Introduction to Photochemistry

K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

Photochemistry studies light induced chemical reactions and physical processes. Electronically excited molecules are formed by the absorption of suitable radiation in the visible and near ultraviolet region. Naturally occurring phenomena of photochemistry are photosynthesis, phototaxis, photoperiodism, vision and mutagenic effects of light. Some applications of photochemistry are synthesis of vitamin D_2 from ergosterol isolated from yeast, synthesis of caprolactam (*i.e.* monomer for nylon 6), manufacture of cleaning solvents, synthesis of some antioxidants, photography, lithoprinting and manufacture of printed circuits for the electronic industry.

Photochemistry is divided into two processes: - (i) **Photophysical process** (*i.e.*, the absorption of light does not result in any chemical reaction), and (ii) **Photochemical process** (*i.e.*, light absorbed by the system results in chemical changes). Photochemical reactions differ from thermal reactions for several reasons: (i) photochemical reactions involve absorption of quantum of radiation, (ii) temperature has very little effect on the rate of a photochemical reaction, (iii) activation energy is acquired by absorption of quanta of radiation of suitable energy, and (iv) the presence of light is an essential requirement for the reaction to take place.

Laws related to electromagnetic radiation

The prolonged existance of the physical world is based on the interaction between electromagnetic radiation and matter, for example, X-rays are used to determine the structures of molecules and to study various types of spectroscopic techniques. Thermal reactions are initiated by heat energy, either through absorption or evolution of heat. In contrast, photochemical reactions take place in the presence of a **chromophore** (an atom or group of a molecule that has been specifically designed to absorb light energy). Thus, photochemical reactions are highly specific reactions.

1. Beer Lambert law

Beer Lambert law states that the concentration (**c**) of the sample and path length (**l**) is directly proportional to the absorbance (**A**) of the light (Fig. 1), which is represented by the equation given below.

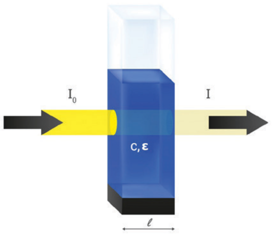

Figure 1. Sample cell with the width (l) exposed to incident light I_o

$$A = \log\left(\frac{I}{I_O}\right) = \varepsilon c l$$

A = absorbance; $\mathbf{I_o}$ = incident light; **I** = transmitted light; **c** = the concentration, ε = molar absorption coefficient and **l** = optical path length of the solution. The Graph of **A** versus **c** of the sample is depicted in Fig. 2.

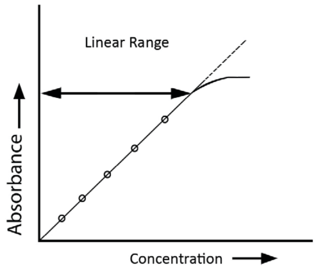

Figure 2. Graph of **A** vs **c** of a sample

Limitations of Beer Lambert law

- The law is valid only for monochromatic radiation.
- The law governs the absorption behaviour of dilute solutions only.
- The temperature of the system should not be allowed to largely vary.

2. Grotthuss-Draper law

It states that “only the light absorbed by a molecule can bring about a photochemical change in the molecule”.

The absorbed light may sometimes result in fluorescence or phosphorescence and in some cases, it may be converted into heat. The law is purely qualitative in nature and does not give any relationship between the amount of light absorbed by a system and the number of reacting molecules.

3. Stark Einstein law

Stark Einstein law states that “for each photon of light absorbed by a chemical system, only one molecule is activated for subsequent reaction”. It is also called the law of photo-equivalence and is given below.

$$\mathbf{E = h\upsilon = hc / \lambda}$$

E = Energy of a photon; **h** = Plank’s constant; **υ** = frequency; **c** = velocity of light; **λ** = its wavelength.

Background of a photochemical reaction

Three different types of electrons are found in molecules, *e.g.*, **σ-electrons** in σ bonds, **π-electrons** in double and triple bonds, and **non-bonding electrons** (*e.g.*, loan pair electrons).

An electron of an atom, ion, or a molecule in its lowest possible energy level (E_1) is called a **ground state electron**. It may absorb light and move to a higher energy level (E_2), now it is called an **excited electron**. The energy (E_p) of the photon absorbed or emitted during these transitions can be represented as shown below.

$$\mathbf{E_p = \Delta E = (E_2 - E_1) = h\upsilon}$$

The overlap of orbitals in atoms results in **bonding** (**σ** or **π**) and **antibonding** molecular orbitals (**σ*** or **π***). **Non-bonding** orbitals (**n**) do not involve in making bonds and they are the lone-pair electrons present in the molecule.

During a photochemical reaction, an electron present in a bonding and non-bonding orbital is excited to the corresponding unoccupied antibonding orbital (Fig. 3). The possible transitions are, σ→σ*, π→π*, and n→π*. The olefin 1,3-butadiene shows only π→π* transition while benzaldehyde shows both π→π* and n→π* transitions. In addition to above mentioned transitions, transition metal complexes show *d-d*, metal to ligand (M→L) and ligand to metal (L→M) transitions.

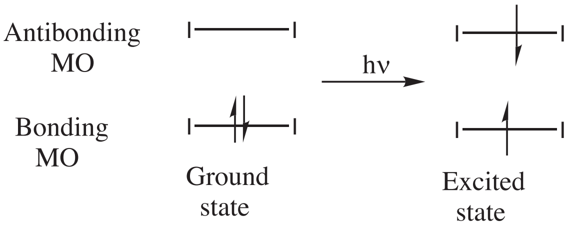

Figure 3. Excitation of an electron

The excited electron may have two different spin orientations which leads to singlet or triplet state.

If the spin of the excited electron remains unchanged, it generates a **singlet excited state**, while the spin-changed excited electron generates a **triplet excited state** (Fig. 4).

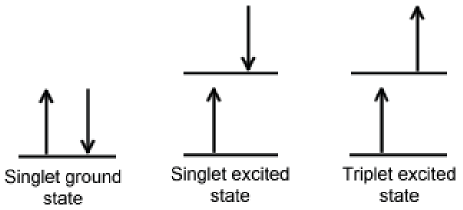

Figure 4. Triplet and singlet excited states

A triplet state is more stable than singlet state due to lesser inter electronic repulsion. This can be explained by the multiplicity theory.

$$\mathbf{Multiplicity\ (n) = 2S+1,\ S = s_1+s_2}$$

s = spin quantum number (±½)

For a singlet state: $n = 2\times(+\frac{1}{2} - \frac{1}{2}) + 1 = 1$

For a triplet state: $n = 2\times(+\frac{1}{2} + \frac{1}{2}) + 1 = 3$

Jablonski energy diagram

The Jablonski energy diagram (Fig. 5) is an energy diagram which explains various excitations and deexcitations in a molecule. Transitions where radiation is absorbed or emitted are called the **radiative** transitions while those not involving in any absorption or emission of radiation are known as **non-radiative** transitions as given in Table 1.

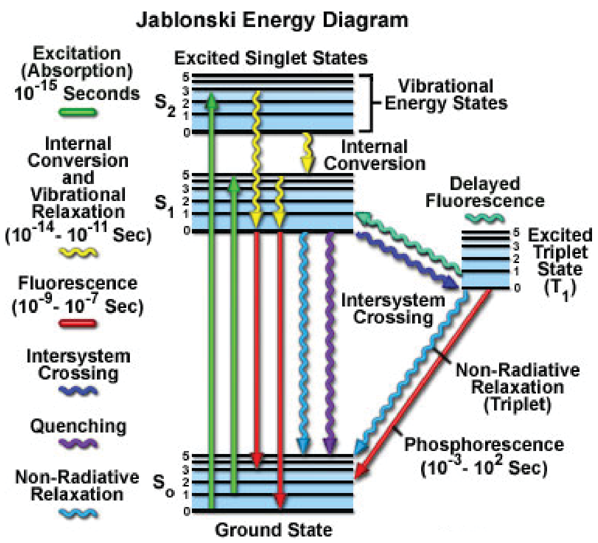

Figure 5. Jablonski energy diagram

Fluorescence is a process of absorption of ultraviolet or visible light by a molecule and the subsequent emission of a photon from (S_1) to the lower energy level (S_0). The light absorbed may be re-emitted almost instantaneously. **It involves no spin change**.

Phosphorescence is a process in which energy absorbed by a molecule is released slowly in the form of light ($T_1 \rightarrow S_0$). In other words, emission of light from a substance exposed to radiation and persisting as an afterglow after the exciting radiation has been switched off. **It involves spin change** and is delayed.

Intersystem crossing (ISC) is a radiation less process involving a transition between two electronic states with different spin multiplicity.

Table 1. Processes & the types of transition

Process	Type of transition	Radiative/ non-radiative
Absorption	$S_0 \rightarrow S_{1,}$ $S_0 \rightarrow S_2$	radiative
Internal Conversion	$S_2 \rightarrow S_1$	non-radiative
Vibrational relaxations	$V_{high} \rightarrow V_{low}$ (same S state)	non-radiative
Intersystem Crossing	$S_1 \rightarrow T_1$	non-radiative
Fluorescence	$S_1 \rightarrow S_0$	radiative
Phosphorescence	$T_1 \rightarrow S_0$	radiative

The quantum yield (Φ)

The quantum yield (Φ) is a measure of the efficiency of photon emission.

$$\Phi = \frac{\text{No. of molecules reacting or formed in a given time}}{\text{No.of quanta of light (photons) absorbed at the same time}}$$

Φ = 1 for a reaction that obeys the Einstein law, *i.e.*, one molecule decomposes per photon is equal to one. Φ = 1 for the reaction between SO_2 and Cl_2 to give SO_2Cl_2.

High Φ is generated, when two or more molecules are decomposed per a photon ($\Phi > 1$). Examples, combination of hydrogen and chlorine ($\Phi = 106$) and combination between CO and Cl_2 ($\Phi = 103$).

Low Φ is generated, when one or lesser than molecules are decomposed per a photon ($\Phi < 1$). Examples, dissociation of NH_3 ($\Phi = 0.25$) and combination between H_2 & Br_2 ($\Phi = 0.01$).

Primary and secondary processes determine the quantum yield of a reaction.

- In primary processes, molecules absorb photons and yield excited molecules or free radicals. They may lose their energy *via* collision, fluorescence, and phosphorescence
- Secondary processes are consisting of propagation and termination reactions. An excited molecule initiates a series of chain reactions.
- Generally, the secondary processes take place of themselves quite independent of the light radiation.

Reasons for High quantum yields

1. Chain reactions of the secondary process (scheme 1)
2. Formation of intermediates or products which act as catalysts and readily propagate the reaction.
3. The secondary reaction may be exothermic which activates other secondary process, as a result more reactant molecules undergo chemical changes without absorbing radiation.

Reaction between H_2 and Cl_2 (scheme 1)

Overall reaction $$H_2 + Cl_2 \longrightarrow 2\,HCl$$

Initiation $$Cl_2 + h\nu \longrightarrow 2\,Cl^{\cdot}$$

Propagation $$Cl^{\cdot} + H_2 \longrightarrow HCl + H^{\cdot}$$
$$H^{\cdot} + Cl_2 \longrightarrow HCl + Cl^{\cdot}$$

Termination $$2\,H^{\cdot} \longrightarrow H_2$$
$$2\,Cl^{\cdot} \longrightarrow Cl_2$$
$$H^{\cdot} + Cl^{\cdot} \longrightarrow HCl$$

Scheme 1. Reaction between H_2 and Cl_2

Reasons for Low quantum yields

1. If excited molecules formed in primary processes are such that they cannot react due to their deactivation by collision or by internal arrangement.
2. Loss of energy due to the collision of excited molecules with non-excited molecules.
3. The excited molecules produced in the primary process may recombine to form the reactant (scheme 2).

Reaction between H_2 and Br_2 (scheme 2)

Overall reaction $$H_2 + Br_2 \longrightarrow 2\,HBr$$

Initiation $$Br_2 + h\nu \longrightarrow 2\,Br^{\cdot}$$

Propagation $$Br^{\cdot} + H_2 \longrightarrow HBr + H^{\cdot}$$
$$H^{\cdot} + Br_2 \longrightarrow HBr + Br^{\cdot}$$
$$H^{\cdot} + HBr \longrightarrow H_2 + Br^{\cdot}$$

Termination $$2\,H^{\cdot} \longrightarrow H_2$$
$$2\,Br^{\cdot} \longrightarrow Br_2$$
$$H^{\cdot} + Br^{\cdot} \longrightarrow HBr$$

Scheme 2. Reaction between H_2 and Br_2

Solvatochromism (Solvent Effect)

The choice of solvent is important in photochemical processes because interactions between the solute and the solvent modify the energies and crossings between the electronic states of the **chromophore**, which give the molecule its color by absorbing visible light.

e.g., Effect of polar and non-polar solvents on benzaldehyde

Benzaldehyde (PhCHO) is a strong chromophore as it has a π-bond as well as a lone pair of electrons. Thus, it can undergo π→π* and n→π* transitions as shown in Fig. 6.

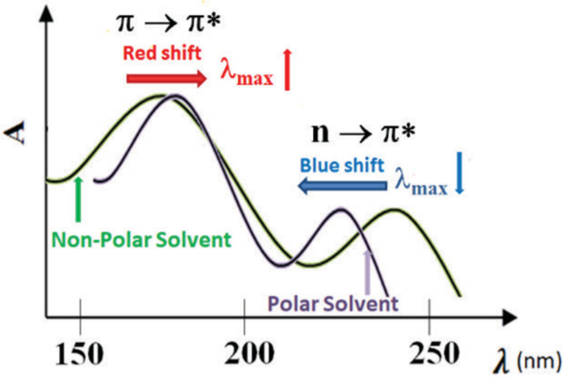

Figure 6. Absorption spectra of benzaldehyde

Effect of solvents on electronic transitions

Let us consider the HOMO-LUMO gap of benzaldehyde in a polar and non-polar solvent.

(a) π→π* transition

The π→π* transition results in a more polar LUMO state due to the partial charge separation of the oxo (C=O) group.

For π→ π* transition

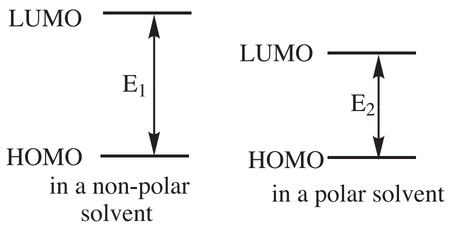

Figure 7. HOMO-LUMO gap of benzaldehyde in a polar and non-polar solvents

Polar solvents can stabilize the LUMO state (Figure 7), thus, the energy gap between the HOMO and LUMO states in a polar solvent E_2 is less than the energy gap E_1 in a non-polar solvent so that λ_{max} is increased in a polar solvent. Thus, π→π* transitions in polar solvents produce a **bathochromic shift** or **red shift** in the absorption spectra.

(b) n→π* transition

The n→π* transition results in a more polar HOMO state than a LUMO state. Polar solvents can stabilize the HOMO state by forming H bonds with the lone pairs on oxygen.

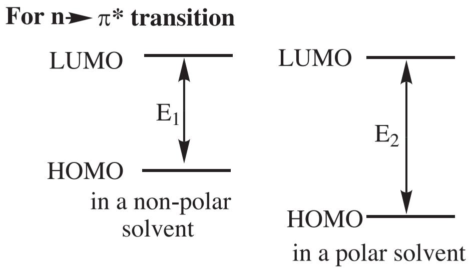

Figure 8. HOMO-LUMO gap of benzaldehyde in a polar and non-polar solvents

The energy gap between the HOMO and LUMO states in a polar solvent E_2 now increased (Figure 8) so that the λ_{max} is decreased in a polar solvent giving a **hypsochromic shift** or **blue shift** in the absorption spectra.

Photosensitization and quenching

Photosensitization is the process of initiating a reaction by using a substance capable of absorbing light and transferring the energy to the desired reactants. Examples of some photosensitizers are Hg, Cd, Zn, benzophenone, SO_2 and chlorophyll.

Quenching is the process of deactivating the excitation. Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample. A variety of molecular interactions can result in quenching. These include excited-state reactions, molecular rearrangements, energy transfer, ground-state complex formation, and collisional quenching.

Upconversion

There are many uses for energy conversion within materials. For example, if one can combine the energy of two particles to form a higher-energy particle, it can be used to activate molecules with higher band gaps. Polycyclic aromatic hydrocarbons are used to achieve upconversion *via* **triplet-triplet** annihilation. Metal complexes of *d*-block and *f*-block elements are capable of undergoing photon upconversion.

Upconversion is a general term referring to nonlinear optical processes that convert two or more lower-energy pump photons to a higher-energy output photon (Fig. 9).

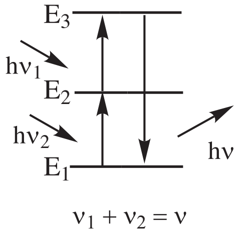

Figure 9. Pictorial presentation of an upconversion process

Upconversion can be utilized to overcome certain limitations associated with traditional photoreactions. One essential application is in photon harvesting and sensitization processes. Upconversion allows the efficient utilization of low-energy light that would not otherwise be absorbed by the photoactive species. This enables photochemical reactions to occur under milder conditions, broadening the range of accessible reaction pathways and enhancing the overall efficiency of the photochemical process. Upconversion plays a significant role in drug release providing a controlled and an on-demand drug delivery.

Down-conversion

Spontaneous parametric down-conversion is a nonlinear instant optical process that converts one photon of higher energy into a pair of photons (namely, a signal photon, and an idler photon) of lower energy. It is an important process in quantum optics, for the generation of entangled photon pairs, and of single photons (Fig. 10).

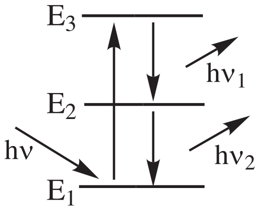

Figure 10. Pictorial presentation of a down-conversion process

In the context of solar cells, down-conversion is employed to enhance the overall efficiency of the photovoltaic conversion process. Solar cells are typically designed to absorb photons with energies corresponding to the bandgap of the semiconductor material used in the cell. However, photons with energies above the bandgap carry excess energy, which can be lost as heat. Down-conversion mechanisms can be integrated into the solar cell design to convert these high-energy photons into multiple lower-energy photons, effectively utilizing a wider range of the solar spectrum and reducing energy losses due to thermalization. This approach helps improve the overall efficiency of solar cells and enhances their power conversion capabilities.

X-ray florescence

X-ray Fluorescence (XRF) is an analytical technique that investigates the interaction between X-rays and a material to determine its elemental composition. XRF is suitable for solids, liquids, and powders, and in most circumstances is non-destructive. It is a very useful method to determine the chemical/elemental composition of metals, ceramics, paintings, glass, and materials related archeology, geology, and forensic science. This technique studies secondary X-rays (florescence) emitted from a material that has been excited by being bombarded with high energy X-rays or gamma rays.

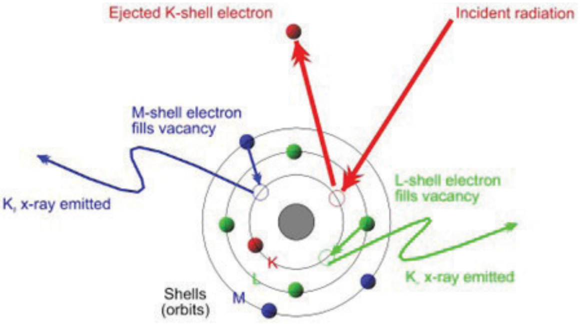

Figure 11. XRF observed by ejecting an electron in the K-shell

In this case (Fig. 11) high energy X-ray photons are made to collide with electrons of a targeted atom to ionize its electrons. Incident radiation removes an electron in the K-shell. The vacancy created in the in the lower K-shell is filled by moving an electron in a higher L-shell (or M-shell) with the emission of X-rays (XRF). The observed XRF is characteristic to the element.

Student Corner

Nucleophilic Attack on Coordinated Ligands

K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

Reactions of nucleophiles with transition metal complexes are useful in the preparation of new metal complexes. Unsaturated ligands such as C≡O, isonitriles, olefins, dienes, and arenes are not normally reactive towards nucleophiles. When these ligands or molecules are coordinated to an electron-deficient metal they become activated towards nucleophilic attack.

The factors which facilitate nucleophilic attack on a coordinated ligands are (i) formal positive charge on the metal, (ii) coordination of π acceptor ligands, (iii) the metal should be coordinatively saturated. and (iv) high reactivity of the nucleophile.

Nucleophilic attack on C≡O

Nucleophiles such as hydride, alkyls, alkoxides, hydroxide and amines can attack the carbon of metal carbonyls without prior coordination to the metal. For example,

1. Attack of hydride ion (H^-) on C≡O produces a formyl (CHO) group in (**1**).

   ($L = CO, PPh_3$; M = Cr, W, Fe; n = 4, 5, 6)

$$\begin{array}{c} H^- + [LM(CO)_n] \\ \downarrow \\ [L(OC)_{n-1}M\text{-}C(=O)H]^- \ \mathbf{(1)} \end{array}$$

2. Attack of an alkyl/aryl reagent produces an acyl group as in (**2**).

$$\begin{array}{c} R^- + [LM(CO)_n] \\ \downarrow \\ [L(OC)_{n-1}M\text{-}C(=O)R]^- \ \mathbf{(2)} \end{array}$$

3. HO^- attacks C≡O in (**3**) to give hydroxy- carbonyl complexes (**4**), which lose CO_2 to form metal hydrides (**5**).