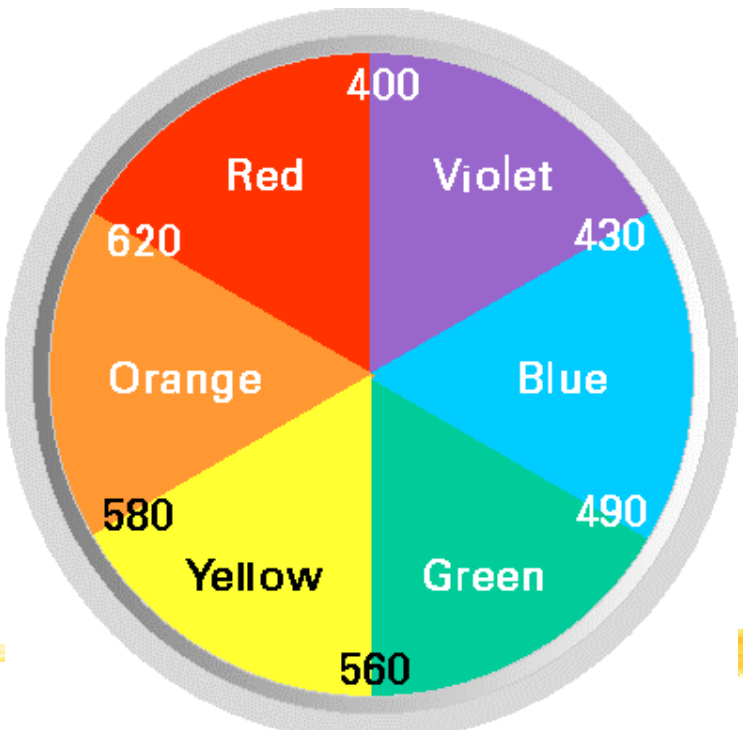
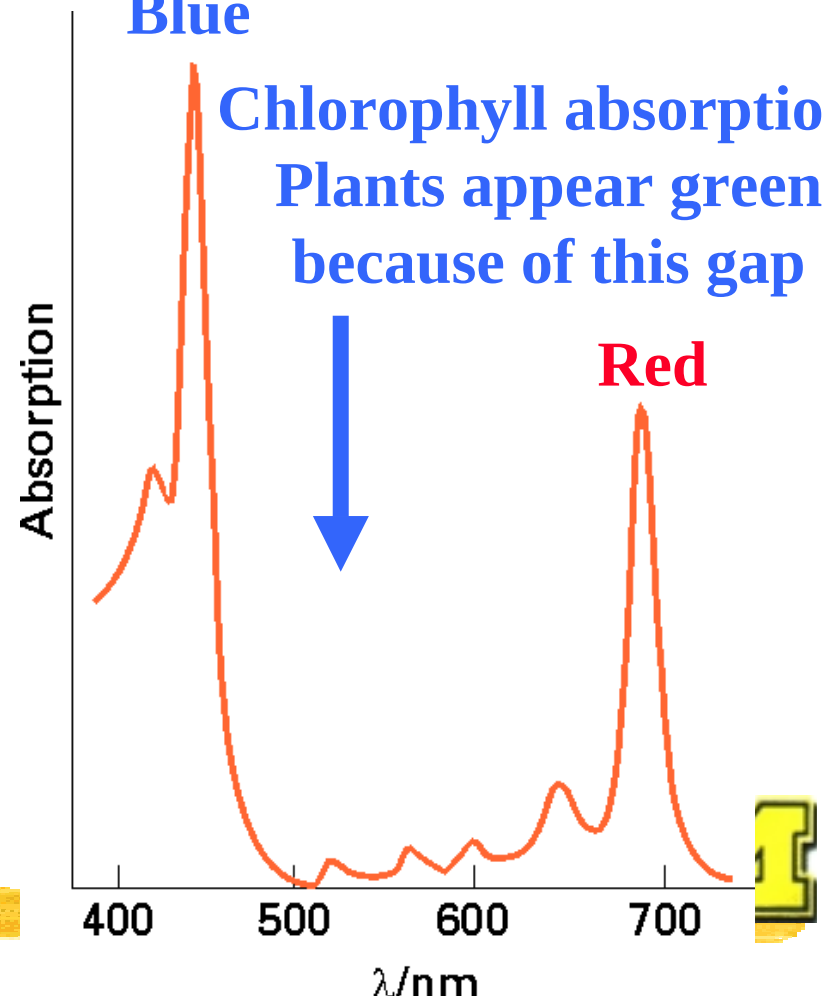
Electronic transitions: The visible electromagnetic spectrum

Atkins, Chapter 18

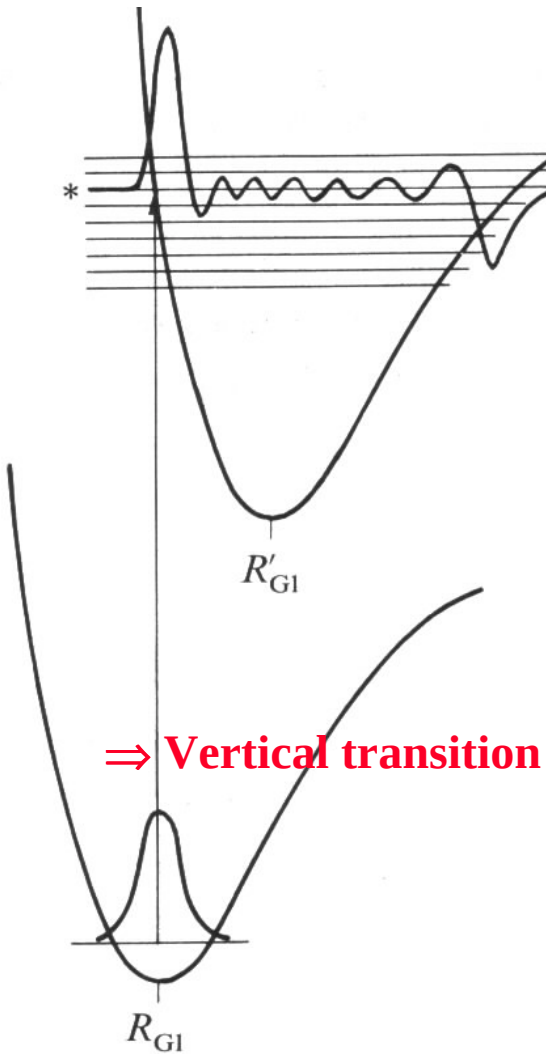
Red light: 14,000 cm^{-1} (171 kJ/mol)
Blue light: 21,000 cm^{-1} (254 kJ/mol)
Ultraviolet radiation: 50,000 cm^{-1} (598 kJ/mol)



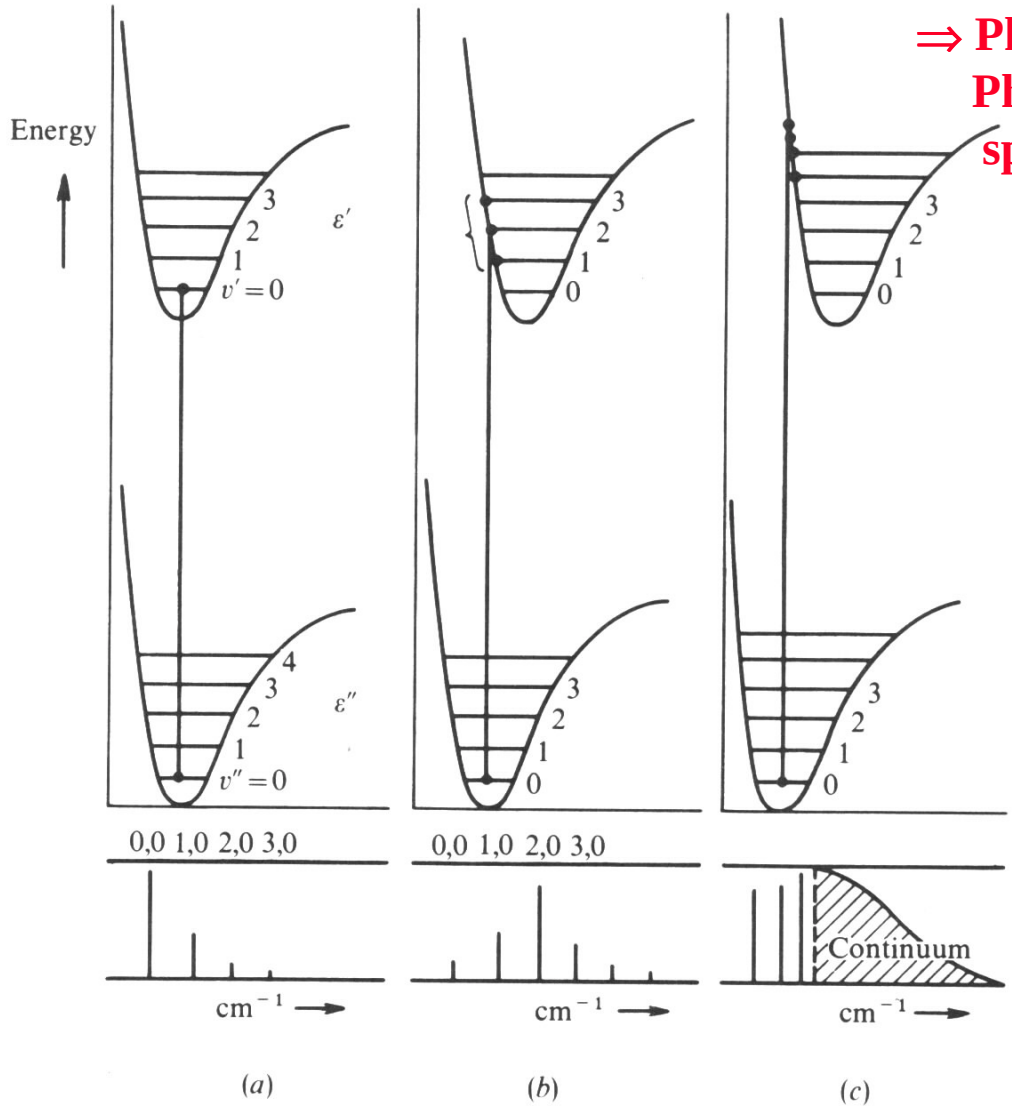


The Franck-Condon principle

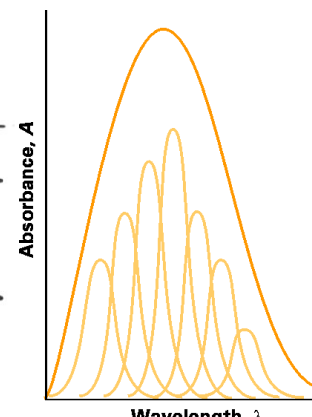
The heavy nuclei don't have time to react to fast changes in the electronic distribution



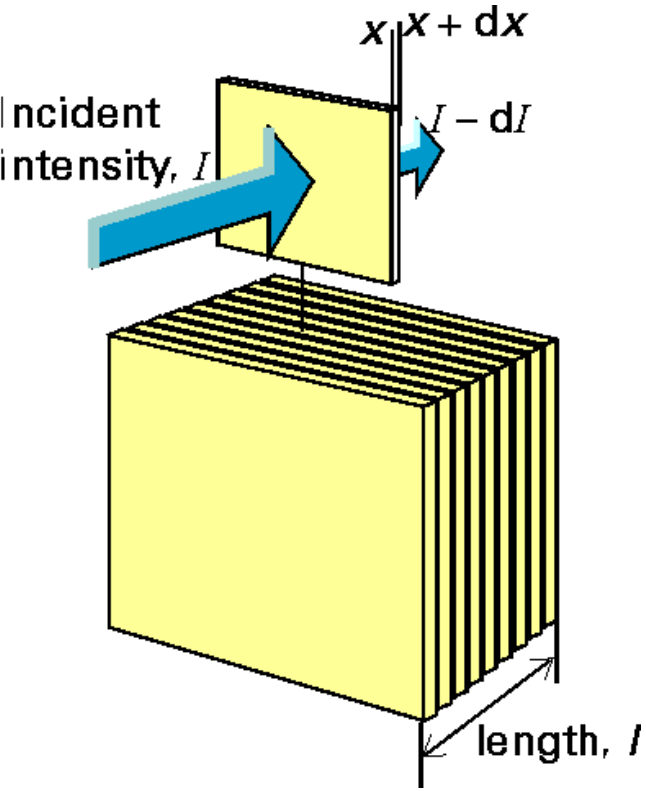
⇒ Vertical transition

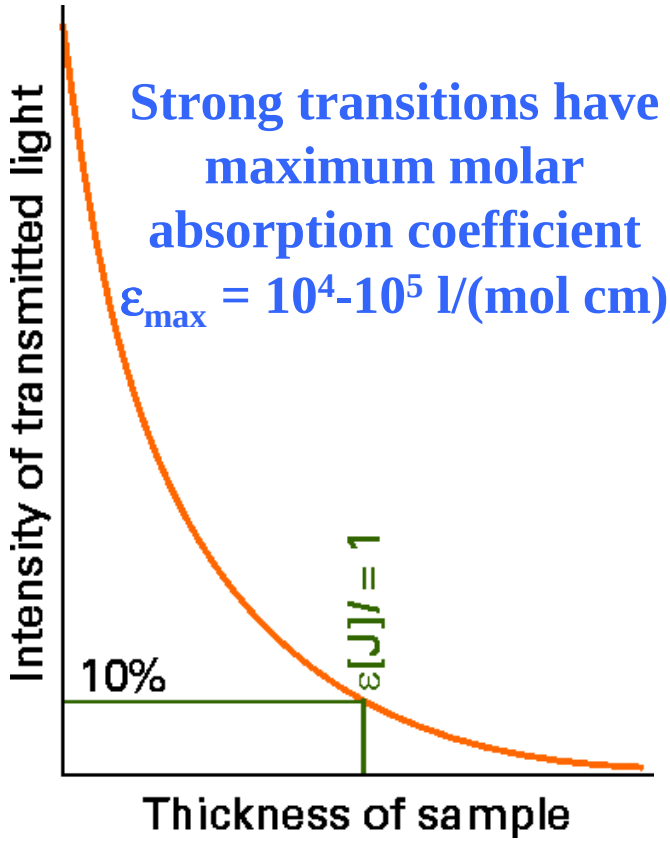


⇒ Photochemistry; Photoelectron spectroscopy



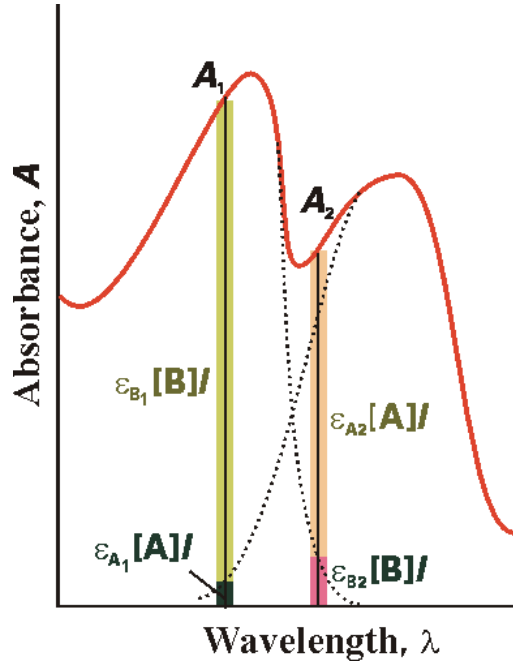
Absorption intensity

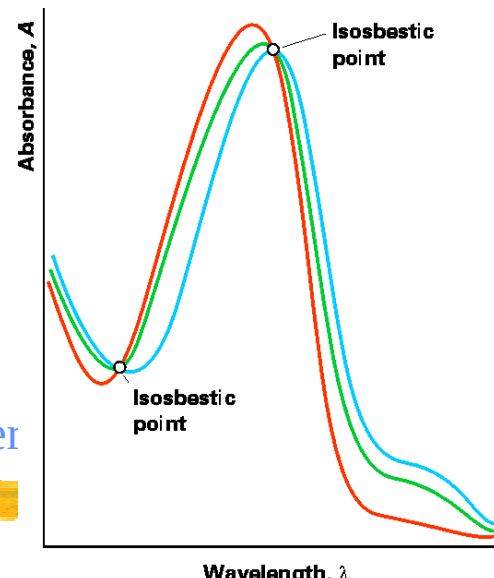




Strong transitions have maximum molar absorption coefficient

$\varepsilon_{max} = 10^4\text{-}10^5$ l/(mol cm)





$$dI = -\kappa[J]Idx$$

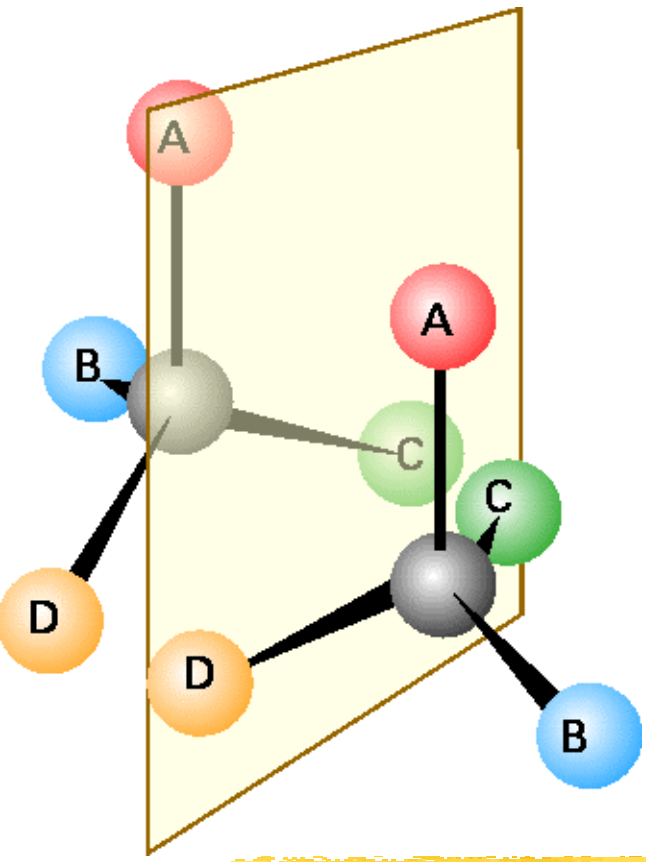
$$\frac{I}{I_0} = 10^{-\varepsilon[J]l}$$

Beer-Lambert law

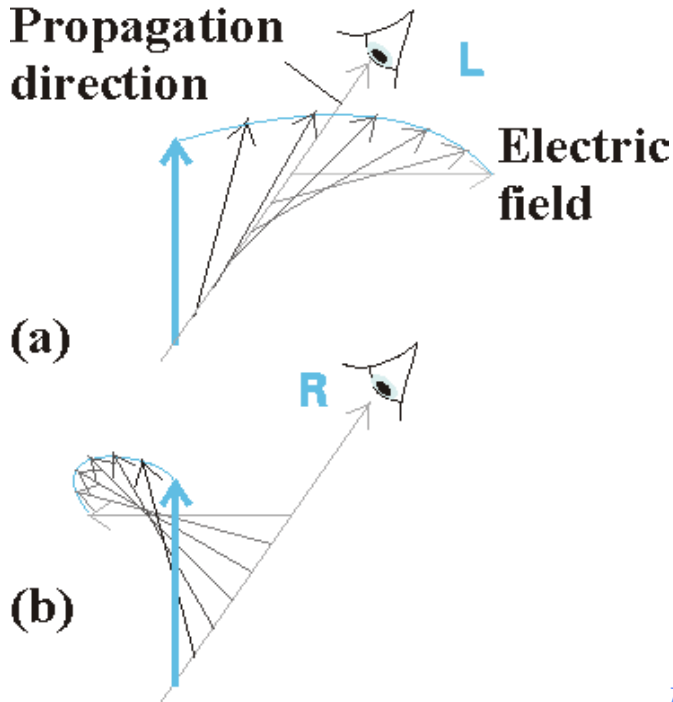
Nils Walter

Circular dichroism

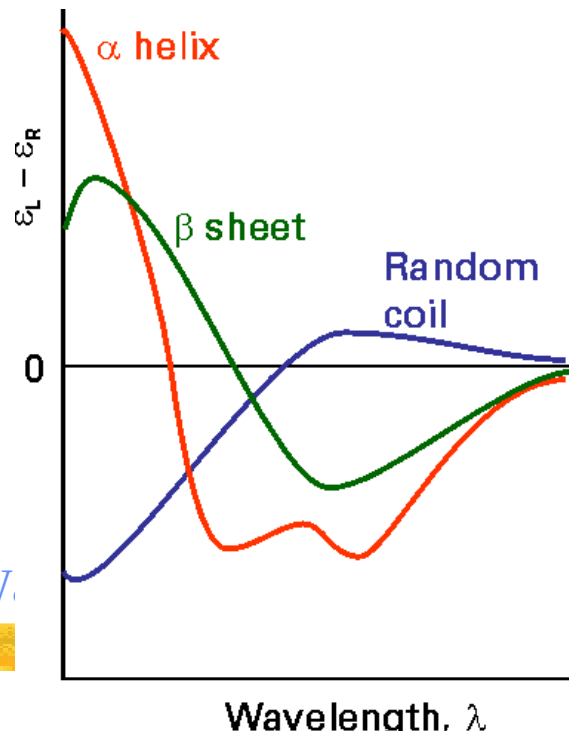
Chiral molecules have optical activity



Light can be left- or right-circularly polarized

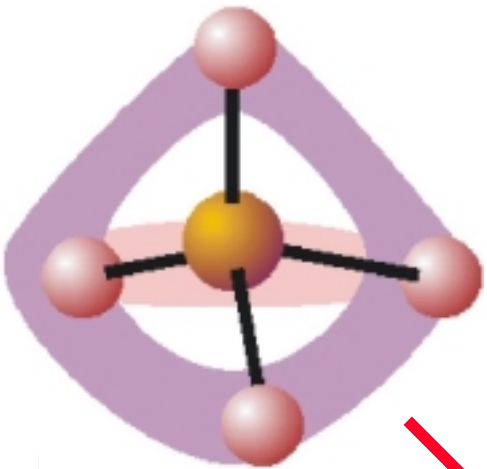


An optically active polypeptide shows differential absorption of left- and right-circularly polarized light

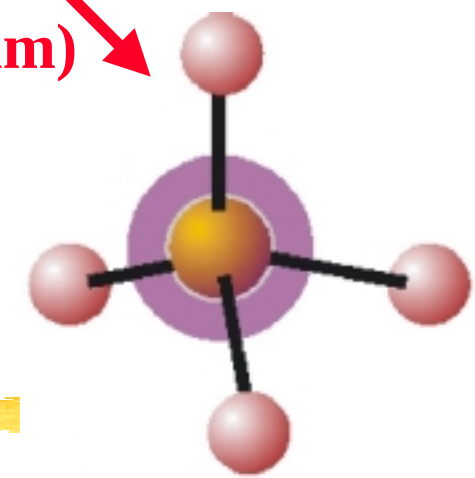


Specific transitions

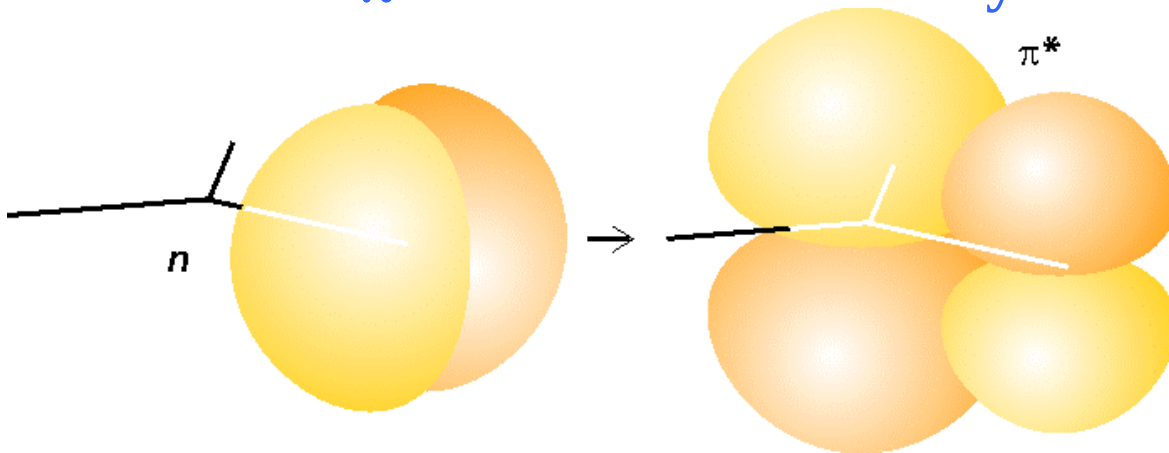
Charge transfer:
Example MnO_4^-



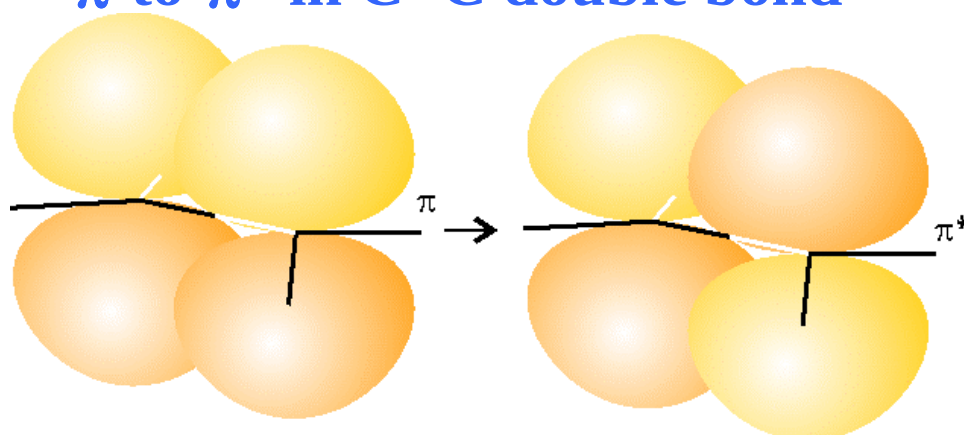
hν (420-700 nm)



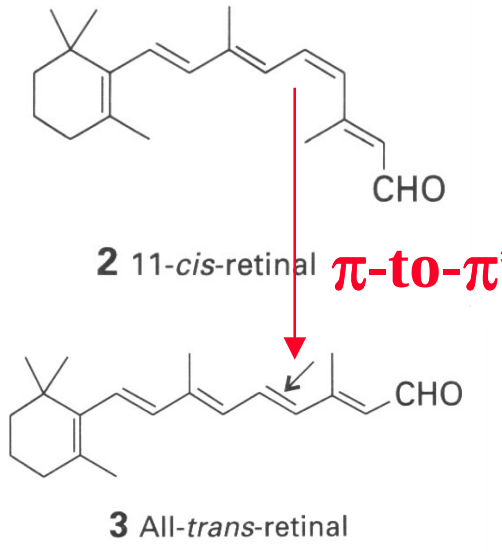
n-to-π* transition in carbonyl

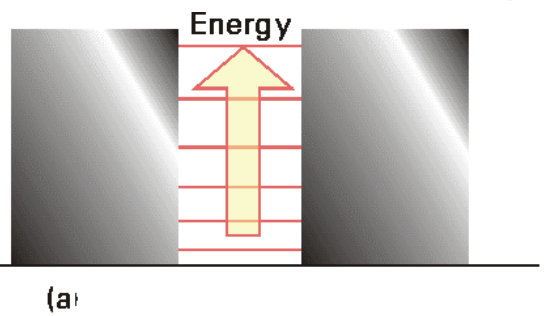


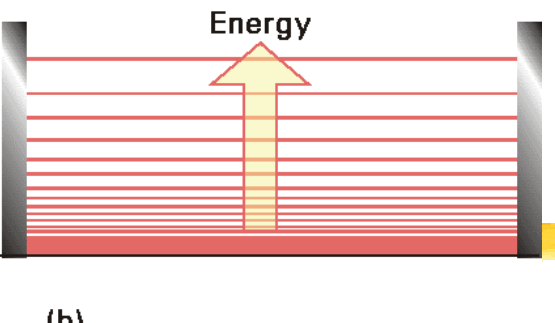
π-to-π* in C=C double bond

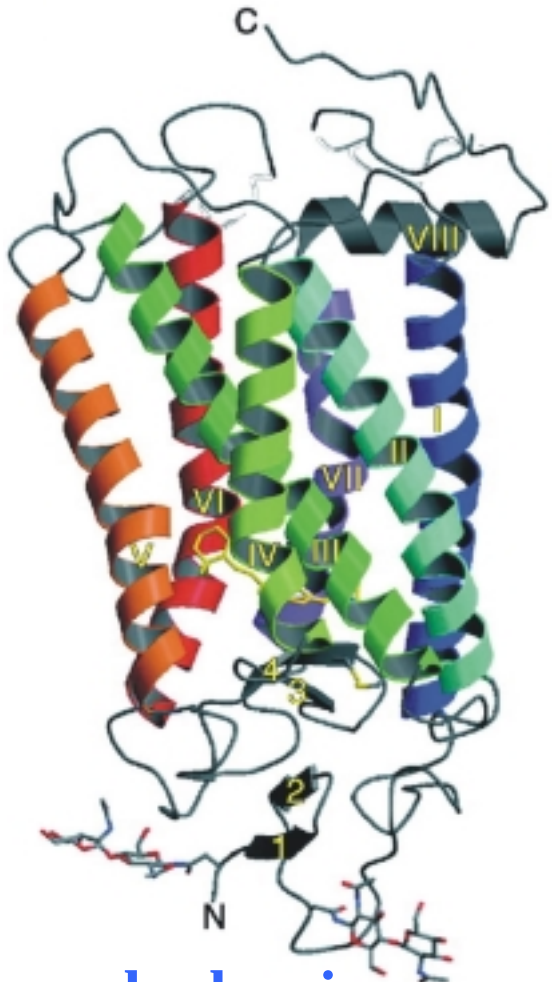


Vision

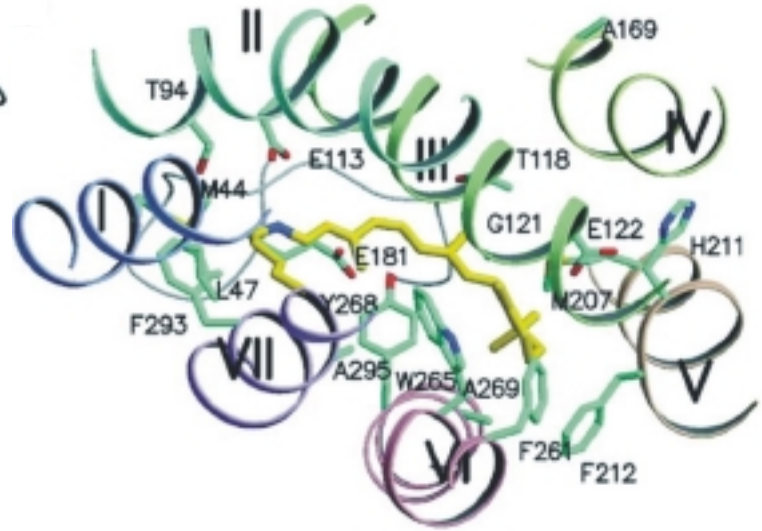


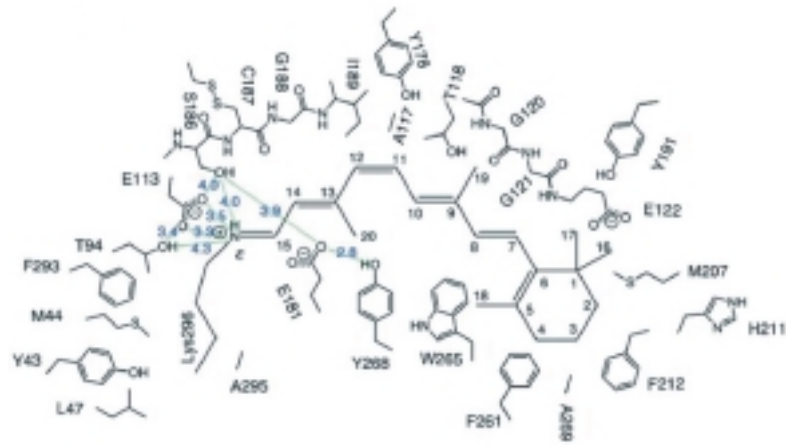






rhodopsin

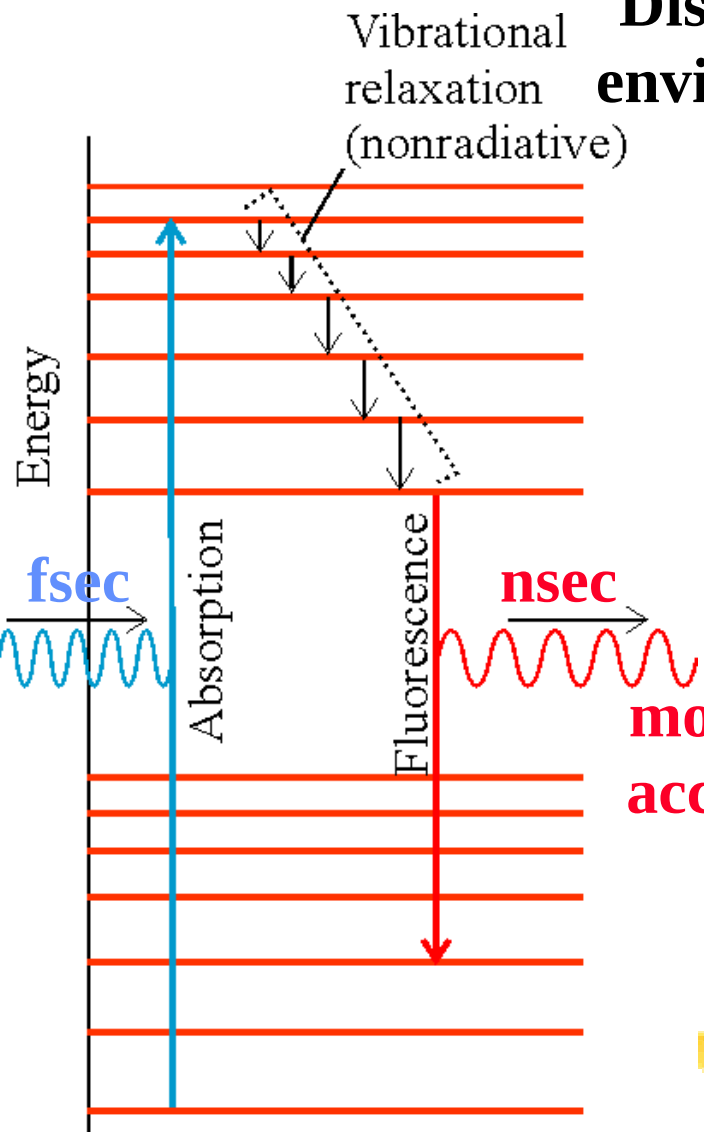




$$E_n = \frac{n^2 h^2}{8mL^2}$$

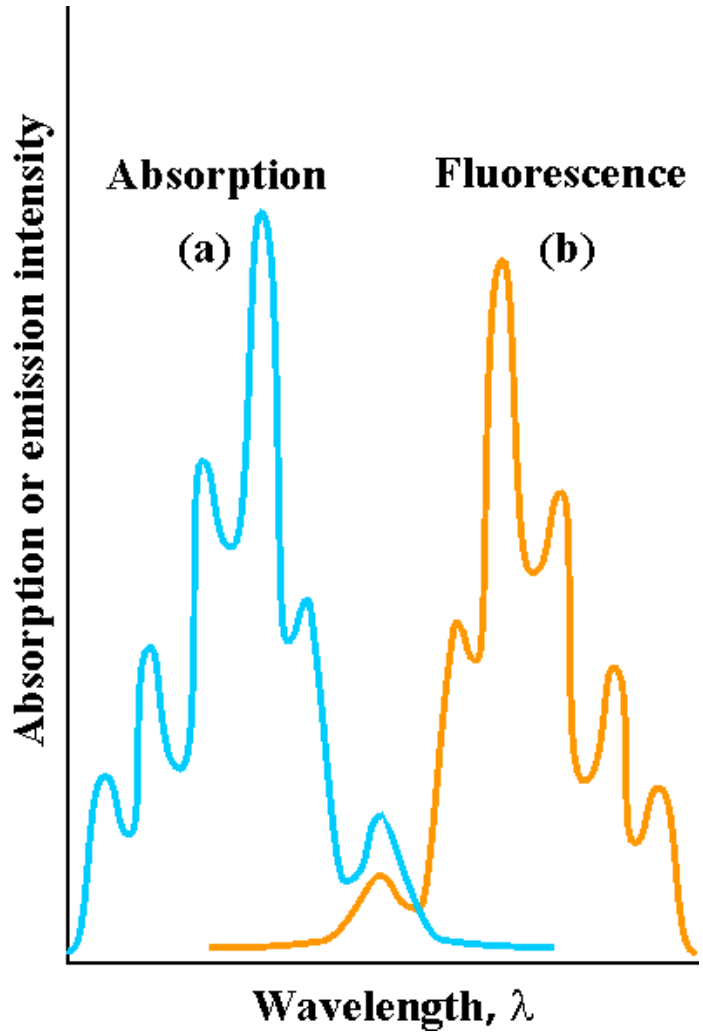
Fluorescence

Jablonski diagram



Dissipation in environment as heat

If colliding molecules cannot accept this larger energy



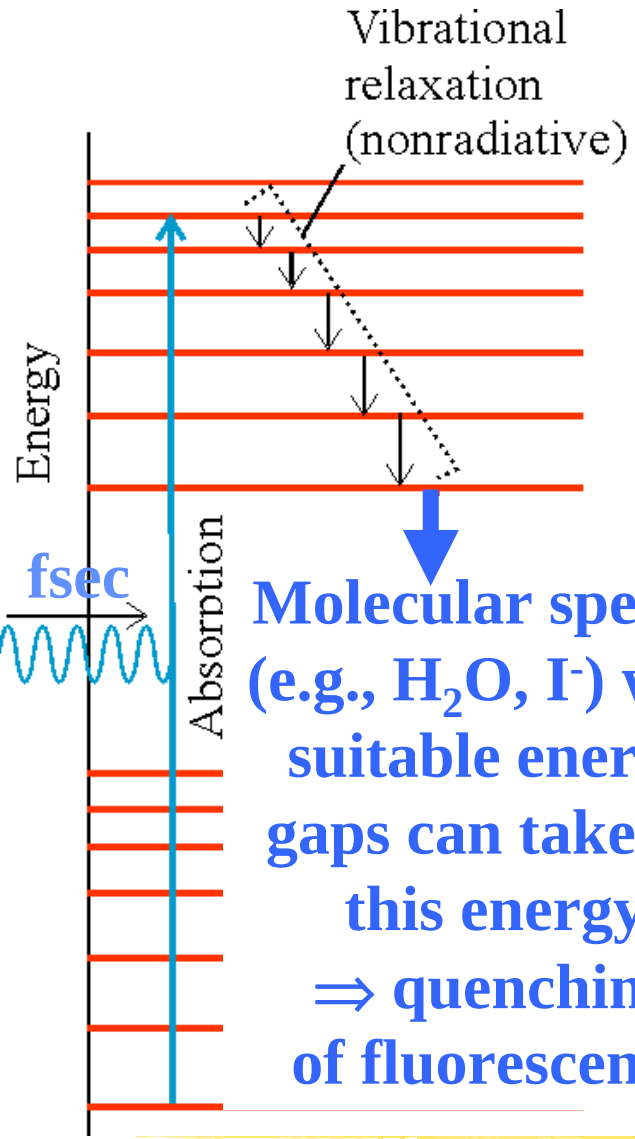
Fluorescence quenching

$\rightarrow M + h\nu_2$(fluorescence, k_f)

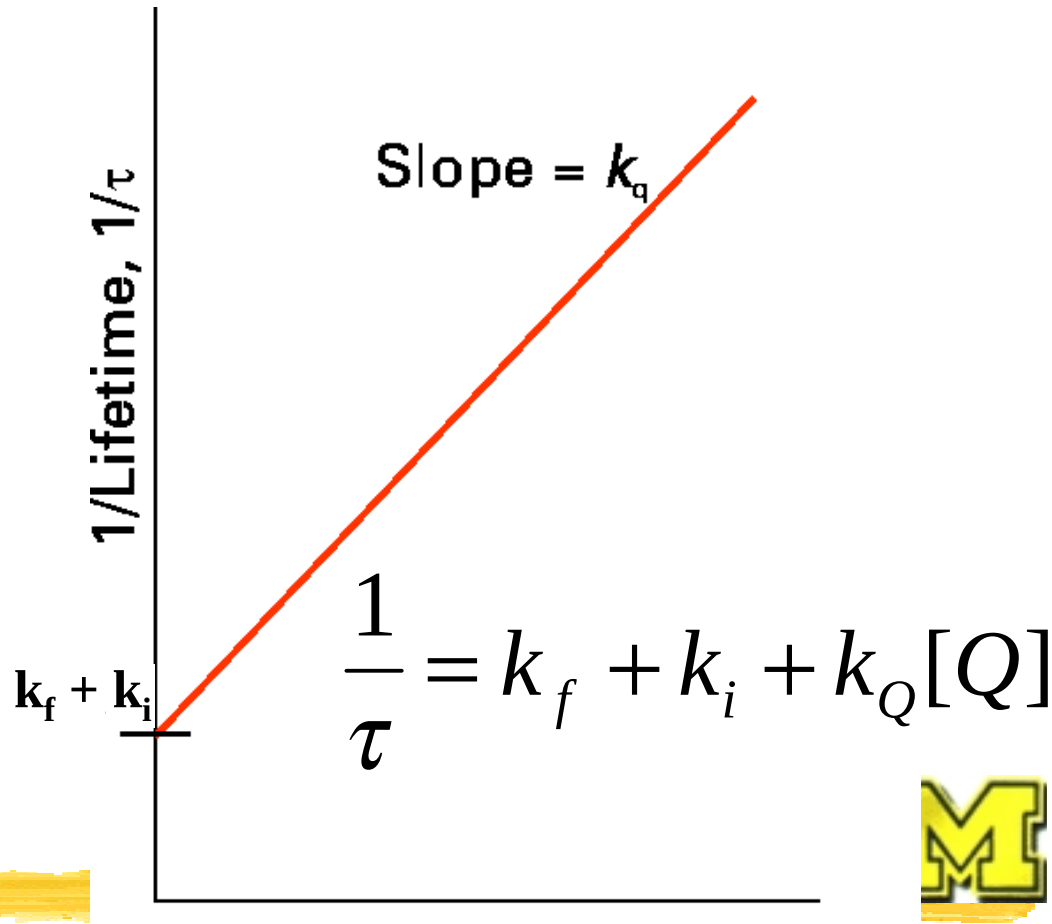
$M + h\nu_1 \rightarrow M^* \rightarrow M$ + heat (internal conversion, k_i)

$+ Q \rightarrow M + Q^*$

$\rightarrow M + Q$ + heat (quenching, k_Q)

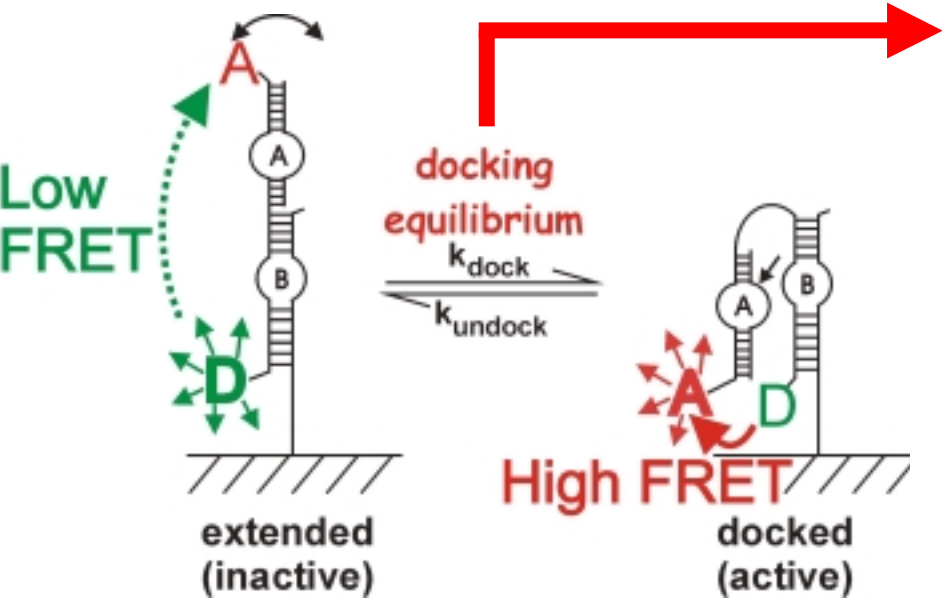


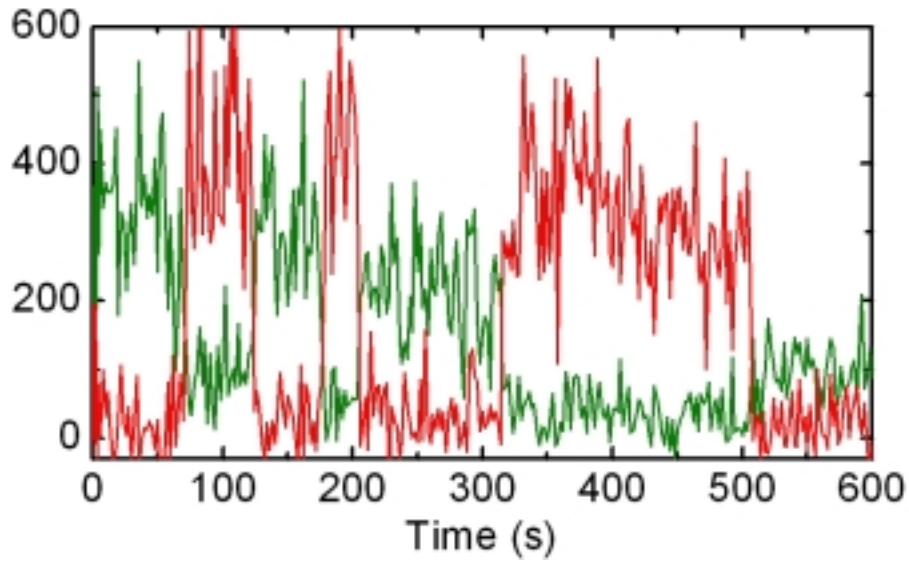
Molecular species (e.g., H_2O, I^-) with suitable energy gaps can take up this energy ⇒ quenching of fluorescence



Fluorescence quenching: An example from actual research

$$k_T = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6 \qquad E_{FRET} = \frac{R_0^{\,6}}{r^6 + R_0^{\,6}}$$



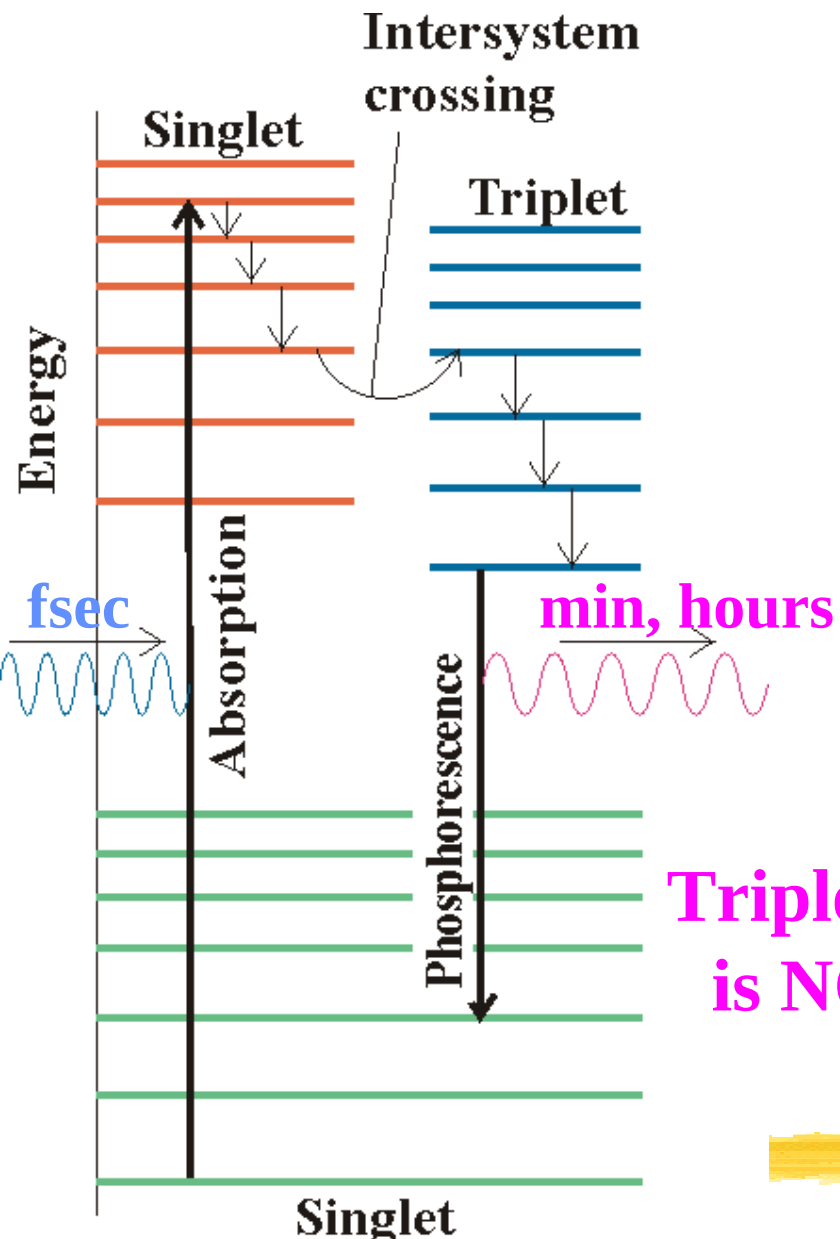


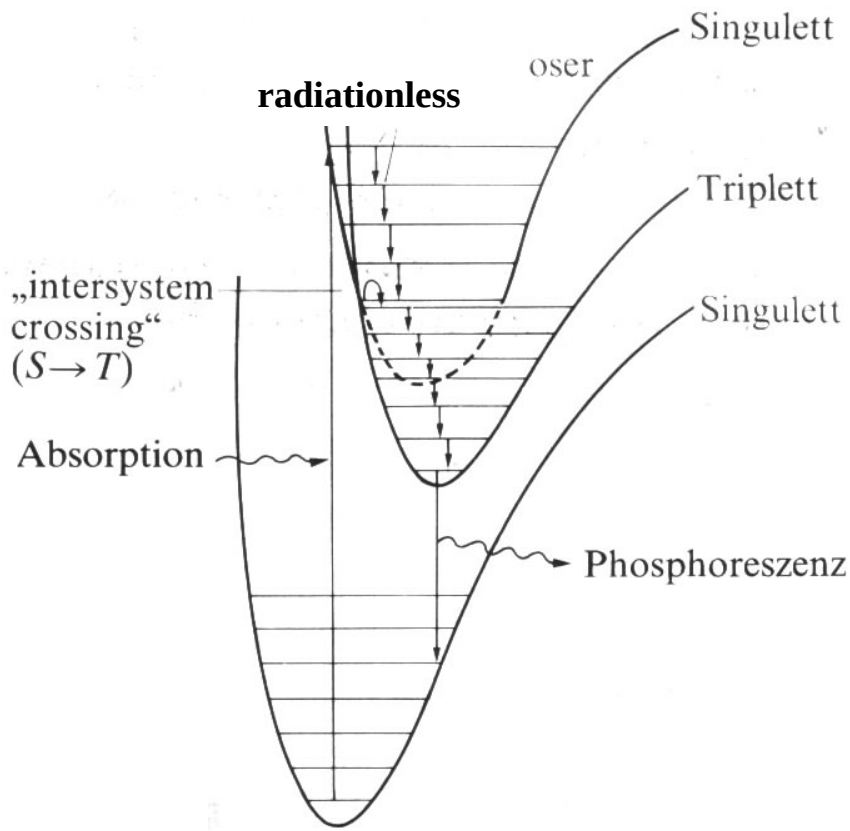
⇓

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

Green: Donor fluorophore
Red: Acceptor fluorophore

Phosphorescence





Triplet→Singlet state transition is NOT allowed ⇒ takes long

Lasers: Light Amplification by Stimulated Emission of Radiation