Surface-enhanced Raman Scattering

HUANG Shaoying

OUTLINE

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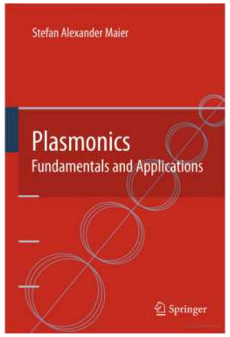
- Single molecule detections
- Working principles
- Enhancement of E-fields
- Summaries

References



Plasmonics: fundamentals and applications

Stefan A. Maier,
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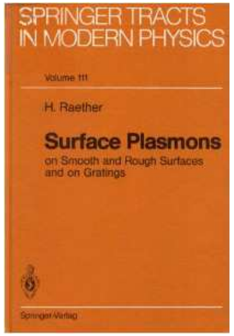
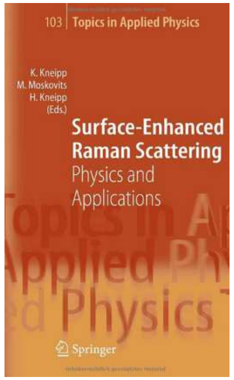


Surface Plasmons on Smooth and Rough Surfaces and on Gratings

Heinz Raether



Surface-Enhanced Raman Scattering: Physics and Applications

Editors: Katrin Kneipp, Martin Moskovits, Harald Kneipp

Raman Scattering

- The observation

1928	C.V. Raman & K.S. Krishnan	Liquids
	G.S. Landsberg & L. I. Mandelshtam	Crystals

- Working principles

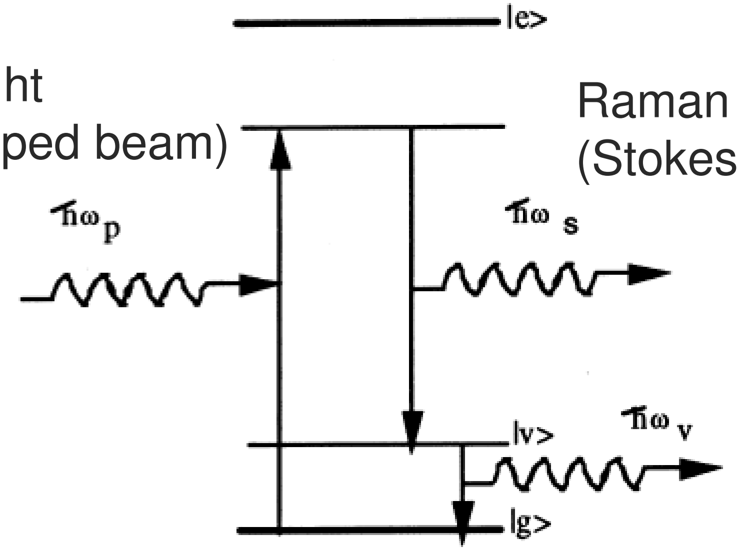
It is an inelastic scattering process between a photon & a molecule, mediated by the vibrational mode of the molecule

The incoming energy, $\hbar\omega_p$, is shifted by the characteristic energy of vibration, $\hbar\omega_v$

Raman Scattering

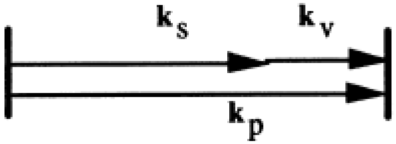
Incident light
(laser pumped beam)

Raman scattered light
(Stokes Raman beam)



Energy conservation: $\omega s = \omega p - \omega v$

Momentum conservation:



If the molecule is at

vibrational ground state

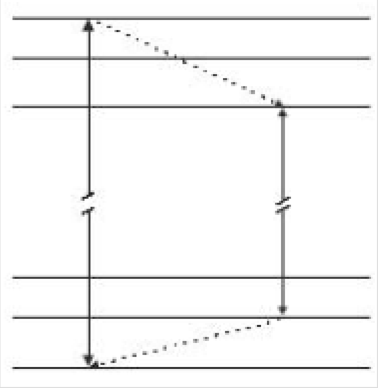
→ excite a vibrational mode→ energy lose→ red-shift (Stokes shift)

vibrational excited state

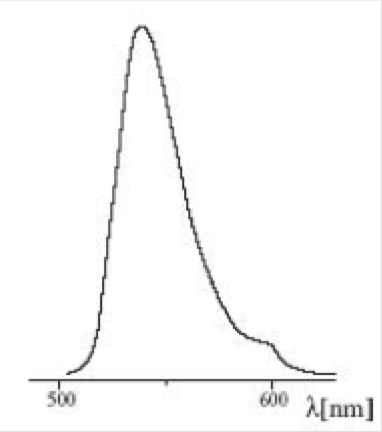
→ de-excitation → energy gain → blue shift (anti-Stokes shift)

Raman Scattering, Fluorescence, SERS

Fluorescence

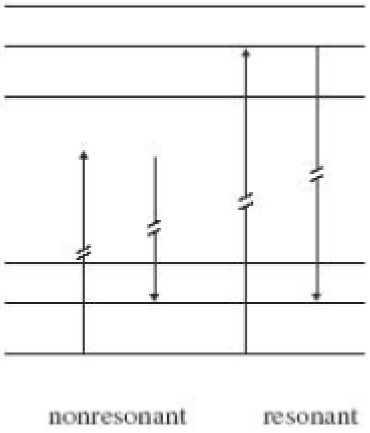


Nonelastic electron relaxation to lower edge of the excited level

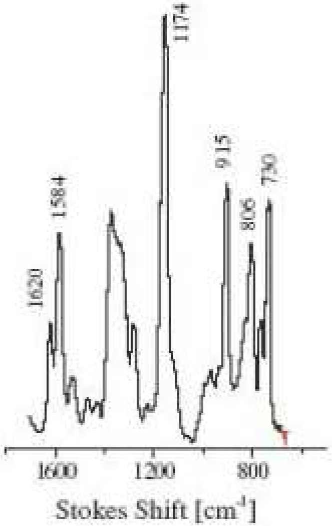


Broad linewidth

Raman scattering (spontaneous)



Inelastic scattering process



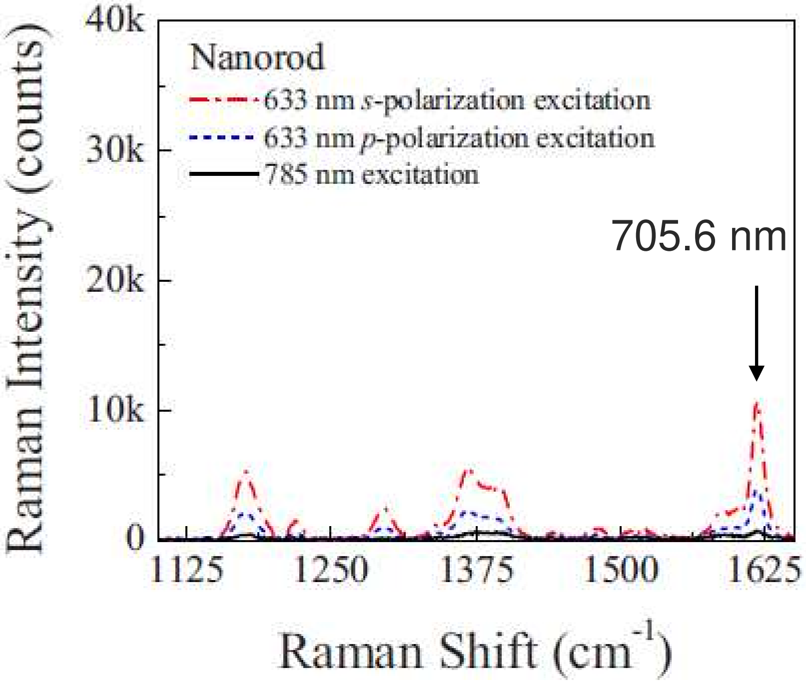
Sharp Raman line

- Resonant case: incoming photons resonate with electronic transition
- Resonant Raman scattering is stronger than normal Raman scattering
- Low efficiency

- Linear process: the total power of the inelastically scattered beam scales linearly with the intensity of the incoming intensity beam

Surface-enhanced Raman scattering: place Raman active molecules within the near-field of a metallic nanostructure (localized surface plasmons & lightning rod effect).

Raman/SERS Spectrum



- In SERS, the wavelength of the scattered light is shifted.
- It is due to the nature of Raman scattering (inelastic scattering)
- Raman shift

$$\Delta w(cm^{-1}) = \left(\frac{1}{\lambda_0(nm)} - \frac{1}{\lambda_1(nm)} \right) \times 10^7 \frac{(nm)}{(cm)}$$

SERS

SERS is a phenomenon that can be readily observed for a range of different molecules when they are adsorbed to curved noble metal* surface.

1974	First observation	Fleischman et al.	Wrong explanations
1977	First discovery	Jeanmaire & Van Duyne Albrecht & Creighton	
1997	Single molecules were detected on single nanoparticles using SERS		

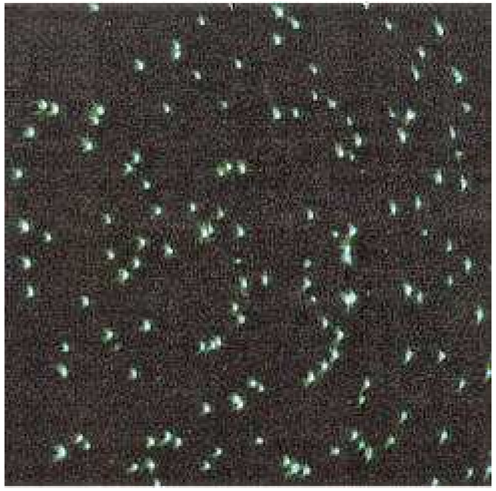
- E-field enhancement (|E|/|E0|) > 100

---

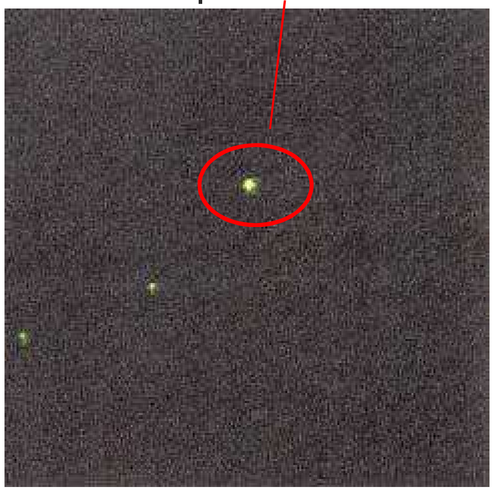
* Noble metals are metals that are resistant to corrosion and oxidation in moist air.

Single Molecule Detections [1]

- One Ag nanoparticle carries a rhodamine 6G (R6G) molecule.
- The particles are immobilized on a polylysine - coated surface.
- The particles are excited by evanescent-wave excitation.



Unfiltered photograph showing laser scattering



Raman scattering particles

Filtered photograph showing Raman scattering

Two mechanisms dominates in the SERS phenomenon

- Classical electromagnetic effect (main [2,3])
- Chemical effects (a factor of 3)

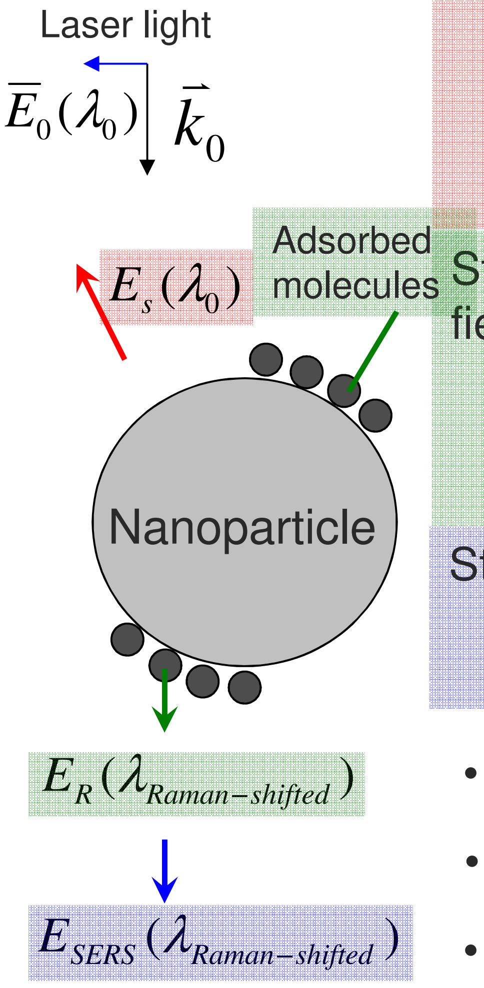
[1] S. Nie, et al, Science vol. 275, 1102, 1997

[2] A. Otto, Light Scattering in Solids IV, vol. 54, 1984

[3] A. Campion and P. Kambhampati, Chem. Soc. Rev., vol. 27, 241, 1998

Working Principles

- E-field induces oscillating surface plasmon multipoles of various orders.
- When the dimension of the particle << λ, dipolar plasmons dominate.



Step 1: Laser light (λ_0) resonates with the dipolar plasmons,

- The scattered fields are amplified/enhanced, $E_s = g(\lambda_0)E_0$
  - g (λ_0): averaged field enhancement factor
  - E_s: averaged magnitude of the radiated field
- It is coherent with the incident field & $\lambda_s = \lambda_0$

Step 2: E_s excites the absorbed molecules to produce Raman-scattered fields, E_R,

- E_R is at λ_R
- $E_R \propto \alpha_R E_s \propto \alpha_R \, g \, E_0$
  - α_R: Raman polarizability of the molecule

Step 3: Raman-scattered fields, E_R are enhanced. $E_{SERS} \propto \alpha_R \, g(\lambda_0) g'(\lambda_R) \, E_0$

- The enhancement factor, $g'(\lambda_R)$
- Wavelength of the scattered-field, $\lambda_R \neq \lambda_0$

- $\Delta\lambda = \lambda_R - \lambda_0$ is much smaller than the linewidth of LSP→ $g(\lambda_0) \cong g'(\lambda_R)$;
- SERS intensity, $I_{SERS} \propto |\alpha_R|^2 |gg'|^2 \, I_0$
- The SERS enhancement factor = $\dfrac{I_{SERS}}{I_0} = \dfrac{|E_{SERS}|^2}{|E_0|^2} \cong |g|^4$

Working Principles

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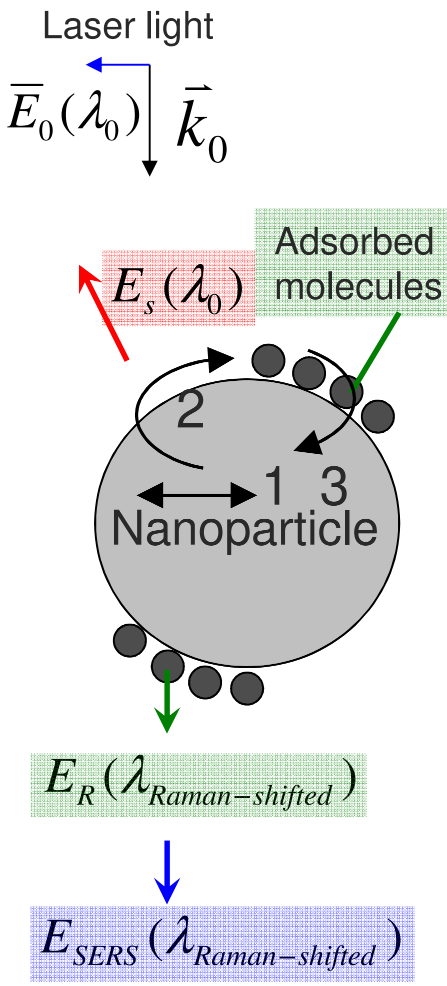
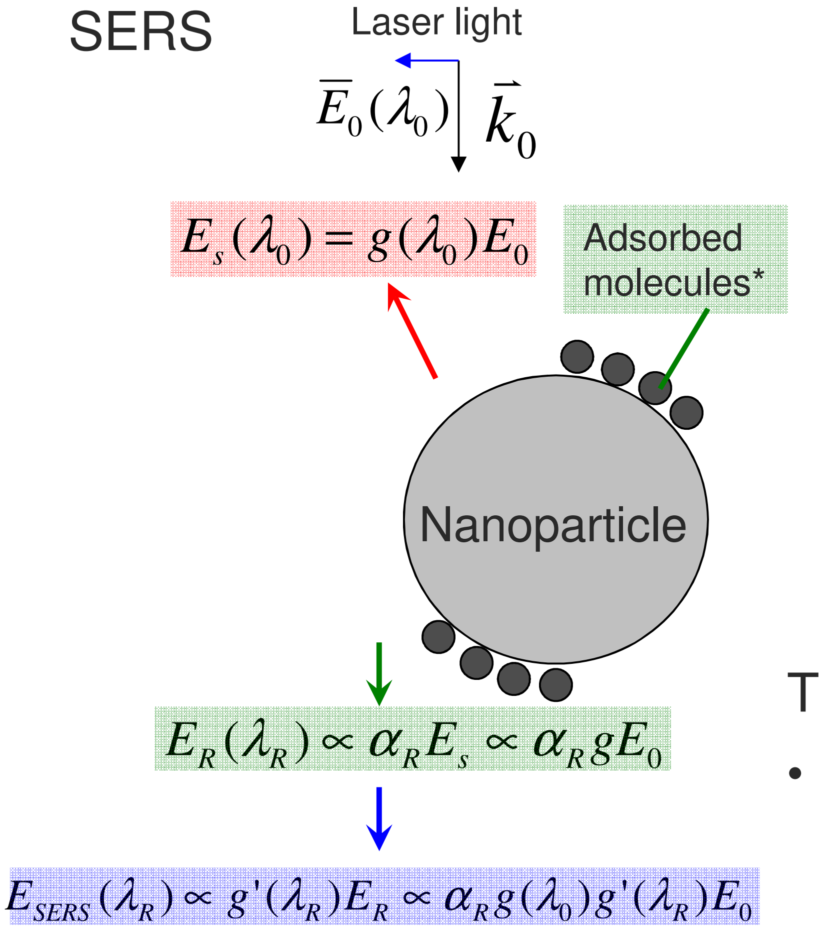


1. E-field enhanced by the nanoparticles
2. Frequency shifted by the molecules
3. E-field enhanced again by the nanoparticles

SERS vs Raman Scattering



SERS

Laser light

$\overline{E}_0(\lambda_0)$ $\vec{k}_0$

$E_s(\lambda_0) = g(\lambda_0)E_0$

Adsorbed molecules*

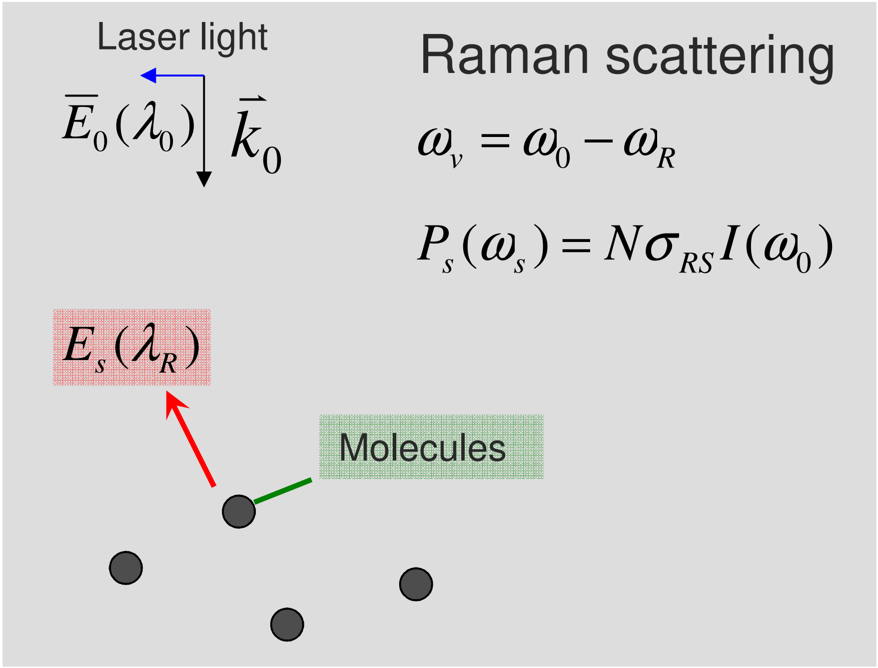
Nanoparticle

$E_R(\lambda_R) \propto \alpha_R E_s \propto \alpha_R g E_0$

$E_{SERS}(\lambda_R) \propto g'(\lambda_R)E_R \propto \alpha_R g(\lambda_0) g'(\lambda_R) E_0$

$$P_{SERS}(\omega_s) = N\sigma_{SERS}\, g^2(\omega_0)\, g'^2(\omega_s)\, I(\omega_0)$$

* The adsorbed molecule is also called probing molecule



Laser light

$\overline{E}_0(\lambda_0)$ $\vec{k}_0$

Raman scattering

$\omega_v = \omega_0 - \omega_R$

$P_s(\omega_s) = N\sigma_{RS} I(\omega_0)$

$E_s(\lambda_R)$

Molecules

The enhancement

- Increased Raman cross section, σ_{SERS} (a maximum factor of 100 → $|E_R|/|E_0|$ ~ 3)
  Chemical/electronic contribution
- EM contribution, E-field enhancement
  - Excitation of localized surface plasmons
  - Crowding of electric field lines (lightning rod effect) at the metal interface

EM Contribution to the Enhancement

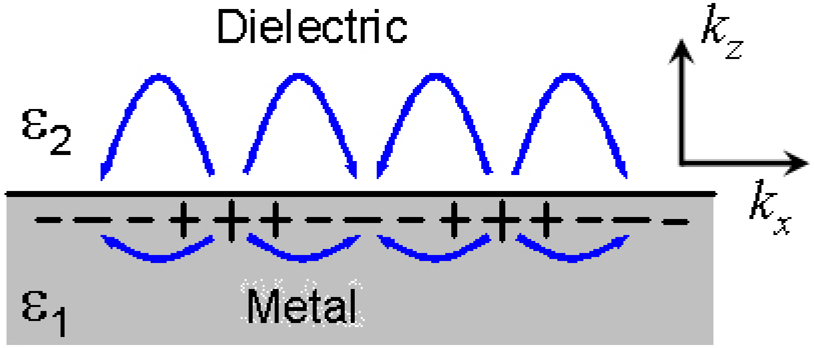
- Localized surface plasmons, $g_{SP}(\omega)$
  - Strong frequency dependence
  - Averaged enhancement factor

- Lightning rod effect, g_{LR}
  - Purely geometric phenomenon of field line crowding
  - The accompanying enhancement near sharp metallic features
  - It exists in structures with tips and/or sharp edges

- Total EM contribution $g(\omega) = g_{SP}(\omega)\, g_{LR}$

Surface Plasmons on Smooth Surfaces

- Surface plasmons are coherent electron oscillations on a dielectric-metal boundary (Re(ε) change signs across the interface).
- The coherent electron oscillations are called surface plasma oscillations.
- TM waves excite SPs.
- It is a longitudinal oscillation, with frequency, ω.
- $k_x = \frac{\omega}{c}\left(\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^{1/2}$



Surface Plasmons on Smooth Surfaces

To obtain the relation: $k_x = \frac{\omega}{c}\left(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{1/2}$

Region 2 (dielectric)

$$\overline{H}_2 = H_{y2}\hat{y}e^{i(k_{x2}x+k_{z2}z-\omega t)}$$

$$\overline{E}_2 = (E_{x2}\hat{x}+E_{z2}\hat{z})e^{i(k_{x2}x+k_{z2}z-\omega t)}$$

Region 1 (metal)

$$\overline{H}_1 = H_{y1}\hat{y}e^{i(k_{x1}x-k1z-\omega t)}$$

$$\overline{E}_1 = (E_{x1}\hat{x}+E_{z1}\hat{z})e^{i(k_{x1}x-k_{z1}z-\omega t)}$$

⇨

- Maxwell's equations
- Boundary conditions

⇩

$$H_{y1} - H_{y2} = 0$$

$$\frac{k_{z1}}{\varepsilon_1}H_{y1} + \frac{k_{z2}}{\varepsilon_2}H_{y2} = 0$$

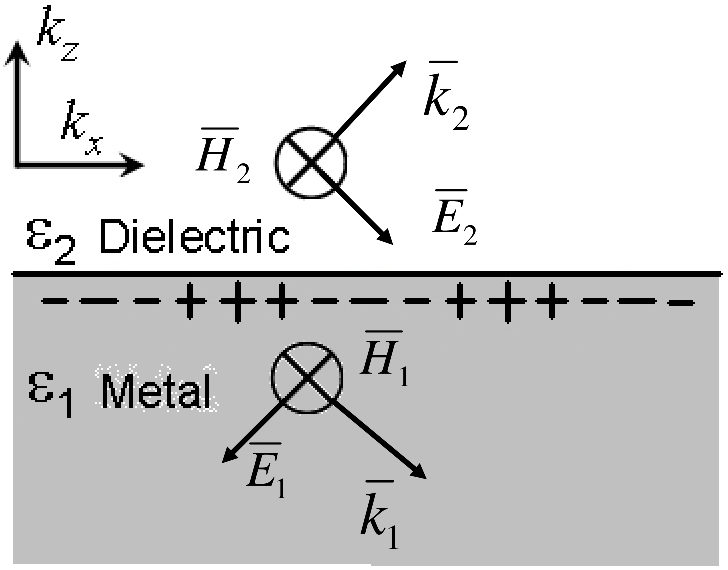
⇨ $D_0 = \frac{k_{z1}}{\varepsilon_1} + \frac{k_{z2}}{\varepsilon_2} = 0$

⇨ Dispersion relation

$$k_x^2 + k_{zi}^2 = \varepsilon_i\left(\frac{\omega}{c}\right)^2$$

⇩

$$k_x = \frac{\omega}{c}\left(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{1/2}$$



Surface Plasmons on Smooth Surfaces

The charge fluctuation is localized in z-direction.

$$k_x^2 + k_{zi}^2 = \varepsilon_i \left(\frac{\omega}{c}\right)^2$$

$$k_x = \frac{\omega}{c}\left(\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^{1/2}$$

⇒

$\varepsilon_1 < 0 \quad |\varepsilon_1| > 1$

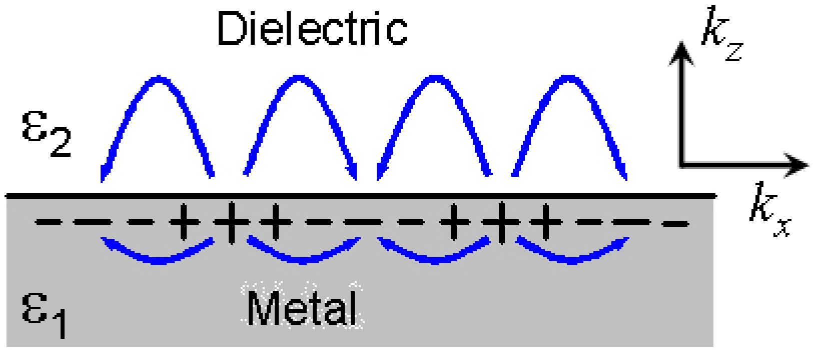
$\varepsilon_2 = 1$

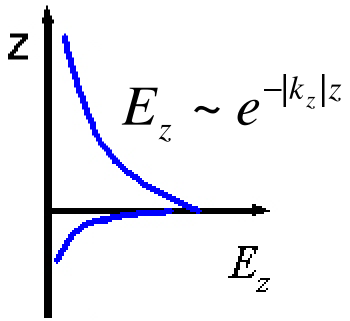
⇒

$$k_x > \frac{\omega}{c}$$

⇒

- k_{z1} is complex in metal
- k_{z2} is imaginary

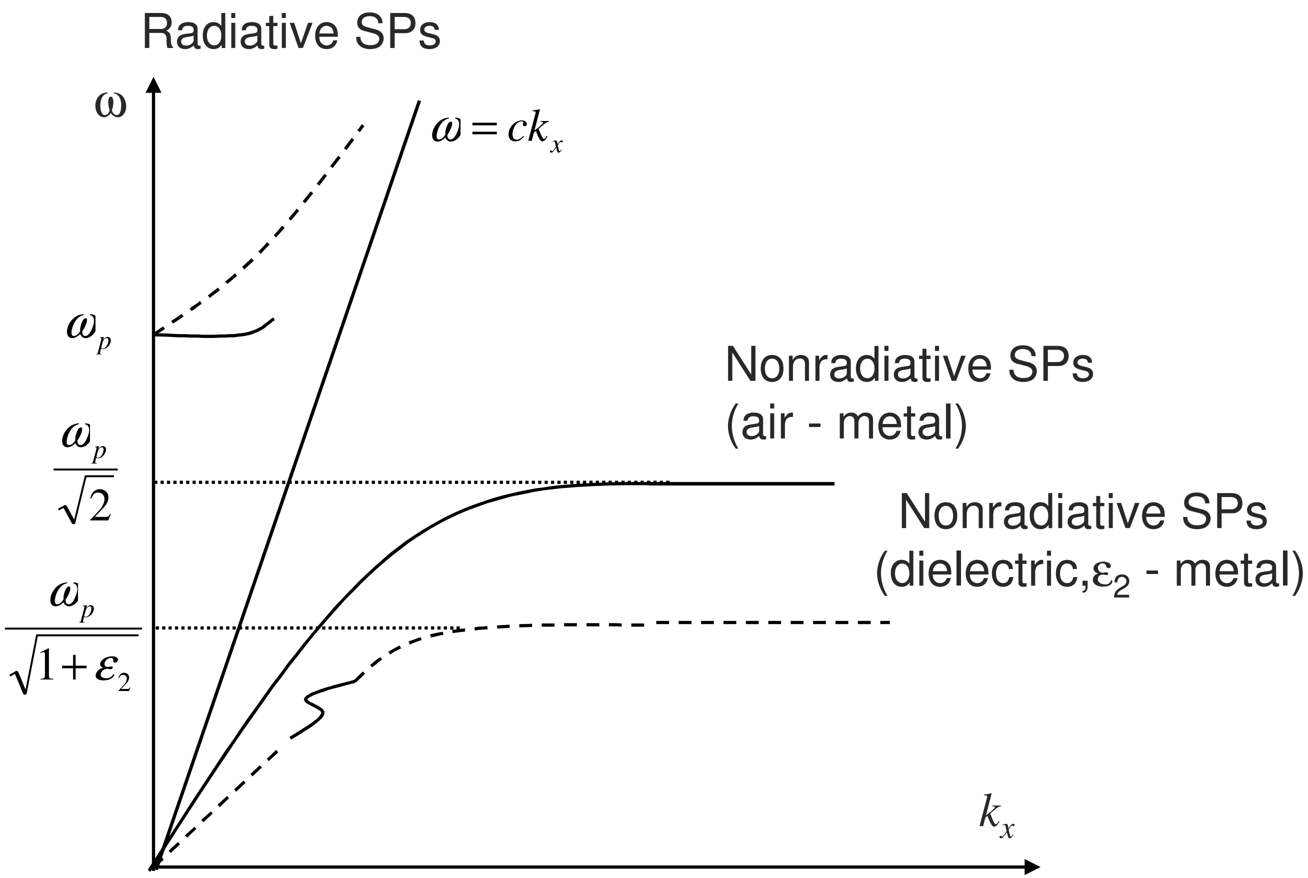




Surface Plasmons on Smooth Surfaces

Dispersion relations

$$k_x = \frac{\omega}{c}\left(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{1/2}$$



- $k_x > \frac{\omega}{c}$ ($\varepsilon_2 = 1$, $\varepsilon_1 < 0$, $|\varepsilon_1| > 1$)
- When $k_x \to \propto$ ($f_x \to \propto, \varepsilon_1 = -\varepsilon_2$) , the asymptotic value of ω is $\frac{\omega_p}{\sqrt{1+\varepsilon_2}}$ (a plasma medium)

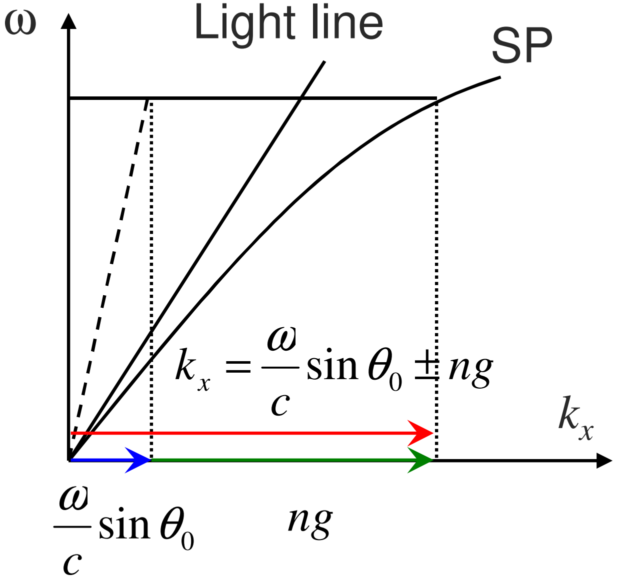
Excitation of Surface Plasmons by Light

Surface plasmons are excited by light - using grating to match phase

Light $k = \frac{\omega}{c}$

SPs $k_x > \frac{\omega}{c}$ $k_x > \frac{\omega}{c}\sin\theta_0$

θ_0 is the incident angle of light



Phase matching using grating coupler (periodicity = a)

Equivalent wavenumber for the grating

$$g = 2\pi / a$$

Thus

$$k_x = \frac{\omega}{c}\sin\theta_0 \pm ng \quad = \frac{\omega}{c}\sqrt{\frac{\varepsilon}{\varepsilon+1}}$$

Localized Surface Plasmons/ localized plasmons

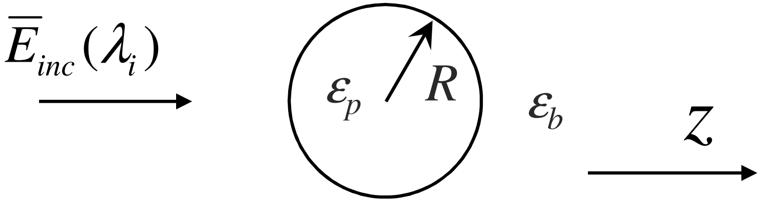
- They are excited by using light illuminating metallic spheres /cylinders
- Non-propagating
- Conditions for exciting localized SPs of a sphere

$$\varepsilon_p(\omega) = -\varepsilon_b \frac{\ell+1}{\ell}, \ell = 1,2,3...$$ (infinite number of modes)

- The lowest mode is the radiative mode (light emission)

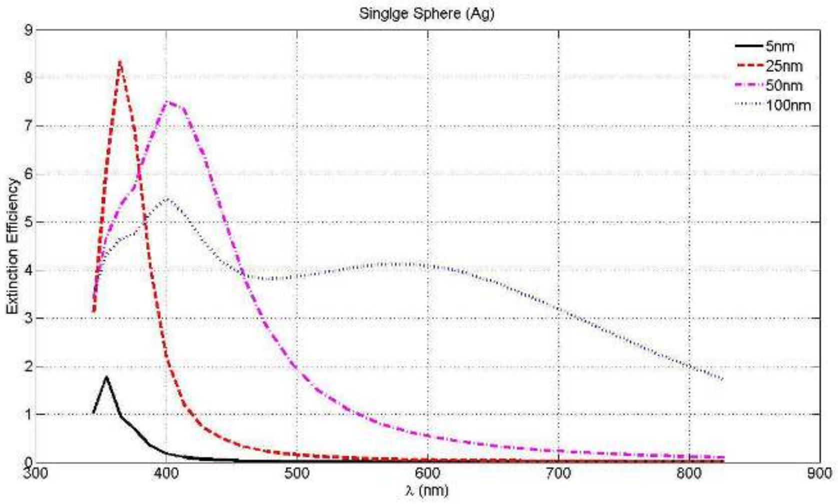
$$\varepsilon_p(\omega) = -2\varepsilon_b$$

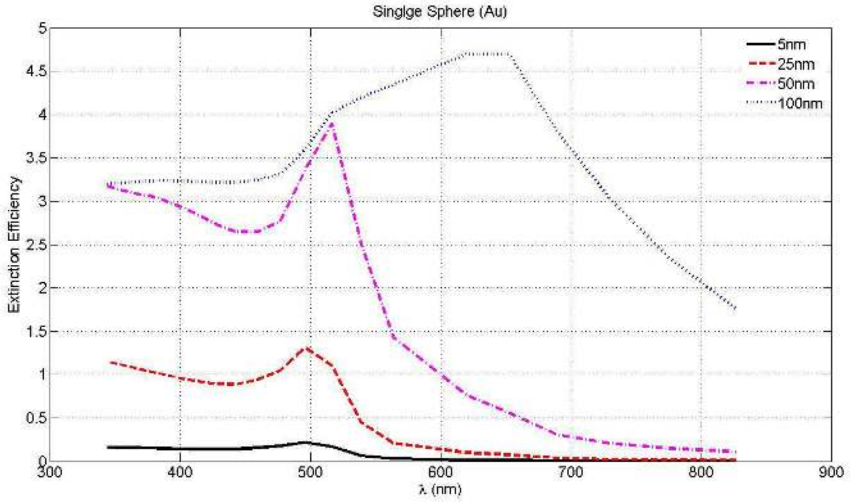
- At R << λ_i, the dipolar mode dominates.



MIE Scattering Theory

- It is applicable to spherical nanoparticles of different dimensions
- The extinction efficiency predicts the resonance of a metallic sphere
- The localized surface plasmon resonances depends on the dimension of the sphere (5 nm < R < 100 nm)





- An increased in R
  - Broadens of the dipole plasmon resonance
  - Red-shifts the resonance

Localized Surface Plasmons (Small Particles)

Quasi-static approximation for small particles (R << λ_i)

- Laplace equation for the potential $\nabla^2\Phi = 0$
- The potentials inside and outside the sphere

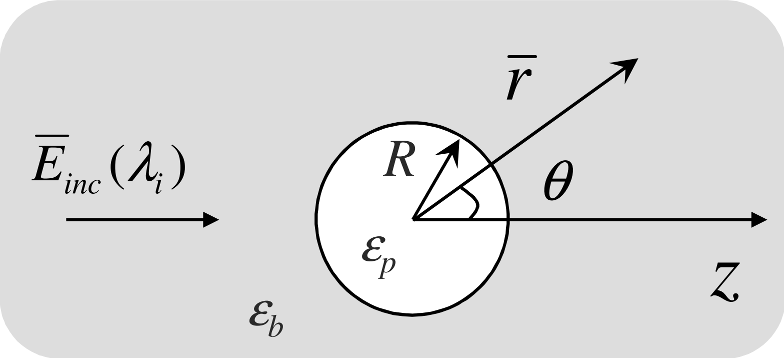
$$\Phi_{in} = -\frac{3\varepsilon_b}{\varepsilon_p(\omega)+2\varepsilon_b}E_0 r\cos\theta \qquad \Phi_{out} = -E_0 r\cos\theta + \frac{\varepsilon_p(\omega)-\varepsilon_b}{\varepsilon_p(\omega)+2\varepsilon_b}E_0 a^3\frac{\cos\theta}{r^2}$$

- The dipole moment

$$\overline{p} = 4\pi\varepsilon_0\varepsilon_b a^3\frac{\varepsilon_p(\omega)-\varepsilon_b}{\varepsilon_p(\omega)+2\varepsilon_b}E_0 \quad \text{thus} \quad \Phi_{out} = -E_0 r\cos\theta + \frac{\overline{p}\cdot\overline{r}}{4\pi\varepsilon_0\varepsilon_b r^3}$$

- The polarizability

$$\alpha = \frac{\overline{p}}{\varepsilon_0\varepsilon_b E_0} \qquad \boxed{\alpha = 4\pi a^3\frac{\varepsilon_p(\omega)-\varepsilon_b}{\varepsilon_p(\omega)+2\varepsilon_b}}$$



- Condition for resonance
  - When $|\varepsilon_p(\omega)+2\varepsilon_b|$ is minimum, α experiences a resonant enhancement
  - Re[$\varepsilon_p(\omega)$]= - 2 ε_b (Flohlich condition)
  - Silver & gold nano-spheres: resonances fall into the visible region (380 nm – 750 nm)

Localized Surface Plasmons (Small Particles)

The E-field inside and outside the sphere $\overline{E} = -\nabla\Phi$

$$\overline{E}_{in} = \frac{3\varepsilon_b}{\varepsilon_p(\omega)+2\varepsilon_b}\overline{E}_0 \qquad \overline{E}_{out} = \overline{E}_0 + 2a^3\frac{\varepsilon_p(\omega)-\varepsilon_b}{\varepsilon_p(\omega)+2\varepsilon_b}\frac{1}{r^3}\overline{E}_0$$

$$\overline{E}_{out}\big|_{r=a} = \overline{E}_0 + 2\frac{\varepsilon_p(\omega)-\varepsilon_b}{\varepsilon_p(\omega)+2\varepsilon_b}\overline{E}_0 = \frac{3\varepsilon_p(\omega)}{\varepsilon_p(\omega)+2\varepsilon_b}\overline{E}_0$$

The enhancement of E-fields

Spheres

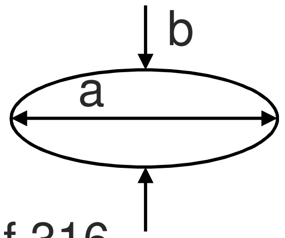
Enhancement of E-fields = $\left|\frac{E_{out}\big|_{r=a}}{E_0}\right| = \left|\frac{3(\varepsilon_{pR}(\omega)+i\varepsilon_{pI}(\omega))}{\varepsilon_{pR}(\omega)+i\varepsilon_{pI}(\omega)+2\varepsilon_b}\right|_{\omega=\omega_R} = \left|\frac{3\varepsilon_{pR}(\omega_R)}{\varepsilon_{pI}(\omega_R)}\right|$

- e.g. Silver (ε = -2+0.28 at 350nm), a small silver sphere has an enhancement factor of |-2*3/0.28| = 21 >> intensity enhancement of 460

Spheroid $\overline{E}_{tip} = \frac{\varepsilon_p(\omega)}{1+(\varepsilon_p(\omega)-1)A}\overline{E}_0$

- Resonance condition: $1+(\varepsilon_{pR}-1)A = 0$
- A is the depolarization factor

Enhancement of E-fields = $\left|\frac{E_{tip}(\omega_R)}{E_0}\right| = \left|\frac{\varepsilon_{pR}(\omega_R)}{\varepsilon_{pI}(\omega_R)A}\right|$



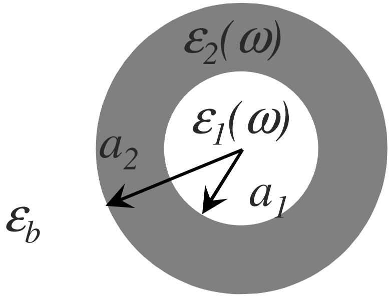
- Small b/a >> small A >> higher enhancement;
- E.g. b/a = 1/3, ε = -9+0.3 at 496nm, an E-field enhancement of 316

Localized Surface Plasmons (Small Particles)

Quasi-static approximation for a core/shell particle

- The dielectric core & a thin, concentric metallic shell
- Wide tunability of the plasmon resonance
- The polarizability

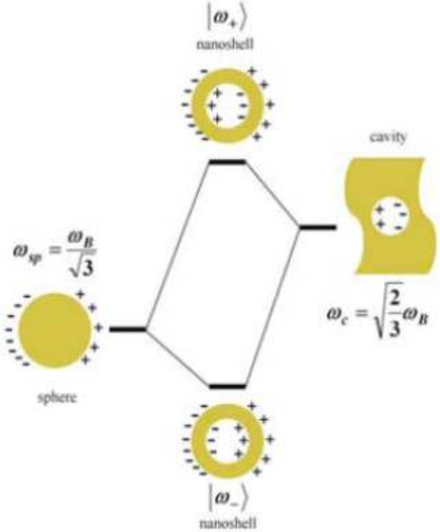
$$\alpha = 4\pi a_2^3 \frac{(\varepsilon_2-\varepsilon_b)(\varepsilon_1+2\varepsilon_2)+(a_1^3/a_2^3)(\varepsilon_1-\varepsilon_2)(\varepsilon_b+2\varepsilon_2)}{(\varepsilon_2+2\varepsilon_b)(\varepsilon_1+2\varepsilon_b)+(a_1^3/a_2^3)(2\varepsilon_2-2\varepsilon_b)(\varepsilon_1-\varepsilon_2)}$$



- Obtain resonance by minimizing the denominator,

$$(\varepsilon_2+2\varepsilon_b)(\varepsilon_1+2\varepsilon_b)+(a_1^3/a_2^3)(2\varepsilon_2-2\varepsilon_b)(\varepsilon_1-\varepsilon_2)$$

- It has two fundamental dipolar modes
- They can be thought to arise via the hybridization of the dipolar modes of
  - Metallic spheres
  - A dielectric void in the metallic substrate



- Applying the hybridization, the particle plasmon is described as an incompressible deformation of the conduction electron gas of the metallic nanostructure

$$\omega_{l,\pm}^2 = \frac{\omega_p^2}{2}\left[1 \pm \frac{1}{2l+1}\sqrt{1+4l\,(l+1)\left(\frac{a}{b}^{2l+1}\right)}\right]$$

Localized Surface Plasmons (Big Particles)

- The polarizability of a sphere of volume V is approximated by taking the first TM mode of Mie theory

$$\alpha_{\text{Sphere}} = \frac{1-\left(\frac{1}{10}\right)(\varepsilon+\varepsilon_m)x^2+O\left(x^4\right)}{\left(\frac{1}{3}+\frac{\varepsilon_m}{\varepsilon-\varepsilon_m}\right)-\frac{1}{30}(\varepsilon+10\varepsilon_m)x^2-i\frac{4\pi^2\varepsilon_m^{3/2}}{3}\frac{V}{\lambda_0^3}+O\left(x^4\right)}V$$

- Red-shift of the resonance

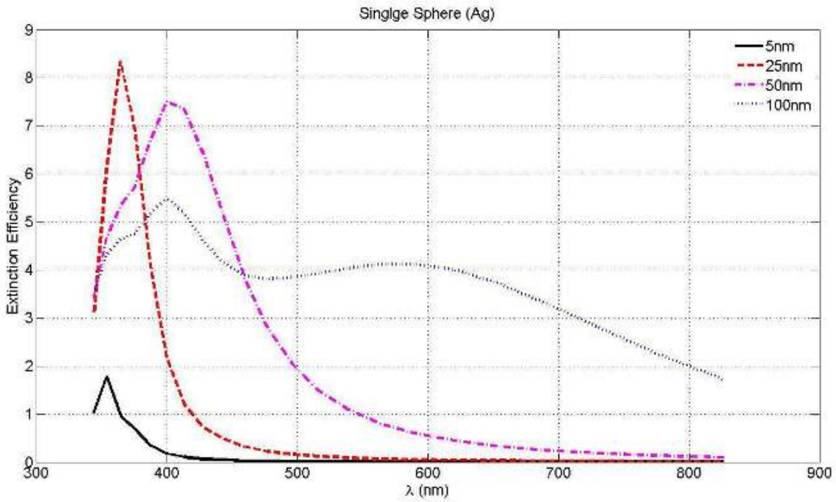
  Reason: the smaller restoring force in a big particle → smaller energy → lower frequency

- Broadened linewidth

  Reason: radiation damping dominates in lager particles

Homogeneous linewidth, $\Gamma = \frac{2\hbar}{T_2}$

T_2 is the dephasing time, $T_2 \approx 2T_1$, population relaxation/decay time



Localized Surface Plasmons (Very Small Particles)

R < 10 nm

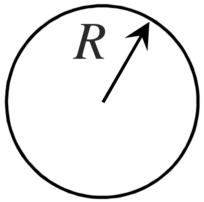
- An additional damping process: chemical interface damping
- 2R < electron free path (30 – 50 nm)

→ elastic scattering at the particle surface

→ the rate of dephasing of coherent oscillation increases

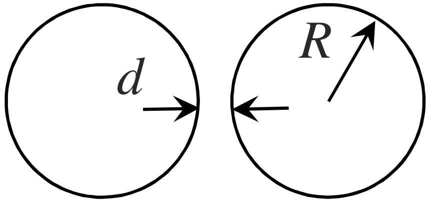
→ decrease in decay time

→ Broad linewidth



R < 1 nm

- Quantum effect sets in
- The coherent electron oscillation breaks down
- The problem has to be treated using the quantum mechanical picture of a multiple-particle excitation



---

d < 0.5 nm, quantum-mechanical effects such as charge transfer become important

[1] Quantum description of the plasmon resonances of a nanopaerticle dimer, Nano Lett. 2009, 9, 887-891

[2] Quantum plasmonics: Optical properties and tunability of metallic nanorods, ACS Nano, 2010,4,5269-5276

SERS Enhancement Factor

- SERS enhancement factor, $$\frac{I_{SERS}}{I_0} = \frac{|E_{SERS}|^2}{|E_0|^2} \cong |g|^4$$
- In SERS experiments,

$$\text{SERS enhancement factor} = \frac{\begin{array}{c}\text{Measured Raman cross section}\\ \text{(in the presence of metal particles)}\end{array}}{\begin{array}{c}\text{Measured Raman cross section}\\ \text{(in the absence of metal particles)}\end{array}}$$

- Average $|E|/|E_0|$ is relevant to conventional SERS measurements
  - Most early experiments utilized large probe volumes
- The peak of $|E|$ is important to single molecule detection
  - The site(s) with the maximum E-field are called hot sites/hot spots

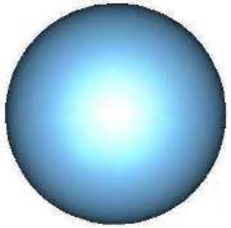
		SERS enhancement factor	**E-field enhancement factor**
Conventional SERS	Silver colloids	10^3-10^6	6-32
Single molecule SERS	Silver and gold colloids	10^{10}-10^{15}	316 - 5623

‘What gives the giant enhancement factor?’

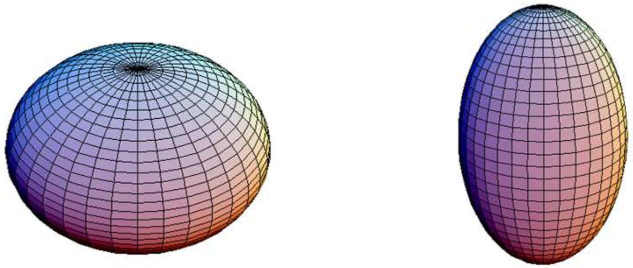
→ There are factors that affect the E-field enhancement

Factors Affecting the E-field Enhancement

1. The shape/geometry of the nanoparticles
   (wet-chemistry methods, lithographic techniques)

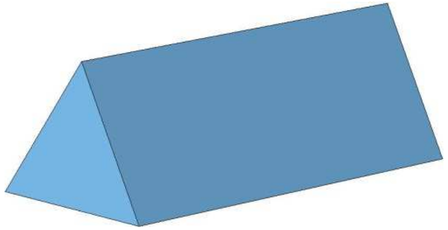


$|E|/|E_0| \sim 10$



$|E|/|E_0| > 30$

- Spheroids have higher E-field enhancement than spheres (quasi-static approximation)
  - Additional field enhancement at the tips due to continuity of $\overline{D}$
  - Lightning rod factor, $g_{LR} = |\varepsilon_p|/|\varepsilon_b|$
- Nanoparticles with tips/sharp edges show high E-field enhancement

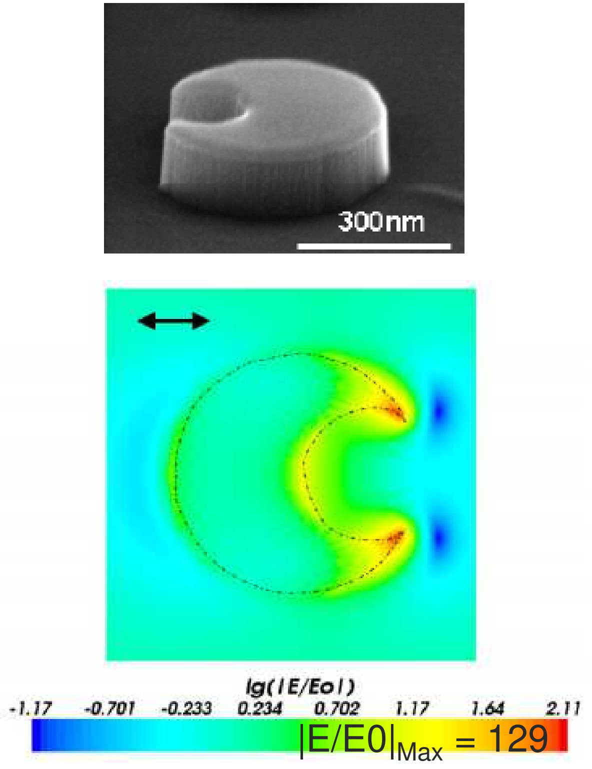


- Nanoparticles with complicated geometries → $|E|/|E_0|$ is cal. numerically

Factors Affecting the E-field Enhancement

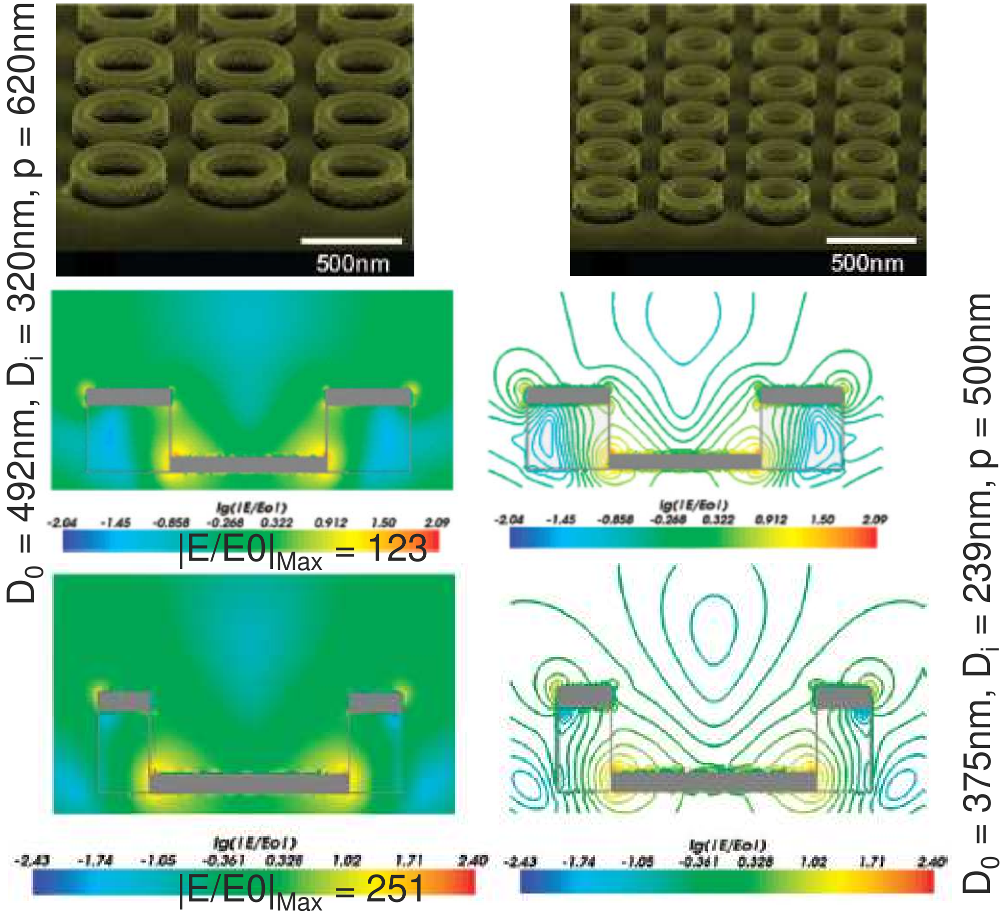
1. The shape/geometry of the nanoparticles (lightning rod effect)
2. The physical size ↔ the incident wavelength (localized surface plasmons)

Nanocrescent [1]



$|E/E0|_{Max} = 129$

Nanowells [2]



$|E/E0|_{Max} = 123$

$|E/E0|_{Max} = 251$

[1] K. Li, et al, Nanotechnology, vol. 19, page 145305, 2008

[2] K. Li, et al, Analytical Chemistry, vol. 80, page 4945, 2008

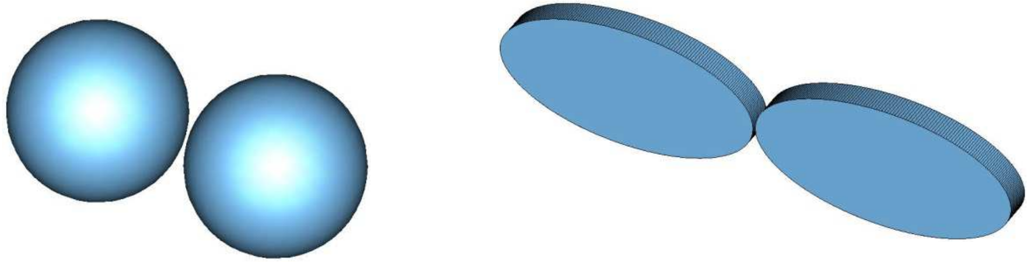
Factors Affecting the E-field Enhancement

3. The number of particles
4. The space between the particles

Monomer: a single nanoparticle

$|E|/|E_0| \sim 10$

Dimers: two nanoparticles that are in close proximity



$|E|/|E_0| > 320$

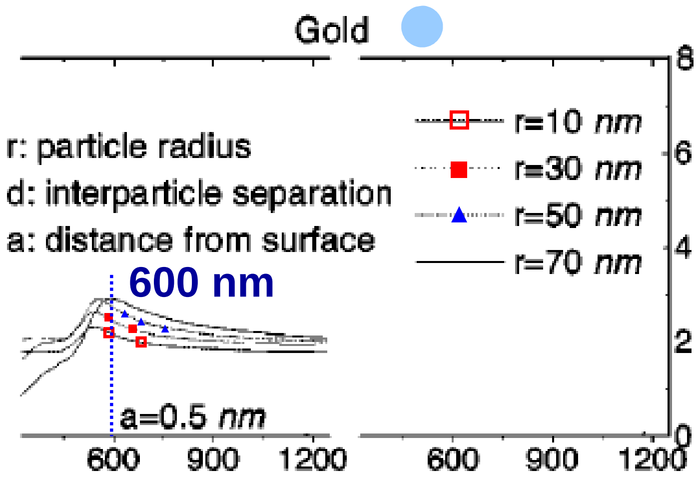
- High E-field enhancement [1,2]
- It is used to interpret high E-field enhancement in single molecule SERS

[1] E. Cai, and G. Schatz, J. Chemical Physics vol. 120, No. 1, p357 – 365, 2004

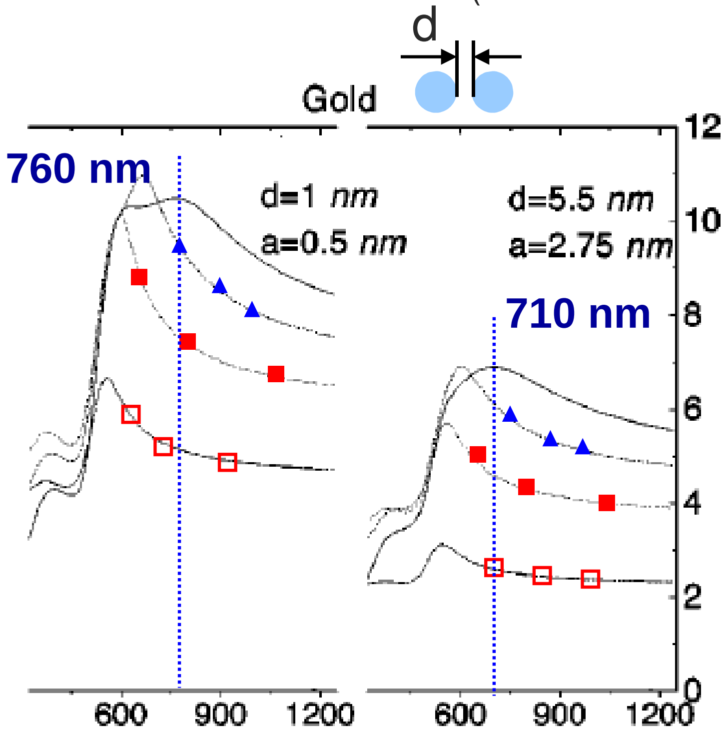
[2] H. Xu, et al. PR E, vol. 62, No. 3, 4318, 2000

Factors Affecting the E-field Enhancement

3. The number of particles
4. The space between the particles



(T-matrix for dimers)



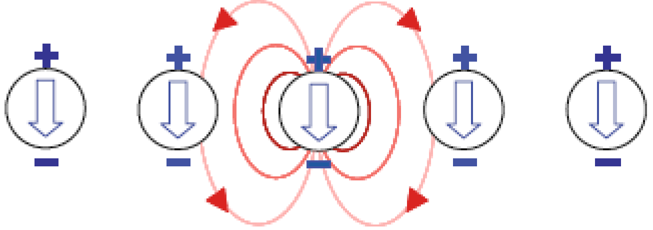
- Dimer has coupling between localized surface plasmons
- The coupling has two effects
  1. Shifting the resonant frequency
  2. Suppress the coupling of the nearby particle & further localize the field

[1] H. Xu, et al. PR E, vol. 62, No. 3, 4318, 2000

Coupling Btw Localized Surface Plasmons

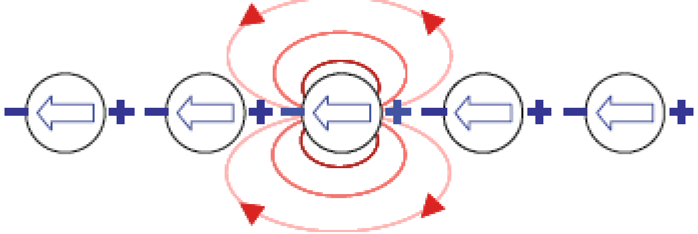
The shifting of resonant frequency

Polarization 1
Transverse excitation (E_T)



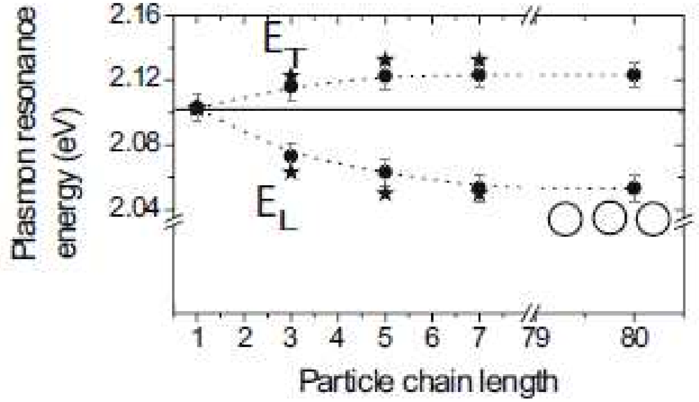
- Higher potential
- Higher frequency
- Blue-shift

Polarization 2
Longitudinal excitzation(E_L)



- Potential cancellation
- Lower frequency
- Red-shift

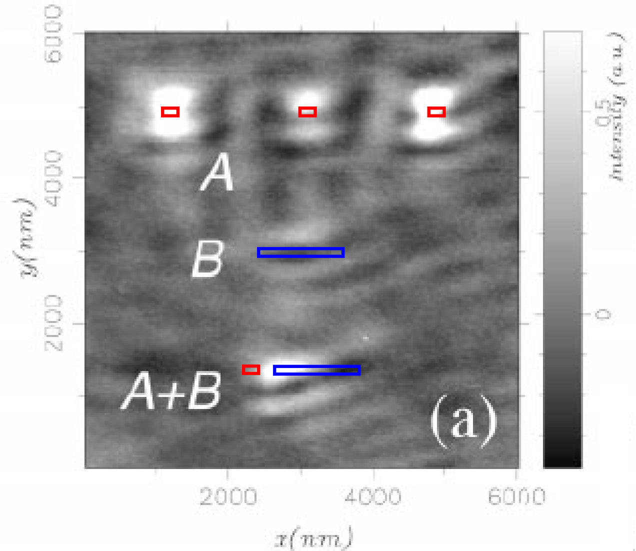
Due to the near-field nature, the effect becomes negligible for a chain length of about 5 particles



Coupling Btw Localized Surface Plasmons

Further enhancement of E-fields

- Experimental observation [1]



A: 120 × 60 × 40 nm^3
B: 660 × 60 × 40 nm^3

Photon scanning tunneling microscope (PSTM) image

- Explanation using interaction between the molecule & an EM cavity mode

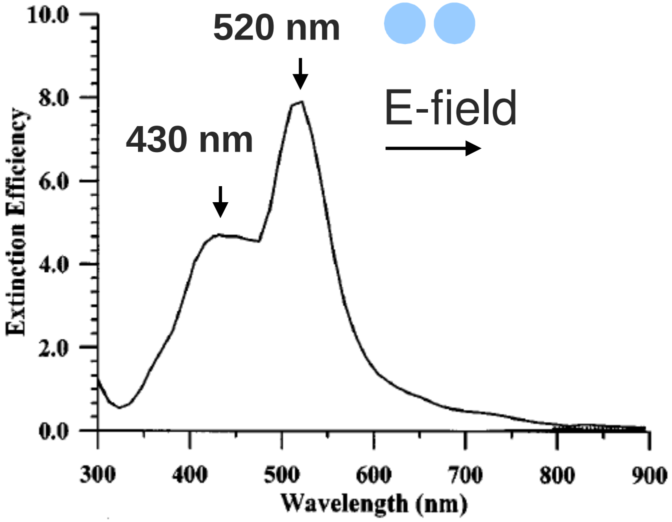
$$\frac{|E_{loc}|^2}{|E_i|^2} = \frac{\gamma_{rad} A_c}{4\pi^2 c^2 \eta \varepsilon_0 \lambda_0} \frac{Q^2}{V_{eff}}$$

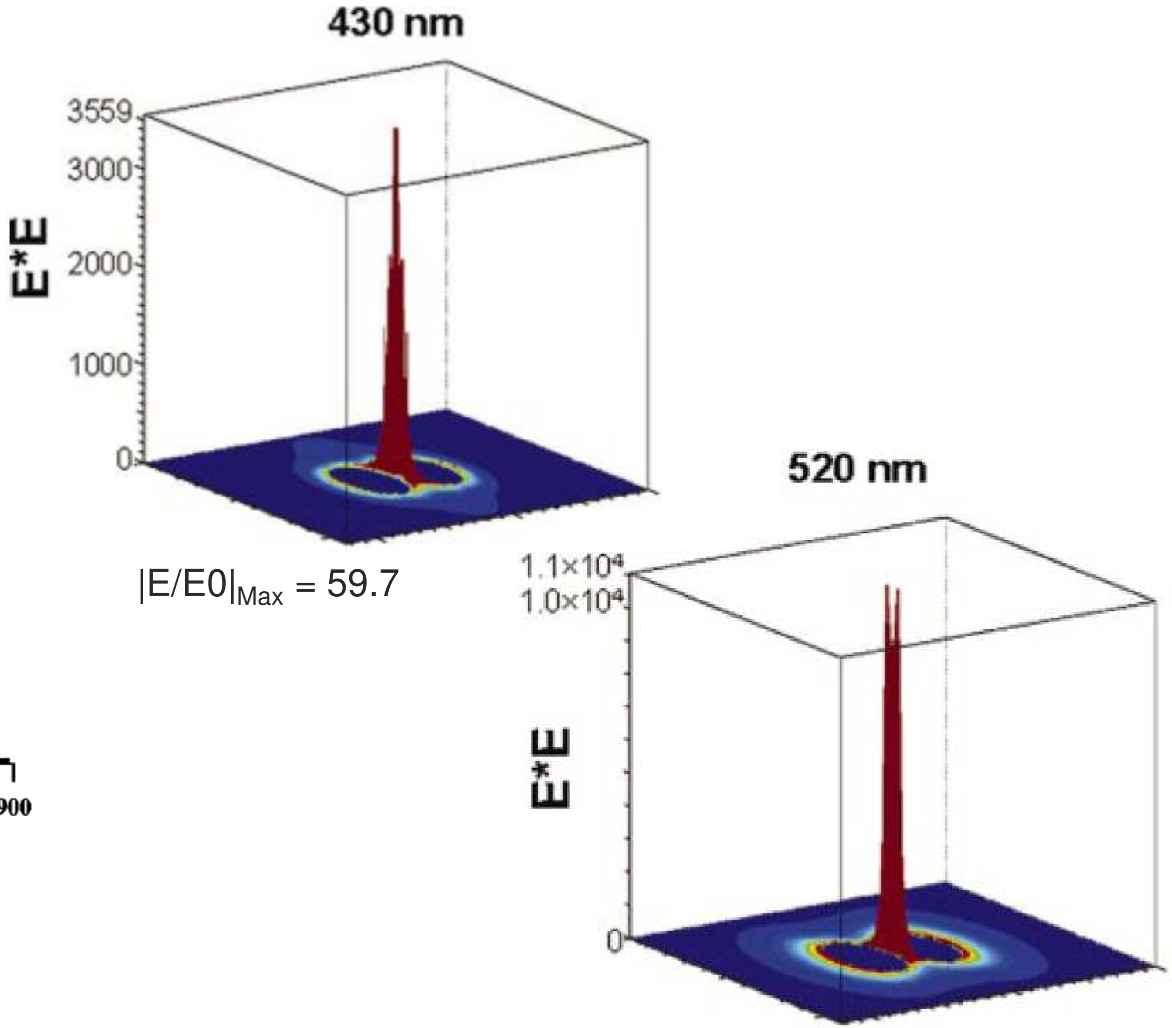
[1] J. R. Krenn, et al, PRL, vol. 82, 2590, 1999

Factors Affecting the E-field Enhancement

3. The number of particles, dimers

Spherical dimers





$|E/E0|_{\text{Max}} = 59.7$

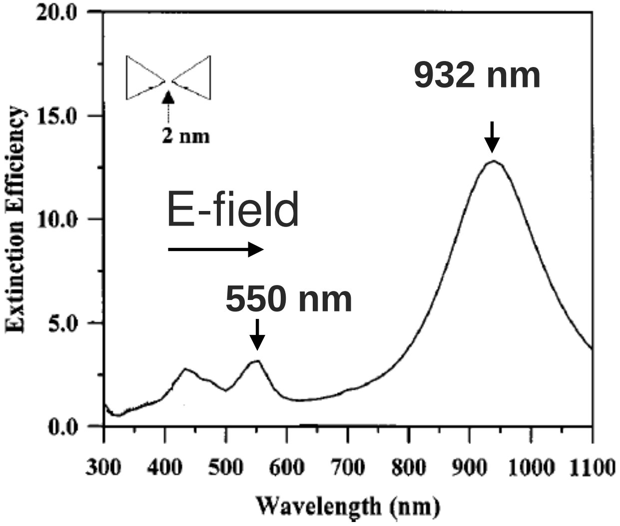
$|E/E0|_{\text{Max}} = 104.9$

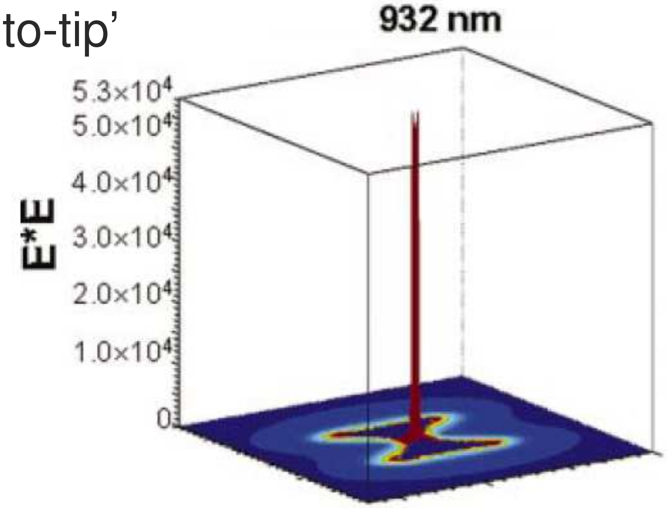
[1] E. Cai, and G. Schatz, J. Chemical Physics vol. 120, No. 1, p357 – 365, 2004

Factors Affecting the E-field Enhancement

3. The number of particles, dimers

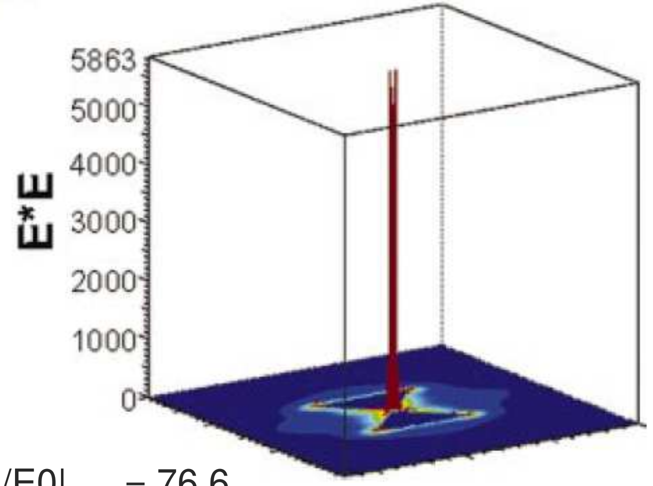
Triangular cylinder dimers, ‘tip-to-tip’





$|E/E0|_{Max}$ = 230.2

550 nm



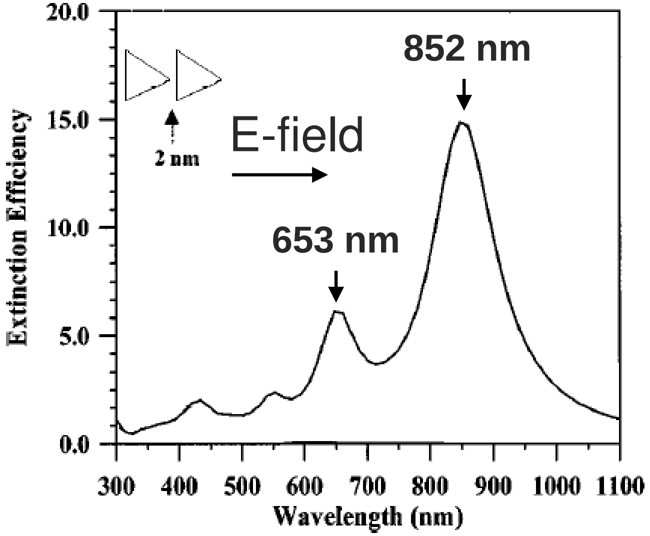
$|E/E0|_{Max}$ = 76.6

[1] E. Cai, and G. Schatz, J. Chemical Physics vol. 120, No. 1, p357 – 365, 2004

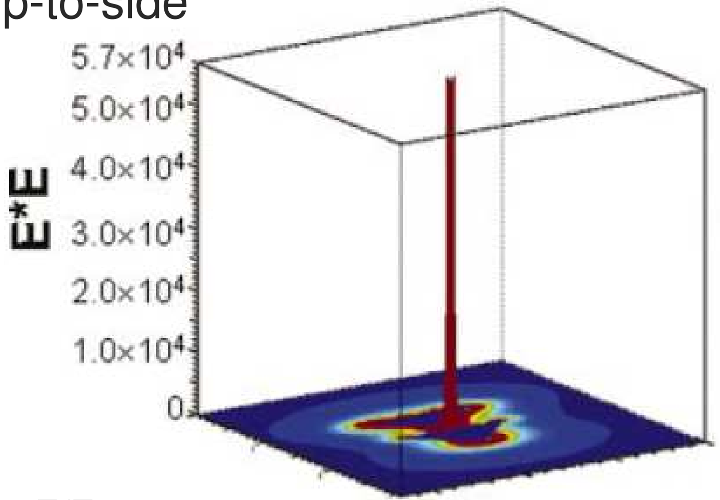
Factors Affecting the E-field Enhancement

3. The number of particles, dimers

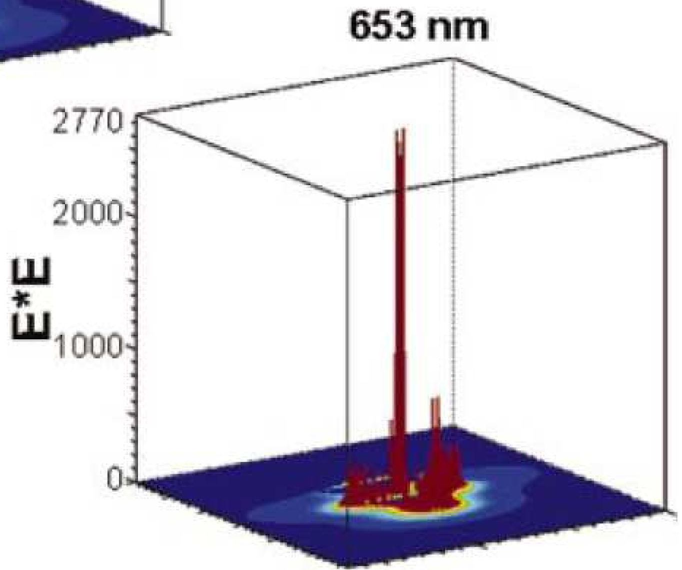
Triangular cylinder dimers, ‘tip-to-side’



852nm



$|E/E0|_{Max} = 238$



$|E/E0|_{Max} = 52.6$

[1] E. Cai, and G. Schatz, J. Chemical Physics vol. 120, No. 1, p357 – 365, 2004

Dimers, Optical Antennas

Dimers with high E-field enhancement working at THz

They are called optical antennas.

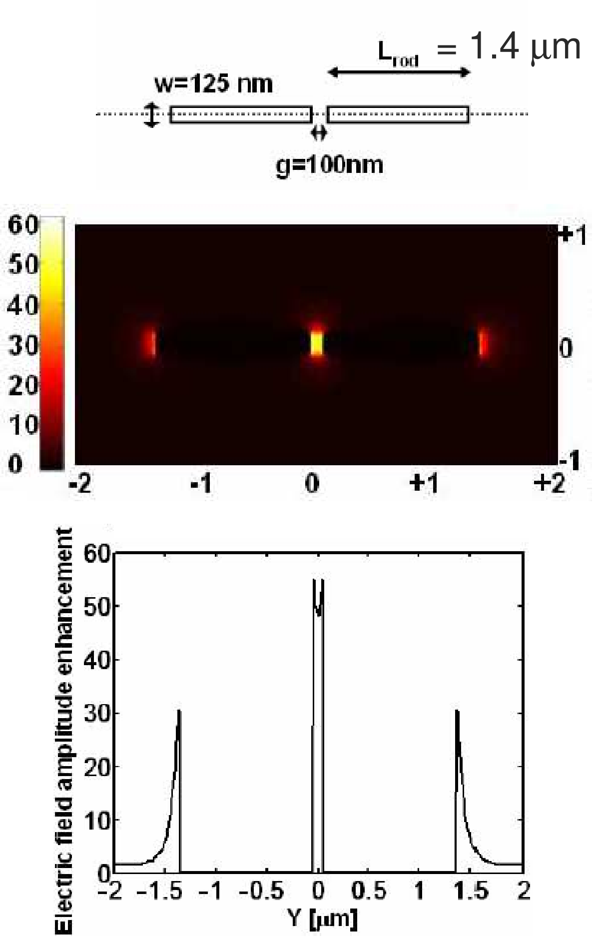
Incident wavelength = 7μm

Schematics

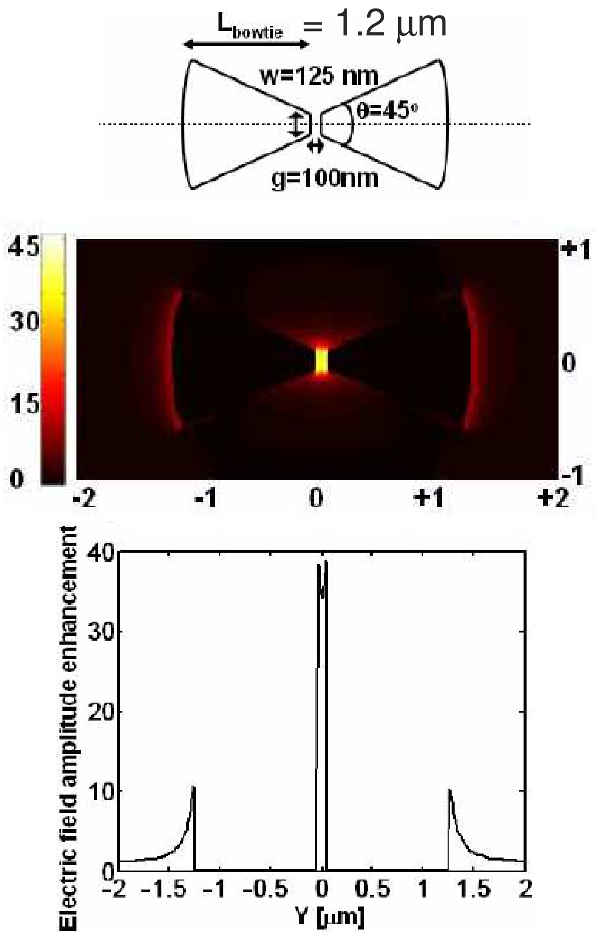
FDTD simulations

Line scans (FDTD with adapted meshing)

Nano-rod



Nano-bowtie [1]



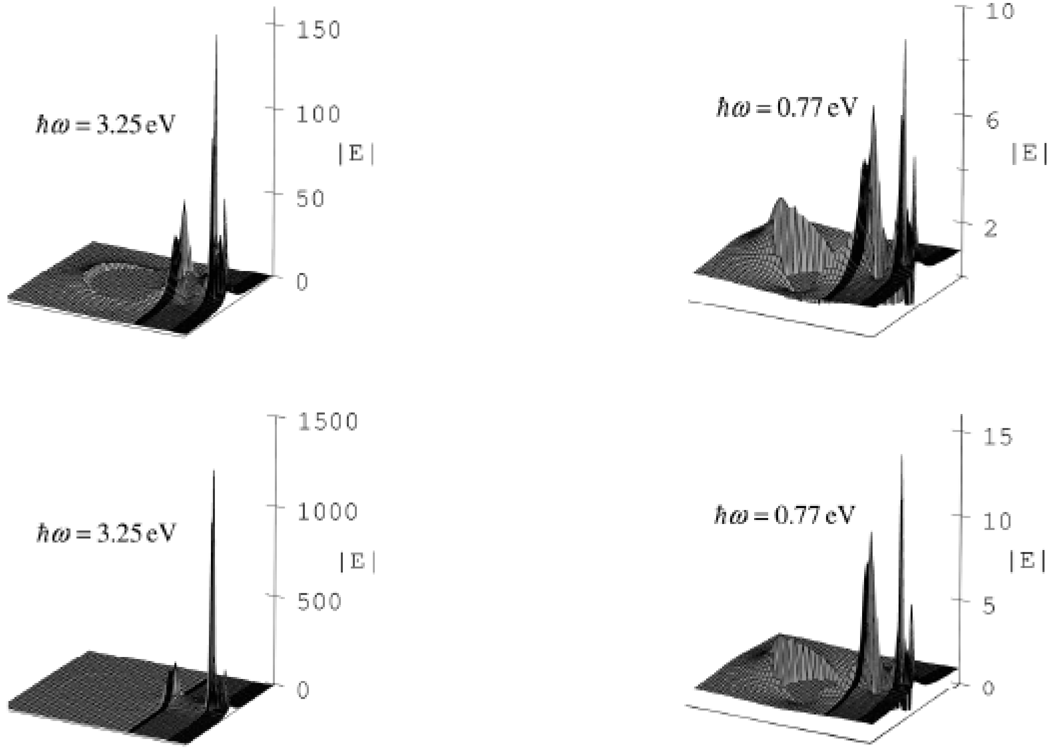
[1] N. Yu, K. B. Crozier, F. Capasso et al, OE, vol. 15, No. 20, 13272, 2007

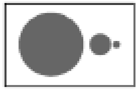
Factors Affecting the E-field Enhancement

4. The space between the particles

$d_{i,i+1} = 0.6R_{i+1}$

$d_{i,i+1} = 0.3R_{i+1}$





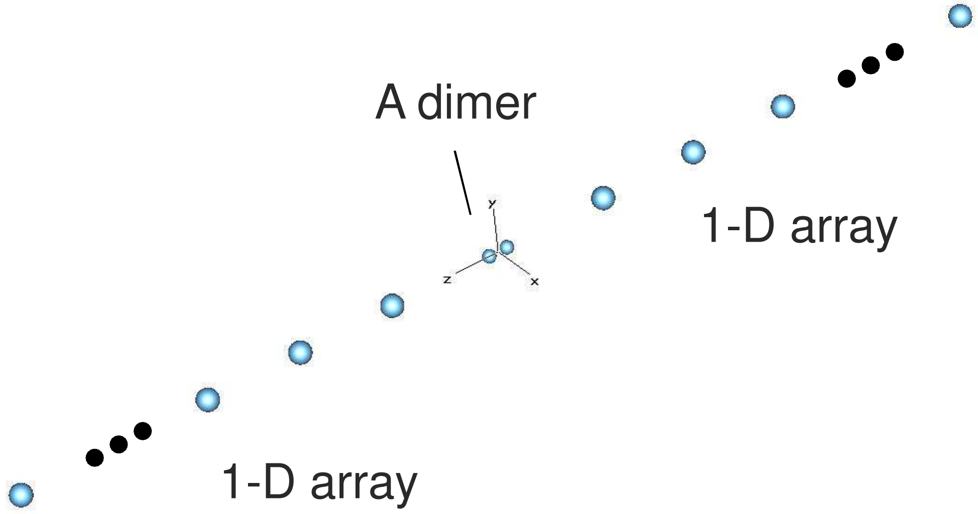
$R_{i+1}/R_i = 1/3$

A self-similar chain of three silver nanospheres at different distance between successive spheres [1]

[1] K. Li, et al, PRL, vol. 91, 227402, 2003

Factors Affecting the E-field Enhancement

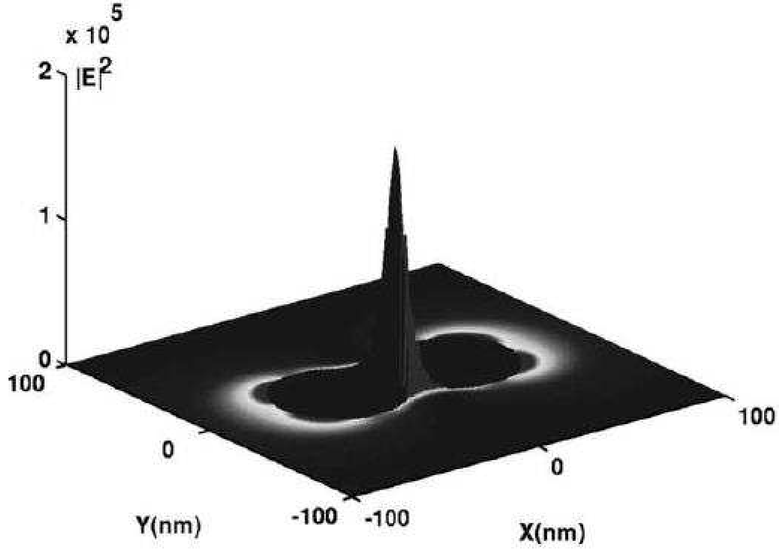
5. The periodicity



A dimer

1-D array

1-D array



A dimer (radius=30nm) in a 1-D sphere array
(radius=50nm, period=470nm) [1]

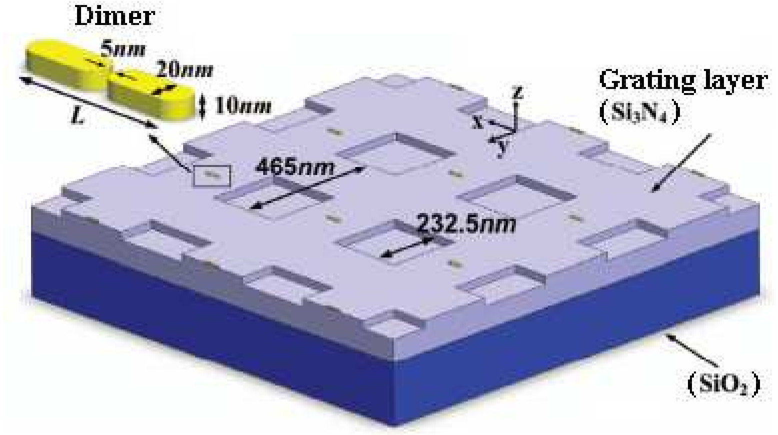
$|E/E_0|$ = 400 at 471.4nm, 4 times of an isolated dimer

[1] S. Zou, et al, Chemical Physics Letters, vol. 403, page 62, 2005

E-field Enhancement

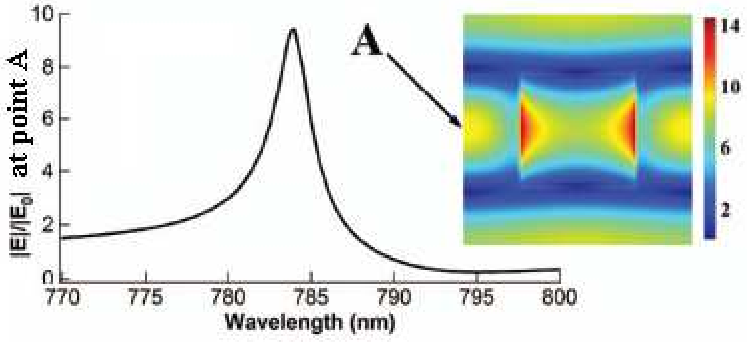
Using structures with grating to provide additional enhancement at resonance [1]

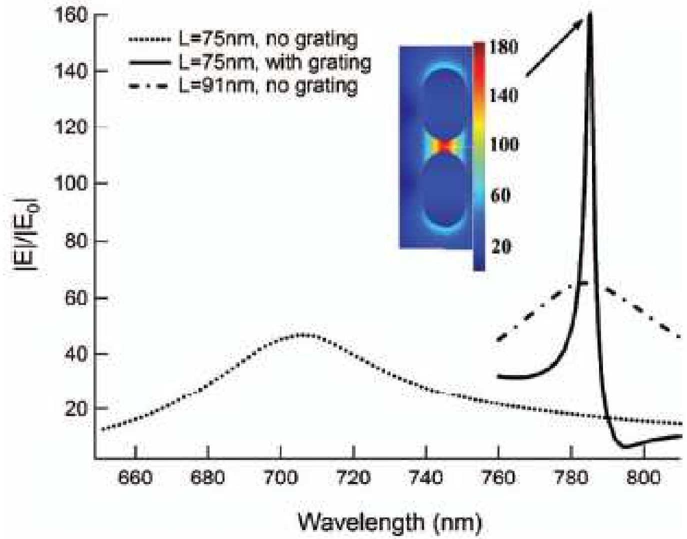
A silver dimer placed on top of a Si3N4 grating layer on a SiO2 substrate



- The dimension of the grating surface is determined to resonate at 785 nm based on rigorous coupled wave analysis (x-polarized normal incident waves)
- Location A
  - Max E-fields
  - Place a dimer

A E-field enhancement of 10 at 785 nm





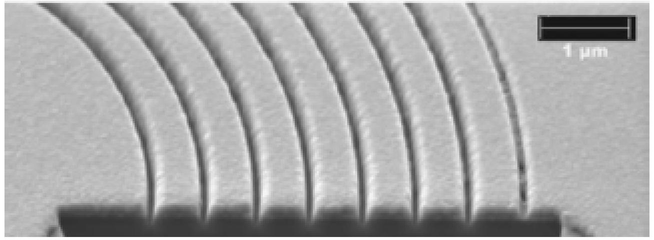
Simulated results using COMSEL. The dimer is resonating by tuning L (L=75 with grating, L = 91 without grating)

[1] J. Li et al, APL, vol. 94, 263114, 2009

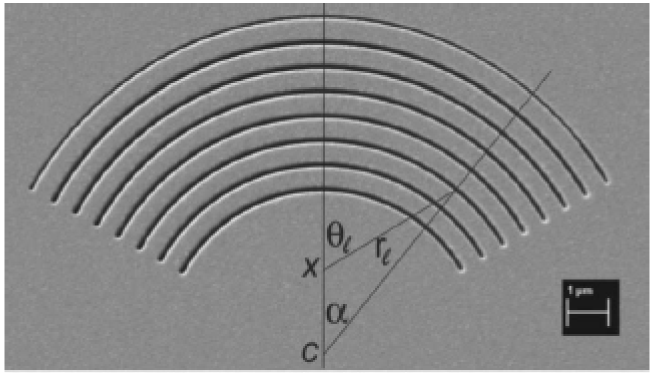
Other SERS Active Substrates

A large variety of structures show / predicted to have large E-field enhancements.

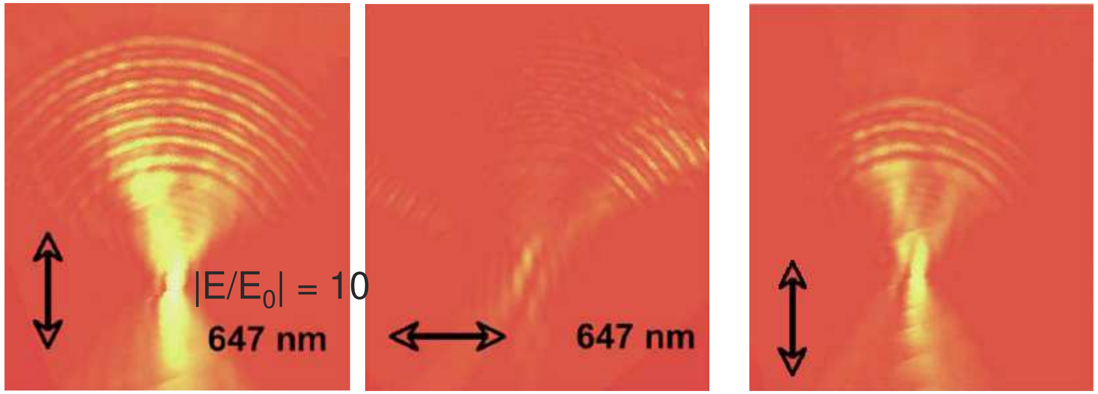
Concentric Arcs Nanoslits



Cross-section [1]



Plane view



$|E/E_0| = 10$

Eight arcs

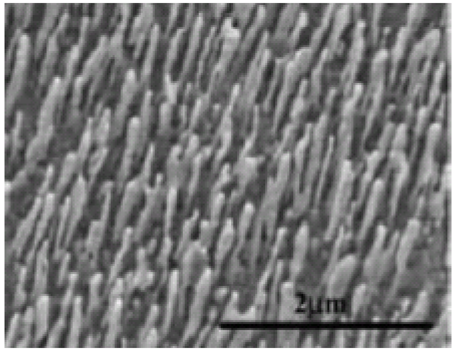
Four arcs

Near-field scanning optical microscope images of the surface plasmon polaritons

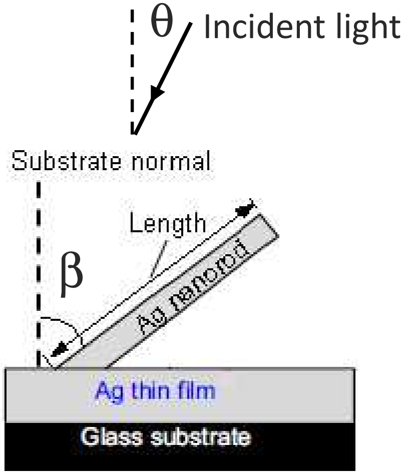
[1] J. T. Bahns, et al, APL, vol. 91, 081104, 2007

Other SERS Active Substrates

Oblique angle deposited Ag nanorod arrays [1][2]



A top view scanning electron microscopy (SEM) image



2-D cross-sectional schematics

E-field enhancement factor of more than 100 is obtained when

- The rod with 508.29±44.86 nm;
- Tilting angle, $50^o < \beta < 60^o$;
- L/diameter of the rod = 5.69 ± 1.49

When $\beta = 73^o$, the optimal incident angle $\theta = 45^o$ [3]

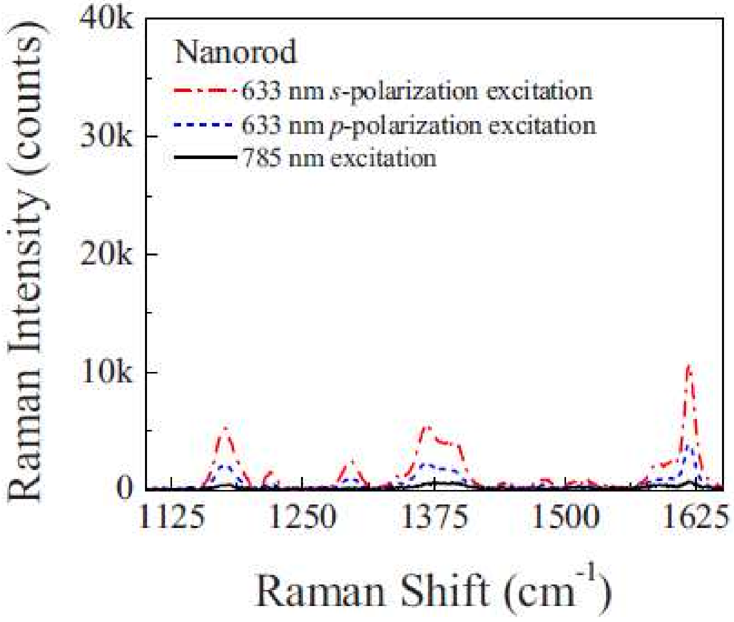
[1] S. B. Chaney, et al, APL, vol. 87, 031908, 2005

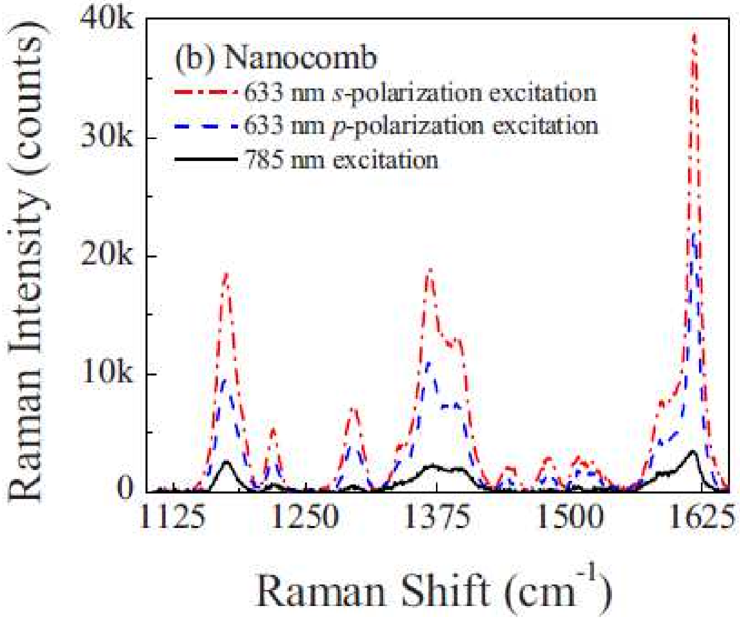
[2] Y-J. Liu, et al, PR-B, vol. 78, 075436, 2008

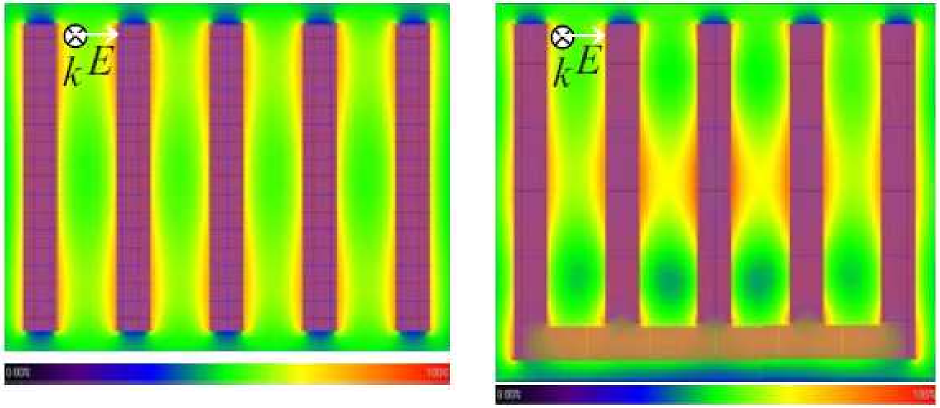
[3] Y-J. Liu, et al, APL, vol. 89, 173134, 2006

Other SERS Active Substrates

Effects of the Ag thin film for oblique angle deposited Ag nanorod arrays [1]







E-field distribution at 633 nm (FDTD)

[1] Y-J. Liu, et al, APL, vol. 94, 033103, 2009

Computation for SERS

Possible contributions: to describe the electrodynamics of nanoparticles with

  - Arbitrary shapes
  - Degree of aggregation
  - Complex external dielectric environments

Methods

- MIE scattering theory >> metal spheres
- Quasi-static approximation >> nanostructure of regular geometries
- Numerical methods
  - Discrete dipole approximation (DDA)
  - FDTD
  - T-matrix methods (multiple multipole method)
  - Modified long wavelength approximation (MLWA)

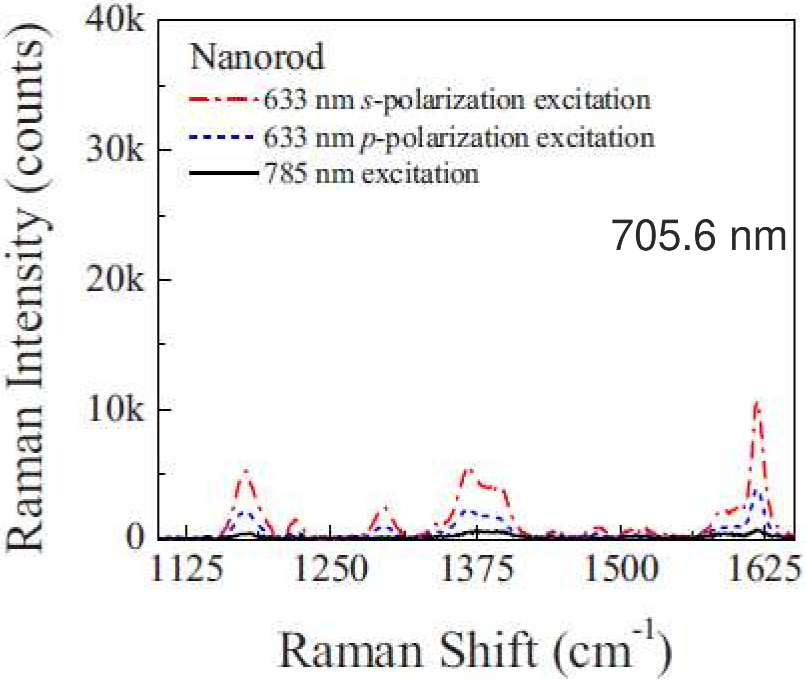
Expected outputs

- Extinction efficiency (far-field) >> resonance of the structure
- Near-field E-field (SERS enhancement) >> suitbale location for molecules

Raman Scattering

- Main applications:
  - Spectroscopic chemical analysis
  - Laser technology
- Raman spectroscopy
  - The laser light interacts with molecular vibrations, phonons, or other excitations in the system ⇨ The energy of the laser photons being shifted up (anti-Stokes) or down (Stokes)
  - The shift in energy gives information about the phonon modes in the system.
- Raman lasers: achieve gain through stimulated Raman scattering (SRS) process

Raman Spectrum



Raman Lines

- The linewidth: it depends on the lifetime of the vibrational excitation
- The intensity: it depends on the effective scattering cross section (the light-matter interaction)

Summary

- Introduction
- Single molecule detections
- Working principles
- Enhancement of E-fields