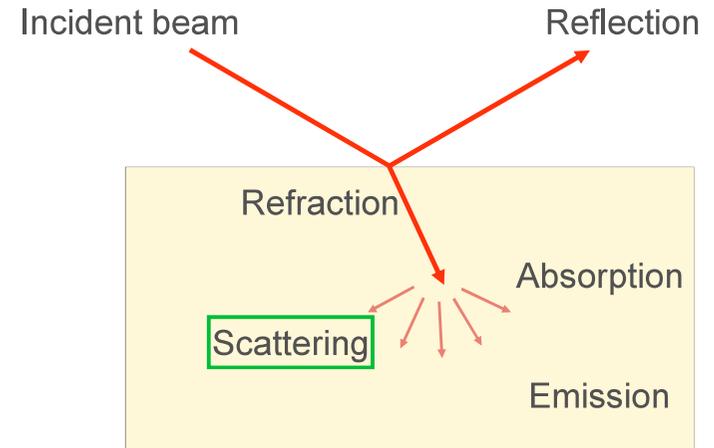


# Interaction of light with matter: Scattering, absorption

# Interaction of light with matter



## Scattering of light

## Scattering of light



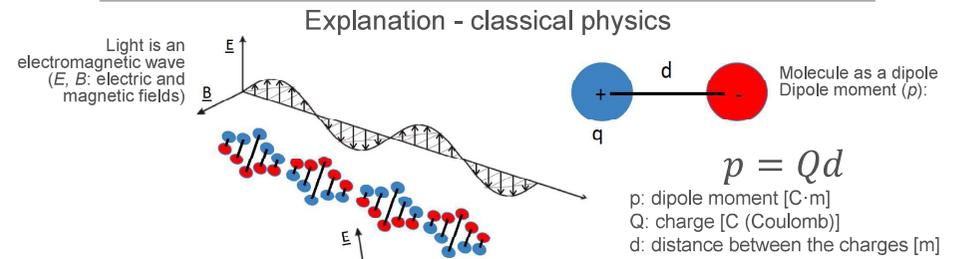
What are these rays?  
Crepuscular rays  
(St. Peter's basilica)



Why is the sky blue?



What makes the sunset red?



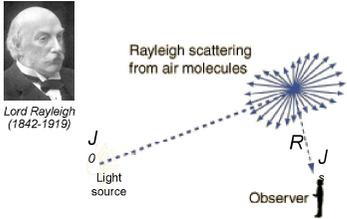
- the incident light (EM wave) interacts with the particle
- the change of the electric field induces a temporary transfer of charges in the particle: induces a dipole
- the temporally varying electrical field vibrates the dipoles which, as oscillators, emit light.

$$\alpha = \frac{p}{E}$$

dipole that is generated by a unit of electric force-field

$\alpha$ : polarizability [C·m<sup>2</sup>·V<sup>-1</sup>]  
 $p$ : dipole moment [C·m]  
 $E$ : electric field strength [V/m]

# Rayleigh scattering



Lord Rayleigh (1842-1919)

- Elastic collision: photon energy (wavelength, frequency) does not change
- $d \ll \lambda$  (particles are smaller than the wavelength)
- Mobile scattering particles, located randomly, relatively far from each other  
 → Disorder of phases, there is no interference



Strong wavelength dependence → enhancement of short wavelengths → blue sky

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

$J_s$ =intensity of scattered light  
 $J_0$ =intensity of incident light  
 $N$ =number of scattering particles  
 $\alpha$ =polarizability (dipole moment per electric field)  
 $\lambda$ =wavelength of light  
 $R$ =distance between scatterer and observer  
 $\Theta$ =angle between light source and observer

$$J_s \sim \frac{1}{\lambda^4}$$



# Mie scattering



Gustav Mie 1868-1957

- Elastic collision: photon energy (wavelength) does not change
- No strong  $\lambda$  dependency



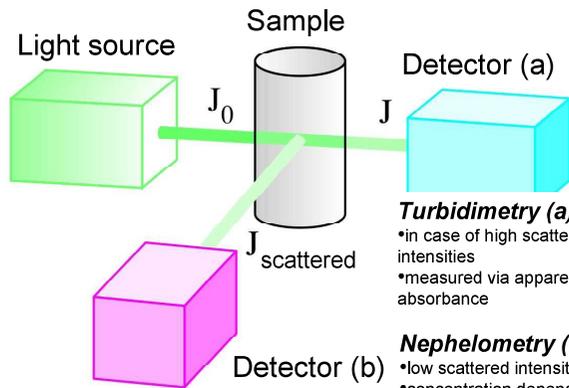
Scatterers are interacting particles the overall size of which is comparable to the wavelength. White or grey colour of clouds is determined by the size of droplets

Bigger particle size ( $> \lambda/10$ ), groups of molecule very close to each other (e.g. water droplets)  
 → oscillate at same phase → interference

## Inelastic scattering

- Energy transition between light and material
- $\lambda, f, \text{ energy are not constant}$
- e.g. Raman scattering, Compton scattering (later)

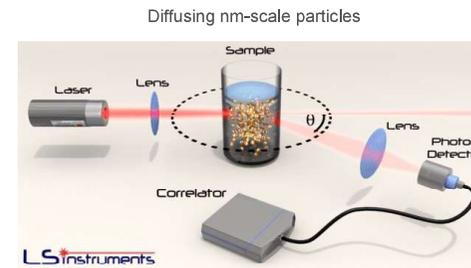
# Biomedical applications of light scattering



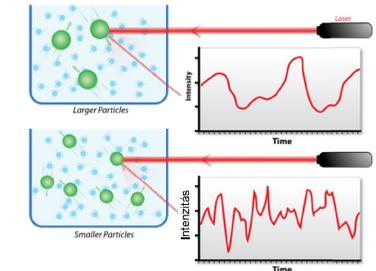
**Turbidimetry (a):**  
 •in case of high scattered intensities  
 •measured via apparent absorbance

**Nephelometry (b):**  
 •low scattered intensity  
 •concentration dependence  
 •concentration measurement of immune complexes

# Dynamic Light Scattering (DLS)



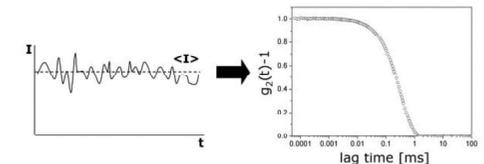
Intensity of scattered light fluctuates in time



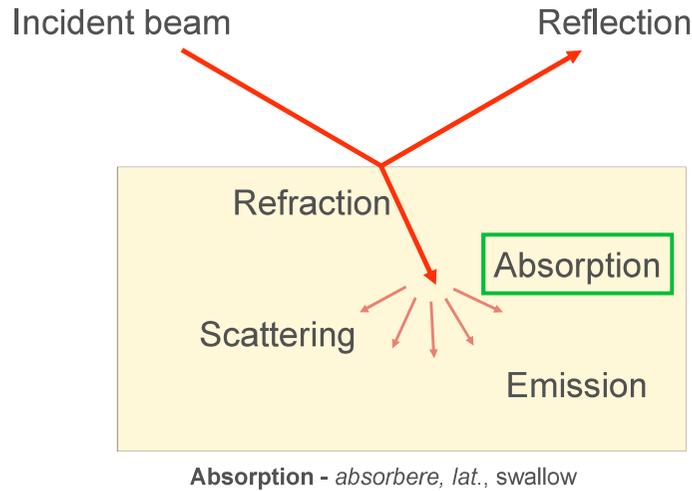
Fluctuation rate depends on particle size

- 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):

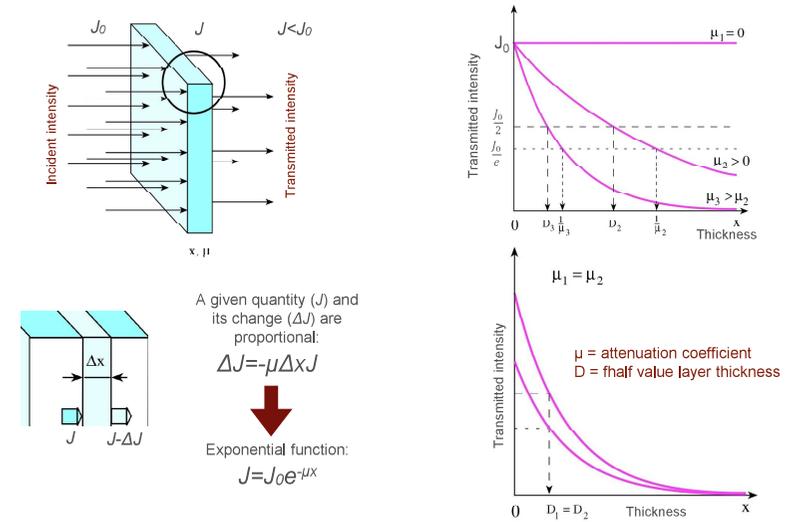
$$D = \frac{kT}{6\pi\eta r}$$



# Interaction of light with matter



# Reminder-General absorption (attenuation) law



# Absorbance

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

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

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

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

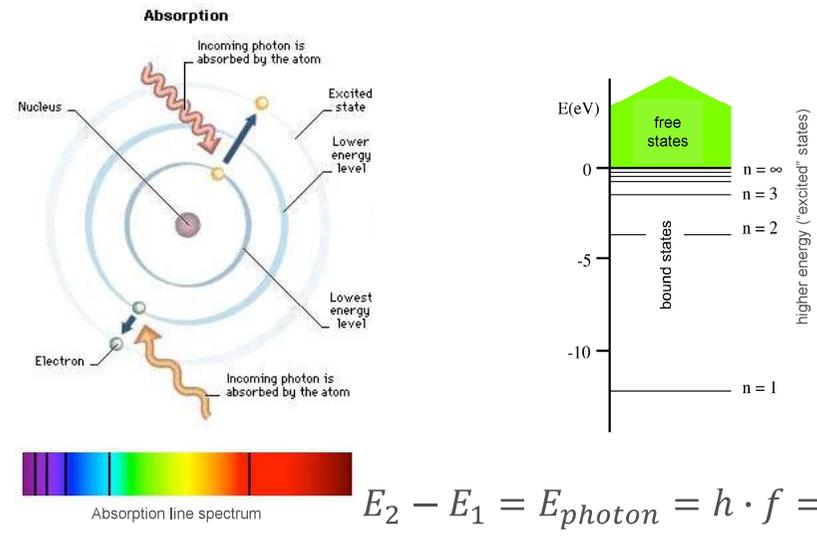
Absorbance (A):  $A = \lg \frac{J_0}{J} = \lg e \cdot \mu \cdot x$

Dimensionless number  
Synonyms: (decadic) extinction, optical density (OD)

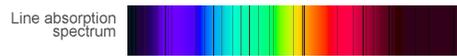
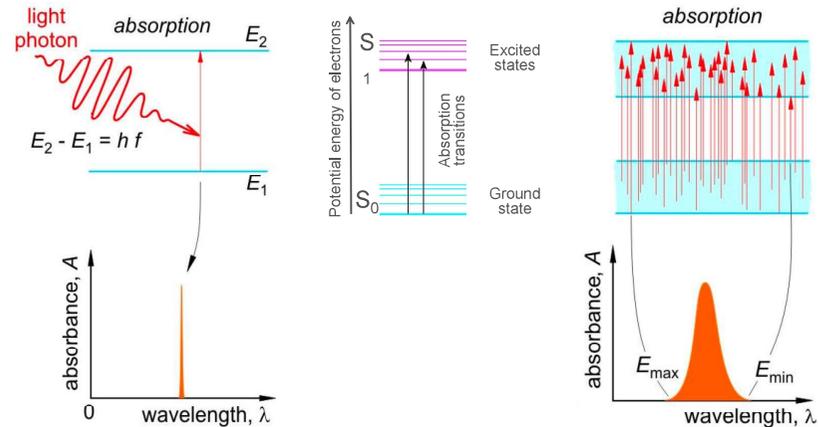
Transmittance (T):  $T = \frac{J}{J_0} \cdot 100\%$

Expressed in percent (%)  
Synonym: transmission coefficient

# Light absorption by an atom



# Origin of the band spectrum



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

**Band spectrum - origin:**

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

# Beer-Lambert law

From the general attenuation law:

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

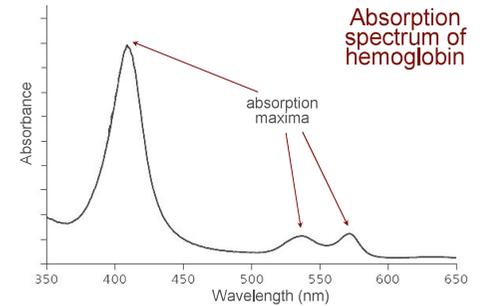
For dilute solutions – Beer-Lambert law:

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

$\varepsilon_{(\lambda)}$  = molar extinction coefficient [ $M^{-1}cm^{-1}$ ]  
(strongly depends on wavelength)

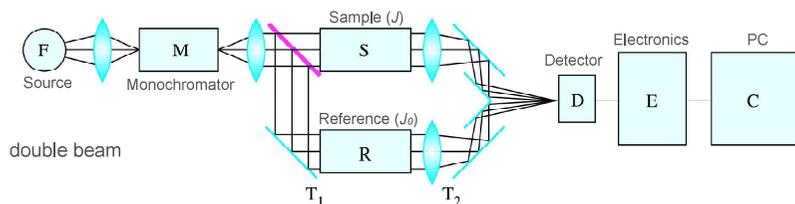
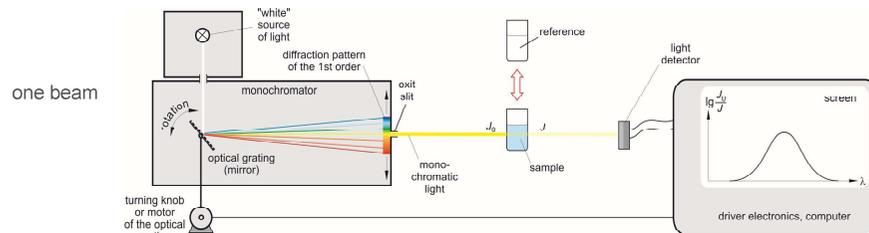
$c$  = concentration [M]

$x$ : thickness [cm]

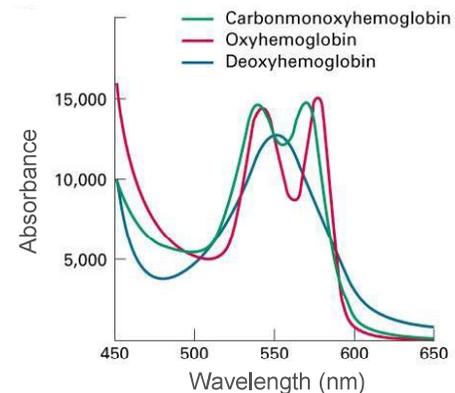


- SI unit of molar extinction coefficient ( $\varepsilon$ ):  $m^2mol^{-1}$ , but the practical unit is  $M^{-1}cm^{-1}$
- Method ideal for concentration measurement of solutions (qualitative analysis)
- Based on the wavelength (at maximum) the material can be identified, transition energy may be calculated (quantitative analysis)

# Absorption spectrophotometer



# Absorption-applications

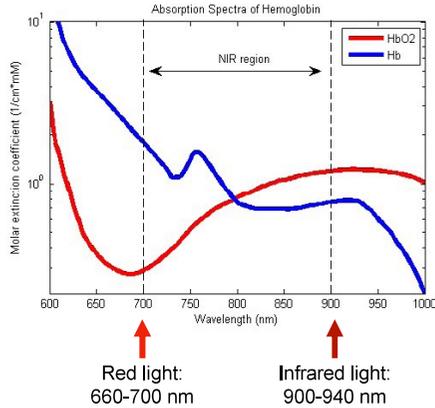
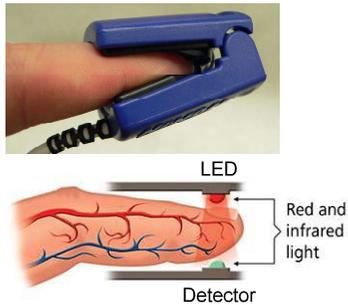


- Spectrum:** intensity (or its derived units, e.g., OD) as a function of photon energy (or its derived units, e.g., frequency, wavelength).
- Spectroscopy:** qualitative analysis of the spectrum.
- Spectrometry, spectrophotometry:** quantitative analysis of the spectrum.
- Applications:** analysis of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

# Pulse oxymetry

Non-invasive measurement of oxygen saturation (SO<sub>2</sub>)

- % of HgB that carries O<sub>2</sub> is measured
- Arterial oxygen saturation (SaO<sub>2</sub>) is estimated from the peripheral (SpO<sub>2</sub>)
- Normal value: 95-99%
- Ratio measurement is carried out (red/IR)

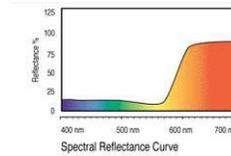


# Why do objects appear the colour they are?

reflection scattering absorption transmission

$$\rho(\lambda) = \frac{J_{\text{reflected}}(\lambda)}{J_0(\lambda)} \quad \sigma(\lambda) = \frac{J_{\text{scattered}}(\lambda)}{J_0(\lambda)} \quad \alpha(\lambda) = \frac{J_{\text{absorbed}}(\lambda)}{J_0(\lambda)} \quad \tau(\lambda) = \frac{J_{\text{transmitted}}(\lambda)}{J_0(\lambda)}$$

$$\rho(\lambda) + \sigma(\lambda) + \alpha(\lambda) + \tau(\lambda) = 1$$

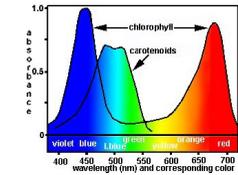


e.g. reflection of red

red object



Influenced by the relative position of the light source and observer, size of particles etc.



e.g. red absorption

green in transmitted light

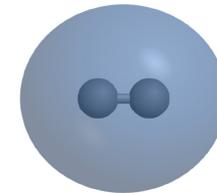
## Problem 2.81.

The decadic extinction of Earth's atmospheric ozone layer (which includes both the absorption and the scattering components) for ultraviolet radiation with 300 nm wavelength is 2.5.

- What percentage of the incident ultraviolet light can pass through the ozone layer?
- By how many fold does the transmitted radiation intensity increase if the thickness of the ozone layer decreases by 20%? For the sake of simplicity consider the ozone layer a homogeneous layer with uniform ozone concentration.

## State of a molecule is affected by its motional modes

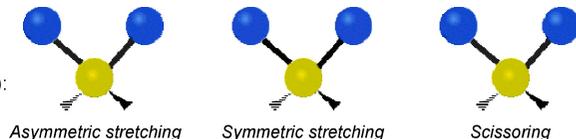
Molecule: atoms connected by chemical bonds  
Simplest case: diatomic molecule (e.g., hydrogen molecule)



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<sub>2</sub>-):



# Energy of a molecule

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Max Born  
(1882-1970)



J. Robert Oppenheimer  
(1904-1967)

Born-Oppenheimer approximation:

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational}$$

**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:

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

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