# NATIONAL OPEN UNIVERSITY OF NIGERIA

## SCHOOL OF SCIENCE AND TECHNOLOGY

## COURSE CODE: CHM 414

# COURSE TITLE: PHOTOCHEMISTRY & PERICYCLIC REACTIONS

# COURSE GUIDE (CHM 414)

## Introduction

The study of chemical reactions, isomerizations and physical behavior that may occur under the influence of visible and/or ultraviolet light is called **Photochemistry**. The Photochemistry course is concerned with the interaction of visible and ultraviolet light with molecules, an important aspect of modern chemistry which is relevant to biology (e.g. photosynthesis, vision), lasers, organic synthesis, reaction kinetics and atmospheric science (e.g. the ozone hole). Some familiarity with concepts such as Hund's rules, the Franck-Condon principle, basic reaction kinetics and the steady-state approximation is expected. On the other hand, pericyclic reactions represent an important class of concerted (single step) processes involving $\pi$-systems. It is a *chemical reaction* in which *concerted* reorganization of bonding takes place throughout a cyclic array of continuously bonded atoms. The term embraces a variety of processes, including *cycloadditions, cheletropic reactions, electrocyclic reactions* and *sigmatropic rearrangements* (provided they are concerted).

## Course Description

In this course (CHM 414) titled "photochemistry and pericyclic reaction", you will be presented information in a structured way to make leaning easier. This course exposes students to the fundamental principles that are foundational to understanding photochemical transformations. Each unit is planned in an easy to follow pattern for beginners in this aspect of chemistry. We have adopted a step-by-step approach in order to introduce you to a fascinating world of excited-state reactions and concerted reactions involving a cyclic flow of electrons through a single transition state. All the units follow the same pattern and so after the first unit the rest will become easy to follow.

## What you will learn in this course

In this course you will learn about the underlying mechanism for all of photobiology. You will find that the energy that is absorbed from light can result in photochemical changes in the absorbing molecule, or in an adjacent molecule (e.g., photosensitization). You will learn about different preference each type of molecule has to get rid of absorbed photon energy either to be given off as heat or as lower energy light, i.e., fluorescence or phosphorescence and which of these different mechanisms it uses in order to return the molecule to its ground state.

In addition, it will become obvious that a pericyclic reaction is characterized by a change in bonding relationships that takes place as a continuous, concerted reorganization of electrons. You will also learn that the term "concerted" specifies that there is one single transition state and therefore no intermediates are involved in the process. To maintain continuous electron flow, pericyclic reactions occur through cyclic transition states. You will find out that the cyclic transition state must correspond to an arrangement of the participating orbitals which has to maintain a bonding interaction between the reaction components throughout the course of the reaction.

## Course Aims

This course aims at providing you the necessary background on the basics of photochemistry so as to enable you understand the underlying mechanism for all photochemical processes. It also intends to enhance a detailed understanding of the concept of the processes of pericyclic reactions and the stereochemical outcomes of these highly stereospecific reactions.

## Course Objectives

On completion of this course you should be able to:

- Distinguish between thermal reactions and photochemical reactions.
- Discuss the role of photochemistry in our everyday living.
- Identify photochemical process in what goes on in your environment.
- Give a concise definition of pericyclic reactions
- Explain the mechanisms of pericyclic reactions
- Explain various approaches to analyzing pericyclic reactions
- Discuss the Frontier molecular orbital theory
- Draw an orbital correlation diagram
- Classify an orbital as symmetric or antisymmetric
- State and explain the generalized and Woodward-Hoffmann orbital symmetry rules

## Working through this course

In order to be able to successfully complete this course, you are required to carefully study each unit along with recommended textbooks and other materials that may be provided by the National Open University. You may also need to exploit other e-reading such as internet for further useful information on the course. Each unit contains self assessment exercise and at certain points in the course you would be required to submit assignment for grading and recording purposes. You are also to participate in the final examination at the end of the course. It is recommended that you devote an abundant time to reading and comprehension. It is highly necessary that you avail yourself the opportunity of attending the tutorial sessions where you will be able to compare your understanding of the course contents with your colleagues.

## Course Materials

You are provided with the following sets of course materials:

1. A course guide which spells out the details of photochemistry and pericyclic reactions including the aims and objectives.

2. The study units (presented in two modules) with detailed learning information. Each study unit has a set of performance objectives along with other relevant learner guide.

## Study Units

A synopsis of the units contained in the course is here presented:

### Module One

Unit 1- The electromagnetic spectrum: This Unit gives the range of all possible frequencies of electromagnetic radiation and the "electromagnetic spectrum" of an object as the characteristic distribution of electromagnetic radiation emitted or absorbed by that object.

Unit 2 – Introduction to photochemistry: Presents photochemistry as the study of the chemical reactions and physical changes that result from interactions between matter and visible or ultraviolet light. This Unit familiarizes the reader with basic ideas relating to light and matter and the interaction between them.

Unit 3 – Light absorption and fate of the excited state: Reveals what happens to molecules when they absorb light, the variety of processes and different mechanistic pathways they undergo.

Unit 4 – Selection rules and photophysical parameters: Looks at the way absorbed or generated photons are analyzed to predict the likelihood that a physical system will change from one state to another or will be unable to make such a transition.

Unit 5 –Lasers: In this Unit the properties of Laser and the wide variety of applications in all walks of life to which Laser has been engaged were discussed.

Unit 6 – Photochemical reactions: Contrasts photochemical reactions with thermal reactions as reactions involving electronic reorganization initiated by electromagnetic radiation and shows the valuable use to which they have been put in organic and inorganic chemistry.

### MODULE TWO

Unit 1 - Mechanism of pericyclic reactions and associated terminologies: Gives a concise definition of pericyclic reactions, explains the mechanisms of pericyclic reactions and its associated terminologies together with the various stereochemical notations as well as characteristics of pericyclic reactions.

Unit 2 - Types of pericyclic reactions: Explains the major categories of pericyclic reactions and compares different types.

Unit 3 - Analysis of pericyclic reactions: This Unit applies orbital correlation diagram method and the frontier molecular orbital (FMO) approach to analyze pericyclic reactions.

The individual units of this book are organized according to the following format: unit title, introduction to the unit, unit learning objectives and text, summary, tutor-marked assignments (TMA) and suggested references for further reading. We chose this format in order to aid the reader in comprehending the material and to stimulate him to probe the unit topics further. The TMAs are meant to test your basic understanding and comprehension of the course materials, which is a prerequisite for achieving the stated aims and objectives of the course.

## Assessment

The course assessment consists of three aspects namely the self assessment exercise, the tutor marked assignment and the written examination/end of course examination. It is essential that you attempt all exercises and assignments and submit appropriately to the course facilitator for grading. Let your answers be concise and as accurate as possible. You are expected to consult other materials in addition to your course materials in order to be able to present accurate answers to the questions. Kindly note that the tutor marked assignment covers only 30% of the total marks for the course.

## Tutor Marked Assignment (TMA)

The TMA is a continuous assessment component of your course. It accounts for 30% of the total score. You will be given a number of TMAs to answer. Nearly all of them must be answered before you are allowed to sit for the end of the course examination. The TMAs will be given to you by your facilitator and returned after you have done the assignment. Note that these assignments are already contained in the assignment file to be given to you. You may do yourself good by reading and researching well before you attempt to answer the questions.

## Facilitators/Tutors and Tutorials

There are few hours of tutorials provided in support of this course. You will be informed appropriately of the name, telephone number and e-mail address of your facilitator. In addition, the time, dates and location of the tutorial lessons will be communicated beforehand. You are required to mail or submit your Tutor Marked Assignment to your facilitator, at least two working days, before the schedule date. Note that all the submitted assignments will be duly marked by the facilitator with further comments that can improve on your performances. The facilitator will from time to time take track record of your comprehension, progress and difficulty in the course. Be kind enough to attend tutorial lessons at the fixed appointment. It is probably the only avenue to meet face to face and discuss with you facilitator. There, you will be able to ask questions or seek clarification on seemingly grey areas in the course material. You may as well have prepared questions and comments for your facilitator before the due date. An active participation during the tutorial lessons will be an added advantage to boost your confidence level. In case any of the situations listed below arises, do not hesitate to intimate your facilitator using his or her telephone number or via e-mail address;

- You do not understand any part of the study or the assigned readings
- You are not skill enough to attempt the self assessment exercise
- The questions in the TMAs are not clearly understood

## Textbooks

There are numerous books and other materials that treat Structure and Bonding; some of these are listed at the end of units. In addition, the internet provides a lot of information relating to the course title; the learner is encouraged to use the internet, though with some level of caution. The learner may wish to consult any of the following resources in aid of effective learning:

- J. Mattay, A. G. Griesbeck: *Photochemical Key Steps in Organic Synthesis*, Wiley-VCH, 1994.
- N. J. Turro, *Modern Molecular Photochemistry* 1991, University Science Books, Mill-Valley, California.
- F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry***,** Plenum Publishing Corporation, 2000.
- A. Gillbert, J. Baggott, *Essentials of Molecular Photochemistry* 1991, Blackwell Scientific Publications, London.
- M. Klessinger, J. Michl, *Excited States and Photochemistry of Organic Molecules*, Wiley-VCH, 1994, New York.
- Woodward, R.B.; Hoffmann, R. *The Conservation of Orbital Symmetry*. Verlag Chemie Academic Press, 2004.

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**MODULE TWO**

# UNIT 1 – THE ELECTROMAGNETIC SPECTRUM

## 1.0. INTRODUCTION

The **electromagnetic spectrum** is the range of all possible frequencies of electromagnetic radiation. The "electromagnetic spectrum" of an object is the characteristic distribution of electromagnetic radiation emitted or absorbed by that object.

The electromagnetic spectrum extends from low particular frequencies used for modern radio communication to gamma radiation at the short-wavelength (high-frequency) end, thereby covering wavelengths from thousands of kilometres down to a fraction of the size of an atom. It is for this reason that the electromagnetic spectrum is highly studied for spectroscopic purposes to characterize matter. The limit for long wavelength is the size of the universe itself, while it is thought that the short wavelength limit is in the vicinity of the Planck length, although in principle the spectrum is infinite and continuous.

## 2.0. OBJECTIVES

After studying this Unit, you should be able to:

- Describe and electromagnetic wave and its properties.
- Describe properties of light in relation to particles and to electromagnetic waves.
- Describe the two components of an electromagnetic radiation
- State the range (various divisions) of the electromagnetic spectrum
- Explain the wave-particle duality of light
- Carry out simple calculations using the parameters of light (wavelength, frequency, velocity, wave number and energy)
- State the physical processes that could take place when electromagnetic radiation interacts with matter

## 3.0. MAIN CONTENT

### 3.1. Range of the spectrum

Electromagnetic waves are typically described by any of the following three physical properties: the frequency $f$, wavelength $\lambda$, or photon energy $E$. Frequencies range from $2.4\times10^{23}$ Hz (1 GeV gamma rays) down to the local plasma frequency of the ionized interstellar medium (~1 kHz). Wavelength is inversely proportional to the wave frequency, so gamma rays have very short wavelengths that are fractions of the size of atoms, whereas wavelengths can be as long as the universe. Photon energy is directly proportional to the wave frequency, so gamma rays have the highest energy (around a billion electron volts) and radio waves have very low energy (around a femto-electronvolt). These relations are illustrated by the following equations:

$$f = \frac{c}{\lambda}, \quad \text{or} \quad f = \frac{E}{h}, \quad \text{or} \quad E = \frac{hc}{\lambda},$$

where:

- $c$ = 299,792,458 m s$^{-1}$ is the speed of light in vacuum
- $h = 6.62606896(33)\times10^{-34}$ J s $= 4.13566733(10)\times10^{-15}$ eV s is Planck's constant.

Whenever electromagnetic waves exist in a medium with matter, their wavelength is decreased. Wavelengths of electromagnetic radiation, no matter what medium they are travelling through, are usually quoted in terms of the *vacuum wavelength*, although this is not always explicitly stated.

Generally, electromagnetic radiation is classified by wavelength into radio wave, microwave, terahertz (or sub-millimeter) radiation, infrared, the visible region we perceive as light, ultraviolet, X-rays and gamma rays. The behaviour of EM radiation depends on its wavelength. When EM radiation interacts with single atoms and molecules, its behaviour also depends on the amount of energy per quantum (photon) it carries.

Spectroscopy can detect a much wider region of the EM spectrum than the visible range of 400 nm to 700 nm. A common laboratory spectroscope can detect wavelengths from 2 nm to 2500 nm. Detailed information about the physical properties of objects, gases, or even stars can be obtained from this type of device. Spectroscopes are widely used in astrophysics. For example, many hydrogen atoms emit a radio wave photon that has a wavelength of 21.12 cm. Also, frequencies of 30 Hz and below can be produced by and are important in the study of certain stellar nebulae and frequencies as high as $2.9\times10^{27}$ Hz have been detected from astrophysical sources.

## 3.2. Interaction of electromagnetic Radiation with Matter

Electromagnetic radiation interacts with matter in different ways in different parts of the spectrum. The types of interaction can be so different that it seems to be justified to refer to different types of radiation. At the same time, there is a continuum containing all these "different kinds" of electromagnetic radiation. Thus we refer to a spectrum, but divide it up based on the different interactions with matter.

| **Region of the spectrum** | **Main interactions with matter** |
|---|---|
| Radio | Collective oscillation of charge carriers in bulk material (plasma oscillation). An example would be the oscillation of the electrons in an antenna. |
| Microwave through far infrared | Plasma oscillation, molecular rotation |
| Near infrared | Molecular vibration, plasma oscillation (in metals only) |
| Visible | Molecular electron excitation (including pigment molecules found in the human retina), plasma oscillations (in metals only) |
| Ultraviolet | Excitation of molecular and atomic valence electrons, including ejection of the electrons (photoelectric effect) |
| X-rays | Excitation and ejection of core atomic electrons, Compton scattering (for low atomic numbers) |
| Gamma rays | Energetic ejection of core electrons in heavy elements, Compton scattering (for all atomic numbers), excitation of atomic nuclei, including dissociation of nuclei |
| High-energy gamma rays | Creation of particle-antiparticle pairs. At very high energies a single photon can create a shower of high-energy particles and antiparticles upon interaction with matter. |

### 3.3. Types of radiation

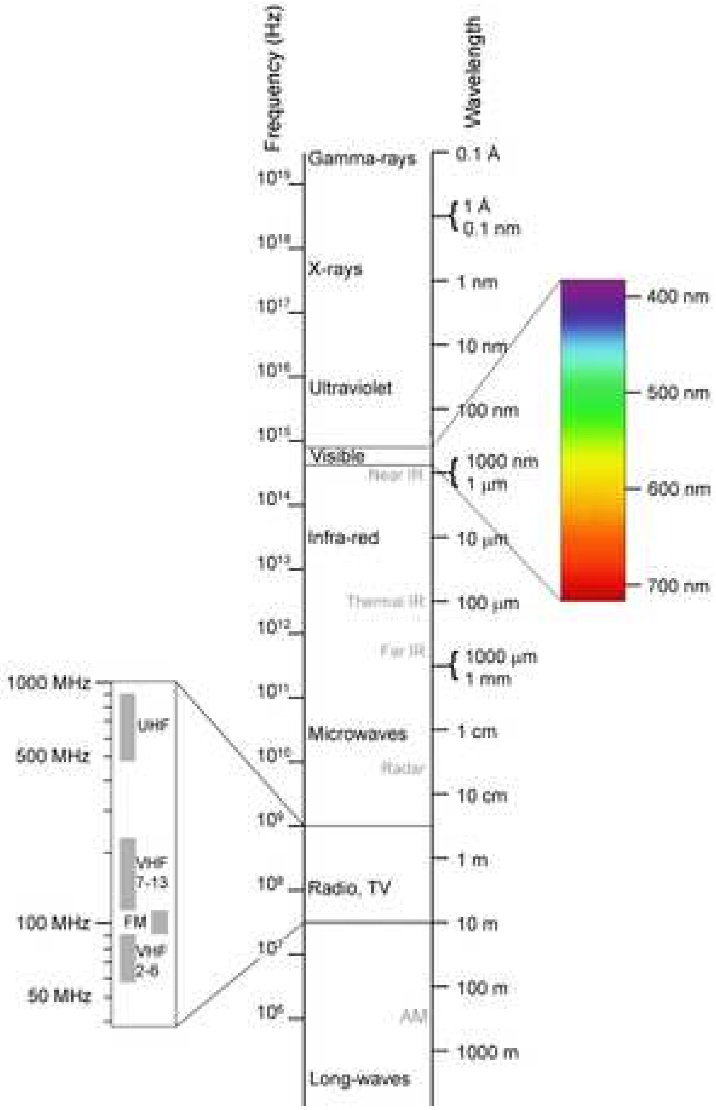


**Figure 1: The electromagnetic spectrum**

The types of electromagnetic radiation are broadly classified into the following classes:

1. Gamma radiation
2. X-ray radiation
3. Ultraviolet radiation
4. Visible radiation
5. Infrared radiation
6. Microwave radiation
7. Radio waves

This classification goes in the increasing order of wavelength, which is characteristic of the type of radiation. While, in general, the classification scheme is accurate, in reality there is often some overlap between neighboring types of electromagnetic energy. For example, SLF radio waves at 60 Hz may be received and studied by astronomers, or may be ducted along wires as electric power, although the latter is, in the strict sense, not electromagnetic radiation at all (see near and far field) The distinction between X-rays and gamma rays is based on sources: gamma rays are the photons generated from nuclear decay or other nuclear and subnuclear/particle process, whereas X-rays are generated by electronic transitions involving highly energetic inner atomic electrons. In general, nuclear transitions are much more energetic than electronic transitions, so gamma-rays are more energetic than X-rays, but exceptions exist. By analogy to electronic transitions, muonic atom transitions are also said to produce X-rays, even though their energy may exceed 6 megaelectronvolts (0.96 pJ), whereas there are many (77 known to be less than 10 keV (1.6 fJ)) low-energy nuclear transitions (e.g., the 7.6 eV (1.22 aJ) nuclear transition of thorium-229), and, despite being one million-fold less energetic than some muonic X-rays, the emitted photons are still called gamma rays due to their nuclear origin.

Also, the region of the spectrum of the particular electromagnetic radiation is reference frame-dependent (on account of the Doppler shift for light), so EM radiation that one observer would say is in one region of the spectrum could appear to an observer moving at a substantial fraction of the speed of light with respect to the first to be in another part of the spectrum. For example, consider the cosmic microwave background. It was produced, when matter and radiation decoupled, by the de-excitation of hydrogen atoms to the ground state. These photons were from Lyman series transitions, putting them in the ultraviolet (UV) part of the electromagnetic spectrum. Now this radiation has undergone enough cosmological red shift to put it into the microwave region of the spectrum for observers moving slowly (compared to the speed of light) with respect to the cosmos. However, for particles moving near the speed of light, this radiation will be blue-shifted in their rest frame. The highest-energy cosmic ray protons are moving such that, in their rest frame, this radiation is blueshifted to high-energy gamma rays, which interact with the proton to produce bound quark-antiquark pairs (pions).

### 3.3.1. Radio frequency

Radio waves generally are utilized by antennas of appropriate size (according to the principle of resonance), with wavelengths ranging from hundreds of meters to about one millimeter. They are used for transmission of data, via modulation. Television, mobile phones, wireless networking, and amateur radio all use radio waves. The use of the radio spectrum is regulated by many governments through frequency allocation.

Radio waves can be made to carry information by varying a combination of the amplitude, frequency, and phase of the wave within a frequency band. When EM radiation impinges upon a conductor, it couples to the conductor, travels along it, and induces an electric current on the surface of that conductor by exciting the electrons of the conducting material. This effect (the skin effect) is used in antennas.

### 3.3.2. Microwaves

The super-high frequency (SHF) and extremely high frequency (EHF) of microwaves come after radio waves. Microwaves are waves that are typically short enough to employ tubular metal waveguides of reasonable diameter. Microwave energy is produced with klystron and magnetron tubes, and with solid state diodes such as Gunn and IMPATT devices. Microwaves are absorbed by molecules that have a dipole moment in liquids. In a microwave oven, this effect is used to heat food. Low-intensity microwave radiation is used in Wi-Fi, although this is at intensity levels unable to cause thermal heating.

Volumetric heating, as used by microwave ovens, transfers energy through the material electromagnetically, not as a thermal heat flux. The benefit of this is a more uniform heating and reduced heating time; microwaves can heat material in less than 1% of the time of conventional heating methods.

When active, the average microwave oven is powerful enough to cause interference at close range with poorly shielded electromagnetic fields such as those found in mobile medical devices and cheap consumer electronics.

### 3.3.3. Infrared radiation

The infrared part of the electromagnetic spectrum covers the range from roughly 300 GHz (1 mm) to 400 THz (750 nm). It can be divided into three parts:

1. **Far-infrared**, from 300 GHz (1 mm) to 30 THz (10 μm). The lower part of this range may also be called microwaves. This radiation is typically absorbed by so-called rotational modes in gas-phase molecules, by molecular motions in liquids, and by phonons in solids. The water in Earth's atmosphere absorbs so strongly in this range that it renders the atmosphere in effect opaque. However, there are certain wavelength ranges ("windows") within the opaque range that allow partial transmission, and can be used for astronomy. The wavelength range from approximately 200 μm up to a few mm is often referred to as "sub-millimeter" in astronomy, reserving far infrared for wavelengths below 200 μm.
2. **Mid-infrared**, from 30 to 120 THz (10 to 2.5 μm). Hot objects (black-body radiators) can radiate strongly in this range. It is absorbed by molecular vibrations, where the different atoms in a molecule vibrate around their equilibrium positions. This range is sometimes called the *fingerprint region*, since the mid-infrared absorption spectrum of a compound is very specific for that compound.
3. **Near-infrared**, from 120 to 400 THz (2,500 to 750 nm). Physical processes that are relevant for this range are similar to those for visible light.

### 3.3.4. Visible radiation (light)

Above infrared in frequency comes visible light. This is the range in which the sun and other stars emit most of their radiation and the spectrum that the human eye is the most sensitive to. Visible light (and near-infrared light) is typically absorbed and emitted by electrons in molecules and atoms that move from one energy level to another. The light we see with our eyes is really a very small portion of the electromagnetic spectrum. A rainbow shows the optical (visible) part of the electromagnetic spectrum; infrared (if you could see it) would be located just beyond the red side of the rainbow with ultraviolet appearing just beyond the violet end.

Electromagnetic radiation with a wavelength between 380 nm and 760 nm (790–400 terahertz) is detected by the human eye and perceived as visible light. Other wavelengths, especially near infrared (longer than 760 nm) and ultraviolet (shorter than 380 nm) are also sometimes referred to as light, especially when the visibility to humans is not relevant. White light is a combination of lights of different wavelengths in the visible spectrum. Passing white light through a prism splits it up in to the several colours of light observed in the visible spectrum between 400 nm and 780 nm.

If radiation having a frequency in the visible region of the EM spectrum reflects off an object, say, a bowl of fruit, and then strikes our eyes, this results in our visual perception of the scene. Our brain's visual system processes the multitude of reflected frequencies into different shades and hues, and through this insufficiently-understood psychophysical phenomenon, most people perceive a bowl of fruit.

At most wavelengths, however, the information carried by electromagnetic radiation is not directly detected by human senses. Natural sources produce EM radiation across the spectrum, and our technology can also manipulate a broad range of wavelengths. Optical fibre transmits light that, although not necessarily in the visible part of the spectrum, can carry information. The modulation is similar to that used with radio waves.

### 3.3.5. Ultraviolet light

Next in frequency comes ultraviolet (UV). The wavelength of UV rays is shorter than the violet end of the visible spectrum but longer than the X-ray.

UV in the very shortest range (next to X-rays) is capable even of ionizing atoms (see photoelectric effect), greatly changing their physical behavior.

At the middle range of UV, UV rays cannot ionize but can break chemical bonds, making molecules to be unusually reactive. Sunburn, for example, is caused by the disruptive effects of middle range UV radiation on skin cells, which is the main cause of skin cancer. UV rays in the middle range can irreparably damage the complex DNA molecules in the cells producing thymine dimers making it a very potent mutagen.

The sun emits a large amount of UV radiation, which could potentially turn Earth's land surface into a barren desert (although ocean water would provide some protection for life there). However, most of the Sun's most-damaging UV wavelengths are absorbed by the atmosphere's nitrogen, oxygen, and ozone layer before they reach the surface. The higher ranges of UV (vacuum UV) are absorbed by nitrogen and, at longer wavelengths, by simple diatomic oxygen in the air. Most of the UV in this mid-range is blocked by the ozone layer, which absorbs strongly in the important 200–315 nm range, the lower part of which is too long to be absorbed by ordinary oxygen in air. The range between 315 nm and visible light (called UV-A) is not blocked well by the atmosphere, but does not cause sunburn and does less biological damage. However, it is not harmless and does cause oxygen radicals, mutation and skin damage. See ultraviolet for more information.

### 3.3.6. X-rays

After UV come X-rays, which, like the upper ranges of UV are also ionizing. However, due to their higher energies, X-rays can also interact with matter by means of the Compton effect. Hard X-rays have shorter wavelengths than soft X-rays. As they can pass through most substances, X-rays can be used to 'see through' objects, the most notable use being diagnostic X-ray images in medicine (a process known as radiography), as well as for high-energy physics and astronomy. Neutron stars and accretion disks around black holes emit X-rays, which enable us to study them. X-rays are given off by stars and are strongly emitted by some types of nebulae.

### 3.3.7. Gamma rays

After hard X-rays come gamma rays, which were discovered by Paul Villard in 1900. These are the most energetic photons, having no defined lower limit to their wavelength. They are useful to astronomers in the study of high-energy objects or regions, and find a use with physicists thanks to their penetrative ability and their production from radioisotopes. Gamma rays are also used for the irradiation of food and seed for sterilization, and in medicine they are used in radiation cancer therapy and some kinds of diagnostic imaging such as PET scans. The wavelength of gamma rays can be measured with high accuracy by means of Compton scattering.

Note that there are no precisely defined boundaries between the bands of the electromagnetic spectrum. Radiations of some types have a mixture of the properties of those in two regions of the spectrum. For example, red light resembles infrared radiation in that it can resonate some chemical bonds.

## 3.4. Nature of Light and Quantum Theory

The early theories describing the atomic structure are based on classical physics. However these theories could not explain the behaviour of atom completely. The modern view of atomic structure is based on quantum theory introduced by Max Planck.

Light is considered as an electromagnetic radiation. It consists of two components i.e., the electric component and the magnetic component which oscillate perpendicular to each other as well as to the direction of path of radiation.

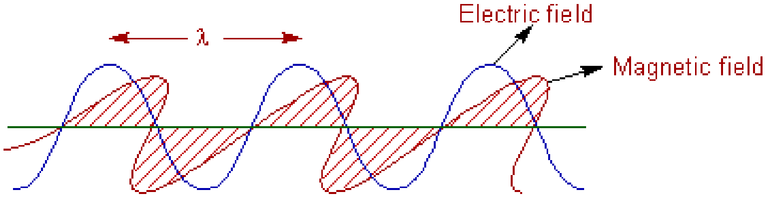


**Figure 2: Electromagnetic Radiation**

The electromagnetic radiations are produced by the vibrations of a charged particle. The properties of light can be explained by considering it as either wave or particle as follows.

### 3.4.1. Wave nature of light

According to the wave theory proposed by Christiaan Huygens, light is considered to be emitted as a series of waves in all directions. The following properties can be defined for light by considering the wave nature.

**Wavelength (λ):** The distance between two successive similar points on a wave is called as wavelength. It is denoted by λ.

Units: cm, Angstroms ($A^o$), nano meters (nm), milli microns (mµ) etc.,
Note:
1 $A^o = 10^{-8}$ cm.
1 nm= $10^{-9}$m = $10^{-7}$cm

**Frequency (ν):** The number of vibrations done by a particle in unit time is called frequency. It is denoted by 'ν'.
Units: cycles per second = Hertz = $sec^{-1}$.

**Velocity (c):** Velocity is defined as the distance covered by the wave in unit time. It is denoted by 'c'.
Velocity of light = c = $3.0 \times 10^8$ $m.sec^{-1}$ = $3.0 \times 10^{10}$ $cm.sec^{-1}$

Note: For all types of electromagnetic radiations, the velocity is a constant value. The relation between velocity (c), wavelength (λ) and frequency (ν) can be given by following equation:
velocity = frequency x wavelength **($c = \nu\lambda$).**

**Wave number($\bar{\nu}$):** The number of waves spread in a length of one centimeter is called wave number. It is denoted by $\bar{\nu}$. It is the reciprocal of wavelength, λ.

$\bar{\nu} = \frac{1}{\lambda}$ units: $cm^{-1}$, $m^{-1}$

**Amplitude:** The distance from the midline to the peak or the trough is called amplitude of the wave. It is usually denoted by 'A' (a variable). Amplitude is a measure of the intensity or brightness of light radiation.

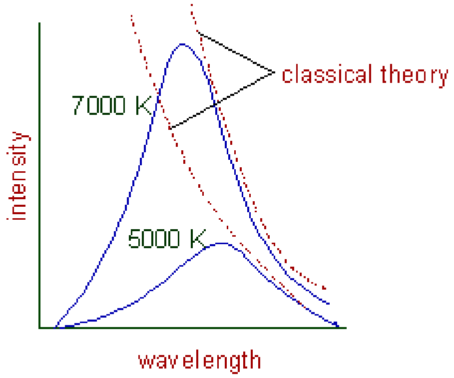
### 3.4.2. Particle nature of light

Though most of the properties of light can be understood by considering it as a wave, some of the properties of light can only be explained by using particle (corpuscular) nature of it. Newton considered light to possess particle nature. In the year 1900, in order to explain black body radiations, Max Planck proposed Quantum theory by considering light to possess particle nature.

### 3.4.3. Planck's quantum theory

**Black body:** The object which absorbs and emits the radiation of energy completely is called a black body. Practically it is not possible to construct a perfect black body. But a hollow metallic sphere coated inside with platinum black with a small aperture in its wall can act as a near black body. When the black body is heated to high temperatures, it emits radiations of different wavelengths.

The following curves are obtained when the intensity of radiations are plotted against the wavelengths, at different temperatures.



Following are the conclusions that can be drawn from above graphs.

1) At a given temperature, the intensity of radiation increases with wavelength and reaches a maximum value and then starts decreasing.

2) With increase in temperature, the wavelength of maximum intensity ($\lambda_{max}$) shifts towards lower wavelengths. According to classical physics, energy should be emitted continuously and the intensity should increase with increase in temperature. The curves should be as shown by dotted line.

In order to explain above experimental observations Max Planck proposed the following theory.

**Quantum theory:**

1) Energy is emitted due to vibrations of charged particles in the black body.

2) The radiation of energy is emitted or absorbed discontinuously in the form of small discrete energy packets called *quanta*.

3) Each *quantum* is associated with definite amount of energy which is given by the equation

$E = h\nu$

Where h = planck's constant = $6.625 \times 10^{-34}$ J. sec = $6.625 \times 10^{-27}$ erg. sec

$\nu$ = frequency of radiation

4) The total energy of radiation is quantized i.e., the total energy is an integral multiple of hν. It can only have the values of 1 hν or 2 hν or 3 hν. It cannot be the fractional multiple of hν.

5) Energy is emitted and absorbed in the form of quanta but propagated in the form of waves.

**The following table gives approximate wavelengths, frequencies, and energies for selected regions of the electromagnetic spectrum:**

**Spectrum of Electromagnetic Radiation**

| **Region** | **Wavelength (Angstroms)** | **Wavelength (centimeters)** | **Frequency (Hz)** | **Energy (eV)** |
|---|---|---|---|---|
| Radio | $> 10^9$ | > 10 | $< 3 \times 10^9$ | $< 10^{-5}$ |
| Microwave | $10^9 - 10^6$ | 10 - 0.01 | $3 \times 10^9 - 3 \times 10^{12}$ | $10^{-5} - 0.01$ |
| Infrared | $10^6 - 7000$ | $0.01 - 7 \times 10^{-5}$ | $3 \times 10^{12} - 4.3 \times 10^{14}$ | 0.01 - 2 |
| Visible | 7000 - 4000 | $7 \times 10^{-5} - 4 \times 10^{-5}$ | $4.3 \times 10^{14} - 7.5 \times 10^{14}$ | 2 - 3 |
| Ultraviolet | 4000 - 10 | $4 \times 10^{-5} - 10^{-7}$ | $7.5 \times 10^{14} - 3 \times 10^{17}$ | $3 - 10^3$ |
| X-Rays | 10 - 0.1 | $10^{-7} - 10^{-9}$ | $3 \times 10^{17} - 3 \times 10^{19}$ | $10^3 - 10^5$ |
| Gamma Rays | < 0.1 | $< 10^{-9}$ | $> 3 \times 10^{19}$ | $> 10^5$ |

**The notation "eV" stands for electron-volts, a common unit of energy measure in atomic physics.**

## 4.0. SUMMARY

The electromagnetic (EM) spectrum is just a name that scientists give a bunch of types of radiation when they want to talk about them as a group. Radiation is energy that travels and spreads out as it goes-- visible light that comes from a lamp in your house and radio waves that come from a radio station are two types of electromagnetic radiation. Other examples of EM radiation are microwaves, infrared and ultraviolet light, X-rays and gamma-rays. Hotter, more energetic objects and events create higher energy radiation than cool objects. Only extremely hot objects or particles moving at very high velocities can create high-energy radiation like X-rays and gamma-rays.

## 5.0. TUTOR-MARKED ASSIGNMENT

1. What are the different types of electromagnetic radiation? What kind of electromagnetic radiation has the shortest wavelength? The longest?
2. List any three physical processes that take place when radiant energy interacts with an object
3. Calculate the wavelength of the electromagnetic radiation whose frequency is 7500 x$10^{12}$ Hz?
4. Calculate the frequency of radiation with a wavelength of 442 nm.
5. Calculate the frequency of radiation with a wavelength of 4.55 x $10^{-9}$ cm.
6. A certain source emits radiation of wavelength 500.0 nm. What is the energy, in kJ, of one mole of photons of this radiation?
7. Determine the wavelength (in meters) of photons with the following energies:
    a) 92.0 kJ/mol
    b) 8.258 x $10^{-4}$ kJ/mol
    c) 1870 kJ/mol

## 6.0. REFERENCES

1.1. en.wikipedia.org/wiki/Electromagnetic_spectrum
1.2. http://www.adichemistry.com/general/atomicstructure/quantumtheory/quantum-theory.html

# UNIT 2 – INTRODUCTION TO PHOTOCHEMISTRY

## 1.0. INTRODUCTION

Today photochemistry has become one of the most powerful research tools. Compounds of different molecules are occurred through various photochemical reactions like $CO_2$, $NH_3$ and methane. Other examples of photochemical reactions are formation of $O_3$, smog, Vitamin D and many more. A new field in photochemistry called photobiology helps us to understand the mechanism of photosynthesis (process by which plants make their own food by the absorption of sunlight).

Also photochemistry helps us to form some typical compounds like Vitamin D, cubanes, and several cleaning agents which all are made by various chemical reactions of photochemistry. The formation of laser light is only possible through photochemistry. LASER stands for Light Amplification by Stimulated Emission of Radiations. LASER contain monochromatic rays with coherent radiations, these rays can be easily focused to a small point. Due to this property, LASER light is used for cutting hard material like metal, diamond etc, also there is some application of LASER light in medical field.

Photochemical reactions occur all around us, being an important feature of many of the chemical processes occurring in living systems and in the environment. The power and versatility of photochemistry is becoming increasingly important in improving the quality of our lives, through health care, energy production and the search for ‘green’ solutions twosome of the problems of the modern world. Many industrial and technological processes rely on applications of photochemistry, and the development of many new devices has been made possible by spin-off from photochemical research.

Photochemistry is the study of the chemical reactions and physical changes that result from interactions between matter and visible or ultraviolet light.

The principal aim of this Unit is to familiarise the reader with basic ideas relating to light and matter and the interaction between them.

## 2.0. OBJECTIVES

After studying this Unit, you should be able to:

- Explain the importance of the electromagnetic radiation in understanding the nature of matter
- Distinguish between thermal and photochemical reactions
- State the classical laws of photochemistry
- Explain the importance of UV-Visible radiation in photochemistry
- Discuss the applications of photochemistry

## 3.0. MAIN CONTENT

### 3.1. Light and matter

The reason that light is so important for our understanding of the Universe is because light interacts with matter, and that interaction can tell us a great deal about the nature of the matter. Thus, it is important to be concerned with how light electromagnetic waves interact with matter. A sound knowledge of the energy level structure of atoms and molecules is necessary to understand the nature of this interaction. Such interactions are at the very heart of spectroscopy. There are lots of spectroscopic processes.

### 3.1.1. Absorption of Light by Atoms and Molecules

The basic ideas:

Light consists of oscillating electric and magnetic fields.

Because nuclei and electrons are charged particles, their motions in atoms and molecules generate oscillating electric fields.

An atom or molecule can absorb energy from light if the frequency of the light oscillation and the frequency of the electron or molecular "transition motion" match. Unless these frequencies match, light absorption cannot occur. The "transition motion" frequency is related to the frequencies of motion in the higher and lower energy states by the equation: $\Delta E = E_2 - E_1 = h\nu$

By measuring the frequencies of light absorbed by an atom or molecule, one can determine the frequencies of the various transition motions that the atom or molecule can have. Thus light absorption can be used to probe the dynamics of atoms and molecules.

These ideas are the basis for the techniques of *spectroscopy*, which is the study of the interaction of light and matter. The word means "measurement of spectrum," where the spectrum of a substance is the array of frequencies of light absorbed by its atoms or molecules.

## 3.2. Differences between thermal and photochemical processes

Many chemical reactions occur only when a molecule is provided the necessary “activation energy”. A simple example can be the combustion of gasoline (a hydrocarbon) into carbon dioxide and water. In this reaction, the activation energy is provided in the form of heat or a spark. In case of photochemical reactions light provides the activation energy. Simplistically, light is one mechanism for providing the activation energy required for many reactions. If laser light is employed, it is possible to selectively excite a molecule so as to produce a desired electronic and vibrational state. Equally, the emission from a particular state may be selectively monitored, providing a measure of the population of that state. If the chemical system is at low pressure, this enables scientists to observe the energy distribution of the products of a chemical reaction before the differences in energy have been smeared out and averaged by repeated collisions.

The absorption of a photon of light by a reactant molecule may also permit a reaction to occur not just by bringing the molecule to the necessary activation energy, but also by changing the symmetry of the molecule’s electronic configuration, enabling an otherwise inaccessible reaction path, as described by the Woodward-Hoffmann selection rules. A 2+2 cycloaddition reaction is one example of a pericyclic reaction that can be analyzed using these rules or by the related frontier molecular orbital theory.

Photochemical reactions involve electronic reorganization initiated by electromagnetic radiation. The reactions are several orders of magnitude faster than thermal reactions; reactions as fast as $10^{-9}$ seconds and associated processes as fast as $10^{-15}$ seconds are often observed. Difference between photochemical reactions and thermal reactions are summarized below:

**Table 1.1 Difference between thermal and photochemical reactions**

| THERMAL REACTIONS | PHOTOCHEMICAL REACTIONS |
|---|---|
| These reactions involve absorption or evolution of heat. | These reactions involve absorption of light. |
| They can take place even in absence of light i.e. dark. | The presence of light is the primary requisite for the reaction to take place. |
| Temperature has significant effect on the rate of a thermochemical reaction. | Temperature has very little effect on the rate of a photochemical reaction. Instead, the intensity of light has a marked effect on the rate of a photochemical reaction. |
| The free energy change ΔG of a thermochemical reaction is always negative. | The free energy change ΔG of a photochemical reaction may not be negative. |
| They are accelerated by the presence of a catalyst. | Some of these are initiated by the presence of a photosensitizer. However a photosensitizer acts in a different way than a catalyst. |

## 3.3. Photochemistry

Photochemistry is the study of how two of the most fundamental components of the universe, **light** and **matter**, interact with each other. The field of photochemistry can be classified in terms of **photophysics** (interaction of light with molecules which results in net physical, not chemical, changes) and **photochemistry** (interaction of light with molecules which results in net chemical changes).

### 3.3.1. Basic laws of photochemistry

**Grotthus-Draper law (1st law of photochemistry)**

In the early 1800s Christian von Grotthus (1785-1822) and John Draper (1811-1882) formulated the first law of photochemistry, which states that only light that is absorbed by a molecule can produce a photochemical change in that molecule. This law relates photochemical activity to the fact that each chemical substance absorbs only certain wavelengths of light, the set of which is unique to that substance. Therefore, the presence of light alone is not sufficient to induce a photochemical reaction; the light must also be of the correct wavelength to be absorbed by the reactant species.

**Stark-Einstein law (2nd law of photochemistry)**

In the early 1900s the development of the quantum theory of light—the idea that light is absorbed in discrete packets of **energy** called photons—led to the extension of the laws of photochemistry. The second law of photo-chemistry, developed by Johannes Stark (1874-1957) and Albert Einstein (1879-1955), states that only one quantum, or one **photon**, of light is absorbed by each molecule undergoing a photochemical reaction. In other words, there is a **one-to-one correspondence** between the number of absorbed photons and the number of excited species. The ability to accurately determine the number of photons leading to a reaction enables the efficiency, or quantum yield, of the reaction to be calculated.

### 3.3.2. Photochemistry Induced By Visible and Ultraviolet Light

Light that can break molecular bonds is most effective at inducing photochemical reactions. The energy required to break a molecular bond ranges from approximately 150 kiloJoules per

**mole** to nearly 1000 kJ $mol^{-1}$, depending on the bond. Visible light, having wavelengths ranging from 400-700 nanometers, corresponds to energies ranging from approximately 300-170 kJ $mol^{-1}$, respectively. Note that this is enough energy to dissociate relatively weak bonds such as the single **oxygen** (O-O) bond in **hydrogen peroxide** (HOOH), which is why **hydrogen** peroxide must be stored in a light-proof bottle.
Ultraviolet light, having wavelengths ranging from 200-400 nm, corresponds to higher energies ranging from approximately 600-300 kJ $mol^{-1}$, respectively. Ultraviolet light can dissociate relatively strong bonds such as the double oxygen (O=O) bond in molecular oxygen ($O_2$) and the double C=O bond in **carbon dioxide** ($CO_2$); ultraviolet light can also remove **chlorine** atoms from compounds such as chloromethane ($CH_3Cl$). The ability of ultraviolet light to dissociate these molecules is an important aspect of the stability—and destruction—of ozone molecules in the upper atmosphere.

A photochemical process may be considered to consist of two steps: the absorption of a photon, followed by reaction. If the absorption of a photon causes an **electron** within an atom or molecule to increase its energy, the species is said to be electronically excited. The absorption and reaction steps for a molecule AB may be written as: $AB + h\nu \rightarrow AB^{*}$ $AB^{*} \rightarrow$ products where hν represents the energy of a photon of **frequency** ν and the asterisk indicates that the species has become electronically excited. The excited species, $AB^{*}$, has the additional energy of the absorbed photon and will react in order to reduce its energy. Although the excited species generally does not live long, it is sometimes formally indicated when writing photochemical reactions to stress that the reactant is an electronically excited species. The possible reactions that an electronically excited species may undergo are illustrated below.

### 3.4. Reaction pathways

Absorption of a photon (electronic excitation)

Followed by:

| | | |
|---|---|---|
| i) | $AB^* \rightarrow A + B$ | Dissociation |
| ii) | $AB^* \rightarrow AB^+ + e^-$ | Ionization |
| iii) | $AB^* \rightarrow BA$ | Isomerization |
| iv) | $AB^* + C \rightarrow AC + B$ or $ABC$ | Reaction |
| v) | $AB^* + DE \rightarrow AB + DE^*$ | Energy Transfer (intermolecular) |
| vi) | $AB^* + M \rightarrow AB + M$ | Physical Quenching |
| vii) | $AB^* \rightarrow AB$ | Energy Transfer (intramolecular) |
| viii) | $AB^* \rightarrow AB + h\nu$ | Luminsecence |

#### 3.4.1. Dissociation

The energy of an absorbed photon may be sufficient to break molecular bonds (path i), creating two or more atomic or molecular fragments. An important example of photodissociation is found in the photochemistry of stratospheric ozone. Ozone ($O_3$) is produced in the stratosphere from molecular oxygen ($O_2$) through the following pair of reactions: $O_2 + h\nu \rightarrow O + O$ and $O + O_2 \rightarrow O_3$ where hν represents the energy of a photon of ultraviolet light with a wavelength less than 260 nm. Ozone is also dissociated by short-wavelength ultraviolet light (200-300 nm) through the reaction: $O_3 + h\nu \rightarrow O_2 + O$. The oxygen atom formed from this reaction may recombine with molecular oxygen to regenerate ozone, thereby completing the ozone cycle. The great importance of stratospheric ozone is that it absorbs harmful short-wavelength ultraviolet light before it reaches the Earth's surface, thus serving as a protective shield.

In recent years, the effect of chlorofluorocarbons, commonly known as Freons or CFCs, on the ozone cycle has become of great concern. CFCs rise into the stratosphere where they are dissociated by ultraviolet light, producing chlorine atoms (Cl) through the reaction: CFC + hν → Cl + CFC(minus one Cl). These chlorine atoms react with ozone to produce ClO and molecular oxygen: $Cl + O_3 \rightarrow ClO + O_2$. ClO reacts with the oxygen atoms produced from the photodissociation of ozone in reaction 5 to produce molecular oxygen and a chlorine atom: $ClO + O \rightarrow O_2 + Cl$. Therefore, the presence of CFCs interrupts the natural ozone cycle by consuming the oxygen atoms that should combine with molecular oxygen to regenerate ozone. The net result is that ozone is removed from the stratosphere while the chlorine atoms are regenerated in a catalytic process to continue the destructive cycle.

An electronically excited species may react with a second species to produce a new product, or set of products (path iv). For example, the products of the ultraviolet dissociation of ozone (reaction 5) are themselves electronically excited: $O_3 + h\nu \rightarrow O^{*} 2 + O^{*}$. These excited fragments may react with other atmospheric molecules such as water: $O^{*} + H_2O \rightarrow OH + OH$. Or they may react with ozone: $O^{*} 2 + O_3 \rightarrow 2O_2 + O$. These reactions do not readily occur for the corresponding non-excited species, confirming the importance of electronic excitation in determining reactivity.

### 3.4.2. Energy Transfer

In some cases the excited species may simply transfer its excess energy to a second species. This process is called intermolecular energy transfer (path v). Photosynthesis relies on intermolecular energy transfer to redistribute the light energy gathered by chlorophyll to a reaction center where the carbohydrates that nourish the plant are produced. Physical quenching (path vi) is a special case of intermolecular energy transfer in which the chemical behavior of the species to which the energy is transferred does not change. An example of a physical quencher is the walls of a container in which a reaction is confined. If the energy transfer occurs within the same molecule, for example, and if the excess electron energy is transferred into internal motion of the molecule, such as vibration, it is called intramolecular energy transfer (path vii).

### 3.4.3. Luminescence

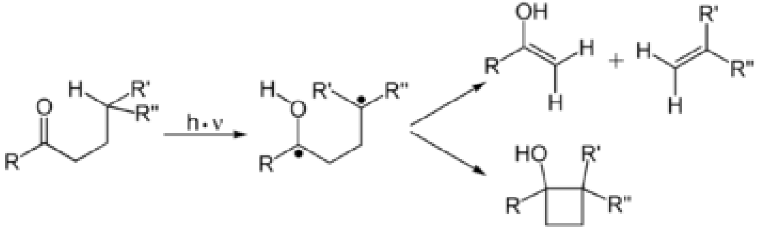
Although it is not strictly a photochemical reaction, another pathway by which the excited species may reduce its energy is by emitting a photon of light. This process is called luminescence (path viii). Luminescence includes the processes of fluorescence (prompt emission of a photon) and phosphorescence (delayed emission of a photon). Optical brighteners in laundry detergents contain substances that absorb light of one wavelength, usually in the ultraviolet range, but emit light at a longer wavelength, usually in the visible range—thereby appearing to reflect extra visible light and making clothing appear whiter. This process is called fluorescence and only occurs while the substance is being illuminated. The related process, phosphorescence, persists after the excitation source has been removed and is used in "glow-in-the-dark" items.

### 3.5. Applications of Photochemistry

Many important processes involve photochemistry. The premier example is photosynthesis, in which most plants use solar energy to convert carbon dioxide and water into glucose, disposing of oxygen as a side-product. Humans rely on photochemistry for the formation of vitamin D. In fireflies, an enzyme in the abdomen catalyzes a reaction that results in bioluminescence.

Photochemistry can also be highly destructive. Medicine bottles are often made with darkened glass to prevent the drugs from photodegradation. A pervasive reaction is the generation of singlet oxygen by photosensitized reactions of triplet oxygen. Typical photosensitizers include tetraphenylporphyrin and methylene blue. The resulting singlet oxygen is an aggressive oxidant, capable of converting C-H bonds into C-OH groups. In photodynamic therapy, light is used to destroy tumors by the action of singlet oxygen.

Many polymerizations are started by photoinitiatiors, which decompose upon absorbing light to produce the free radicals for Radical polymerization.



In the area of photochemistry, a **photochemical reaction** is a chemical reaction that is induced by light. Photochemical reactions are valuable in organic and inorganic chemistry because they proceed differently than thermal reactions. Photochemical reactions are not only very useful but also can be a serious nuisance, as in the photodegradation of many materials, e.g. polyvinyl chloride. A large-scale application of photochemistry is photoresist technology, used in the production of microelectronic components. Vision is initiated by a photochemical reaction of rhodopsin.

### 3.6. Experimental set-up

Photochemical reactions require a light source that emits wavelengths corresponding to an electronic transition in the reactant. In the early experiments (and in everyday life), sunlight was the light source, although it is polychromatic. Mercury-vapor lamps are more common in the laboratory. Low pressure mercury vapour lamps mainly emit at 254 nm. For polychromatic sources, wavelength ranges can be selected using filters. Alternatively, LEDs (light emitting diodes) and Rayonet lamps emit monochromatically.

The emitted light must of course reach the targeted functional group without being blocked by the reactor, medium, or other functional groups present. For many applications, quartz is used for the reactors as well as to contain the lamp. Pyrex absorbs at wavelengths shorter than 275 nm. The solvent is an important experimental parameter. Solvents are potential reactants and for this reason, chlorinated solvents are avoided because the C-Cl bond can lead to chlorination of the substrate. Strongly absorbing solvents prevent photons from reaching the substrate. Hydrocarbon solvents absorb only at short wavelengths and are thus preferred for photochemical experiments requiring high energy photons. Solvents containing unsaturation absorb at longer wavelengths and can usefully filter out short wavelengths. For example, cyclohexane and acetone "cut off" (absorb strongly) at wavelengths shorter than 215 and 330 nm, respectively.

### 3.6.1. Excitation

Photoexcitation is the first step in a photochemical process where the reactant is elevated to a state of higher energy, an excited state. The photon can be absorbed directly by the reactant or by a photosensitizer, which absorbs the photon and transfers the energy to the reactant. The opposite process is called quenching when a photoexited state is deactivated by a chemical reagent.

Most photochemical transformations occur through a series of simple steps known as primary photochemical processes. One common example of these processes is the excited state proton transfer (ESPT).

## 3.7. Organic photochemistry

Examples of photochemical organic reactions are electrocyclic reactions, photoisomerization and Norrish reactions.

Alkenes undergo many important reactions that proceed via a photon-induced $\pi$ to $\pi^*$ transition. The first electronic excited state of an alkene lack the $\pi$-bond, so that rotation about the C-C bond is rapid and the molecule engages in reactions not observed thermally. These reactions include cis-trans isomerization, cycloaddition to other (ground state) alkene to give cyclobutane derivatives. The cis-trans isomerization of a (poly)alkene is involved in retinal, a component of the machinery of vision. The dimerization of alkenes is relevant to the photodamage of DNA, where thymine dimers are observed upon illuminating DNA to UV radiation. Such dimers interfere with transcription. The beneficial effects of sunlight are associated with the photochemically induced retro-cyclization (decyclization) reaction of ergosterol to give vitamin D. In the DeMayo reaction, an alkene reacts with a 1,3-diketone reacts via its enol to yield a 1,5-diketone. Still another common photochemical reaction is Zimmerman's Di-pi-methane rearrangement.

In an industrial application, about 100,000 tonnes of benzyl chloride are prepared annually by the gas-phase photochemical reaction of toluene with chlorine. The light is absorbed by chlorine molecule, the low energy of this transition being indicted by the yellowish color of the gas. The photon induces homolysis of the Cl-Cl bond, and the resulting chlorine radical converts toluene to the benzyl radical:

$$Cl_2 + h\nu \rightarrow 2\,Cl\cdot$$
$$C_6H_5CH_3 + Cl\cdot \rightarrow C_6H_5CH_2\cdot + HCl$$
$$C_6H_5CH_2\cdot + Cl\cdot \rightarrow C_6H_5CH_2Cl$$

Mercaptans can be produced by photochemical addition of hydrogen sulfide ($H_2S$) to alpha olefins.

## 3.8. Inorganic and organometallic photochemistry

Coordination complexes and organometallic compounds are also photoreactive. These reactions can entail cis-trans isomerization. More commonly photoreactions result in dissociation of ligands, since the photon excites an electron on the metal to an orbital that is antibonding with respect to the ligands. Thus, metal carbonyls that resist thermal substitution undergo decarbonylation upon irradiation with UV light. UV-irradiation of a THF solution of molybdenum hexacarbonyl gives the THF complex, which is synthetically useful:

$$Mo(CO)_6 + THF \rightarrow Mo(CO)_5(THF) + CO$$

In a related reaction, photolysis of iron pentacarbonyl affords diiron nonacarbonyl (see figure):

$2\ Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO$

## 4.0. SUMMARY

- The concept of photochemistry is introduced and explained.
- Interaction of radiation with matter is discussed and difference between thermal and photochemical processes highlighted.
- Laws of photochemistry: Grothus-Draper law and Stark-Einstein law provide basis for understanding photochemical transformations.
- Examples of photochemical organic reactions are electrocyclic reactions and photoisomerization
- The photoactivity of coordination and inorganic compounds is highlighted
- Many important processes involve photochemistry. The premier example is photosynthesis, in which most plants use solar energy to convert carbon dioxide and water into glucose, disposing of oxygen as a side-product.

## 5.0. TUTOR-MARKED ASSIGNMENT

1.2.1.1. What is photochemistry?
1.2.1.2. Give four areas of application of photochemistry in everyday life
1.2.1.3. State the laws of photochemistry
1.2.1.4. State the differences between photochemical and thermal reactions?

## 6.0. REFERENCES

1. http://en.wikipedia.org/wiki/Photochemistry
2. http://science.jrank.org/pages/5157/Photochemistry

# UNIT 3 – LIGHT ABSORPTION AND FATE OF THE EXCITED STATE

## 1.0. INTRODUCTION

Photochemistry is the study of what happens to molecules when they absorb light. Therefore it is important to consider the factors affecting whether and how efficiently molecules absorb. In addition, in the very short time-frame after a molecule has absorbed light, it can undergo a variety of processes. In applications, we may desire a particular process, so again an understanding of what pathways are available to excited states is important so that systems can be optimised as required (e.g. by changing solvent, modifying the molecule).

Electronic excited states are thermodynamically unstable. They persist for lifetimes that are normally about 10 nanoseconds for many medium sized organic molecules. A number of transition metal complexes have lifetimes of about 1 microsecond. Triplet states, resulting from a spin inter-conversion process in the excited state, have quite long lifetimes, sometimes to beyond 1 millisecond.

Closed shell organic species that are electrically neutral always have single electronic ground states; electronic selection rules require that absorption of light can occur only when the electronic spin multiplicity is unchanged during the transition. However, molecular vibrations and interactions between neighbouring molecules provide mechanisms for molecules to jump between electronic energy levels either with the same or different spin multiplicity.

As molecules relax from excited states, they can proceed along many different mechanistic pathways. A simple fate of an excited state molecule is to emit ***fluorescence***. ***Fluorescence*** is the light emission that occurs from the $v' = 0$ excited electronic state back down to the ground electronic state. ***Spontaneous emission*** is the normal fluorescence that occurs with a random probability. ***Stimulated emission*** is the reverse of a (***stimulated***) ***absorption*** transition, where a photon of precisely the correct wavelength and direction comes along and knocks the excited state down to the ground state, taking with it a second identical photon. ***LASERs*** (Light Amplification by Stimulated Emission of Radiation) function when an excited state reaches a population inversion, and all of the photons emitted from the gain medium have the same characteristics. Lasers misbehave, or cease to function when stimulated emission starts to lose the rate competition against spontaneous emission.

## 2.0. OBJECTIVES

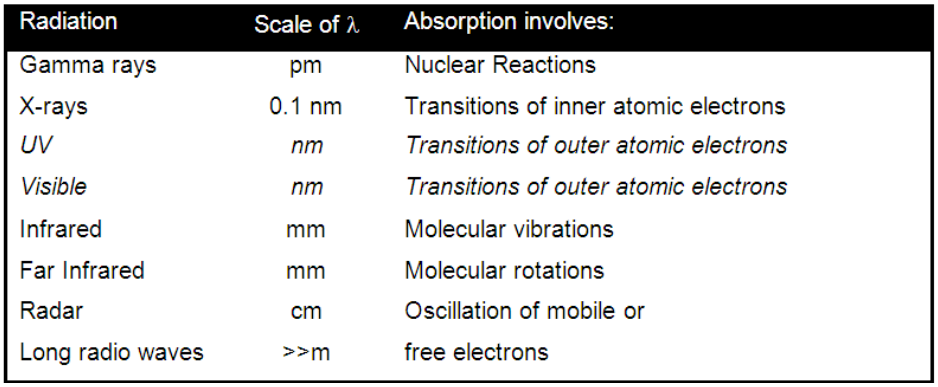
After studying this Unit, you should be able to:

- Describe the process of light absorption by an atom or molecule
- Describe the fate of an electronically excited molecule
- Explain the impact of electromagnetic radiation on atomic and molecular structure
- State and explain the Franck-Condon Principle
- List the important photophysical processes
- Draw the Jablonski diagram and use it to explain the fate of an electronically excited molecule
- Discuss the relationship between the Franck-Condon principle and the Stokes' shift

## 3.0. MAIN CONTENT

### 3.1. Light Absorption – Formation of the Excited State

Photochemistry is based on the reaction/reactivity of molecules in their excited state after they have absorbed light. By “light”, we mean that part of the electromagnetic spectrum that can promote electrons in the outer atomic orbitals to unoccupied orbitals – i.e. electrons near or at the highest occupied molecular orbital (HOMO) to orbitals near or including the lowest unoccupied molecular orbital (LUMO). To do this, the light must be of sufficient energy to promote electrons between electronic energy levels, and this is found to be light in the UV/visible region of the electromagnetic spectrum. For this reason, the region of the spectrum $200 \text{ nm} < \lambda < 800 \text{ nm}$ is sometimes referred to as the “photochemical window”. The range of wavelengths in the spectrum and the result of absorption by the atom/molecule is shown below.



| Radiation | Scale of λ | Absorption involves: |
|---|---|---|
| Gamma rays | pm | Nuclear Reactions |
| X-rays | 0.1 nm | Transitions of inner atomic electrons |
| *UV* | *nm* | *Transitions of outer atomic electrons* |
| *Visible* | *nm* | *Transitions of outer atomic electrons* |
| Infrared | mm | Molecular vibrations |
| Far Infrared | mm | Molecular rotations |
| Radar | cm | Oscillation of mobile or |
| Long radio waves | >>m | free electrons |

**Figure 1: Regions of the electromagnetic spectrum and their impact on atom structure**

Therefore, absorption of a photon of light of wavelength 200 – 800 nm may result in a HOMO-LUMO transition. A very clear indication of this is observed in d-block complexes. For example, a ruthenium (II) complex has six d-electrons and has a low spin octahedral configuration $t_{2g}^6$. On absorption of visible light ($\lambda$ ~450 nm), an electron is promoted to an $e_g$ orbital, giving the complex its red-orange colour. This transition is in the visible region. For $d^0$ complexes such as $TiO_2$, a d-d transition is not possible, and a transition from the oxide ligand to the metal centre – a ligand – to metal charge transfer (LMCT) transition occurs, but only if the molecule is irradiated by UV light ($\lambda < 390$ nm). Hence $TiO_2$ is white, as it does not absorb any visible light.

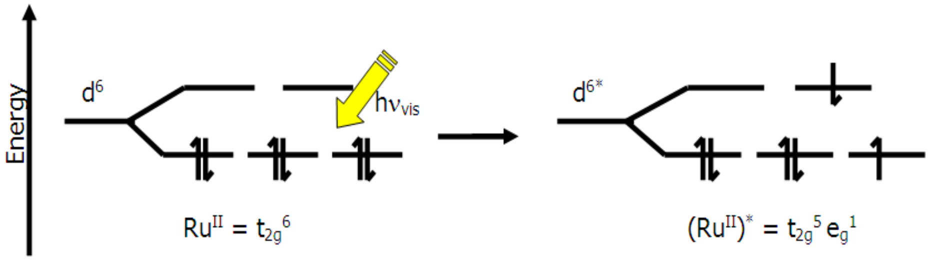


**Figure 2: Absorption of a photon of visible light causes a d-d transition in Ru(II) giving the molecule a visible colour.**

### 3.1.1. Excited electronic states carry vibrational and rotational excitation immediately after their creation.

Though absorption of light most often occurs from ground electronic states for which the vibrational quantum number is v = 0, the rotational quantum number *J* is zero only for very cold, isolated molecules (such as those prepared in a gas-phase supersonic free jet expansion, or kept in a liquid helium cryostat for condensed phase samples). However, the Franck-Condon principle shows that we can access a number of excited vibrational states during the electronic transition.

### 3.1.2. The Franck-Condon Principle

The principle states that the absorption of a photon is a practically instantaneous process, since it involves only the rearrangement of virtually inertia-free electrons. During light absorption, which occurs in femtoseconds ($10^{-15}$ s), electrons can move, not the nuclei. The much heavier atomic nuclei have no time to readjust themselves during the absorption act, but have to do so after it is over, and this readjustment swings them into vibration. Excitation according to Franck-Condon principle is not to the lowest vibrational level (corresponding to a non-vibrational state), but somewhere higher (Franck-Condon state), and the transition involved, a vertical transition (Figure 2). This means that the molecule finds itself, after the absorption act, in a non-equilibrium state and begins to vibrate like a spring. The periods of these vibrations are of the order of $10^{-13}$ sec. Since the usual lifetimes of excited electronic states are of the order $10^{-9}$ sec, there is enough time during the excitation period for many thousands of vibrations. During this period, equilibrium can be established through a non-radiative relaxation to the non-vibrational $v_0$ state.

## 3.2. A catalogue of several important photophysical processes.

Photo-induced excited states are created by absorption or scattering of one or more photons. Scattering and multi-photon processes require the intense light fields available only from lasers. Multi-photon and light scattering processes are called ***nonlinear optical*** phenomena, because unlike stimulated absorption, they do not depend linearly on the excitation intensity (or power). Some of the most important excited state relaxation processes are listed below:

- **Fluorescence** (stimulated and spontaneous emission)
- **Intersystem Crossing** (jumps between electronic excited state manifolds of different spin multiplicity)
- **Internal Conversion** (downward energy jump from higher to lower lying excited states having the same spin multiplicity)
- **Phosphorescence** (lower energy spontaneous emission occurring from longer-lived excited states, usually triplet multiplicity)
- **Energy Transfer** (excitation transfer, or exciton annihilation-photosynthetic antenna proteins, diode lasers)
- **Photochemical Reactions** (photosynthesis, photo-induced electron-transfer, photo- dissociation).
- **Excited State Solvatochromism** (relaxation of molecular excited state caused by strong electric interactions with solvent)

The photophysical processes f***luorescence, vibrational relaxation, internal conversion, intersystem crossing, and phosphorescence*** are illustrated schematically in the diagram below. In the colored diagram above, three electronic states for a diatomic molecule are represented by the Morse potential curves. The ground electronic state $S_0$ is a singlet (paired-spin, or filled shell) configuration, typical of most neutral organic molecules. The first single excited state, $S_1$, is coloured blue. The lowest energy unpaired-spin configuration is a triplet state labelled $T_1$, shown at top right as the dark green curve.

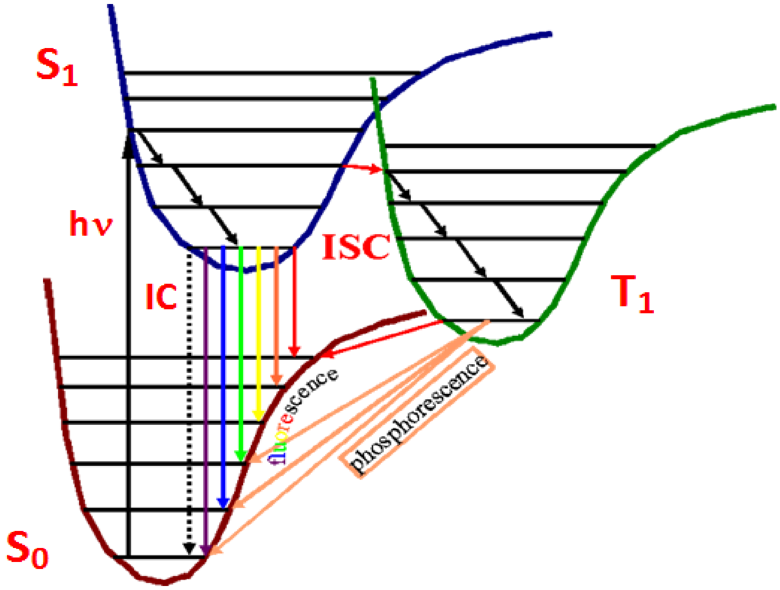


**Figure 3: The photophysical processes f*luorescence, vibrational relaxation, internal conversion, intersystem crossing, and phosphorescence.***

Each of the three Morse potential curves have the first several vibrational levels shown explicitly. Rotational levels are much more densely spaced, and though quite important, are not shown.

### 3.2.1. The Jablonski diagram

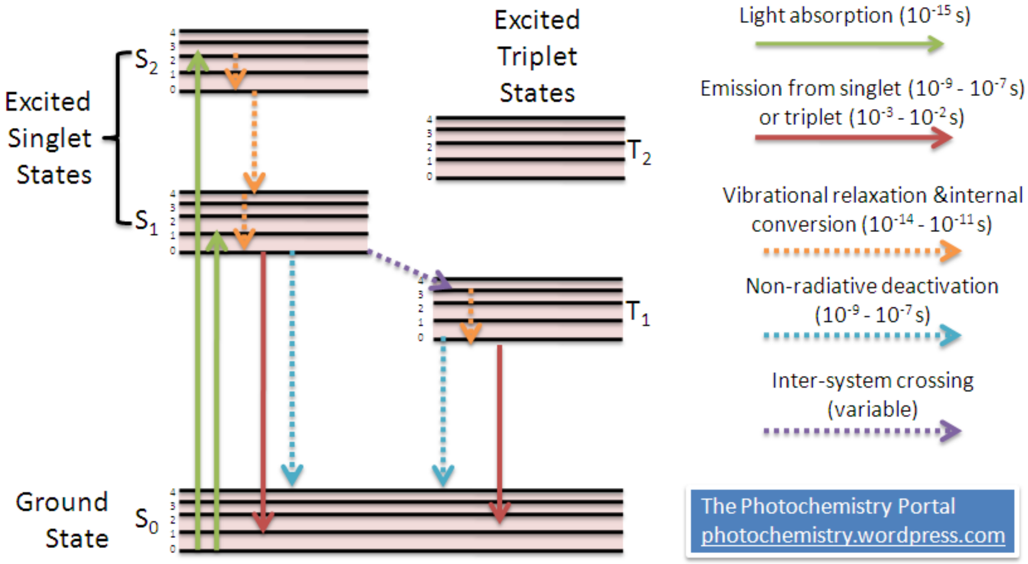


**Figure 4: A Jablonksi diagram for an organic molecule.**

Radiative processes (those which are "vertical" in energy transfer) are shown in solid lines whereas non-radiative processes ("horizontal" energy transfer) are shown using dotted lines. Indicative timescales are shown, although are molecule-dependant.

In principle the Jablonski diagram is similar to the transitions in the potential energy curves, shown above, except the potential energy curves are usually not represented. A simple Jablonski diagram for an organic molecule is shown above. Note that a similar diagram for an inorganic compound will also include metal orbitals, so will be different in style.

### 3.3. Photo-excitation by Stimulated Absorption

Photo-excitation can induce a stimulated absorption transition from $S_0$ to $S_1$ indicated in Figure 2 by the vertical energy jump labelled hν, connecting the $S_{0,\ v=0}$ state to the $_{S1,\ v=3}$ state. The vertical Franck-Condon transition in energy occurs nearly instantaneously, without the atomic nuclei being able to respond yet. One can think of the relevant time scales for the vertical energy transition as follows: The transition is will likely occur within one period T=1/ν of the optical cycle. If we consider that typical wavelengths for electronic transitions for diatomic molecules are in the ultraviolet, an estimate for a UV wavelength of 300 nm (3 x $10^{-7}$ m) and the speed of light c (3 x $10^{8}$ m/s) corresponds to a frequency ν = 1015 Hz, or 1 PetaHertz. The period T is then $10^{-15}$ seconds, or one femtosecond.

Immediately following the transition, the diatomic molecule now resides on the potential energy curve (surface, for a polyatomic molecule) with the geometry of the ground state, and begins to vibrate with characteristics of the excited state v=3 level. Note that the blue $S_1$ potential energy curve is broader than the dark red $S_0$ curve. For this case, it means that the excited state characteristic vibrational frequency will be lower than in the ground state.

### 3.4. Vibrational Relaxation

A given vibronic excited state for a diatomic molecule such as the $S_{1,v=3}$ state shown above may be stable for nanoseconds to even one second, depending on environment and temperature. However, the general case for polyatomic molecules is in general very different. For medium and larger sized molecules (10 or more atoms), the density of the several vibrational potential energy curves leads to a multi-dimensional excited-state potential energy surface that is densely packed with both vibrational and rotational levels. The black diagonal arrows indicate the direction of the relaxation process in normal organic molecules: the $S_{1,v=3}$ state will relax rapidly to the $S_{1,v=2}$ state, followed by subsequent relaxation to the $S_{1,v=1}$ and $S_{1,v=0}$ vibronic levels. The larger the molecule, the more rapid the relaxation can become. For a molecule such as an amino acid, a tetrapyrrole (such as chlorophyll a, or a heme), the vibrational population relaxation can be complete in < 25 femtoseconds. In addition to intramolecular pathways made possible by the coupling between a high density of anharmonic states, interactions with neighbouring molecules (gas-phase collisions, or low-frequency collective vibrations in liquids or phonons in solids) also enhance the rate of vibrational relaxation. While much has been learned both theoretically and experimentally about the vibrational relaxation processes, there is no quantitative theory that can predict the vibrational relaxation a priori.

### 3.4.1. Radiative versus Non-Radiative Excited State Decay Pathways

After vibrational relaxation has occurred over the time scale of some tens of femtoseconds to many picoseconds, the molecule will be metastable in the $S_{1,v=0}$ state for a time frame ranging from hundreds of picoseconds ($10^{-10}$ s) to hundreds of nanoseconds ($10^{-7}$ s). From the $S_{1,v=0}$ level, the eventual relaxation to the ground state can proceed by two general pathways: one radiative, in which light is emitted from the molecular excited state, and the other non-radiative, where a jump is made from the $S_1$ excited-state electronic manifold to the $S_0$ manifold. A third less probable possibility, intersystem crossing, is discussed below.

## 3.5. Radiative Decay: Fluorescence

The six downward-pointing arrows connecting the S1 excited-state electronic state represent the spectrum of colours of light that might be emitted from a molecular excited state. The purple, blue, green, yellow, orange, and red arrows represent radiative decay pathways connecting $S_{1,v=0}$ to the states $S_{0,v=0}$ through $S_{0,v=5}$ ground electronic states, respectively. The fluorescence will be emitted with peaks at different colours in the UV-visible spectrum because all of the transitions can be allowed, depending on their Franck-Condon overlap integrals, or Franck-Condon factors.

***Fluorescence*** is a very powerful spectroscopic method, because we have detectors capable of recording single photons. Hence we can use fluorescence to identify where a molecule is (*e.g.*, in a microscope image), how many are present (we can detect a single molecule), and what the relative orientation of the molecule is.

***Fluorescence*** is very sensitive to changes in the chemical environment. For molecules that have substantial changes between their ground and first excited electronic states, the excited state energy evolves with the reorganization of the dipole moments of a polar solvent. This process is called solvatochromism, and is of great value for characterizing the dynamical changes in environment that an excited state molecule experiences. Understanding these phenomena are still an active research problem, and are crucial for understanding all of the features that affect the outcomes of photophysical and photochemical processes occurring from excited electronic states.

## 3.6. Non-Radiative Decay: Internal Conversion

Internal conversion is the non-radiative decay mechanism by which higher-lying electronic states can rapidly relax to lower-lying states that have the same spin multiplicity. This can hold true for singlet-singlet, triplet-triplet, and other states as well. The case shown in the diagram above represents internal conversion from $S_{1,v=0}$ to $S_{0,v=0}$. Normally, internal conversion can occur between any vibrational levels in the initial and final electronic state. Theoretical work done in the 1970s by Prof. Karl Freed and co-workers showed that the probability for internal conversion increases with the energy gap between the initial and final states. Internal conversion from higher-lying singlet states is very important to life processes. Some examples include the non-radiative decay of the nucleic acid bases, and in chlorophyll and related light-harvesting pigments.

### 3.6.1. Internal Conversion: Importance to Life Processes

The measured excited state lifetimes of the five nucleic acid bases would be expected to be about 10 nanoseconds based on their structural similarity to a large number of other organic molecules. However, when illuminated by ultraviolet light in the 250-285 nm wavelength range, the five nucleic acid bases cytosine, adenine, thymidine, guanine, and uracil decay by a factor of about 20,000 times more rapidly than we might otherwise expect: the lifetimes of the nucleic acid bases range from 0.29 to 0.72 picoseconds. It is precisely because of this unique property of the nucleic acid electronic structure that life forms on this planet with genetic material based on DNA/RNA are able to survive when our primary energy source is derived from sunlight: the rapid internal conversion prevents other damaging excited-state photochemical processes from occurring in DNA/RNA. When illumination by ultraviolet light is too intense, then even this rapid molecular mechanism for dumping the UV light energy fails: photochemistry occurs, especially oxidative damage to guanines; carcinogenic lesions form, mutation rates skyrocket, and the organism dies from a number of causes.

Another major example of the importance of ***internal conversion*** to life processes is the fact that tetrapyrrole molecules (including porphyrins, hemes, and chlorophyll *a*, shown below) have very rapid relaxation from their higher-lying excited singlet states to a stable lowest excited state from which all photochemical reactions and photophysical processes (such as intermolecular energy transfer) can occur. A common feature of the excited-state configurations of tetrapyrroles is that they have an extremely intense transition at the edge of the UV-visible range (near 390-445 nm), with a molar extinction coefficient of about $10^6$ $M^{-1}cm^{-1}$. This state is referred to not by its spectroscopic or electronic state label of $S_2$ or $S_3$, but rather as the Soret transition. The $S_2$ and $S_1$ states of chlorophyll a are called the Qx and Qy transitions, respectively. Because these three transitions absorb strongly in the near UV to blue and red spectral ranges, chlorophyll *a* appears bright green in colour, since green is the only color of the visible spectrum not absorbed, hence giving grass and tree leaves their green hue. Because the *Soret* excited state relaxes in about 1 picosecond via ***internal conversion***, then proteins are engineered to make use of energy absorbed from sunlight by all three excited states, with the subsequent photochemical and photophysical processes needing to be optimized only for the lowest energy excited state, $\boldsymbol{S_1}$.

### 3.7. Non-Radiative Decay: Intersystem Crossing

Intersystem crossing Connects Spin-Paired (singlet) states to the Unpaired-Spin (triplet) States.

Though intersystem crossing in general is not a high probability event, it is a mechanism that links formally spin-forbidden transitions between states of different multiplicity. For example, a spin- paired organic molecule in an excited singlet state can transform to a spin-unpaired state by a flip of the lone electron remaining in the Highest Occupied Molecular Orbital (HOMO). The probability for such a spin-flip transition is negligible, except in the case where a vibronic energy level of the singlet is nearly degenerate with the energy of a triplet vibronic state. In the diagram above, The $S_{1,v=2}$ state has been drawn to be only marginally higher in energy than the $T_{1,v=4}$ state. When such a situation occurs, then the probability for the spin-flip intersystem crossing process is greatly enhanced. When a triplet state such as the green potential curve labelled $T_1$ shown above is populated by intersystem crossing, the vibrational relaxation process will normally occur quite rapidly, lowering the energy of the triplet $T_1$ state to the bottom of its vibronic potential energy well $T_{1,v=0}$. As shown above, the $T_{1,v=0}$ state lies substantially below the $S_{1,v=0}$ state, making a reverse intersystem crossing process have a very much lower probability than in the forward direction. Thus, the only decay channel for $T_{1,v=0}$ is to await the very low probability event that the $T_{1,v=0}$ state can return to the $S_0$ vibronic manifold. As discussed immediately above, the $T_{1,v=0}$ excited-state decay can be either radiative or non-radiative. Unless there is an accidental near degeneracy (which occurs less frequently than in the excited state case, as one can see by thinking carefully about the density of states in an enharmonic Morse potential for $S_1$, $T_1$, and $S_0$) the $T_1$ state can be quite long-lived. At room temperature, triplet states may last for milliseconds, while at reduced temperatures, the triplet state can persist for minutes to hours.

### 3.8. Phosphorescence: Radiative Decay from Triplet States

In the event that a triplet state $T_1$ is populated from an excited singlet state (such as $S_1$), the transition back to the ground electronic state $S_0$ has a very low probability of occurring, and thus occurs infrequently. However, such transitions do occur both non-radiatively (as in $T_1$ to S1 intersystem crossing) and radiatively. When the transitions are accompanied by emission of light, this light has different spectral, but more importantly, different time profiles for occurring. Because of the low transition probability, the time scale for emission from triplet to singlet states via phosphorescence is on the millisecond to hour time frame, as is the case for non-radiative decay. By observing the time profile of the emission as well as the wavelength spectrum, the singlet-singlet fluorescence emission will occur on the nanosecond time scale, and the phosphorescence will occur much more slowly, on the millisecond and longer time scale. In the event that the intersystem crossing from the excited singlet state S1 to the triplet state $T_1$ is very efficient, then nearly all of the excited singlet states can be converted to triplets. In this event, (which normally can only occur for some special cases of planar, symmetric molecules at low temperatures) the total phosphorescence emission can be quite intense, and easily observable by the human eye. However, the probability for the phosphorescence transition is very low at any given instant.

### 3.9. Photosensitization

Photosensitization is the process of initiating a reaction through the use of a substance capable of absorbing light and transferring the energy to the desired reactants. The technique is commonly employed in photochemical work, particularly for reactions requiring light sources of certain wavelengths that are not readily available. A commonly used sensitizer is mercury, which absorbs radiation at 1849 and 2537 angstroms; these are the wavelengths of light produced in high-intensity mercury lamps. Also used as sensitizers are cadmium; some of the noble gases, particularly xenon; zinc; benzophenone; and a large number of organic dyes.

In a typical photosensitized reaction, as in the photodecomposition of ethylene to acetylene and hydrogen, a mixture of mercury vapour and ethylene is irradiated with a mercury lamp. The mercury atoms absorb the light energy, there being a suitable electronic transition in the atom that corresponds to the energy of the incident light. In colliding with ethylene molecules, the mercury atoms transfer the energy and are in turn deactivated to their initial energy state. The excited ethylene molecules subsequently undergo decomposition. Another mode of photosensitization observed in many reactions involves direct participation of the sensitizer in the reaction itself.

### 3.10. The Franck-Condon Principle and the Stokes' shift

The energy levels are indicated, as they usually are in spectroscopy, by properly spaced horizontal lines. The lowest line represents the ground state, $E_0$, of the atom or molecule in which it exists in the absence of external activation. The higher lines ($E_1$ and $E_2$) represent *excited electronic* states--the only kind of excited states possible in an atom. In a diatomic or polyatomic *molecule*, one or several series of (also quantized) *vibrational* and rotational states are superimposed on each electronic state. If the molecule is complex, the various vibrational and rotational states lie very close together. The sharp absorption (and emission) lines of atoms, or structured bands of simple molecules, are replaced by broad, continuous bands. The absorption lines (or bands) are represented, in schemes of this type, by arrows directed upwards and the emission lines or bands by arrows directed downwards (see the figure shown above). The energy of the quanta of emission or absorption is proportional to the lengths of the arrows. An atom or molecule can absorb only energy quanta corresponding to the distances between the permitted energy states. Once it is excited, say to state $E_2$, it can release energy represented by downward arrows, leading from *E2* to a lower energy state $E_1$. The wavy arrow in the above figure (from $E_2$ to $E_1$ ) relates to another, radiationless way in which a transition can occur by energy loss to surrounding molecules, or by its "internal conversion" into vibrational energy of the excited molecule. The fall from $E_2$ to $E_1$ in one big jump is *fluorescence*. In *fluorescence*, light absorption leading, say, from $E_0$ to $E_1$ is reversed by light emission leading from $E_1$ to $E_0$. When a photon is absorbed, the molecule usually is not merely transferred into an excited electronic state, but also acquires some vibrational energy. According to the so-called ***Franck-Condon principle***, the absorption of a photon is a practically instantaneous process, since it involves only the rearrangement of practically inertia-free electrons. James Frank recognized the obvious: the nuclei are enormously heavy as compared to the electrons. Thus, during light absorption, which occurs in femtoseconds, electrons can move, not the nuclei. The much heavier atomic nuclei have no time to readjust themselves during the absorption act, but have to do it after it is over, and this readjustment brings them into vibrations. This is best illustrated by potential energy diagrams, such as that shown in Figure 4. It is an expanded energy level diagram, with the abscissa acquiring the meaning of distance between the nuclei, $r_{xy}$. The two potential curves show the potential energy of the molecule as a function of this distance for two electronic states, a ground state and an excited state. Excitation is represented, according to the Franck-Condon principle, by a *vertical* arrow *(A)*. This arrow hits the upper curve, except for very special cases, not in its lowest point, corresponding to a non-vibrating state, but somewhere higher. This means that the molecule finds itself, after the absorption act, in a non-equilibrium state and begins to vibrate like a spring. This vibration is described, in the figure, by the molecule running down, up, down again, etc., along the upper potential curve, like a pendulum. The periods of these vibrations are of the order of $10^{-13}$, or $10^{-12}$ seconds. Since the usual lifetimes of excited electronic states are of the order of $10^{-9}$ s, there is enough time during the excitation period for many thousands of vibrations. During this time, much (if not all) of the extra vibrational energy is lost by energy exchange (temperature equalization) with the medium. The molecule, while it remains extremely "hot" as far as its electronic state is concerned, thus acquires the ambient "vibrational temperature." Fluorescence, when it comes, originates from near the bottom of the upper potential curve, and follows a vertical arrow down *(F)*, until it strikes the lower potential curve. Again, it does not hit it in its deepest point, so that some excitation energy becomes converted into vibrational energy. The cycle absorption-emission thus contains two periods of energy dissipation. Because of this, the fluorescence arrow *(F)* is always shorter (that is, the fluorescence frequency is lower) than that of absorption *(A)*. In other words, the wavelengths of the fluorescence band are longer than of the absorption band. This displacement of fluorescence bands towards the longer wavelengths compared to the absorption bands **(Stokes' shift)** was a long-established experimental fact before the Franck-Condon principle provided its interpretation. Obviously, the extent of the shift depends on the difference between the two potential curves.

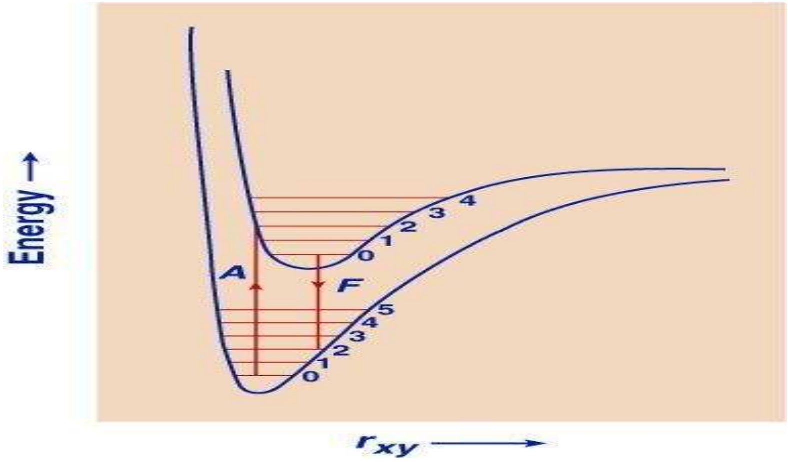


**Figure 5: Frank-Condon Principle. Potential energy curves for the ground state and an excited state of a diatomic molecule. (r, interatomic distance; A, absorption; F, fluorescence; numbers indicate vibrational states.)**

### 3.10.1. How did it become known as Franck-Condon Principle?

A historical suggestion was that of James Franck (1925, who had shared, with Hertz, the 1925 Nobel Prize in Physics for the experimental verification of the quantum theory). He argued simply that because of the large masses of the nuclei in a molecule, their relative momentum cannot be directly affected by an electronic transition, so that those transitions will be most likely that conform most closely to a Principle. The nuclei do not move during an electronic transition. Thus, on a diagram of energy (ordinate) versus distance between the nuclei of a diatomic molecule (abscissa), this transition is vertical promoting the electron from the lowest vibrational state of a molecule in the ground state to a higher vibrational state of the excited state (e.g. $S_1$ or $S_2$) of the molecule. The molecule in the excited state then dissipates immediately (within 10 to 100 fs) some energy as heat and the electron reaches the lowest vibrational level of the excited state. When the molecule relaxes to the ground state giving off light (fluorescence), it generally occurs at longer wavelength than the absorbing wavelength (Rotverschiebung, the red shift, Franck, 1927). The Franck-Condon principle, then, explains the observed red shift (Stokes, 1852) of the fluorescence spectrum from the absorption spectrum. The history of how the principle became known as the Franck-Condon principle was beautifully presented by Condon (1947). The original idea is in a paper at a Faraday Society meeting in London by Franck (1925); the proofs of this paper were sent to his student Hertha Sponer, who was then at the University of California at Berkeley on an International Education Board Fellowship. She generously shared the proofs with Condon; he was able to generalize Franck's ideas (Condon, 1926). Condon (1947) states: "This work was all done in a few days. Doctor Sponer showed me Franck's paper one afternoon, and a week later all the quantitative work for my 1926 paper was done."

### 3.11. The stokes' Shift

If a molecule is in an isolated environment, such as in a gas phase, then the fluorescence is emitted from the lowest vibrational level of the excited state to the ground state and its vibrationally excited levels. This emission has a spectrum which is a mirror image of the absorption spectrum. Where emission is excited by a narrow spectral source such as a laser, some emission is at the same wavelength as the excitation, and is known as "resonance fluorescence". For molecules in solution, the excited state can usually reduce its energy through rearrangement of the solvent 'cage' around the molecule prior to emission. In this case, although the emission spectrum is often still rather similar to a mirror image of the excitation spectrum, the absorption peak and the emission peak do not coincide. The emission maximum is now at longer wavelength (lower energy) than the excitation, and is said to be red-shifted.

Several factors influence the magnitude of the Stokes' shift. If the environment is rigid so that little rearrangement is possible then the Stokes shift is expected to be small. The magnitude of the shift depends on factors such as solvent polarity, viscosity and polarizability. It also depends on whether the excited state can undergo any specific interactions such as proton transfer or charge transfer to other molecules or (sometimes) within the same molecule.

Sometimes, there could be non-conformity to the mirror image rule. Such deviation is indicative of a change in geometry of the absorbing species soon after excitation and prior to emission. This implies that the ground state and the excited states now have different geometrical arrangements of their nuclei. Apart from change in geometry, excited state reactions could also result in a breakdown of the mirror image rule. For example the absorption and emission spectra of anthracene (in the presence of diethylaniline) are not mirror images, due to the formation of a charge-transfer complex between the excited state of anthracene and diethyaniline.

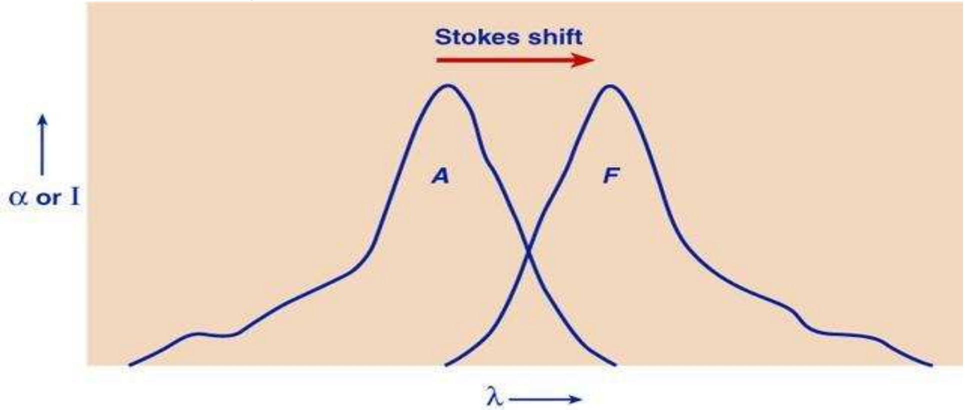


**Figure 6: The Stokes' shift (displacement of fluorescence band compared to the absorption band of a molecule). Approximate mirror symmetry of the two bands exists when the shapes of the potential curves in the ground state and the excited state are similar.**

## 4.0. SUMMARY

Light absorption can result in the formation of an (electronically) excited state, which has different chemical properties to the ground state. The intensity and shape of absorption spectra are a result of the nature of excitation between ground and excited states. Various processes result in the deactivation of the excited state. The timescales of these indicate their efficiency, and we will look at these in more detail in future posts.

## 5.0. TUTOR-MARKED ASSIGNMENTS

1. State the major laws of photochemistry.
2. With the aid of a simple Jablonski diagram, discuss the fate of a photochemically excited molecule.
3. State and explain the Franck-Condon principle
4. Discuss briefly how the Franck-Condon principle provided an interpretation for the phenomenon of Stokes' shift.
5. Write short notes on the followings:
   (a) Absorption
   (b) Fluorescence
   (c) Internal conversion
   (d) Intersystem crossing
   (e) Phosphorescence
6. What do you understand by the term 'photosensitization'?

## 6.0. REFERENCES

1. Gilbert, A. and Baggott, J. E., *Essentials of molecular photochemistry*, Blackwell Scientific: London, 1991.
2. Turro, N. J., Ramamurthy, V. and Scaiano, J. C., *Principles of molecular photochemistry: an introduction*, University Science Books: Sausalito, 2009. Despite the title, a detailed text with lots on the various photophysical processes that occur on light absorption. These three authors are among the best known photochemists today. Turro's classic, *Modern Molecular Photochemistry*, was for a long time the bible for photochemistry.
3. http://www.life.illinois.edu/govindjee/biochem494/Abs.html
4. http://www.britannica.com/EBchecked/topic/458153/photosensitization

# UNIT 4 – SELECTION RULES AND PHOTOPHYSICAL PARAMETERS

## 1.0. INTRODUCTION

We have looked at the way photons are absorbed. Photons of UV and visible light cause electrons to promote between orbitals. In this Unit, we shall look at the way this photon absorption is analysed by spectroscopists. When a photon is absorbed or generated, we must conserve the total angular momentum in the overall process. So we must start by looking at some of the ‘rules’ that allow for intense UV-visible bands (caused by electronic motion).

Selection rules are a set of restrictions governing the likelihood that a physical system will change from one state to another or will be unable to make such a transition. Selection rules, accordingly, may specify "allowed transitions," those that have a high probability of occurring, or "forbidden transitions," those that have minimal or no probability of occurring.

It is advisable to employ a high-power lamp when performing a photochemical reaction because it produces more photons than a low-power lamp. Its flux is greater. When we looked at the laws of photochemistry, we saw how the second law stated the idea that when a species absorbs radiation, one particle is excited for each quantum of radiation absorbed. This (hopefully) obvious truth now needs to be investigated further. The ‘quantum yield’ Φ is a useful concept for quantifying the number of molecules of reactant consumed per photon of light. It may be defined mathematically by

$$\Phi = \frac{\text{number of molecules of reactant consumed}}{\text{number of photons consumed}}$$

## 2.0. OBJECTIVES

After studying this Unit, you should be able to:

- Explain the concept of selection rules
- Define and carry out simple calculations on quantum yields
- Determine the number of photons absorbed by a sample in a photochemical process
- Define the lifetime of an excited species
- Derive an expression for the lifetime of an excited species
- Calculate the rate constants for the various photophysical parameters
- Use the Stern-Volmer equation to analyze the fluorescence quenching of a fluorophore

## 3.0. MAIN CONTENT

### 3.1. Selection rules

A selection rule is a quantum mechanical rule that describes the types of quantum mechanical transitions that are permitted. Transitions not permitted by selection rules are said to be “forbidden,” although in practice, such transitions are generally forbidden “to first order” only, which means they may occur in practice but with low probability. Light absorption is a resonant process; hence the most fundamental condition for absorption is that the energy of the incoming photon must match the difference in energy between the two energy states involved in the transition ($\Delta E = h\nu$). In addition to this energy matching, the probability of an electronic transition is predicted using a set of selection rules, which may be summarized as follows:

### 3.1.1. Spin selection rule ($\Delta S = 0$)

Transitions involving spin changes (S→T, or T→S) are strongly forbidden. This rule can be relaxed in the presence of heavy atoms and paramagnetic species. The fact that spin-forbidden transitions can be observed at all is as a result of the phenomenon of *spin-orbit coupling*, which is the interaction of the electron's spin magnetic moment with its orbital magnetic moment. This interaction introduces a new term into the Hamiltonian operator which operates on both spin and space variables. In the presence of this new term, the zero-order wave functions of the system, which were hitherto pure singlets and triplets, are combined to form new wave functions of mixed multiplicity. S→T and T→S transitions therefore become somewhat probable because the singlet state is no longer pure singlet but has some triplet character mixed with it. The triplet state also has some singlet character.

### 3.1.2. LaPorte selection rule (g↔u; $\Delta l = \pm 1$)

Whether spin-allowed or spin-forbidden, some transitions (e.g. d-d) are generally very weak. This could be due to the LaPorte rule which forbids transitions involving no change of parity (p↔p, d↔d, f↔f). If the sign of the wave function changes on reflection through a centre of smmetry, then the symmetry is referred to as *ungerade* denoted *u*; if it is unchanged, it is termed *gerade* denoted *g*. Then according to this rule, g→u and u→g transitions are allowed, while u→u and g→g transitions are forbidden. The corollary of the LaPorte rule is that d↔p and s↔p transitions are allowed, while d↔d, and s↔d transitions are forbidden. The selection rule which states that transitions which cause a large change in linear of angular momentum of the molecule are forbidden is also consistent with the LaPorte rule. However, the LaPorte rule does not strictly apply in the presence of minor static distortions or non-totally symmetric vibrational motions which remove the exact centrosymmetry. This could be responsible for the observed intensities of the d→d transitions in octahedral complexes.

### 3.1.3. Franck-Condon Selection Rule

The classical Franck-Condon principle requires that, because an electronic transition is "instantaneous", the nuclear coordinates and momenta do not change. As a result of this transition, electron density is rapidly built up in new regions of the molecule and removed from others. The change in electron density causes a new force field on the stationary nuclei, which causes the molecules to vibrate. The most probable transition is from the ground state to the vibrational state lying vertically above it. In terms of the quantum mechanics, transitions are most probable when the wave function of the upper vibrational state most closely resembles the ground state vibrational wave function.

### 3.1.4. Orbital Overlap Selection Rule

Orbitals involved in an electronic transition need to overlap. For example, the $\pi\rightarrow\pi^*$ transition in carbonyls is highly probable because the orbitals involved do overlap. This is not the case for the $n\rightarrow\pi^*$ transition, which is forbidden.

### 3.2. The Quantum Yield

The **quantum yield (Φ)** of a radiation-induced process is the number of times a specific event occurs per photon absorbed by the system. The "event" is typically a kind of photophysical or photochemical process.

By definition, quantum yield is the number of defined events which occur per photon absorbed by the system. The quantum yield (ϕ) represents and quantifies the efficiency of a photophysical or photochemical process.

$$\phi = \frac{\text{number of events}}{\text{number of photons absorbed}}$$

This definition emanates from the first and second laws of photochemistry, which proposed that for any photochemical process to take place, there must be absorption of photons, and that one photon activates only one molecule. Many factors, intrinsic and extrinsic to the system, can influence the efficiency of a photochemical process. Quantum yield is a measure of the efficiency of such processes after light absorption. The efficiencies of all photochemical and photophysical processes are quantified by the quantum yield.

Its value can lie anywhere in the range $10^{-6}$ to $10^{6}$. A value of $10^{-6}$ implies that the photon absorption process is very inefficient, with only one molecule absorbed per million photons. In other words, the energetic requirements for reaction are not being met. Conversely, a quantum yield Φ of greater than unity cannot be achieved during a straightforward photochemical reaction, since the second law of photochemistry clearly says that one photon is consumed per species excited. In fact, values of $\Phi > 1$ indicate that a secondary reaction(s) has occurred. A value of $\Phi > 2$ implies that the product of the photochemical reaction is consumed by another molecule of reactant, e.g. during a chain reaction, with one photon generating a simple molecule of, say, excited chlorine, which cleaves in the excited state to generate two radicals. Each radical then reacts in propagation reactions until the reaction mixture is exhausted of reactant.

To help clarify the situation, we generally define two types of quantum yield: primary and secondary. The magnitude of the primary quantum yield refers solely to the photochemical formation of a product so, from the second law of Photochemistry, the value of $\Phi_{\text{primary}}$ cannot be greater than unity. The so-called secondary quantum yield refers to the total number of product molecules formed via secondary (chemical) reactions; its value is not limited. The primary quantum yield should always be cited together with the photon pathway occurring: it is common for several possible pathways to coexist, with each characterized by a separate value of Φ. As a natural consequence of the second law of photochemistry, the sum of the primary quantum yields cannot be greater than unity.

The quantum yield of a photophysical process is directly related to the ‘allowedness’ of the process. For example, phosphorescence (T→S transition) is a spin-forbidden process; hence its quantum yield is expected to be small.

The quantum yields for some photophysical and photochemical processes are defined thus:

**Fluorescence quantum yield:** $\phi_F = \frac{\text{n}\underline{\text{o}}\text{ of fluorescing molecules}}{\text{n}\underline{\text{o}}\text{ of photons absorbed}}$

**Internal conversion:** $\phi_{IC} = \frac{\text{n}\underline{\text{o}}\text{ of molecules undergoing internal conversion}}{\text{n}\underline{\text{o}}\text{ of photons absorbed}}$

**Intersystem crossing:** $\phi_{ISC} = \frac{\text{n}\underline{\text{o}}\text{ of molecules undergoing intersystem crossing}}{\text{n}\underline{\text{o}}\text{ of photons absorbed}}$

**Phosphorescence:** $\phi_P = \frac{\text{n}\underline{\text{o}}\text{ of Phosphorescing molecules}}{\text{n}\underline{\text{o}}\text{ of photons absorbed}}$

**Photoreaction:** $\phi_R = \frac{\text{n}\underline{\text{o}}\text{ of molecules undergoing photoreaction}}{\text{n}\underline{\text{o}}\text{ of photons absorbed}}$

### 3.2.1. Calculating the Number of Photons Absorbed

Photons are the particles of light. Properties of photons:

- Photons always move with the speed of light.
- Photons are electrically neutral.

Two pieces of information are needed to determine the number of photons absorbed by a sample:

1. The power (or energy) of the incident light

Light emanating from a source (laser, flash light, incandescent light bulb, etc) is characterized by its power output (e.g., 80 W, 80 $Js^{-1}$).

The relationship between power ($J\ s^{-1}$ or W) is energy of an incident radiation is:

$E_{incident}$ (J) = $Power_{incident}$ ($J\ s^{-1}$) x time (s).

2. The quantity of energy per emitted photon (energy of 1 photon)

Photons have no mass, but they have energy E = hν = $\frac{h\square}{\lambda}$. Here h = 6.626 $x10^{-34}$ Js is a universal constant called **Planck's constant**. The energy of each photon is inversely proportional to the wavelength of the associated electromagnetic wave. The shorter the wavelength, the more energetic is the photon, the longer the wavelength, the less energetic is the photon.

$$E_{photon} = h\nu_{photon} = \frac{hc}{\lambda_{photon}}$$

Knowing these two quantities, then the number of photons incident photons ($N_{incident}$) is given as:

$$N_{incident} = \frac{E_{incident}}{E_{photon}}$$

The number of photons absorbed ($N_{absorbed}$) is given as

$$N_{absorbed} = \alpha . N_{incident}$$

Where α is the fraction of incident photons absorbed i.e., the efficiency of absorption. α is sometimes given as %-absorption.

**Example 1:**

Calculate the number of photons emitted by a 100 W yellow lamp in 1.0 s. Take the wavelength of yellow light as 560 nm and assume 100 % efficiency.

**Solution:**

Power = 100 W = 100 J $s^{-1}$

Time = 1.0 s

Wavelength (λ) = 560 nm = 5.6 $x10^{-7}$ m

$E_{incident}$ = Power x Time = 100 x 1

= 100 J

$$E_{photon} = \frac{hc}{\lambda_{photon}} = \frac{6.63 \text{ x}10^{-34} \text{ x } 3 \text{ x}10^{8}}{5.6 \text{ x}10^{-7}} = 3.55 \text{ x}10^{-19} \text{ J}$$

$N_{incident} = \frac{100}{3.55 \text{ x}10^{-19}}$ = 2.815 $x10^{20}$ photons

**Example 2:**

When a sample of 4-heptanone was irradiated with 313 nm light with a power output of 50 W under conditions of total absorption for 100 s, it was found that 2.8 $x10^{-3}$ mol $C_2H_4$ was formed. What is the quantum yield for the formation of ethane?

**Solution:**

No. of moles of $C_2H_4$ formed = 2.8 $x10^{-3}$ mol

Power = 50 W = 50 J $s^{-1}$

Time = 100 s

Wavelength (λ) = 313 nm = 3.13 $x10^{-7}$ m

$E_{incident}$ = Power x Time = 50 x 100

$= 5000 \text{ J}$

$$E_{photon} = \frac{hc}{\lambda_{photon}} = \frac{6.63 \times 10^{-34} \times 3 \times 10^{8}}{3.13 \times 10^{-7}} = 6.36 \times 10^{-19} \text{ J}$$

$$N_{incident} = \frac{5000}{6.36 \times 10^{-19}} = 7.86 \times 10^{21} \text{ photons}$$

Total absorption implies 100 % absorption (i.e., $\alpha = 1$).

Therefore, $N_{incident} = N_{absorbed}$

$\text{No. of moles of photons absorbed} = \frac{N_{absorbed}}{N_A}$, where $N_A$ is the Avogadro's number.

$$\text{No. of moles of incident photons} = \frac{7.86 \times 10^{21}}{6.02 \times 10^{23}} = 1.31 \times 10^{-2} \text{ mol}$$

$$\Phi_{ethene} = \frac{\text{no. of mol of ethene formed}}{\text{no. of mol of photons absorbed}} = \frac{2.8 \times 10^{-3}}{1.31 \times 10^{-2}} = 0.21$$

**Self Assessment Questions**

i. How many photons does a monochromatic (single-frequency) infrared rangefinder of power 1 mW and wavelength 1000 nm emit in 0.1 s? (Answer: $5 \times 10^{14}$)
ii. The overall quantum yield for a reaction at 290 nm is 0.30. For what length of time must irradiation with a 100 W source continue in order to destroy 1.0 mol of molecules? (Answer: 3.8 hrs)

### 3.3. The excited state lifetime

In the field of photochemistry, two important excited states are known: the singlet and the triplet excited states. The lifetime of these states are designated $\tau_F$ and $\tau_T$ respectively. However, there exists a term called the radiative lifetime, designated as $\tau_0$. The photophysical processes that deactivated the first excited singlet state are:

| | | |
|---|---|---|
| $S_0 + h\nu \rightarrow S_1$ | Rate = $I_a$ | Absorption |
| $S_1 \rightarrow S_0 + h\nu_F$ | Rate = $k_F[S_1]$ | Fluorescence |
| $S_1 \longrightarrow S_0 + \text{heat}$ | Rate = $k_{IC}[S_1]$ | Internal conversion |
| $S_1 \longrightarrow T_1$ | Rate = $k_{ISC}[S_1]$ | Intersystem crossing |

The radiative lifetime, $\tau_0$, is a measure of the probability of emission, which is related to the probability of absorption. The radiative lifetime is represented by:

$$\tau_0 = \frac{1}{k_F}$$

By definition, $\tau_0$ is the lifetime of an excited molecule in the absence of radiationless transitions. The radiative lifetime is not the actual lifetime of the excited state; it is the lifetime if fluorescence was the only process deactivating the excited state, and it is the reciprocal of the first order rate constant of fluorescence. Following excitation, the molecule will also relax by internal conversion and intersystem crossing, in addition to fluorescence; so that the rate of decay of the singlet excited state is the sum of these three decay processes.

$$\frac{-d[S_1]}{dt} = (k_F + k_{IC} + k_{ISC})[S_1]$$

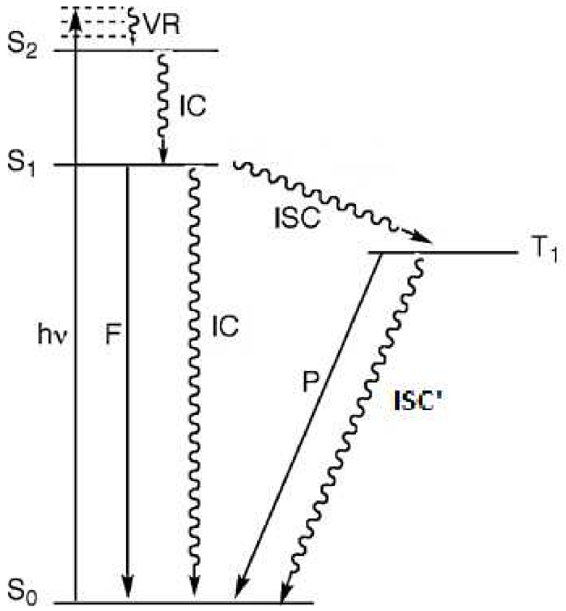


Figure X: Jablonski diagram showing processes at the $S_1$ and $T_1$ states

The lifetime of the excited state ($S_1$) is the reciprocal of the first order rate constant for decay.

$$\tau_F = \frac{1}{k_F + k_{IC} + k_{ISC}}$$

However, $\tau_0 = \frac{1}{k_F}$

There

The triplet state ($T_1$) formed can undergo further relaxation processes:

| | | |
|---|---|---|
| $T_1 \rightarrow S_0 + h\nu_P$ | Rate = $k_P[T_1]$ | Phosphorescence (radiative) |
| $T_1 \rightarrow S_0$ | Rate = $k'_{ISC}[T_1]$ | Intersystem crossing (non-radiative) |

Where $k_P$ is the rate constant for phosphorescence; and k′ISC is the rate constant for intersystem crossing from $T_1$ state to $S_0$.

Typically, the rate of triplet formation is much faster than the rate of triplet decay, i.e., $k_{ISC} > (k_P + k'_{ISC})$.

As in the case of the singlet state,

$$\frac{-d[T_1]}{dt} = (k_P + k'_{ISC})[T_1]$$

And the phosphorescence (triplet) lifetime is given by:

$$\tau_T = \frac{1}{(k_P + k'_{ISC})}$$

In all cases, the excited triplet state is longer lived than the singlet counterpart because of the decay (radiative or non-radiative) of the $T_1$ to the $S_0$ state is forbidden. Table X gives a description of the common photophysical processes.

**Table X: Description of the regular photophysical properties**

| **Process** | **Notation** | **Efficiency description** | **Timescale (s)** | **Kinetic description** |
|---|---|---|---|---|
| **Absorption** | Abs | $\varepsilon$ ($M^{-1}$ $cm^{-1}$) | $10^{-15}$ | |
| **Vibrational Relaxation** | VR | $\phi_{VR}$ | $10^{-13}$ | $k_{VR}$ |
| **Internal Conversion** | IC | $\phi_{IC}$ | $10^{-12}$ | $k_{IC}$ |
| **Fluorescence** | F | $\phi_F$ | $10^{-9}$ | $k_F$ |
| **Intersystem Crossing** | ISC | $\phi_{ISC}$ | $10^{-12}$ | $k_{ISC}$ |
| **Phosphorescence** | Ph | $\phi_P$ | $10^{-6}$ | $k_P$ |

### 3.3.1. Exponential Decay of the Excited State

The lifetime ($\tau$) of a chemical species, which decays in a first-order process, is the time needed for a concentration of this species to decrease to 1/e of its original value. Statistically, $\tau$ represents the mean life expectancy of an excited species. In a reacting system in which the decrease in concentration of a particular chemical species is governed by a first-order rate law, $\tau$ is equal to the reciprocal of the sum of the (pseudo) unimolecular rate constants of all processes, which cause the decay.

For any molecular entity which decays in a first order kinetics,

$$\text{Rate of decay} = \frac{\text{- dA}}{\text{dt}} = k_d[A]$$

$k_d$ is the first order decay constant. Rearranging this equation, we have:

$$\frac{dA}{[A]} = -k_d dt$$

Integrating,

$$\int_{A_0}^{A} \frac{1}{[A]} dA = -k_d \int_0^t dt$$

and

$In[A] – In[A]_o \;=\; -k_d t$

$$\ln \frac{[A]}{[A]_0} = -k_d t$$

From the definition above,

t = τ, when $[A] = \frac{[A]_0}{e}$

Substituting, we have:

$$\ln\left(\frac{1}{e}\right) = -k_d\tau$$

$$\tau = \frac{\ln e}{k_d}$$

And

$$\tau = \frac{\log_e e}{k_d} = \frac{1}{k_d}$$

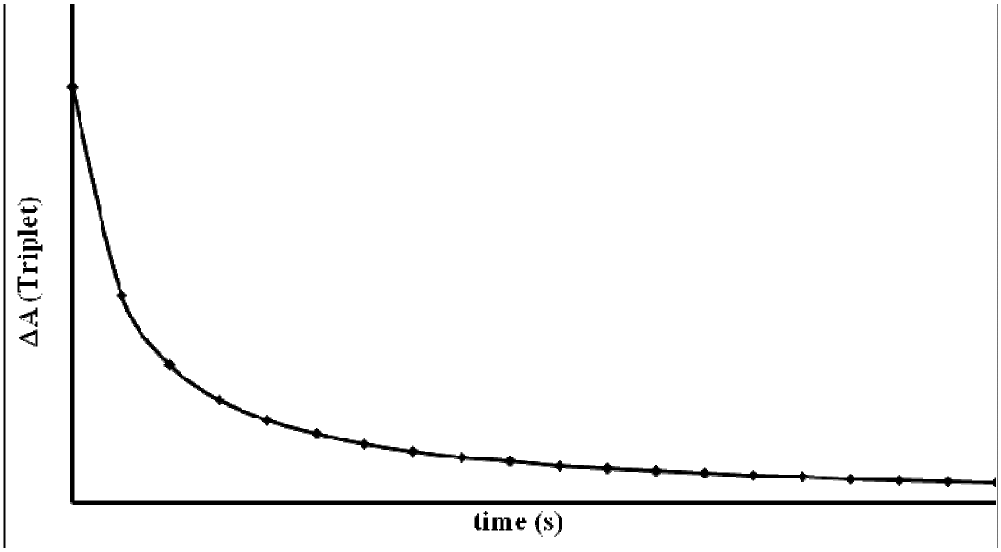


**Figure X: A typical triplet absorption curve (simulated)**

### 3.4. Rate Constants for Excited State Deactivation

An alternative description of the quantum yield of a process emanating from an excited state is in terms of the relationship between the rate constant for the specified process and the sum of rate constants of all processes deactivating the excited state. For example, the quantum yield of fluorescence ($\Phi_F$) is given as:

$$\Phi_F = \frac{k_F}{k_F + k_{IC} + k_{ISC}}$$

However, it is also known that $\tau_F = \frac{1}{k_F + k_{IC} + k_{ISC}}$

Therefore, $\Phi_F = k_F.\tau_F$

It is known that

$$\tau_F = \frac{1}{k_F + k_{IC} + k_{ISC}} \text{; and } \tau_0 = \frac{1}{k_F}$$

Therefore, it follows that $\dfrac{k_F}{k_F + k_{IC} + k_{ISC}} = \dfrac{\tau_F}{\tau_0} = \Phi_F$

If the lifetime of an excited state and the quantum yields of all processes deactivating it are known, it is possible to calculate the rate constants for the deactivating processes.

The following equations give the expressions for rate constants for the intrinsic processes (fluorescence, F; internal conversion, IC and intersystem crossing, ISC), which deactivate the excited singlet state of a molecule:

$$k_F = \frac{\Phi_F}{\tau_F}$$

$$k_{IC} = \frac{\Phi_{IC}}{\tau_F}$$

$$k_{ISC} = \frac{\Phi_{ISC}}{\tau_F}$$

Also, remember that $\Phi_{\square} = \frac{\sqcup_{\square}}{\square_{0}}$

**Question:**

For naphthalene in a glassy matrix at 77 K excited to the $S_1$ state, the quantum yield of fluorescence is 0.20, the quantum yield of triplet formation is 0.80, and the quantum yield of phosphorescence is 0.018.

a) Using the measured lifetime of fluorescence of 96 ns, determine the rate constant for intersystem crossing from $S_1$ to $T_1$.

b) From the measured phosphorescence lifetime of 2.6 s, determine the rate constant for intersystem crossing from $T_1$ to $S_0$.

**Answer:**

a) From the $S_1$ state,

$\Phi_F = 0.2$; $\Phi_T = 0.8$; $\Phi_{ISC} = 0.0$, and $\tau_F = 9.6 \text{ x}10^{-8}$ s

$$k_{ISC} = \frac{\Phi_{ISC}}{\tau_F} = \frac{\Phi_T}{\tau_F} = \frac{0.8}{9.6 \text{ x}10^{-8}} = 8.33 \text{ x}10^{6} \text{ s}^{-1}$$

b) From the $T_1$ state,

$\Phi_P = 0.2$, and $\tau_T = 2.6$ s

$\Phi'_{ISC} = \Phi_T - \Phi_P = 0.80 - 0.018 = 0.792$

$$\therefore\ k'_{ISC} = \frac{\Phi'_{ISC}}{\tau_T} = \frac{0.792}{2.6} = 0.305\,s^{-1}$$

### 3.5. Fluorescence quenching

When a fluorescent dye is excited at a particular wavelength, it is promoted to an excited state. In the absence of a quencher, the excited dye emits light in returning to the ground state. When a quencher is present, the excited fluorophore can return to the ground state by transferring its energy to the quencher without the emission of light. This is fluorescence quenching.

Quenching depends on the ability of the fluorophore to transfer energy to the quencher without the emission of light. Collisional quenchers do this by partaking in close molecular interactions with the fluorophore,

When only the three intrinsic processes (F, IC and ISC) deactivate the excited singlet state, i.e., no external factor contributing to the singlet decay; the fluorescence lifetime of a fluorophore can be expressed as:

$$\frac{1}{\tau_F^0} = k_F + k_{IC} + k_{ISC}$$

$\tau_F^0$ is the fluorescence intensity in the absence of a quencher.

However in the presence of a reactant (Q, also known as a quencher) that intercepts the $S_1$ state, the following excited state reaction takes place:

$$S_1 + Q \xrightarrow{k_Q} S_0 + Q^*$$

The rate law for this reaction is written as:

Rate = $k_Q[S_1][Q]$

Where $k_Q$ is the bimolecular quenching constant; $[S_1]$ and $[Q]$ are the concentrations of the $S_1$ state and the quencher respectively.

Assuming that the reaction is pseudo-unimolecular with $[Q] >> [S_1]$, we can state that:

Rate = $k'[S_1]$

Where

$k' = k_Q[Q]$

As a result of this quenching reaction, the fluorescence lifetime of the fluorophore is lowered; the quenching term is introduced into the expression for the $S_1$ state deactivation, and we now have:

$$\frac{1}{\tau_F} = k_F + k_{IC} + k_{ISC} + k_Q[Q]$$

Taking ratios,

$$\frac{\tau_F^0}{\tau_F} = \frac{k_F + k_{IC} + k_{ISC} + k_Q[Q]}{k_F + k_{IC} + k_{ISC}}$$

Simplification yields:

$$\frac{\tau_F^0}{\tau_F} = 1 + k_Q[Q].\tau_F^0$$

A vital assumption made in the treatment of fluorescence quenching data is that the rate constants for the intrinsic processes do not change in the presence of a quencher. This implies that for any system,

$$\frac{\tau_F^0}{\tau_F} = \frac{\Phi_F^0}{\Phi_F} = \frac{I_0}{I}$$

Hence, one can state that

$$\frac{I_F^0}{I_F} = 1 + k_Q[Q].\tau_F^0$$

This is the familiar Stern-Volmer (S-V) equation, which is usually written as:

$$\frac{I_0}{I} = 1 + K_{SV}[Q]$$

Where $k_Q$ ($M^{-1}$ $s^{-1}$) is the bimolecular quenching rate constant; the Stern-Volmer constant ($K_{SV}$, $M^{-1}$) is defined by as:

$$K_{SV} = k_Q \tau_F^0$$

A plot of $\frac{I_0}{I}$ versus [Q] should give a straight line with intercept 1 and slope $K_{SV}$. The observation of a straight line from this plot would indicate that the quenching process is solely by a collisional mechanism (dynamic quenching).

## 4.0. SUMMARY

A selection rule is a quantum mechanical rule that describes the types of quantum mechanical transitions that are permitted. The familiar selection rules are: spin selection rule, LaPorte selection rule, Franck-Condon selection rule and orbital overlap section rule.

The **quantum yield (Φ)** of a radiation-induced process is the number of times a specific event occurs per photon absorbed by the system.

Two pieces of information are needed to determine the number of photons absorbed by a sample:

Three types of lifetime exist in photochemistry: fluorescence lifetime ($\tau_F$), triplet lifetime ($\tau_T$) and the radiative lifetime ($\tau_0$). By definition, $\tau_0$ is the lifetime of an excited molecule in the absence of radiationless transitions. The radiative lifetime is not the actual lifetime of the excited state; it is the lifetime if fluorescence was the only process deactivating the excited state.

The fluorescence of a substance is said to be quenched if the addition of another substance to it reduces the intensity of fluorescence, provided that no chemical reaction occurs between the fluorescing substance (fluorescer or fluorophore) and the quenching material (quencher). According to Stern and Volmer, the quenching process is a reaction of the second order, which competes with all other molecular and radiative processes, and is subject to the equation:

$$\frac{I_0}{I} = 1 + k_{SV}[Q]$$

## 5.0. TUTOR-MARKED ASSIGNMENT

1. (a) What are selection rules in photochemistry?

   (b) Describe the spin selection rule and the La Porte selection rule.

2. The quantum yield for a photochemical reaction is 0.91. The absorbing substance was exposed to 320 nm radiation from a 87.5 W source. The intensity of the transmitted light was 0.257 that of the incident light. As a result of the irradiation, 0.324 mol of the absorbing substance decomposed. For what length of time must the irradiation have persisted?

3. Derive the Stern-Volmer equation for the reaction of a fluorophore ($S_1^*$) with a quencher (Q); after which the fluorophore was deactivated and the quencher excited.

4. 1-Chloronaphthalene fluoresces with $\phi_F = 0.06$ and phosphoresces with $\phi_P = 0.54$; fluorescence lifetime $\tau_F$ and phosphorescence lifetime $\tau_P$ are $10^{-9}$ and 0.3 seconds respectively. If the quantum yield of internal conversion is 0.01, calculate (i) Rate constants for $S_1 \rightarrow T_1$ intersystem crossing, (ii) Rate constant for $T_1 \rightarrow S_0$ intersystem crossing, (iii) Rate constant for fluorescence, and (iv) Rate constant for phosphorescence.

5. The change in fluorescence intensity of a zinc(II) phthalocyanine derivative varies with the concentration of benzoquinone (BQ) quencher in DMF is as follows:

| [BQ]/M | 0 | 0.0028 | 0.2256 | 0.0084 | 0.0112 |
|---|---|---|---|---|---|
| I | 324.5 | 280.78 | 263.2 | 240.2 | 224.6 |

Given that the fluorescence lifetime of the zinc(II) phthalocyanine derivative in DMF is 4.10 ns, determine the bimolecular rate constant.

## 6.0. REFERENCES

1. N. J. Turro, Molecular Photochemistry, Benjamin, New York, 1967.
2. J. R. Lakowicz, Principles of Fluorescence Spectroscopy, Springer, New York, 2006.

## UNIT 5 - LASERS

### 1.0. INTRODUCTION

Lasers are devices that produce intense beams of light which are *monochromatic*, *coherent*, and *highly collimated*. The wavelength (colour) of laser light is extremely pure monochromatic) when compared to other sources of light, and all of the photons (energy) that make up the laser beam have a fixed phase relationship (coherence) with respect to one another. Light from a laser typically has very low divergence. It can travel over great distances or can be focused to a very small spot with a brightness which exceeds that of the sun. Because of these properties, lasers are used in a wide variety of applications in all walks of life.

The basic operating principles of the laser were put forth by Charles Townes and Arthur Schalow from the Bell Telephone Laboratories in 1958, and the first actual laser, based on a pink ruby crystal, was demonstrated in 1960 by Theodor Maiman at Hughes Research Laboratories. Since that time, literally thousands of lasers have been invented (including the edible "Jello" laser), but only a much smaller number have found practical applications in scientific, industrial, commercial, and military applications. The helium neon laser (the first continuous-wave laser), the semiconductor diode laser, and air-cooled ion lasers have found broad OEM application. In recent years the use of diode-pumped solid-state (DPSS) lasers in OEM applications has been growing rapidly. The term "laser" is an acronym for (L)ight (A)mplification by (S)timulated (E)mission of (R)adiation.

### 2.0. OBJECTIVES

After studying this Unit, you should be able to:

- Define the following properties of laser light:
- Define the following terms that relate to the lasing process:
- Describe in a short paragraph and with a diagram the process of stimulated emission.
- Draw and label diagrams that illustrate the four basic elements of the following types of lasers:
- List the seven safety precautions to be followed when operating a low powered, helium-neon gas laser.

### 3.0. MAIN CONTENT

The invention of the LASER is one of the most significant developments in science and engineering. A thorough understanding and appreciation of the operation of this unique device requires an understanding of the behaviour and the properties of light itself. The term "LASER" is an acronym for **Light Amplification by Stimulated Emission of Radiation**, although common usage today is to use the word as a noun - laser - rather than as an acronym - LASER. A laser is a device that creates and amplifies a narrow, intense beam of coherent light. To understand the processes of amplification of light requires familiarity with the nature of light and absorption and emission of light. Atoms emit radiation. For example, "excited" neon atoms in a neon sign emit light, which is normally radiated in random directions at random times. The result is incoherent light (a technical term for a jumble of photons going in all directions). To generate a coherent light (nearly monochromatic and going in one precise direction); it is imperative to find the right atoms and an environment which would make the all light given up to go in one direction.

There are many different types of lasers, with output wavelengths ranging from ultraviolet to far infra-red. Lasers are broadly classified into solid, liquid and gas lasers. Most solid and gas lasers are only able to produce photons at a fixed wavelength, and this tends to limit their utility for chemical applications. Liquid lasers (which contain dye solutions and nearly operate mostly in the visible and near UV) on the other hand can be adjusted (tuned) over a certain wavelength range. A major advantage of lasers over other light sources is that they are capable of producing highly energetic and nearly monochromatic photons. The processes that go on inside them differing greatly from one laser type to another, hence, it is easy to become distracted by detail that might apply to one type of laser only. The features described here are those that lasers have in common.

## 3.1. Characteristics of Laser radiation

The light emitted by lasers is different from that produced by more common light sources such as incandescent bulbs, fluorescent lamps, and high-intensity arc lamps. An understanding of the unique properties of laser light may be achieved by contrasting it with the light produced by other, less unique sources.

### 3.1.1. Monochromaticity

Laser light consists of essentially one wavelength, having its origin in stimulated emission from one set of atomic energy levels.

All light consists of waves travelling through space. The colour of the light is determined by the length of those waves, as illustrated in Figure 1.

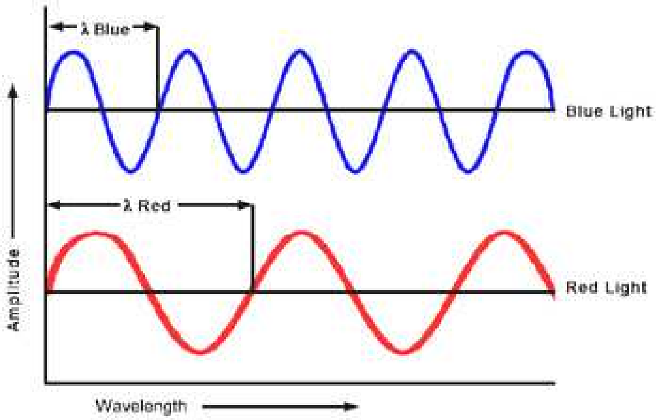


**Figure 1:** Comparison of the wavelengths of red and blue light

**Wavelength** is the distance over which the wave repeats itself and is represented by the Greek letter λ (lambda). Each colour of visible light has its own characteristic wavelength.

White light consists of a mixture of many different wavelengths. A prism can be used to disperse white light into its component wavelengths (colours), as in Figure 2.

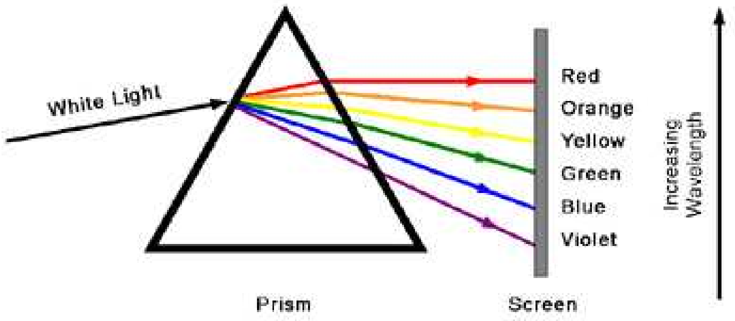


**Figure 2:** Dispersion of white light by a prism

All common light sources emit light of many different wavelengths. White light contains all, or most, of the colours of the visible spectrum. Ordinary coloured light consists of a broad range of wavelengths covering a particular portion of the visible-light spectrum. A green traffic light, for example, emits the entire green portion of the spectrum, as well as some wavelengths in the neighbouring yellow and blue regions.

The beam of a helium-neon gas laser, on the other hand, is a very pure red colour. It consists of an extremely narrow range of wavelengths within the red portion of the spectrum. It is said to be nearly **"monochromatic,"** or nearly "single-coloured." **Near**-monochromaticity is a unique property of laser light, meaning that it consists of light of almost a single wavelength.

Perfectly monochromatic light cannot be produced even by a laser, but laser light is many times more monochromatic than the light from any other source. In some applications, special techniques are employed to further narrow the range of wavelengths contained in the laser output and, thus, to increase the monochromaticity.

### 3.1.2. Directionality

Figure 3 depicts light being emitted from a light bulb in all directions. All conventional light sources emit light in this manner. Devices such as automobile headlights and spotlights contain optical systems that collimate the emitted light, such that it leaves the device in a directional beam; however, the beam produced always diverges (spreads) more rapidly than the beam generated by a laser.

**Figure 3**: Conventional source

Figure 4 illustrates the highly directional nature of light produced by a laser. **"Directionality"** is the characteristic of laser light that causes it to travel in a single direction within a narrow cone of divergence.

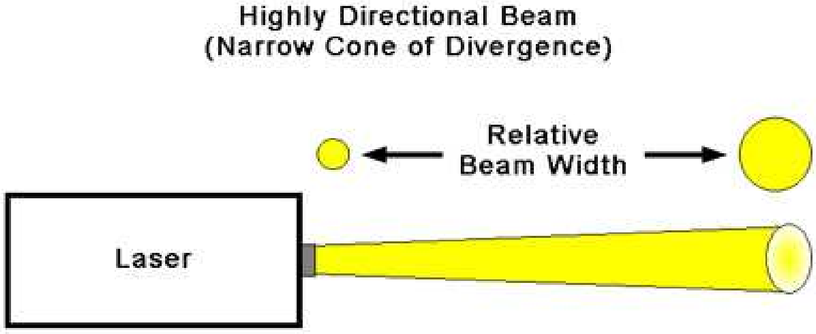


**Figure 4**: Directionality of laser light

But again, perfectly parallel beams of directional light—which we refer to as collimated light—cannot be produced. All light beams eventually spread (diverge) as they move through space. But laser light is more highly collimated, that is, it is far more directional than the light from any conventional source and thus less divergent. In some applications, optical systems are employed with lasers to improve the directionality of the output beam. One system of this type can produce a spot of laser light only one-half mile in diameter on the moon (a distance of 250,000 miles).

### 3.1.3. Coherence

Figure 5 depicts a parallel beam of light waves from an ordinary source traveling through space. None of these waves has any fixed relationship to any of the other waves within the beam. This light is said to be "incoherent," meaning that the light beam has no internal order.

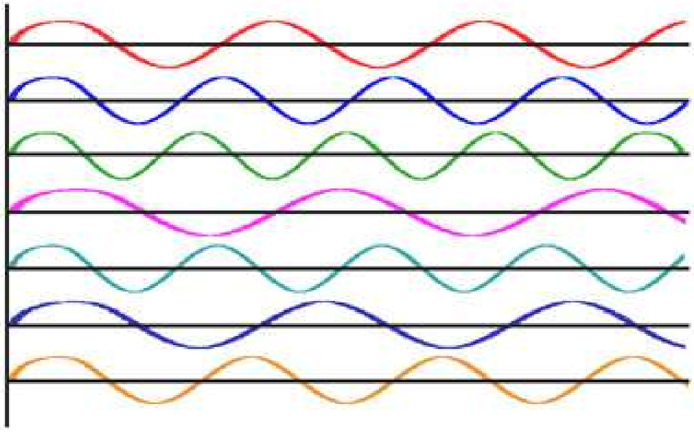


**Figure 5:** Incoherent light waves

Figure 6 illustrates the light waves within a highly collimated laser beam. All of these individual waves are in step, or "in phase," with one another at every point. "Coherence" is the term used to describe the in-phase property of light waves within a beam.

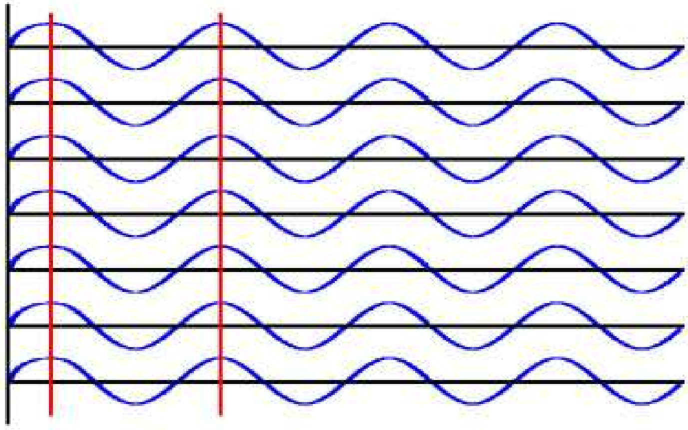


**Figure 6:** Coherent light waves

Just as laser light cannot be perfectly monochromatic or perfectly directional, it cannot have perfect coherence; yet laser light is far more coherent than light from any other source. Techniques currently in use greatly improve the coherence of light from many types of lasers.

Coherence is the most fundamental property of laser light and distinguishes it from the light from other sources. Thus, a laser may be defined as a source of coherent light. The full importance of coherence cannot be understood until other concepts have been introduced, but evidence of the coherence of laser light can be observed easily.

In Figure 7, the beam of a low-powered laser strikes a rough surface, such as paper or wood, and is reflected in all directions. A portion of this light reaches the eye of an observer several meters away. The observer will see a bright spot that appears to be stippled with many bright and dark points. This "speckled" appearance is characteristic of coherent light, and is caused by a process called "interference," which will be discussed in a later module.

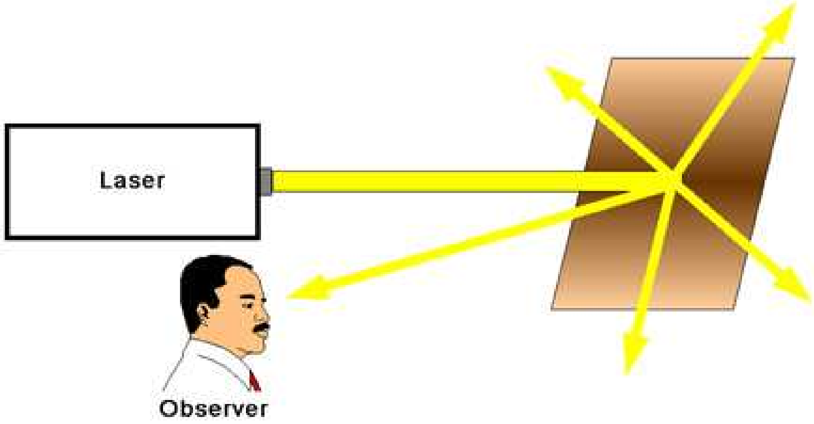


**Figure 7**

#### 3.1.4. High Irradiance Intensity

**Irradiance** is the power of electromagnetic radiation per unit area (radiative flux) incident on a surface.

### 3.2. Emission and Absorption of Light

A laser produces coherent light through a process termed "stimulated emission." The word **"LASER"** is an acronym for "**L**ight **A**mplification by **S**timulated **E**mission of **R**adiation." A brief discussion of the interaction of light with atoms is necessary before stimulated emission can be described.

#### 3.2.1. Energy Levels in Atoms

An atom is the smallest particle of an element that retains the characteristics of the element. An atom consists of a positive nucleus surrounded by a "cloud" of negative electrons. All neutral atoms of a given element have the same number of positive charges (protons) in the nucleus and negative charges (electrons) in the cloud. The energy content of atoms of a particular type may vary, however, depending on the energies contained by the electrons within the cloud.

Each type of atom can contain only certain amounts of energy. When an atom contains the lowest amount of energy that is available to it, the atom is said to be in its **"atomic ground**

**state."** If the atom contains additional energy over and above its ground state, it is said to be in an **"excited atomic state."**

Figure 8 is a simplified energy-level diagram of an atom that has three energy levels. This atom can contain three distinct amounts of energy and no others. If the atom has an energy content of $E_l$, it is in the atomic ground state and is incapable of releasing energy. If it contains energy content $E_2$ or $E_3$, it is in an excited state and can release its excess energy, thereby dropping to a lower energy state. Real atoms may have hundreds or even thousands of possible distinct energy states. The three-level mode is utilized here for purposes of clarity.

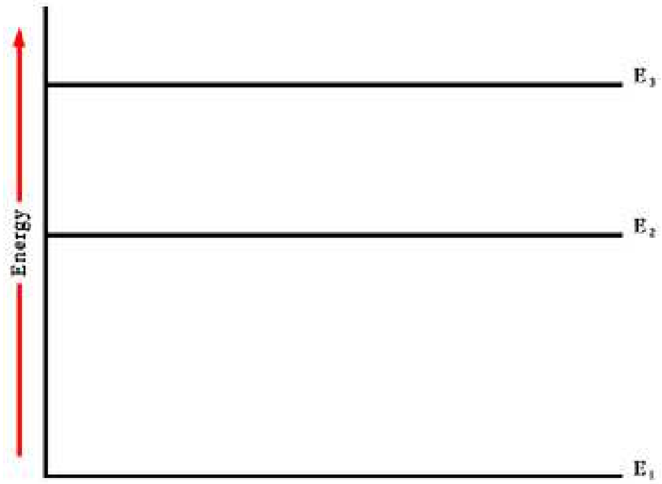


**Figure 8**: Atomic energy-level diagram

### 3.2.2. Spontaneous Emission of Light

An atom in an excited state is unstable and will release spontaneously its excess energy and return to the ground state. This energy release may occur in a single transition or in a series of transitions that involve intermediate energy levels. For example, an atom in state $E_3$ of Figure 8 could reach the ground state by means of a single transition from $E_3$ to $E_l$, or by two transitions, first from $E_3$ to $E_2$ and then from $E_2$ to $E_1$. In any downward atomic transition, an amount of energy equal to the difference in energy content of the two levels must be released by the atom. In many cases, this excess energy appears as a photon of light. A **photon** is a quantum of light having a characteristic wavelength and energy content; in fact, the wavelength of the photon is determined by its energy. A photon of longer wavelength (such as that for red light) possesses less energy than one of shorter wavelength (such as that for blue light), as illustrated in Figure 9.

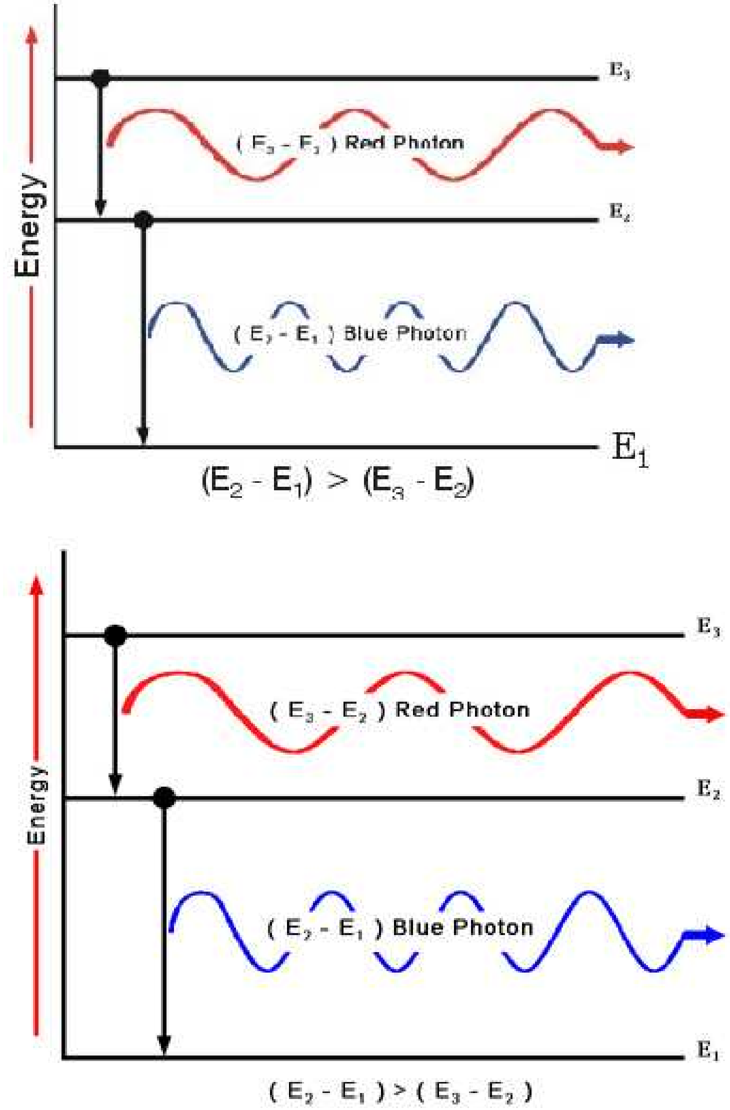


**Figure 9**: Spontaneous emission

In ordinary light sources, individual atoms release photons at random. Neither the direction nor the phase of the resulting photons is controlled in any way, and many wavelengths usually are present. This process is referred to as "spontaneous emission" because the atoms emit light spontaneously, quite independent of any external influence. The light produced is neither monochromatic, directional, nor coherent.

### 3.2.3. Stimulated Emission of Light

The coherent light of the laser is produced by a "stimulated-emission" process (Figure 10). In this case, the excited atom is stimulated by an outside influence to emit its energy (photon) in a particular way.

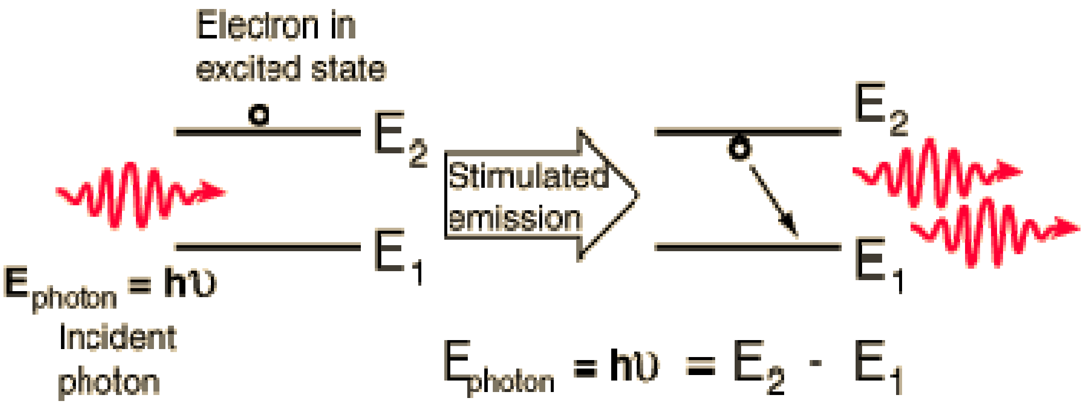


**Figure 10**: Stimulated emission

The stimulating agent is a photon whose energy ($E_3$–$E_2$) is exactly equal to the energy difference between the present energy state of the atom, $E_3$ and some lower energy state, $E_2$. This photon stimulates the atom to make a downward transition and emit, in phase, a photon identical to the stimulating photon. The emitted photon has the same energy, same wavelength, and same direction of travel as the stimulating photon; and the two are exactly in phase. Thus, stimulated emission produces light that is monochromatic, directional, and coherent. This light appears as the output beam of the laser.

### 3.2.4. Absorption of Light

Figure 11 illustrates another process that occurs within a laser. Here, a photon strikes an atom in energy state $E_2$ and is absorbed by that atom. The photon ceases to exist; and its energy appears as increased energy in the atom, which moves to the $E_3$ energy level. The process of absorption removes energy from the laser beam and reduces laser output.

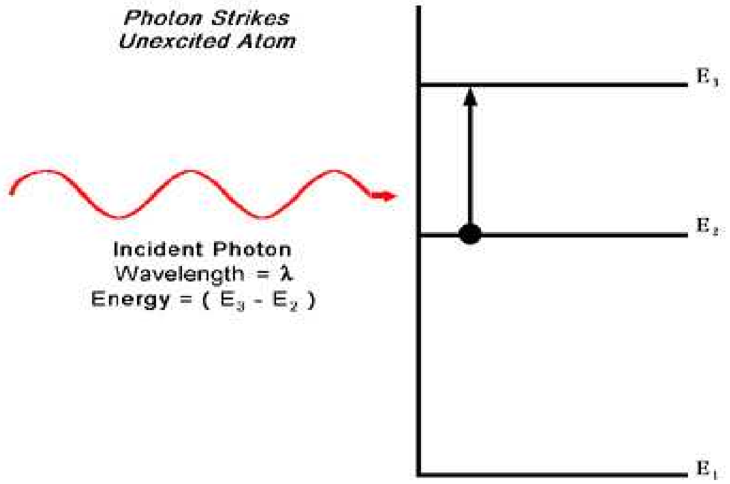


**Figure 11**: Absorption of light

### 3.2.5. Population Inversion

In order for a laser to produce an output, more light must be produced by stimulated emission than is lost through absorption. For this process to occur, more atoms must be in energy level $E_3$ than in level $E_2$, which does not occur under normal circumstances. In any large collection of atoms in matter at any temperature T, most of the atoms will be in the ground state at a particular instant, and the population of each higher energy state will be lower than that of any of the lower energy states. This is called a "normal population distribution."

Under "normal" circumstances, each energy level contains many more atoms than the energy level just above it, and so on up the energy lever ladder. For example, at room temperature, if there are $N_o$ atoms in the ground state of Neon (He-Ne laser) there are only $10^{-33}N_o$ atoms in the first excited state, even fewer in the second excited state and so forth. The population of the ascending energy levels decreases exponentially.

Thus, in any large collection of atoms in matter at any temperature T, most of the atoms will be in the ground state at a particular instant, and the population of each higher energy state will be lower than that of any of the lower energy states. This is called a "normal population distribution."

A **population inversion** exists whenever more atoms are in an excited atomic state than in some lower energy state. The lower state may be the ground state, but in most cases it is an excited state of lower energy. Lasers can produce coherent light by stimulated emission only if a population inversion is present. And a population inversion can be achieved only through external excitation of the atomic population.

## 3.3. Elements of a Laser

All lasers have three basic components namely: energy source, the active medium and the feedback mechanism.

**Energy source (Energizer)**: Often electricity, but a very intense light, flash tube, chemical reaction or even another laser can also be used.

**The active medium (Amplifying medium)**: Can be a solid, a liquid or a gas. Whatever its physical form, the amplifying medium must contain atoms, molecules or ions, a high proportion of which can store energy that is subsequently released as light.

**The feedback mechanism:** This consists of two mirrors or other highly reflective surfaces placed at each end of the active medium.

### Energizing the active medium

The process of energizing an active medium is known in laser terminology as “pumping” Pumping an amplifying medium by irradiating it with intense light is referred to as optical pumping.

### 3.3.1. Amplification

A laser consists of a pumped active medium positioned between two mirrors (Figure 12). The purpose of the mirrors is to provide what is described as 'positive feedback'. This means simply that some of the light that emerges from the active medium is reflected back into it for amplification. One of the mirrors is a total reflector, and reflects almost all of the light that falls upon it. The other mirror, known as the output coupler, is only partially reflective. The light that is not reflected being transmitted through the mirror, and constitutes the output beam of the laser.

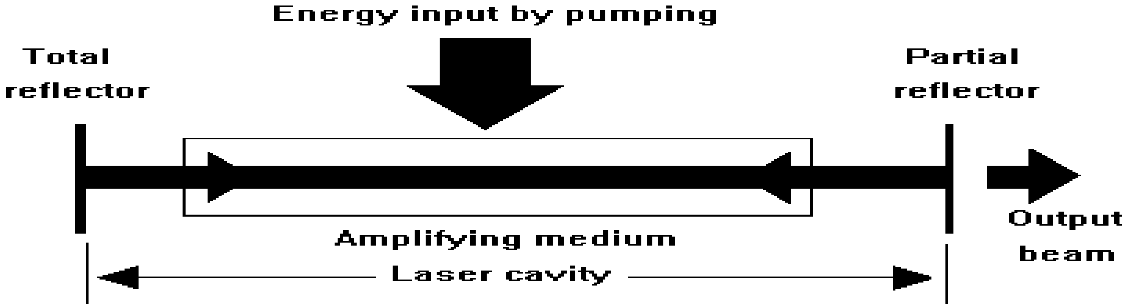


**Figure 12: Light amplification in the LASER cavity**

The process of light amplification could be accounted for by a consideration of the interaction of light with individual atoms within the active medium. Light absorption is a resonant process, and so there will be no absorption if there is no pair of energy states such that the photon energy can elevate the system from the lower to the upper state, i.e., there must be an energy matching between the photon and the separation of the two electronic states. If an electron is already in an excited state (an upper energy level, in contrast to its lowest possible level or "ground state"), then an incoming photon for which the quantum energy is equal to the energy difference between its present level and a lower level can kindle a transition to that lower level, producing a second photon of the same energy. This process is termed **“stimulated emission”**. When a sizable population of electrons resides in upper levels, this condition is called a **"population inversion"**, and it sets the stage for stimulated emission of multiple photons. This is the precondition for the light amplification that occurs in a **laser,** and since the emitted photons have a definite time and phase relation to each other, the light has a high degree of coherence. The **stimulated emission** of light is the crucial quantum process necessary for the operation of a laser.

### 3.3.2. Creating a population inversion

Population inversion is an indispensable prerequisite for laser action. Electrons normally reside in the lowest available energy state. This population inversion is the condition required for stimulated emission to overcome absorption and so give rise to the amplification of light. Simple absorption and spontaneous emission cannot give rise to amplification of light. A population inversion cannot be achieved with just ‘two levels’ (Figure 13) because the probabilities of absorption and spontaneous emission are exactly the same. There should be a non-radiative transition to a metastable excited level having a relatively long lifetime. This long lifetime allows a high proportion of the active medium in the metastable level so that a population inversion can occur. In order to establish a population inversion, the upper state must be populated by pump energy, and the lower state must be depopulated. This could be achieved by using either the 3-level laser or the 4-level laser.

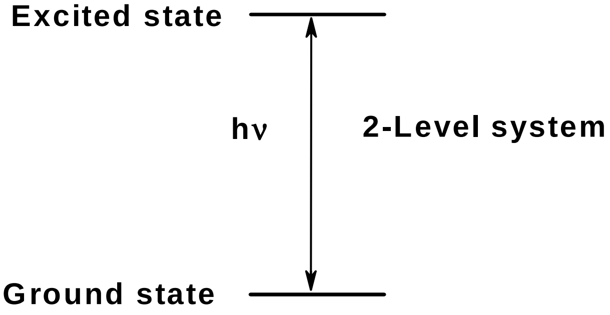


**Figure 13: A two-level system. Population inversion not achievable**

In the 3-level scheme, the particles are first excited to an excited state **higher in energy than the upper laser state** (Figure 14). The particles then quickly decay down into the upper laser state. It is important for the pumped state to have a short lifetime for spontaneous emission compared to the upper laser state. The upper laser state should have as long a lifetime (for spontaneous emission) as possible, so that the particles live long enough to be stimulated and thus contribute to the **gain**. The gain is the factor by which the intensity of the light is increased by the active (amplifying) medium. In this 3-level laser system, the lower state is the ground state, so in order to depopulate it; a large amount of pump energy must be put in so that the ground state is actually in lower concentration than the excited state. The only way to depopulate the ground state is to put in more and more pump energy.

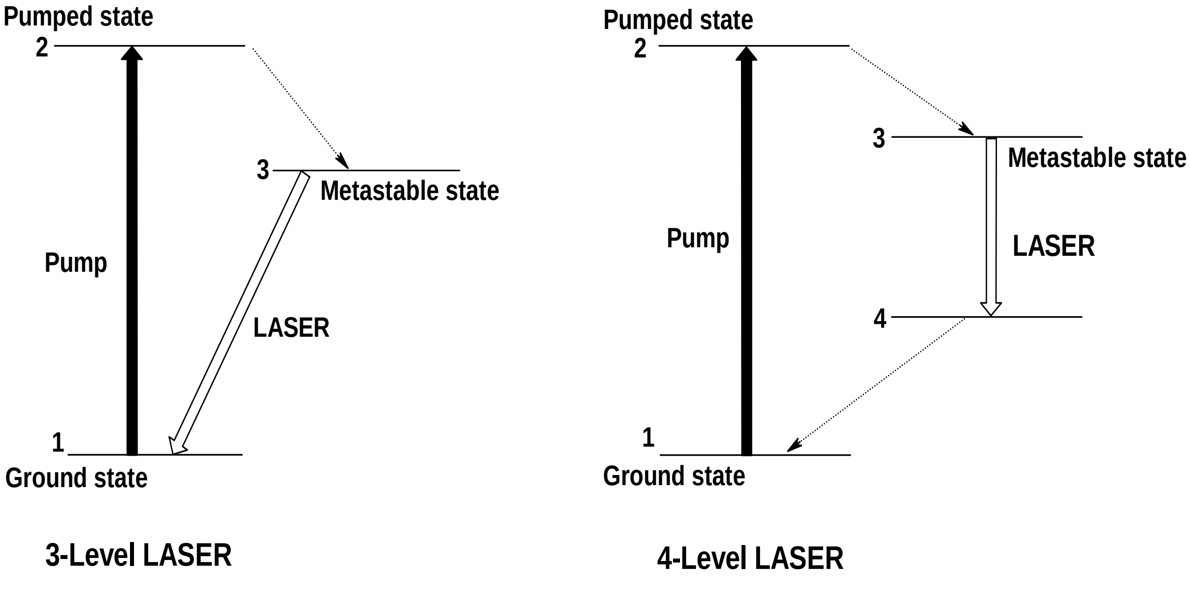


**Figure 14: 3-level and 4-level LASER systems**

In the case of the **“4-level” scheme** (Figure 14), only a modest pump energy may be sufficient to establish a population inversion between higher laser state (3) and lower laser state (4) if the upper state is relatively long lived (metastable) and lower state is relatively short lived (unstable). Laser transition takes place between the states (3) and (4) and so a rapid depopulation of state (3) to the ground state is required to ensure that the upper level is always full and the lower level always (almost) empty (Figure 15).

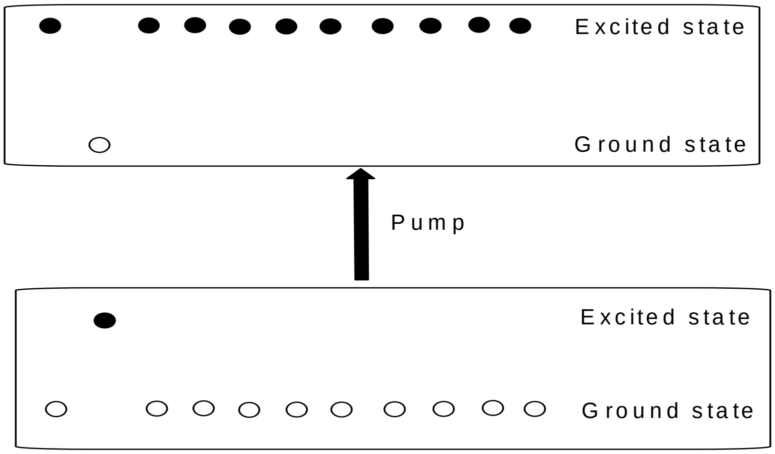


**Figure 15: Population inversion in LASER systems**

### 3.4. Applications of Lasers

Soon after its invention over four decades ago, the laser was spoken of as a “solution in search of a problem”. However, this status rapidly vanished as the laser earned itself a reputation as a valuable tool in many scientific, medical and industrial applications. The development of laser instruments that operate at ultraviolet wavelengths and those based on nonlinear materials has even broadened the spectrum of laser applications.

The followings are some important areas where lasers find huge application:

**Scientific**

- Laser spectroscopy
- Photochemistry
- Photophysics
- Raman spectroscopy

**Medical**

- Cosmetic surgery (tattoo, hair, scar, stretch mark, sunspot, wrinkle & birthmark removal)
- Eye surgery (LASIK, etc...)
- Laser scalpel (gynecological, urology, laparoscopic)
- Dental procedures
- Imaging

**Military**

- "Death ray": A hand-held device that might replace the gun as a weapon for infantry
- "Laser cannon": Able to destroy tanks, ships and aircraft

- Laser sight (to enhances the targetting of other weapons systems)
- Saber 203 Laser Illuminator (U.S. Air Force)
- laser target designator used to indicate a target for a laser guided munition, e.g., missile

**Industrial and Commercial**

- Cutting, welding, marking,
- Isotope separaton
- Rangefinder / surveying,
- LIDAR / pollution monitoring,
- CD/DVD player,
- Laser printing, scanners,
- Laser engraving of printing plates,
- Laser pointers, holography, laser light displays
- Photolithography,
- Optical communications.
- Optical tweezers

## 4.0. SUMMARY

The laser is a light source that exhibits unique properties and a wide variety of applications. Lasers are used in welding, surveying, medicine, communication, national defence, and as tools in many areas of scientific research. Many types of lasers are commercially available today, ranging in size from devices that can rest on a fingertip to those that fill large buildings. All these lasers have certain basic characteristic properties in common.

A laser is a coherent and highly directional radiation source. **LASER** stands for Light Amplification by Stimulated Emission of Radiation.

A laser consists of at least three components:

- a gain medium that can amplify light that passes through it
- an energy pump source to create a population inversion in the gain medium
- two mirrors that form a resonator cavity

The gain medium can be solid, liquid, or gas and the pump source can be an electrical discharge, a flash lamp, or another laser. The specific components of a laser vary depending on the gain medium and whether the laser is operated continuously (cw) or pulsed.

If light of the right colour hits an atom, it will bump an electron up to a higher energy level. And later the electron falls back down, giving off light of the same colour in some random direction.
But when a photon hits an atom that is already excited, the atom releases a new photon that is completely identical to the incoming photon; same colour, going in the same direction. We call this process "stimulated emission". This is basic of all lasers.

## 5.0. TUTOR-MARKED ASSIGNMENTS

1. Define the following properties of laser light:
    1. Monochromaticity
    2. Directionality
    3. Coherence

2. Define the following terms or phrases related to lasing action:
    - (a) Atomic ground state
    - (b) Excited atomic state
    - (c) Population inversion
    - (d) Wavelength
    - (e) Photon

4. Describe stimulated emission with the aid of a diagram.
5. Draw and label a diagram that illustrates the four elements of a laser.
6. State the purpose of each element of a laser, using the concepts of stimulated emission and population inversion, and the principle of feedback.
7. Population inversion is an indispensable prerequisite for laser action. Give a brief discussion on this statement.

## 6.0. REFERENCES

1. http://utopia.cord.org/cm/leot/course01_mod01/mod01-01frame.htm
2. Ogunsipe, A.O., “Photophysical and Photochemical Studies on Non-transition Metal Phthalocyanone Derivatives”, Ph.D thesis, Rhodes University, 2004.

# UNIT 6 – PHOTOCHEMICAL REACTIONS

## 1.0. INTRODUCTION

A photochemical reaction is a chemical reaction that is induced by light. Photochemical reactions are valuable in organic and inorganic chemistry because they proceed differently from thermal reactions. Photochemical reactions involve electronic reorganization initiated by electromagnetic radiation. The reactions are several orders of magnitude faster than thermal reactions; reactions as fast as $10^{-9}$ seconds and associated processes as fast as $10^{-15}$ seconds are often observed. The light required for a photochemical reaction may come from many sources. Giacomo Ciamician, regarded as the "father of organic photochemistry", used sunlight for much of his research at the University of Bologna in the early 1900's. Depending on the compounds being studied and the information being sought, bright incandescent lamps (chiefly infrared and visible light), low, medium and high pressure mercury lamps (185 - 255 nm, 255 -1000 nm & 220 -1400 nm respectively), high intensity flash sources and lasers have all been used.

The process by which a photochemical reaction is carried out is called *photolysis.* Photolysis is usually initiated by infrared, visible, or ultraviolet light. A primary photochemical reaction is the immediate consequence of the absorption of light. Subsequent chemical changes are called secondary processes.

Photochemical reactions are utilized in synthetic chemistry to produce various organic molecules. In addition, many common processes are photochemical in nature and have important applications. For example: photosynthesis involves the absorption of light by the chlorophyll in plants to produce carbohydrates from carbon dioxide and water.

Photography uses the action of light on grains of silver chloride or silver bromide to produce an image. Ozone formation in the upper atmosphere results from action of light on oxygen molecules. Solar cells, which are used to power satellites and space vehicles, convert light energy from the sun to chemical energy and then release that energy in the form of electrical energy.

In this unit we shall focus chiefly on the nature and behaviour of the electronic excited states formed when a photon is absorbed by a chromophoric functional group. As a rule, such excitation results in a change in molecular orbital occupancy, an increase in energy, and changes in local bonding and charge distribution.

## 2.0. OBJECTIVES

After studying this Unit you should be able to:

- Define a photochemical reaction
- Explain photochemical reaction pathway
- List the features of photochemical reactions
- Classify photochemical reactions with examples

## 3.0. MAIN CONTENT

### 3.1. Features of Photochemical Reactions

1. Photochemical reactions do not take place in dark but take place in the presence of light by absorbing it.

2. Since different coloured radiations in the range of visible light have different frequencies and hence different energies, therefore all radiations may not be able to initiate a particular reaction. For example, a photon of violet light has highest frequency and hence the highest energy. Hence a reaction which is initiated by violet light may not be initiated by other colored radiations of visible light. On the other hand, a photon of red light has lowest frequency and energy. Therefore a reaction that can be initiated by red light can be initiated by all other radiations as well.

3. Temperature has very little effect on the rate of a photochemical reaction. Instead, the intensity of light has marked effect on the rate of photochemical reaction.

4. The free energy change of a photochemical reaction may not be negative.

5. There are many substances which do not react directly when exposed to light. However, if another substance is added, the photochemical reaction starts

#### 3.1.1. Why are photochemical reactions interesting?

1. The excited states are rich in energy. Therefore reactions may occur that are highly endothermic in the ground state. Using the equation $E = h \times \nu$ we can correlate light of a wavelength of 350 nm with an energy of 343 kJ/mol.

2. In the excited state anti-bonding orbitals are occupied. This may allow reactions which are not possible for electronic reasons in the ground state.

3. Photochemical reaction can include singlet and triplet states; thermal reactions usually only show singlet states. In photochemical reaction intermediates may be formed which are not accessible at thermal

#### 3.1.2. Essential criteria for all photochemical reactions:

- Molecule must absorb light
- Radiation energy must match energy difference of ground and excited state

Typical absorption range of some important classes of organic compounds:

| | |
|---|---|
| Simple alkene | 190 - 200 nm |
| Acylic diene | 220 - 250 nm |
| Cyclic diene | 250 - 270 nm |
| Styrene | 270 - 300 nm |
| Saturated ketones | 270 - 280 nm |
| α,β-Unsaturated ketones | 310 - 330 nm |
| Aromatic ketones/aldehydes | 280 - 300 nm |
| Aromatic compounds | 250 - 280 nm |

### 3.1.3. Factors Determining Outcome of a Photochemical Reaction

The wide variety of molecular mechanisms of photochemical reactions makes a general discussion of such factors very difficult. The chemical nature of the reactant(s) is definitely among the most important factors determining chemical reactivity initiated by light. However, a better understanding of this aspect may be gained from a closer examination of the individual groups of chemical compounds. The nature of excited states involved in a photoreaction is directly related to the electronic structure of the reactant(s). Environmental variables, i.e., parameters that are not directly related to the chemical nature of the reacting systems, may also strongly affect photochemical reactivity. It is useful to distinguish between variables that are common for thermal and photochemical reactions, and those that are specific for the reactions of excited species. The first group includes reaction medium, reaction mixture composition, temperature, isotope effects to name the most important. The distinctive feature of photochemical reactions is that these parameters almost always operate under conditions when one or more photophysical processes compete with a photoreaction. The result of a photo-induced transformation can only be understood as the interplay of several processes corresponding to passages on and between at least two potential energy surfaces.

Reaction medium may directly modify the potential energy surfaces of the ground and excited states and hence affect the photo-reactivity. The outcome of some reactions changes dramatically when solvent polarity and hydrogen bonding capacity are changed. The protolytic photo-dissociation of 1-naphthol is completely suppressed in aprotic solvents because of unfavourable solvation energies both for the anion and proton. Under such conditions, proton transfer reaction cannot compete with the deactivation.

Solvent viscosity will strongly affect photoreactions where the encounter of two reactants or a substantial structural change is required. In highly viscous or solid solutions the loss of excitation via light emission or unimolecular non-radiative deactivation is more probable than a chemical modification of the excited species. On the other hand, slow diffusion in viscous solutions may prevent self-deactivation of the triplet state via a bimolecular process called triplet-triplet annihilation and enhance the efficiency of a photoreaction from this state. Triplet-triplet annihilation belongs to electronic-energy transfer processes, which may be classified as quenching of excited states. Quenching rate is a very important factor in discussing effects of

## 3.2. The Photochemical Process

To begin a photochemical process, an atom or molecule must absorb a quantum of light energy from a photon; when this occurs, the energy of the atom or molecule increases above its normal level. The atom or molecule is now in an excited (or activated) state. If a quantum of visible or ultraviolet light is absorbed, then an electron in a relatively low energy state of the atom or molecule is excited into a higher energy state. If infrared radiation is absorbed by a molecule, then the excitation energy affects the motions of the nuclei in the molecule.

After the initial absorption of a quantum of energy, the excited molecule can undergo a number of primary photochemical processes. A secondary process may occur after the primary step. The absorption step can be represented by where the molecule M absorbs a quantum of light of appropriate energy to yield the excited M* molecule.

### 3.2.1. Primary Photochemical Processes

The figure below indicates the various primary processes that the excited M* molecule can undergo: The highly energized - or excited - molecule may return to its initial state according to any of three physical processes:

1) It can release its excitation energy by emitting luminescent radiation through fluorescence or phosphorescence.

2) It may transfer its energy to some other molecule, C, with which it collides, without emitting light. The latter energy transfer process results in a normal molecule, M, and an excited molecule, C*.

3) As a result of the initial light absorption step, an electron ($e^-$) in the atom or molecule may absorb so much energy that it may escape from the atom or molecule, leaving behind the positive M+ ion. This process is called *photoionization.* If the excited M* molecule (or atom) does react, then it may undergo any of the following chemical processes: photodissociation, intramolecular (or internal) rearrangement, and reaction with another molecule C. Photodissociation may result when the excited molecule breaks apart into atomic and/or molecular fragments A and B. A rearrangement (or photoisomerization) reaction involves the conversion of molecule M into its isomer N - a molecule with the same numbers and types of atoms but with a different structural arrangement of the atoms. The conversion of *trans*-1,2-dichloroethylene into the *cis* isomer is an example of intramolecular rearrangement. The reaction is shown below:

In the *trans* isomer the chlorine atoms lie on opposite sides of the double bond, whereas in the *cis* isomer they are on the same side of the double bond.

### 3.2.2. Secondary Photochemical Processes

Secondary processes may occur upon completion of the primary step. Several examples of such processes are described below.

**Formation of Ozone**

Ozone (O3) is formed in the upper atmosphere from ordinary oxygen (O2) gas molecules according to the reaction:

After a quantum of ultraviolet light is absorbed (step 1), the excited oxygen molecule dissociates into two oxygen atoms (step 2). An oxygen atom then reacts with O2 to form ozone (step 3).

**Destruction of Ozone in the Upper Stratosphere**

Certain chlorofluoromethanes, such as CCl3F and CCl2F2, are used as refrigerants and-in some countries-as propellants in aerosol cans. These compounds eventually diffuse into the stratosphere, where the molecules undergo photodissociation to produce chlorine (Cl) atoms, which then react with ozone molecules according to the formula Cl + O3 → ClO + O2.

This decrease in the ozone content of the upper atmosphere allows more ultraviolet radiation to reach the surface of the earth.

### 3.2.3. Chain Reactions

If the primary photochemical process involves the dissociation of a molecule into radicals (unstable fragments of molecules), then the secondary process may involve a chain reaction. A chain reaction is a cyclic process whereby a reactive radical attacks a molecule to produce another unstable radical. This new radical can now attack another molecule, thereby reforming the original radical, which can now begin a new cycle of events.

The hydrogen-chlorine reaction is an example of a chain reaction. The overall reaction between hydrogen and chlorine gases in the presence of violet or ultraviolet light forms hydrogen chloride; it is given by This reaction actually proceeds according to the following series of steps:

According to the above mechanism, a suitable quantum of light dissociates a chlorine molecule into atoms (step 1). The reactive Cl atom attacks a hydrogen molecule to yield hydrogen chloride and a hydrogen atom (step 2). The reactive hydrogen atom attacks a chlorine molecule, which regenerates the Cl atom (step 3). This chlorine atom can then react with another H2 molecule according to step 2, beginning a new cycle of steps. Steps 2 and 3 will occur many times until either of the two reactants, H2 and Cl2, is completely consumed or until the H or Cl radicals attack a new substance that has been introduced into the reaction chamber.

## 3.3. Types of Photoreactions

There exists a plethora of photoreactions practically for each class of chemical compounds. These reactions may be categorized according to chemical composition and structure. They may also be classified under different types by using theoretical models for the description of the excited state(s) or structure of the potential energy surface. However, for our introductory discussion it seems to be more appropriate just to consider some examples classified by general reaction types (Figure 3.1).

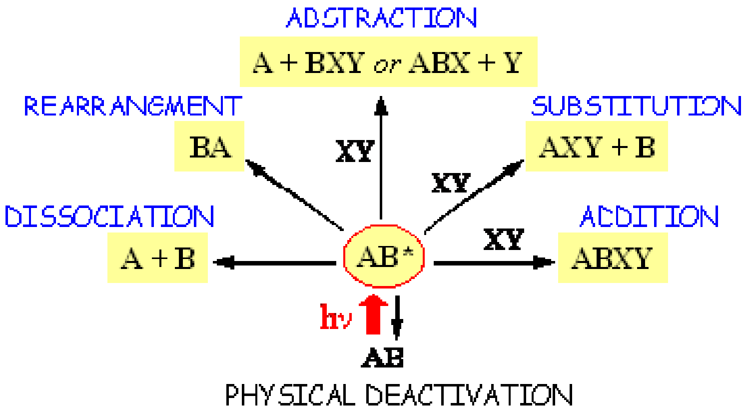
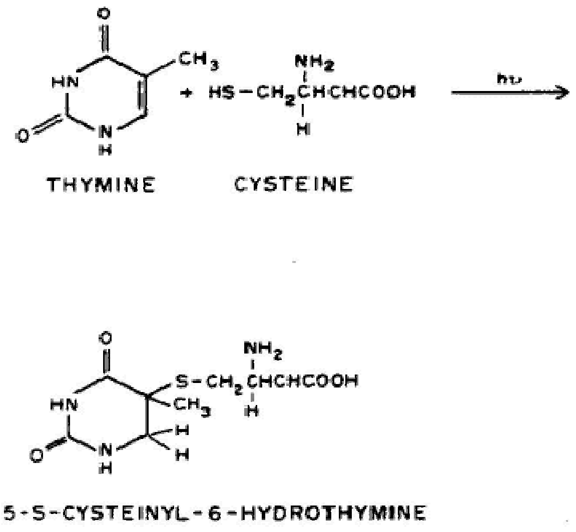


**Figure 3.1:** Multiple reaction pathways for electronically excited species.

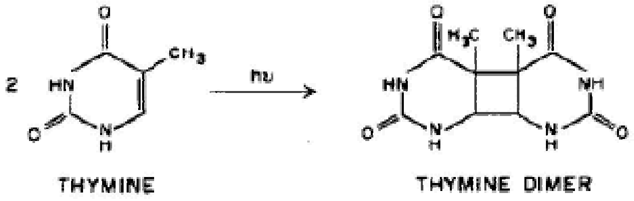
### 3.3.1. Linear addition to an unsaturated molecule

The pyrimidine base, thymne, in DNA can combine with the amino acid residue, cysteine, in proteins. This is a model for the photochemical crosslinking of DNA and proteins by UV radiation.



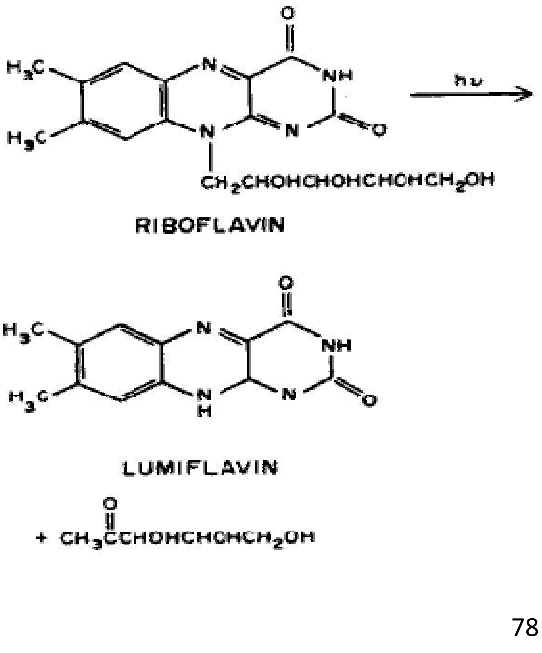
### 3.3.2. Cycloaddition of unsaturated molecules

Two thymines can react to form a ring product, the thymine dimer, an important class of products formed in DNA by UV radiation.



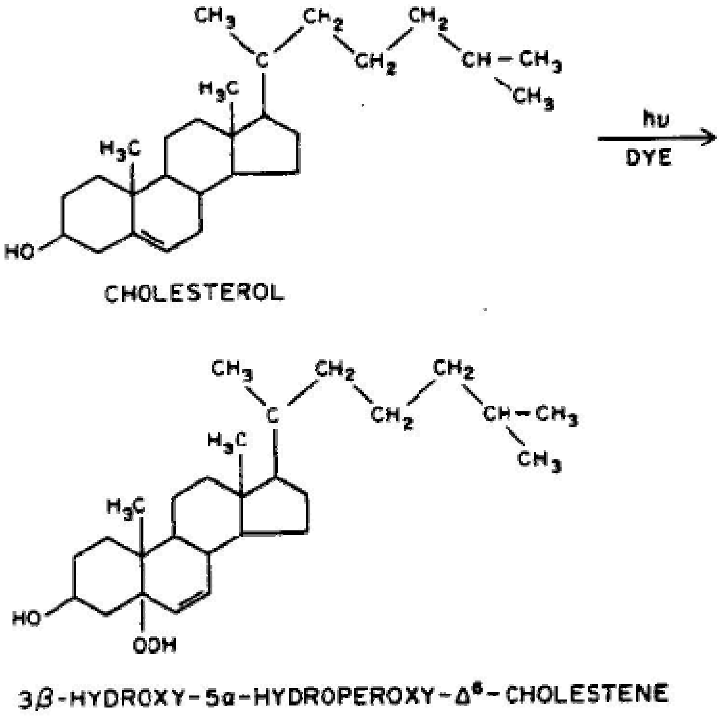
### 3.3.3. Photofragmentation

The side chain of riboflavin can split off to form lumiflavin.



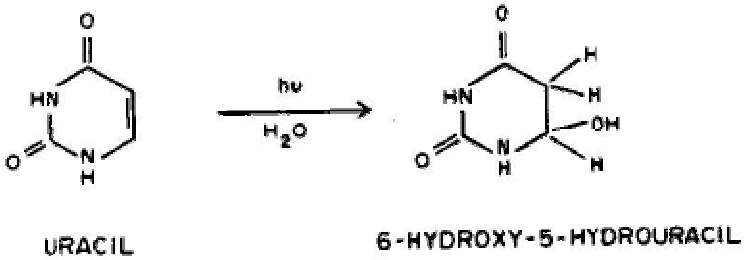
### 3.3.4. Photooxidation

Singlet oxygen is an easily available reagent. It can be generated from triplet oxygen in many solvents by a broad variety of sensitizers. The reaction of organic compounds with singlet oxygen can lead to reactive molecules, such as hydroperoxides, 1, 2-dioxetanes and endoperoxides. These compounds are useful for subsequent transformations, e.g., the ring structure of cholesterol can add a peroxy group.



### 3.3.5. Photohydration

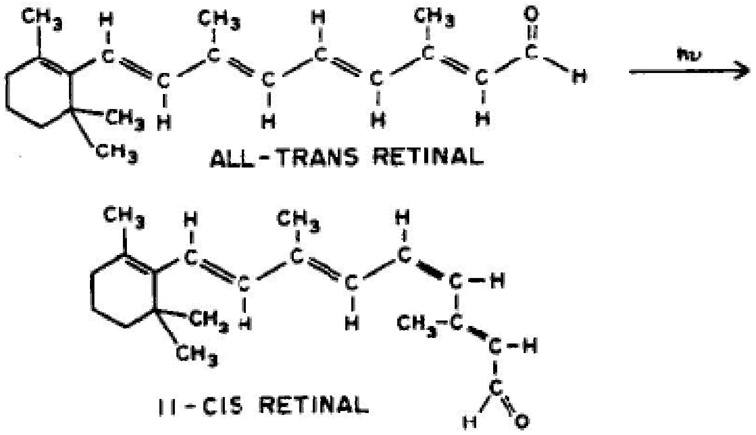
Uracil can add a molecule of water to it 5-6 double bond when UV irradiated.



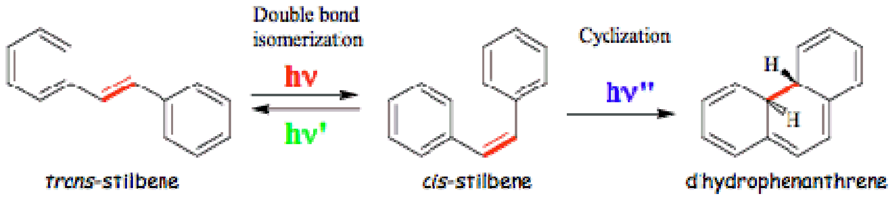
A photohydrolysis reaction in aqueous solution (substitution with $OH^-$) was utilized to provide the rapid light-controlled release of biologically active molecules, such as aminoacids, nucleotides, etc. Biologically inert compounds affording such release upon photoirradiation are referred to as "caged" compounds. Two-photon photochemistry is of great interest for such studies, because one can utilize red light or IR radiation, which is not absorbed by biomolecules, and is biologically benign.

### 3.3.6. Cis-Trans Isomerization

All-*trans* retinal can be converted to 11-*cis* retinal.



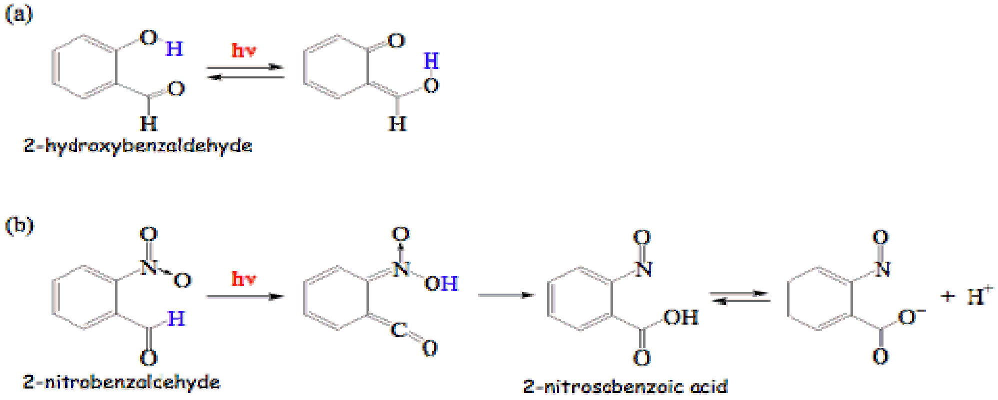
Rearrangements of electronically excited molecules present one of the most exciting chapters in photochemistry in the sense that they follow reaction pathways that are usually inaccessible for the ground state (activation barriers in the ground state are very high). The *cis*-*trans* isomerization of double bonds belongs to such reactions. The azobenzene reaction provides an instructive example. Scheme 1 shows photoinduced rearrangements of stilbene that has been extensively studied. In addition to double bond isomerization, *cis*-stilbene undergoes also cyclization with a lower quantum yield to form dihydrophenanthrene. The *cis*-*trans* isomerization of stilbene occurs through rotation around the double bond. In the ground state this rotation encounters a large barrier, i.e., there is a maximum on the ground-state potential energy surface at the geometry corresponding to a twist angle of about $90^o$. In contrast, both the first singlet excited state and triplet state have a minimum approximately at the same geometry. The close proximity of the minimum and maximum facilitates a jump to the ground state. The *cis*-*trans* isomerization of azobenzene may proceeds not only through rotation, but also through nitrogen inversion, i.e. in-plane motion of the phenyl ring.



**Scheme 1**

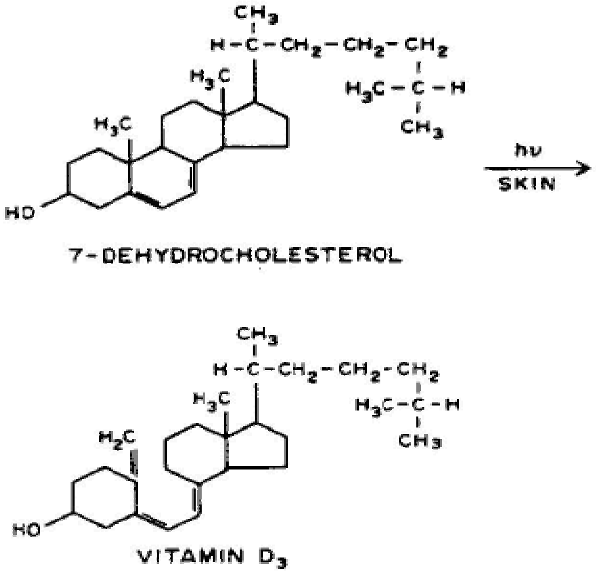
### 3.3.7. Photorearrangement

Two illuminating examples of photoinduced rearrangements of substituted benzaldehydes are presented in Scheme 2. Intramolecular hydrogen transfer in 2-hydroxybenzaldehyde is an extremely fast reaction in the singlet excited state. However, the process is completely reversed upon a jump to the ground state. Overall, no chemical conversion is observed and excitation energy is either dissipated as heat or emitted as light, but with a longer wavelength. This behavior is typical for aromatic carbonyl compounds with *ortho*-hydroxy groups, and they found application as UV protectors, in sunscreens for example. Molecules acting as UV protectors absorb light that is harmful for biological molecules, and convert light into heat or radiation that is biologically benign. In contrast, an intramolecular hydrogen transfer in 2-nitrobenzaldehyde initiates a sequence of the ground-state reactions that leads to 2-nitrosobenzoic acid. The latter molecule is a moderately strong acid, and dissociates in aqueous solutions so that the photochemistry of 2-nitrobenzaldehyde can be used to create a rapid pH-jump in solution. Many biological macromolecules, such as proteins and nucleic acids, show pH-dependent conformational changes. Those changes can be monitored in real time by using the light-induced pH-jump.



**Scheme 2**

Another important example is the conversion of 7-dehydrocholesterol to vitamin $D_3$.



### 3.3.8. Energy Transfer (Photosensitization)

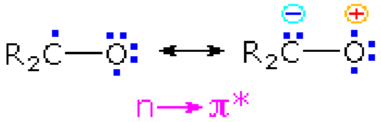
When a second molecule is located near an electronically excited molecule, the excitation can be transferred from one to the other through space. If the second molecule is chemically different, there can be a substantial change in the luminescence. For example, the chemiluminescence of a jellyfish is actually blue, but, because the energy is transferred to GFP, the observed fluorescence is green.

Photosensitized molecular oxygen is a powerfully oxidative species that severely hampers the photosynthetic efficiency of plants and causes health problems such as cataracts in humans. The ground state of molecular oxygen is very unusual in that it is a triplet; hence, it can accept electronic energy from more-energetic triplet states of other molecules in a process called quenching (as in the case of the space shuttle wing described above). When this occurs, the donor molecule begins in its triplet state and undergoes a change in spin to its singlet ground state. The molecular oxygen begins in its triplet ground state and also changes spin to a singlet excited state. Because the total spin between the two molecules is unchanged, the transfer of energy can occur rapidly and efficiently. The resulting molecular oxygen singlet state phosphoresces in the far red and the near infrared. Moreover, it is both a strong oxidant and peroxidant and, if formed, may chemically attack (oxidize) a nearby molecule, often the same molecule that sensitized the molecular oxygen. The oxidation reaction often changes the molecule to a form without colour. This light-induced bleaching (one kind of photodamage) can be observed in nearly any coloured material left in sunlight. In fact, the photosynthetic systems in plants must be continuously dismantled, repaired, and rebuilt because of photodamage (primarily from singlet molecular oxygen).

Some organisms use photodamage to their advantage. A remarkably effective plant-pathogenic fungus, *Cercospora*, produces a pigment that efficiently sensitizes singlet molecular oxygen. Peroxidation of the plant cell membrane causes the cells of the infected plants to burst, giving nutrients to the fungus.

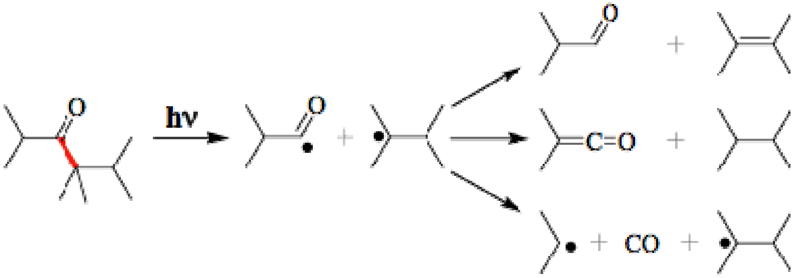
### 3.3.9. Carbonyl compounds

The n → π* excited states of carbonyl compounds display a rich chemistry in their own right.



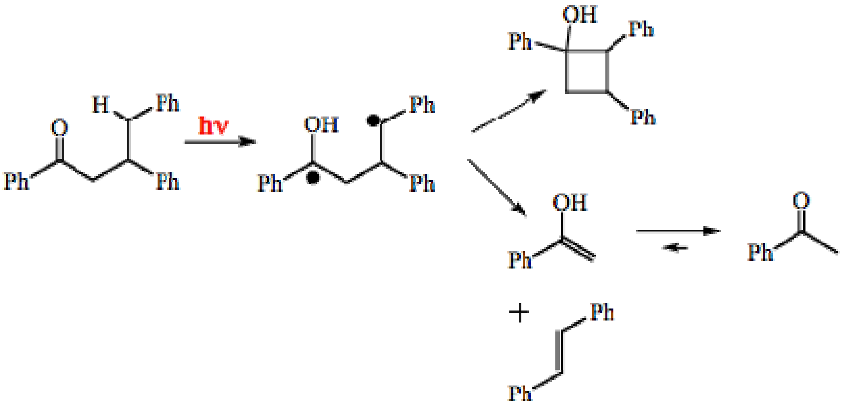
Since the oxygen has an unpaired electron, it behaves in much the same way as an alkoxy radical. Hydrogen abstraction and addition to double bonds are typical reactions. Cleavage of neighboring carbon-carbon bonds may also occur, the two most common of these being designated **Type I** and **Type II**.

An important primary photoprocess of carbonyl compounds is α cleavage, also known as a Norrish Type I reaction (Scheme 3). Besides recombination, the acyl and the alkyl radicals formed in the primary reaction can undergo numerous secondary reactions that are responsible for the multitude of final products.



**Scheme 3**

Intramolecular hydrogen abstraction is a common photoreaction of carbonyl compounds with a hydrogen atom attached to the fourth carbon atom (Scheme 4). The resulting diradical can form cycloalkanol or undergo C-C bond fission to give an alkene and enol. The latter is usually thermodynamically unfavorable and converts to a ketone. Intramolecular abstraction of a ϒ-hydrogen is known as a Norrish Type II process.



**Scheme 4**

## 4.0. SUMMARY

In this unit you have learnt that photochemical reactions are chemical reactions initiated by the absorption of energy in the form of light. They involve electronic reorganization initiated by electromagnetic radiation. The consequence of molecules absorbing light is the creation of transient excited states whose chemical and physical properties differ greatly from the original molecules. These new chemical species can fall apart, change to new structures, combine with each other or other molecules, or transfer electrons, hydrogen atoms, protons, or their electronic excitation energy to other molecules. Excited states are stronger acids and stronger reductants than the original ground states. It is this last property that is crucial in the most important of all photochemical processes, photosynthesis, upon which almost all life on earth depends. What you have learned in this unit concerns the chemistry that distinguishes photochemical reactions from other reactions. It has served to introduce you to the peculiar types of photochemical reactions such as photo-isomerization, photo-oxidation, photo-fragmentation, photo-rearrangement and photosensitization.

## 5.0. TUTOR-MARKED ASSIGNMENT

(1) A photochemical reaction occurs when internal conversion and relaxation of an excited state leads to a ground state isomer of the initial substrate molecule. Illustrate this with stilbene.

(2) Explain how solvent viscosity affects the outcome of a photochemical reaction.

(3) Write short notes on photo-fragmentation and its applications

## 6.0. REFERENCES

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# MODULE TWO

# PERICYCLIC REACTION

## UNIT 1 - MECHANISM OF PERICYCLIC REACTIONS AND ASSOCIATED TERMINOLOGIES

### 1.0. INTRODUCTION

For the synthetic organic chemist, the development of a general procedure that leads to the formation of carbon-carbon bonds is considered a laudable achievement. A general method that results in the simultaneous formation of two carbon-carbon bonds is worthy of a Nobel Prize. In 1950, two chemists, Otto Diels and Kurt Alder, received that accolade for their discovery of a general method of preparing cyclohexene derivatives that is now known as the Diels-Alder reaction. The Diels-Alder reaction is one type of a broader class of reactions that are known as pericyclic reactions. Pericyclic reactions are the *concerted* reactions involving reorganization of electrons which occur by the way of a single *cyclic transition state*. Pericyclic reactions represent an important class of concerted (single step) processes involving π-systems. The fact that the reactions are concerted gives fine stereochemical control of the product; however, this module is more concerned with the general types of pericyclic reaction, than with regio and stereochemical control. In 1965 two other Nobel laureates, Robert B.Woodward and Roald Hoffmann, published a series of short communications in which they presented a theoretical basis for these well known, but poorly understood pericyclic reactions. Their theory is called orbital symmetry theory. Subsequently other chemists published alternative interpretations of pericyclic reactions, one called frontier orbital theory, and another named aromatic transition state theory. All of these theories are based upon MO theory. In this module we will use the Diels-Alder reaction to illustrate aspects of each of these theories.

Pericyclic reactions that involve a redistribution of bonding and non-bonding electrons in a cyclic, concerted manner are an important class of organic reactions. Since the publications of the Woodward-Hoffmann rules on the conservation of orbital symmetry and the frontier molecular orbital theory (FMO) by Fukui first described in the late 1960s, the underlying principles of these processes at the molecular level have become fully understood. Many modern organic chemistry textbooks include pericyclic reactions as a major topic. They are usually covered in detail in a typical introductory organic chemistry course. Among the two fundamental approaches to pericyclic reactions, the FMO approach has gained some popularity at the undergraduate teaching level. It is simpler and can be based on a pictorial approach. A detailed understanding of molecular orbital theories and symmetry is not required.

- Pericyclic reactions have a *cyclic* transition state.
- While in this transition state, a concerted rearrangement of the electrons takes place that causes σ and π-bonds to simultaneously break and form.
- Pericyclic reactivity can be understood in terms of frontier molecular orbital (FMO) theory and the outcome of reactions can be predicted using the Woodward-Hoffmann rules.

Pericyclic reactions are popular with synthetic chemists because the reagents and conditions are mild and the reactions are usually very "clean" unlike so many organic chemical reactions that result in the formation of large quantities of brown-black, smelly by-product of unknown composition.

## 2.0. OBJECTIVES

After studying this Unit, you should be able to:

- Give a concise definition of pericyclic reactions
- Explain the mechanisms of pericyclic reactions and its associated terminologies
- State the characteristics of pericyclic reactions
- Explain various stereochemical notations

## 3.0 MAIN CONTENT

### 3.1 Mechanism of pericyclic reactions

Pericyclic reaction involves several simultaneous bond-making and bond-breaking processes with a cyclic transition state involving delocalized electrons. The combination of steps is called a ***concerted process*** where intermediates are skipped. We distinguish between ***concerted*** and ***stepwise*** reaction mechanisms on the basis of absence and presence of intermediate(s). Historically, pericyclic reactions were unusual in that they were clearly important in practice but seemed to have “no mechanism”; i.e., no intermediates could be identified. A concerted reaction mechanism may be ***synchronous*** or ***asynchronous***. The term “synchronous” is used when multiple bond-making or bond-breaking events occur to the same extent at the transition state. Of course, perfect synchronicity is rarely achieved. The HOMO is the “highest occupied molecular orbital”. The LUMO is the “lowest unoccupied molecular orbital”. Together, these are the ***frontier molecular orbitals*** **(FMO)**. If there is an orbital at the same energy level as a p orbital, this is an NBMO (nonbonding molecular orbital). In compounds for which a MO has just one electron, the orbital occupied by that electron is a SOMO (singly occupied molecular orbital).

Reactions that proceed by nearly simultaneous reorganization of bonding electron pairs by way of cyclic transition states have been termed pericyclic reactions. A pericyclic reaction is characterized as a change in bonding relationships that takes place as a ***continuous, concerted reorganization of electrons***. The term "***concerted***" specifies that there is ***one single transition state*** and therefore ***no intermediates*** are involved in the process. To maintain ***continuous electron flow***, pericyclic reactions occur through ***cyclic transition states***. The cyclic transition state must correspond to an arrangement of the ***participating orbitals*** which has to ***maintain a bonding interaction*** between the reaction components throughout the course of the reaction.

### 3.2 Characteristics of pericyclic reactions

Main characteristics of pericyclic reactions are:

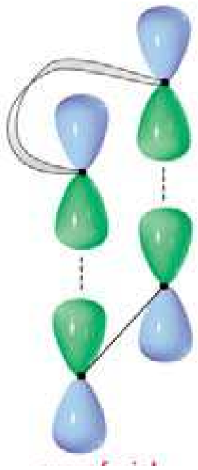
1. The pericyclic reactions occur in single step and hence there is no intermediate formed during the reaction.
2. They are relatively unaffected by solvent changes, the presence of radical initiators or scavenging reagents, or by electrophilic or nucleophilic catalysts.
3. They proceed by a simultaneous (concerted) series of bond breaking and bond making events in a single kinetic step, in a cyclic transition state, often with high stereospecificity.

4. No ionic, free radical or other discernible intermediates lie on the reaction path.

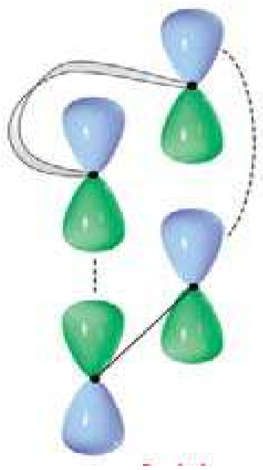
5. The configuration of the product depends on: (i) the configuration of reactants (ii) The number of electron pairs undergoing reorganization and (iii) the reaction conditions (like thermal or photochemical).

### 3.3 Stereochemical Notations

***3.3.1 Suprafacial and antarafacial shifts*** For pericyclic reactions, new stereo chemical designations are needed. **Cycloaddition reactions** and **sigmatropic rearrangements** both involve pairs of σ- bond-making events (or a coupled bond-making & bond-breaking) associated with a π-electron system.If all the bonding events take place on the same face of the π-system the configuration of the reaction is termed suprafacial. If the bonding events occur on opposite sides or faces of the π-system the reaction is termed antarafacial. For π systems and lone pairs, suprafacial interactions involve same face; antarafacial interactions involve opposite faces. For σ systems, the terms are defined as shown.



**Suprarafacial**



**Antarafacial**

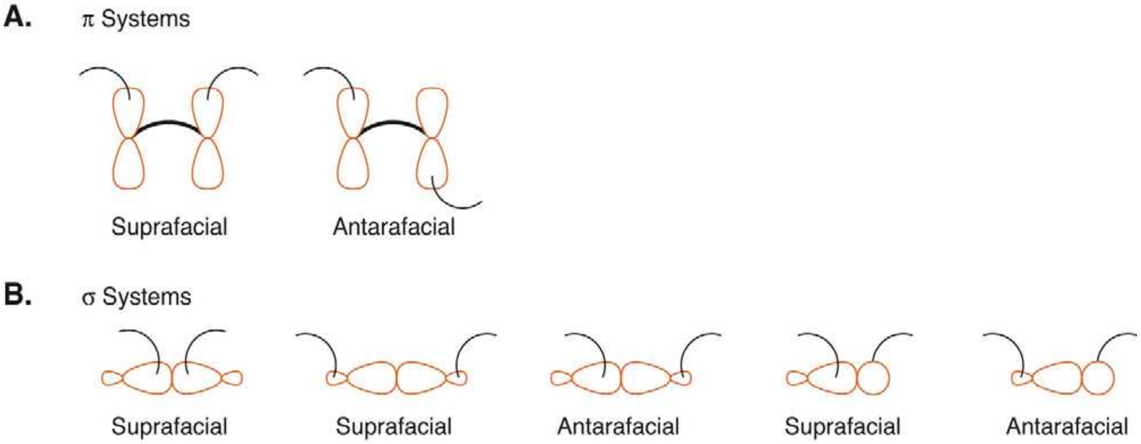
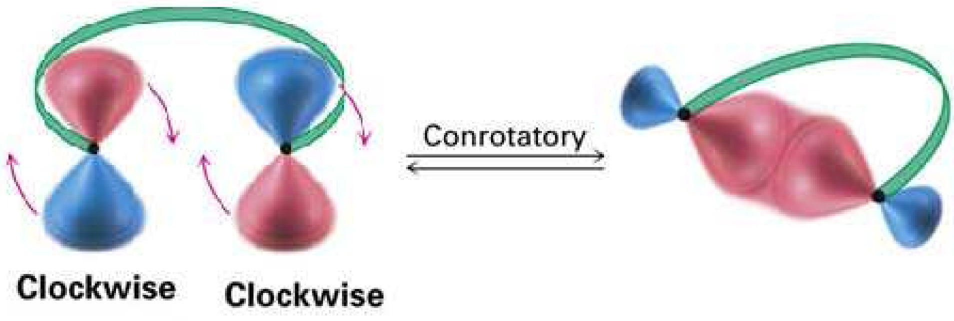


**Figure 1: Suprafacial and Antarafacial Interactions**

A different notation for configurational change is required for **electrocyclic** reactions. In these cases a σ-bond between the ends of a conjugated π-electron system is either made or broken with a corresponding loss or gain of a π-bond. For this to happen, the terminal carbon atoms of the conjugated π- electron system must be rehybridized with an accompanying rotation or twisting of roughly $90^{0}$. The lobes of like sign can be either on the same side or on opposite sides of the molecule. For a bond to form, the outermost pi lobes must rotate so that favorable bonding interaction is achieved. If lobes of like sign are on opposite sides of the molecule: both orbitals must rotate in the same direction, clockwise or counterclockwise .Woodward called this motion conrotatory .That is, when viewed along the axis of rotation, the two end groups may turn in the same direction, termed **conrotatory.** If two lobes of like sign are on the same side of the molecule, the two orbitals must rotate in opposite directions-one clockwise and one counterclockwise .Woodward called this a disrotatory opening or closure. When viewed along the axis of rotation, the two end groups may turn in the opposite directions, termed **disrotatory.** The prefixes **con** and **dis** may be remembered by association with their presence in the words *concur & disagree*. These two modes electrocyclic reaction are shown in the diagram in the general form in which they are most commonly observed. To form the new σ-bond in the electrocyclic reaction, the p orbitals at the end of the conjugated system must overlap head-to-head.



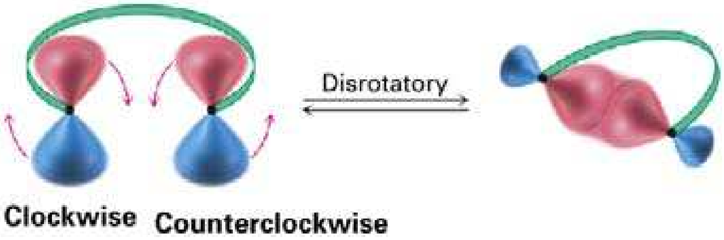
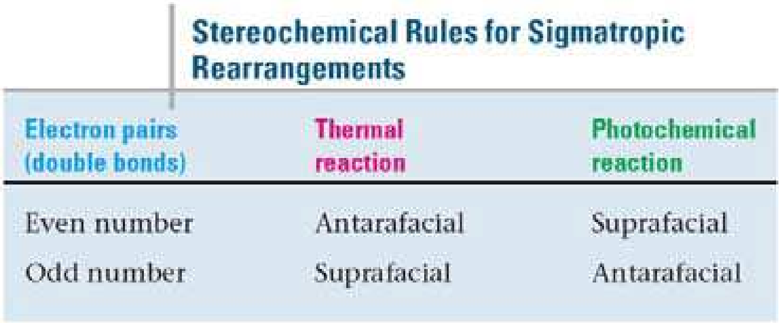


**Figure 2: Conrotatory and Disrotatory twisting**

Migration of a group across the same face of the pi system is a suprafacial rearrangement
Migration of a group from one face of the pi system to the other face is called an antarafacial rearrangement



**Stereochemical Rules for Sigmatropic Rearrangements**

| Electron pairs (double bonds) | Thermal reaction | Photochemical reaction |
|---|---|---|
| Even number | Antarafacial | Suprafacial |
| Odd number | Suprafacial | Antarafacial |

***3.3.2 Cycloadditions*** Two or more molecules or molecular components (from now on, "components") react together to form two or more bonds in a new ring. It should be noted for a sense of completeness that not all cycloadditions are pericyclic, and that they can occur in a stepwise manner. This allows the selection rules to be broken (i.e. [2+2] additions etc. can occur). The reactions can be made stepwise by equipping one reagent with a powerful electron-donating group (nucleophilic) and the other with a powerful electron withdrawing group (electrophilic). In assigning a cycloaddition to a class we assign descriptors π-, σ- or ω- to the electrons *directly involved* in the process (i.e. those that move when curly arrows are drawn), count how many electrons are involved in each component, and identify whether the components are reacting in suprafacial (s) or antarafacial (a) modes.

***3.3.3 Forbidden reactions and allowed reactions*** Not all cycloaddition reactions are allowed. For example, [2+2] reactions are not. This is due to a kinetic barrier to reaction (2 alkenes forming a 4 membered ring is thermodynamically favourable, but kinetically impossible). A "forbidden" reaction is expected to have an electronic barrier on the reaction pathway due to unfavorable orbital properties. An "allowed" reaction is not expected to have such a barrier. These terms are perhaps overly dramatic, but they indicate accurately the tendencies of certain reactions to occur or not to occur. Generally, a thermal pericyclic reaction is allowed if the number of electrons involved can be expressed as 4n+2. 4n is forbidden. Crudely, an odd number of curly arrows is allowed while an even number is forbidden. Conversely, photochemical pericyclic reactions are allowed if the number of electrons is 4n, but not if it is 4n+2. Note though that when putting that much energy into a reaction, other mechanisms may take precedence.

## 4.0 SUMMARY

In this unit you have learned that a pericyclic reaction is a chemical reaction in which concerted reorganization of bonding takes place throughout a cyclic array of continuously bonded atoms. It may be viewed as a reaction proceeding through a fully conjugated cyclic transition state. The number of atoms in the cyclic array is usually six, but other numbers are also possible. The term embraces a variety of processes, including cycloadditions, cheletropic reactions, electrocyclic reactions and sigmatropic rearrangements (provided they are concerted). Concerted means that all bonding changes occur at the same time and in a single step (no intermediates).

## 5.0 TUTOR-MARKED ASSIGNMENTS

1. Distinguish between (i) concerted and stepwise processes (ii) synchronous and asynchronous systems.
   (b)List four types of pericyclic reactions and give an example of each.

2. (a) What do the following acronyms stand for (i) HOMO (ii) LUMO (iii) SOMO?

## 6.0 REFERENCES

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2 .Barltrop, J.A., Coyl, J.D. *Excited states in organic chemistry*, 1975, London; New York: Wiley.
3. Pericyclic reaction - Wikipedia, the free encyclopedia

## UNIT 2 - TYPES OF PERICYCLIC REACTIONS

### 1.0 INTRODUCTION

More simply, the term “pericyclic” covers all concerted reactions involving a cyclic flow of electrons through a single transition state. While in this transition state, a concerted rearrangement of the electrons takes place which causes sigma and π- bonds to simultaneously break and form. Pericyclic reactions can be predicted and controlled to a great degree, which makes them very useful in synthesis. Pericyclic reactions are popular with synthetic chemists because the reagents and conditions are mild and the reactions are very "clean"... unlike so many organic chemical reactions that result in the formation of large quantities of brown-black, smelly by-product of unknown composition. Pericyclic reactivity can be understood in terms of frontier molecular orbital (FMO) theory and the outcome of reactions can be predicted using the Woodward-Hoffmann rules.

### 2.0 OBJECTIVES

At the end of this Unit, you should be able to:

- Explain the major categories of pericyclic reactions
- Give appropriate examples of each category of pericyclic reactions
- Compare different types of pericyclic reactions

### 3.0 MAIN CONTENT

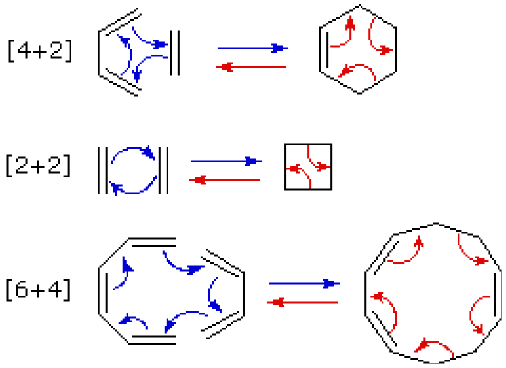
#### 3.1 General classification of pericyclic reactions

Pericyclic reactions are usually rearrangement reactions. The major classes of pericyclic reactions are: cycloaddition, electrolytic reaction, sigmatropic reaction, group transfer reaction, cheletropic reaction and dyotropic reaction. Within each subclass, it is common that reactions can either be induced to occur under thermal conditions with simple heating, or under photochemical conditions. The two methodologies are complementary.

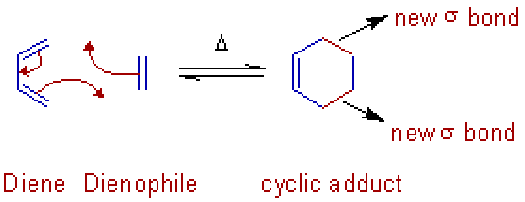
#### 3.2 Cycloaddition Reactions

A cycloaddition is a reaction that simultaneously forms at least two new bonds, and in doing so, converts two or more open-chain molecules into rings. The transition state for these reactions typically involves the electrons of the molecules moving in continuous rings, making it a pericyclic reaction. A concerted combination of two π-electron systems to form a ring of atoms having two new σ bonds and two fewer π bonds is called a cycloaddition reaction. The number of participating π- electrons in each component is given in brackets preceding the name, and the reorganization of electrons may be depicted by a cycle of curved arrows - each representing the movement of a pair of electrons. Ring-opening process is cycloreversion.

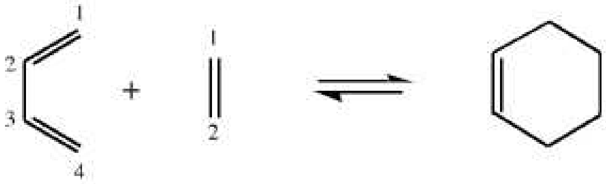
The most common cycloaddition reaction is the [4π+2π] cyclization known as the Diels-Alder reaction. In Diels-Alder terminology the two reactants are referred to as the diene and the dienophile. The following diagram shows examples of [4π+2π], a light induced [2π+2π] and [6π+4π] cycloadditions.



Cycloaddition reactions involve the formation of a cyclic product due to addition of two different π bond containing components, which are joined by newly formed two σ bonds at their ends at the expense of two π bonds. It is usually reversible and the backward reaction is also referred to as retro-cycloaddition or a cycloreversion. The classic example of cycloaddition is Diels-Alder reaction between a Diene and a Dienophile to give a cyclic adduct. Cycloaddition, and the reverse process retrocycloaddion, can be observed in the reaction between 1,3-butadiene and ethene to give cyclohexene.



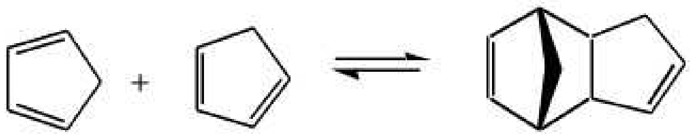
That is:



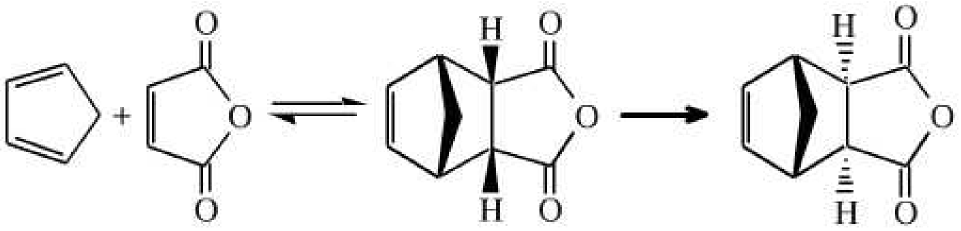
The 1,3-butadiene is a conjugated π-system with 4 π-electrons and the ethene is a conjugated π-system with 2 π-electrons. The reaction between 1,3-butadiene and ethene to give cyclohexene is described as a [4+2] cycloaddition reaction. This type of cycloaddition is also called a Diels-Alder reaction. In a Diels-Alder reaction the 4 π-electron system is referred to as "the diene" and the 2 π-electron system as the "dieneophile". These terms are used in related [4+2] reaction systems even when the functional groups are not actually dienes or alkenes.

Cycloaddition is a type of X + Y ⟶ X-Y complexation, and it follows the usual thermochemistry rules. The formation of the *Diels-Alder adduct* is an exothermic reaction. It follows that high temperatures favour retrocycloaddition and low temperatures favour adducts formation.

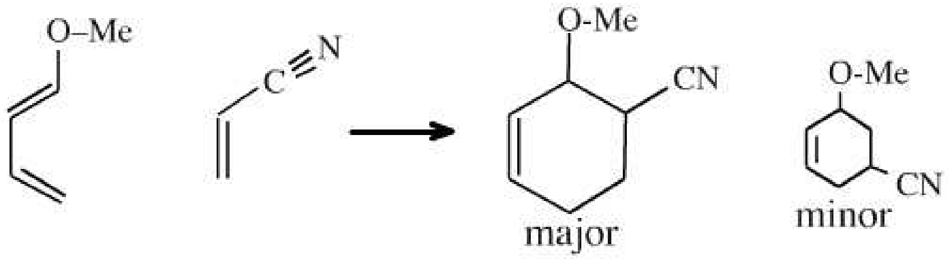
However, many cycloaddition reactions require moderate heating to overcome the activation energy. So a cycloaddition may require heating to make the reaction "go", but if it is heated too much the equilibrium will favour retrocycloaddition. The compound cyclopentadiene slowly undergoes cycloaddition with itself: one molecule of cyclopentadiene acts as a 4 π-electron diene and the other as a 2 π-electron dieneophile. The product is a Diels-Alder "adduct", often called dicyclopentadiene. This dimeric material can be *cracked* back to cyclopentadiene by heating at 150°C for an hour and then distilling off the diene monomer.



Diels-Alder cycloaddition reactions proceed more efficiently if the diene is electron rich and the dienophile is electron poor. Cyclopentadiene is electron rich. The way to make the dieneophile electron poor is to add electron withdrawing groups, such as carbonyl functions. Maleic anhydride is an electron poor dieneophile which reacts with cyclopentadiene to give an endo Diels-Alder adduct. Upon heating at 190°C, the endo conformation adduct adopts the more stable exo-adduct conformation.

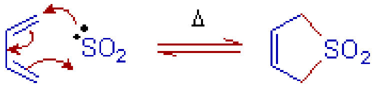


1-Methoxy-1,3-butadiene reacts with acrylonitrile to give 3-methoxy-4-cyanocyclohexene rather than the 3-methoxy-5-cyanocyclohexene isomer. This "ortho" regioselectivity of this reaction can be rationalised using FMO theory.



### 3.3 Cheletropic reactions

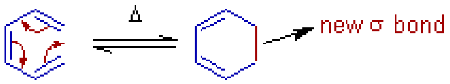
These are a special class of cycloadditions or retro-cycloadditions in which the two σ-bonds are either made or broken to the same atom. For example, the reversible addition of sulfur dioxide to 1,3-butadiene is an example of cheletropic reaction, in which the two new σ-bonds are made to the sulfur atom.



Note: In this reaction, a lone pair on sulfur atom is equivalent a π-bond and is reorganized. One π-bond and a lone pair are disappeared, whereas two σ-bonds are formed. Also note that sulfur atom is oxidized from +4 to +6 state.

### 3.4 Electrocyclic reactions

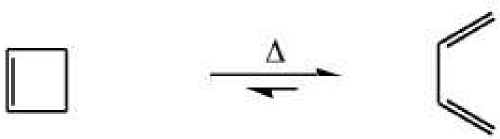
Electrocyclic reactios are intramolecular pericyclic reactions which involve the rearrangement of π-electrons in an open conjugated system leading to formation of a cyclic product with a new σ bond at the expense of a π-bond. However the electrocyclic reactions not only involve ring-closure but also ring opening, which are referred to as retro-electrocyclic reactions. For example, the formation of Cyclohexa-1,3-diene by heating Hexa-1,3,5-triene is an example of ring-closure electrocyclic reaction.



That is:

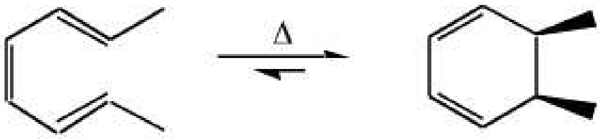
Note that the 3-alkene must be *cis* for the reaction to occur.

The reverse, or *retroelectrocyclic*, reaction can also occur. This is seen with the ring opening of cyclobutene to 1,3-butadiene:

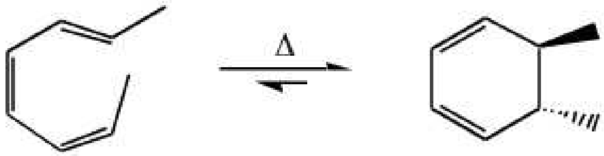


Electrocyclic reactions, like all pericyclic processes, exhibit great stereoselectivity. Consider two 1,3,5-hexatriene systems embedded into longer hydrocarbon chains.

*trans*-*cis*-*trans*-2,4,6-Octatriene will ring-close to give a *cis* ring:

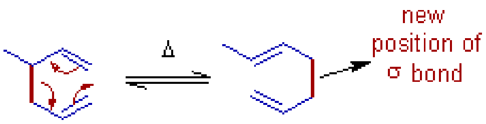


*trans*-*cis*-*cis*-2,4,6-Octatriene will ring close to give a *trans* ring:



### 3.5 Sigmatropic rearrangements

Sigmatropic rearrangements are concerted unimolecular isomerization reactions characterized by the overall movement of a σ-bond from one position to another with an accompanying rearrangement of π-electrons of conjugated system so as to accommodate the new σ-bond. The total number of σ-bonds and π-bonds remain unchanged. For example, the [3,3] Cope rearrangement. The σ-bond undergoing movement is shown as thick line.

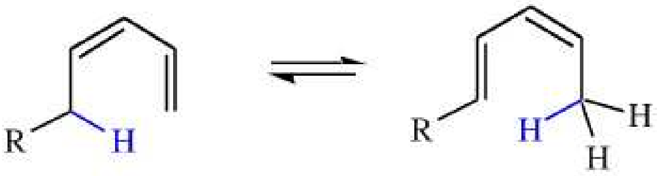


Note: Though looking like electrocyclic reactions, there is no reduction in the number of π-bonds in sigmatropic reactions.

Like electrocyclic reactions, sigmatropic rearrangements are unimolecular processes. Sigmatropic reactions involve the movement of a sigma-bond with the simultaneous rearrangement of the π-system.

Two examples illustrate this:

The [1,5] shift of hydrogen in a 1,3-pentadiene system:



The [3,3] Cope rearrangement:

Note that the generic "R" functions have been added so that the product can be distinguished from the starting materials.

The biosynthesis of vitamin D has photochemical step, and the reaction takes place in skin cells. A 1,3-cyclohexadiene system associated with the b ring of a steroid undergoes a photoactivated, retroelectrocyclisation to give 1,3,5-hexatriene system. The thermal reaction is not allowed because it would be necessary to form a six membered ring with a *trans*-alkene, a sterically impossible structure. 1,3,5-hexatriene system then undergoes a thermal [1,7] sigmatropic rearrangement to give vitamin D3. This is further processed in the liver.

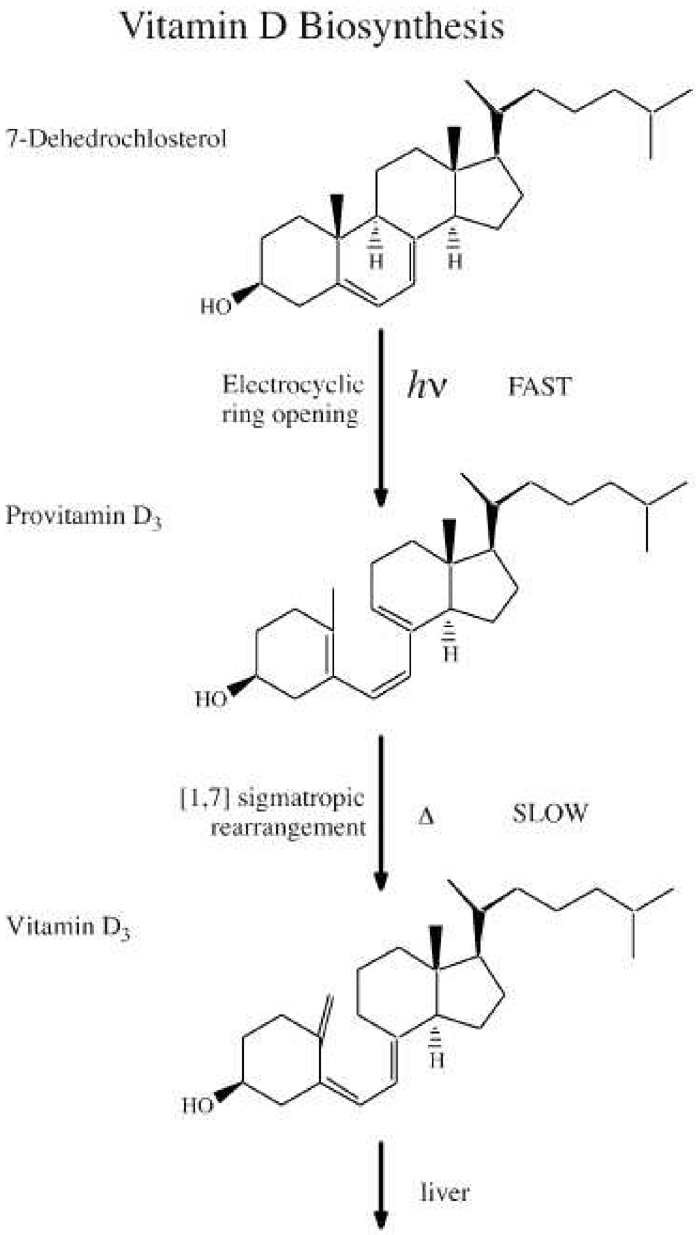
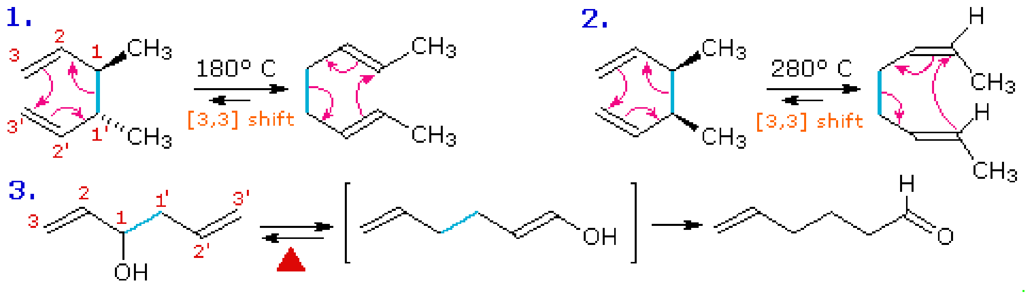


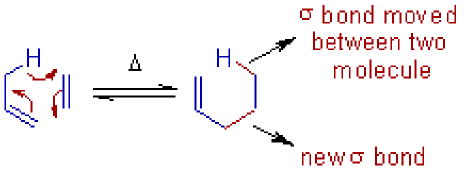
**Figure 1 Sigmatropic rearrangement in biosynthesis of vitamin D**

The [3,3] sigmatropic rearrangement of 1,5-dienes or allyl vinyl ethers, known respectively as the **Cope and Claisen rearrangements**, are among the most commonly used sigmatropic reactions. Three examples of the Cope rearrangement are shown in the following diagram. Reactions **1** and **2** demonstrate the stereospecificity of this reaction. Since each allyl segment is the locus of a [1,3] shift, the overall reaction is classified as a **[3,3] rearrangement**. The three curved arrows describe the redistribution of three bonding electron pairs in the course of this reversible rearrangement. The diene reactant in the third reaction is drawn in an extended conformation.



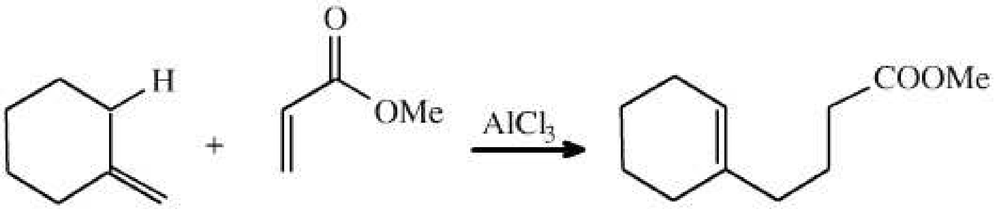
### 3.6 Group transfer pericyclic reaction

The concerted transfer of a group from one molecule to another due to concomitant movement of a σ-bond (from one molecule to another) and formation of a new σ-bond (between two molecules) at the expense of a π-bond is generally referred to as **group transfer** pericyclic reaction. For example, the ene reaction between propene and ethene to give 1-pentene is a classic example of group transfer reaction.

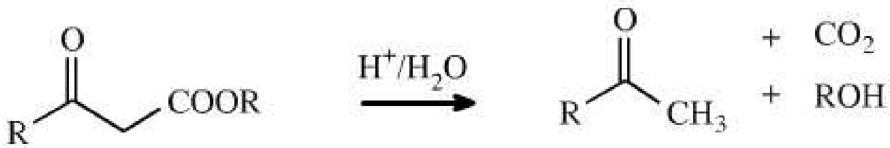


These reactions resemble sigmatropic rearrangements, since a σ-bond moves. However sigmatropic reactions are unimolecular reactions whereas the group transfer reactions are bimolecular. They also resemble cycloadditions, since a new σ-bond is formed at the expense of a π-bond. However, in group transfer reactions, no ring is formed.

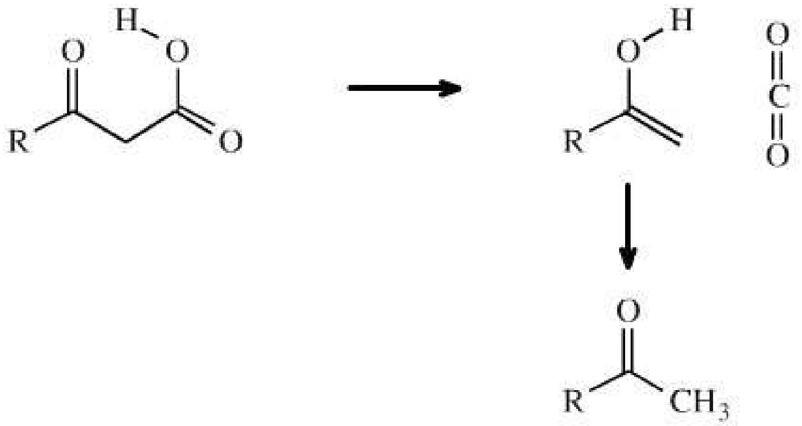
Another example of an ene reaction is seen with the reaction of methylenecyclohexene and methyl acrylate. (An aluminium chloride catalyst is required to "activate" the enone system.)



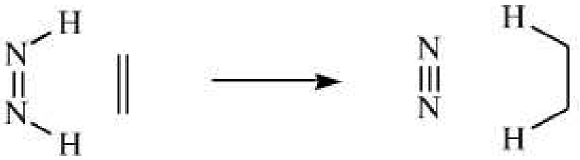
A common reaction in organic synthesis is the acid catalysed decarboxylation of a β-ketoester. The ester is hydrolysed to the β-ketoacid by the aqueous acid this rapidly loses carbon dioxide.



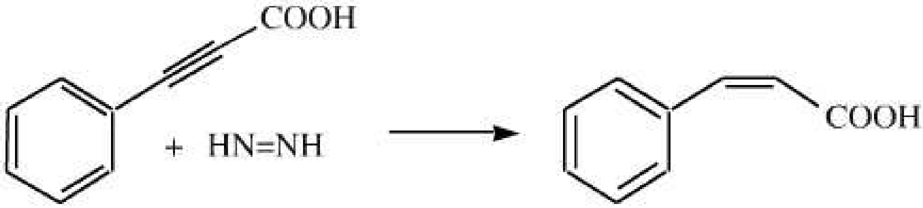
The reaction proceeds as a retroene reaction to give carbon dioxide and an enol system. The loss of $CO_2$ drives the reaction to the right hand side. The enol rapidly tautomerises to the methyl ketone:



Diimide is used as a reducing agent, it adds $H_2$ to C=C and N=N bonds and leaves other functions untouched:



For example, 3-phenylpropynoic acid is reduced to *cis*-3-phenylpropenic acid (*cis*-cinnamic acid) by diimide:



### 3.7 Dyotropic rearrangements

The pericyclic reactions which involve concerted intramolecular migration of two σ-bonds simultaneously are known as **dyotropic rearrangements**. However dyotropic reactions can also occur stepwise. There are two types of dyotropic rearrangements:

**Type-I:** Two migrating groups interchange their relative positions

**Type-II:** The σ-bonds are migrated to new bonding sites without any positional interchange for groups.

All types of pericyclic reactions are concerted and involve cyclic transition state without any intermediate formed during the reaction. The characteristics which differentiate them from each other are tabulated below.

***SAS 7:*** *Define pericyclic reactions.*

**Table 1 Comparison of different types of pericyclic reactions**

| **S.no** | **Type of pericyclic reaction** | **change in no. of σ bonds** | **change in no. of π bonds** | **comments** |
|---|---|---|---|---|
| **1)** | **Cycloaddition reactions** | +2 | -2 | A cyclic product is formed; may be intermolecular or intramolecular. |
| **2)** | **Electrocyclic reactions** | +1 | -1 | Intramolecular. |
| **3)** | **Sigmatropic reactions** | 0 | 0 | Intramolecular; migration of a σ-bond; rearrangement of π-electrons |
| **4)** | **Group transfer reactions** | +1 | -1 | Intermolecular transfer of a group; migration of a σ-bond from one molecule to another; formation of new σ-bond at the expense of one π-bond. |

| | | | | |
|---|---|---|---|---|
| **5)** | **Cheletropic reactions** | +2 | -1 (π-bond)<br>-1 (lone pair) | A cyclic product is formed; two σ-bonds are formed to same atom;<br>A lone pair is disappeared. |
| **6)** | **Dyotropic reactions** | 0 | 0 | Simultaneous migration of two σ-bonds. |

***SAS 8:*** *Name three pericyclic reactions.*

## 4.0 SUMMARY

Pericyclic reactions represent an important class of concerted (single step) processes involving π-systems. The fact that the reactions are concerted gives fine stereochemical control of the product. Pericyclic reactions have a *cyclic* transition state. While in this transition state, a concerted rearrangement of the electrons takes place that causes σ- and π-bonds to simultaneously break and form. A pericyclic reaction is a reaction that occurs as a result of reorganizing the electrons in the reactant(s). The electrocyclic reactions and sigmatropic rearrangements are intramolecular reactions while the cycloaddition reactions are usually intermolecular reactions. An electrocyclic reaction is a pericyclic process that involves the cyclization of a conjugated polyene**.**

Common features among the pericyclic reactions, they are:
- Concerted reactions
- Highly stereoselective
- Not affected by catalysts

## 5.0 TUTOR-MARKED ASSIGNMENTS

1. Classify cycloaddition reactions according to the number of pi electrons that interact in the reaction.
2. Show how electrons are redistributed in Cope and Claissen rearrangements
3. Give three examples of intramolecular pericyclic reactions.

## 6.0 REFERENCES

1. Woodward, R. B., Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: 1971, New York.
2. Barltrop, J.A., Coyl, J.D. () *Excited states in organic chemistry*; 1975, London; New York: Wiley.

# UNIT 3-ANALYSIS OF PERICYCLIC REACTIONS

## 1.0 INTRODUCTION

The Diels-Alder reaction is one type of a broader class of reactions that are known as pericyclic reactions. In 1965 two other Nobel laureates, Robert B.Woodward and Roald Hoffmann, published a series of short communications in which they presented a theoretical basis for these well known, but poorly understood pericyclic reactions. Their theory is called orbital symmetry theory. Subsequently other chemists published alternative interpretations of pericyclic reactions, one called frontier orbital theory, and another named aromatic transition state theory. All of these theories are based upon MO theory. In this unit we will use the Diels-Alder reaction to illustrate aspects of each of these theories.

## 2.0 OBJECTIVES

At the end of this Unit you should be able to:

- Analyze pericyclic reactions using the orbital correlation diagram method, the frontier molecular orbital (FMO) approach.
- Give the reaction conditions for pericyclic reactions
- Use Woodward-Hoffmann rules to predict allowed pericyclic reaction

## 3.0 MAIN CONTENT

### 3.1Analysis of Pericyclic reactions

Principal methods of analyzing pericyclic reactions are the orbital correlation diagram method, the frontier molecular orbital (FMO) approach, and the Mobius-Huckel transition state aromaticity approach.

### 3.2 Orbital correlation diagram method

The original approach of Woodward and Hoffmann involved construction of an "orbital correlation diagram" for each type of pericyclic reaction. The symmetries of the appropriate reactant and product orbitals were matched to determine whether the transformation could proceed without a symmetry imposed conversion of bonding reactant orbitals to anti bonding product orbitals. If the correlation diagram indicated that the reaction could occur without encountering such a symmetry-imposed barrier, it was termed symmetry allowed. If a symmetry barrier was present, the reaction was designated symmetry-forbidden.

In applying orbital correlation analysis, care must be taken to recognize the pertinent σ and π molecular orbitals and their delocalization as required by the symmetry of the transition state. This must be done for both the bonding and antibonding orbitals, and when necessary for n (nonbonded pair) orbitals. The following principles should be observed:

1**.** Bonding orbitals undergoing significant change in the reaction, and their antibonding counterparts, should be identified.

2. If polyene moieties are involved, all the molecular orbitals of that conjugated system must be used.

3. Ignoring non-participating substituents and heteroatoms, the symmetry elements of the essential molecular skeleton must be identified. All orbitals not clearly symmetric or antisymmetric with respect to these molecular symmetry elements need to be mixed or until they become so. In the construction of the orbital correlation diagram caution is exercised in choosing the symmetry elements.In this respect, the only important symmetry elements are those that bisect bonds that are made or broken in the reaction. Mixing is usually required for σ orbital analysis.

4. Each bonding and antibonding orbital included in the correlation is assigned one or more symmetry designations, S for symmetric, A for antisymmetric, depending on its fit with each characteristic symmetry element
5. The molecular orbitals are then arrayed according to their energy (increasing vertically), and location on the reaction coordinate (horizontally). Correlations of reactant and product orbitals are drawn so that orbitals of like symmetry are connected.

### 3.3 Orbital symmetry diagram (Orbital correlation diagram)

**3.3.1 Conservation of Orbital Symmetry Theory:** Explains the relationship among the structure and configuration of the reactant, the conditions (thermal or photochemical) under which the reaction takes place, and the configuration of the products. In 1965 R. B. Woodward and Roald Hoffmann of Harvard University proposed and demonstrated orbital symmetry rule, states that in-phase orbitals overlap during the course of a pericyclic reaction. Concerted reactions proceed most readily when there is congruence between the orbital symmetries of the reactants and products. In other words, when the bonding character of all occupied molecular orbitals is preserved at all stages of a concerted molecular reorganization, that reaction will most likely take place. The greater the degree of bonding found in the transition state for the reaction, the lower will be its activation energy and the greater will be the reaction rate. A symmetry-allowed pathway is one in which in-phase orbitals overlap. If a reaction is symmetry-forbidden, it cannot take place by a concerted pathway. If the symmetries of both reactant and product orbitals match the reaction is said to be symmetry allowed under the Woodward-Hoffmann Rules. If the symmetries of reactant and product orbitals do not correlate, the reaction is symmetry-disallowed and there are no low energy concerted paths.

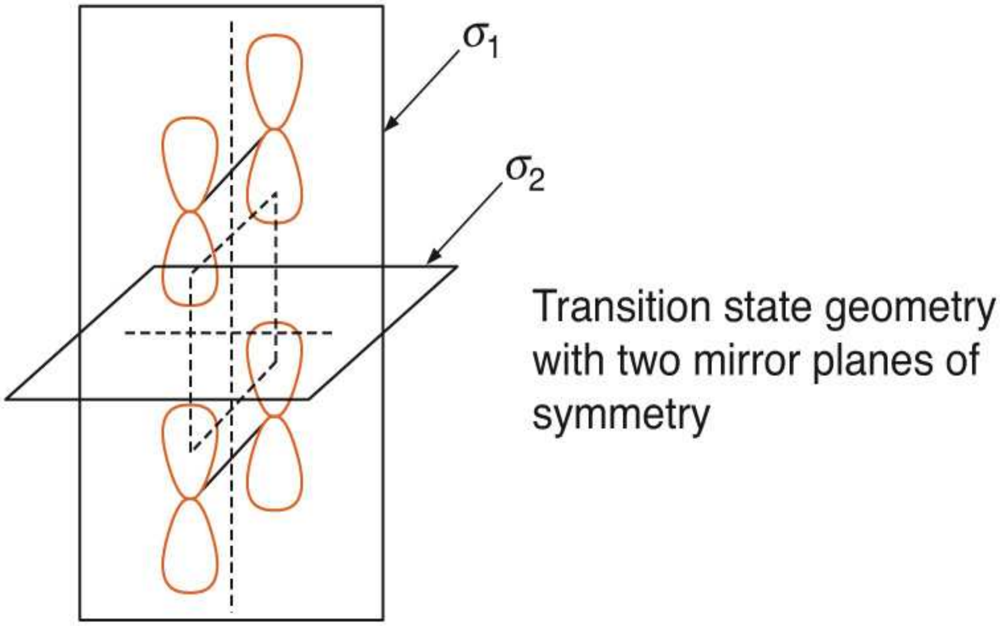
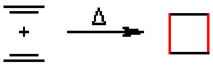


**Figure 1: Transition state geometry with two mirror planes of symmetry**

The fundamental feature of the orbital symmetry analysis is to draw the MOs of the reactant(s) and the MOs of the product(s). One then considers how the symmetries of the orbitals relate to each other. Orbitals of reactants are transformed smoothly into orbitals of products, with **conservation of orbital symmetry.**

### 3.3.2 Analysis of cycloaddition reaction by orbital correlation diagram method

Consider the [2+2] cycloaddition of two ethylene molecules. Let us assume that the two molecules approach each other with their π systems arranged symmetrically (i.e., a symmetric pericyclic transition state). If so, then we can identify two symmetry elements: two mirror planes, as shown. Each pair of interacting pi orbitals in the reactant combination leads to one σ bond in the cyclobutane product.



(2)

Figure 2 defines the conditions implied by the term head-to-head, namely that the reactants approach each other in parallel planes with the pi orbitals overlapping in the head-to-head fashion required for the formation of sigma bonds. The sigma-bonded atoms of each ethene lie in the two parallel planes shown in black in the figure. The p orbitals on each carbon lie in the vertical plane which is shown in blue. The two planes shown in red are symmetry planes. Plane 1 bisects the C-C bond of each ethene, while plane 2 lies half way between the two planes shown in black.

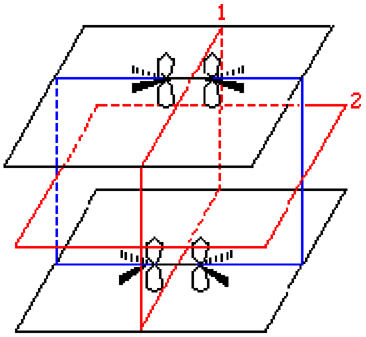
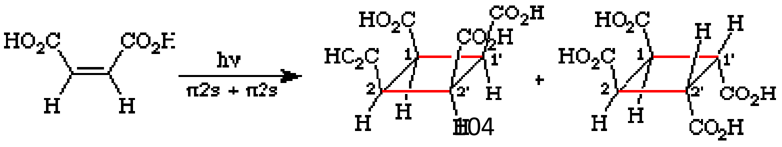


**Figure 2: Two ethylene molecules going Head-to-Head**

According to the conventions of orbital symmetry theory, the reaction shown in Figure 2 is classified as a π2s + π2s cycloaddition, where π indicates that the reaction involves a π system, the number 2 is the number of electrons in the reacting π system, and the letter s stands for suprafacial: if one lobe of a p orbital is considered as the top face, while the other lobe is called the bottom face, then a suprafacial interaction is one in which the bonding occurs on the same face at both ends of the π system. The orientation of the interacting ¼ systems depicted in Figure 2 implies something about the stereochemical outcome of the reaction. Consider the π2s + π2s cycloaddition shown in Equation 3, where the two new sigma bonds are shown in red.



(3)

Because the interacting π systems approach each other in a "head-to-head" fashion, the relative stereochemistry is the same in the products as it is in the reactants, i.e. the two carboxyl groups that are "*cis*" to each other in the alkene are "*cis*" to each other in the products.

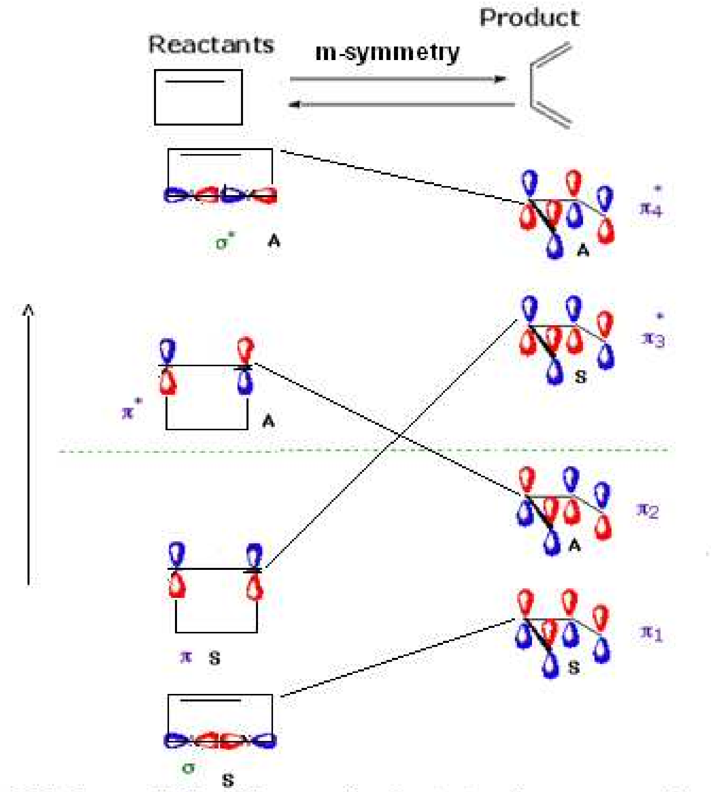
The alternative to a suprafacial interaction is an antarafacial reaction: in this case bonding occurs on the top face at one end of the πsystem and on the bottom face of the other. We will consider these ideas again when we discuss the Diels-Alders reaction. Molecular orbital theory describes the formation of the product in reaction 2 in terms of linear combinations the molecular orbitals of the reactants. Each reactant has two pi molecular orbitals of interest, $\psi_1$ and $\psi_2$. There are four combinations of these pi orbitals possible: $\psi_{1A} + \psi_{1B}$, $\psi_{1A} - \psi_{1B}$, $\psi_{2A} + \psi_{2B}$, and $\psi_{2A} - \psi_{2B}$, where the subscripts A and B are used to distinguish one ethene from the other. These combinations transform into the four sigma molecular orbitals in the product: $\sigma_{1A} + \sigma_{1B}$, $\sigma_{1A} - \sigma_{1B}$, $\sigma_{2A} + \sigma_{2B}$, and $\sigma_{2A} - \sigma_{2B}$. The diagram depicting the correlation of the reactant and product orbitals is shown in Figure 4. The numbers 1 and 2 in the diagram refer to the symmetry planes 1 and 2 in Figure 2.

### 3.3.3 Analysis of electrolytic reaction by orbital correlation diagram method

**Example 1: Interconversion of cyclobutene to butadiene.** For the disrotatory process not all the orbitals correlate with ground state orbitals of butadiene. The following conclusions can be drawn from the correlation diagram.

1. We expect a thermal transformation to take place only when the ground state orbitals of cyclobutene correlate with the ground state orbitals of butadiene. Even though σ correlates with π1, the π orbital of cyclobutene is not correlating with π2 of butadiene. Thus thermal transformation of cyclobutene to butadiene by disrotatory process is symmetry forbidden.
2. Irradiation of cyclobutene causes excitation with electron distribution σ2, π1, π*1, which correlates with first excited state orbitals of butadiene. The photochemical process is symmetry allowed.

$$\sigma^2, \pi^1, \pi^{*1} \rightleftarrows \pi_1^2, \pi_2^1, \pi_3^{*1}$$



Orbital correlation diagram for disrotatory inter conversion cyclobutene-butadiene

**Eample 2: Conrotaory ring opening of cyclobutene –butadiene –$C_2$ symmetry.** From the correlation diagram two conclusions can be drawn:

1. since there are correlation between the ground state orbitals of cyclobutene and butadiene.

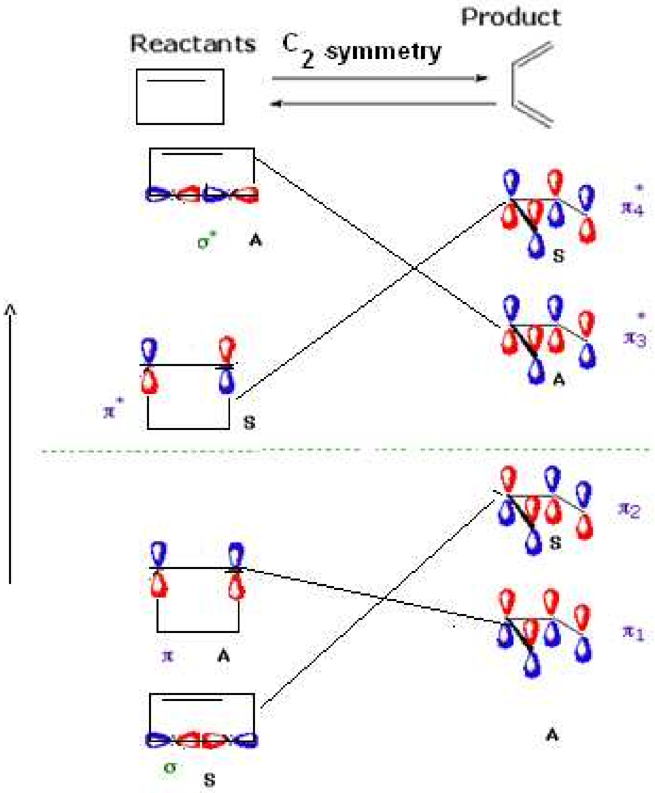
$$\sigma^2, \pi^2 \rightleftarrows \pi_1^2 , \pi_2^2$$

A thermal conrotatory process is symmetry allowed.

2. The first excited state of cyclobutene($\sigma_2$, $\pi_1$, $\pi^*{}_1$) correlates with not first excited state but an upper excited state of butadienethe process is symmetry forbidden.

$$\sigma^2, \pi^2, \pi^{*1} \cancel{\rightleftarrows} \pi_1^2 , \pi_2^1, \pi_3^{*1}$$

Similarly the first excited state of butadiene is correlating with a higher energy upper excited state of cyclobutene .i.e., a photochemical conrotatory process in either direction is symmetry forbidden.



Orbital correlation diagram for

conrotatory interconversion of cyclobutene- butadiene
($C_2$ symmetry)

On similar grounds we can work out the disrotatory and conrotatory modes interconversion of hexatriene – cyclohexadiene. It can be noted that the thermal disrotatory and photochemical conrotatory processes are symmetry allowed.
These generalizations are Woodward –Hoffmann rules for electro cyclic reactions which can be summarized as

### 3.4 Frontier Molecular Orbital Theory

Frontier Molecular Orbital Theory was developed in the 1960s by Kenichi Fukui who recognized that chemical reactivity can often be explained in terms of interacting Highest Occupied MOs (HOMOs), Lowest Unoccupied MOs (LUMOs) and Singly Occupied MOs (SOMOs).

- HOMO + LUMO -> bonding MO
- HOMO + HOMO -> antibonding MO

- LUMO + LUMO -> null interaction (no electrons)
- SOMO + SOMO -> bonding MO

The FMO approach was developed by Woodward & Hoffmann in the late nineteen sixties who used it to explain an apparently diverse set of reactions involving π-systems, including Diels-Alder cycloaddition. Hoffmann used the approach to explore transition metal complexes.

According to Frontier Orbital Theory it is possible to determine if a pericyclic reaction is allowed or forbidden by simply considering the symmetry relationship of the frontier orbitals of the reactants. The frontier orbitals are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The interaction between these orbitals, a so-called HOMO-LUMO interaction, is a concept that is similar to Lewis acid-Lewis base chemistry which involves the interaction of a filled orbital of the base with an empty orbital of the acid. According to Frontier Orbital Theory, a pericyclic reaction is allowed when the HOMO of one reactant has the same symmetry as the LUMO of the other. The bonding or antibonding interactions of the frontier molecular orbital(s) determine whether the reactions are thermally or photochemically allowed or forbidden.

Cycloaddition can be explained using frontier molecular orbital (FMO) theory. The alkene (dienophile) component has two electrons is a "single" π-bond. FMO theory, here, identifies the HOMO and LUMO components of this system:

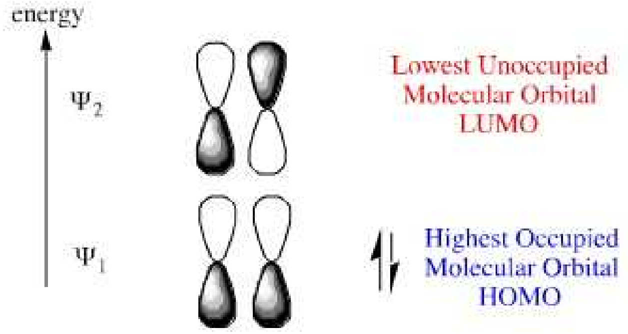


**Figure 3: HOMO/LUMO components of a dienophile**

Likewise, the diene which has four electrons in its conjugated π-system can have its HOMO and LUMO identified within FMO theory:

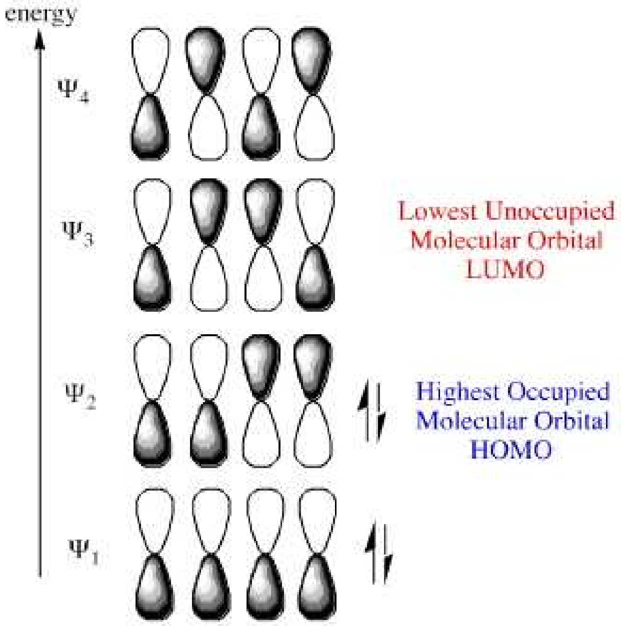


**Figure 4: HOMO/LUMO components of a diene**

If we examine the phases at the ends (termini) of the diene and dieneophile we find that the LUMO/HOMO interactions are phase matched:

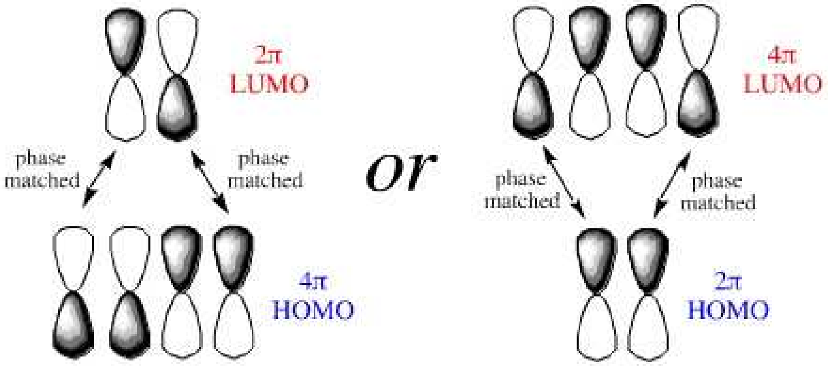


**Figure 5: LUMO/HOMO interactions of diene and dienophile**

Notice that the phases match whichever species is defined as the HOMO or LUMO. In reality, the electron rich species reacts via its HOMO and the electron poor species via its LUMO.

In the FMO diagrams above, the sizes or *coefficients* are all the same size, but usually they are of different sizes. The rule is that the coefficients match as well: small with small and large with large:

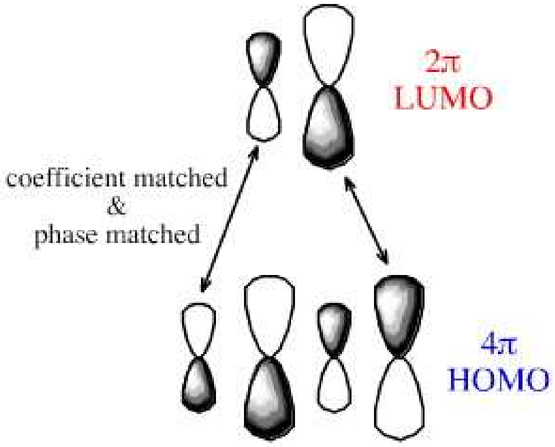


**Figure 6: Coefficient and phase matched HOMO/LUMO**

We can use Hückel MO theory to calculate the sizes of the coefficients at each of the atoms. (There is a web based HMO calculator, here, although at *meta-synthesis* we use a stand alone package: HMO by Allan Wissner.)

If the coefficients are calculated for 1-methoxy-1,3-butadiene the termini are +0.3 and –0.58 (or –0.3 and and +0.58). For acrylonitrile the coefficients are +0.2 and –0.66 (or –0.2 and +0.66).

The cycloaddition reaction proceeds so the coefficients "match", both in in terms of phase (*essential*) and in terms of coefficient magnitude: +0.3 with +0.2 and –0.58 with –0.66.

Thus, the regioselectivity of the cycloaddition can be explained:

Fukui realized that a good approximation for reactivity could be found by looking at the frontier orbitals (HOMO/LUMO). This was based on three main observations of molecular orbital theory as two molecules interact:

1. The occupied orbitals of different molecules repel each other.
2. Positive charges of one molecule attract the negative charges of the other.
3. The occupied orbitals of one molecule and the unoccupied orbitals of the other (especially the HOMO and LUMO) interact with each other causing attraction.

From these observations, frontier molecular orbital (FMO) theory simplifies reactivity to interactions between the HOMO of one species and the LUMO of the other. This helps to explain the predictions of the Woodward–Hoffmann rules for thermal pericyclic reactions, which are summarized in the following statement:

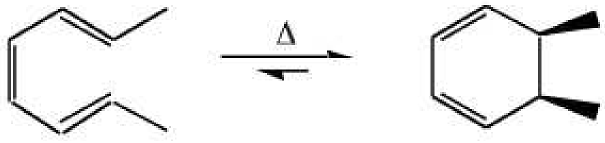
*"A ground-state pericyclic change is symmetry-allowed when the total number of* $(4q+2)_s$ *and* $(4r)_a$ *components is odd"*

$(4q+2)_s$ refers to the number of aromatic, suprafacial electron systems; likewise, $(4r)_a$ refers to antiaromatic, antarafacial systems. It can be shown that if the total number of these systems is odd then the reaction is thermally allowed.

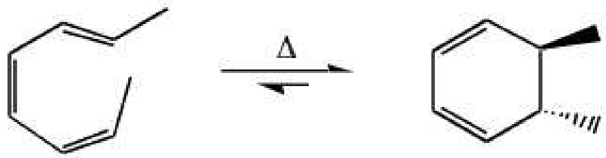
### 3.4.1 Analysis of Electrocyclic reactions by FMO

Electrocyclic reactions, like all pericyclic processes, exhibit great stereoselectivity. Consider two 1,3,5-hexatriene systems embedded into longer hydrocarbon chains.

*trans*-*cis*-*trans*-2,4,6-Octatriene will ring close to give a *cis* ring:



*trans*-*cis*-*cis*-2,4,6-Octatriene will ring close to give a *trans* ring:



As with cycloaddition, this selectivity can be explained by examining the FMOs, specifically the HOMO:

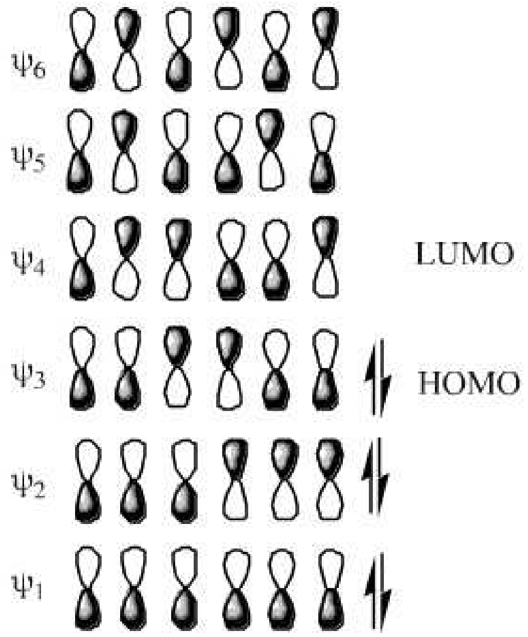


**Figure 7: Superimposition of HOMO upon triene system**

If the termini of the HOMO are superimposed upon the triene system, it can be seen that the end groups must rotate in a disrotatory manner (twist in opposite directions, when viewed front-on) to form the bond:

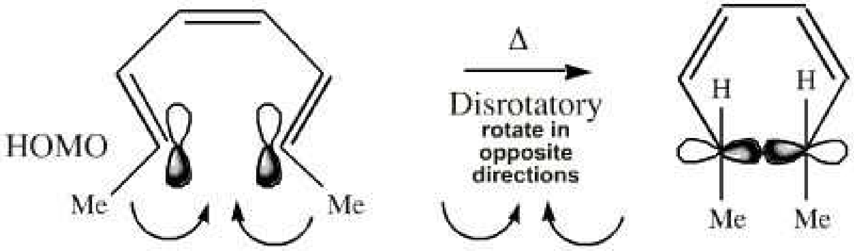


**Figure 8: Disrotatory twist of HOMO**

However, electrocyclic reactions can also occur photochemically. When photoactivated, an electron moves from the HOMO to the next orbital, the LUMO. (Now this orbital contains an electron it is no longer unoccupied, it is either a SOMO or an excited state HOMO).

The photoexcited system will ring-close in the opposite manner to the thermal system and the groups conrotate (twist the same way) to form the sigma bond:

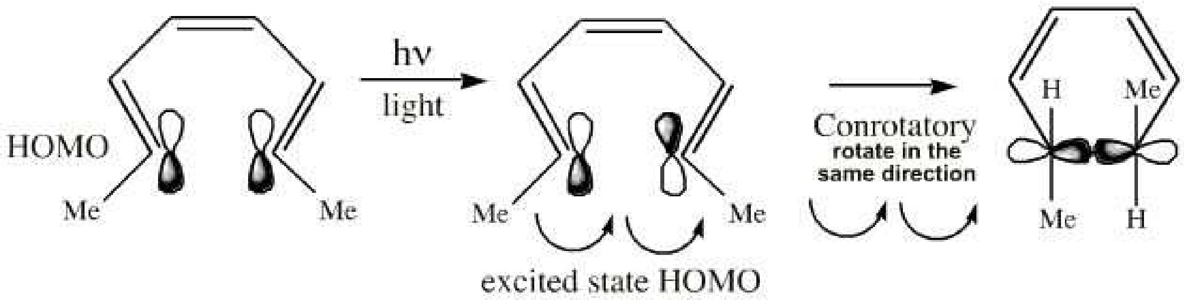


**Figure 9: Conrotation of photoexcited System**

The two products have different stereochemistry and are diastereomers.

This thermal and photo selectivity can be exploited in the reaction sequence below in which 1,3,5-cyclononatriene is converted into bicyclic systems, first with *cis* and then *trans* ring junctions.

The initial 1,3,5-cyclononatriene is all *cis*. This is thermally ring closed in a disrotatory manner and then photo-ring opened at -20°C in a conrotatory manner. The 1,3,5-cyclononatriene now has two *cis* and one *trans* double bonds, however, the nine membered ring is able to accommodate the strain of a *trans* alkene. Thermal ring closure gives the *trans*-ring junction.

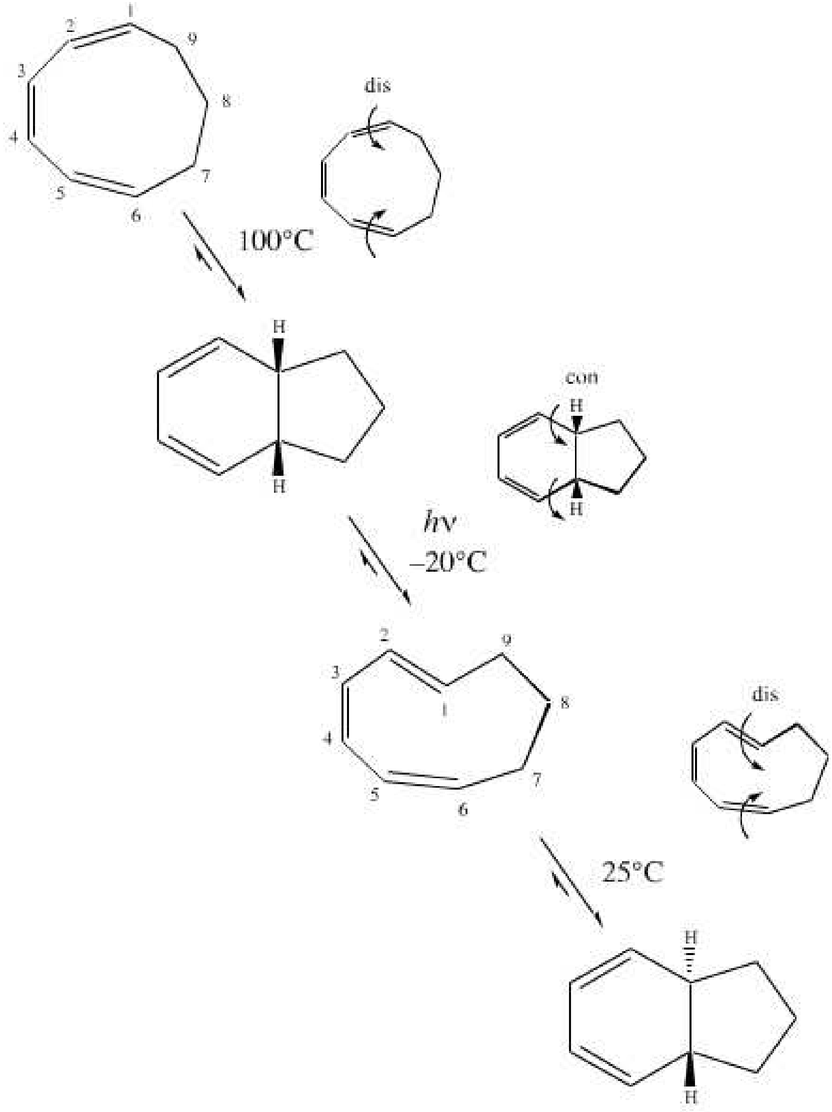
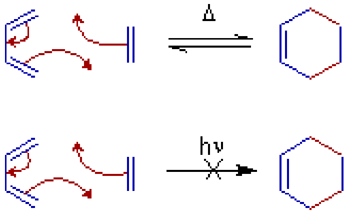


**Figure 10 Conrotatory twist of 1,3,5-cyclononatriene**

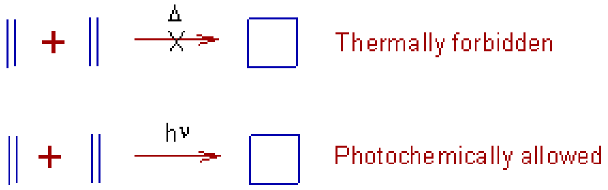
### 3.5 Reaction conditions for pericyclic reactions

It is observed that some of the pericyclic reactions occur only upon heating, whereas others are possible only under photochemical conditions e.g. the Diels-Alder reaction, a [4+2] cycloaddition occurs under thermochemical conditions and is not possible under photochemical conditions.



Diels Alder reaction
Allowed Thermally
but forbidden photochemically

Whereas the following [2+2] cycloaddition is forbidden under thermal conditions. But the reaction is possible under photochemical conditions.



## 3.6 Woodward-Hoffmann rules

To predict whether a pericyclic reaction is allowed or not under given condition, Woodward and Hoffmann proposed following set of rules Woodward-Hoffmann rules concept.

***A thermal pericyclic reaction is allowed in the ground state, when the total number of $(4q + 2)_s$ and $(4r)_a$ components is odd.Otherwise, if the total of $(4q + 2)_s$ and $(4r)_a$ components is even, the pericyclic reaction is allowed in the excited state i.e., under photochemical conditions.***

**Table 2** Woodward-Hoffmann rules for predicting allowed pericyclic reaction

| **Number of $(4q + 2)_s$ and $(4r)_a$ components** | **The condition under which the reaction is allowed** |
|---|---|
| odd | Thermal |
| even | Photochemical |

**Component:** A bond(s) or an orbital(s) taking part in the pericyclic reaction as a single unit can be considered as a component. It can have any number of electrons but may not have mixtures of π and σ electrons. E.g. A double bond is considered as a ${}_{\pi}2$ component, since there are two π electrons. A conjugated diene can be considered as ${}_{\pi}4$ component, since there are four π electrons. **'s'** represents suprafacial. A suprafacial component forms new bonds on the same face at its both ends. **'a'** represents antarafacial. An antarafacial component forms new bonds on the opposite faces of its both ends. E.g. ${}_{\pi}2_s$ represents a component containing two π electrons and forming new bonds in suprafacial manner. $_{\pi}4_{a}$ represents a component containing four π electrons and is going to form new bonds in antarafacial manner.

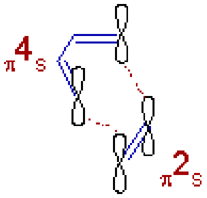
**q & r:** These are integers.

**$(4q + 2)_s$ component:** The suprafacial component which may have either 2 or 6 or 10 or _ _ _ electrons of same type. These numbers are obtained by substituting 'q' by 0 or 1 or 2 or _ _ _.

**$(4r)_a$ component:** The antarafacial component which may have either 4 or 8 or 12 or _ _ _ electrons of same type. These numbers are obtained by substituting 'r' by 1 or 2 or 3 or _ _ _.

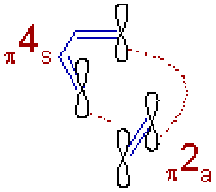
Likewise the meanings of **$(4q + 2)_a$ & $(4r)_s$** can be understood.

**Application:** Let us assume the diene and dienophile in Diels-Alder reaction are approaching suprafacially as shown below.



thermally allowed
suprafacial addition

Since there are 4 π electrons in diene, which is making bonds in suprafacial manner it is a **$(4q + 2)_s$** component**.** i.e, there is one $(4q + 2)_s$ component. And the alkene is a **$(4r)_s$** component, since it has 2 π electrons and is approaching the diene suparfacially i.e., there are **no** $(4r)_a$ components. Hence, the total number of $(4q + 2)_s$ and $(4r)_a$ components = 1 + 0 = 1, an odd number. Therefore Diels-Alder reaction is thermally allowed in ground state when both the components are approaching suprafacially. Hence it is termed as $_{\pi}4_{s}$ + $_{\pi}2_{s}$ cycloaddition. Antarafacial addition is not allowed under thermal conditions but is theoretically allowed under photochemical conditions in the excited state. However, the strain in the transition state while doing so forbids to do so.



photochemically allowed
antarafacial addition
but never takes place
under these conditions

**Note:** The orbitals shown in above diagrams are simple 'p' orbitals and are not the frontier molecular orbitals. Do not mix descriptions of FMO theory with Woodward-Hoffmann rules.

### 3.6.1 Simplified Woodward-Hoffmann rules

Application of above Woodward-Hoffmann rules to pericyclic reactions is tedious and cumbersome; following simplified rules can be used to predict theoretically allowed modes of pericyclic reactions under given conditions.

**Table 3 Simplified Woodward-Hoffmann rules**

| **No. of π electrons** | **Reaction conditions** | **Allowed mode** |
|---|---|---|
| (4n+2)<br>A Huckel number | Thermal | Supra (or) Dis |
| | Photochemical | Antara (or) Con |
| (4n)<br>A non Huckel number | Thermal | Antara (or) Con |
| | Photochemical | Supra (or) Dis |

Remember that even though the pericyclic reactions are allowed theoretically under both the conditions in either of the modes, sometimes the factors like steric hindrance and strain in the transition state may forbid the reaction to occur.

**Table 4 Pericyclic Reaction Rules**

| **Designation** | **Thermal** | **Photochemical** |
|---|---|---|
| π2s + π2s | forbidden | allowed |
| π2s + π4s | allowed | forbidden |
| π2s + π2a | allowed | forbidden |
| π2s + π4a | forbidden | allowed |
| π2a + π2a | forbidden | allowed |
| π2a + π4a | allowed | forbidden |

Before we move on, it is worthwhile to clarify the implications of the words allowed and forbidden. An allowed reaction is simply one with a low activation relative to some other pathway, while a forbidden reaction is a process for which there is significant activation energy. In terms of transition states, an allowed reaction proceeds via an aromatic transition state, while a forbidden reaction does not occur because the transition state would be "anti-aromatic."

## 4.0 SUMMARY

In this unit you have learnt the various rules of pericyclic reactions. All of the theories just described involve two basic assumptions

1. The orbitals overlap suprafacially on both π systems.
2. The reaction is thermally induced.

Given these assumptions, we can state the following:

- A thermally induced π2s + π4s cycloaddition reaction is allowed.
- A thermally induced π2s + π2s cycloaddition reaction is forbidden.

The rules are reversed when the reaction is photochemically induced:

- A photochemically induced π2s + π4s cycloaddition reaction is forbidden.
- A photochemically induced π2s + π2s reaction is allowed.

These rules are summarized in Table 4.4. Note that changing just one of the variables, i.e. faciality, energy source, or number of electrons (two electrons at a time), changes an allowed reaction to a forbidden one and vice versa. Below are some other fine points:

- A *cycloaddition reaction* is a reaction in which two unsaturated molecules add to one another, yielding a cyclic product
- It is controlled by orbital symmetry; it takes place when a bonding interaction occurs between the HOMO of one reactant and the LUMO of the other.
- Major examples: 1) Diels-Alder reaction (thermal); 2) [2+2] cycloaddition (photochemical)
- *Woodward-Hoffman Rules***:** pericyclic reactions can only take place if the symmetries of the reactant molecular orbitals are the same symmetries as the product molecular orbitals (*lobes of reactant MO's must be of the correct algebraic sign for bonding to occur in the transition state leading to the product*).
- *Frontier Orbital Theory:* we need to consider only *two* molecular orbitals, the HOMO and LUMO, to predict the structure of the product; called frontier MO's.
- *Conservation of Orbital Symmetry Theory:* explains the relationship among the structure and configuration of the reactant, the conditions (thermal or photochemical) under which the reaction takes place and the configuration of the products and states that in-phase orbitals overlap during the course of a pericyclic reaction.

## 5.0 TUTOR-MARKED ASSIGNMENTS

1 Show the formation of Cyclohexa-1,3-diene from Hexa-1,3,5-triene in an electrocyclic reaction.

2(a) State the Woodward-Hoffmann's rule for pericyclic reactions
(b) Explain the terms allowed and forbidden reactions.

## 6.0 REFERENCES

3. Woodward, R. B., Hoffmann, R. (1971). *The Conservation of Orbital Symmetry*; Academic Press: New York
4. Barltrop, J.A., Coyl, J.D. (1975) *Excited states in organic chemistry*. London ; New York: Wiley.

## SOLUTIONS TO SELF ASSESSMENT EXERCISES

1). Photochemical equivalence law or photoequivalence law.
2). Return of an excited molecule to the ground state by emission of light (luminescence, fluorescence, phosphorescence).
3).Photodissociation results when the excited molecule breaks apart into atomic and/or molecular fragments A and B.

*4).* Fluorescence, phosphorescence, internal conversion and intersystem crossing.

5). Internal conversion and intersystem crossing.

6). Phototropism.

7).Pericyclic reactions are concerted and involve cyclic transition state without any intermediate formed during the reaction.

8). Three types of pericyclic reactions: 1) electrocyclic, 2) cycloaddition, 3) sigmatropic rearrangement.

**Course Developer: Mr O. I. Adeniran**