Spectroscopy

T.Y.B.Sc. Chemistry

Sem VI

ELECTROMAGNETIC SPECTRUM

Most organic spectroscopy uses **electromagnetic energy, or radiation,** as the physical stimulus.

Electromagnetic energy (such as visible light) has no detectable mass component. In other words, it can be referred to as “pure energy.”

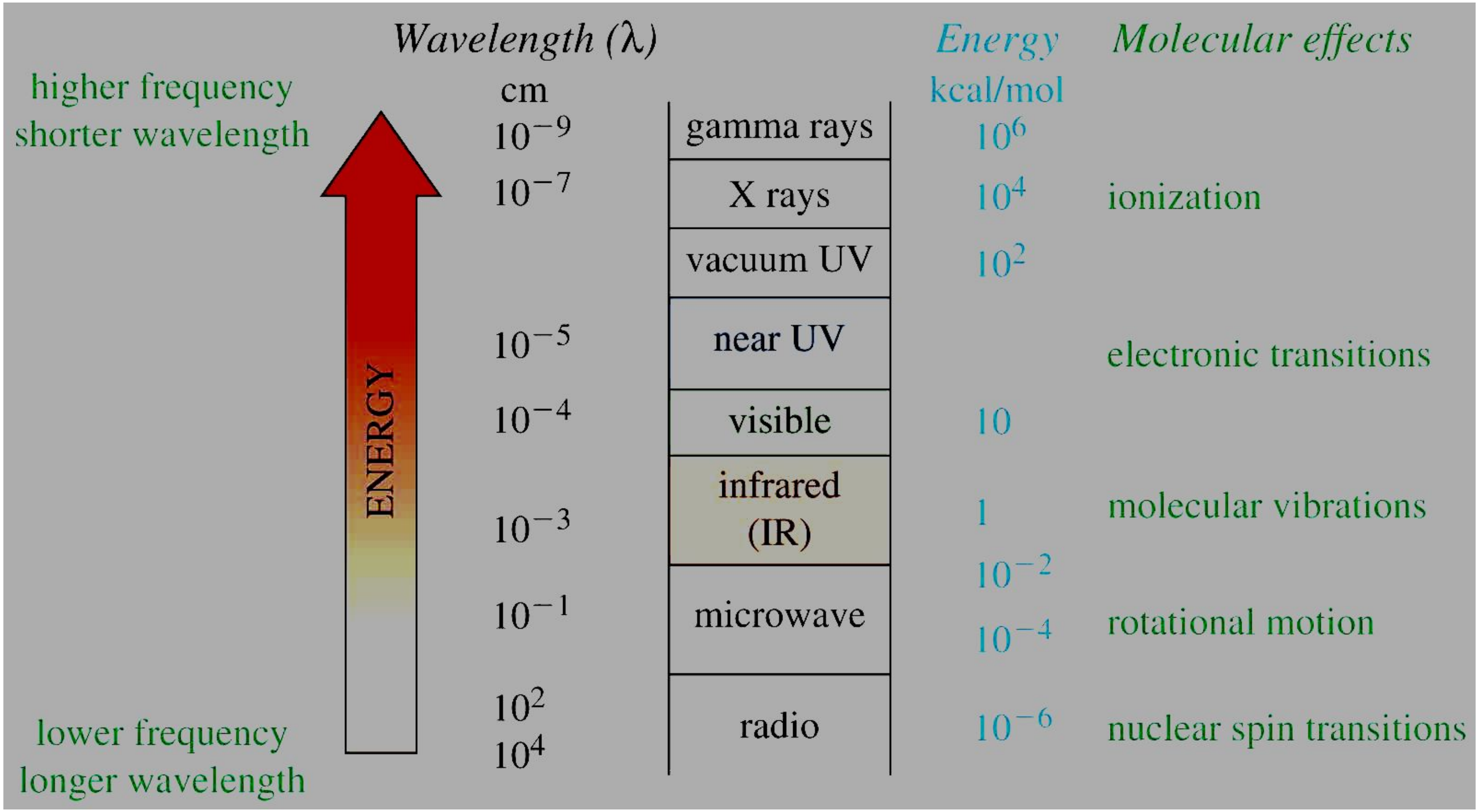
Other types of radiation such as alpha rays, which consist of helium nuclei, have a detectable mass component and therefore cannot be categorized as electromagnetic energy.

The important parameters associated with electromagnetic radiation are:

- **Energy (E)**: Energy is directly proportional to frequency, and inversely proportional to wavelength, as indicated by the equation below.
- **Frequency (μ)**
- **Wavelength (λ)**

$$\boxed{E = h\mu}$$

EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES

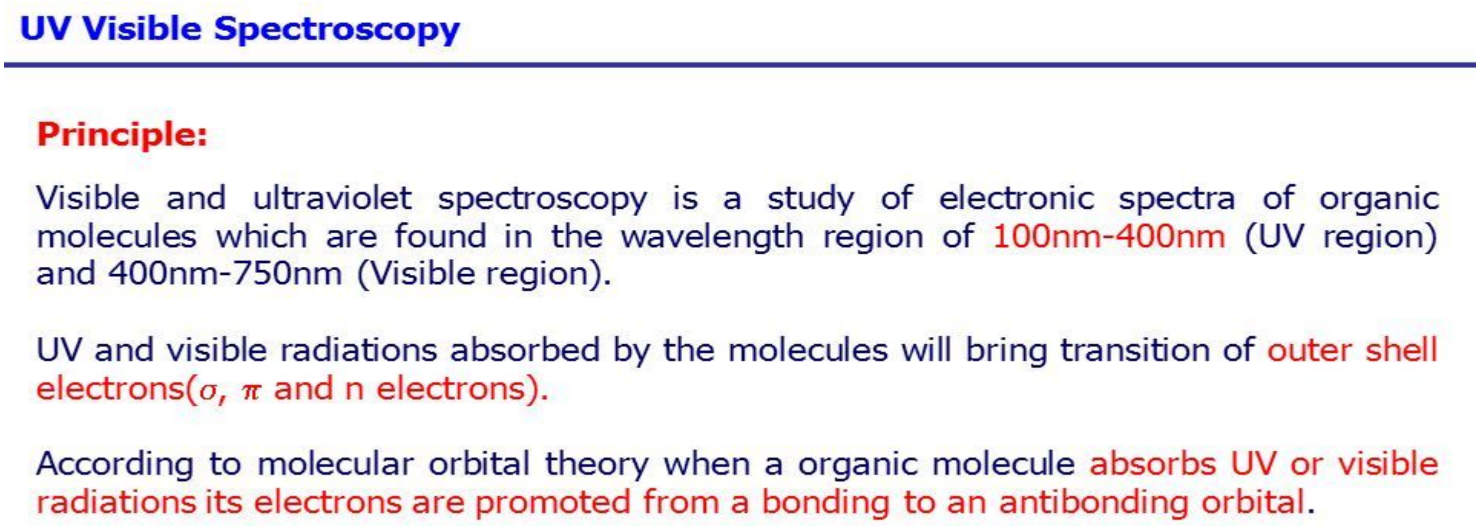


Wavelength (λ) cm		*Energy* kcal/mol	*Molecular effects*
10^{-9}	gamma rays	10^{6}	
10^{-7}	X rays	10^{4}	ionization
	vacuum UV	10^{2}	
10^{-5}	near UV		electronic transitions
10^{-4}	visible	10	
10^{-3}	infrared (IR)	1	molecular vibrations
10^{-1}	microwave	10^{-2} 10^{-4}	rotational motion
10^{2} 10^{4}	radio	10^{-6}	nuclear spin transitions

Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

UV Visible Spectroscopy

Basic Theory



UV Visible Spectroscopy

Principle:

Visible and ultraviolet spectroscopy is a study of electronic spectra of organic molecules which are found in the wavelength region of 100nm-400nm (UV region) and 400nm-750nm (Visible region).

UV and visible radiations absorbed by the molecules will bring transition of outer shell electrons(σ, π and n electrons).

According to molecular orbital theory when a organic molecule absorbs UV or visible radiations its electrons are promoted from a bonding to an antibonding orbital.

UV / VISIBLE SPECTROSCOPY

UV Radiation – Wavelength range 220 - 380nm

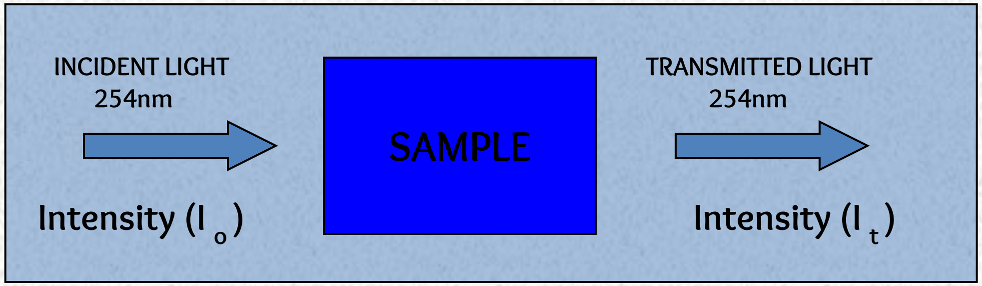
VISIBLE Radiation – Wavelength range 380 - 780nm

Substances can absorb varying amounts of UV and/or Visible radiation at particular wavelengths – Coloured compounds absorb energy in both UV and visible region of the electromagnetic spectrum.

Substances can be liquids or solids and measurements are made with instruments called SPECTROPHOTOMETERS or SPECTROMETERS.

Modern instruments can be coupled to microscopes which allow solid samples and very small samples of solids and liquids to be analysed both qualitatively and quantitatively.

UV / VISIBLE SPECTROSCOPY - THEORY



INCIDENT LIGHT
254nm

Intensity (I_o)

SAMPLE

TRANSMITTED LIGHT
254nm

Intensity (I_t)

- **If a particular wavelength of UV or Visible radiation can be isolated from the source and passed through a sample which can ABSORB some of the radiation then the TRANSMITTED light intensity (I_t) will less than the INCIDENT light intensity (I_o).**

- **The amount of light transmitted with respect to the incident light is called TRANSMITTANCE (T) ie.,**

$$T = \frac{I_t}{I_o}$$

- **Sample can absorb all or none of the incident light and therefore**
- **transmittance often quoted as a percentage eg.,**

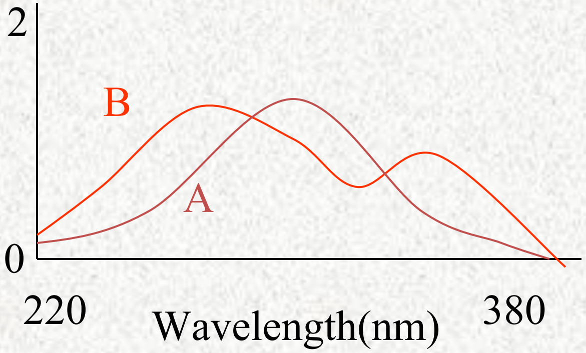
$$\% \ T = \frac{I_t}{I_o} \quad X\ 100$$

UV / VISIBLE SPECTROSCOPY - THEORY

ABSORBANCE $A = -\log_{10} T$

$$A = -\log_{10} \left(\frac{I_t}{I_o} \right)$$

$$A = \log_{10} \left(\frac{I_o}{I_t} \right)$$



For of %T = 0 and 100 the corresponding absorbance values will be 0 and 2 respectively

By plotting Absorbance vs wavelength an ABSORBANCE SPECTRUM is generated. The absorbance spectra for the same compounds A and B are shown.

With the advantage that absorbance measurements are usually linear with Concentration, absorbance spectra are now used

The possible electronic transitions are

1. $\sigma \rightarrow \sigma^*$ transition
2. $\pi \rightarrow \pi^*$ transition
3. $n \rightarrow \sigma^*$ transition
4. $n \rightarrow \pi^*$ transition
5. $\sigma \rightarrow \pi^*$ transition
6. $\pi \rightarrow \sigma^*$ transition

1 • σ → σ* transition

- σ electron from orbital is excited to corresponding anti-bonding orbital σ*.

- The energy required is large for this transition.

- e.g. Methane (CH_4) has C-H bond only and can undergo σ → σ* transition and shows absorbance maxima at 125 nm.

2. π → π* transition

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π*.
- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo π → π* transitions.
- e.g. Alkenes generally absorb in the region 170 to 205 nm.

3 • n → σ* transition

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of n → σ* transition.

- These transitions usually requires less energy than σ → σ* transitions.

- The number of organic functional groups with n → σ* peaks in UV region is small (150 – 250 nm).

4

• n → π^* transition

- An electron from non-bonding orbital is promoted to anti-bonding π^* orbital.

- Compounds containing double bond involving hetero atoms ($C=O$, $C\equiv N$, $N=O$) undergo such transitions.

- n → π^* transitions require minimum energy and show absorption at longer wavelength around 300 nm.

5

- $\sigma \rightarrow \pi^*$ transition

&

- $\pi \rightarrow \sigma^*$ transition

6

- These electronic transitions are forbidden transitions & are only theoretically possible.

- Thus, $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ electronic transitions show absorption in region above 200 nm which is accessible to UV-visible spectrophotometer.

- The UV spectrum is of only a few broad of absorption.

3| Solvent can also absorb in UV-vis spectrum.

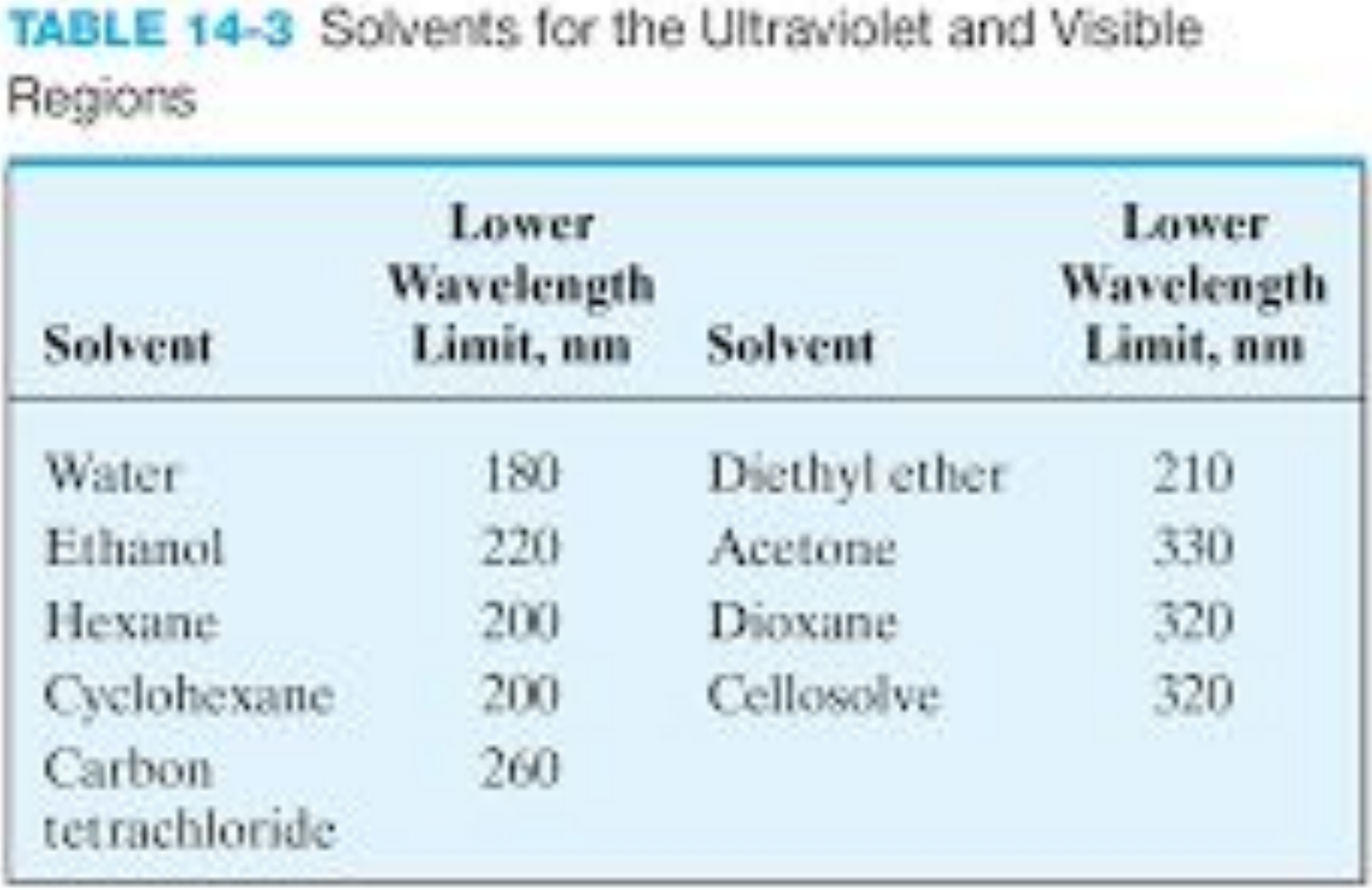
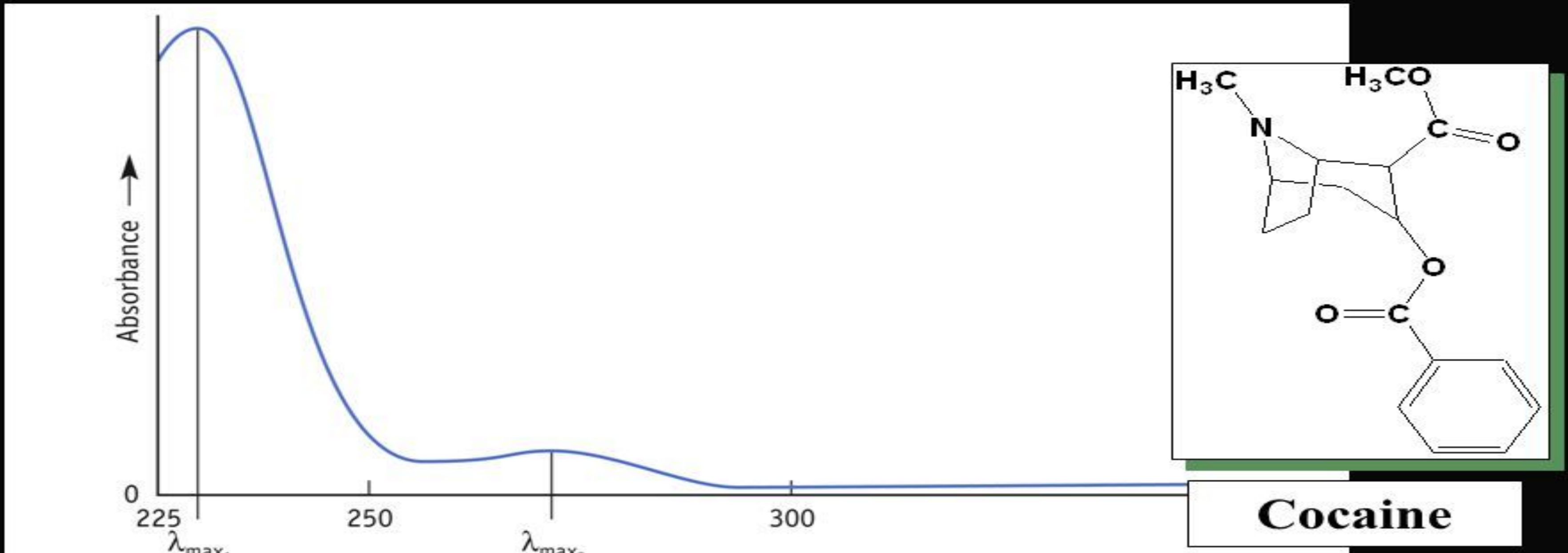


TABLE 14-3 Solvents for the Ultraviolet and Visible Regions

Solvent	Lower Wavelength Limit, nm	Solvent	Lower Wavelength Limit, nm
Water	180	Diethyl ether	210
Ethanol	220	Acetone	330
Hexane	200	Dioxane	320
Cyclohexane	200	Cellosolve	320
Carbon tetrachloride	260		

Nature of UV visible absorption Spectra

UV-Visible Spectroscopy



Cocaine

The aqueous ultraviolet absorption spectrum of cocaine hydrochloride

Spectrum recorded by Andrew Jackson, Staffordshire University, UK.

Chromophore

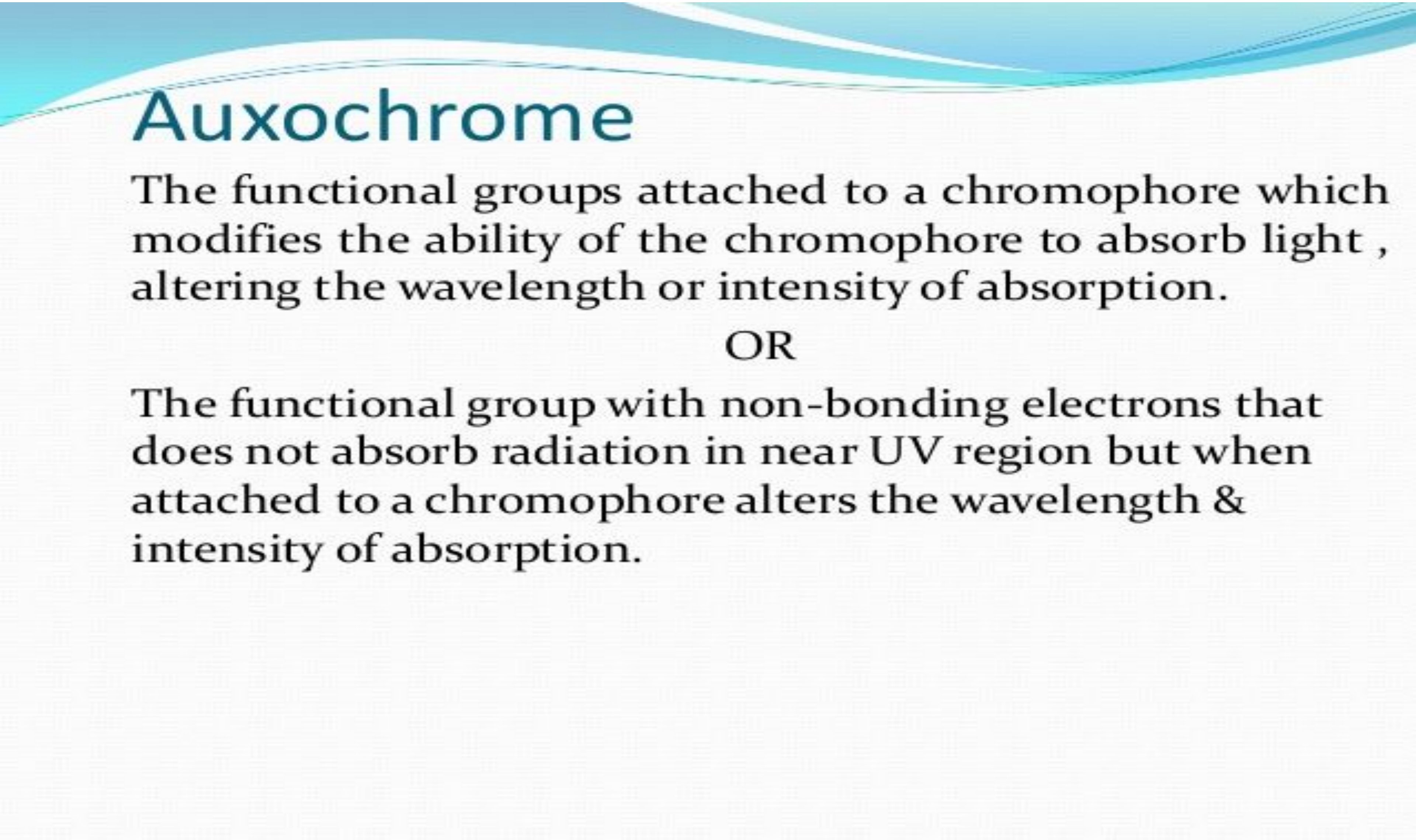
The part of a molecule responsible for imparting color, are called as chromospheres.

OR

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

e.g. NO_2, N=O, C=O, C=N, C≡N, C=C, C=S, etc

Concept Chromophore and Auxochrome



Auxochrome

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

OR

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

Some terms related to UV-Vis spectrophotometer:

1- Bathochromic shifts:

The shift of absorption to a longer wavelength due to substitution or solvent effect **(red shift)**

2- Hypsochromic shifts:

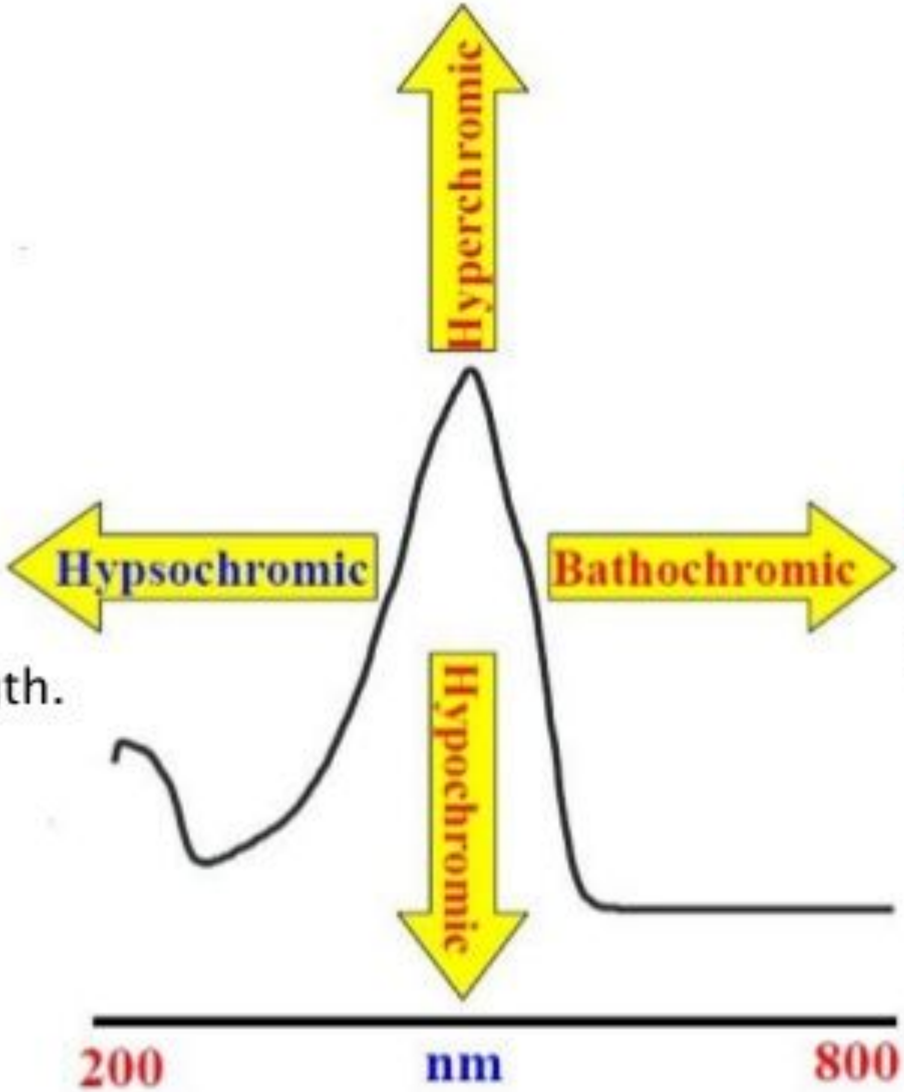
The shift of absorption to a shorter wavelength due to substitution or solvent effect **(blue shift)**

3- Hyperchromic effect:

It is increase in absorption intensity.

4- Hypochromic effect:

It is simply a decrease in the absorption intensity.

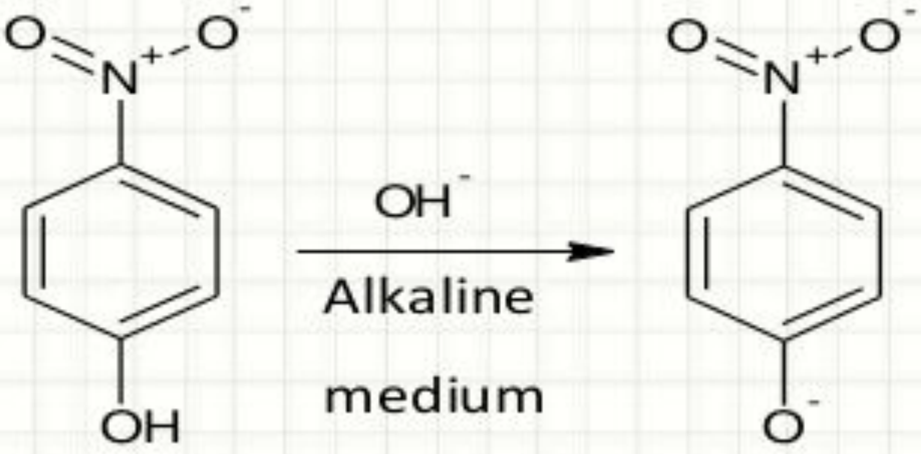


Blue Shift
(Hypsochromic)
Peaks shift to
shorter wavelength.

Red Shift
(Bathochromic)
Peaks shift to longer
wavelength.

1 • Bathochromic Shift (Red Shift)

- In alkaline medium, p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.



p-nitrophenol

λ_{max} = 255 nm λ_{max} = 265 nm

2 • Hypsochromic Shift (Blue Shift)

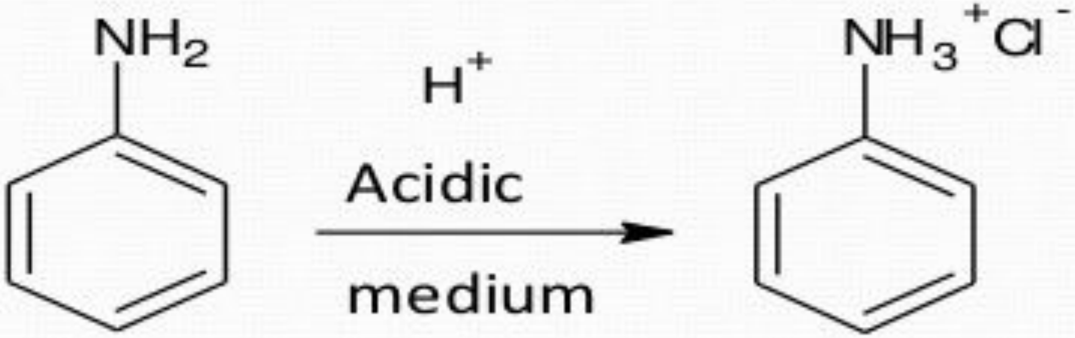
- When absorption maxima (λ_{max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.

- The effect is due to presence of an group causes removal of conjugation or by the change of solvent.

2

• Hypsochromic Shift (Blue Shift)

- Aniline shows blue shift in acidic medium, it loses conjugation.



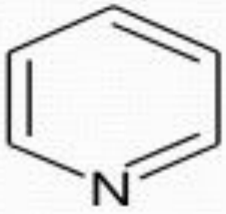
Aniline

λ_{max} = 280 nm

λ_{max} = 265 nm

3 • Hyperchromic Effect

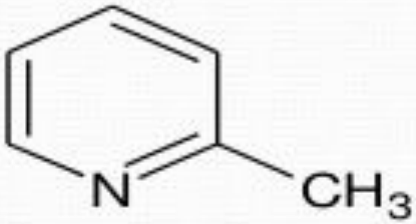
- When absorption intensity (ε) of a compound is increased, it is known as hyperchromic shift.
- If auxochrome introduces to the compound, the intensity of absorption increases.



Pyridine

$\lambda_{max} = 257$ nm

$\varepsilon = 2750$



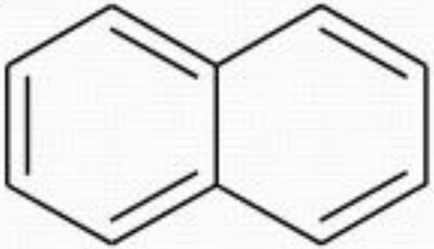
2methylpyridine

$\lambda_{max} = 260$ nm

$\varepsilon = 3560$

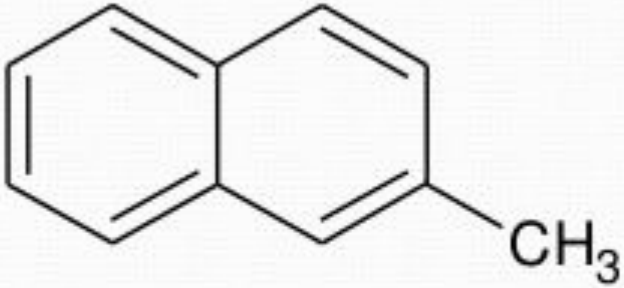
4 • Hypochromic Effect

- When absorption intensity (ε) of a compound is decreased, it is known as hypochromic shift.



Naphthalene

$\varepsilon = 19000$



2-methyl naphthalene

$\varepsilon = 10250$

Chromophore

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

OR

The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to n → π* & π → π* transitions.

e.g. NO_2, N=O, C=O, C=N, C≡N, C=C, C=S, etc

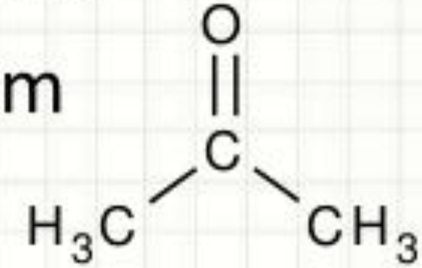
Chromophore

3. Conjugation of C=C and carbonyl group shifts the λ_{max} of both groups to longer wavelength.

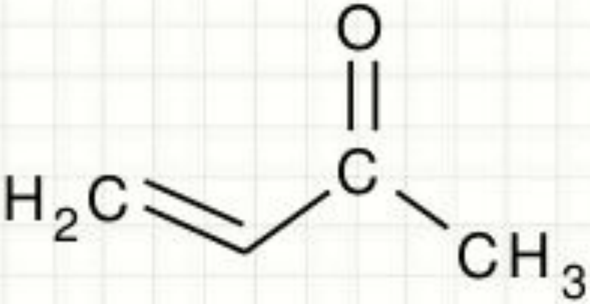
e.g. Ethylene has λ_{max} = 171 nm

Acetone has λ_{max} = 279 nm

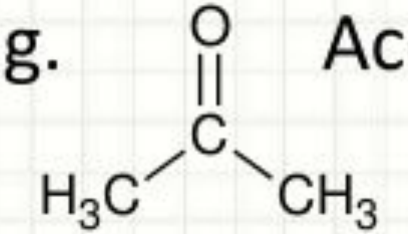
$H_2C{=}CH_2$



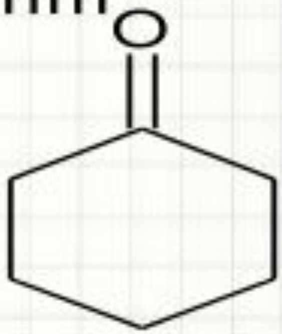
Crotonaldehyde has λ_{max} = 290 nm



Chromophore

e.g. 

Acetone which has λ_{max} = 279 nm

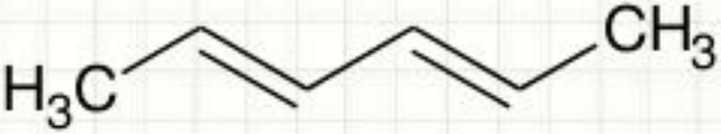


and that cyclohexane has λ_{max} = 291 nm.

When double bonds are conjugated in a compound λ_{max} is shifted to longer wavelength.

e.g. 1,5 - hexadiene has λ_{max} = 178 nm

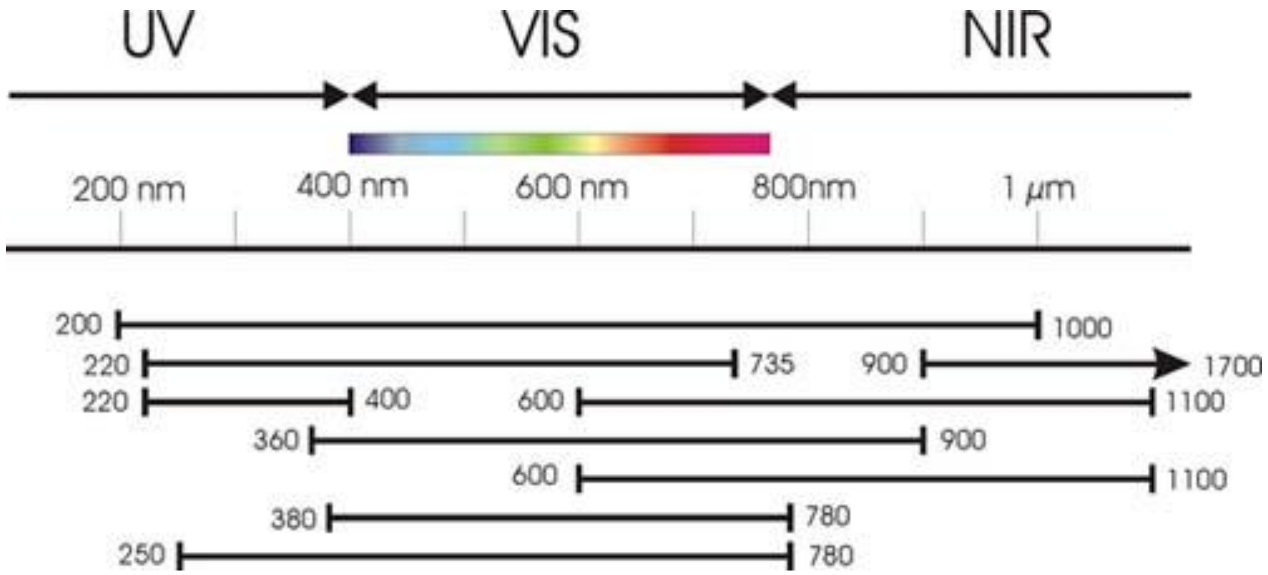
2,4 - hexadiene has λ_{max} = 227 nm



INFRA RED SPECTROSCOPY

Principle of IR

- In the context of infra red spectroscopy the term "infra red" covers the range of the electromagnetic spectrum between 0.78 and 1000 mm.



Wavenumbers

- wavelength is measured in "wavenumbers„
- wavenumber = 1 / wavelength
- in centimetersIt is useful to divide the infra red region into three sections; *near*, *mid* and *far* infra red;

Regions of wavelength range

- **Wavenumber range** (cm-1)
- Near0.78 - 2.51   2800 – 4000
- Middle2.5 – 504000- 200
- Far50 -1000200 - 10
- The most useful I.R. region lies between 4000 - 670cm-1.

Theory of infra red absorption

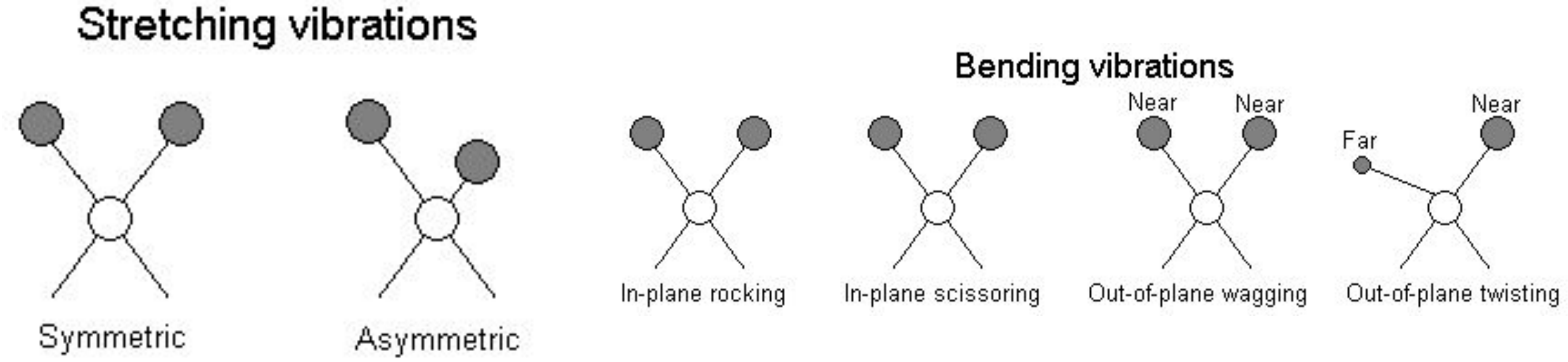
- IR radiation does not have enough energy to induce electronic transitions as seen with UV.
- Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states.
- For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule.

Molecular rotations

- Rotational transitions are of little use to the spectroscopist.
- Rotational levels are quantized, and absorption of IR by gases yields line spectra.
- However, in liquids or solids, these lines broaden into a continuum due to molecular collisions and other interactions.

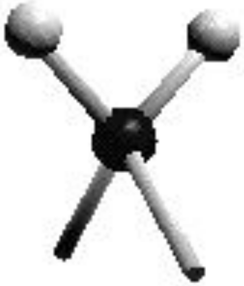
Molecular vibrations

- The positions of atoms in a molecules are not fixed; they are subject to a number of different vibrations.

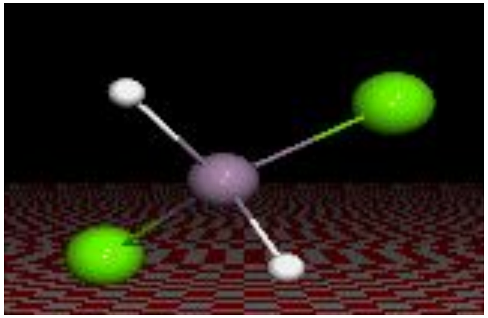


symmetric

asymmetric



In-plane scissoring



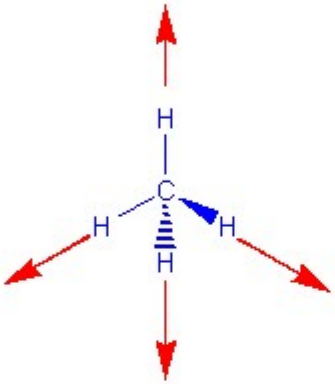
Out-of-plane twisting

In-plane rocking

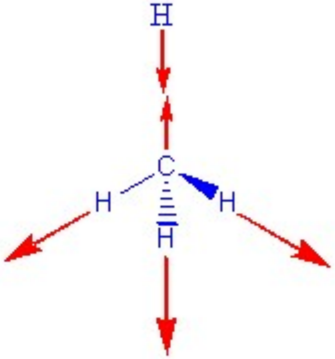
Out-of-plane wagging

Another Illustration of Molecular Vibrations

The stretching modes of CH_4

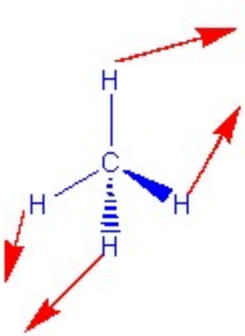


Symmetrical stretch

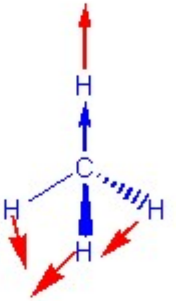


Asymmetric stretch-

The bending modes of CH_4



Symmetric bend



Asymmetric bend

1. Coupling interaction

- It is expected that there is a stretching absorption frequency for an isolated C-H bond. But in case of Methylene(-CH2-) group, two absorption occurs which corresponds to symmetric & asymmetric vibrations.
- Asymmetric vibration always takes place at high wave number compared with symmetric vibration.
- These are knows as coupled vibrations because vibration occurs at different frequencies than that required for an isolated C-H stretching.

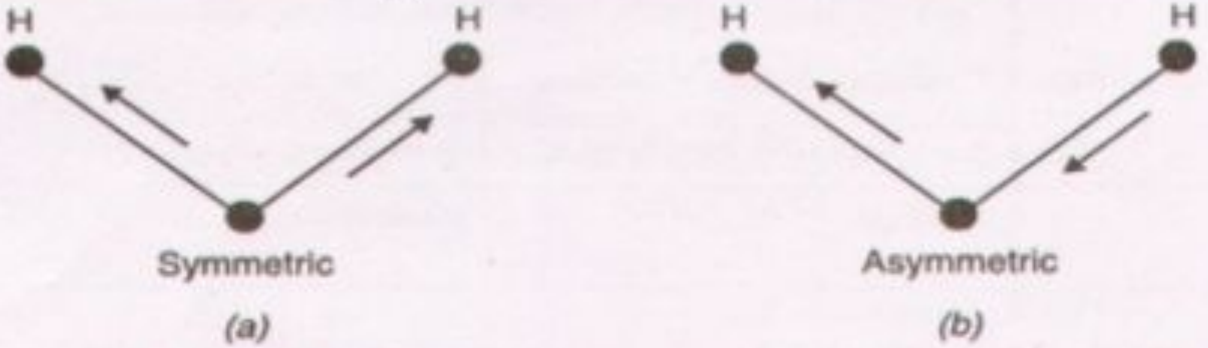


Fig. 3.25 : Stretching vibrations in methylene group.

Selection Rules

- During the transition, there must be a change in the **dipole moment** of the molecule:
  - if there is a large change, the light / molecule interaction is strong and many photons are absorbed:
    large area or intense bands → intense colour
  - if there is a small change, the light / molecule interaction is weak and few photons are absorbed:
    low area or weak bands → weak colour
  - If there is no change, there is no interaction and **no** photons are absorbed

Selection rules tell us which transitions give no change in dipole moment and hence which will have zero intensity

NATURE OF IR SPECTRA

- IR spectrum is a graph of band intensities on ordinate versus position of band on abscissa.
- Band intensities can be given in terms of transmittance(T) or absorbance(A).
- Position of band can be expressed in terms of wave number (n) or wavelength(λ).
- In IR spectra, wave numbers (n) are used instead of wavelength (λ) for mentioning the characteristic peak as this unit has advantage of being linear with energy of radiation (E) .

$E = h\,c/\lambda$ or, $E = h\,c\,n$

[$n = 1/\lambda$, c= velocity of light, h= Planck's constant]

Infrared Spectra of Some Common Functional Groups

- n-Alkanes

  - look for stretching and bending of C–H and C–C bonds
    - C–C bends: ca. 500 cm^{-1} (out of spectral window)
    - C–C stretches: 1200–800 cm^{-1}, weak bands not of value for interpretation (fingerprint)

  More characteristic
    - C–H stretches: occurs from 3000 - 2840 cm^{-1}

      CH_3: 2962 cm–1, asymmetrical stretch
      2872 cm–1, symmetrical stretch
      CH_2: 2926 cm–1, asymmetrical stretch
      2853 cm–1, symmetrical stretch

    - C–H bends:

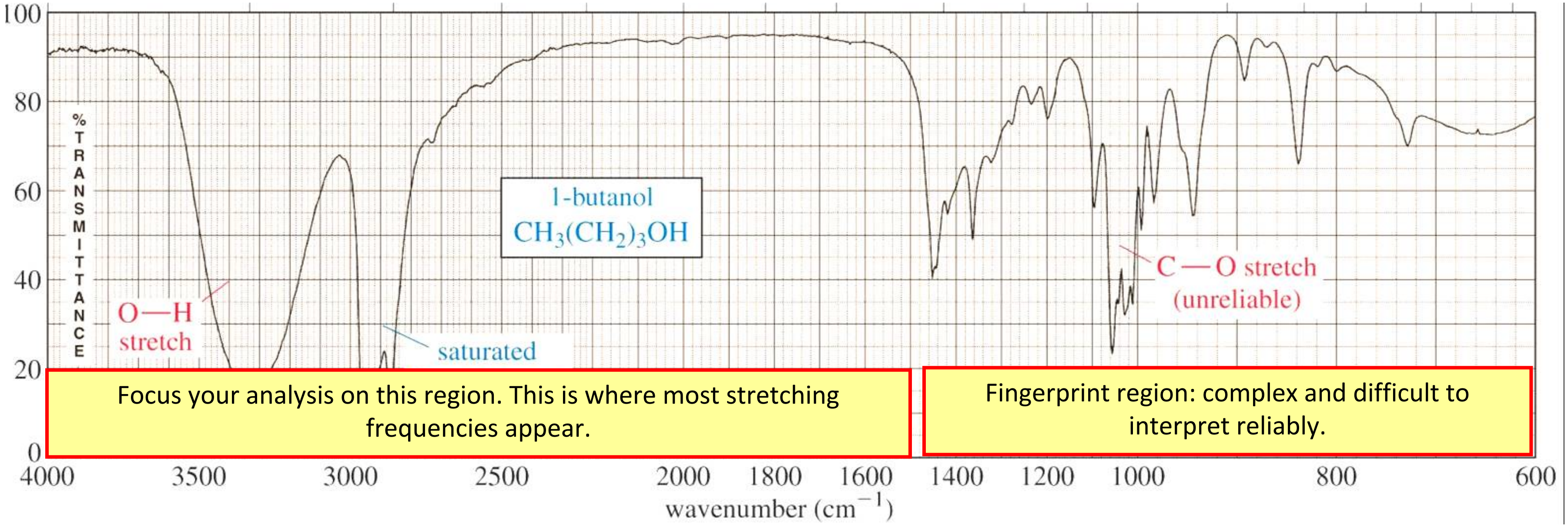
      CH_3: ca. 1375 cm–1
      CH_2: ca. 1465 cm–1

Table 10.1 Typical vibrational frequencies of functional groups

Bond	Molecule	Wavenumber (cm^{-1})
C–O	Alcohols, ethers, esters, carboxylic acids, etc.	1300 – 1000
C=O	Aldehydes, ketones, esters, carboxylic acids	1750 – 1680
C=O	Amides	1680 – 1630
N–H (Stretching)	Amines and amides	3500 – 3100
–N–H (Bending)	Amines and amides	1640 – 1550
O–H	Alcohols	3650 – 3200
C–N	Amines	1350 – 1000
S–H	Mercaptans	2550

THE FINGERPRINT REGION

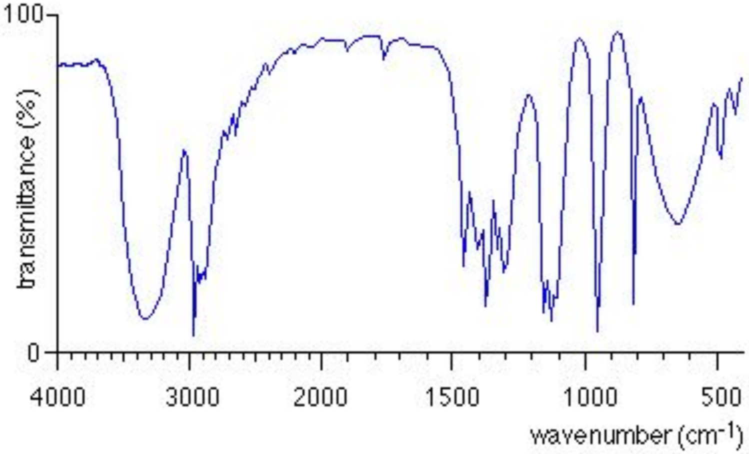
Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm^{-1}** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm^{-1}.



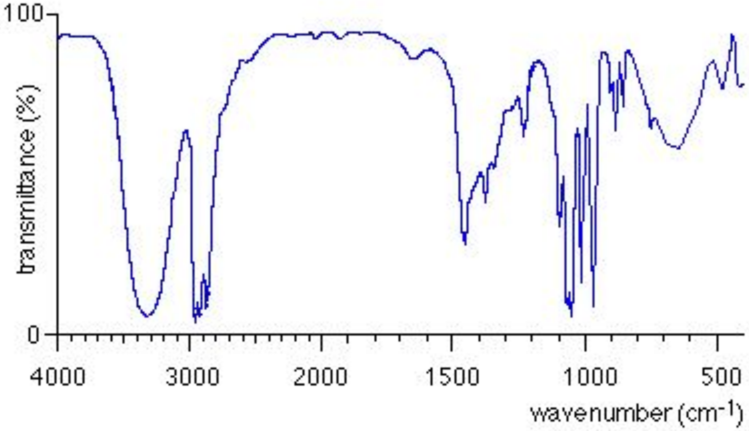
Focus your analysis on this region. This is where most stretching frequencies appear.

Fingerprint region: complex and difficult to interpret reliably.

Graphics source: Wade, Jr., L.G.*Organic Chemistry,* 6th ed. Pearson Prentice Hall Inc., 2006

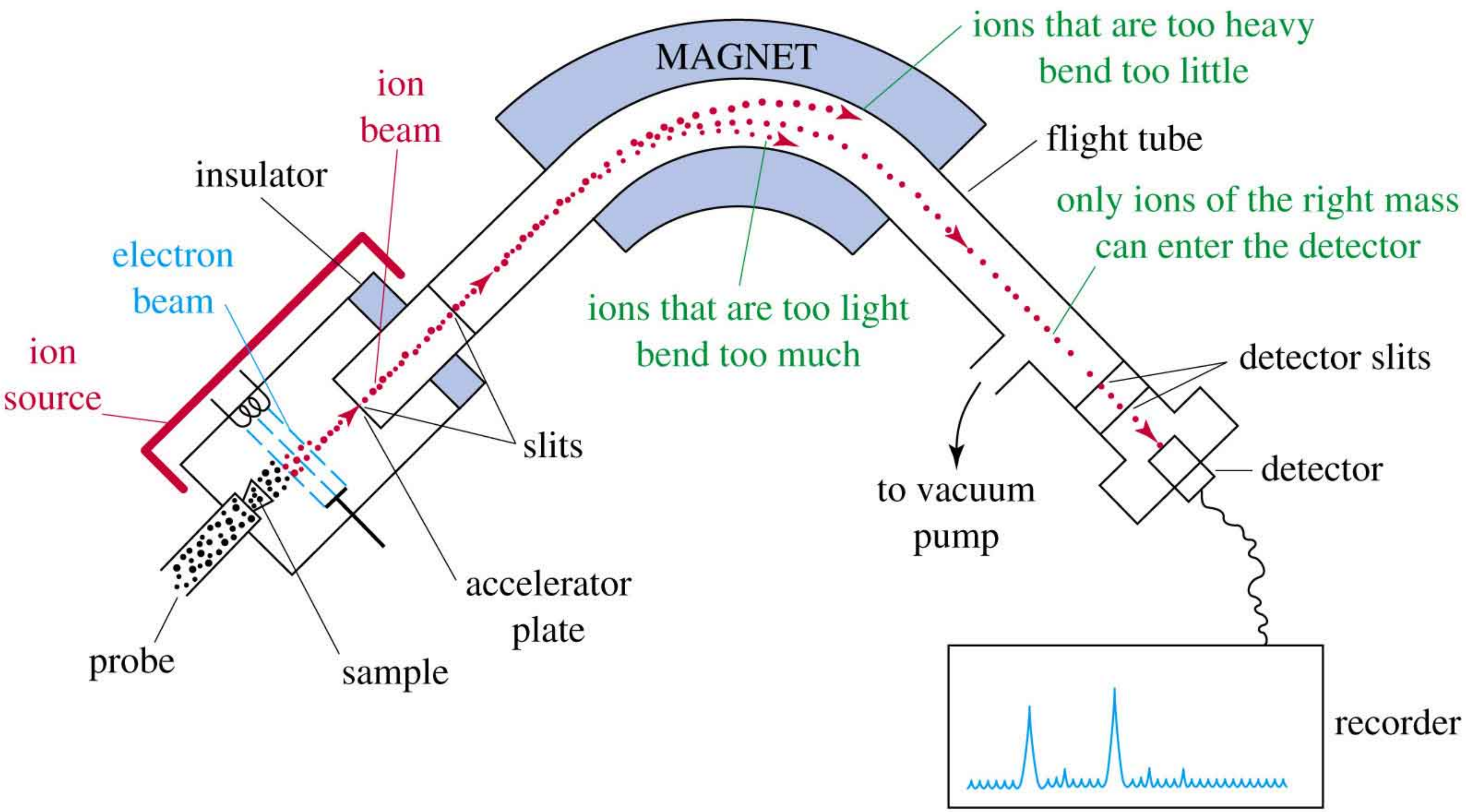


infra-red spectrum of propan-2-ol, $\mathrm{CH_3\underset{\substack{|\\ OH}}{C}HCH_3}$



infra-red spectrum of propan-1-ol, $CH_3CH_2CH_2OH$

Mass Spectrometer



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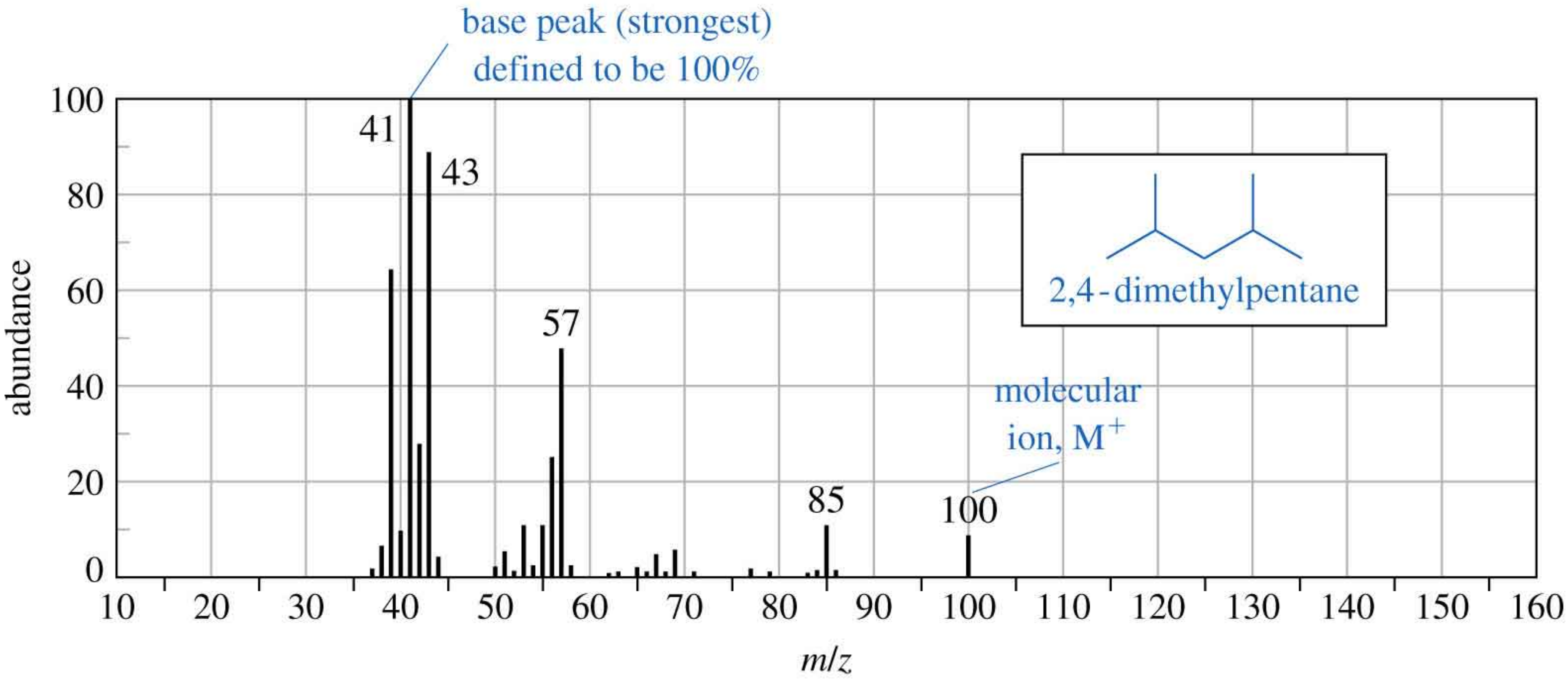
The Mass Spectrum

Masses are graphed or tabulated according to their relative abundance.



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