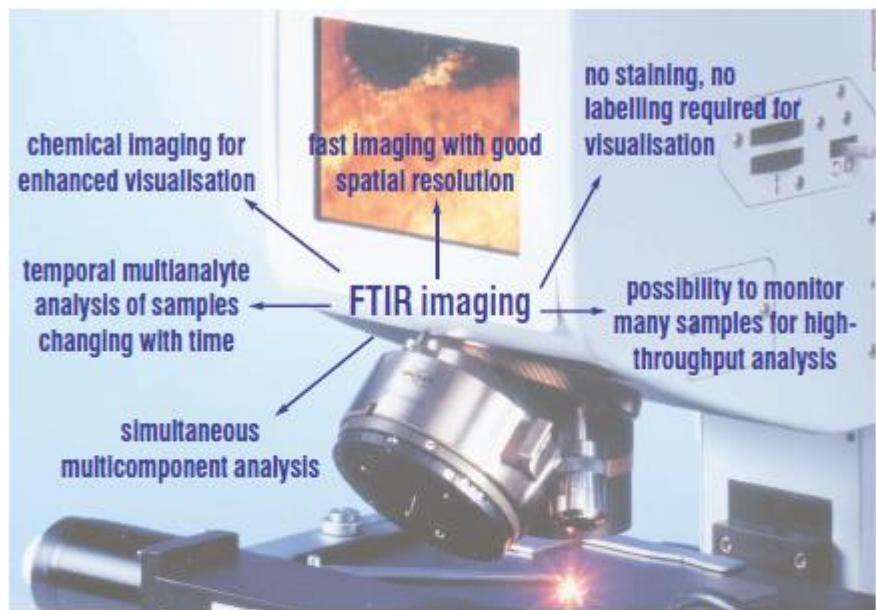
Spatial resolution  
beyond diffraction limit  
with micro-ATR



Biomaterials for tissue engineering



Emulsions Tablets



# A closer look at polymers

FTIR imaging is emerging as a powerful technique for analysing polymer mixtures. By providing simultaneous chemical and spatial information, heterogeneous polymeric materials can be characterised easily. *Sergei Kazarian & Julia Higgins explain.*

## In Brief

- Optimum blends achieved through process visualisation with FTIR microscopy
- Produces a spatial distribution map and no staining is needed
- Applications include medicine, engineering, pharmaceuticals and materials science
- Exhibits generality, specificity and sensitivity

**Blends** of different polymers are often explored in the search for polymeric materials with desirable properties. A recently emerged technology, Fourier-transform infrared (FTIR) imaging, provides a new and powerful method to characterise these blends.

FTIR imaging can be used to analyse multilayer polymer films, polymer-drug formulations, composite materials and polymeric fibres. In many cases, these materials are mixtures.

By mixing a relatively expensive polymer with an inexpensive one, the

overall cost of the product can be significantly reduced. Mixing might also result in a material with new mechanical properties, when, for example, a glassy and a rubbery polymer are mixed. The properties of polymer blends can be tuned by changing the ratio of the components. However, properties largely depend on mixing efficiency. Adding a compatibiliser can improve mixing by reducing interfacial tension between the polymer phases. Compatibilisers can also help to achieve better dispersion and im-

This article is available on the BB

Please also look at the web-site of my research group for further information on FTIR imaging:  
[www.imperial.ac.uk/vsci](http://www.imperial.ac.uk/vsci)

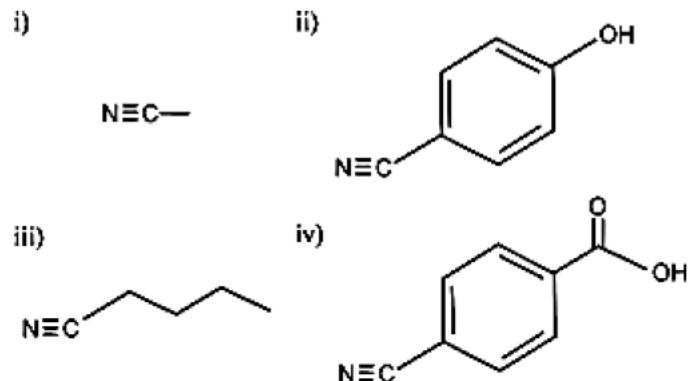
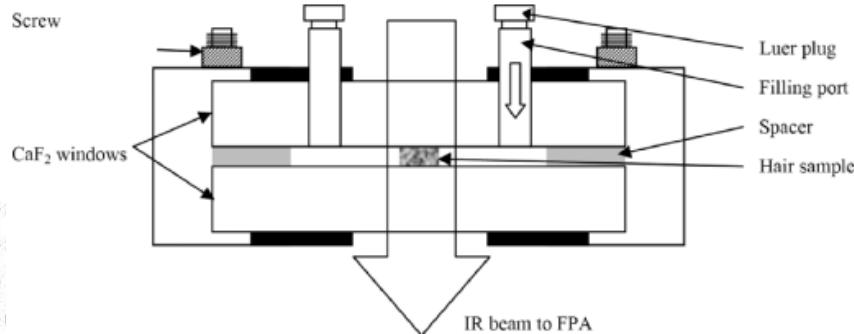
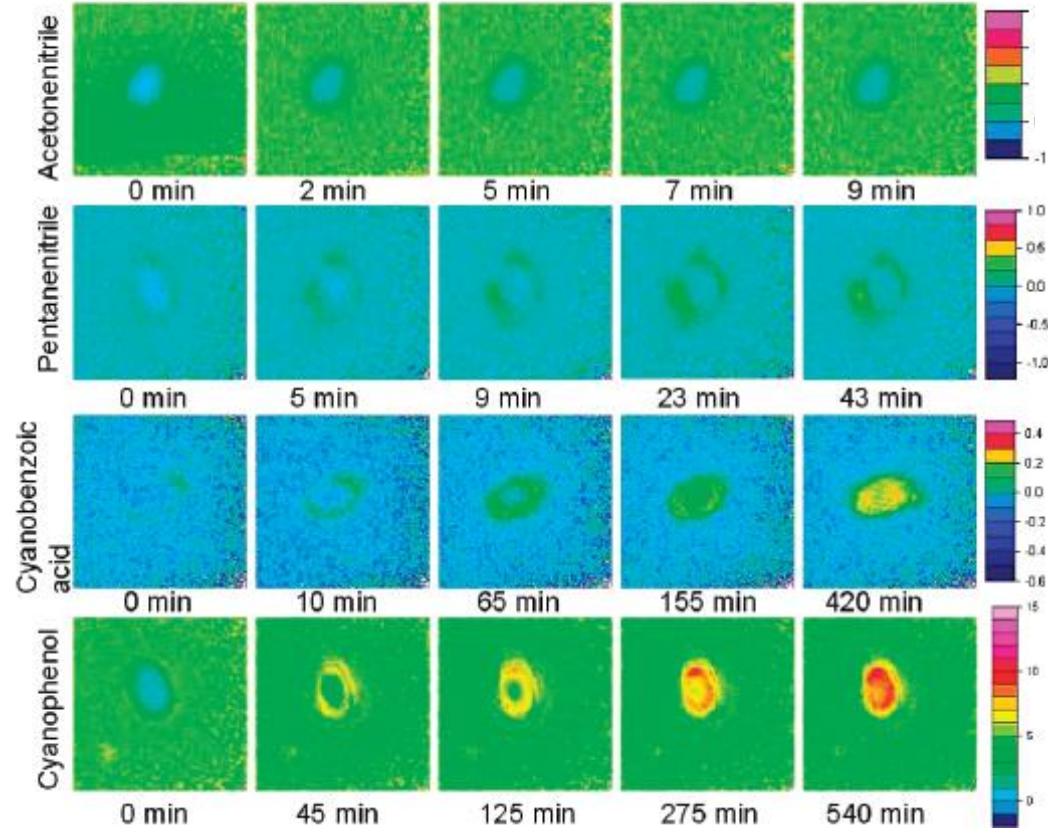
“FTIR imaging is set to find broad applications in forensic, materials colloid science, engineering and pharmaceuticals” S. Kazarian

IR spectroscopy is “most nearly universal chemical spectroscopy. As a structural tool, its generality, sensitivity and specificity are hard to match” Richard Palmer

# In situ diffusion in human hair with transmission FTIR imaging

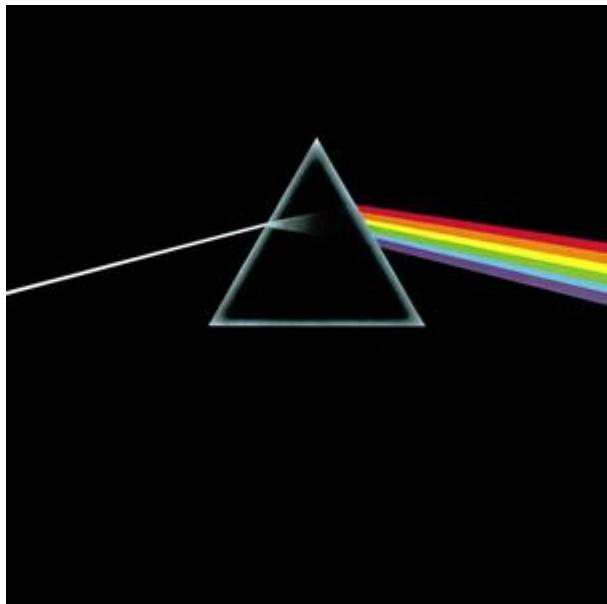
Collaboration with Unilever:

Demonstration of the potential of in situ FT-IR imaging to study the diffusion of model chemicals across the hair cross-section.

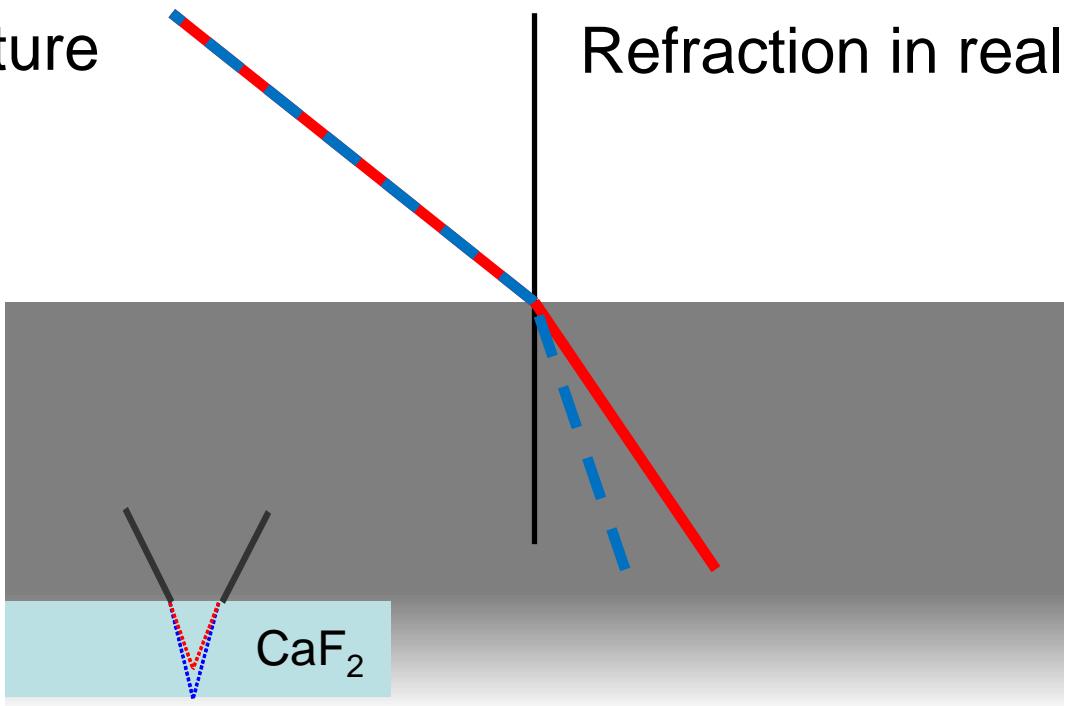


# Refraction and Chromatic Aberration

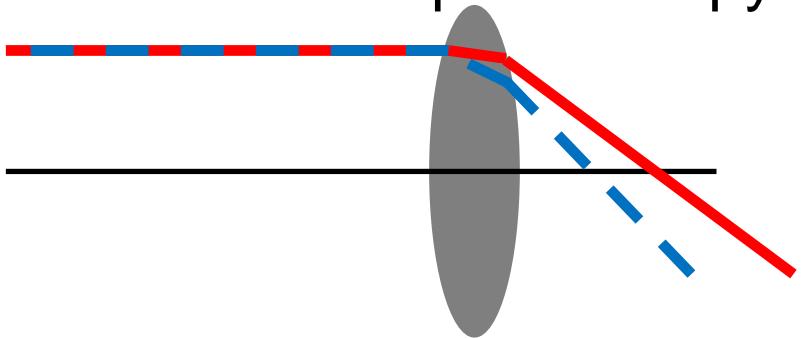
Refraction in popular culture



Refraction in reality



Refraction in spectroscopy



- Light of shorter wavelengths bent more than longer wavelengths, giving chromatic aberration.
- In transmission, effects of refraction are unavoidable

?

# Effect of refraction

CaF<sub>2</sub>

REVIEW OF SCIENTIFIC INSTRUMENTS

VOLUME 72, NUMBER 3

MARCH 2001

## Resolution limits for infrared microspectroscopy explored with synchrotron radiation

G. L. Carr<sup>a)</sup>

National Synchrotron Light Source, Brookhaven National Laboratory, U.S.A.

IR microspectroscopy 1617

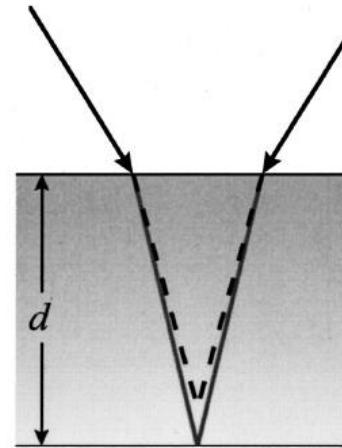
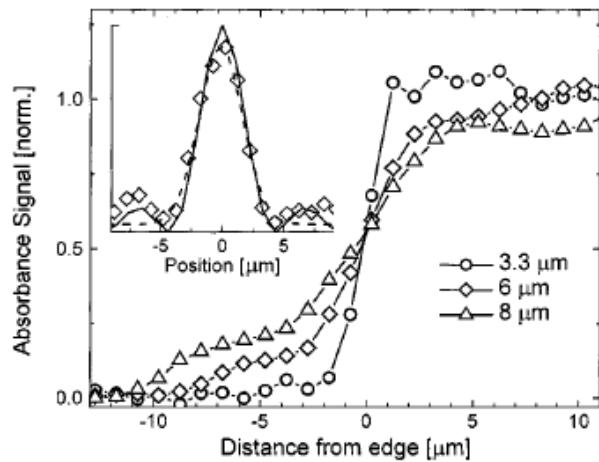
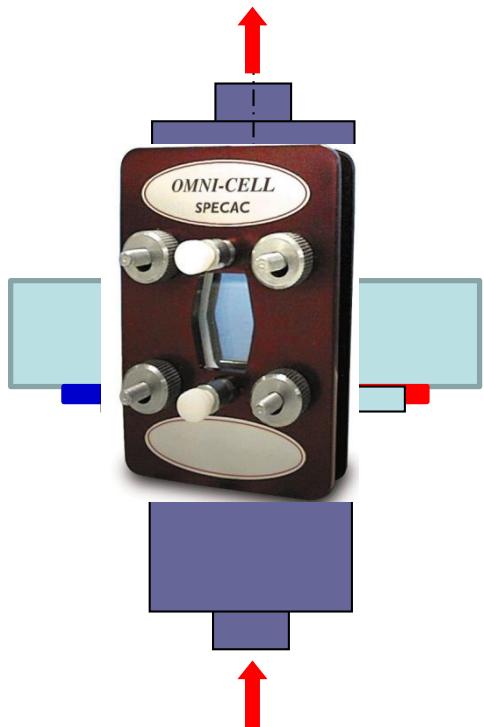


Illustration of the focus shift that occurs for dispersive substrates.

“There are cases where this problem cannot be avoided, for example, samples sandwiched between two substrates as in a liquid or compression cell. In order to achieve optimal spatial resolution, the measurement must be repeated for each wavelength range of interest, adjusting the instrument’s focus to match the spectral range.” (Carr G. L. Review Sci. Instrum. 72, 1613, 2001.)



# Effect of refraction on FTIR images measured in transmission

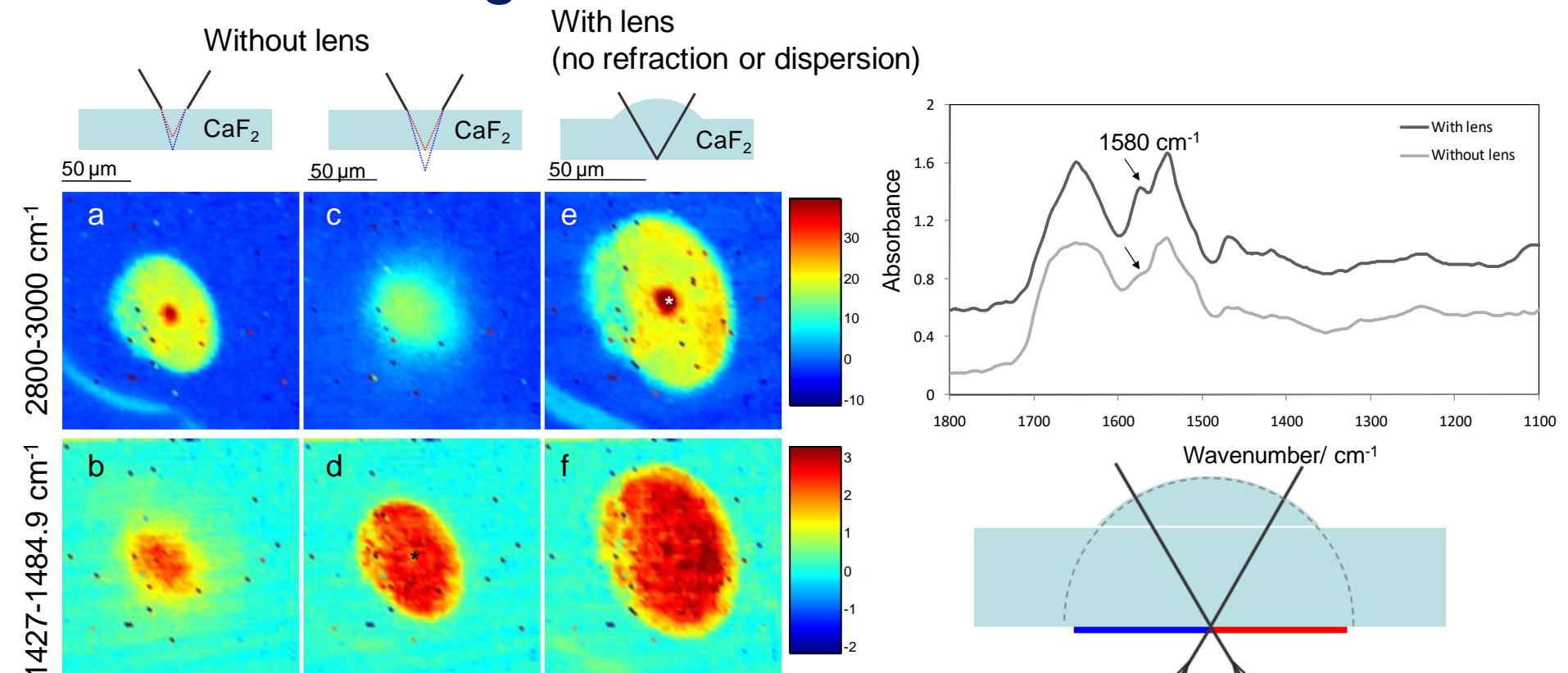


through a flat infrared transparent window; refraction makes the focal length depending on wavelength (chromatic aberration)

through a hemisphere light does not refract

through a pseudo hemisphere by placing a lens on top of window; no refraction

# Removal of refraction of light in FTIR images measured in transmission



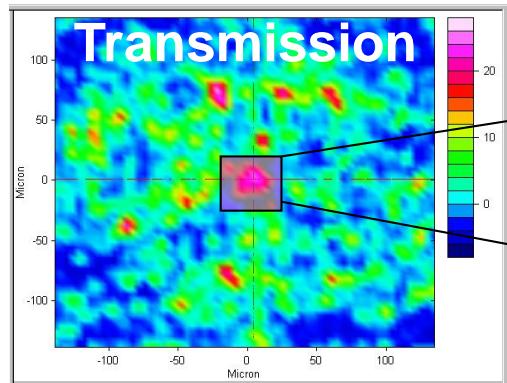
Size of images a-d is 170  $\mu\text{m} \times 170 \mu\text{m}$

Size of images e and f is 120  $\mu\text{m} \times 120 \mu\text{m}$

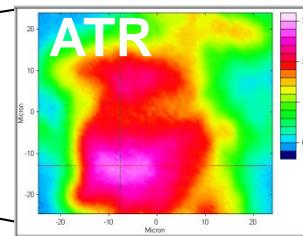
(refractive index of CaF<sub>2</sub> is 1.4)

# Fields of view in transmission and in micro ATR imaging

Transmission

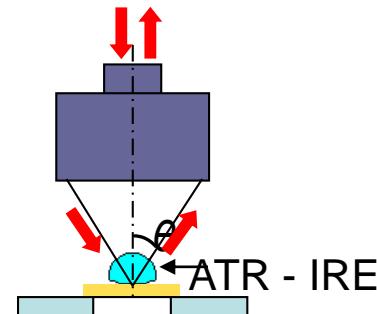
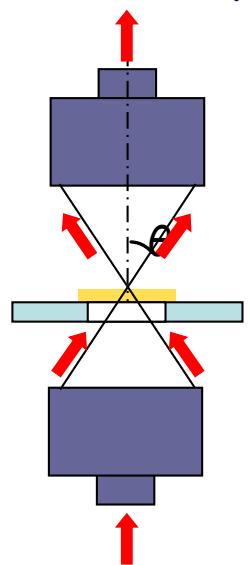


Micro ATR

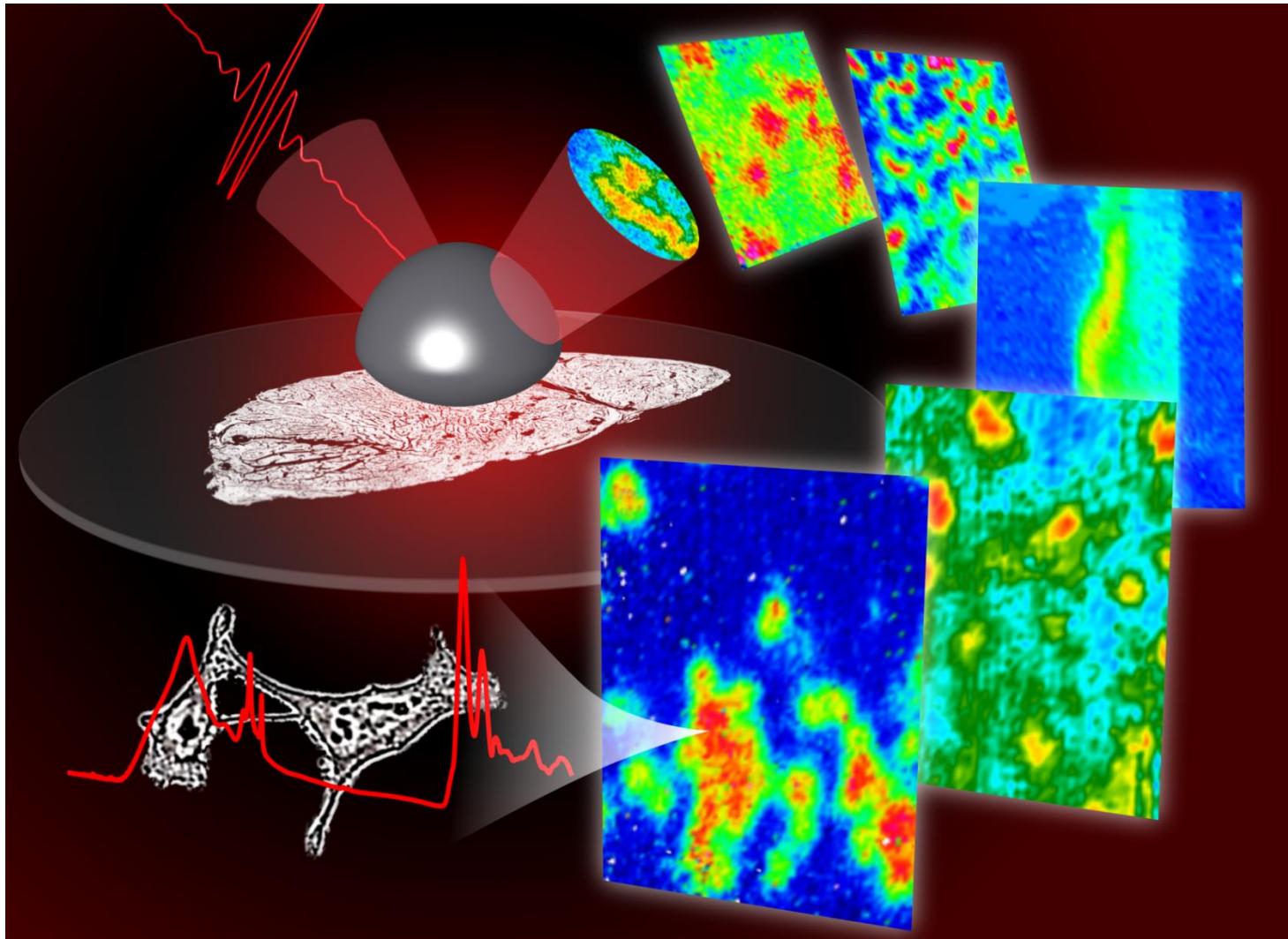


50 x 50  $\mu\text{m}^2$

300 x 300  $\mu\text{m}^2$



# Label-free chemical imaging of live cells and tissues with micro ATR-FTIR imaging



**Fast imaging with good  
spatial resolution**

**Chemical imaging for  
enhanced visualisation**

**No staining, no labelling is  
required for visualisation**

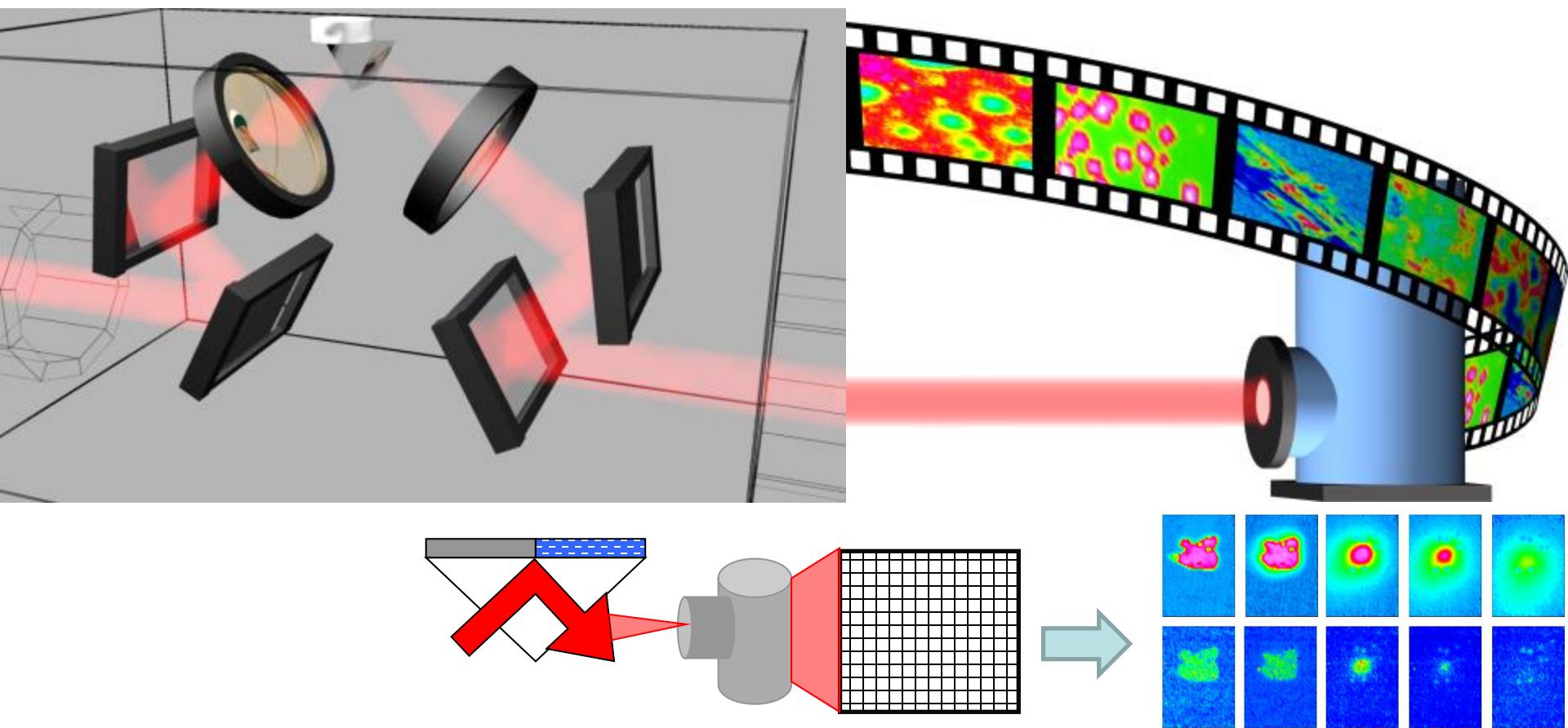
## **FT-IR Imaging**

**Simultaneous  
multicomponent analysis**

**Possibility to monitor  
many samples for high-  
throughput analysis**

**Temporal multianalyte  
analysis of samples  
changing with time**

# From chemical photography to chemical movies: macro ATR-FTIR imaging of dynamic systems



Spectroscopic imaging enables a variety of dynamic phenomena to be simultaneously observed due to chemical specificity and spatial resolution, such as diffusion, dissolution, drug release, crystalisation, sorption, etc. [www.imperial.ac.uk/vsci](http://www.imperial.ac.uk/vsci)

# Raman spectroscopy

**How can we detect gaseous nitrogen or oxygen?**

**Sir Chandrasekhara Venkata Raman**



**1888 - 1970**

He showed that the interaction of vibrating molecules with photons passing through altered the spectrum of the scattered light, either increasing or decreasing it by fixed amount. He was knighted by the British government in 1929.

# Raman Scattering

## A new type of secondary radiation

C.V. Raman and K.S. Krishnan, Nature, **121**, 501 (1928)

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**.



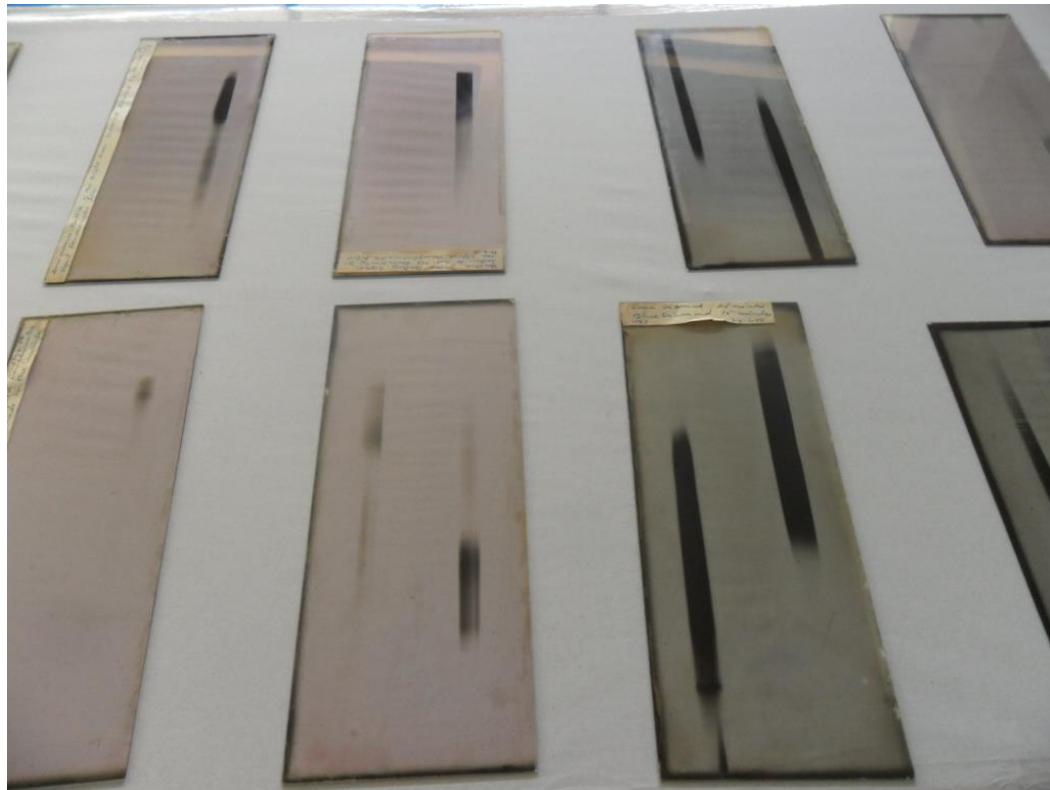
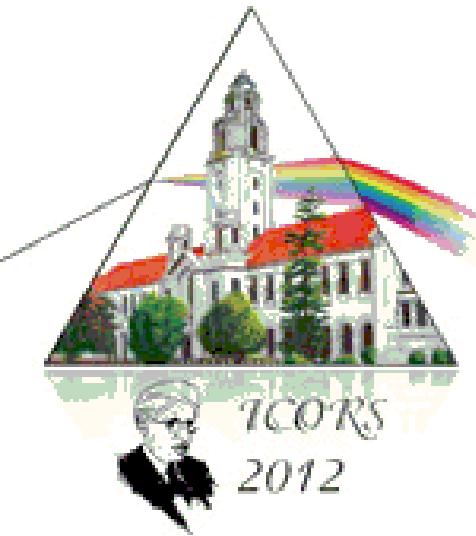
Figure 3(1)  
Incident Spectrum.

Figure 3(2)  
Scattered Spectrum.

C. V. Raman was awarded the Nobel Prize in Physics in 1930

G. Landsberg and L. Mandelstam, Naturwissenschaften, 1928, **16**, 557. "Combinatorial Scattering of Light "

# Raman spectroscopy



First spectra measured by Raman

*23rd International Conference on Raman Spectroscopy  
IISc - Bangalore, India, August 12 - 17, 2012*

# Raman spectroscopy

Analyst

RSC Publishing

EDITORIAL

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[View Journal](#) | [View Issue](#)

Cite this: *Analyst*, 2013, **138**, 729

## Rayleigh, Ramsay, Rutherford and Raman – their connections with, and contributions to, the discovery of the Raman effect†

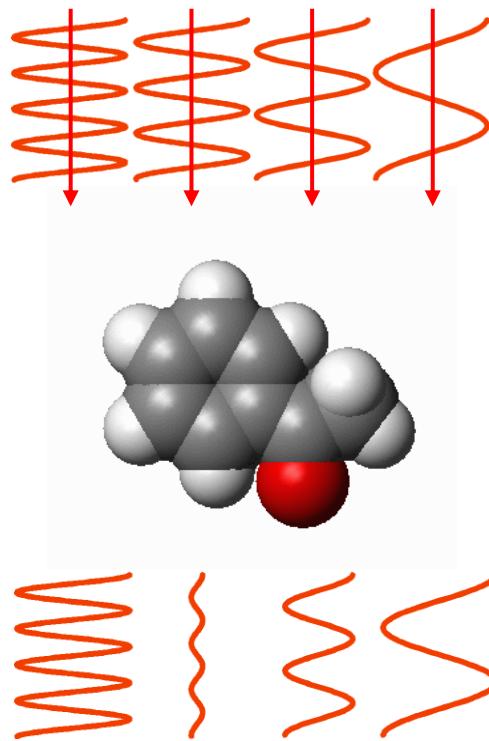
Robin J. H. Clark\*

The key contributions of the four great Nobel Laureates – Lord Rayleigh, Sir William Ramsay, Lord Rutherford and Sir Chandrasekhara Raman – to the understanding of light scattering, to the identification and classification of the rare gases, and to the discovery in 1928 of the Raman effect are outlined. The interactions between these scientists are explored, in particular those of Rayleigh with Ramsay (in establishing the physics and chemistry of the rare gases), Ramsay with Rutherford (on studies of the radioactivity of radium dibromide and on the discovery of radon and its position in the periodic table), and Rutherford with Raman (in supporting Raman's career *via* the Royal Society and as a nominee for the Nobel Prize). The resilience and dedication of these scientific pioneers is emphasised,

*Analyst*, 2013, **138**, 729–734 |

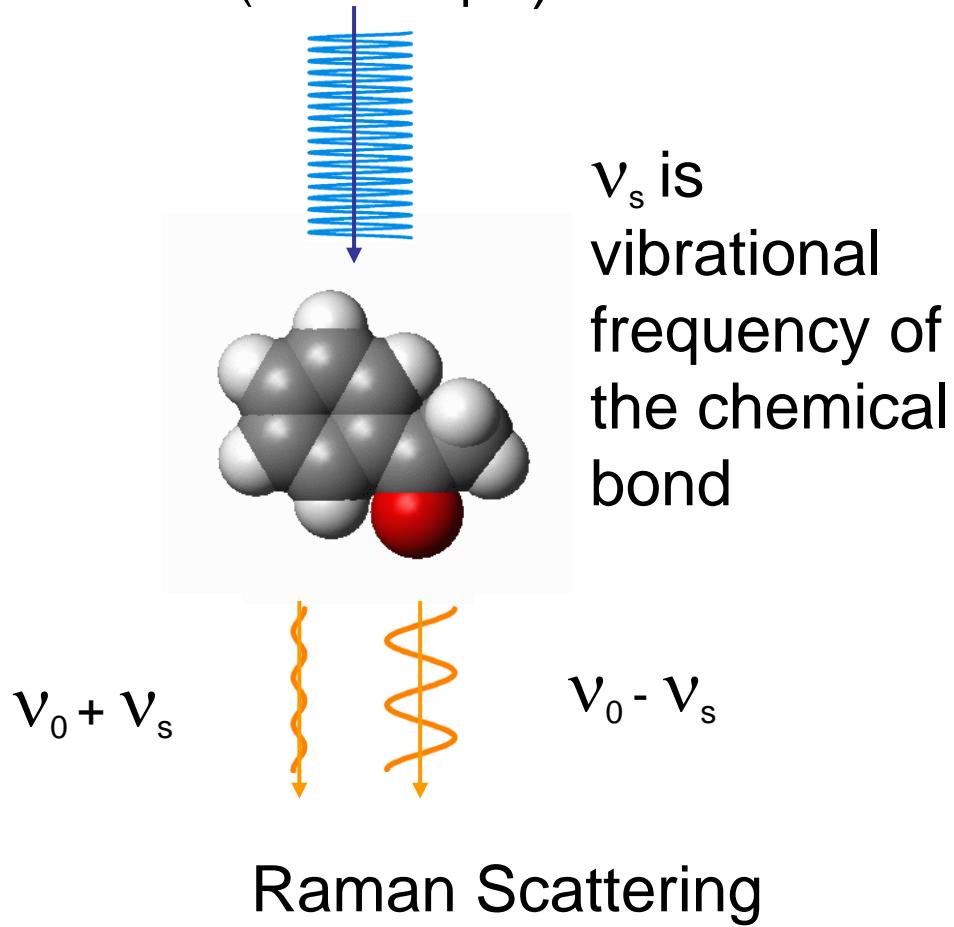
# Infrared and Raman Spectroscopy

2-20 micrometers



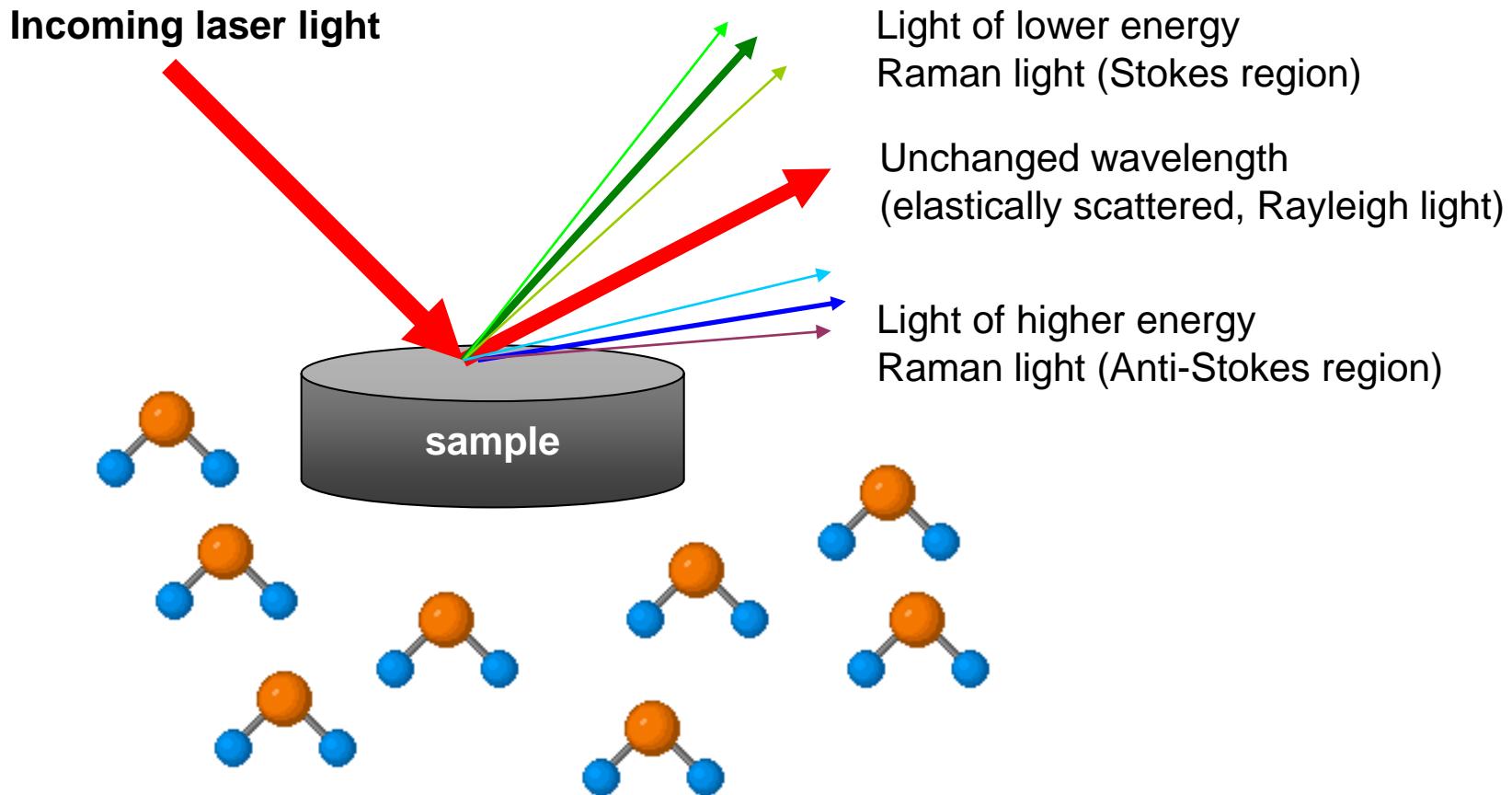
$\nu_0 = 1.064$  micrometers

(for example)



# Key idea of Raman spectroscopy

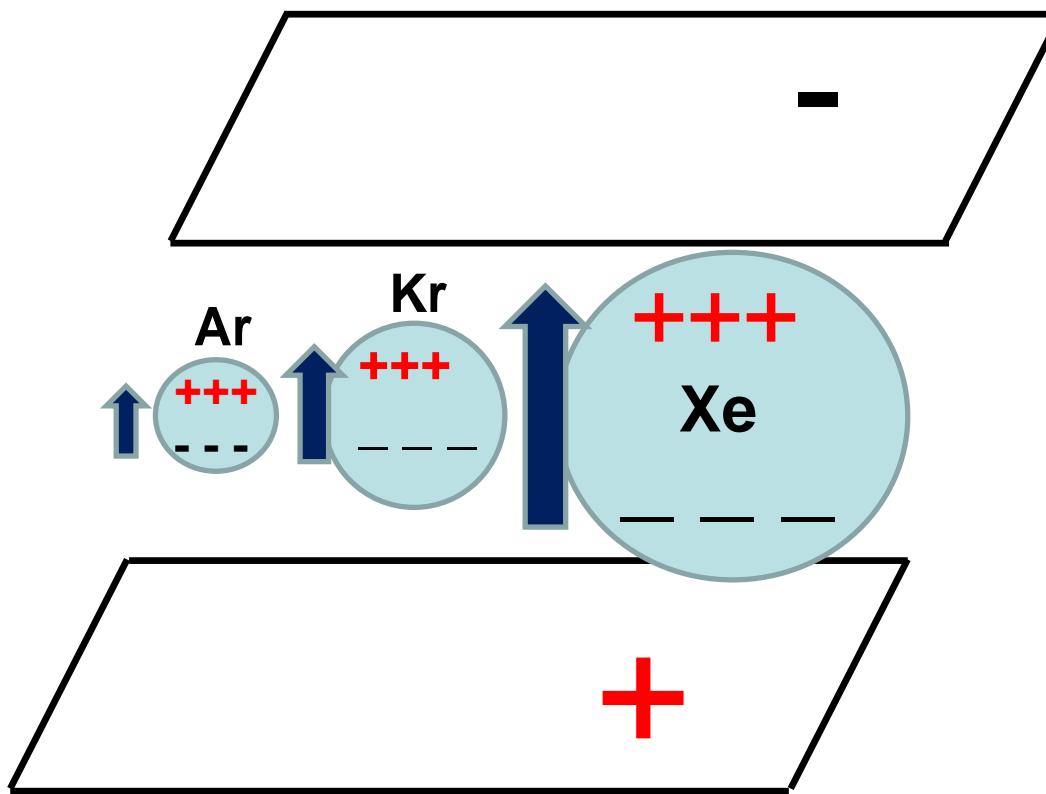
Inelastic scattering during which vibrational energy exchanged



Schematics of Raman scattering; why is the scattered light represented by 3 green arrows and 3 blue arrows?

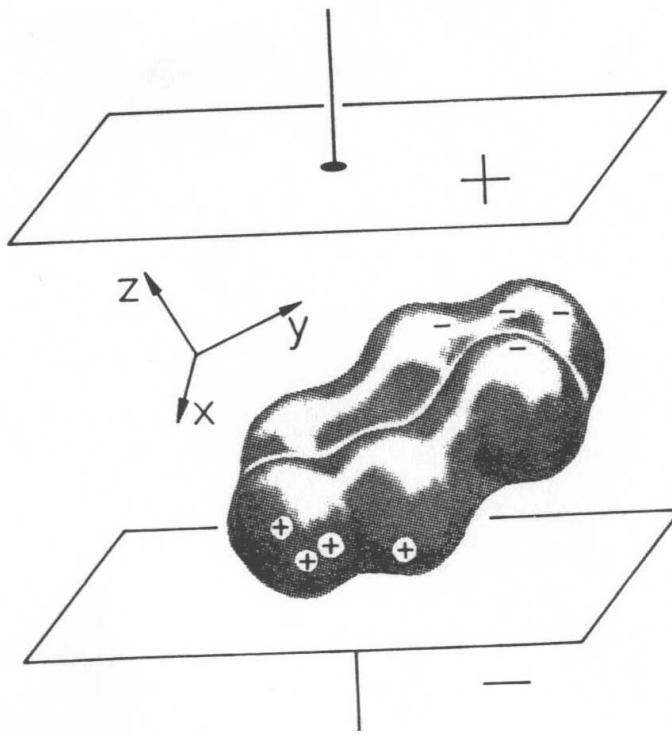
# Polarizability

$$\text{dipole moment, } \mu = q \times r$$



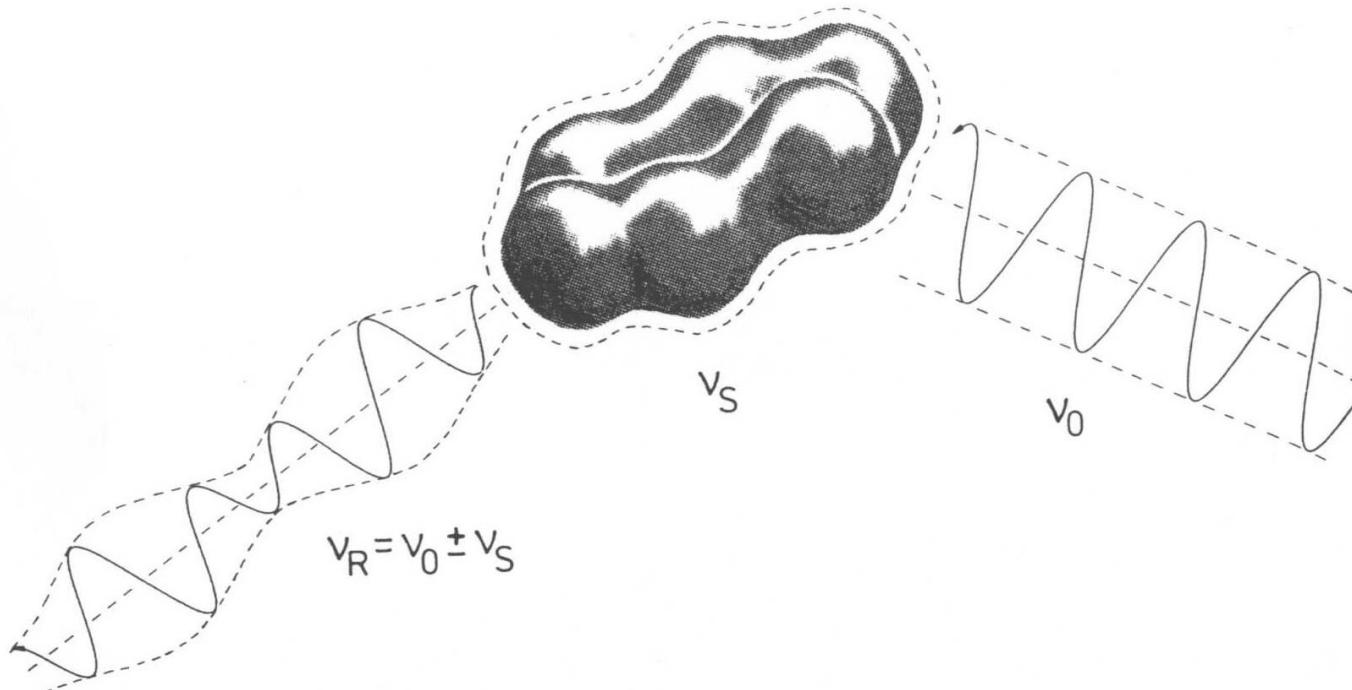
Schematics of a capacitor and the effect of its electrical field on polarisation of three different atoms: Argon, Krypton and Xenon. It is clear that the same magnitude of electric field results in different induced dipole moments of atoms

# Molecular dipole moment is induced by an electric field (benzene) $\mu = \alpha E$



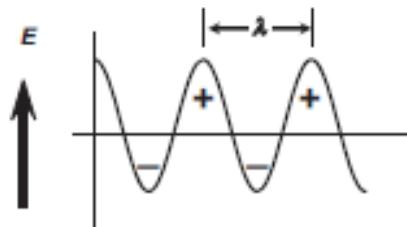
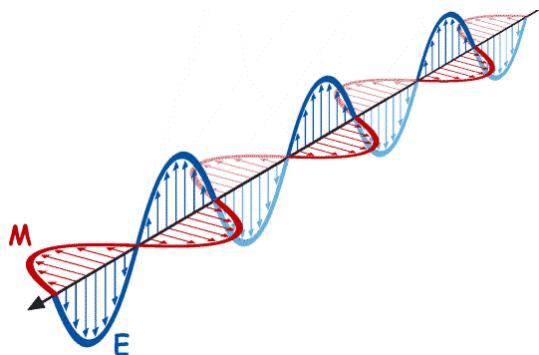
The polarizability,  $\alpha$ , represents the ability of an applied electric field  $E$  to induce a dipole moment  $\mu$  in atom or molecule. Polarizabilities of atoms are isotropic, whereas polarizabilities of molecules may vary with positions of atoms in the molecule, depending on molecule's symmetry.

# Modulation of the scattered light by a molecular vibration

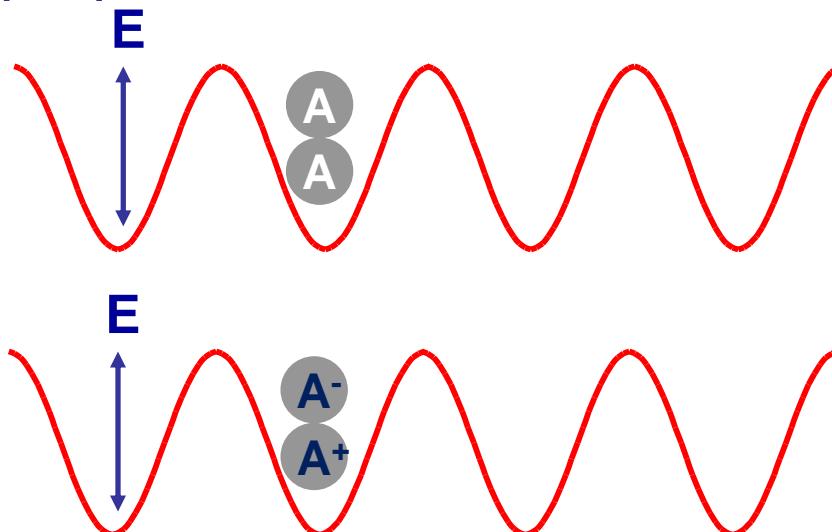


The analogy would be that a molecule behaves like the radio antenna of an AM station, which emits signals produced by amplitude modulation of a certain carrier frequency with a signal frequency ( $v_s$ ).

# Polarizability and Raman spectroscopy



Light or electromagnetic radiation consists of an alternating electric field, E, and a magnetic field, H, perpendicular to the propagating direction and perpendicular to each other.



Oscillating electric field of light can induce charge separation in molecules (dipole moment)

Light may interact with molecules if they have some movement of charges and in this case light induces such oscillation of charges (induced dipole moment)

# Polarizability and Raman spectroscopy

- The flexibility of electrons and nuclei in a molecule depends upon their mutual distance.
- For a small distance, an external field has a weak influence (compact molecule, tightly bound)
- For a large distance, the field has a strong influence (expansive molecule, weakly bound)
- The polarizability ( $\alpha$ ) of a molecule and the induced dipole moment can therefore be modulated by a vibration.

$$\frac{\partial \alpha}{\partial r} \neq 0$$

# Principles of Raman scattering

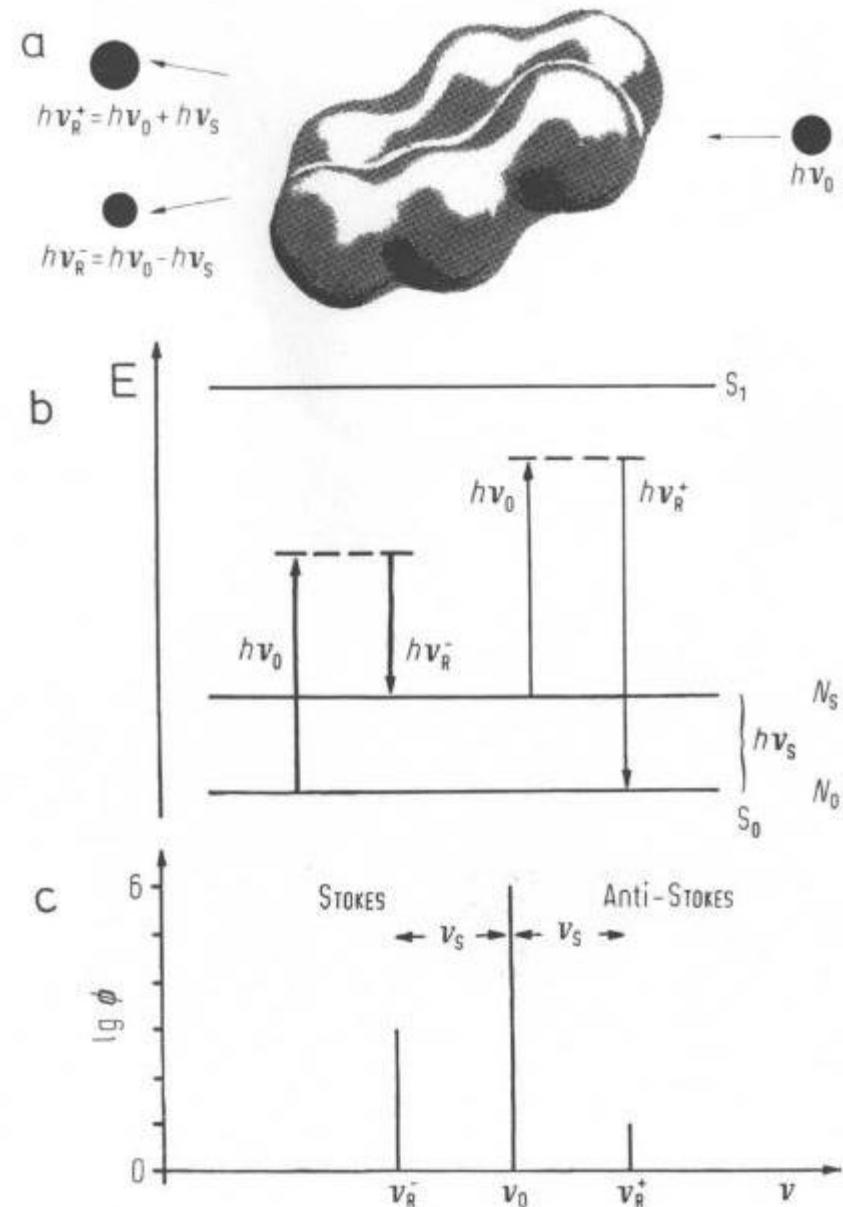
## Schematic

Implication of Boltzmann distribution on the intensities of bands in Raman spectrum

$$\frac{N_s}{N_0} = \exp\left[\frac{-\Delta E}{kT}\right]$$

## Energy diagram

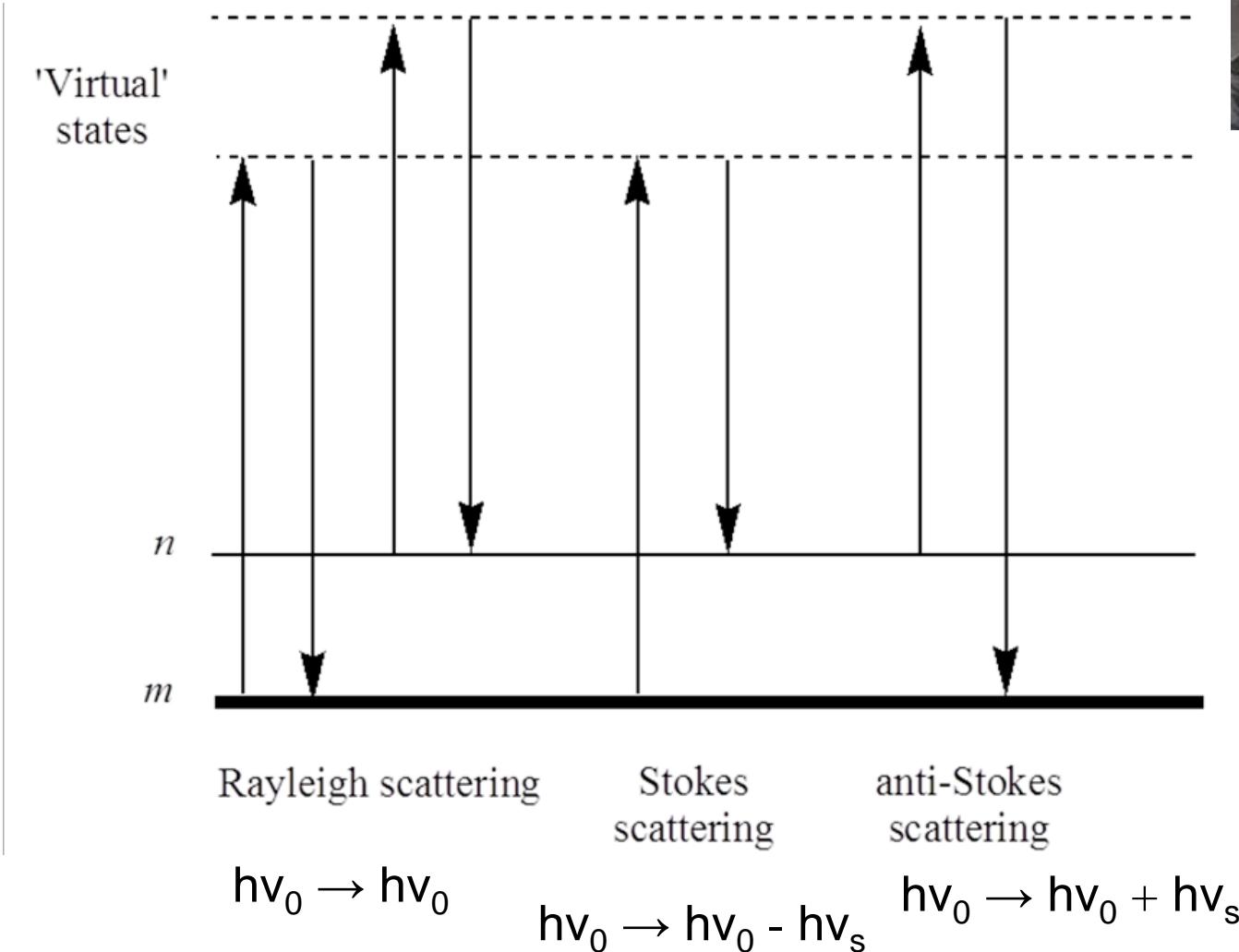
## Raman spectrum



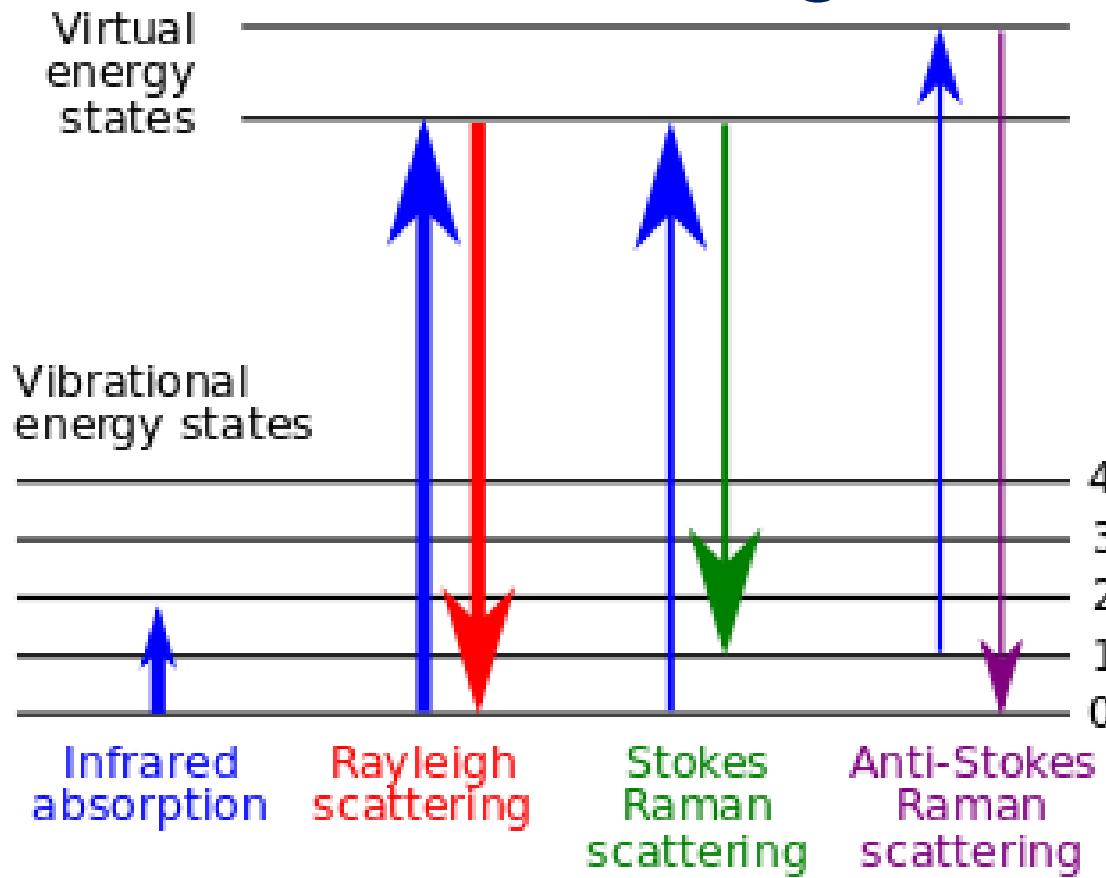
# Energy diagram for Raman scattering



Sir George  
Stokes



# Energy diagram for Raman scattering



Energy-level diagram showing the states involved in Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions.

# Anisotropic Polarizability

$$\mu'_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z$$

$$\mu'_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z$$

$$\mu'_z = \alpha_{xz}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z$$

These correspond to the matrix multiplication:

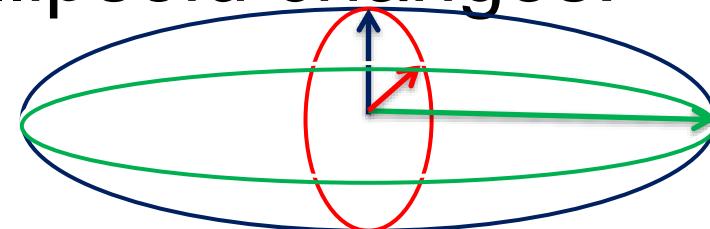
$$\begin{bmatrix} \mu'_x \\ \mu'_y \\ \mu'_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{xz} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

All of the nine components  $\alpha_{ij}$  are the components of the polarisability **tensor  $\alpha$** .

# Polarizability Ellipsoids

(see brief notes on Raman on BB)

- For a given molecule, can draw an ellipsoid that shows polarizability in each direction (dimension is proportional to  $1/\alpha^{1/2}$  , see reading notes for this lecture provided on Blackboard)
- Such ellipsoids can be used to visualise change of polarizability during vibrations.
- If a vibration in molecules changes size, shape or orientation of ellipsoid changes:  
→ Raman activity



# Polarizability Ellipsoids

## Raman Spectroscopy and Molecular Polarizability

The charge distribution in molecules is distorted / polarised by electric fields ( $E = \nabla\phi$ ), resulting in an induced electric dipole moment ( $\mu$ ):

$$\mu = \alpha E \quad [1]$$

where  $\phi$  is the electric potential and  $\alpha$  is the polarisability of the molecule.

As shown in Fig. 1, electrons forming the bond in the diatomic molecule  $H_2$ , are more easily displaced by the field along the bond axis than that across the bond; the polarisability is said to be *anisotropic*.

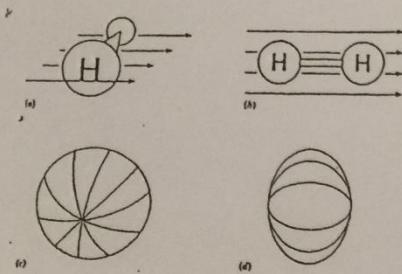


Fig. 1. Hydrogen molecule in an electric field and its polarisability ellipsoid.

The polarisability of a molecule in various directions is conventionally represented by drawing a polarisability ellipsoid, which for hydrogen has the shape of a squashed sphere, like a tangerine. Fig. 1(c) shows a view looking down on to the top of the tangerine, just off its axis and Fig. 1(d) shows a sideways view; these viewpoints correspond to those for the hydrogen molecule in Fig. 1(a) and (b), respectively. All diatomic molecules have ellipsoids of the same general tangerine shape as  $H_2$ , as do linear polyatomic molecules, such as  $CO_2$ ,  $HC\equiv CH$ , etc.; they differ only in the relative sizes of their major and minor axes.

In general, a polarisability ellipsoid is defined as a three-dimensional surface, whose distance from the electrical centre of the molecule (in  $H_2$  this is also the centre of gravity) is proportional to  $1/\sqrt{\alpha_i}$  where  $\alpha_i$  is the polarisability along the line joining a point  $i$  on the ellipsoid with the electrical centre. Thus, where the polarisability is greatest, the axis of the ellipsoid is least, and vice versa.

If we imagine applying an electric field across the bond axis of  $H_2$ , as in Fig. 1(a), a certain amount of polarization of the molecule will occur. If we also imagine the molecule rotating out its bond axis, it is obvious that it will present exactly the same aspect to the electric field at all orientations - i.e. its polarisability will be exactly the same in any direction across axis. This means that a section through the polarisability ellipsoid will be circular, as in 1(c).

If a field is applied along the bond axis, as in Fig. 1(b), the polarisability is greater, so the

cross-section of the ellipsoid is less, as shown in Fig. 1(d). Where the electron density is greatest, the electrons are further from the nucleus and so are most easily polarized, represented by a small axis for the polarisability ellipsoid.

If, in addition, the molecule undergoes some internal motion, such as vibration or rotation, which changes the polarisability periodically, then the oscillating dipole will have the vibrational or rotational oscillation superimposed upon it.

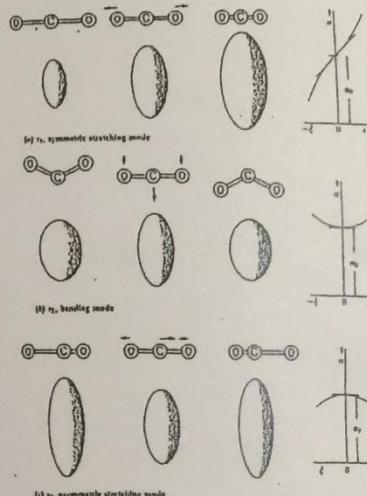


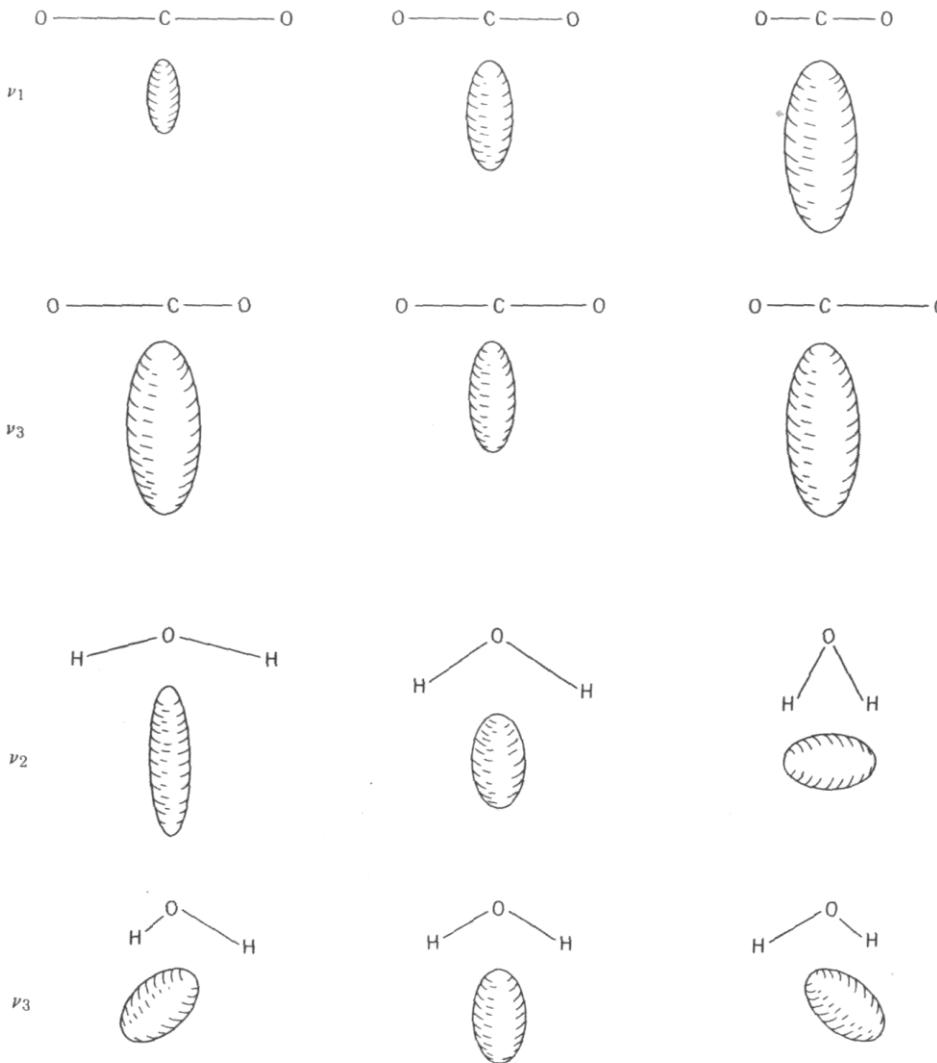
Figure 2. The changes in the polarisability ellipsoid of carbon dioxide during its vibrations, and a graph showing the variation of the polarisability,  $\alpha$ , with the displacement coordinate,  $\xi$ , during each vibration.

Fig. 2. Changes in polarisability ellipsoid of  $CO_2$  with displacement coordinate  $\xi$ .

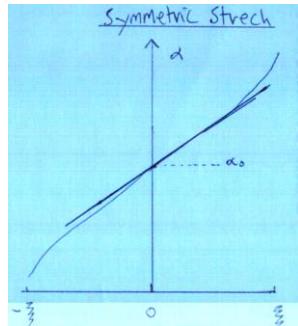
For a stretching motion, the displacement coordinate,  $\xi$ , is a measure of the extension (positive  $\xi$ ) or compression (negative  $\xi$ ) of a bond, while for a bending mode,  $\xi$  measures the displacement of the bond angle from its equilibrium value, positive and negative  $\xi$  referring to opposite displacement directions.

Fig. 2 shows the three fundamental vibrational modes and the extreme and equilibrium configurations of the linear triatomic molecule  $CO_2$ , together with their approximate polarisability ellipsoids. If the equilibrium value of the polarisability is  $\alpha_0$  (second picture) then, when the bonds stretch symmetrically in the  $v_1$  mode, ( $\xi$  positive),  $\alpha$  increases, while when the bonds contract (negative  $\xi$ )  $\alpha$  decreases, as shown on the right of Fig. 2. Hence, for small displacements about the equilibrium position ( $\xi=0$ ),  $d\alpha/d\xi \neq 0$ , so the motion produces a change in polarisability and so is Raman active.

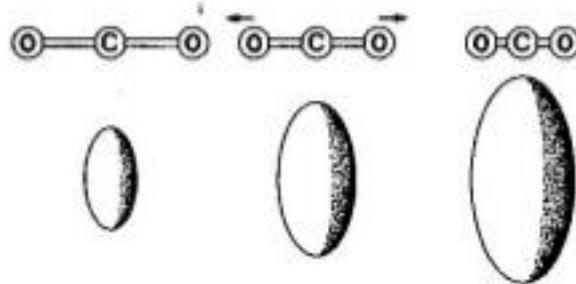
# Changes in ellipsoids of polarizability during vibrations of CO<sub>2</sub> and H<sub>2</sub>O



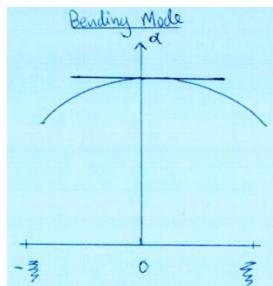
# Raman Activity – CO<sub>2</sub>



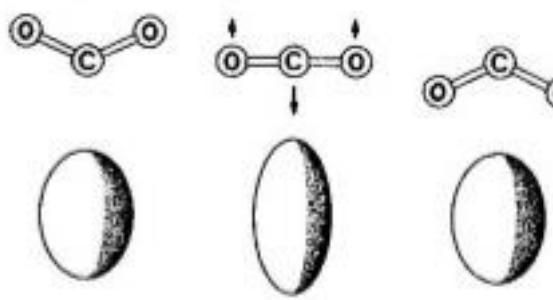
$$\frac{\partial \alpha}{\partial r} \neq 0$$



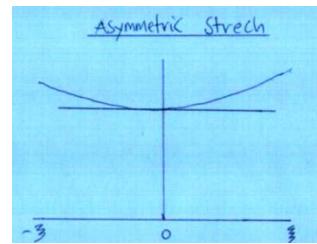
**v<sub>1</sub>**



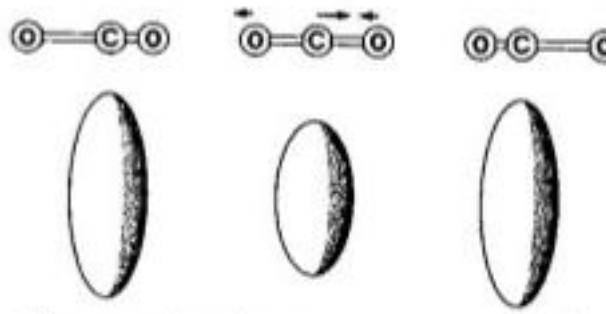
$$\frac{\partial \alpha}{\partial r} \approx 0$$



**v<sub>2</sub>**



$$\frac{\partial \alpha}{\partial r} \approx 0$$



**v<sub>3</sub>**

# Comparison of polarizability and dipole moment variations for CO<sub>2</sub>

Molecule			
Mode of vibration			
Variation of polarizability with normal coordinate (schematic)			
Polarizability derivative at equilibrium position	$\neq 0$	= 0	= 0
Raman activity	Yes	No	No
Variation of dipole moment with normal coordinate (schematic)			
Dipole moment derivative at equilibrium position	= 0	$\neq 0$	$\neq 0$
Infrared activity	No	Yes	Yes

From D.A. Long

**Figure 3.6** Polarizability and dipole moment variations in the neighbourhood of the equilibrium position and vibrational Raman and infrared activities for a linear ABA molecule.

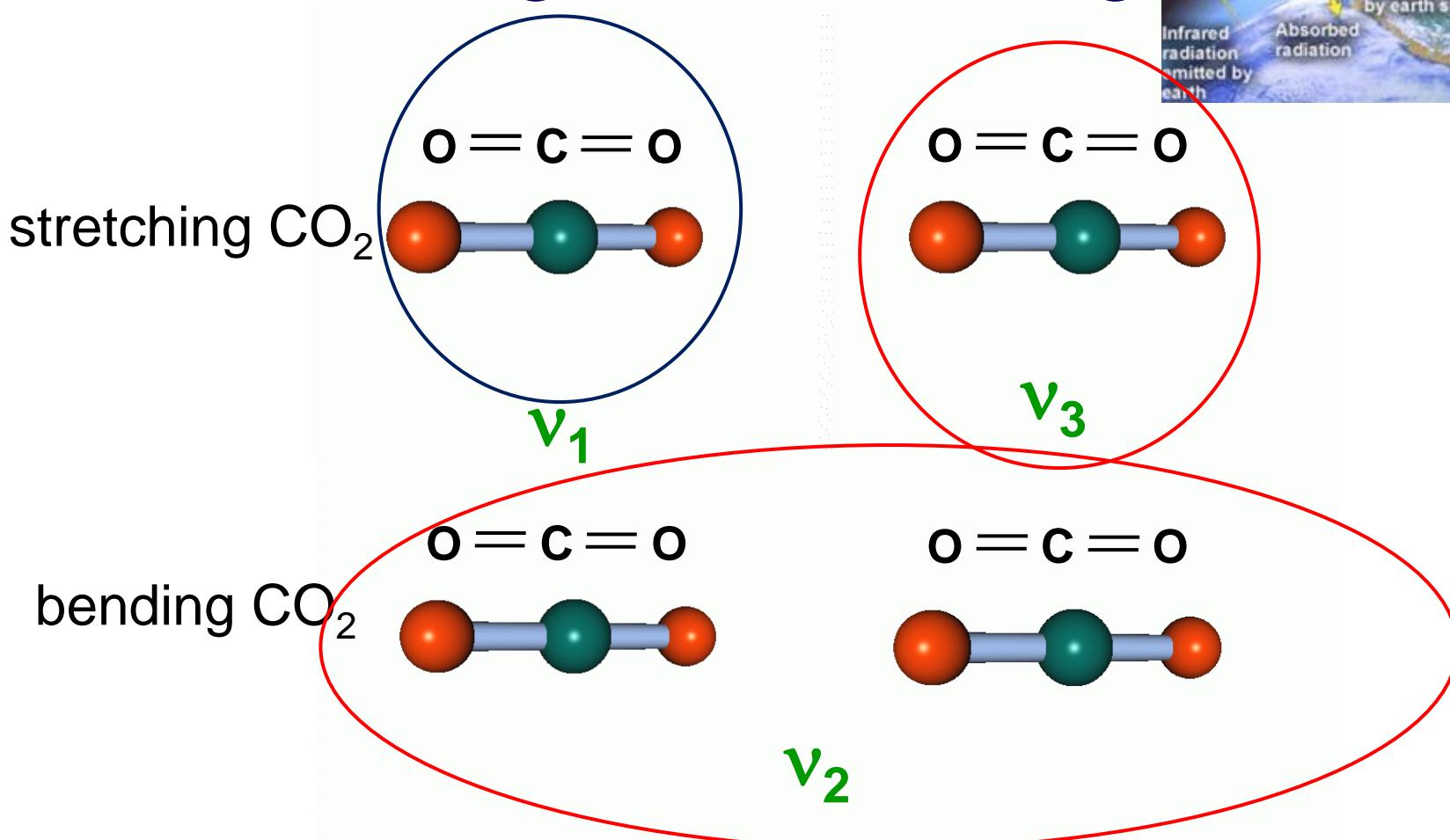
# Comparison of polarizability and dipole moment variations for two molecules

Molecule		
Mode of vibration		
Variation of polarizability with normal coordinate (schematic)		
Polarizability derivative at equilibrium position	$\neq 0$	$\neq 0$
Raman activity	Yes	Yes
Variation of dipole moment with normal coordinate (schematic)		
Dipole moment derivative at equilibrium position	$= 0$	$\neq 0$
Infrared activity	No	Yes

From D.A. Long

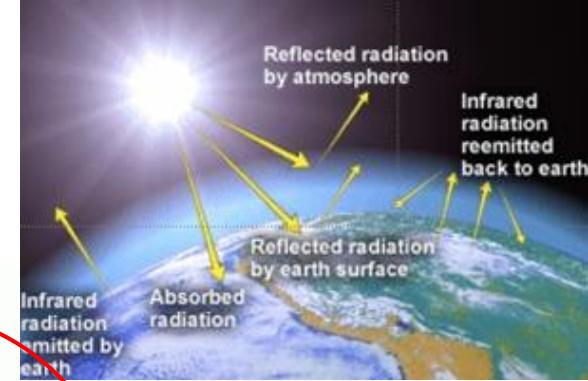
**Figure 3.5** Comparison of polarizability and dipole moment variations in the neighbourhood of the equilibrium position and vibrational Raman and infrared activities for an  $A_2$  and an  $AB$  molecule.

# Vibrations of CO<sub>2</sub> and global warming



Vibrations of CO<sub>2</sub> molecules is an excellent example to understand why some vibrations of CO<sub>2</sub> absorb infrared radiation

Symmetric vibration  $v_1$  is Raman active.



# Combined in situ ATR-IR and confocal Raman spectroscopy

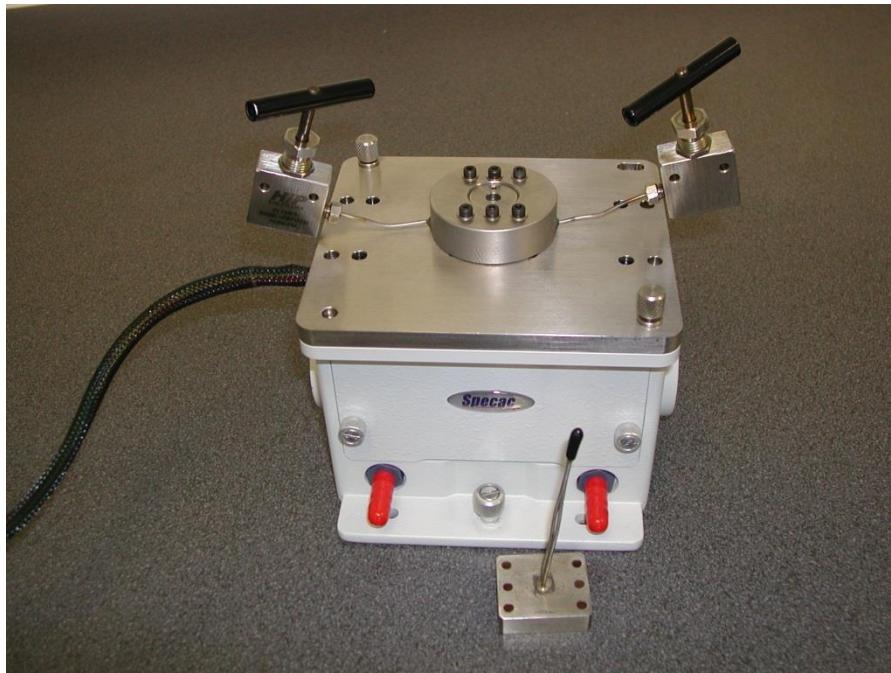
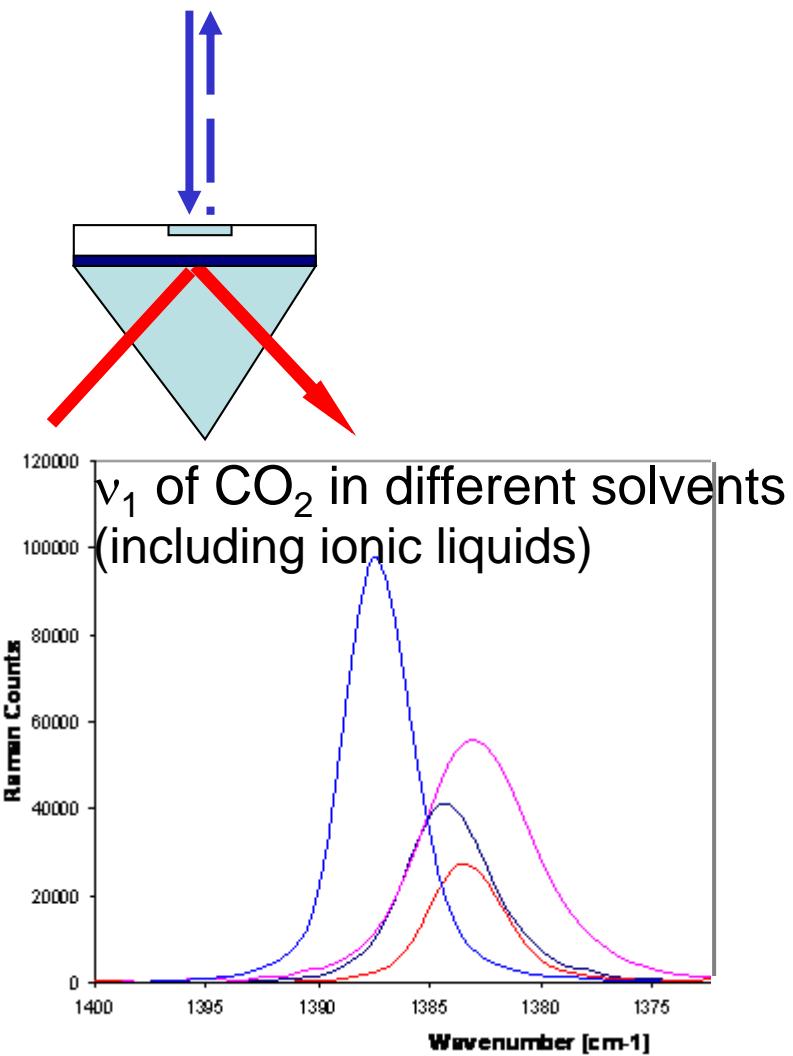
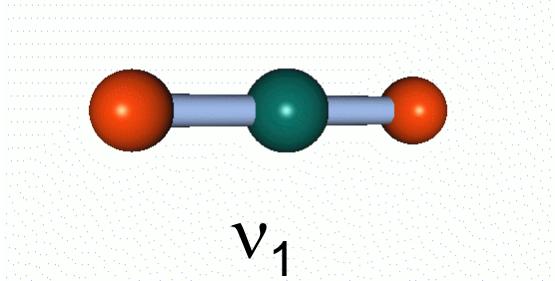
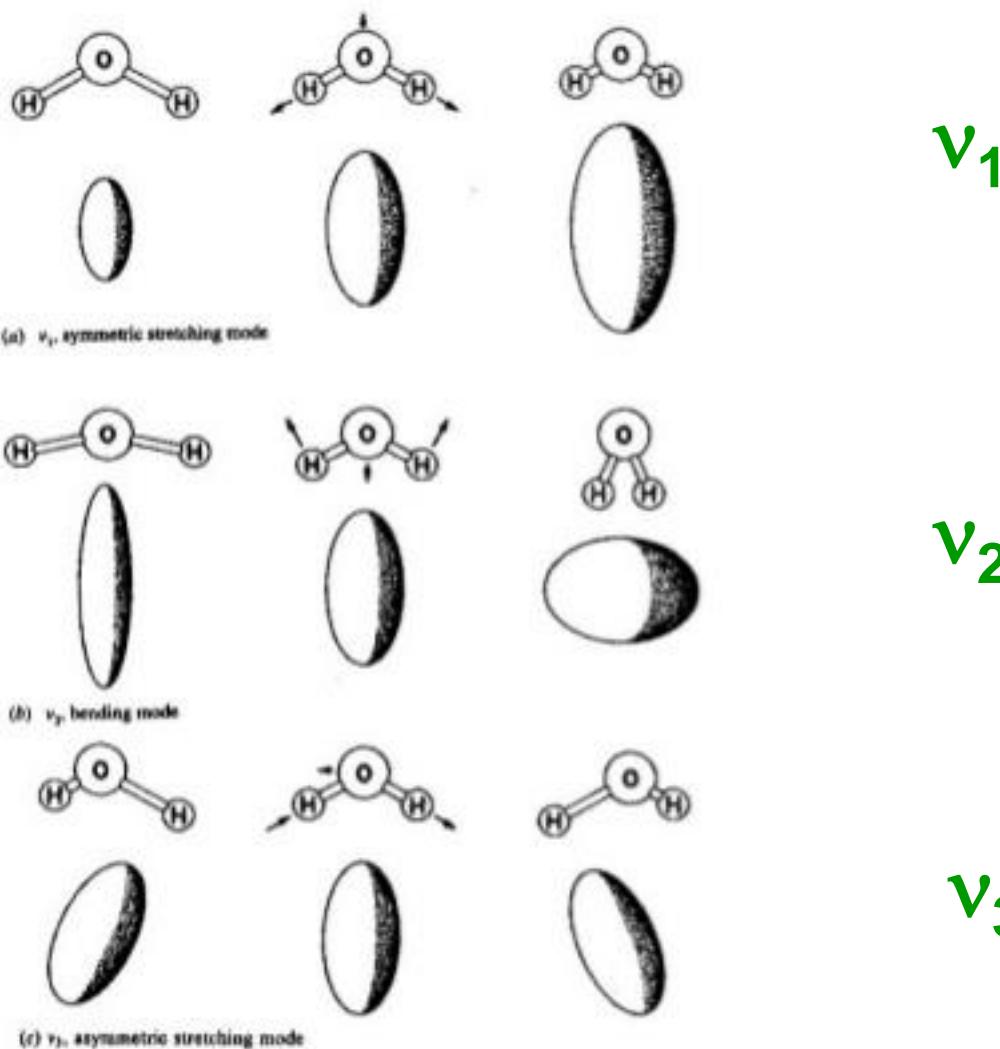


Photo of an accessory and high-pressure cell for Raman measurements



# Raman Activity – H<sub>2</sub>O

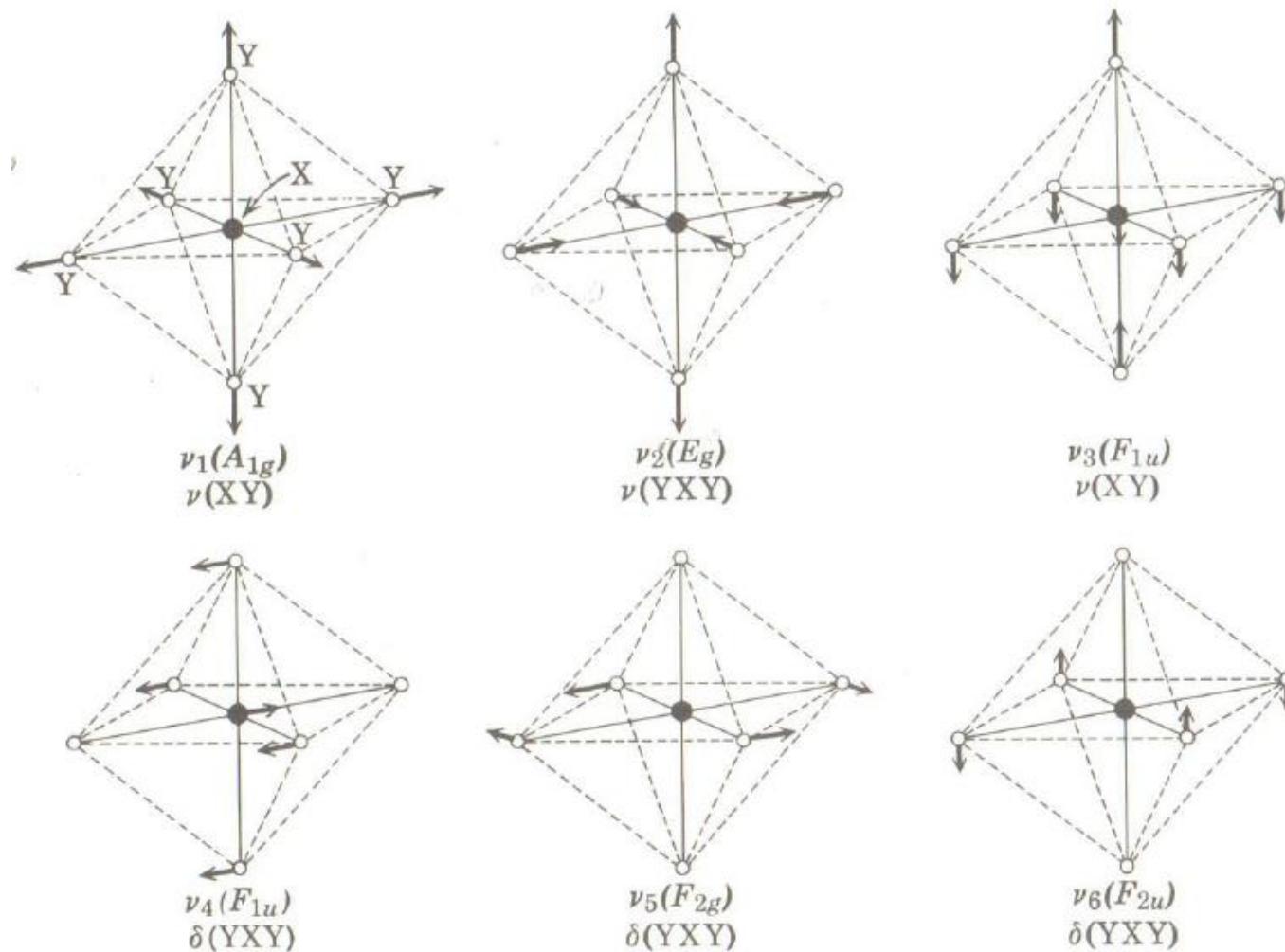


# Question

- Which of the following molecules may show
  - a) infrared absorption spectra
  - b) Raman spectra

HCl, C<sub>6</sub>H<sub>6</sub>, SF<sub>6</sub>, N<sub>2</sub>, O<sub>3</sub>

# Vibrations of $SF_6$ (or $UF_6$ )



**Fig. II-15.** Normal modes of vibration of octahedral  $XY_6$  molecules.

Which of these vibrations will be Raman active?

# Selection rules

$$\Delta v = \pm 1 \quad (\text{for harmonic oscillator})$$

$$\frac{\partial \mu}{\partial r} \neq 0 \quad \begin{aligned} & \mu \text{ is a dipole moment} \\ & \text{Infrared active} \end{aligned}$$

$$\frac{\partial \alpha}{\partial r} \neq 0 \quad \begin{aligned} & \alpha \text{ is polarizability} \\ & \text{Raman active} \end{aligned}$$

$3N - 5$  for a linear molecule (which requires 2 rotational co-ordinates).

$3N - 6$  for a non-linear molecule (which requires 3 rotational co-ordinates).

# How can we detect gaseous nitrogen or oxygen?

Question: If we excite with a laser at 532 nm, where should the Stokes vibrational oxygen Raman peak appear?

$$\text{Stoke shift / line: } \nu_0 - \nu_s$$

Calculate the oxygen Raman wavelength: according to the Raman shift is  $1556 \text{ cm}^{-1}$ .

With an excitation wavelength at 532 nm the oxygen Stokes line will appear at  $1/532 \text{ nm} - 1556 \text{ cm}^{-1} = 18797 \text{ cm}^{-1} - 1556 \text{ cm}^{-1} = 17241 \text{ cm}^{-1} = 580 \text{ nm}$

# How can we detect gaseous nitrogen or oxygen?

Question: If we excite with a laser at 532 nm, where should the Stokes vibrational oxygen Raman peak appear?

$$\text{Stoke shift / line: } \nu_0 - \nu_s \quad h\nu_0 \rightarrow h\nu_0 - h\nu_s$$

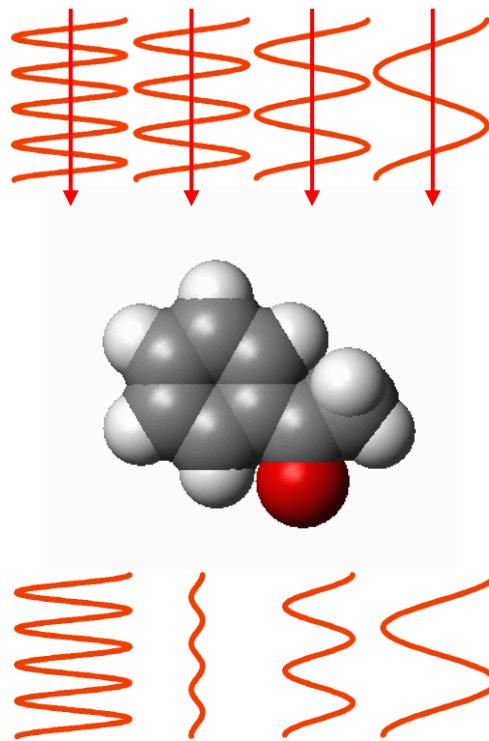
$$\Delta E = h\nu = hc\tilde{\nu} \quad \lambda = \frac{c}{\nu} \quad \tilde{\nu} = \frac{1}{\lambda} \quad \tilde{\nu} = \frac{\nu}{c}$$

Calculate the oxygen Raman wavelength: according to the Raman shift of oxygen is 1556 cm<sup>-1</sup>.

With an excitation wavelength at 532 nm the oxygen Stokes line will appear at  $1/532 \text{ nm} - 1556 \text{ cm}^{-1} = 18797 \text{ cm}^{-1} - 1556 \text{ cm}^{-1} = 17241 \text{ cm}^{-1} = 580 \text{ nm}$

# Infrared and Raman Spectroscopy

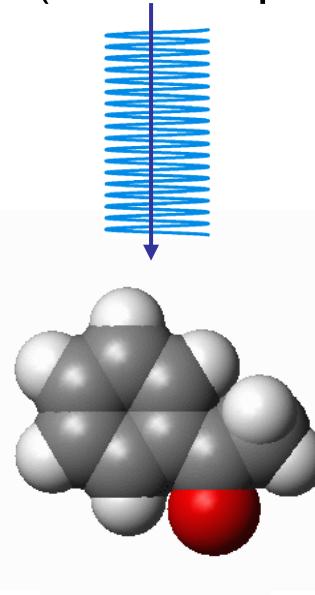
2-20 micrometers



IR - Absorption

$\nu_0 = 1.064$  micrometers

(for example)



$\nu_s$  is  
vibrational  
frequency of  
the chemical  
bond

$$\nu_0 + \nu_s$$

$$\nu_0 - \nu_s$$

Raman Scattering

# Raman Spectroscopy: choice of wavelength

In general: Raman Scattering Cross Section

$$\sigma \sim 1/\lambda^4$$

But:

- (i) Fluorescence Background
- (ii) Scattering Background
- (iii) Photodamage
- (iv) Resonance Effects
- (v) Substrate



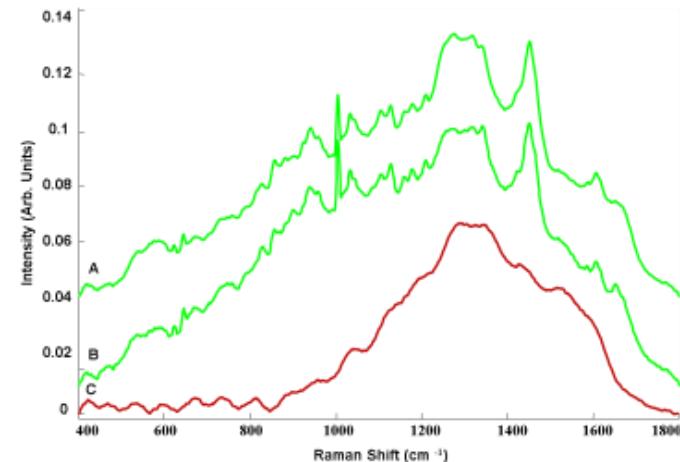
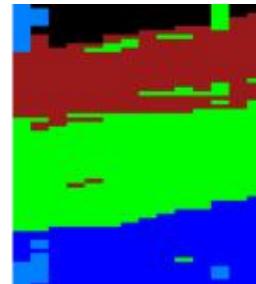
# Raman Spectroscopy: Tissue Fluorescence

[www.raman4clinics.eu](http://www.raman4clinics.eu) is a network for Raman in clinic

Table 1  
The principal chromophores of skin<sup>a</sup>

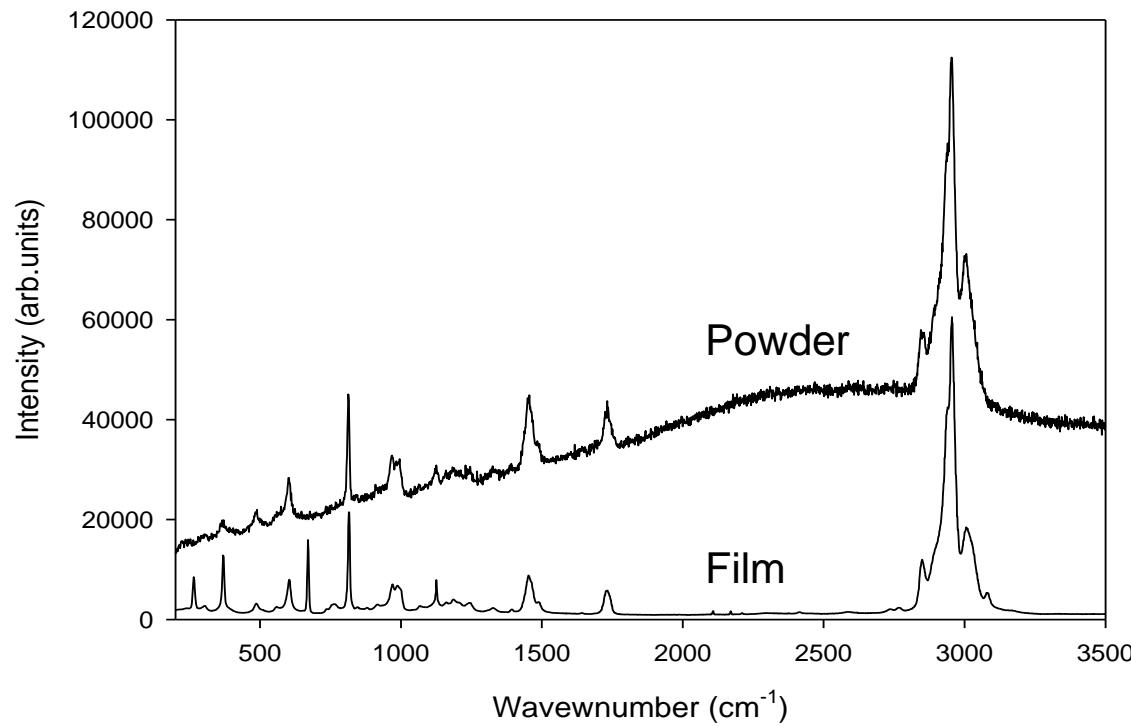
Skin chromophore	Spectral range of absorption	Fluorescence	Principal absorption maxima (nm)
Oxyhemoglobin	UV-VIS	NO	412, 542, 577
Deoxyhemoglobin	UV-VIS	NO	430, 555, 760
Melanin	UV-VIS	NO	Monotonic increase to short wavelengths
Water	IR-long VIS	NO	760, 900, 1250, 1400, etc.
Porphyrins	VIS	Yes	Ex: ~405; Em: 600
Bilirubin	VIS	NO	460
NAD/NADH	UV	Yes	Ex: ~350; Em: 460
DNA/RNA	UV	NO	260
Tryptophan	UV	Yes	Ex: 295; Em: 340–350
Urocanic acid	UV	NO	280
Collagen x-links	UV	Yes	Ex: 335, 370; Em: 380, 460
Elastin x-links	UV-VIS	Yes	Ex: 420, 460; Em: 500, 540
Keratin (dry), horn	UV	Yes	Ex: 370; Em: 460

<sup>a</sup> NO: not observable; Ex: excitation wavelength; Em: emission wavelength.



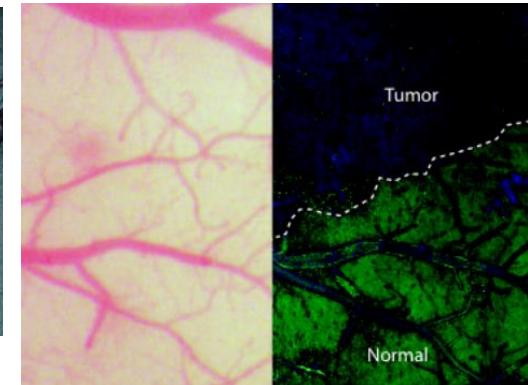
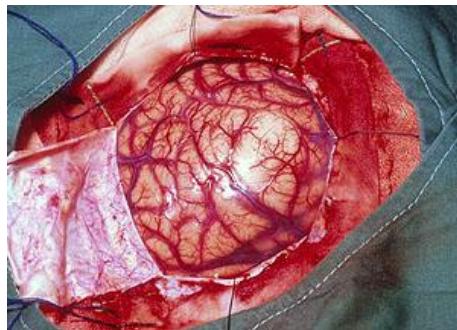
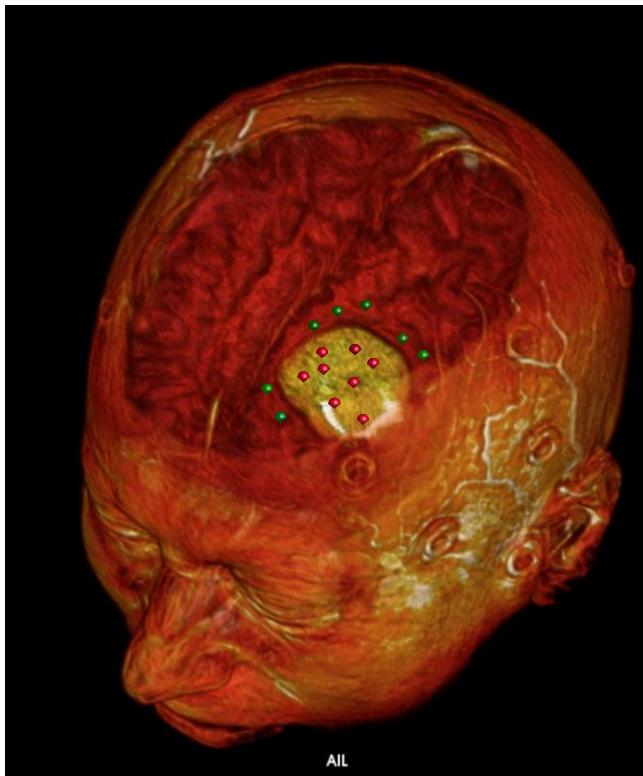
Fluorescence of impurities or of the sample itself may strongly interfere with Raman

# Fluorescence in Raman

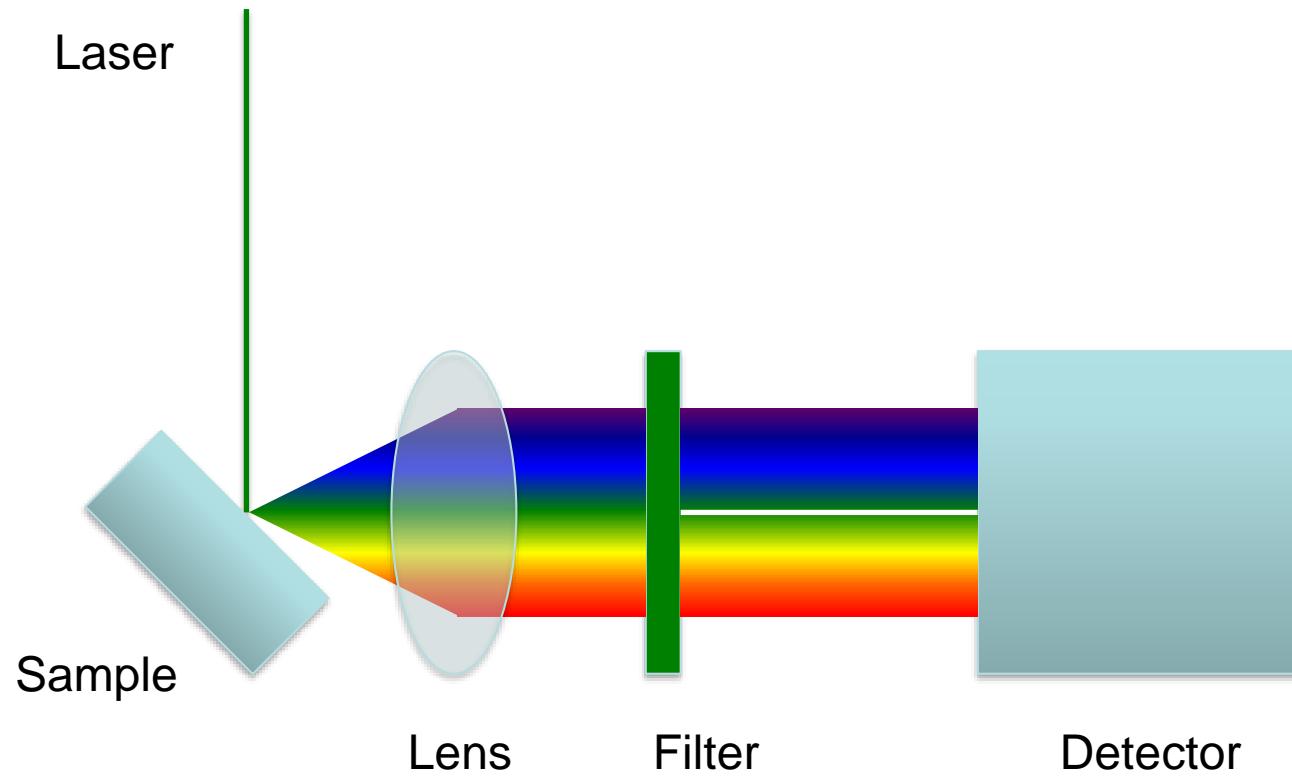


PMMA Powder and Film

# Raman in brain surgery

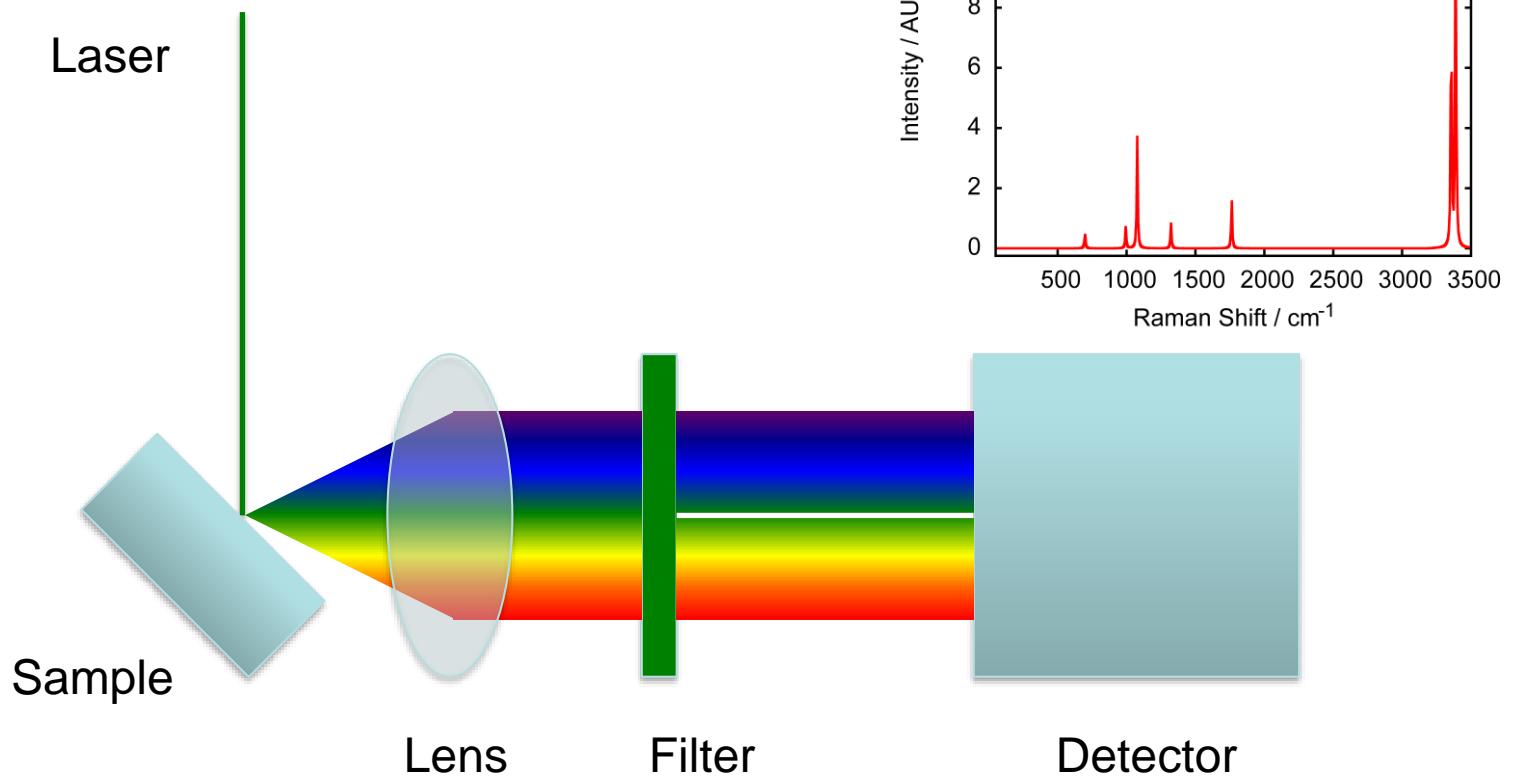


# Raman Spectrometer Schematic



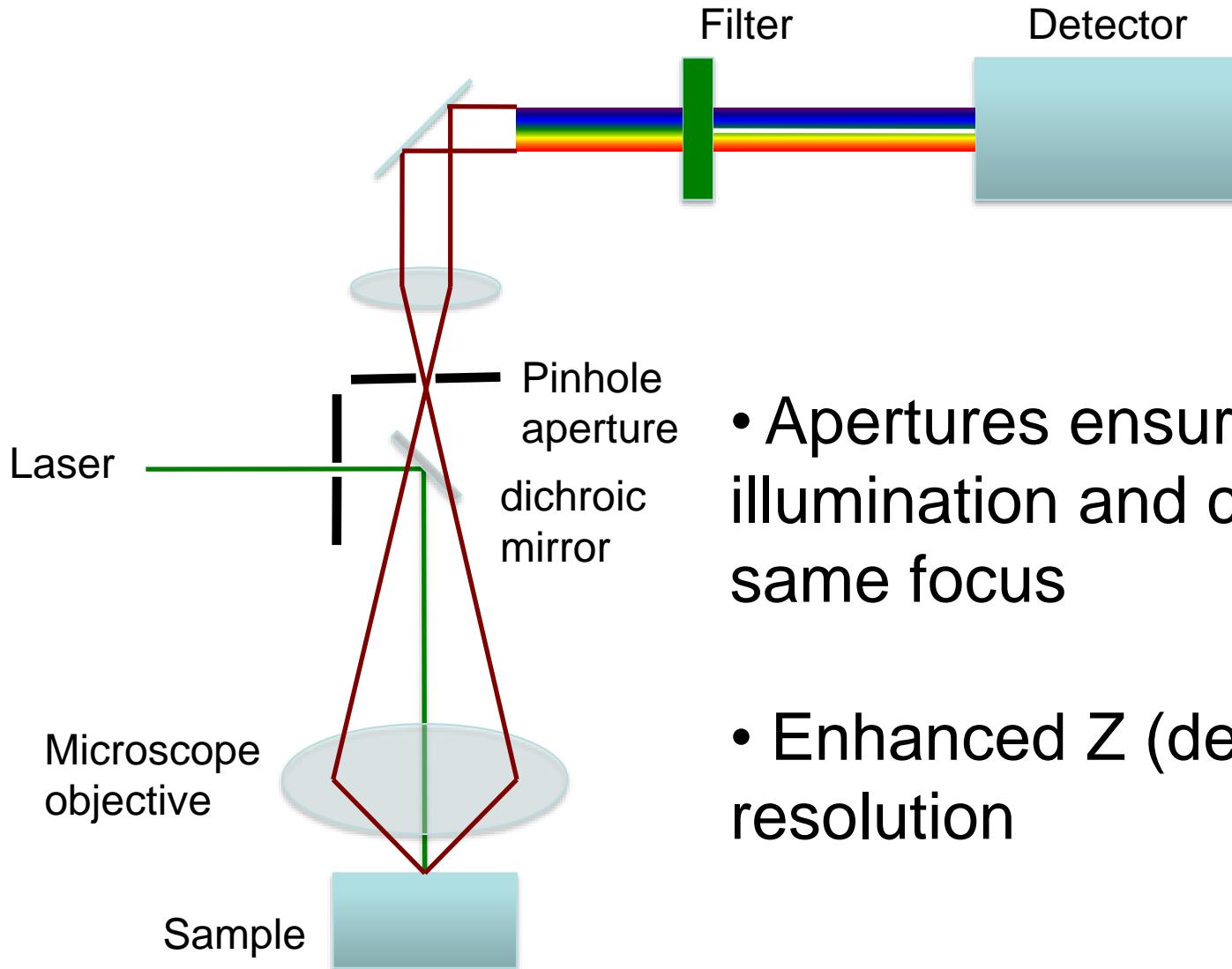
As light scattered in all directions, angle of collection not important

# Raman Spectrometer Schematic



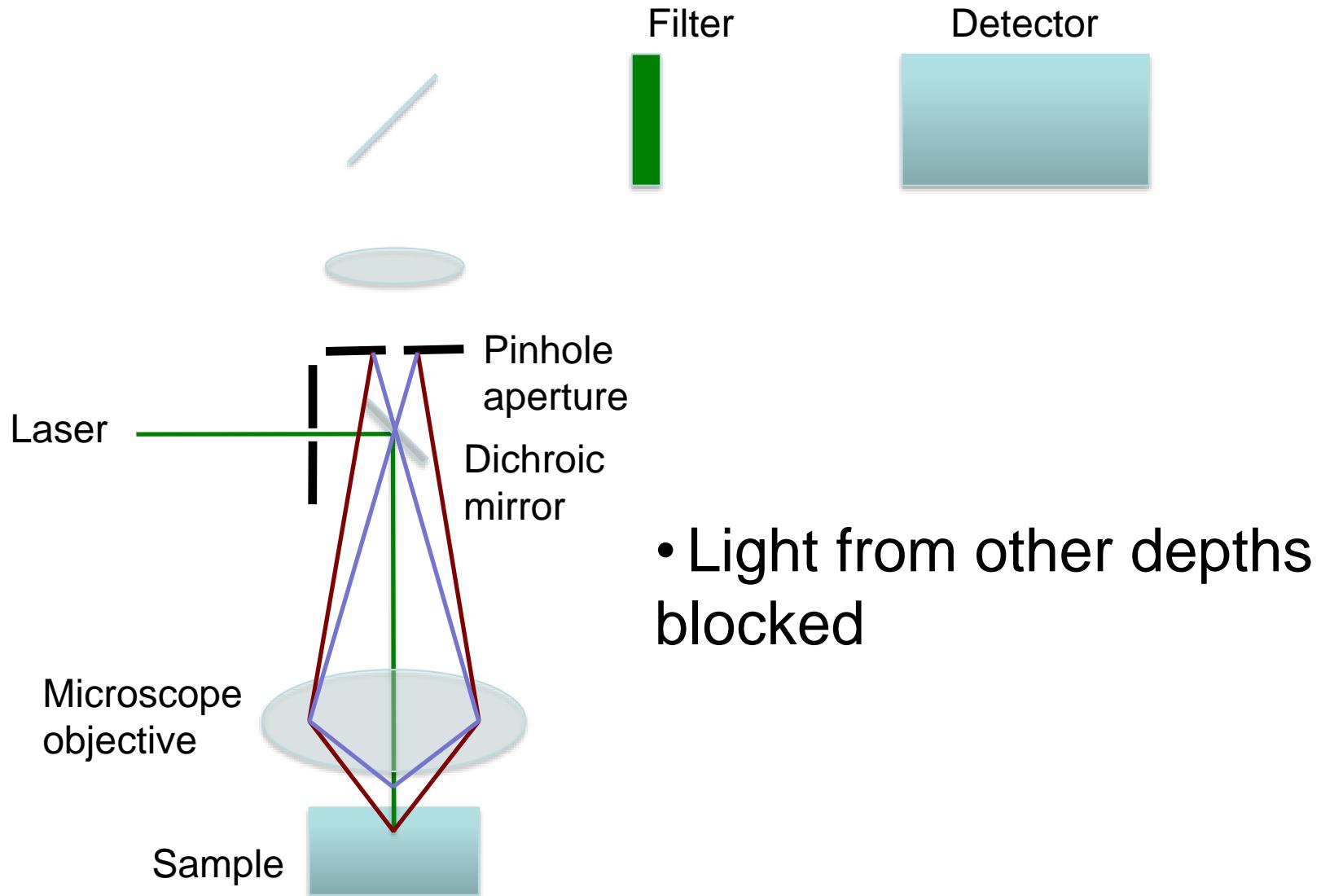
As light scattered in all directions, angle of collection not important

# Confocal Raman for obtaining depth profiles of samples

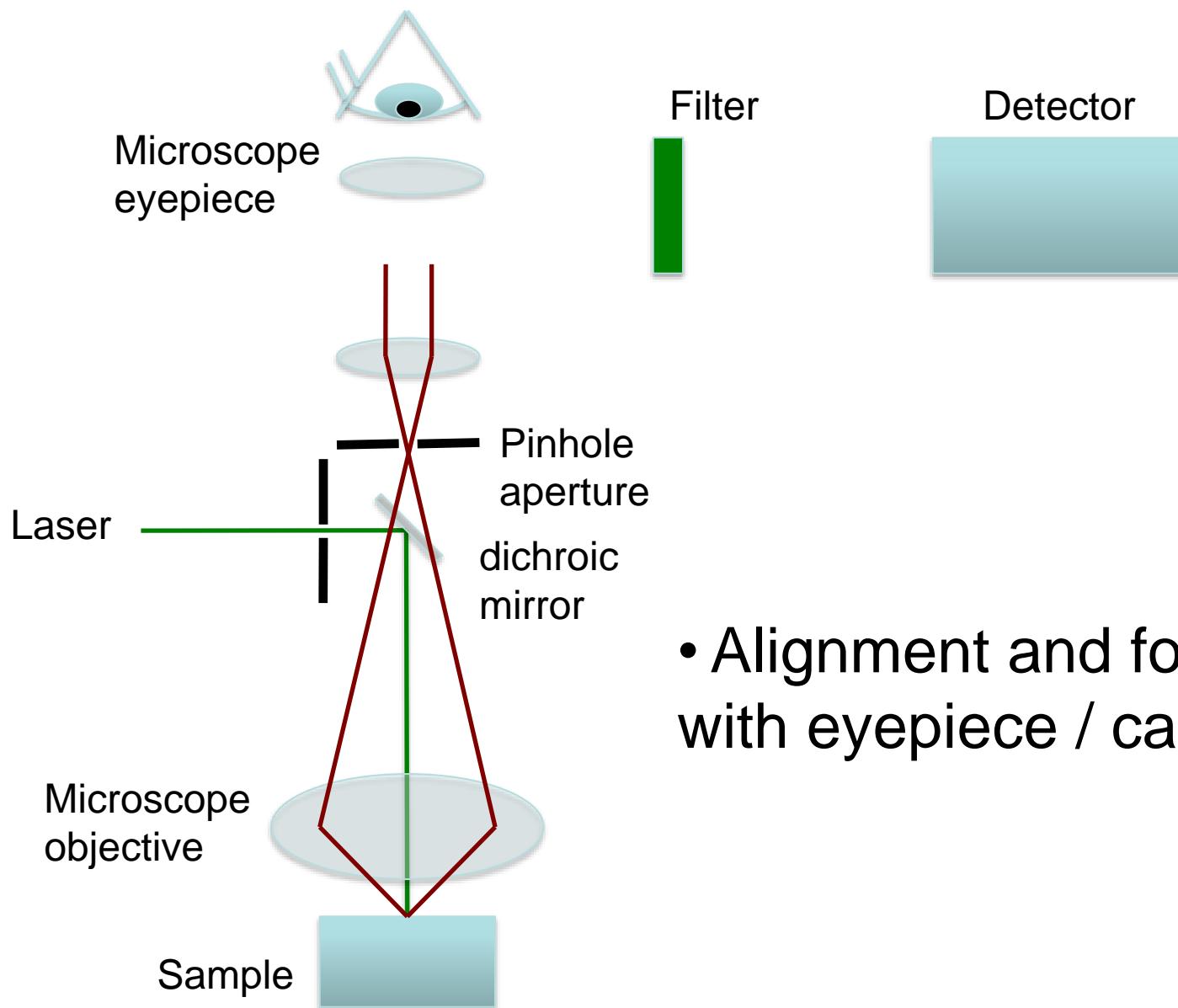


- Apertures ensure illumination and collection at same focus
- Enhanced Z (depth) resolution

# Confocal Raman



# Confocal Raman



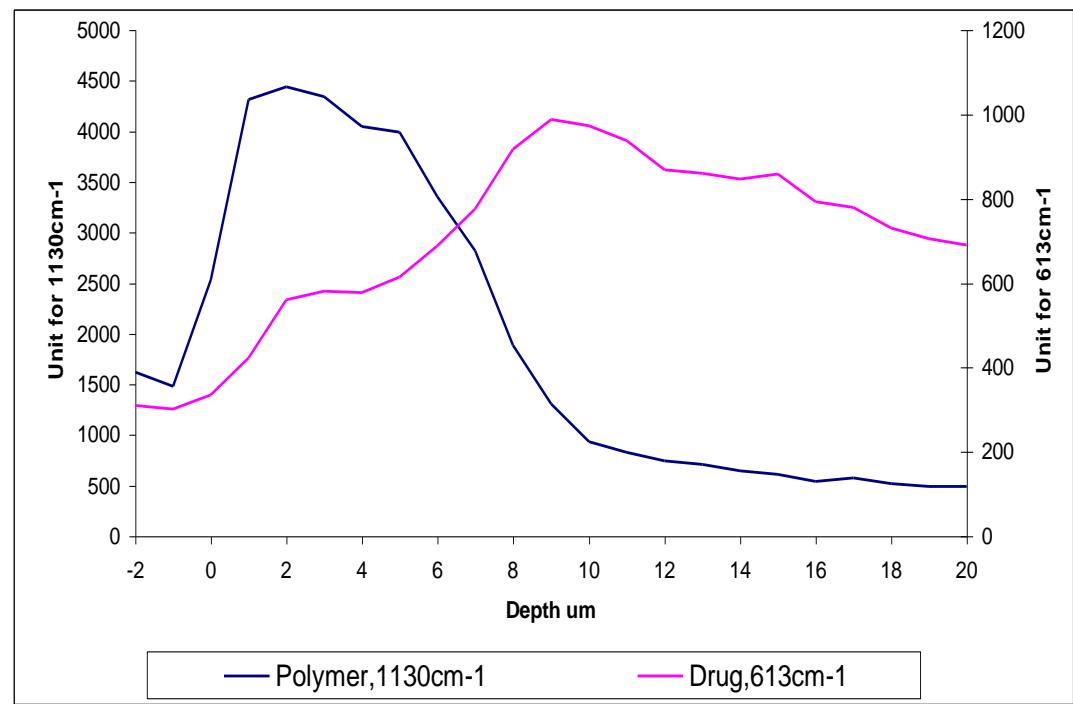
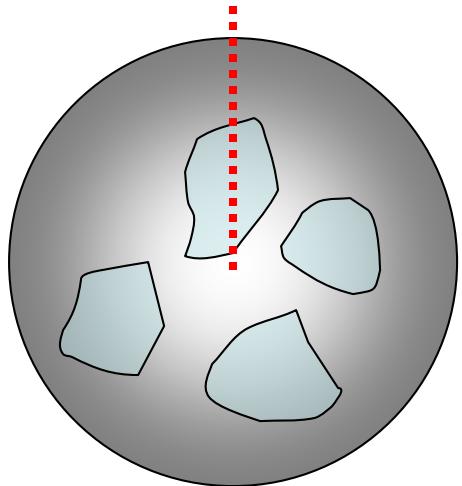
- Alignment and focusing with eyepiece / camera

# One of Raman spectrometers combined with confocal microscopes

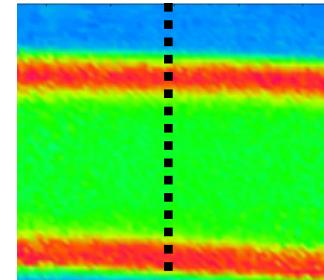


# Confocal Raman Study of Pharmaceuticals

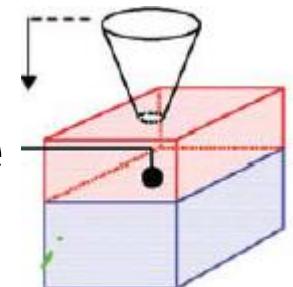
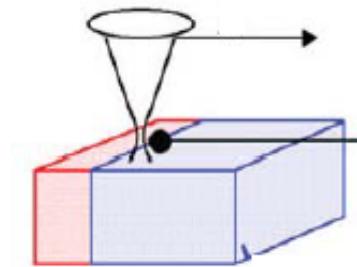
Blue line shows intensity change of polymer band with depth  
Pink line shows intensity change of drug band with depth



# Confocal Raman microscopy

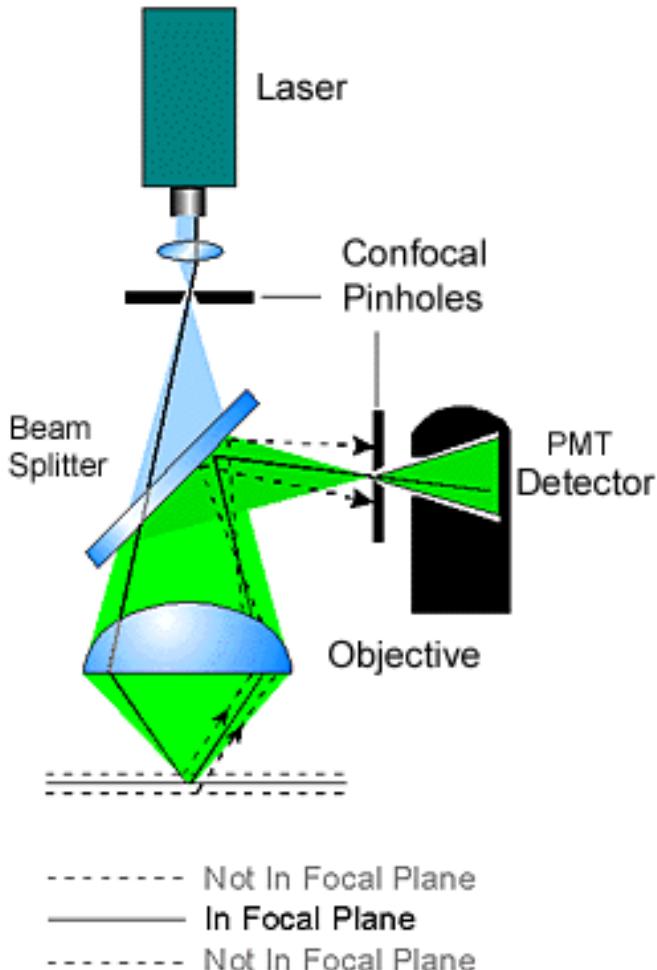


- Point mapping: film is microtomed, spectra are recorded at  $1\mu\text{m}$  increments on the line normal to the surface
- Confocal Raman: non-destructive depth profile without need to microtome

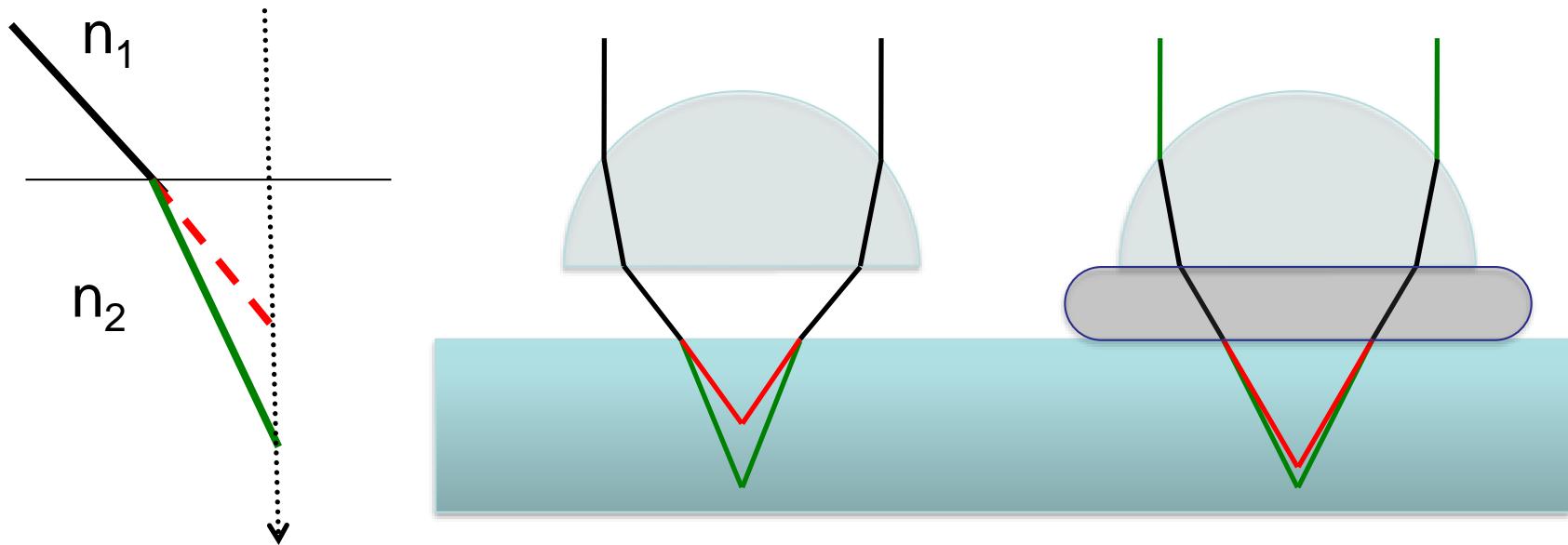


# Depth Profile with Confocal Raman Microscopy

- Measurements recorded below the surface
  - Chemical information as a function of depth
- Restriction of out of focus regions entering the detector
- Depths profiling up to 100 micrometers

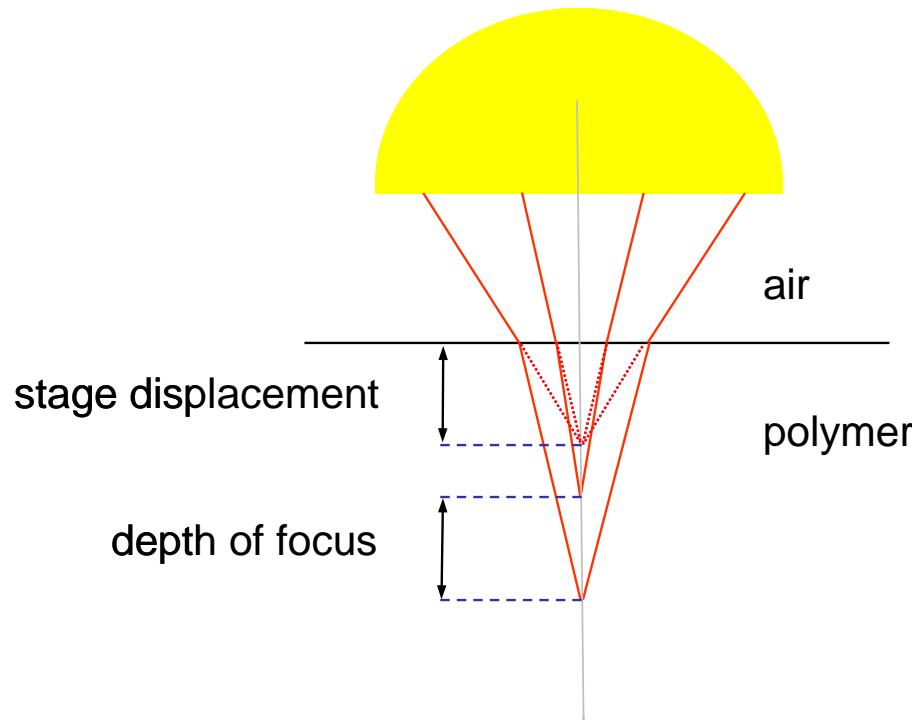


# Confocal Raman Microscopy: Refraction Effect (similar effect in IR as will be discussed in Lecture 3, now it is in Raman)

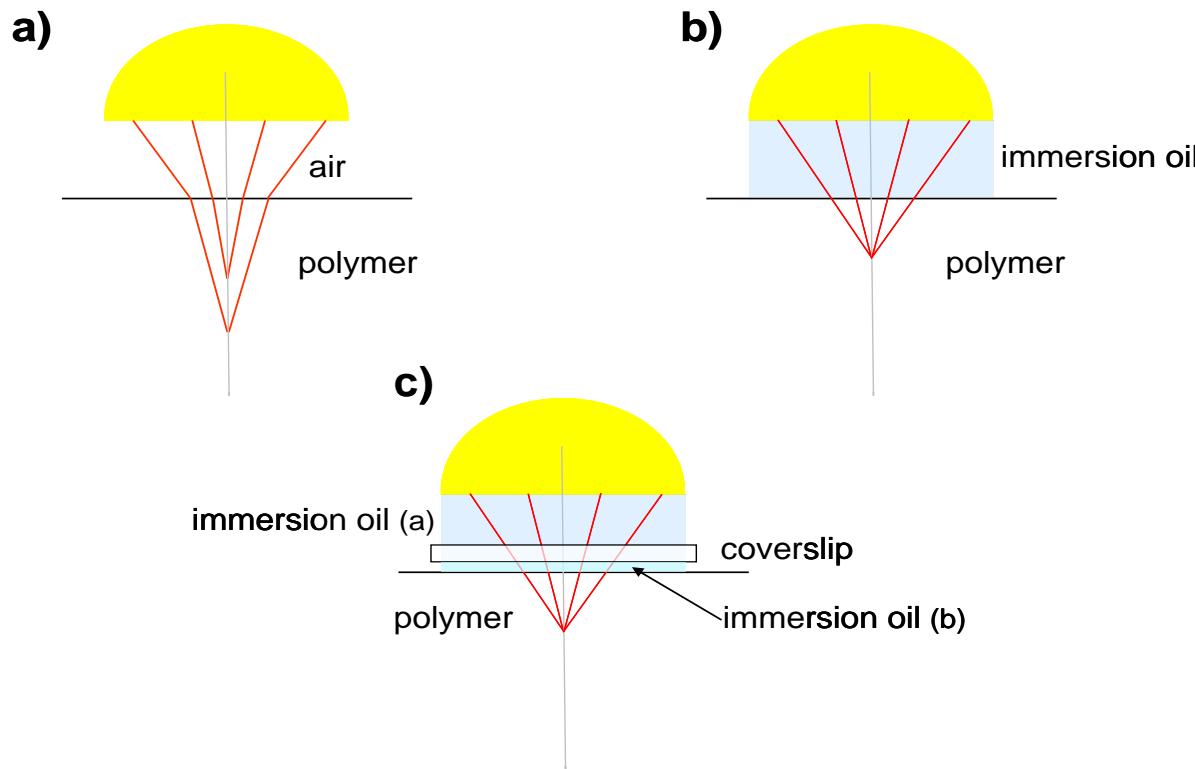


- Refractive index mismatch at the air/sample interface
- Oil immersion objective improves the depth resolution

# Schematic representation of light refraction occurring at air/polymer interface



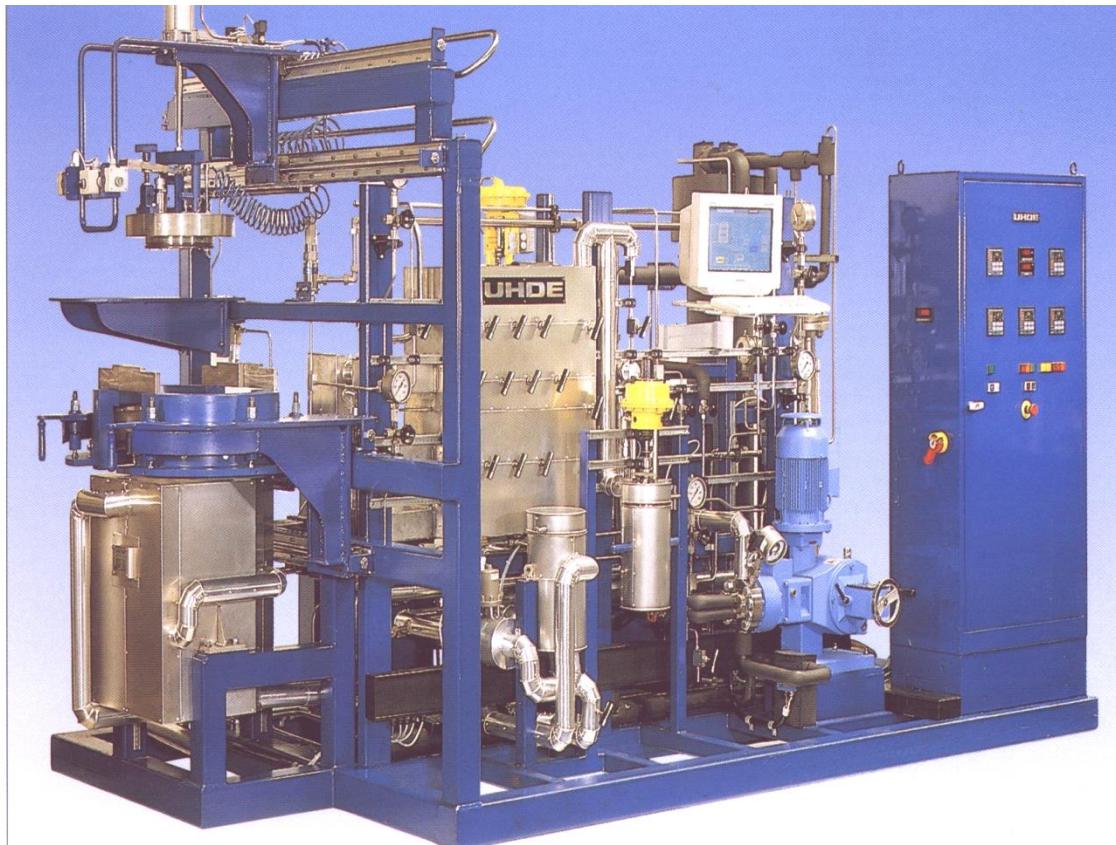
# Confocal Raman Microscopy: Refraction Effects



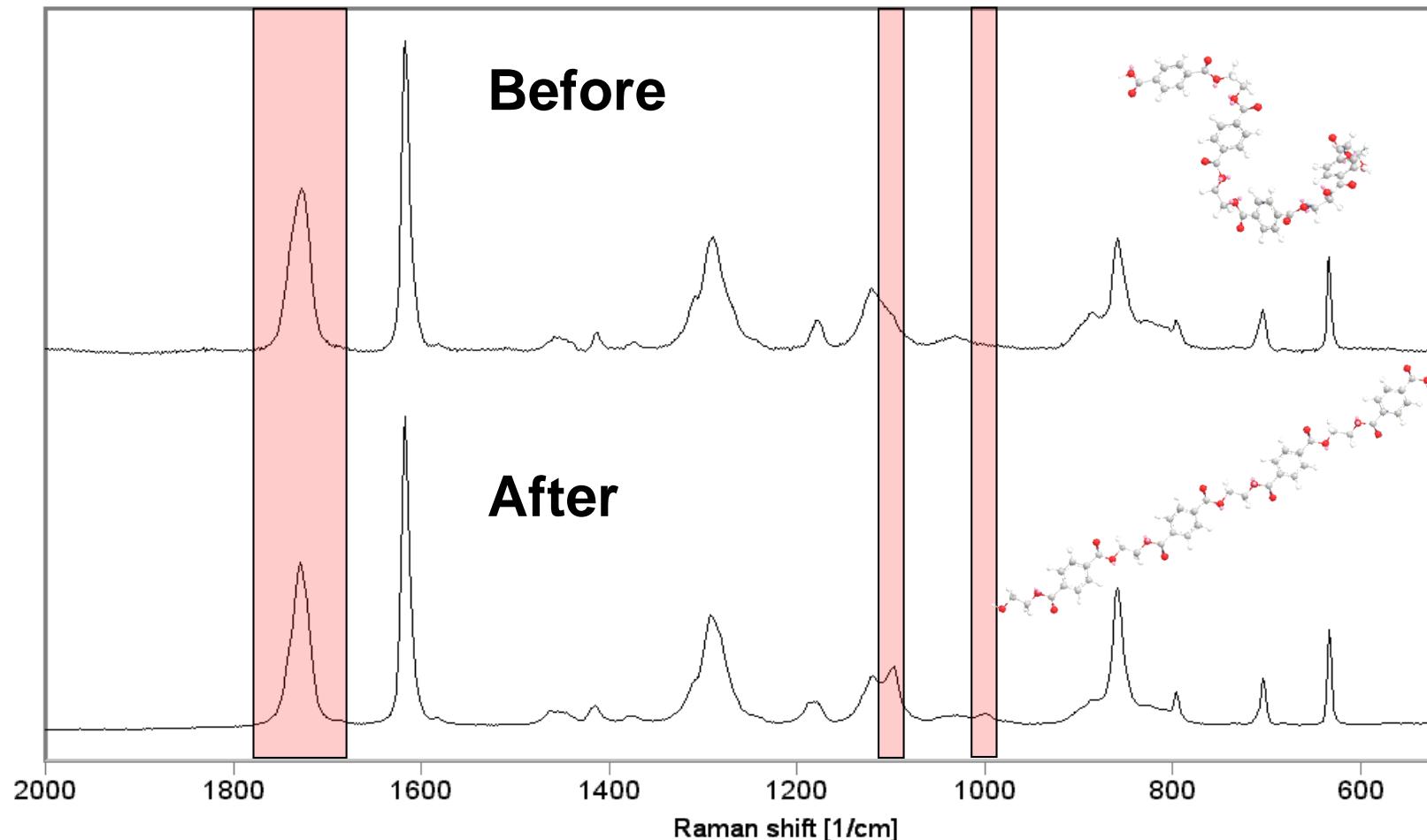
- Refractive index mismatch at the air/sample interface (a)
- Oil immersion (b and c) objective improves the depth resolution

# Applications of Confocal Raman:

## Dyeing to be clean: dyeing fabric with supercritical fluids

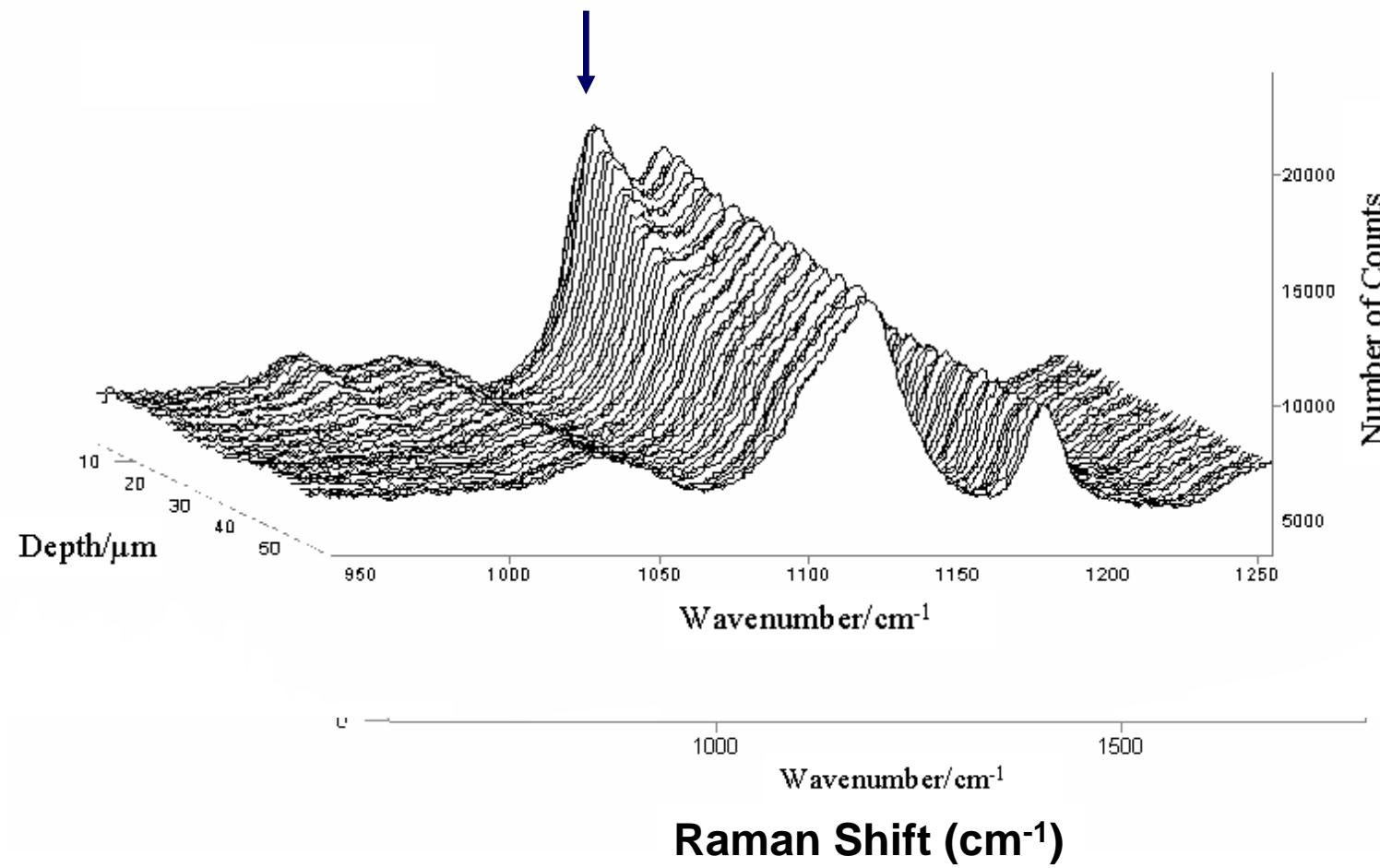


# Raman Spectra of PET Film Processed with scCO<sub>2</sub>



# PET Film After scCO<sub>2</sub>: Raman Spectra as a Function of Depth

1096 cm<sup>-1</sup> band is indication of induced crystallinity



# Normalisation of Raman bands

For quantitative analysis Raman band normalisation is required in order to correct spectra for changes in focus, alignment, laser intensity, and signal attenuation, etc.

Therefore, to compare the two different bands from depth profiles it is necessary to account for possible laser power fluctuations, which was accomplished using band area normalisation.

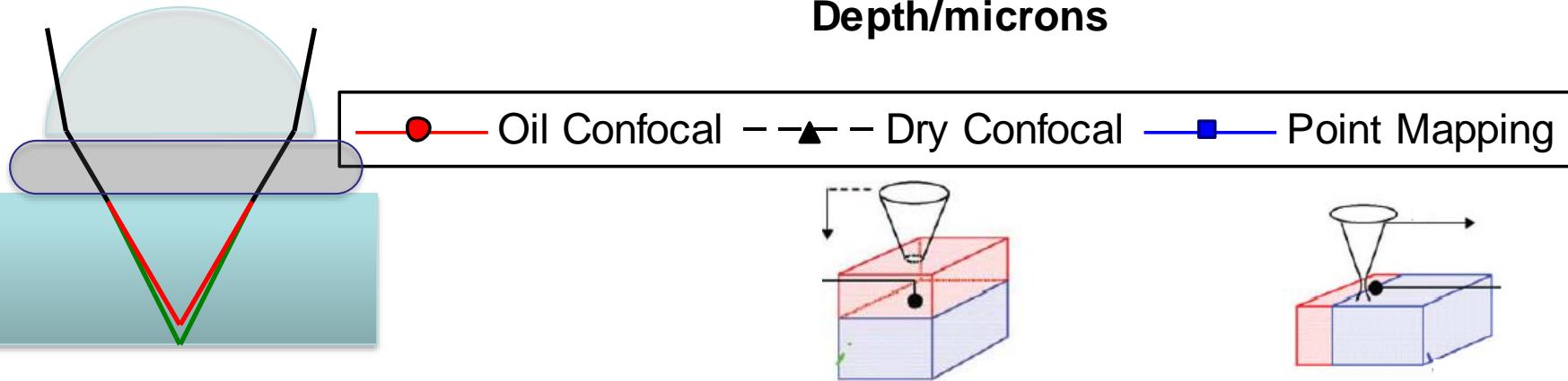
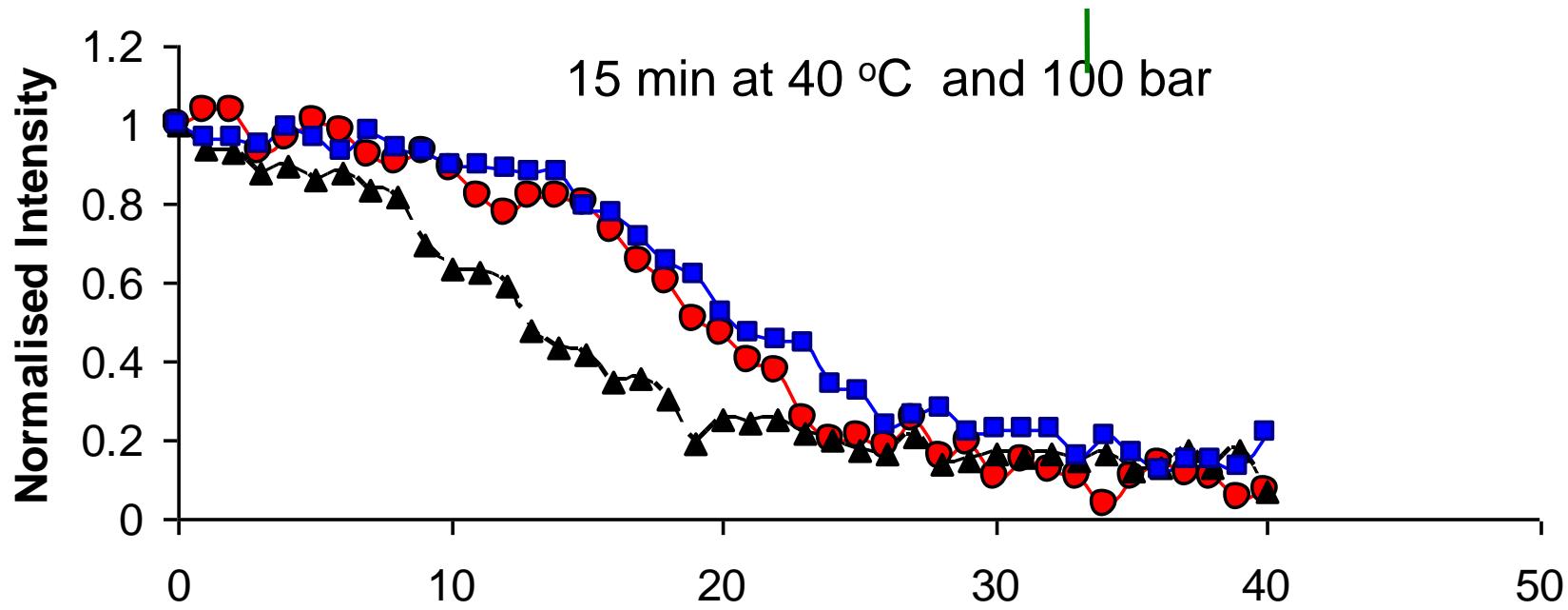
In order for the  $1096\text{ cm}^{-1}$  band (crystalline PET) to be assessed it is necessary to normalise its intensity with respect to a band that is unaffected by crystallinity.

The band at  $795\text{ cm}^{-1}$  was selected for normalization as it is known to be insensitive to conformation or crystallinity.

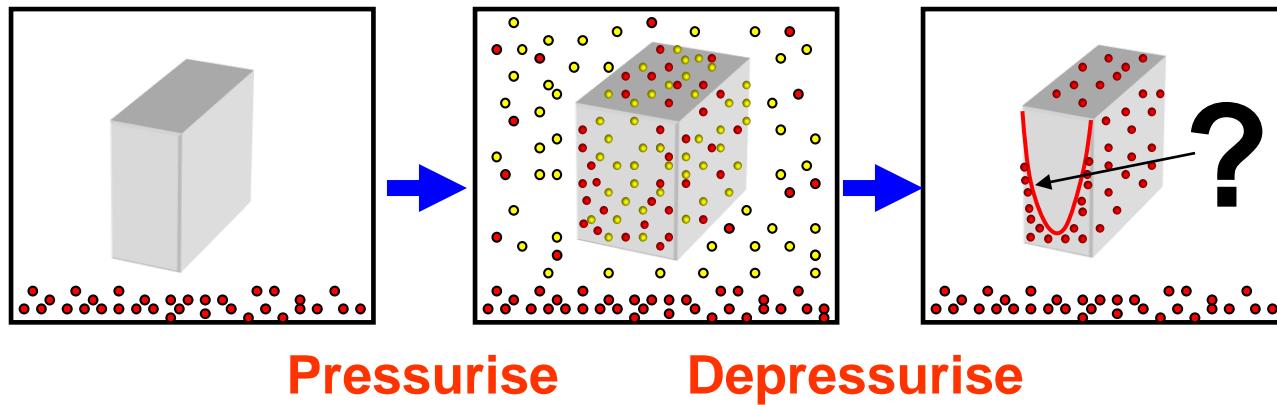
Band normalisation is performed by dividing the area of the  $1096\text{ cm}^{-1}$  band by the area of the band at  $795\text{ cm}^{-1}$

Similar procedure used for assessment of dye impregnation into PET fibers

# Depth Profile of CO<sub>2</sub>-Induced PET Crystallinity as a Function of Depth: Validation of Confocal Raman

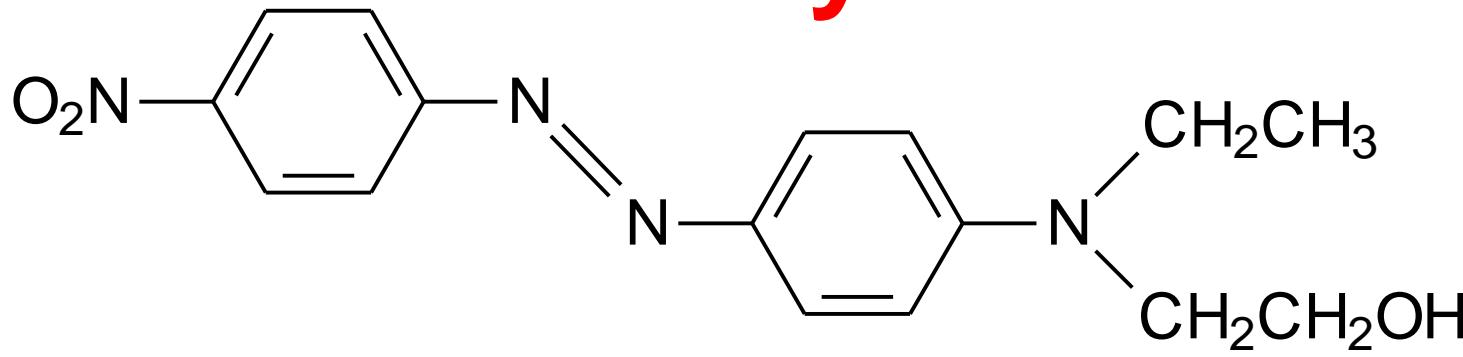


# scCO<sub>2</sub>-assisted impregnation of dyes (or drugs)

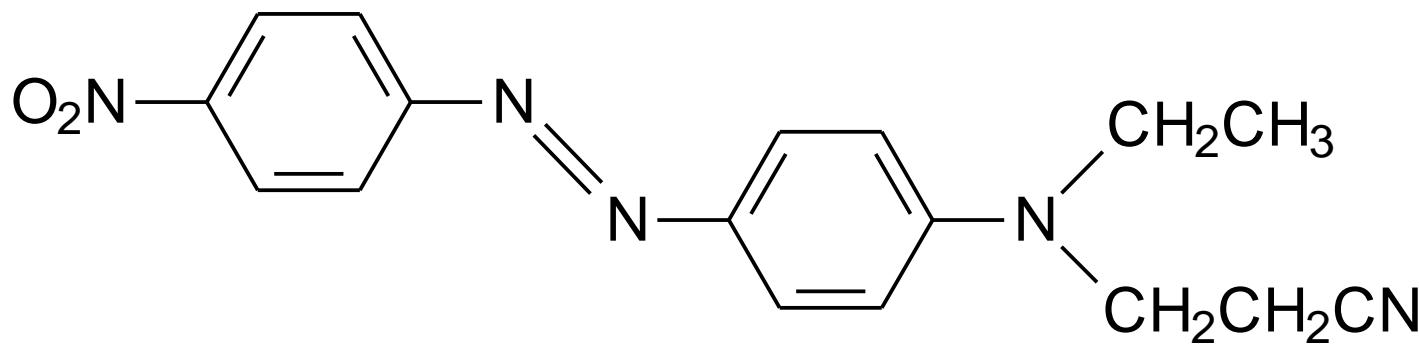


- Diffusion may be assessed from the spatial distribution of solute
- Information may be acquired using confocal Raman microscopy and mapping of cross-sections

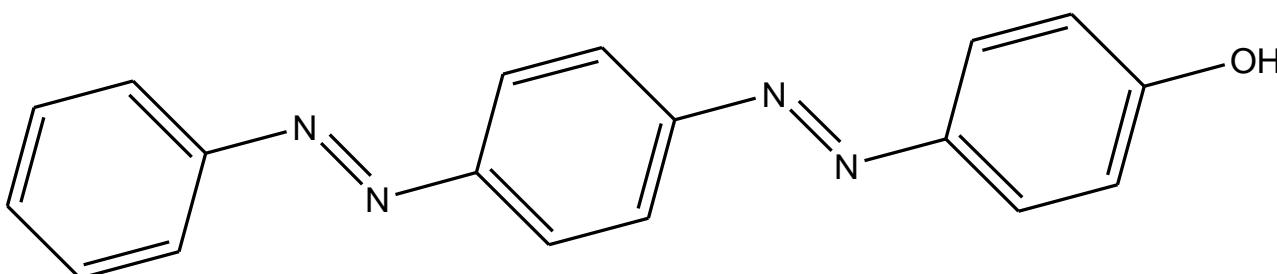
# Dyes



Disperse  
Red 1  
(DR1)

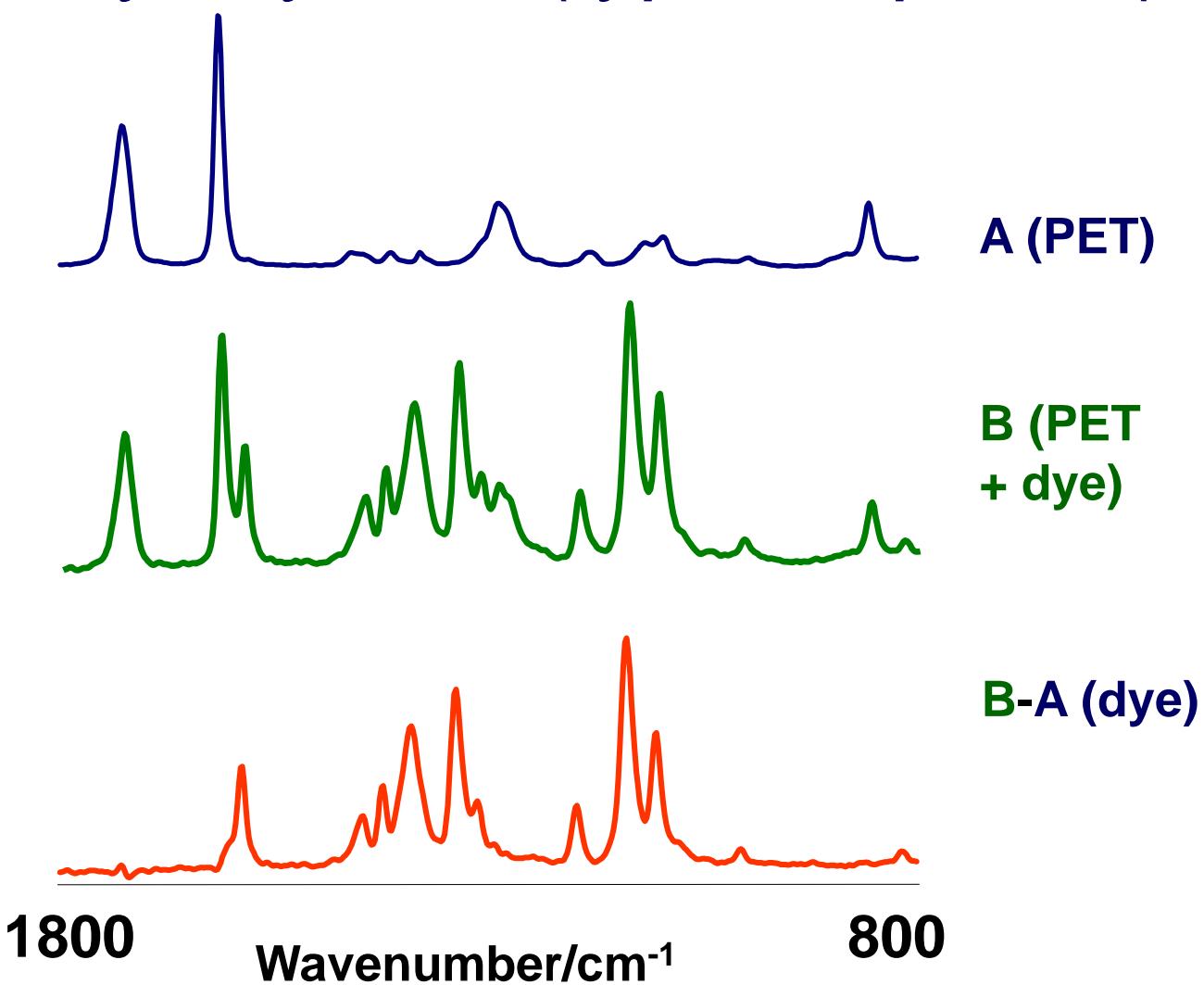


Disperse  
Orange 25  
(DO25)



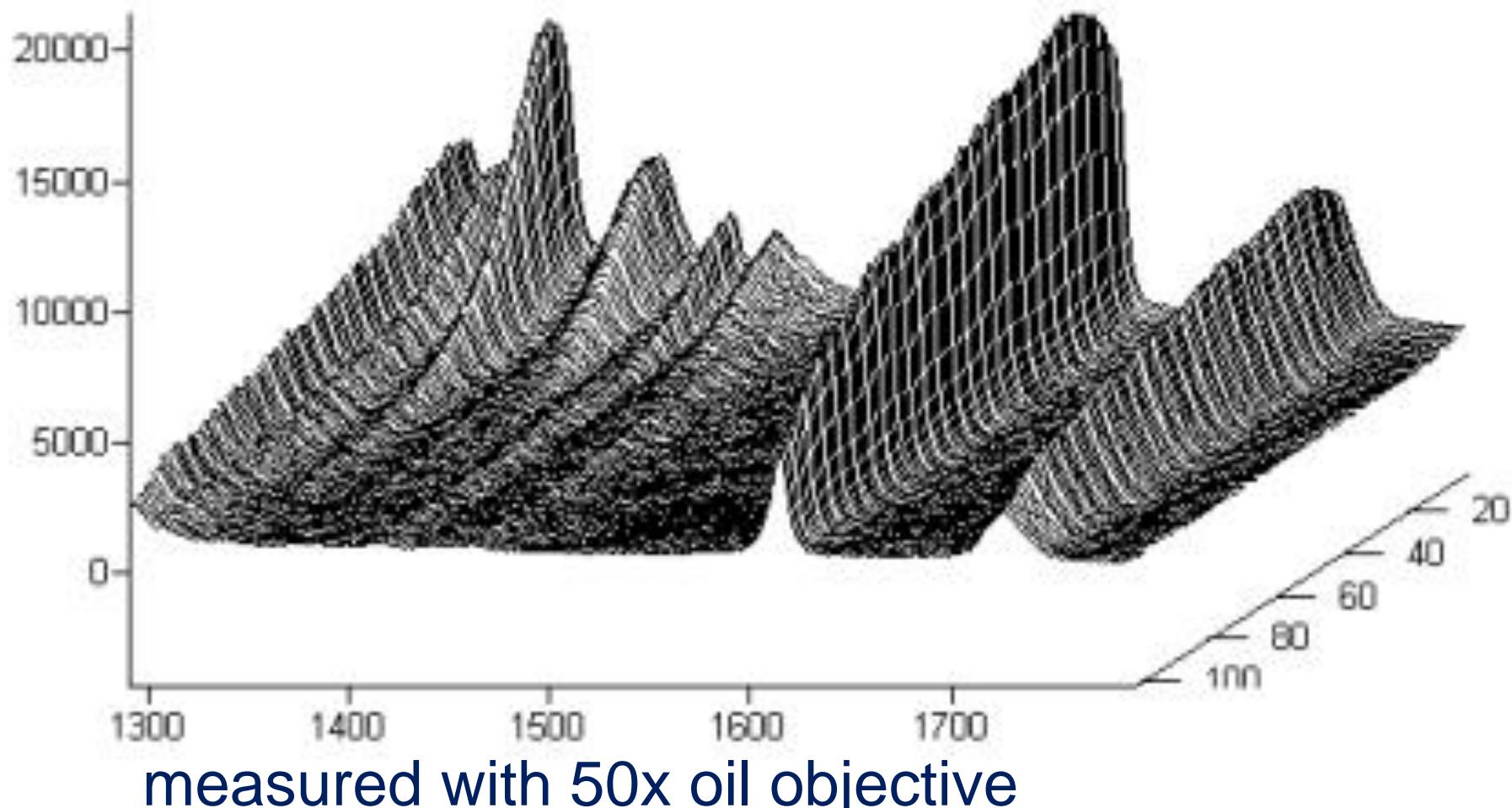
Disperse  
Yellow 23

# Raman spectrum of PET/dye system (typical spectra)



Detection of a dye in polymeric matrix at different depths is possible by using spectral subtraction as shown above. Confocal Raman provides high-quality spectra

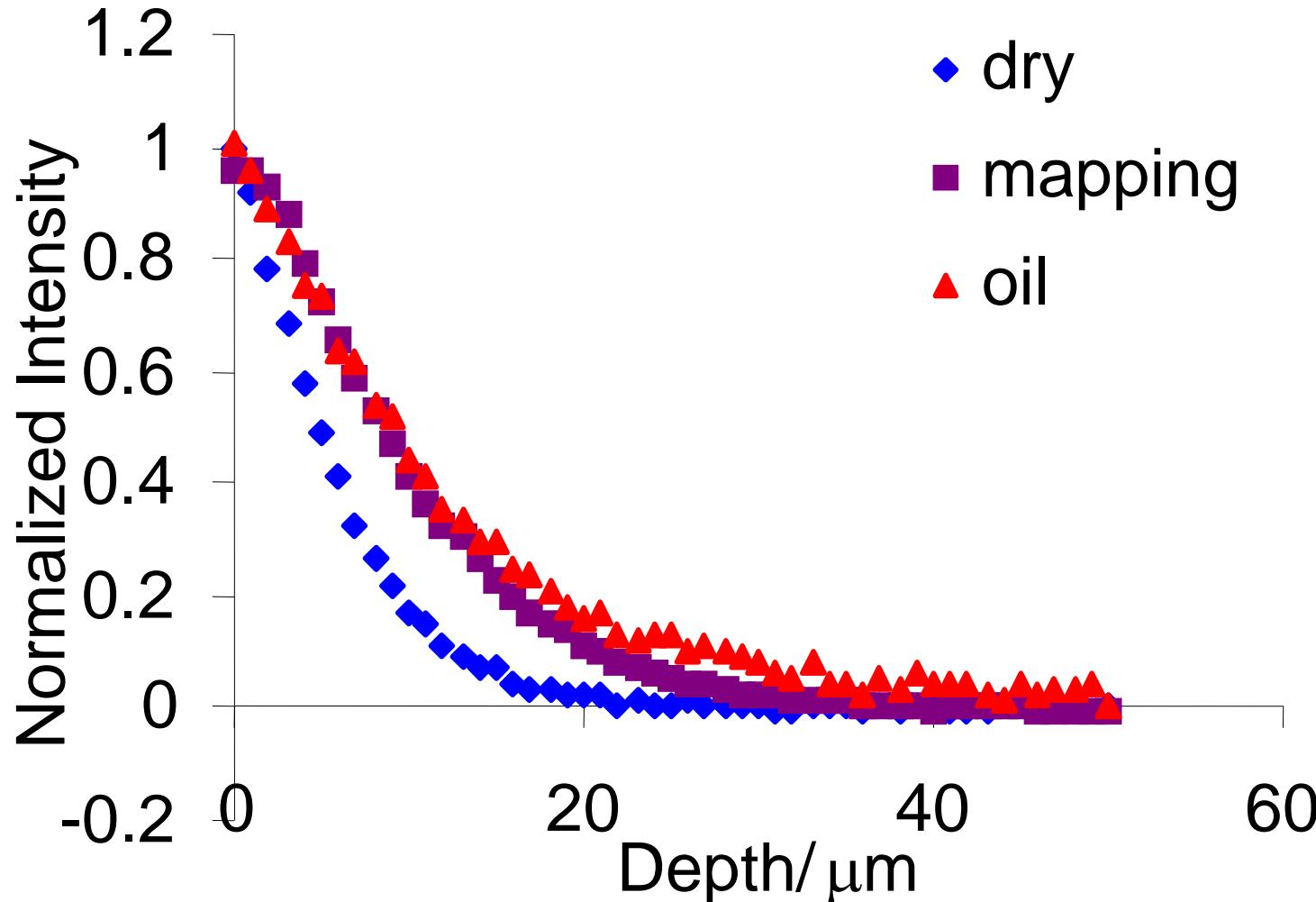
# Confocal Raman spectra of PET/DR1 as a function of depth



Note that intensities of all Raman spectra bands decrease here as a function of depth (because laser power decays with depth) but intensities of the bands of dyes decrease faster because of gradient in the distribution of dye within PET matrix

# Depth profiles of DR1 in PET after exposure for 14 hours

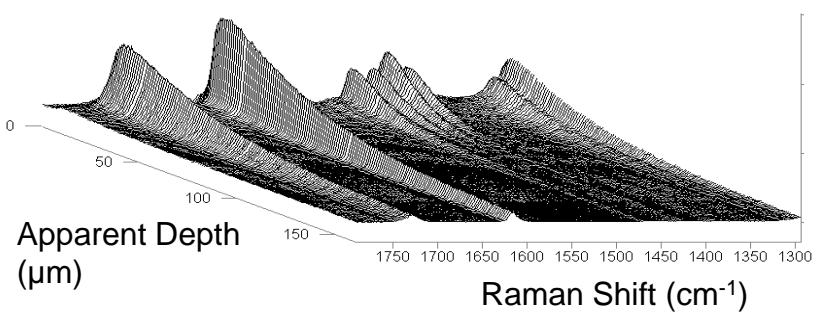
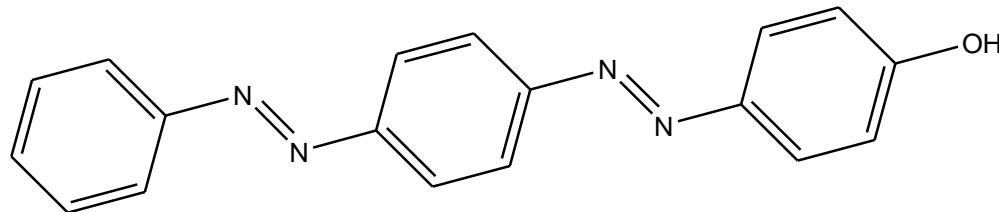
Validation of Confocal Raman using oil objective



Normalised intensities of a spectral band of dye as a function of depth

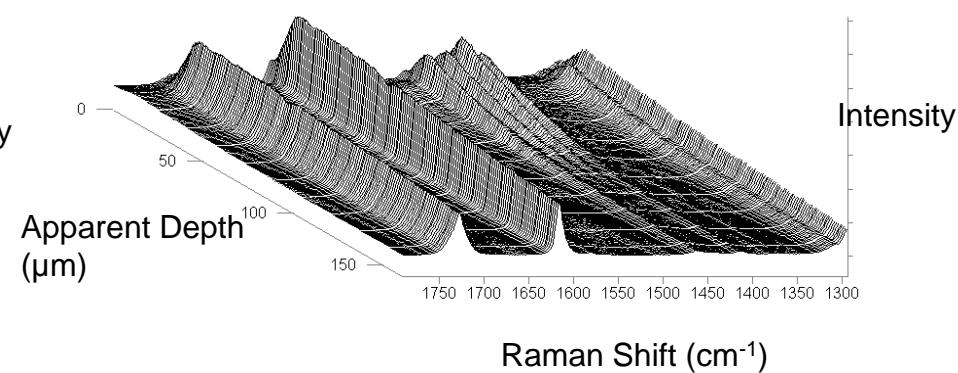
# Confocal Raman Spectra of PET Fibers Dyed with DY 23

: Disperse Yellow 23  
280 bar and 130 °C



Dry objective

Depths up to 100 – 150  $\mu\text{m}$



Oil objective

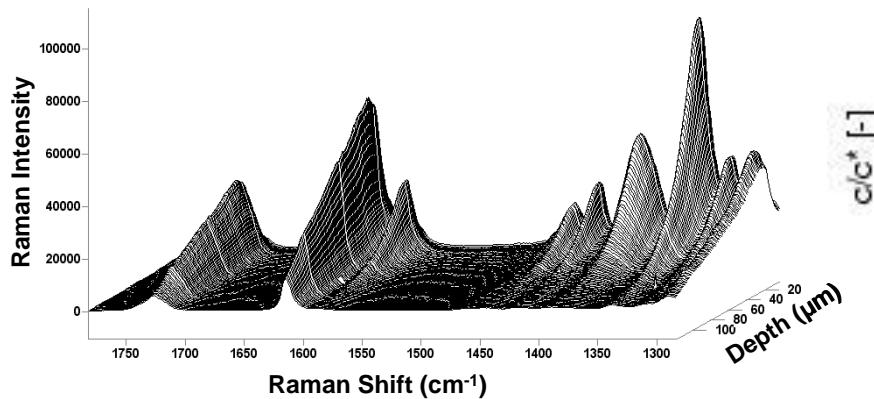
**Diffusion coefficient,  $D = 3.5 \times 10^{-13} \text{ m}^2\text{s}^{-1}$**

*POLYMER, 46, 2943, 2005*

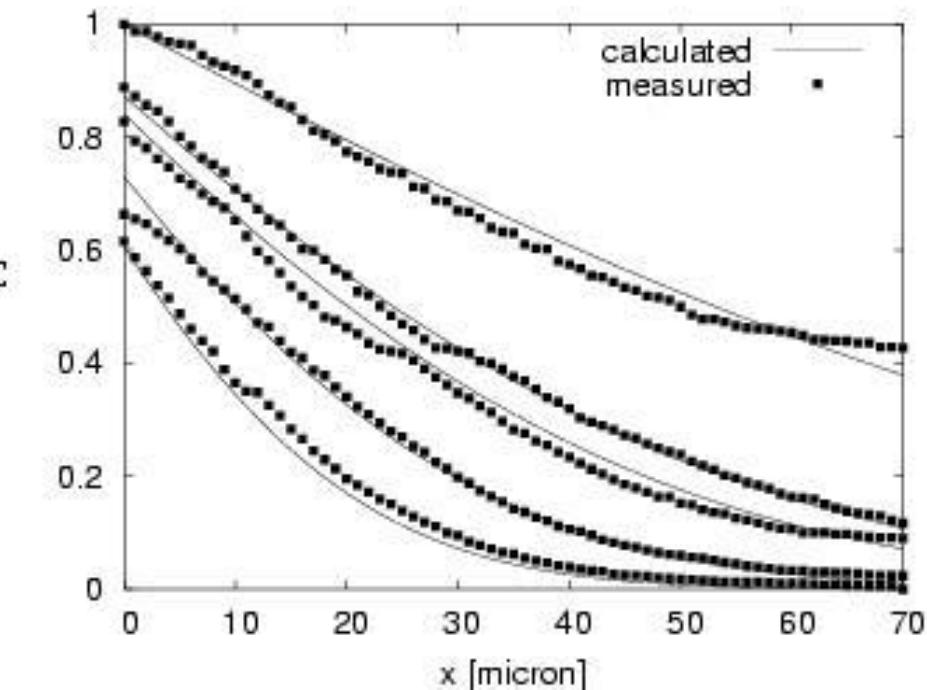
# Confocal Raman and Modelling of Dye Diffusion in PET impregnated from scCO<sub>2</sub>



200 bar and 80 °C



$$\frac{\partial c}{\partial t} = D^s \frac{\partial^2 c}{\partial x^2}$$



Time: 1,2,4,5 and 15h

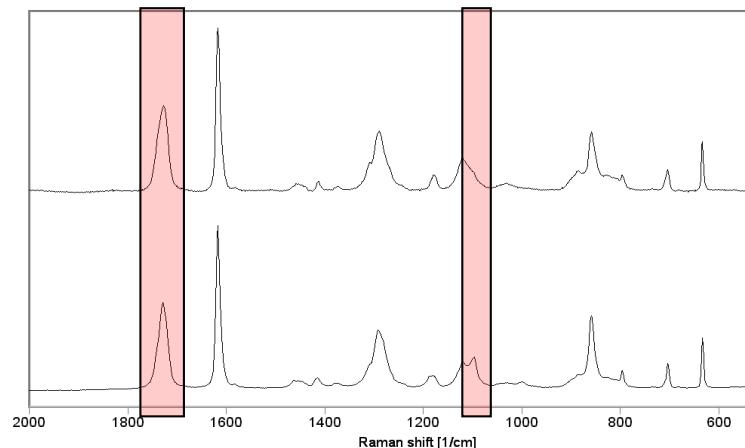
A one-dimensional Fickian diffusion model was used to evaluate the diffusion coefficient of the dye from the Raman microscopy data by non-linear least squares regression, calculated diffusion coefficient  $D = 6.75 \times 10^{-14} \text{ m}^2 \text{s}^{-1}$

# Normalisation of Raman bands

Achieving quantitative analysis with Raman spectroscopy is complicated by the fact that the intensities of Raman bands are sensitive to the scattering geometry, roughness of the surface, laser power fluctuations, etc.

Fortunately, the relative concentrations of the components can be determined by measuring the ratio of the bands corresponding to each component.

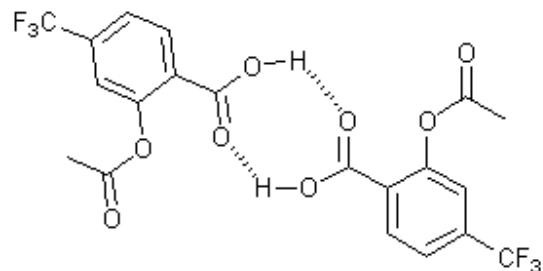
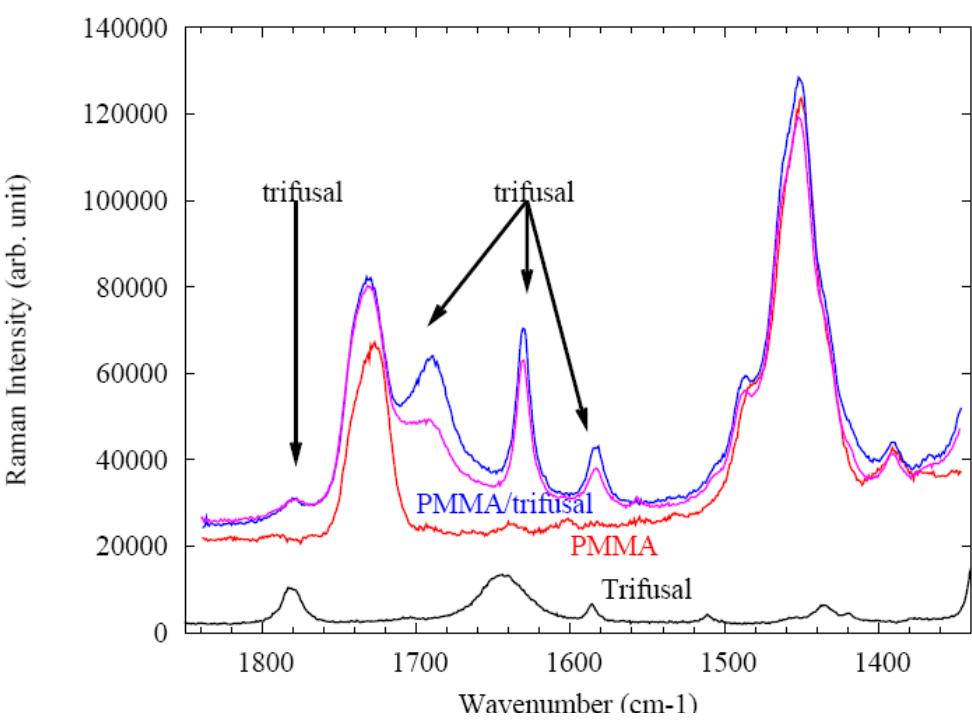
Thus, if distinct Raman bands corresponding to the different components are identified, then the relative concentrations of these components can be obtained quite precisely.



# Raman spectroscopy for in pharmaceutical applications

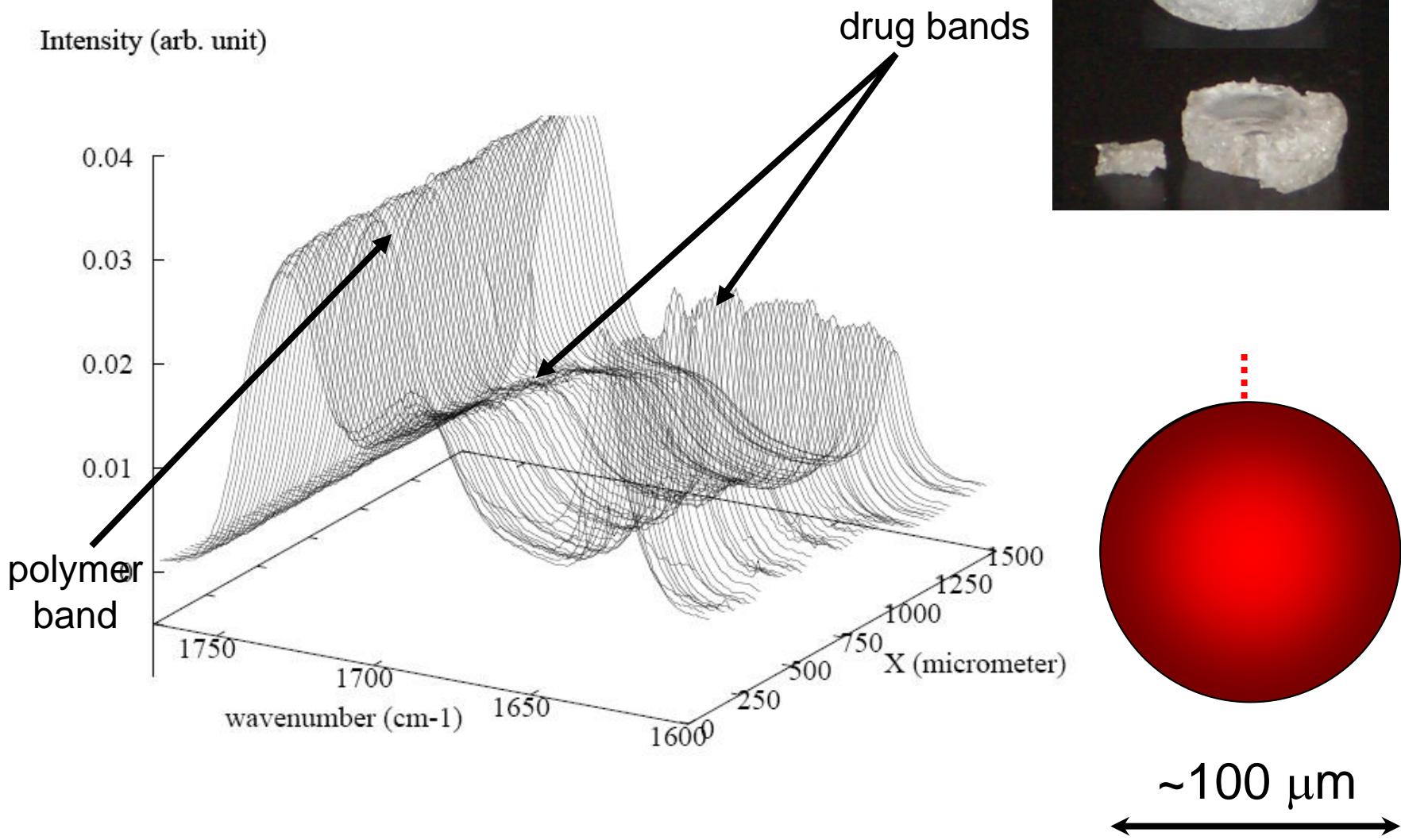
- Raman spectroscopy for drug identification
- Raman mapping for analysis of distribution of drug in tablet (obtaining chemical images similar to FTIR imaging but by mapping)
- Depth profile analysis - a key for drug release
- Studies of polymorphs
- On line analysis and detection of drugs through the packaging material
- Forensics

# Impregnation of drug (triflusal, TRF) in PMMA matrix

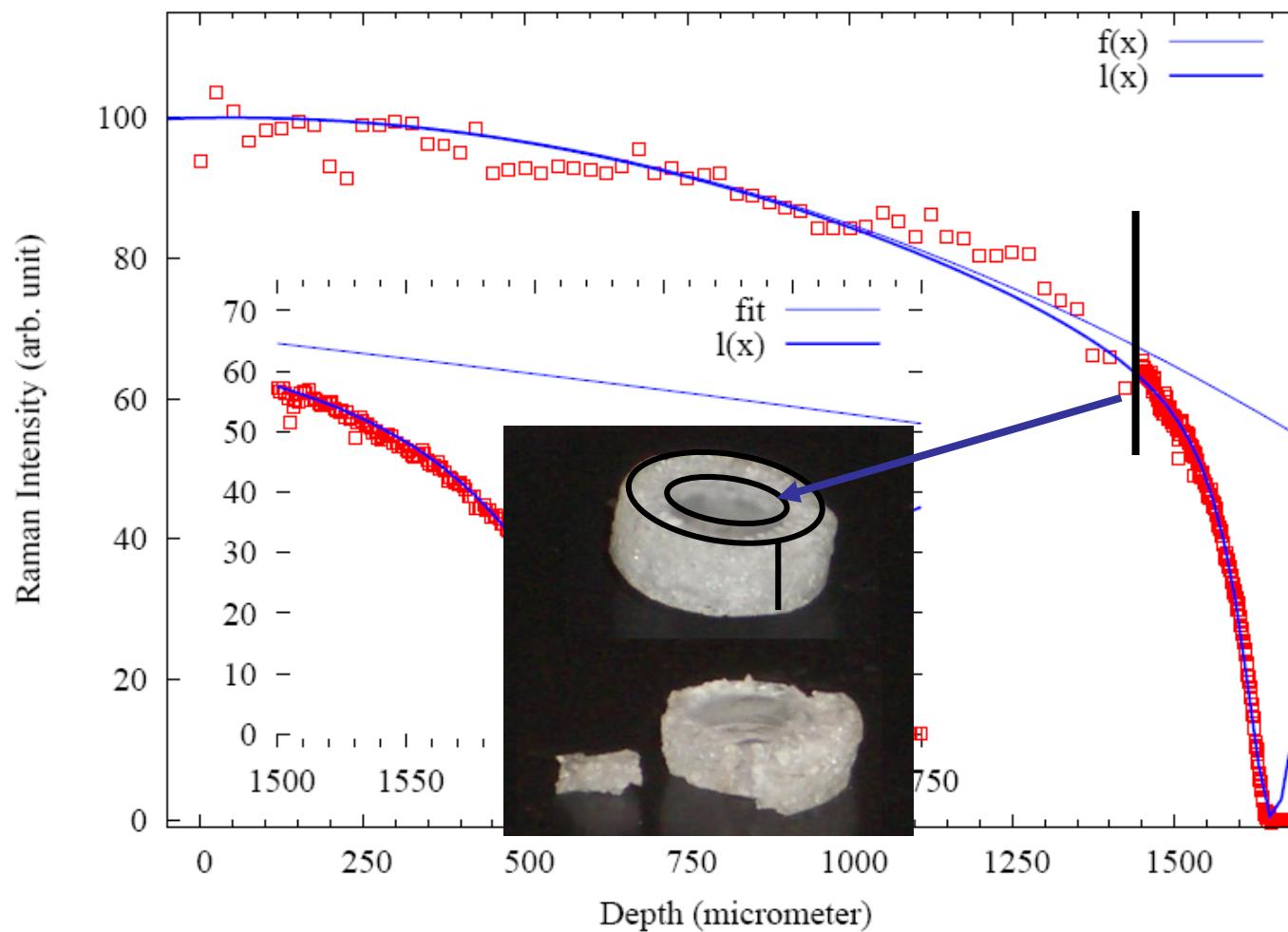


Vib. Spectroscopy 49 (2009) 183

# Depth profile by Raman microscopy: distribution of a drug in polymer matrix



# Distribution of TRF as a function of depth in PMMA rod

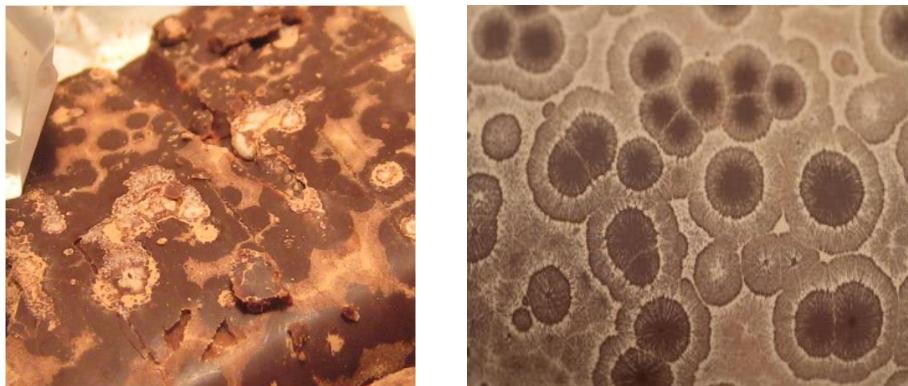


- concentration of drug is relatively homogenous in part of polymer swollen by scCO<sub>2</sub>
- drug also diffuses in first 75 μm in transparent part of the rod

# Polymorphism

## Definition:

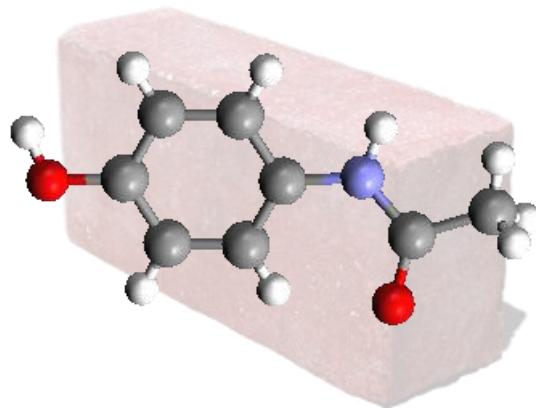
**A solid material with at least two different molecular arrangements that give distinct crystal species**



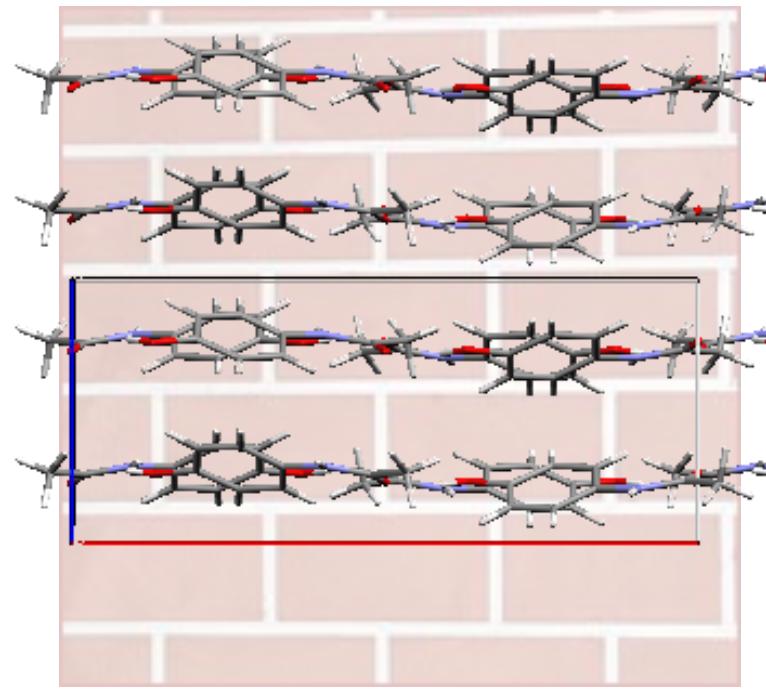
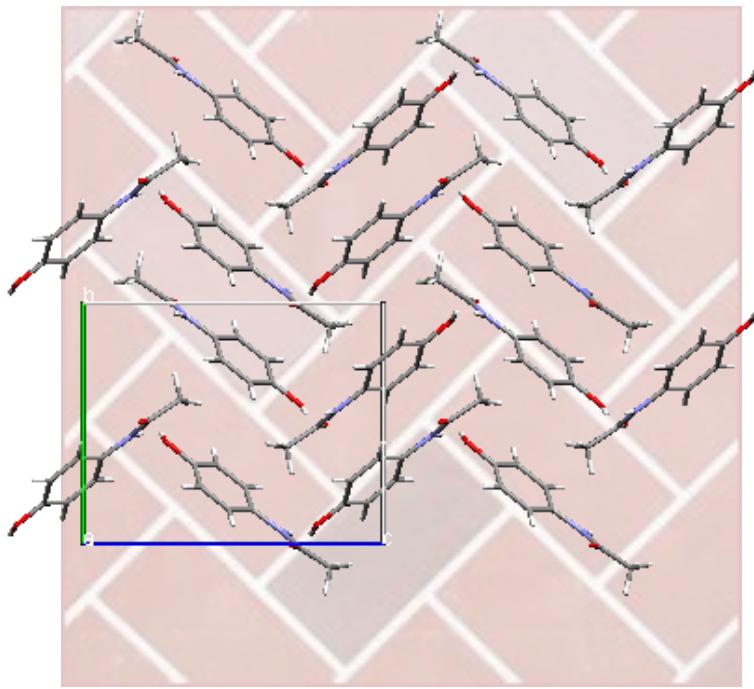
Polymorph	Melting point °C
sub- $\alpha$ (I)	17.3
$\alpha$ (II)	23.3
$\beta'$ (III)	25.5
$\beta'$ (IV)	27.5
$\beta$ -V	33.8
$\beta$ -VI	36.3

# Polymorphism in paracetamol

**Monoclinic  
(Form I)**



**Orthorhombic  
(Form II)**

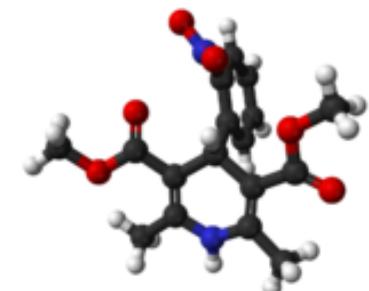
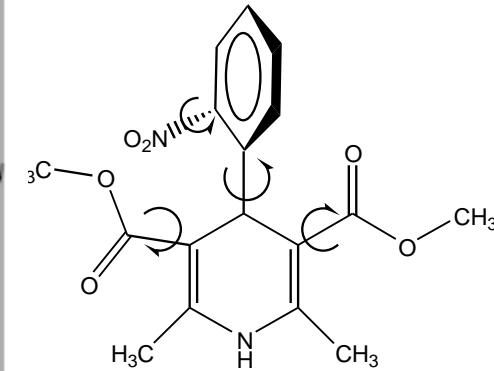
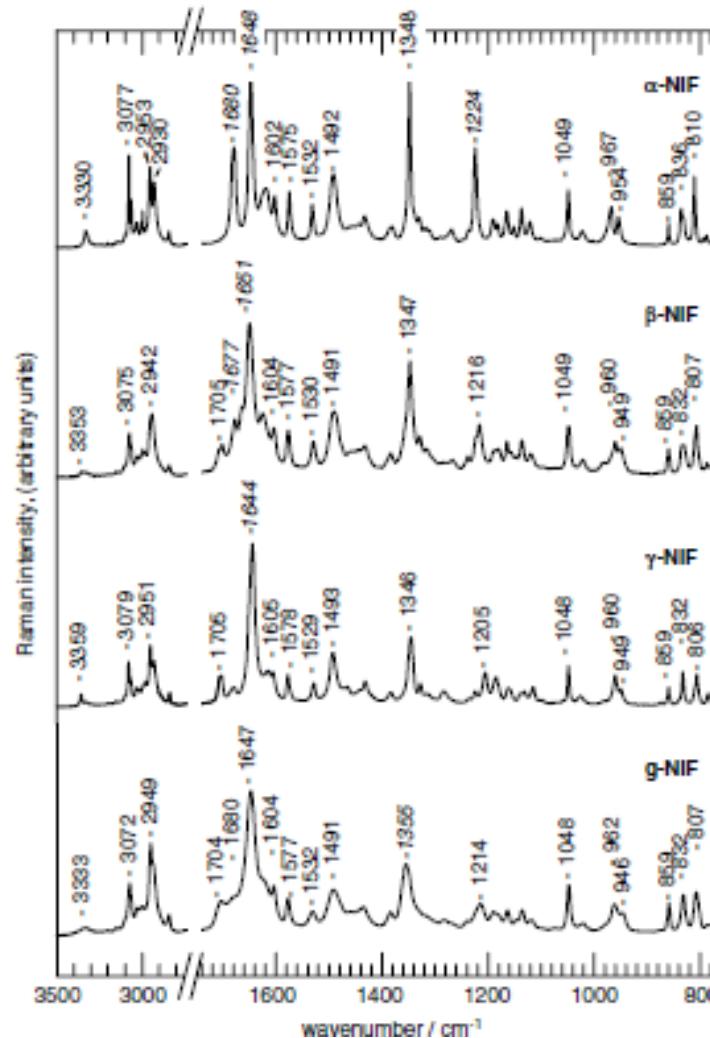
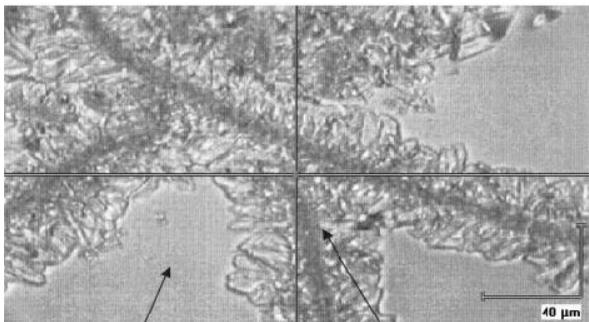


# Stability study: nifedipine

## Raman spectra identify different polymorphs:

### Raman spectra of various forms of nifedipine

- Amorphous
- $\beta$ -crystalline
- $\alpha$ -crystalline
- $\gamma$ -crystalline



Stability of the drug depends on its molecular state. Stability tests may be accelerated by increasing the temperature and/or relative humidity <sup>112</sup>

# Stability of the drug molecular state

- Several delivery technologies for poorly soluble drugs rely on stabilising the drug in its amorphous form to increase its dissolution and bioavailability
- Amorphous forms are better maintained at below  $T_g$  temperature and under dried condition
- Processing (e.g. milling or micronising) can sometime makes crystalline materials partially amorphous – increase complexity, creating unpredictable outcomes
- All forms, amorphous or meta stable crystals, eventually convert to the most stable, slowest dissolving crystalline form which can make the drug therapeutically ineffective
- Stability tests may be accelerated by increasing the temperature and/or relative humidity

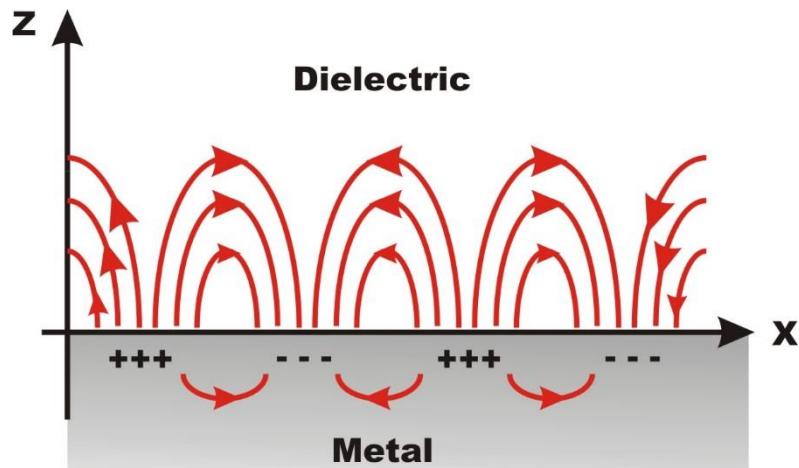
# SERS

Surface-enhanced Raman spectroscopy or surface-enhanced Raman scattering (SERS) is a surface-sensitive technique that enhances Raman scattering by molecules adsorbed on rough metal surfaces or by nanostructures

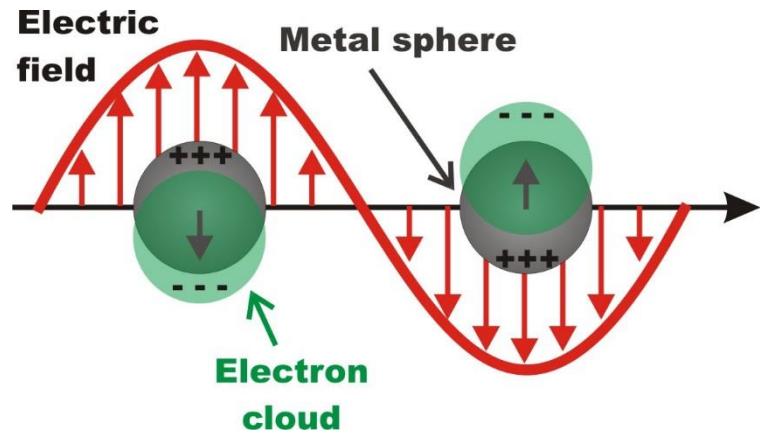
# What is a surface plasmon?

A collective oscillation of surface conduction electrons in materials with a *negative real* and *small positive imaginary* dielectric constant

## Propagating surface plasmons (surface plasmon polaritons)



## Localized surface plasmons

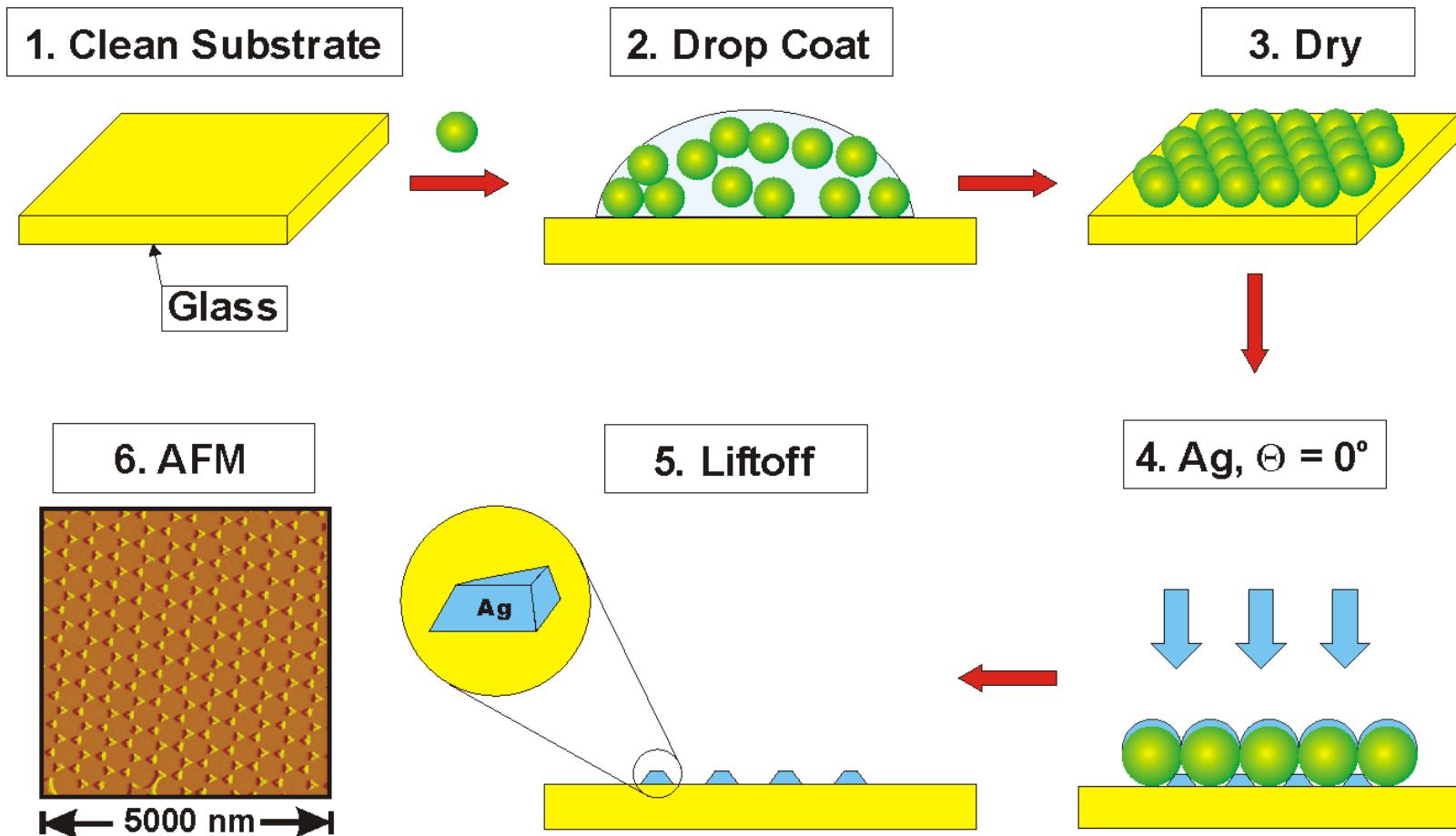


- Thin metal films ( $\sim 50$  nm)
- Propagate 10-100  $\mu\text{m}$  along x-y
- $l_d \sim 200$  nm

- Particle size  $\ll \lambda$
- Plasmon is localized
- $l_d \sim 5$  nm

# Fabrication: Nanosphere Lithography (NSL)

Single Layer Periodic Particle Array



# Applications of SERS

## Single Molecule SERS

Frequency Domain Existence Proof of Single Molecule SERS

Structure & Electrodynamics of “Hot Spots” in SMSERS

Charge Transfer Transitions in SMSERS?

Wavelength Scanned SMSERS Excitation Spectroscopy

## Electrochemical SERS

Electrochemical SERRS: Cytochrome c, ET at Biological/Electrode Interface

## Surface Science & Catalysis

UHV SERS and Temperature Programmed Desorption Spectroscopy

Toward *Operando* SERS

Tip-Enhanced Raman Spectroscopy (TERS)

## Chemical & Biological Sensing

*In Vivo* Glucose Sensing by SERS

Rapid Detection of an Anthrax Biomarker by SERS

Rapid Detection of Chemical Agents by SERS

## Art Conservation

# Single Molecule SERS: EF ~ $10^{14}$ !!

0.5 Molecules per nanoparticle

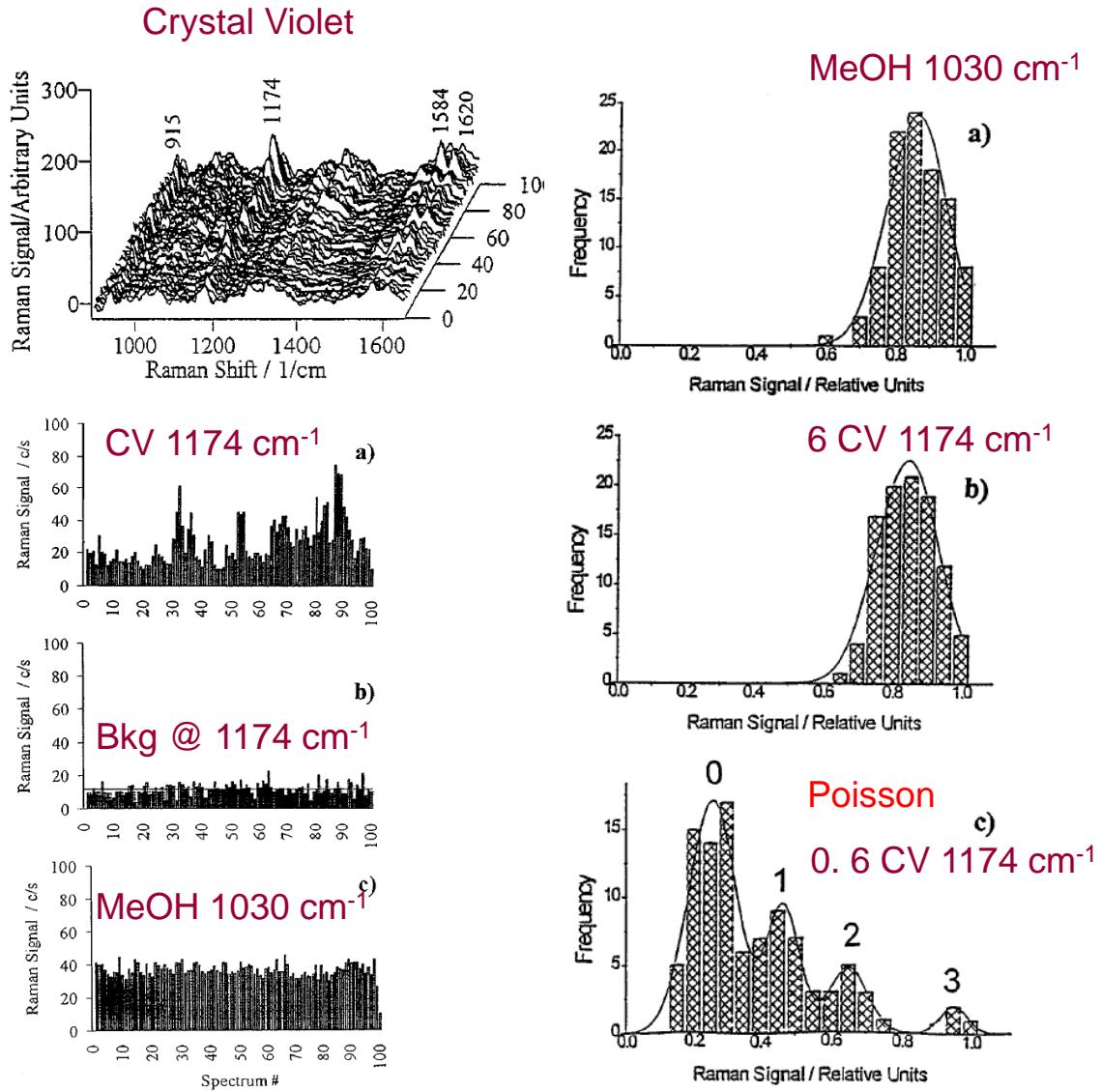
Crystal Violet

830nm excitation

200mW  
Focused Illumination

Brownian Motion

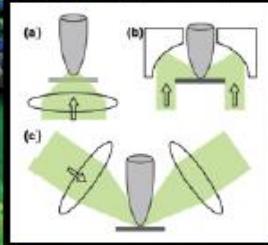
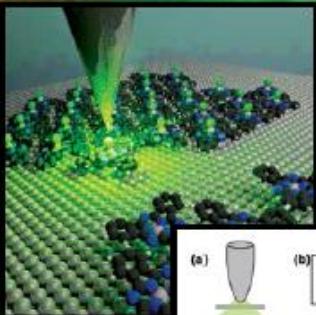
In  $\text{H}_2\text{O} + \text{O}_2$



# Applied Spectroscopy

An International Journal of Spectroscopy

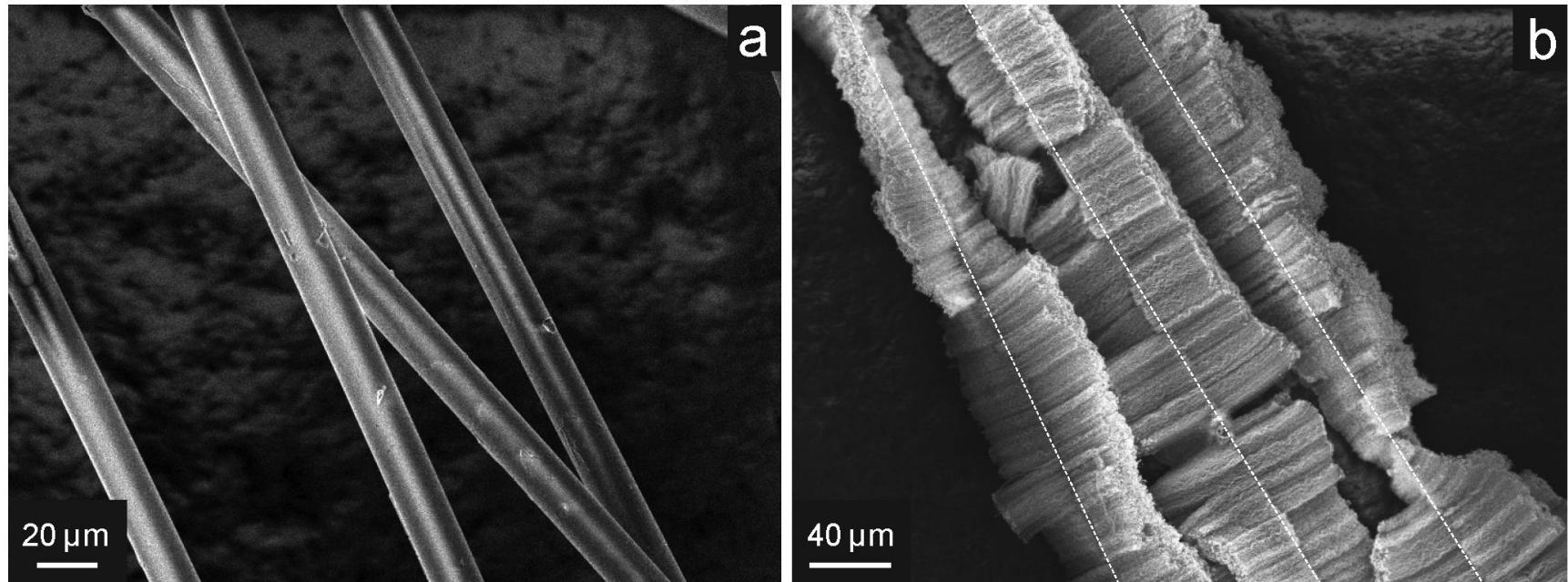
SPECIAL SERS-TERS ISSUE • IN MEMORY OF RICHARD VAN DUYNE  
GUEST EDITORS: AMANDA HAES AND NAN JIANG



# Raman spectroscopy for Nanotechnology

# SEM images of silica fibres before and after the CNT growth

## for preparation of Hierarchical polymer nanocomposites



Collaboration with Prof. A. Bismarck  
Qian et al. Carbon 48, 277 (2010)  
Qian et al. Nanoscale 3, 4759 (2011)

# Raman mapping around carbon nanotubes grafted silica fibres in polymer nanocomposites

## Nanoscale

Cite this: DOI: 10.1039/c1nr10497g

[www.rsc.org/nanoscale](http://www.rsc.org/nanoscale)

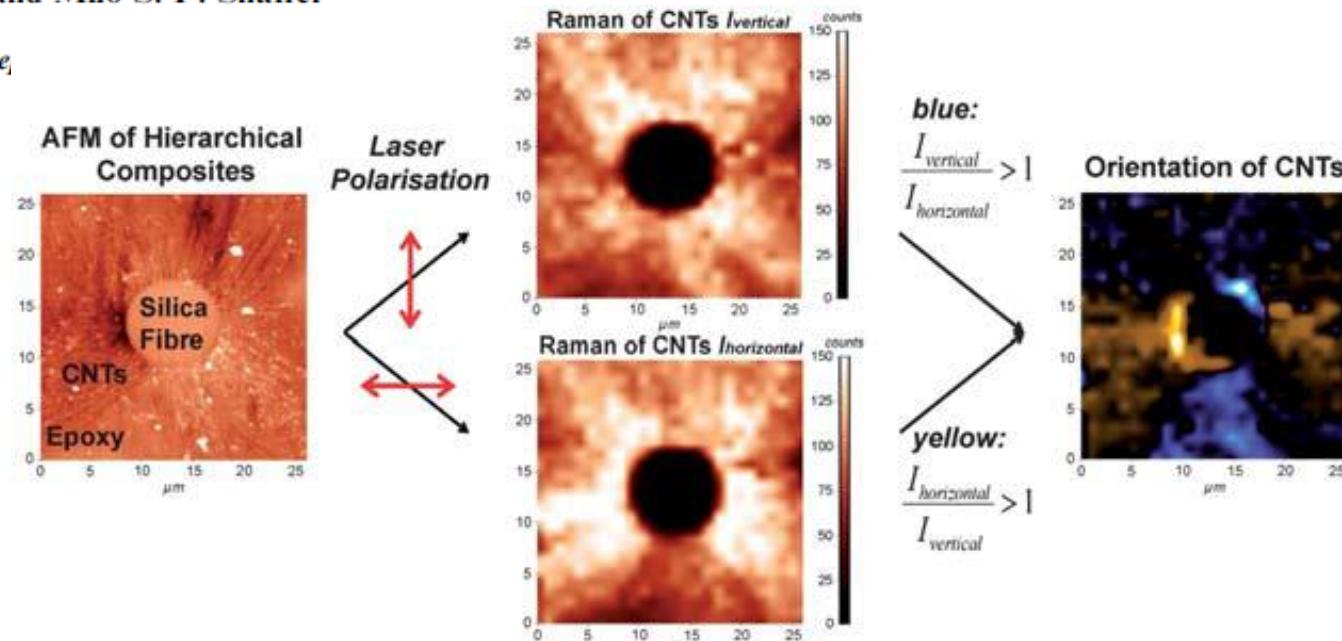
PAPER

### ■ Mapping local microstructure and mechanical performance around carbon nanotube grafted silica fibres: Methodologies for hierarchical composites†

Hui Qian,<sup>abc</sup> Gerhard Kalinka,<sup>d</sup> K. L. Andrew Chan,<sup>e</sup> Sergei G. Kazarian,<sup>e</sup> Emile S. Greenhalgh,<sup>a</sup> Alexander Bismarck<sup>\*ac</sup> and Milo S. P. Shaffer<sup>\*ab</sup>

Received 16th May 2011, Accepted 1st July 2011

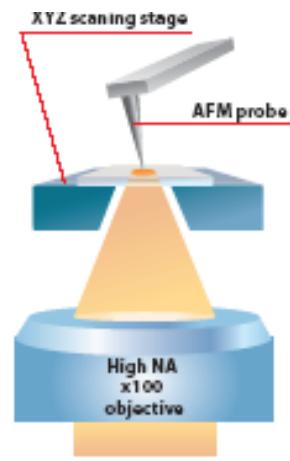
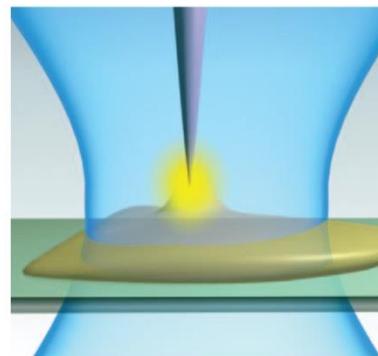
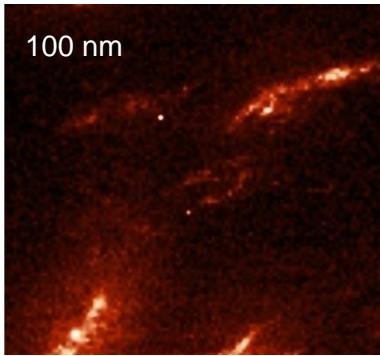
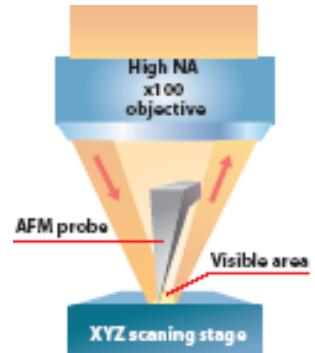
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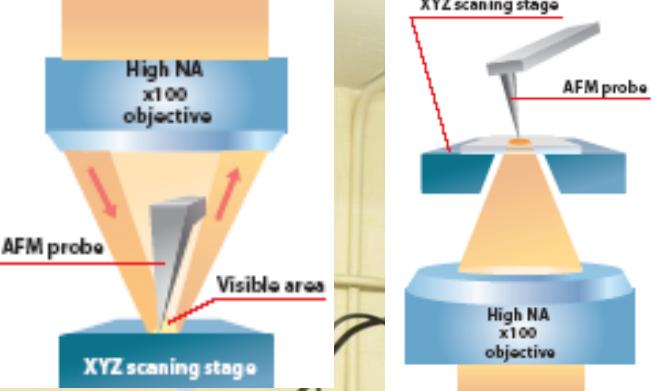


# Summary - nanotubes grafted silica fibres

- The combined AFM (Atomic Force Microscopy) /Raman approach is useful tool for characterisation of hierarchical composites
- It provides information about distribution and orientation of CNT around main fibres.

# Tip-enhanced Raman/AFM: nanoscale resolution

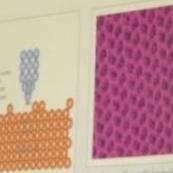




## SPM study

### STM techniques

• Contour Current mode



Individual carbon nanotubes imaged in the SPM surface has size 232 nm  
Image courtesy of Iridium (U)

• AFM

• EFM

**RENISHAW**  
inVia Raman Microscope

Confocal Raman  
spectrometer

M. D. - intensity of carbon  
Top-Enhanced Raman  
spatial resolution as  
Gorenstein, NT-MDT

NT-MDT  
Molecular Device and Tools for Spectroscopy

# Tip-enhanced Raman/AFM: nanoscale resolution

IOP PUBLISHING

Nanotechnology 21 (2010) 445704 (6pp)

NANOTECHNOLOGY

doi:10.1088/0957-4484/21/44/445704

## Finding a needle in a chemical haystack: tip-enhanced Raman scattering for studying carbon nanotubes mixtures

K L Andrew Chan and Sergei G Kazarian

Department of Chemical Engineering, Imperial College London, SW7 2AZ, UK

E-mail: [s.kazarian@imperial.ac.uk](mailto:s.kazarian@imperial.ac.uk)

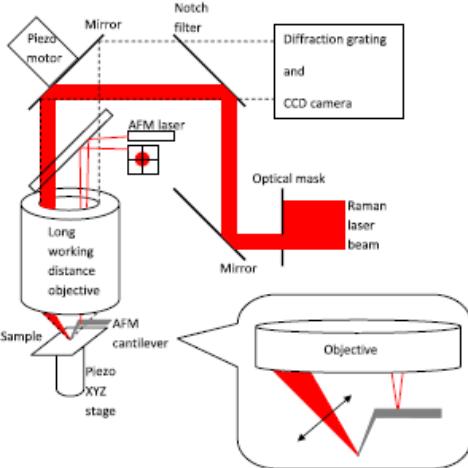
Nanotechnology, 21, 445704 (2010)

Nanotechnology, 22, 175701 (2011)

Received 5 August 2010, in final form 31 August 2010

Published 8 October 2010

Online at [stacks.iop.org/Nano/21/445704](http://stacks.iop.org/Nano/21/445704)



IOP PUBLISHING

Nanotechnology 22 (2011) 175701 (5pp)

NANOTECHNOLOGY

doi:10.1088/0957-4484/22/17/175701

## Tip-enhanced Raman mapping with top-illumination AFM

K L Andrew Chan and Sergei G Kazarian

Department of Chemical Engineering, Imperial College London, SW7 2AZ, UK

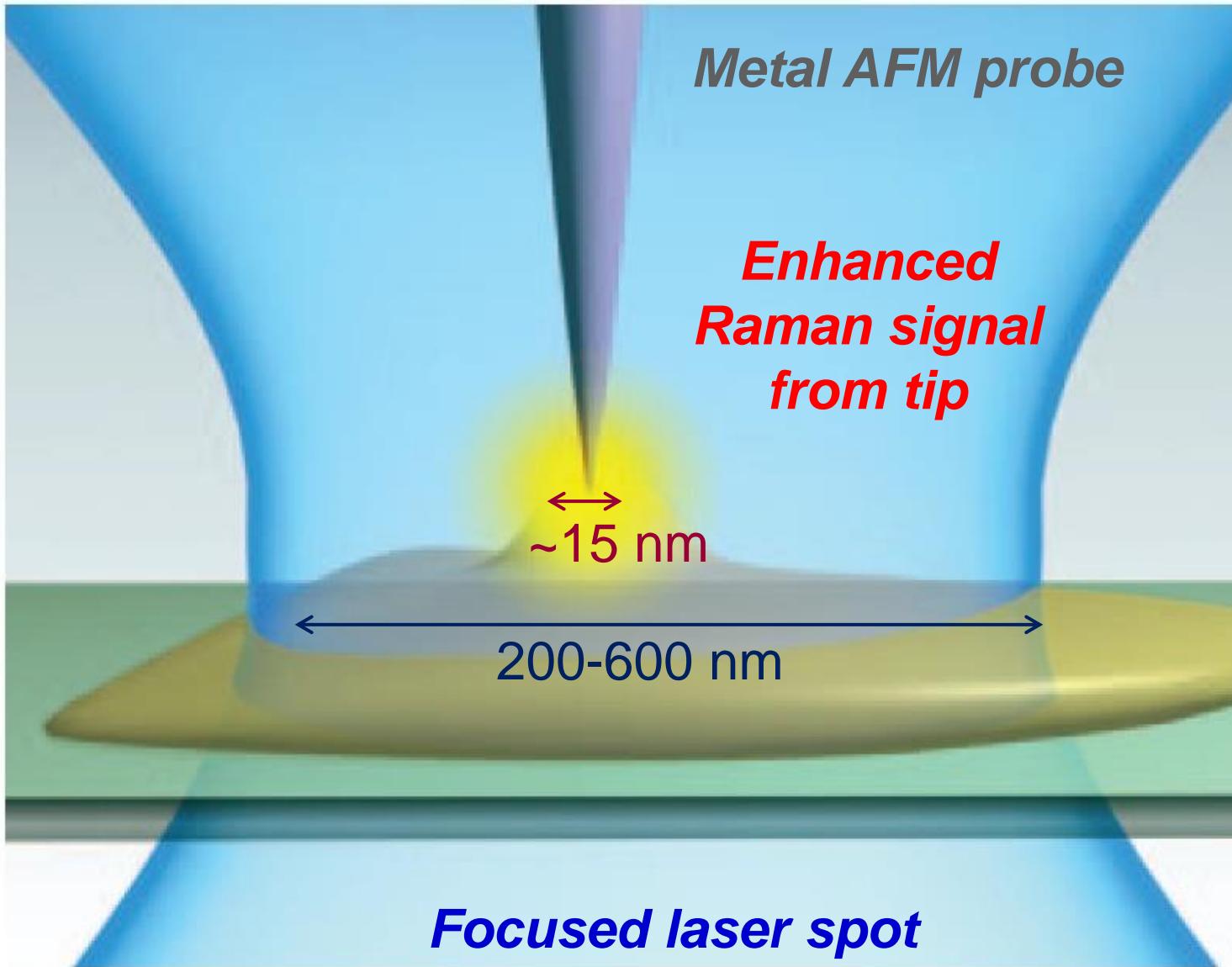
E-mail: [s.kazarian@imperial.ac.uk](mailto:s.kazarian@imperial.ac.uk)

Received 2 January 2011, in final form 10 February 2011

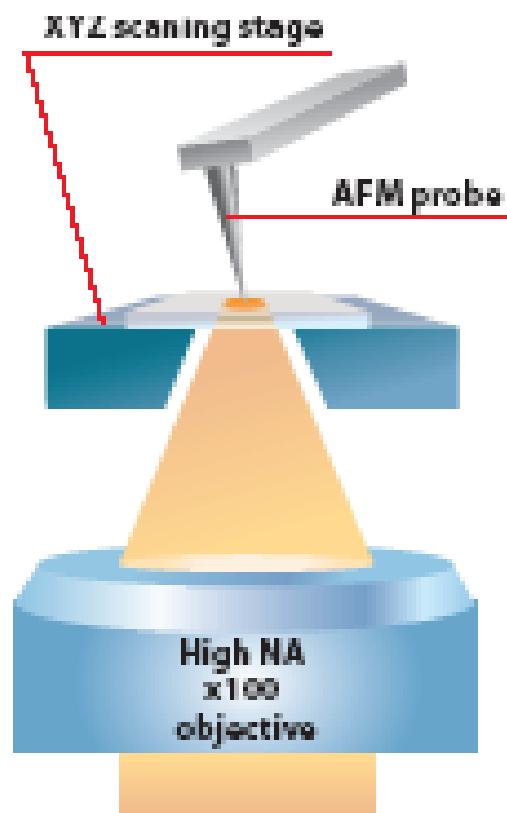
Published 16 March 2011

Online at [stacks.iop.org/Nano/22/175701](http://stacks.iop.org/Nano/22/175701)

# Principles of Tip Enhanced Raman microscopy



# TERS - Inverted configuration

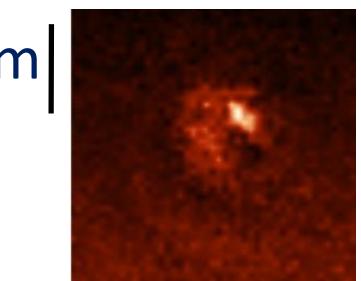
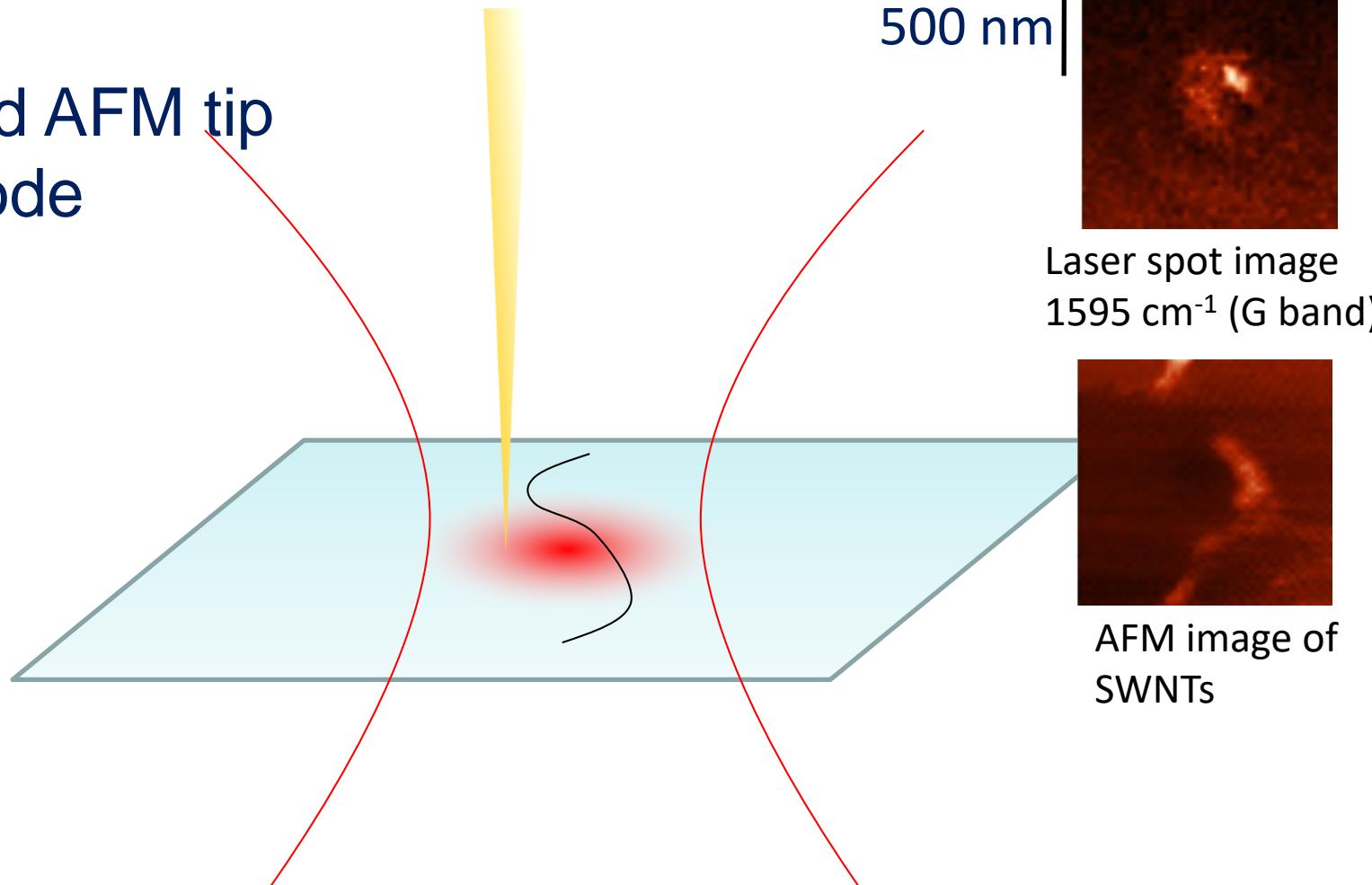


# Aligning tip to laser spot

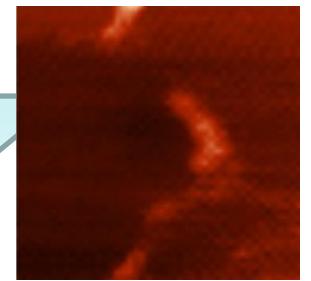
Wavelength = 633 nm

Laser power = 0.01 mW

Gold coated AFM tip  
Contact mode



Laser spot image  
 $1595 \text{ cm}^{-1}$  (G band)



AFM image of  
SWNTs

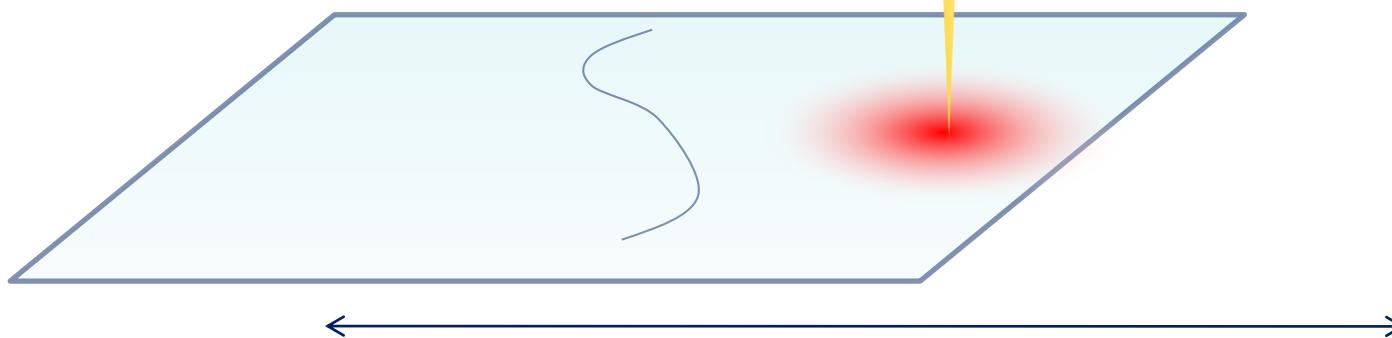
# Scanning sample

Wavelength = 633 nm

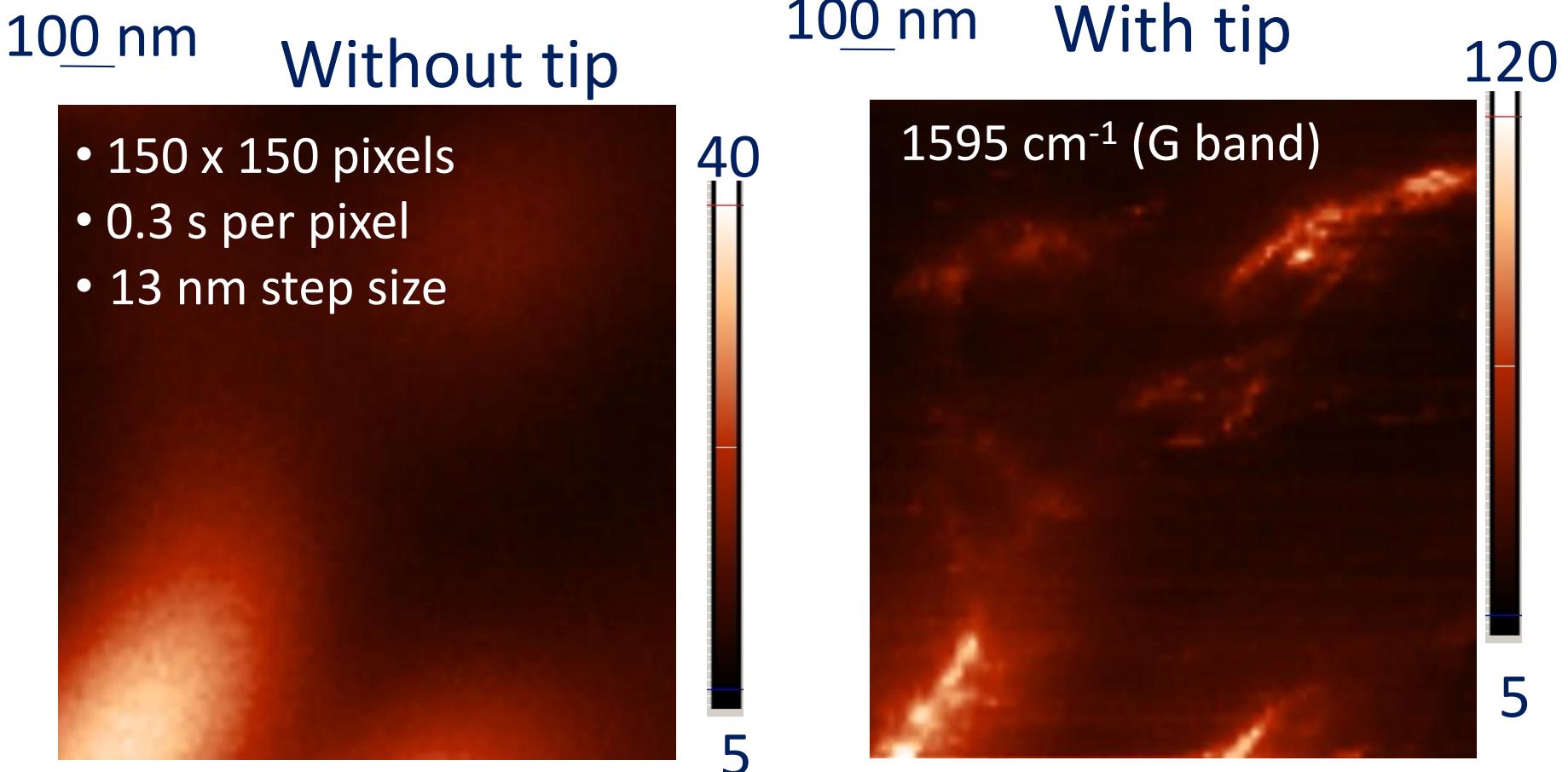
Laser power = 0.01 mW

Gold coated AFM tip  
fixed at “hot spot”

0.3 s per spectrum



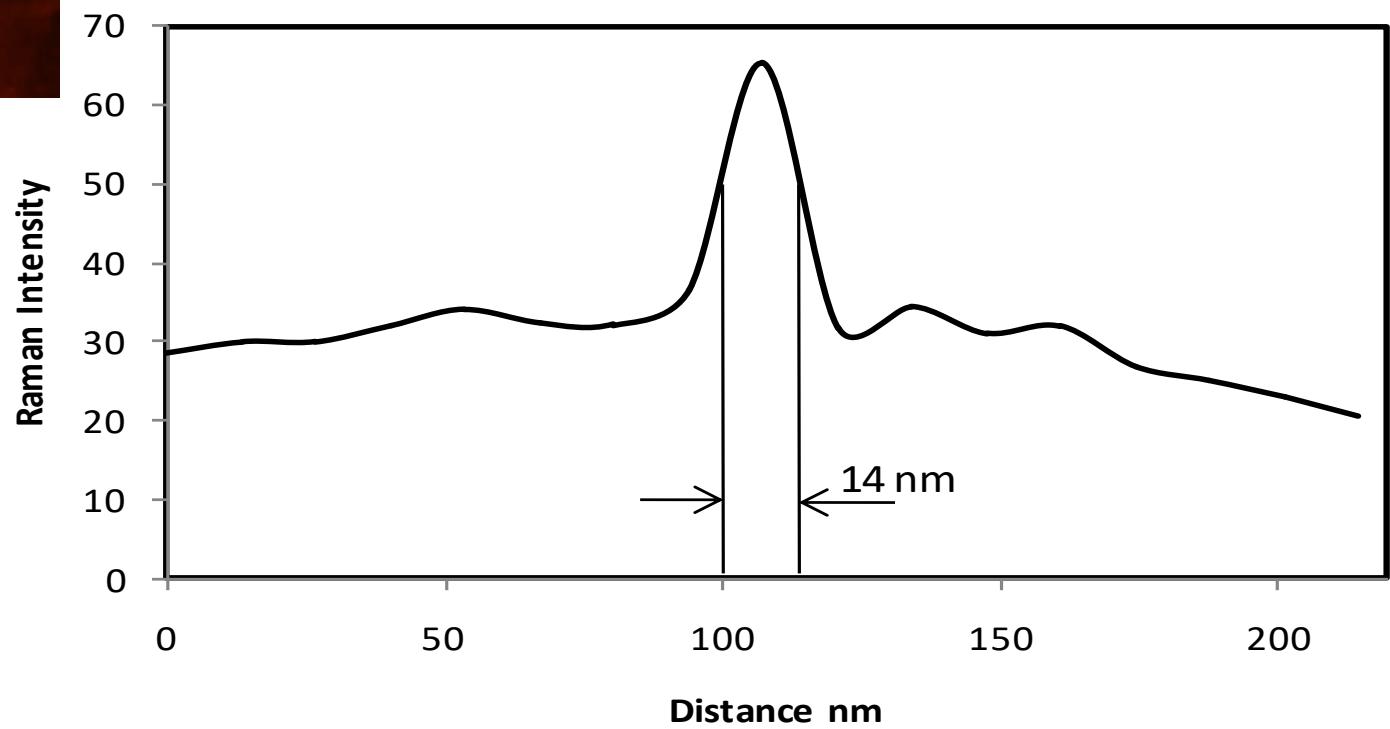
# TERS images in inverted configuration of dispersed carbon nanotubes (HiPCo SWNT)



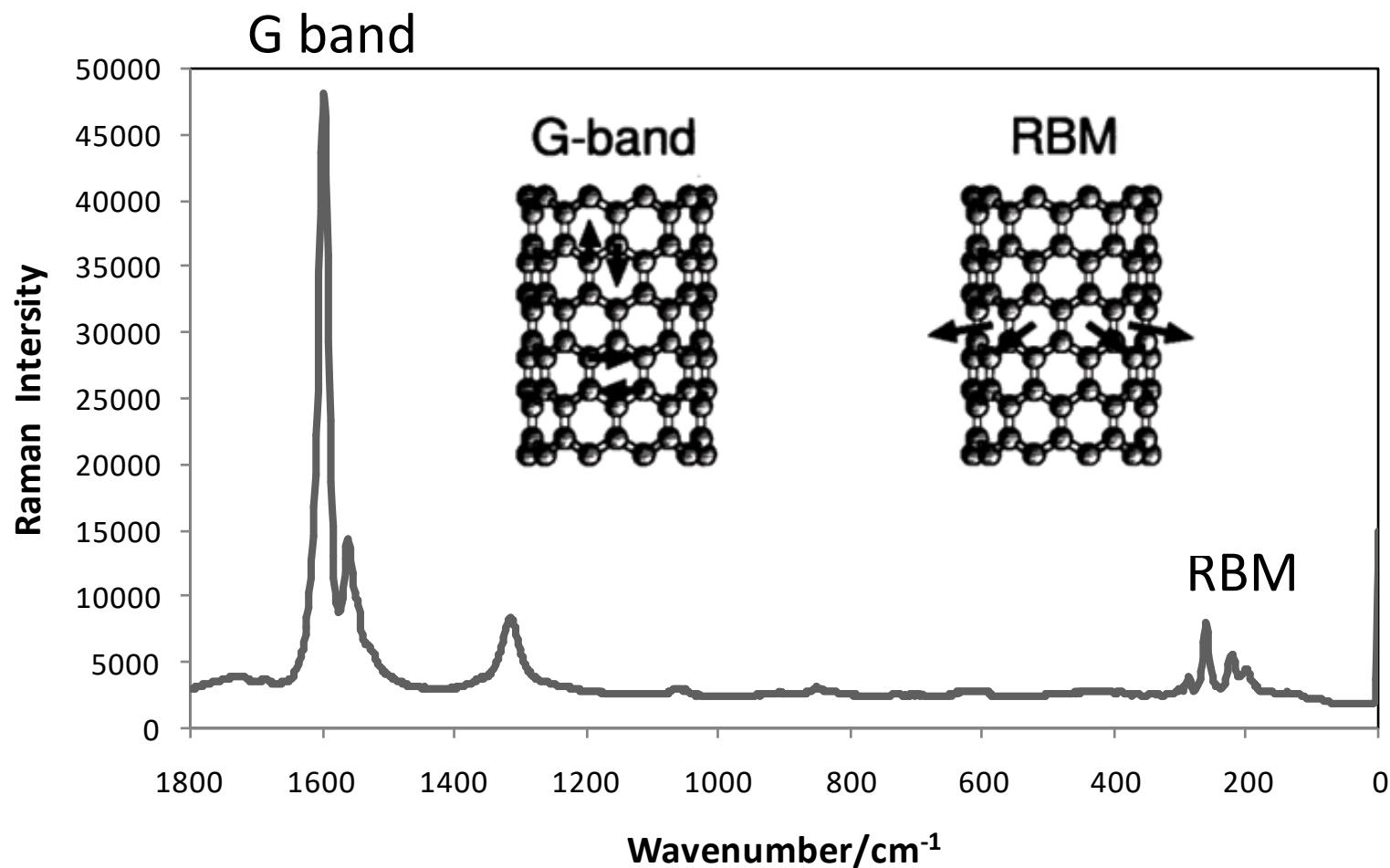
Chan and Kazarian, Nanotechnology, 21, 2010, 445704

Instability of the tip at higher laser power

# Raman intensity profile across the nanotubes

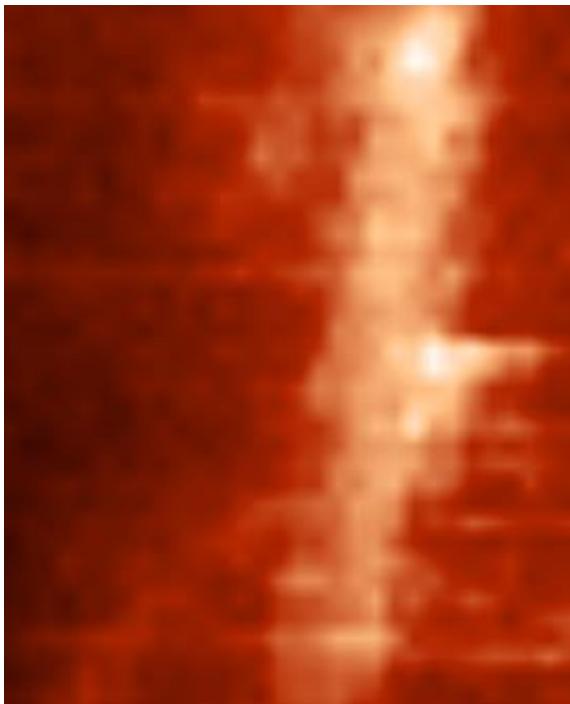


# Raman spectrum of HiPCo SWNTs



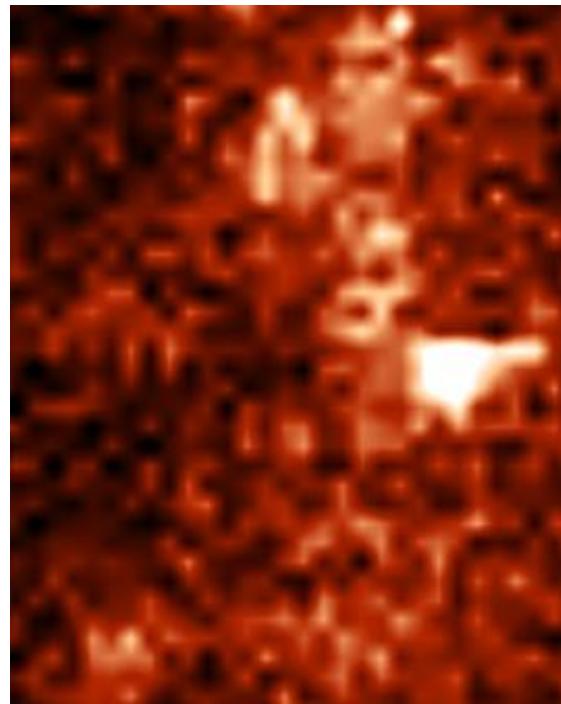
# TERS images SWNTs in inverted configuration

$1595\text{ cm}^{-1}$  (G band)

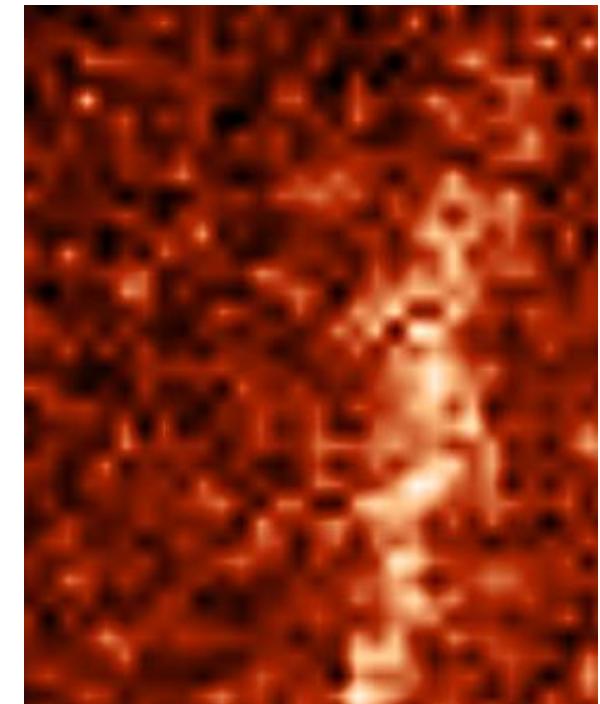


50 nm

$287\text{ cm}^{-1}$

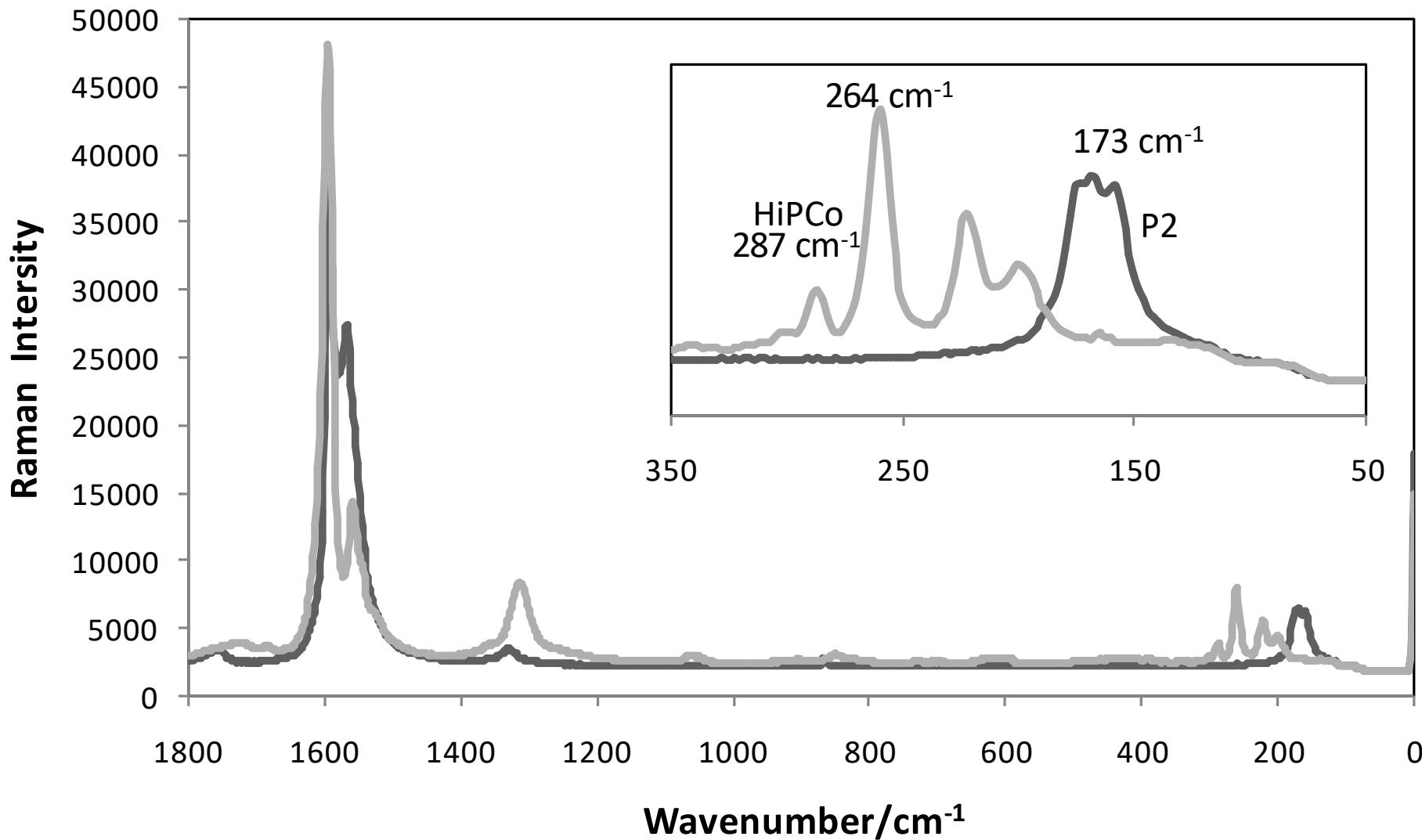


$264\text{ cm}^{-1}$



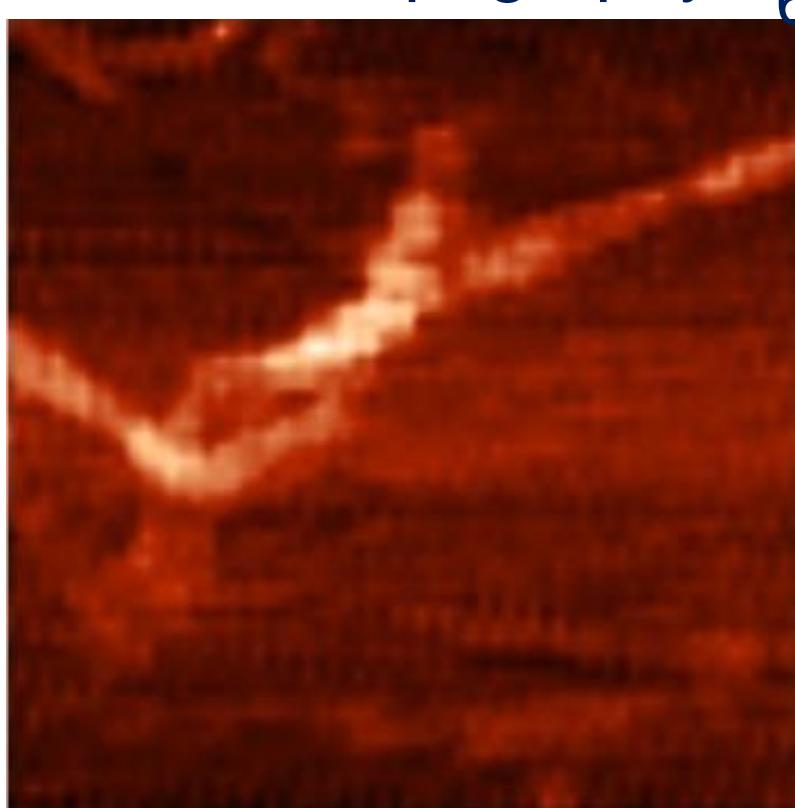
- $25 \times 35$  pixels, 8 nm step size
- 0.3 s per pixel
- HiPCo SWNT

# Raman spectra of pre-mixed HiPCo and P2-SWNT



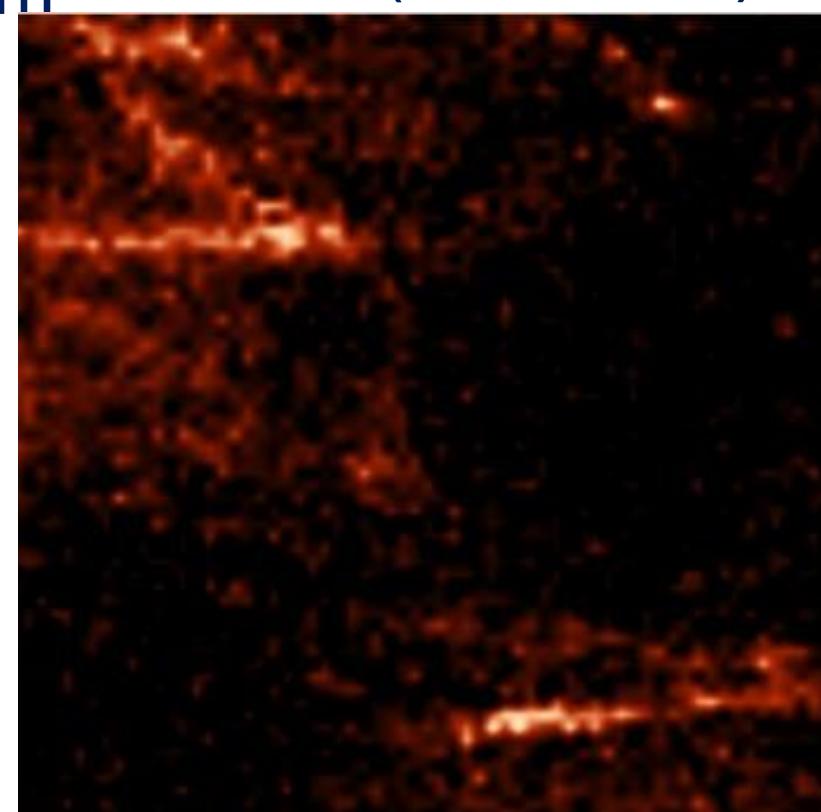
# AFM and TERS images of SWNT mixture: differentiating carbon nanotubes

100 nm Topography



60 nm

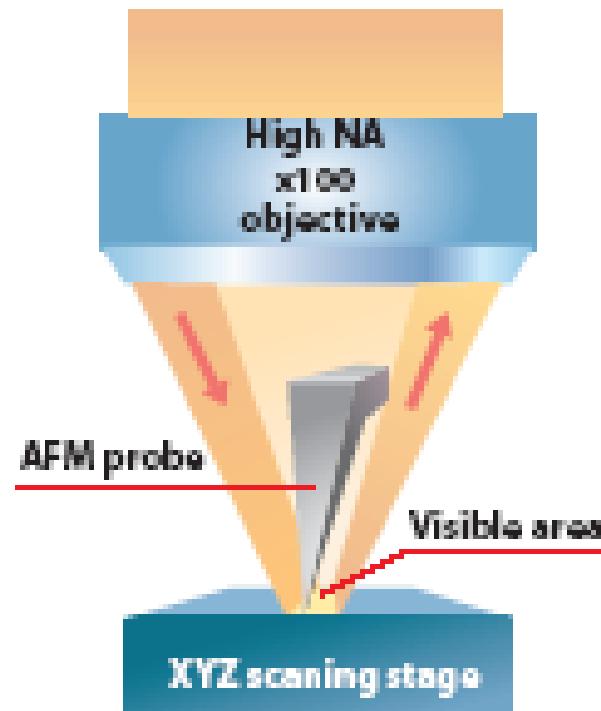
P2 ( $173 \text{ cm}^{-1}$ )



5

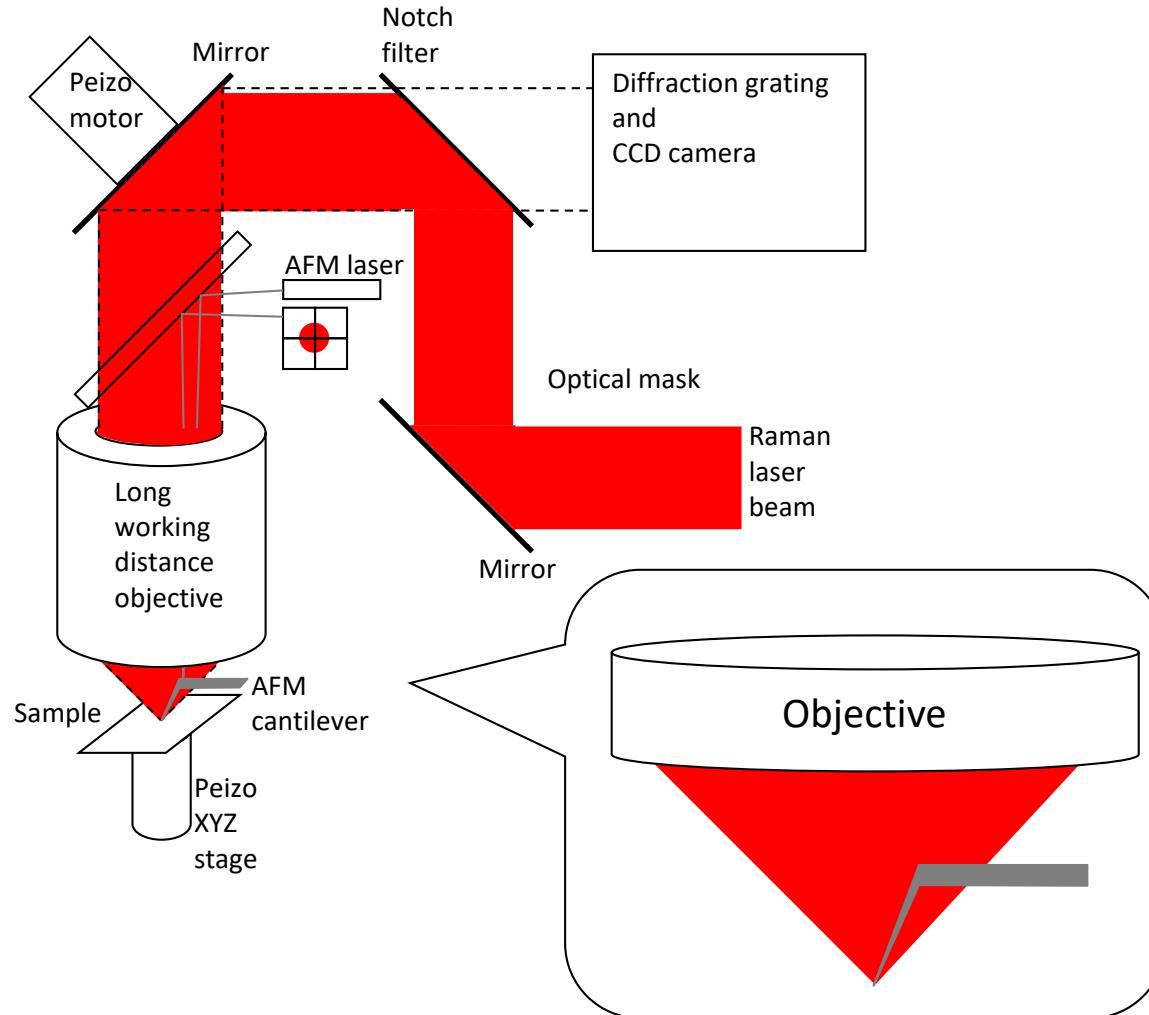
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# TERS - Upright configuration

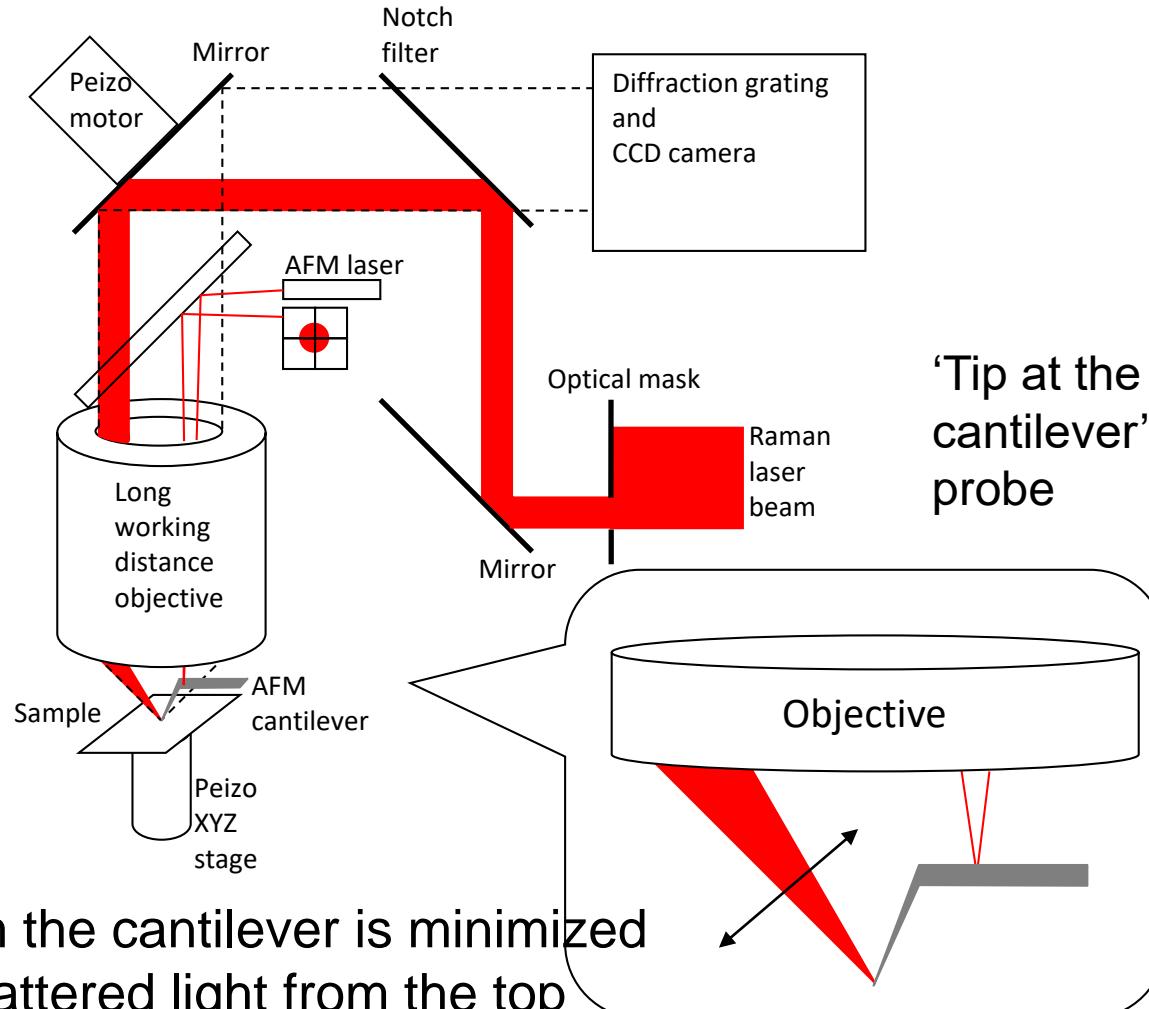


The laser beam is focused and the scattered light is collected by the same objectives

# Upright configuration for TERS of non-transparent or thick samples



# Upright configuration for TERS of non-transparent or thick samples



- Shadowing from the cantilever is minimized
- Reduction of scattered light from the top surface of cantilever

# Aligning laser spot to tip

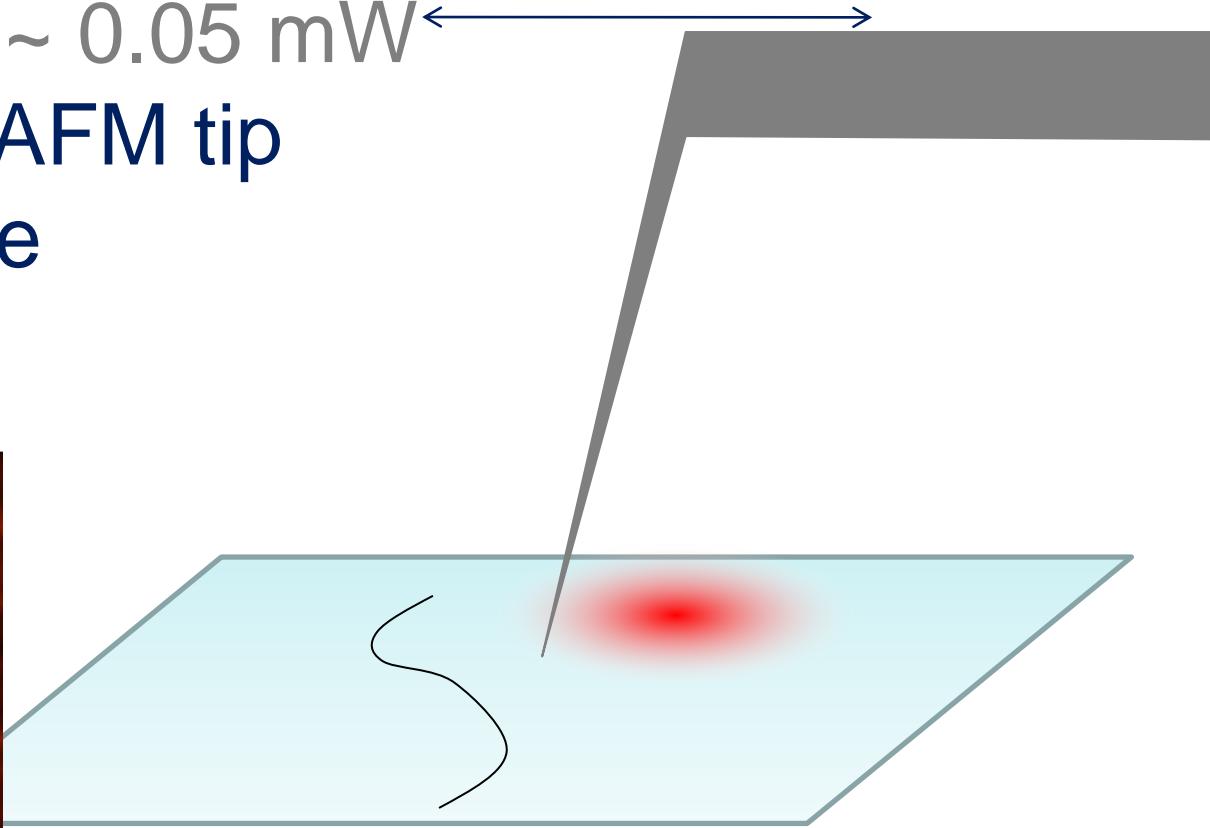
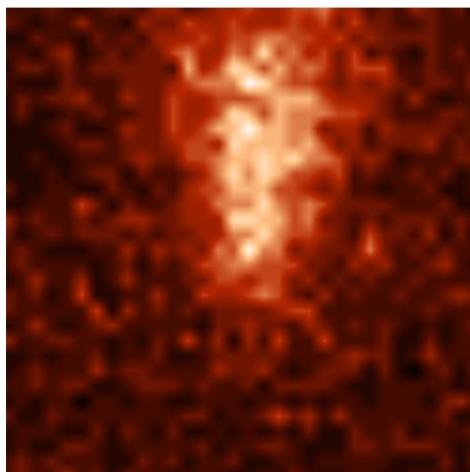
Wavelength = 633 nm

Laser power ~ 0.05 mW

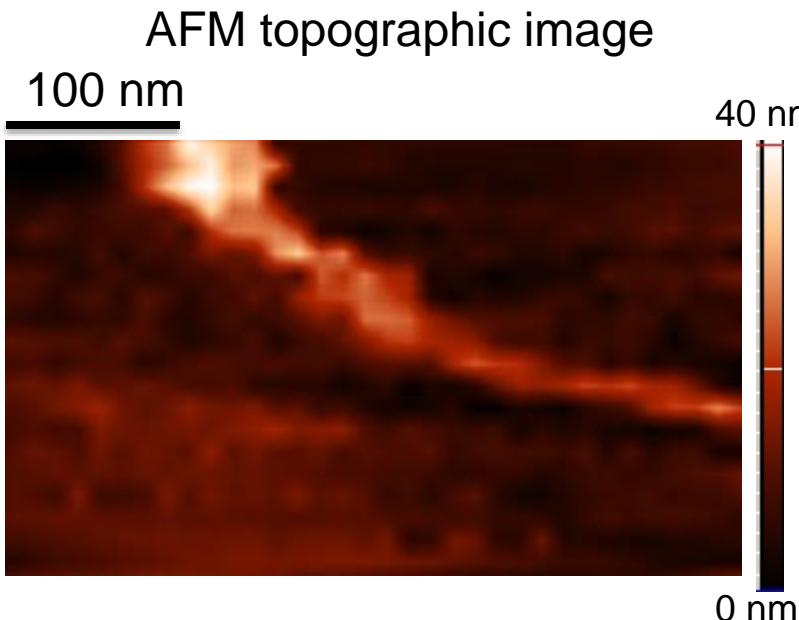
Gold coated AFM tip

Contact mode

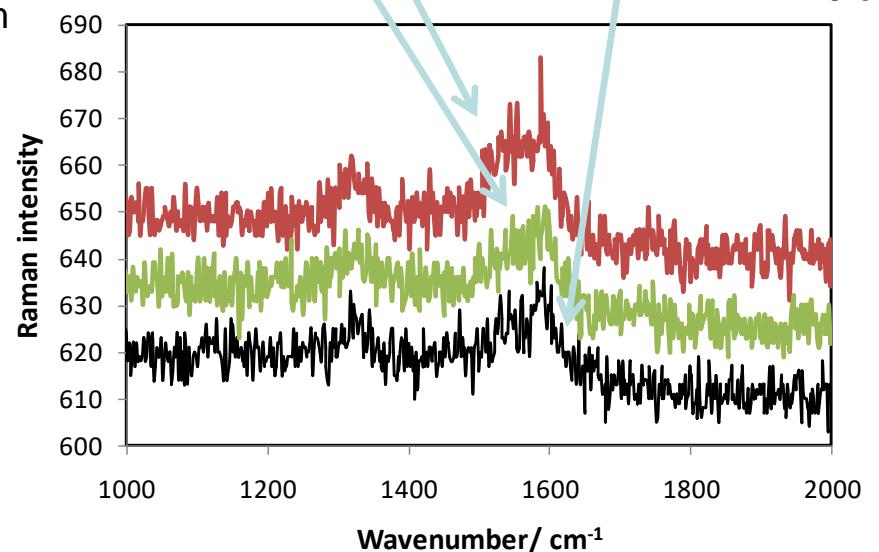
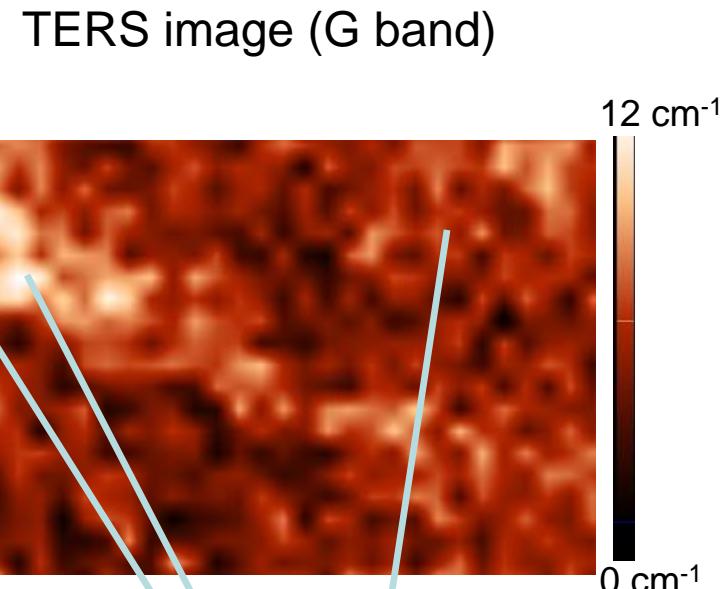
1 μm



# Upright configuration TERS of SWNTs

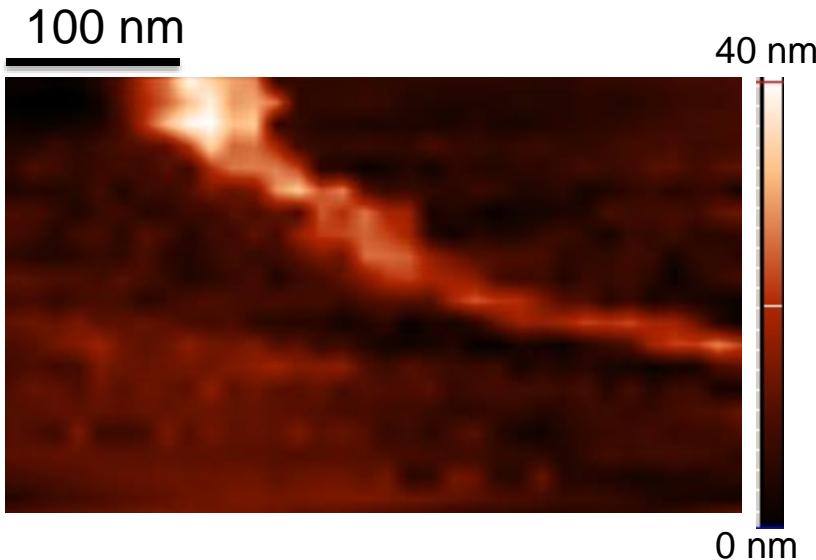


1 s per pixel

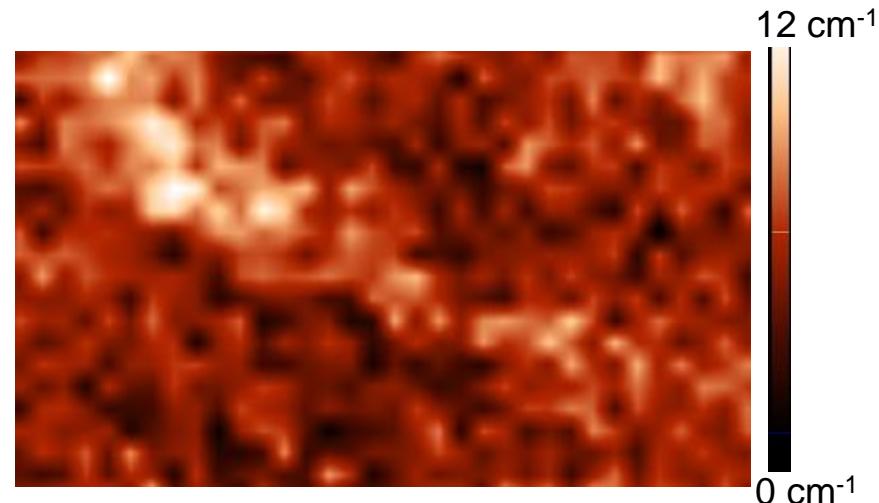


# Upright configuration TERS of SWNTs

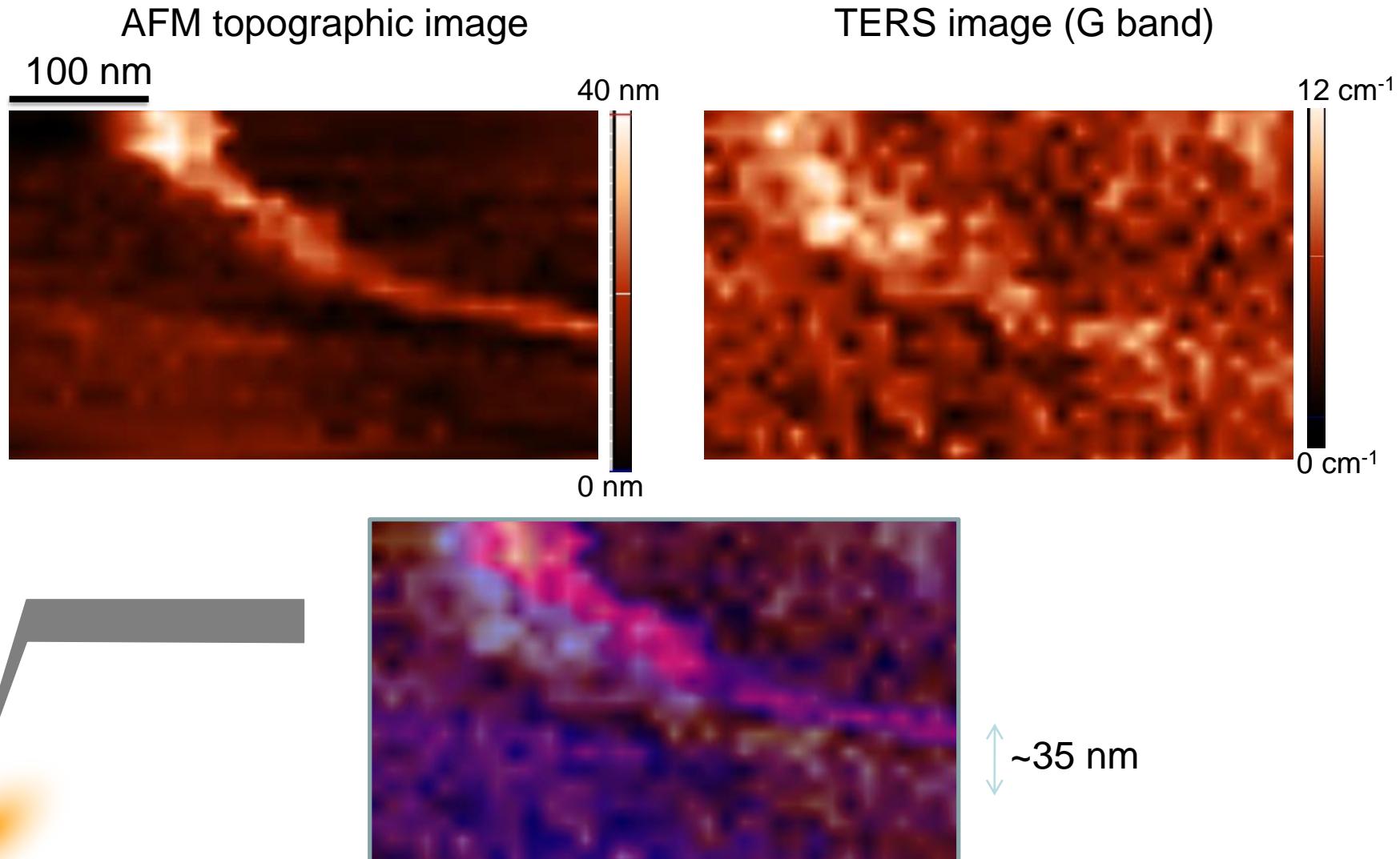
AFM topographic image



TERS image (G band)



# Upright configuration TERS of SWNTs



TERS image of the carbon nanotubes is slightly offset lower to the topographic image by approximately 35 nm. This indicates that the enhancement zone is on the side of the tip apex rather than at the end of the tip.

# Key points on TERS

## Inverted TERS

- Imaging with ca.10 nm spatial resolution
- Higher Raman collection efficiency
- Transparent or very thin samples only

## Upright TERS

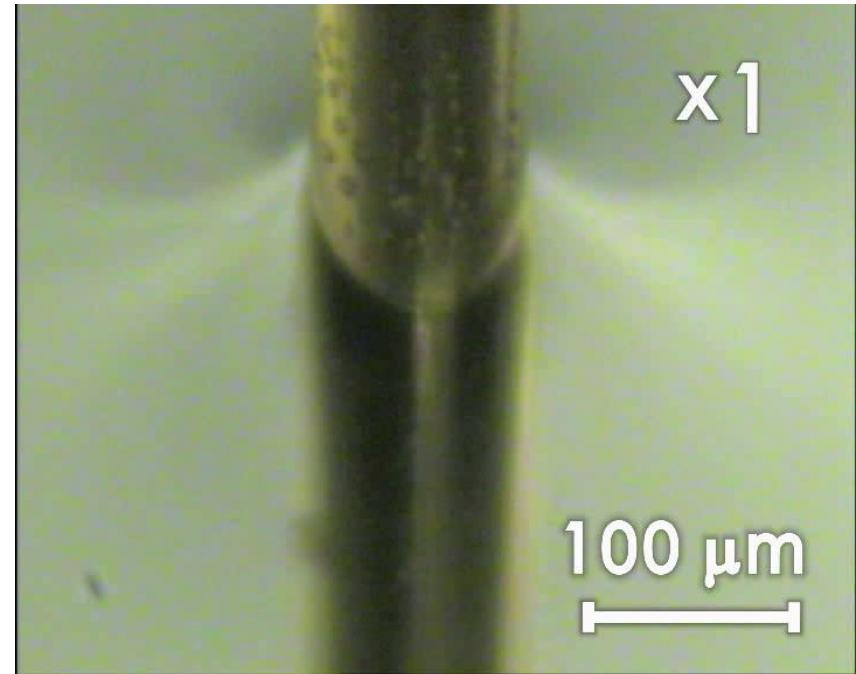
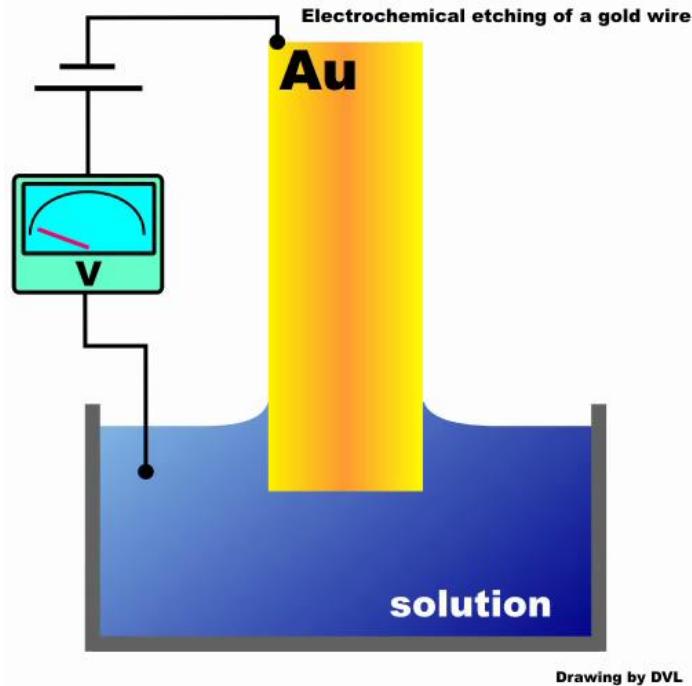
- Imaging with 20-50 nm spatial resolution
- More difficult to obtain optimal polarisation
- Suitable for opaque and thick samples

# Towards different tips: electrochemical etching of gold wires

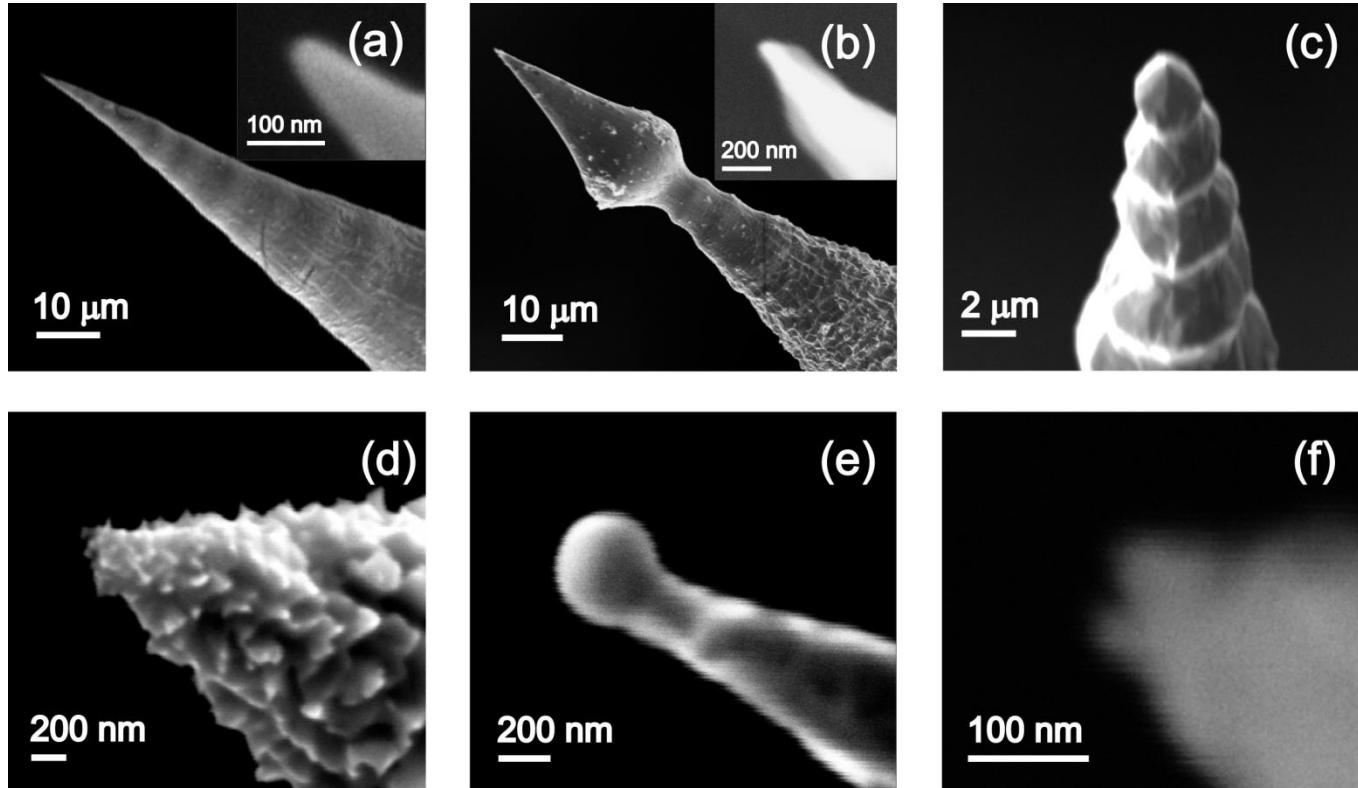
Electrochemical Etching of Au wires

Bin Ren et al. Appl. Phys. Lett. 101105 (2007)

Kharintsev, et al J. Phys. D: Appl. Phys. **46**, 145501 (2013).

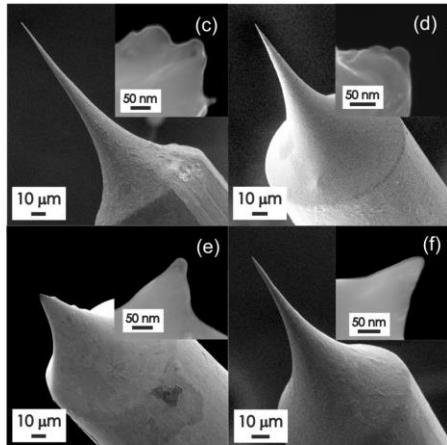
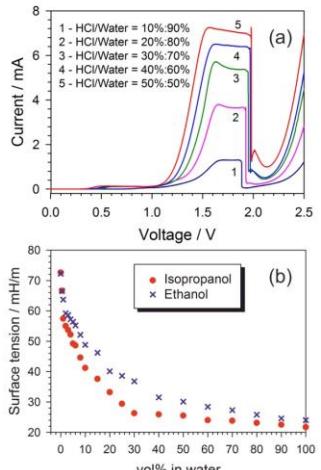


# Towards well-defined tips



S. S. Kharintsev, et al J. Phys. D: Appl. Phys. **46**, 145501 (2013)

# Tip-enhanced Raman: nanoscale resolution



## Tip-Enhanced Raman Spectroscopy (TERS) for *in Situ* Identification of Indigo and Iron Gall Ink on Paper

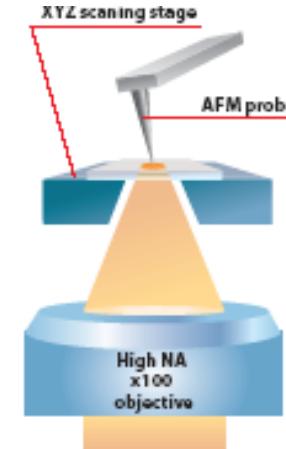
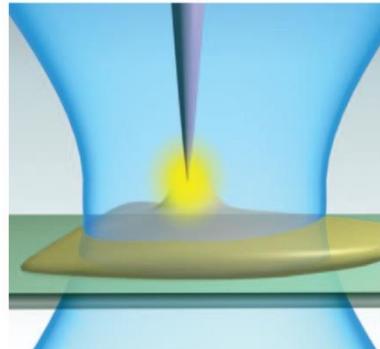
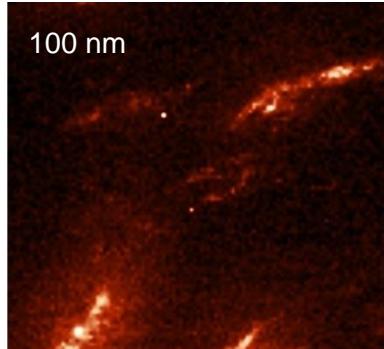
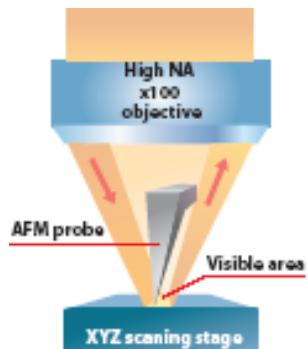
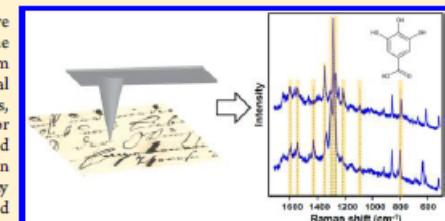
Dmitry Kurouski,<sup>†</sup> Stephanie Zaleski,<sup>†</sup> Francesca Casadio,<sup>‡</sup> Richard P. Van Duyne,<sup>\*†</sup> and Nilam C. Shah<sup>\*†</sup>

<sup>†</sup>Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois United States

<sup>‡</sup>The Art Institute of Chicago, 111 S. Michigan Avenue, Chicago, Illinois United States

### Supporting Information

**ABSTRACT:** Confirmatory, nondestructive, and noninvasive identification of colorants *in situ* is of critical importance for the understanding of historical context and for the long-term preservation of cultural heritage objects. Although there are several established techniques for analyzing cultural heritage materials, there are very few analytical methods that can be used for molecular characterization when very little sample is available, and a minimally invasive approach is required. Tip-enhanced Raman spectroscopy (TERS) is a powerful analytical technique whose key features include high mass sensitivity, high spatial resolution, and precise positioning of the tip. In the current proof-of-concept study we utilized TERS to identify indigo dye and iron gall ink *in situ* on Kinwashi paper. In addition, TERS was used to identify iron gall ink on a historical document with handwritten text dated to the 19th century. We demonstrate that TERS can identify both of these colorants directly on paper. Moreover, vibrational modes from individual components of a complex chemical mixture

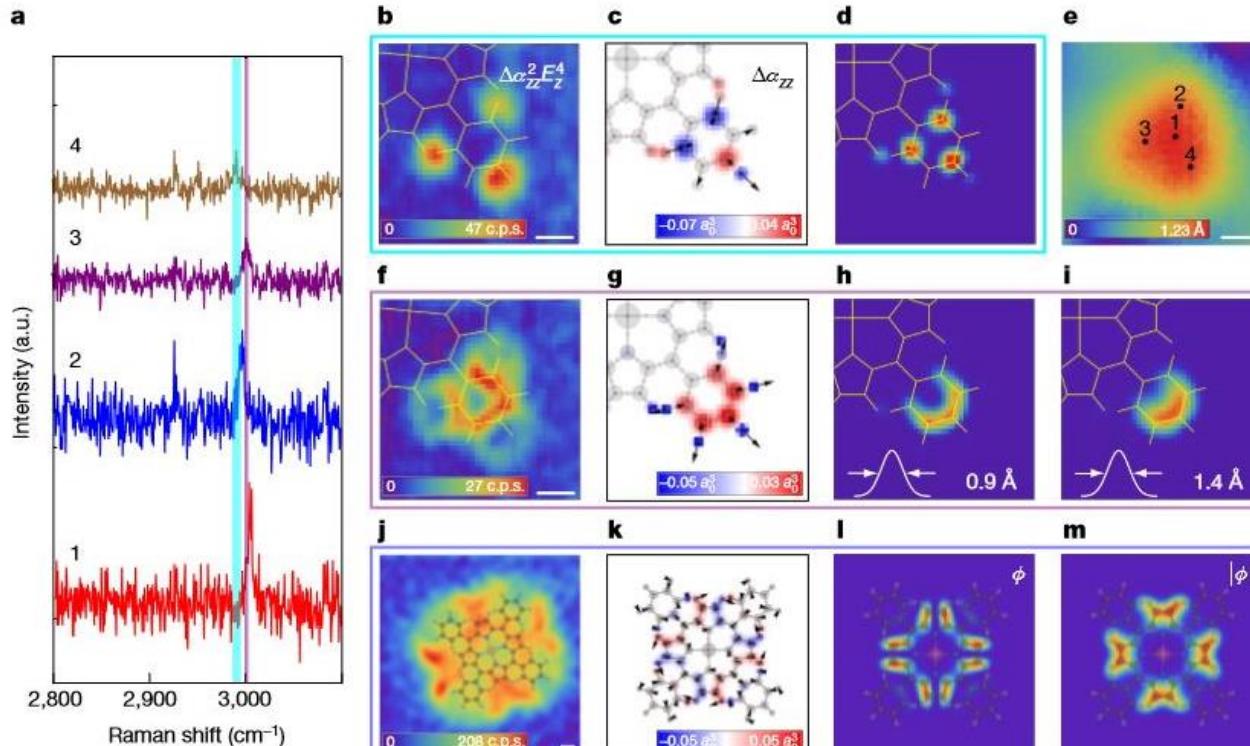


# Tip-enhanced Raman/AFM: ångström-scale resolution

NATURE Apkarian et al  
Volume: 568 Issue: 7750  
Pages: 78-- Published: 2019

## LETTER

RESEARCH LETTER

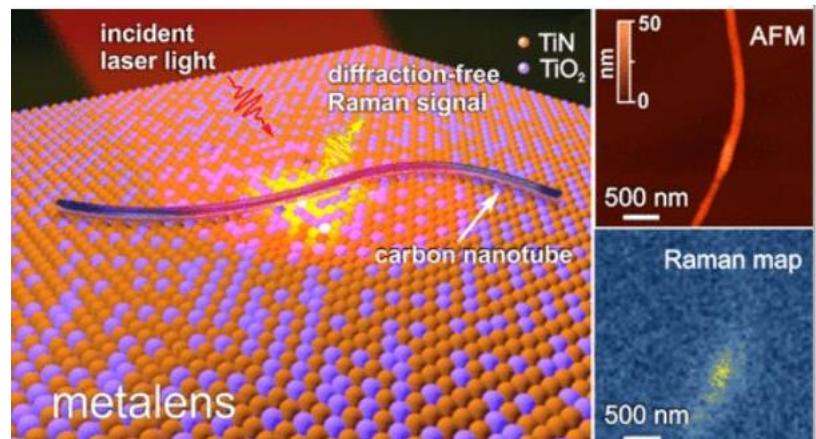


**Fig. 4 | Close-ups of TER-SM images and their simulations.** **a**, Variation of the C–H stretching frequency within a phenyl group is shown by four representative spectra recorded on the points indicated in the scanning tunnelling microscope (STM) topography in **e**. The spectra are extracted from a hyperspectral image recorded on a  $40 \times 40$  grid with 4-s integration time per grid point. **b–d**, TERS map of the asymmetric C–H stretching mode, integrated over the blue band ( $2,986\text{--}2,995\text{ cm}^{-1}$ ) in **a** (**b**); colour-coded atomic partitioning of the polarizability differences

topography ( $11 \times 11\text{ \AA}^2$ ) of the lower-right phenyl group in Fig. 2b. **f–i**, TERS map integrated over the purple band ( $2,999\text{--}3,003\text{ cm}^{-1}$ ; **f**),  $\Delta\alpha_{zz}$  (**g**), and images obtained using a Gaussian with FWHM of  $0.9\text{ \AA}$  (**h**) and  $1.4\text{ \AA}$  (**i**). **j–m**,  $29 \times 29\text{ \AA}^2$  Raman map ( $80 \times 80$  grid) integrated over a band ( $1,538\text{--}1,572\text{ cm}^{-1}$ ; **j**),  $\Delta\alpha_{zz}$  map ( $20 \times 20\text{ \AA}^2$ ; **k**) and images obtained using signed polarizability differences (phase  $\phi$  preserved) versus their magnitudes (**l**, **m**). Scale bars are  $2\text{ \AA}$ . Experimental Raman maps in **b–m** are low-pass-filtered for clarity.

# Most recent advances

**Disordered Nonlinear Metalens for Raman Spectral Nanoimaging**  
ACS Applied Materials & Interfaces 2020



Nanoscale

Nanoscale, 2019



PAPER

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[View Journal](#) | [View Issue](#)



Cite this: *Nanoscale*, 2019, **11**, 7710

**Superresolution stimulated Raman scattering microscopy using 2-ENZ nano-composites**

# Tip-enhanced Raman: nanoscale resolution

## Tip-enhanced Raman Spectroscopy

Kirsty F. Gibson and Sergei G. Kazarian  
Imperial College London, London, UK

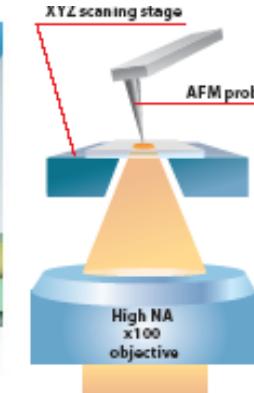
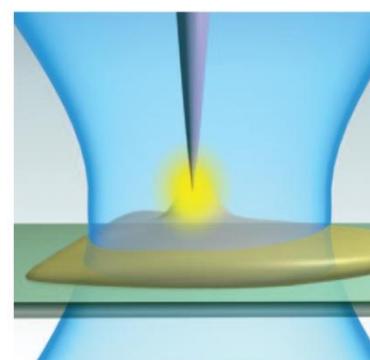
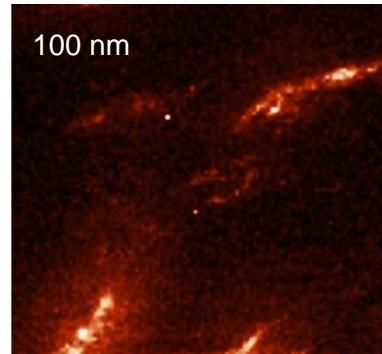
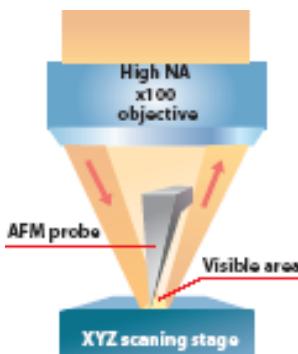
<b>1</b> Introduction	<b>1</b>
<b>2</b> Tip-enhanced Raman Spectroscopy Concept and Underlying Theory	<b>2</b>
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2.3 Sub-diffraction Limited Microscopy	2
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*Tip-enhanced Raman spectroscopy (TERS) is a powerful analytical technique for chemical analysis at the nanoscale. Three different SPM/TERS (scanning probe microscopy/tip-enhanced Raman spectroscopy) modes allow the analysis of a wide range of samples. TERS has been shown to be of great use in materials-based applications, particularly for nanostructured materials and in the analysis of biologically relevant systems. In this article, the fundamentals and theoretical aspects of TERS, the instrumentation required to perform a TERS experiment, and examples of a range of practical applications are discussed.*

K. F. Gibson, S. G. Kazarian “Tip-enhanced Raman spectroscopy”  
Encyclopedia of Analytical Chemistry, Online Wiley, 2014

K. F. Gibson, S. G. Kazarian, S. S. Kharintsev “Tip-enhanced Raman spectroscopy” Encyclopedia of Analytical Chemistry, Online Wiley, 2019



# Selection rules for Infrared and Raman

$$\Delta v = \pm 1 \quad (\text{for harmonic oscillator})$$

$$\frac{\partial \mu}{\partial r} \neq 0 \quad \begin{aligned} & \mu \text{ is a dipole moment} \\ & \text{Infrared active} \end{aligned}$$

$$\frac{\partial \alpha}{\partial r} \neq 0 \quad \begin{aligned} & \alpha \text{ is polarizability} \\ & \text{Raman active} \end{aligned}$$

$3N - 5$  for a linear molecule (which requires 2 rotational co-ordinates).

$3N - 6$  for a non-linear molecule (which requires 3 rotational co-ordinates).

# Thank you!

## Questions?

