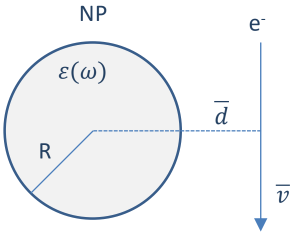
4. LSPR Imaging

4.2 Electron Energy Loss Spectroscopy (EELS)

EELS basics

Excitation induced by fast electrons (100 - 300 keV) passing close to a NP



Electron trajectory

$$\overline{r}(t) = \overline{d} + \overline{v}\,\mathrm{t}$$

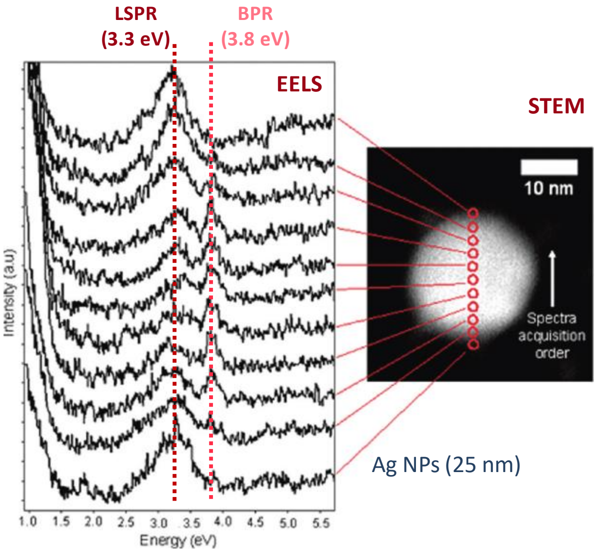
Energy Loss

$$\Delta E = \int e\overline{v} \cdot \overline{E}_{ind}[\overline{r}(t), t]\, dt = \int_0^{\infty} \Gamma(\omega)\, d\omega$$

Loss Probability

$$\Gamma(\omega) = \frac{1}{\pi} \int Re(e\overline{v} \cdot \overline{E}_{ind}[\overline{r}(t), \omega] e^{-i\omega t})\, dt$$

LSPR in Ag NP: EELS



Probe ~ 1 nm
ΔE ~ 0.2 eV

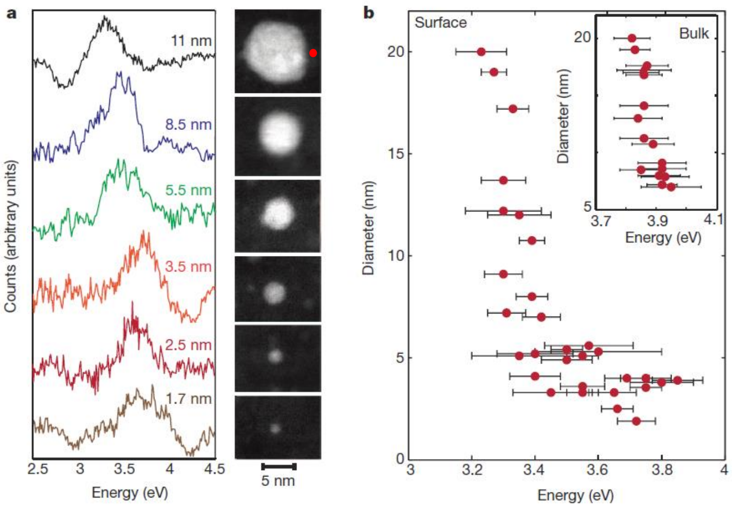
LSPR @ 3.3 eV = 380 nm

BPR @ 3.8 eV = 320 nm

Ag – core NP (25 nm)
Citrate Shell (1 nm)

A. L. Koh, et al. "Electron Energy-Loss Spectroscopy (EELS) of Surface Plasmons in Single Silver Nanoparticles and Dimers: Influence of Beam Damage and Mapping of Dark Modes," ACS Nano **3**, 3015–3022 (2009).

LSPR in Ag NP: EELS



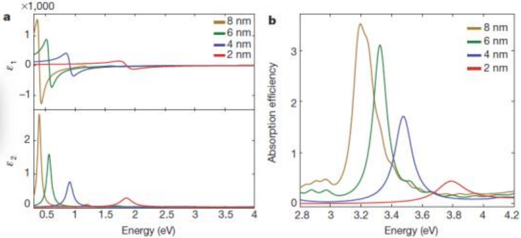
Quantum to Classical transition

J. A. Scholl, A. L. Koh, and J. A. Dionne, "Quantum plasmon resonances of individual metallic nanoparticles," Nature **483**, 421–427 (2012).

LSPR in Ag NP: EELS

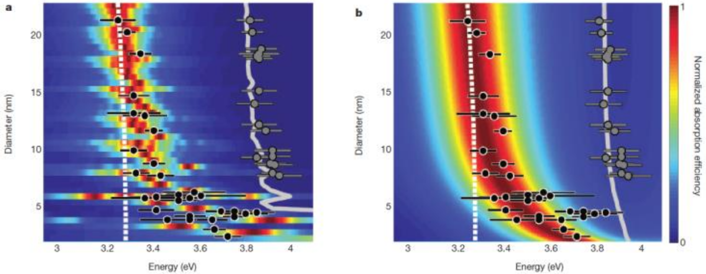
Analytic model for $\varepsilon(\omega)$

$$\varepsilon(\omega) = \varepsilon_{\mathrm{IB}} + \omega_{\mathrm{p}}^2 \sum_i \sum_f \frac{S_{if}}{\omega_{if}^2 - \omega^2 - i\gamma\omega}$$



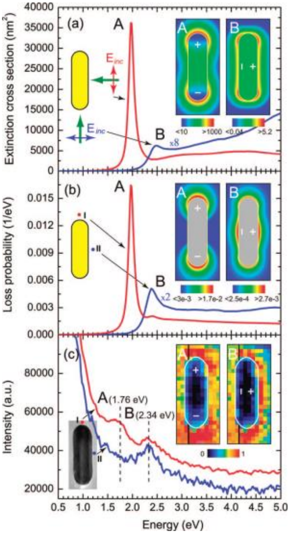
Analytic model for $\varepsilon(\omega)$

DFT model for $\varepsilon(\omega)$



J. A. Scholl, A. L. Koh, and J. A. Dionne, "Quantum plasmon resonances of individual metallic nanoparticles," Nature **483**, 421–427 (2012).

LSPR in Au NRods: EELS



Theory:
Light induced $|E|^2$

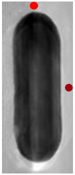
Theory:
EEL probability map

Exp:
EEL intensity maps and profiles

Transmission Electron Microscope

STEM – FEI Tecnai F20

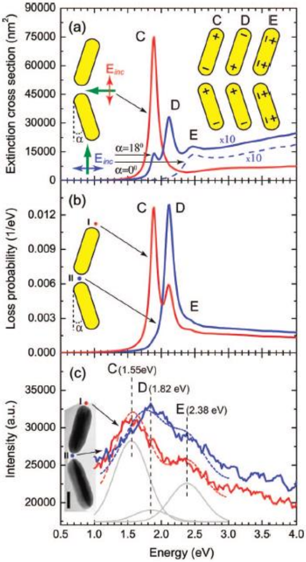
- E=200keV
- ΔE = 0.22 eV (Wien-filter)
- Beam size: 2 nm



25nm

M.-W. Chu, et al., "Probing Bright and Dark Surface-Plasmon Modes in Individual and Coupled Noble Metal Nanoparticles Using an Electron Beam," Nano Lett. **9**, 399–404 (2009).

LSPR in Au NRods: EELS



Theory:
Light induced |E|^2

Theory:
EEL probability map

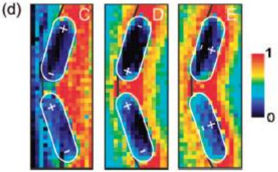
Exp:
EEL spectra and intensity map

Transmission Electron Microscope

STEM – FEI Tecnai F20

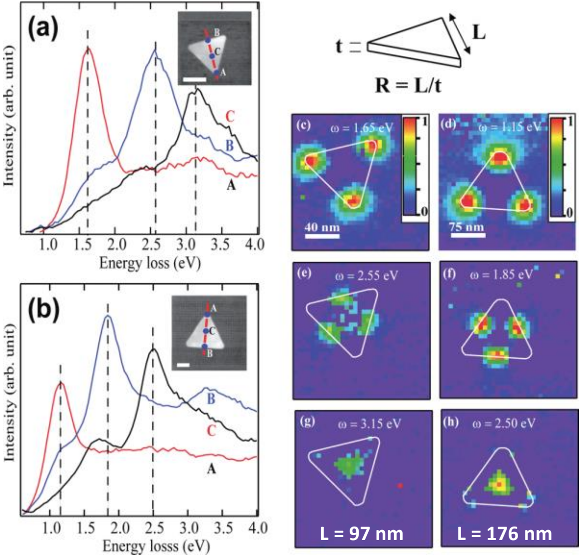
- E=200keV
- ΔE = 0.22 eV (Wien-filter)
- Beam size: 2 nm

Plasmonic
Dark Modes (D)



M.-W. Chu, et al., "Probing Bright and Dark Surface-Plasmon Modes in Individual and Coupled Noble Metal Nanoparticles Using an Electron Beam," Nano Lett. **9**, 399–404 (2009).

LSPR in Ag NPrisms: EELS



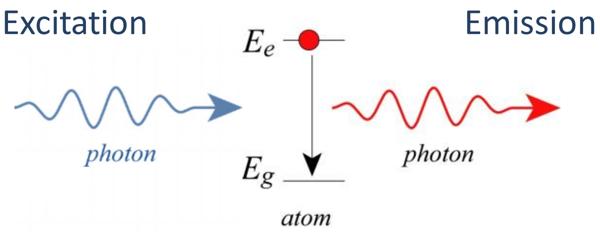
(a)
t = 4 nm
L = 97 nm

(b)
t = 6 nm
L = 176 nm

J. Nelayah et al., "Two-Dimensional Quasistatic Stationary Short Range Surface Plasmons in Flat Nanoprisms," Nano Lett. **10**, 902–907 (2010).

Nanostructure - Emitter interaction

Spontaneous emission



Spontaneous emission of a two-level emitter:

Initial state: excited state + 0 photons.

Final state: ground state emitter + 1 photon in some photon state

Fermi's Golden Rule

- unperturbed emitter eigenfunction is $|\psi_i>$
- The photon field perturbs the Hamiltonian H_0 as $H = H_0 + V$

$$V = -\boldsymbol{p} \cdot \boldsymbol{E}$$

Dipole operator Electric field

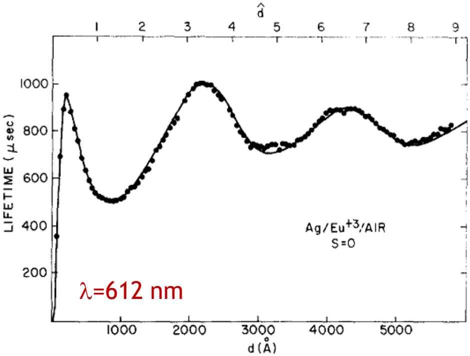
The interaction induces a transition from $|\psi_i>$ to $|\psi_f>$ (energy conservation)

Fermi's Golden Rule: rate of decay of the initial state ψ_i

$$\gamma = \gamma_r = \frac{2\pi}{\hbar}\sum_f \left|\langle\psi_f|V|\psi_i\rangle\right|^2 \delta\left(\epsilon_f - \epsilon_i\right) = \frac{2\pi}{\hbar}\rho(\epsilon_f)\left|\langle\psi_f|V|\psi_i\rangle\right|^2$$

$\gamma_{meas} = \gamma = \gamma_{nr} + \gamma_r$ real emitter (radiative & non-radiative decays)

emitter-film interaction



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INFLUENCE OF A DIELECTRIC INTERFACE ON FLUORESCENCE DECAY TIME

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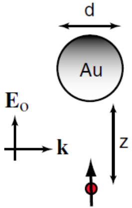
IBM Research Laboratory, San Jose, California, USA

When a mirror is placed near a fluorescing molecule, not only the angular distribution of the fluorescence is affected, but also the decay time. This effect is considered for the case of the reflecting interface between two dielectrics of different refractive indices. The fluorescence decay time varies markedly due to the presence of such an interface. In case of fluorescing molecules placed directly at the interface between a medium of refractive index 1.54 and air, the decay time is lengthened by a factor of 1.08 if their transition moment is oriented parallel to the interface, and by a factor of 3.61 if the transition moment is oriented perpendicular to the interface. These considerations are compared with measurements on monomolecular layers of an europium dibenzoylmethane complex which were held at a variable, but well defined distance from the interface.

fluorescence lifetime variation as a function of the distance of Eu ions from a Ag mirror.

Nano-antennas: emitter-NP interaction



Emitter at $\mathbf{r}_m$

Fluorescence rate

$$\gamma_{em} = \gamma_{exc} q_a = \gamma_{exc} \frac{\gamma_r}{\gamma_r + \gamma_{nr}} = \gamma_{exc} \frac{\gamma_r}{\gamma}$$

$\gamma_{\rm exc} \propto |\mathbf{p} \cdot \mathbf{E}|^2$ $\quad \mathbf{E}(\mathbf{r}_m, \omega)$ $\quad \mathbf{E}_m(\mathbf{r}) = (k^2/\varepsilon_0)\ \overleftrightarrow{\mathbf{G}}(\mathbf{r}, \mathbf{r}_m)\mathbf{p}$

$$\gamma = \frac{2\omega}{3\hbar\varepsilon_0} |\mathbf{p}|^2 \rho(\mathbf{r}_m, \omega)$$

DoS $\quad \rho(\mathbf{r}_m, \omega) = \frac{6\omega}{\pi c^2} [\mathbf{n}_p \cdot \mathrm{Im}\{\overleftrightarrow{\mathbf{G}}(\mathbf{r}_m, \mathbf{r}_m\} \cdot \mathbf{n}_p]$

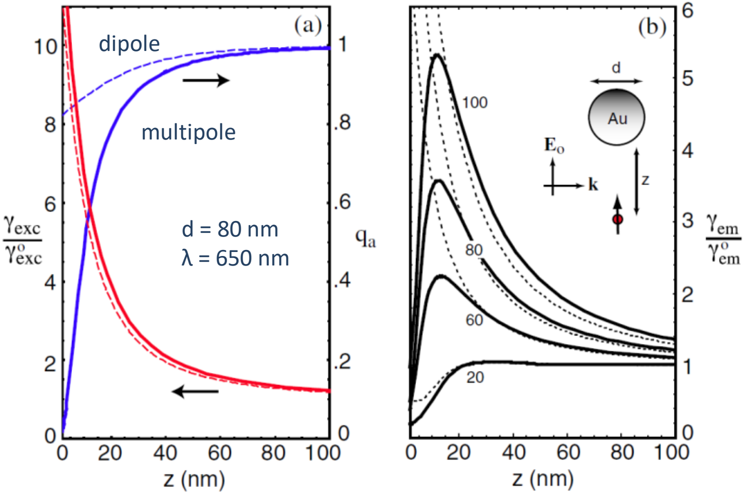
$\gamma_0 = \omega^3 |\mathbf{p}|^2 / (3\pi\varepsilon_0 \hbar c^3)$ $\quad \rho = \omega^2/(\pi^2 c^3)$ (Vacuum)

$$\gamma_{\rm exc}/\gamma_{\rm exc}^0 = |[\mathbf{n}_p \cdot \mathbf{E}(\mathbf{r}_m)]/[\mathbf{n}_p \cdot \mathbf{E}_0(\mathbf{r}_m)]|^2$$

$$\frac{\gamma_{\rm nr}}{\gamma_0} = \frac{1}{P_0} \frac{1}{2} \int_V \mathrm{Re}\{\mathbf{j}(\mathbf{r}) \cdot \mathbf{E}_m^*(\mathbf{r})\} d\mathbf{r}^3$$

P. Anger *et al.*, Enhancement and Quenching of Single-Molecule Fluorescence. *Phys. Rev. Lett.* **96**, 113002 (2006).

Nano-antennas

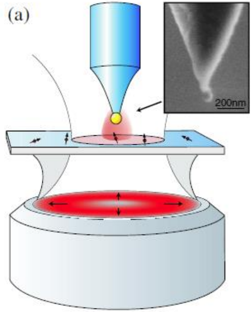


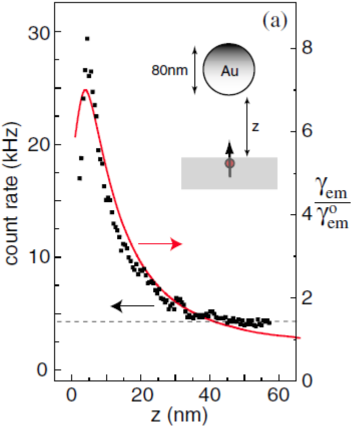
Fluorescence rate

$$\gamma_{em} = \gamma_{exc} q_a = \gamma_{exc} \frac{\gamma_r}{\gamma_r + \gamma_{nr}}$$

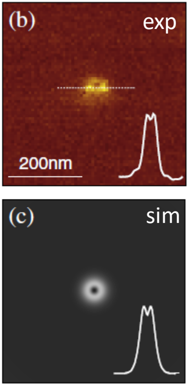
P. Anger *et al*., Enhancement and Quenching of Single-Molecule Fluorescence. *Phys. Rev. Lett.* **96**, 113002 (2006).

Nano-antennas





Fluorescence imaging



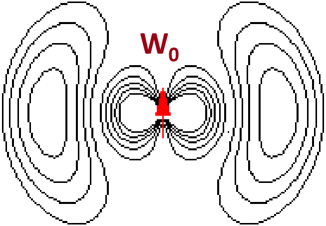
z = 2 nm
central dark spot = quenching

Fluorescence rate

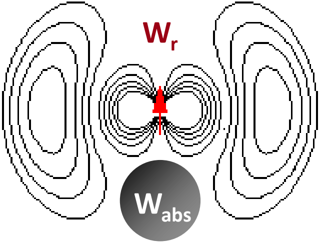
$$\gamma_{em} = \gamma_{exc} q_a = \gamma_{exc} \frac{\gamma_r}{\gamma_r + \gamma_{nr}}$$

P. Anger *et al.*, Enhancement and Quenching of Single-Molecule Fluorescence. *Phys. Rev. Lett.* **96**, 113002 (2006).

Nanoantennas



$$q_0 = \frac{\gamma_{r,0}}{\gamma_{r,0} + \gamma_{nr,0}}$$



$$q = \frac{\gamma_r / \gamma_{r,0}}{\gamma_r / \gamma_{r,0} + \gamma_{abs}/\gamma_{r,0} + (1 - q_0)/q_0}$$

$$\frac{\gamma_r}{\gamma_{r,0}} = \frac{W_r^{na}}{W_{r,0}} \quad \frac{\gamma_{abs}}{\gamma_{r,0}} = \frac{W_{abs}^{na}}{W_{r,0}}$$

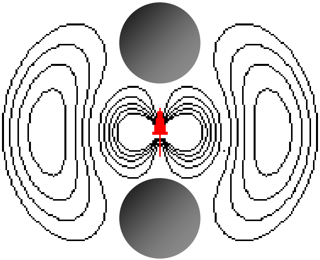
$$\frac{\gamma_{nr}}{\gamma_{r,0}} = \frac{\gamma_{abs} + \gamma_{nr,0}}{\gamma_{r,0}}$$

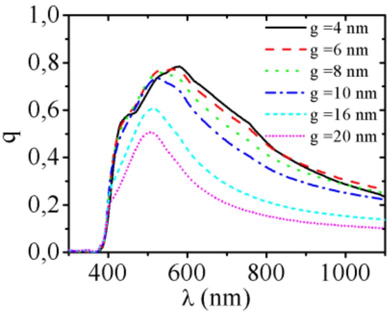
Quantum Efficiency enhancement

Pellegrini, G., Mattei, G. & Mazzoldi, P. Tunable, directional and wavelength selective plasmonic nanoantenna arrays. *Nanotechnology* **20**, 065201 (2009).

Nanoantennas

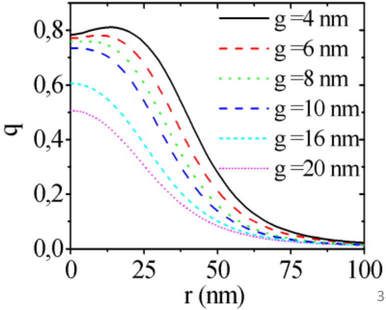
q_0=0.01
D=60 nm





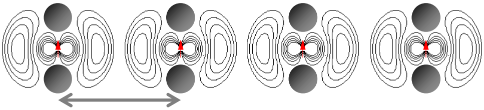
q ~ 0.8

(q > 0.5 if r < 25 nm)

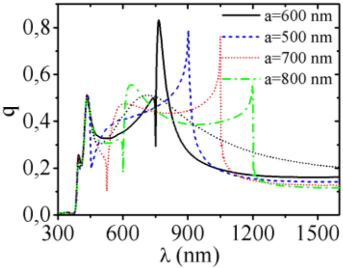


Nanoantennas

- D= 100 nm
- N_S=1200
- a variable, g = 20 nm
- λ_{res}~ n × a



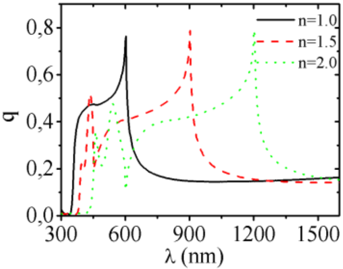
a variable, n=1.5



q ~ 0.8

λ ~ 500 nm
λ = 1.5 μm

n variabile, a=600 nm



Pellegrini, G., Mattei, G. & Mazzoldi, P. Tunable, directional and wavelength selective plasmonic nanoantenna arrays. *Nanotechnology* **20**, 065201 (2009).