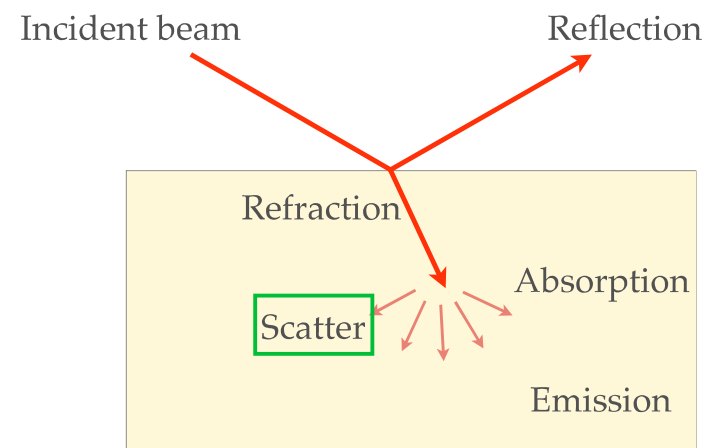


INTERACTION OF LIGHT WITH MATTER: SCATTER, ABSORPTION

MIKLÓS KELLERMAYER

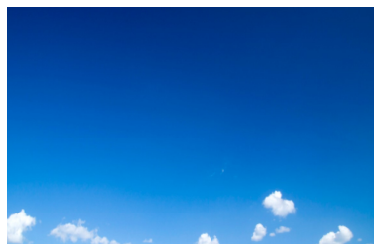
INTERACTION OF LIGHT WITH MATTER



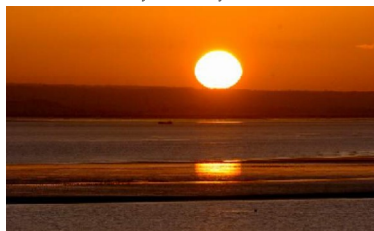
SCATTERING OF LIGHT



What are these rays?
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: $Qd t^{-1}$

How large is the scattered ("re-radiated") light's power? (P_{scatt} , dimension $W = F d t^{-1}$)

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

Dimensional derivation

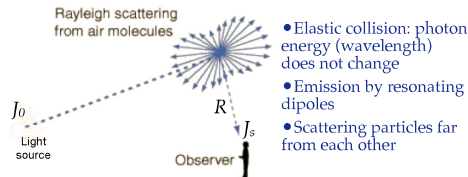
Physical parameter	Dimension	Operation
p_0^2	$Q^2 d^2$	Square
p_0^2 / c^3	$Q^2 d^{-2} d^4 = F d^4$	Expand with $d^2 d^{-2}$
$(p_0^2 / c^3) \omega^4$	$F d t^{-1} = W$	Divide by c^3 ($d^3 t^{-3}$) Multiply by ω^4 (t^{-4})

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

LIGHT SCATTERING



Lord Rayleigh
(1842-1919)



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

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

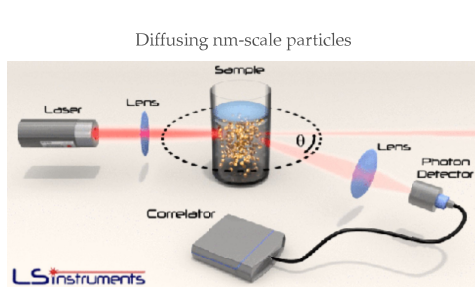


Strong wavelength dependence → enhancement of short wavelengths → blue sky

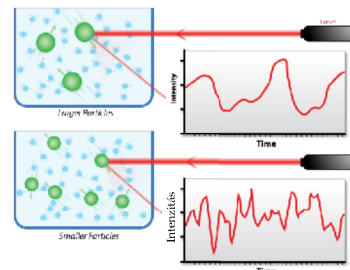


If scatterers are interacting particles the the overall size of which is comparable to the wavelength → interference, cancellation → gray clouds

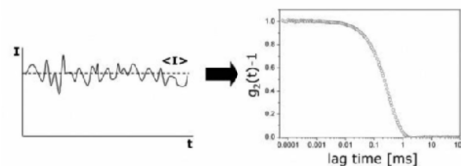
DYNAMIC LIGHT SCATTERING (DLS)



Intensity of scattered light fluctuates in time



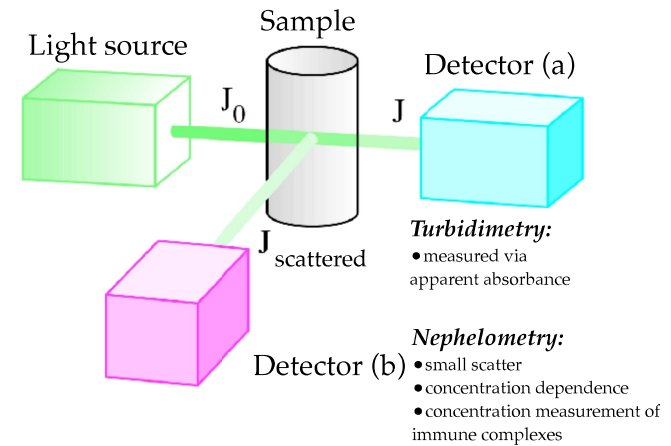
Fluctuation rate depends on particle size



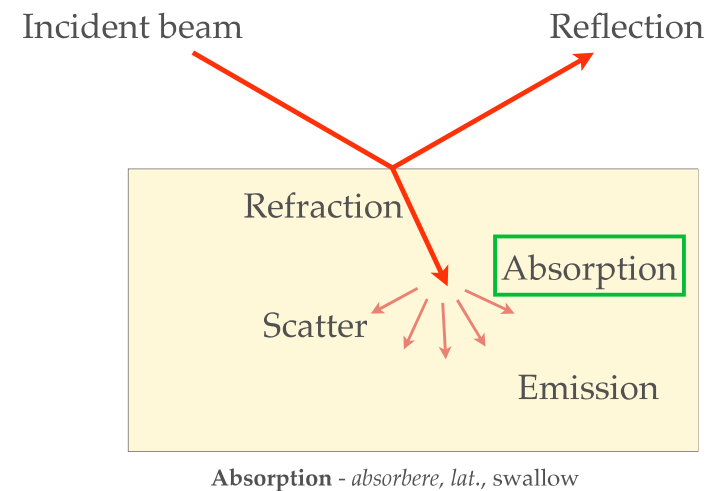
- From the autocorrelation function ("self-similarity") of temporal intensity fluctuation the diffusion constant (D) can be calculated.
- From the diffusion constant the radius (r) of the spherical particle can be calculated (Stokes-Einstein):

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

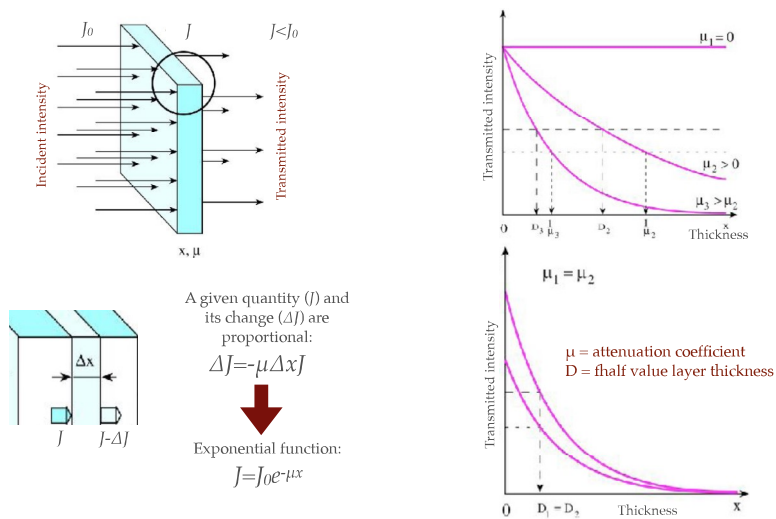
BIOMEDICAL APPLICATIONS OF LIGHT SCATTERING



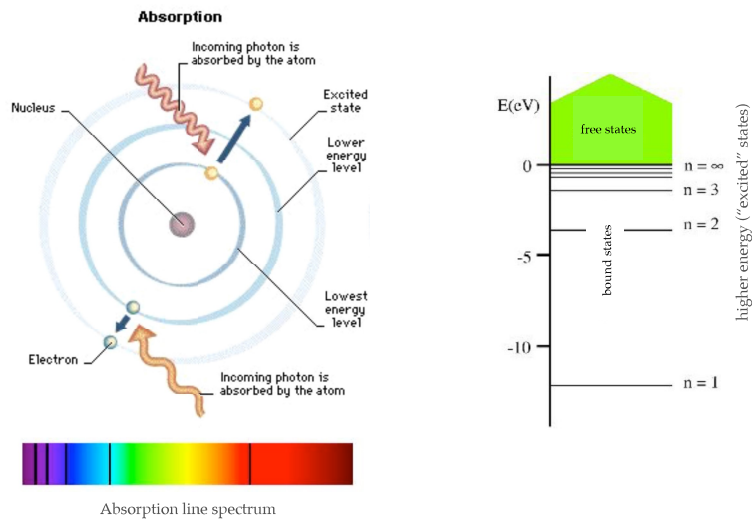
INTERACTION OF LIGHT WITH MATTER



GENERAL ABSORPTION (ATTENUATION) LAW



LIGHT ABSORPTION BY AN ATOM

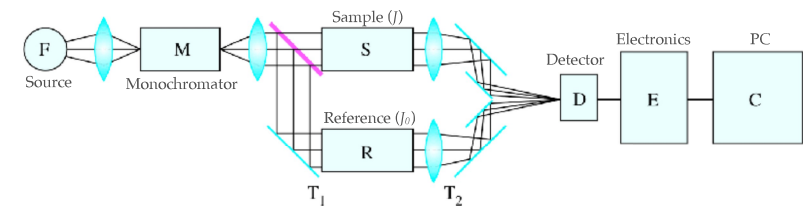


PARAMETERS AND MEASUREMENT OF ABSORPTION

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

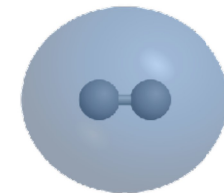
Transmittance (T): $T = \frac{J}{J_0} \cdot 100$ Expressed in percent (%)
Synonym: transmission coefficient

Photometry
("measurement of light"):



STATE OF A MOLECULE IS AFFECTED BY ITS MOTIONAL MODES

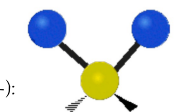
Molecule: atoms connected by chemical bonds
Simplest case: diatomic molecule (e.g., hydrogen molecule)



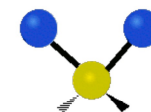
Molecules *vibrate* and *rotate*!

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

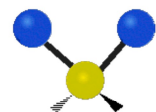
Examples of vibrational motion in the triatomic methylene group (-CH2-):



Asymmetric stretching



Symmetric stretching



Scissoring

ENERGY OF A MOLECULE



Max Born
(1882-1970)



J. Robert Oppenheimer
(1904-1967)

Born-Oppenheimer approximation:

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

Important notions:

Types of energy states are independent (not coupled)

Energy states are non-continuous, but discrete

Transition between states involves packets (quanta) of energy

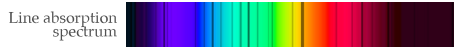
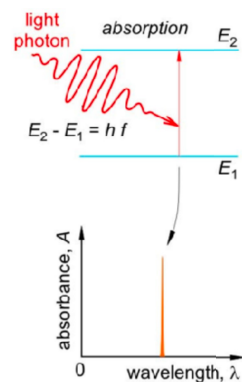
Scales of transition energies between different states are different:

$$E_e \sim 100\times E_v \sim 100\times E_r$$

$$\sim 3 \times 10^{-19} \text{ J } (\sim 2 \text{ eV}) > \sim 3 \times 10^{-21} \text{ J } > \sim 3 \times 10^{-23} \text{ J }$$

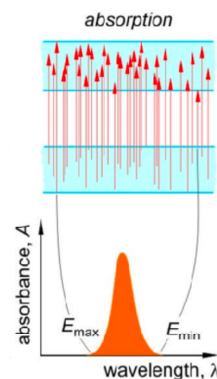
ORIGIN OF THE BAND SPECTRUM

Individual atoms



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

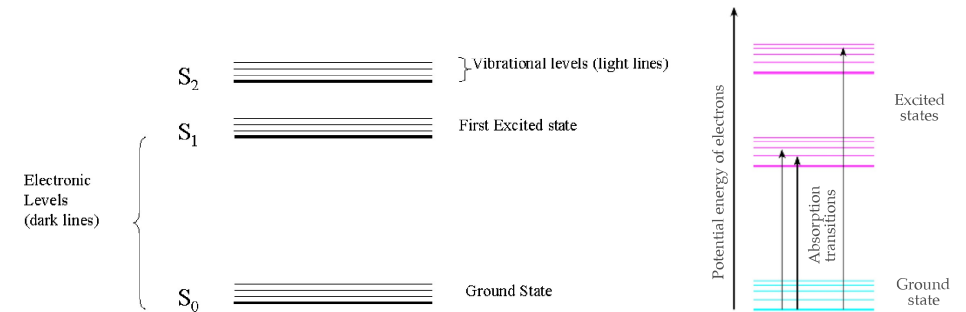
REPRESENTATION OF ENERGY STATES

Jabłoński diagram:

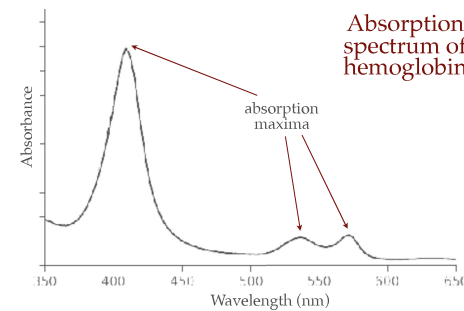
illustrates the electronic states of a molecule and the transitions between them (with arrows)



Alexander Jabłoński
(1898-1980)



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:

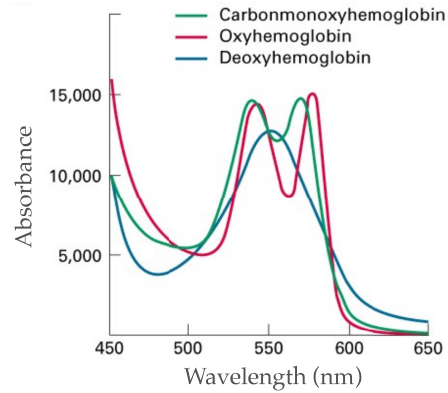
$$A_\lambda = \lg \frac{J_0}{J} = \epsilon_\lambda \cdot c \cdot x$$

ϵ_A = molar extinction coefficient
 c = concentration

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

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

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.

INTERACTION OF LIGHT WITH MATTER

