

Metallic nanoantennas for Field-Enhanced Spectroscopy and Microscopy: from Visible to TeraHertz

DONOSTIA INTERNATIONAL
PHYSICS CENTER



Javier Aizpurua

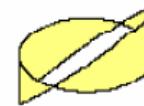


*Centro de Física de Materiales CSIC-UPV/EHU
and Donostia International Physics Center (DIPC),
Donostia-San Sebastián, Spain*

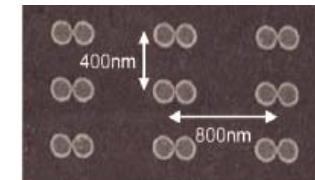
***Summer School on Plasmonics
September 13-17, 2009
Porquerolles Island, Côte d'Azur, France***

Outline

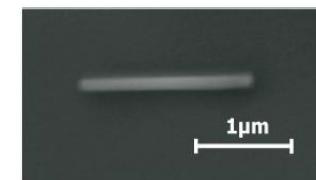
- Basics: Localized Plasmons



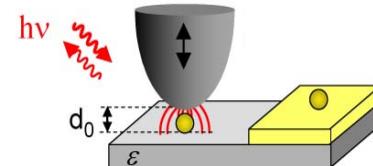
- Optical antennas for SERS



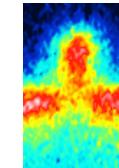
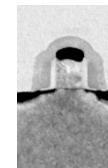
- Infrared antennas for SEIRA



- Substrate-Enhanced Infrared Near-Field Microscopy



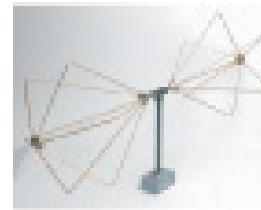
- THz Near-field Nanoscopy



Radio Frequency Antennas



Half wave
dipole antennas



Biconical antenna



Monopole antenna



CombiLog antenna



Yagi-Uda antenna



Horn antenna

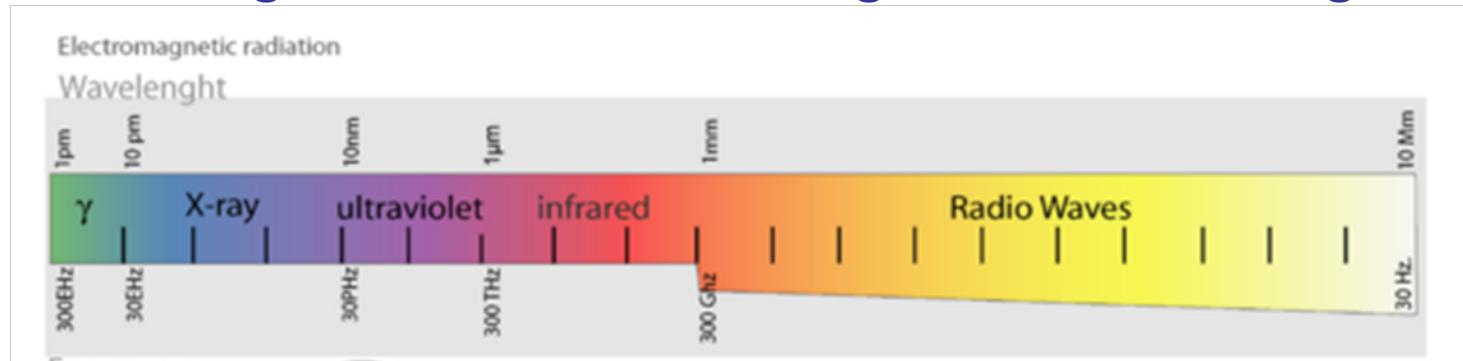


Parabolic antenna



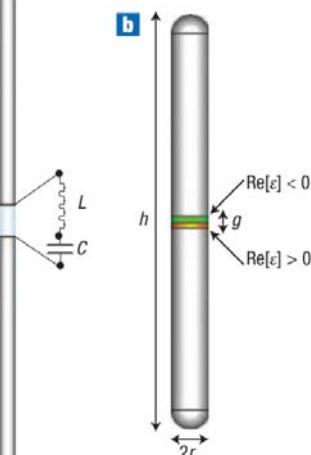
Active loop antenna

Scaling down in size \leftarrow Scaling down in wavelength

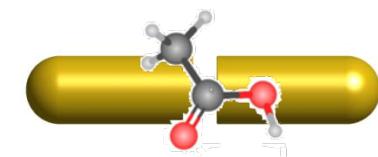
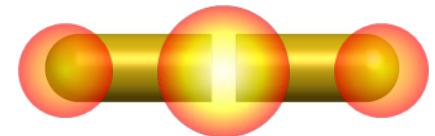
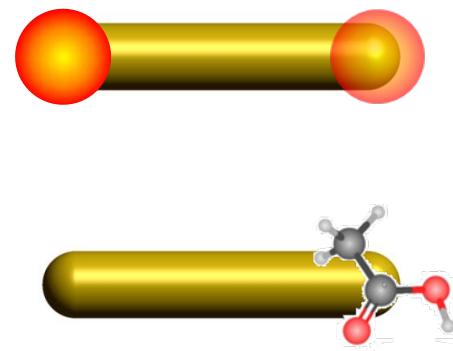


a

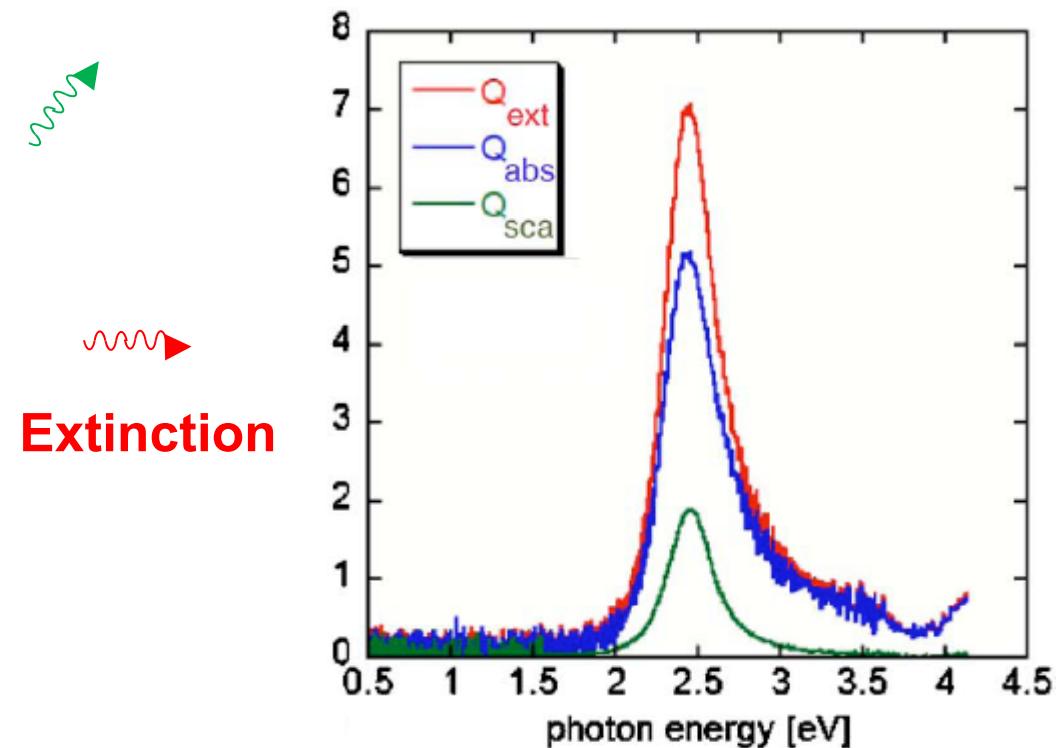
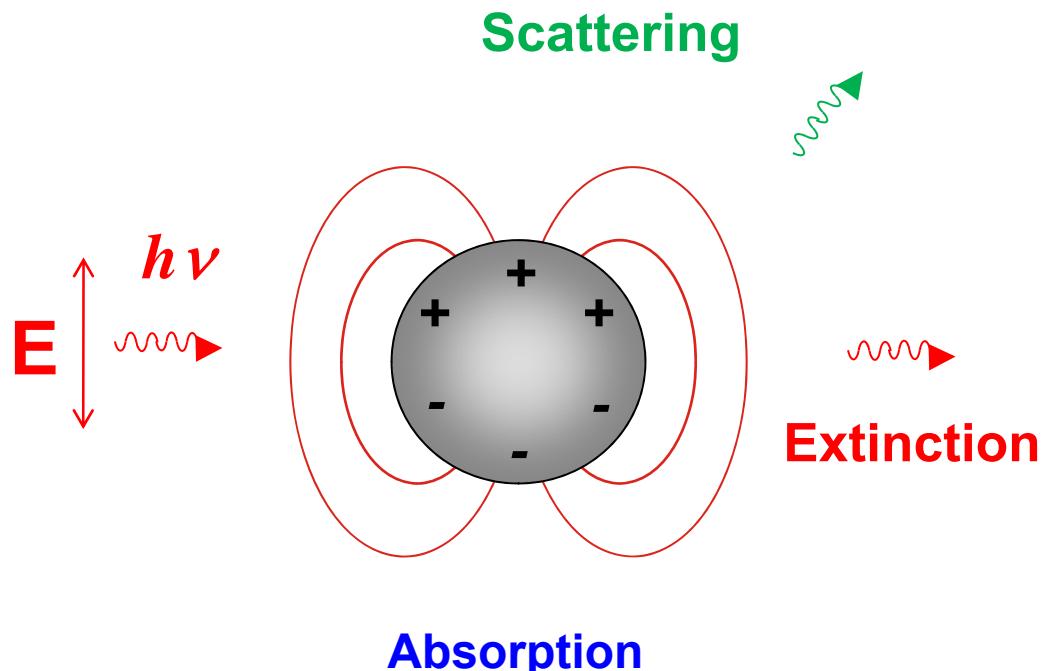
Visible light \rightarrow Optical antenna \rightarrow Nanoantenna



$\lambda/2$ nanoantenna



The simplest optical antenna: a metallic particle



Enhancement of absorption and emission:
Bringing effectively the far-field into the near-field

Metal particle plasmons

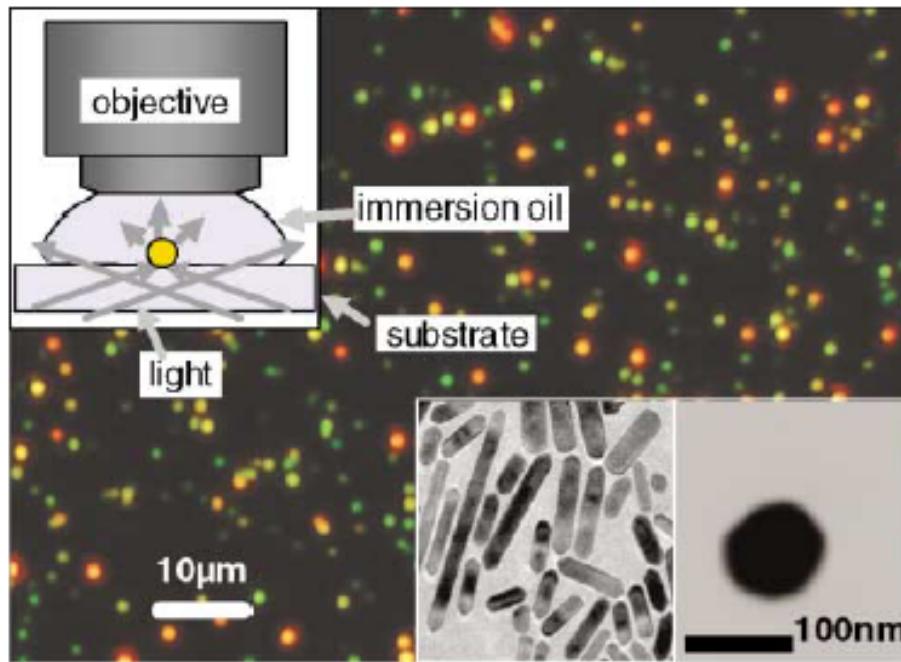
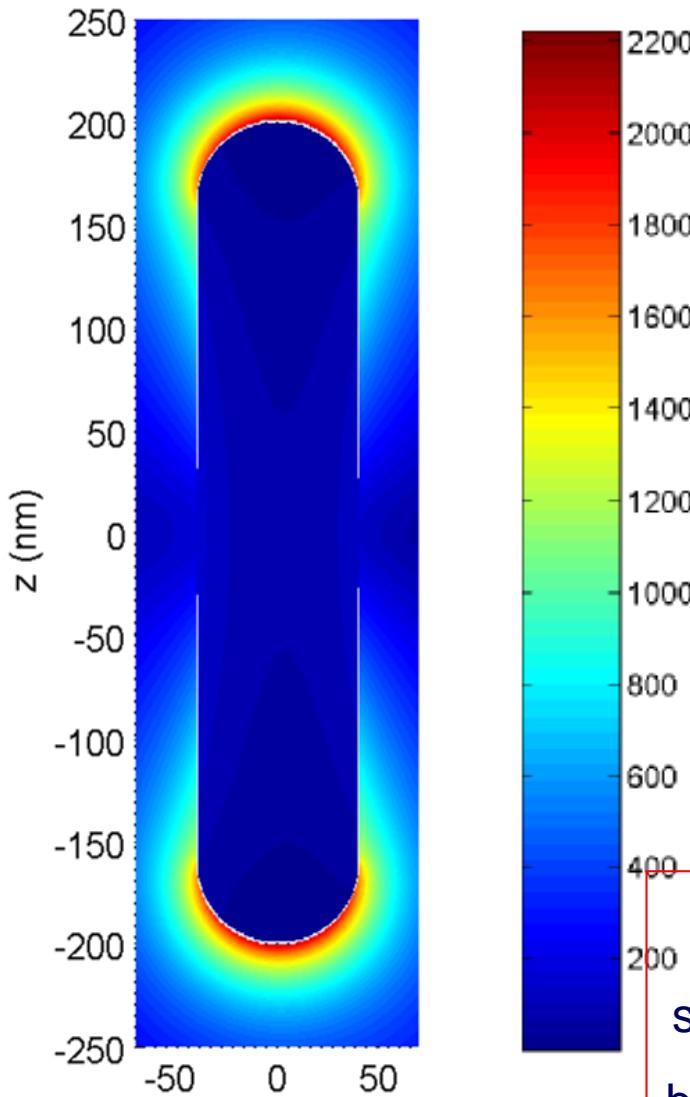


FIG. 2 (color). True color photograph of a sample of gold nanorods (red) and 60 nm nanospheres (green) in dark-field illumination (inset upper left). Bottom right: TEM images of a dense ensemble of nanorods and a single nanosphere.

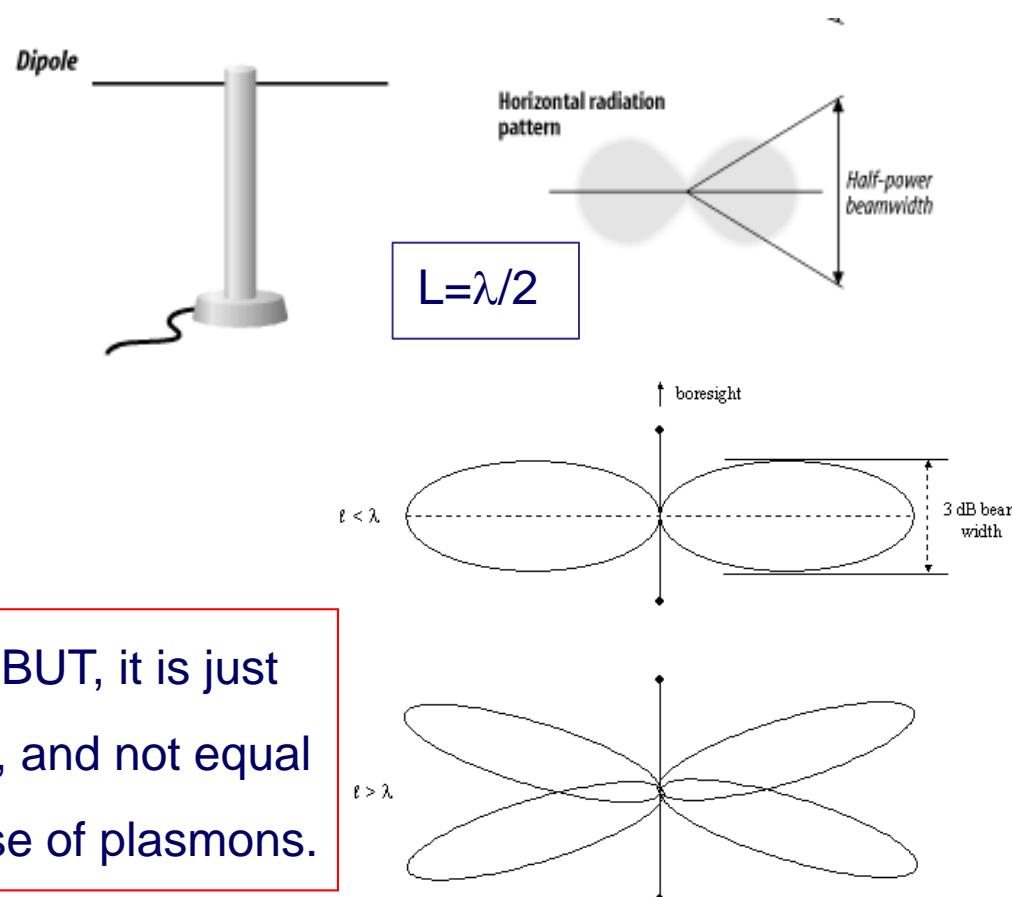
Standard textbooks:

- Kreibig, Vollmer, Optical properties of metal clusters, Springer 1995
- Bohren, Huffmann, Absorption and scattering of light by small particles, Wiley 1983

Metallic nanorod as a $\lambda/2$ optical antenna



In analogy to a $\lambda/2$ radiowave antenna,
we call a nanosized rod-like metallic
structure a $\lambda/2$ optical antenna .



YES BUT, it is just
similar, and not equal
because of plasmons.

Bulk plasmons

A plasmon is a collective oscillation of the conduction electrons

Bulk plasmon:

The rigid displacement of the electrons induces a dipolar moment and an electric field opposing the displacement



Newton's equation for $\delta(t)$:

Electron density

$$nm_e \frac{d^2}{dt^2} \delta(t) = -enE(t) = -4\pi n^2 e^2 \delta(t)$$

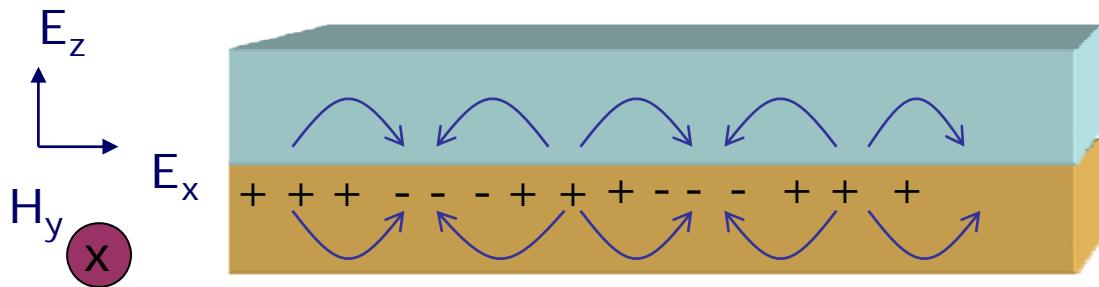
=> Harmonic oscillator

$$\omega_p = \sqrt{\frac{4\pi n_e e^2}{m_e}}$$

All the electrons are involved in the oscillation. The energy of those oscillations in typical metals might be triggered out by external probes.

Surface plasmons

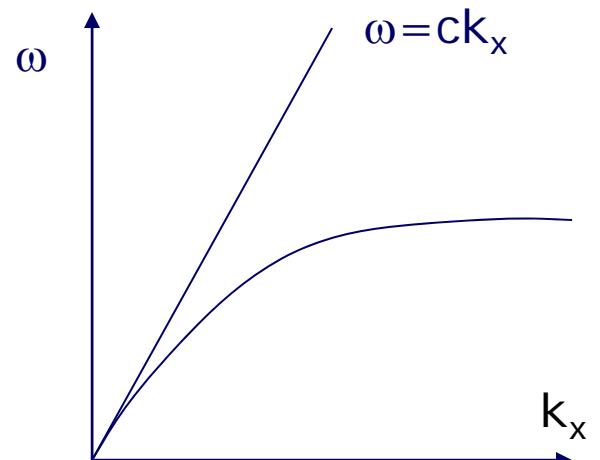
Electromagnetic surface waves which exist at the interface between 2 media whose ϵ have opposite sign.



$$E^{(1)} = E_o^{(1)} e^{i(k_x x - \omega t) - \alpha^{(1)} |z|}$$

$$k_x = k_x' + ik_x'' = \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \left(\frac{\omega}{c} \right)$$

Dispersion relation



Drude model

$$\epsilon' = 1 - \frac{\omega_p^2}{\omega^2}$$

Surface plasmons

$$\omega_s = \frac{\omega_p}{\sqrt{2}}$$

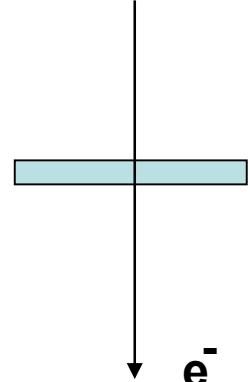
Plasma Losses by Fast Electrons in Thin Films*

R. H. RITCHIE

Health Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received February 7, 1957)

The angle-energy distribution of a fast electron losing energy to the conduction electrons in a thick metallic foil has been derived assuming that the conduction electrons constitute a Fermi-Dirac gas and that the fast electron undergoes only small fractional energy and momentum changes. This distribution exhibits both collective interaction characteristics and individual interaction characteristics, and is more general than the result obtained by other workers. Describing the conduction electrons by the hydrodynamical equations of Bloch, it has been shown that for very thin idealized foils energy loss may occur at a value which is less than the plasma energy, while as the foil thickness decreases below $\sim v/\omega_p$ the loss at the plasma energy becomes less than that predicted by more conventional theories. The net result is an increase in the energy loss per unit thickness as the foil thickness is decreased. It is suggested that the predicted loss at subplasma energies may correspond to some of the low-lying energy losses which have been observed by experimenters using thin foils.



Now let us define

$$P(k_1, \omega) = \{aP_\infty'(k_1, \omega) + P_b(k_1, \omega)\},$$

where P_∞' is the transition probability per unit foil thickness in an infinite foil and P_b is the term introduced by the boundary effect. Then one may write, inserting the expression for ϵ ,

$$P_b = \frac{e^2}{\pi^2 \hbar v^2} \frac{2k_1}{(k_1^2 + \omega^2/v^2)^2} \frac{g\omega_p^4}{\omega} \cdot \left\{ \frac{\frac{1}{4}\omega_p^2}{(\omega^2 - \frac{1}{2}\omega_p^2)^2 + g^2\omega^2} - \frac{\omega_p^2}{(\omega^2 - \omega_p^2)^2 + g^2\omega^2} \right\}. \quad (25)$$

$$P(k_1, \omega) \rightarrow \frac{e^2 a}{\hbar \pi^2 v^2} \left\{ \frac{\text{Im}(1/\epsilon)}{(k_1^2 + \omega^2/v^2)} - \frac{2k_1}{a(k_1^2 + \omega^2/v^2)^2} \text{Im} \left(\frac{(1-\epsilon)^2}{\epsilon(1+\epsilon)} \right) \right\}$$

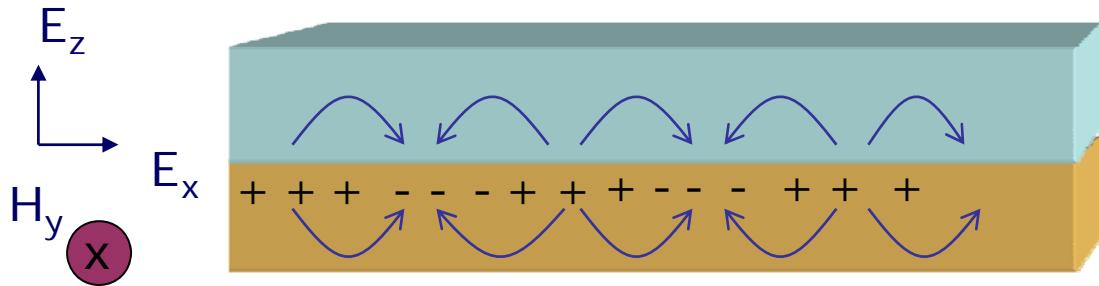
Now let us define

$$P(k_1, \omega) = \{aP_\infty'(k_1, \omega) + P_b(k_1, \omega)\},$$

One notes that the effect of the boundary is to cause a decrease in loss at the plasma frequency and an additional loss at $\omega = \omega_p/\sqrt{2}$. Call the probabilities for these

Surface plasmons

Electromagnetic surface waves which exist at the interface between 2 media whose ϵ have opposite sign.



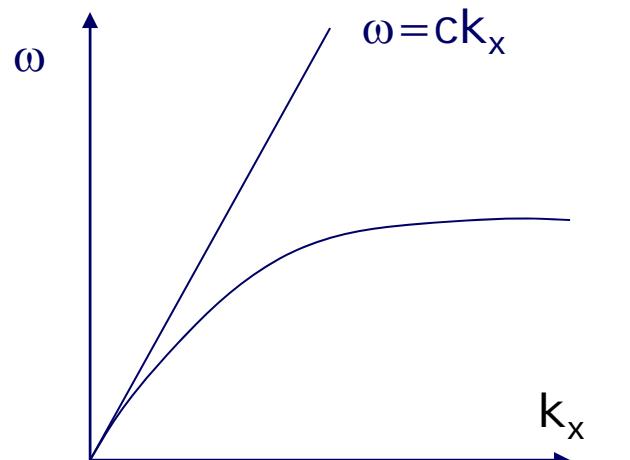
Metal ($\epsilon_1 = \epsilon_1' + i\epsilon_1''$)

Dielectric ($\epsilon_2 = \epsilon_2' + i\epsilon_2''$)

$$E^{(1)} = E_o^{(1)} e^{i(k_x x - \omega t) - \alpha^{(1)} |z|}$$

$$k_x = k_x' + ik_x'' = \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \left(\frac{\omega}{c} \right)$$

Dispersion relation



$$\frac{\omega_p}{\sqrt{2}}$$

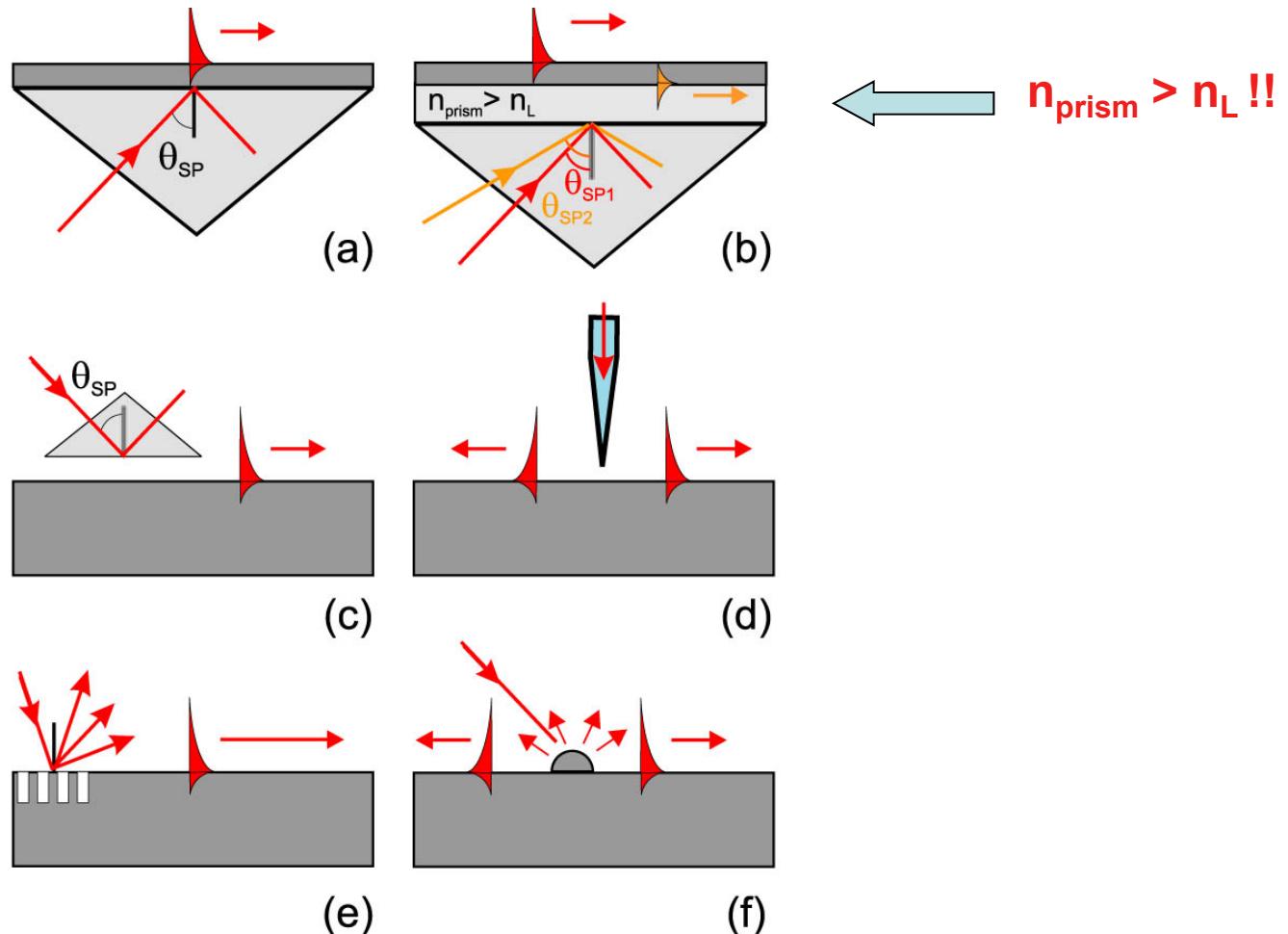
Drude model

$$\epsilon' = 1 - \frac{\omega_p^2}{\omega^2}$$

Surface plasmons

$$\omega_s = \frac{\omega_p}{\sqrt{2}}$$

Methods of SPP excitation



SPP excitation configurations: (a) Kretschmann geometry, (b) two-layer Kretschmann geometry, (c) Otto geometry, (d) excitation with an SNOM probe, (e) diffraction on a grating, and (f) diffraction on surface features.

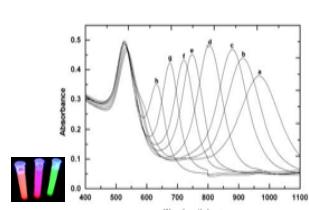
Nano-optics with localised plasmons

Characteristics

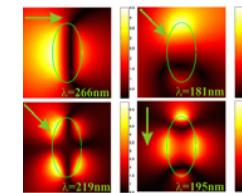
- Confined fields:
- *Nano optics*
- Enhanced field:
- *Lighting rod effect*
- Tunability:
- *Geometry*
- Coupling:
- Wavelength range:
- *Visible* → *Infrared*

Resonances dependence

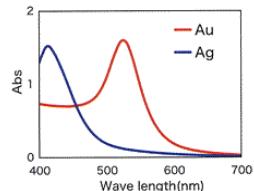
with size



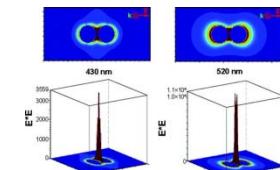
with shape



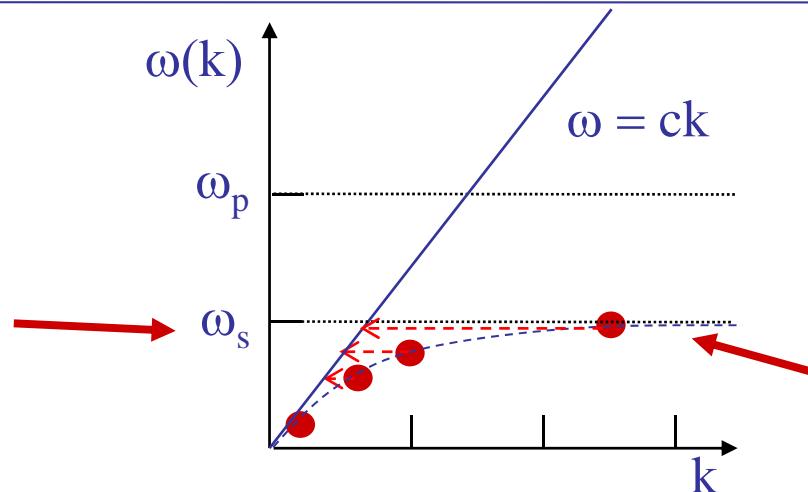
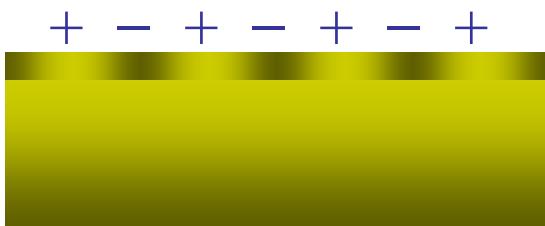
with material



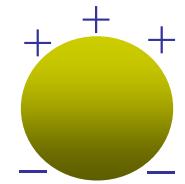
with coupling



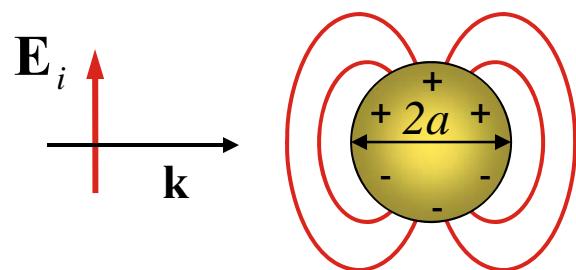
Plasmon polariton



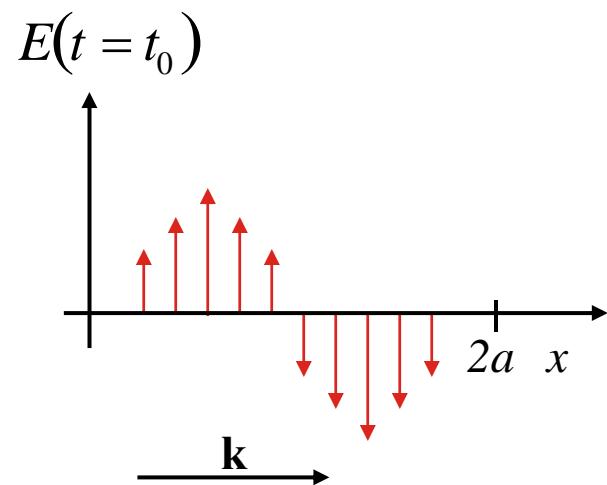
Confined plasmon



Light-particle interaction

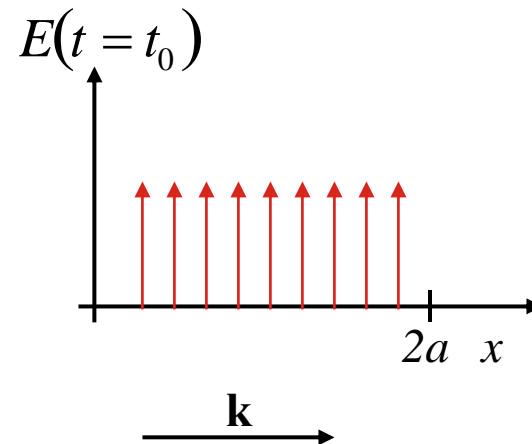


General case: $\lambda \leq a$



Phase shifts in the particles:
retardation, multipole excitations

Quasi-static case: $\lambda \gg a$



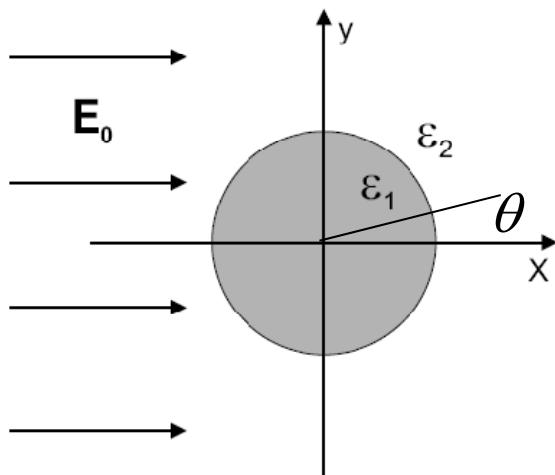
Homogeneous polarization:
All points of an object respond simultaneously
to the incoming (exciting) field.

→ Helmholtz eq. reduces to Laplace
equation:

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

→ el. field: $\mathbf{E} = -\nabla \Phi$

Small sphere



The electric fields inside (E_1) and outside (E_2) the sphere can be obtained from the scalar potentials $\Phi = \Phi(r, \theta, \varphi)$

$$\mathbf{E}_1 = -\nabla\Phi_1 \quad \text{with} \quad \nabla^2\Phi_1 = 0$$

$$\mathbf{E}_2 = -\nabla\Phi_2 \quad \text{with} \quad \nabla^2\Phi_2 = 0$$

$$\Phi_2 = \Phi_{\text{scatter}} + \Phi_0$$

Solve Laplace equation in spherical coordinates:

$$\frac{1}{r^2 \sin \theta} \left[\sin \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \varphi^2} \right] \Phi(r, \theta, \varphi) = 0$$

Boundary conditions:

$$\frac{\partial \Phi_1}{\partial \theta} = \frac{\partial \Phi_2}{\partial \theta} \quad (r = a)$$

continuity of the tangential electric fields

$$\epsilon_1 \frac{\partial \Phi_1}{\partial r} = \epsilon_2 \frac{\partial \Phi_2}{\partial r} \quad (r = a)$$

continuity of the normal component of the electric displacement

Small sphere

Homogeneous electric field along x-direction: $\Phi_0 = -E_0 x = -E_0 r \cos \theta$

The following potentials satisfy the Laplace equation and boundary conditions:

$$\Phi_1 = -E_0 \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} r \cos \theta$$

$$\Phi_2 = -E_0 r \cos \theta + E_0 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} a^3 \frac{\cos \theta}{r^2}$$

From $\mathbf{E} = -\nabla\Phi$ we obtain

$$\mathbf{E}_1 = E_0 \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} (\cos \theta \mathbf{e}_r - \sin \theta \mathbf{e}_\theta) = E_0 \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \mathbf{e}_x$$

$$\mathbf{E}_2 = E_0 (\cos \theta \mathbf{e}_r - \sin \theta \mathbf{e}_\theta) + \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \frac{a^3}{r^3} E_0 (2 \cos \theta \mathbf{e}_r + \sin \theta \mathbf{e}_\theta)$$

The field is independent of the azimuth angle ϕ which is a result of the symmetry implied by the direction of the applied electric field.

Small sphere

Small sphere:

$$\Phi_2 = -E_0 r \cos\theta + E_0 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} a^3 \frac{\cos\theta}{r^2}$$

Dipole:

$$\Phi_{dipole} = \frac{p}{4\pi\epsilon_2} \frac{\cos\theta}{r^2}$$

- The field outside the sphere is the superposition of the applied field and the field of an ideal dipole at the sphere origin

The dipole moment is given by

$$\mathbf{p} = 4\pi\epsilon_0\epsilon_2 a^3 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \mathbf{E}_0$$

Generally the dipole moment is defined by $\mathbf{p} = \epsilon_0\epsilon_2\alpha\mathbf{E}_0$

- **Polarizability of the sphere:**

$$\alpha = 4\pi a^3 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2}$$

Small sphere

We can describe the light scattering of a small sphere by plane wave scattering at an ideal point dipole with dipole moment derived on the previous slides. The dipole field is given by:

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{e^{ikr}}{r} \left\{ k^2 [(\mathbf{n} \times \mathbf{p}) \times \mathbf{n}] + \frac{1}{r} \left(\frac{1}{r} - ik \right) [3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}] \right\} e^{i\omega t}$$

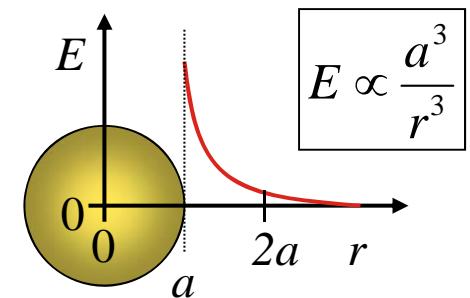
with $\mathbf{n} = \frac{\mathbf{r}}{r}$

Near-field zone:
 $kr \ll 1$ ($r \ll \lambda$)

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{3\mathbf{n}(\mathbf{n} \cdot \mathbf{p}) - \mathbf{p}}{r^3} e^{-i\omega t}$$

electrostatic
dipole field

harmonic time
dependency

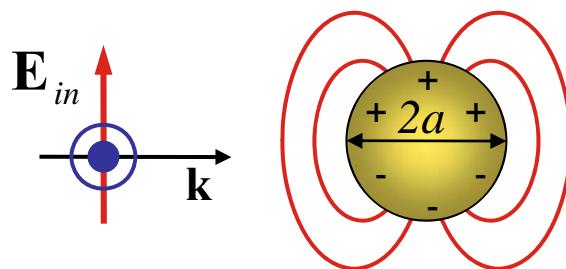


Radiation zone:
 $kr \gg 1$ ($r \gg \lambda$)

$$\mathbf{E}(\mathbf{r}) = \frac{(\mathbf{n} \times \mathbf{p}) \times \mathbf{n}}{r} \frac{k^2}{4\pi\epsilon_0} e^{i(kr - \omega t)}$$

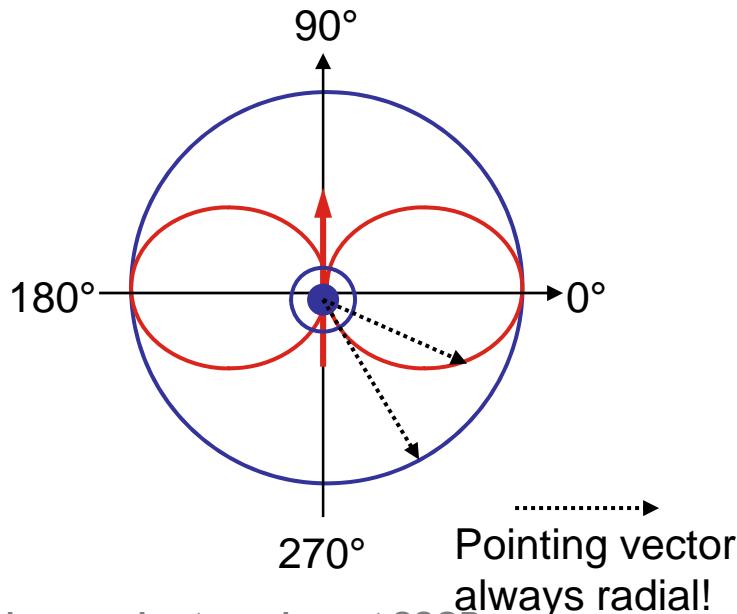
propagating
wave

Far- and near-field calculations for a sphere $a \ll \lambda$

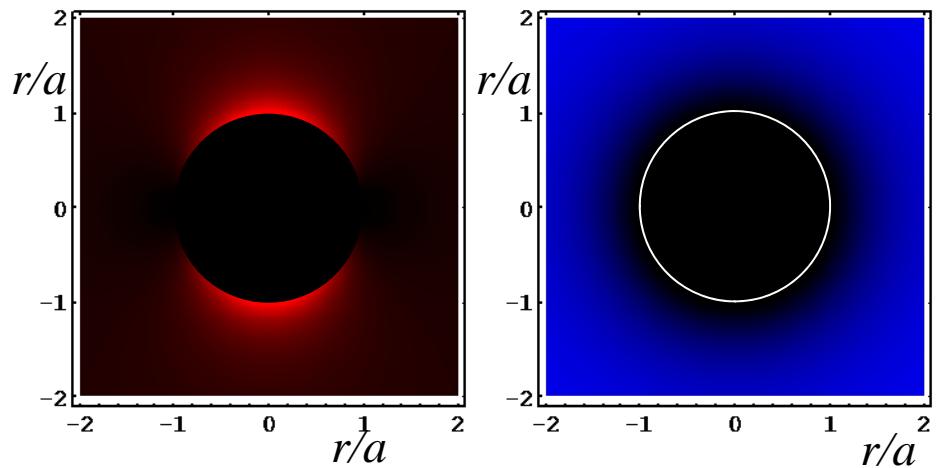


Near-field scattering

Far-field scattering
(transverse fields)



$$I = |\mathbf{E}_{in} + \mathbf{E}_{particle}|^2$$



Pointing vector is
not always radial

Optical cross sections of small spheres

Integrating the Poynting vector \mathbf{S}_{sca} (\mathbf{S}_{abs}) over a close spherical surface we obtain the totally scattered (absorbed) power P_{sca} (P_{abs}) from which we can calculate the scattering (absorption) cross section $C_{\text{sca}} = P_{\text{sca}}/I_i$ ($C_{\text{abs}} = P_{\text{abs}}/I_i$):

Scattering cross section:

$$C_{\text{sca}} = \frac{8\pi}{3} k^4 a^6 \left| \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right|^2 = \frac{k^4}{6\pi} |\alpha|^2$$

Absorption cross section:

$$C_{\text{abs}} = 4\pi k a^3 \operatorname{Im} \left\{ \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right\} = k \operatorname{Im}\{\alpha\}$$

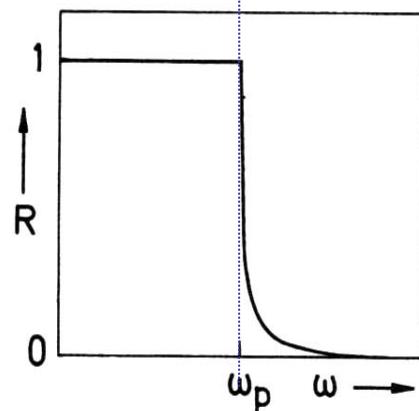
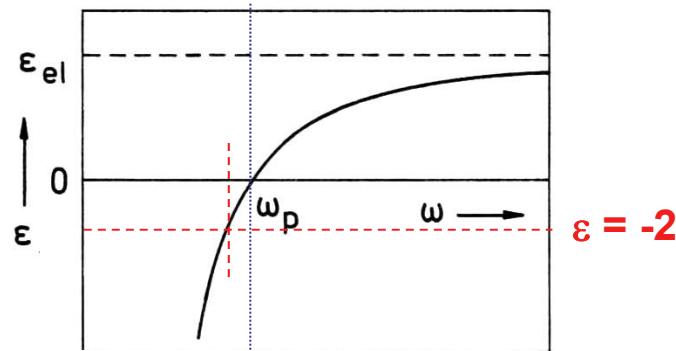
$$\implies C_{\text{sca}} \propto \frac{a^6}{\lambda^4} \qquad \qquad \qquad \implies C_{\text{abs}} \propto \frac{a^3}{\lambda}$$

- stronger scattering at shorter wavelength (Rayleigh scattering, blue sky)
- for large particle extinction is dominated by scattering whereas for small particles it is associated with absorption
- scattering of single particles <10nm is difficult to measure (low signal/noise and low signal/background)

Dielectric function of metals and polar crystals

Metal

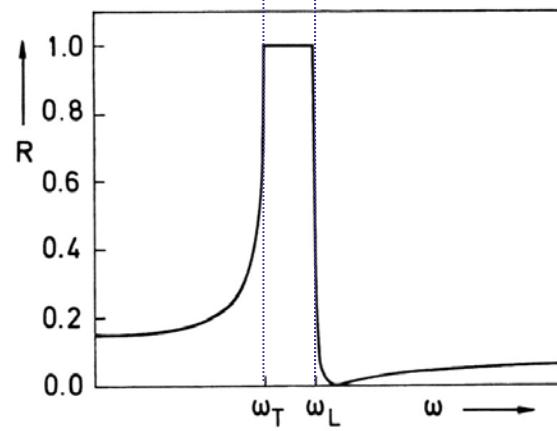
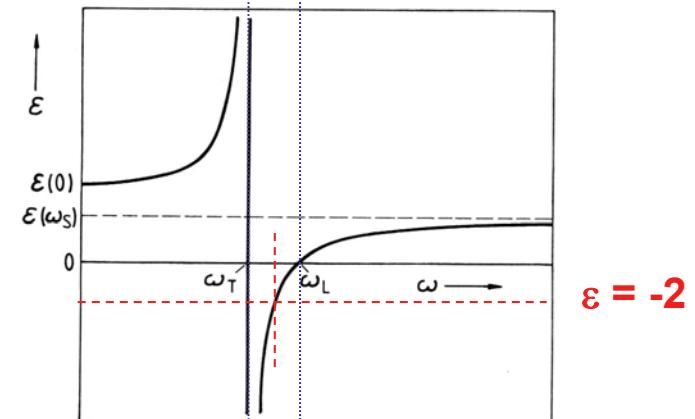
collective free electron oscillations (plasmons)



plasma frequency
(longitudinal oscillation)

Polar crystal

strong lattice vibrations (phonons)



transversal optical phonon frequency, TO longitudinal optical phonon frequency, LO

Plasmon vs. Phonon

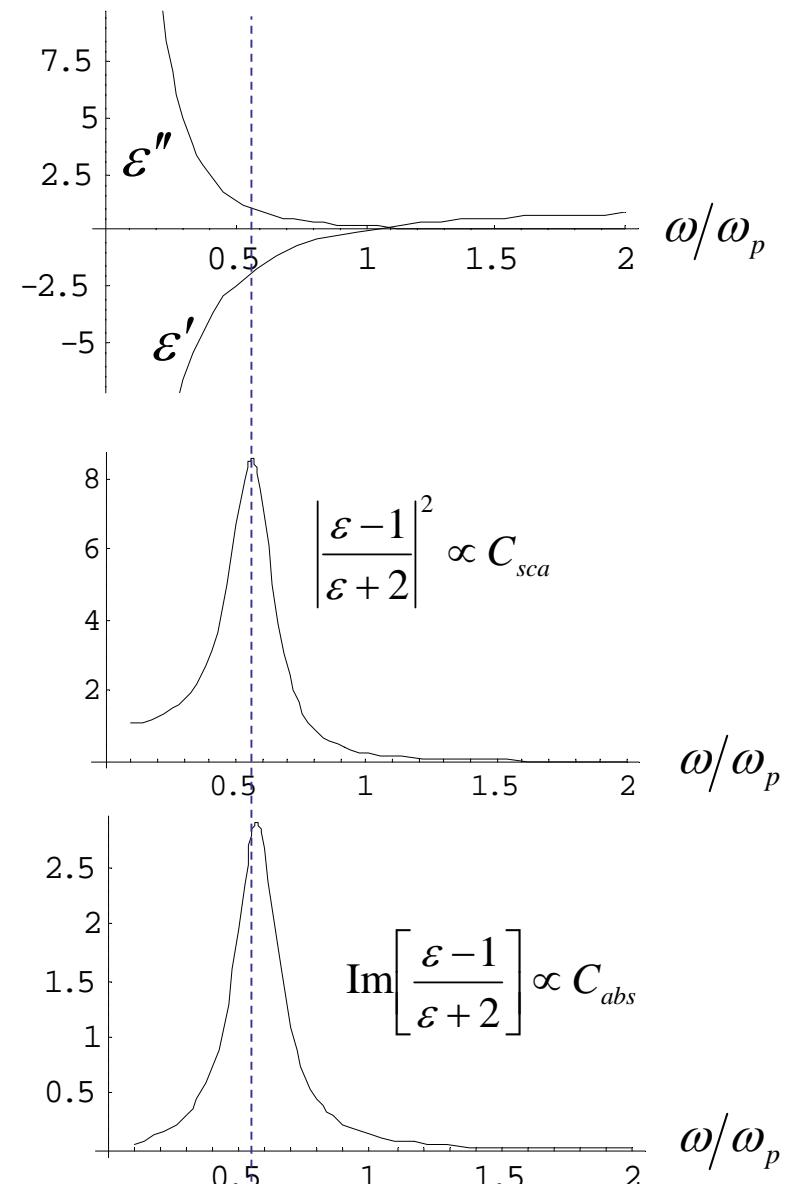
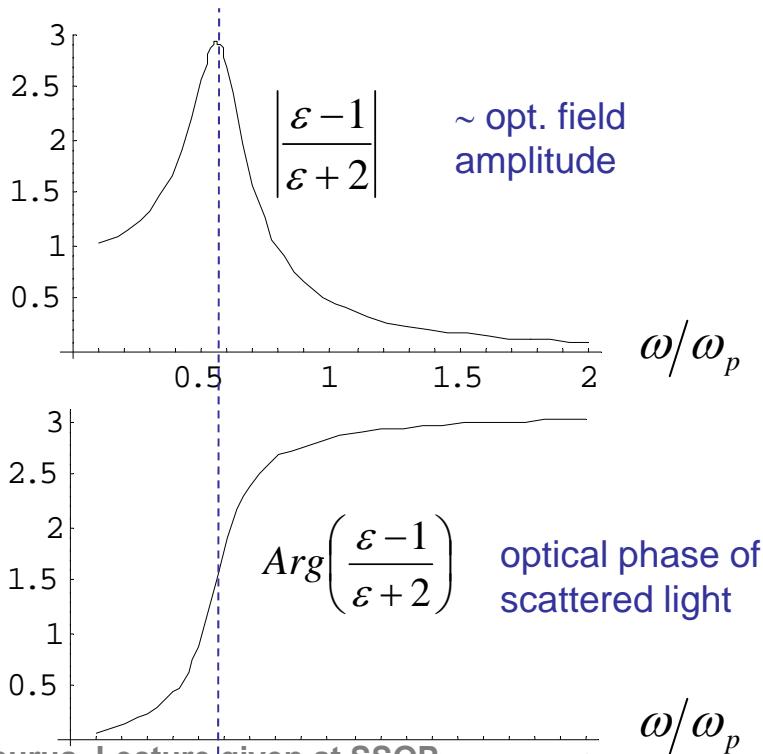
Plasmon polaritons:	Phonon polaritons:
<p>Light - electron coupling in</p> <ul style="list-style-type: none">• metals• semiconductors	<p>Light - optical phonon coupling in polar crystals</p> <ul style="list-style-type: none">• SiC, SiO₂• III-V, II-VI-semiconductors
<p>typically visible (<i>metals</i>) typically IR and terahertz (<i>doped SC</i>)</p>	<p>mid-infrared to terahertz</p>
<p>resonant excitation of collective electron oscillation</p>	<p>resonant excitation of optical lattice vibrations</p>

surface polariton resonances @ $\epsilon \approx 1$

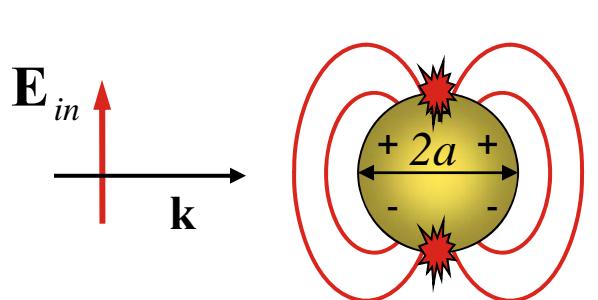
Optical cross sections of small spheres

Drude model

$$\epsilon = 1 - \frac{\omega_p^2}{\omega^2 + 0.2i\omega}$$



Small particle resonances

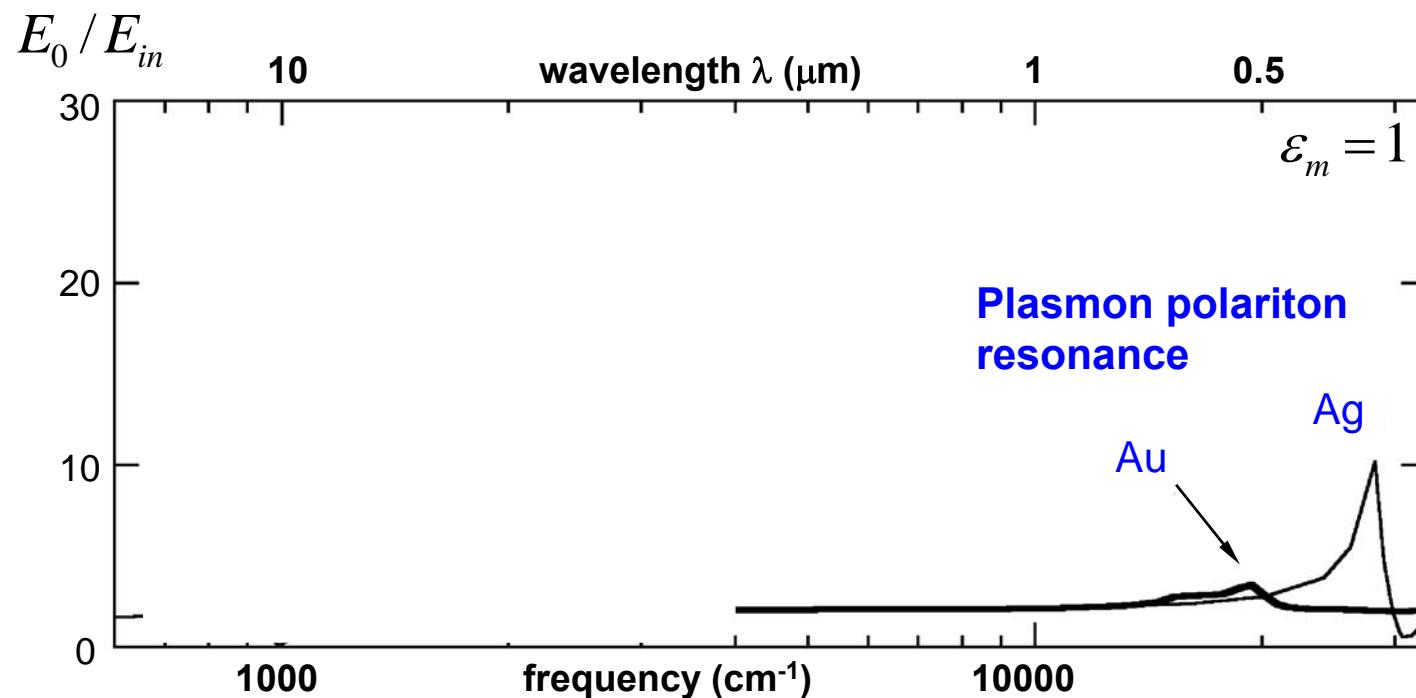


E_0 = enhanced field at

$$E_0 = 2 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} E_{in}$$

resonance at

$$\epsilon = -2\epsilon_m$$



Nanotechnology with plasmonics: before the nanorevolution

Lycurgus Cup

(British Museum; 4th century AD)

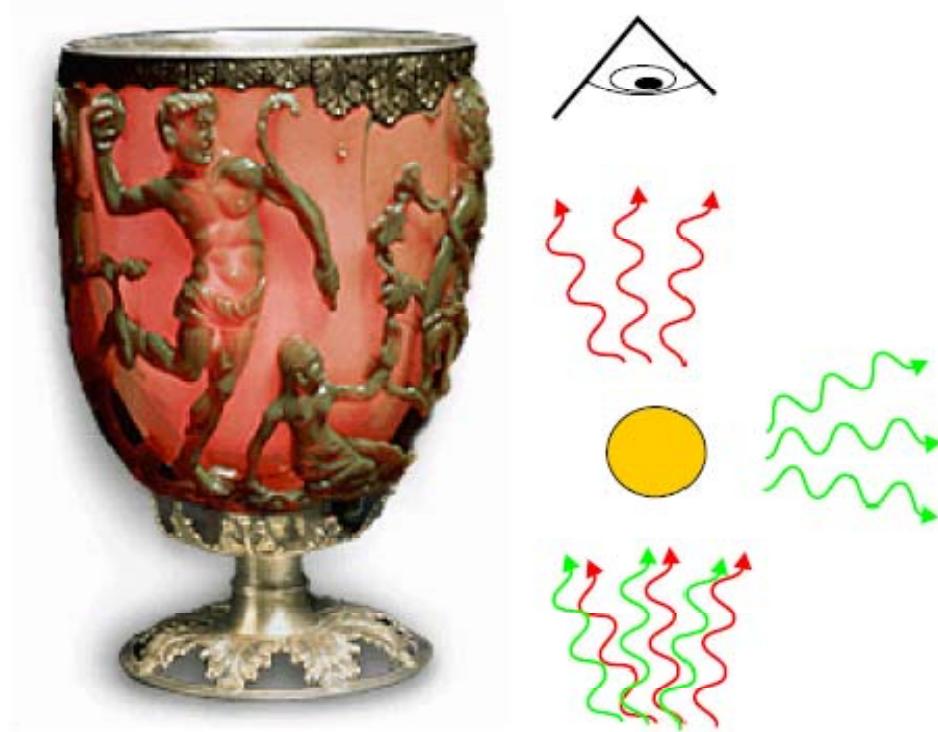


Illumination: from outside

from inside

(strong absorption at and below 520 nm)

Extinction vs. scattering

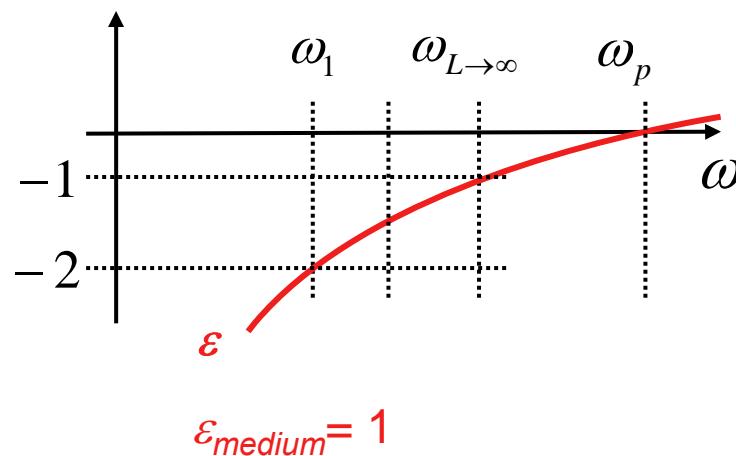


Ancient roman Lycurgus cup illuminated by a light source from behind. Light absorption by the embedded gold particles leads to a red color of the transmitted light whereas scattering at the particles yields a greenish color. From <http://www.thebritishmuseum.ac.uk/science/lycuguscup/sr-lycugus-p1.html>.

Higher multipole resonances in quasistatic limit

In the quasistatic limit the Mie theory yields the resonance positions of the higher multipoles at

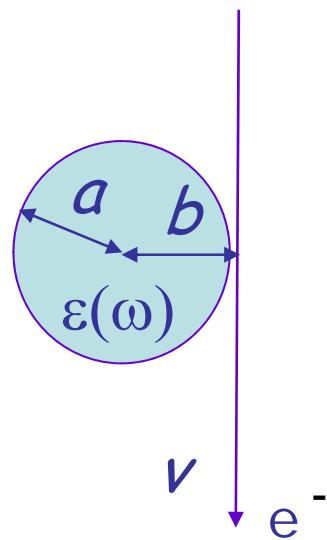
$$\varepsilon_L = -\varepsilon_{\text{medium}} \frac{l+1}{l} \quad \xrightarrow{\text{Drude}} \quad \omega_L = \omega_p \frac{1}{\sqrt{1 + \frac{l+1}{l} \varepsilon_{\text{medium}}}}$$



However, higher multipoles in the quasistatic limit are negligible compared to the dipole contribution ($l=1$)

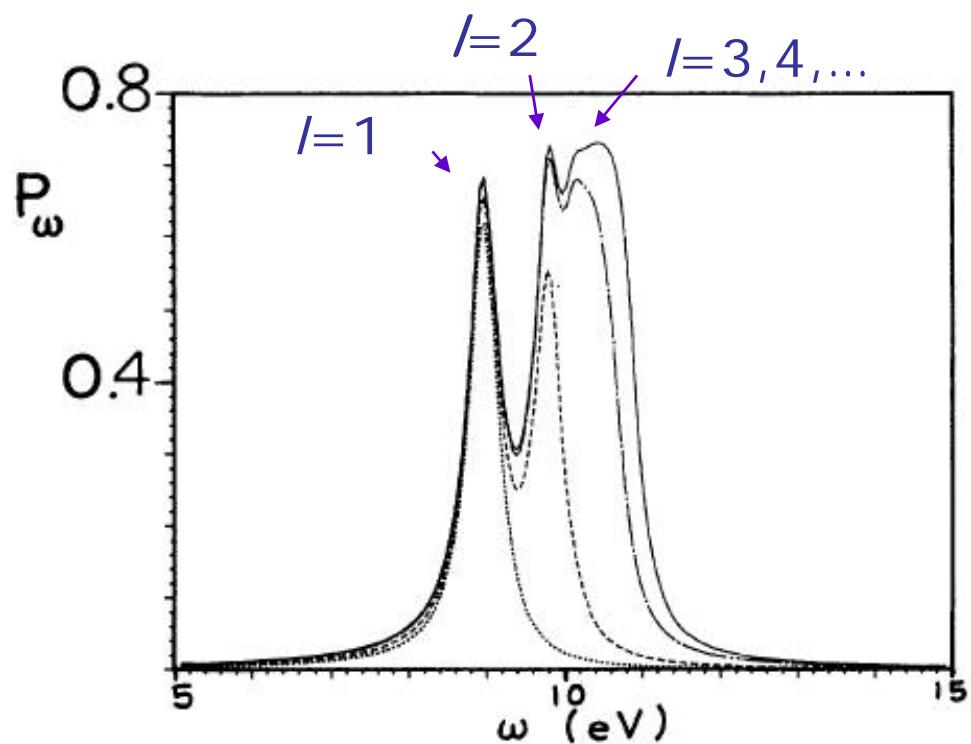
An alternative to excite high order modes in a sphere

EELS in nanoparticles



$$\alpha_l(\omega) = \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + (l+1)/l} a^3$$

Ferrell and Echenique, PRL 55, 1526 (1985)



$$P_\omega(a, b, v) = \frac{4q^2}{\pi v^2 a^2} \sum_{l=0}^{\infty} \sum_{m=0}^l A_{lm} \left(\frac{\omega a}{v} \right)^{2l} K_m^2 \left(\frac{\omega b}{v} \right) \text{Im}[\alpha_l(\omega)]$$

Probability of losing energy $\hbar\omega$ for a 50-keV electron moving at grazing incidence on an aluminum sphere of radius $a=10\text{nm}$

Mie-theory

2.1.3 Exact Electrodynamic Calculation of Spherical Metal Clusters (Mie Theory)

Kreibig/Vollmer

The above discussion of the *quasi-static regime* serves as a first rough estimate which only holds for sufficiently small particles and needs to be extended considerably in order to account for larger particle sizes and particle-size distributions.

The general solution of the diffraction problem of a single sphere of arbitrary material within the frame of electrodynamics was first given by Mie in 1908 [2.19]. He applied Maxwell's equations with appropriate boundary conditions in spherical coordinates using multipole expansions of the incoming electric and magnetic fields. Input parameters were the particle size and the optical functions of the particle material and of the surrounding medium. His solution was based upon the determination of scalar electromagnetic potentials from which the various fields were derived. In particular there are two sets of potentials Π , solving the wave equation

$$\Delta\Pi + |\mathbf{k}|^2\Pi = 0 \quad (2.15a)$$

in spherical coordinates: $\Pi_{e,m}^{inc}$ of the incident plane wave

$\Pi_{e,m}^{in}$ of the wave inside the cluster

$\Pi_{e,m}^{sca}$ of the outgoing scattered wave

The indices e and m indicate the sets of *electrical* and *magnetical* partial waves, respectively. The solutions can be separated in spherical coordinates

$$\Pi = R(r)\Theta(\theta)\Phi(\phi) \quad (2.15b)$$

and have the form

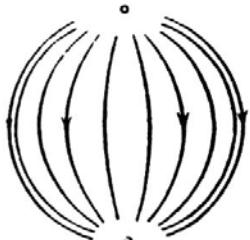
$$\begin{aligned} \Pi = & \{\text{cylindrical fct.}\} \cdot \{\text{Legendre spherical fct.}\} \\ & \cdot \{\text{trigonometric fct.}\} \end{aligned} \quad (2.15c)$$

The relevant parameter in all formulas is the size parameter $x = |\mathbf{k}|R$ which distinguishes the regime of geometrical optics ($x \gg 1$) from the one important for clusters ($x \ll 1$) (a compressed description is given in [2.9]).

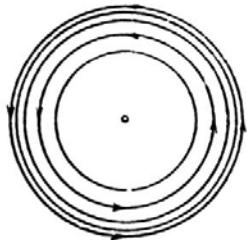
Mie-theory is an electrodynamic theory for optical properties of spherical particles. The solution is divided into two parts: the electromagnetic one which is treated from first principles (Maxwell equations) and the material problem which is solved by using phenomenological dielectric functions taken from experiments or model calculations

See also Bohren/Huffman

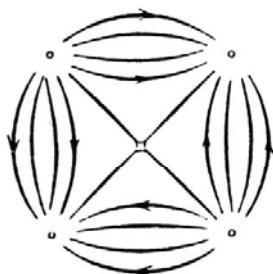
Mie theory - results



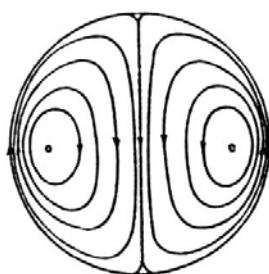
Electric field L = 1



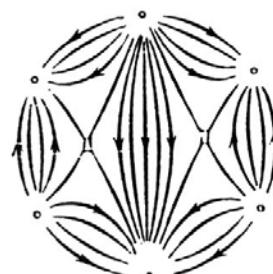
Magnetic field L = 1



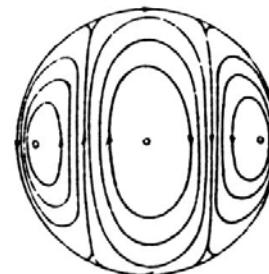
Electric field L = 2



Magnetic field L = 2



Electric field L = 3



Magnetic field L = 3

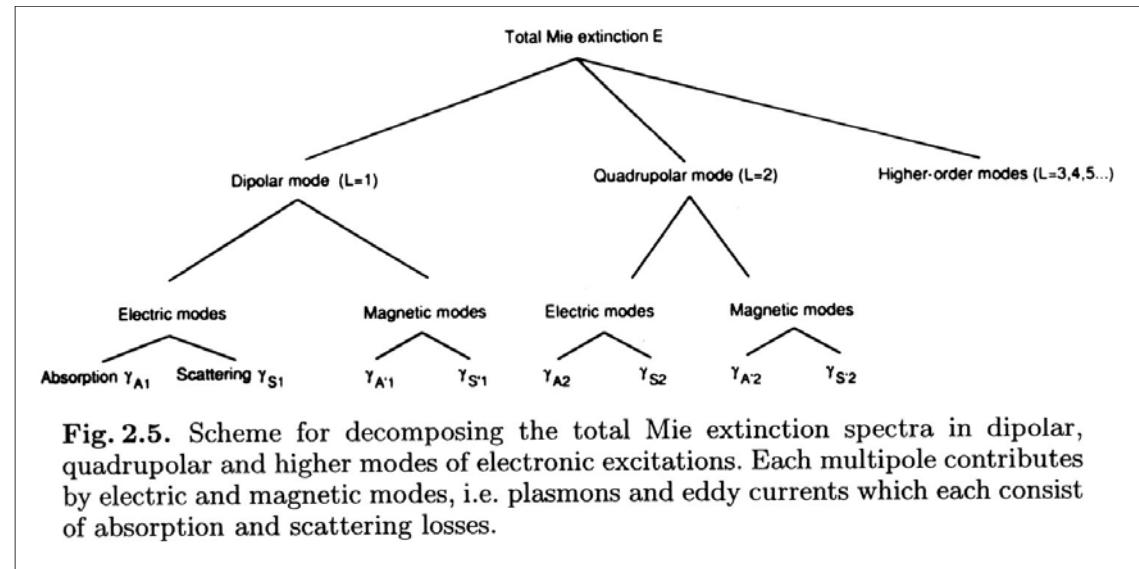
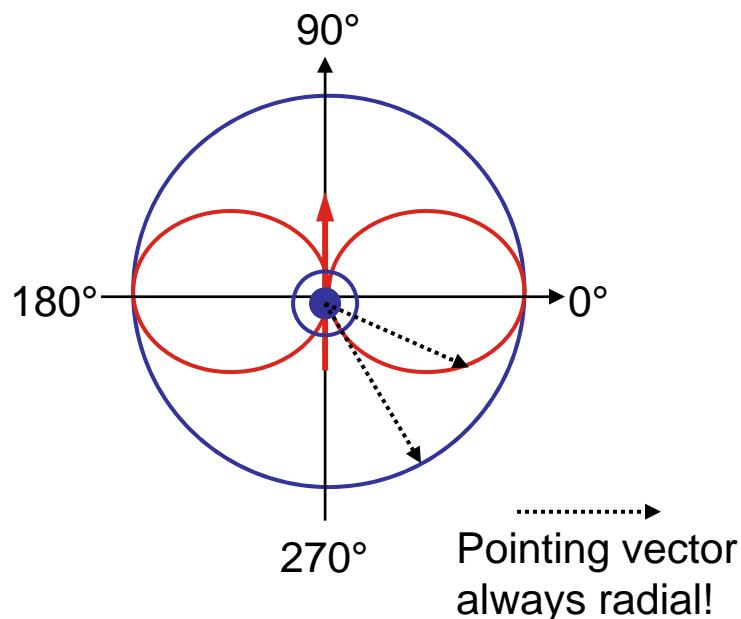


Fig. 2.6. Electric and magnetic fields far away from the clusters, of the $L = 1, 2,$ and 3 electric partial wave, i.e. the electric dipole, quadrupole, and octupole mode. The same field distributions hold for the magnetic partial waves, if electric and magnetic fields are interchanged (after [2.19]).

Fig. 2.6 shows farfield distribution at the surface of a large sphere centered at the small cluster

Scattering characteristics (far-field)

Small particle



Large particle (Mie calculation)

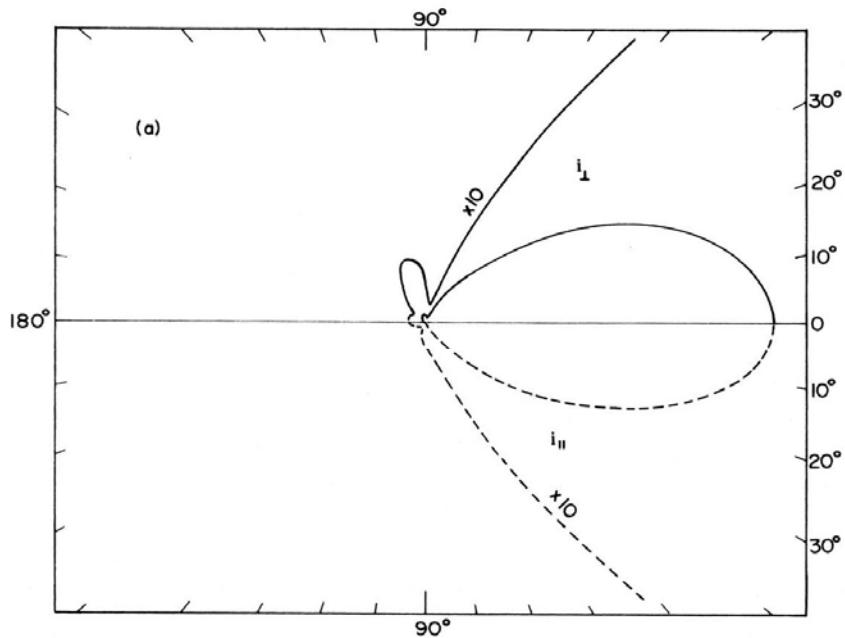
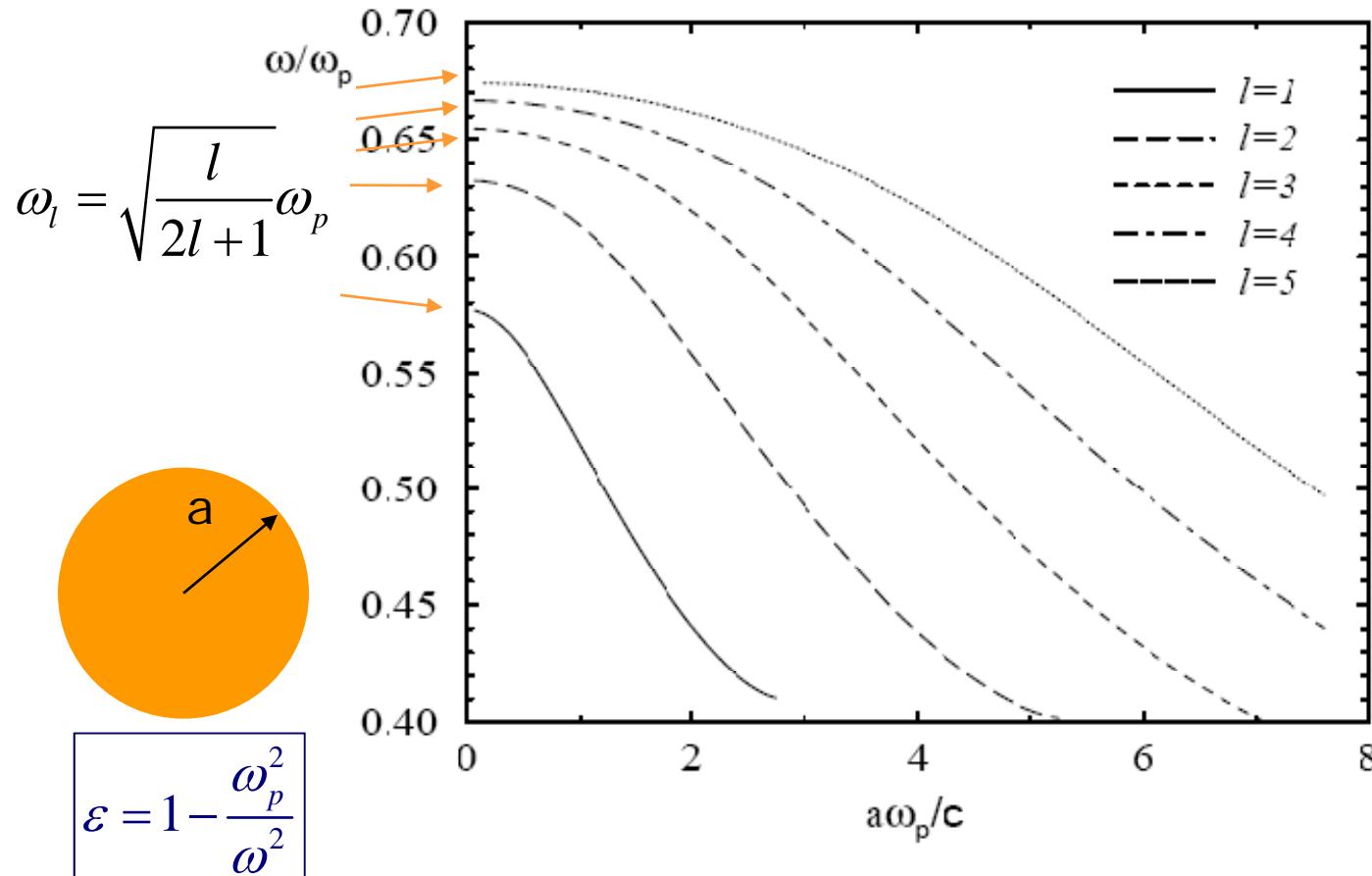


Figure 4.9 Scattering by a sphere with $x = 3$ and $m = 1.33 + i10^{-8}$.

→ **Strong forward scattering**

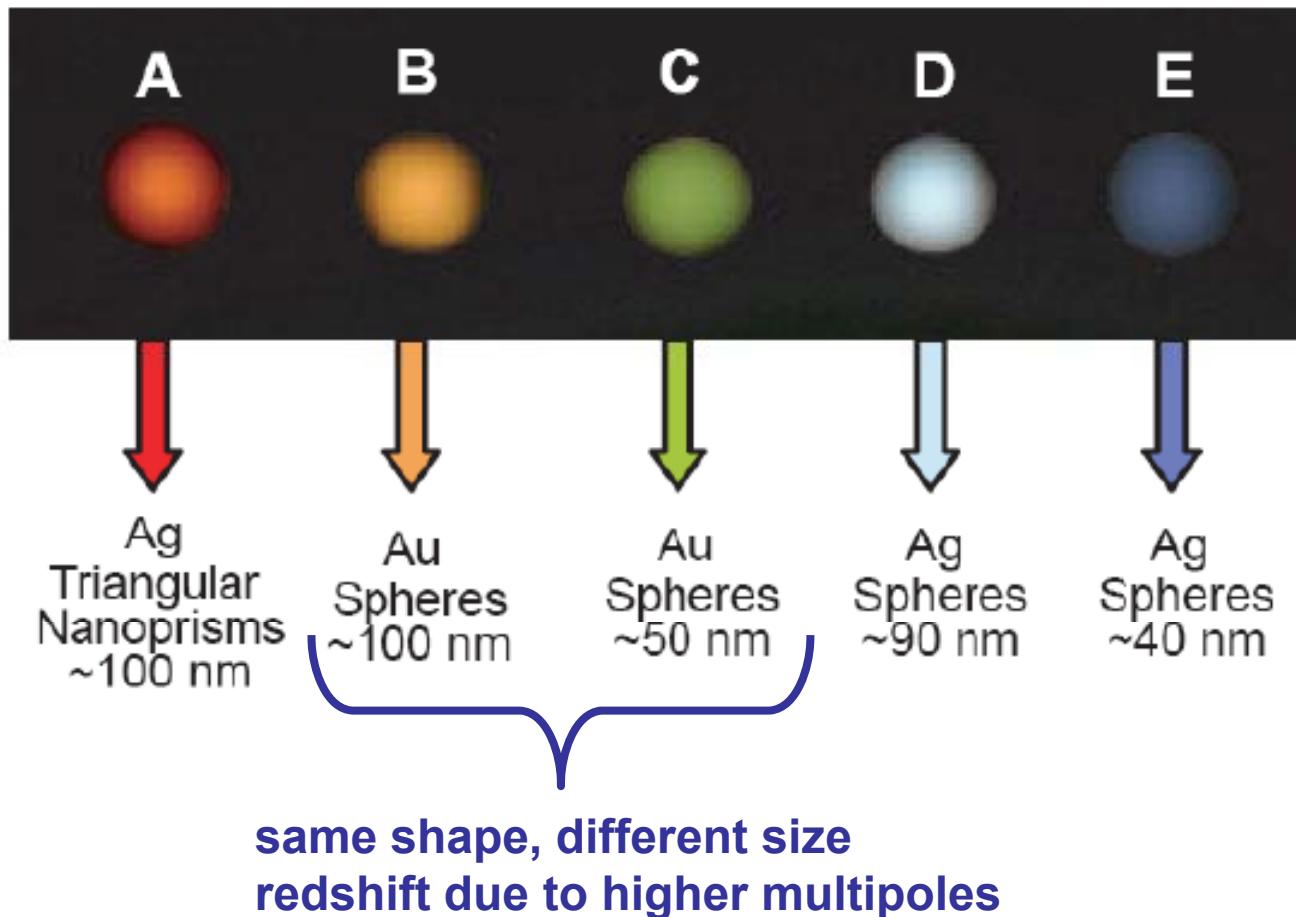
Spherical plasmons: Mie modes derivaded from Maxwell's equations



Drude-like metal

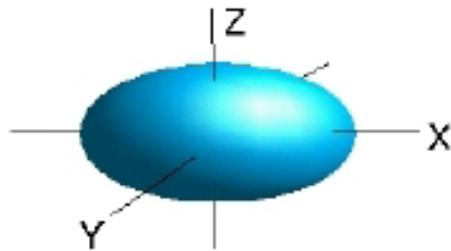
J. Aizpurua, Lecture given at SSOP
Porquerolles, Sept. 2009

Effect of finite size on the resonant frequency



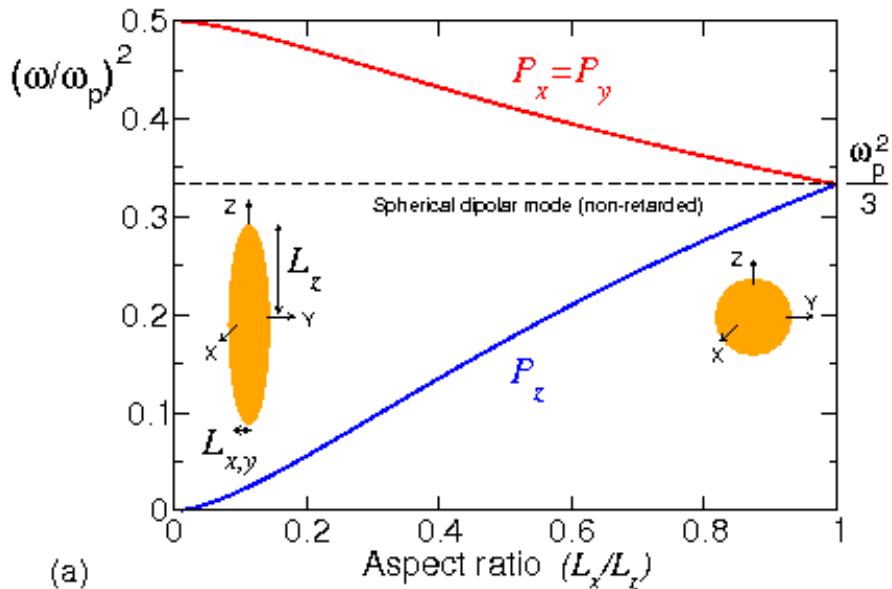
Jin et. al., Science 294, 1901 (2001)

Shape: Polarizability of small ellipsoids



quasistatic approximation:

$$\alpha_{xyz} = \frac{4}{3} \pi abc \frac{\epsilon - \epsilon_m}{\epsilon_m + L_{xyz}(\epsilon - \epsilon_m)}$$



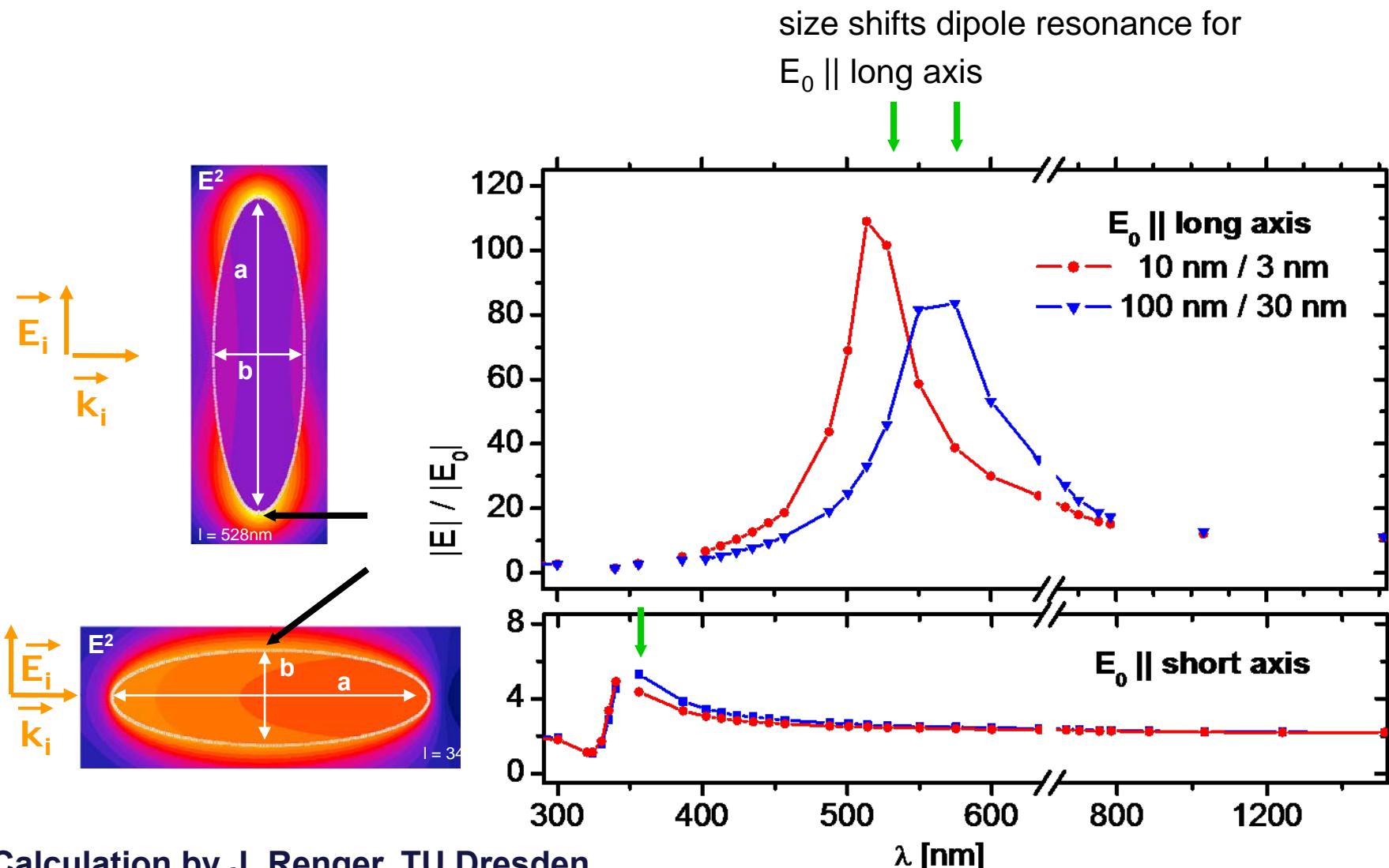
geometrical factors

sphere: $L_x = L_y = L_z = \frac{1}{3}$

generally: $L_x \neq L_y \neq L_z$

→ 3 resonances at $\epsilon = \epsilon_m \left(1 - \frac{1}{L_{xyz}} \right)$

Silver ellipsoid illuminated by a plane wave



Calculation by J. Renger, TU Dresden

Plasmon resonances: dependence on the geometry

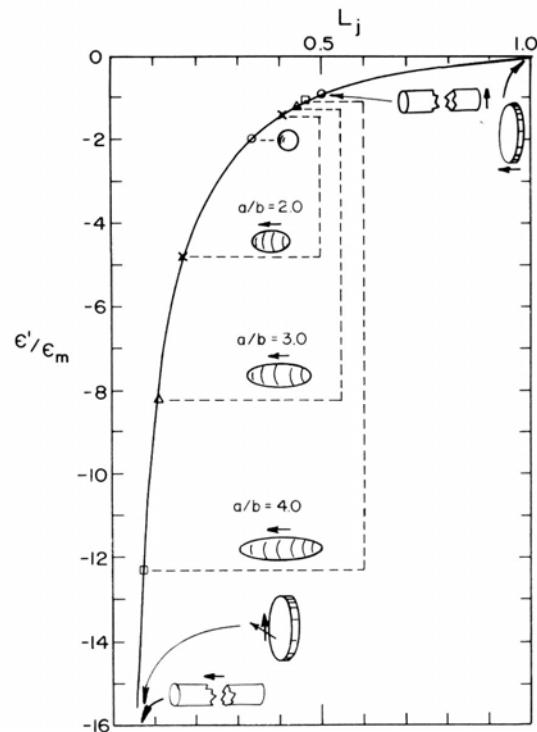


Figure 12.5 Effect of shape on the position of the lowest-order surface mode of small spheroids. Arrows next to the various shapes show the direction of the electric field.

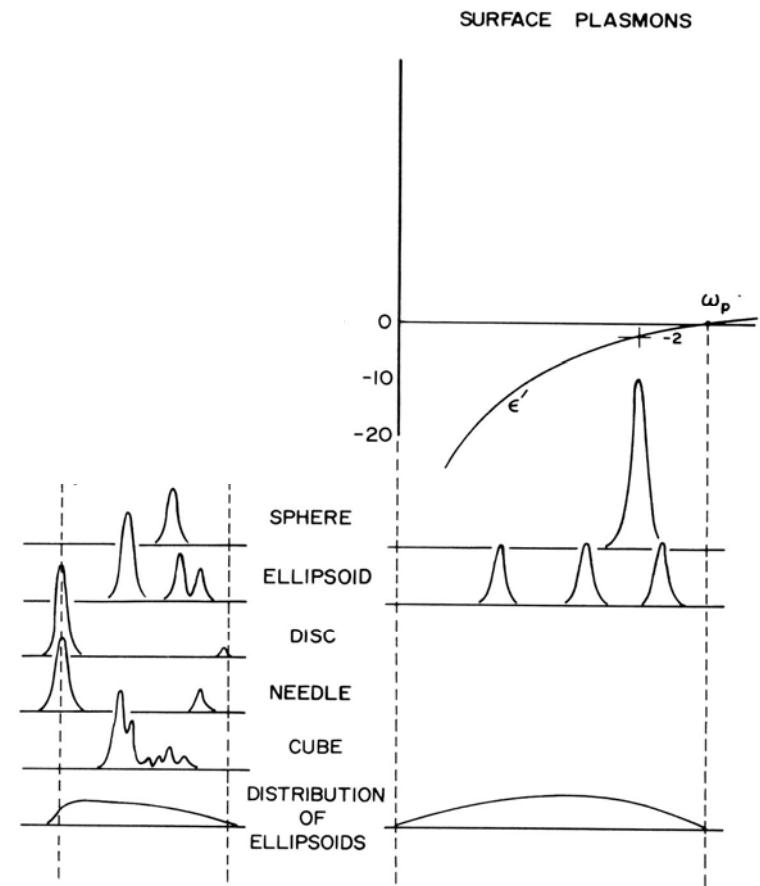


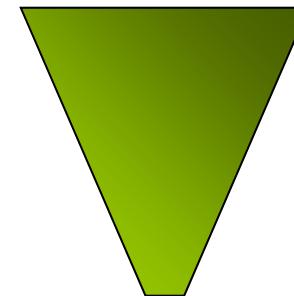
Figure 12.11 Surface mode frequencies for insulating and metallic particles of various shapes.

More complex geometries

Control over the plasmon frequencies by playing with particle **shapes** and **coupling**

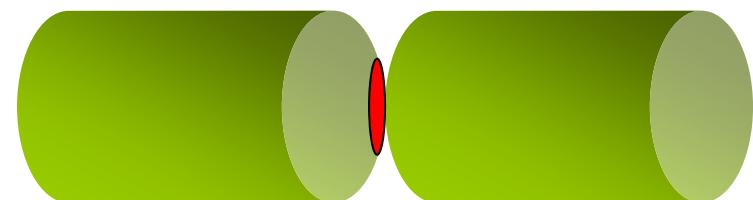
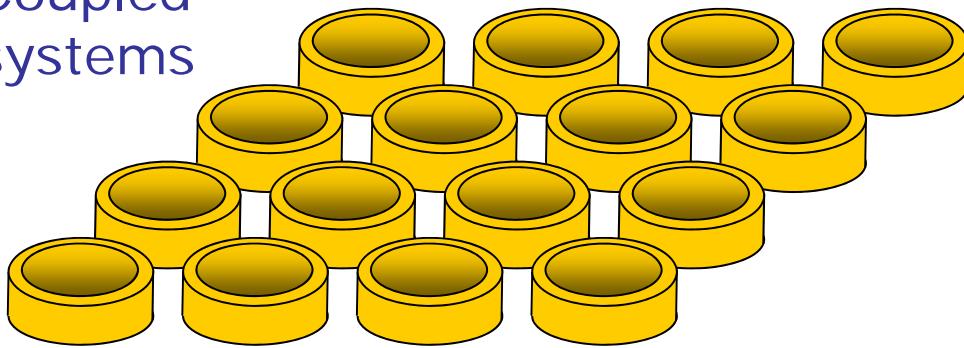


Nanorods, nanoshells,
nanorings, dimers,.....



Apertureless
NSOM

Coupled
systems



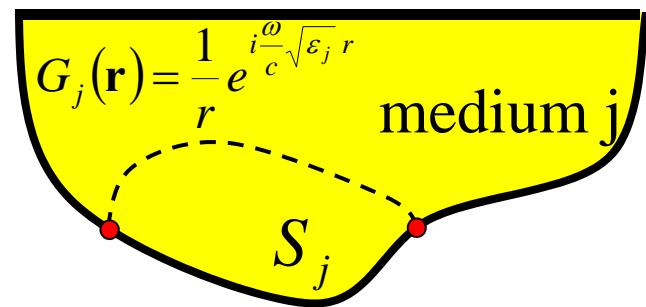
Nanometrology, sensing,
spectroscopy

Boundary Element Method

$$\mathbf{E}(\mathbf{r}) = i \frac{\omega}{c} \mathbf{A}(\mathbf{r}) - \nabla \phi(\mathbf{r})$$

$$\mathbf{A}(\mathbf{r}) = \mathbf{A}^{\text{ext}}(\mathbf{r}) + \int_{S_j} d\mathbf{s} G_j(\mathbf{r}-\mathbf{s}) \mathbf{h}_j(\mathbf{s})$$

$$\phi(\mathbf{r}) = \phi^{\text{ext}}(\mathbf{r}) + \int_{S_j} d\mathbf{s} G_j(\mathbf{r}-\mathbf{s}) \sigma_j(\mathbf{s})$$

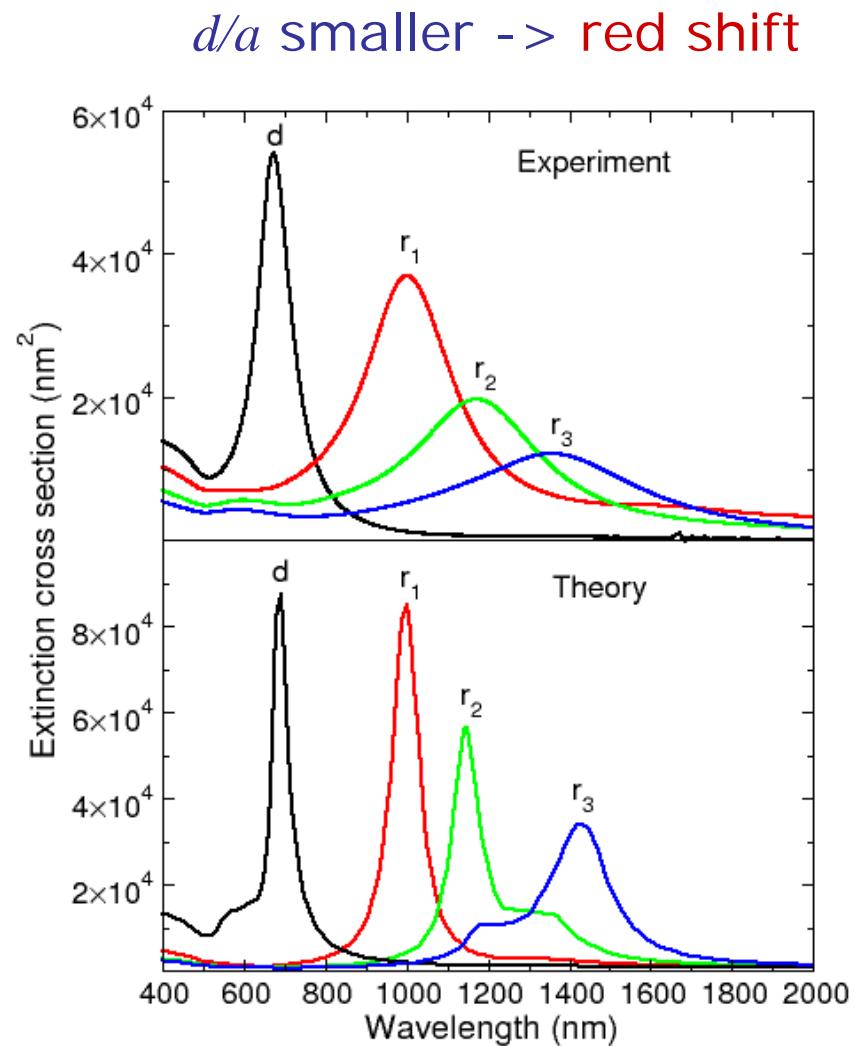
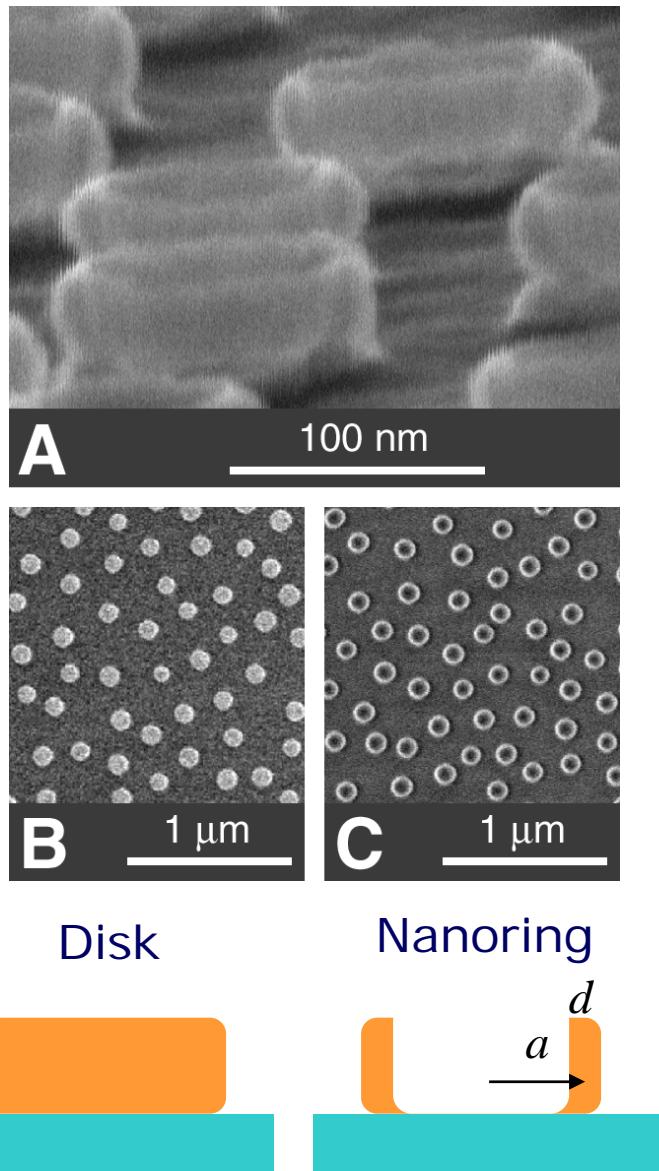


The boundary conditions lead to a set of surface integral equations with the interface currents \mathbf{h}_j and charges σ_j as variables. For example, the continuity of ϕ leads to

$$\int_{S_j} d\mathbf{s}' \left[G_1(\mathbf{s}-\mathbf{s}') \sigma_1(\mathbf{s}') - G_2(\mathbf{s}-\mathbf{s}') \sigma_2(\mathbf{s}') \right] = \phi_2^{\text{ext}}(\mathbf{s}) - \phi_1^{\text{ext}}(\mathbf{s}),$$

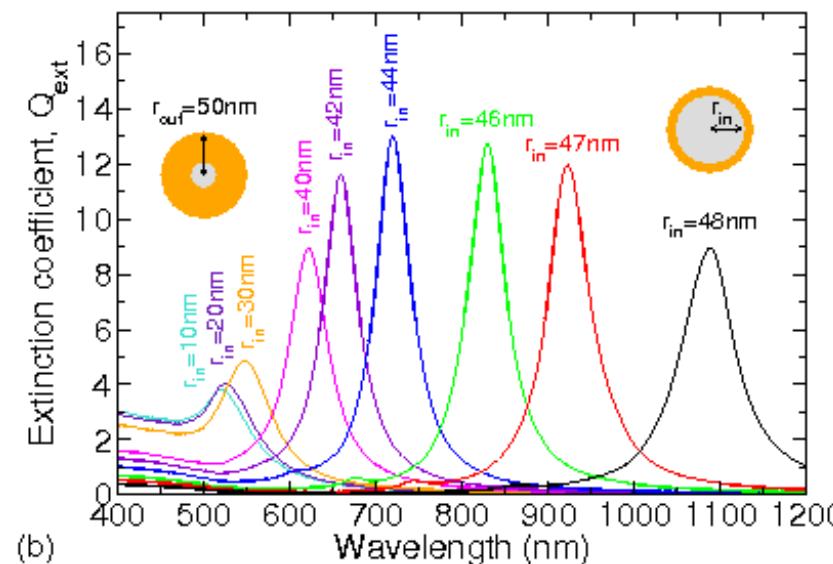
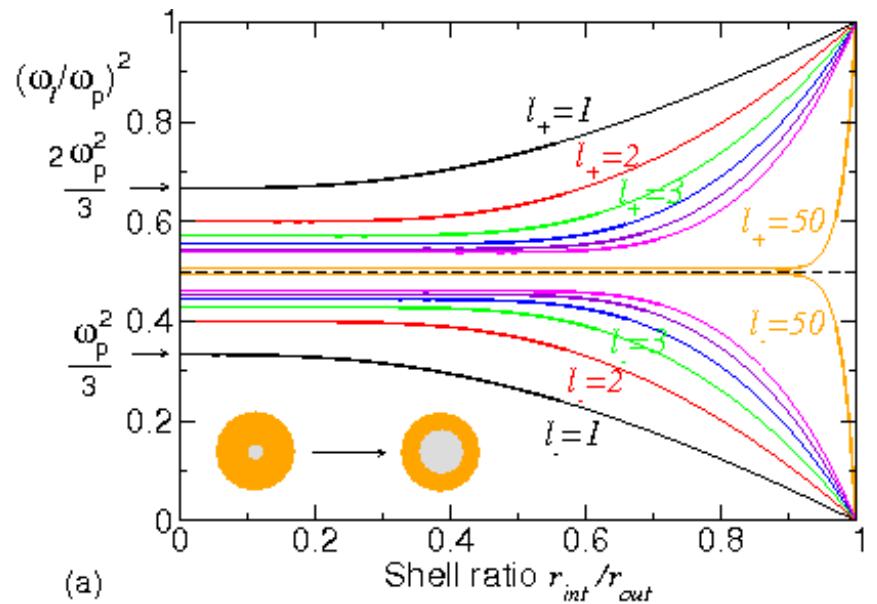
(1 and 2 refer to the interface sides). The surface integrals are now discretized using N representative points \mathbf{s}_i . This leads to a system of $8N$ linear equations with $\mathbf{h}_1(\mathbf{s}_i)$, $\mathbf{h}_2(\mathbf{s}_i)$, $\sigma_1(\mathbf{s}_i)$, and $\sigma_2(\mathbf{s}_i)$ as unknowns.

Optical properties of metallic nanorings



Optical properties of metallic nanoshells

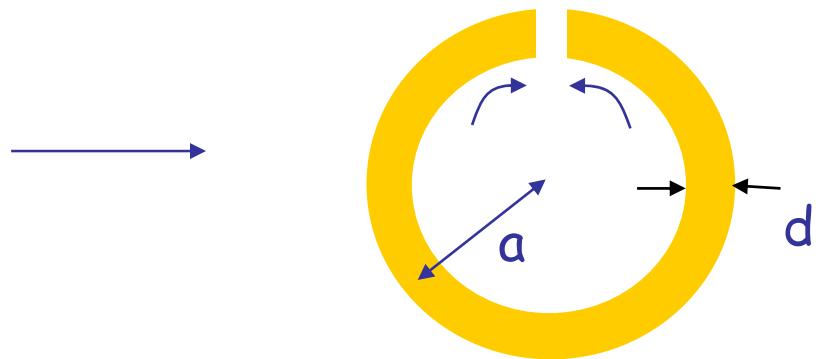
Mode tuning
thanks to the
aspect ratio



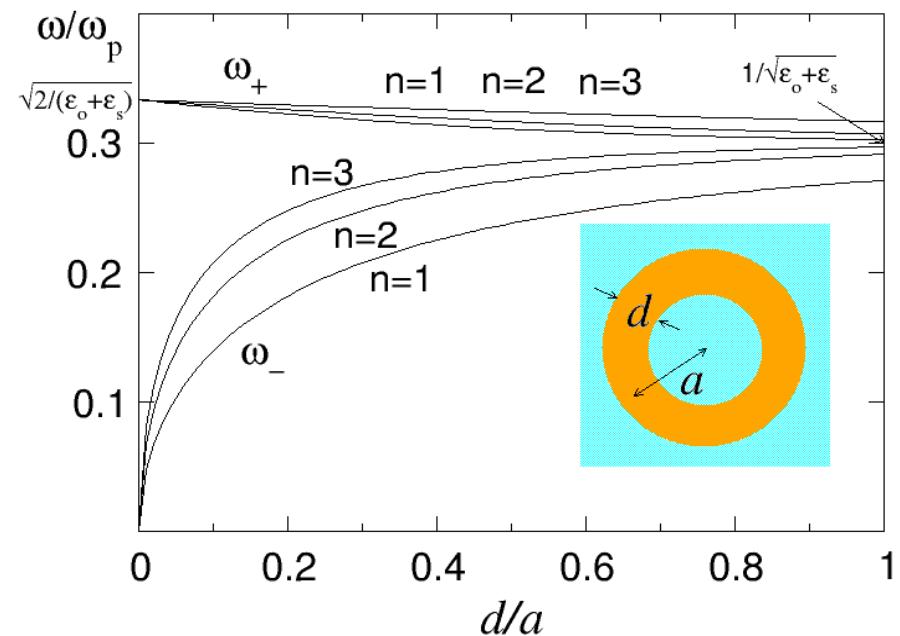
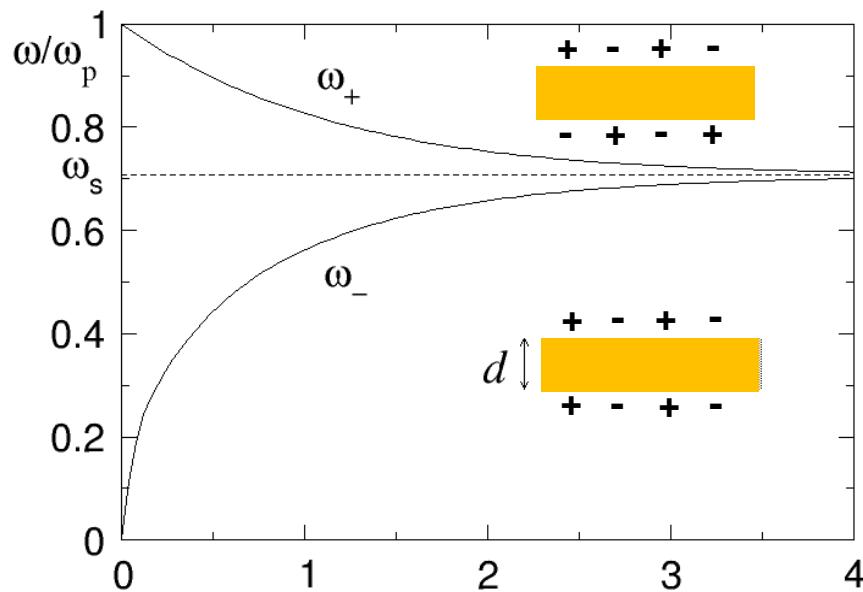
Modes in a nanoring. The twisted slab



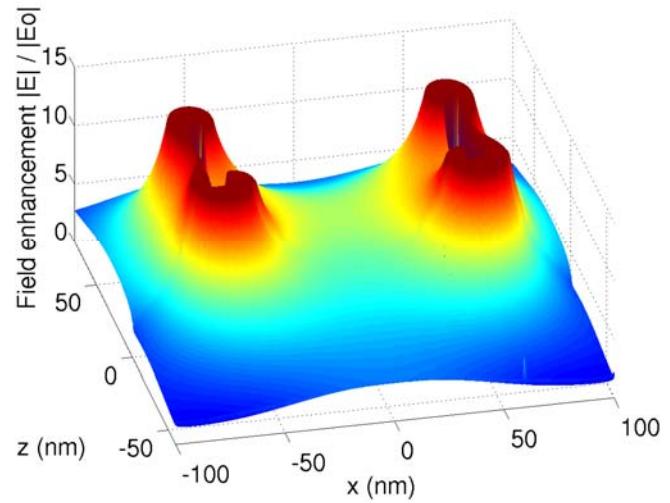
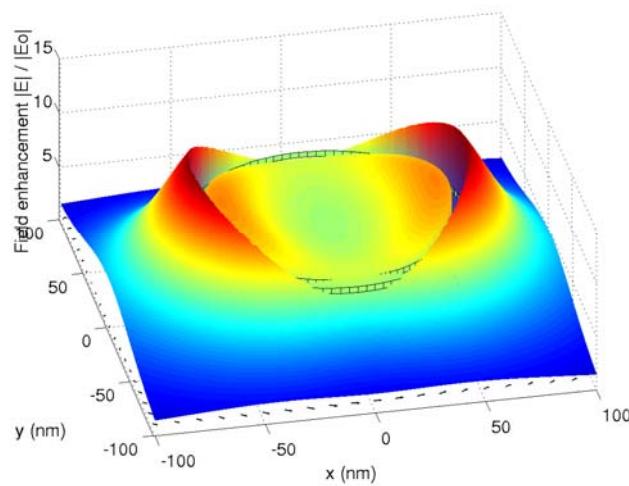
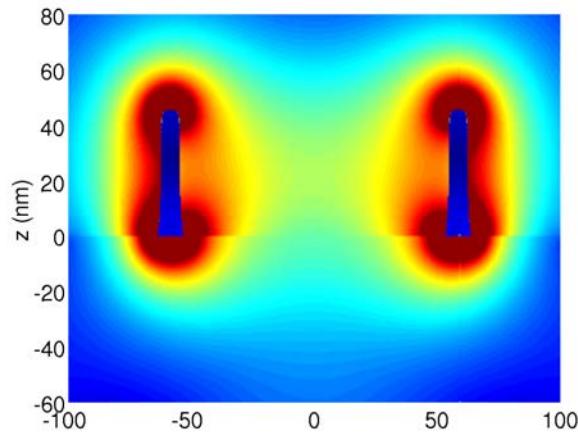
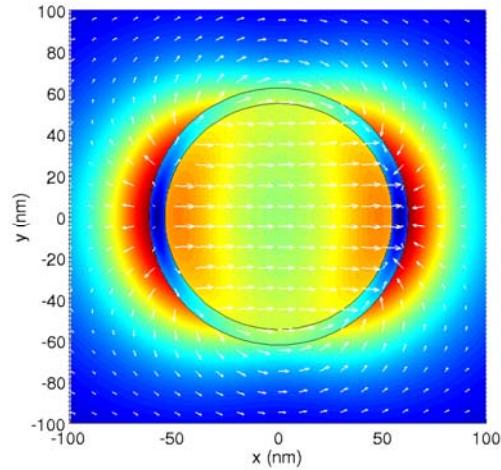
$$\omega_{\pm} = \omega_s (1 \pm e^{-kd})^{1/2}$$



$$kd = n \frac{2\pi}{L} d = n \frac{d}{a}$$



Field-enhancement in a nanoring



Different types of radio antennas

$\lambda/4$ antenna



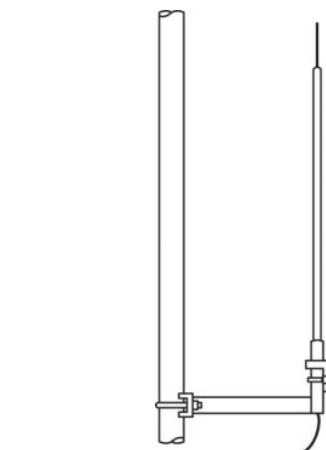
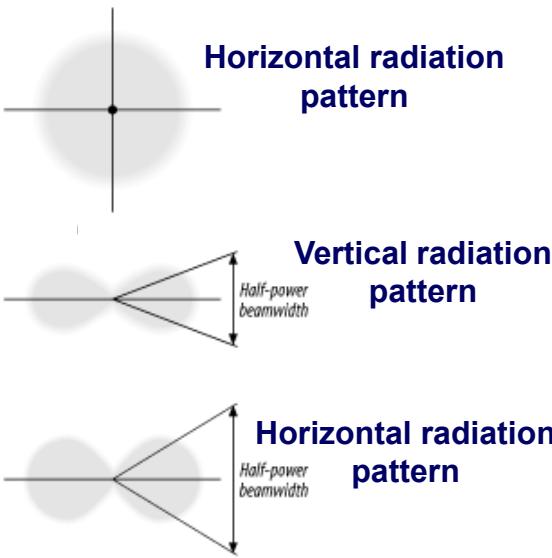
$\lambda/2$ Dipole



Yagi



Parabolic

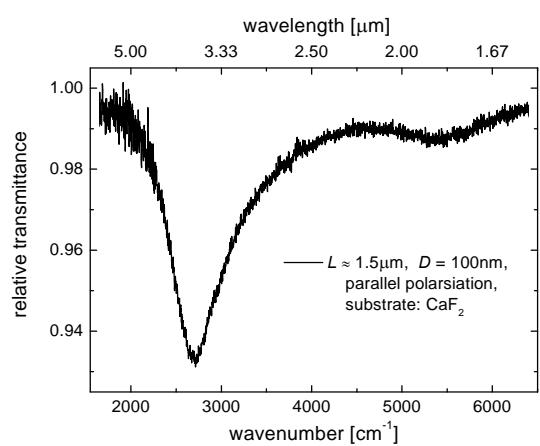
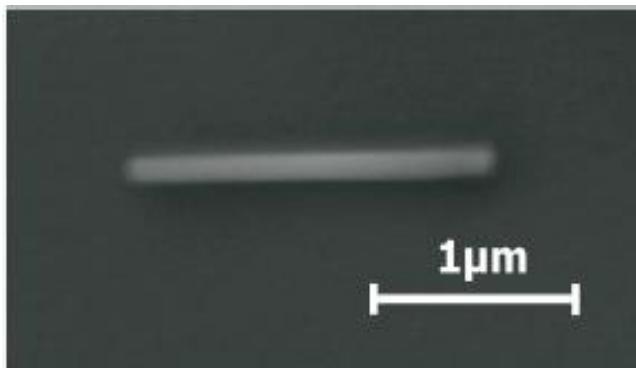


Omni-directional antenna
often used at master station sites



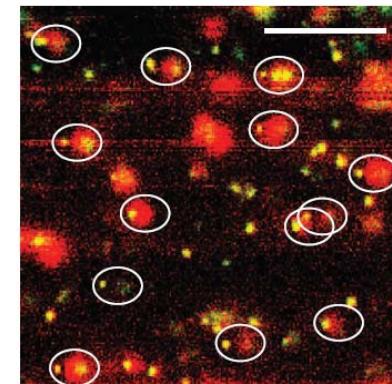
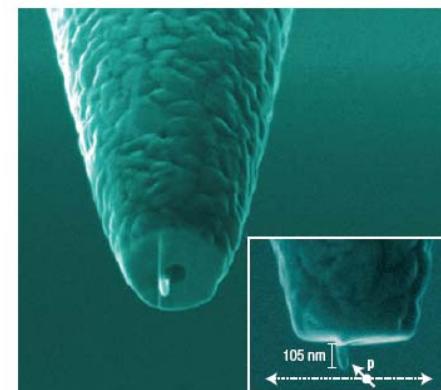
Directional Yagi antenna
Commonly used at remote field sites

$\lambda/2$ nanoantenna



Neubrech *et al.*,
App. Phys. Lett. 89, 253104 (2006)

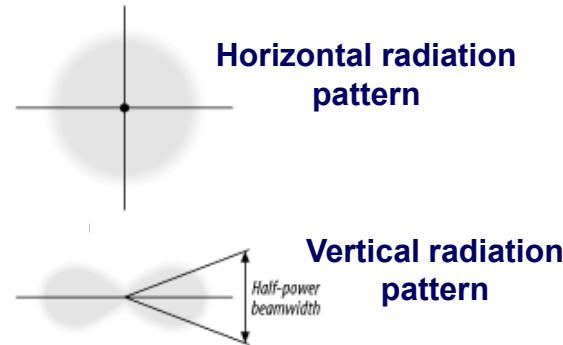
$\lambda/4$ optical antenna



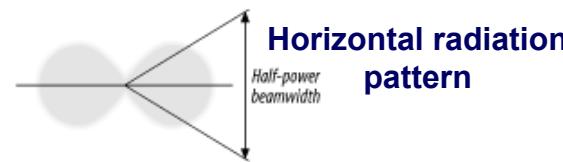
Taminiau *et al.*,
Nature Photonics 2, 234 (2008)

Different types of radio antennas

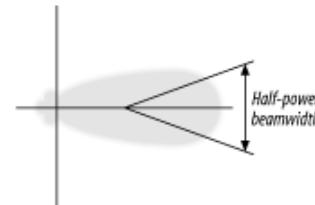
Vertical



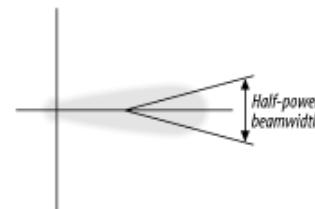
Dipole



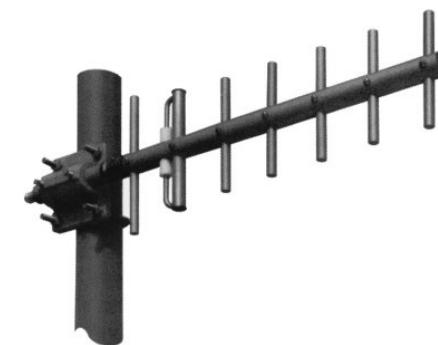
Yagi



Parabolic

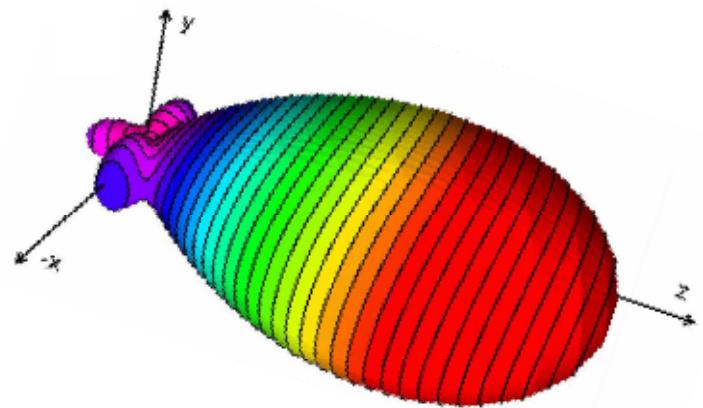
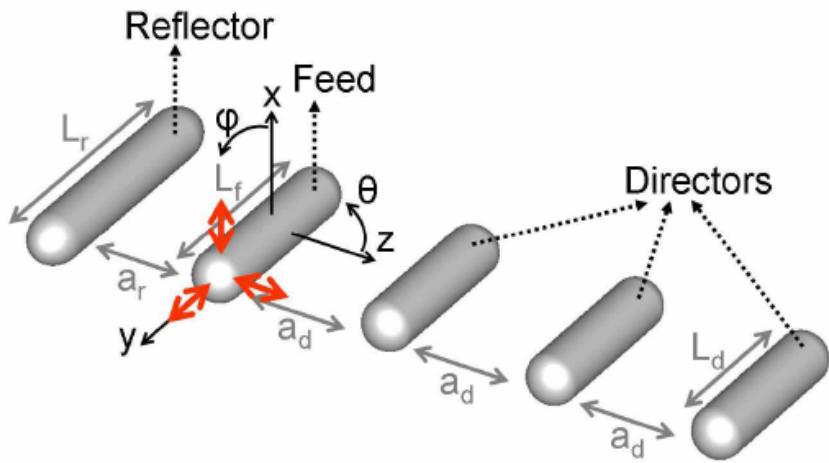


Omni-directional antenna
often used at master station sites



Directional Yagi antenna
Commonly used at remote field sites

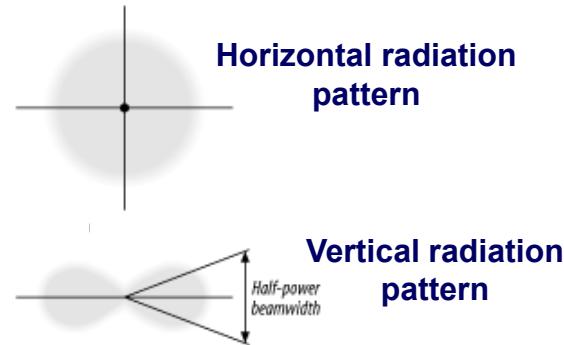
Yagi-Uda antenna



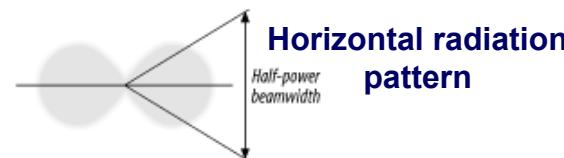
Taminiau et al.,
Optics Express 14, 10858 (2008)

Different types of radio antennas

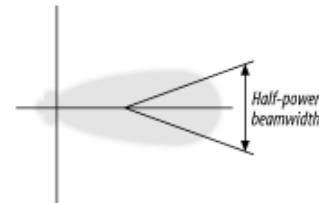
Vertical



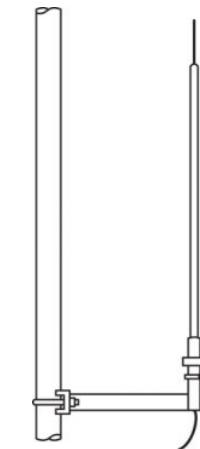
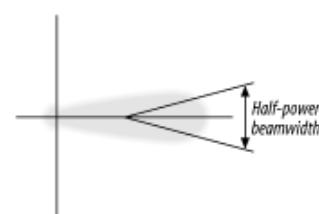
Dipole



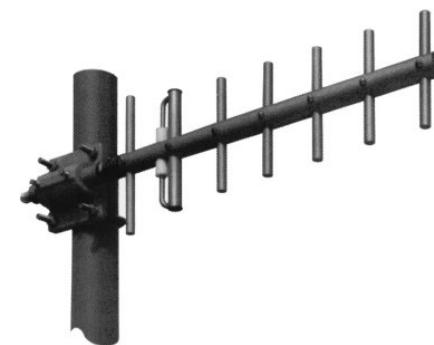
Yagi



Parabolic

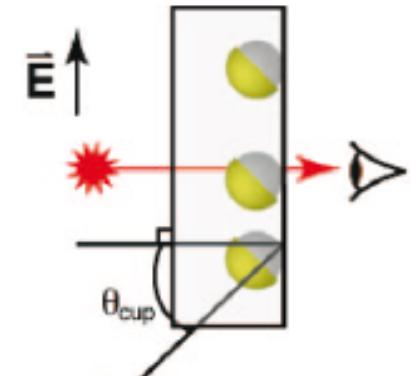
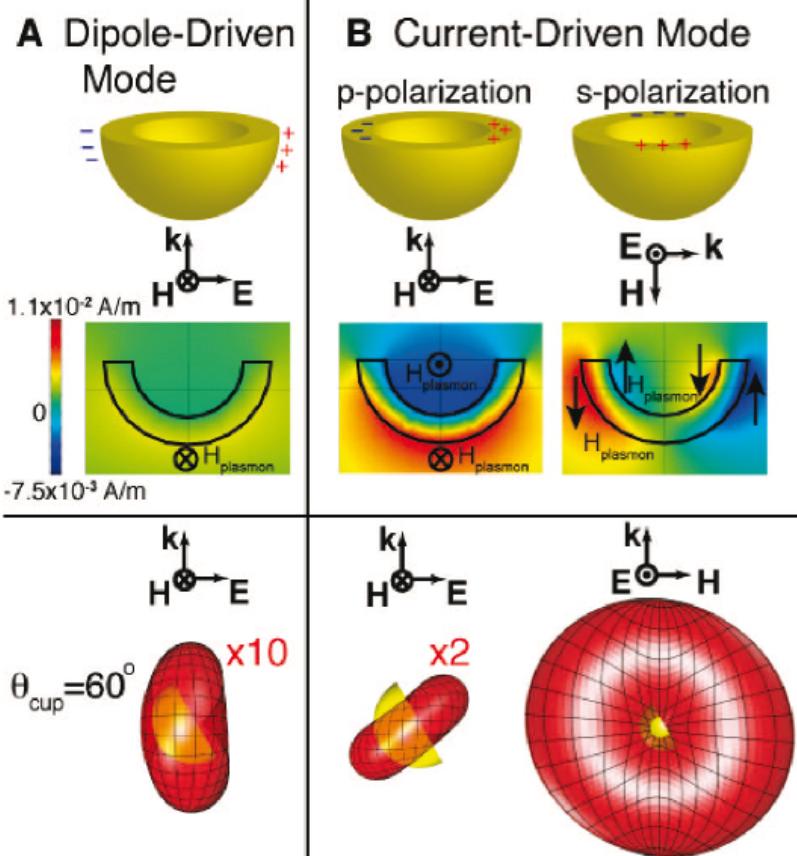


Omni-directional antenna
often used at master station sites



Directional Yagi antenna
Commonly used at remote field sites

Parabolic-like optical nanoantennas

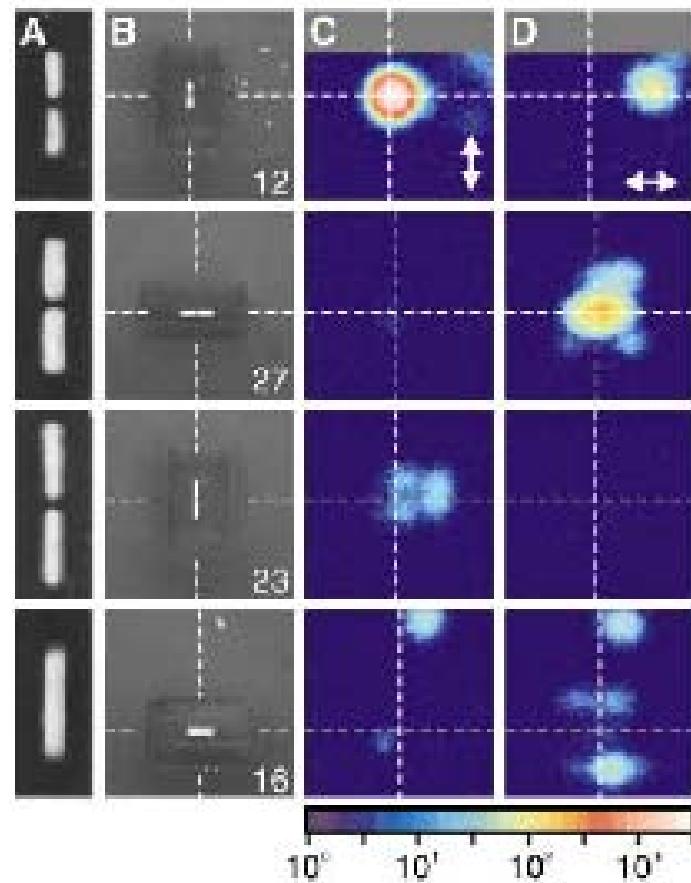
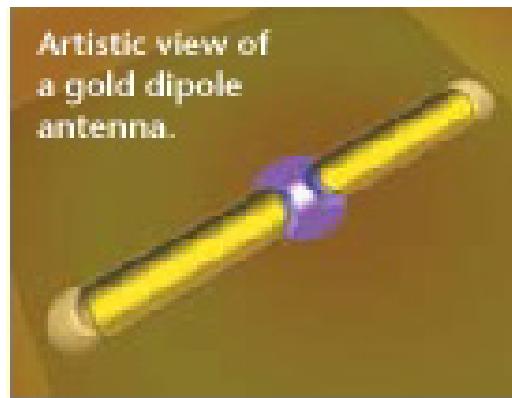
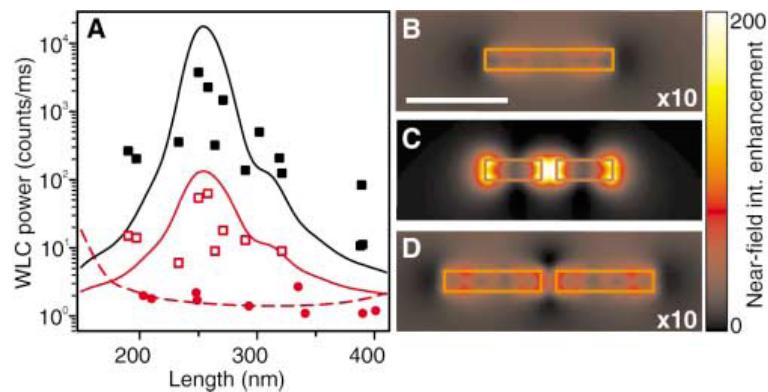


N. Mirin and N. Halas, Nano Letters 9, 1255 (2009)

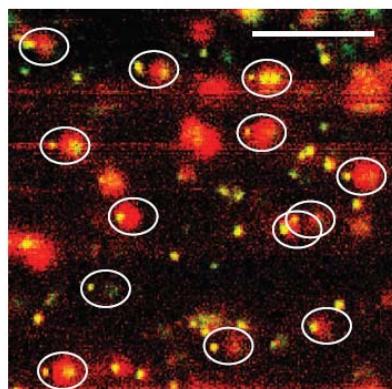
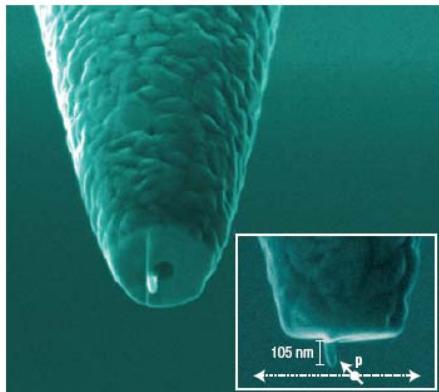
Resonant Optical Antennas

P. Mühlischlegel,¹ H.-J. Eisler,¹ O. J. F. Martin,² B. Hecht,^{1*}
D. W. Pohl¹

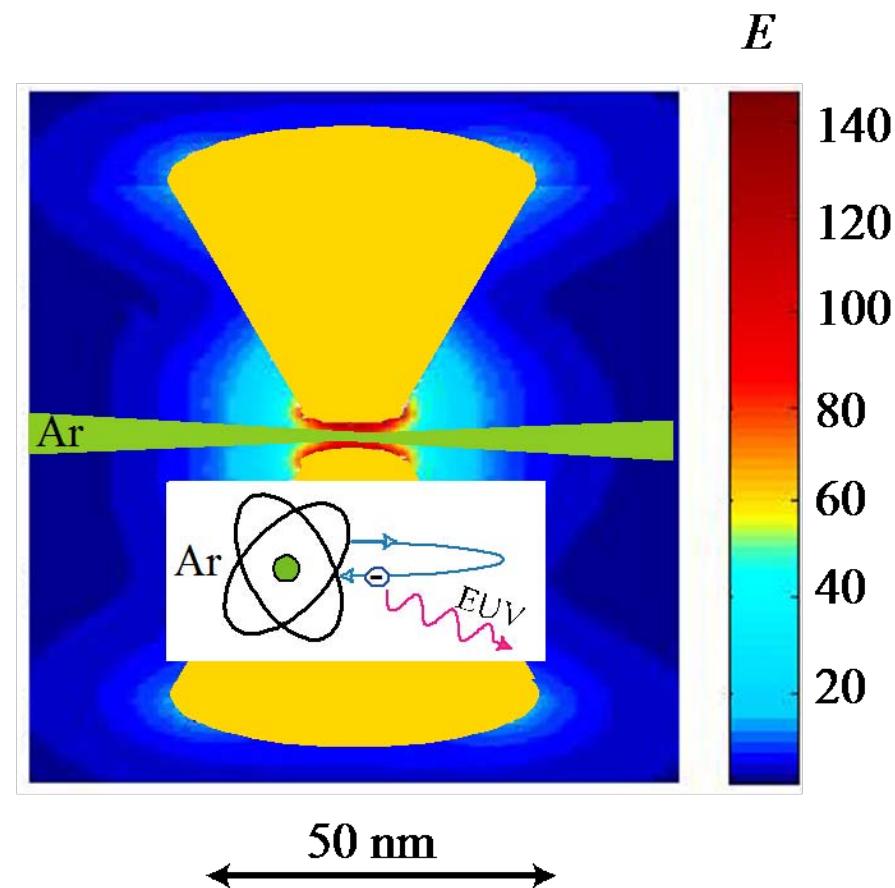
SCIENCE VOL 308 10 JUNE 2005



$\lambda/4$ optical antenna



Bowtie antennas



Taminiau *et al.*,

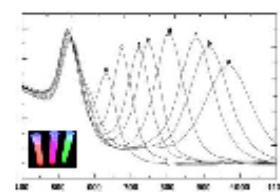
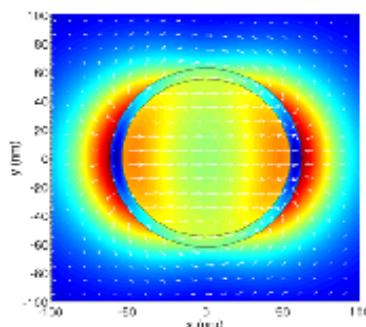
Nature Photonics 2, 234 (2008)

J. Aizpurua, Lecture given at SSOP

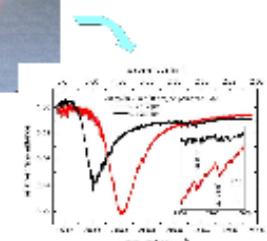
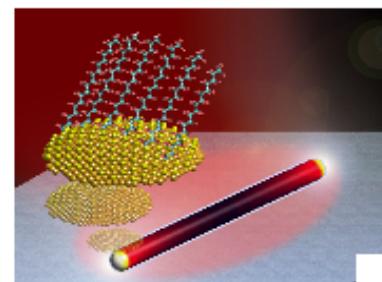
Porquerolles, Sept. 2009

Nature 453, 731 (2008)

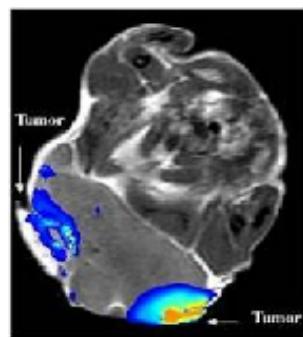
Fundamentals of metallic nano-optical components (optical response)



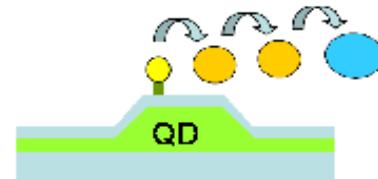
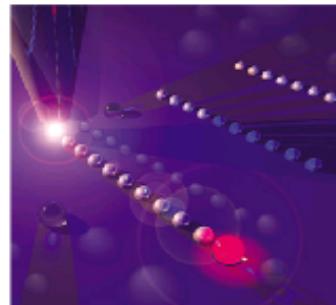
Plasmon-enhanced spectroscopies and microscopies (SERS, SEIRA, s-SNOM)



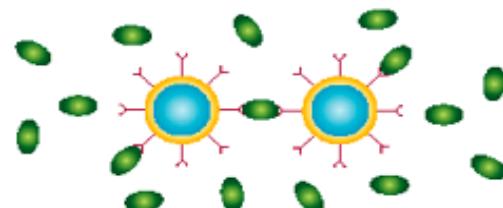
Biomedical applications



Optical guides, interconnects in opto-electronic devices

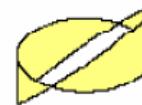


Sensing and biolabeling

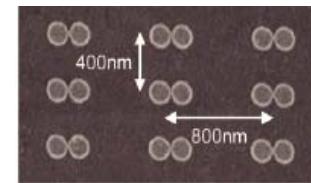


Outline

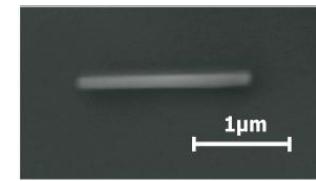
- Basics: Plasmonics



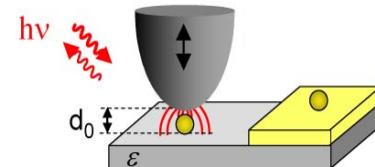
- Optical antennas for SERS
(Surface-Enhanced Raman Scattering)



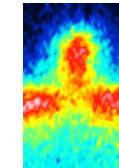
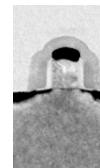
- $\frac{1}{2} \lambda$ dipole Infrared antennas for SEIRA



- Substrate-Enhanced Infrared
Near-Field Microscopy



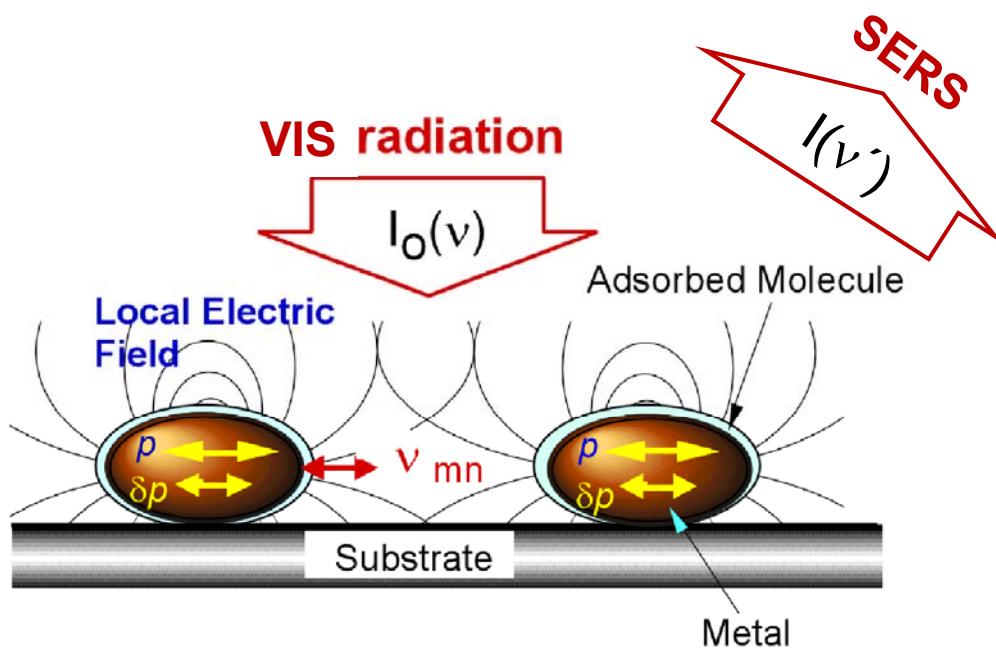
- THz Near-field Nanoscopy



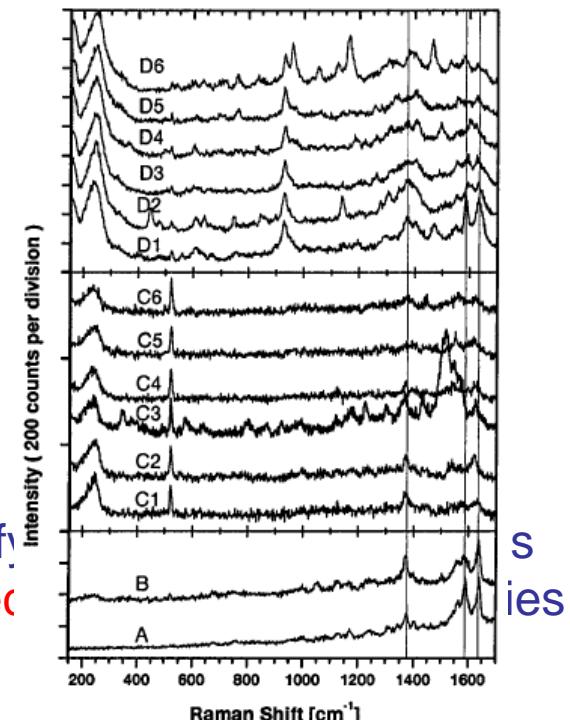
Surface-Enhanced Raman Scattering (SERS)

Resonant antennas for enhanced signal of molecular vibrations

Concept



Molecular fingerprints



Identify
for select

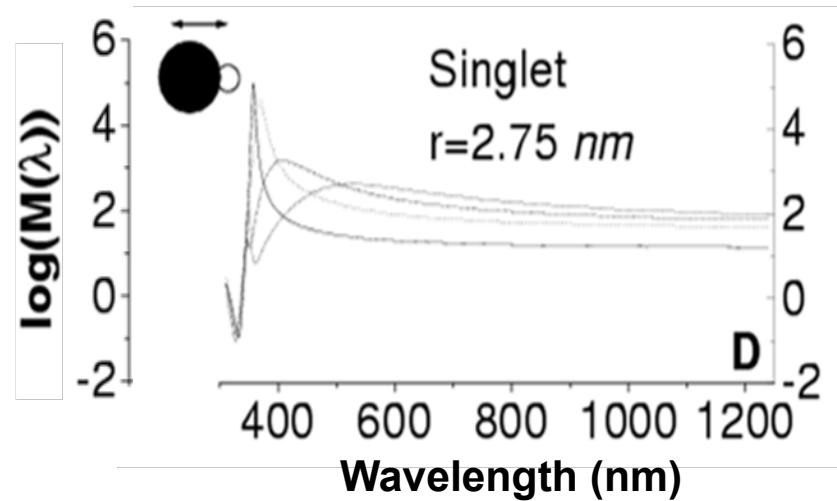
Surface Enhanced Raman Scattering, SERS

Electromagnetic effect

$$M_i^{EM} = \left| E^L(\omega_I) / E^I(\omega_I) \right|^2 \cdot \left| E^L(\omega_I - \omega_v) / E^I(\omega_I - \omega_v) \right|^2$$

If $\omega_v \ll \omega_I$

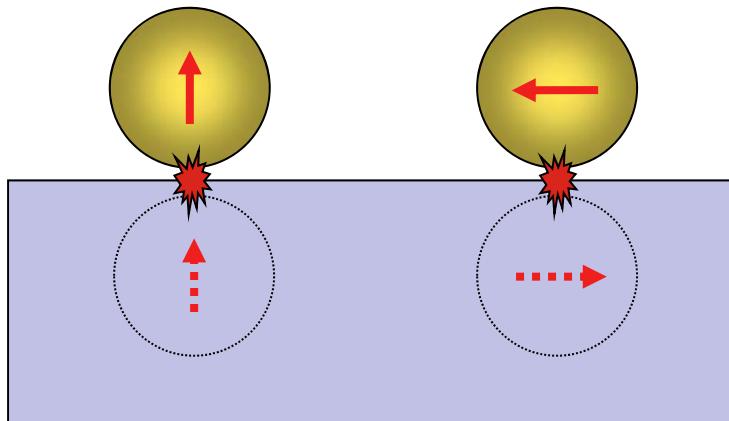
$$M_i^{EM} = \left| E^L(\omega_I) / E^I(\omega_I) \right|^4$$



H. Xu, J. Aizpurua, M. Käll and P. Apell, Phys. Rev. E. **62**, 4318 (2000)

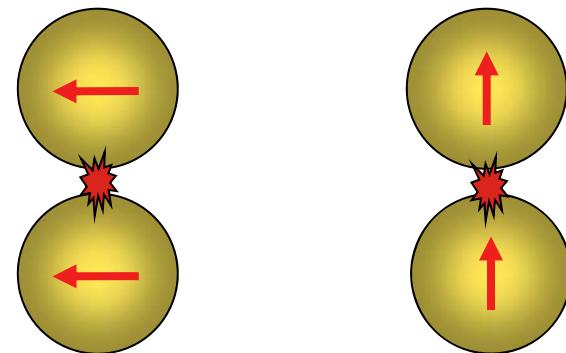
Near-field coupling – simple systems

Sphere - plane



dipole – mirror dipole near-field interaction

Sphere - sphere



dipole – dipole near-field interaction

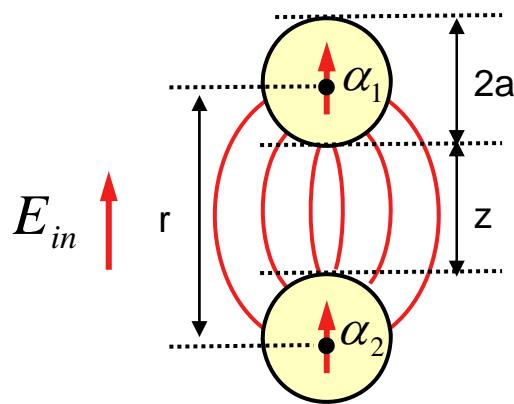
- High field enhancement in the gap due to resonant near-field coupling
- - local light sources
 - enhanced Raman signals (detection of single molecule Raman signals)
 - nonlinear effects

Dipolar sphere-sphere near-field interaction

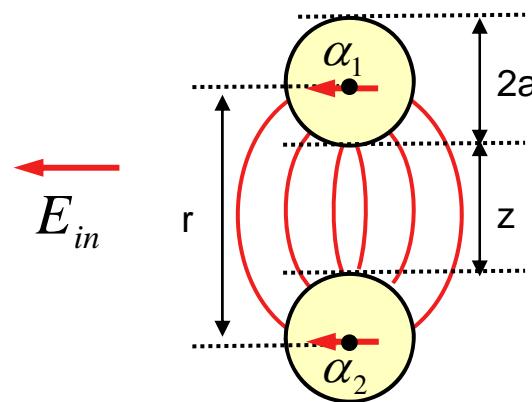
Polarizability of spheres: $\alpha_i = 4\pi a_i^3 \frac{\epsilon_i - 1}{\epsilon_i + 2}$

Scattered field:
 $E_{sca} \propto \alpha_{eff} E_{in}$

Effective polarizability of interacting dipoles (dipole approximation):



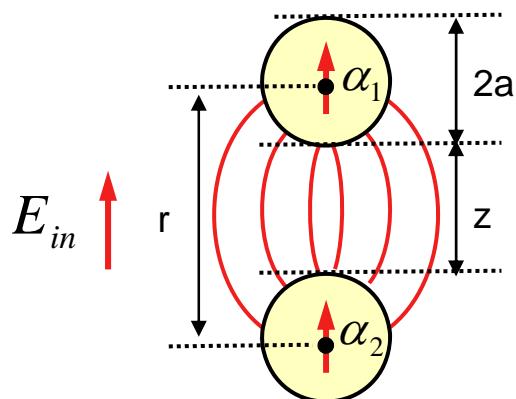
$$\alpha_{eff} = \frac{\alpha_1 + \alpha_2 + \frac{\alpha_1 \alpha_2}{\pi r^3}}{1 - \frac{\alpha_1 \alpha_2}{4\pi^2 r^6}}$$



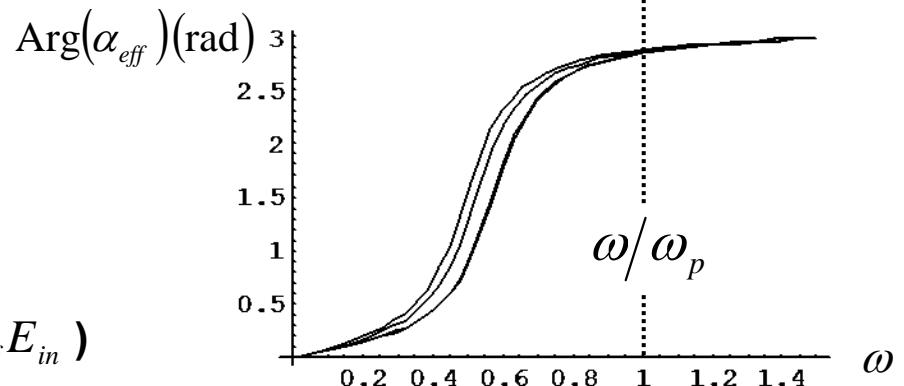
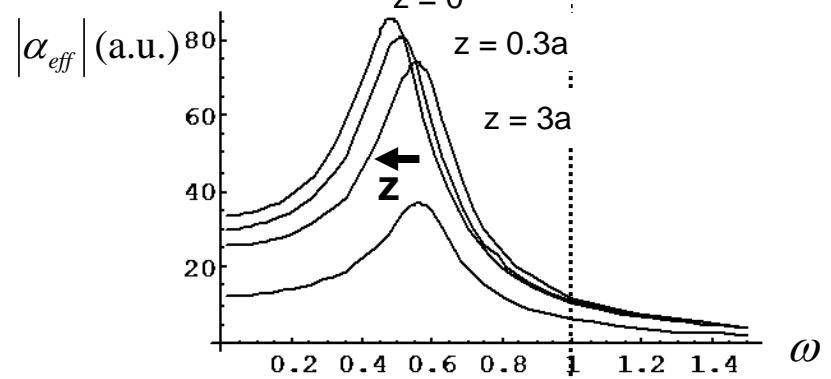
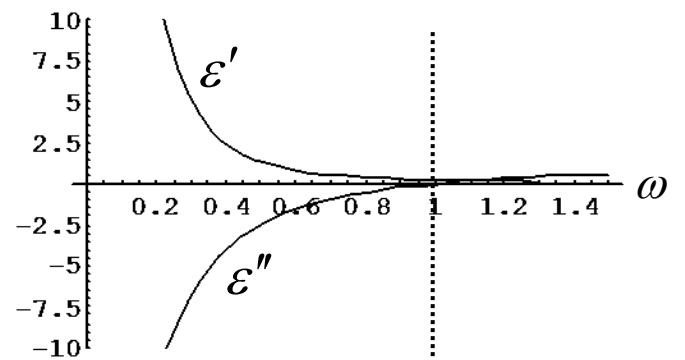
$$\alpha_{eff} = \frac{\alpha_1 + \alpha_2 - \frac{\alpha_1 \alpha_2}{2\pi r^3}}{1 - \frac{\alpha_1 \alpha_2}{16\pi^2 r^6}}$$

Resonance shift effects – two resonant spheres

2 metal spheres: $\epsilon_1 = \epsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$
 (drude term) $\gamma = 0.2$



$$\alpha_{eff} = \frac{\alpha_1 + \alpha_2 + \frac{\alpha_1 \alpha_2}{\pi r^3}}{1 - \frac{\alpha_1 \alpha_2}{4\pi^2 r^6}}$$

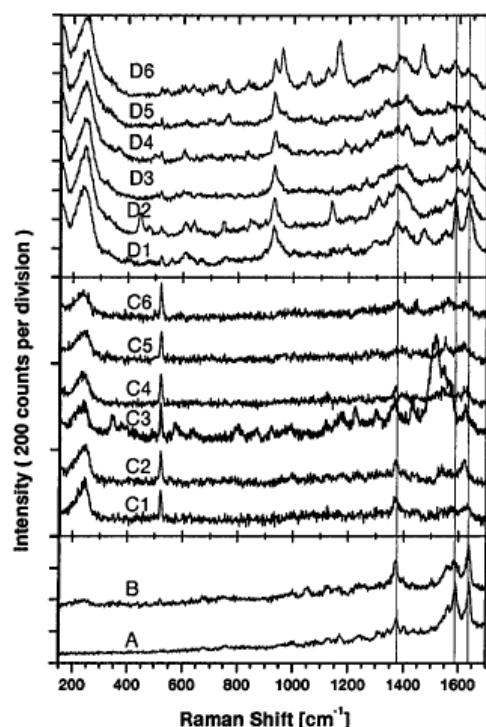
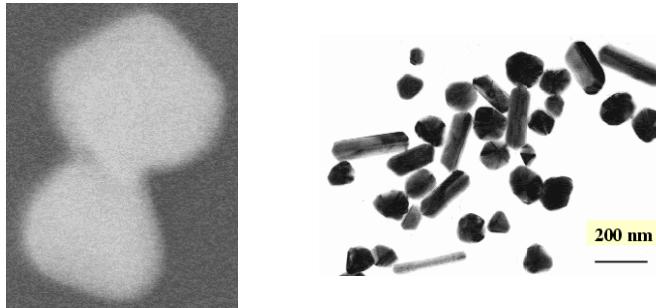


→ dipolar approximation predicts

- resonance shifts
- field enhancement ($E_{sca} \propto \alpha_{eff} E_{in}$)

Dimers assisting in spectroscopy: SERS

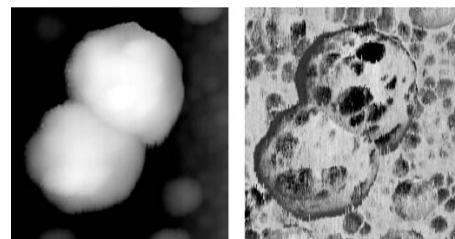
Xu et al. Phys Rev. Lett. (1999)



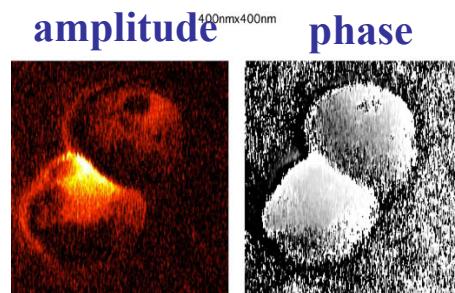
Xu, Aizpurua, Käll and Apell, Phys. Rev. E. **62**, 4318 (2000)

Hot sites

topography



amplitude



phase

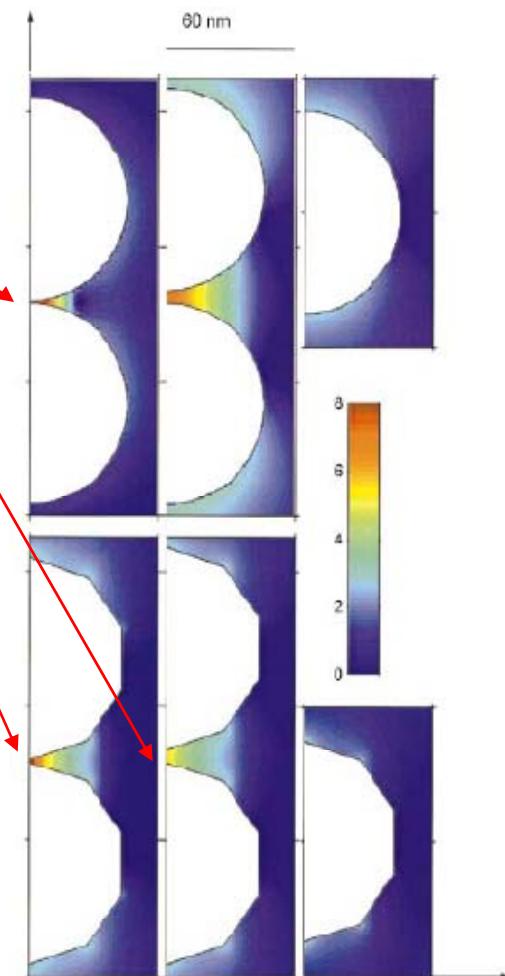


Image obtained by R. Hillenbrand,
(Max Planck, Munich)

Two near-field interacting gold discs I

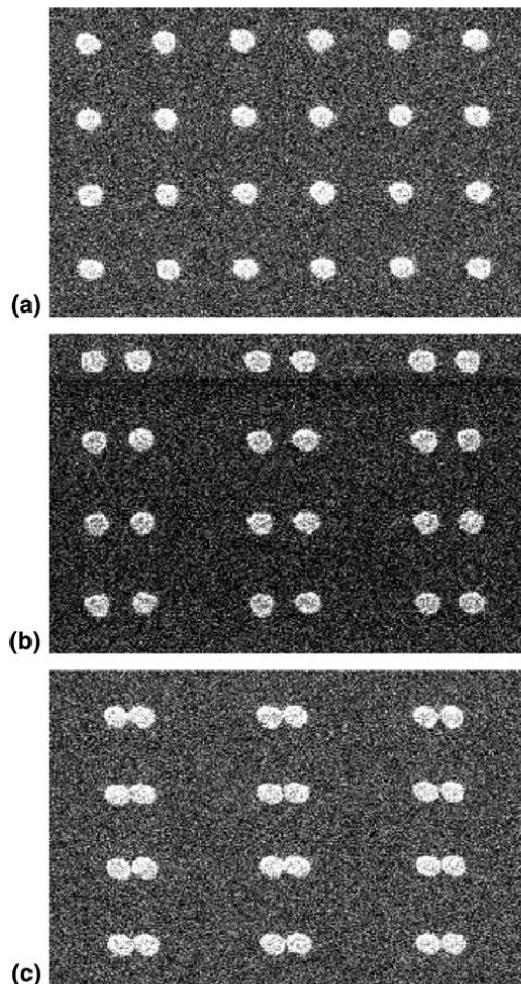
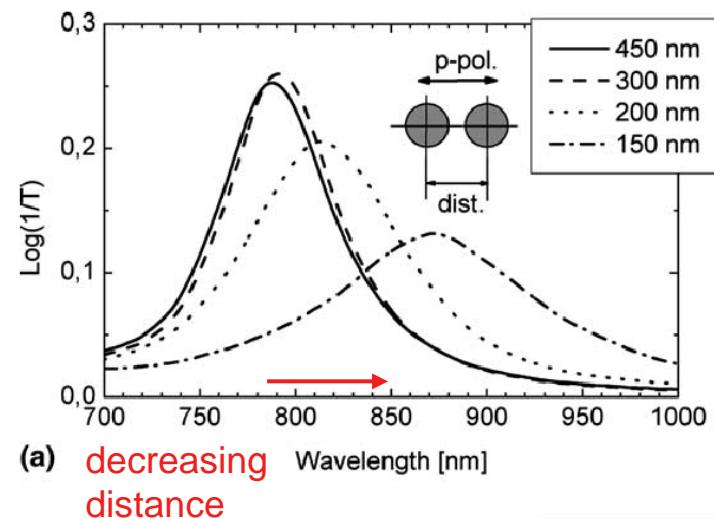
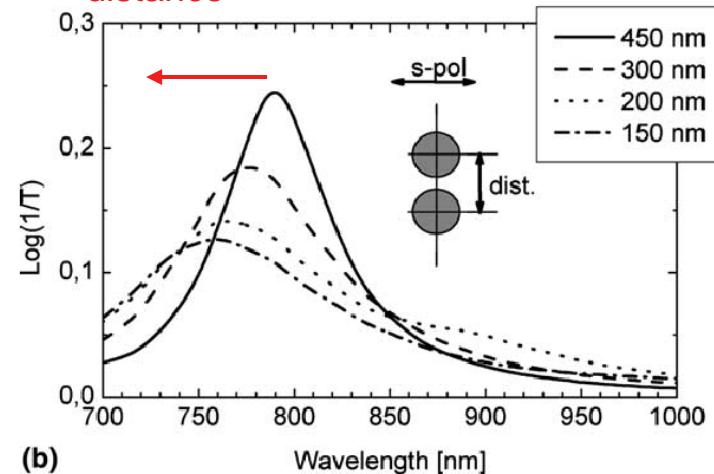


Fig. 1. SEM images of particle pair samples with varying interparticle distance (center-to-center) of (a) 450 nm, (b) 300 nm and (c) 150 nm. The particle diameter is 150 nm, the particle height is 17 nm.

W. Rechenberger et.al., Opt. Commun. **220**, 137 (2003)
 J. Aizpurua, Lecture given at SSOP
 Porquerolles, Sept. 2009



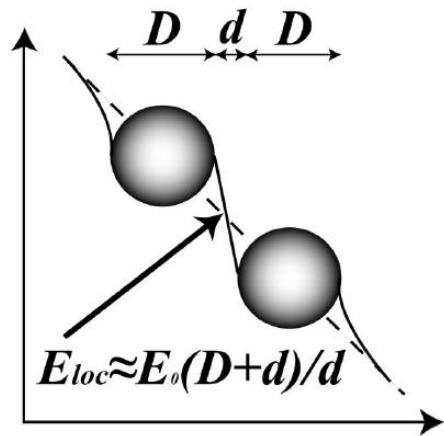
(a) decreasing distance Wavelength [nm]



(b) Wavelength [nm]

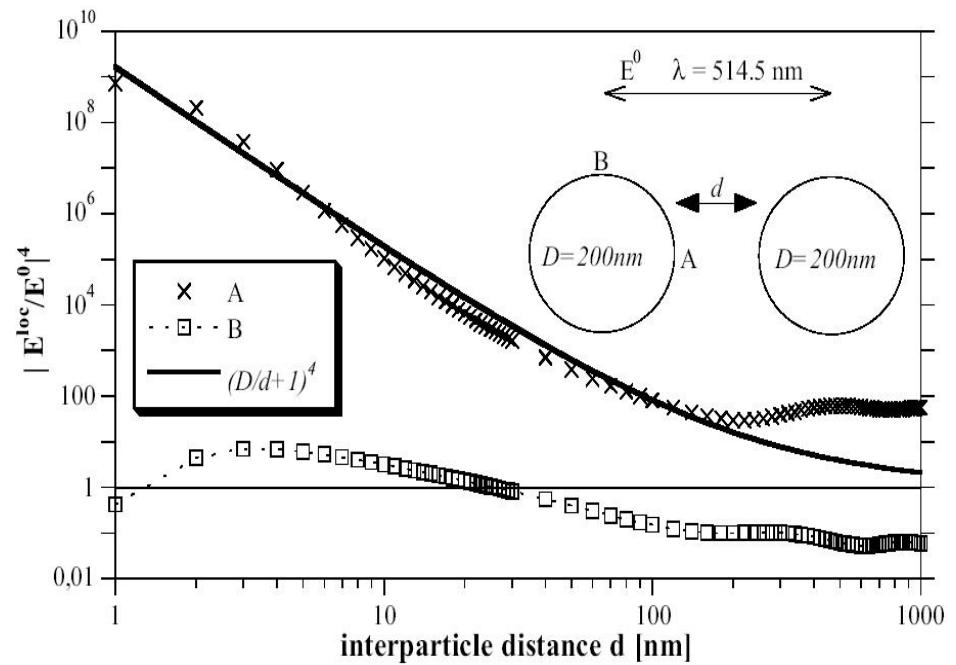
Fig. 2. Extinction (=log(1/Transmission)) spectra of a 2D array of the Au nanoparticle pairs with the interparticle center-to-center distances as the parameter. The orthogonal particle separation is kept constant, as can be seen in Fig. 1. The polarization direction of the exciting light is (a) parallel to the long particle pair axis and (b) orthogonal to it.

Field-enhancement: geometrical squeezing



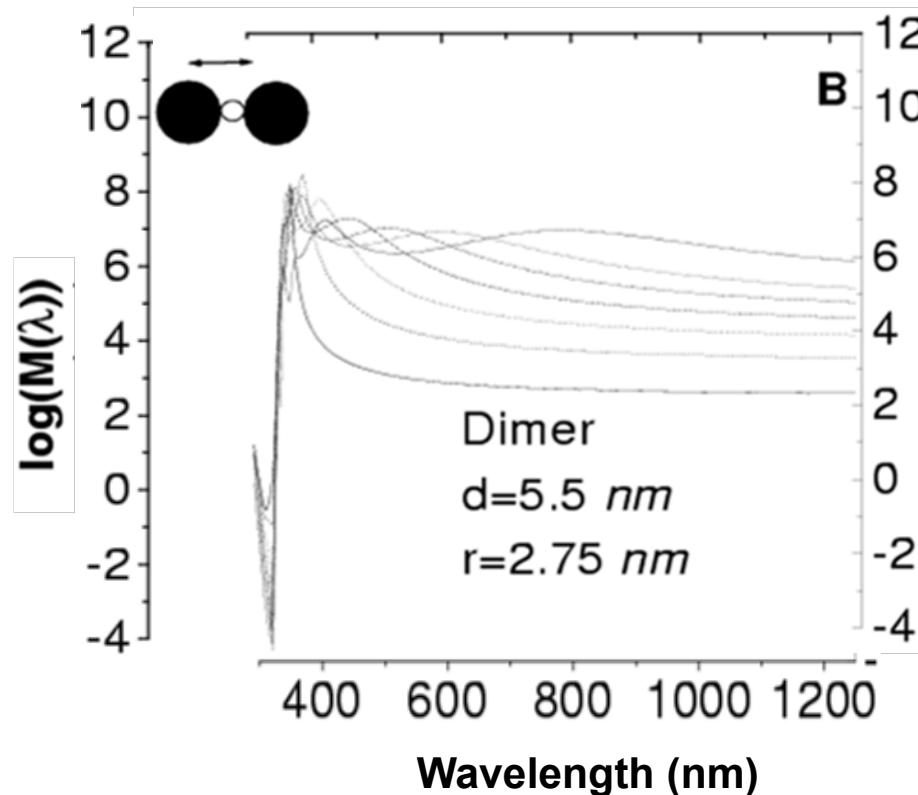
$$E_{loc} = E_0(D + d) / d$$

$$M = \left(\frac{D}{d} + 1\right)^4$$



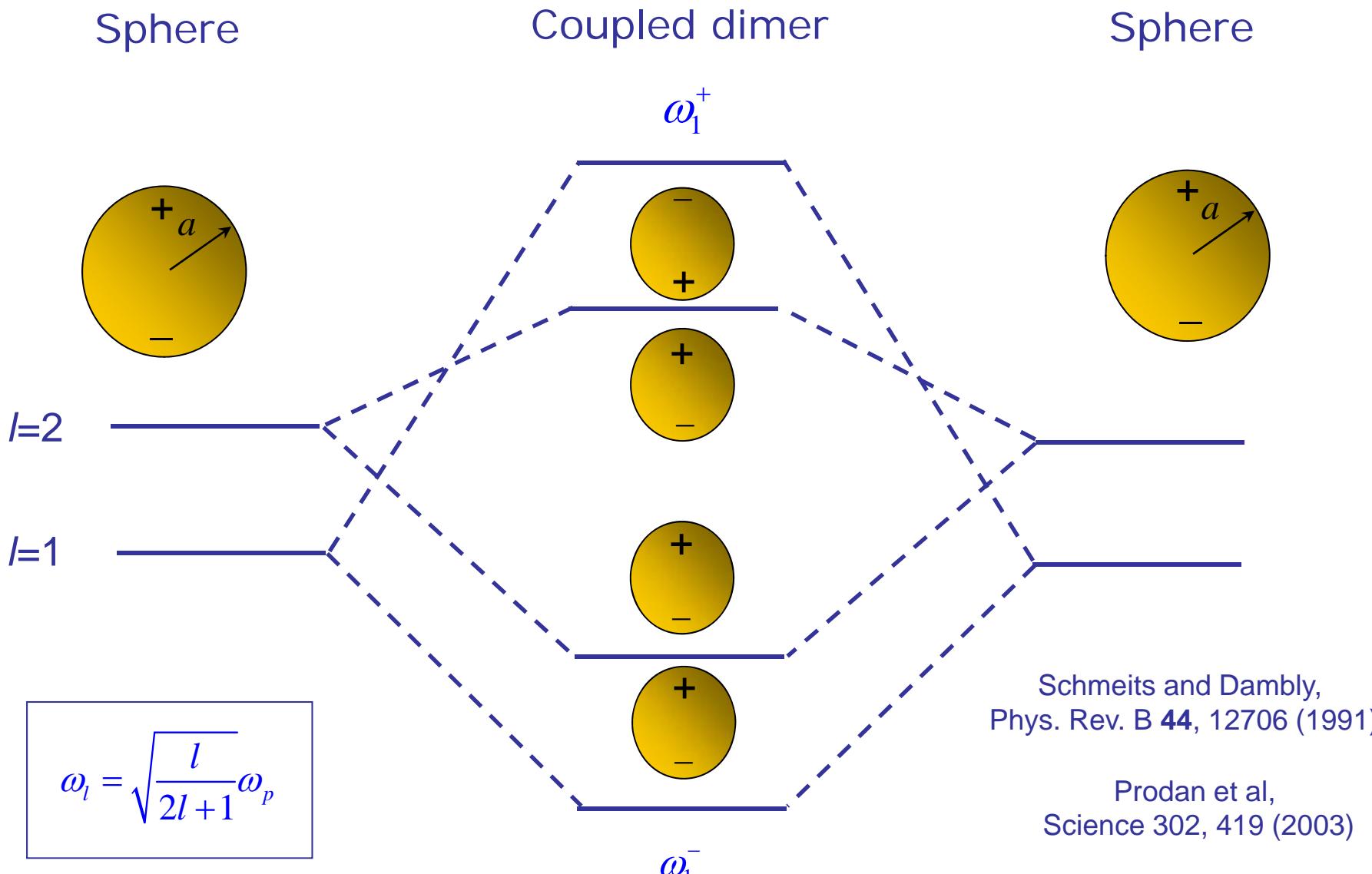
Dimers assisting in spectroscopy: SERS

$$M_i^{EM} = \left| E^L(\omega_i) / E^I(\omega_i) \right|^4$$

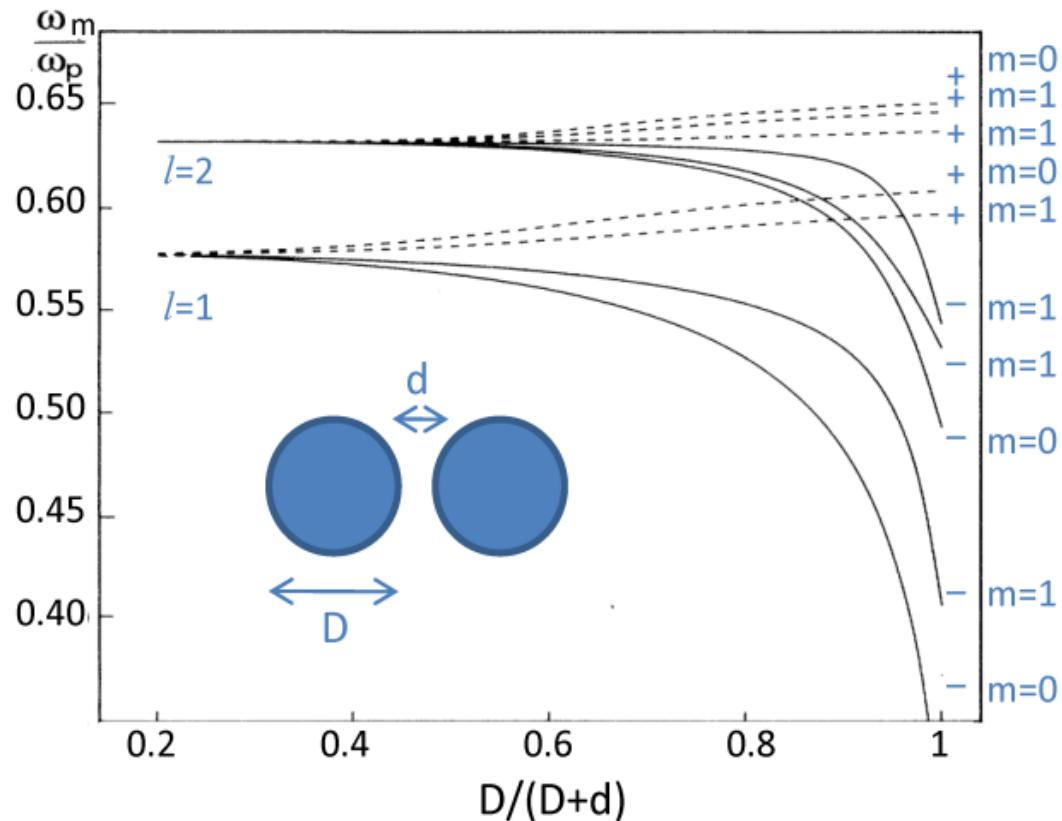
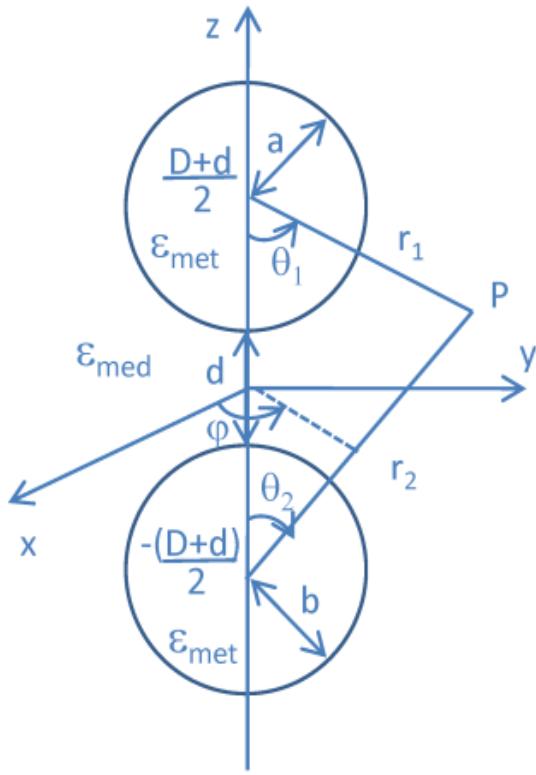


H. Xu, J. Aizpurua, M. Käll and P. Apell, Phys. Rev. E. **62**, 4318 (2000)

Plasmon hybridization



Coupled modes in a metallic dimer



$$\Psi^{(1)}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=+l} \left(\frac{r_1}{a}\right)^l A_{lm} Y_{lm}(\theta_1, \varphi) e^{im\varphi} \quad \text{for } r_1 < a,$$

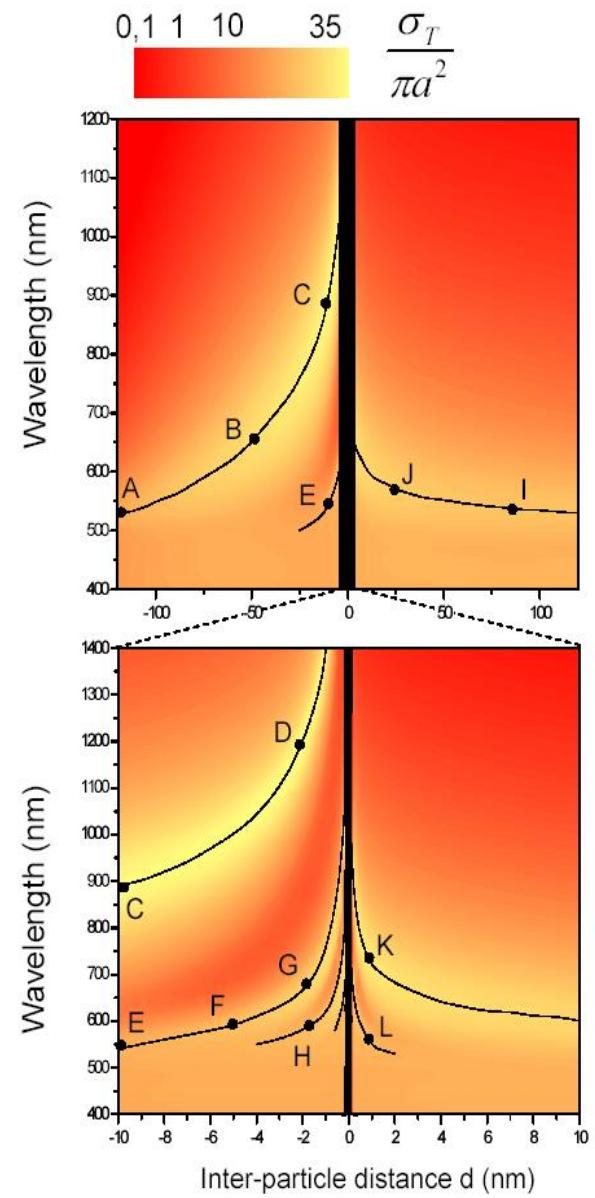
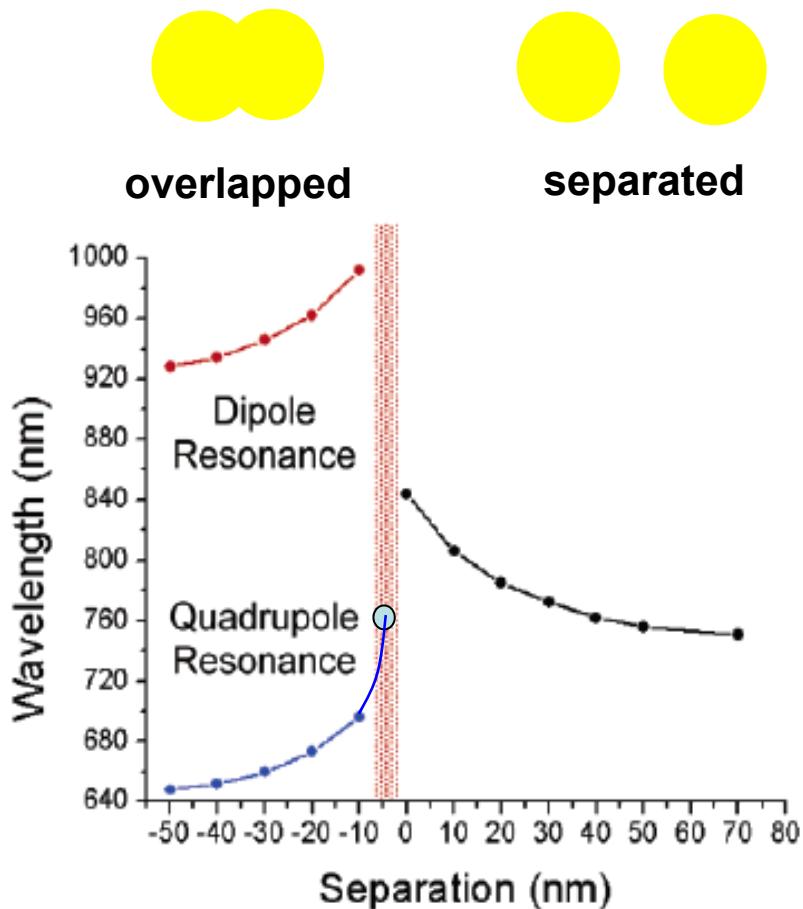
$$\Psi^{(2)}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=+l} \left(\frac{r_2}{b}\right)^l D_{lm} Y_{lm}(\theta_2, \varphi) e^{im\varphi} \quad \text{for } r_2 < b,$$

$$\Psi^{(3)}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=+l} \left[\left(\frac{a}{r_1}\right)^{l+1} B_{lm} Y_{lm}(\theta_1, \varphi) + \left(\frac{b}{r_2}\right)^{l+1} C_{lm} Y_{lm}(\theta_2, \varphi) \right] e^{im\varphi}$$

$$\left(\frac{\omega_{m=0;l=1}}{\omega_p}\right)_{\pm}^2 = \frac{\left(1 \pm 2 \left(\frac{D/2}{D+d}\right)^3\right)}{3}$$

Nanoparticles in the touching limit

Map of the resonances

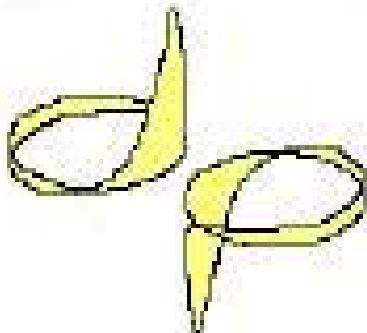


I. Romero, et al. Optics Express 14, 9988 (2006)

Charge density modes

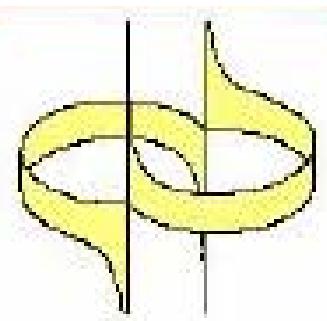
Low frequency modes of non-touching and touching dimers are distinctly different

NOT TOUCHING

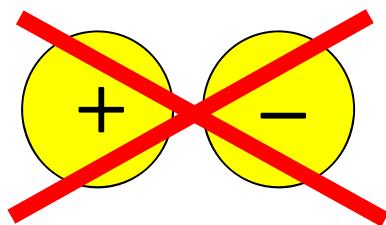


Neutral charge in each particle

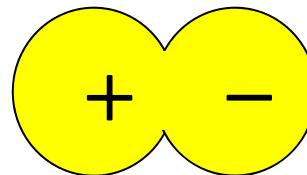
TOUCHING



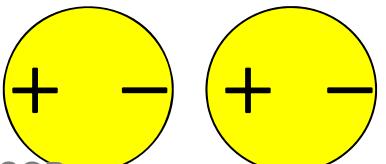
Net electrical charge in each half of the dimer



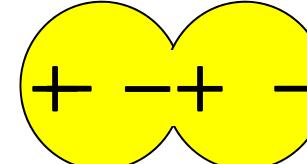
Unphysical mode



1st physical mode



1st physical mode

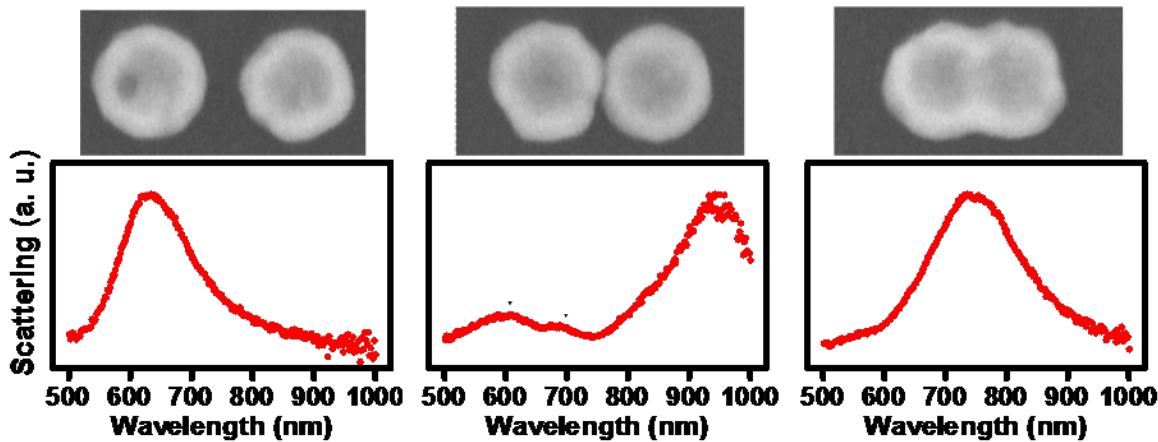


2nd physical mode

Close Encounters between Two Nanoshells

J. Britt Lassiter,^{†,II} Javier Aizpurua,[†] Luis I. Hernandez,^{II} Daniel W. Brandl,^{†,II} Isabel Romero,[†] Surbhi Lal,^{†,II} Jason H. Hafner,^{†,§,II} Peter Nordlander,^{†,‡,II} and Naomi J. Halas^{*†,§,II}

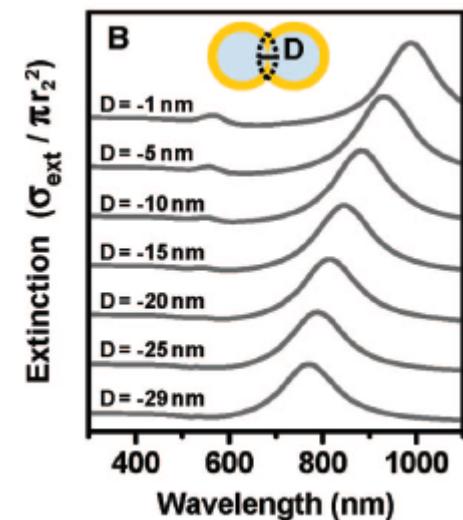
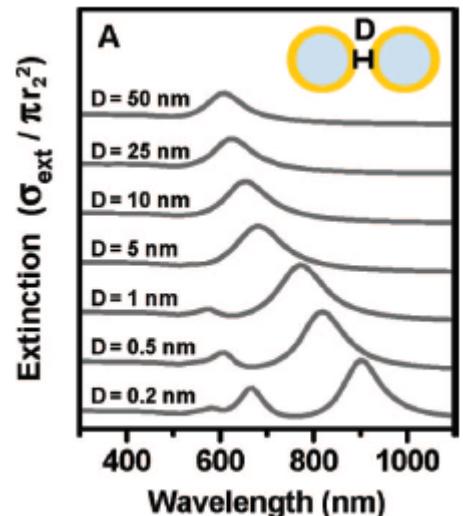
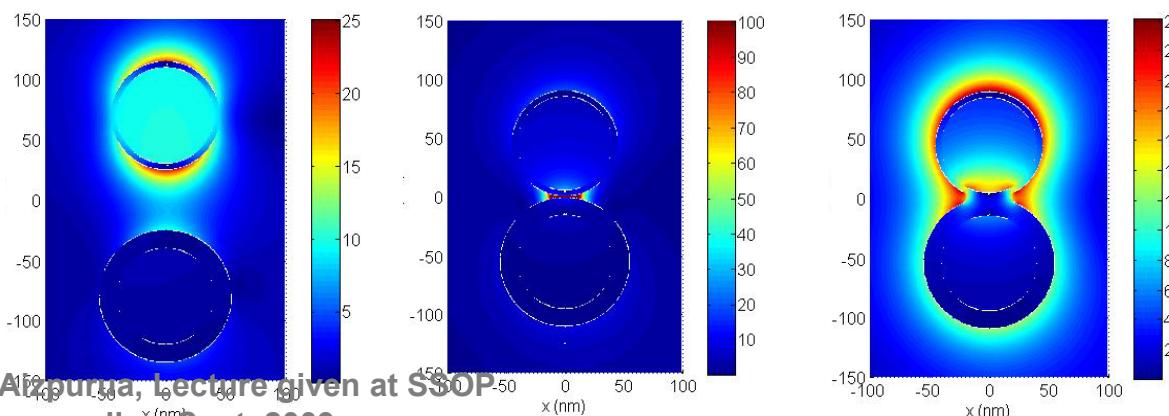
NANO
LETTERS
2008
Vol. 8, No. 4
1212-1218



Slightly close:
Slight shift

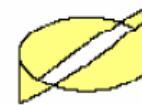
Close proximity:
red shift

Overlapped:
Blue-shift

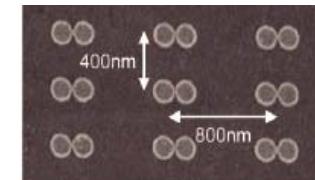


Outline

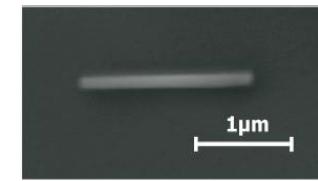
- Basics: Plasmonics



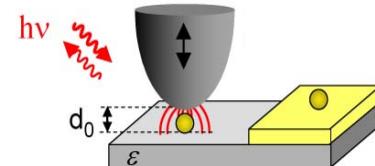
- Optical antennas for SERS



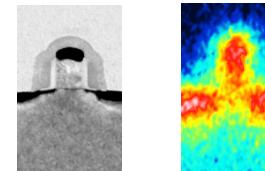
- Infrared antennas for SEIRA
(Surface-Enhanced IR Absorption)



- Substrate-Enhanced Infrared
Near-Field Microscopy



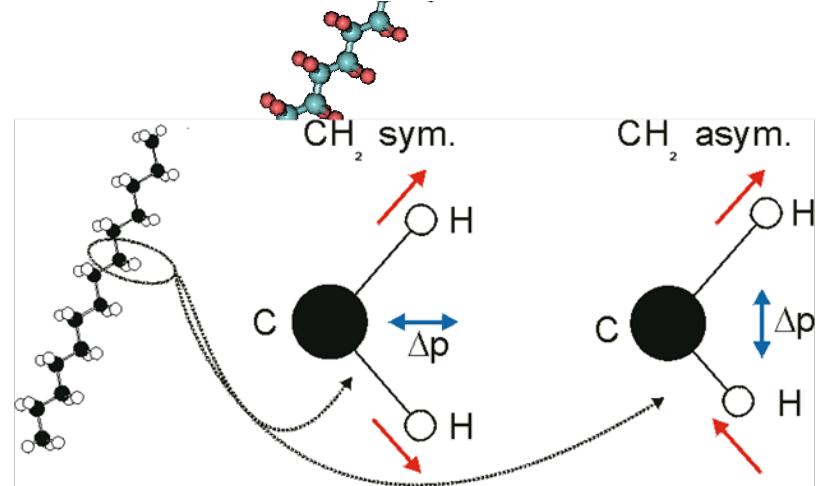
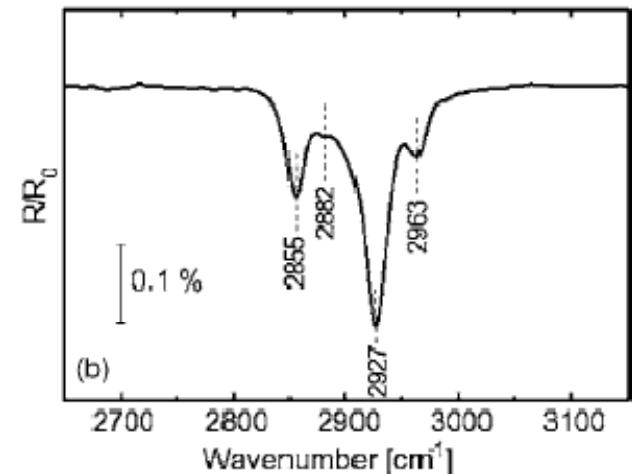
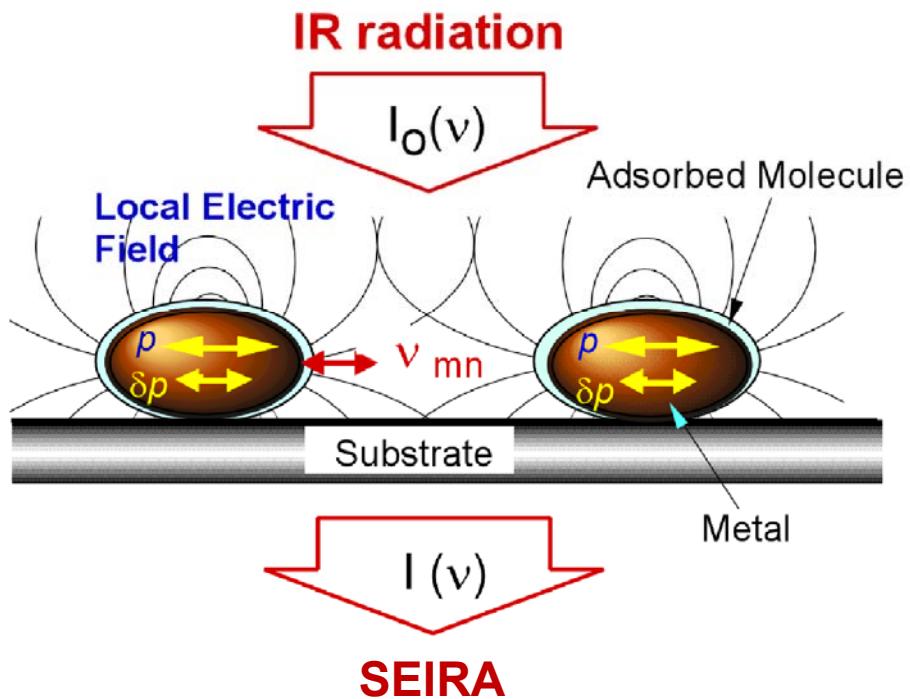
- THz Near-field Nanoscopy



Surface-enhanced IR absorption (SEIRA)

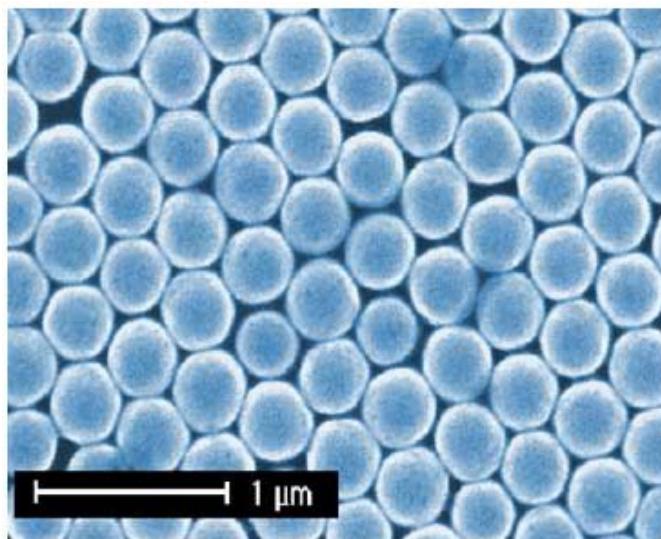
Resonant antennas for enhanced signal of molecular vibrations

Concept



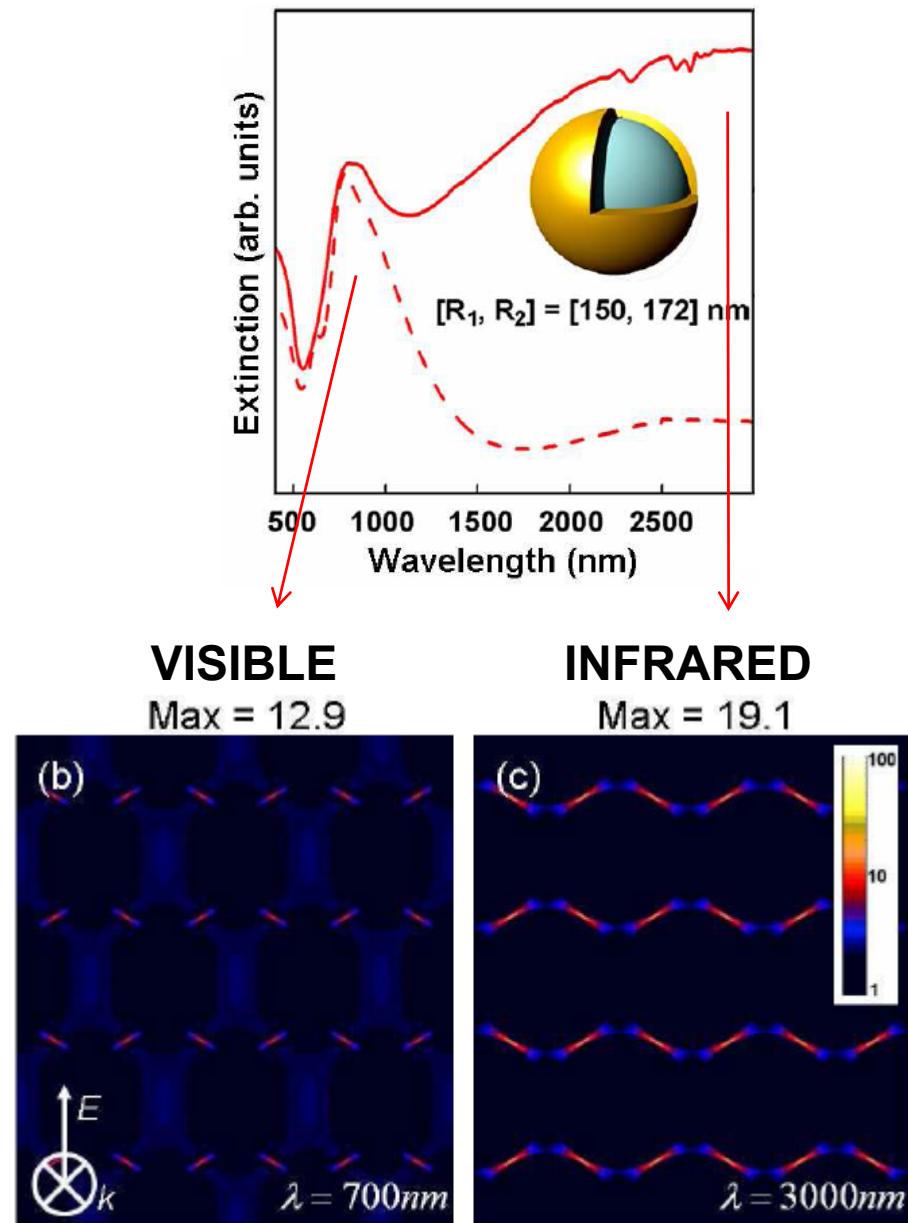
Nanoshell arrays: Substrates for infrared spectroscopy

Metallic nanoparticle arrays for SERS and SEIRA



Kundu et al. Angew. Chem. (2007)
Halas group, Rice Univ.

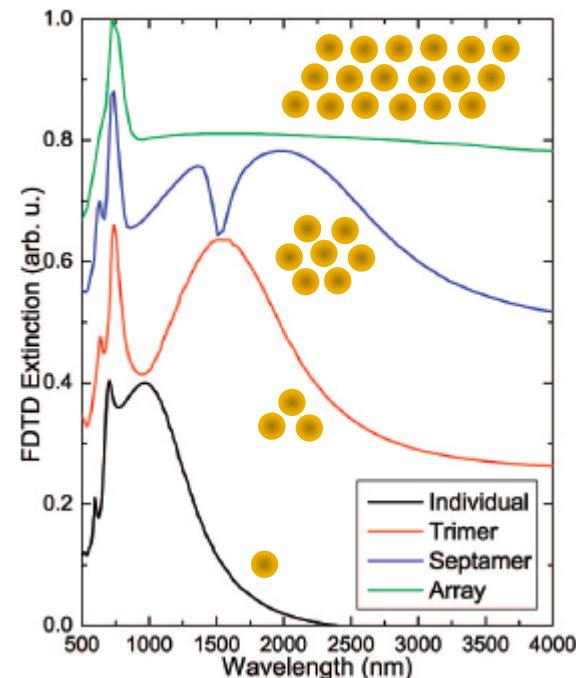
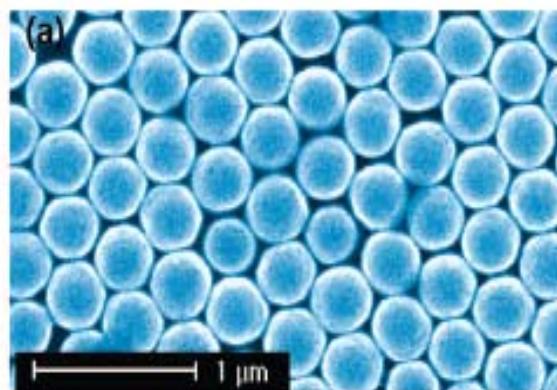
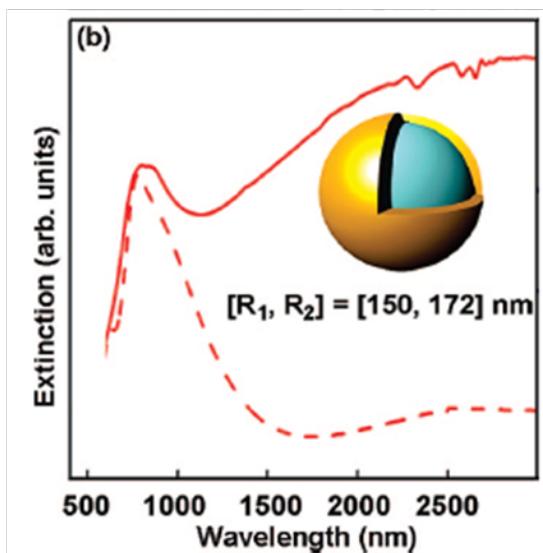
Fei et al. ACS Nano. 2, 707 (2008)
In collaboration with P. Nordlander's group



Metallic Nanoparticle Arrays: A Common Substrate for Both Surface-Enhanced Raman Scattering and Surface-Enhanced Infrared Absorption

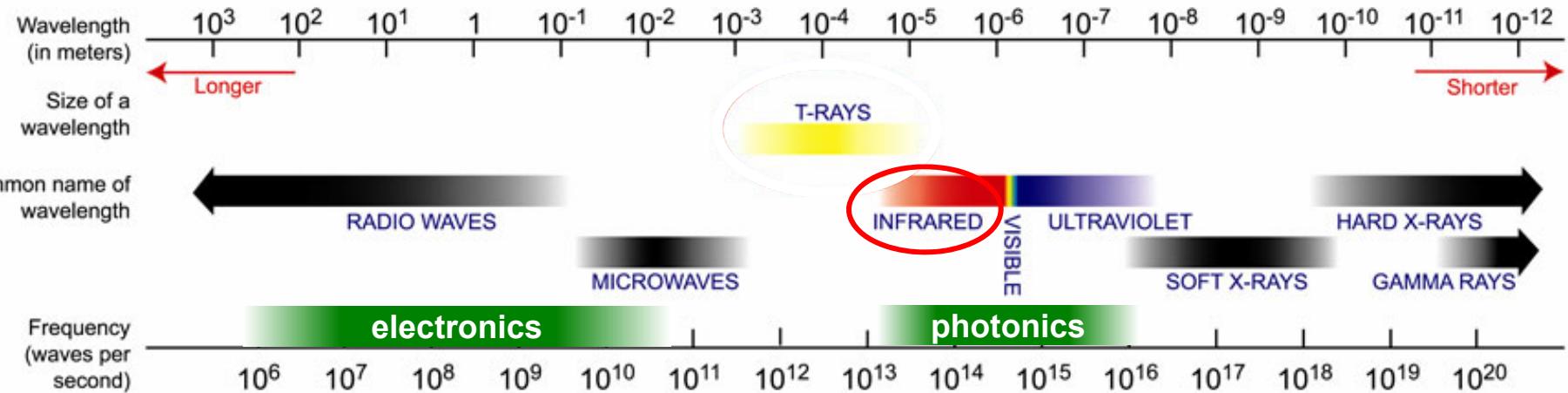
ACSNANO
2, 707 (2008)

Fei Le,[†] Daniel W. Brandl,[†] Yaroslav A. Urzhumov,[‡] Hui Wang,[§] Janardan Kundu,[§] Naomi J. Halas,^{§,⊥} Javier Aizpurua,^{||} and Peter Nordlander^{†,⊥,*}



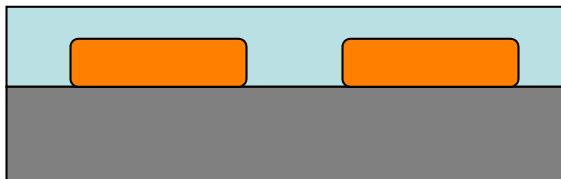
Surface-enhanced IR absorption (SEIRA)

Resonant antennas for enhanced signal of molecular vibrations



Single antenna for infrared resonant spectroscopy

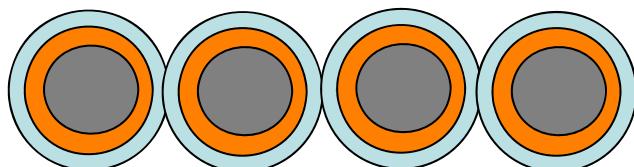
Resonant triangles (coated)



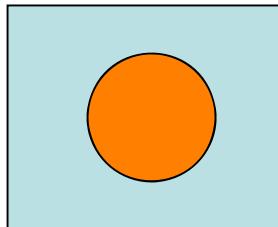
T.R. Jensen et al., J. Phys. Chem B, 104, 10549 (2000)

Resonant structure
Layer to be investigated
Non-resonant structure

Nanoshell arrays

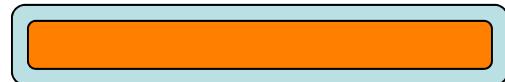


H. Wang et al., Angew. Chem. **46**, 9040 (2007)



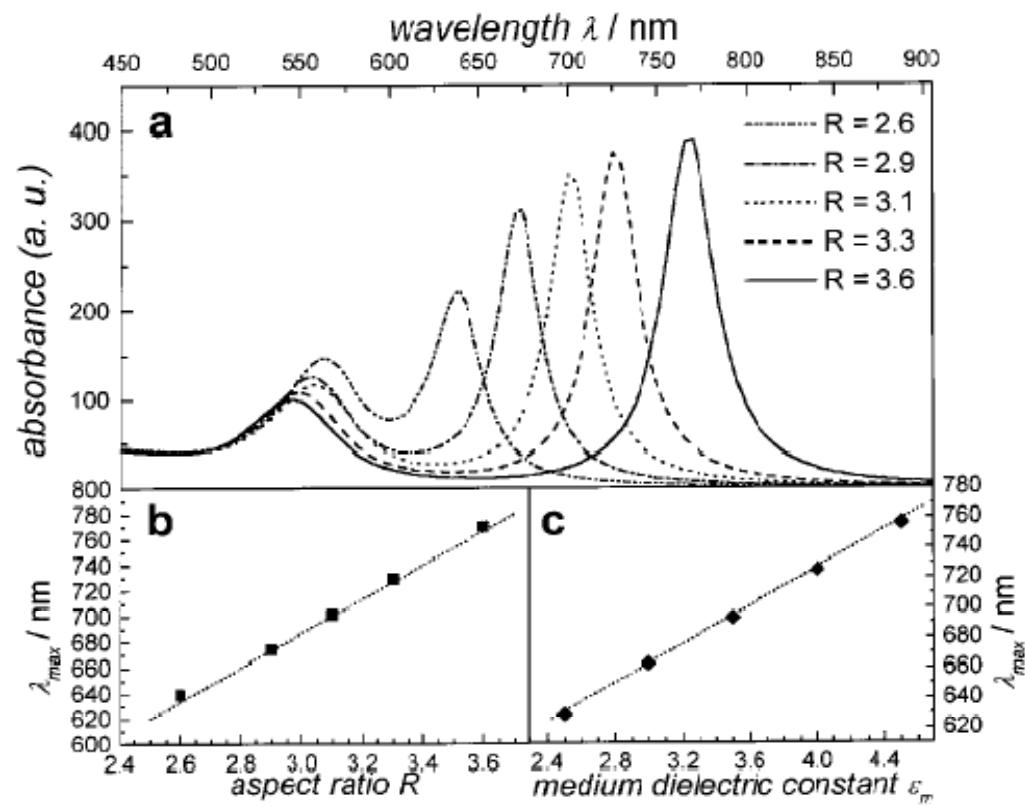
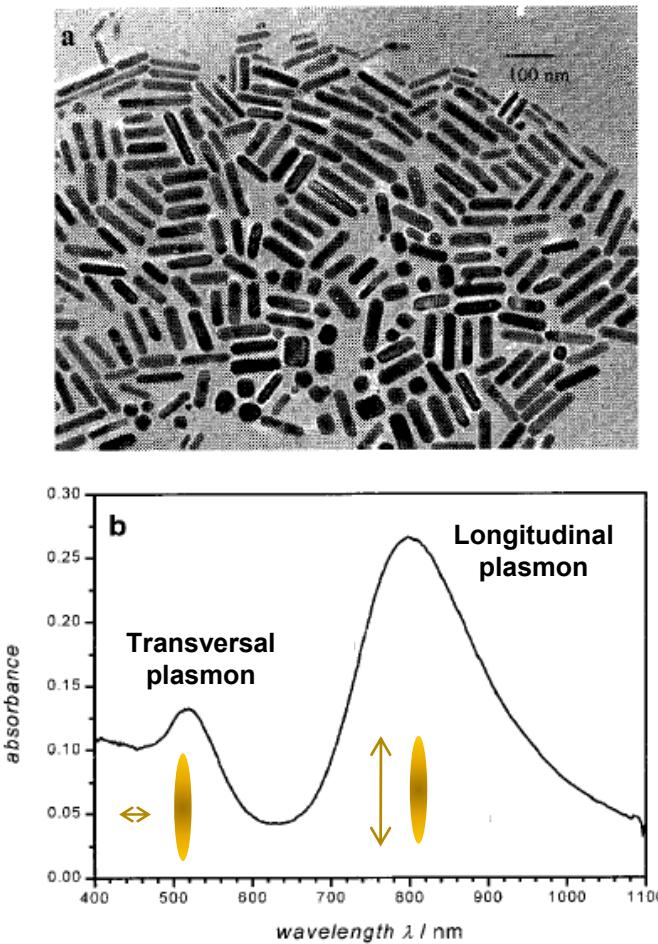
M.S. Anderson, App. Phys. Lett. **83**, 2964 (2003)

Resonant rod (coated)



F. Neubrech et al.,
Phys. Rev. Lett. **101**, 157403 (2008)

Basics of nanorods



$$L = \lambda/m \ ?$$

S. Link and M.A. El-Sayed. J. Phys. Chem. B 103, 8410 (1999).

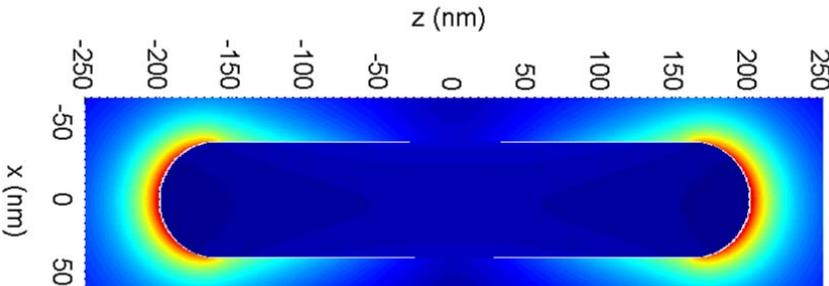
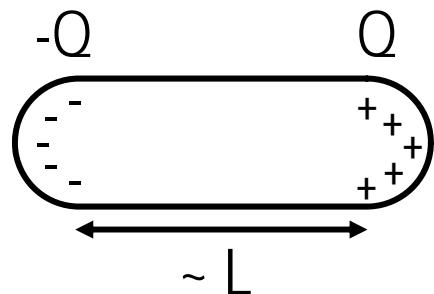
Calculation of gold antenna modes

Antenna modes:

D=80nm,L=200nm; ratio=2.5

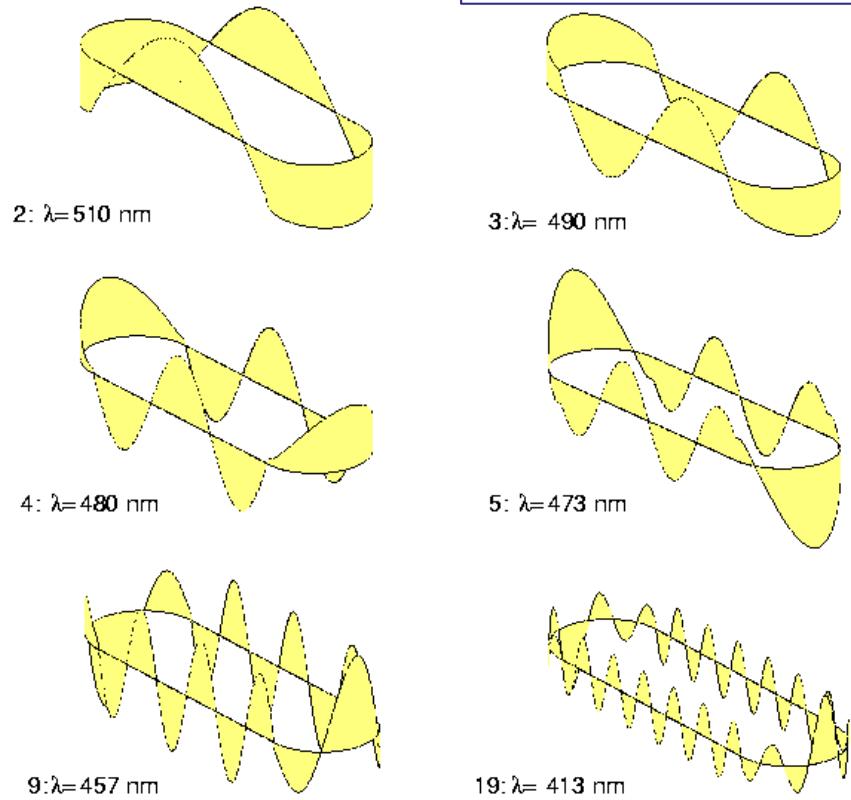
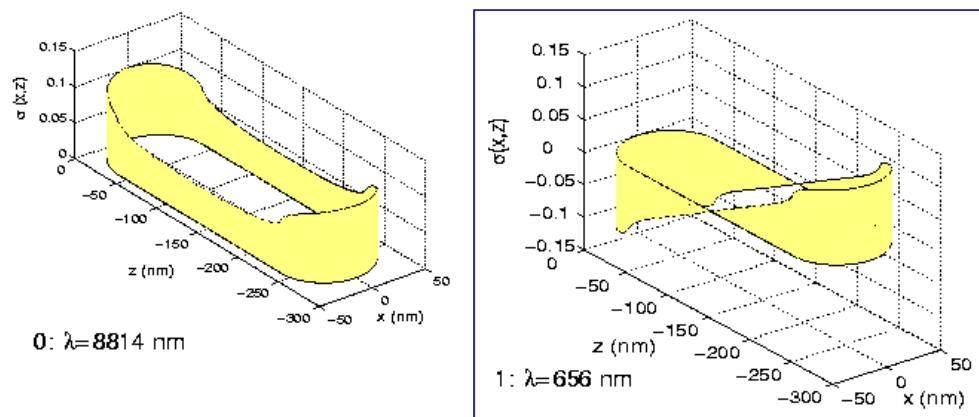
Dipole response:

$$L \propto \lambda/2$$

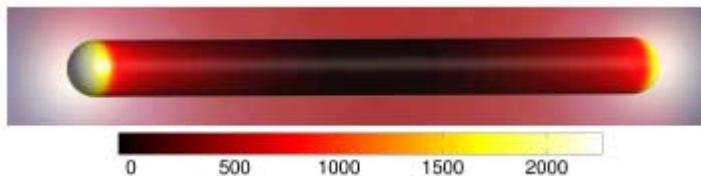


Aizpurua et al. Physical Review B 71, 235420 (2005)

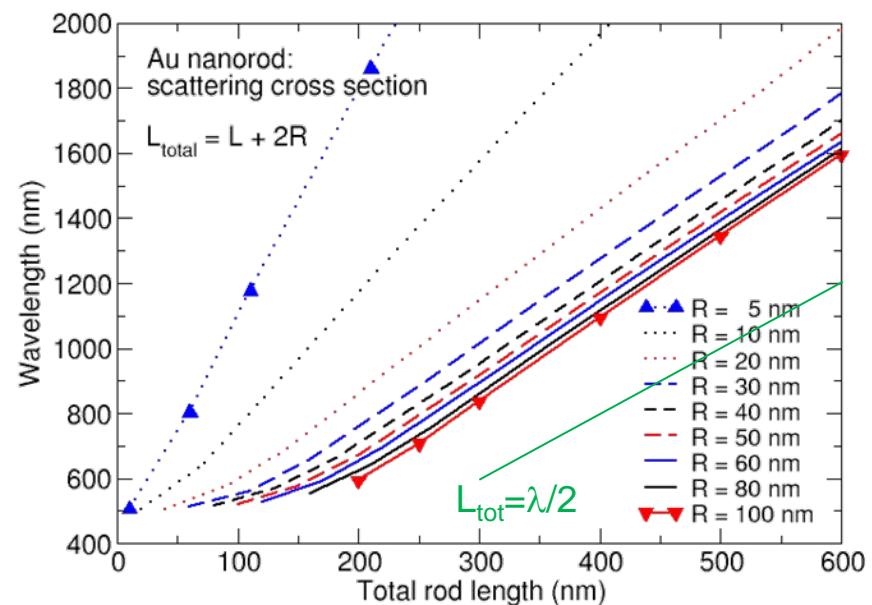
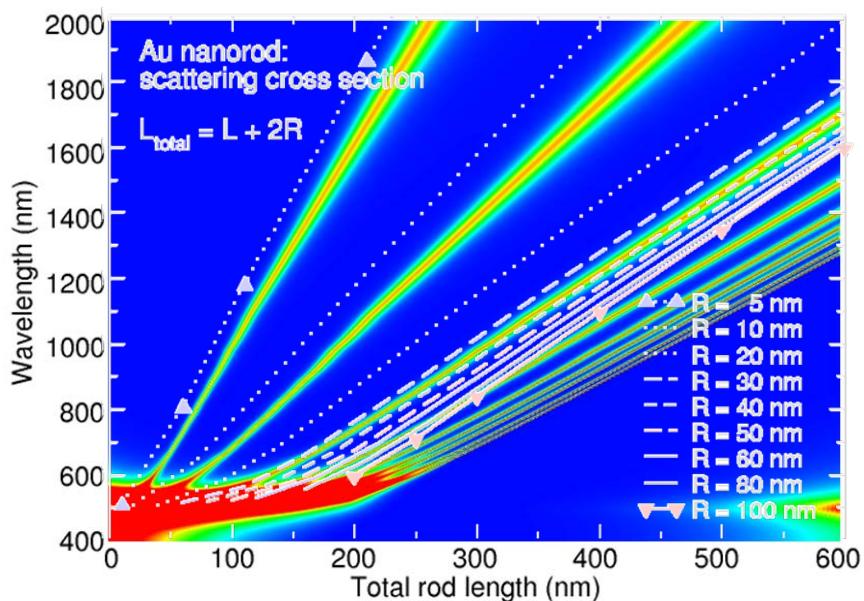
J. Aizpurua, Lecture given at SSOP
Porquerolles, Sept. 2009



Metallic nanorod as a $\lambda/2$ optical antenna



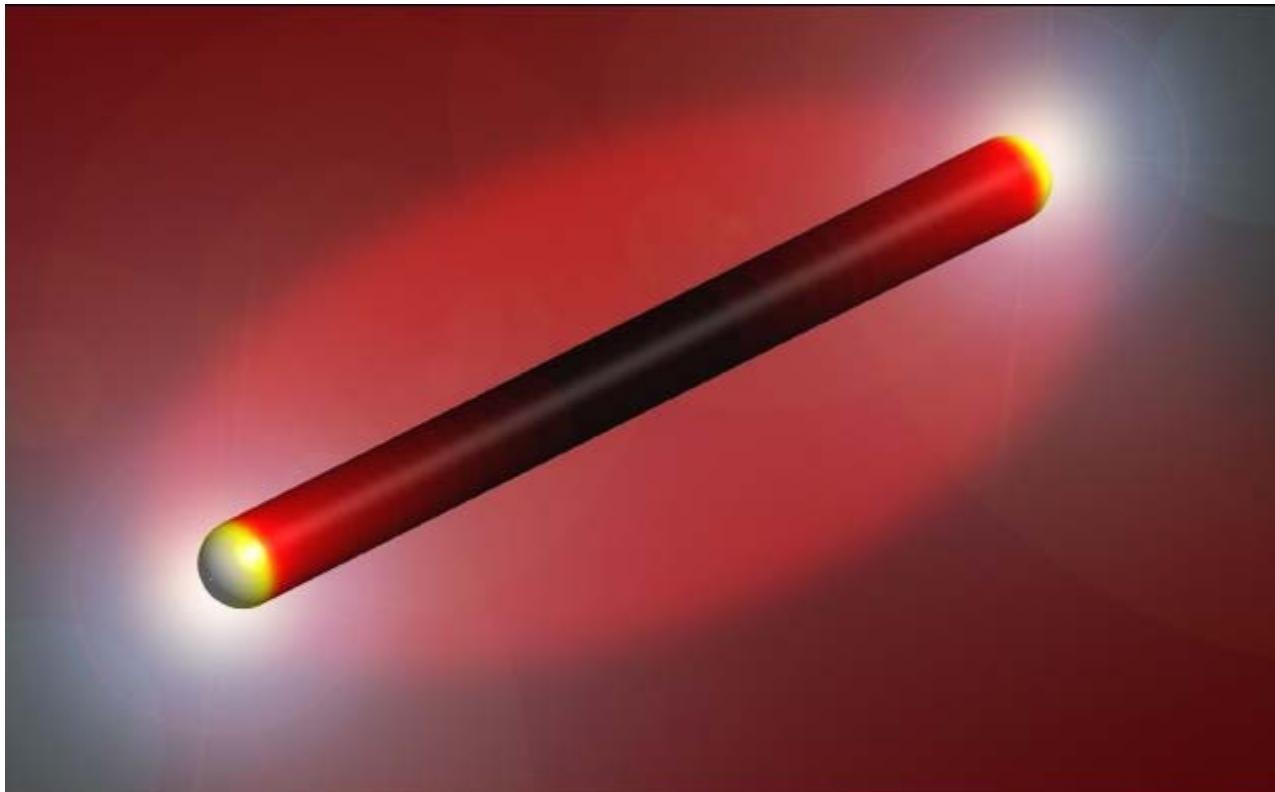
Mapping the plasmon resonances of metallic nanoantennas



$$(q^2 - \varepsilon k^2)^{\frac{1}{2}} I_0((q^2 - \varepsilon k^2)^{\frac{1}{2}} R) K_1((q^2 - k^2)^{\frac{1}{2}} R) + \varepsilon (q^2 - k^2)^{\frac{1}{2}} I_1((q^2 - \varepsilon k^2)^{\frac{1}{2}} R) K_0((q^2 - k^2)^{\frac{1}{2}} R) = 0$$

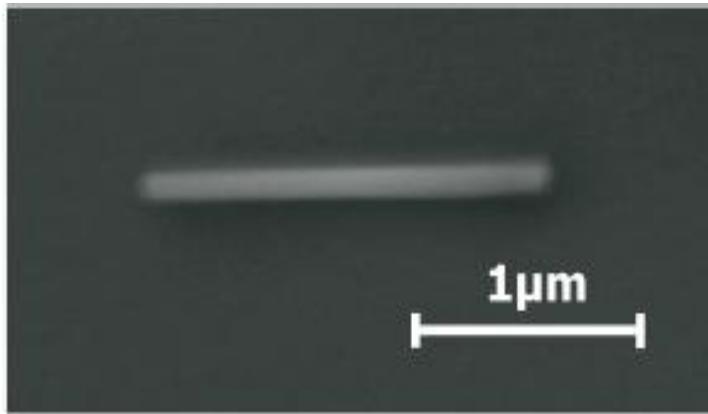
$$q = \pi/L_{\text{tot}}$$

Optical nanoantenna resonant at $\lambda=3.41\mu\text{m}$
with $L=1.31\mu\text{m}$ and $D=100\text{nm}$



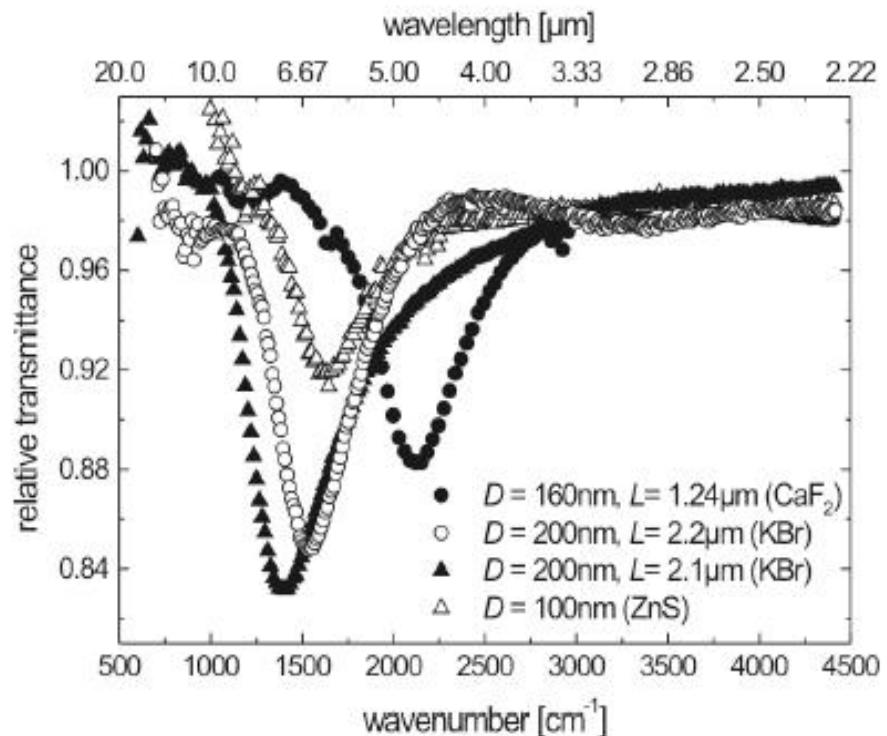
Finding the right nanowire resonance for IR spectroscopy

Experiments by Prof. A. Pucci's group (Heidelberg, Germany)



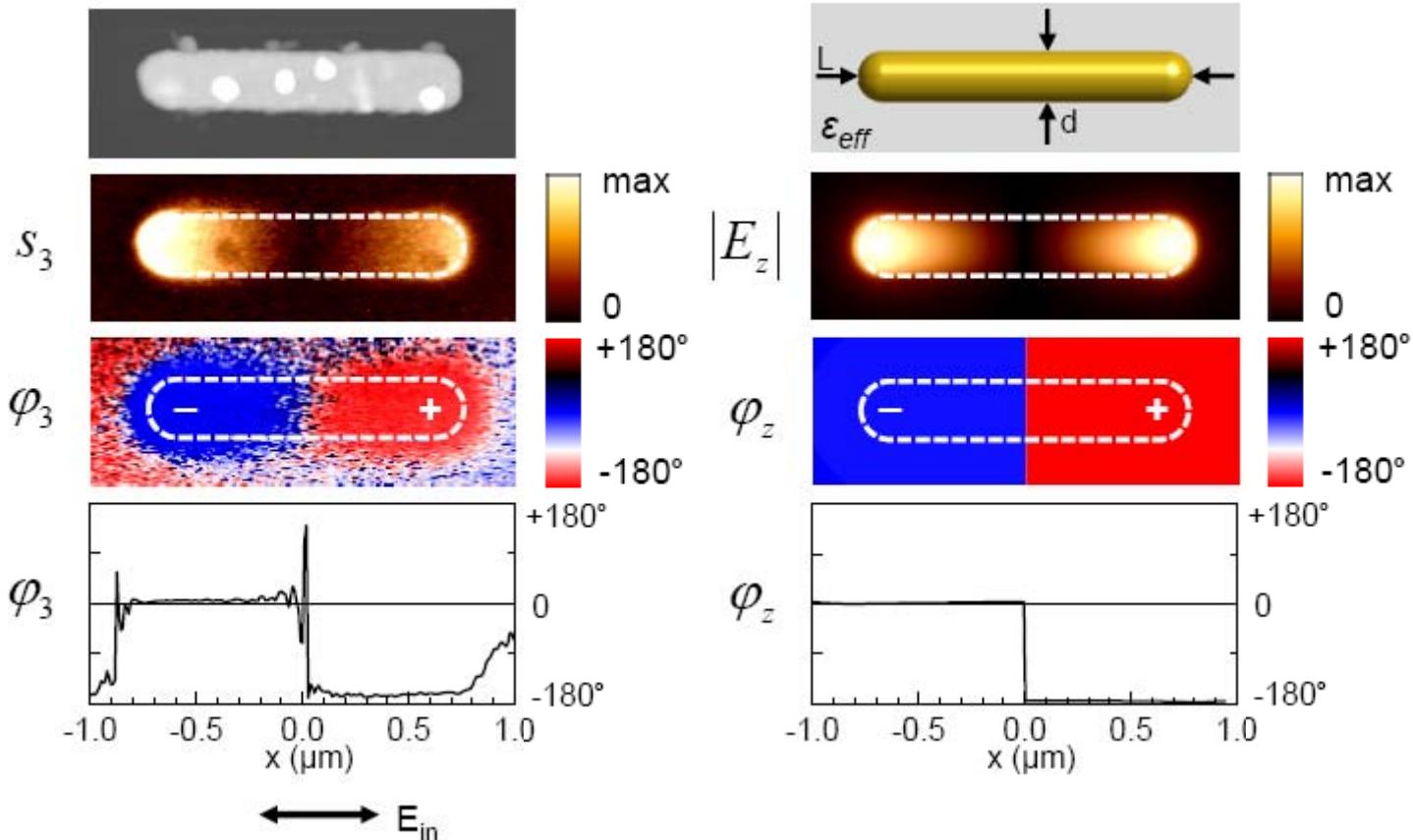
Gold nanowire ($L=1.5\mu\text{m}$ and $D=100\text{nm}$,
on a silicon wafer)

SEM image: perfect cylindrical shape



Relative IR transmittance spectra
Electric field along the long wire axis

Near-field mapping of IR nanoantennas

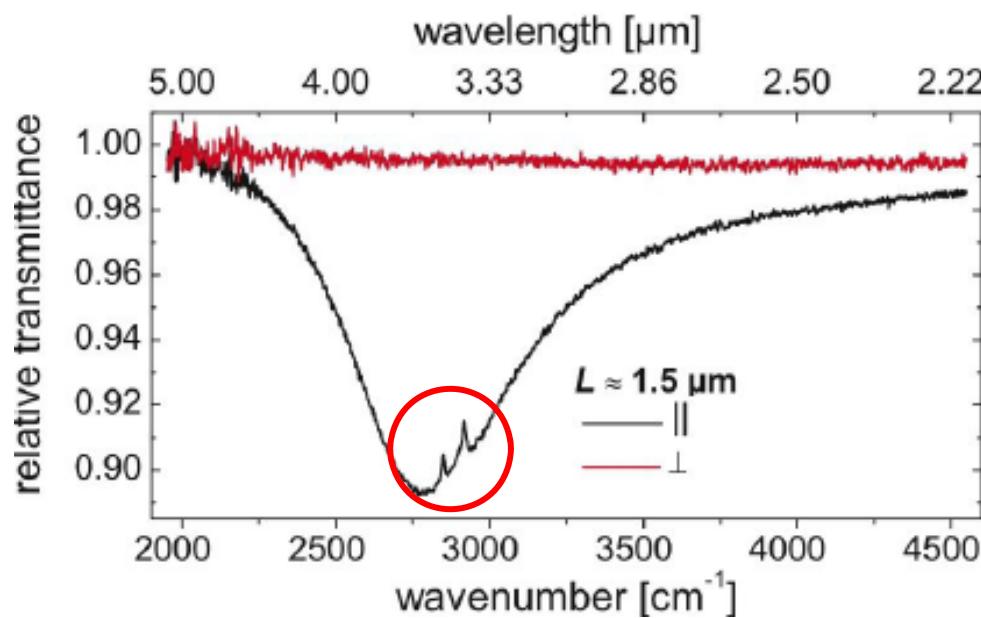
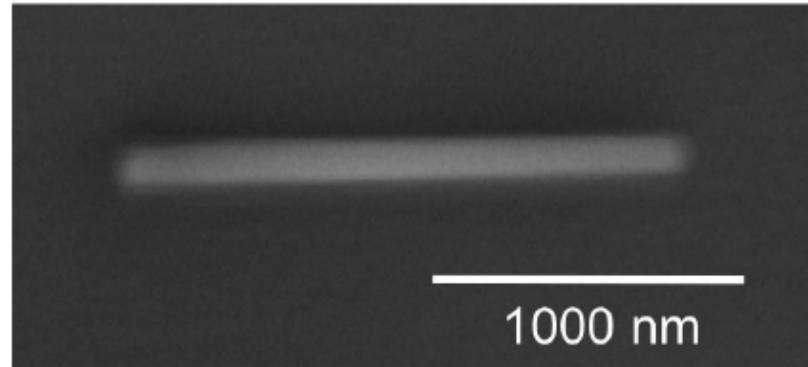


Experiment by Martin Schnell,
R. Hillenbrand's group

Calculation by A. Garcia-Etxarri,
San Sebastian

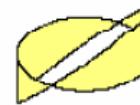
$\lambda/2$ antenna enhanced IR spectroscopy

Relative IR transmittance of ODT molecules on a gold nanowire

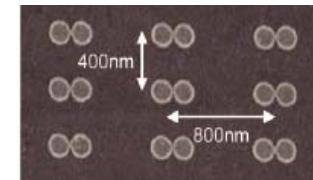


Outline

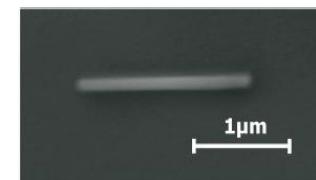
- Basics: Plasmonics



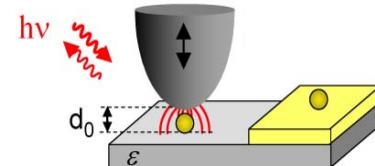
- Optical antennas for SERS



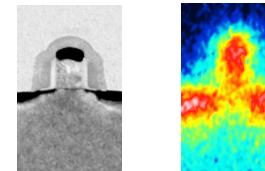
- $\frac{1}{2} \lambda$ dipole Infrared antennas for SEIRA

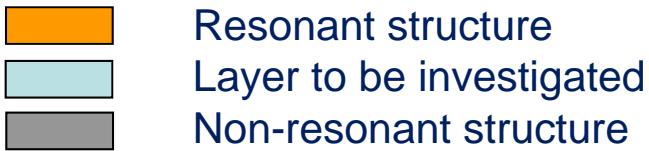


- Substrate-Enhanced Infrared Near-Field Microscopy

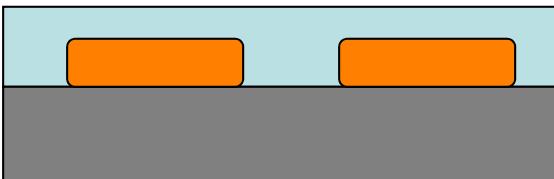


- THz Near-field Nanoscopy

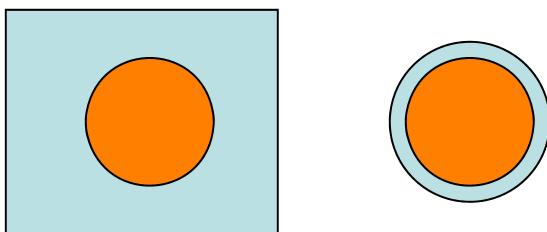




Resonant triangles (coated)

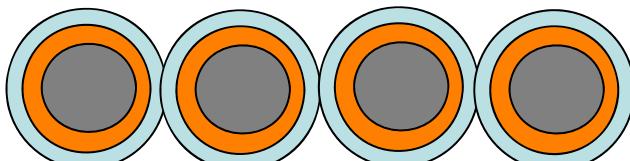


T.R. Jensen et al., J. Phys. Chem B, 104, 10549 (2000)



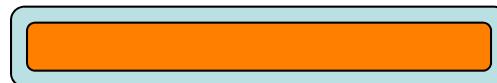
M.S. Anderson, App. Phys. Lett. **83**, 2964 (2003)

Nanoshell arrays



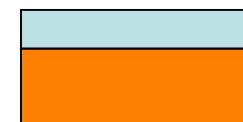
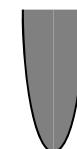
J. Aizpurua, Lecture given at SSOP
H. Wang et al., Angew. Chem. **46**, 9040 (2007)
Porquerolles, Sept. 2009

Resonant rod (coated)

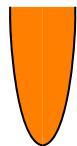
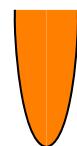


F. Neubrech et al., APL **89**, 253104 (2006)

Near-field IR spectroscopy



Resonant substrate



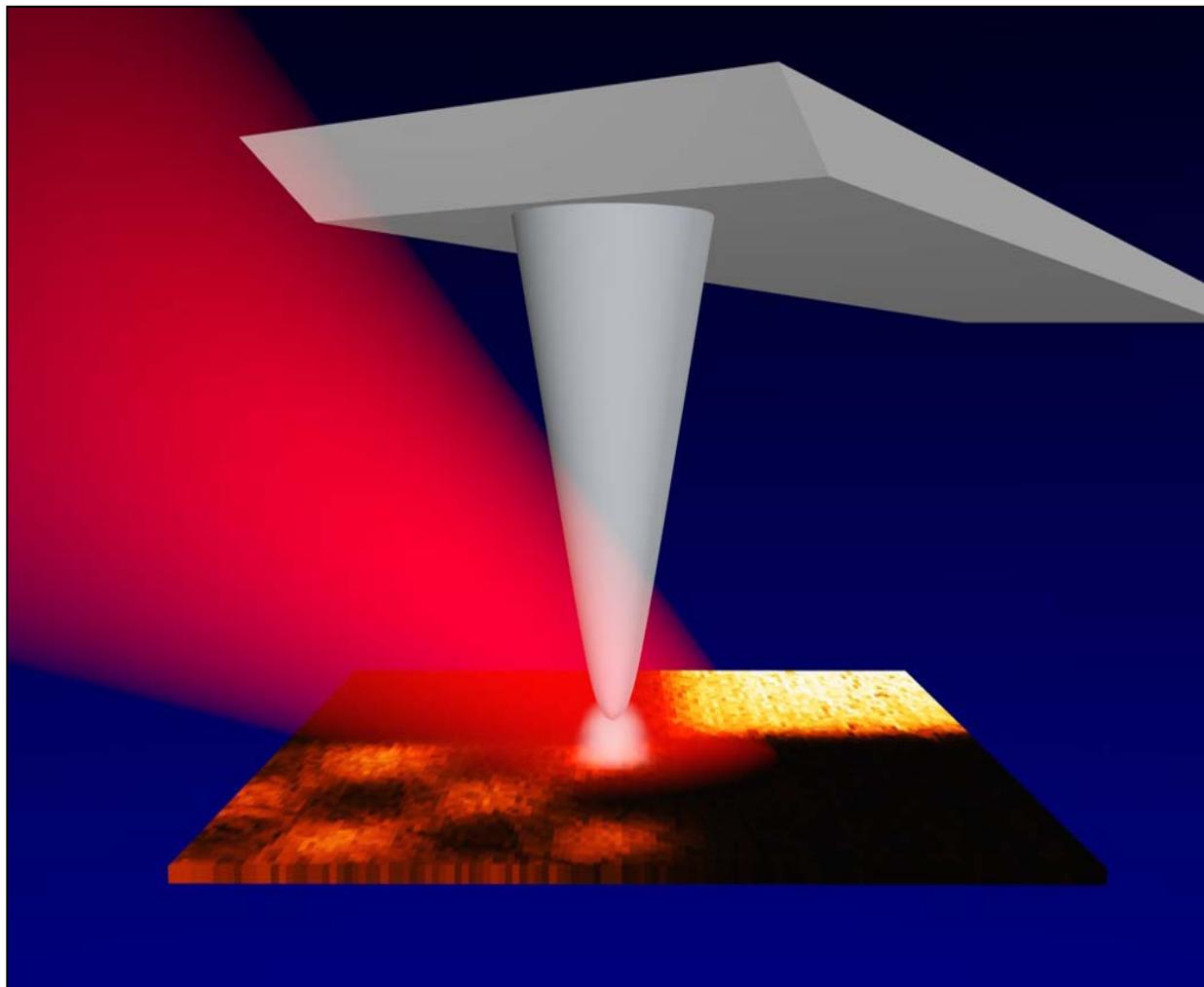
Resonant tip

Resonant tip & substrate

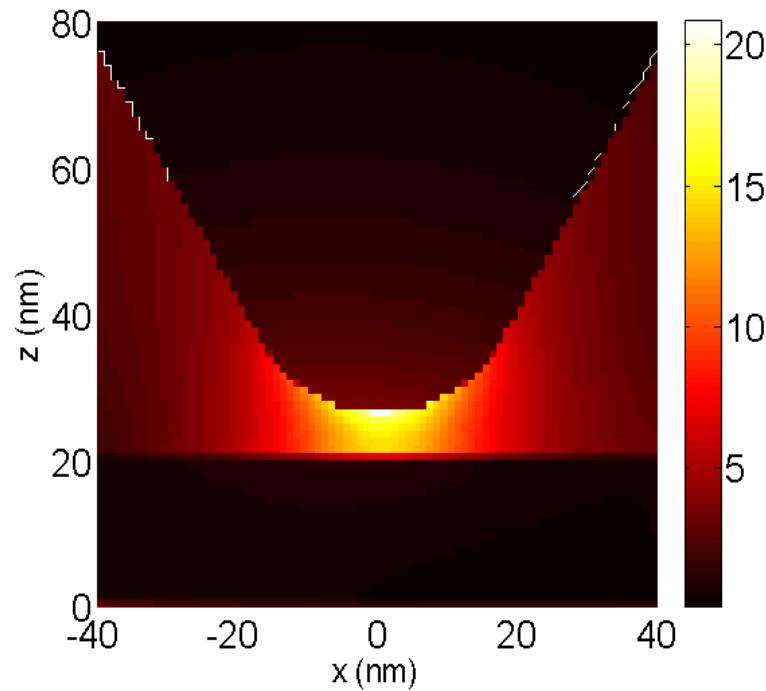
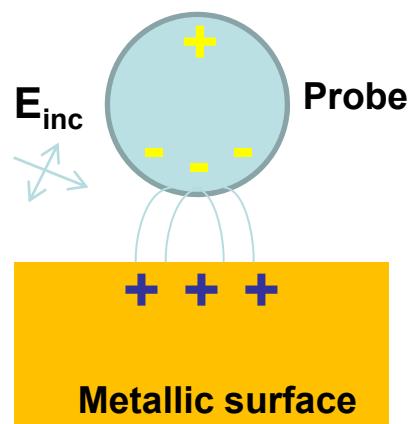
J. Aizpurua et al., Optics Exp 16, 1529 (2008)

Scattering-type Near Field Optical Microscopy

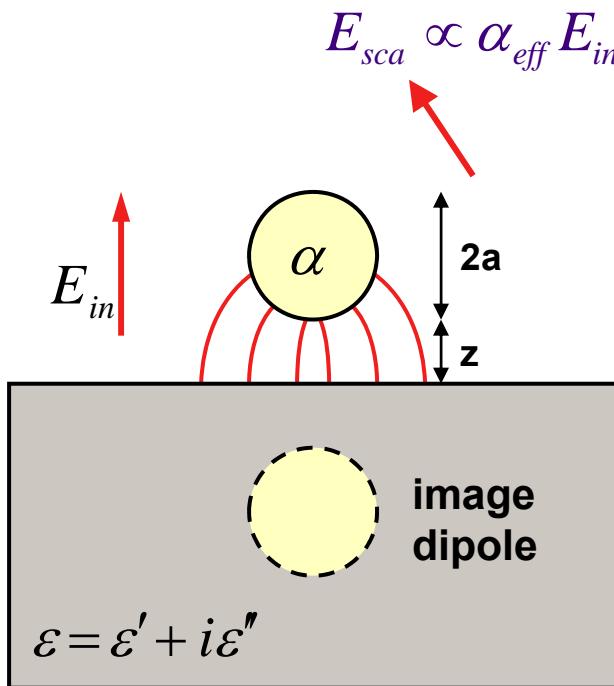
Rainer Hillenbrand



Localization of plasmons by a probe



Dipolar sphere-plane near-field interaction



Polarizability of the tip

$$\alpha = 4\pi a^3 \frac{\epsilon - 1}{\epsilon + 2}$$

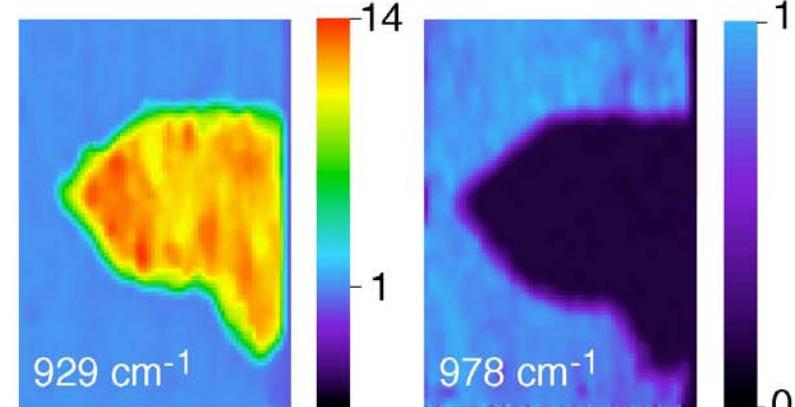
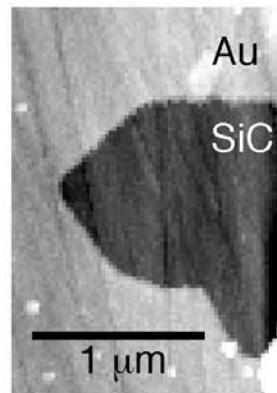
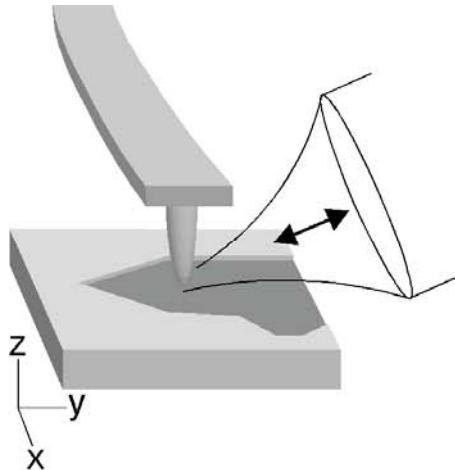
Effective polarizability of interacting dipoles

$$\alpha_{eff} = \frac{\alpha(1+\beta)}{1 - \frac{\alpha\beta}{16\pi(z+a)^3}} \quad \text{with} \quad \beta = \frac{\epsilon - 1}{\epsilon + 1}$$

- near-field interaction modifies amplitude and phase of E_{sca}
- resonance through a) sphere $\epsilon_p = -2$
b) plane $\epsilon = -1$

No multipoles included in this description

s-SNOM contrast of SiC/Au



**phonon-enhanced
near-field interaction**

- strong signals
- high spectral sharpness
- optical fingerprint

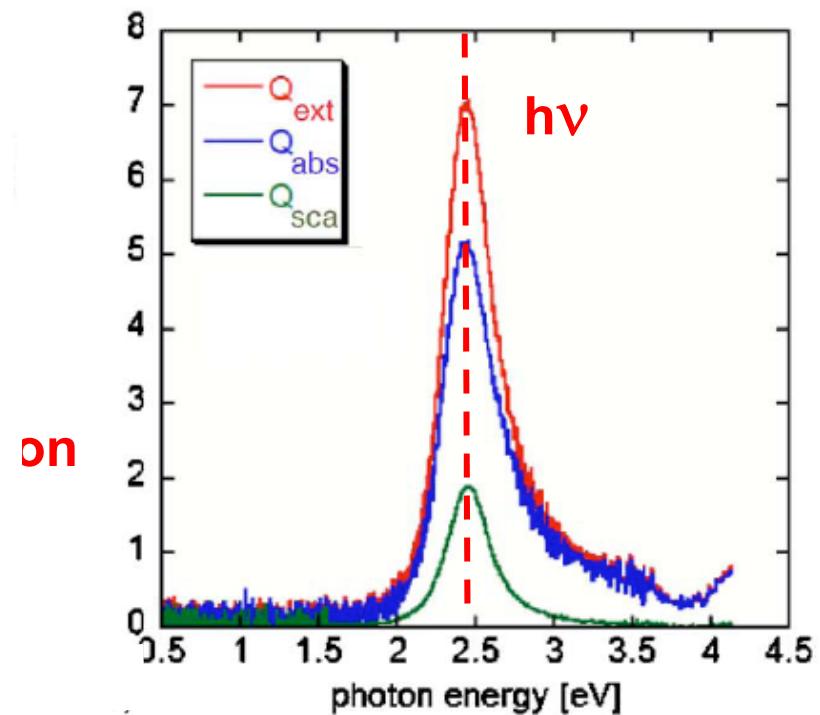
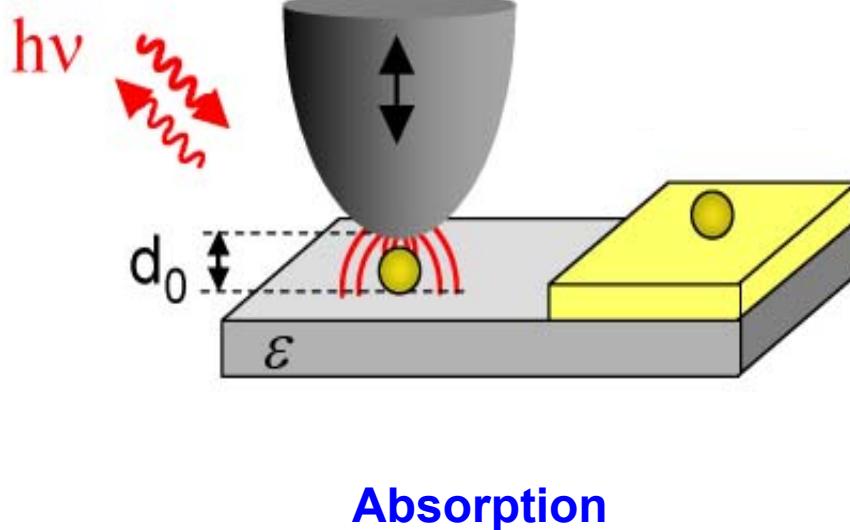


**identification of materials at
nanoscopic spatial resolution**

< $\lambda / 100$!

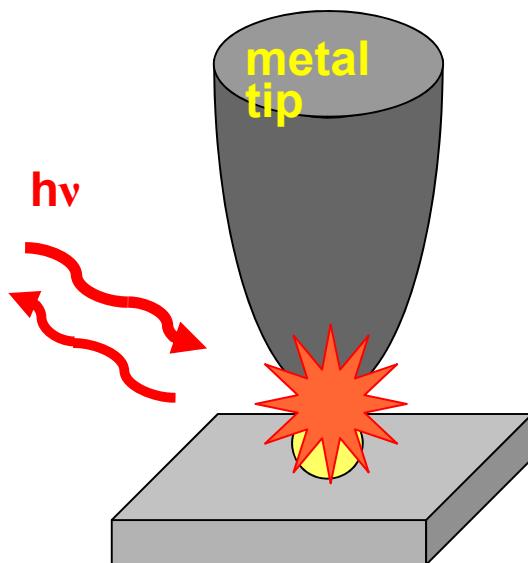
Can we do the same in a simple optical antenna?

Mapping the fields of a metal-nanoparticle



Imaging nanoparticles in the IR

Label-free high-resolution optical imaging of nanoparticles



Probing - tip based chemically specific methods

IR

$$C_{sca} \sim d^6/\lambda^4$$

$$10^{-28} \text{ cm}^2$$

(1 nm particle @ mid-IR)

Raman

$$C_{sca} \sim$$

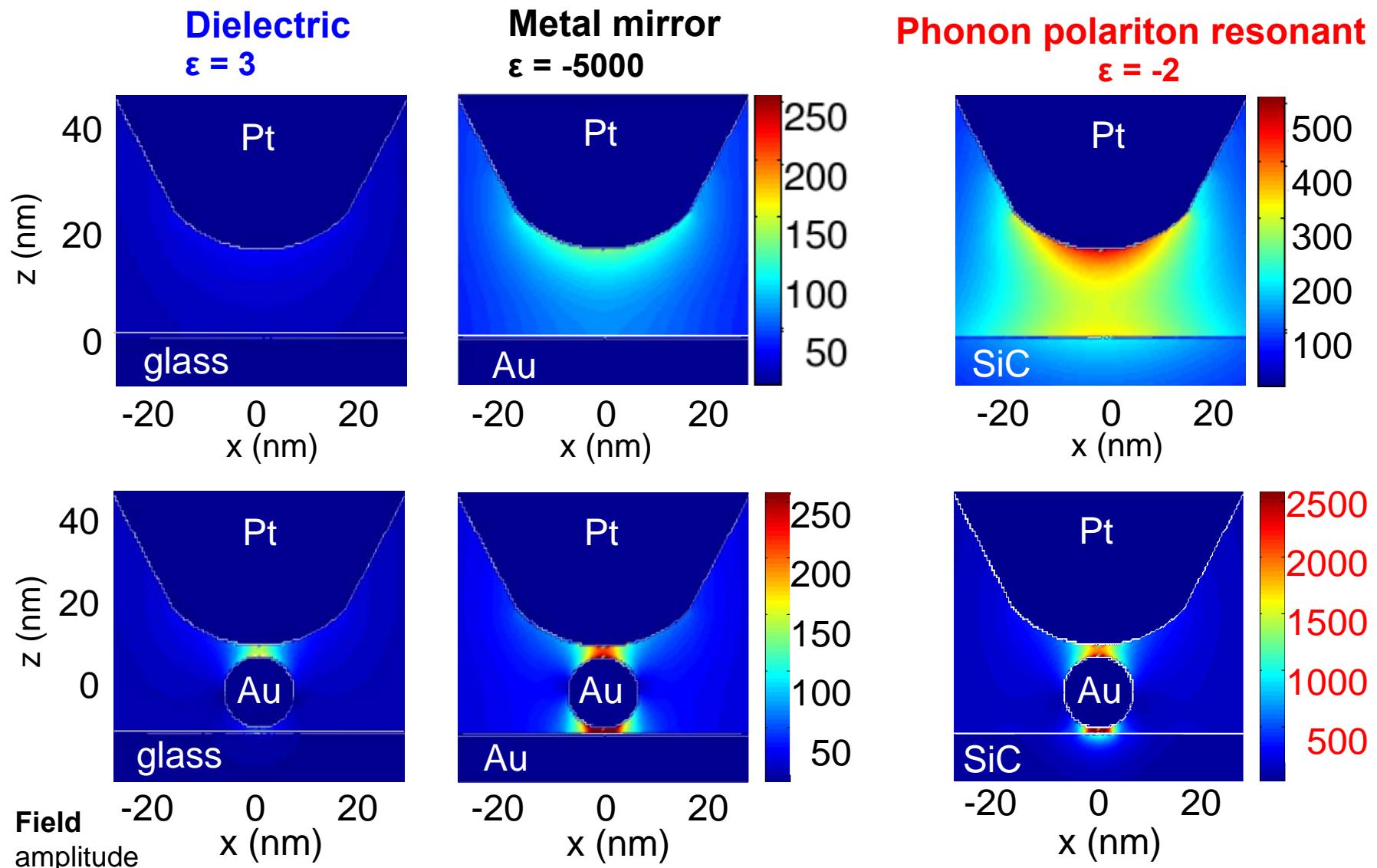
$$10^{-30} \text{ cm}^2$$

(typical molecule)

extremely small scattering cross-sections !

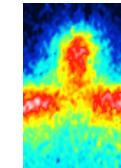
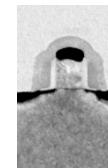
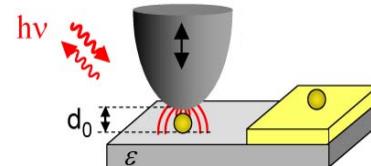
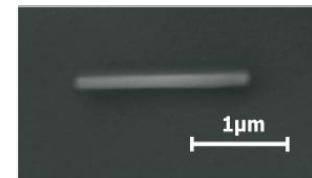
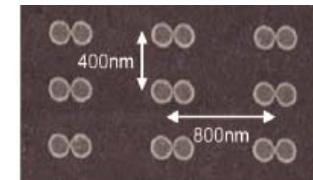
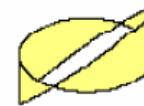
Solution \longrightarrow field enhancement in an antenna cavity!

Substrate-enhanced IR microscopy

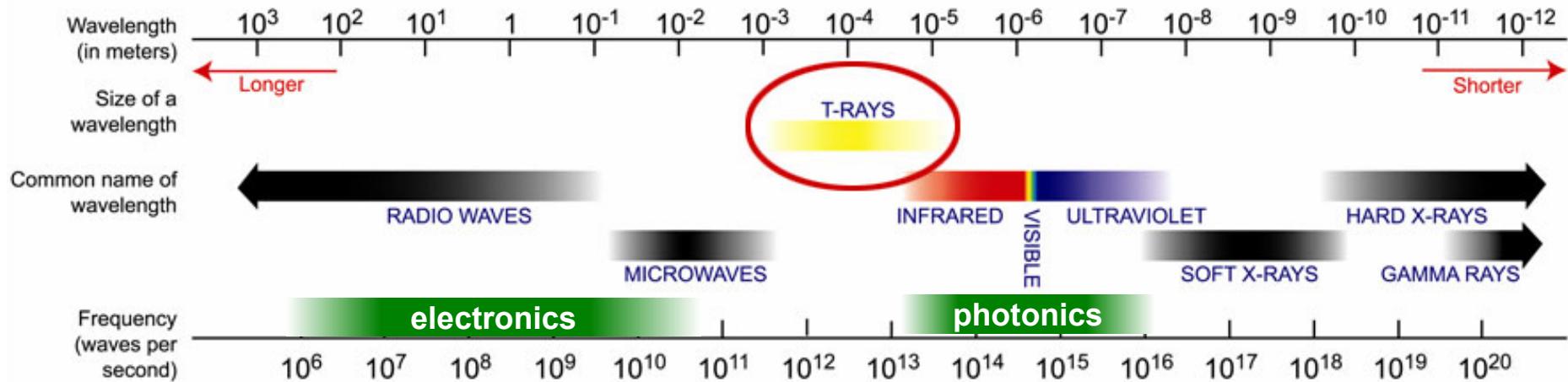


Outline

- Basics: Plasmonics
- Optical antennas for SERS
- Infrared antennas for SEIRA
- Substrate-Enhanced Infrared Near-Field Microscopy
- THz Near-field Nanoscopy

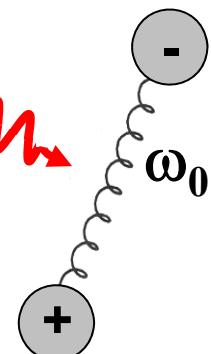


Terahertz radiation (THz, T-RAYS)



Frequencies between IR and THz (far-IR) are highly sensitive to

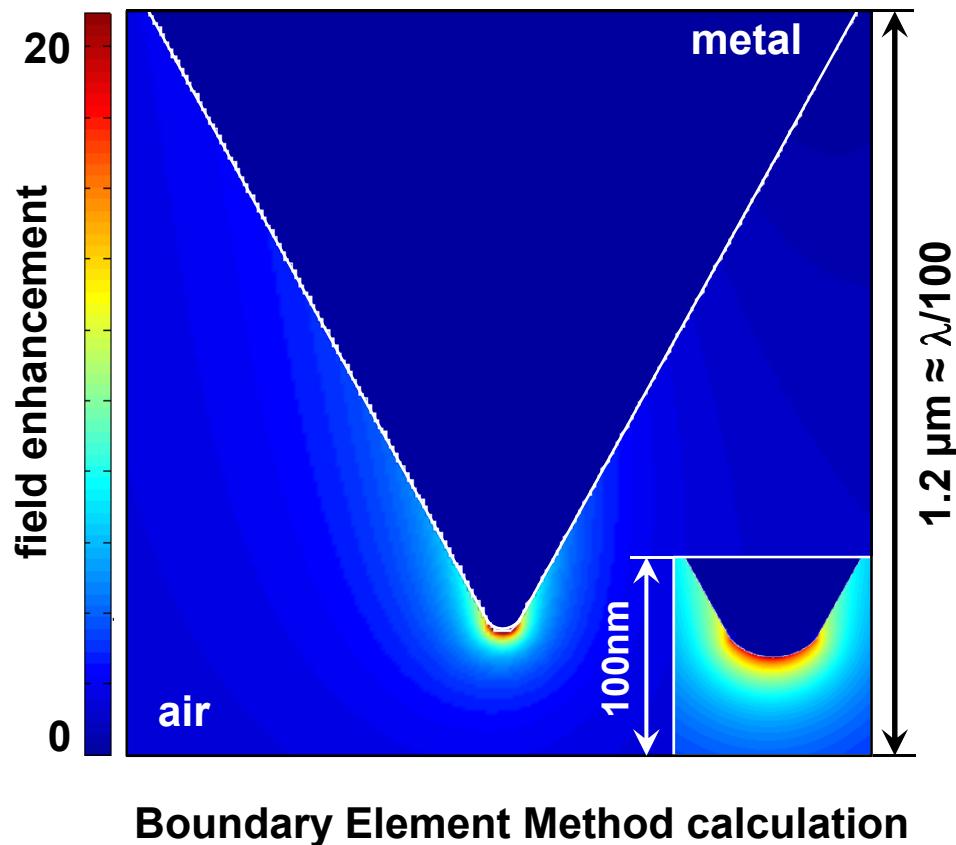
- molecular vibrations → chemical composition
- crystal lattice vibrations → structural properties
- plasmons in doped semiconductors → electron properties 
-



BUT: spatial resolution $> \lambda/2 \approx 10\text{-}100 \mu\text{m}$

Theory predicts nanoscale confined THz fields

- Full electrodynamic calculation
- for **2.54 THz ($\lambda \approx 118 \mu\text{m}$)** predicts field enhancement at tip apex
- Tip length: **1 μm ($\approx \lambda / 118$)**
- **30 nm field confinement** at tip apex, like for VIS or IR frequencies
- Mechanism: **lightning-rod effect**



nanoscale confinement of THz fields can be achieved with metal tips much smaller than the wavelength, e.g. AFM tips

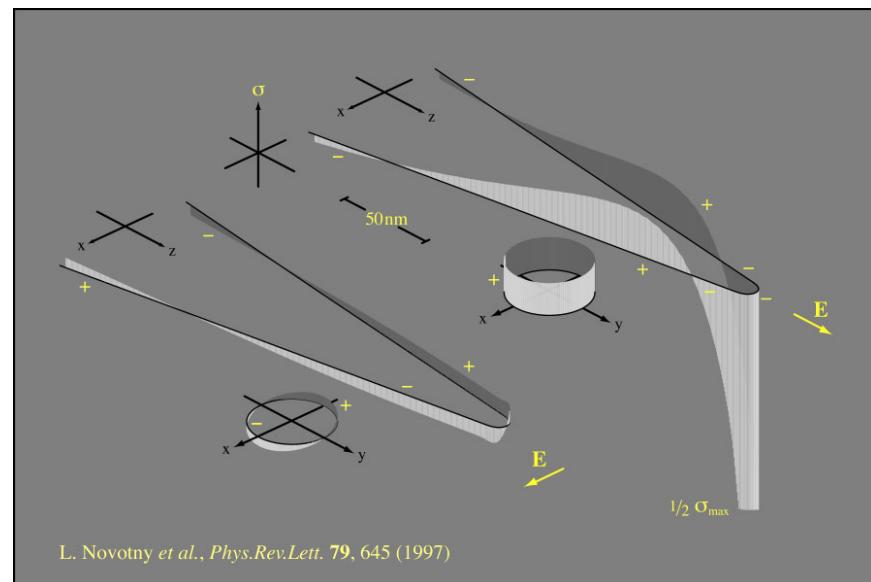
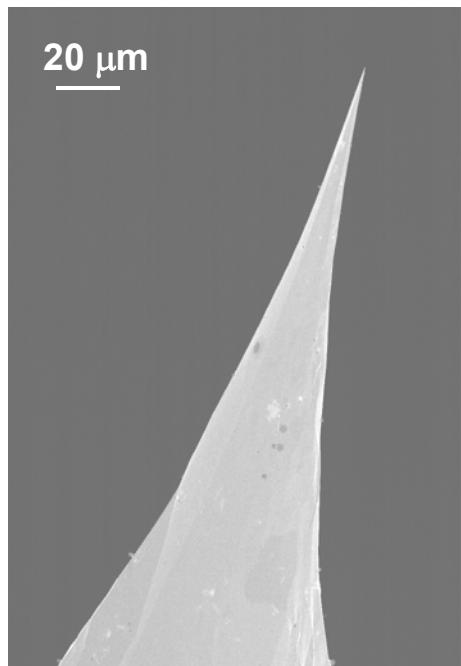
Lightning rod effect



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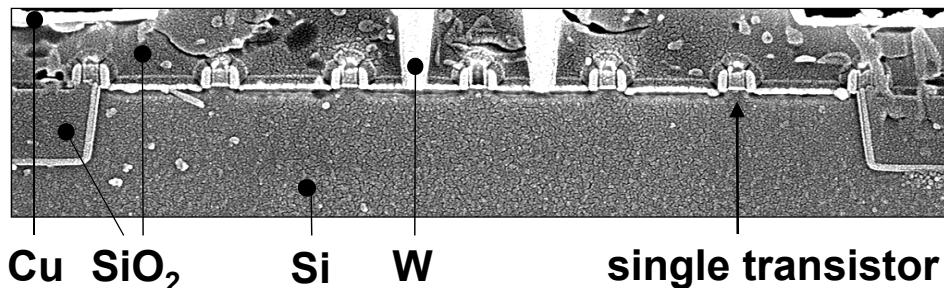
- **Lightning rod effect**
- Needs:**
- Geometric singularity
 - Proper polarization
 - Good conductor



L. Novotny *et al.*, Phys.Rev.Lett. **79**, 645 (1997)

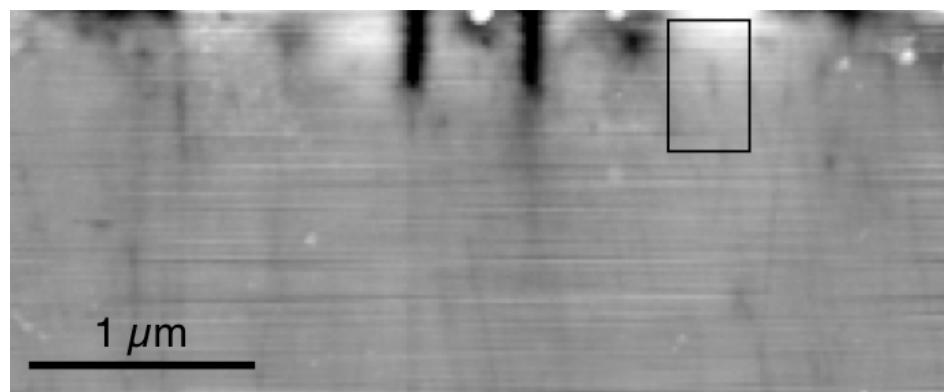
THz s-SNOM can map free carriers in semiconductor devices

SEM

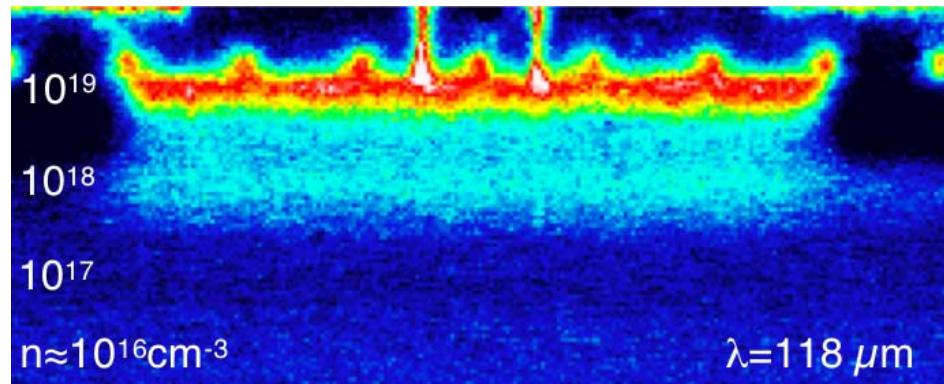


test structure
containing transistors of
65 nm - technology

Topography

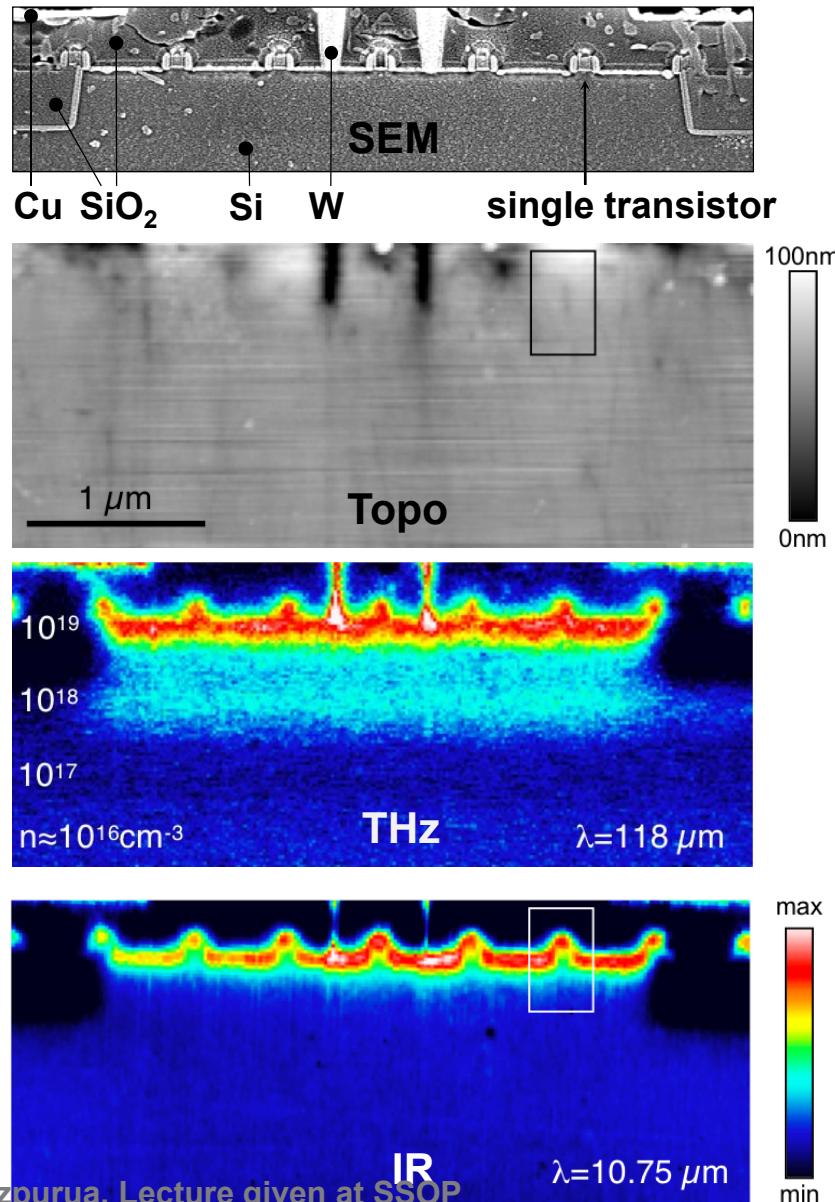


THz image



THz image exhibits
material and
free-carrier contrast

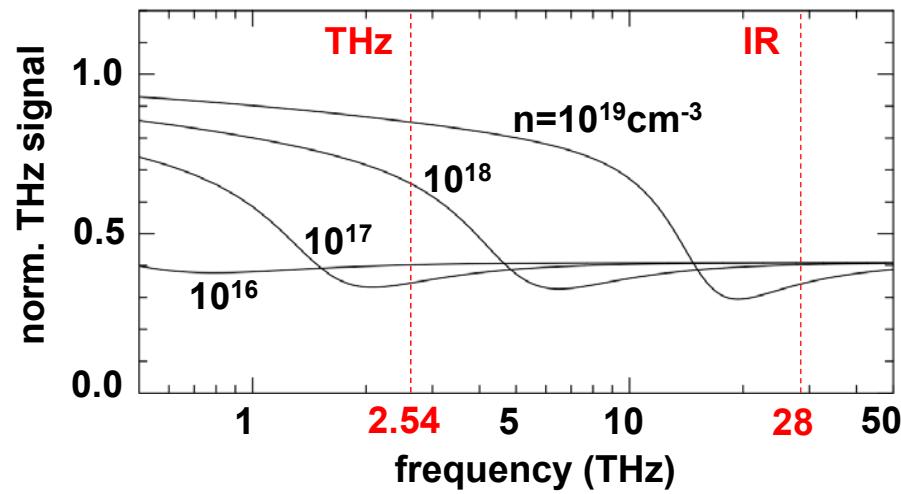
THz s-SNOM can map free carriers in semiconductor devices



For doped semiconductors $\epsilon(\omega)$ depends on concentration of free carriers:

$$\epsilon(\omega) = \epsilon_{\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \right) \text{ with } \omega_p^2 = \frac{n e^2}{\epsilon_0 \epsilon_{\infty} m \cdot m_0}$$

Dipole model explains free-carrier contrast



A. Huber et al. Nano Letters 8, 3766 (2008)