



IIT ROORKEE



NPTEL ONLINE
CERTIFICATION COURSE

Lecture 14: Plasmons- V

Localized Surface Plasmons, Sensing

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History



The Lycurgus Cup made by the Romans dates to the fourth century AD.

Reflected light, (in daylight) ➡ Green.

Transmitted Light ➡ Red.



The First Nanotechnologists



“Labors of the Months”
Norwich, England, ca.1480
(The ruby color is probably
due to gold nanoparticles)

Ancient stained glass makers

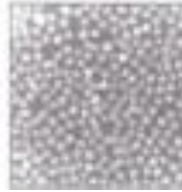
Size and Shape Dependence of Physical Properties



Gold

Silver

Size: 25 nm
Shape: sphere
Color reflected

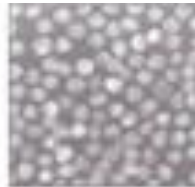
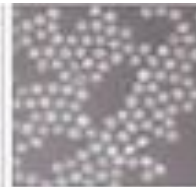


Size: 100 nm
Shape: sphere
Color reflected



By placing small amounts of tiny nanoparticles in some particular fashion, the physical properties of a material can be tailored.

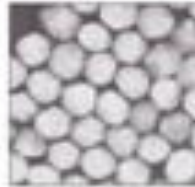
Size: 50 nm
Shape: sphere
Color reflected



Size: 40 nm
Shape: sphere
Color reflected



Size: 100 nm
Shape: sphere
Color reflected

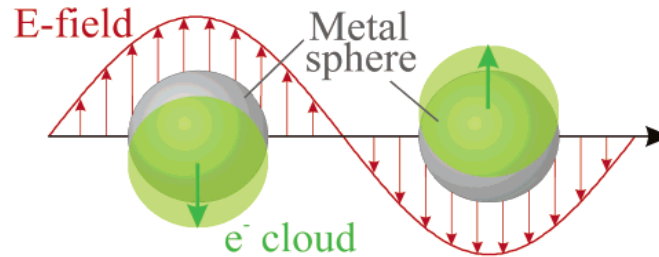


Size: 100 nm
Shape: Pyramid
Color reflected



Plasmons Resonances of Metal Nanoparticles

❖ Localized surface plasmons (LSPs) are the quanta of charge density oscillations in metal nanoparticles



❖ Excited when the frequency of the incident light becomes equal to the oscillation frequency of conduction electrons. This is attributed as **localized surface plasmon resonance (LSPR)**

❖ The resonance frequency as well as the absorbance is highly dependent on the size, shape and environment of the nanoparticles

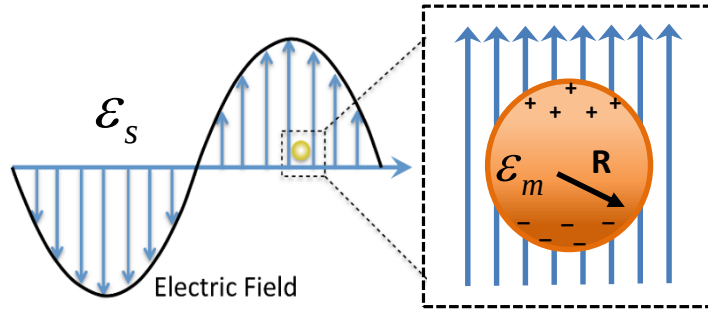
Hutter & Fendler, Adv. Mater. 16, 1685-1706 (2004)

Advantageous Features

- ❖ LSPs being confined to the particle, the field gets extremely enhanced in the local environment
- ❖ Can be excited directly by the light of appropriate frequency. Thus they don't require any phase matching technique
- ❖ Excitation of LSPs does not require polarized light beams as in the case of propagating SPs
- ❖ Can be employed in biosensing

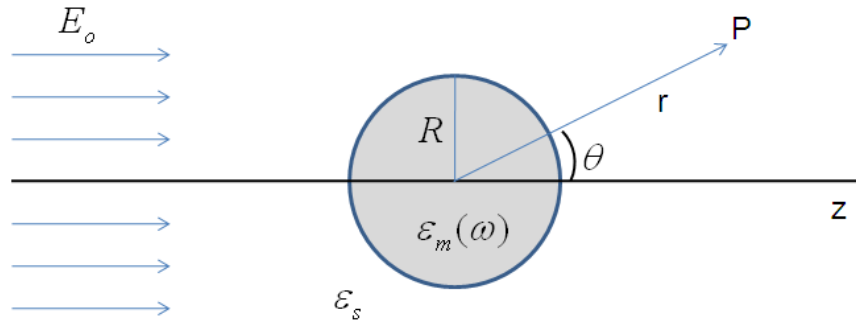


LSPR in a Metal Sphere: Quasi static Approximation



Laplace Equation $\nabla^2 \Phi = 0$

Electric Field $\vec{E} = -\nabla \Phi$



Azimuthal Symmetry

General solution:

$$\Phi(r, \theta) = \sum_{l=0}^{\infty} [A_l r^l + B_l r^{-(l+1)}] P_l(\cos \theta)$$

Legendre Polynomials

$$\Phi_{in}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos \theta)$$

$$\Phi_{out}(r, \theta) = \sum_{l=0}^{\infty} [B_l r^l + C_l r^{-(l+1)}] P_l(\cos \theta)$$

Boundary conditions

(i) $\Phi_{in} = \Phi_{out}$

(ii) $\epsilon_m \frac{\partial \Phi_{in}}{\partial r} = \epsilon_s \frac{\partial \Phi_{out}}{\partial r}$

$$\lim_{r \rightarrow \infty} \Phi_{out} = -E_o z = -E_o r \cos \theta$$

$$\Phi_{in} = -\frac{3\epsilon_s}{\epsilon_m + \epsilon_s} E_o r \cos \theta$$

$$\Phi_{out} = -E_o r \cos \theta + \frac{\epsilon_m - \epsilon_s}{\epsilon_m + 2\epsilon_s} E_o R^3 \frac{\cos \theta}{r^2} = -E_o r \cos \theta + \frac{\vec{p} \cdot \vec{r}}{4\pi\epsilon_o\epsilon_s r^3}$$



Superposition of potentials due to the incident field and that due to a dipole located at the center of the nanoparticle

Electric Fields

$$\vec{E}_{in} = \frac{3\epsilon_s}{\epsilon_m + 2\epsilon_s} \vec{E}_o \quad \vec{E}_{out} = \vec{E}_o + \frac{3\vec{n}(\vec{n} \cdot \vec{p}) - \vec{p}}{4\pi\epsilon_o\epsilon_s r^3}$$

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

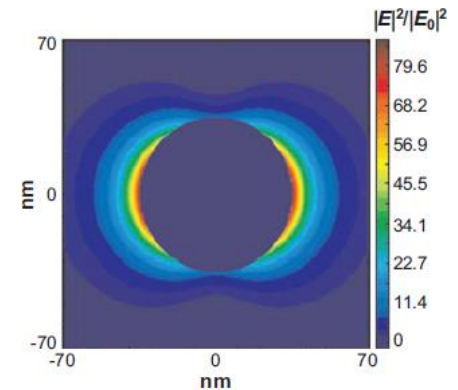
Field Enhancement in a 35 nm Ag NP

Polarizability

$$\alpha = 4\pi R^3 \frac{\epsilon_m - \epsilon_s}{\epsilon_m + 2\epsilon_s}$$

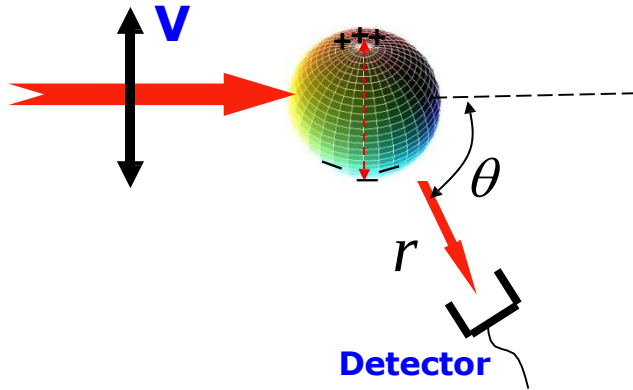
Frölich condition

$$\epsilon_{m1} = -2\epsilon_s$$

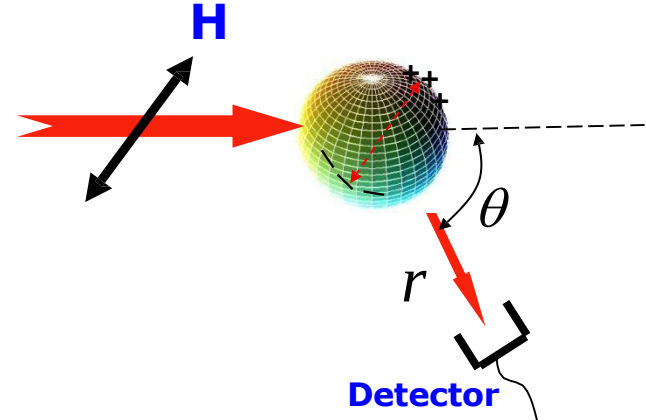


Sites et al., Annu. Rev. Anal. Chem. **1**, 601 (2008)

LSPR Excitation at Small Spherical Particle



$$\frac{I_{scat-V}}{I_0} = \frac{16\pi^4}{r^2 \lambda^4} |\alpha|^2$$



$$\frac{I_{scat-H}}{I_0} = I_{scat-V} \cos^2 \theta$$

Absorption and Scattering at Small Particles: Extinction

Scattering cross section:

$$C_{scat} = \frac{8\pi}{3} k^4 |\alpha|^2$$

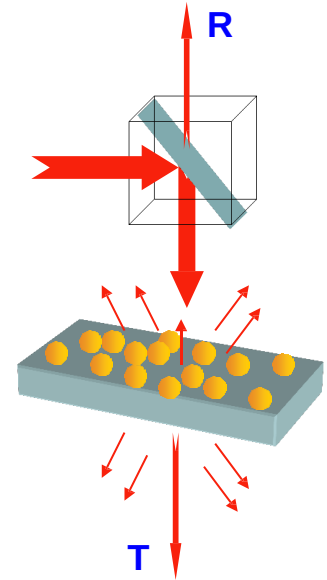
Absorption cross section:

$$C_{abs} = k \operatorname{Im}(\alpha)$$

Extinction cross section

$$C_{ext} = C_{abs} + C_{sca} \cong 4\pi k \operatorname{Im}(\alpha)$$

$$\text{Extinction} = 1 - T - R$$



LSPR in Small Anisotropic Nanoparticles

$$\alpha_j = \frac{abc}{3} \left(\frac{\epsilon_p - \epsilon_m}{L_j(\epsilon_p - \epsilon_m) + \epsilon_m} \right)$$

Resonance when

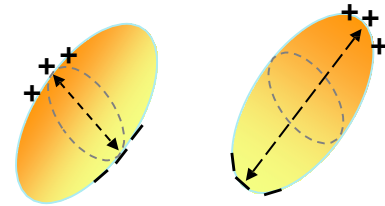
$$\text{Re}(\epsilon_p) = \epsilon_m(1 - 1/L_j)$$

The geometrical factor:

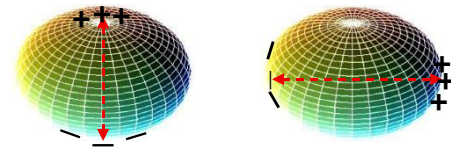
$$L_j = \frac{abc}{2} \int_0^\infty \frac{ds}{(x_j^2 + s) \sqrt{(a^2 + s)(b^2 + s)(c^2 + s)}}$$

where $j = 1, 2, 3$ and $x_1 = a, x_2 = b, x_3 = c$

Prolate Spheroid $a > b = c$



Oblate Spheroid $a = b > c$



For a sphere: $L_a = L_b = L_c = 1/3$

Extinction Cross-section

(Absorption + Scattering)

$$E(\omega, V) = \frac{9\omega V \varepsilon_s^{3/2}}{c} \frac{\varepsilon_{m2}(\omega, V)}{[(\varepsilon_{m1}(\omega, V) + \chi \varepsilon_s)^2 + \varepsilon_{m2}^2(\omega, V)]}$$

V = volume of the nanoparticle $\varepsilon_s = n^2$, n = refractive index of the surrounding medium

χ = parameter depending on the shape of the nanoparticle

$$\varepsilon(\omega, R) = \varepsilon_{m1}(\omega, R) + i\varepsilon_{m2}(\omega, R) : \text{Metal Dielectric Function}$$

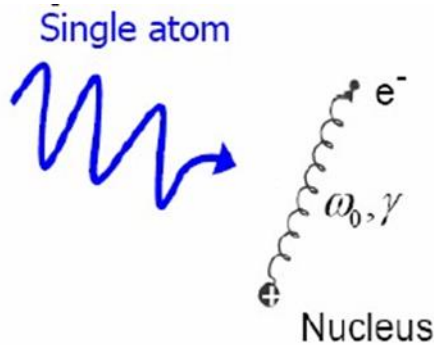
Resonance Condition

$$\varepsilon_{m1} = -\chi \varepsilon_s$$

Maier, Plasmonics: Fundamentals and Applications, Springer, 2007



Summary of Plasmon Frequencies at the Metal-Air Interface



ω_p = plasma frequency
 γ = restoring force (spring) constant

$$E = -4\pi P \quad \ddot{x} + \omega_p^2 x = 0$$

$$\ddot{x} = -(e/m)E \quad P = -Nex$$

$$\omega_p = \left(\frac{Ne^2}{\epsilon_0 m} \right)^{\frac{1}{2}}$$

Plasma resonances for various geometries

Material	Resonance condition	Resonance Frequency
Bulk Metal	$\epsilon_{eff} = 0$	ω_p
Planar Surface	$\epsilon_{eff} = -\epsilon_d$	$\frac{\omega_p}{\sqrt{2}}$
Sphere	$\epsilon_{eff} = -2\epsilon_d$	$\frac{\omega_p}{\sqrt{3}}$
Ellipsoid	$\epsilon_{eff} = -\frac{1-L_M}{L_M}$	$\omega_p L_M$

Optical Properties of Metal Clusters
 Kreibig and Vollmer, 1995

Size Effects

Extrinsic size effects

$$\lambda_p \approx \sqrt{3} \lambda_{pb}$$

Intrinsic size effects

$$\lambda_c = \left[\lambda_{cb}^{-1} + \frac{v_f}{2\pi Rc} \right]^{-1}$$

For Gold

$$\lambda_{pb} = 0.138 \mu m \quad \& \quad \lambda_{cb} = 46.3 \mu m$$

Meiwes-Broer, *Metal clusters at surfaces: structure, quantum properties, physical chemistry* (Springer, 2000).

[Link et.al., Journal of Physical Chemistry B **103**(21), 4212-4217 (1999).

Ordal et.al., Appl. Opt. **22**(7), 1099-1119 (1983).



Sensing with LSPR

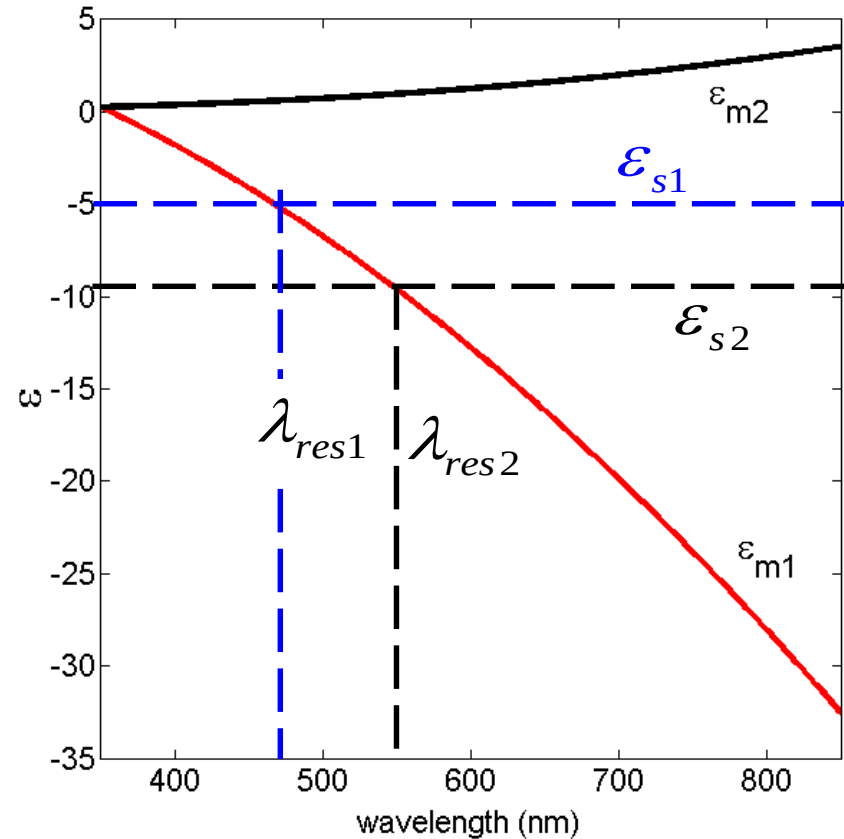
Spherical AuNP case

Extinction Cross-section

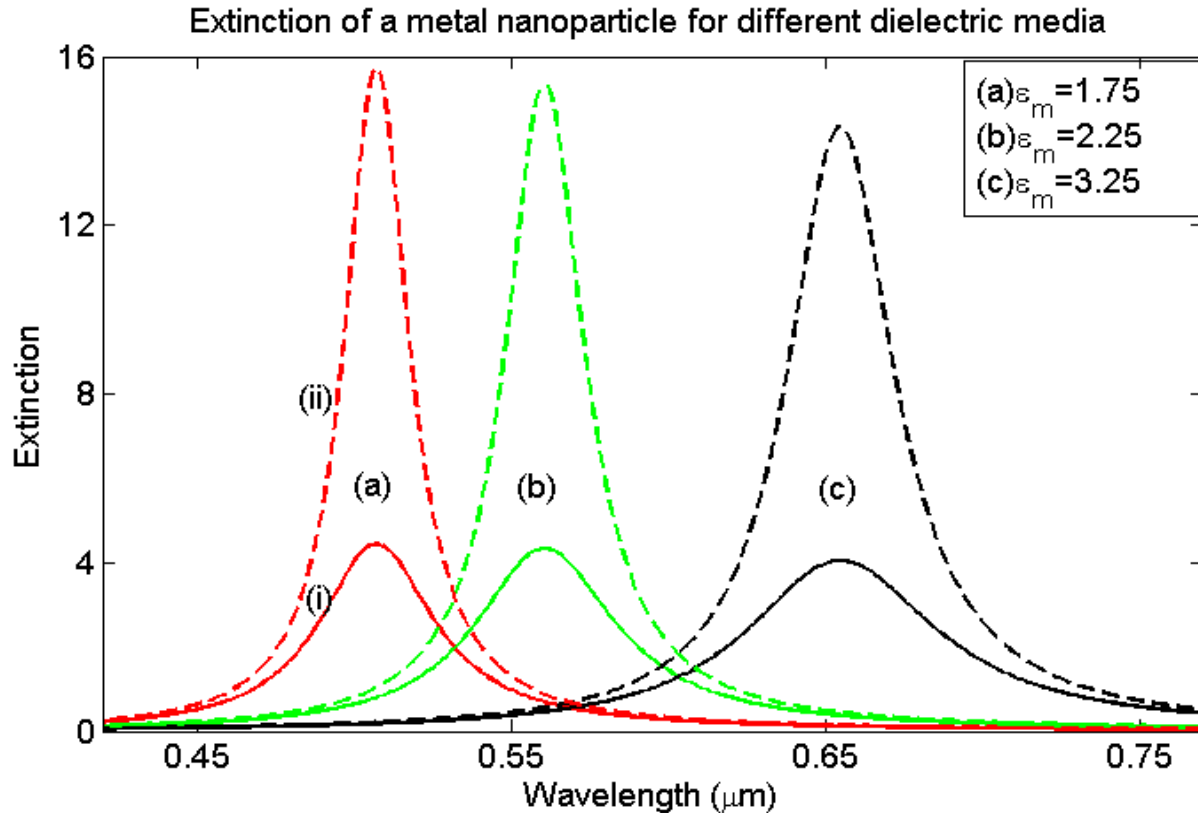
$$E = \frac{24\pi R \epsilon_s^{3/2}}{\lambda} \frac{\epsilon_{m2}}{[(\epsilon_{m1} + 2\epsilon_s)^2 + \epsilon_{m2}^2]}$$

Resonance Condition

$$\epsilon_{m1}(\lambda) = -2\epsilon_s$$

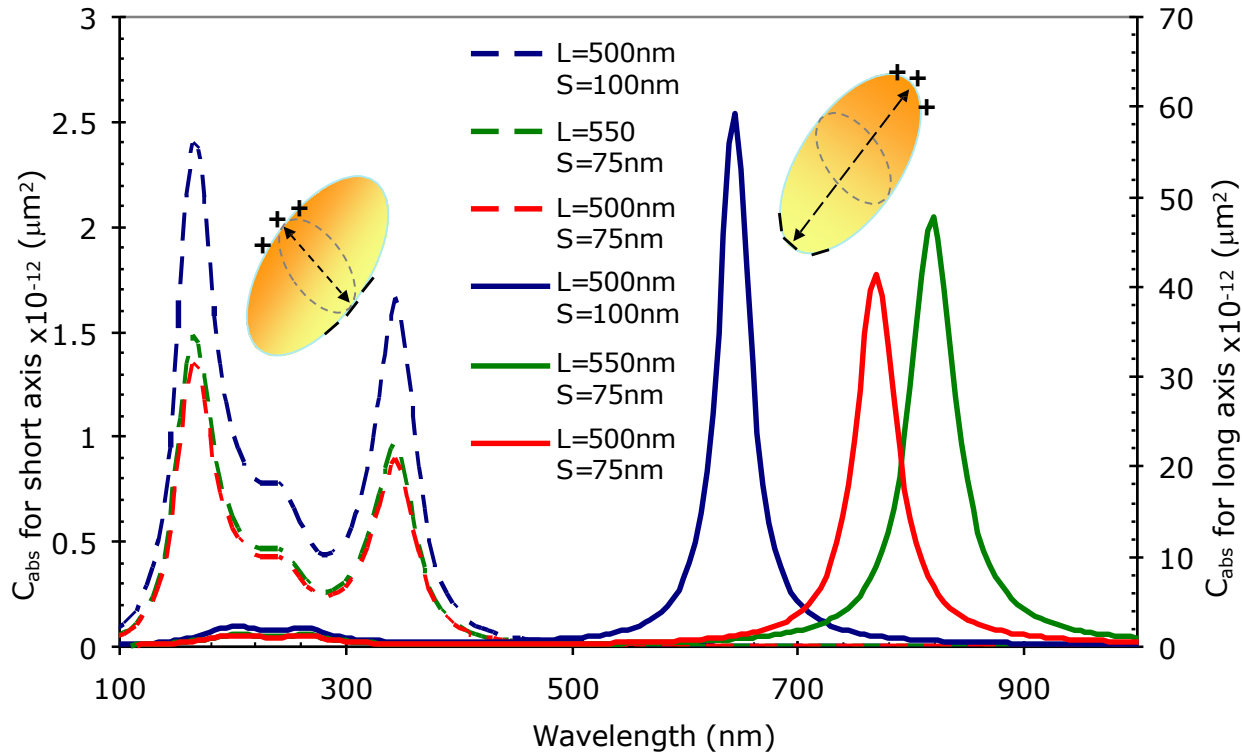


Au Spherical Nanosphere

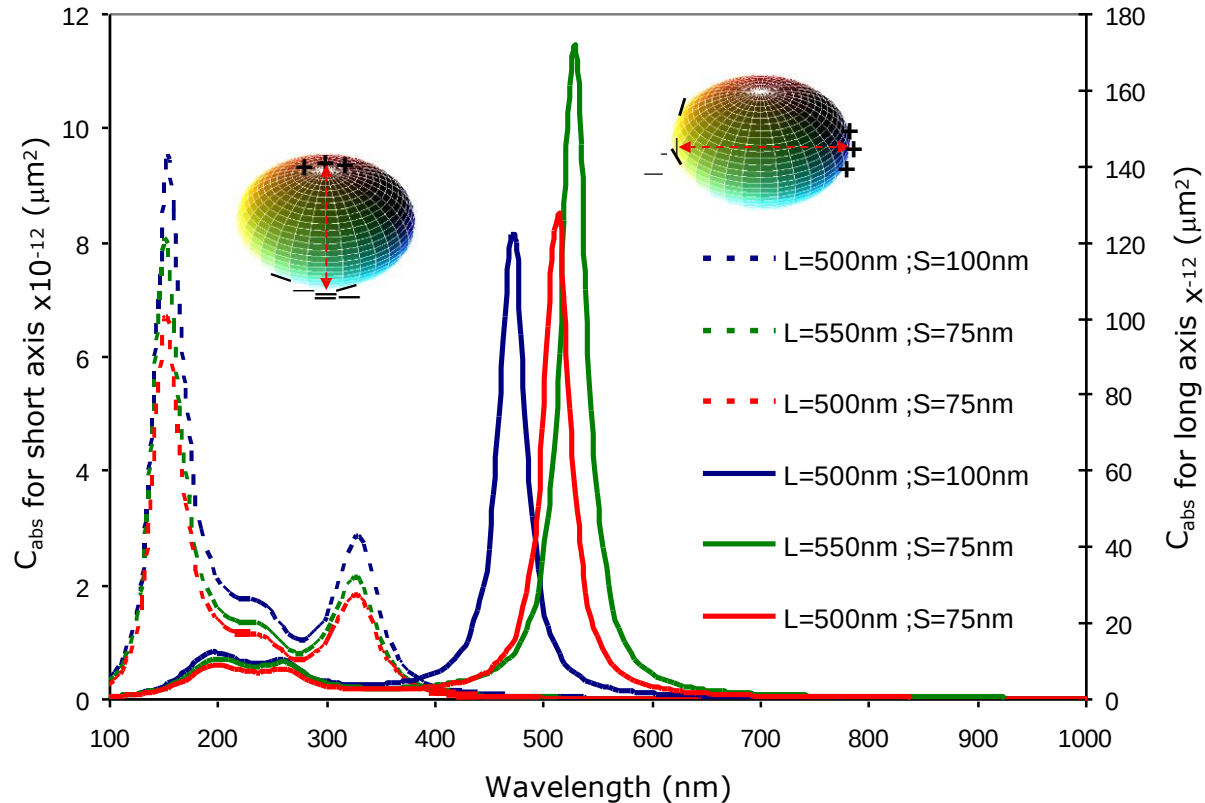


- (i) $R = 5\text{nm}$ (solid line)
- (ii) $R = 10\text{nm}$ (dotted line)

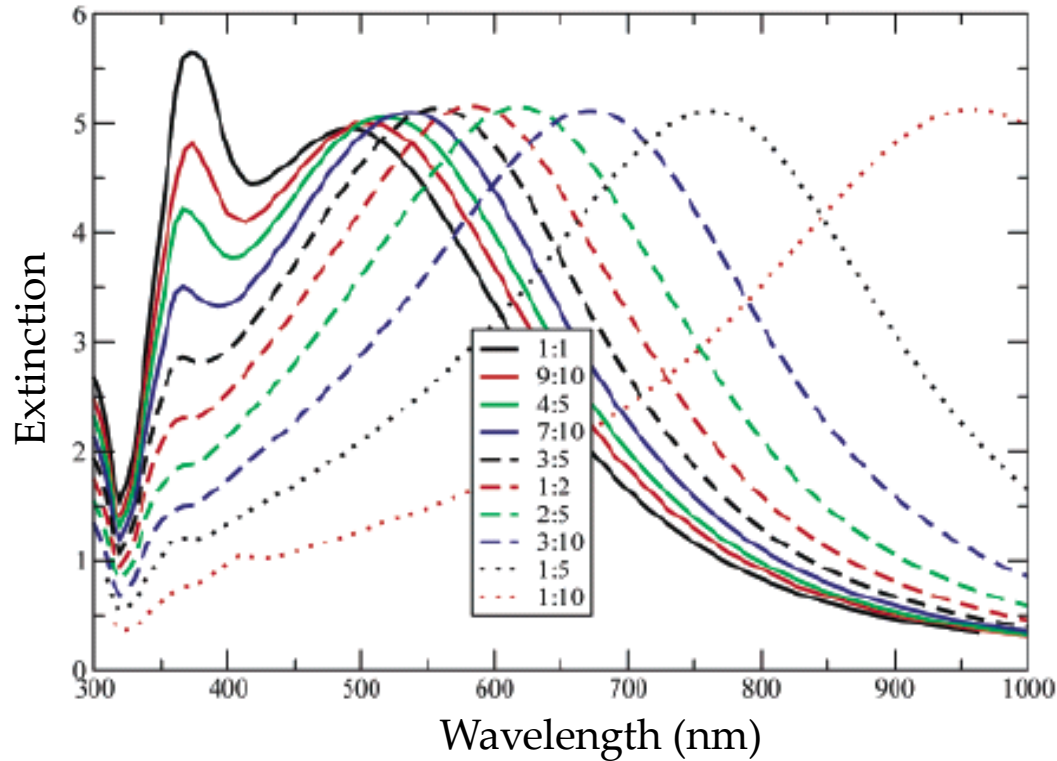
Example: Absorption Resonances of Ag Prolate Spheroids



Example: Absorption Resonances of Ag Oblate Spheroids



More Exact Calculation for Prolate Spheroids



K.L. Kelly, E. Coronado, L. L. Zhao and G. C. Schatz, The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, J. Phys. Chem. B 107, 668-677 (2003).

Summary

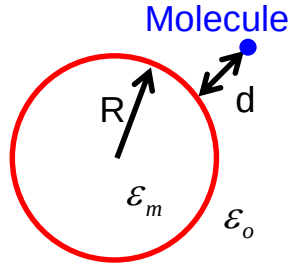
1. Localized surface plasmon resonance (LSPR) was introduced and some historical examples were presented.
2. An analytical expression based on quasi-static approach was presented to study LSPR theoretically for both spherical and anisotropic nanoparticles
3. Sensing potential of LSPR for both spherical and non-spherical nanoparticles was assessed.

Thank You





Estimation of Electromagnetic Enhancement



Metal Nanosphere

$$E_{mole} = E_o + E_{plas}$$

E_o = Incident Field

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

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

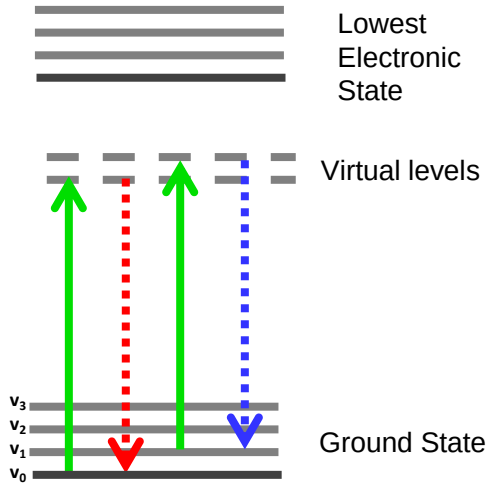
$$A(\nu) = \frac{E_{mol}(\nu)}{E_o(\nu)} \square \frac{\epsilon_m(\nu) - \epsilon_o}{\epsilon_m(\nu) + 2\epsilon_o} \frac{R^3}{(R + d)^3}$$

Experimental estimation of enhancement factor

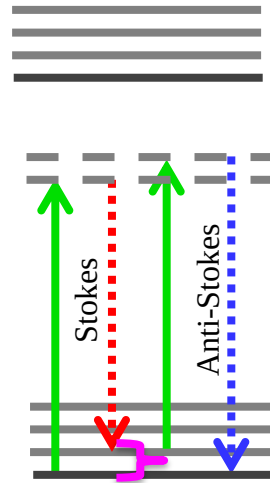
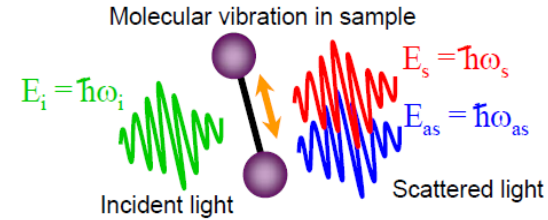
$$\text{Enhancement Factor} = \frac{I_{SEF} / N_{Ads}}{I_{Bulk} / N_{Bulk}}$$

Raman Spectroscopy

Rayleigh Scattering



Raman Scattering

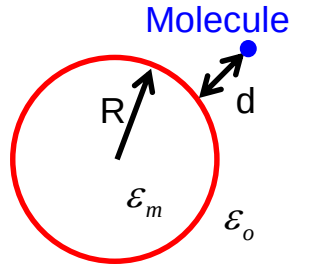


- 'Fingerprint' of molecular bonds and crystalline structure
- Very low cross-section: **1 in 10^7** photons

Surface Enhanced Raman Spectroscopy

Enhancement of Raman signal near a metallic rough surface or nanostructure

Estimation of Electromagnetic Enhancement



Metal Nanosphere

$$E_{mole} = E_o + E_{plas}$$

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

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

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

Electromagnetic enhancement factor for Stokes signal power

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

E^4 Enhancement

Highly localized phenomenon

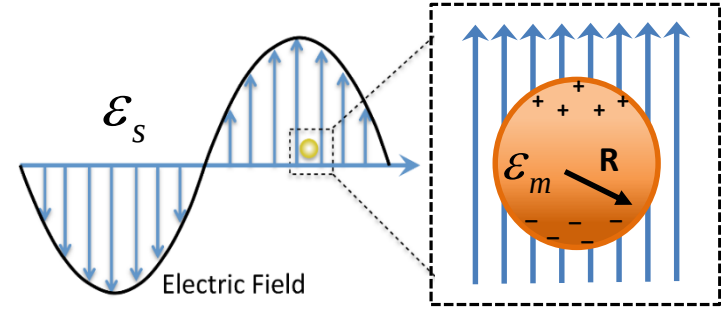
Localized Surface Plasmon Resonance

- Resonant collective oscillations of free electrons in metallic nanostructures
- Light confines in structures much smaller than the wavelength.
- Enhanced electromagnetic fields
- Characterized by extinction

Extinction of a spherical metallic nanoparticle

V = volume of the nanoparticle

$\epsilon_s = n^2$, n = refractive index of the surrounding medium



$$\epsilon_m = \epsilon_{m1} + i\epsilon_{m2}$$

$$E = \frac{24\pi R \epsilon_s^{3/2}}{\lambda} \frac{\epsilon_{m2}}{[(\epsilon_{m1} + 2\epsilon_s)^2 + \epsilon_{m2}^2]}$$

Resonance Condition

$$\epsilon_{m1} = -2\epsilon_s$$

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

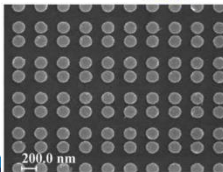
SERS Stokes Power

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

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

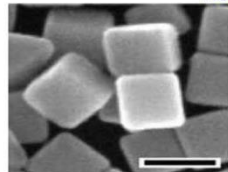
$$\text{Enhancement Factor} = \frac{I_{SERS} / N_{Ads}}{I_{Bulk} / N_{Bulk}}$$

Nano rings 4.2×10^6



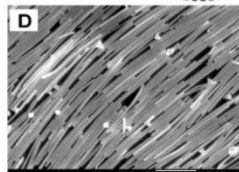
Banaee et al., (2010)

Dimer nano-cubes 3×10^6



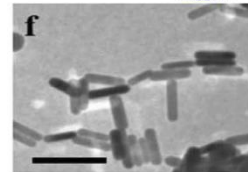
Camargo et al., (2010)

Ag nano-wires 2×10^5



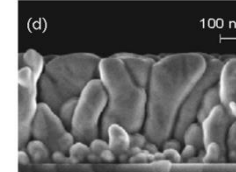
Tao et al., (2003)

Ag nano-rods 2×10^6



Orendorff et al., (2006)

Ag nSTFs 10^8



Shalabney et al., (2012)

LSPR Sensitivity to the Refractive Index

Using:

$$\lambda_{res} = \lambda_p / \sqrt{\frac{1}{\epsilon_{\infty} - (1 - 1/L_j)\epsilon_m} - (\Gamma/\omega_p)^2} \approx \lambda_p \sqrt{\epsilon_{\infty} - (1 - 1/L_j)\epsilon_m}$$

Sensitivity

$$\frac{\partial \lambda_{res}}{\partial n_m} = - \frac{\lambda n_m (1 - 1/L_j)}{\epsilon_{\infty} - (1 - 1/L_j)\epsilon_m}$$

For a spherical particle

$$\frac{\partial \lambda_{res}}{\partial n_m} = \frac{2\lambda n_m}{1 + 2n_m^2}$$

without damping and no interband transitions:

$\epsilon_{\infty} = 1$, $L_j = 1/3$ we get:

At 600nm for water sensing we get:

$$\frac{\partial \lambda_{res}}{\partial n_m} = 576 \text{ nm} / \text{RIU}$$

This is higher than the measured one about 200nm/RIU, perhaps due to size effects of the nanoparticle which need to be taken into account.















