CHM 696-11: Week 8

Instructor: Alexander Wei

Optical Properties of Metal Nanoparticles and Nanoparticle Assemblies

Review:

Wei, Q.; Wei, A. In *Supramolecular Chemistry of Organic–Inorganic Hybrid Materials* (Chapter 10), Mañez, R. M.; Rurack, K., Eds.; Wiley and Sons: New York, 2010; pp. 319-349

Plasmon-resonant nanoparticles

Surface plasmon (SP): collective excitation of conduction electrons, using light at a resonant (visible to NIR) frequency

Plasmon-enhanced extinction:

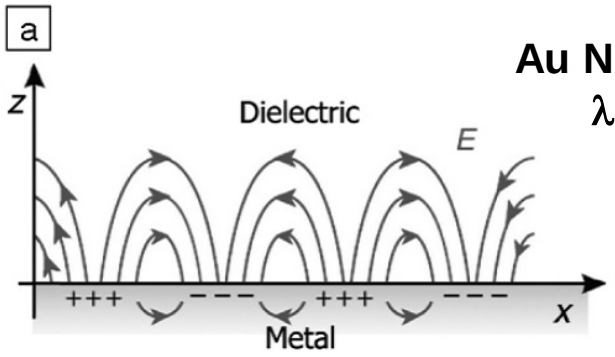
$\varepsilon = 10^{9}–10^{11}\ M^{-1}\,cm^{-1}$

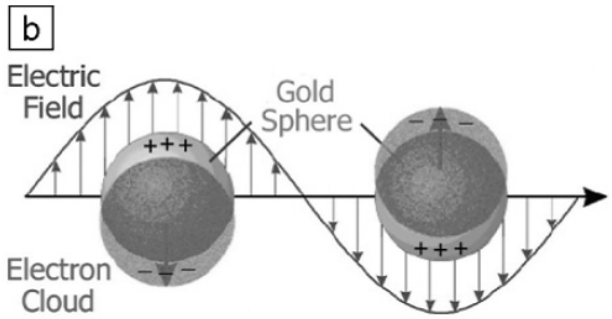
$C_{sca} = 10^{-13}–10^{-9}\ cm^{2}$

$\phi_{sca} = 0.04–0.90$

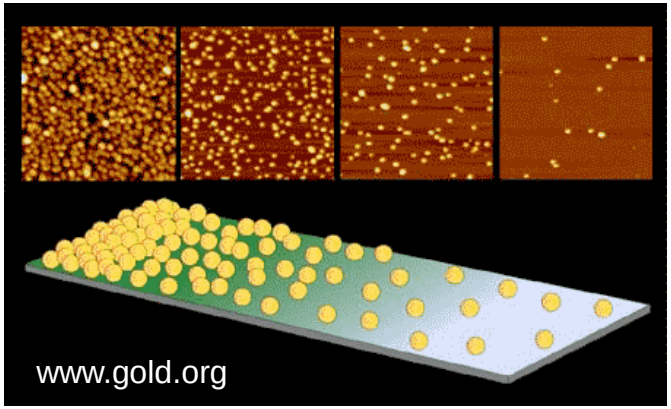
Ag NPs (20–150 nm):
$\lambda_{SP} = 380–600$ nm

Au NPs (20–150 nm):
$\lambda_{SP} = 520–660$ nm





Scattering from single Au nanospheres



Lycurgus Cup, 4th century A.D.

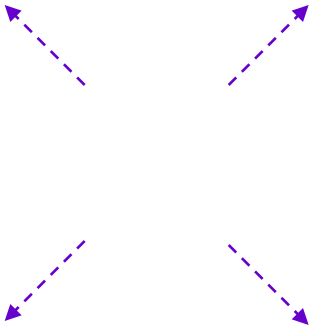
(Ag-Au NP's embedded in glass)

Absorption: red **Scattering: green**

British Museum, London

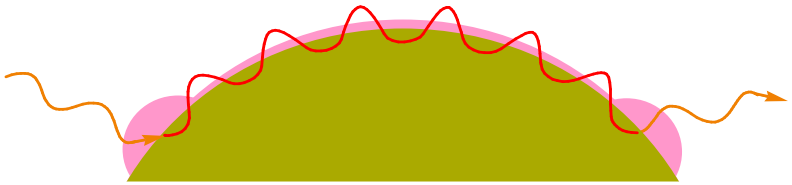
Manifestations of Surface Plasmons

λ_{inc}

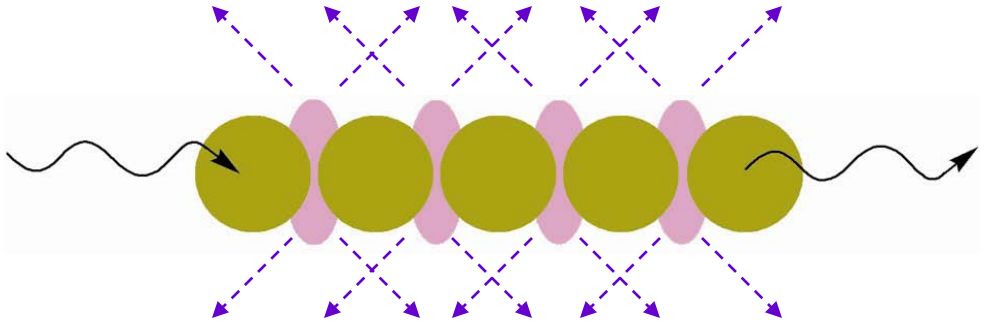


I. Localized surface plasmon resonance (LSPR) in metal nanoparticles ($d<\lambda_p$)

λ_{em}



II. Surface plasmon waves (polaritons) propagating along smooth metal surface ($d>\lambda_p$)



III. Coupled plasmons in nanoparticle aggregate or array

For a primer on surface plasmons, see: *Nanoparticles: Building Blocks for Nanotechnology*, Ed. V. M. Rotello, Kluwer Academics: New York, 2004; Chapter 7 (Wei)

Physical description of localized SPRs

Free-electron behavior in metals: the Drude model

Polarizability or oscillator strength α defined by the Clausius-Mosotti (a.k.a. Lorentz-Lorenz) equation:

$$\alpha = 4\pi\varepsilon_0 R^3 \left| \frac{\varepsilon - \varepsilon_d}{\varepsilon + 2\varepsilon_d} \right|$$

Complex dielectric function $\varepsilon = \varepsilon'(\omega) + i\varepsilon''(\omega)$;

Resonance achieved with $\varepsilon'(\omega) = -2\varepsilon_d$, $\varepsilon''(\omega) << 1$

Given a plasma frequency ω_p such that $\varepsilon(\omega_p) = 0$:

$$\varepsilon'(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} \qquad \varepsilon''(\omega) \approx \frac{\omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)}$$

where Γ is the plasma relaxation frequency.

Ideally, $\omega_{SP} \approx \dfrac{\omega_p}{\sqrt{2\varepsilon_d + 1}}$

However, free-electron response is coupled with interband transitions (e.g., Au(5*d*→6*s*)), which changes ω_{SP}

Only metals with low $\varepsilon''(\omega)$ at ω_{SP} will exhibit strong plasmon resonance: **Ag > Au > Cu**

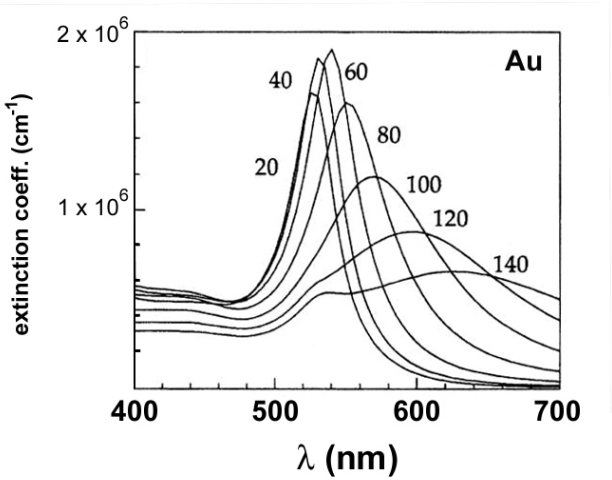
Physical description of plasmons (cont'd)

Electrodynamic Mie Theory

Can calculate dipolar optical response with great accuracy, especially if performed under "quasi-static" conditions (valid when particle size is less than 30 nm)

Generalized Mie Theory:

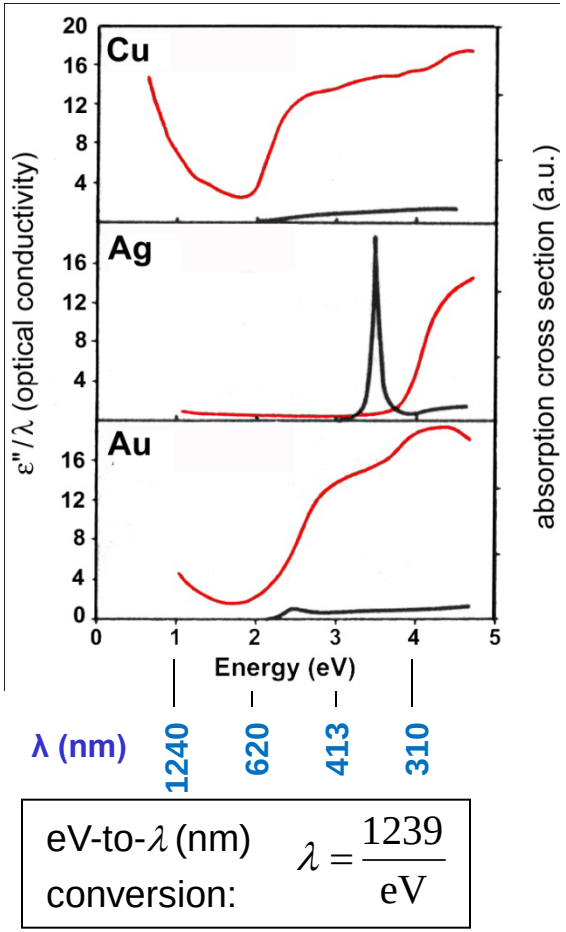
Can calculate approximate optical response for metal nanoparticles of all shapes and sizes; accounts for higher-order effects such as phase retardation, quadrupolar resonances, etc.



Calculated plasmon response from spherical Au nanoparticles in H_2O:

Yguerabide, *Anal. Biochem*. **1998**, *262*, 137.

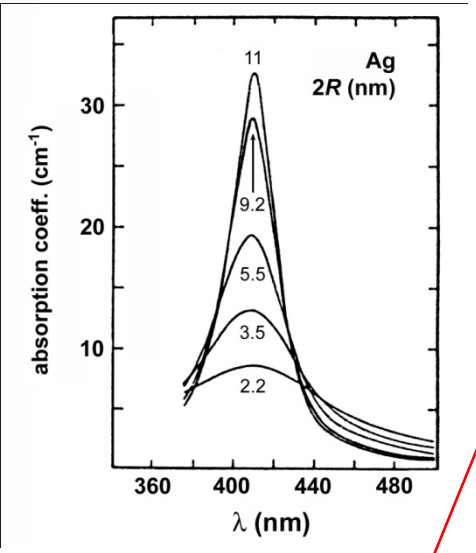
Calculated response (extinction) from metal nanoparticles (in air):



eV-to-λ (nm) conversion: $\lambda = \frac{1239}{\text{eV}}$

Kriebig and Vollmer, *Optical Properties of Metal Clusters, c.*1995.

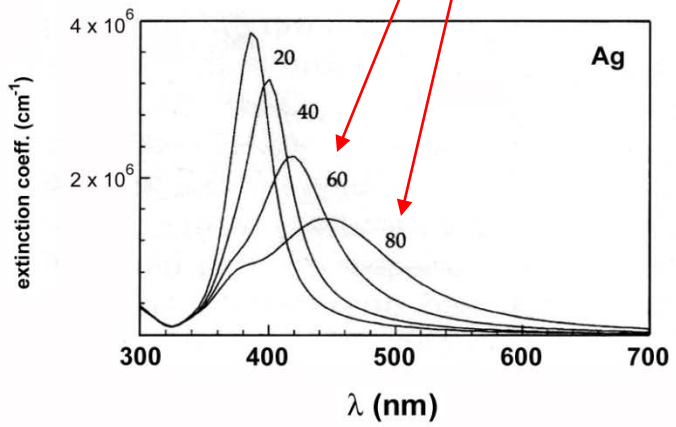
Size effects on localized SPRs

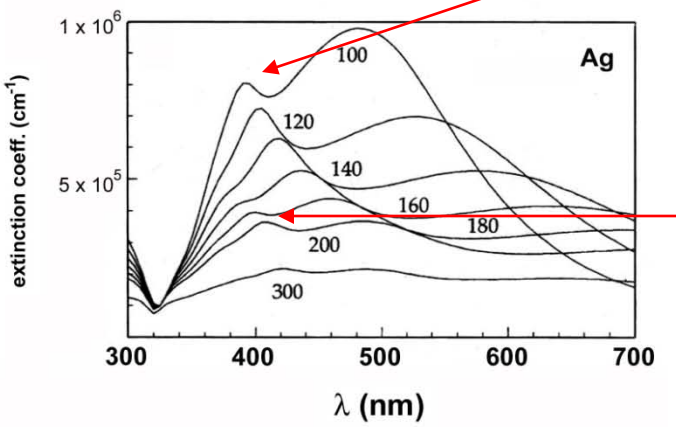


Surface scattering of oscillating electrons: plasmon lineshape (Γ) broadens with 1/R

Phase retardation: redshift and broadening of λ_{SP} for particles greater than L_E, the electron mean free path (40-50 nm)

Higher-order plasmon resonances: increase in probability with larger particle size (also a function of L_E)





Dipolar mode

Quadrupolar mode

Octupolar mode

Calculated plasmon response from spherical Ag nanoparticles in H_2O:
Yguerabide, *Anal. Biochem*. **1998**, *262*, 137.