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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT-I – Electronic Spectroscopy – SCYA7301

1. Introduction

Electromagnetic Radiation (EMR)

- Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic fields perpendicular to each other, traveling through a vacuum or matter at constant velocity

Characteristics of EMR

- ***Wavelength (λ):*** The linear distance between successive crests or trough of a wave is known as wavelength. It is usually expressed in centimetre or millimetre.
- ***Frequency (ν):*** The number of vibrations or oscillations per second is known as frequency. It is expressed in Hertz.
- ***Wave number ($\bar{\upsilon}$):*** The reciprocal of wavelength is known as wave number. It is expressed in cm^{-1}.
- ***Energy of EMR (E):*** Electromagnetic radiations consist of particles having small packets of energies called quanta or photons.
- Photons possess the characteristic of wave and travel with the speed of light. The amount of energy corresponding to one photon is expressed by ***Planck's equation*** as E

$$E = h\nu \text{ or } E = hc/\lambda \text{ or } E = hc\bar{\upsilon}$$

where h – Planck's constant (6.62x10-34J)

ν - frequency in Hz

λ – wavelength in cm

c – Velocity of light m/s

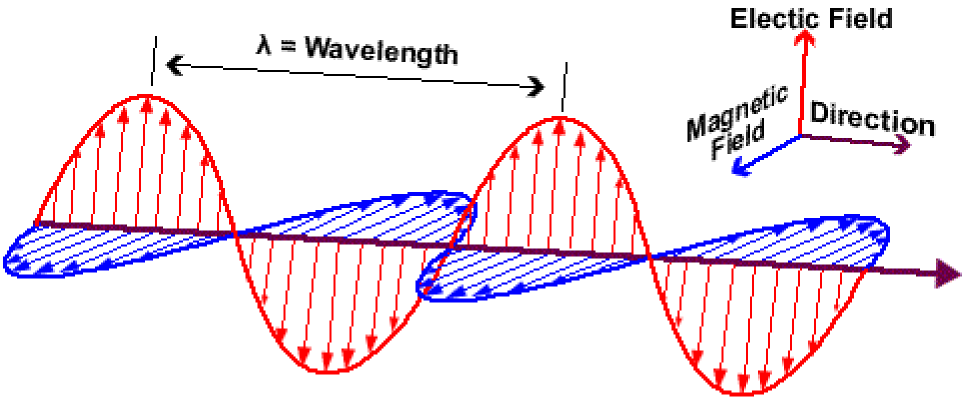


Figure 1: Electromagnetic Radiation (Source:www.nde-ed.org)

2. Electronic Transitions

Spectroscopy

- ***Spectroscopy:*** It is the branch of science dealing with the study of interaction of electromagnetic radiation (EMR) with matter like atoms and molecules.
- The interaction of EMR with matter gives rise to two types of spectra namely
- ***Atomic spectra:*** It is the spectrum of frequencies of electromagnetic radiation emitted or absorbed during transitions of electrons between energy levels within an atom
- ***Molecular spectra:*** It is the spectrum of frequencies of electromagnetic radiation emitted or absorbed by particular substance from which structural and compositional information can be determined
- Molecular spectrum involves transition of electrons between rotational and vibrational energy levels in addition to electronic transition.
- Thus Molecular spectra is more complex
- ***Absorption:*** An atom or molecule absorb energy from EMR and undergo a transition from energy state E_1 (ground state) to E_2 (Excited higher energy state)
- ***Emission:*** An atom or molecule returns from E_2 to E_1 state, an equivalent amount of energy is emitted
- ***Absorption and Emission Spectra***
- Absorption (excitation) of photon of EMR occurs only if the energy of EMR corresponds to energy difference ΔE between two energy states (E_1 and E_2)
- ΔE will correspond to certain frequency ν or wavelength λ of EMR
- The relationship between the energy of a transition and the frequency is given by

$$\Delta E = h\nu \text{ or } \Delta E = hc/\lambda \text{ or } \Delta E = hc\bar{\upsilon}$$

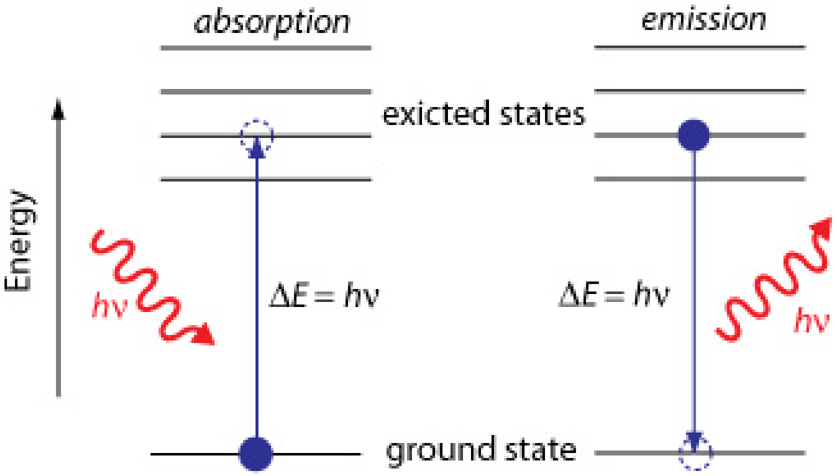


Figure 2: Energy diagram of Absorption and Emission

(Source: https://community.asdlib.org)

- The energy of a particular transition is thus proportional to frequency and wavenumber ($\bar{\upsilon}$= 1/λ) and inversely proportional to the wavelength.

- Thus spectroscopy is the study of interaction of molecules and electromagnetic radiation

- ***Absorption Spectra:*** It consists of peaks or bands corresponding to frequencies of light transmitted with dark bands when energy is absorbed by the electrons in the ground state to get excited to higher energy states.

- ***Emission Spectra:*** When energy is absorbed by electrons of an atom, they move from lower energy level to higher energy levels. These excited electrons release energy to return to ground states from the excited state. The emission spectra are formed by peaks or bands corresponding to the frequencies of these emitted light.

- The Emission spectra has different coloured lines in the spectrum whereas an absorption spectrum has dark-coloured lines in the spectrum

- Emission spectra can emit all the colours in an EMR, whereas the absorption spectrum can have a few colours missing due to absorption of photons.

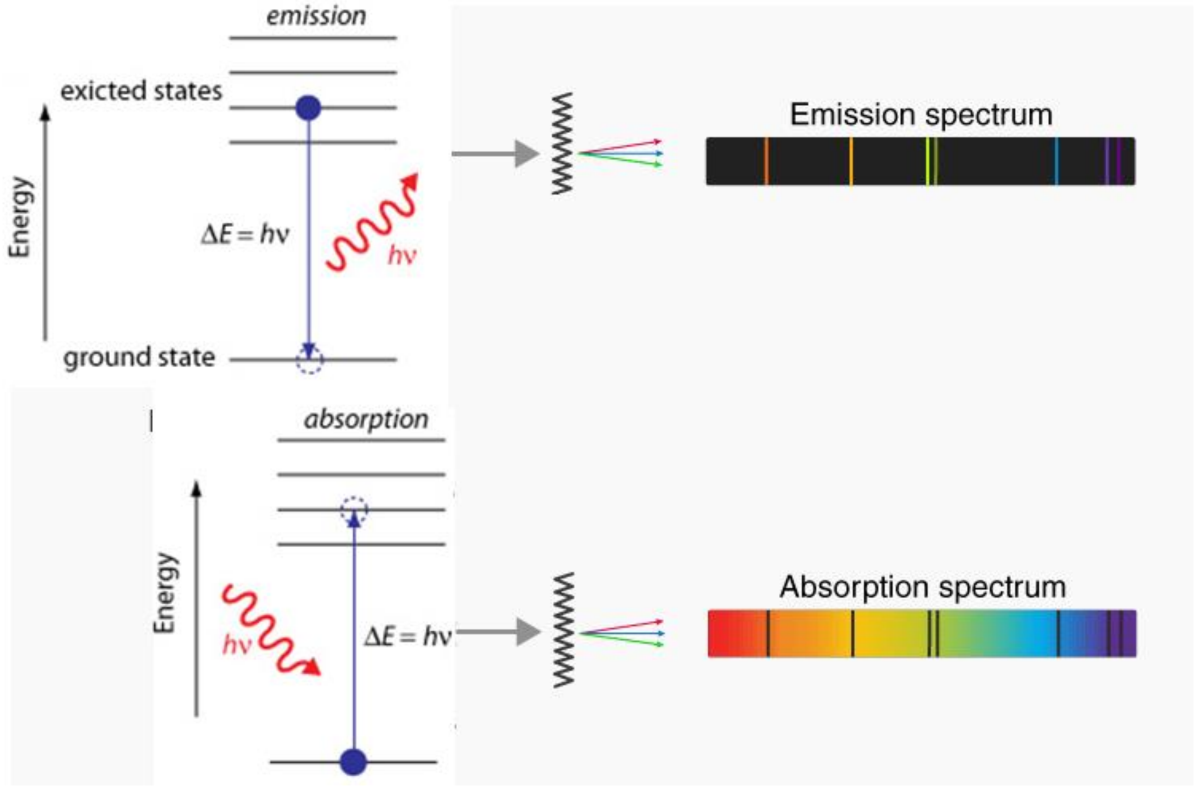


Figure 3: Absorption and Emission spectra (Source: https://byjus.com and https://community.asdlib.org)

Energy levels in molecules

- In molecules, there are many electronic energy levels (they are widely spaced- E_1,E_2,E_3 etc)

- In between the electronic energy levels, there are vibrational energy levels (they are narrow than electronic energy levels- V_1,V_2, V_3 etc)

- In between the vibrational energy levels, there are rotational energy levels (they are still narrow than vibrational energy levels- J_1,J_2,J_3 etc)

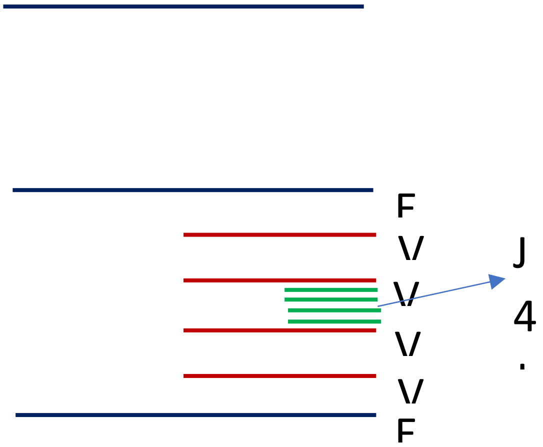


Figure 4: Electronic, Vibrational and Rotational energy levels in molecules

Electromagnetic Spectrum (EM)

- The electromagnetic (EM) spectrum is the range of all types of EM radiation
- The electromagnetic spectrum is the range of frequencies (the spectrum) of electromagnetic radiation and their respective wavelengths (or frequency) and photon energies.

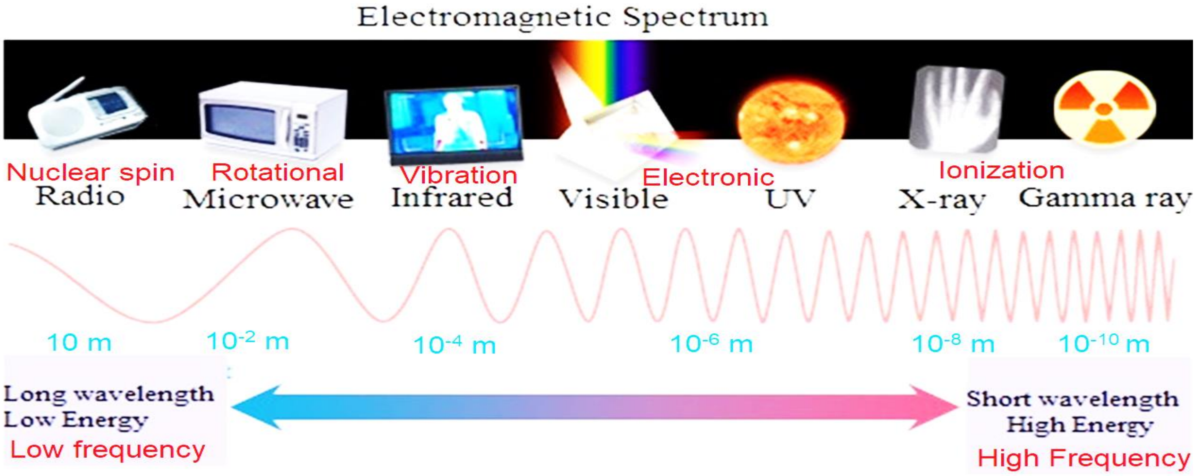


Figure 5: Various Electromagnetic radiations and its significance (Source: https://quizlet.com)

7 Major regions of Electromagnetic spectrum

- *Radiowaves:*
    - λ=10 m, $\nu=10^6 - 10^{10}$ Hz
    - NMR and ESR spectroscopy
    - Energy change involved in reversal of nucleus or electron
- *Microwaves:*
    - $\lambda=10^{-2}$ m, $\nu=10^{10} - 10^{12}$ Hz
    - Rotational spectroscopy
    - Rotational transitions lead to rotation of molecule

- *Infrared:*
    - $\lambda=10^{-4}$ m, $\nu=10^{12} – 10^{14}$ Hz
    - Vibrational spectroscopy
    - Vibrations of bonds in molecule
- *Ultraviolet - Visible:*
    - $\lambda=10^{-6}$ m, $\nu=10^{16} – 10^{18}$ Hz
    - Electronic spectroscopy
    - Electronic transitions lead to excitation of molecule – absorption and emission
- *X-ray:*
    - $\lambda=10^{-8}$ m, $\nu=10^{16} – 10^{18}$ Hz
    - X-ray spectroscopy
    - Energy change involved in inner electron of atom or molecule
- *γ-ray:*
    - $\lambda=10^{-10}$ m, $\nu=10^{18} – 10^{20}$ Hz
    - γ-ray spectroscopy
    - Energy change involved rearrangement of nuclear particles

Energy levels and Absorption bands/Absorption Lines

- ***Absorption lines:***
    - With only few energy levels
    - When the spacing between them is large enough
    - A line spectrum is obtained.
- ***Absorption bands:***
    - When there are many closely spaced sublevels in each energy levels
    - A broad band is obtained (since the individual lines are not resolved)

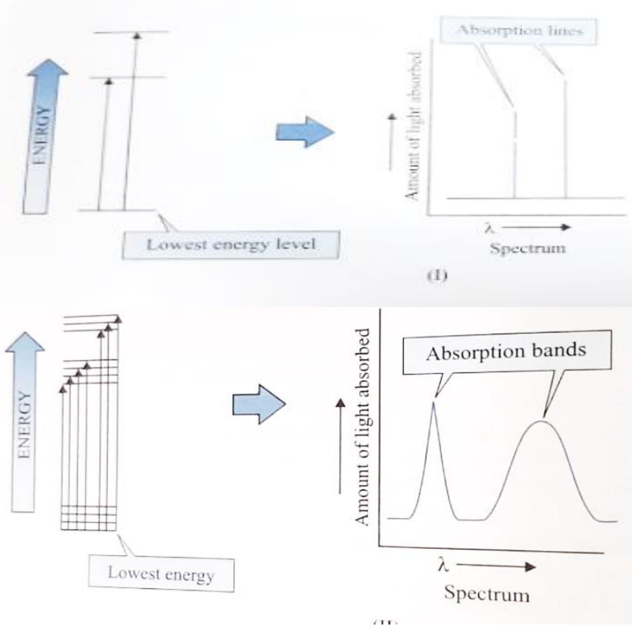


Figure 6: Absorption lines and Absorption bands in spectrum (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Absorption Spectrum and Units

- In UV-Vis or IR spectrophotometer, light of given frequency is allowed to pass through the sample and the amount of transmitted light (not absorbed) is measured
- The instrument detects the intensity of the transmitted light with that of the incident light
- Spectrum (graph) is recorded between absorbance (A) or transmittance (% T) versus frequency or wavelength
- ***Absorbance*** is the measure of the absorption of radiation by a sample
- A = log (Original Intensity/Intensity)
- An increase in absorption appears s an increase of the signal (and not decrease)
- ***Percent transmittance*** is the percent of the intensity of the original radiation which passes through the sample
- % T = (Intensity/Original intensity) x 100
- When a compound does not absorb any radiation at a particular wavelength, % transmission is 100 at that wavelength

Introduction to Electronic Spectroscopy

- The absorption of ultraviolet/visible radiation by a molecule leads to transitions among the electronic energy levels of the molecule
- The application of electronic spectroscopy is its ability to measure the extent of multiple bond or aromatic conjugation within molecules.
- The non-bonding electrons on oxygen, nitrogen and sulfur may also be involved in extending the conjugation of multiple-bond systems
- Electronic spectroscopy can differentiate conjugated dienes from non-conjugated dienes, conjugated dienes from conjugated trienes, α,β-unsaturated ketones from their β,γ-analogs, etc
- The position of absorption may also be influenced by substituents
- The method is used in the study of aromatic and heteroaromatic systems which is completely unobtainable from any other spectroscopic technique
- The longer the conjugation the longer the wavelength maximum (λ_{max}) of the absorption spectrum

Electronic Spectroscopy: UV-Vis Spectroscopy

- Ultraviolet and Visible spectroscopy (electronic spectroscopy) is primarily used to measure the multiple bonds or aromatic conjugation within molecules
- In electronic spectroscopy an electron is promoted from the HOMO to the LUMO
- As the conjugation increases, the HOMO-LUMO gap decreases and the position of the π-π^* adsorption shifts to longer wavelengths (lower energy)

- Simple aldehydes and ketones like simple alkenes do not have a π-π^* absorption in the region of UV spectrum readily accessible to most spectrometers
- UV-Vis spectroscopy requires electromagnetic radiation of high energy
- The visible region corresponds to 400 – 800 nm and Ultraviolet region to 200 – 400 nm
- The amount of energy available in this radiation, ranging from 143 Kcal/mol (600 KJ/mol) to 36 Kcal/mol (150 Kcal/mol) is sufficient to cause an electronic transition to excite an electron in a molecule from an occupied MO to an antibonding MO.

Chromophore

- The electronic excitations are typically characteristic of chromophores. Although the entire molecule is in excited energy state, the excited state is mainly localized within the chromophore for simple transitions.
- A chromophore is a part of the molecule containing the electrons involved in the electronic transition leading to an absorption.
- Chromophore is defined as an unsaturated group (or collection of groups) that is responsible for absorption of UV or visible light
- Originally, the term chromophore was applied to the system responsible for imparting color to a compound. (The derivation is from the Greek chromophoros, or colour carrier.) Thus, in azo dyes the aryl conjugated azo group (Ar – N = N – Ar) is clearly the principal chromophore; in nitro compounds the yellow color is carried by $-NO_2$; etc

Auxochrome

- An auxochrome was an earlier-defined term for a group that could enhance the color-imparting properties of a chromophore without being itself a chromophore, examples being –OR, $-NH_2$, $-NR_2$, etc
- Auxochrome is defined as a substituent (usually saturated) that alters the wavelength and molar extinction coefficient of the absorption maximum (intensity of peak) when it is attached to a chromophore
- Eg. OH is an auxochrome. The lone pair of electrons on oxygen is available to interact with the π-electron cloud of the benzene ring and his interaction increases λ_{max}
- ***Effect of an auxochrome on benzene***
- The anilinium ion does not have an auxochrome, its λ_{max} is similar to that of benzene
- The phenolate ion increases λ_{max} when compared to phenol, this ion has an additional lone-pair. Similarly, on protonation λ_{max} is decreased in anilinium ion

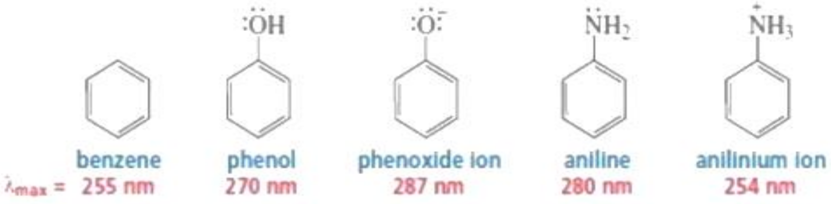


Figure 7: Effect of Auxochrome on Benzene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- **Bathochromic shift (or Red shift):** The shift of the absorption maximum to longer wavelength (larger λ) caused by either substitution onto chromophore (by an auxochrome) or a change in the solvent
- **Hypsochromic shift (or Blue shift):** The shift to shorter wavelength (smaller λ) as a result of substitution or solvent change

Electronic Transitions and Electronic Energy Levels

- ***Types of electrons in orbitals:***
- *Bonding σ–orbital:* electron in a single covalent bond is tightly bound and hence radiation of high energy is required to excite them.
- *Non-bonding n-orbital:* electrons attached to atoms as loan pair. These electrons are not involved in bonds. For example: Oxygen, Nitrogen and Chlorine. The non-bonding electrons can be excited at a lower energy than tightly bound bonding electrons.
- *Bonding π-orbital:* electrons in double or triple bond can be excited relatively easily. Molecules containing a series of alternating double bonds, the πelectrons are delocalized and require less energy for excitation.
- There are four transitions that can occur (possible) in the electronic spectroscopy.
- σ → σ* Transition
- π → π* Transition
- n → π* Transition
- n → σ* Transition

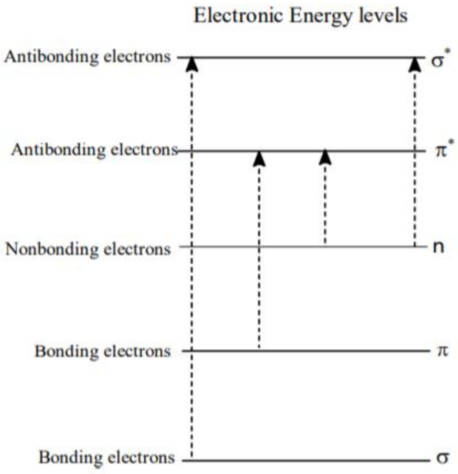


Figure 8: Types of electrons in electronic energy levels

σ → σ Transition*

- The electronic transitions that can involve the excitation of an electron from a bonding (σ) MO to an antibonding (σ*) MO is a high energy transition σ → σ* transition (λ_{max} = 135 nm)
- Eg. Saturated alkanes like ethane, the HOMO is sigma bonding MO and the LUMO is sigma antibonding MO

- λ_{max} is the wavelength where absorption band has maximum absorbance
- Energy separation ΔE between sigma σ bonding and antibonding MO is very large
- Therefore alkanes are transparent in the accessible UV region above 200 nm and are often used as solvent for obtaining UV spectra of other compounds
- The UV-Visible spectrometers easily detect in 200 – 800 nm range but at higher energy (i.e < 200 nm) the atmosphere absorb strongly and thus spectrometers require vacuum in this region

π → π* Transition and n → π* Transition

- Most common transitions that occur in UV-Visible region are π → π* transition and n → π* transition
- n → π* transition requires low energy for the promotion of a non-bonding (lone-pair) electron (n) into π* antibonding molecular orbital transition.
- π → π* transition requires still higher energy for the promotion of a π bonding electron into π* antibonding molecular orbital transition.
- Acetone has both π electrons and non-bonding electrons. In UV spectra, two absorption bands: one band at λ_{max} =195 nm (π → π* transition) and another band at λ_{max} =274 nm (n → π* transition).
- The π → π* transition corresponds to the shorter wavelength as it requires higher energy than n → π* transition
- The absorption bands are broad because each electronic state has vibrational sublevels

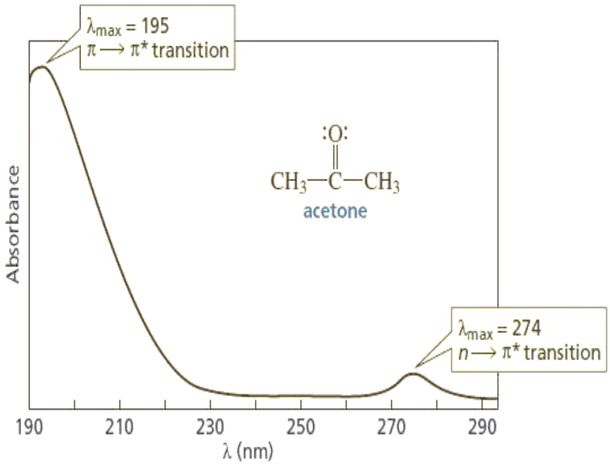


Figure 9: UV spectrum of acetone (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

n → σ* Transition

- This transition involves saturated compounds with one heteroatom with unshared pair of electrons (n electrons) ie. Saturated halides, ethers, aldehydes, ketones, amines etc.
- These transitions require comparatively less energy than σ → σ* transition

- Eg. Water absorbs at 167 nm, methyl alcohol at 174 nm, methyl chloride at 169 nm and methyl iodide at 258 nm
- Methyl iodide absorb at lower energy than methyl chloride due to the higher electronegativity of Cl compared to that of Iodine atom. Thus easy to excite electron in iodine than in Cl.
- n → σ* transitions are sensitive to hydrogen bonding. Eg. Alcohols form hydrogen bonding with solvent molecules and thus requires higher energy to excite the electrons.

Effect of Conjugation on UV spectra (λ_{max})

- Important application of UV spectroscopy is to detect and identify conjugated systems such as C=C–C=C and C=C–C=O, where the $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition occur at lower energy and higher wavelengths and can be measured in the UV region.
- In general, increasing number of substituents attached to conjugated systems or adding more conjugated double bonds increases the absorption maximum.
- Conjugation in a system reduces the energy gap between the HOMO and LUMO and this pushes the position of the lowest energy absorption to longer wavelength (lower energy)
- On extending the degree of conjugation, the HOMO-LUMO gap becomes so small that the absorption enters the visible range (highly conjugated polyenes are coloured).
- An intense absorption above 210 nm shows the presence of a conjugated system.
- The longer the wavelength the longer is the chromophore and with enough conjugated double bonds, the compound will absorb visible light (λ_{max} > 400 nm) and will be coloured
- The wavelength of the absorption maximum depends on the energy difference between the two energy levels
- β – carotene present in carrot and lycopene in tomatoes contains sufficient conjugation (11 conjugated bonds) to shift the absorption of visible region (orange and red)
- 1,3-Butadiene absorbs UV radiation of longer wavelengths (less energy) while ethene absorbs shorter wavelength (higher energy)

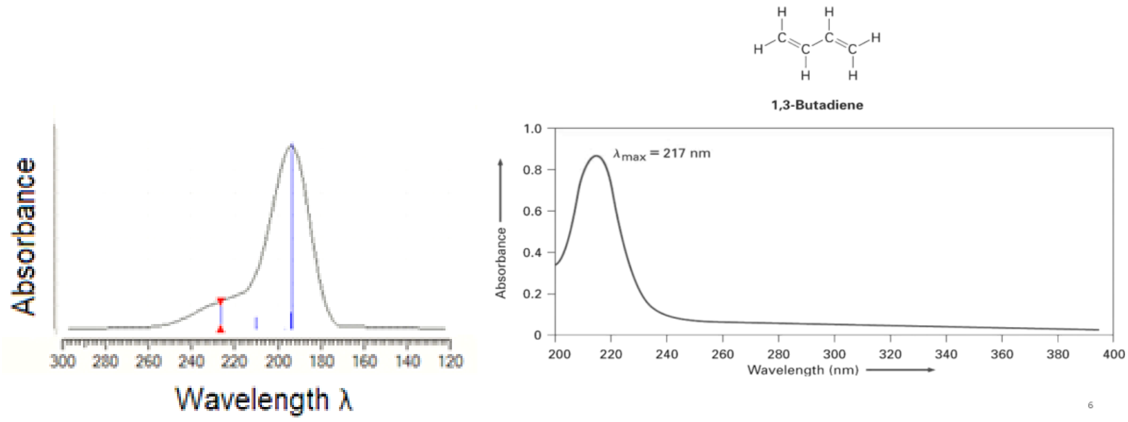


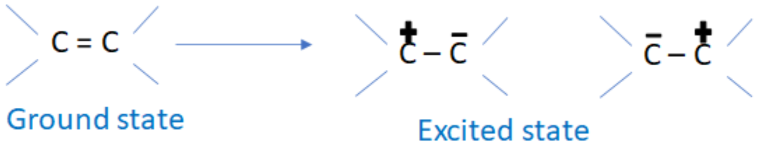
Figure 10: UV-Vis spectrum of Ethylene and 1,3-Butadiene

3. Effect of Solvent in Electronic Transitions

- All molecules have absorption bands
- The solvent must be transparent in the wavelength region being used
- Solvent in which the absorption spectrum is measured influence the position of λ_{max}
- According to Franck-Codon principle, during a electronic excitation, atoms donot move but electrons-including electrons of the solvent may reorganize themselves.
- When the solvent electrons arrange in a way to stabilize the excited state of a molecule, the energy difference between the electronic levels of the molecule gets lowered and the absorption moves to higher wavelength.

Effect of Solvent - Polarity of Solvent

- ***$\pi \rightarrow \pi^*$ Transition of alkenes***
- Polar solvent – the excited state is readily stabilized by dipole-dipole interactions compared to ground state.
- The energy gap between HOMO-LUMO decreases and results in 10 – 50 nm shift to longer wavelength (lower energy) in ethanol compared with hexane – Bathochromic shift or red shift occurs



These dipoles will be stabilized by a polar solvent

- ***$n \rightarrow \pi^*$ Transition of carbonyl group***
- Ground state forms hydrogen-bonding more readily than excited state
- Thus electronic excitation requires more energy in hydrogen bonding solvents (polar solvent) than with non-polar solvent (hexane)
- λ_{max} shift about 15 nm to shorter wavelength – Hypsochromic shift or blue shift
- Higher energy EMR is required when carbonyl compound is recorded in ethanol than cyclohexane
- Thus for $\pi \rightarrow \pi^*$ transition polar solvent is preferred and for $n \rightarrow \pi^*$ transition non-polar is preferred

4. Beer – Lambert Law

- When a beam of monochromatic radiation passes through a transparent absorbing medium, the absorbance of the medium is directly proportional to the thickness and concentration of absorbing medium.
  - $A = \varepsilon c l$
    - where A = Absorbance of the medium = $\log (I_o/I)$
    - I_o = Intensity of incident radiation
    - I = Intensity of transmitted radiation

- c = Concentration of the medium, mol L^{-1}
- l= Length or thickness of the medium (path length), cm
- ε = Molar absorptivity (L mol^{-1} cm^{-1})

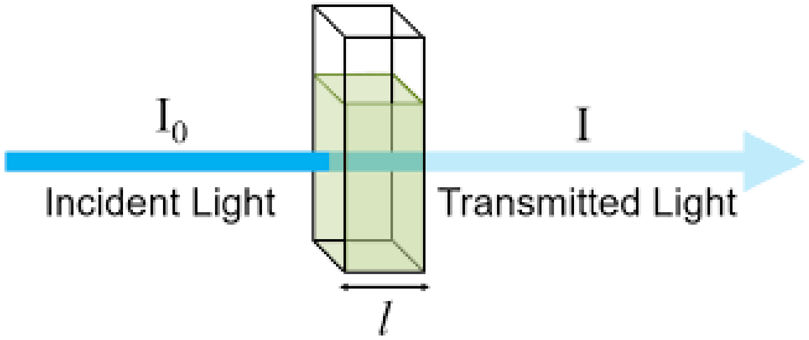


Figure 11: Beer-Lambert's law (Source: https://www.edinst.com)

Terms involved in Beer – Lambert law

- ***Transmittance:*** It is defined as the fraction of the incident light that is transmitted by a given species
- $T = I/I_o$
- Where I = Intensity of transmitted light and I_o = Intensity of incident light
- Taking log on both sides
- $\log T = \log (I / I_o)$
- $– \log T = \log (I_o / I)$ [Since $\log (I_o / I) = A = \varepsilon cl$]
- – log T is called as absorbance A or optical density
- **Absorbance or Optical Density (A):** It is defined as the negative logarithm to the base 10 of the transmittance (T) of the solution
- $– \log_{10} T = A$
- $\log (1/T) = A$
- Since $A = \varepsilon c l$

  $\therefore \log (1/T) = \varepsilon cl$
- The absorbance (A) is zero for a perfect transparent medium and infinity for perfect opaque medium

  The transmittance (T) is 100 for perfect transparent medium and zero for a perfect opaque medium
- ***The molar absorptivity (ε)*** of a compound is a constant and is characteristic of the compound at particular wavelength. It relates the observed absorbance (at particular λ) to the molar concentration and path length.

- ***Molar absorptivity (ε)*** is defined as the absorbance of a sample solution of 1 M concentration placed in a cell of length 1 cm.
- ***Unit:*** If c is represented in mol.dm^{-3}, then ε is given in dm^3 mol^{-1} cm^{-1}
- If c is given in g.dm^{-3}, then ε is given in dm^3 g^{-1} cm^{-1}
- Since absorbance is proportional to concentration, the concentration of a sample can be determined from Beer – Lambert law if ε and A are known.
- Molar extinction coefficient (ε) is a measure of how strongly a chemical species or substance absorbs light at a particular wavelength. It is an intrinsic property of chemical species that is dependent upon their chemical composition and structure.
- The molar extinction coefficient is frequently used in spectroscopy to measure the concentration of a solute in solution.
- Molar extinction coefficient is used to determine the brightness of a fluorescent molecule, by using the following equation:
- ***Brightness = Extinction Coefficient (ε) x Fluorescence Quantum Yield φ***
- ***Fluorescence quantum yield φ*** is a measure of the efficiency of photon emission through fluorescence, which is the loss of energy by a substance that has absorbed light via emission of a photon.
- It is often defined as the ratio of the number of photons emitted to the number of photons absorbed.

Validity, Applications and Limitations of the Beer – Lambert Law

- ***Validity:***
- The Beer – Lambert law can be validated is a straight line through the origin is obtained in a plot of absorbance versus concentration
- The absorbance is measured as log (I_o / I) for solution of different concentrations using a UV-Vis spectrometer
- ***Applications:***
- The relationship between energy absorption and concentration is of great importance for the purpose of analysis
- From the absorbance, the concentration of any solution can be determined.
- From the molar absorptivity the intensity (how strong the compound absorbs the UV light) of absorption
- ***Limitations:***
- The Beer – Lambert law is obeyed only by dilute solutions. Deviations from Beer – Lambert law are observed when

- The absorbing solute dissociates or associates in solution
- The concentration of solution is higher, the straight line bends towards the concentration axis and deviates from Beer – Lambert law
- Light is scattered due to particulates in the solution

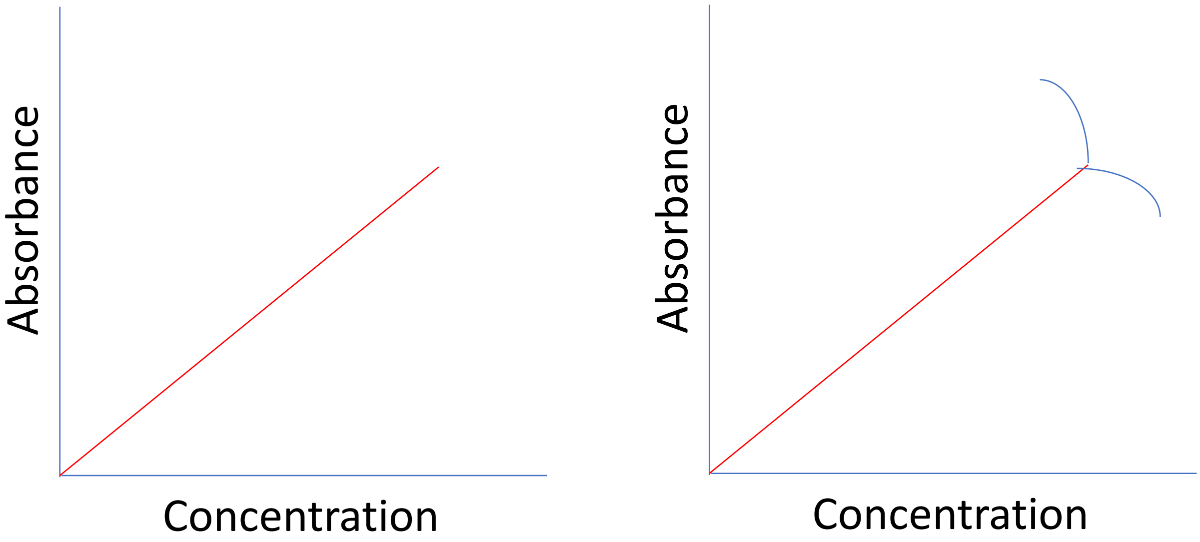


Figure 12: Deviation of Beer-Lambert's law

General Applications of UV Spectroscopy

- UV Spectroscopy is mostly used for conjugated systems
- Practical purpose: 750 nm for red and 400 nm for violet, ultraviolet commences around 400 nm.
- For organic applications- Region above 200 nm (near UV region) and hardly in region below 200 nm (far UV region)
- ***Significant applications of UV spectroscopy to organic chemistry***
    - Extent of conjugation
    - Distinction between conjugated and Non-conjugated compounds
    - Detection of a chromophore in an unknown compound
    - Identification of a chromophore (functional group)
    - Study of Geometric Isomerism
    - Effect of Geometric Isomerism and Steric Effects
    - Study of Tautomerism
    - Study of Structural features in different solvents
    - As an analytical tool
    - Effect of S-Cis (cisoid) and S-Trans (transoid) conformations
    - Effect of Alkyl Substitution and Ring residues
    - Effect of Exocyclic double bonds

- ***Extent of conjugation***
    - The longer the conjugation, longer the absorption maximum λ_{max}
    - Isomeric conjugated dienes, conjugated trienes, conjugated tetraenes etc. show appropriate increase in λ_{max}
    - Sufficient conjugation shifts the absorption maximum λ_{max} to visible region and the compound will be coloured. Eg. Lycopene-compound with 11 conjugated bonds gives red colour to tomatoes

- ***Distinction between conjugated and Non-conjugated compounds***
    - Conjugated compounds show λ_{max} at longer wavelength whereas non-conjugated compounds shows λ_{max} at shorter wavelength
    - UV spectroscopy can differentiate conjugated dienes from non-conjugated dienes, conjugated dienes from conjugated trienes, α,β-unsaturated ketones from their β,γ-analogs, etc

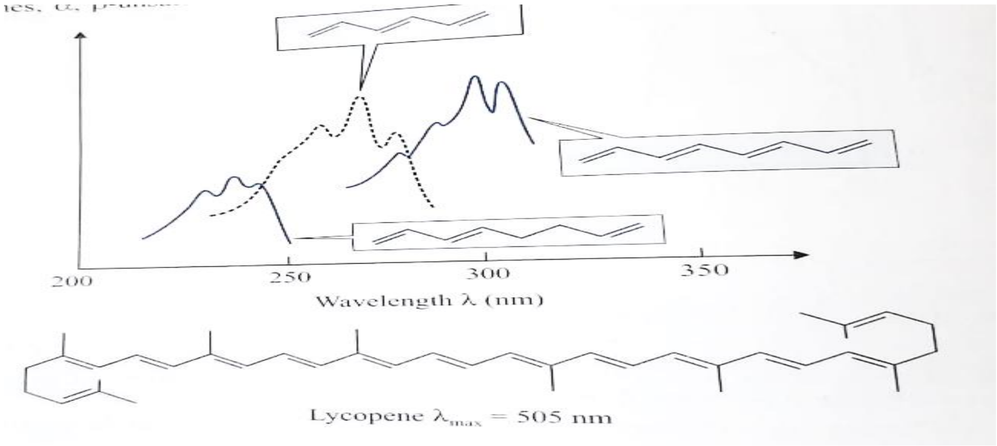


Figure 13: UV-Vis spectrum of Lycopene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- ***Detection of a chromophore in an unknown compound by comparison of its spectrum with that of a known compound***
    - Absorption in the near UV (above 200 nm) is invariably associated with the presence of unsaturated groups or atoms with unshared pairs of electrons- Presence of chromophore
    - Eg. Cholest-4-en-3-one have a α,β-unsaturated ketone moiety similar to mesityl oxide. The UV spectrum of known small molecule (mesityl oxide) is comparable with an unknown larger molecule (Cholest-4-en-3-one) indicating presence of same chromophore

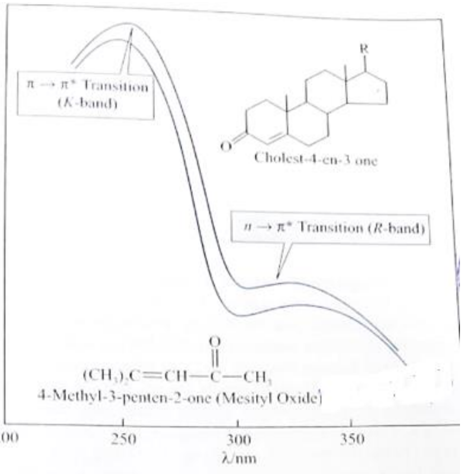
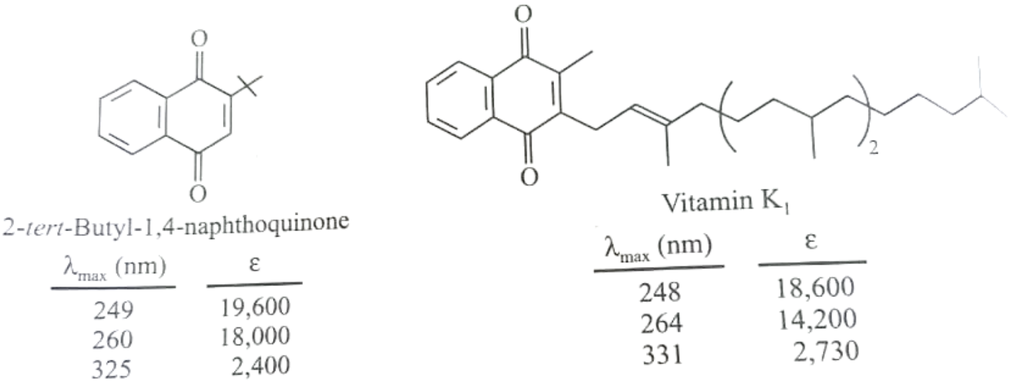


Figure 14: π-π* transition and n-π* transition of mesityl oxide (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- Presence of 1,4-naphthoquinone system in vitamin K1 can be confirmed



2-*tert*-Butyl-1,4-naphthoquinone

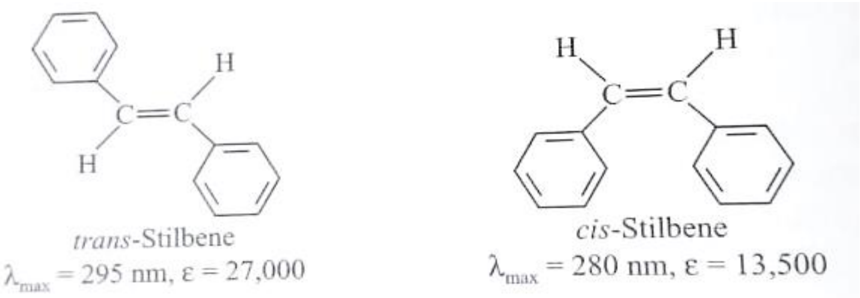
λ_{max} (nm)	ε
249	19,600
260	18,000
325	2,400

Vitamin K_1

λ_{max} (nm)	ε
248	18,600
264	14,200
331	2,730

Figure 15: λ_{max} and ε values of 2-tert-butyl-1,4-naphoquinone and vitamin K_1 (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- ***Identification of a chromophore (functional group)***
  - Simple conjugated dienes and α,β-unsaturated ketone have ε value of 10000 – 20000
  - Low intensity absorption bands around 270 – 350 nm with ε values 10 – 100 corresponds to n – π* transition of ketone
  - In-between these extremes, the presence of absorption bands with ε values of 1000 – 10000 indicate presence of aromatic system
- ***Study of Geometric Isomerism***
  - Trans- isomer absorbs at a longer wavelength and with larger molar absorptivity than cis- isomer
- ***Effect of Geometric Isomerism and Steric Effects***
  - In compounds where geometrical isomerism is possible such as Stilbene, the trans-isomer (E-isomer) absorbs at a longer wavelength with greater intensity than cis- isomer (Z-isomer) due to steric effect.
  - Thus coplanarity is needed for the most effective overlap of the π- orbitals and increased ease of π – π* transition.
  - The Z- isomer is forced into a nonplanar conformation due to steric effects
  - The greater the distance between the ends of a conjugated chromophore the greater is ε_{max}



trans-Stilbene
λ_{max} = 295 nm, ε = 27,000

cis-Stilbene
λ_{max} = 280 nm, ε = 13,500

Figure 16: λ_{max} and ε values of cis-Stilbene and trans-Stilbene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- ***Study of Tautomerism***
  - Ultraviolet spectroscopy can be used to identify stable tautomeric species
  - β keto ester exist as tautomeric form and their UV spectroscopy shows strong absorption due to conjugated double bond (enol form) and weak absorption due to keto carbonyl group in ethylacetoacetate

  - The keto form exhibit low intensity band around 275 nm whereas the enol form shows high intensity band around 245 nm
  -

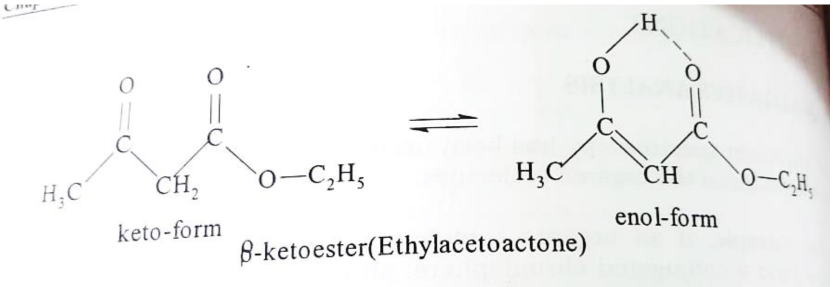


Figure 17: **Keto-form and Enol-form of β-keto ester**

- ***As an analytical tool***
  - The reaction rates and pKa values can be determined using UV spectroscopy
  - The reaction rate can be measured by UV spectroscopy provided one of the reactants or products absorb UV or visible light at a wavelength where the other reactants for products have no absorbents
  - Example: Anion of nitroethane λ_{max} at 240 nm but neither water not the other reactants show any significant absorbents at this wavelength
  - The Hydroxide ion remove a Proton from nitroethane
  - Nitroethane is added to cell containing a basic solution and the rate of the reaction is determined by monitoring the rate of increase in the absorbent at 240 mm

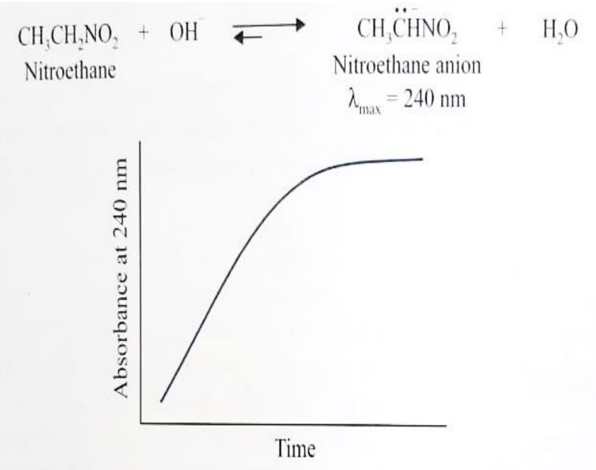


Figure 18: Absorbance Vs Time plot of nitroethane with NaOH (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- ***Study of Structural features in different solvents***
  - Chloral hydrate in hexane shows absorption maximum λ_{max} at 290 nm which is not seen in UV spectrum of same compound in Aqueous medium

- ***Effect of S-Cis (cisoid) and S-Trans (transoid) conformations***
  - Mono- and polycyclic dienes fall into two classes depending on whether the double bonds are in same ring or in different rings
  - Members of first class are called homoannular dienes and have S-Cis arrangement and their absorption closely resemble 1,3- cyclohexadiene. The

second category are heteroannular dienes and have S-trans arrangement and are spectrally related to butadiene

- ***S-cis***: The conformation of a single bond separating two double bonds in which the double bonds have a dihedral angle of 0° (the double bonds lie in the same plane and point in the same direction). The 's' in s-cis stands for 'single'.
- ***S-trans***: The conformation of a single bond separating two double bonds in which the double bonds have a dihedral angle of 180° (the double bonds lie in the different plane and point in the same direction).

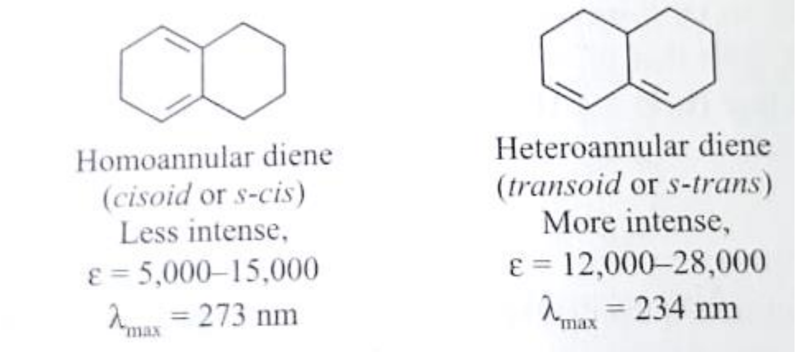


Figure 19: λ_{max} and ε values of Homoannular diene and Heteroannular diene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

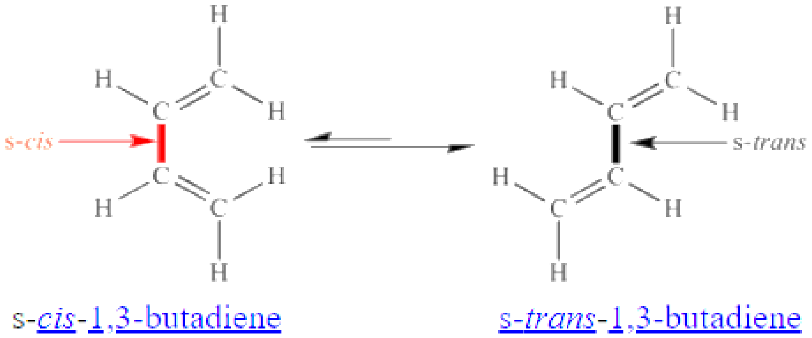


Figure 20: s-cis-1,3-butadiene and s-trans-1,3-butadiene (Source: www.chemucla.edu)

- ***Effect of Alkyl Substitution and Ring residues***
  - Each alkyl substituents or ring residue attached to the conjugated diene chromophore displaces λ_{max} by about 5 nm towards longer wavelength
  - Example: Butadiene λ_{max} 217 nm in 2,3- dimethyl-1,3-butadiene then the two added methyl groups on C2 and C3 of the basic conjugated dienes system result in a 5 + 5 or 10nm increase in λ_{max}
  - Similarly in 1,3- pentadiene the observed λ_{max} is close to the calculated value

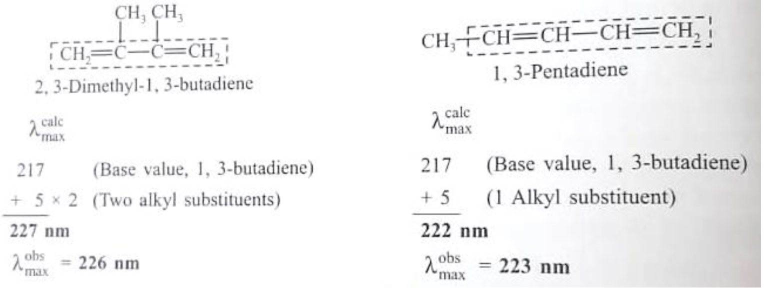


Figure 21: Calculated λ_{max} and observed λ_{max} values of 2,3-dimethyl-1,3-butadiene and 1,3-pentadiene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- ***Effect of Exocyclic double bonds***
  - In 1- methyl cyclohexene the double bond is inside the ring called endocyclic position and this is a stable isomer that has double bond inside the ring
  - The less stable isomer has double bond projecting outside the ring are called exocyclic position
  - Each exocyclic double bond causes a displacement of λ_{max} by 5 nm towards longer wavelength redshift and may be regarded as 1,3- butadiene derivative in which the two hydrogen atoms of one of the terminal CH2 group are replaced by 2 ring Residue.
  - These ring residues add 2 x 5 nm to the λ_{max}. The double bond attached to the cyclohexane is exocyclic therefore additional 5 nm must be added.
  - Thus it is important to locate the exocyclic position of a double bond in a compound

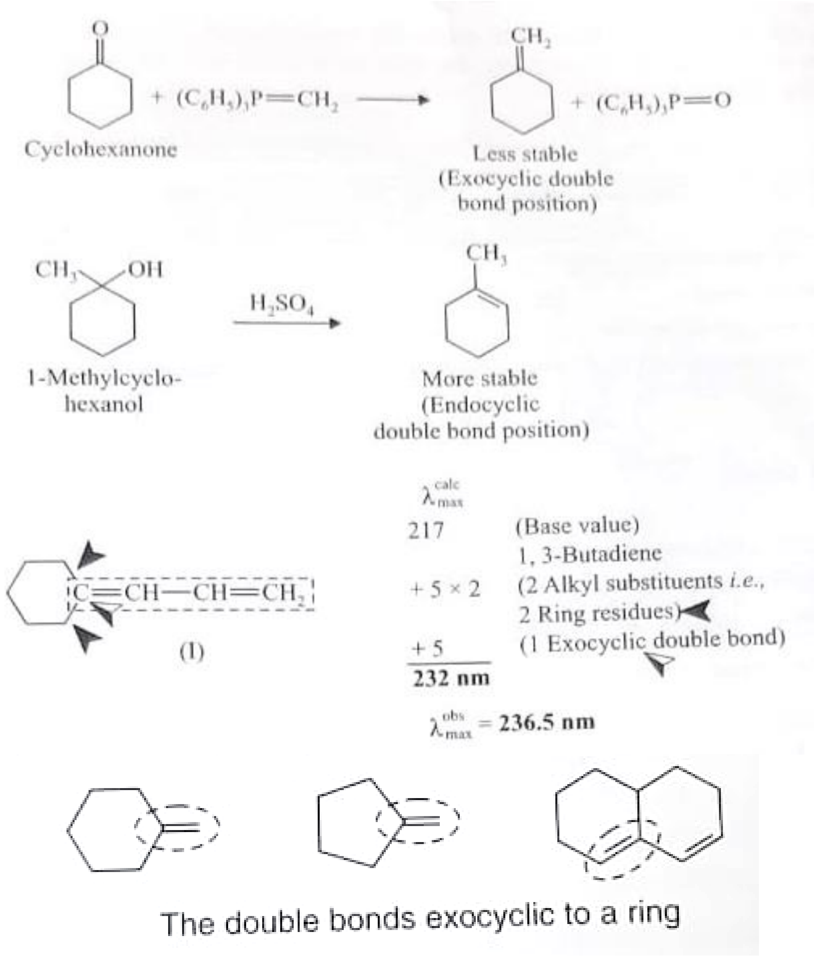


Figure 22: Exocyclic double bonds in compounds (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

5. Woodward-Fieser Rules

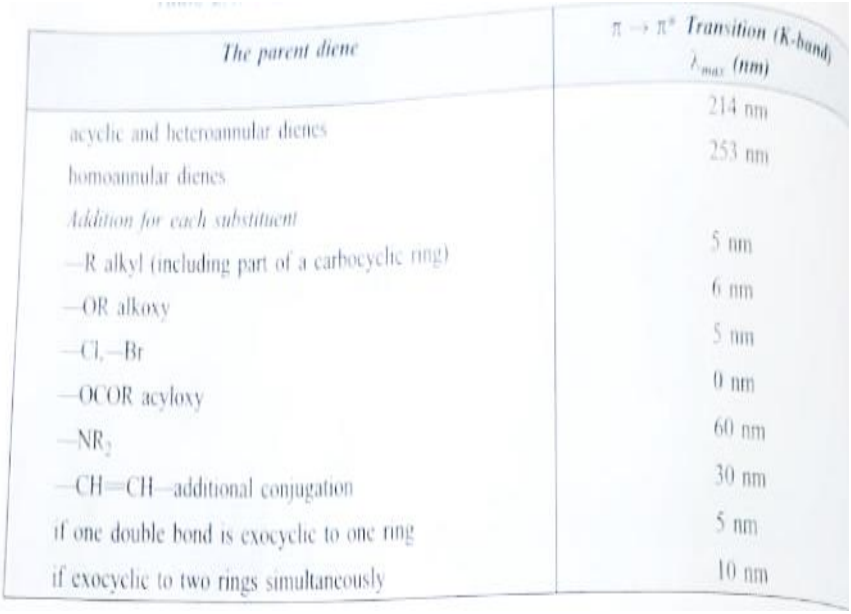
- ***Woodward–Fieser rules*** are several sets of empirically derived rules which attempt to predict the wavelength of the absorption maximum (λ_{max}) in an ultraviolet-visible spectrum of a given compound. Inputs used in the calculation are based on the type of chromophores present, the auxochromes (substituents on the chromophores) present and the solvent used.

- ***Steps involved in calculation of λ_{max}***
- Each type of diene or triene or α, β-unsaturated aldehydes or ketones have a certain fixed value where absorption takes place- Base value
- The contribution made by various alkyl substituents or ring residues or double bond extension conjugation or polar groups such as Br, Cl etc are added to base value to obtain the λ_{max} for a particular compound.
- λ_{max} = Base value + ΣSubstituent contribution + ΣOther contribution
- There are three sets of rules
    - 1. Woodword – Fieser rule for conjugated dienes and polyenes
    - 2. Woodword – Fieser rule for carbonyl compounds
    - 3. Woodword – Fieser rule for aromatic compounds

Woodward-Fieser Rules for Conjugated Dienes and Trienes

- Woodword - Fieser rules are used for calculation of absorption maximum λ_{max} wavelength in conjugated dienes and trienes
- The diene absorption is influenced by its structure
- Woodword gave rules for calculating λ_{max} which was improved by Fieser.
- Unlike the base value 217 nm used for predicting the λ_{max} values (1,3-butadiene) Woodword - Fieser fix this value at 214 nm.
- Calculated and experimental values of λ_{max} match within 5 nm
- In case of acyclic diene such as myrcene there is only alkyl i.e., C-substituent on the dienes system

Table 1: λ_{max} values of π-π* transition of various diene



The parent diene	$\pi \rightarrow \pi^*$ *Transition (K-band)* λ_{max} *(nm)*
acyclic and heteroannular dienes	214 nm
homoannular dienes	253 nm
Addition for each substituent	
—R alkyl (including part of a carbocyclic ring)	5 nm
—OR alkoxy	6 nm
—Cl, —Br	5 nm
—OCOR acyloxy	0 nm
—NR_2	60 nm
—CH=CH—additional conjugation	30 nm
if one double bond is exocyclic to one ring	5 nm
if exocyclic to two rings simultaneously	10 nm

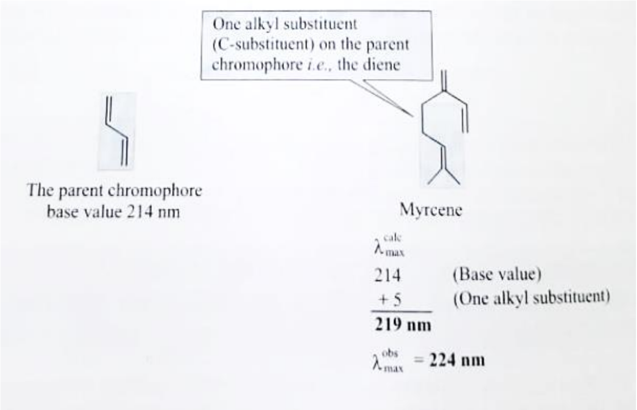


Figure 23: Calculated λmax and observed λmax values of Myrcene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- Monocyclic system such as β-phellandrene, two additional factors need consideration
- There are two ring residues on the diene system and one double bond is exocyclic to the ring
- α-Terpinene is homoannular diene with four carbon substituents on it and these are methyl groups, an isopropyl group and two ring residue
- In α-phellandrene there are only 3 substituent

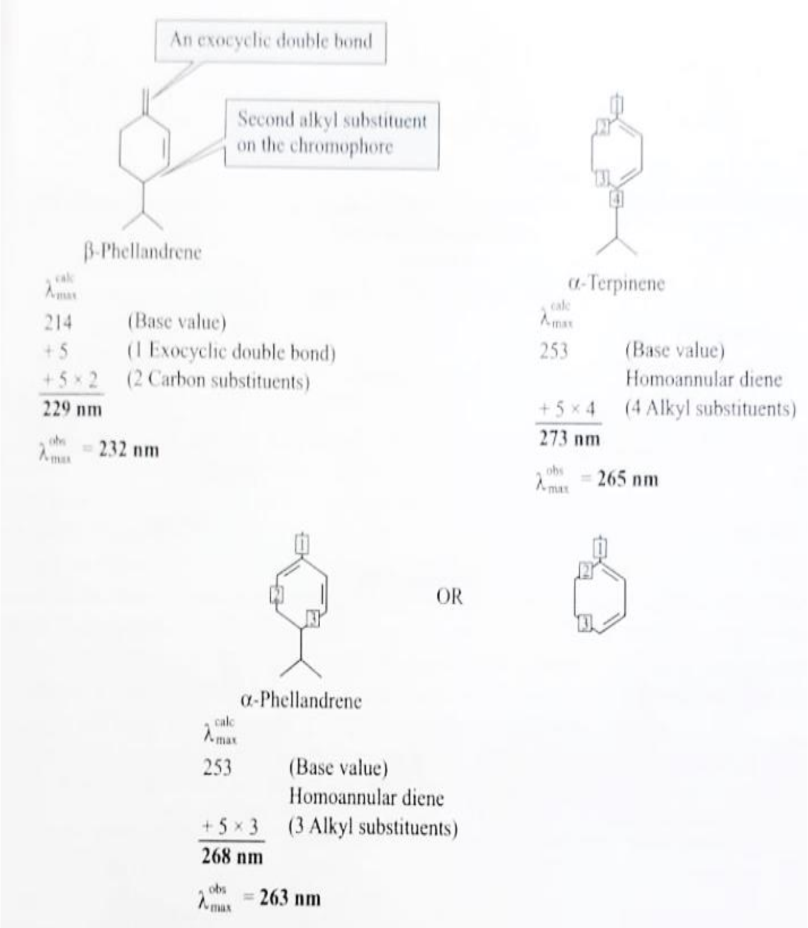


Figure 24: Calculated λmax and observed λmax values of β-phellandrene, α-Terpinene and α-phellandrene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- Both the dienes I and II are homoannular and can be calculated to have a λ_{max} at 273 nm
- In (I) diene double bond is exocyclic to ring B while none of the double bond in diene (II) has exocyclic position
- Diene (I) has 3 ring residue while in (II) diene there are 4 ring residue instead to make the total same in both the cases
- Diene (III) is heteroannular and base value taken as 214 nm and contains 3 ring residues and one exocyclic double bond

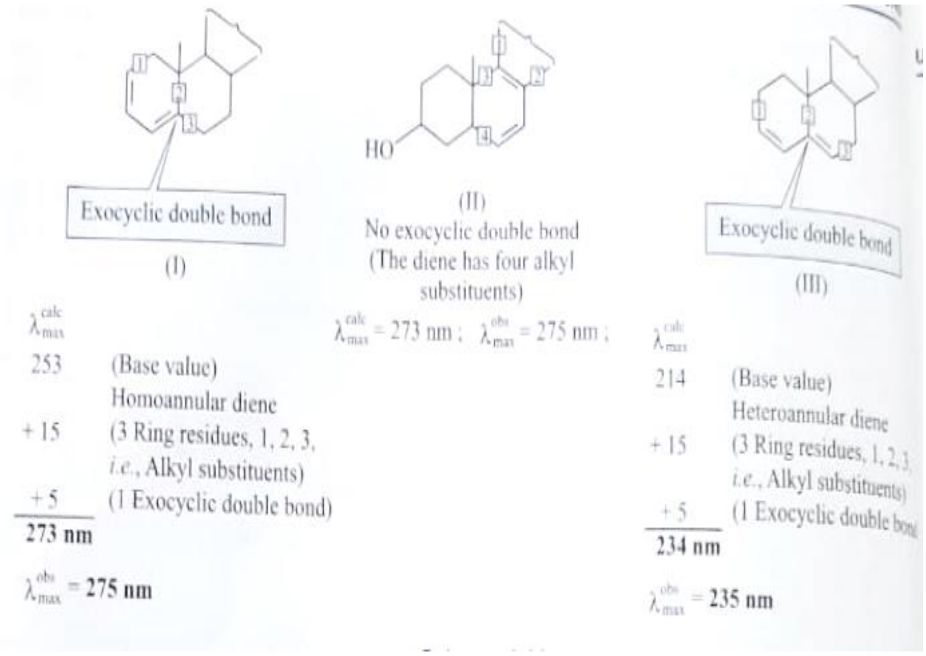
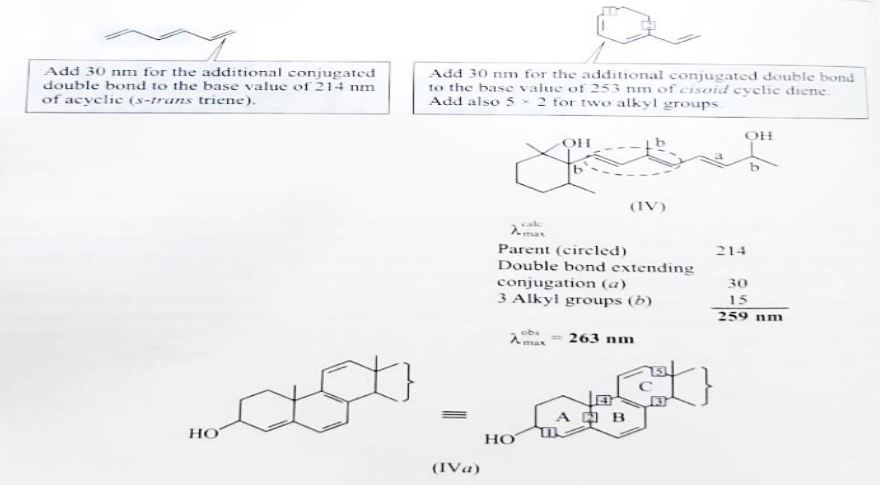
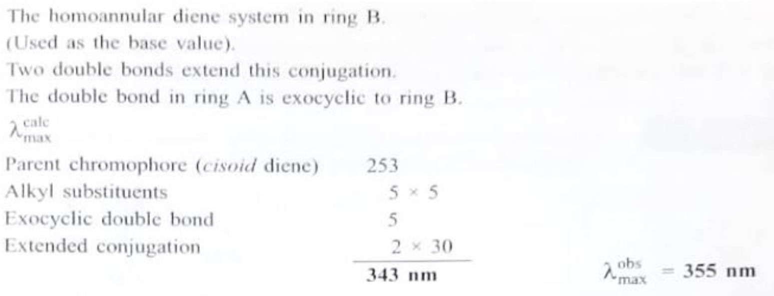


Figure 25: Calculated λ_{max} and observed λ_{max} values of homoannular diene and Heteroannular diene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- In compounds that contain both homoannular and heteroannular diene system the calculations are based on homoannular diene system
- When one or two double bond extend the conjugation, 30 nm is added for each extension on the entire conjugated system as shown for compounds IV and IV a





The homoannular diene system in ring B.
(Used as the base value).
Two double bonds extend this conjugation.
The double bond in ring A is exocyclic to ring B.

λ_{max}^{calc}

Parent chromophore (*cisoid* diene)	253
Alkyl substituents	5 × 5
Exocyclic double bond	5
Extended conjugation	2 × 30
	343 nm

λ_{max}^{obs} = 355 nm

Figure 26: Calculated λ_{max} and observed λ_{max} values of s-cisoid and s-transoid dienes (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Effect of strain around the diene chromophore - Exceptions to Woodward rules

- Woodward rules for conjugated dienes do not give reliable results if strain is present around the chromophore
- The strain may lead to red or blue shift depending on the nature of strain
- Compared to β -phellandrene (V), the compound Verbenene (VI) has an λ_{max} at 245 nm while the calculated value for both is 229 nm
- In diene (VII) the distortion of the chromophore, presumably out of planarity with consequent loss of conjugation causes the λ_{max} as low as 220 nm – Blue shift
- Calculated λ_{max} = 214 + 2 x 5 (exo) + 2 x 5 (alkyl) = 234 nm
- In diene (VIII) however the coplanarity of the diene is more likely and it gives a maximum at 243 nm but still does not agree with the expected value that is 234 nm – Red shift

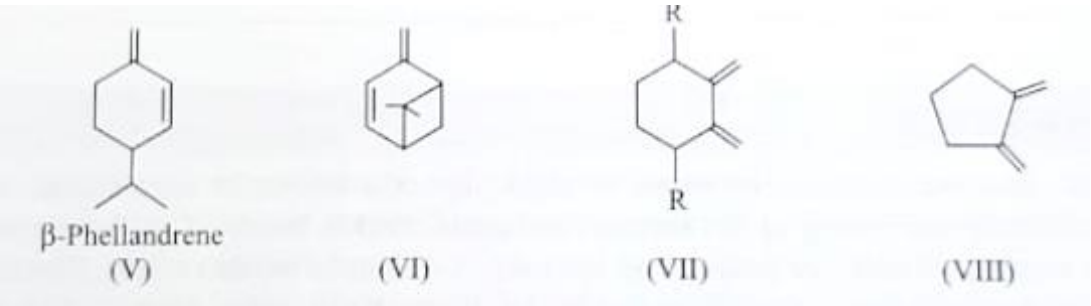
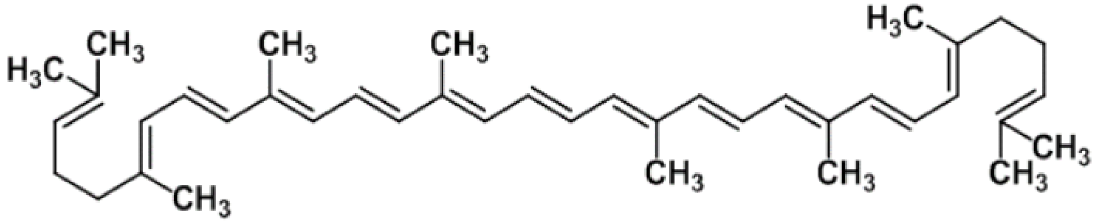


Figure 27: Strained diene chromophore systems (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

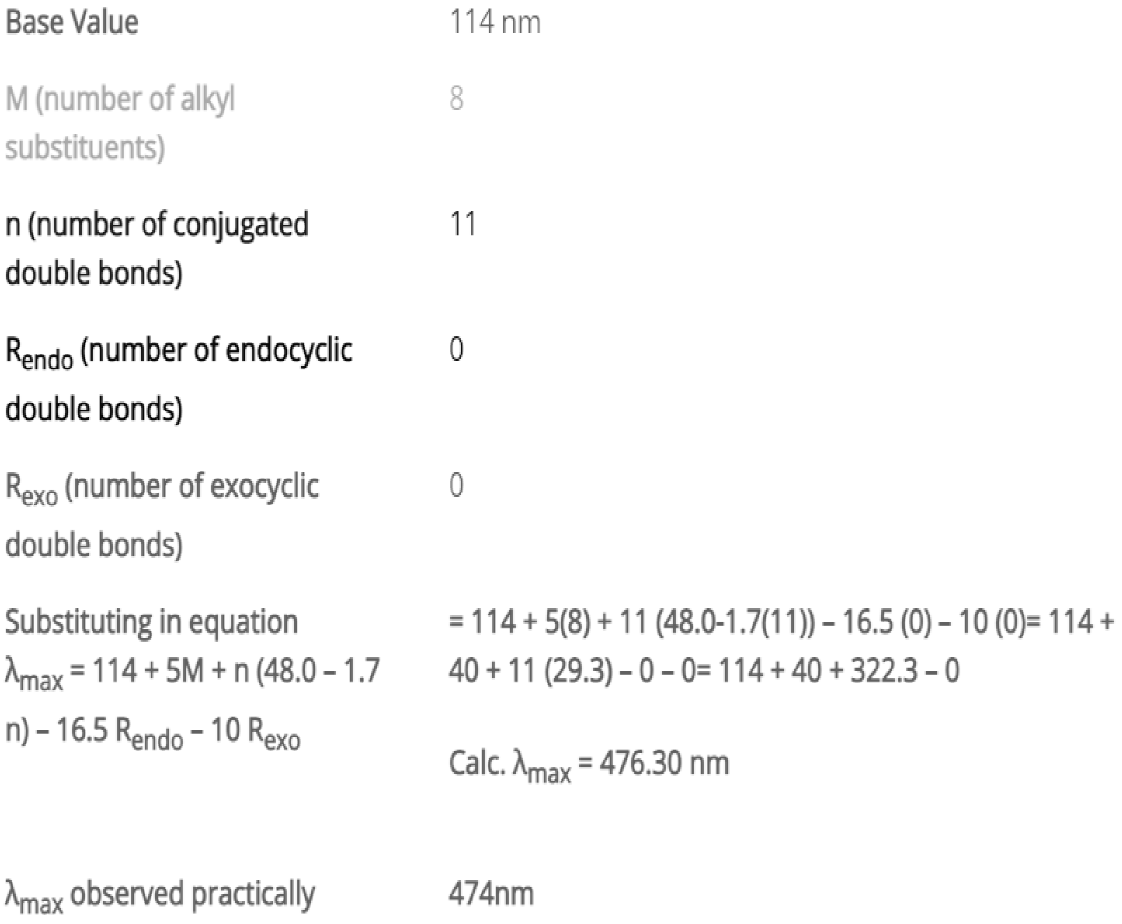
Fieser – Kuhn Rules for Polyenes

- Polyenes - Plant pigments like Carotenoids which are extended polyenes containing upto eleven conjugated double bonds
- The Woodward – Fieser rule work well only for conjugated systems of 4 double bonds or less
- For conjugated polymers having more than four double bonds Fieser - Kuhn rules are used
- When applied to All-trans-lycopene λ_{max} is obtained at 474 nm

- In this compound of the 13 double bonds only eleven are conjugated (n=11)
- There are 8 substituents (Methyl groups and chain residues on the polyene system (M=8)
- There are no ring systems or exocyclic or endocyclic double bonds ($R_{exo} = R_{endo} = 0$)

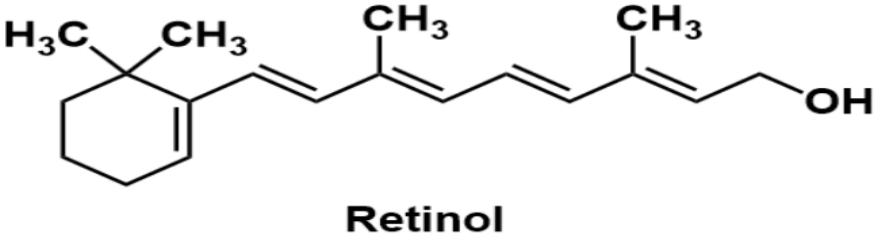


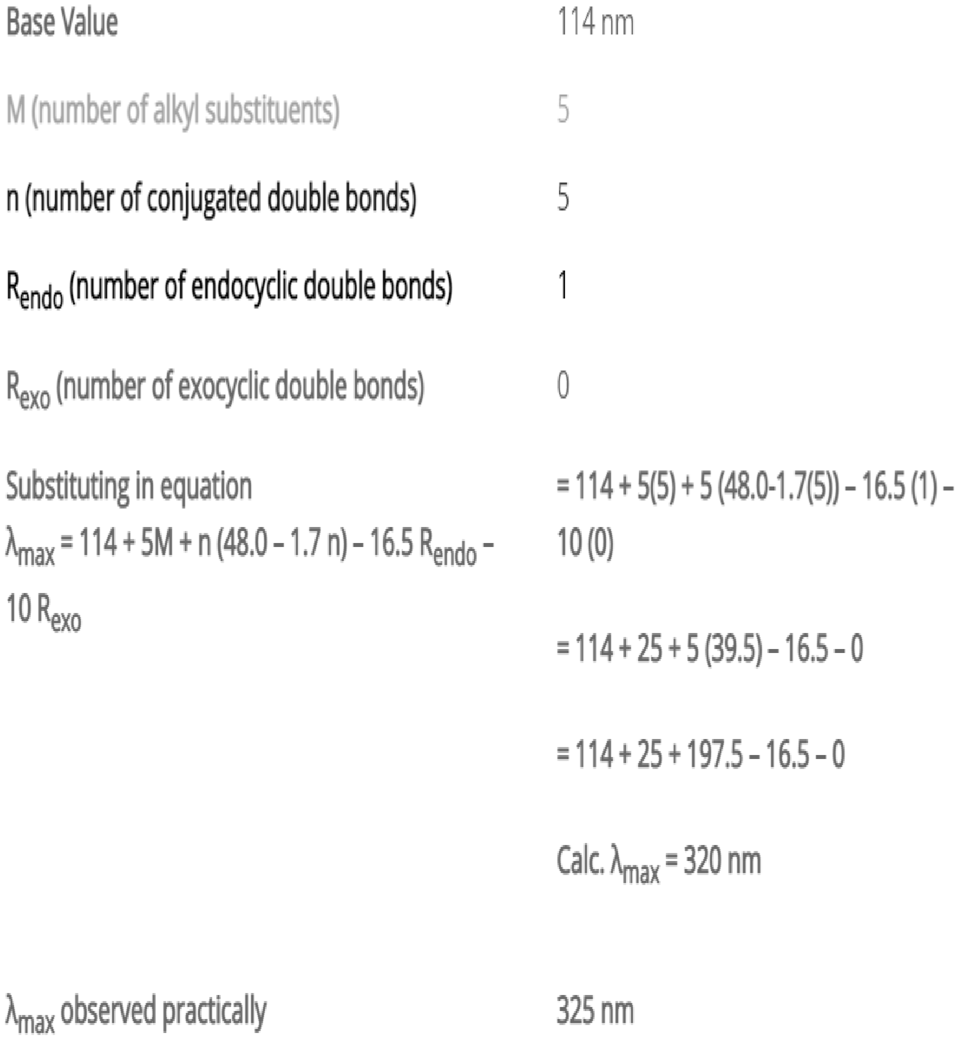
all-*trans*-lycophene



Base Value	114 nm
M (number of alkyl substituents)	8
n (number of conjugated double bonds)	11
R_{endo} (number of endocyclic double bonds)	0
R_{exo} (number of exocyclic double bonds)	0
Substituting in equation $\lambda_{max} = 114 + 5M + n (48.0 – 1.7 n) – 16.5 R_{endo} – 10 R_{exo}$	= 114 + 5(8) + 11 (48.0-1.7(11)) – 16.5 (0) – 10 (0)= 114 + 40 + 11 (29.3) – 0 – 0= 114 + 40 + 322.3 – 0 Calc. λ_{max} = 476.30 nm
λ_{max} observed practically	474nm

Figure 28: Calculated λ_{max} values of All-trans-lycopene by Fieser-Kuhn rule





Base Value	114 nm
M (number of alkyl substituents)	5
n (number of conjugated double bonds)	5
R_{endo} (number of endocyclic double bonds)	1
R_{exo} (number of exocyclic double bonds)	0
Substituting in equation $\lambda_{max} = 114 + 5M + n\,(48.0 - 1.7\,n) - 16.5\,R_{endo} - 10\,R_{exo}$	$= 114 + 5(5) + 5\,(48.0\text{-}1.7(5)) - 16.5\,(1) - 10\,(0)$
	$= 114 + 25 + 5\,(39.5) - 16.5 - 0$
	$= 114 + 25 + 197.5 - 16.5 - 0$
	Calc. λ_{max} = 320 nm
λ_{max} observed practically	325 nm

Figure 29: Calculated λ_{max} values of Retinol by Fieser-Kuhn rule

6. UV Bands of Carbonyl compounds

- ***n-π* Transition (R band)***
- Saturated aldehydes and ketones display two significant absorption bands a weak symmetry forbidden band around 270 nm is n-π* Transition (R band) and intense π-π* Transition (K band) and results from the excitation of oxygen lone pair electrons to antibonding π-orbital of the carbonyl group.
- This band is used for identification of ketones

- Polar substituents such as the halogen on the α- carbon in case of an aliphatic ketone has no effect of the n-π* Transition
- In cyclic ketones, the presence of such substituents raise by 10 - 30 nm (when axial) or lower by 4 – 10 nm (when equatorial), the λ_{max} of the parent compound
- Thus compared with parent and substituted steroid (I), the 6-α -bromo derivative (II, equatorial Br) shows a decrease in λ_{max} while the 6-β-epimer (III, axial Br) displays a wavelength shift of +26 nm with intensification of the absorption
- The preferred confirmation in a non rigid system, thus 2-chlorocyclohexanone may have either confirmation (IV) or (V)
- Compared with cyclohexanone (λ_{max}=283nm), 2-chlorocyclohexanone absorbs at 293 nm corresponding to a shift of +11 nm to indicate that the more important confirmation is (IV)

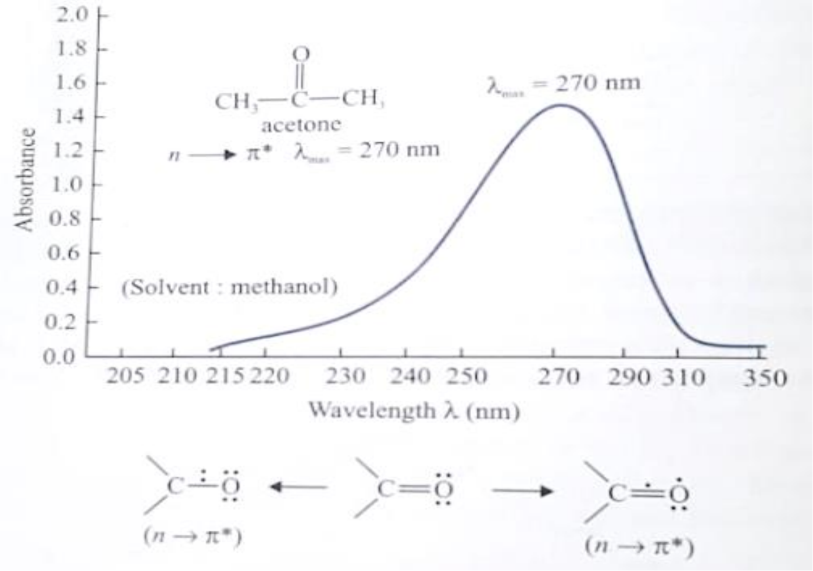


Figure 30: UV spectrum of acetone (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

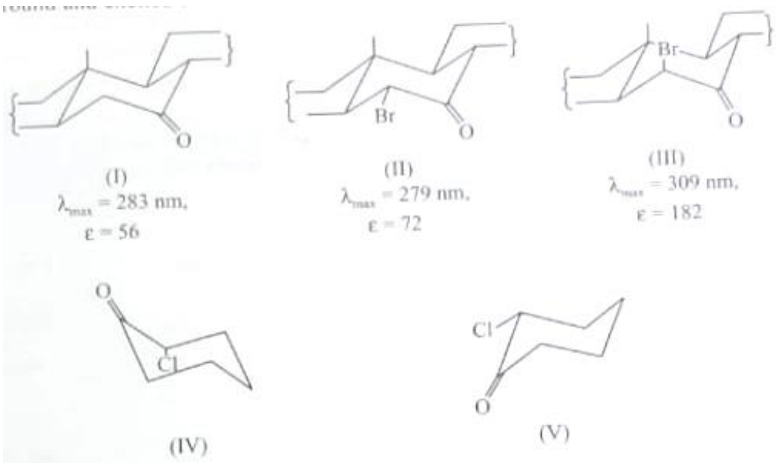


Figure 31: λ_{max} and ε values of substituted cyclohexanones (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Distinction between the carbonyl group in aldehydes and ketones from Carboxylic acids, esters and amides

- When the carbonyl group is substituted by an auxochrome, for example: an Ester (OR) or an amide (NH2), the π* orbital is raised but the n level of the Lone pair is not much affected
- As a consequence the n-π* transition of these compounds is shifted to shorter wavelength (200 - 220 nm) range
- Thus compared to acetaldehyde λ_{max} = 293 nm the R-bands of ethylacetate, acetic acid and acetamide are shifted to 207,204 and 220 nm respectively
- The presence of a weak band in 275 - 295 nm region is positive identification of Ketone or aldehyde carbonyl group

α,β-Unsaturated aldehydes and ketones

- Compounds in which carbon-oxygen double bond is conjugated with a carbon-carbon double bond (enones) have their absorption at longer wavelengths due to a decrease in the energy difference between ground and excited states
- Thus both the n-π*(R-band) and π-π* transitions (K-band) are at a longer wavelength (lower energies) in 3-buten-2-one (methyl vinyl ketone) than in the non-conjugated acetone
- The excited state is relatively more stabilized by conjugation than the ground state as a result the magnitude of the energy transition is decreased
- The enones can be easily characterized by an intense absorption band (K-band) in 215 - 250 nm region (e_{max} usually 10000 to 20000) and a weak n-π* band (R-band) at 310 - 330 nm
- The change of solvent polarity affect the wavelength of the transition

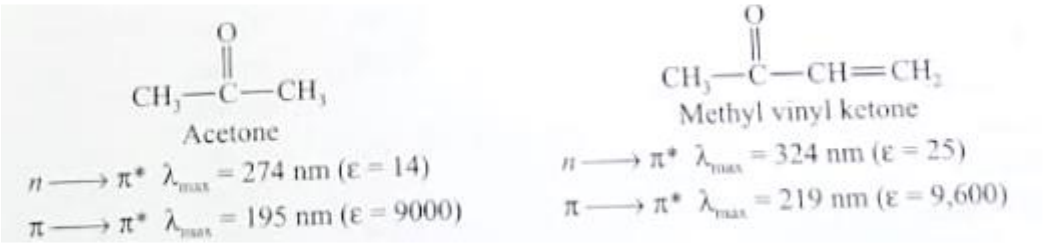
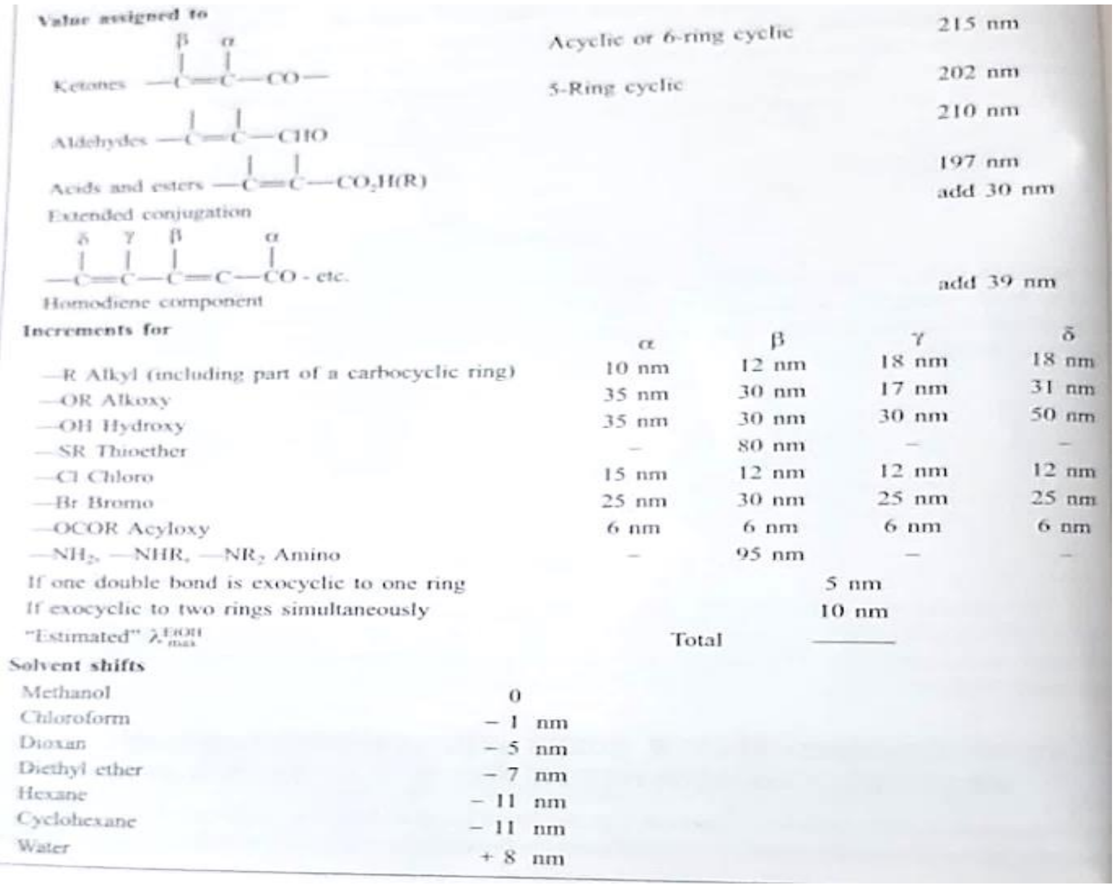


Figure 32: λ_{max} and ε values of n-π* and π-π* transitions of acetone and methylvinyl ketone (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Table 2: Base values and substituent λ_{max} values of ketones and aldehydes (Source: Spectroscopy of Organic compounds, P.S. Kalsi)



Value assigned to

Ketones $-\overset{\beta}{C}=\overset{\alpha}{C}-CO-$	Acyclic or 6-ring cyclic	215 nm
	5-Ring cyclic	202 nm
Aldehydes $-C=C-CHO$		210 nm
Acids and esters $-C=C-CO_2H(R)$		197 nm
Extended conjugation		add 30 nm
$-\overset{\delta}{C}=\overset{\gamma}{C}-\overset{\beta}{C}=C-\overset{\alpha}{C}O$ - etc.		
Homodiene component		add 39 nm

Increments for

	α	β	γ	δ
—R Alkyl (including part of a carbocyclic ring)	10 nm	12 nm	18 nm	18 nm
—OR Alkoxy	35 nm	30 nm	17 nm	31 nm
—OH Hydroxy	35 nm	30 nm	30 nm	50 nm
—SR Thioether	–	80 nm	–	–
—Cl Chloro	15 nm	12 nm	12 nm	12 nm
—Br Bromo	25 nm	30 nm	25 nm	25 nm
—OCOR Acyloxy	6 nm	6 nm	6 nm	6 nm
$-NH_2$, —NHR, $-NR_2$ Amino	–	95 nm	–	–

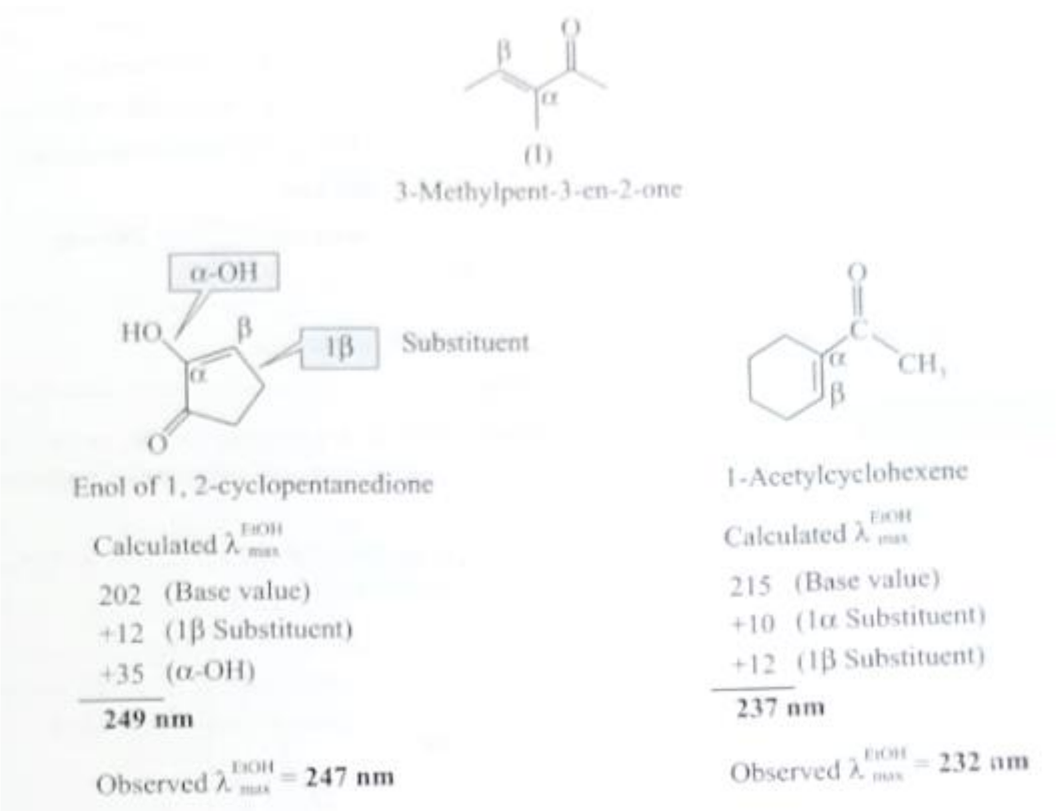
If one double bond is exocyclic to one ring		5 nm
If exocyclic to two rings simultaneously		10 nm
"Estimated" λ_{max}^{EtOH}	Total	———

Solvent shifts

Methanol	0
Chloroform	− 1 nm
Dioxan	− 5 nm
Diethyl ether	− 7 nm
Hexane	− 11 nm
Cyclohexane	− 11 nm
Water	+ 8 nm

Woodward-Fieser Rules for α,β-Unsaturated Ketones and Aldehydes for π-π* Transition

- The Woodward rules are used to calculate the position of intense π-π* Transition not the weak and n-π* Transition for alpha beta unsaturated carbonyl compounds
- The λ_{max} for a π-π* absorption band in the UV spectrum of compound I is calculated by taking the base value = 215 nm; for one α-alkyl group add 10 nm; for one beta alkyl group add 12 nm. Thus the total is 215 + 10 + 12 = 237 nm this is within one nm of the observed value (for which e_{max} is 4600)
- If the spectrum is recorded in water λ_{max} would move to 245 nm that is π-π* bands undergo a red shift



(I)
3-Methylpent-3-en-2-one

Enol of 1, 2-cyclopentanedione

Calculated λ_{max}^{EtOH}

202 (Base value)
+12 (1β Substituent)
+35 (α-OH)
249 nm

Observed λ_{max}^{EtOH} = **247 nm**

1-Acetylcyclohexene

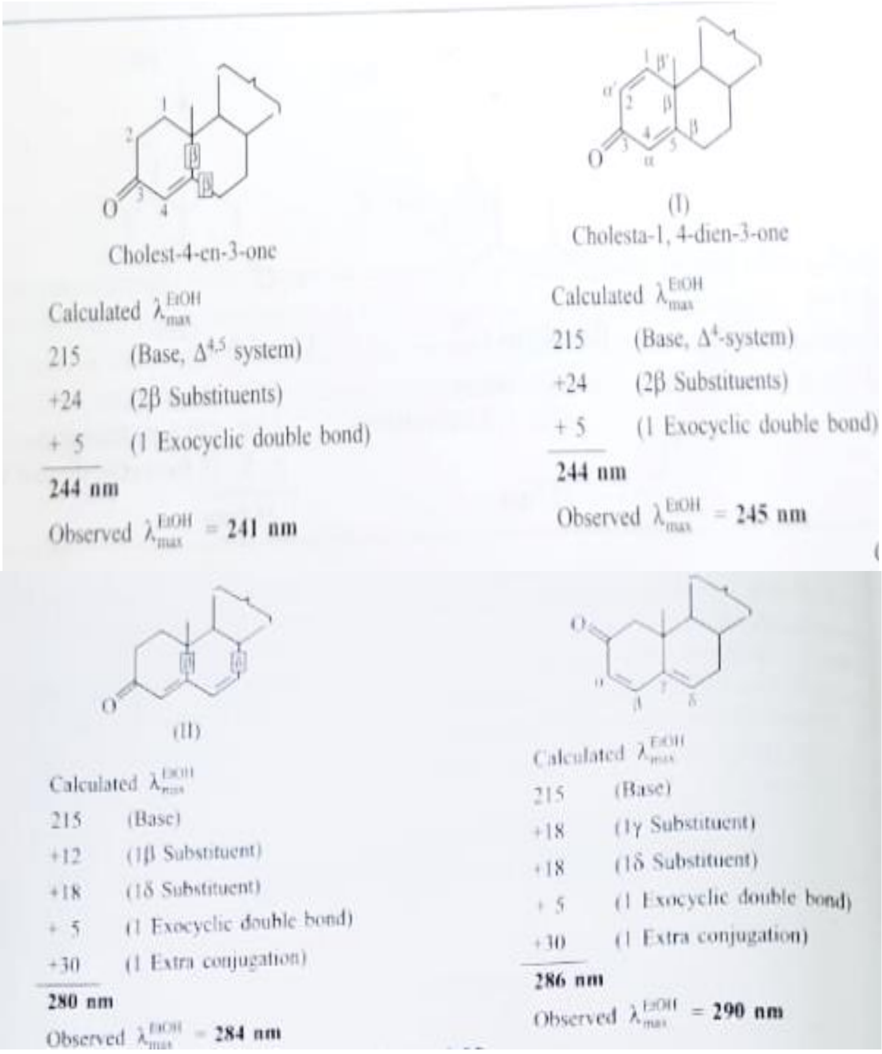
Calculated λ_{max}^{EtOH}

215 (Base value)
+10 (1α Substituent)
+12 (1β Substituent)
237 nm

Observed λ_{max}^{EtOH} = **232 nm**

Figure 33: Calculated λmax and observed λmax values of aliphatic and cyclic ketones (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- When cross conjugation (α,β-unsaturation on both sides of carbonyl group) is present in a compound then the value of λ_{max} is calculated by considering the most highly substituted conjugated system (i.e) the more active monoenone chromophore
- Thus in case of structure I the calculations do not take into account the 1,2-double bond or for the β group on it
- The UV spectroscopy therefore can distinguish the structure I and II
- The extended dienone (II) absorbs fully 30 nm to longer wavelength
- In the case of compound I the calculations taking into account the $\Delta^{1,2}$ system on the other hand gives 227 nm as predicted value


Cholest-4-en-3-one

Calculated λ_{max}^{EtOH}

215 (Base, $\Delta^{4,5}$ system)
+24 (2β Substituents)
+ 5 (1 Exocyclic double bond)

244 nm

Observed λ_{max}^{EtOH} = **241 nm**

(I)
Cholesta-1, 4-dien-3-one

Calculated λ_{max}^{EtOH}

215 (Base, Δ^{4}-system)
+24 (2β Substituents)
+ 5 (1 Exocyclic double bond)

244 nm

Observed λ_{max}^{EtOH} = **245 nm**

(II)

Calculated λ_{max}^{EtOH}

215 (Base)
+12 (1β Substituent)
+18 (1δ Substituent)
+ 5 (1 Exocyclic double bond)
+30 (1 Extra conjugation)

280 nm

Observed λ_{max}^{EtOH} = **284 nm**

Calculated λ_{max}^{EtOH}

215 (Base)
+18 (1γ Substituent)
+18 (1δ Substituent)
+ 5 (1 Exocyclic double bond)
+30 (1 Extra conjugation)

286 nm

Observed λ_{max}^{EtOH} = **290 nm**

Figure 34: Calculated λ_{max} and observed λ_{max} values of cyclic conjugated ketones (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

7. UV bands for Aromatic system benzene and its substituted derivatives

- Benzene (I) shows three absorption bands at 184 nm (ε_{max} = 60000), 203 nm (ε_{max} = 7400, K-band) and 254 nm (ε_{max} = 204, B-band)
- The intense band near 180 nm is a result of an allowed transition while the weak K-band and B-band near 200 and 260 nm respectively result from forbidden transitions in the highly symmetrical benzene molecule
- The B-band of benzene and many of its homologues show a great deal of fine structure in the vapour phase or in non polar solvents. The fine structure originate from sublevels of vibrational absorption upon which the electronic absorption is superimposed
- When the spectrum is determined in polar solvents interactions occur between solute and solvent which tend to reduce the fine structure

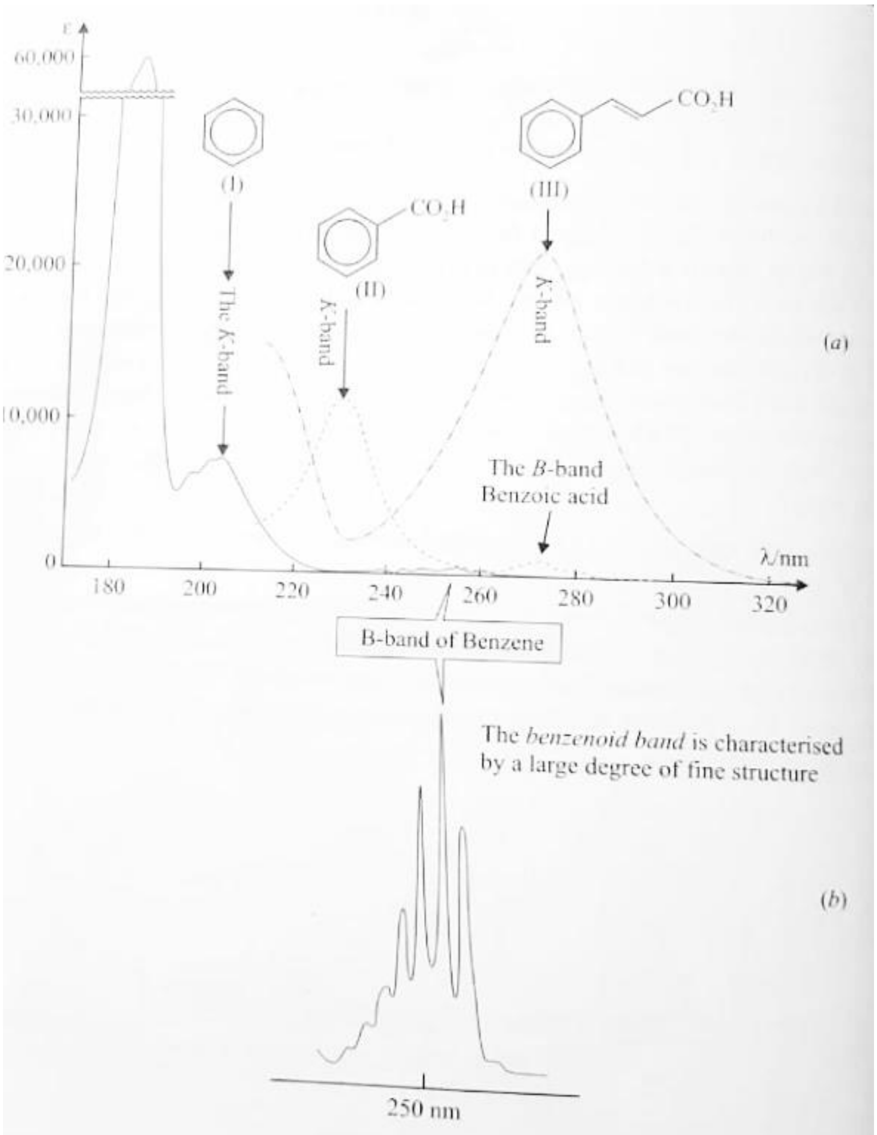


Figure 35: Absorption bands in benzene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- when Benzene is substituted by simple alkyl groups the absorption are shifted slightly to longer wavelength and the fine structure remains intact
- This small bathochromic shift is ascribed to hyperconjugation between the alkyl group and π system of the Ring
- The second alkyl group is most effective in producing a red shift if it is in the para position
- The para isomer absorbs at the longest wavelength where as the ortho isomer is observed at the shorter wavelength
- This effect is due to their weak interaction between the ortho substituents which effectively reduced hyperconjugation

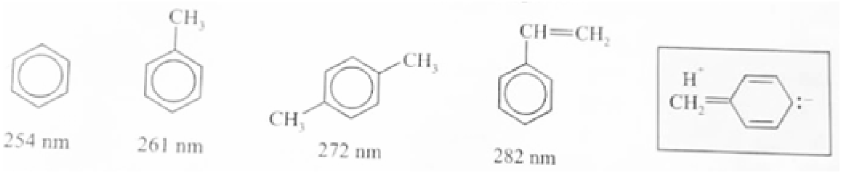


Figure 36: λmax of aromatic hydrocarbons (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- When non bonding pair substituents (-OH, -NH2, -OR etc) are present on the benzene ring the absorptions are shifted substantially to longer wavelengths and the fine structure of the band is either seriously diminished or wholly eliminated because of n-π conjugation
- In case of disubstituted benzene when electronically complementary group (i.e) an amino and nitro are situated Para to each other show a pronounced red shift in the main absorption band (K- band)
- This effect of presence of an electron donating and electron attracting groups Para to one another leads to the extension of chromophore through the benzene ring
- This extension of the chromophore is not possible when these groups are located ortho or meta to each other or if the para disposed to groups are not complementary
- In these cases the spectrum displays close resemblance with the separate non reacting chromophores

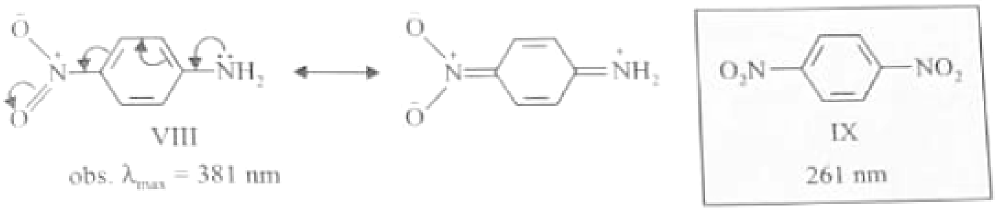
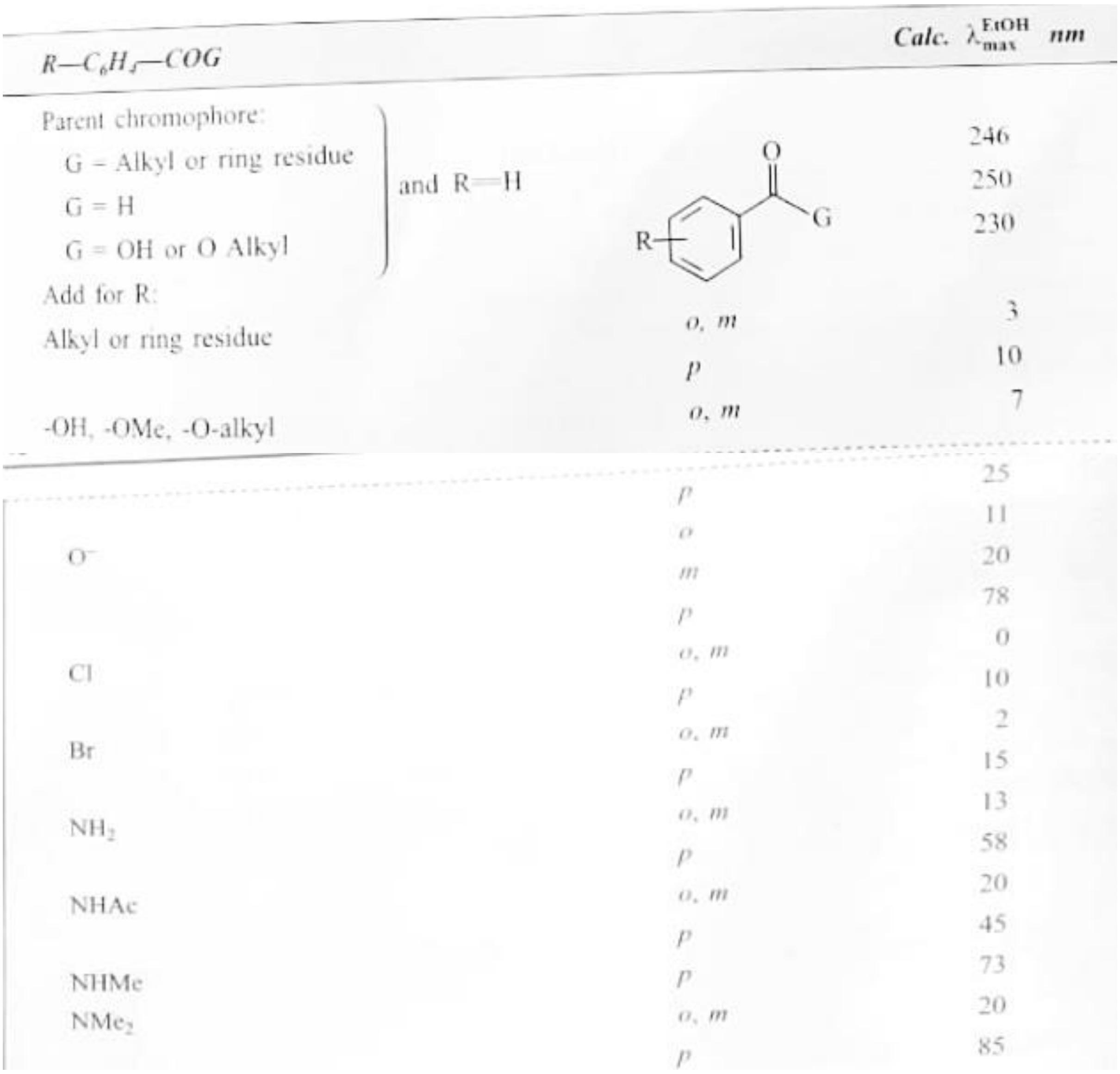


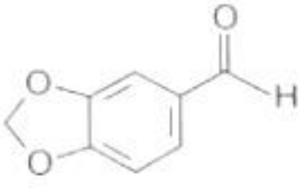
Figure 37: λmax for disubstituted benzene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- **Rules for calculating λmax of substituted benzenes**
- λ_{max} = Parent aromatic carbonyl + Σ other contributions (-o,-m,-p substituents in ring)

Table 3: λ_{max} for parent chromophore and various substitutents



$R—C_6H_4—COG$		Calc. λ_{max}^{EtOH} nm
Parent chromophore:		
G = Alkyl or ring residue and R = H		246
G = H and R = H		250
G = OH or O Alkyl and R = H		230
Add for R:		
Alkyl or ring residue	o, m	3
	p	10
-OH, -OMe, -O-alkyl	o, m	7
	p	25
O^-	o	11
	m	20
	p	78
Cl	o, m	0
	p	10
Br	o, m	2
	p	15
NH_2	o, m	13
	p	58
NHAc	o, m	20
	p	45
NHMe	p	73
NMe_2	o, m	20
	p	85

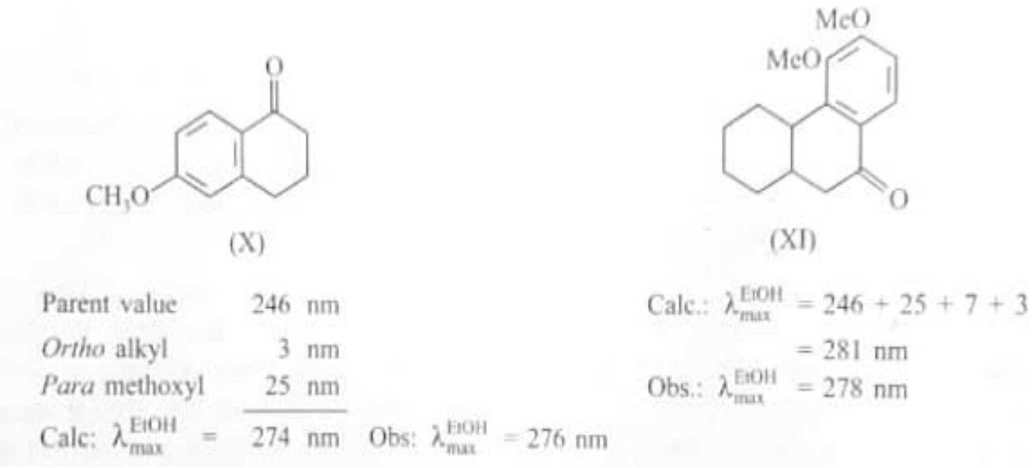


Piperonal

ANSWER: Calculated λ_{max}

250	(Parent aromatic carbonyl G = H)
+ 7	(*Meta* substituent)
+ 25	(*Para* substituent)
282 nm	

Observed λ_{max} = 280 nm


(X)

(XI)

Parent value	246 nm
Ortho alkyl	3 nm
Para methoxyl	25 nm
Calc: λ_{max}^{EtOH} =	274 nm

Obs: λ_{max}^{EtOH} = 276 nm

Calc.: λ_{max}^{EtOH} = 246 + 25 + 7 + 3 = 281 nm

Obs.: λ_{max}^{EtOH} = 278 nm

Figure 38: Calculated λ_{max} for substituted cyclic ketones (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

UV Bands for Polycyclic aromatic Hydrocarbons

- The UV spectra of polycyclic aromatic compounds are highly complicated but unique of each aromatic system and provide useful fingerprints for identification purposes
- The introduction of relatively non-polar substituents like alkyl or acetoxy groups have little influence on λ_{max} or ε_{max}
- Thus methylanthracene are readily recognized to have the anthracene chromophore by a comparison of their UV spectra
- As the number of condensed rings increases the absorption moves progressively to longer wavelengths until it occurs in the visible region
- For example: in case of pentacene (λ_{max} = 580 nm blue) 5 benzene rings joint in a linear fashion

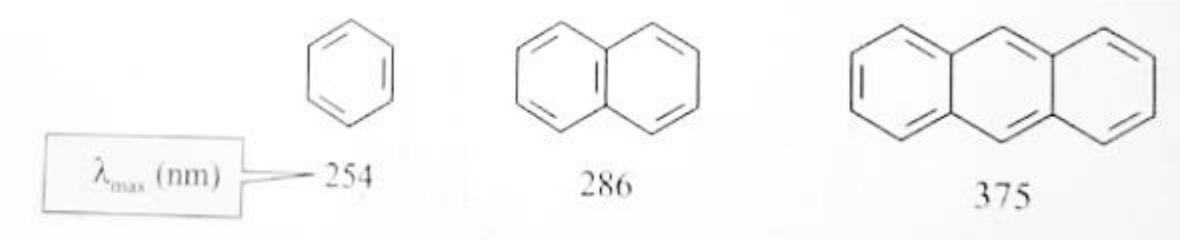


Figure 39: λ_{max} for aromatics (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

UV Bands for Heteroaromatic Compounds

- The UV spectra of heteroaromatic compounds are similar to their corresponding hydrocarbons
- The absorption of 5 membered ring aromatic compounds are comparable with that of cyclopentadiene (intense absorption near 200 nm and moderately intense absorption near 238 nm)

- Similarly the spectrum of pyridine is comparable with that of benzene the only difference being that the B-band of pyridine is more intense with diminished fine structure
- This transition is allowed for pyridine but Forbidden for the more symmetrical benzene molecule
- An increase in the solvent polarity does not affect either the position or intensity of B-band of benzene but produces a hyperchromic effect on B-band of pyridine and its homologues
- This effect is assigned to hydrogen bonding through the lone pair of electrons of Nitrogen atom
- Generation of tautomeric system is seen in 2-hydroxy pyridine which tautomerizes entirely to 2-pyridones

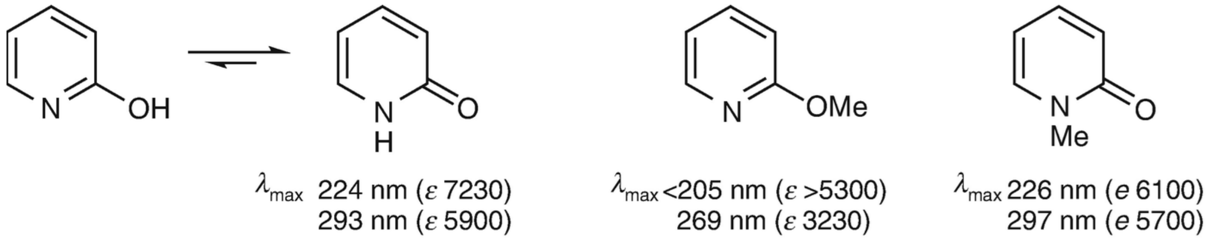
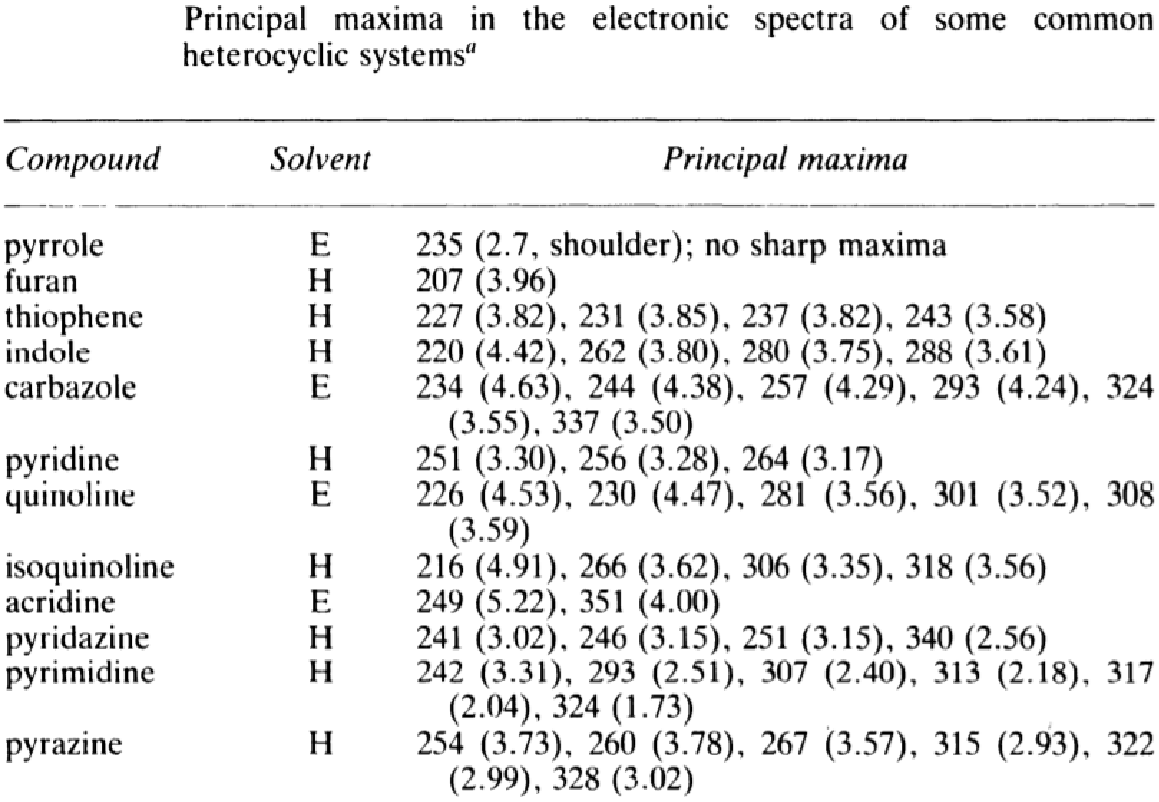


Figure 40: λ_{max} for heteroaromatic compounds (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Table 4: λ_{max} for various heteroaromatic compounds



Principal maxima in the electronic spectra of some common heterocyclic systems[a]

Compound	*Solvent*	*Principal maxima*
pyrrole	E	235 (2.7, shoulder); no sharp maxima
furan	H	207 (3.96)
thiophene	H	227 (3.82), 231 (3.85), 237 (3.82), 243 (3.58)
indole	H	220 (4.42), 262 (3.80), 280 (3.75), 288 (3.61)
carbazole	E	234 (4.63), 244 (4.38), 257 (4.29), 293 (4.24), 324 (3.55), 337 (3.50)
pyridine	H	251 (3.30), 256 (3.28), 264 (3.17)
quinoline	E	226 (4.53), 230 (4.47), 281 (3.56), 301 (3.52), 308 (3.59)
isoquinoline	H	216 (4.91), 266 (3.62), 306 (3.35), 318 (3.56)
acridine	E	249 (5.22), 351 (4.00)
pyridazine	H	241 (3.02), 246 (3.15), 251 (3.15), 340 (2.56)
pyrimidine	H	242 (3.31), 293 (2.51), 307 (2.40), 313 (2.18), 317 (2.04), 324 (1.73)
pyrazine	H	254 (3.73), 260 (3.78), 267 (3.57), 315 (2.93), 322 (2.99), 328 (3.02)

8. UV bands for Charge Transfer Complexes and dd- Transitions

- Charge transfer complexes called (EDA) the electron donor-acceptor complexes

- The donor may donate an unshared pair or a pair of electrons in π-orbital of a double bond or an aromatic system
- The evidence for formation of this type of complexes is Electronic spectroscopy
- Such complexes generally display a spectrum (charge transfer spectrum) which is not the sum of spectra of parent individual molecules
- These complexes are often coloured due first excited state of the complex is relatively close to the ground state
- Consequently there is usually a peak in the visible or near UV region does the colourless components tetracyanoethylene and paracyclophane give a coloured complex λ_{max} = 521 nm in CH_2Cl_2 (I)
- Another example of such complex is the formation of a picrate between picric acid and aromatic hydrocarbon like anthracene (II)
- Complexes, in which the iodine accept electron from benzene probably via the expansion of the outer shell to hold on to 10 electrons
- For the reason of complex formation iodine loses its purple colour in Benzene III

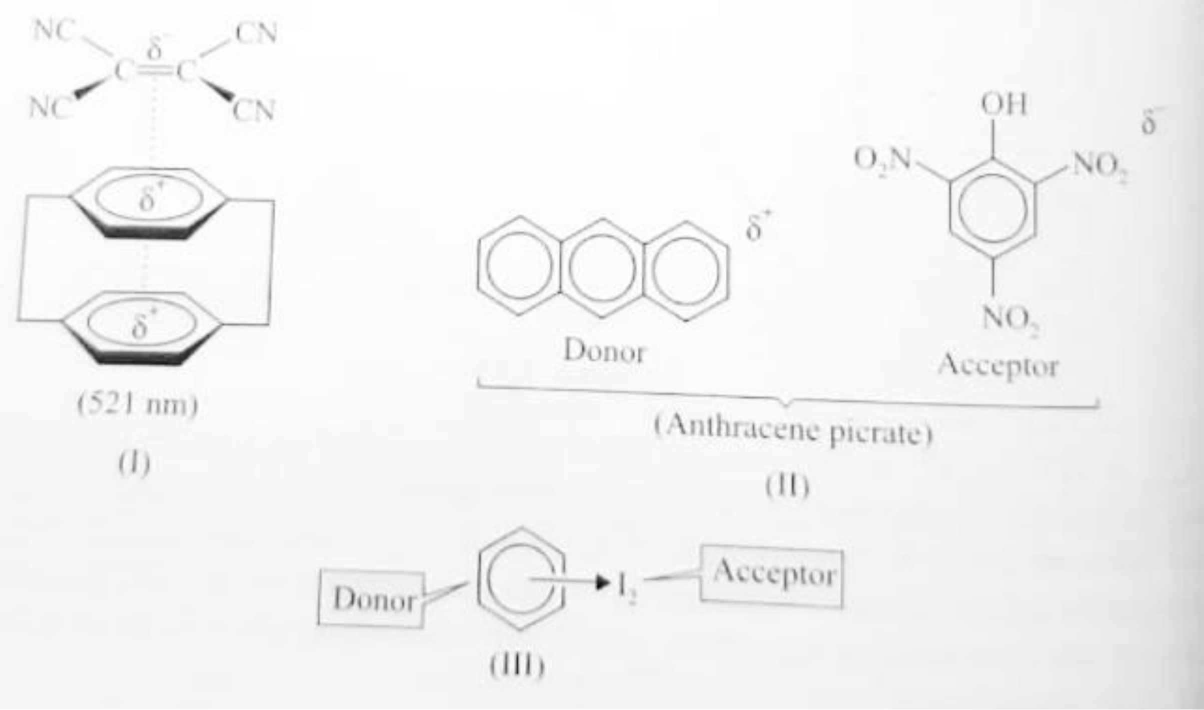


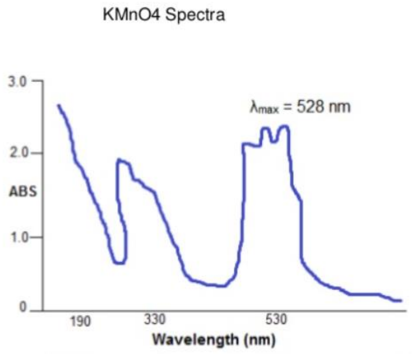
Figure 41: Complex formation of Donor and Acceptor (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

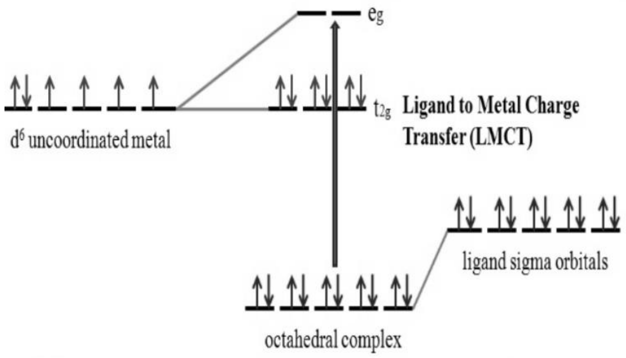
Charge Transfer complexes

- Charge transfer means transfer of charge (electron) from a donor to acceptor
- **Types of Charge transfer complexes**
- Ligand to Metal Charge Transfer Complex
- Metal to Ligand Charge Transfer Complex
- Metal to Metal Charge Transfer Complex
- Ligand to Ligand Charge Transfer Complex

Ligand to Metal Charge Transfer Complex (LMCT)

- **Condition for LMCT complex formation**
  - Presence of π donor ligands –
    - F^-, Cl^-, Br^-, I^-, H2O, RS^- etc
  - Metal ions are devoid of d electrons
  - Example:Transition metal oxo compounds





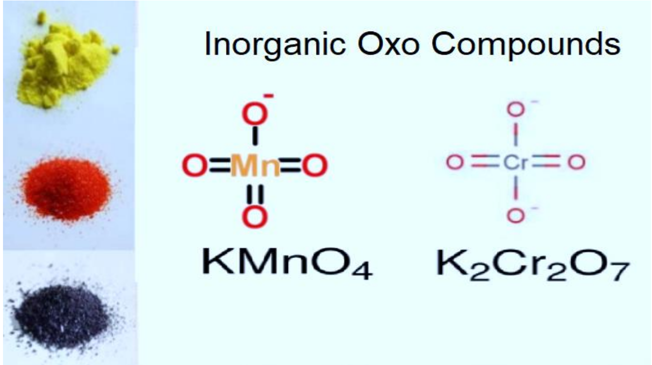


Figure 42: UV spectrum of Ligand to Metal complex (Source: Chemistry Libre text)

Metal to Ligand Charge Transfer Complex (MLCT)

- **Condition for MLCT complex formation**
  - Presence of π accepting ligands –
    - CO, NO, CN-, bipy, C=C, etc
  - Metal in 0, +1, +2 oxidation states (low oxidation state)
- Example: Transition metal halide compounds

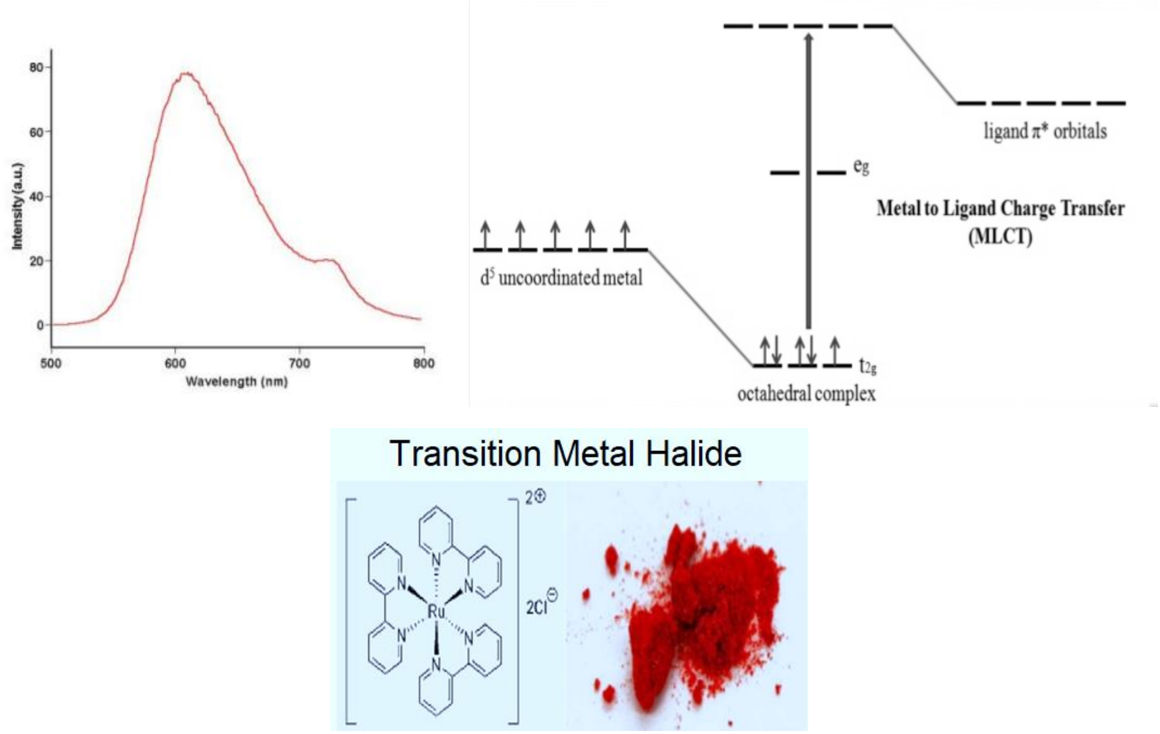


Figure 43: UV spectrum of Metal to Ligand complex (Source: Chemistry Libre text)

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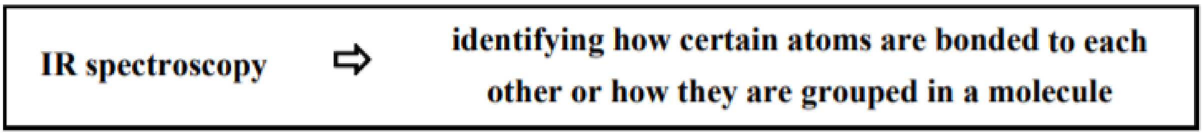
SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT-2 – IR Spectroscopy – SCYA7301

1. IR Spectroscopy – Principle

- **IR Spectroscopy:** It is the spectroscopy which deals IR region of electromagnetic spectrum with longer wavelength and lower frequency (wavenumber =4000–400 cm^{-1}) than visible light.
- Infrared spectroscopy is used to study the vibrational motions of molecules.
- Energy of IR photon insufficient to cause electronic excitation but can cause vibrational excitation
- The different motions (vibrational motion) among different groups of atoms cause the molecule to absorb different amounts of energy.
- These transitions determine the kinds of atoms that are bonded or grouped in an unknown compound, which in turn gives clues to the chemical nature and molecular structure.
- **Principle:**
- When molecules containing either permanent dipole moment or dipole moment arising due to vibration of atoms in molecules are subjected to IR radiation of particular frequency, it induces an oscillating dipole moment and excite them to undergo vibrational transition.
- Vibrational transition is produced by the absorption of energy (suitable IR radiation)



IR spectroscopy ⇨ **identifying how certain atoms are bonded to each other or how they are grouped in a molecule**

IR region subdivided into 3 sub-regions

- Near IR region (Nearest to the visible)
    - **780 nm to 2.5 µm** (12,800 to 4000 cm^{-1})
- Mid IR region
    - **2.5 to 50 µm** (4000 – 200 cm^{-1})
- Far IR region
    - **50 to 1000 µm** (200 – 10cm^{-1})

Features of IR Spectroscopy

- IR spectroscopy is mostly used for qualitative analysis.
- IR absorption spectra is recorded as transmittance.
- Absorption in the infrared region arise from molecular vibrational transitions
- Absorption for every substance are at specific wavelengths where IR spectra provides more specific qualitative information.
- IR spectra is called “fingerprints” because no other chemical species will have similar IR spectrum.

IR Spectra

- The IR spectrum is a plot of % transmittance (or absorbance) of the radiation through the molecule versus wave number of the radiation.
- The transmittance spectra provide better contrast between intensities of strong and weak bands compared to absorbance spectra.
- The IR spectra is normally plotted in the wavenumber range 4000–600 cm^{-1}

Functional group region and Fingerprint region

- Infrared spectrum is the graph of percentage transmittance versus either increasing wavelength or decreasing frequency
- Infrared spectrum shows percentage transmittance versus frequency expressed as wave numbers which have the units of cm^{-1} or wavelength in microns or micrometres
- Each dip in the spectrum is called a band or peak which represents absorption of infrared radiation at the frequency by the sample
- A 100 Percent transmittance means no absorption and if all the radiation is absorbed the transmittance is zero
- **Functional group region:**
    - It is region from 4000 - 1650 cm^{-1} and is termed high frequency region or functional group region.
    - This region is especially useful for identification of various functional groups
    - This region shows absorption arising from stretching modes
    - This region 0often contains only a few bands
- **Fingerprint region:**
    - Many of the vibrational modes in the fingerprint region depend on complex vibrations involving the entire molecule
    - It is impossible for any two different compounds to have precisely the same infrared spectrum
    - This region is from 1650 to 600 cm^{-1} and is called the fingerprint region because the pattern of absorption in this region are unique to any particular compound just as a person's fingerprints are unique

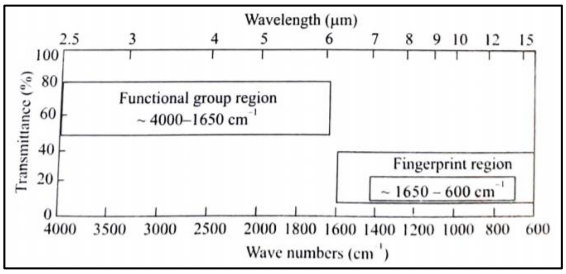
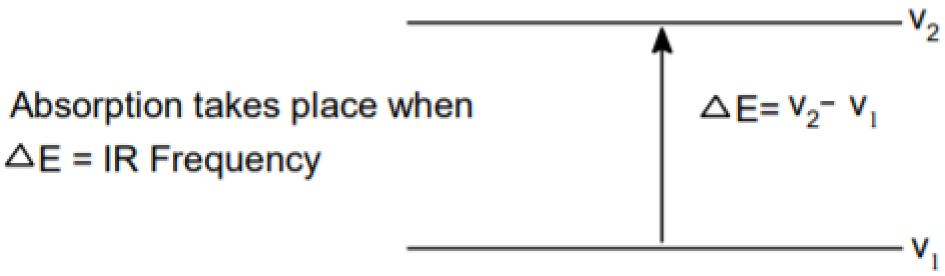


Figure 1: Functional group region and Fingerprint region in IR spectrum (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- **Conditions for IR spectroscopy to occur**
    - There must be change in dipole moment of the molecule during the vibration.
    - Energy of IR radiation must match the energy difference between the two vibrational energy levels.
    - No absorption can occur if both rules above are not met.
    - **Types of Vibrations:**
        - ✓ Stretching – Symmetric and Asymmetric
        - ✓ Bending – Inplane and Out of plane



IR transition in a molecule

What happen when a molecule absorbs IR radiation?

- Absorption of IR radiation corresponds to energy changes on the order of 8 to 40 kJ/mole.
    - Radiation in this energy range corresponds to stretching and bending vibrational frequencies of the bonds in most covalent molecules.
    - In the absorption process, those frequencies of IR radiation which match the natural vibrational frequencies of the molecule are absorbed.
- The energy absorbed will increase the amplitude of the vibrational motions of the bonds in the molecule.
- NOT ALL bonds in a molecule are capable of absorbing IR energy. Only those bonds that have change in dipole moment are capable to absorb IR radiation.
- **The larger the dipole change, the stronger the intensity of the band in an IR spectrum.**

What is dipole moment?

- A dipole moment arises in any system in which there is a separation of charge.
- They can arise in ionic bonds as well as in covalent bonds.
- Dipole moments occur due to the difference in electronegativity between two chemically bonded atoms.

- A bond dipole moment is a measure of the polarity of a chemical bond between two atoms in a molecule.
- It involves the concept of electric dipole moment, which is a measure of the separation of negative and positive charges in a system.
- In heteronuclear diatomic molecule, because of the difference in electronegativities of the two atoms, one atom acquires a small positive charge (δ+), the other a negative charge (δ-).
- This molecule is then said to have a dipole moment whose magnitude, $\mu = qr$

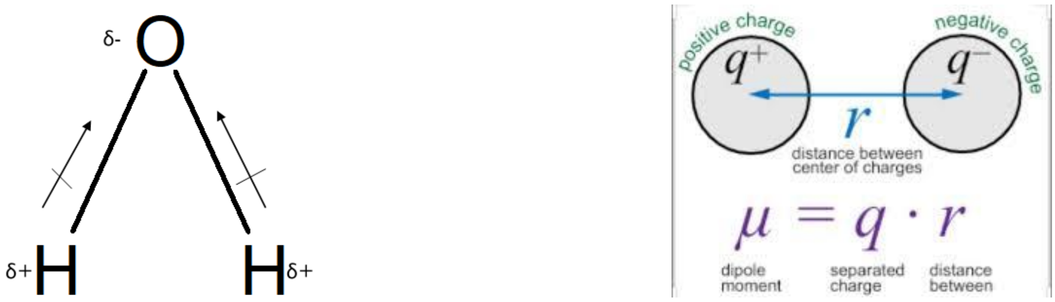


Figure 2: Dipole moment representation (Source: Socratic.org)

Molecular Species That Absorb IR

- **Compound absorb in IR region**
  - Organic compounds, carbon monoxide

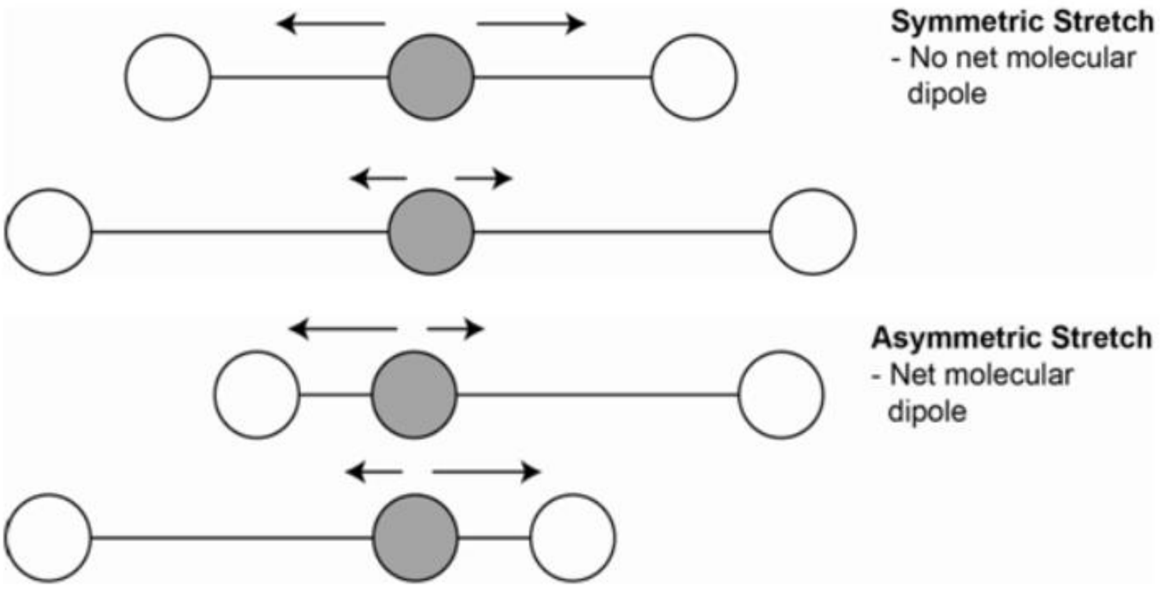


Figure 3: Symmetric stretch and Asymmetric stretch (Source: chem.libretexts.org)

- **Compounds DO NOT absorb in IR region**
    - O_2, H_2, N_2, Cl_2

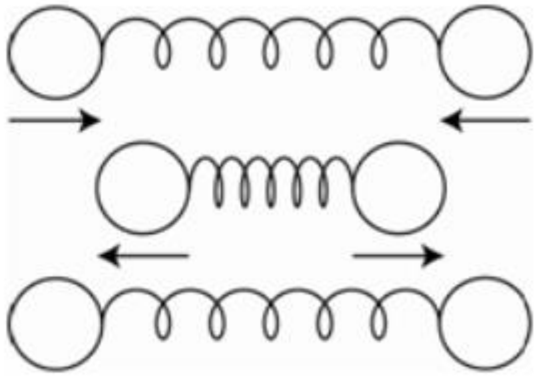


Figure 4: Stretching vibration of homonuclear molecules (Source: chem.libretexts.org)

Types of Molecular Vibration

- Periodic displacement of atoms or nuclei from their equilibrium position is called vibration.
- **Classification:** There are two types of molecular vibrations namely stretching and bending vibrations.
- **Stretching Vibrations:** The change in bond length between connecting atoms without altering the bond axis or bond angle is known as Stretching vibration.
- Stretching vibration are two types
    - **a. Symmetric stretching vibration:** At the time of vibration reference bonds subjected to either expansion or compression (i.e. Opposite direction of movement)
    - **b. Asymmetric stretching vibration:** At the time of vibration reference bonds subjected to compressed and other is expanded (i.e. same direction of movement)
- **Bending Vibrations:** The change in bond angle between connecting atom by changing the bond angle in and out of the bond axis plane is known as bending vibration.
- Bending vibration are four types
    - **a. Scissoring:** One connecting atom joined to a central atom move towards and another connecting atom moves away from each other in the same plane and change the bond angle.
    - **b. Rocking:** Both the connecting atoms joined to a central atom move towards or away in the same direction.
    - **c. Twisting:** One of the atom moves up (or front) the plane while the other atom moves down (or back) the plane with respect to the central atom.
    - **d. Wagging:** Both the two atoms move up (front) or below (back) the plane with respect to the central atom.

- In bending vibrations, rocking and scissoring vibrations occur in the same plane (in plane vibrations) whereas twisting and wagging vibrations occur out of plane.
- In some cases, because of symmetry factors two or more vibrational modes may be identical with same energy which are referred to as degenerate modes

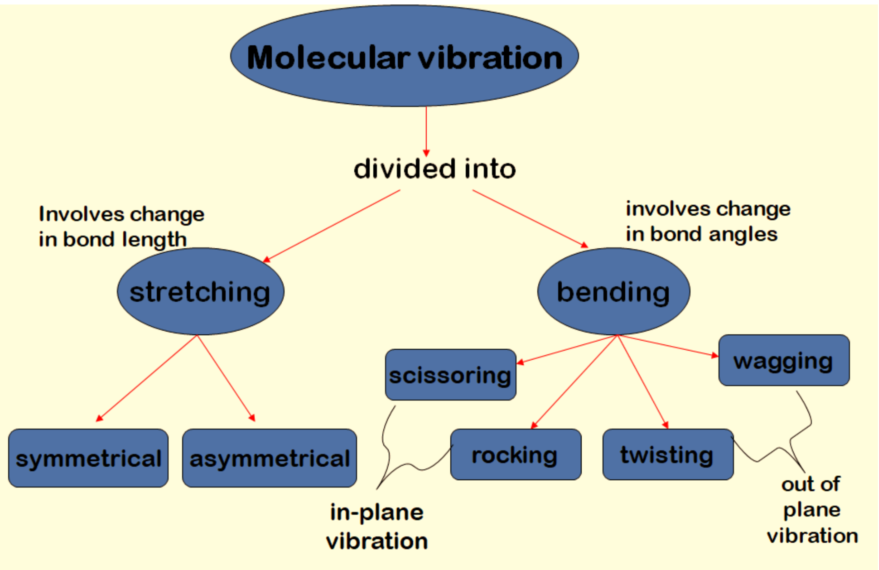


Figure 5: Types of Molecular Vibrations

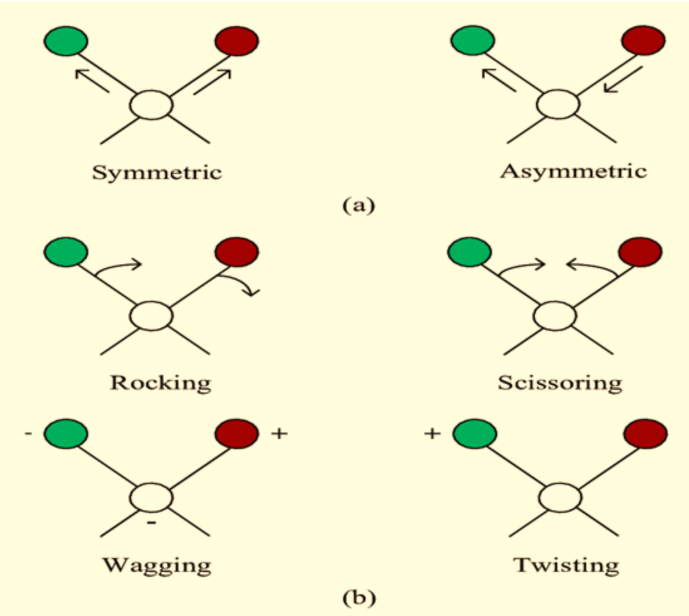


Figure 6: a) Symmetric and Asymmetric stretching IR vibrations and b) Bending IR vibrations (Source: DOI: 10.3390/polym11071111**)**

Degrees of Freedom

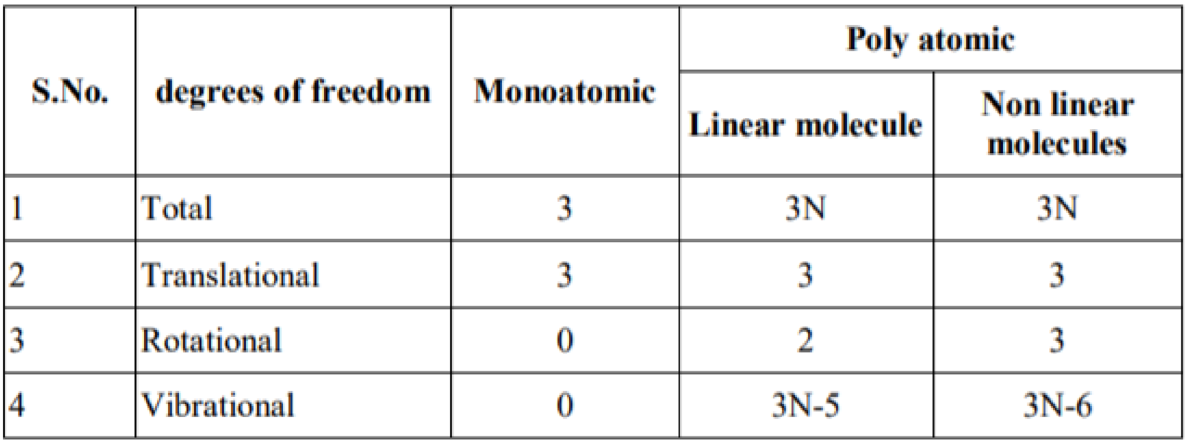
- **Degrees of freedom:** The number of variables required to describe the motion of molecule or atom completely

- A molecule can have three types of degrees of freedom and a total of 3N degrees of freedom, where N equals the number of atoms in the molecule.
- These degrees of freedom can be broken down into 3 categories
- **Translational:** These are the simplest of the degrees of freedom. These entail the movement of the entire molecule. This movement can be completely described by three orthogonal vectors and thus contains 3 degrees of freedom.
- **Rotational:** These are rotations around the center of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. This again means that this category contains only 3 degrees of freedom.
- However, in the case of a linear molecule only two degrees of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.
- **Vibrational:** These are any other types of movement not assigned to rotational or translational movement and thus there are 3N – 6 degrees of vibrational freedom for a nonlinear molecule and 3N – 5 for a linear molecule.
- These vibrations include bending, stretching, wagging and many other aptly named internal movements of a molecule.
- These various vibrations arise due to the numerous combinations of different stretches, contractions, and bends that can occur between the bonds of atoms in the molecule.

Types of Motion in molecule

- **Translational motion:** The atom shifts from one point to another point in three dimensional space. It is a permanent displacement.
- **Rotational motion:** Rotation of an atom through fixed axis.
- **Vibrational motion:** The motion brings change in bond angle and bond distance between connecting atoms
- **Normal mode:** It is a molecular vibration where some or all atoms vibrate together with the same frequency in a defined manner.
- Poly atomic molecules show more than one fundamental vibrational absorption bands.
- The number of these fundamental bands is related to the degrees of freedom in a molecule.
- The number of degrees of freedom is equal to the sum of coordinates necessary to locate all the atoms of a molecule in space.
- Each atom has three degrees of freedom corresponding to the three Cartesian coordinates (X, Y, Z) which necessary to describe its position on relative to other atoms in a molecule.
- Therefore the total number of degrees of freedom in a molecule containing N-atoms is equal to 3N which includes rotational, vibrational and translation degrees of freedom.
- **Total number of degrees of freedom (3N) = Translational + Vibrational + Rotational**

Table 1: Degrees of Freedom of monoatomic and diatomic molecules



S.No.	degrees of freedom	Monoatomic	Poly atomic	
			Linear molecule	Non linear molecules
1	Total	3	3N	3N
2	Translational	3	3	3
3	Rotational	0	2	3
4	Vibrational	0	3N-5	3N-6

Vibrational Degrees of Freedom for Linear Molecule

- If the molecule is linear then two independent modes of rotation about x and y axis are possible. Therefore the number of coordinates or degrees of freedom necessary to specify the vibrational transition is
- **Total degrees of freedom for polyatomic molecule = Translational + Rotational + Vibrational**
- 3N = 3 + 2 + Vibrational
- Vibrational Degrees of freedom = 3N-5
- For example: CO_2, CO, HCl, Acetylene
- Vibrational Degrees of freedom for CO = 3N-5
- =3 x 2 – 5 = 1
- Vibrational Degrees of freedom for C_2H_2
- = 3N-5 =3 x 4 – 5 = 7
- Vibrational Degrees of freedom for CO_2
- = 3N-5 =3 x 3 – 5 = 4

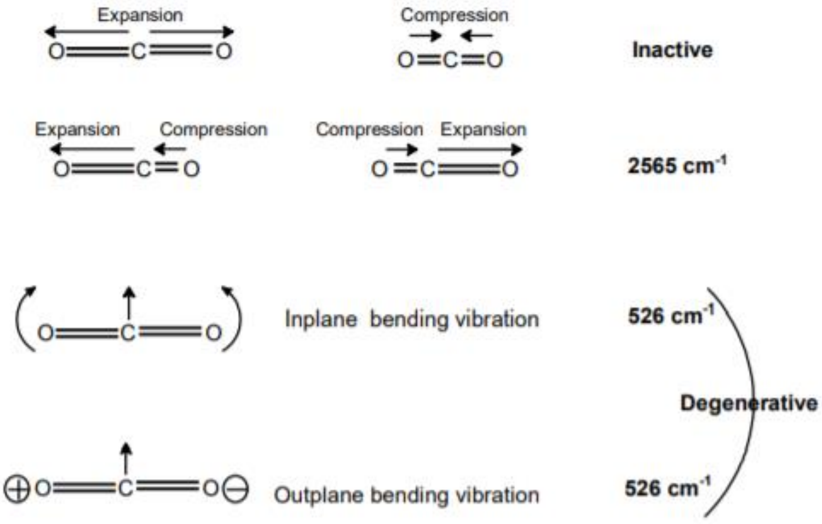
Degrees of Freedom of Vibration for Non-linear Molecule

- In case of non-linear molecules, 3 rotational coordinates(x,y,z) are needed to specify the molecular orientation about the centre of gravity.
- **Total degrees of freedom for polyatomic molecule = Translational + Rotational + Vibrational**
- 3N = 3 + 3 + Vibrational
- Vibrational degrees of freedom = 3N – 6
- Vibrational Degrees of freedom for H_2O
- = 3N-6 = 3 x 3 – 6 = 3

- Vibrational Degrees of freedom for CH_4
- = 3N-6 = 3 x 5 – 6 = 9
- Vibrational Degrees of freedom for NH_3
- = 3N-6 = 3 x 4 – 6 = 6
- Vibrational Degrees of freedom for C_6H_6
- = 3N-6 = 3 x 12 – 6 = 30

Vibration Modes of CO_2 Molecule

- CO_2 is a linear triatomic molecule,
- Therefore it has 3N – 5 = 3 x 3 – 5 = 4 fundamental modes of vibration.
- The four modes of vibration are symmetrical stretching, antisymmetrical stretching and two bending modes.
- During the stretching vibration, there is no change in the dipole moment.
- Hence, this symmetrical stretch will not absorb radiation, and hence it is IR inactive.

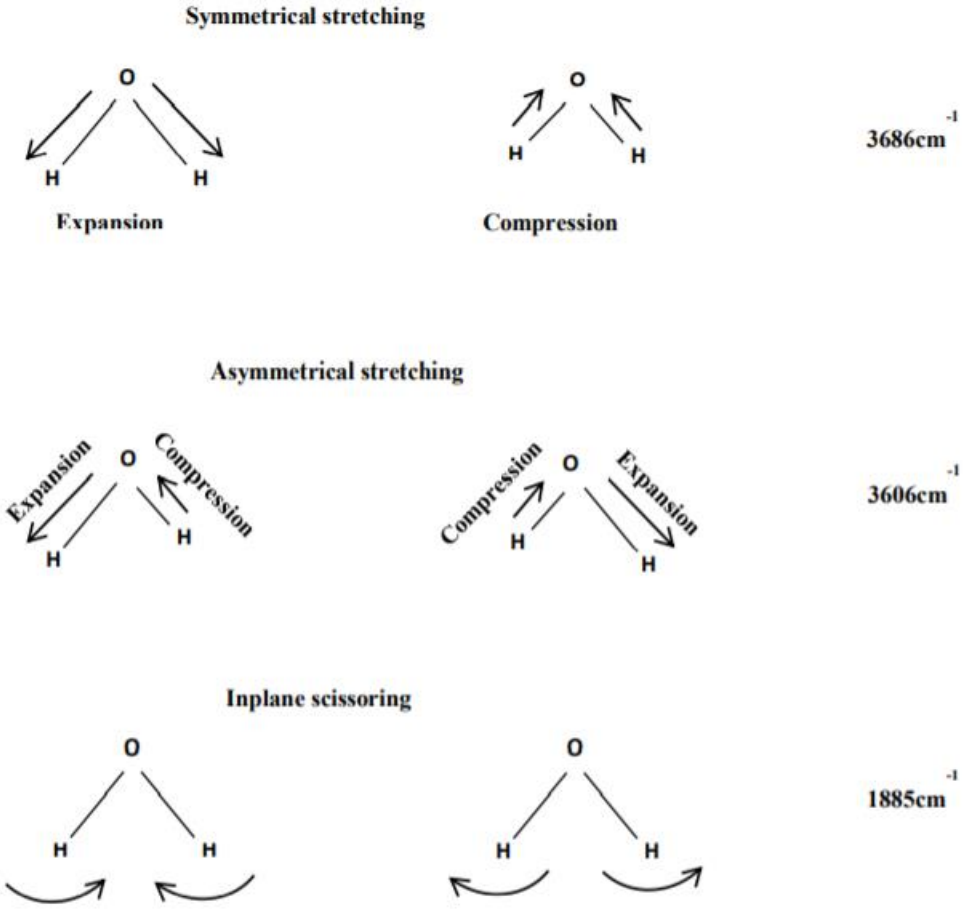


Representation of stretching and bending molecular vibrations of CO_2 Molecule

Figure 7: Molecular Vibrations of CO_2 molecule

Vibrations modes of H_2O molecule

- Water is a bent, non-linear triatomic molecule.
- Therefore it has 3N – 6 = 3 x 3 – 6 = 3 fundamental modes of vibrations.
- The three modes of vibrations are a bending mode, a symmetrical stretching and an unsymmetrical stretching mode.
- All the three modes of vibration involve changing in dipole moment and hence they are IR active.



Representation of stretching and bending molecular vibrations of H_2O Molecule

Figure 8: Molecular Vibrations of H_2O molecule

2. IR spectrum of important organic compounds

Detection of some important functional groups

- IR region is divided into two main regions
- **The functional group region**
- It is further subdivided into several regions only three of these are considered here and fourth region fall in the fingerprint region where the C – O stretching bands of alcohol, phenol, carboxylic acid and some C – N stretching bands of amines and amides can be identified
- **The Hydrogen region**
- Due to comparatively low mass of a hydrogen atom single bonds to hydrogen C – H, O – H, N – H stretching occurs here
- the position of band depends on the bond strength which increases in the order C – H < N – H < O – H

- **Double bond region**
- this region contains most of the carbonyl stretching bands of aldehydes ketones, carboxylic acid, amides and esters
- the stretching bands occur around 1640 CM inverse
- **Triple bond region**
- the C≡C and C≡N stretching bonds occur near 2200 CM^{-1}
- A part of the fingerprint region is often useful to identify stretching bands of alcohol, phenol, carboxylic acid and Ester also some C – N stretching bands of amines and amides

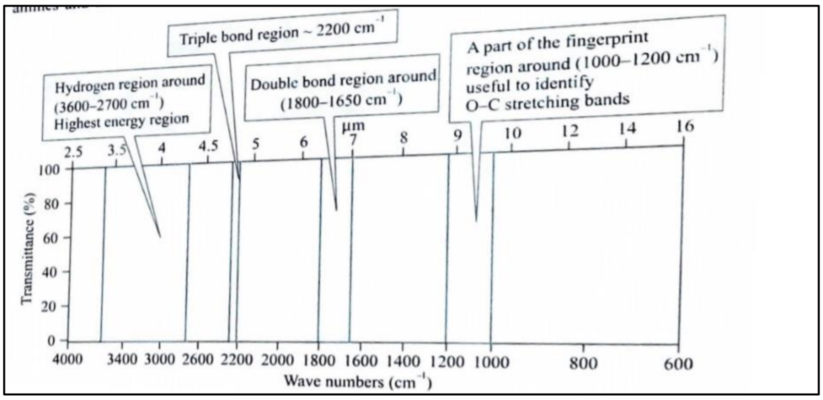


Figure 9: Hydrogen region, Double bond region and Triple bond region in IR spectrum (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

IR spectrum of cyclohexanol

- The bands at the left end of the spectrum have high vibrational (stretching) energy and band in 3600 – 2700 cm^{-1} (hydrogen region) arise from stretching of bonds to H atoms
- In cyclohexanol there are only two types of bonds of this type C – H bond and O – H bond. Thus there are two bands in the highest energy region (3600 – 2700 cm^{-1})
- The symmetrical strong and broadband at 3,300 cm^{-1} is due to O – H stretching
- The ragged (split) band centered at 2950 cm^{-1} is composed of several overlapping bands due to vibrations of several different bonds of the same general type
- There is only one O – H bond in the molecule while there are 11 sp3 C – H bonds
- The ragged (split) band around 2950 cm^{-1} arises due to sp3 C - H stretching vibrations while the band at 3300 cm^{-1} is the O - H stretching band
- The area under a band has little to do with the number of bonds which gives rise to it the single O – H bond has a much broader band compared to 11 C – H bonds
- Another very strong band is seen at 1050 cm^{-1}

- This band occurs in fingerprint region and this region 1000 – 1200 cm^{-1} is typical for single bond stretching vibrations (except those which involve hydrogen) of the single bond
- The position of O – C stretch can often be used to make distinction between primary secondary and tertiary alcohols. In phenol OC stretched is at highest frequency 1200 cm^{-1}
- There are several bands which remained unassigned
- The C – C bonds do not give prominence bands while the same kind of bond can undergo various other kinds of bending vibrations (scissoring, wagging and twisting vibrations)
- A very broad and rather weak band centered around 670 cm^{-1} is typically due to O – H bending vibrations
- The stretching bands are more easily recognized than others and these bands give key information in detecting the presence of functional groups

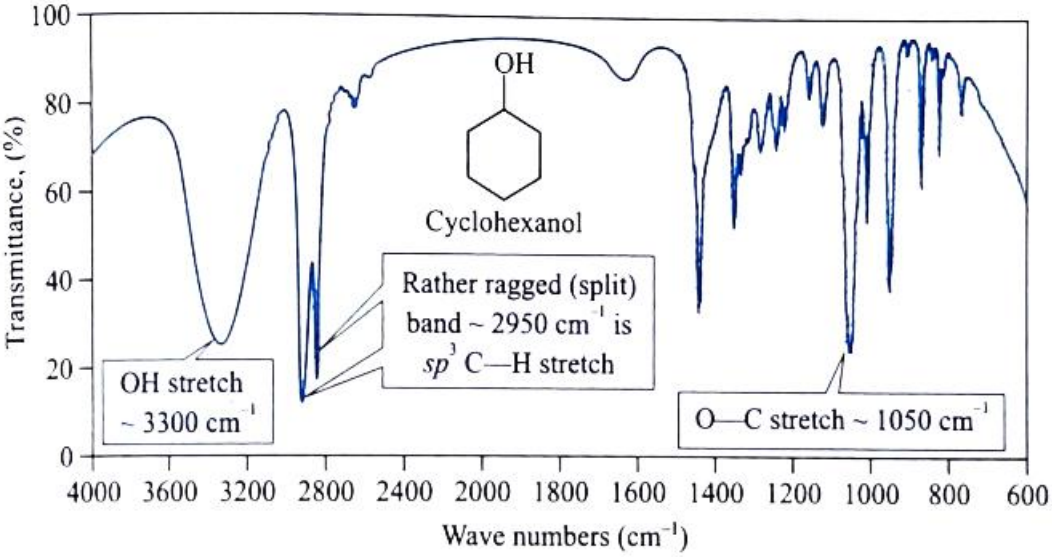


Figure 10: IR spectrum of Cyclohexanol (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Infrared spectrum of cyclohexanone

- There are three bands in the high frequency (hydrogen region)
- There is no strong symmetrical and broadband around 3300 cm^{-1} which shows the absence of O – H group
- A very small absorption around 3300 cm^{-1} in which is not due to trace of moisture (H – OH, since the sample is dry) but represents an overtone of C = O stretch frequency about twice that of C = O stretch
- The presence of weak overtone bands is the C = O is one of the factor which complicates the infrared spectrum

- A strong band at 1715 cm^{-1} is the C = O stretching band of cyclohexanone
- The carbonyl band is always strong and unmistakable
- The C = C stretching which also occurs in the double bond region is always weaker and narrower than a carbonyl band
- Cyclohexanone shows a strong and ragged band around 2950 cm^{-1} as in cyclohexanol and represents sp3 C – H stretch

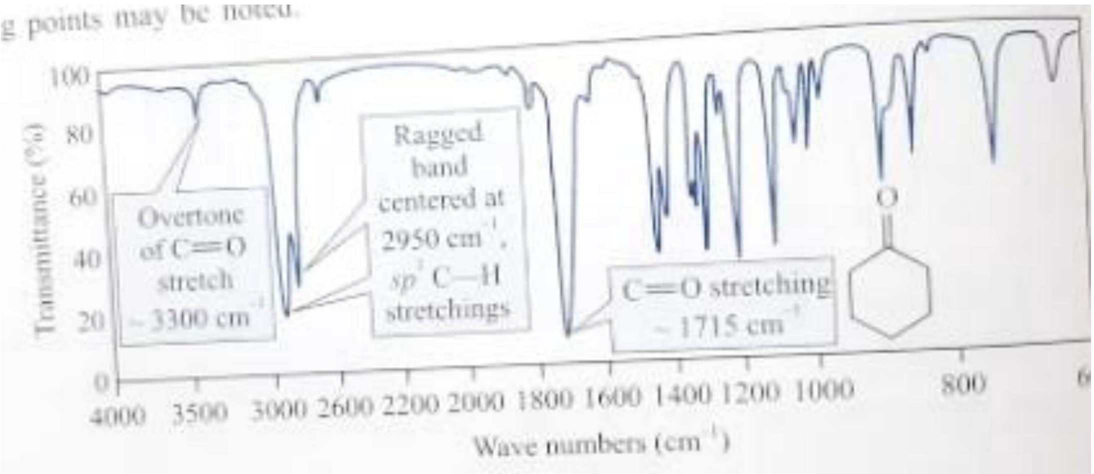


Figure 11: IR spectrum of Cyclohexanone (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Intensity of infrared bands

- The bands in an infrared spectrum are classified by intensity strong (s), medium (m), weak (w) and variable (v)
- The position of all bands is given in cm^{-1}
- The number of similar groups in a molecule changes the relative strength of the absorption bands in a spectrum
- For example, the stretching band of a single O – H group in a compound display itself as a relatively strong absorption at 3300 cm^{-1} whereas a single C – H Stretch is comparatively weaker
- If a molecule has many C – H bond the collective effect of the C – H absorption gives a band which is strong as in the case of sp3 C – H stretching band at 2950 cm^{-1}

Overtones and Combination band

- Overtone may arise in two ways
- **First type:**

  - when a molecule in the lowest or first vibrational state is excited to third vibrational levels the energy needed is almost twice that required for excitation to the second vibrational level
  - It is not exactly twice since the higher levels tend to lie closer together than the lower levels
- **Second type:**
  - Another type of overtone commonly called a combination band occurs when a single photon has precisely the correct energy to excite two vibration at once
  - For this to happen the energy of the combination band must be exact sum of the two independent absorptions
- Most of these vibrations are called fundamental vibrations which occur when a molecule absorbs IR radiation of appropriate energy needed to promote it from the ground state to its first vibrationally excited state
- Other bands also occur corresponding to excitation to the second, third or even 4th excited states
- These bands (overtones) are very weak but these are important for characterization of certain classes of compounds particularly benzene derivatives
- The presence of week overtone or combination bands from 2000 – 1667 cm^{-1} is sufficient to indicate the compound to be benzene derivatives

Infrared spectrum of benzaldehyde

- Spectrum of benzaldehyde shows weak overtone/combination bands between 1667 – 2000 cm^{-1}
- These weak absorptions are indication for the presence of an aromatic ring
- The shape and number of these peaks is related to the kind of ring substitution
- In benzaldehyde, the aromatic ring is monosubstituted
- It shows four absorption bands in the high frequency (hydrogen region 3600 – 2700 cm^{-1}
- The ragged band at highest frequency 3050 cm^{-1} is the sp2 C – H stretch of =C – H system of the aromatic ring
- This band is typical of other sp2 C - H stretches of alkenes as well
- The value of this which is typically slightly greater than 3000 cm^{-1}
- Typical band around 1700 cm^{-1} is located at a lower frequency than observed for cyclohexanone (at 1715 cm^{-1})
- The strong C = O stretching is in the double bond region and the lower frequency is due to conjugation with the phenyl group
- The typical band of medium intensity at 2720 cm^{-1} is aldehydic C – H stretch

- This is C – H stretch with SP3 C – H present in most organic compounds with typical value 2950 cm^{-1} and sp2 C – H bond stretches associated with aromatic hydrocarbons and alkenes which absorbs slightly at a higher frequencies (3080 cm^{-1})
- In case of benzaldehyde the sp2 switches that 3050 cm^{-1}

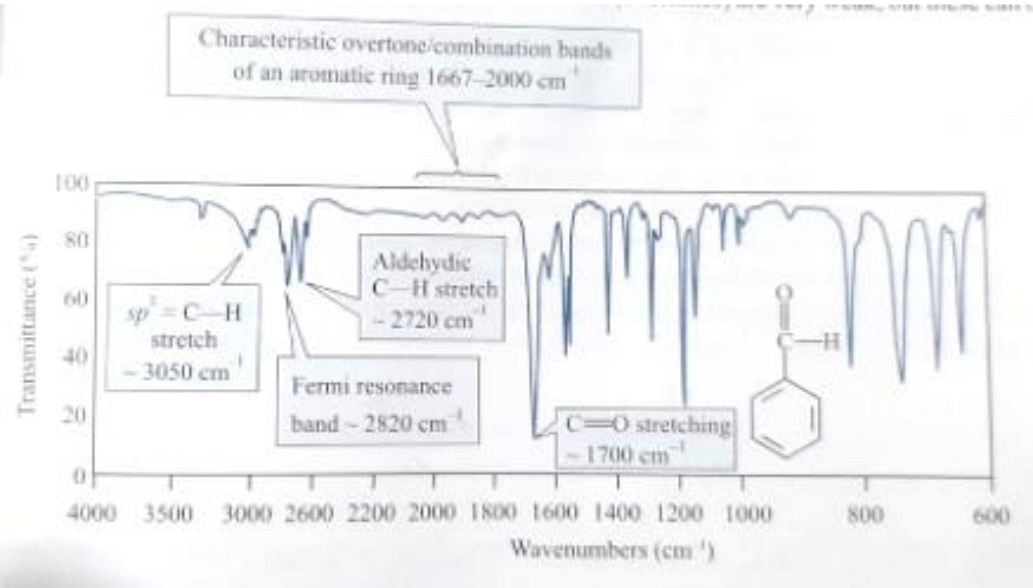


Figure 12: IR spectrum of Benzaldehyde (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

3. Characteristic Vibrational Frequencies

Characteristic Vibrational Frequencies of Alkanes, Alkenes and Alkynes

- **Identification of an alkane Residue**
- Most organic molecules contain alkane residues and it is important to identify the main absorption bands in an alkane
- **Identify the sp3 C-H stretch centered around 2950 cm^{-1}**
- The C-H stretching modes of both methyl and methylene groups (asymmetric and symmetric C-H stretching modes) gives four absorption bands just below 3000 cm^{-1}
- All the four bands overlap but when resolved the four bands may be clearly visible and two of these are centered around 2950 cm^{-1}

- **C-H bending vibrations of methyl and methylene groups**
- The bending vibrations of C-H bonds of methylene and methyl groups occur at 1450 cm^{-1} and 1380 cm^{-1}
- These C-H bend absorptions are called C-H deformation band

- The symmetrical C-H bending vibrations of CH3 groups occur at 1380 cm^{-1} while the asymmetric bending vibrations at 1450 cm^{-1}
- Fourth band at 720 cm^{-1} represents the methylene rocking vibration
- This band generally appears for straight chain alkanes containing at least 4 adjacent methylene groups (- (CH2)$_n$ -, n > 4)
- These bands are easily detected in the IR spectrum of n-hexane

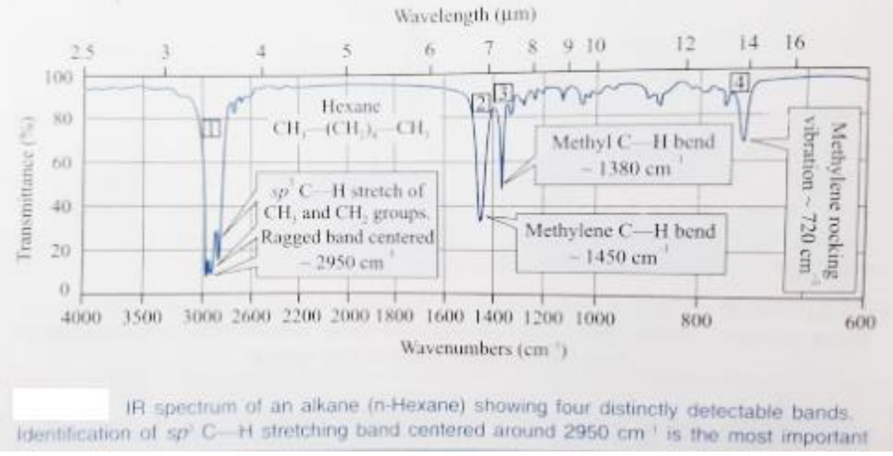
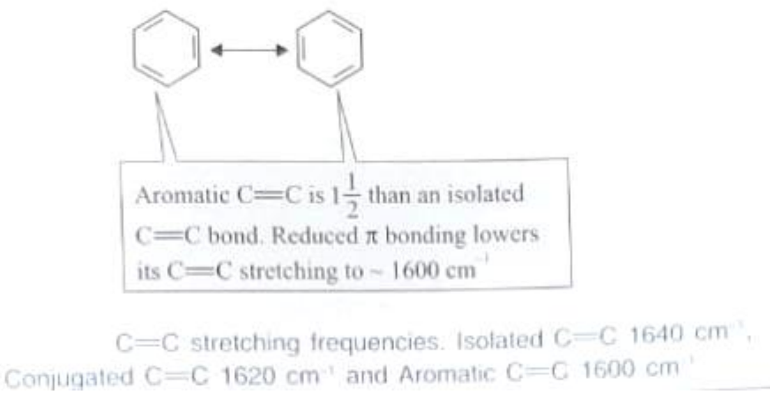


Figure 13: IR spectrum of Cyclohexanol (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Identification of unsaturation alkene, alkyne and aromatic Residue

- **Alkane system**
- Primary unsaturation in an organic compound can be detected from carbon – carbon bond stretching (C=C and C≡C) and carbon – hydrogen bond stretching (sp2-C=C-H and sp-C=C-H)
- **Carbon – Carbon Bond stretching**
- Most double bonds unsymmetrically substituted give observable stretching absorptions around 1640 cm^{-1}
- Conjugation lowers the absorption frequency of double bond by 20 cm^{-1}
- Thus compared to an isolated double bond (C=C stretch at 1640 cm^{-1}) conjugated C=C stretch is around 1620 cm^{-1}
- The effect of conjugation is even more pronounced in aromatic compounds and aromatic C=C bond are like 1 ½bonds than true double bonds
- The consequent reduced π bonding leads to less stiff double bonds with lower stretching frequencies at 1600 cm^{-1}
- The double bonds of aromatic system C=C double bond ring stretching in Benzene normally displays three bands 1400, 1500 and 1600 cm^{-1}

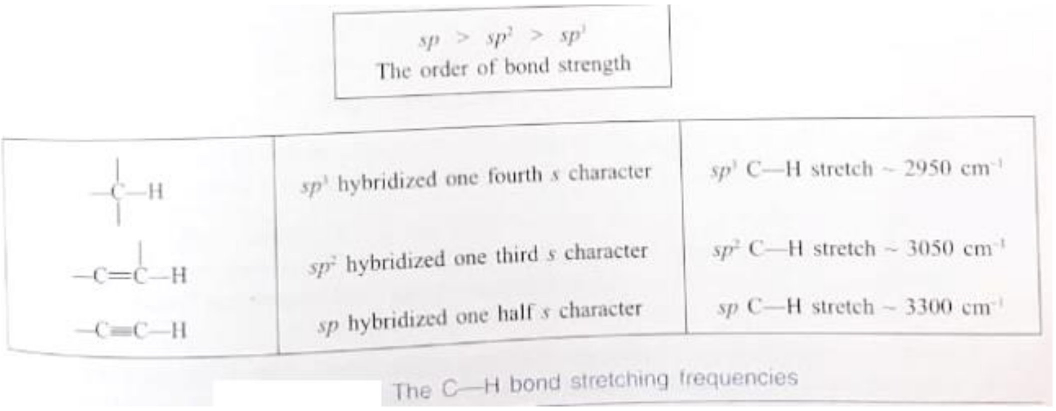


Aromatic C=C is $1\frac{1}{2}$ than an isolated C=C bond. Reduced π bonding lowers its C=C stretching to ~ 1600 cm^{-1}

C=C stretching frequencies. Isolated C=C 1640 cm^{-1}, Conjugated C=C 1620 cm^{-1} and Aromatic C=C 1600 cm^{-1}

Figure 14: Vibrational frequency of isolated C=C, conjugated C=C and aromatic C=C (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- **Carbon – Hydrogen bond stretching**
- Alkanes, alkenes and alkynes have typical and characteristics C-H stretching frequencies
- The C-H bond stretch is explained by the amount of s character in the carbon orbital used to form the bond
- Since the S orbital is closer to the nucleus than the p orbitals and stronger, therefore stiffer bonds arise from orbitals with more s character
- Thus C-H bonds involving sp hybridized carbon are strongest and those involving sp3 hybridized carbon are weakest
- The order of Bond strength is given as



$sp > sp^2 > sp^3$
The order of bond strength

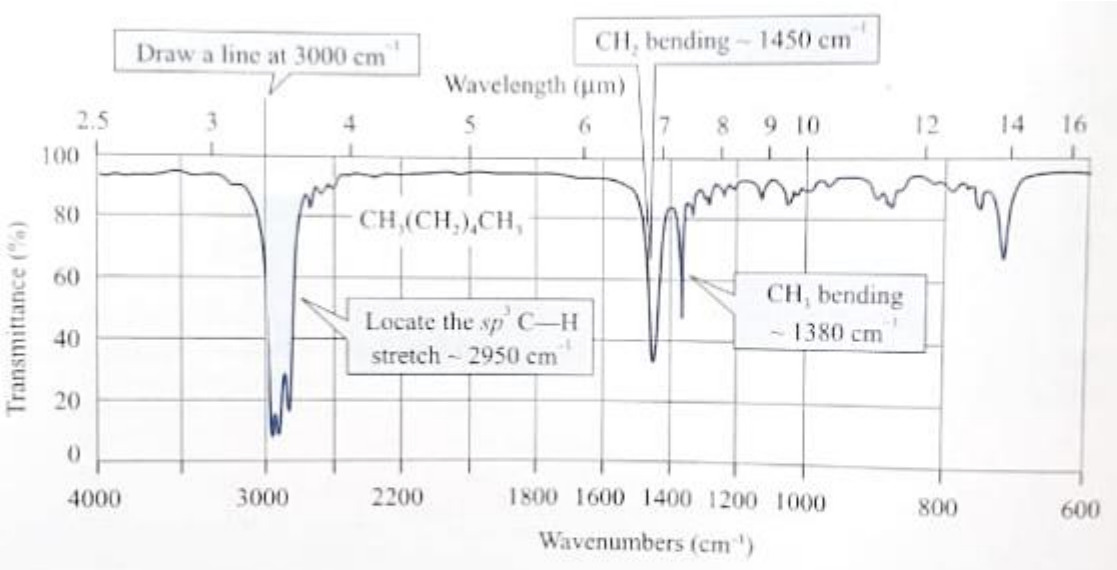
$-\overset{|}{\underset{|}{C}}-H$	sp^3 hybridized one fourth *s* character	sp^3 C—H stretch ~ 2950 cm^{-1}
$-C=\overset{|}{C}-H$	sp^2 hybridized one third *s* character	sp^2 C—H stretch ~ 3050 cm^{-1}
$-C\equiv C-H$	*sp* hybridized one half *s* character	*sp* C—H stretch ~ 3300 cm^{-1}

The C—H bond stretching frequencies

Figure 15: Vibrational frequency of sp3 C – H, sp2 C – H and sp C – H (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

- The C-H stretching band of hydrogen atoms attached to sp2 hybridized carbon atoms including aromatic rings absorb around 3050 cm^{-1}
- **Interpretation of IR spectra from C-H stretching region**
- Locate the sp3 C-H stretch of CH3 and CH2 groups which is around 2950 cm^{-1}

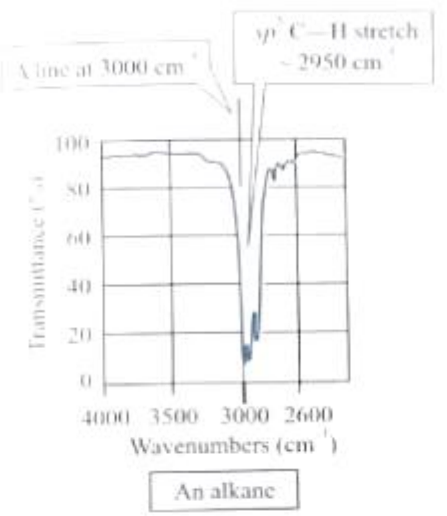
- This band shows a fine structure due to coupled vibrations (i.e) symmetric and asymmetric stretching bands
- Draw a line at 3000 cm^{-1} in the spectrum separating unsaturated and saturated C-H stretching bands
- Generally hydrogens attached to sp and sp^2 carbon will display bands above 3000 cm^{-1}
- The C-H stretch for terminal alkynes is generally a sharp, intense band at 3300 cm^{-1}
- This band is typically stronger and higher than the band's associated with sp2 C-H stretching of C=C bond or aromatic rings at 3050 cm^{-1}



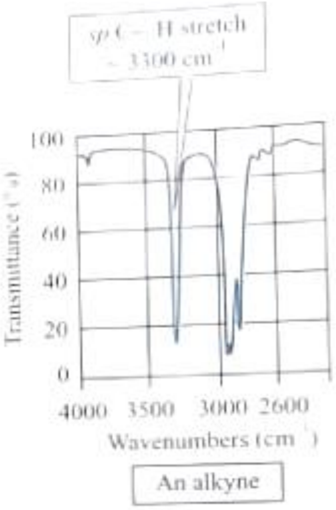
IR spectrum of an alkane emphasizing the role of line drawn at 3000 cm^{-1} to identify saturated and unsaturated hydrocarbon features

Figure 16: IR spectrum of sp3 C – H, sp2 C – H and sp C – H (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

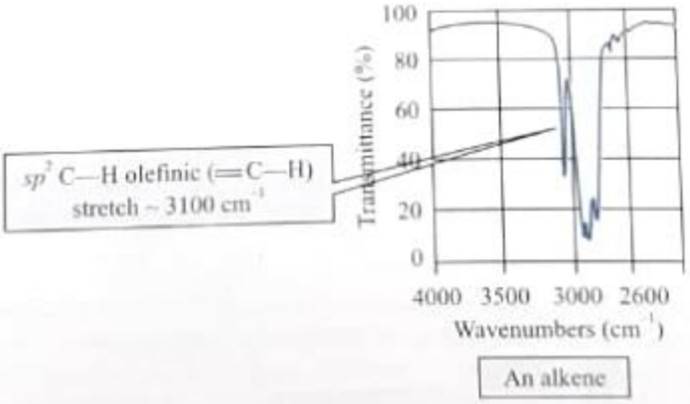
- Just below 3000 cm^{-1} line around 2950 cm^{-1} sp3 C-H stretching frequencies and sp2 C-H stretching absorption bands of both alkenyl C-H bonds and C-H groups of aromatic rings give absorption bands at 3050 cm^{-1}
- The complete absence of absorption in the region from 3300 to 3100 cm^{-1} indicates the absence of hydrogen atoms bonded to C=C or C≡C (i.e) absence of unsaturation of any kind acetylenic, olefinic or aromatic
- Even if C=C stretching of an alkene is weak or absent, the unsaturated C-H stretch at 3050 cm^{-1} shows the presence of a double bond
- The complete absence of absorption in the region from 3300 to 3500 cm^{-1} indicates the absence of hydrogen atom bonds (OH, NH, etc)



With only sp^3 C—H stretch ~ 2950 cm^{-1} below 3000 cm^{-1} line ($R—CH_2—CH_2—CH_3$)



$R—CH_2—CH_2—C≡C—H$
With both sp^3 C—H stretch at 2950 cm^{-1} (below 3000 cm^{-1} line) and above 3000 cm^{-1} lina at 3300 cm^{-1} —C≡C—H, sp C—H stretch.



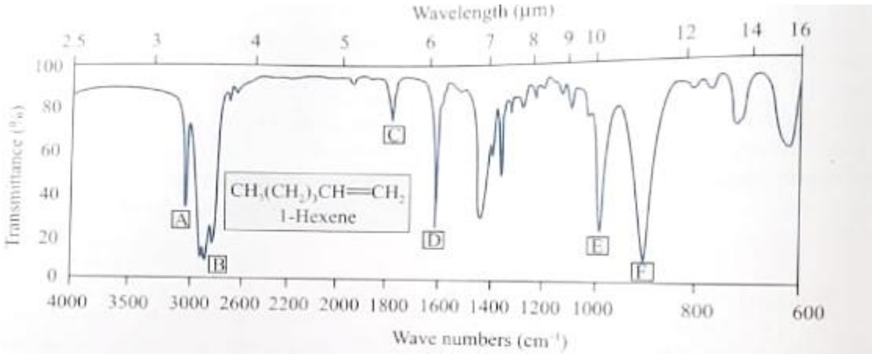
$R—CH_2—CH_2—CH═CH_2$
with both sp^3 C—H stretch and olefinic (C═C—H) C—H stretch around 3050 cm^{-1} (sp^2 C—H stretch).

Partial infrared spectra of an alkane, an alkyne and an alkene. Identification of sp C—H stretch (—C≡C—H) of a terminal alkyne, sp^2 C—H stretch (>C═C—H) of an alkene or an aromatic ring in relation to typically a medium to strong intensity band (shaded) ~ 2950 cm^{-1} due to sp^3 C—H stretching vibrations

Figure 17: Identification of sp3 C – H, sp2 C – H and sp C – H bands in IR spectrum (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

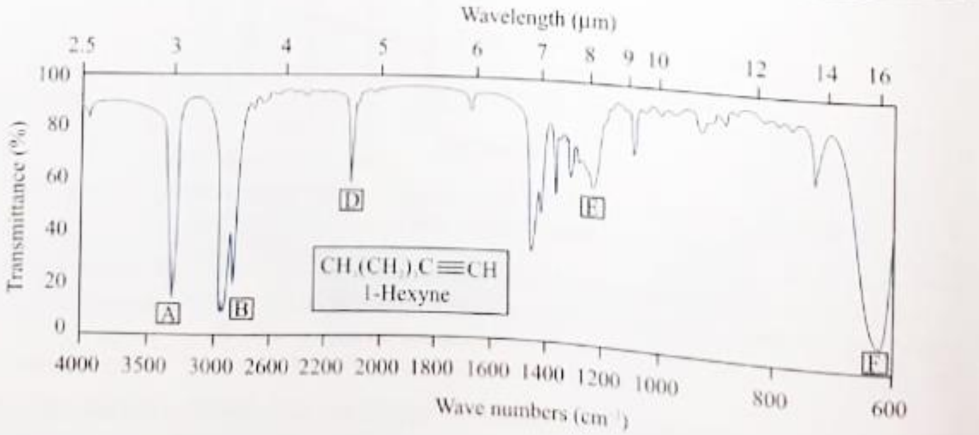
- **A comparison of IR spectra of 1-hexene and 1-hexyne** with n-hexane reveal some interesting and helpful features for interpretation of IR spectra
- For the presence of functional groups in the high frequency region 3600 – 2700 cm^{-1} and double bond region 1800 – 1650 cm^{-1}
- The spectrum of n-hexane shows the absence of any IR active functional groups

- The spectrum of n-hexane shows sp3 C – H stretch at 2950 cm^{-1}
- The spectrum of 1-hexene shows characteristic additional absorption bands of a double bond around 3050 cm^{-1} to alkenes C – H stretch
- The absorption around 1640 cm^{-1} is for C=C stretching
- 1-hexene contains a vinyl double bond show band at 1000 and 900 cm^{-1} for C – H bending
- Absorption band at 1820 cm^{-1} is the overtone of intense band at 900 cm^{-1}



1-Hexene. A, the alkene C—H stretch ~3050 cm^{-1}; B, the sp^3 C—H stretch ~2950; C, overtone of the intense out of plane =C—H bending ~1820 cm^{-1} of the intense band ~900 cm^{-1}; D, the C=C stretch ~ 1640 cm^{-1} E and F are the typical =C—H bending vibrations of a vinyl double bond ~1000 and 900 cm^{-1}

Figure 18: IR spectrum of 1-Hexene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

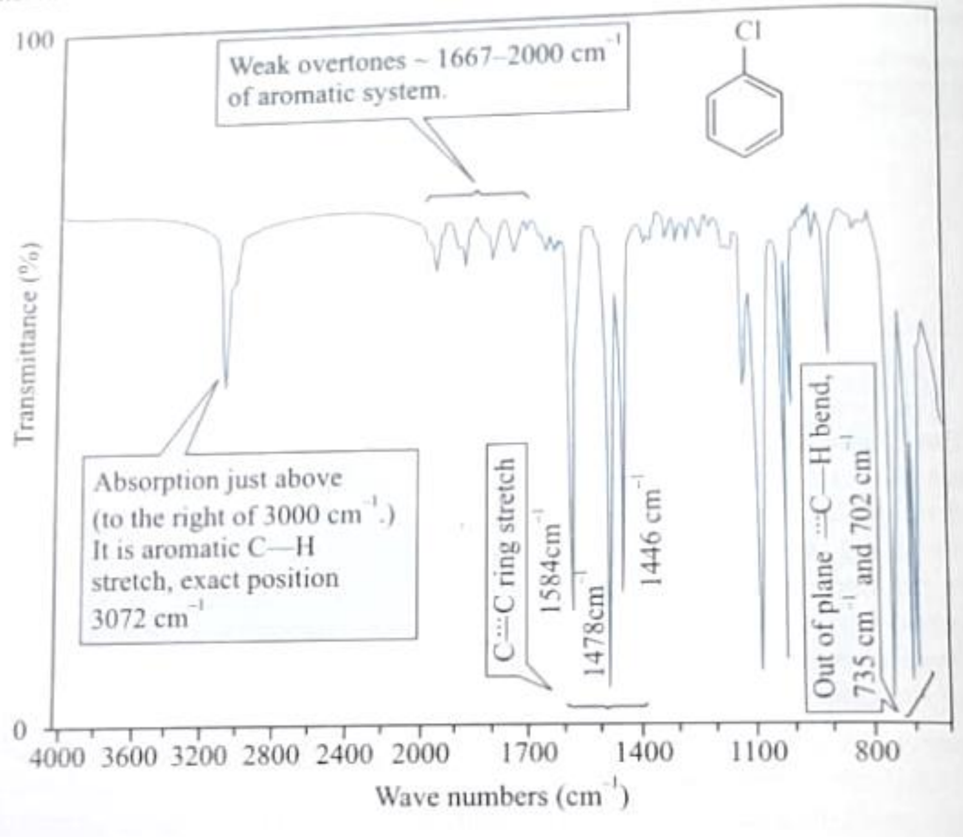


1-Hexyne. A, the alkynyl ≡C—H stretch ~3300 cm^{-1}; B, the alkane sp^3 C—H stretch (ragged) ~ 2950 cm^{-1}; D, the C≡C stretch ~2200 cm^{-1}; E, the ≡C—H bend overtone ~1250 cm^{-1}; F, the ≡C—H bend ~630 cm^{-1}

Figure 19: IR spectrum of 1-Hexyne (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Interpretation of spectra of aromatic systems

- Spectrum of chlorobenzene does not have a methyl or methylene group therefore doesnot show sp3 C – H stretching band at 2950 cm^{-1}
- The presence of band at 3050 cm^{-1} show the presence of sp2 C – H stretch (=C – H stretch)
- The band at 1446 cm^{-1} corresponds to C=C bond ring stretching of benzene. The other bands for this stretching mode are 1584 cm^{-1} and 1478 cm^{-1}
- It contains an aromatic C – H stretch at 3072 cm^{-1}
- A strong absorption below 900 cm^{-1} corresponds to out-of-plane C=C – H bend)
- Strong absorption at 735 and 702 cm^{-1} indicate its aromaticity
- The weak set of bands between 1667 - 2000 cm^{-1} (overtones) helps in labelling a compound aromatic

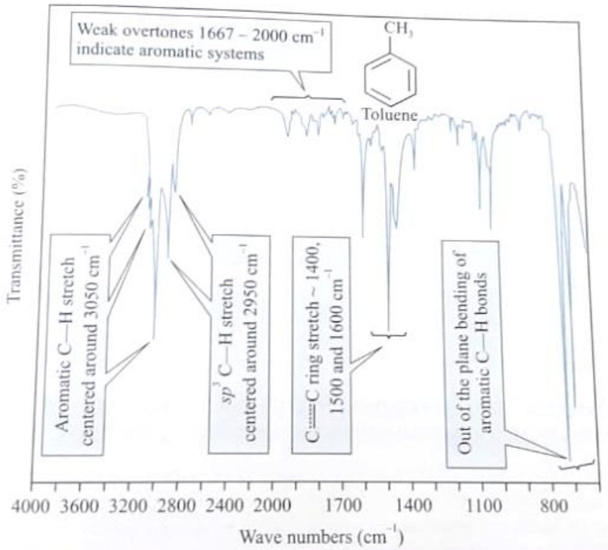


IR spectrum of chlorobenzene. Aromatic =C—H stretch is at 3072 cm^{-1}. It does not show absorption just below 3000 cm^{-1} around 2950 cm^{-1} to show absence of —CH_3 and —CH_2 groups (sp^3 C—H stretch). The aromatic character is shown by overtone bands (1667–2000 cm^{-1}), presence of aromatic C=C stretching bands around 1400, 1500 and 1600 cm^{-1} and one or more strong bands below 900 cm^{-1}

Figure 20: IR spectrum of aromatic (Chlorobenzene) (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Spectrum of Alkyl benzene

- Toluene have a methyl therefore show sp3 C – H stretching band at 2950 cm^{-1}

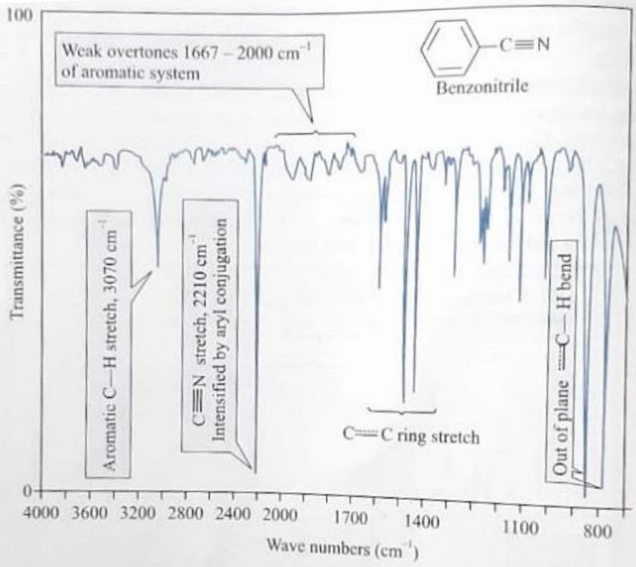


IR spectrum of toluene is comparable with that of chlorobenzene. However, in toluene bands are both above 3000 cm^{-1} (~3050 cm^{-1} aromatic = C—H stretch) and below 3000 cm^{-1} (ragged) showing sp^3 C—H stretch centered around 2950 cm^{-1}. These IR spectral features show the compound to be an alkylbenzene

Figure 21: IR spectrum of Toluene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Spectrum of Cyano benzene

- Benzonitrile have a cyano group therefore show C≡ N stretching band at 2200 cm^{-1}



The infrared spectrum of benzonitrile has bands at comparable positions to that in chlorobenzne, the distinctive and characteristic feature is the presence of strong C≡N stretch ~2200 cm^{-1}

Figure 22: IR spectrum of Benzonitrile (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Characteristic Vibrational Frequencies of Alcohol

- Presence of strong broadband at 3300 cm^{-1} indicates O – H Stretching
- Strong C – O stretching band at 1200 – 1000 cm^{-1}
- C – O band above 1200 cm^{-1} suggest it is phenol (particularly when it is accompanied by bands indicating an aromatic ring structure)
- Most saturated aliphatic alcohols absorb near 1050 cm^{-1} if it is primary, near 1110 cm^{-1} if it is secondary and near 1175 cm^{-1} if it is tertiary

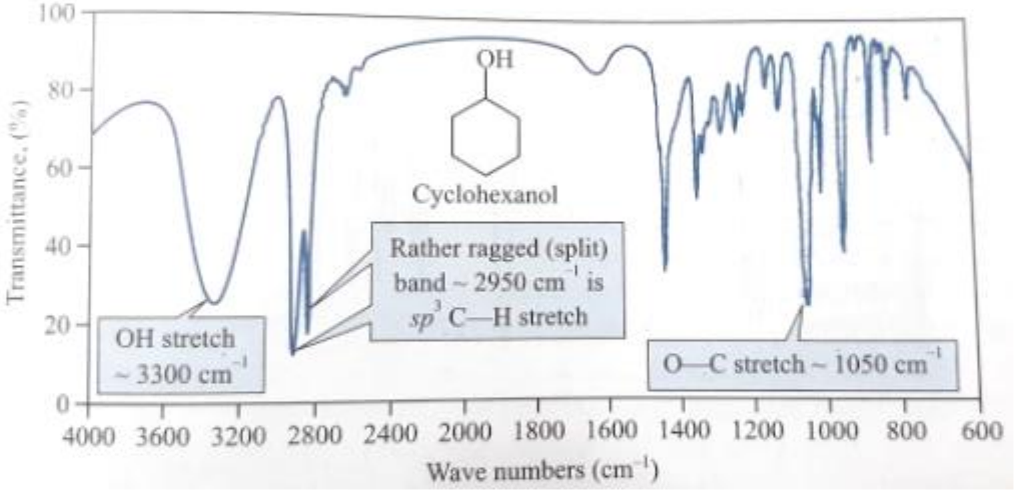
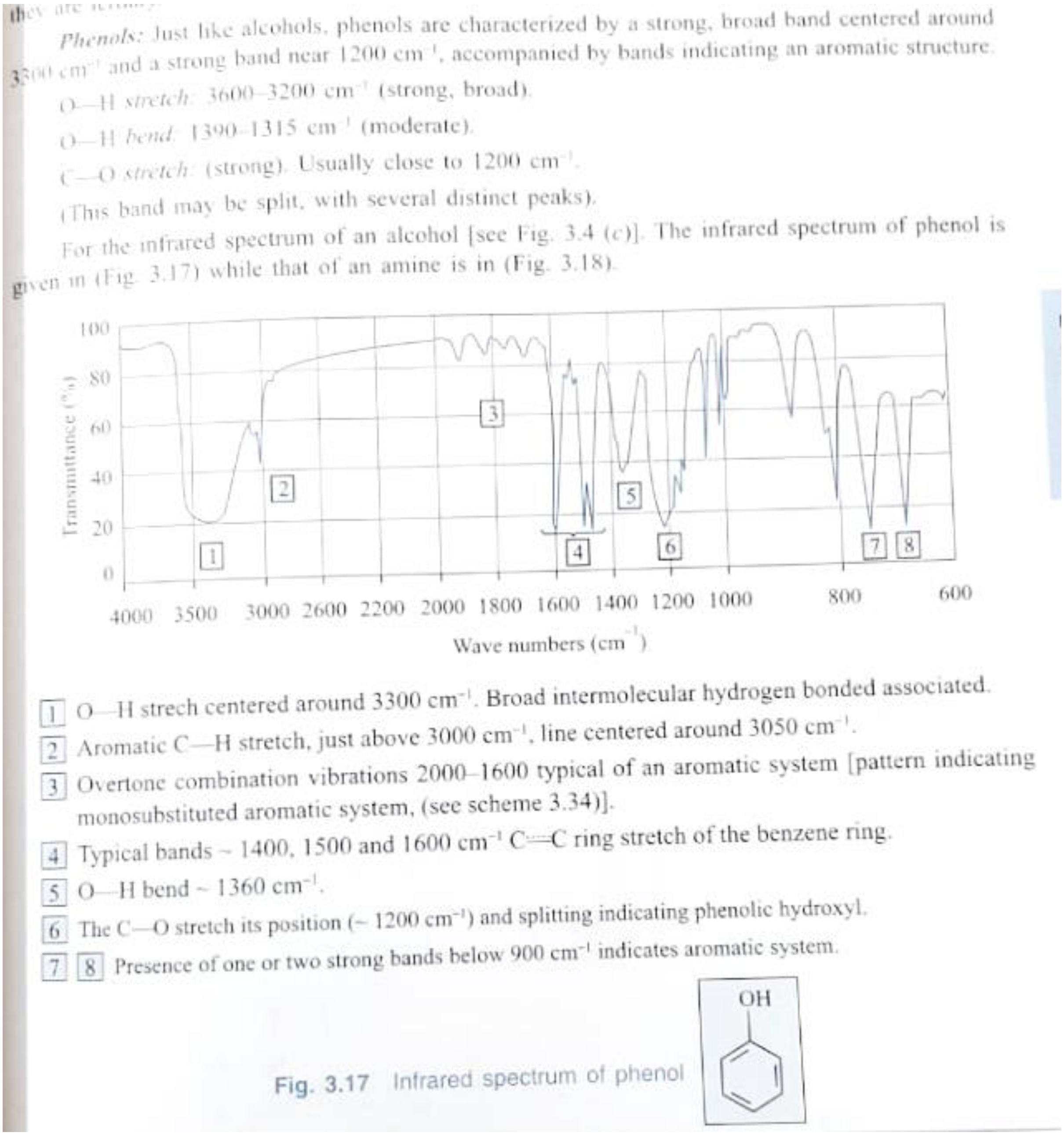


Figure 23: IR spectrum of Cyclohexanol (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Characteristic Vibrational Frequencies of Phenol

- Phenol just like alcohols phenols are characterized by strong broadband at 3300 cm^{-1} and strong band near 1200 cm^{-1} accompanied by bands indicating an aromatic structure
- O – H stretch: 3600 – 3200 cm^{-1} (strong, broad)
- O – H bend: 1390 – 1315 cm^{-1} (moderate)
- C – O stretch: (strong) usually close 1200 cm^{-1}
- O – H stretch at 3300 cm^{-1} (broad intramolecular hydrogen bonded associated)
- Aromatic C–H stretch, just above 3000 cm^{-1} (3050 cm^{-1})
- Overtone combination vibrations 2000 – 1600 cm^{-1} (typical of an aromatic system)
- Typical bands at 1400, 1500 and 1600 cm^{-1} (C=C ring stretch of the benzene ring)
- O – H bend at 1360 cm^{-1}
- C – O stretch its position at 1200 cm^{-1} and splitting indicating phenolic hydroxyl
- Presence of one or two strong bands below 900 cm^{-1} indicates aromatic system



they are

Phenols: Just like alcohols, phenols are characterized by a strong, broad band centered around 3300 cm^{-1} and a strong band near 1200 cm^{-1}, accompanied by bands indicating an aromatic structure.

O—H *stretch:* 3600–3200 cm^{-1} (strong, broad).

O—H *bend:* 1390–1315 cm^{-1} (moderate).

C—O *stretch:* (strong). Usually close to 1200 cm^{-1}.

(This band may be split, with several distinct peaks).

For the infrared spectrum of an alcohol [see Fig. 3.4 (*c*)]. The infrared spectrum of phenol is given in (Fig. 3.17) while that of an amine is in (Fig. 3.18).

1 O—H strech centered around 3300 cm^{-1}. Broad intermolecular hydrogen bonded associated.

2 Aromatic C—H stretch, just above 3000 cm^{-1}, line centered around 3050 cm^{-1}.

3 Overtone combination vibrations 2000–1600 typical of an aromatic system [pattern indicating monosubstituted aromatic system, (see scheme 3.34)].

4 Typical bands ~ 1400, 1500 and 1600 cm^{-1} C═C ring stretch of the benzene ring.

5 O—H bend ~ 1360 cm^{-1}.

6 The C—O stretch its position (~ 1200 cm^{-1}) and splitting indicating phenolic hydroxyl.

7 8 Presence of one or two strong bands below 900 cm^{-1} indicates aromatic system.

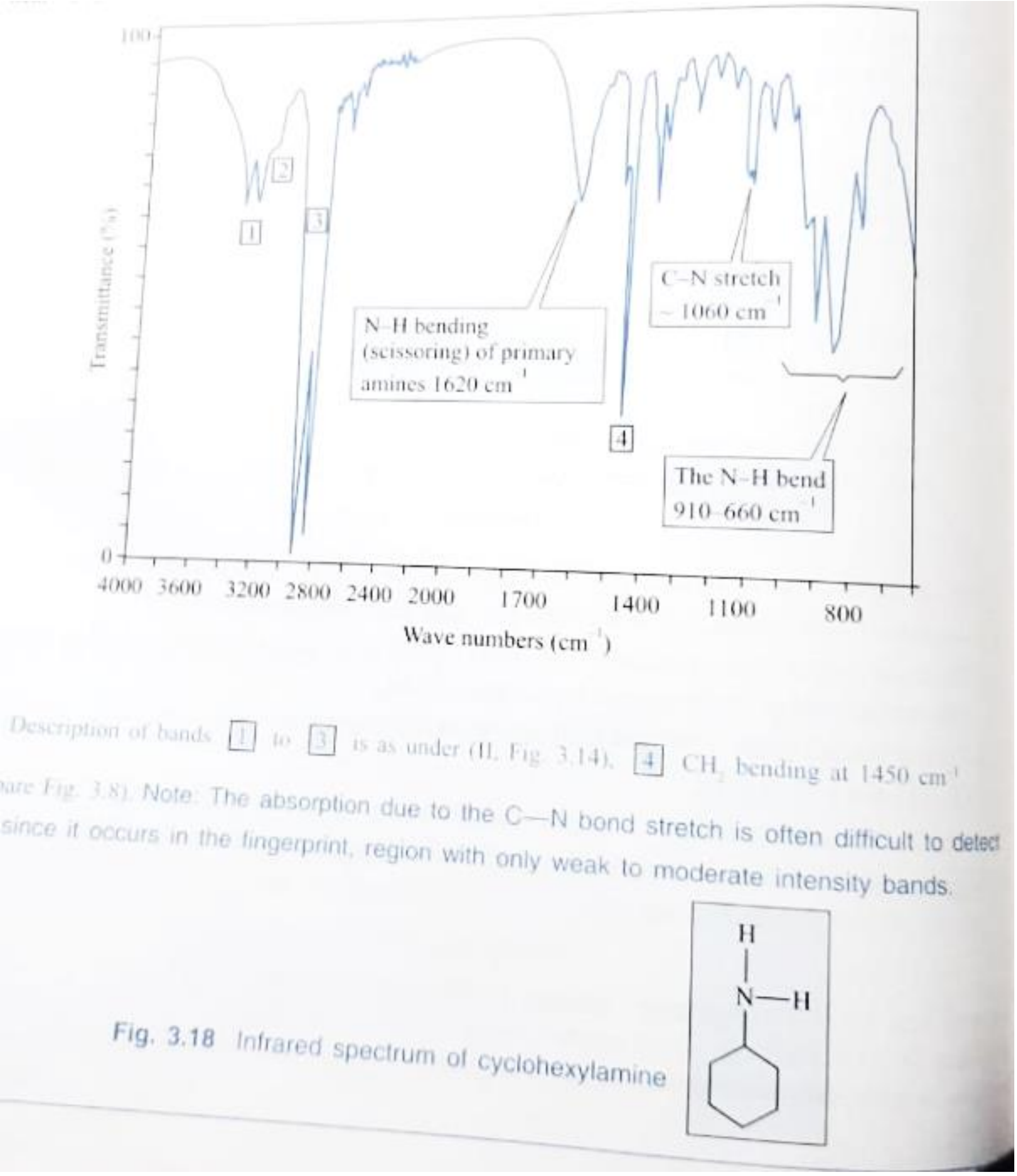
Fig. 3.17 Infrared spectrum of phenol

Figure 24: IR spectrum of Toluene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Characteristic Vibrational Frequencies of Amine

- **N – H stretch:**
- Primary amine display a typical 2 prolonged band near 3350 cm^{-1} and 2 Bands near 1615 and 800 cm^{-1}
- Secondary amines have single weak band near 3300 cm^{-1} and broadband near 715 cm^{-1}
- Tertiary amine have none and can be distinguished by the presence of C – N band

- Primary and secondary aromatic amines absorb at slightly higher frequencies
- **N – H bend (scissoring): 1650 – 1500 cm^{-1}**
- usually near 1615 cm^{-1} for primary amine, seldom observed for secondary aliphatic amines and secondary aromatic amines absorb near 1515 cm^{-1}
- **N – H bend (wagging): 910 – 667 cm^{-1}**
- Strong and very broad around the 910 – 770 cm^{-1} for primary amines and near 715 cm^{-1} for secondary amine
- **C – N stretch:** 1250 cm^{-1} for aromatic amine and 1250 – 1020 cm^{-1} for aliphatic amines



Description of bands 1 to 3 is as under (II, Fig. 3.14). 4 CH$_2$ bending at 1450 cm^{-1}

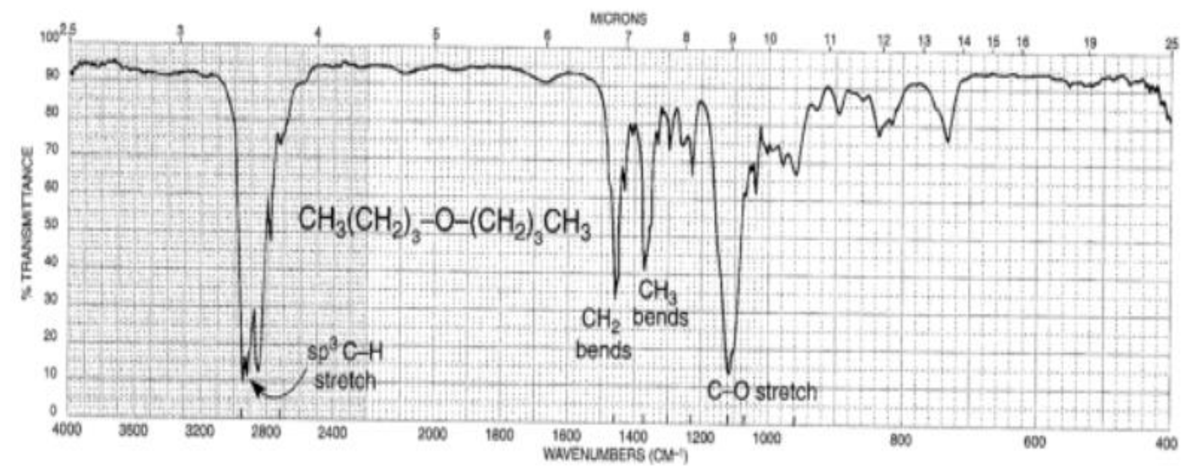
are Fig. 3.8). Note: The absorption due to the C—N bond stretch is often difficult to detect since it occurs in the fingerprint, region with only weak to moderate intensity bands.

Fig. 3.18 Infrared spectrum of cyclohexylamine

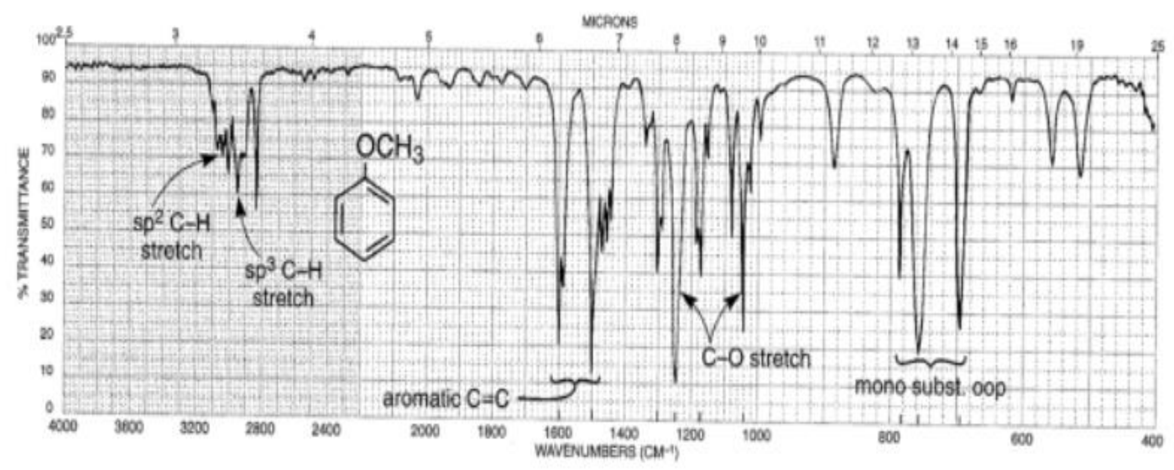
Figure 25: IR spectrum of Toluene (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Characteristic Vibrational Frequencies of Ether

- The obvious way to know a molecule is an ether is to see a C – O peak, but no C=O or O – H
- Since the absence of a C=O or O – H stretch confirms it is not an ester, acid, alcohol
- The C – O stretch is found between 1000 – 1300 cm^{-1}
- Aliphatic ethers give one strong asymmetric stretch around 1120 cm^{-1}, and a very weak symmetric stretch around 850 cm^{-1}.
- Aryl alkyl ethers give two bands around 1250 cm^{-1} symmetric and 1040 cm^{-1}, asymmetric respectively.



Dibutyl ether



Anisole

Figure 26: IR spectrum of Dibutyl ether and Anisole (Source: blogspot.com)

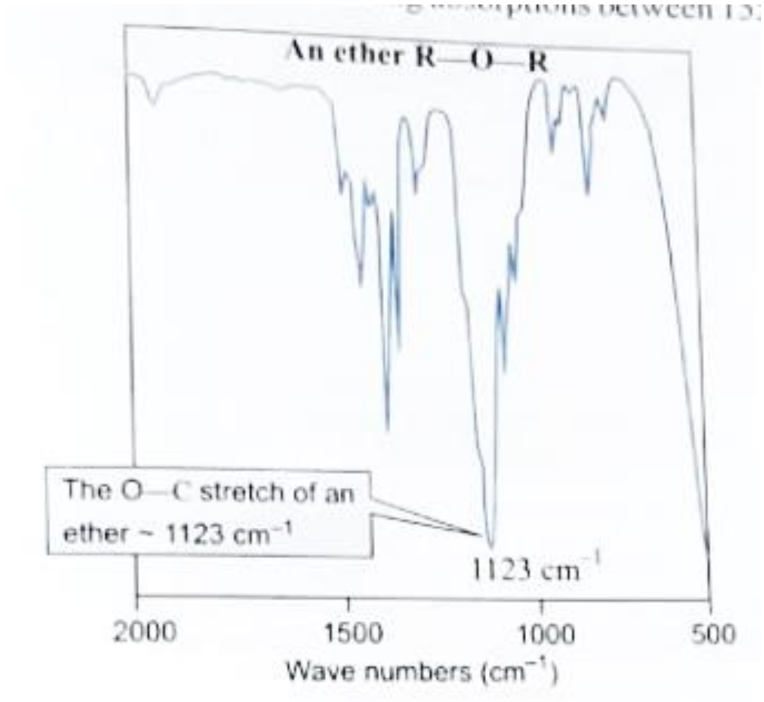
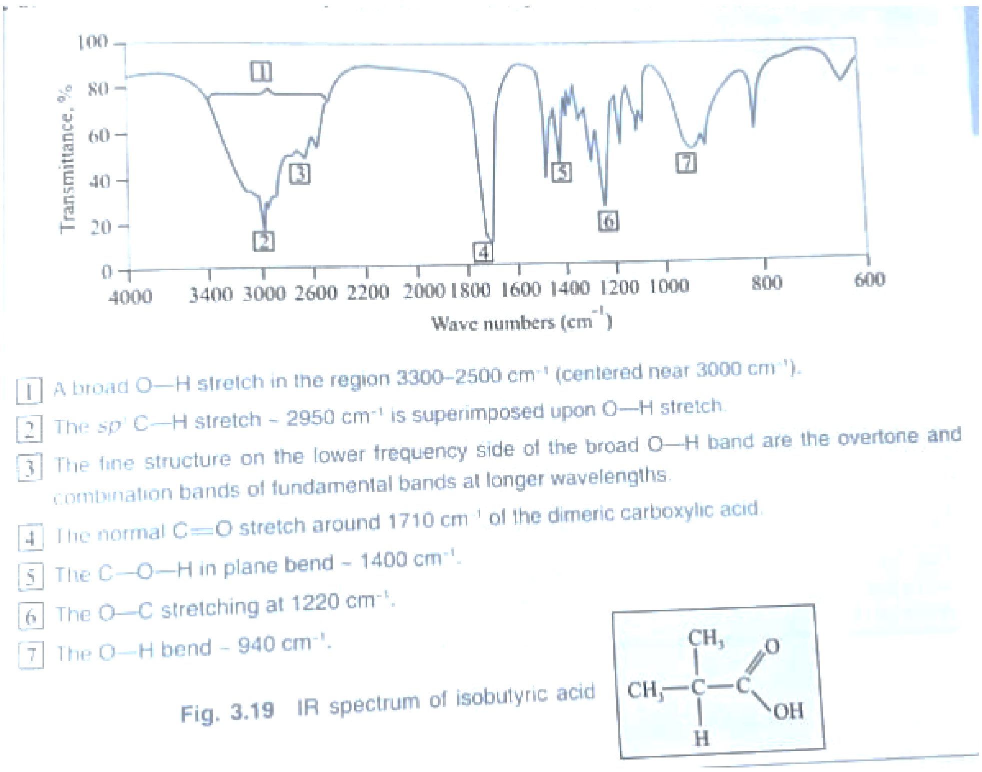


Figure 27: O – C stretch of ether in IR spectrum (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

4. Characteristic Vibrational Frequencies of Carbonyl compounds

Characteristic Vibrational Frequencies of Carbonyl compound- Carboxylic acid



1 A broad O—H stretch in the region 3300–2500 cm⁻¹ (centered near 3000 cm⁻¹).

2 The sp^3 C—H stretch ~ 2950 cm⁻¹ is superimposed upon O—H stretch.

3 The fine structure on the lower frequency side of the broad O—H band are the overtone and combination bands of fundamental bands at longer wavelengths.

4 The normal C═O stretch around 1710 cm⁻¹ of the dimeric carboxylic acid.

5 The C—O—H in plane bend ~ 1400 cm⁻¹.

6 The O—C stretching at 1220 cm⁻¹.

7 The O—H bend ~ 940 cm⁻¹.

Fig. 3.19 IR spectrum of isobutyric acid

Figure 28: IR spectrum of isobutyric acid (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Vibrational Frequencies of Carbonyl compound- Amide

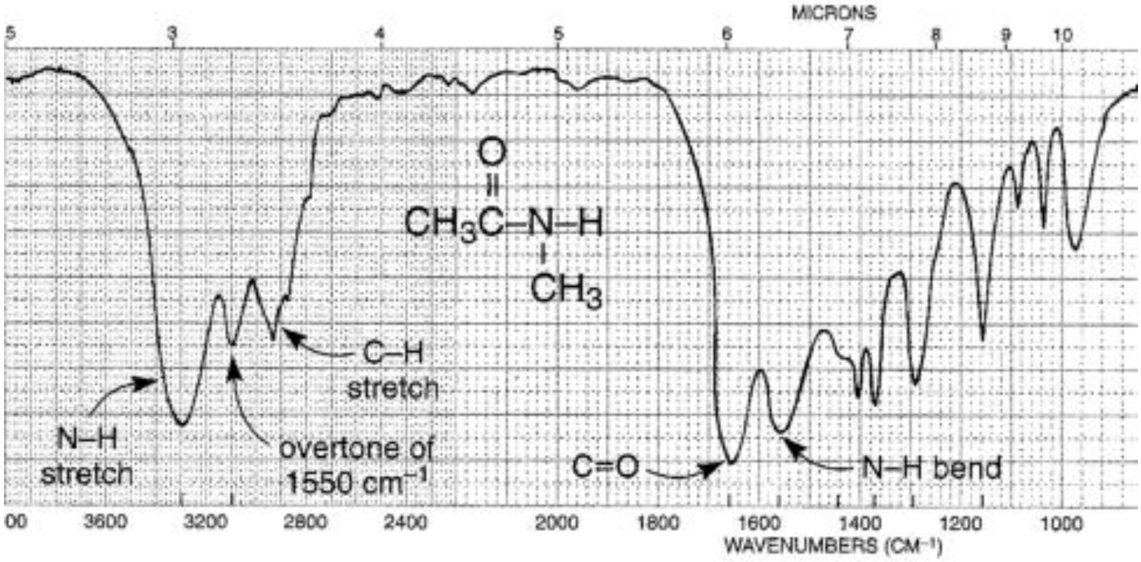


Figure 29: IR spectrum of N-methyl acetamide (Source: blogspot.com)

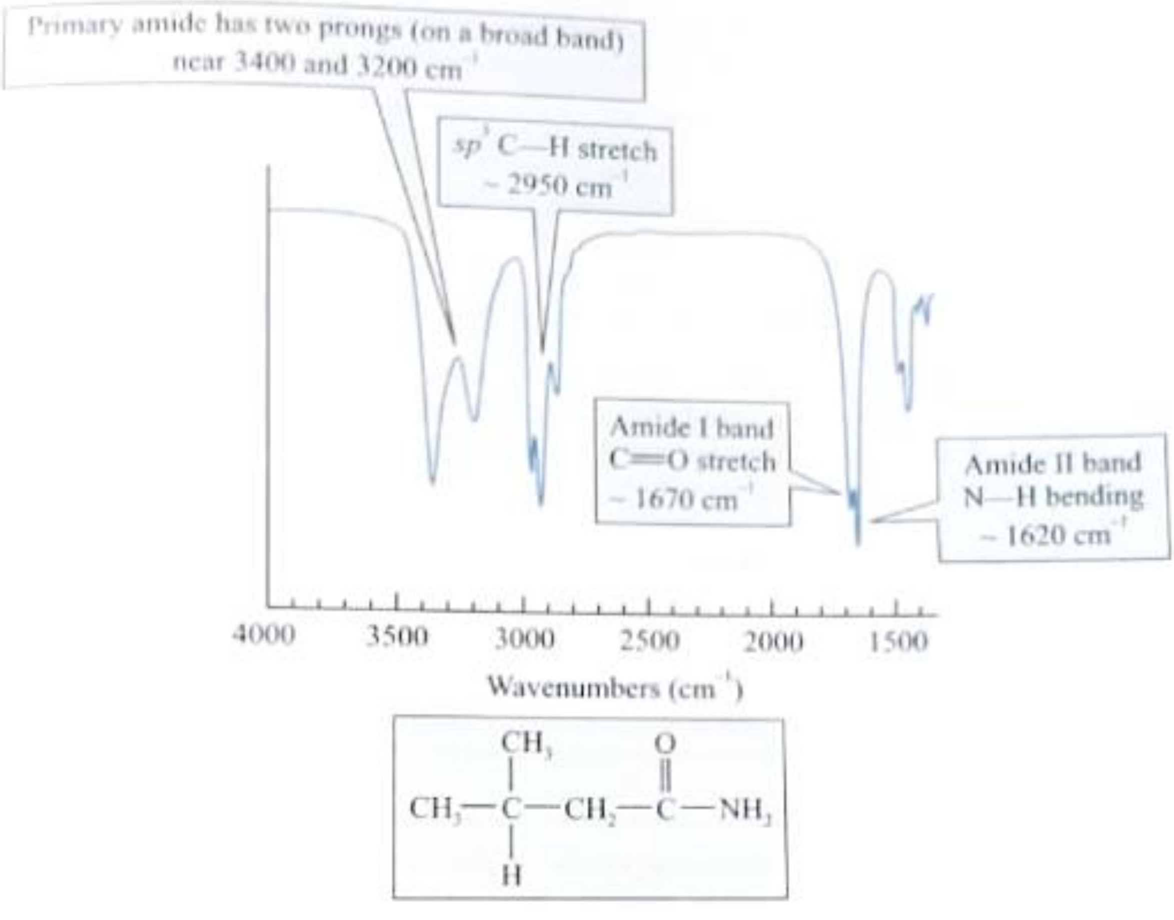


Figure 30: IR spectrum of Amide (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Characteristic Vibrational Frequencies of Carbonyl compound- Ketone and Aldehyde

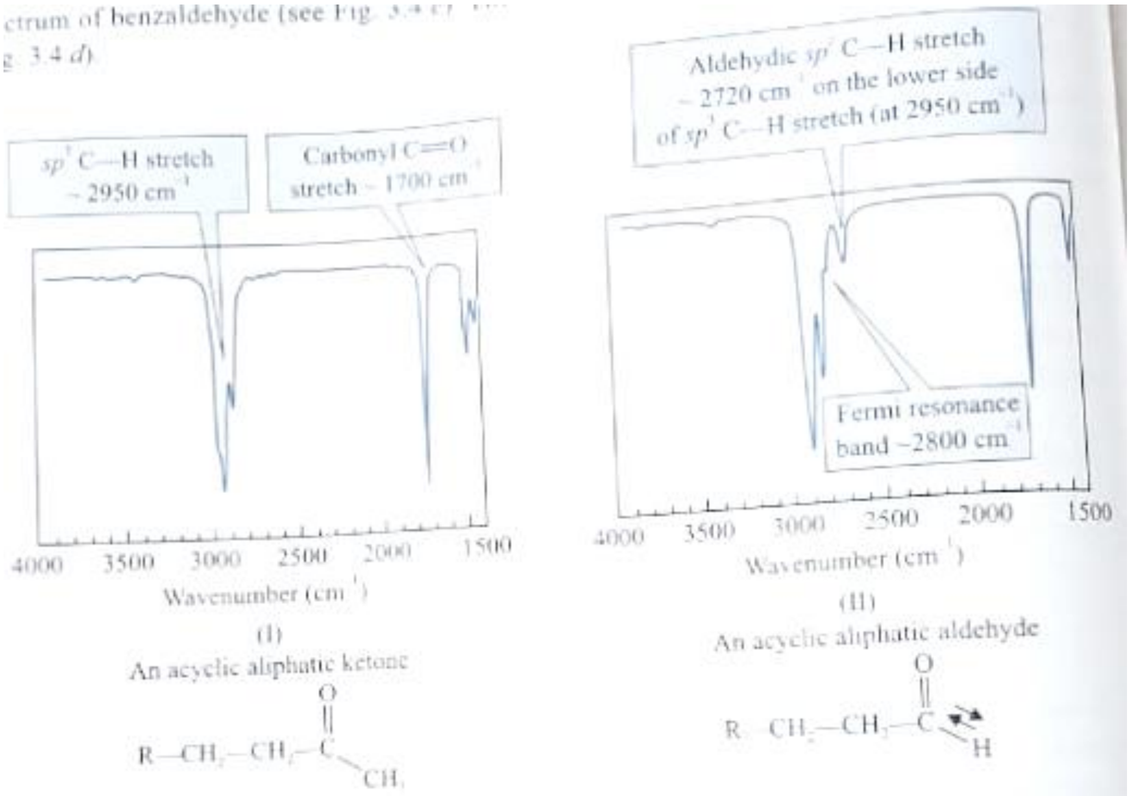


Figure 31: IR spectrum of aliphatic ketone and Aldehyde (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Characteristic Vibrational Frequencies of Carbonyl compound- Ester

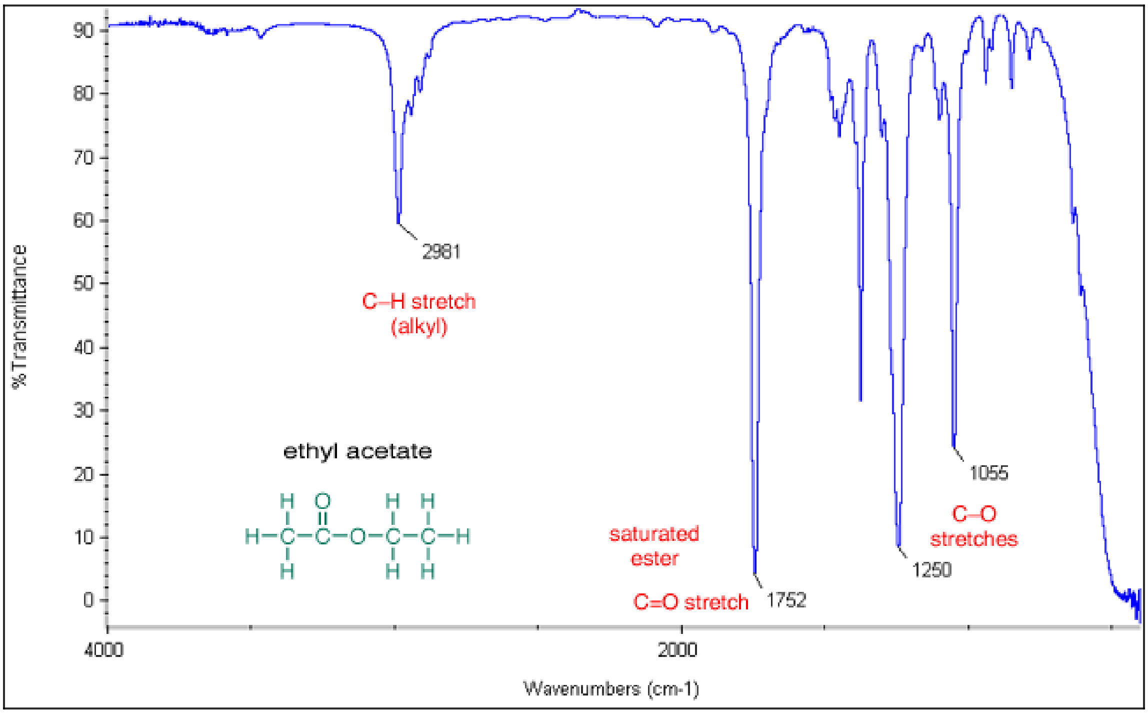


Figure 32: IR spectrum of ethyl acetate (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

Characteristic Vibrational Frequencies of Carbonyl compound- Lactam

- N – H Stretching: Strong band at 3200 cm^{-1}
- C = O stretching: One Intense band near 1670 cm^{-1}
- Whereas for Amides 2 bands appear 1670 and 1620 cm^{-1}

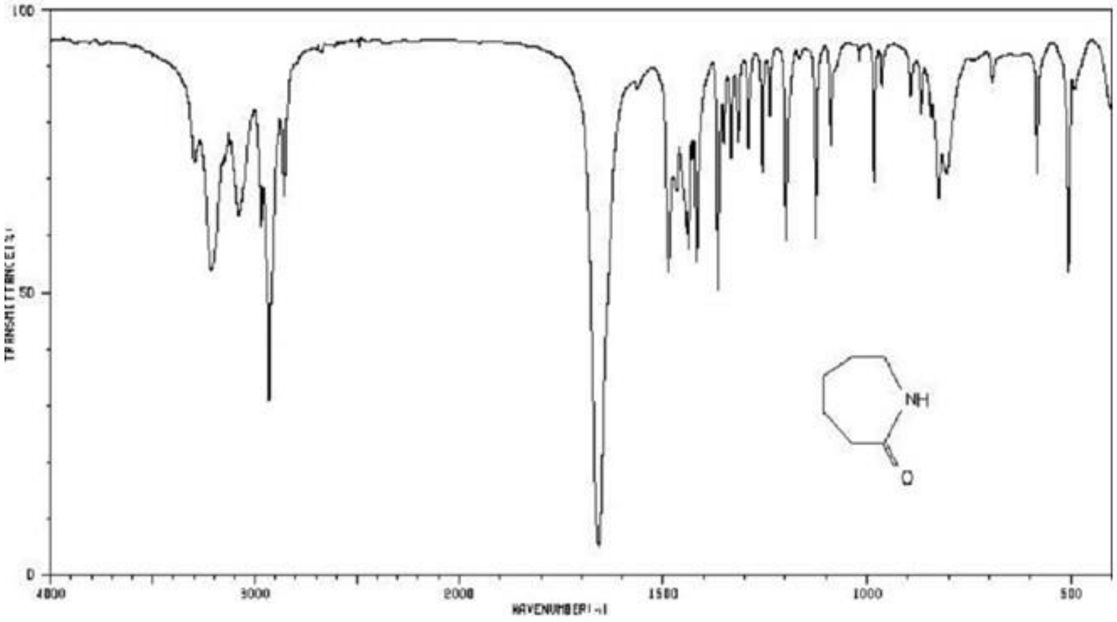


Figure 33: IR spectrum of Lactam (Source: chem.pg.edu.pl)

Characteristic Vibrational Frequencies of Carbonyl compound- Acid Anhydride

- Acid anhydride show two C=O stretching absorptions (1820 and 1760 cm^{-1} (with separation of 60 cm^{-1}
- C – O Stretching in region 1300 – 1050 cm^{-1}

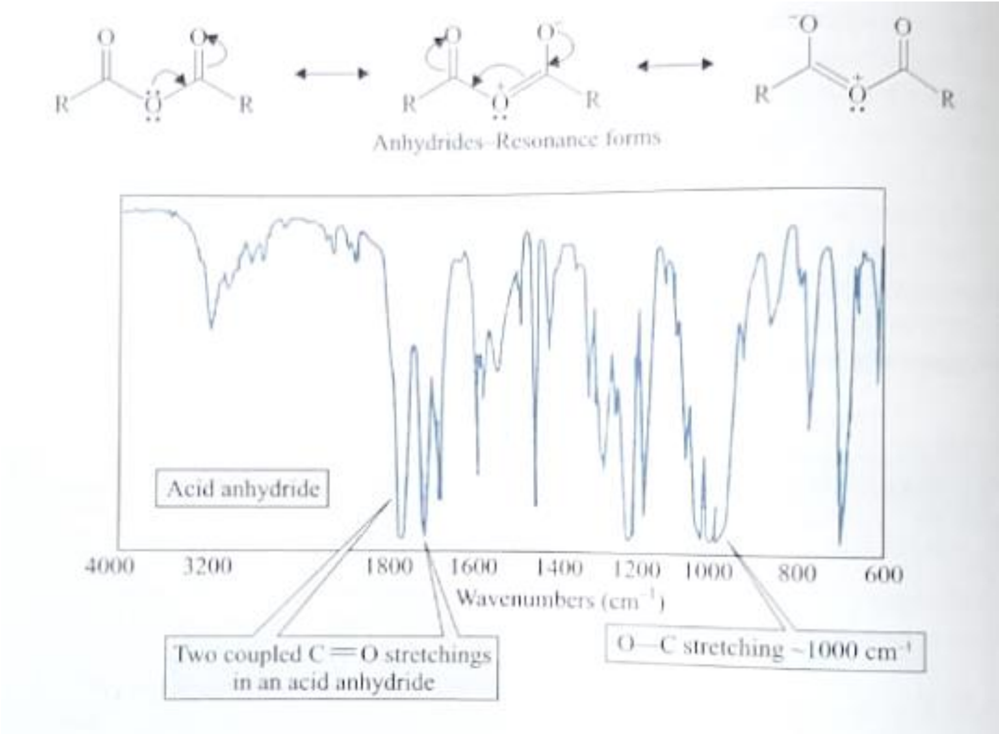


Figure 34: IR spectrum of acid anhydride (Source: Spectroscopy of Organic compounds, P.S. Kalsi)

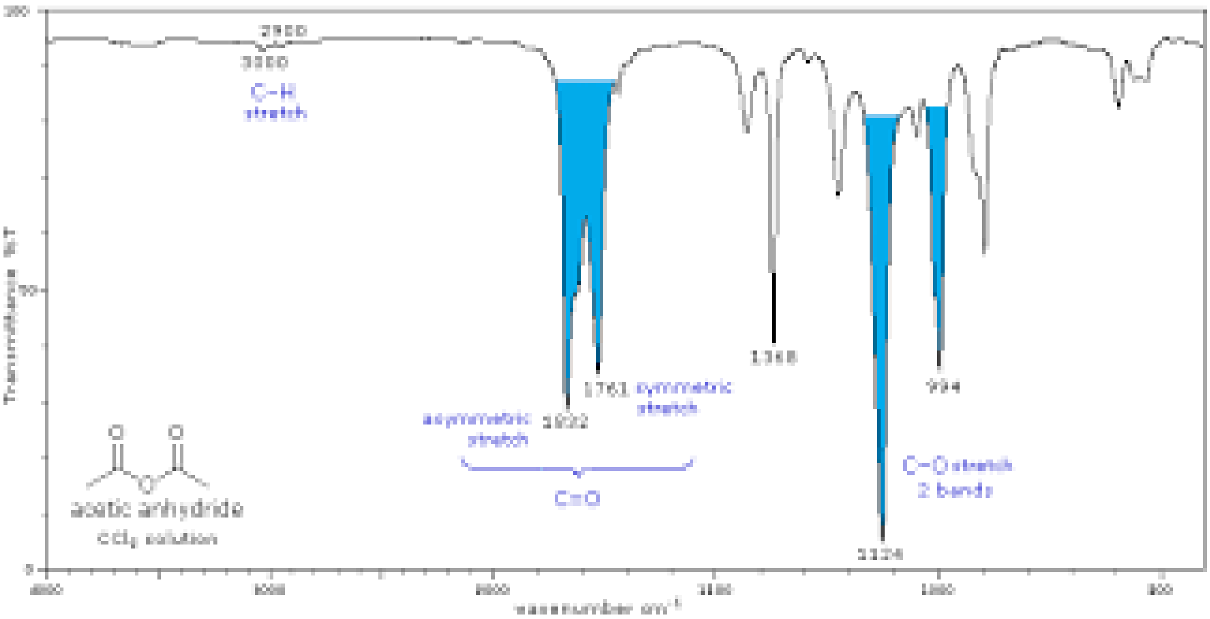
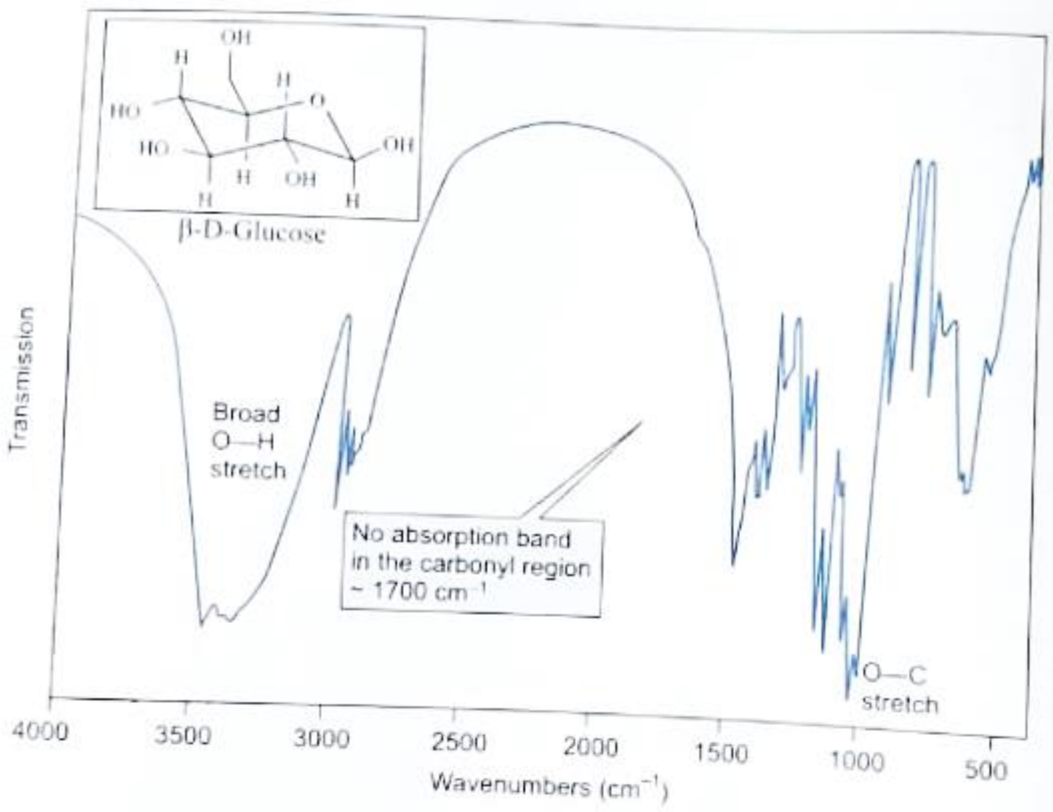


Figure 35: IR spectrum of acetic anhydride (Source: chem.pg.edu.pl)

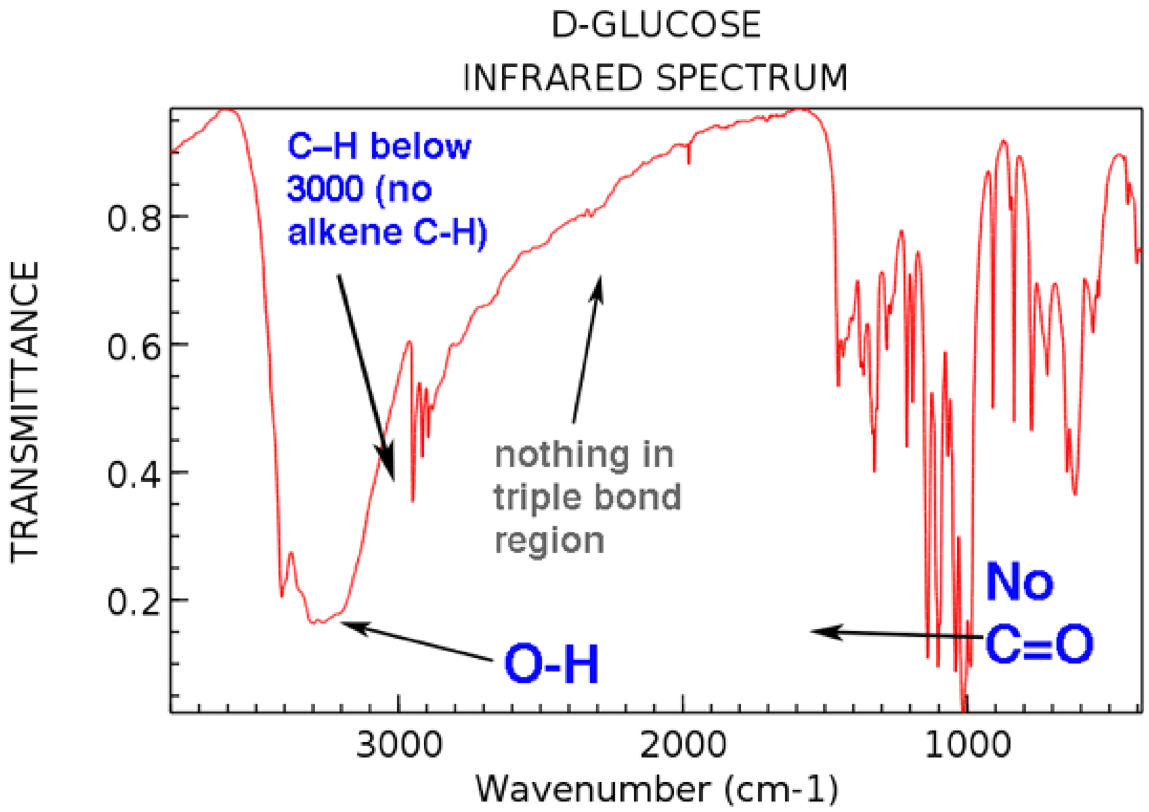
Characteristic Vibrational Frequencies of Carbonyl compound- Lactone

- D- Glucose (Lactone):
- No C = O peak at 1700 cm^{-1}

- O – H stretch: Broad band at 3300 cm^{-1}
- O – C stretch: Band at 1000 cm^{-1}

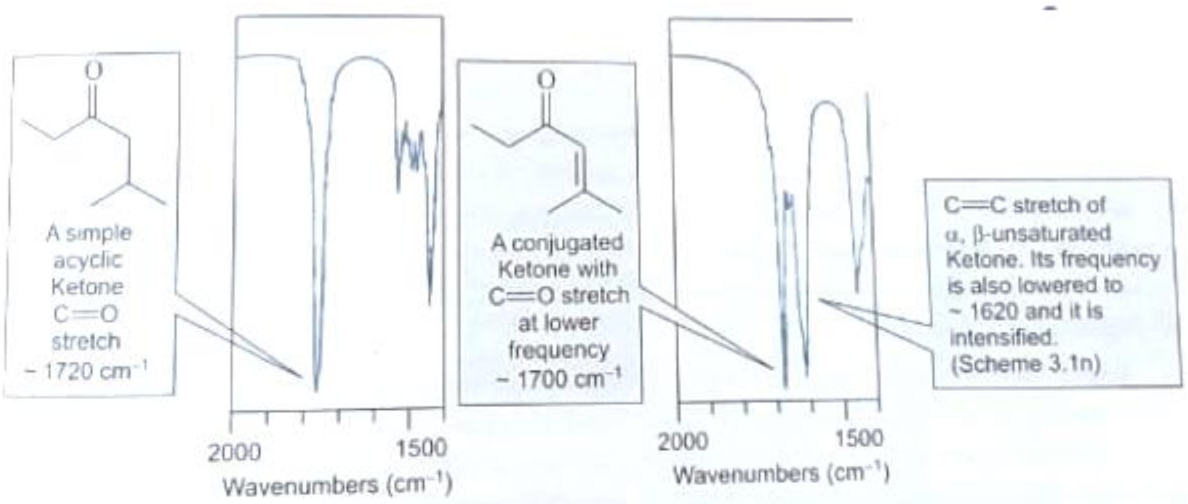


IR Spectrum of glucose



Characteristic Vibrational Frequencies of Carbonyl compound- Conjugated Ketone

- Conjugation lowers the frequency of both C = O and C = C stretching vibrations (conjugation due to α,β-unsaturation or aromatic ring) by about 20 and 30 cm^{-1} respectively

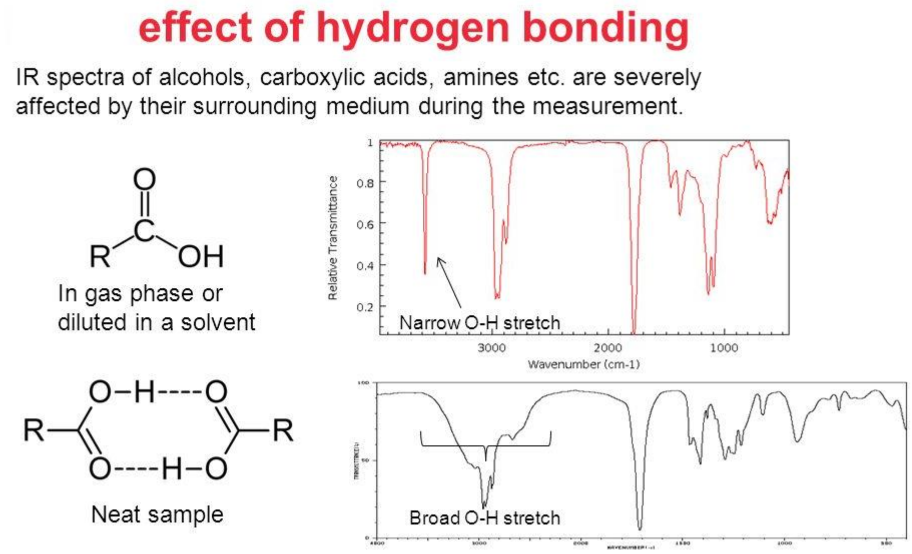


Partial IR spectra in the double bond region of a simple and a conjugated ketone

Unit 2 – IR Spectroscopy

Effect of Hydrogen bonding and Study of Linkage isomerism

Effect of Hydrogen bonding



effect of hydrogen bonding

IR spectra of alcohols, carboxylic acids, amines etc. are severely affected by their surrounding medium during the measurement.

In gas phase or diluted in a solvent

Narrow O-H stretch

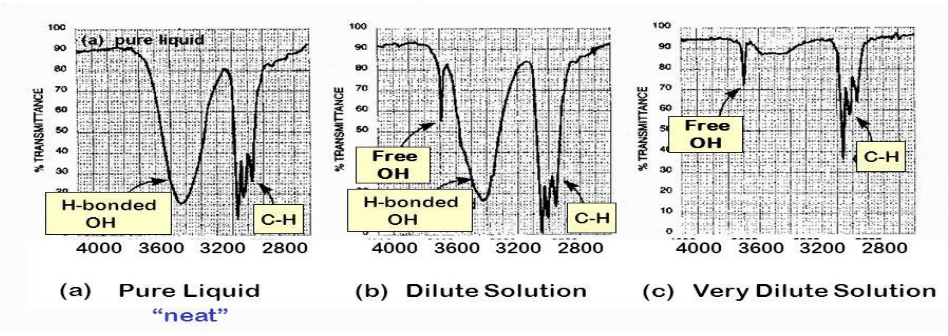
Neat sample

Broad O-H stretch

- Intermolecular hydrogen bonds gives rise to broad bands, while intramolecular hydrogen bonds give sharp and well defined bands.

- The inter and intramolecular hydrogen bonding can be distinguished by dilution.

- Intramolecular hydrogen bonding remains unaffected on dilution and as a result the absorption band also remains unaffected where as in intermolecular, bonds are broken on dilution and as a result there is a decrease in the bonded O-H absorption .

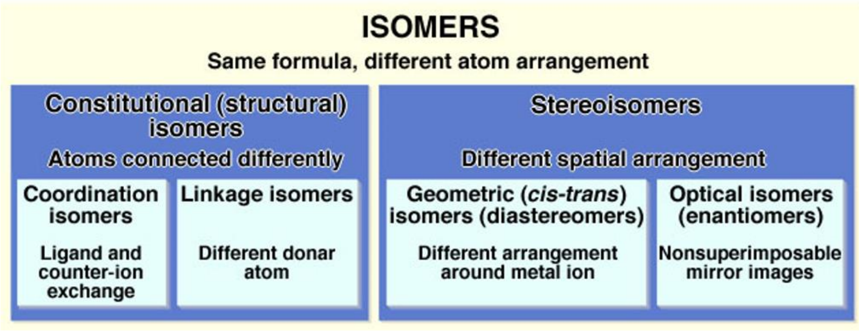


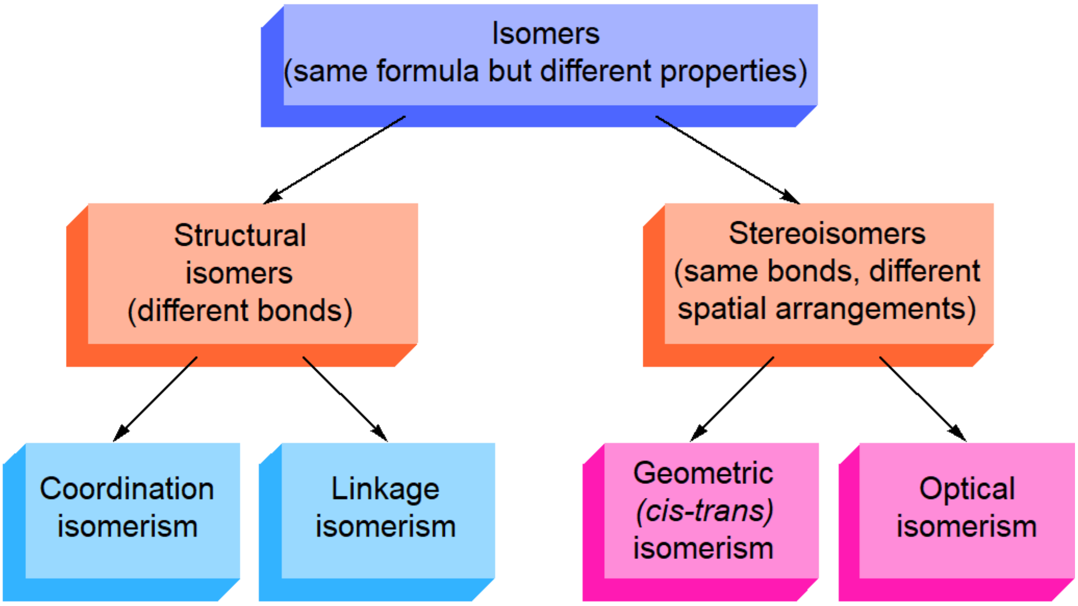
(a) Pure Liquid "neat"

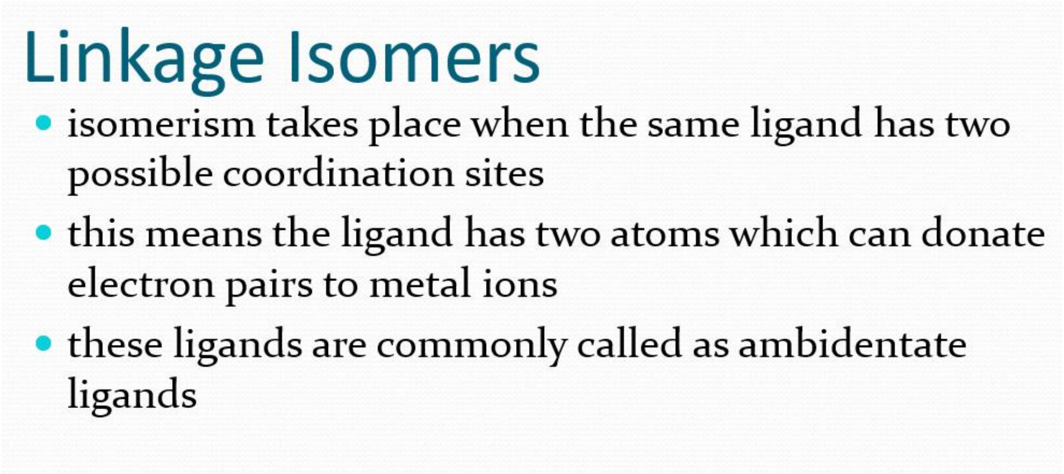
(b) Dilute Solution

(c) Very Dilute Solution

Isomerism in Coordination Compounds



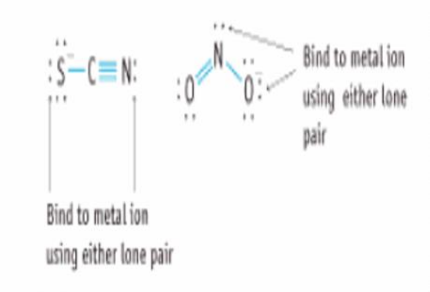




Linkage Isomers

- isomerism takes place when the same ligand has two possible coordination sites
- this means the ligand has two atoms which can donate electron pairs to metal ions
- these ligands are commonly called as ambidentate ligands

Ambidentate ligands



CN- (cyano) links to C

NC- (isocyano) links to N

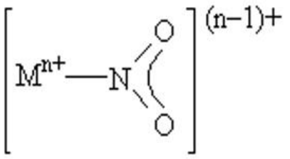
OCN- (cyanato) links to O

NCO- (isocyanato) links to N

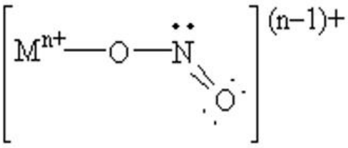
SCN- (thiocyanato) links to S

NCS- (isothiocyanato) links to N atoms

Nitrate Ion



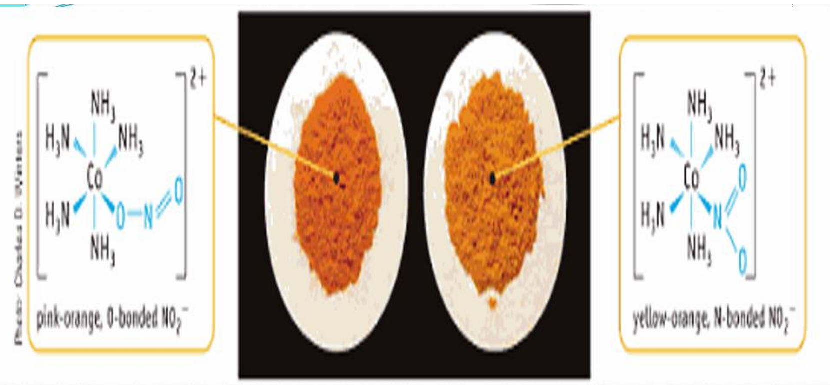
Nitro linkage



Nitrito linkage

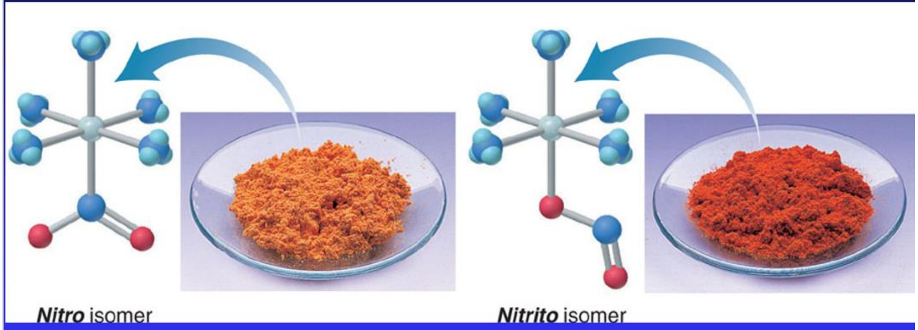
- two different resonance structures, each with the negative charge on a different oxygen atom.
- binds through the lone pair of the central atom: nitrogen for the nitro form and oxygen for the nitrito form.

- Linkage isomerism arises in a coordination compound containing ambidentate ligand.
- A simple example is provided by complexes containing the thiocyanate ligand, NCS–, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN.
- Jørgensen discovered such behaviour in the complex [Co(NH3)5(NO2)]Cl2, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen (–NO2).



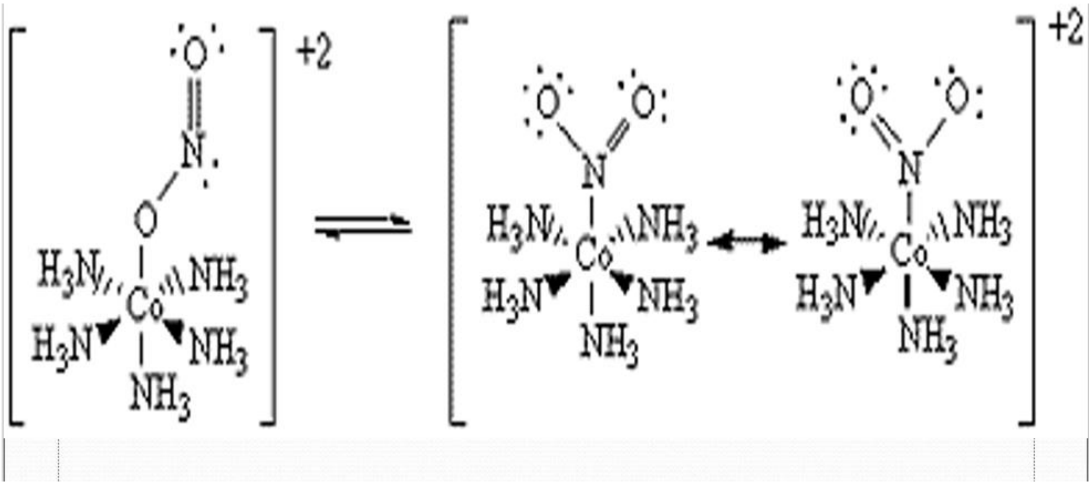
- Nitrito and Nitro isomer

Linkage Isomers

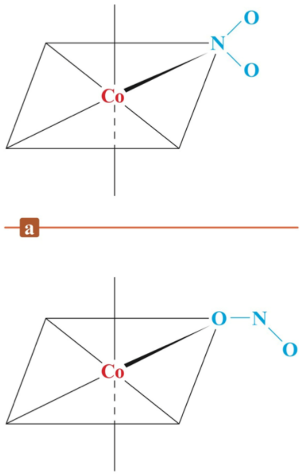


$[Co(NH_3)_5(NO_2)]Cl_2$
Pentaamminenitrocobalt(III) chloride

$[Co(NH_3)_5(ONO)]Cl_2$
Pentaamminenitritocobalt(III) chloride



Linkage Isomerism of NO_2^-

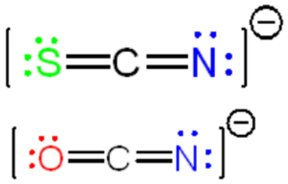


Linkage isomers

- **Occur when a ligand has two alternative donor atoms.**
-

Thiocyanate ion

cyanate ion

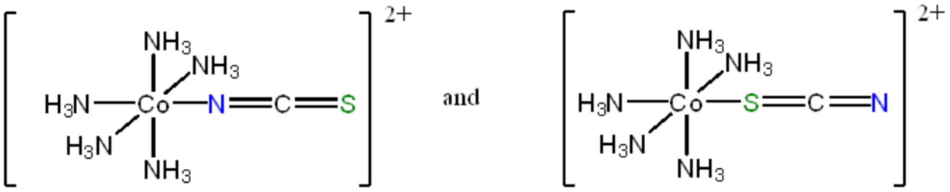


Thiocyanato NCS:→

Isothiocyanato SCN:→

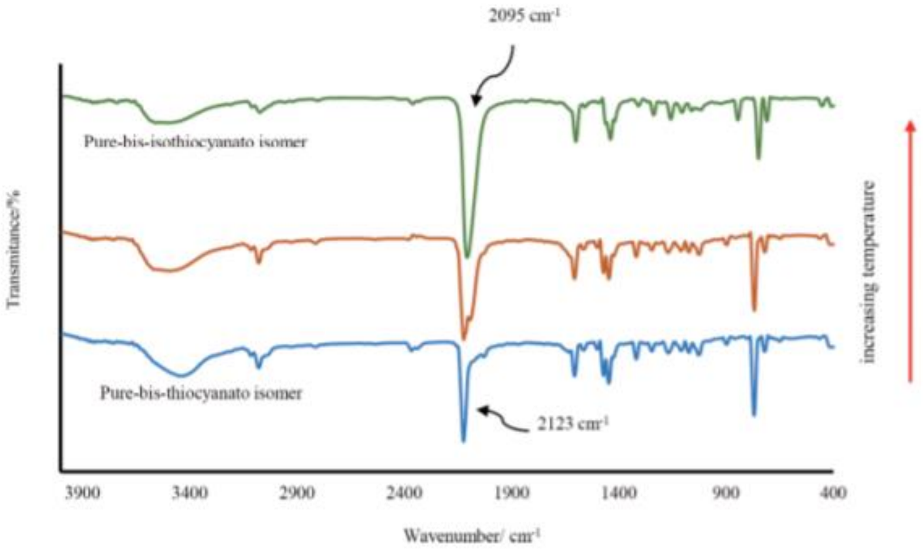
cyanato NCO:→

isocyanato OCN:→



Pentaammineisothiocyanatocobalt(III) pentaamminethiocyanatocobalt (III)

- The IR spectra of pure sample of [Pt(SCN)2(bipy)],
- for (–SCN)2 isomer (lower spectra), the sharp peak at 2123 cm–1 is related to CN stretching frequency.
- Upon increasing temperature, the (–SCN)2 species is being converted into the (–NCS)2 ones through a plausible (–SCN)(–NCS) isomer.
- The CN stretching frequencies are higher in S-bonded complexes than in Nbonded one, so appearance of a double peak at regions of 2121 and 2093 cm–1 can be attributed to the appearance of (–SCN)(–NCS) species.
- By increasing temperature, the CN peak shifted to frequency of 2095 cm–1, that represents the (–NCS)2 isomer.

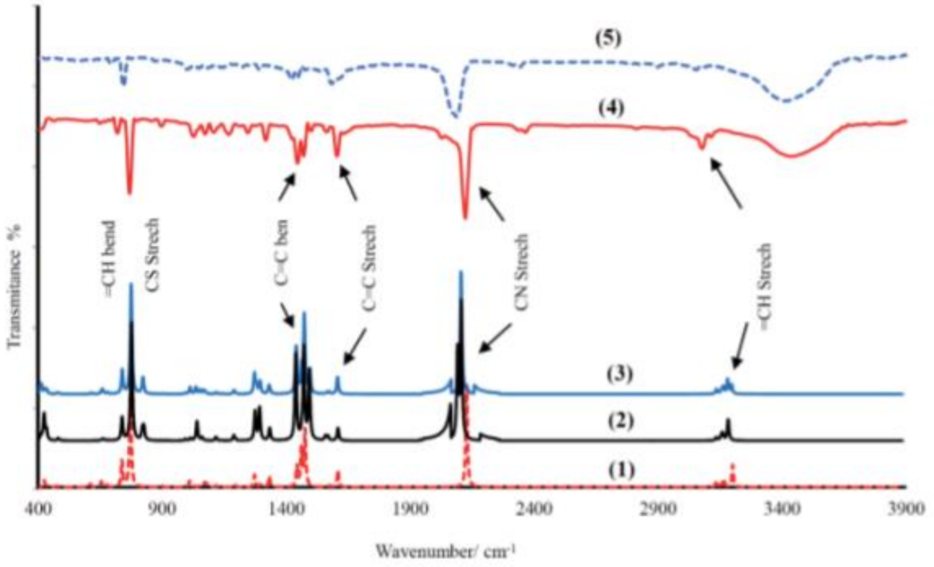


The experimental IR spectra of the bis-thiocyanato and bis-isothiocyanato isomers.

Table 3. The C–N stretching frequencies and the colors of the linkage isomers of thiocyanato Pt^{II} complexes.

Sample	C–N stretching /cm^{-1}	Color
$[Pt(SCN)_2(bipy)]$	2123	light yellow
$[Pt(SCN)(NCS)(bipy)]$	2121–2093	yellow-orange
$[Pt(NCS)_2(bipy)]$	2095	red

IR spectra of Thiocyanato and Isothiocyanato complexes



Computed IR spectra for the bis-thiocyanato (1), thiocyanato–isothiocyanato (2), and bis-isothiocyanato (3) linkage isomers in the gas phase (lower curves). Experimental IR spectra (upper curves) for the bis-thiocyanato (4) and bis-isothiocyanato isomers (5).

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT-3 – ^{1}H-NMR and ^{13}C-NMR Spectroscopy – SCYA7301

1. ^{1}H-NMR Spectroscopy

Introduction

Nuclear Magnetic Resonance (NMR) is a branch of spectroscopy in which electromagnetic radiation (usually of radiowave frequency) is absorbed by molecules possessing nuclei with non-zero spins, *i.e.* **nuclear** spin **I > 0**. NMR is similar to **Electron Paramagnetic Resonance (EPR)** which deals with the species of non-zero **electronic** spins, **S > 0**.

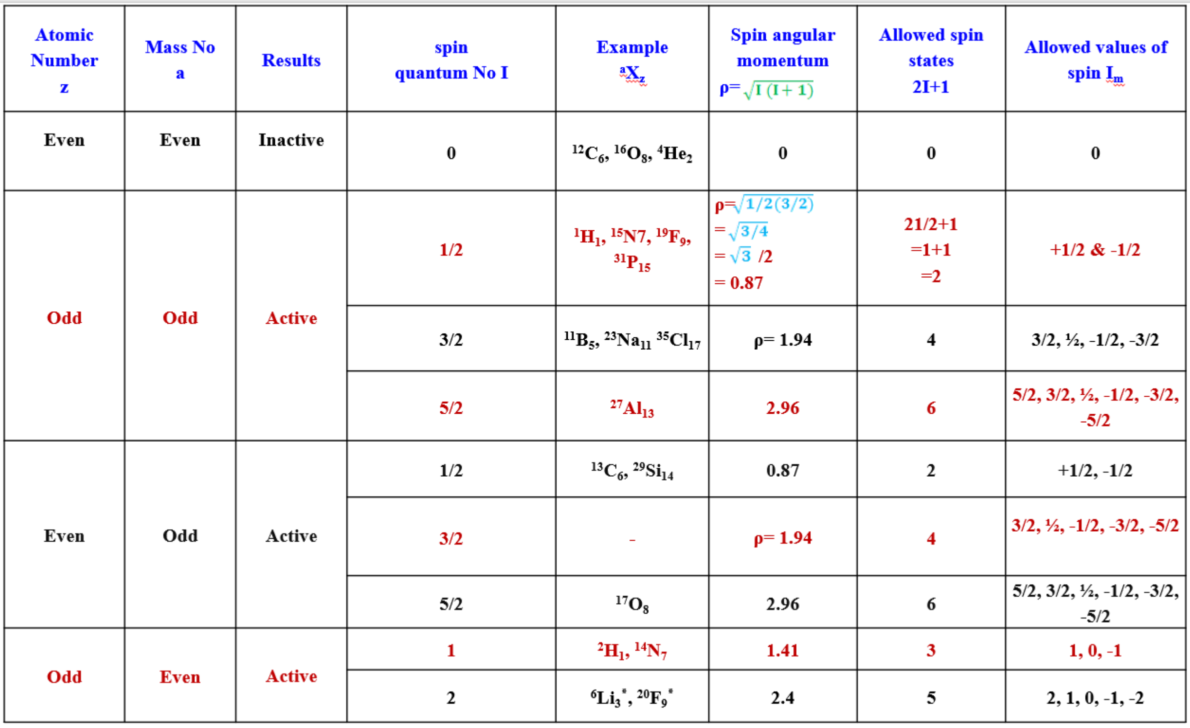
In both ESR and NMR, the sample material is immersed in a strong static magnetic field and exposed to an **orthogonal** low-amplitude high-frequency field. ESR usually requires microwave-frequency radiation (GHz), while NMR is observed at lower radio frequencies (MHz).

Nature of Spinning Particles

- The NMR experiment is made possible by magnetic properties of various nuclei
- All nuclei carry a charge
- In some nuclei this charge spins on a nuclei axis
- This generates a magnetic dipole along the axis
- The angular momentum of the spinning charge is described in terms of spin quantum number I
- The spin quantum number have values 0, ½, 1, 3/2 and so on
- The magnitude of the generated dipole is expressed in terms of nuclear magnetic moment (μ)
- Each proton and neutron has its own spin and I is the resultant of these spins
- If the sum of protons and neutrons is even, I is zero or integral
- If the sum is odd, I is a half integral
- If both protons and neutrons are even numbered I is 0
- Example: ^{1}H, ^{19}F, ^{13}C, ^{31}P …….. I = ½
- ^{2}H, ^{14}N…….. I = 1
- ^{11}B, ^{35}Cl, ……. I = 3/2
- If a particular nucleus is composed of p protons and n neutrons, its total mass is p + n , its Total charges is +p and its total spin will be a vector combination of p+n spins each of magnitude ½

- The atomic mass is specified for each nucleus as a prefix to the nuclear symbol, for example ^{12}C indicates in nucleus of carbon having a mass of 12.
- The atomic charges is 6 for this nucleus (6 protons and 6 neutrons)
- The nucleus 13C isotope of carbon has 6 protons and 7 neutrons
- The spin of hydrogen nucleus ^{1}H is ½ since it consists of one Proton only
- Deuterium an isotope of hydrogen containing one proton and one neutron that is ^{2}H is 1
- The Helium nucleus containing two protons and two neutrons ^{4}He has zero spin
- Nuclei with both p and n even (hence charge and mass even) have zero spin for example ^{4}He, ^{12}C, ^{16}O
- Nuclei with both p and n odd (hence charge odd but mass=p+n, even) have integral spin. For example ^{2}H, ^{14}N (spin=1)
- Nuclei with odd mass have half integral spin. For example ^{1}H, ^{15}N (spin= ½)

Table 1: Spin quantum number, Allowed spin states and allowed values of Spins of various nucleus



Atomic Number z	Mass No a	Results	spin quantum No I	Example $^{a}X_{z}$	Spin angular momentum $\rho=\sqrt{I\ (I+1)}$	Allowed spin states 2I+1	Allowed values of spin I_m
Even	Even	Inactive	0	$^{12}C_6$, $^{16}O_8$, $^{4}He_2$	0	0	0
Odd	Odd	Active	1/2	$^{1}H_1$, $^{15}N7$, $^{19}F_9$, $^{31}P_{15}$	$\rho=\sqrt{1/2(3/2)}$ $=\sqrt{3/4}$ $=\sqrt{3}\ /2$ = 0.87	21/2+1 =1+1 =2	+1/2 & -1/2
			3/2	$^{11}B_5$, $^{23}Na_{11}$ $^{35}Cl_{17}$	ρ= 1.94	4	3/2, ½, -1/2, -3/2
			5/2	$^{27}Al_{13}$	2.96	6	5/2, 3/2, ½, -1/2, -3/2, -5/2
Even	Odd	Active	1/2	$^{13}C_6$, $^{29}Si_{14}$	0.87	2	+1/2, -1/2
			3/2	-	ρ= 1.94	4	3/2, ½, -1/2, -3/2, -5/2
			5/2	$^{17}O_8$	2.96	6	5/2, 3/2, ½, -1/2, -3/2, -5/2
Odd	Even	Active	1	$^{2}H_1$, $^{14}N_7$	1.41	3	1, 0, -1
			2	$^{6}Li_3^{*}$, $^{20}F_9^{*}$	2.4	5	2, 1, 0, -1, -2

- The spin quantum number I determine the number of orientation a nucleus may assume in an external uniform magnetic field in accordance with the formula (2I +1)
- The spin quantum number I of the proton is ½
- According to the formula the proton has two orientation in the applied uniform magnetic field

- In one orientation the spin of the proton is parallel with the applied field (aligned with the field)
- In another orientation the spin of the proton is anti-parallel with the applied magnetic field (aligned against the field)
- The first one is the low-energy stable state
- The second one is the unstable high energy state
- The energy levels depend on the nuclear magnetic moment μ and the strength of the applied external magnetic field (H_o)

Larmor equation

- When exposed to static magnetic field B_0 the spinning Nucleus ^1H Behaves like a gyroscope. The spinning axis coincides with the magnetic momentum vector μ precesses about B_0. The angular frequency, ω in radius per second is related to B_0 as
- $\omega = \gamma B_0$ …….. 1
- But $\gamma = \omega/2\pi$:- $\omega = 2\pi\nu$ …….2
- $B_0\gamma = \omega$ or $\gamma = \omega/B_0$
- γ= gyromagnetic ratio ν= frequency
- Equating Equation 1 and 2
- $B_0\gamma = 2\pi\nu$ or $\nu = B_0\gamma/2\pi$
- γ is a unique constant for each nucleus and in an applied field strength of B_0, the frequency of precession $\nu = B_0\gamma/2\pi$
- In contrast to bar magnet, the magnetic moment of spinning nuclei do not align in the direction of B_0, no matter how strong the magnetic field is involved the larmor precession is accelerated by increasing the strength B_0
- $\nu \alpha B_0$
- γ is gyromagnetic ratio which is constant for the given nucleus and 2π is constant

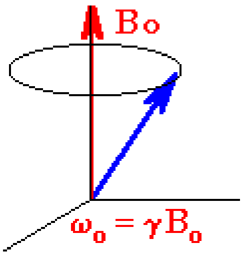


Figure 1: Angular frequency in Larmor equation

Nuclear Magnetic Energy Levels

- All ^{1}H isotopes have an intrinsic magnetic moment μ = 2.7927 nuclear magnetons.
- This magnetic moment is always present, no matter what the environment of the proton is.
- The *energies* of the protons in a magnetic field B_0, two spin states with different energies exist.
- Each level corresponds to a magnetic quantum number, m=± ½
- When B_0=0, the two spin states have the same energy, because there is no magnetic field to split their energy states.

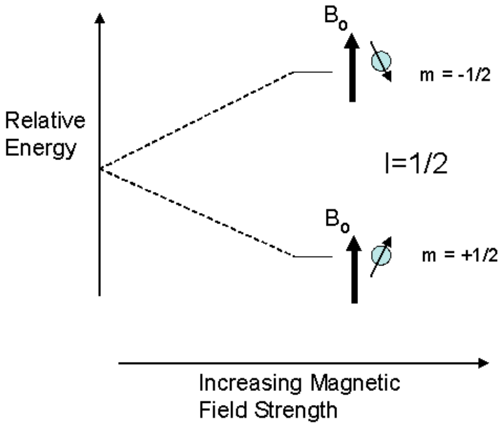
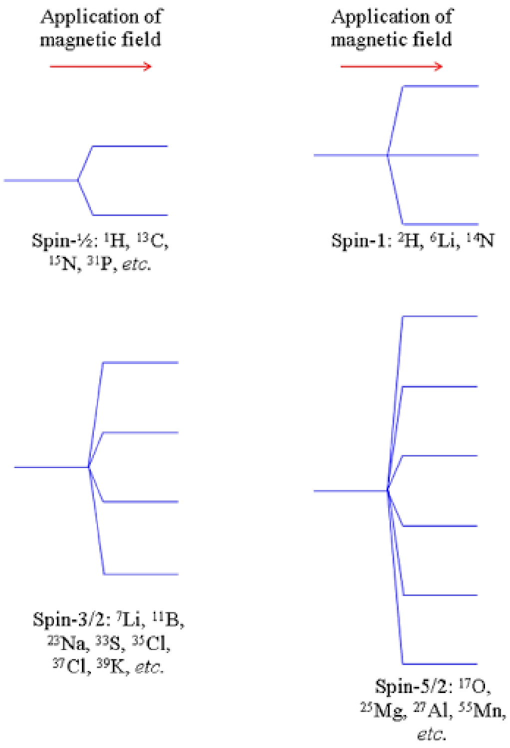


Figure 2: Energy of spin states of nuclei with I = 1/2



Spin-½: ^{1}H, ^{13}C, ^{15}N, ^{31}P, *etc.*

Spin-1: ^{2}H, ^{6}Li, ^{14}N

Spin-3/2: ^{7}Li, ^{11}B, ^{23}Na, ^{33}S, ^{35}Cl, ^{37}Cl, ^{39}K, *etc.*

Spin-5/2: ^{17}O, ^{25}Mg, ^{27}Al, ^{55}Mn, *etc.*

Figure 3: Energy of spin states of various nuclei with different I values

Spin-Spin relaxation and Spin-Lattice relaxation

- **Two Radiationless Process**
- **Spin – spin relaxation** is effected by the mutual exchange of spins by two nuclei in close proximity to one another. It is called as T_2 (Transverse relaxation time)
- **Spin lattice relaxation** is effected by the loss of energy of nucleus in higher energy state to its environment and return to the low energy state. It is also called as T_1 (Longitudinal relaxation time)
- **Relaxation process:** The mechanism (radiationless process) by which excess spin energy (nucleus in upper state returns to lower spin state) is shared either with the surrounding or with the other nuclei.
- **Relaxation Time:** The time taken for a fraction $1/e = 0.37$ of the excess energy to be dissipated.
- The natural width of a spectral line is inversely proportional to the average time the system spends in the excited state.
- Sharp resonance lines are observed for states of extended excitations
- Broad lines are observed for short lived excited states

NMR Process

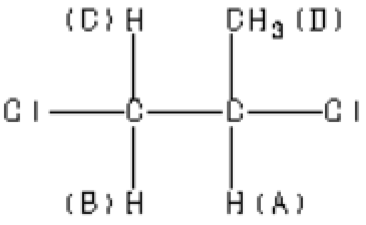
- If a proper frequency is introduced, it will resonate with the precessional frequency
- Due to resonance, the energy of the applied frequency can thus be absorbed by the nucleus
- The nucleus in general or the proton can be flipped from the low energy level to the high energy level
- At a given radiofrequency all protons in an organic molecule may give NMR signals at different applied field strength
- The number of signals tells us about the number of protons of each kind
- The splitting of a signal into several peaks tells us about the environment of a proton with respect to other nearby protons

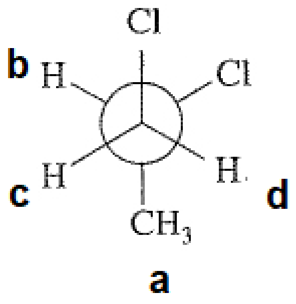
Number of Signals

- The set of protons with the same environment are said to be equivalent
- They absorb the same applied field strength
- Protons with different environment absorb at different applied field strength
- $CH_3 – CH_2 – Cl$ $\qquad$ $CH_3 – CHCl – CH_3$

  a $\quad$ b $\qquad\qquad$ a $\quad$ b $\quad$ a

- Ethyl chloride gives 2 signals and Isopropyl chloride gives 2 signals
- To be chemically equivalent, protons must also be stereochemically equivalent
- $CH_3 – CH_2 – CH_2 – Cl$ $\qquad$ For example: n-propyl chloride gives only
  a $\quad$ b $\quad$ c $\qquad$ 3 signals
- $CH_3 – CHCl – CH_2 – Cl$ $\qquad$ For example: 1,2-Dichloropropane must give only
  a $\quad$ b $\quad$ c $\qquad$ 3 signals but gives 4 signals (because stereochemically four different protons are present as shown in Newmann Projection formula. The environment of ‘c’ differs from ‘d’)





Position of Signals- Chemical Shift

- An isolated nuclei without influence of electrons is practically not possible. All nucleus are surrounded by electrons.
- When placed in a magnetic field the surrounding electron cloud tend to circulate in such a direction to produce a field opposing that applied field
- The exact resonance frequency depends on the nature of electron cloud surrounding the nucleus

- The total field experienced by the nucleus is
- $B_{effective} = B_{applied} - B_{induced}$
- Since Induced field is directly proportional to the applied field
- $B_{induced} = \sigma B_{applied}$
- Where σ is a constant called the shielding (σ is a measure of the ability of the electrons to alter B_0.
- $B_{effective} = B_0 (1 - \sigma)$
- Shielding varies from compound to compound and even within the individual compound.
- The resonance frequency of the nucleus therefore depends on its electronic environment, as well as on B_0 and Υ.

$$\boldsymbol{\upsilon} = \frac{\boldsymbol{\gamma}}{\mathbf{2}\boldsymbol{\pi}}\boldsymbol{B_o}(\mathbf{1} - \sigma)$$

$$\boldsymbol{\sigma} = \mathbf{1} - \left(\frac{\mathbf{2}\boldsymbol{\pi\upsilon}}{\boldsymbol{\gamma B_o}}\right)$$

- Nuclei are said to be shielded or screened by the surrounding electrons
- Variation of the resonance frequency with electronic structure has been termed the chemical shift

Chemical Shift

- The difference in the absorption position of a particular proton (nucleus) from the absorption position of a reference proton (nucleus) is called the Chemical Shift of the particular proton (nucleus)
- Generally used reference proton is TMS tetramethyl silane. It is chemically inert, magnetically isotropic, volatile and insoluble in most organic solvents. It gives a single sharp absorption peak and absorbs at a higher field than almost all organic protons

- If ν_0 is the frequency at which TMS absorbs and sample is the frequency at which the sample proton absorbs at a given magnetic field, the chemical shift of the sample proton is defined as

$$\delta_{sample} = \left(\frac{\upsilon_{sample} - \upsilon_{reference}}{\upsilon_{reference}}\right) \times 10^6$$

- Chemical shift can be expressed in terms of τ values
- T = 10 - δ
- δ increases from left to right. Tincreases from right to left
- The existence of the chemical shift is due to the screening effect of the electrons about the nucleus
- **TMS signal (Reference)**

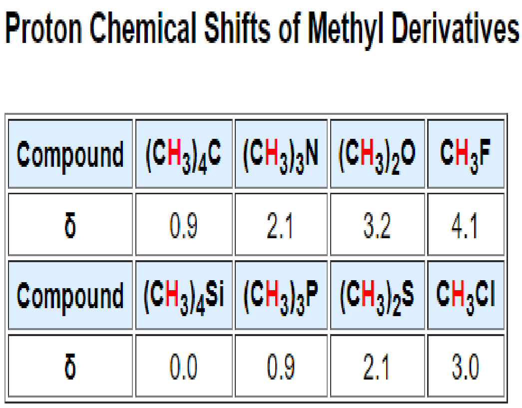
  NMR absorbances appear in a spectrum as a series of sharp spikes or peaks. Although there is no vertical scale on the spectrum, the relative height of each peak corresponds roughly to the strength of the absorption. The horizontal scale does not show proton resonances in simple wavelength units. Instead, the position of each peak is normally measured relative to the absorption of the protons in the compound tetramethylsilane, $(CH_3)_4Si$. Tetramethylsilane is an inert liquid added in small amounts to the compound being analyzed. All 12 of its hydrogen atoms absorb at the same position to give a single sharp peak, which is arbitrarily assigned a positional value of zero. This peak is then used as a reference point for all other peaks in the spectrum. The hydrogen atoms in the molecule being analyzed generally appear to the left of the reference peak because they absorb radiation of higher energy than the hydrogens of tetramethylsilane.

Deshielded and Shielded Protons

- When a molecule is placed in a magnetic field, its electrons circulate and due to this, induced magnetic field is generated
- This opposes the applied field and the actual magnetic field experienced on the proton is less than the applied field

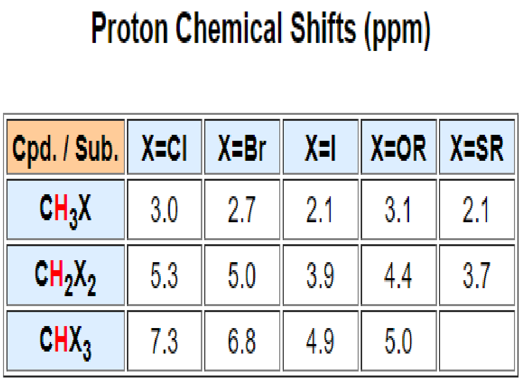
- The nucleus is shielded
- Circulation of electrons, specifically π electrons generates a field that can either oppose or reinforce depending on the location of the proton.
- If the induced field reinforces the applied field, the nucleus is said to be shielded
- Compared with naked proton, a shielded proton requires a higher applied field strength and a deshielded proton requires a lower field strength i.e, a shielded proton is found upfield whereas a deshielded proton is seen downfield.
- $R - CH_3 = 0.9\ \delta$
- $R_2CH_2 = 1.3\ \delta$
- $R_3CH = 1.5\ \delta$
- Aromatic protons appear far downfield (Ar – H = 6 to 8.5 δ)
- Attachment of chlorine to the carbon bearing protons causes a downfield shift
- Most proton chemical shift may be explained by two general effects
- 1. Electron withdrawing or donation by induction, resonance or hybridization alters the electron density at the resonating proton. Higher electron density results in an upfield shift, lower density in a downfield shift
- 2. Diamagnetic anisotropy influences the position of protons in the vicinity of nonspherical substituents and is largely responsible for proton shifts of aromatics, acetylenes, aldehydes, cyclopropane, etc

Table 2: Proton chemical shifts of Methyl derivatives



Proton Chemical Shifts of Methyl Derivatives

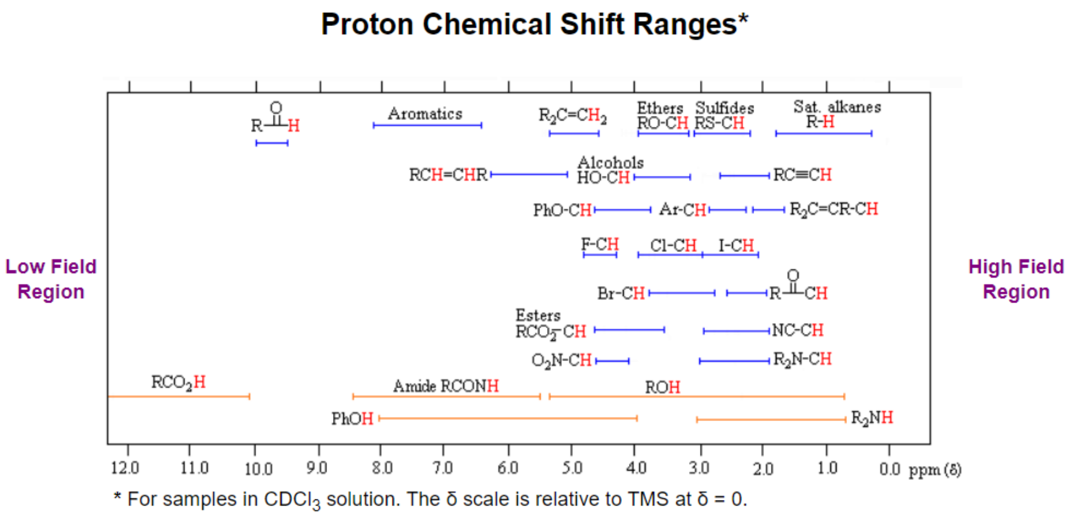
Compound	$(CH_3)_4C$	$(CH_3)_3N$	$(CH_3)_2O$	CH_3F
δ	0.9	2.1	3.2	4.1
Compound	$(CH_3)_4Si$	$(CH_3)_3P$	$(CH_3)_2S$	CH_3Cl
δ	0.0	0.9	2.1	3.0



Proton Chemical Shifts (ppm)

Cpd. / Sub.	X=Cl	X=Br	X=I	X=OR	X=SR
CH_3X	3.0	2.7	2.1	3.1	2.1
CH_2X_2	5.3	5.0	3.9	4.4	3.7
CHX_3	7.3	6.8	4.9	5.0	

Table 3: Proton chemical shift range of various organic compounds



Spin Spin splitting

- In the bromoethane example, the CH_3 peak is split into three distinct peaks, called a triplet.
- The CH_2 peak is split into four peaks, called a quartet.
- These multiple peaks are caused by nearby hydrogen atoms through a process termed *spin-spin splitting*.
- Each set of equivalent hydrogens on a given carbon is split into an n+1 multiplet by adjacent hydrogen atoms that are nonequivalent to the hydrogens of the given carbon.
- These splittings are generally observed for all nonequivalent hydrogens bonded to one or two adjoining carbon atoms.
- In the bromoethane spectrum, the CH_3 absorption appears as a triplet owing to the effects of the two hydrogens on the adjacent CH_2 group.
- Reciprocally, the CH_2 absorption is a quartet because of the effects of the three hydrogen atoms on the neighbouring CH_3 group.

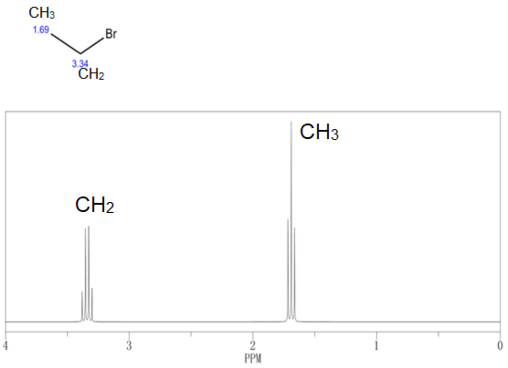


Figure 4: Spin-Spin splitting in ^{1}H-NMR spectrum of Bromoethane

Spin-spin coupling between spinning nuclei

The interaction between the spin magnetic moments of the different sets of H atoms in the molecule under study, is known as spin-spin coupling. It is imperative that a minimum of 2 sets of protons are present in adjacent positions. The magnetic spins of these resonating nuclei interact with each other and affect each other's precession frequencies. The effective magnetic field (B_{eff}) experienced by neighboring protons as a result of magnetic spins thereby affect the chemical shift values. In addition to the chemical shifts, the nature of the peaks in the NMR spectrum is also affected.

Peak splitting in NMR spectroscopy

A closer analysis of an NMR spectrum reveals that each signal on the graph represents one kind of proton present in the molecule. It is commonly observed that this signal is not always a single peak but has multiple peaks. This multiplicity of the signal is a very important determinant for the structure of the molecule. This phenomenon by which the spins of resonating protons cause the peaks on NMR spectrum to multiply is known as peak splitting. The splitting of NMR signal gives precise information about the number of neighboring protons in a molecule. There is a formula to calculate the multiplicity of the peaks in the NMR spectrum.

$2nI + 1$

n= Number of neighbouring protons

I= spin number of protons

Since I is always ½, we can rewrite the formula as n+1.

The other relevant information which comes along with knowing the number of peaks is the intensity of the peaks (which is seen as the height of the peaks). As a general rule, the height of the peaks or in other words, the relative intensities of the peaks can be determined by using Pascal's triangle.

Pascal's triangle

This is a number pattern invented by a famous French mathematician, Blaise Pascal. We can use the n+1 rule to determine the number of peaks. The height of the peaks, caused due to spin-spin coupling is in proportion to the values in the row (corresponding to the value n) in Pascal's triangle. If we look at the figure below and consider a quartet, we would observe that the peak of the extreme signals is 1/3rd of the first and the last peak.

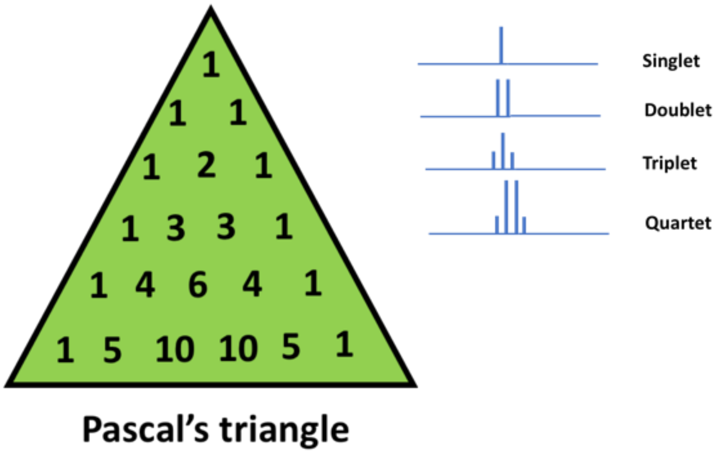


Figure 5: Pascal triangle for Intensity of peak signals in ^1H-NMR spectrum

With n=0 (or 0 neighboring protons), we get a single peak. This is depicted as 1 at the apex of the Pascal's triangle

Similarly, for n=1 (or 1 neighboring proton), we get a doublet (using the n+1 rule). This is written as 1 on either side of the second row in the Pascal's triangle

Moving on, for n=2 (or 2 neighboring protons), we get a triplet. In this case, the number 1 is written at the left and right of the triangle and the sum (1+1) is shown in the middle.

For n=3, we get a quartet. In this case, again 1 is written at the ends and the neighboring numbers are added. Therefore, we end up with the sequence 1 3 3 1

We can explain the rest of the Pascal's triangle in a similar way. This method of generating numbers is known as binomial expansion.

Let us try to understand peak splitting using the following molecule as an example;

CH_3CH_2Cl (Ethyl chloride)

Let us calculate the multiplicity for the hydrogen atoms.

There are 2 sets of hydrogen atoms in Ethyl Chloride and we should expect to get 2 peaks in the NMR spectrum. This, however, is not true when it comes to visualizing the actual spectrum. Each of the hydrogen atoms will influence the neighbours in an applied magnetic field and would lead to multiple peaks. To determine how many peaks we can get for hydrogen atoms in CH_2 or CH_3, we need to apply the above rule of multiplicity determination.

Let us look at the hydrogen atoms in CH_2 which are under the influence of 3 hydrogen atoms of the CH_3 group. Therefore,

$n=3$

$I=1/2$

After applying the formula,

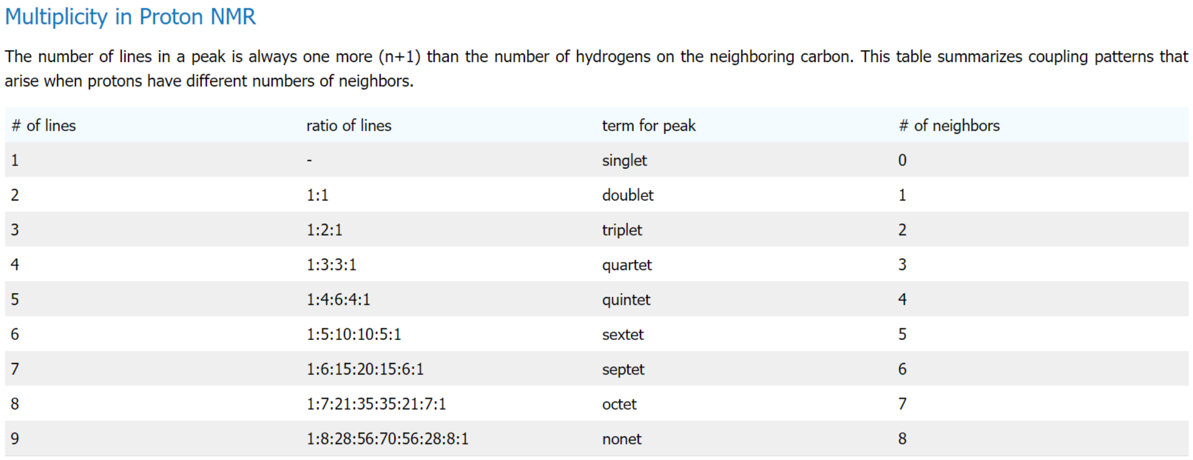
$2nI+1 = (2x3x1/2) + 1= 4$

Therefore, there will be 4 peaks for hydrogen atoms in CH_2

Similarly, there would be 3 peaks for hydrogen atoms in CH_3

The position of the split peaks on the chemical shift scale (also known as the delta value) would be further influenced by the presence of the electronegative atom (chloride) in close proximity to hydrogen atoms in CH_2

Table 4: Multiplicity in ^{1}H-NMR spectrum



Multiplicity in Proton NMR

The number of lines in a peak is always one more (n+1) than the number of hydrogens on the neighboring carbon. This table summarizes coupling patterns that arise when protons have different numbers of neighbors.

# of lines	ratio of lines	term for peak	# of neighbors
1	-	singlet	0
2	1:1	doublet	1
3	1:2:1	triplet	2
4	1:3:3:1	quartet	3
5	1:4:6:4:1	quintet	4
6	1:5:10:10:5:1	sextet	5
7	1:6:15:20:15:6:1	septet	6
8	1:7:21:35:35:21:7:1	octet	7
9	1:8:28:56:70:56:28:8:1	nonet	8

Proton counting

Two more features of NMR spectra are important aids to structure assignment. The first is the area of space enclosed by the absorption peaks. The area under the peaks is directly proportional to the number of hydrogen atoms contributing to the peak. NMR spectrometers have a feature, called integration, which, when selected by the user, calculates the area under each peak and plots the result as a line that is displaced vertically at a peak by an amount proportional to the area under the peak. The integration of the bromoethane spectrum, for example, shows that the absorption peaks around 1.6 ppm have an area that is 1.5 times greater than the area of the peaks at 3.3 ppm. This is consistent with, and supports, the assignment of the peaks to the CH_3 and CH_2 groups because the ratio of the area of the CH_3 peak to the CH_2 peak is expected to be 3:2, or 1.5:1, for the numbers of hydrogen atoms are in a 3:2 ratio.

The second additional feature is the pattern of the absorption peaks. In the bromoethane example, the CH_3 peak is split into three distinct peaks, called a triplet. The CH_2 peak is split into four peaks, called a quartet. These multiple peaks are caused by nearby hydrogen atoms through a process termed *spin-spin splitting*. Each set of equivalent hydrogens on a given carbon is split into an n+1 multiplet by adjacent hydrogen atoms that are nonequivalent to the hydrogens of the given carbon. These splittings are generally observed for all nonequivalent hydrogens bonded to the one or two adjoining carbon atoms. In the bromoethane spectrum, the CH_3 absorption appears as a triplet owing to the effects of the two hydrogens on the adjacent CH_2 group. Reciprocally, the CH_2 absorption is a quartet because of the effects of the three hydrogen atoms on the neighbouring CH_3 group.

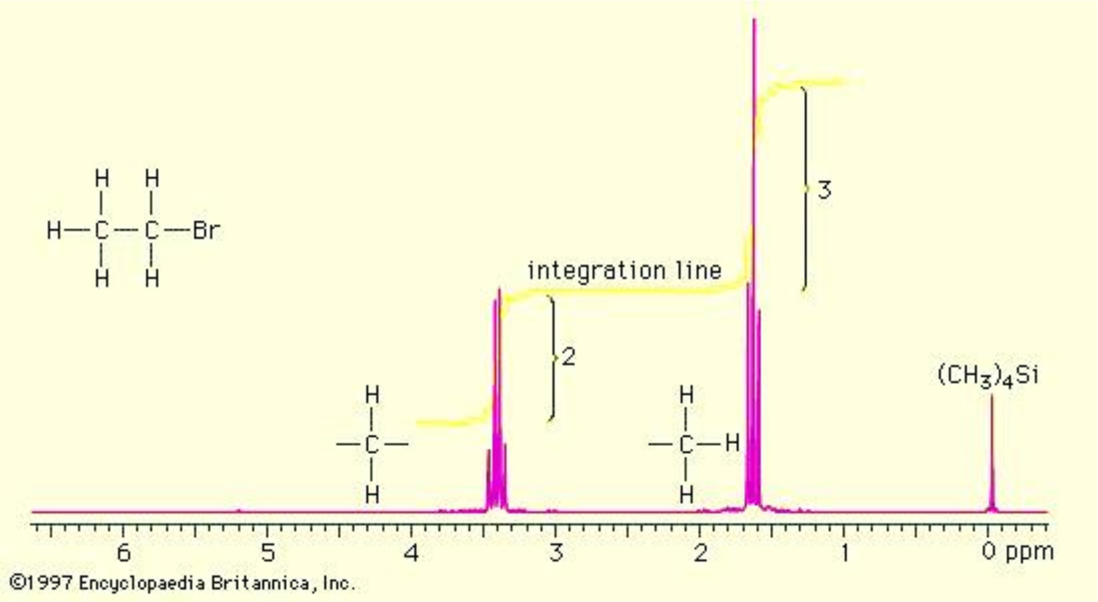


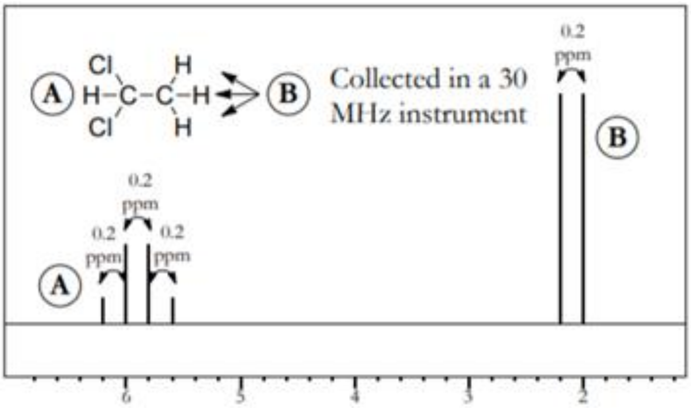
Figure 6: Integration line of 1H-NMR spectrum for Bromoethane

Coupling Constants and the Karplus Equation

When two protons couple to each other, they cause splitting of each other's peaks. The spacing between the peaks is the same for both protons, and is referred to as the coupling constant or J constant. This number is always given in hertz (Hz), and is determined by the following formula: J Hz = Δ ppm x instrument frequency

Δ ppm is the difference in ppm of two peaks for a given proton. The instrument frequency is determined by the strength of the magnet, and will always be 30 MHz for all spectra collected on the organic teaching lab NMR.

Figure 7, below shows the simulated NMR spectrum of 1,1-dichloroethane, collected in a 30 MHz instrument. This compound has coupling between A (the quartet at 6 ppm) and B (the doublet at 2 ppm).

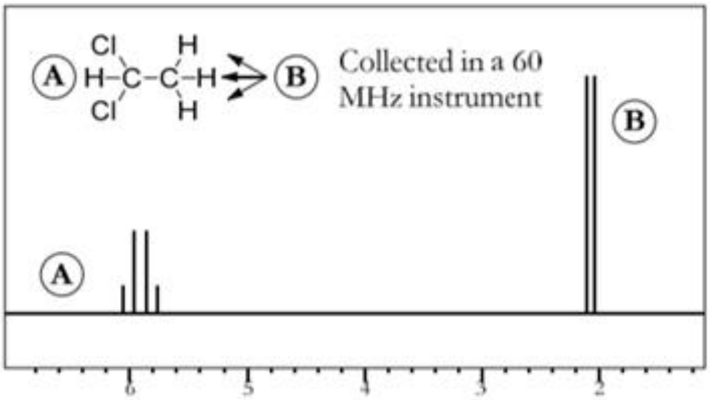


The NMR spectrum of 1,1-dichloroethane, collected in a 30 MHz instrument. For both A and B protons, the peaks are spaced by 0.2 ppm, equal to 6 Hz in this instrument.

Figure 7: Coupling constant determination of 1,1-dichloroethane in 30 MHz instrument

For both A and B, the distance between the peaks is equal. In this example, the spacing between the peaks is 0.2 ppm (for example, the peaks for A are at 6.2, 6.0, 5.8, and 5.6 ppm). This is equal to a J constant of (0.2 ppm x 30 MHz) = 6 Hz. Since the shifts are given in ppm or parts per million, you should divide by 10^6. But since the frequency is in megahertz instead of hertz, you should multiply by 10^6. These two factors cancel each other out, making calculations nice and simple.

Figure 8, below shows the NMR spectrum of the same compound, but this time collected in a 60 MHz instrument.



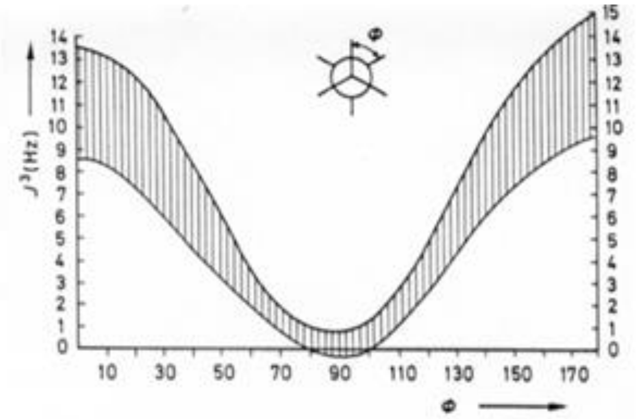
The NMR spectrum of 1,1-dichloroethane, collected in a 60 MHz instrument. For both A and B protons, the peaks are spaced by 0.1 ppm, equal to 6 Hz in this instrument.

Figure 8: Coupling constant determination of 1,1-dichloroethane in 60 MHz instrument

This time, the peak spacing is 0.1 ppm. This is equal to a J constant of (0.1 ppm x 60 MHz) = 6 Hz, the same as before. This shows that the J constant for any two particular protons will be the same value in hertz, no matter which instrument is used to measure it.

The Karplus equation

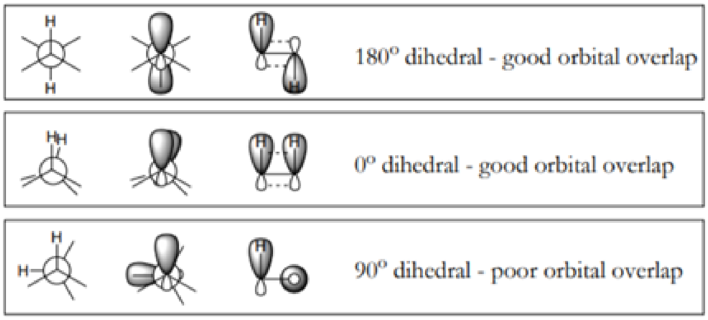
In molecules where the rotation of bonds is constrained (for instance, in double bonds or rings), the coupling constant can provide information about stereochemistry. The Karplus equation describes how the coupling constant between two protons is affected by the dihedral angle between them. The equation follows the general format of **$J = A + B (\cos \theta) + C (\cos 2\theta)$**, with the exact values of A, B and C dependent on several different factors. In general, though, a plot of this equation has the shape shown in Figure 9. Coupling constants will usually, but not always, fall into the shaded band on this graph.



The plot of dihedral angle vs. coupling constant described by the Karplus equation.

Figure 9: Karplus equation plot

The highest coupling constants will occur between protons that have a dihedral angle of either 0° or 180°, and the lowest coupling constants will occur at 90°. This is due to orbital overlap – when the orbitals are at 90°, there is very little overlap between them, so the hydrogens cannot affect each other's spins very much (Figure 10).



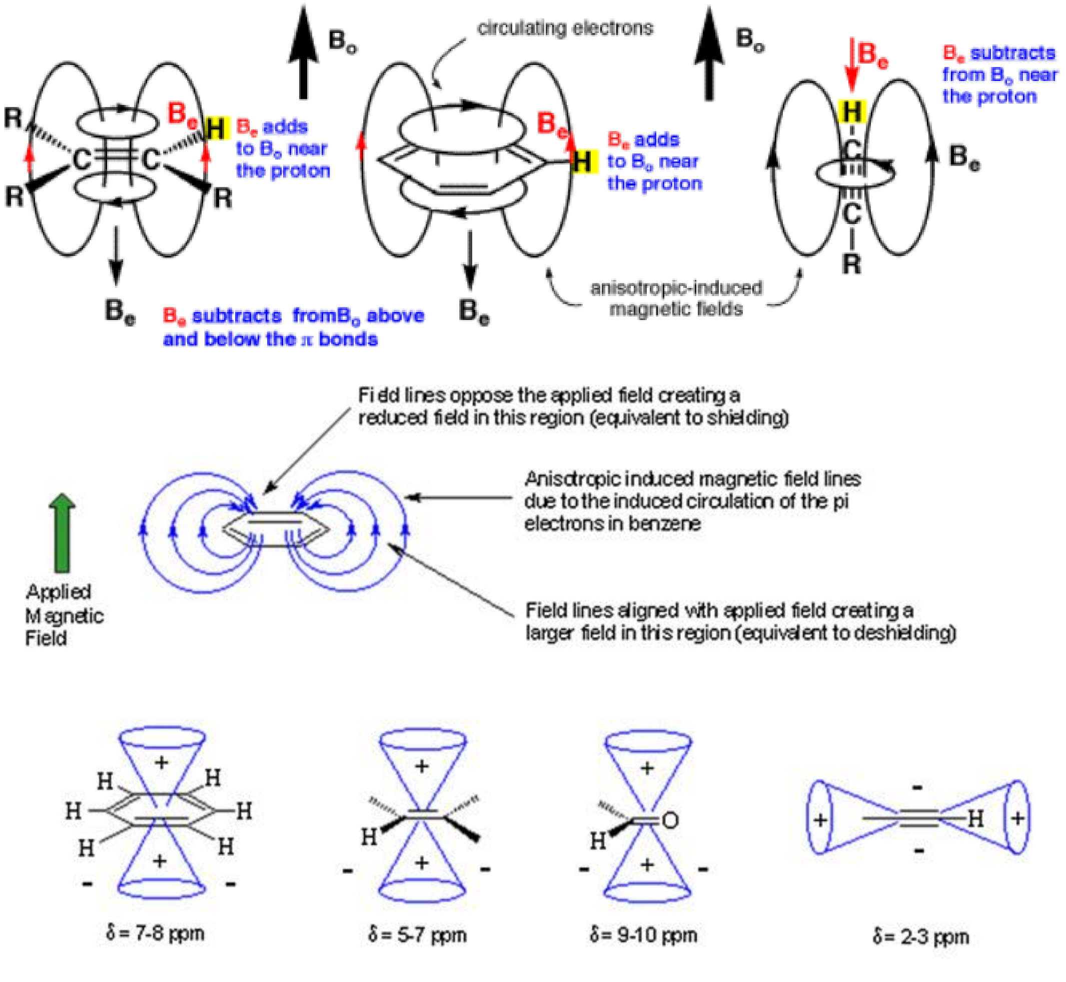
The best orbital overlap occurs at 180° or 0°, which is why the coupling constant is higher for those angles.

Figure 10: Good orbital overlap and poor orbital overlap for coupling constant

Anisotropy- π Electron Function

- The low field resonance of hydrogens bonded to double bond or aromatic ring carbons is puzzling, as is the very low field signal from aldehyde hydrogens.
- The hydrogen atom of a terminal alkyne, in contrast, appears at a relatively higher field.
- All these anomalous cases seem to involve hydrogens bonded to pi-electron systems, and an explanation may be found in the way these pi-electrons interact with the applied magnetic field.
- Pi-electrons are more polarizable than are sigma-bond electrons.
- The field induced pi-electron movement produces strong secondary fields that perturb nearby nuclei.
- The pi-electrons associated with a benzene ring provide a striking example of this phenomenon.
- The electron cloud above and below the plane of the ring circulates in reaction to the external field so as to generate an opposing field at the center of the ring and a supporting field at the edge of the ring.
- This kind of spatial variation is called anisotropy, and it is common to nonspherical distributions of electrons.
- Regions in which the induced field supports or adds to the external field are said to be deshielded, because a slightly weaker external field will bring about resonance for nuclei in such areas.
- However, regions in which the induced field opposes the external field are termed shielded because an increase in the applied field is needed for resonance.

- Shielded regions are designated by a plus sign, and deshielded regions by a negative sign.



Schematic diagram of shielding cones for common pi systems.
The + denotes shielding areas and - denotes deshielding areas.
Remember shielding lowers the chemical shift, δ and
deshielding increases δ. Typical H δ values are also shown.

Figure 11: Anisotropic systems showing induced magnetic field

2. ^{13}C-NMR Spectroscopy

Carbon-13 (C13) nuclear magnetic resonance (most commonly known as **carbon-13 NMR** or **^{13}C NMR** or sometimes simply referred to as **carbon NMR**) is the application of nuclear magnetic resonance (NMR) spectroscopy to carbon. It is analogous to proton NMR (^{1}H NMR) and allows the identification of carbon atoms in an organic molecule just as proton NMR identifies hydrogen atoms. As such ^{13}C NMR is an important tool in chemical structure elucidation in organic chemistry.

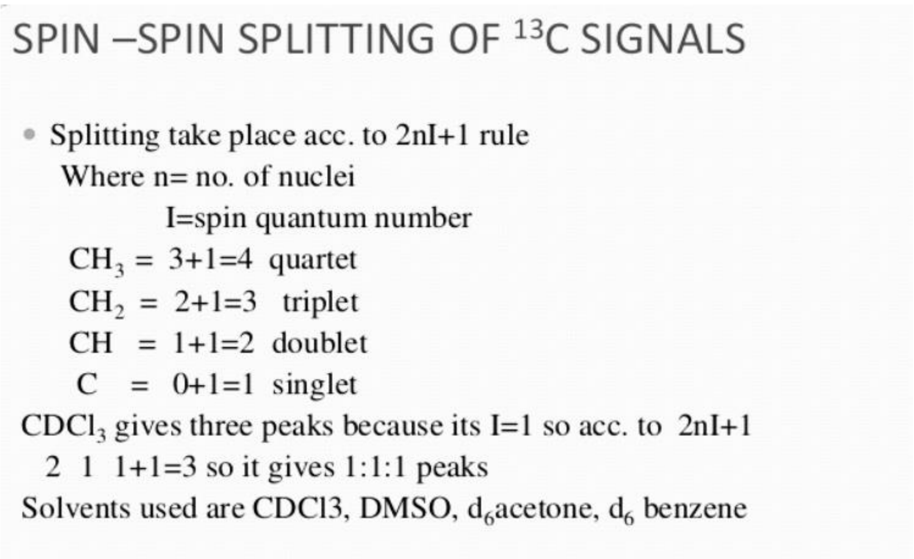
^{13}C NMR detects only the ^{13}C isotope of carbon, whose natural abundance is only 1.1%, because the main carbon isotope, ^{12}C, is not detectable by NMR since its nucleus has zero spin.

^{13}C chemical shifts follow the same principles as those of ^{1}H, although the typical range of chemical shifts is much larger than for ^{1}H (by a factor of about 20). The chemical shift reference standard for ^{13}C is the carbons in tetramethylsilane (TMS), whose chemical shift is considered to be 0.0 ppm.

Sensitivity

^{13}C NMR has a number of complications that are not encountered in proton NMR. ^{13}C NMR is much less sensitive to carbon than ^{1}H NMR is to hydrogen since the major isotope of carbon, the ^{12}C isotope, has a spin quantum number of zero and so is not magnetically active and therefore not detectable by NMR. Only the much less common ^{13}C isotope, present naturally at 1.1% natural abundance, is magnetically active with a spin quantum number of 1/2 (like ^{1}H) and therefore detectable by NMR. Therefore, only the few ^{13}C nuclei present resonate in the magnetic field, although this can be overcome by isotopic enrichment of e.g. protein samples. In addition, the gyromagnetic ratio ($6.728284\ 10^{7}$ rad T^{-1} s^{-1}) is only 1/4 that of ^{1}H, further reducing the sensitivity. The overall *receptivity* of ^{13}C is about 4 orders of magnitude lower than ^{1}H.

In a typical run on an organic compound, a ^{13}C NMR may require several hours to record the spectrum of a one-milligram sample, compared to 15–30 minutes for ^{1}H NMR, and that spectrum would be of lower quality. The nuclear dipole is weaker, the difference in energy between alpha and beta states is one-quarter that of proton NMR, and the Boltzmann population difference is correspondingly less.

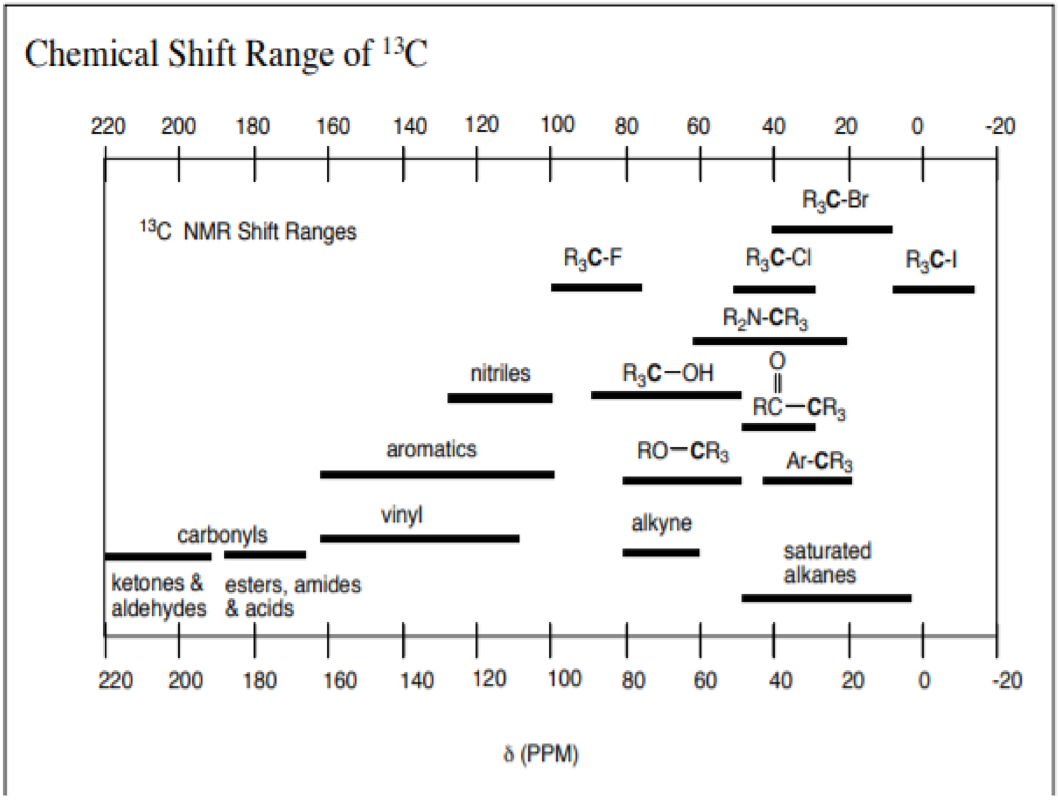


SPIN –SPIN SPLITTING OF ^{13}C SIGNALS

- Splitting take place acc. to 2nI+1 rule
  Where n= no. of nuclei
  I=spin quantum number
  CH_3 = 3+1=4 quartet
  CH_2 = 2+1=3 triplet
  CH = 1+1=2 doublet
  C = 0+1=1 singlet

$CDCl_3$ gives three peaks because its I=1 so acc. to 2nI+1
2 1 1+1=3 so it gives 1:1:1 peaks
Solvents used are CDCl3, DMSO, $d_6$acetone, d_6 benzene

Table 5: ^{13}C-NMR chemical shift range of various organic compounds



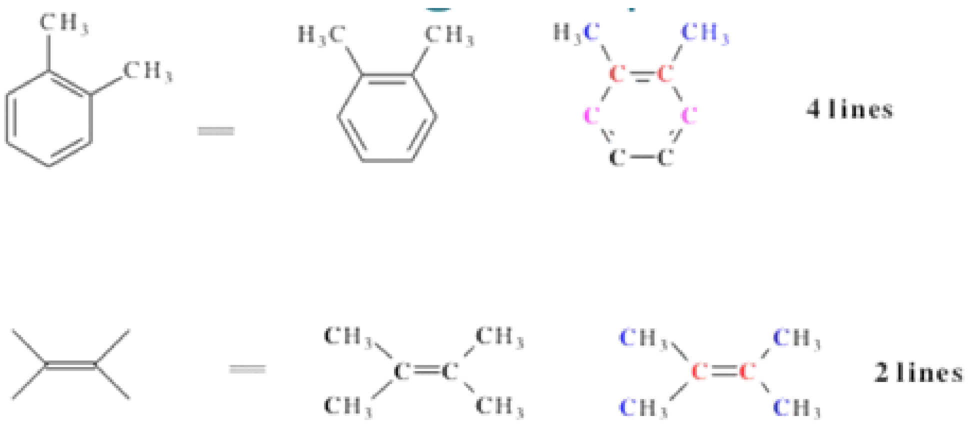


Figure 12: Predicting number of lines in ^{13}C spectra

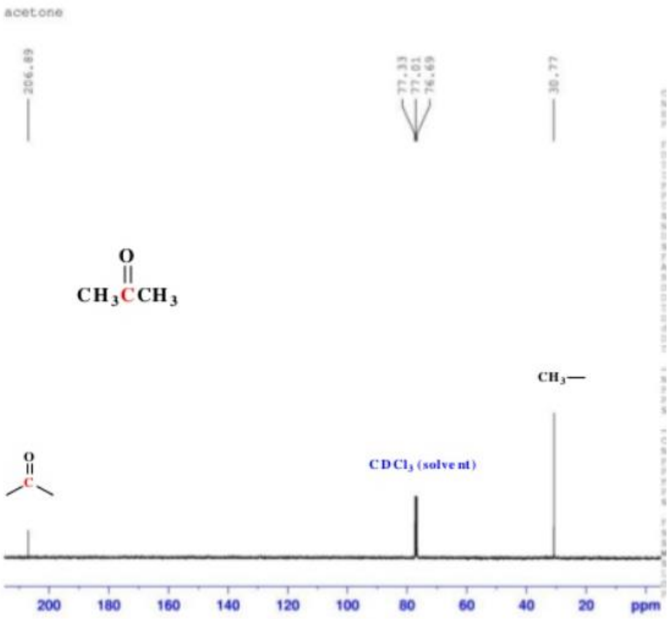


Figure 13: ^{13}C-NMR spectra of Acetone

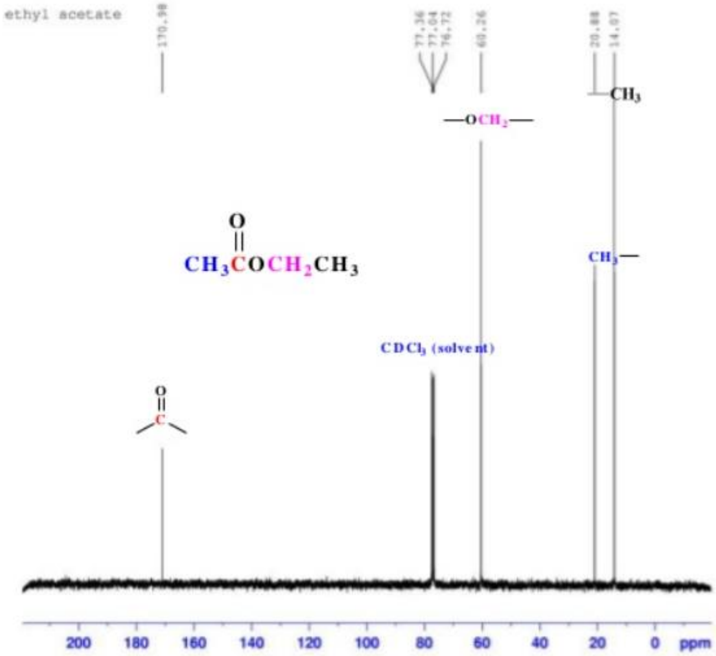


Figure 14: ^{13}C-NMR spectra of Ethyl acetate

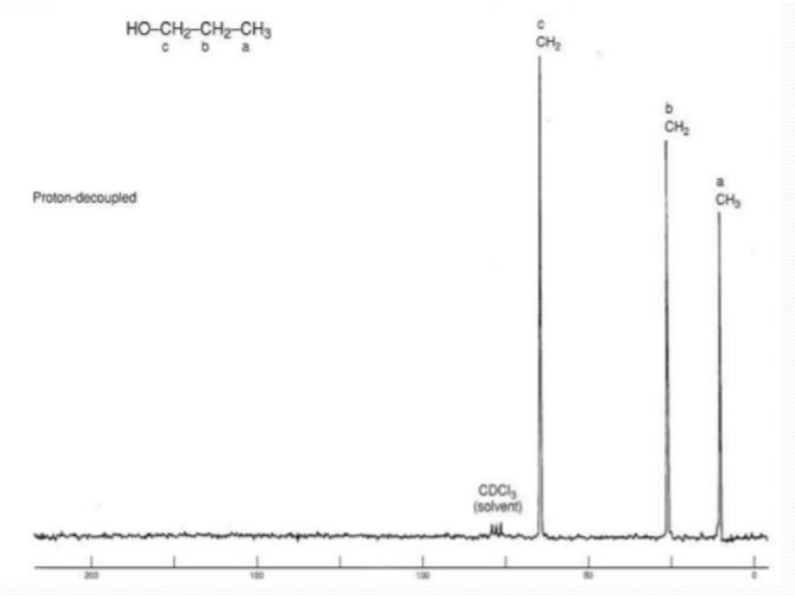


Figure 15: ^{13}C-NMR spectra of propanol

Coupling modes

Another potential complication results from the presence of large one bond J-coupling constants between carbon and hydrogen (typically from 100 to 250 Hz). In order to suppress these couplings, which would otherwise complicate the spectra and further reduce sensitivity, carbon NMR spectra are usually proton decoupled to remove the signal splitting. Couplings between carbons can be ignored due to the low natural abundance of ^{13}C. Hence in contrast to typical proton NMR spectra which show multiplets for each proton position, carbon NMR spectra show a single peak for each chemically non-equivalent carbon atom.

In further contrast to ^{1}H NMR, the intensities of the signals are not normally proportional to the number of equivalent ^{13}C atoms and are instead strongly dependent on the number of surrounding spins (typically ^{1}H). Spectra can be made more quantitative if necessary by allowing sufficient time for the nuclei to relax between repeat scans.

The most common modes of recording ^{13}C spectra are proton-noise decoupling (also known as noise, proton, or broadband decoupling), off-resonance decoupling, and gated decoupling. These modes are meant to address the large J values for ^{13}C - H (110–320 Hz), ^{13}C - C - H (5–60 Hz), and ^{13}C - C - C - H (5–25 Hz) which otherwise make completely proton coupled ^{13}C spectra difficult to interpret.

With proton-noise decoupling, in which most spectra are run, a noise decoupler strongly irradiates the sample with a broad (approximately 1000 Hz) range of radio frequencies covering the range (such as 100 MHz for a 23,486 gauss field) at which protons change their nuclear spin. The rapid changes in proton spin create an effective heteronuclear decoupling, increasing carbon signal strength on account of the nuclear Overhauser effect (NOE) and simplifying the spectrum so that each nonequivalent carbon produces a singlet peak. The relative intensities are unreliable because some carbons have a larger spin-lattice relaxation time and others have weaker NOE enhancement.

^{1}H NMR Vs ^{13}C NMR

- It is useful to compare and contrast H-NMR and C-NMR as there are certain differences and similarities:
- ^{13}C has only about 1.1% natural abundance (of carbon atoms)
- ^{12}C does not exhibit NMR behaviour (I=0)
- ^{13}C nucleus is also a spin 1/2 nucleus
- ^{13}C nucleus is about 400 times less sensitive than H nucleus to the NMR phenomena
- Due to the low abundance, we do not usually see ^{13}C-^{13}C coupling
- Chemical shift range is normally 0 to 220 ppm
- Chemical shifts are also measured with respect to tetramethylsilane, $(CH_3)_4Si$ (*i.e.* TMS)
- Similar factors affect the chemical shifts in ^{13}C as seen for H-NMR
- Long relaxation times (excited state to ground state) mean no integrations
- "Normal" ^{13}C spectra are "broadband, proton decoupled" so the peaks show as single lines
- Number of peaks indicates the number of types of C
- The general implications of these points are that ^{13}C-NMR spectra take longer to acquire than H-NMR, though they tend to look simpler. Accidental overlap of peaks is much less common than for H-NMR which makes it easier to determine how many

types of C are present. In comparison to ^{1}H NMR spectroscopy, ^{13}C NMR spectra are more easily interpreted and give following information:

- 1. The common range of energy absorption for ^{13}C is wide δ 0 – 200 relative to TMS, contrasted with δ 0-15 for ^{1}H NMR. Thus fewer peaks overlap in ^{13}C NMR spectra
- 2. Because only 1.1% of carbon in a compound is ^{13}C, ^{13}C- ^{13}C coupling is negligible and thus is not observed. Therefore, in one type of ^{13}C NMR Spectra(proton decoupled) each magnetically non equivalent carbon gives a single unsplit peak
- The presence of plane of symmetry in an organic molecule may render some carbons chemically equivalent to others. This may lead to discrepancy between the apparent number of peaks and the actual number of carbon atoms present in the molecule
- 3. The area under the peaks in ^{13}C NMR Spectra are not necessarily proportional to the number of carbons giving rise to the signals.
- 4. The proton coupled spectra, the signal for each carbon (or a group of magnetically equivalent carbons) is split by the protons bonded directly to that carbon and n+1 rule is followed.[3]
- Carbon -13 NMR spectroscopy is similar to proton NMR in that the no. of the peaks in the spectrum normally corresponds to the number of different carbon enviornments and the chemical shifts of carbon signals provide some indication of nature of each enviornment.
- Carbon -13 NMR differs from proton NMR in that integration is normally
- There are *three* short-comings of 13C-NMR spectra, namely :
- (1) Only 1% of the carbon in the molecule is carbon-13,
- (2) Sensitivity is consequently low, and
- (3) Recording the NMR-spectra is a tedious and time consuming process. However, with the advent of recent developments in NMR-spectroscopy it is quite possible to eliminate some of these short comings adequately. They are :
- (*a*) Development of powerful magnets (‘supercon’ magnets) has ultimately resulted in relatively stronger NMR-signals from the same number of atoms,

- (*b*) Improved hardware in NMR-spectroscopy has gainfully accomplished higher sensitivity, and
- (*c*) Development of more sensitive strategies has made it possible to record these C—H correlation spectra in a much easier manner.[8]
- Whereas carbon-carbon signal splitting does not occur in ^{13}C NMR spectra, hydrogen atoms attached to carbon can split ^{13}C NMR signals into multiplet peaks. However it is useful to simplify the appearance of ^{13}C NMR spectra by initially eliminating signal splitting for ^{1}H -^{13}C coupling. This can be done by choosing instrumental parameters that decouple the proton-carbon interactions and such a spectra is said to be broadband (BB) proton decoupled, thus in a broadband proton decoupled ^{13}C NMR spectrum each carbon atom in a unique environment gives a signal consisting of only one peak. Most ^{13}C NMR spectra are obtained in the simplified broadband mode first and then in modes that provide information from the ^{1}H-^{13}C couplings.

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT-4 – Mass Spectrometry – SCYA7301

1. Introduction

Organic chemists use mass spectrometry in three principal ways:

- To measure relative molecular masses (molecular weights) with very high accuracy
    - from which exact molecular formulae can be deduced
- To detect within a molecule the places at which it prefers to fragment
    - from this the presence of recognizable groupings within the molecule can be deduced
- As a method for identifying analytes by comparison of their mass spectra with libraries of digitized mass spectra of known compounds

2. Basic Principle of Mass Spectra

- In the simplest mass spectrometer, organic molecules are bombarded with electrons and converted to highly energetic positively charged ions (molecular ions or parent ions)
- This molecular ion, can break up into smaller ions (fragment ions, or daughter ions)
- The loss of an electron from a molecule leads to a radical cation, and we can represent this process as

$$\mathrm{M} \rightarrow \mathrm{M}^{+\cdot}$$

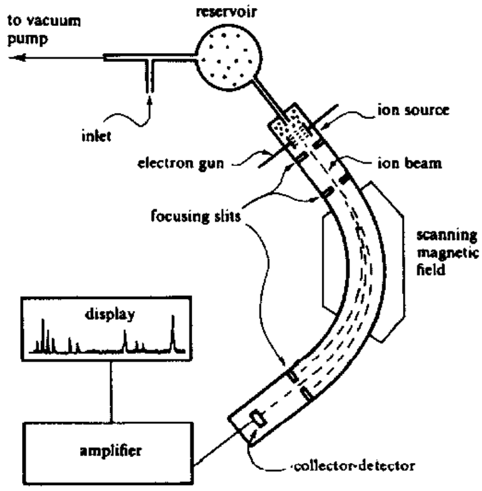
- The molecular ion $\mathrm{M}^{+\cdot}$ commonly decomposes to a pair of fragments, which may be either a radical plus an ion, or a small molecule plus a radical cation. Thus

$$\mathrm{M}^{+\cdot} \rightarrow \mathrm{m}_1^{+} + \mathrm{m}_2^{\cdot} \quad \text{or} \quad \mathrm{m}_1^{+\cdot} + \mathrm{m}_2$$

- The molecular ions, the fragment ions and the fragment radical ions are separated by deflection in a variable magnetic field according to their mass and charge
- This generate a current (the ion current) at the collector in proportion to their relative abundances.

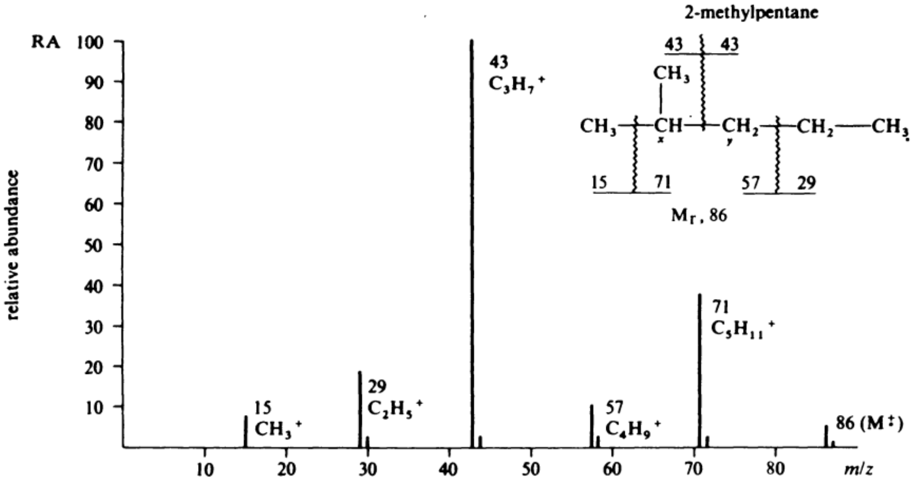
3. Representation of Mass spectrum

- A mass spectrum is a plot of relative abundance against the ratio mass/charge (the m/z value).
- For singly charged ions, the lower the mass the more easily is the ion deflected in the magnetic field.
- Doubly charged ions are occasionally formed: these are deflected twice as much as singly charged ions of the same mass
- They appear in the mass spectrum at the same value as the singly charged ions of half the mass, since $2m/2z = m/z$.
- Neutral particles produced in the fragmentation, whether uncharged molecules (m_2) or radicals ($m_2^{\cdot}$), cannot be detected directly in the mass spectrometer.



A simple mass spectrometer. Molecules drift from the reservoir into the ion source, where they are ionized by electron bombardment. The resulting ion beam consists of molecular ions, fragment ions and neutral fragments; the ions are deflected by the magnetic field onto the collector-detector.

Figure 1: A Simple Mass Spectrometer



Simplified mass spectrum of 2-methylpentane showing how the chain can break in several places; but breaks occur preferentially at the branching point, the most abundant ion being m/z 43 ($C_3H_7^+$).

Figure 2: A simplified line-diagram representation of the mass spectrum of 2-methylpentane (C_6H_{14})

- The most abundant ion has m/z value of 43 (corresponding to $C_3H_7^+$), showing that the most favored point of rupture occurs between C_x and C_y
  - This most abundant ion (the base peak) is given an arbitrary abundance of 100, and all other intensities are expressed as a percentage of this (relative abundances).
- The small peak at m/z 86 is obviously the molecular ion.
- The peaks at m/z 15, 29 and 71 correspond to CH_3^+, $C_2H_5^+$ and $C_5H_{11}^+$, respectively, etc.

  - The fragment ions arise from the rupture of the molecular ion, either directly or indirectly, and the analysis of many thousands of organic mass spectra has led to comprehensive semiempirical rules about the preferred fragmentation modes of every kind of organic molecule.

- The mass spectrum of a compound can be obtained on a smaller sample size (in extremis down to 10^{-12} g) than for any other of the main spectroscopic techniques

- Mass spectrometry is unlike the other spectroscopic techniques does not measure the interaction of molecules with the spectrum of energies found in the electromagnetic spectrum

- The principal disadvantages
  - The destructive nature of the process, which precludes recovery of the sample
  - The difficulty of introducing small sample into the high-vacuum system
  - Needed to handle the ionic species involved
  - The high cost of the instrument.

4. The Molecular Ion

- **Structure of the Molecular Ion**

- Organic molecules react on electron bombardment in two ways: either an electron is captured by the molecule, giving a radical anion, or an electron is removed from the molecule, giving a radical cation:

- $M \xrightarrow{e} M^{-\cdot}$ or $M \xrightarrow{-e} M^{+\cdot} + 2e$

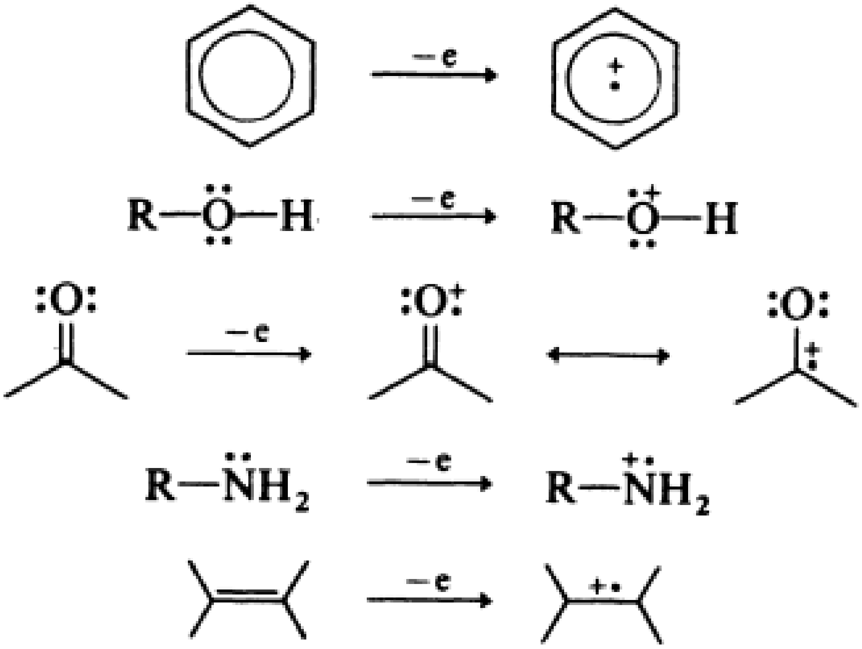
- The molecular ion represented as $M^{+\cdot}$ is a radical cation produced when a neutral molecule loses an electron

- For electron bombardment around their ionization potentials, it is possible to say which are the likeliest orbitals to lose an electron in organic molecules.

- The highest occupied orbitals of aromatic systems and nonbonding orbitals on oxygen and nitrogen atoms readily lose an electron; the π electrons of double and triple bonds are also vulnerable.

- The molecular ion is frequently written in square brackets (for example, [C5H5]$^{+\cdot}$ or [C4H7]$^{+\cdot}$

Examples of Molecular ion



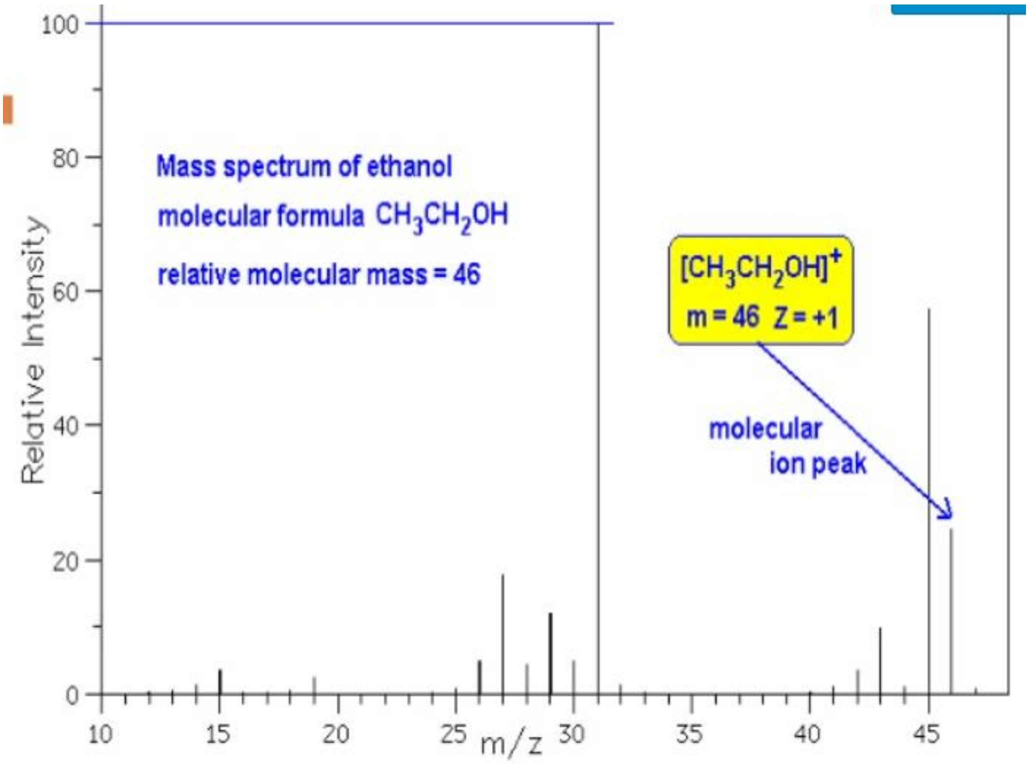


Figure 3: Molecular ion peak in Mass spectrum

5. Types of Ions in Mass Spectra

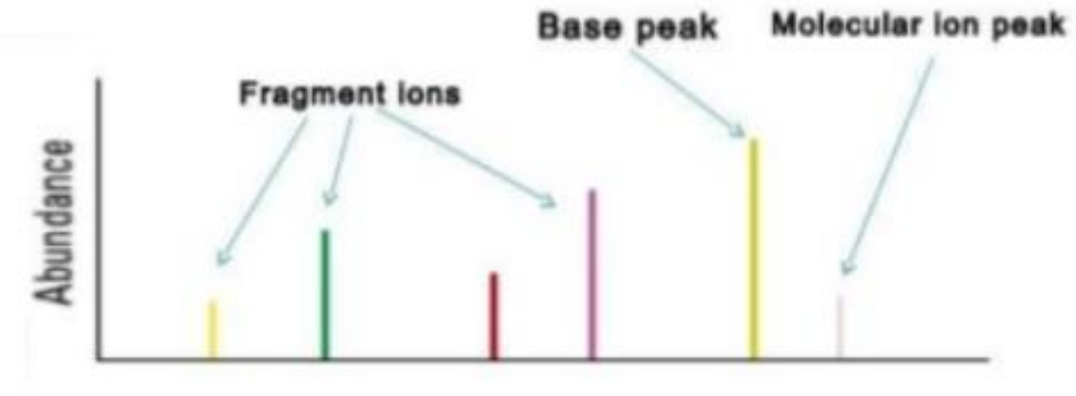


Figure 4: Various types of ions in Mass Spectra

Recognition of the Molecular Ion

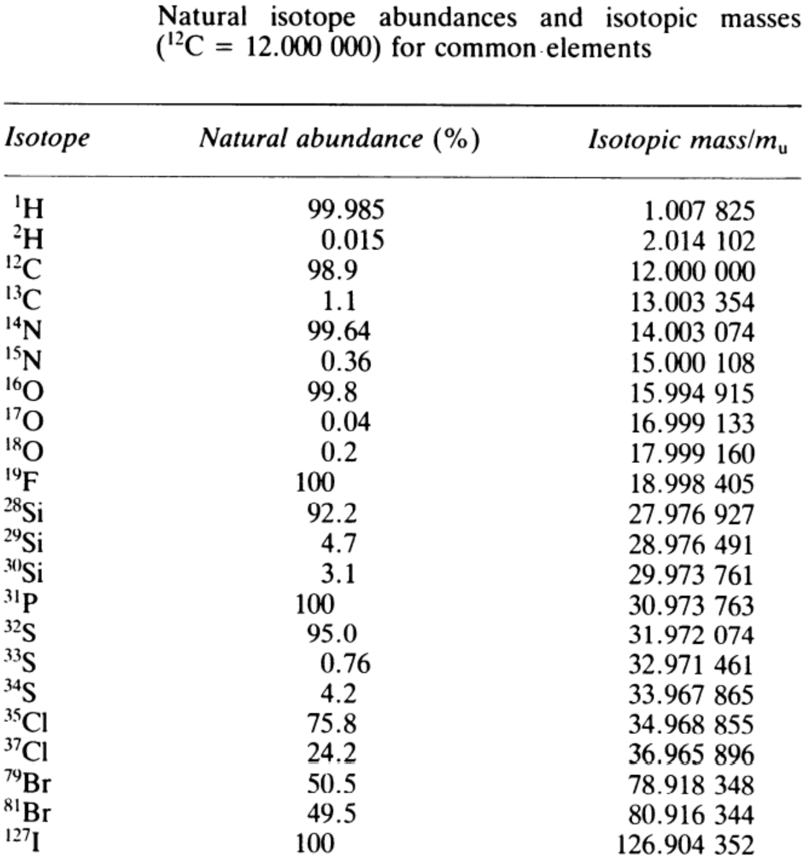
- The molecular ions of roughly 20 per cent of organic compounds decompose so rapidly $< 10^{-5}$ s) that they may be very weak or undetected in a routine 70 eV spectrum.
- For most unknown compounds, the ion cluster appearing at highest m/z value is likely to represent the molecular ion with its attendant M + 1 peaks, etc.,
- Abundant molecular ions are given by aryl amines, nitriles, fluorides and chlorides.
- Aromatic hydrocarbons & heteroaromatic compounds give strong $\mathbf{M}^{+\cdot}$ peaks provided that no side-chain of C_2 or longer is present
  - The $\mathbf{M}^{+\cdot}$ peak is often the base peak (Most Abundant ions)
  - Doubly charged ions may often be observed in the mass spectra of these compounds appearing at m/2z values
- Aryl bromides and iodides lose halogen too readily to give strong molecular ion peaks.
- Absence of molecular ions (or an extremely weak $\mathbf{M}^{+\cdot}$ peak) is characteristic of highly branched molecules whatever the functional class.
- Alcohols and molecules with long alkyl chains also fragment easily and lead to very weak $\mathbf{M}^{+\cdot}$ peaks.
- Isotope abundances should correlate with the appearance of the molecular-ion cluster. The intensities of M + 1, M + 2 peaks, etc., are obviously most easily measured and of greatest value when the $\mathbf{M}^{+\cdot}$ peak is fairly abundant
- Common fragment ions in the spectrum contribute positive support for the assignment of $\mathbf{M}^{+\cdot}$
- Unusual fragment ions should make one suspicious: for example, molecular ions can give rise to a series of weaker ions at M - 1, M - 2 and M - 3 due to successive loss of hydrogen, but a specific fragmentation leading directly to M - 3 (or M - 4 or M - 5) is never observed.

6. Effect of Isotopes on Mass Spectra

Isotope Abundances

- Few elements are monoisotopic
- **Monoisotopic mass** is the sum of the masses of the atoms in a molecule using the most abundant isotope for each element
- **Monoisotopic element** is one of the 26 chemical elements which have only one stable isotope
- Ions containing different isotopes appear at different m/z values.
- For an ion containing n carbon atoms, there is a probability that approximately 1.1 % of these atoms will be ^{13}C
- This will give rise to an ion of mass one higher than the ion that contains only ^{12}C atoms.
- The molecular ion for 2-methylpentane has an associated M + 1 ion, whose intensity is approximately 6.6 per cent of that of the molecular ion (molecular ion has only ^{12}C atoms, the M + 1 ion contains ^{13}C atoms)

Table 1: Natural Abundance and isotopic masses for common elements



Natural isotope abundances and isotopic masses (^{12}C = 12.000 000) for common elements

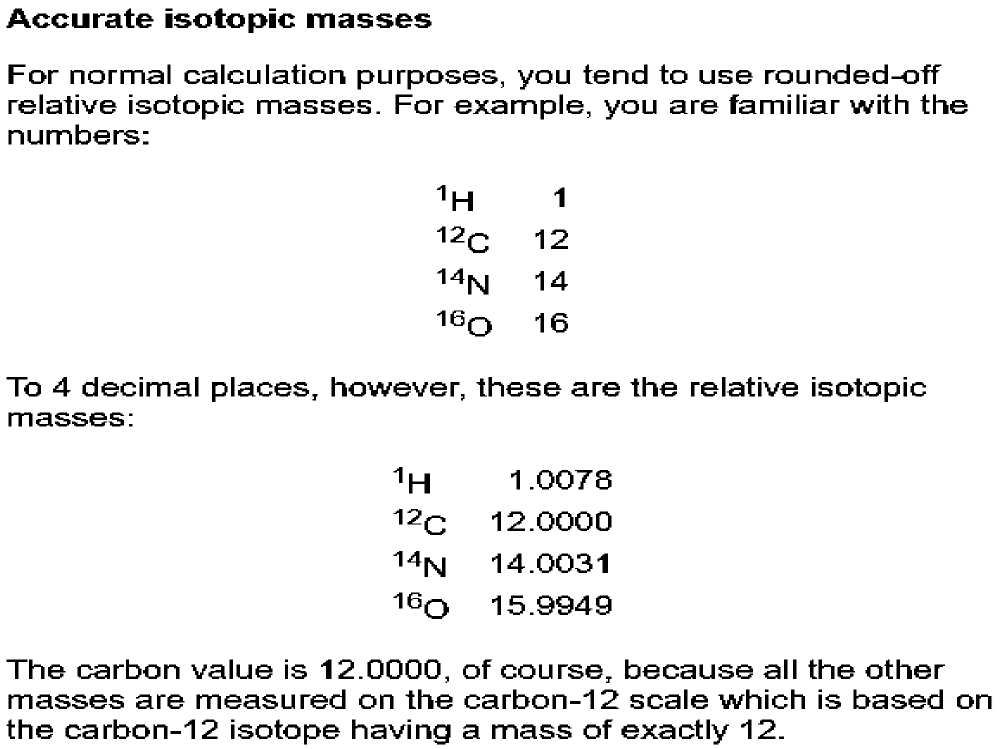
Isotope	*Natural abundance* (%)	*Isotopic mass*/m_u
^{1}H	99.985	1.007 825
^{2}H	0.015	2.014 102
^{12}C	98.9	12.000 000
^{13}C	1.1	13.003 354
^{14}N	99.64	14.003 074
^{15}N	0.36	15.000 108
^{16}O	99.8	15.994 915
^{17}O	0.04	16.999 133
^{18}O	0.2	17.999 160
^{19}F	100	18.998 405
^{28}Si	92.2	27.976 927
^{29}Si	4.7	28.976 491
^{30}Si	3.1	29.973 761
^{31}P	100	30.973 763
^{32}S	95.0	31.972 074
^{33}S	0.76	32.971 461
^{34}S	4.2	33.967 865
^{35}Cl	75.8	34.968 855
^{37}Cl	24.2	36.965 896
^{79}Br	50.5	78.918 348
^{81}Br	49.5	80.916 344
^{127}I	100	126.904 352

- A second associated peak can arise at m/z is M + 2 if two ^{13}C atoms are present in the same ion (or if two ^{2}H atoms, or one ^{13}C and one ^{2}H, are present)
- The probabilities can be calculated and may be helpful in deciding the formula for an ion in the absence of exact mass measurement.
- For example, the two ions $C_8H_{12}N_3^+$ and $C_9H_{10}O_2^+$ have the same unit mass (m/z 150), and the M + 1 relative abundances are similar (9.98 per cent and 9.96 percent respectively)
- However, the M + 2 abundances are sufficiently different to enable differentiation of the structures (0.45 per cent and 0.84 per cent, respectively).
- The ability to see M + 2 peaks of such low abundance depends on there being a large $\mathbf{M}^{+\cdot}$ peak.

7. Determination of Molecular Formula

- For an unknown organic compound, the ability to measure its relative molecular mass (molecular weight) to within four decimal places leads immediately to an accurate molecular formula for the compound.
- In the mass spectrum of an organic molecule, each peak corresponds to an ion of a particular isotopic composition, and its m/z value is calculated from the isotopic masses and not from the relative atomic masses of the elements.
- Similarly, in calculating the molecular formula from the molecular ion, we must be sure that we know which isotopes are present in that ion.
- In the case of compounds containing only C, Hand 0, we can easily identify the ^{13}C isotope peak and ^{2}H and $^{17}0$ are at extremely low abundance; the main peak in the molecular ion cluster then corresponds solely to a combination of ^{12}C, ^{1}H and $^{16}0$.
- As an example, consider an unknown compound X whose relative molecular mass (to the nearest integer) is measured at low resolution to be 100.
- From this and other evidence the compound could be either (A) $C_6H_{12}0$ or (B) $C_4H_40_3$
- High-resolution mass measurement of the molecular ion gives m/z 100.08871, proving that the correct structure is A.

Table 2: Accurate Isotopic Masses of Common elements for Calculation purpose



Accurate isotopic masses

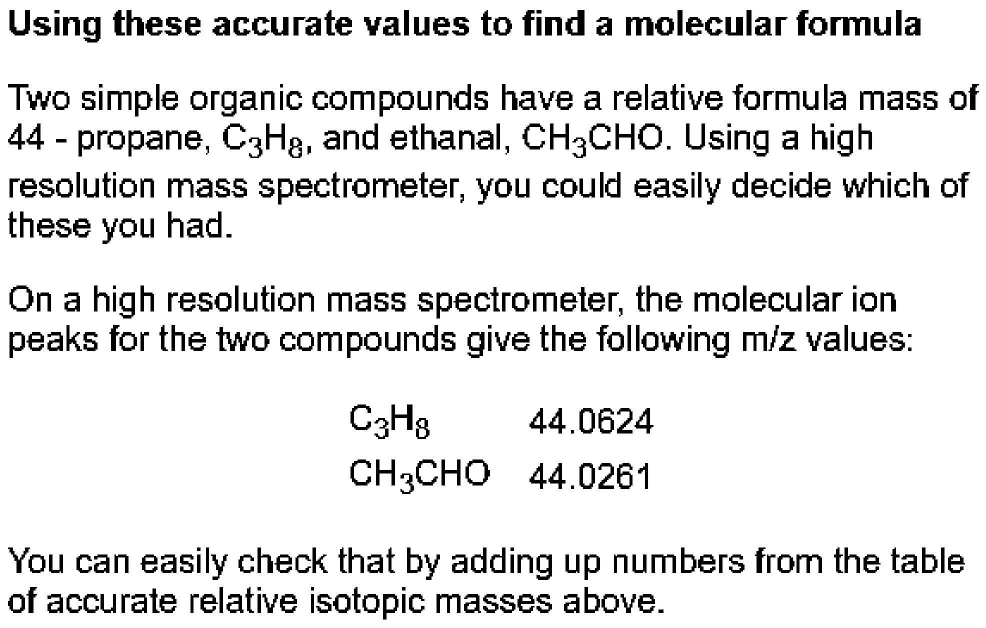
For normal calculation purposes, you tend to use rounded-off relative isotopic masses. For example, you are familiar with the numbers:

^{1}H	1
^{12}C	12
^{14}N	14
^{16}O	16

To 4 decimal places, however, these are the relative isotopic masses:

^{1}H	1.0078
^{12}C	12.0000
^{14}N	14.0031
^{16}O	15.9949

The carbon value is 12.0000, of course, because all the other masses are measured on the carbon-12 scale which is based on the carbon-12 isotope having a mass of exactly 12.



Using these accurate values to find a molecular formula

Two simple organic compounds have a relative formula mass of 44 - propane, C_3H_8, and ethanal, CH_3CHO. Using a high resolution mass spectrometer, you could easily decide which of these you had.

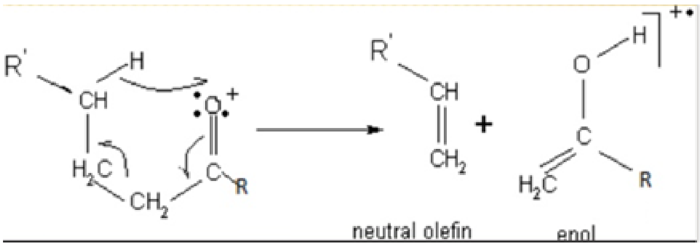
On a high resolution mass spectrometer, the molecular ion peaks for the two compounds give the following m/z values:

C_3H_8	44.0624
CH_3CHO	44.0261

You can easily check that by adding up numbers from the table of accurate relative isotopic masses above.

8. McLafferty Rearrangement

- Fragmentation due to rearrangement of molecular or parent Ion: Here cleavage of Bond in molecular ion is due to the intramolecular atomic rearrangement
- This leads to fragmentation whose origin cannot be described by simple cleavage of bonds
- When fragments are accompanied by bond formation as well as bond for breaking, a rearrangement process is said to have occurred
- Such rearrangement involves the transfer of hydrogen from one part of molecular Ion to another via preferably a 6 member cyclic transition state
- This process is favoured energetically because as many bonds are formed as are broken
- Compound containing hydrogen atom at position gamma to carbonyl group have been found to a relative intense peak
- This is probably due to rearrangement and fragmentation and is accompanied by the loss of neutral molecule. This rearrangement is known as Mclafferty rearrangement
- The rearrangement results in the formation of charged in all and a neutral olefin
- To undergo Mclafferty rearrangement, the molecules must poses
    - An appropriately located heteroatom (example oxygen)
    - A double bond
    - An abstractable hydrogen atom which is Gamma to C = O system



- **Aldehydes**
- The molecular Ion peak of aliphatic aldehydes is weak
- Aromatic aldehyde show moderate intense peak
- Characteristic feature of aldehyde especially aromatic aldehyde is loss of Alpha (α) hydrogen
- Second common feature of aliphatic aldehyde is beta (β) cleavage
- For example, aldehyde with CH_2CHO end-group gives rise to characteristic M -43 peaks

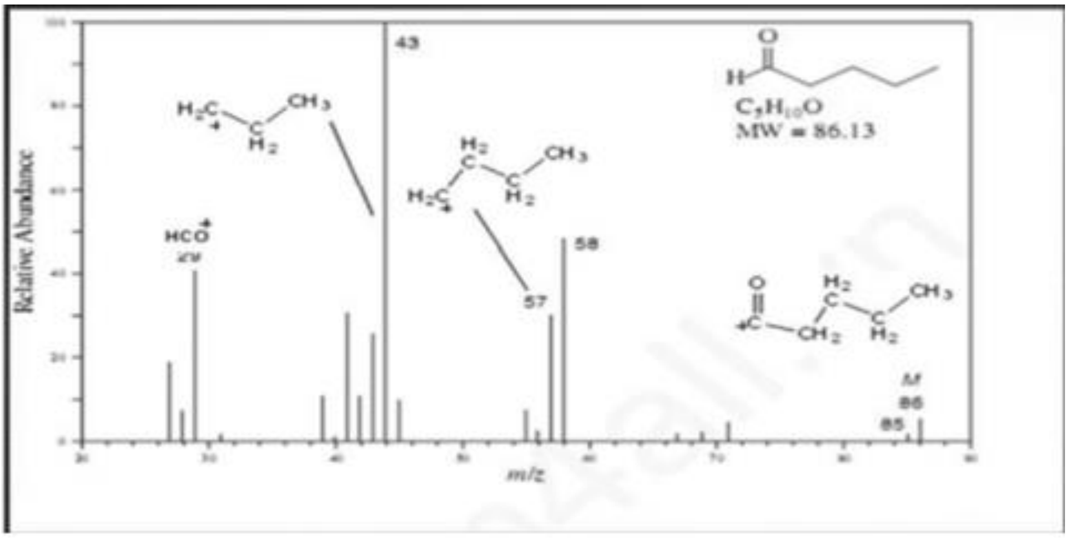


Figure 5: Mass Spectra of Valeraldehyde

- **Ketones**
- The molecular Ion peak are more intense than aldehyde
- Most of the abundant I on in the mass spectra of ketones can be accounted by Alpha cleavage and McLafferty rearrangement
- Strong molecular Ion peak
- Formation of acylium ion ($RC{\equiv}O^+$)

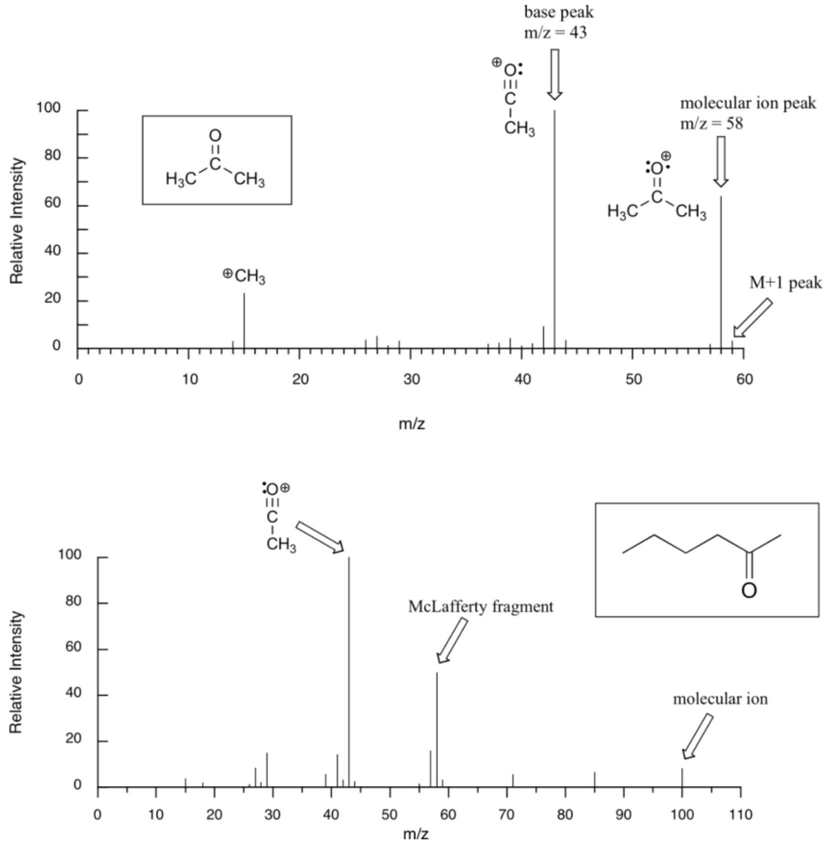
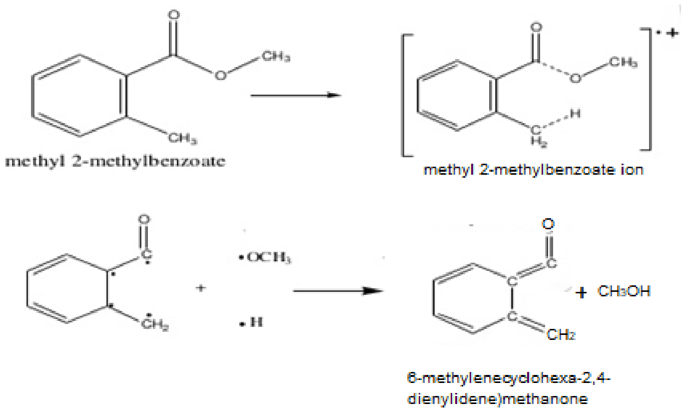
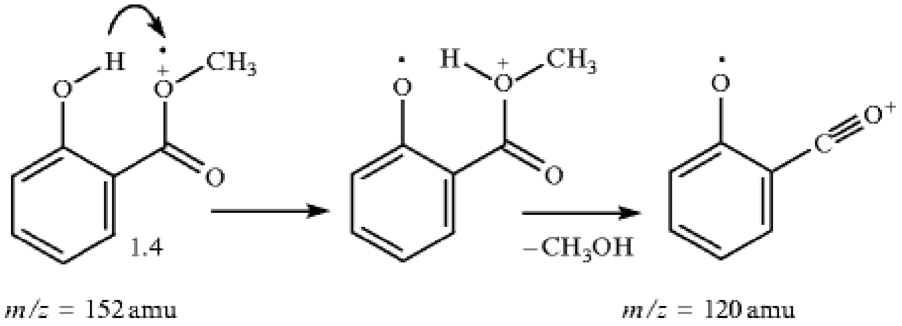


Figure 6: Mass Spectra of Acetone and Methyl butyl Ketone

9. Ortho effect

In the case of substituted aromatic compounds the substitute and carbon come into proximity (if present in ortho position) has help in elimination of neutral molecule. This effect is called Ortho effect.





10. Metastable Ions

The Nature of Metastable Ions

- In mass spectrum the broad peaks at non-integer masses m/z 60.2 and m/z 43.4 – Metastable peaks
- The ions producing these peaks are termed metastable ions :
  - They have lower kinetic energy than have normal ions,
  - They are formed from fragmentations that take place during the flight down the ion tube rather than in the ionization chamber.
- The exact position where they are formed in the tube determines whether or not we can easily observe them.
- Depending on the inherent stability of an ion, and on the amount of excitation energy absorbed on bombardment, ion lifetimes will vary
- Suppose a large number of molecules of M are converted to molecular ions $M^{+\cdot}$ not all of the ions will possess the same excitation energy and therefore some will have longer lifetimes than others

- The $M^{+\cdot}$ ions with shortest lifetimes may decompose in the ionization chamber to stable daughter ions A^+ and radicals $B^{\cdot}$ (the daughter ions A^+ will be detected at the collector normally).
- The molecular ions that leave the ion source intact will be accelerated by the accelerator voltage and will then possess a translational energy eV.
- Some of these $M^{+\cdot}$ ions may survive intact to the collector and be detected normally.
- If, however, others of these $M^{+\cdot}$ ions decompose to A^+ and $B^{\cdot}$ immediately after acceleration, the translational energy of the parent $M^{+\cdot}$ will be shared between A^+ and $B^{\cdot}$ which is in proportion to their masses (principle of conservation of momentum).
- The translational energy of the daughter ion A^+ must then be lower than that of the parent ion , and will arrive at the collector differently from the 'normal' A^+ ion produced in the ion source.
- The ion A^+ with 'abnormal' translational energy is a metastable ion.
- Note that metastable A^+ ions have the same mass as normal A^+ ions, but simply have less translational energy.

Calculation of Metastable Ion M/Z Values

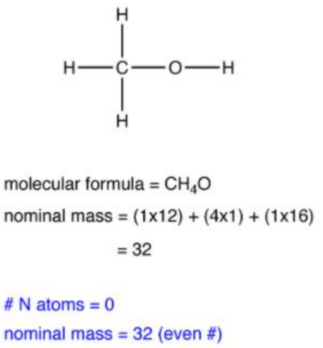
- The apparent mass of a metastable ion A^+ (m^*) can be calculated fairly accurately from the masses of the parent ion (m_1) and the normal daughter ion A^+ (m_2) from the equation
- $$m^* = \frac{(m_2)^2}{m_1}$$
- This equation often gives an apparent mass 0.1-D.4 mass units lower than is in fact observed.
- Calculate the expected apparent mass of the metastable ion produced when m/z= 77 decomposes by loss of CH≡CH to m/z= 51
- Solution: The equation $m^* = \frac{(m_2)^2}{m_1}$ becomes $(51)^2/77 = 33.4$
- As an example, the mass spectrum of toluene shows strong peaks at m/z 91 and m/z 65, together with a strong broad metastable peak at m/z 46.4. Now $(65)^2/91 = 46.4$,
- we can interpret that the ion m/z 91 is decomposing by loss of 26 mass units to the daughter ion m/z 65, and that some of this fragmentation takes place in the second field-free region , leading to a metastable ion peak of m/z 46.4.
- The value 46.4 is the apparent mass of the metastable ion, the real mass being the same as that of the normal daughter- (i.e) 65
- It is worth restating that some of the m/z 91 ions will decompose before and after the second field-free region , producing m/z 65 ions, which are not focused at m/z 46.4

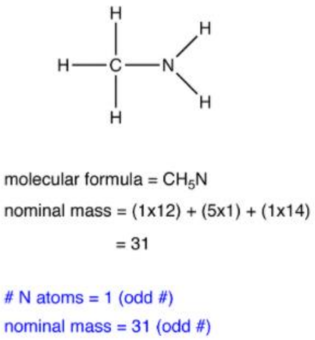
Significance of Metastable Ions

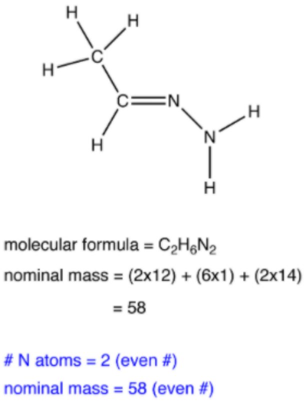
- The presence of a metastable ion in a mass spectrum is taken as very good evidence that
    - The parent ion undergoes decomposition in one step to the daughter ions
    - one-step processes occurring in the mass spectrometer that do not produce metastable-ion peaks, so the absence of such peaks cannot be used to infer the absence of a one-step transition.
- Establish fragment routes
- Distinguish between fragmentation process which occur in few microseconds

11. Nitrogen Rule

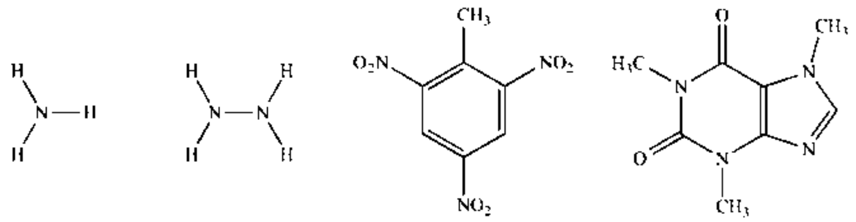
- The nitrogen rule states that a molecule that has no or even number of nitrogen atoms has an even nominal mass, whereas a molecule that has an odd number of nitrogen atoms has an odd nominal mass.







- m/ ever corresponding molecular formula has an even number of nitro
- When m/z for M has an odd mass (odd number of amu), the corresponding molecular formula has an odd number of nitrogen atoms (1, 3, 5, etc.).



Molecule:	Ammonia	Hydrazine	TNT	Caffeine
Formula:	NH_3	N_2H_4	$C_7H_5N_3O_6$	$C_8H_{10}N_4O_2$
m/z (M):	17	32	227	194
	One nitrogen m/z (M) is odd	Two nitrogens m/z (M) is even	Three nitrogens m/z (M) is odd	Four nitrogens m/z (M) is even

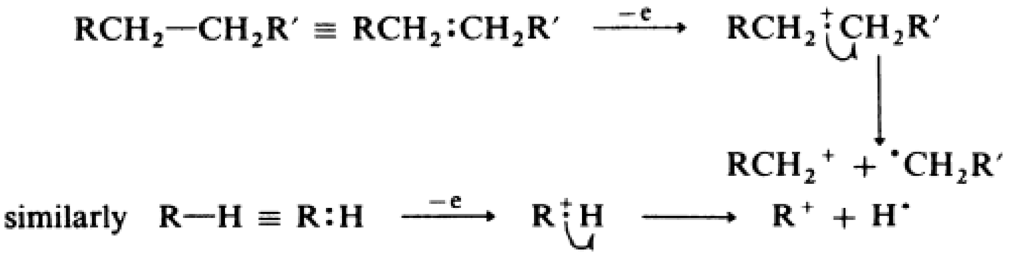
12. General Fragmentation Modes

Representation of Fragmentation Processes

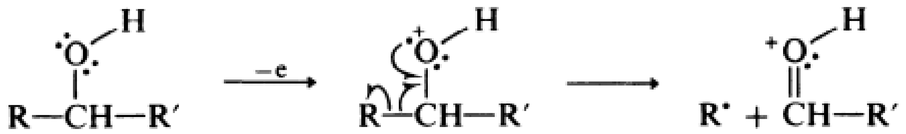
- If a molecular ion loses a methyl radical ($CH_3^{\cdot}$), the mass spectrum will show an ion 15 mass units below the molecular ion
- $M^{+\cdot} \rightarrow CH_3^{\cdot} + (M - 15)^+$
- An alternative is to write the fragment ion as M - CH_3
- These ions are represented as M - 18, M - 24, M - CO, M – H_2S, etc.,
- These are even-electron ions-for example, $(M - 15)^+$ or odd electron radical ions – for example, $(M - 18)^{+\cdot}$
- The same convention can be used to represent fragment ions as m^+ (or $m^{+\cdot}$ and these may, in turn, fragment to m - 1, m - CH_3, m – C_2H_5, etc

Basic Fragmentation Types and Rules

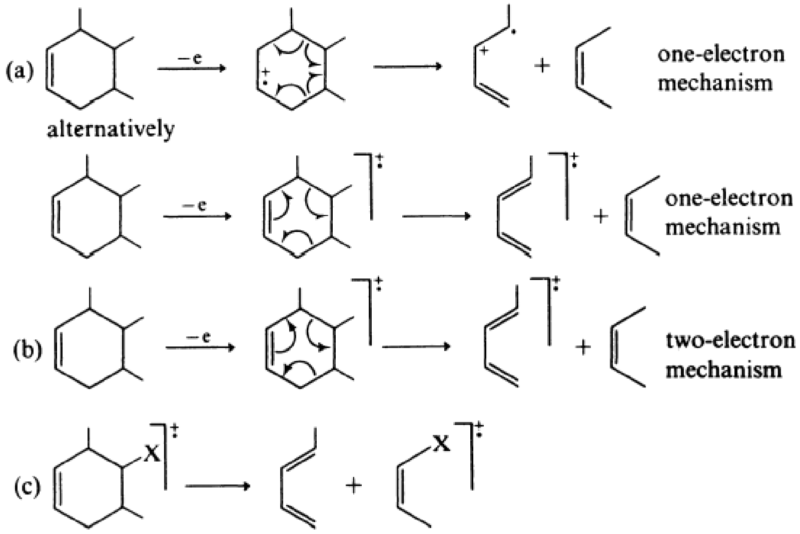
- Electron-pair processes (such as bond heterolysis) are represented by the conventional curved arrow, and one-electron processes (such as bond homolysis) by the fish-hook arrow
- Many fragmentations can be represented as occurring either by one-electron or two-electron processes.
- The molecular ion, because of its excess energy, may take part in processes that have no counterpart in test-tube chemistry.
- **α-Bond rupture in alkane groups**
- At the instant of ionization, sufficient excitation energy is concentrated on the rupturing bond to ionize it



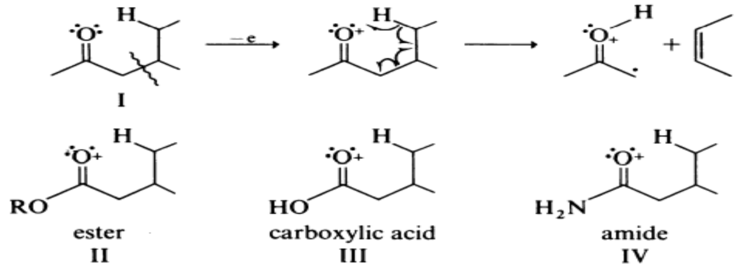
- **α-Bond rupture near functional groups**
- This may be facilitated by the easier ionization of that group's orbitals, as in alcohols, where the nonbonding orbitals of oxygen are more easily ionized than the σ orbitals.
- Other groups in this category are ethers, carbonyl groups and compounds containing halogen, nitrogen, double bonds, phenyl groups, etc



- **Elimination by multiple σ-bond rupture**
- Elimination by multiple σ-bond rupture may occur , leading to the extrusion of a neutral molecule such as CO, C_2H_4, C_2H_2 etc.
- A well-known example is the retro-Diels-Alder reaction of cyclohexenes, which can be represented as in (a) or (b). Highly stabilized ene fragments may cause charge retention to be in part reversed, as in (c)



- **Rearrangements**
- These are common, the most frequently encountered having been described by F. W. McLafferty. (McLafferty Rearrangement)
- In the case of a carbonyl compound (I) by the elimination of an alkene,
- This is also exhibited by ions such as II, Ill, IV, etc.
- **The even-electron rule**:
- The even-electron rule is a rule-of-thumb interpretation of sound thermodynamic principles
- It states that an even-electron species (an ion also as a radical ion) will not normally fragment to two odd-electron species (that is, it will not degrade to a radical and a radical ion), since the total energy of this product mixture would be too high:



I

ester
II

carboxylic acid
III

amide
IV

$$\underset{\text{even}}{A^{+}} \not\longrightarrow \underset{\text{odd}}{B^{\dot{+}}} + \underset{\text{odd}}{C^{\cdot}}$$

In preference, an ion will degrade to another ion and a neutral molecule:

$$\underset{\text{even}}{A^{+}} \longrightarrow \underset{\text{even}}{B^{+}} + \underset{\text{even}}{C}$$

Radical ions, being odd-electron species, can extrude a neutral molecule, leaving a radical ion as coproduct:

$$\underset{\text{odd}}{A^{\dot{+}}} \longrightarrow \underset{\text{odd}}{B^{\dot{+}}} + \underset{\text{even}}{C}$$

Radical ions can also degrade to a radical and an ion

$$\underset{\text{odd}}{A^{\dot{+}}} \longrightarrow \underset{\text{even}}{B^{+}} + \underset{\text{odd}}{C^{\cdot}} \text{ (or } \underset{\text{odd}}{B^{\cdot}} + \underset{\text{even}}{C^{+}}\text{)}$$

Factors Influencing Fragmentations

- **Functional groups**
    - Some functional groups may direct the course of fragmentation profoundly, while other functional groups may have little effect.
- **Thermal decomposition**
    - Thermal decomposition of thermolabile compounds may occur in the ion source, and commonly leads to difficulty in interpreting the mass spectra of alcohols, which may dehydrate before ionization.
    - In the case of alcohols, loss of water gives rise to a peak at M - 18 whether the loss occurs before or after ionization, but thermal dehydration may be extensive enough to eliminate entirely the appearance of a molecular ion in the spectrum.
    - If thermal decomposition is suspected, the compound can be ionized in a cooled ion source , so that electron bombardment of the whole molecule takes place .
    - An alternative solution is to convert the alcohol to the more volatile trimethylsilyl derivative
- **Bombardment energies**
- For routine organic spectra bombarding energy = 70 eV.
- Even with these high energies, molecular ions possess a maximum of 6 eV in excess of their ionization potentials, and there is little change in the fragmentation pattern if this 70 eV is reduced to 20 eV
- However, the ion yield (that is, the efficiency of ionization) is reduced, and the spectra are weaker in intensity overall.

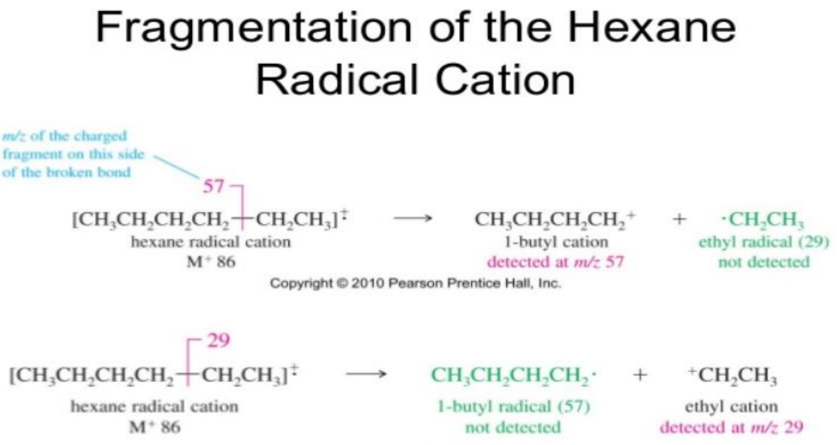
- From > 20 eV down to the ionization potential of the molecule , the spectrum becomes progressively simpler, since only the most favored fragmentations are occurring.
- It follows from these observations that the relative abundances of ions in a spectrum are only reproducible when bombardment energies are constant.
- **Relative rates of competing fragmentation routes**
- These also are important in dictating relative abundances.
- In the simple case of $A^{+\cdot}$ going either to B^+ and $C^{\cdot}$ or to $B^{+\cdot}$ and C
- The equilibrium abundances of $A^{+\cdot}$, B^+ and $B^{+\cdot}$ depend on the relative rate constants for the two competing reactions:
    - The rate constants depend on the excitation energy possessed by $A^{+\cdot}$ and will certainly depend on the heats of formation of all the products.
    - Calculations involving these and other parameters are the basis of the so-called quasi equilibrium theory (QET) of mass spectrometry.
- It is misleading to use the intensity of an ion peak as a simple measure of the particular fragmentation route, unless it is certain that the ion cannot be produced by another route.
- At low resolution there is the additional complication that the peak may be associated with two ions of equal mass (such as $C_3H_7^+$ and CH_3C0^+, at m/z 43).

Fragmentations Associated with Functional Groups

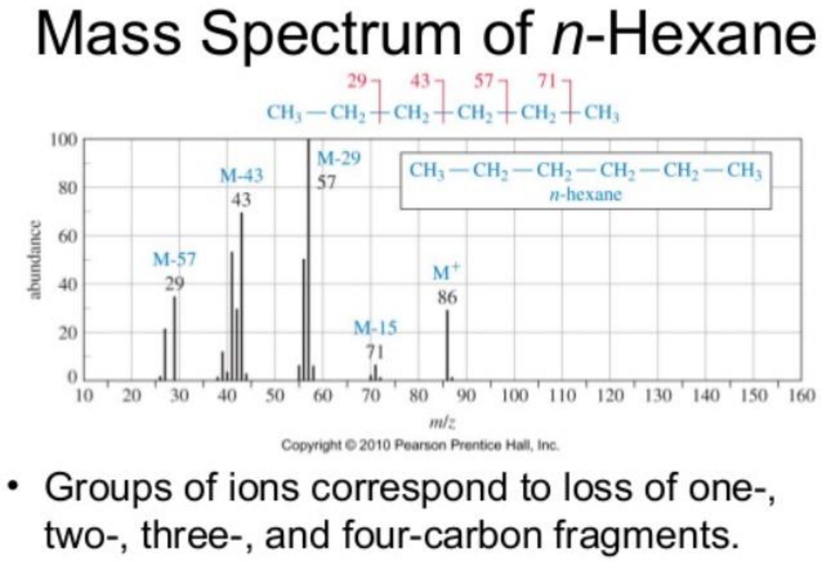
- For simple monofunctional compounds we can predict the mass spectrum based on
    - a) the nature of the carbon skeleton (whether alkane, alkene, aromatic, etc)
    - b) the nature of the functional group
- For difunctional compounds, a more complex interaction can be expected, depending on the relative powers of the two functional groups to direct the fragmentation .
- It is always easier to interpret the mass spectrum of a known structure than to deduce the structure of an unknown compound
- Other spectroscopic evidence for the presence of functional groups should ideally always be required.

13. Mass Spectra of Hydrocarbons

a. Mass Spectra of Alkanes



Fragmentation of the Hexane Radical Cation



Mass Spectrum of *n*-Hexane

- Groups of ions correspond to loss of one-, two-, three-, and four-carbon fragments.

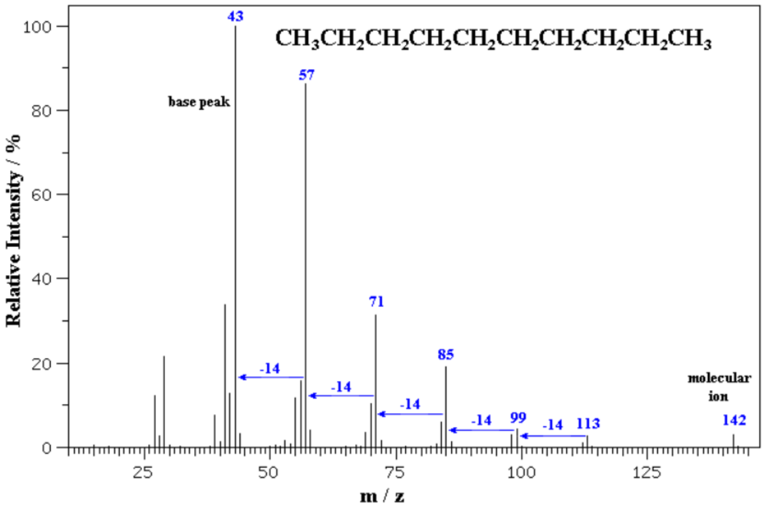
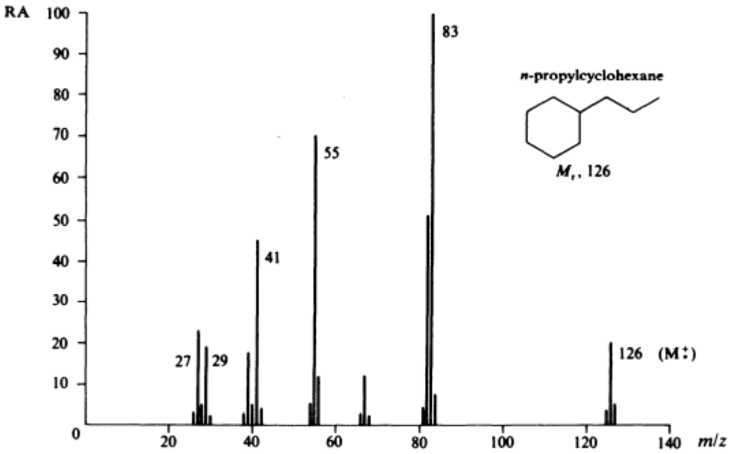


Figure 7: Fragmentation pattern and Mass Spectrum of n-Hexane and Mass Spectrum of n-Decane

b. Mass Spectra of Cycloalkanes

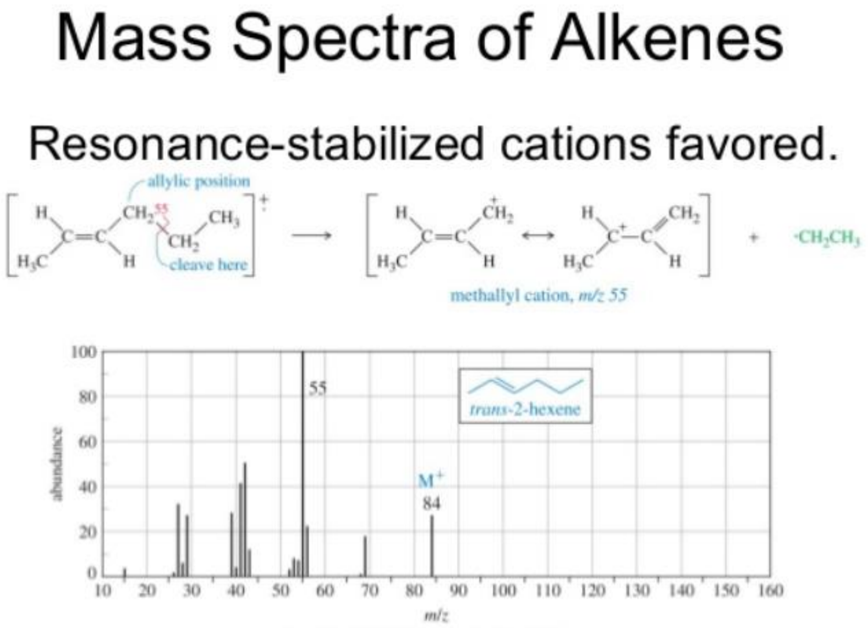
- Complex fragmentations usually occur for cycloalkanes, ring size obviously being important in relation to ion stability.
- Typically, for the simple members the molecular ion peak will be easily seen, its intensity reducing as branching increases.
- Common fragmentations are loss of alkenes or alkenyl ions and the splitting off of the side-chains with charge retention by the ring remnant
- side-chain loss is simply a special case of fragmentation at a branching point.



Mass spectrum of n-propylcyclohexane: because of branching, m/z 57 is no longer a prominent fragment.

Figure 8: Mass spectrum of substituted cyclohexane

c. Mass Spectra of Alkenes



Mass Spectra of Alkenes

Resonance-stabilized cations favored.

Figure 9: Mass Spectra of Trans-2-hexene

d. Mass Spectra of Alkynes

- No simple pattern emerges for the fragmentation of alkynes, which can be applied to complex molecules.
- Thus, for 1-butyne and 2-butyne the molecular ion peak is the base peak, but the molecular ion peak for higher members is weak.
- Loss of alkyl radicals gives prominent peaks in many cases (at M - 15, M - 29, etc .) and extrusion of alkenes may give M - 28 and M - 42 peaks, etc .

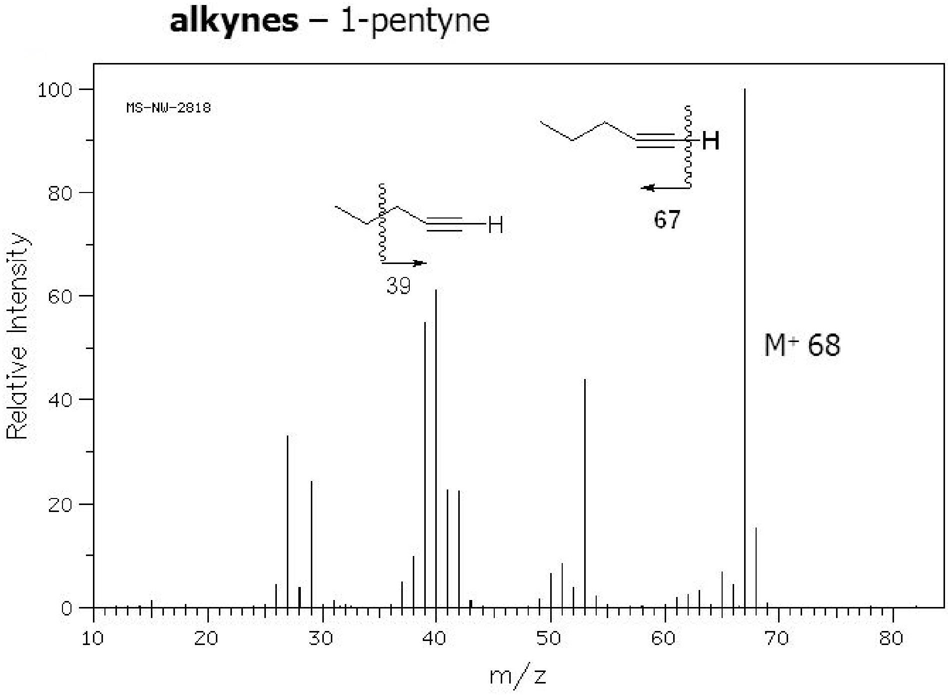
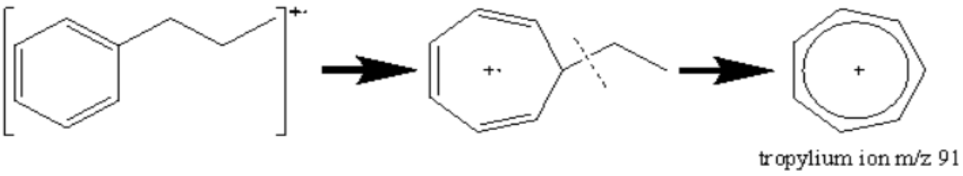


Figure 10: Mass Spectra of 1-Pentyne

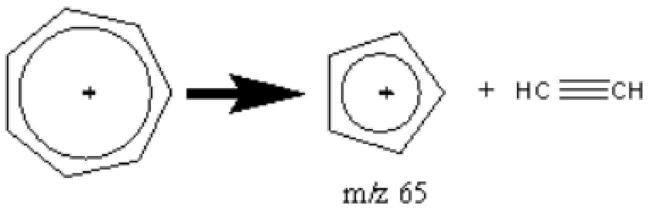
e. Mass Spectra of Aromatic hydrocarbons

Fragmentation of Aromatics

- The presence of an aromatic ring in a compound results in a prominent molecular ion. A common peak at [M – 1] results from the loss of a hydrogen atom from the benzene ring. Alkyl substituted benzene rings result in a prominent peak at *m/z* 91. In most cases, the peak at *m/z* 91 is the result of a tropylium ion caused by the following rearrangement.



- The peak observed in most aromatic compounds at *m/z* 65 results from the elimination of an acetylene molecule from the tropylium ion.



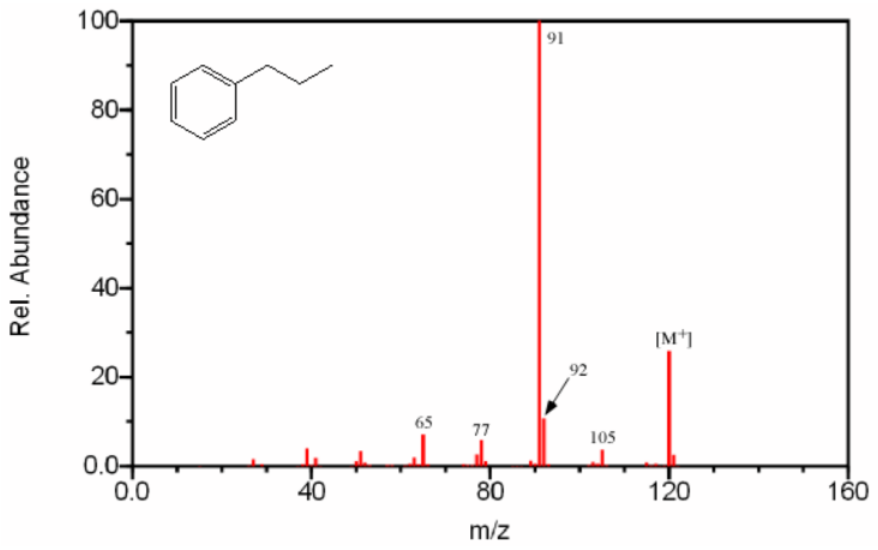


Figure 11: Mass Spectra of n-Propyl benzene

f. Mass Spectra of Alcohols

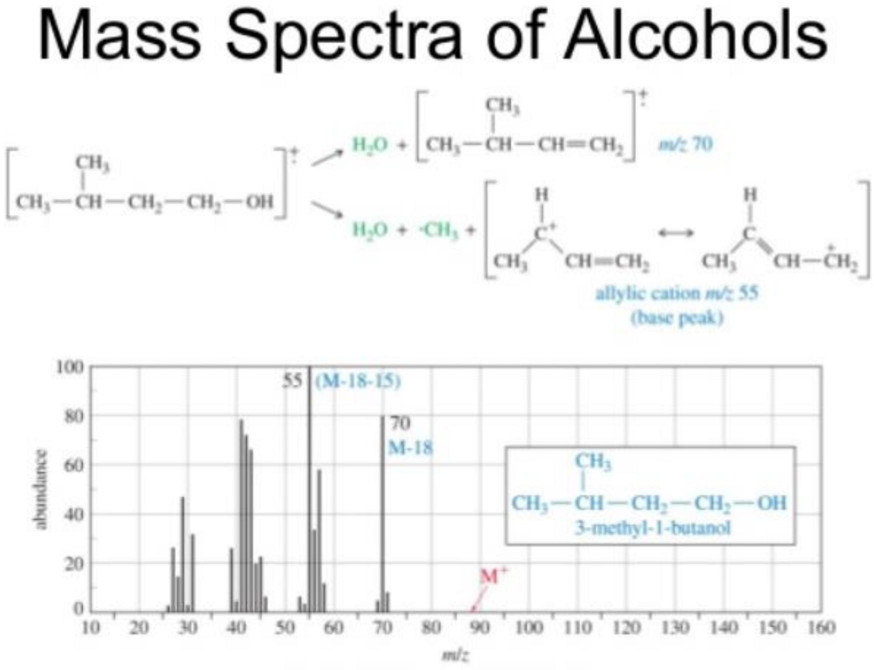
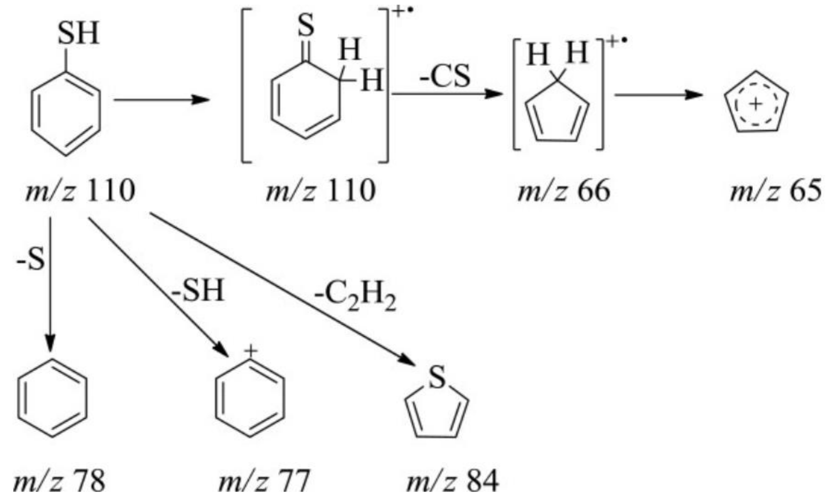


Figure 12: Fragmentation pattern and Mass Spectra of Alcohol

g. Mass Spectra of Thiophenol

Fragmentation of Thiophenol



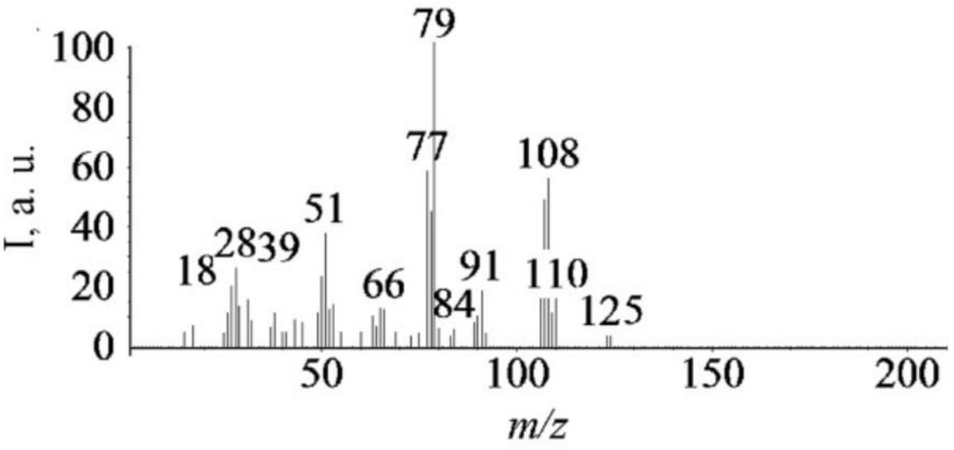
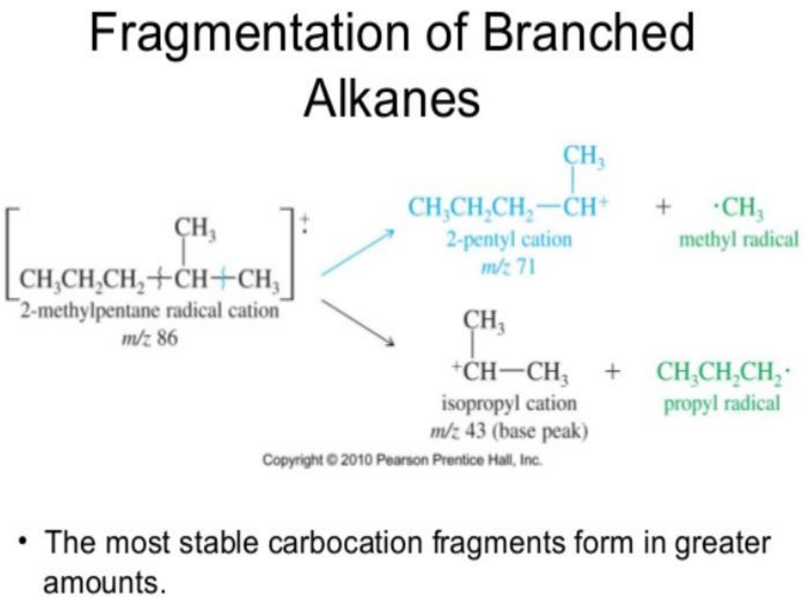


Figure 13: Mass Spectra of Thiophenol

h. Mass Spectra of Branched Hydrocarbons



Fragmentation of Branched Alkanes

$[CH_3CH_2CH_2CH(CH_3)CH_3]^{+\cdot}$ 2-methylpentane radical cation m/z 86

$CH_3CH_2CH_2CH^+(CH_3)$ 2-pentyl cation m/z 71 + $\cdot CH_3$ methyl radical

$^+CH(CH_3)-CH_3$ isopropyl cation m/z 43 (base peak) + $CH_3CH_2CH_2\cdot$ propyl radical

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- The most stable carbocation fragments form in greater amounts.

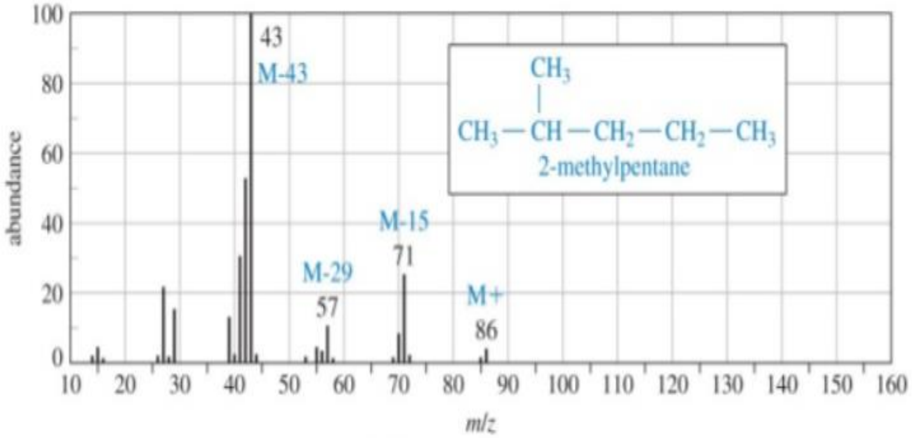
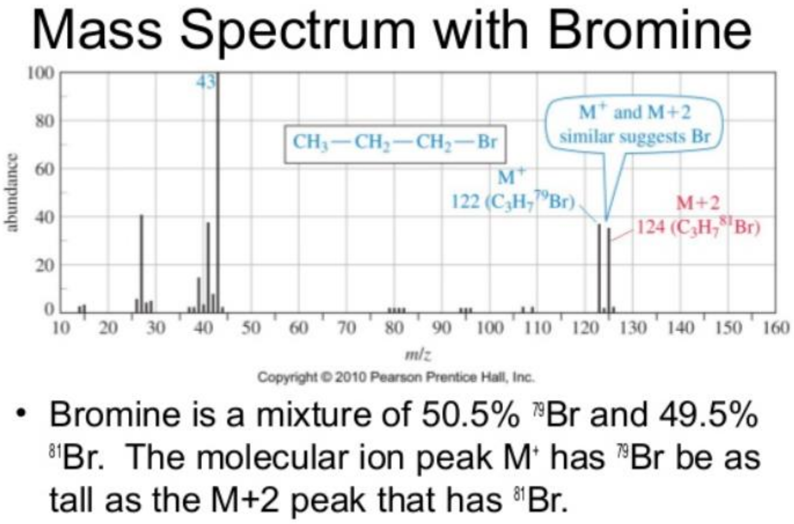


Figure 14: Fragmentation pattern and Mass Spectra of Branched Hydrocarbon

i. Mass Spectra of Chlorine and Bromine substituted compounds



Mass Spectrum with Bromine

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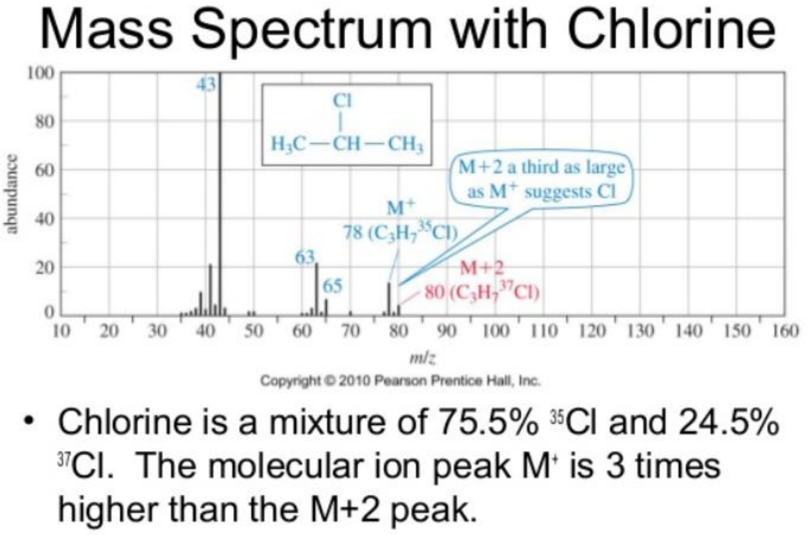
- Bromine is a mixture of 50.5% ^{79}Br and 49.5% ^{81}Br. The molecular ion peak M$^+$ has ^{79}Br be as tall as the M+2 peak that has ^{81}Br.



Mass Spectrum with Chlorine

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- Chlorine is a mixture of 75.5% ^{35}Cl and 24.5% ^{37}Cl. The molecular ion peak M$^+$ is 3 times higher than the M+2 peak.

Figure 15: Mass Spectra Bromine and Chlorine Substituted hydrocarbons

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT-5 – ESR AND Mossbauer Spectroscopy – SCYA7301

1. Electron spin resonance spectroscopy

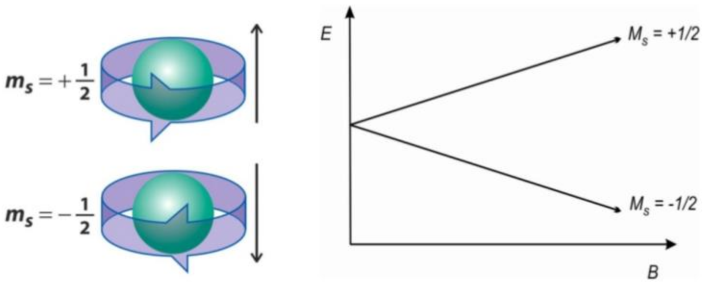
- ESR Spectroscopy is also known as electron paramagnetic resonance
- It is absorption spectroscopy similar to NMR possible only with molecules having unpaired electrons
- Instead of radio waves in NMR microwaves is used in ESR

Principle:

- The Phenomenon of electron spin resonance (ESR) is based on the fact that an electron is a charged particle
- It spins around its axis and this causes it to act like the tiny bar magnet
- When a molecule or compound with an unpaired electron is placed in a strong magnetic field.
- The spin of the unpaired electrons can align in two different ways creating two spin states ms = ± ½
- The alignment can either be along the direction (parallel) to magnetic field which corresponds to the lower energy state ms= - ½
- Opposite (anti-parallel) to the direction of the applied magnetic field ms= +½
- The two alignment have different energies and this difference in energy lifts the degeneracy of the electron spin states
- The energy difference is given by

  $$\Delta E = E_+ - E_- = h\nu = gm\beta B$$

  where h is Planck's Constant (6.626×10^{-34}Js)
  ν is frequency of the radiation
  β is Bohr magneton ($9.274 \times 10^{-24}\ JT^{-1}$)
  B is Strength of the magnetic field in Tesla
  g is g-factor
- The g-factor is a unit less measurement of the intrinsic magnetic moment of the electron and its value for a free electron is 2.0 023



Resulting energy levels of an electron in a magnetic field

Figure 1: Energy Levels of electron in magnetic field

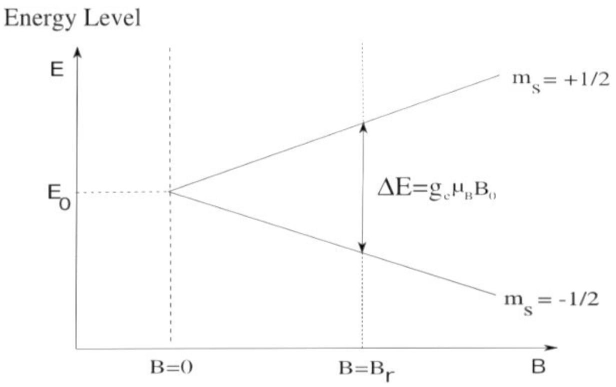


Figure 2: Alignment of electron spin states

- The unpaired electrons are excited to high energy state under the magnetic field by the absorption of microwave
- The excited electron changes its direction of spin and relaxes into the ground state by emitting photons
- Microwave absorption is measured as a function of the magnetic field by ESR
- A chemical species with an odd number of electrons exhibits characteristic magnetic properties much like the nucleus
- The spinning action of an unpaired electron generates a magnetic moment μ
- If an intense magnetic field is applied, the electron assume orientations aligned with (lower energy $-\mu B$) or against (higher energy $+\mu B$) the field
- An electron in a magnetic field is able to absorb energy of the proper frequency $\Delta E = h\nu$ which will catapult it from lower to higher energy level
- This phenomenon is known as electron resonance and the technique employed to study this type of behaviour is called as electron spin resonance spectrometry
- In a magnetic field of the order 3400 gauss, the appropriate quantum of energy is obtained from radiation in the microwave region of electromagnetic spectrum
- It is common practice to subject the sample to differing magnetic intensities keeping the microwave frequency constant.
- The magnetic field is varied till resonance occurs
- The area of ESR peak is directly proportional to the number of unpaired electrons in the sample investigated and thus to the concentration of the sample
- In quantitative analysis, peak areas of the sample are compared to the peak area of a standard which contains a known quantity of unpaired electrons
- ESR spectra do not exhibit hyperfine splitting which is caused by interaction between the spinning electrons and adjacent spinning magnetic nuclei
- ESR spectra show no phenomenon like chemical shift as seen in NMR

Hyperfine splitting

- The ESR signal is due to the transition of electron from the spin state ms = – ½ and spin state ms = +½ – Spin Flip
- This state may interact with magnetic moment of nuclei, with which the unpaired electron may be partially or wholly associated
- This interaction will lead to splitting of resonance signals into several lines
- This is hyperfine splitting

Spin – Spin splitting (Hyperfine splitting)

- Magnetic resonance can also occur without an external magnetic field from the interaction of the electron and nuclear spin
- Such resonance produces fine and hyperfine structure of atomic spectra
- The nuclei of atoms in a molecule or complex often have magnetic moment which produces a local magnetic field at the electron
- The interaction between and unpaired electron an nuclei with non-zero nuclear spin is called hyperfine interactions
- This leads to splitting of ESR line and is known as hyperfine spectrum

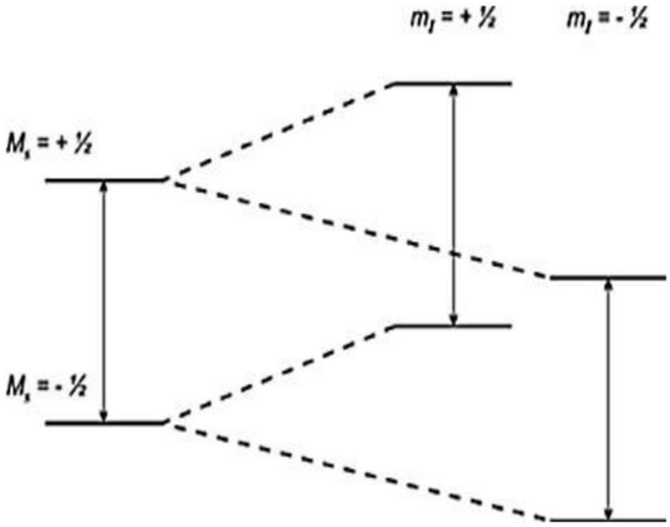
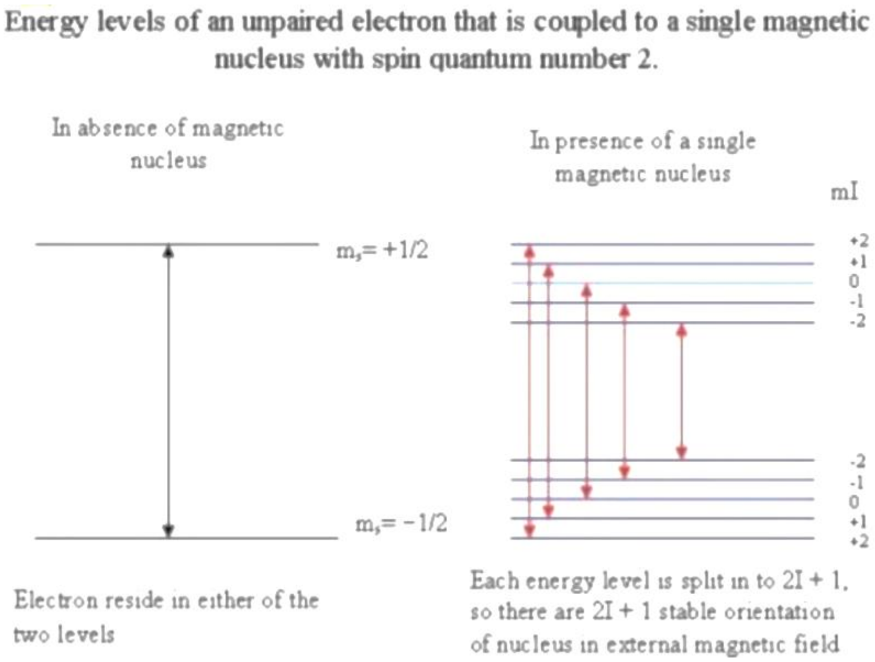


Figure 3: Hyperfine Interactions



Energy levels of an unpaired electron that is coupled to a single magnetic nucleus with spin quantum number 2.

Electron reside in either of the two levels

Each energy level is split in to 2I + 1, so there are 2I + 1 stable orientation of nucleus in external magnetic field

Figure 4: Splitting of energy levels in absence and presence of Magnetic field

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1

Figure 5: Signal Intensities-Follow Pascal's triangle

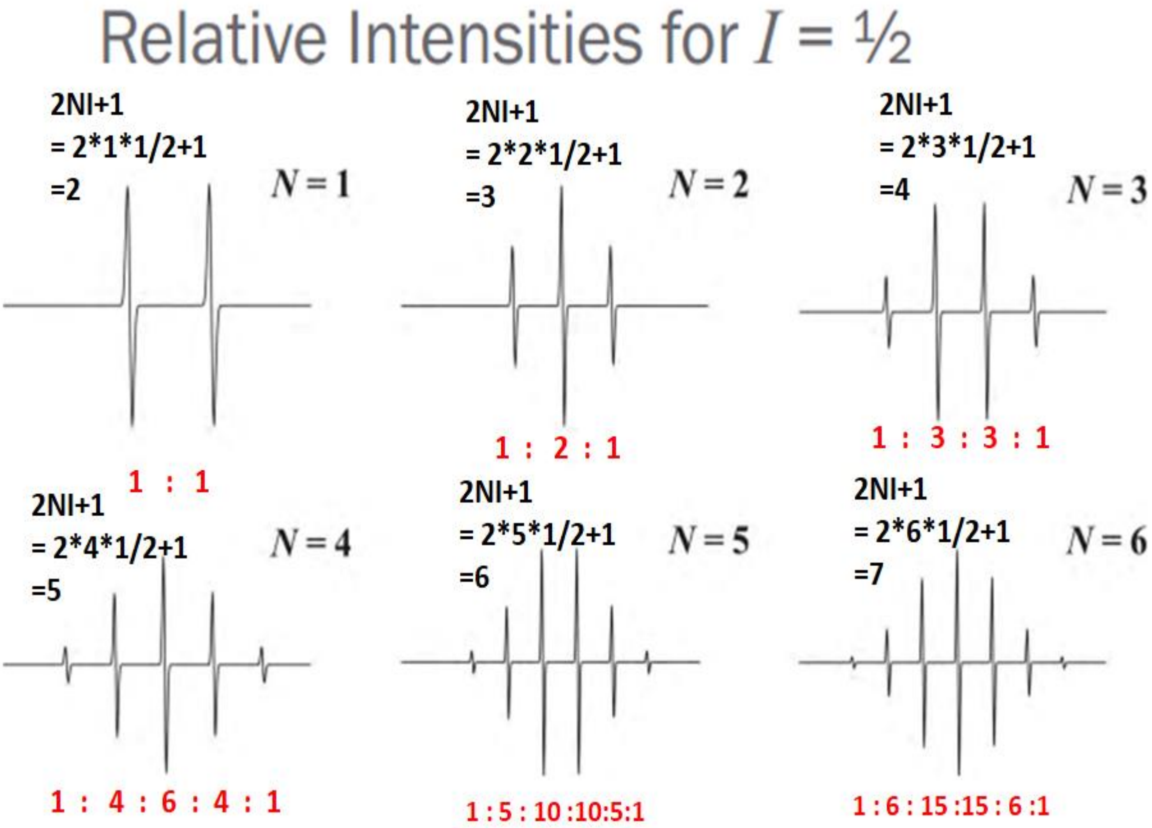


Figure 6: ESR Spectral intensities for Nucleus with I = 1/2

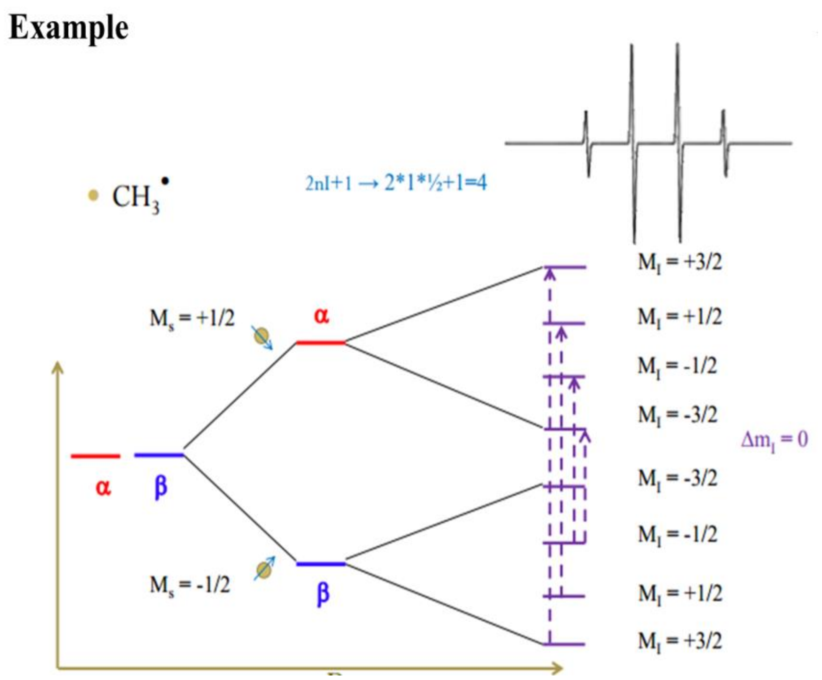
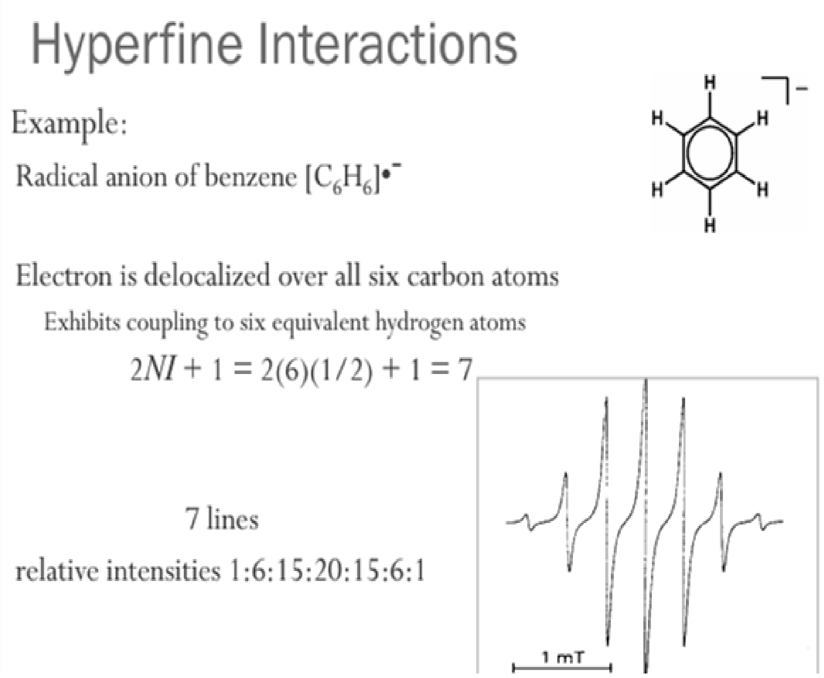


Figure 7: ESR hyperfine splitting of CH$_3$ radical



Hyperfine Interactions

Example:

Radical anion of benzene $[C_6H_6]^{•-}$

Electron is delocalized over all six carbon atoms

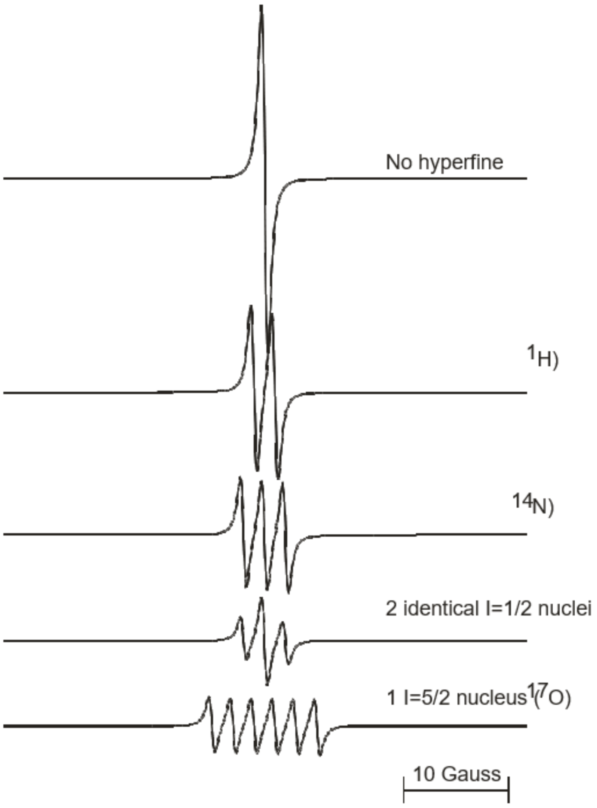
Exhibits coupling to six equivalent hydrogen atoms

$$2NI + 1 = 2(6)(1/2) + 1 = 7$$

7 lines

relative intensities 1:6:15:20:15:6:1

Figure 8: ESR hyperfine splitting of Benzene radical

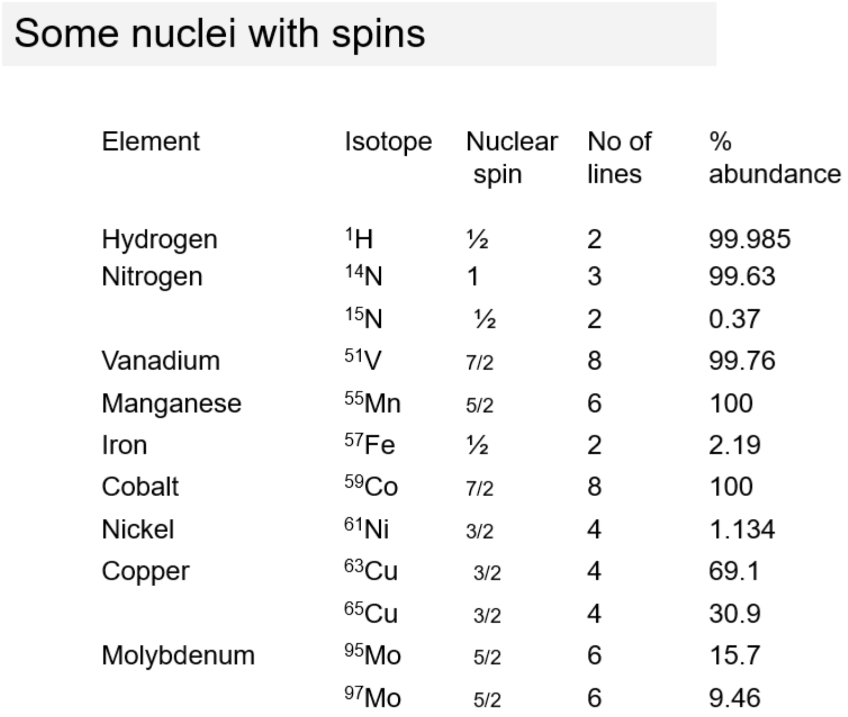


Hyperfine coupling

If the electron is surrounded by *n* spin-active nuclei with a spin quantum number of I, then a (*2nI+1*) line pattern will be observed in a similar way to NMR.

In the case of the hydrogen atom *(I*= ½), this would be 2(1)(½) + 1 = 2 lines.

Table: 1- Spins of various Nuclei



Some nuclei with spins

Element	Isotope	Nuclear spin	No of lines	% abundance
Hydrogen	^{1}H	½	2	99.985
Nitrogen	^{14}N	1	3	99.63
	^{15}N	½	2	0.37
Vanadium	^{51}V	7/2	8	99.76
Manganese	^{55}Mn	5/2	6	100
Iron	^{57}Fe	½	2	2.19
Cobalt	^{59}Co	7/2	8	100
Nickel	^{61}Ni	3/2	4	1.134
Copper	^{63}Cu	3/2	4	69.1
	^{65}Cu	3/2	4	30.9
Molybdenum	^{95}Mo	5/2	6	15.7
	^{97}Mo	5/2	6	9.46

Hyperfine interactions

- Coupling pattern same as in NMR
- More common to see coupling to nuclei with spins greater than ½
- The number of lines: 2NI + 1
- N = number of equivalent nuclei
- I = Spin
- Only determine the number of lines - not the intensities
- Relative intensities determined by the number of interacting nuclei
- If only one nucleus interacting: all lines have equal intensity
- If multiple nuclei interacting: Distributions derived based upon spin
- For spin ½ (most common), intensities follow Binomial Distribution

Quadruple nuclei

- A quadrupolar nucleus is one that has a Quantum spin number I greater than ½
- Example: Vanadium and Nitrogen containing compounds
- Example: $VO(acac)_2$
- Interaction with vanadium nucleus
- For vanadium, I = 7/2
- So, 2NI + 1 = 2(1)(7/2) + 1 = 8
- Thus expected eight lines of equal intensity
- Pyrazine anion (electron delocalized over ring)
- Exhibits coupling to two equivalent N (*l* =1)
- 2NI + 1 = 2(4)(½) + 1 = 5
- So spectrum should be quintet with intensities 1:2:3:2:1 and each of those lines should be split into quintets with intensities 1:4:6:4:1

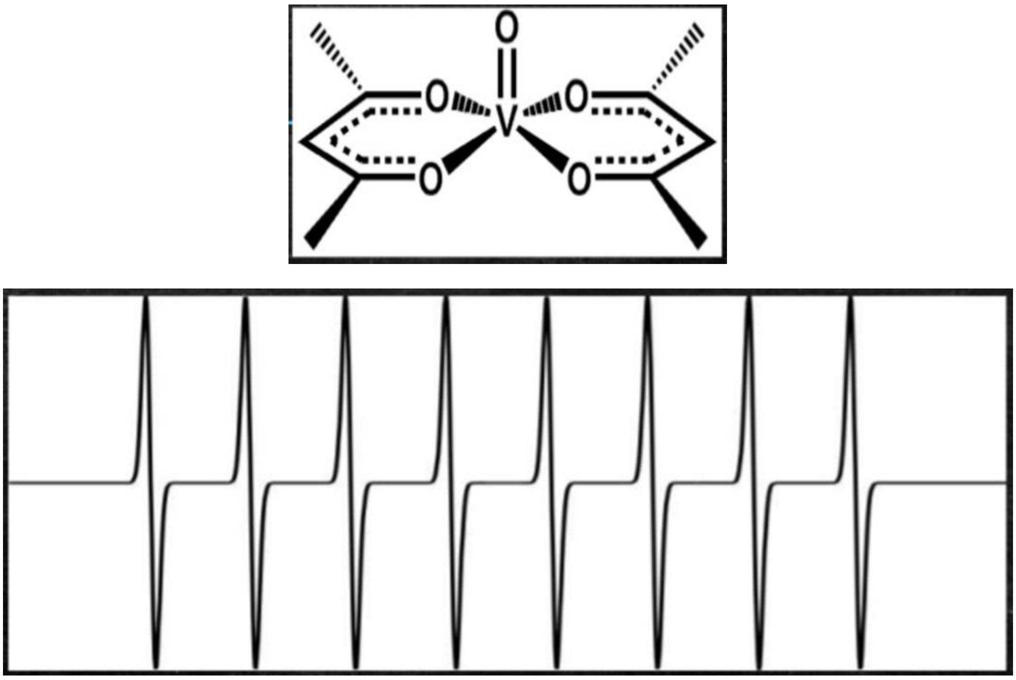


Figure 9: ESR Hyperfine splitting of Quadrapole nuclei - $VO(acac)_2$

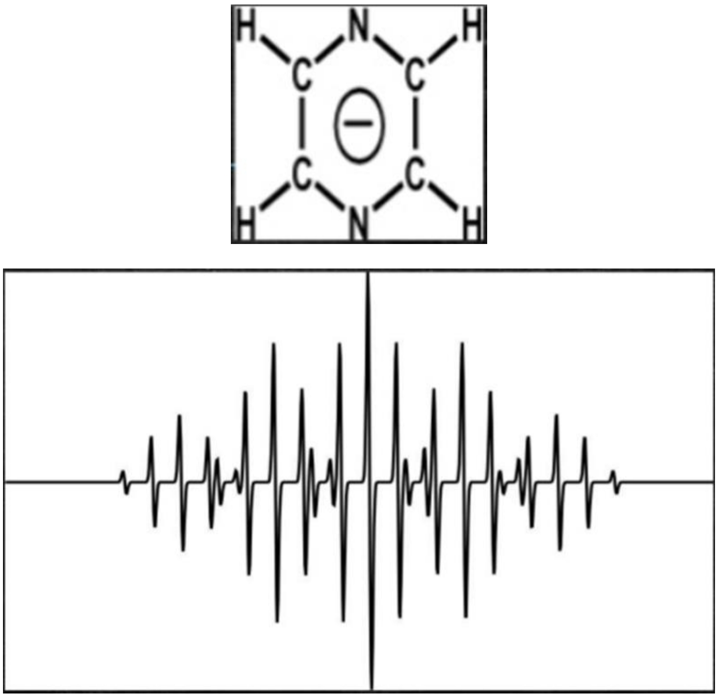


Figure 9: ESR Hyperfine splitting of Quadrapole nuclei – Pyrazine anion

Superhyperfine Splitting

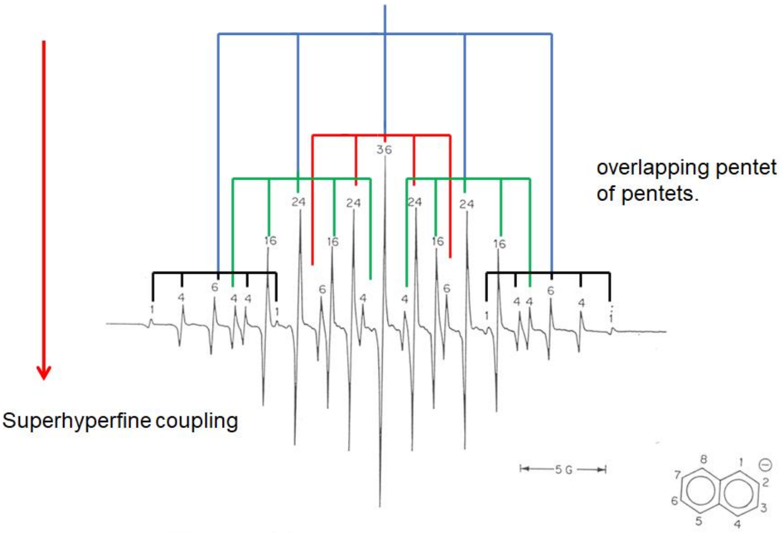
- Further splitting may occur by the unpaired electron if the electron is subject to the influence of multiple sets of equivalent nuclei.
- This splitting is on the order of 2nI+1 and is known as superhyperfine splitting.
- As hyperfine structure splits fine structure into smaller components, superhyperfine structure further splits hyperfine structure.
- For example, in a CH_2OH radical, an EPR spectrum would show a triplet of doublets.
- The triplet would arise from the three protons, but superhyperfine splitting would cause these to split further into doublets.
- This is due to the unpaired electron moving to the different nuclei but spending a different length of time on each equivalent proton.
- In the methanol radical example, the electron lingers the most on the CH_2 protons but does move occasionally to the OH proton.
- Carbon compound; I(C) = 0; 2(0) + 1 = 1 peak…. But:
- If the odd, unpaired electron spends time around multiple sets of equivalent nuclei, additional splitting is observed: 2nI + 1; this is called “superhyperfine splitting.”

ESR spectrum of CH_2OH radical at pH 1.03

ESR spectrum of the methyl radical in aqueous solution

ESR spectrum of p-benzosemiquinone anion

Figure 10: ESR spectrum of CH_2OH and p-benzosemiquinone anion



ESR spectrum of the naphthalene anion (K^+ is the counterion) at 298 K. The numbers above each line are the degeneracies of the corresponding nuclear spin states. These numbers correspond approximately to the relative derivative amplitudes.

Figure 11: ESR spectrum of Naphthalene anion

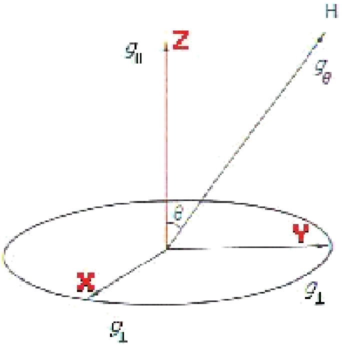
Hyperfine splitting and anisotropy

- In solution the molecules are under continuous motion so interactions in all the directions are same
- So hyperfine interactions is called isotropic
- In the case of solid state depending upon the orientation of the Crystal Field experienced will change indifferent direction, so A is anisotropic
- Usually field is considered to be applied along Z axis. So A along Z axis is called A_{ll}
- A values along X and Y directions are called $A_\perp$
- $A_{ave} = 1/3[A_{ll} +$ e a parallel $+ A_\perp]$

Anisotropy in g and A

- Many measurements are made in the solid state in EPR spectroscopy
- The ability of EPR to obtain useful information from amorphous (glassy) and
- polycrystalline (powders) as well as from single crystal materials has attracted

- much biology and biochemistry research
- Usually : g_X, g_Y, g_Z are not all equal, so g is anisotropic. Same for A_X, A_Y, A_Z.



For EPR the local symmetry at an unpaired electron center is categorised as :

- *Cubic*. If x = y = z is cubic (*cubal*, *octahedral*, *tetrahedral*) No anisotropy in g and A.
- *Uniaxial (Axial)*. If x = y, and z is unique.
  Linear rotation symmetry (at least 3-fold). Two principal values each for g and A. For an arbitrary orientation:

$$g_\theta^2 = g_\perp^2 \sin^2\theta + g_{II}^2 \cos^2\theta$$

- *Rhombic*. Three unequal components for g and A
- For an arbitrary orientation:

$$g^2 = g_{XX}^2 \sin^2\theta \cos^2\phi + g_{YY}^2 \sin^2\theta \sin^2\phi + g_{ZZ}^2 \cos^2\phi$$

Anisotropic systems

- Anisotropy shown his solids, frozen solutions, radical prepared by irradiation of crystalline materials, radical trapped in host matrices, paramagnetic point defect in single crystals
- For systems with spherical or cubic symmetry g is isotropic
- For systems with lower symmetry,
- g = g_{II} and g = gxx, gyy, gzz
- ESR absorption lines shapes should distinctive envelope

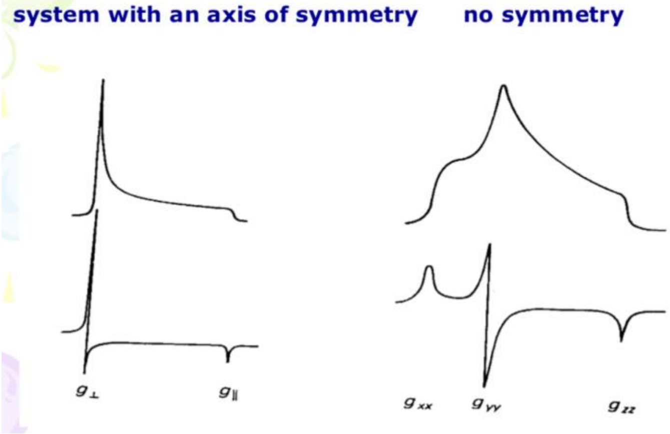


Figure 12: g_{II} and g_{xx}, g_{yy} and g_{zz} for system with axis of symmetry and no symmetry

Zero–field splitting (ZFS)

- The splitting of spin levels even in the absence of magnetic field is called zero–field splitting.
- Occurs mainly in in transition metal complexes where there are more than one unpaired electrons.
- Removes the degeneracy of transitions and more transitions are observed than expected , in the presence of external magnetic field.
- Fine structure in ESR spectrum is obtained.

Causes & Mechanism :

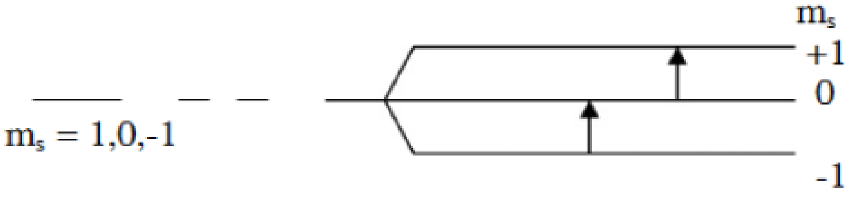
Dipolar interactions among electrons:
i. In a d2 system, S=1 both electrons being parallel. Since each spin produces a small magnetic field in the vicinity of its partner. The dipolar interactions for m_S= +1 and m_S = -1 or same and m_S=0 has different dipolar interaction than +1 or -1 states. Thus -1 and +1 m_S states are raised than m_S=0 state.

ii. Spin orbit coupling

iii. A strong internal electric field which results in the perturbations to the energy levels of m_S= +1 and -1 states but not of m_S = 0 state.

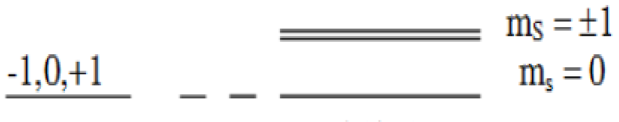
Kramer's degeneracy /Rule :

- Crystal field lifts the spin degeneracy of two or more unpaired electrons in a complex due to electrostatic interactions (ZFS).
- When the species contains an odd number of unpaired electrons, the spin degeneracy of every level remains doubly degenerate.
- This is known as Kramer's degeneracy
- When the number of unpaired electrons is even, crystal field may remove the spin degeneracy entirely.
- *Some examples :*
- Example 1: In a d2 system with two unpaired electrons, S = +½ + ½ = 1.
- Therefore, m_s= -1, 0, +1.
- In the absence of zero-field splitting, two transitions are possible

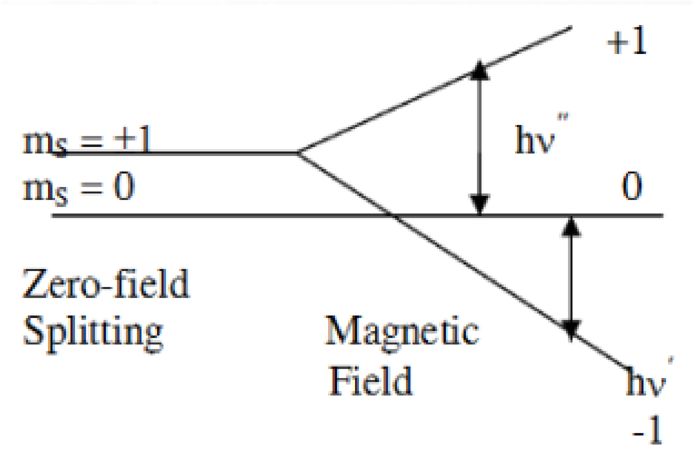


- The first transition is m_s= 0 to +1 and the second transition is m_s= -1 to 0.

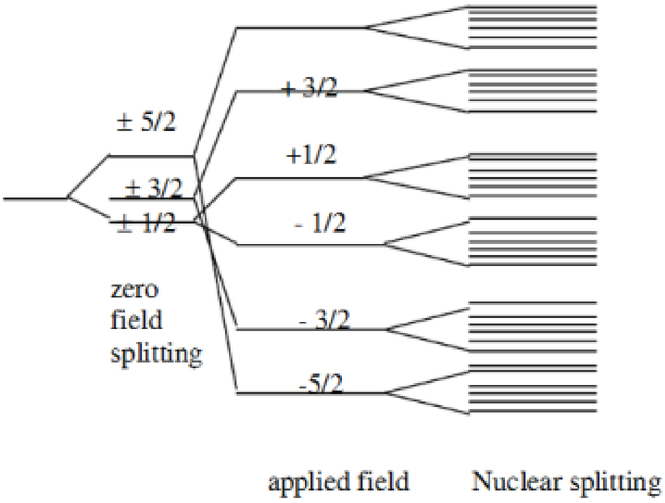
- These transitions have equal energy (i.e. degenerate) and only one signal is observed.
- This system has even number of unpaired electrons.
- Hence, Kramer’s degeneracy is not operative.
- That is, each level will not be doubly degenerate.
- If zero-field splitting is present, it removes the degeneracy in m_S as shown below:



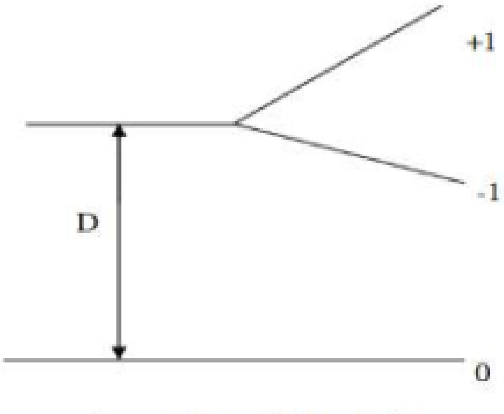
- Subsequent magnetic field splits the levels further as shown below :



- Here, two transitions are not degenerate. 2 peaks =>ZFS present, 1 peak =>ZFS absent.
- Example 2: In a d5 system like Mn(2+), there is an odd number of unpaired electrons.
- So, Kramer’s degeneracy is operative here.
- The zero-field splitting produces three doubly degenerate spin states, namely, m_S = +5/2, +3/2,+½ (Kramer ’s degeneracy)



- Consequences of ZFS :
- Large ZFS => transitions fall out of the microwave region. e.g. In V(3+) m_S= 0 to m_S= +1 transition is not observed. However, a weak transition between m_S= +1 and m_S= -1 has been observed (forbidden).
- Number of peaks observed in the spectrum is more. The spectrum becomes much more complex when hyperfine splitting is also incorporated.



2. Mossbauer spectroscopy

Introduction

- Discovered by German physicist Rudolf Mossbauer in 1958
- It is also known as Nuclear Gamma Resonance Spectroscopy
- Based on the resonance fluorescence of Gamma (γ)-radiations (Mossbauer effect)
- Elements used are ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{129}I, etc
- It is found to have wide application in elucidating the nature of chemical bond in inorganic solid state chemistry and biological Science, for instance bonding in haemoglobin and oxyhaemoglobin

Basic Principle

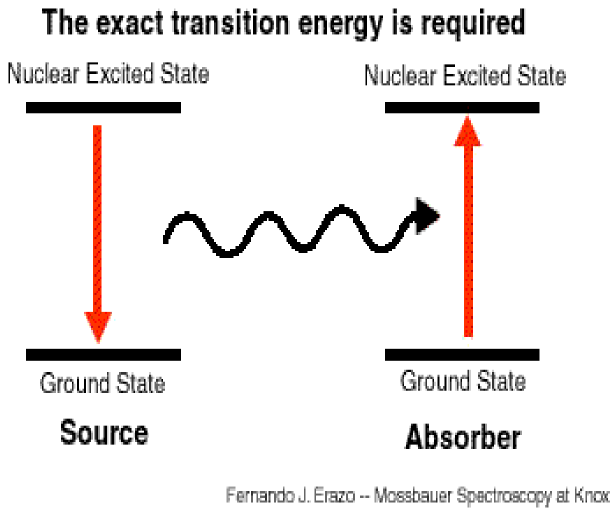
- It involves recoilless emission and absorption of Gamma (γ)- rays by nuclei
- Atoms in source emitting Gamma (γ)-rays must be of same isotope as atoms in sample absorbing them

Mossbauer Effect

- The Mossbauer Effect: **Recoil-Free Nuclear Radiation**
- The Mossbauer effect states that when some atoms are held tightly in crystalline atomic structures, the gamma radiation emitted by their nuclei are very close to being recoil-free.
- This implies that the emitted photon has the exact frequency that corresponds to the transition energy between the nuclear ground state and the excited state.

- When this photon carrying the full nuclear transition energy strikes another similar nucleus also embedded in a tight crystalline structure, absorption may occur.

- Because the nuclear energy levels are very sharply defined, only such a photon - one that carries the exact transition energy - may excite another nucleus (of course, only if absorber doesn't recoil either).



Fernando J. Erazo -- Mossbauer Spectroscopy at Knox

Figure 13: Source and Absorber in Mossbauer Effect

Difficulty in Mossbauer Spectroscopy:

- The only suitable source of Gamma radiation is the excited nuclei of the same isotope in the course of radioactive decay
- No way of tuning the energy of the emitter γ photon
- The energies involved are much higher and in the order of KeV
- Recoil effect

Recoil effect:

- Whenever a high-energy particle is released from a body at rest the releasing body feel a back- kick that is it is pushed backward (just like a gun), this is called recoil effect
- So the energy of Gamma (γ)-rays is slightly less than natural energy of transition
- Similarly for a nucleus at rest to absorb Gamma (γ)- ray, the energy of Gamma (γ)- rays should be slightly less than natural energy
- Energy of recoil $E_R = \frac{E_\gamma}{2mC^2}$
- E_γ = energy of Gamma ray (energy between ground state and excited state)
- m = mass of nucleus
- C = velocity of light
- recoiling effect depends upon the effective mass so as mass increases, the recoil effect decreases
- So, for the free nucleus this nuclear resonance, that is absorption and emission of Gamma Rays by identical nuclei, is not an observable
- But when the nuclei is present in solid crystal, there is little very little loss as recoil energy

- A nucleus with Z protons and N neutrons in an excited state of energy E_e undergoes transition to the ground state of energy E_g by emitting a gamma quantum of energy Ee – Eg .
- The gamma quantum may be absorbed by the nucleus of the same kind (same Z and N) in its ground state, whereby transition to the excited state of energy E_e takes place (resonance absorption).
- The subsequent transition to the ground state emits a conversion electron e- or a γ-quantum (resonance fluorescence).

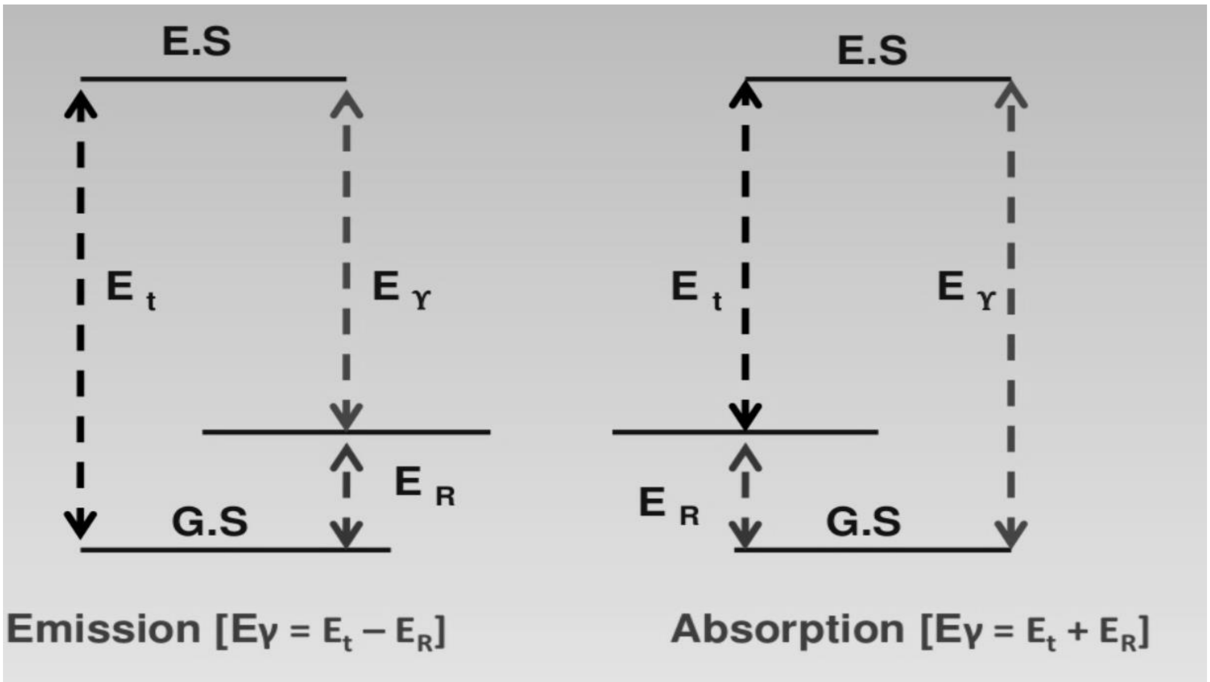


Figure 14: Emission and Absorption in Mossbauer Spectroscopy

- Radioactive ^{57}Co with 270 days halflife, which may be generated in a cyclotron and diffused into a noble metal like rhodium, serves as the gamma radiation source for ^{57}Fe Mössbauer spectroscopy.
- ^{57}Co decays by electron capture (EC from K-shell, thereby reducing the proton number, from 27 to 26 corresponding to ^{57}Fe) and initially populates the 136 keV nuclear level of ^{57}Fe with nuclear spin quantum number I = 5/2.
- This excited state decays and populates, with 85 % probability the 14.4 keV level by emitting 122 keV gamma quanta, with 15 % probability the 136 keV level decays directly to the ground state of ^{57}Fe.
- The 14.4 keV nuclear state has a halflife of ca. 100 ns.
- Both the halflife and the emitted gamma quanta of 14.4 keV energy are ideally suited for ^{57}Fe Mössbauer spectroscopy.
- I = 3/2 and I = 1/2 are the nuclear spin quantum numbers of the excited state (14.4 keV) and the ground state, respectively.

- The internal conversion coefficient = 9.7 (the number of ejected K-shell electrons for each γ-quantum interacting with the K-shell)

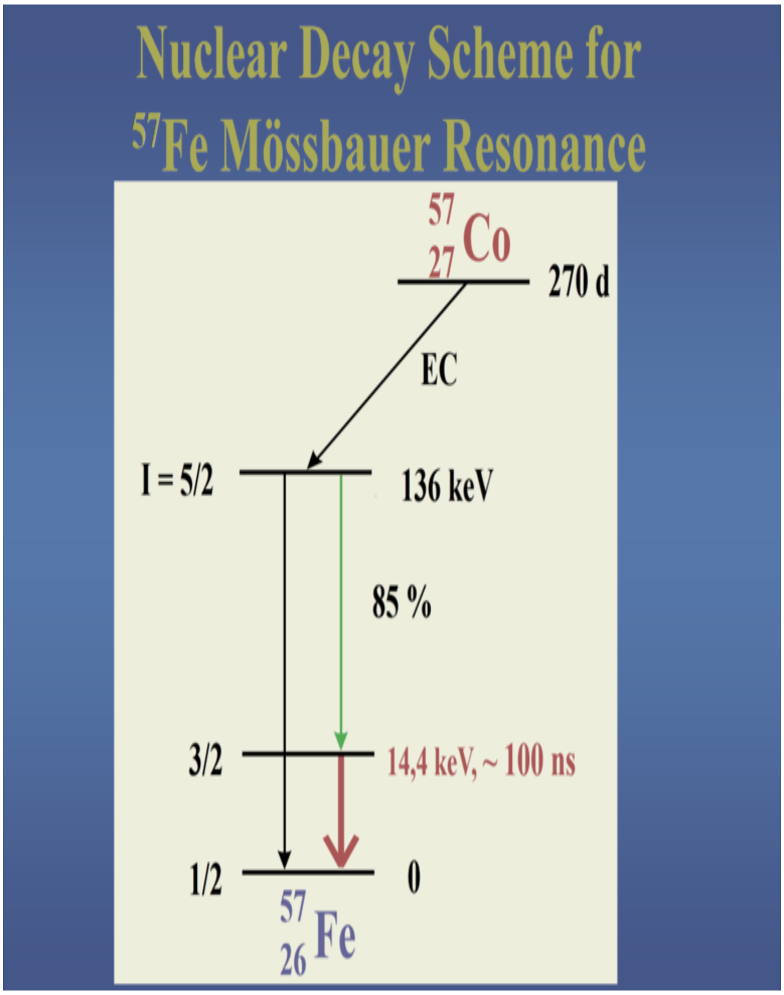


Figure 15: ^{57}Fe Mossbauer Spectroscopy

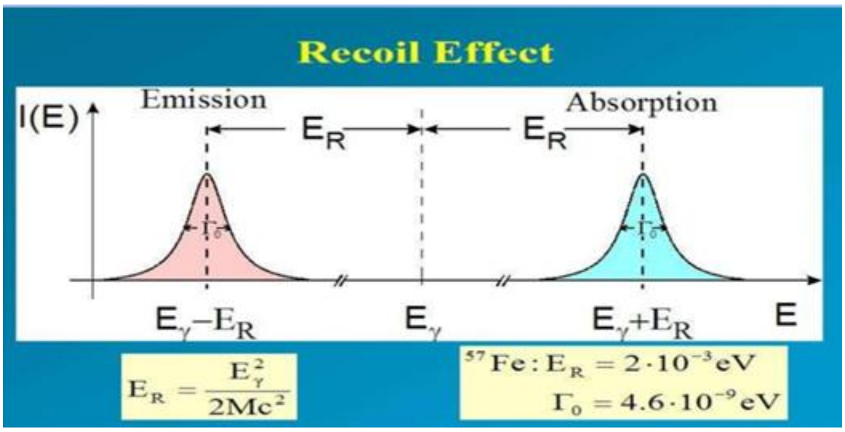


Figure 16: Recoil Effect for Emission and Absorption

- The figure shows the intensity I(E) as a function of the transition energy for emission and absorption of gamma quanta.

- The width at half maximum of the spectral line is called the natural line width Γo and is determined by the mean life time $\tau = t_{1/2} / \ln 2 = 1.43 \times 10^{-7}$ s for the 14.4 keV level of ^{57}Fe, for which $\Gamma o = h/2\pi\tau = 4.6 \times 10^{-9}$eV.

- The symbol Γo is used here for the natural linewidth to differentiate from the experimental line width, which in actual experiments is always broader than the natural line width due to various broadening effects.

- If a free atom or molecule with mass m emits or absorbs a gamma quantum of energy Eγ , a linear momentum with recoil energy E_R is imparted to the atom and molecule, respectively, which according to the formula given in the Figure (c = velocity of light) amounts to 2×10^{-3} eV and thus is six orders of magnitude larger than the transition energy Eγ .

- The recoil effect reduces the transition energy by E_R for the emission process and increases the transition energy by E_R for the absorption process.

- Thus the emission and the absorption lines are shifted away from each other by $2E_R \approx 10^6$ Γo , and in view of the huge difference between Γo and E_R an appreciable overlap resonance is not possible.

- This means, that the Mössbauer effect cannot be observed for freely moving atoms or molecules, i.e. in gaseous or liquid state.

- If the emitting and absorbing nuclei were in identical chemical environment then the transition energies would be equal and nuclei resonance
- But if chemical environment is different, it will cause the shift in nuclear energy less.
- To bring the nuclei in resonance the energy of Gamma (γ)- rays is slightly changed by Doppler Effect

Mossbauer Effect:

- It involves the resonant and recoil-free emission and absorption of Gamma radiation by atomic nuclei bound in a solid
- In the Mossbauer effect, a narrow resonance for nuclear gamma emission and absorption results from the momentum of recoil being delivered to a surrounding crystal lattice rather than to the emitting or absorbing nucleus alone
- When this occurs, no gamma energy is lost to the kinetic energy of recoiling nuclei at either emitting or absorbing end of a Gamma transition: emission and absorption occurs at the same energy, resulting in strong, resonant absorption
- It should be noted that Mossbauer effect cannot be observed in liquids and gases because the recoil energy cannot be dissipated in these state in matters

Doppler Effect:

- Doppler effect or Doppler Shift is the change in frequency or wavelength of a wave in relation to an observer who is moving relative to the wave source
- A common example is the change of pitch heard when a vehicle sounding a horn approaches and recedes from an observer
- Compared to the emitted frequency, the received frequency is a higher during the approach, identical at the instant of passing by and lower during the recession

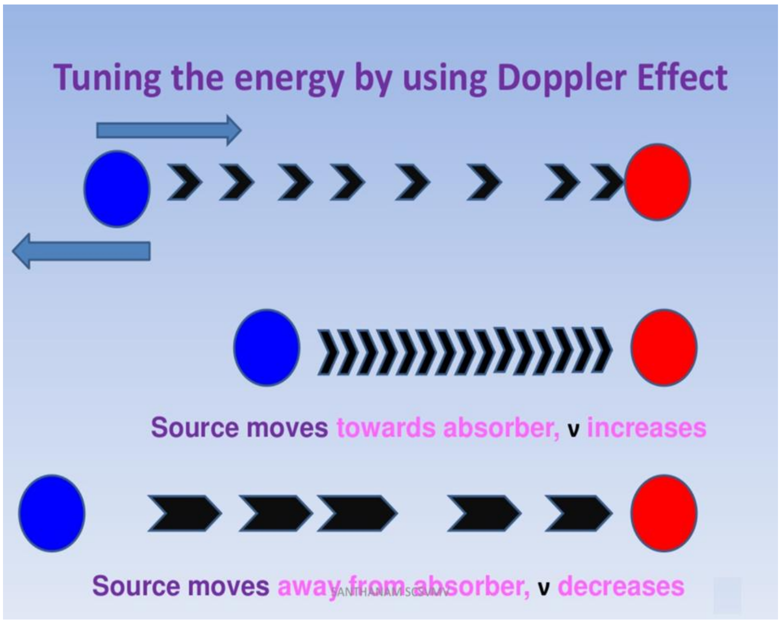


Figure 17: Doppler Effect

Instrumentation

Driver or Absorber: It is used to move the source relative to sample

Source: ^{57}Co source for Gamma ray emission and generally kept at room temperature

Collimator: It is used to narrow the gamma rays

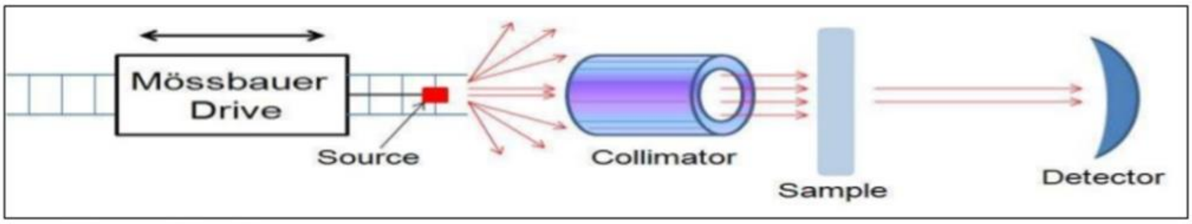


Figure 18: Block diagram of Mossbauer Spectrophotometer

Sample:

- It contains the sample to be analysed
- Must be in solid phase and in crystalline structure
- Usually requires a large amount of sample
- Applied as a thin layer on sample holder and irradiated

Selecting a sample:

- Excited state should be of relatively low energy
- Small change of energy between ground and excited state
- Too large a change of energy results in no resonant emission
- Relatively long lasting life of excited state

Detector:

- Choice of detector depends on Gamma ray energies
- Cannot be seen using traditional examination methods of electromagnetic radiation

- Observes effect of Gamma Rays on a material that absorbs them

Resonance detectors

- Distance and angle of detector is crucial
- Two types:

1. Gas filled and 2. Scintillation

1. ***Gas filled:***
   - Sensitive volume of gas between two electrodes
   - Not often used

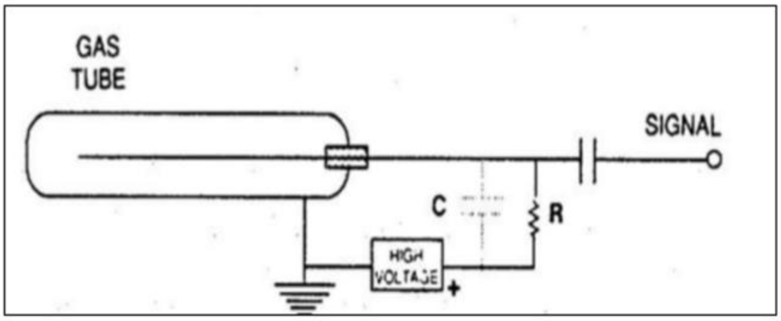


Figure 19: Gas filled Detector

2. ***Scintillation:***
   - Sensitive material is luminescent material
   - Gamma rays interact with luminescent materials
   - Gamma rays are detected by an optical detector
   - Usually used detector

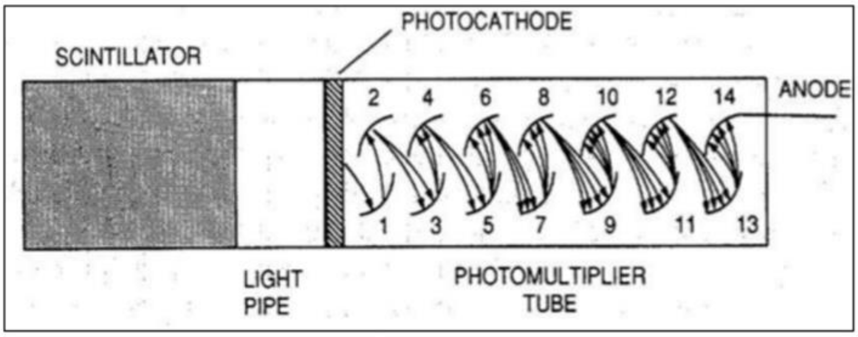


Figure 20: Scintillator Detector

Components of Mossbauer Spectrometer

- The schematic diagram shows the main components of a Mössbauer spectrometer.

- ***Source:*** For ^{57}Fe spectroscopy, ^{57}Co/Rh, is mounted on the shaft of a vibrator at room temperature

- ***Absorber (sample under study):*** Thermostated in a cryostat for cooling down to liquid nitrogen or liquid helium temperatures, or for controlled heating in an oven.

- ***Detector:*** The γ-rays are detected by a scintillation counter, gas proportional counter detector. The pulses from the detector are amplified and pass through a discriminator¸ where most of the non-resonant background radiation is rejected, and finally are fed into the analyser

- ***Analyser (e.g. a computer):*** with several hundred channels, which is synchronised with the vibrator making use of the so-called feed-back control system. A constant frequency clock synchronises a voltage waveform (usually triangular yielding a linear Doppler velocity scale) which serves as a reference signal to the servo-amplifier controlling the electromechanical vibrator.

- ***Amplifier:*** The difference between the monitored signal and the reference signal is amplified and drives the vibrator at the same frequency

- ***Collector:*** The incoming γ-counts are collected in their corresponding channels during the sequential accessing e.g. 50 times per second, until satisfactory resolution is reached.

- **Calibration:** The measured Mössbauer spectrum is analysed using special least squares fitting programs.

Hyperfine Interactions

Three quantities called hyperfine interactions are studied:

- Isomer shift
- Quadrupole splitting
- Magnetic splitting (Nuclear Zeeman splitting/ Magnetic hyperfine splitting)

Isomer (chemical) shift:

- Arises due to the non-zero volume of the nucleus and the electron charge density due to s-electrons within it
- This leads to a monopole (coulomb) interaction, altering the nuclear energy levels
- Any difference in s-electron environment between the source and absorber that produces a shift in the resonance energy of the transition
- This shifts the whole spectrum positively or negatively depending upon s-electron density and sets the centroid of the spectrum
- As the shift cannot be measured directly, it is quoted relative to a known absorber.
- Example: ^{57}Fe Mossbauer spectra will often be quoted relative to alpha-iron at room temperature
- It is useful for determining valency states, ligand bonding states, electron shielding and electron drawing power of electronegative groups.
- Example: Electron configurations for Fe^{+2} and Fe^{+3} are $3d^6$ and $3d^5$ respectively
- Ferrous ions have less s-electrons at the nucleus due to greater screening of the d-electrons
- Thus ferrous ions have larger positive isomer shift than the ferric ions

Quadrupole splitting

- Nuclei in States with the angular momentum quantum number $I > 1/2$ have a non-spherical charge distribution
- This produces a nuclear quadrupole moment
- In presence of an asymmetrical electric field (produced by an asymmetric electronic charge distribution or ligand arrangement), this splits the nuclear energy levels

- The charge distribution is characterized by a single quantity called Electric Field Gradient (EFG)
- In case of an isotope with a I > 3/2 ES, such as ^{57}Fe or ^{119}Sn, the ES is split into two substates $m_I = \pm \frac{1}{2}$ and $m_I = \pm 3/2$. The figure gives a 2 line spectrum of doublet

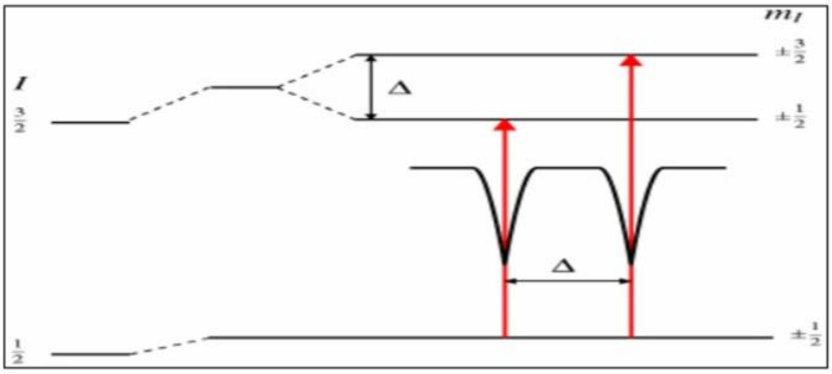


Figure 21: Quadrapole Splitting

Magnetic splitting

- In presence of magnetic field (MF), the nuclear spin moment experiences are dipolar interact with the MF, i.e, Zeeman splitting
- There are many sources of MFs that can be experienced by the nucleus
- Total effective MF at the nucleus, Beff is given by,
- $B_{eff} = (B_{contact} + B_{orbital} + B_{Dipolar}) + B_{applied}$
- The first three terms being due to the atom’s own partially filled electron shells
- $B_{contact}$ is due to spin on those electrons polarizing the spin density at the nucleus
- $B_{orbital}$ is due to the orbital moment on those electrons
- $B_{Dipolar}$ is the bipolar field due to spin of those electrons
- This MF splits nuclear levels with a spin of 1 into (2I+1) substates
- This is shown in the figure for ^{57}Fe
- These interactions, Isomer shift, Quadrupole splitting and magnetic splitting, alone or in combination are the primary characteristics of many Mossbauer spectra
- Mossbauer Spectroscopy is useful analytical tool for studying a variety of systems and phenomena

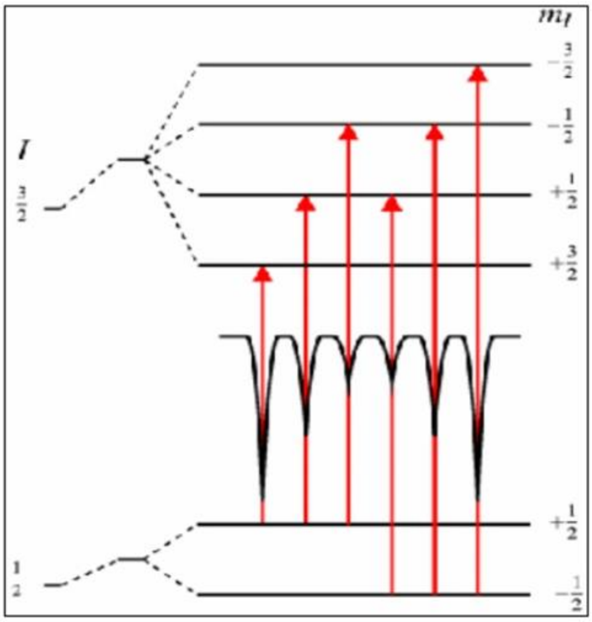


Figure 22: Magnetic Splitting

Mossbauer spectra of high and low-spin Fe(II) and Fe(III) compounds

- In each spectrum the more intense quadrupole doublet marked in red corresponds to the two high spin Fe(III)-HS ions and the less intense doublet is for the one high spin Fe(II) ion.
- The ratio of the area fractions of Fe(III) to Fe(II) is close to 2 at low temperatures.
- Towards higher temperatures it tends to become larger than 2, which is due to the larger Lamb-Mössbauer factor of Fe(III) compared to that of Fe(II).
- At room temperature, complex C shows a single doublet that is a time-averaged signal for all three Fe ions in the Fe_3O complex.

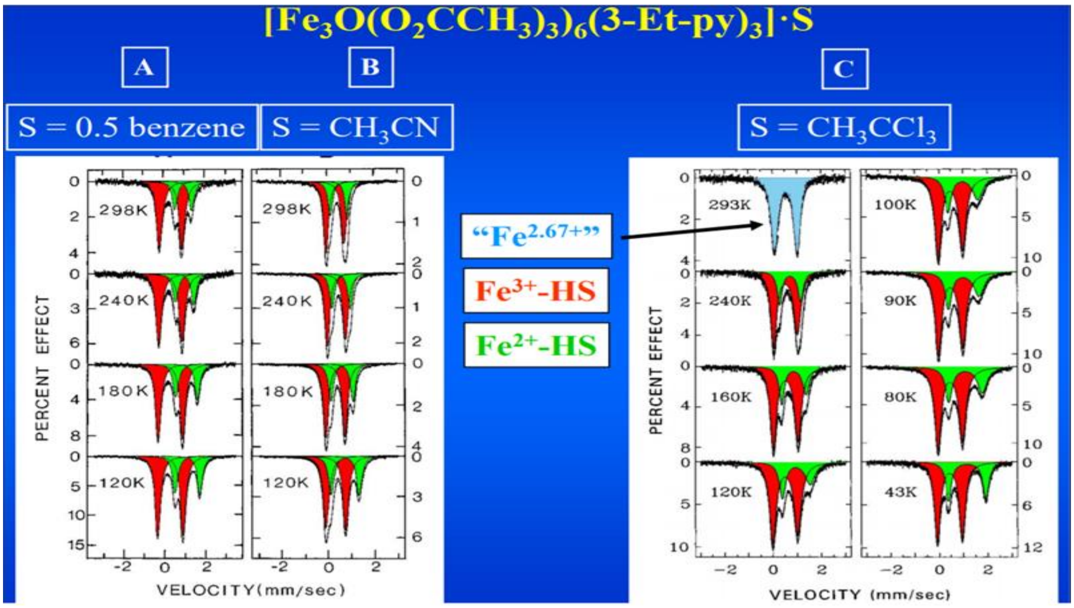
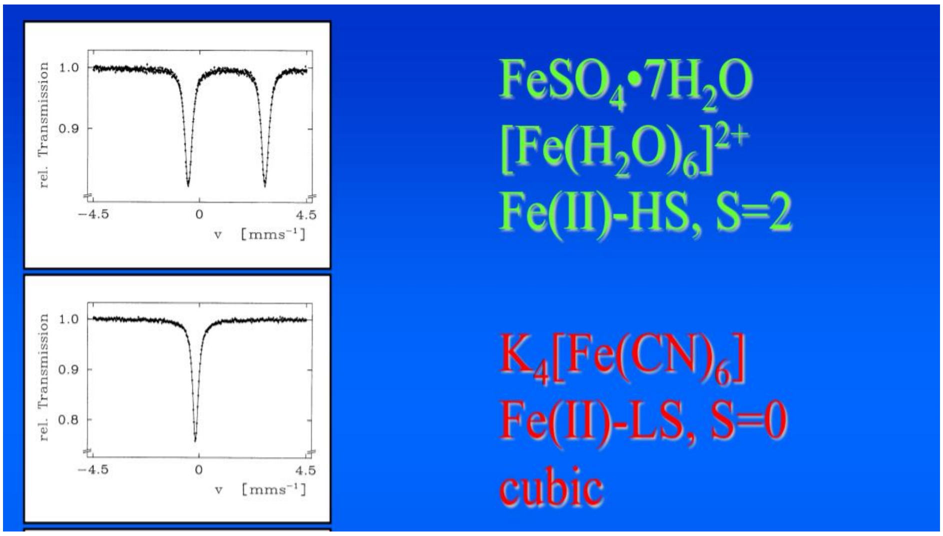


Figure 23: Mossbauer spectra of high spin Fe(II) and Fe(III) compounds



$FeSO_4 \cdot 7H_2O$

$[Fe(H_2O)_6]^{2+}$

Fe(II)-HS, S=2

$K_4[Fe(CN)_6]$

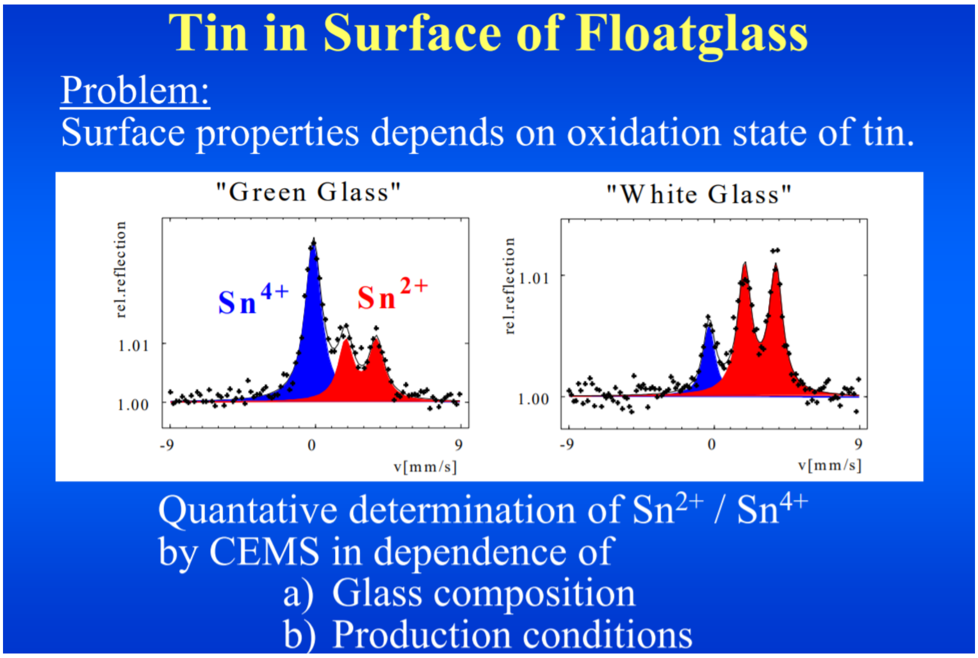
Fe(II)-LS, S=0

cubic

Figure 24: Mossbauer spectra of high and low-spin Fe(II) compounds

Discovering oxidation states of Sn - Sn(II), Sn(IV) compounds

- Tin is usually an additive in the production of floatglass.
- It has been found that the surface properties of floatglass depends on the oxidation state of tin.
- In order to have control over the surface properties it is necessary to control the oxidation state of tin, which is difficult to do with conventional methods.
- ^{119}Sn Mössbauer spectroscopy using the conversion electron detection.
- The two spectra shown here confirm convincingly that the oxidation state of tin in floatglass can be determined qualitatively and quantitatively.
- The production of floatglass can now be conducted considering various parameters like glass composition and production conditions.



Tin in Surface of Floatglass

Problem:
Surface properties depends on oxidation state of tin.

Quantative determination of Sn^{2+} / Sn^{4+}
by CEMS in dependence of
a) Glass composition
b) Production conditions

Figure 25: Mossbauer spectra of surface of Floatglass in determining the oxidation states of Sn - Sn(II), Sn(IV) compounds