



IIT ROORKEE



NPTEL ONLINE
CERTIFICATION COURSE

Lecture 15: Plasmons- VI

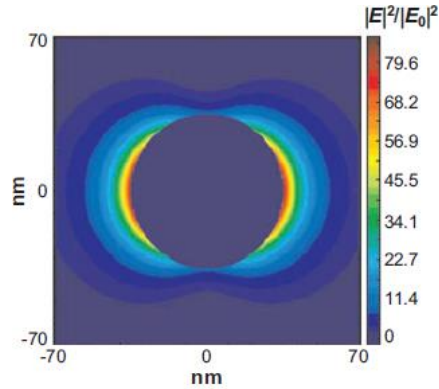
LSPs: Enhanced EM Fields, Surface Enhanced Raman Spectroscopy, Sensors

Sachin Kumar Srivastava

Department of Physics



Field Near Metallic Nanoparticles: Quasi static approx.



$$\vec{E}_{in} = \frac{3\epsilon_s}{\epsilon_m + 2\epsilon_s} \vec{E}_o$$

$$\vec{E}_{out} = \vec{E}_o + \frac{3\vec{n}(\vec{n} \cdot \vec{p}) - \vec{p}}{4\pi\epsilon_o\epsilon_s r^3}$$

$$\vec{p} = 4\pi\epsilon_o\epsilon_s R^3 \frac{\epsilon_m - \epsilon_s}{\epsilon_m + 2\epsilon_s} \vec{E}_o$$

Total Electric Field

$$\vec{E} = \frac{1}{4\pi\epsilon_o\epsilon_s} \left[k^2 (\vec{n} \times \vec{p}) \times \vec{n} \frac{e^{ikr}}{r} + \{3\vec{n}(\vec{n} \cdot \vec{p}) - \vec{p}\} \left(\frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr} \right]$$

$$E_{plas} \approx \frac{\epsilon_m - \epsilon_s}{\epsilon_m + 2\epsilon_s} \frac{R^3}{(R + d)^3} E_o$$

Sites et al., Annu. Rev. Anal. Chem. **1**, 601 (2008)

Field Enhancement Near Metallic Nanoparticles

$$\vec{E} = \vec{E}_{inc} + (1 - \tilde{L}) \frac{4\pi}{V} \tilde{\alpha} \vec{E}_{inc}$$

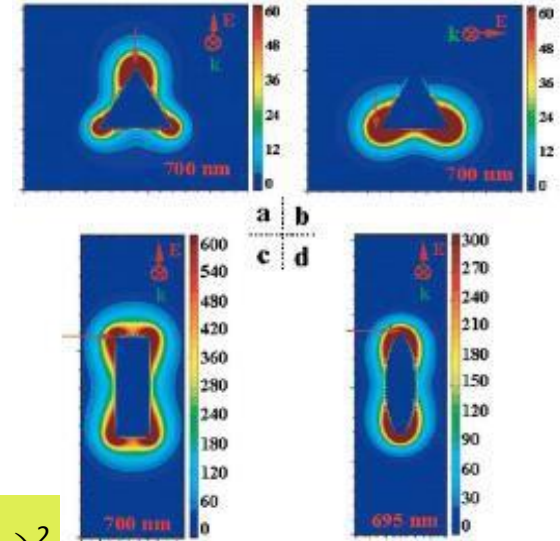
Hence the field enhancement near the tip j of a spheroid:

$$\eta_{E_j} = \left| \frac{E_j}{E_{inc}} \right|^2 = \left| 1 + (1 - L_j) \left(\frac{\epsilon_m - \epsilon_s}{L_j(\epsilon_m + \epsilon_s) + \epsilon_s} \right) \right|^2 = \left| \frac{\epsilon_m}{L_j(\epsilon_m + \epsilon_s) + \epsilon_s} \right|^2$$

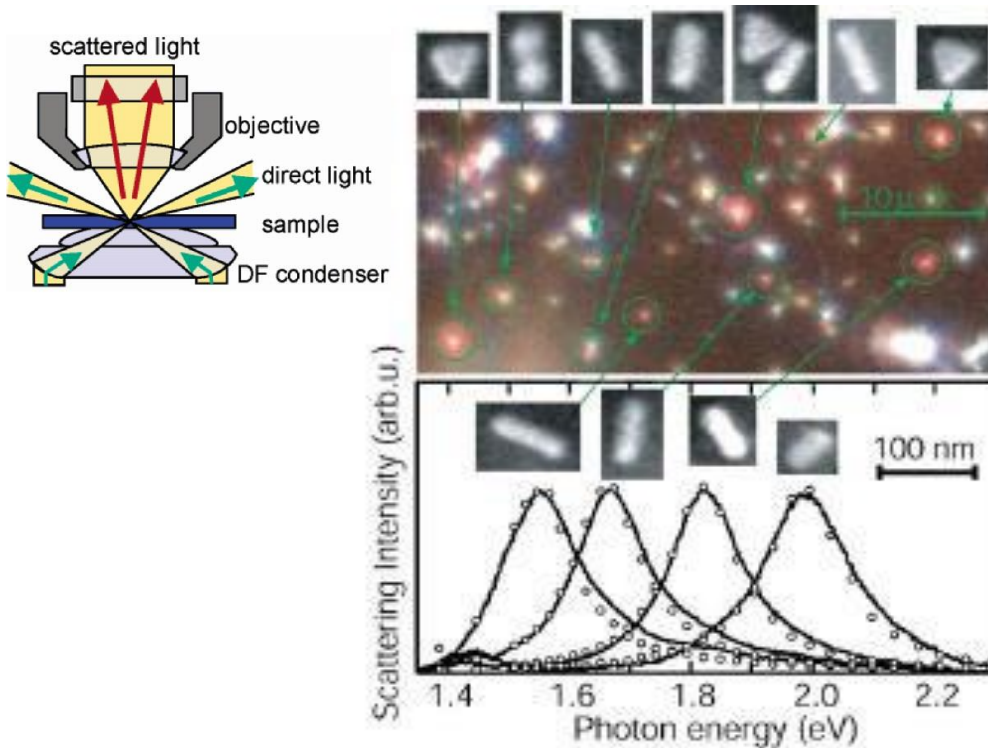
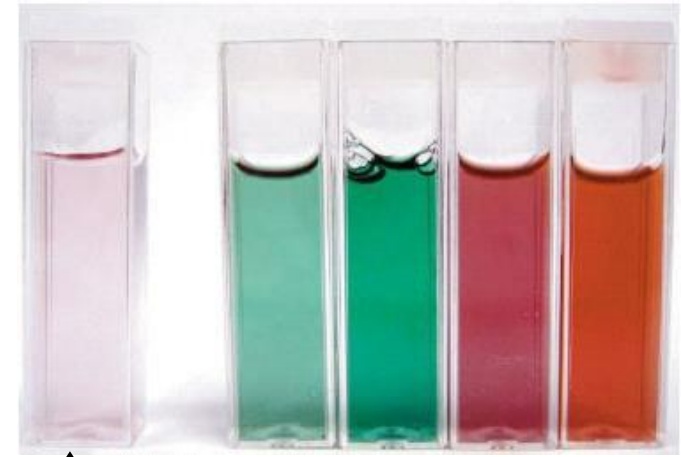
$$\eta_{E_j} = \left| \left(\frac{\epsilon_{mr}^2 + \epsilon_{mi}^2}{|L_j(\epsilon_{mr} + \epsilon_s) + \epsilon_s|^2 + |L_j \epsilon_{mi}|^2} \right) \right|^2 \Rightarrow \eta_{E_j}^{Max} = \left(\frac{\epsilon_{mr}^2 + \epsilon_{mi}^2}{L_j^2 \epsilon_{mi}^2} \right) \approx \left(\frac{\epsilon_{mr}}{L_j \epsilon_{mi}} \right)^2$$

Vanishes at the resonance

Hao et.al., J.Chem.Phys. 120, 357 (2004)



Observing LSPR in Metal Nanoparticles



Au nanorods
in water

Ag shell on Au
nanorods in water

Increasing shell thickness

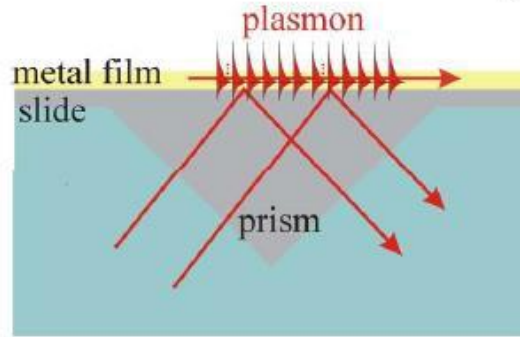
Kawata et.al., Appl.Phys.Lett. 83, 4625 (2003)

Pelton et.al., Laser and Photonics Review 3, 136-159 (2008)

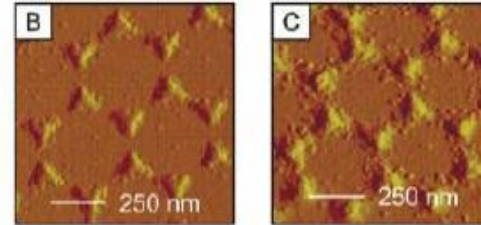


Plasmonic Structures

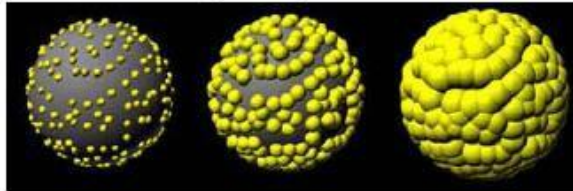
Surface Plasmon Resonance (SPR)



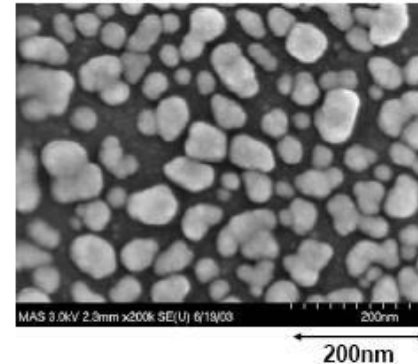
Structured LSPR or SERS films



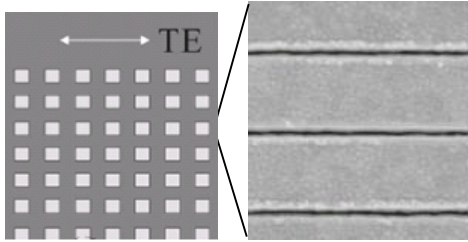
Nanoshells (LSPR)



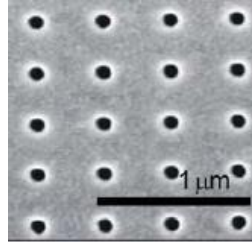
Metal-dielectric semicontinuous films



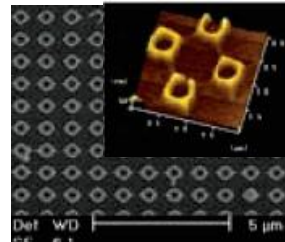
Plasmonic Structures



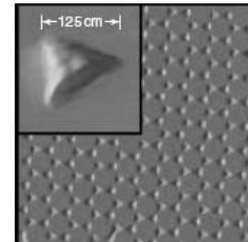
Arrays of nanoslits



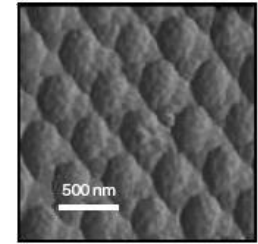
Nanoholes array



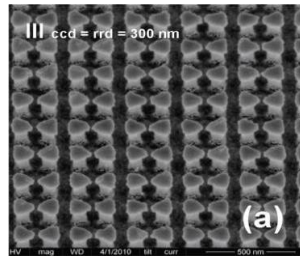
Nanorings array



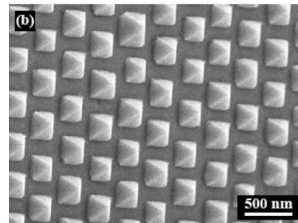
Triangles array



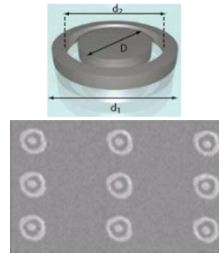
Film over nanospheres



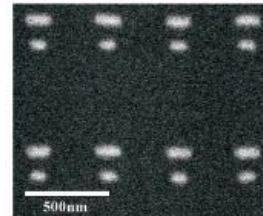
Bowties array



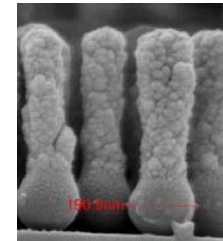
NanoPyramides array



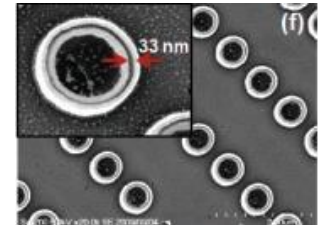
Disk in nanoring array



Array of pairs of nanorods

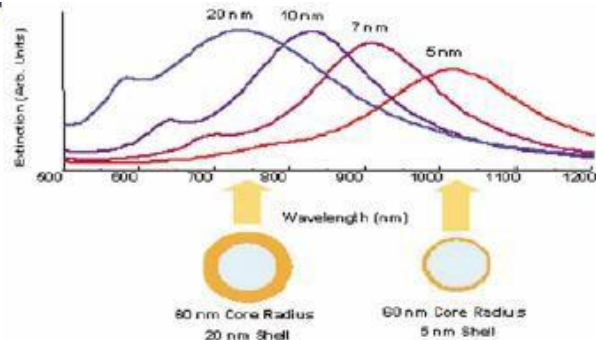


Nanocolumns on nanospheres

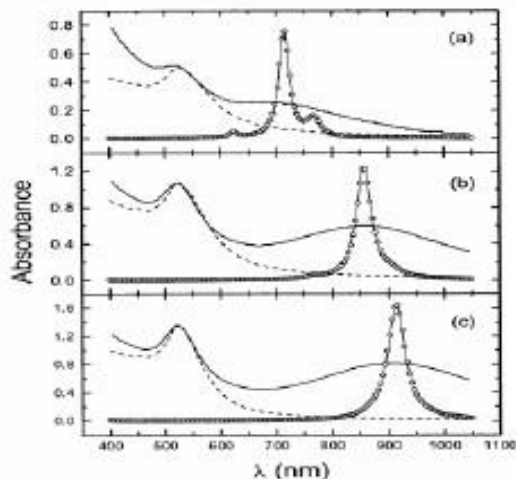


2D array of double Au nanopillars

Nano-Shells LSPR



Optical resonances of gold-silica core nanoshells as a function of their core/shell ratio.



Calculated – circles
Experimental – solid
Solid gold spheres - dashed

$$r_1 = 4.1, r_2 = 5.1 \text{ nm}$$



8.6, 9.9



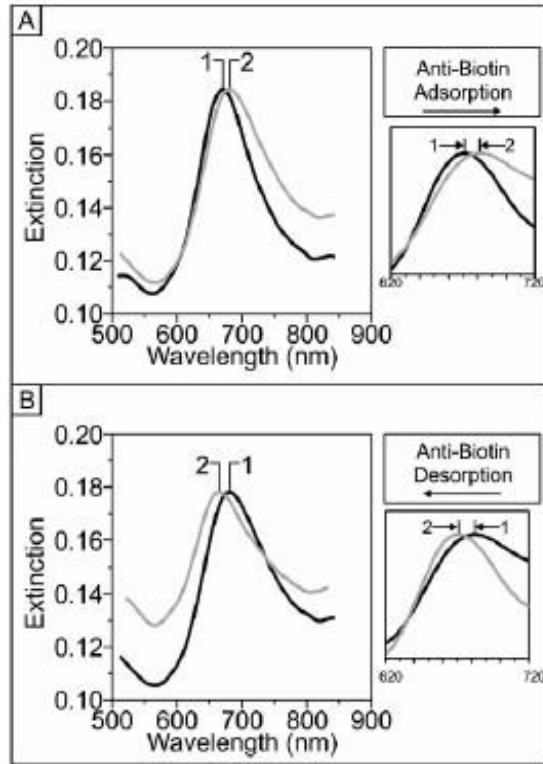
13.1, 14.9



- More sensitive than simple nanoparticles. (gain $\sim r_2/r_1$)
- Resonance frequency is a strong function of geometry
- More resonant frequencies possible

Technology in Cancer Research & Treatment, 3, 1, 2004
Nano Lett., 3, 10, 1411-1414, 2003.

Biosensing with Ag Nano-Particles



- 1 – Ag nanoparticles
- 2 – Anti-biotin added

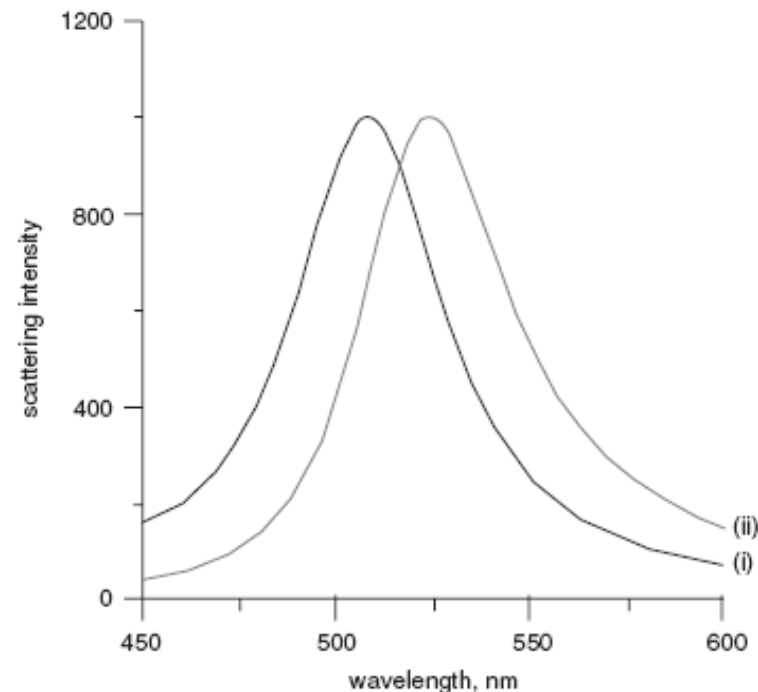
Peak
671.1 nm
681.8 nm

- 1 – Ag with Anti-biotin
- 2 – Biotin added

Peak
681.8 nm
670.2 nm

R.P.V. Duyne, J. Fluorescence, 14, 2004

Single Ag Particle BioSensor



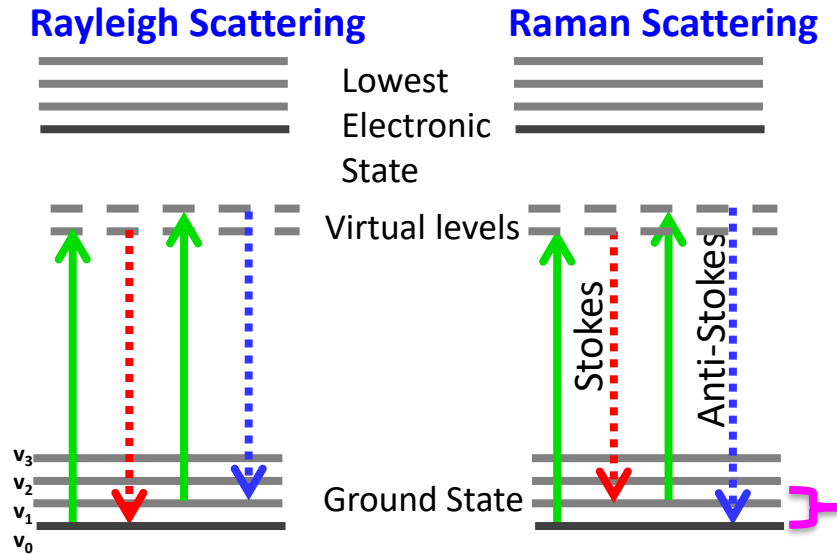
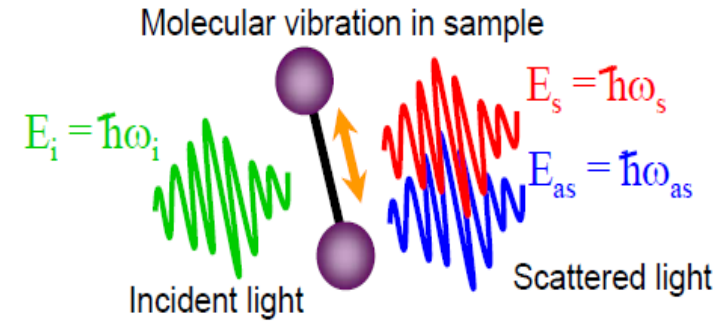
Individual Ag nanoparticle sensor before and after exposure to 10 nM streptavidin. All measurements were collected in a nitrogen environment

(i) Biotinylated Ag nanoparticle, $\lambda_{\text{max}} = 508.0 \text{ nm}$.

(ii) After streptavidin incubation, $\lambda_{\text{max}} = 520.7 \text{ nm}$.

I. Abdulhalim, BOSMI Lecturs

Raman Spectroscopy



- 'Fingerprint' of molecular bonds and crystalline structure
- Very low cross-section: **1 in 10^7** photons

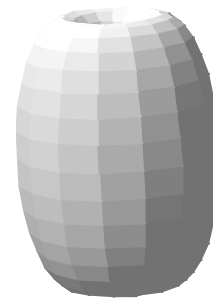
Polarizability Tensor & Raman Modes

In actual molecules, the nice linear relationship does not hold since both P and E are vectors. Then the equation must be written as

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

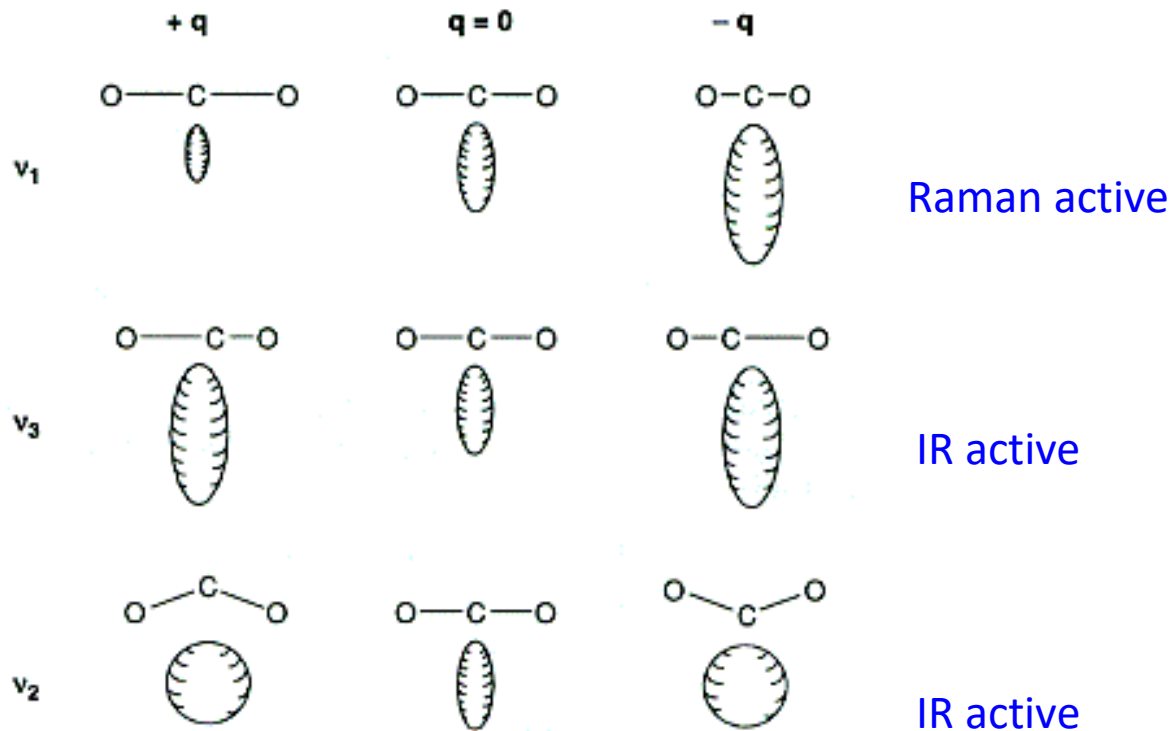
$$P = \alpha E$$

The matrix is called the *polarizability tensor*. We can plot α_i (a in the i direction) in all directions we get a 3D surface. Conventionally we plot $1/\sqrt{\alpha_i}$ instead, and get a *polarizability ellipsoid*.



Advanced Vitreous State 2007,
Raman spectroscopy L1, M.
Affatigato

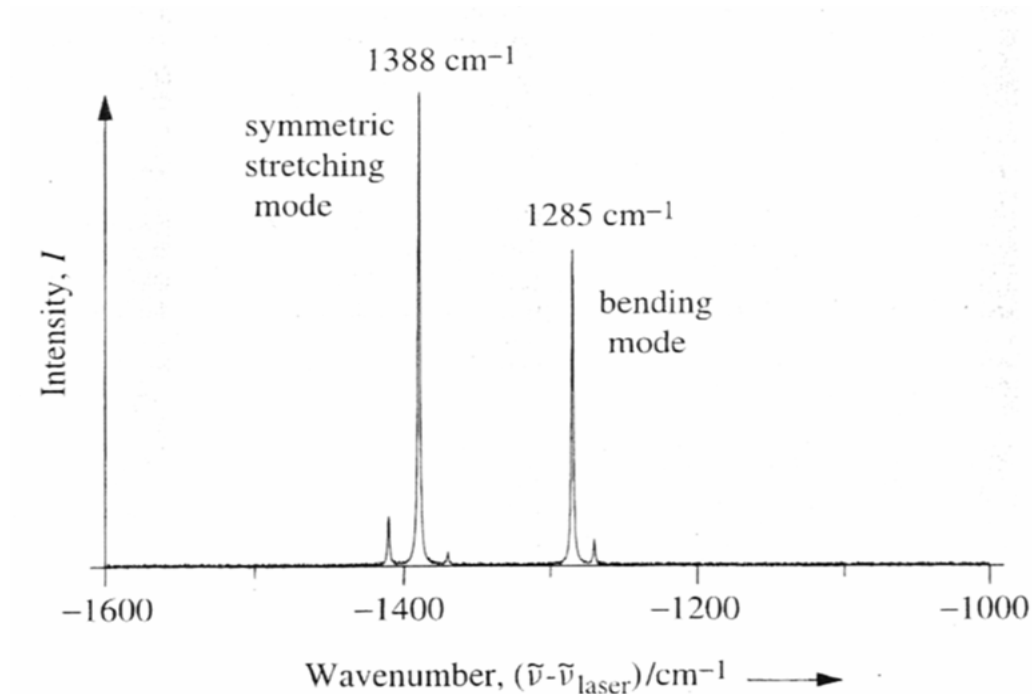
CO₂ Polarizability Ellipsoids



Advanced Vitreous State 2007, Raman spectroscopy L1, M. Affatigato

Example: Polarizability changes CO_2

Vibrational modes of CO_2



C. Hess, 2006

Raman Spectroscopy to stop Fraud

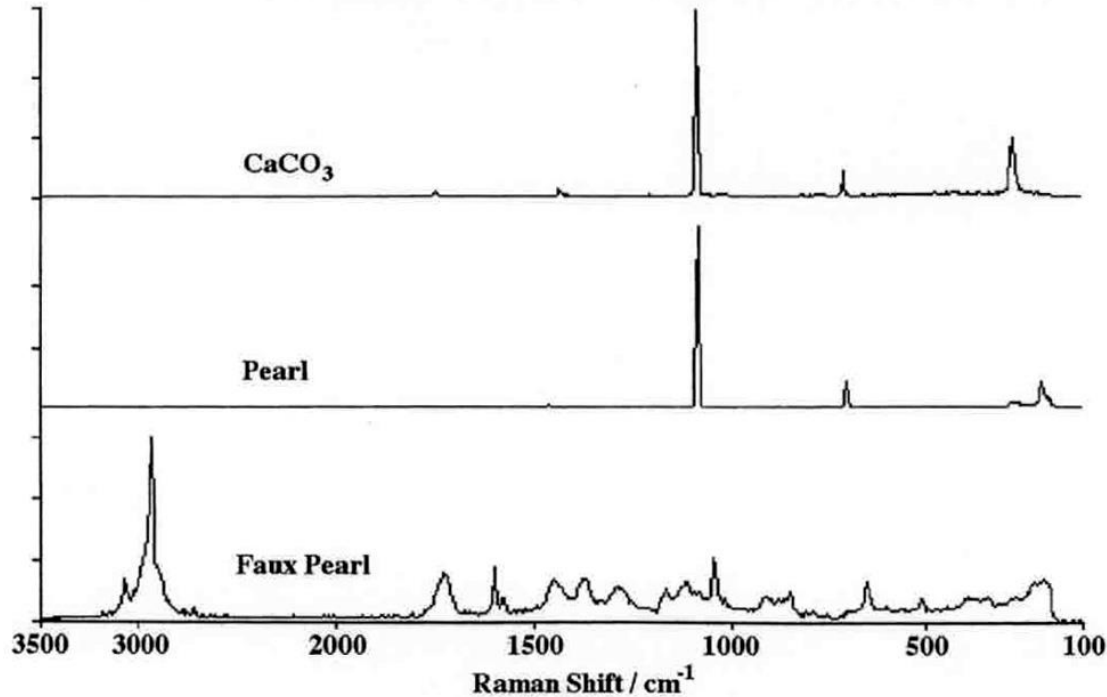
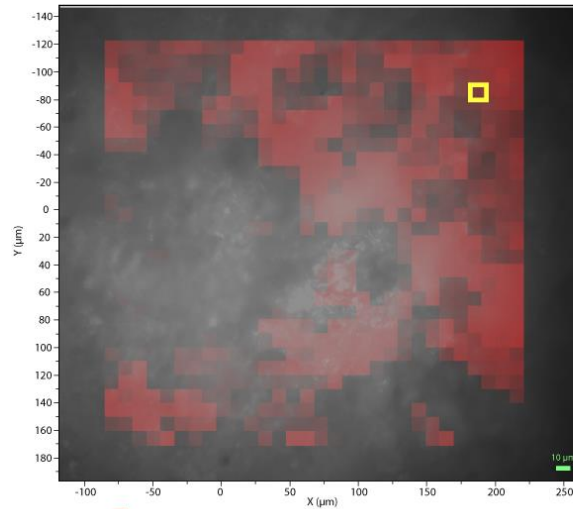
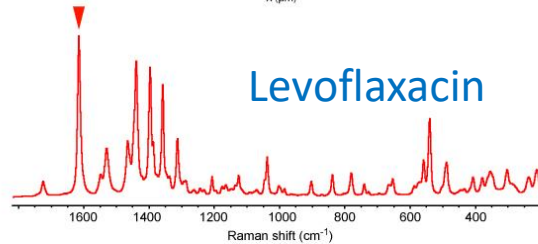
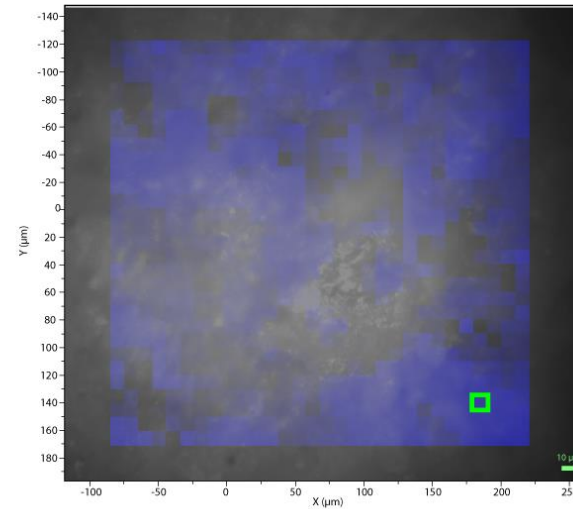
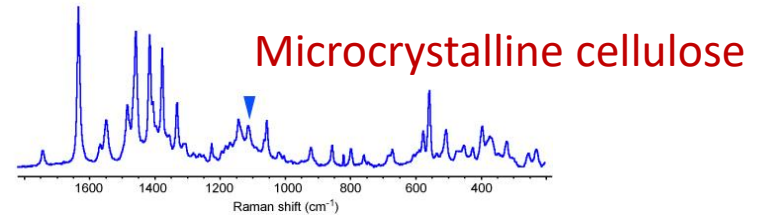


Figure 3 The Raman spectra of calcium carbonate (top), natural pearl (middle), and faux pearl (bottom). (Adapted with permission from Ref. 9.)



Lewis, et.al., *Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line*, Marcel Dekker, New York: 2001

Mapping a Drug Tablet with Raman Microscopy



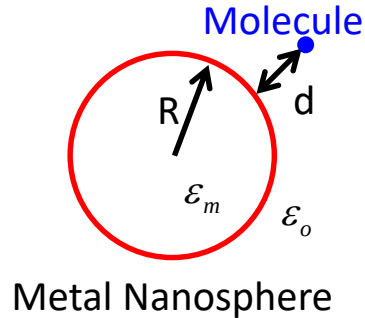
Am. Pharm. Rev., **2010**, 13, 58-65.



Surface Enhanced Raman Spectroscopy

Enhancement of Raman signal near a metallic rough surface or nanostructure

Estimation of Electromagnetic Enhancement



$$E_{mole} = E_o + E_{plas} \quad E_o = \text{Incident Field}$$

$$E_{plas} = \frac{\epsilon_m - \epsilon_o}{\epsilon_m + 2\epsilon_o} \frac{R^3}{(R + d)^3} E_o$$

$$\text{Field enhancement factor} = \frac{\text{Field at the position of molecule}}{\text{Incident field}}$$

$$A(\nu) = \frac{E_{mol}(\nu)}{E_o(\nu)} \square \frac{\epsilon_m(\nu) - \epsilon_o}{\epsilon_m(\nu) + 2\epsilon_o} \frac{R^3}{(R + d)^3}$$

Electromagnetic enhancement factor for Stokes signal power

$$G_{em}(\nu_S) = \underbrace{|A(\nu_L)|^2 |A(\nu_S)|^2}_{\text{E}^4 \text{ Enhancement}} \frac{\varepsilon_m(\nu_L) - \varepsilon_0}{\varepsilon_m(\nu_L) + 2\varepsilon_0} \frac{\varepsilon_m(\nu_S) - \varepsilon_0}{\varepsilon_m(\nu_S) + 2\varepsilon_0} \underbrace{\left(\frac{R}{R+d} \right)^{12}}_{\text{Highly localized phenomenon}}$$

E⁴ Enhancement

Highly localized phenomenon

Raman Stokes Power

$$P^{RS}(\nu_S) = N \sigma_{free}^R I(\nu_L)$$

N = No. of molecules, σ^R = Raman Cross-section $I(\nu_L)$ = Intensity of the laser

SERS Stokes Power

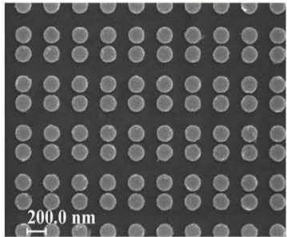
$$P^{SERS}(\nu_S) = N \underbrace{\sigma_{ads}^R}_{<10^2} \underbrace{|A(\nu_L)|^2 |A(\nu_S)|^2}_{10^{5-9}} I(\nu_L)$$

$A(\nu_L)$ and $A(\nu_S)$ = Enhancement factors for laser and Raman scattered fields

Experimental Determination of Enhancement Factor

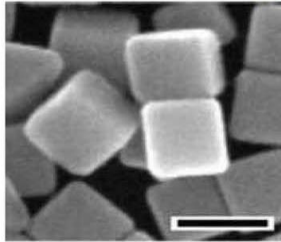
$$\text{Enhancement Factor} = \frac{I_{SERS} / N_{Ads}}{I_{Bulk} / N_{Bulk}}$$

Nano rings 4.2×10^6



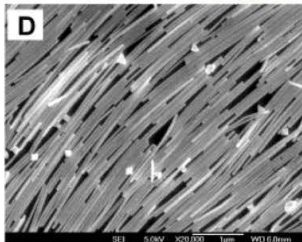
Banaee et al., (2010)

Dimer nano-cubes 3×10^6



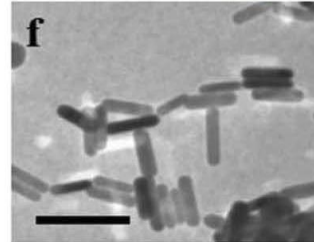
Camargo et al., (2010)

Ag nano-wires 2×10^5



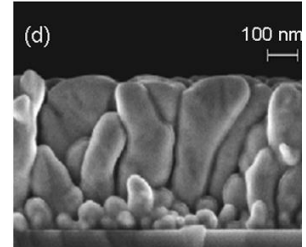
Tao et al., (2003)

Ag nano-rods 2×10^6



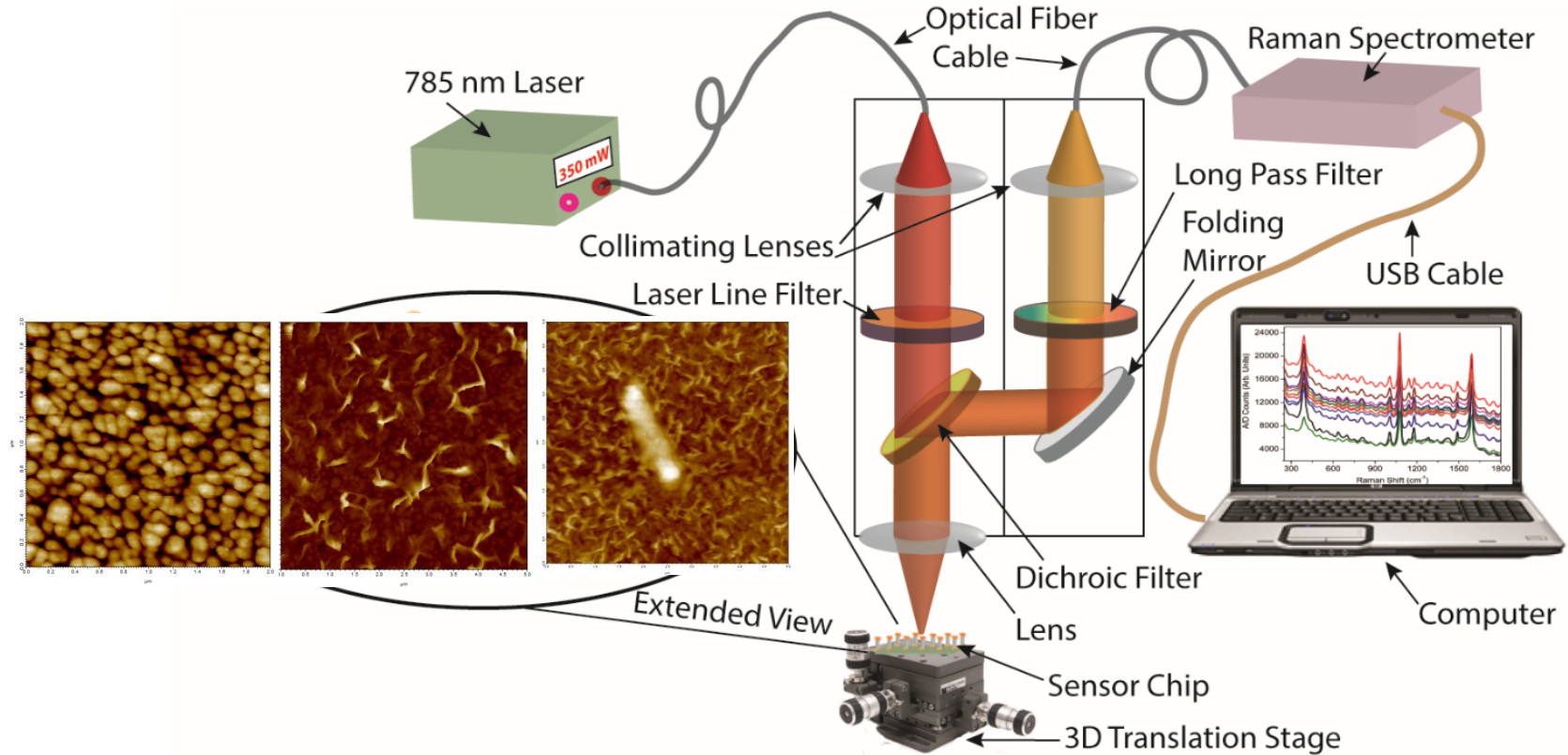
Orendorff et al., (2006)

Ag nSTFs 10^8

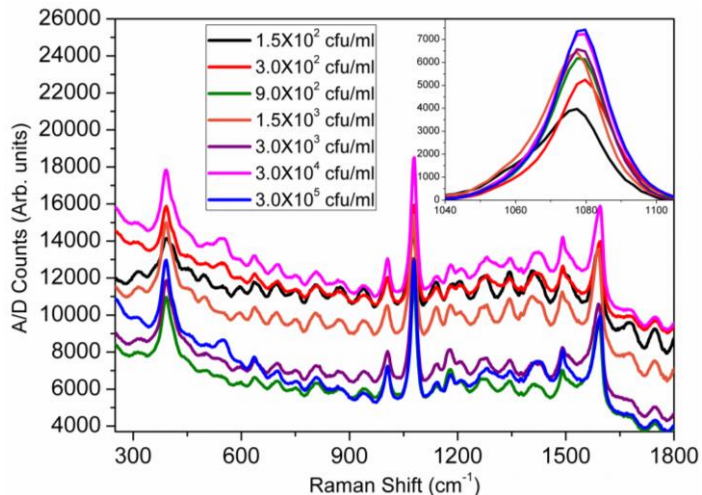


Shalabney et al, (2012)

Experimental Setup (Highly Sensitive E.coli Detection)



SERS Spectra for Varying Bacterial Concentrations



Sample volume: 10 μ l

Interaction time: 10 minutes

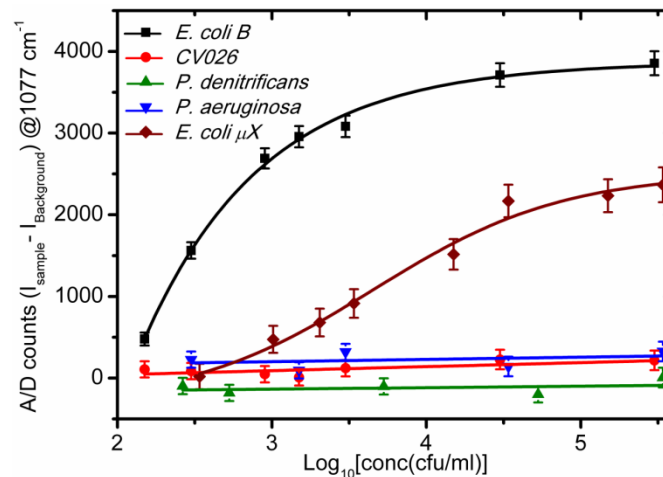
Limit of detection (LOD)

150 cfu/ml = 1.5 bacterium/ 10 μ l $\approx$ 1 bacterium/ 10 μ l

No change in the differential Raman enhancement is observed for other kinds of bacteria

E. coli μ X has smaller affinity than *E. coli* B

Quantitative Analysis



Srivastava et al., Analyst, 140, 3201 (2015)



Summary

1. Expression for Electric field enhancement in Localized surface plasmon resonance was obtained and discussed.
2. Various LSPR configurations and some biosensing applications were discussed
3. Raman spectroscopy and SERS were discussed and the electromagnetic enhancement was estimated analytically.
4. Applications of Raman and SERS in sensing were presented

Thank You

