

Electronic Transitions and Photochemistry

CHEM 361B: Introduction to Physical Chemistry

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Lecture 19

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Learning Objective:

- Quantify electronic transitions in molecules as well as reaction rates for photochemical reactions

References:

- Atkins and de Paula Topic 11D and 11E
- Engel and Reid Chapter 25 and §36.9

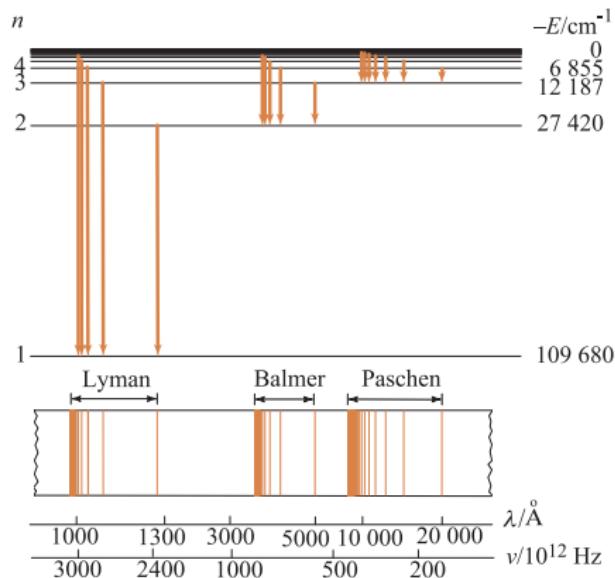
What Wavelengths Govern Electronic Transitions

Type of spectroscopy	Usual λ range	Type of quantum transition
γ -ray emission	0.005 - 1.4 Å	Nuclear
X-ray absorption, emission, fluorescence, and diffraction	0.1 - 100 Å	Inner electron
Vacuum UV absorption	10 - 180 nm	Bonding electrons
UV/VIS absorption, emission, and fluorescence	180 - 780 nm	Bonding electrons
IR absorption and Raman scattering	0.78 - 300 μ m	Rotation/vibration of molecules
Microwave absorption	0.75 - 3.75 mm	Rotation of molecules
Electron spin resonance	3 cm	Spin of electrons in a magnetic field
NMR	0.6 - 10 m	Spin of nuclei in a magnetic field

Electronic Transitions from Atomic Orbitals

These transitions can come from atomic orbitals:

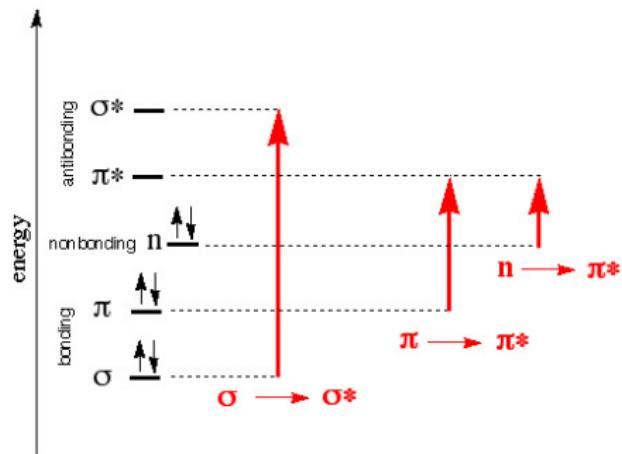
- Here is the hydrogen spectrum where the Balmer series are transitions that emit light in the visible spectrum.
- Sodium is principally characterised by its transition between its 3p and 3s orbitals which determines its characteristic yellow glow.



Electronic Transitions from Molecular Orbitals

They can also come from molecular orbitals

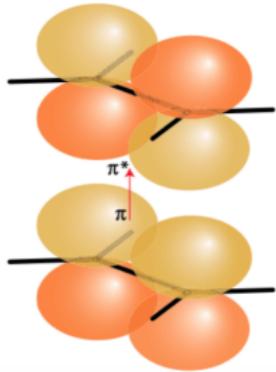
- The wavelength of the photon measured from these transitions depends on the energy separation between the orbitals.



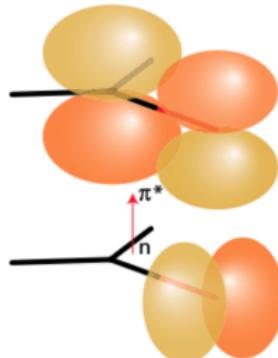
Chromophores

A **chromophore** is a chemical entity embedded within a molecule that adsorbs radiation at nearly the same wavelength in different molecules. Common ones include:

- C=C Bonds



- C=O Bonds



- Example of a π -to- π^* transition

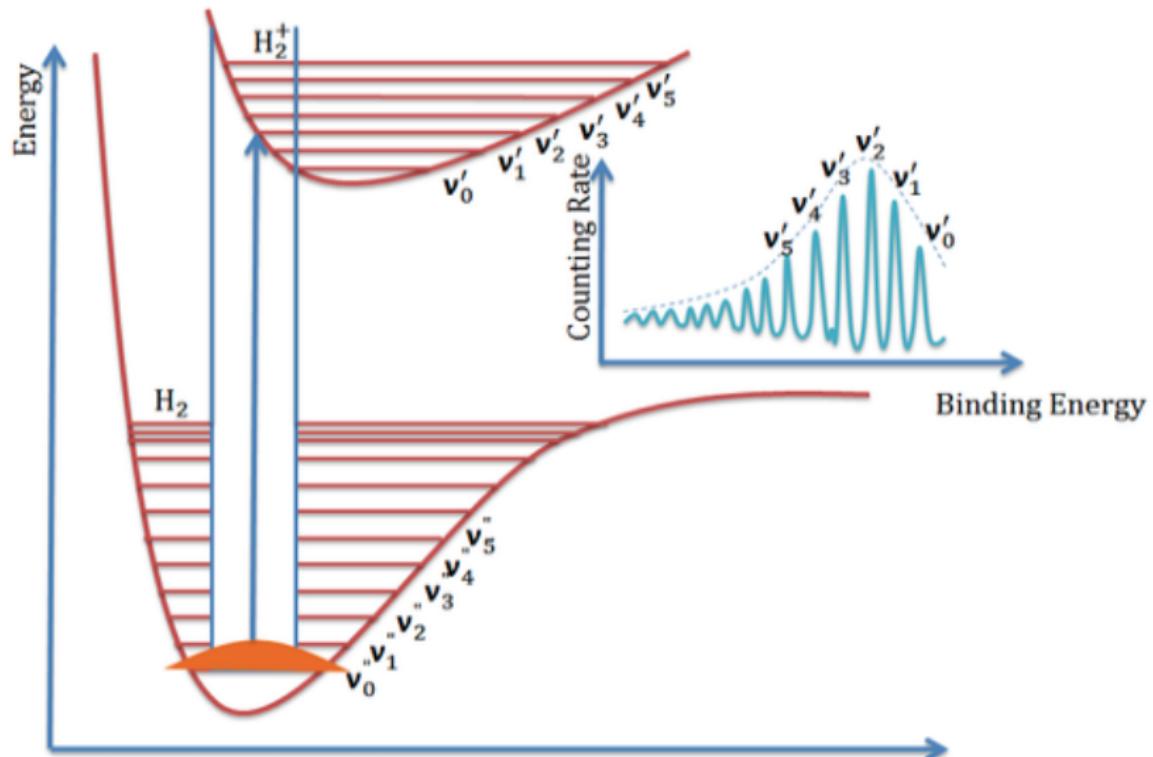
- Example of an n -to- π^* transition

Molecular Orbital Transition Data

- In a C=C bond, absorption can lift a π electron into an antibonding π^* orbital ($\pi \rightarrow \pi^*$)
 - Unconjugated C=C bonds: the energy is ≈ 7 eV corresponding to $\lambda \approx 180\text{nm}$ (UV).
 - Conjugated chain: the energy is lower and this transition is shifted into the visible.
- In a C=:O: bond, an electron belonging to a lone pair may be excited to a π^* orbital ($n \rightarrow \pi^*$). Their absorption energies are ≈ 4 eV ($\lambda \approx 290\text{ nm}$).

In general, π -to- π^* transitions are more intense than n-to- π^* transitions.

Electronic-Vibrational Transition



Redrawn from data of Sharp, T. E.,
Atomic Data, 2, 119 (1971)

Internuclear Separation

The Bohn-Oppenheimer Approximation

- Born-Oppenheimer Approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated.
- This leads to molecular wavefunctions that are given in terms of the electron positions (r_i) and the nuclear positions (R_j):

$$\psi_{molecule}(r_i, R_j) = \psi_{electrons}(r_i, R_j)\psi_{nuclei}(R_j)$$

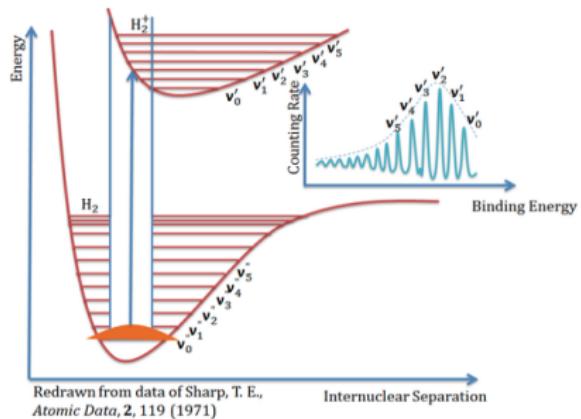
- This involves the following assumptions:
 - ① Electronic wavefunction depends on nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
 - ② The nuclear motion (e.g., rotation, vibration) sees a smeared out potential from the fast-moving electrons.

Franck-Condon Principle

The **Franck-Condon Principle** states that transitions between electronic states correspond to vertical lines on an energy versus internuclear distance diagram.

- Electronic transitions occur much more quickly than vibrational motions
 - Nuclei are much too massive to respond quickly
- The initial, equilibrium separation becomes an end point in the excited nuclear vibration
 - A vertical line is drawn from the initial equilibrium separation to where a vibrational energy level meets the excited potential energy curve
 - Multiple excited vibrational states could be selected

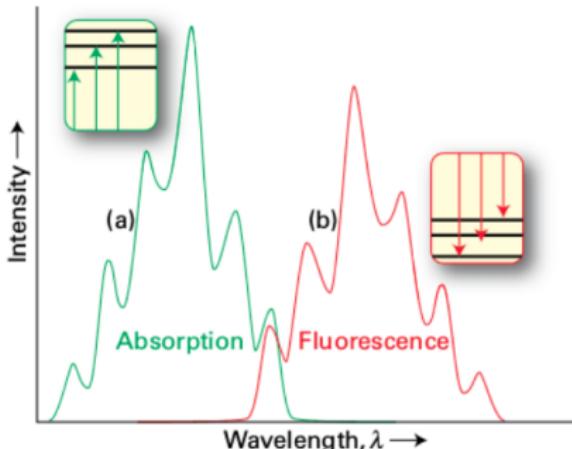
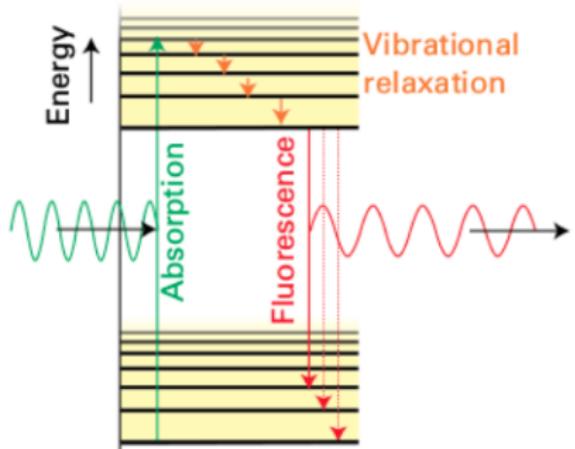
Franck-Condon Factor



Mathematically, in one dimension, the intensity of each vibrational state is expressed as the **Franck-Condon Factor**, S , where:

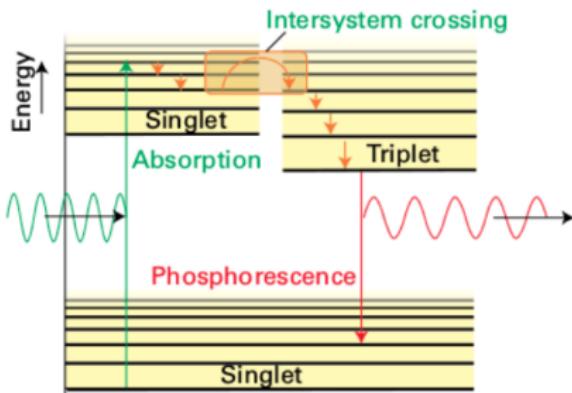
$$S^2 = \left| \int_{-\infty}^{\infty} (\psi_{final}^{vibrational})^* (\psi_{initial}^{vibrational}) dx \right|^2$$

Fluorescence



Fluorescence is the spontaneously emitted radiation immediately following absorption.

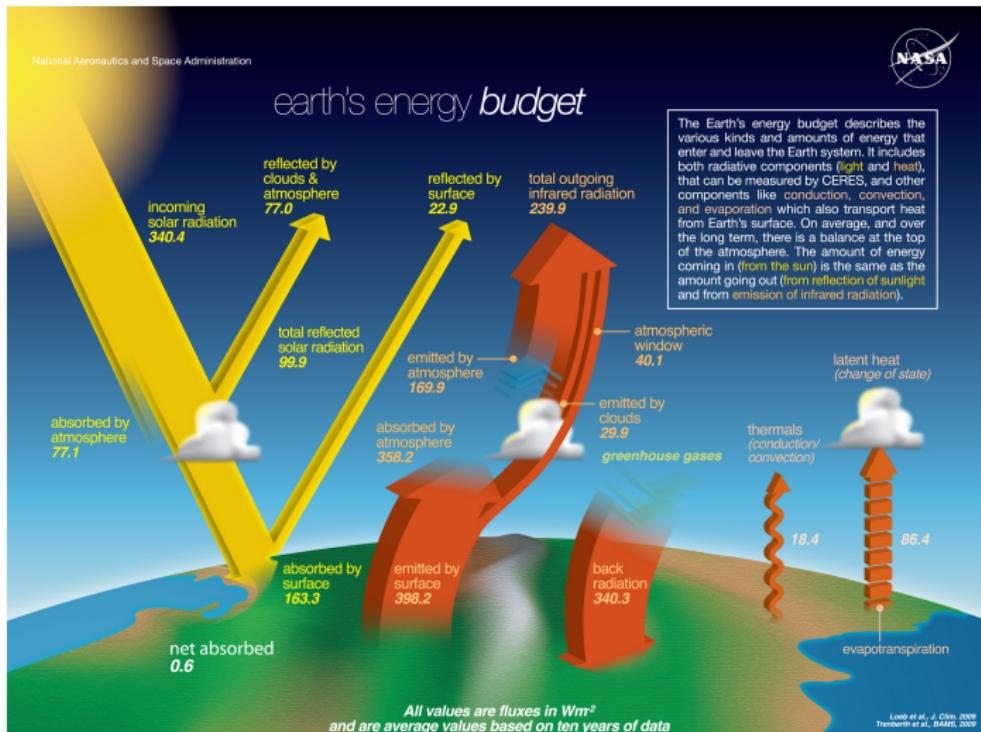
Phosphorescence



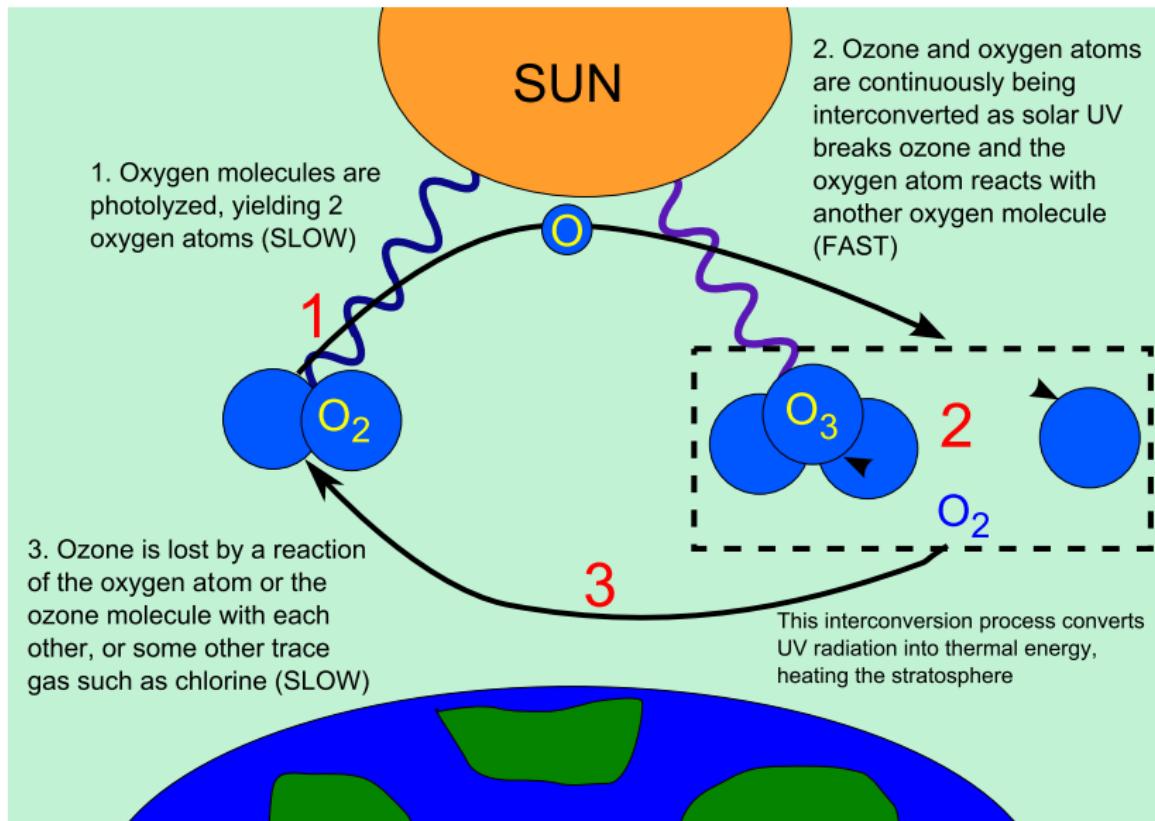
- With **Phosphorescence** the spontaneous emission may persist for long periods.
- Due to intersystem crossing from singlet ($\uparrow\downarrow$) to triplet ($\uparrow\uparrow$) state

Photochemistry in Action

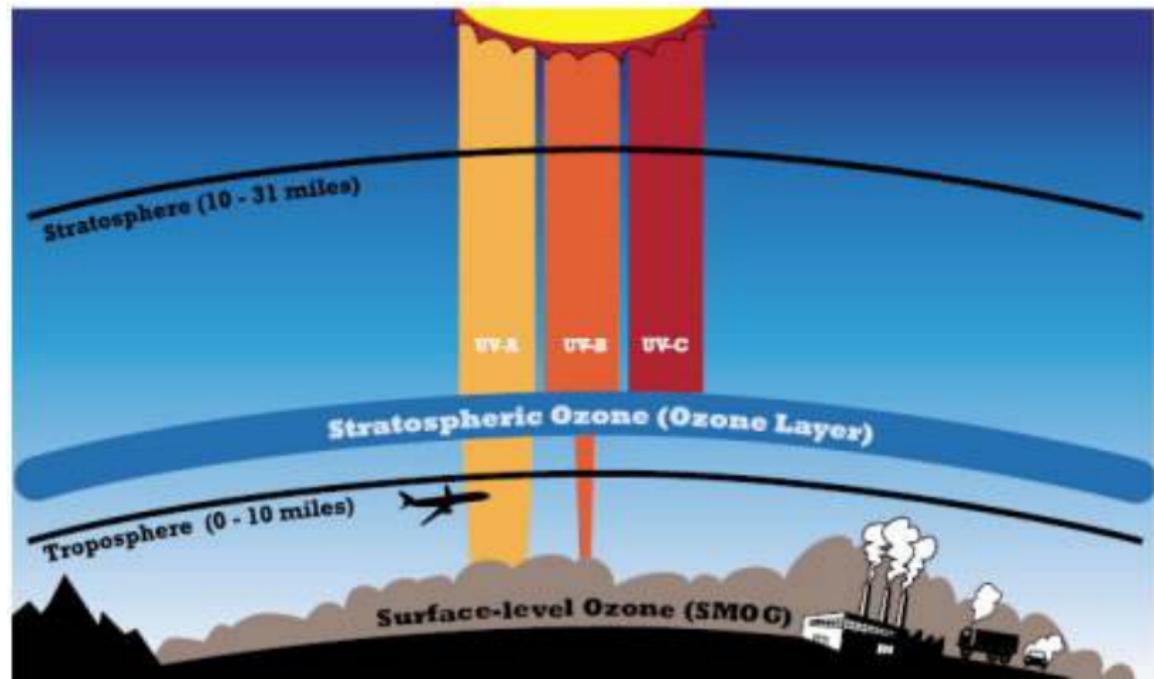
Photochemistry is the study of chemical reaction that are initiated by light.



Photochemistry in Action: The Ozone Layer

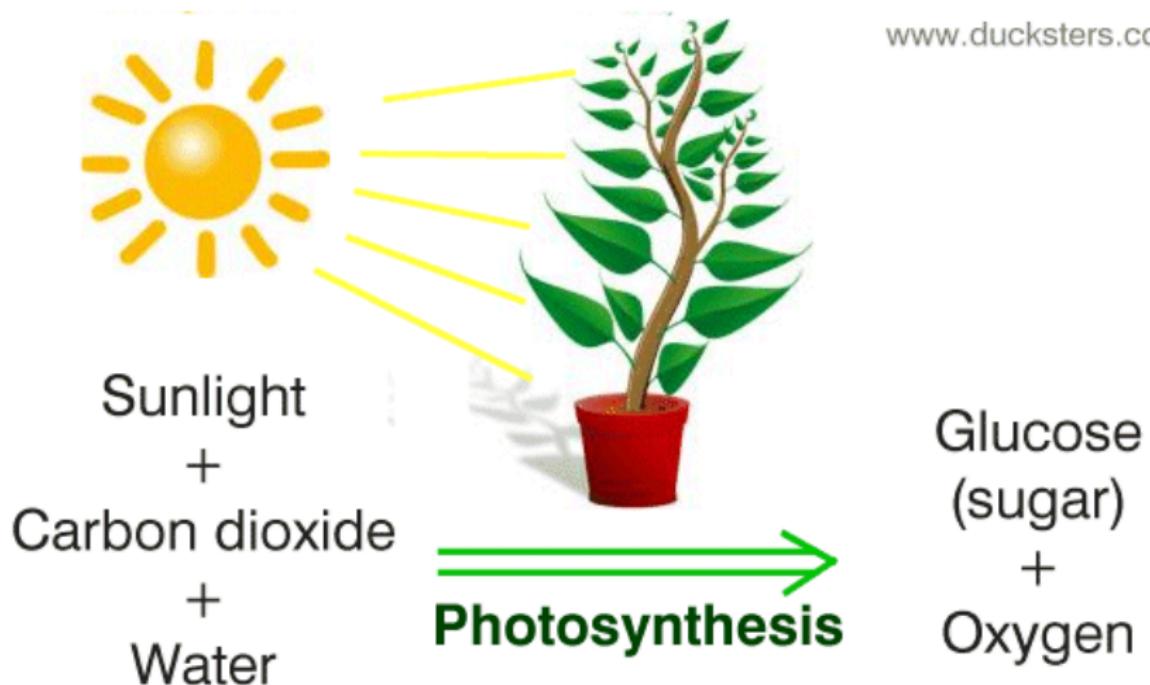


Photochemistry in Action: The Ozone Layer (cont.)



Photochemistry in Action: Photosynthesis

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Quantum Yield

The **quantum yield** of a process is defined as

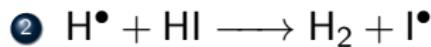
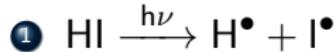
$$\phi = \frac{\nu}{I_{abs}}$$

where

- ν is the rate of an event
- I_{abs} is the rate of photon adsorption

Quantum Yield (cont.)

Quantum Yields can be higher than 1. Take the photochemical decomposition of HI:

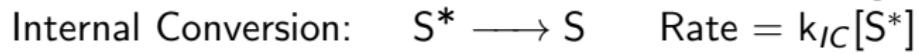
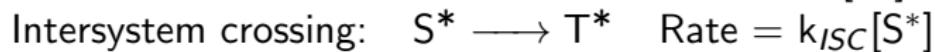
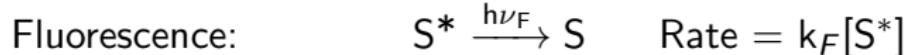
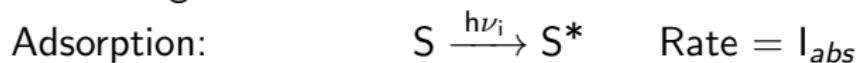


In this mechanism, the adsorption of **one** photon results in the loss of **two** HI molecules.

- The quantum yield, $\phi = 2$

Mechanisms of Decay

The following steps are present in the formation and decay of an excited singlet state S^* :



Overall rate of decay (after light source is turned off):

$$\begin{aligned}-\frac{dS^*}{dt} &= k_f[S^*] + k_{ISC}[S^*] + k_{IC}[S^*] \\ &= (k_f + k_{ISC} + k_{IC})[S^*]\end{aligned}$$

Observed Fluorescence Lifetime

This is a first order process where the integrated rate law is

$$[S^*] = [S^*]_0 e^{-(k_f + k_{ISC} + k_{IC})t} = [S^*]_0 e^{-t/\tau_0}$$

where the observed fluorescence lifetime, τ_0 is

$$\tau_0 = \frac{1}{k_f + k_{ISC} + k_{IC}}$$

Quantum Yield of Fluorescence

The **quantum yield of fluorescence** is defined by

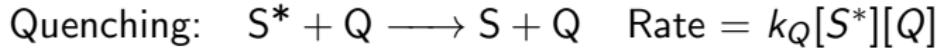
$$\begin{aligned}\Phi_{F,0} &= \frac{\text{Rate of Fluorescence}}{\text{Rate of photon adsorption}} \\ &= \frac{k_f[S^*]}{(k_f + k_{ISC} + k_{IC})[S^*]} \\ &= \frac{k_f}{k_f + k_{ISC} + k_{IC}} \\ &= k_f \tau_0\end{aligned}$$

Quenching

Other species in the system can interact with the excited state to remove its energy. We will examine three processes:

- ① Collisional deactivation
- ② Fluorescence Resonance Energy Transfer
- ③ Electron Transfer

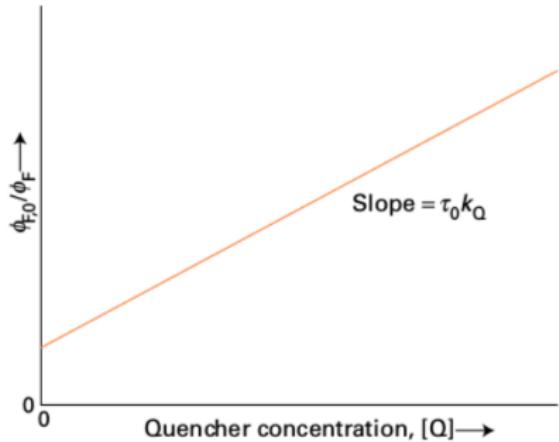
Mechanisms for collisional decay are quantified as



This means that when quenching is taken into account the new rate law is:

$$-\frac{dS^*}{dt} = k_f[S^*] + k_{ISC}[S^*] + k_{IC}[S^*] + k_Q[S^*][Q]$$

Quantifying Collisional Quenching: Stern-Volmer Plots

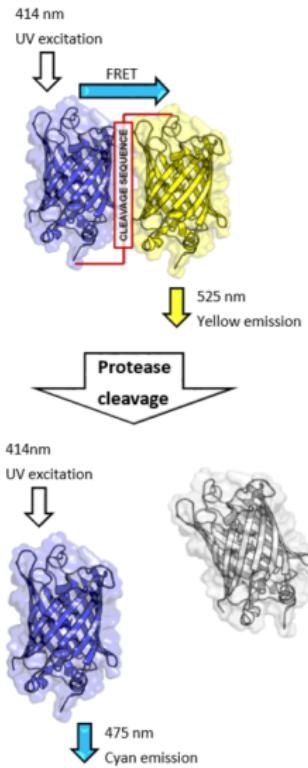


The relationship between the fluorescence quantum yields $\Phi_{F,0}$ and Φ_F in the absence and presence, respectively, of a quencher Q is given by the Stern-Volmer equation:

$$\frac{\Phi_{F,0}}{\Phi_F} = 1 + \tau_0 k_Q [Q]$$

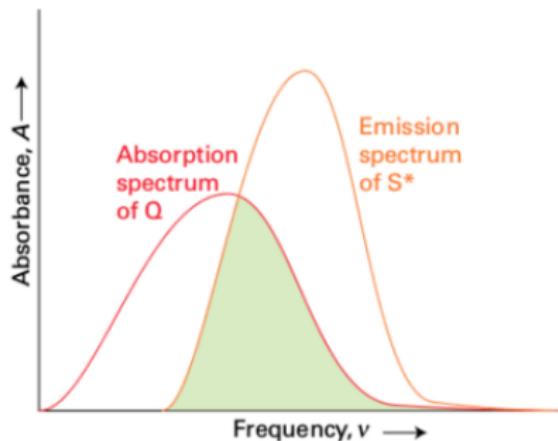
Fluorescence Resonance Energy Transfer

Through a dipole-dipole interaction, the energy from absorbing a photon in one region of a molecule can be transferred to another part. This is called **Fluorescence Resonance Energy Transfer**. Its mechanism of decay is:



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FRET Efficiency

- The efficiency of this process is determined by

$$\eta_{FRET} = \frac{\Phi_{F,0} - \Phi_F}{\Phi_{F,0}}$$

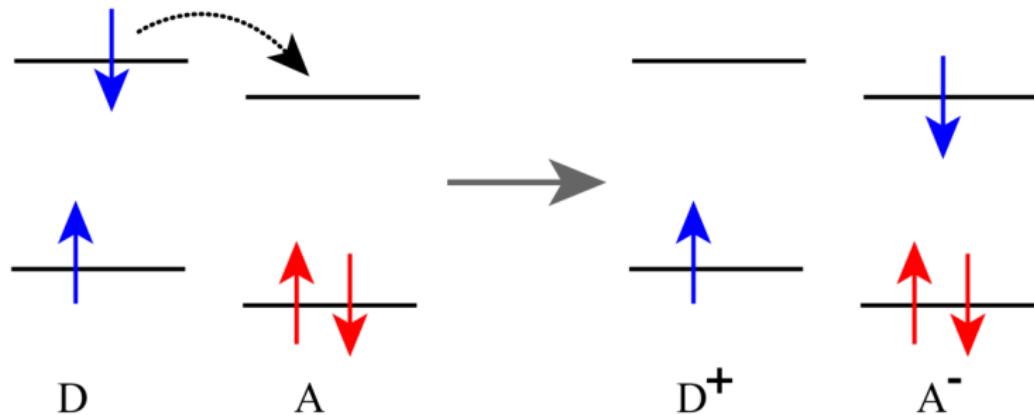
- Förster theory** quantifies the efficiency of this energy transfer through covalent bonds or protein scaffolds as a function of the distance between the two parts:

$$\eta_{FRET} = \frac{R_0^6}{R_0^6 + R^6}$$

where R_0 is a parameter that is characteristic of each donor-acceptor pair (values typically close to 4 nm)

Electron Transfer

Electron transfer is a quenching process where an electron is transferred from the excited molecule to the quenching molecule



Rate of Electron Transfer - Marcus Theory

The observed rate constant depends on two factors

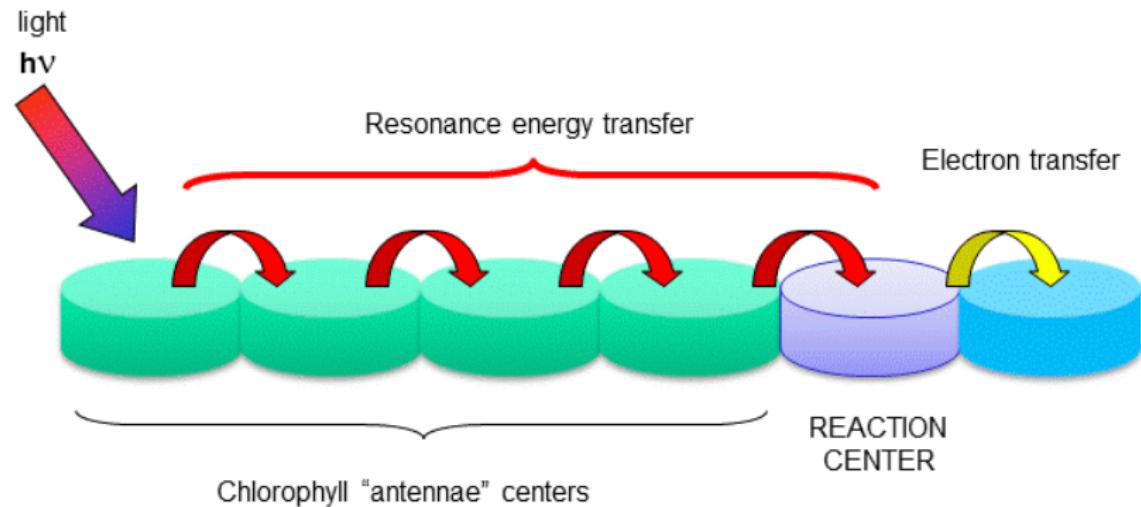
- ① The separation between the donor and the acceptor and
- ② The Gibbs energy of activation (ΔG^\ddagger)

These two factors put together give

$$k_{\text{exp}} \propto e^{-\beta r} e^{-\Delta G^\ddagger / k_b T}$$

where β is a constant that varies as a function of the system of interest and the medium in which electron transfer occurs

Back to Photosynthesis



Summary - Electronic Transitions

- The energy for electronic transitions are the largest of the three types of molecular excitations ($E_{electronic} > E_{vibrational} > E_{rotational}$)
- A **chromophore** is a chemical entity embedded within a molecule that absorbs radiation at nearly the same wavelength in different molecules. Can be used to ID certain transitions.
- The **Franck-Condon Principle** states that transitions between electronic states correspond to vertical lines on an energy versus internuclear distance diagram. Used to predict the dominant vibrational state in the excited molecule.
- **Fluorescence** is the spontaneously emitted radiation immediately following absorption.
- **Phosphorescence** is a spontaneous emission which may persist for long periods.

Summary - Photochemistry

- The interaction of molecules with light plays a key role in supporting life on Earth
- The rate at which excited molecules decay can be described with standard kinetic theory
- The rate at which systems relax can be accelerated by quenching molecules