Empa
Materials Science and Technology

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Advanced materials processing with intelligent systems

Light materials interaction

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References:
https://micro.magnet.fsu.edu/primer/virtual/virtual.html

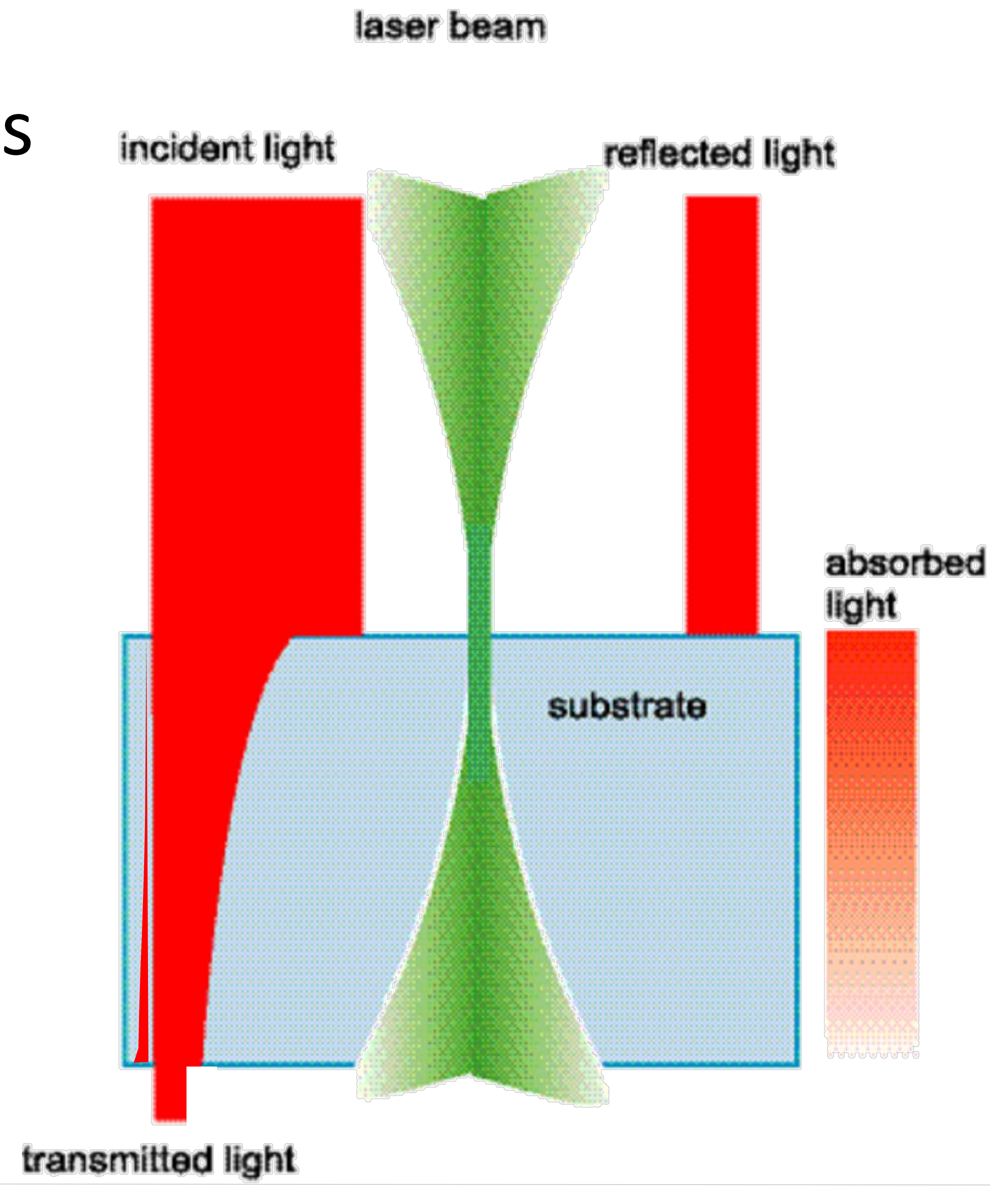
Content

Content

- Light meets materials
  - Reflection
  - Absorption
  - Transmission
  - Scattering

Light meets material

- Light meets materials
  - Reflexion
  - Absorption
  - Transmission
  - Scattering



Fresnel Equations

Light intensity (Power) coefficients:

$$R^{\sigma} = \left(r^{\sigma}\right)^2$$

$$R^{\pi} = \left(r^{\pi}\right)^2$$

In case of normal incidence:

$$R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2$$

Do not forget to use complex refractive index, if absorption is present!

$$R = \left(\frac{\tilde{n}_1 - \tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2}\right)^2_{\text{normal incidence}}$$

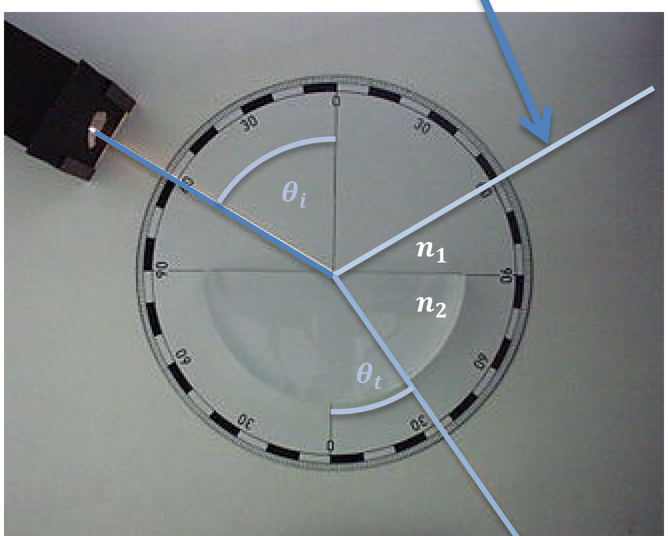
$$R^{\sigma} = \left(\frac{\tilde{n}_1 \cos(\theta_1) - \tilde{n}_2 \cos(\theta_2)}{\tilde{n}_1 \cos(\theta_1) + \tilde{n}_2 \cos(\theta_2)}\right)^2_{\text{general case}}$$

, etc.

Fresnel coefficients

- The materials refractive index determines the fraction of reflected light R

Can the reflected light intensity be calculated?



The reflexion coefficient R is polarization dependent:

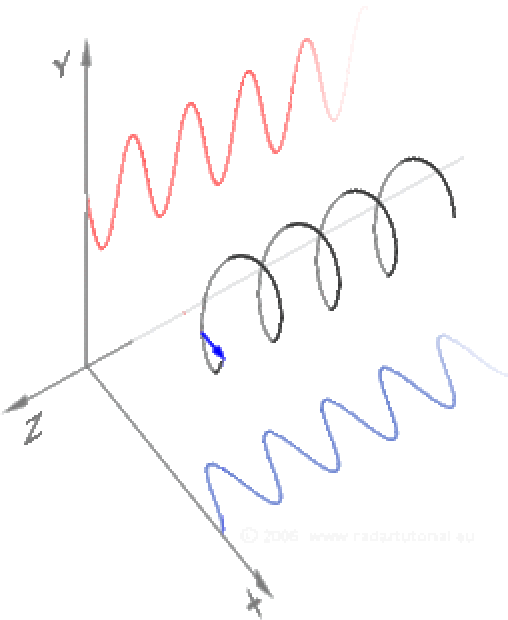
$$R_s = \left| \frac{n_1 \cdot \cos\theta_i - n_2 \cdot \cos\theta_t}{n_1 \cdot \cos\theta_i + n_2 \cdot \cos\theta_t} \right|^2$$

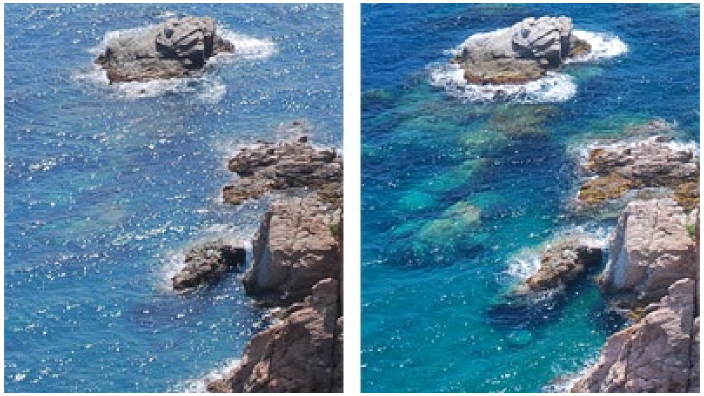
$$R_p = \left| \frac{n_2 \cdot \cos\theta_i - n_1 \cdot \cos\theta_t}{n_2 \cdot \cos\theta_i + n_1 \cdot \cos\theta_t} \right|^2$$

- $n_{1,2}$ refractive index of medium 1 et 2
- θ_i incident angle
- θ_t transmitted angle

Polarisation

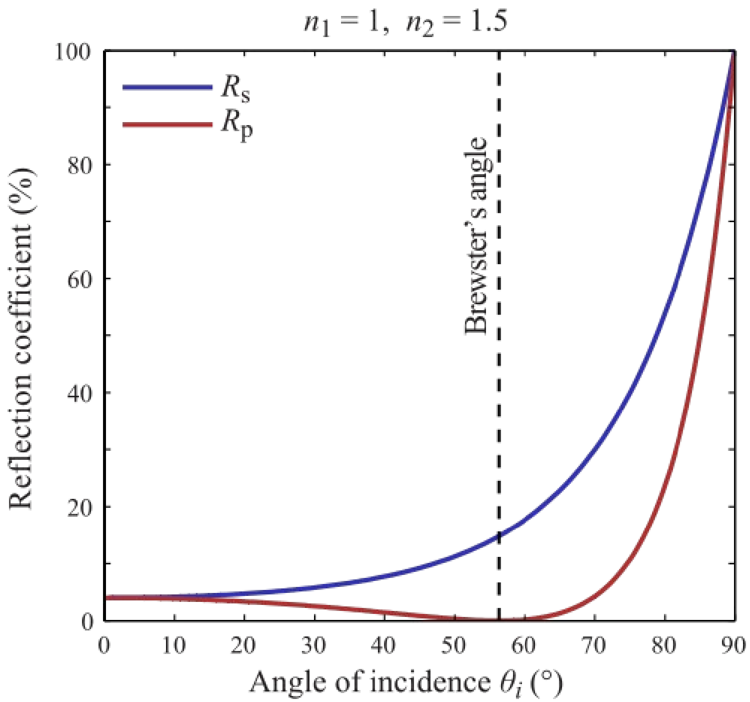
- What is polarization?
- For linearly polarized light:
  - s – polarisation ⊥ (senkrecht; german for perpendicular)
    - Electric field vector perpendicular to light propagation plane
  - p - polarisation II (parallel)
    - Electric field vector lies in the light propagation plane





polarization filters are often used in photographie

Angle de Brewster



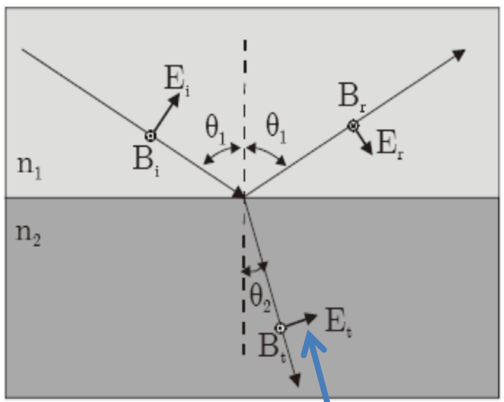
$$R_p = \left| \frac{n_2 \cdot \cos\theta_i - n_1 \cdot \cos\theta_t}{n_2 \cdot \cos\theta_i + n_1 \cdot \cos\theta_t} \right|^2 = 0$$

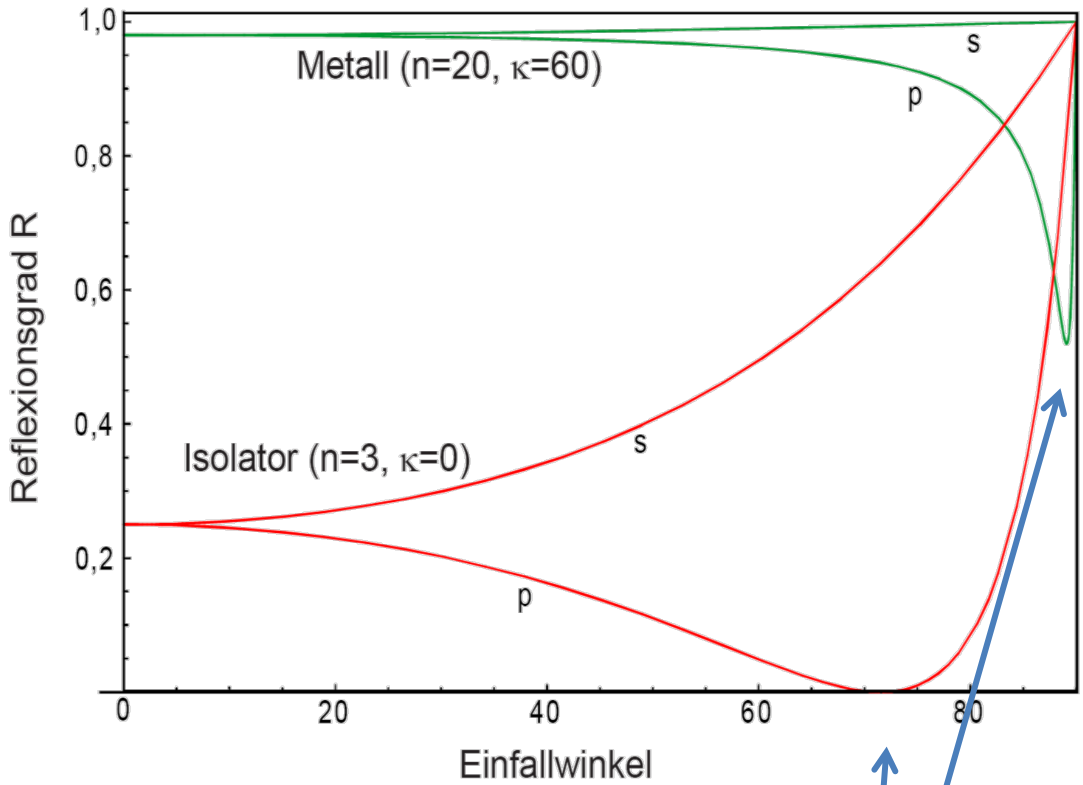
with Snell-Descartes law

$$\theta_B = \arctan\left(\frac{n_2}{n_1}\right)$$

Reflection

π-polarization (TM)
(Transversal Magnetic field)





Excited dipoles cannot reemit light in the direction parallel to the dipole vector ⇒ no reflected light if,

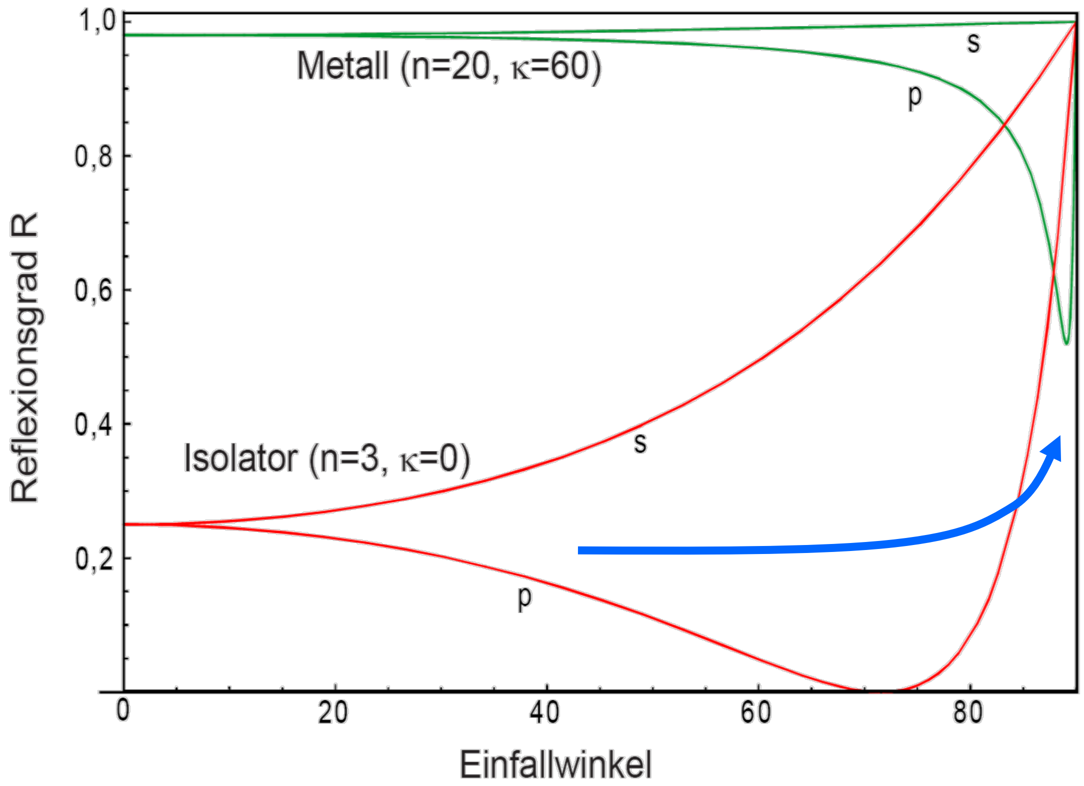
$$\theta_1 + \theta_2 = 90°$$

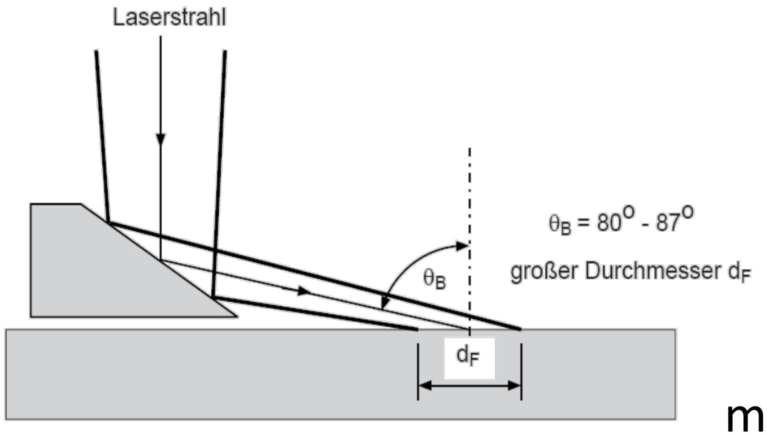
$$\theta_1^B = \arctan \frac{n_2}{n_1}$$

Brewster Angle

Reflection

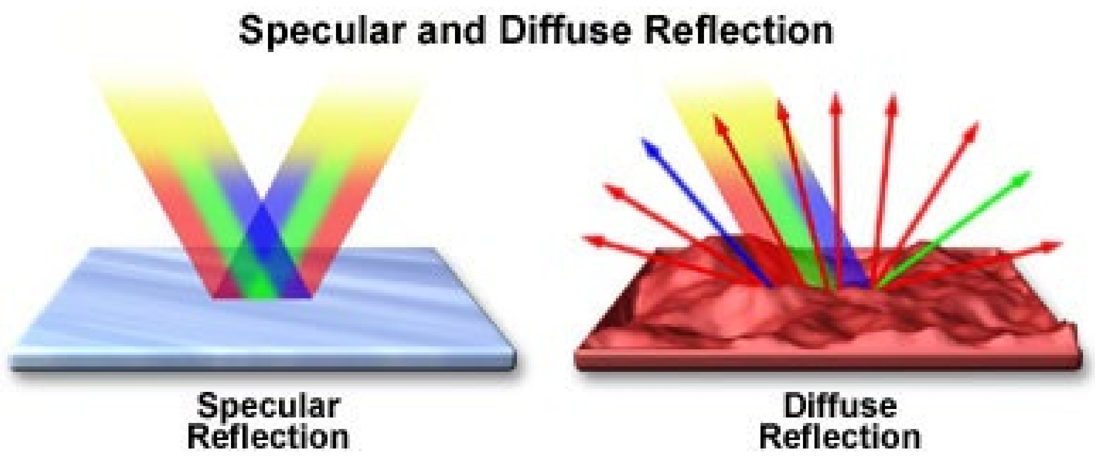
$$\theta_1^B = \arctan\frac{n_2}{n_1}$$



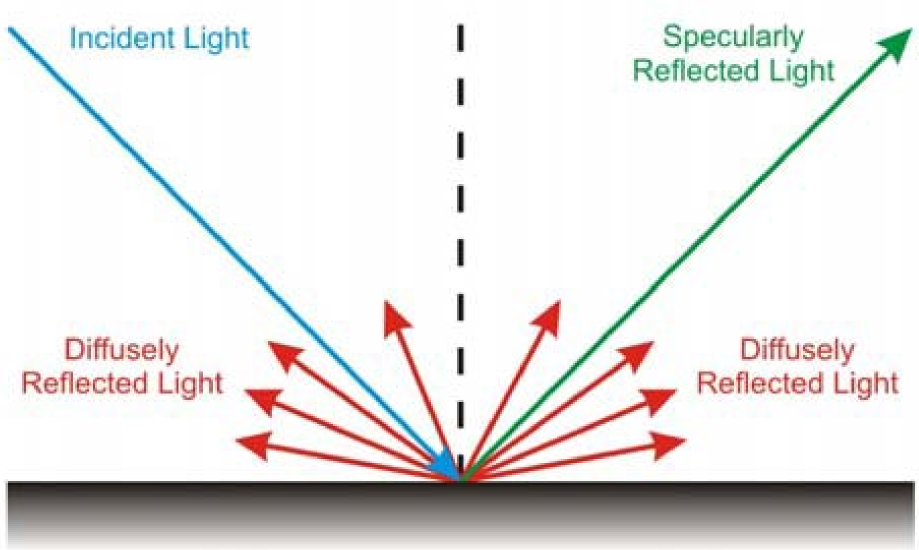


machining under Brewster angle
(increase absorption for metals)

Diffuse reflectance

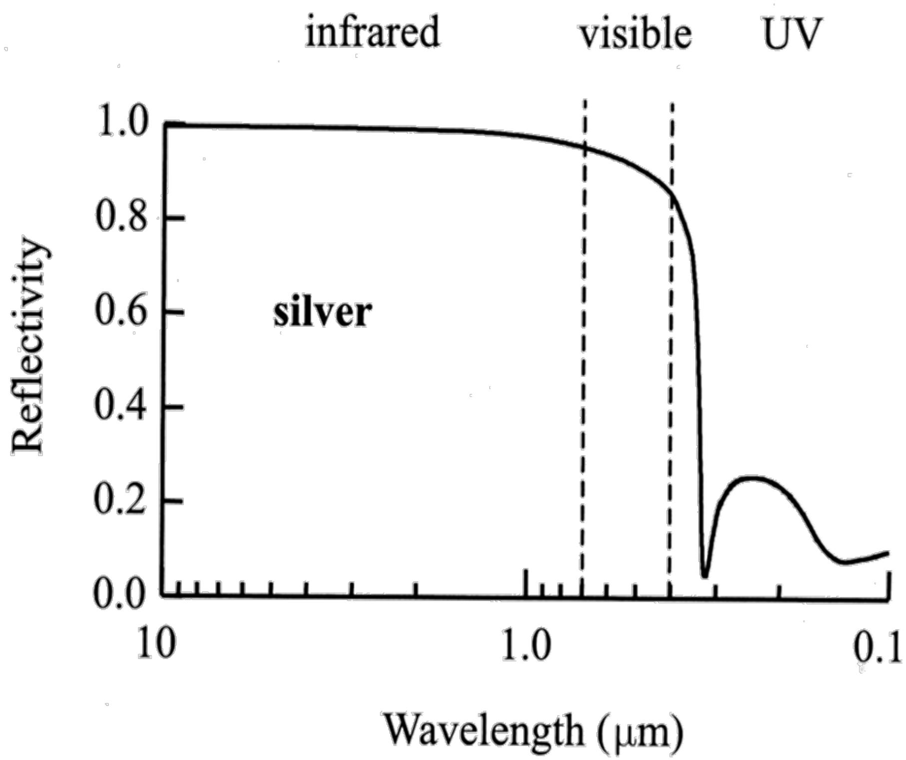


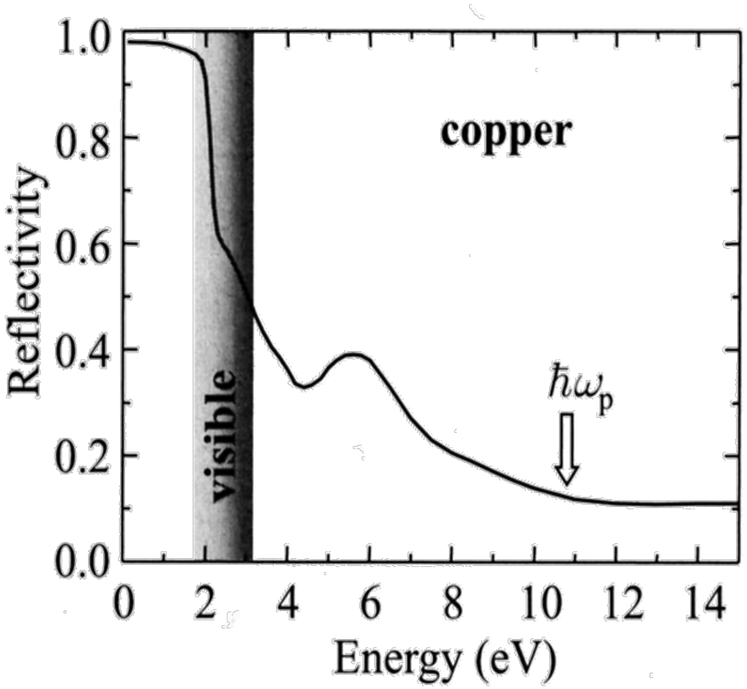
https://micro.magnet.fsu.edu/primer/java/reflection/specular/index.html



Optical properties of Metals

Metals are shiny and typically not transparent





What would be the best laser for metal processing?

Electrons in Metal

in metal electrons are not bounded $\Rightarrow$ free-electron plasma

$$m_0 \frac{d^2 x}{dx^2} + m_0 \gamma \frac{dx}{dt} + \cancel{m_0 \omega^2 x} = -eE(t) = -eE_0 \mathrm{e}^{-i\omega t}$$

acceleration — damping — E-field driving force

"spring" (returning force) term is not present

solution:

$$x = \frac{e}{m_0(\omega^2 + i\omega\gamma)} E(t)$$

$$\downarrow$$

$$P = -N_e \cdot e \cdot x = \varepsilon_0 (\varepsilon - 1) E \longrightarrow$$

dielectric constant for free-electron plasma (in first approximation for metals):

$$\varepsilon(\omega) = 1 - \frac{N_e e^2}{\varepsilon_0 m_0} \frac{1}{\left(\omega^2 + i\gamma\omega\right)} = 1 - \frac{\omega_p}{\left(\omega^2 + i\gamma\omega\right)}$$

$$\omega_p = \sqrt{\frac{N_e e^2}{\varepsilon_0 m_0}}$$ plasma frequency

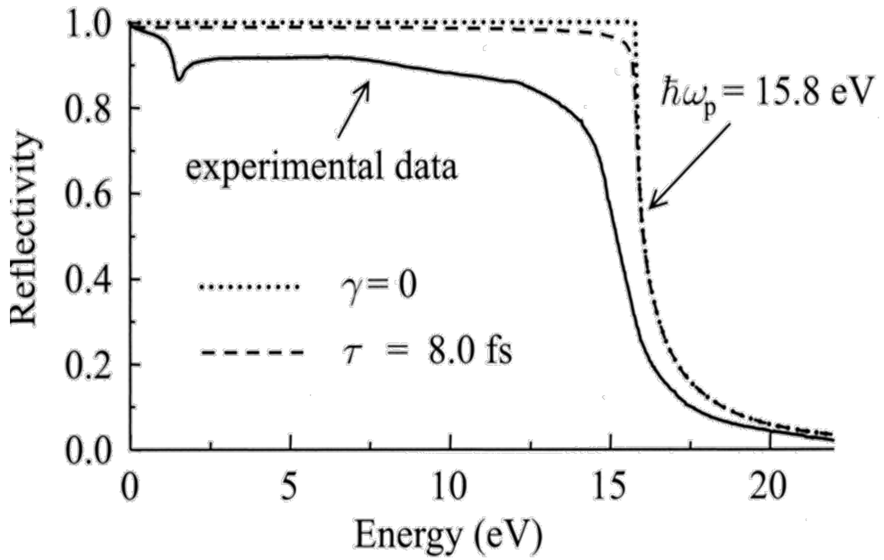
Theoretical Plasma Frequencies

Table 7.1 Free electron density and plasma properties of some metals. The figures are for room temperature unless stated otherwise. The electron densities are based on data taken from Wyckoff (1963). The plasma frequency ω_p is calculated from eqn 7.6, and λ_p is the wavelength corresponding to this frequency.

Metal	Valency	N (10^{28} m^{-3})	$\omega_p/2\pi$ (10^{15} Hz)	λ_p (nm)
Li (77 K)	1	4.70	1.95	154
Na (5 K)	1	2.65	1.46	205
K (5 K)	1	1.40	1.06	282
Rb (5 K)	1	1.15	0.96	312
Cs (5 K)	1	0.91	0.86	350
Cu	1	8.47	2.61	115
Ag	1	5.86	2.17	138
Au	1	5.90	2.18	138
Be	2	24.7	4.46	67
Mg	2	8.61	2.63	114
Ca	2	4.61	1.93	156
Al	3	18.1	3.82	79

$$\varepsilon(\omega) = 1 - \frac{\omega_p}{\left(\omega^2 + i\gamma\omega\right)}$$

reflectivity of free-electron gas and real metal (Al)



$$\gamma = \frac{1}{\tau}$$

γ – damping coefficient

τ – momentum scattering time

Dielectric Constant and Conductivity

$$\varepsilon(\omega) = 1 - \frac{\omega_p}{\omega^2 + i\gamma\omega}$$

$$\varepsilon(\omega) = 1 + \frac{i\sigma(\omega)}{\varepsilon_0\omega},$$

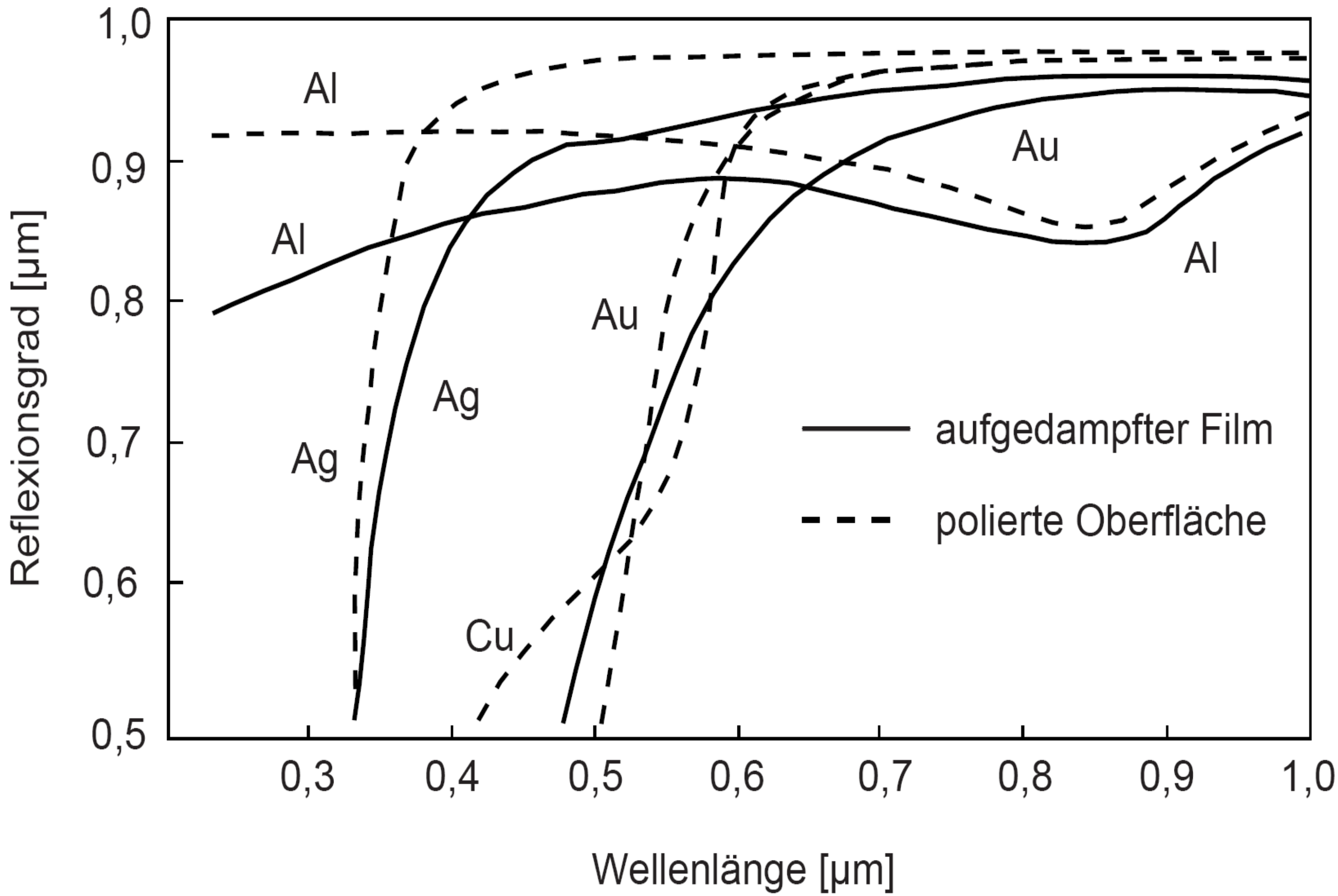
$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau} - \text{ AC conductivity}$$

$$\sigma_0 = \frac{N_e e^2 \tau}{m_0} - \text{ DC conductivity}$$

$$\sigma_0 = \omega_p^2 \varepsilon_0 \tau$$

conductivity and plasma frequency of a metal are directly linked (link between optical and electrical properties)

Reflection of Al, Ag & Au



Reflection coefficients and penetration depth for some Materials

maté-riaux	l_α (250 nm)	R (250 nm)	l_α (500 nm)	R (500 nm)	l_α (1060 nm)	R (1060 nm)	l_α (10.6 µm)	R (10.6 µm)
KCl	> 1 cm	0.05	> 1 cm	0.04	> 1 cm	0.04	> 1 cm	0.03
SiO_2	> 1 cm	0.06	> 1 cm	0.04	> 1 cm	0.04	40 µm	0.2
Ge	7 nm	0.42	15 nm	0.49	200 µm	0.38	1 mm	0.36
Si	6 nm	0.61	500 nm	0.36	200 µm	0.33	1 mm	0.3
Ag	20 nm	0.30	14 nm	0.98	12 nm	0.99	12 nm	0.99
Al	8 nm	0.92	7 nm	0.92	10 nm	0.94	12 nm	0.98
Au	18 nm	0.33	22 nm	0.48	13 nm	0.98	14 nm	0.98
W	7 nm	0.51	13 nm	0.49	23 nm	0.58	20 nm	0.98

for metals for frequencies between:

$1/\tau_e < \omega < \omega_p$ (optical, vis.)

$$\alpha \approx \frac{2\omega_p}{c}$$

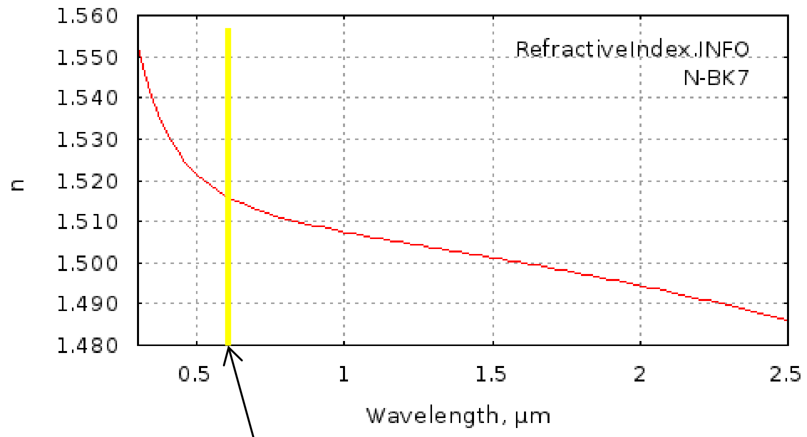
$$l_\alpha \approx \frac{c}{2\omega_p}$$

Table 1: Energies de gap pour les examples

Matériaux	Gap (eV)	λ (nm)
Si	1.1	1130
SiO_2	6.9	180

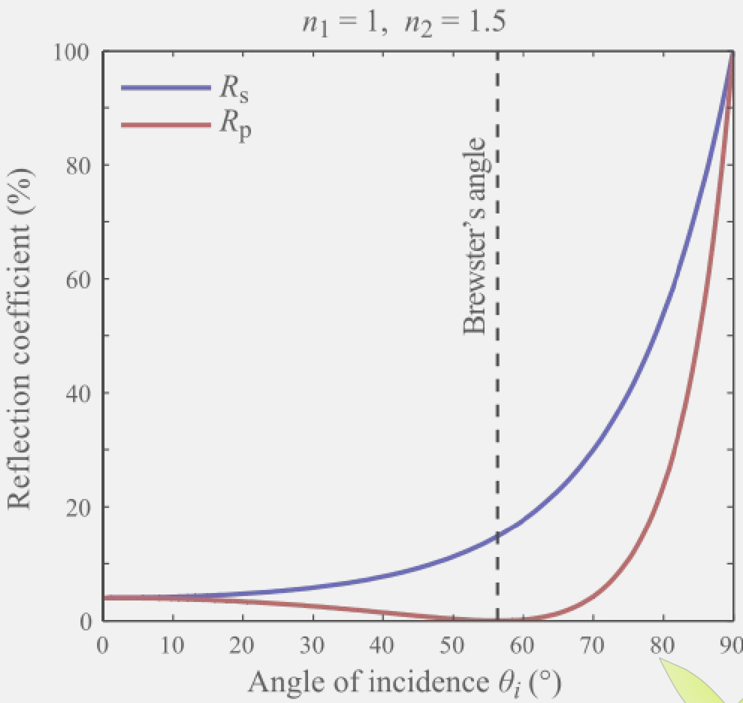
dependances

Index of refraction is wavelength dependent



589 nm sodium Na line

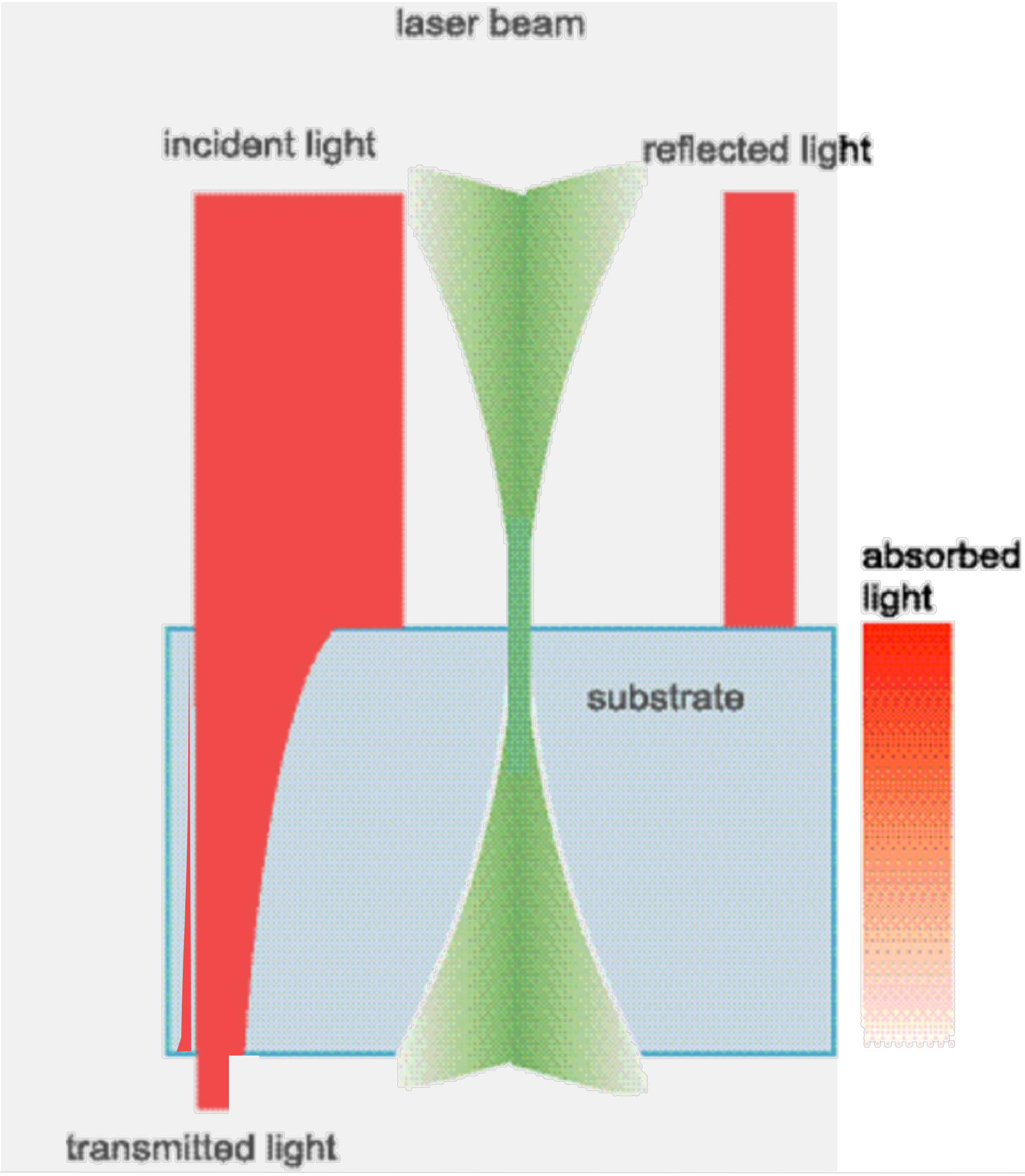
Reflection depends on polarisation



$n_{1,2}$ indice de réfraction des milieux 1 et 2

Light meets material

- Light meets materials
  - Reflexion
  - Absorption
  - Transmission
  - Scattering



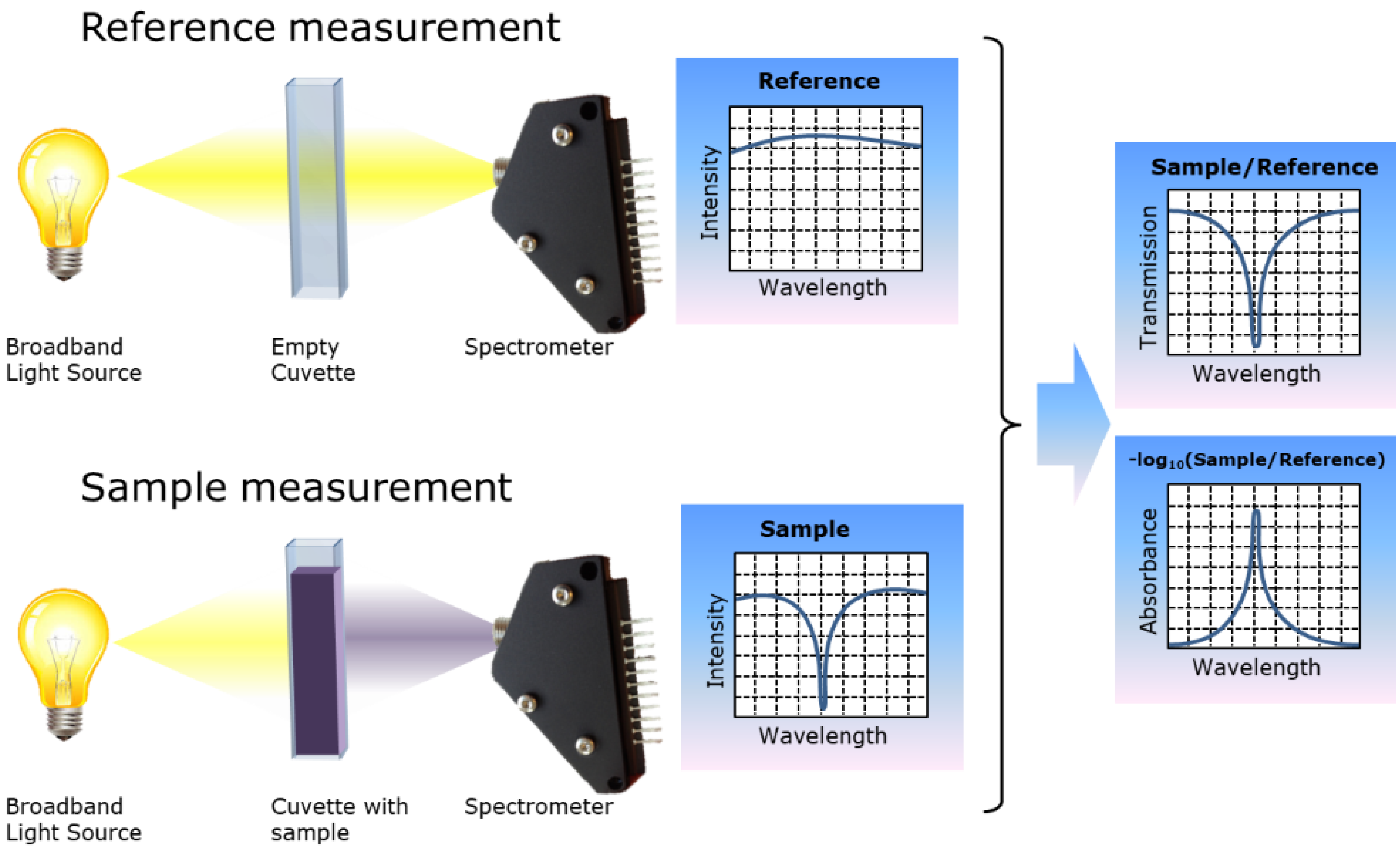
Light absorption

- Light that is absorbed makes a photon disappear !
  - Where is the energy going?

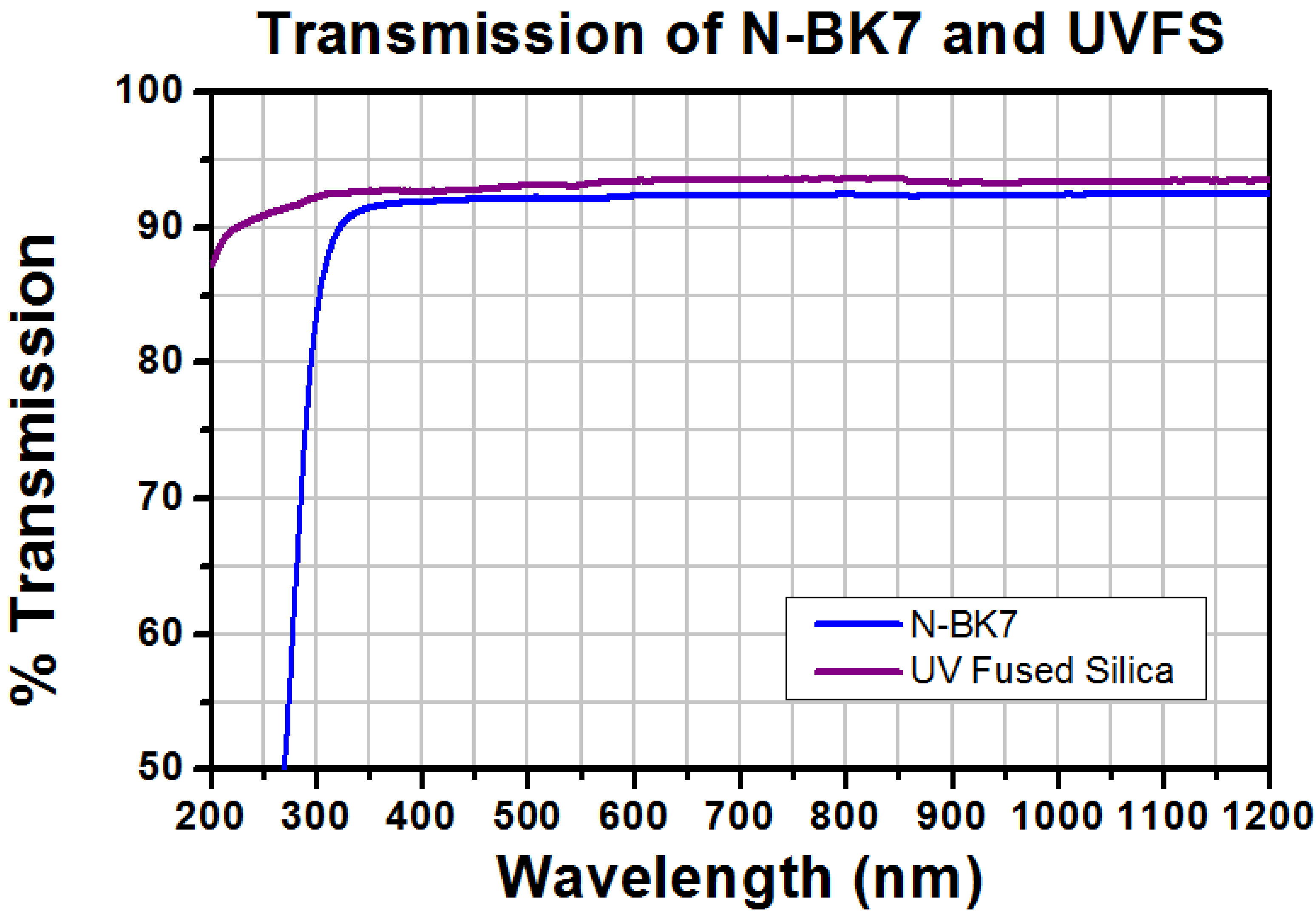
- Light that is deviated only, does not loose energy!
  - Reflection
  - Transmission
  - Scattering

Absorption

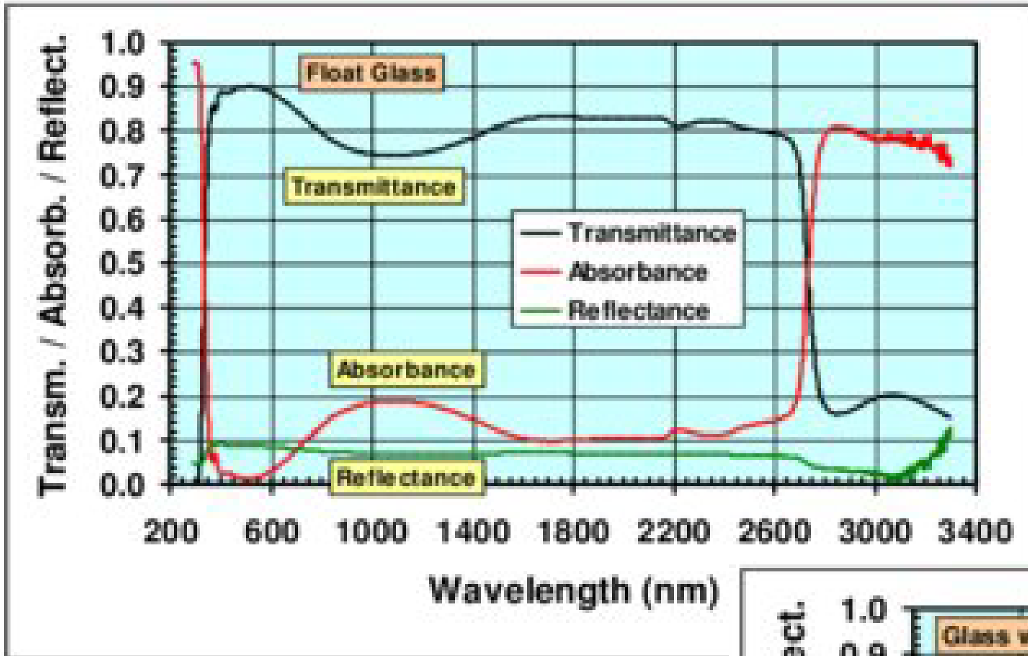
- Light meets materials
  - Absorption



Absorption – Transmission index of refraction



Absorption – Transmission index of refraction



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SOLAR RADIATION GLAZING FACTORS FOR ELECTROCHROMIC WINDOWS FOR BUILDING APPLICATIONS

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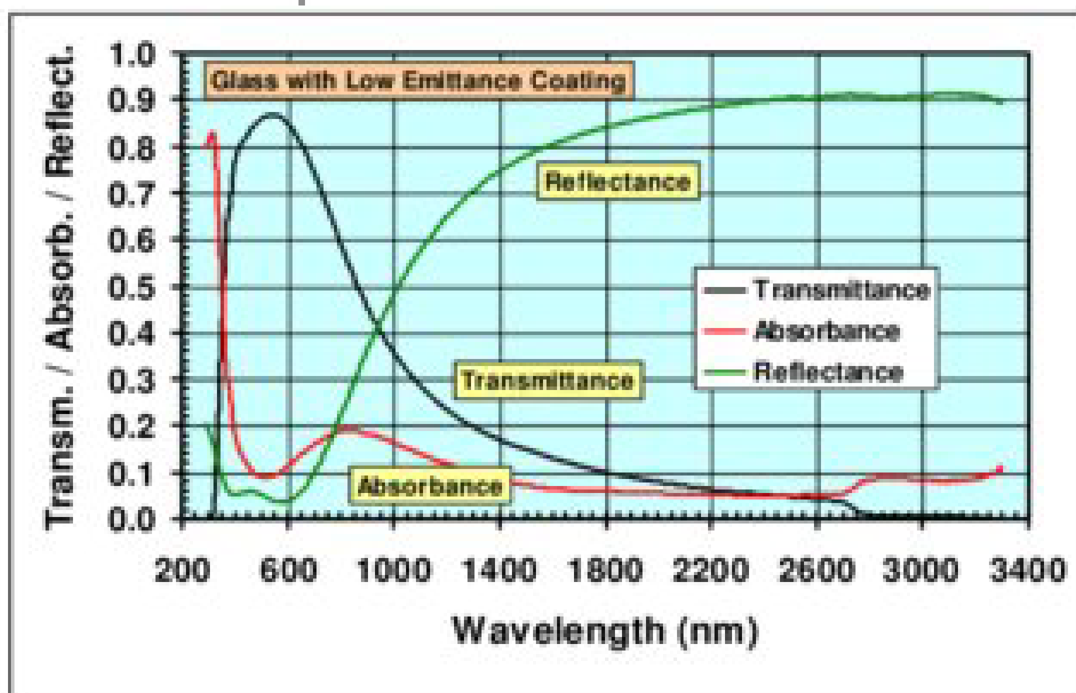
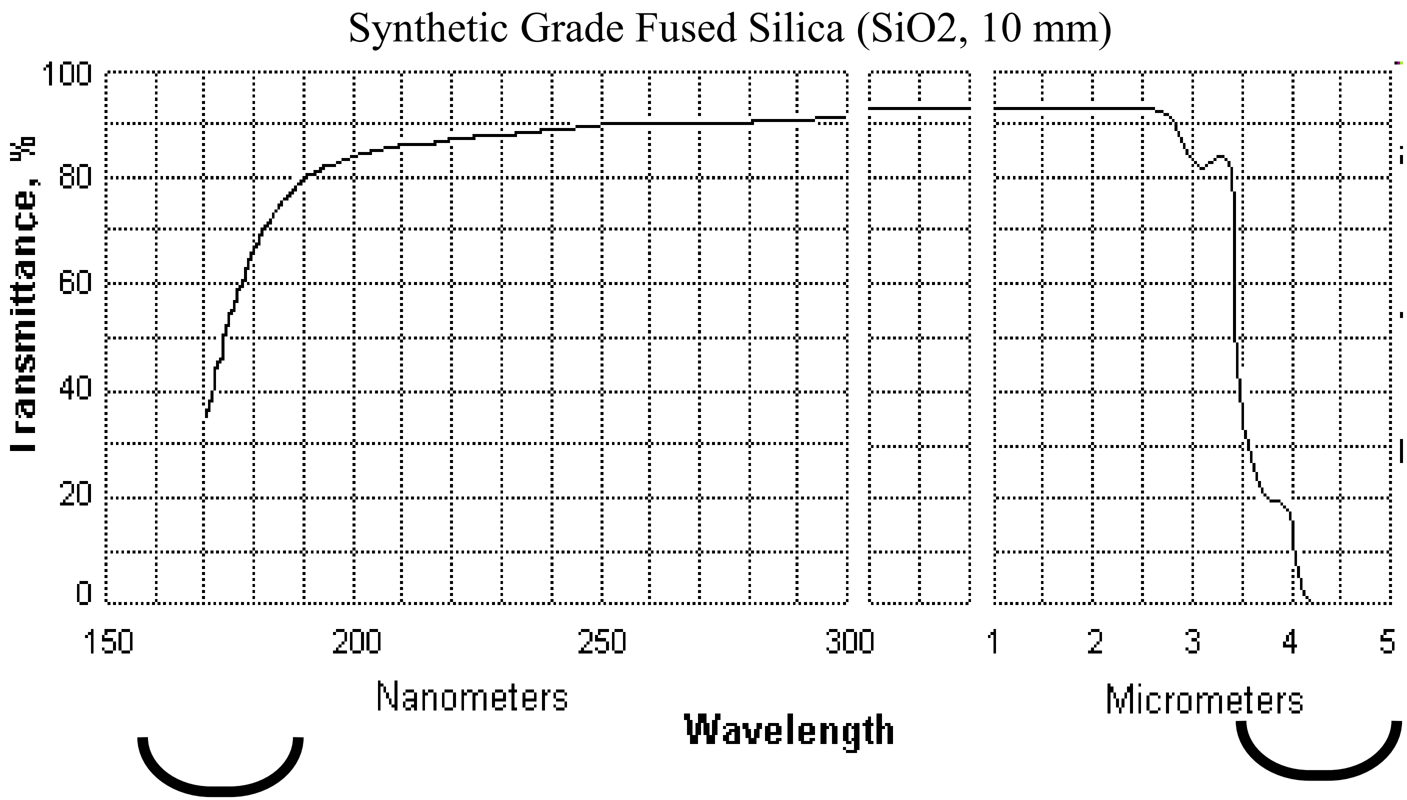


Transmission Spectra (Fused Silica)



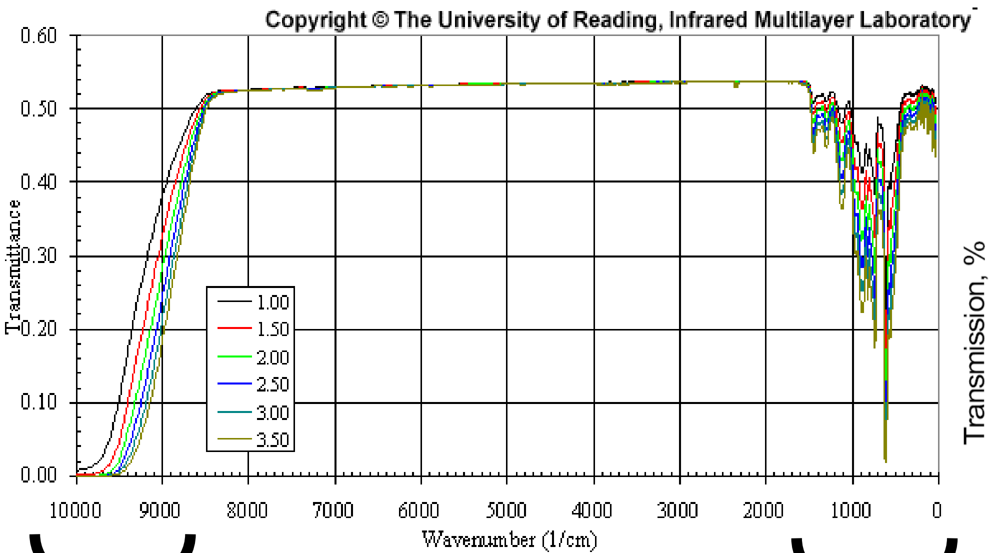
Absorption due to electronic band to band transitions (band gap)

Absorption due to excitation of lattice vibrations (phonons)

Almaz Optics Inc.
http://www.almazoptics.com

Transmission Spectra (Silicon)

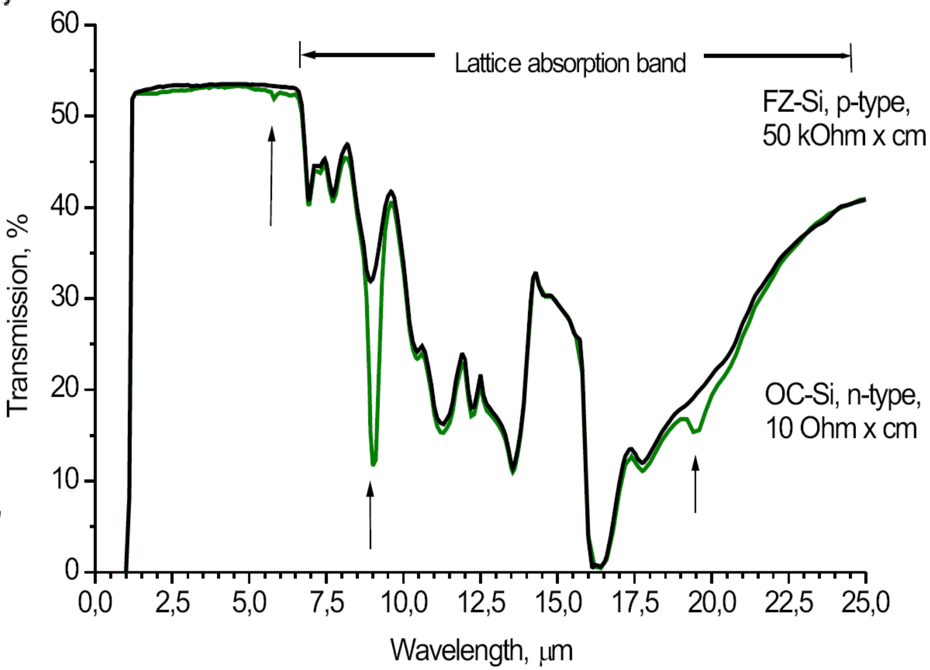
Calculated transmission profiles of hyperpure Fz Silicon (Si) at 293K for substrate thicknesses between 1.0 and 3.5mm



Absorption due to electronic band to band transitions (band gap)

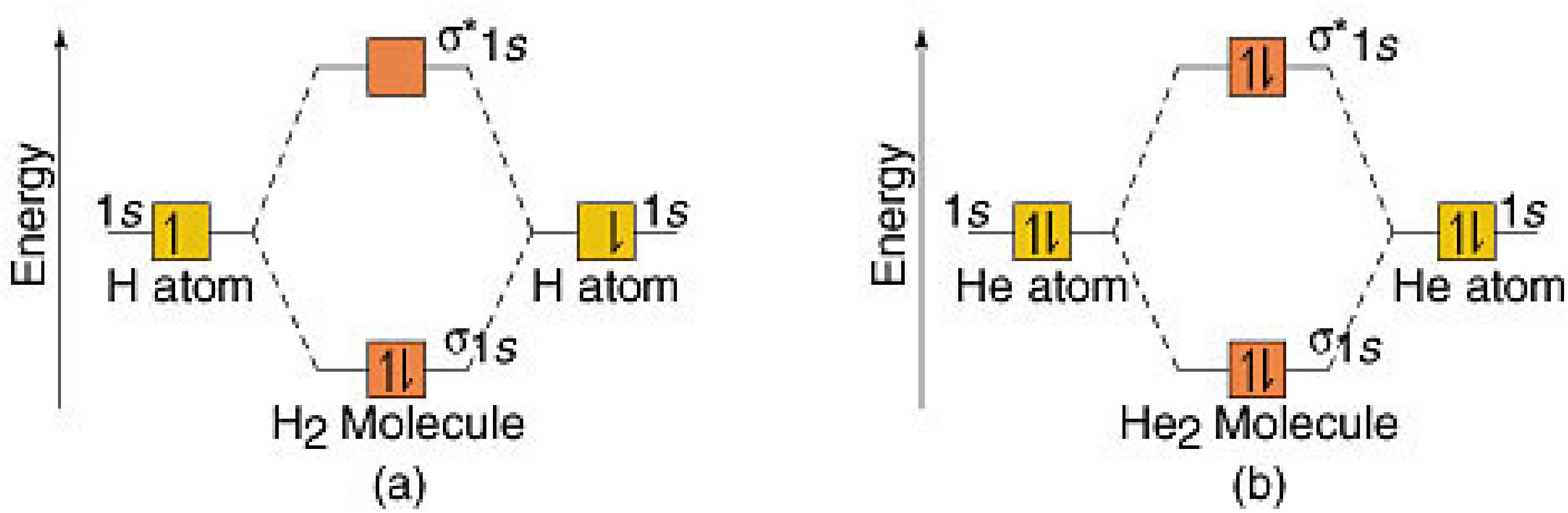
Absorption due to excitation of lattice vibrations (phonons)

Silicon (5 mm) transmission. (pure and oxygen contaminated) Arrows point to the oxygen absorption peaks.

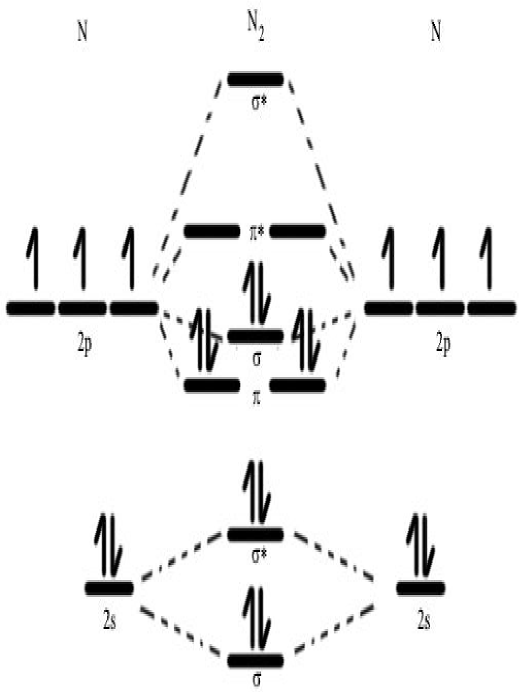


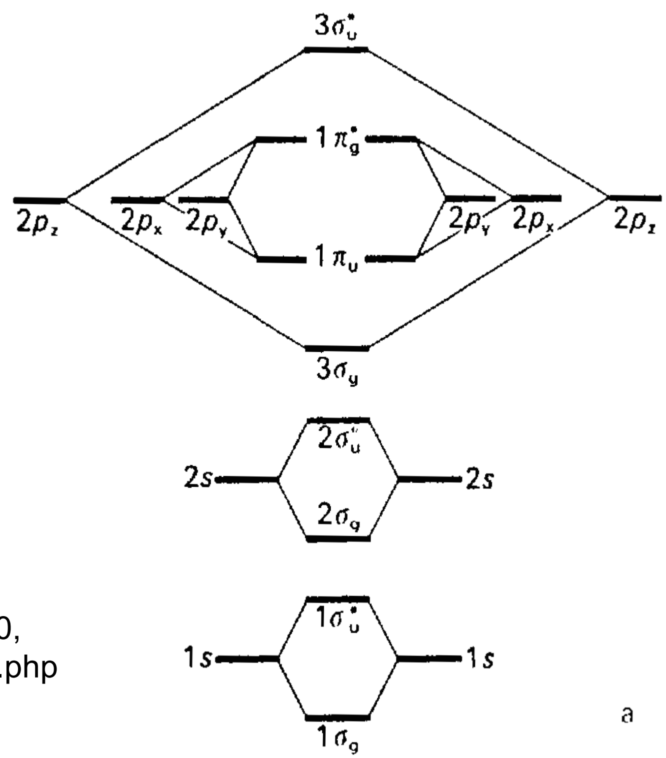
Tydex J.S.Co
http://www.tydex.ru

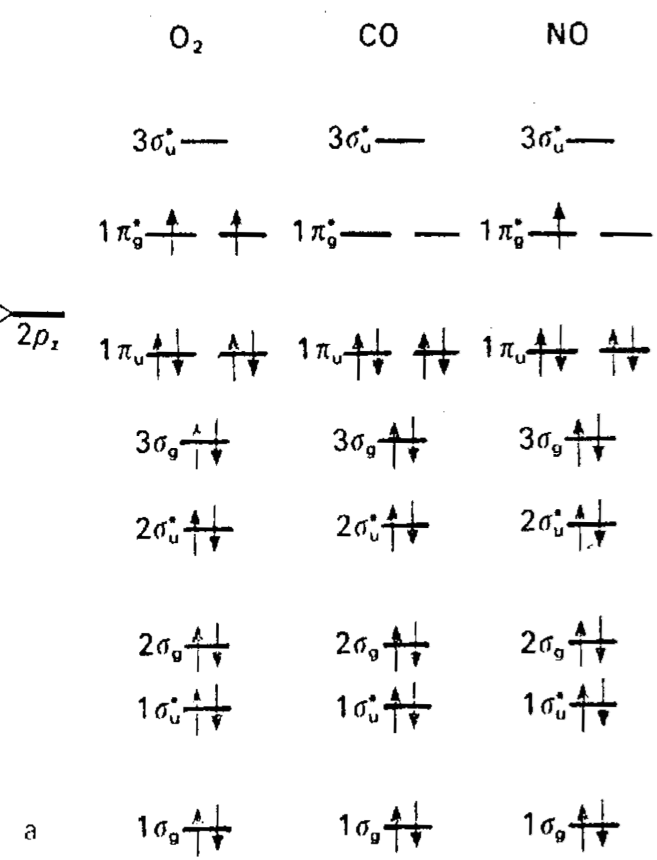
Electronic absorption: Energy Levels



Light absorption in a Gaseous Molecule

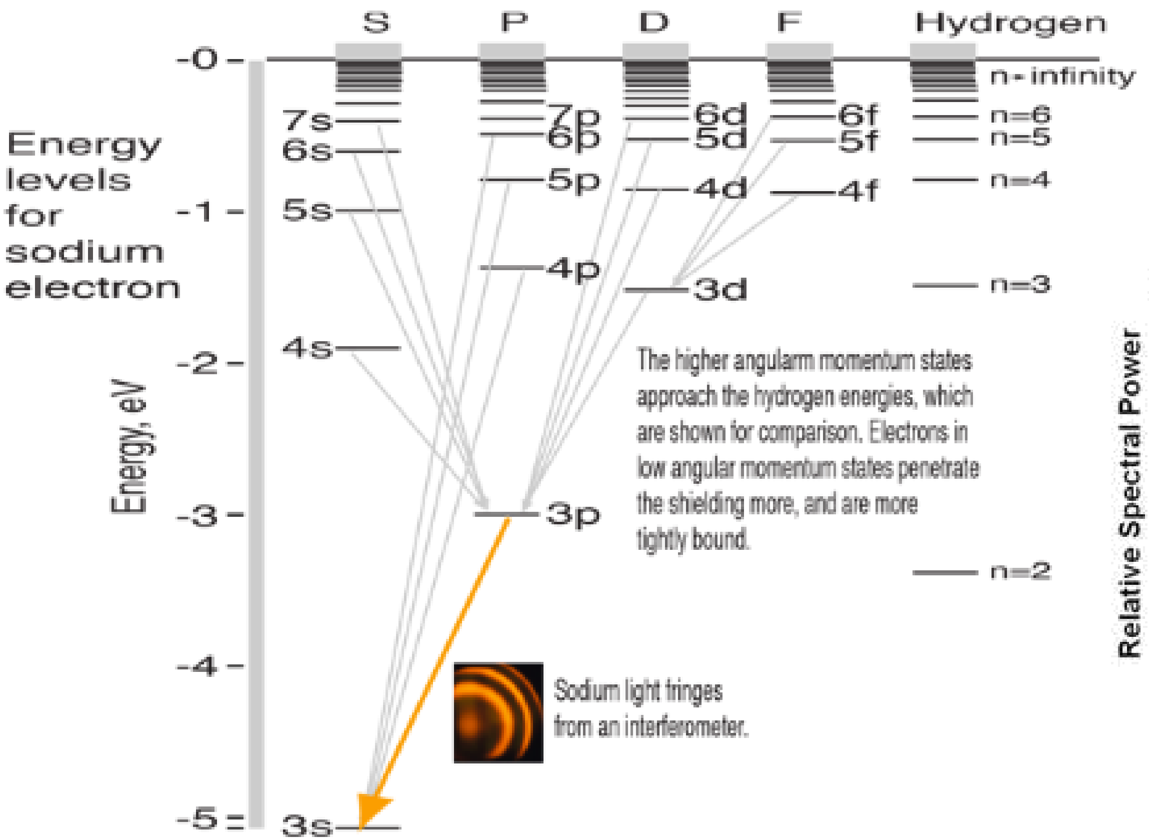


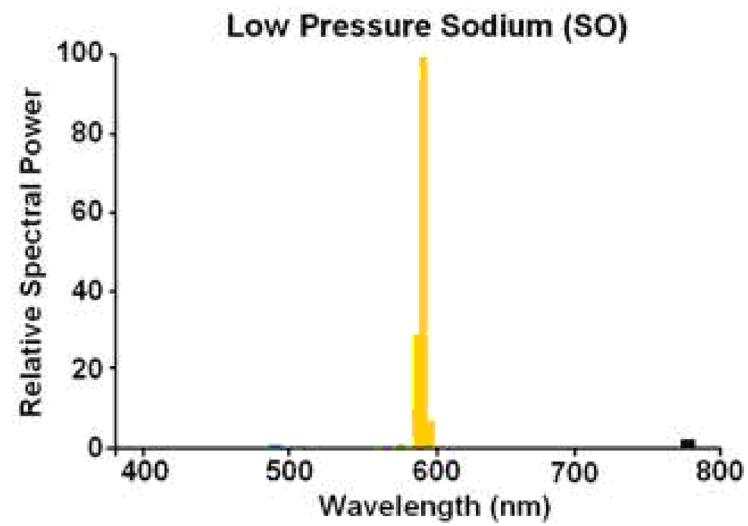




Sodium D-line

Cold sodium vapor (300°C) emits only light at 589,00nm and 589,59nm this sodium - D-line for doublet is almost monochromatic

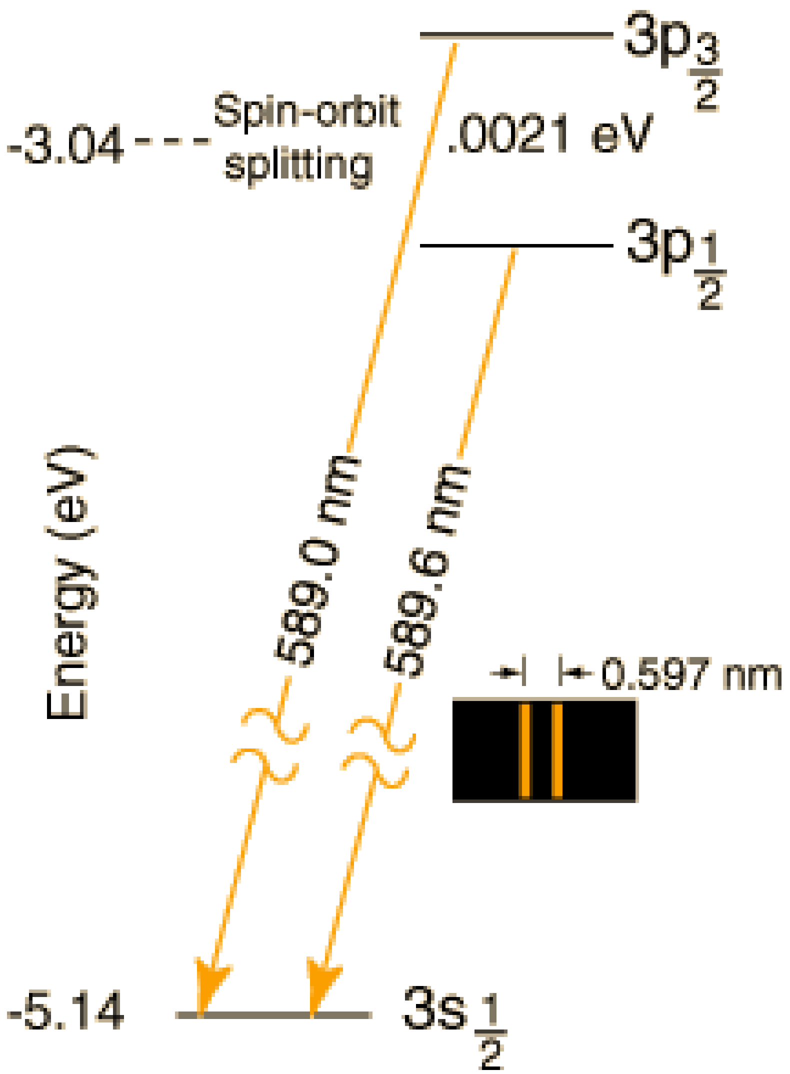




Sodium D-line – why is it a doublet ?

What happens if you put the Na vapor in a magnetic field ?

Could not have asked Pieter Zeeman when he discovered the effect in 1896 !



Absorption

$$I = I_0 \cdot e^{-\alpha \cdot z} = I_0 \cdot e^{-z/l_\alpha}$$

macroscopic ("black box") description of absorption

Types of Absorption /Excitation

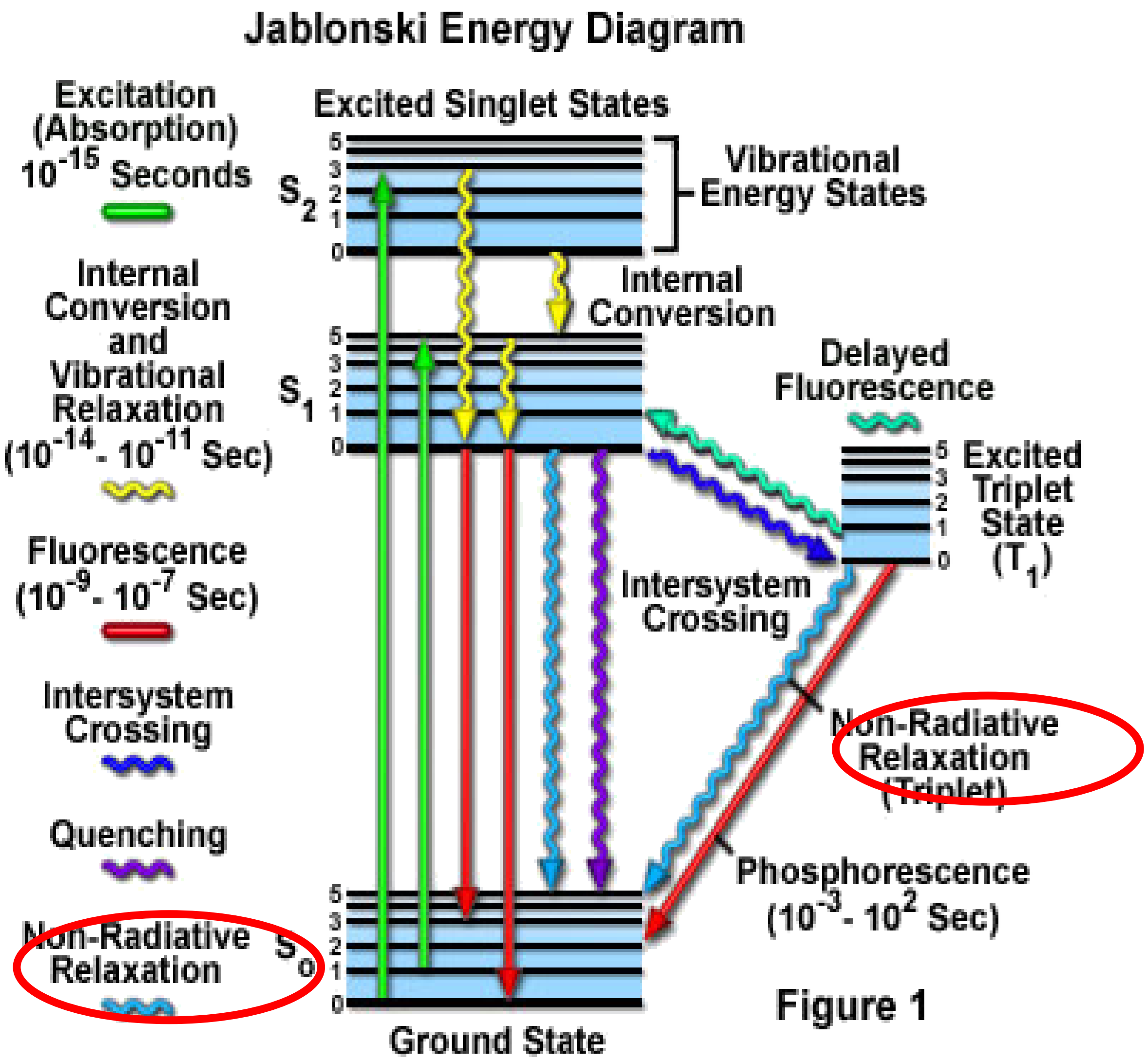
Absorption	Wavelength (nm)
electronic molecular(σ, π)	10-150 – 1000-2000
electronic interband	150 – 1000-2000
vibrational	900 – 10'000
rotational	> 10'000

Absorption & Fluorescence

Absorption & fluorescence in a single molecule, ion, atom

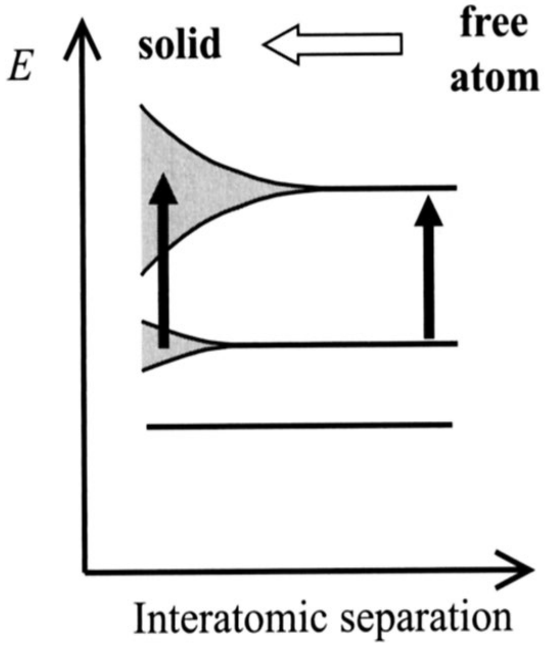
!

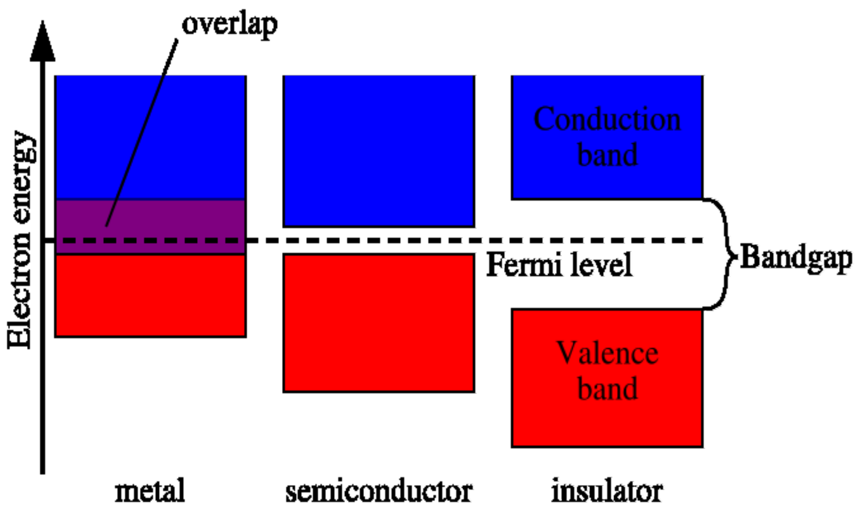
non-radiative transition → transformation into heat



http://micro.magnet.fsu.edu/primer/techniques/fluorescence/fluorescenceintro.html

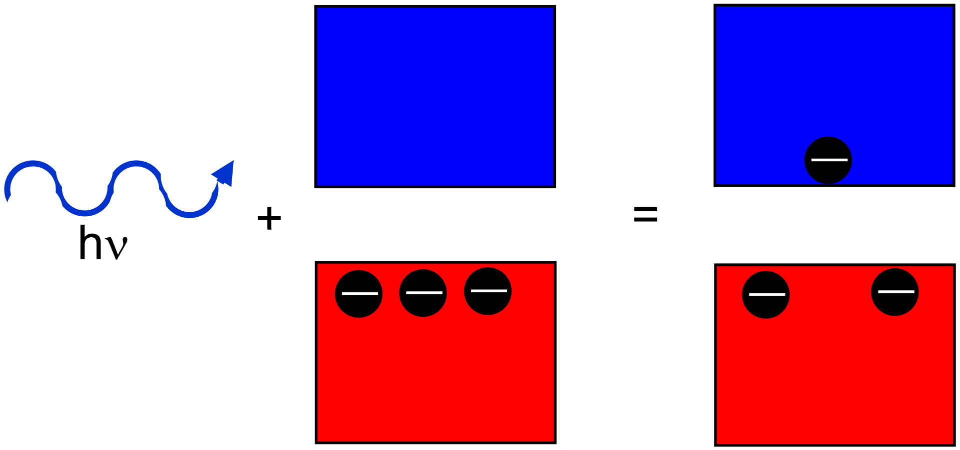
Band Structure of Solids





http://en.wikipedia.org/wiki/Band_structure

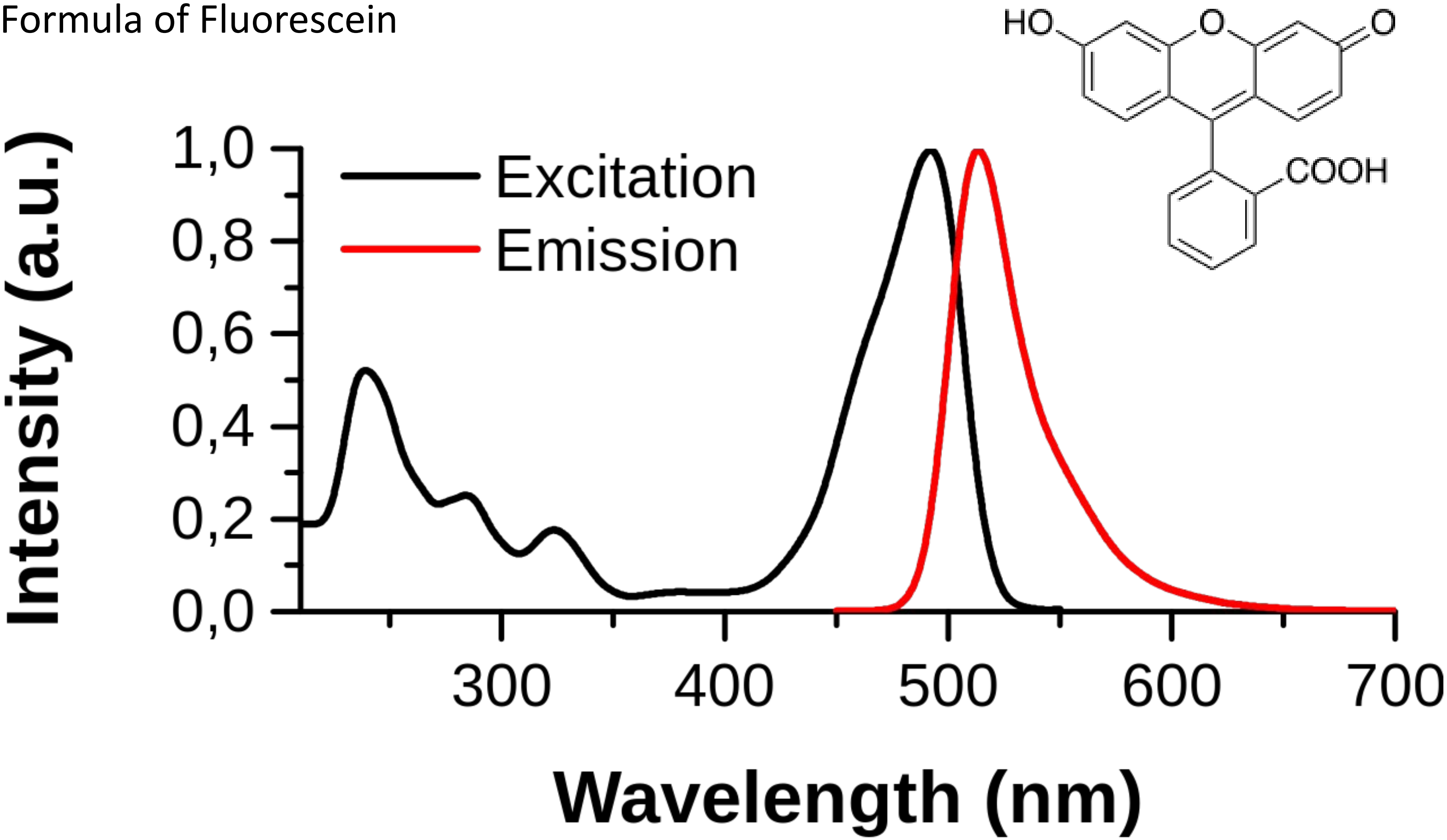
Band Gap Absorption



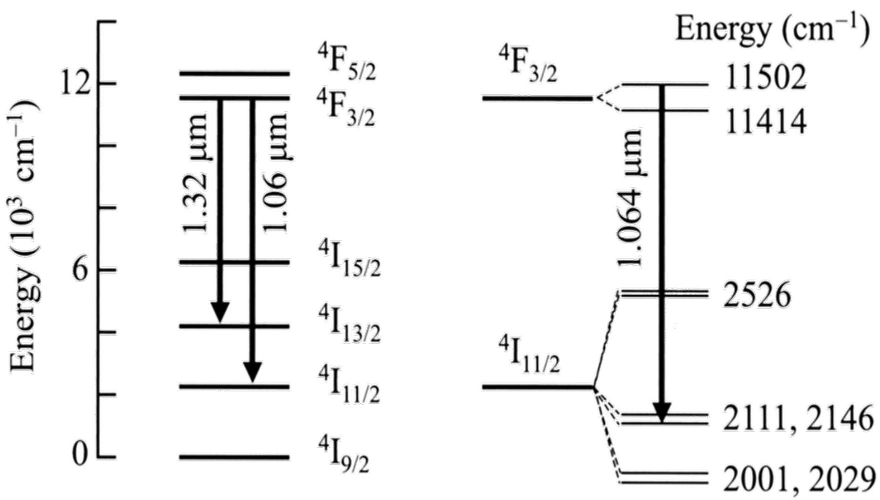
Only photons with energy larger than the band gap of material are absorbed
Inter band absorption grates free charge carriers – new centers of absorption

Fluorescein

Formula of Fluorescein

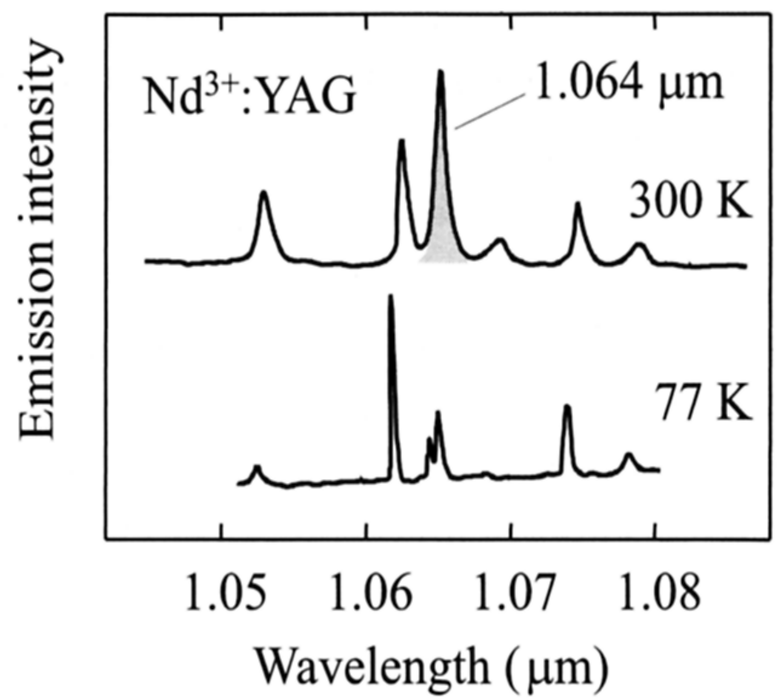


Absorption/Luminescence Centers in Solids

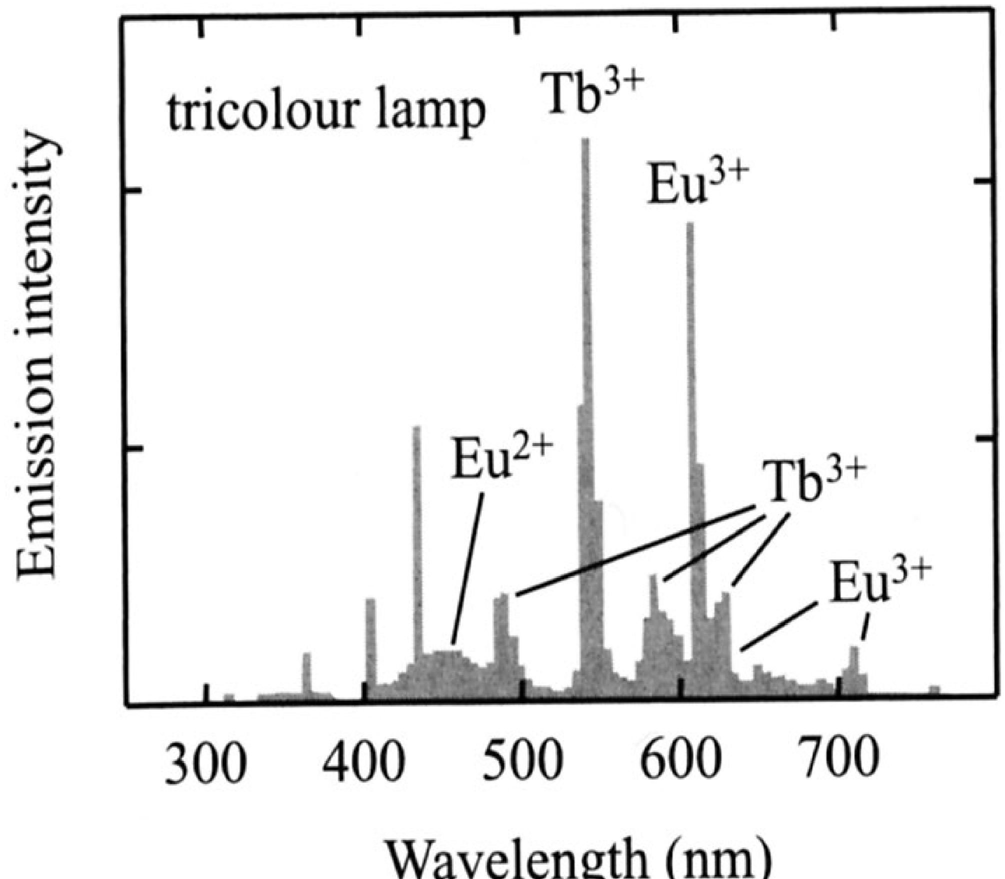


Energy Level Diagram of Nd^{3+}-ion in YAG crystal

Emission spectrum of Nd^{3+}-ion in YAG crystal



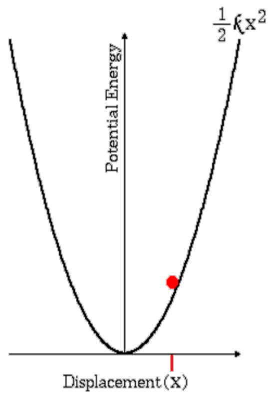
Emission of Luminescent Lamp

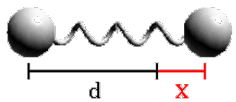


emission of luminescent lamp is composed of narrow line emission of a mixture of phosphors

Vibronic Transitions and Infrared Spectroscopy

Vibration of a di-atomic molecule

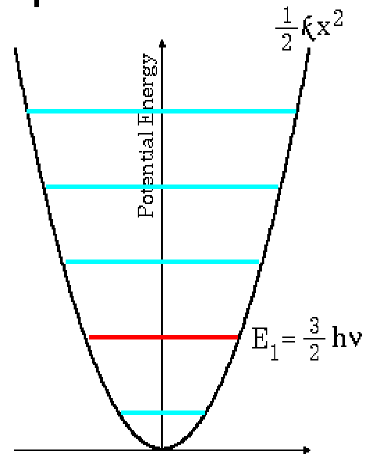




The **vibration frequency** ν is related to the force constant k and mass m by the equation:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

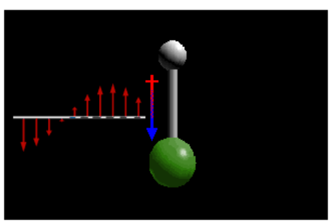
quantized harmonic oscillator



In the quantum mechanical model, a molecule in may only absorb (or emit) light of an energy equal to the spacing between two levels. Furthermore, for a harmonic oscillator these transitions can only occur from one level to the next higher (or lower) level, i.e. **Δn = ±1**. This is called the **selection rule**. Press the buttons below to see absorbtion and emission:

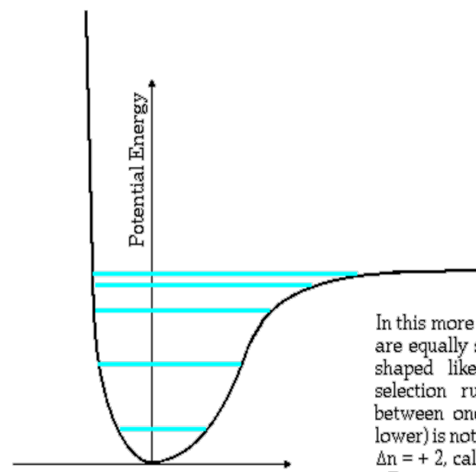
Absorb Emit

Selection rules for oscillation to be visible in IR spectroscopy: the dipole moment of a molecule have to change when undergoing the transition



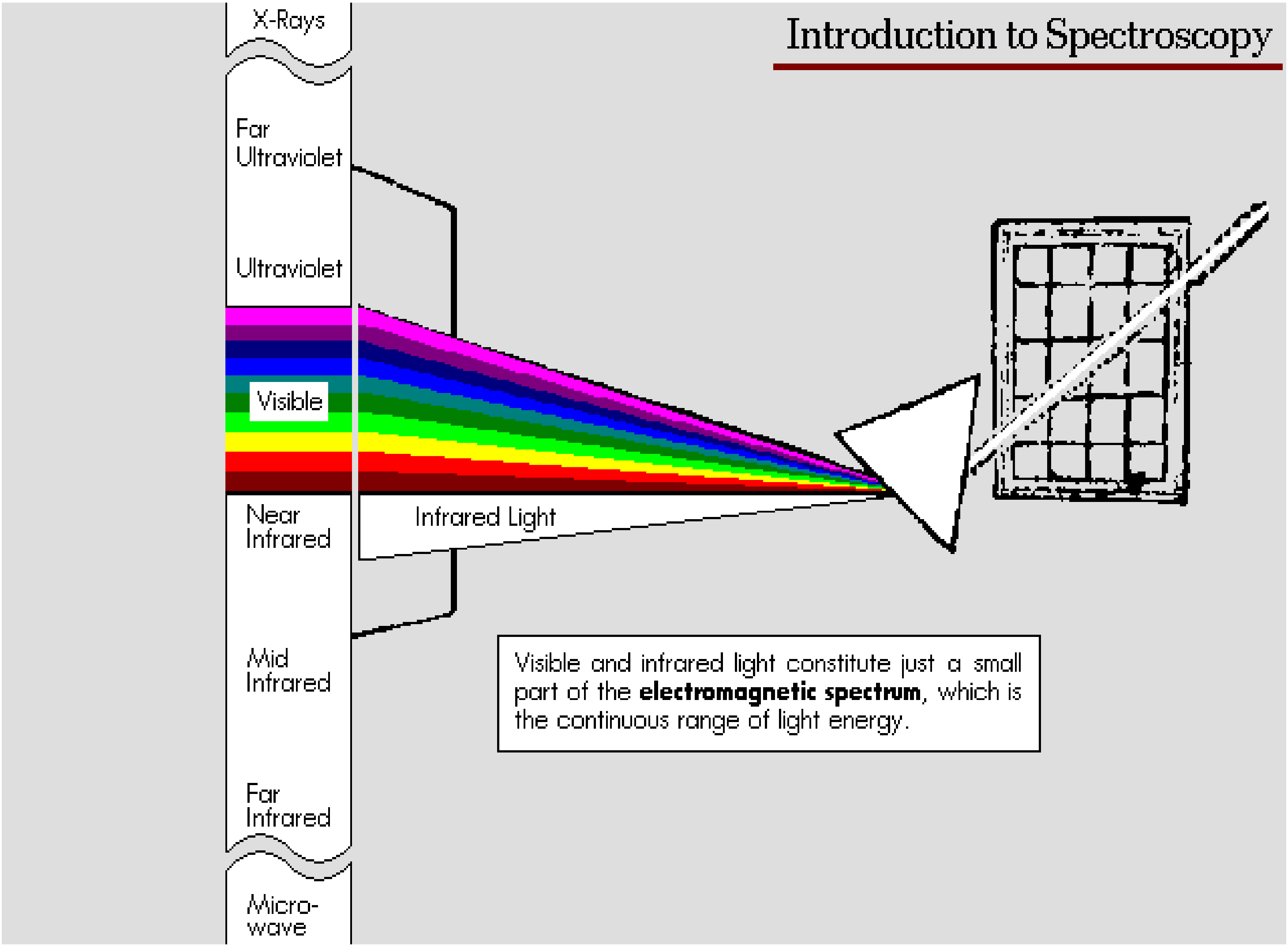
However, HCl does have a dipole change as it stretches. When this dipole aligns with the electric field of a beam of light, the light is absorbed (so long as the frequency is correct). The intensity of the absorption is related to the magnitude of the dipole change.

quantized unharmonic oscillator



In this more realistic model, the energy levels are equally spaced only in the region that is shaped like the harmonic potential. The selection rule, which allowed transitions between one level and the next higher (or lower) is not rigorously true. A transition with Δn = + 2, called an **overtone**, corresponds to ΔE approximately 2 hν.

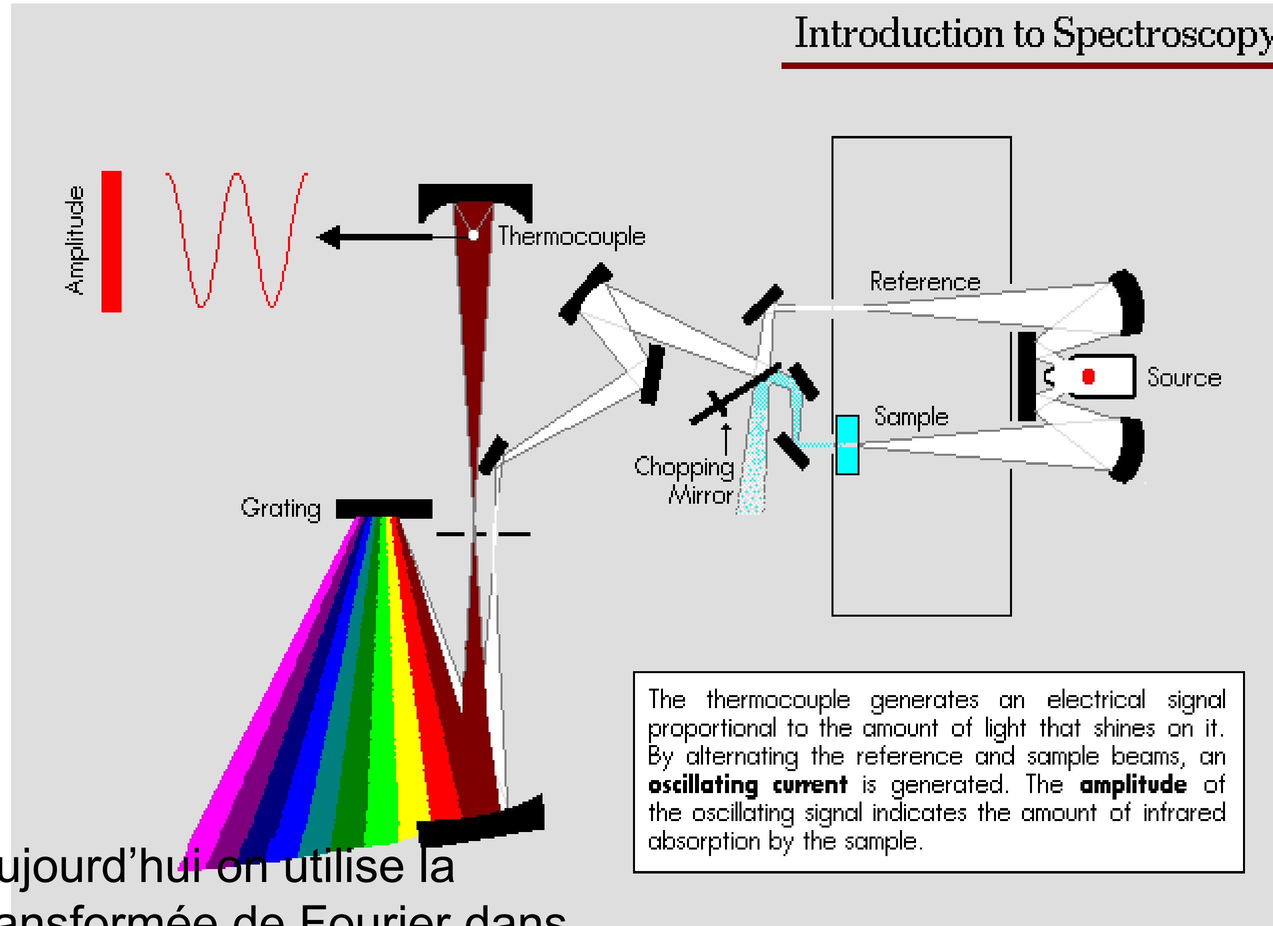
Infrared Spectroscopy



Schematic of Infrared Spectroscopy

En pivotant le réseau (en anglais *grating*, prisme réflectif), la longueur d'onde arrivant sur l'échantillon est scannée. L'absorption dans l'échantillon varie avec la longueur d'onde.

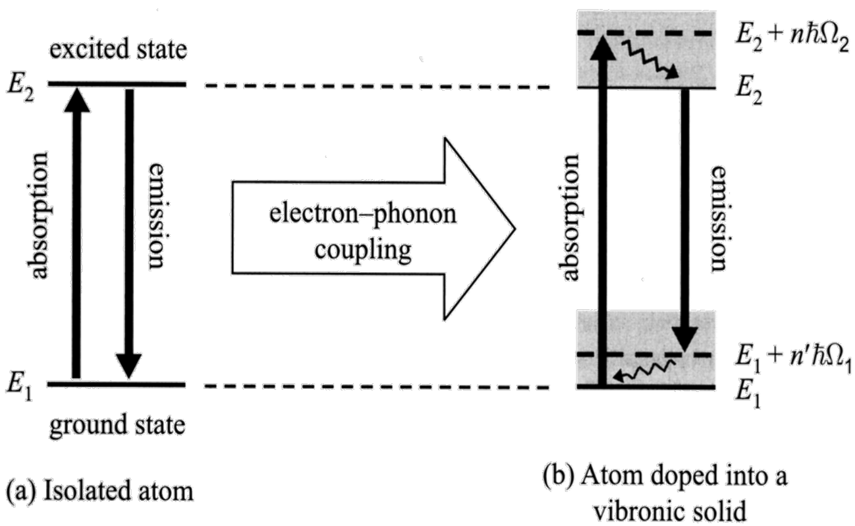
On obtient sur le détecteur un spectre IR.

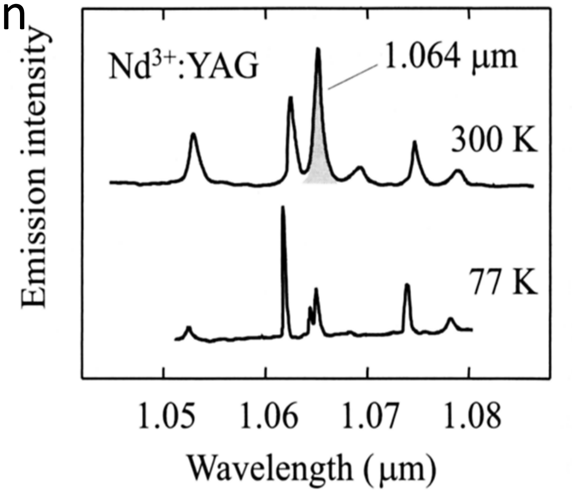


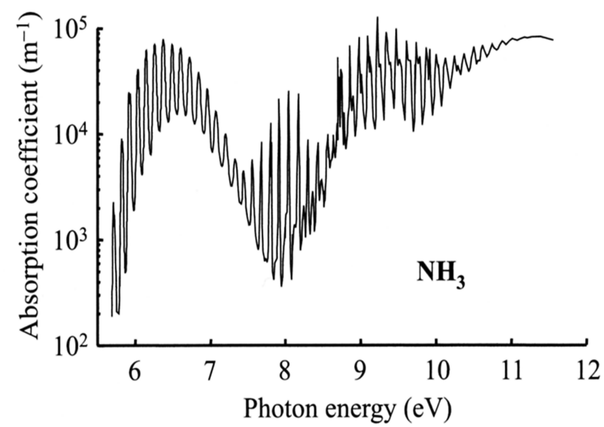
Aujourd'hui on utilise la transformée de Fourier dans les machines, pour augmenter la vitesse et la precision.

Electronic and Vibronic Trasitions

electronic and vibronic transition often interact – broadening of the transitions (emission / absorption peaks)







Absorption

for linear absorption lost intensity in a thin layer is proportional to incident intensity

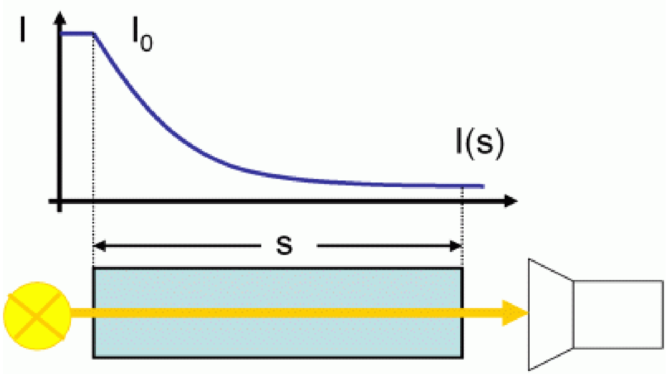
$$\frac{dI(z)}{dz} = -\alpha \cdot I(z)$$

which results in a Beer-Lambert law

$$I = I_0 \cdot e^{-\alpha \cdot z} = I_0 \cdot e^{-z/l_\alpha}$$

α - absorption coefficient

$l_\alpha = 1/\alpha$ - penetration depth (characteristic absorption length)



Measures of Absorption

absorption coefficient and extinction coefficient

$$\alpha = 4\pi \frac{k}{\lambda}$$

optical density – a logarithmic unit:

$$O.D. = -\log_{10} \frac{I(l)}{I_0} = \frac{\alpha \cdot l}{\log_e 10}$$

complex refractive index and complex dielectric constant:

$$\tilde{n}^2 = (n + ik)^2 = \varepsilon' + i\varepsilon'' = \tilde{\varepsilon}$$

$$n^2 - k^2 = \varepsilon'$$

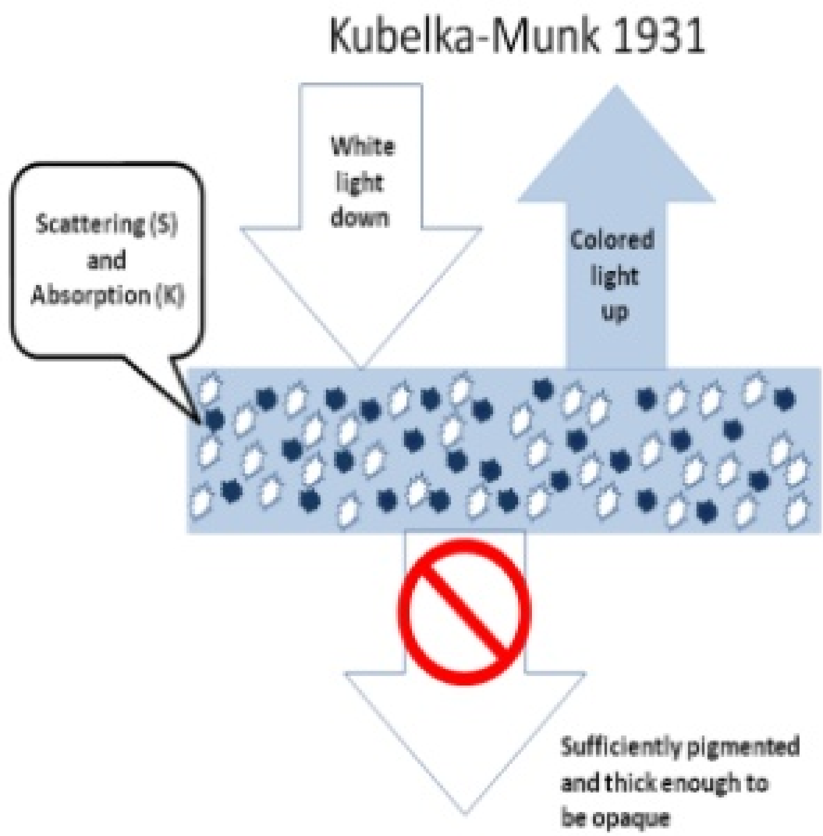
$$2nk = \varepsilon''$$

$$n = \sqrt{\frac{\varepsilon' + \sqrt{\varepsilon'^2 + \varepsilon''^2}}{2}}, k = \sqrt{\frac{-\varepsilon' + \sqrt{\varepsilon'^2 + \varepsilon''^2}}{2}}$$

Partially transparent scattering media

Kubelka–Munk analysis

- Consider the simple case of a light beam passing vertically through a very thin
- pigmented layer of thickness d*x in a paint film (Figure 1.28). We consider separately*
- the downward (incident) and upward (reflected) components of the incident light
- beam, assuming that the absorption coefficient is represented by *K and the scattering* coefficient by *S.*



2

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Kubelka - Munk

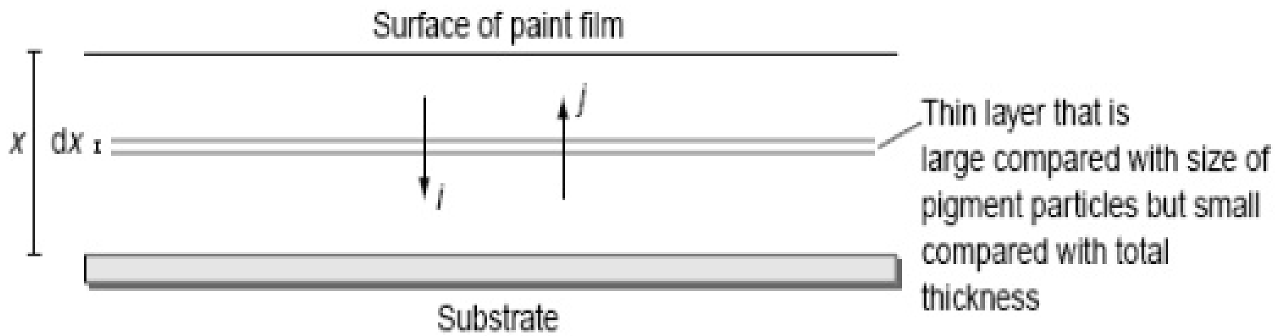

Figure 1.28 Kubelka–Munk analysis

- The downward flux (intensity *I*) *is:*
- – decreased by absorption = – *KI dx*
- – decreased by scattering = – *SI dx*
- – increased by backscatter = + *SJ dx (from the radiation*

$$dI = -KI\,dx - SI\,dx + SJ\,dx$$
$$= -(K+S)I\,dx + SJ\,dx$$

- At the same time, the upward flux (intensity *J) is:*
- – decreased by absorption = – *kJ dx*
- – decreased by scattering = – *SJ dx*
- – increased by backscatter = + *SI dx (from the radiation proceeding downward)*

$$dJ = -KJ\,dx - SJ\,dx + SI\,dx$$
$$= -(K+S)J\,dx + SI\,dx$$

3

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Kubelka - Munk

Kubelka–Munk analysis

- For an iso-tropically absorbing and scattering layer of infinite thickness
- **(or at least so thick that the background layer reflection is negligible), it leads to the**
  - wic ession (Eqn 1.22):

$$K/S = \frac{(1-R_\infty)^2}{2R_\infty}$$

where R_∞ *= Jo/Io is the reflection factor at the surface for a sample of infinite thickness.*

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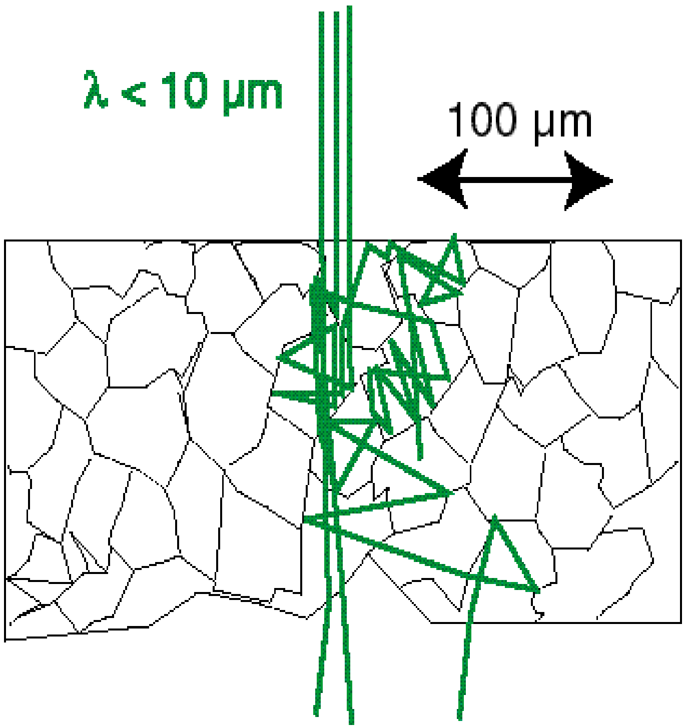
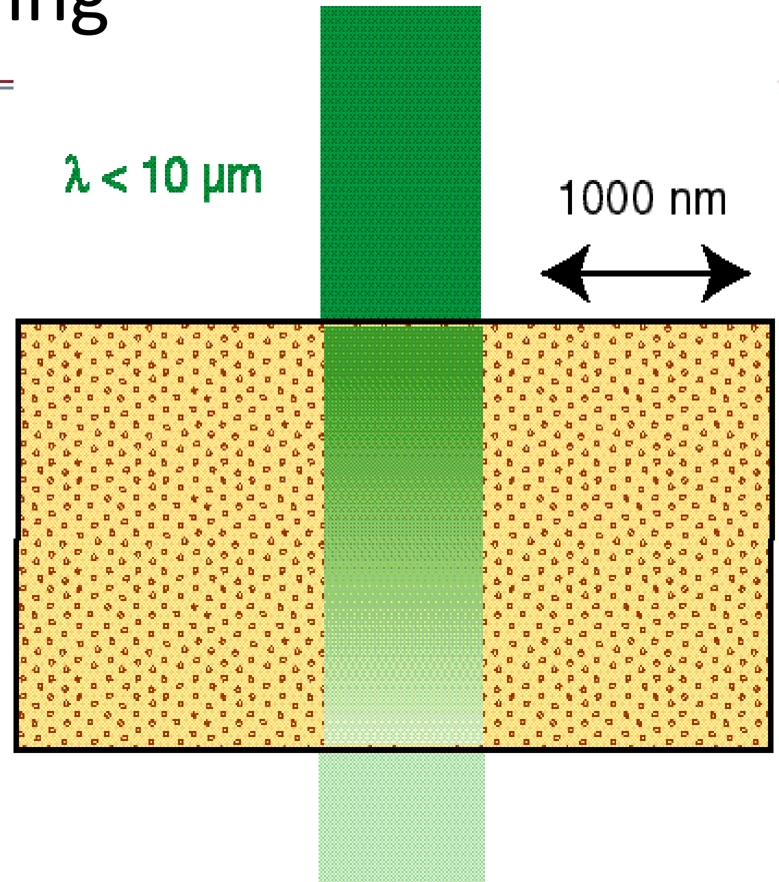
Scattering



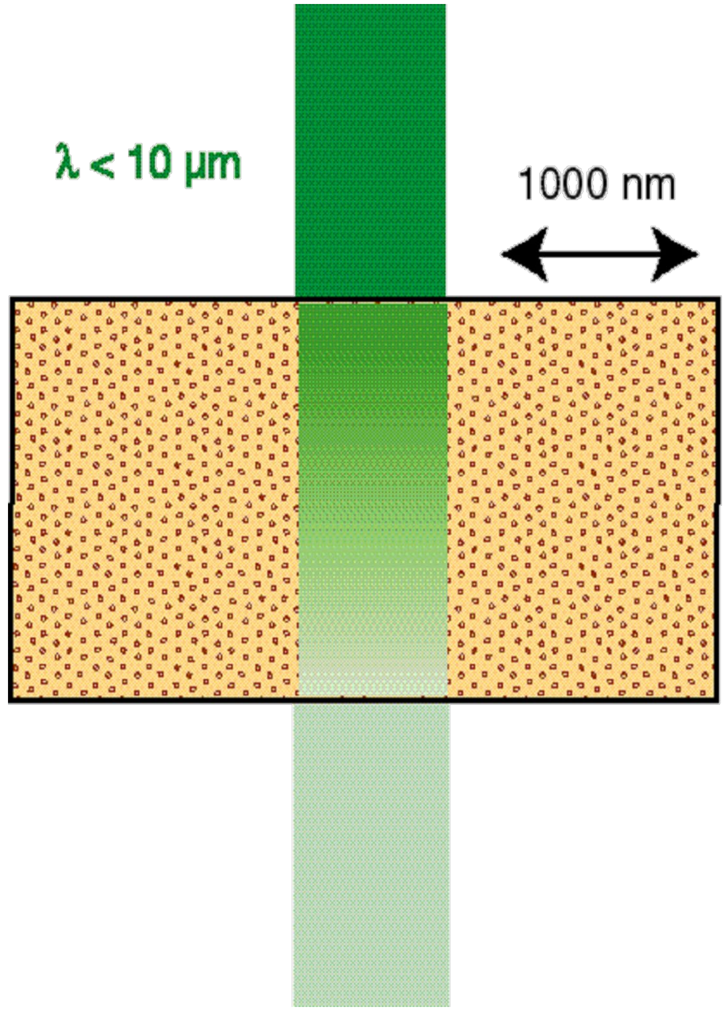


$\lambda \sim d \Rightarrow$ Mie Scattering

$\lambda >> d \Rightarrow$ Rayleigh Scattering

Effective Medium Approximation

ε_1 - inclusion dielectric constant
ε_0 - matrix medium dielectric constant
ε_{eff} – effective dielectric constant
η_1 – volume fraction of inclusions



Maxwell-Garnett Equation

$$\frac{\varepsilon_{eff}-\varepsilon_0}{\varepsilon_{eff}+2\varepsilon_0}=\eta_1\frac{\varepsilon_1-\varepsilon_0}{\varepsilon_1+2\varepsilon_0}$$

formula valid only for low concentraitions η_1 and small difference between ε_1 and ε_0