Interaction of liht with matter: scatter, absorption

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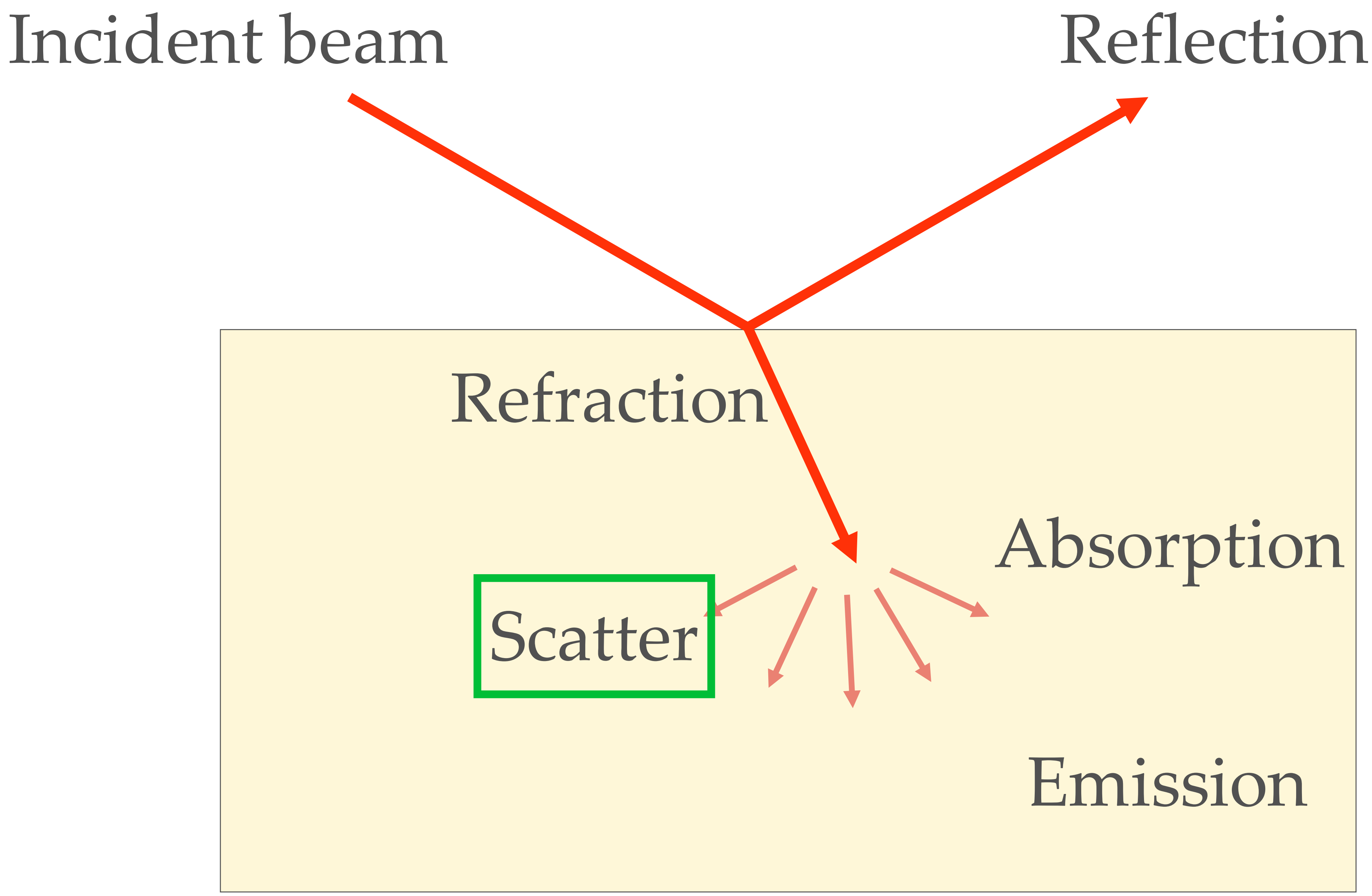
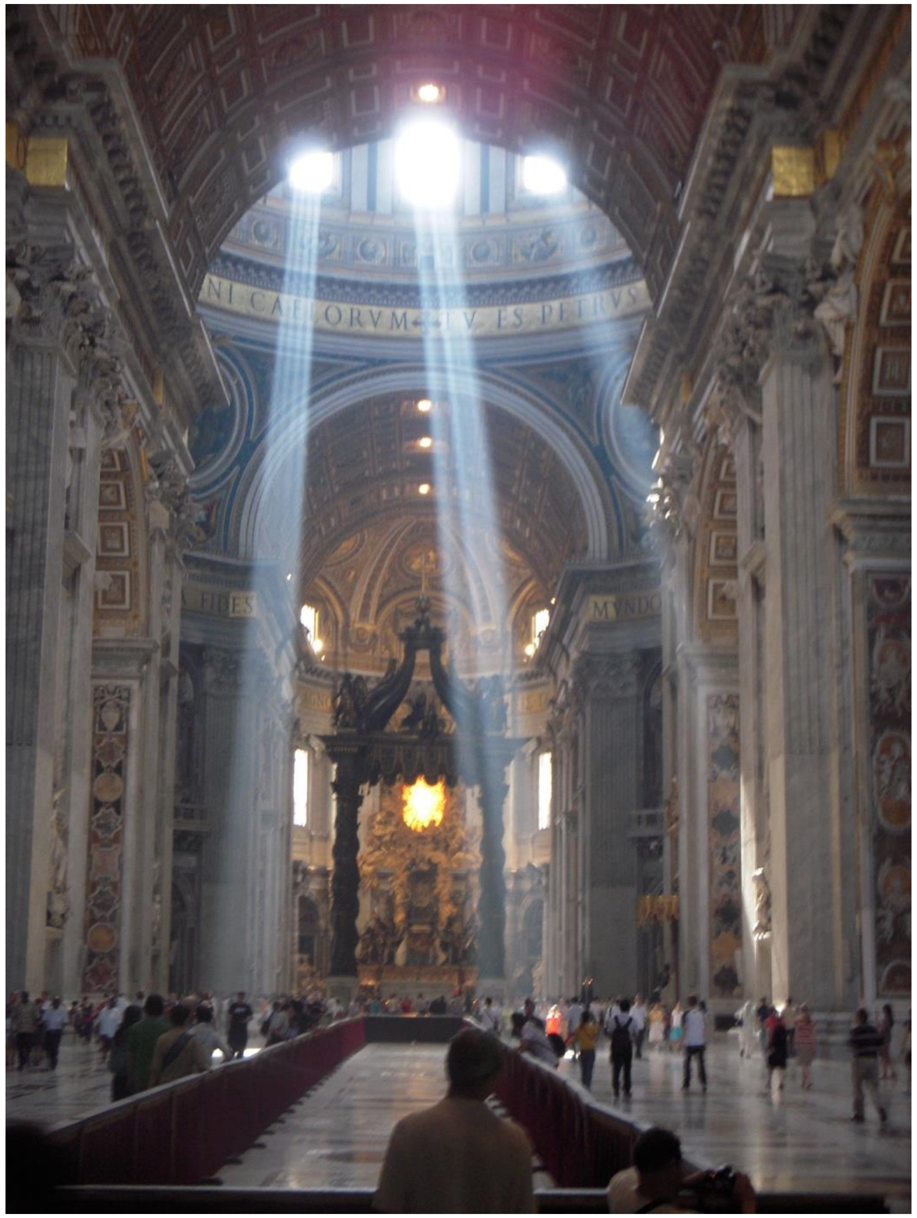
SEMMELWEIS
EGYETEM 1769

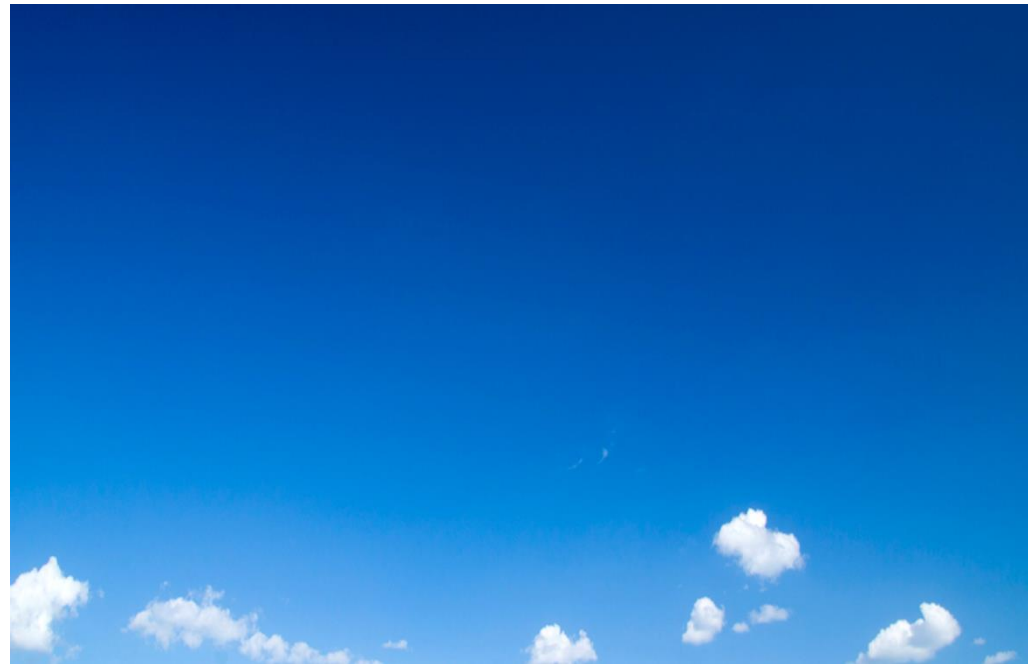
interaction of light with matter



Scattering of light



What are these days?
Crepuscular rays
(St. Peter’s basilica)



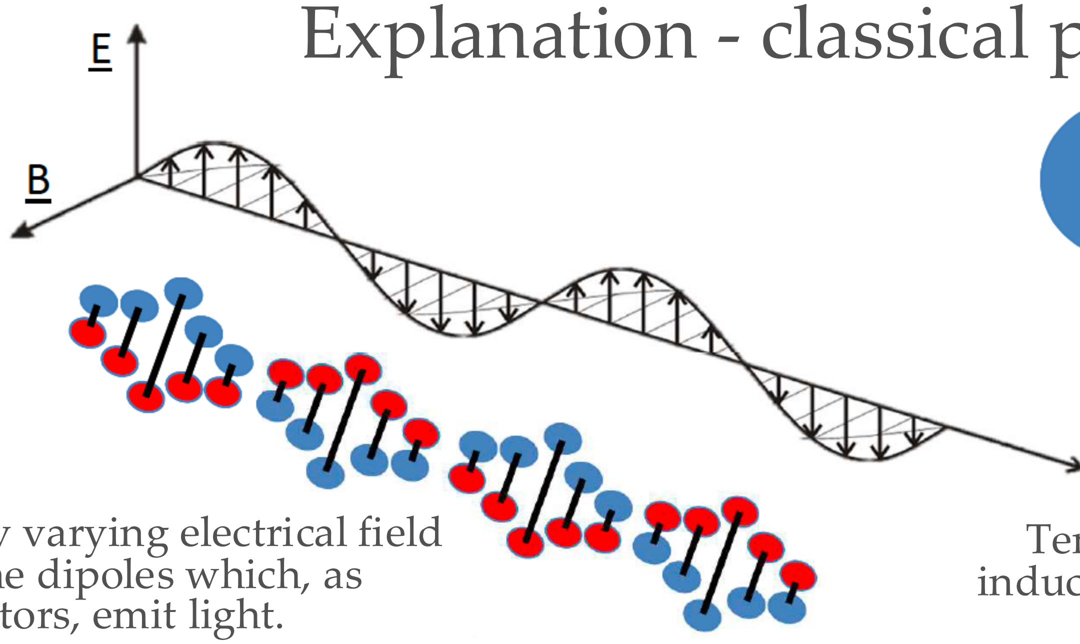
Why is the sky blue?

What makes the sunset red?

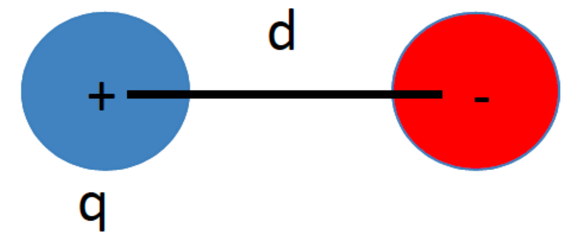
Scattering of light

Explanation - classical physics

Light is an electromagnetic wave (E, B: electric and magnetic fields)



The temporally varying electrical field vibrates the dipoles which, as oscillators, emit light.



Molecule as a dipole
Dipole moment (p_0):

$$p_0 = Qd$$

Temporally varying dipole moment induced by the varying electrical field: $p = p_0 \sin \omega t$

Dimension: Qdt^{-1}

How large is the scattered ("re-radiated") light's power? (P_{scatt}; dimension $W = Fdt^{-1}$)

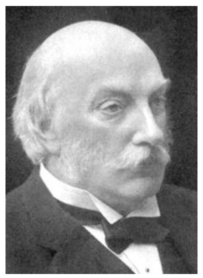
N.B. - Coulomb's law: $F \sim \dfrac{Q_1 Q_2}{r^2}$ (dimension $Q^2 d^{-2}$)

Dimensional derivation

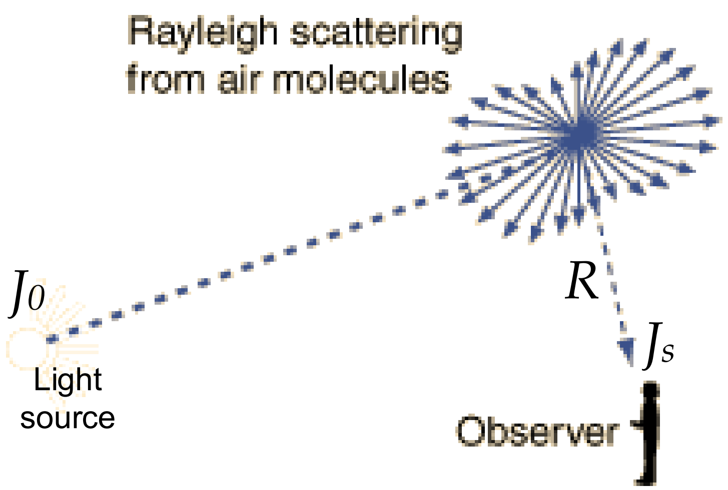
Physical parameter	Dimension	Operation
p_0^2	$Q^2 d^2$	Square
p_0^2	$Q^2 d^{-2} d^4 = Fd^4$	Expand with $d^2 d^{-2}$
p_0^2 / c^3	Fdt^3	Divide by c^3 ($d^3 t^{-3}$)
$(p_0^2 / c^3)\omega^4$	$Fdt^{-1} = W$	Multiply by ω^4 (t^{-4})

$$P_{scatt} = \frac{p_0^2}{c^3}\omega^4$$

Light scattering



Lord Rayleigh (1842-1919)



- Elastic collision: photon energy (wavelength) does not change
- Emission by resonating dipoles
- Scattering particles far from each other

$$J_s = J_0 \frac{8\pi^4 N\alpha^2}{\lambda^4 R^2}\left(1+\cos^2\Theta\right)$$

J_s=intensity of scattered light
J_0=intensity of incident light
N=number of scattering particles
α=polarizability (dipole moment per electric field)
λ=wavelength of light
R=distance between scatterer and observer
Θ=angle between light source and observer

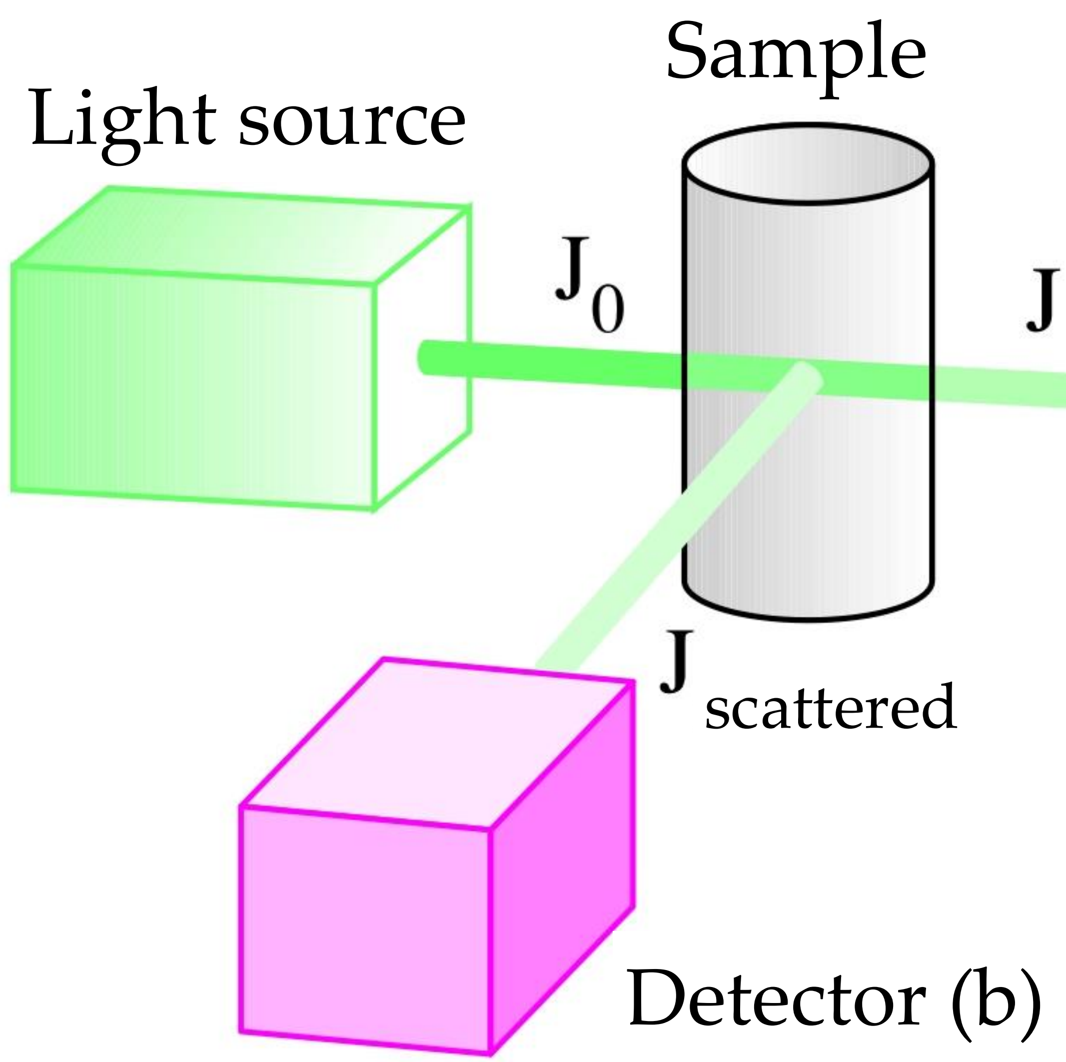
Strong wavelength dependence ➛ enhancement of short wavelengths ➛ blue sky

If scatterers are interacting particles the overall size of which is comparable to the wavelength ➛ interference, cancellation ➛ gray clouds

Mie scatter
(d~λ)
(J_s λ-independent)

Gustav Mie (1868-1957)

Biomedical applications of light scattering



Turbidimetry:

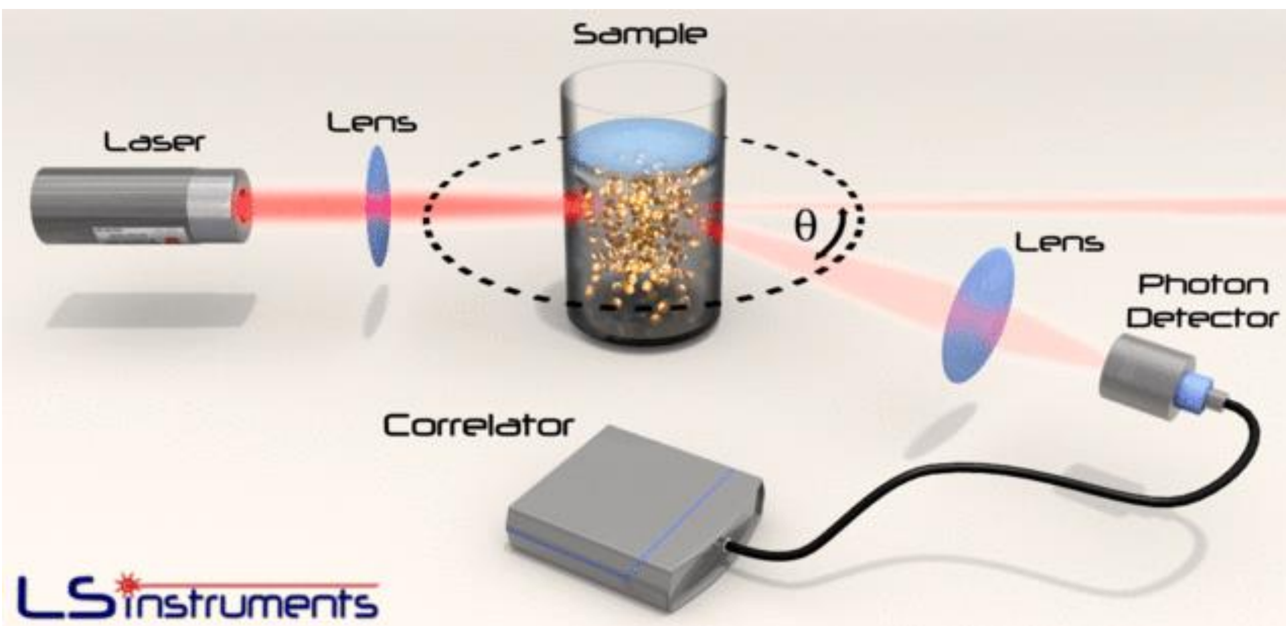
- measured via apparent absorbance

Nephelometry:

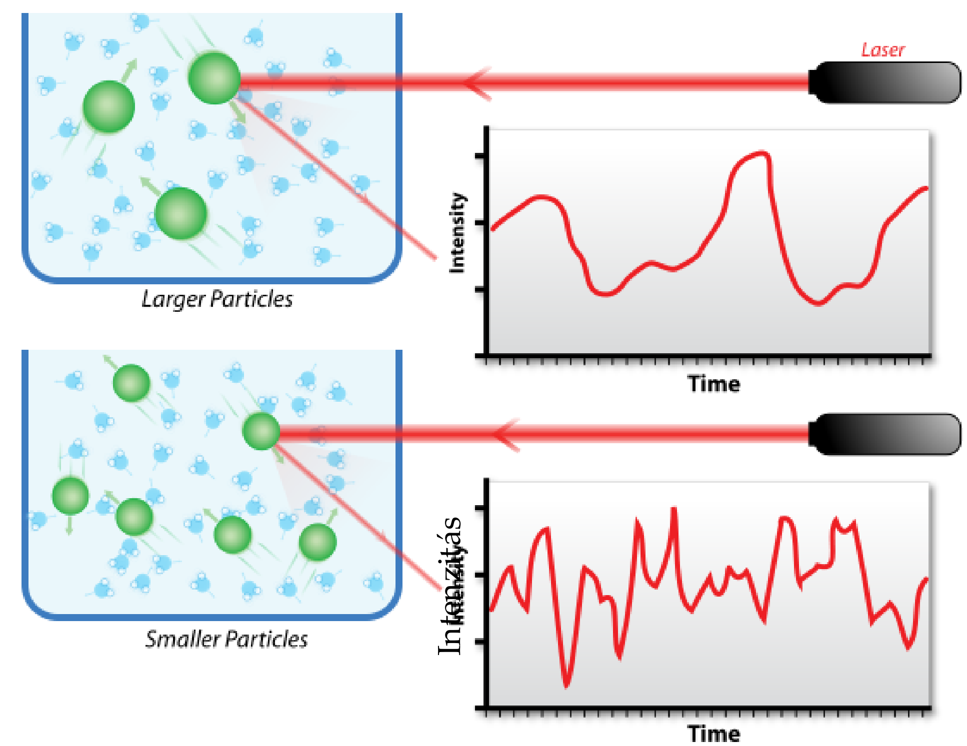
- small scatter
- concentration dependence
- concentration measurement of immune complexes

Dynamic Light Scattering (DLS)

Diffusing nm-scale particles



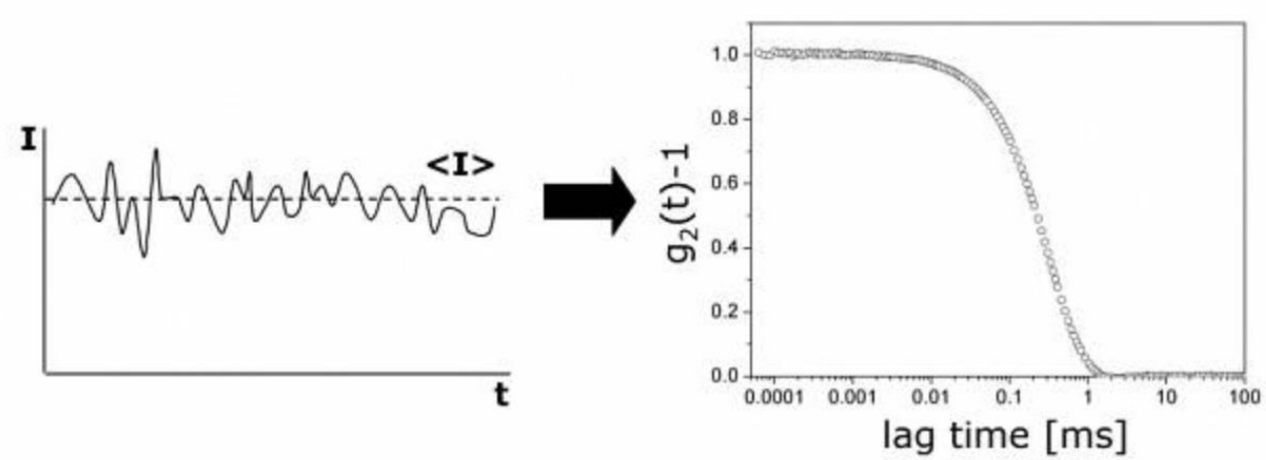
Intensity of scattered light fluctuates in time



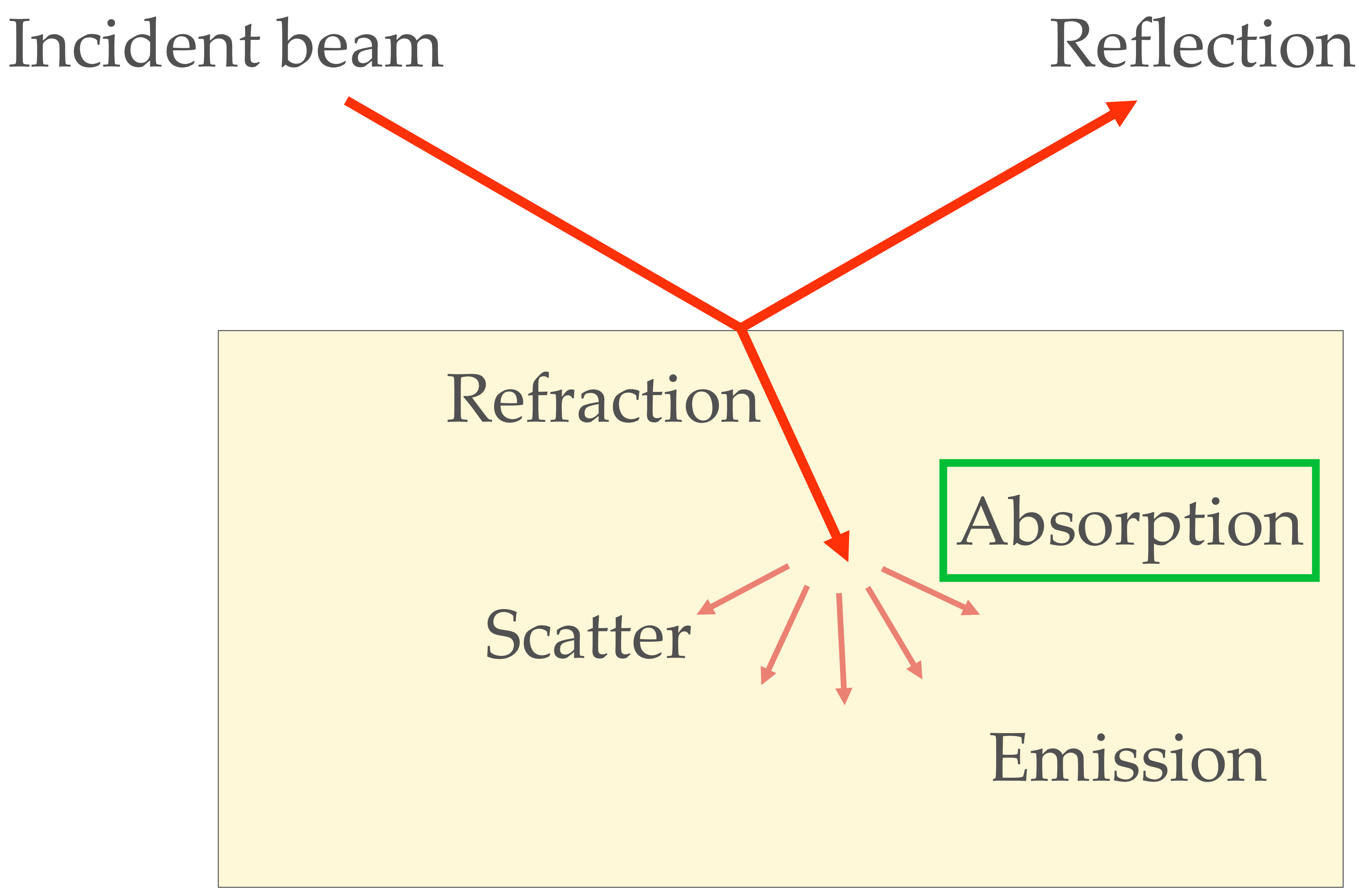
Fluctuation rate depends on particle size

- From the autocorrelation function ("self-similarity") of temporal intensity fluctuation the diffusion constant (D) can be calculated.
- From the diffusion constant the radius (r) of the spherical particle can be calculated (Stokes-Einstein):

$$D = \frac{k_B T}{6\pi\eta r}$$

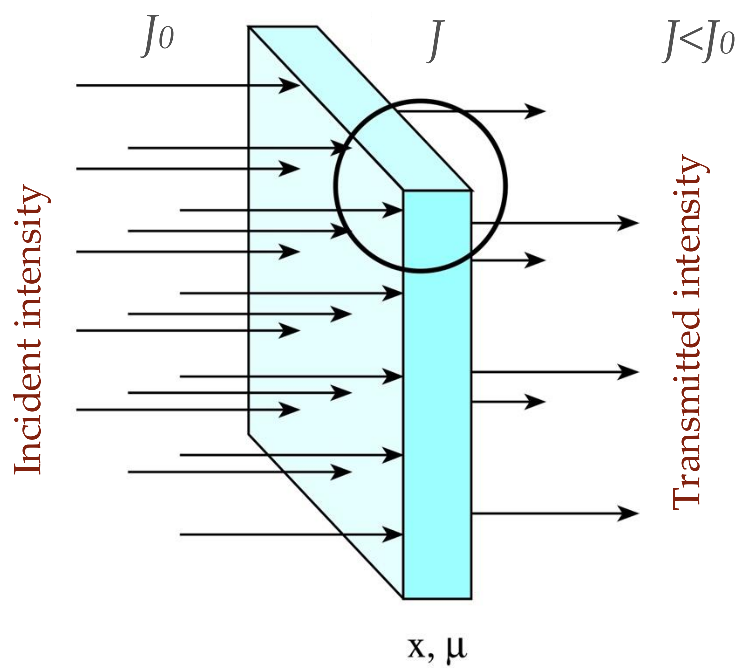


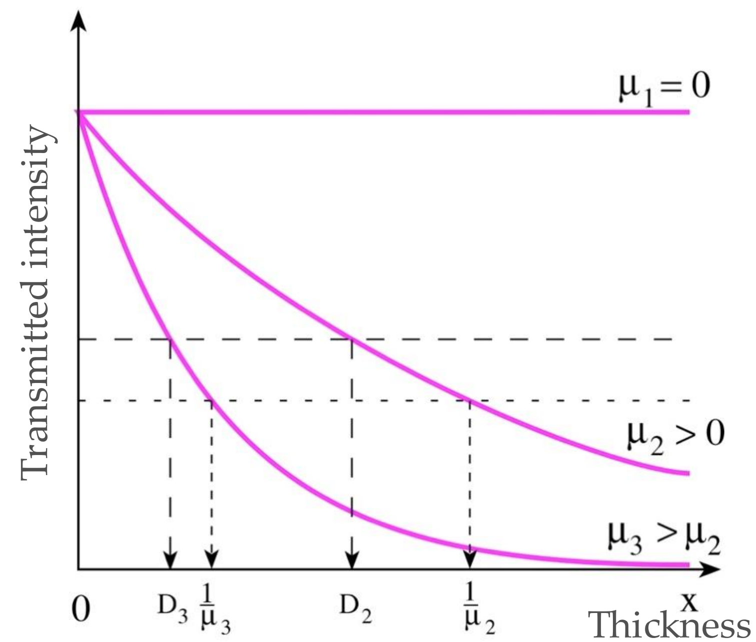
interaction of light with matter

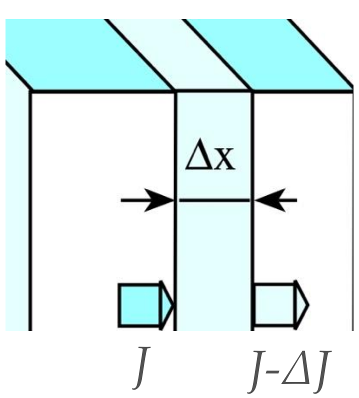


Absorption - *absorbere, lat.*, swallow

General absorption (attenuation) law





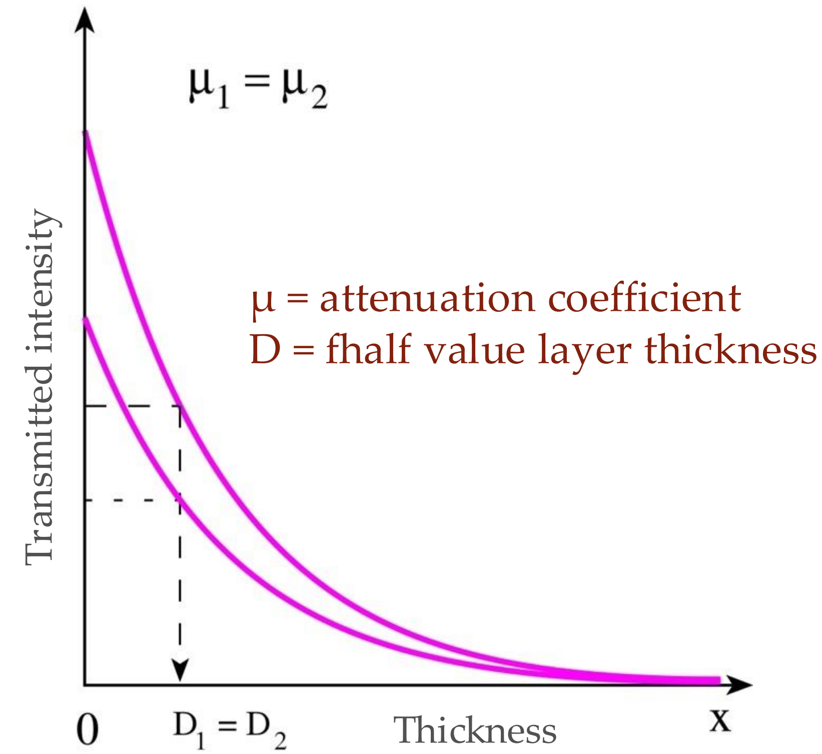


A given quantity (J) and its change (ΔJ) are proportional:

$$\Delta J = -\mu \Delta x J$$

Exponential function:

$$J = J_0 e^{-\mu x}$$

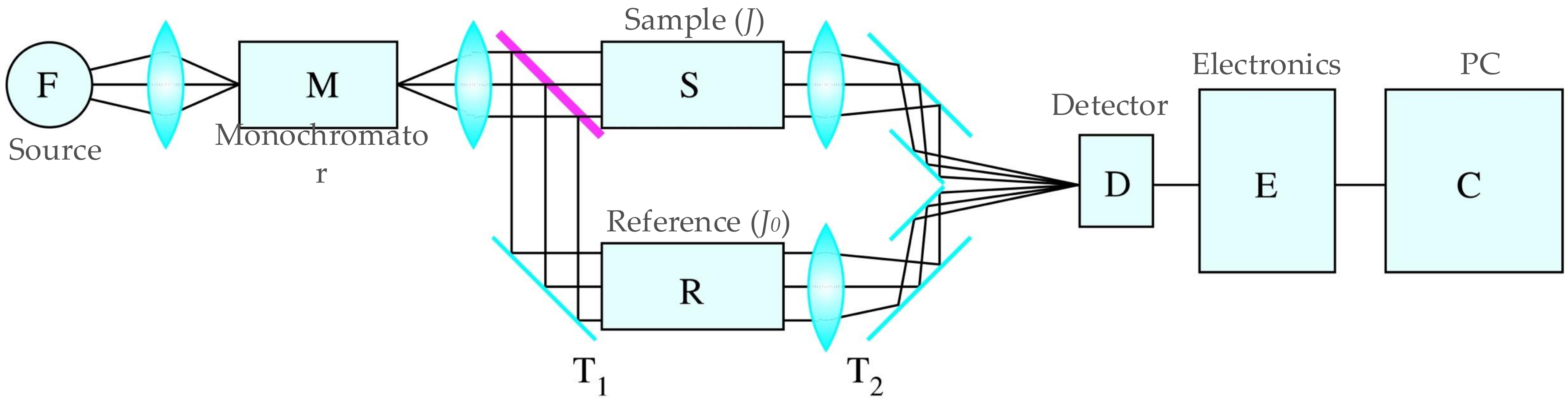


Parameters and measurement of absorption

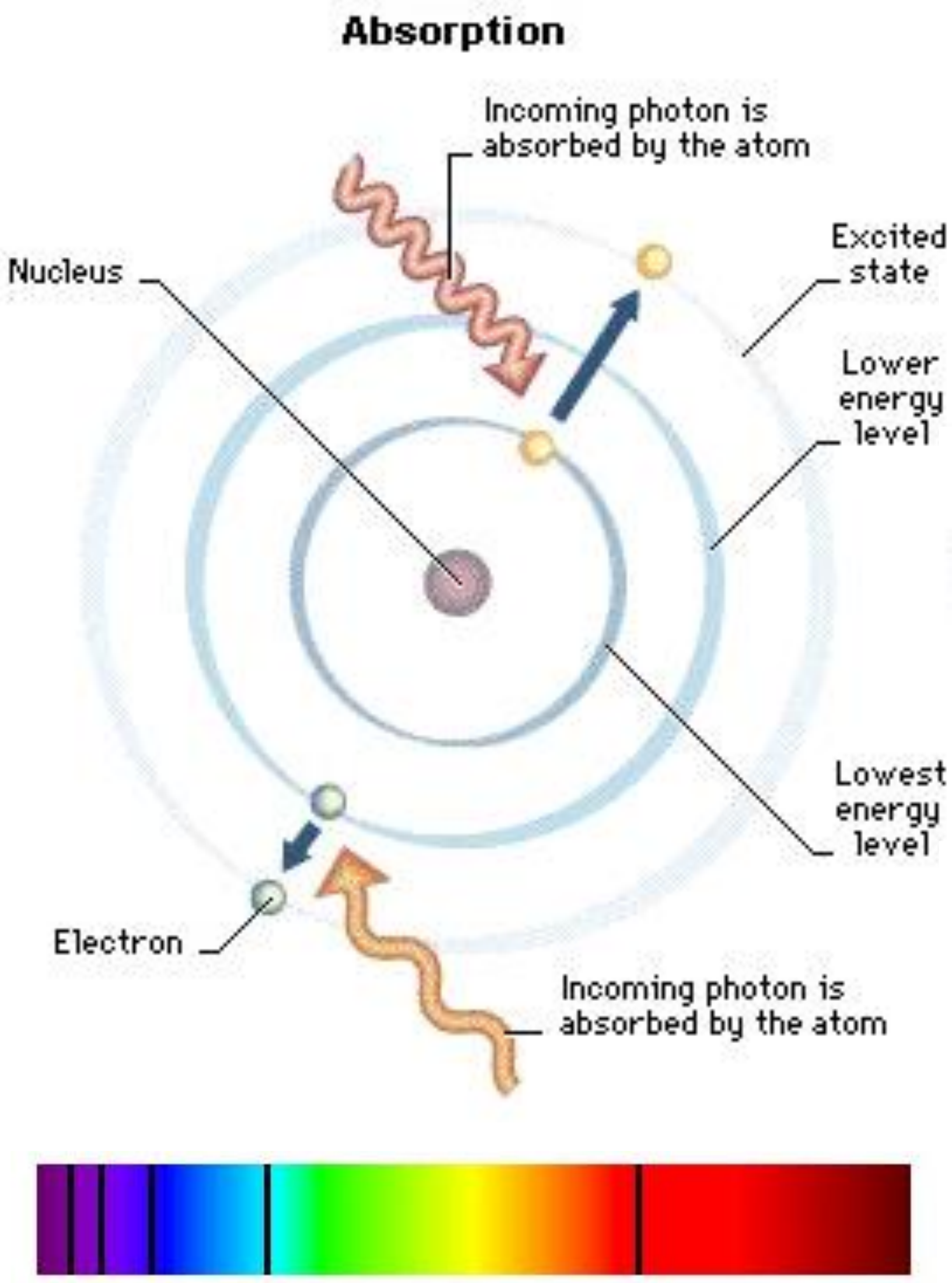
Absorbance (A): $$A = \lg \frac{J_0}{J} = \lg e \cdot \mu \cdot x$$ Dimensionless number
Synonyms: extinction, optical density (OD)

Transmittance (T): $$T = \frac{J}{J_0} \cdot 100$$ Expressed in percent (%)
Synonym: transmission coefficient

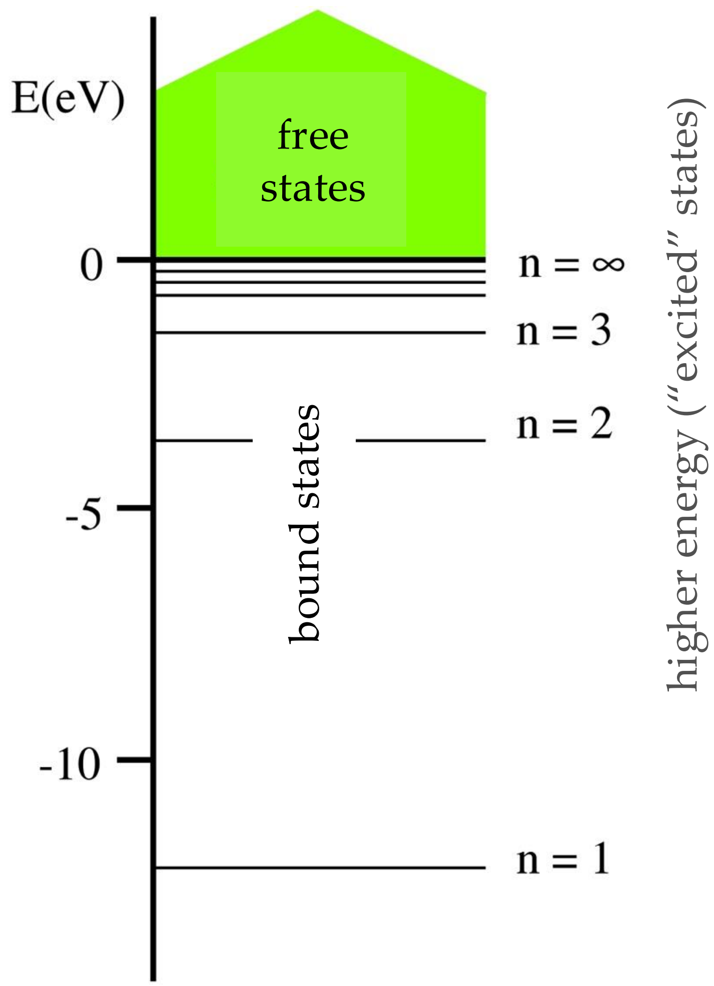
Photometry
("measurement of light"):



Light absorption by an atom

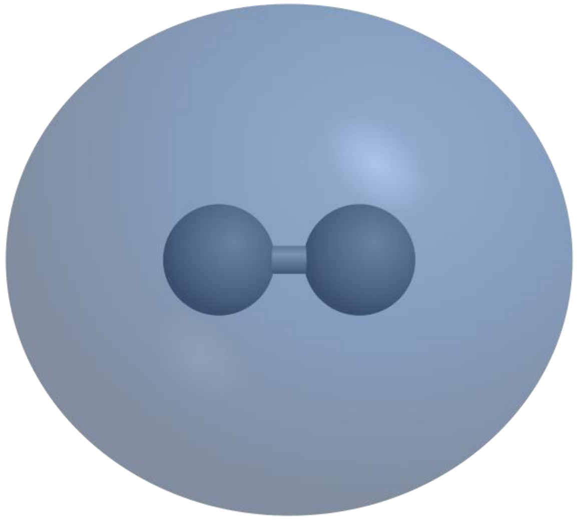


Absorption line spectrum



State of a molecule is affected by its motional modes

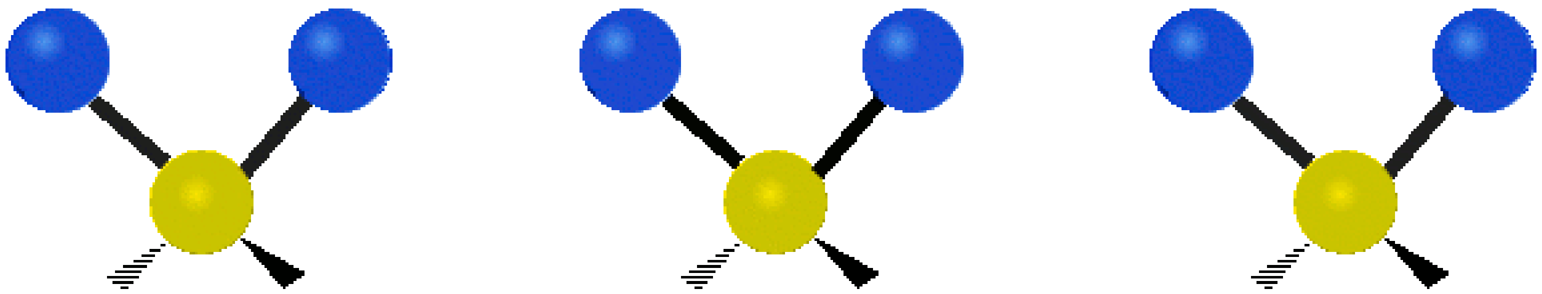
Molecule: atoms connected by chemical bonds
Simplest case: diatomic molecule (e.g., hydrogen molecule)



Molecules ***vibrate*** and ***rotate***!

Vibration: periodic motion ***along*** the axis of the covalent bond
Rotation: periodic motion ***around*** the axis of the covalent bond

Examples of vibrational motion in the triatomic methylene group (-CH_2-):



Asymmetric stretching *Symmetric stretching* *Scissoring*

Energy of a molecule

Max Born
(1882-1970)

J. Robert Oppenheimer
(1904-1967)

Born-Oppenheimer approximation:

$$E_{total} = E_e + E_v + E_r$$

Iportant notions:
Types of energy states are independent (not coupled)
Energy states are non-continuous, but discrete
Transition between states involves packets (quanta) of energy
Scales of transition energies between different states are different:

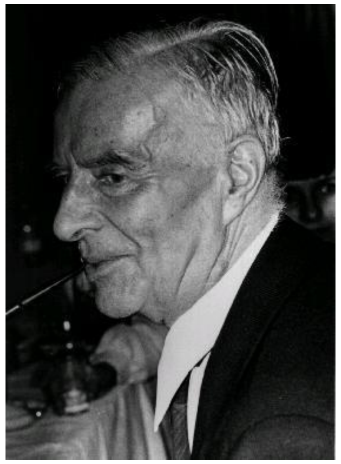
$$E_e \overset{\sim 100x}{>} E_v \overset{\sim 100x}{>} E_r$$

$\sim 3x10^{-19}$ J (~2 eV) > $\sim 3x10^{-21}$ J > $\sim 3x10^{-23}$ J

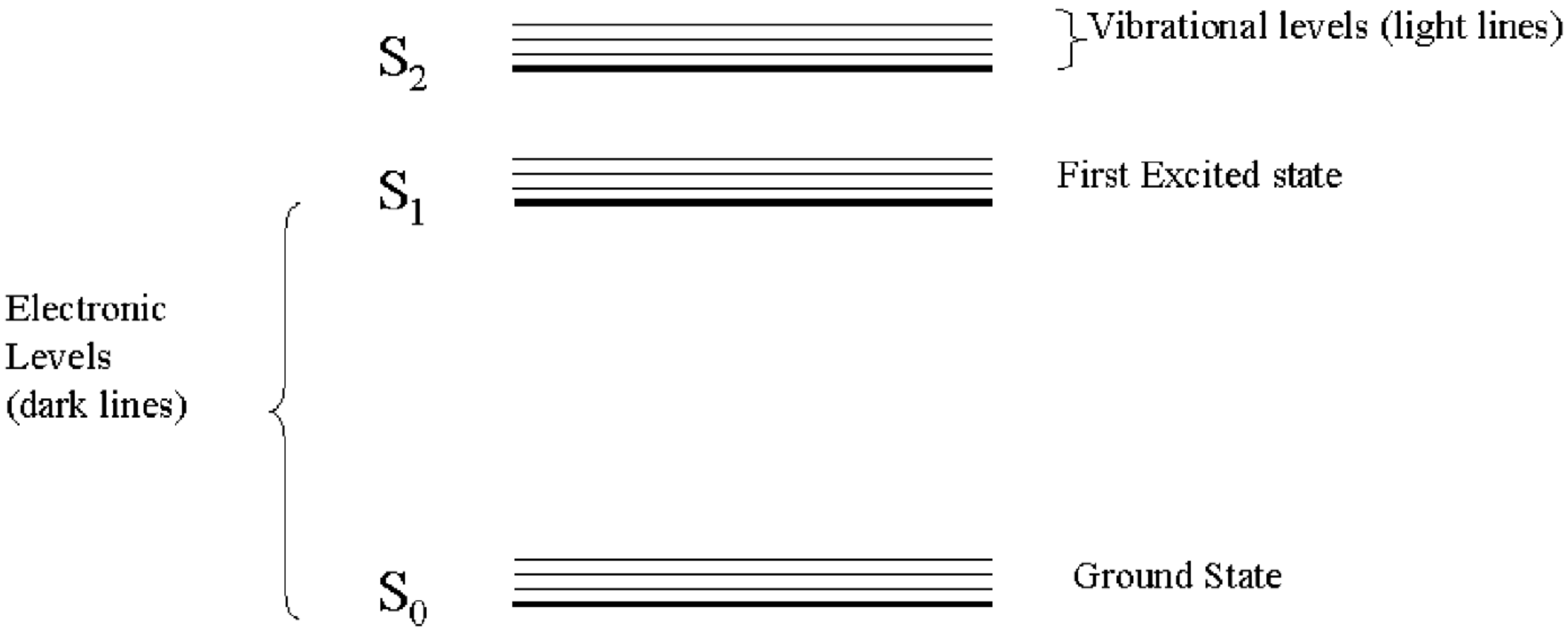
Representation of energy states

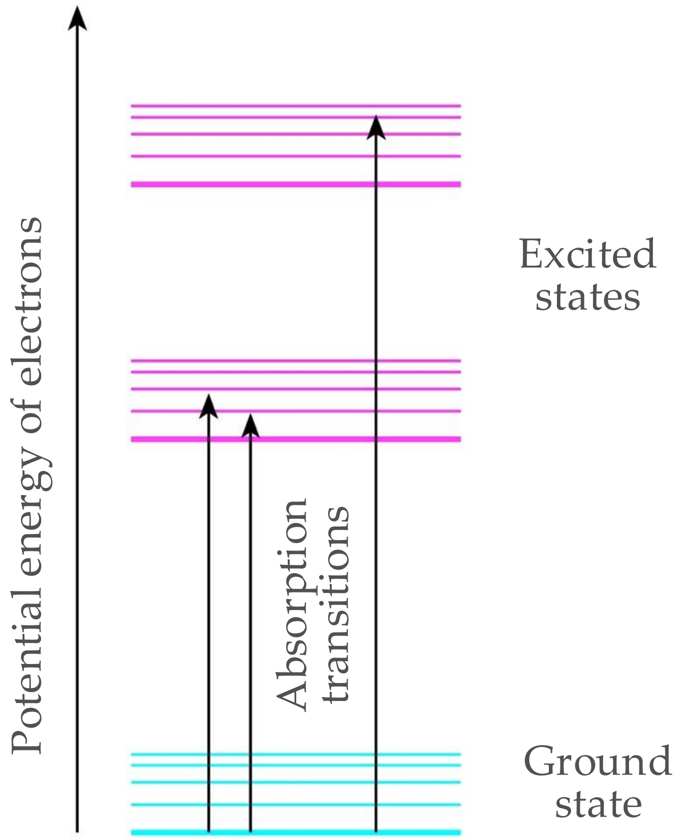
Jabłoński diagram:

illustrates the electronic states of a molecule and the transitions between them (with arrows)



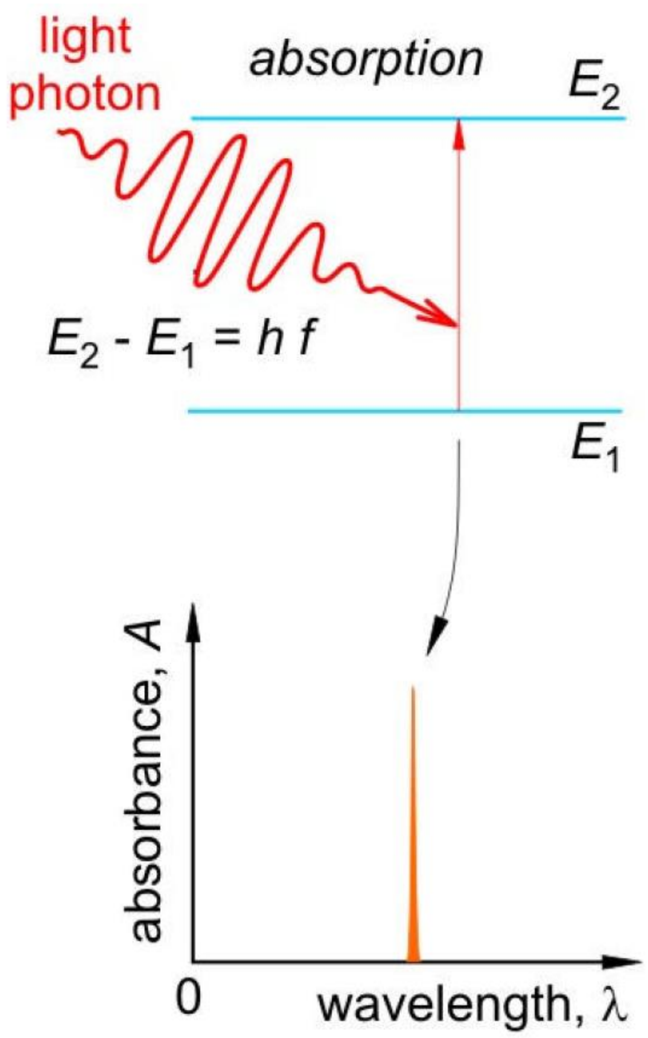
Alexander Jabłoński
(1898-1980)



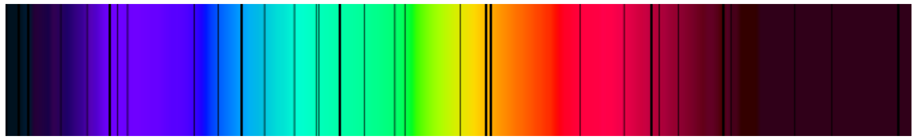


Origin of the band spectrum

Individual atoms

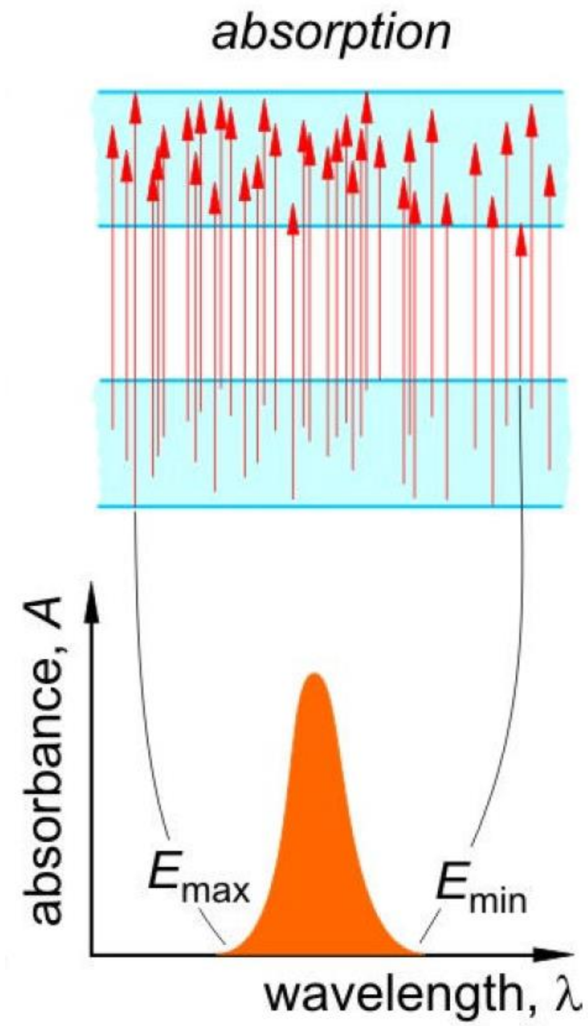


Line absorption spectrum



Narrow black lines ("missing colors") appear in the spectrum of the light source: absorption lines

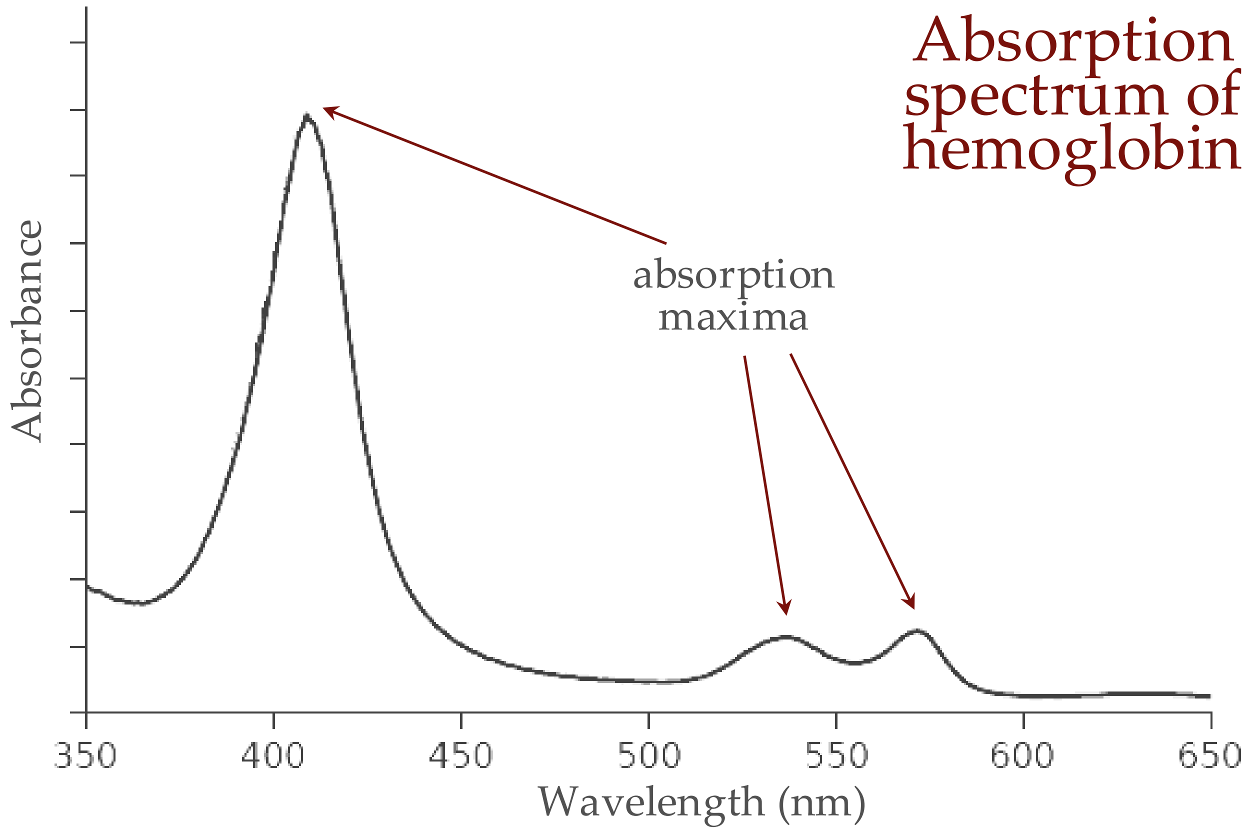
Molecules



Band spectrum - origin:

- chemically identical molecules are in different energy states
- thermal motion
- solvent conditions

Molecules have band absorption spectra



General attenuation law:

$$A = \lg \frac{J_0}{J} = \lg e \cdot \mu \cdot x$$

For dilute solutions - Lambert-Beer law:

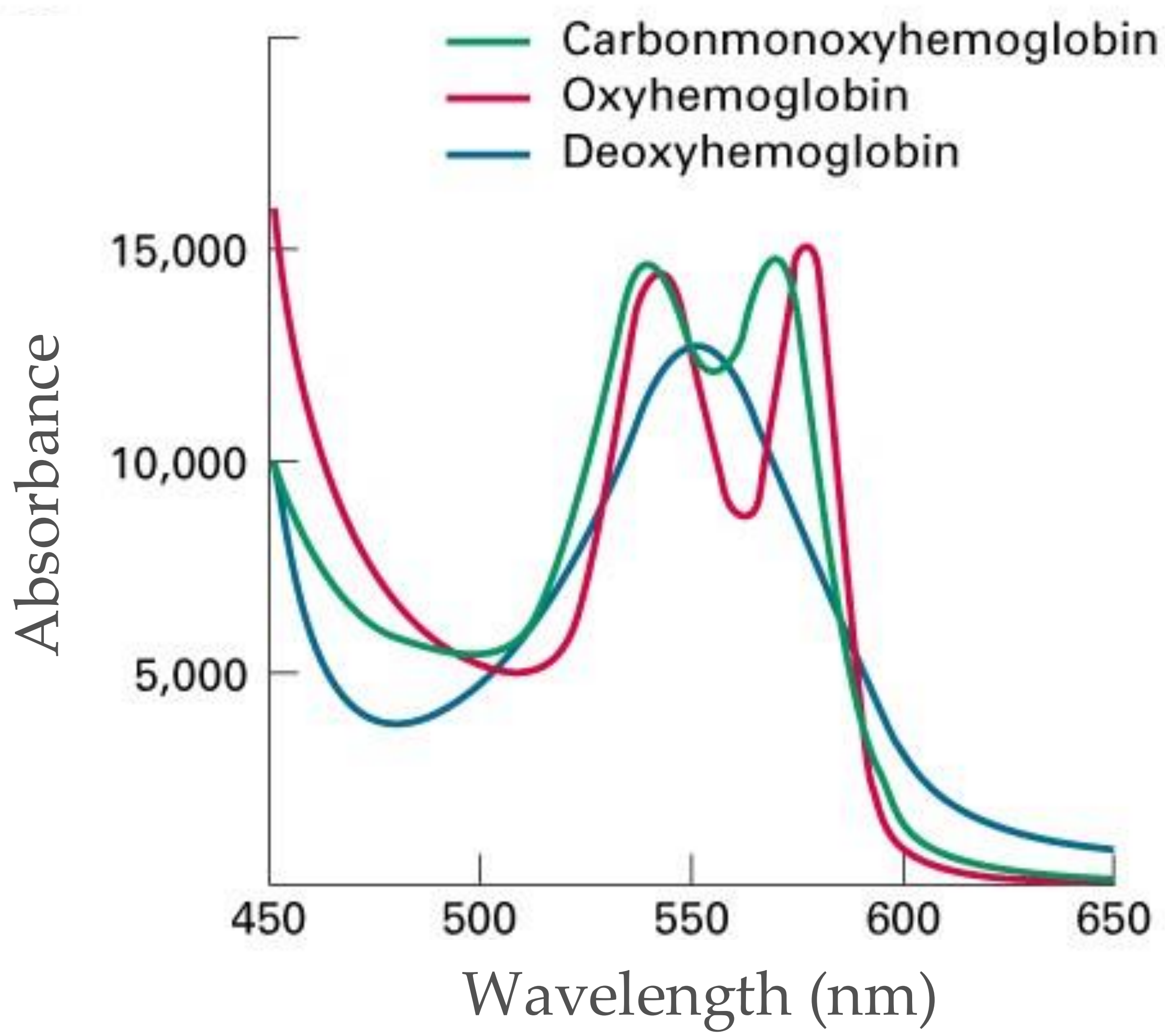
$$A_\lambda = \lg \frac{J_0}{J} = \varepsilon_\lambda \cdot c \cdot x$$

$\varepsilon\lambda$ = molar extinction coefficient
c = concentration

- SI unit of molar extinction coefficient ($\varepsilon\lambda$) : m^2mol^{-1}
- Method ideal for concentration measurement
- Based on the wavelength (at maximum) the transition energy may be calculated:

$$E_2 - E_1 = E_{foton} = h \cdot f = h \cdot \frac{c}{\lambda}$$

Absorption spectroscopy

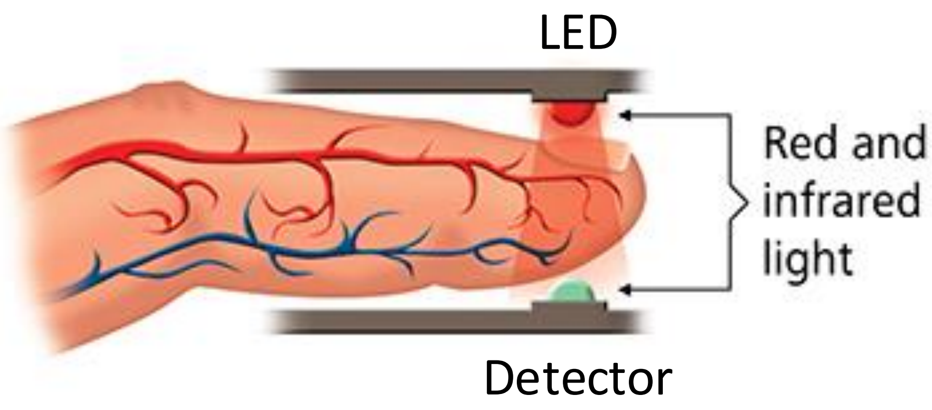


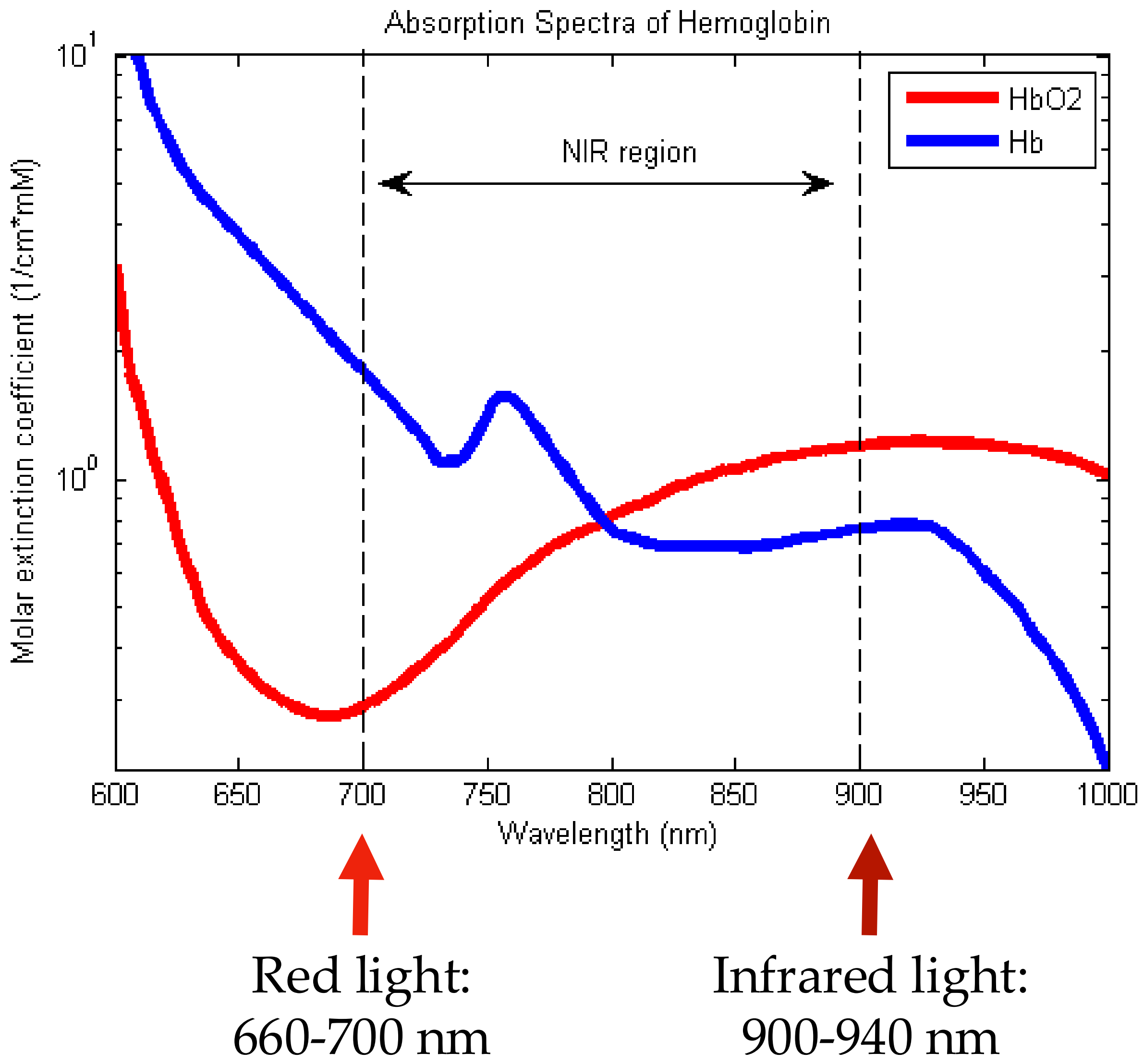
- *Spectrum*: intensity (or its derived units, e.g., OD) as a function of photon energy (or its derived units, e.g., frequency, wavelength).
- *Spectroscopy*: qualitative analysis of the spectrum.
- *Spectrometry, spectrophotometry*: quantitative analysis of the spectrum.
- *Applications*: analysis of chemical structure, concentration measurement, etc.

Pulse oxymetry

Non-invasive meaurement of oxygen saturation (SO_2)

- % of HgB that carries O_2 is measured
- Arterial oxygen saturation (SaO_2) is estimated from the peripheral (SpO_2)
- Normal value: 95-99%
- Ratio measurement is carried out (red/IR)





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