

Photochemistry

Photochemistry

- Photochemistry is the underlying mechanism for all of photobiology. When a molecule absorbs a photon of light, its electronic structure changes, and it reacts differently with other molecules. The energy that is absorbed from light can result in photochemical changes in the absorbing molecule, or in an adjacent molecule (e.g., photosensitization). The energy can also be given off as heat, or as lower energy light, i.e., fluorescence or phosphorescence, in order to return the molecule to its ground state. Each type of molecule has a different preference for which of these different mechanisms it uses to get rid of absorbed photon energy, e.g., some prefer fluorescence over chemistry.

The Basic Laws of Photochemistry

- *The First Law of Photochemistry*

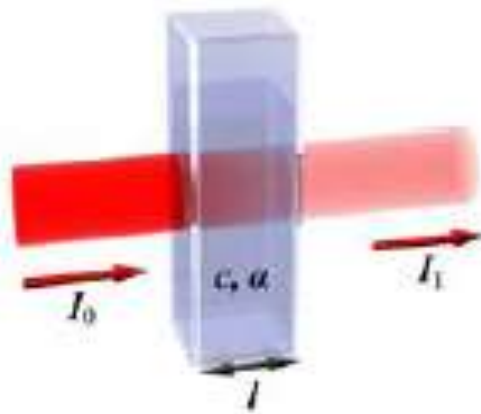
The First Law of Photochemistry states that light must be absorbed for photochemistry to occur. This is a simple concept, but it is the basis for performing photochemical and photobiological experiments correctly. If light of a particular wavelength is not absorbed by a system, no photochemistry will occur, and no photobiological effects will be observed, no matter how long one irradiates with that wavelength of light.

The Second Law of Photochemistry

- *The Second Law of Photochemistry* states that for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction. This law is true for ordinary light intensities, however, with high-powered lasers, two-photon reactions can occur, i.e., the molecule is raised to a higher energy state than produced by single-photon absorption.

Beer - Lambert Law

- **Fundamental Law of Spectrophotometry**



http://en.wikipedia.org/wiki/File:Beer_lambert.png

$$\text{Transmittance} = T = \frac{P}{P_0} = \frac{S}{B}$$

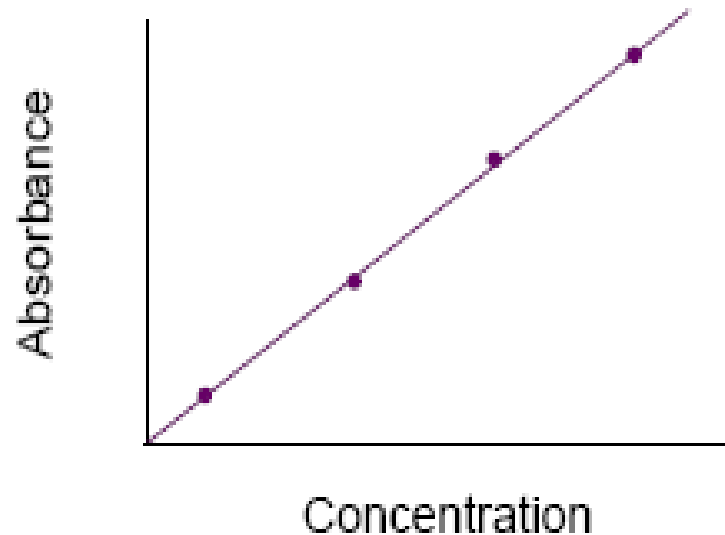
$$\text{Absorbance} = -\log T$$

$$A = -\log \frac{P}{P_0} = \epsilon bc$$

- Assumes:
 - monochromatic radiation
 - system not saturated in light
 - absorbers behave independently and are distributed homogeneously
- The product corresponds to the number of absorbers per cm^2 area as beam passes through cell.
- $A = abc$ vs $A = \epsilon bc$

Beer - Lambert Law

- Typical analytical application: Calibration curve



- Also works for mixtures: For a given λ ,

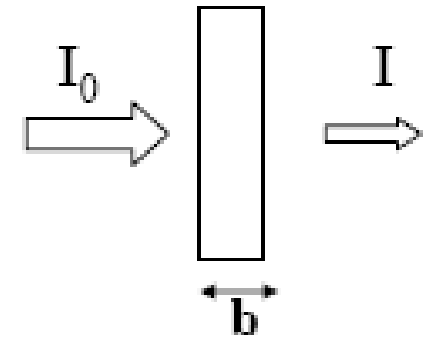
$$A_{\text{net}} = A_1 + A_2 + A_3 + \dots$$

$$A_{\text{net}} = \epsilon_1 b c_1 + \epsilon_2 b c_2 + \epsilon_3 b c_3 + \dots$$

Principle

Beer Lamberts Law

$$A = \epsilon b c$$



A → absorbance (-)

ϵ → molar absorptivity with units of $L \text{ mol}^{-1} \text{ cm}^{-1}$

b → path length of the sample (cuvette)

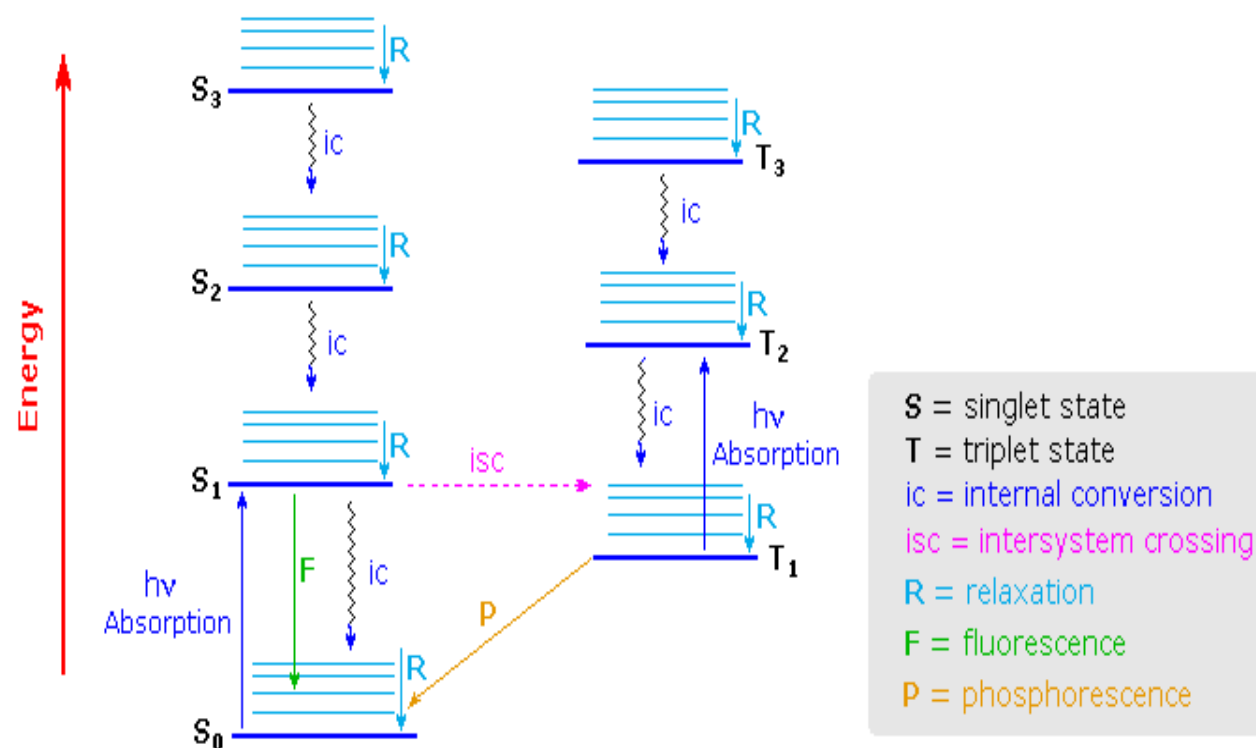
c → Concentration of the compound in solution, expressed in mol L^{-1}

3. If a higher vibrational level of the excited state is populated, either by the initial Franck-Condon transition or by collisional activation, the molecule may cleave into two $X\cdot$ atoms. Note that vibrational level 5 of the excited state is roughly coincident with bond breaking.

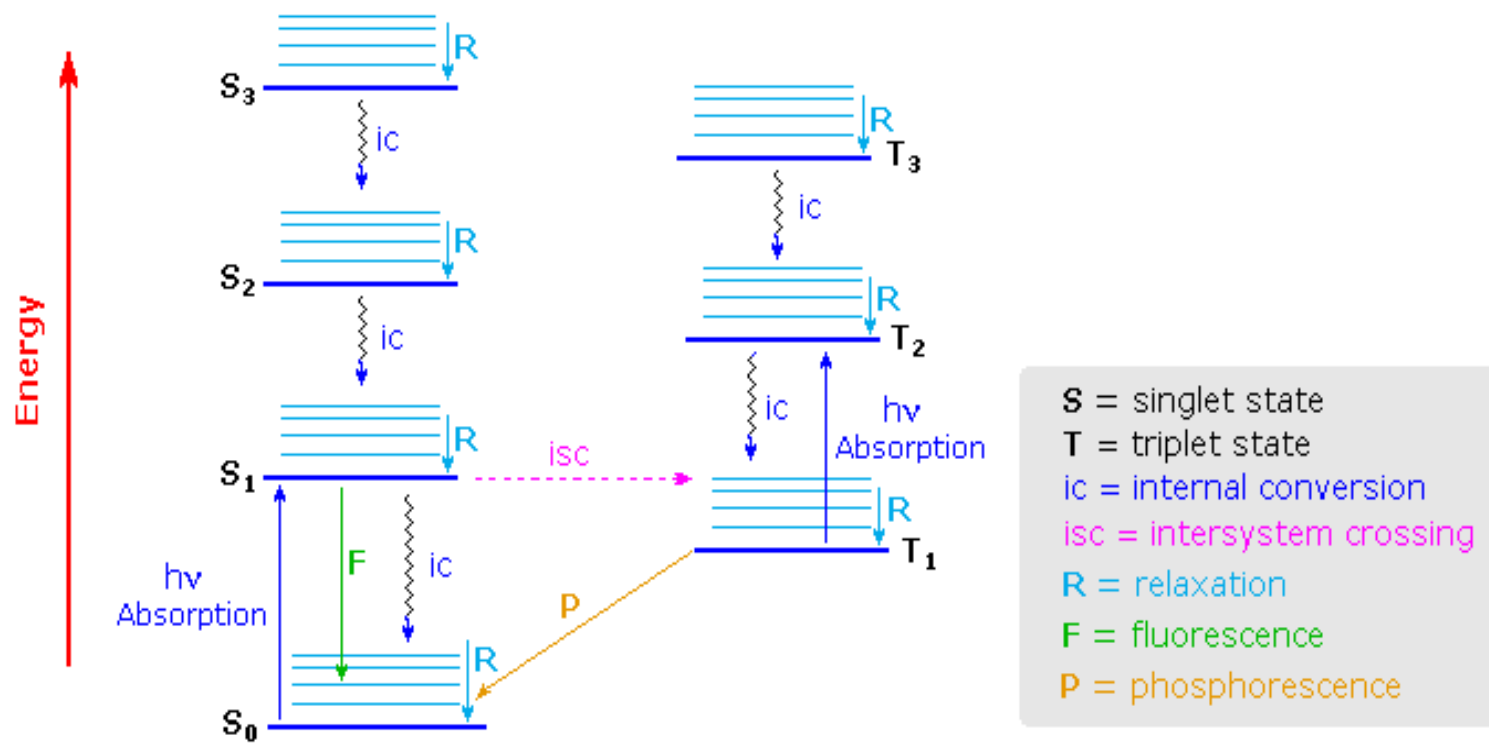
Virtually all organic compounds have more than two atoms, so the potential energy state diagram of X_2 must be adjusted for the increased number of bonding relationships. One way of doing this is to retain the energy coordinate while dispensing with the dimensional (r) coordinate. The **Jablonski diagram** shown below is an example, in which the spatial orientation of the various electronic states is not specified. Nevertheless, Franck-Condon transitions are expected.

One important feature conveyed by the diagram is that more than one electronic excited state is likely to exist for a given molecule, six are drawn and labeled in the diagram. Each electronic state will have a group of vibrational (and rotational) states, depicted by light blue lines above each state marker. Transitions between electronic states often occur to higher vibrational levels which then relax to lower levels by collisional loss of heat (translational energy).

A Jablonski Diagram



A Jablonski Diagram



may be classified as **singlet** or **triplet** based upon their electron spin angular momentum. The electrons in most non-metals are paired (opposite spins) in bonding and non-bonding orbitals, resulting in a net zero spin diamagnetic molecule for the ground state. Electronic states in which two electrons with identical spins (the Pauli exclusion principle) have a net spin of 1 ($2 \cdot 1/2$) and are paramagnetic. In a magnetic field such states have three degenerate energy levels and are called triplets. Molecular [oxygen](#) is a rare example of a triplet ground electronic state. The distinction between singlet and triplet states is important because photon induced excitation always leads to a state of the same multiplicity, i.e. singlet to singlet or triplet to triplet. Since ground states are singlets, this means that the excited states initially formed by absorption of light must also be singlets. **Internal conversion** between energy states of the same multiplicity takes place rapidly with loss of heat energy (relaxation). Alternatively, an excited state can decay to a lower energy state by emitting a photon (radiative decay). In the study of acetone [described above](#), nearly 80% of the excited singlet states decay by internal conversion and about 3% by fluorescence. Conversion of a singlet state to a lower energy triplet state, or vice versa, is termed **intersystem crossing**. Radiative decay from a triplet state is called phosphorescence and is generally quite slow.

Laws of Photochemistry

1. Only light that is absorbed can produce photochemical change (**Grotthus, Draper**)
2. A molecule absorbs a single quantum of light is becoming **excited** (**Stark, Einstein**)

Energy of photons (A. Einstein)

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

h = Planck's constant ($6.6 \cdot 10^{-34}$ Js)

c = speed of light ($3 \cdot 10^8$ ms⁻¹)

λ = wavelength

ν = frequency

Einstein's Equivalency Principle

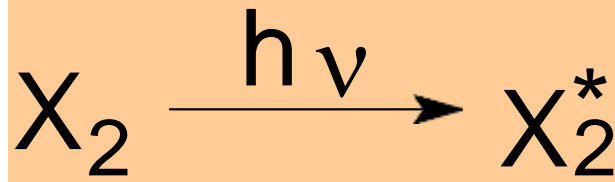
One particle of a chemical substance can absorb only *one photon* from a light beam: $\Delta E = h\nu$

For one mole: $\Delta E = Nh\nu$

$N = \text{Avogadro's number } (6.02 \cdot 10^{23})$

Mechanisms of Light Absorption

Excitation:



A bonding electron is lifted to a higher energy level (higher orbital)

INTERACTION OF LIGHT AND MATERIALS:

a) $X_2^* \rightarrow X_2 + M^*$ (excess energy transferred to the surrounding)

b) $X_2^* \rightarrow X_2 + h\nu$ (fluorescence or phosphorescence)

c) $X_2^* + Y \rightarrow$ **chemical reaction** (excess energy supplies the activation energy of the reaction)

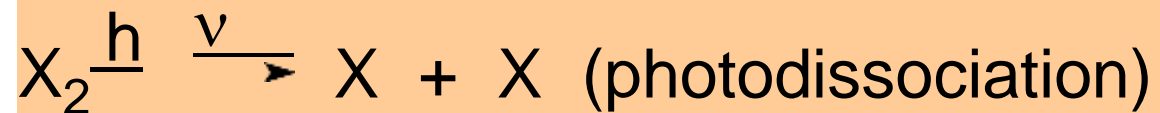
Types of photochemical reactions:

a) **Photodissociation**

b) **Photosynthesis**: when a larger molecule is formed from simple ones

c) **Photosensitized reactions**: when an excited molecule supplies activation energy for the reactants

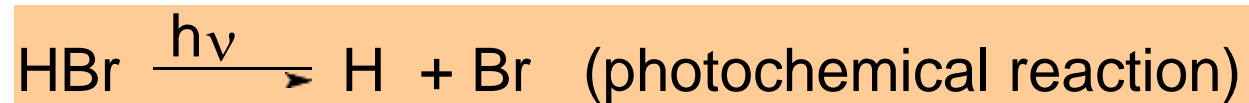
2.



(energy of the photon supplies the „dissociation heat“)

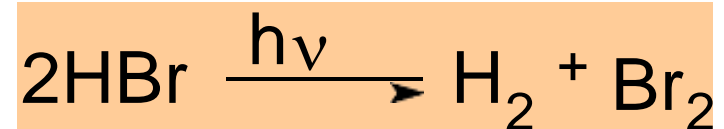
Photodissociation

Photolysis of hydrogen bromide



(dark reactions)

Overall:



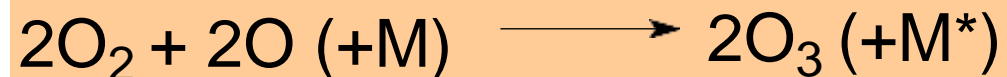
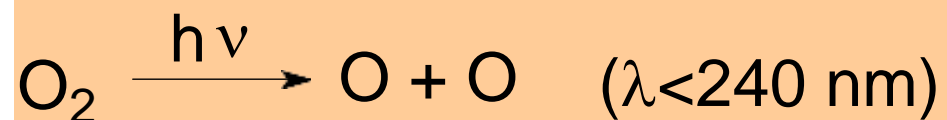
Note:

1 photon absorbed, 2 molecules of HBr dissociated:

$$\text{QUANTUM YIELD} = \frac{2}{1} = 2$$

$$\Phi = \frac{\text{number of molecules undergoing the process}}{\text{number of quanta absorbed}}$$

Ozone formation in the atmosphere
(at about 25 km altitude)



Notes: M absorbs energy released in the reaction

$$\text{QUANTUM YIELD} = \frac{2}{1} = 2$$

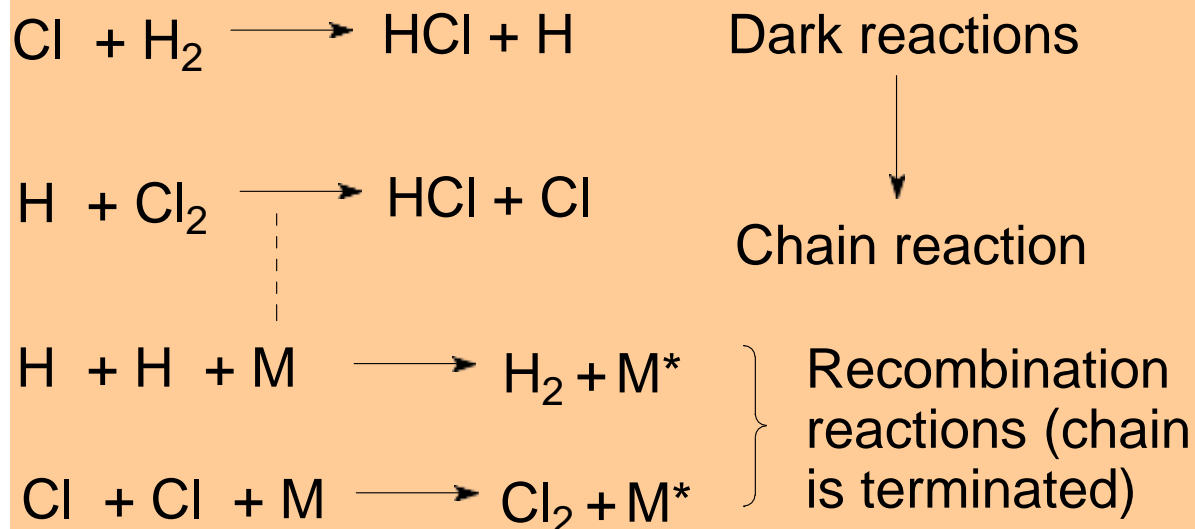
Photosynthesis

The photosynthesis of hydrogen chloride

Overall reaction:



Mechanism:



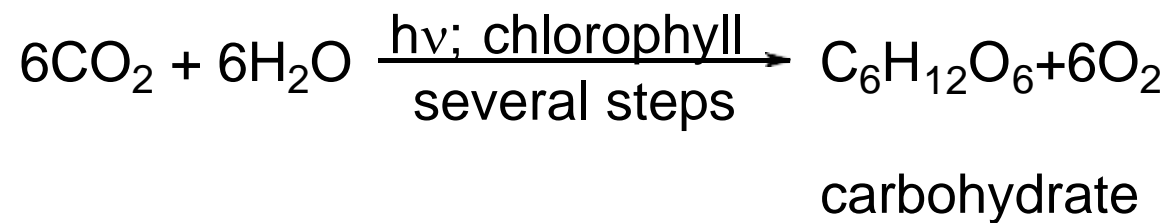
Note:

Quantum yield is about 10^6 (explosion)

Photosensitized reactions

Photosynthesis in plants

Overall reaction:



Notes:

1. Chlorophyll acts as a catalyst absorbing and transferring the photon energy for reduction of carbon dioxide to carbohydrate

2. This reaction maintains the life on the Earth:

