Chapter 5

Spectroscopy and Green Chemistry

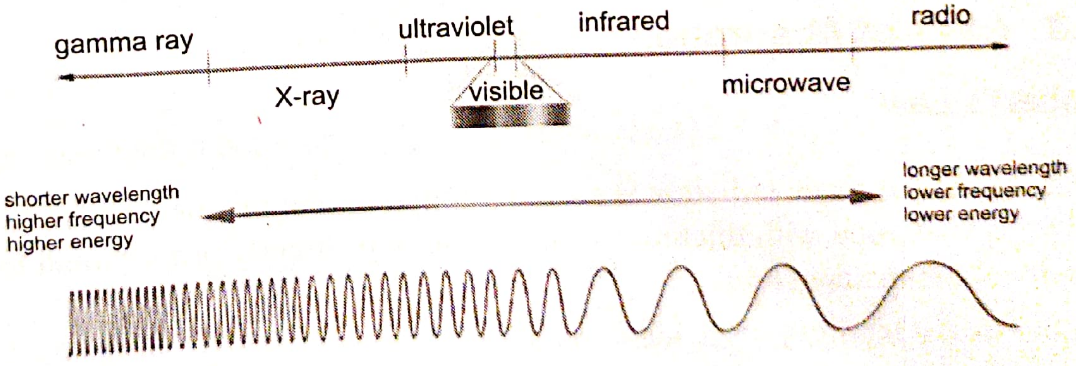
5.1 Spectroscopy

5.1.1 Introduction

It is the branch of science that deals with the study of interaction of matter with light or electromagnetic radiation.

5.1.2 Electromagnetic Spectrum

Electromagnetic spectrum or EM spectrum is the range of all types of electromagnetic radiation. The distribution of the radiation is based on their wavelength and frequency. The waves that have shorter wavelength are more energetic while the waves with longer wavelength are less energetic. Based on wavelength and frequency, the spectrum is divided into seven electromagnetic waves. They are measured in Hertz.



Comparison of wavelength, frequency and energy for the electromagnetic spectrum.

Types of Electromagnetic Waves:

Following is the list of types of electromagnetic waves:

Gamma rays: These are part of electromagnetic spectrum which includes visible as well as invisible radiations and their wavelength is below 0.01nm. These have the highest frequency which is greater than 10 Hz.

X-rays: These are parts of the electromagnetic spectrum and their wavelength is in the range 0.01nm to 10nm. They find applications in healthcare industry.

Ultraviolet (UV) rays: These are the part of electromagnetic spectrum with wavelength between 10nm to 400nm. When there is a continuous exposure of the skin to these rays, they tans skin and create burns. These will be produced by hot materials in space.

Visible light: These are part of the electromagnetic spectrum which lies between UV rays and infrared rays. The wavelengths of these light are 400nm to 750nm. These are generated by light bulbs.

Infrared radiation: These are the part of electromagnetic spectrum and their wavelength range is between 750nm to 1mm. These are also referred to as thermal waves as they have heat inducing property.

Microwaves: These are part of electromagnetic spectrum and is known as microwave radiation. Their wavelength range is between 1mm to 1m. In the electromagnetic spectrum series, microwaves is between infrared radiation and radio waves.

Radio waves: These are part of electromagnetic spectrum and have the longest wavelengths and huge band of frequencies. Their wavelength is greater than 1m. They find applications in radio communication, broadcasting etc.

5.1.3 Laws of Absorption

Lambert's Law

When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light.

Let I be the intensity of incident radiation.

x be the thickness of the solution. Then

$$-\frac{dI}{dx}\alpha I$$

$$\text{So, } -\frac{dI}{dx} = KI$$

Integrate equation between limit I= I_0 at $x = 0$ and $I = I$ at $x = l$, We get,

$$\ln\frac{I}{I_0} = -Kl$$

$$2.303\log\frac{I_0}{I} = Kl$$

$$\log\frac{I_0}{I} = \frac{K}{2.303}l$$

$$\text{where, } \log\frac{I_0}{I} = A \quad \text{Absorbance}$$

$$\frac{K}{2.303} = E \quad \text{Absorption coefficient}$$

$$A = E.l \quad \text{Lambert's Law}$$

Beer's Law

When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light as well as concentration of the solution.

Let I– be the intensity of incident radiation.

x– be the thickness of the solution.

C– be the concentration of the solution. Then

$$-\frac{dI}{dx} \alpha C.I$$

$$\text{So, } -\frac{dI}{dx} = K.C.I$$

Integrate equation between limit $I = I_0$ at $x = 0$ and $I = I$ at $x = l$,

We get,

$$\ln\frac{I}{I_0} = -k.c.l$$

$$2.303\log\frac{I_0}{I} = k.c.l$$

$$\log\frac{I_0}{I} = \frac{k}{2.303}c.l$$

$$\text{where, } \log\frac{I_0}{I} = A \quad \text{Absorbance}$$

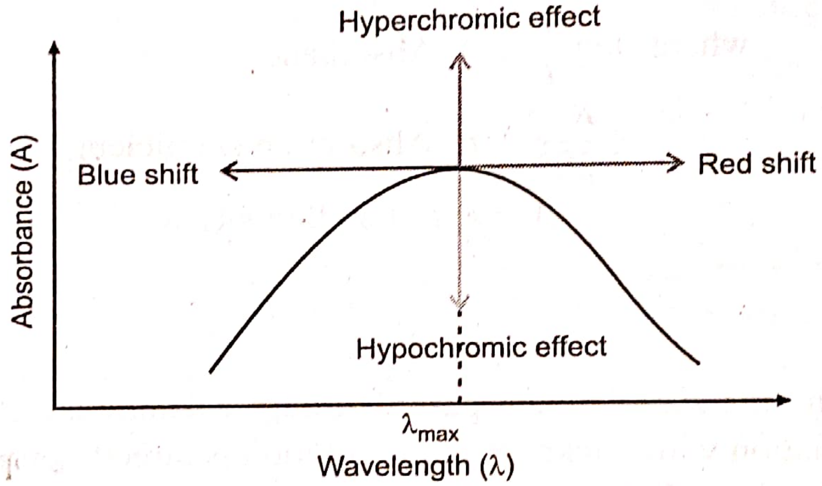
$$\frac{k}{2.303} = \in \quad \text{Molar extinction coefficient}$$

$$A = \in .C.l \quad \text{Beer's Law}$$

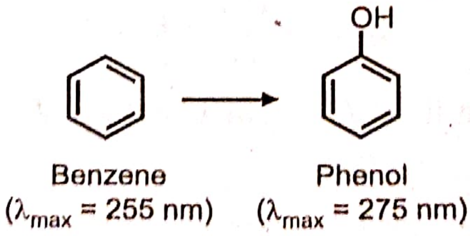
From the equation it is seen that the absorbance which is also called as optical density (OD) of a solution in a container of fixed path length is directly proportional to the concentration of a solution.

5.1.4 Absorption and Intensity Shifts

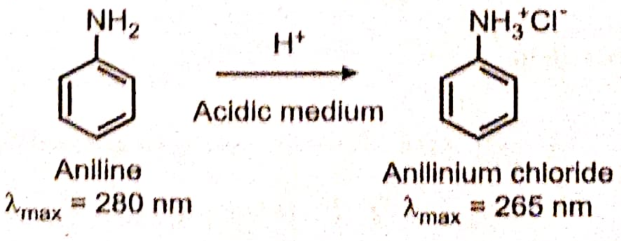
There are four types of shifts observed in the UV spectroscopy.



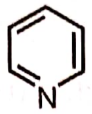
a) **Bathochromic effect:** This type of shift is also known as red shift. Bathochromic shift is an effect by virtue of which the absorption maximum is shifted towards the longer wavelength due to the presence of an auxochrome or change in solvents.The nonbonding to pie* transition of carbonyl compounds observes bathochromic or red shift.



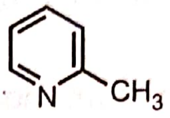
b) **Hypsochromic shift:** This effect is also known as blue shift. Hypsochromic shift is an effect by virtue of which absorption maximum is shifted towards the shorter wavelength. Generally, it is caused due to the removal of conjugation or by changing the polarity of the solvents.



c) **Hyperchromic shift:** Hyperchromic shift is an effect by virtue of which absorption maximum increases. The introduction of an auxochrome in the compound generally results in the hyperchromic effect.

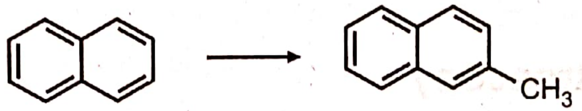


Pyridine
$\lambda_{max} = 257$ nm
$\epsilon_{max} = 2750\ Mol^{-1}cm^{-1}$



2-methyl pyridine
$\lambda_{max} = 262$ nm
$\epsilon_{max} = 3560\ Mol^{-1}cm^{-1}$

d) **Hypochromic shift:** Hypochromic shift is defined as the effect by virtue of intensity of absorption maximum decreases. Hypochromic shift occurs due to the distortion of the geometry of the molecule with an introduction of new group.



Naphthalene
$\epsilon_{max} = 19000\ Mol^{-1}cm^{-1}$

2-Methyl Naphthalene
$\epsilon_{max} = 10250\ Mol^{-1}cm^{-1}$

5.1.5 Concept of Chromophore and Auxochrome

Chromophore

The part of a molecule responsible for imparting color, are called as chromophores.

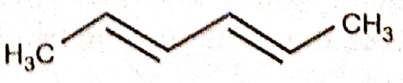
(OR)

The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ transitions.

e.g. $NO_2, N=O, C=O, C=N, C \rightarrow N, C=C, C=S$, etc.

- Non-conjugated alkenes show an intense absorption below 200 nm & are therefore inaccessible to UV spectrophotometer.
- When double bonds are conjugated in a compound λ_{max} is shifted to longer wavelength.

1,5 - hexadiene has $\lambda_{max} = 178$ nm



2,4 - hexadiene has $\lambda_{max} = 227$ nm

Auxochrome

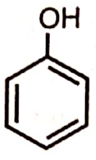
The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of absorption.

(OR)

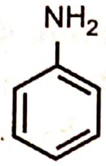
The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

Ex:- $-OH, NH_2, NR_2, NHR, SH, OR$, etc.

Benzene λ_{max} = 255 nm



Phenol λ_{max} = 275 nm



Aniline λ_{max} = 280 nm

5.1.6 UV Spectroscopy

UV spectroscopy is an important tool in analytical chemistry. The other name of UV (Ultra-Violet) spectroscopy is Electronic spectroscopy as it involves the promotion of the electrons from the ground state to the higher energy or excited state.

Introduction to UV spectroscopy

UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (10nm-400nm) is absorbed by the molecule. Absorption of the ultra-violet radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the ultra-violet radiation that are absorbed is equal to the energy difference between the ground state and higher energy states ($\Delta E = h\upsilon$).

Principle of UV spectroscopy

Any molecule has either n, π or σ or a combination of these electrons. These bonding ($\sigma \& \pi$) and non-bonding (n)electrons absorb the characteristic radiation and undergoes transition from ground state to excited state.

By the characteristic absorption peaks, the nature of the electrons presents and hence the molecular structure can be elucidated.

- When the molecule absorbs ultraviolet or visible light, its electrons get promoted from the ground state to the higher energy state.

In the ground state, the spins of the electrons in each molecular orbital are essentially paired.

- In the higher energy state, if the spins of the electrons are paired, then it is called an excited singlet state.
- On the other hand, if the spins of the electrons in the excited state are parallel, it is called an excited triplet state.
- The triplet state is always lower in energy than the corresponding excited singlet state.
- Therefore, triplet state is more stable as compared to the excited singlet state.
- An excited singlet state is converted to excited triplet state with the emission of energy as light.
- The higher energy states are designated as high energy molecular orbitals and also called antibonding orbitals.
- Energy absorbed in the ultraviolet region produces changes in the electronic energy of the molecule resulting from transition of valence electrons in the molecule.
- Three distinct types of electrons are involved organic molecule. These are as follows 'σ' electrons, 'π' electrons, 'n' electrons.

The electrons in a molecule can be of one of three types: namely σ (single bond), π (multiple-bond), or non-bonding (n- caused by lone pairs). These electrons when imparted with energy in the form of light radiation get excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and the resulting species is known as the excited state or anti-bonding state.

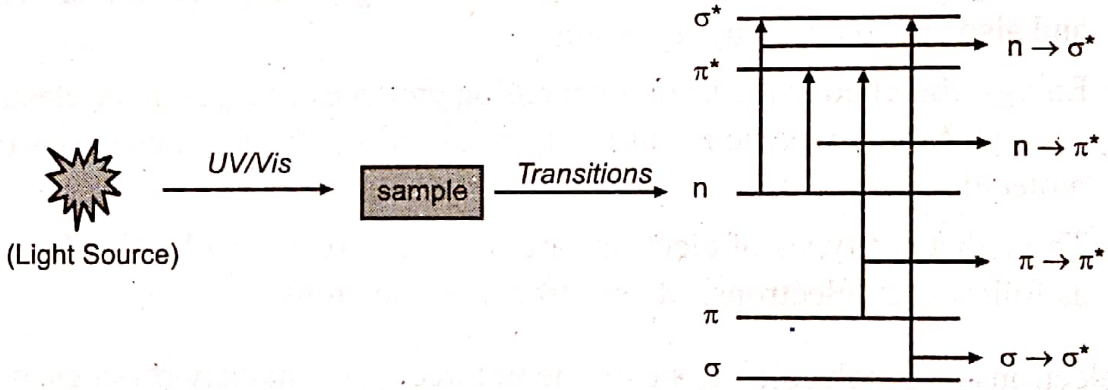
1. σ-bond electrons have the lowest energy level and are the most stable electrons. These would require a lot of energy to be displaced to higher energy levels. As a result these electrons generally absorb light in the lower wavelengths of the ultraviolet light and these transitions are rare.
2. π-bond electrons have much higher energy levels for the ground state. These electrons are therefore relatively unstable and can be excited more easily and would require lesser energy for excitation. These electrons would therefore absorb energy in the ultraviolet and visible light radiations.
3. n-electrons or non-bonding electrons are generally electrons belonging to lone pairs of atoms. These are of higher energy levels than π-electrons and can be excited by ultraviolet and visible light as well.

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy.

Types of Transitions

In U.V spectroscopy molecule undergo electronic transition involving σ, π and n electrons. Four types of electronic transition are possible.

i. $\sigma \rightarrow \sigma^*$ transition
ii. $\pi \rightarrow \pi^*$ transition
iii. $n \rightarrow \sigma^*$ transition
iv. $n \rightarrow \pi^*$ transition



i. $\sigma \rightarrow \sigma^*$ Transition:

- An electron in a bonding ? orbital of a molecule is excited to the corresponding anti-bonding orbital by the absorption of radiation.
- To induce a $\sigma \rightarrow \sigma^*$ transition it requires large energy.

Ex: Methane (CH_4) contain only single C-H bonds it undergo only $\sigma \rightarrow \sigma^*$ transition only, it gives absorption maximum at 125nm.

ii. $\pi \rightarrow \pi^*$ transitions

- π electron in a bonding orbital is excited to corresponding anti-bonding π^*.
- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, aromatic compounds, etc undergo $\pi \rightarrow \pi^*$ transitions.

Ex: Alkenes generally absorb in the region 170 to 205 nm.

iii. $n \rightarrow \sigma^*$ transition

- Saturated compounds containing atoms with lone pair of electrons like O,N,S and halogens are capable of $n \rightarrow \sigma^*$ transition.
- It require less energy than the $\sigma \rightarrow \sigma^*$ type.
- Most of the absorption peaks appearing below 200nm.
- In the presence of polar solvents the absorption maximum tend to shift shorter wavelength.

Ex: Water, ethanol.In this the peaks in U.V region relatively small.

iv. $n \rightarrow \pi^*$ transitions

- An electron from non-bonding orbital is promoted to anti-bonding π^* orbital.
- Compounds containing double bond involving hetero atoms (C=O, N=O) undergo such transitions.
- $n \rightarrow \pi^*$ transitions require minimum energy and show absorption at longer wavelength around 300 nm.

Ex: Carbonyl compounds.

Applications of UV Spectroscopy

1. **Structure elucidation of organic compounds:** UV-Visible absorption spectroscopy is useful in the structure elucidation of organic compounds such as the presence or absence of unsaturation or hetero atoms etc.
2. **Detection of impurities:** Impurities present in organic compounds can be detected by UV-Visible absorption spectroscopy.
3. **Detection of extent of conjugation:** The extent of conjugation in the polyenes can be detected with the help of UV spectroscopy. With the increase in double bonds the absorption shifts towards the longer wavelength.
4. **Identification of an unknown compound:** An unknown compound can be identified with the help of UV spectroscopy. The spectrum of unknown compound is compared with the spectrum of a reference compound and if both the spectrums coincide then it confirms the identification of the unknown substance.
5. **Detection of functional groups:** UV-Visible absorption spectroscopy is used to detect the presence of certain functional groups present in compounds.

6. **Detection of geometrical isomers (Trans and Cis):** In the case of geometrical isomers, trans isomers exhibit slightly longer wavelength than the corresponding cis isomers.

5.1.7 Infrared (IR) [OR] Vibrational Rotational Spectroscopy

- IR spectroscopy is the study of interaction between infrared radiations and matter.
- Infrared radiations refers broadly to that part of electromagnetic spectrum between visible and microwave region.
- IR spectroscopy is an important analytical technique for determining the structure of both inorganic & organic compounds.
- But it is particularly used to identify different functional groups present in organic molecules.
- IR spectroscopy is also useful in molecular structure determination.
- The radiation sources used are incandescent lamp, Nernst glower etc., and the detectors used are thermal and photon detectors.

Range: In terms of wavenumber IR region is from 12500 cm^{-1} to 50 cm^{-1}. (The wavelength region from 0.8 μm to 200 μm. But representation in wavelength is not common for IR spectroscopy).

Near IR region: 12500 - 4000 cm^{-1} (0.8 - 2.5 μm).

Mid IR region: 4000 - 667 cm^{-1} (2.5 - 15 μm),

4000 - 1450 cm^{-1} is functional group region.

1450 - 667 cm^{-1} is fingerprint region.

Far IR region: 667 - 50 cm^{-1} (15 - 200 μm)

Mid IR region is the main important region. Almost all functional groups absorb in this region.

Principle of IR Spectroscopy

- The principle of IR spectroscopy is related to the vibrational and rotational energy of a molecule.
- When the frequency of the IR radiation is equal to the natural frequency of vibration, the molecule absorb IR radiation and a peak is observed.
- Absorption of IR radiation causes an excitation of molecule from a lower to the higher vibrational level.

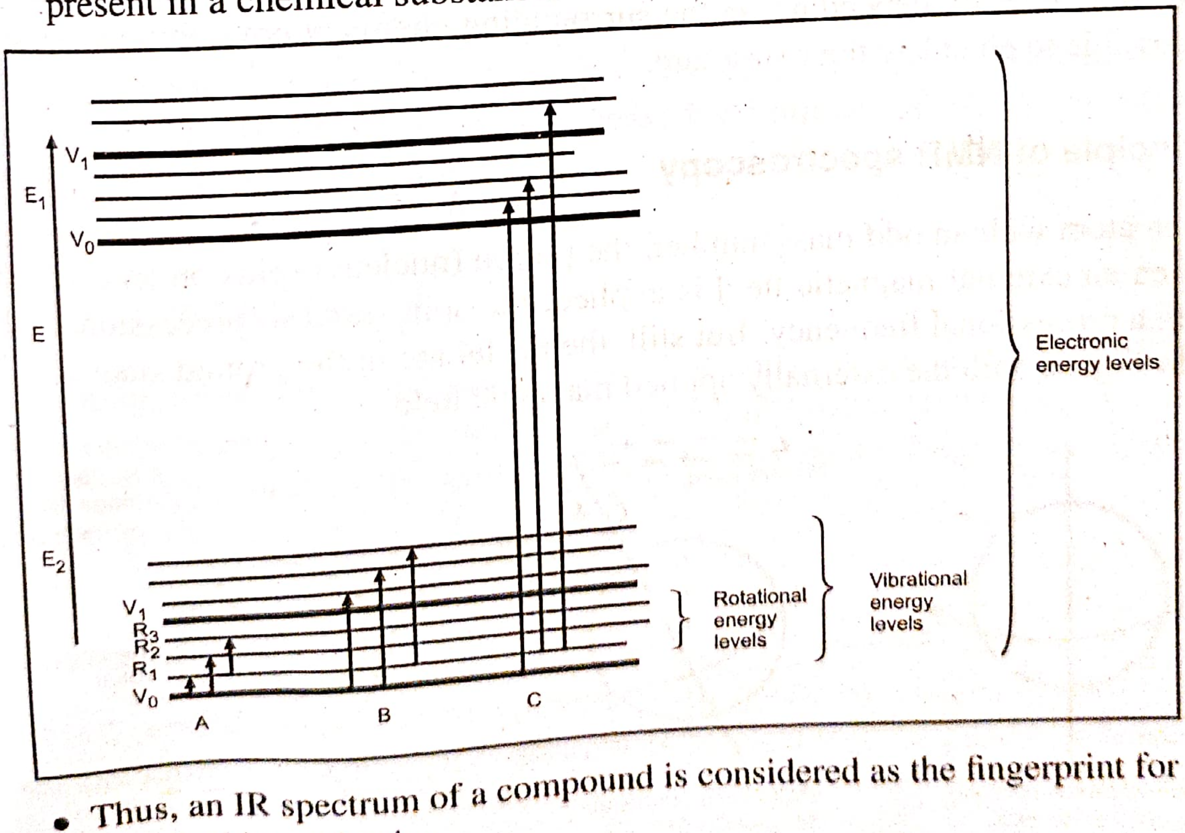
- Each vibrational level is associated with a number of closely placed rotational level.
- Therefore the IR spectroscopy is also called as "vibrational-rotational spectroscopy"
- All the bonds in a molecule are not capable of absorbing IR energy but those bonds which are accompanied by a change in dipole moment will absorb in the IR region and such transitions are called IR active transitions.
- The transitions which are not accompanied by a change in dipole moment of the molecule are not directly observed and are considered as IR inactive.
- In IR spectroscopy the changes in the vibrational energy depends upon

  i. Mass of the atoms present in a molecule

  ii. Strength of the bonds

  iii. Arrangement of atoms within the molecule

- The bands correspond to the characteristic functional groups and the bonds present in a chemical substance.



- Thus, an IR spectrum of a compound is considered as the fingerprint for its chemical identification.
- There are 3 main process by which a molecule can absorb radiation, each of these route involve an increase of energy which is proportional to the light absorbed.

i. First route occurs when absorption of radiation leads to a higher rotational energy level in a rotational transition.

ii. Second occurs when absorption of radiation leads to a higher vibrational energy level in a vibrational transition.

iii. Third occurs when absorption of radiation leads to a higher electronic energy level in its electronic transitions.

5.1.8 NMR Spectroscopy

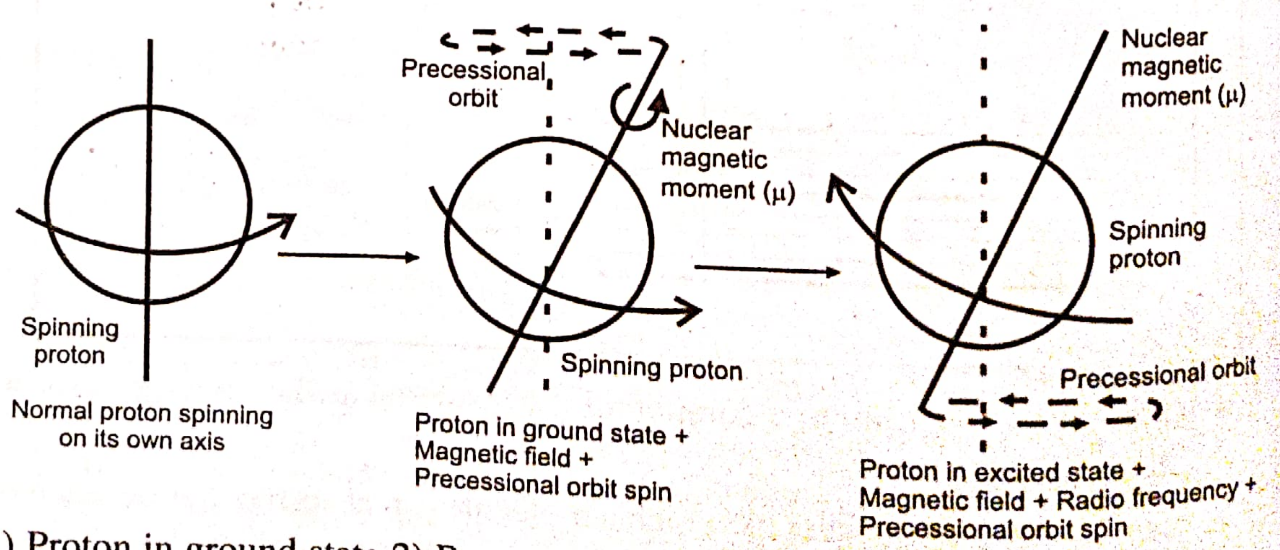
NMR Spectroscopy is abbreviated as Nuclear Magnetic Resonance spectroscopy.

Nuclear magnetic resonance spectroscopy is one that studies the spin changes at the nuclear level: This spin change occurs when a radio frequency (Rf) electromagnetic radiations is absorbed by the nucleus in the presence of a strong magnetic field.

Nuclear magnetic resonance (NMR) spectroscopy is a crucial analytical tool. Not only can it provide information on the structure of the molecule, it can also determine the content and purity of the sample. Proton (1H) NMR is one of the most widely used NMR methods. The protons present in the molecule will behave differently depending on the surrounding chemical environment, making it possible to elucidate their structure.

Principle of NMR spectroscopy

In an atom with an odd mass number, the proton (nucleus) spins on its own axis. When an external magnetic field is applied, the spin shifts to precessional orbit with a precessional frequency. But still, the nuclei are in the ground state with its spin aligned with the externally applied magnetic field.



1) Proton in ground state 2) Proton under the magnetic field and 3) Proton under radio-frequency + magnetic field.

To this atom, if radio-frequency energy is applied such that the applied frequency is equal to precessional frequency, then the absorption of energy occurs leading to an NMR signal.

Since the energy is absorbed, the nucleus moves from the ground state to the excited state with its spin oriented in the opposite or anti-parallel direction.

If the application of radio frequency energy is stopped, then the nucleus returns to the ground state with parallel orientation spinning is precessional orbit.

If even the magnetic field is removed, the nucleus will return to its normal spin on its own axis instead of precessional orbit.

Hence, application of magnetic filed only makes the nucleus to spin in the precessional orbit while the application of radio frequency energy leads to NMR signal.

This indicates that both the application of the magnetic field as well as the radio frequency energy are needed to produce NMR signal.

It may be pointed here that the character of NMR spectra is not solely determined by nuclear properties, but also by the environment. In other words, the frequency of radiation absorbed by a given nucleus is strongly influenced by the kind of environment in which it exists. For example, CH_3-CH_2-OH contains 6 protons. So its NMR spectra contains 3 peaks for 3 protons of CH_3, 2 protons of CH_2 and 1 proton of $-OH$ respectively.

Coupling constant (J)

The coupling constant J (usually in frequency units, Hz) is a measure of the interaction between a pair of protons. In a vicinal system of the general type, then the coupling of H_a with H_b is J_{ab} must be equal to the coupling of H_b with H_a is J_{ba}, therefore $J_{ab} = J_{ba}$

Chemical shift (δ)

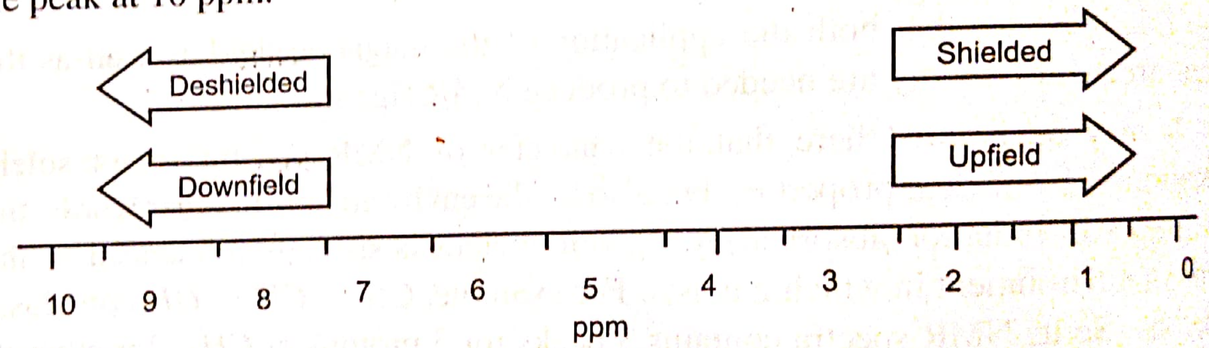
- All other absorptions are measured by their shift away from the TMS line on the NMR spectrum. This is called the chemical shift (δ), and is measured in units of parts per million (ppm).
- The relative energy of resonance of a particular nucleus resulting from its local environment is called chemical shift.
- NMR spectra show applied field strength increasing from left to right. Left part is downfield, the right is upfield.

- Nuclei that absorb on upfield side are strongly shielded where nuclei that absorb on downfield side is weakly shielded.
- An NMR Spectrum is a plot of the radio frequency applied against absorption.

Chemical shift can be calculated as follows

$$\text{Chemical shift} = \frac{\text{Frequency of signal - Frequency of reference}}{\text{spectrometer frequency}} \times 10$$

The relative positions in the NMR Spectrum. For Example ,a peak at a chemical shift of 10 ppm is said to be the down field or deshielded with respect to a peak at 5 ppm, or if you prefer, the peak at 5 ppm is up field or shielded with respect to the peak at 10 ppm.



Chemical shift scale

Typically for field strength of 4.7τ the resonance frequency of a proton will occur around 200MHz and for a carbon 50.4MHz. The reference compound is the same for both, Tetramethylsilane (Si $(CH_3)_4$ often just referred to as TMS.

Factors Influencing Chemical shift

The following are the various factors affecting chemical shift

- Inductive effects by electronegative groups
- Magnetic anisotropy
- Hydrogen bonding

Applications of NMR spectroscopy

1. **Structural elucidation:** Most organic compounds have hydrogen in them. NMR helps to identify the number of hydrogen atoms, their types, position and other characters. Thus it helps to understand the structure of a compound.

2. **Quantitative assay of components:** A component or more can be estimated without separation. Even the percentage of hydrogen in a compound, the chain length of polymers like polythene, moisture content, etc. can be analyzed.
3. **Identification of properties of molecules** like the isomerism, hydrogen bonding, tautomerism, etc. can be determined by using NMR spectroscopy.

5.1.9 MRI (Magnetic Resonance Imaging) Scan

Magnetic resonance imaging (MRI) is a type of scan that uses strong magnetic fields, radio waves and a computer to create a detailed, cross-sectional image of internal organs and structures. Figure shows outlook of MRI scan(no need to draw).

- The scanner itself typically resembles a large tube with a table in the middle, allowing the patient to slide in.
- An MRI scan differs from CT scans and X-rays, as it does not use potentially harmful ionizing radiation.

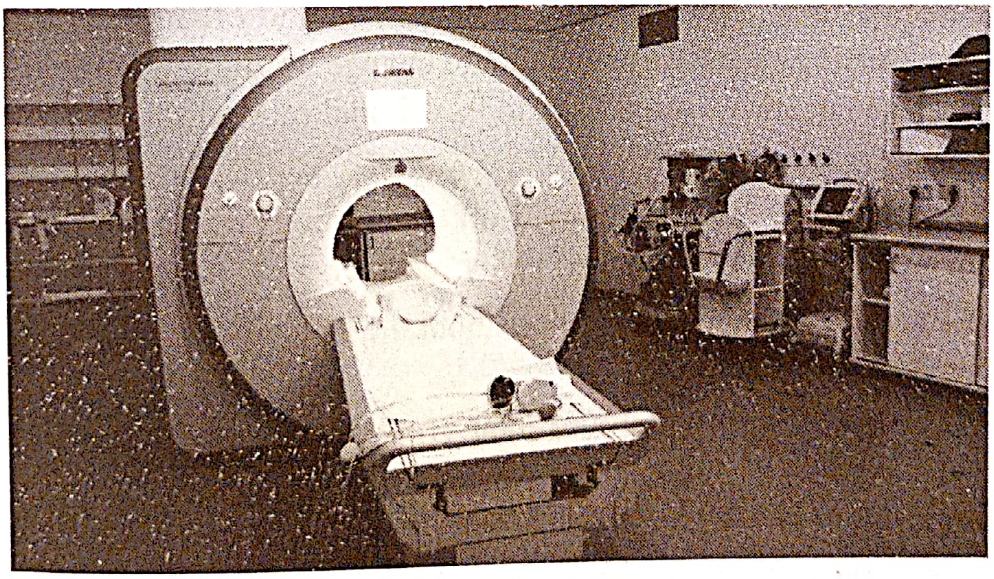


Figure. 5.1 MRI scan outlook

As the MRI scanner produces strong magnetic fields, it's important to remove any metal objects from your body.

These include:

- Watches
- Jewellery, such as earrings and necklaces

- Piercings, such as ear, nipple and nose rings
- Dentures (false teeth)
- Hearing aids
- Wigs (some wigs contain traces of metal)

Procedure

MRI scans work by rearranging water molecules in the body with magnets.

An MRI scanner contains two powerful magnets. These are the most important parts of the equipment.

- The human body is largely made of water molecules, which are comprised of hydrogen and oxygen atoms. At the center of each atom lies an even smaller particle called a proton. Protons are like tiny magnets and are very sensitive to magnetic fields.
- Normally, the water molecules in the body are randomly arranged, but on entering an MRI scanner, the first magnet causes the water molecules to align in one direction, either north or south.
- The second magnetic field is then turned on and off in a series of quick pulses, causing each hydrogen atom to change its alignment when switched on and then quickly switch back to its original relaxed state when switched off.
- When the radio waves are turned off, the protons realign. This sends out radio signals, which are picked up by receivers.
- These signals provide information about the exact location of the protons in the body.
- Passing electricity through gradient coils, which also cause the coils to vibrate, creates the magnetic field, causing a knocking sound inside the scanner.
- Although the patient cannot feel these changes, the scanner can detect them and, in conjunction with a computer, can create a detailed cross-sectional image for the radiologist.

Applications

The development of the MRI scan represents a huge milestone for the medical world. Doctors, scientists, and researchers are now able to examine the inside of the human body in high detail using a non-invasive tool.

The following are examples in which an MRI scanner would be used:

- Anomalies of the brain and spinal cord.
- Tumors, cysts, and other anomalies in various parts of the body.
- Breast cancer screening for women who face a high risk of breast cancer.
- Injuries or abnormalities of the joints, such as the back and knee.
- Certain types of heart problems.
- Diseases of the liver and other abdominal organs.
- The evaluation of pelvic pain in women, with causes including fibroids and endometriosis.
- Suspected uterine anomalies in women undergoing evaluation for infertility.

5.2 Green Chemistry

5.2.1 Introduction

To meet the demands of modern civilization, variety of chemical products and industries have evolved which lead to the formation of hazardous substances. In order to prevent or minimize the formation and use of such hazardous substances, the chemists are required to develop the novel technologies which has inspired the generation of new branch of chemistry called Green chemistry.

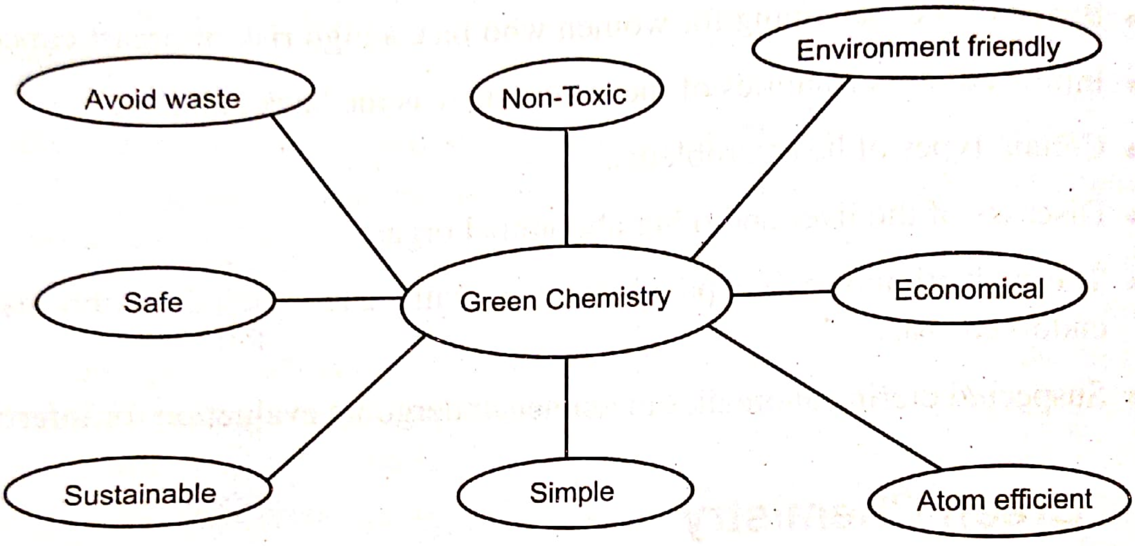
- Basic idea of Green chemistry is a new approach which provides the design of chemical products and process that minimize the use and formation of hazardous substances so that it is inherently of less risk to human health and the environment.
- Laboratory chemistry plays a key role to develop green chemical methods to prevent the pollution in the environment. Now, the revolution of green chemistry begins with new challenges for chemists involved with the discovery, Manufacture and use of chemicals.

Definition

A branch of chemistry which designs the chemical products and processes that minimize the use and formation of hazardous substances is known as Green chemistry.

5.2.2 The need of Green chemistry

The 20th century is very successful and highest scientific development with respect to various benefits to the mankind, but all this was responsible for a number of environmental problems at the local and global levels.



- Industrial discharges, pesticides and herbicides fill the skies and seas.
- Our technological power is increased day by day but the side effects and potential hazardous also increased.
- To maintain our current standard of living and improve our quality of life, society has come to depend on the products of chemical industry.
- Now a day the public is equally aware of hazardous substances used and generated by the chemical processes.
- Our environment, which is endowed by nature, needs to be protected from ever increasing chemical pollution associated with contemporary life styles and emerging technologies.
- Developments in water treatment, waste disposal method agricultural pesticides and fungicides, polymers, material sciences, detergents, petroleum, additives and so forth have all contributed to the improvement in our quality of life.
- Green chemistry concept is to avoid toxic substance, reduce energy requirement, and use renewable materials.
- Green chemistry includes any chemical process or technology that improves the environment and thus our quality of life.
- The risk of human health and environment can be eliminated through fundamental chemical methodologies in green chemistry.

5.2.3 The principles of green chemistry

Chemistry plays an important role in our lives like clothes, food, building etc. on the earth. But in another way it leads to the adverse effects of land, water and atmosphere. This is caused mainly due to effects of byproducts such as pollution of land, water and atmosphere. One of the most important new aspects of chemistry is the development of Green Chemistry. Green Chemistry has emerged as an important aspect of all chemistry Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

Green Chemistry is based on Twelve Principles

1. **Minimization of the waste product formation (or) Prevention:-**

   The first principle aims to develop zero waste technology (ZWT).In terms of ZWT, in a chemical synthesis, waste product should be zero or minimum. It also aims to use the waste product of one system as the raw material for other systems. As for example, bottom ash of thermal power station can be used as a raw material for cement and brick industry.

2. **Atom Economy:-** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product or to minimize the formation of by product.

$$\% \text{ Atom economy} = \frac{\text{mass of desired product}}{\text{total mass of reactants}} \times 100\%$$

3. **Less Hazardous Chemical Syntheses:-**

   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals:-**

   Chemical products should be designed to effect their desired function while minimizing their toxicity.

5. **Safer Solvents and Auxiliaries:-** The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. **Design for Energy Efficiency:-**

   Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstock's:-**

   A raw material or feed stock should be renewable rather than depleting whenever technically and economically practicable.

8. **Reduce Derivatives:-**

   Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes)should beminimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis:-**

   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation:-**

    Chemical products should be designed so that at the end of their function they breakdown in to innocuous degradation products and do not persist in the Environment.

11. **Real-time analysis for Pollution Prevention:-**

    Analytical methodologies need to be further developed to allow for real-time, in- process monitoring and control prior to the formation of hazardous substances.

12. **Inherently Safer Chemistry for Accident Prevention:-**

    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

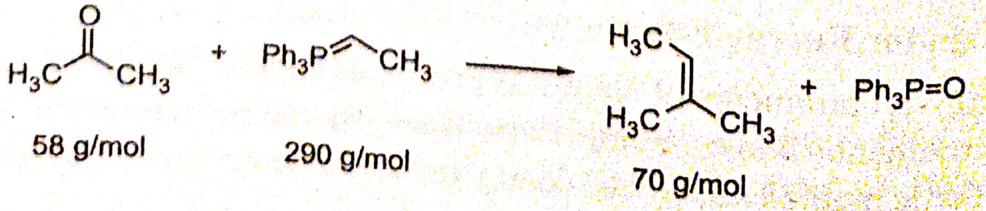
5.2.4 Examples of Clean Technology

1. **Example for Atom Economy:-**

   "synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product".

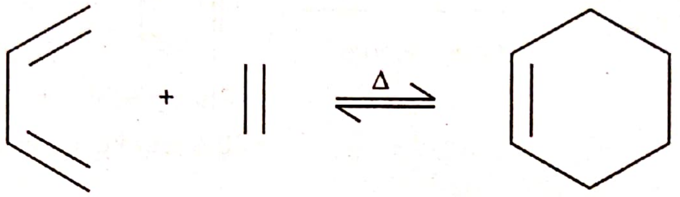
$$\% \text{ Atom economy} = \frac{\text{mass of desired product}}{\text{total mass of reactants}} \times 100\%$$

Wittig Reaction



$$\begin{aligned}\%\ \text{Atom economy} &= \frac{\text{mass of desired product}}{\text{total mass of reactants}} \times 100\% \\ &= \frac{70}{348} \times 100\% \\ &= 20.11\%\end{aligned}$$

Diels Alder Reaction



$$\begin{aligned}\%\ \text{Atom economy} &= \frac{\text{mass of desired product}}{\text{total mass of reactants}} \times 100\% \\ &= \frac{82}{82} \times 100\% \\ &= 100\%\end{aligned}$$

So, Diels Alder reaction is the Green chemical Reaction

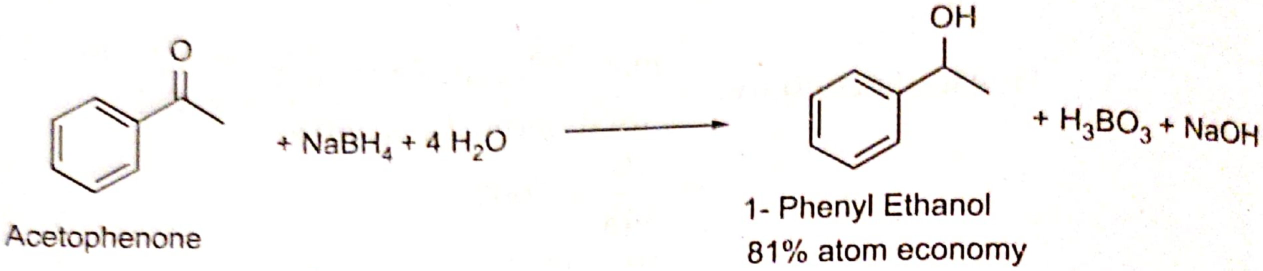
2. **Example for Catalysis:-**

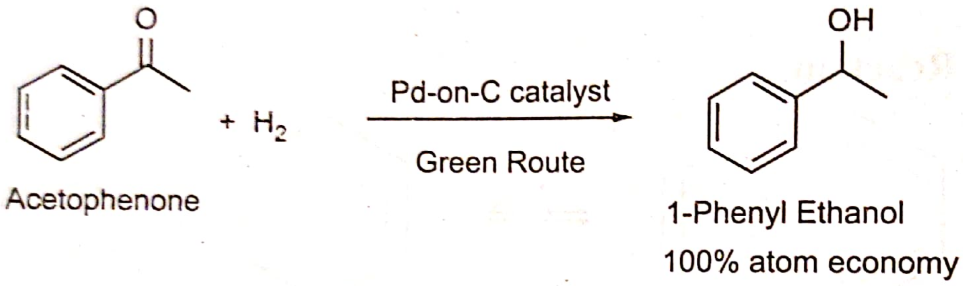
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

The chemical substance that is used to accelerate the rate of a chemical reaction by lowering its activation energy this also nas the ability to regenerate itself at the end of the reaction is known as a catalyst.

- It is used in small quantities.
- The use of catalyst reduces the energy demand by lowering the temperature and pressure of the chemical reaction.
- The enable the other side reactions and by this way, better atom economy can be obtained and waste material production is minimized.

In the first reaction no catalyst is used so obtained atom economy is only 81%. While in the second reaction pd on carbon is used as a catalyst so it increases the atom economy i.e 100%.


O
+ NaBH$_4$ + 4 H$_2$O
OH
+ H$_3$BO$_3$ + NaOH
Acetophenone
1- Phenyl Ethanol
81% atom economy


O
+ H$_2$
Pd-on-C catalyst
Green Route
OH
Acetophenone
1-Phenyl Ethanol
100% atom economy

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