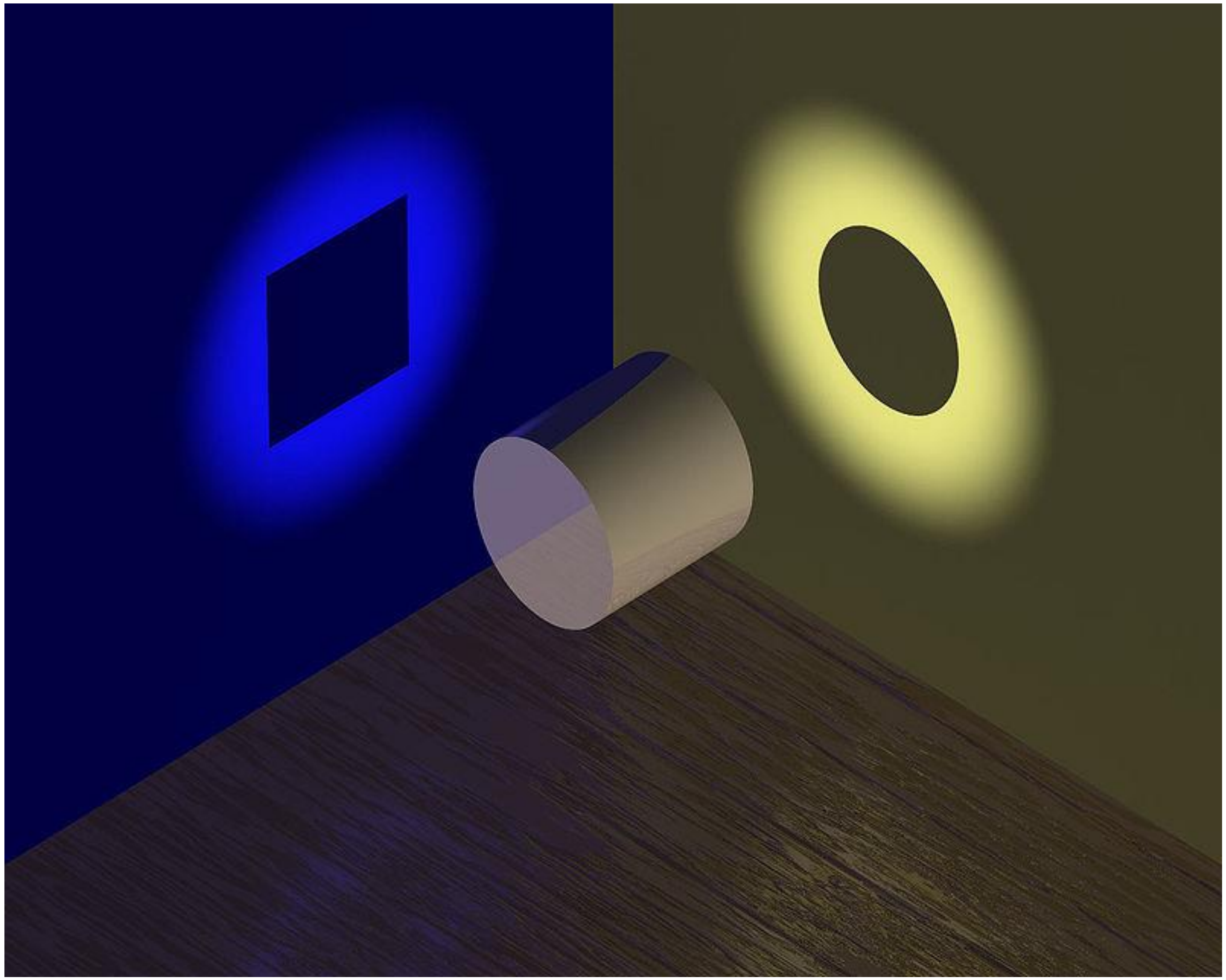
The Dao of Surface Plasmons
表面等离子共振之道

Stefan Franzen

NC State University

Two ways to look at nature …



… as a wave or a particle.

An ancient idea: Opposing views confront each other

"大曰逝，逝曰远，远曰反。"

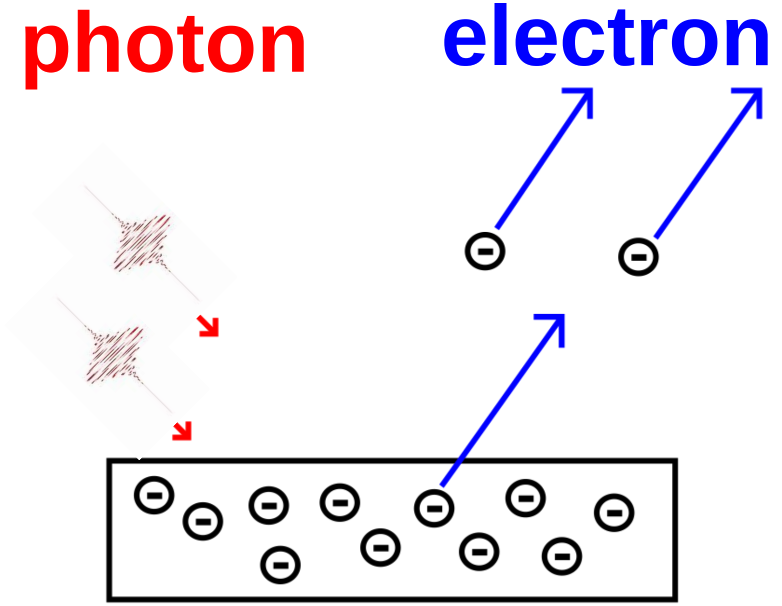
"反者道之动，弱者道之用"

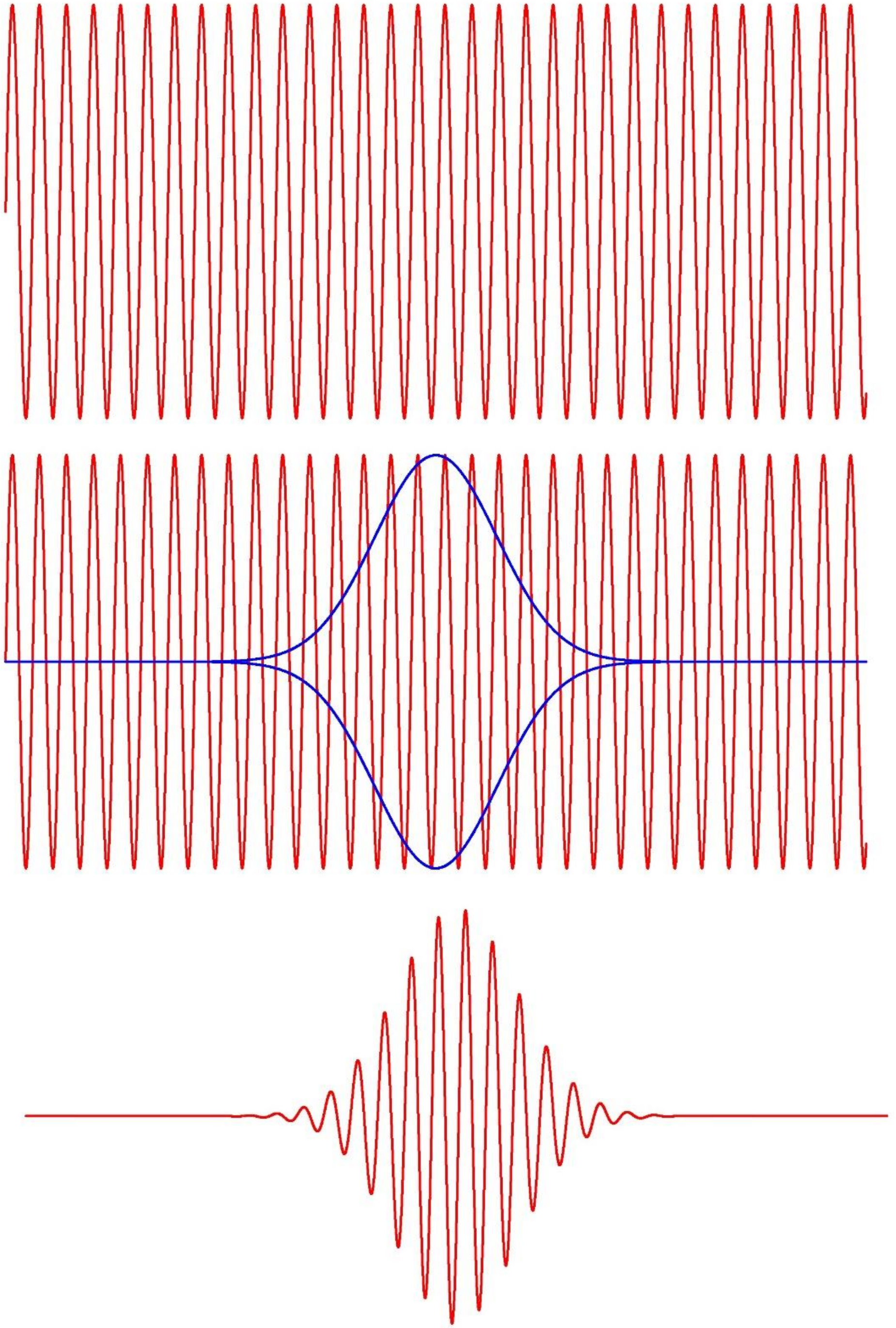
循环往复的运动变化，是道的运动。老子揭示出诸如长短、 高下、美丑、难易、有无、前后、祸福、刚柔、 损益、强弱、 大小、生死、智愚、胜败、巧拙、轻重、进退、攻守、荣辱等一系列矛盾.

This ancient way of looking at nature is analogous to the central feature of quantum mechanics, the wave-particle duality.

Wave-Particle Duality
波粒二象性

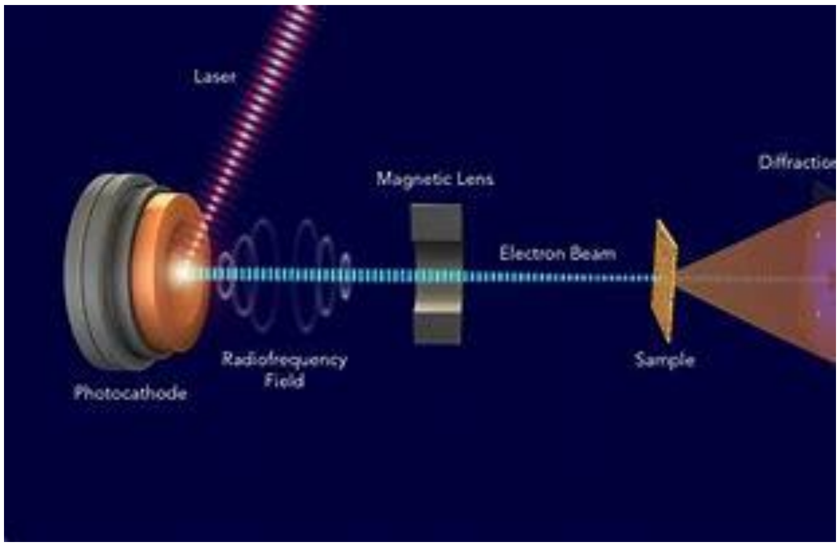
Photoelectric Effect
光电效应

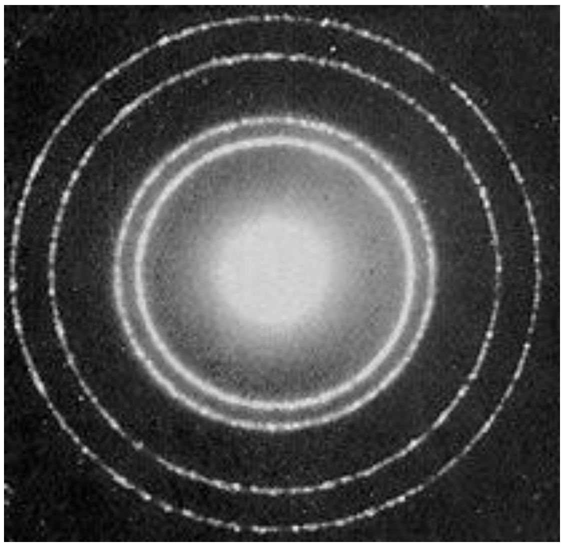




“对立统一”

If a wave acts like a particle, then a particle must act like a wave.   Example: electron diffraction





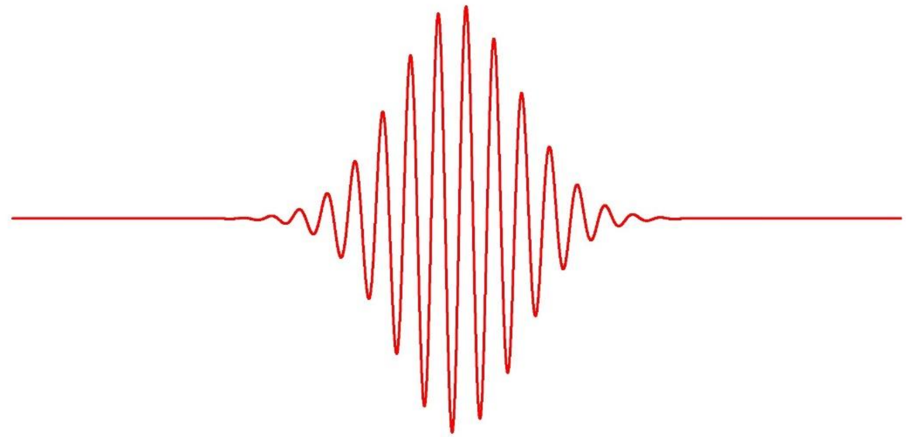
The yin and yang of complex numbers

复数的阴阳

Real

In phase

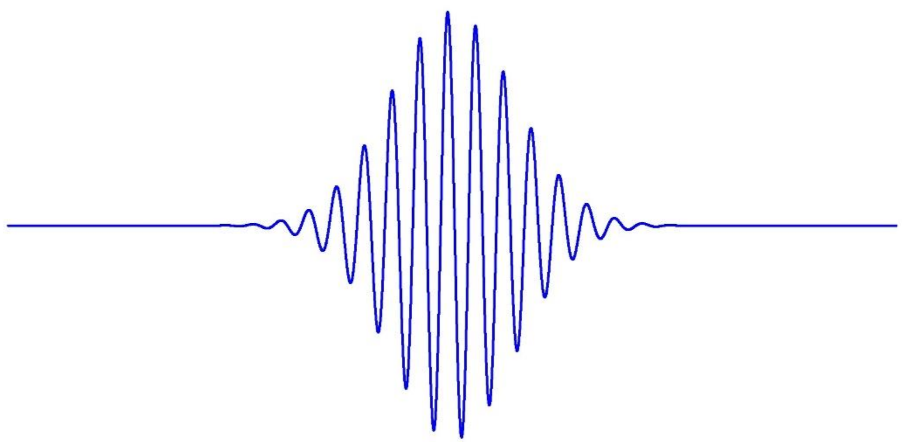
实部



Imaginary

Out of phase

虚部

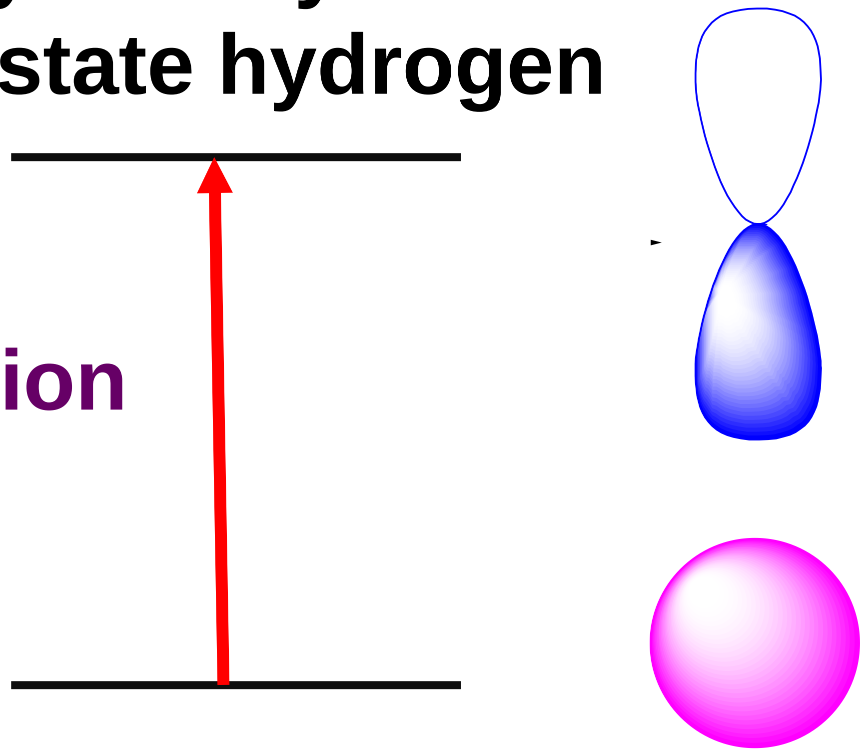


This applies to both waves and particles.

Absorption of light by hydrogen

Nodal symmetry of excited state hydrogen

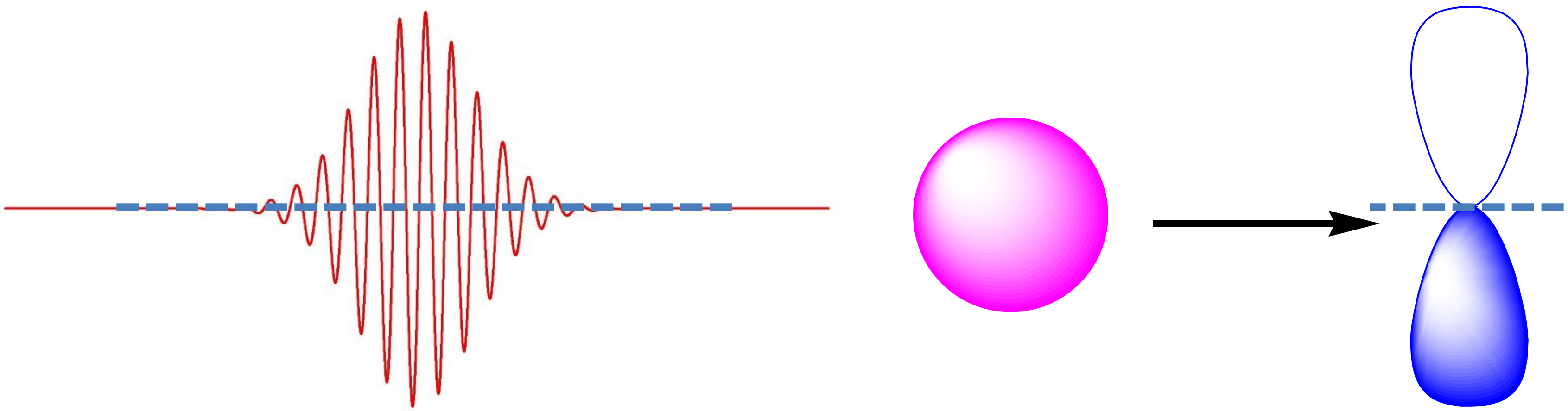
Conservation Of Energy



Spherical symmetry of ground state hydrogen

Symmetry breaking by electromagnetic wave

Conservation of angular momentum

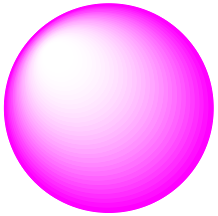


	Photon	1s	np
Nodes	1	0	1
Ang mom	$\ell = 1$	$\ell = 0$	$\ell = 1$

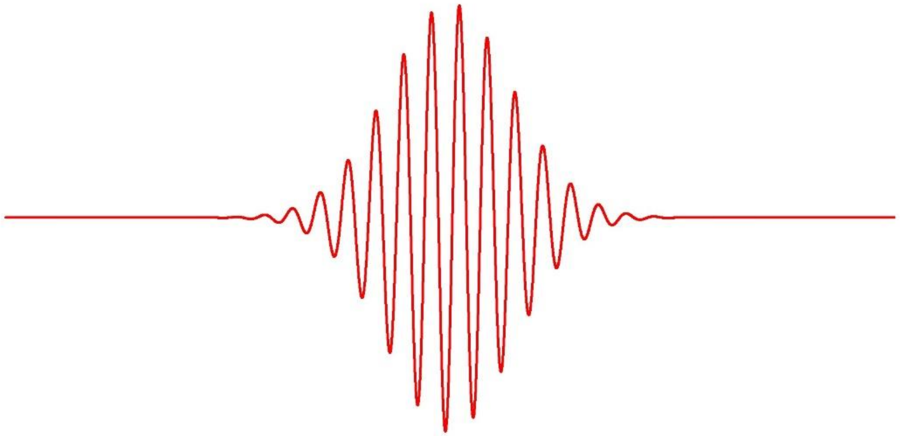
In-phase oscillation breaks the symmetry

Nodes

0



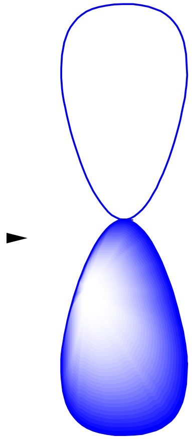
1



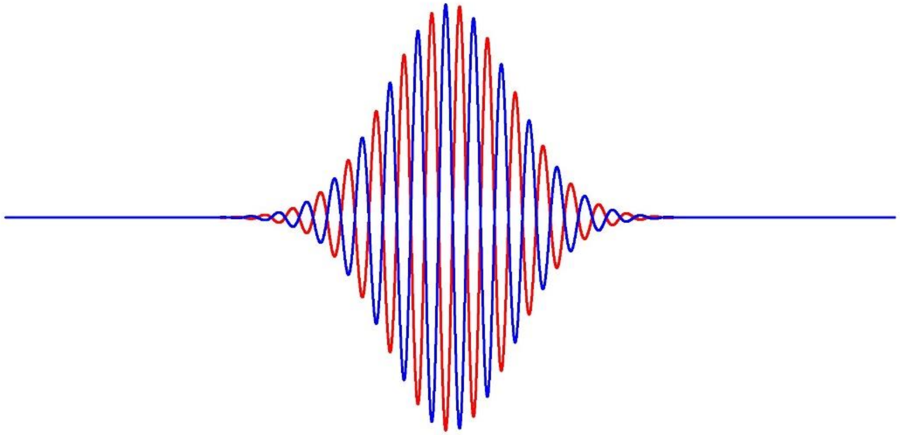
Out-of-phase oscillation transfers momentum

Nodes

1



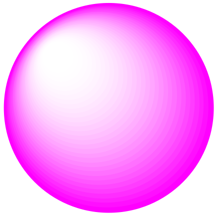
0



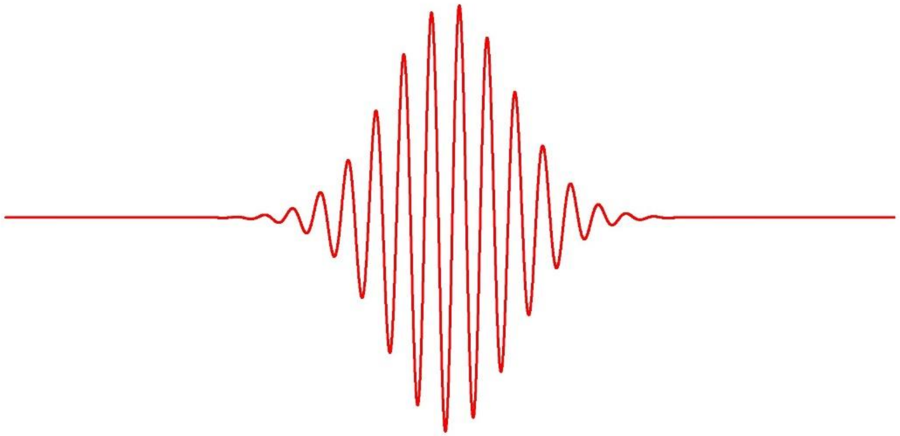
Net change from one photon and one atom….

Nodes

0



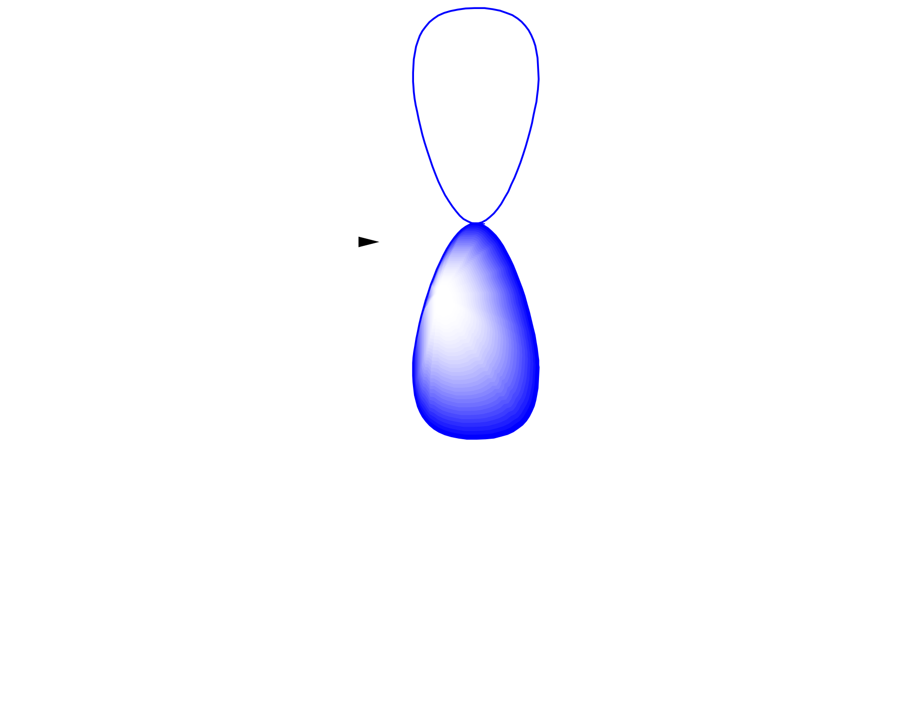
1



…to an excited state atom and no photon.

Nodes

1

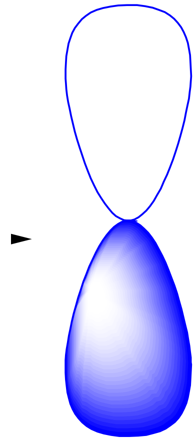


0

“对立统一”

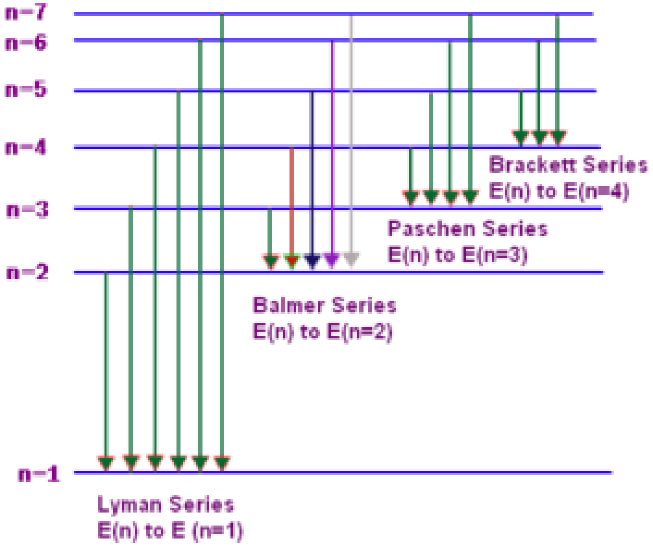
Nodes

1



0

We can predict the H atom absorption and emission lines



Hydrogen absorption spectrum

Hydrogen emission spectrum

道可道非常道

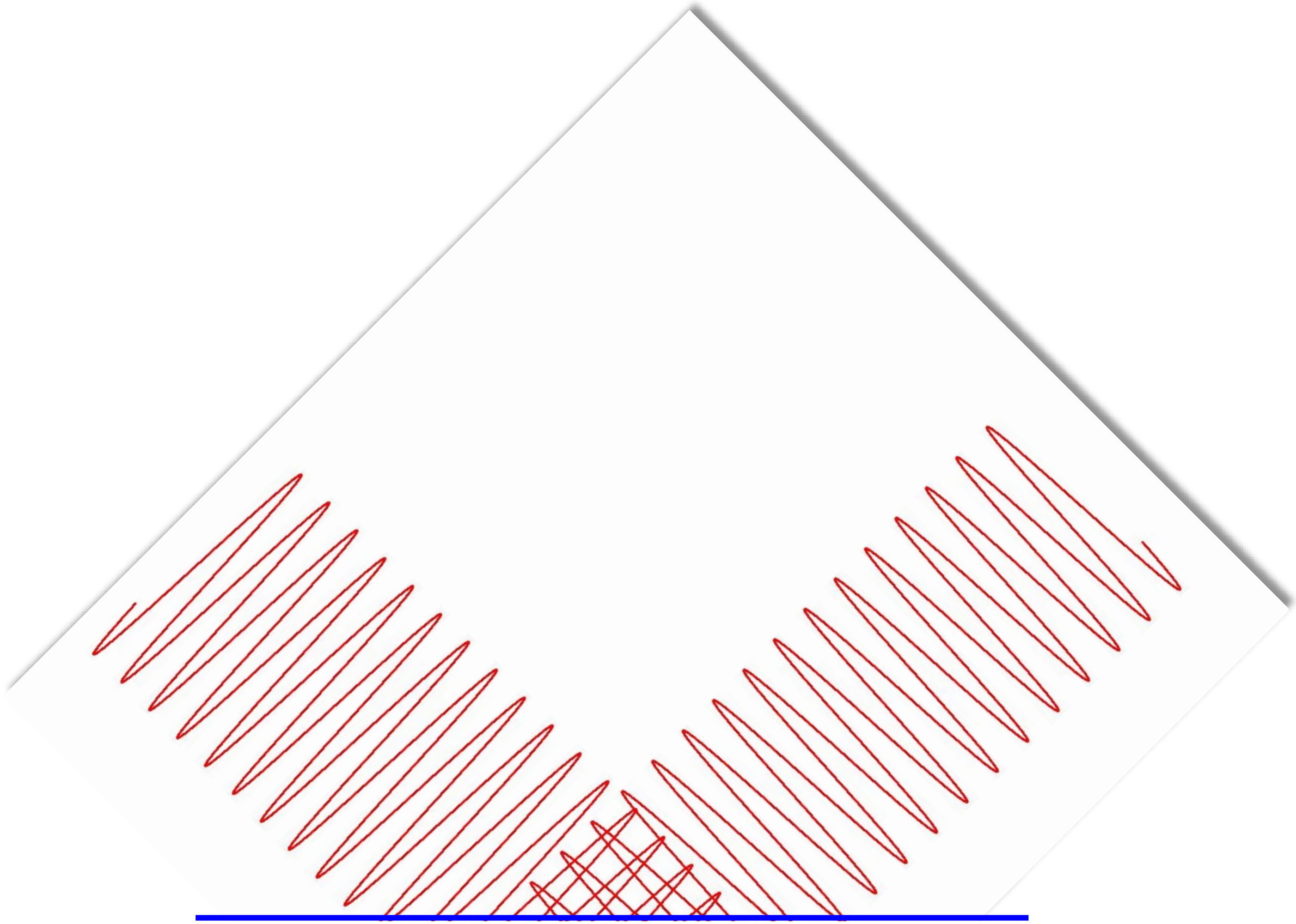
The way to understand nature is to realize the limitations of our individual viewpoints, but then to look for unifying principles or concepts.

Our goal is to understand surface plasmon resonance using an optical “way”. We use an intuitive picture rather than mathematics to describe the phenomenon.

人法地，地法天，天法道，道法大自然。

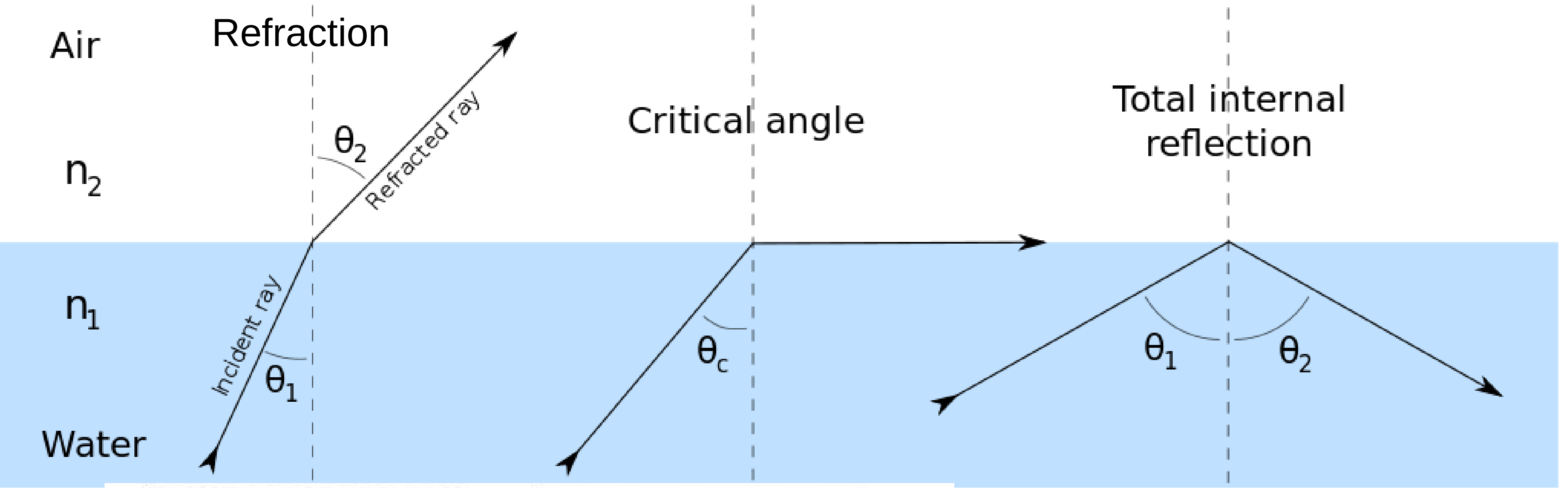
We can obtain understanding directly from nature.

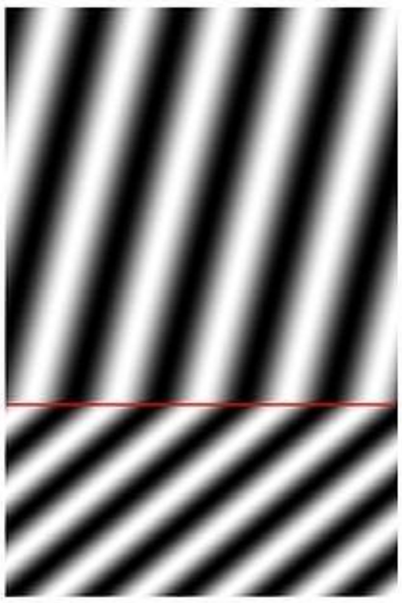
Reflection and refraction preserve phase

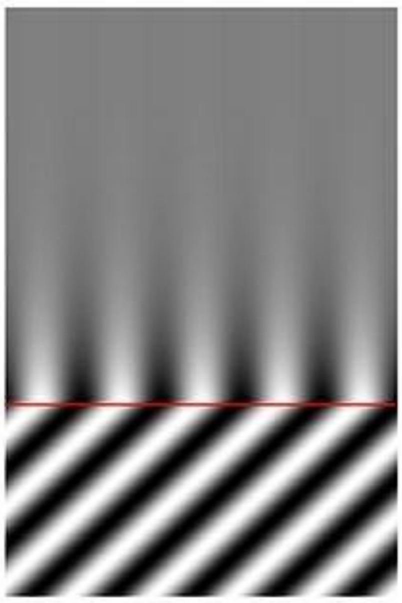


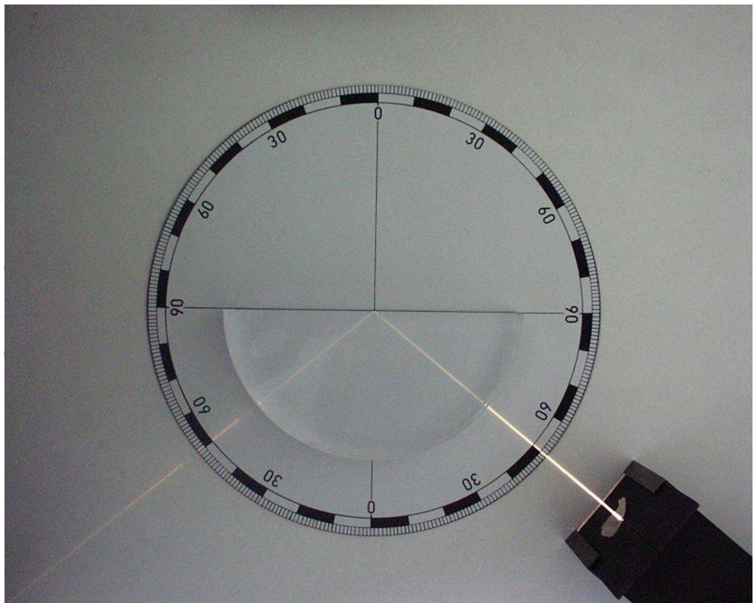
The induced field must be opposite in sign in a conducting medium. Therefore, the dielectric function is negative.

Total internal reflection 全内反射





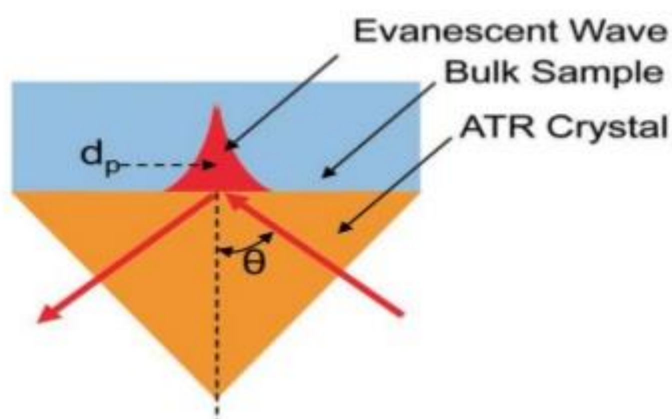




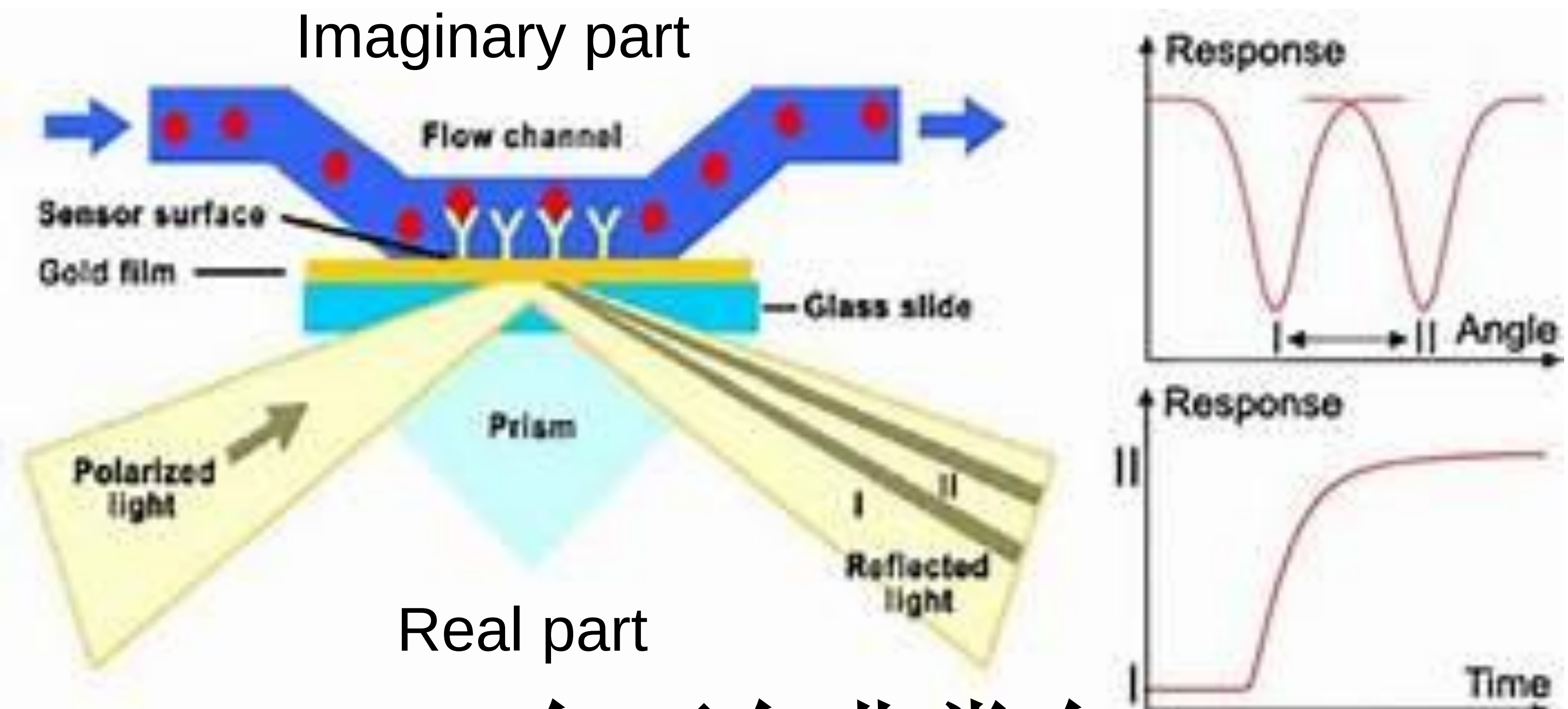
Attenuated total reflection (ATR) Fourier transform infrared (FTIR)

Imaginary part

Real part



Surface plasmon resonance (SPR)
is a special case of ATR spectroscopy



名可名非常名

The name we give to something determines "what it is", yet there are many possible ways to name something. There are many ways to observe a natural phenomenon.

A plasmon is a collective oscillation of conduction electrons

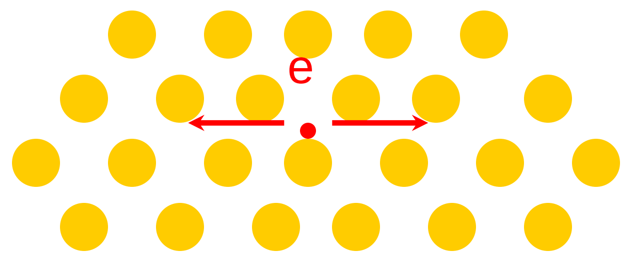
等离子体共振是传导电子的集体振荡

表面等离共振可以说是金属的属性（比如说金或者银）但是基本上是无论任何导体的属性。

Force + Friction = Driving term

Electron motion

Conductor

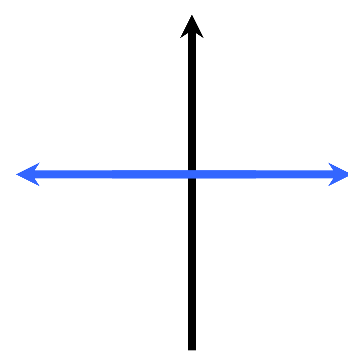


导体

Dipole

Polarization (dipole per unit volume)

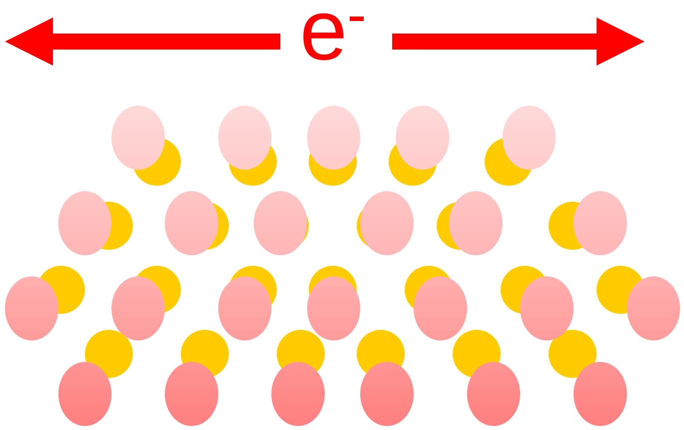
Susceptibility: measure of polarization in an electric field



Electric vector of light

Conductor 导体

Natural frequency of electronic oscillation



Conductor 导体

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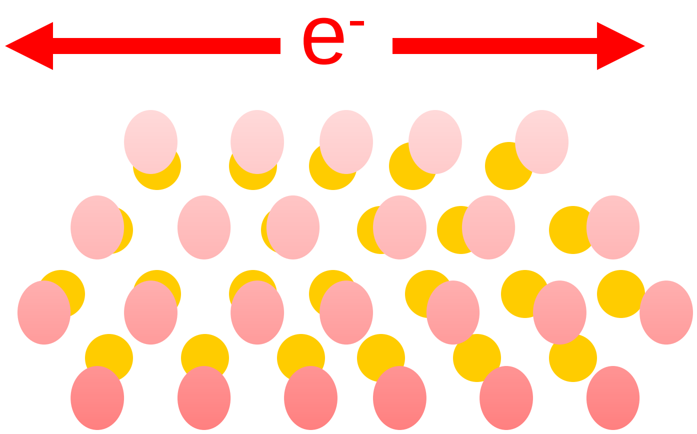

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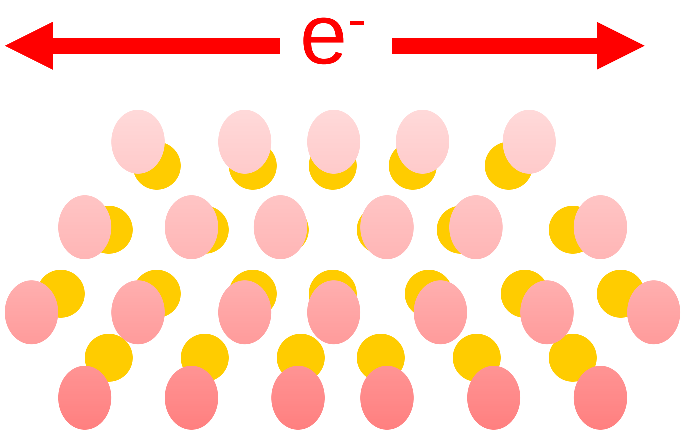

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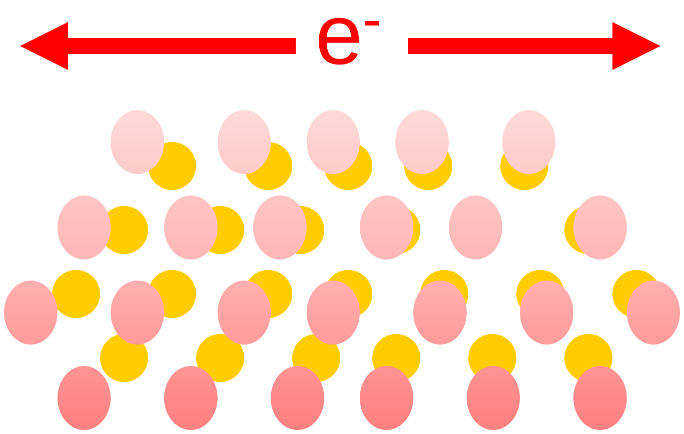

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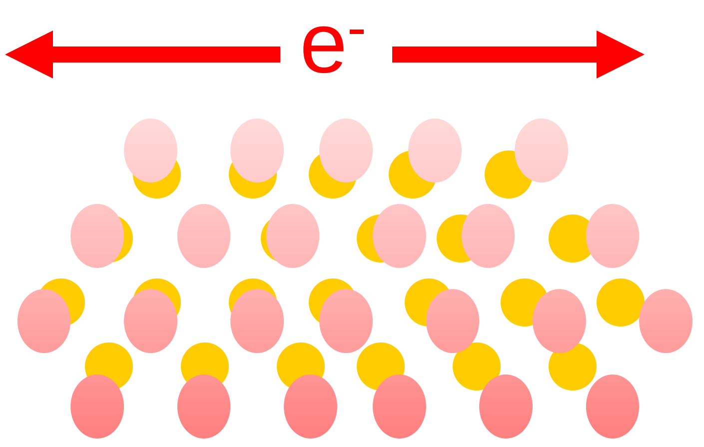
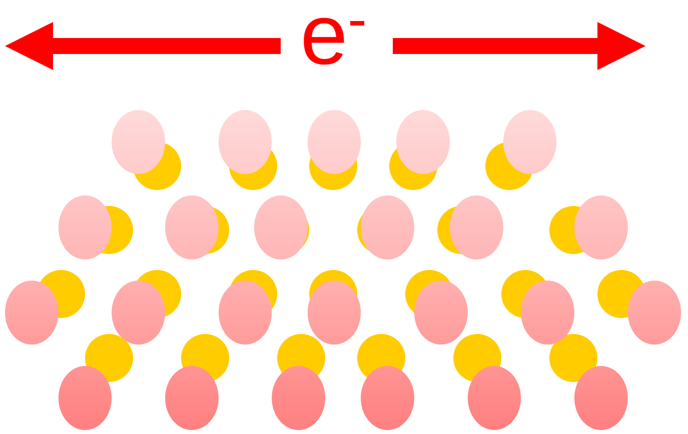


Dipole moment →

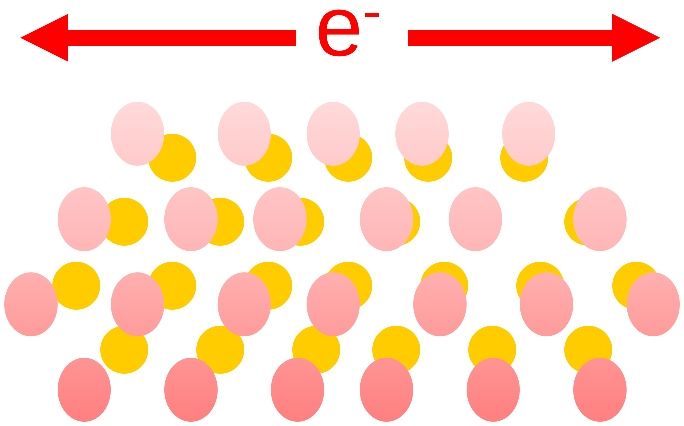
Conductor 导体

Natural frequency of electronic oscillation



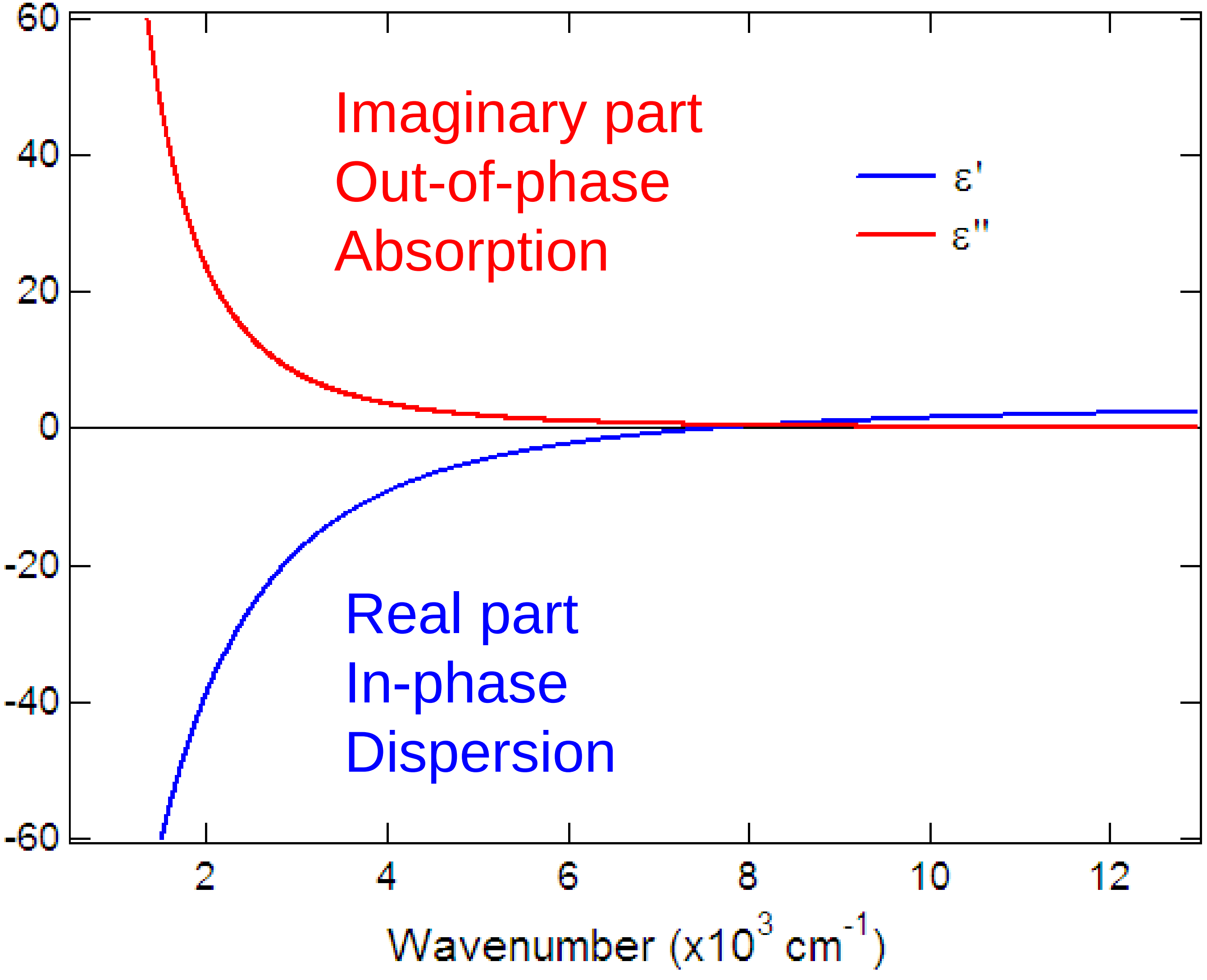
Conductor 导体

Natural frequency of electronic oscillation

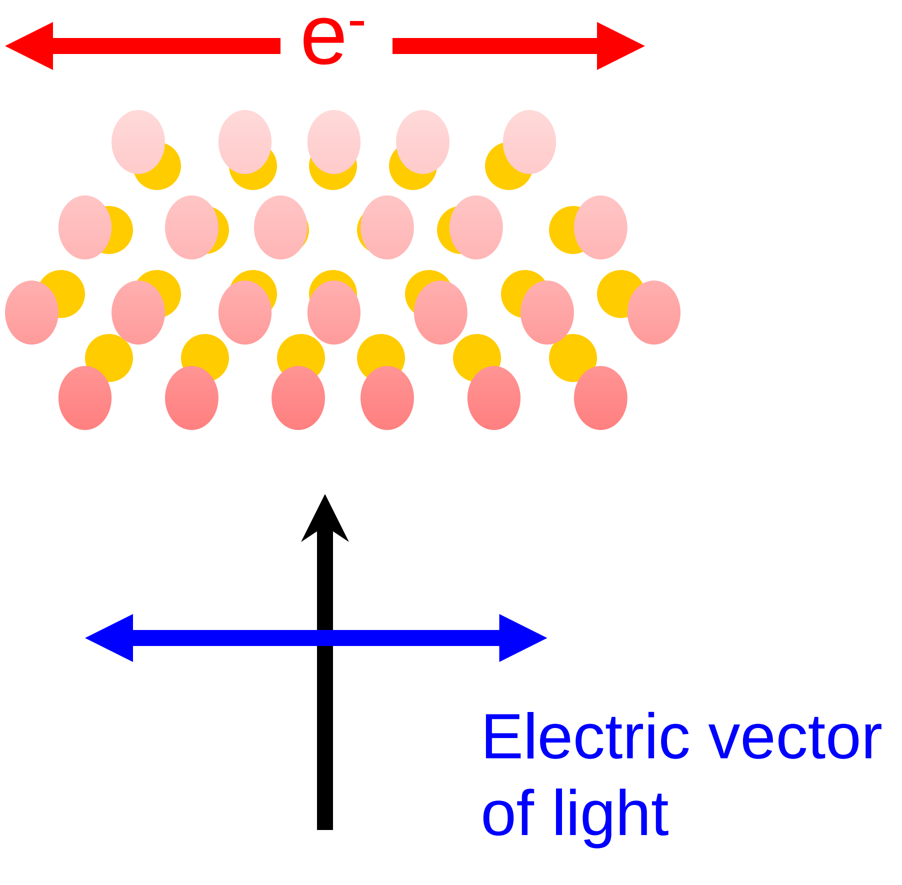


Dipole moment

Dielectric functions for a free electron conductor



Electric field driving oscillation at the natural frequency



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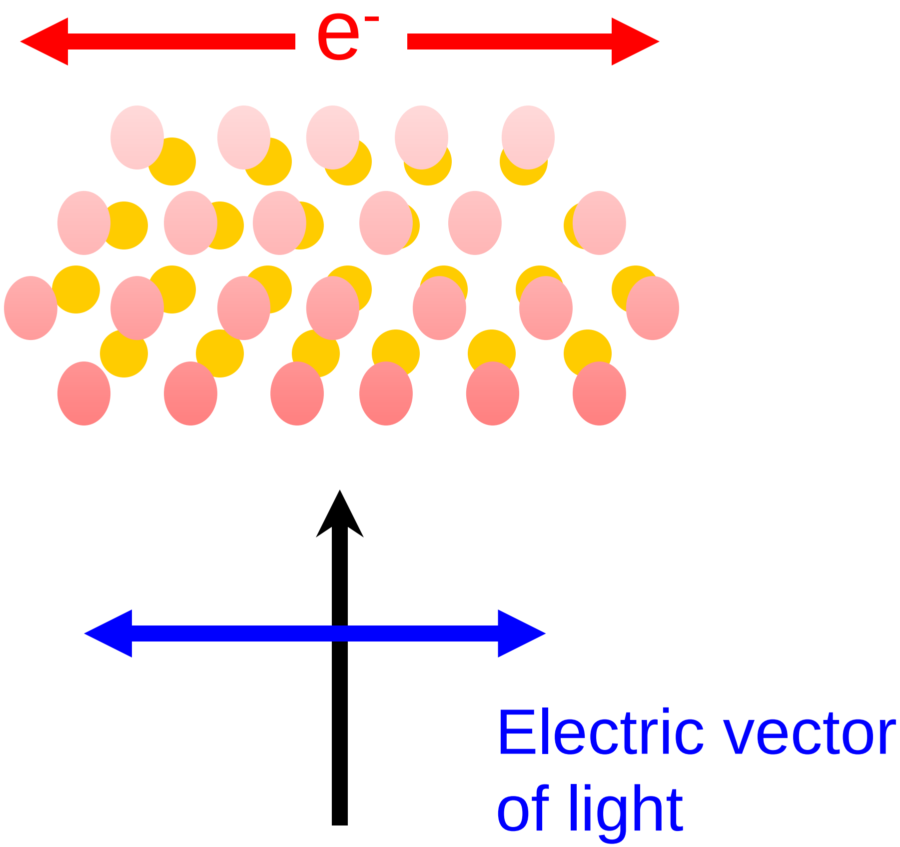

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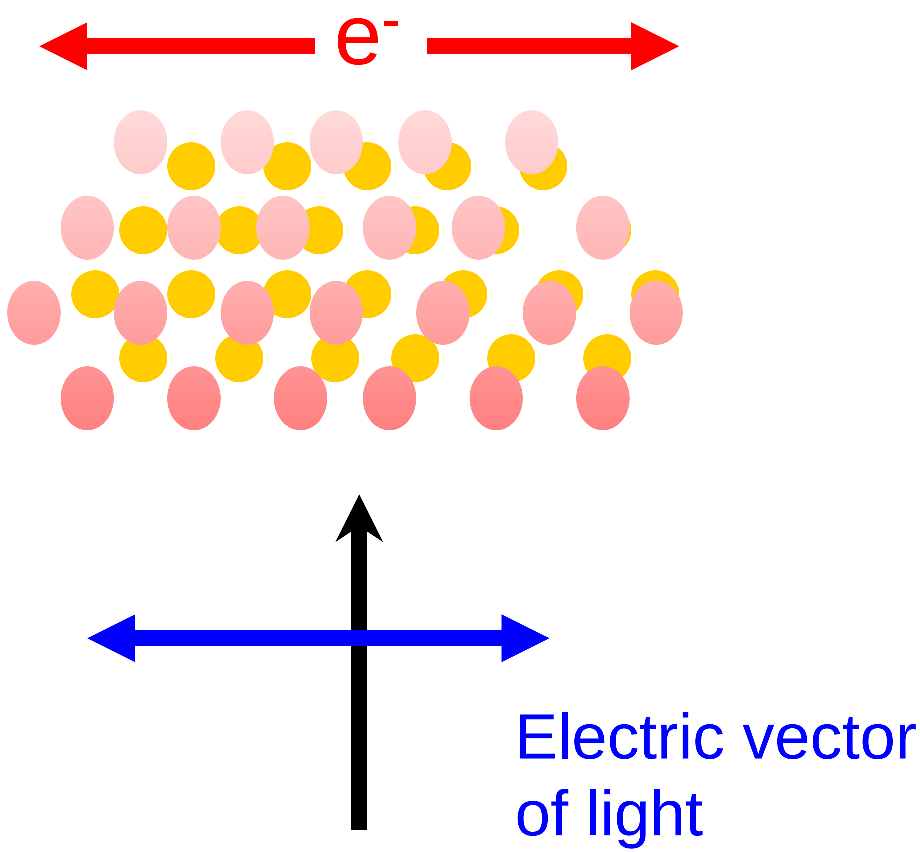

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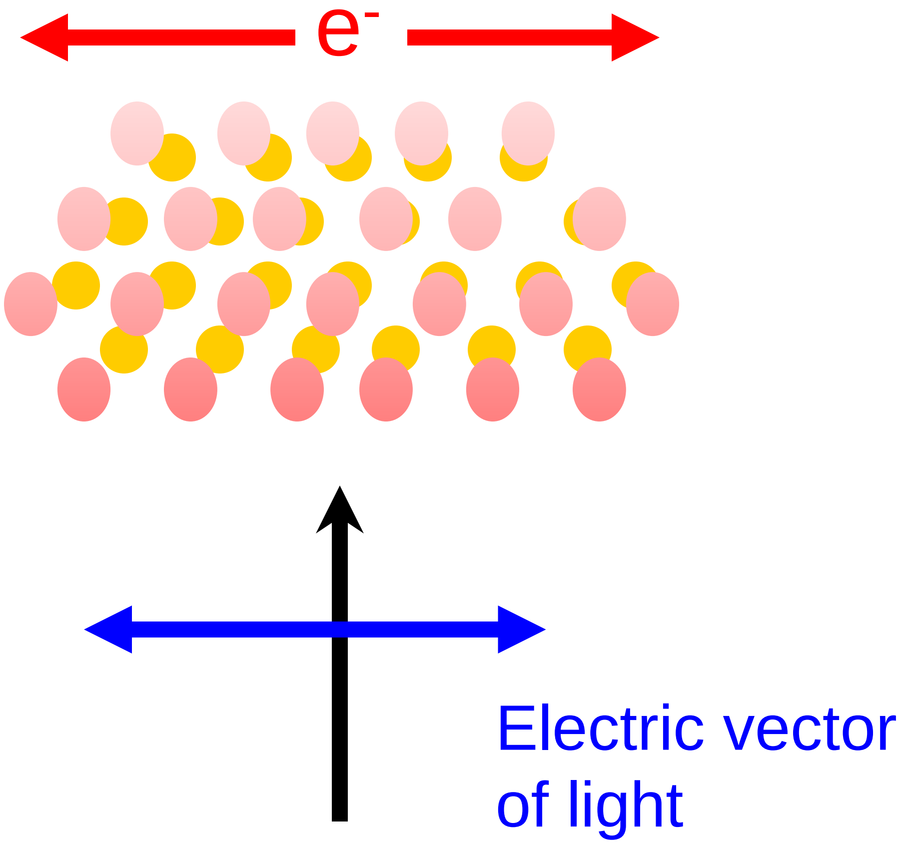

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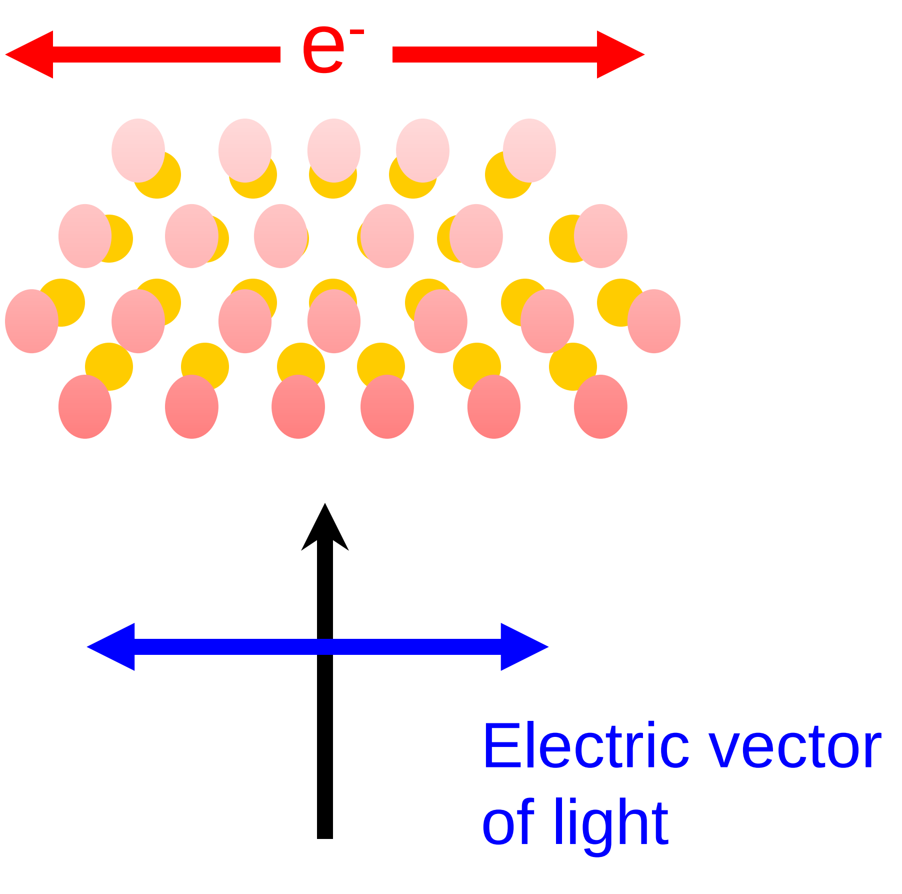

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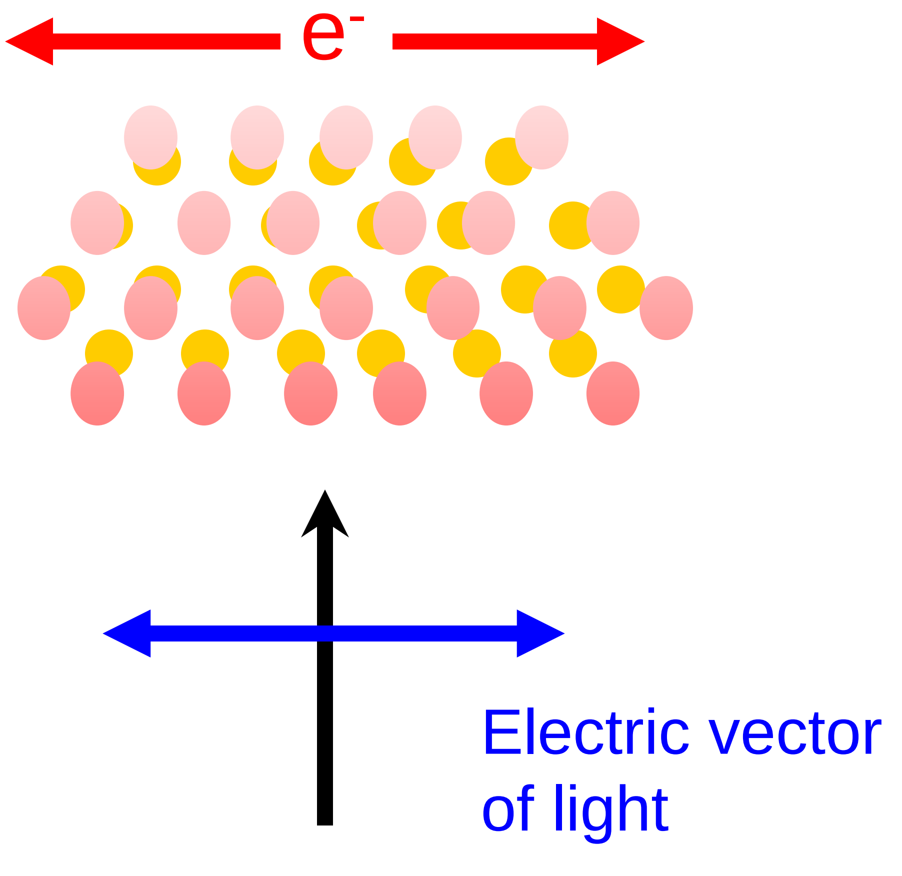

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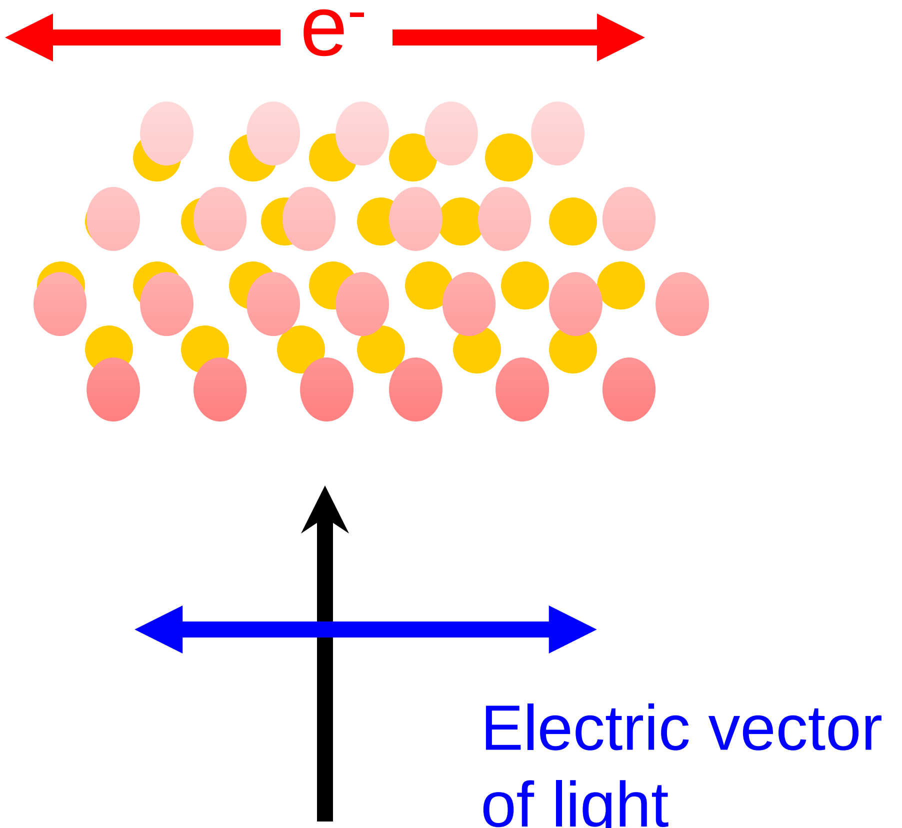

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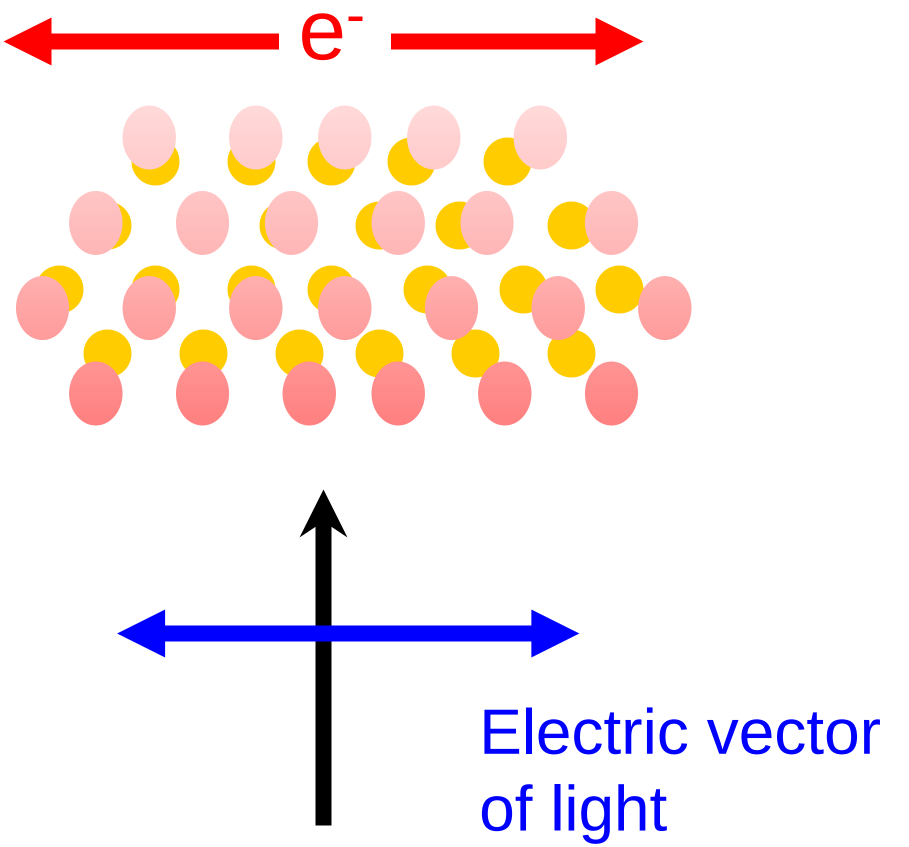

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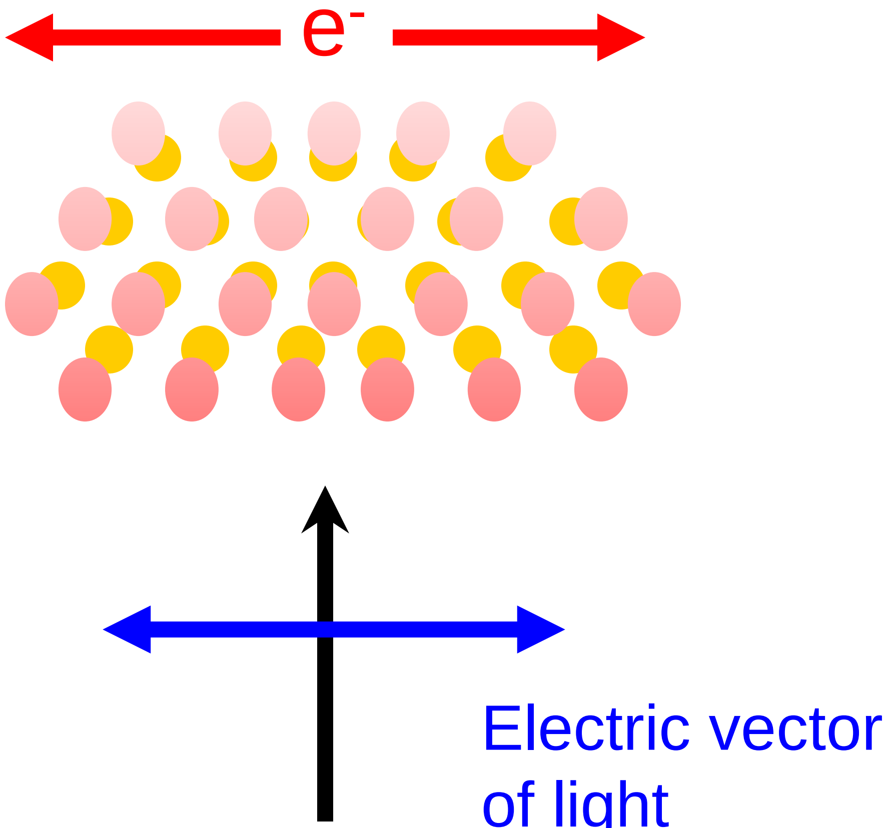
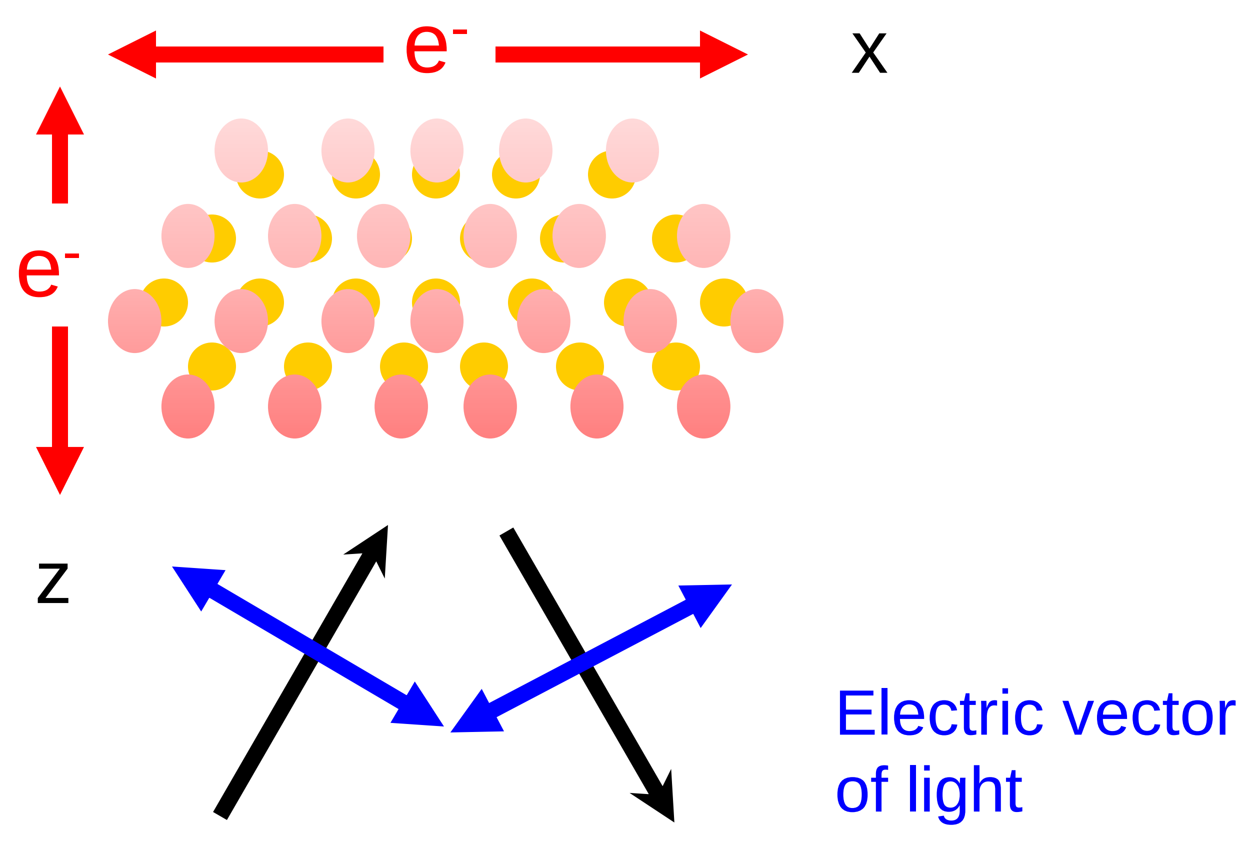


Electric field driving oscillation at the any frequency lower than the natural frequency = reflection



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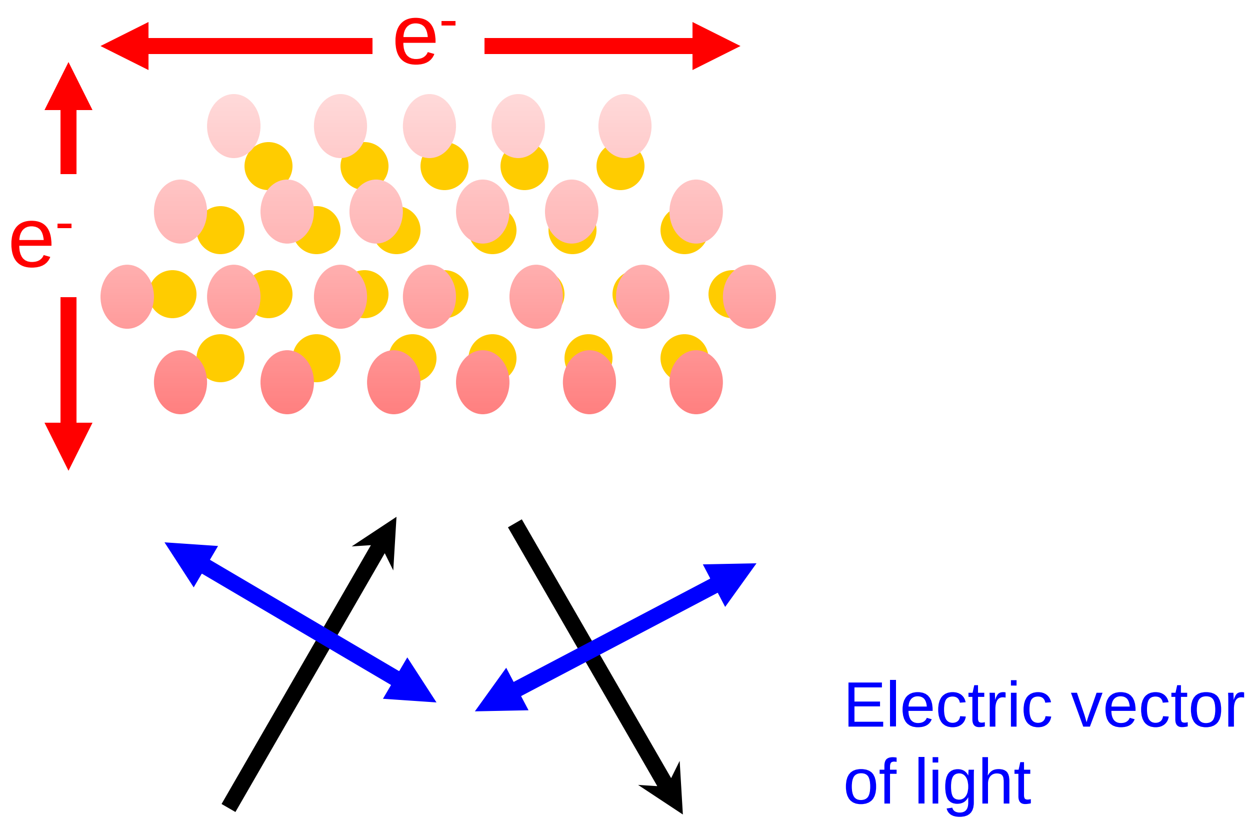

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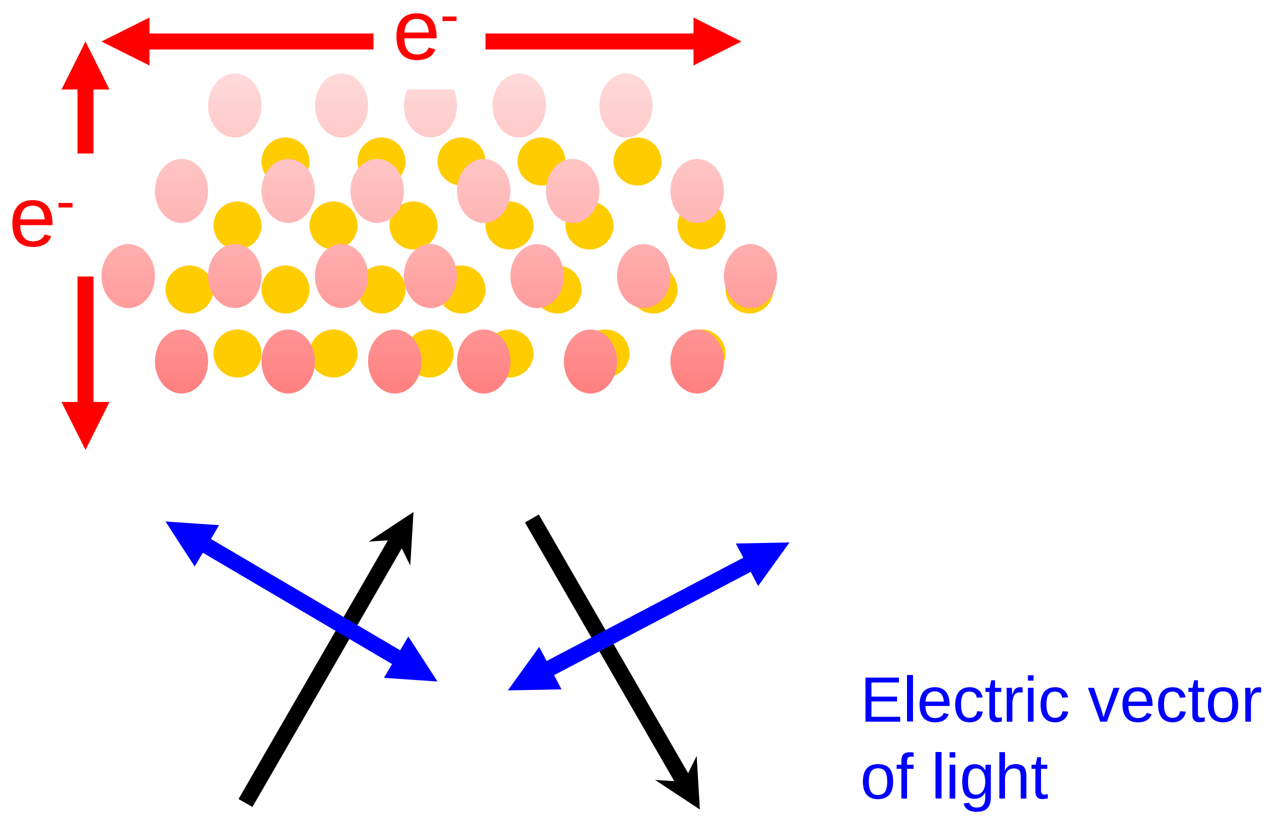
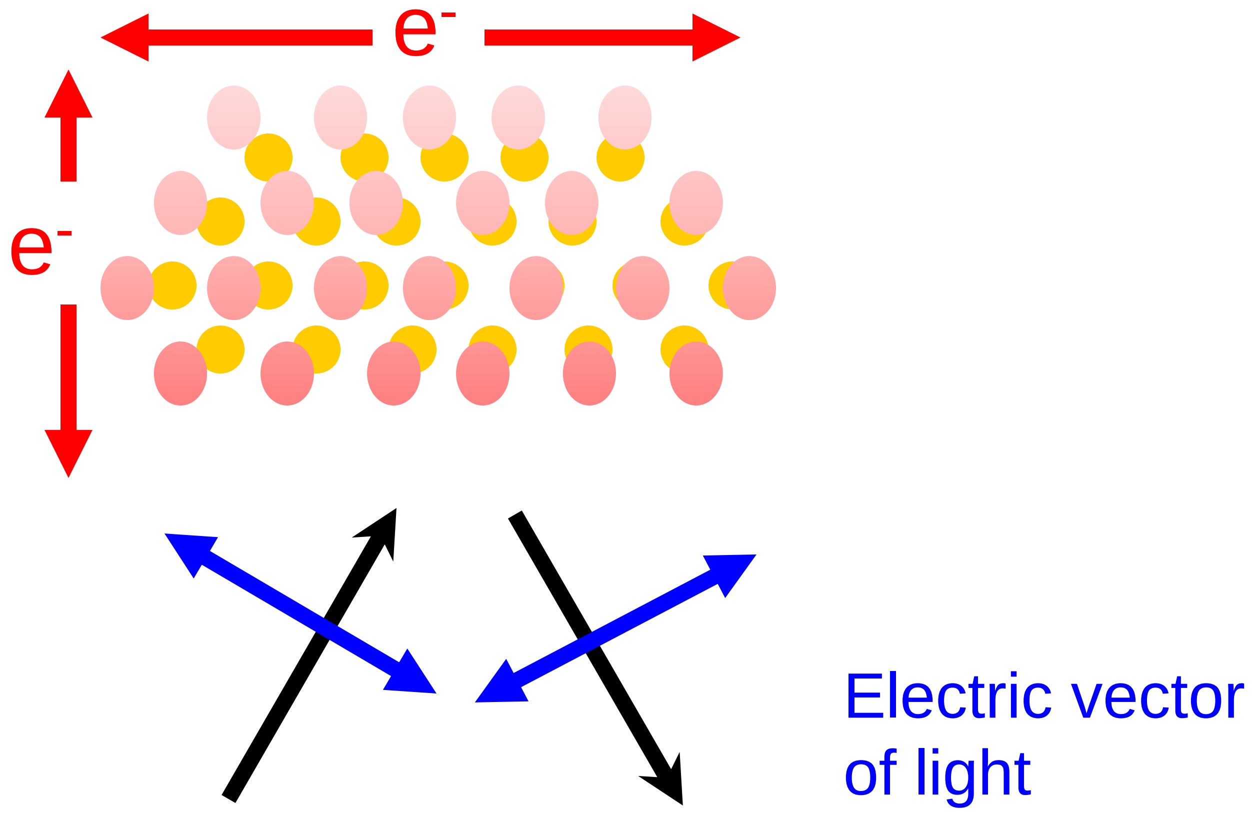
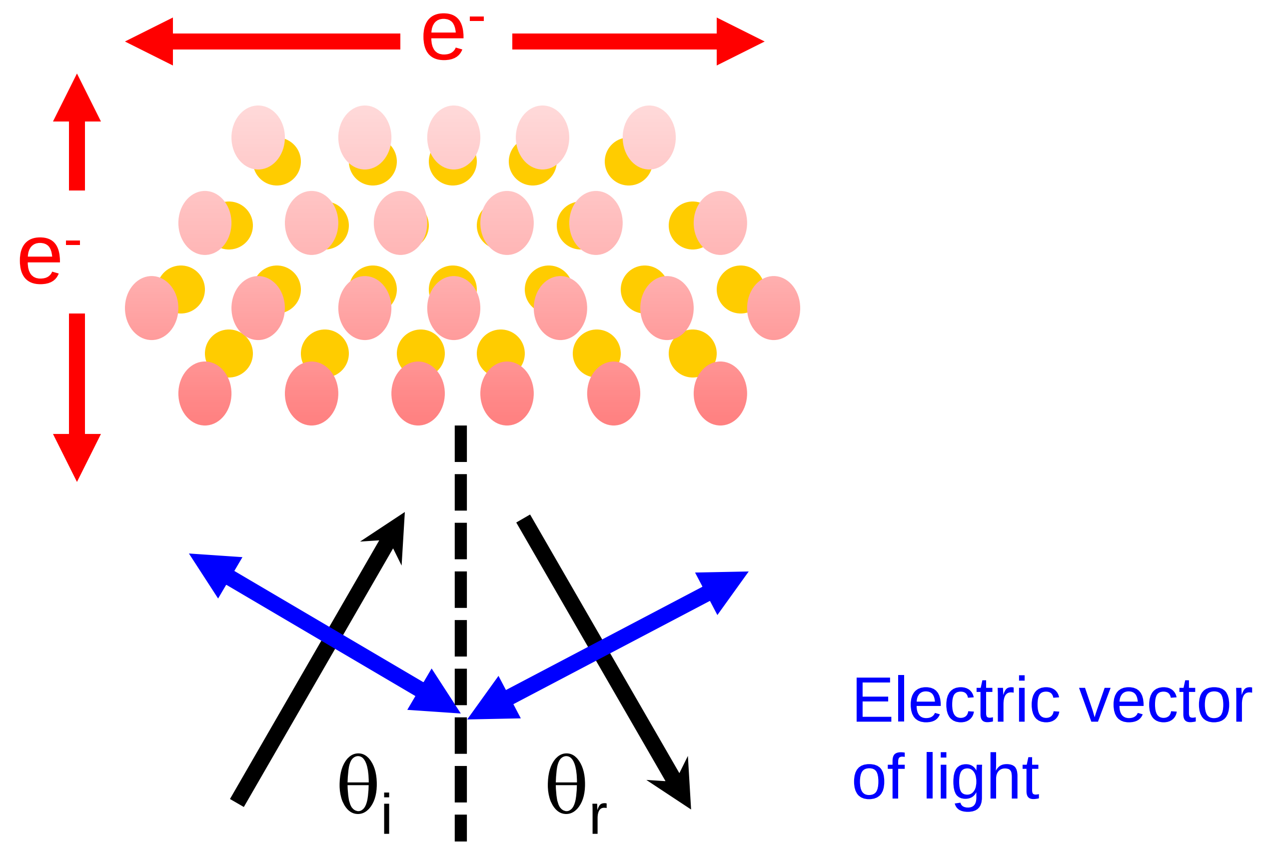


Electric field driving oscillation at the any frequency lower than the natural frequency = reflection

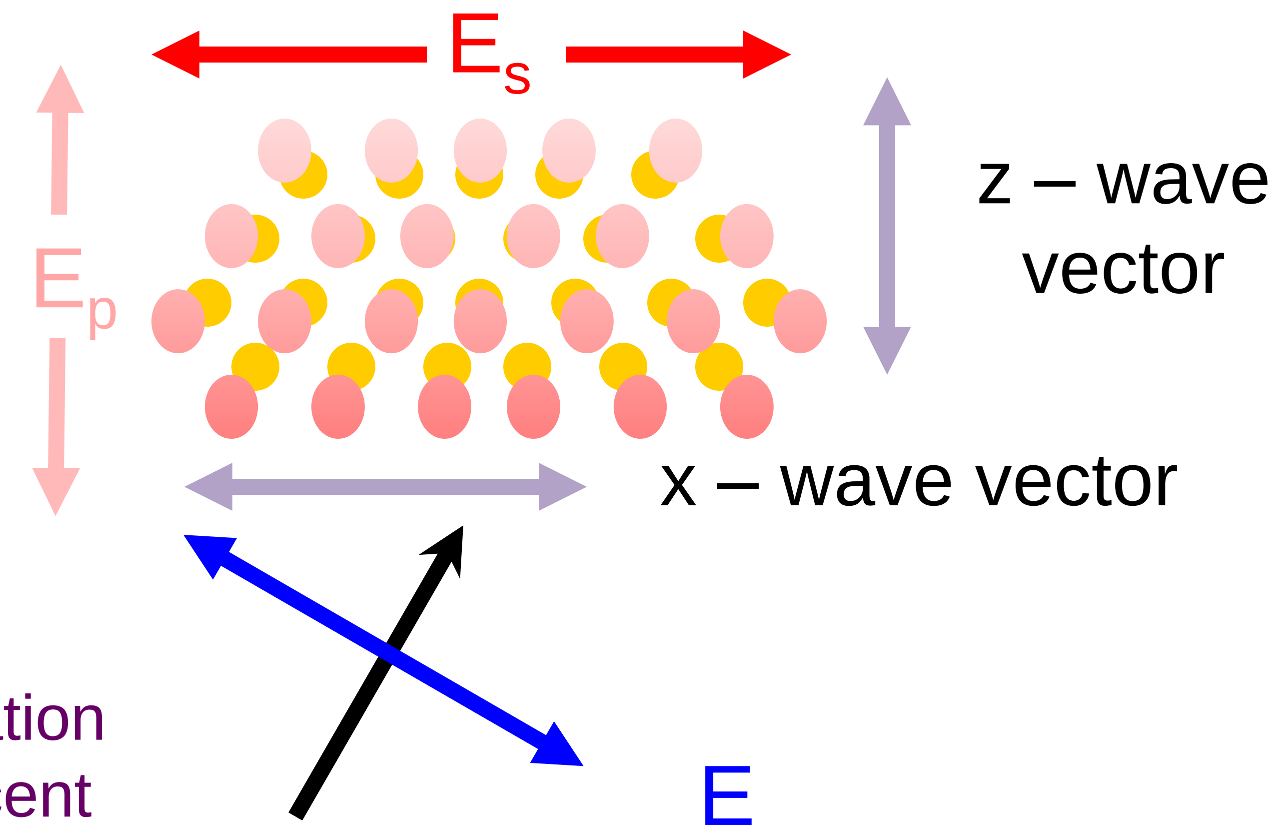


Electric field driving oscillation at the any frequency lower than the natural frequency = reflection



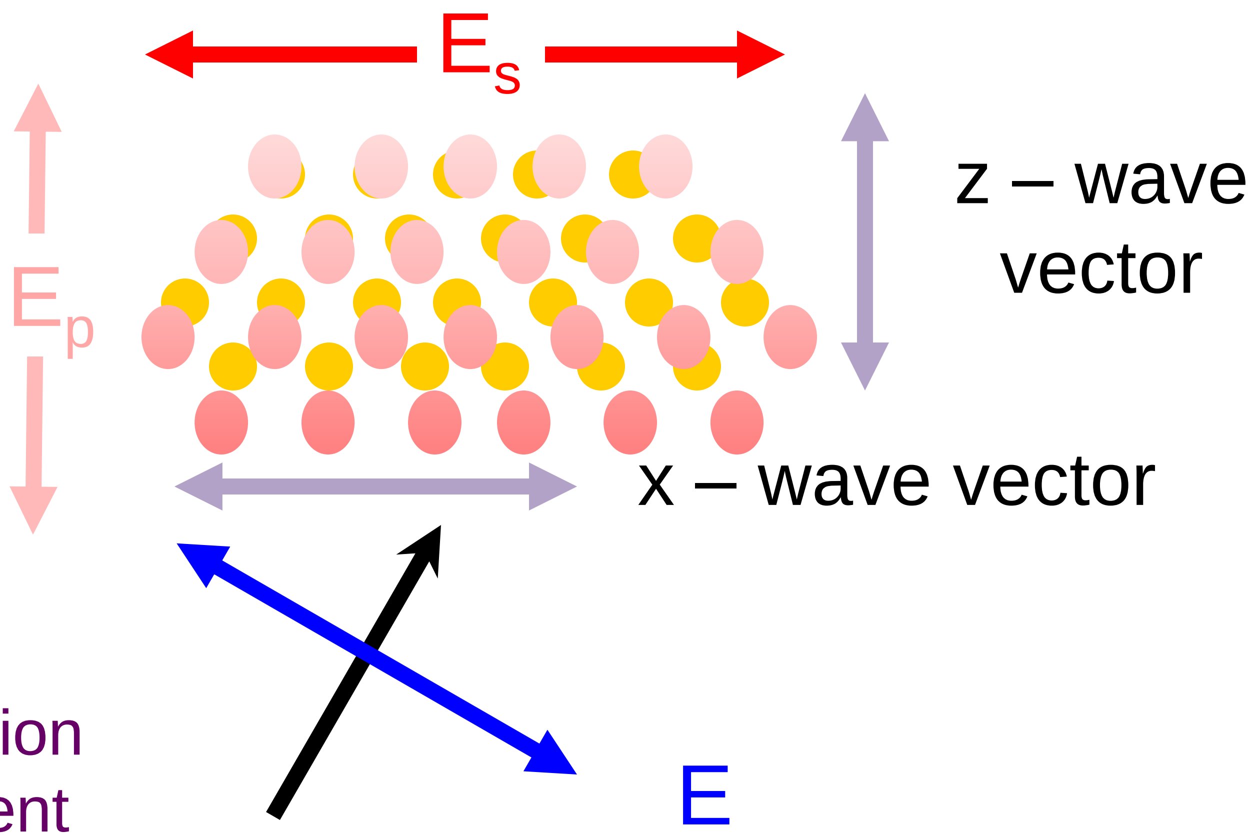
This oscillation gives rise to reflection by conductors.

Electric field driving oscillation at the natural frequency and matched wave vector



The z-polarization is an evanescent save (like ATR)

Electric field driving oscillation at the natural frequency and matched wave vector



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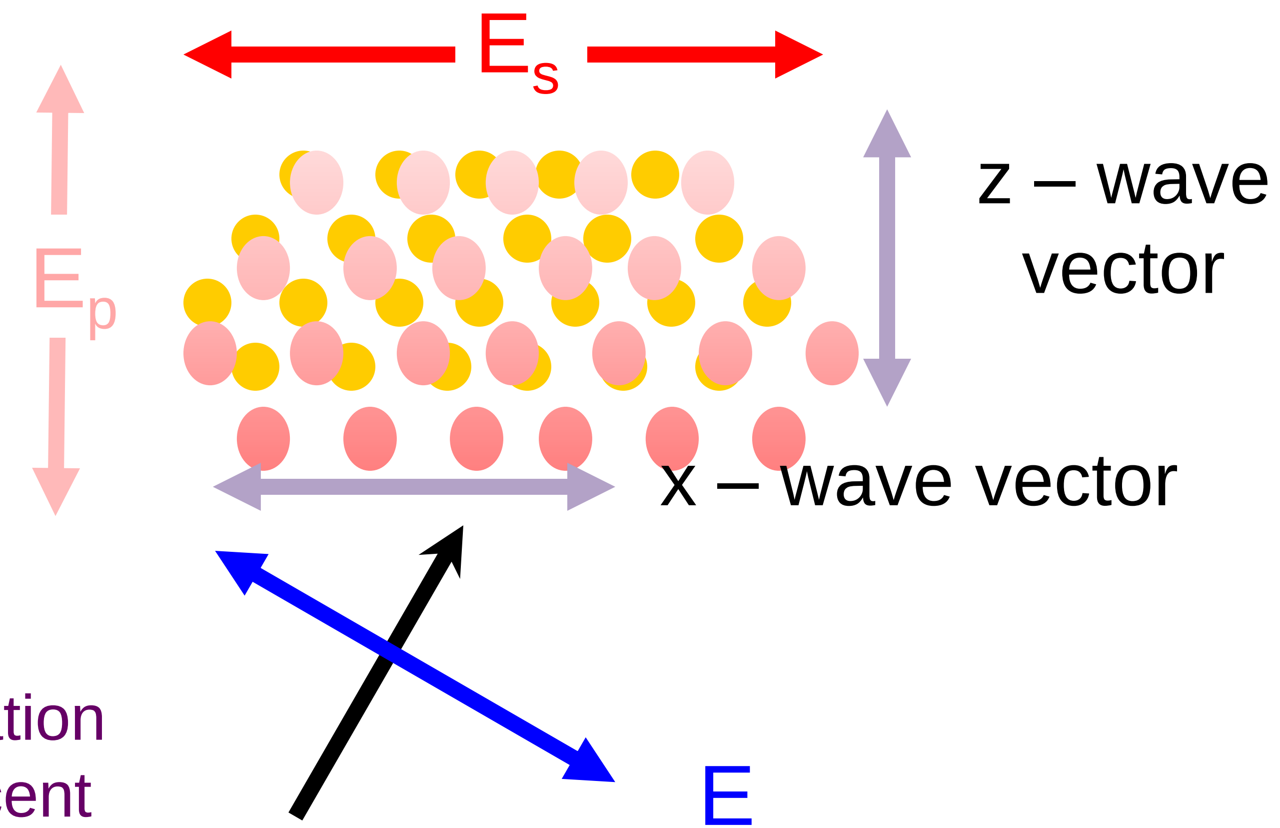

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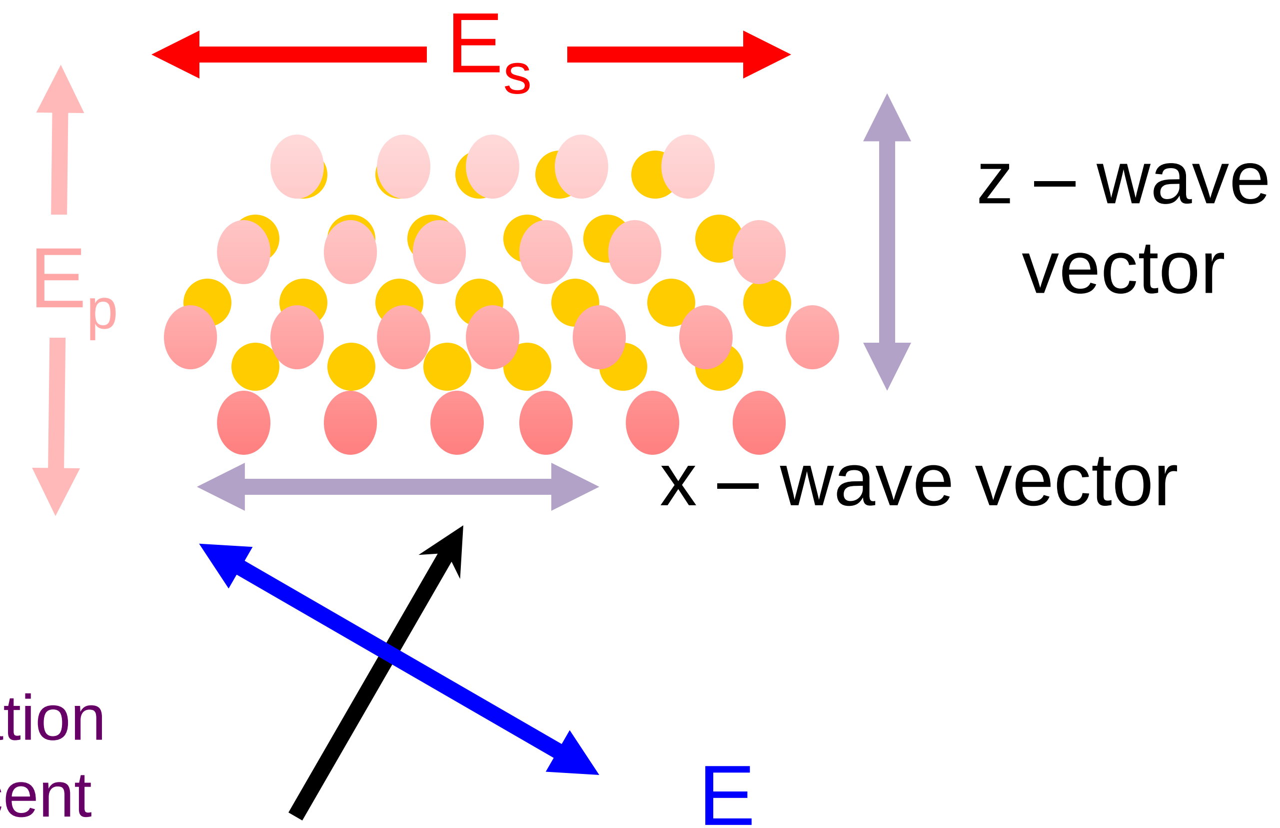

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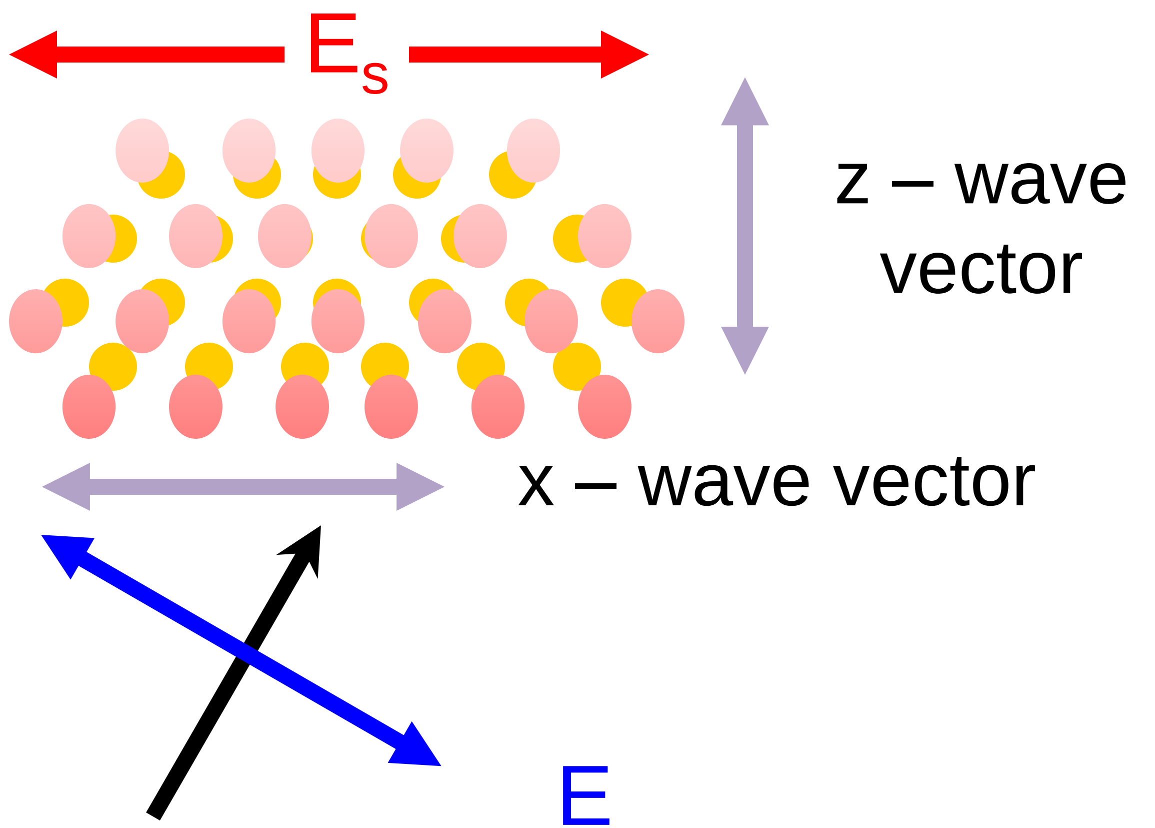

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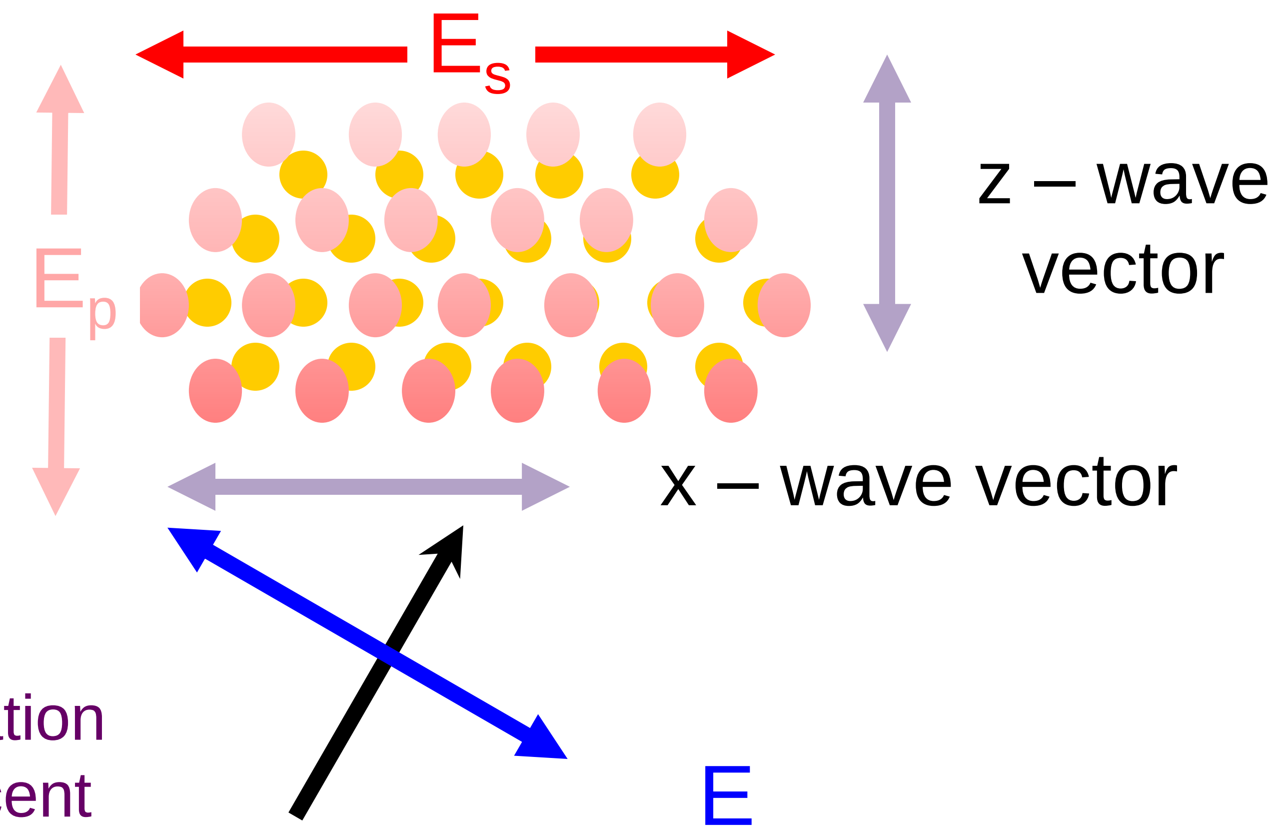

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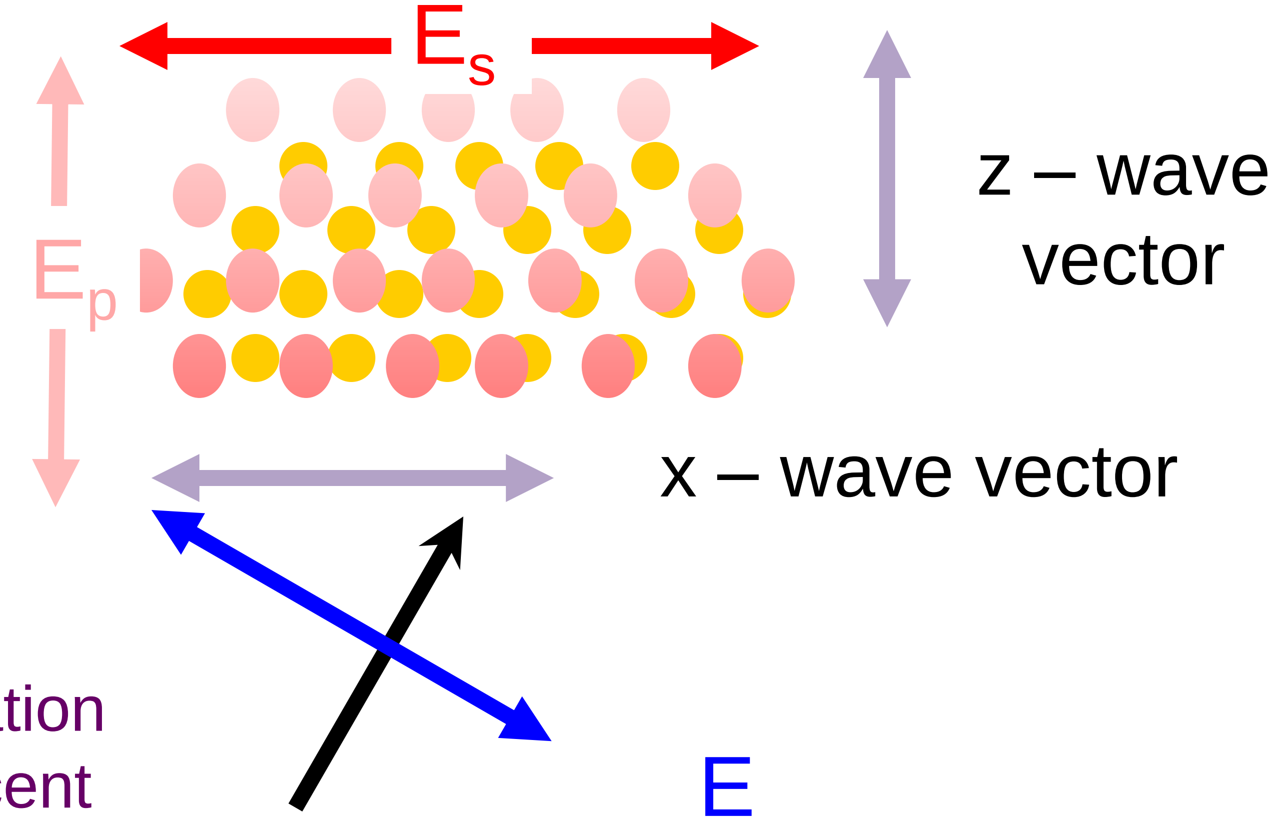

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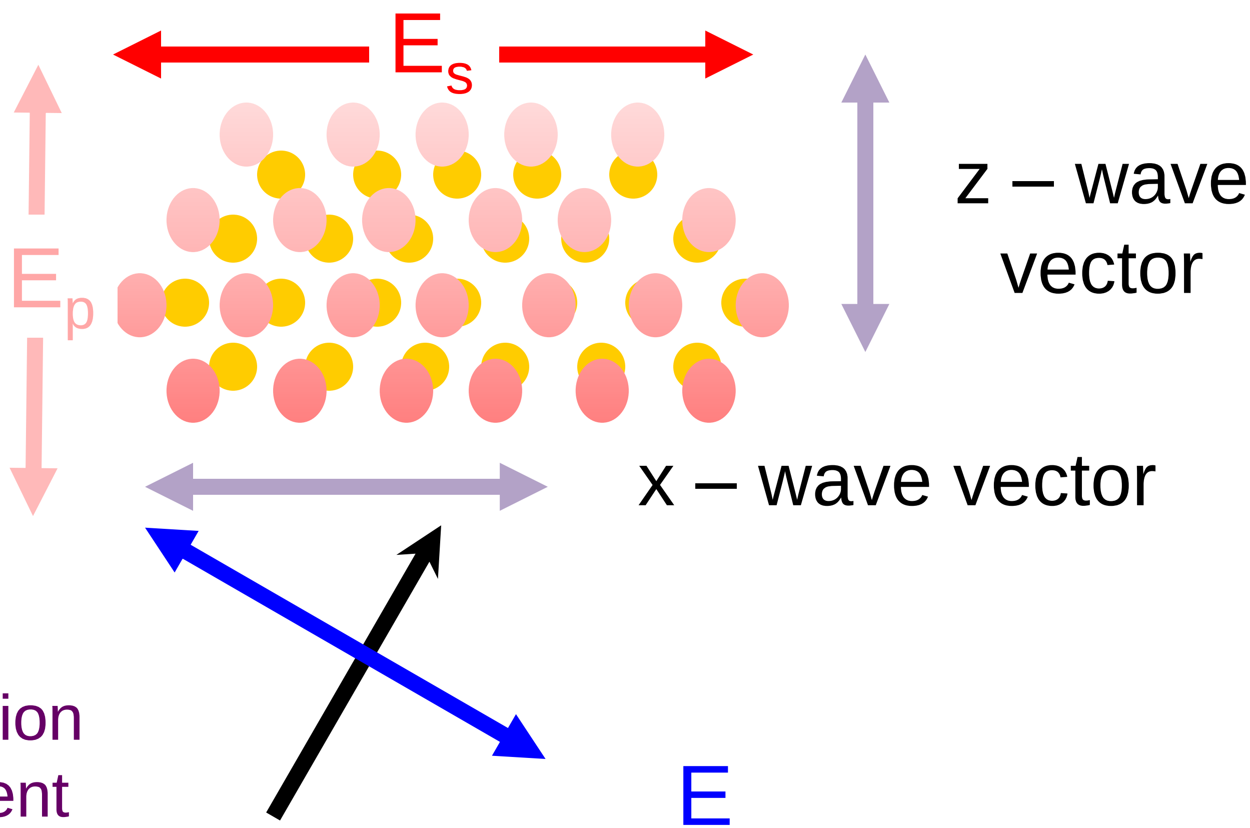

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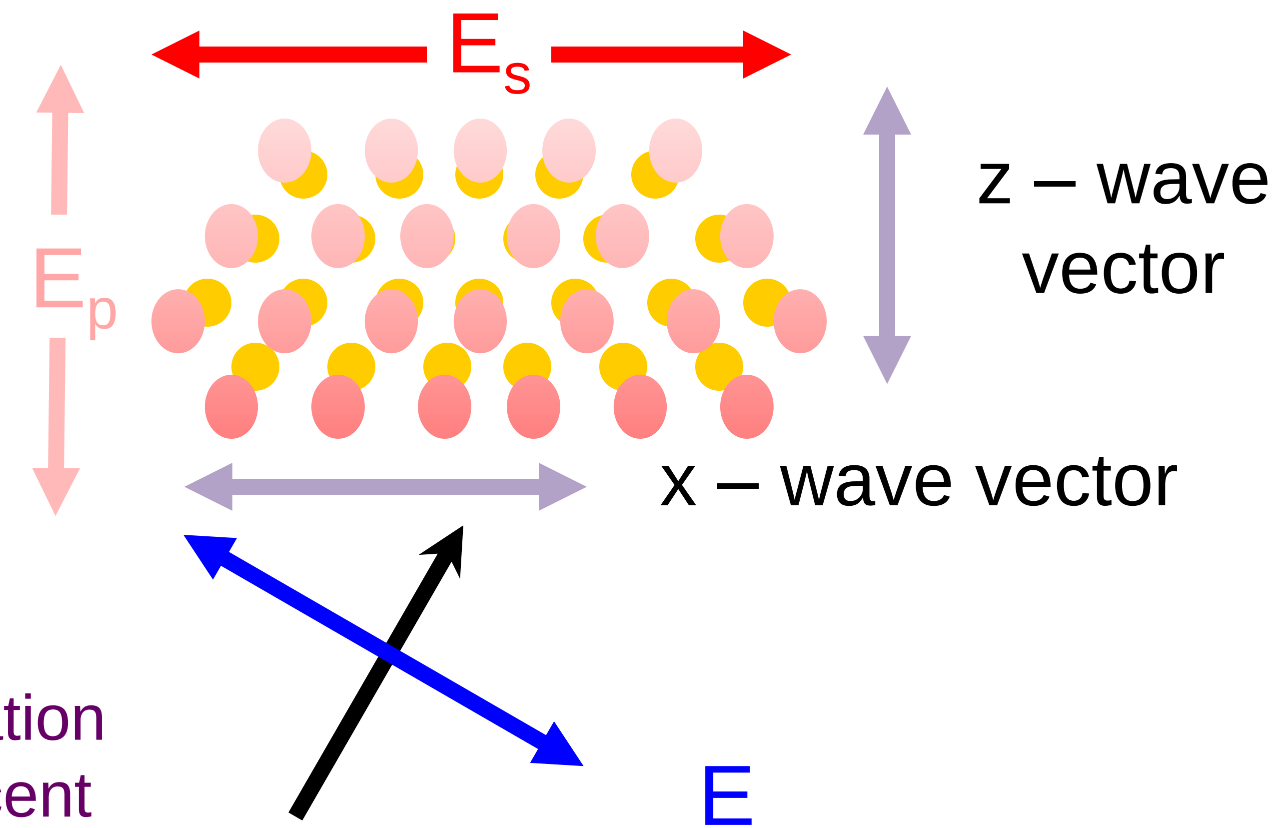


The z-polarization is an evanescent save (like ATR)

Conditions for absorption by surface plasmon

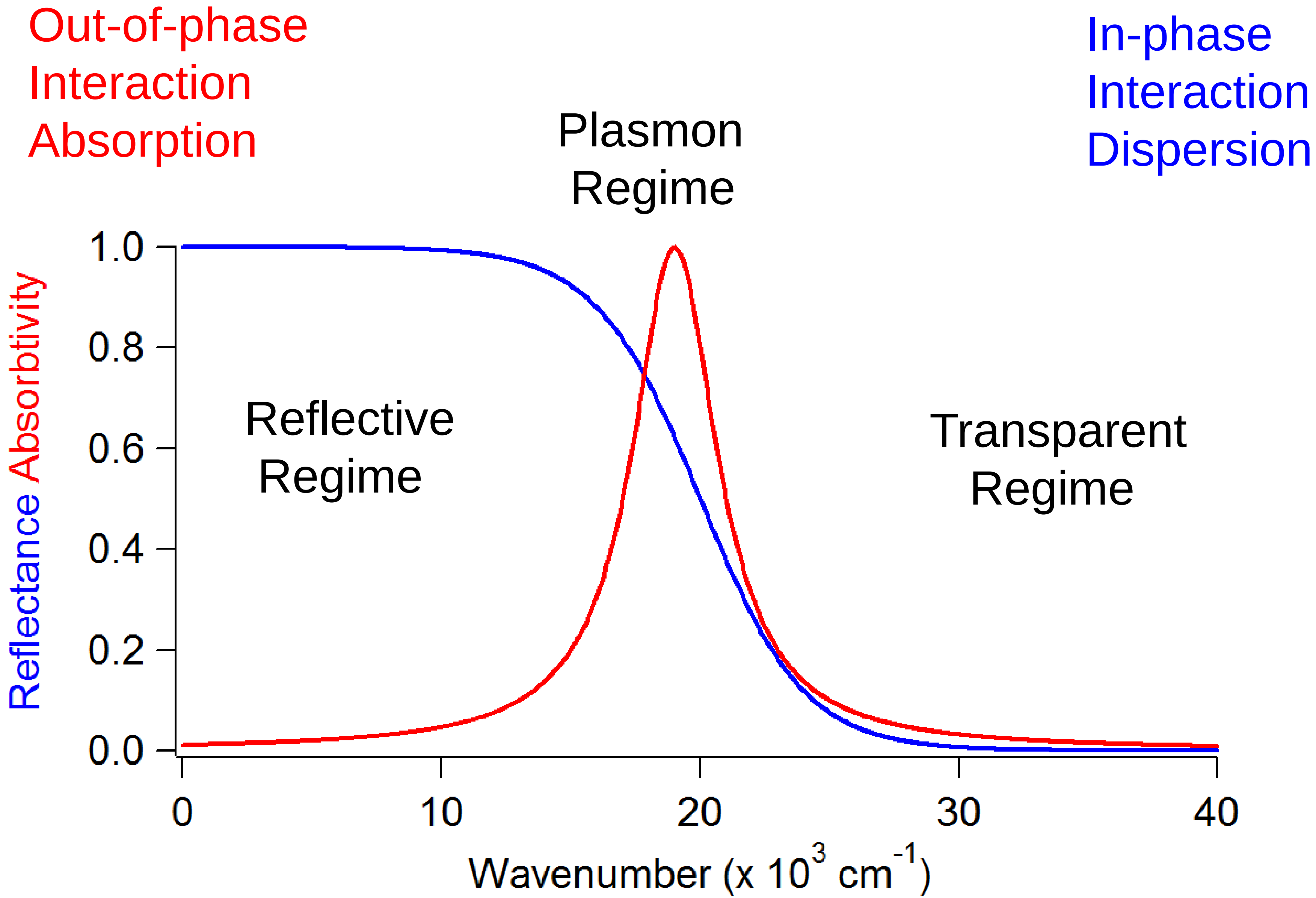
The **forcing term** is the electric field of the incident light.

Conservation of energy: the frequency of the incident light matches the frequency of the plasmon.

Conservation of momentum: the angle of the incident light matches the spatial distribution of the plasmon.

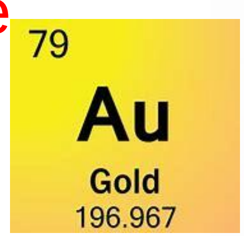
These conditions do not require a noble metal or even a metal, but they do require a conductor of electricity.

Optical properties of conductors

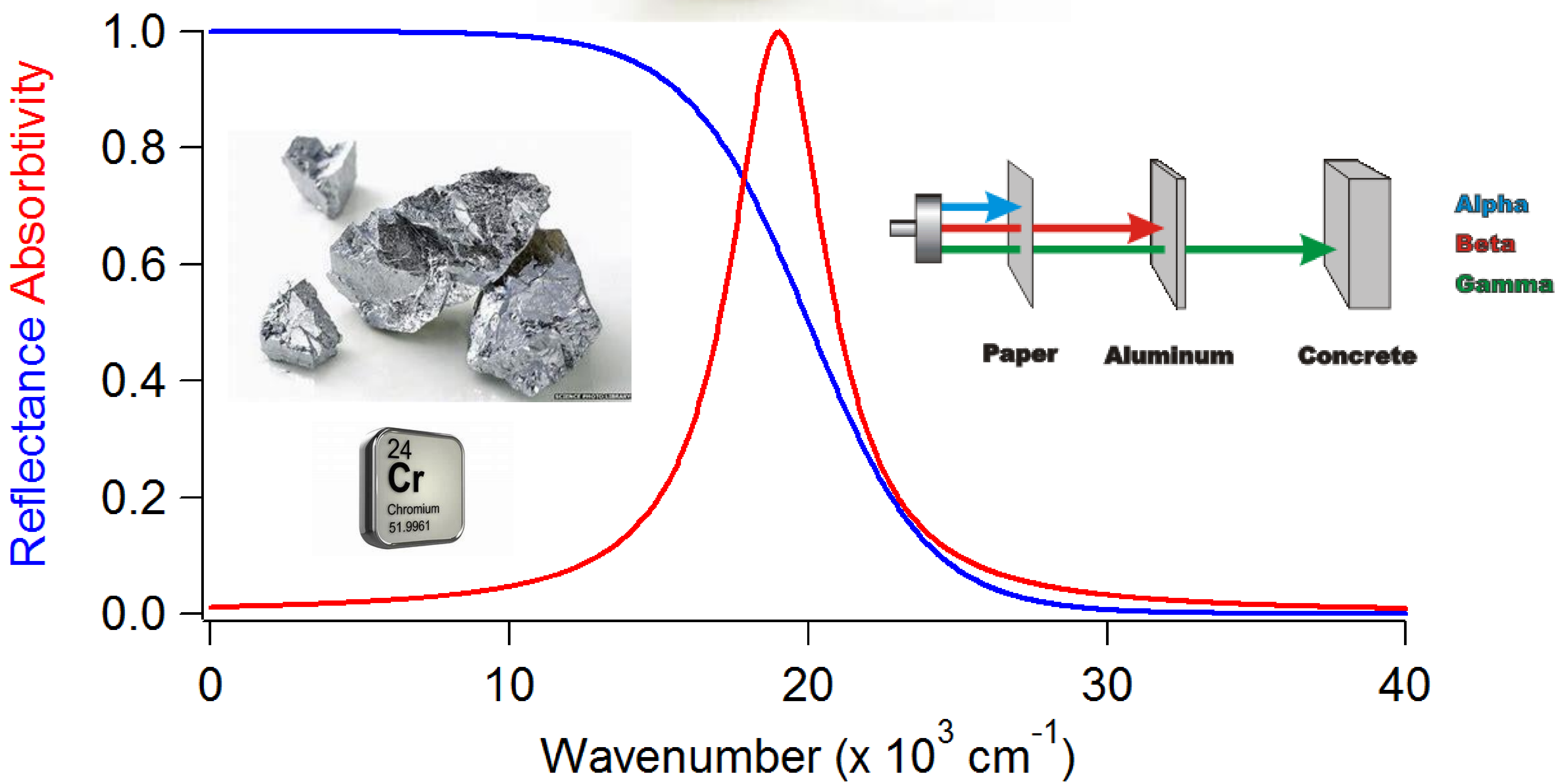


Optical properties of conductors

Out-of-phase
Interaction
Absorption



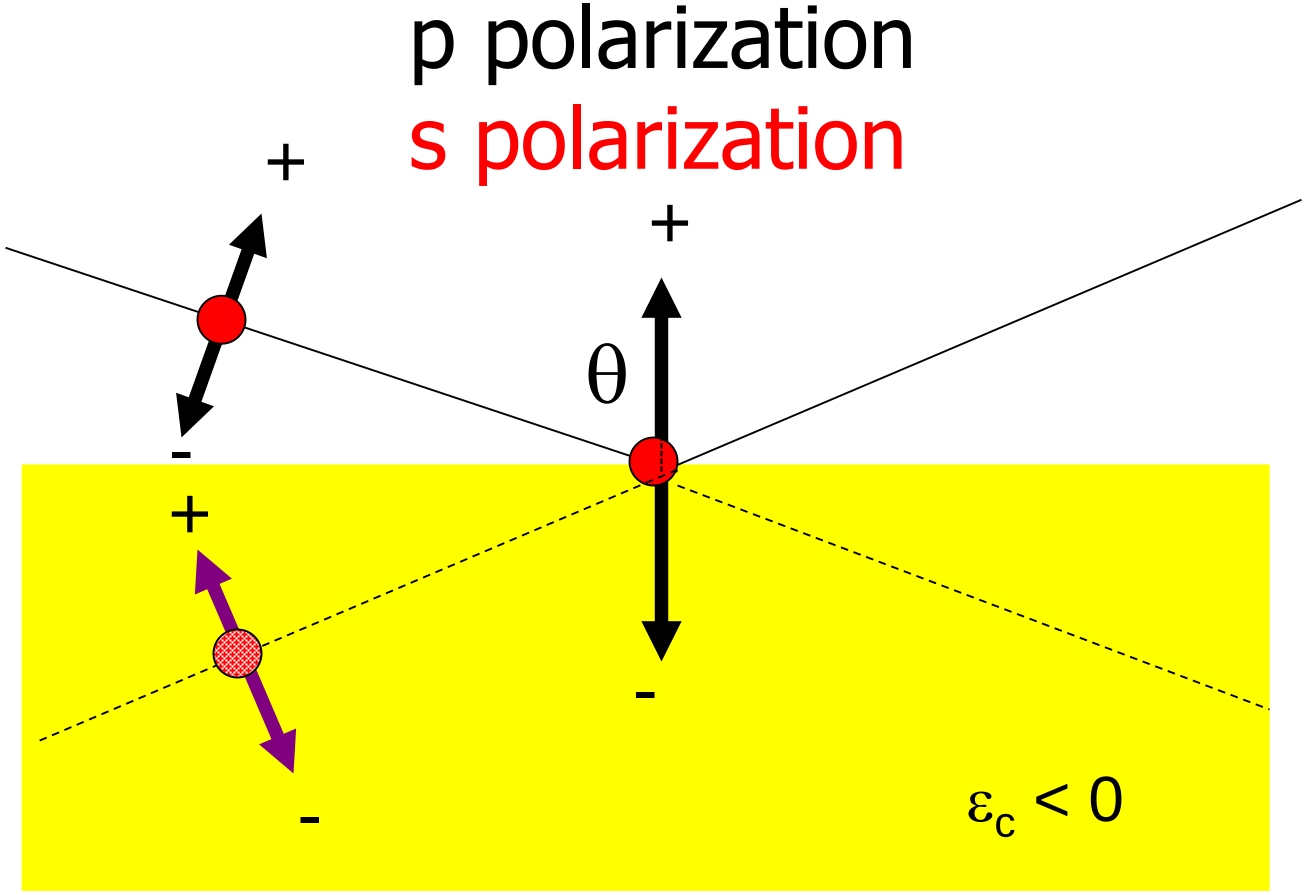
In-phase
Interaction
Dispersion



Surface selection rules

Reflective Regime

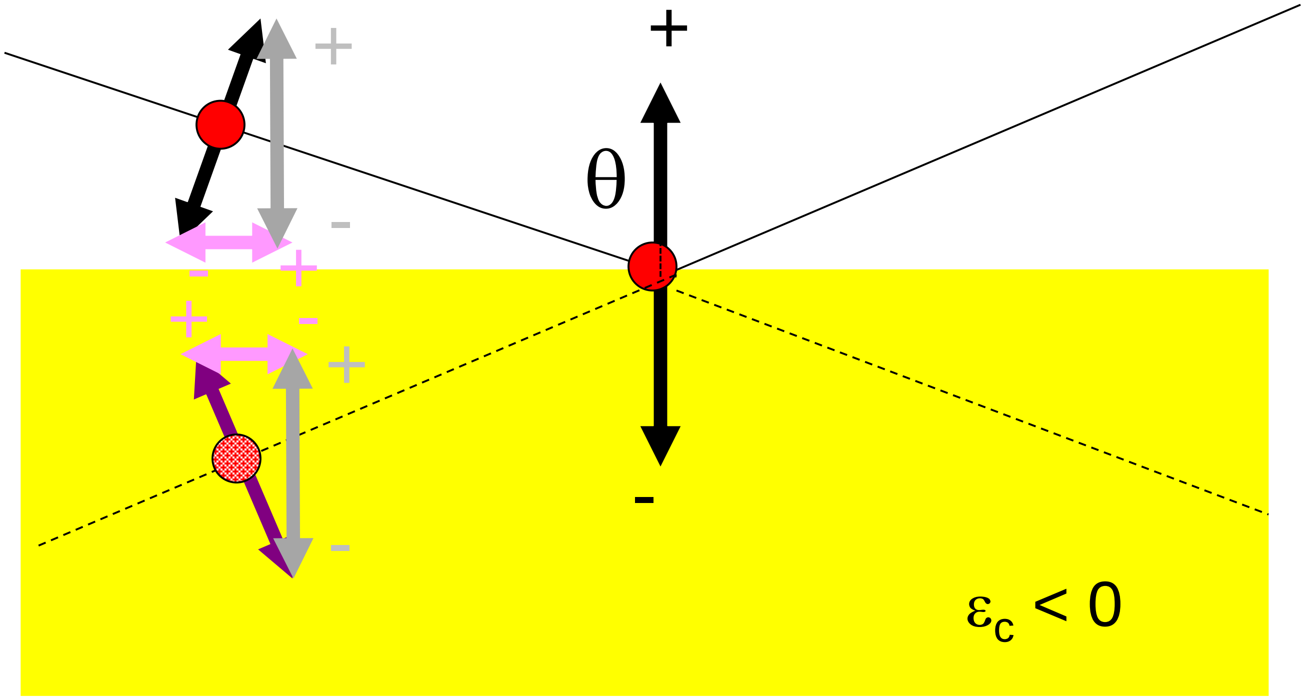
For $\varepsilon_c < 0$ the p-polarized image charge adds constructively to the incident field.



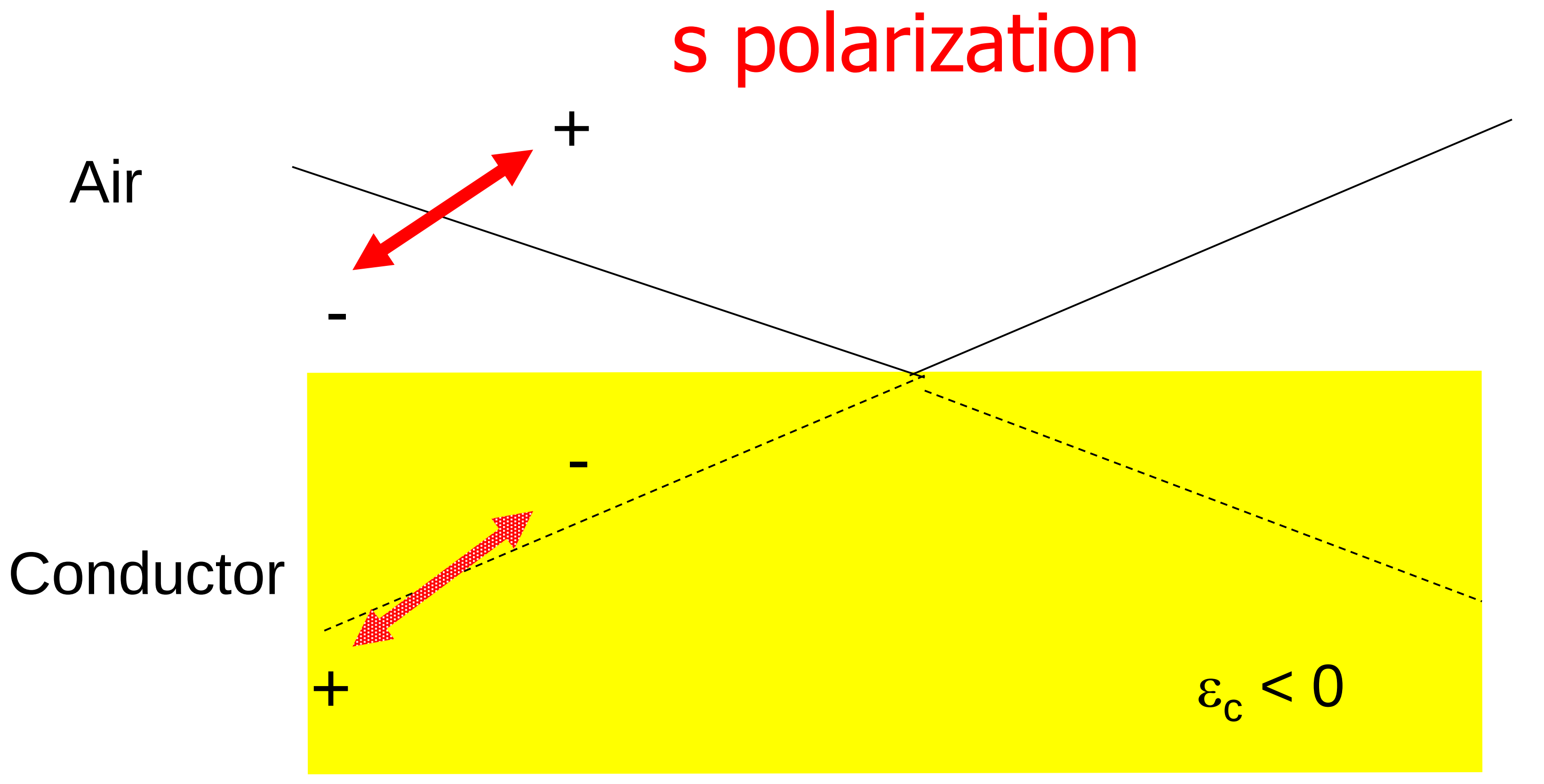
For $\varepsilon_c < 0$ the p-polarized image charge adds constructively to the incident field.

p polarization

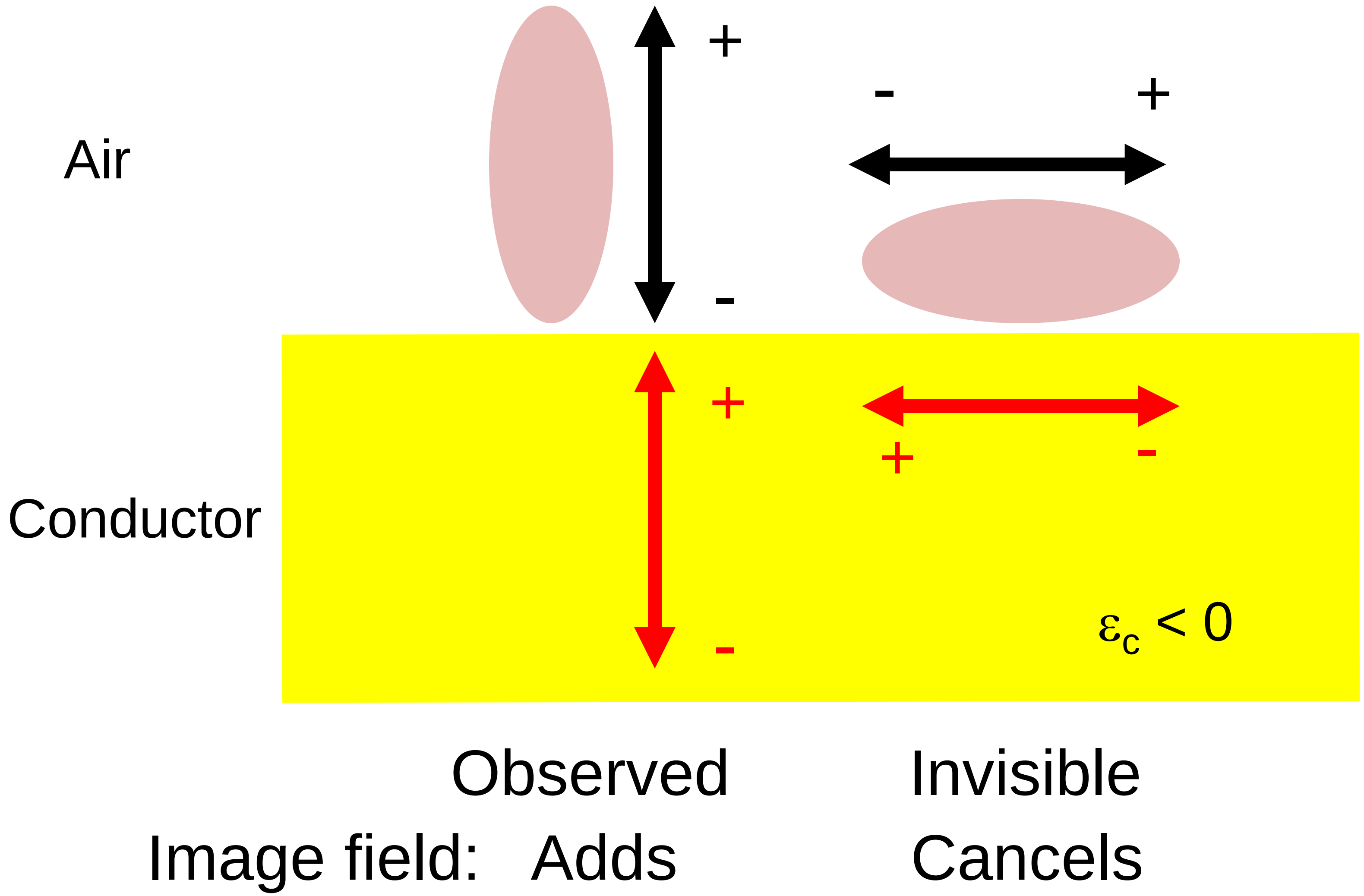
parallel, perpendicular



For $\varepsilon_c < 0$ the s-polarized image charge adds destructively to the incident field.



Only the parallel component of a transition Dipole moment is observed on a conductor



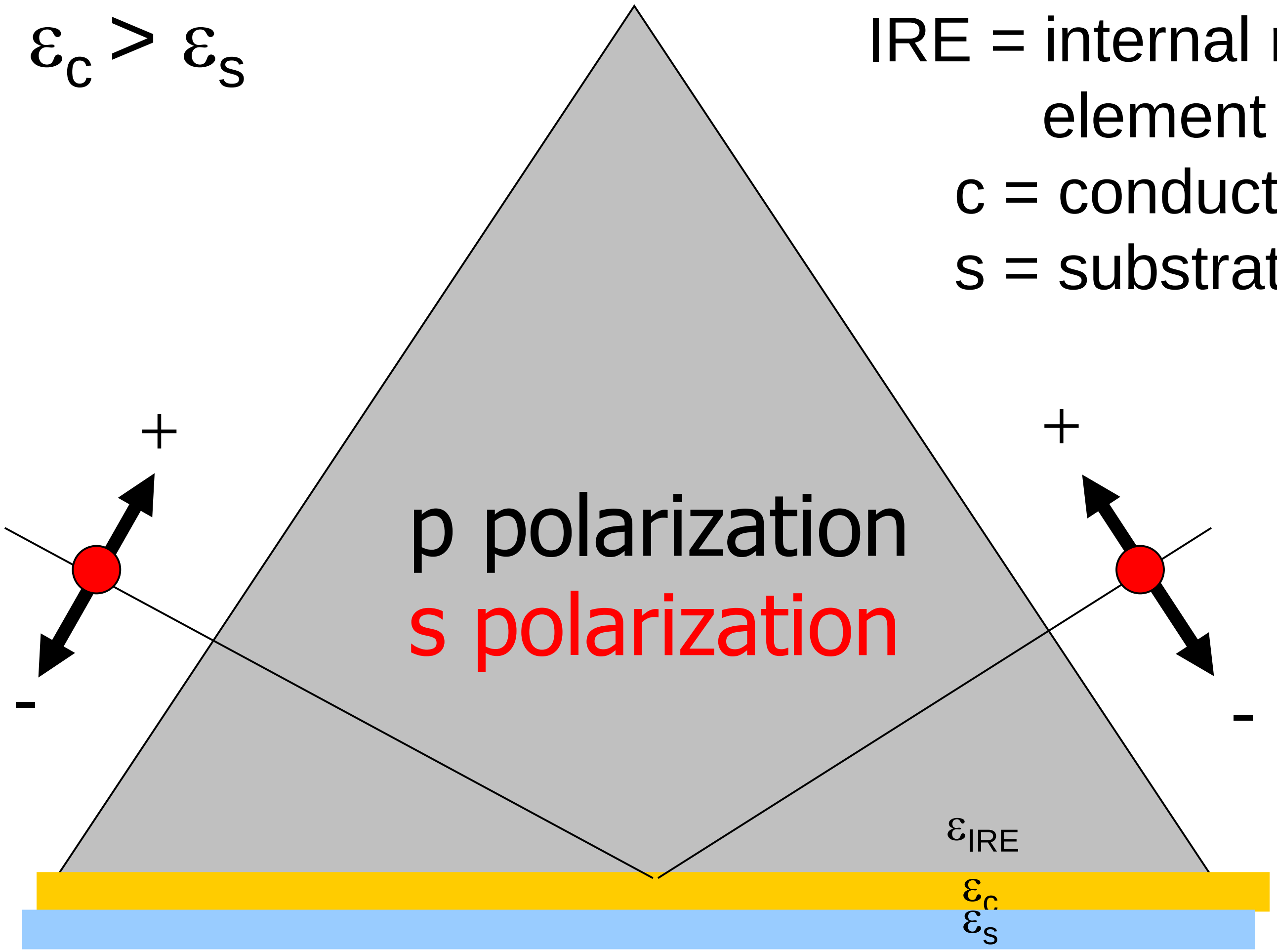
Surface selection rules

Plasmon Regime

Kretschmann configuration

$\varepsilon_{IRE} > \varepsilon_c > \varepsilon_s$

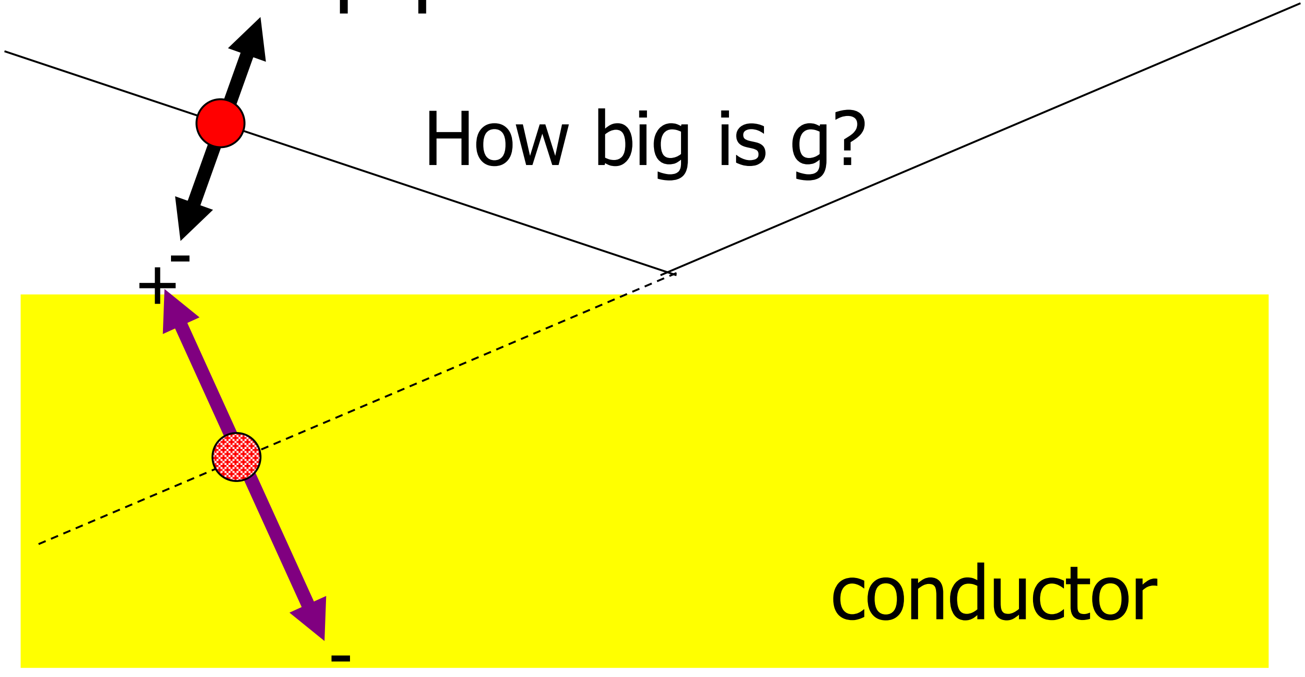
IRE = internal reflecting element
c = conductor
s = substrate



Thin conducting film on a prism

On a metal surface there is a local field
The image field is critically damped

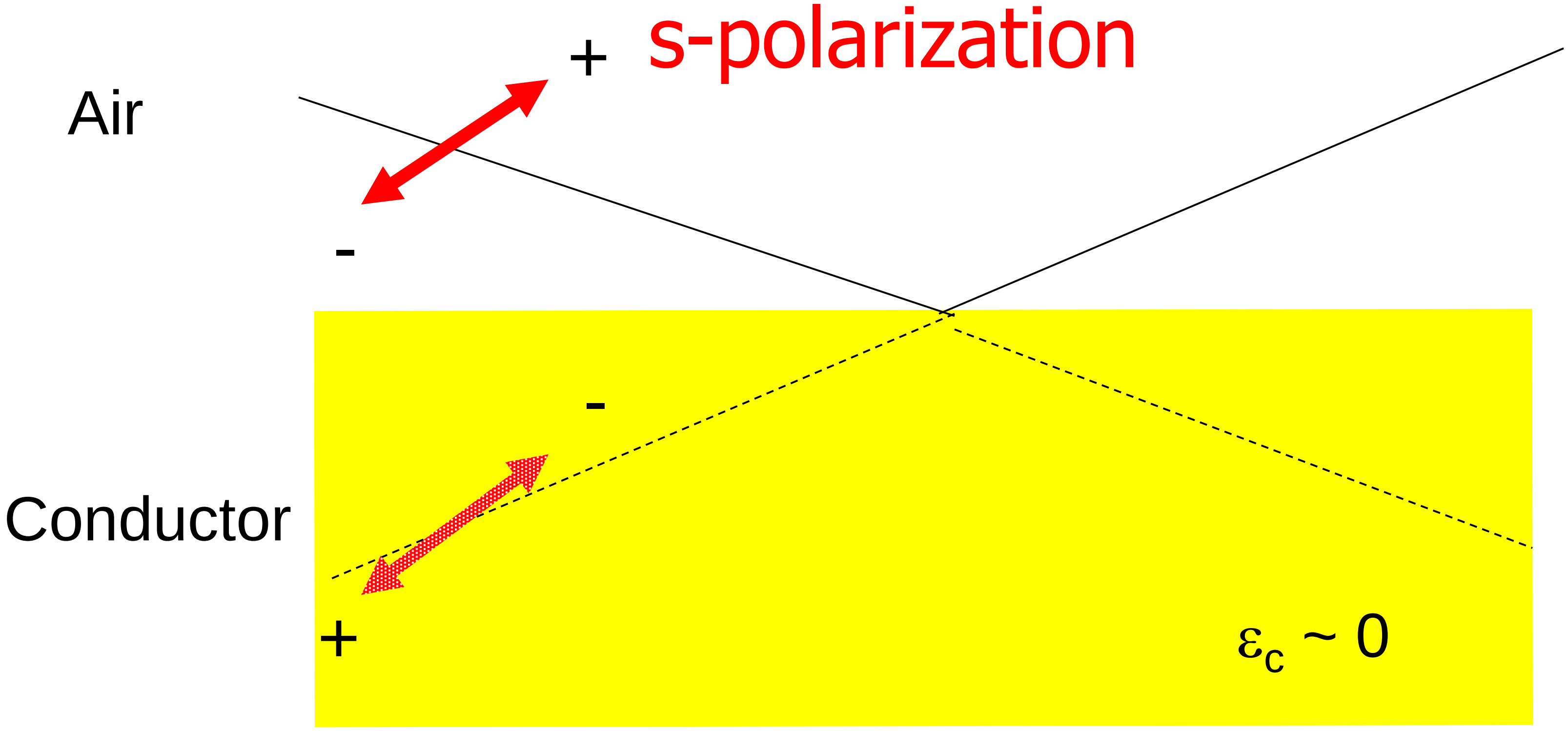
wave vector matching is required
+ p-polarization



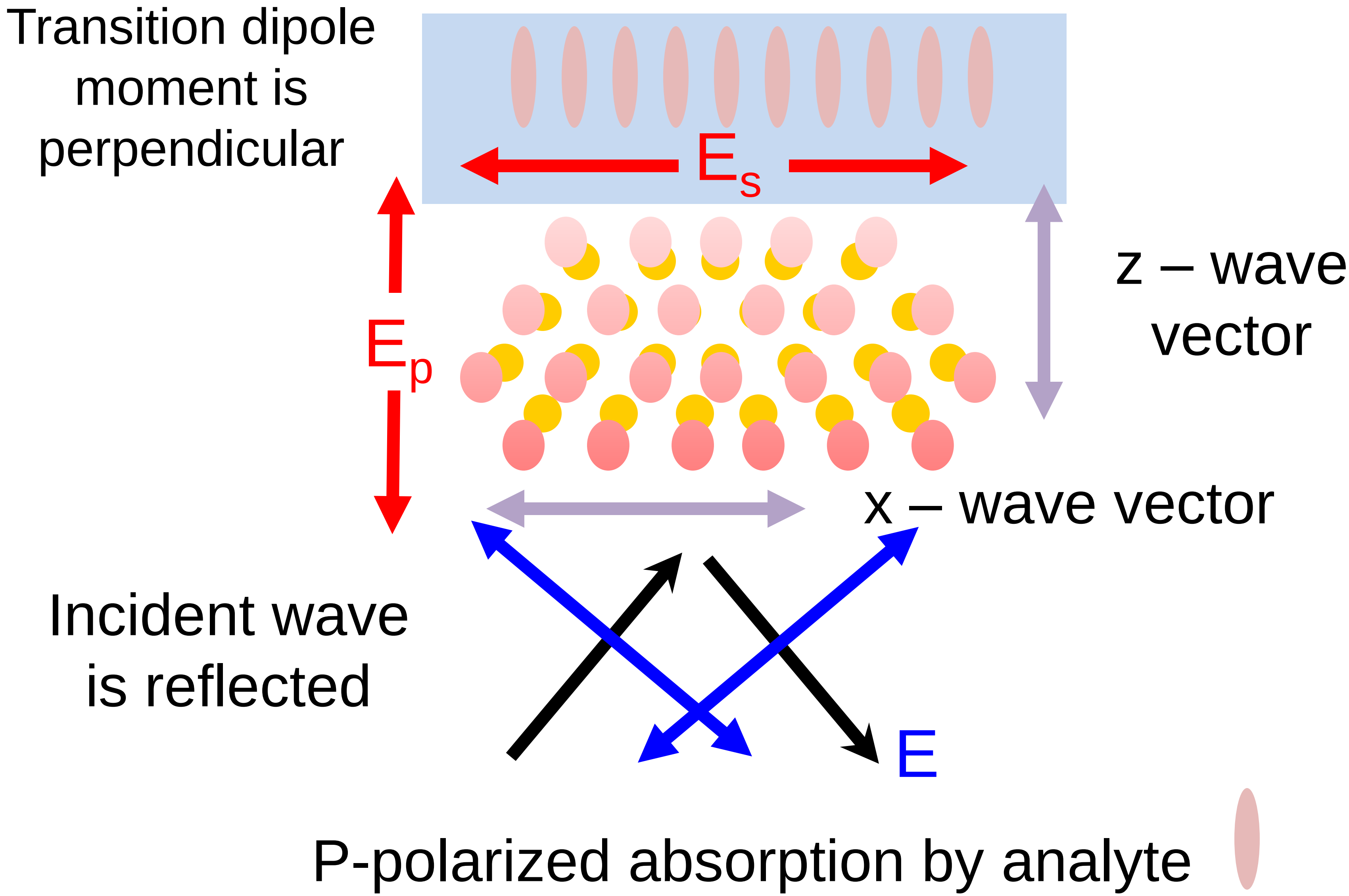
Local field $E_p = gE_i$

No local field enhancement is possible on a surface for s-polarization

k-vector matching is not possible

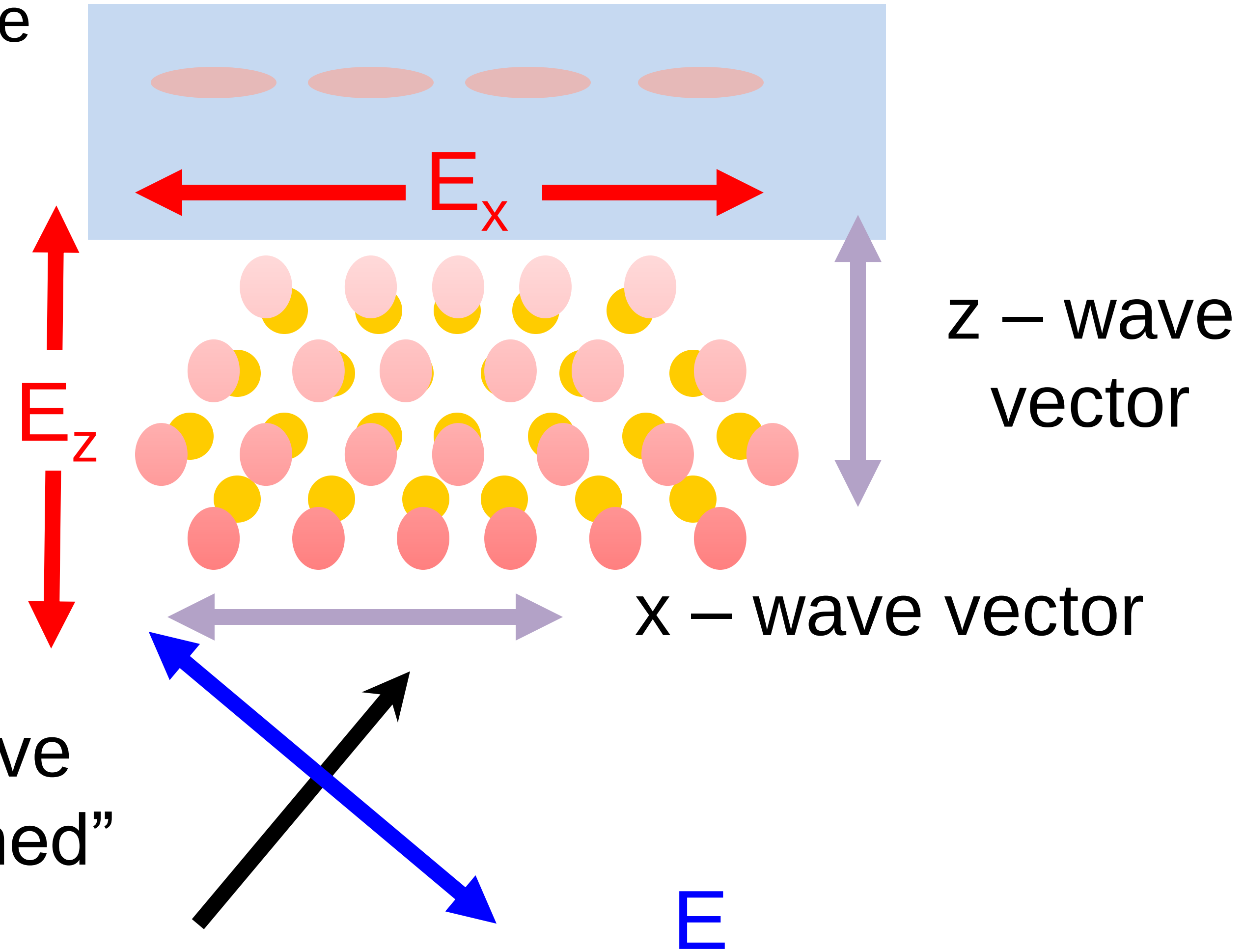


Non-SPR resonant condition
ATR spectroscopy on a metal



SPR resonant condition
Plasmon enhancement is possible

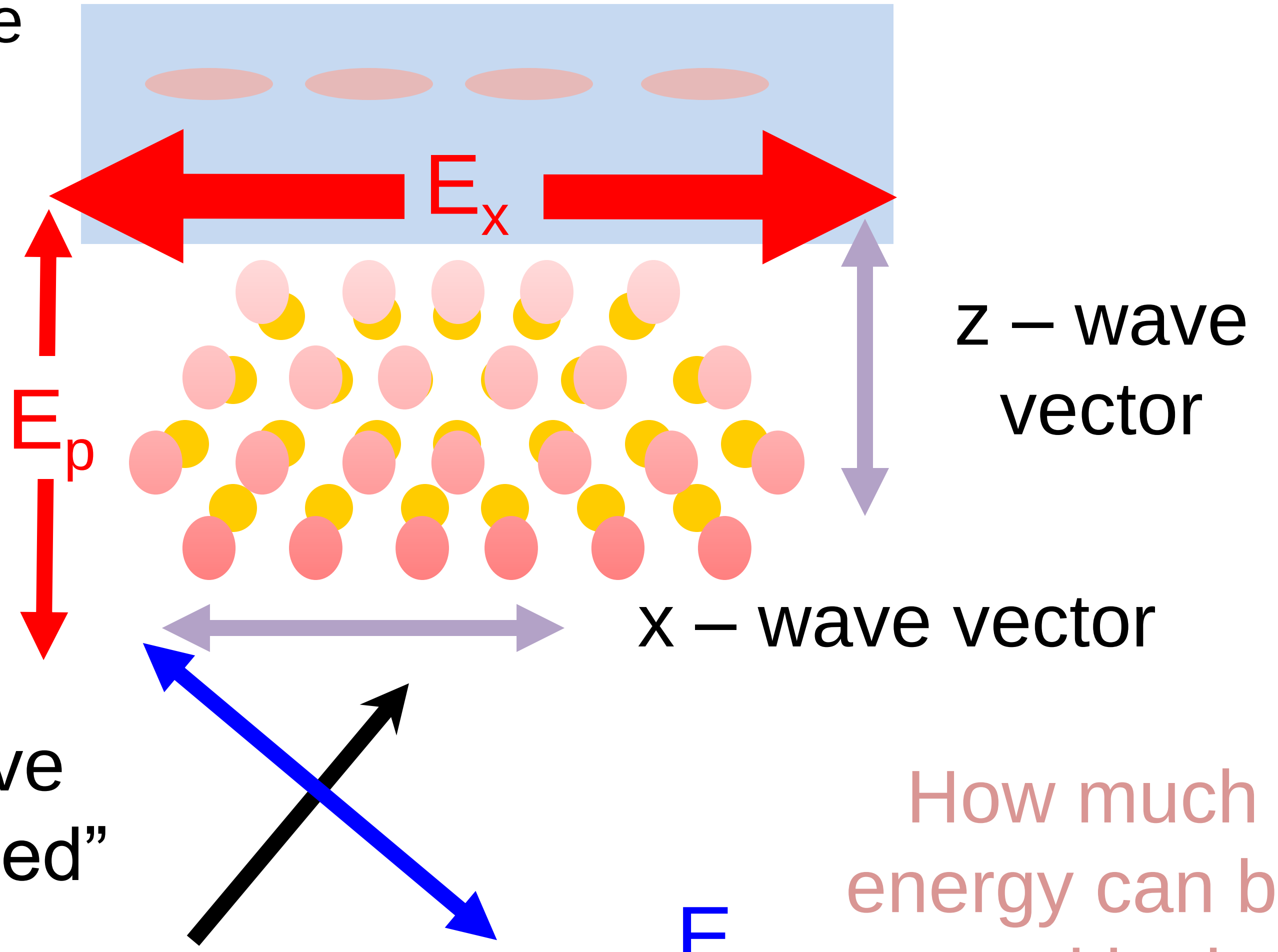
Transition dipole moment is perpendicular



Incident wave is “extinguished”

SPR resonant condition
Plasmon enhancement is possible

Transition dipole
moment is
perpendicular

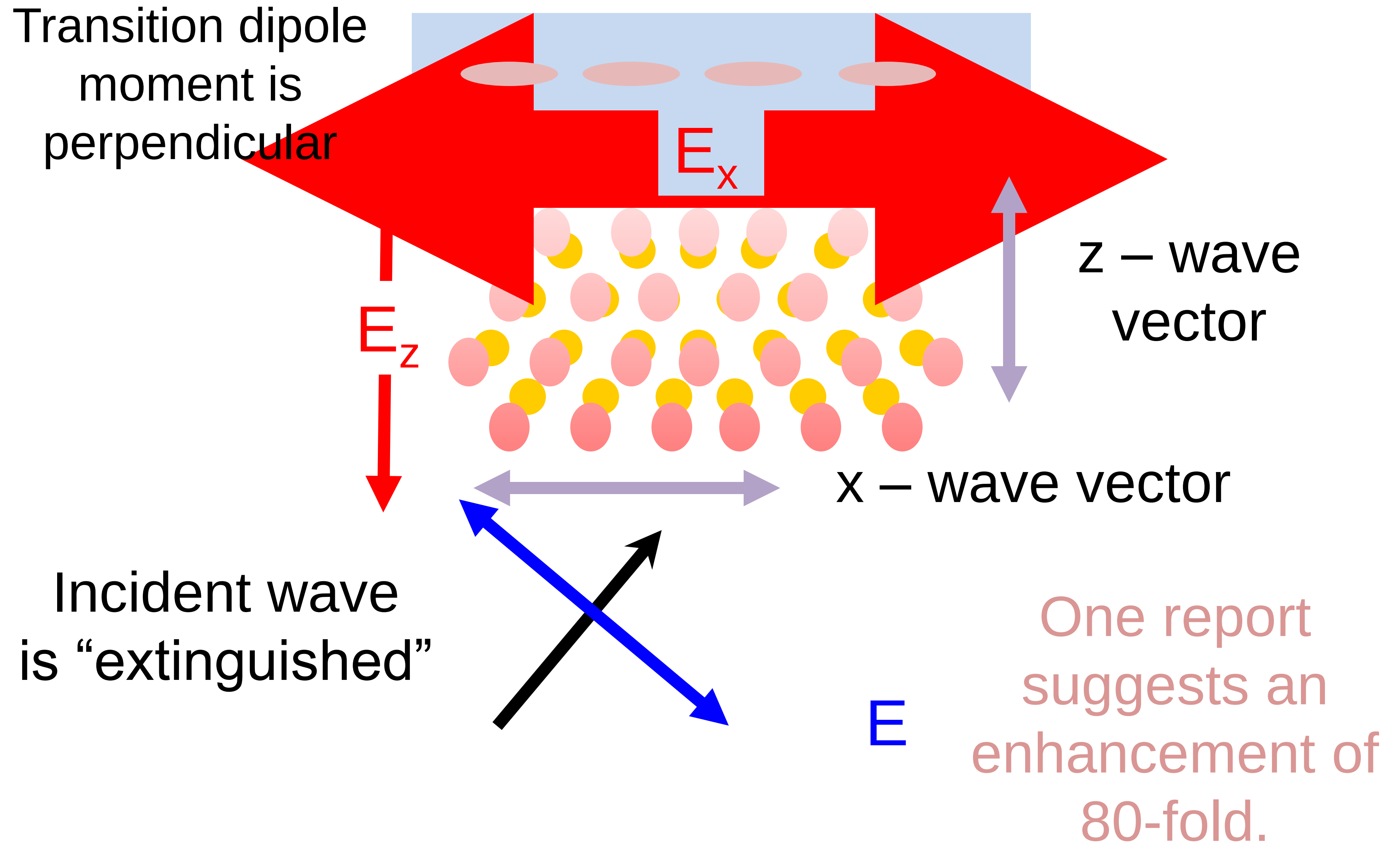


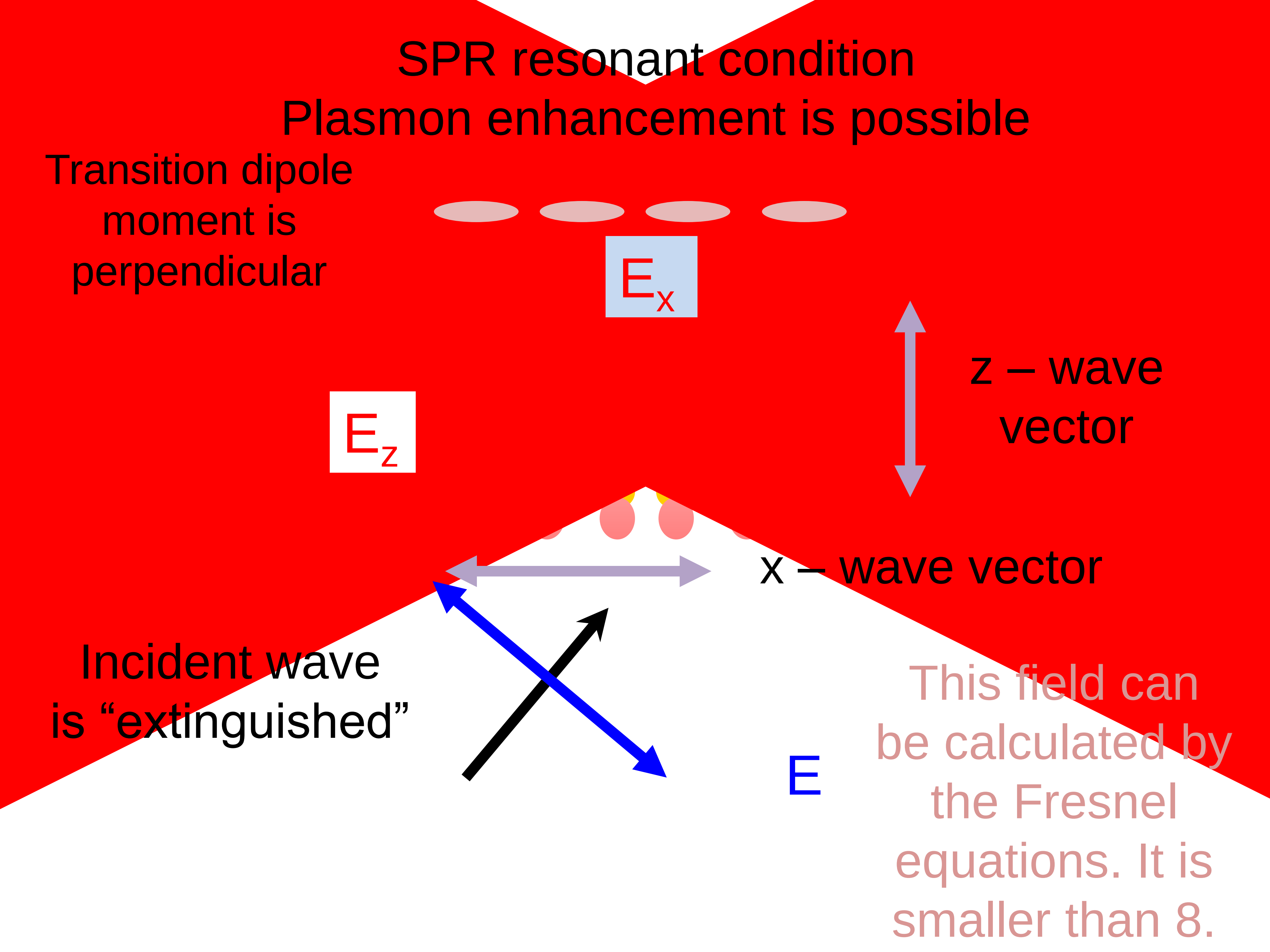
Incident wave
is “extinguished”

How much
energy can be
stored in the
conductor?

SPR resonant condition

Plasmon enhancement is possible

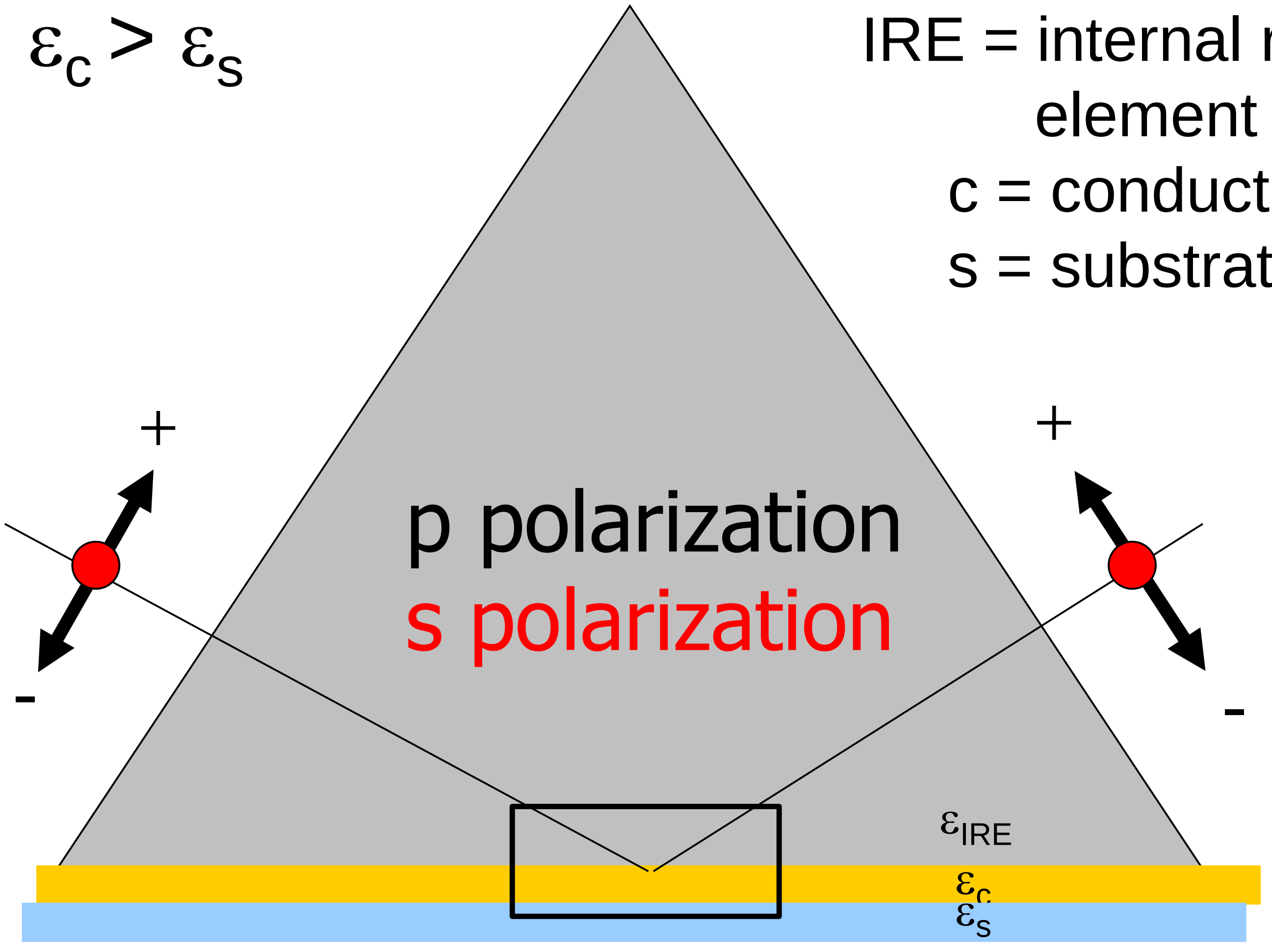



SPR resonant condition
Plasmon enhancement is possible
Transition dipole moment is perpendicular
E_x
E_z
z – wave vector
x – wave vector
Incident wave is "extinguished"
E
This field can be calculated by the Fresnel equations. It is smaller than 8.

Kretschmann configuration

$\varepsilon_{IRE} > \varepsilon_c > \varepsilon_s$

IRE = internal reflecting element
c = conductor
s = substrate



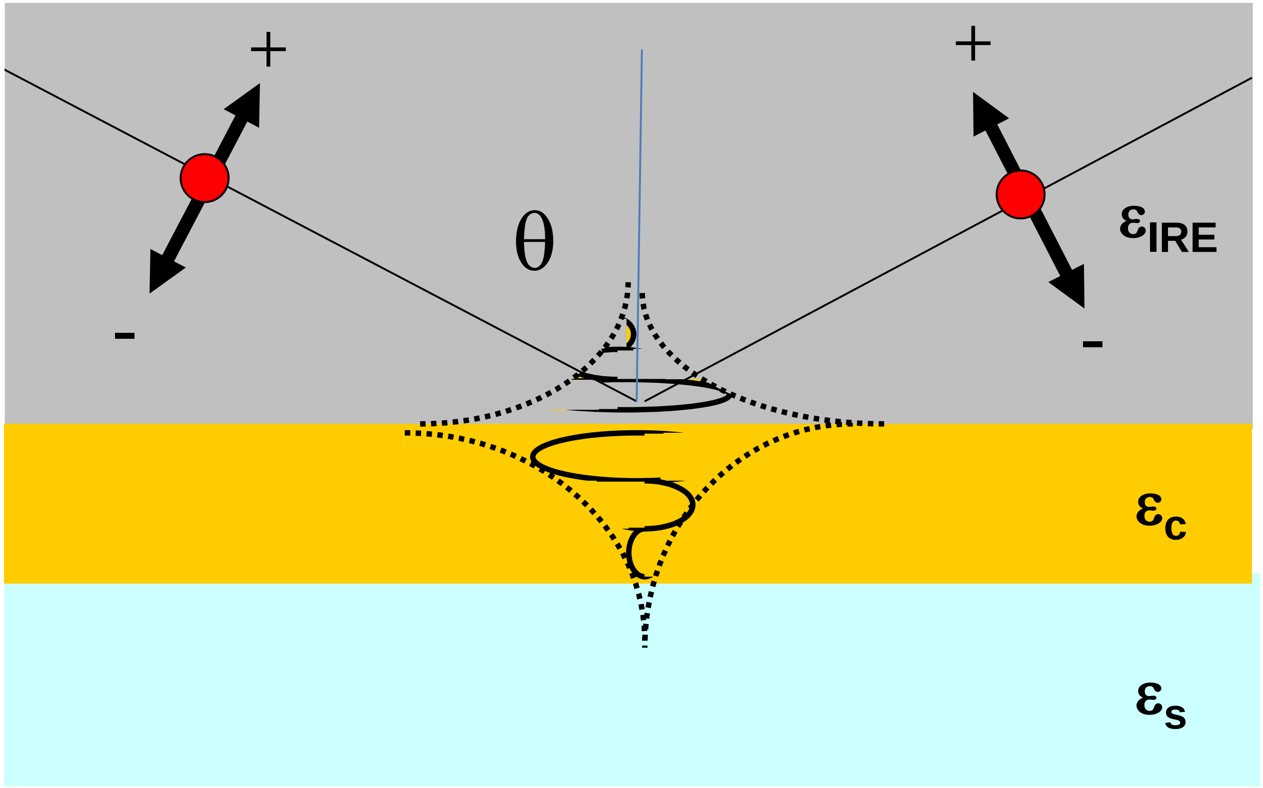
Thin conducting film on a prism

Attenuated total reflection ($\theta > \theta_{critical}$)

Condition for surface plasmon resonance

p polarization

s polarization



Surface Plasmons: A special case of ATR

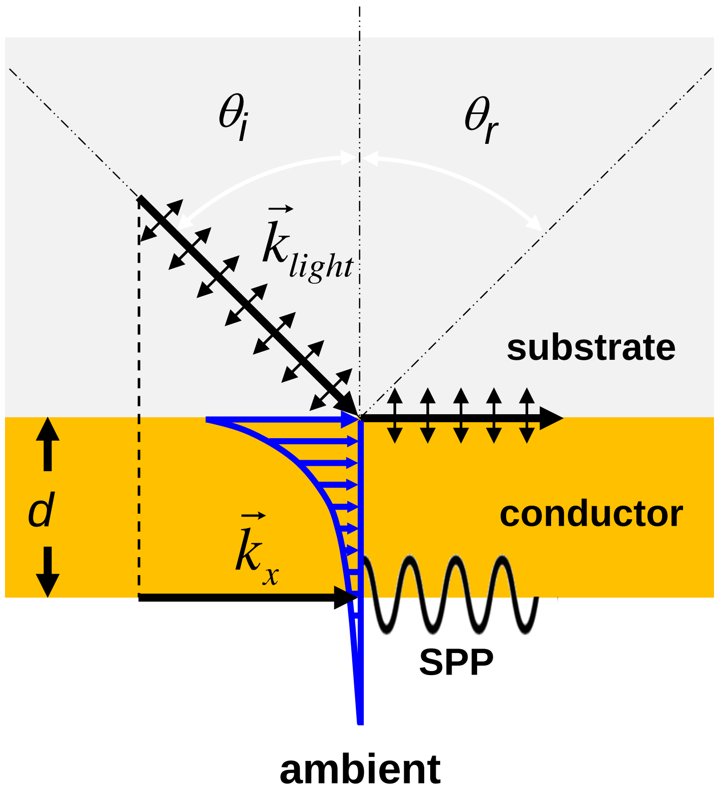
Monitor SPPs in the *Kretschmann-Raether* configuration

When $\theta_i > \theta_c$, total internal reflection of *p*-polarized light

Evanescent field extends from the conductor interface to the conductor surface

In-plane wavevector (k_x) depends on incident angle (θ_i)

Couple to the surface plasmon polariton when $k_x = k_{SPP}$



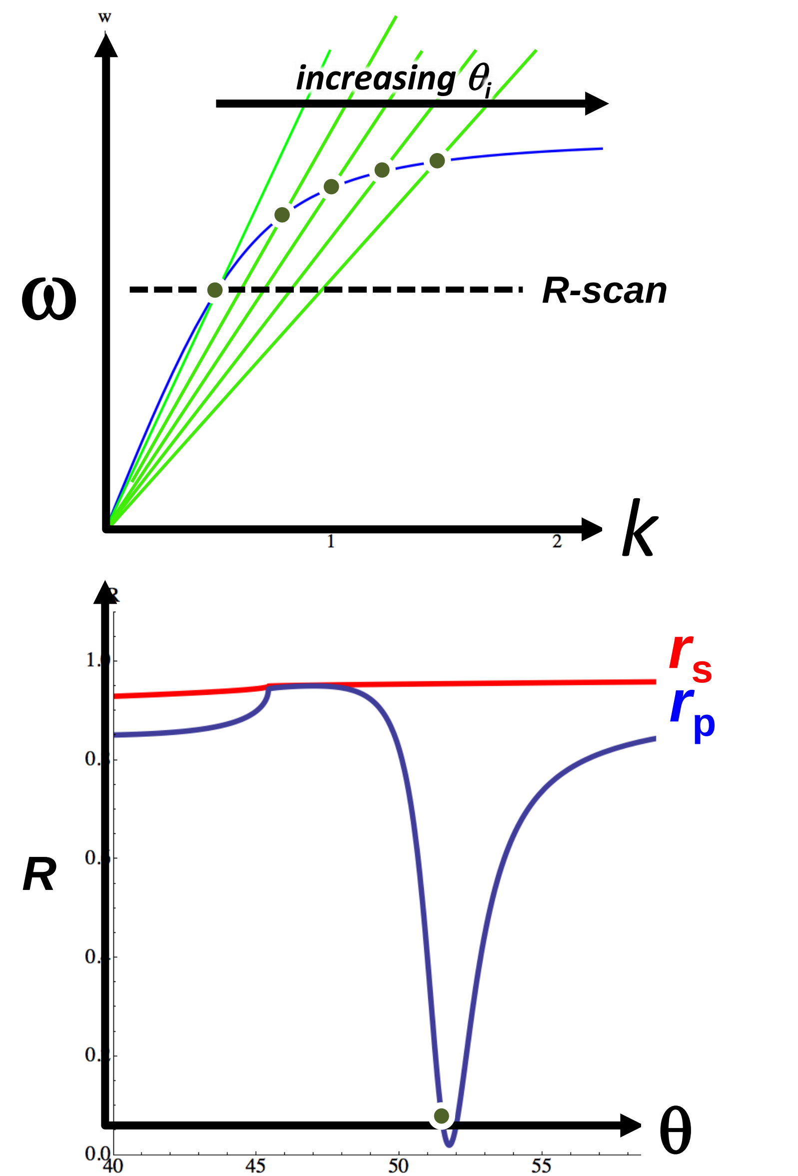
Surface Plasmons: Observation

Each incident angle has a unique k_x for plasmon coupling

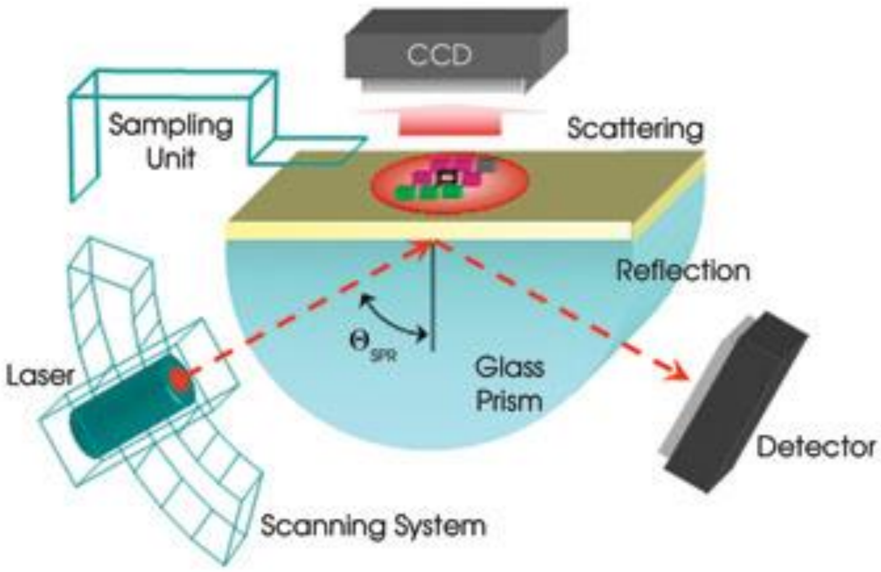
At resonance there is no reflected light, all energy couples to the SPP

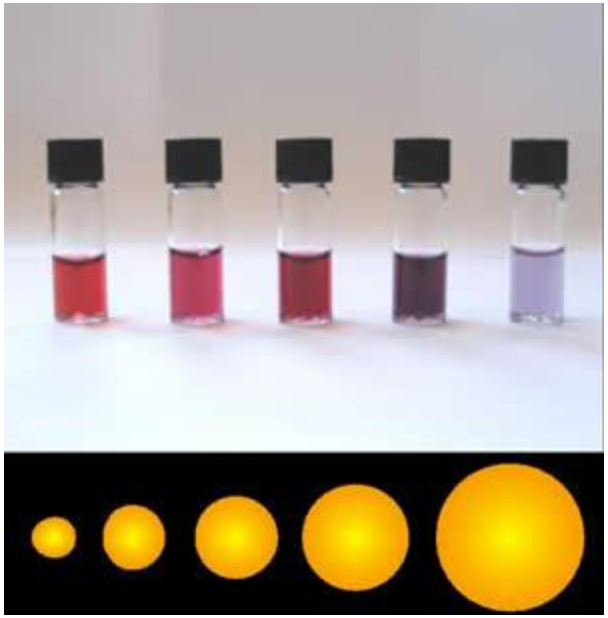
SPPs are visible as a dip in reflected intensity as a function of incident angle at constant w

This only occurs for incidence light with electric field component in the x-direction, thus only for *p*-polarization



Surface Plasmon Resonance on Gold
Localized surface plasmon resonance



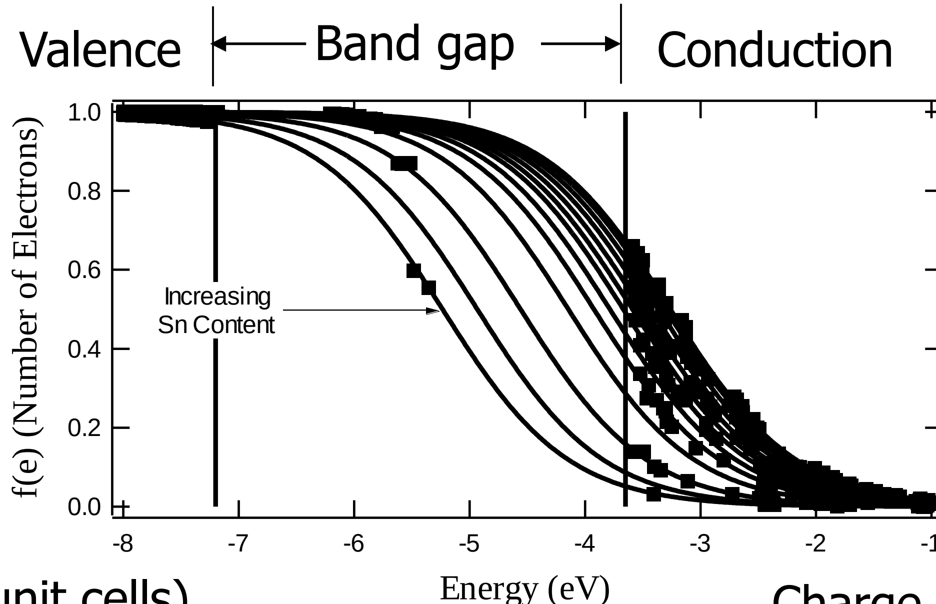


SPR

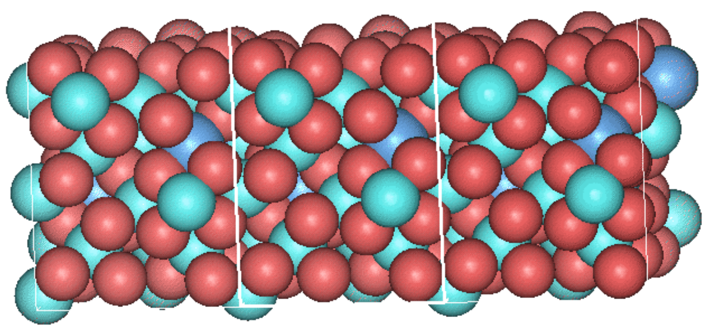
LSPR

What is the relationship?

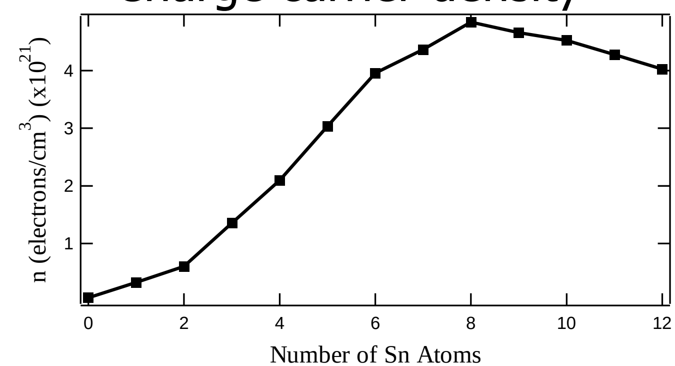
Indium Tin Oxide (ITO)
Transparent conducting thin film



$In_{28}Sn_4O_{48}$ (three unit cells)



Charge carrier density

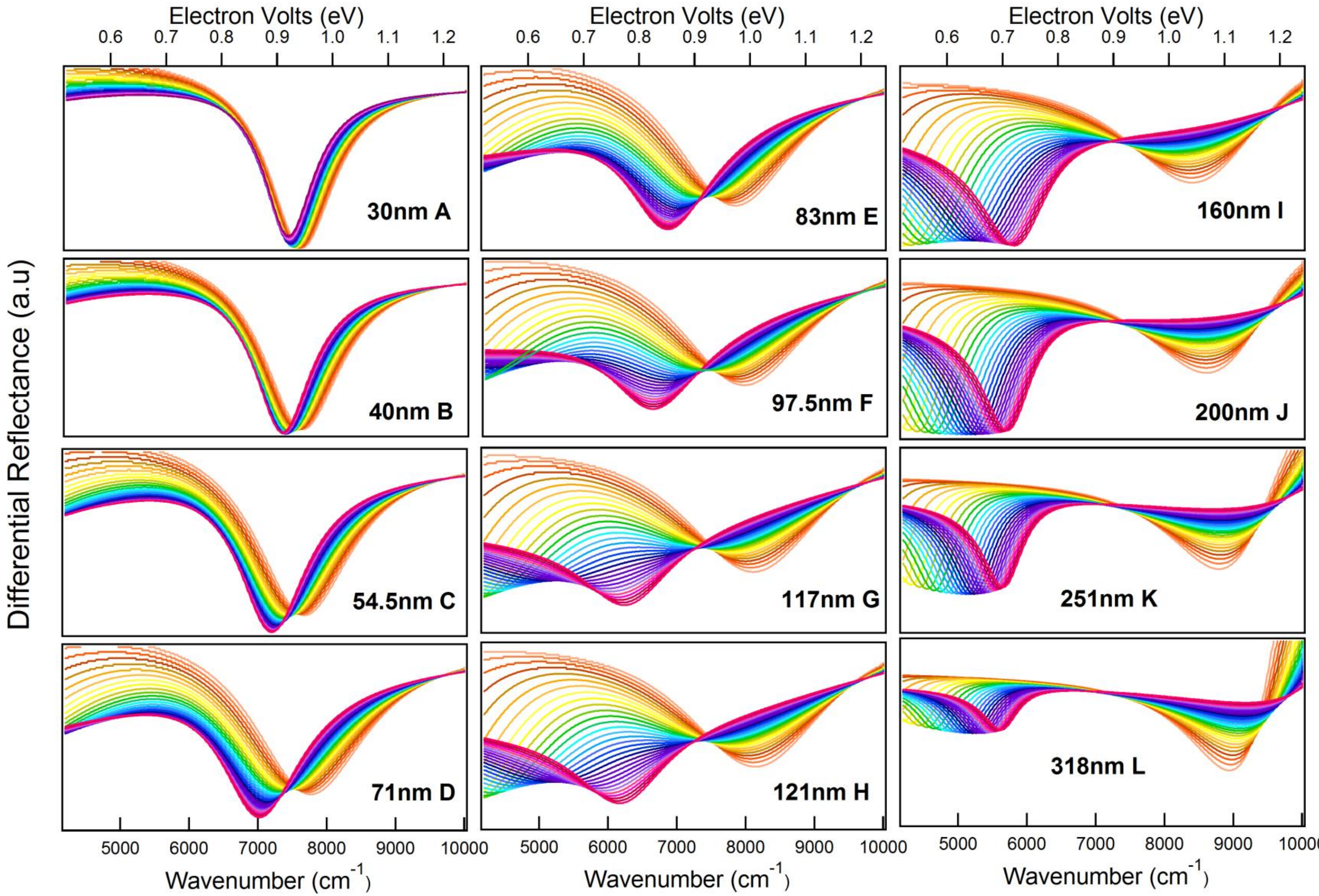


Brewer, S. H.; Franzen, S. "Calculation of the Electronic and Optical Properties of Indium Tin Oxide by Density Functional Theory" Chem. Phys., **2003**, <u>119</u>, 751-858

Surface Plasmon Resonance on ITO

Calculated

Angle Range: 42°-53°

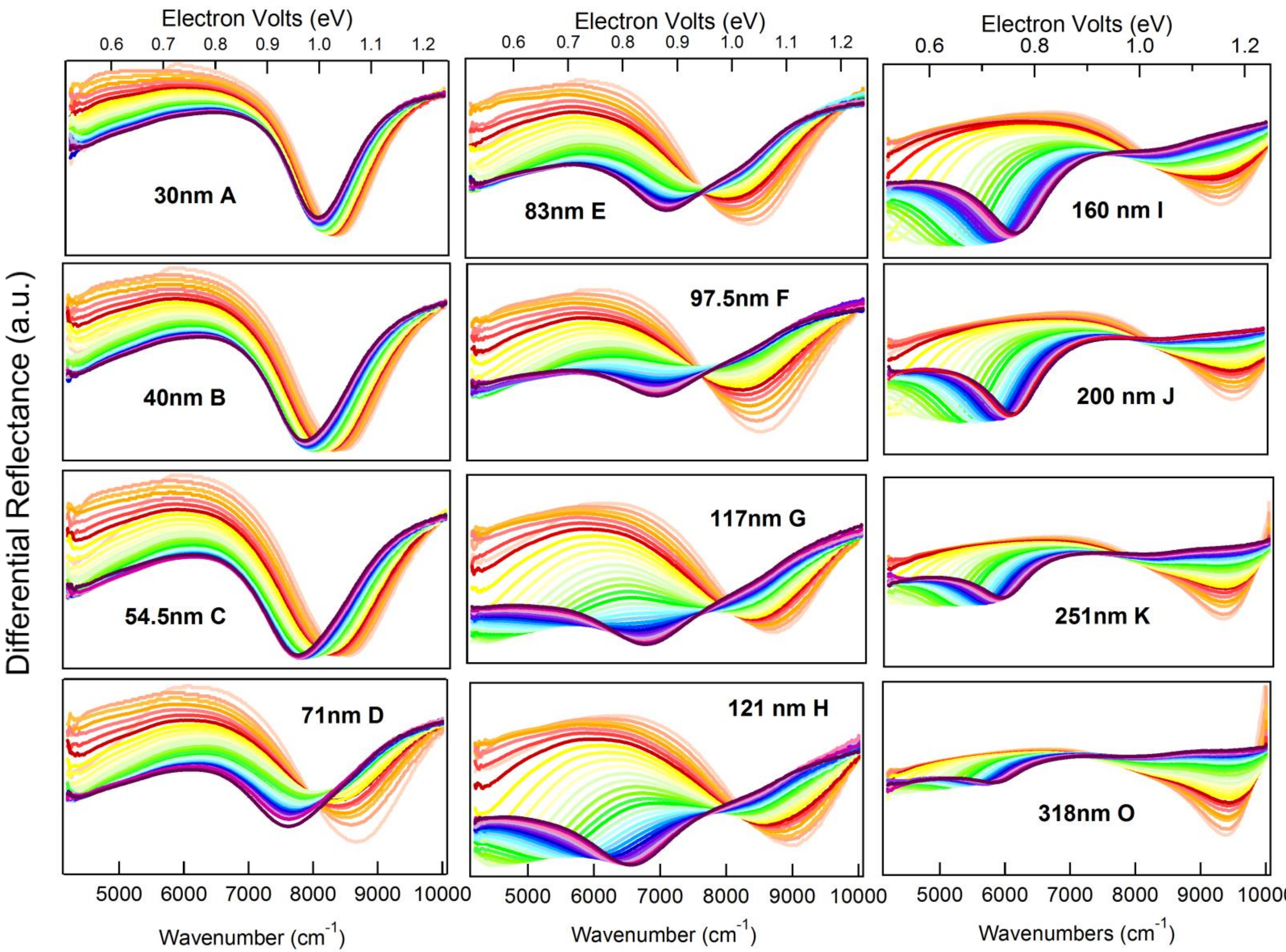


Rhodes, C.L. ; Aspnes, D.E. ; Maria, J.-P.; Franzen, S. et al. "Dependence of Plasmon Polaritons on the Thickness of Indium Tin Oxide Thin Films" J. Appl. Phys. **2008,** 103, Art. No. 093108

Surface Plasmon Resonance on ITO

Experimental

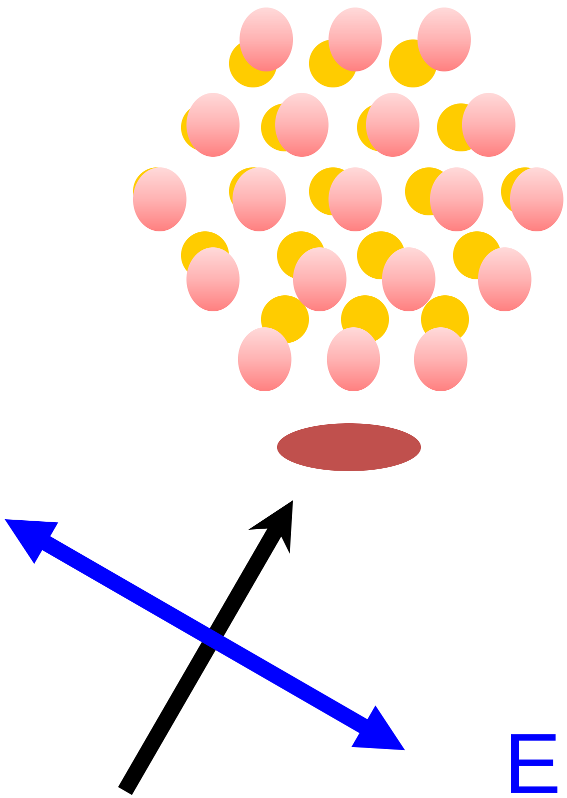
Angle Range: 42°-53°



Rhodes, C.L. ; Aspnes, D.E. ; Maria, J.-P.; Franzen, S. et al. "Dependence of Plasmon Polaritons on the Thickness of Indium Tin Oxide Thin Films" J. Appl. Phys. **2008,** 103, Art. No. 093108

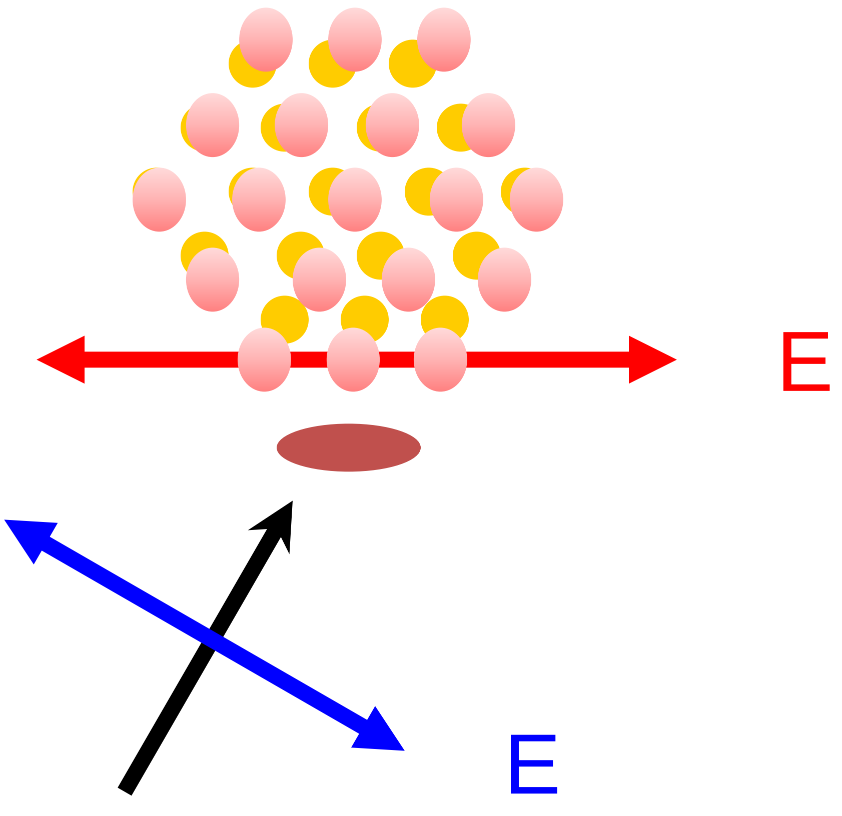
Concept of a LSPR
Localized Surface Plasmon Resonance

$\lambda >> d$



Teranishi et al. *J. Am. Chem. Soc.*, **2009**, *131*, 17736–17737

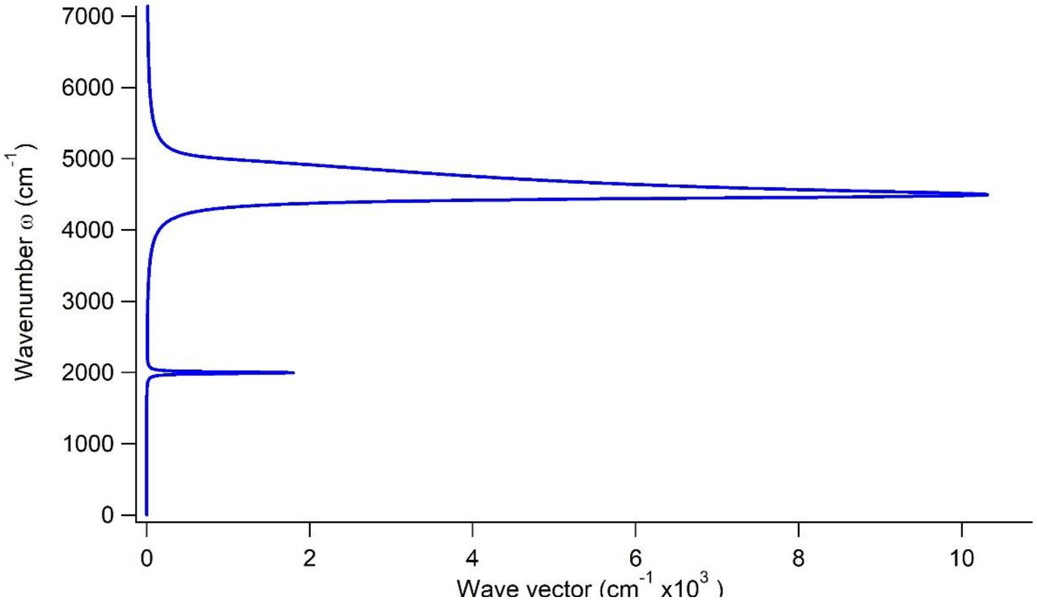
Concept of a LSPR
Localized Surface Plasmon Resonance
Field at molecule = E + E



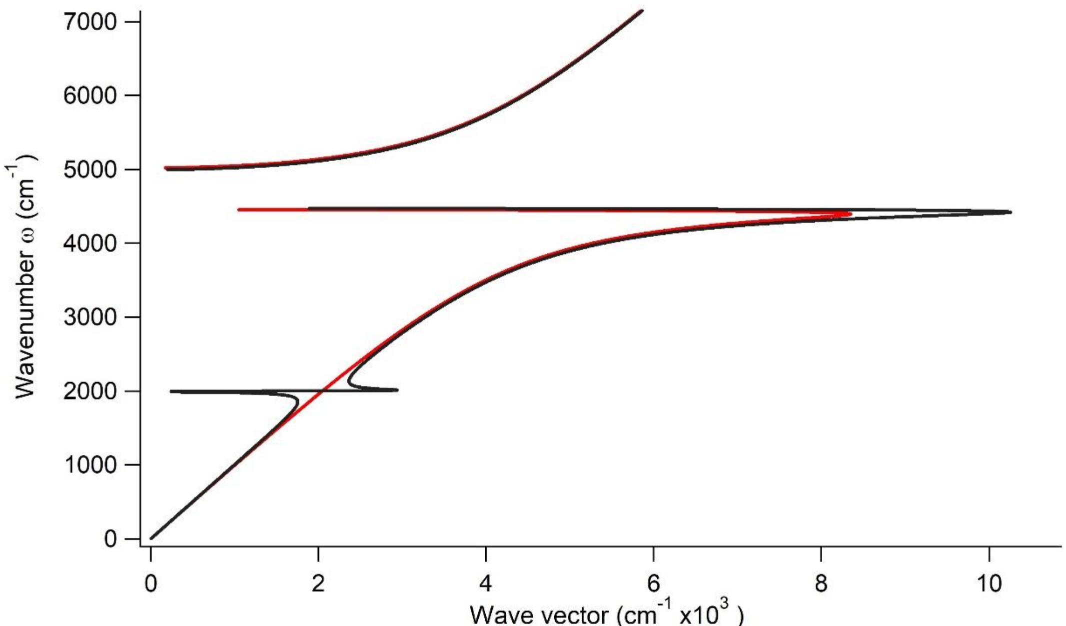
Are the phases the same?

This is a requirement for enhancement!

How are LSPR and SPR related?

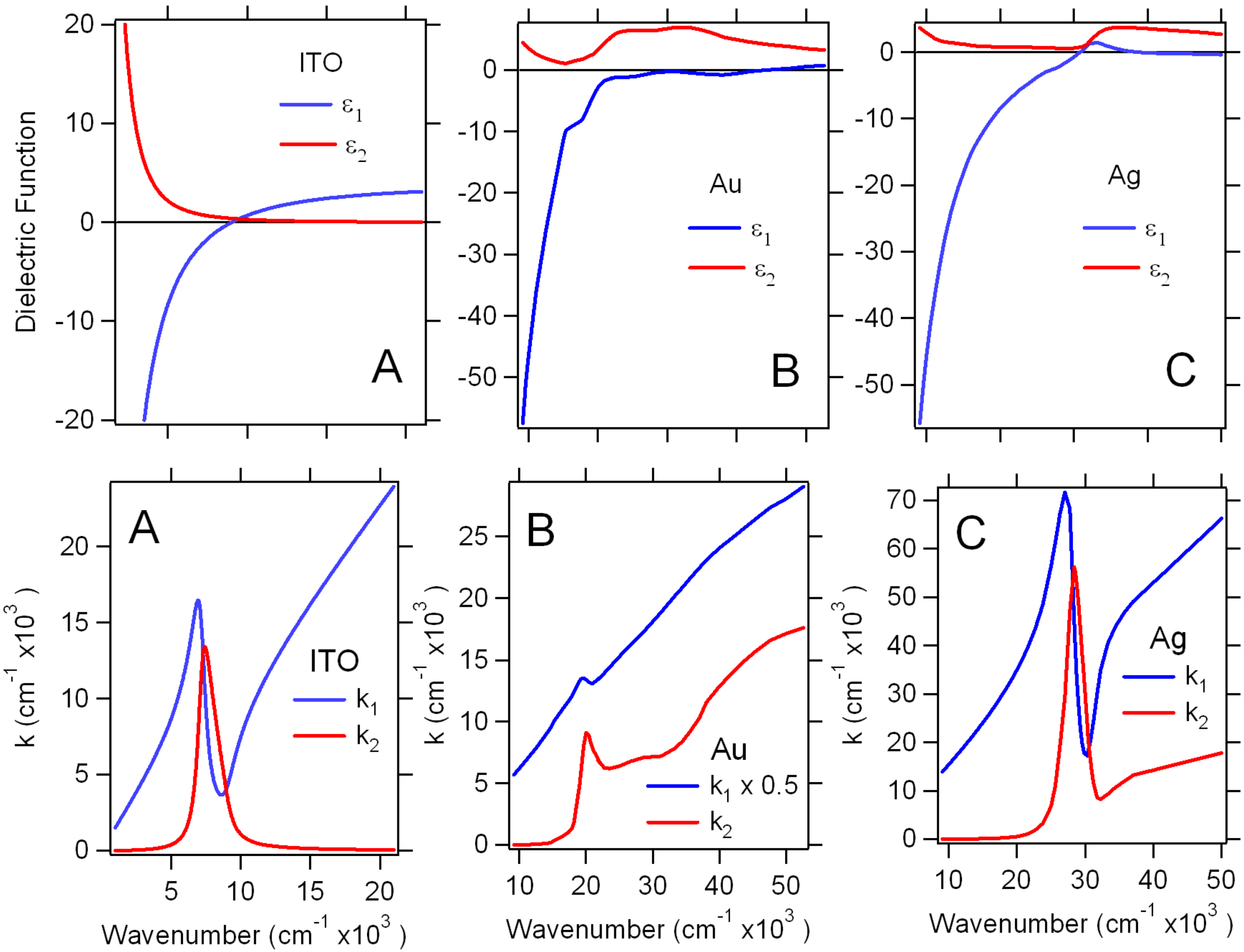


LSPR
Imaginary part
Absorption



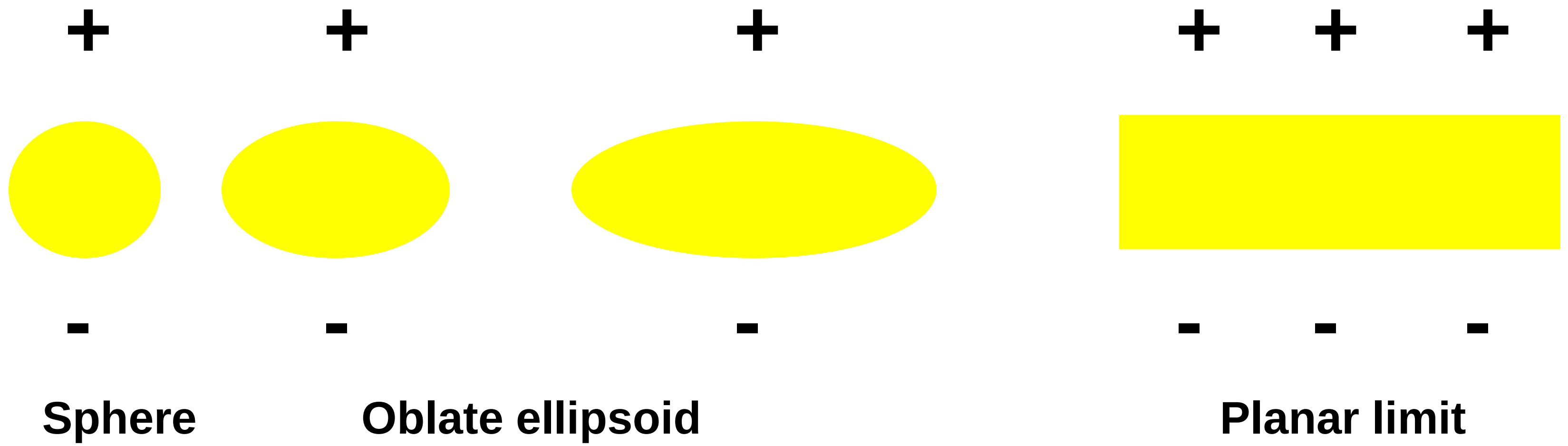
SPR
Real part
Disperson

Absorption and dispersion in conductors



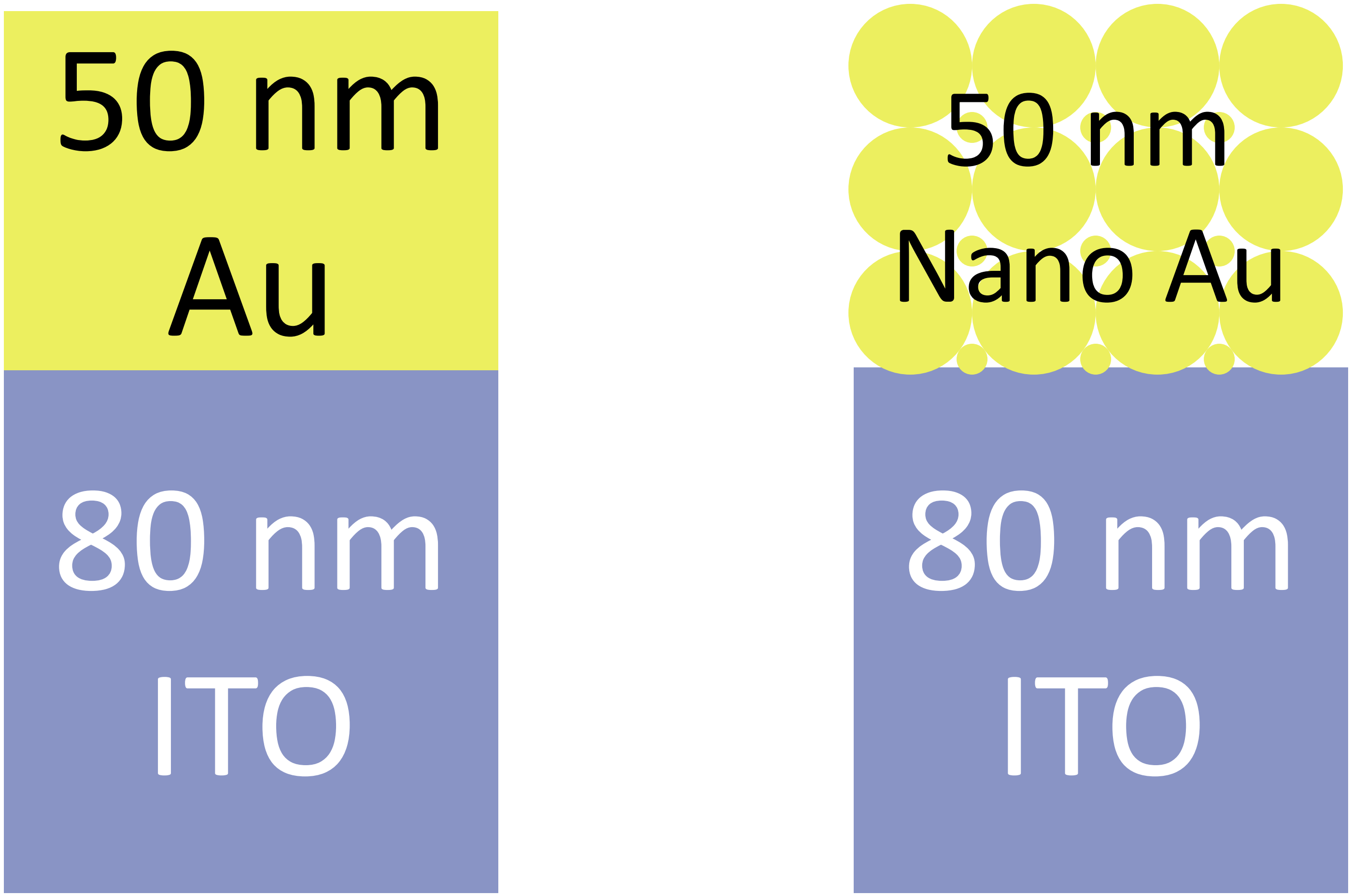
Franzen, S. "Surface Plasmon Polaritons and Plasma Absorption in Indium Tin Oxide Compared to Silver and Gold" J. Phys. Chem. C 2008, 112, 6027-6032

The planar limit of LSPR as a limiting case of an oblate spheroid



The planar limit of LSPR as a collection of nanoparticles

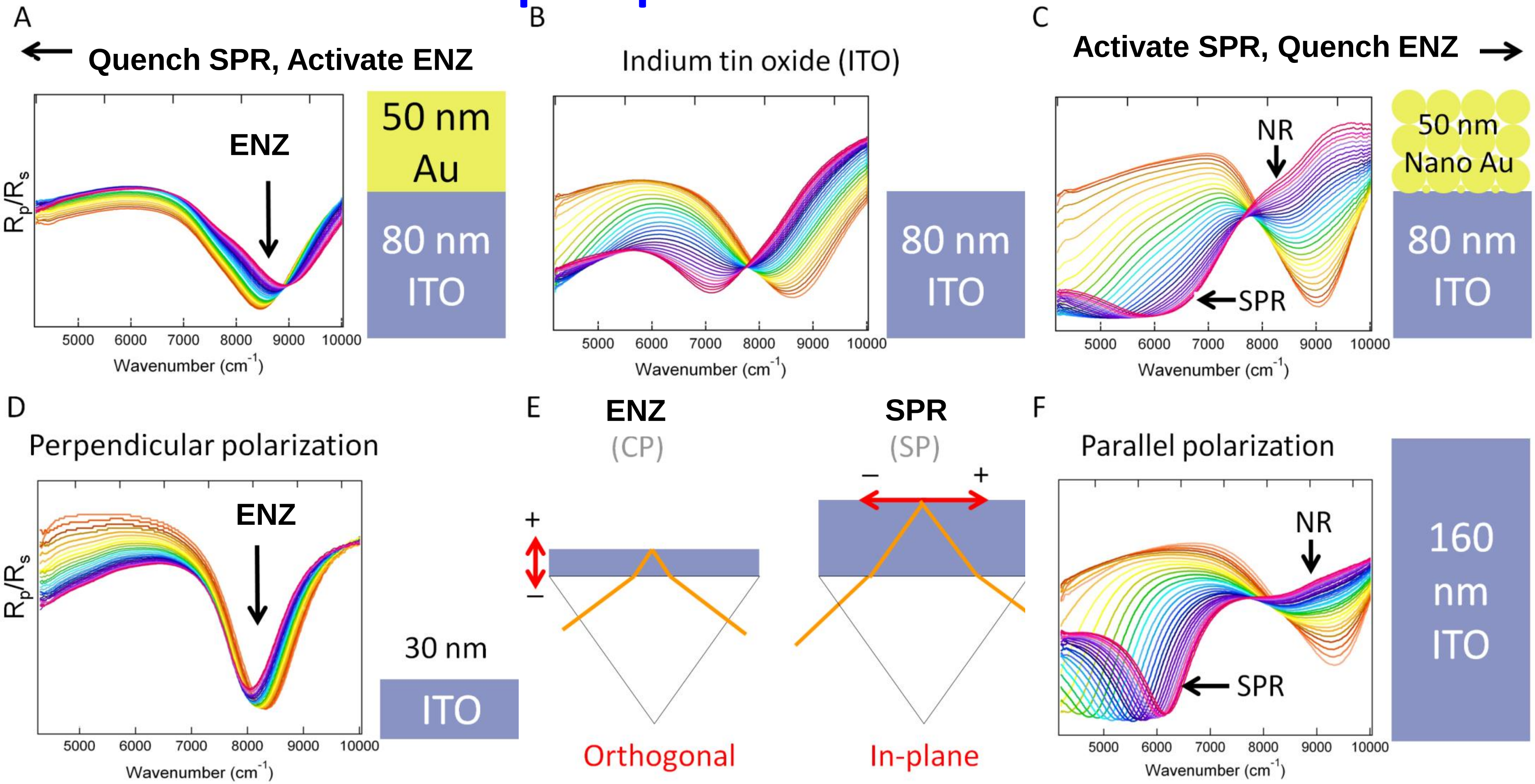
Hybrid plasmons



1. Franzen. S; Rhodes C.; Cerruti, M.; Efremenko, A.Y.; Gerber, R.W.; Losego, M.; Maria, J.-P.; Aspnes D.; "Equivalences between Gold and Indium Tin Oxide as Plasmonic Materials" Opt. Lett., 2009, 34, 2867-2869

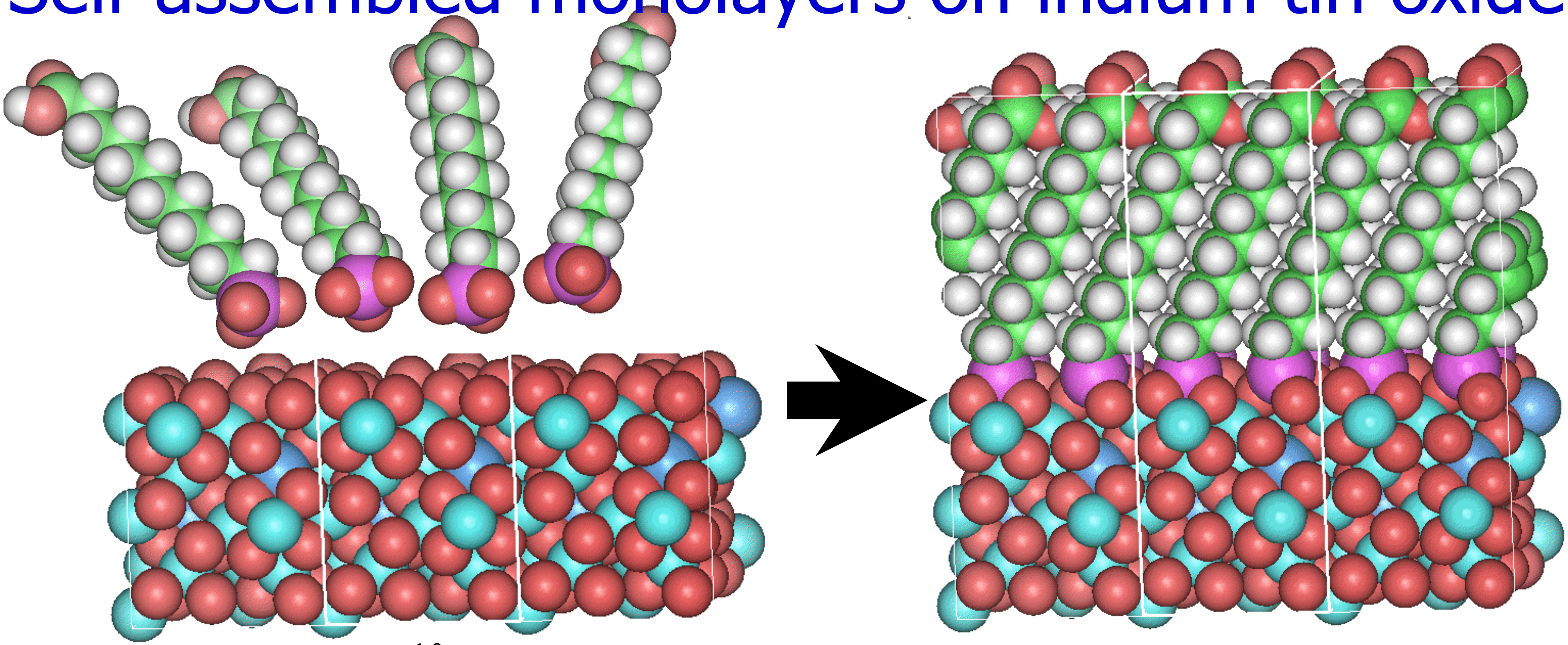
2. Gerber, R.W.; Leonard, D.N.; Franzen. S; "Conductive thin film multilayers of gold on glass formed by self-assembly of multiple size gold nanoparticles" Thin Solid Films, 2009, 517, 6303-6308

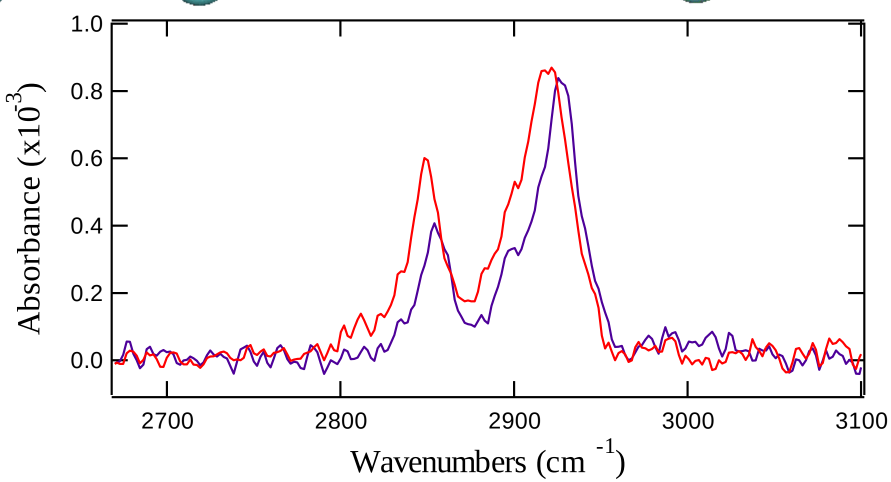
Optical proof of parallel polarization Of SPR and perpendicular ENZ mode



1. Franzen. S; Rhodes C.; Cerruti, M.; Efremenko, A.Y.; Gerber, R.W.; Losego, M.; Maria, J.-P.; Aspnes D.; "Equivalences between Gold and Indium Tin Oxide as Plasmonic Materials" Opt. Lett., 2009, 34, 2867-2869
2. Gerber, R.W.; Leonard, D.N.; Franzen. S; "Conductive thin film multilayers of gold on glass formed by self-assembly of multiple size gold nanoparticles" Thin Solid Films, 2009, 517, 6303-6308

Self-assembled monolayers on indium tin oxide





Brewer, S. H.; Brown, D. A.; Franzen, S. "Formation of thiolate and phosphonate adlayers on indium tin oxide: Optical and electronic characterization of the bonding" Langmuir **2002**, 18, 6857-6865

A new mid-IR plasmonic material that is a “good as gold and better”

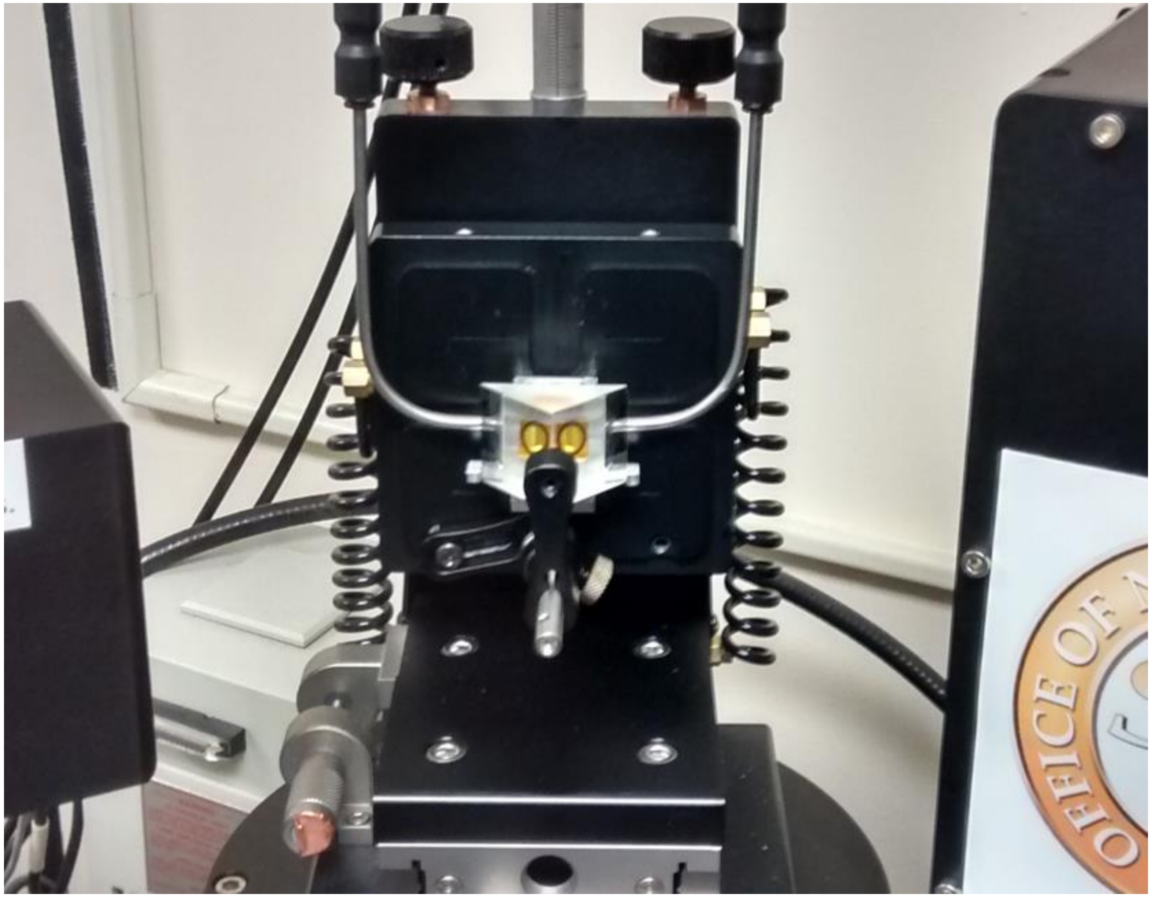
CdO:X (doped cadmium oxide)

Khamh, H.; Sachet, E.; Kelley, K. ; Maria, J.-P.; Franzen, S.; “As good as gold and better: conducting metal oxide materials for mid-infrared plasmonic applications” *J. Mater. Chem.* **2018**, 31, 8326-8342

Sachet, E.; Shelton , C.; Harris , J.; Gaddy , B.; Irving , D.; Donovan , B.; Hopkins, P.; Sharma , P.; Sharma, A.L.; Ihlefeld , J.; Franzen, S.; Maria, J.-P.; Curtarolo, S. " Dysprosium doped cadmium oxide: A gateway material for mid-infrared plasmonics " *Nature Materials*, 2015, 14, 414-420

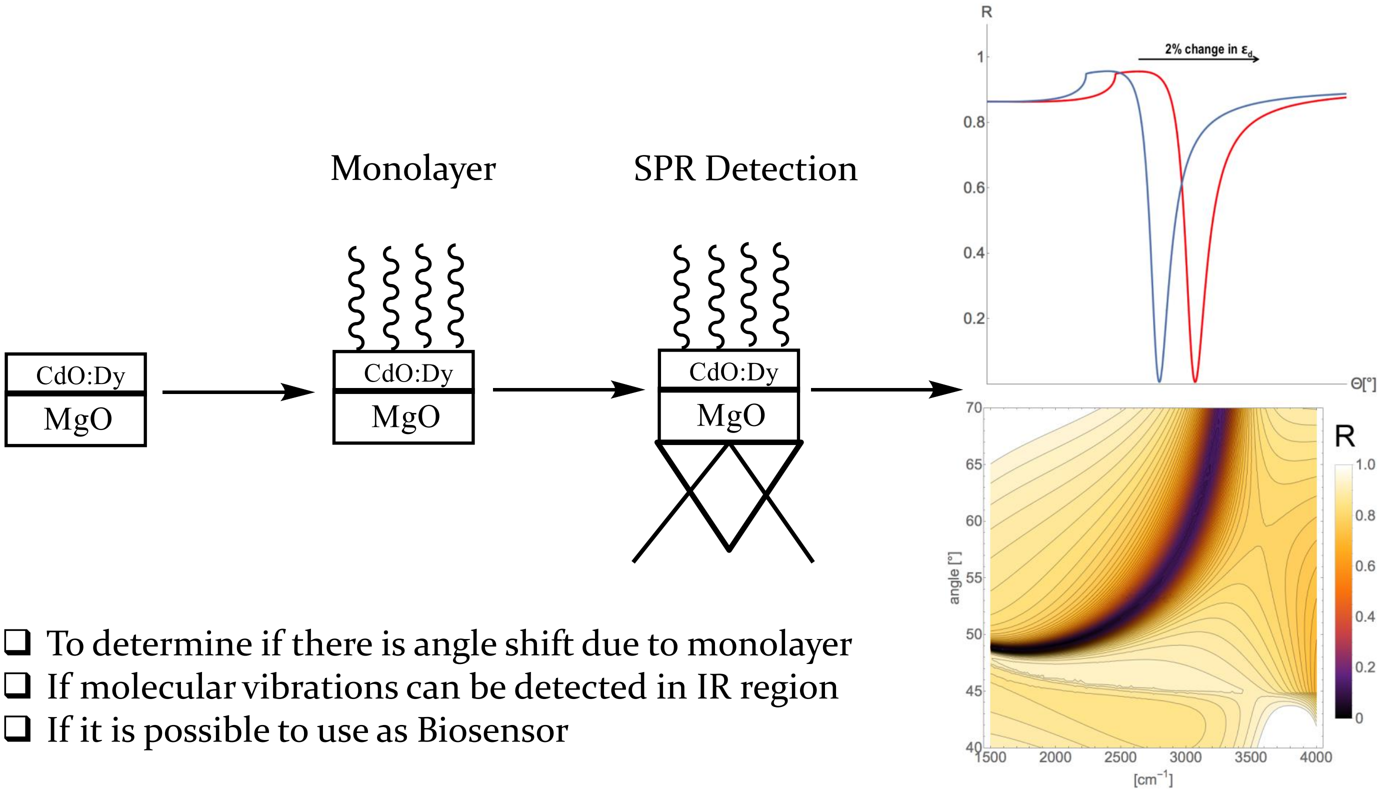
CdO:Dy for spectroscopy

Flow cell to record SPR maps at various pressures of N_2O



CdO:Dy SPR of monolayers

Motivation



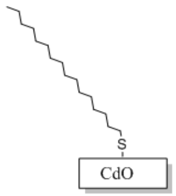
- ❑ To determine if there is angle shift due to monolayer
- ❑ If molecular vibrations can be detected in IR region
- ❑ If it is possible to use as Biosensor

NC STATE UNIVERSITY

Figures: Sachet, E. *Igarss 2014* 1–5 (2014). doi:10.1007/s13398-014-0173-7.2

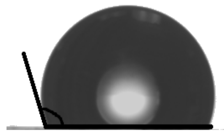
IR-SPR shows shifts as large as Au

Hexadecanethiol (HDT) SAM on CdO:Dy

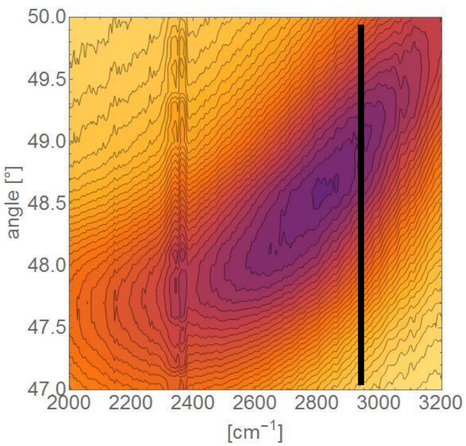


HDT: Hexadecanethiol

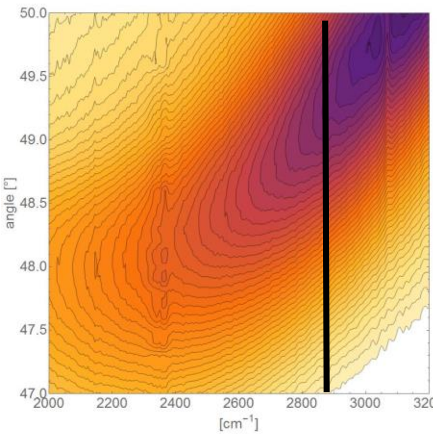
104^0



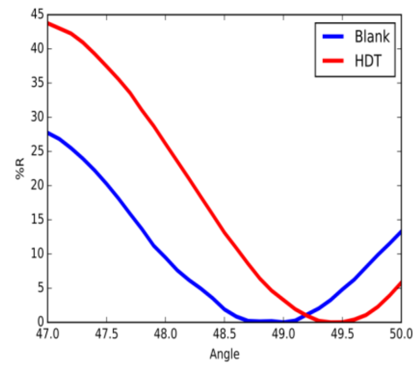
Method: 10 mM of HDT in THF for 1 hr at room temperature



$\mathbf{r_p/r_s}$



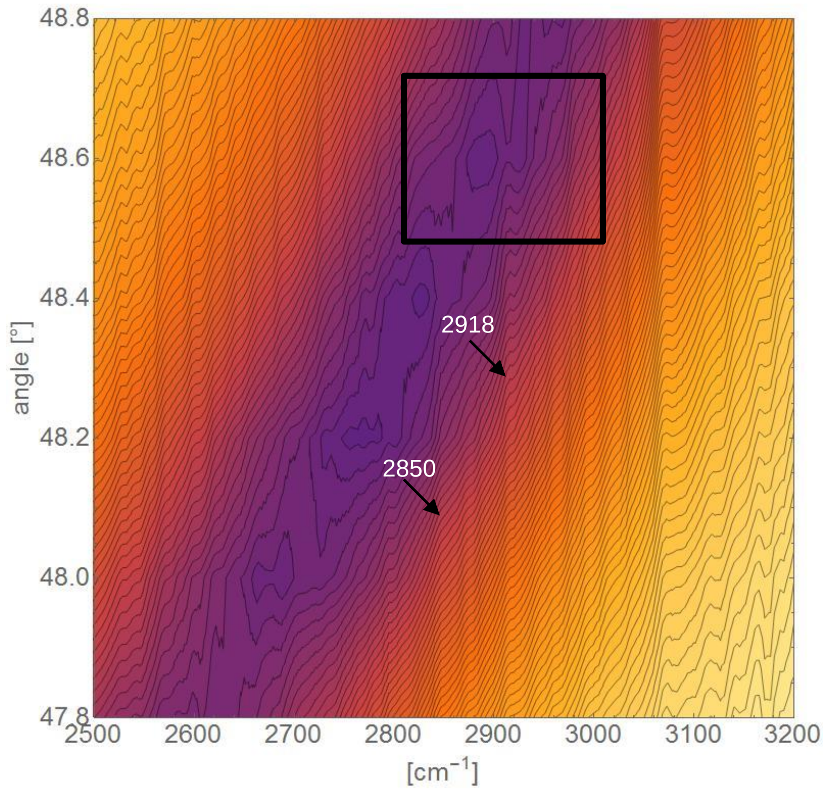
0.4^0 Angle Shift @ 2920 cm^{-1}

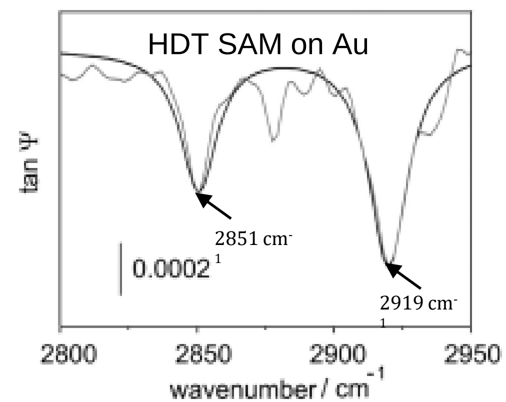


d = 250 nm, n = 2.6 x 10^{20} cm^{-3}, μ = 310 cm^{2}V^{-1}s^{-1}

NC STATE UNIVERSITY

Self-assembled monolayer packing is not optimal on metal oxides





Peak	Position [cm^{-1}]
$\nu_{as}(CH_3)_{ip}$	2964
$\nu_s(CH_3)_{FR}$	2937
$\nu_{as}(CH_2)$	2920
$\nu_s(CH_3)_{FR}$	2877
$\nu_s(CH_2)$	2850

Schröter, A., Kalus, M. & Hartmann. *Beilstein J. Nanotechnol.* **3,** 65–74 (2012)
Rosu, D. M. *et al*. *Langmuir* **25,** 919–23 (2009).

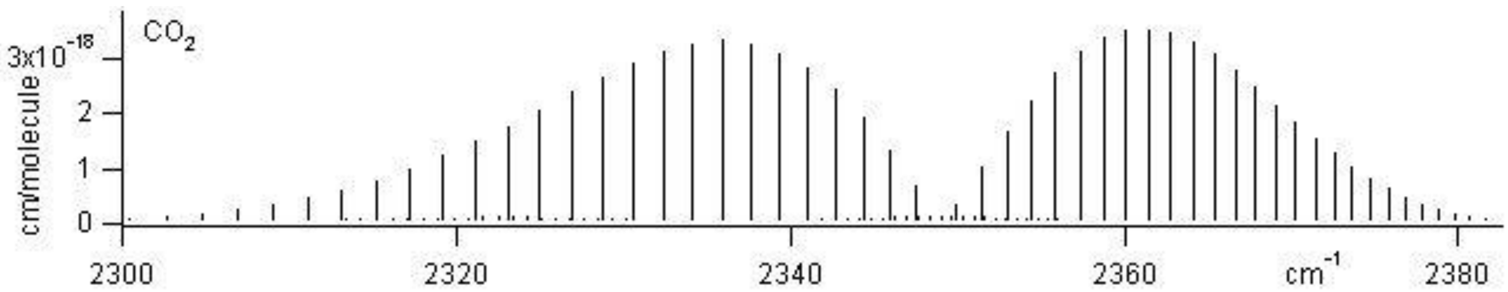
How can we detect surface enhancement parallel to the surface?

SEIRA (surface enhanced infrared)

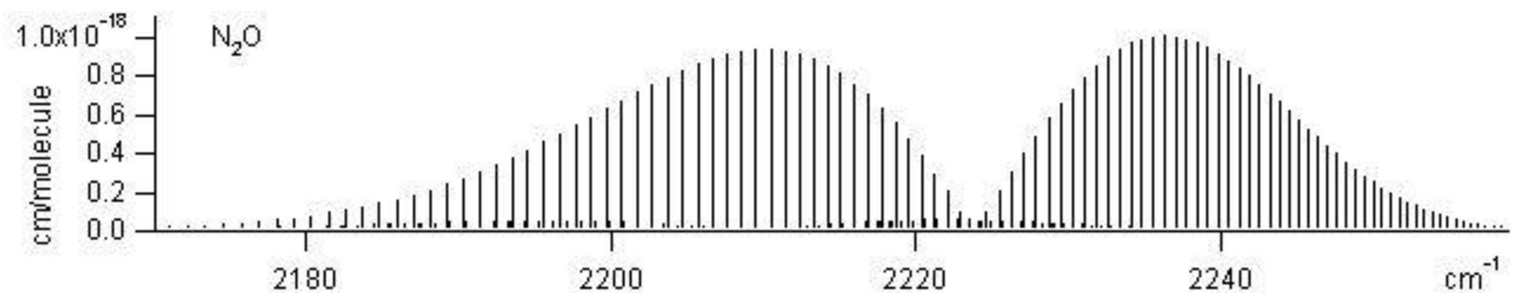
Gas absorption bands in the IR

Absorption bands alter the dielectric function of the environment

CO_2



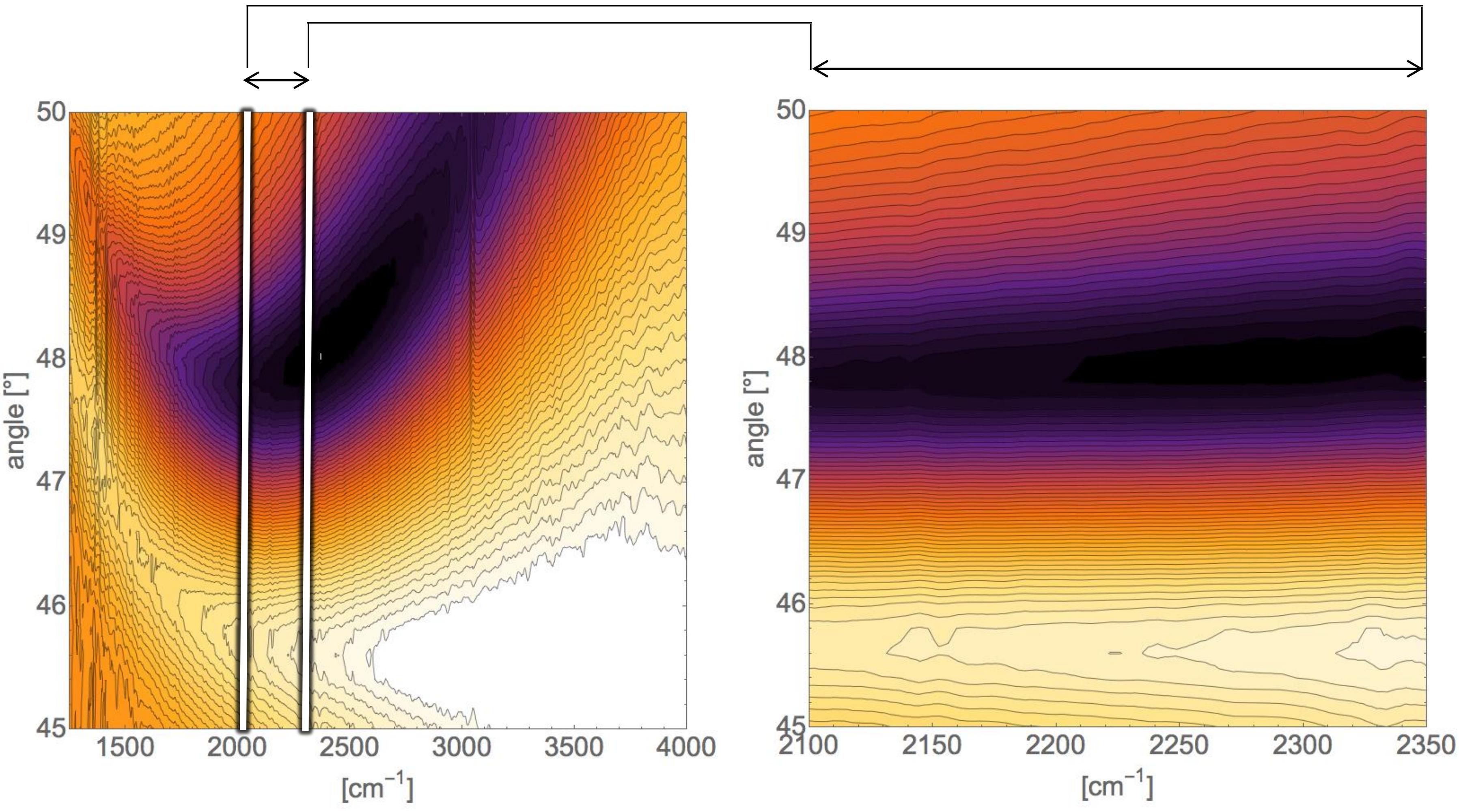
N_2O



[HITRAN 2004 database]

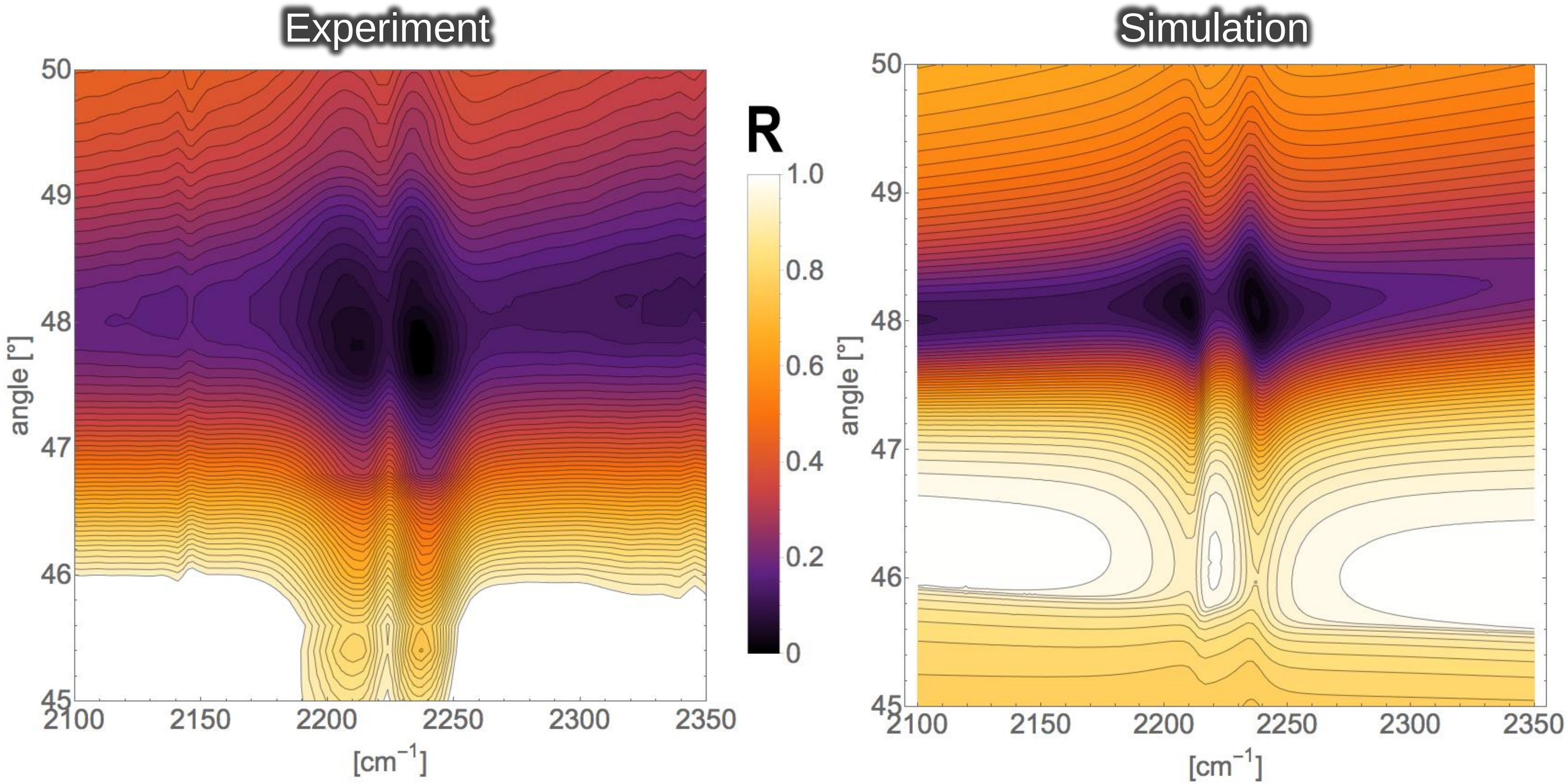
CdO:Dy for spectroscopic dection

CdO:Dy sample in air represents the background



Detection of gas phase N_2O by IR-SPR

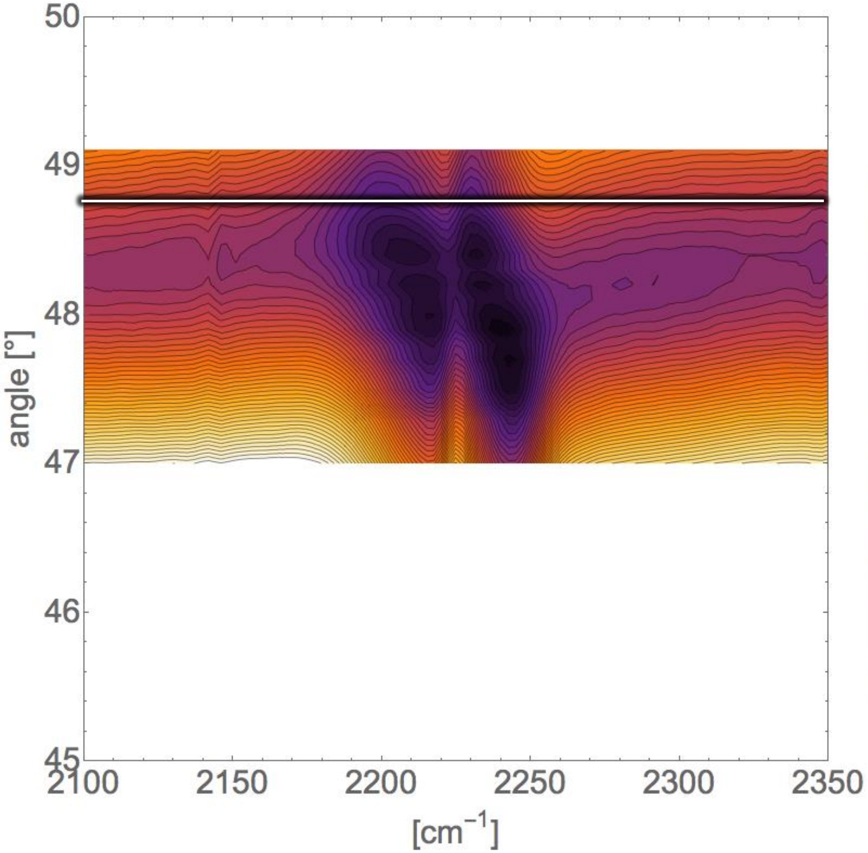
20 PSI of N_2O



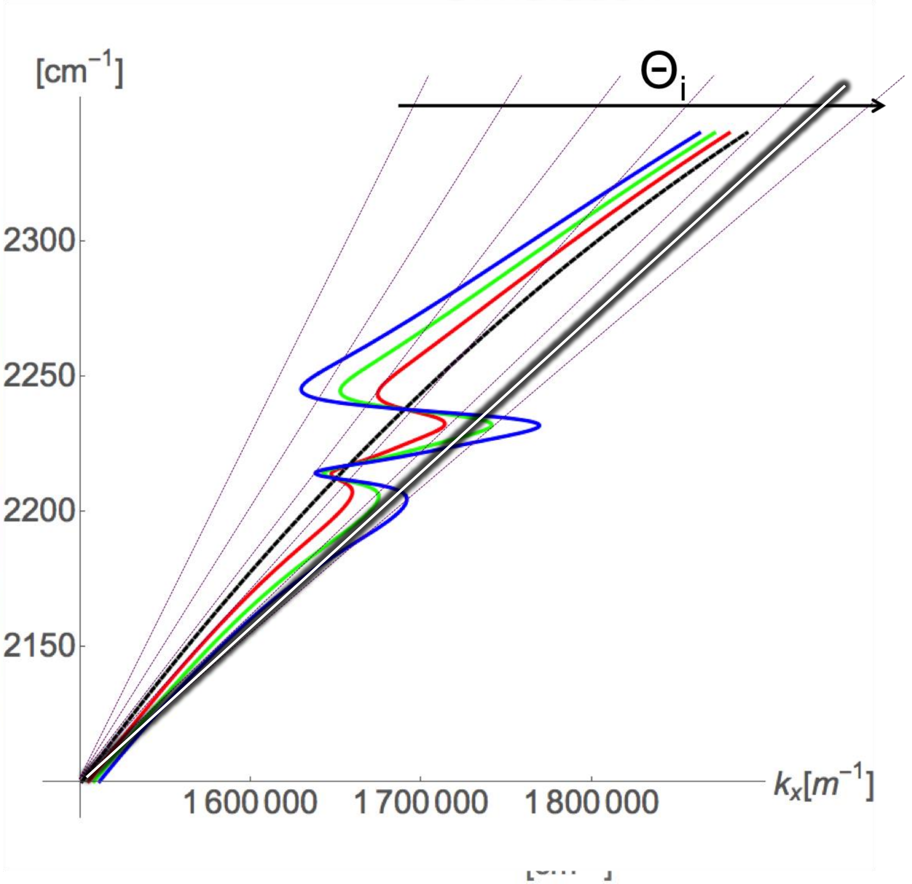
Detection of gas phase N_2O by IR-SPR

80 PSI of N_2O

Experiment



Simulation



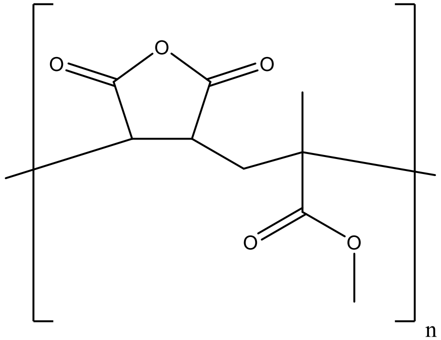
How can we use these materials?

SEIRA (surface enhanced infrared) is a sensitive way to detect optical responses in polymers

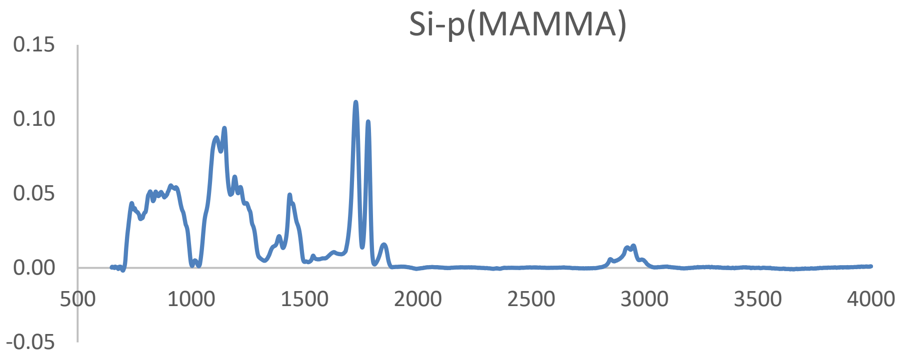
This is analogous to Biacore, but much more sensitive

Polymers for systematic detection

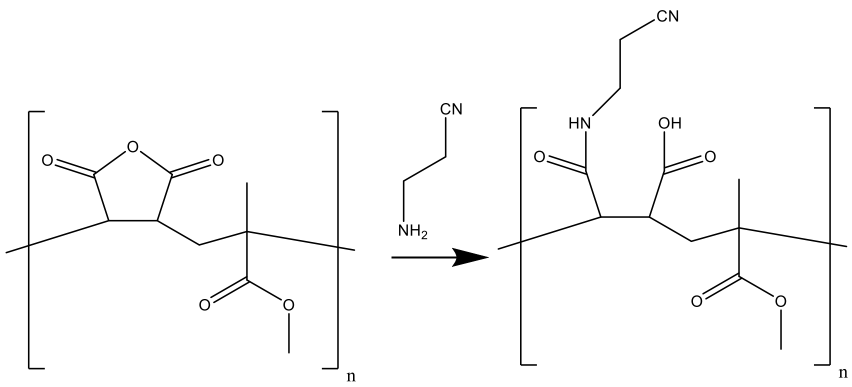
Poly(methyl methacrylate-*alt*-maleic anhydride) - PMAMMA

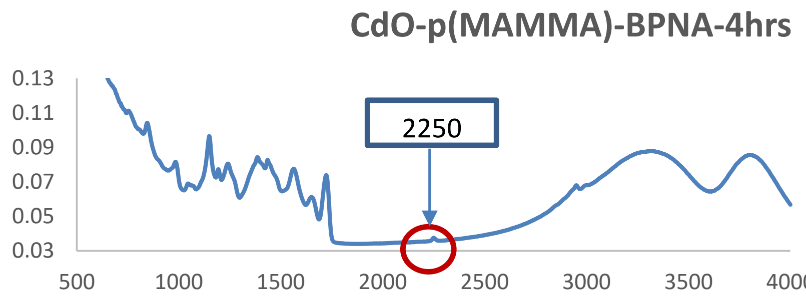


ATR data



Poly(methyl methacrylate-*alt*-maleic anhydride) + β-aminopropionitrile (PMAMMA+BAPN)

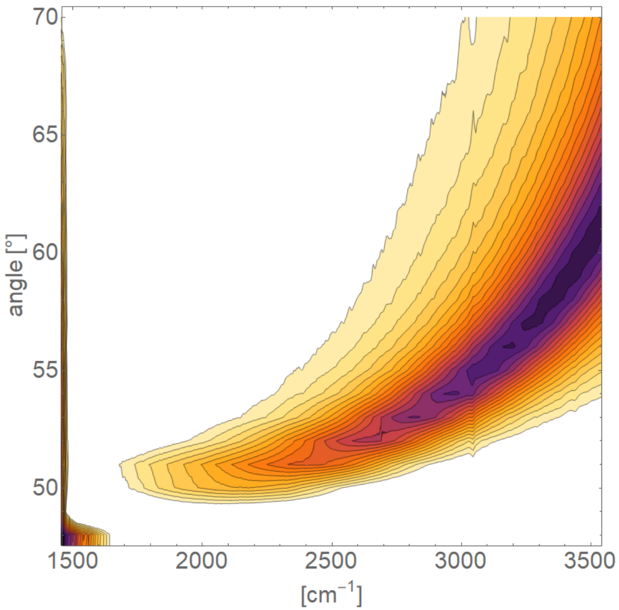




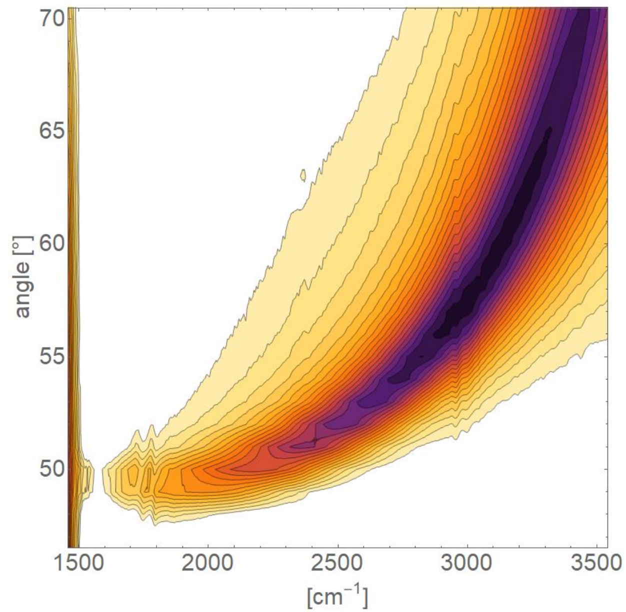
Polymers for systematic detection

Data showing 2000 – 2500 cm^{-1}

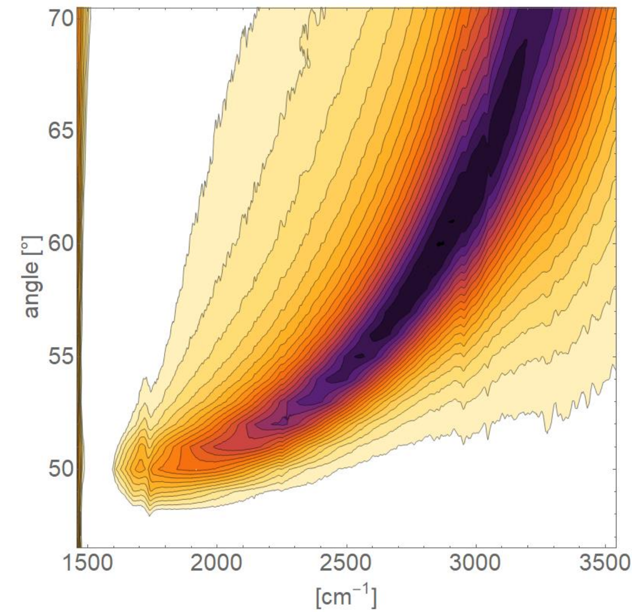
Bare

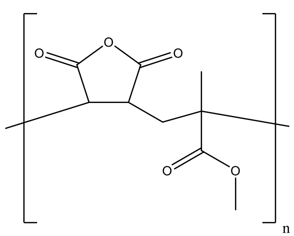


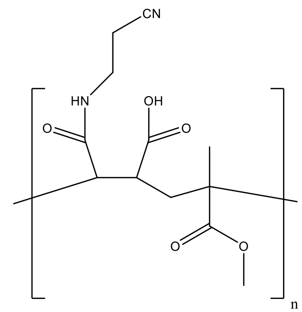
Poly(MAMMA)



Poly(MAMMA)-BAPN



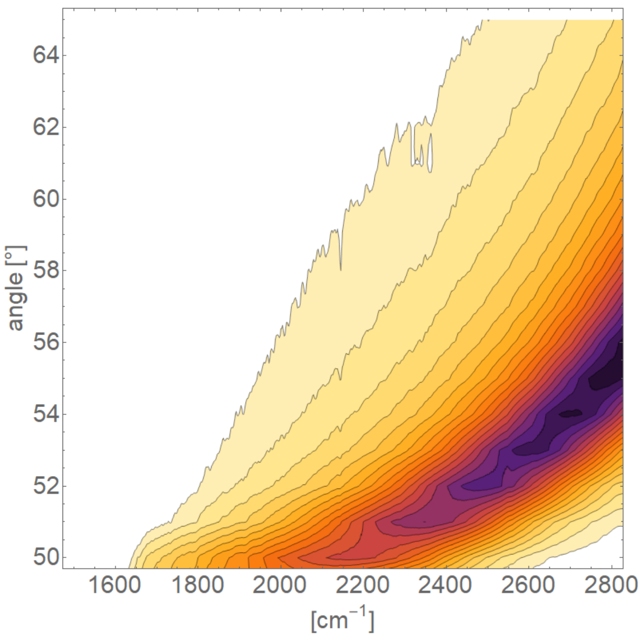




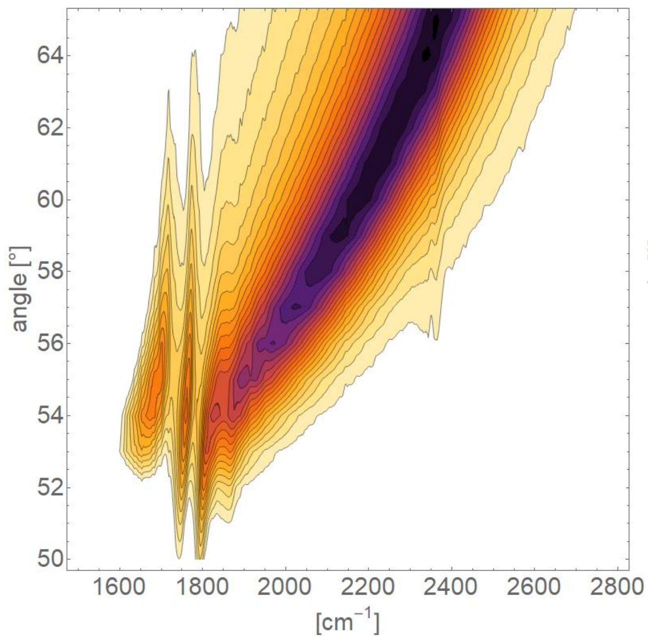
Polymers for systematic detection

3.5% PMAMMA Solution Spin Coated + BAPN

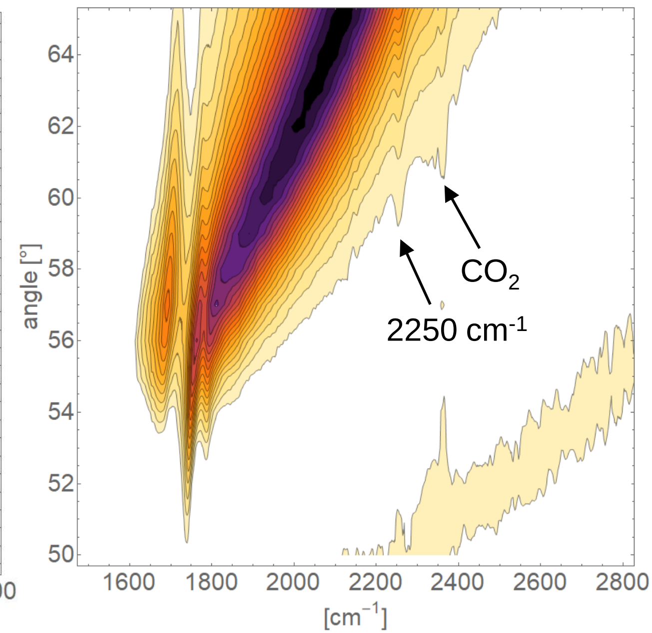
Blank

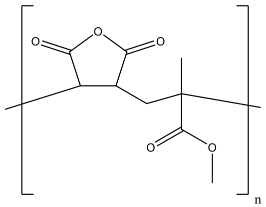


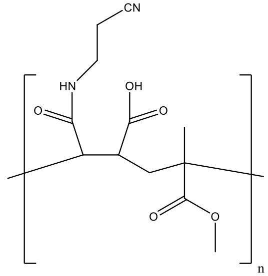
p(MAMMA)



p(MAMMA)-

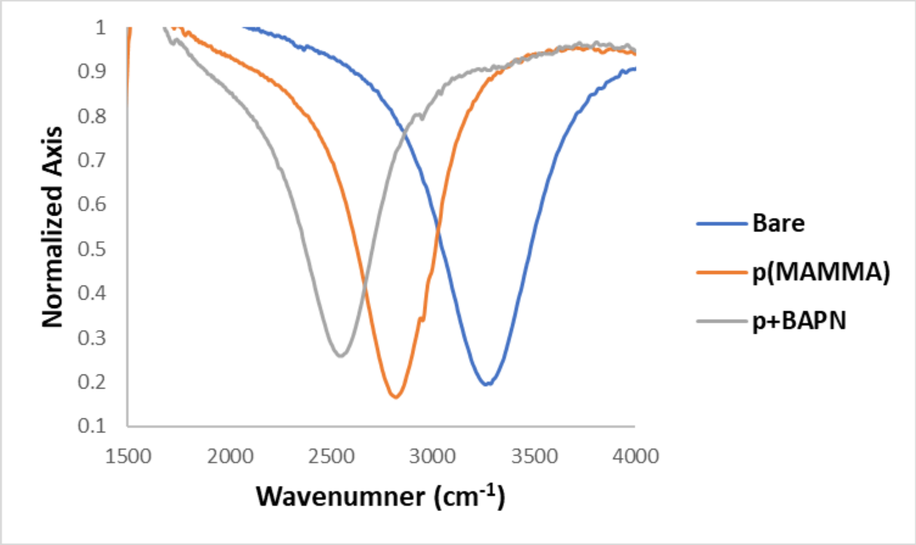




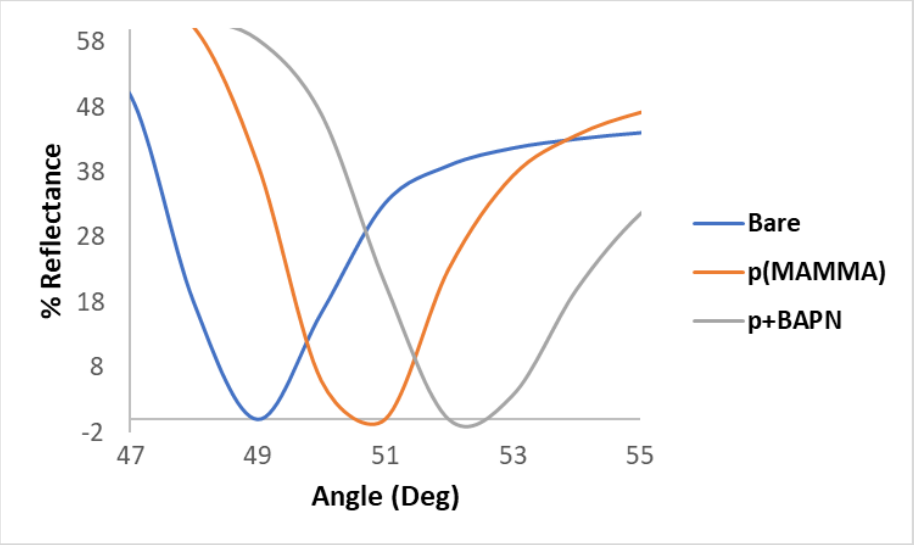


Polymers for systematic detection

SPR r_p/r_s at 55° Angle



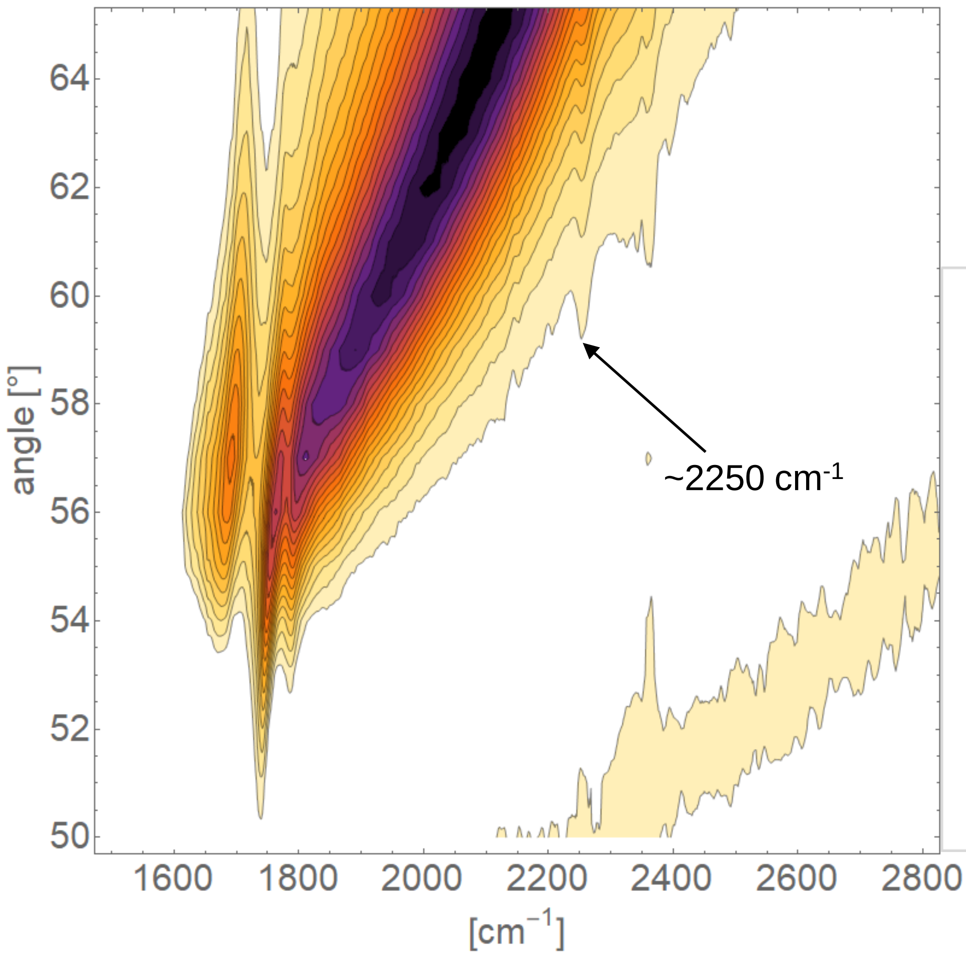
Angle Shift at 2250.8 cm^{-1}



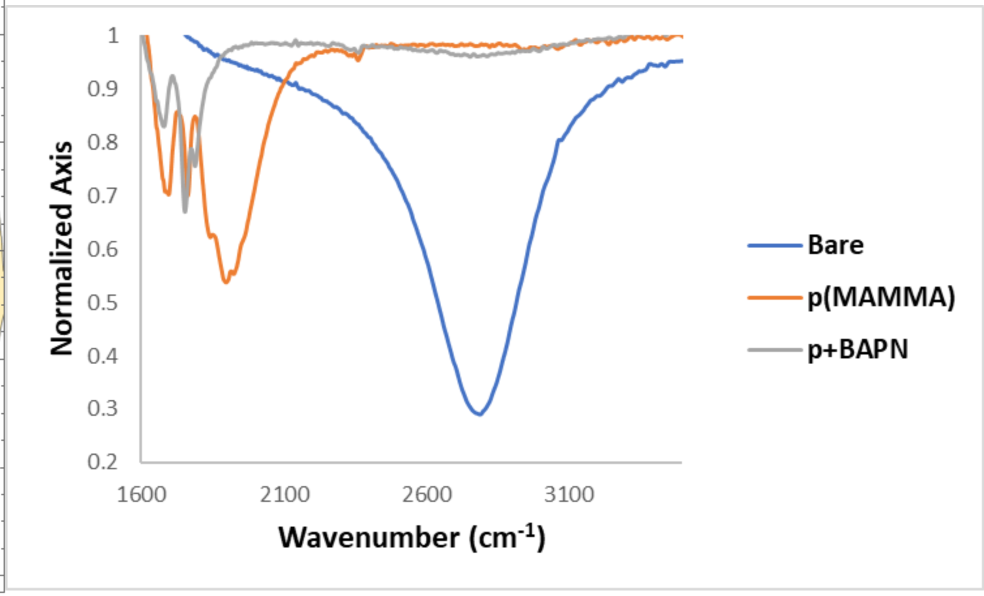
Bare -> p(MAMMA) = 2° shift
P(MAMMA) -> p+BAPN = 1° shift
Overall -> 3° shift

Polymers for systematic detection

3.5% Poly(MAMMA) + BAPN

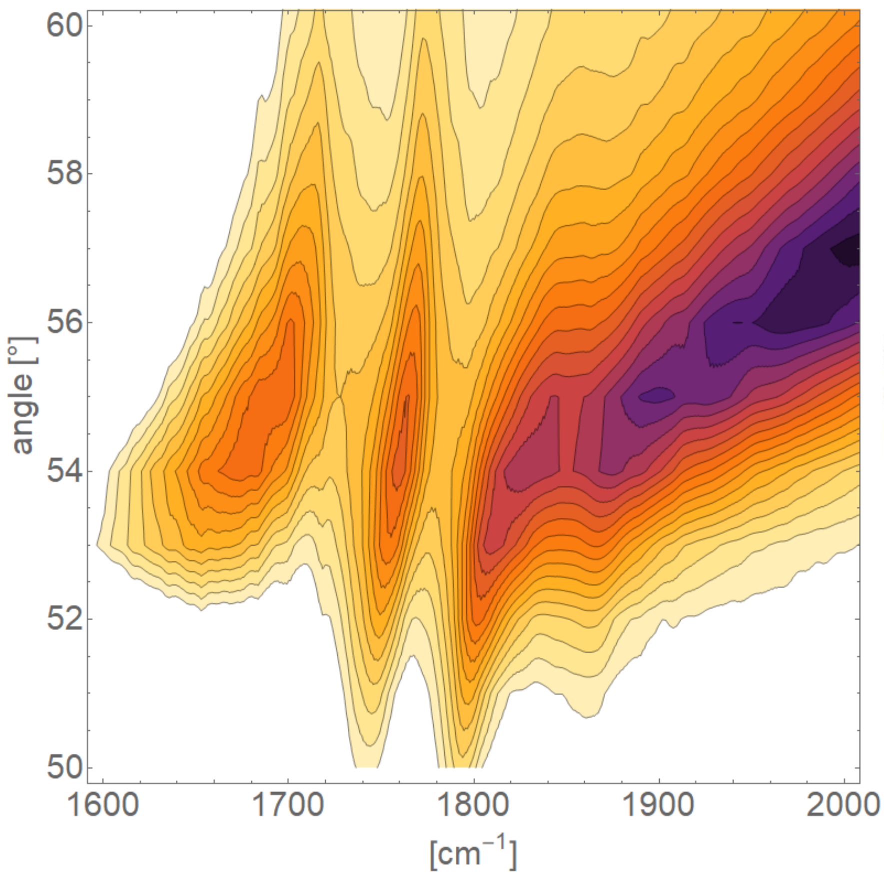


SPR r_p/r_s at 55° Angle

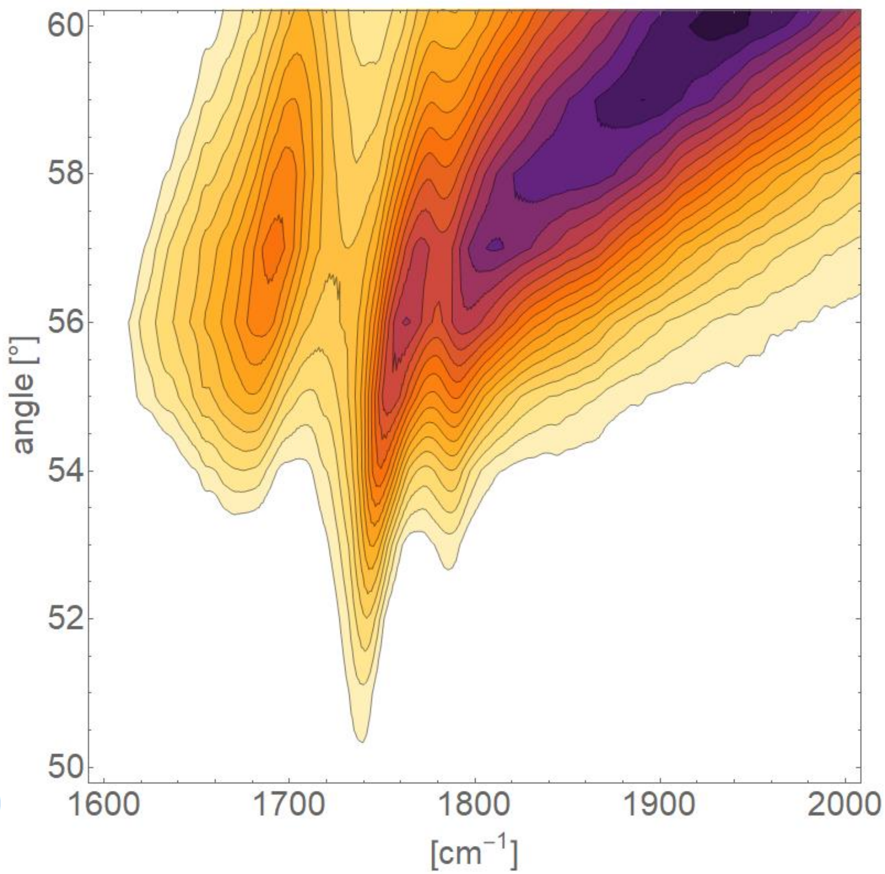


Polymers for systematic detection

3.5% poly(MAMMA)



3.5% poly(MAMMA) + BAPN



Conclusion

This research demonstrates the equivalence of noble metals (Au and Ag) with conducting metal oxides (CMOs) as materials for surface plasmon resonance. Since CMOs have bulk plasma frequencies that are in the infrared region, they are natural materials for studies of the interaction of molecular infrared transitions due to vibrations and the SPR phenomena. Although Ag and Au can be used to SEIRA, CMOs have the advantage that they can be tuned and the vibrations can be studied both on and off resonance. We find that molecular vibrations are weakly coupled to surface plasmons. There is no evidence of strong coupling or Rabi splitting in these systems.