Interaction of molecules with light (Chapter 17)

- general aspects of spectroscopy
- molecular excited states
- photochemistry and other photoinduced processes
- photoionization spectroscopy
- atmospheric chemistry

Prerequisites:
Quantum Mechanics and Molecular Structure (Chapter 16)

- Born-Oppenheimer approximation
- molecular orbitals
- quantum picture of the chemical bond
Light

Electromagnetic waves

Wavelength $\lambda$
Frequency $\nu$

$$\nu = \frac{c}{\lambda}$$

$c = 3 \times 10^8 \text{ m/s}$
Energy of light

\[ E = h \nu = \frac{hc}{\lambda} \]

- \( h = 6.626 \times 10^{-3} \text{ Js} \) - Plank constant
- \( c = 3 \times 10^8 \text{ m/s} \) - speed of light
- \( \lambda (\text{m}) \) - wavelength (nm=10^{-9} m)
- \( \nu (\text{s}^{-1} \text{ or Hz}) \) - frequency
The diagram illustrates the electromagnetic spectrum, showing the range of wavelengths from $10^{-12}$ to $10^4$ meters. The spectrum includes gamma rays, X rays, ultraviolet, visible light, infrared, microwaves, and radio waves. The visible light spectrum is further divided into FM, shortwave, and AM radio bands.
Quantum Mechanics: energy is quantized

Atomic energy levels: s, p, d, f, g, etc...

Molecular quantized energy levels: electronic, vibrational, rotational
Transitions between discrete molecular levels can be induced by light.

Light can be absorbed or emitted upon such transitions.

Various energy levels in the hydrogen atom.
Born-Oppenheimer approximation and molecules

Electrons: adjust to nuclear positions
Nuclei: feel mean-field created by electrons -> molecular potential energy curves
Different electronic states -> different potentials
For each electronic state -> different nuclear motions and energy levels
Molecular Energy Levels

\[ E_{\text{tot}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} \]

- Rotational levels
- Vibrational states
- Electronic states (different arrangements of electrons in molecular orbitals)
Photochemical processes

Light can induce $\sigma-\sigma^*$ transition ->
reduces bond order to zero ->
dissociation

$\sigma_{1s}$ and $\sigma_{1s}^*$ are molecular orbitals in the H$_2$ molecule.
Photodissociation

E

Photon energy

R_{eq}

Bond energy

H + H

R_{H-H}
Demo: Photoinduced chain reaction of chlorine and hydrogen

\[ \text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl} \]

\[ \Delta E = 92.3 \text{ kJ/mol} \]

\[ \text{Cl}_2 + \text{light} \rightarrow 2\text{Cl} \]
\[ \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \]
\[ \text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl} \]
\[ \text{H} + \text{Cl} \rightarrow \text{HCl} \]
\[ \text{Cl} + \text{Cl} \rightarrow \text{Cl}_2 \]
\[ \text{H} + \text{H} \rightarrow \text{H}_2 \]

Bond energy in Cl\(_2\): 230 kJ/mol
Bond energy in H\(_2\): 432 kJ/mol
Visible light: 400-700 nm = 171-299 kJ/mol
Quantitative description of adsorption: Beer-Lambert Law

Probability that light is absorbed by a molecule in the cell:
- concentration C
- length of the cell

The absorbance, $A$, is defined as: $A = -\ln \frac{I_s}{I_R}$

where $I_s$ - light transmitted through the filled cell
$I_R$ - light transmitted through the reference cell
**Beer-Lambert Law**

\[ A = -\ln \frac{I_s}{I_R} = \varepsilon c l \]

where

- \( \varepsilon \) - molar extinction coefficient
- \( c \) - concentration
- \( l \) - cell length

\[ A_g = -\log \frac{I_s}{I_R} = \varepsilon_g c l \]

\[ \varepsilon_g = \frac{\varepsilon_n}{\ln 10} = \frac{\varepsilon_n}{2.303} \]