Spectroscopy Analyses by Laser Technology

Raman Spectroscopy

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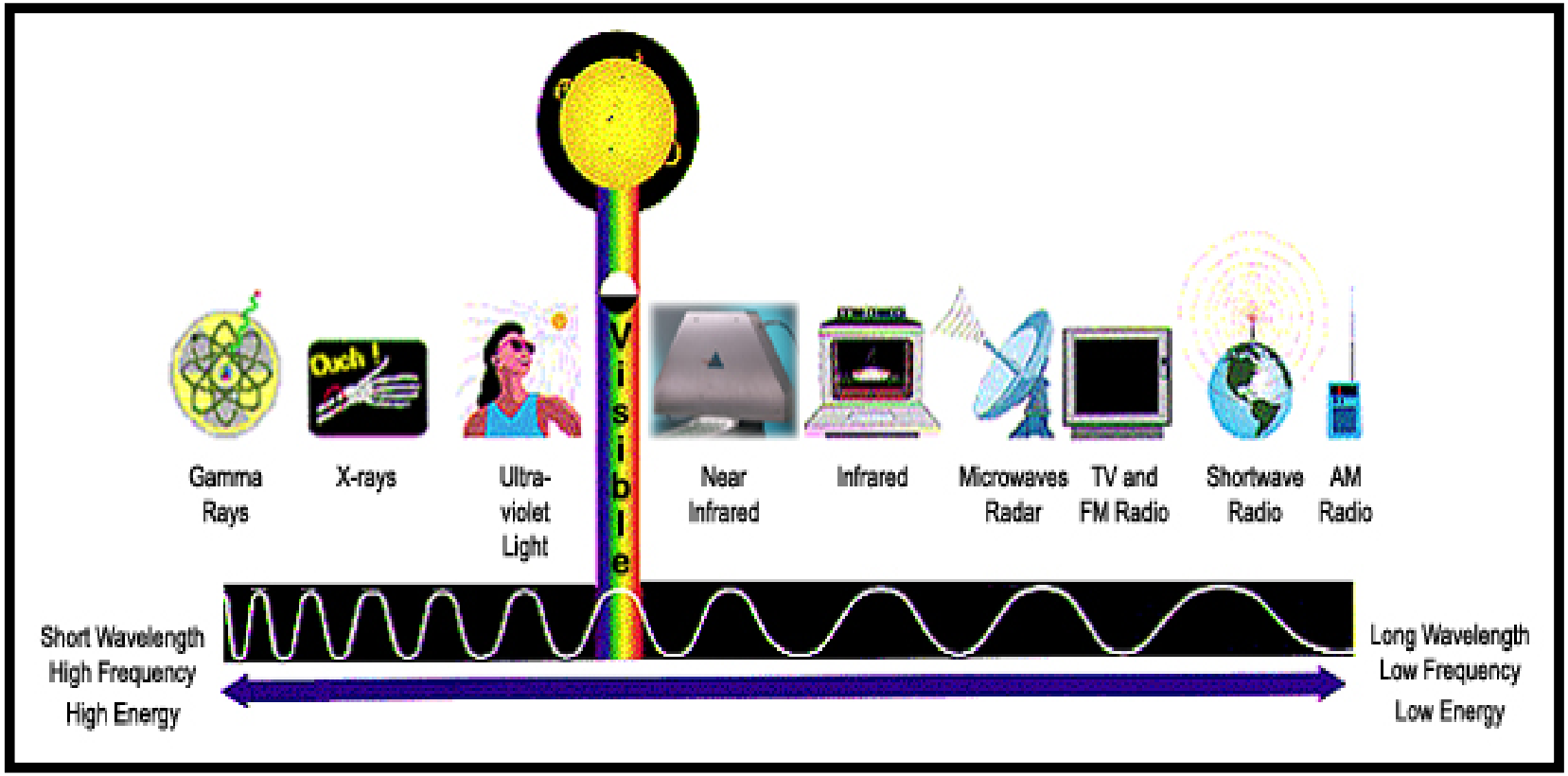
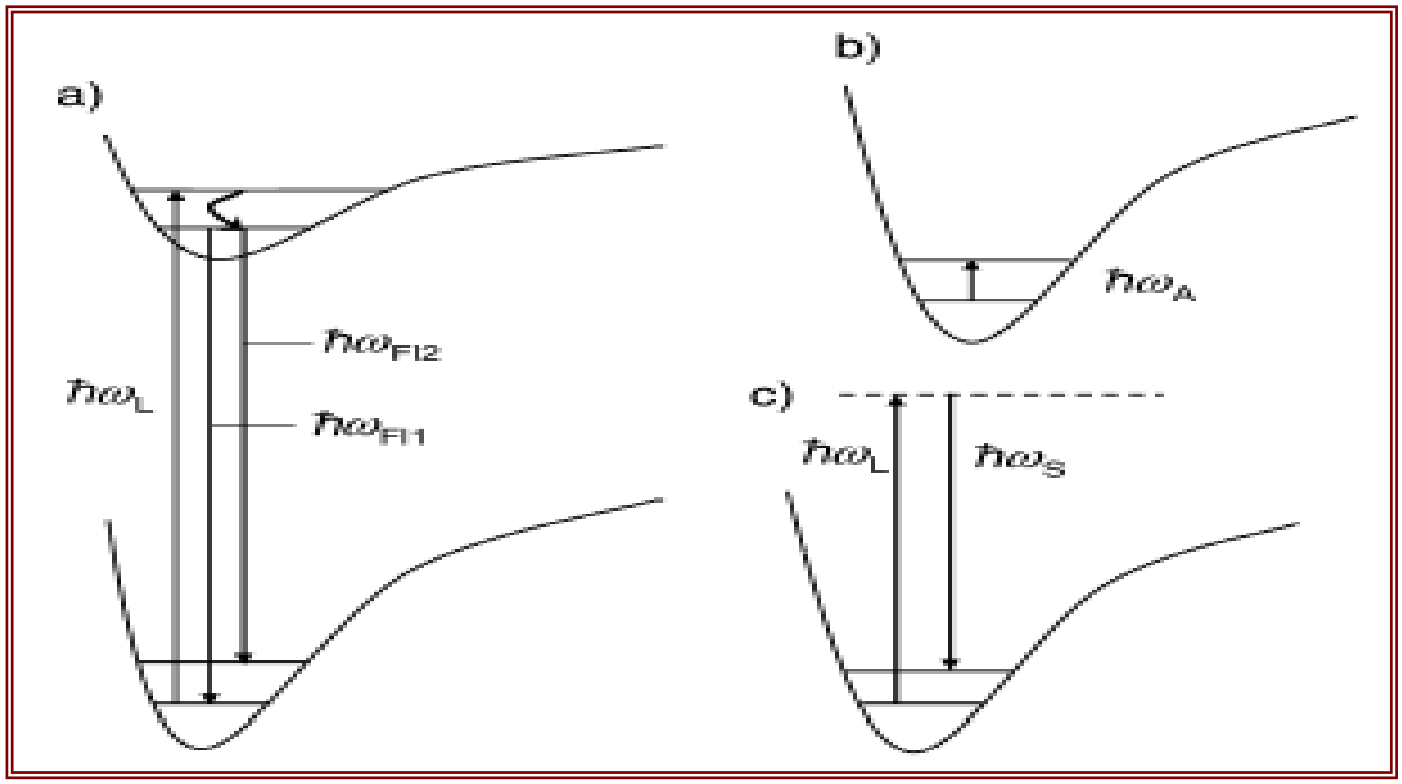
Light Range and its function



Near Infrared Region ~700-3000nm
UV to Visible~180-700nm

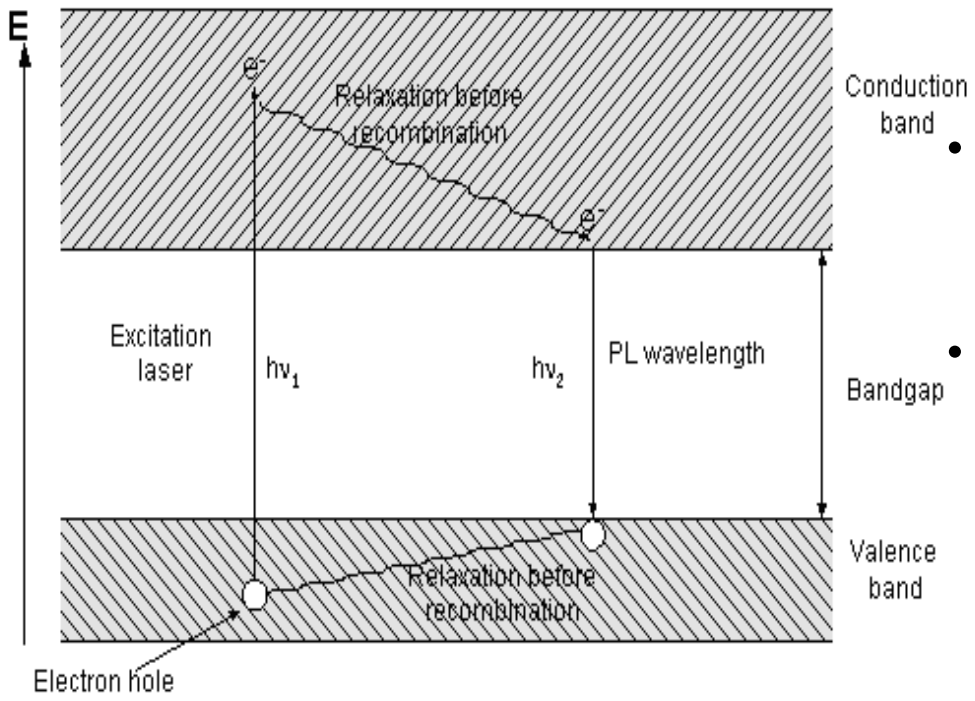
General Aspects of Raman Scattering



Simple model illustrating (a) fluorescence, (b) IR absorption, and (c) Raman scattering

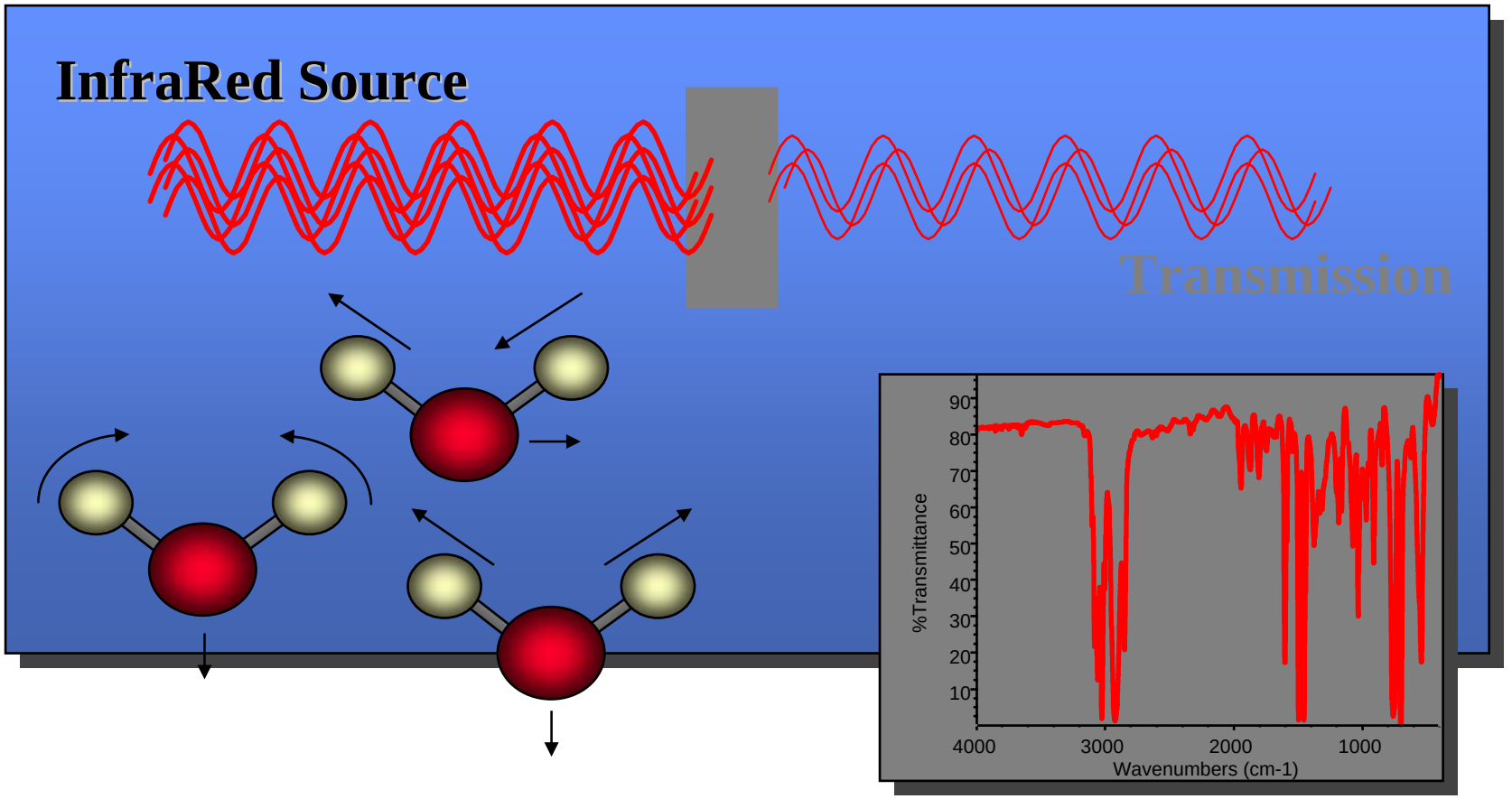
ω_L = laser frequency, ω_{F11}, ω_{F11} = **frequency 1, 2 (fluoroscence);** ω_A = **absorption frequency,** ω_S = **frequency of Stokes scattered light**

Principal of PL



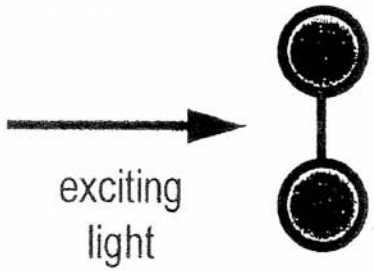
- In a Semiconductor material, the outer band of electrons is known as the **Valence Band**
- The Excited state for these electrons is know as the **Conduction Band**
- The Energy required to move an electron from the Valence to Conduction band is called the **Bandgap**

InfraRed Spectroscopy

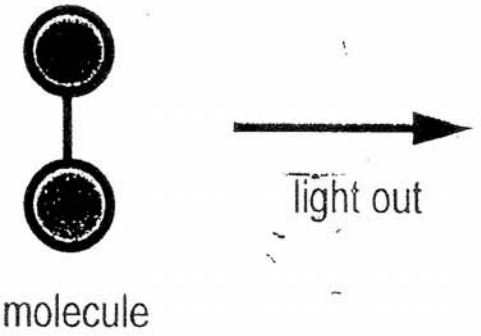


Rayleigh Scattering

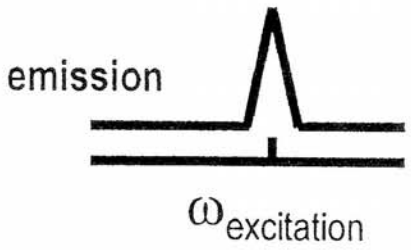
- Elastic (Rayleigh) scattering dominates
- Before...



After...

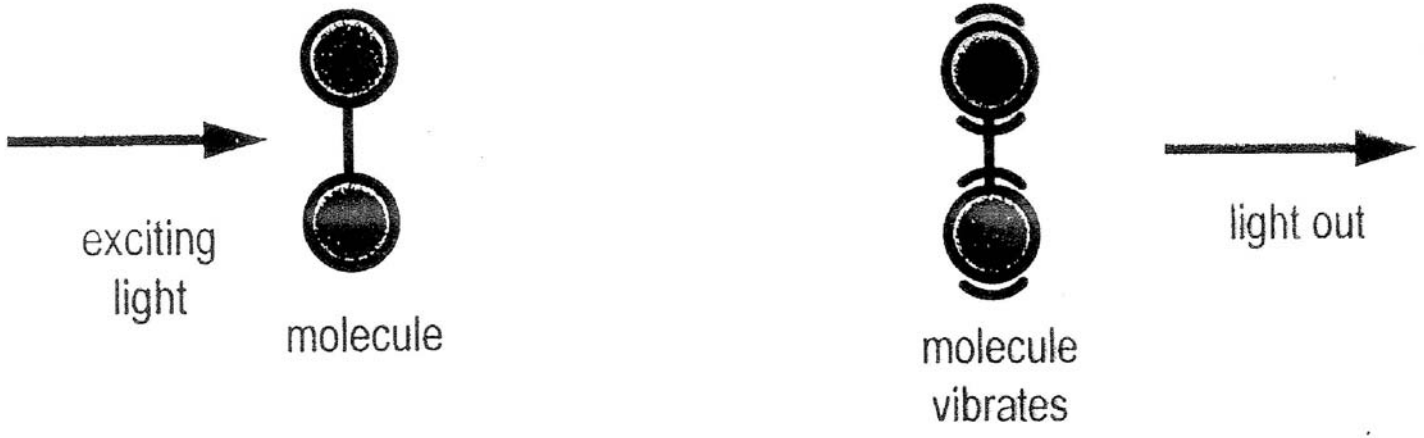


- Light out has same frequency as light in

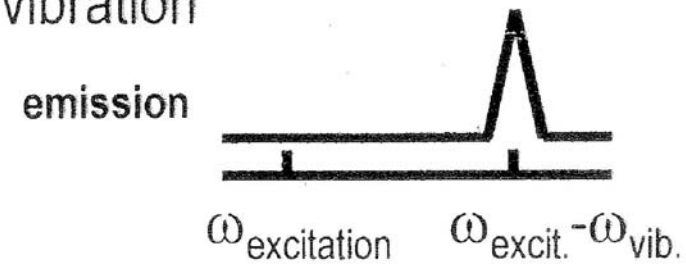


Raman Scattering

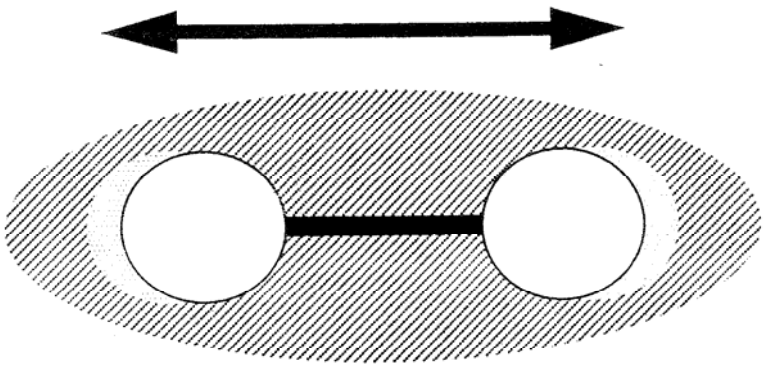
- 1 part in 10^8 is inelastically (Raman) scattered
- Before… After…



- Light loses energy to the molecule vibration



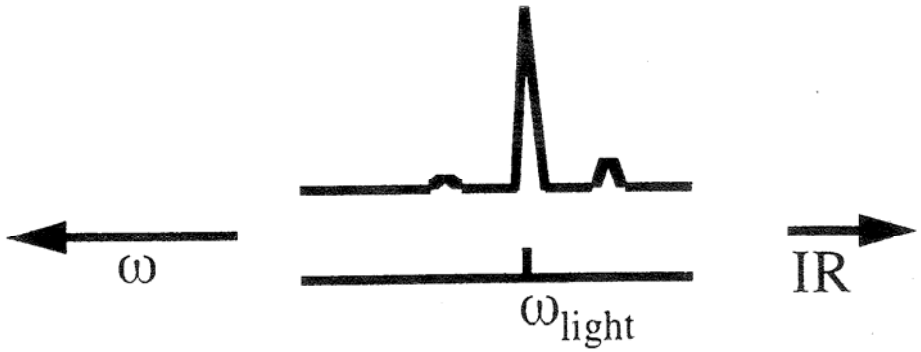
Raman Scattering



$$E = E_0 \sin\omega_{light} t$$

$$x = x_0 \sin(\omega_{vibration} t + \delta)$$

- Incoming light sets electron cloud vibrating **and** atoms vibrating
- Radiated light has frequencies $\omega = \omega_{light} \pm \omega_{vibration}$

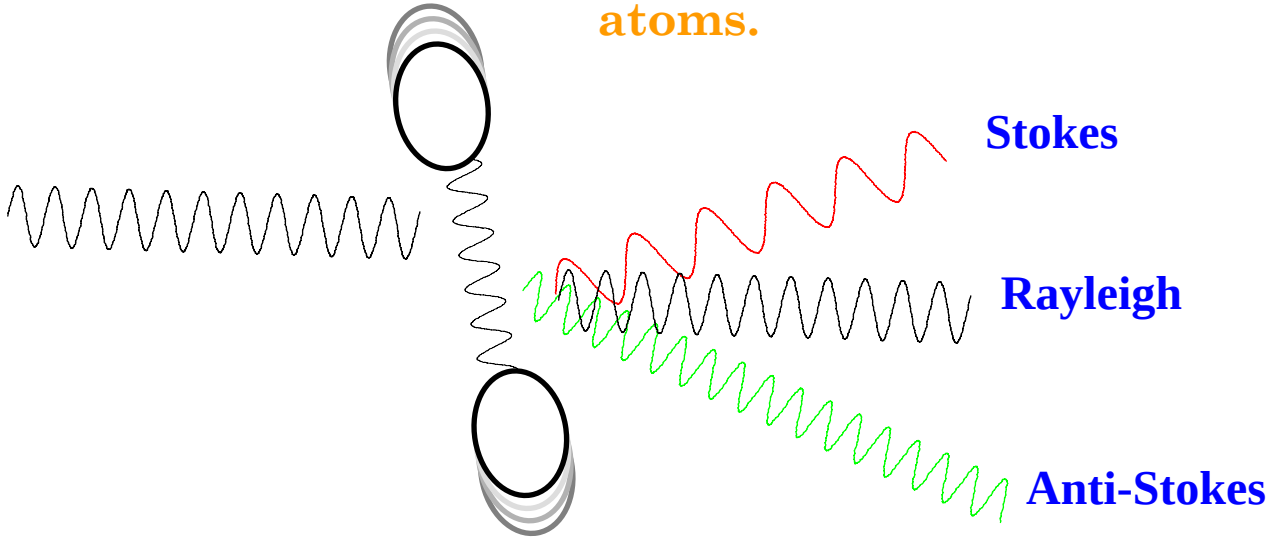


Raman Scattering from Molecular Vibrations

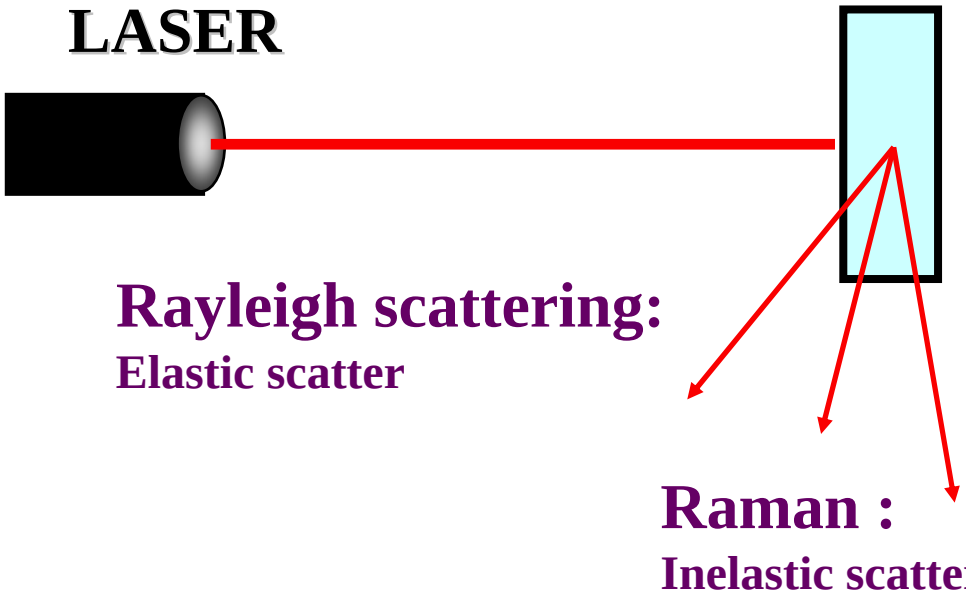
$$\nu = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

ν = Vibrational frequency
k = Spring force constant
μ = Reduced mass of atoms, $m_1m_2/(m_1+m_2)$

Higher vibrational frequency with stronger chemical bond and lighter atoms.

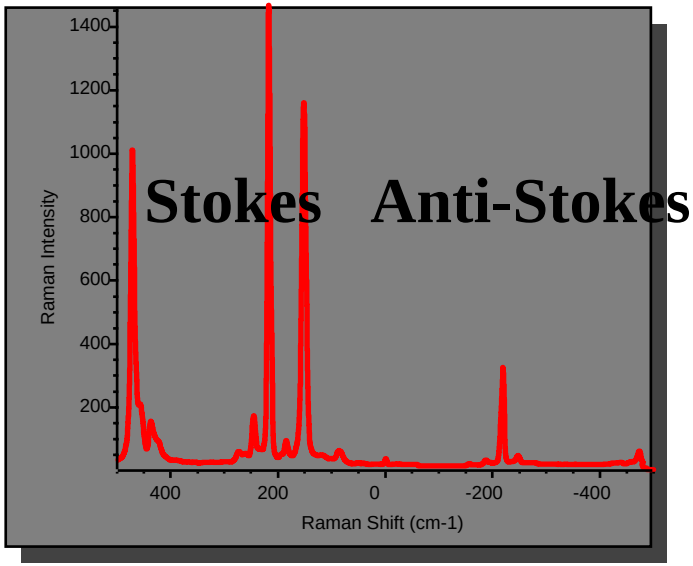


What is Raman Spectroscopy?



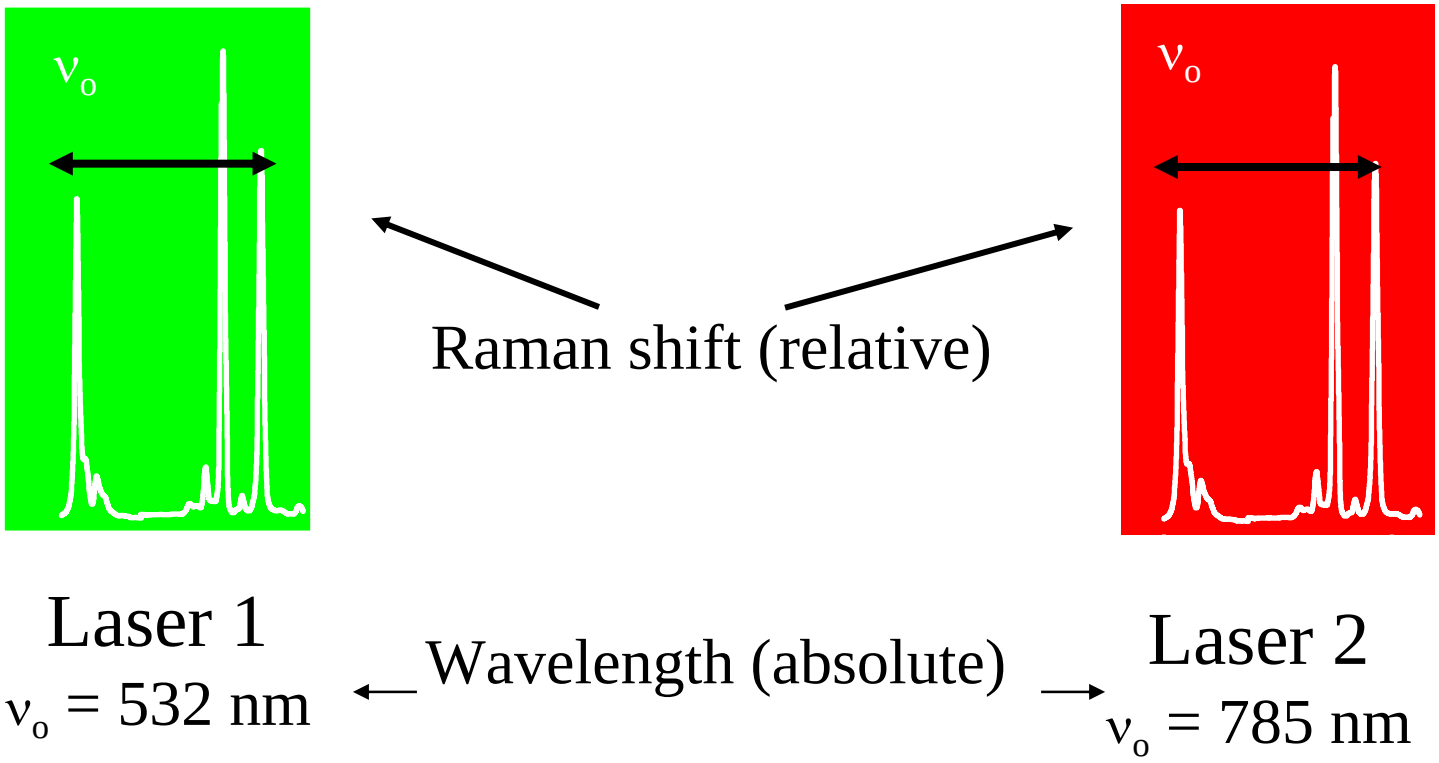
Rayleigh scattering:
Elastic scatter

Raman :
Inelastic scatter

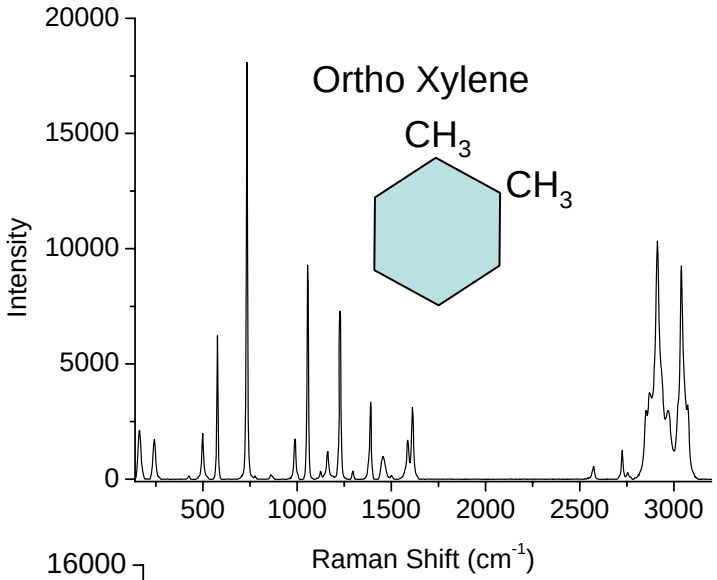


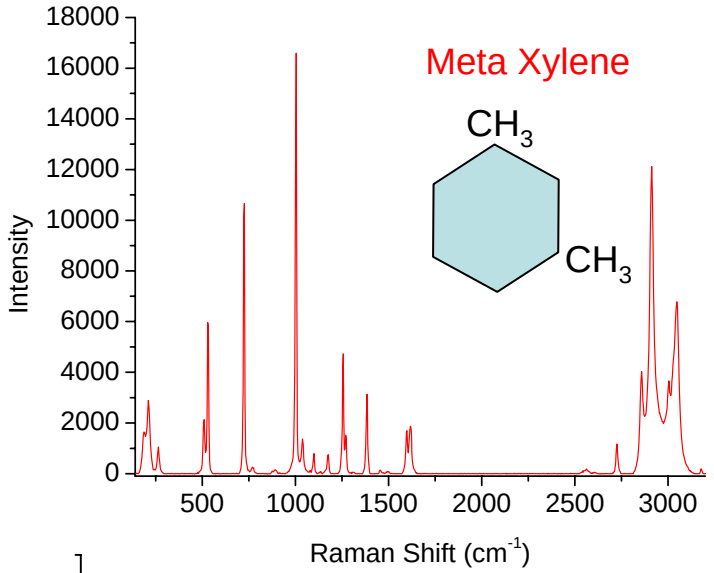
Raman Shift – The Great Equalizer

- Displayed Raman spectrum is independent of laser wavelength
- Sample characteristics and analytical goals may determine laser choice

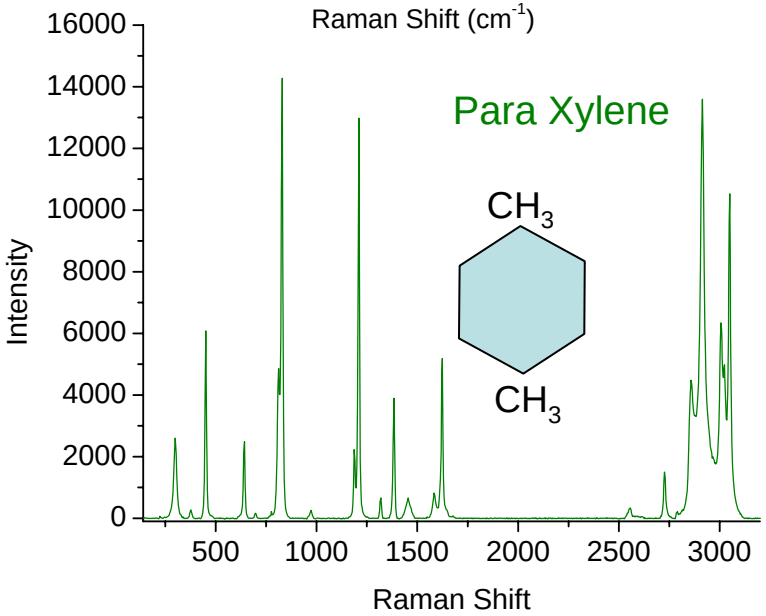


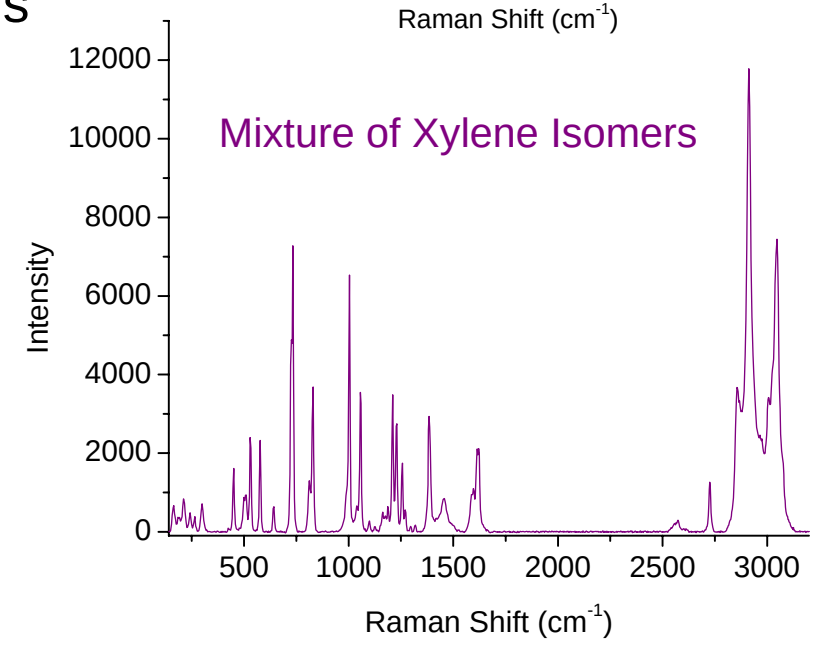
Xylene Spectra





Xylene Isomers





Polarizability of a Diatomic Molecule

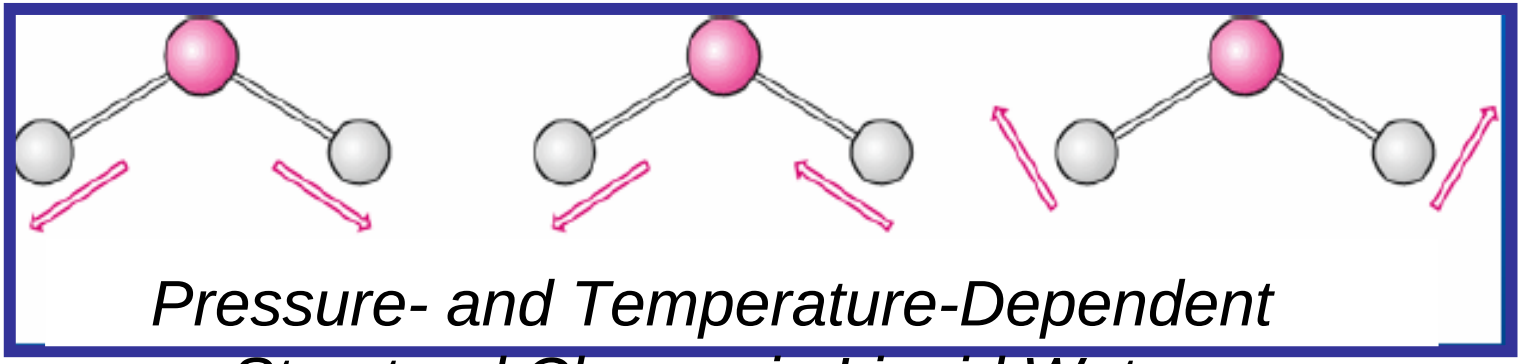
- For the molecule vibrating with a frequency ν_R, the nuclear displacement q is written

$$q = q_0 \cos 2\pi \nu_R t$$

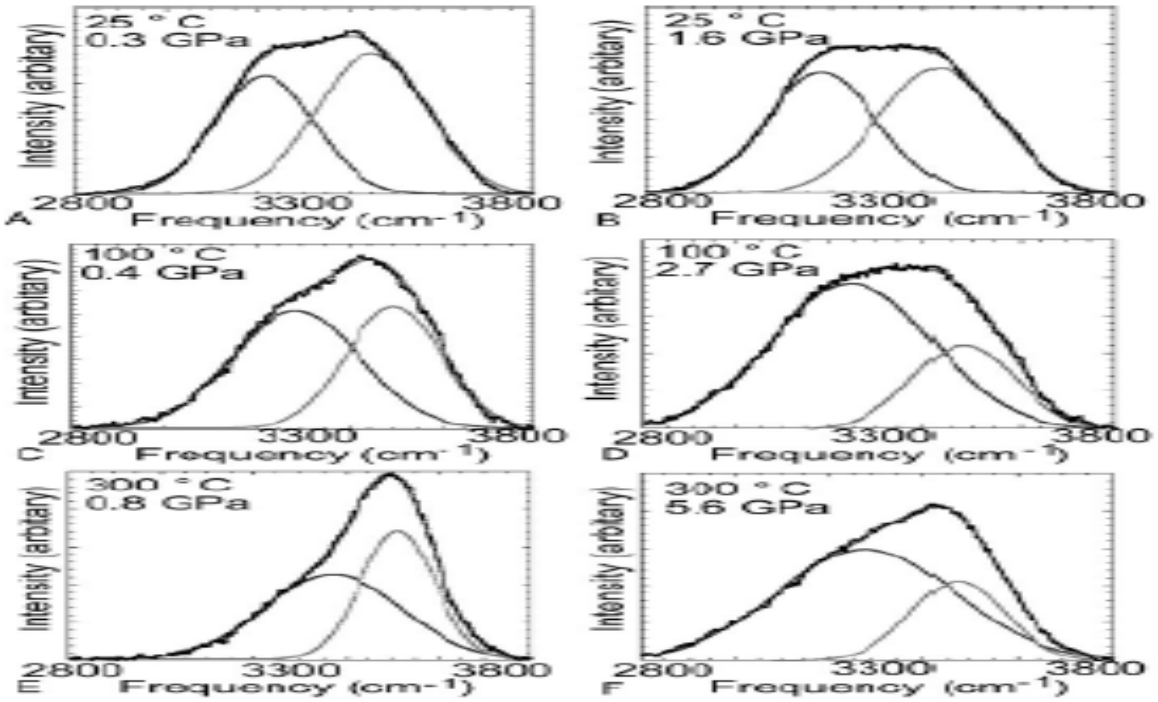
  - Where q_0 is the vibrational amplitude.
- If the vibration is small, then

$$\alpha = \alpha_0 + \left(\partial\alpha / \partial q \right)_0 q + \cdots$$

  - Here α_0 is the polarizability at the equilibrium position, and $\left(\partial\alpha/\partial q\right)_0$ is the rate of change of α with respect to the change in q, evaluated at the equilibrium position

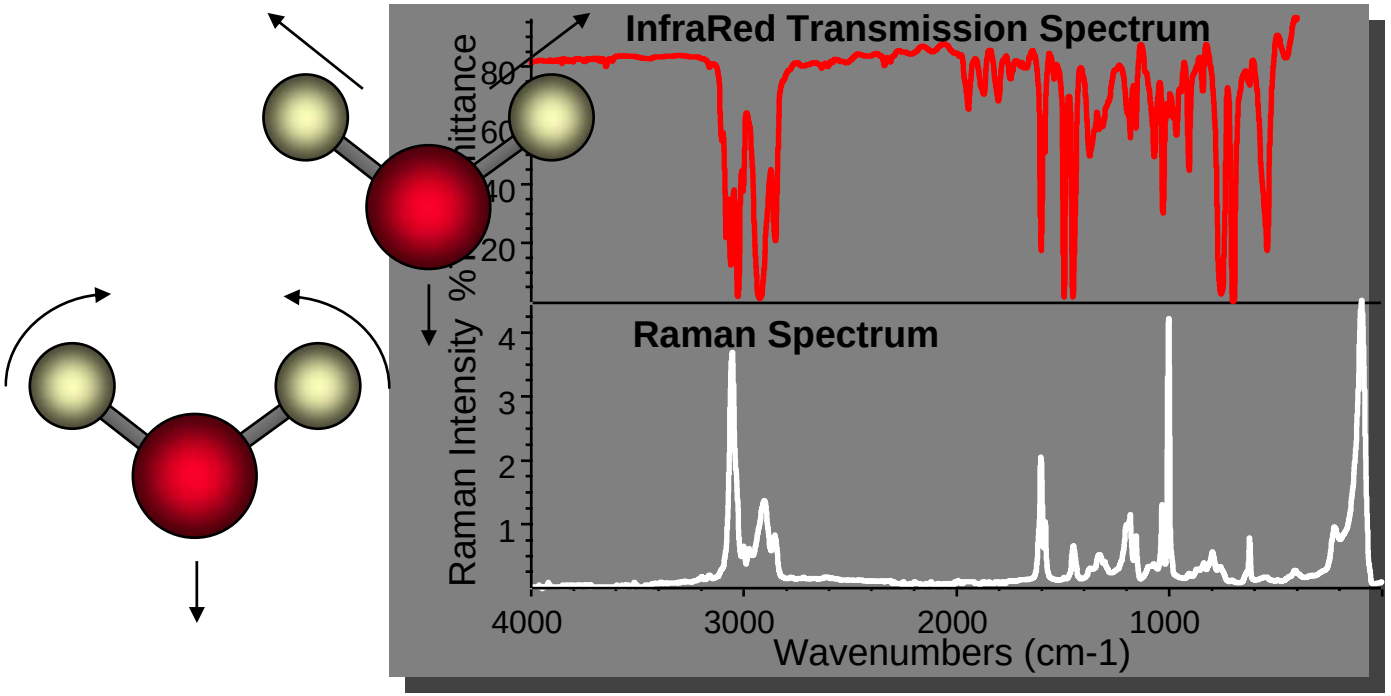


Pressure- and Temperature-Dependent Structural Change in Liquid Water



Band analysis of Raman spectra of water.

IR and Raman Spectra



- Raman spectroscopy gives us information about the vibrational energies of molecules
- Raman is complementary to IR, producing relatively stronger peaks for symmetrical stretching vs. anti-symmetrical stretching modes
- Raman spectra tend to be less cluttered than IR, much less affected by water and it is usually easier to implement/sample than IR

Comparing FT-IR and Raman

FT-IR

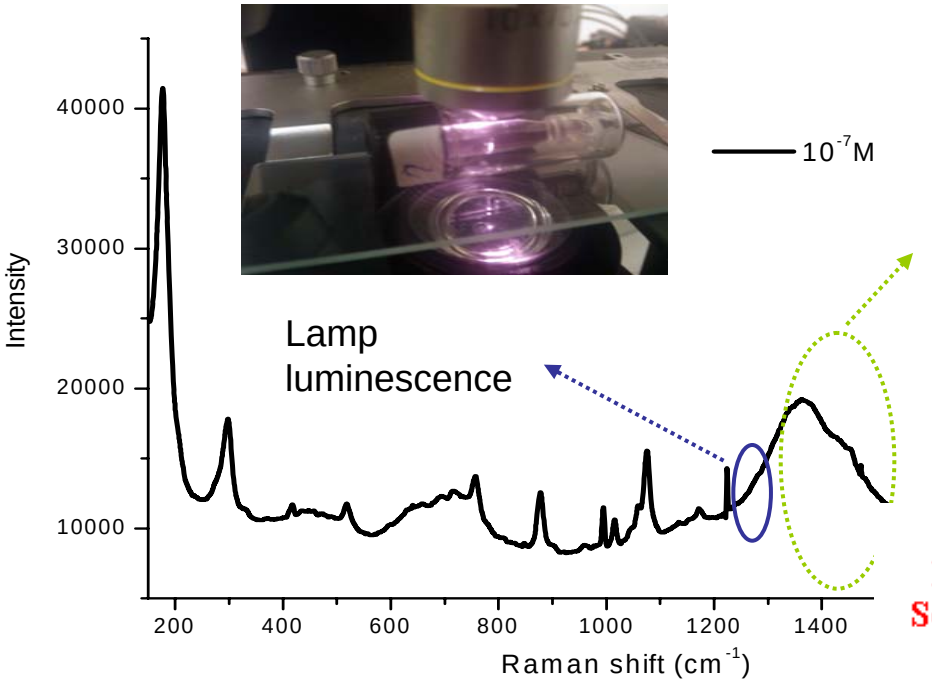
- Absorption
- Fundamental information
- Sample preparation (most)
- Process measurements less flexible
- High spectral density
- Organics
- Dipoles
  - O-H, C=O, N-H
- Water a problem

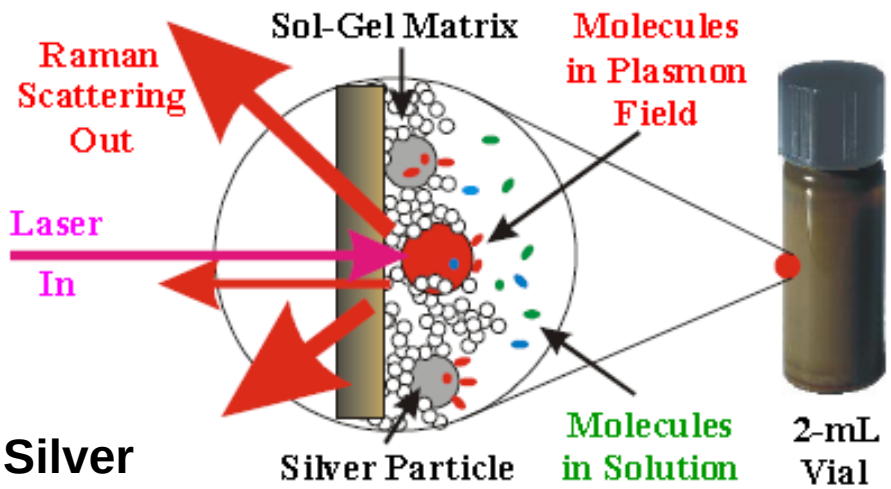
Raman

- Emission
- Fundamental information
- No sample preparation
- Process measurements
- High spectral density
- Static sampling challenges
- Organics and inorganics
- Polarizability
  - Aromatics, C=C
- Water not an issue

Wet- Substrates for SERS

The total amount of the measured solution is 200 ul.





Gold or Silver

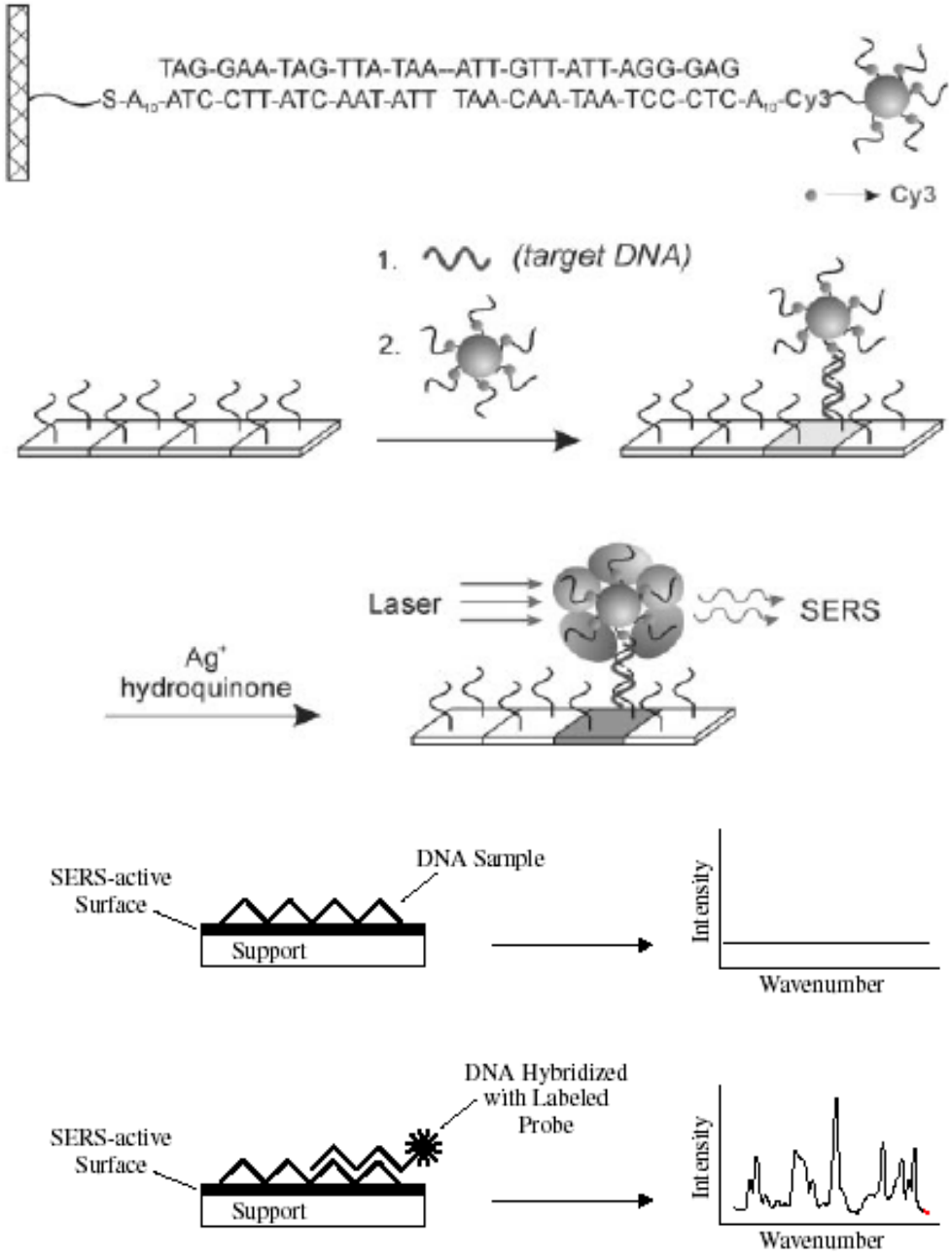
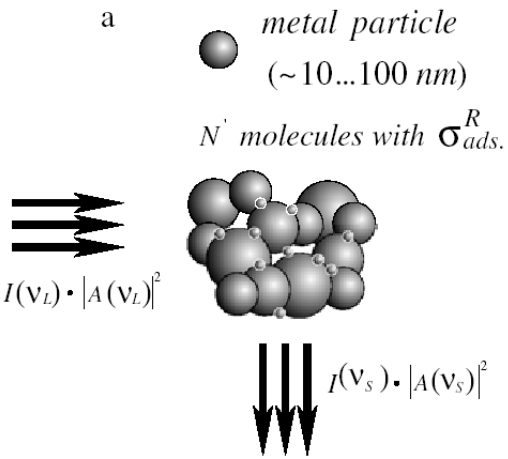
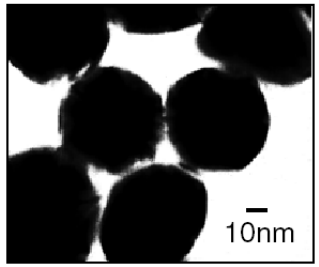


Figure 14. Schematic diagram of DNA hybridization detection using a SERS label [138].

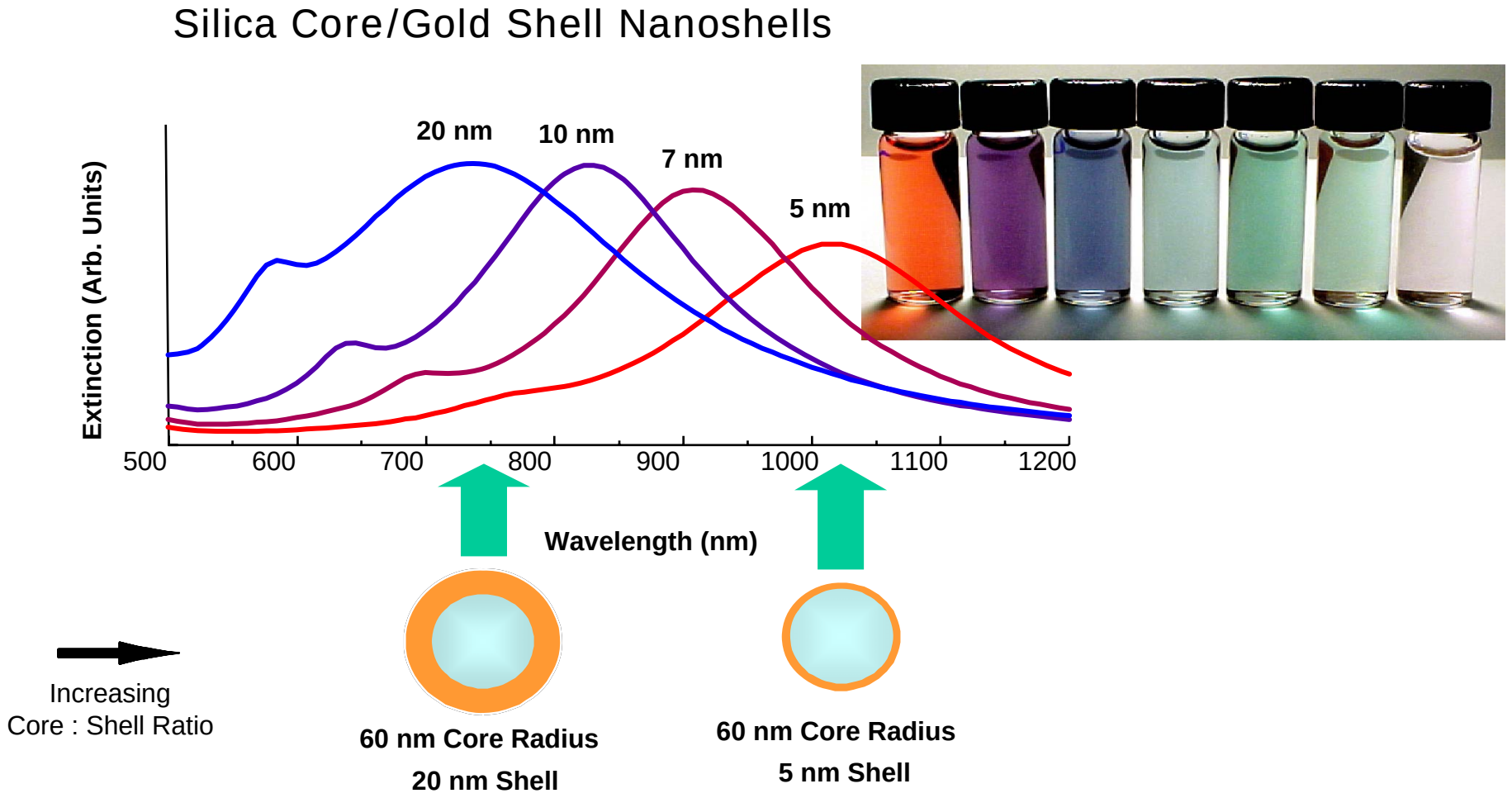


b



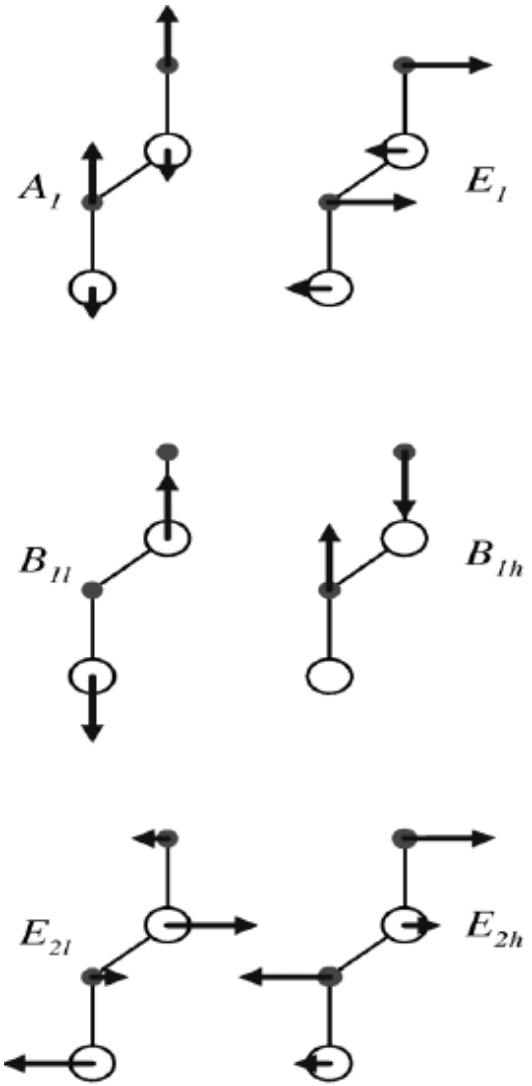
Nanoparticles with Raman Spectroscopic Fingerprints for DNA and RNA

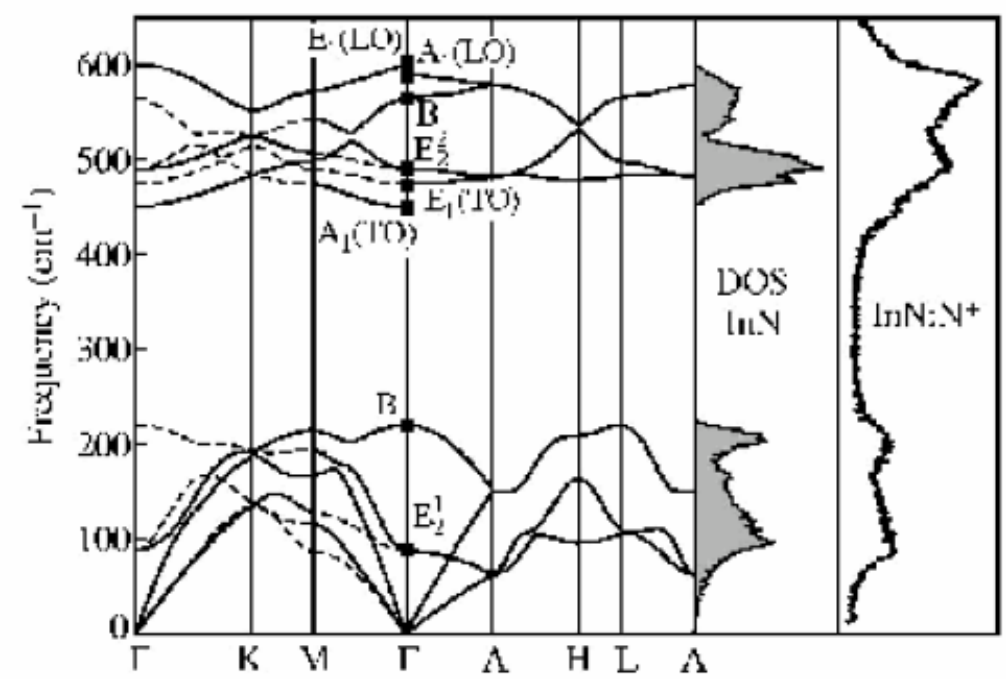
Plasma factor

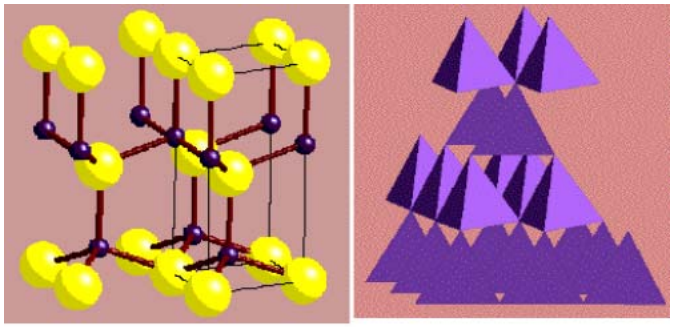


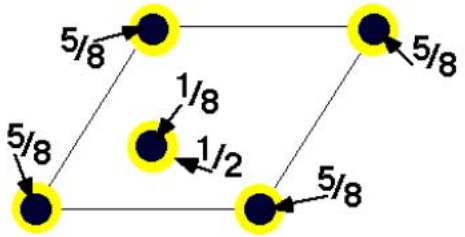
S. J. Oldenburg, R. D. Averitt, S. L. Westcott and N. J. Halas, Chem. Phys. Lett., 288, 243-247 (1998)

Wurtzite Structure $C6v^4$-$P6_3mc$

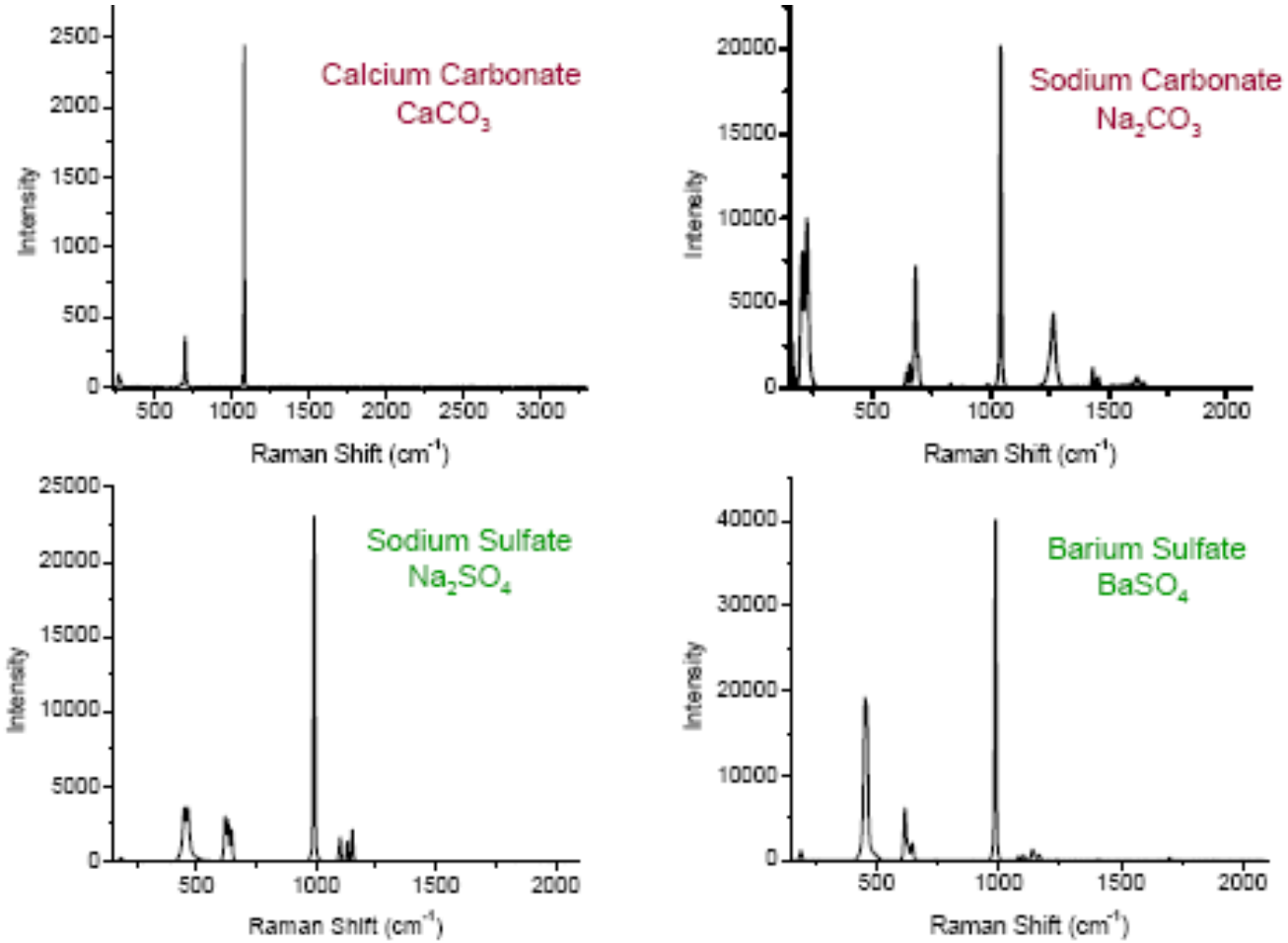








Spectra for Inorganic Samples



Rayleigh and Raman Scattering

- The first term represents an oscillating dipole that radiates light of frequency ν
  - Rayleigh Scattering
- The second term corresponds to the Raman scattering of frequency $\nu+\nu_R$ (Anti-Stokes) and $\nu-\nu_R$ (Stokes shift)
- To observe Raman scattering, $(\partial\alpha/\partial q)_0$ the rate of change of polarizability with the vibration must not be zero.

Placzek's Equation for Raman Scattering Intensity

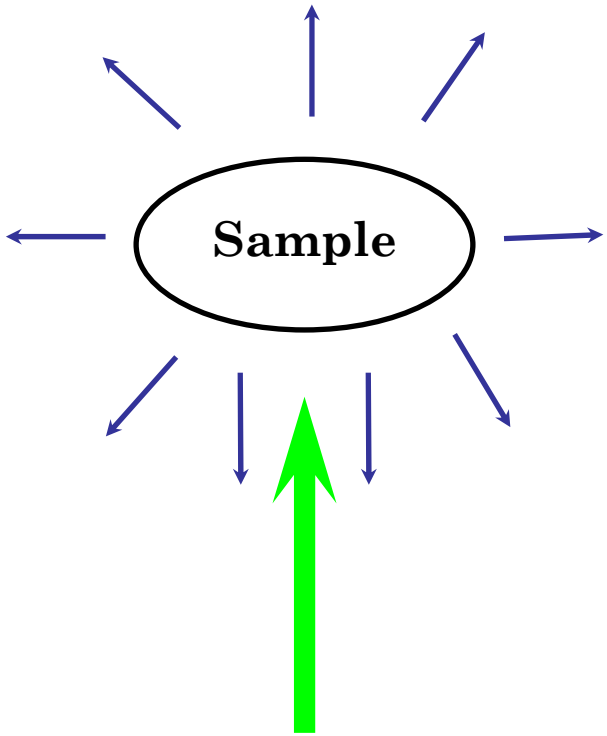
$$I_R = \frac{2^4\pi^3}{(45)(3^2)c^4}\frac{hI_L N(\nu_0-\nu)^4}{\mu\nu(1-e^{-h\nu/kT})}[45(\alpha_a')^2+7(\gamma_a')^2]$$

- I_R proportional to I_L
- I_R proportional to N
- I_R stronger at shorter wavelength
- Statistical factor: $(1-e^{-h\nu/kT})$

Where

c = speed of light
h = Planck's constant
I_L = laser intensity
N = number of scattering molecules
ν = molecular vibrational frequency in Hz
ν_L = laser excitation frequency, in Hz
μ = reduced mass of the vibrating atoms
k = Boltzmann's constant
T = absolute temperature
α_a' = mean value invariant of the polarizability tensor
γ_a' = anisotropy invariant of the polarizability tensor

Analytical Raman Spectroscopy



$$I_\lambda = \sigma L C I$$

I_λ = Raman intensity

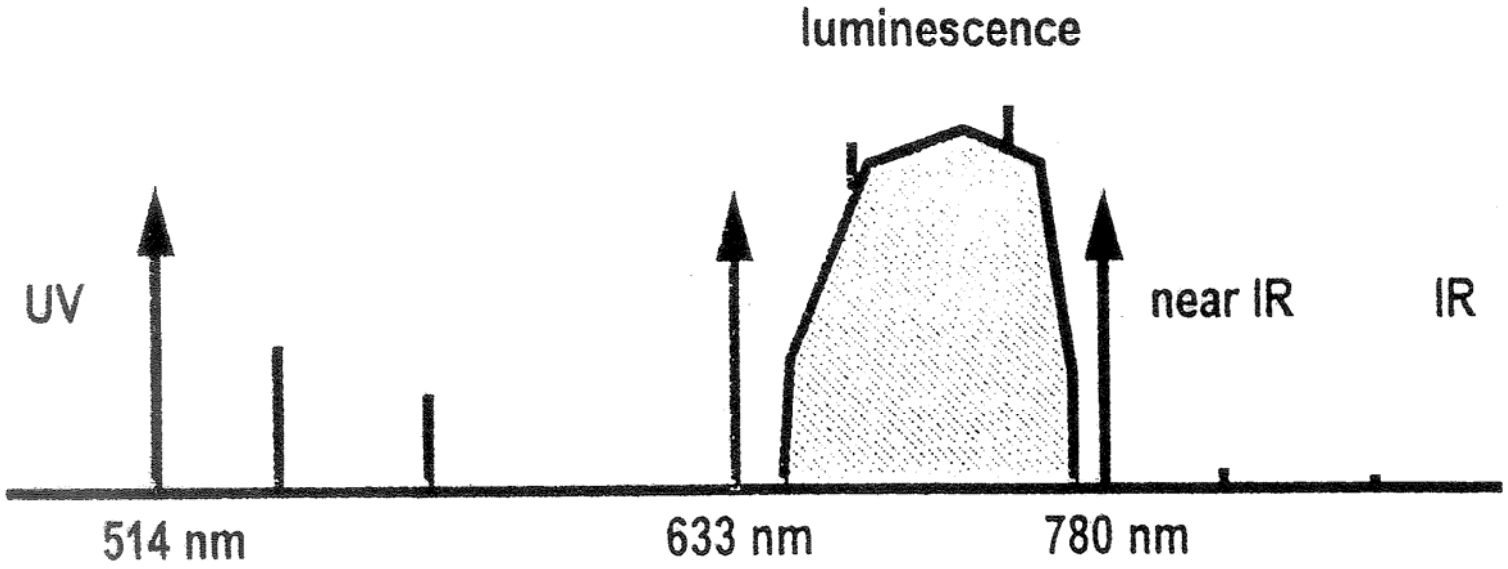
σ = Raman cross section

L = Pathlength

C = Concentration

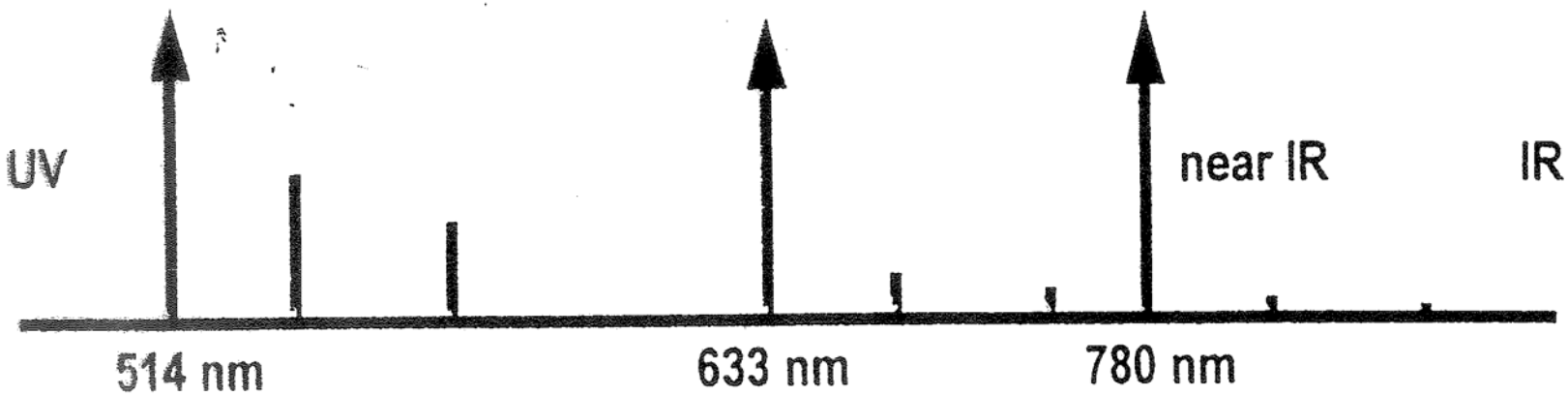
I = Instrument parameters

Choices of Excitation Wavelength



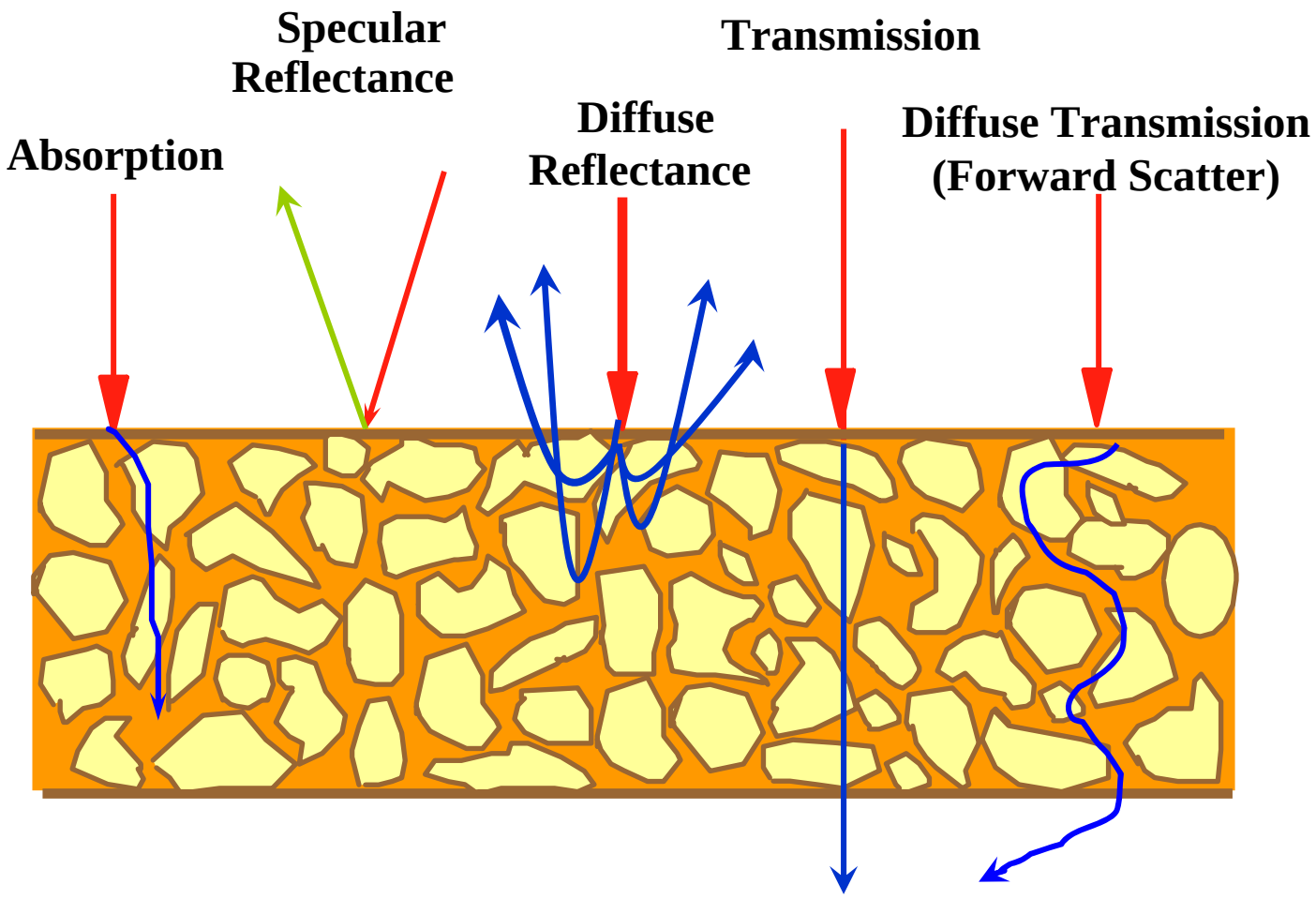
Luminescence problems can often be solved by choosing an appropriate excitation wavelength

Choices of Excitation Wavelength

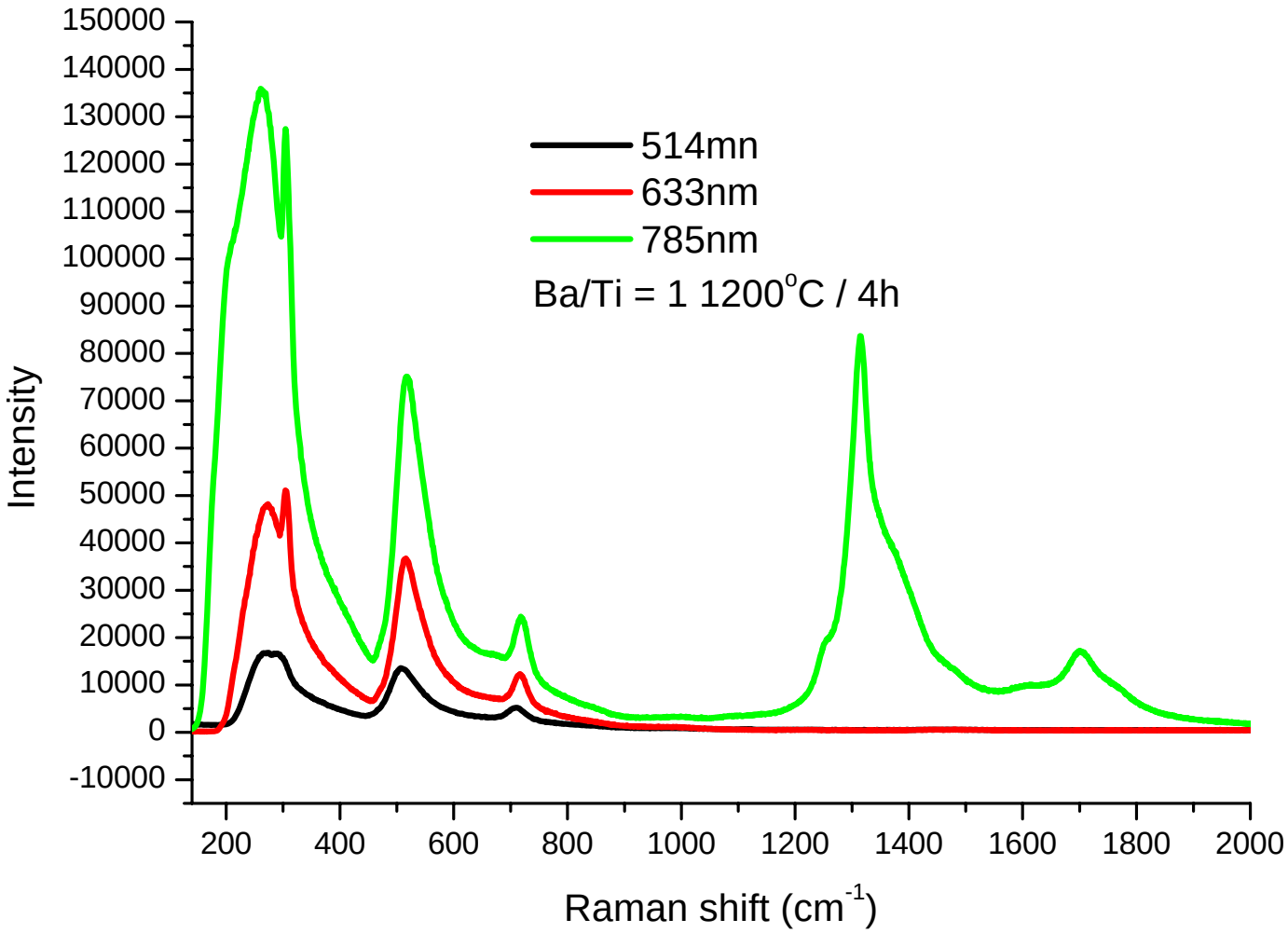


- Shorter wavelength lasers excite Raman scattering more efficiently
- $\text{Efficiency}_{514\ nm}$ - 5 x $\text{Efficiency}_{780\ nm}$

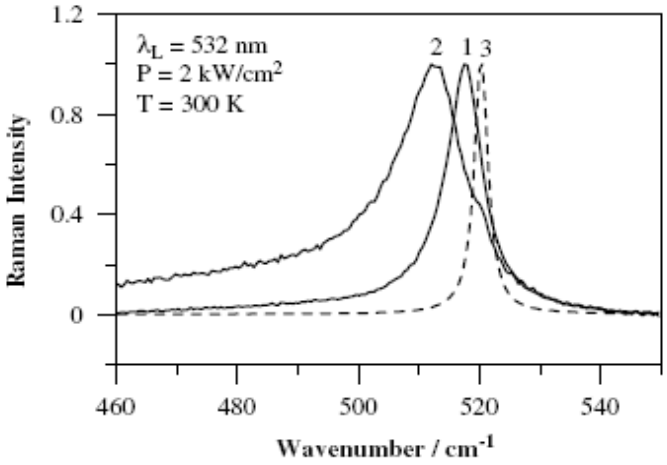
Modes of material interaction



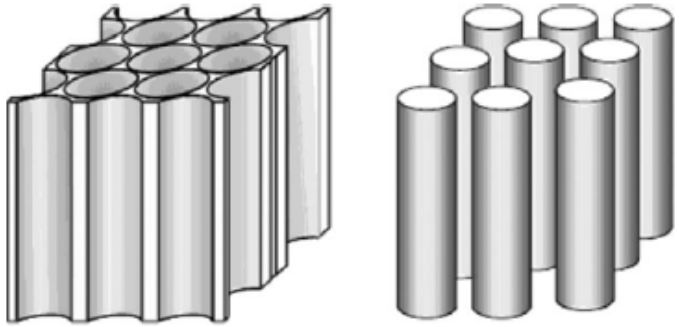
$BaTiO_3$ System

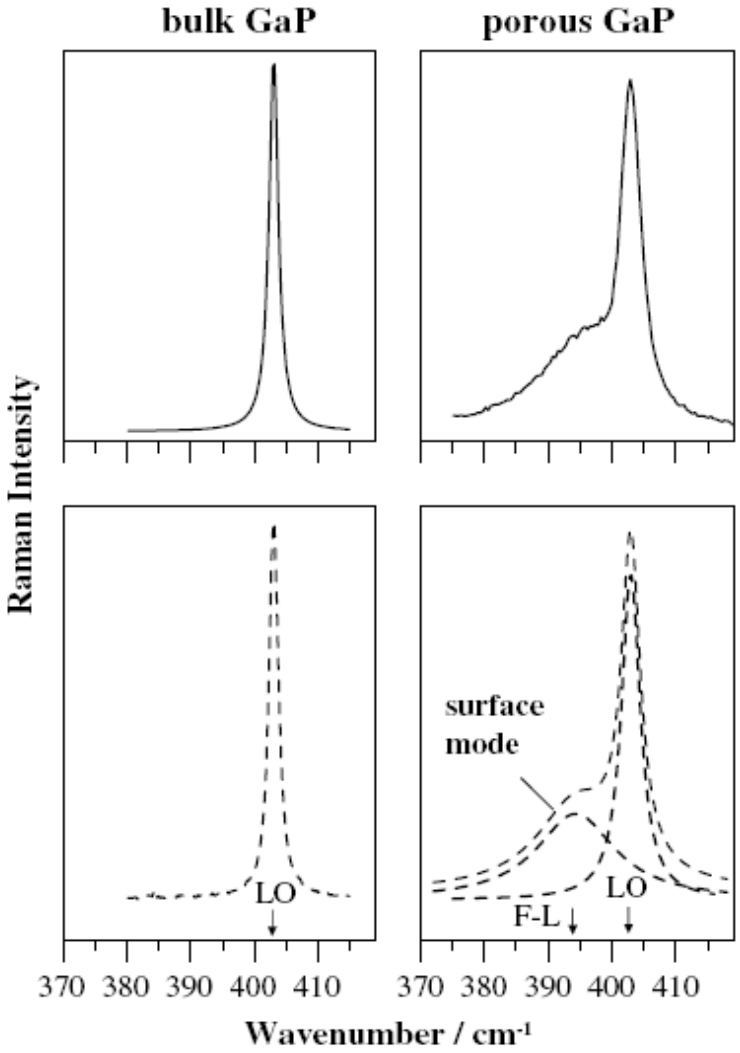


Raman in Nanoporous semiconductors

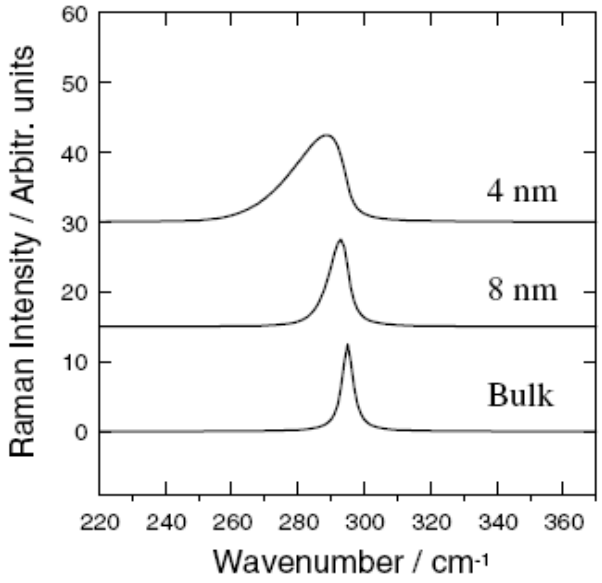


Two porous Si Layers

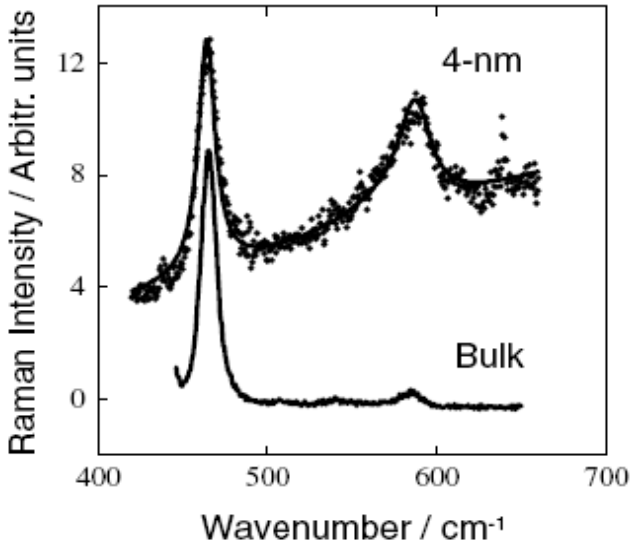




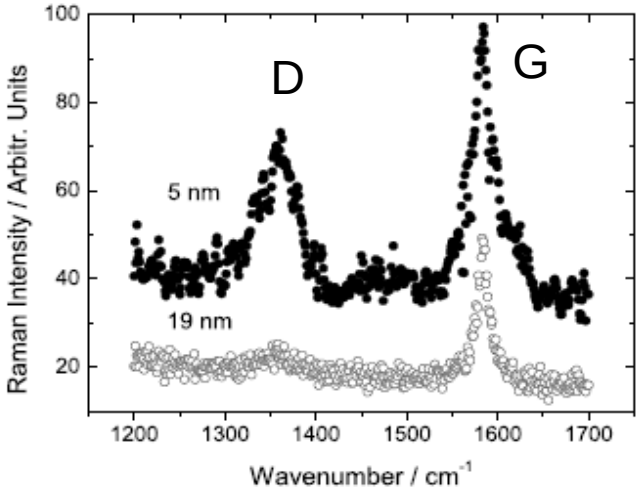
Size effect



GaAs

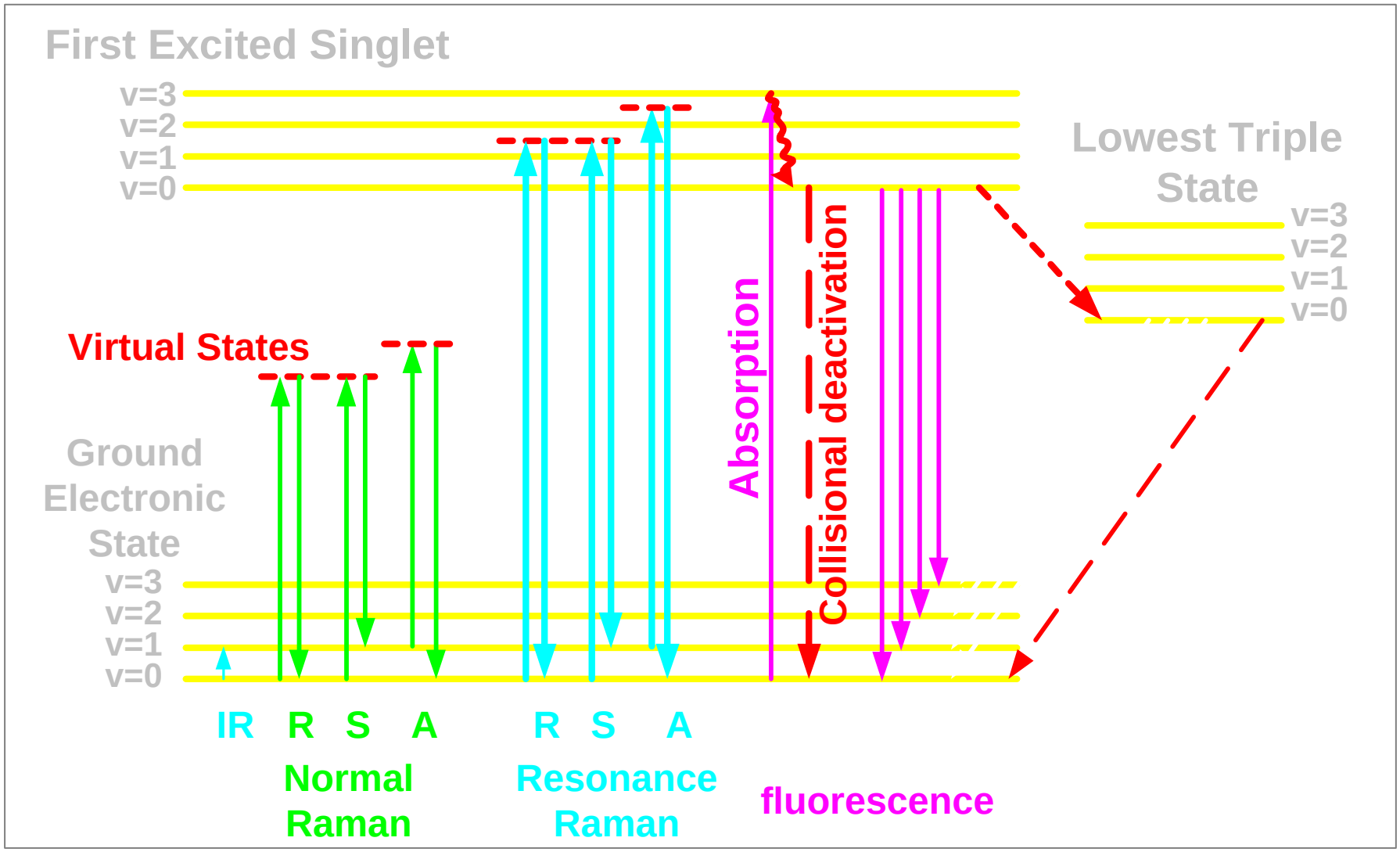


ZnO_2

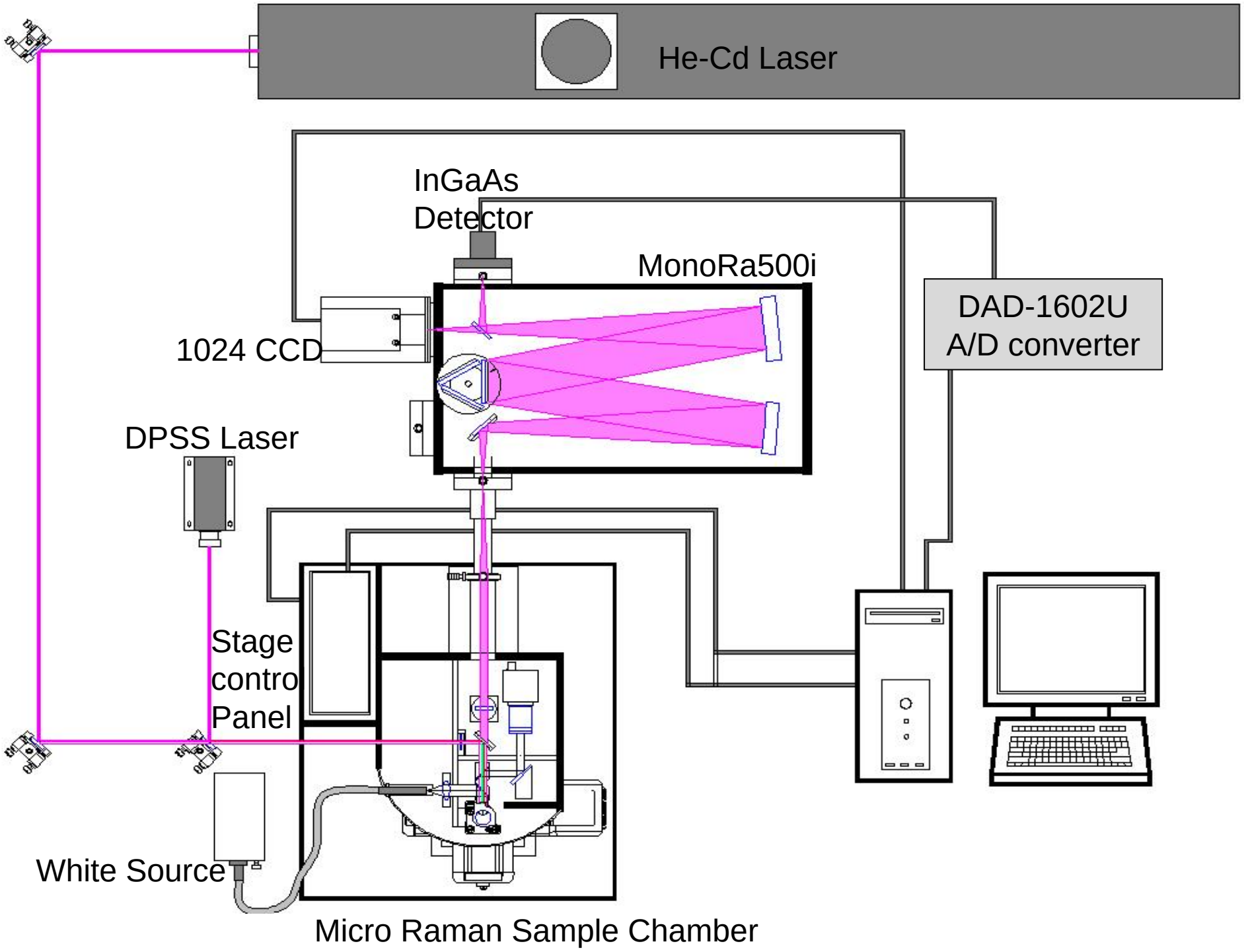


Graphite

Schematic Energy Level Diagram

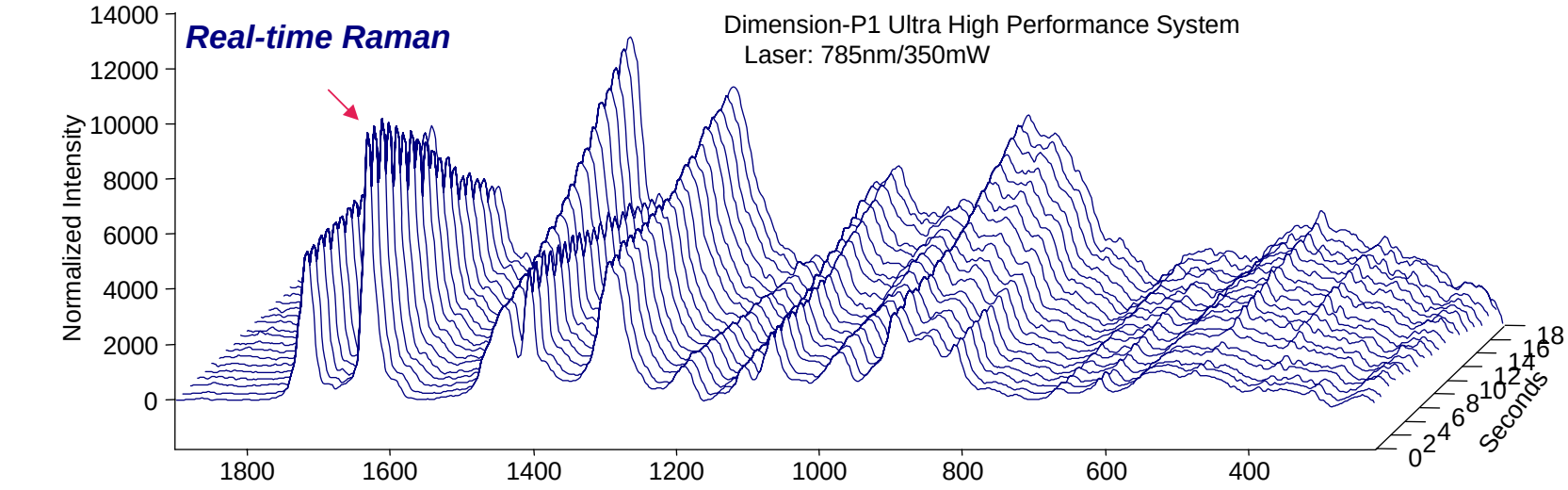


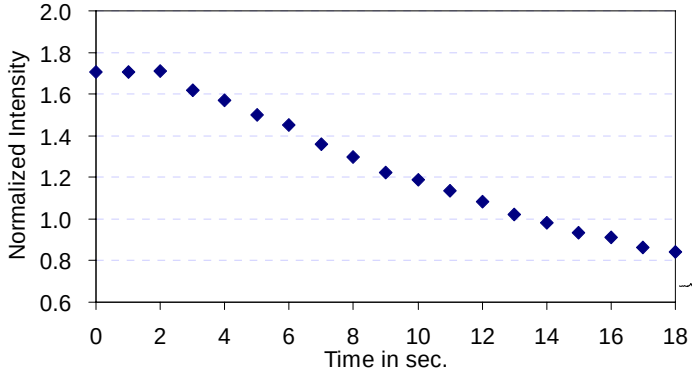
Instruments

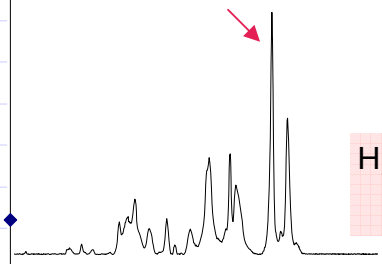

He-Cd Laser
InGaAs
Detector
MonoRa500i
1024 CCD
DAD-1602U
A/D converter
DPSS Laser
Stage
contro
Panel
White Source
Micro Raman Sample Chamber

Plastic and Polymer

Real-time Raman analysis of UV induced polymerization

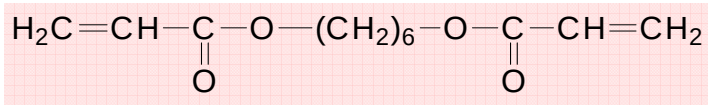






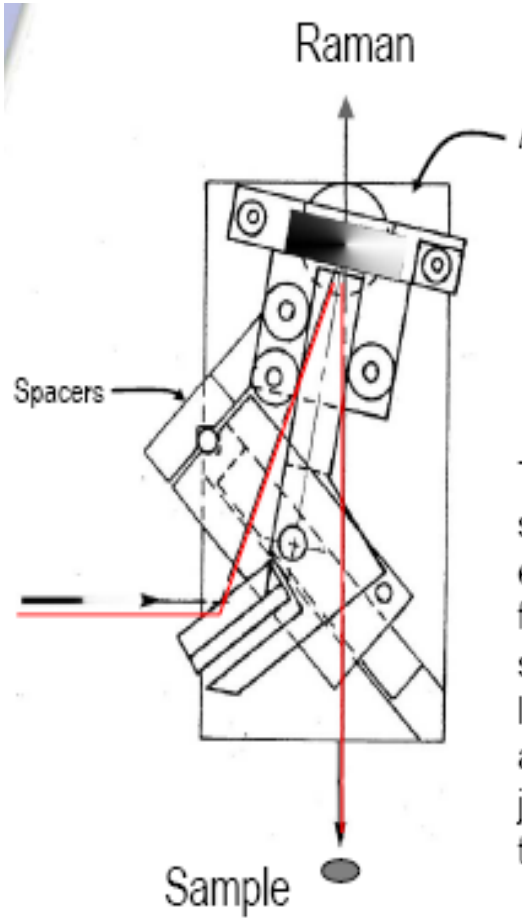
C=C stretch
1630 cm^{-1}

1,6-hexanediol diacrylate/Irgacure 369



Optical Filters set

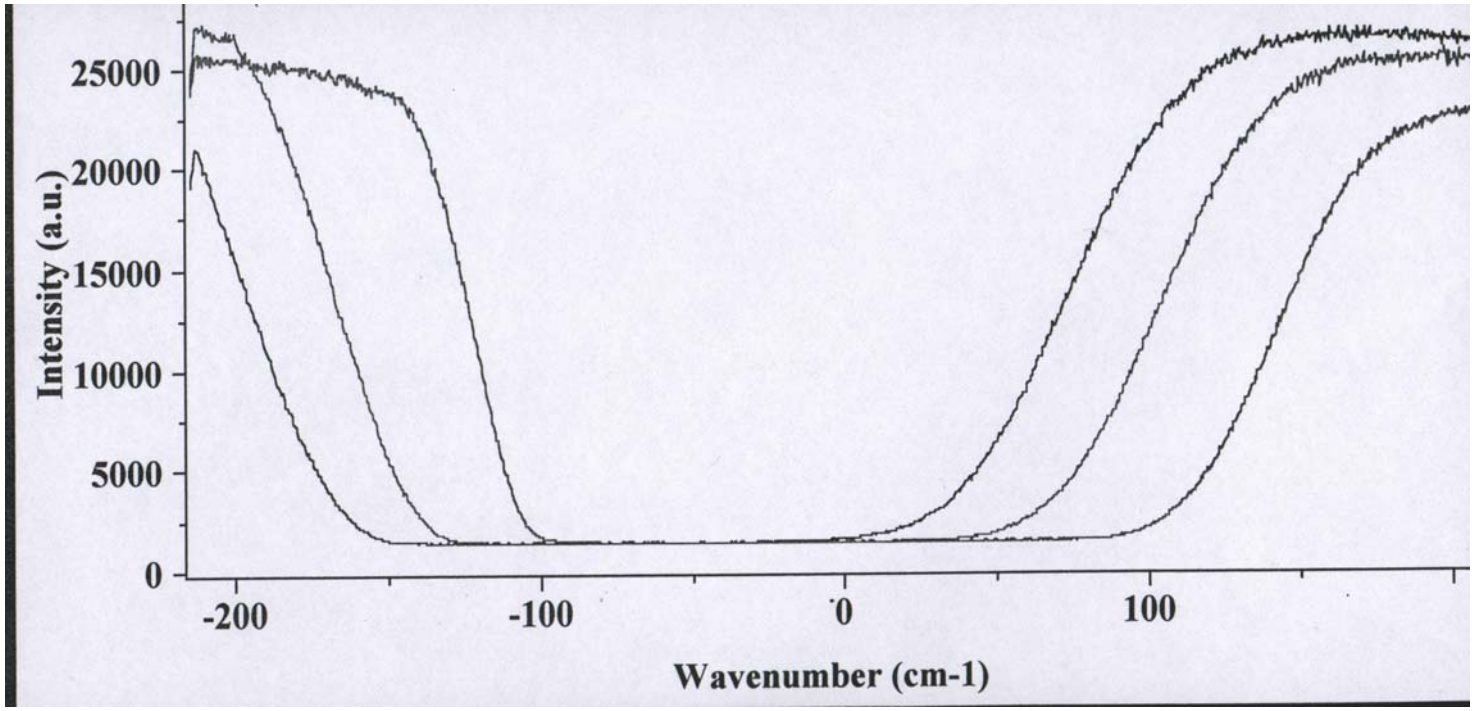
- **Plasma or intereference filter**
- **Edge filter**
- **Notch filter**
- **Grating**



L1003 kinematic filter system

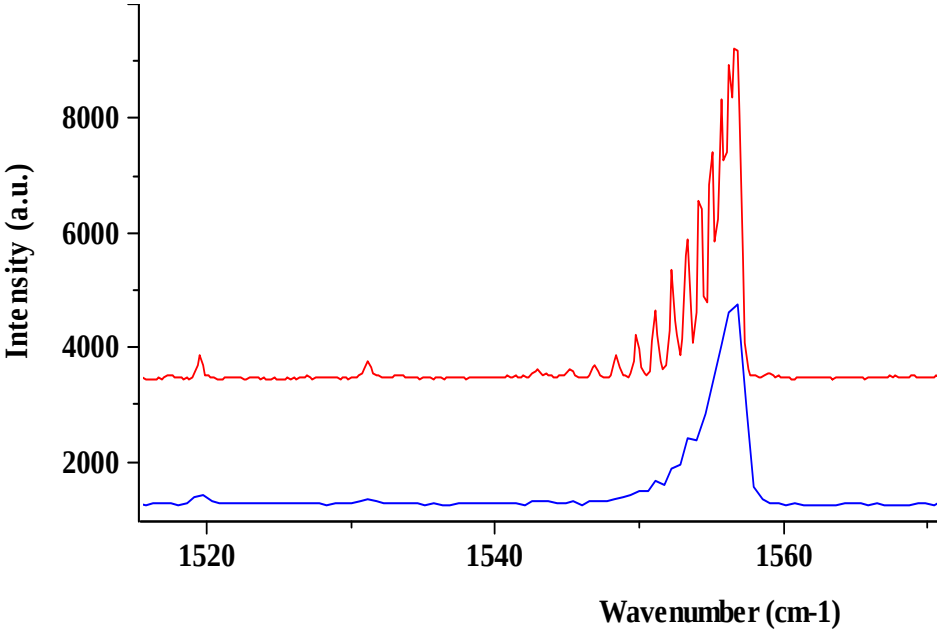
The Unique L1003 kinematic filter system allows the notch filter to be exchanged quickly and the angle of the filter to be adjusted with simple spacers. The optical alignment of the laser and microscope is maintained and requires NO adjustment. So, in just a second, the angle adjustment of the filter can be obtained.

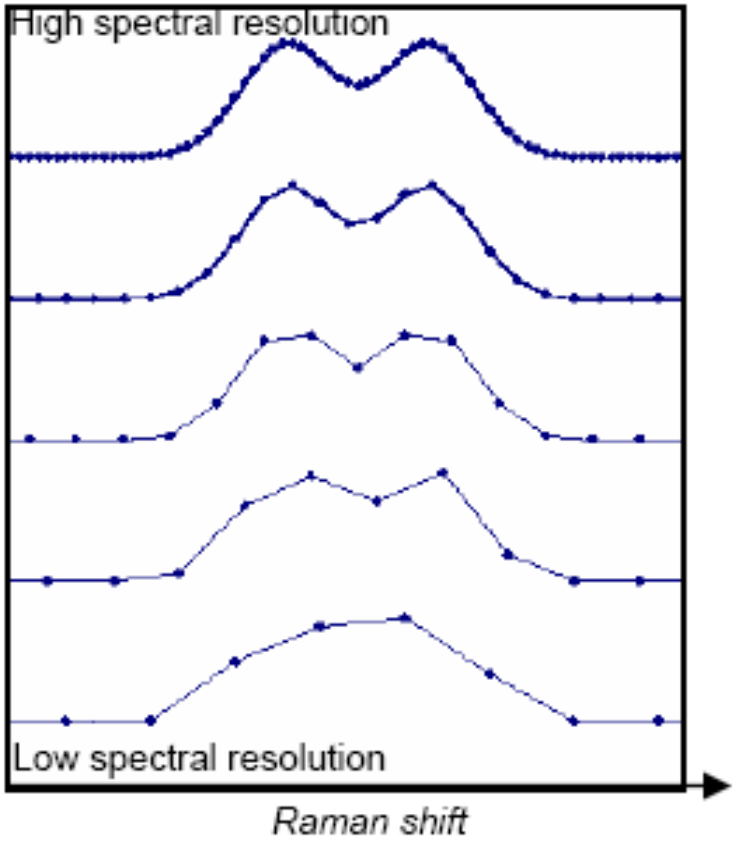
Real cut-off response of a Notch filter

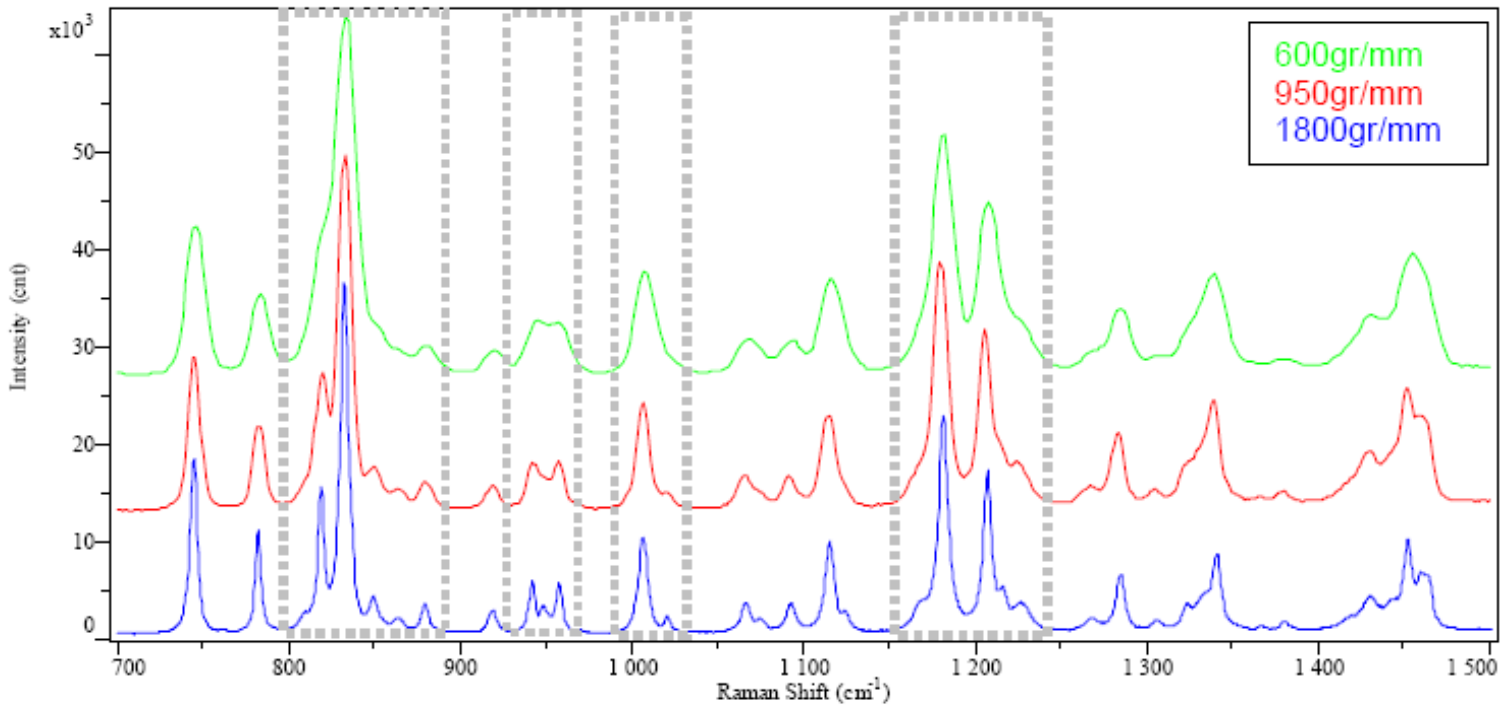


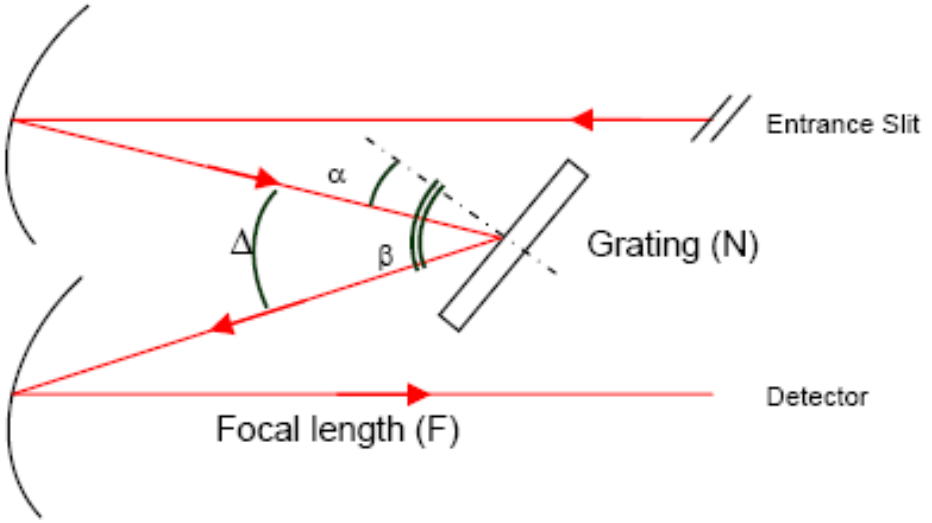
The spectral range on which the filter reflects light shifts with the tilt angle of the filter in the beam

High Resolution Data

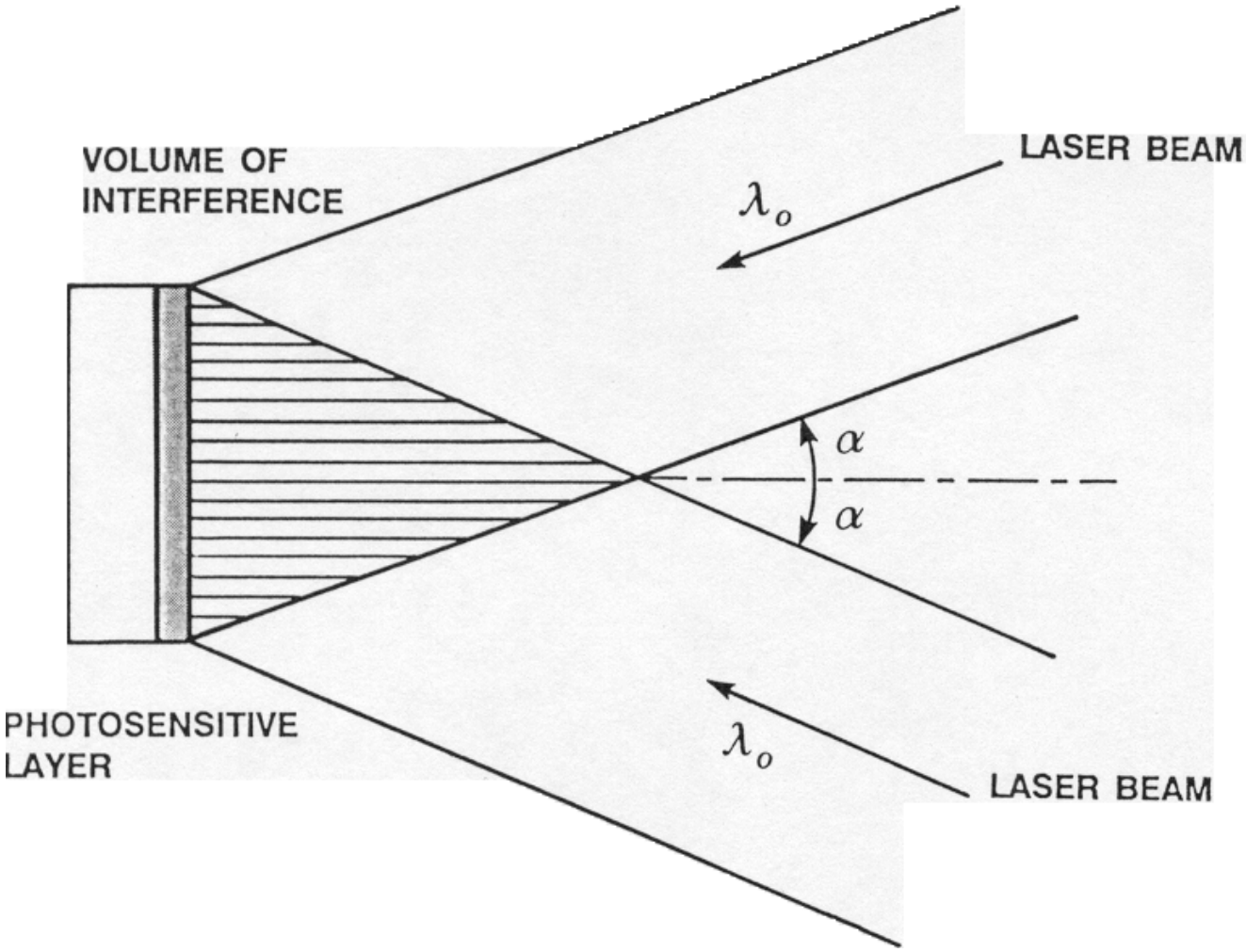





x10^3
50
40
30
20
10
0
Intensity (cnt)
700
800
900
1 000
1 100
1 200
1 300
1 400
1 500
Raman Shift (cm^-1)
600gr/mm
950gr/mm
1800gr/mm

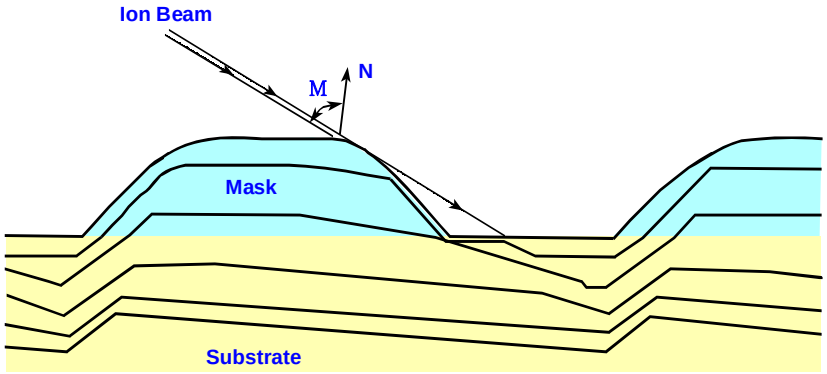

Entrance Slit
α
Δ
β
Grating (N)
Detector
Focal length (F)

HOLOGRAPHIC RECORDING



ION-ETCHING PROCESS

Evolution of groove profile simulated throught faceting model of ion beam erosion

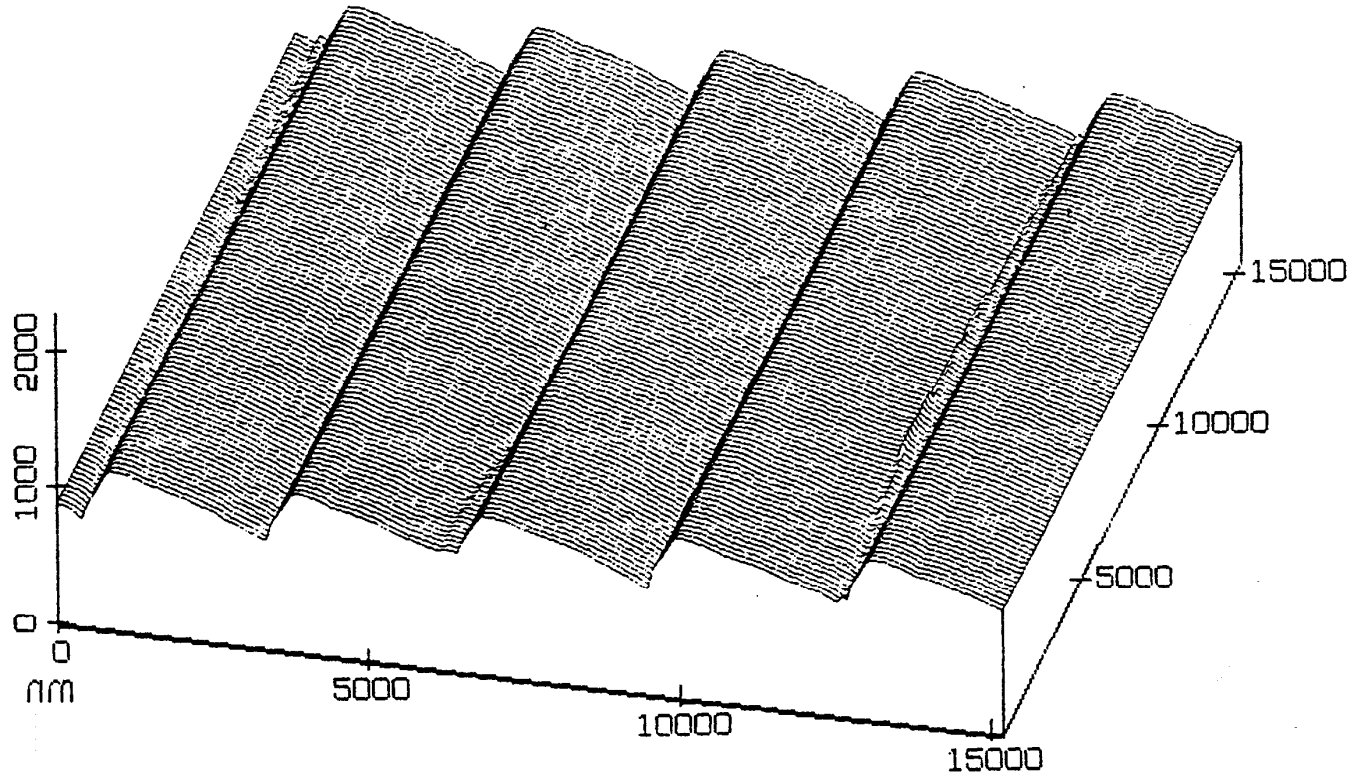


M : Angle of maximum etch rate
t_0 : *Initial mask profile*

An holographic mask, symetric and sinusoidal profile is transformed into a sawtooth profile :

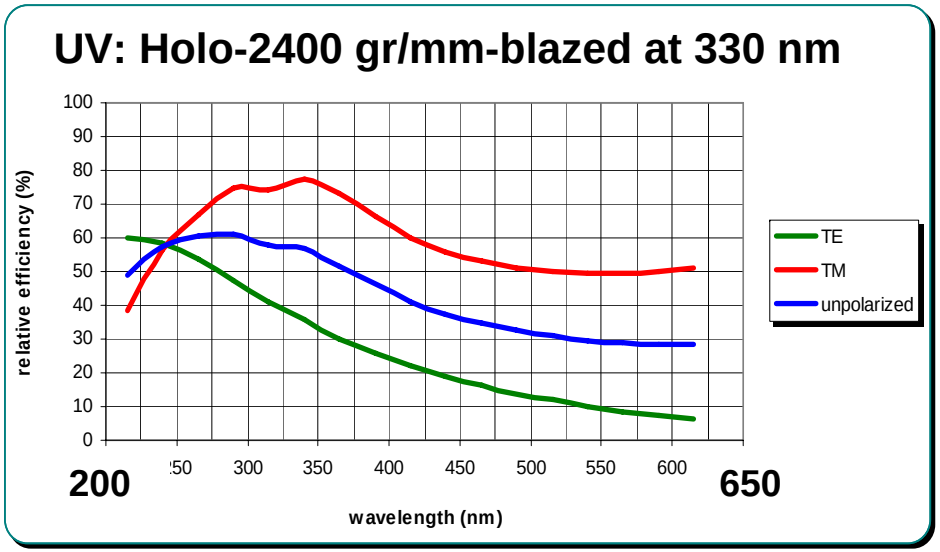
- higher efficiency
- still all advantages of holographic gratings

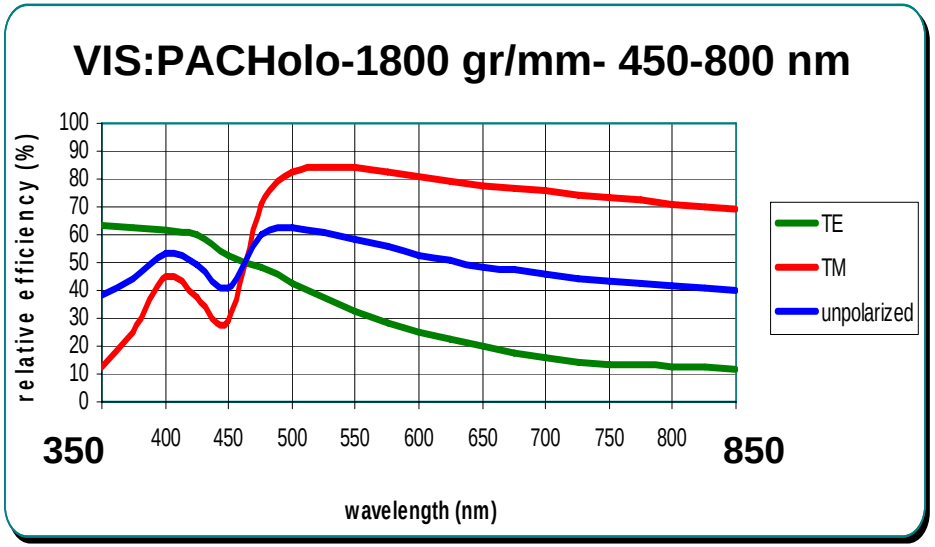
HOLOGRAPHIC BLAZED GRATING MADE BY ION-ETCHING

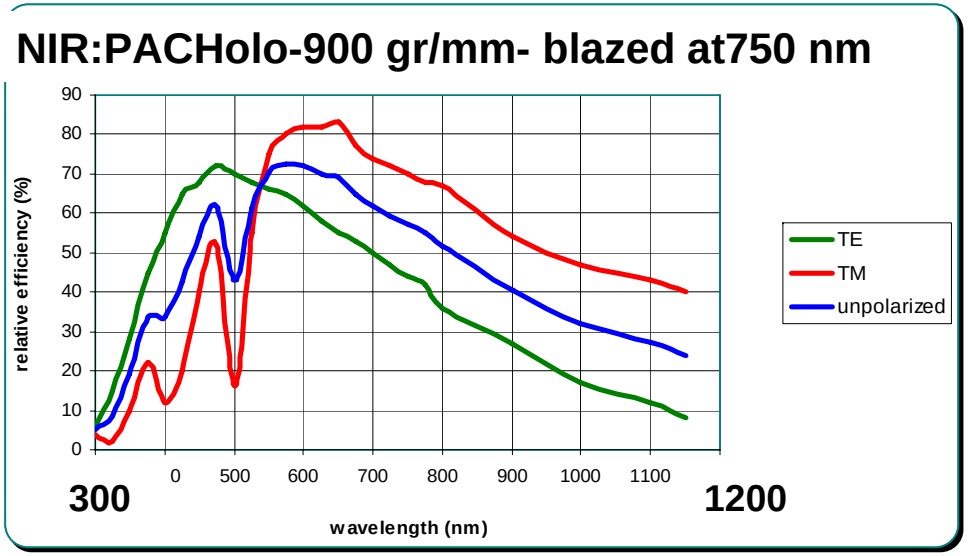


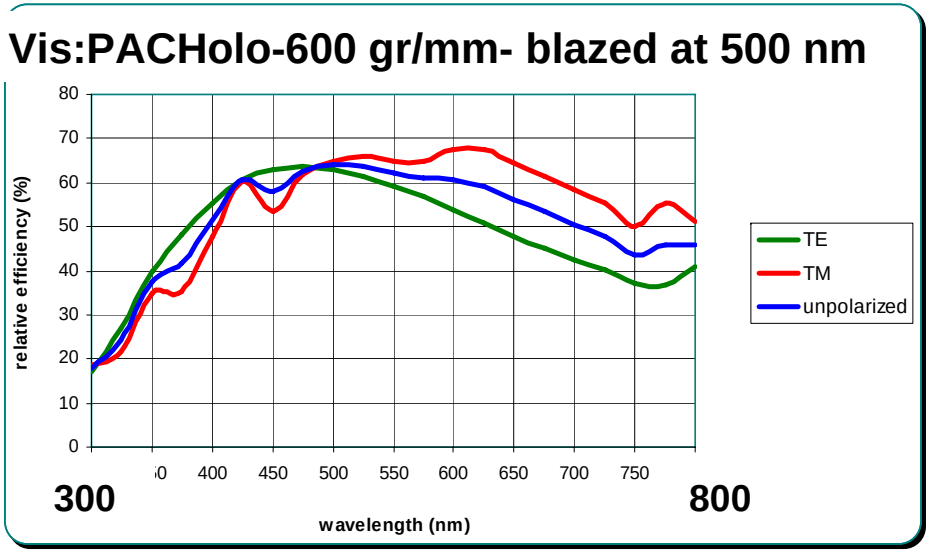
Scanning Tunneling Microscope Profile

Efficiency curves of some gratings

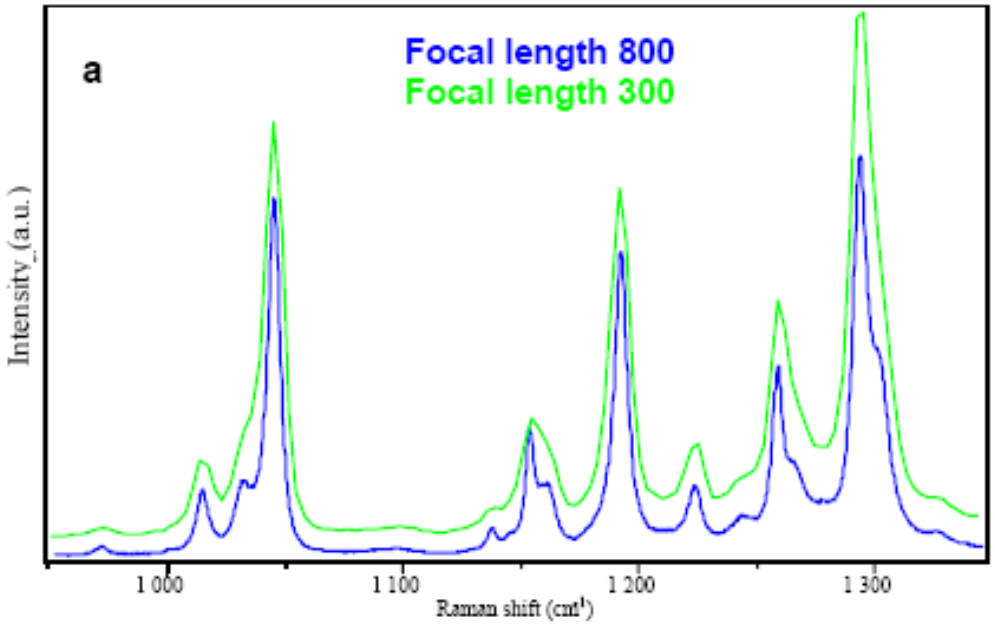


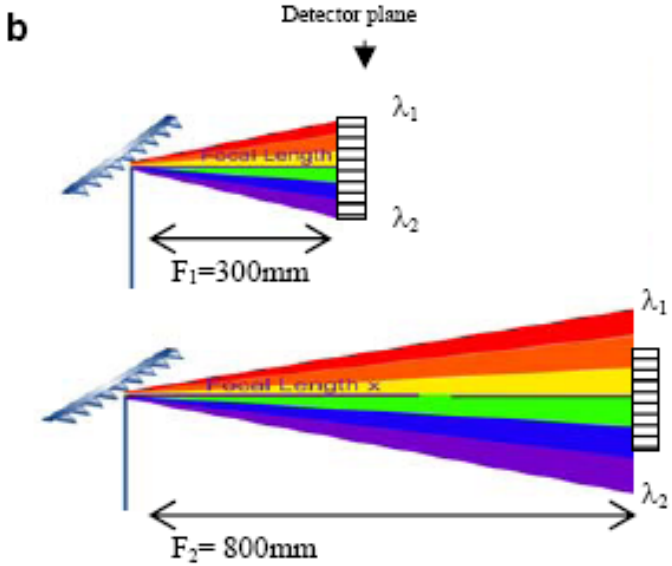


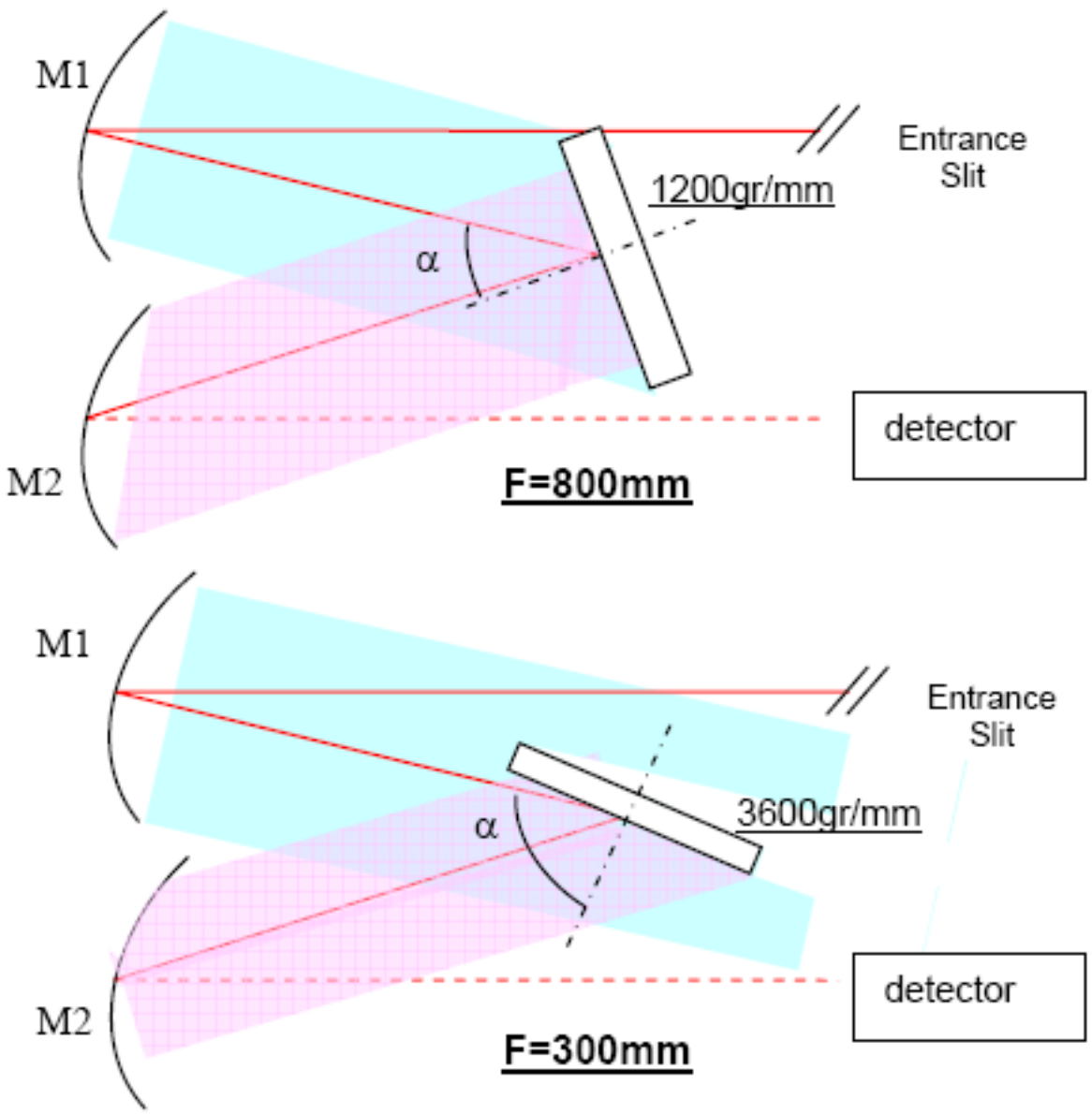




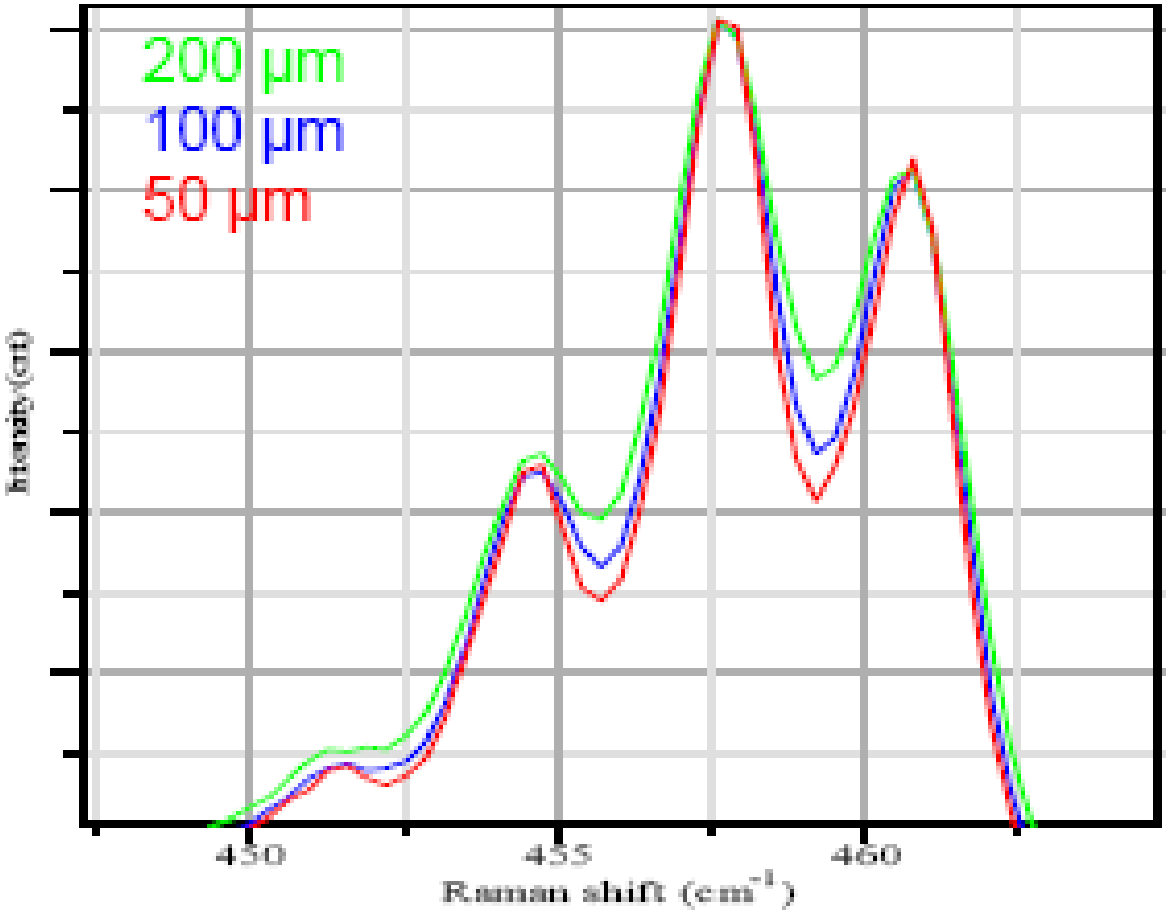
Focal length problem



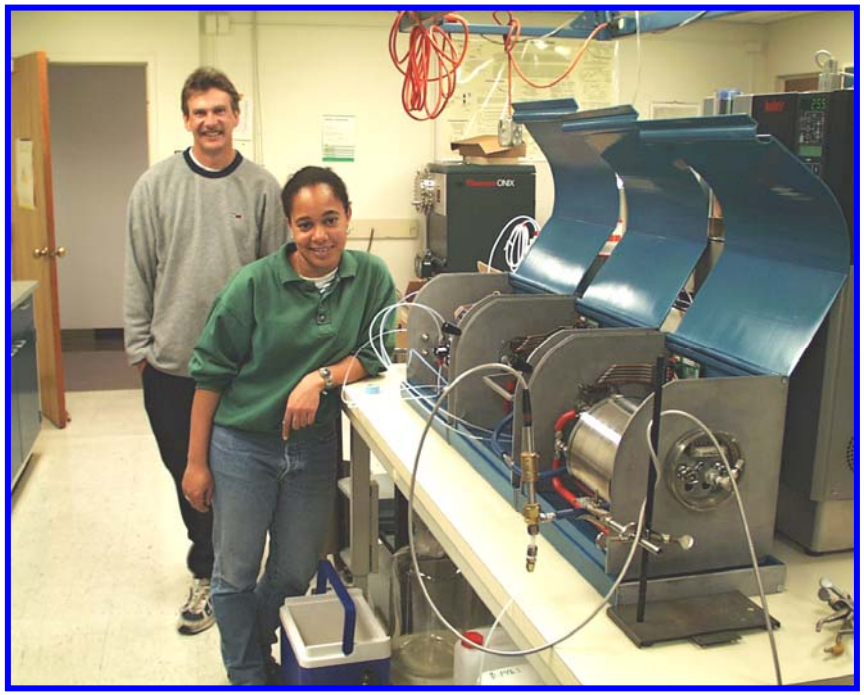



M1
Entrance
Slit
1200gr/mm
α
detector
M2
F=800mm
M1
Entrance
Slit
3600gr/mm
α
detector
M2
F=300mm

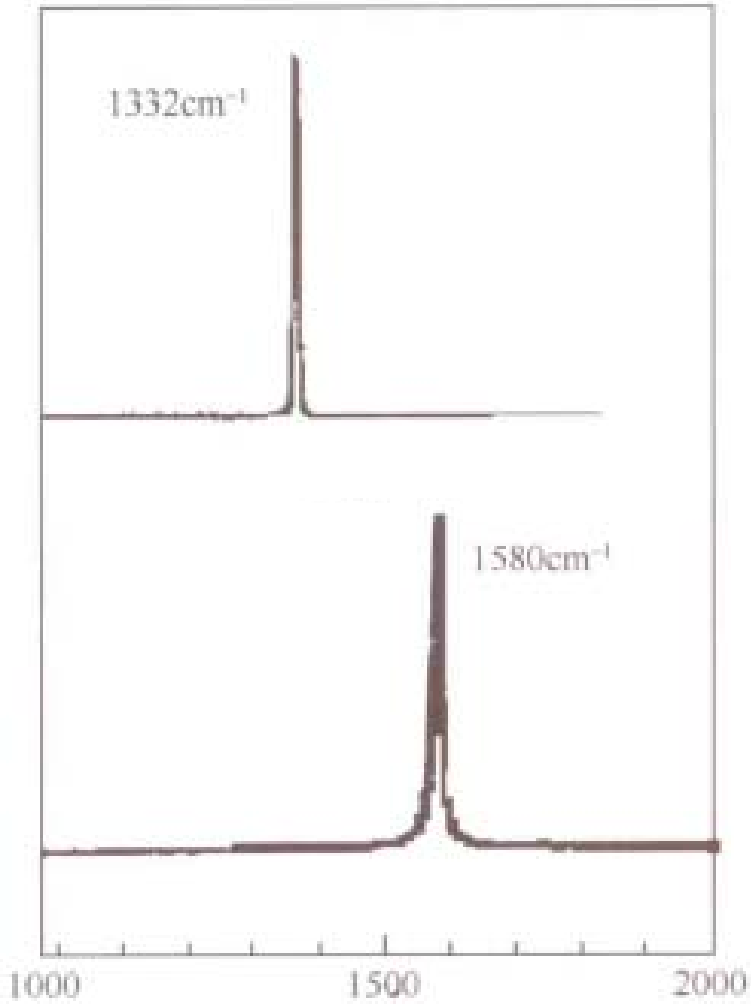
Slit size



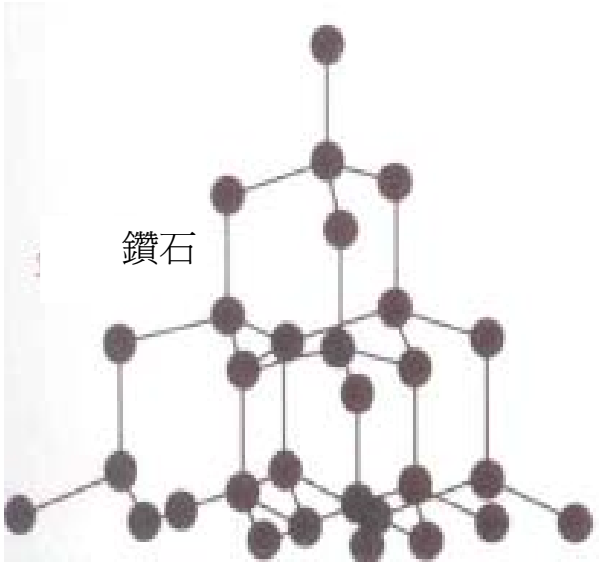
Applications

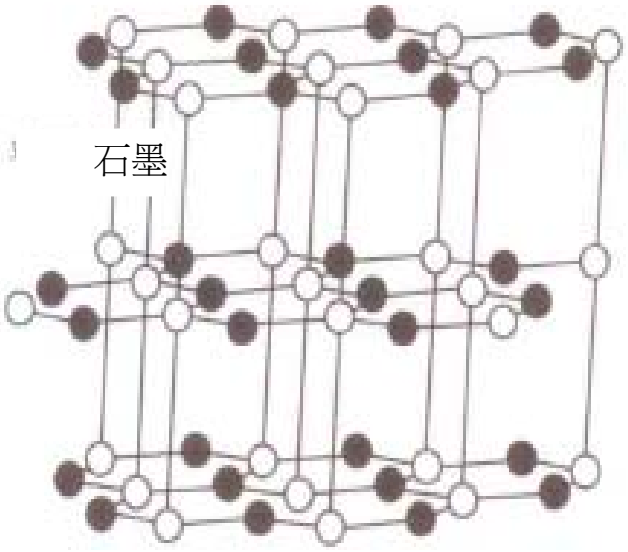


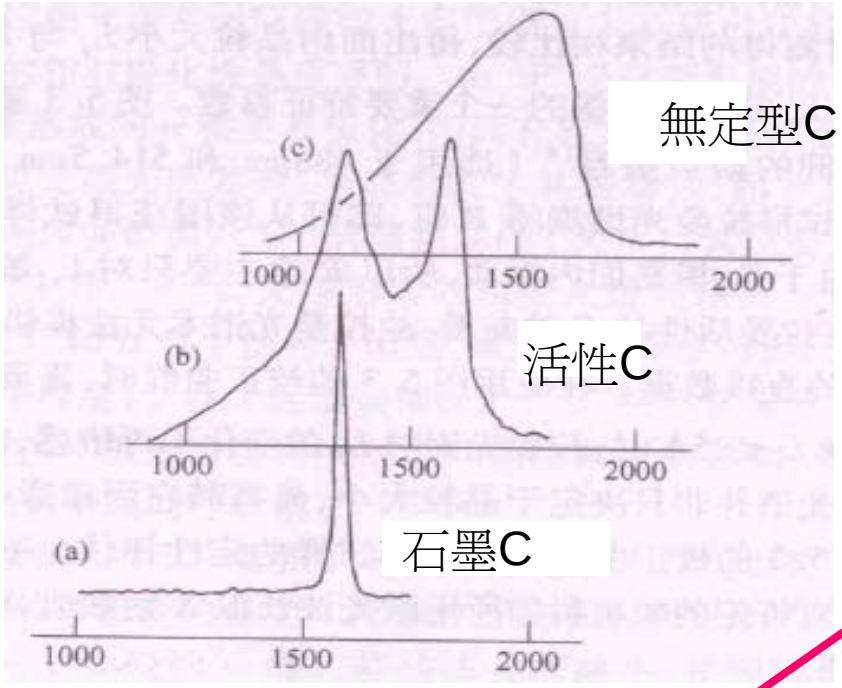
Carbon Nanotubes



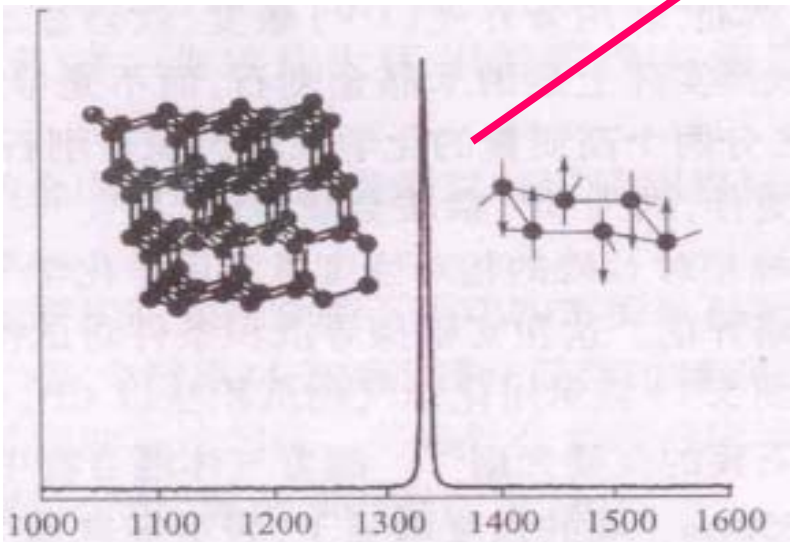
Raman shift cm-1



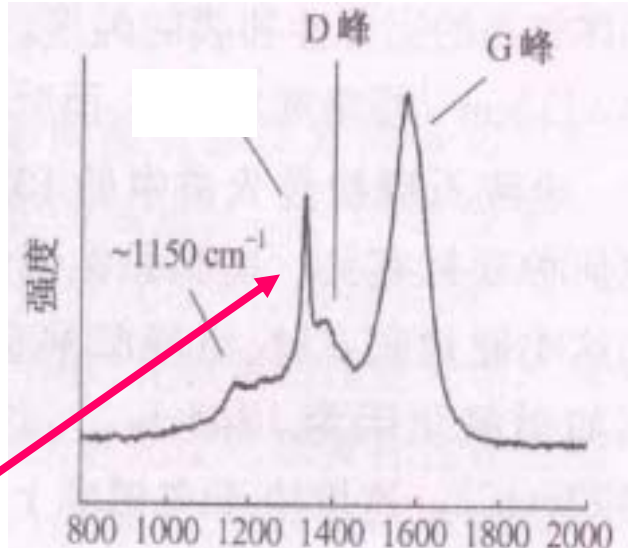




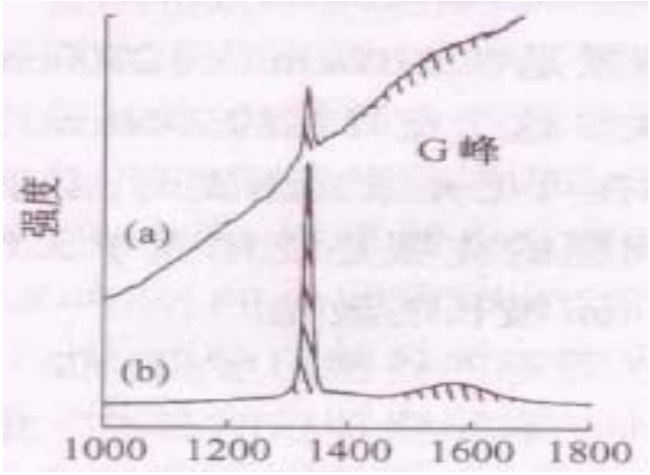
Raman shift



單晶鑽石結構



325nm laser

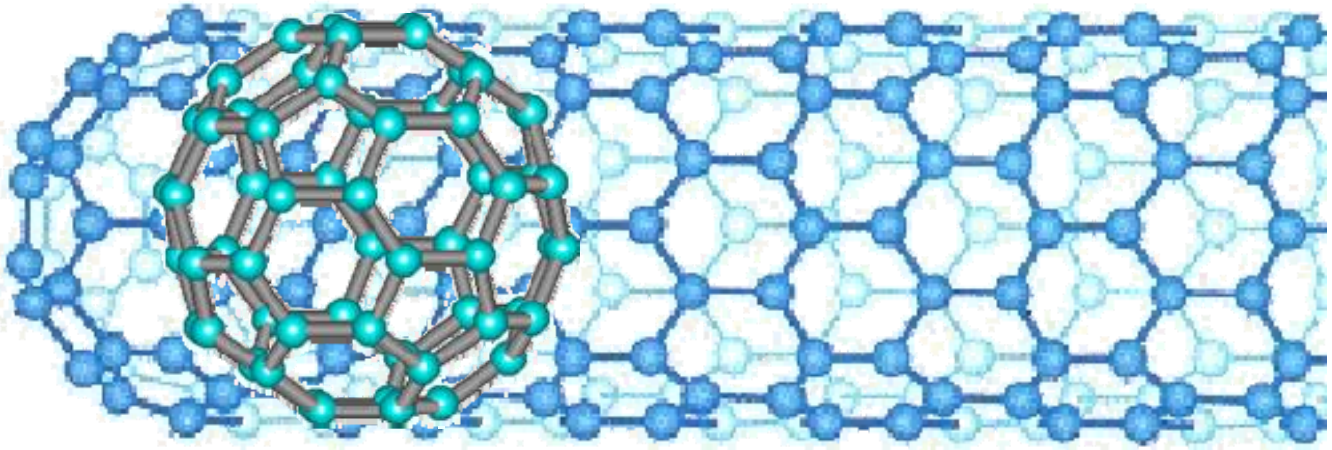


微晶鑽石膜

(a) 532nm laser

(b) 325nm laser

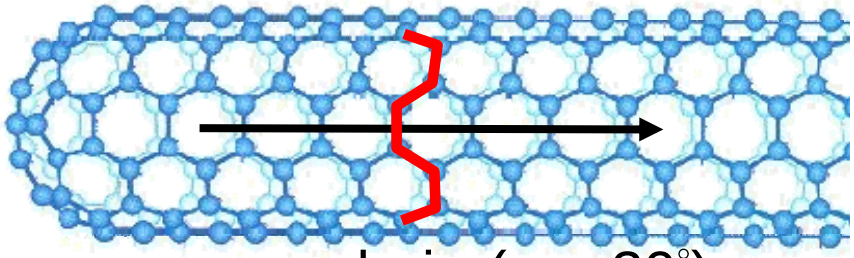
Carbon Nanostructures



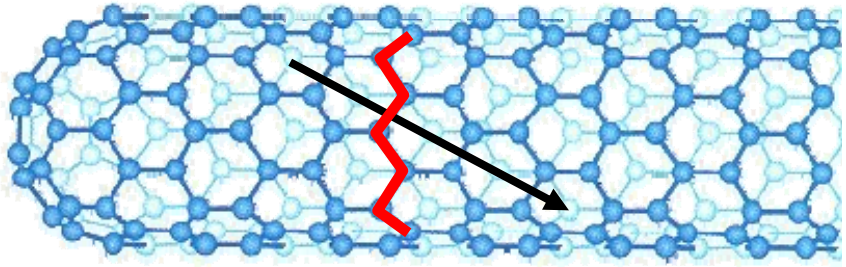
C_{60} (Buckminsterfullerene)

Single-walled Carbon Nanotube (SWNT)

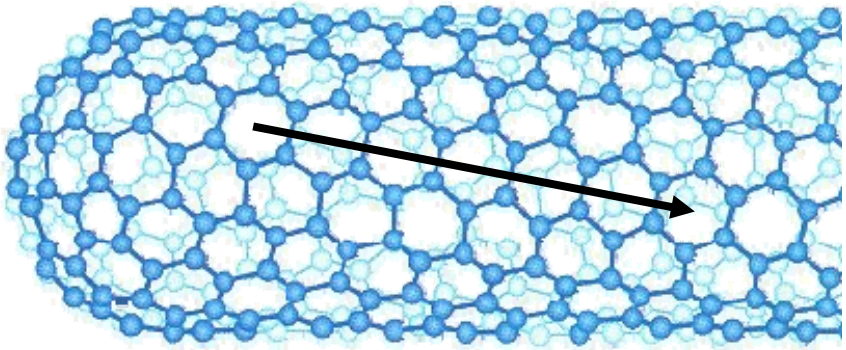
Many SWNT Structures Exist
(different diameters and angles)



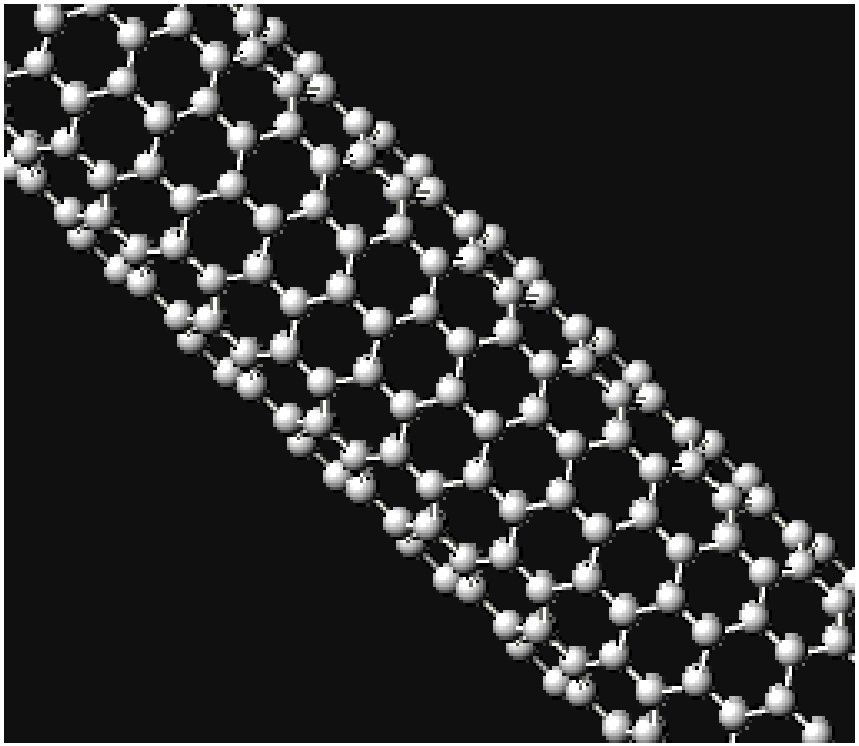
armchair ($\alpha = 30^{\circ}$)



zigzag ($\alpha = 0^{\circ}$)

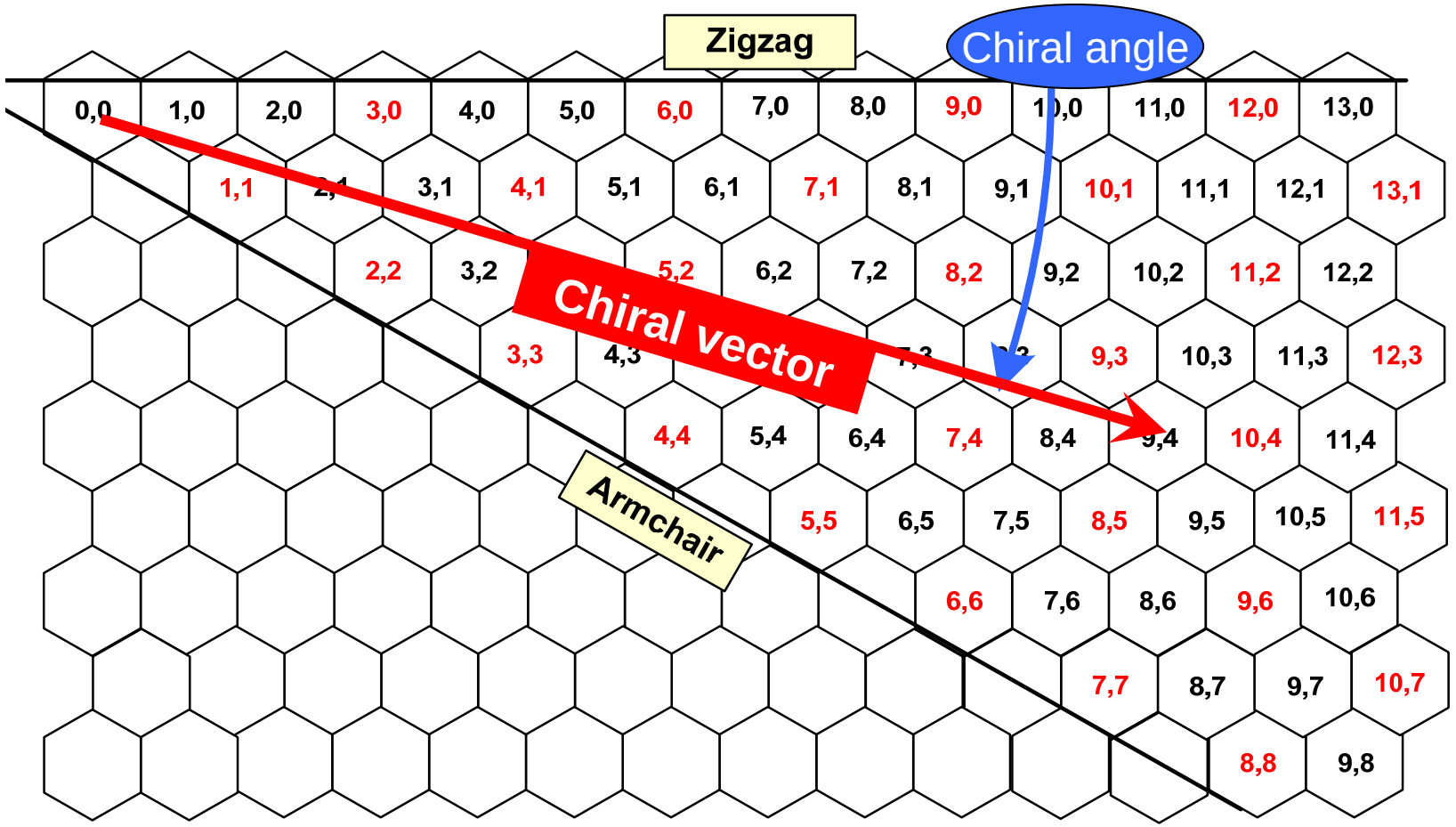


intermediate ($0 < \alpha < 30^{\circ}$)



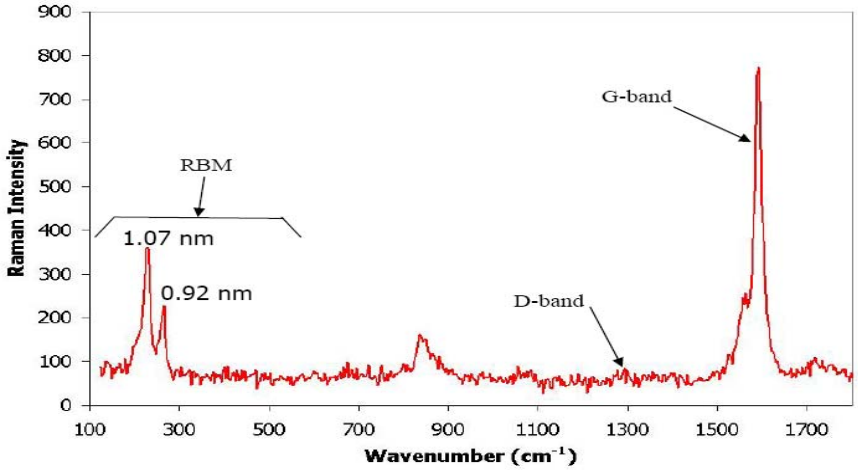
zigzag

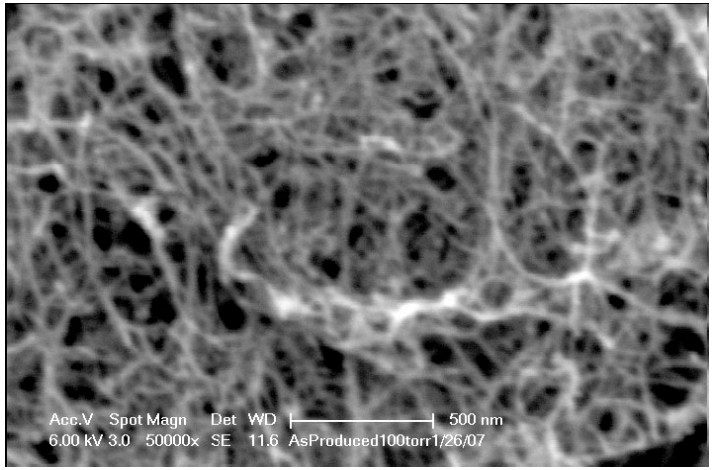
Constructing Nanotubes from a Graphene Sheet

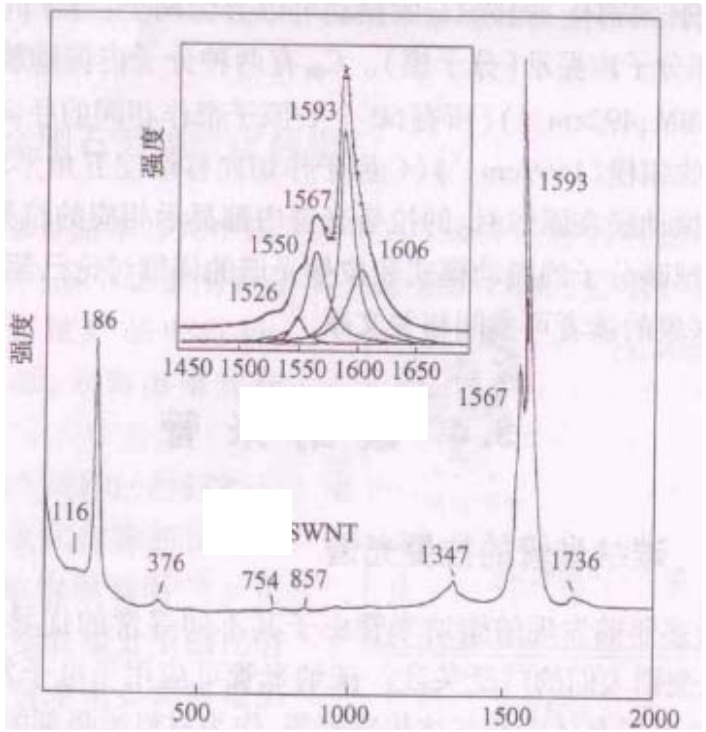


Each possible nanotube structure is labeled by two integers, (*n*,*m*), that uniquely define its diameter and chiral angle.

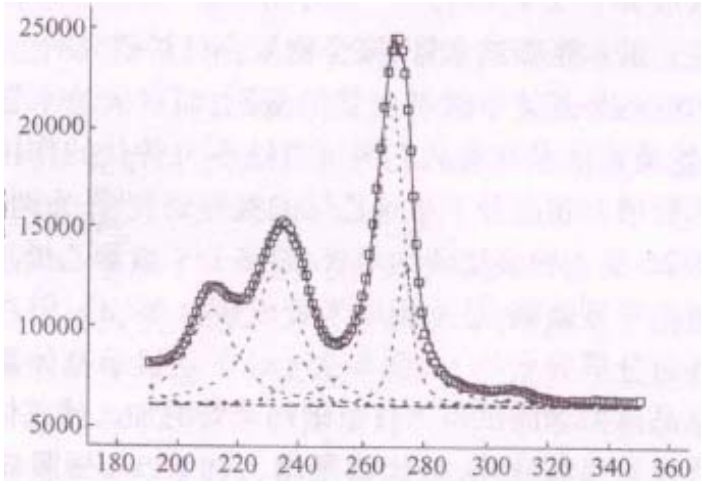
SWCNT



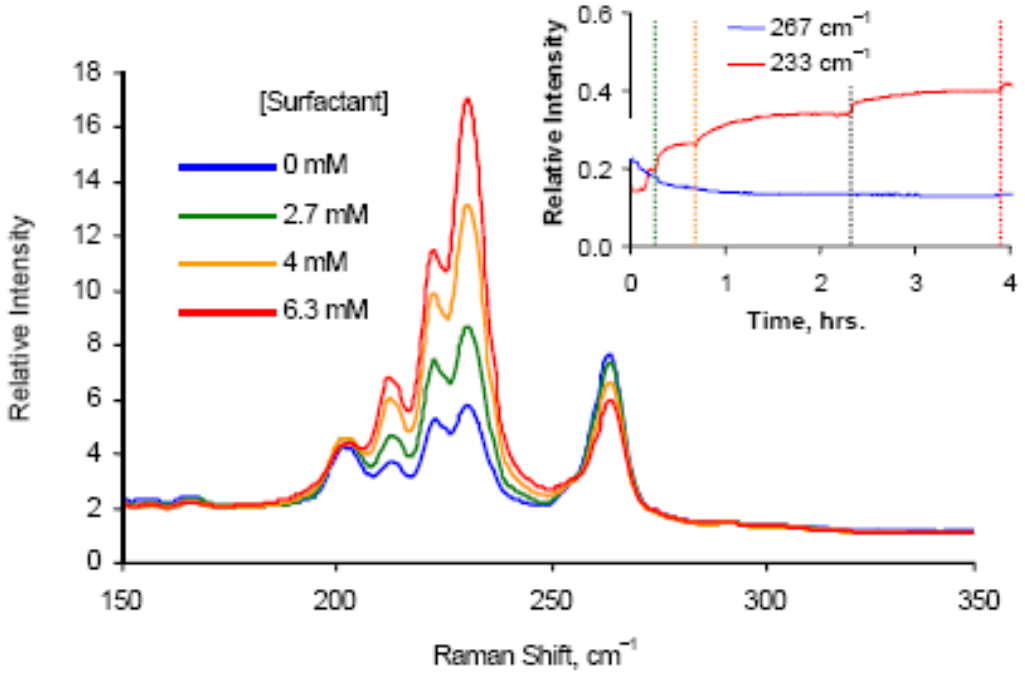




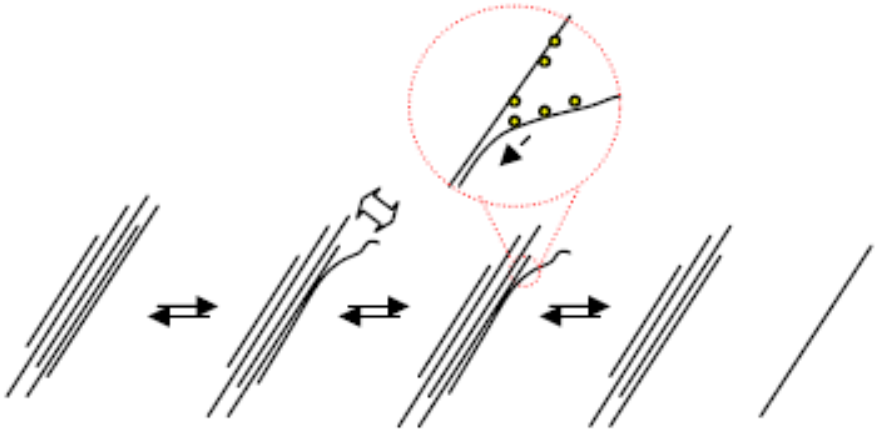
G mode identification with five peaks fitting



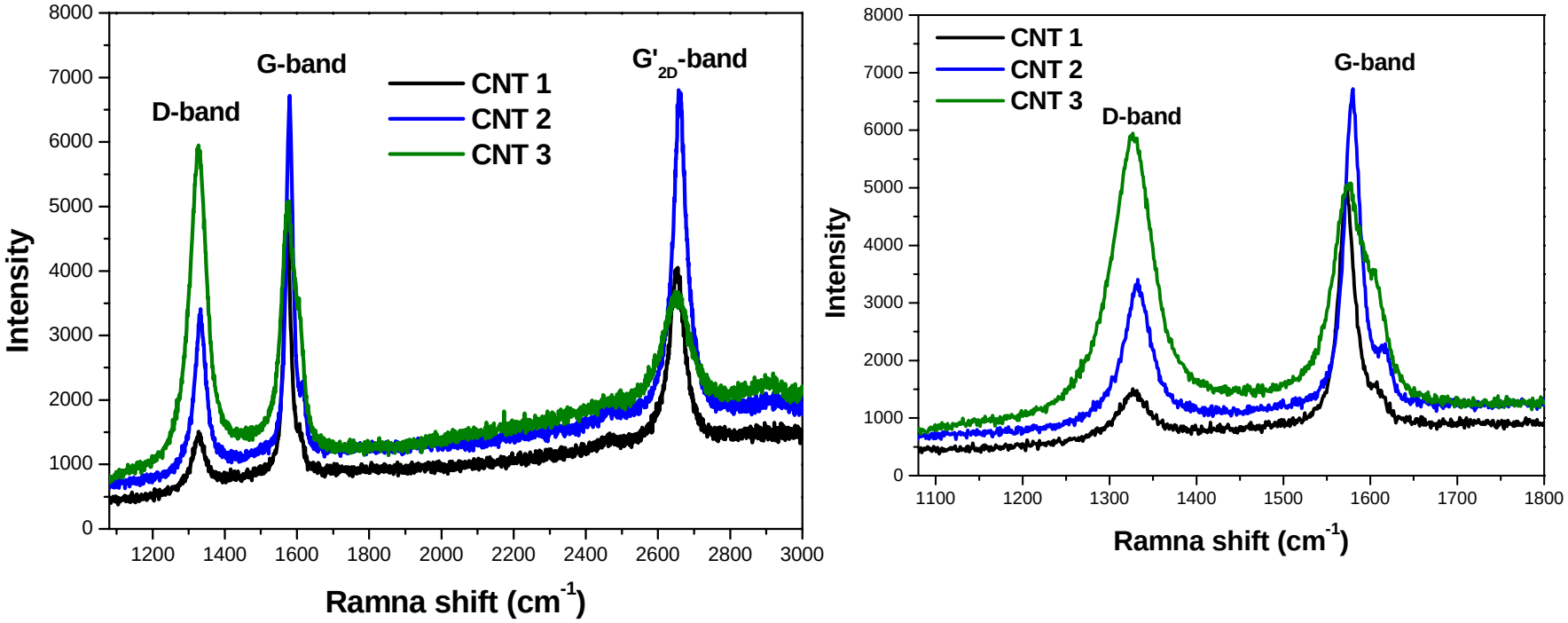
Raman shift



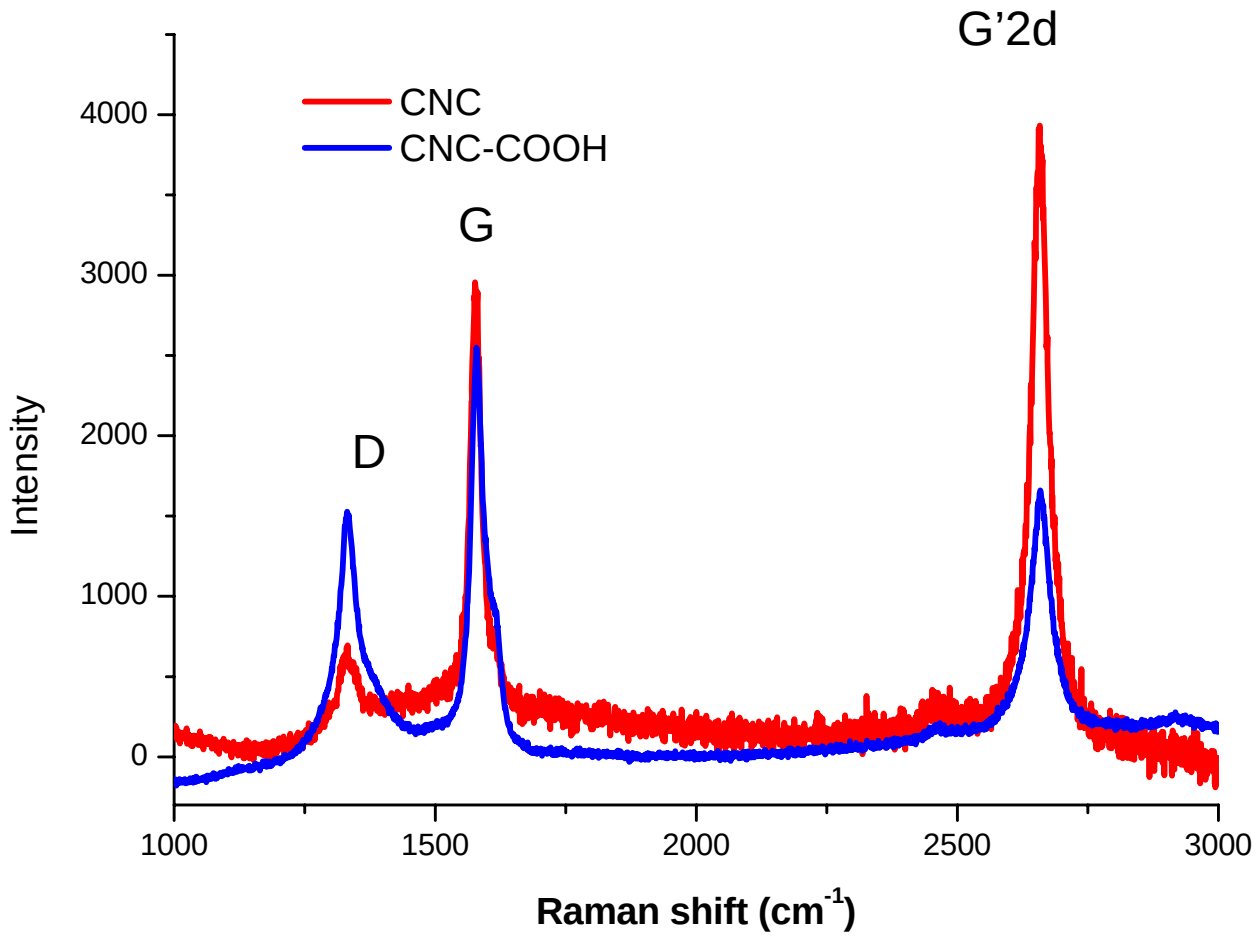
Raman shift of RBM for SMCNT:
210, 232, 238, 268, 272 cm-1



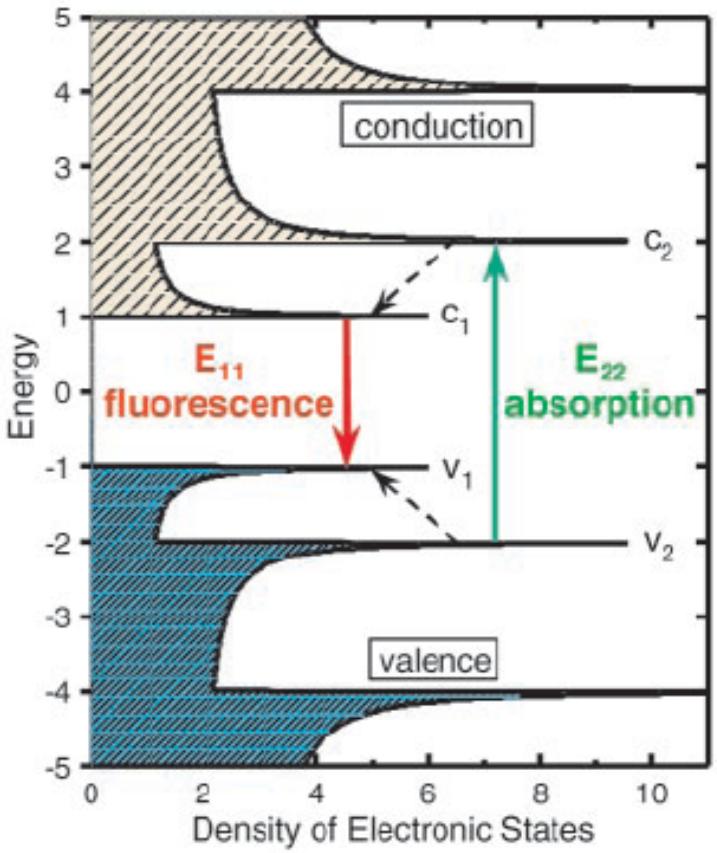
Five ring effect

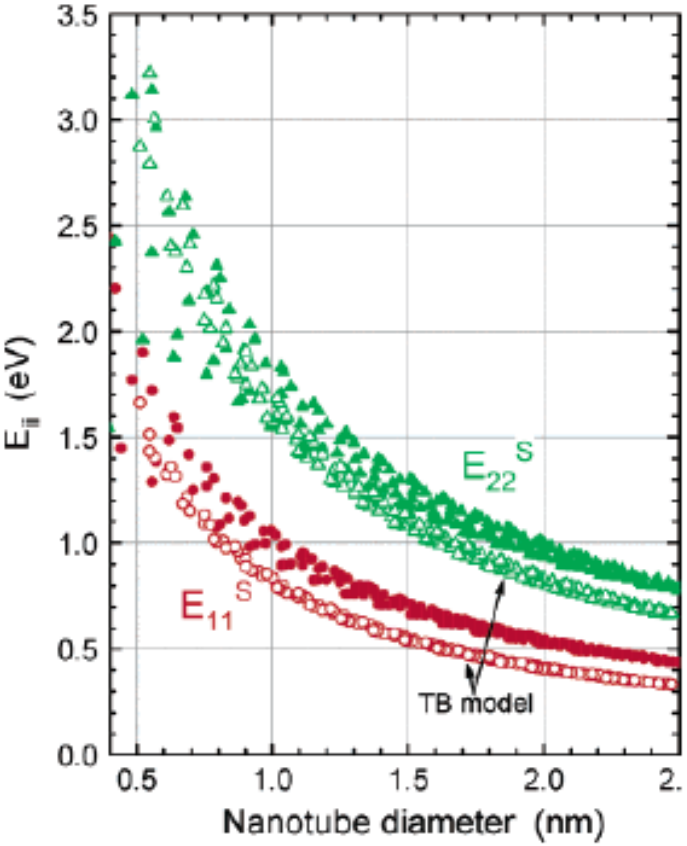


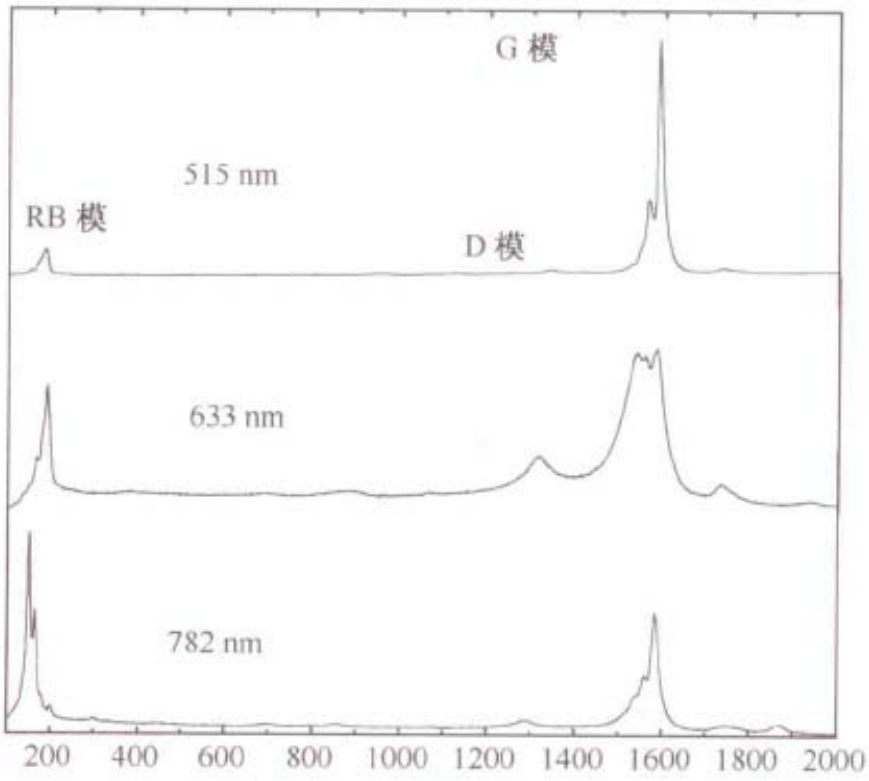
The small shoulder should be different electron contribution, indicating that the CNT might have two kinds of carbon rings like as five-ring or six-ring, which is called G+ and G– bands. Moreover, the three CNTs have different band shape, implying that the CNTs show a non-consistent double- or single- wall carbon.



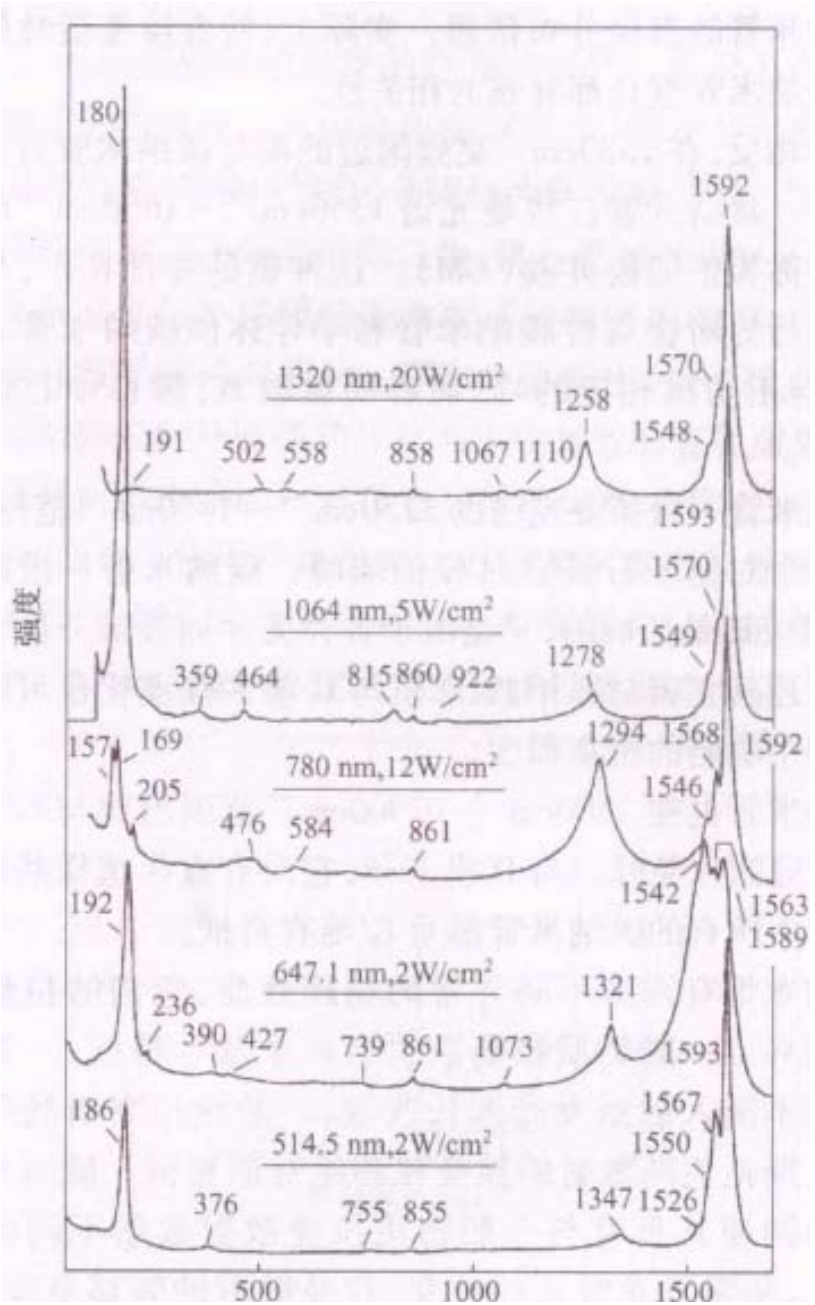
CNC經由表面處理後，其所產生之CNC之炭化度(G/D ratio)下降，且相對應之G/G'2d亦下降。 Wavelength = 633 nm


conduction
valence
C_2
C_1
V_1
V_2
E_{11} fluorescence
E_{22} absorption
Energy
Density of Electronic States


E_{ii} (eV)
E_{22}^S
E_{11}^S
TB model
Nanotube diameter (nm)

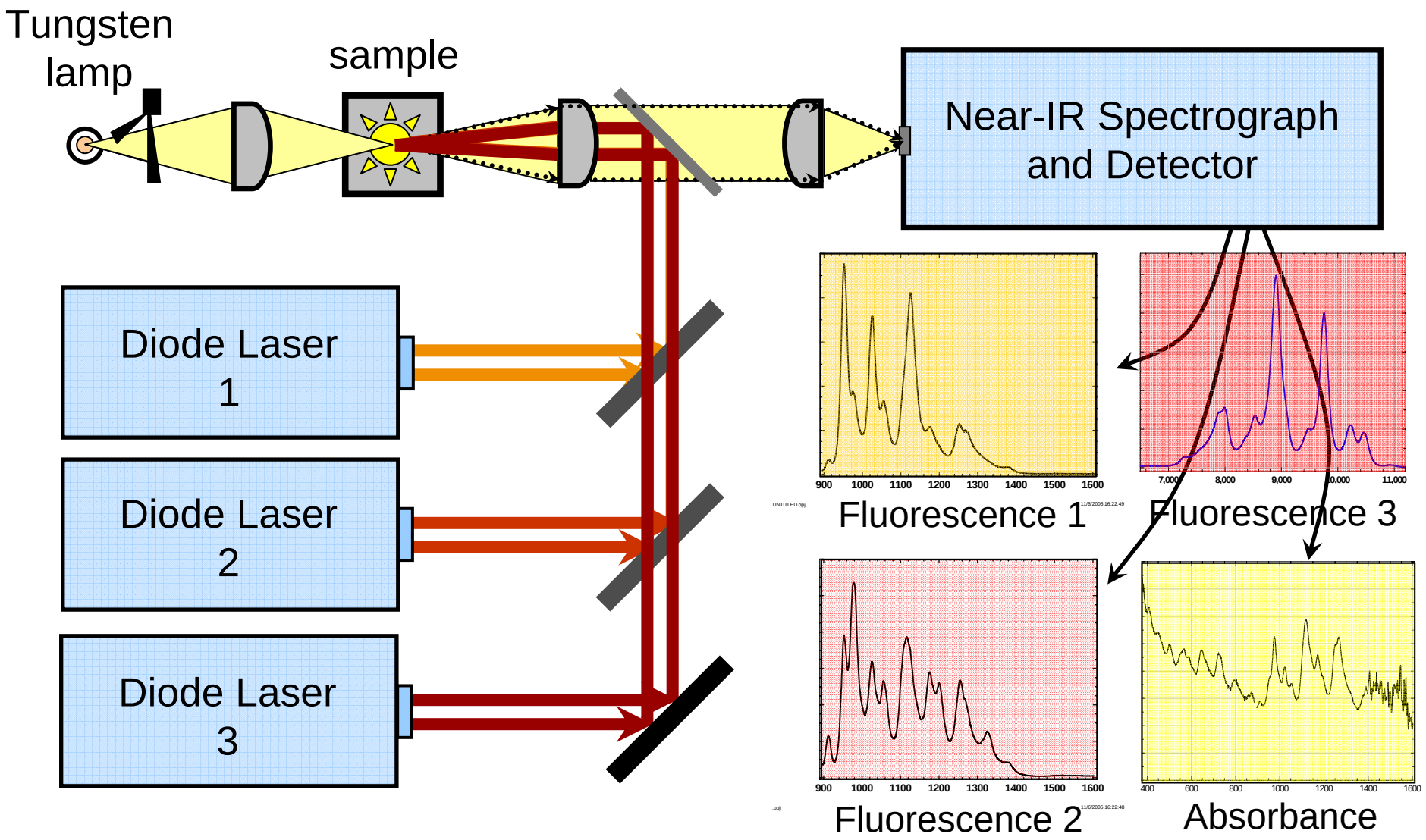


Raman shift cm-1

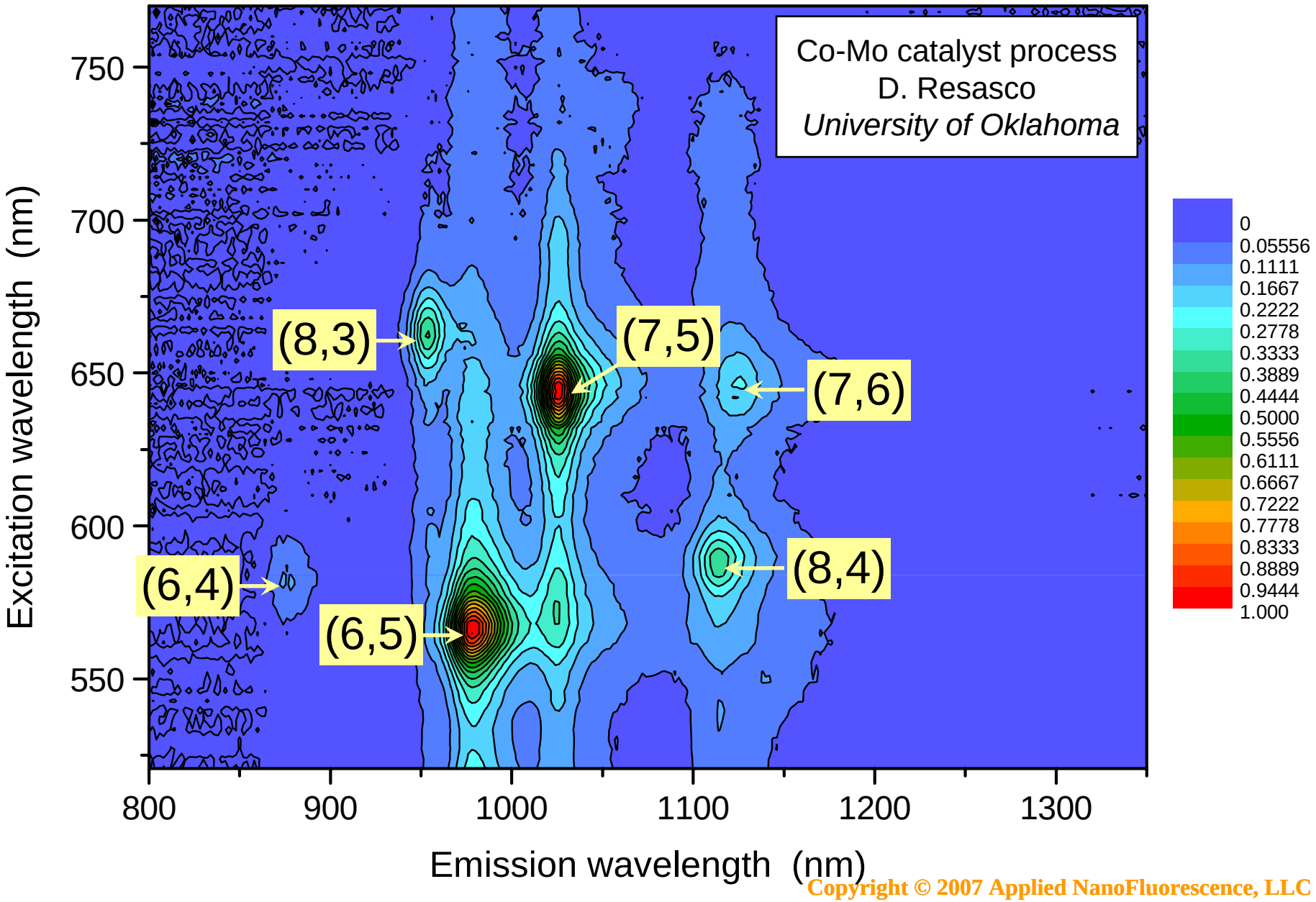


Raman shift cm-1

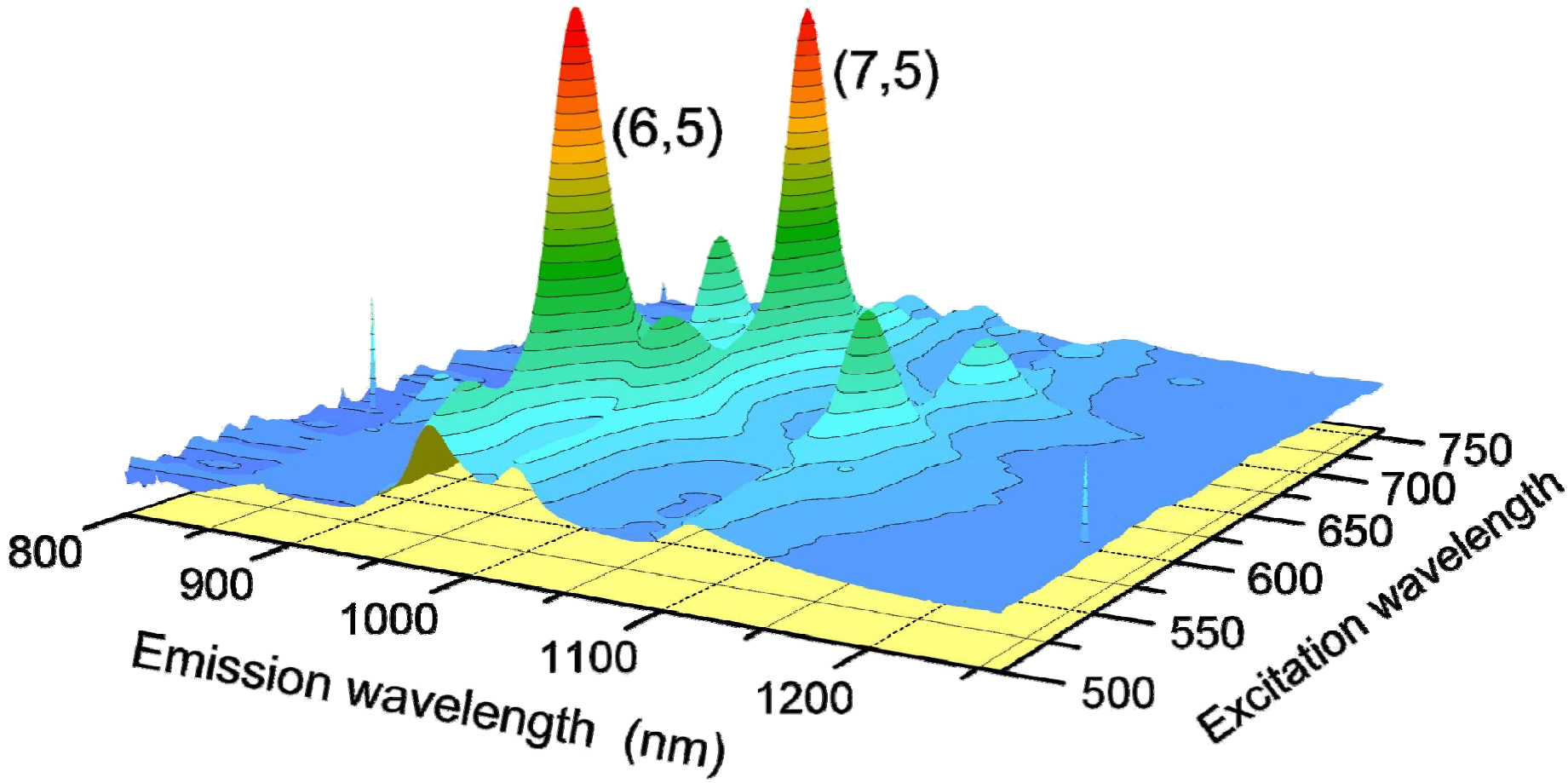
NanoSpectralyzer® Operation



Fluorimetric analysis from a full 2-D scan



2-D scan shows that two abundant SWCNT species are present



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Thanks for your attention