

Size dependent properties

Progressive Generation of Nanostructures

Small size results in new quantum phenomena

Quantum Confinement

Achieving quantum confinement requires confining at least one of the three dimensions of a solid (length, width or height) to be less than 100 nm.

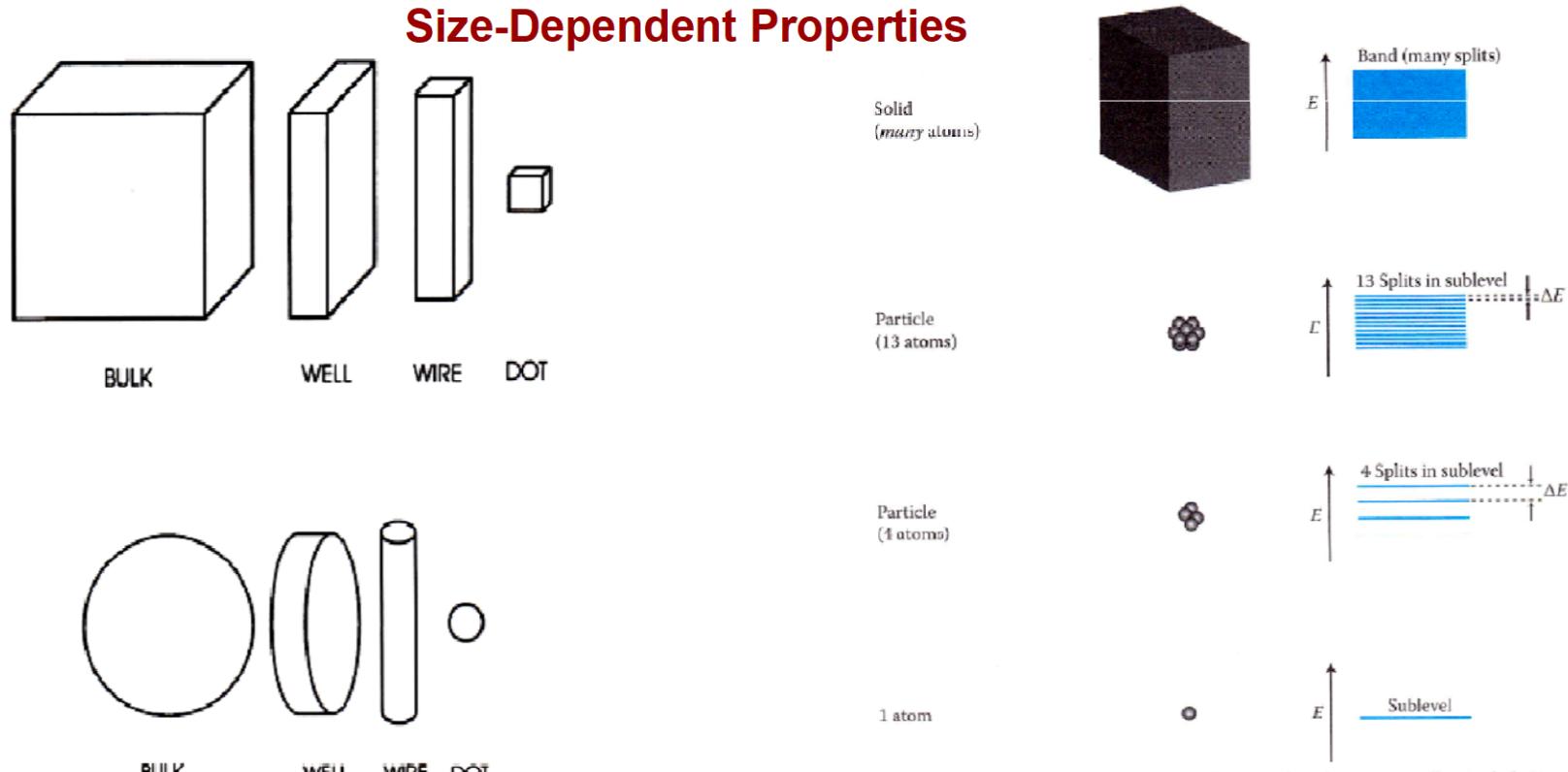
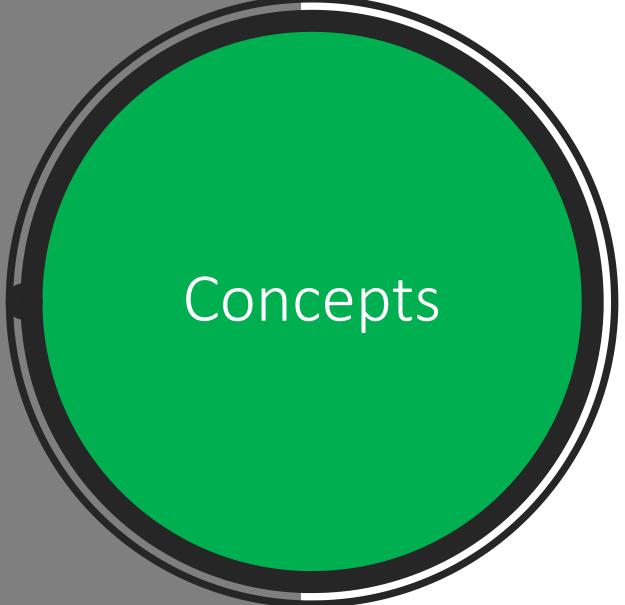


FIGURE 6.8 The spacing between energy states gets larger as the volume gets smaller. At the bottom, a single atom has just one energy state per sublevel. As atoms group together to form particles, there are as many splits per sublevel as there are atoms in the particle. If the particle is small enough, we can discern these splits within the sublevel. As the volume increases to the size of a solid, the spacing between splits gets so tight that the sublevel is best characterized as a band.

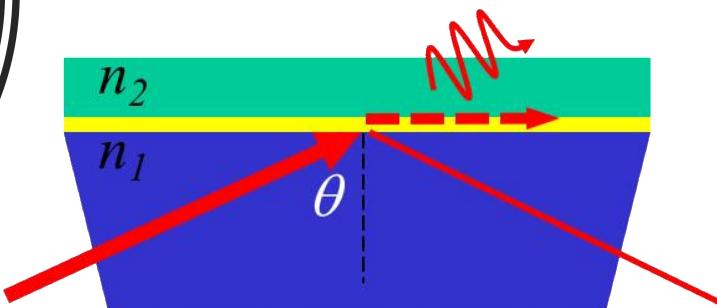


Concepts

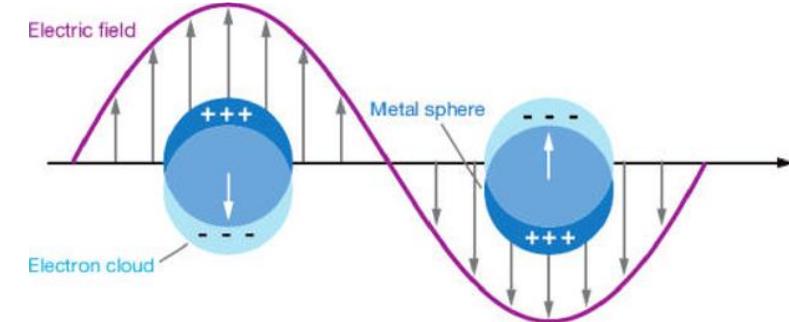
- *Plasmons:*
 - collective oscillations of the “free electron gas” density, often at optical frequencies.
- *Surface Plasmons:*
 - plasmons confined to surface (interface) and interact with light resulting in polaritons.
 - propagating electron density waves occurring at the interface between metal and dielectric.
- *Surface Plasmon Resonance:*
 - light (λ) in resonance with surface plasmon oscillation

SPR vs. LSPR

Surface Plasmon Resonance (SPR)

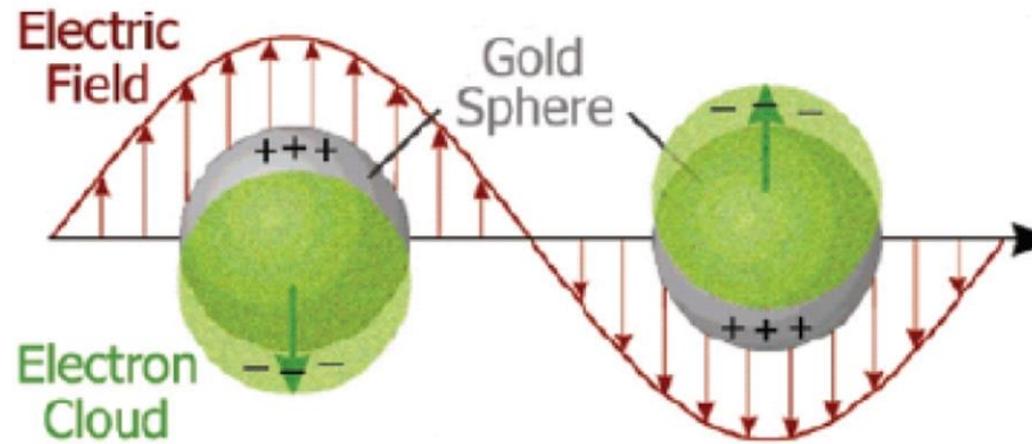


Localized Surface Plasmon Resonance (LSPR)



Localized Surface Plasmon Resonance (LSPR)

Localized Surface Plasmon Resonance (LSPR)



The schematic diagram demonstrated the interaction between incident light and electrons of a metal nanoparticle with **dimensions less than the wavelength of light**, showing the displacement of the conduction electron charge cloud relative to the nuclei

Free electron oscillations are confined to metal nanoparticles



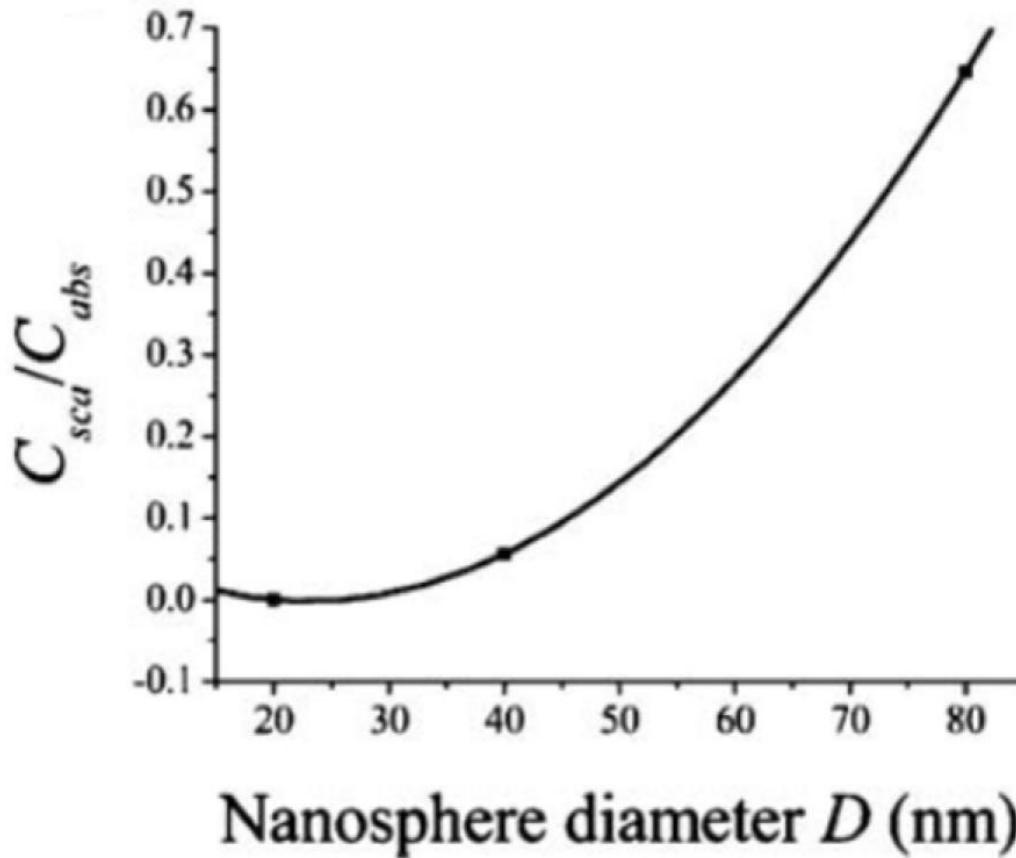
LSPR (continued)

When the frequency of incident light matches metal surface plasmon frequency, resonance occurs at surface of metal nanoparticles and there are three results:

- Intense incident light absorption (appearance of surface plasmon absorption bands)
- Strong incident light scattering
- Enhancement of the local electromagnetic fields

LSPR
(continued)

Ratio of scattering to absorption as a function of Au nanosphere diameter



Jain, PK; Huang, X; El-Sayed, IH; El-Sayed, MA. Plasmonics, 2007, 2, 107-118

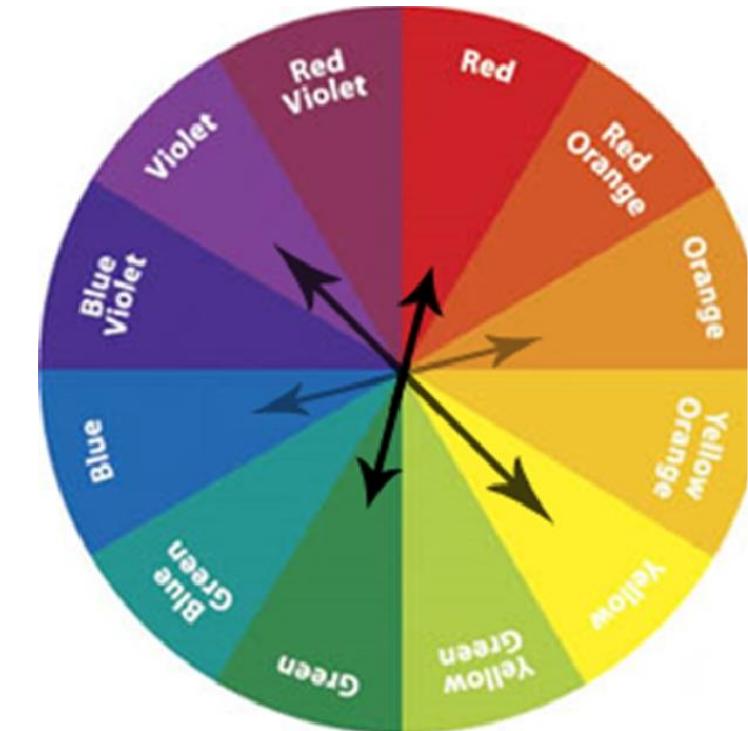


Gold
nanoparticles

The intense red color of aqueous dispersions of colloidal gold particles is a manifestation of localized surface plasmon resonance:
Light absorption at ~ 520 nm

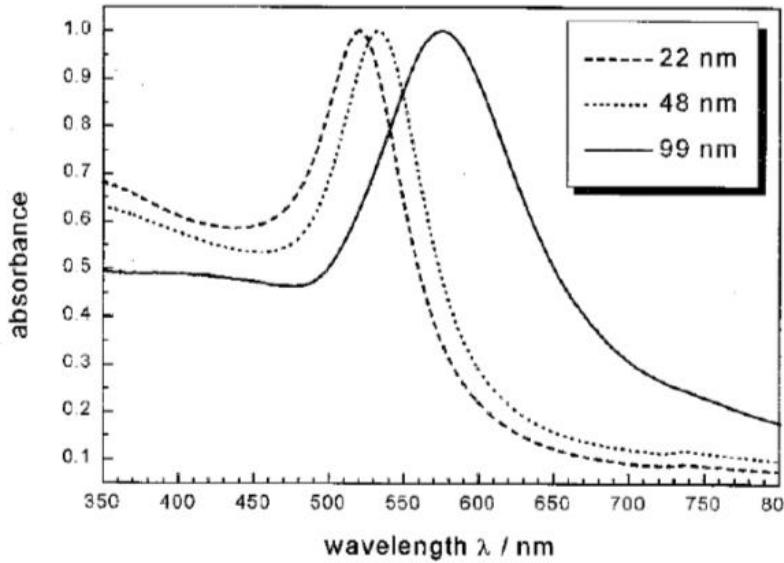
color	wavelength interval
red	$\sim 700\text{--}635$ nm
orange	$\sim 635\text{--}590$ nm
yellow	$\sim 590\text{--}560$ nm
green	$\sim 560\text{--}490$ nm
blue	$\sim 490\text{--}450$ nm
violet	$\sim 450\text{--}400$ nm

Complementary color wheel



Dependence
on size,

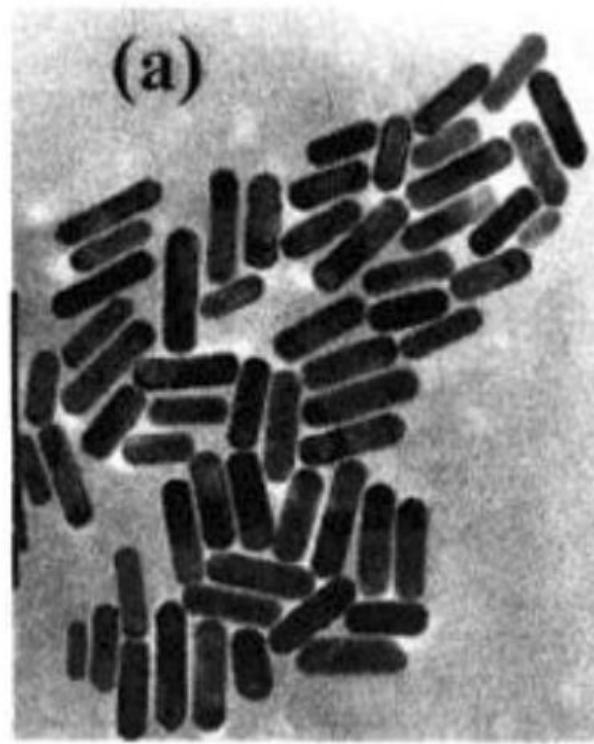
The frequency and intensity of the surface plasmon absorption bands are characteristic of the **type of material**, and are sensitive to the **size** and **shape** of the nanostructures, as well as to the **environment** which surround them



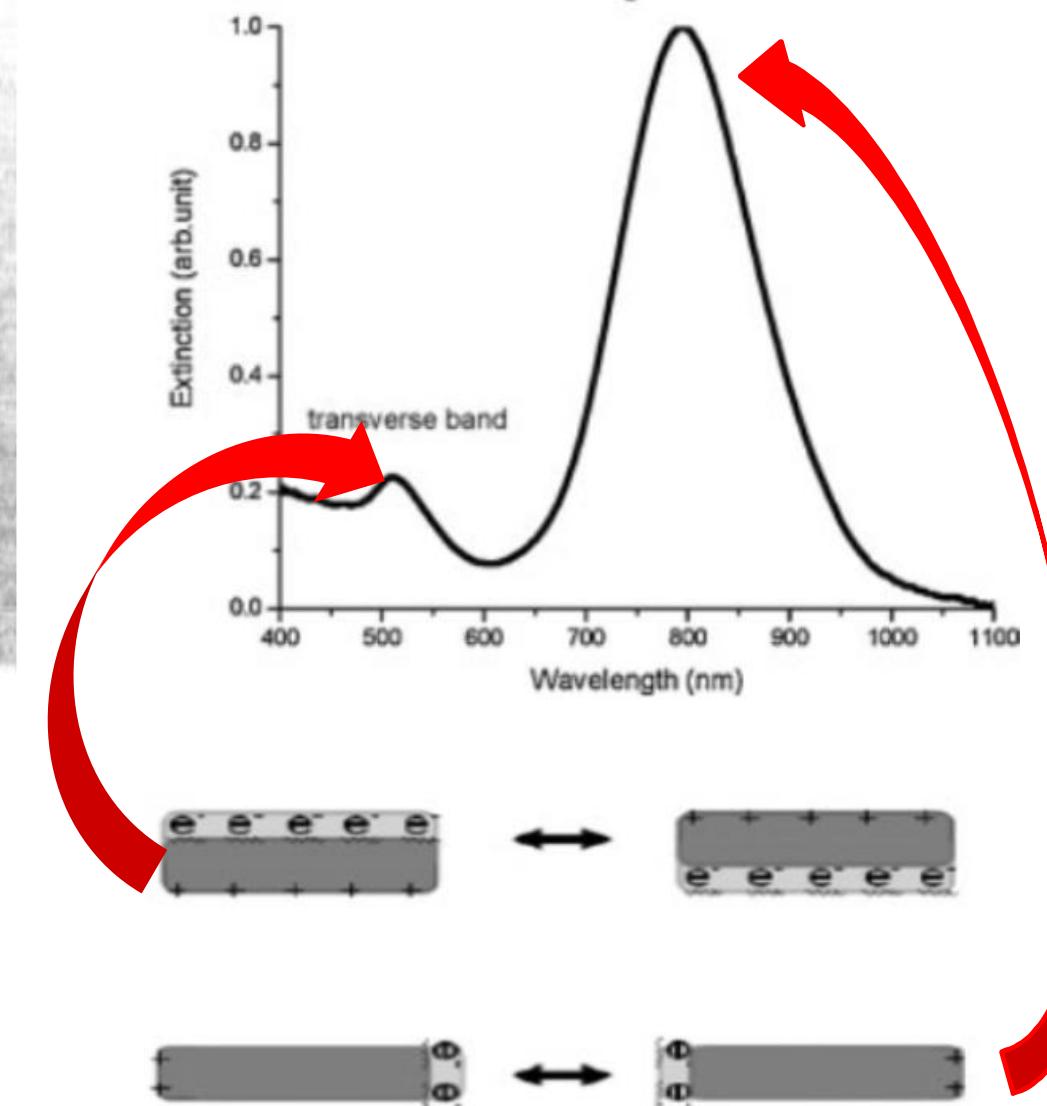
Optical absorption spectra of 22, 48 and 99 nm spherical gold NPs

As gold nanoparticles (NPs) increase in size, the optical absorption spectra shift toward larger wavelength (red end), not very sensitive to size though

Gold
nanorods
transverse
vs.
longitudinal

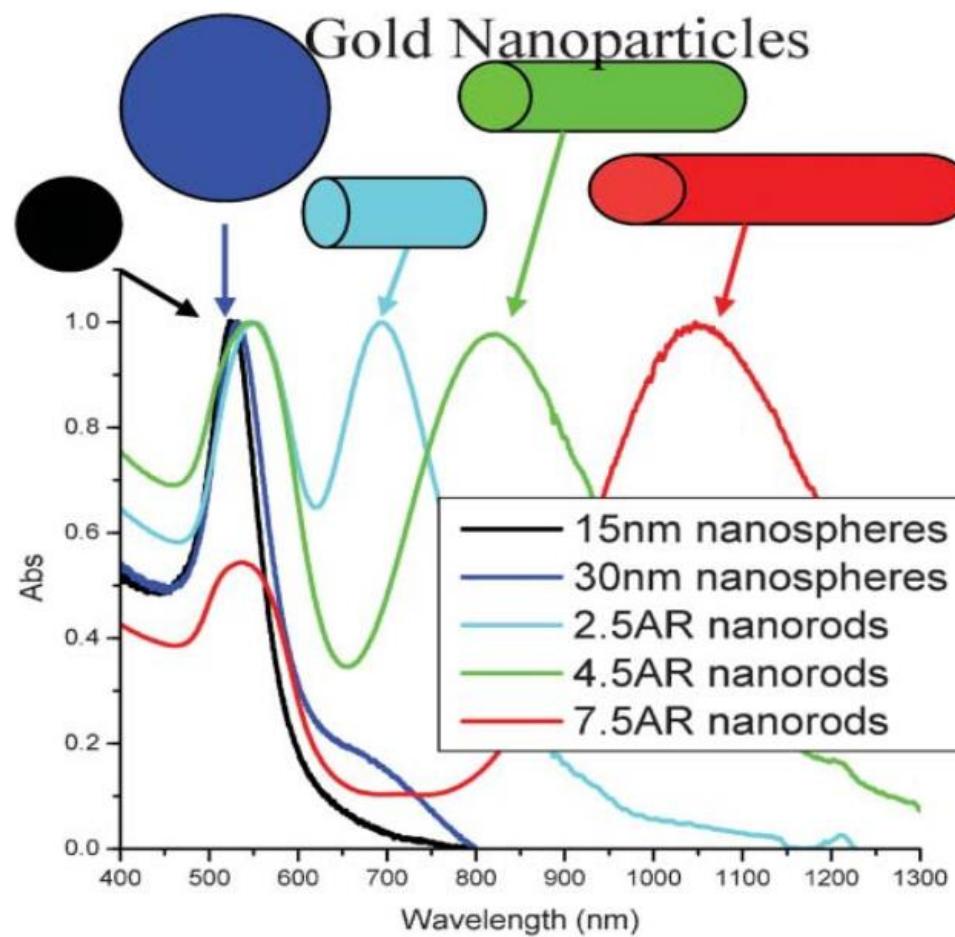


Gold nanorods



Huang, X; Neretina, S; El-Sayed, MA. Adv. Mater. 2009, 21, 4880-4910.

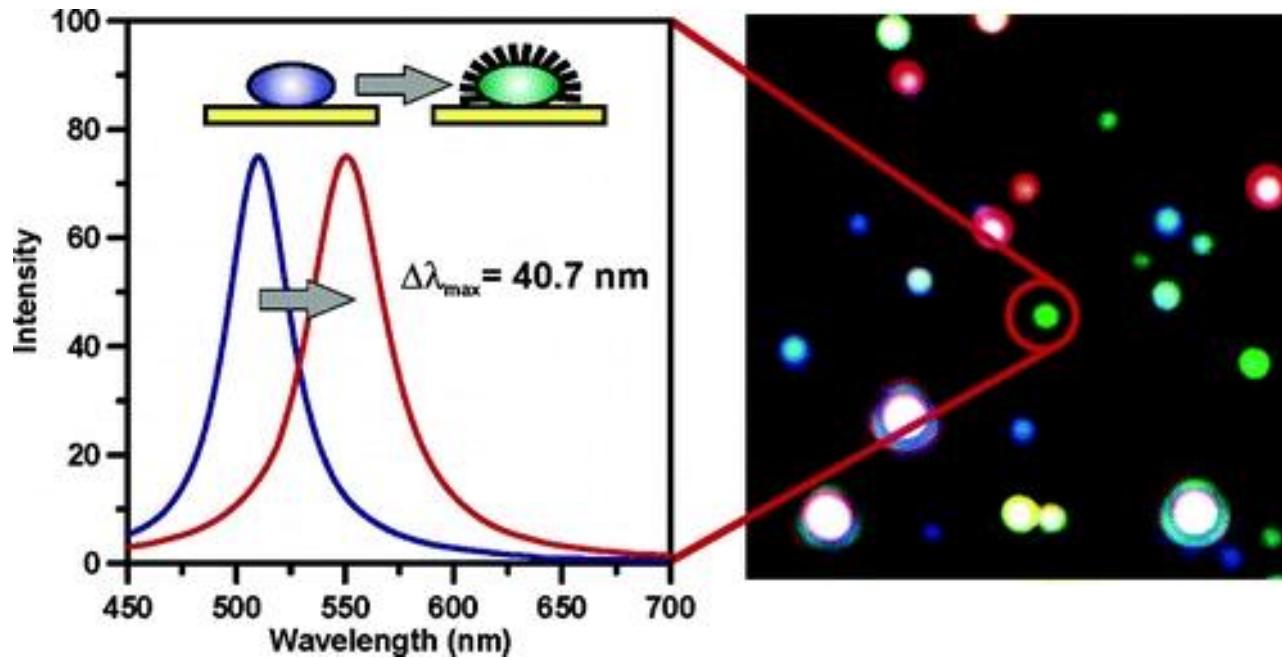
Shapes effects



Eustis, S; El-Sayed, MA. Chem. Soc. Rev., 2006, 35, 209-217.

- The transverse band is not very sensitive to the diameter of the nanorods
- The longitudinal band is red-shifted largely from the visible to near-infrared region with increasing aspect ratio (AR) L/D

Behavior of Silver nanoparticles after functionalization



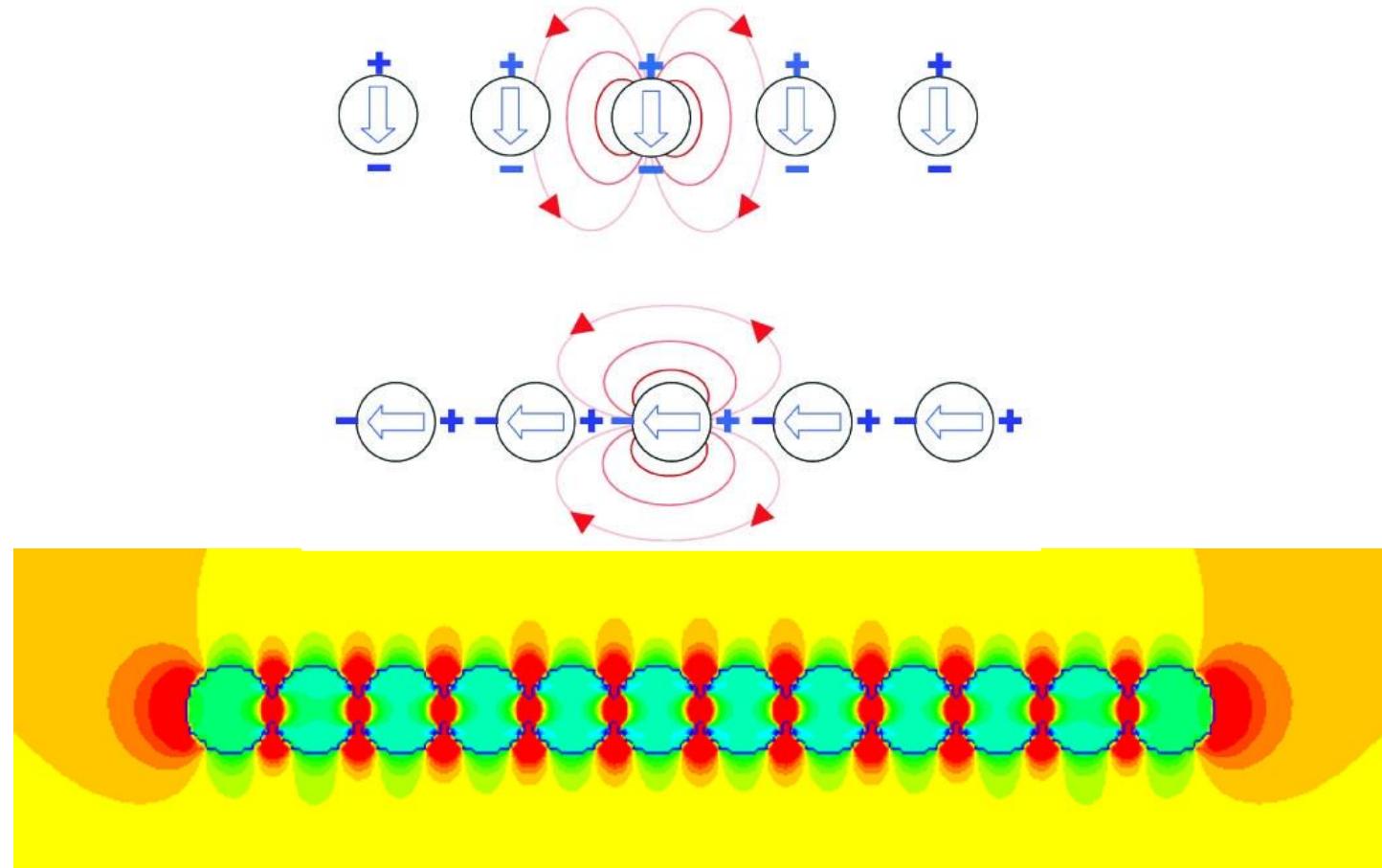
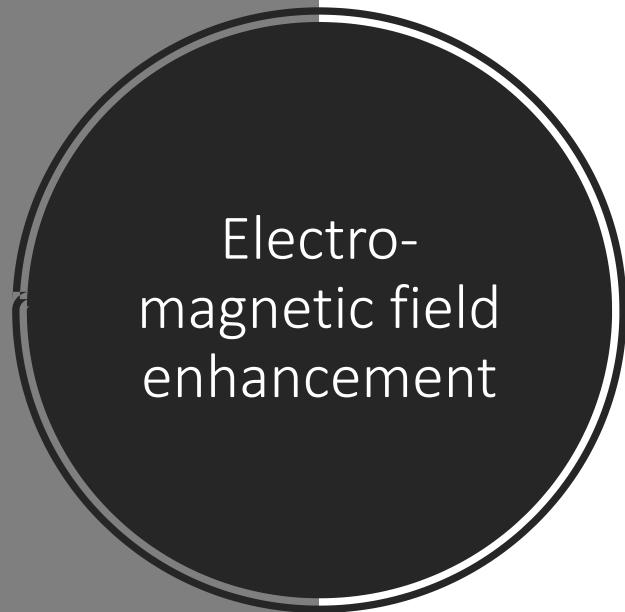
Left: Scattering spectrum of an individual Ag nanoparticle sensor before and after functionalization with hexadecanethiol
Right: A dark-field optical image of a field of Ag nanoparticles

The change of environment make the LSPR frequency shift
Scattering color change → Sensing

McFarland, AD; Van Duyen, RP. Single silver nanoparticles as real-time optical sensors with zeptomole sensitivity. *Nano Letters*, 2003, 3: 1057-1062

Large local electromagnetic field enhancement between nanoparticles

Near-field coupling in metal nanoparticle arrays



Surface Plasmon Resonance

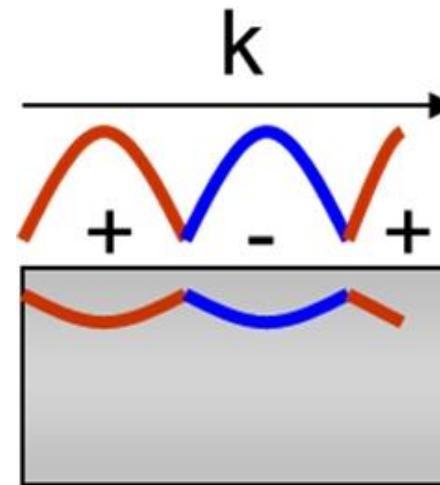


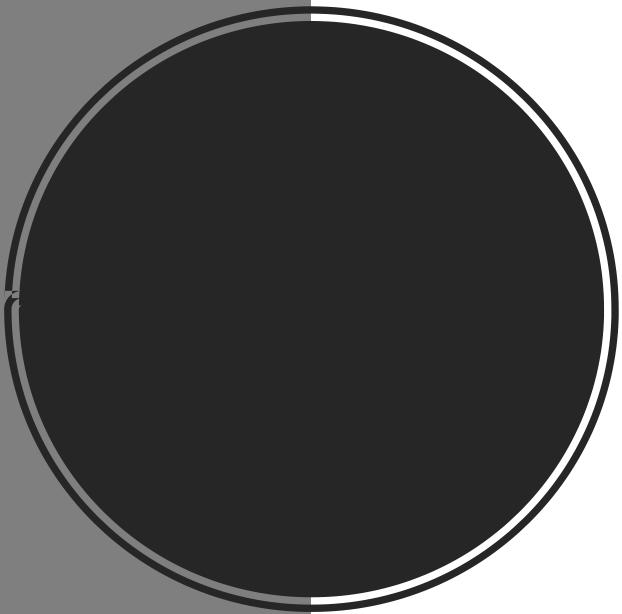
Surface Plasmon Resonance (SPR)

- As an electromagnetic wave that imposes on a metal surface only has a certain penetration depth, only the electrons on the surface have the most significant oscillations and their collective oscillations are termed surface plasmons
- Surface plasmon resonance
The resonance condition is established when the frequency of incident light matches the natural frequency of surface plasmon

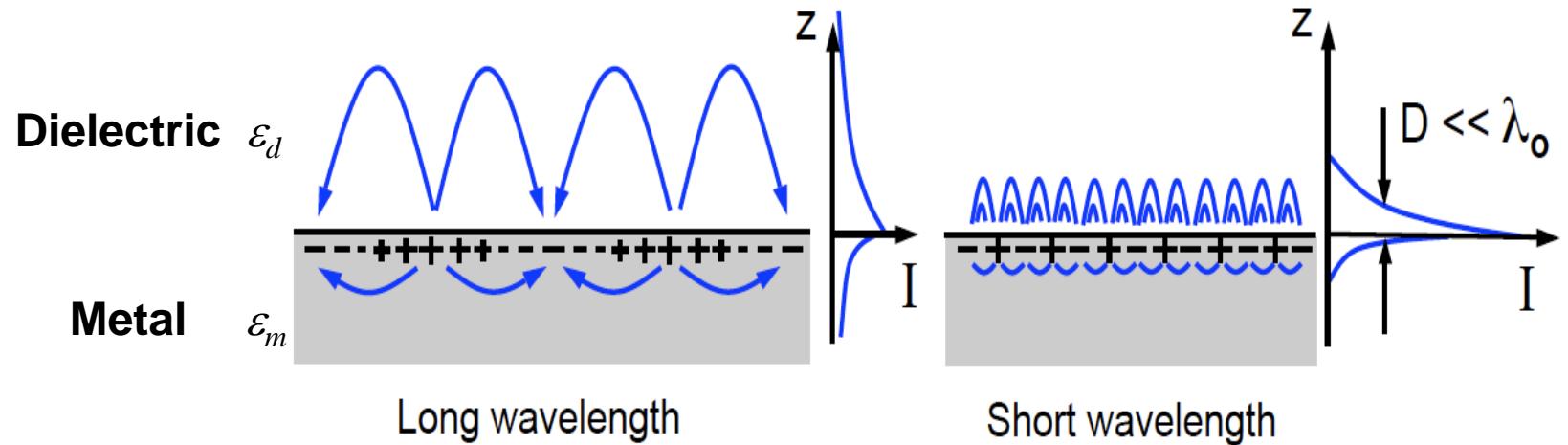
Surface Plasmon Polaritons

Plasmons confined to metal surfaces can interact with incident light to form propagating “surface plasmon polaritons (SPP)” (electromagnetic waves on bulk metal surface)



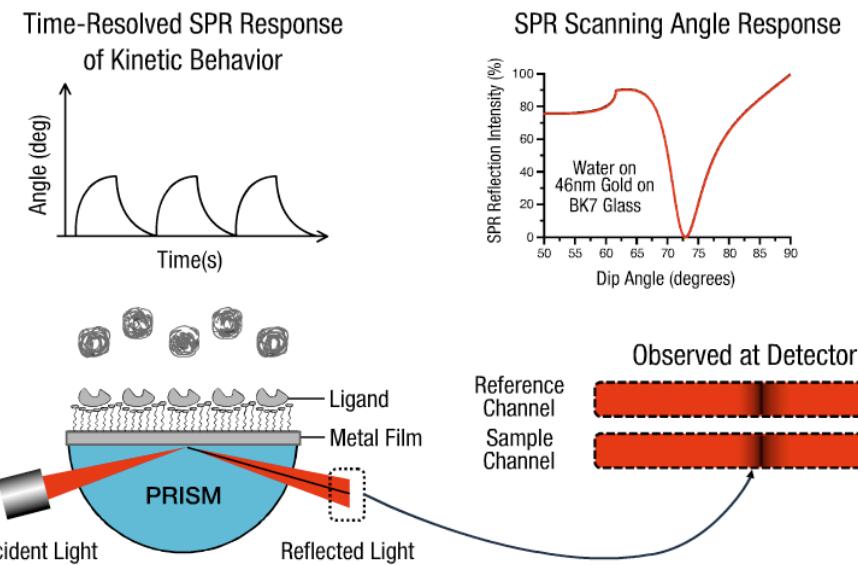
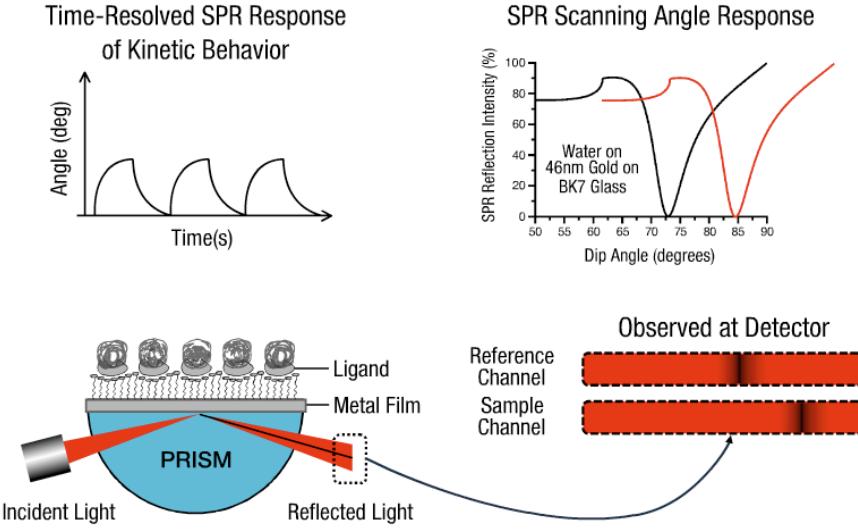


- Surface plasmons (SPs) are coherent electron oscillations.
- SPs exist at the interface between any two materials, such as metal and dielectric layer, where the real part of the dielectric function changes sign across the interface.
- SPs can be excited by both photons and electrons



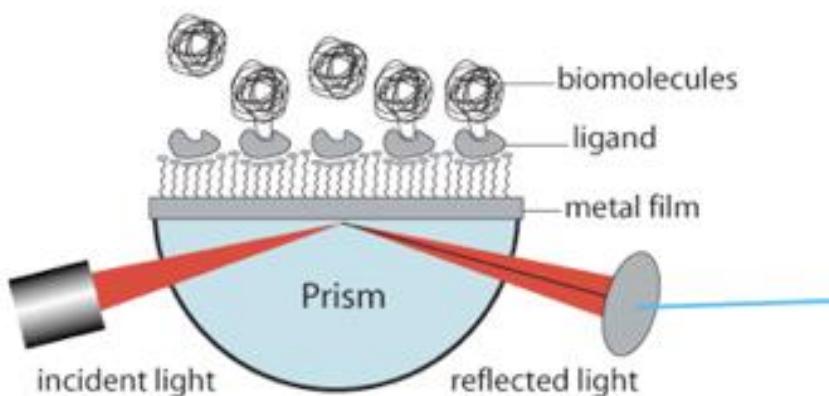
SPR Biosensors

<http://www.biosensingusa.com/index.html>

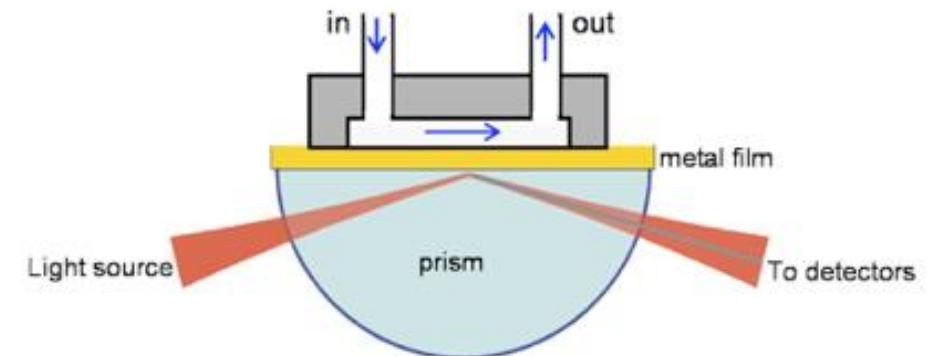


SPR Sensing Principle

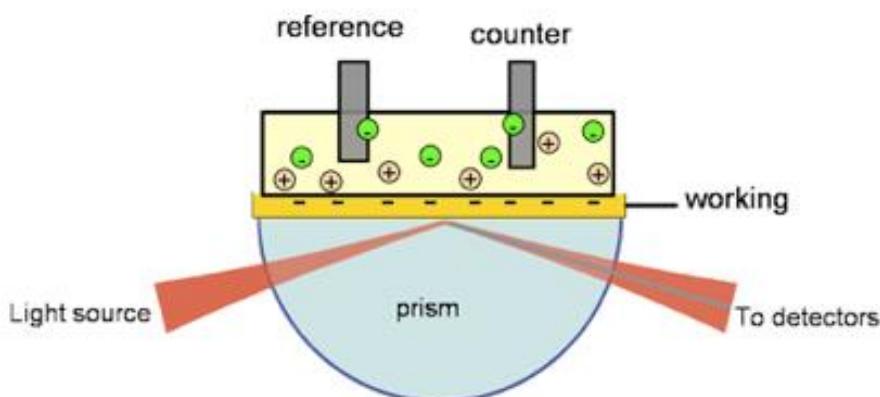
Biomolecular SPR



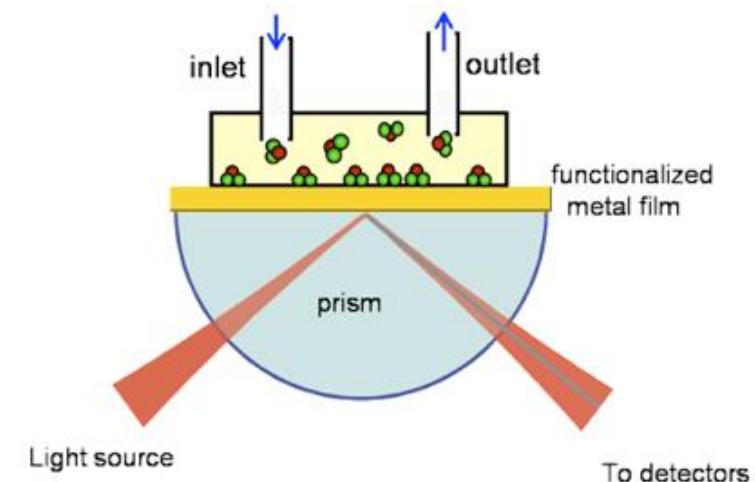
Flow Injection SPR



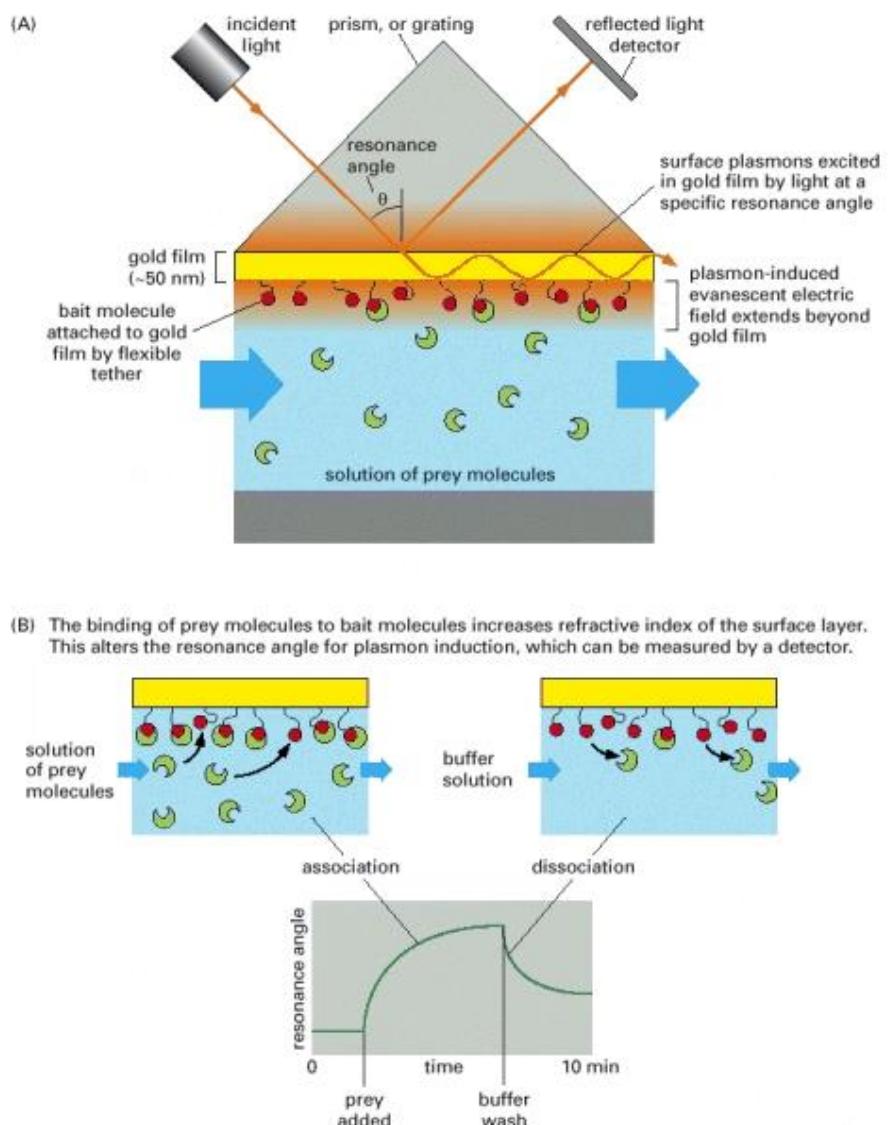
Electrochemical SPR



Gas Phase SPR



Quantum Mechanical SPR



Interactions of Light + Metal + Molecules

1. Photons (totally reflected) create electric field at the interface.
2. Localized electric field on metal thin film oscillates EM and form an evanescent wave.
3. Free electrons in metal thin film act as resonator.
Energy for the resonance comes from the evanescent wave produced by TIR photons.
4. Coupling resonance between the plasma oscillations of free electrons on the metal and the EM field of the reflected photons matches if conditions of the wavelength, incident angle, and the index of refraction of prism, metal, liquid layer matched.
Momentum of the incident light =
Momentum of the plasma EM field.
5. Photons are absorbed and converted to surface plasmons.

Applications of SPR

Ligand fishing

Bacteriology

Virology

Epitope mapping

Molecular engineering

Cell biology

Cell adhesion

Signal transduction

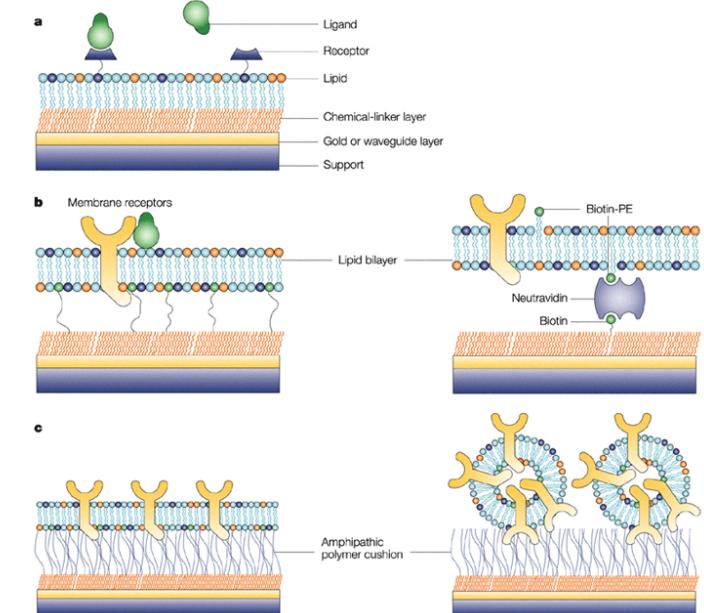
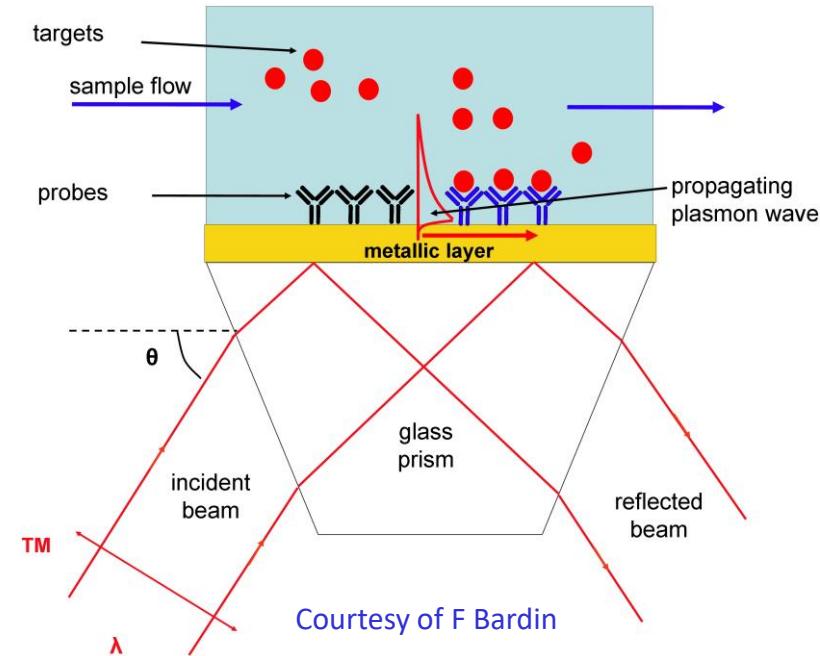
Nucleotide-nucleotide binding

Nucleotide-protein binding

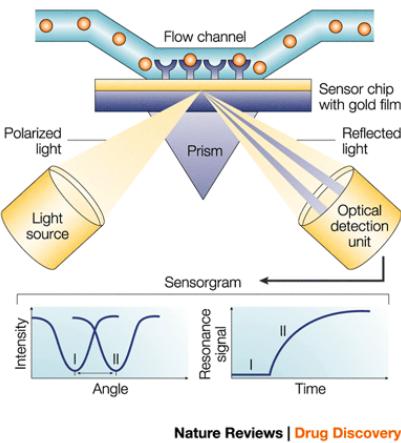
Enzyme mechanism

Small-molecule binding to immobilized receptors

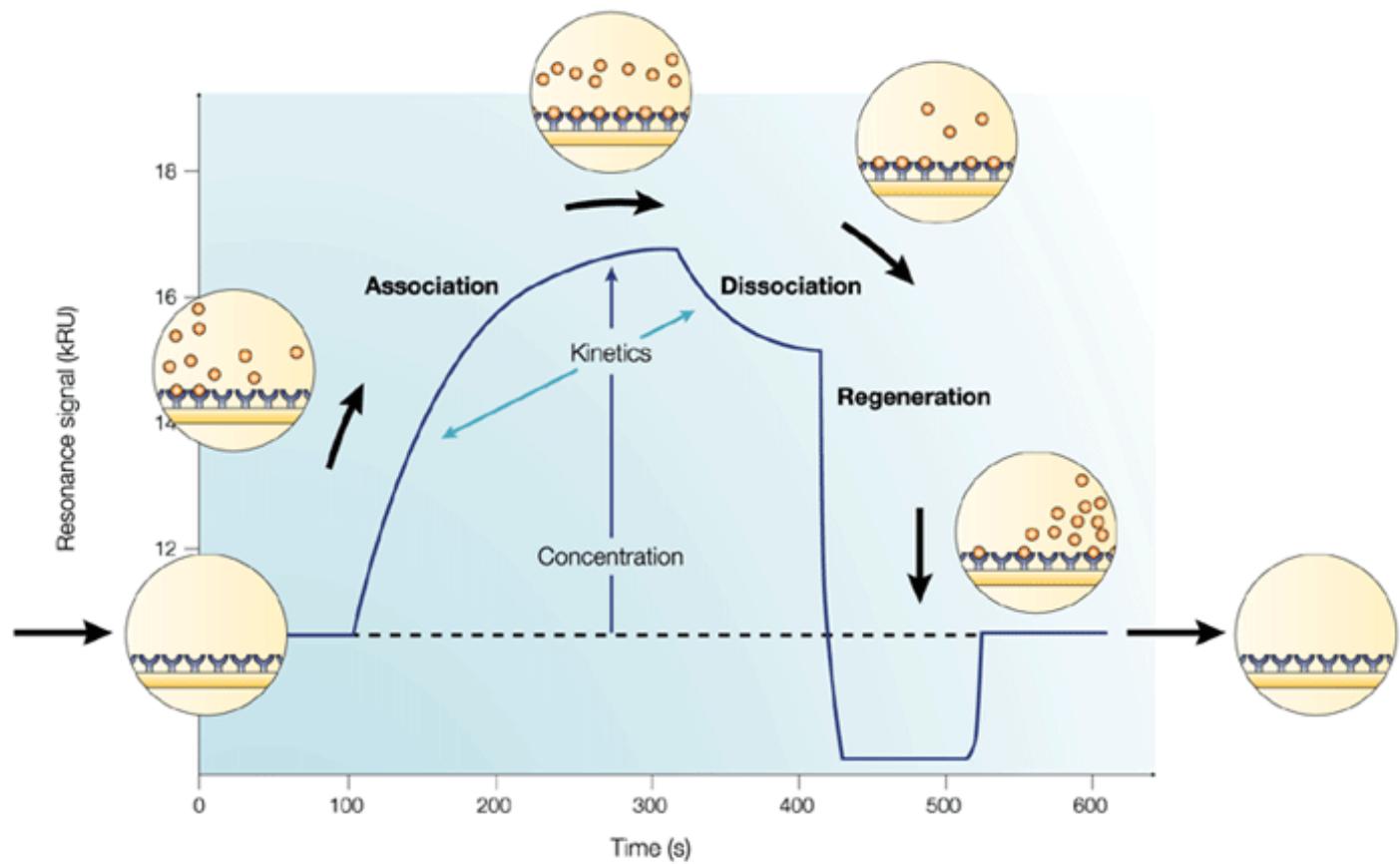
Analysis of biomolecular interactions.



Binding Cycle Detection by SPR



Nature Reviews | Drug Discovery

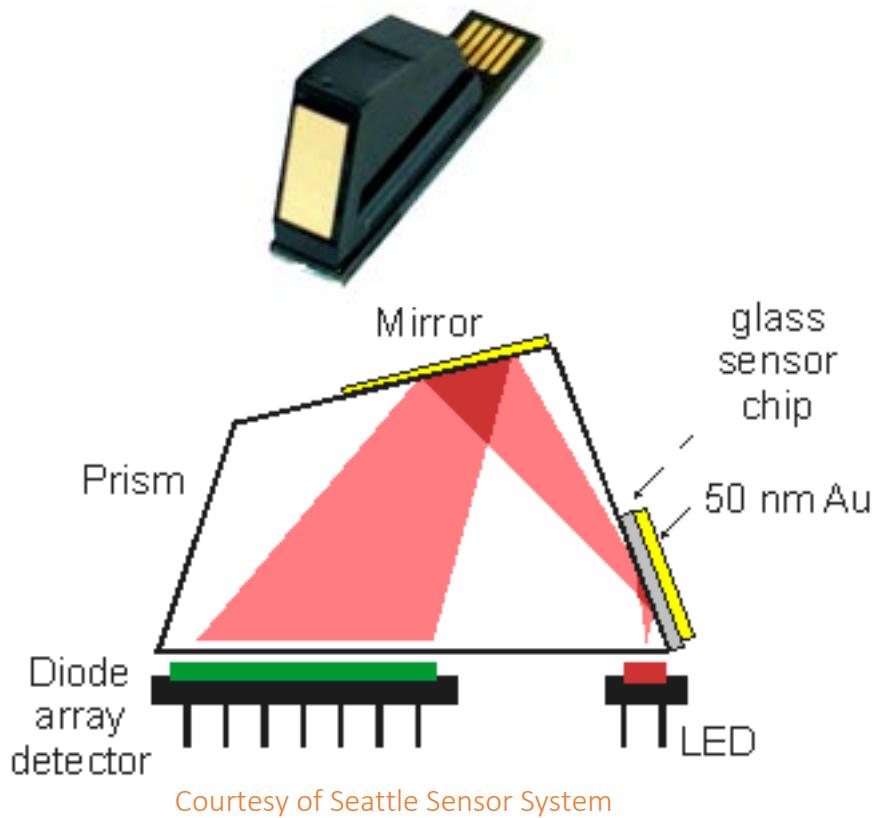


Nature Reviews | Drug Discovery

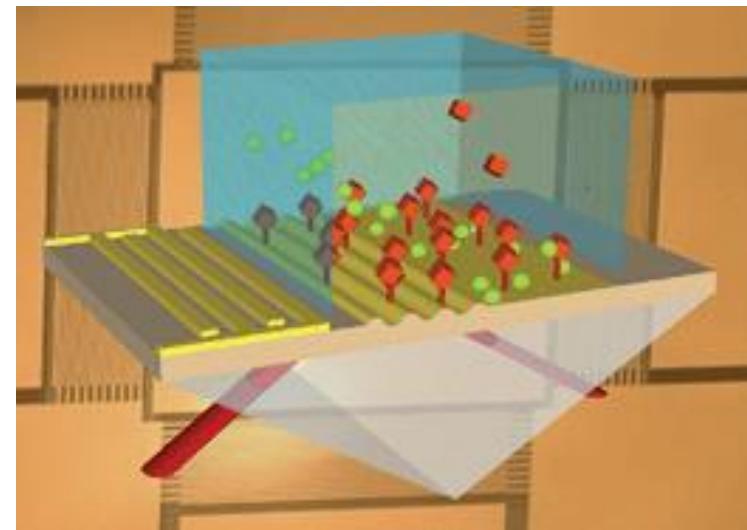
Matthew A. Cooper, *Nature Reviews Drug Discovery* 1, 515-528

Miniaturized SPR Systems

Integrated SPR System

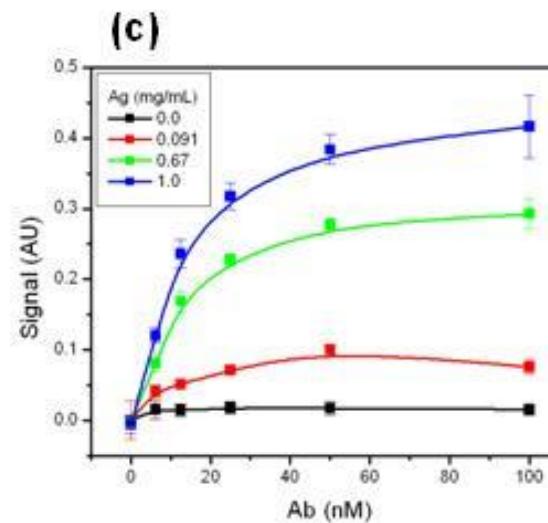
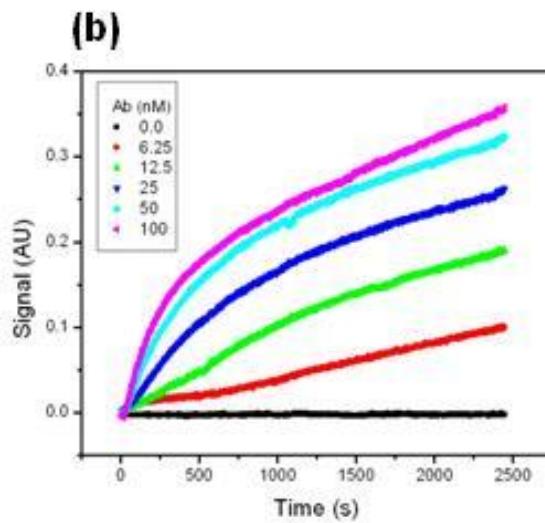
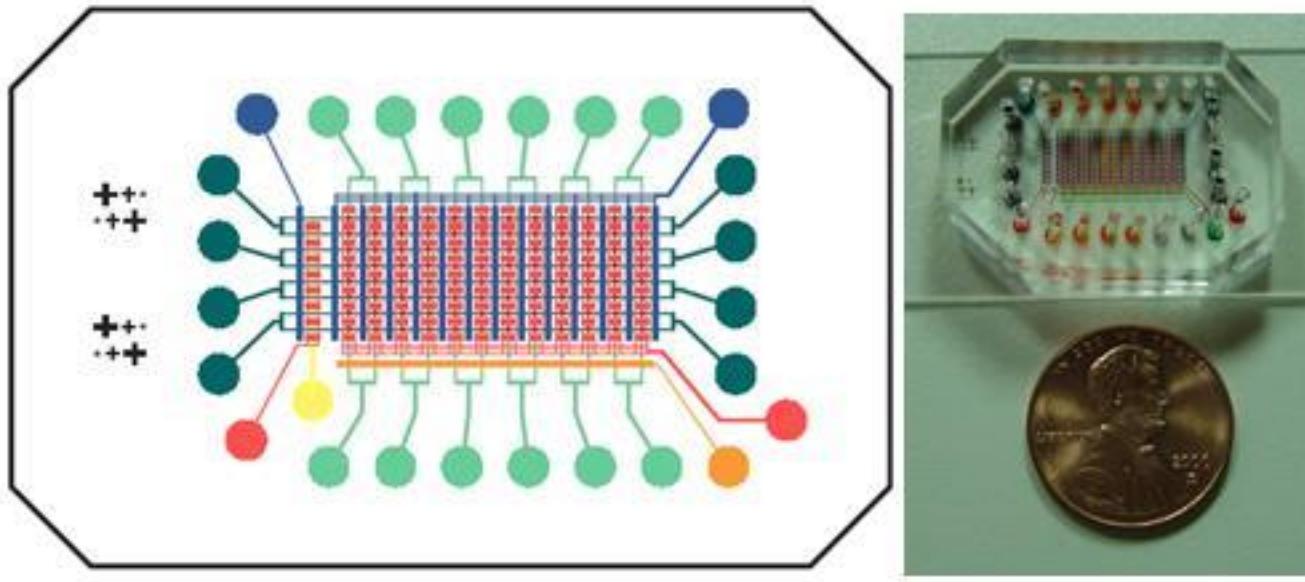


Integrated SPR and SAW



Renaudin A. et al., (*Lab Chip*, 2010)

Multiplexed SPR



Courtesy of Prof. Zare



List of
Applications

Surface Plasmon Resonance Sensing (Biosensing)

Surface Enhanced Raman Scattering (SERS)
for single molecule detection

Heat generation of metal nanoparticles

Metal nanoparticle-derived polymer thermal
processing

Photothermal therapy of cancer

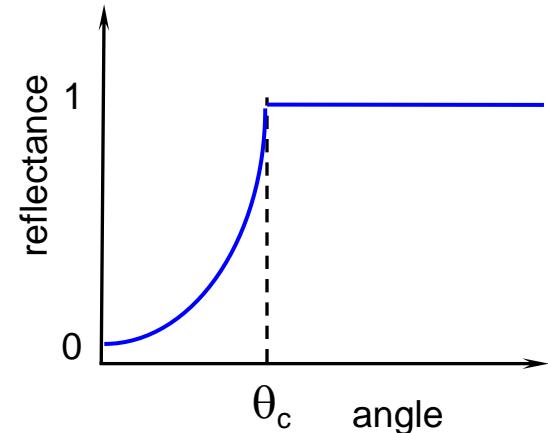
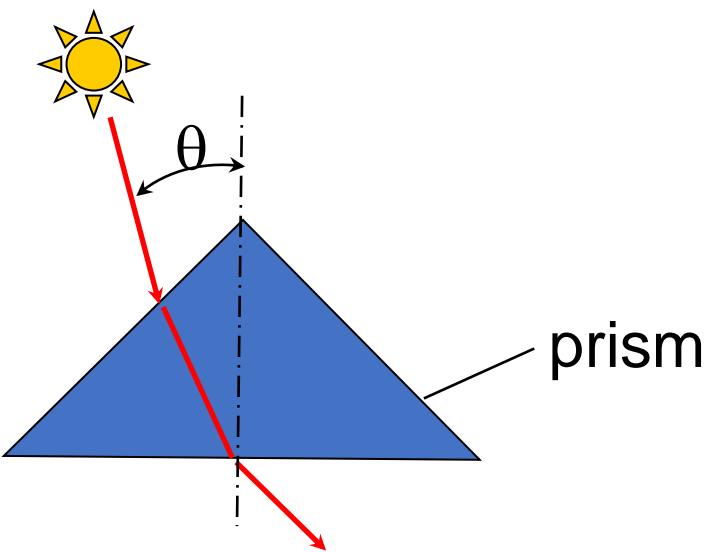
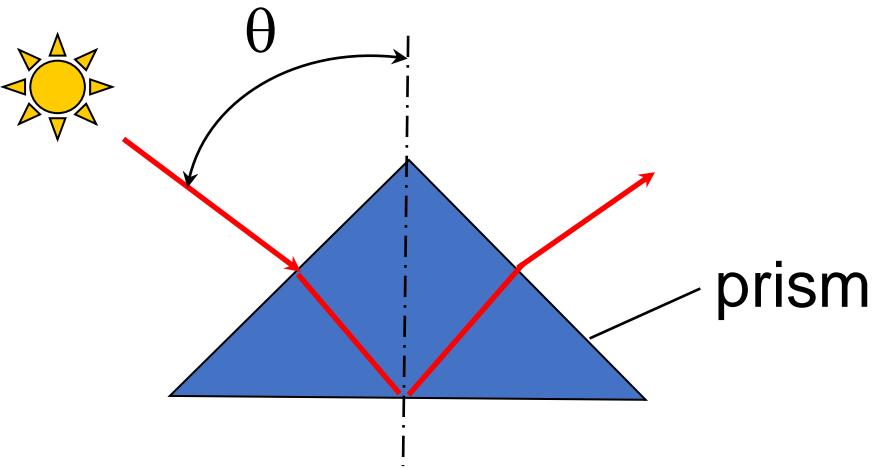
Surface Plasmon-assisted Spectroscopy

<i>Technique</i>	<i>Largest enhancement factor</i>
Surface enhanced raman	10^{14}
SERS	Nie and Emery, <i>Science</i> , 1997, 275, 1102.
Surface enhanced IR	10^4
SEIRA	Tsang, et.al., <i>Phys. Rev. Lett.</i> , 1980, 45, 201.
Sum frequency generation	10^4
SESFG	Baldelli, et.al., <i>J. Chem.Phys.</i> , 2000, 113, 5432.
Second harmonic generation	10^4
SESHG	Chen, et.al., <i>Phys. Rev. Lett.</i> , 1981, 46, 145.
Surface enhanced fluorescence	~ 100
SEF	

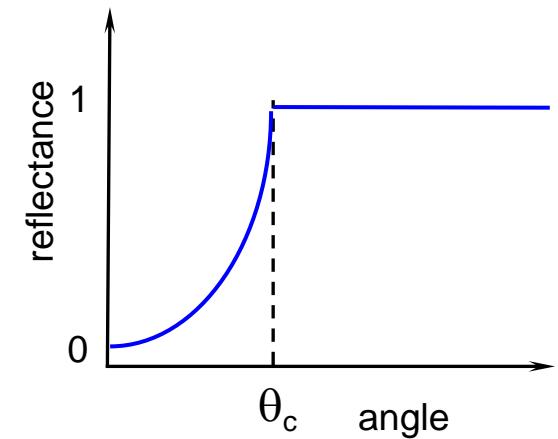
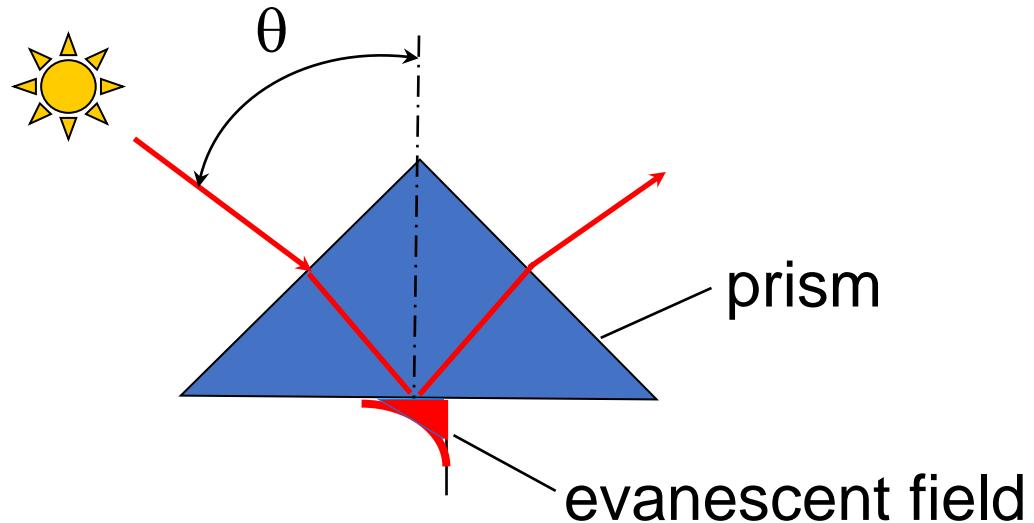


Evanescence Waves

Total reflection on a prism



Evanescence Wave

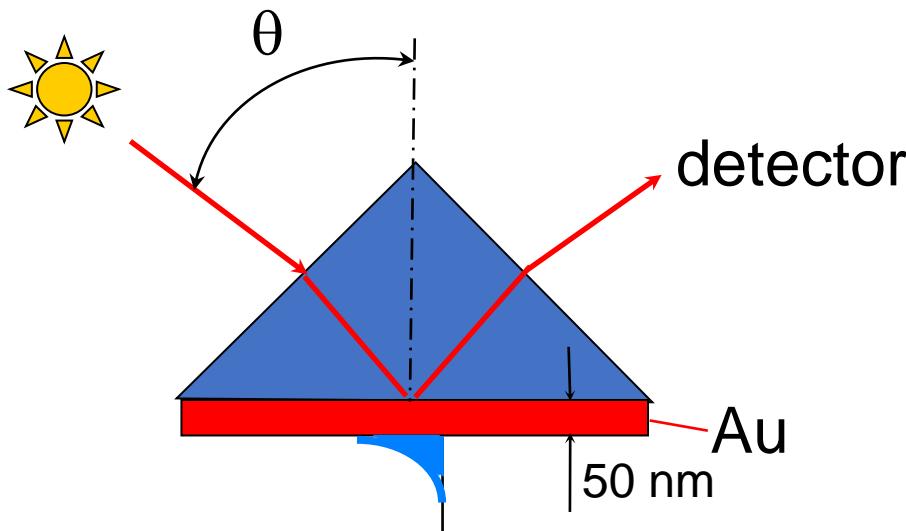


evanescent wave:

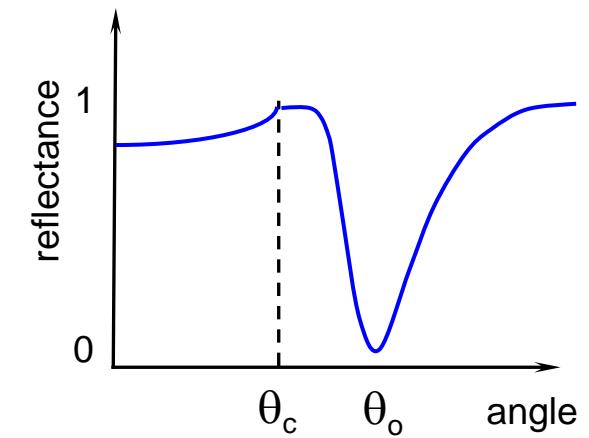
- nearfield standing wave,
- extends about $1/2 \lambda$,
- decays exponentially with the distance

Surface Plasmon Resonance

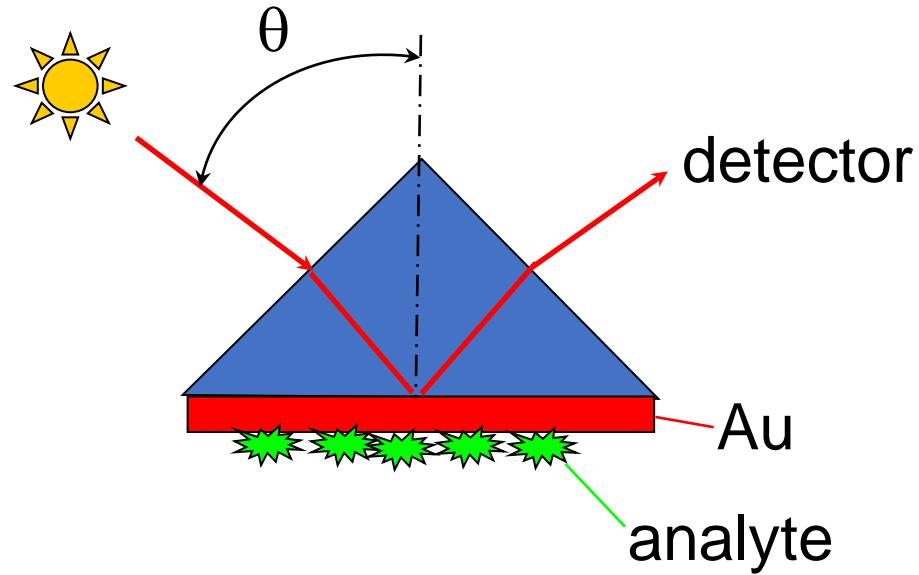
Surface
Plasmon
Resonance



(Kretschmann)

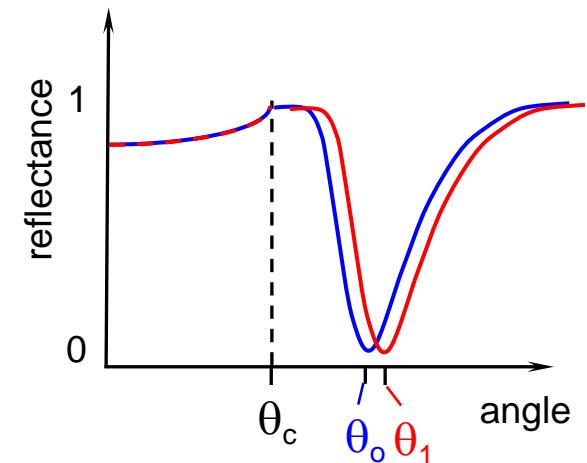


Surface Plasmon Resonance Spectroscopy



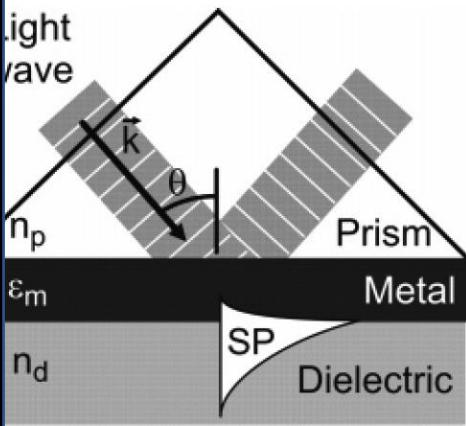
To measure:

- thickness changes,
- density fluctuation,
- molecular adsorption

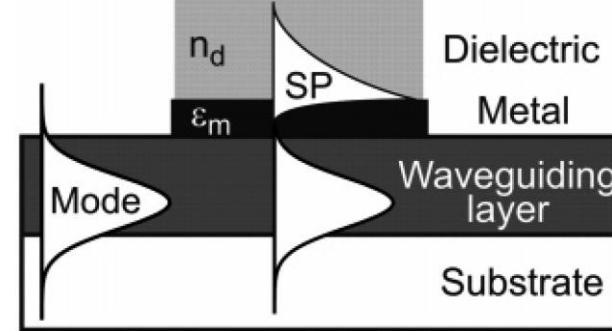


Coupling of Light to Surface Plasmon

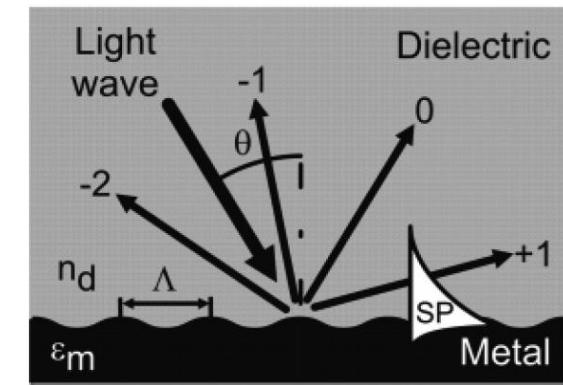
Coupling of Light to Surface Plasmon



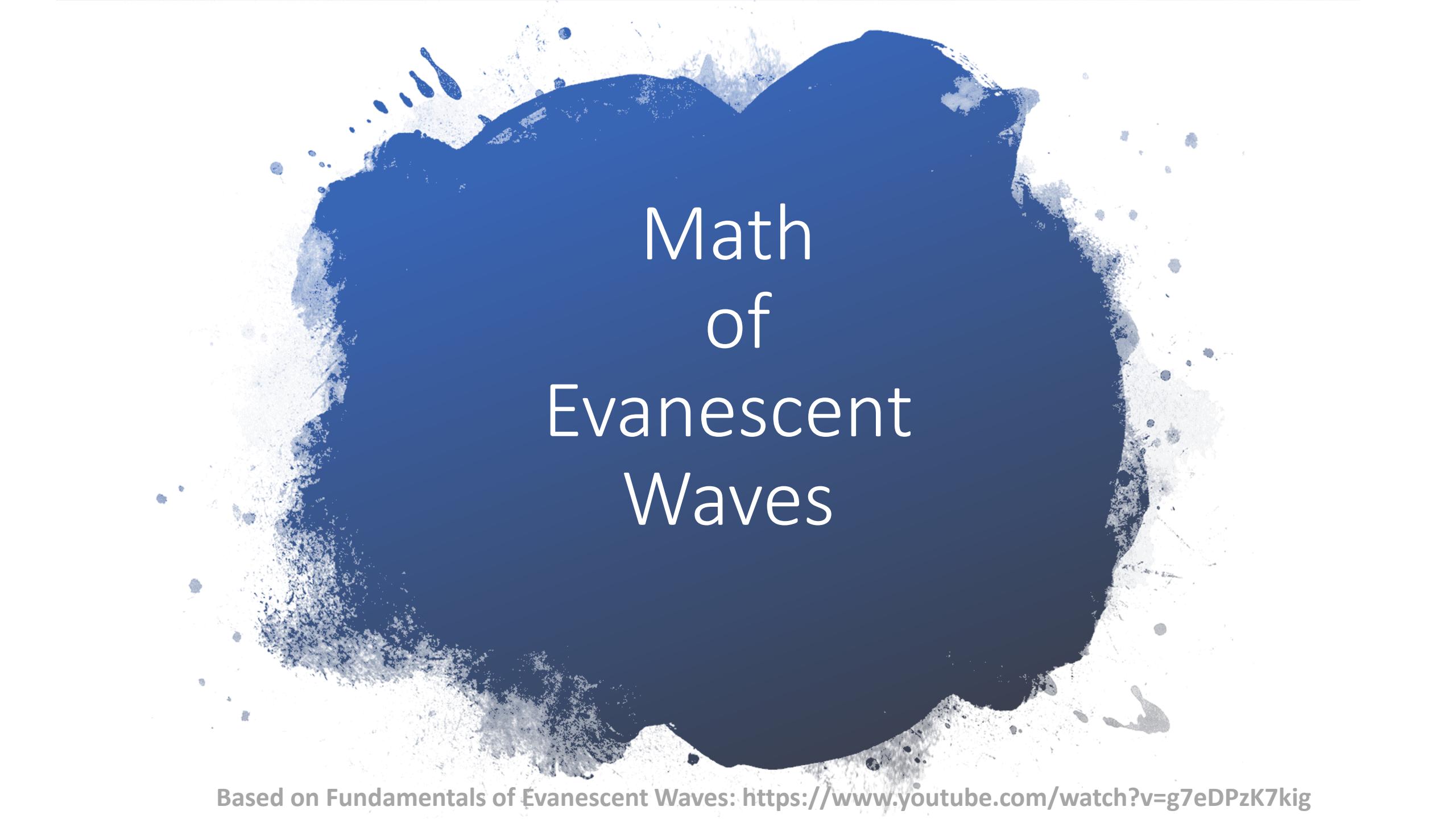
Prism coupler
Kretschmann)



Waveguide coupler



Grating coupler

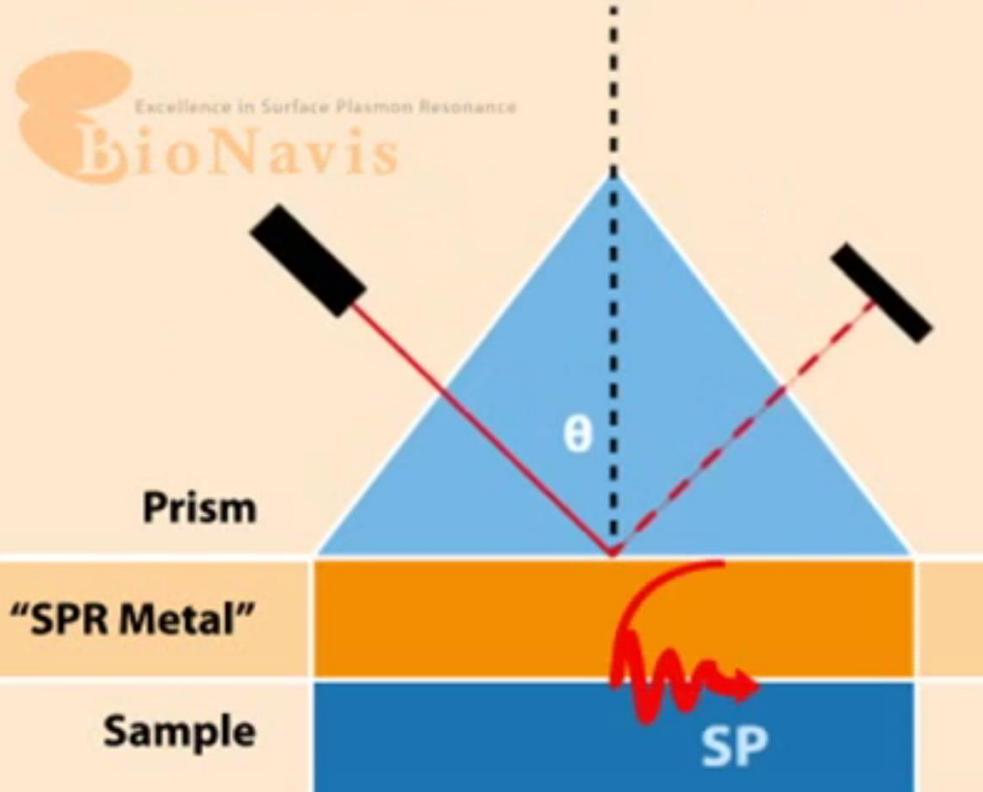


Math of Evanescent Waves

Based on Fundamentals of Evanescent Waves: <https://www.youtube.com/watch?v=g7eDPzK7kig>

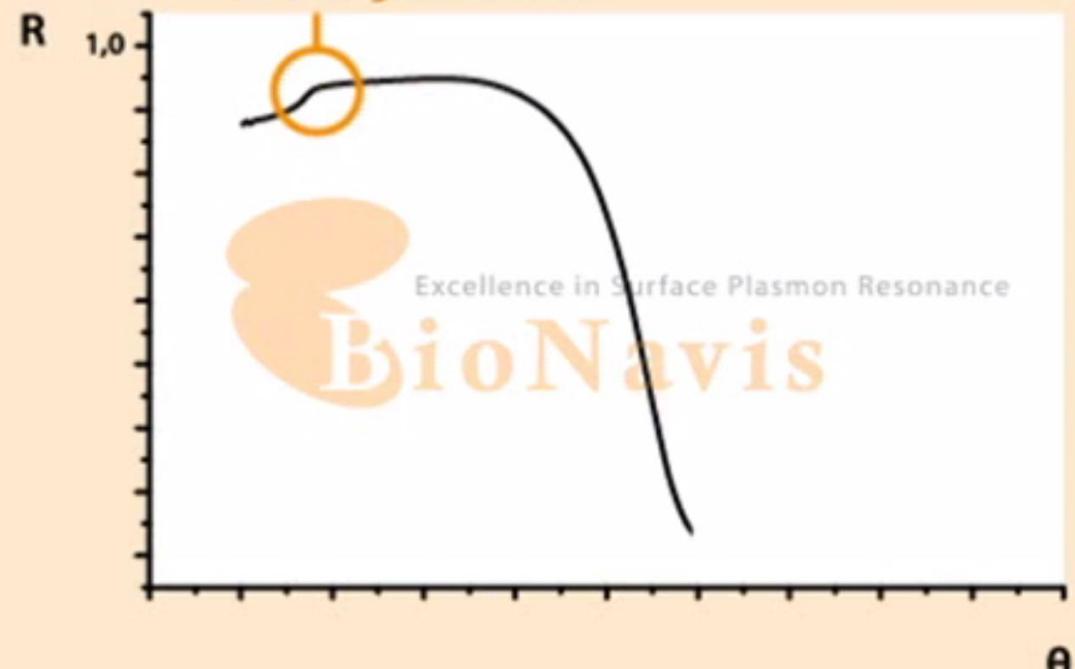
Excitation of surface Plasmon using EVANESCENT WAVE

Laser, p-polarized light

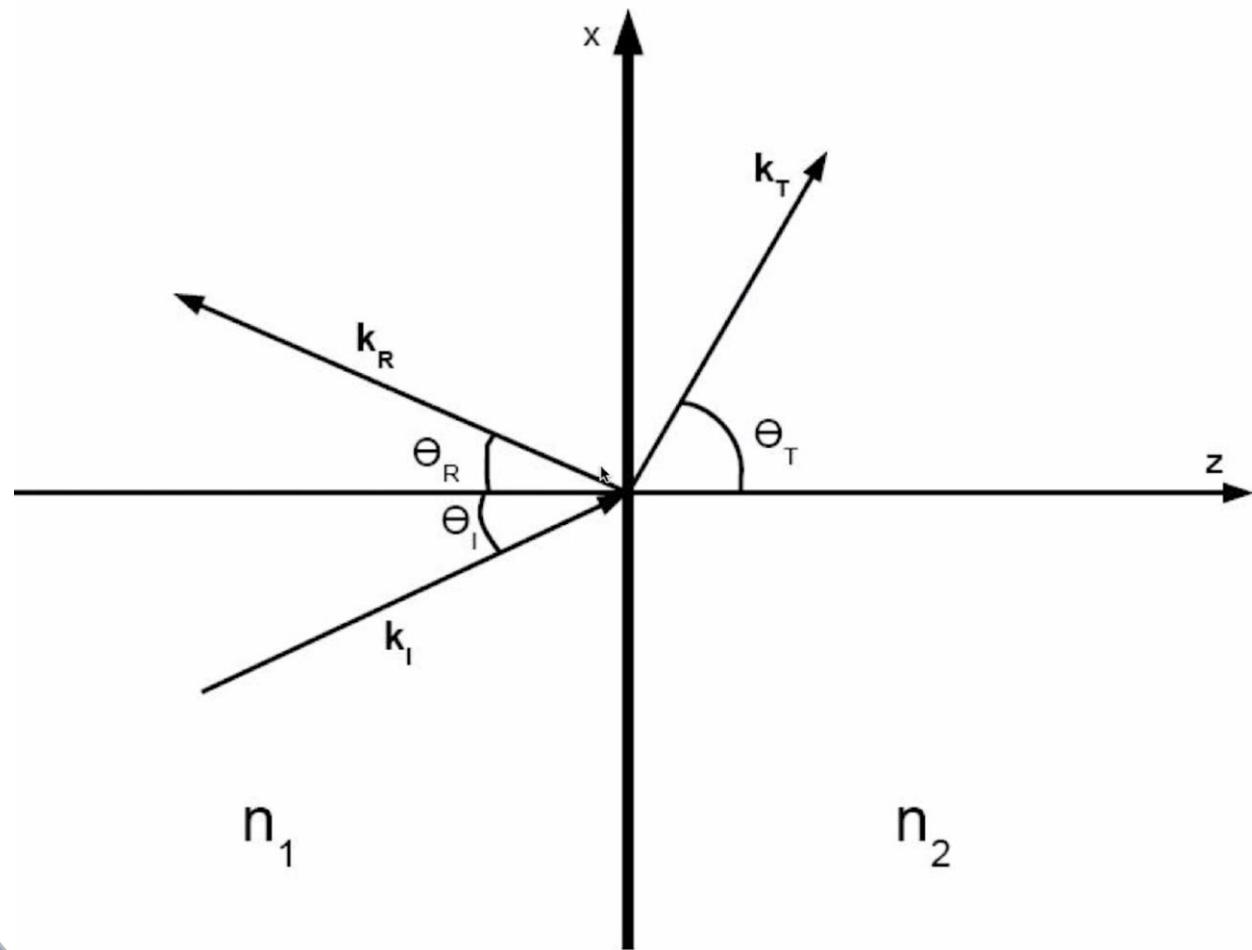


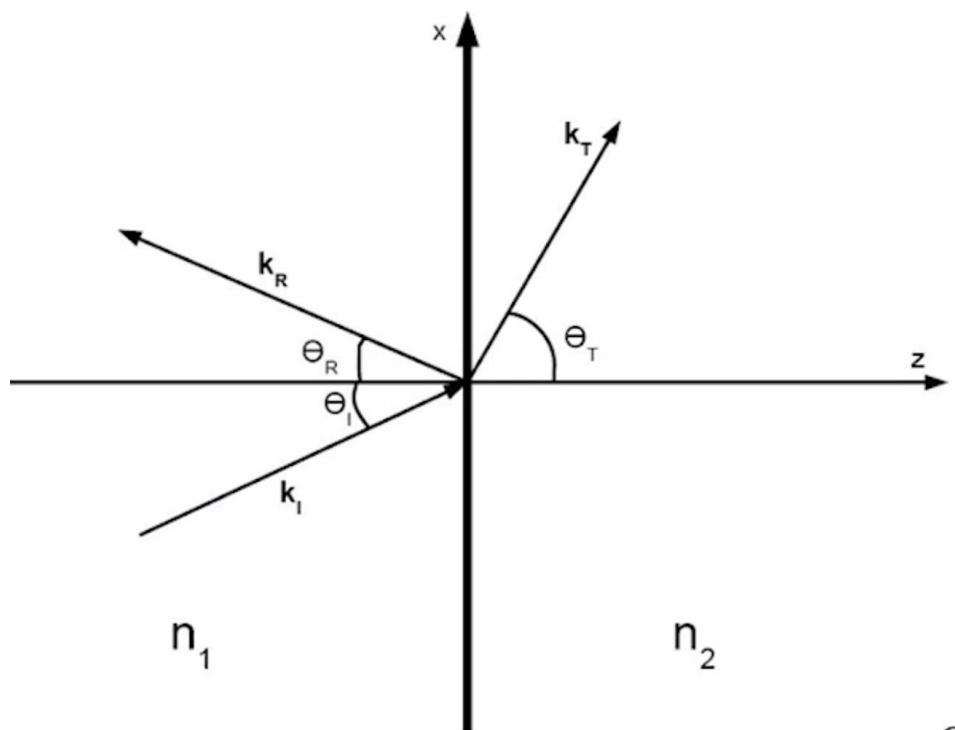
Photodetector

Total Internal Reflection (TIR)
100 % of light is reflected



- The propagation constant of the evanescent wave depends on the incidence angle.





$$n_1 \sin \theta_I = n_2 \sin \theta_T$$

Snell's law

$$\theta_T = \sin^{-1} \left(\frac{n_1}{n_2} \sin \theta_I \right)$$

$$\sin \theta_I > \frac{n_2}{n_1}$$

$$\frac{n_1}{n_2} \sin \theta_I > 1$$

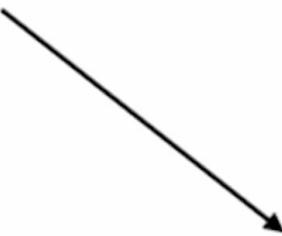
$$\theta_C = \sin^{-1} \left(\frac{n_2}{n_1} \right)$$

Critical Angle

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right) \text{ Critical Angle}$$

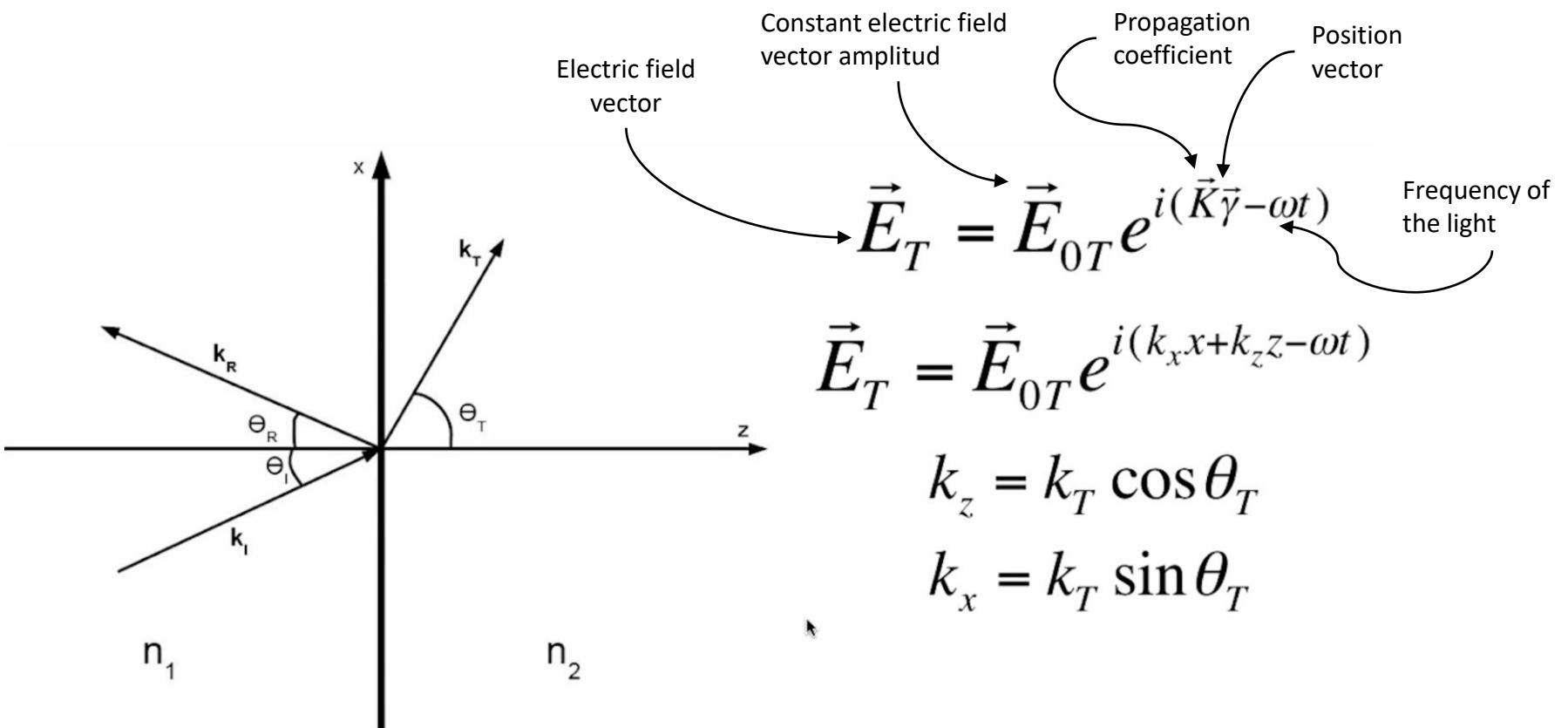
$$\theta_I > \theta_c$$

“Total” Internal reflection



Light incident on surface completely reflects off of it back into the medium from where it came

$$\theta_c = \sin^{-1} \left(\frac{n_2}{n_1} \right)$$
$$\theta_I > \theta_c$$
$$\sin^{-1} \left(\frac{n_2}{n_1} \sin \theta_T \right) > \theta_c$$
$$\sin \theta_T > 1$$



$$\vec{E}_T = \vec{E}_{0T} e^{i(k_T \sin \theta_T) x} e^{i(k_T \cos \theta_T) z} e^{-i\omega t}$$

$$\vec{E}_T = \vec{E}_{0T} e^{i(k_T \sin \theta_T) x} e^{i(k_T \cos \theta_T) z} e^{-i\omega t}$$

$$\cos \theta_T = \sqrt{1 - \sin^2 \theta_T} \quad \sin \theta_T > 1$$

$$\cos \theta_T \quad \text{imaginary}$$

$$k_T = \frac{n_2 \omega}{c} \quad \text{real}$$

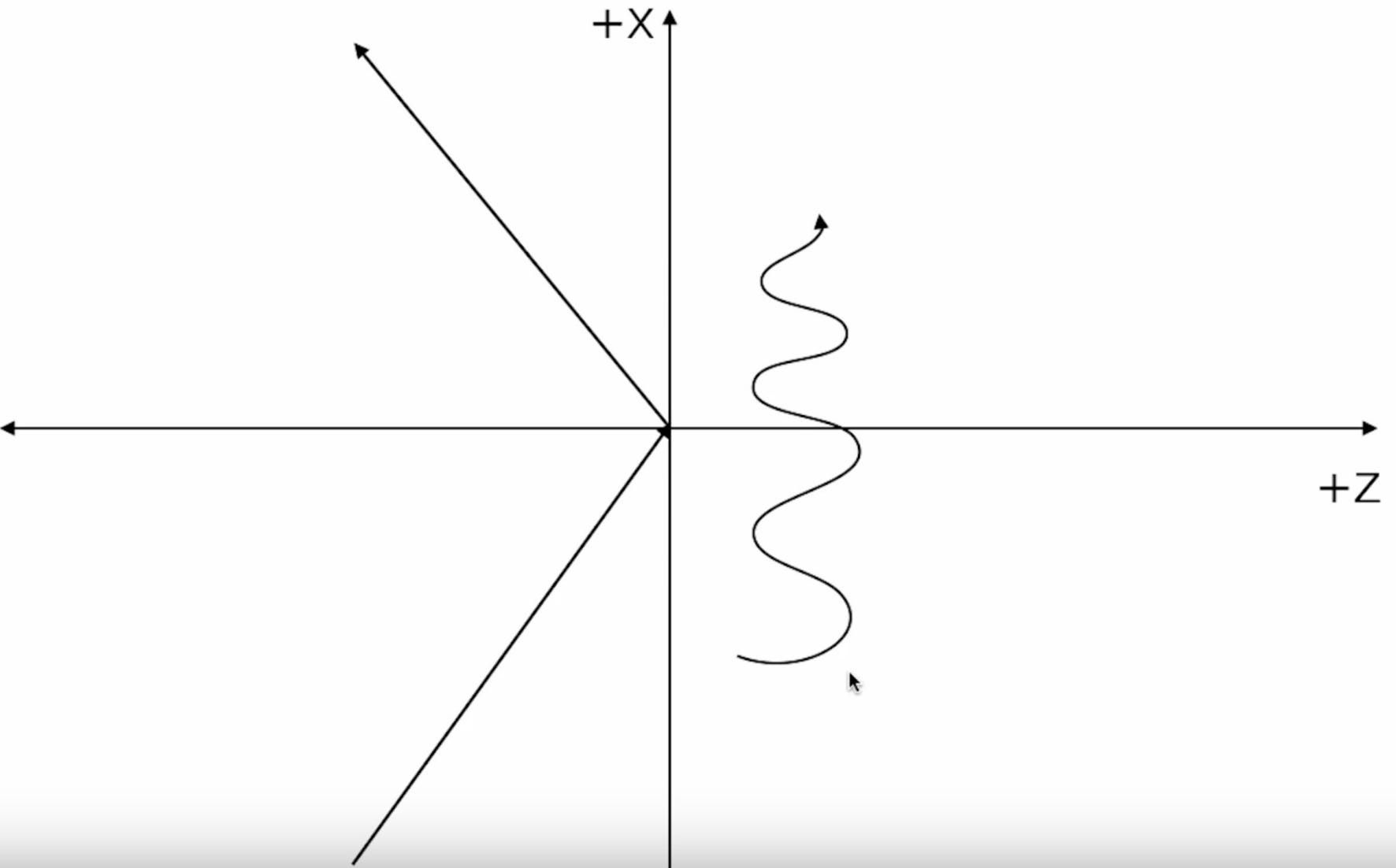
$$k_T \cos \theta_T = A i$$

$$\vec{E}_T = \vec{E}_{0T} e^{i(k_T \sin \theta_T) x} e^{i(k_T \cos \theta_T) z} e^{-i\omega t}$$
$$k_T \cos \theta_T = A i$$

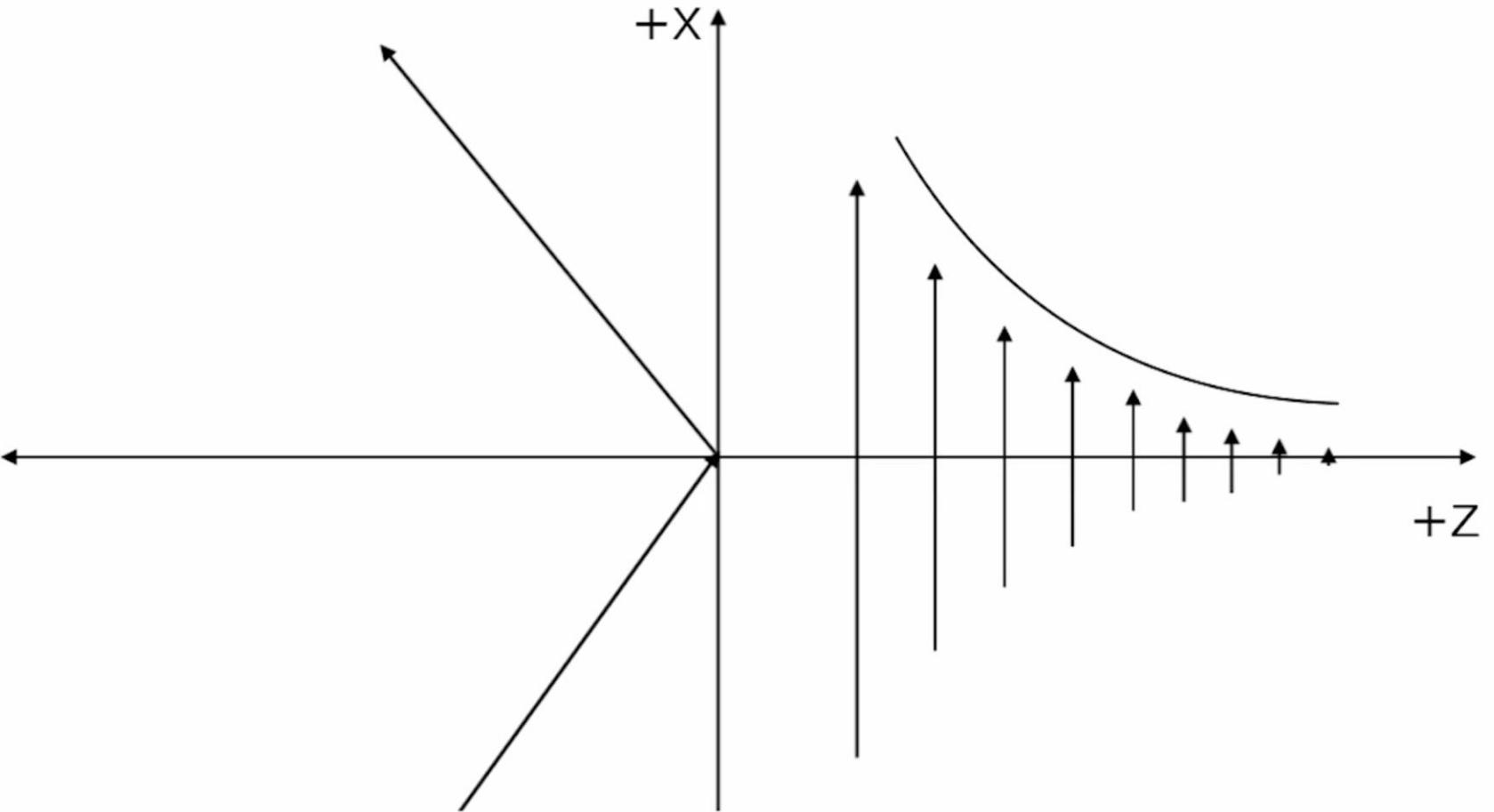
$$\vec{E}_T = \left(\vec{E}_{0T} e^{i(k_T \sin \theta_T) x} e^{-i\omega t} \right) e^{-A z}$$

$$\text{Re}(\vec{E}_T) = \vec{E}_{0T} \cos((k_T \sin \theta_T) x - \omega t) e^{-A z}$$

$$\operatorname{Re}(\vec{E}_T) = \vec{E}_{0T} \cos((k_T \sin \theta_T) x - \omega t) e^{-Az}$$



$$\operatorname{Re}(\vec{E}_T) = \vec{E}_{0T} \cos((k_T \sin \theta_T) x - \omega t) e^{-Az}$$



Evanescence Wave

Therefore

Evanescence Wave

It does not propagate as an electromagnetic wave

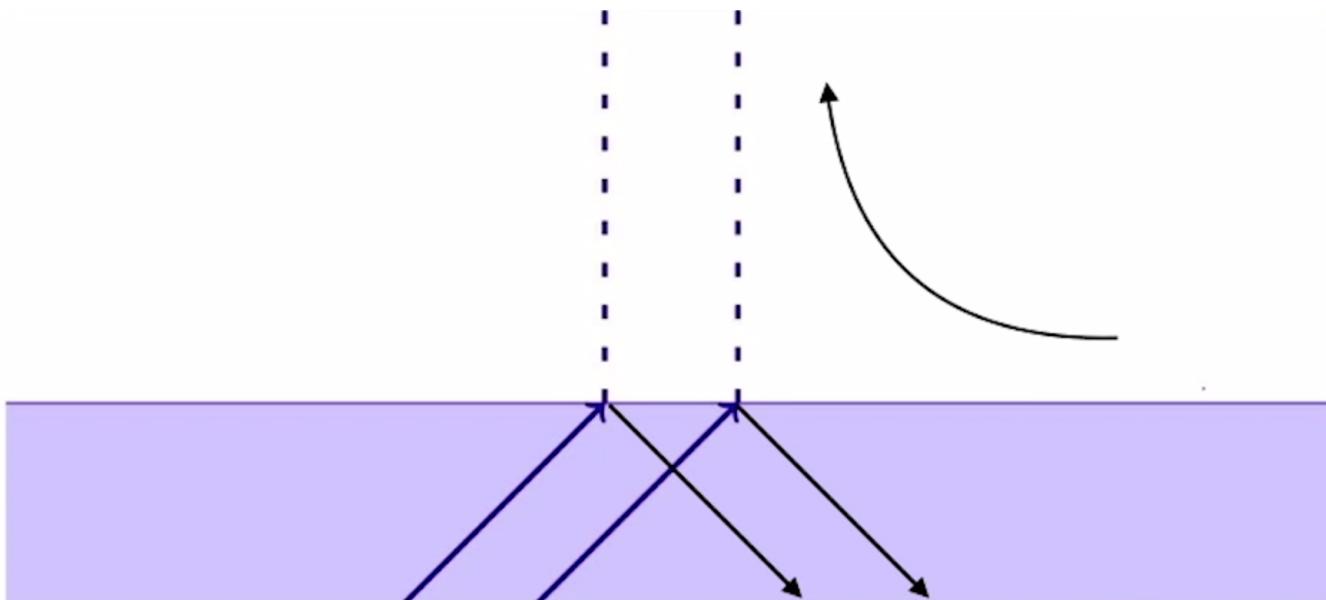
Its energy is concentrated spatially in the vicinity of the source, in this case, the boundary between the materials

There is no net energy flow . i.e. The Poynting Vector when averaged algebraically over a complete oscillation results in zero

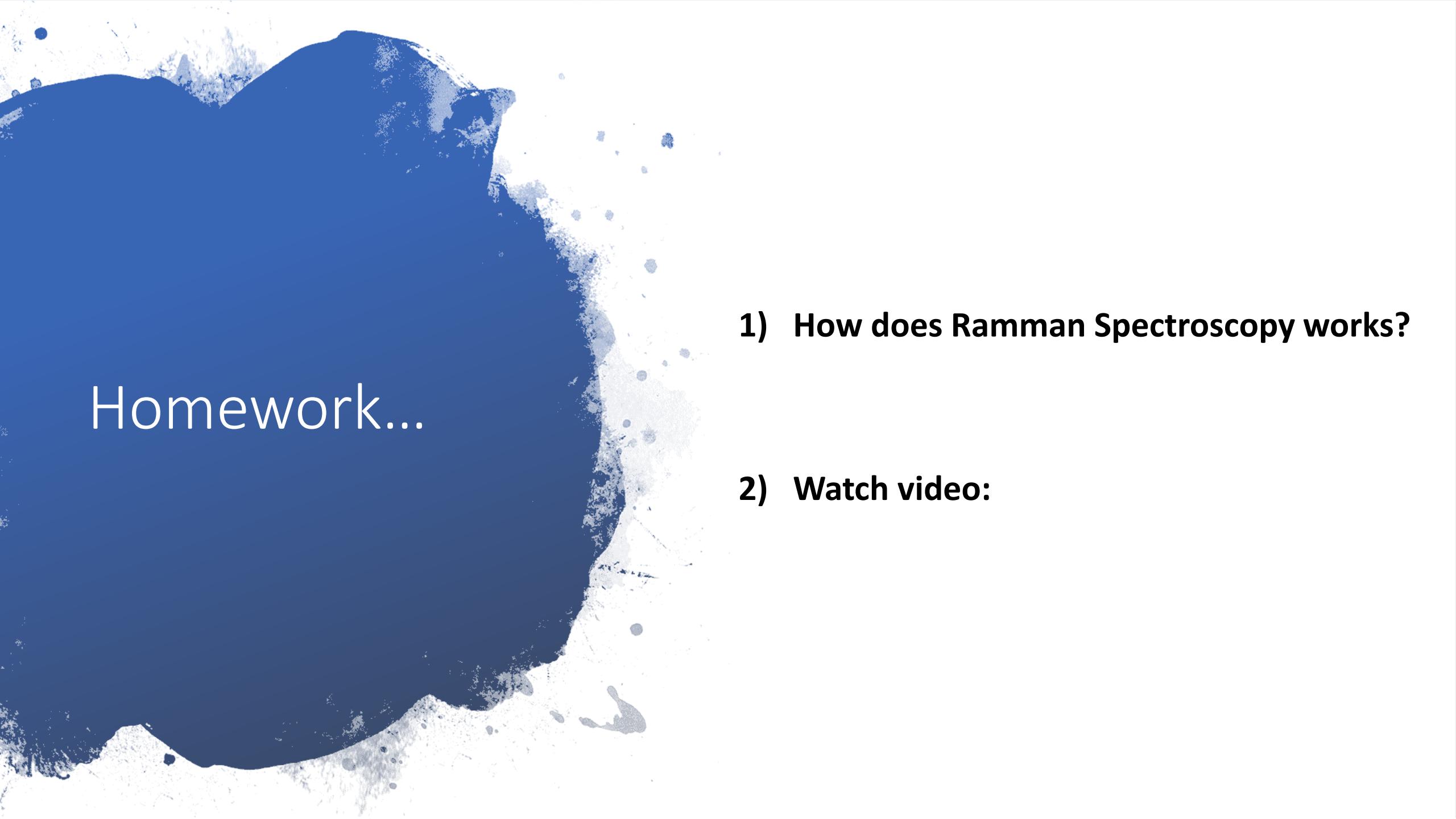
The physical explanation for the existence of the evanescent waves is that the electric and magnetic fields cannot be discontinuous at a boundary

... and if you
put another
glass

Detection



Frustrated Total Internal Reflection



Homework...

- 1) How does Raman Spectroscopy works?**

- 2) Watch video:**