



**The Abdus Salam  
International Centre for Theoretical Physics**



**2328-11**

**Preparatory School to the Winter College on Optics and the Winter College on  
Optics: Advances in Nano-Optics and Plasmonics**

*30 January - 17 February, 2012*

**Optical antennas: Spectroscopy, Microscopy and other applications**

J. Aizpurua

*Center for Materials Physics, CSIC-UPV/EHU and Donostia International Physics  
Center - DIPIC  
Spain*

# Optical antennas: Spectroscopy, Microscopy and other applications

*Javier Aizpurua*



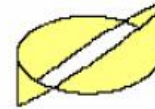
<http://cfm.ehu.es/nanophotonics>

*Center for Materials Physics, CSIC-UPV/EHU  
and Donostia International Physics Center - DIPC  
Donostia-San Sebastián, the Basque Country, Spain*

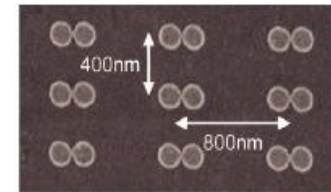
***Winter College on Optics: Advances in Nano-Optics and Plasmonics  
February 6-17, 2012  
The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy***

# Outline

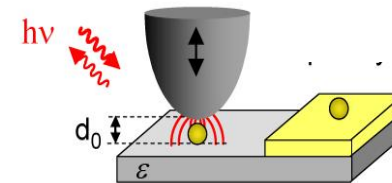
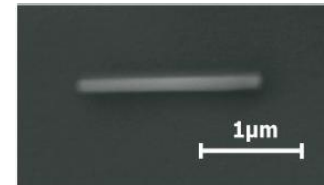
- Optical antennas: Basics



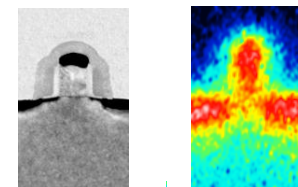
- Playing with antenna modes



- Optical antennas for Enhanced Spectroscopy: Coupling for SERS

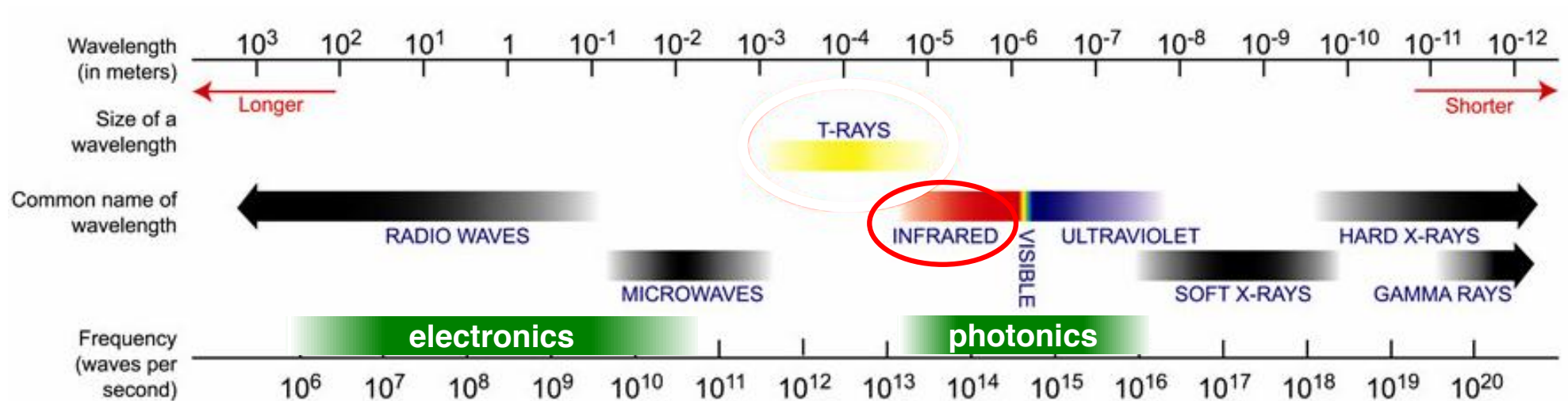


- More applications of optical antennas

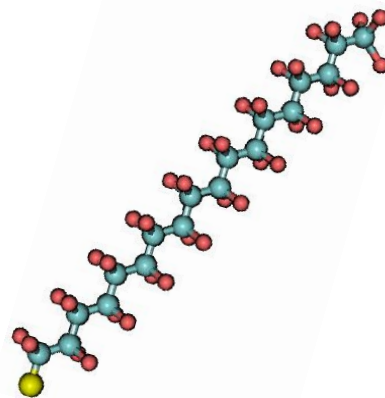


# Infrared spectroscopy

Resonant antennas for enhanced signal of molecular vibrations



**Molecular fingerprints**



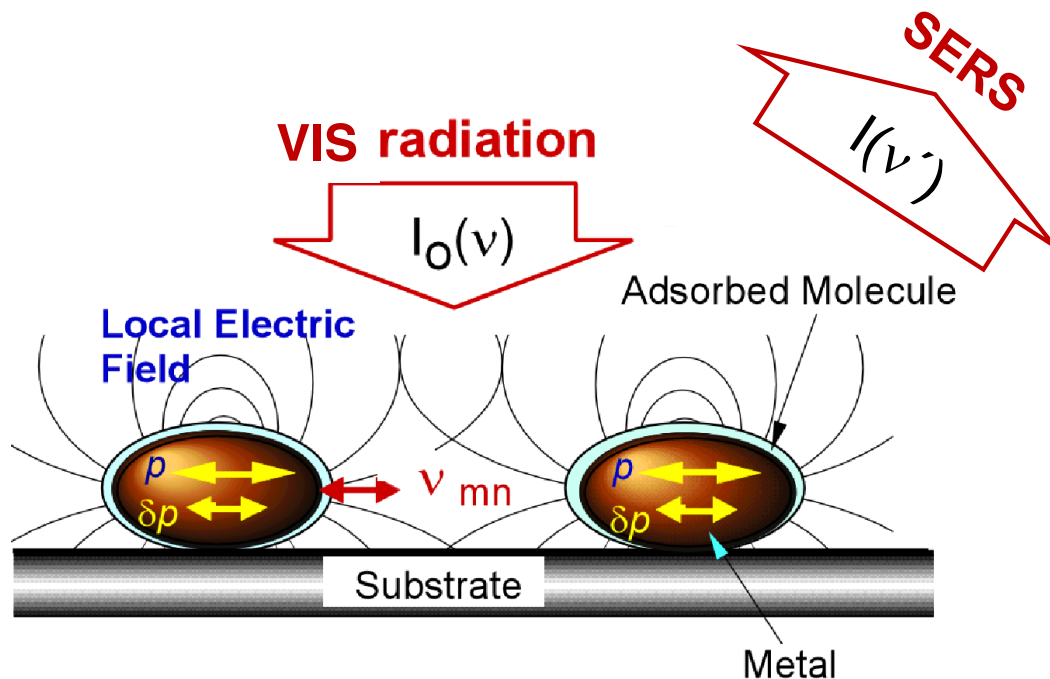
**Raman spectroscopy**

**IR absorption spectroscopy**

# Surface-Enhanced Raman Scattering (SERS)

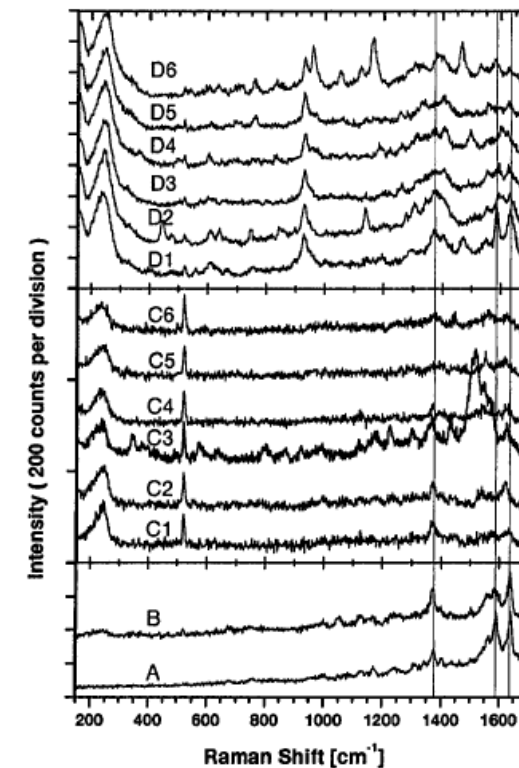
Resonant antennas for enhanced signal of molecular vibrations

## Concept



## Molecular fingerprints

Identifying molecular vibrations for **selective** detection of species in **small volumes**



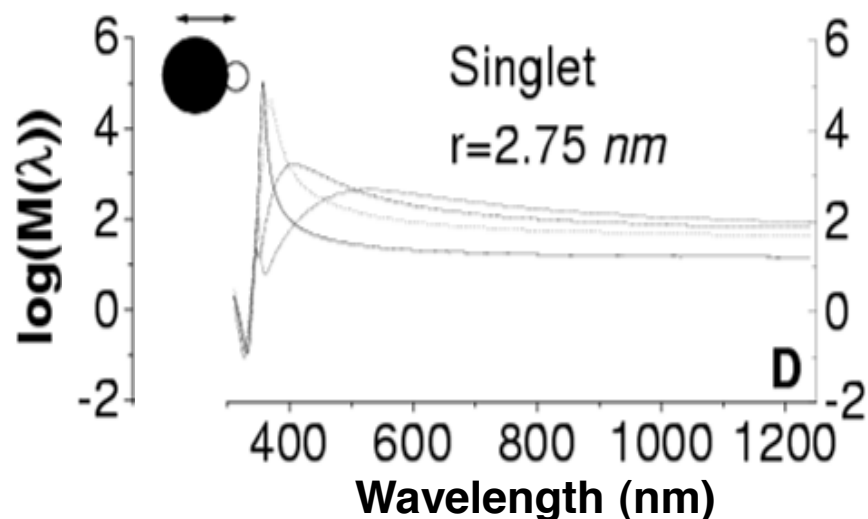
# Surface Enhanced Raman Scattering, SERS

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  $\omega_V \ll \omega_I$

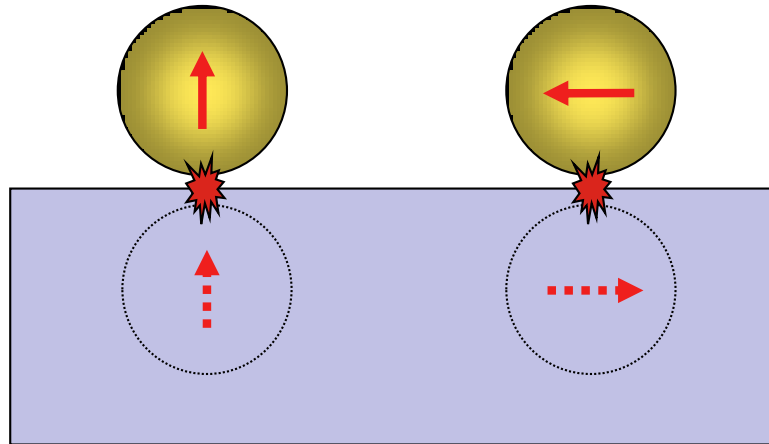
$$M_i^{EM} = \left| E^L(\omega_I) / E^I(\omega_I) \right|^4$$



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

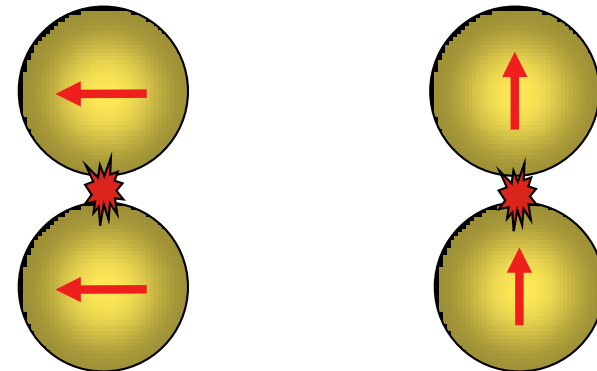
# Near-field coupling – simple systems

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

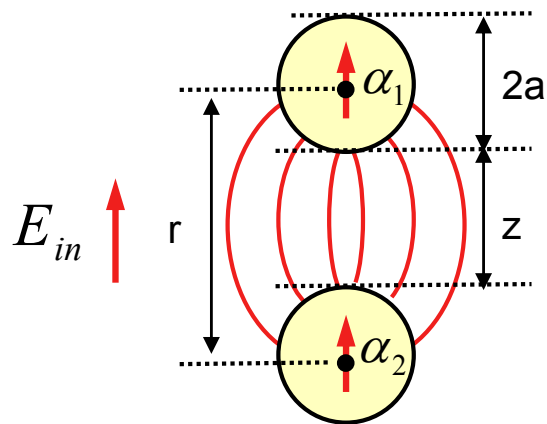
# Dipolar sphere-sphere near-field interaction

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

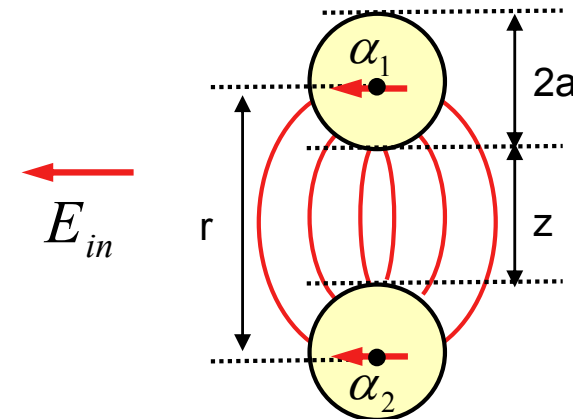
Scattered field:

$$E_{sca} \propto \alpha_{eff} E_{in}$$

Effective polarizability of interacting dipoles (dipole approximation):



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

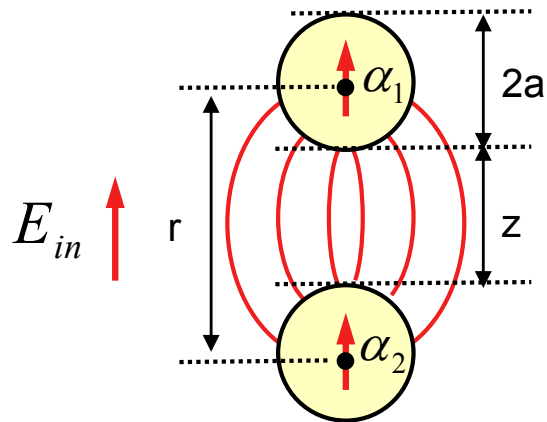


$$\alpha_{eff} = \frac{\alpha_1 + \alpha_2 - \frac{\alpha_1 \alpha_2}{2\pi r^3}}{1 - \frac{\alpha_1 \alpha_2}{16\pi^2 r^6}}$$



# Resonance shift effects – two resonant spheres

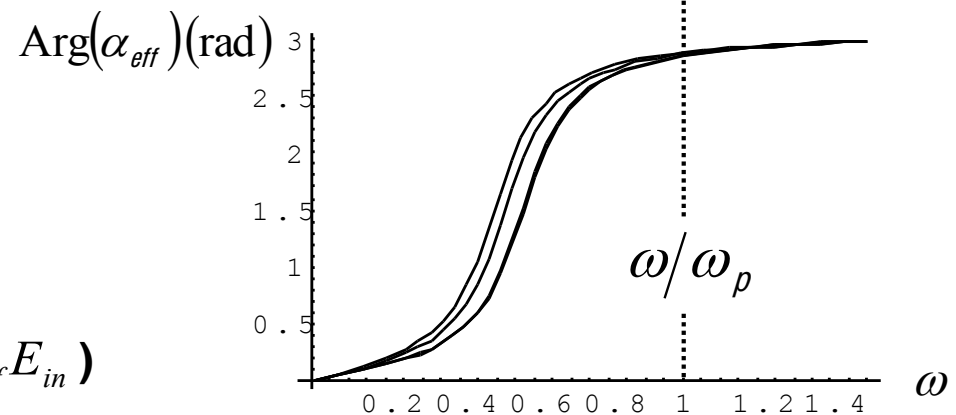
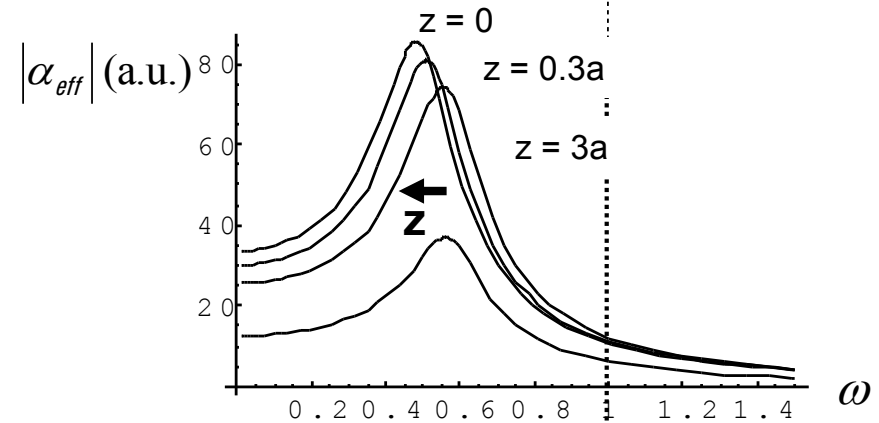
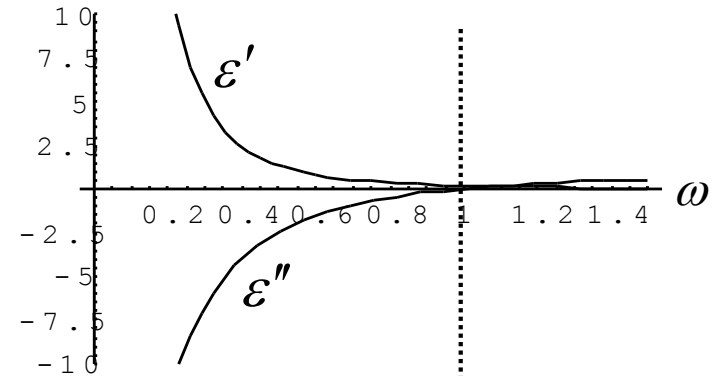
2 metal spheres:  $\epsilon_1 = \epsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$   
 (drude term)  $\gamma = 0.2$



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

→ dipolar approximation predicts

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



# Two near-field interacting gold discs I

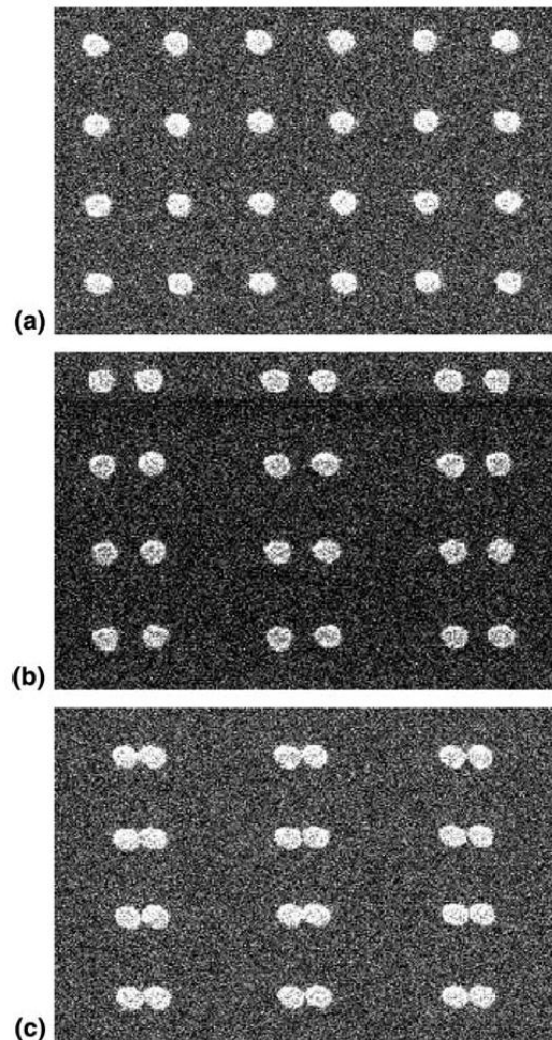
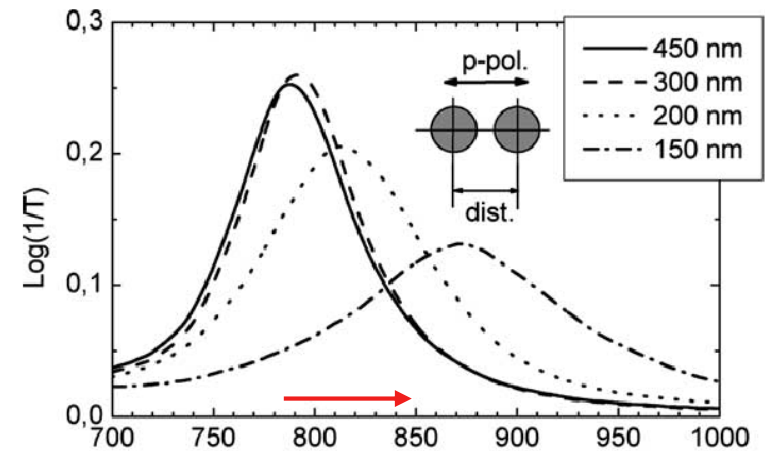
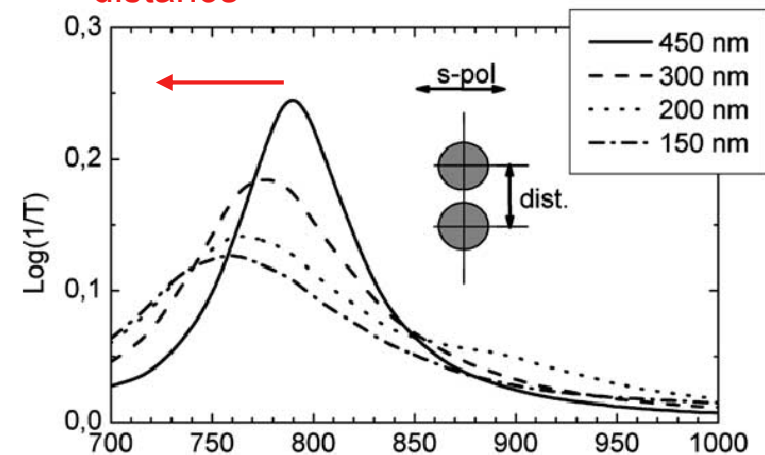


Fig. 1. SEM images of particle pair samples with varying interparticle distance (center-to-center) of (a) 450 nm, (b) 300 nm and (c) 150 nm. The particle diameter is 150 nm, the particle height is 17 nm.

W. Rechenberger et.al., *Opt. Commun.* **220**, 137 (2003)



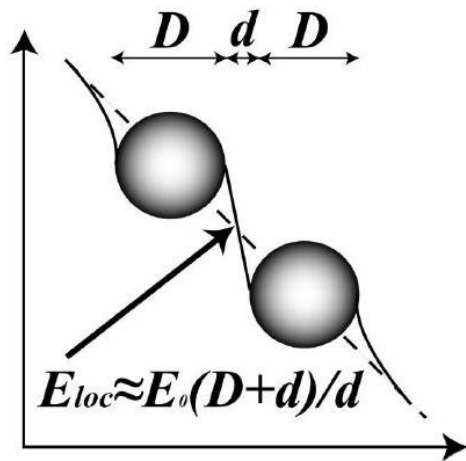
(a) decreasing distance



(b)

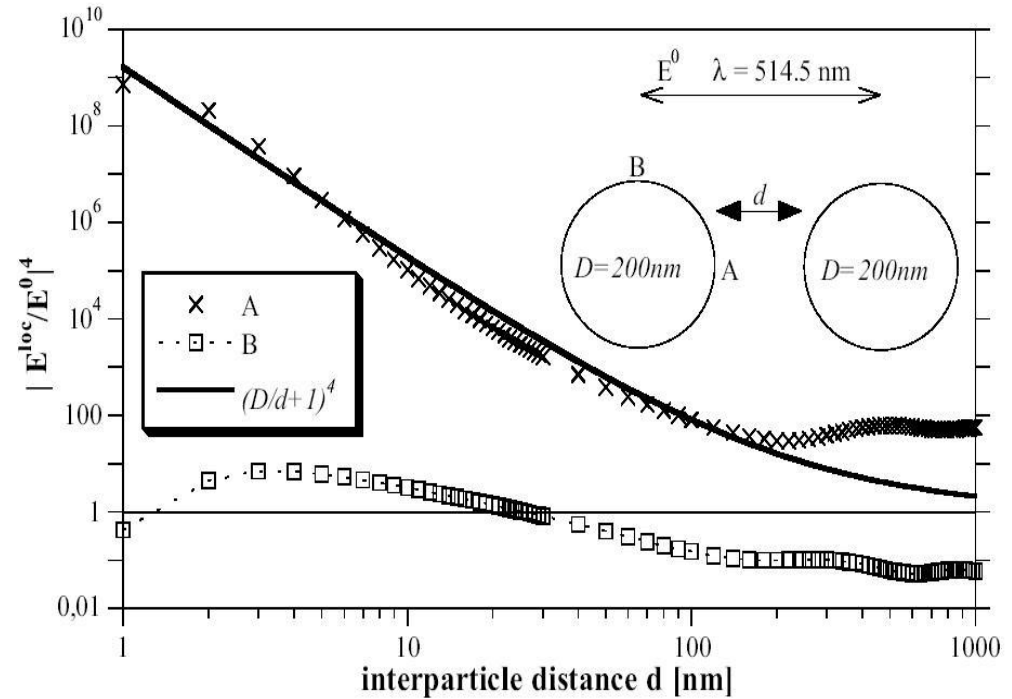
Fig. 2. Extinction ( $=\log(1/\text{Transmission})$ ) spectra of a 2D array of the Au nanoparticle pairs with the interparticle center-to-center distances as the parameter. The orthogonal particle separation is kept constant, as can be seen in Fig. 1. The polarization direction of the exciting light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

## Field-enhancement: geometrical squeezing



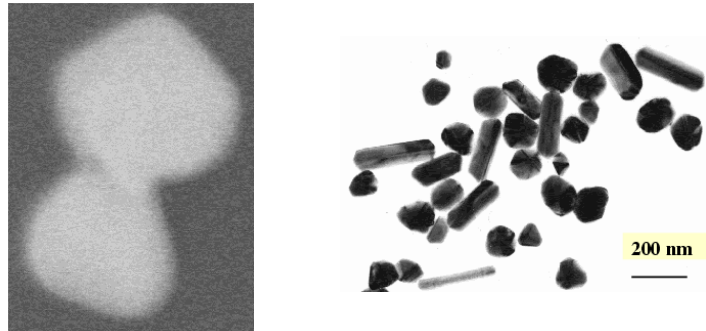
$$E_{loc} = E_0 (D+d)/d$$

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



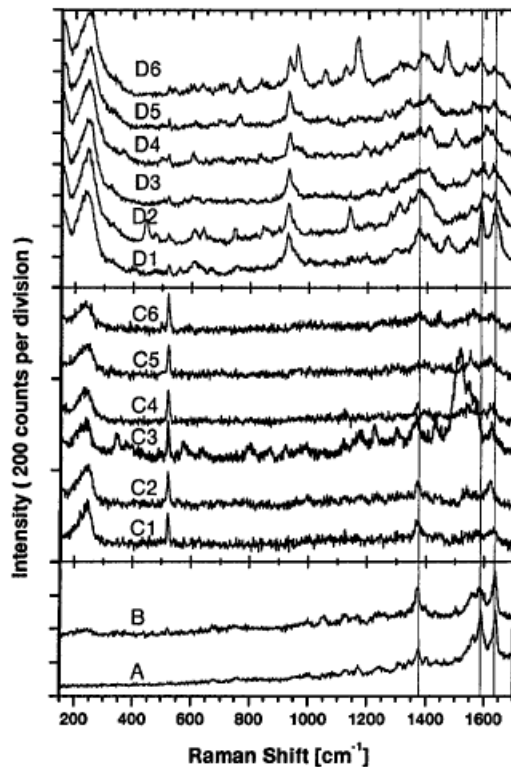
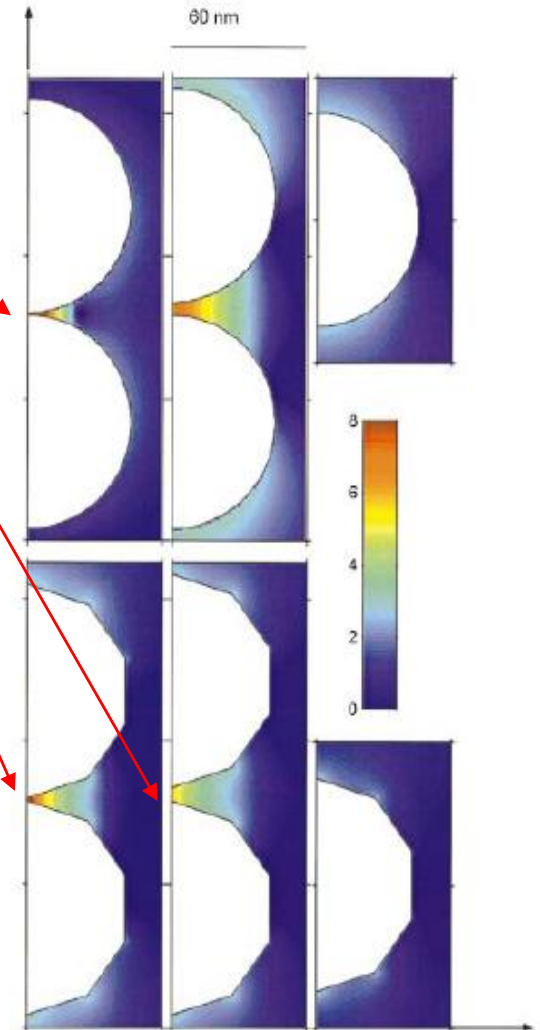
# Dimers assisting in spectroscopy: SERS

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

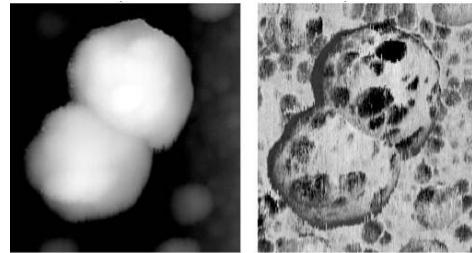


Xu, Aizpurua, Käll and Apell, Phys. Rev. E. **62**, 4318 (2000)

Hot sites



topography



amplitude

phase

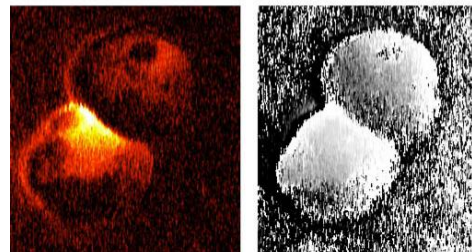
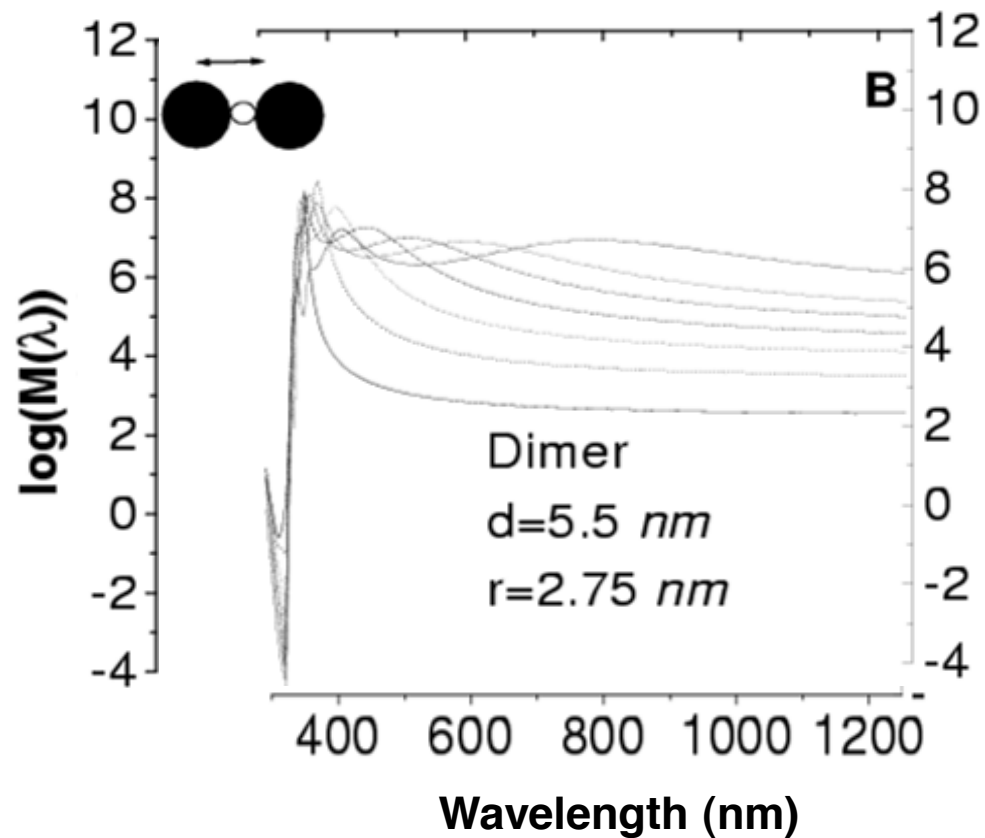


Image obtained by R. Hillenbrand,  
(Max Planck, Munich)

# Dimers assisting in spectroscopy: SERS

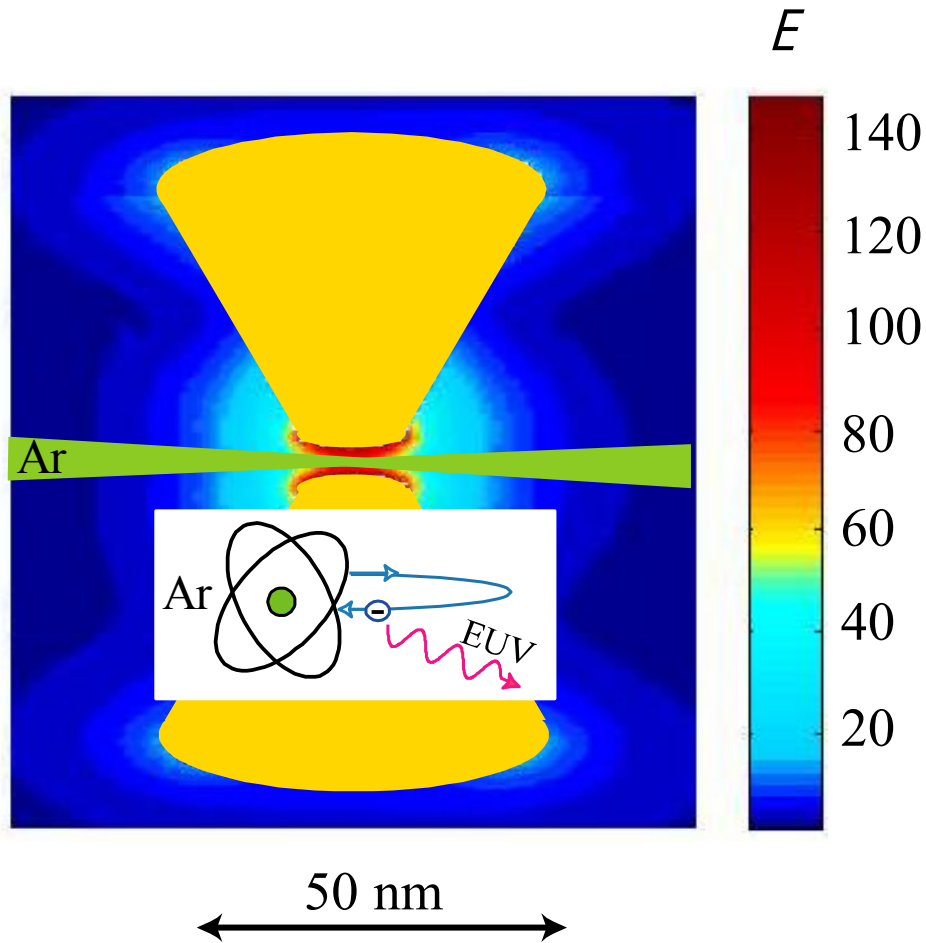
$$M_i^{EM} = \left| E^L(\omega_i) / E^I(\omega_i) \right|^4$$



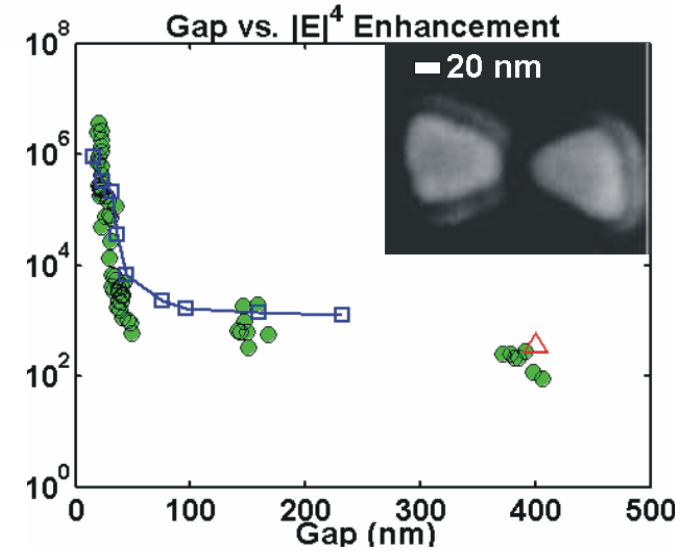
H. Xu, J. Aizpurua, M. Käll and P. Apell, Phys. Rev. E. **62**, 4318 (2000)



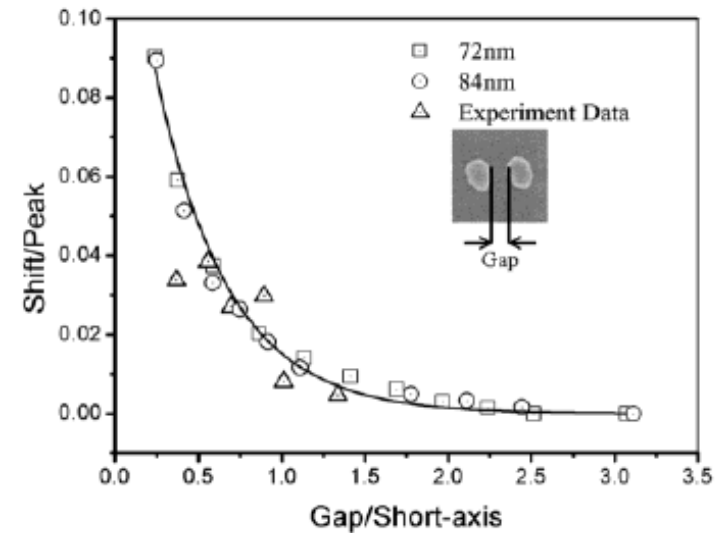
# Bowtie nanoantennas



Nature 453, 731 (2008)

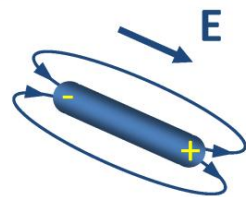


P. J. Schuck, et al, *Phys. Rev. Lett.* **94**, 017402 (2005)

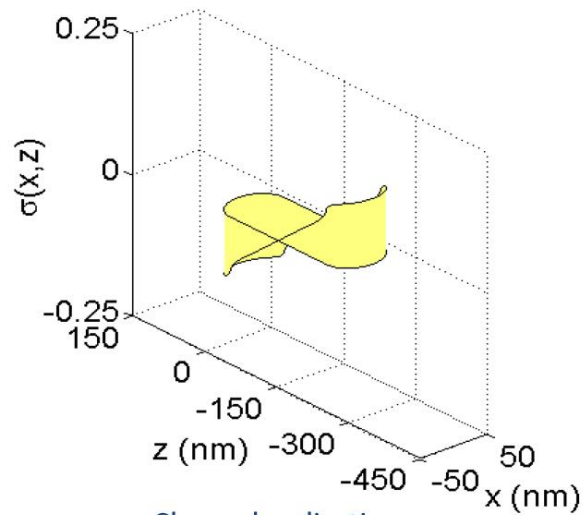


K. H. Su et al, *Nano Lett.* **3**, 1087 (2005)

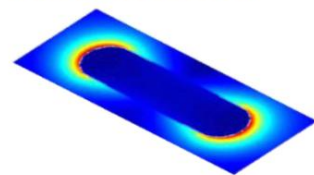
Dipole antenna



Single nanoparticles

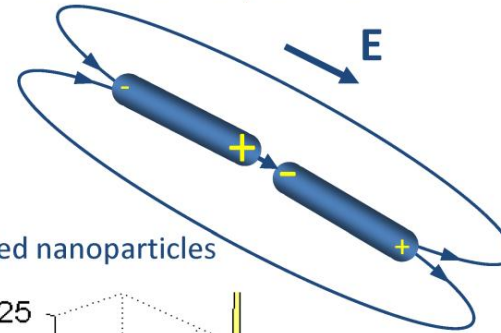


Charge localization

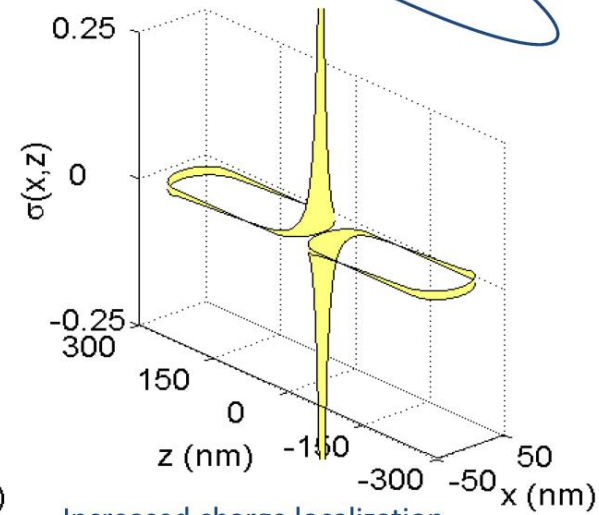


Field hot spots

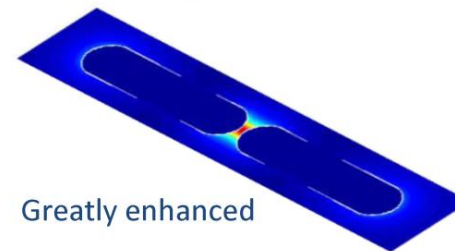
“Distorted” dipole antenna



Coupled nanoparticles

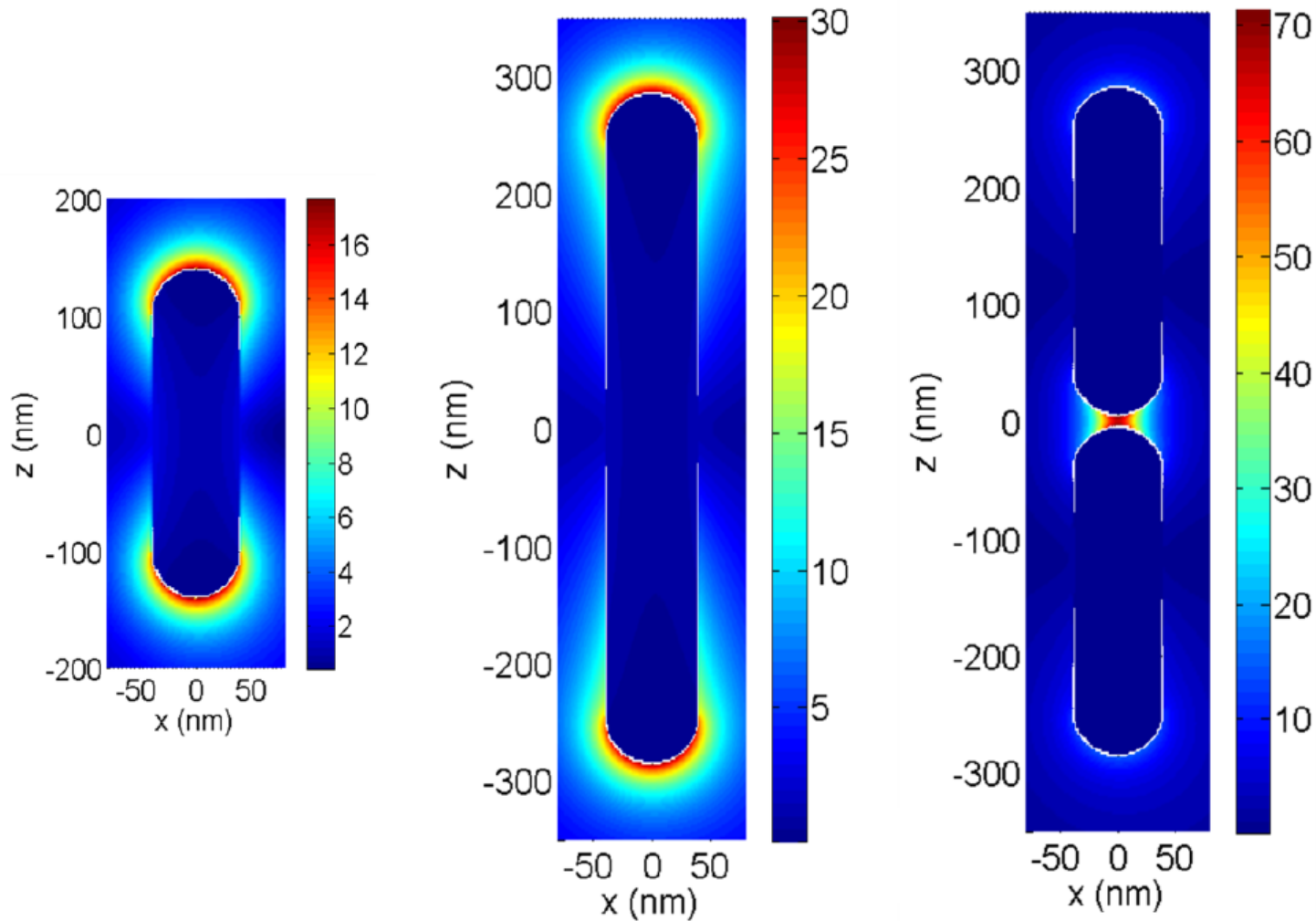


Increased charge localization



Greatly enhanced hot spots and field localization

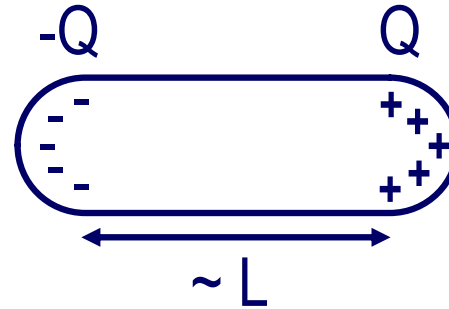
# Gap antenna: localization and field-enhancement: hot-sites



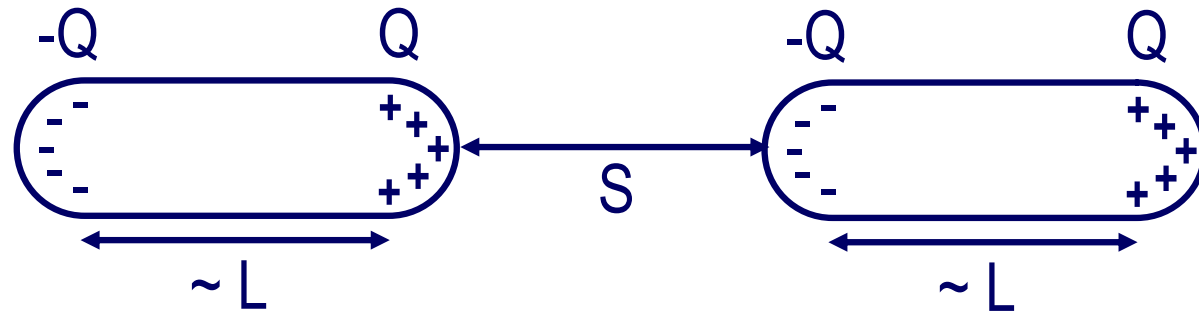


# Distorted dipole

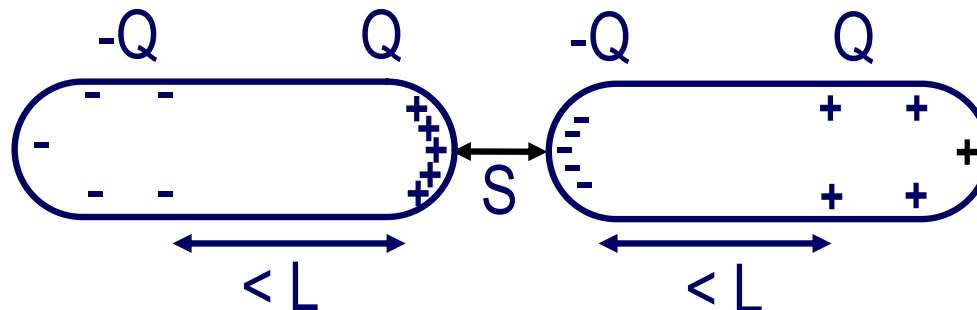
Isolated rod: dipole



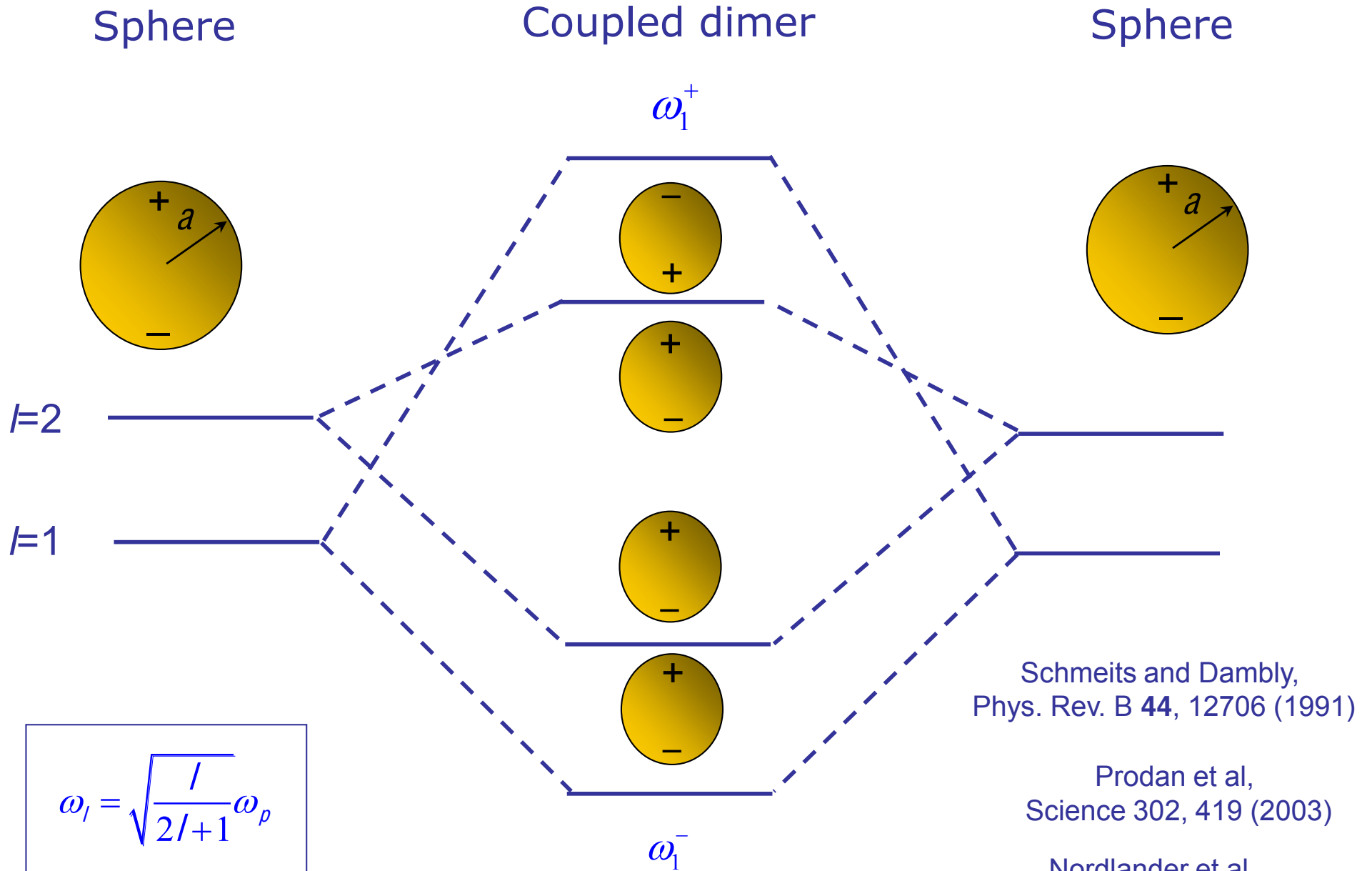
Weak coupling:  
two dipoles



Strong coupling:  
distorted dipoles

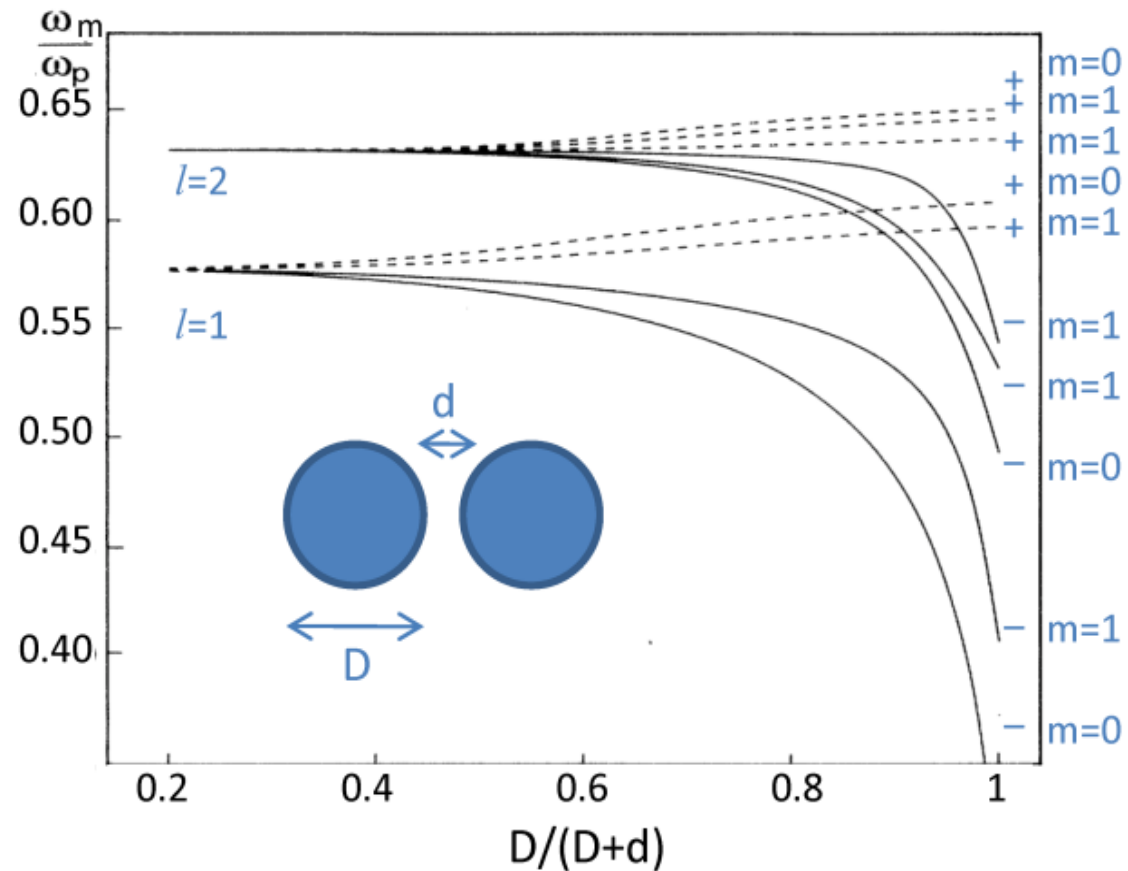
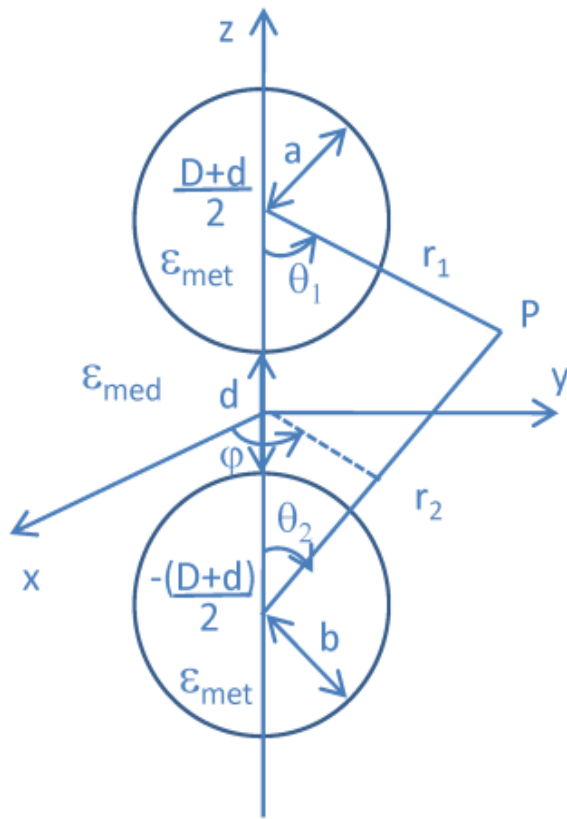


# Plasmon hybridization



$$\omega_l = \sqrt{\frac{l}{2l+1}} \omega_p$$

# Coupled modes in a metallic dimer



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

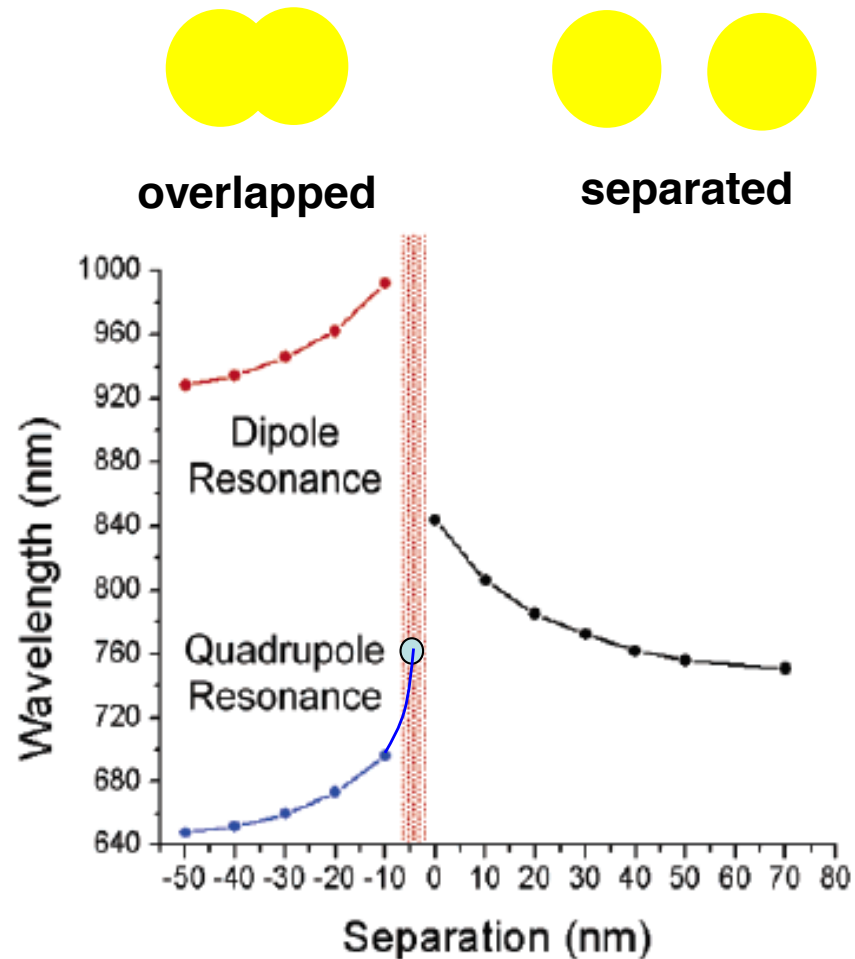
$$\Psi^{(2)}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=+l} \left(\frac{r_2}{b}\right)^l D_{lm} Y_{lm}(\theta_2, \varphi) e^{im\varphi} \quad \text{for } r_2 < b,$$

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

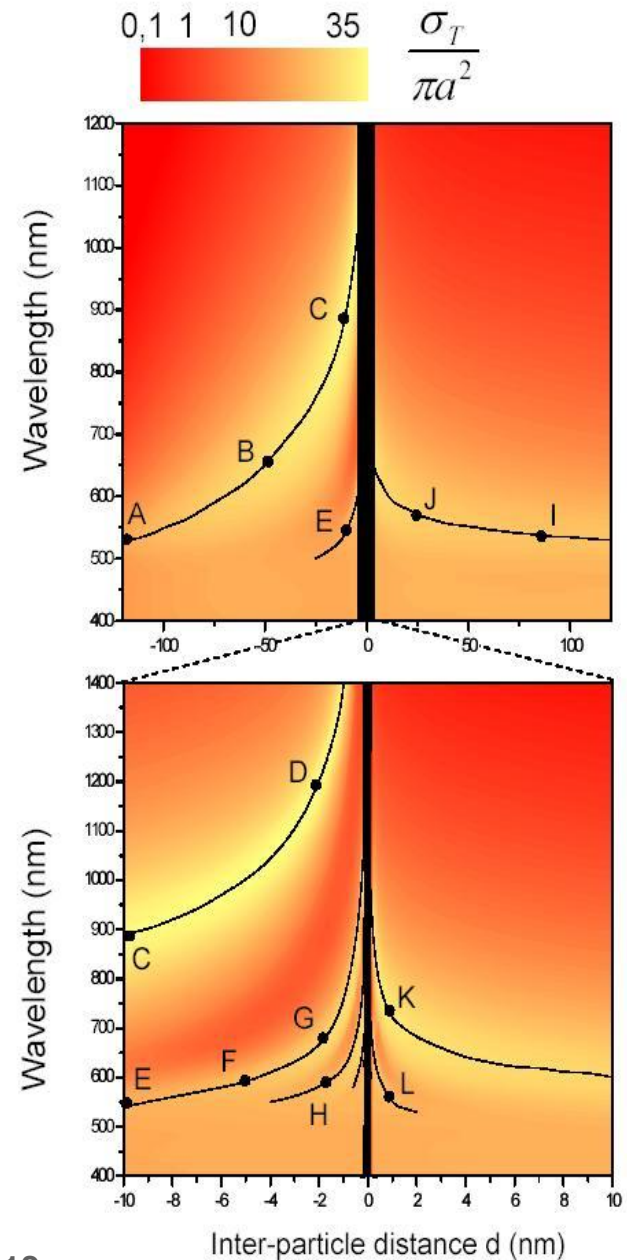
$$\left(\frac{\omega_{m=0;l=1}}{\omega_p}\right)_{\pm}^2 = \frac{\left(1 \pm 2\left(\frac{D/2}{D+d}\right)^3\right)}{3}$$

# Nanoparticles in the touching limit

## Map of the resonances



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



# Charge density modes

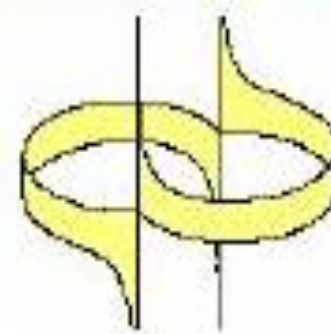
Low frequency modes of non-touching and touching dimers are distinctly different

## NOT TOUCHING



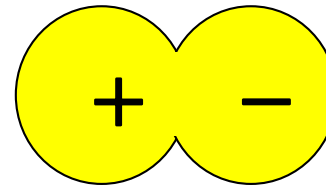
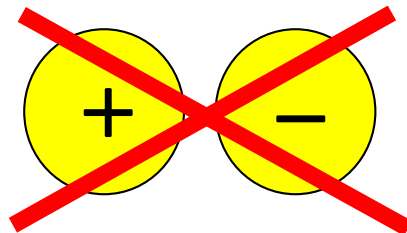
Neutral charge in each particle

## TOUCHING



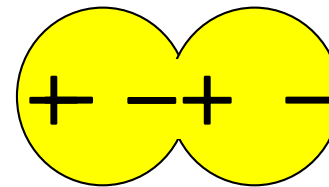
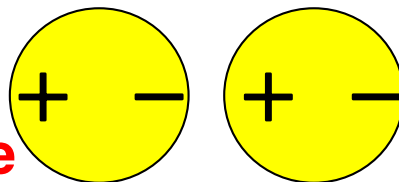
Net electrical charge in each half of the dimer

**Unphysical mode**



**1st physical mode**

**1st physical mode**



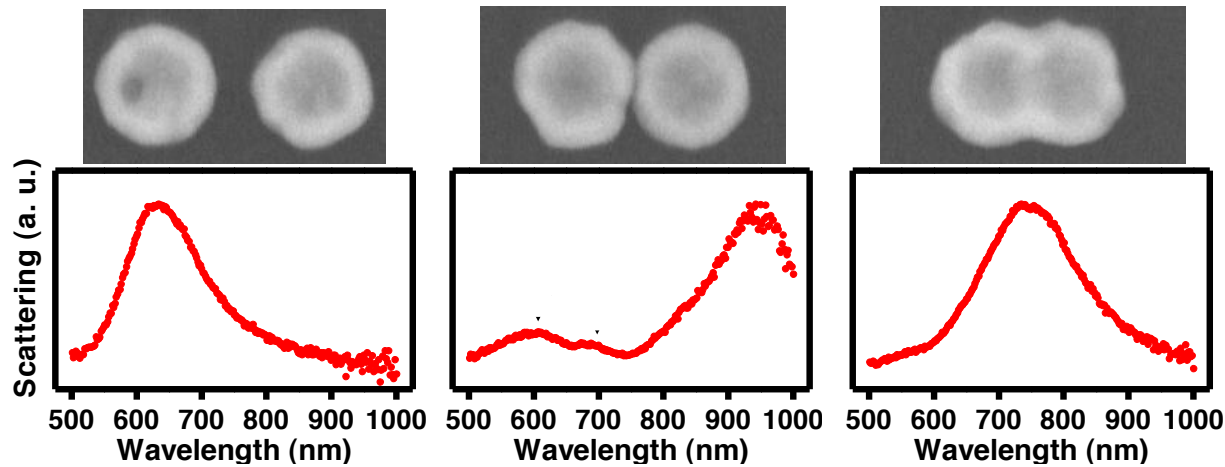
**2nd physical mode**

# Close Encounters between Two Nanoshells

J. Britt Lassiter,<sup>†,||</sup> Javier Aizpurua,<sup>‡</sup> Luis I. Hernandez,<sup>||</sup> Daniel W. Brandl,<sup>†,||</sup> Isabel Romero,<sup>‡</sup> Surbhi Lal,<sup>‡,||</sup> Jason H. Hafner,<sup>†,§,||</sup> Peter Nordlander,<sup>†,‡,||</sup> and Naomi J. Halas<sup>\*,‡,§,||</sup>

NANO  
LETTERS

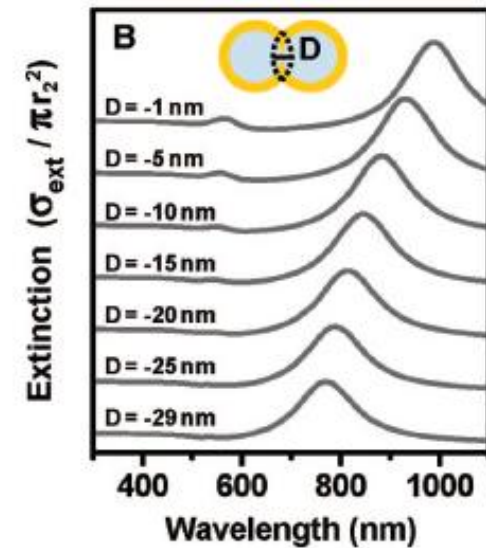
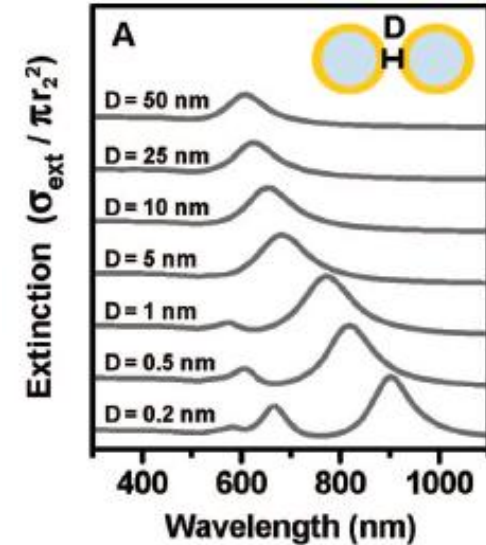
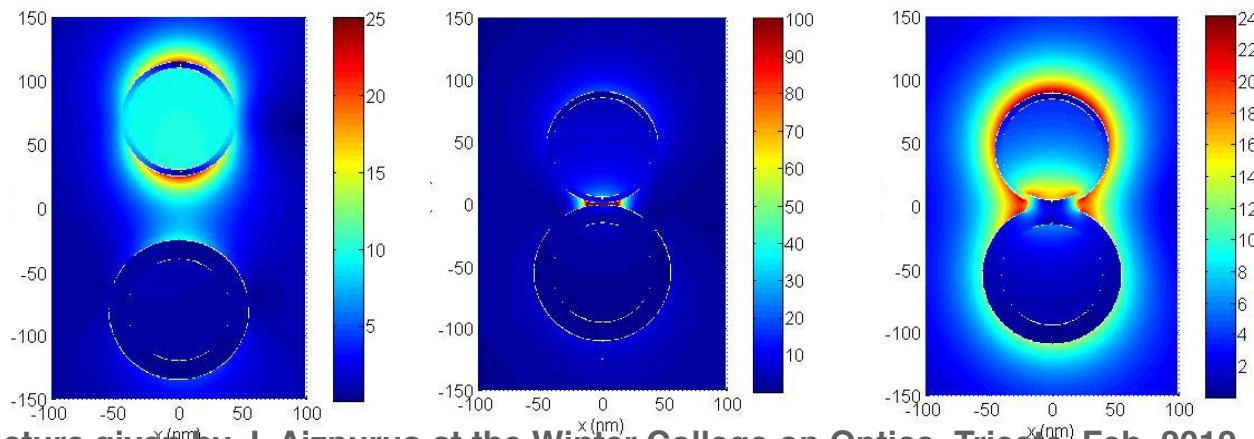
2008  
Vol. 8, No. 4  
1212-1218



**Slightly close:  
Slight shift**

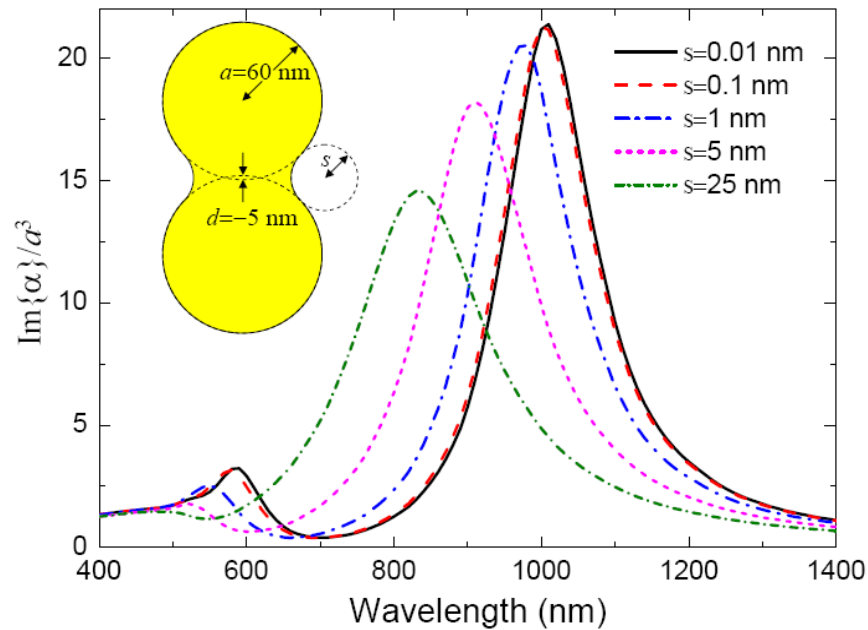
**Close proximity:  
red shift**

**Overlapped:  
Blue-shift**

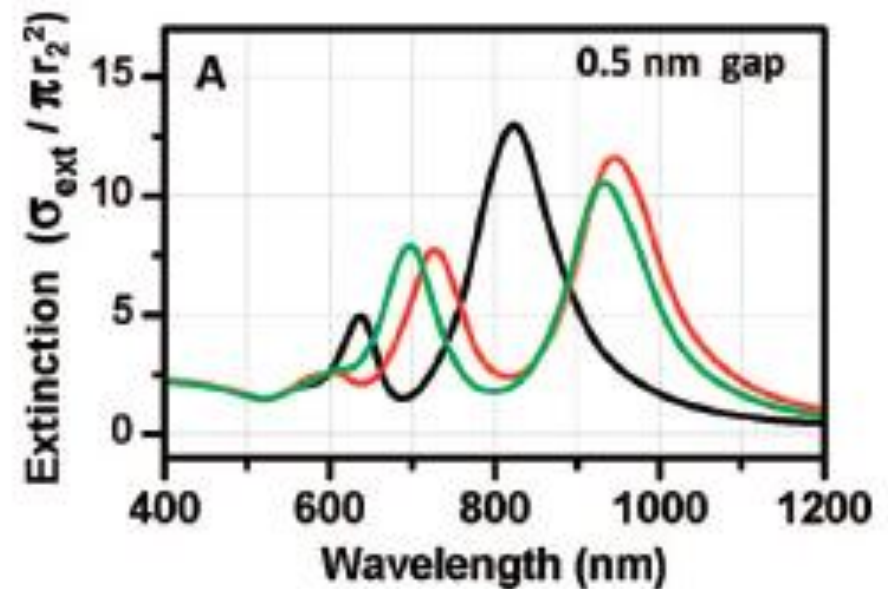
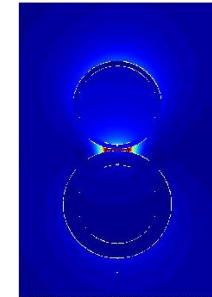


# The fine detail of the junction matters!!!

Specially for resonant spectroscopy



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

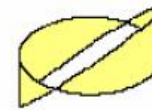


J.B. Lassiter, *Nano Letters* 8, 1212 (2008)

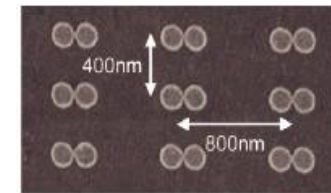


# Outline

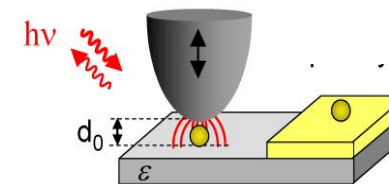
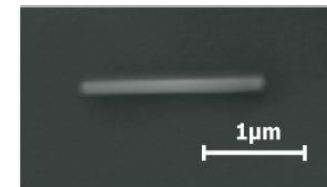
- Optical antennas: Basics



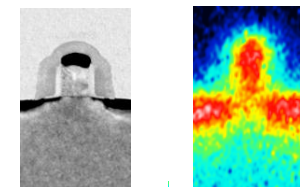
- Playing with antenna modes



- Optical antennas for Enhanced Spectroscopy : **SEIRA**



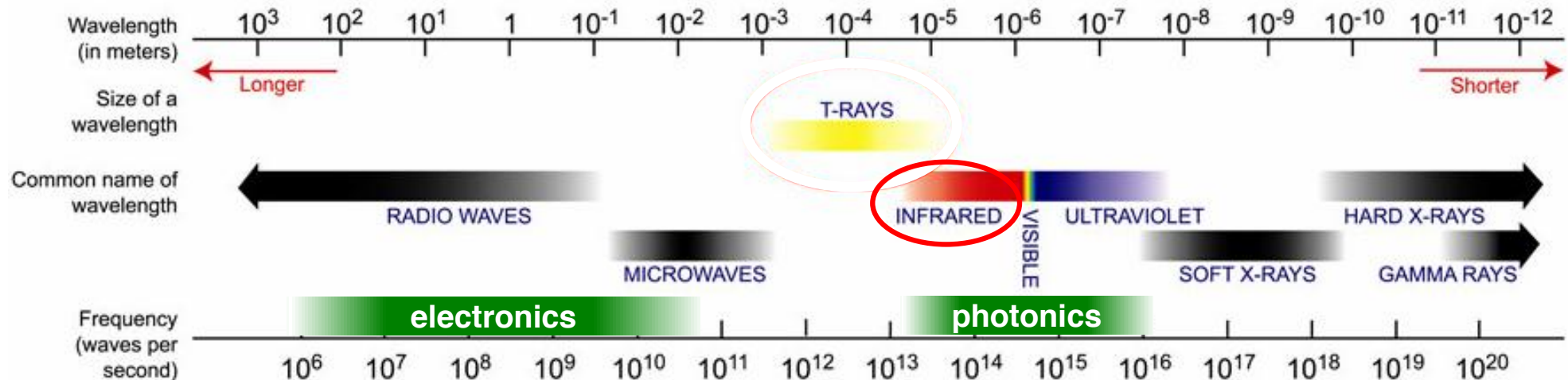
- More applications of optical antennas





# Surface-enhanced IR absorption (SEIRA)

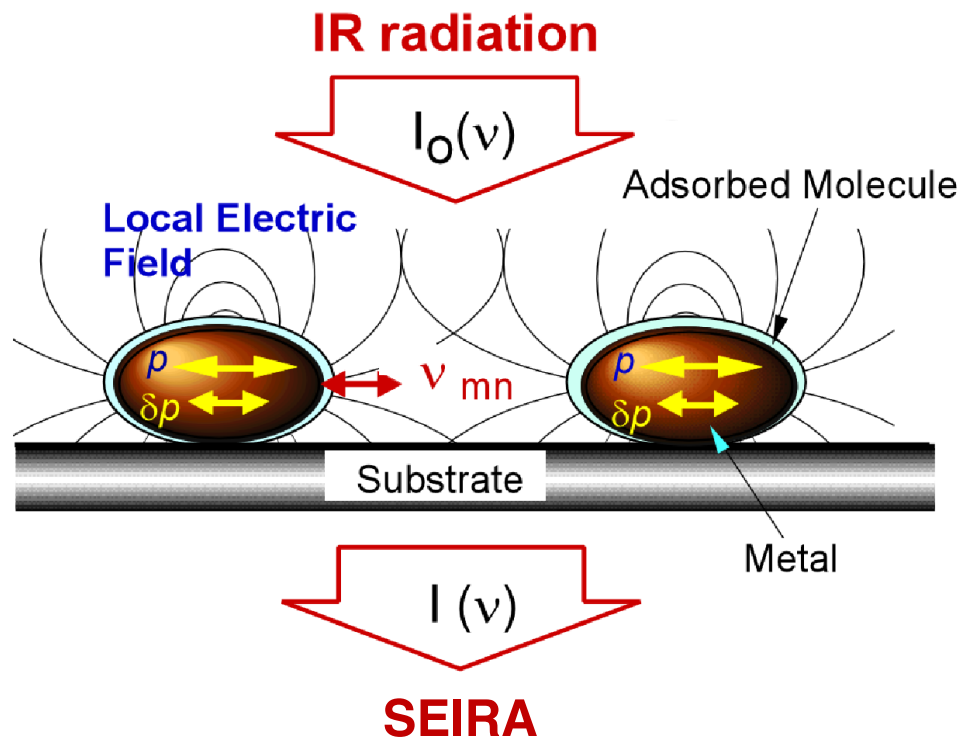
Resonant antennas for enhanced signal of molecular vibrations



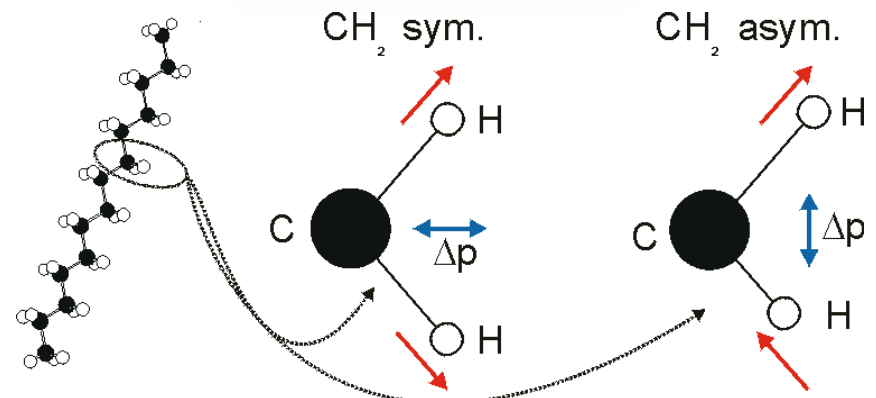
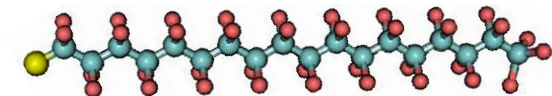
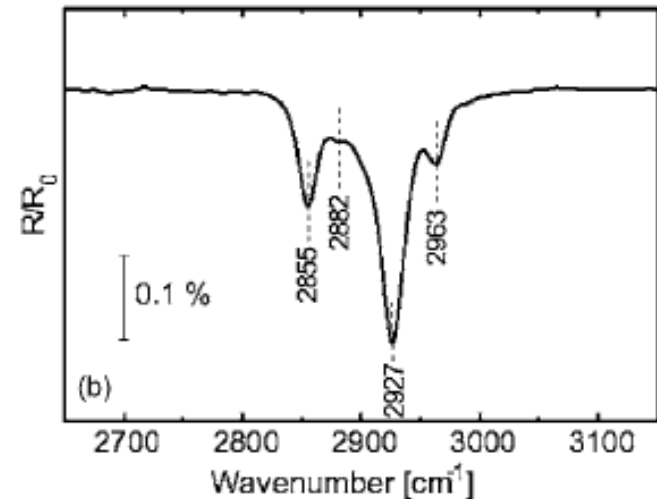
# Surface-enhanced IR absorption (SEIRA)

Resonant antennas for enhanced signal of molecular vibrations

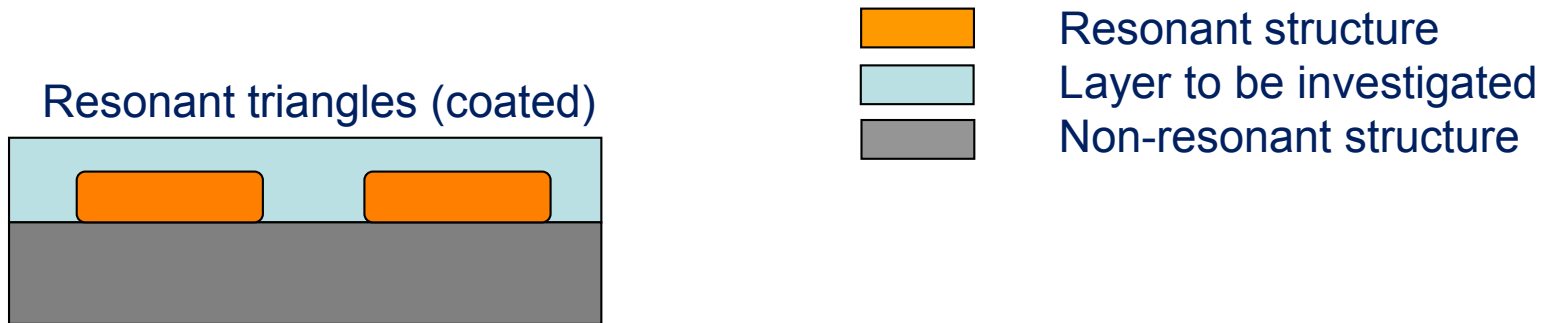
## Concept



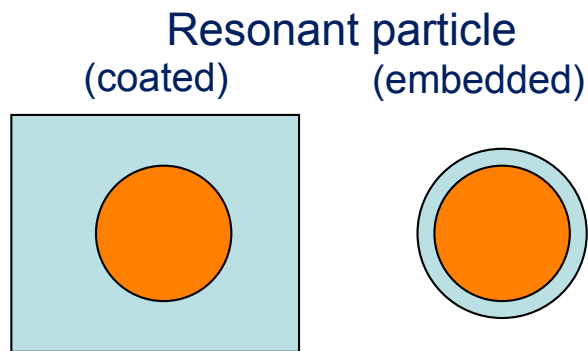
## ODT Molecular fingerprints



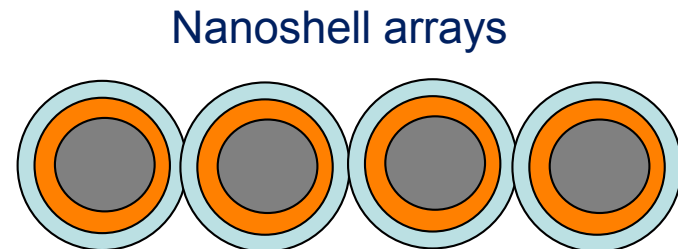
# How to bring resonances of nanoscale objects to the mid-infrared ??



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



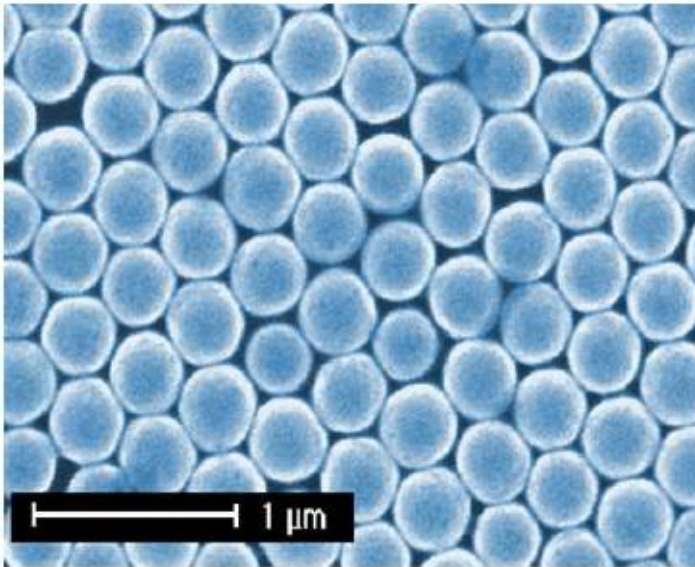
M.S. Anderson, App. Phys. Lett. 83, 2964 (2003)



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

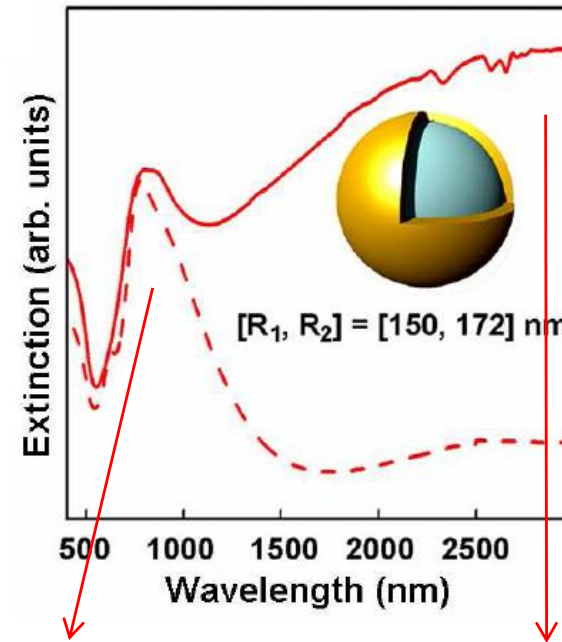
# Nanoshell arrays: Substrates for infrared spectroscopy

## Metallic nanoparticle arrays for SERS and SEIRA



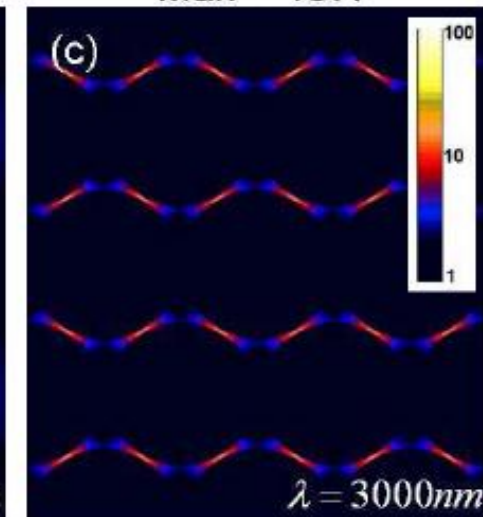
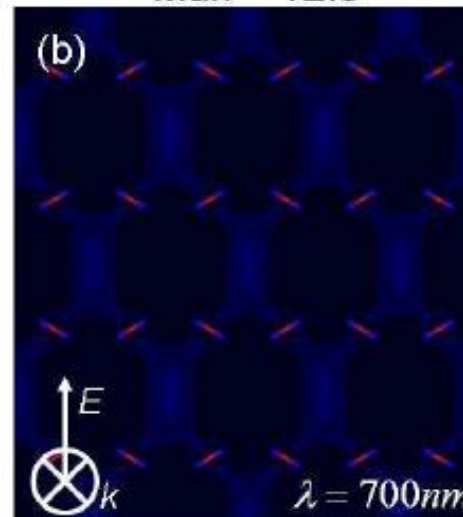
Kundu et al. *Angew. Chem.* (2007)  
Halas group, Rice Univ.

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



**VISIBLE**  
Max = 12.9

**INFRARED**  
Max = 19.1

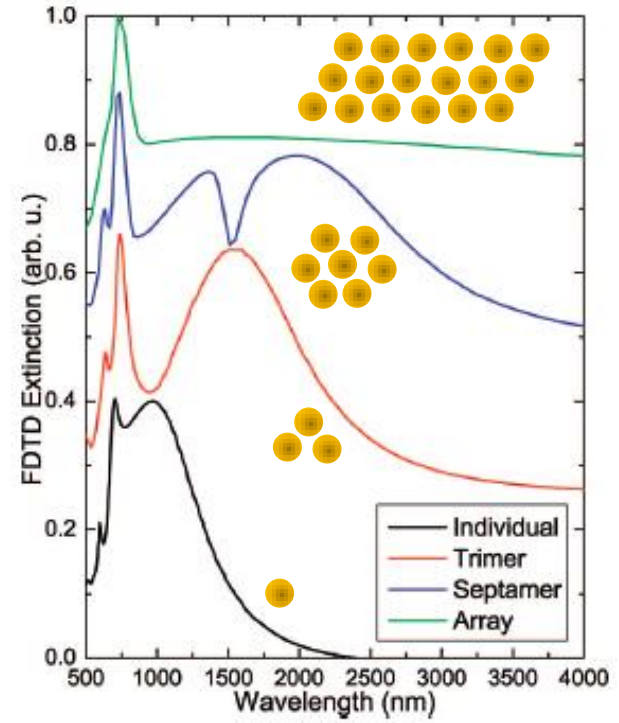
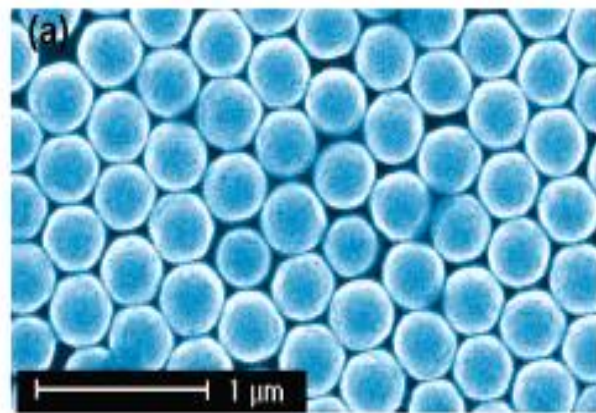
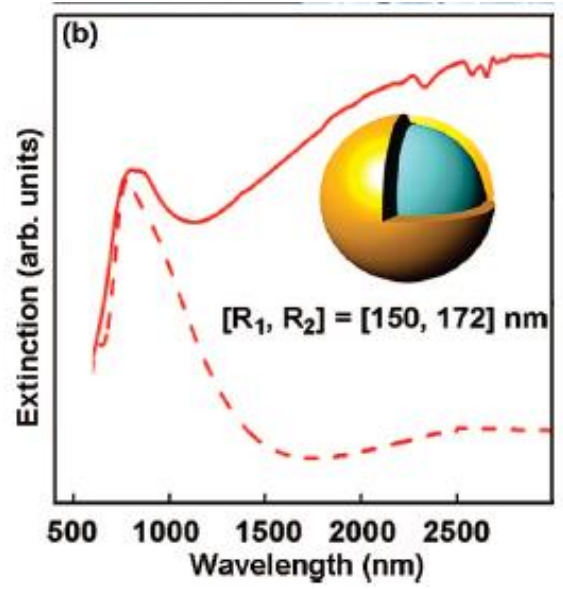


# Metallic Nanoparticle Arrays: A Common Substrate for Both Surface-Enhanced Raman Scattering and Surface-Enhanced Infrared Absorption



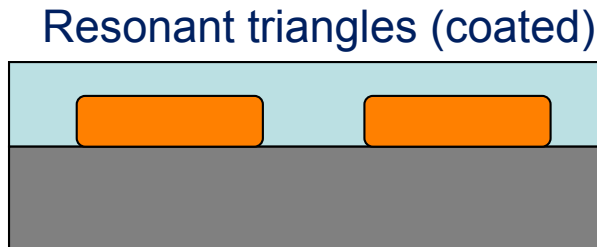
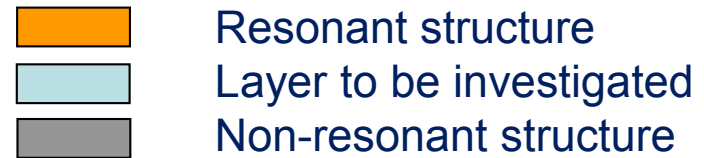
2, 707 (2008)

Fei Le,<sup>†</sup> Daniel W. Brandl,<sup>†</sup> Yaroslav A. Urzhumov,<sup>‡</sup> Hui Wang,<sup>§</sup> Janardan Kundu,<sup>§</sup> Naomi J. Halas,<sup>§,⊥</sup> Javier Aizpurua,<sup>||</sup> and Peter Nordlander<sup>†,⊥,\*</sup>

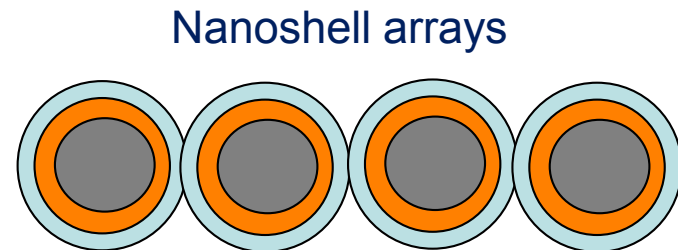




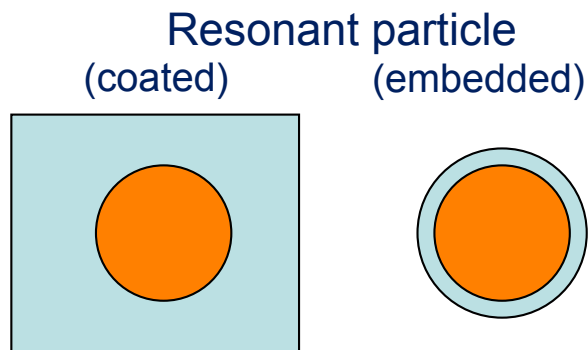
# Single antenna for infrared resonant spectroscopy



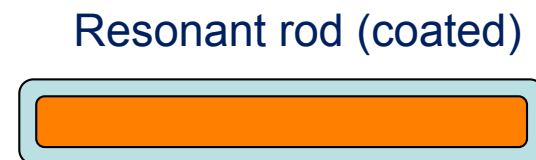
T.R. Jensen et al., *J. Phys. Chem B*, 104, 10549 (2000)



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

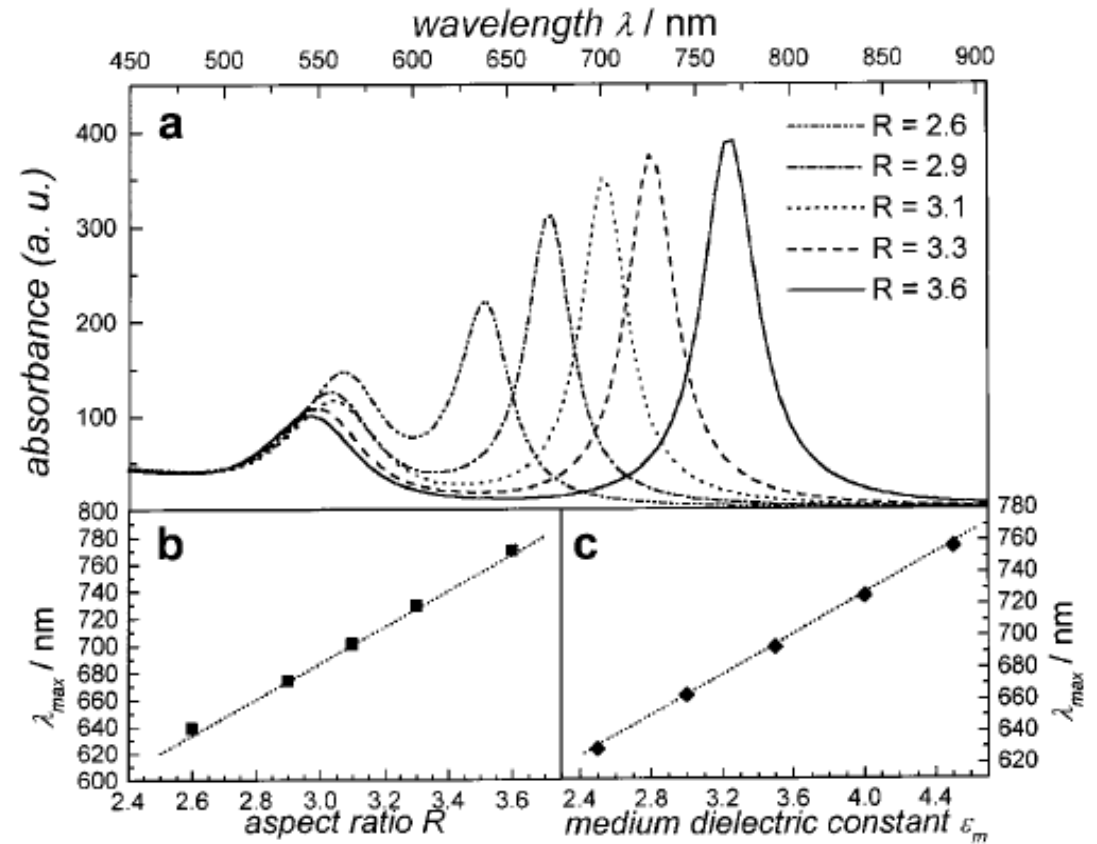
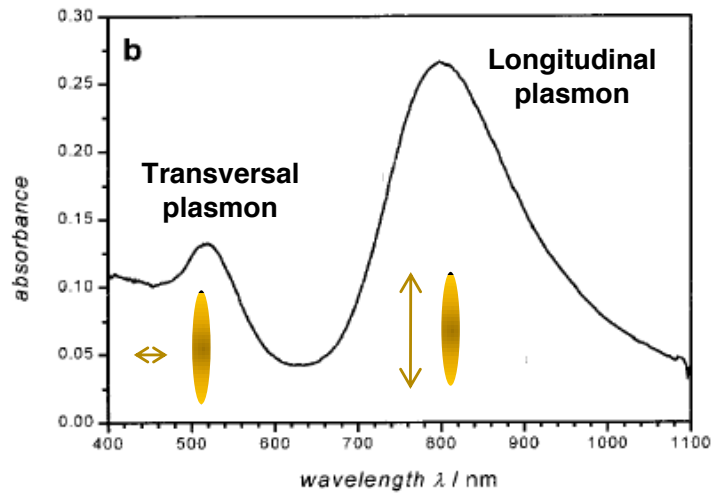
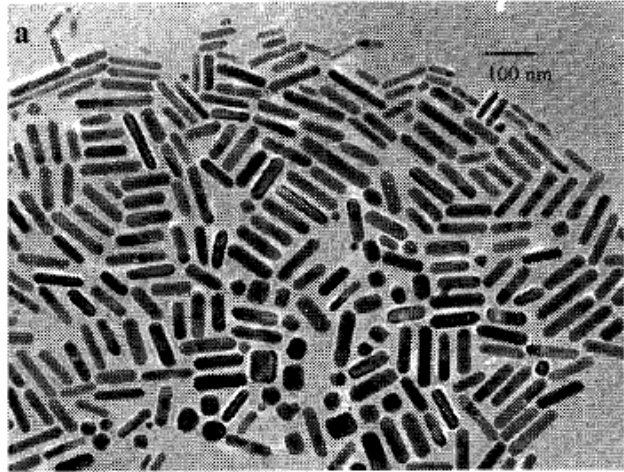


M.S. Anderson, *App. Phys. Lett.* 83, 2964 (2003)



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

# Basics of nanorods



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

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

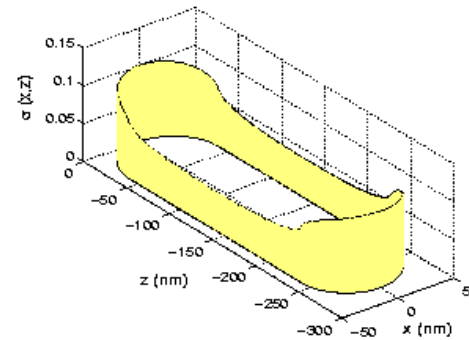
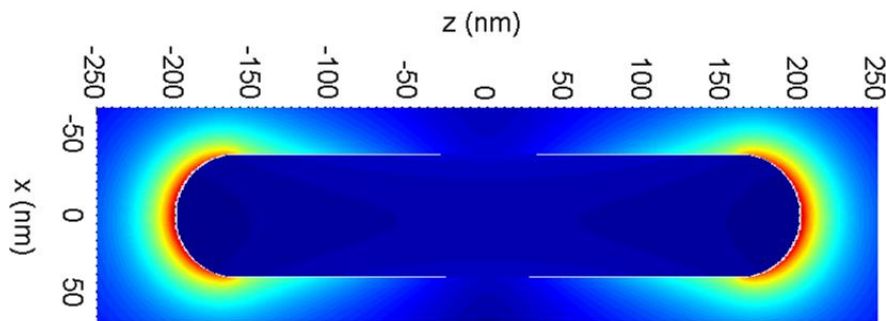
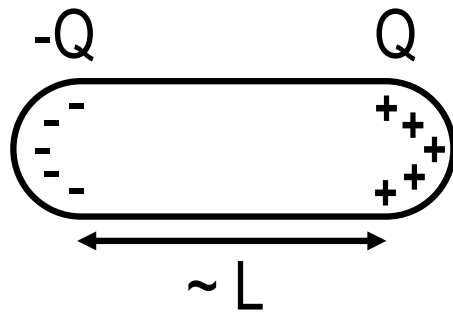
# Calculation of gold antenna modes

Antenna modes:

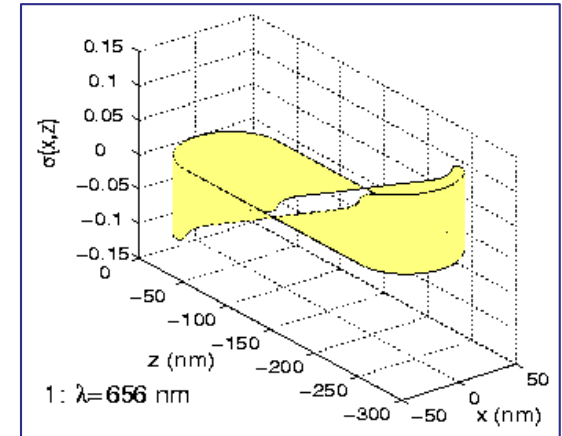
$D=80\text{nm}, L=200\text{nm}; \text{ ratio}=2.5$

Dipole response:

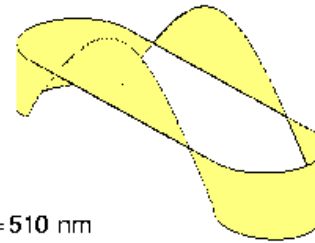
$$L \propto \lambda/2$$



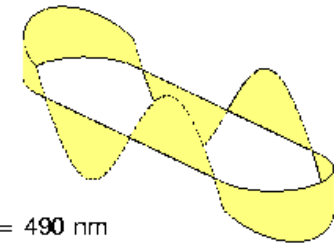
0:  $\lambda=8814 \text{ nm}$



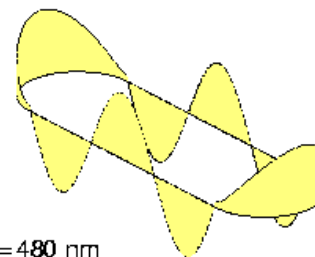
1:  $\lambda=656 \text{ nm}$



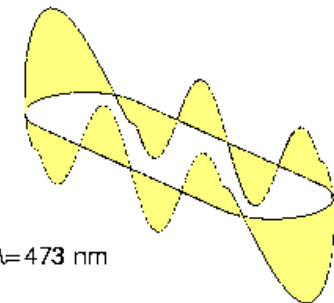
2:  $\lambda=510 \text{ nm}$



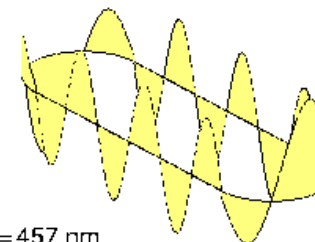
3:  $\lambda=490 \text{ nm}$



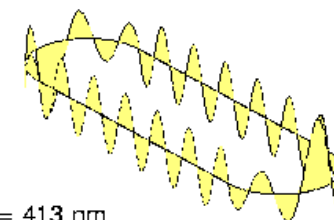
4:  $\lambda=480 \text{ nm}$



5:  $\lambda=473 \text{ nm}$



9:  $\lambda=457 \text{ nm}$



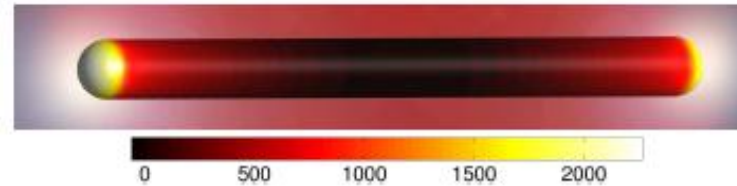
19:  $\lambda=413 \text{ nm}$

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

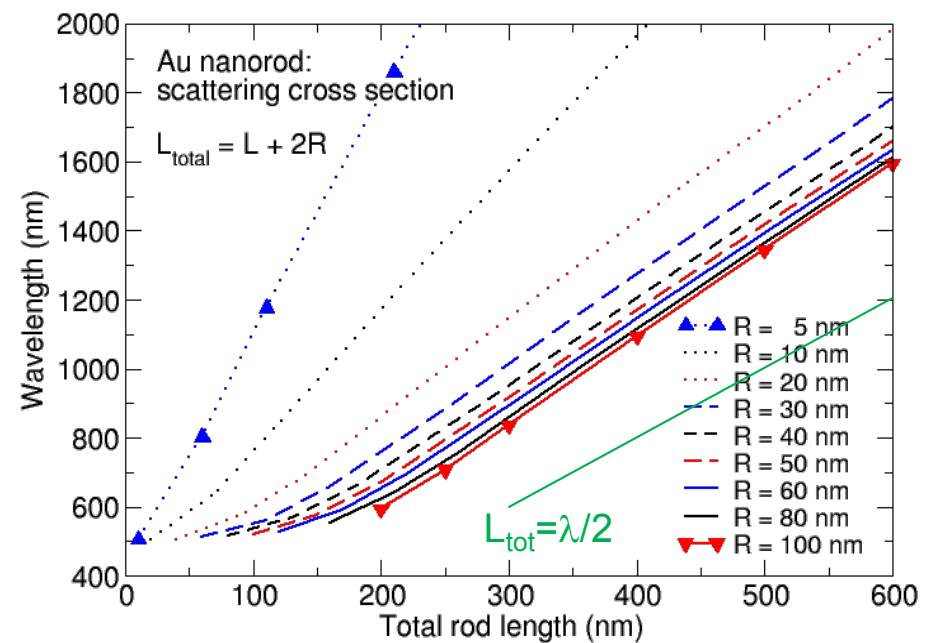
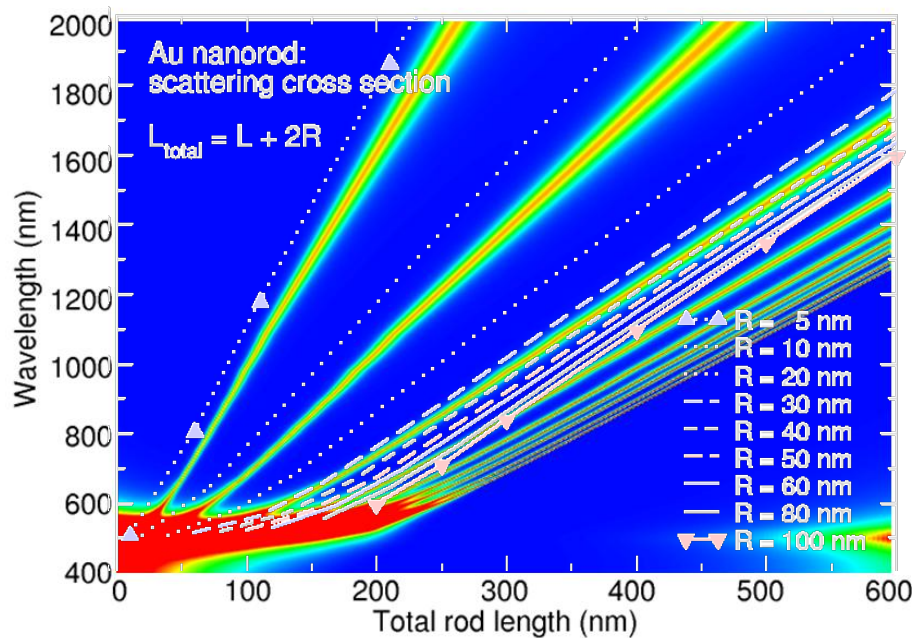
Lecture given by J. Aizpurua at the Winter College on Optics, Trieste, Feb. 2012



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



## Mapping the plasmon resonances of metallic nanoantennas



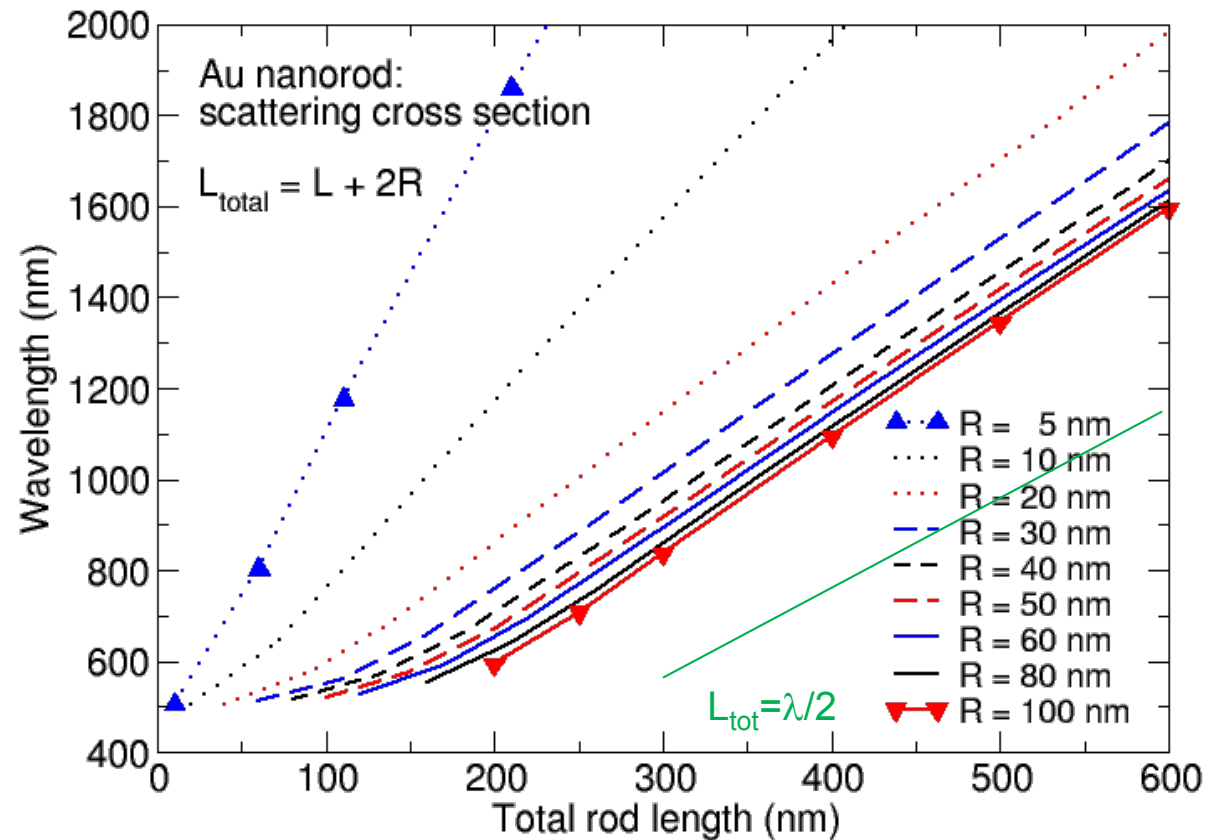
$$(q^2 - \epsilon k^2)^{1/2} I_0((q^2 - \epsilon k^2)^{1/2} R) K_1((q^2 - k^2)^{1/2} R) + \epsilon (q^2 - k^2)^{1/2} I_1((q^2 - \epsilon k^2)^{1/2} R) K_0((q^2 - k^2)^{1/2} R) = 0$$

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

G.W. Bryant, F.J. García de Abajo and J. Aizpurua, Nano Lett. **8**, 631 (2008)

# Dependence of the $\lambda/2$ antenna resonance with the length L

## Au nanowire with hemispherical ends

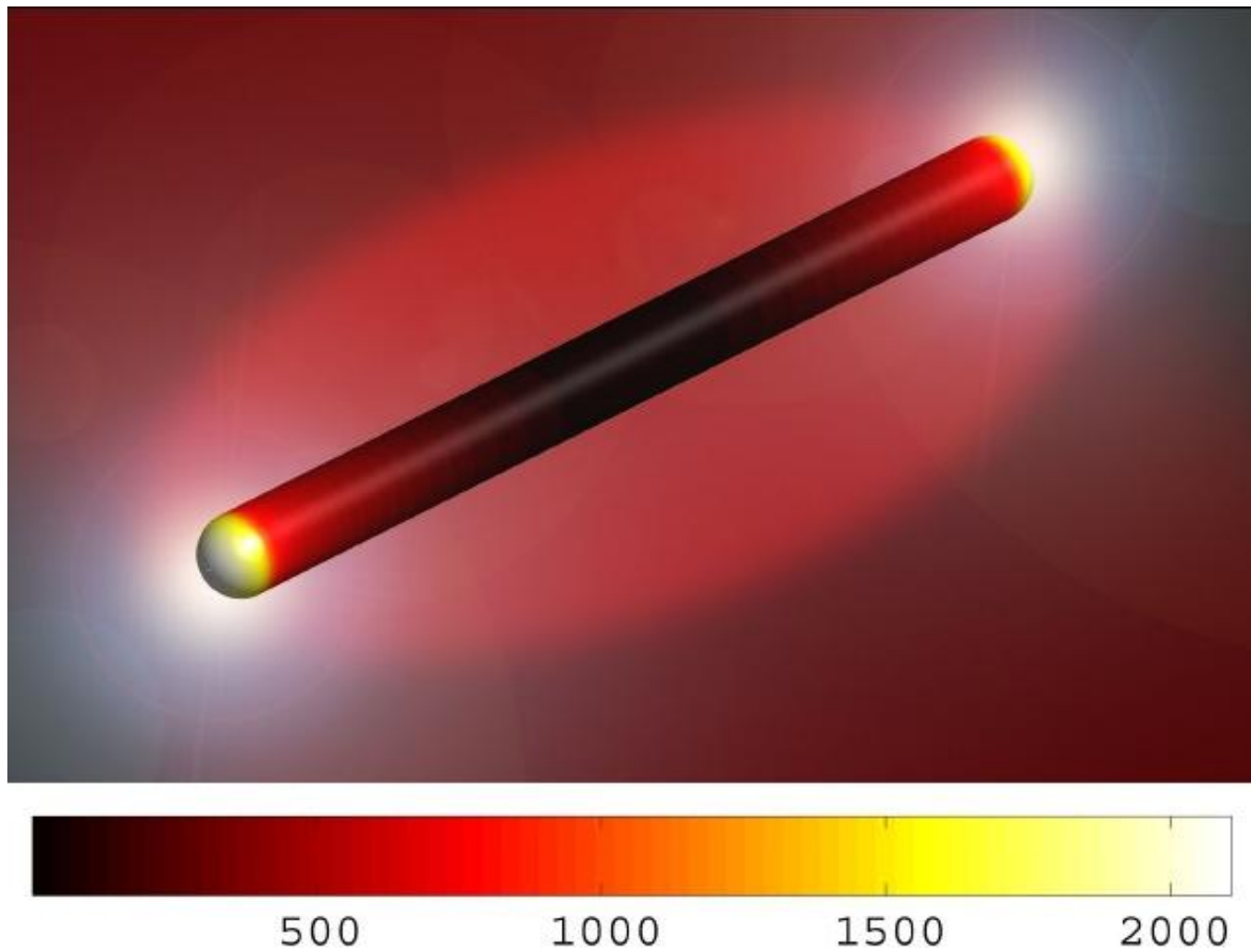


The resonance follows  $L \propto \lambda/3 - \lambda/10$  !!!!; not like in ideal antenna theory  $L \propto \lambda/2$

Aizpurua et al. Physical Review B **71**, 235420 (2005); L. Novotny, Phys. Rev. Lett. **98**, 266802 (2007)

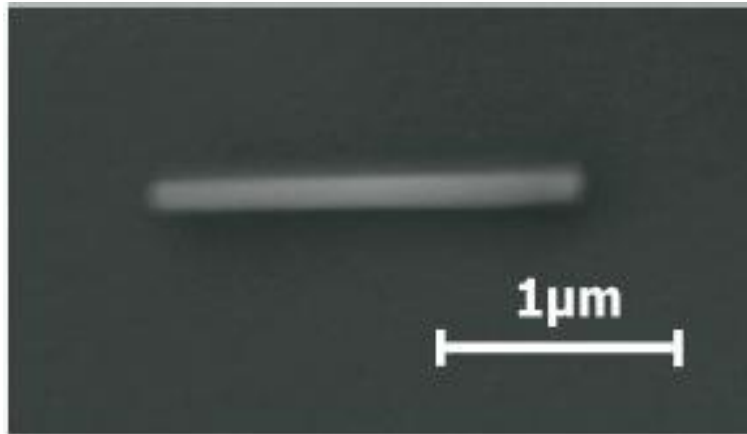
G.W. Bryant, F.J. García de Abajo and J. Aizpurua, Nano Lett., **8**, 631 (2008)

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



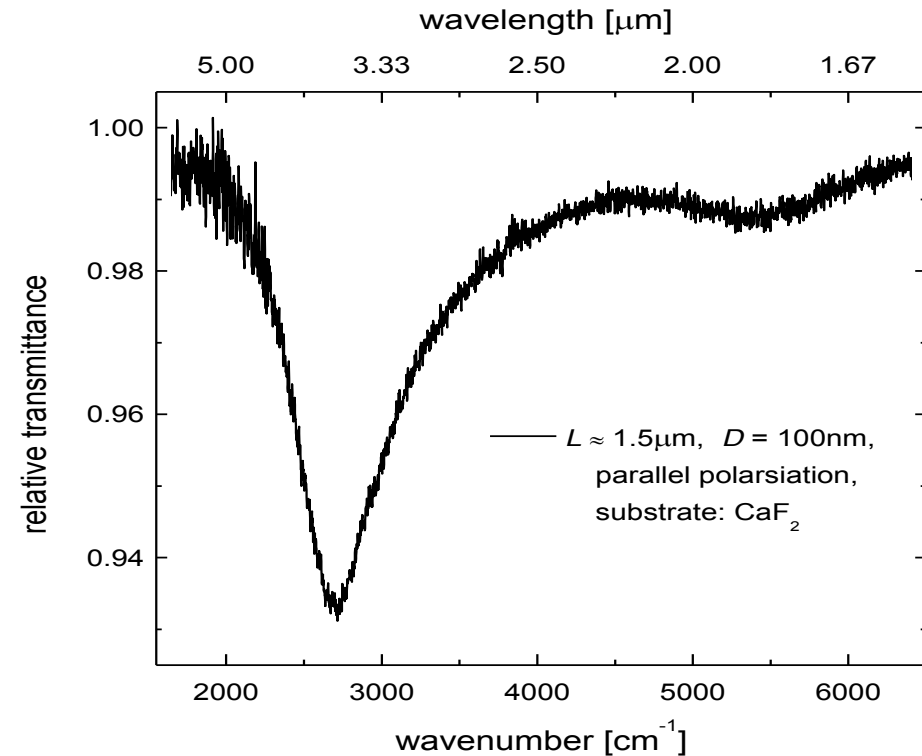
# Finding the right nanowire resonance for IR spectroscopy

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)

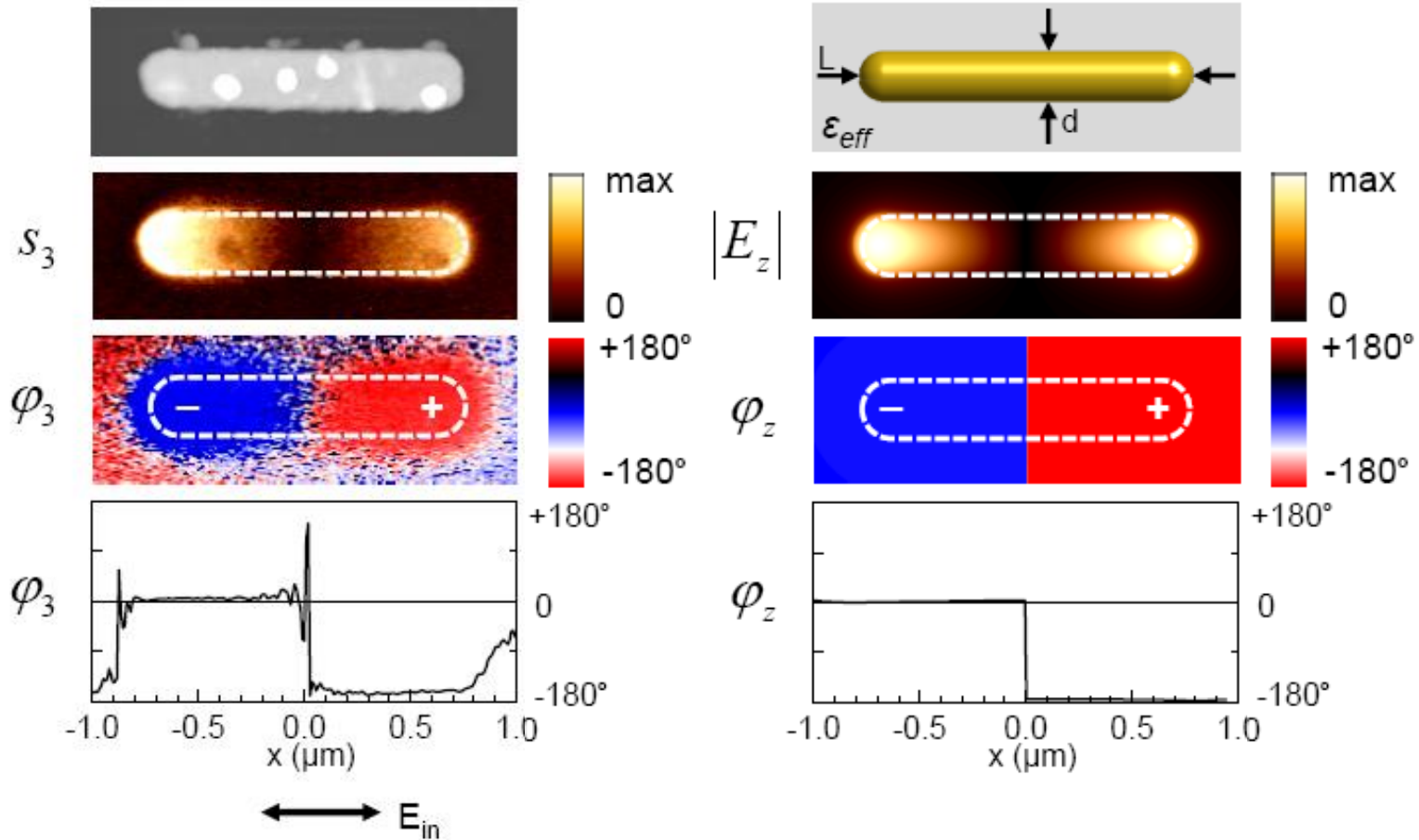
SEM image: perfect cylindrical shape



Relative IR transmittance spectra  
Electric field along the long wire axis

F. Neubrech et al. Appl. Phys. Lett. 89, 253104 (2006)

# Near-field mapping of IR nanoantennas



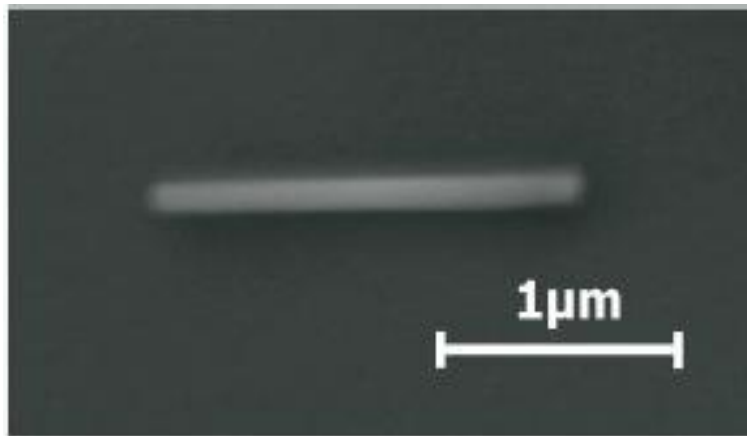
Experiment by Martin Schnell,  
R. Hillenbrand's group

Calculation by A. Garcia-Etxarri,  
San Sebastian

M. Schnell *et al.*, Nature Photonics 3, 287 (2009)

# Finding the right nanowire resonance for IR spectroscopy

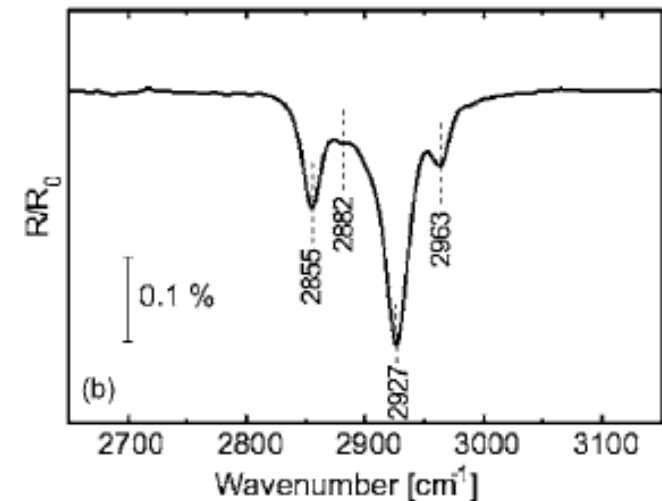
Experiments by Prof. A. Pucci's group (Heidelberg, Germany)



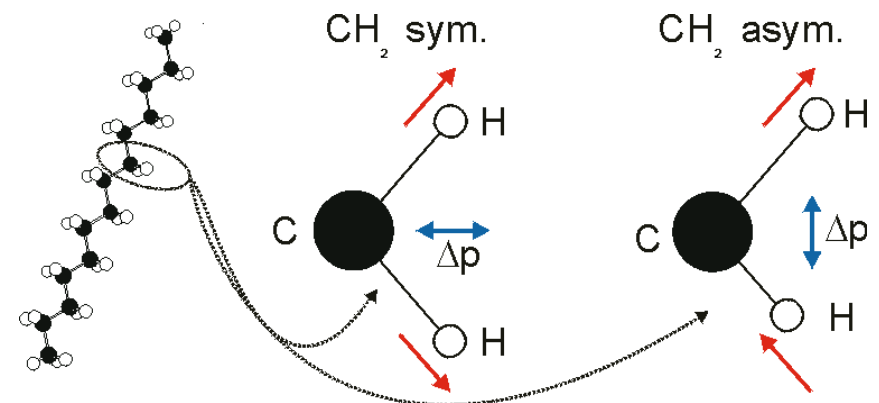
Gold nanowire ( $L=1.7\mu\text{m}$  and  $D=100\text{nm}$ , on a silicon wafer)

SEM image: perfect cylindrical shape

## Absorption bands in ODT



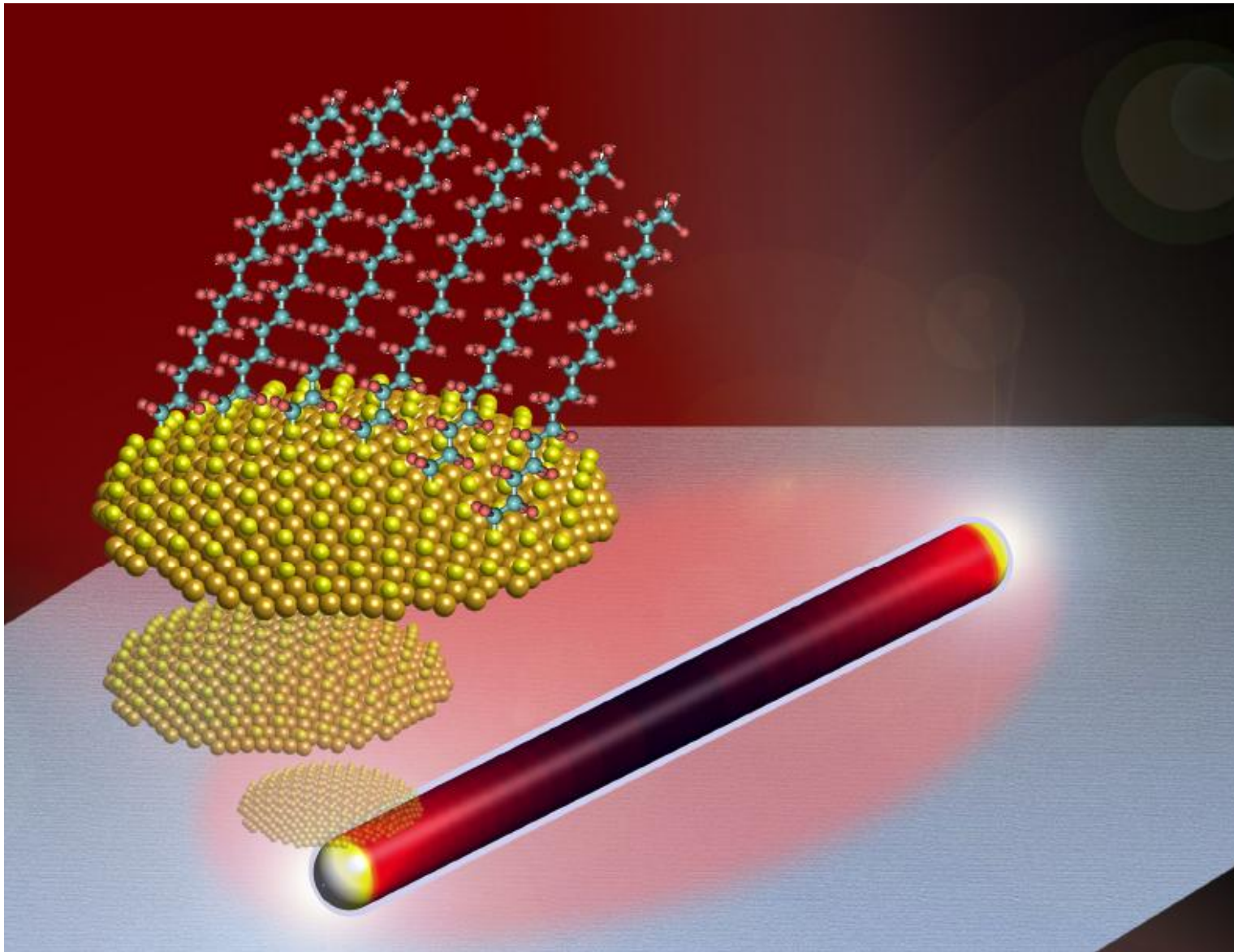
## Vibration modes in $\text{CH}_2$



F. Neubrech et al. Appl. Phys. Lett. 89, 253104 (2006)

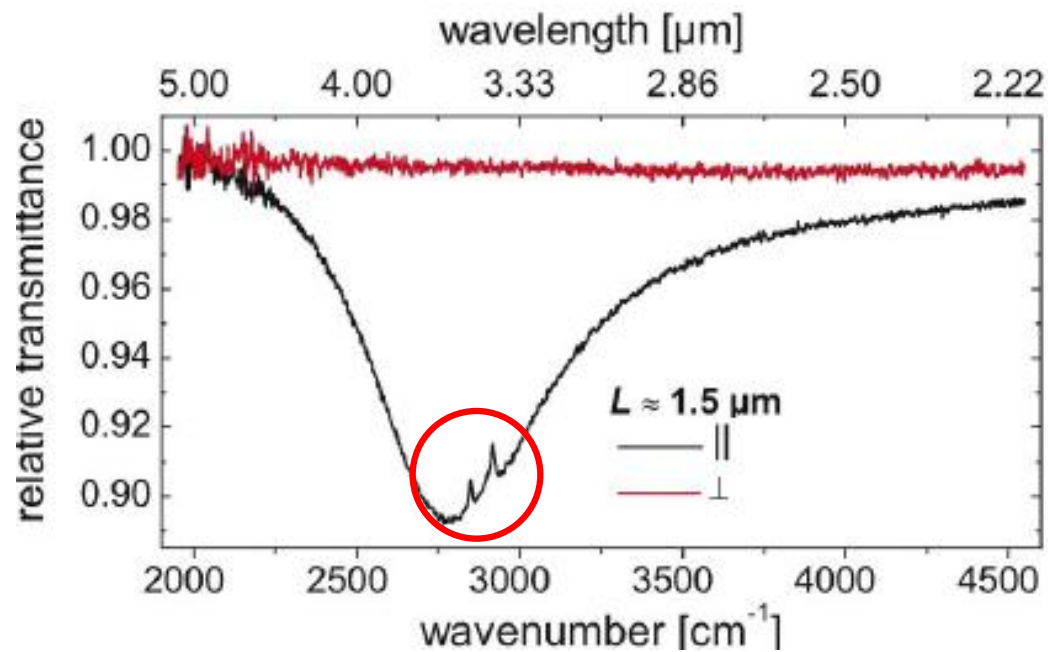
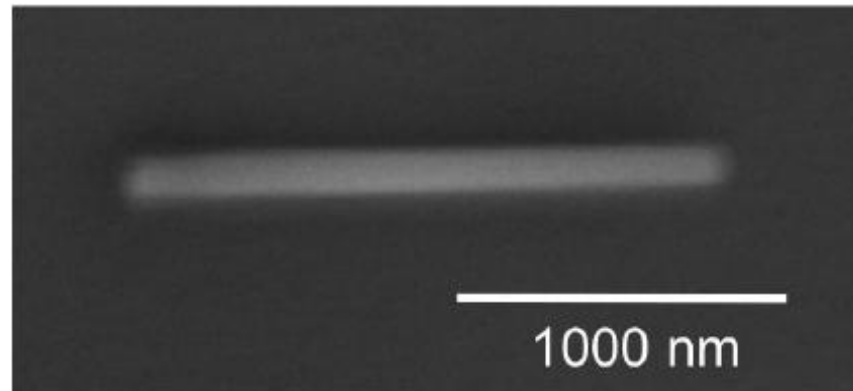


## ODT covered nanoantenna



Sample and reference obtained in the spectral range of  $600\text{ cm}^{-1}$  to  $7000\text{ cm}^{-1}$  (res.  $2\text{ cm}^{-1}$ )

# Relative IR transmittance of ODT molecules on a gold nanowire



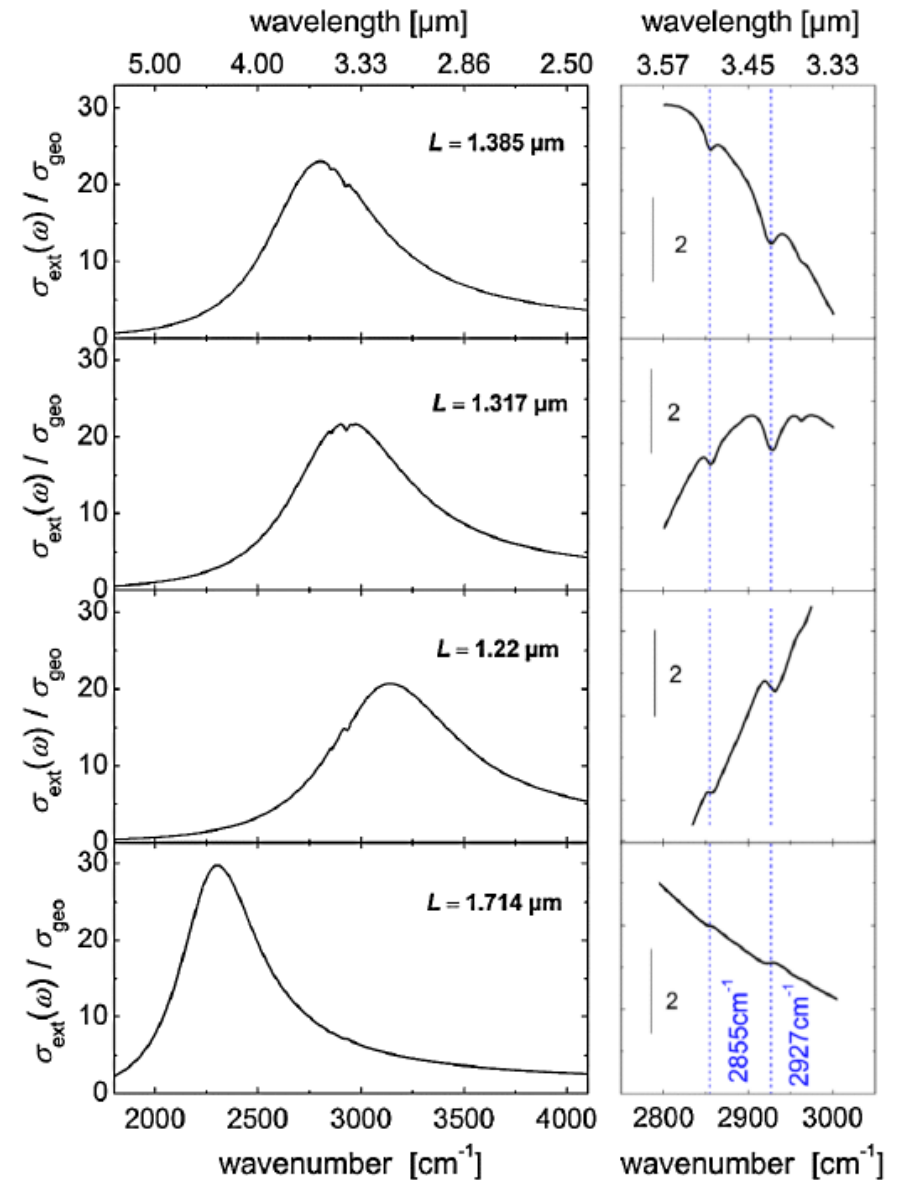
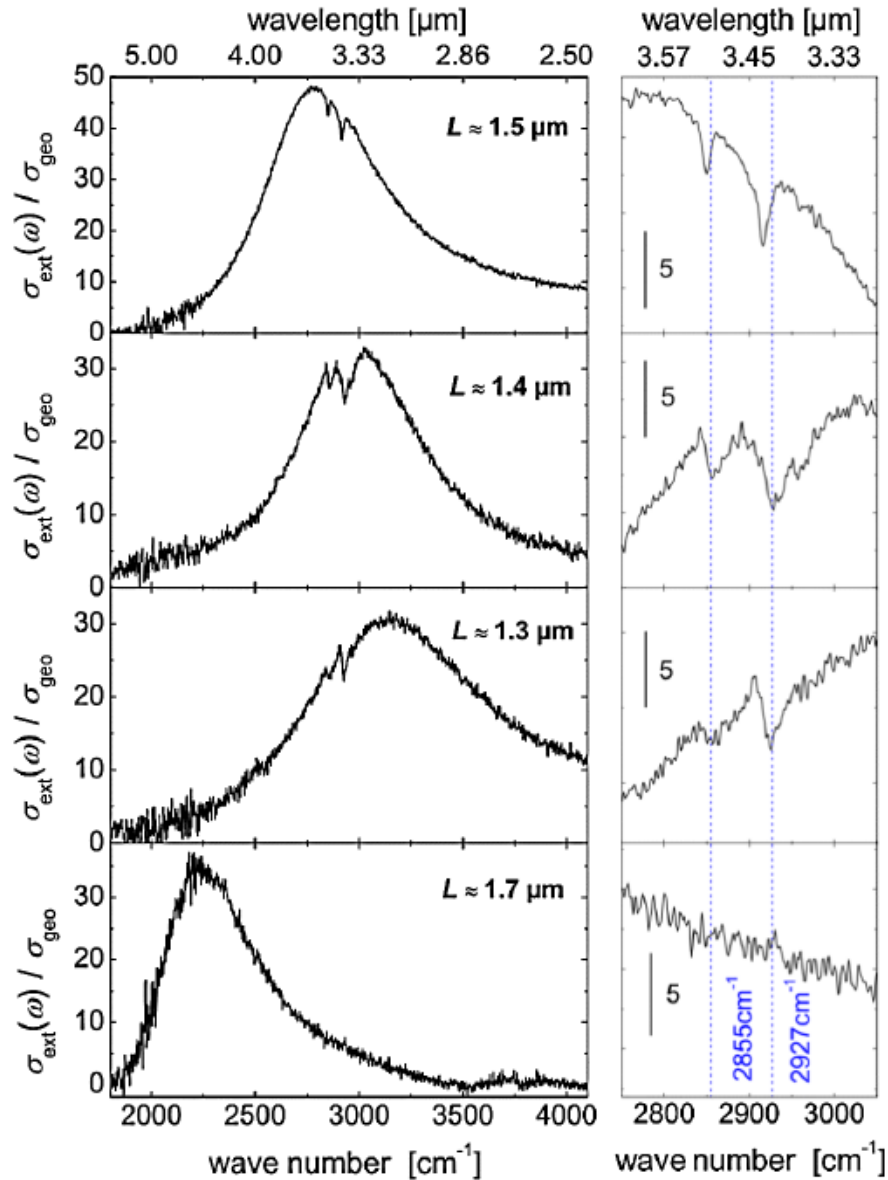
F. Neubrech et al. Phys. Rev. Lett. **101**, 157403 (2008)



# Tailoring the nanoantenna for signal optimization

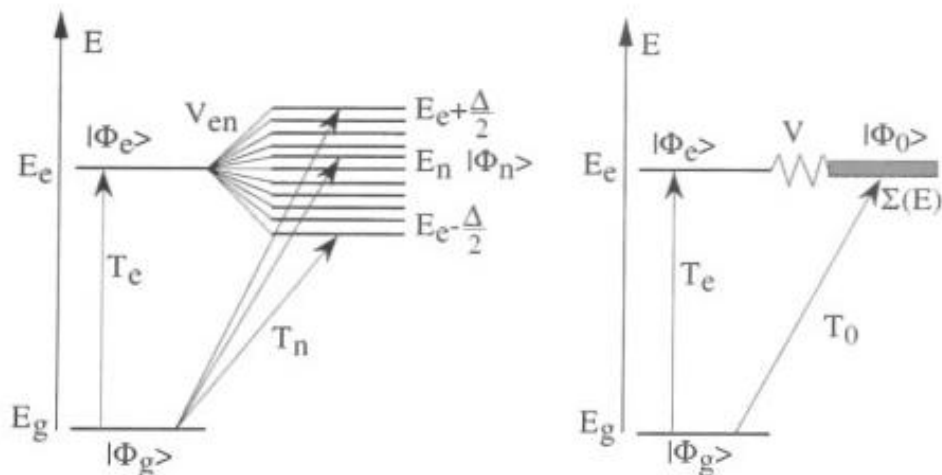
## Experiments

## Theory



# Classical analog of Fano effect

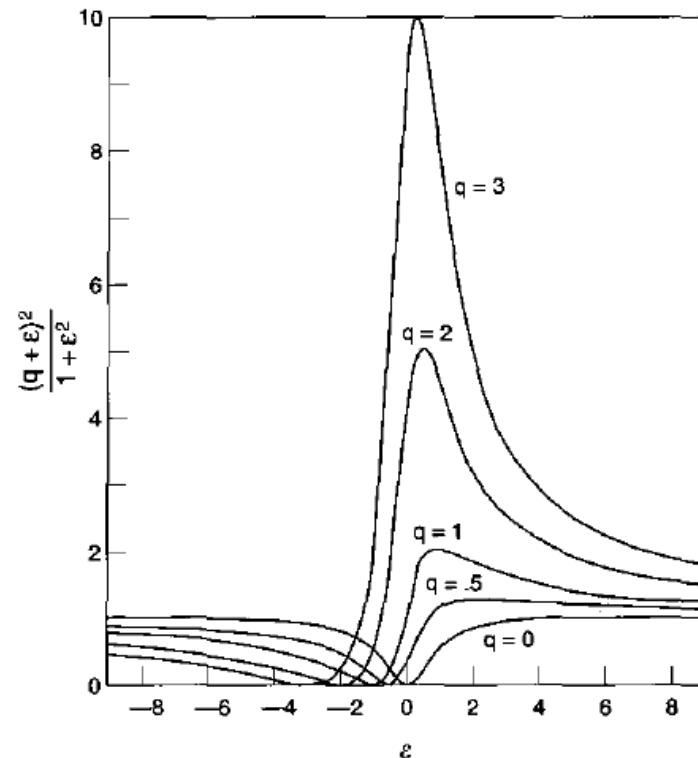
## Discrete state coupled to a continuum



$$|T_F(q, \omega)|^2 = |T_o|^2 \frac{(\omega - \omega_o' + \Gamma q)^2}{(\omega - \omega_o')^2 + \Gamma^2}$$

$$= |T_o|^2 \left( 1 + \frac{2q\Gamma(\omega - \omega_o') + \Gamma^2(q^2 - 1)}{(\omega - \omega_o')^2 + \Gamma^2} \right)$$

$$\Gamma = 2\pi \frac{|V|^2}{\Delta} \quad \varepsilon = \frac{\omega - \omega_o'}{\Gamma/2} \quad q = \frac{1}{\pi} \frac{T_e}{T_o} \frac{\Delta}{V}$$



$$|T_F|^2 = |T_o|^2 \frac{1}{\Delta} \frac{|\varepsilon + q|^2}{\varepsilon^2 + 1} = |T_o|^2 \frac{1}{\Delta} \left[ 1 + \frac{q^2}{\varepsilon^2 + 1} + \frac{2q\varepsilon - 1}{\varepsilon^2 + 1} \right]$$

# Classical analog of Fano effect

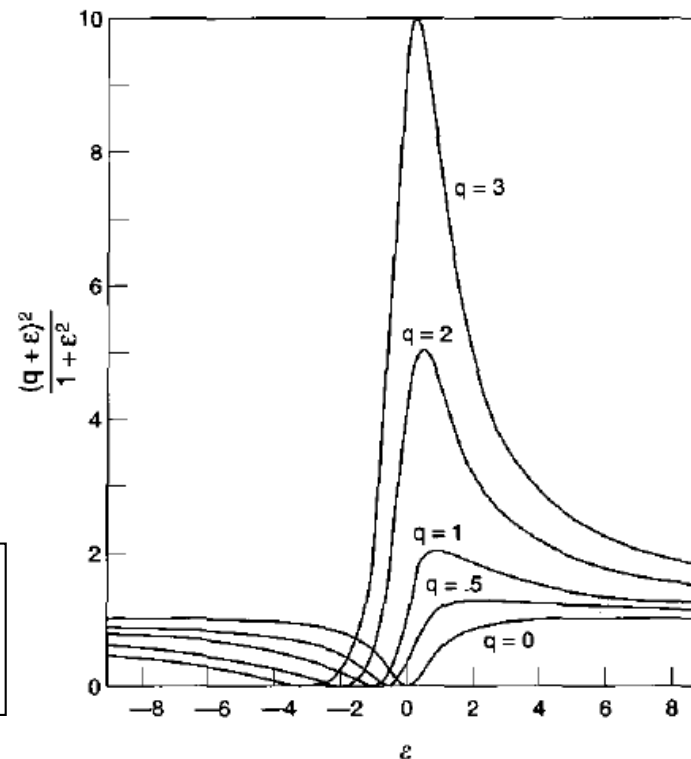
## Discrete state coupled to a continuum

$$|T_F(q, \omega)|^2 = |T_o|^2 \frac{(\omega - \omega_o' + \Gamma q)^2}{(\omega - \omega_o')^2 + \Gamma^2}$$

$$= |T_o|^2 \left( 1 + \frac{2q\Gamma(\omega - \omega_o') + \Gamma^2(q^2 - 1)}{(\omega - \omega_o')^2 + \Gamma^2} \right)$$

$$\Gamma = 2\pi \frac{|V|^2}{\Delta} \quad \varepsilon = \frac{\omega - \omega_o'}{\Gamma/2} \quad q = \frac{1}{\pi} \frac{T_e}{T_o} \frac{\Delta}{V}$$

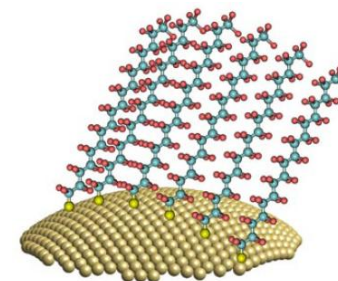
$$|T_F|^2 = |T_o|^2 \frac{1}{\Delta} \frac{|\varepsilon + q|^2}{\varepsilon^2 + 1} = |T_o|^2 \frac{1}{\Delta} \left[ 1 + \frac{q^2}{\varepsilon^2 + 1} + \frac{2q\varepsilon - 1}{\varepsilon^2 + 1} \right]$$



## Electromagnetic interference

$$|T_t|^2 = |T|^2 \left( 1 - 4\pi^2 \frac{d}{\lambda} \sqrt{\varepsilon_o} N \alpha_o \omega_o R^i \frac{(\omega - \omega_o) + \frac{1+R^r}{R^i} \frac{\gamma}{2}}{(\omega - \omega_o)^2 + \left(\frac{\gamma}{2}\right)^2} \right)$$

$$\frac{1+R^r}{R^i} = \frac{q^2 - 1}{2q}$$



# Optical antennas: Spectroscopy, Microscopy and other applications

*Javier Aizpurua*



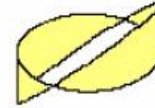
<http://cfm.ehu.es/nanophotonics>

*Center for Materials Physics, CSIC-UPV/EHU  
and Donostia International Physics Center - DIPC  
Donostia-San Sebastián, the Basque Country, Spain*

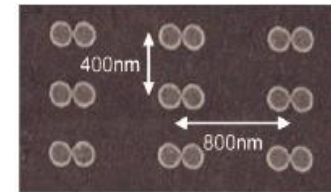
***Winter College on Optics: Advances in Nano-Optics and Plasmonics  
February 6-17, 2012  
The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy***

# Outline

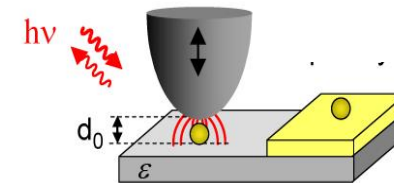
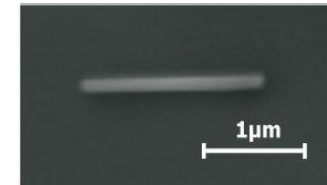
- Optical antennas: Basics



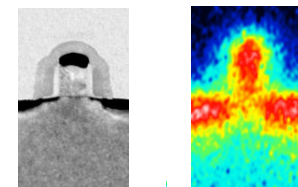
- Playing with antenna modes



- Optical antennas for Enhanced Spectroscopy

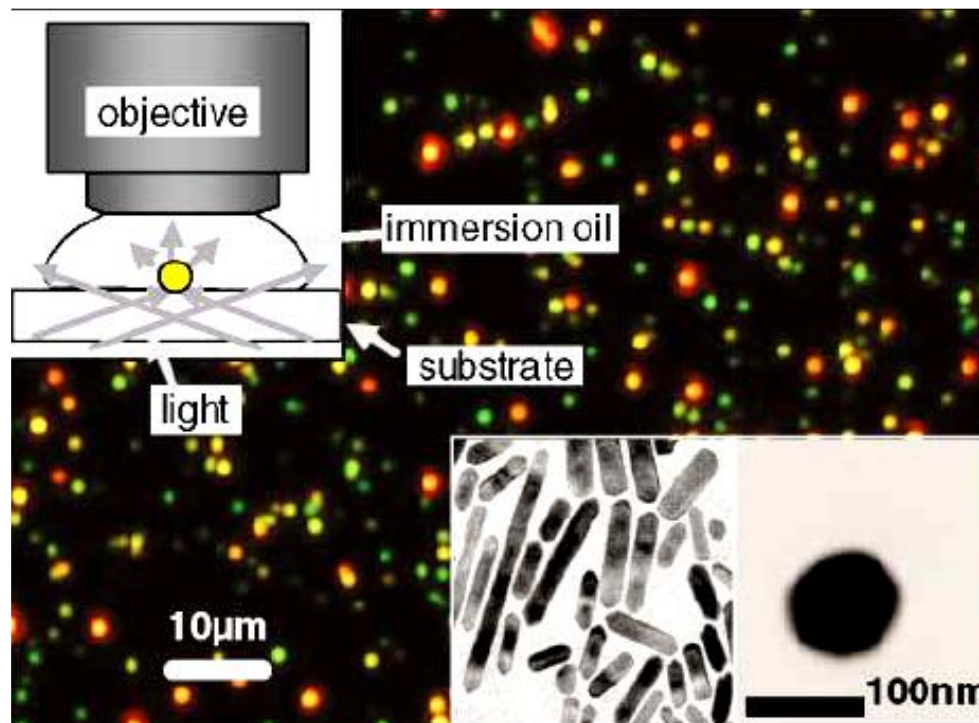


- More applications of optical antennas:  
Microscopy and Biomedicine.



# Near-field Optical Microscopy

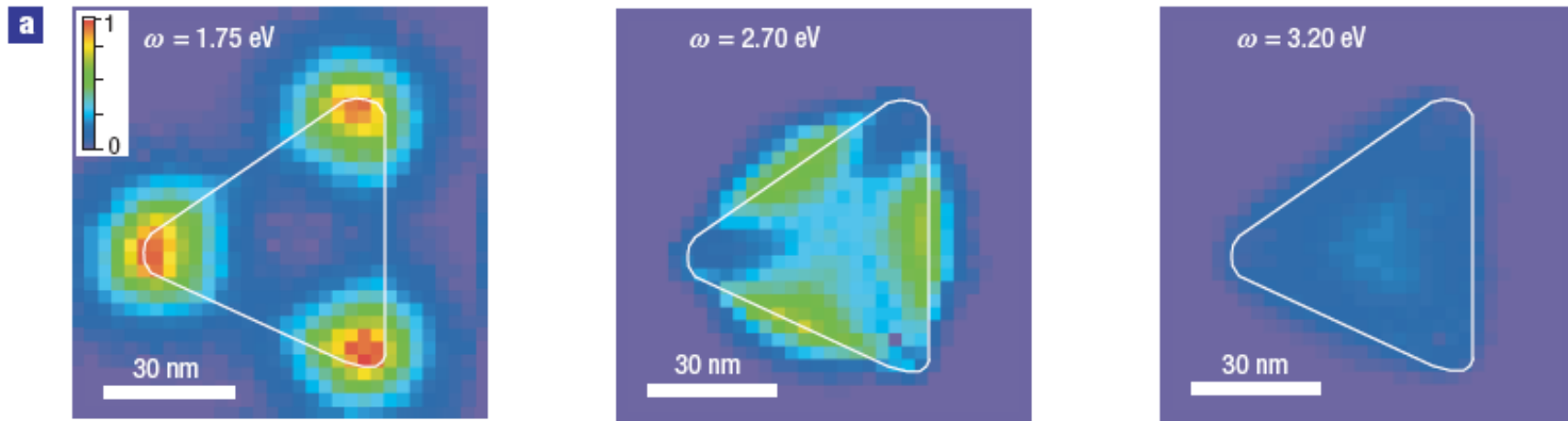
- **Far field** information is commonly accessible:
  - Dark field optical spectroscopy



C. Sönnichsen *et al.*,  
*Phys. Rev. Lett.* **88**,  
077402 (2002)

# Near-field Optical Microscopy

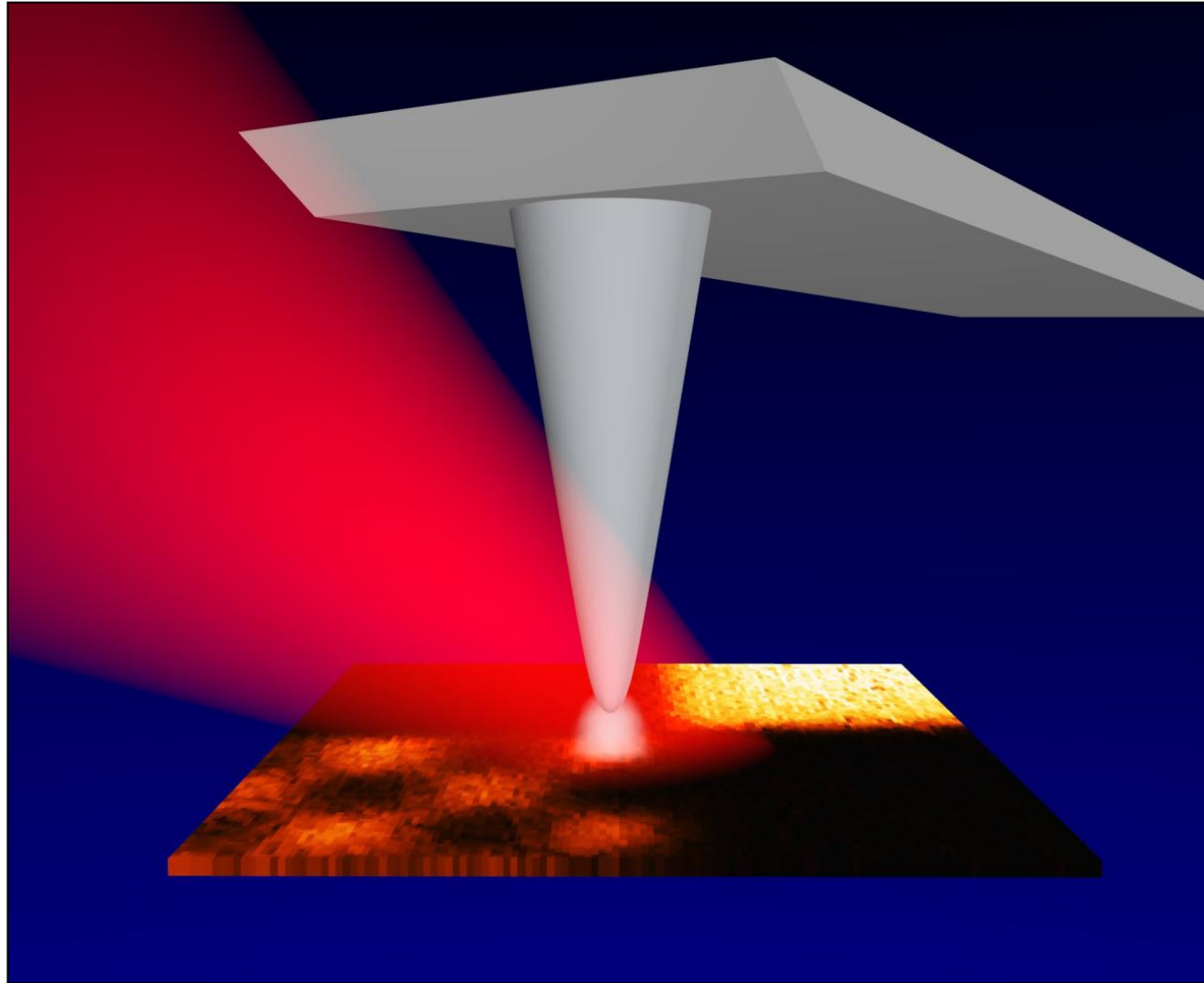
- **Near-Field** is more challenging to access
- One possibility: EELS
  - Does not resolve the phase



*J. Nelayah et al.,  
Nature Physics 3, 348  
(2007)*

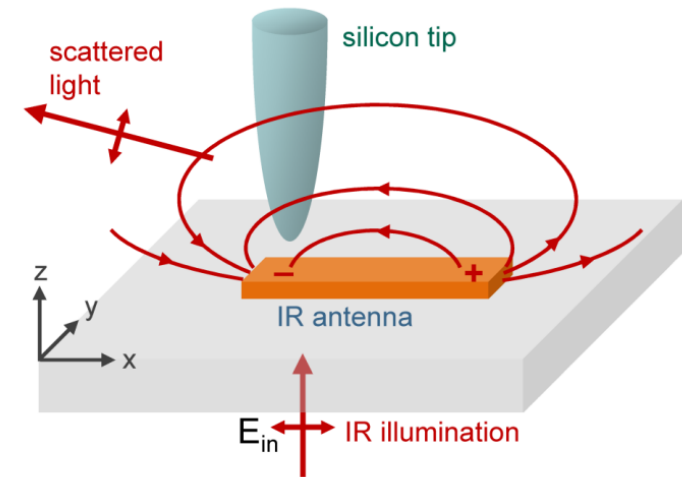
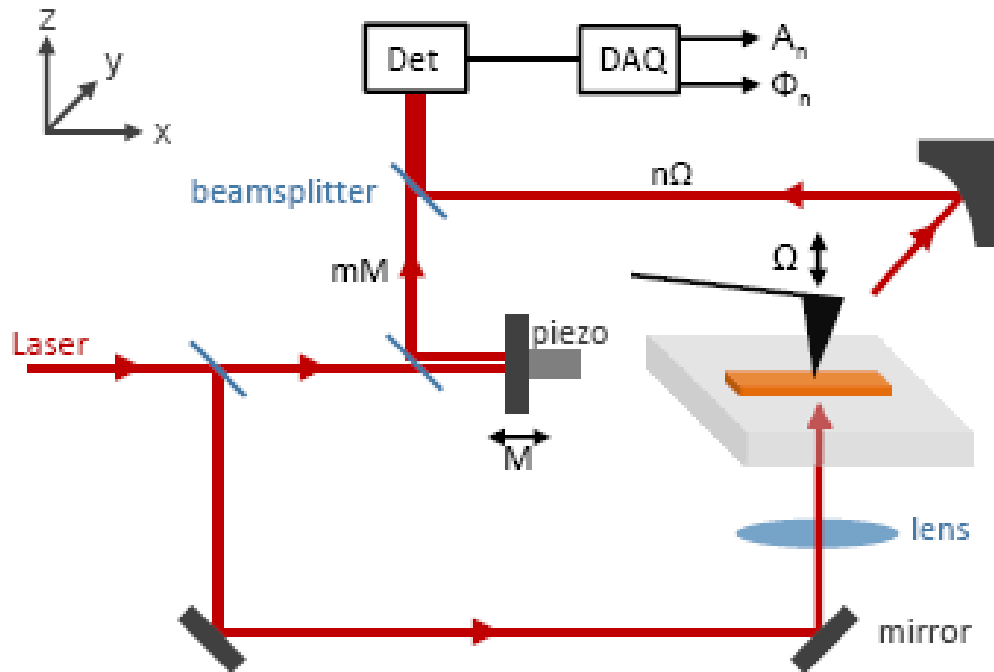


## Scattering-type Near Field Optical Microscopy; Mapping both amplitude and phase in the nanoscale



# Transmission mode s-SNOM for near-field mapping

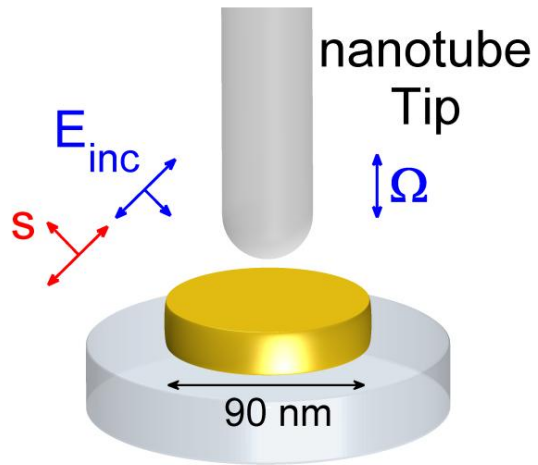
Rainer Hillenbrand



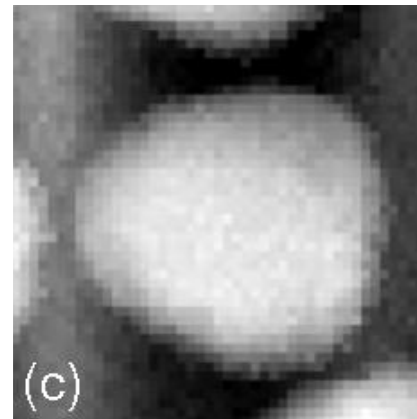
- **Transmission-mode for homogeneous illumination, also side illumination**
- **AFM tip scatters antenna near fields** R. Hillenbrand et al. *APL* 83 (2003)
- **Pseudoheterodyne detection measures amplitude and phase** *APL* 89 (2006)

# Which scattering tip to use?

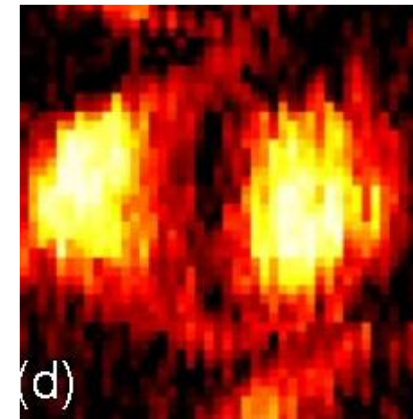
## Weakly interacting Tip



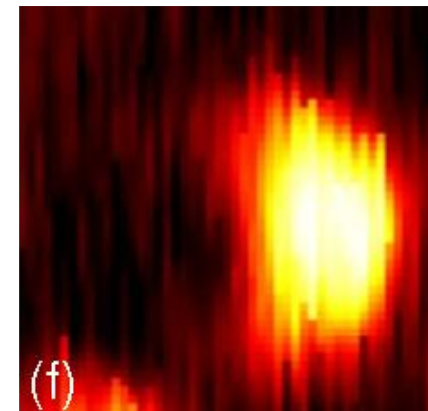
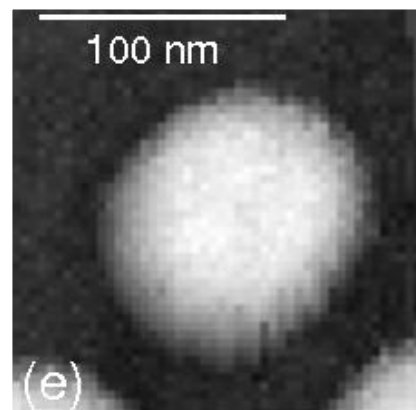
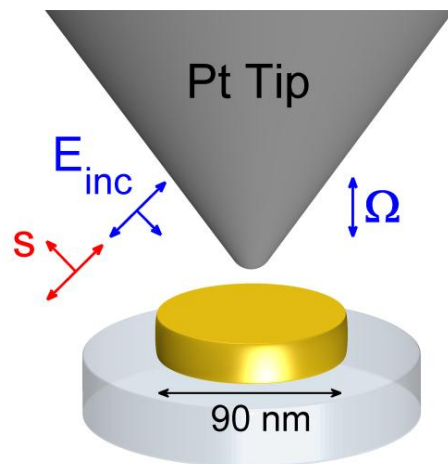
## Topography



## Near-field image



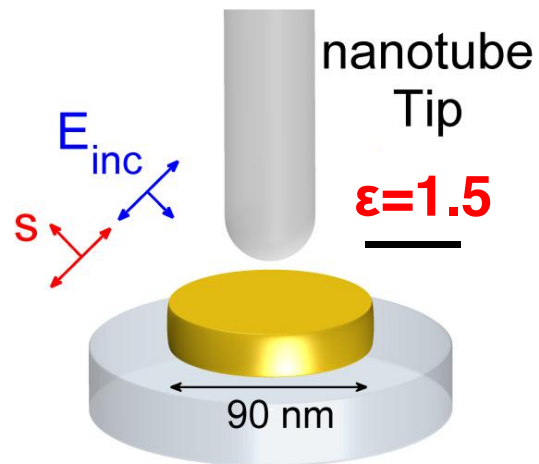
## Strongly interacting Tip



Experiments by R. Hillenbrand,  
nanoGUNE and Max Planck Institute  
(Donostia and Munich)

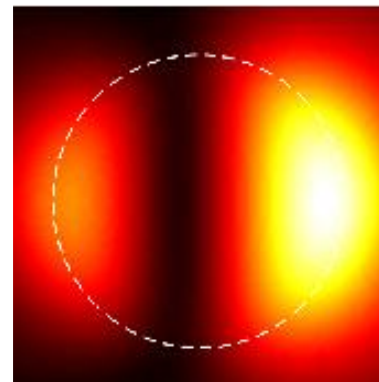
# Which scattering tip to use?

**Weakly** interacting regime

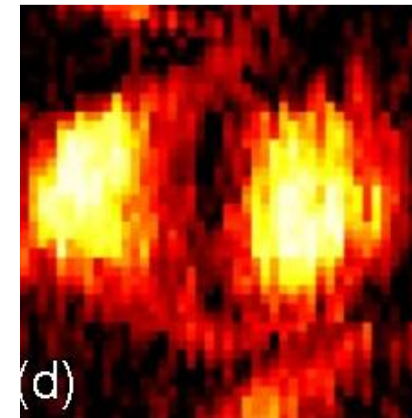


**Theory**

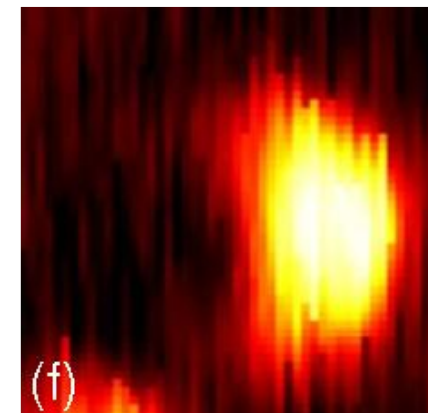
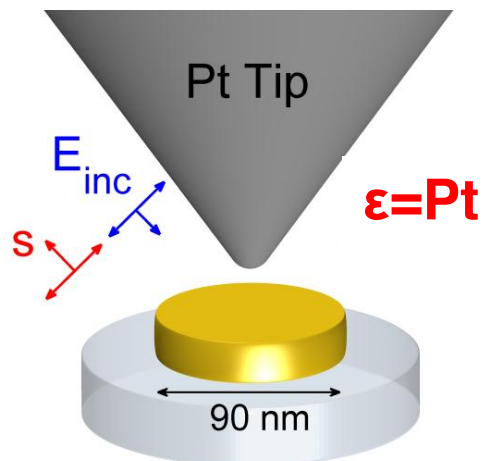
**Original NF  
(no Tip)**



**Experiment**

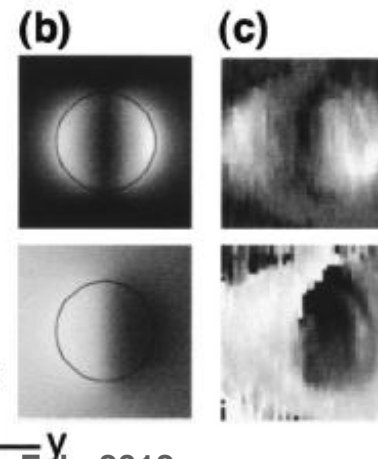
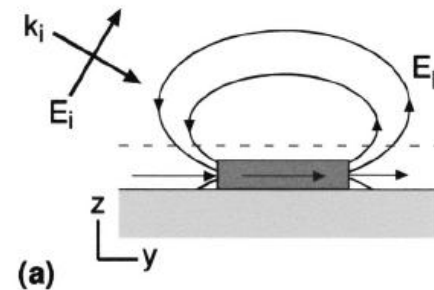
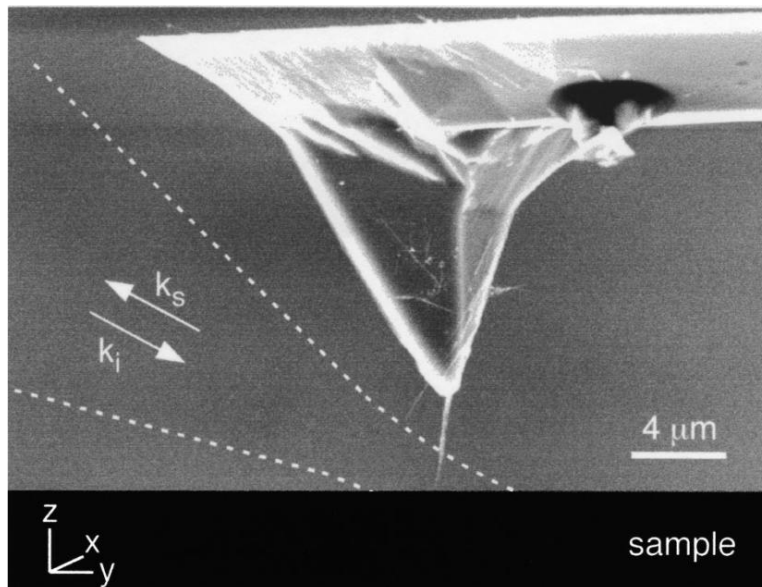


**Strongly** interacting regime



# Accessing the NF information: s-SNOM weak scattering tip:carbon nanotube

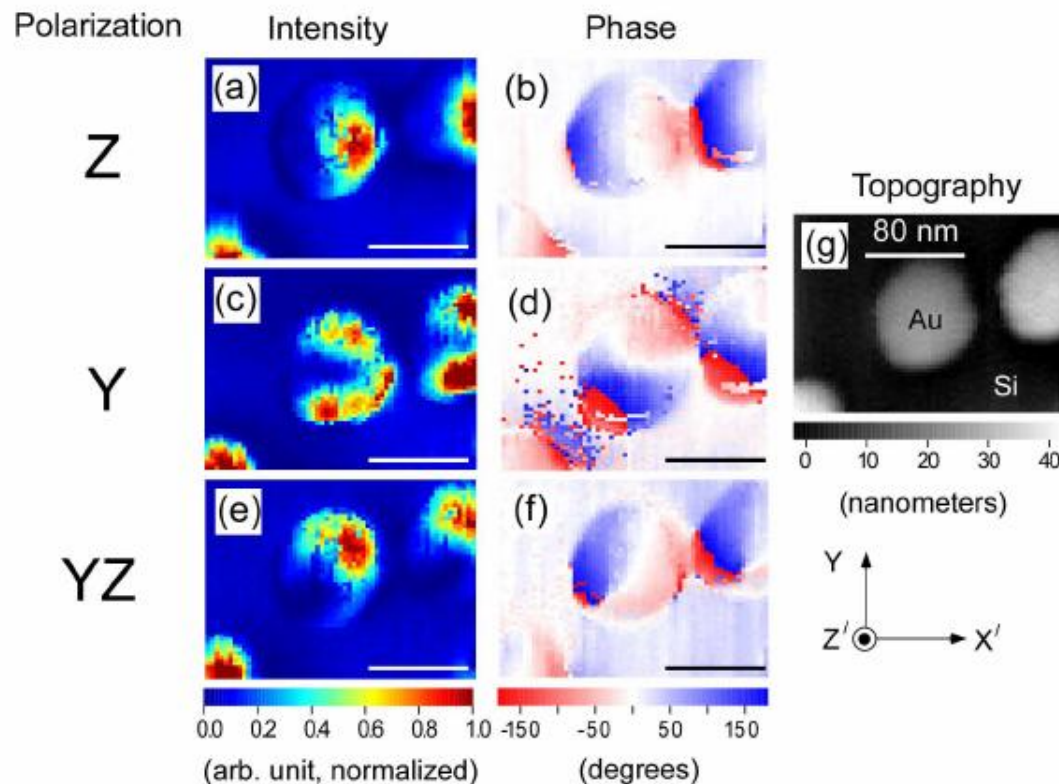
- Scattering-type scanning near-field optical microscopy (s-SNOM) maps both amplitude and phase information in the nanoscale



R. Hillenbrand  
*et al.*, *Appl.*  
*Phys. Lett.* **83**,  
**368 (2003)**

# Accessing the phase information: s-SNOM

- Scattering-type scanning near-field optical microscopy (s-SNOM) maps both amplitude and phase information in the nanoscale

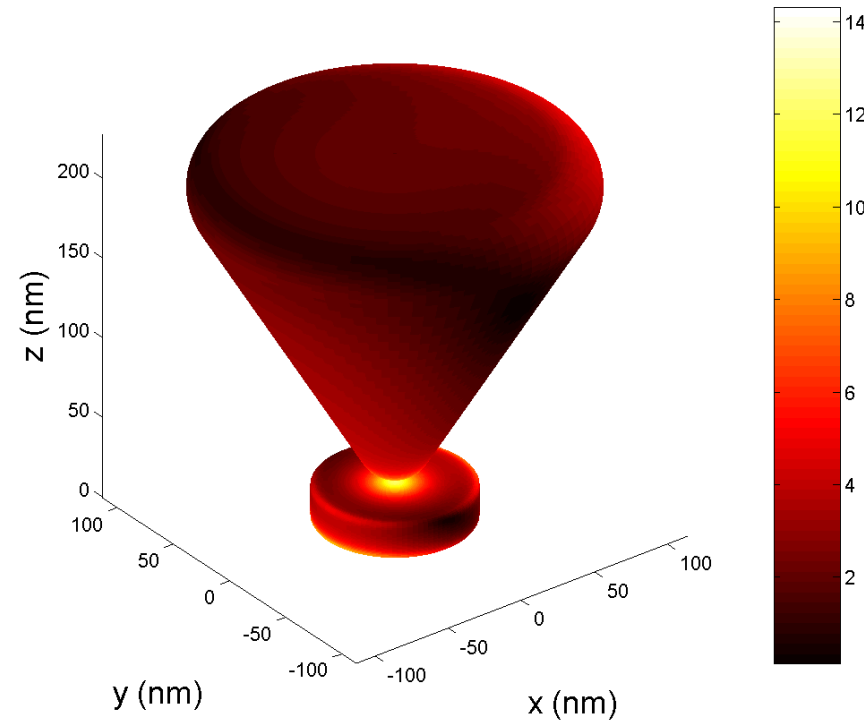
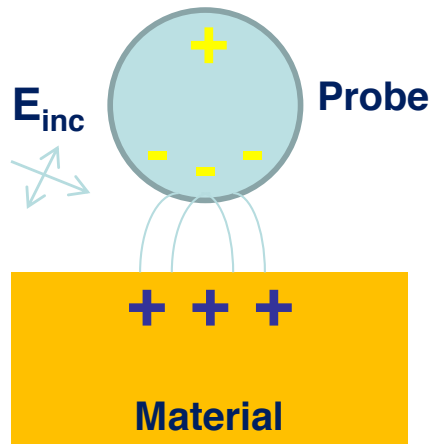


Z. H. Kim and S. R. Leone, *Opt. Express* 16, 1733 (2008)



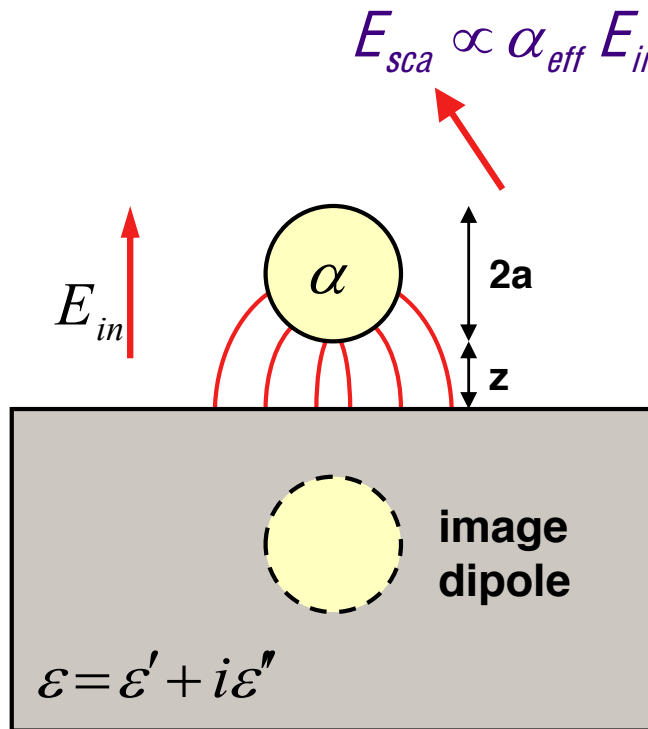
# Any advantage of a strong scattering tip?

## Localization of plasmons by a probe



## Material properties mapping

# Dipolar sphere-plane near-field interaction



Polarizability of the tip

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

Effective polarizability of interacting dipoles

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

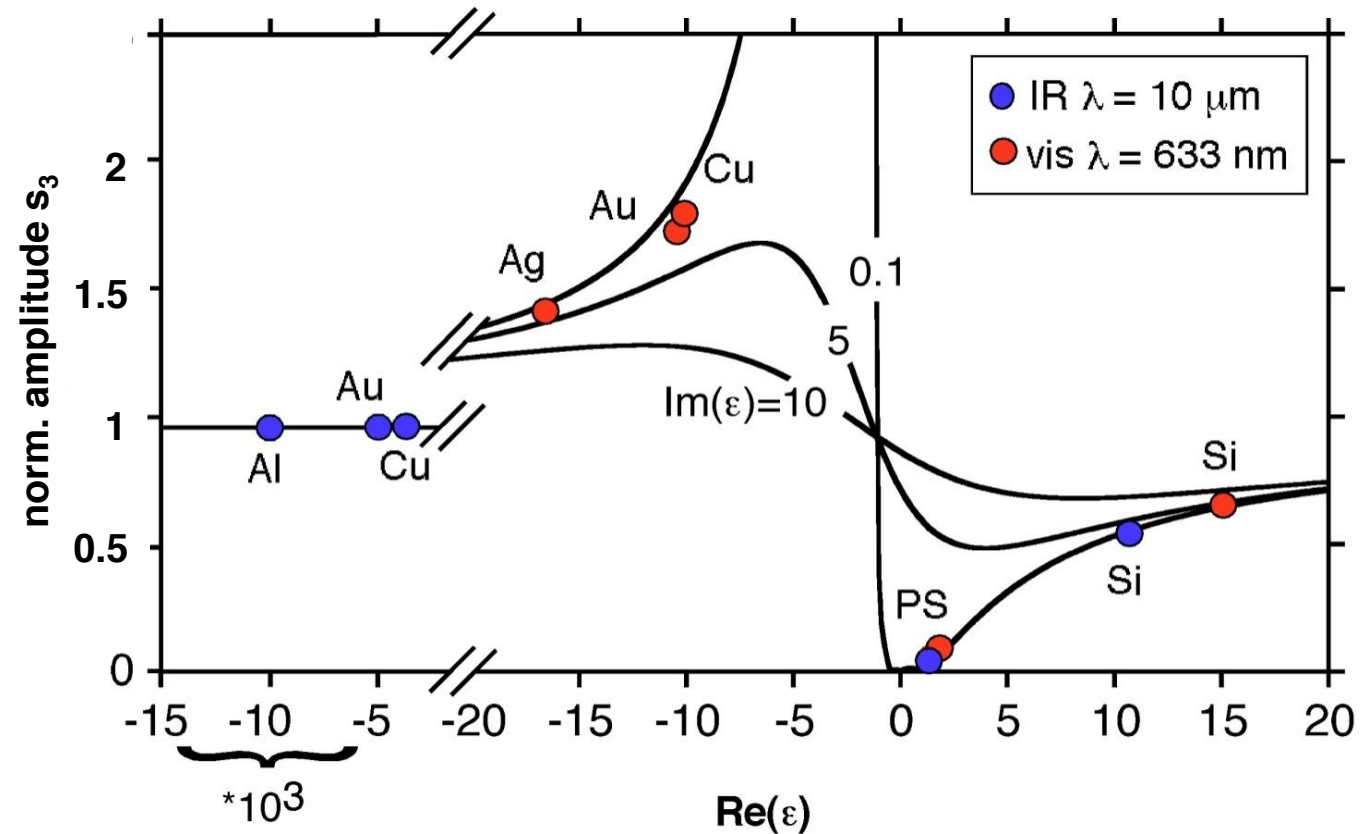
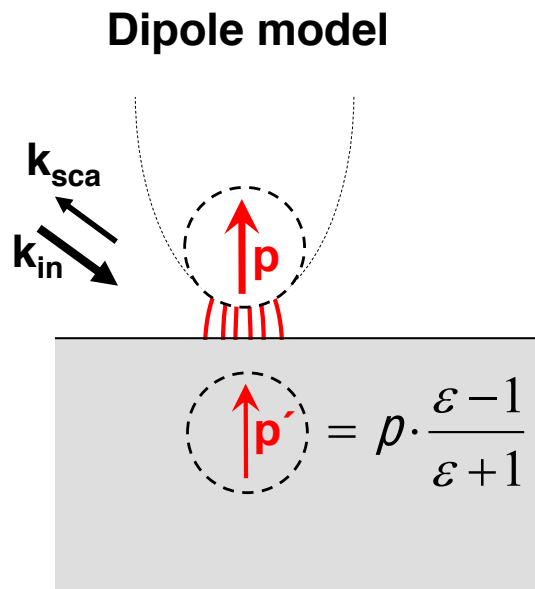
→ near-field interaction modifies amplitude and phase of  $E_{sca}$

→ resonance through a) sphere  $\varepsilon_p = -2$

b) plane  $\varepsilon = -1$

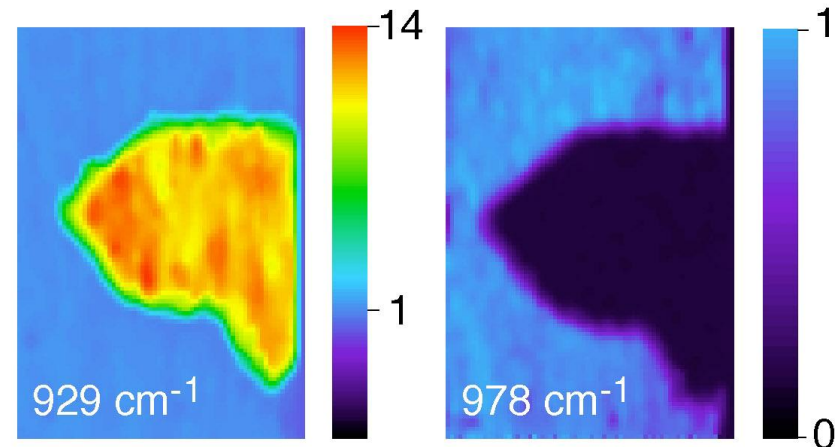
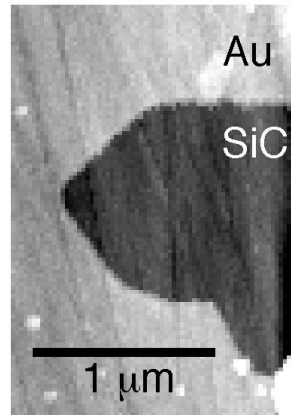
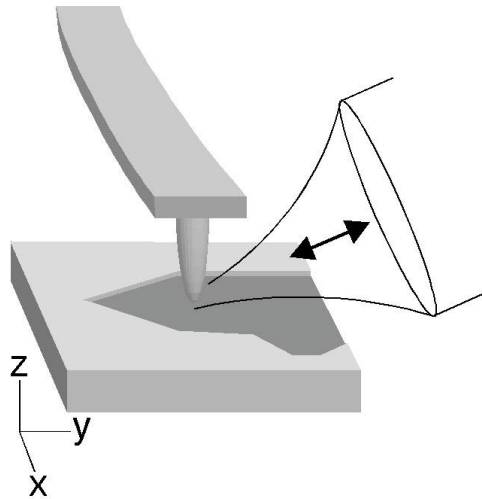
**No multipoles included in this description**

# Dipole model explains near-field material contrasts from visible to IR frequencies



T. Taubner, R. Hillenbrand, F. Keilmann, J. Microsc. 210, 311 (2003)

# s-SNOM contrast of SiC/Au



**phonon-enhanced  
near-field interaction**

- strong signals
- high spectral sharpness
- optical fingerprint



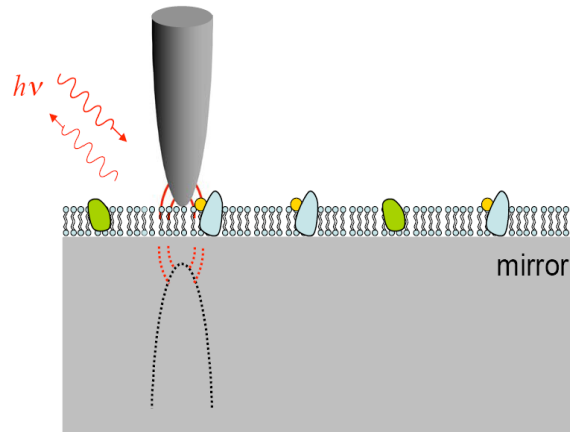
**identification of materials at  
nanoscopic spatial resolution**

**<  $\lambda / 100$  !**

R. Hillenbrand, T. Taubner, F. Keilmann, Nature 418, 159-162 (2002)

# Applications

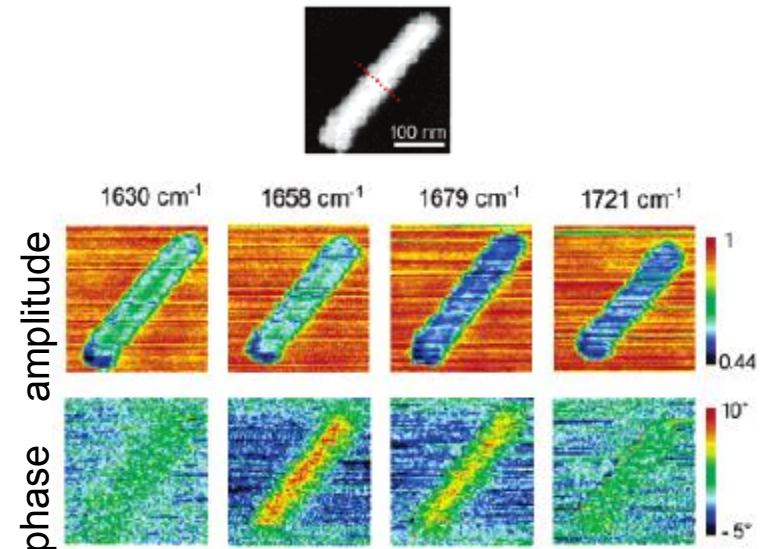
## Hig resolution biolabeling imaging



Au particle → biolabel

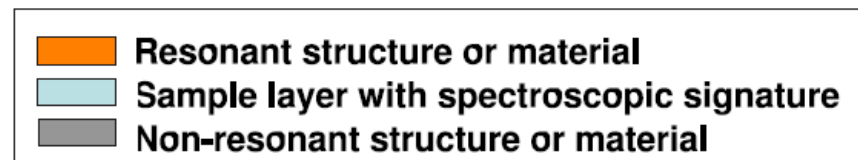
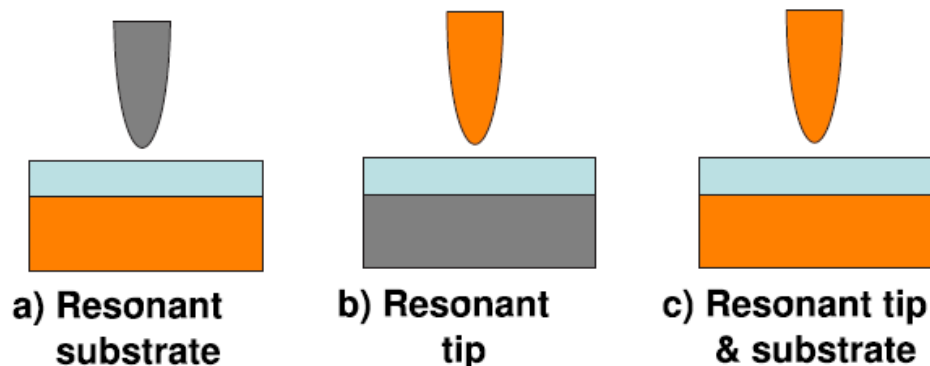
Resonant substrate → mirror

## IR near-field spectroscopy

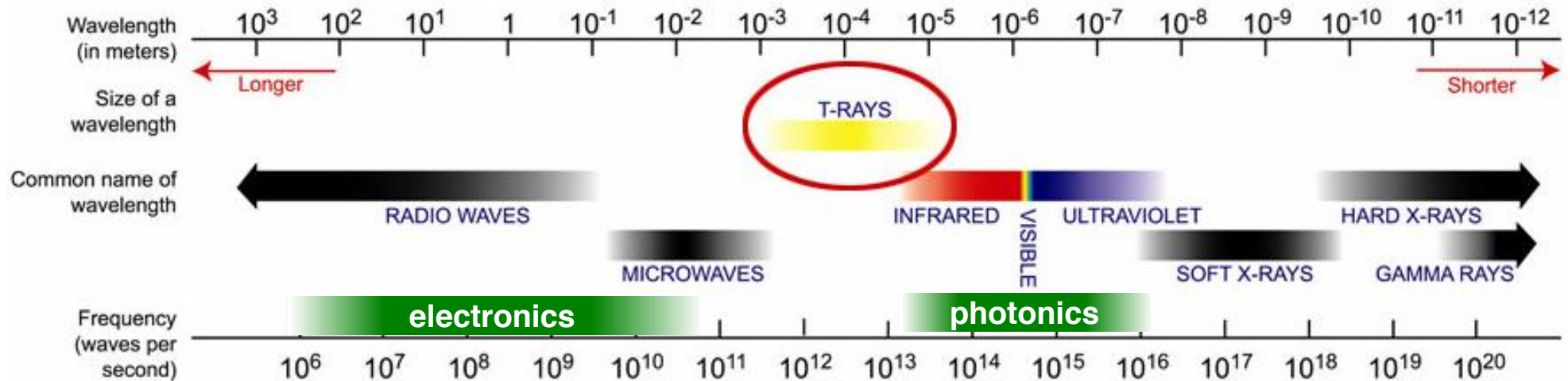


IR Near-fiel imaging of a single tobacco virus on Si

M. Brehm et al, Nano Lett. 6, 1307 (2006)



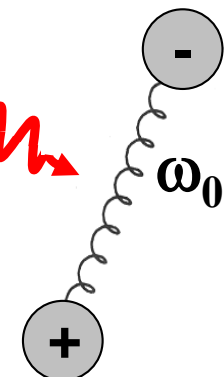
# Terahertz radiation (THz, T-RAYS)



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
- .....

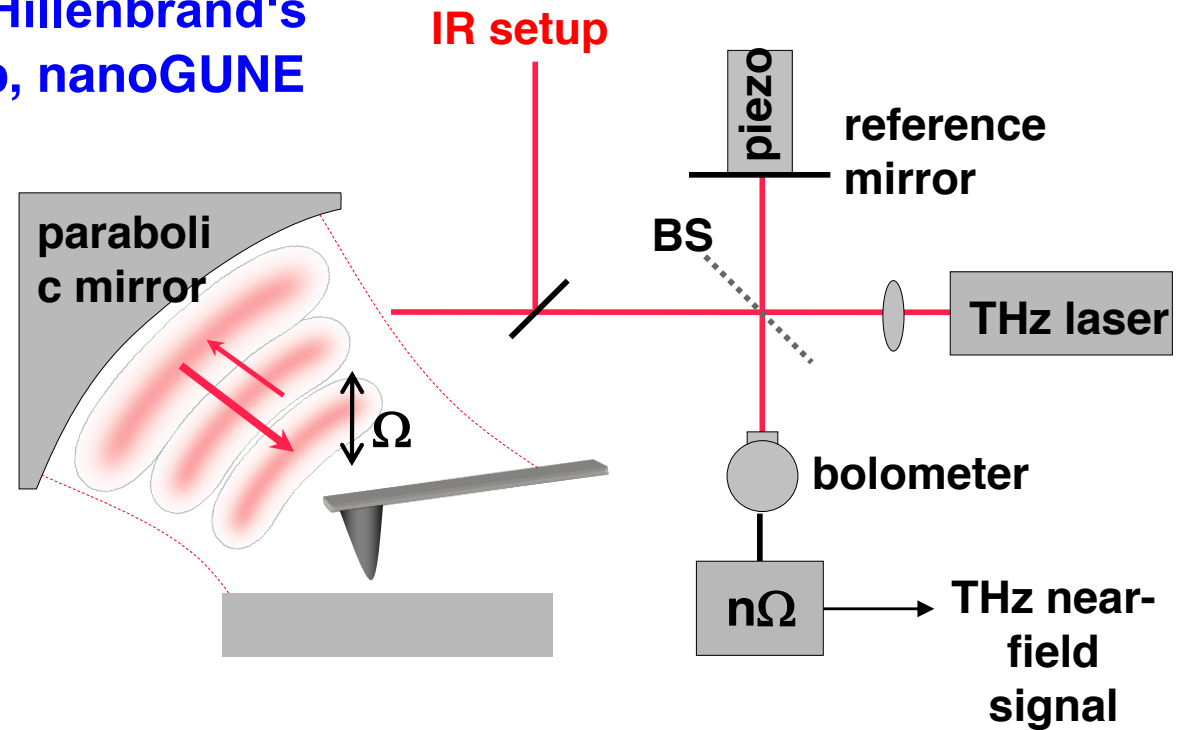
**BUT: spatial resolution  $> \lambda/2 \approx 10\text{-}100 \mu\text{m}$**





# Scattering-type THz near-field microscope based on AFM

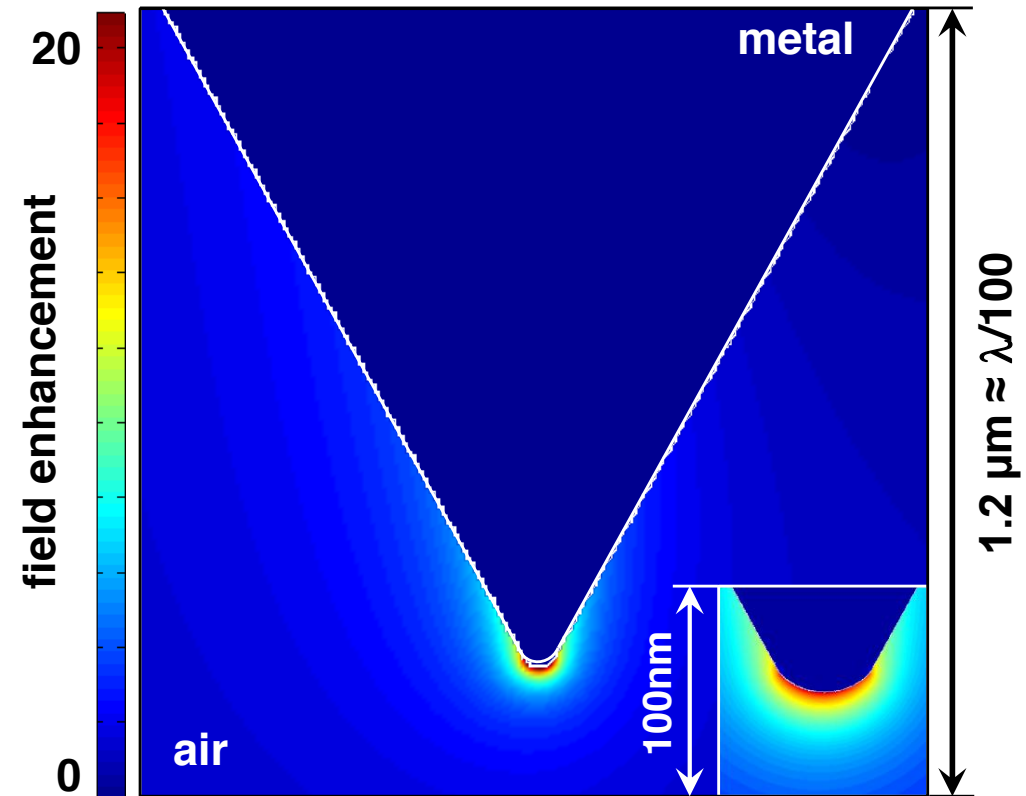
## THz s-SNOM at R. Hillenbrand's group, nanoGUNE



- Use of **commercial AFM tips** (tip length  $L \approx 10 - 20 \mu\text{m} \ll$  wavelength  $\lambda \approx 100 - 200 \mu\text{m}$ )
- Modulation of tip-sample distance (**tapping mode**, frequency  $\Omega$ )
- **Interferometric detection** of THz radiation backscattered by tip
- **Background suppression** by signal demodulation at **higher harmonics  $n\Omega$**
- Use of **single laser frequency** (high laser power, ca. **100 mW**)
- Integration in existing s-SNOM setup: **simultaneous THz and IR s-SNOM**

# 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  $\mu\text{m}$**  ( $\approx \lambda / 118$ )
- **30 nm field confinement** at tip apex, like for VIS or IR frequencies
- Mechanism: **lightning-rod effect**

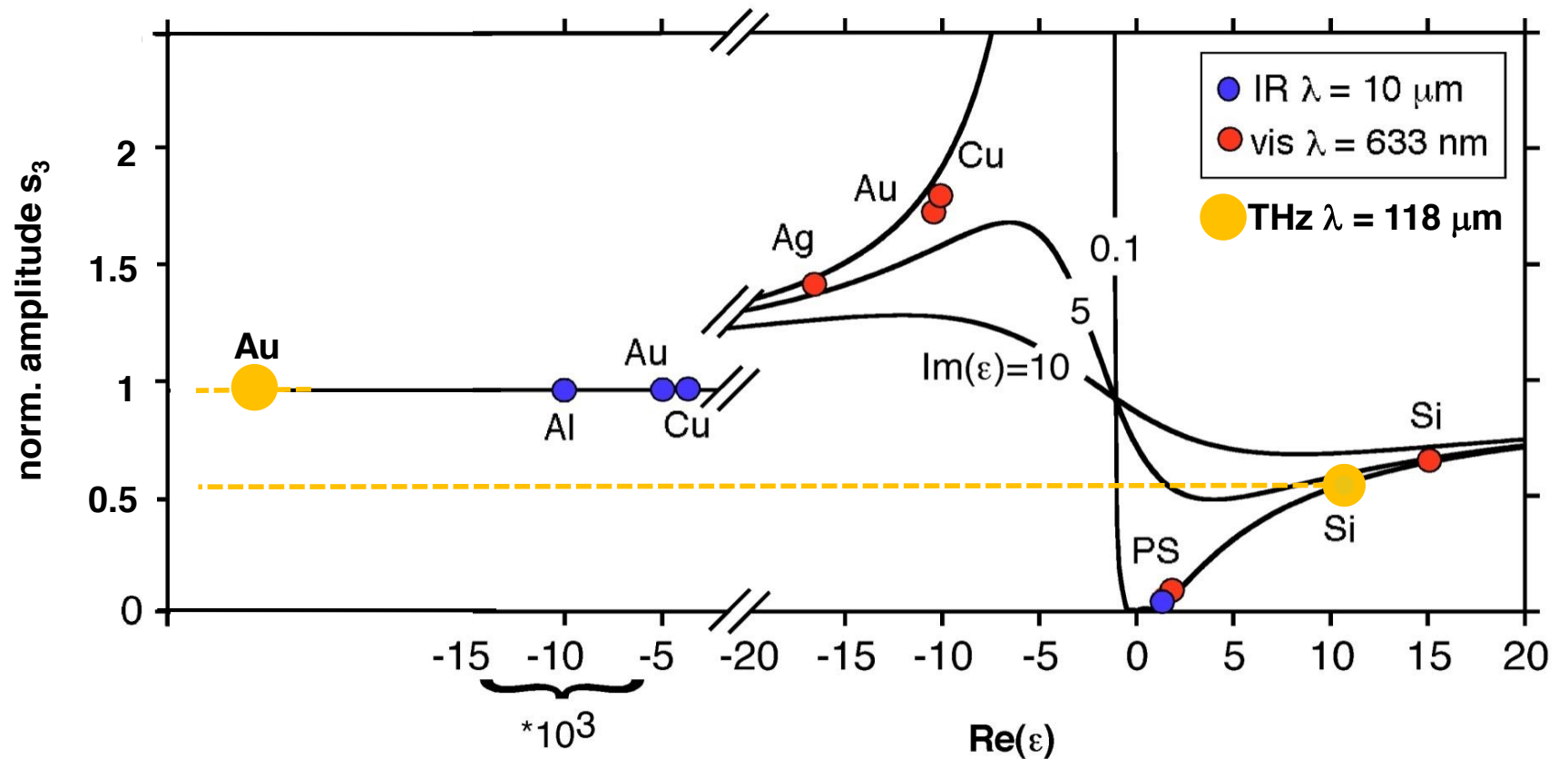


Boundary Element Method calculation



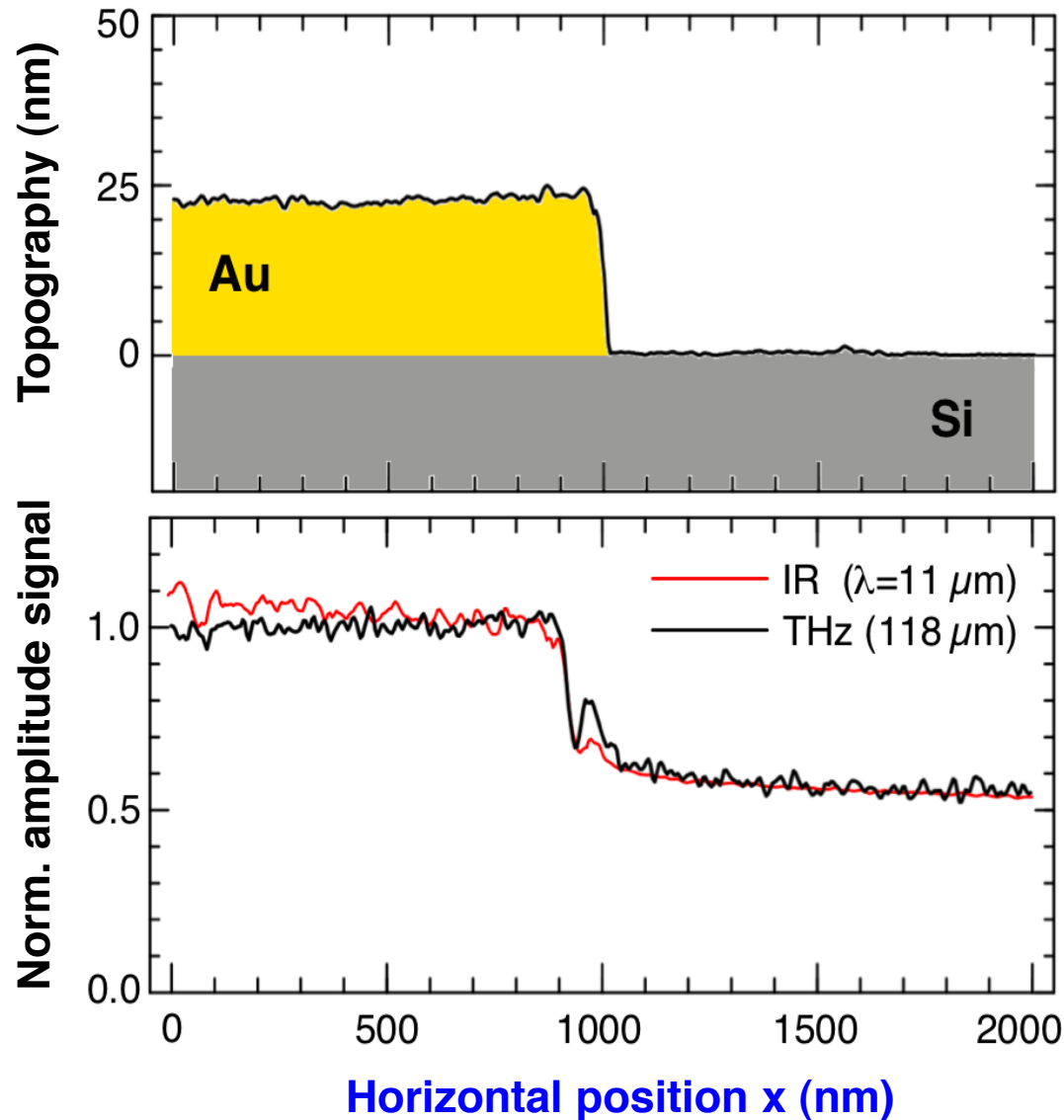
**nanoscale confinement of THz fields can be achieved with metal tips much smaller than the wavelength, e.g. AFM tips**

# Dipole model explains near-field material contrasts from visible to THz frequencies



T. Taubner, R. Hillenbrand, F. Keilmann, J. Microsc. 210, 311 (2003)

# Au/Si test sample demonstrates strong THz material contrast



Recording THz signal as a function of tip-sample position x:

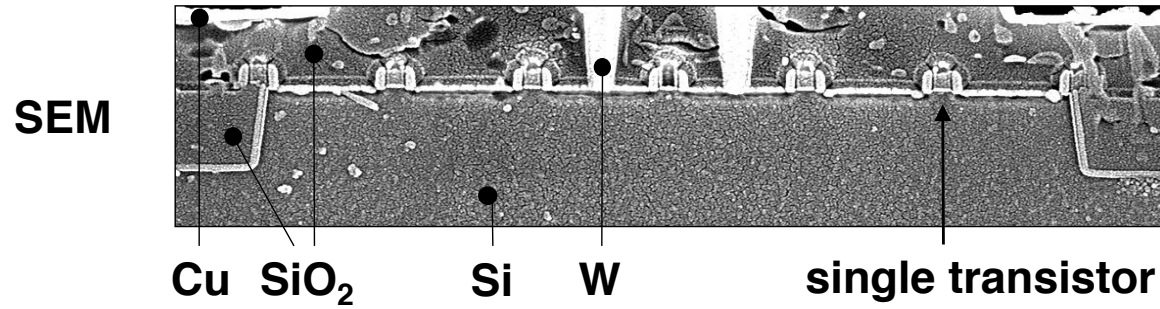


Optical properties for Au and Si are the same at THz and IR frequencies



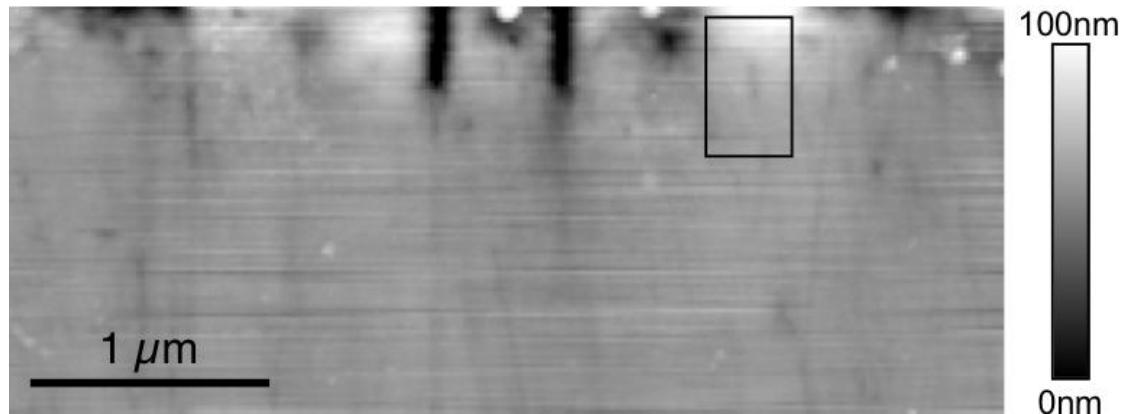
similar near-field contrast mechanism at IR and THz frequencies

# THz s-SNOM can map free carriers in semiconductor devices

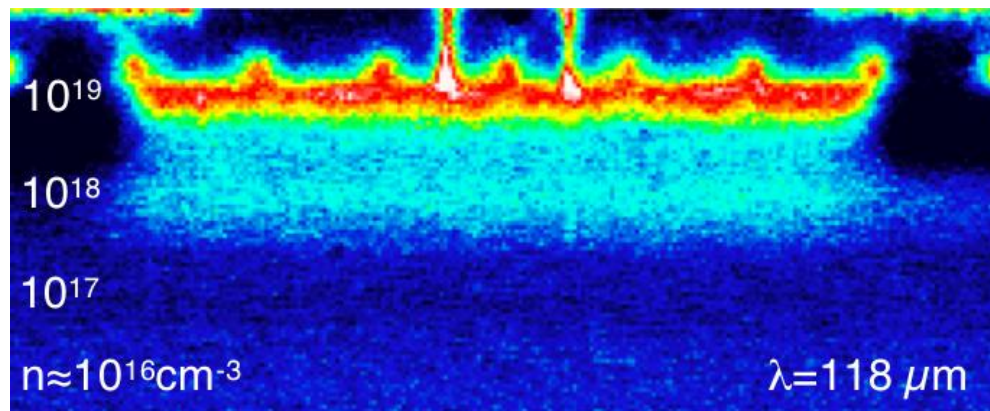


test structure  
containing transistors of  
65 nm - technology

Topography



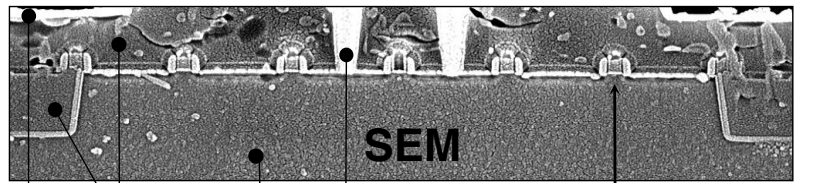
THz image



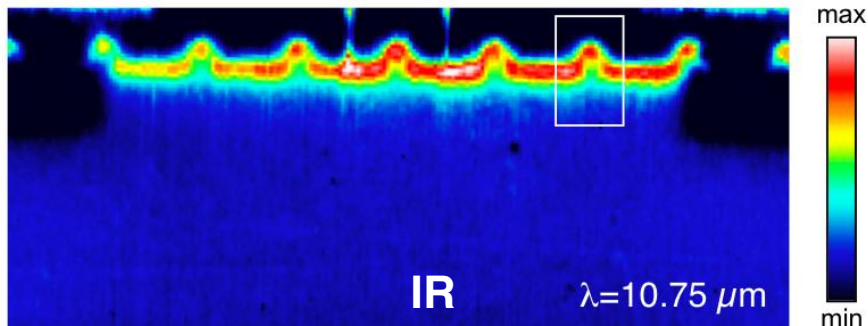
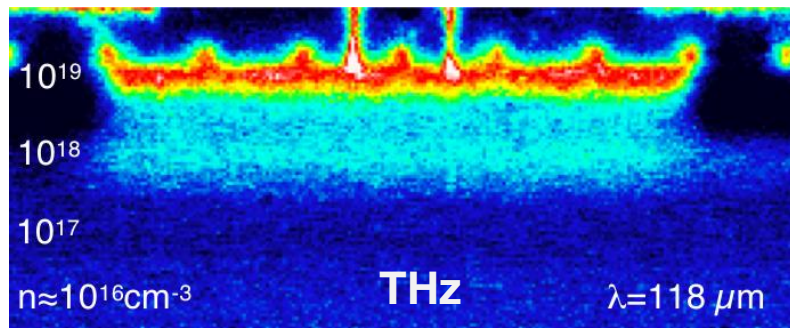
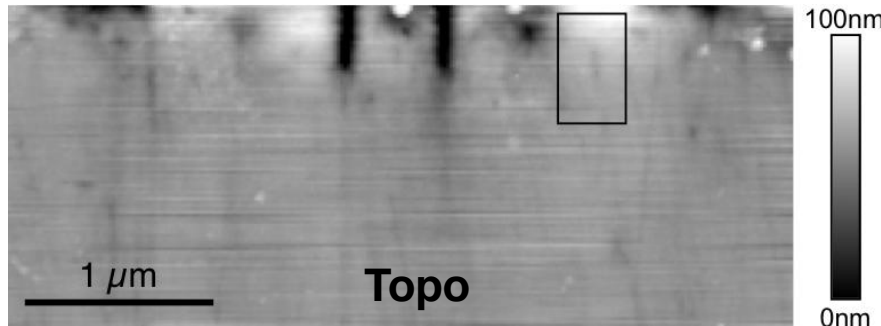
THz image exhibits  
**material and  
free-carrier contrast**



# THz s-SNOM can map free carriers in semiconductor devices



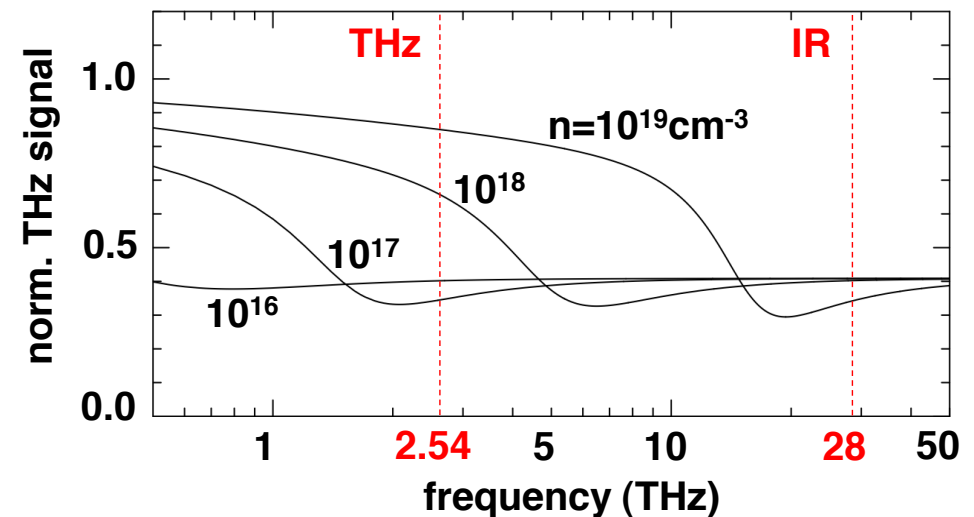
Cu SiO<sub>2</sub> Si W single transistor



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

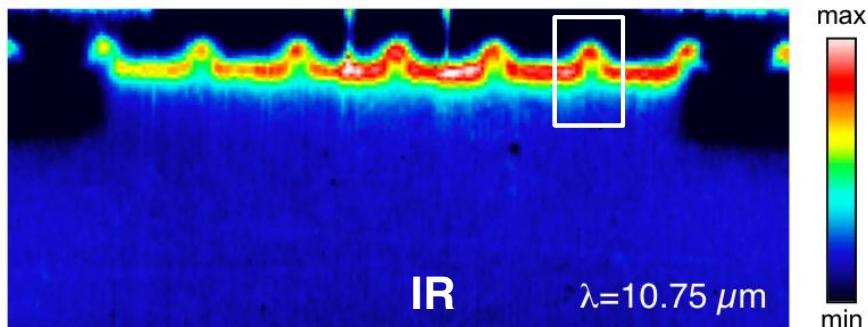
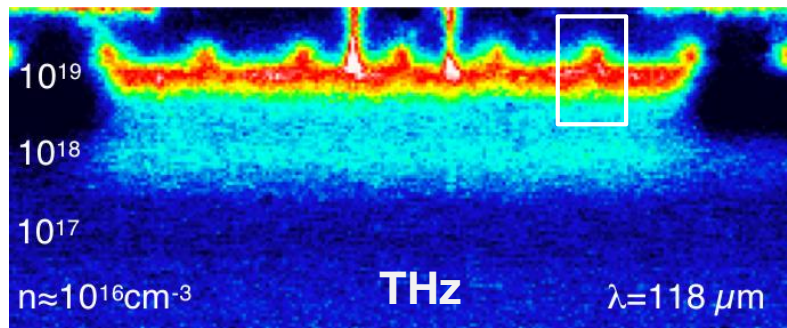
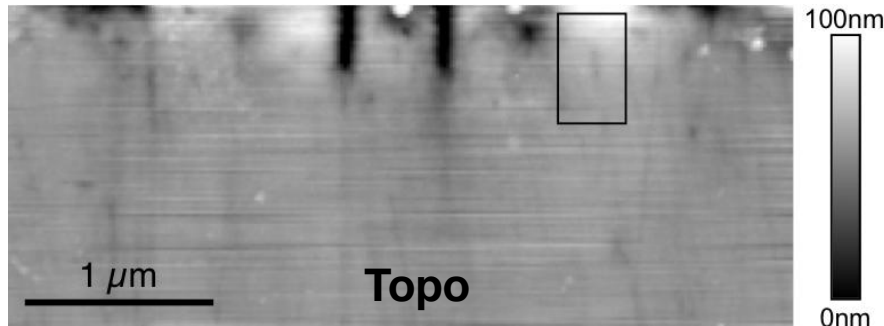
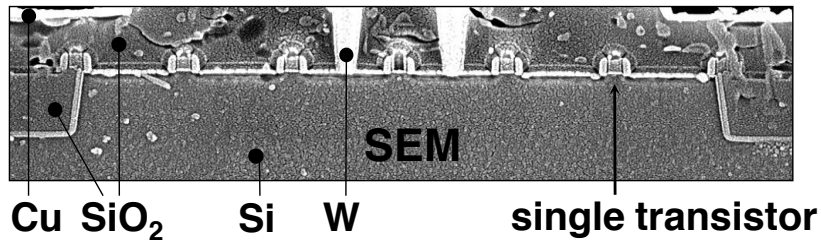
$$\epsilon(\omega) = \epsilon_{\infty} \left( 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \right) \text{ with } \omega_p^2 = \frac{n e^2}{\epsilon_0 \epsilon_{\infty} m \cdot m_0}$$

Dipole model explains free-carrier contrast

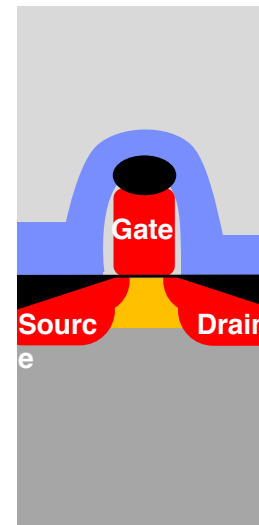




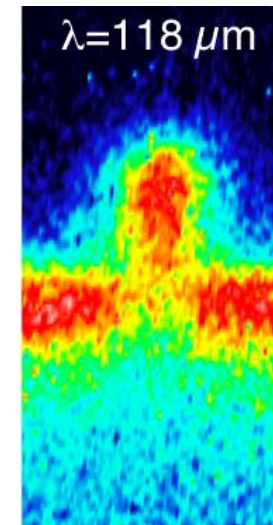
# THz s-SNOM resolves source, drain and gate of single transistors



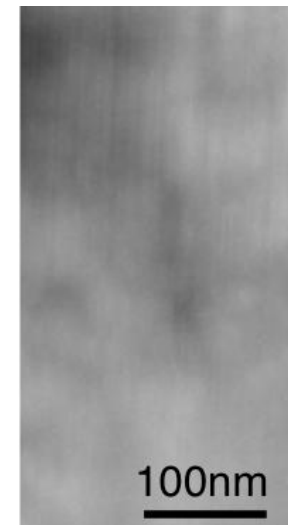
Single 65 nm - transistor



design

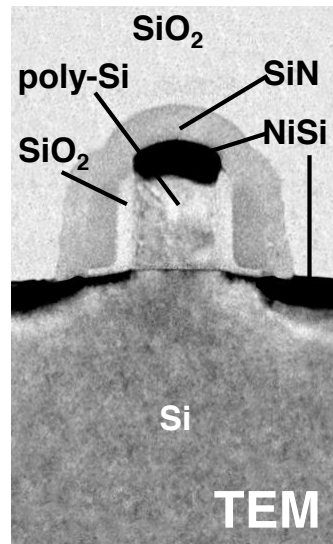


THz



Topo

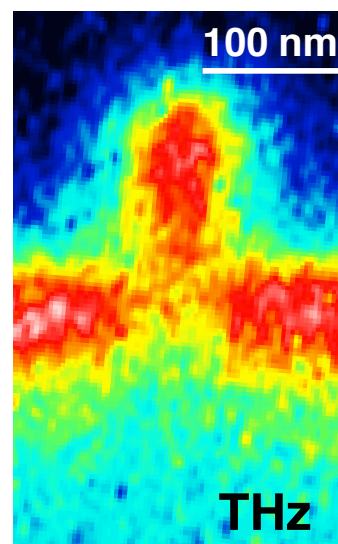
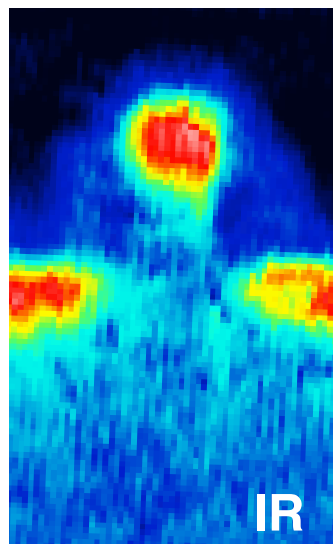
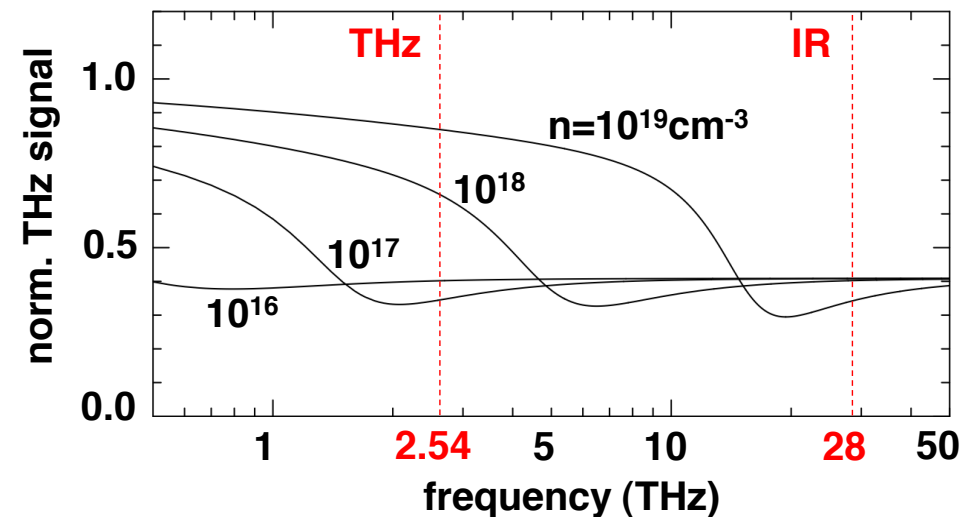
# THz s-SNOM maps free carriers with nanometric resolution



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

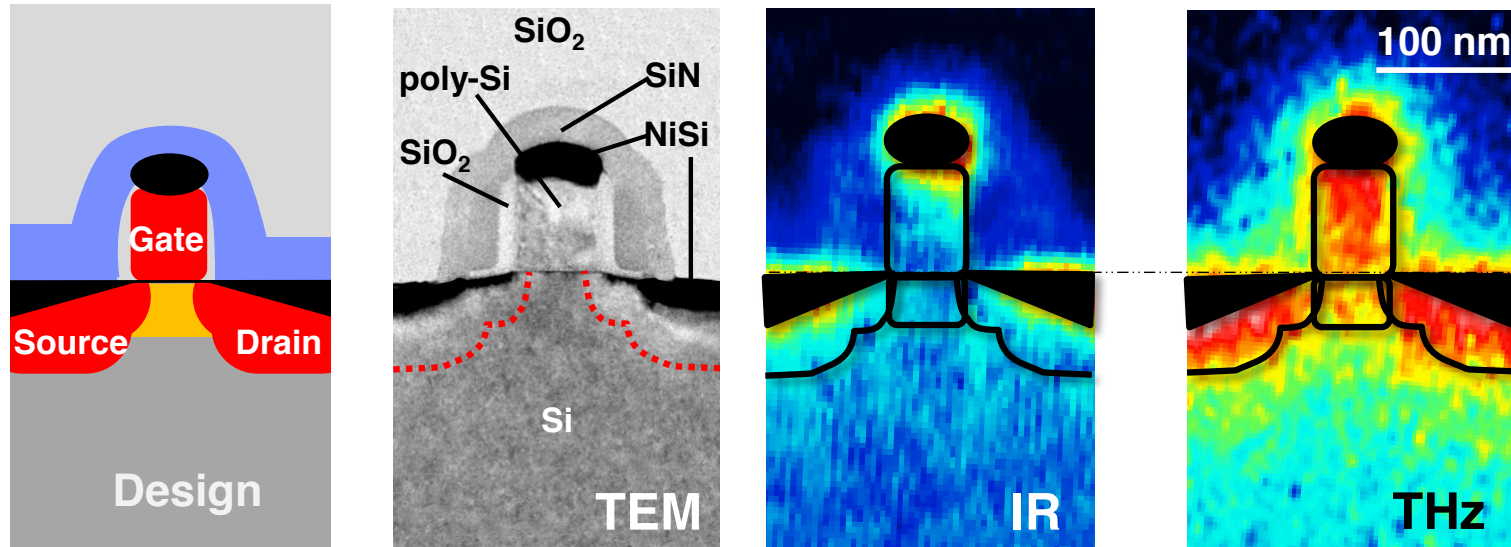
$$\epsilon(\omega) = \epsilon_{\infty} \left( 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \right) \quad \text{with} \quad \omega_p^2 = \frac{n e^2}{\epsilon_0 \epsilon_{\infty} m \cdot m_0}$$

Dipole model explains free-carrier contrast



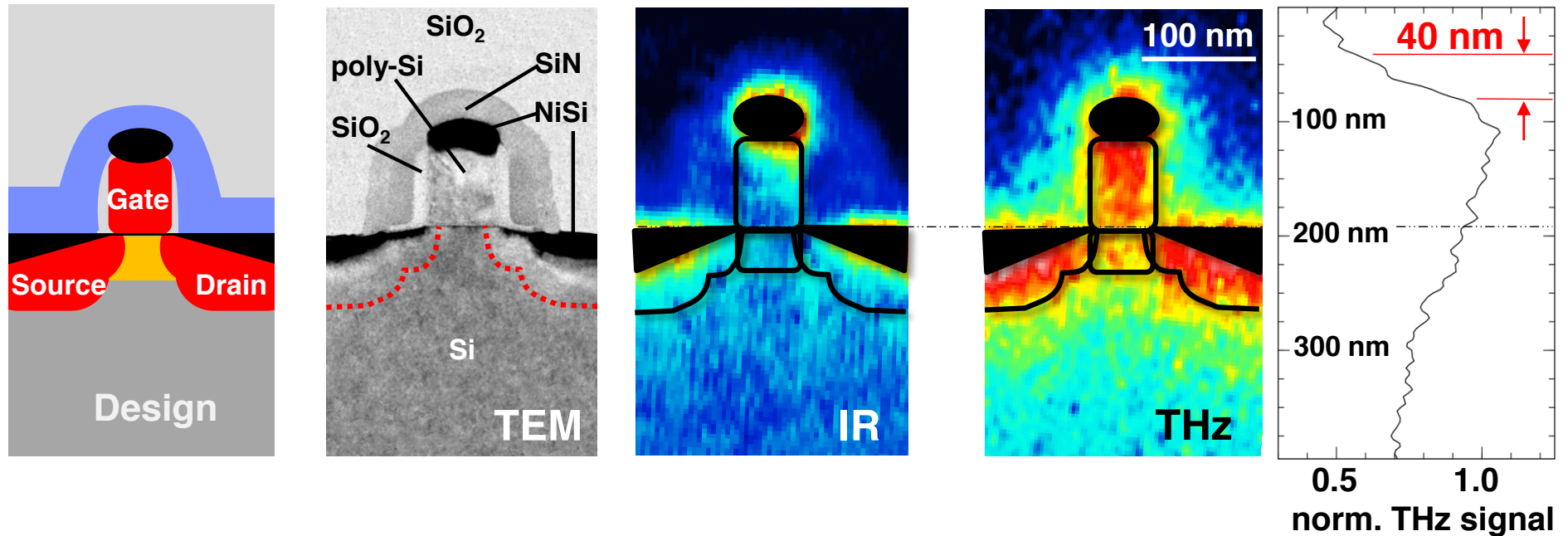
A. Huber et al. Nano Lett. 8, 3766 (2008)

# THz s-SNOM maps free carriers in single 65 nm-transistor



- metallic NiSi contacts
- highly doped Si,  $n = 10^{19} \text{ cm}^{-3}$
- medium doped Si,  $n = 10^{18} \text{ cm}^{-3}$

# THz s-SNOM achieves a resolution of about 40 nm



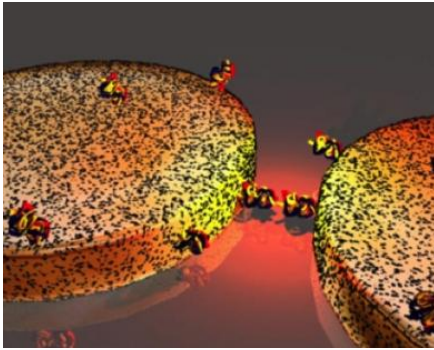
⇒ substructure of single 65 nm-transistor can be characterized with THz

- ⇒ s-SNOM offers nanoscale spatial resolution at THz frequencies
- ⇒ Achieve 40 nm resolution at 118  $\mu\text{m}$  ( $= \lambda/3000$ )
- ⇒ THz near-field contrast maps materials and free-carrier concentration
- ⇒ Promises quantitative and nanoscale resolved mapping of free carriers)

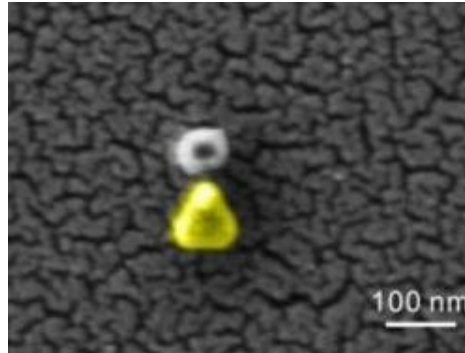


# Optical nanoantennas

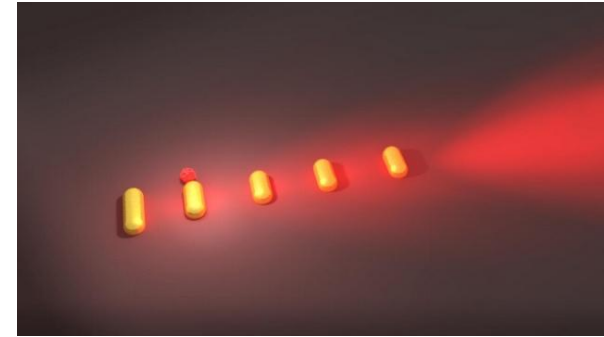
- Applications: biosensing, nonlinear optics / SERS, fluorescence, quantum optics,...



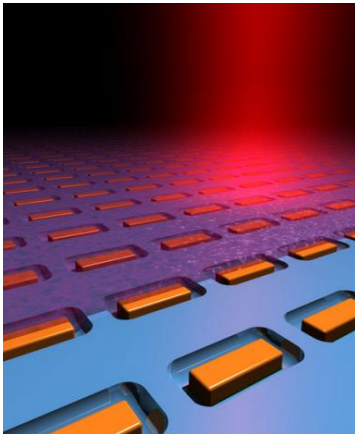
**Quidant, ICFO**  
**Antenna-gap sensing**



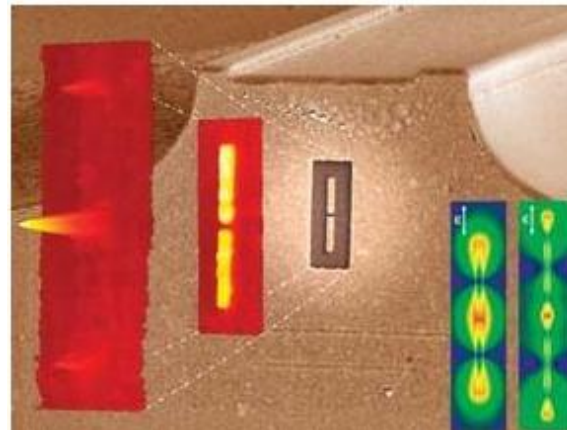
**Alivisatos, Giessen**  
**Pd-antenna sensor**



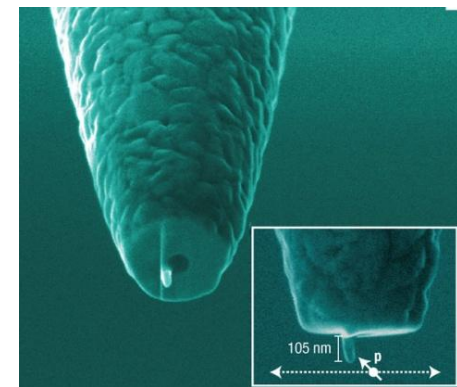
**Van Hulst, ICFO - Single molecule, scanning probe**



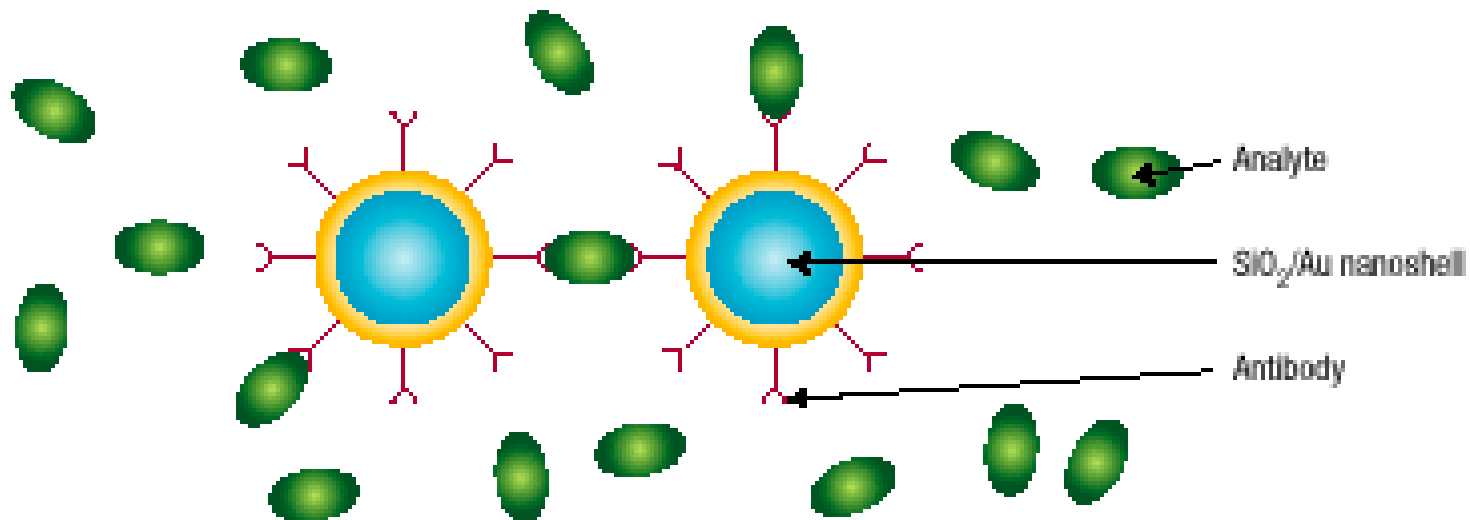
**Halas, Nordlander**  
**Plasmonic photodetector**



**Capasso**  
**Antenna QCL**



# Nanoantennas as nanoproboscopes: bio applications



Sensing via coupling

... frequency shift

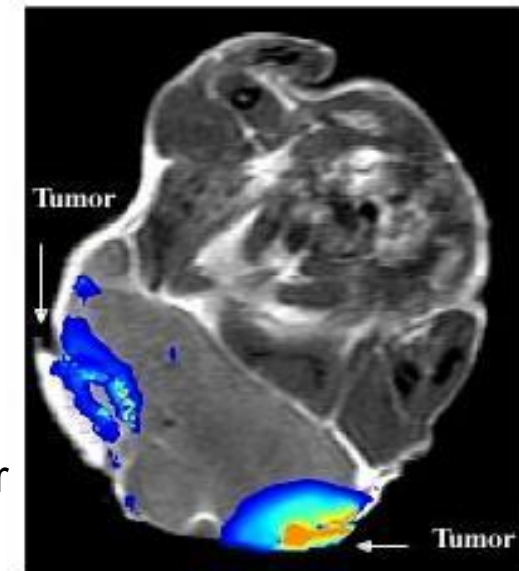
... nanoantenna for scattering

**We review this aspect now!**

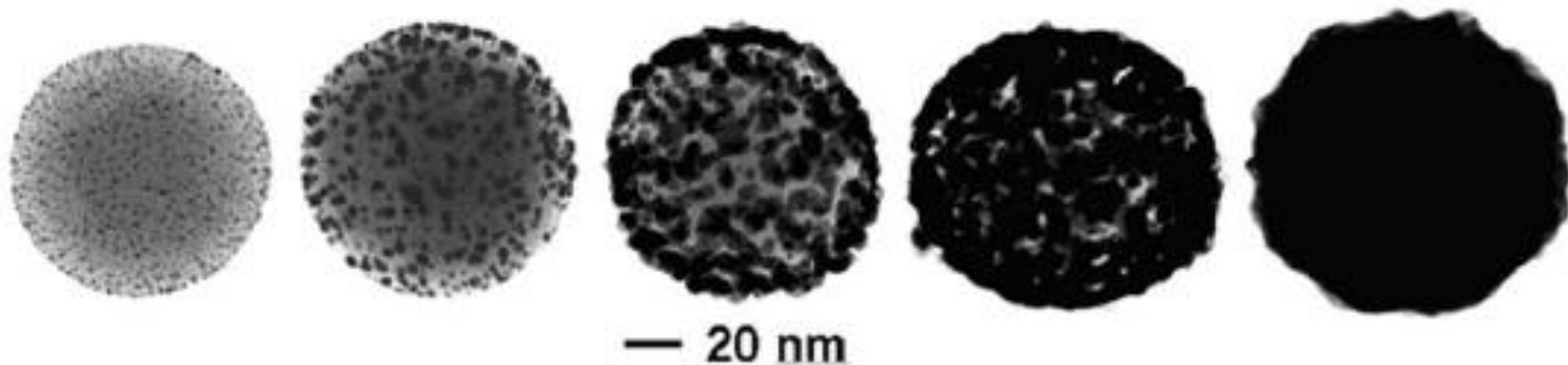
Local heating

... tagging

... nanoantenna for absorption



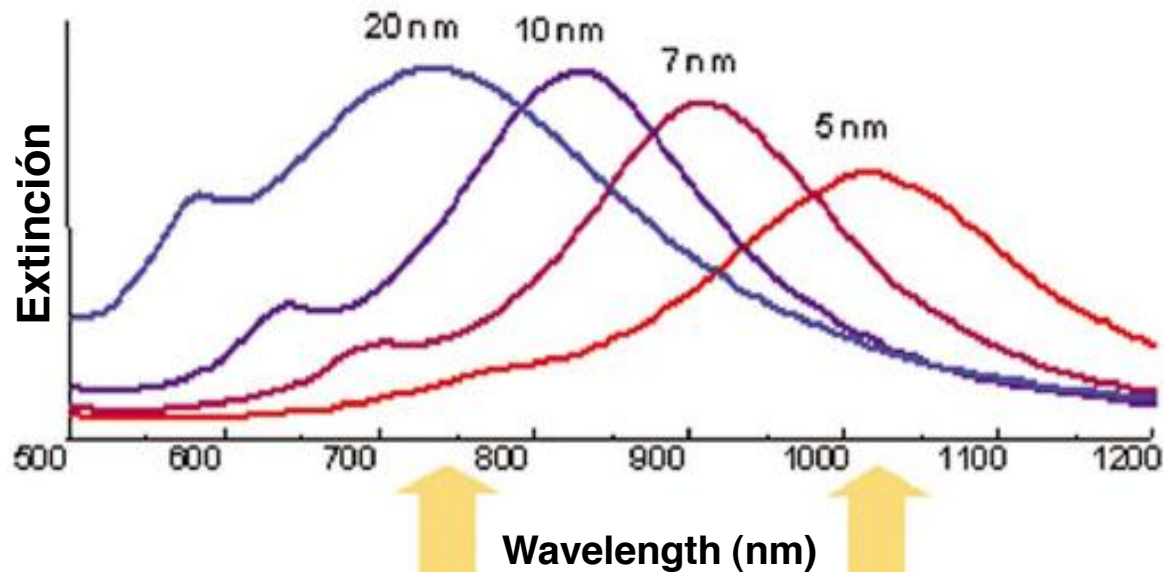
# Electrochemical synthesis of metallic nanoshells



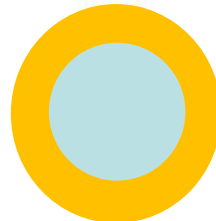
**N. Halas Group, Rice University, Houston, EEUU.**



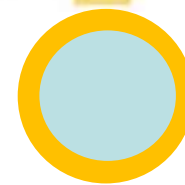
# Visible and infrared radiation absorption by metallic nanoshells



Core radius: 60 nm  
Nanoshell: 20 nm



Core radius: 60 nm  
Nanoshell: 5 nm



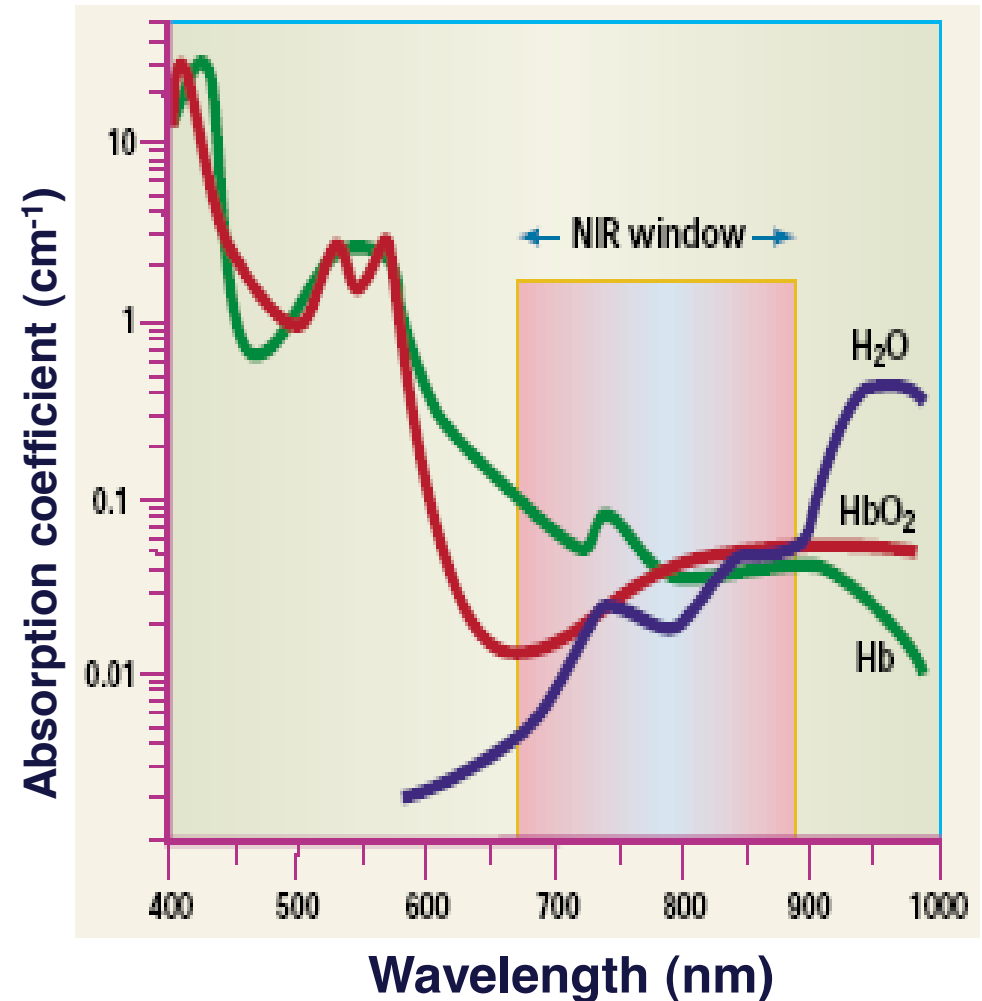
# Gold Nanoshells: an ideal nano-bio Interface

Gold nanoshells are completely biocompatible

Small enough to pass through circulatory system ( $< 3 \mu\text{m}$ )

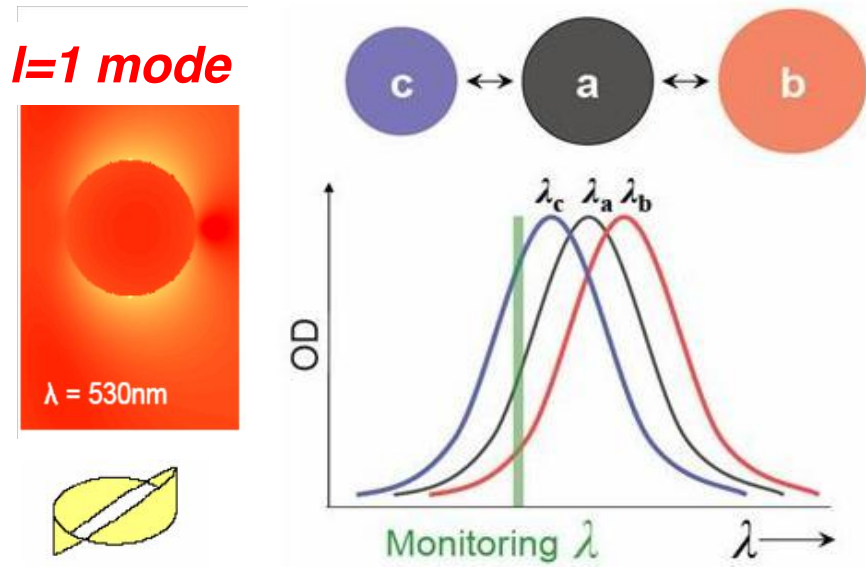
Easily attached to antibodies for specific cellular targeting

Gold nanoshells are strong absorbers and scatterers of light in the near infrared, where light penetrates several inches into the human body !

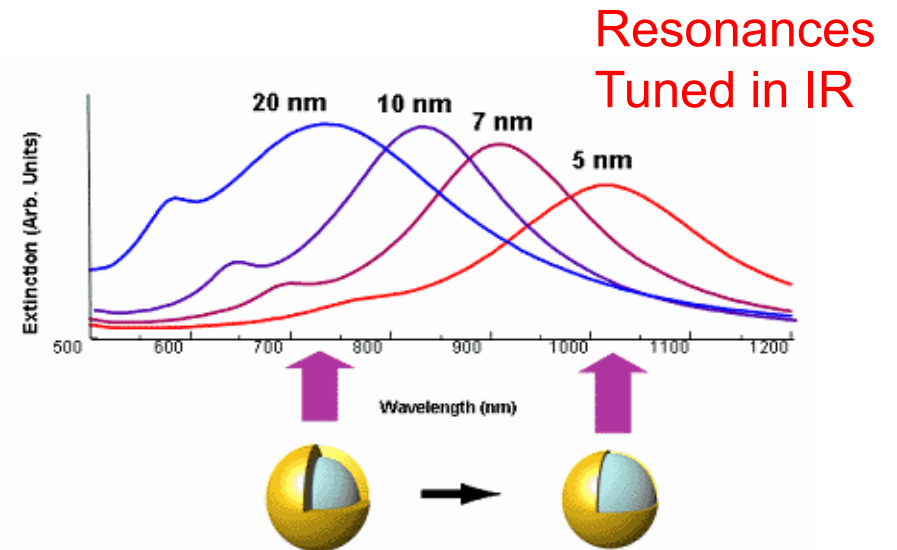


# Plasmonics for Cancer Therapy

Sphere Localized plasmon ( $\lambda=530\text{nm}$ )



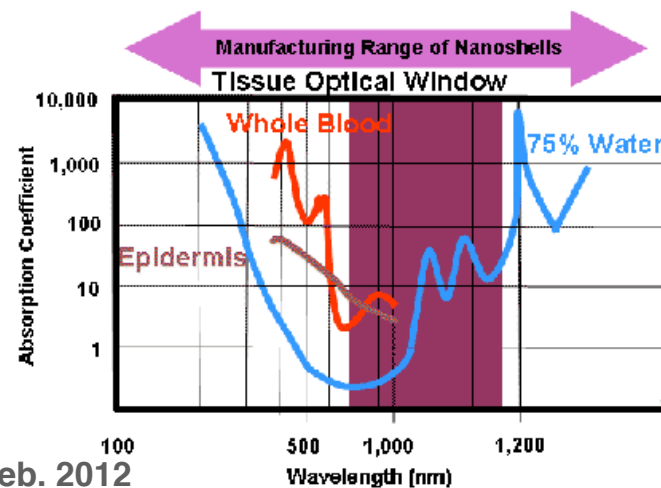
Nanoshell plasmons (infrared)



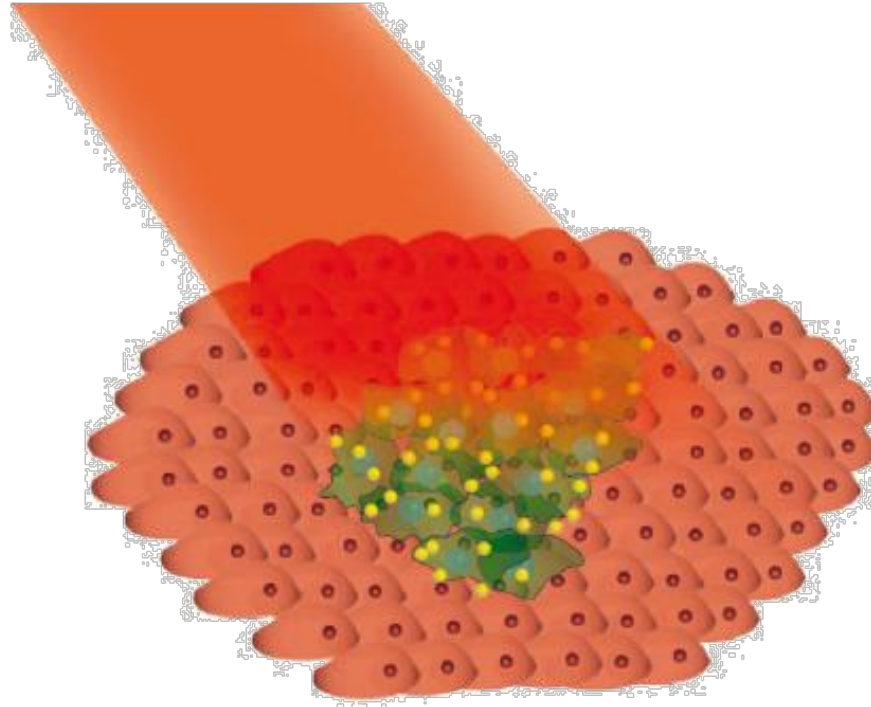
Localized surface plasmons are tuned to the infrared due to the thickness of the shell →

Nanoshell functionalization to get attached to cancer cells →

IR Absorption → high temperature → cancer cell destruction



# Enhanced permeability and retention (EPR) effect



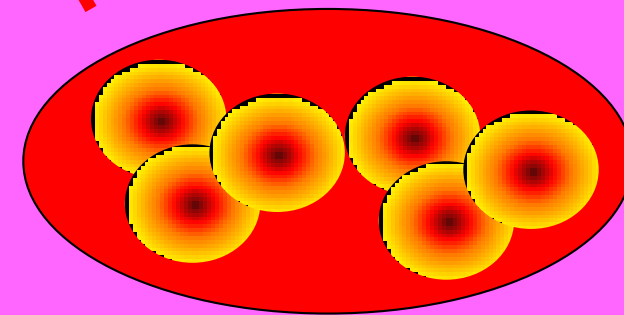
**H. Maeda, Adv. Enzyme Regul. 41, 189-207 (2001)**

# Nanoshell–assisted Seamless Integration of Screening and Therapy: “See and Treat”

nanoshells provide vivid contrast enhancement, increase image resolution

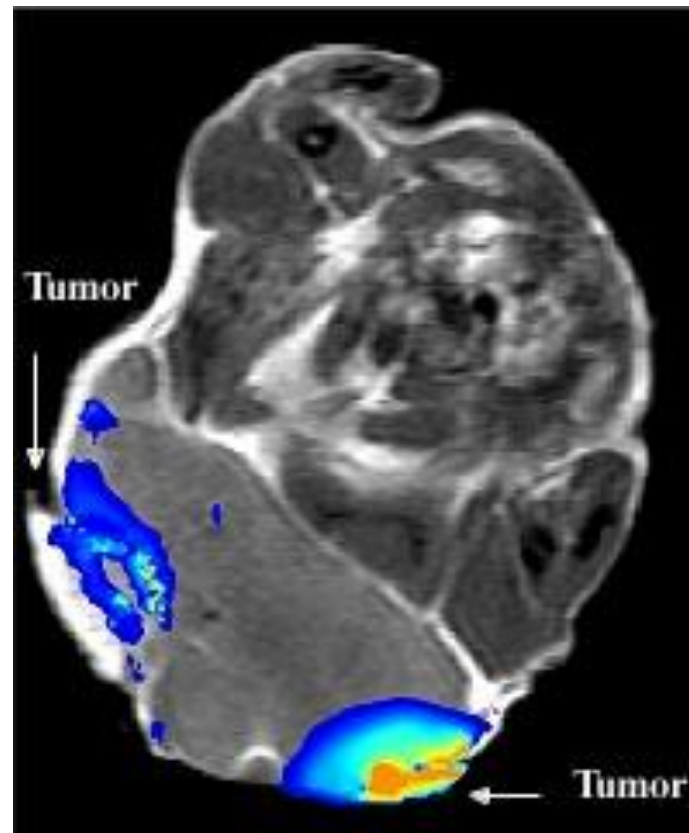
nanoshells are a photothermal heat source for remote destruction of tumors

scattered light also provides information for identifying malignancy– using pH (Nanoshell–enhanced Raman Scattering):



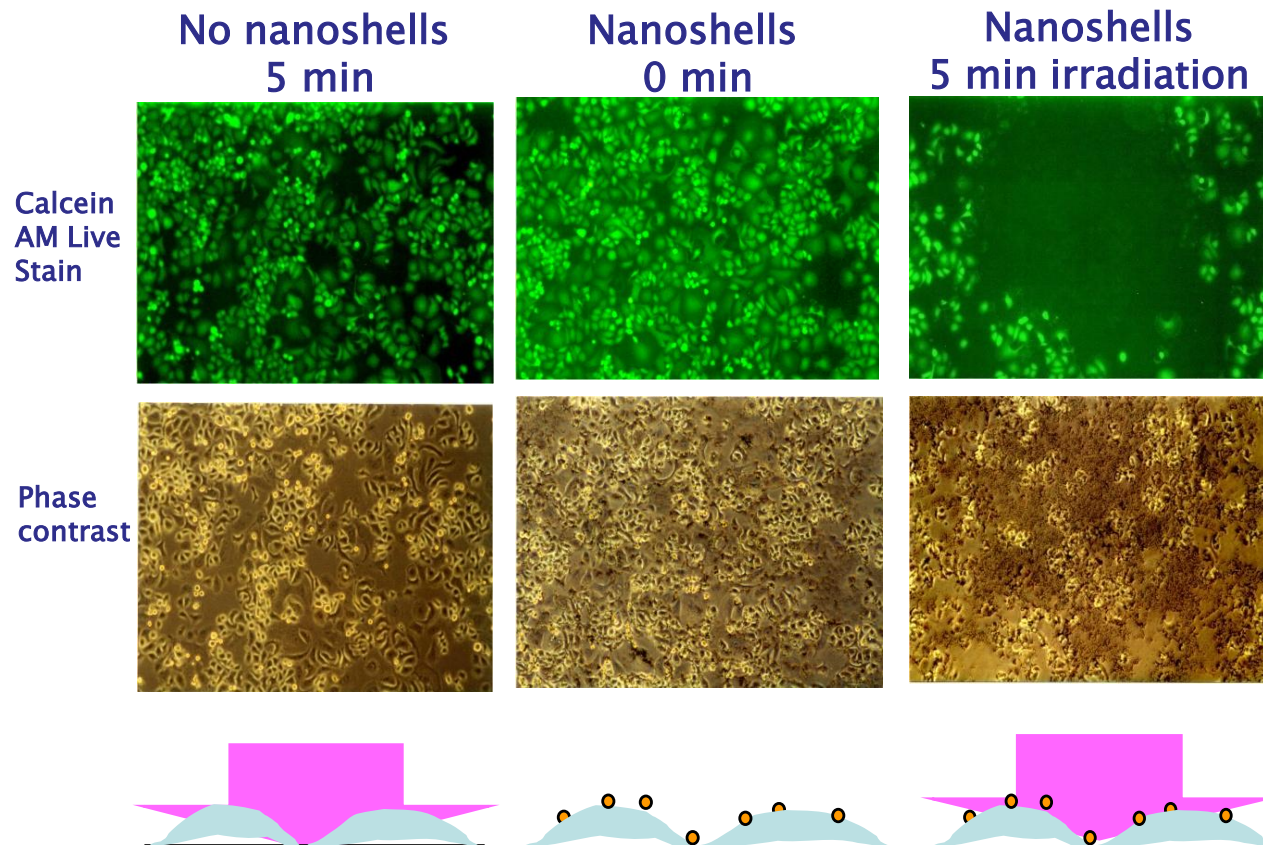
**deliver nanoshells to tumor site**

# Metallic Nanoshells in diagnosis



**Nanospectra Biosciences Ltd.**

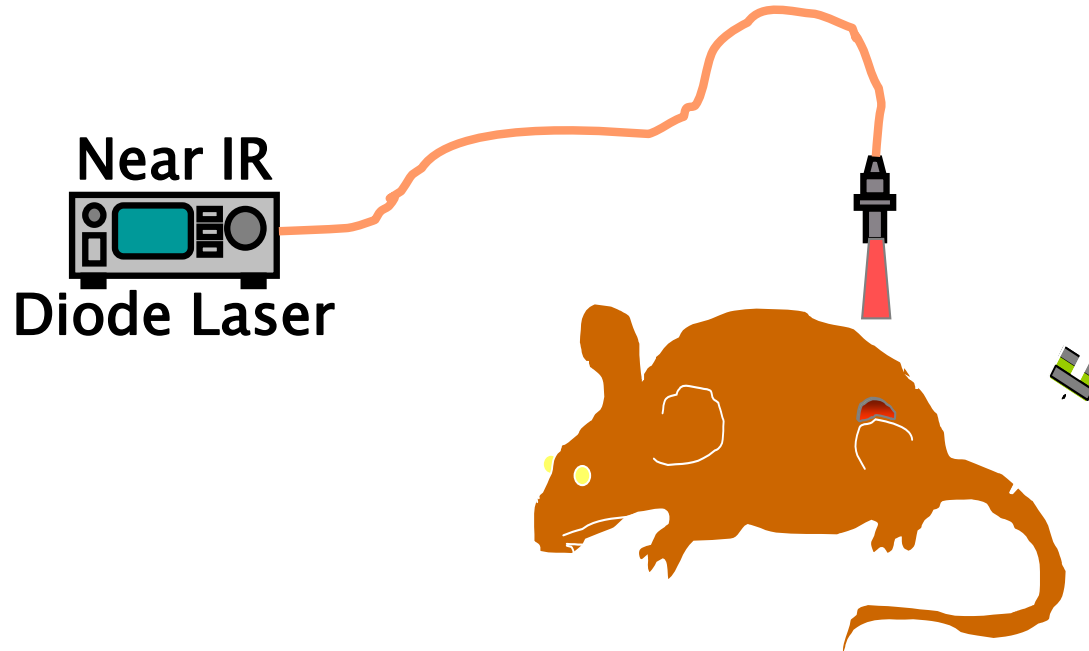
# Nanoshell-assisted Cancer Therapy





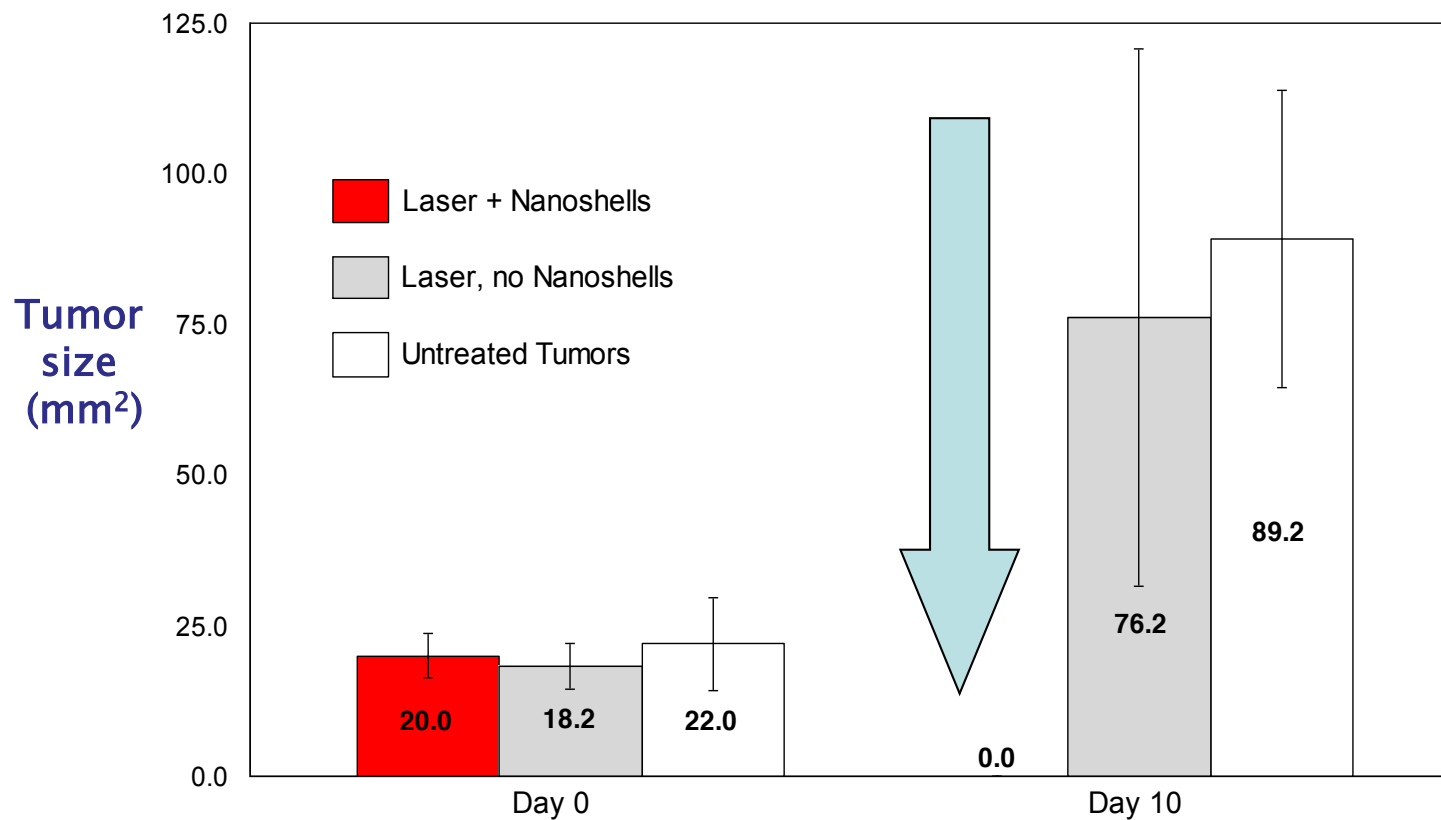
# Systemically delivered nanoshell therapy

*no targeting used!*



- mice inoculated with mouse colon carcinoma cell line
- Systemically delivered nanoshells via tail vein injection
- 6 hrs post injection, tumors irradiated with near infrared light through the skin ( $4 \text{ W/cm}^2$  810 nm diode laser source) for 3 min
- Tumor surface temp. monitored using infrared thermometer
- Resultant tumor size monitored for up to 2 months

# Tumor size before and after therapy



No measurable tumor mass was found in any nanoshell/laser treatments after 10 days

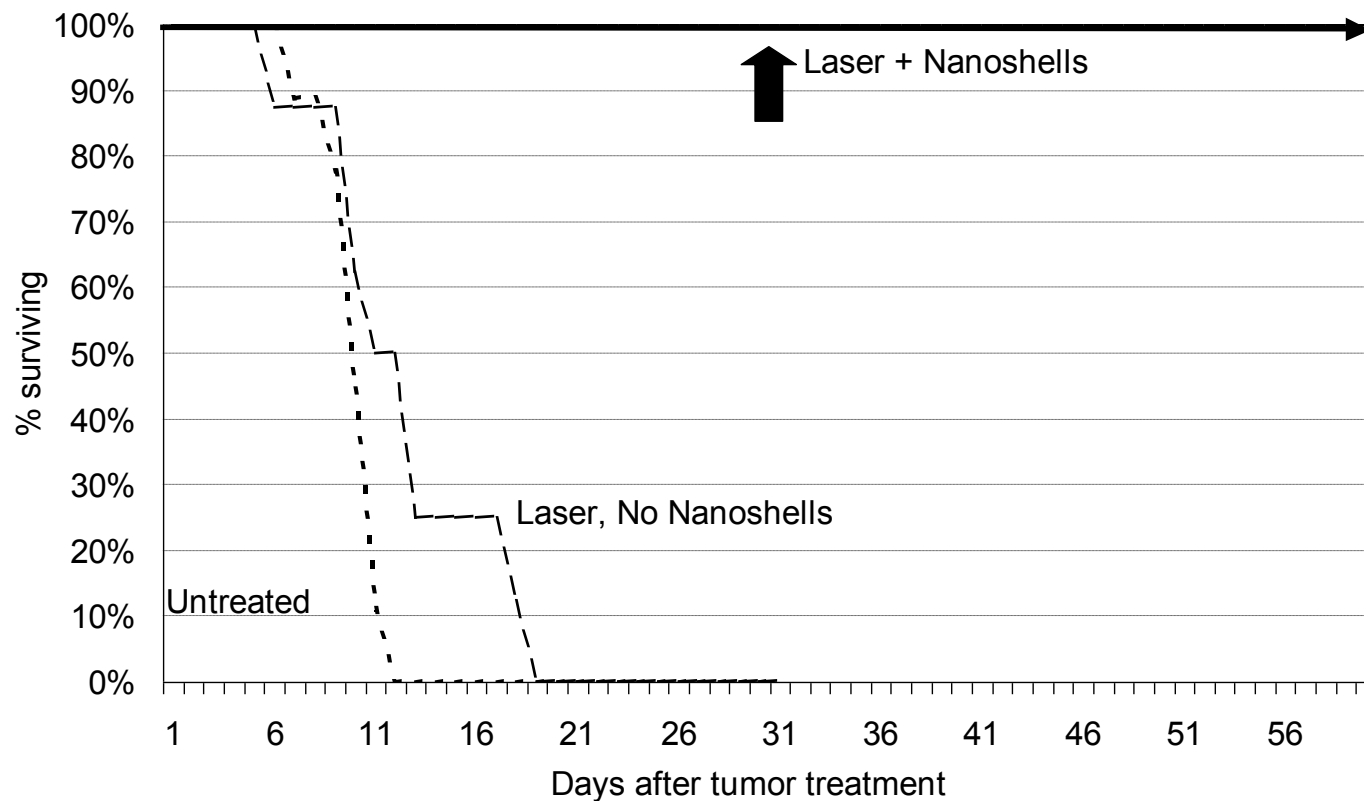
Complete regression of all tumors receiving nanoshell/laser treatments

# Treatment in mice



**J. M. Stern et al., J. Urol. 179, 748-753 (2008)**

# Mouse Survival after Therapy

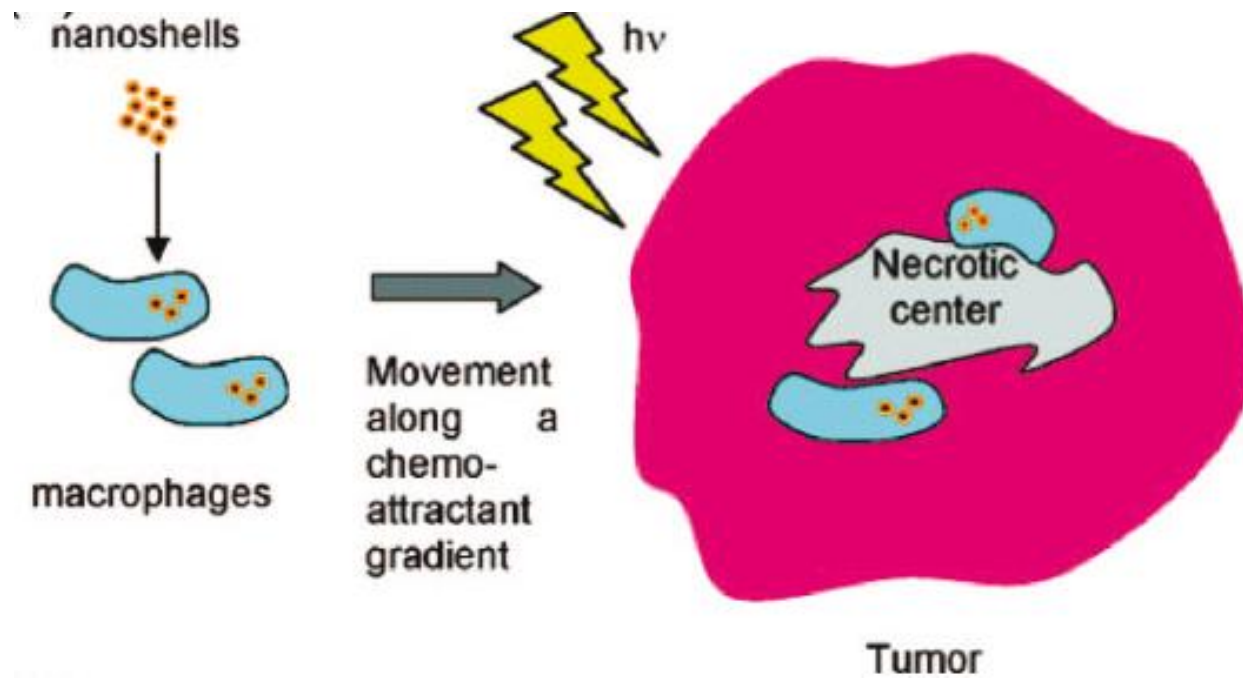


Untreated tumors:  
- Mean survival of 10 days

Laser controls:  
- Mean survival of 12.5 days

100% of all mice receiving nanoshell/laser therapy survived to end of study (60 days)

# Access to hipoxic regions



**S. Lal, N. Halas et al., Accounts of Chemical Research. 41, 1842 (2008)**

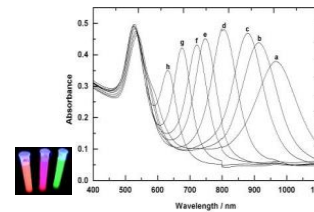
# Summary: Nano-optics with localised plasmons

## Characteristics

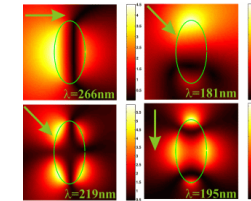
- Confined fields:
  - *Nanooptics*
- Enhanced field:
  - *Lighting rod effect*
- Tunability:
  - *Geometry*
- Coupling:
- Wavelength range:
  - *Visible → Infrared*

## Resonances dependence

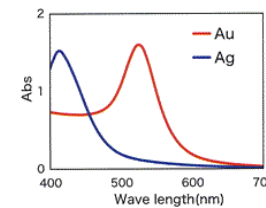
with size



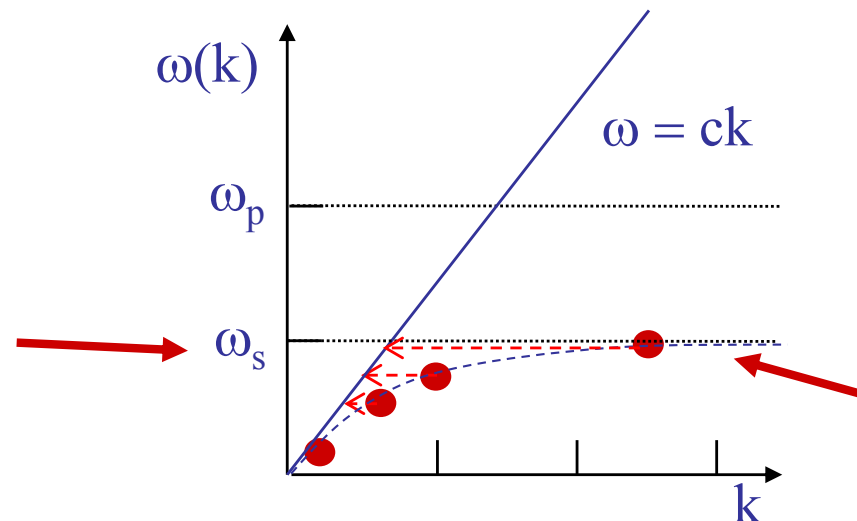
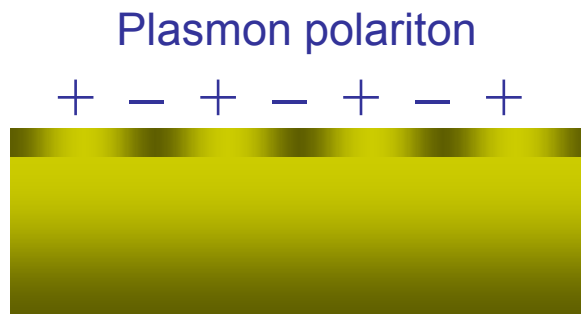
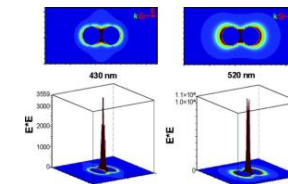
with shape



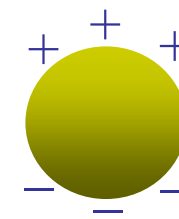
with material



with coupling



Confined plasmon







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**Thank you for your attention!**

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