Interaction of light with matter:
Scatter, absorption

Miklós Kellermayer

Interaction of light with matter

Incident beam   Reflection

Refraction

Scatter   Absorption

Emission
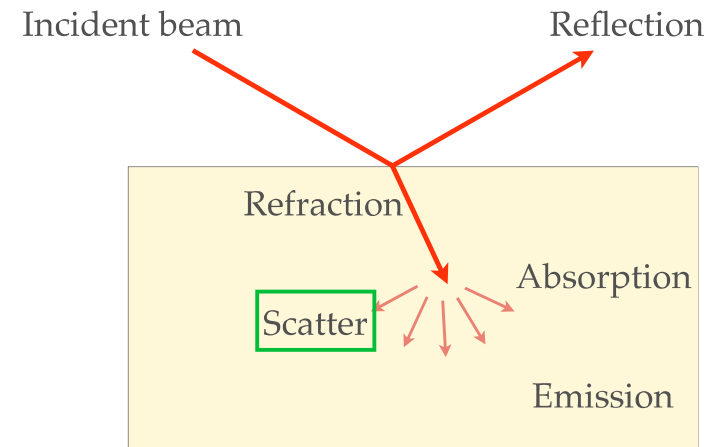
Scattering of light

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)

Molecule as a dipole
Dipole moment (p_0):

$$p_0 = Qd$$

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

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 $Q^2 d^{-2}$)

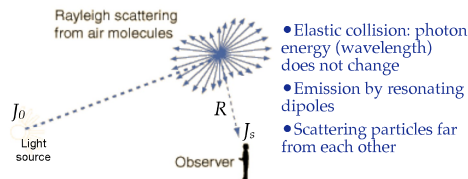| Physical parameter	Dimension	Operation
p_0^2	$Q^2 d^2$	Square
p_0^2	$Q^2 d^{-2} d^4 = Fd^4$	Expand with $d^2 d^{-2}$
p_0^2 / c^3	Fdt^3	Divide by c^3 ($d^3 t^{-3}$)
$\left(p_0^2 / c^3\right)\omega^4$	$Fdt^{-1} = W$	Multiply by ω^4 (t^{-4})

Dimensional derivation

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

Light scattering

Lord Rayleigh
(1842-1919)

Rayleigh scattering from air molecules

J_0 Light source

R

J_s

Observer

- 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
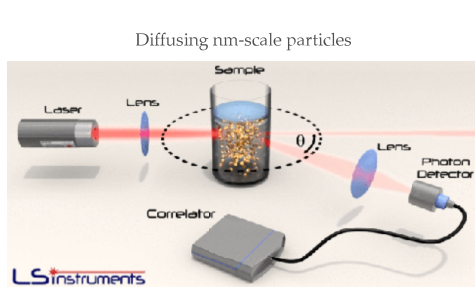Θ=angle between light source and observer

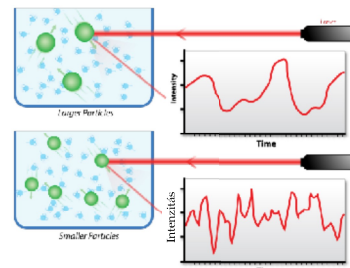Strong wavelength dependence ➤ enhancement of short wavelengths ➤ blue sky
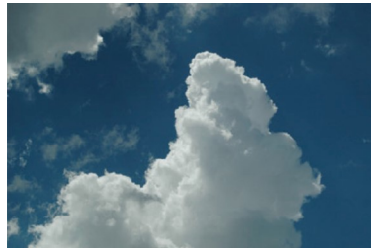
If scatterers are interacting particles the the overall size of which is comparable to the wavelength ➤ interference, cancellation ➤ gray clouds
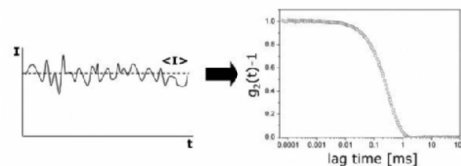
Biomedical applications of light scattering

Light source

Sample

Detector (a)

J_0

J

J scattered

Detector (b)

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
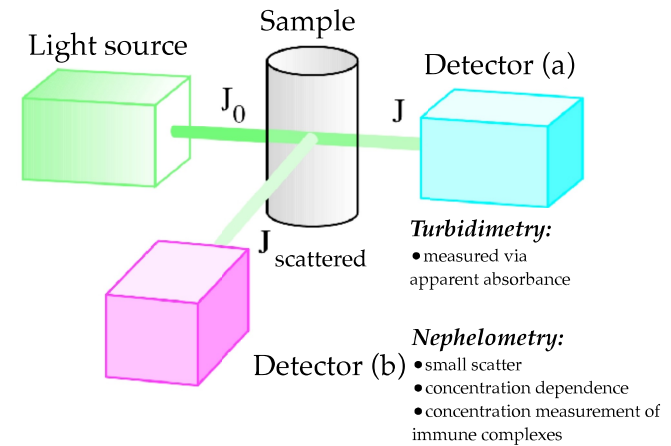
Fluctuation rate depends on particle size

- From the autocorrelation function ("self-similarity") of temporal intensity fluctuation the diffusion constant (D) can be calculated.
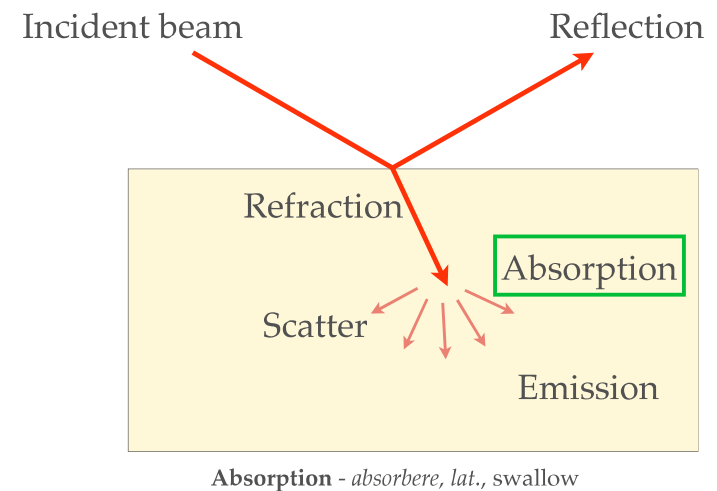- From the diffusion constant the radius (r) of the spherical particle can be calculated (Stokes-Einstein):
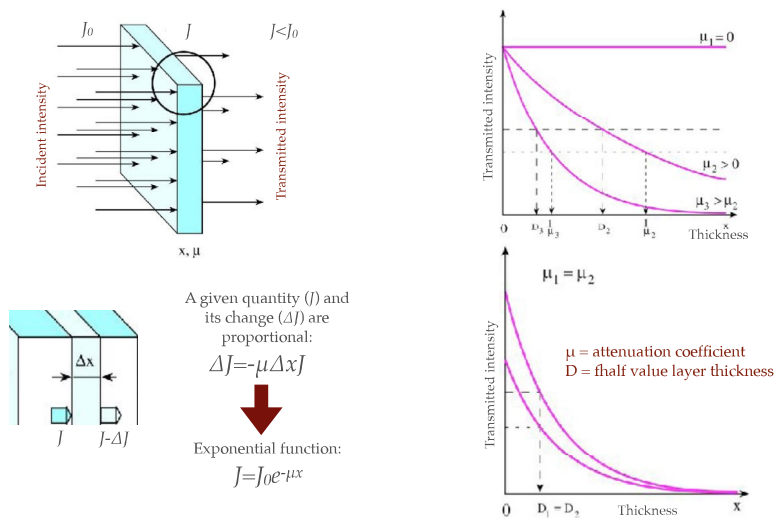
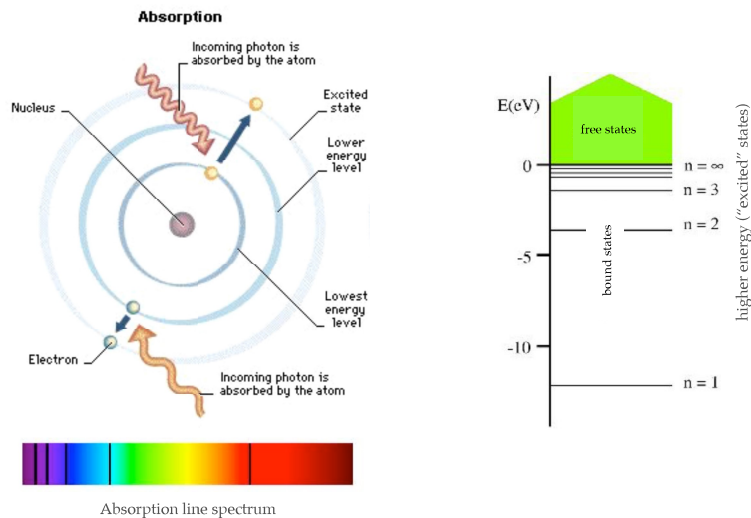$$D = \frac{k_B T}{6\pi\eta r}$$

lag time [ms]

interaction of light with matter

Incident beam

Reflection

Refraction

Absorption

Scatter

Emission

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:

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

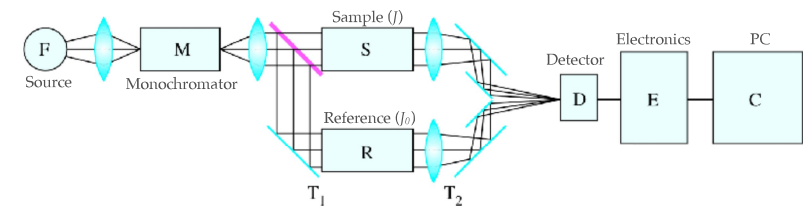μ = attenuation coefficient
D = fhalf value layer thickness

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)
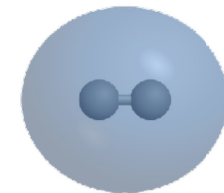
Molecules *vibrate* and *rotate*!

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*
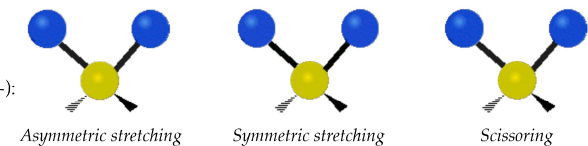
Energy of a molecule

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
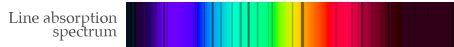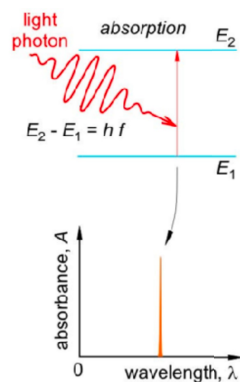Transition between states involves packets (quanta) of energy
Scales of transition energies between different states are different:

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

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

S_2]Vibrational levels (light lines)

S_1 First Excited state

Electronic Levels (dark lines)

S_0 Ground State

Potential energy of electrons

Absorption transitions

Excited states

Ground state

Origin of the band spectrum

Individual atoms

light photon

absorption E_2

$E_2 - E_1 = h f$

E_1

absorbance, A

0   wavelength, λ

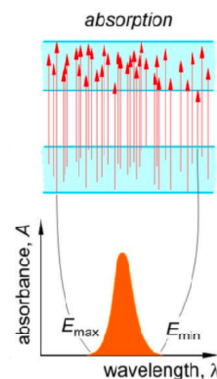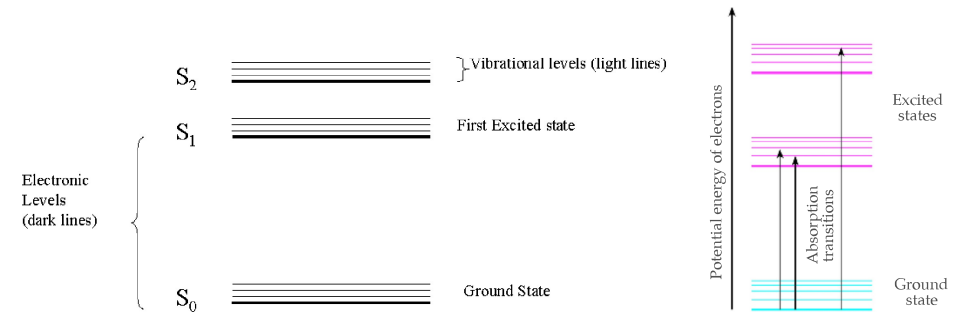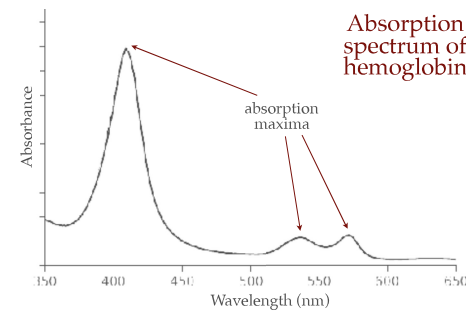Line absorption spectrum

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

Molecules

absorption

absorbance, A

E_{max} E_{min}

wavelength, λ

Band spectrum - origin:
• chemically identical molecules are in different energy states
• thermal motion
• solvent conditions

Molecules have band absorption spectra

Absorbance

Absorption spectrum of hemoglobin

absorption maxima

350   400   450   500   550   600   650
Wavelength (nm)

• SI unit of molar extinction coefficient (ε_λ) : m²mol⁻¹
• Method ideal for concentration measurement
• Based on the wavelength (at maximum) the transition energy may be calculated:

General attenuation law:

$$A = \lg \frac{J_0}{J} = \lg e \cdot \mu \cdot x$$
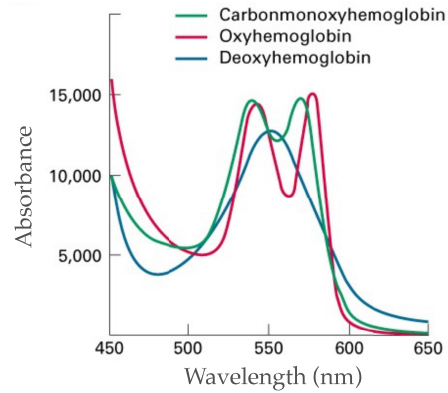
For dilute solutions - Lambert-Beer law:

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

ε_λ = molar extinction coefficient
c = concentration

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

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.

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