Electronic transitions: The visible electromagnetic spectrum
Atkins, Chapter 18

Red light: 14,000 cm\(^{-1}\) (171 kJ/mol)
Blue light: 21,000 cm\(^{-1}\) (254 kJ/mol)
Ultraviolet radiation: 50,000 cm\(^{-1}\) (598 kJ/mol)

Chlorophyll absorption: Plants appear green because of this gap
The Franck-Condon principle

The heavy nuclei don’t have time to react to fast changes in the electronic distribution

⇒ Vertical transition

⇒ Photochemistry; Photoelectron spectroscopy
Absorption intensity

\[
dI = -\kappa [J] I dx
\]

\[
\frac{I}{I_0} = 10^{-\varepsilon [J] I}
\]

**Beer-Lambert law**

Strong transitions have maximum molar absorption coefficient \(\varepsilon_{\text{max}} = 10^4-10^5 \text{ l/(mol cm)}\)
Circular dichroism

Chiral molecules have optical activity

Light can be left- or right-circularly polarized

An optically active polypeptide shows differential absorption of left- and right-circularly polarized light
Specific transitions

Charge transfer:
Example MnO₄⁻

$n$-to-$\pi^*$ transition in carbonyl

$\pi$-to-$\pi^*$ in C=C double bond

$h\nu (420-700 \text{ nm})$
Vision

11-cis-retinal → rhodopsin

Energy diagram

\[ E_n = \frac{n^2 \hbar^2}{8mL^2} \]
Fluorescence

Jablonski diagram

Dissipation in environment as heat

If colliding molecules cannot accept this larger energy

Absorption (a)  Fluorescence (b)

Wavelength, $\lambda$

Nils Walter: Chem 260
Fluorescence quenching

Molecular species (e.g., H$_2$O, I⁻) with suitable energy gaps can take up this energy ⇒ quenching of fluorescence

\[ M + h\nu_1 \rightarrow M^* \rightarrow M + \text{heat (internal conversion, } k_i) \]
\[ + Q \rightarrow M + Q^* \rightarrow M + Q + \text{heat (quenching, } k_Q) \]

\[ \frac{1}{\tau} = k_f + k_i + k_Q[Q] \]

Slope = $k_q$
Fluorescence quenching:
An example from actual research

\[ k_T = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6 \]

\[ E_{FRET} = \frac{R_0^6}{r^6 + R_0^6} \]

Green: Donor fluorophore
Red: Acceptor fluorophore

The molecular dynamics of a single biomolecule can be observed by modern fluorescence techniques.
Phosphorescence

Triplet → Singlet state transition is NOT allowed ⇒ takes long
Lasers: **Light Amplification by Stimulated Emission of Radiation**

- **Population inversion**
- **Radiationless transition**
- **Laser transition**
- **Pump**
- **Relaxation**

**Equilibrium population**

**Inverted population**

**Laser effect**