**Semester-I**

**17CHP104**      **ORGANIC AND INORGANIC SPECTROSCOPY**   **4H**   **4C**

**Instruction Hours/week:L: 4 T:0 P:0**     **Marks: Internal:40 External: 60 Total:100**

**Scope**

Spectroscopic analysis is based on an atom or compound's interaction with electromagnetic radiation of specific wavelength. Spectroscopy provides information on chemical identity of a compound, quantity present and structure based on the technique selected and the wavelength of electromagnetic spectrum.

**Programme Outcome**

Students are able

1. To learn about Electronic spectroscopy.
2. To understand about IR spectroscopy.
3. To learn the different aspects of NMR spectroscopy.
4. To learn about the Mass spectroscopy and Mossbauer spectroscopy.
5. To learn about the invaluable tools in synthetic chemistry for the confirmation of known molecules and elucidation of shape and structures of unknown compounds of high complexity with a high degree of certainty.

**Programme Learning Outcome**

Students understood the basic principles of Ultra-violet and Infrared spectroscopy. Students know theory and principles of Nuclear magnetic resonance spectroscopy like Proton and Carbon NMR spectroscopy. Student will have an ability to understand the mass spectroscopy and Mossbauer spectroscopy.

**Methodology**
Blackboard teaching, Powerpoint presentation and group discussion.

**UNIT- I**
**Ultraviolet and Visible Spectroscopy**: Electronic spectra of diatomic molecules - laws of photochemistry - electronic absorption transitions-correlation of electronic structure with

molecular structure - simple chromophoric groups - effects of conjugation - Woodward -Fisher rules for α, β unsaturated carbonyl compounds & dienes - aromatic systems with extended conjugation - applications to organic and inorganic compounds - Instrumentation**.**

## UNIT-II

**Infrared Spectroscopy:** The vibrating diatomic molecules-the simple harmonic oscillator and anharmonic oscillator - the diatomic rotor - factors influencing vibrational frequencies - identification of fundamental groups. Fingerprint region-application to organic and inorganic compounds-Instrumentation**.**

## UNIT-III

**NMR Spectroscopy:** Principle of NMR spectroscopy – description of the PMR instrument, factors affecting chemical shifts-chemical shift equivalence and magnetic equivalence - spin-spin coupling - first order and non first order spectra - Hetero nuclear coupling in $^1$H NMR - deuterium exchange - high field spectra - double resonance-shift reagents-applications to organic and inorganic compounds. FT NMR.

$^{13}$C NMR spectroscopy-factors affecting the chemical shifts - broad band and off-resonance decoupling - applications in organic chemistry.

## UNIT – IV
**Mass Spectroscopy:** Principles of mass spectrometry – resolution - description of single focusing and double focusing electron impact mass spectrometers - presentation and analysis of spectra - determination of molecular formulae - Nitrogen rule- Stevenson's rule - isotope abundance analysis - meta stable ions and peaks the molecular ion peak - fragmentation processes - Retro Diels - Alder rearrangement - McLaffertty rearrangement - ortho effect - fragmentation associated with functional groups - aldehydes, ketones, carboxylic acids, esters, amides, alcohols, thiols, amine, ethers, sulphides and halides..

## UNIT – V
**Mossbauer and Problems:** Mossbauer spectroscopy – principles - spectrometer - isomer shift - quadrapole interaction - nuclear zeeman splitting – applications.

Problems involving UV, IR, NMR, Mass spectral data (for compounds not more than 10 carbon atoms).

**SUGGESTED READINGS:**

**Text Books:**

1.	Jag Mohan. (2007). *Organic Spectroscopy: Principles and Applications* (II Edition). New Delhi: Narose Publishing House.
2.	Kemp, W. (2004). *Organic Spectroscopy* (III Edition). New York: Palgrave Macmillan.
3.	Sharma, Y. R. (2007). Elementary Organic Spectroscopy: Principles and Chemical Applications (V Edition). New Delhi: S. Chand & Company Limited.
4.	Silverstein, R. M., Webster, F. X., & Kiemle, D. (2005). *Spectroscopy of Organic Compounds* (VI Edition). New York: John Wiley & Sons.

**Reference Books:**

1.	Levine, I. N. (2004). *Quantum Chemistry* (V Edition). New Delhi: Pearson Education Pvt. Ltd.
2.	Prasad, R. K. (2004). *Quantum Chemistry* (II Edition). New Delhi: New Age International Publishers Pvt. Ltd.
3.	Drago, R .S. (1965). *Physical Methods in Inorganic Chemistry*. New York: Reinhold Publishing Corporation.
4.	Banwell.,(1994). *Fundamentals of Molecular & Spectroscopy,* McGraw-Hill Education (India) Pvt. Limited

## LECTURE PLAN

**Name of the Faculty : Dr. M.R.Ezhilarasi**          **Department : Chemistry**

**Title of the course   : Organic & Inorganic spectroscopy**     **Course Code : 17CHP104**

**Class                  : I M.Sc**          **Semester       : I**

**Completed Hours    : 60 Hours**

**UNIT-I       UV Spectroscopy**                              **Hours required: 12**

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|------|------|---------------------|------------------|
| 1. | 1 | Ultraviolet and Visible Spectroscopy-Introduction | T1: 9-14 |
| 2. | 1 | Electronic spectra of diatomic molecules | T1: 1-7 |
| 3. | 1 | laws of photochemistry | T1: 6-7 |
| 4. | 1 | Electronic absorption transitions | T1: 14-15 |
| 5. | 1 | correlation of electronic structure with molecular structure | T1: 18-19 |
| 6. | 1 | Simple chromophoric groups, | T1: 19-26 |
| 7. | 1 | Effects of conjugation | T1:25-27 |
| 8. | 1 | Woodward -Fisher rules for $\alpha,\beta$ unsaturated carbonyl compounds and dienes | T1: 36-42 |
| 9. | 1 | Aromatic systems with extended conjugation | T1: 36-38 |
| 10 | 1 | Applications to Organic and Inorganic compounds | T1: 52-54 |
| 11 | 1 | Discussion | |
| 12 | 1 | ESE Question paper discussion | |

**References:**
**Text book:**

T1: Y.R. Sharma, 2010, Elementary organic sectroscopy, S. Chand and company ltd.

**UNIT-II**　　　　　**IR Spectroscopy**　　　　　**Hours required: 12**

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|------|------|------|------|
| 1. | 1 | Infrared Spectroscopy-Introduction, | T1: 69-76 |
| 2. | | Instrumentation | |
| 3. | 1 | The vibrating diatomic molecules | T1: 70-72 |
| 4. | 1 | The simple harmonic oscillator | T1: 70-73 |
| 5. | 1 | Unharmonic oscillator the diatomic rotor | T1: 70-77 |
| 6. | 1 | Factors influencing vibrational frequencies-hydrogen bond | T1: 77-83, T2: 35-39 |
| 7. | 1 | Factors influencing vibrational frequencies- coupled vibration, and electrinic effects | T1: 77-83 T2: 35-39 |
| 8. | 1 | Identification of fundamental groups | T1:137-140 |
| 9. | 1 | Fingerprint region | T1:86-90 |
| 10 | 1 | Application to organic inorganic compounds | T1:90-95, |
| 11 | 1 | Discussion | |
| 12 | 1 | ESE Question paper discussion | |

**References:**
**Text books:**

T1- Y.R. Sharma, 2010, Elementary organic sectroscopy, S. Chand and company ltd.

T2: Robert M. Silverstein and Francis X. Webstir, 1998. Spectroscopy of organic compounds, VI Edition, Wiley Publication.

## UNIT-III    NMR Spectroscopy                    Hours required: 15

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|------|--------------|----------------------|-------------------|
| 1. | 1 | NMR Spectroscopy-Introduction | T1:182-185 |
| 2. | 1 | Principle of NMR spectroscopy | T1:185-189 |
| 3. | 1 | Description of the PMR instrument, factors affecting chemical shifts | T1:194-198 |
| 4. | 1 | Chemical shift equivalence and magnetic equivalence | T1:189-191, |
| 5. | 1 | Spin-spin coupling | T2: 90-138 |
| 6. | 1 | First order and non first order spectra | T2:135-138 |
| 7. | 1 | Hetero nuclear coupling in $H^1$ NMR- deuterium exchange | T1:230-233 |
| 8. | 1 | high field spectra - double resonance- | T1:194-198 |
| 9. | 1 | shift reagents | T2: 90-138 |
| 10. | 1 | applications to organic and inorganic compounds, | T1:236-238 |
| 11. | 1 | FT NMR. | T2:150-160 |
| 12. | 1 | $C^{13}$ NMR spectroscopy- introduction | T1:233-235 |
| 13 | 1 | factors affecting the chemical shifts, broad band and off-resonance decoupling | T1:194-198 <br> T1:202-210 |
| 14 | 1 | applications in organic chemistry | T1:236-238 |
| 15 | 1 | Question paper discussion | |

**References:**
**Text book:**

T1: Y.R. Sharma, 2010, Elementary organic sectroscopy, S. Chand and company ltd.

T2: Robert M. Silverstein and Francis X. Webstir, 1998. Spectroscopy of organic compounds, VI Edition, Wiley Publication.

**UNIT-IV    Mass Spectroscopy**                                  **Hours required: 10**

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|------|--------------|----------------------|-------------------|
| 1. | 1 | Mass Spectroscopy- Introduction | T1:280-281 |
| 2. | 1 | Resolution - description of single focusing and double focusing electron impact mass spectrometers | T1:281-284 |
| 3. | 1 | Presentation and analysis of spectra, determination of molecular formulae | T1:294-297 <br><br> T1:286-287 |
| 4. | 1 | Nitrogen rule, Stevenson's rule | T1:287-291 |
| 5. | 1 | Isotope abundance analysis - meta stable ions and peaks the molecular ion peak | T1:288-290 |
| 6. | 1 | Fragmentation processes - Retro Diels - Alder rearrangement, McLaffertty rearrangement- Ortho Effect | T1:284-287 |
| 7. | 1 | Fragmentation associated with functional groups - aldehydes, ketones, carboxylic acids, esters | T1:315-318 |
| 8. | 1 | Fragmentation associated with functional groups - amides, alcohols, thiols | T1:304-310, |
| 9 | 1 | Fragmentation associated with functional groups - amine, sulphides and halides. | T1:321-324, |
| 10. | 1 | Revision  and Question paper discussion | |

**References:**
**Text book:**

T1:Y.R. Sharma, 2010, Elementary organic sectroscopy, S. Chand and company ltd.

**UNIT-V   Mossbauer Spectroscopy and Spectral Problems        Hours required: 11**

| S.No | Lecture Hour | Topics to be Covered | Support Materials |
|------|------|------|------|
| 1. | 1 | Mossbauer spectroscopy- Introduction | W1 |
| 2. | 1 | Principles, Mossbauer Spectrometer | W1 |
| 3. | 1 | Isomer shift, Quadrapole interaction, | W1 |
| 4. | 1 | Nuclear Zeeman Splitting, Applications | W1, W2 |
| 5. | 1 | Problems involving UV | T1:38-51 |
| 6. |  | Problem involving IR spectral data | T1: 91-133 |
| 7. | 1 | Problems involving NMR spectral data, | T1: 258-276 |
| 8. | 1 | Problem involving Mass spectral data | T1: 297-320 |
| 9. | 1 | ESE question paper discussion |  |
| 10 | 1 | ESE question paper discussion |  |
| 11 | 1 | ESE question paper discussion |  |

**References:**
**Text book:**

T1: Y.R. Sharma, 2010, Elementary organic sectroscopy, S. Chand and company ltd.


**Website:**

W1: http://www.rsc.org/membership/networking/interestgroups/mossbauerspect/intropart1.asp

W2: http://csep10.phys.utk.edu/astT162/lect/light/zeeman-split.html

**Signature of the Staff**                                                      **HOD**

**Unit-I**

**Ultraviolet and Visible Spectroscopy**

**1. Background**

An obvious difference between certain compounds is their color. Thus, quinone is yellow; chlorophyll is green; the 2,4-dinitrophenylhydrazone derivatives of aldehydes and ketones range in color from bright yellow to deep red, depending on double bond conjugation; and aspirin is colorless. In this respect the human eye is functioning as a spectrometer analyzing the light reflected from the surface of a solid or passing through a liquid. Although we see sunlight (or white light) as uniform or homogeneous in color, it is actually composed of a broad range of radiation wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. As shown on the right, the component colors of the visible portion can be separated by passing sunlight through a prism, which acts to bend the light in differing degrees
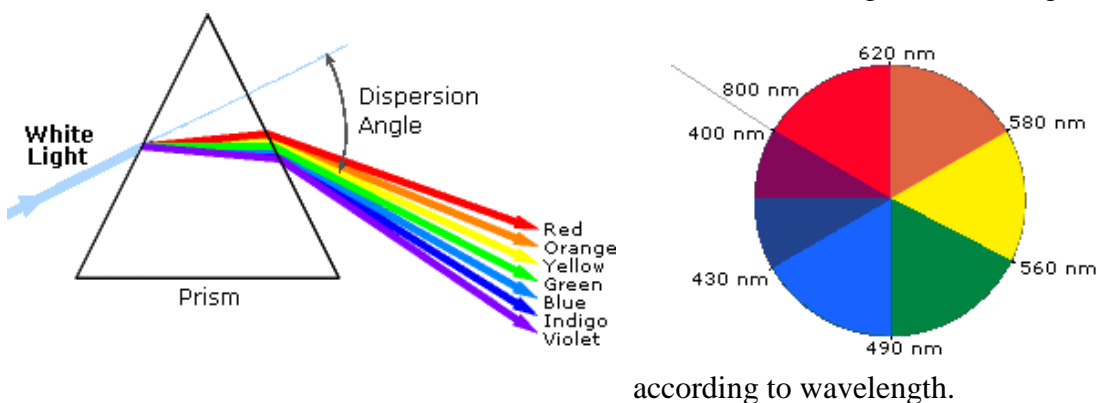


according to wavelength.

Electromagnetic radiation such as visible light is commonly treated as a wave phenomenon, characterized by a wavelength or frequency. **Wavelength** is defined on the left below, as the distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or nanometers ($10^{-9}$ meters). **Frequency** is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz). Visible wavelengths cover a range from approximately 400 to 800 nm. The longest visible wavelength is red and the shortest is violet. Other common colors of the spectrum, in order of decreasing wavelength, may be remembered by the mnemonic: **ROY G BIV**. The wavelengths of what we perceive as particular colors in the visible portion of the spectrum are displayed and listed below. In horizontal diagrams, such as the one on the bottom left, wavelength will increase on moving from left to right.
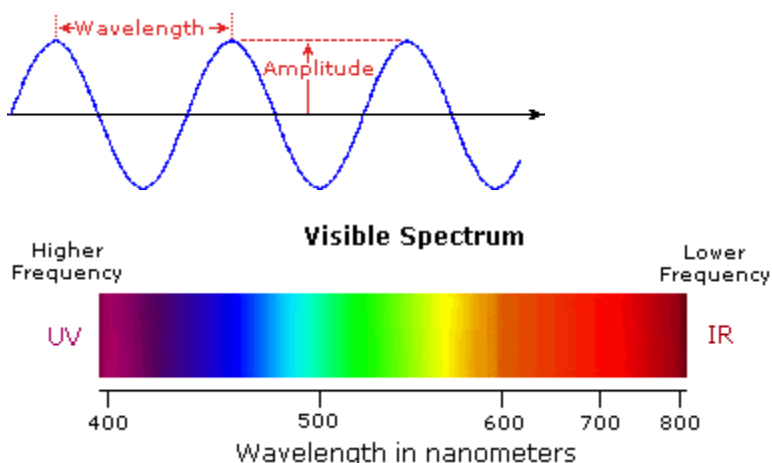
- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown on the right. Here, complementary colors are diametrically opposite each other. Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absoption close to 400 nm as well as absorption near 800 nm. Early humans valued colored pigments, and used them for decorative purposes. Many of these were inorganic minerals, but several important organic dyes were also known. These included the crimson pigment, kermesic acid, the blue dye, indigo, and the yellow saffron pigment, crocetin. A rare dibromo-indigo derivative, punicin, was used to color the robes of the royal and wealthy. The deep orange hydrocarbon carotene is widely distributed in plants, but is not sufficiently stable to be used as permanent pigment, other than for food coloring. A common feature of all these colored compounds, displayed below, is a system of **extensively conjugated pi-electrons**.
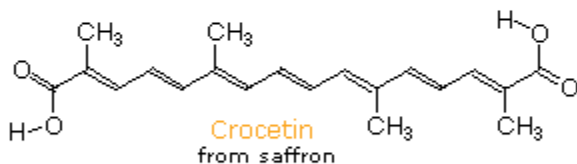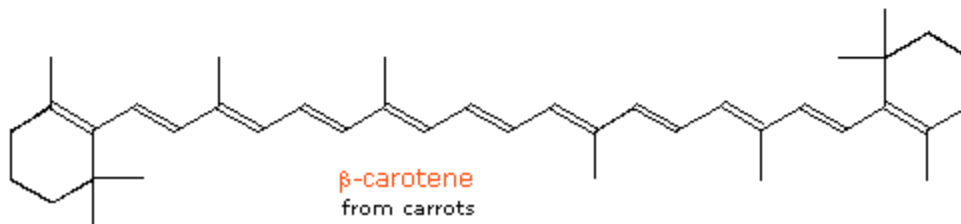
## Some Natural Organic Pigments
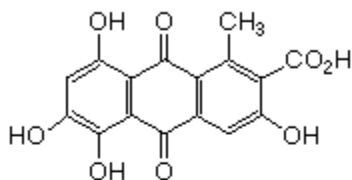


Kermesic Acid
(Carminic Acid)
from the insect *Coccus cacti*
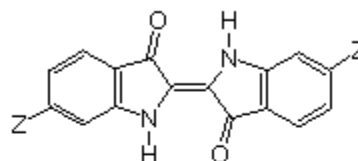
Z=H
Indigo
from *Isatis tinctoria* (woad)

Z=Br
Punicin or Tyrian Purple
from mollusks of the genus *Murex*

Crocetin
from saffron

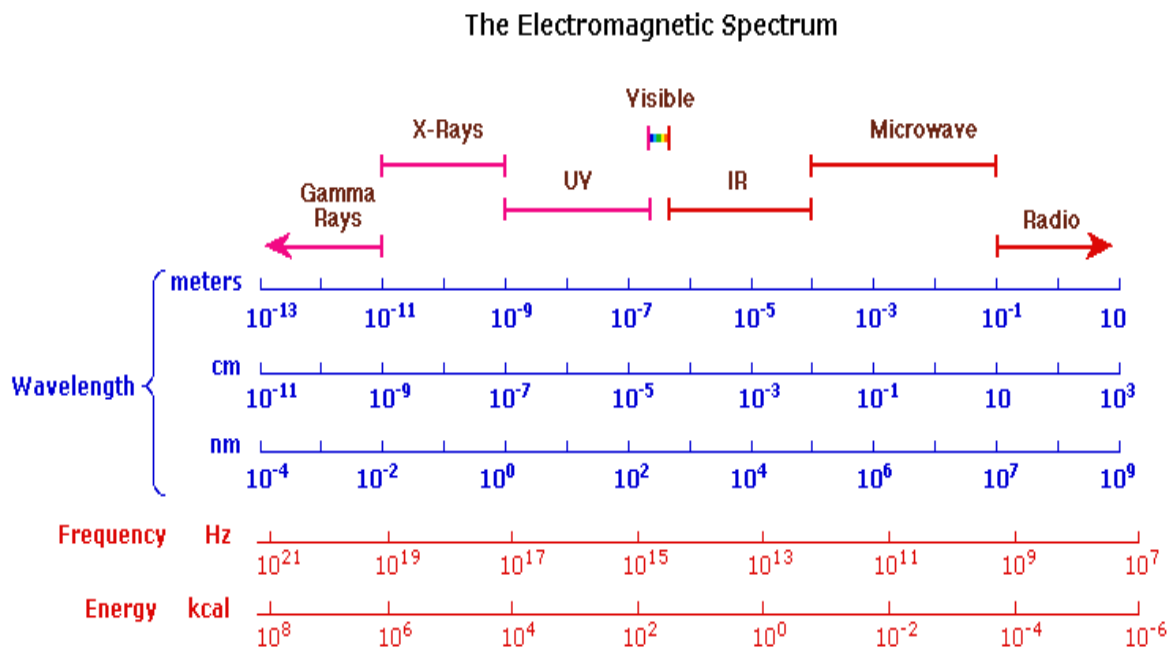β-carotene
from carrots

## 2. The Electromagnetic Spectrum

The visible spectrum constitutes but a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This **electromagnetic spectrum** ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency (shown in the top equation below the chart).

The energy associated with a given segment of the spectrum is proportional to its frequency. The bottom equation describes this relationship, which provides the energy carried by a photon of a given wavelength of radiation.

$\upsilon = c/\lambda$   $\upsilon$=frequency, $\lambda$=wavelength, c=velocity of light (c=3•$10^{10}$ cm/sec)
$\Delta E = h\upsilon$   E=energy, $\upsilon$=frequency, h=Planck's constant (h=6.6•$10^{-27}$ erg sec)

To obtain specific frequency, wavelength and energy values use this calculator.

## The Electromagnetic Spectrum

Visible

X-Rays          Microwave

Gamma          UV          IR
Rays                                    Radio

| meters | $10^{-13}$ | $10^{-11}$ | $10^{-9}$ | $10^{-7}$ | $10^{-5}$ | $10^{-3}$ | $10^{-1}$ | 10 |
|---|---|---|---|---|---|---|---|---|
| cm | $10^{-11}$ | $10^{-9}$ | $10^{-7}$ | $10^{-5}$ | $10^{-3}$ | $10^{-1}$ | 10 | $10^{3}$ |
| nm | $10^{-4}$ | $10^{-2}$ | $10^{0}$ | $10^{2}$ | $10^{4}$ | $10^{6}$ | $10^{7}$ | $10^{9}$ |

Wavelength

| Frequency Hz | $10^{21}$ | $10^{19}$ | $10^{17}$ | $10^{15}$ | $10^{13}$ | $10^{11}$ | $10^{9}$ | $10^{7}$ |
|---|---|---|---|---|---|---|---|---|
| Energy kcal | $10^{8}$ | $10^{6}$ | $10^{4}$ | $10^{2}$ | $10^{0}$ | $10^{-2}$ | $10^{-4}$ | $10^{-6}$ |

## Introduction

Many molecules absorb ultraviolet or visible light. The absorbance of a solution increases as attenuation of the beam increases. Absorbance is directly proportional to the path length, *b*, and the concentration, *c*, of the absorbing species. *Beer's Law* states that

*A = □bc*, where □ is a constant of proportionality, called the *absorbtivity*.

Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule. For example, the absorption that is observed in the UV region for the carbonyl group in acetone is of the same wavelength as the absorption from the carbonyl group in diethyl ketone.

## Introduction

Many compounds absorb ultraviolet (UV) or visible (Vis.) light. The diagram below shows a beam of monochromatic radiation of radiant power $P_0$, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power $P$.
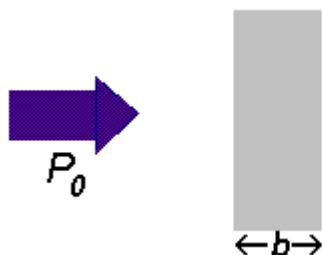
The amount of radiation absorbed may be measured in a number of ways:

**Transmittance**, $T = P / P_0$
**% Transmittance**, $\%T = 100\,T$

**Absorbance**,
$A = log_{10}\,P_0 / P$
$A = log_{10}\,1 / T$
$A = log_{10}\,100 / \%T$
$A = 2 - log_{10}\,\%T$

$P_0$

$\leftarrow b \rightarrow$

The last equation, $A = 2 - log_{10}\,\%T$, is worth remembering because it allows you to easily calculate absorbance from percentage transmittance data.

The relationship between absorbance and transmittance is illustrated in the following diagram:

**% Transmittance**

| 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |

2.0 1.5    1.0    0.8  0.7    0.6   0.5    0.4        0.3        0.2        0.1      0.05      0.00
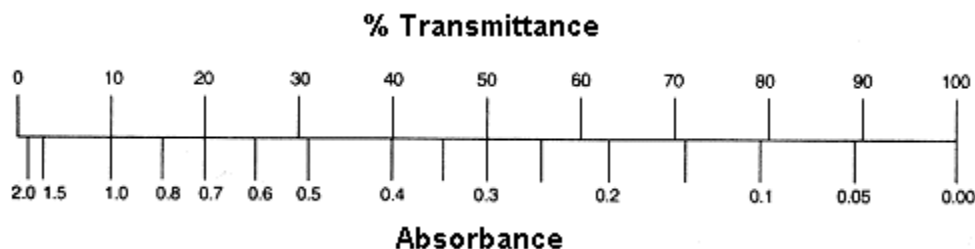
**Absorbance**

So, if all the light passes through a solution *without* any absorption, then absorbance is zero, and percent transmittance is 100%. If all the light is absorbed, then percent transmittance is zero, and absorption is infinite.

**The Beer-Lambert Law**

Now let us look at the Beer-Lambert law and explore it's significance. This is important because people who use the law often don't understand it - even though the equation representing the law is so straightforward:

**A=□bc**

Where A is absorbance (no units, since $A = log_{10} P_0 / P$ )
$\square$ is the molar absorbtivity with units of L mol$^{-1}$ cm$^{-1}$
**b** is the path length of the sample - that is, the path length of the cuvette in which the sample is contained. We will express this measurement in centimetres.

**c** is the concentration of the compound in solution, expressed in mol L-1

The reason why we prefer to express the law with this equation is because absorbance is directly proportional to the other parameters, as long as the law is obeyed. We are not going to deal with deviations from the law.

Let's have a look at a few questions...

**Question :** Why do we prefer to express the Beer-Lambert law using absorbance as a measure of the absorption rather than %T ?

**Answer :** To begin, let's think about the equations...

$A=\square bc$

$\%T = 100\ P/P_0 = e^{-\square bc}$

Now, suppose we have a solution of copper sulphate (which appears blue because it has an absorption maximum at 600 nm). We look at the way in which the intensity of the light (radiant power) changes as it passes through the solution in a 1 cm cuvette. We will look at the reduction every 0.2 cm as shown in the diagram below. **The Law says that the fraction of the light absorbed by each layer of solution is the same.** For our illustration, we will suppose that this fraction is 0.5 for each 0.2 cm "layer" and calculate the following data:

| Path length / cm | 0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
|---|---|---|---|---|---|---|
| %T | 100 | 50 | 25 | 12.5 | 6.25 | 3.125 |
| Absorbance | 0 | 0.3 | 0.6 | 0.9 | 1.2 | 1.5 |
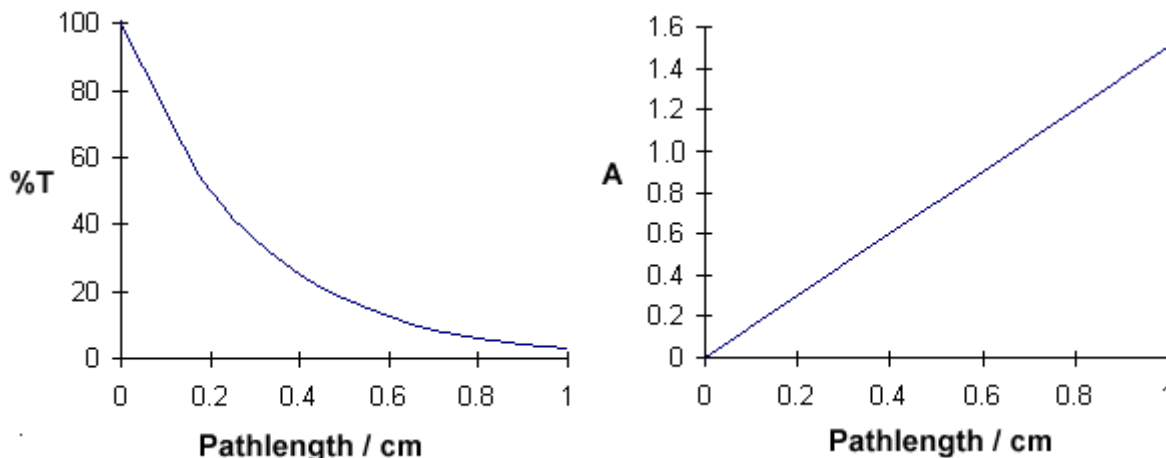
$A = \varepsilon bc$ tells us that absorbance depends on the total quantity of the absorbing compound in the light path through the cuvette. If we plot absorbance against concentration, we get a straight line passing through the origin (0,0).
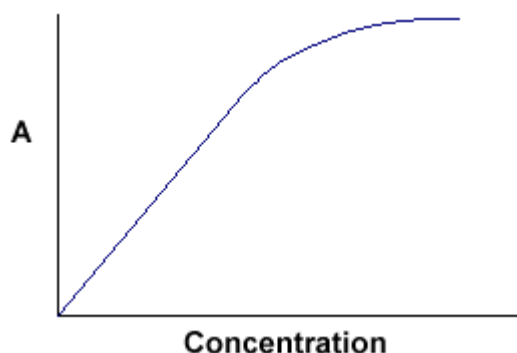


Note that the Law is not obeyed at high concentrations. This deviation from the Law is not dealt with here.

The linear relationship between concentration and absorbance is both simple and straightforward, which is why we prefer to express the Beer-Lambert law using absorbance as a measure of the absorption rather than %T.

**Question :** What is the significance of the molar absorbtivity, $\varepsilon$ ?

**Answer :** To begin we will rearrange the equation $A = \varepsilon bc$ :

$\varepsilon = A / bc$

In words, this relationship can be stated as "$\varepsilon$ is a measure of the amount of light absorbed per unit concentration".

Molar absorbtivity is a constant for a particular substance, so if the concentration of the solution is halved so is the absorbance, which is exactly what you would expect.

Let us take a compound with a very high value of molar absorbtivity, say 100,000 L mol$^{-1}$ cm$^{-1}$, which is in a solution in a 1 cm pathlength cuvette and gives an absorbance of 1.

$\square$ = 1 / 1$\square$ c

Therefore, c = 1 / 100,000 = 1 $\square\square\square\square^{-5}$ mol L$^{-1}$

Now let us take a compound with a very low value of $\square$, say 20 L mol$^{-1}$ cm$^{-1}$ which is in solution in a 1 cm pathlength cuvette and gives an absorbance of 1.

$\square$ = 1 / 1$\square$ c

Therefore, c = 1 / 20 = 0.05 mol L$^{-1}$

The answer is now obvious - a compound with a high molar absorbtivity is very effective at absorbing light (of the appropriate wavelength), and hence low concentrations of a compound with a high molar absorbtivity can be easily detected.

**Question :** What is the molar absorbtivity of Cu$^{2+}$ ions in an aqueous solution of CuSO$_4$ ? It is either 20 or 100,000 L mol$^{-1}$ cm$^{-1}$

**Answer :** I am guessing that you think the higher value is correct, because copper sulphate solutions you have seen are usually a beautiful bright blue colour. However, the actual molar absorbtivity value is 20 L mol$^{-1}$ cm$^{-1}$ ! The bright blue colour is seen because the concentration of the solution is very high.

$\square$-carotene is an organic compound found in vegatables and is responsible for the colour of carrots. It is found at exceedingly low concentrations. You may not be surprised to learn that the molar absorbtivity of $\square$-carotene is 100,000 L mol$^{-1}$ cm$^{-1}$ !

**3. UV-Visible Absorption Spectra**

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum.

> **For a description of a UV-Visible spectrometer Click Here.**

The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole.



Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.

The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy". A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**, and the resulting species is called an **excited state**. For a review of molecular orbitals click here. When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.

Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when

comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). **Molar absorptivity** ($\varepsilon$) is defined as:

**Molar Absorptivity, $\varepsilon$ = $A / c \, l$**      (where $A$= absorbance, $c$ = sample concentration in moles/liter & $l$ = length of light path through the sample in cm.)

If the isoprene spectrum on the right was obtained from a dilute hexane solution (c = 4 * $10^{-5}$ moles per liter) in a 1 cm sample cuvette, a simple calculation using the above formula indicates a molar absorptivity of 20,000 at the maximum absorption wavelength. Indeed the entire vertical absorbance scale may be changed to a molar absorptivity scale once this information about the sample is in hand. Clicking on the spectrum will display this change in units.

| Chromophore | Example | Excitation | $\lambda_{max}$, nm | $\varepsilon$ | Solvent |
|---|---|---|---|---|---|
| C=C | Ethene | $\pi \rightarrow \pi^*$ | 171 | 15,000 | hexane |
| C≡C | 1-Hexyne | $\pi \rightarrow \pi^*$ | 180 | 10,000 | hexane |
| C=O | Ethanal | $n \rightarrow \pi^*$ <br> $\pi \rightarrow \pi^*$ | 290 <br> 180 | 15 <br> 10,000 | hexane <br> hexane |
| N=O | Nitromethane | $n \rightarrow \pi^*$ <br> $\pi \rightarrow \pi^*$ | 275 <br> 200 | 17 <br> 5,000 | ethanol <br> ethanol |
| C-X    X=Br <br>        X=I | Methyl bromide <br> Methyl Iodide | $n \rightarrow \sigma^*$ <br> $n \rightarrow \sigma^*$ | 205 <br> 255 | 200 <br> 360 | hexane <br> hexane |
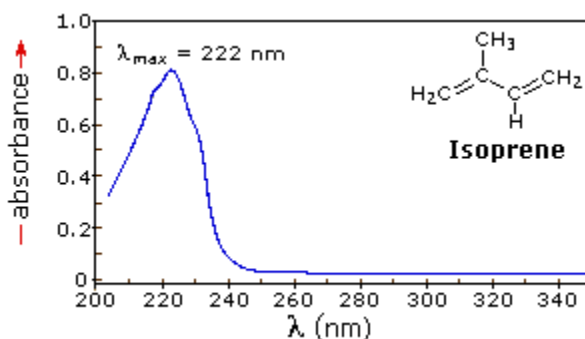


From the chart above it should be clear that the only molecular moieties likely to absorb light in the 200 to 800 nm region are pi-electron functions and hetero atoms having non-bonding valence-shell electron pairs. Such light absorbing groups are referred to as

**chromophores**. A list of some simple chromophores and their light absorption characteristics is provided on the left above. The oxygen non-bonding electrons in alcohols and ethers do not give rise to absorption above 160 nm. Consequently, pure alcohol and ether solvents may be used for spectroscopic studies. The presence of chromophores in a molecule is best documented by UV-Visible spectroscopy, but the failure of most instruments to provide absorption data for wavelengths below 200 nm makes the detection of isolated chromophores problematic. Fortunately, conjugation generally moves the absorption maxima to longer wavelengths, as in the case of isoprene, so conjugation becomes the major structural feature identified by this technique. Molar absorptivities may be very large for strongly absorbing chromophores (>10,000) and very small if absorption is weak (10 to 100). The magnitude of ε reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore.

## 4. The Importance of Conjugation

A comparison of the absorption spectrum of 1-pentene, $\lambda_{max}$ = 178 nm, with that of isoprene (above) clearly demonstrates the importance of chromophore conjugation. Further evidence of this effect is shown below. The spectrum on the left illustrates that conjugation of double and triple bonds also shifts the absorption maximum to longer wavelengths. From the polyene spectra displayed in the center diagram, it is clear that each additional double bond in the conjugated pi-electron system shifts the absorption maximum about 30 nm in the same direction. Also, the molar absorptivity (ε) roughly doubles with each new conjugated double bond. Spectroscopists use the terms defined in the table on the right when describing shifts in absorption. Thus, extending conjugation generally results in bathochromic and hyperchromic shifts in absorption. The appearance of several absorption peaks or shoulders for a given chromophore is common for highly conjugated systems, and is often solvent dependent. This fine structure reflects not only the different conformations such systems may assume, but also electronic transitions between the different vibrational energy levels possible for each electronic state. Vibrational fine structure of this kind is most pronounced in vapor phase spectra, and is increasingly broadened and obscured in solution as the solvent is changed from hexane to methanol.
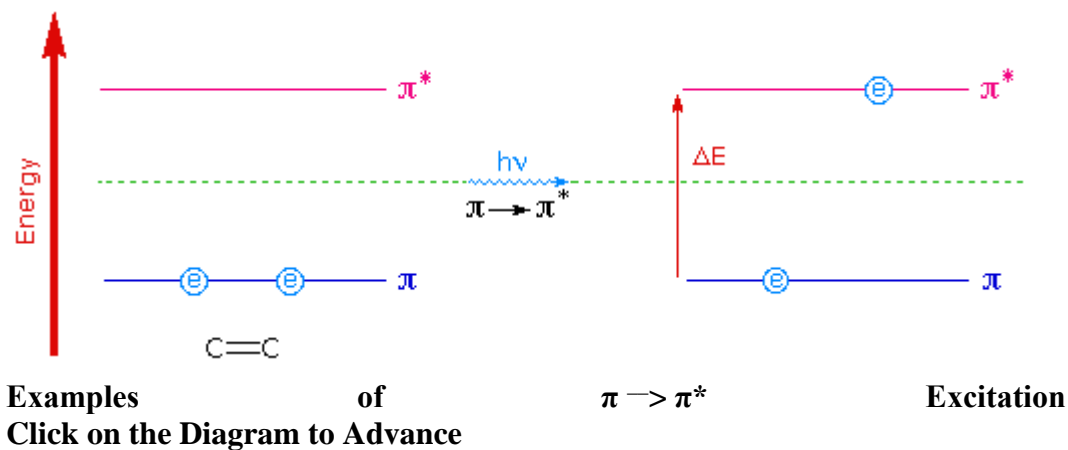
$\lambda_{max} = 230$ nm $\varepsilon = 11,600$

$R(CH=CH)_nR$
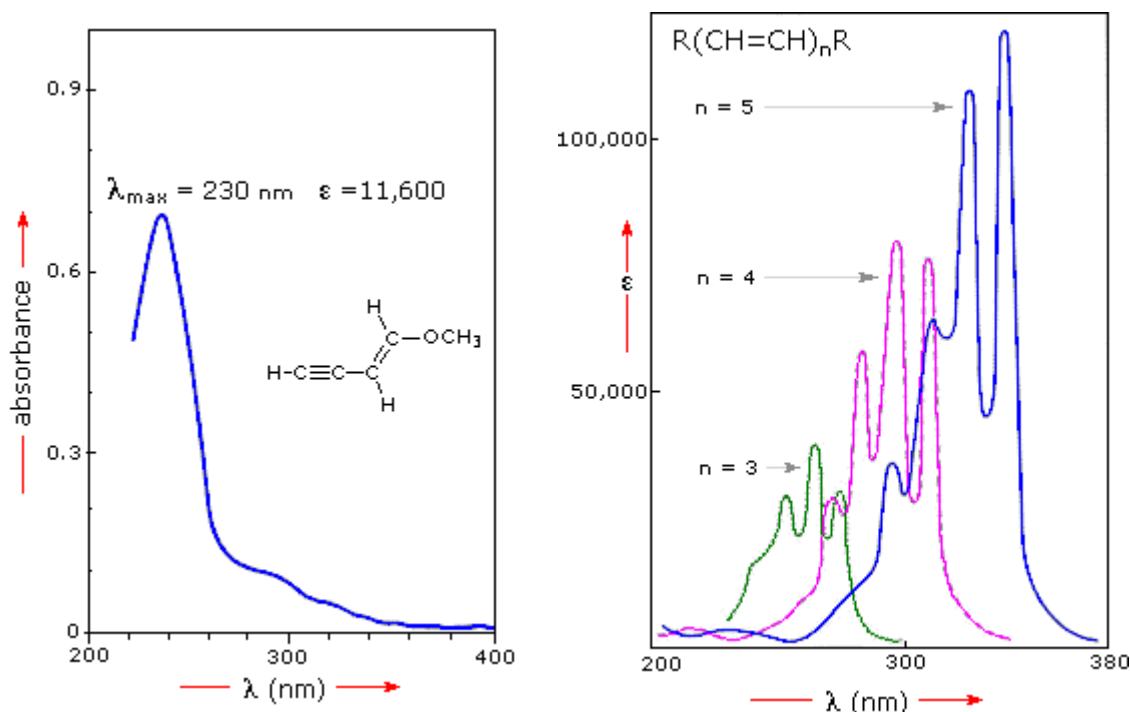
**Terminology for Absorption Shifts**

| Nature of Shift | Descriptive Term |
|---|---|
| To Longer Wavelength | Bathochromic |
| To Shorter Wavelength | Hypsochromic |
| To Greater Absorbance | Hyperchromic |
| To Lower Absorbance | Hypochromic |

To understand why conjugation should cause bathochromic shifts in the absorption maxima of chromophores, we need to look at the relative energy levels of the pi-orbitals. When two double bonds are conjugated, the four p-atomic orbitals combine to generate four pi-molecular orbitals (two are bonding and two are antibonding). This was described earlier in the section concerning diene chemistry. In a similar manner, the three double bonds of a conjugated triene create six pi-molecular orbitals, half bonding and half antibonding. The energetically most favorable $\pi \longrightarrow \pi^*$ excitation occurs from the highest energy bonding pi-orbital (**HOMO**) to the lowest energy antibonding pi-orbital (**LUMO**).

The following diagram illustrates this excitation for an isolated double bond (only two pi-orbitals) and, on clicking the diagram, for a conjugated diene and triene. In each case the HOMO is colored blue and the LUMO is colored magenta. Increased conjugation brings the HOMO and LUMO orbitals closer together. The energy ($\Delta E$) required to effect the electron promotion is therefore less, and the wavelength that provides this energy is increased correspondingly (remember $\lambda = h \cdot c/\Delta E$ ).



**Examples                    of                    $\pi \longrightarrow \pi^*$                    Excitation**
**Click on the Diagram to Advance**

Many other kinds of conjugated pi-electron systems act as chromophores and absorb light in the 200 to 800 nm region. These include unsaturated aldehydes and ketones and aromatic ring compounds. A few examples are displayed below. The spectrum of the unsaturated ketone (on the left) illustrates the advantage of a logarithmic display of molar absorptivity. The $\pi \longrightarrow \pi^*$ absorption located at 242 nm is very strong, with an $\varepsilon = 18,000$. The weak n $\longrightarrow \pi^*$ absorption near 300 nm has an $\varepsilon = 100$.
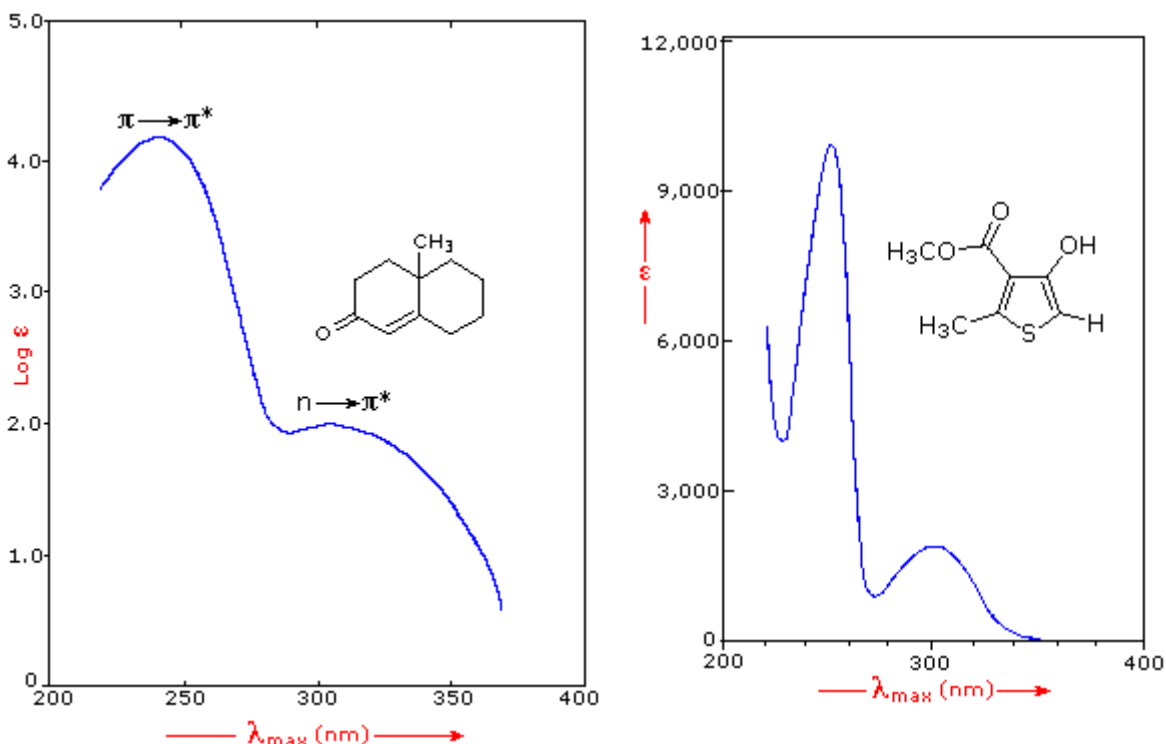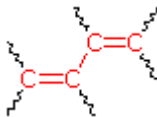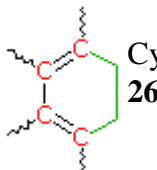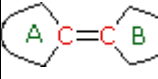
Benzene exhibits very strong light absorption near 180 nm ($\varepsilon > 65{,}000$) , weaker absorption at 200 nm ($\varepsilon = 8{,}000$) and a group of much weaker bands at 254 nm ($\varepsilon = 240$). Only the last group of absorptions are completely displayed because of the 200 nm cut-off characteristic of most spectrophotometers. The added conjugation in naphthalene, anthracene and tetracene causes bathochromic shifts of these absorption bands, as displayed in the chart on the left below. All the absorptions do not shift by the same amount, so for anthracene (green shaded box) and tetracene (blue shaded box) the weak absorption is obscured by stronger bands that have experienced a greater red shift. As might be expected from their spectra, naphthalene and anthracene are colorless, but tetracene is orange.
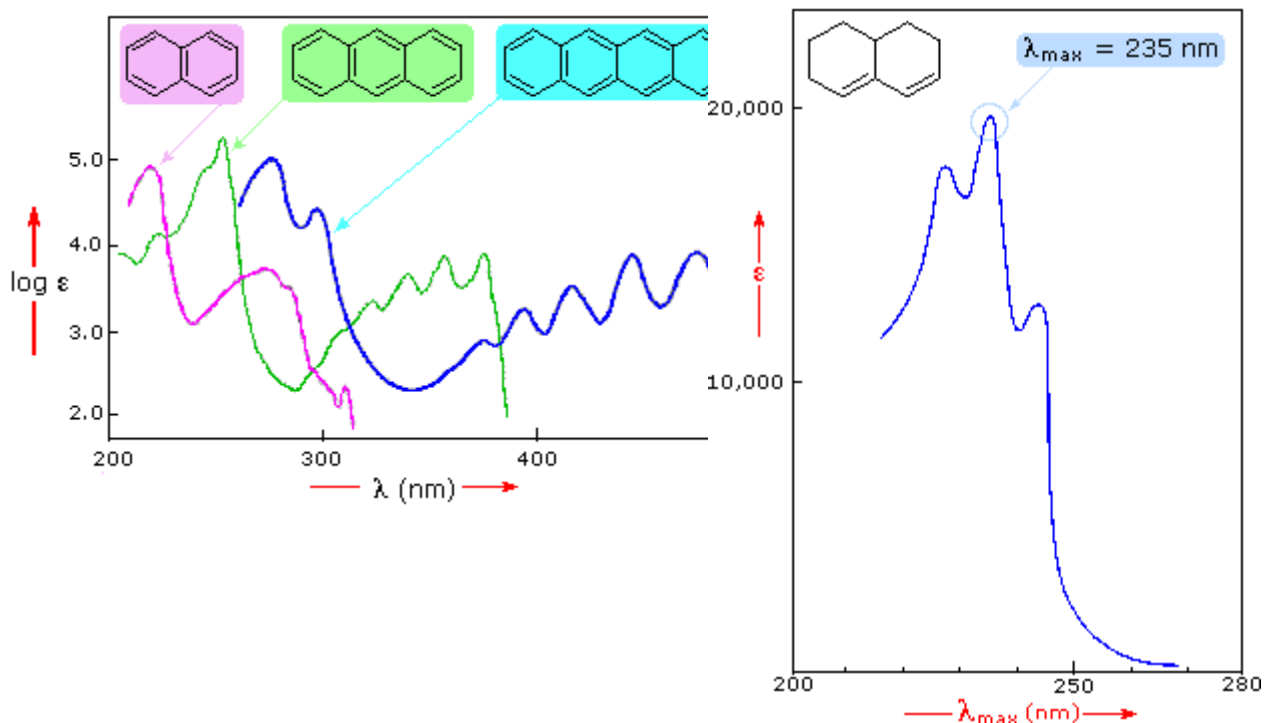
The spectrum of the bicyclic diene (above right) shows some vibrational fine structure, but in general is similar in appearance to that of isoprene, shown above. Closer inspection discloses that the absorption maximum of the more highly substituted diene has moved to a longer wavelength by about 15 nm. This "substituent effect" is general for dienes and trienes, and is even more pronounced for enone chromophores.

**Empirical Rules for Absorption Wavelengths of Conjugated Systems**

| Woodward-Fieser Rules for Calculating the $\lambda_{max}$ of Conjugated Dienes and Polyenes | |
|---|---|
| **Core Chromophore** | **Substituent and Influence** |
|  Transoid Diene **215 nm** | R- (Alkyl Group) .... **+5 nm** <br> RO- (Alkoxy Group) .. **+6** <br> X- (Cl- or Br-) ......... **+10** <br> RCO$_2$- (Acyl Group) .... **0** <br> RS- (Sulfide Group) .. **+30** <br> R$_2$N- (Amino Group) .. **+60** <br> **Further $\pi$ -Conjugation** <br> C=C (Double Bond) ... **+30** <br> C$_6$H$_5$ (Phenyl Group) ... **+60** |
|  Cyclohexadiene* **260 nm** | |

**(i)** Each exocyclic double bond adds **5 nm**. In the example on the right, there are two exo-double bond components: one to ring A and the other to ring                                                                                                                     B.
**(ii)**              Solvent              effects              are              minor.
\* When a homoannular (same ring) cyclohexadiene chromophore is present, a base value of 260 nm should be chosen. This includes the ring substituents. Rings of other size have a lesser influence.
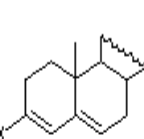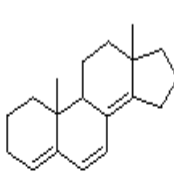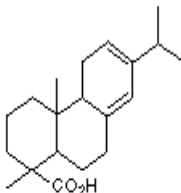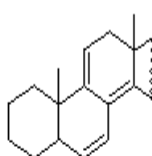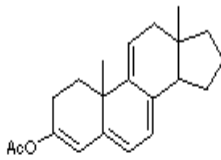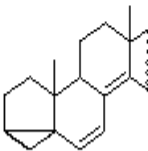
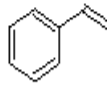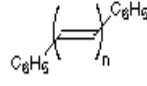$\lambda_{max}$ (calculated) = **Base** (215 or 260) + **Substituent Contributions**

**Some examples that illustrate these rules follow.**

UV Data Sheet
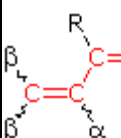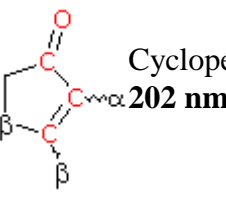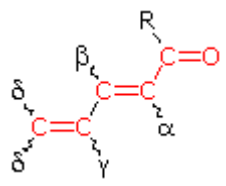
Absorption maxima ($\lambda_{max}$) are in nanometers, molar absorptivities ($\varepsilon$) are in parentheses.
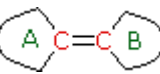


| X | $\lambda_{max}$ | ($\varepsilon$) | calc |
|---|---|---|---|
| H | 235 | 19000 | 235 |
| EtO | 241 | 22000 | 240 |
| MeS | 268 | 22600 | 265 |
| Br | 238 | 23000 | 240 |

233 (33,000)
calc: 235

Base: 215
conj: 30
subs: 25
exo: 15
285

235 (9,100)
(calc: homo: 260 + 15 + 15 = 290)
(calc: hetero: 215 + 20 + 10 = 245)

273 (7,000)
calc: 270

355 (19,700)
(calc: 260 + 60 + 15 + 15 + = 350)

261 (26,800)
calc: 355

244
(2,500)

256
(8,000)

248
(7,400)

228
(5,600)

| $\lambda_{max}$ | ($\varepsilon$) | Type |
|---|---|---|
| 203 | 58,000 | E |
| 248 | 14,000 | K |
| 282 | 750 | B |
| 291 | 500 | B |

| n | $\lambda_{max}$ | ($\varepsilon$) |
|---|---|---|
| 2 | 328 | 56,000 |
| 3 | 358 | 75,000 |
| 4 | 384 | 86,000 |
| 5 | 403 | 94,000 |
| 6 | 420 | 113,000 |

| Woodward-Fieser Rules for Calculating the $\pi \rightarrow \pi^*$ $\lambda_{max}$ of Conjugated Carbonyl Compounds | |
|---|---|
| **Core Chromophore** | **Substituent and Influence** |
|  R = Alkyl    **215 nm** <br> R  = H       **210 nm** <br> R = OR'  **195 nm** | **α-**                                                                          **Substituent** <br>      R-      (Alkyl      Group)                          **+10**      **nm** <br>      Cl-      (Chloro      Group)                                      **+15** |

**M . R . E z h i l a r a s i    D e p a r t m e n t   O f   C h e m i s t r y ,   K A H E    16 | 21**

Cyclopentenone **202 nm**



| | | | |
|---|---|---|---|
| Br- | (Chloro | Group) | **+25** |
| HO- | (Hydroxyl | Group) | **+35** |
| RO- | (Alkoxyl | Group) | **+35** |
| $RCO_2$- | (Acyl | Group) | **+6** |

**β-** **Substituent**

| | | | |
|---|---|---|---|
| R- | (Alkyl | Group) | **+12** nm |
| Cl- | (Chloro | Group) | **+12** |
| Br- | (Chloro | Group) | **+30** |
| HO- | (Hydroxyl | Group) | **+30** |
| RO- | (Alkoxyl | Group) | **+30** |
| $RCO_2$- | (Acyl | Group) | **+6** |
| RS- | (Sulfide | Group) | **+85** |
| $R_2N$- | (Amino | Group) | **+95** |

**γ & δ- Substituents**

R- (Alkyl Group) **+18** nm (both γ & δ)
HO- (Hydroxyl Group) **+50** nm (γ)
RO- (Alkoxyl Group) **+30 nm** (γ)

**Further π -Conjugation**
C=C (Double Bond) ... **+30**
$C_6H_5$ (Phenyl Group) ... **+60**


**(i)** Each exocyclic double bond adds **5 nm**. In the example on the right, there are two exo-double bond components: one to ring A and the other to ring B.
**(ii)** Homoannular cyclohexadiene component adds **+35 nm** (ring atoms must be counted separately as substituents)
**(iii)** Solvent Correction: water = **–8**; methanol/ethanol = **0**; ether = **+7**; hexane/cyclohexane = **+11**

$λ_{max}$ (calculated) = **Base + Substituent Contributions and Corrections**

---

**Some examples that illustrate these rules follow.**

**UV Data Sheet**

Absorption maxima ($\lambda_{max}$) are in nanometers, molar absorptivities ($\varepsilon$) are in parentheses.
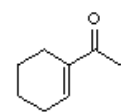


233  (13,000)
calc: 237
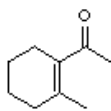
245  (6,500)
calc: 249
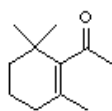
243  (1,400)
calc: 249
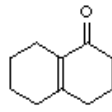
246  (12,300)
calc: 249
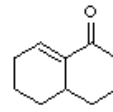
245  (5,500)
calc: 242
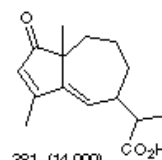
281  (14,000)
calc: 283
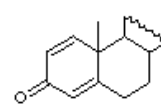
245  (15,000)
calc: 244 or 237
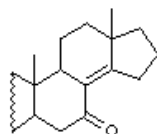
259  (9,500)
calc: 259
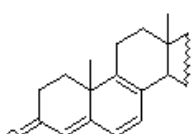
388  (18,000)
calc: 381

| Base: | 215 |
| conj: | 60 |
| subs: | 66 |
| exo: | 5 |
| 6-ring: | 35 |
| | 381 |
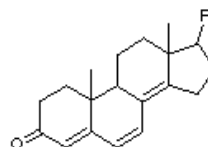
348  (40,000)
calc: 356

| Base: | 215 |
| conj: | 60 |
| subs: | 66 |
| exo: | 15 |
| | 356 |
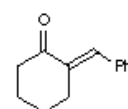
294  (17,000)
calc: 290
215 + 10 + 5 + 60 = 290
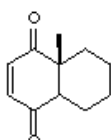
225
calc: 225
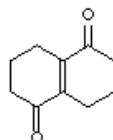
275
calc: 249
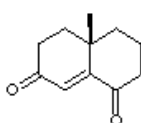
252
calc: 244
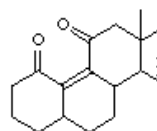
260
calc: 259
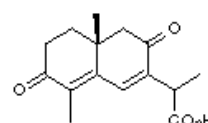
311  (20,000)
calc: 309 or 314
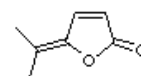
270  (23,000)
calc: 273 or 276

**POSSIBLE QUESTIONS**

**MULTIPLE CHOICE QUESTIONS**

1. UV absorption spectroscopy is powerful tool for ------------ analysis
   a)**Quantitative**      b)Qualitative      c)Physical
   d)Environmental

2. As the number of double bonds in conjugation increases, $\lambda_{max}$ --------
   a)  **Increases**      b) Decreases      c) Remains zero      d)Zero

3. The alkyl subsitution in an alkene causes a ---------- shift
   a)**Bathochromic**      b)Hypsochromic      c)Isomeric
   d)Chromophoric

4. What is the forbidden transition in the following?
   a)$\sigma$- $\sigma^*$      b)**n-$\pi^*$**      c)n-$\sigma^*$      d)$\pi$- $\pi$ *

5. In $\pi$- $\pi^*$ transition, solvent polarity results in------------ shift
   a) **Bathochromic**      b) hypsochromic      c) Isobestic point      d)hyperchromic

6. In the case of alcohol $\lambda_{max}$ small, the effect due to
   a) Covalent bonding      b) **Hydrogen bonding**      c. Co ordinate bonding.
   D. Ionic bonding

7. The arrangement of all type of electromagnetic radiation in the order of --------
   wavelength is called electromagnetic spectrum.
   a)**Increasing**      b)Decreasing      c)Same      d)Approximate

8. Which of the following spectroscopy otherwise known as electronic spectroscopy
   a) **UV**      b) IR      c) NMR      d) ESR

9. Which of the energy not accounted in total energy state of electronic absorption by
   Born-oppenhiemer approximation?
   a) $E_{elec}$      b) $E_{rot}$      c) **$E_{trans}$**      d) $E_{vib}$

10. The relative intensity of molecular spectra both in absorption and emission may be
    interpreted in terms of
    a)**Frank-condom principle**  b)Hiesenberg principle      c)Paulis principle
    d)Hooks law.

11. Beer-Lamberts law implies the fractional change in light intensity is proportional to
    a)**concentration of solution and thickness of solution**
    b)concentration only
    c) thickness of the solution only      d) intensity of emitted light.

12. Bathochromic shift also called

a)blue shift                     b)**red shift**             c)yellow shift
d)orange shift

13. Among the following electromagnetic radiations, which has the maximum wavelength?

      a) IR           b) UV          c) **Radio wave**       d) X-ray

14. Which of the following radiation has the maximum energy?

      a) **UV**         b) far IR     c) visible          d) near IR

15. Which of the following colours of visible light is bent most as it passes through a prism?

      a) Yellow      b) Red        c) **Blue**            d) Green

16. A frequency of 1000 cm$^{-1}$ is in the ------ region

      a)UV          b) **IR**       c) visible     d) microwave

17. What is the calculated value for cyclohexa 1,3-diene

      a) 261 mμ      b) 262 mμ     c) **263 mμ**    d)264 mμ

18. Upon irradiation with UV-radiation, benzene displaces ---- bonds due to its transition

      a) 1           b) 2         c) **3**         d) 4

19. If water used as solvent in UV absorption studies, ------ nm to be added with parent value.

      a) -4          b) +4        c) + 8        d) **-8**

20. Cycles/sec is unit for

      a) Wavelength         b) Frequency        c) Wave number     d) **Energy**

**8 MARKS QUESTION**

1. (i)Explain the electronic transitions involved in UV spectroscopy?
   (ii). Explain the various parts and functions of a UV-visible spectrophotometer

2. Explain the Woodward-Fieser rules for calculating absorption maximum for α,β-unsaturated carbonyl compounds with examples.

3. (i)**.**Explain the description of double beam UV spectrophotometer.
   (ii). How will you determine the structure of α, β – unsaturated compounds and conjugated dienes by   UV spectroscopy?

4. (i). Explain the various applications of UV spectroscopy.
   (ii). Explain the absorption laws in detail.

5. Explain the Woodward-Fieser rules for calculating absorption maximum in dienes with examples.

6. (i). Explain absorption and intensity shifts in detail.
   (ii). Explain the keto enol tautomerism in UV spectroscopy?

7. Explain the instrumentation of UV spectrophotometer.

8. (i). Explain the various applications of UV spectroscopy.
   (ii). Explain the absorption laws in detail.

9. Explain the Woodward-Fieser rules for calculating absorption maximum in dienes and α,β-unsaturated carbonyl compounds with an examples.

10. Explain the applications of UV spectroscopy?

11. Discuss the following terms:
    (a)(i)Bathochromic shift   (ii) hypochromic shift   (iii) A chromophore   (iv)Hyper chromic effect
    (b) On what effects do (i) and (ii) depend?

**KARPAGAM ACADEMY OF HIGHER EDUCATION**
**COIMBATORE-641021**
**(For the candidates admitted on 2015 onwards)**
**DEPARTMENT OF CHEMISTRY**
**I - SEMESTER**
**ORGANIC CHEMISTRY**

OBJECTIVE TYPE QUESTIONS( EACH QUESTION CARRY ONE MARK)

Unit-1  Ultraviolet spectroscopy (17CHP104)

| S.No | Question | option a | option b | option c | option d | answer |
|---|---|---|---|---|---|---|
| 1 | An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.This principle is known as | a. Paulis principle | b. Heisenberg principle | c. Franck condon principle. | d.Uncertinity principle | c. Franck condon principle. |
| 2 | Which among the following is the laws of Photochemistry | a.Hooks law | b.Beer-Lambertz law | c. Charls law | d.Avagdros law. | b.Beer-Lambertz law |
| 3 | Reciprocal of transmittance is called | a. Absorbance | b. Opacity | c. Incidence | d.Molar exinction coefficient | b. Opacity |
| 4 | The quantity Ecl is known as | a.Absorbance | b.Opacity | c.Transmittance | d.absorbtivity | a.Absorbance |
| 5 | Structural information deducible from UV spectra is mainly about | a. Inductive effect | b.Conjugation | c.Steric hiderance | d.Mesomeric effect | b.Conjugation |
| 6 | UV absorption spectroscopy is powerful tool for ------------ analysis | a. Quantitative | b. qualitative | c.physical | d environmental | a. Quantitative |
| 7 | As the number of double bonds in conjucation increases, $\lambda_{max}$ -------- | a.    increases | b. decreases | c.  remains zero | d.zero | a.    increases |
| 8 | The alkyl subsitution in an alkene causes a -------- shift | a.Bathochromic | b.Hypsochromic | c. isomeric | d.Chromophoric | a.Bathochromic |
| 9 | What is the forbidden transition in the following | a.$\sigma$- $\sigma$* | b.n-$\pi$* | c.n-$\sigma$* | d. $\pi$- $\pi$ * | b.n-$\pi$* |
| 10 | Saturated aldehyde exhibit ------- type of transition | A.both .n-$\pi$* and $\pi$-$\pi$* | b. both .$\sigma$- $\sigma$* and $\pi$-$\pi$ * | c. .both .$\sigma$- $\sigma$*   and n-$\pi$* | d.only n- $\pi$ * | A.both .n-$\pi$* and $\pi$- $\pi$* |
| 11 | Methyl chloride is an example for ------- type of transition | a. .n-$\pi$* | b.$\pi$- $\pi$* | c. .$\sigma$- $\sigma$* | d. n-$\sigma$* | d. n-$\sigma$* |
| 12 | In $\pi$- $\pi$* transition, solvent polarity results in------------ shift | a. Bathochromic | b. hypsochromic | c. both | d.none | a. Bathochromic |
| 13 | In the case of alcohol $\lambda_{max}$ small, the effect due to | a.Covalent bond | b.H-bonding | c.co ordinate bonding. | D.none | b.H-bonding |
| 14 | Transition in UV absorption depend on | a.size of the atom | b.Electronegativity | c. H-bonding | d.all the above | d.all the above |

| # | Question | a | b | c | d | Answer |
|---|----------|---|---|---|---|--------|
| 15 | According to Woodward-Fieser rule, the value of absorbance depend on | a.no of alkyl sustituents | b. no of double bond | c.presence of polar group | d.all the above | d.all the above |
| 16 | Parent value for Buta diene system is | a.217mµ | b.218 mµ | c.219 mµ | d.220 mµ | a.217mµ |
| 17 | According to Woodward-Fieser rule, to correct strain correction in bicyclic system----- should be added | a. 5 mµ | b.10 mµ | c.15 mµ | d.20 mµ | c.15 mµ |
| 18 | What is the $\lambda_{max}$ for the 2,4-hexa diene | a. 217 mµ | b.227 mµ | c.272 mµ | d.271 mµ | b.227 mµ |
| 19 | What is the calculated value for cyclohexa 1,3-diene | a. 261 mµ | b. 262 mµ | c.263 mµ | d.264 mµ | c.263 mµ |
| 20 | Upon irradiation with UV-radiation, benzene displaces ---- bonds due to its transition | a. 1 | b.2 | c. 3 | d.4 | c. 3 |
| 21 | If water used as solvent in UV absorption studies, ------ nm to be added with parent value. | a. -4 | b.+4 | c.+ 8 | d.-8 | d.-8 |
| 22 | Cycles/sec is unit for | a. Wavelength | b.frequency | c.wave number | d.energy | d.energy |
| 23 | The arrangement of all type of electromagnetic radiation in the order of ------- wavelength is called electromagnetic spectrum. | a.increasing | b.decreasing | c.same | d.approximate | a.increasing |
| 24 | Which of the following spectroscopy otherwise known as electronic spectroscopy | a.UV | b.IR | c.NMR | d.ESR | a.UV |
| 25 | Greater value of Molar extinction coefficient indicates that the probability of transition------- | a.less | b.more | c.  nil | d.zero | b.more |
| 26 | Molar extinction coefficient value less than ------- is called forbidden transition | a.1 | b.10 | c.100 | d.1000 | c.100 |
| 27 | When electronegativity increases, $\lambda_{max}$ ---------- | a.increases | b.decreases | c.remains same | d.becomes zero | b.decreases |
| 28 | Increase of solvent polarity results in --------- of $\lambda_{max}$ of absorption. | a.increase | b.decrease | c. increase and decrease | d.zero | b.decrease |
| 29 | Sufficient condition for absorption of energy of energy is that the interaction must create | a.dipole moment | b.frequency of oscillation | c.both the above | d.none | c.both the above |
| 30 | According to spin conservation rule,which of the following is allowed transition | a.singlet to singlet | b.singlet to triplet | c.triplet to singlet | d.none | a.singlet to singlet |
| 31 | The time taken for an electronic transition is very small compared to time taken for one vibration.This principle is known as | a.Paulis principle | b.Frank-condon principle | c.predissociation | d.Hunds principle | b.Frank-condon principle |

| # | Question | a | b | c | d | Answer |
|---|---|---|---|---|---|---|
| 32 | In predissociation, some molecules dissociation occur at ------ energy | a.Higher | b.lower | c.zero | d.without | b.lower |
| 33 | Radiation source used in UV instrumentation is | a.Hydrogen | b.deuterium lamp | c. xenon discharge lamp | d.Hydrogen, deutrium and xenon lamp | d.Hydrogen, deutrium and xenon lamp |
| 34 | Which of the energy not accounted in total energy state of electronic absorption by Born-oppenhiemer approximation? | a.$E_{elec}$ | b. $E_{rot}$ | c. $E_{trans}$ | d. $E_{vib}$ | c. $E_{trans}$ |
| 35 | The relative intensity of molecular spectra both in absorption and emission may be interpreted in terms of | a.Frank-condom principle | b.Hiesenberg principle | c.Paulis principle | d.Hooks law. | a.Frank-condom principle |
| 36 | Beer-Lamberts law implies the fractional change in light intensity is proportional to | a.concentration of solution and thickness of solution | b.concentration only | c.thickness of the solution only | d.intensity of emitted light. | a.concentration of solution and thickness of solution |
| 37 | Bathochromic shift also called | a.blue shift | b.red shift | c.yellow shift | d.orange shift | b.red shift |
| 38 | Water has the electronic transition | a. .n-$\pi^*$ | b.$\pi$- $\pi^*$ | c. .$\sigma$- $\sigma^*$ | d. n-$\sigma^*$ | d. n-$\sigma^*$ |
| 39 | If a molecule exists in two tautomeric form,the preference of one form to another can be detected by ------- spectroscopy | a.UV | b.IR | c,NMR | d.ESR | a.UV |
| 40 | Addition in unsaturation with the increase in the number of double bonds shifts the absorption to------- wavelength | a.shorter | b.longer | c.no change | d.maximum | b.longer |
| 41 | Which of the following is an electromagnetic radiation | a.alpha rays | b.beta rays | c.gammarays | d. anode rays | c.gammarays |
| 42 | Which of the following statements is true | a. X-rays are affected by electric field | b. X-rays are affectedby magnetic field | c. gamma rays are more energetic than X-rays | d.gamma rays are a stream of position | c. gamma rays are more energetic than X-rays |
| 43 | The wave length of x-rays is of the order of | a.$10^{-8}$m | b.$10^{-8}$ cm | c. $10^{-23}$ cm | d. 40000A° | b.$10^{-8}$ cm |
| 44 | The wave length of 1000 A° is in the ------ region | a. far UV | b.Visible | c.near UV | d. IR | a. far UV |
| 45 | Of the following radiations, which represents the visible region? | a. 0-100 nm | b. 100-200 nm | c.200-400 nm | d.400-800 nm | d.400-800 nm |
| 46 | Among the following electromagnetic radiations, which has the maximum wavelength? | a. IR | b.UV | c.radio wave | d. X-ray | c.radio wave |
| 47 | Which of the following radiation has the maximum energy | a.UV | b. far IR | c.visible | d. near IR | a.UV |
| 48 | Which of the following colours of visible light is bent most as it passes through a prism? | a. Yellow | b. Red | c. Blue | d. Green | c. Blue |

| | | | | | |
|---|---|---|---|---|---|
| 50 | A frequencyof 1000 cm$^{-1}$ is in the ------ region | a.UV | b. IR | c.visible | d. microwave | b. IR |
| 51 | One electron- volt of energy is equivalent to a photon with a wave lengthof about | a. 300 A° | b. 30 A° | c. 3000A° | d.12000A° | d.12000A° |
| 52 | Which among the following radiation will not ionise a gas? | a. X-rays | b. $\alpha$-particles | c.$\beta$-particles | d. neutrons | d. neutrons |
| 53 | Radiation which has the least energy ( among the following) | a.alpha rays | b.beta rays | c.gammarays | d. electrica; waves | d. electrica; waves |
| 54 | One nm is equal to | a. 10A° | b. 0.1 A° | c. $10^{-9}$ cm | d. $10^{-8}$ cm | a. 10A° |
| 55 | Which of the following transition require the least energy? | a. .n-$\pi$* | b.$\pi$- $\pi$* | c. .$\sigma$- $\sigma$* | d. n-$\sigma$* | a. .n-$\pi$* |
| 55 | Which of the following molecule has the shortest wavelength absorption band? | a. $H_2O$ | b.$CH_4$ | c. $CH_3Cl$ | d. $CH_3CHO$ | b.$CH_4$ |
| 56 | Which compound does not involve the $\pi$-$\pi$* transition in UV spectroscopy | a. alkenes | b. azo compound | c. alcohols | c. cyanides | c. alcohols |
| 57 | Which one is acidic auxochromic group? | a. -OH | b. -$NO_2$ | c. -OR | d.$NH_2$ | b. -$NO_2$ |
| 58 | What will be the theoritical number of vibrational degrees of freedom in benzene,$CO_2$, SO2 respectively | a. 12,4,3 | b. 3,4,12 | c. 30,4,3 | d. 30,3,3 | c. 30,4,3 |
| 59 | The number of vibrational degrees of freedom in $C_6H_5CH_3$ | a. 39 | b. 15 | c. 18 | d. 40 | a. 39 |
| 60 | Which one is the correctbasic value of $\lambda_{max}$ for a homoanular ddiene-- | a.214 | b.217 | c.253 | d.215 | c.253 |

**UNIT – II:**
**Infrared spectroscopy**

**Infrared spectroscopy** (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher energy near-IR, approximately 14000–4000 $cm^{-1}$ (0.8–2.5 μm wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately 4000–400 $cm^{-1}$ (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 $cm^{-1}$ (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

**Theory**

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling.

In particular, in the Born–Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are determined by the normal modes corresponding to the molecular electronic ground state potential energy surface. Nevertheless, the resonant frequencies can be in a first approach related to the strength of the bond, and the mass of the atoms at either end of it. Thus, the frequency of the vibrations can be associated with a particular bond type.

**Number of vibrational modes**

In order for a vibrational mode in a molecule to be "IR active," it must be associated with changes in the permanent dipole.

A molecule can vibrate in many ways, and each way is called a *vibrational mode.* Linear molecules have $3N - 5$ degrees of vibrational modes whereas nonlinear molecules have $3N - 6$ degrees of vibrational modes (also called vibrational degrees of freedom). As an example $H_2O$, a non-linear molecule, will have $3 \times 3 - 6 = 3$ degrees of vibrational freedom, or modes.

Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g. $N_2$, the band is not observed in the IR spectrum, but only in the Raman spectrum. Unsymmetrical diatomic molecules, e.g. CO, absorb in the IR spectrum. More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex, i.e. big molecules have many peaks in their IR spectra.

The atoms in a $CH_2$ group, commonly found in organic compounds, can vibrate in six different ways: **symmetric and antisymmetric stretching**, **scissoring**, **rocking**, **wagging** and **twisting**:
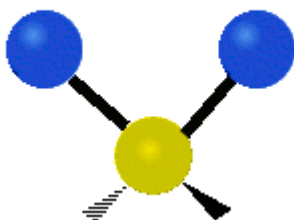
**Symmetrical stretching**  **Antisymmetrical stretching**  **Scissoring**
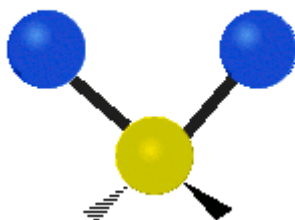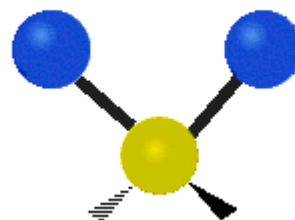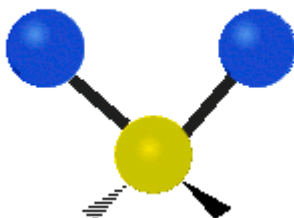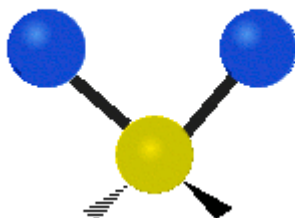
**Rocking**  **Wagging**  **Twisting**
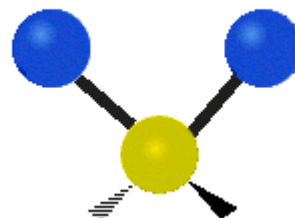
(These figures do not represent the "recoil" of the C atoms, which, though necessarily present to balance the overall movements of the molecule, are much smaller than the movements of the lighter H atoms).

**Special effects**

The simplest and most important IR bands arise from the "normal modes," the simplest distortions of the molecule. In some cases, "overtone bands" are observed. These bands arise from the absorption of a photon that leads to a doubly excited vibrational state. Such bands appear at approximately twice the energy of the normal mode. Some vibrations, so-called 'combination modes," involve more than one normal mode. The phenomenon of Fermi resonance can arise when two modes are similar in energy, Fermi resonance results in an unexpected shift in energy and intensity of the bands.

**Practical IR spectroscopy**

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs.

This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures.

**Sample preparation**

Gaseous samples require a sample cell with a long pathlength (typically 5–10 cm), to compensate for the diluteness.

Liquid samples can be sandwiched between two plates of a salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide or calcium fluoride are also used). The plates are transparent to the infrared light and do not introduce any lines onto the spectra.

Solid samples can be prepared in a variety of ways. One common method is to crush the sample with an oily mulling agent (usually Nujol) in a marble or agate mortar, with a pestle. A thin film of the mull is smeared onto salt plates and measured. The second method is to grind a quantity of the sample with a specially purified salt (usually potassium bromide) finely (to remove scattering effects from large crystals). This powder mixture is then pressed in a mechanical press to form a translucent pellet through which the beam of the spectrometer can pass. A third technique is the "cast film" technique, which is used mainly for polymeric materials. The sample is first dissolved in a suitable, non hygroscopic solvent. A drop of this solution is deposited on surface of KBr or NaCl cell. The solution is then evaporated to dryness and the film formed on the cell is analysed directly. Care is important to ensure that the film is not too thick otherwise light cannot pass through. This technique is suitable for qualitative analysis. The final method

is to use microtomy to cut a thin (20–100 μm) film from a solid sample. This is one of the most important ways of analysing failed plastic products for example because the integrity of the solid is preserved.

It is important to note that spectra obtained from different sample preparation methods will look slightly different from each other due to differences in the samples' physical states.

**Comparing to a reference**
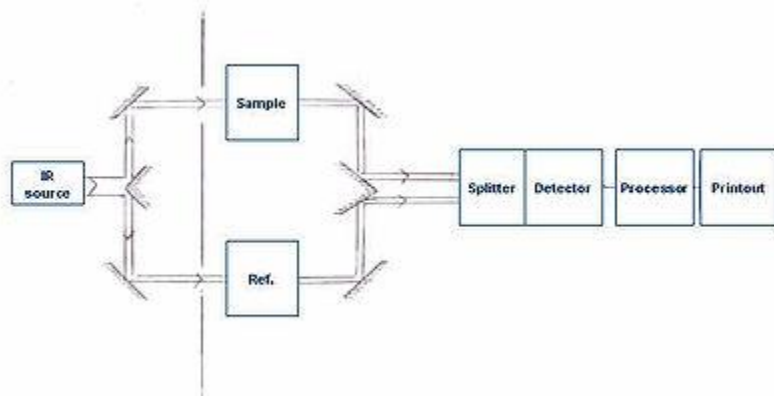


Schematics of a two-beam absorption spectrometer. A beam of infrared light is produced, passed through an interferometer (not shown), and then split into two separate beams. One is passed through the sample, the other passed through a reference. The beams are both reflected back towards a detector, however first they pass through a splitter, which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained. This "two-beam" setup gives accurate spectra even if the intensity of the light source drifts over time.

To take the infrared spectrum of a sample, it is necessary to measure both the sample and a "reference" (or "control"). This is because each measurement is affected by not only the light-absorption properties of the sample, but also the properties of the instrument (for example, what light source is used, what detector is used, etc.). The reference measurement makes it possible to eliminate the instrument influence. Mathematically, the sample transmission spectrum is divided by the reference transmission spectrum.

The appropriate "reference" depends on the measurement and its goal. The simplest reference measurement is to simply remove the sample (replacing it by air). However, sometimes a different reference is more useful. For example, if the sample is a dilute solute dissolved in water in a beaker, then a good reference measurement might be to measure pure water in the same beaker. Then the reference measurement would cancel out not only all the instrumental properties (like what light source is used), but also the light-absorbing and light-reflecting properties of the water and beaker, and the final result would just show the properties of the solute (at least approximately).

A common way to compare to a reference is sequentially: First measure the reference, then replace the reference by the sample, then measure the sample. This technique is not perfectly reliable: If the infrared lamp is a bit brighter during the reference measurement, then a bit dimmer during the sample measurement, the measurement will be distorted. More elaborate methods, such as a "two-beam" setup (see figure), can correct for these types of effects to give very accurate results.

**FTIR**

Fourier transform infrared spectroscopy
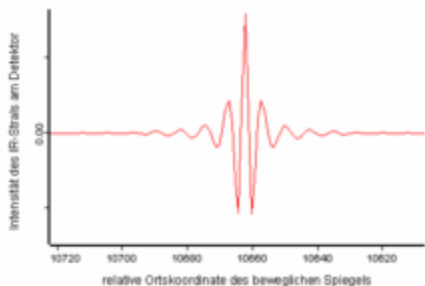


An interferogram from an FTIR measurement. The horizontal axis is the position of the mirror, and the vertical axis is the amount of light detected. This is the "raw data" which can be Fourier transformed to get the actual spectrum.

**Fourier transform infrared (FTIR) spectroscopy** is a measurement technique that allows one to record infrared spectra. Infrared light is guided through an interferometer and then through the sample (or vice versa). A moving mirror inside the apparatus alters the distribution of infrared light that passes through the interferometer. The signal directly recorded, called an "interferogram", represents light output as a function of mirror position. A data-processing technique called Fourier transform turns this raw data into the desired result (the sample's spectrum): Light output as a function of infrared wavelength (or equivalently, wavenumber). As described above, the sample's spectrum is always compared to a reference.

There is an alternate method for taking spectra (the "dispersive" or "scanning monochromator" method), where one wavelength at a time passes through the sample. The dispersive method is more common in UV-Vis spectroscopy, but is less practical in the infrared than the FTIR method. One reason that FTIR is favored is called "Fellgett's advantage" or the "multiplex advantage": The information at all frequencies is collected simultaneously, improving both speed and signal-to-noise ratio. Another is called "Jacquinot's Throughput Advantage": A dispersive measurement requires detecting much lower light levels than an FTIR measurement. There are other advantages, as well as some disadvantages, but virtually all modern infrared spectrometers are FTIR instruments.

**Absorption bands**

Infrared Spectroscopy Correlation Table
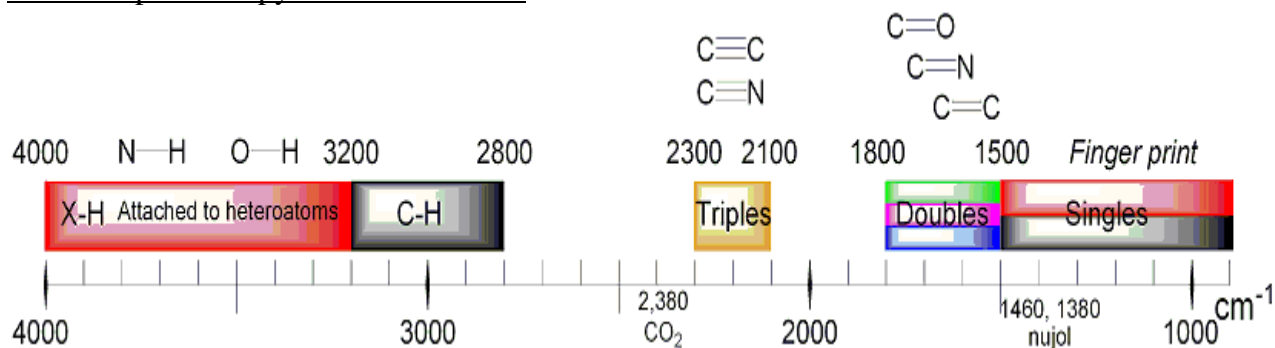


Wavenumbers listed in cm$^{-1}$.

## Uses and applications

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and dynamic measurement. It is also used in forensic analysis in both criminal and civil cases, enabling identification of polymer degradation for example.

The instruments are now small, and can be transported, even for use in field trials. With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment). Some instruments will also automatically tell you what substance is being measured from a store of thousands of reference spectra held in storage.

By measuring at a specific frequency over time, changes in the character or quantity of a particular bond can be measured. This is especially useful in measuring the degree of polymerization in polymer manufacture. Modern research instruments can take infrared measurements across the whole range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.

Infrared spectroscopy has been highly successful for applications in both organic and inorganic chemistry. Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics: for example, infrared spectroscopy can be applied to semiconductors like silicon, gallium arsenide, gallium nitride, zinc selenide, amorphous silicon, silicon nitride, etc.

## Isotope effects

The different isotopes in a particular species may give fine detail in infrared spectroscopy. For example, the O–O stretching frequency (in reciprocal centimeters) of

oxyhemocyanin is experimentally determined to be 832 and 788 cm$^{-1}$ for v($^{16}$O–$^{16}$O) and v($^{18}$O–$^{18}$O), respectively.

By considering the O–O bond as a spring, the wavenumber of absorbance, v can be calculated:

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where $k$ is the spring constant for the bond, $c$ is the speed of light, and $\mu$ is the reduced mass of the A–B system:

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

($m_i$ is the mass of atom $i$).

The reduced masses for $^{16}$O–$^{16}$O and $^{18}$O–$^{18}$O can be approximated as 8 and 9 respectively. Thus

$$\frac{\nu(^{16}O)}{\nu(^{18}O)} = \sqrt{\frac{9}{8}} \approx \frac{832}{788}.$$

Where v is the wavenumber; [wavenumber = frequency/(speed of light)]

The effect of isotopes, both on the vibration and the decay dynamics, has been found to be stronger than previously thought. In some systems, such as silicon and germanium, the decay of the anti-symmetric stretch mode of interstitial oxygen involves the symmetric stretch mode with a strong isotope dependence. For example, it was shown that for a natural silicon sample, the lifetime of the anti-symmetric vibration is 11.4 ps. When the isotope of one of the silicon atoms is increased to $^{29}$Si, the lifetime increases to 19 ps. In similar manner, when the silicon atom is changed to $^{30}$Si, the lifetime becomes 27 ps.

**Two-dimensional IR**

**Two-dimensional infrared correlation spectroscopy analysis** is the application of 2D correlation analysis on infrared spectra. By extending the spectral information of a perturbed sample, spectral analysis is simplified and resolution is enhanced. The 2D synchronous and 2D asynchronous spectra represent a graphical overview of the spectral changes due to a perturbation (such as a changing concentration or changing temperature) as well as the relationship between the spectral changes at two different wavenumbers.

Two-dimensional infrared spectroscopy
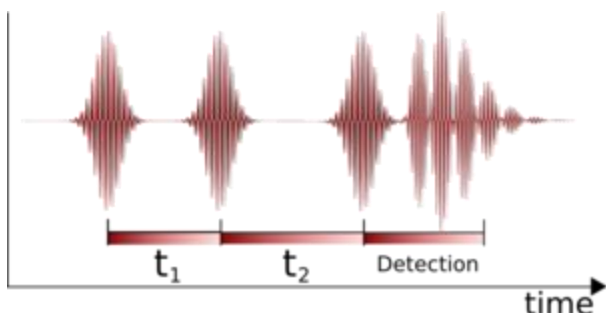
Pulse Sequence used to obtain a two-dimensional Fourier transform infrared spectrum. The time period $\tau_1$ is usually referred to as the coherence time and the second time period $\tau_2$ is known as the waiting time. The excitation frequency is obtained by Fourier transforming along the $\tau_1$ axis.

**Nonlinear two-dimensional infrared spectroscopy** is the infrared version of correlation spectroscopy. Nonlinear two-dimensional infrared spectroscopy is a technique that has become available with the development of femtosecond infrared laser pulses. In this experiment, first a set of pump pulses are applied to the sample. This is followed by a waiting time, wherein the system is allowed to relax. The typical waiting time lasts from zero to several picoseconds, and the duration can be controlled with a resolution of tens of femtoseconds. A probe pulse is then applied resulting in the emission of a signal from the sample. The nonlinear two-dimensional infrared spectrum is a two-dimensional correlation plot of the frequency $\omega_1$ that was excited by the initial pump pulses and the frequency $\omega_3$ excited by the probe pulse after the waiting time. This allows the observation of coupling between different vibrational modes; because of its extremely high time resolution, it can be used to monitor molecular dynamics on a picosecond timescale. It is still a largely unexplored technique and is becoming increasingly popular for fundamental research.

As with two-dimensional nuclear magnetic resonance (2DNMR) spectroscopy, this technique spreads the spectrum in two dimensions and allows for the observation of cross peaks that contain information on the coupling between different modes. In contrast to 2DNMR, nonlinear two-dimensional infrared spectroscopy also involves the excitation to overtones. These excitations result in excited state absorption peaks located below the diagonal and cross peaks. In 2DNMR, two distinct techniques, COSY and NOESY, are frequently used. The cross peaks in the first are related to the scalar coupling, while in the later they are related to the spin transfer between different nuclei. In nonlinear two-dimensional infrared spectroscopy, analogs have been drawn to these 2DNMR techniques. Nonlinear two-dimensional infrared spectroscopy with zero waiting time corresponds to COSY, and nonlinear two-dimensional infrared spectroscopy with finite waiting time allowing vibrational population transfer corresponds to NOESY. The COSY variant of nonlinear two-dimensional infrared spectroscopy has been used for determination of the secondary structure content proteins.

**Organic Compound Identification Using Infrared Spectroscopy**
**Description**

This exercise is intended to familiarize you with the identification of functional groups in organic compounds using infrared spectra. Before you can use this technique, you need to have an introduction to infrared spectroscopy and to what an IR spectrum is.

Infrared spectroscopy deals with the interaction of infrared light with matter. The energy of an infrared photon can be calculated using the Planck energy relation.

$$E = hn$$

where $h = 6.6 \times 10^{-34}$ joule second and $n$ = frequency of the photon. This shows that high energy photons have high frequency.

The frequency, n, and speed of light, c, are related through the relation

$$c = ln$$

where $c = 3.0 \times 10^{8}$ meter/second and $l$ = wavelength for the light
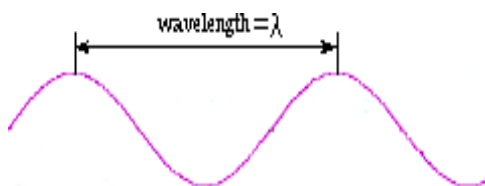


These two equations can be used to identify a common spectroscopic unit called *wavenumber*, $\bar{v}$, which is the reciprocal of the wavelength.

$$E = hn = h \, c\left(\tfrac{1}{\lambda}\right); E = hn = h \, c\,\bar{v};$$

$\bar{v}$= wavenumber = $\left(\tfrac{1}{\lambda}\right)$ has units of (cm$^{-1}$)

You can see that both frequency and wavenumber are directly proportional to energy.

Molecules are flexible, moving collections of atoms. The atoms in a molecule are constantly oscillating around average positions. Bond lengths and bond angles are continuously changing due to this vibration. A molecule absorbs infrared radiation when the vibration of the atoms in the

Bond stretch    Normal bond length    Bond compressed

molecule produces an oscillating electric field with the same frequency as the frequency of incident IR "light".
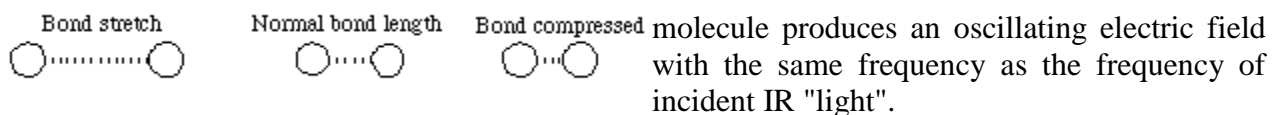
All of the motions can be described in terms of two types of molecular vibrations. One type of vibration, a stretch, produces a change of bond length. A stretch is a rhythmic movement along the line between the atoms so that the interatomic distance is either increasing or decreasing.

The second type of vibration, a bend, results in a change in bond angle. These are also sometimes called scissoring, rocking, or "wig wag" motions.

Bond angle compressed     Normal bond angle     Bond angle widened

Scissoring or bending of bond angle
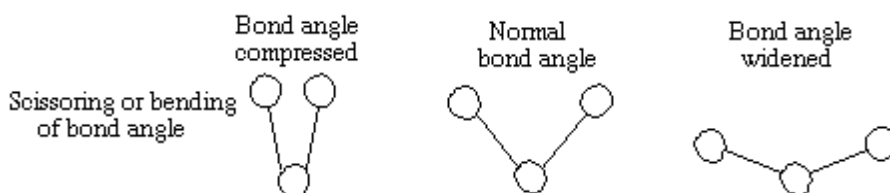
Each of these two main types of vibration can have variations. A stretch can be symmetric or asymmetric. Bending can occur in the plane of the molecule or out of plane; it can be scissoring, like blades of a pair of scissors, or rocking, where two atoms move in the same direction.

Different stretching and bending vibrations can be visualized by considering the $CH_2$ group in hydrocarbons. The arrows indicate the direction of motion. The stretching motions require more energy than the bending ones.

Symmetric stretch
~2853 cm$^{-1}$

Asymmetric stretch
~2926 cm$^{-1}$
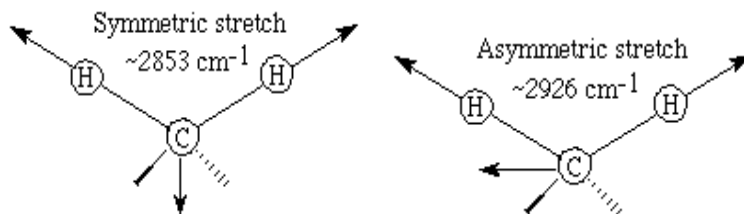
Note the high wavenumber (high energy) required to produce these motions.

The bending motions are sometimes described as wagging or scissoring motions.

In-plane bending or scissoring
~ 1465 cm$^{-1}$

In-plane bending or rocking
~ 720 cm$^{-1}$
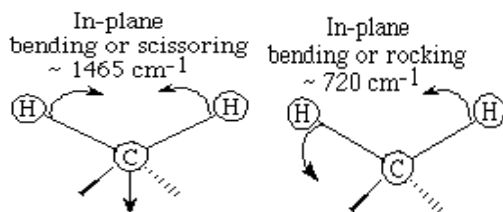
You can see that the lower wavenumber values are consistent with lower energy to cause these vibrations.

A molecule absorbs a unique set of IR light frequencies. Its IR spectrum is often likened to a person's fingerprints. These frequencies match the natural vibrational modes of the molecule. A molecule absorbs only those frequencies of IR light that match vibrations that cause a change in the dipole moment of the molecule. Bonds in symmetric N2 and H2 molecules do not absorb IR because stretching does not change the dipole moment, and bending cannot occur with only 2 atoms in the molecule. Any individual bond in an organic molecule with symmetric structures and identical groups at each end of the bond will not absorb in the IR range. For example, in ethane, the bond between the carbon atoms does not absorb IR because there is a methyl group at each end of the bond. The C-H bonds within the methyl groups do absorb.

In a complicated molecule many fundamental vibrations are possible, but not all are observed. Some motions do not change the dipole moment for the molecule; some are so much alike that they coalesce into one band.

Even though an IR spectrum is characteristic for an entire molecule, there are certain groups of atoms in a molecule that give rise to absorption bands at or near the same wavenumber, $\bar{\nu}$,

(frequency) regardless of the rest of the structure of the molecule. These persistent characteristic bands enable you to identify major structural features of the molecule after a quick inspection of the spectrum and the use of a correlation table. The correlation table is a listing of functional groups and their characteristic absorption frequencies.

The infrared spectrum for a molecule is a graphical display. It shows the frequencies of IR radiation absorbed and the % of the incident light that passes through the molecule without being absorbed. The spectrum has two regions. The *fingerprint* region is unique for a molecule and the *functional group* region is similar for molecules with the same functional groups.
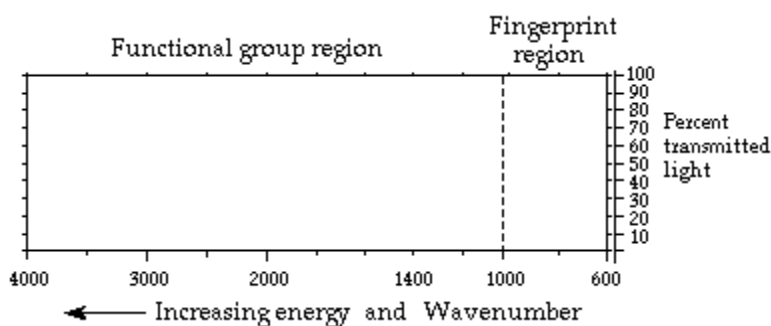


The nonlinear horizontal axis has units of wavenumbers. Each wavenumber value matches a particular frequency of infrared light. The vertical axis shows % transmitted light. At each frequency the % transmitted light is 100% for light that passes through the molecule with no interactions; it has a low value when the IR radiation interacts and excites the vibrations in the molecule.

A portion of the spectrum where % transmittance drops to a low value then rises back to near

100% is called a "band". A band is associated with a particular vibration within the molecule. The width of a band is described as broad or narrow based on how large a range of frequencies it covers. The efficiencies for the different vibrations determine how "intense" or strong the absorption bands are. A band is described as strong, medium, or weak depending on its depth.

In the hexane spectrum below the band for the CH stretch is strong and that for the CH bend is medium. The alkane, hexane ($C_6H_{14}$) gives an IR spectrum that has relatively few bands because there are only CH bonds that can stretch or bend. There are bands for CH stretches at about 3000 $cm^{-1}$. The $CH_2$ bend band appears at approximately 1450 $cm^{-1}$ and the $CH_3$ bend at about 1400 $cm^{-1}$. The spectrum also shows that shapes of bands can differ.
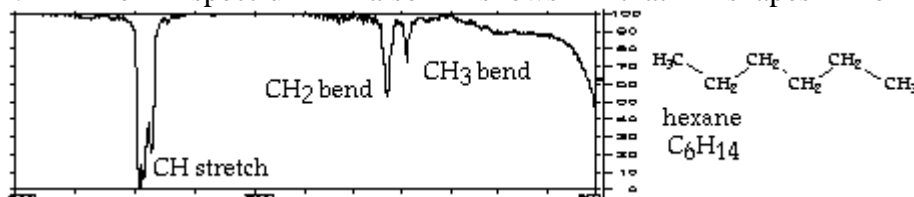


**Procedure**

Every molecule will have its own characteristic spectrum. The bands that appear depend on the types of bonds and the structure of the molecule. Study the sample spectra below, noting similarities and differences, and relate these to structure and bonding within the molecules.

The spectrum for the alkene, 1-hexene, $C_6H_{12}$, has few strong absorption bands. The spectrum has the various CH stretch bands that all hydrocarbons show near 3000 $cm^{-1}$. There is a weak alkene CH stretch above 3000 $cm^{-1}$. This comes from the C&emdash;H bonds on carbons 1 and 2, the two carbons that are held together by the double bond. The strong CH stretch bands below 3000 $cm^{-1}$ come from carbon-hydrogen bonds in the $CH_2$ and $CH_3$ groups. There is an out-of-plane CH bend for the alkene in the range 1000-650 $cm^{-1}$. There is also an alkene CC double bond stretch at about 1650 $cm^{-1}$ .
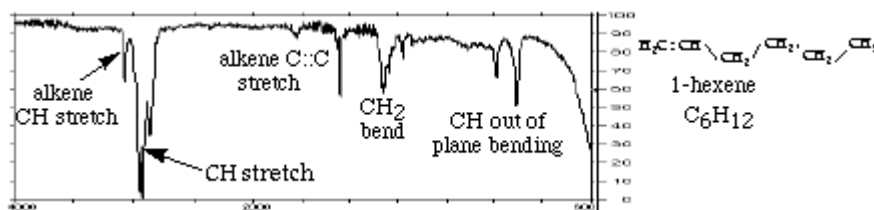


The spectrum for cyclohexene, ($C_6H_{10}$) also has few strong bands. The main band is a strong CH stretch from the $CH_2$ groups at about 3000 $cm^{-1}$. The CH stretch for the alkene CH is, as always, to the left of 3000 $cm^{-1}$. The $CH_2$ bend appears at about 1450 $cm^{-1}$. The other weaker bands in the range 1000-650 $cm^{-1}$ are for the out of plane CH bending . There is a very weak alkene CC double bond stretch at about 1650 $cm^{-1}$.

cyclohexene $C_6H_{10}$
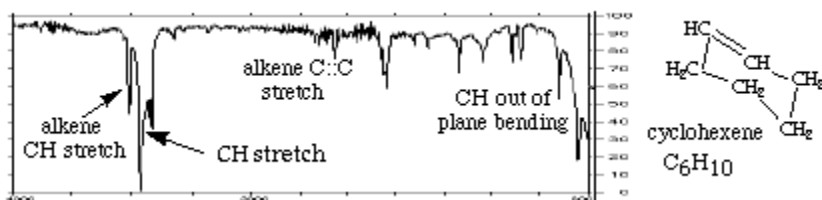
The IR spectrum for benzene, $C_6H_6$, has only four prominent bands because it is a very symmetric molecule. Every carbon has a single bond to a hydrogen. Each carbon is bonded to two other carbons and the carbon-carbon bonds are alike for all six carbons. The molecule is planar. The aromatic CH stretch appears at 3100-3000 $cm^{-1}$ There are aromatic CC stretch bands (for the carbon-carbon bonds in the aromatic ring) at about 1500 $cm^{-1}$. Two bands are caused by bending motions involving carbon-hydrogen bonds. The bands for CH bends appear at approximately 1000 $cm^{-1}$ for the in-plane bends and at about 675 $cm^{-1}$ for the out-of-plane bend.



Benzene $C_6H_6$
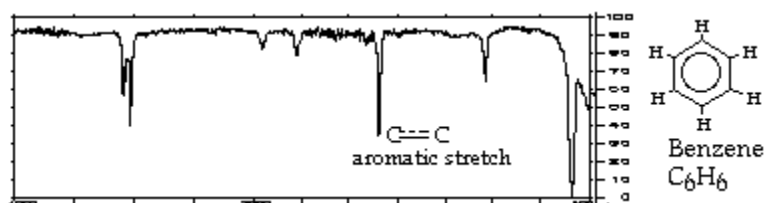
The IR spectrum for the alcohol, ethanol ($CH_3CH_2OH$), is more complicated. It has a CH stretch, an OH stretch, a CO stretch and various bending vibrations. The important point to learn here is that no matter what alcohol molecule you deal with, the OH stretch will appear as a broad band at approximately 3300-3500 $cm^{-1}$. Likewise the CH stretch still appears at about 3000 $cm^{-}$



Ethanol
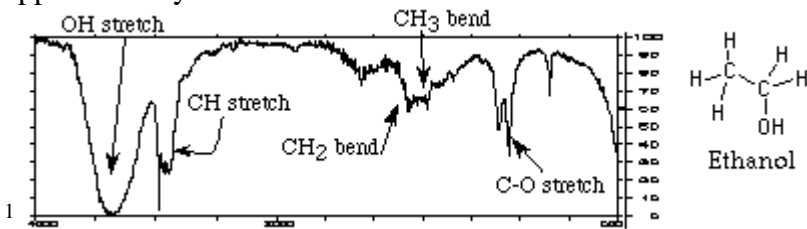
The spectrum for the aldehyde, octanal ($CH_3(CH_2)_6CHO$), is shown here. The most important features of the spectrum are carbonyl CO stretch near 1700 $cm^{-1}$ and the CH stretch at about 3000 $cm^{-1}$. If you see an IR spectrum with an intense strong band near 1700 cm-1 and the compound contains oxygen, the molecule most likely contains a carbonyl group,

$\rangle$C=O

CH bend

CH stretch

C=O stretch

octanal
$C_8H_{16}O$
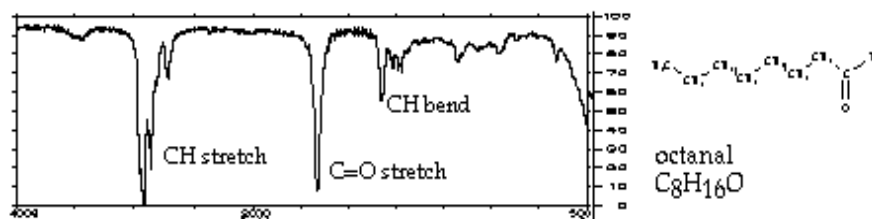
The spectrum for the ketone, 2-pentanone, appears below. It also has a characteristic carbonyl band at 1700 cm⁻¹. The CH stretch still appears at about 3000 cm⁻¹, and the CH2 bend shows up at approximately 1400 cm⁻¹. You can see the strong carbonyl CO stretch at approximately 1700 cm⁻¹. You can also see that this spectrum is different from the spectrum for octanal. At this point in your study of IR spectroscopy, you can't tell which compound is an aldehyde and which is a ketone. You can tell that both octanal and a 2-pentanone contain C-H bonds and a carbonyl group.

CH stretch

CO carbonyl stretch

2-pentanone
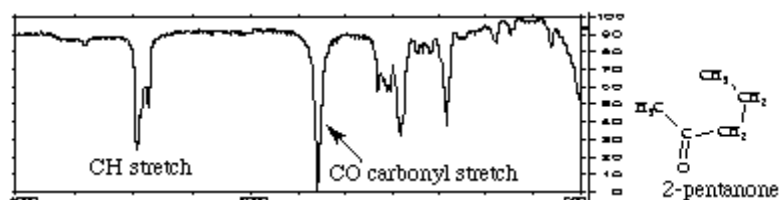
Carboxylic acids have spectra that are even more involved. They typically have three bands caused by bonds in the COOH functional group. The band near 1700 cm⁻¹ is due to the CO double bond. The broad band centered in the range 2700-3300 cm⁻¹ is caused by the presence of the OH and a band near 1400 cm⁻¹ comes from the CO single bond . The spectrum for the carboxylic acid, diphenylacetic acid, appears below. Although the aromatic CH bands complicate the spectrum, you can still see the broad OH stretch between 2700-3300 cm⁻¹. It overlaps the CH stretch which appears near 3000 cm⁻¹. A strong carbonyl CO stretch band exists near 1700 cm⁻¹. The CO single bond stretch shows up near 1200 cm⁻¹.

OH stretch

CH stretch

CO carbonyl stretch

diphenylacetic acid
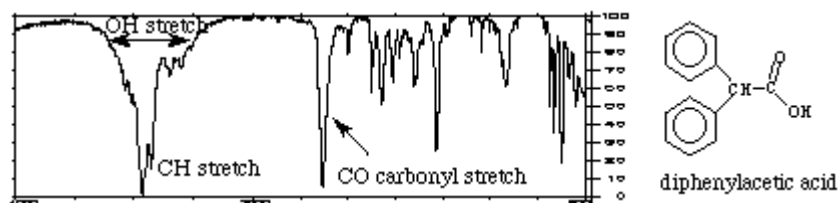
The spectrum for 1-bromobutane, $C_4H_9Br$, is shown here. This is relatively simple because there are only CH single bonds and the CBr bond. The CH stretch still appears at about 3000 cm-1. The $CH_2$ bend shows up near 1400 cm⁻¹, and you can see the CBr stretch band at approximately 700

cm$^{-1}$.



1-bromobutane
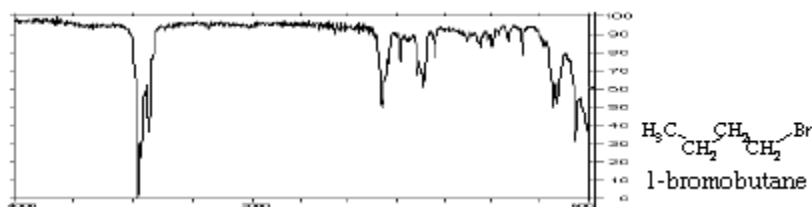
IR spectra can be used to identify molecules by recording the spectrum for an unknown and comparing this to a library or data base of spectra of known compounds. Computerized spectra data bases and digitized spectra are used routinely in this way in research, medicine, criminology, and a number of other fields.

In this exercise you will try to identify the outstanding bands characteristic of certain bonds and functional groups in the spectra you examine. You are certainly not expected to identify all the absorption bands in each IR spectrum at this point in your work.

**Table 1. A summary of the principle infrared bands and their assignments.**

**R is an aliphatic group.**

| Functional Group | Type | | Frequencies cm-1 | Peak Intensity |
|---|---|---|---|---|
| C-H | sp3 hybridized | R3C-H | 2850-3000 | M(sh) |
| | sp2 hybridized | =CR-H | 3000-3250 | M(sh) |
| | sp hybridized | C-H | 3300 | M-S(sh) |
| | aldehyde C-H | H-(C=O)R | 2750, 2850 | M(sh) |
| N-H | primary amine, amide | RN-H2, RCON-H2 | 3300, 3340 | S,S(br) |
| | secondary amine, amide | RNR-H, RCON-HR | 3300-3500 | S(br) |
| | tertiary | RN(R3), | none | |

| | amine, amide | RCONR2 | | |
|---|---|---|---|---|
| O-H | alcohols, phenols | free O-H | 3620-3580 | W(sh) |
| | | hydrogen bonded | 3600-3650 | S(br) |
| | carboxylic acids | R(C=O)O-H | 3500-2400 | S(br) |
| CN | nitriles | RCN | 2280-2200 | S(sh) |
| CC | acetylenes | R-CC-R | 2260-2180 | W(sh) |
| | | R-CC-H | 2160-2100 | M(sh) |
| C=O | aldehydes | R(C=O)H | 1740-1720 | S(sh) |
| | ketones | R(C=O)R | 1730-1710 | S(sh) |
| | esters | R(CO2)R | 1750-1735 | S(sh) |
| | anhydrides | R(CO2CO)R | 1820, 1750 | S, S(sh) |
| | carboxylates | R(CO2)H | 1600, 1400 | S,S(sh) |
| C=C | olefins | R2C=CR2 | 1680-1640 | W(sh) |
| | | R2C=CH2 | 1600-1675 | M(sh) |
| | | R2C=C(OR)R | 1600-1630 | S(sh) |
| -NO2 | nitro groups | RNO2 | 1550, 1370 | S,S(sh) |

**Effect of resonance and conjugation on infrared frequencies**

Let's continue our discussion of the importance of resonance but shift from the nitro group to the carboxylate anion. The carboxylate anion is represented as a resonance hybrid by the following figure:
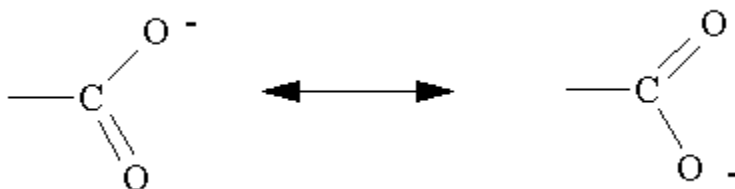


Unlike the nitro group which contained functional groups we will not be discussing, the carboxyl group is made up of a resonance hybrid between a carbon oxygen single bond and a carbon oxygen double bond. According to resonance, we would expect the C-O bond to be an average between a single and double bond or approximately equal to a bond and a half. We can use the carbonyl frequency of an ester of 1735 cm-1 to describe the force constant of the double bond. We have not discussed the stretching frequency of a C-O single bond for the simple reason that it is quite variable and because it falls in the fingerprint region. However the band is known to vary from

1000 to 1400 cm-1. For purposes of this discussion, we will use an average value of 1200 cm-1. The carbonyl frequency for a bond and a half would be expected to fall halfway between 1735 and 1200 or at approximately 1465 cm-1. The carboxyl group has the same symmetry as the nitro and CH2 groups. Both a symmetric and asymmetric stretch should be observed. The infrared spectrum of sodium benzoate is given in Figure 42. An asymmetric and symmetric stretch at 1410 and 1560 cm-1 is observed that averages to 1480 cm-1, in good agreement with the average frequency predicted for a carbon oxygen bond with a bond order of 1.5. While this is a qualitative argument, it is important to realize that the carboxylate anion does not show the normal carbonyl and normal C-O single bond stretches (at approximately 1700 and 1200 cm-1) suggested by each of the static structures above.

In the cases of the nitro group and the carboxylate anion, both resonance forms contribute equally to describing the ground state of the molecule. We will now look at instances where two or more resonance forms contribute unequally to describing the ground state and how these resonance forms can effect the various stretching frequencies.

**Carbonyl frequencies**

Most carbonyl stretching frequencies are found at approximately 1700 cm-1. A notable exception is the amide carbonyl which is observed at approximately 1600 cm-1. This suggests that the following resonance form makes a significant contribution to describing the ground state of amides:
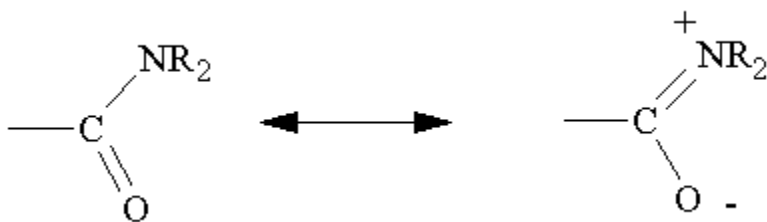


You may recall that resonance forms that lead to charge separation are not considered to be very important. However the following information support the importance of resonance in amides. X-ray crystal structures of amides show that in the solid state the amide functional group is planar. This suggests sp2 hybridization at nitrogen rather than sp3. In addition the barrier to rotation about the carbon nitrogen bond has been measured. Unlike the barrier of rotation of most aliphatic C-N bonds which are of the order of a few kcal/mol, the barrier to rotation about the carbon nitrogen bond in dimethyl formamide is approximately 18 kcal/mol. This suggests an important contribution of the dipolar structure to the ground state of the molecule and the observed frequency of 1600 cm-1, according to the arguments given above for the carboxylate anion, is consistent with more C-O single bond character than would be expected otherwise.

Conjugation of a carbonyl with a C=C bond is thought to lead to an increase in resonance interaction. Again the resonance forms lead to charge separation which clearly de-emphasizes their importance.
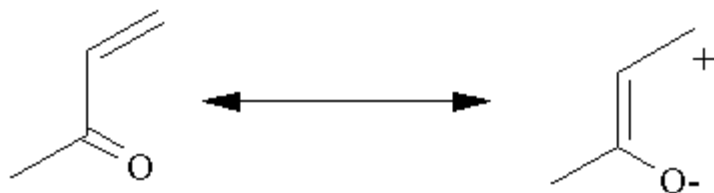
However this conjugative interaction is useful in interpreting several features of the spectrum. First it predicts the small but consistent shift of approximately 10 cm-1 to lower frequency, observed when carbonyls are conjugated to double bonds or aromatic rings. This feature is summarized in Table 4 for a variety of carbonyl groups. Next, the dipolar resonance form suggests a more polar C=C than that predicted for an unconjugated C=C. In terms of the change in dipole moment, contributions from this structure suggest that the intensity of infrared absorption of a C=C double bond would increase relative to an unconjugated system. Comparison of Figures 9, 10 and 35 with Figures 43, and 44-47 shows this to be the case. Conjugation is associated with an increase in intensity of the C=C stretching frequency. Finally, examination of Figures 43-46 reveals an intricacy not previously observed with simple non-conjugated carbonyls. The carbonyls of Figures 43-46 which are all conjugated appear as multiplets while those unconjugated carbonyls such as those in Figures 14 and 35 appear as single frequencies. Note however that not all conjugated carbonyls appear as multiplets (Figures 15 and 47. Resolution of this additional complicating feature can be achieved if we consider that conjugation requires a fixed conformation. For most conjugated carbonyls, two or more conformations are possible. The *s-cis* form is shown above and the *s-trans* form is shown below.
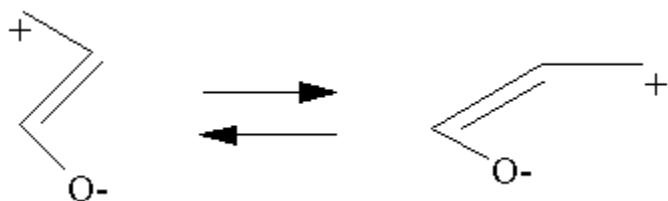


If the resonance interaction in these two forms differ, the effect of resonance on the carbonyl will differ leading to similar but different frequencies. The presence of multiple carbonyl frequencies is a good indication of a conjugated carbonyl. In some conjugated systems such as benzaldehyde

**Table 4. The effect of conjugation on carbonyl frequencies**.

| Non-conjugated Compound | Frequency cm-1 | Conjugated Compound | Frequency cm-1 | | Frequency cm-1 |
|---|---|---|---|---|---|
| butanal | 1725 | 2-butenal | 1691 | benzaldehyde | 1702 |
| 2-butanone | 1717 | methyl vinyl ketone | 1700, 1681 | acetophenone | 1685 |

| propanoic acid | 1715 | propenoic acid | 1702 | benzoic acid | 1688 |
|---|---|---|---|---|---|
| ethyl propionate | 1740 | ethyl acrylate | 1727 | ethyl benzoate | 1718 |
| butanoic anhydride | 1819, 1750 | 2-butenoic anhydride | 1782, 1722 | benzoic anhydride | 1786, 1726 |
| *cis*-cyclohexane-1,2- dicarboxylic anhydride | 1857, 1786 | 1-cyclohexene-1,2- dicarboxylic anhydride | 1844, 1767 | phthalic anhydride | 1852, 1762 |

and benzyl 4-hydroxyphenylketone (Figures 15 and 47), only one conformation by symmetry is possible and conjugation does not lead to any additional carbonyl frequencies. It should also be noted that in many of the examples given above, *cis-trans* isomerization about the carbon-carbon double bond is also possible. Some of the observed bands may also be due to the presence of these additonal isomers. Since the intensity of the peak is determined by the change in dipole moment, the presence of a small amount of geometric isomer can still lead to a detectable peak.

**Fingerprint Region of the Molecule** :

Fingerprint Region of the Molecule Whole-molecule vibrations and bending vibrations are also quantitized. No two molecules will give exactly the same IR spectrum (except enantiomers). Simple stretching: 1600-3500 cm-1. Complex vibrations: 600-1400 cm-1, called the "fingerprint region."

**REFERENCES**
Chandra A.K, 2002. Quantum Chemistry. IV Edition, Tata McGraw – Hill Publishing Company Ltd., New Delhi.
Jag Mohan, 2001. Organic Spectroscopy Principles and Applications. Narose Publishing House, New Delhi.
Kemp W., 2004. Organic Spectroscopy. III Edition, Pal Grave, New York.
Y.R.Sharma, Organic Spectroscopy III Edition, Pal Grave, New York

## POSSIBLE QUESTIONS

## MULTIPLE CHOICE QUESTIONS

1. The most important region in IR is

  a)15μ-200 μ  b) **2.5 μ-15 μ**  c) 0.8 μ-2.5μ  d) 20μ–50μ

2. Stretching Vibrations require ---------- energy than bending vibration

  a)Less  b) **More**  c) Same  d) Equal

3. The vibrational frequency is given by

  a)**$υ = 1/2πc\sqrt{k/μ}$**  b) $υ = 1/4πc\sqrt{μ/R}$  c) $υ/c = 1/2πc\sqrt{μ/R}$  d) $υ = 1/2πc * μ/R$

4. The vibrational energy of a chemical bond is given by

  a.)**Evib=[v+1\2]hν**  b)Evib=[v+1]hν  c)Evib=[v+1\2]3\2hν
  d)Evib=[v_1\2]v

5. Zero point energy of diatomic S.H.O. of vibrational frequency ν is

a)**h ν**  b) 1\2h ν  c)1\4h ν  d)0

6. The relation between De and Do the diossociation energies, of an S.H.O.is

a)**De=Do+h ν\2**  b)Do=De+h ν\2  c)De=Do+h ν  d)De=Do+2h ν

7. The selection rule for a vibrational transition in S.H.O.is

a)**Δv = +1**  b) Δv=+0  c) Δv=+or-2  d) Δn= 0

8. Very important requirement for a molecule to show an I.R spectrum is that

a) **Change in dipole moment**  b) Change in force constant  c) Change in electronic energy  d)Change in wave number

9. In IR C—H s tretching vibration occur at the region

  a)1470—1430cm$^{-1}$  b)**2960-2850cm$^{-1}$**  c)1300-1800cm$^{-1}$
  d)1000-1300cm$^{-1}$

10. In IR,C=C stretching has the frequency in the region

  a)970—980cm$^{-1}$  b)650-610cm$^{-1}$  c)**1680-1620cm$^{-1}$**
  d)995-985cm$^{-1}$

11. Absorbance is defined as

  a)**A=log$_{10}$(1\T)**  b)A=e$^-$1\T  c)A=1\T
  d)A=2\T

12. For a non linear molecule there are ------degrees of vibrational degree of freedom

  a)3n-2  b)**3n-6**  c)3n-3  d)3n-4

13. The number of vibrational degrees of freedom of watermolecule is

  a) 4  b) 9  c) 2  d) **3**

14. Which of the following molecules has the smallest spacing in the fine structure of IR spectrum?

        a) HCl          b) HBr          c) CO          d) **HI**

15. Carbonyl group shows a characteristic intense band in the IR. This high intensity is due to

        a) high reactivity of the carbonyl group
        b) the presence of lone pair of electrons which are easily excited
        c) **high polarity of the group**
        d) large force constant of the group

16. The vibrational frequency of HD is less than that of $H_2$becausce

        a) $H_2$ has a higher force constant          b) $H_2$ has a lower force constant
        c) **HD has a higher mass**      d) HD has a higher mass and lower force constant

17. The characteristic bond stretching frequency for C-Ois about---

        a)$10^4$ cm$^{-1}$          b) $10^5$ cm$^{-1}$          c) **$10^3$ cm$^{-1}$**          d) $10^2$cm$^{-1}$

18. In practical organic chemistry tetramethyl silane is used mainly for--

        a) Making volatile derivatives of alcohols          b) **A spectroscopic standard**
c) A solvent for IR spectra                       d) An antinock in gasolines

19. The spectra resulting from changes in vibrational energy levels for the same electronic state fall in which region of the spectrum

        a) Microwave          b)Visible          c) UV          d)**IR**

20. Which of the following isboth IR and microwave active?

        a)$Br_2$          b)**HBr**          c) $CS_2$          d) $CO_2$

## 8 MARKS QUESTION

1. Write the expected infrared peaks for the following compounds.

    (i) Acetamide   (ii) Benzophenone

    (ii). Discuss the features of the infrared spectra which could help in distinguishing the following pairs. $H_2N$ $CH_2C_6$ $H_4$ $COCl$ and $H_2$ $N$ $C_6$ $H_4$ $CH_2$ $COCl$

        .

2. (i).Obtain the selection rules for linear molecules, symmetric top molecules, asymmetric molecules for IR spectrum.

  (ii). Discuss briefly about the techniques employed for preparing solid samples in IR spectrum.

3. (i). Explain the following effects on vibrational frequency shift in IR spectrum.

    (a)    Coupled vibration
    (b)    Field effect and Bond angle
    (ii).What is the effect of ring size on carbonyl absorption in case of cycloketones?

4. How will you distinguish between the following pairs on the basis of IR spectroscopy?

    (i)      Fundamental vibrations and overtones.

    (ii)     Fermi resonamce and overtones

    (iii)    Inplane bending and out of plane bending virbrations

    (iv)    Inter and intramolecular hydrogen bonding.

5. (i). Compare the relative frequencies for C-C, C=C, and C≡C bonds.

   (ii). How can you distinguish among 1-hexane, 1 – hexene and 1 – hexyne on the basis of infrared spectroscopy.

**6**. Discuss in detail the various types of vibration and the factors influencing vibrational frequency.

7. (i)Explain the following effects on vibrational frequency shift in IR spectrum.

   (a) Coupled vibration

   (b) Field effect and Bond angle

   (ii) What is the effect of ring size on carbonyl absorption incase of cycloketones?

8. Explain the applications of IR spectroscopy in organic compounds?

9. (i). Compare the relative frequencies for C-C, C=C, and C≡C bonds.

   (ii). How can you distinguish among 1-hexane, 1 – hexene and 1 – hexyne on the basis of infrared spectroscopy.

10. Discuss in detail the various types of vibration and the factors influencing Vibrational frequency .

11. (a) Write the expected IR peaks for the following compounds:

   (i) p-nitro phenol (ii) p-nitro benzoic acid (iii) acetic anhydride

   (b) An organic compound (a) with molecular formula $C_3H_7NO$ gives absorption peak in the regions 3413 (m), 3236 (m), 3030-2899 (m), 1667 (s), 1634(s), and 1460 cm$^{-1}$ (s). Give its possible structure.

**KARPAGAM ACADEMY OF HIGHER EDUCATION**
**COIMBATORE-641021**
**(For the candidates admitted on 2015 onwards)**
**DEPARTMENT OF CHEMISTRY**
**I- SEMESTER**
**ORGANIC AND INORGANIC SPECTROSCOPY**

Unit-2  Infrared Spectroscopy   (17CHP104)

| S.No | Questions | Option a | Option b | Option c | Option d | Answer |
|---|---|---|---|---|---|---|
| 1 | The most important region in IR is | a)15μ-200 μ | b) 2.5 μ-15 μ | c) 0.8 μ-2.5μ | d) 20μ–50μ | b) 2.5 μ-15 μ |
| 2 | Stretching Vibration require ---------- energy than bending vibration | a)less | b) more | c) same | d) equal | b) more |
| 3 | The vibrational frequency is given by | a)$\upsilon = 1/2\pi c\sqrt{k/\mu}$ | b) $\upsilon = 1/4\pi c\sqrt{\mu/R}$ | c) $\upsilon/c = 1/2\pi c\sqrt{\mu/R}$ | d) $\upsilon = 1/2\pi c * \mu/R$ | a)$\upsilon = 1/2\pi c\sqrt{k/\mu}$ |
| 4 | The vibrational energy of a chemical bond is given by | a.)Evib=[v+1\2]hv | b)Evib=[v+1]hv | c)Evib=[v+1\2]3\2hv | d)Evib=[v_1\2]v | a.)Evib=[v+1\2]hv |
| 5 | The energy of fundamental band is | a)ΔEvib= hυ | b) ΔEvib=( hυ+3\2) | c) ΔEvib=3 hυ | d) ΔEvib= hυ\2 | a)ΔEvib= hυ |
| 6 | The energy of first overtone is | a)ΔEvib= 2hυ | b) ΔEvib= hυ+3\2 | c) ΔEvib= 3hυ | d) ΔEvib= hυ\2 | a)ΔEvib= 2hυ |
| 7 | The number of vibrational degree of freedom for $C_6H_6$ is | a)40 | b )60 | c)30 | d)10 | c)30 |
| 8 | The spectra caused in the IR region by the transition in vibrational levels in different modes of vibrations are called | a)rotational spectra | b)electronic spectra | c)vibrational spectra | d)absorption spectra | c)vibrational spectra |
| 9 | The IRspectra of a comgpound helps in | a)proving the identity of compounds | b)showing the presence of certain functional groups in the molecule | c)neither of the above | d)both (a) and (b) | d)both (a) and (b) |
| 10 | The wave numbers are expressed in | a)sec | b)cmsec | c)cm | d)cmsec[1] | c)cm |
| 11 | The internal energy of a molecule is its | a)rotational energy | b) vibrational energy | c)translational energy | d)all of these | d)all of these |
| 12 | The frequency and wavelength are related to each other by the formula | a) ν = c ν | b) ν=cv | c) ν=h ν | d) ν=h c/λ | d) ν=h c/λ |
| 13 | The molecule which is IR inactive but Raman active is | a)Hcl | b)$N_2$ | c)$SO_2$ | d)protein | d)protein |
| 14 | Number of translationa; rotational and vibrational degree of freedom in CO2 are respectively | a)3,2,4 | b)3,4,2 | c)3,3,3 | d)4,3,2 | a)3,2,4 |
| 15 | Zero point energy of diatomic S.H.O. of vibrational frequency ν is | a)h ν | b) 1\2h ν | c)1\4h ν | d)0 | a)h ν |
| 16 | The relation between De and Do the diossociation energies, of an S.H.O.is | a)De=Do+h ν\2 | b)Do=De+h ν\2 | c)De=Do+h ν | d)De=Do+2h ν | a)De=Do+h ν\2 |
| 17 | The selection rule for a vibrational transition in S.H.O.is | a)Δv = +1 | b) Δv=+0 | c) Δv=+or-2 | d) Δn= 0 | a)Δv = +1 |
| 18 | Very important requirement for a molecule to show an I.R.spectrum is that | a)change in dipolemoment | b)change in force constant | c)change in electronic energy | d)change in wave number | a)change in dipolemoment |

| # | Question | a) | b) | c) | d) | Answer |
|---|----------|----|----|----|----|--------|
| 19 | The rotational energy of a rigid rotar is | a)$E_{rot} = h^2/4\pi^2 IJ(J+1)$ | b.$E_{rot} = h^2/8\pi^2 IJ(J+1)$ | c. $E_{rot} = h/8\pi IJ(J+1)$ | d.$h/2I(J+1)$ | b.$E_{rot} = h^2/8\pi^2 IJ(J+1)$ |
| 20 | The IR spectrum od rigid rotator consist of ------ equally spaced lines with a spacing of each side of band origin | a)B | b)2B | c)4B | d)3B | a)B |
| 21 | The $\Delta J=0$ transition gives rise to a new group of lines called | a)R branch | b)S branch | c)Qbranch | d)Pbranch | c)Qbranch |
| 22 | To get parallel band in IR for$CO_2$,the oscillating dipole moment is ------- to the molecular axis is | a)parallel | b)perpendicular | c)angular | d)linear | a)parallel |
| 23 | To get parallel band in IR the selection rule is | a)$\Delta V=+1, \Delta J=+1$ | b) $\Delta V= 1, \Delta J =+1$ | c) $\Delta V=+1, \Delta J = 1$ | d) $\Delta V=+2, \Delta J=+3$ | a)$\Delta V=+1, \Delta J=+1$ |
| 24 | The selection rule to get the perpendicular band in spectrum is | a) $\Delta V=+1, \Delta J = -1$ | b) $\Delta V=+1, \Delta J = -1, O$ | c) $\Delta V=O, \Delta J=+ -1$ | d) $\Delta V=+2 \Delta J = 1^2$ | b) $\Delta V=+1, \Delta J = -1, O$ |
| 25 | Due to the +I effect of methyl group absorbtion takes place at ------- wave number in IR spectrum | a)higher | b)lower | c)same | d)none of above | b)lower |
| 26 | Introduction of electronegative atoms (or)groups-------the wave number absorption | a)increases | b)decreases | c)same | d)none of the above | a)increases |
| 27 | In IR C—H s tretching vibration occur at the region | a)$1470—1430cm^{-1}$ | b)$2960-2850cm^{-1-}$ | c)$1300-1800cm^{-1}$ | d)$1000-1300cm^{-1}$ | b)$2960-2850cm^{-1-}$ |
| 28 | In IR,C=C stretching has the frequency in the region | a)$970—980cm^{-1}$ | b)$650-610cm^{-1}$ | c)$1680-1620cm^{-1}$ | d)$995-985cm^{-1}$ | c)$1680-1620cm^{-1}$ |
| 29 | Absorbance is defined as | a)$A=\log10(1\backslash T)$ | b)$A=e^{-1}\backslash T$ | c)$A=1\backslash T$ | d)$A=2\backslash T$ | a)$A=\log10(1\backslash T)$ |
| 30 | For a non linear molecule there are ------degrees of vibrational degree of freedom | a)$3n-2$ | b)$3n-6$ | c)$3n-3$ | d)$3n-4$ | b)$3n-6$ |
| 31 | Position of C—O stretching band for primary alcohol occur at ----in IR | a)$1050cm^{-1}$ | b)$1500cm^{-1}$ | c)$1800cm^{-1}$ | d)$200cm^{-1}$ | a)$1050cm^{-1}$ |
| 32 | The O-H stretching of Phenol exibit a strong broad band in the range in IR | a)$3600-3200cm^{-1}$ | b)$1600-1700cm^{-1}$ | c)$2300-2500cm^{-1}$ | d)$900-100cm^{-1}$ | a)$3600-3200cm^{-1}$ |
| 33 | The potential energy of an anhormonic oscillator is | a)$V_r=D_e[1-\exp a(r-re)]^2$ | b)$V_r=D_e[1-a(ro-r)]^2$ | c)$V_r=D_e[1\backslash ro-r]^2$ | d)$V_r=a[D_o-(r-ro)]^2$ | a)$V_r=D_e[1-\exp a(r-re)]^2$ |
| 34 | $\mu$/For a molecule to be IR active | a)$d\mu/dr=o$ | b) $dr/d\mu =o$ | c) $d\mu/dr$ not equal to 0 | d) $d¥/dc$ not equal to 0 | c) $d\mu/dr$ not equal to 0 |
| 35 | >C=O stretching of aldehudes occur in the region in the IR region. | a)$2770-2700 cm^{-1}$ | b)$1740-1720cm^{-1}$ | c)$700-970cm^{-1}$ | d)$3300-3400^{-1}cm$ | b)$1740-1720cm^{-1}$ |
| 36 | The type of H-bonding which give rise to broad lines in IR Techinque is ----- | a)Intermolecular | b)Intramolecular | c)C-H stretching | d)C-H bending | b)Intramolecular |
| 37 | The type of H-bonding which give rise to sharp lines in IR Techinque is ------ | a)Sym.stretching | b)Anti.sym.stretching | c)Intramoleclulear | d)Intercular | a)Sym.stretching |
| 38 | In which region we get absorbtiion bands and shoulders | a)Far infradredf | b)near infrared | c)mid-infrared | d)finger print region | d)finger print region |

| No. | Question | a | b | c | d | Answer |
|---|---|---|---|---|---|---|
| 39 | N-H bending vibration for primary amines occurs in the region | a)700-900cm$^{-1}$ | b)800-700cm$^{-1}$ | c)1600-1500cm$^{-1}$ | d)800-700cm$^{-1}$ | c)1600-1500cm$^{-1}$ |
| 40 | In a double beam instrument ,the beamspilts into-----parts | a)one | b)three | c)two | d)none of the above | c)two |
| 41 | The radiation used to study the vibrational spectra of a molecule is | a. microwave | b.radiowave | c.UV | d.IR | d.IR |
| 42 | The number of vibrational degrees of freedom of watermolecule is | a. 4 | b.9 | c.2 | d. 3 | d. 3 |
| 43 | Which of the following molecules has the smallest spacing in thefine structureof Irspectrum? | a. HCl | b.HBr | c.CO | d.HI | d.HI |
| 44 | Carbonyl group shows a characteristic intenseband in the IR. This high intensity is due to | a. high reactivity of the carbonyl group | b. the presence of lone pair of electrons which areeasily excited | c. high polarity of the group | d. largeforce constant of thegroup | c. high polarity of the group |
| 45 | The vibrational frequency of HD is less than that of H$_2$becausce | a. H$_2$ has a higher force constant | b. H$_2$has a lower force constant | c. HD has a higher mass | d. HD has a higher mass and lower force constant | c. HD has a higher mass |
| 46 | Which one of the following spectroscopy is known as magnetic radiation absorption spectroscopy? | a. MS | b.NMR | c. IR | d. UV | c. IR |
| 47 | Which one of thefollowing region in IR is known as functional group region | a. 1300-4000 cm$^{-1}$ | b. 900-1300 cm$^{-1}$ | c. 650-900 cm$^{-1}$ | d)1000-1300cm$^{-1}$ | a. 1300-4000 cm$^{-1}$ |
| 48 | Whatwill be the C=O stretching band in IR of CH$_2$=CHCOCH$_3$ | a. 1700 cm$^{-1}$ | b. 1710 cm$^{-1}$ | c. 1680 cm$^{-1}$ | d. 1780 cm$^{-1}$ | c. 1680 cm$^{-1}$ |
| 49 | Which one of thefollowing statement is false for IR spectroscopy | a. Conjugation decreases the C=O stretching frequency | b. higher the frequency if more strained the alicyclic ring containig C=O group | c. Electron releasing substituents decreases the frequency of C=O band | d. Electran withdrawing subtituents decreases thefrequencyof C=O band | d. Electran withdrawing subtituents decreases thefrequencyof C=O band |
| 50 | An alcohol having mol-formula C$_4$ H gives C-O stretching band at1120 cm$^{-1}$ will be | a. 1-butanol | b.2.butanol | c. 2-methyl-2-propanol | d. isobutanol | b.2.butanol |
| 51 | Pedict thenumber of translational ,rotational and vibrational degree offreedom in neon-- | a. 3,0,0 | b. 3,1,0 | c.3,0,1 | d.3,1,1 | a. 3,0,0 |
| 52 | Which one of the following is microwave inactive? | a. HCl | b.HBr | c.Cl$_2$ | d. NO | c.Cl$_2$ |
| 53 | The rotational constant (B) of a diatomicmolecule is | a. h/4π$^2$I | b.h$^2$/4π$^2$I | c. h$^2$/8π$^2$I | d. h/8π$^2$I | d. h/8π$^2$I |
| 54 | The degree of degeneracy for a rid rotor in energy level with quantum number J is-- | a.J | b.2J | c.2J-1 | d.2J+1 | d.2J+1 |
| 55 | From the pure rotation spectrum of HF information can beobtained about | a. the force constant | b. The proton spin | c. The hydrogen bonding | d. the internuclear distance | d. the internuclear distance |
| 56 | The characteristic bond stretching frequency for C-Ois about--- | a.10$^4$ cm$^{-1}$ | b. 10$^5$ cm$^{-1}$ | c. 10$^3$ cm$^{-1}$ | d.10$^2$cm$^{-1}$ | c. 10$^3$ cm$^{-1}$ |

| | | a. | b. | c. | d. | |
|---|---|---|---|---|---|---|
| 57 | In practical organic chemistry tetramethyl silane is used mainly for-- | a. Making volatile derivatives of alcohols | b. A spectroscopic standard | c. A solvent for IR spectra | d. An antinock in gasolines | b. A spectroscopic standard |
| 58 | The spectra resulting from changes in vibrational energy levels for the same electronic state fall in which region of thespectrum | a. microwave | b.Visible | c. UV | d.IR | d.IR |
| 59 | Which of the following isboth IR and microwave active? | a.Br$_2$ | b.HBr | c.CS$_2$ | d.CO$_2$ | b.HBr |
| 60 | The symmetric C=C stretching ibration of €-2 butene is mesuredby which one of thefollowing spectroscopic methods | a. microwave | b.Visible | c. Raman | d.IR | c. Raman |

# Unit-III:
# NMR spectroscopy

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is the name given to a technique that exploits the magnetic properties of certain nuclei. For details regarding this phenomenon and its origins, refer to the nuclear magnetic resonance article. The most important applications for the organic chemist are proton NMR and carbon-13 NMR spectroscopy. In principle, NMR is applicable to any nucleus possessing spin.

Many types of information can be obtained from an NMR spectrum. Much like using infrared spectroscopy (IR) to identify functional groups, analysis of a NMR spectrum provides information on the number and type of chemical entities in a molecule. However, NMR provides much more information than IR.

The impact of NMR spectroscopy on the natural sciences has been substantial. It can, among other things, be used to study mixtures of analytes, to understand dynamic effects such as change in temperature and reaction mechanisms, and is an invaluable tool in understanding protein and nucleic acid structure and function. It can be applied to a wide variety of samples, both in the solution and the solid state.

## Theory of nuclear magnetic resonance

### Nuclear spin and the splitting of energy levels in a magnetic field

Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as $^{12}C$) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as $^{1}H$ and $^{13}C$) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons **and** the number of protons are both even, then the nucleus has **NO** spin.
2. If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

The overall spin, *I*, is important. Quantum mechanics tells us that a nucleus of spin *I* will have $2I + 1$ possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number, m.*

## Energy levels for a nucleus with spin quantum number 1/2
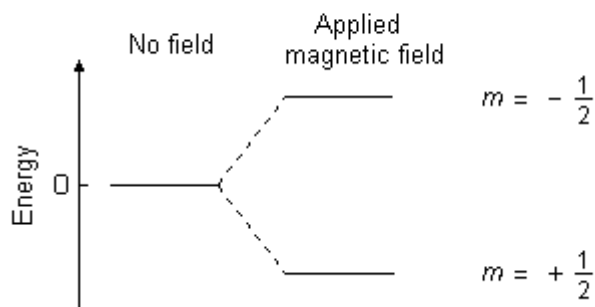


When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that **the lower energy level will contain slightly more nuclei than the higher leve**l. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels

## Nuclear spin and magnets

All nucleons, that is neutrons and protons, composing any atomic nucleus, have the intrinsic quantum property of spin. The overall spin of the nucleus is determined by the spin quantum number $S$. If the number of both the protons and neutrons in a given nuclide are even then $S = 0$, i.e. there is no overall spin; just as electrons pair up in atomic orbitals, so do even numbers of protons or even numbers of neutrons (which are also spin-$\frac{1}{2}$ particles and hence fermions) pair up giving zero overall spin.

However, a proton and neutron will have lower energy when their spins are parallel, **not anti-parallel**, as this parallel spin alignment does not infringe upon the Pauli principle, but instead has to do with the quark structure of these two nucleons. Therefore, the spin ground state for the deuteron (the deuterium nucleus, or the $^2$H isotope of hydrogen)—that has only a proton and a neutron—corresponds to a spin value of **1**, *not of zero*; the single, isolated deuteron is therefore exhibiting an NMR absorption spectrum characteristic of a quadrupolar nucleus of spin **1**, which in the 'rigid' state at very low temperatures is a characteristic ('Pake') *doublet*, (not a singlet as for a single, isolated $^1$H, or any other isolated fermion or dipolar nucleus of spin 1/2). On the other hand, because of the Pauli principle, the (radioactive) tritium isotope has to have a pair of anti-parallel spin neutrons (of total spin zero for the neutron spin couple), plus a proton of spin 1/2; therefore, the character of the tritium nucleus ('triton') is again magnetic dipolar, *not quadrupolar*—like its non-radioactive deuteron neighbor—and the tritium nucleus total spin value is again 1/2, just like for the simpler, abundant hydrogen isotope, $^1$H nucleus (the *proton*). The NMR absorption (radio) frequency for tritium is however slightly higher than that of $^1$H because the tritium nucleus has a slightly higher gyromagnetic ratio than $^1$H. In many other cases of *non-radioactive* nuclei, the overall spin is also non-zero.

For                               example,                               the
Al nucleus has an overall spin value $S = {}^5\!/_2$.

A non-zero spin is thus always associated with a non-zero magnetic moment ($\mu$) via the relation $\mu = \gamma S$, where $\gamma$ is the gyromagnetic ratio. It is this magnetic moment that allows the observation of NMR absorption spectra caused by transitions between nuclear spin levels. Most nuclides (with some rare exceptions) that have both even numbers of protons and even numbers of neutrons, also have zero nuclear magnetic moments-and also have zero magnetic dipole and quadrupole moments; therefore, such nuclides do not exhibit any NMR absorption spectra. Thus, 18O is an example of a nuclide that has no NMR absorption, whereas 13C, 31P, 35Cl and 37Cl are nuclides that do exhibit NMR absorption spectra; the last two nuclei are quadrupolar nuclei whereas the preceding two nuclei (13 C and 31P) are dipolar ones.

Electron spin resonance (ESR) is a related technique which detects transitions between electron spin levels instead of nuclear ones. The basic principles are similar; however, the instrumentation, data analysis and detailed theory are significantly different. Moreover, there is a much smaller number of molecules and materials with unpaired electron spins that exhibit ESR (or electron paramagnetic resonance (EPR)) absorption than those that have NMR absorption spectra. Significantly also, is the much greater sensitivity of ESR and EPR in comparison with NMR. Furthermore, ferromagnetic materials and thin films may exhibit 'very unusual', highly resolved ferromagnetic resonance (FMR) spectra, or ferromagnetic spin wave resonance (FSWR) excitations in non-crystalline solids such as ferromagnetic metallic glasses, well beyond the common single-transitions of most routine NMR, FMR and EPR studies.

## Values of spin angular momentum

The angular momentum associated with nuclear spin is quantized. This means both that the magnitude of angular momentum is quantized (i.e. $S$ can only take on a restricted range of values), and also that the orientation of the associated angular momentum is quantized. The associated quantum number is known as the magnetic quantum number, $m$, and can take values from $+S$ to $-S$, in integer steps. Hence for any given nucleus, there is a total of $2S + 1$ angular momentum states.

The z-component of the angular momentum vector ($\mathbf{S}$) is therefore $S_z = m\hbar$, where $\hbar$ is the reduced Planck constant. The z-component of the magnetic moment is simply:

$$\mu_z = \gamma S_z = \gamma m \hbar$$

## Spin behavior in a magnetic field
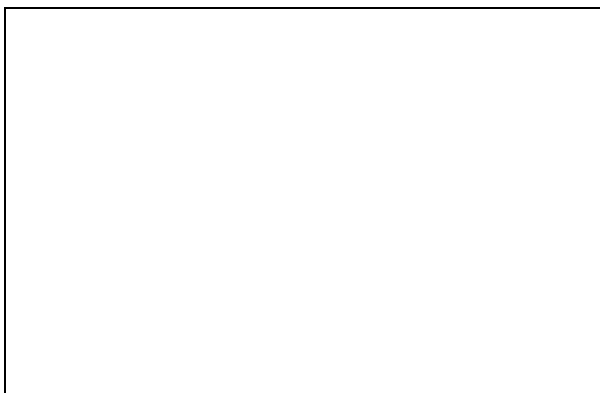
Splitting of nuclei spin states in an external magnetic field

Consider nuclei which have a spin of one-half, like 1H, 13C or 19F. The nucleus has two possible spin states: $m = \frac{1}{2}$ or $m = -\frac{1}{2}$ (also referred to as spin-up and spin-down, or sometimes α and β spin states, respectively). These states are degenerate, that is they have the same energy. Hence the number of atoms in these two states will be approximately equal at thermal equilibrium.

If a nucleus is placed in a magnetic field, however, the interaction between the nuclear magnetic moment and the external magnetic field mean the two states no longer have the same energy. The energy of a magnetic moment $\boldsymbol{\mu}$ when in a magnetic field $\mathbf{B}_0$ is given by:
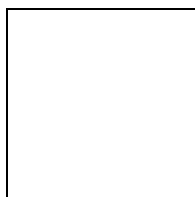
Usually the $z$ axis is chosen to be along $\mathbf{B}_0$, and the above expression reduces to:
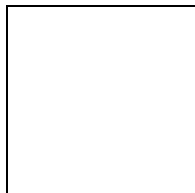
or alternatively:
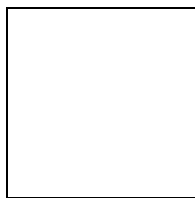
As a result the different nuclear spin states have different energies in a non-zero magnetic field. In hand-waving terms, we can talk about the two spin states of a spin $\frac{1}{2}$ as being *aligned* either with or against the magnetic field. If $\gamma$ is positive (true for most isotopes) then $m = \frac{1}{2}$ is the lower energy state.

The energy difference between the two states is:
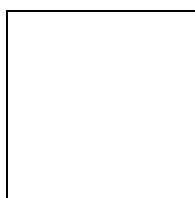
and this difference results in a small population bias toward the lower energy state.

## Magnetic resonance by nuclei

Resonant absorption by nuclear spins will occur only when electromagnetic radiation of the correct frequency (e.g., equaling the Larmor precession rate) is being applied to match the energy difference between the nuclear spin levels in a constant magnetic field of the appropriate strength. The energy of an absorbed photon is then $E = hv_0$, where $v_0$ is the resonance radiofrequency that has to match (that is, it has to be equal to) the Larmor precession frequency $v_L$ of the nuclear magnetization in the constant magnetic field $\mathbf{B}_0$. Hence, a magnetic resonance absorption will only occur when $\Delta E = hv_0$, which is when $v_0 = \gamma B_0/(2\pi)$. Such magnetic resonance frequencies typically correspond to the radio frequency (or RF) range of the electromagnetic spectrum for magnetic fields up to ~20 T. It is this magnetic resonant absorption which is detected in NMR

## Calculating transition energy

The nucleus has a positive charge and is spinning. This generates a small magnetic field. The nucleus therefore possesses a magnetic moment, $\mu$, which is proportional to its spin,*I*.
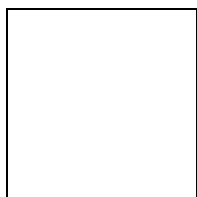
The constant, γ, is called the *magnetogyric ratio* and is a fundamental nuclear constant which has a different value for every nucleus. *h* is Plancks constant.

The energy of a particular energy level is given by;
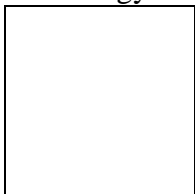
Where *B* is the strength of the magnetic field **at the nucleus**.

The difference in energy between levels (the transition energy) can be found from
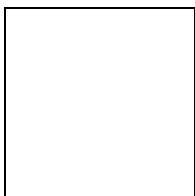
This means that if the magnetic field, *B*, is increased, so is ΔE. It also means that if a nucleus has a relatively large magnetogyric ratio, then ΔE is correspondingly large.

If you had trouble understanding this section, try reading the next bit (The absorption of radiation by a nucleus in a magnetic field) and then come back.
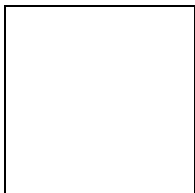
## The absorption of radiation by a nucleus in a magnetic field

In this discussion, we will be taking a "classical" view of the behaviour of the nucleus - that is, the behaviour of a charged particle in a magnetic field.

Imagine a nucleus (of spin 1/2) in a magnetic field. This nucleus is in the lower energy level (i.e. its magnetic moment does not oppose the applied field). The nucleus is spinning on its axis. In the presence of a magnetic field, this axis of rotation will *precess* around the magnetic field;
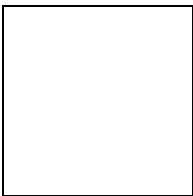
The frequency of precession is termed the *Larmor frequency*, which is identical to the transition frequency.

The potential energy of the precessing nucleus is given by;

$E = - \mu B \cos \theta$

where $\theta$ is the angle between the direction of the applied field and the axis of nuclear rotation.

If energy is absorbed by the nucleus, then the angle of precession, $\theta$, will change. For a nucleus of spin 1/2, absorption of radiation "flips" the magnetic moment so that it **opposes** the applied field (the higher energy state).
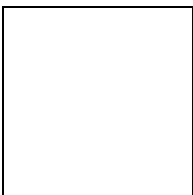
It is important to realise that only a small proportion of "target" nuclei are in the lower energy state (and can absorb radiation). There is the possibility that by exciting these nuclei, the populations of the higher and lower energy levels will become equal. If this occurs, then there will be **no** further absorption of radiation. The spin system is *saturated*. The possibility of saturation means that we must be aware of the relaxation processes which return nuclei to the lower energy state.

## Nuclear shielding

It might appear from the above that all nuclei of the same nuclide (and hence the same *g*) would resonate at the same frequency. This is not the case. The most important perturbation of the NMR frequency for applications of NMR is the 'shielding' effect of the surrounding electrons. In general, this electronic shielding reduces the magnetic field *at the nucleus* (which is what determines the NMR frequency).

As a result the energy gap is reduced, and the frequency required to achieve resonance is also reduced. This shift in the NMR frequency due to the electrons' molecular orbital coupling to the external magnetic field is called chemical shift, and it explains why NMR is able to probe the chemical structure of molecules which depends on the electron

density distribution in the corresponding molecular orbitals. If a nucleus in a specific chemical group is shielded to a higher degree by a higher electron density of its surrounding molecular orbital, then its NMR frequency will be shifted "upfield" (that is, a lower chemical shift), whereas if it is less shielded by such surrounding electron density, then its NMR frequency will be shifted "downfield" (that is, a higher chemical shift).

Unless the local symmetry of such molecular orbitals is very high (leading to "isotropic" shift), the shielding effect will depend on the orientation of the molecule with respect to the external field ($\mathbf{B}_0$). In solid-state NMR spectroscopy, magic angle spinning is required to average out this orientation dependence in order to obtain values close to the average chemical shifts. This is unnecessary in conventional NMR investigations of molecules, since rapid molecular tumbling averages out the chemical shift anisotropy (CSA). In this case, the term "average" chemical shift (ACS) is used.

## Relaxation

There are two major relaxation processes;

- Spin - lattice (longitudinal) relaxation
- Spin - spin (transverse) relaxation

**Spin - lattice relaxation**
Nuclei in an NMR experiment are in a sample. The sample in which the nuclei are held is called the *lattice*. Nuclei in the lattice are in vibrational and rotational motion, which creates a complex magnetic field. The magnetic field caused by motion of nuclei within the lattice is called the *lattice field*. This lattice field has many components. Some of these components will be equal in frequency and phase to the Larmor frequency of the nuclei of interest. These components of the lattice field can interact with nuclei in the higher energy state, and cause them to lose energy (returning to the lower state). The energy that a nucleus loses increases the amount of vibration and rotation within the lattice (resulting in a tiny rise in the temperature of the sample).

The relaxation time, $T_1$ (the average lifetime of nuclei in the higher energy state) is dependant on the magnetogyric ratio of the nucleus and the mobility of the lattice. As mobility increases, the vibrational and rotational frequencies increase, making it more likely for a component of the lattice field to be able to interact with excited nuclei. However, at extremely high mobilities, the probability of a component of the lattice field being able to interact with excited nuclei decreases.

**Spin - spin relaxation**
Spin - spin relaxation describes the interaction between neighbouring nuclei with identical precessional frequencies but differing magnetic quantum states. In this situation, the nuclei can exchange quantum states; a nucleus in the lower energy level will be excited, while the excited nucleus relaxes to the lower energy state. There is no **net** change in the populations of the energy states, but the average lifetime of a nucleus in the excited state will decrease. This can result in line-broadening.

## Chemical shift

Depending on the local chemical environment, different protons in a molecule resonate at slightly different frequencies. Since both this frequency shift and the fundamental resonant frequency are directly proportional to the strength of the magnetic field, the shift is converted into a *field-independent* dimensionless value known as the chemical shift. The chemical shift is reported as a relative measure from some reference resonance frequency. (For the nuclei $^1$H, $^{13}$C, and $^{29}$Si, TMS (tetramethylsilane) is commonly used as a reference.) This difference between the frequency of the signal and the frequency of the reference is divided by frequency of the reference signal to give the chemical shift. The frequency shifts are extremely small in comparison to the fundamental NMR frequency. A typical frequency shift might be 100 Hz, compared to a fundamental NMR frequency of 100 MHz, so the chemical shift is generally expressed in parts per million (ppm). To detect such small frequency differences the applied magnetic field must be constant throughout the sample volume. High resolution NMR spectrometers use shims to adjust the homogeneity of the magnetic field to parts per billion (ppb) in a volume of a few cubic centimeters.

By understanding different chemical environments, the chemical shift can be used to obtain some structural information about the molecule in a sample. The conversion of the raw data to this information is called *assigning* the spectrum. For example, for the $^1$H-NMR spectrum for ethanol ($CH_3CH_2OH$), one would expect three specific signals at three specific chemical shifts: one for the C$H_3$ group, one for the C$H_2$ group and one for the O$H$ group. A typical $CH_3$ group has a shift around 1 ppm, a $CH_2$ attached to an OH has a shift of around 4 ppm and an OH has a shift around 2–3 ppm depending on the solvent used.

Because of molecular motion at room temperature, the three methyl protons *average* out during the course of the NMR experiment (which typically requires a few ms). These protons become degenerate and form a peak at the same chemical shift.

The shape and size of peaks are indicators of chemical structure too. In the example above—the proton spectrum of ethanol—the $CH_3$ peak would be three times as large as the OH. Similarly the $CH_2$ peak would be twice the size of the OH peak but only 2/3 the size of the $CH_3$ peak.

Modern analysis software allows analysis of the size of peaks to understand how many protons give rise to the peak. This is known as integration—a mathematical process which calculates the area under a curve. The analyst must integrate the peak and not measure its height because the peaks also have *width*—and thus its size is dependent on its area not its height. However, it should be mentioned that the number of protons, or any other observed nucleus, is only proportional to the intensity, or the integral, of the NMR signal, in the very simplest one-dimensional NMR experiments. In more elaborate experiments, for instance, experiments typically used to obtain carbon-13 NMR spectra, the integral of the signals depends on the relaxation rate of the nucleus, and its scalar and dipolar coupling constants. Very often these factors are poorly known - therefore, the

integral of the NMR signal is very difficult to interpret in more complicated NMR experiments.

The magnetic field at the nucleus is **not** equal to the applied magnetic field; electrons around the nucleus shield it from the applied field. The difference between the applied magnetic field and the field at the nucleus is termed the *nuclear shielding*.

Consider the s-electrons in a molecule. They have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased for the nucleus to absorb at its transition frequency. This *upfield shift* is also termed *diamagnetic shift*.
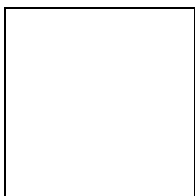
Electrons in p-orbitals have **no** spherical symmetry. They produce comparatively large magnetic fields at the nucleus, which give a *low field shift*. This "deshielding" is termed *paramagnetic shift*.

In proton ($^1$H) NMR, p-orbitals play no part (there aren't any!), which is why only a small range of chemical shift (10 ppm) is observed. We can easily see the effect of s-electrons on the chemical shift by looking at substituted methanes, $CH_3X$. As X becomes increasingly electronegative, so the electron density around the protons decreases, and they resonate at lower field strengths (increasing $\delta_H$ values).

*Chemical shift* is defined as *nuclear shielding / applied magnetic field*. Chemical shift is a function of the nucleus and its environment. It is measured relative to a reference compound. For $^1$H NMR, the reference is usually tetramethylsilane, Si $(CH_3)_4$.

## J-coupling

Some of the most useful information for structure determination in a one-dimensional NMR spectrum comes from **J-coupling** or **scalar coupling** (a special case of spin-spin coupling) between NMR active nuclei. This coupling arises from the interaction of different spin states through the chemical bonds of a molecule and results in the splitting of NMR signals. These splitting patterns can be complex or simple and, likewise, can be straightforwardly interpretable or deceptive. This coupling provides detailed insight into the connectivity of atoms in a molecule.

| Multiplicity | Intensity Ratio |
|---|---|
| Singlet (s) | 1 |
| Doublet (d) | 1:1 |
| Triplet (t) | 1:2:1 |
| Quartet (q) | 1:3:3:1 |
| Quintet | 1:4:6:4:1 |
| Sextet | 1:5:10:10:5:1 |
| Septet | 1:6:15:20:15:6:1 |

Coupling to *n* equivalent (spin ½) nuclei splits the signal into a *n+1* **multiplet** with intensity ratios following Pascal's triangle as described on the right. Coupling to additional spins will lead to further splittings of each component of the multiplet e.g. coupling to two different spin ½ nuclei with significantly different coupling constants will lead to a *doublet of doublets* (abbreviation: dd). Note that coupling between nuclei that are chemically equivalent (that is, have the same chemical shift) has no effect of the NMR spectra and couplings between nuclei that are distant (usually more than 3 bonds apart for protons in flexible molecules) are usually too small to cause observable splittings. *Long-range* couplings over more than three bonds can often be observed in cyclic and aromatic compounds, leading to more complex splitting patterns.

For example, in the proton spectrum for ethanol described above, the $CH_3$ group is split into a *triplet* with an intensity ratio of 1:2:1 by the two neighboring $CH_2$ protons. Similarly, the $CH_2$ is split into a *quartet* with an intensity ratio of 1:3:3:1 by the three neighboring $CH_3$ protons. In principle, the two $CH_2$ protons would also be split again into a *doublet* to form a *doublet of quartets* by the hydroxyl proton, but intermolecular exchange of the acidic hydroxyl proton often results in a loss of coupling information.

Coupling to any spin ½ nuclei such as phosphorus-31 or fluorine-19 works in this fashion (although the magnitudes of the coupling constants may be very different). But the splitting patterns differ from those described above for nuclei with spin greater than ½ because the spin quantum number has more than two possible values. For instance, coupling to deuterium (a spin 1 nucleus) splits the signal into a *1:1:1 triplet* because the spin 1 has three spin states. Similarly, a spin 3/2 nucleus splits a signal into a *1:1:1:1 quartet* and so on.

Coupling combined with the chemical shift (and the integration for protons) tells us not only about the chemical environment of the nuclei, but also the number of *neighboring* NMR active nuclei within the molecule. In more complex spectra with multiple peaks at similar chemical shifts or in spectra of nuclei other than hydrogen, coupling is often the only way to distinguish different nuclei.

## Spin - spin coupling

Consider the structure of ethanol;
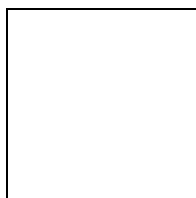


The ^{1}H NMR spectrum of ethanol (below) shows the methyl peak has been split into three peaks (a *triplet*) and the methylene peak has been split into four peaks (a *quartet*). This occurs because there is a small interaction (*coupling*) between the two groups of protons. The spacings between the peaks of the methyl triplet are equal to the spacings

between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the *coupling constant, J*.
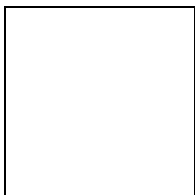
To see why the methyl peak is split into a triplet, let's look at the **methylene** protons. There are two of them, and each can have one of two possible orientations (aligned with or opposed against the applied field). This gives a total of four possible states;
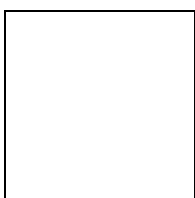
In the first possible combination, spins are paired and opposed to the field. This has the effect of reducing the field experienced by the **methyl** protons; therefore a slightly higher field is needed to bring them to resonance, resulting in an upfield shift. Neither combination of spins opposed to each other has an effect on the methyl peak. The spins paired in the direction of the field produce a downfield shift. Hence, the methyl peak is split into three, with the ratio of areas 1:2:1.

Similarly, the effect of the methyl protons on the methylene protons is such that there are eight possible spin combinations for the three methyl protons;
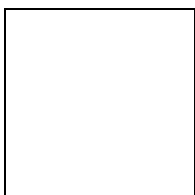
Out of these eight groups, there are two groups of three magnetically equivalent combinations. The methylene peak is split into a quartet. The areas of the peaks in the quartet have the ration 1:3:3:1.

In a *first-order* spectrum (where the chemical shift between interacting groups is much larger than their coupling constant), interpretation of splitting patterns is quite straightforward;

- The multiplicity of a multiplet is given by the number of equivalent **protons** in **neighbouring** atoms plus one, i.e. *the n + 1 rule*

- Equivalent nuclei do not interact with each other. The three methyl protons in ethanol cause splitting of the neighbouring methylene protons; they do not cause splitting among themselves
- The coupling constant is not dependant on the applied field. Multiplets can be easily distinguished from closely spaced chemical shift peaks.

## Second-order (or strong) coupling

The above description assumes that the coupling constant is small in comparison with the difference in NMR frequencies between the inequivalent spins. If the shift separation decreases (or the coupling strength increases), the multiplet intensity patterns are first distorted, and then become more complex and less easily analyzed (especially if more than two spins are involved). Intensification of some peaks in a multiplet is achieved at the expense of the remainder, which sometimes almost disappear in the background noise, although the integrated area under the peaks remains constant. In most high-field NMR, however, the distortions are usually modest and the characteristic distortions (*roofing*) can in fact help to identify related peaks.

Second-order effects decrease as the frequency difference between multiplets increases, so that high-field (i.e. high-frequency) NMR spectra display less distortion than lower frequency spectra. Early spectra at 60 MHz were more prone to distortion than spectra from later machines typically operating at frequencies at 200 MHz or above.

## Magnetic inequivalence

More subtle effects can occur if chemically equivalent spins (i.e. nuclei related by symmetry and so having the same NMR frequency) have different coupling relationships to external spins. Spins that are chemically equivalent but are not indistinguishable (based on their coupling relationships) are termed magnetically inequivalent. For example, the 4 H sites of 1,2-dichlorobenzene divide into two chemically equivalent pairs by symmetry, but an individual member of one of the pairs has different couplings to the spins making up the other pair. Magnetic inequivalence can lead to highly complex spectra which can only be analyzed by computational modeling. Such effects are more common in NMR spectra of aromatic and other non-flexible systems, while conformational averaging about C-C bonds in flexible molecules tends to equalize the couplings between protons on adjacent carbons, reducing problems with magnetic inequivalence.

# Correlation spectroscopy

For more details on this topic, see 2D-NMR.

**Correlation spectroscopy** is one of several types of two-dimensional nuclear magnetic resonance (NMR) spectroscopy or 2D-NMR. This type of NMR experiment is best known by its acronym, COSY. Other types of two-dimensional NMR include J-spectroscopy, exchange spectroscopy (EXSY), Nuclear Overhauser effect spectroscopy (NOESY), total correlation spectroscopy (TOCSY) and heteronuclear correlation experiments, such as HSQC, HMQC, and HMBC. Two-dimensional NMR spectra provide more information about a molecule than one-dimensional NMR spectra and are especially useful in determining the structure of a molecule, particularly for molecules that are too complicated to work with using one-dimensional NMR. The first two-dimensional experiment, COSY, was proposed by Jean Jeener, a professor at Université Libre de Bruxelles, in 1971 This experiment was later implemented by Walter P. Aue, Enrico Bartholdi and Richard R. Ernst, who published their work in 1976

# Solid-state nuclear magnetic resonance

A variety of physical circumstances does not allow molecules to be studied in solution, and at the same time not by other spectroscopic techniques to an atomic level, either. In solid-phase media, such as crystals, microcrystalline powders, gels, anisotropic solutions, etc., it is in particular the dipolar coupling and chemical shift anisotropy that become dominant to the behaviour of the nuclear spin systems. In conventional solution-state NMR spectroscopy, these additional interactions would lead to a significant broadening of spectral lines. A variety of techniques allows to establish high-resolution conditions, that can, at least for $^{13}$C spectra, be comparable to solution-state NMR spectra.

Two important concepts for high-resolution solid-state NMR spectroscopy are the limitation of possible molecular orientation by sample orientation, and the reduction of anisotropic nuclear magnetic interactions by sample spinning. Of the latter approach, fast spinning around the magic angle is a very prominent method, when the system comprises spin 1/2 nuclei. A number of intermediate techniques, with samples of partial alignment or reduced mobility, is currently being used in NMR spectroscopy.

Applications in which solid-state NMR effects occur are often related to structure investigations on membrane proteins, protein fibrils or all kinds of polymers, and chemical analysis in inorganic chemistry, but also include "exotic" applications like the plant leaves and fuel cells.

# NMR spectroscopy applied to proteins

Much of the recent innovation within NMR spectroscopy has been within the field of protein NMR, which has become a very important technique in structural biology. One common goal of these investigations is to obtain high resolution 3-dimensional structures of the protein, similar to what can be achieved by X-ray crystallography. In contrast to X-ray crystallography, NMR is primarily limited to relatively small proteins, usually smaller than 35 kDa, though technical advances allow ever larger structures to be solved. NMR spectroscopy is often the only way to obtain high resolution information on

partially or wholly intrinsically unstructured proteins. It is now a common tool for the determination of Conformation Activity Relationships where the structure before and after interaction with, for example, a drug candidate is compared to its known biochemical activity. Proteins are orders of magnitude larger than the small organic molecules discussed earlier in this article, but the basic NMR techniques and some of the NMR theory also applies. Because of the much higher number of atoms present in a protein molecule in comparison with a small organic compound, the basic 1D spectra become crowded with overlapping signals to an extent where direct spectra analysis becomes untenable. Therefore, multidimensional (2, 3 or 4D) experiments have been devised to deal with this problem. To facilitate these experiments, it is desirable to isotopically label the protein with $^{13}$C and $^{15}$N because the predominant naturally occurring isotope $^{12}$C is not NMR-active, whereas the nuclear quadrupole moment of the predominant naturally occurring $^{14}$N isotope prevents high resolution information to be obtained from this nitrogen isotope. The most important method used for structure determination of proteins utilizes NOE experiments to measure distances between pairs of atoms within the molecule. Subsequently, the obtained distances are used to generate a 3D structure of the molecule by solving a distance

# Carbon-13 NMR

## Introduction

Many of the molecules studied by NMR contain carbon. Unfortunately, the carbon-12 nucleus does not have a nuclear spin, but the carbon-13 (C-13) nucleus does due to the presence of an unpaired neutron. Carbon-13 nuclei make up approximately one percent of the carbon nuclei on earth. Therefore, carbon-13 NMR spectroscopy will be less sensitive (have a poorer SNR) than hydrogen NMR spectroscopy. With the appropriate concentration, field strength, and pulse sequences, however, carbon-13 NMR spectroscopy can be used to supplement the previously described hydrogen NMR information. Advances in superconducting magnet design and RF sample coil efficiency have helped make carbon-13 spectroscopy routine on most NMR spectrometers.

The *sensitivity* of an NMR spectrometer is a measure of the minimum number of spins detectable by the spectrometer. Since the NMR signal increases as the population difference between the energy levels increases, the sensitivity improves as the field strength increases. The sensitivity of carbon-13 spectroscopy can be increased by any technique which increases the population difference between the lower and upper energy levels, or increases the density of spins in the sample. The population difference can be increased by decreasing the sample temperature or by increasing the field strength. Several techniques for increasing the carbon-13 signal have been reported in the NMR literature.

Unfortunately, or fortunately, depending on your perspective, the presence of spin-spin coupling between a carbon-13 nucleus and the nuclei of the hydrogen atoms bonded to the carbon-13, splits the carbon-13 peaks and causes an even poorer signal-to-noise ratio.

This problem can be addressed by the use of a technique known as decoupling, addressed in the next section.

**Carbon-13 NMR** ($^{13}$**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 (1H 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 13C isotope of carbon, whose natural abundance is only 1.1%, because the main carbon isotope, 12C, is not detectable by NMR since it has zero net spin.

# Implementation

$^{13}$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 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 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.

High field magnets with internal bores capable of accepting larger sample tubes (typically 10 mm in diameter for $^{13}$C NMR versus 5 mm for $^1$H NMR), the use of relaxation reagents, for example Cr(acac)$_3$ (chromium (III) acetylacetonate, CAS number 21679-31-2), and appropriate pulse sequences have reduced the time needed to acquire quantitative spectra and have made quantitative carbon-13 NMR a commonly used technique in many industrial labs. Applications range from quantification of drug purity to determination of the composition of high molecular weight synthetic polymers.

$^{13}$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.
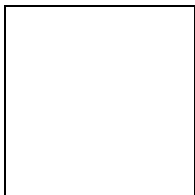
Typical chemical shifts in $^{13}$C-NMR

# DEPT spectra
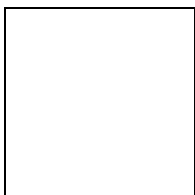
DEPT spectra of propyl benzoate

DEPT stands for **D**istortionless **E**nhancement by **P**olarization **T**ransfer. It is a very useful method for determining the presence of primary, secondary and tertiary carbon atoms. The DEPT experiment differentiates between CH, CH$_2$ and CH$_3$ groups by variation of the selection angle parameter (the tip angle of the final $^1$H pulse):

- 45° angle gives all carbons with attached protons (regardless of number) in phase
- 90° angle gives only CH groups, the others being suppressed
- 135° angle gives all CH and CH$_3$ in a phase opposite to CH$_2$

Signals from quaternary carbons and other carbons with no attached protons are always absent (due to the lack of attached protons).

The polarization transfer from $^1$H to $^{13}$C has the secondary advantage of increasing the sensitivity over the normal $^{13}$C spectrum (which has a modest enhancement from the NOE (Nuclear Overhauser Effect) due to the $^1$H decoupling).

## Decoupling

The signal-to-noise ratio in an NMR spectrometer is related to the population difference between the lower and upper spin state. The larger this difference the larger the signal. We know from chapter 3 that this difference is proportional to the strength of the $B_o$ magnetic field.

To understand decoupling, consider the familiar hydrogen NMR spectrum of HC-$(CH_2CH_3)_3$. The HC hydrogen peaks are difficult to see in the spectrum due to the splitting from the 6 -$CH_2$- hydrogens. If the effect of the 6 -$CH_2$- hydrogens could be removed, we would lose the 1:6:15:20:15:6:1 splitting for the HC hydrogen and get one peak. We would also lose the 1:3:1 splitting for the $CH_3$ hydrogens and get one peak. The process of removing the spin-spin splitting between spins is called decoupling. Decoupling is achieved with the aid of a saturation pulse. If the affect of the HC hydrogen is removed, we see the following spectrum. Similarly, if the affect of the -$CH_3$ hydrogens is removed, we see this spectrum.

A saturation pulse is a relatively low power $B_1$ field left on long enough for all magnetization to disappear. A saturation pulse applied along X' rotates magnetization clockwise about X' several times. As the magnetization is rotating, $T_2$ processes cause the magnetization to dephase. At the end of the pulse there is no net Z, X, or Y magnetization. It is easier to see this behavior with the use of plots of $M_Z$, $M_{X'}$, and $M_{Y'}$ as a function of time. Since the $B_1$ pulse is long, its frequency content is small. It therefore can be set to coincide with the location of the -$CH_2$- quartet and saturate the -$CH_2$- spin system. By saturating the -$CH_2$- spins, the -$CH_2$- peaks and the splittings disappear, causing the height of the now unsplit HC- and -$CH_3$ peaks to be enhanced.

Now that the concept of decoupling has been introduced, consider the carbon-13 spectrum from $CH_3I$. The NMR spectrum from the carbon-13 nucleus will yield one absorption peak in the spectrum. Adding the nuclear spin from one hydrogen will split the carbon-13 peak into two peaks. Adding one more hydrogen will split each of the two carbon-13 peaks into two, giving a 1:2:1 ratio. The final hydrogen will split each of the previous peaks, giving a 1:3:3:1 ratio. If the hydrogen spin system is saturated, the four lines collapse into a single line having an intensity which is eight times greater than the outer peak in the 1:3:3:1 quartet since 1+3+3+1=8 . In reality, we see a single line with a relative intensity of 24. Where did the extra factor of three come from?

## NOE

The answer to the question raised in the previous paragraph is the nuclear Overhauser effect (NOE). To understand the NOE, consider a set of coupled hydrogen and carbon-13 nuclei. Assume that the red-green nuclei are carbon-13 and the blue-pink nuclei are hydrogen.

$T_{1CC}$ is $T_1$ relaxation due to interactions between carbon-13 nuclei. $T_{1HH}$ is $T_1$ relaxation due to interactions between hydrogen nuclei. $T_{1CH}$ is $T_1$ relaxation due to interactions between carbon-13 and hydrogen nuclei.

$M_Z(C)$ is the magnetization due to carbon-13 nuclei. $M_o(C)$ is the equilibrium magnetization of carbon-13. $M_Z(H)$ is the magnetization due to hydrogen nuclei. $M_o(H)$ is the equilibrium magnetization of hydrogen.

The equations governing the change in the Z magnetization with time are:
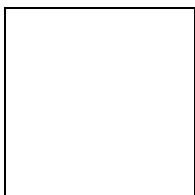
If we saturate the hydrogen spins, $M_Z(H) = 0$.
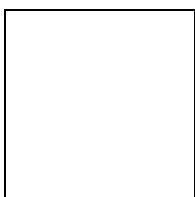
Letting the system equilibrate, d $M_Z(C)$ /dt = 0 .
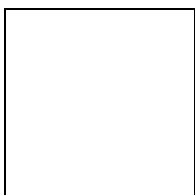
Rearranging the previous equation, we obtain an equation for $M_Z(C)$ .
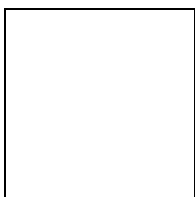
Note that $M_Z(C)$ has increased by $M_o(H)$ $T_{1CC}$ / $T_{1CH}$ which is approximately 2 $M_o(C)$, giving a total increase of a factor of 3 relative to the total area of the undecoupled peaks. This explains the extra factor of three (for a total intensity increase of 24) for the carbon-13 peak when hydrogen decoupling is used in the carbon-13 spectrum of $CH_3I$.

The following spin-echo sequence has been modified to decouple the hydrogen spins from the carbon-13 spins. The signal is recorded as the second half of the echo.

## Population Inversion

Another method of improving the NMR signal in systems with spin-spin coupling is population inversion. To understand the concept of a population inversion, that Boltzmann statistics tell us that there are more spins in the lower spin state than the upper one of a two spin state system. Population inversion is the interchange of the populations of these two spin states so that there are more spins in the upper state then the lower one.

To understand how a population inversion improves the signal-to-noise ratio in a spectrum, consider the $CHI_3$ molecule. $CHI_3$ will have four energy levels ($L_1$, $L_2$, $L_3$, and $L_4$) due to C-H spin-spin coupling. There are two carbon-13 absorption frequencies $f_1$ and $f_2$ and two hydrogen absorption frequencies $f_3$ and $f_4$. The population distribution between the four levels is such that the lowest state has the greatest population and the highest the lowest population. The two intermediate states will have populations between the outer two as indicated by the thickness of the levels in the accompanying diagram. The four lines in the spectrum will have intensities related to the population difference between the two levels spanned by the frequency. The two carbon-13 absorption lines ($f_1$ and $f_2$) will have a lower intensity than the hydrogen lines ($f_3$ and $f_4$) due to the smaller population difference between the two states joined by $f_1$ and $f_2$.

If the populations of $L_3$ and $L_1$ are inverted or interchanged with a frequency selective 180 degree pulse at $f_3$, the signal at $f_2$ will be enhanced because of the greater population difference between the states joined by $f_2$. It should be noted that the signal at $f_1$ will be inverted because the upper state of the two joined by $f_1$ has a greater population than the lower one. An example of a population inverting pulse sequence designed to enhance the carbon-13 spectral lines is depicted in the animation window. The 180 degree pulse at $f_3$ has a narrow band of frequencies centered on $f_3$ that selectively rotates only the magnetization at $f_3$ by 180 degrees.

## 1-D C-13 Spectra

The following table of compounds contains links to their corresponding one-dimensional carbon-13 NMR spectra. The spectra were recorded on a 300 MHz NMR spectrometer with a delay time between successive scans of two seconds. This relatively short delay time may cause differences in the peak heights due to variations in $T_1$ values. Other differences may be caused by variations in the nuclear Overhauser effect. In spectra recorded with deuterated chloroform ($CDCl_3$) as the lock solvent, the three peaks at = 75 are due to splitting of the $CDCl_3$ carbon-13 peak by the nuclear spin = 1 deuterium nucleus.
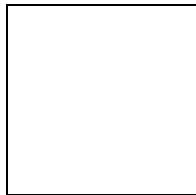
| Molecule | Formula | Solvent |
|---|---|---|
| cyclohexane | $C_6H_{12}$ | $CDCl_3$ |
| benzene | $C_6H_6$ | $CDCl_3$ |

| toluene | $C_6H_5CH_3$ | $CDCl_3$ |
|---|---|---|
| ethyl benzene | $C_6H_5CH_2CH_3$ | $CDCl_3$ |
| acetone | $CH_3(C=O)CH_3$ | $CDCl_3$ |
| methyl ethyl ketone | $CH_3(C=O)CH_2CH_3$ | $CDCl_3$ |
| ethanol | $CH_3CH_2OH$ | $CDCl_3$ |
| ethanol | $CH_3CH_2OH$ | $D_2O$ |
| 1-propanol | $CH_3CH_2CH_2OH$ | $CDCl_3$ |
| 2-propanol | $(CH_3)_2CHOH$ | $CDCl_3$ |
| t-butnol | $(CH_3)_3COH$ | $CDCl_3$ |
| 2-butanol | $CH_3CH_2CH(OH)CH_3$ | $CDCl_3$ |
| pyridine | $C_5H_5N$ | $CDCl_3$ |

# Applications of NMR Spectroscopy

NMR spectroscopy can provide an enormous amount of information—including physical, chemical, structural, and electronic—about samples under analysis. NMR spectroscopy has applications in medicine, chemistry and other fields of scientific research, industry,

**Determining molecular structure and conformation** of a sample and examining interactions between molecules can often only be achieved via NMR spectroscopy in conjunction with mass spectroscopy. Very often this type of research is critical to further or complete a given project (and determining structure and conformation is also important in obtaining intellectual property rights).

NMR spectroscopy is also vital for **studying cell metabolism**, due to the fact that metabolism is based on interactions between molecules and cells. NMR allows these types of studies to be carried out non-invasively, as it can be used to detect the presence of metabolites and chemical energy produced by cells.

**Industrial processes** such as reaction and process monitoring, and content and purity checks, often involve NMR spectroscopy. The specificity of NMR makes it highly suitable for monitoring and optimizing dynamic reactions and processes. Content and purity checks use NMR spectroscopy to monitor the quality and purity of batches of certain types of manufactured products, and to determine the composition of mixtures. NMR-based monitoring and testing is particularly useful because it can be done non-destructively—that is, without destroying the item being examined.

The ability of NMR spectroscopy to provide non-destructive analysis is actually highly useful in biological research because samples can be studied for extended periods using NMR, whereas biochemical experiments might destroy the samples.

**REFERENCES**

Chandra A.K, 2002. Quantum Chemistry. IV Edition, Tata McGraw – Hill Publishing Company Ltd., New Delhi.

Donald A. Mc Quarrie, 2003. Viva Books Pvt. Ltd, New Delhi.

James E. House, 2005. Fundamental of Quantum Chemistry. II Elsevier Academic Press, New Delhi.

Jag Mohan, 2001. Organic Spectroscopy Principles and Applications. Narose Publishing House, New Delhi.

Kemp W., 2004. Organic Spectroscopy. III Edition, Pal Grave, New York.

Levine, Ira.N , 2001.Quantum Chemistry. Prentice – Hall of India Pvt. Ltd., New Delhi.

Prasad R.K. 2002. Quantum Chemistry. II New Age International Pvt. Ltd., New Delhi.

Russell S. Drago, 1965. Physical Methods in Inorganic Chemistry. Reinhold Publishing Corporation, New York.

<u>**POSSIBLE QUESTIONS**</u>

## MULTIPLE CHOICE QUESTIONS

1. What is precessional motion
   a) **top moves around the vertical**           b)moves away the horizontal
   c) top moves away from the vertical           d)moves around the horizontal

2. The gyromagnetic ratio is
   a) **2 pi M/Hi**           b) 2C pi  M/hI           c) hI/2 pi M    d) hI/ 2C pi M.

3. What is flipping?
   a) Energy **transfer within the molecule**  b) Energy transfer outside the molecule
   c) Energy transfer from one energy        d) No energy has been transfer

4. Acetone gives
   a) **One signal NMR**   b) Two signal NMR       c) Three signal NMR        d) Four
signal NMR

5. Propanal gives
   a) 1 NMR signal        b) **2 NMR signal**      c) 3 NMR signal        d) 4 NMR signal

6. The DMSO is a
   a) **Highly polar solvent**           b) Highly non polar solvent
   c) Weakly polar solvent           d) Weakly non polar solvent

7. NMR spectrum obtained in
   a) Microwave region           b) **Radiofrequency region**
   c) IR region           d) Far IR region

8. For NMR, (a) downfield due to deshielding (b) up field due to shielding
   a) **both are true**           b) a true b false
   c) b true  a false           d)both are false

9. What is anisotropic effect
   a. **$\delta$ for protons attached to C=C in alkenes**        b. $\delta$ for protons attached to
   C=C in alkynes        c. $\delta$ for protons attached to cyclo hexanes
   d. $\delta$ for protons attached to para hexanes

10. The resultant spin of $^1$H NMR is
    a) 0-100 nm           b) 1           c) **½**           d) 3/2

11. The nucleus which gives NMR spectrum is
    a) $^{16}_8$O           b) $^{10}_5$**B**           c) $^{12}$O           d) $^4_2$He

12. The $^1$H spectrum $CH_2$ (Cl)CH(Cl)OCH$_3$ would show
    a) **a 3 proton singlet, I proton triplet and 2 proton doublet**
    b) a 3 proton doublet 1 proton triplet and 2 proton singlet
    c) a 3 proton triplet 1 proton doublet 2 proton doublet
    d) a 3 proton singlet 1 proton singlet 2 proton doublet

13. The chemical shift of a proton on the $\delta$ scale is 4. The value of the $\tau$ scale is---
    a) 14           b) **6**           c) 2.5           d) 4

14. The fine structure and intensity ratios expected in the proton NMR spectrum of $NH_4^+$ ion (for $^{14}N$, I=1) are

      a) Singlet        b) Doublet 1:1        c) **Triplet 1:1:1**        d) triplet1:2:1

15. In the proton NMR spectrum of toluene, the resonance due to $CH_3$, group is expected to

      a) δ 0.5        b) δ 1.25        c) **δ2.5**        d) δ 3.5

16. How many NMR signals are found in cis dimethyl cyclopropane and trans dimethyl cyclopropane?

      a) 2, 3        b) **3, 4**        c) 1,2        d) 8,10

17. The nucleus which gives NMR spectrum is

      a) $^{16}_8O$        b) $^{10}_5B$        c) $^{12}O$        d) $^4_2He$

18. The $^1_1H$ spectrum $CH_2$ (Cl)CH(Cl)OCH_3$ would show

      a) **a 3 proton singlet,I proton triplet and 2 proton doublet**

      b) a 3 proton doublet 1 proton triplet and 2 proton singlet

      c) a 3 proton triplet 1 proton doublet 2 proton doublet

      d) a 3 proton singlet 1 proton singlet 2 proton doublet

19. The chemical shift of $^1_1H$ on the δ scale is 2.56. The value on ϒ scale is

      a) 12.56        b) **7.44**        c) 2.56        d) 1.44

20. The bond length on NO is 0.116 nm. Its rotational constant is

      a) $5.0^{30}$ x $10^{10}$ sec        b) $1.23$x $10^{10}$ sec

      c) **$5.030$x$10^{10}$ sec$^{-1}$**        d) $1.23$x $10^{10}$ sec-1


### 8MARKS QUESTION

1. Describe with examples the various factors which affect the magnitude of the chemical shift in NMR spectra?.

2. What is double resonance and spin tickling? How these are helpful in simplifying the spectra?

3. Describe $^{13}C$ NMR spectroscopy. What are the advantages of it over proton magnetic resonance spectroscopy?

4. Explain (i). Qualitative analysis

      (ii).Quantitative analysis using NMR spectra?

      (iii). Explain heteronuclear coupling with examples?

5. (i). Explain first order and non-first order NMR spectra with example?

      (ii).What are the factors that influencing germinal coupling (b) vicinal coupling (c) Long range coupling?

6. (i). What are lanthanide shift reagents and chemical shift reagents?
   (ii). Explain spin-spin coupling and spin-spin splitting are resonance phenomenon?

7. Describe $^{13}$C NMR spectroscopy. What are the advantages of it over proton magnetic resonance spectroscopy?

8. (i).Explain the qualitative analysis using NMR spectra?
      (ii). Explain heteronuclear coupling with examples?

9.      (i). Explain first order and non-first order NMR spectra with example?
         (ii).What are the factors that influencing germinal coupling (b) vicinal coupling (c) Long range coupling?

10.     (i). What are lanthanide shift reagents and chemical shift reagents?
         (ii). Explain spin-spin coupling and spin-spin splitting are resonance phenomenon?

11. Explain the application of NMR spectroscpy.

[17CHP104

**KARPAGAM ACADEMY OF HIGHER EDUCATION**

**COIMBATORE-21**

**DEPARTMENT OF CHEMISTRY**

**M.SC CHEMISTRY 2017-2019 BATCH**

**I SEMESTER**

**ORGANIC AND INORGANIC SPECTROSCOPY**

**Unit-3     Nuclear Magnetic Resonance Spectroscopy  (17CHP104)        OBJECTIVE TYPE QUESTIONS EACH QUESTIONS CARRY ONE MARK**

| S.No | Questions | option a | Option b | Option c | Option d | Answer |
|---|---|---|---|---|---|---|
| 1 | What is precessional motion | a.top moves around the vertical | b.top moves away the vertical | c.top moves away from the vertical | d.none of the above | a.top moves around the vertical |
| 2 | The gyromagnetic ratio is | a.2 pi M/Hi | b.2C pi  M/hI | c.hI/2 pi M | d.hI/ 2C pi M. | a.2 pi M/Hi |
| 3 | What is flipping | a.energy transfer within the molecule | b.energy transfer outside the molecule | c. .energy transfer from one energy | d.none of the above | a.energy transfer within the molecule |
| 4 | Acetone gives | a.one signal NMR | b. two signal NMR | c. three signal NMR | d. four signal NMR | a.one signal NMR |
| 5 | Methyl cyclo propane gives | a.one signal NMR | b. two signal NMR | c. three signal NMR | d. four signal NMR | c. three signal NMR |
| 6 | For non viscous system NMR gives | a.splitting signal | b.sharp signal | c.broad signal | d.none of the above | b.sharp signal |
| 7 | The relationship between delta value in ppm and frequency in hertz is fundamental | a. $\delta x = v_x - v_{TMS/V0}$ | b. $\delta x = v_{TMS} - v_{x/V0}$ | c. $v_0/ v_x - v_{TMS}$ | d. $v_0/ v_{TMS} - v_x$ | a. $\delta x = v_x - v_{TMS/V0}$ |
| 8 | What is the rule of spectral multiplicity | a.I(n+1) | b.n(I+1) | C.n+1 | d.n-1 | C.n+1 |
| 9 | Which compound gives AMX spectrum | a.poly styrene compound | b.poly ehylene compound | c.vinyl compound | d. polyvinyl compound | c.vinyl compound |
| 10 | What is karplus equation | a.    Ǿ between 0° and 90° $Jvic = 8.5COS^2 Ǿ-0.28$ | b.    Ǿ between 0° and 90° $Jvic = 9.5COS^2 Ǿ-0.28$ | c.    Ǿ between 0° and 180° $Jvic = 8.5COS^2 Ǿ-0.28$ | d.    None of the above | a.    Ǿ between 0° and 90° $Jvic = 8.5COS^2 Ǿ-0.28$ |
| 11 | What is double resonance | a.At a time use of two radio frequency source | b.alternate use of two radio frequency source | c.simultaneous  use of two radio frequency source | d.combined use of two radio frequency source | a.At a time use of two radio frequency source |
| 12 | What is NOE signal | a.nucleous oriented energy level | b.nucleous over effect | c.nuclear over hauser effect | d.nucleous opposite energy level | c.nuclear over hauser effect |
| 13 | How many double bond present in norborene | a.single | b.double | c.triple | d.multiplet | b.double |
| 14 | How many nitrogen present in imidazole | a.1 | b. 2 | c.3 | d.5 | b. 2 |
| 15 | What is SPI | a.spin permittive intense peak | b.selective population inversion | c.selective possible interaction | d.spin pulse energy intensive peak. | b.selective population inversion |
| 16 | (i)Magnetically equivalent protons are chemically equivalent (ii)each signal corresponds to a set of equivalent protons | a.(i) and (ii) are true | b.(i) true | c.(ii) true | d.(i) and (ii) false | a.(i) and (ii) are true |

| No. | Question | a | b | c | d | Answer |
|---|---|---|---|---|---|---|
| 17 | Propanal gives | a.1 NMR signal | b.2 NMR signal | c.3 NMR signal | d.4 NMR signal | b.2 NMR signal |
| 18 | The DMSO is a | a.highly polar solvent | b.highly non polar solvent | c.weakly polar solvent | d.weakly non polar solvent | a.highly polar solvent |
| 19 | NMR spectrum obtained in | a.microwave region | b.radiofrequency region | c.IR region | d.none of the above | b.radiofrequency region |
| 20 | For NMR, (a) downfield due to deshielding (b)upfield due to shielding | a.both are true | b. a true  b false | c.b true  a false | d.both are false | a.both are true |
| 21 | What is Geminal coupling a.protons attached as the same carbon having different chemical environment b. protons attached as the same carbon having same chemical environment | a. a and b are true | b. a and d are flase | c. b and a flase | d. both are flase | a. a and b are true |
| 22 | I=0 | a. NMR signals observed | b. NMR signals not observed | c. half NMR signals | d. none of the above | b. NMR signals not observed |
| 23 | How many gem methyl group present in ∝-pinene | a) one | b) two | c) three | d) zero | b) two |
| 24 | For NMR the aromatic character relates to cyclic delocalization of | a. (4n+2) π electrons | b. (2n+4) π electrons | c. (4n+π) 2 electrons | d. (2n+π) 4 electrons | a. (4n+2) π electrons |
| 25 | What is magnetic equivalence | a)chemical shift equivalence | b)coupling equivalence | c)chemical equivalence | d)magnetic equivalence | c)chemical equivalence |
| 26 | What is accidental equivalence | a.chemical shift of 2 proton are equal | b)environment of 2 protons are equal | c)coupling constants are equal | d)magnetic field of 2 protons are equal | a.chemical shift of 2 proton are equal |
| 27 | For NMR the number of orientatins is | a) (2m+I) | b) (2I+1) | c) (2n+1) | d) (2n+1) | b) (2I+1) |
| 28 | Oppose orientation most stable and alligned orientation least stable a)most stable     b)least stale | a) both are true | b) a true b flase | c) both are flase | d) a flase b true | a) both are true |
| 29 | How many methyl group present I methanol | a) 2 | b) 3 | c) 4 | d) 0 | b) 3 |
| 30 | Which is used as a lanthanide shift reagent | a) Europium | b) Tms | c) 6-methyl quinoline | d) combination of europium and TMS | c) 6-methyl quinoline |
| 31 | What is the natural abundance of $^{13}C$ NMR | a) 1% | b) 0.1% | c) 1.1% | d) 11% | c) 1.1% |
| 32 | What is the chemical shift range of $^{1}H$ spectrum | a) 4ppm | b) 40 ppm | c) 80 ppm | d) none | c) 80 ppm |
| 33 | What is the chemical shift range of | a) 4ppm | b) 40 ppm | c) 80 ppm | d) 120 ppm | a) 4ppm |
| 34 | What is "CI  DNP" | a. Chemically induced dynamic nuclear polymerization | b. Chemically induced dinuclear polarisation | c. Chemically induced dynamic number polarisation | d. magentically indued | a. Chemically induced dynamic nuclear polymerization |

| # | Question | a | b | c | d | Answer |
|---|---|---|---|---|---|---|
| 35 | What is MRI | a)magnetic radio frequency imagine | b)magnetic resolution imagine | c)magnetic resonance imagine | d)none | c)magnetic resonance imagine |
| 36 | What is "COSY" | a)2D NMR-Shift correlation spectra | b)2D NMR-Shift corrected spectra | c)NMR shift corrected spectra | d)NMR shift correction spectra | a)2D NMR-Shift correlation spectra |
| 37 | The energy of free spin is related to give their envirnment is called as | a. spin-spin relaxation | b. spin-spin coupling | c. spin-lattice relaxation | d. spin-lattice coupling | c. spin-lattice relaxation |
| 38 | How many number of hydrogen present in annulene | a) 12H | b) 14H | c) 16 H | d) 18 H | d) 18 H |
| 39 | What is shielding | a. spin oppose to magnetic field | b. spin allign to magnetic field | c. spin lateral to magnetic field | d. spin oppose lateral to magnetic field | b. spin allign to magnetic field |
| 40 | What is anisotropic effect | a. $\delta$ for protons attached to C=C in alkenes | b. $\delta$ for protons attached to C=C in alkynes | c. $\delta$ for protons attached to cyclo hexanes | d. $\delta$ for protons attached to para hexanes | a. $\delta$ for protons attached to C=C in alkenes |
| 41 | The resultant spin of $^1_1H$ is | a. 0-100 nm | b. 1 | c. 1/2 | d.3/2 | c. 1/2 |
| 42 | The nucleus which gives NMR spectrum is | a. $^{16}_8O$ | b. $^{10}_5B$ | c.$^{12}O$ | d. $^4_2He$ | b. $^{10}_5B$ |
| 43 | The $^1_1H$ spectrum CH$_2$(Cl)CH(Cl)OCH$_3$ would show | a. a 3 proton singlet,I proton triplet and 2 proton doublet | b. a 3 proton doublet 1 proton triplet and 2 proton singlet | c. a 3 proton triplet 1 proton doublet 2 proton doublet | d. a3 proton singlet 1 proton singlet 2 proton doublet | a. a 3 proton singlet,I proton triplet and 2 proton doublet |
| 44 | The chemical shift of $^1_1H$ on the $\delta$ scale is 2.56. The value on ϒ scale is | a. 12.56 | b. 7.44 | c.2.56 | d. 1.44 | b. 7.44 |
| 45 | The bond length on NO is 0.116 nm. Its rotational constant is | a. $5.0^{30} \times 10^{10}$ sec | b. $1.23 \times 10^{10}$ sec | c. $5.030 \times 10^{10}$ sec$^{-1}$ | d. $1.23 \times 10^{10}$ sec-1 | c. $5.030 \times 10^{10}$ sec$^{-1}$ |
| 46 | Among the following which does not give NMR spectra | a. $^{16}_8O$ | b. $^{10}_5B$ | c. $^{15}_7N$ | d.$^1_1H$ | a. $^{16}_8O$ |
| 47 | The NMR spectroscopy is based on the magnetic moment by the spinning of a | a. Atom | b. Charged nucleus | c. Electron | d. neutrons | b. Charged nucleus |
| 48 | In the PMR spectrum FCH$_2$ CHF$_2$ would give | a. 4 signals | b. 3 signals | c. 2 signals | d.1 signals | c. 2 signals |
| 49 | In a NMR spectrum number of protons of each kind in a molecule is indicated by the | a. number of signals | b. Intensity of signals | c.Splitting of a signals | d. Charged nucleus | b. Intensity of signals |
| 50 | In a low resolution NMR spectrum of ethanol, the area under the peak corresponding to OH, CH$_2$ and CH$_3$ protons respectively will be in the ratio | a. 3:2:1 | b. 1:3:2 | c.3:1:2 | d.1:2:3 | a. 3:2:1 |

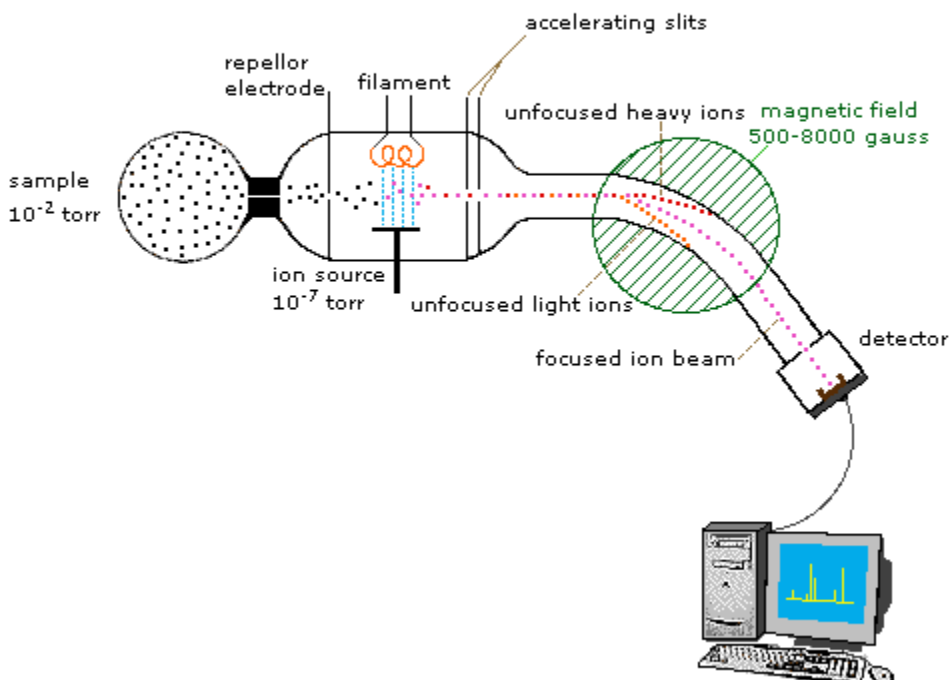| | | | | | |
|---|---|---|---|---|---|
| 51 | What is the spin number of thefollowing nuclei $^{11}B$, $^{35}Cl$, $^{79}Br$, $^{81}Br$? | a. 3/2 | b. 1/2 | c. 1 | d. 5/2 | a. 3/2 |
| 52 | The spin angular momentum of thenucleus, H is---- | a. root of 1/2x h/2π | b.root of 1/2x11/2 | c. rootof 1/2x1 1/2xh/2π | d.root of 1/2 | c. rootof 1/2x1 1/2xh/2π |
| 53 | The Bohr magneton is aunit of---and it is nearly--- times the nuclear magneton | a. Magnetic field 1850 | b. Magnetic moment,1850 | c. Magnetic field 1/1850 | d. Magnetic moment, 1/1850 | b. Magnetic moment,1850 |
| 54 | The proton magnetic resonance is studied in--- | a. Radiofrequency | b. microwave region | c.IR region | d.Visible region | a. Radiofrequency |
| 55 | Underhigh resolution, ethanol containing acid inpurity gives---PMR signals and the hydroxyl proton appears as a | a.3 triplet | b.3.singlet | c.2 singlet | d. 3 quintet | a.3 triplet |
| 56 | The chemical shift of a proton on the δ scale is 4. The value of the τ scale is--- | a. 14 | b.6 | c. 2.5 | d.4 | b.6 |
| 57 | The fine structure and intensity ratios expected in the proton NMRspetrum of $NH_4^+$ ion (for $^{14}N$,I=1) are | a. singlet | b. Doublet 1:1 | c. Trplet 1:1:1 | d.triplet1:2:1 | c. Trplet 1:1:1 |
| 58 | In the proton NMR spectrum of toluene,the resonancedue to $CH_3$, group is expected to | a. δ 0.5 | b.δ 1.25 | c.δ2.5 | d. δ 3.5 | c.δ2.5 |
| 59 | How many NMR signals are found in cis dimethyl cyclopropane and transdimethyl cyclopropane? | a. 2,3 | b.3,4 | c. 1,2 | d. 8,10 | b.3,4 |
| 60 | In NMR spectroscopy the value of coupling constant(5) | a. Changes with ield strength | b. Changes with temperature | c.Changeswith solvent | d. Is independent to field strength, temperature and solvent | d. Is independent to field strength, temperature and solvent |

### Unit IV : Mass Spectrometry
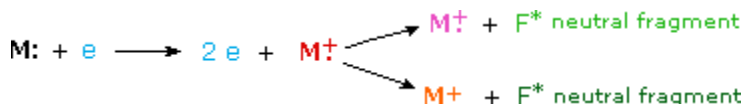
### The Mass Spectrometer

In order to measure the characteristics of individual molecules, a mass spectrometer converts them to ions so that they can be moved about and manipulated by external electric and magnetic fields. The three essential functions of a mass spectrometer, and the associated components, are:

1. A small sample is ionized, usually to cations by loss of an electron. **The Ion Source**
2. The ions are sorted and separated according to their mass and charge. **The Mass Analyzer**
3. The separated ions are then measured, and the results displayed on a chart. **The Detector**

Because ions are very reactive and short-lived, their formation and manipulation must be conducted in a vacuum. Atmospheric pressure is around 760 torr (mm of mercury). The pressure under which ions may be handled is roughly $10^{-5}$ to $10^{-8}$ torr (less than a billionth of an atmosphere). Each of the three tasks listed above may be accomplished in different ways. In one common procedure, ionization is effected by a high energy beam of electrons, and ion separation is achieved by accelerating and focusing the ions in a beam, which is then bent by an external magnetic field. The ions are then detected electronically and the resulting information is stored and analyzed in a computer. A mass spectrometer operating in this fashion is outlined in the following diagram. The heart of the spectrometer is the ion source. Here molecules of the sample (black dots) are bombarded by electrons (light blue lines) issuing from a heated filament. This is called an **EI** (electron-impact) source. Gases and volatile liquid samples are allowed to leak into the ion source from a reservoir (as shown). Non-volatile solids and liquids may be introduced directly. Cations formed by the electron bombardment (red dots) are pushed away by a charged repeller plate (anions are attracted to it), and accelerated toward other electrodes, having slits through which the ions pass as a beam. Some of these ions fragment into smaller cations and neutral fragments. A perpendicular magnetic field deflects the ion beam in an arc whose radius is inversely proportional to the mass of each ion. Lighter ions are deflected more than heavier ions. By varying the strength of the magnetic field, ions of different mass can be focused progressively on a detector fixed at the end of a curved tube (also under a high vacuum).

When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** (colored red in the following diagram). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller **fragment ions** (colored pink and orange). The molecular ion is a radical cation, but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral fragment. An animated display of this ionization process will appear if you click on the ion source of the mass spectrometer diagram.



## 2. The Nature of Mass Spectra

A mass spectrum will usually be presented as a vertical bar graph, in which each bar represents an ion having a specific mass-to-charge ratio (m/z) and the length of the bar indicates the relative abundance of the ion. The most intense ion is assigned an abundance of 100, and it is referred to as the **base peak**. Most of the ions formed in a mass spectrometer have a single charge, so the m/z value is equivalent to mass itself.

Modern mass spectrometers easily distinguish (resolve) ions differing by only a single atomic mass unit (amu), and thus provide completely accurate values for the molecular mass of a compound. The highest-mass ion in a spectrum is normally considered to be the molecular ion, and lower-mass ions are fragments from the molecular ion, assuming the sample is a single pure compound. The following diagram displays the mass spectra of three simple gaseous compounds, carbon dioxide, propane and cyclopropane. The molecules of these compounds are similar in size, $CO_2$ and $C_3H_8$ both have a nominal mass of 44 amu, and $C_3H_6$ has a mass of 42 amu. The molecular ion is the strongest ion in the spectra of $CO_2$ and $C_3H_6$, and it is moderately strong in propane. The unit mass resolution is readily apparent in these spectra (note the separation of ions having m/z=39, 40, 41 and 42 in the cyclopropane spectrum). Even though these compounds are very similar in size, it is a simple matter to identify them from their individual mass spectra. By clicking on each spectrum in turn, a partial fragmentation analysis and peak assignment will be displayed. Even with simple compounds like these, it should be noted that it is rarely possible to explain the origin of all the fragment ions in a spectrum. Also, the structure of most fragment ions is seldom known with certainty.
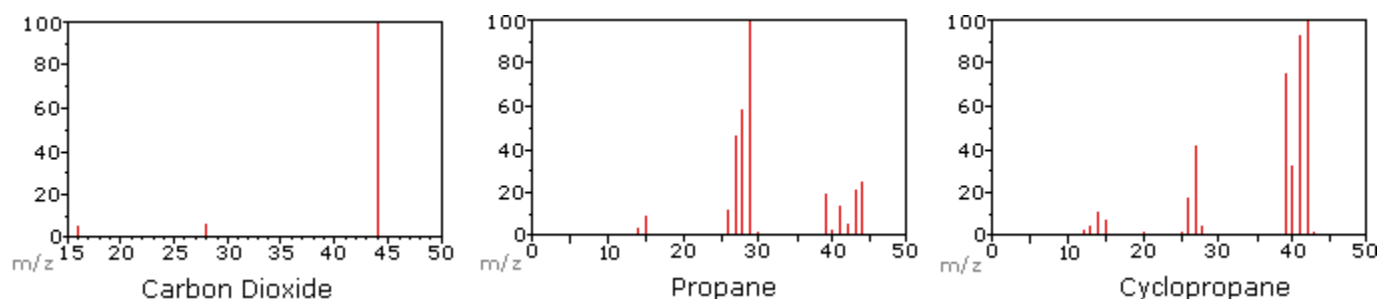


Since a molecule of carbon dioxide is composed of only three atoms, its mass spectrum is very simple. The molecular ion is also the base peak, and the only fragment ions are CO (m/z=28) and O (m/z=16). The molecular ion of propane also has m/z=44, but it is not the most abundant ion in the spectrum. Cleavage of a carbon-carbon bond gives methyl and ethyl fragments, one of which is a carbocation and the other a radical. Both distributions are observed, but the larger ethyl cation (m/z=29) is the most abundant, possibly because its size affords greater charge dispersal. A similar bond cleavage in cyclopropane does not give two fragments, so the molecular ion is stronger than in propane, and is in fact responsible for the the base peak. Loss of a hydrogen atom, either before or after ring opening, produces the stable allyl cation (m/z=41). The third strongest ion in the spectrum has m/z=39 ($C_3H_3$). Its structure is uncertain, but two possibilities are shown in the diagram. The small m/z=39 ion in propane and the absence of a m/z=29 ion in cyclopropane are particularly significant in distinguishing these hydrocarbons.

Most stable organic compounds have an even number of total electrons, reflecting the fact that electrons occupy atomic and molecular orbitals in pairs. When a single electron is removed from a molecule to give an ion, the total electron count becomes an odd number, and we refer to such ions as **radical cations**. The molecular ion in a mass spectrum is always a radical cation, but the fragment ions may either be even-electron

cations or odd-electron radical cations, depending on the neutral fragment lost. The simplest and most common fragmentations are bond cleavages producing a neutral radical (odd number of electrons) and a cation having an even number of electrons. A less common fragmentation, in which an even-electron neutral fragment is lost, produces an odd-electron radical cation fragment ion. Fragment ions themselves may fragment further. As a rule, odd-electron ions may fragment either to odd or even-electron ions, but even-electron ions fragment only to other even-electron ions. The masses of molecular and fragment ions also reflect the electron count, depending on the number of nitrogen atoms in the species.

| **Ions with no nitrogen or an even # N atoms** | odd-electron ions even-number mass | even-electron ions odd-number mass |
|---|---|---|
| **Ions having an odd # N atoms** | odd-electron ions odd-number mass | even-electron ions even-number mass |

This distinction is illustrated nicely by the following two examples. The unsaturated ketone, 4-methyl-3-pentene-2-one, on the left has no nitrogen so the mass of the molecular ion (m/z = 98) is an even number. Most of the fragment ions have odd-numbered masses, and therefore are even-electron cations. Diethylmethylamine, on the other hand, has one nitrogen and its molecular mass (m/z = 87) is an odd number. A majority of the fragment ions have even-numbered masses (ions at m/z = 30, 42, 56 & 58 are not labeled), and are even-electron nitrogen cations. The weak even-electron ions at m/z=15 and 29 are due to methyl and ethyl cations (no nitrogen atoms). The fragmentations leading to the chief fragment ions will be displayed by clicking on the appropriate spectrum. Repeated clicks will cycle the display.
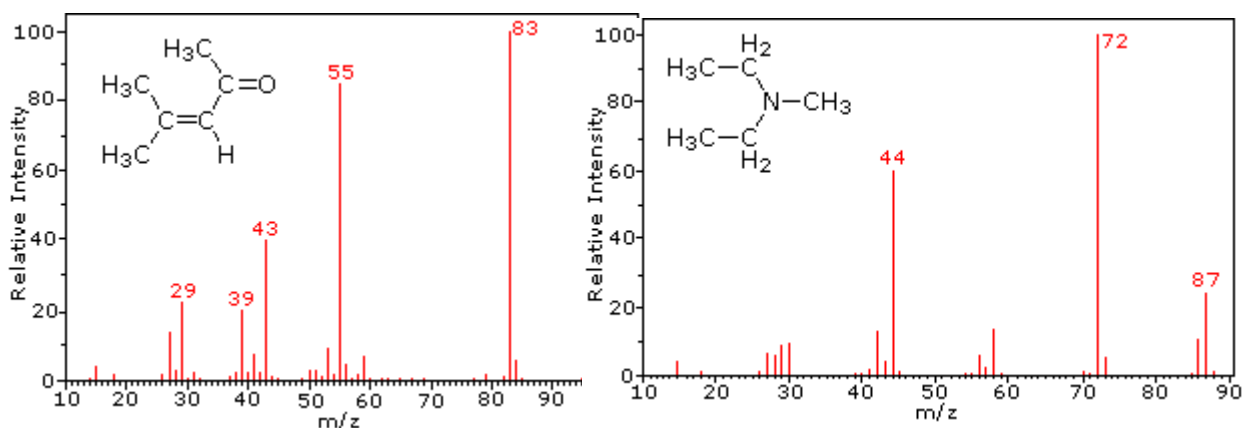
**4-methyl-3-pentene-2-one**                    **N,N-diethylmethylamine**

When non-bonded electron pairs are present in a molecule (e.g. on N or O), fragmentation pathways may sometimes be explained by assuming the missing electron is partially localized on that atom. A few such mechanisms are shown above. Bond

cleavage generates a radical and a cation, and both fragments often share these roles, albeit unequally.

## Isotopes

Since a mass spectrometer separates and detects ions of slightly different masses, it easily distinguishes different isotopes of a given element. This is manifested most dramatically for compounds containing bromine and chlorine, as illustrated by the following examples. Since molecules of bromine have only two atoms, the spectrum on the left will come as a surprise if a single atomic mass of 80 amu is assumed for Br. The five peaks in this spectrum demonstrate clearly that natural bromine consists of a nearly 50:50 mixture of isotopes having atomic masses of 79 and 81 amu respectively. Thus, the bromine molecule may be composed of two $^{79}$Br atoms (mass 158 amu), two $^{81}$Br atoms (mass 162 amu) or the more probable combination of $^{79}$Br-$^{81}$Br (mass 160 amu). Fragmentation of $Br_2$ to a bromine cation then gives rise to equal sized ion peaks at 79 and 81 amu.



**bromine**                    **vinyl chloride**                    **methylene chloride**
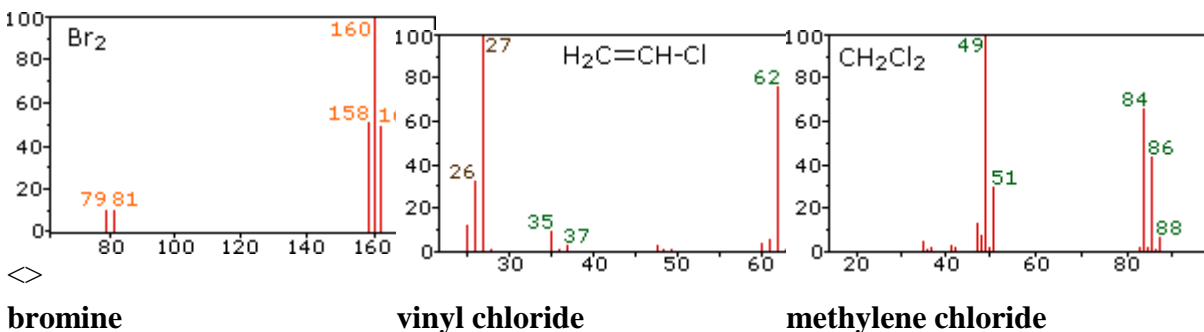
The center and right hand spectra show that chlorine is also composed of two isotopes, the more abundant having a mass of 35 amu, and the minor isotope a mass 37 amu. The precise isotopic composition of chlorine and bromine is:
**Chlorine:** 75.77% $^{35}$Cl and 24.23% $^{37}$Cl
**Bromine:** 50.50% $^{79}$Br and 49.50% $^{81}$Br

The presence of chlorine or bromine in a molecule or ion is easily detected by noticing the intensity ratios of ions differing by 2 amu. In the case of methylene chloride, the molecular ion consists of three peaks at m/z=84, 86 & 88 amu, and their diminishing intensities may be calculated from the natural abundances given above. Loss of a chlorine atom gives two isotopic fragment ions at m/z=49 & 51amu, clearly incorporating a single chlorine atom. Fluorine and iodine, by contrast, are monoisotopic, having masses of 19 amu and 127 amu respectively. It should be noted that the presence of halogen atoms in a molecule or fragment ion does not change the odd-even mass rules given above.

Two other common elements having useful isotope signatures are carbon, $^{13}$C is 1.1% natural abundance, and sulfur, $^{33}$S and $^{34}$S are 0.76% and 4.22% natural abundance respectively. For example, the small m/z=99 amu peak in the spectrum of 4-methyl-3-pentene-2-one (above) is due to the presence of a single $^{13}$C atom in the molecular ion. Although less important in this respect, $^{15}$N and $^{18}$O also make small contributions to higher mass satellites of molecular ions incorporating these elements.

The calculator on the right may be used to calculate the isotope contributions to ion abundances 1 and 2 amu greater than the molecular ion (M). Simply enter an appropriate subscript number to the right of each symbol, leaving those elements not present blank, and press the "Calculate" button. The numbers displayed in the M+1 and M+2 boxes are relative to M being set at 100%.
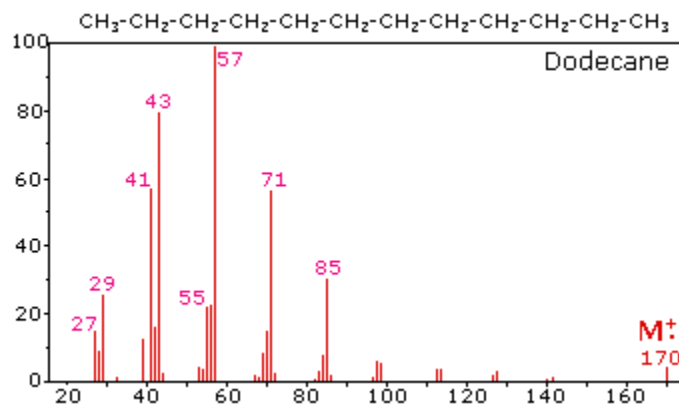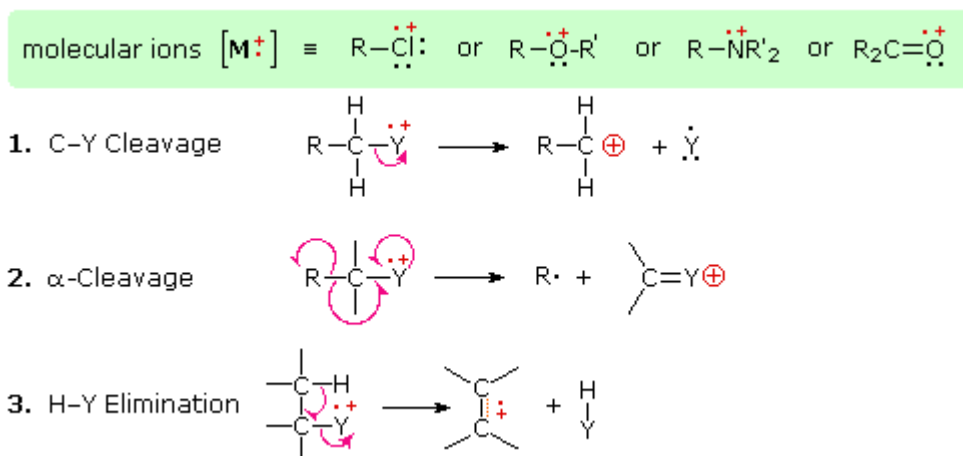


## 4.FragmentationPatterns

The fragmentation of molecular ions into an assortment of fragment ions is a mixed blessing. The nature of the fragments often provides a clue to the molecular structure, but if the molecular ion has a lifetime of less than a few microseconds it will not survive long enough to be observed. Without a molecular ion peak as a reference, the difficulty of interpreting a mass spectrum increases markedly. Fortunately, most organic compounds give mass spectra that include a molecular ion, and those that do not often respond successfully to the use of milder ionization conditions. Among simple organic compounds, the most stable molecular ions are those from aromatic rings, other conjugated pi-electron systems and cycloalkanes. Alcohols, ethers and highly branched alkanes generally show the greatest tendency toward fragmentation.

The mass spectrum of dodecane on the right illustrates the behavior of an unbranched alkane. Since there are no heteroatoms in this molecule, there are no non-bonding valence shell electrons. Consequently, the radical cation character of the molecular ion (m/z = 170) is delocalized over all the covalent bonds. Fragmentation of C-C bonds occurs because they are usually weaker than C-H bonds, and this produces a mixture of alkyl radicals and alkyl carbocations. The positive charge commonly resides on the smaller fragment, so we see a homologous series of hexyl (m/z = 85), pentyl (m/z = 71), butyl (m/z = 57), propyl (m/z = 43), ethyl (m/z = 29) and methyl (m/z = 15) cations. These are accompanied by a set of corresponding alkenyl carbocations (e.g. m/z = 55, 41 &27) formed by loss of 2 H. All of the significant fragment ions in this spectrum are even-electron ions. In most alkane spectra the propyl and butyl ions are the most abundant.

The presence of a functional group, particularly one having a heteroatom Y with non-bonding valence electrons (Y = N, O, S, X etc.), can dramatically alter the fragmentation pattern of a compound. This influence is thought to occur because of a "localization" of the radical cation component of the molecular ion on the heteroatom. After all, it is easier

to remove (ionize) a non-bonding electron than one that is part of a covalent bond. By localizing the reactive moiety, certain fragmentation processes will be favored. These are summarized in the following diagram, where the green shaded box at the top displays examples of such "localized" molecular ions. The first two fragmentation paths lead to even-electron ions, and the elimination (path #3) gives an odd-electron ion. Note the use of different curved arrows to show single electron shifts compared with electron pair shifts.



The charge distributions shown above are common, but for each cleavage process the charge may sometimes be carried by the other (neutral) species, and both fragment ions are observed. Of the three cleavage reactions described here, the alpha-cleavage is generally favored for nitrogen, oxygen and sulfur compounds. Indeed, in the previously displayed spectra of 4-methyl-3-pentene-2-one and N,N-diethylmethylamine the major fragment ions come from alpha-cleavages. Further examples of functional group influence on fragmentation are provided by a selection of compounds that may be examined by clicking the left button below. Useful tables of common fragment ions and neutral species may be viewed by clicking the right button.

Nitrogen rule
***

The **nitrogen rule** states that organic compounds containing exclusively hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens either have 1) an *odd nominal mass* that indicates an *odd number* of nitrogen atoms are present or 2) an *even nominal mass* that indicates an *even number* of nitrogen atoms are present in the molecular ion. The nitrogen rule is not a rule, *per se*, as much as a general principle which may prove useful when attempting to solve organic mass spectrometry structures.

Formulation of the rule
***

This rule is derived from the fact that, perhaps coincidentally, for the most common chemical elements in neutral organic compounds (hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens), elements with even numbered nominal masses form even numbers of covalent bonds, while elements with odd

numbered nominal masses form odd numbers of covalent bonds, with the exception of nitrogen, which has a nominal (or integer) mass of 14, but has a valency of 3.

The nitrogen rule is only true for neutral structures in which all of the atoms in the molecule have a number of covalent bonds equal to their standard valency (counting each sigma bond and pi bond as a separate covalent bond for the purposes of the calculation). Therefore, the rule is typically only applied to the molecular ion signal in the mass spectrum.

Mass spectrometry generally operates by measuring the mass of ions. If the measured ion is generated by creating or breaking a single covalent bond (such as protonating an amine to form an ammonium center or removing a hydride from a molecule to leave a positively charged ion) then the nitrogen rule becomes reversed (odd numbered masses indicate even numbers of nitrogens and vice versa). However, for each consecutive covalent bond that is broken or formed, the nitrogen rule again reverses.

Therefore, a more rigorous definition of the nitrogen rule for organic compounds containing exclusively hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens would be as follows:

An even nominal mass indicates that a net even number of covalent bonds have been broken or formed and an even number of nitrogen atoms are present, or that a net odd number of covalent bonds have been broken or formed and an odd number of nitrogen atoms are present. An odd nominal mass indicates that a net even number of covalent bonds have been broken or formed and an odd number of nitrogen atoms are present, or that a net odd number of covalent bonds have been broken or formed and an even number of nitrogen atoms are present.

Inorganic molecules do not necessarily follow the rule. For example, the nitrogen oxides NO and $NO_2$ have an odd number of nitrogens but even masses of 30 and 46, respectively.

**Rearangement Mechanisms in Fragmentation**

**4-nonanone**
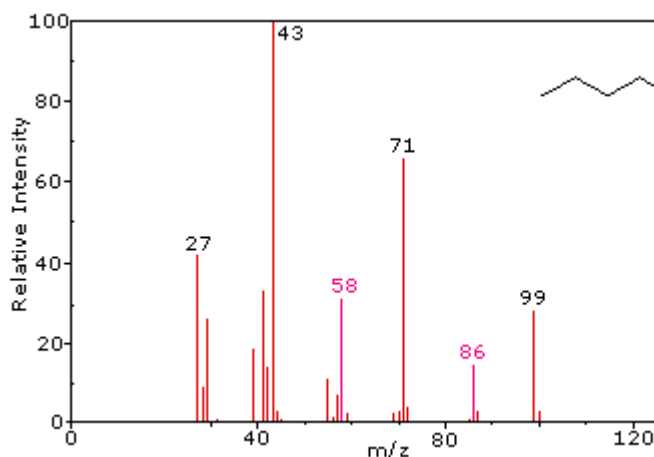


The odd-electron fragment ions at m/z = 86 and 58 are the result of a McLafferty rearrangement, involving the larger alkyl chain, and a subsequent loss of ethene (the "double-McLafferty" rearrangement).

Alpha-cleavage leads to the m/z = 99, 71 and 43 ions. The charge is apparently distributed over both fragments.
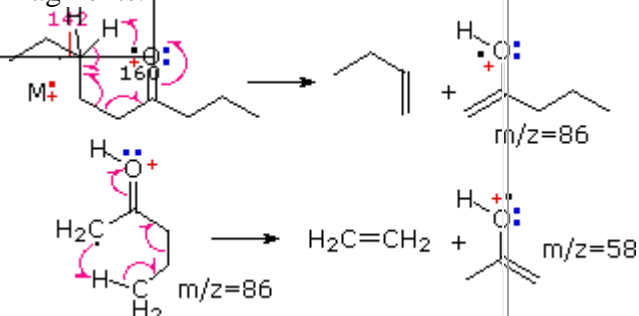


**butylpentanoate**
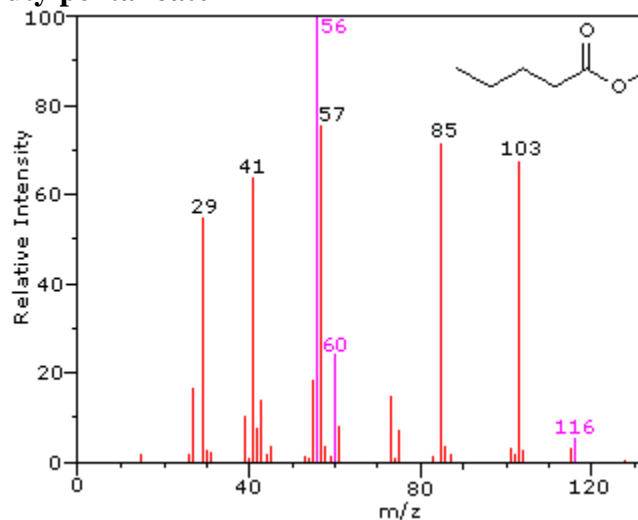


Alpha-cleavage gives ions at m/z=57 & 85 amu. The McLafferty rearrangement on the acid side generates a m/z=116 ion. Subsequent rearrangement on the alcohol side generates m/z=60 and 56 ions. The m/z=103 ion is probably $C_4H_9CO_2H_2^{(+)}$.
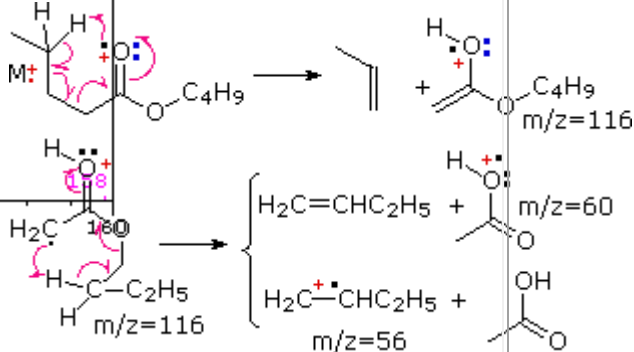
## 5-methyl-5-hexen-3-ol
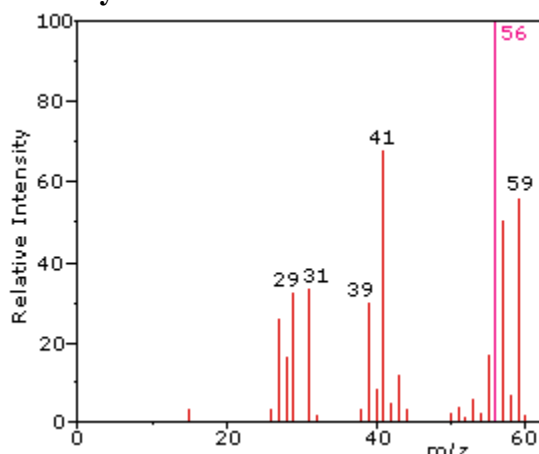


The molecular ion (m/z=114 amu) is not observed under electron impact ionization conditions. The highest mass ion (m/z=85) is due to an alpha-cleavage of ethyl; the other alpha-cleavage generates m/z=59. The rearrangement cleavage shown here generates the m/z=56 ion.

## 4,4-dimethylcyclohexene



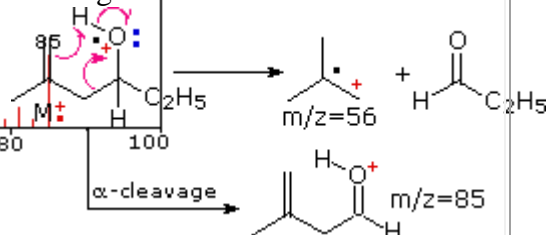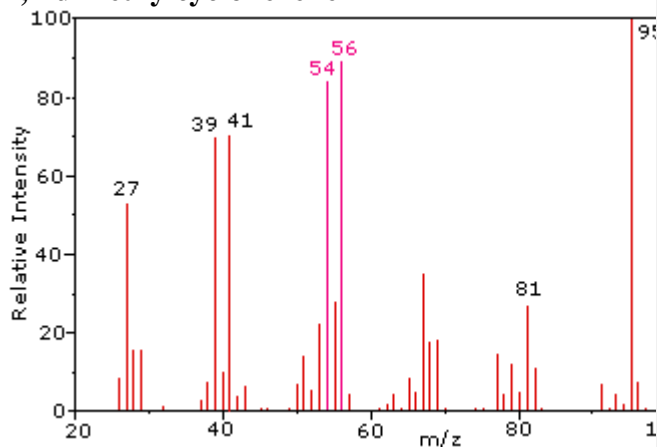The loss of a methyl radical generates the base peak at m/z=95 amu. The m/z=81 & 67 ions are smaller homologues of this ion (14 mass units less). Cyclohexene compounds undergo a retro-Diel-Alder rearrangement to give diene and alkene fragments. The charge may reside on either fragment, with the larger usually predominating. In this case both ions are relatively strong (m/z=54 & 56).
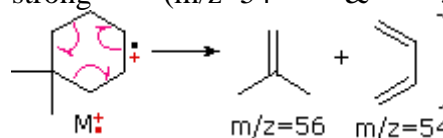
The complexity of fragmentation patterns has led to mass spectra being used as "fingerprints" for identifying compounds. Environmental pollutants, pesticide residues on food, and controlled substance identification are but a few examples of this application. Extremely small samples of an unknown substance (a microgram or less) are sufficient for such analysis. The following mass spectrum of cocaine demonstrates how a forensic laboratory might determine the nature of an unknown street drug. Even though extensive fragmentation has occurred, many of the more abundant ions (identified by magenta numbers) can be rationalized by the three mechanisms shown above. Plausible assignments may be seen by clicking on the spectrum, and it should be noted that all are even-electron ions. The m/z = 42 ion might be any or all of the following: $C_3H_6$, $C_2H_2O$ or $C_2H_4N$. A precise assignment could be made from a high-resolution m/z value (next section).
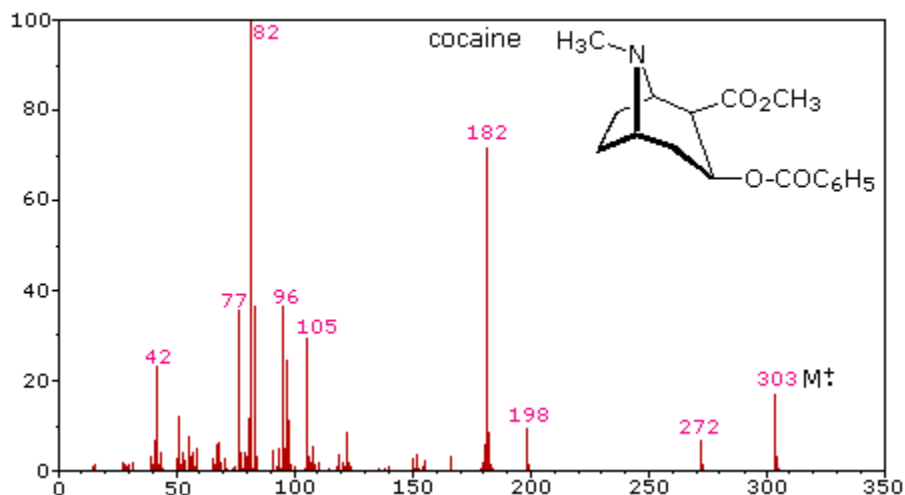
Odd-electron fragment ions are often formed by characteristic rearrangements in which stable neutral fragments are lost. Mechanisms for some of these rearrangements have been identified by following the course of isotopically labeled molecular ions. A few examples of these rearrangement mechanisms may be seen by clicking the following button.

## 5. High Resolution Mass Spectrometry

In assigning mass values to atoms and molecules, we have assumed integral values for isotopic masses. However, accurate measurements show that this is not strictly true. Because the strong nuclear forces that bind the components of an atomic nucleus together vary, the actual mass of a given isotope deviates from its nominal integer by a small but characteristic amount (remember $E = mc^2$). Thus, relative to $^{12}C$ at 12.0000, the isotopic mass of $^{16}O$ is 15.9949 amu (not 16) and $^{14}N$ is 14.0031 amu (not 14).

By designing mass spectrometers that can determine m/z values accurately to four decimal places, it is possible to distinguish different formulas having the same nominal mass. The

| Formula | $C_6H_{12}$ | $C_5H_8O$ | $C_4H_8N_2$ |
|---------|-------------|-----------|-------------|
| **Mass** | 84.0939 | 84.0575 | 84.0688 |

table on the right illustrates this important feature, and a double-focusing high-resolution mass spectrometer easily distinguishes ions having these compositions. Mass spectrometry therefore not only provides a specific molecular mass value, but it may also establish the molecular formula of an unknown compound. Tables of precise mass values for any molecule or ion are available in libraries; however, the mass calculator provided below serves the same purpose. Since a given nominal mass may correspond to several molecular formulas, lists of such possibilities are especially useful when evaluating the spectrum of an unknown compound. Composition tables are available for this purpose, and a particularly useful program for calculating all possible combinations of H, C, N & O that give a specific nominal mass has been written by Jef Rozenski.

Molecular formula determination

**Nitrogen rule**

The nitrogen rule states that organic molecules that contain hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens have an odd nominal mass if they have an odd number of nitrogen atoms or an even mass if they have an even number of nitrogen atoms are present. The nitrogen rule is true for structures in which all of the atoms in the molecule have a number of covalent bonds equal to their standard valency, counting each sigma bond and pi bond as a separate covalent bond.

## Rings plus double bonds

From degree of unsaturation principles, molecules containing only carbon, hydrogen, halogens, nitrogen, and oxygen follow the formula

Rings + $\pi$ bonds= $\mu$ = C-H/2- X/2 + N/2 +1

where C is the number of carbons, H is the number of hydrogens, X is the number of halogens, and N is the number of nitrogen.

## Even electron rule

The **even electron rule** states that ions with an even number of electrons (cations but not radical ions) tend to form even-electron fragment ions and odd-electron ions (radical ions) form odd-electron ions or even-electron ions.[9] Even-electron species tend to fragment to another even-electron cation and a neutral molecule rather than two odd-electron species.

$OE^{+\bullet} \rightarrow EE^+ + R^\bullet$, $OE^{+\bullet} \rightarrow OE^{+\bullet} + N$

## Stevenson's rules

The more stable the product cation ion, the more abundant the corresponding decomposition process . Several theories can be utilized to predict the fragmentation process, such as the electron octet rule, the resonance stabilization and hyperconjugation and so on.

## Rule of 13

The **Rule of 13** is a simple procedure for tabulating possible chemical formula for a given molecular mass. The first step in applying the rule is to assume that only carbon and hydrogen are present in the molecule and that the molecule comprises some number of CH "units" each of which has a nominal mass of 13. If the molecular weight of the molecule in question is $M$, the number of possible CH units is $n$ and

M/13= n+ r/13

where r is the remainder. The base formula for the molecule is

$C_n H_{n+r}$

and the degree of unsaturation is

$$\mu = n-r+2 \quad / \ 2$$

A negative value of $u$ indicates the presence of heteroatoms in the molecule and a half-integer value of $u$ indicates the presence of an odd number of nitrogen atoms. On addition of heteroatoms, the molecular formula is adjusted by the equivalent mass of carbon and hydrogen. For example, adding N requires removing $CH_2$ and adding O requires removing $CH_4$.

**Isotope effects**

Isotope peaks within a spectrum can help in structure elucidation. Compounds containing halogens (especially chlorine and bromine) can produce very distinct isotope peaks. The mass spectrum of methylbromide has two prominent peaks of equal intensity at $m/z$ 94 (M) and 96 (M+2) and then two more at 79 and 81 belonging to the bromine fragment.

Even when compounds only contain elements with less intense isotope peaks (carbon or oxygen), the distribution of these peaks can be used to assign the spectrum to the correct compound. For example, two compounds with identical mass of 150 Da, $C_8H_{12}N_3^+$ and $C_9H_{10}O_2^+$, will have two different M+2 intensities which makes it possible to distinguish between them.

Fragmentation

The fragmentation pattern of the spectra beside the determination of the molar weight of an unknown compound also suitable to give structural information, especially in combination with the calculation of the degree of unsaturation from the molecular formula (when available). Neutral fragments frequently lost are carbon monoxide, ethylene, water, ammonia, and hydrogen sulfide. There are several fragmentation processes, as follows.

**α - cleavage**

Fragmentation arises from a homolysis processes.This cleavage results from the tendency of the unpaired electron from the radical site to pair up with an electron from another bond to an atom adjacent to the charge site, as illustrated below. This reaction is defined as a homolytic cleavage since only a single electron is transferred. The driving forces for such reaction is the electron donating abilities of the radical sites: N > S, O,π > Cl, Br > H. An example is the cleavage of carbon-carbon bonds next to a heteroatom.In this depiction, single-electron movements are indicated by a single-headed arrow.
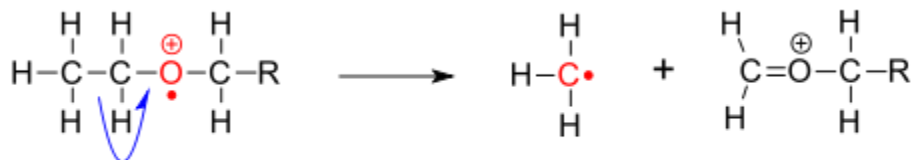


**Sigma bond cleavage**

The ionization of alkanes weakens the C-C bond, ultimately resulting in the decomposition. As bond breaks, A charged, even electron species (R+) and a neutral radical species (R•) are generated. Highly substituted carbocations are more stable than the nonsubstituted ones. An example is depicted as below.



Sigma bond cleavage example

**Inductive cleavage**

This reaction results from the inductive effect of the radical sites, as depicted below.This reaction is defined as a heterolytic cleavage since a pair of electrons is transferred. The driving forces for such reaction are the electronegativities of the radical sites: halogens > O, S >> N, C. this reaction is less favored than radical-site reactions.



**McLafferty rearrangement**

The McLafferty rearrangement can occur in a molecule containing a keto-group and involves β-cleavage, with the gain of the γ-hydrogen atom. Ion-neutral complex formation involves bond homolysis or bond heterolysis, in which the fragments do not have enough kinetic energy to separate and, instead, reaction with one another like an ion-molecule reaction.
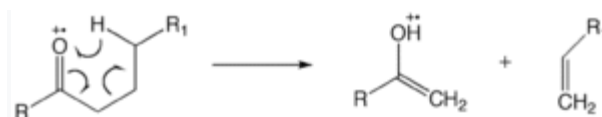


An example of the McLafferty rearrangement

**Hydrogen rearrangement to a saturated heteroatom**

The "1,5 " hydrogen shift cause transfer of one γ- hydrogen to a radical site on a saturated heteroatom. The same requirements for McLafferty rearrangement apply to hydrogen rearrangement to a saturated heteroatom. Such rearrangement initiates charge-site reaction, resulting in the formation of an odd electron ion and a small neutral molecule ( water, or acid and so on). For alcohols, this heterolytic cleavage releases a water molecule. Since the charge-site reactions are dominant in the less bulky alcohols, this reaction is favored for alcohols as primary > secondary > tertiary.[11]

**Double-hydrogen rearrangement**

The "1,5 " hydrogen shift cause transfer of two γ- hydrogen to two radical sites on two different unsaturated atoms. The same requirements for McLafferty rearrangement apply to double-hydrogen rearrangement. This reaction is observed for three unsaturated functional groups, namely thioesters, esters and amides.

**Ortho rearrangement**

The "1,5 " hydrogen shift cause transfer of two γ- hydrogen to two radical sites on two different unsaturated atoms. The same requirements for The "1,5 " hydrogen shift occur

between proper substituents in the ortho positions of the aromatic rings. The same requirements for McLafferty rearrangement apply to ortho rearrangement except for the strong α,β carbon-carbon double bond. Such rearrangement initiates charge-site reaction, resulting in the formation of an odd electron ion and a small neutral molecule ( water, or HCl and so on). This reaction can be utilized to differentiate ortho from para and meta isomersMcLafferty rearrangement apply to double-hydrogen rearrangement. This reaction is observed for three unsaturated functional groups, namely thioesters, esters and amides.[11]



Ortho Rearrangement
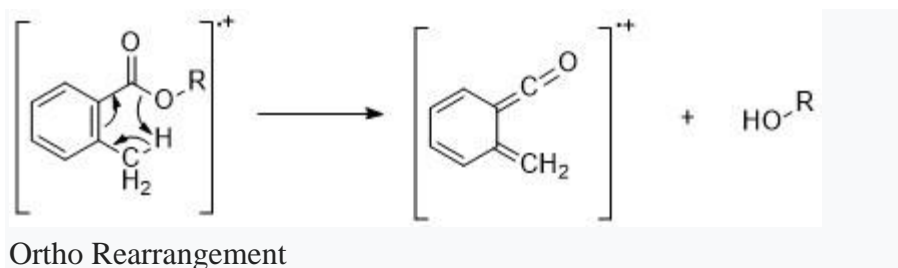
## Retro-Diels-Alder reaction

This reaction occurs mainly in cyclohexene and it's derivatives. Upon ionization, the pi electrons are excited and generate a charge site and a radical site. Following this, two successive α cleavages yield a butadiene radical and a neutral ethene since ethene has a higher ionisation energy than butadiene ( Stevenson's rules).



Retro Diels-Alder reaction producing neutral ethylene
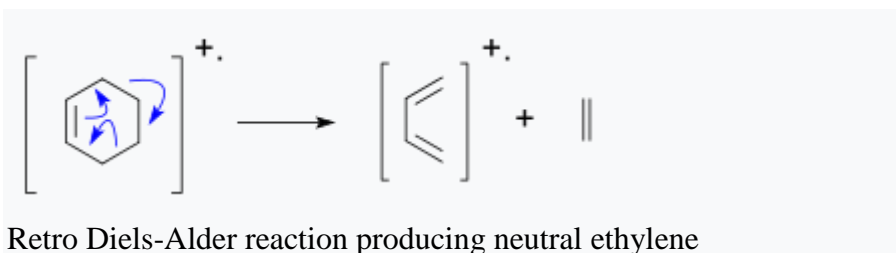
## Cycloreversion reaction

This reaction occurs mainly in four-membered cyclic molecules. Once ionized, it produces a distonic ion and then further fragments to yield an ethene radical ion and a neutral ethene molecule.

Fragmentation patterns of specific compound classes

## Alkanes

For linear alkanes, molecular ion peaks are often observed. However, for long chain compounds, the intensity of the molecular ion peaks are often weak. Linear fragments often differ by 14 Da ($CH_2 = 14$). For example, hexane fragmentation patterns. The m/z=57 butyl cation is the base peak, and other most abudant peaks in the spectrum are alkyl carbocations at m/z=15, 29, 43 Da.
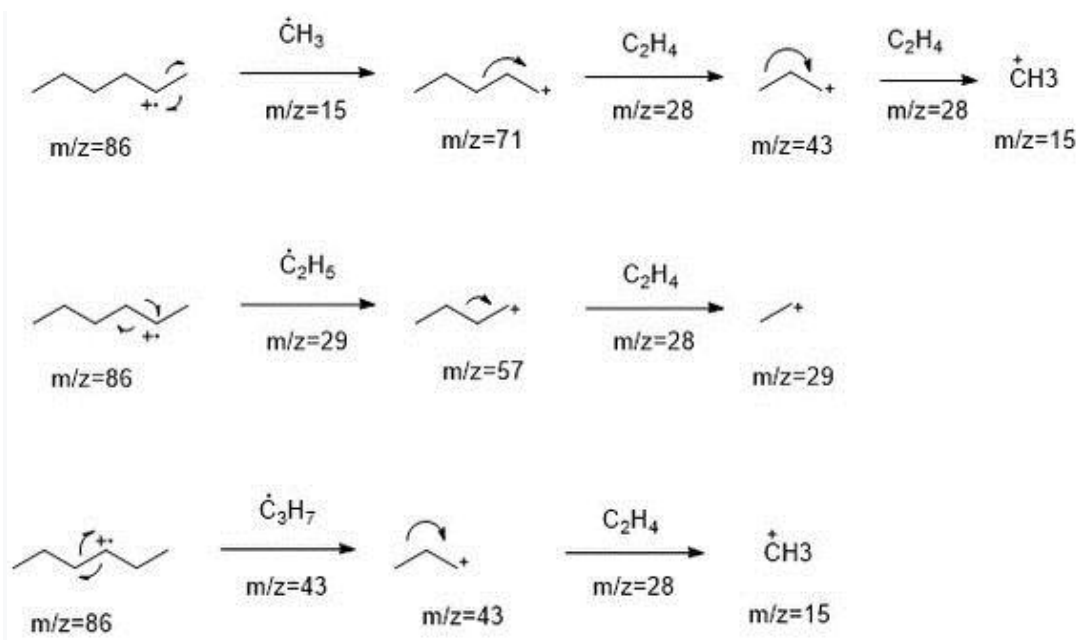
The possible mechanisms for EI ionization spectra of hexane

Branched alkanes have somewhat weaker molecular ion peaks in the spectra.They tend to fragment at the branched point. For the 2,3-dimethylbutane, an isopropyl cation peak (m/z=43) is very strong.
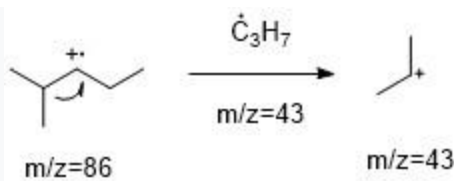


Branched alkane

Cycloalkanes have relatively intense molecular ion peaks (two bonds have to break). Alkene fragmentation peaks are often most significant mode. Loss of "CH$_2$CH$_2$" (= 28) is common, if present. However, for the substituted cycloalkanes, they prefer to form the cycloalkyl cations by cleavage at the branched points.
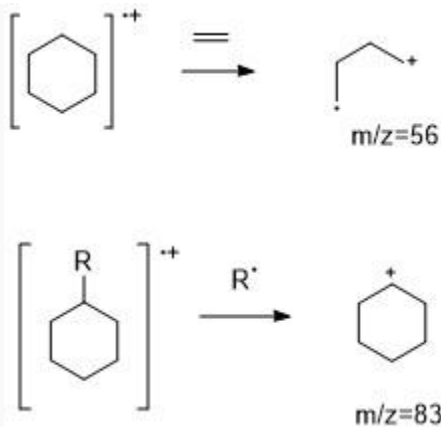


**Alkenes**

Alkenes often produce stronger molecular ion peaks than alkanes due to the lower ionization energy of a pi electron than a σ electron. After the ionization, double bonds can migrate easily, resulting in almost impossible determination of isomers. Allylic cleavage is most significant fragmentation mode due to resonance stabilization.[11]



Most possible ionization mechanism of acyclic alkenes

McLafferty-like rearrangements are possible (similar to carbonyl pi bonds). Again, bond migration is possible.



m/z=84

McLafferty-like rearragements of alkenes

Cyclohexenes often undergo retro Diels-Alder reactions.

**Alkynes**

Similar to alkenes, alkynes often show strong molecular ion peak. Propargylic cleavage is a most significant fragmentation mode.
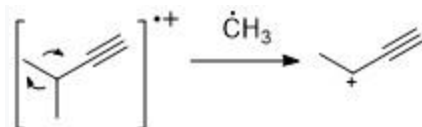


Most possible ionization mechanism of alkyne

**Aromatic hydrocarbons**

Aromatic hydrocarbons show distinct molecular ion peak.benzylic cleavage is pretty common.When alkyl groups are attached to the ring, a favorable mode of cleavage is to lose a H-radical to form the tropylium cation (m/z 91).
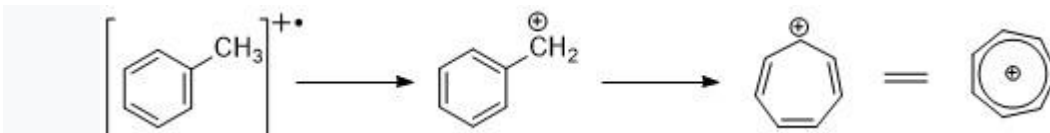


Benzylic cleavage

Alkyl substituted benzenes can fragment via the kinetic controlled process to form $C_6H_5^+$, $C_6H_6^+$ ions.



m/z=77    m/z=78    m/z=79
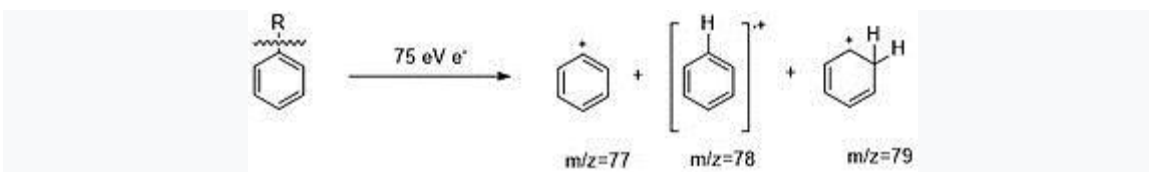
Benzene derivatives' fragmentation process

Another common mode of fragmentation is the McLafferty rearrangement, which requires the alkyl chain lengh to be at least longer than 3 carbons.[11]
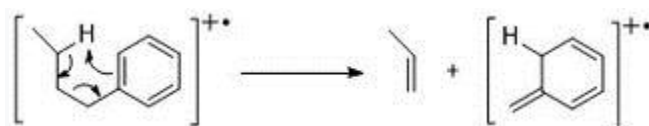


McLafferty rearrangement of aromatics

**Alcohols**

Alcohols generally have weak molecular ion peaks due to the strong electronegativity of oxygen. "Alpha" cleavage is common due to the resonance stabilization. The largest alkyl group will be lost.
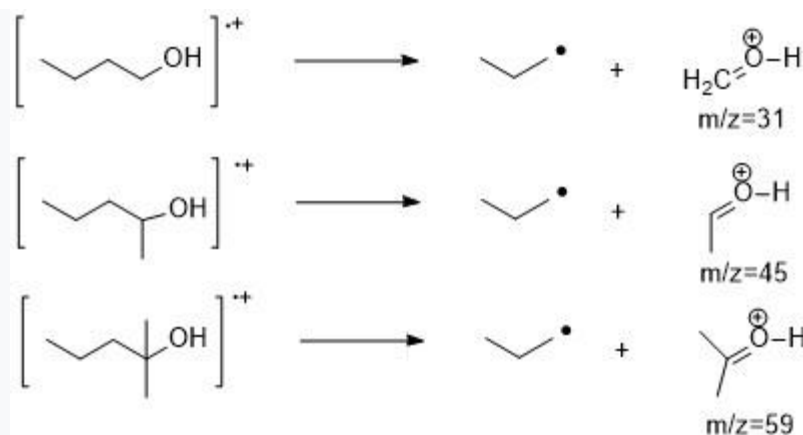


α-cleavage fragmentation mechanism of alcohols

Another common fragmentation mode is dehydration (M-18). For longer chain alcohols, a McLafferty type rearrangement can produce water and ethylene (M -46).
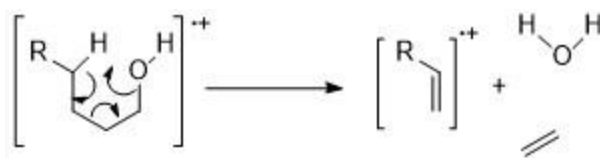


McLafferty type rearrangement for long chain alcohols

Cyclic alcohols tend to show stronger M+ peaks than linear chains. And they follow similar fragmentation pathways: Alfa cleavage and dehydration.

**Phenol**

Phenol exhibit a strong molecular ion peak. Loss of H· is observed (M − 1), CO (M − 28) and formyl radical (HCO·, M − 29) is common observed.
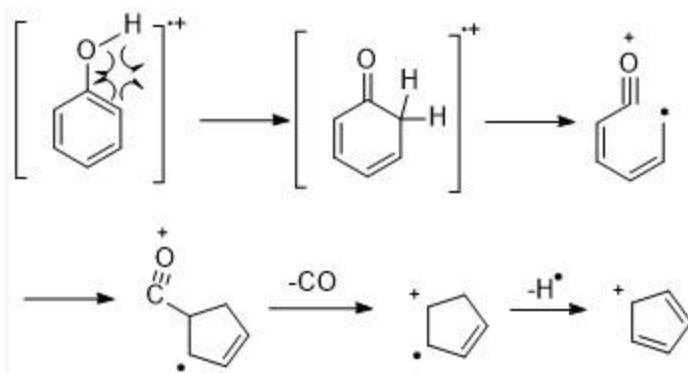
Possible fragmentation mechanism of phenols

## Ether

Ethers produce slightly more intense molecular ion peaks compared to the corresponding alcohols or alkanes. There are two common cleavage modes. α-cleavage and C-O bond cleavage.
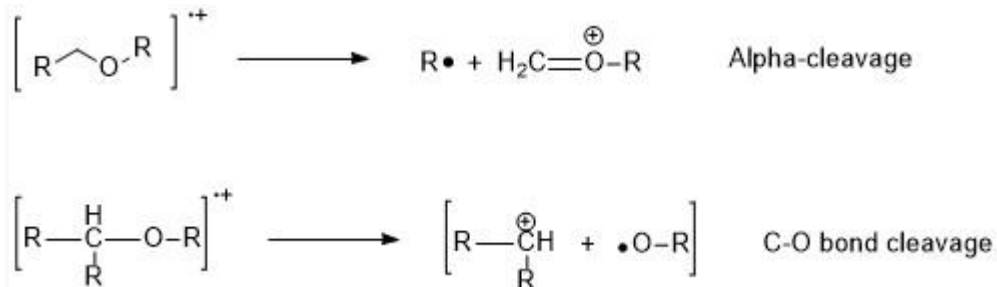


Fragmentation modes of aliphatic ethers

Aromatic ethers can generate the C6H5O+ ion by loss of the alkyl group rather than H; this can expel CO as in the phenolic degradation.
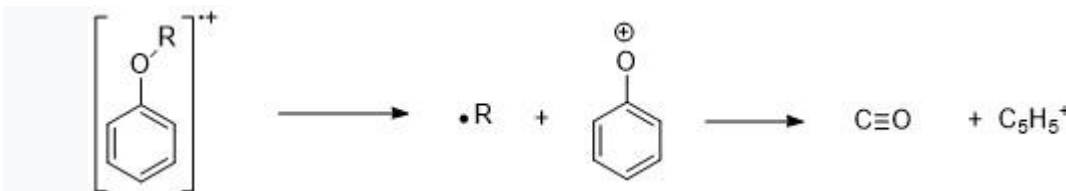


Fragmentation mechanism of aromatic ethers

## Carbonyl compounds

There are five types of carbonyl compounds, including aldehydes, ketones, carboxylic acids and esters. The principal fragmentation modes are described as follows:

Alpha-cleavage can occur on either side of the carbonyl functional group since an oxygen lone pair can stabilize the positive charge.
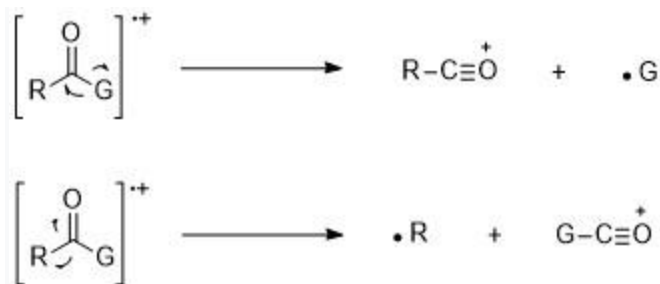
Alpha cleavage of carbonyl compounds

β-cleavage is a characteristic mode of carbonyl compounds' fragmentation due to the resonance stabilization.
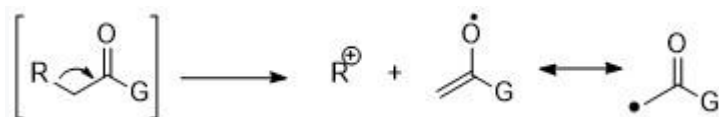


Beta cleavage of carbonyl compounds

For longer chain carbonyl compounds ( carbon number is bigger than 4), McLafferty rearrangements are dominant.
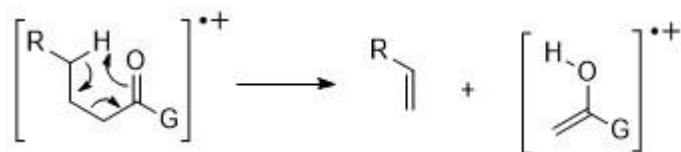


McLafferty rearrangement of carbonyl compounds

According to these fragmentation patterns, the characteristic peaks of carbonyl compounds are summarized in the following table.

| | | m/z of ion observed | | | | |
|---|---|---|---|---|---|---|
| Fragmentation | Path | Aldehydes G = H | Ketones G=CH$_3$ | Esters G=OCH$_3$ | Acids G = OH | Amides G = NH2 |
| Alpha-cleavage | Loss of R radical | 29 | 43 | 59 | 45 | 44 |
| Alpha-cleavage | Loss of G radical | M-1 | M-15 | M-59 | M-45 | M-44 |
| Beta-cleavage | | M-43 | M-57 | M-73 | M-59 | M-58 |
| McLafferty rearrangement | | 44 | 58 | 74 | 60 | 59 |

For aromatic carbonyl compounds, Alpha-cleavages are favorable primarily to lose G· (M − 1,15, 29…) to form the C6H5CO+ ion (m/z=105), which can further lose CO (m/z= 77) and HCCH (m/z=51).
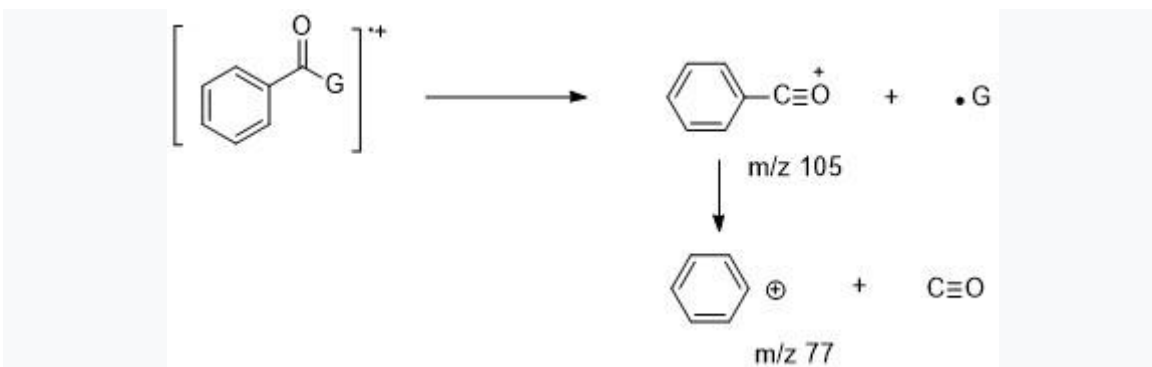


Aromatic carbonyl compound fragmentation mechanism

**Amines**

Amines follow nitrogen rule. Odd molecular ion mass to charge ratio suggests existence of odd numbers of nitrogens. Nonetheless, molecular ion peaks are weak in aliphatic amines due to the ease of fragmentation next to amines. Alpha-cleavage reactions are the most important fragmentation mode for amines; for 1° n-aliphatic amines, there is an intense peak at m/z 30.



Alpha cleavage of amines

Aromatic amines have intense molecular ion peaks. For anilines, they prefer to lose a hydrogen atom before the expulsion of HCN.
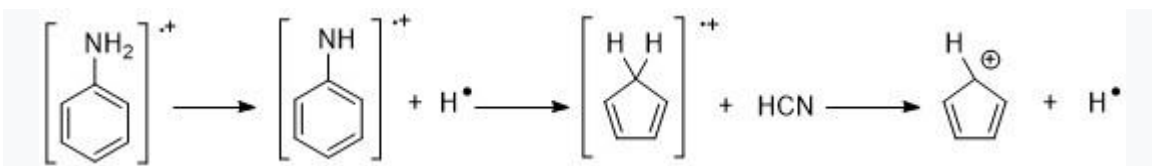


Aniline fragmentation mechanism

**Nitriles**

The principle fragmentation mode is the loss of an H-atom (M − 1) from the carbon next to the CN group due to the resonance stabilization. McLafferty rearrangement can be observed when they have longer chain lengths.[6]
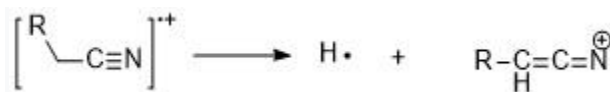


Nitrile fragmentation

**Nitro compounds**

The aliphatic nitro compounds normally show weak molecular ion peaks while the aromatic nitro compounds give a strong peak.Common degradation mode is loss of $NO^+$ and $NO^{2+}$ .



Nitro compound fragmentation
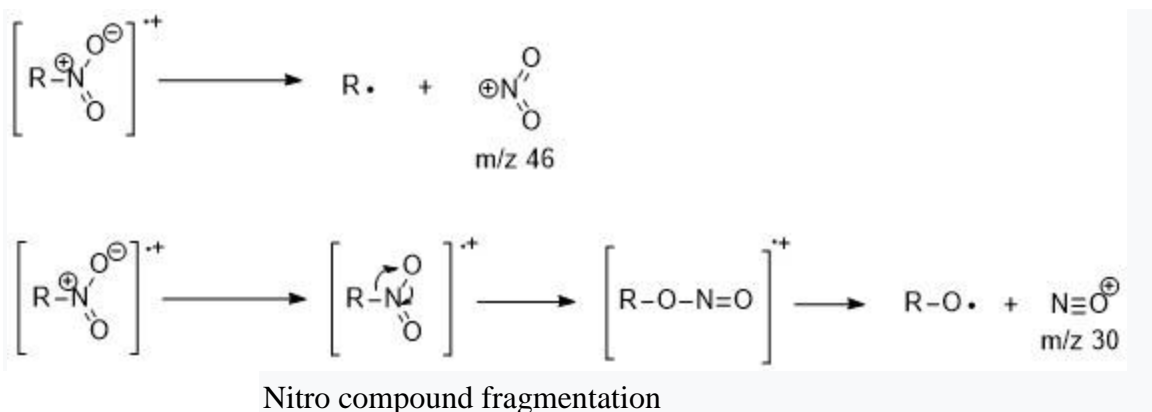
Electrospray and atmospheric pressure chemical ionization

Electrospray and atmospheric pressure chemical ionization have different rules for spectrum interpretation due the different ionization mechanisms.

## POSSIBLE QUESTIONS

## MULTIPLE CHOICE QUESTIONS

1. In Mass spectroscopy, molecules are bombarded with a beam of energetic
   a) Neutrons      b) Positrons      c) **Electrons**      d) Nucleons

2. The intensity of the base peak is taken as
   a) 80      b) **100**      c) 87      d) 57

3. The energy required for removing one electron from the neutral parent molecule is usually
   a) **10ev**      b) 30ev      c) 70ev      d) 25ev

4. The energy required for the fragmentation of parent ion is

a) 40ev  b) 100ev  c) 80ev  d) **70ev**

5. Position at metastable peak m* due to the reaction $M_1^{+-------}m_1*$ is such that

a)$m*=m_1^2/M_1$  b)$M_{1=}m_1^2/m*$  c)$m*=m_1^2M$  d)$\mathbf{m_1*M=m_1^2}$

6. The relative abundance of the metastable peak m*is often of the order or less compared to the abundance of parent ion

a) $\mathbf{10^{-2}}$  b)$10^{-1}$  c)$10^{-3}$  d)$10^{-5}$

7. Conjugated olefins show ------intense molecular ion peak as compared to the corresponding non-conjugated olefins

a) **less**  b)more  c)same  d)poor

8. Double focusing mass spectrometers are capable of attaining much-------resolving power than single focusing instruments

a) higher  b)**lower**  c)same  d)poor

9. In aliphatic acids carboxyl group is directly eliminated by

a) **β-cleavage**  b) α-cleavage  c) γ-cleavage  d) δ-cleavage

10. Primary amides gives a strong peak at m/e=44 due to

a) $H_2N$  b) $\mathbf{NH_3}$  c) $NH_4$  d) $H_2N-C=O$

11. For primary amines, the base peak is formed at m/e 30 due to $CH_2=N^+ H2$ by

a) α-cleavage  b) β- cleavage  c) γ- cleavage  d) **δ- cleavage**

12. The Position of metastable peak m* is for $m_1=108$, $m_1=123$

a) **100**  b) 70  c) 94.8  d) 90

13. In aromatic primary amines, a parent ion is formed by the loss of -------- electron from the lone pair present on the nitrogen atom

a) 1  b) 2  c) 3  d) **4**

14. A very weak parent ion peak and a prominent $(M^+-18)$ peak would probably indicate

a) **Alcohol**  b) Ketone

c) Aldehyde  d) Presence of isotope of Oxygen

15. The compound whose mass spectrum shows m/e values at 156 (M+, base peak), 127 and 29 is

a) ethyl bromide  b) methyl iodide

c) methyl bromide  d) **ethyl iodide**

16. For mass spectrum of n-propyl benzene, the m/e value of tropiliun ion is

a) **91**  b)85  c) 41  d)51

17. The molecular ion peak in phenol is--

a) **Intense**  b) less abundance  c) more abundance

d) significant

18. In catechol the molecular ion peak is---
    a) **Intense**        b) less abundance        c) more abundance
    d) significant

19. In aliphatic aldehydes and ketones the major fragmentation processes are
    a) alpha cleavage        b) beta cleavage
    c) gamma cleavage        d) **alpha and beta cleavage**

20. The intensity of molecular ion peak ---as the alkyl chain length---
    a) **decreases, increases**        b) increases, increases
    c) decreases, decreases        d) increases, decreases

## 8MARKS QUESTION

1. Explain the following rearrangements in the mass spectra

    (i) McLafferty rearrangement
    (ii) Retero – Diels Alder's rearrangement

2. What is Mossbauer Effect? Explain the principle and theory of Mossbauer Spectroscopy

3. (i).What are the factors that influencing the fragmentation process?

    (ii).What are the factors that governing the reaction pathways in mass spectroscopy. Explain any two.

    4. (i). Write brief notes on isotropic and anisotropic system
     (ii). Explain the factors affecting the magnitude of the g-value.

5. Write notes on

    (i). Metastable peaks

    (ii). Molecular ion peaks

    (iii). Relative abundance of the parent and the fragment ions

6. (i). What is DPPH? Explain the importance of DPPH?
    (ii) Write notes on hyperfine splitting

7. Explain the effect of external field on the energy states for an electron in hyperfine splitting.

8. What are the applications of mass spectroscopy?

9. Write notes on

   (i). Metastable peaks?

   (ii). Molecular ion peaks?

   (iii). Relative abundance of the parent and the fragment ions?

10. (i).Explain the Biochemical applications in mossbauer spectroscopy?
    (ii). what do you mean by isomer shift? Explain the Isomer shift for iron and tin
        Compounds in different states of oxidation?

11. Determine the structure of compound which shows m/e peaks at 88, 70, 55, 42, 31 (much intense) and 29.

**KARPAGAM ACADEMY OF HIGHER EDUCATION**
**COIMBATORE-641021**
**(For the candidates admitted on 2015 onwards)**
**DEPARTMENT OF CHEMISTRY**
**I - SEMESTER**
**ORGANIC CHEMISTRY**

OBJECTIVE TYPE QUESTIONS( EACH QUESTION CARRY ONE MARK)

Unit-4 Mass Spectroscopy  (17CHP104)

| S.No | Questions | Option a | Option b | Option c | Option d | Answer |
|---|---|---|---|---|---|---|
| 1 | In Mass spectroscopy, molecules are bombarded with a beam of energetic | a.)neutrons | b)positrons | c)electrons | d)nucleons | c)electrons |
| 2 | The intensity of the base peak is taken as | a)80 | b)100 | c)87 | d)57 | b)100 |
| 3 | The energy required for removing one electron from the neutral parent molecule is usually | a)10ev | b)30ev | c)70ev | d)25ev | a)10ev |
| 4 | The energy required for the fragmentation of parent ion is | a)40ev | b)100ev | c)80ev | d)70ev | d)70ev |
| 5 | In Mass spectrometer the positive ions are separated according to their | a)m/e ratio | b)e/mratio | c)h/mratio | d)e/v ratio | a)m/e ratio |
| 6 | The molecular ion peak in aromatic compounds ia relatively much intense due to the presence of | a)$\sigma$-electron system | b)non-bonding electron system | c)$\pi$-electron sy;stem | d)unpaired electron system | c)$\pi$-electron sy;stem |
| 7 | In case of bromo compounds $M^{+}+2$ and $M^{+}$ peaks are formed in the intensity ratio | a)1:2 | b)3:1 | c)1:1 | d)3:4 | c)1:1 |
| 8 | Incase of choloro compounds $M^{+}$ and $M^{+}+2$ peaks are formed in the intensity ratio | a)1:3 | b)2:1 | c)4:1 | d)3:1 | a)1:3 |
| 9 | McLafferty rearrangement involves the | a)cleavage of a $\beta$-bond followed by a $\gamma$-hydrogen tra;nsfer | b)cleavage of $\gamma$-bond followed by $\beta$-hydrogen transfer | c)cleavage of $\alpha$-bond followed by $\gamma$-hydrogen transfer | d)cleavage of $\delta$-bond and followed by $\gamma$-hydrogen transfer | a)cleavage of a $\beta$-bond followed by a $\gamma$-hydrogen tra;nsfer |
| 10 | InMcLafferty rearrangement ,mechanism involves a ------- membered transition state | a)4 | b)8 | c)5 | d)6 | a)4 |
| 11 | Position at metastable peak m* due to the reaction $M_1^{+\text{-------}}m_1*$ is such that | a)$m*=m_1^2/M_1$ | b)$M_1=m_1^2/m*$ | c)$m*=m_1^2M$ | d)$m_1*M=m_1^2$ | d)$m_1*M=m_1^2$ |
| 12 | The relative abundance of the metastable peak m*is often of the order or lesscompared to the abundance of parent ion | a)$10^{-2}$ | b)$10^{-1}$ | c)$10^{-3}$ | d)$10^{-5}$ | a)$10^{-2}$ |

| | | | | | |
|---|---|---|---|---|---|
| 13 | Conguated olefins show ------ intense molecular ion peak as compared to the corresponding non-conjugated olefins | a)less | b)more | c)same | d)poor | a)less |
| 14 | Double foussing mass spectrometers are capable of attaining much-------resolving power than single focusing instruments | a)higher | b)lower | c)same | d)poor | b)lower |
| 15 | The Retro-Diels-Alder reaction is an example of a multicentered fragmentation mode which is characteristic of | a)olefins | b)alkanes | c)cyclicolefines | d)ketones | a)olefins |
| 16 | Nitogen containing compolyunds with an odd number of nitrlogen atoms in the molecule must have an ---molecular weight | a)even | b)odd | c)fractional | d)decimal | c)fractional |
| 17 | An-----number of nitrogen atoms ,or no nitrogen at all,leads to an even molelcular weight according toNitrogen rule | a)even | b)whole | c)fractional | d)odd | b)whole |
| 18 | The metastable A+ions have the same mass as normal ,but simply have less | a)rotational energy | b)vibrational energy | c)translational energy | d)electronic energly | a)rotational energy |
| 19 | The first field fre region ,in double fouccing instr;ument,lilies between the | a)electrostatic and magnetic analyzer | b)ion source and the eletrostatic analyzer | c)recorder and ion soouorce | d)ion source and magnetic analyzer | c)recorder and ion soouorce |
| 20 | The second field freeanalyser region in a double focusing instrlu;ment lies between | a)electroatatilc and magnetic anallyser | b)ionsource and magnetic analyzer | c)ion source and electrostatic analyzer | d)detectoe and ion source | b)ionsource and magnetic analyzer |
| 21 | According toeven electron rule,an evenelectron species will not normally fragment to two | a)even electron species | b)odd electron species | c)even ,odd electron species | d)only neutral molecule | a)even electron species |
| 22 | In the homologous series of alkanes the relative height of the parent peak decreases with the-------of molecular mass | a)decrease | b) Increase | c) same value | d) Less value | b) Increase |
| 23 | The molelcular ion peak is not detected in | a)primary alcohol | b)secondary alcohol | c)tertiary alcohol | d)olefins | b)secondary alcohol |
| 24 | Primary alhols show $M^+$ peaks corresponding to the loss of | a)water | b)$H^+$ion | c)$OH^-$ion | d)$O^{2-}$ion | c)$OH^-$ion |
| 25 | The ----is the most significant peak in thespectra of primary alcohols | a)$CH_2=OH^+$ | b)$OH^-$ | c)$CH_2^+$ | d)$CH_3$ | a)$CH_2=OH^+$ |
| 26 | In aliphatic ethers alkyl cation (or)an oxonium ion is formed by | a)α-cleavage | b)β-cleavage | c)γ-cleavage | d)δ-cleavage | a)α-cleavage |
| 27 | In aliphatic acids carboxyl group is directly eliminated by | a)β-cleavage | b)α-cleavage | c)γ-cleavage | d)δ-cleavage | a)β-cleavage |

| # | Question | a | b | c | d | Answer |
|---|---|---|---|---|---|---|
| 28 | Primary amides gives a strong peak at m/e=44 due to | a)$H_2N^-$ | b)$NH_3$ | c)$NH_4$ | d)$H_2N-C=O^-$ | b)$NH_3$ |
| 29 | For primary amines ,the base peak is formed at m/e 30 due to $CH_2=NH2$ by | a)α-cleavage | b)β- cleavage | c)γ- cleavage | d)δ- cleavage | d)δ- cleavage |
| 30 | The Position of metastable peak m* is for $m_1=108$, $m_1=123$ | a) 100 | b) 70 | c) 94.8 | d) 90 | a) 100 |
| 31 | The substituent group like –OH,-OR,-NH2 etc., which lower the ionization potential ----------- the relative abundance in aromatic compounds. | a) increase | b) decrease | c) Alter | d) influence | c) Alter |
| 32 | The substituent group like ------ etc., which increase the ionization potential, decrease the relative abundance of the aromatic compounds. | a)$–NO_2$ , -CN | b) $–OH,-OR,-NH_2$ | c) $R^+$ | d) $H^+$ ion | a)$–NO_2$ , -CN |
| 33 | In mass spectroscopy, the base peak is | a) Farthest to the right of the plot | b) Farthest to the left | c) Tallest peak | d) Peak preceding the isotope peaks | a) Farthest to the right of the plot |
| 34 | Mass Spectroscopy is a | a) Low pressure technique | b) High pressure technique | c) High pressure technique | d) Low temperature technique | c) High pressure technique |
| 35 | In mass spectroscopy, the compound containing Chlorine & Bromine show charecteristic ------ peak. | a) Base peak | b) Isotope peak | c) Both | d) None | a) Base peak |
| 36 | For primary amines the base peak is formed at -------- due to $CH_2=NH_2^+$ | a) m/e=30 | b) m/e=40 | c) m/e= 50 | d) m/e= 60 | b) m/e=40 |
| 37 | In the case a Cyclohexanol molecular ion peak appears at------- | a) m/e=100 | b) m/e=108 | c) m/e= 99 | d) m/e= 101 | a) m/e=100 |
| 38 | A benzyl group will show a very important fragment at m/e values | a) 92 | b) 78 | c) 77 | d) 91 | a) 92 |
| 39 | In aromatic primary amines , a parent ion is formed by the lose of ------ eletron from the lone pair present on the nitrogen atom | a) 1 | b) 2 | c) 3 | d) 4 | d) 4 |
| 40 | A very weak parent ion peak and a prominent $(M^+-18)$ peak would probably indicate | a) Alcohol | b) Ketone | c) Aldehyde | d) Presence of isotope of Oxygen | a) Alcohol |
| 41 | The compound whose mass spectrum shows m/e values at 156 (M+, base peak),127 and 29is | a.ethylbromide | b.methyliodide | c.methylbromide | d.ethyliodide | d.ethyliodide |
| 42 | For mass spectrum of n-propylbenzene, the m/e value of tropiliun ion is | a.91 | b.85 | c.41 | d.51 | a.91 |

| # | Question | a | b | c | d | Answer |
|---|----------|---|---|---|---|--------|
| 43 | Which of the following will not show ESR spectra? | a.$O_2$ | b.$C_2H_5$ | c. $N_2$ | d.$Cu^{2+}$ | c. $N_2$ |
| 44 | Predict the number of lines in the ESR spectra of thefollowing systems respectively?1.$CH_3CH_2$ , 2.$CH_3$ 3. $C_6H_6^-$ | a. 4,7,6 | b. 2,1,6 | c. 5,3,6 | d. 12,4,7 | d. 12,4,7 |
| 45 | In mass spectrum of ethylbenzene some of the prominent peaksappearat m/e=106, 91 and 65. Which of the species given below is not responsible for these peaks? | a. Ethyl benzene | b.Ethane | c.Tropiliuum ion | d.$C_5H_5^+$ | b.Ethane |
| 46 | In mass spectrum the base peak is | a. lowest peak in themass spectrum | b. the largest peak in the mass spectrum | c.medium peak in the massspectrum | d.both lowest and highest peak in the mass spectrum | b. the largest peak in the mass spectrum |
| 47 | The largest mass spectrum is always the | a.Parent peak | b.first fragment ion peak | c.meclaffetry rearranged ion peak | d.base peak | d.base peak |
| 48 | In malaffetry rearrangent what type of hydrogen involes the cleavage of β bond | a.alpha | b.beta rays | c.gammarays | d.delta | c.gammarays |
| 49 | A molecule is fagmented with--- from an electron in mass | a. excessof energy | b. no energy | c.medium energy | d.higher energy | a. excessof energy |
| 50 | In the mass spectrum of cyclohexene, the peak at m/e--- is formed in the fairly high abundance | a.82 | b.54 | c.28 | d.14 | b.54 |
| 51 | Mclaffetry rearrangement ion formed at m/e-- from pentene due to loss of ethylene molecule | a.42 | b.15 | c.28 | d.14 | a.42 |
| 52 | The tropilium ion has the m/e value at | a.91 | b.85 | c.41 | d.51 | a.91 |
| 53 | The molecular ion peak inphenol is-- | a.intense | a.less abundane | c.more abundance | d.significant | a.intense |
| 54 | In catechol the molecular ion peak is--- | a.intense | a.less abundane | c.more abundance | d.significant | a.intense |
| 55 | In aliphatic aldehydes and ketones the major fragmentation process are | a.alpha cleavage | b.beta cleavage | c.gammacleavage | d. alpha and beta cleavage | d. alpha and beta cleavage |
| 56 | The intensity of molecular ion peak --as the alkyl chain length--- | a. decreases,increases | b.increases,increases | c.decreases,decreases | d.increases,decreases | a. decreases,increases |
| 57 | In aldehydes and ketones containing -- atom | a)α-hydrogen | b)β- hydrogen | c)γ- hydrogen | d)δ- hydrogen | c)γ- hydrogen |
| 58 | In esters the molecular ion peak is | a. strong | b.less intense | c.more intense | d.weak | d.weak |
| 59 | The molecular ion abundance of a particular alkyl halide---as the electronegativity of the halogen substituent---- | a. decreases,increases | b.increases,increases | c.decreases,decreases | d.increases,decreases | d.increases,decreases |
| 60 | The ion peak of aliphatic nitriles is | a. strong | b.less intense | c.more intense | d.weak | d.weak |

**UNIT-V**
**Mössbauer Spectroscopy**

**Introduction to Mössbauer Spectroscopy**

Mössbauer spectroscopy is a versatile technique that can be used to provide information in many areas of science such as Physics, Chemistry, Biology and Metallurgy. It can give very precise information about the chemical, structural, magnetic and time-dependent properties of a material. Key to the success of the technique is the discovery of recoilless gamma ray emission and absorption, now referred to as the 'Mössbauer Effect', after its discoverer Rudolph Mössbauer, who first observed the effect in 1957 and received the Nobel Prize in Physics in 1961 for his work.

This introduction to the theory and applications of Mössbauer spectroscopy is composed of four sections. First the theory behind the Mössbauer effect is explained. Next how the effect can be used to probe atoms within a system is shown. Then the principal factors of a Mössbauer spectrum are illustrated with spectra taken from research work. Finally a bibliography of books and web sites is given for further and more detailed information.

**The Mössbauer Effect**
Nuclei in atoms undergo a variety of energy level transitions, often associated with the emission or absorption of a gamma ray. These energy levels are influenced by their surrounding environment, both electronic and magnetic, which can change or split these energy levels. These changes in the energy levels can provide information about the atom's local environment within a system and ought to be observed using resonance-fluorescence. There are, however, two major obstacles in obtaining this information: the 'hyperfine' interactions between the nucleus and its environment are extremely small, and the recoil of the nucleus as the gamma-ray is emitted or absorbed prevents resonance.

In a free nucleus during emission or absorption of a gamma ray it recoils due to conservation of momentum, just like a gun recoils when firing a bullet, with a recoil energy $E_R$. This recoil is shown in Fig1. The emitted gamma ray has $E_R$ less energy than the nuclear transition but to be resonantly absorbed it must be $E_R$ *greater* than the transition energy due to the recoil of the absorbing nucleus. To achieve resonance the loss of the recoil energy must be overcome in some way.



*Fig1: Recoil of free nuclei in emission or absorption of a gamma-ray*
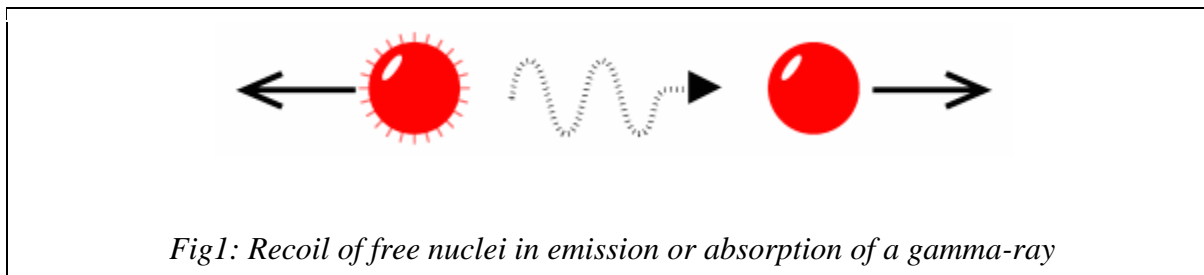
As the atoms will be moving due to random thermal motion the gamma-ray energy has a spread of values $E_D$ caused by the Doppler effect. This produces a gamma-ray energy profile as shown in Fig2. To produce a resonant signal the two energies need to overlap and this is shown in the red-shaded area. This area is shown exaggerated as in reality it is extremely small, a millionth or less of the gamma-rays are in this region, and impractical as a technique.
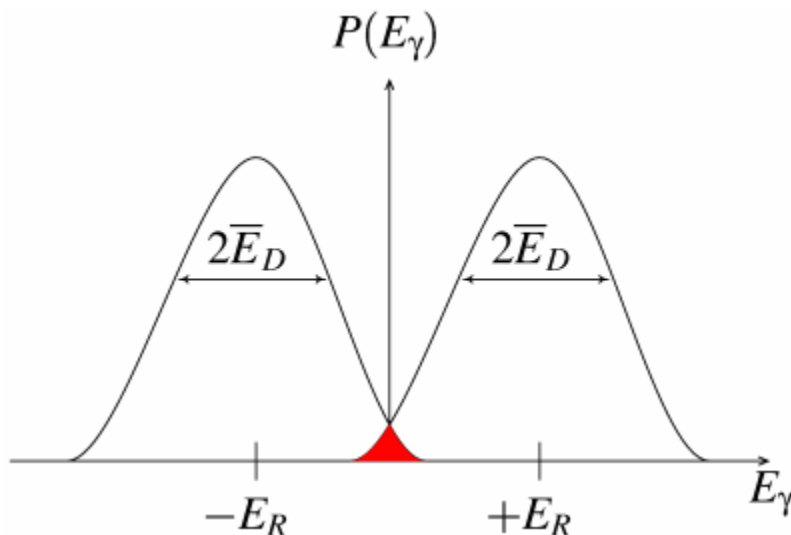
*Fig2: Resonant overlap in free atoms. The overlap shown shaded is greatly exaggerated*

What Mössbauer discovered is that when the atoms are within a solid matrix the effective mass of the nucleus is very much greater. The recoiling mass is now effectively the mass of the whole system, making $E_R$ and $E_D$ very small. If the gamma-ray energy is small enough the recoil of the nucleus is too low to be transmitted as a phonon (vibration in the crystal lattice) and so the whole system recoils, making the recoil energy practically zero: a recoil-free event. In this situation, as shown in Fig3, if the emitting and absorbing nuclei are in a solid matrix the emitted and absorbed gamma-ray is the same energy: resonance!
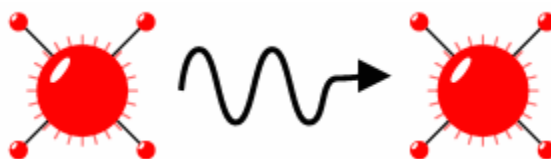


*Fig3: Recoil-free emission or absorption of a gamma-ray when the nuclei are in a solid matrix such as a crystal lattice*

If emitting and absorbing nuclei are in identical, cubic environments then the transition energies are identical and this produces a spectrum as shown in Fig4: a single absorption line.

*Fig4: Simple Mössbauer spectrum from identical source and absorber*

Now that we can achieve resonant emission and absorption can we use it to probe the tiny hyperfine interactions between an atom's nucleus and its environment? The limiting resolution now that recoil and doppler broadening have been eliminated is the natural linewidth of the excited nuclear state. This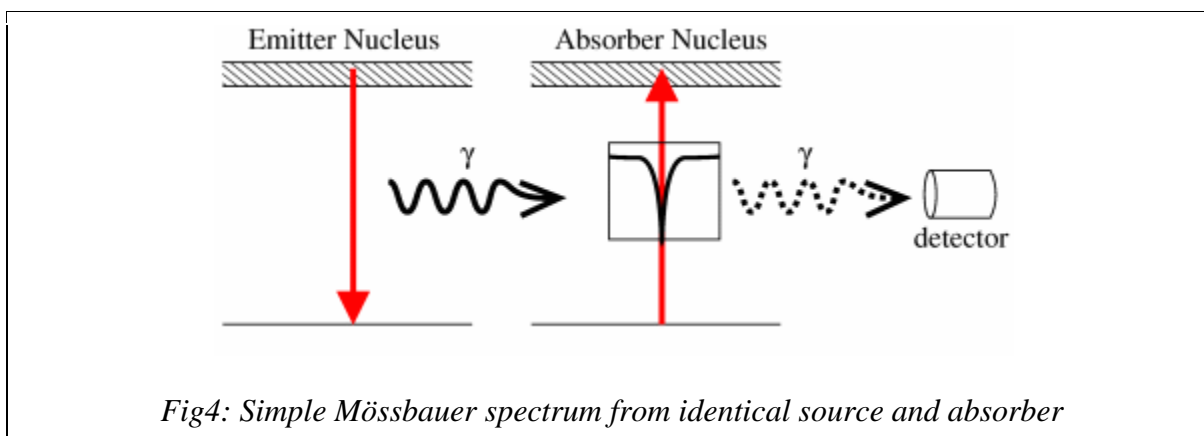 is related to the average lifetime of the excited state before it decays by emitting the gamma-ray. For the most common Mössbauer isotope, $^{57}$Fe, this linewidth is $5 \times 10^{-9}$ev. Compared to the Mössbauer gamma-ray energy of 14.4keV this gives a resolution of 1 in $10^{12}$, or the equivalent of a small speck of dust on the back of an elephant or one sheet of paper in the distance between the Sun and the Earth. This exceptional resolution is of the order necessary to detect the hyperfine interactions in the nucleus.

As resonance only occurs when the transition energy of the emitting and absorbing nucleus match exactly the effect is isotope specific. The relative number of recoil-free events (and hence the strength of the signal) is strongly dependent upon the gamma-ray energy and so the Mössbauer effect is only detected in isotopes with very low lying excited states. Similarly the resolution is dependent upon the lifetime of the excited state. These two factors limit the number of isotopes that can be used successfully for Mössbauer spectroscopy. The most used is $^{57}$Fe, which has both a very low energy gamma-ray and long-lived excited state, matching both requirements well. Fig5 shows the isotopes in which the Mössbauer effect has been detected.



Fig5: Elements of the periodic table which have known Mössbauer isotopes (shown in red font).

So far we have seen one Mössbauer spectrum: a single line corresponding to the emitting and absorbing nuclei being in identical environments. As the environment of the nuclei in a system we want to study will almost certainly be different to our source the hyperfine interactions between the nucleus and the its environment will change the energy of the nuclear transition. To detect this we need to change the energy of our probing gamma-rays. This section will show how

this is achieved and the three main ways in which the energy levels are changed and their effect on the spectrum.

## Fundamentals of Mössbauer Spectroscopy

As shown previously the energy changes caused by the hyperfine interactions we will want to look at are very small, of the order of billionths of an electron volt. Such miniscule variations of the original gamma-ray are quite easy to achieve by the use of the doppler effect. In the same way that when an ambulance's siren is raised in pitch when it's moving towards you and lowered when moving away from you, our gamma-ray source can be moved towards and away from our absorber. This is most often achieved by oscillating a radioactive source with a velocity of a few mm/s and recording the spectrum in discrete velocity steps. Fractions of mm/s compared to the speed of light ($3x10^{11}$ mm/s) gives the minute energy shifts necessary to observe the hyperfine interactions. For convenience the energy scale of a Mössbauer spectrum is thus quoted in terms of the source velocity, as shown in Fig1.



*Fig1: Simple spectrum showing the velocity scale and motion of source relative to the absorber*
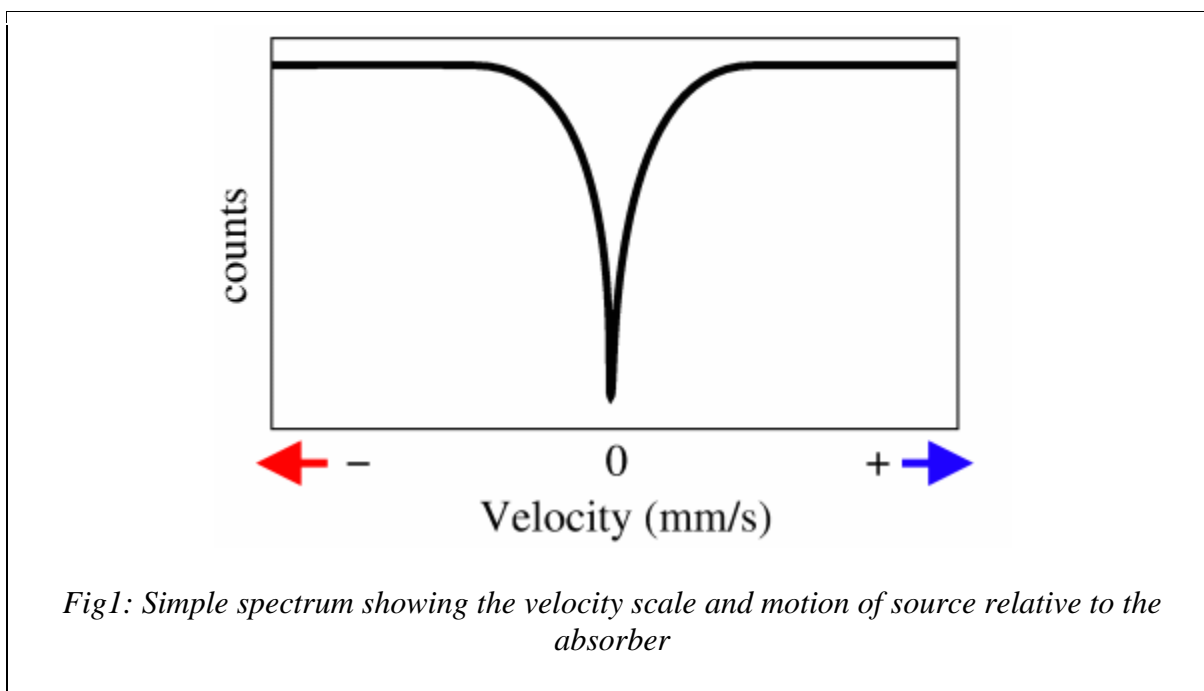
With an oscillating source we can now modulate the energy of the gamma-ray in very small increments. Where the modulated gamma-ray energy matches precisely the energy of a nuclear transition in the absorber the gamma-rays are resonantly absorbed and we see a peak. As we're seeing this in the transmitted gamma-rays the sample must be sufficiently thin to allow the gamma-rays to pass through, the relatively low energy gamma-rays are easily attenuated.

In Fig1 the absorption peak occurs at 0mm/s, where source and absorber are identical. The energy levels in the absorbing nuclei can be modified by their environment in three main ways: by the Isomer Shift, Quadrupole Splitting and Magnetic Splitting.

## Isomer Shift

The isomer 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 the s-electron environment between the source and absorber

thus produces a shift in the resonance energy of the transition. This shifts the whole spectrum positively or negatively depending upon the 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. For example $^{57}$Fe Mössbauer spectra will often be quoted relative to alpha-iron at room temperature.

The isomer shift is useful for determining valency states, ligand bonding states, electron shielding and the electron-drawing power of electronegative groups. For example, the electron configurations for $Fe^{2+}$ and $Fe^{3+}$ are $(3d)^6$ and $(3d)^5$ respectively. The ferrous ions have less s-electrons at the nucleus due to the greater screening of the d-electrons. Thus ferrous ions have larger positive isomer shifts than ferric ions.

## Quadrupole Splitting

Nuclei in states with an angular momentum quantum number I>1/2 have a non-spherical charge distribution. This produces a nuclear quadrupole moment. In the 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 characterised by a single quantity called the Electric Field Gradient (EFG).

In the case of an isotope with a I=3/2 excited state, such as $^{57}$Fe or $^{119}$Sn, the excited state is split into two substates $m_I=\pm 1/2$ and $m_I=\pm 3/2$. This is shown in Fig2, giving a two line spectrum or 'doublet'.



*Fig2: Quadrupole splitting for a 3/2 to 1/2 transition. The magnitude of quadrupole splitting, Delta, is shown*
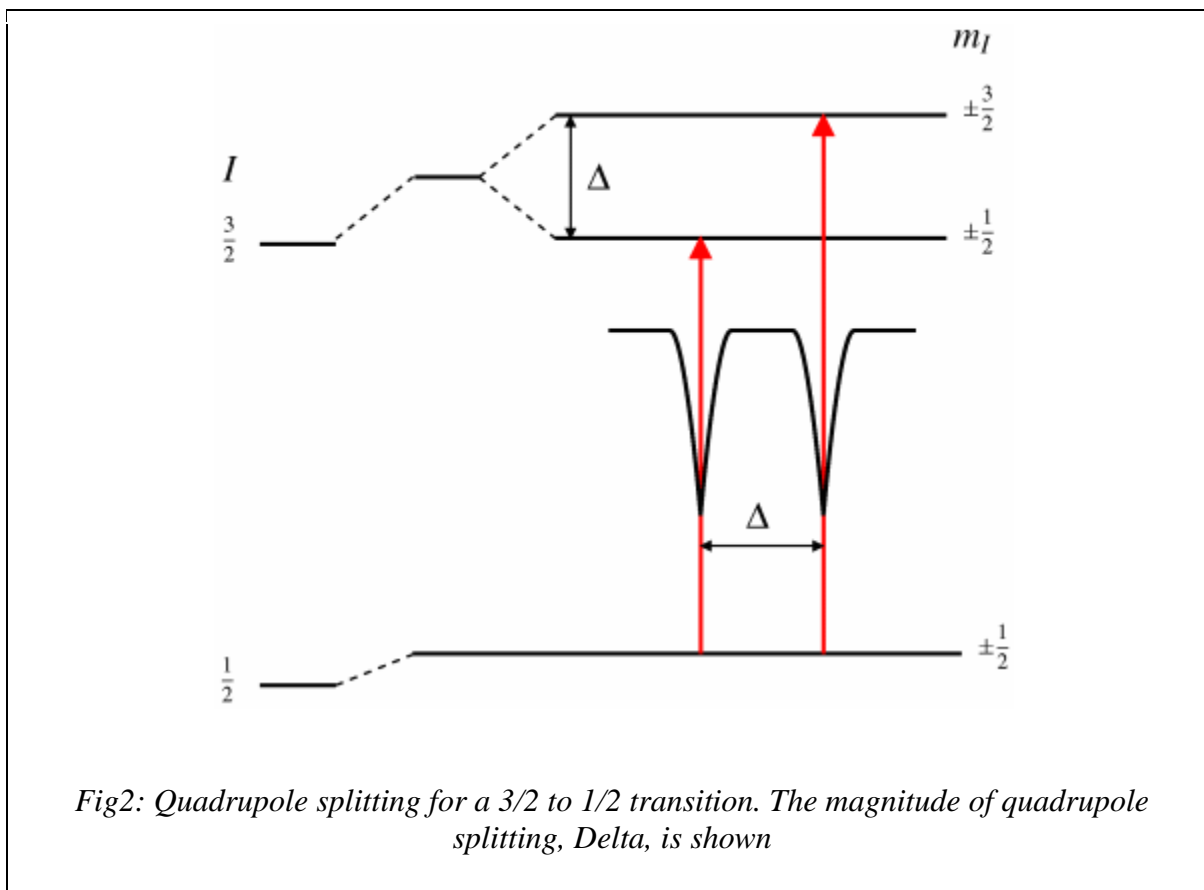
The magnitude of splitting, Delta, is related to the nuclear quadrupole moment, Q, and the principle component of the EFG, $V_{zz}$, by the relation Delta=eQ$V_{zz}$/2.

## Magnetic Splitting

In the presence of a magnetic field the nuclear spin moment experiences a dipolar interaction with the magnetic field ie Zeeman splitting. There are many sources of magnetic fields that can be experienced by the nucleus. The total effective magnetic field at the nucleus, $B_{eff}$ 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 the spin on those electrons polarising the spin density at the nucleus, $B_{orbital}$ is due to the orbital moment on those electrons, and $B_{dipolar}$ is the dipolar field due to the spin of those electrons.

This magnetic field splits nuclear levels with a spin of I into (2I+1) substates. This is shown in Fig3 for $^{57}$Fe. Transitions between the excited state and ground state can only occur where $m_I$ changes by 0 or 1. This gives six possible transitions for a 3/2 to 1/2 transition, giving a sextet as illustrated in Fig3, with the line spacing being proportional to $B_{eff}$.
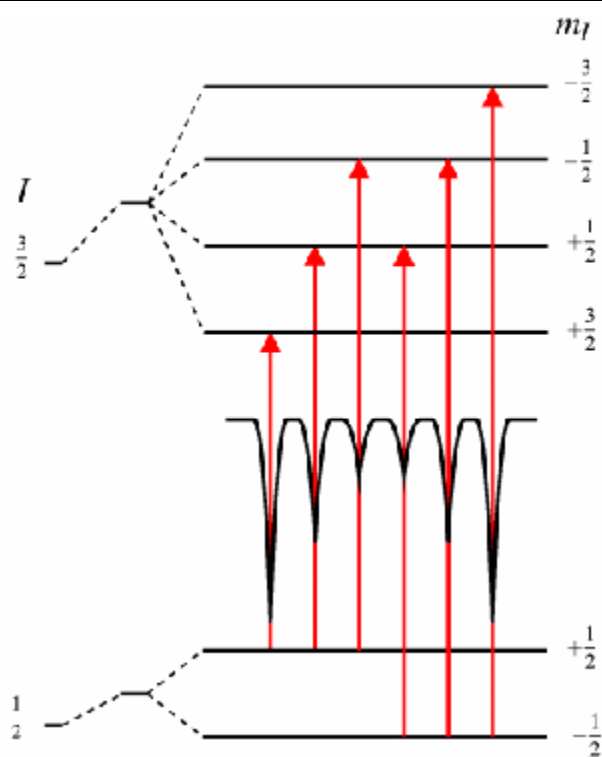


*Fig3: Magnetic splitting of the nuclear energy levels*

The line positions are related to the splitting of the energy levels, but the line *intensities* are related to the angle between the Mössbauer gamma-ray and the nuclear spin moment. The outer, middle and inner line intensities are related by:

3 : (4sin$^2$theta)/(1+cos$^2$theta) : 1

meaning the outer and inner lines are always in the same proportion but the middle lines can vary in relative intensity between 0 and 4 depending upon the angle the nuclear spin moments make to the gamma-ray. In polycrystalline samples with no applied field this value averages to 2 (as in Fig3) but in single crystals or under applied fields the relative line intensities can give information about moment orientation and magnetic ordering.

These interactions, Isomer Shift, Quadrupole Splitting and Magnetic Splitting, alone or in combination are the primary characteristics of many Mössbauer spectra. The next section will show some recorded spectra which illustrate how measuring these hyperfine interactions can provide valuable information about a system.

This section shows how Mössbauer spectroscopy can be a useful analytical tool for studying a variety of systems and phenomena. The spectra have been taken from active research projects and chosen to visually represent the hyperfine interactions presented in Part 2 and how they can be interpreted.

**Example Spectra**

**Tin dioxide assisted antimony oxidation**
Antimony-containing tin dioxide is an important catalyst for selective oxidation of olefins. Of particular importance in studying these systems to is to know the relative concentrations of the antimony charge states (3+ and 5+) during the catalytic process.

Fig1 shows three $^{121}$Sb spectra taken at various stages during the catalytic process: 1) fresh $Sb_2O_3$, 2) $Sb_2O_3$ calcined at 1000C and 3) the calcined material after catalysis. Firstly the isotope-specificity of Mössbauer spectroscopy picks out only the antimony atoms from the Sn-Sb-O composite. Readily apparent from spectrum 1 is that practically all of the antimony is in a single state (the red component). Comparison with previous experiments shows that the isomer shift for this majority component matches that of Sb3+. The asymmetric shape is due to the quadrupole splitting in this isotope, which has 8 lines (it is a 7/2 to 5/2 transition).

*Fig1 shows three $^{121}$Sb spectra taken at various stages during the catalytic process: 1) fresh Sb$_2$O$_3$, 2) Sb$_2$O$_3$ calcined at 1000C and 3) the calcined material after catalysis. Firstly the isotope-specificity of Mössbauer spectroscopy picks out only the antimony atoms from the Sn-Sb-O composite. Readily apparent from spectrum 1 is that practically all of the antimony is in a single state (the red component). Comparison with previous experiments shows that the isomer shift for this majority component matches that of Sb3+. The asymmetric shape is due to the quadrupole splitting in this isotope, which has 8 lines (it is a 7/2 to 5/2 transition).*

After calcining the spectrum is now composed of two components of equal area. The second (green) component corresponds to the Sb5+ ion. The component areas give the relative proportion of each site within the compound, in this case 1:1 indicating either Sb$_2$O$_4$ or Sb$_6$O$_{13}$. After the catalysis in spectrum 3 we can see that the antimony is now all in the 3+ charge state again.

Tin spectra were also recorded, showing a single line spectrum of identical isomer shift during all parts of the process, indicating no change in the tin charge state.

In cases like this basic deductions can be made even without computer analysis: one can simply see one component appear and disappear and the differences in isomer shift are readily apparent. Unfortunately it isn't always quite this obvious!

**Off-center tin atoms in PbSnTeSe**

Off-center impurities are those which can be displaced from their regular positions in a crystal lattice. They can be considered as existing in an asymmetric double potential well. Such atoms can change their position as the temperature changes. Unfortunately there are often many other phenomena in such systems that can mask the off-centering effect.

Mössbauer spectroscopy provides a good tool for observing this effect. Firstly the movement of the off-center atom within the lattice will change the symmetry of the electric field it is in: hence changing the quadrupole splitting. Mössbauer spectroscopy is also isotope and site specific, meaning we can observe the off-center single component without any masking from other elements or effects.

A compound which was thought to exhibit off-centering is $Pb_{0.8}Sn_{0.2}Te_{0.8}Se_{0.2}$, with tin as an off-center atom. Spectra are shown in Fig2 from this sample at 200K and 20K. There are two components: one from an off-center site and one from a normal single-potential site. It can be seen in the highlighted region that the small green component develops from a single line to a (broad) doublet. The quadrupole splitting is increasing, indicating the electric field environment around these particular atoms is become more asymmetrical. This is consistent with an atom moving within an asymmetric potential well.
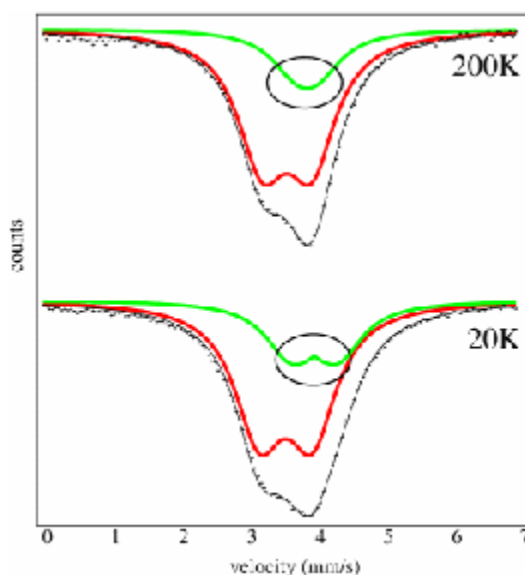


*Fig2: $^{119}$Sn Mössbauer spectra showing the quadrupole splitting as an off-center atom changes position with a change in temperature*

The other component shows no variation in quadrupole splitting. A series of spectra were taken in a temperature cycle and a hysteresis was observed in the values of quadrupole splitting. These results show that tin is an off-center atom in this compound and that there are two tin sites within it: one normal and one off-center.

**Uranium/Iron multilayers**

Magnetic multilayers are very important in today's technology, particularly in the areas of data storage and retrieval. A recent development is the use of actinides, such as uranium. Uranium in the right environment displays very large orbital magnetic moments, crucial to engineering systems with strong magnetic anisotropy and for magneto-optical applications. As part of this research sputtered Uranium/Iron multilayers have been produced and Mössbauer spectroscopy has been used to investigate the state of the iron within them.

As these samples are sputtered onto a thick substrate we cannot use conventional Mössbauer spectroscopy in Transmission Mode (TM) as the substrate would block the gamma-rays and we would receive no signal at all. There is a technique known as Conversion Electron Mössbauer Spectroscopy or CEMS which records the conversion electrons emitted by the resonantly excited nuclei in the absorber. In TM mode we record the absorption peaks as the gamma-rays are resonantly absorbed and so see dips, whilst in CEMS we record the electrons emitted from those excited nuclei and so see emission peaks. As the electrons are strongly attenuated by the sample as they pass through it most of the signal only comes from the uppermost 1000Angstroms.

Fig3 shows [57]Fe CEMS spectra from three Uranium/Iron multilayers of varying layer thicknesses. They are composed of three components: two sextets and one doublet. The hyperfine parameters of the two sextets correspond to alpha-iron, the red component being fully crystalline and the green component being from diffuse and poorly crystalline alpha-iron. The magnetic splitting shows that the iron in these two components is magnetically ordered.
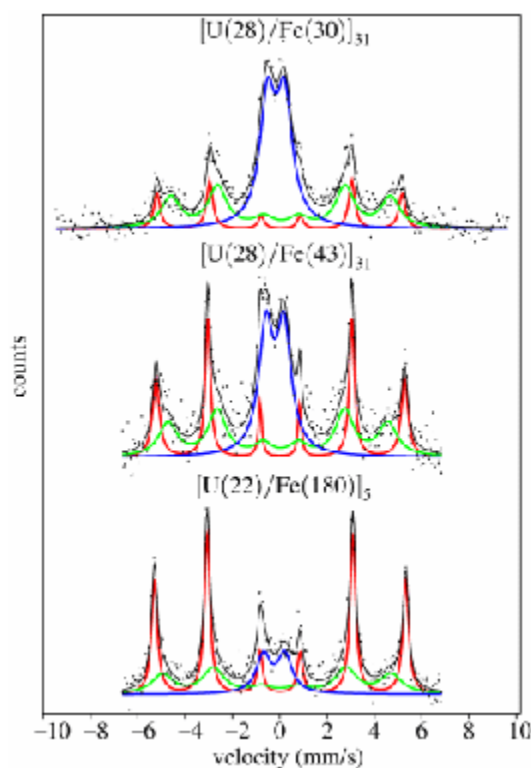


*Fig3: [57]Fe CEMS spectra taken from U/Fe multilayers of varying layer thicknesses*

The third component has an isomer shift and quadrupole splitting consistent with previous work on the $UFe_2$ intermetallic. This is paramagnetic at room temperature, as shown by the doublet. It is a doublet and not a sextet even though the intermetallic has a magnetic moment as the moment direction changes much faster in the paramagnetic state than the time it takes Mössbauer spectroscopy to record it and thus the experienced hyperfine field averages to zero.

As the iron layer thickness is increased to 43Angstroms the relative proportion of alpha-iron to $UFe_2$ increases and also the proportion of fully crystalline iron increases. As the iron layer is increased further to 180Angstroms this proportion becomes even greater. We can deduce from this that the thicker the iron layer the greater the *proportion* of crystalline iron, but more detailed analysis of the component areas compared to the layer thickness shows that the absolute thicknesses of the poorly crystalline iron and $UFe_2$ stay roughly constant.

Mössbauer spectroscopy has easily shown the existence of the three different iron sites within the sample and how their proportion has varied with layer thickness.

Superspin glass transition in $Al_{49}Fe_{30}Cu_{21}$

The magnetic properties of granular alloys and heterogeneous nanostructures built by ferromagnetic and non-magnetic components attract much attention due both to the fundamental interest of their rich phenomenology and to their potential applications, for instance in magnetoresistive devices and magnetic recording. Of particular interest are superspin glasses but their study is made difficult by the different possible sources for non-equilibrium magnetic behaviour and the mixtures of particle phases within the samples.

Mössbauer spectroscopy, as seen in the previous examples, is very good at distinguishing particular sites or phases within a sample. And as seen in the previous example can show the difference between magnetically ordered and paramagnetic sites. As the superspin glass phase reaches its freezing temperature the atoms become magnetically ordered and this will show up in the spectra as a sextet appearing.

A series of [57]Fe spectra were recorded from a ball-milled sample of $Al_{49}Fe_{30}Cu_{21}$ with decreasing temperature, shown in Fig4. At 40K, above the freezing temperature, there are two components of unequal proportion, both doublets. As the temperature is reduced the smaller component starts to spread outwards into a magnetic sextet. The peaks are broad and diffuse due to there being a distribution of grain sizes within the sample and hence a distribution of magnetic hyperfine fields. Plotting the recorded hyperfine field against temperature can then give the superspin glass transition temperature for this compound.
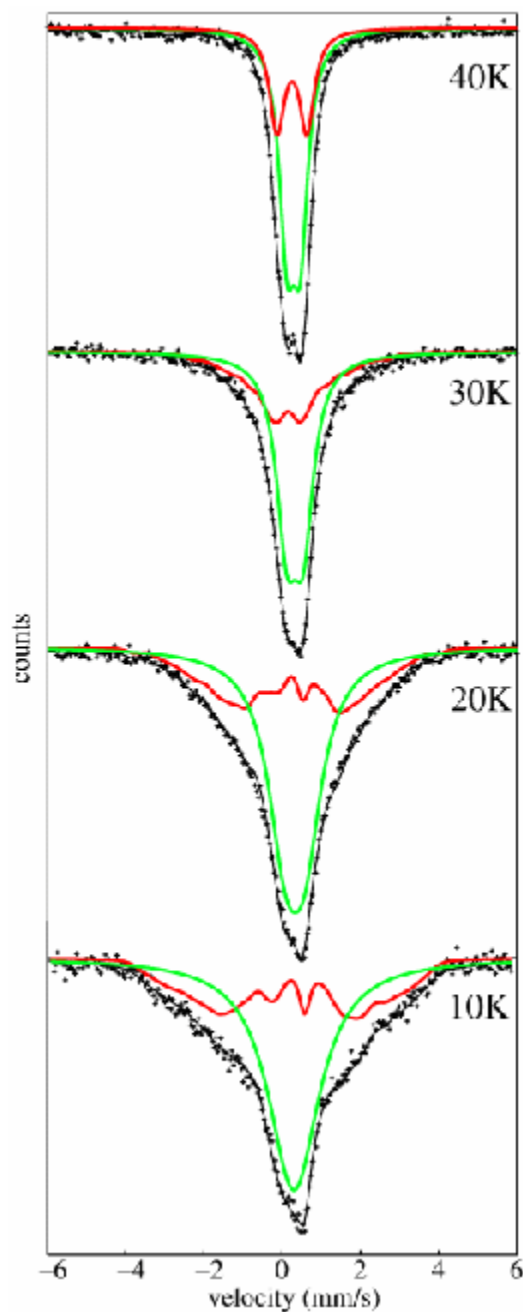
*Fig4: Series of $^{57}$Fe Mössbauer spectra showing the superspin glass transition in nanogranular $Al_{49}Fe_{30}Cu_{21}$*

Mössbauer spectroscopy showed quite readily the onset of the superspin glass 'freezing' and the proportion of the magnetic particles and their surrounding non-magnetic matrix. Analysis of the hyperfine field distribution also proved consistent with that expected for a superspin glass.This section shows how Mössbauer spectroscopy can be a useful analytical tool for studying a variety

of systems and phenomena. The spectra have been taken from active research projects and chosen to visually represent the hyperfine interactions presented in Part 2 and how they can be interpreted.

# Ultraviolet-Visible (UV-Vis) Spectroscopy – Sample Problems Using Woodward-Fieser Rules

Introduction
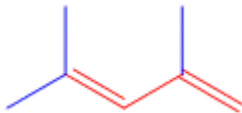
In this page we discuss a few examples of how we can utilize the Woodward-Fieser rules to determine the wavelength of maximum absorption for some molecules. We highly recommend that you read up the first two sections on the Woodward rules to calculate the λmax for conjugated dienes and the Woodward rules to calculate the λmax for unsaturated carbonyl compounds, before you read this page.

*Note: Numerical values for Woodward-Fieser rules differ slightly from one textbook to another. We have tried to compile an extensive list of numerical values from online resources, textbooks and journal articles based on the popularity of the number. It is recommended that you learn on how to apply the values for the contributors and then follow the values given in a text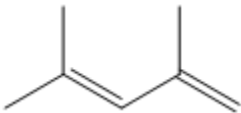 book recommended by your teacher, or use our values. We believe that learning how to apply the rules is more essential than actually getting the exact answer. Other's opinions may vary.*

In these sample problems you will be shown the structure, then the structure is highlighted to show you key features which would affect the λmax of the molecule. Then the table will show you the solutions on how to solve to get the wavelength of maximum absorption, with a final calculated λmax using the Woodward-Fieser rules. In some cases if we have an observed λmax for comparison, it may be given as well.
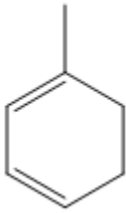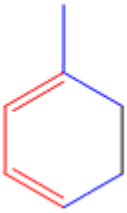
*Note-* If you have your own problems please write the IUPAC name in the comments section and I will attempt to solve it and add it to this list of examples.

## Example/Sample Problem 1
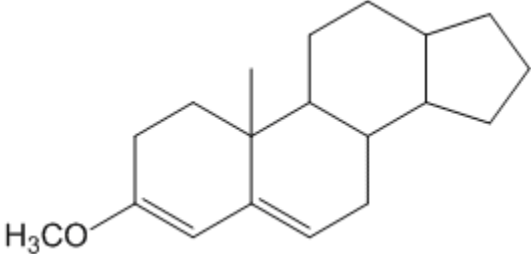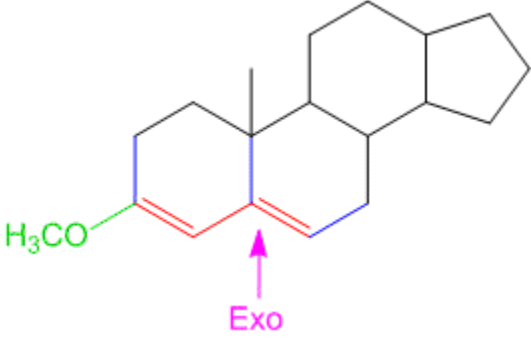
|  |  |
|---|---|
| **Name of Compound** | 2,4-dimethylpenta-1,3-diene |
| **Woodward Component** | **Contribution** |
| **Core-** Transoid/Heteroannular Diene | + 215 nm |
| **Substituents-** 3 alkyl groups | 3 x 5 = + 15 nm |

| Other Effects | 0 |
|---|---|
| | |
| **Calculated λmax** | **230 nm** |
| **Observed λmax** | 234 nm |
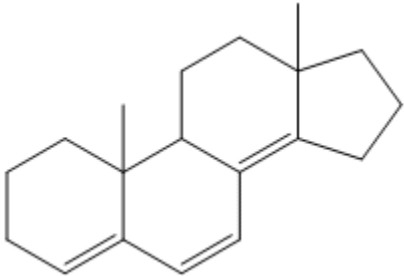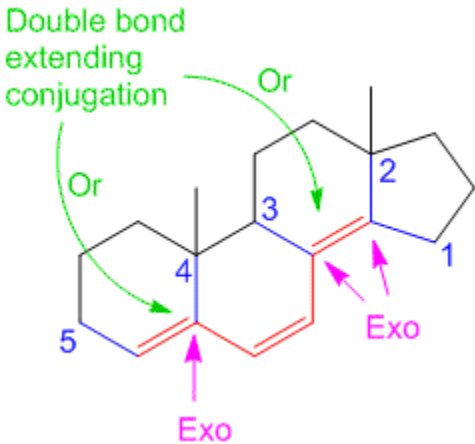
## Example/Sample Problem 2



| **Name of Compound** | 1-methylcyclohexa-1,3-diene |
|---|---|
| **Woodward Component** | **Contribution** |
| **Core-** Cisoid/Homoannular Diene | + 253 nm |
| **Substituents-** 3 alkyl groups | 3 x 5 = + 15 nm |
| **Other Effects** | 0 |
| | |
| **Calculated λmax** | **268 nm** |
| **Observed λmax** | N/A |

## Example/Sample Problem 3

| Name of Compound | 3-methoxy-10-methyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthrene |
|---|---|
| **Woodward Component** | **Contribution** |
| **Core-** Transoid/Heteroannular Diene | + 215 nm |
| **Substituents-** 3 alkyl groups<br><br>1 alkoxy group | 3 x 5 = + 15 nm<br><br>+ 6 nm |
| **Other Effects-** Exocyclic Double Bond | + 5 nm |
| | |
| **Calculated λmax** | **241 nm** |
| **Observed λmax** | N/A |
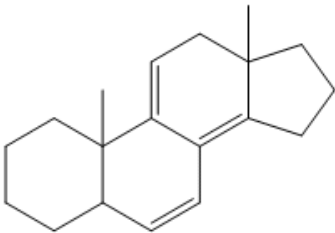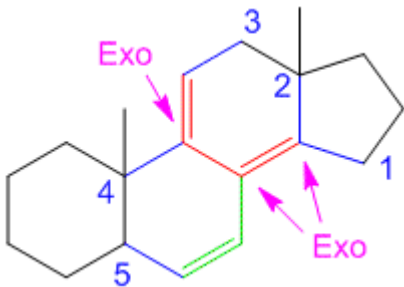
## Example/Sample Problem 4

| Name of Compound | 10,13-dimethyl-2,3,9,10,11,12,13,15,16,17-decahydro-1H-cyclopenta[a]phenanthrene |
|---|---|
| **Woodward Component** | **Contribution** |
| **Core-** Transoid/Heteroannular | + 215 nm |
| **Substituents-** 5 alkyl groups<br><br>1 Double bond extending conjugation | 5 x 5 = + 25 nm<br><br>+ 30 nm |
| **Other Effects-** 3 Exocyclic Double Bond | + 15 nm |
|  |  |
| **Calculated λmax** | **285 nm** |
| **Observed λmax** | 283 nm |
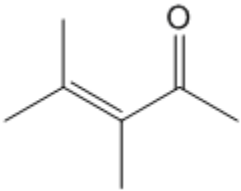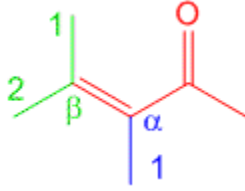
## Example/Sample Problem 5

*Note-* In this example the molecule **contains both, a homoannular diene system and a heteroannular diene** system. In such a molecule the core chromophore is considered to be the homoannular system and accordingly the calculations are performed.

**Homoannular system**
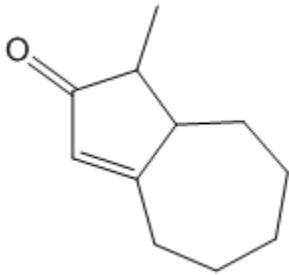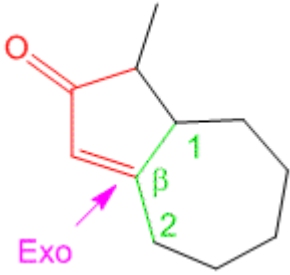
| Component | Contribution |
|---|---|
| **Core-** Homoannular/Cisoid diene | + 253 nm |
| **Substituents**– 5 alkyl substituents<br><br>Double bond extending conjugation | 5 x 5 = + 25 nm<br><br>+ 30 nm |
| **Other Effects-** 3 Exocyclic double bonds | 3 x 5 = + 15 nm |
| **Calculated** $\lambda_{max}$ | **323 nm** |
| **Observed** $\lambda_{max}$ | n/a |

## Example/Sample Problem 6
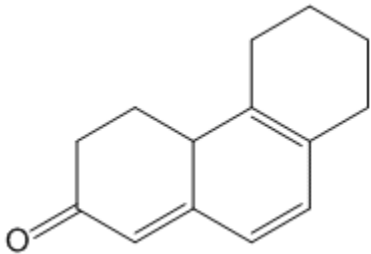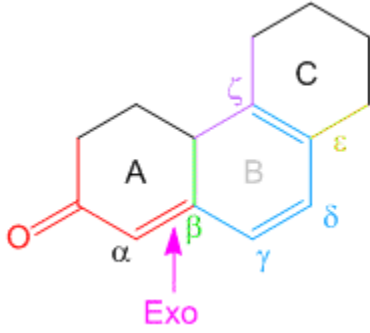


| Name of Compound | 3,4-dimethylpent-3-en-2-one |
|---|---|
| **Component** | **Contribution** |
| **Core-** α,β-unsaturated ketone | + 215 nm |

| Substituents at α-position- 1 alkyl group | + 10 nm |
|---|---|
| Substituents at β-position- 2 alkyl groups | 2 x 12 = 24 nm |
| Other Effects | 0 |
| Calculated λ$_{max}$ | **249 nm** |
| Observed λ$_{max}$ | 249 nm |
| | |

## Example/Sample Problem 7

|  |  |
|---|---|
| **Name of Compound** | 1-methyl-4,5,6,7,8,8a-hexahydroazulen-2(1H)-one |
| **Component** | **Contribution** |
| **Core-** cyclopentenone | + 202 nm |
| **Substituents at α-position** | 0 |
| **Substituents at β-position-** 2 alkyl groups | 2 x 12= + 24 nm |
| **Other Effects-** 1 Exocyclic Double Bond | + 5 nm |
| **Calculated λ$_{max}$** | **231 nm** |
| **Observed λ$_{max}$** | 226 nm |
| | |

## Example/Sample Problem 8



| Name of Compound | 4,4a,5,6,7,8-hexahydrophenanthren-2(3H)-one |
|---|---|
| **Component** | **Contribution** |
| **Core-** cyclohexenone | + 215 nm |
| **Substituents at α-position:** | 0 |
| **Substituents at β-position:** 1 alkyl group | + 12 nm |
| **Substituents at γ-position:** | 0 |
| **Substituents at δ-position:** | 0 |
| **Substituents at ε-position:** 1 alkyl group | + 18 nm |
| **Substituents at ζ-position:** 2 alkyl group | 2 x 18 = + 36 nm |
| **Other Effects:** 2 Double bonds extending conjugation<br><br>Homoannular Diene system in ring B<br>1 Exocyclic double bond | 2 x 30 = + 60 nm<br><br>+ 35 nm<br><br>+ 5 nm |
| **Calculated λ_max** | **381 nm** |

| Observed $\lambda_{max}$ | 388 nm |
|---|---|

*Note-* If you have your own problems please write the IUPAC name in the comments section and I will attempt to solve it and add it to this list of examples.

**IR Spectroscopy: Some Simple Practice Problems**

*By itself,* Infrared (IR) spectroscopy isn't a great technique for solving the structure of an unknown molecule. However, we've seen that IR spectroscopy can a great technique for identifying *certain* functional groups in an unknown molecule – especially functional groups containing OH or C=O.

For instance, in an earlier post on the structure determination of deer tarsal gland pheromone, we saw how the authors of the study used IR spectroscopy to identify the presence of a lactone functional group (i.e. a cyclic ester) by its characteristic absorbance at 1775 cm$^{-1}$.

Additionally, if you've narrowed down a structure to several possibilities, it can be very helpful in ruling various possibilities *out.*

In this post we're going to go through four (simple) practice problems where you'll be provided with an IR spectrum and the molecular formula, and are then charged with the task of figuring out which molecule **best** fits the spectrum.

Everything you need to know about IR in order to solve the problems below was presented in the previous post on how to do quick analyses of IR spectra, so go back and read that if you haven't done so already.

Let's begin.

(answers to each problem, along with analysis, are at the bottom of the post. **Don't peek until you've given each problem a thorough attempt**).

---

**Problem #1:** Unknown molecule with molecular formula $C_5H_{10}O$. Which of these five molecules is it most likely to be?

Which of these molecules best corresponds to the IR spectrum below?
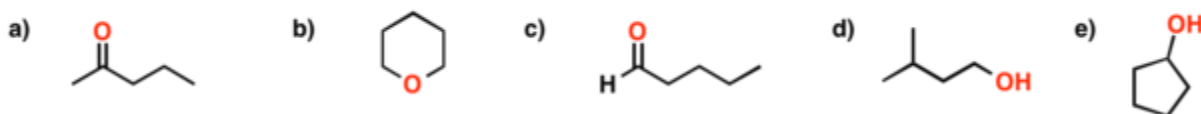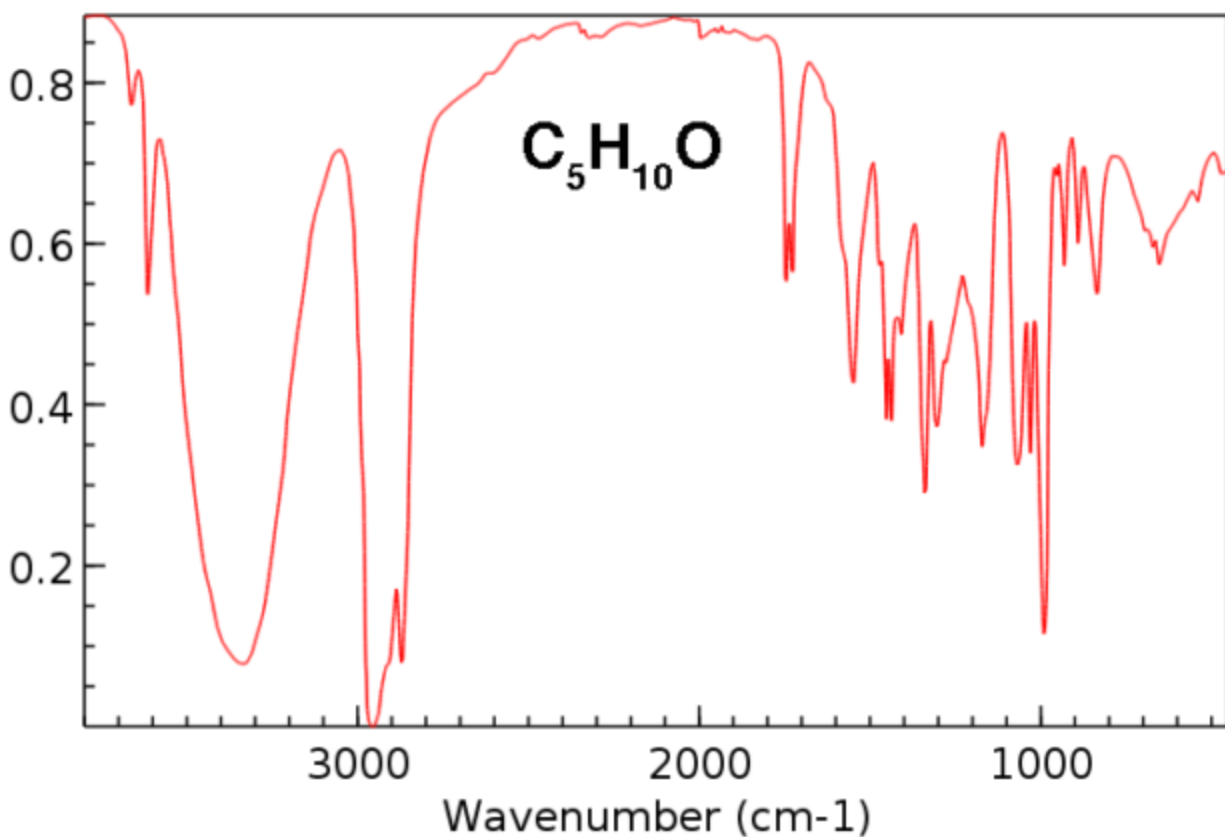
**Problem #2:** Unknown molecule with molecular formula $C_6H_{12}O$.

Which of these molecules best corresponds to the IR spectrum below?

IR spectrum labeled $C_6H_{12}O$ with y-axis values 0.8, 0.6, 0.4, 0.2 and x-axis Wavenumber (cm-1) at 3000, 2000, 1000.
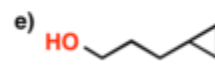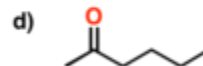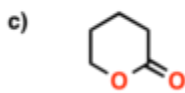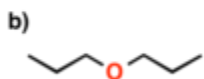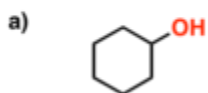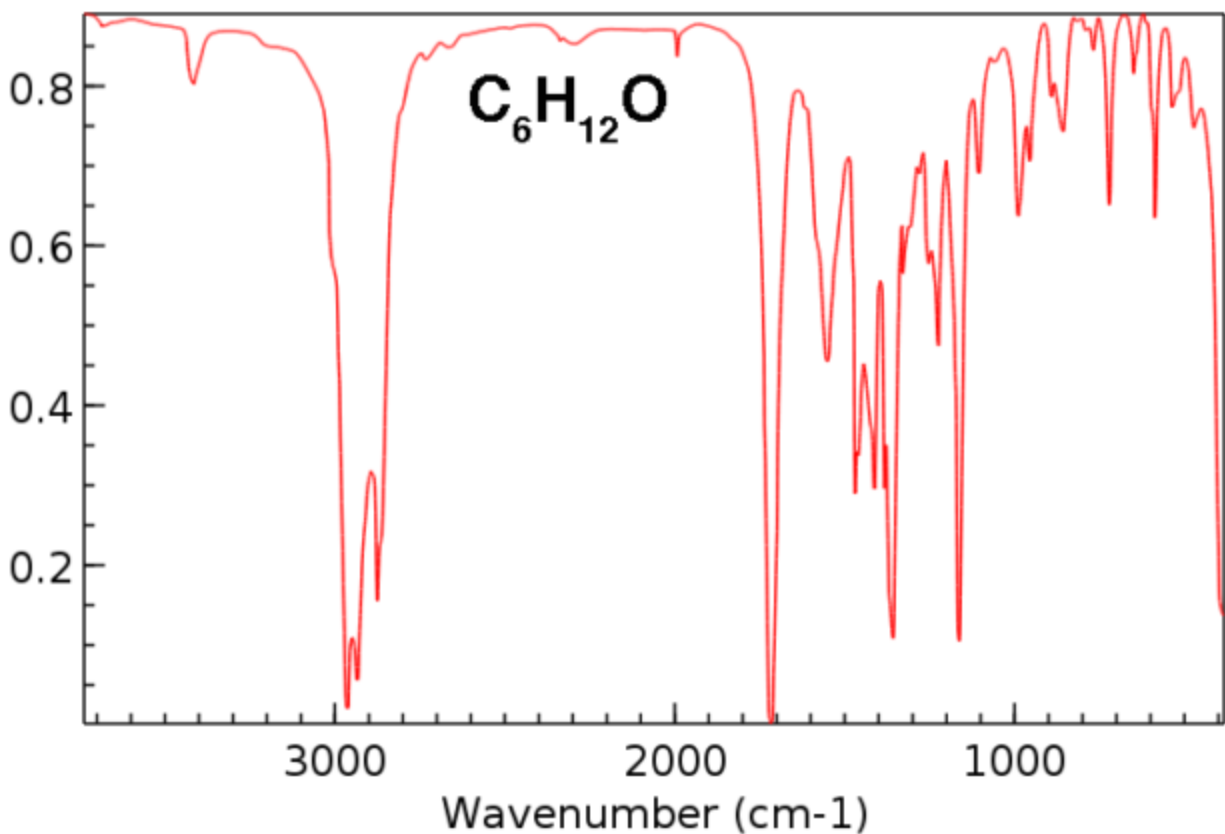
**Problem #3:** Unknown molecule with molecular formula $C_6H_{14}O$ .

Which of these molecules best corresponds to the IR spectrum below with molecular formula $C_6H_{14}O$ ?

a) [structure with OH]  b) [structure with OH]  c) [ether structure]  d) [aldehyde structure]  e) [epoxide structure]
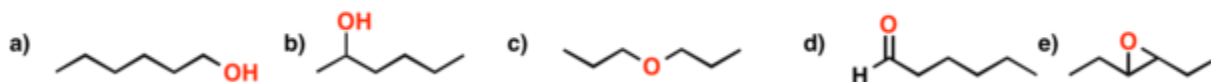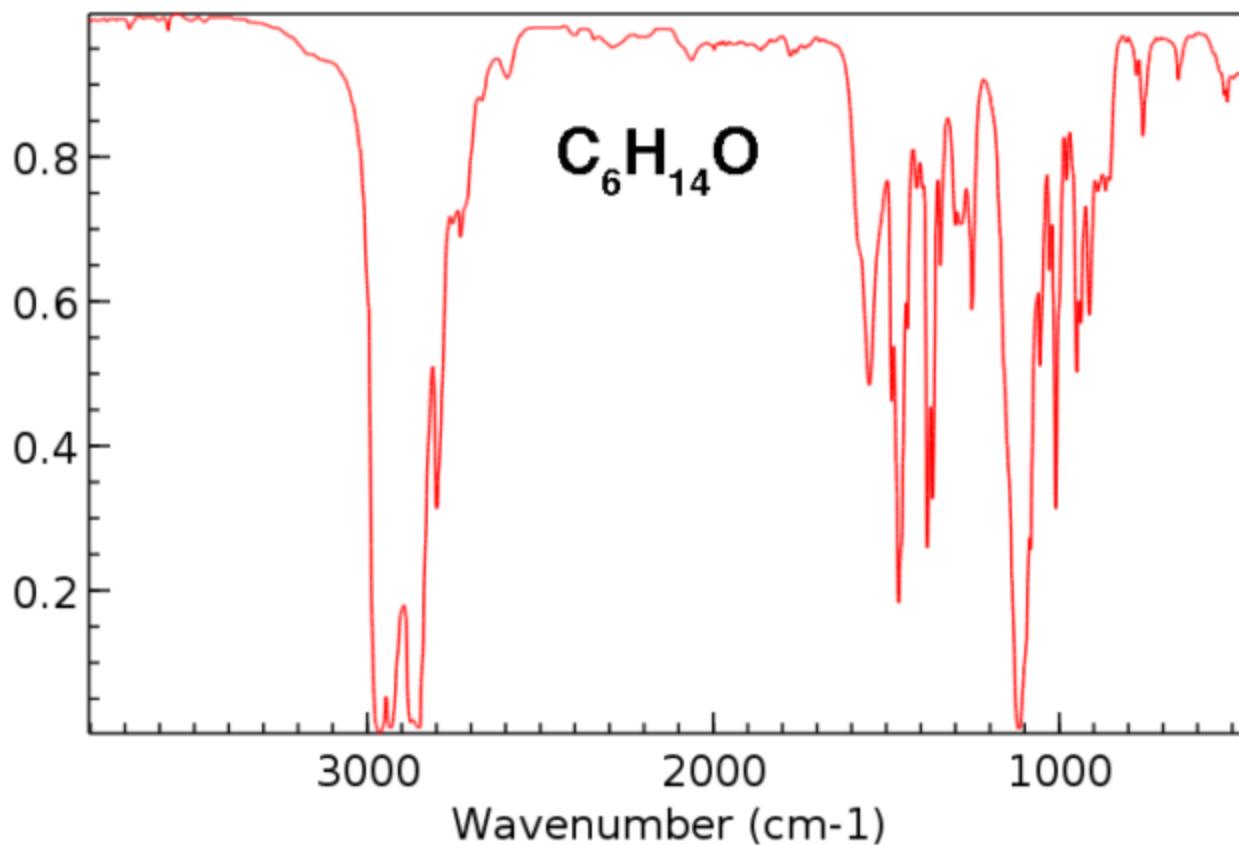
**Problem #4:** Unknown molecule with formula $C_4H_8O_2$ (Also, smells like vomit)

Which of these molecules best corresponds to the IR spectrum below?

a) $H_3C$—O—...  b) ...OH  c) ...  d) HO—...  e) HO—OCH₃
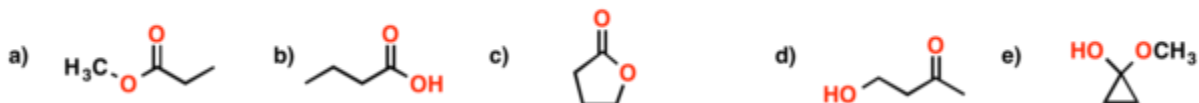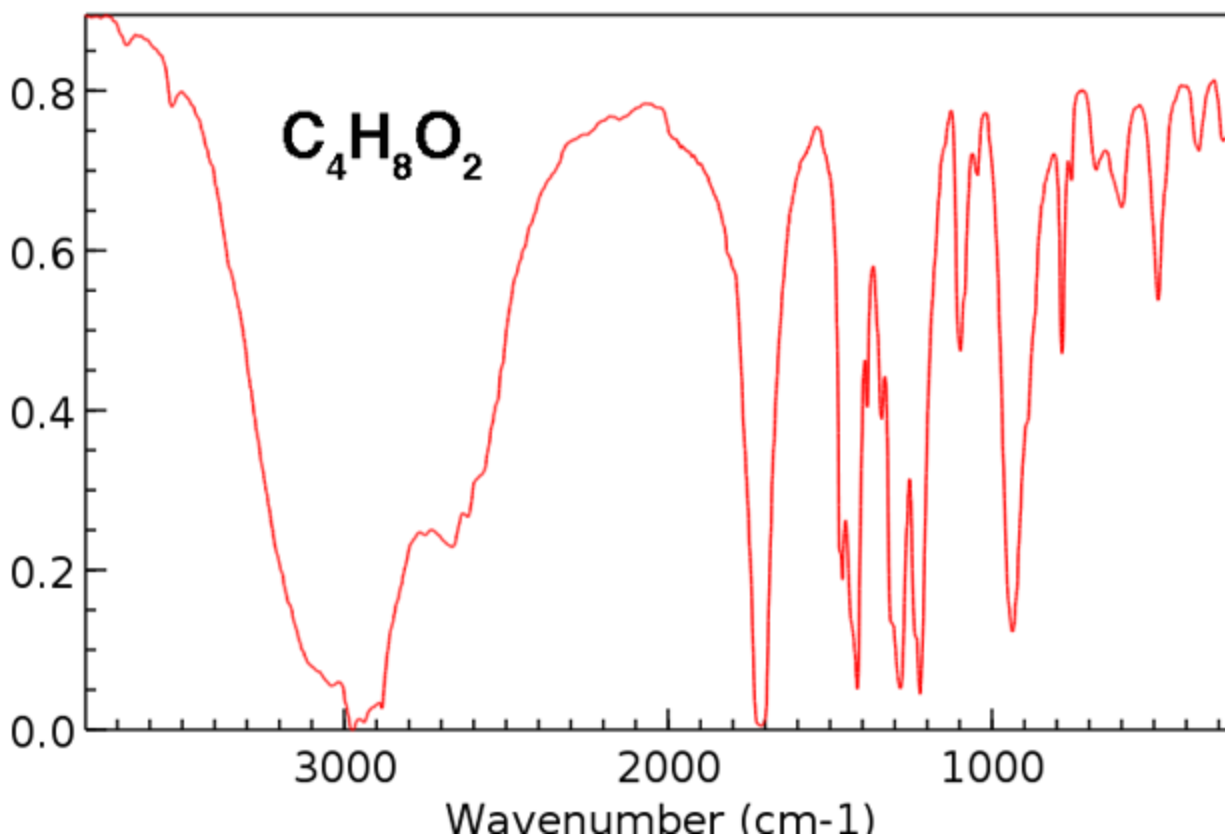
**Answers**

**Problem 1:**
▪ You're given the molecular formula, which is $C_5H_{10}O$. This corresponds to an index of hydrogen deficiency (IHD) of 1, so either a double bond or ring is present in the molecule. This immediately rules out **d)** whose IHD is zero and thus has a molecular formula of $C_5H_{12}O$.
▪ Looking at the spectrum we see a broad peak at 3300 $cm^{-1}$ and no dominant peak around 1700 $cm^{-1}$ (That peak halfway down around 1700 $cm^{-1}$? It's too weak to be a C=O.)
▪ That broad peak at 3300 tells us that we have an alcohol (OH group). The only option that makes sense is **e)** (cyclopentanol) since it has both an OH group and an IHD of 1. It can't be **b)** since that molecule lacks OH.
▪ **a)** and **c)** are further ruled out by the absence of C=O ; B is ruled out by the presence of the OH at 33oo

**Problem 2:**
▪ A molecular formula of C6H12O corresponds to an IHD of 1 so either a double bond or ring is present in the molecule.

- There is no strong OH peak around 3200-3400 cm$^{-1}$ (that little blip around 3400 cm$^{-1}$ is too weak to be an OH). We can immediately rule out **a)** and **e)** .
- However, we do see a peak a little above 1700 cm$^{-1}$ that is one of the strongest peaks in the spectrum. This is a textbook C=O peak. We can safely rule out **b)** which lacks a carbonyl.
- The only option that makes sense is **d)** (2-hexanone) since **c)** doesn't match the molecular formula (two oxygens, five carbons).
- Note also that the C-H region shows all peaks below 3000 cm$^{-1}$ which is what we would expect for a saturated ("aliphatic") ketone.

**Problem 3**:

- A molecular formula of $C_6H_{14}O$ corresponds to an IHD of zero. No double bonds or rings are present in the molecule.
- Using this we can immediately rule out **d)** and **e)** since their structures cannot correspond to molecular formula (they are both $C_6H_{12}O$)
- There is no OH peak visible around 3200-3400 cm$^{-1}$. We can rule out **a)** and **b)** .
- This leaves us with **c)** . It's an ether.
- Useful tip: ethers are "silent" in the prominent parts of the IR spectrum; this functional group is best identified through a process of deduction. Seeing an O in the formula but no OH or C=O peaks, the only logical selection is **c)** .
- Final note: **e)** is a cyclic ether called an "epoxide". The important clue to distinguish **c)** and **e)** was the fact that we were given the molecular formula. In the absence of that information it would have been difficult to tell the difference without a close consultation of an IR peak table.

**Problem 4:**

- The immediate giveaway is the smell of puke. That's butyric acid for sure!
- More seriously: the formula of $C_4H_8O_2$ corresponds to an IHD of 1. We can immediately rule out **c)** .
- Looking at the IR spectrum we see a huge peak in the 3300-2600 cm$^{-1}$ region that blots out everything else. This seems like a textbook "hairy beard" typical of a carboxylic acid, but let's look for more information before confirming it. We can at least rule out **a)** , which has no OH peaks.
- We also see a strong peak a little above 1700 cm$^{-1}$ which is typical of a C=O. We can safely rule out **e)** which lacks carbonyl groups entirely.
- This leaves us with two reasonable choices: **b)** (the carboxylic acid) and **d)** the ketone / alcohol. *How to choose between the two?* The "hairy beard" is diagnostic. Alcohol OH peaks don't fill up 600 wavenumber units the way that carboxylic acid peaks do. [Go back and look at a few examples from the previous post if you'd like confirmation]  A more subtle way to

distinguish the two might be the position of the carbonyl peak, but carboxylic acids (1700-1725 cm$^{-1}$) show up largely in the same range as do ketones (1705-1725 cm$^{-1}$).

You might recognize that in each of these four examples we followed a simple procedure:

1. Since we were given the molecular formula, we calculated the **index of hydrogen deficiency.** This is a quick calculation and gives us useful information. We were able to use it to "rule out" a few answers which you might classify as "trick questions".

2. Next, we examined the **hydroxyl region** around 3200-3400 cm for *broad, rounded peaks* ("tongues") typical of OH groups . The most important question we want to answer is: "is there an OH present"?

3. Then, we looked at the **carbonyl region** from about 1650 – 1830 cm for *sharp, strong peaks* ("swords") typical of C=O groups. Here we want to quickly know if there are any C=O groups present.

4. Using these three pieces of information we could then rule out various options that were given to us, narrowing down the possible options. Granted, these were relatively simple examples (only C,H, and O), but the thought process is what's important.

Two final notes in conclusion:

- It's nice to be able to get a positive ID on a functional group, but **ruling things out can be valuable too.** The *absence* of an OH or C=O peak (or both) is still helpful information! We used this in Problem 3 to **infer** the existence of an ether by the absence of an OH or C=O.

- A related point: information you get about a molecule from various sources (e.g. molecular formula, UV-Vis, IR, mass spec, 13-C and 1H NMR) is self-consistent and should not contradict. I like to think of structure determination as being a bit like trying to infer the structure of a three-dimensional object by analyzing the shadows it casts from lights at various angles (or different *wavelengths*, to use a slightly more apt analogy) Through logic and deduction (and perhaps one or two intuitive leaps) we can use the varying layers of information to work backwards to the shape of the object that casts the shadow in the first place.

It's crucial to be able integrate each of these sources of information together. In this post we saw examples of using both index of unsaturation and IR together to draw conclusions about the functional groups present in the molecule. As we move towards increasingly complex spectral techniques, this skill of "integration" will become increasingly more important! As we'll see, solving the structure of an unknown is a bit like filling out one of those "logic squares" you've likely encountered in grade school.

|  | Red | Yellow | Green | Blue | 12 | 15 | 18 | 21 | Marmite | Honey | Marmalade | Jam |
|---------|-----|--------|-------|------|----|----|----|----|---------|-------|-----------|-----|
| Peter   |     |        |       |      |    | X  |    |    |         |       |           |     |
| Jane    |     |        | X     |      |    | X  |    |    |         |       |           |     |
| Simon   |     |        |       |      | X  | ●  | X  | X  |         |       |           |     |
| Alice   |     |        |       |      |    | X  |    |    |         |       |           |     |
| Marmite |     |        |       |      |    |    |    |    |         |       |           |     |
| Honey   |     |        |       |      |    |    |    |    |         |       |           |     |
| Marmalade |   |        |       |      |    |    |    |    |         |       |           |     |
| Jam     |     |        |       |      |    |    |    |    |         |       |           |     |
| 12      |     |        |       |      |    |    |    |    |         |       |           |     |
| 15      |     |        |       |      |    |    |    |    |         |       |           |     |
| 18      |     |        |       |      |    |    |    |    |         |       |           |     |
| 21      |     |        |       |      |    |    |    |    |         |       |           |     |

## POSSIBLE QUESTIONS

## MULTIPLE CHOICE QUESTIONS

17. The energies of the emitted γ-ray is
  a) 10 to 150 kev  b) **10 to 100 kev**  c)10 to 200 kev  d)10 to 175 kev

18. The Mossbauer Effect is based on
  a) Electromagnetic radiation  b) Recoil momentum
  c) **Recoil energy of the nucleus**  d) Radioactive source

19. Most commonly used isotopes in Mossbauer spectroscopy is
  a) $U^{235}$  b) $\mathbf{Sn^{119}}$  c) $I^{131}$  d) $Fe^{35}$

20. Isomer shift is denoted by
  a) **δ**  b) γ  c) λ  d) η

17. Quadrupole interaction is related to
  a) S-electron density  b) nuclear energy level
  c) **Symmetry of electron cloud**  d) Selection rule

18. Isomer shift is related to
a) **S-electron density**  b) nuclear energy level
c) symmetry of electron cloud  d) Selection rule

19. Example for ferromagnetic and antiferro magnetic substance
a) Co and Cu  b) **Mn and Cr**  c) Ni and I  d)K and Mn

20. The shift of the resonance curve from zero velocity is termed as
a) quadrupole interaction  b)nuclear-Zeeman splitting
c)Doppler shift  d) **Isomer shift**

17. Who have investigated the magnetic moments in metals by Mossbauer effect ?
  a) Johnson  b) Lang and marshall  c)**Hufner and steiner**  d)Zavoisky

18. Mossbauer data for a large number of biochemical have actually been compiled by
  a) Jhonson  b) **Bhide**  c) Hufner and Steiner  d) Lang and marshall

19. Mossbauer data for a large number of biochemical have actually been compiled by bhide in………….
  a) **1973**  b) 1975  c) 1985  d) 1978

20. The value of β is

a) β = **0.9723 x 10$^{-20}$**      b) β=0.6723 x 10$^{-22}$

c) β =0.9723 x 10$^{-22}$      d) β =0.6723 x 10$^{-20}$

17. Mossbauer effect is also related with resonance fluorescence of---
    a) beta rays       b) alpha rays       c) **gamma rays**       d) X-rays

18. Which one is not used as radioactive isotopes for Mossbauer Effect?
    a) Fe$^{57}$       b) Zn$^{67}$       c) Sn$^{119}$       d) **P$^{31}$**

19. Hufner and Steiner have investigated the magnetic moments in………. By Mossbauer Effect
    a) Metals       b) rocks       c) woods       d) dust

20. Who have prepared spin orientation diagram in rare earth cubic compounds
    a) Hufner and Steiner       b) **Atzmony and Dariel**
    c) Johnson       d) Muir

17. In spectroscopy cm-1 is also known as
    a) Candela       b) **Kayser**       c) Lux       d)Lumen

18. The resonance gamma ray of 67Zn has a width at half height of only
    a) **4.8 x 10$^{-11}$ ev**       b) 4.2x 10$^{-12}$ ev       c) 4.4 x 10$^{-11}$ ev       d) 4.6 x 10$^{-11}$ ev

19. Who demonstrated the resonance absorption in iredium by a different system?
    a) **R.L.Mossbauer**       b) Moon       c) Johnson       d) Lang and marshall

20. Benzene in proton NMR spectroscopy gives
    a) no signal       b) **only one signal**       c) 2 signal       d) six signal

## 8MARKS QUESTION

1. Calculate the $\lambda_{max}$ of the following compounds?.



a.      b.      c.



d.
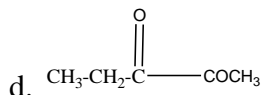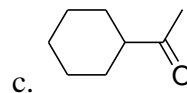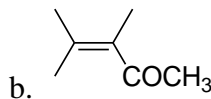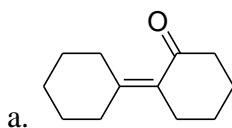
2. Write notes on types of bands in UV?

3. How will you detect the following types of compounds by infra-red spectroscopy?

a. $\diagdown C=C-C=C \diagup$
b. $\diagup C=C \diagdown$ (with H, H)
c. $C=C$ (with H, H)
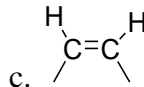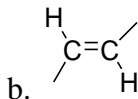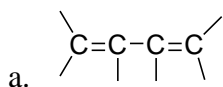
4. Discuss in detail the various factors that influence the vibrational frequency of a particular group. Give examples.

5. (i) Give the probable chemical shift values to the various kinds of protons in the compound, $CH_2=CH-C=CH_2$ with respect to TMS as the standard.

(ii). A hydrocarbon containing 90.9% carbon shows the following four signals:

1. Unsymmetrical multiple = $2.82\tau$ (5H)

2. Triplet 0.9 ppm (2H)

3. Triplet 1.15 ppm (2H)

4. Singlet 1.4 ppm (3H)

What is the structure of the compound?

(a) Explain the applications of Mossbauer spectroscopy.

6. What are the applications of mass spectroscopy?

7. a. How would you distinguish between Ethylamine and triethylamine on the basis of mass spectroscopy?

8. Explain the instrumentation of Mossbauer spectroscopy.

9. (i) Give the probable ppm values to the various kinds of protons in the compound,

$CH_2=CH-C=CH_2$ with respect to TMS as the standard.

(ii). A hydrocarbon containing 90.9% carbon shows the following four signals:

1. Unsymmetrical multiplet = $2.82\tau$ (5H)

2. Triplet 0.9ppm (2H)

3. Triplet 1.15ppm (2H)

4. Singlet 1.4ppm (3H)

What is the structure of the compound?

10. Illustrate Mossbauer effect and explain with suitable example?

11. Write a note on Moss Bauer spectroscopy principles, Isomer shift and Quadra pole Interaction.

**KARPAGAM ACADEMY OF HIGHER EDUCATION**
**COIMBATORE-641021**
**(For the candidates admitted on 2015 onwards)**
**DEPARTMENT OF CHEMISTRY**
**I - SEMESTER**
**ORGANIC CHEMISTRY**

**OBJECTIVE TYPE QUESTIONS( EACH QUESTION CARRY ONE MARK)**

Unit-5 Mossbauer Spectroscopy and spectral problems (17CHP104)

| S.No | Questions | Option a | Option b | Option c | Option d | Answer |
|---|---|---|---|---|---|---|
| 1 | The energies of the emitted $\gamma$-ray is | a) 10 to 150 kev | b)10 to 100 kev | c)10 to 200 kev | d)10 to 175 kev | b)10 to 100 kev |
| 2 | The massbauer effect is based on | a)electromagnetic radiation | b)recoil momentum | c)recoil energy of the nucleus | d)radioactive source | c)recoil energy of the nucleus |
| 3 | The most commonly used isotopes in mossbauer spectroscopy is | a)$U^{235}$ | b)$Sn^{119}$ | c)$I^{131}$ | d)$Fe^{35}$ | b)$Sn^{119}$ |
| 4 | Isomer shift is denoted by | a) $\delta$ | b) $\gamma$ | c) $\lambda$ | d)$\eta$ | a) $\delta$ |
| 5 | Unit of isomer shift is | a) $mms^2$ | b) $mm^{-1}s^3$ | c) $mms^{-1}$ | d) mms | c) $mms^{-1}$ |
| 6 | Mossbouer effect increases as the temperature | a)decreases | b) increases | c)decreases with increases | d)remains constant | a)decreases |
| 7 | Which type of absorber used in $Fe^{57}$ | a)Barium Stannate | b)sodium nitroprusside | c)potassium ferrocyanide | d)Ferrous ammonium sulphate | b)sodium nitroprusside |
| 8 | Which type of absorber used in $Sn^{119}$ | a)Barium Stannate | b)sodium nitroprusside | c)potassium ferrocyanide | d)Ferrous ammonium sulphate | a)Barium Stannate |
| 9 | Quadrupole interaction is related to | a)S-electron density | b)nuclear energy level | c)symmetry of electron cloud | d)Selection rule | c)symmetry of electron cloud |
| 10 | Isomer shift is related to | a)S-electron density | b)nuclear energy level | c)symmetry of electron cloud | d)Selection rule | a)S-electron density |
| 11 | Example for ferromagnetic and antiferro magnetic substance | a)Co and Cu | b)Mn and Cr | c)Ni and I | d)K and Mn | b)Mn and Cr |
| 12 | The shift of the resonance curve from zero velocity is termed as | a)quadrupole interaction | b)nuclear-zeeman splitting | c)Doppler shift | d)isomer shift | d)isomer shift |
| 13 | The quadrupole moment is denoted by | a)eQ | b)Eq | c)Ea | d)Qe | a)eQ |
| 14 | The field gradient is denoted by | a)S | b)q | c)r | d)e | b)q |
| 15 | The unit of quadrupole moment is | a)$cm^{-1}$ | b)cm | c)$cm^2$ | d)$cm^{-2}$ | c)$cm^2$ |
| 16 | Mossbauer work on biological molecule has also been carried out on | Iron sulphur proteins | Iron-phosporous proteins | iron manganees proptein | Iron magnesium protein | Iron sulphur proteins |
| 17 | Who made the first systematic study of biological molecules with these proteins using mossbauer effect? | Lang and marshall | Jhonson | Roberts | Shenoy | Lang and marshall |
| 18 | Who have used mossbauer effect in the study of iron-sulphur proteins? | Lang and marshall | Jhonson | c)Owen | d)Zavoisky | Jhonson |
| 19 | Who have investigated the magnetic moments in metals by mossbauer effect? | Jhonson | Lang and marshall | Hufner and steiner | d)Zavoisky | Hufner and steiner |
| 20 | Mossbauer data for a large number of biochemicals have actually been compiled by | Jhonson | Bhide | Hufner and steiner | Lang and marshall | Bhide |

| # | Question | a | b | c | d | Answer |
|---|---|---|---|---|---|---|
| 21 | Mossbauer data for a large number of biochemicals have actually been compiled by bhide in…………. | 1973 | 1975 | 1985 | 1978 | 1973 |
| 22 | The value of β is | a) $\beta = 0.9723 \times 10^{-20}$ | b) $\beta = 0.6723 \times 10^{-22}$ | c) $\beta = 0.9723 \times 10^{-22}$ | d) $\beta = 0.6723 \times 10^{-20}$ | a) $\beta = 0.9723 \times 10^{-20}$ |
| 23 | Unit of Bohr magneton is | a) $erg/gauss^4$ | b) $erg/gauss^2$ | c) $erg/gauss$ | d) $erg/gauss^3$ | c) $erg/gauss$ |
| 24 | The first measurements of the mossbauer spectrum of 57Fe in haemin were reported by………. | Gnoser | Jhonson | Bhide | Lang and marshall | Gnoser |
| 25 | The first measurements of the mossbauer spectrum of 57Fe in haemin were reported by gnoser in……………. | 1962 | 1965 | 1982 | 1972 | 1962 |
| 26 | The recoilless fraction of gamma-rays emitted from a source imbedded in a solid lattice is called……………. | Lamb Mossbauer Factor | Chemical shift | Resonance | Crompton effect | Lamb Mossbauer Factor |
| 27 | The Debye temperature QD of the crystal structure is ---- | Small | remains constant | high | medium | high |
| 28 | Isomer shift in the mossbauer spectra reflects differences in the ----------- density around the emitterand absorber nuclei. | s-electron | p-electron | d-electron | f-electron | s-electron |
| 29 | Isomer shift------as the s-electron densityandhence the oxidation state----- | decreases, increases | increases,increases | decreases,decreases | increases,decreases | decreases, increases |
| 30 | Unit of hyperfine coupling constant is | a) tesla | b) $tesla^2$ | c) $tesla^3$ | d) $tesla^4$ | a) tesla |
| 31 | Who has studied various phase transitions through mossbauer effect | Shenoy | Roberts | Johnson | Greenwood | Shenoy |
| 32 | Mossbauer effect has been used to study the | effect of temperature | effect of pH | effect of concentration | effect of pressure | effect of temperature |
| 33 | The nitroxide molecules bound to macromolecules are called | a)spin free | b)spin resonance | c)spin tables | d)spin paired | c)spin tables |
| 34 | Commonly used nitroxide is | a)TEMPLO | b)TEMPOL | c)TEMMOL | d)TEPPOL | b)TEMPOL |
| 35 | The Droppler energy shift | V/c | V/e | C/V | e/V | V/c |
| 36 | In copper protein complex, copper is | a)monovalent | b)divalent | c)trivalent | d)tetravalent | b)divalent |
| 37 | In biologically active copper complex, copper is | a)trivalent | b)monovalent | c)divalent | d)tetravalent | b)monovalent |
| 38 | The temperature of the crystal source is | big | constant | small | high | small |
| 39 | ELDOR is | a)electron nuclear double resonance | b)electron double resonance | c)electron nuclear resonance | d)electron spin resonance | b)electron double resonance |
| 40 | ELDOR technique has been used to study the | a)free radical mechanism | b)spin pair mechanism | c)relaxation mechanism | d)proton mechanism | c)relaxation mechanism |
| 41 | Mossbauer effect is also related withresonance fluoresence of--- | a.beta rays | b. alpha rays | c.gammarays | d.X-rays | c.gammarays |
| 42 | Which one is not used as radioactiveisotopes for Massbauer effect? | a. $Fe^{57}$ | b. $Zn^{67}$ | c. $Sn^{119}$ | d. $P^{31}$ | d. $P^{31}$ |

| | | | | | |
|---|---|---|---|---|---|
| 43 | Hufner and Steiner have investigated the magnetic moments in………. By mossbauer effect | Metals | rocks | woods | dust | Metals |
| 44 | Who have preparedspin oreintation diagram in rare earth cubic compounds | Hufner and steiner | Atzmony and Dariel | Johnson | Muir | Atzmony and Dariel |
| 45 | Johnson have used mossbauer effect in the study of --------- | Iron sulphur proteins | Iron-phosporous proteins | iron manganees proptein | Iron magnesium protein | Iron sulphur proteins |
| 46 | Rubredoxins contain only -----iron sulphur group per molecule | one | two | three | four | one |
| 47 | Plant ferredoxins and hydroxylase proteins contain----------iron atoms per molecule | one | two | three | four | two |
| 48 | The source of radiationoperating in microwave region used in EPR spectrometer is | a.Klystron | b.W.lamp | c.hydrogen discharge tube | d.Nernst filament | a.Klystron |
| 49 | In spectroscopy cm-1 is also known as | a.Candela | b. Kayser | cLux | d.Lumen | b. Kayser |
| 50 | The resonancegamma ray of 67Zn has a width at half height of only | 4.8 x 10-11 ev | 4.2x 10-12 ev | 4.4 x 10-11 ev | 4.6 x 10-11 ev | 4.8 x 10-11 ev |
| 51 | Who demonstrated the resonance absorption in iredium by a different system | R.L.Mossbauer | Moon | Johnson | Lang and marshall | R.L.Mossbauer |
| 52 | Benzene in proton NMR spectroscopy gives | a.no signal | b.only one signal | c.2 signal | d. six signal | b.only one signal |
| 53 | An organic compound of molecular formula $C_4H_{10}O$, exhibits in its infra red spectrum a strong band around 1120cm$^{-1}$, but no absorption above 300 cm$^{-1}$. the most likely structure of the compound is | a.Diethyl ether | 1-butanol | c. isopropyl alcohol | d. tertiary alcohol | a.Diethyl ether |
| 54 | Which of the following is the value of λ max for alkenes? | a.175nm | b.170nm | c.165nm | d.185nm | a.175nm |
| 55 | In which of the following regio NMR spectra obtained | a.microwave region | b.Radio wave | c.IR region | d.UV visible | b.Radio wave |
| 56 | The energy of the gamma radiationnshould be in the range | a.10-200KeV | b.20-200KeV | c.100-200KeV | d.1000-2000KeV | a.10-200KeV |
| 57 | Lamb mossbauer factor (f) is given by | a. $f=exp(-E/h\omega_E)$ | b.$f=exp(+e/h\omega_E)$ | c.$f=exp(E/h\omega)$ | c.$f=exp(+E/h\omega)$ | a. $f=exp(-E/h\omega_E)$ |
| 58 | Which of the compounds will have multiplets in their NMR spectra? | a.2-methyl propene | b.2-chloropropene | c.Cyclohexane | d.Methyl chloride | b.2-chloropropene |
| 59 | The quantum number involved in the tracition which gave the line at 169 cm-1 are--- | a. 9 and 10 | b.10 and 11 | c.6 and7 | d.8 and 9 | a. 9 and 10 |
| 60 | The molecular formula of a compound is XY2. If thismolecule shows three IR bands, speculate the structure of the molecule- | a.bent | b.linear | c.bent and linear | d. angle 120° | c.bent and linear |

Reg. No...................                                    [17CHP104]

### KARPAGAM ACADEMY OF HIGHER EDUCATION
(For the candidates admitted from 2017 & onwards)
#### COIMBATORE-21
#### DEPARTMENT OF CHEMISTRY
#### I MSC CHEMISTRY
#### ORGANIC AND INORGANIC SPECTROSCOPY
*Internal test-I*

DATE:                                              SUBJECT CODE: 17CHP104

TIME: 2.00 HRS                                     TOTAL: 50 MARKS

#### PART-A (20 x 1=20 MARKS)

#### ANSWER ALL THE QUESTIONS

1. UV absorption spectroscopy is powerful tool for ----------- analysis
   a)Quantitative      b)Qualitative      c)Physical      d)Environmental

2. As the number of double bonds in conjugation increases, $\lambda_{max}$ --------
   a) Increases      b) Decreases      c) Remains zero      d) Zero

3. The alkyl substitution in an alkene causes a --------- shift
   a)Bathochromic      b)Hypsochromic      c)Isomeric      d)Chromophoric

4. What is the forbidden transition in the following?
   a)$\sigma$-$\sigma^*$      b)n-$\pi^*$      c)n-$\sigma^*$      d)$\pi$-$\pi^*$

5. The wave length of x-rays is in the order of
   a.$10^{-8}$m      b.$10^{-4}$ cm      c. $10^{-23}$ cm      d. 40000A°

6. The wave length of 1000 A° is in the ------ region
   a. far UV      b.Visible      c.near UV      d. IR

7. Of the following radiations, which represents the visible region?
   a. 0-100 nm      b. 100-200 nm      c.200-400 nm      d.400-800 nm

8. Among the following electromagnetic radiations, which has the maximum wavelength?
   a. IR      b.UV      c. radio wave      d. X-ray

9. Which of the following radiation has the maximum energy
   a.UV      b. far IR      c.visible      d. near IR

10. Which of the following colours of visible light is bent most as it passes through a prism?
    a. Yellow      b. Red      c. Blue      d. Green

11. Number of translational, rotational and vibrational degree of freedom in $CO_2$ is respectively

    a)3,2,4      b)3,4,2      c)3,3,3      d)4,3,2

12. The selection rule for a vibrational transition in S.H.O.is
    a)$\Delta v = +1$      b) $\Delta v = +0$      c) $\Delta v=+2$ or -2      d) $\Delta n= 0$

13. Very important requirement for a molecule to show an I.R.spectrum is that
    a) Change in dipole moment      b) Change in force constant
    c) Change in electronic energy      d) Change in wave number

14. The rotational energy of a rigid rotar is
    a)$E_{rot}=h^2/4\pi^2IJ(J+1)$      b.$E_{rot}=h^2/8\pi^2IJ(J+1)$      c. $E_{rot}=h/8\pi IJ(J+1)$
    d.$h/2I(J+1)$

15. An alcohol having the molecular-formula $C_4H_{10}O$, it gives C-O stretching band at1120 cm' will be
    a. 1-butanol      b.2.butanol      c. 2-methyl-2-propanol      d. isobutanol

16. Predict the number of translational, rotational and vibrational degree of freedom in neon--
    a. 3,0,0      b. 3,1,0      c.3,0,1      d.3,1,1

17. Which one of the following is microwave inactive?
    a. HCl      b.HBr      c.$Cl_2$      d. NO

18. The rotational constant (B) of a diatomic molecule is
    a. $h/4\pi^2I$      b.$h^2/4\pi^2I$      c. $h^2/8\pi^2I$      d. $h/8\pi^2I$

19. The degree of degeneracy for a rid rotor in energy level with quantum number J is--
    a.J      b.2J      c.2J-1      d.2J+1

20. The characteristic bond stretching frequency for C-O is about---
    a.$10^4$ cm$^{-1}$      b. $10^3$ cm$^{-1}$      c. $10^3$ cm$^{-1}$      d.$10^2$ cm$^{-1}$

#### PART-B (3 x 2=6 MARKS)

#### ANSWER ALL THE QUESTIONS

21. Define the term chromophore.

22. How will you distinguish between an aliphatic and an aromatic compound by using IR spectroscopy?

23.What is meant by the term chemical shift?

#### PART-C (3 x 8=24 MARKS)

#### ANSWER ALL THE QUESTIONS

24. (a). (i)Explain the electronic transitions involved in UV spectroscopy?

   (ii). Explain the absorption laws in detail.

Reg. No………………. [17CHP104]

**KARPAGAM ACADEMY OF HIGHER EDUCATION**
**(For the candidates admitted from 2017 & onwards)**
**COIMBATORE-21**
**DEPARTMENT OF CHEMISTRY**
**I MSC CHEMISTRY**
**ORGANIC AND INORGANIC SPECTROSCOPY**
***Internal test-I***

 DATE: SUBJECT CODE: 17CHP104

TIME: 2.00 HRS TOTAL: 50 MARKS

***Answer key***


**PART-A (20 x 1=20 MARKS)**


1. b)Qualitative

2. a)   Increases

3. a)Bathochromic

4. b)n-π*

5. b)$10^{-8}$ cm

6. a). far UV

7.d) 400-800nm

8. c) radiowave

9. a) UV

10. c) blue

11. a)3,2,4

12. a)$\Delta v = +1$

13. a) Change in dipole moment

14. b.$E_{rot}$-=$h^2$/8 л$^2$IJ(J+1)

15. b) 2-butanol

16.a) 3,0,0

17. c) $Cl_2$

18. d. $h/8\pi^2 I$

19. d) $2J+1$

20. c. $10^3$ cm$^{-1}$

## PART-B (3 x 2=6 MARKS)

## ANSWER ALL THE QUESTIONS

21. Define the term chromophore.
A chromophore is the part of a molecule responsible for its color. The color that is seen by our eyes is the one not absorbed within a certain wavelength spectrum of visible light. The chromophore is a region in the molecule where the energy difference between two separate molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophore can thus be absorbed by exciting an electron from its ground state into an excited state.

22. How will you distinguish between an aliphatic and an aromatic compound by IR spectroscopy?
In the aliphatic compounds C-H stretching absorption frequencies appeared at 2800-2950cm$^{-1}$, but in the aromatic C-H stretching absorption freuqncies appeared at 3000-3100 cm$^{-1}$.

23. What is meant by the term chemical shift?

Chemical shift $\delta$ is usually expressed in parts per million (ppm) by frequency, because it is

calculated from:       $\delta = v_{sample} - v_{ref} / v_{ref}$

where $v_{sample}$ is the absolute resonance frequency of the sample and $v_{ref}$ is the absolute resonance frequency of a standard reference compound, measured in the same applied magnetic field $B_0$. Since the numerator is usually expressed in hertz, and the denominator in megahertz, $\delta$ is expressed in ppm.

The detected frequencies (in Hz) for $^1$H, $^{13}$C, and $^{29}$Si nuclei are usually referenced against TMS (tetramethylsilane) or DSS, which by the definition above have a chemical shift of zero if chosen as the reference. Other standard materials are used for setting the chemical shift for other nuclei.

## PART-C (3 x 8=24 MARKS)

## ANSWER ALL THE QUESTIONS

**24.** (a). (i)Explain the electronic transitions involved in UV spectroscopy?

The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole.

Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.

The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy". A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an excited state.When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.

Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way

   (ii). Explain the absorption laws in detail.

**Beer's Law** (**Beer**-Lambert **Law**): The amount of energy absorbed or transmitted by a solution is proportional to the solution's molar absorptivity and the concentration of solute. ... A demonstration of **Beer's Law**.

Here is an example of directly using the **Beer's Law**Equation (Absorbance = e L c) when you were given the molar absorptivity constant (or molar extinction coefficient). In this equation, e is

the molar extinction coefficient. L is the path length of the cell holder. c is the concentration of the solution.
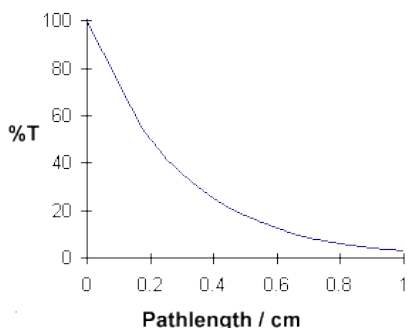


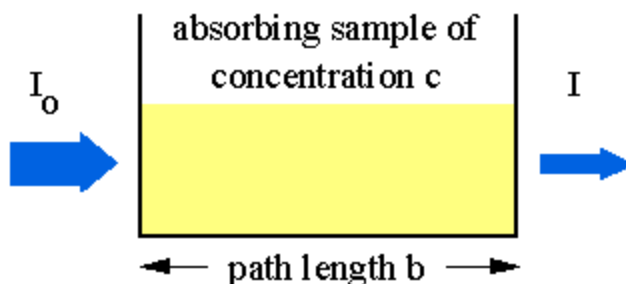**Lambert's law** stated that absorbance of a material sample is directly proportional to its thickness (path length). Much later, August Beer discovered another attenuation relation in 1852. Beer's **law** stated that absorbance is proportional to the concentrations of the attenuating species in the material sample.



The Beer-Lambert law can be derived from an approximation for the absorption coefficient for a molecule by approximating the molecule by an opaque disk whose cross-sectional area, $\sigma$, represents the effective area seen by a photon of frequency $w$. If the frequency of the light is far from resonance, the area is approximately 0, and if $w$ is close to resonance the area is a maximum. Taking an infinitesimal slab, dz, of sample:
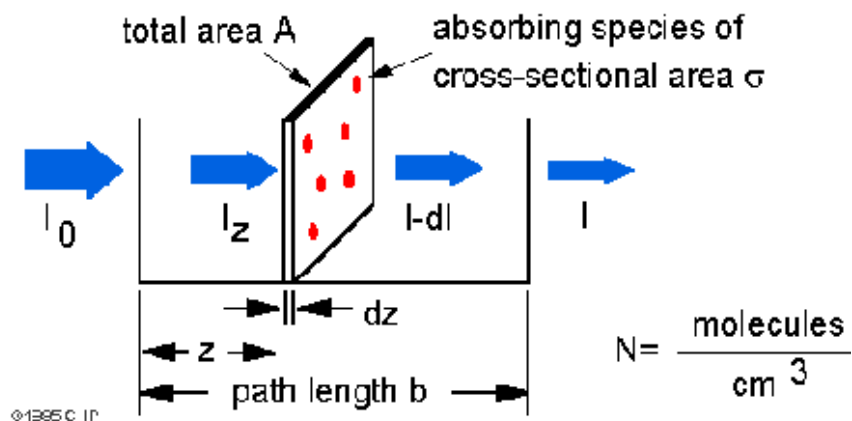
$I_o$ is the intensity entering the sample at z=0, $I_z$ is the intensity entering the infinitesimal slab at z, dI is the intensity absorbed in the slab, and I is the intensity of light leaving the sample. Then, the total opaque area on the slab due to the absorbers is $\sigma * N * A * dz$. Then, the fraction of photons absorbed will be $\sigma * N * A * dz / A$ so,

$dI / I_z = - \sigma * N * dz$

Integrating this equation from z = 0 to z = b gives:

$\ln(I) - \ln(I_o) = - \sigma * N * b$

or $- \ln(I / I_o) = \sigma * N * b$.

Since N (molecules/cm$^3$) * (1 mole / 6.023x10$^{23}$ molecules) * 1000 cm$^3$ / liter = c (moles/liter) and 2.303 * log(x) = ln(x) then

$- \log(I / I_o) = \sigma * (6.023x10^{20} / 2.303) * c * b$

$- \log(I / I_o) = A = \varepsilon * b * c$

where $\varepsilon = \sigma * (6.023x10^{20} / 2.303) = \sigma * 2.61x10^{20}$

Typical cross-sections and molar absorptivities are:

|  | $\sigma$ (cm$^2$) | $\varepsilon$ (M$^{-1}$ cm$^{-1}$) |
|---|---|---|
| absorption - atoms | 10$^{-12}$ | 3x10$^8$ |
| molecules | 10$^{-16}$ | 3x10$^4$ |
| infrared | 10$^{-19}$ | 3x10 |
| Raman scattering | 10$^{-29}$ | 3x10$^{-9}$ |

**Limitations of the Beer-Lambert law**
The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

- deviations in absorptivity coefficients at ***high concentrations (>0.01M)*** due to electrostatic interactions between molecules in close proximity
- **scattering of light due to particulates** in the sample
- **fluoresecence or phosphorescence** of the sample
- changes in refractive index at high analyte concentration
- shifts in chemical equilibria as a function of concentration
- non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
- stray light

(OR)

(b). Explain the various parts and functions of a UV-visible spectrophotometer

**Introduction**

Have a look at this schematic diagram of a double-beam UV-Vis. spectrophotometer;
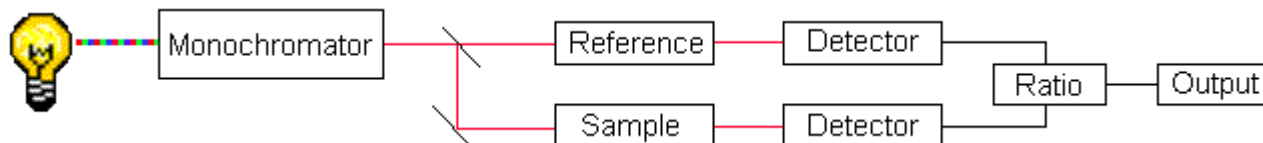


Instruments for measuring the absorption of U.V. or visible radiation are made up of the following components;

1. Sources (UV and visible)
2. Wavelength selector (monochromator)
3. Sample containers
4. Detector
5. Signal processor and readout

Each of these components will be considered in turn.

**Instrumental components**

*Sources of UV radiation*

It is important that the power of the radiation source does not change abruptly over it's wavelength range.

The electrical excitation of deuterium or hydrogen at low pressure produces a continuous UV spectrum. The mechanism for this involves formation of an excited molecular species, which breaks up to give two atomic species and an ultraviolet photon. This can be shown as;

$$D_2 + \text{electrical energy} \circledR D_2^* \circledR D' + D'' + h\nu$$
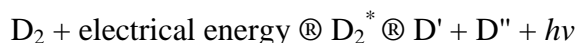
Both deuterium and hydrogen lamps emit radiation in the range 160 - 375 nm. Quartz windows must be used in these lamps, and quartz cuvettes must be used, because glass absorbs radiation of wavelengths less than 350 nm.

*Sources of visible radiation*

The tungsten filament lamp is commonly employed as a source of visible light. This type of lamp is used in the wavelength range of 350 - 2500 nm. The energy emitted by a tungsten filament lamp is proportional to the fourth power of the operating voltage. This means that for the energy output to be stable, the voltage to the lamp must be *very* stable indeed. Electronic voltage regulators or constant-voltage transformers are used to ensure this stability.

Tungsten/halogen lamps contain a small amount of iodine in a quartz "envelope" which also contains the tungsten filament. The iodine reacts with gaseous tungsten, formed by sublimation, producing the volatile compound $WI_2$. When molecules of $WI_2$ hit the filament they decompose, redepositing tungsten back on the filament. The lifetime of a tungsten/halogen lamp is approximately double that of an ordinary tungsten filament lamp. Tungsten/halogen lamps are very efficient, and their output extends well into the ultra-violet. They are used in many modern spectrophotometers.

*Wavelength selector (monochromator)*
All monochromators contain the following component parts;

- An entrance slit
- A collimating lens
- A dispersing device (usually a prism or a grating)
- A focusing lens
- An exit slit

Polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit.

**Czerney-Turner grating monochromator**
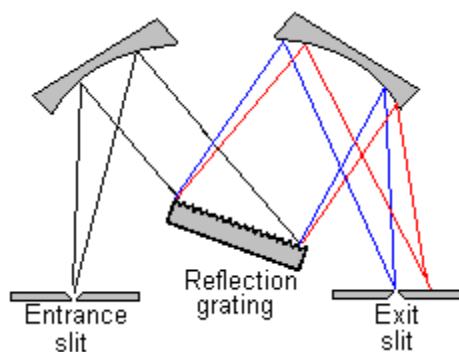


*Cuvettes*

The containers for the sample and reference solution must be transparent to the radiation which will pass through them. Quartz or fused silica cuvettes are required for spectroscopy in the UV region. These cells are also transparent in the visible region. Silicate glasses can be used for the manufacture of cuvettes for use between 350 and 2000 nm.

*Detectors*

**The photomultiplier tube** is a commonly used detector in UV-Vis spectroscopy. It consists of a *photoemissive cathode* (a cathode which emits electrons when struck by photons of radiation), several *dynodes*(which emit several electrons for each electron striking them) and an *anode*.

A photon of radiation entering the tube strikes the cathode, causing the emission of several electrons. These electrons are accelerated towards the first dynode (which is 90V more positive than the cathode). The electrons strike the first dynode, causing the emission of several electrons for each incident electron. These electrons are then accelerated towards the second dynode, to produce more electrons which are accelerated towards dynode three and so on. Eventually, the electrons are collected at the anode. By this time, each original photon has produced $10^6$ - $10^7$ electrons. The resulting current is amplified and measured.

Photomultipliers are very sensitive to UV and visible radiation. They have fast response times. Intense light damages photomultipliers; they are limited to measuring low power radiation.

**Cross section of a photomultiplier tube**
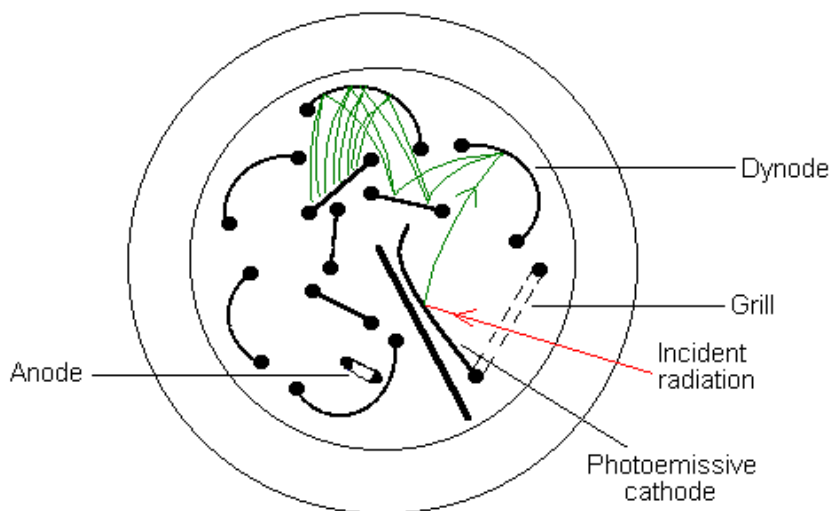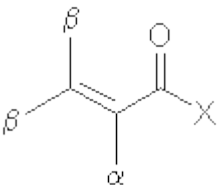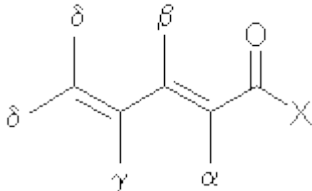


**The linear photodiode array** is an example of a *multichannel photon detector*. These detectors are capable of measuring all elements of a beam of dispersed radiation simultaneously.

A linear photodiode array comprises many small silicon photodiodes formed on a single silicon chip. There can be between 64 to 4096 sensor elements on a chip, the most common being 1024 photodiodes. For each diode, there is also a storage capacitor and a switch. The individual diode-capacitor circuits can be sequentially scanned.

In use, the photodiode array is positioned at the focal plane of the monochromator (after the dispersing element) such that the spectrum falls on the diode array. They are useful for recording UV-Vis. absorption spectra of samples that are rapidly passing through a sample flow cell, such as in an HPLC detector.

**Charge-Coupled Devices (CCDs)** are similar to diode array detectors, but instead of diodes, they consist of an array of photocapacitors.

25. (a). (i)Explain the Woodward-Fischer rules for calculating absorption maximum for α, β unsaturated carbonyl compounds with examples.
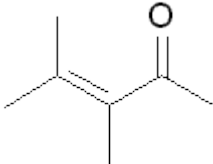
| Woodward's Rules for Conjugated Carbonyl Compounds | | |
|---|---|---|
|  |  | |
| Base values: | | |
| | X = R | |
| | Six-membered ring or acyclic parent enone | $\lambda$=215 nm |
| | Five-membered ring parent enone | $\lambda$=202 nm |
| | X = H | $\lambda$=208 nm |
| | X = OH, OR | $\lambda$=195 nm |
| Increments for: | | |
| | Double bond extending conjugation | 30 |
| | Exocyclic double bond | 5 |
| | Endocyclic double bond in a 5- or 7-membered ring for X = OH, OR | 5 |
| | Homocyclic diene component | 39 |
| | Alkyl substituent or ring residue | $\alpha$ | 10 |

| | | β | 12 |
|---|---|---|---|
| | | γ or higher | 18 |
| Polar groupings: | | | |
| | -OH | α | 35 |
| | | β | 30 |
| | | δ | 50 |
| | -OC(O)CH$_3$ | α,β,γ,δ | 6 |
| | -OCH$_3$ | α | 35 |
| | | β | 30 |
| | | γ | 17 |
| | | δ | 31 |
| | -Cl | α | 15 |
| | | β,γ,δ | 12 |
| | -Br | β | 30 |
| | | α,γ,δ | 25 |
| | -NR$_2$ | β | 95 |
| Solvent correction[*]: | | | variable |
| | | λ$_{max}$ (calc'd) | total |

| Solvent | $\lambda_{max}$ shift (nm) |
|---|---|
| water | + 8 |
| chloroform | - 1 |
| ether | - 7 |
| cyclohexane | - 11 |
| dioxane | - 5 |
| hexane | - 11 |
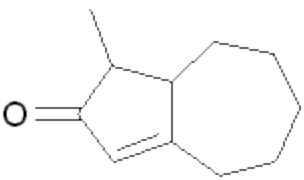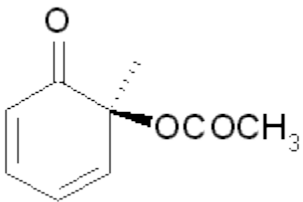
**Example 1:**



| Acyclic enone: | | 215 nm |
|---|---|---|
| $\alpha$-Alkyl groups or ring residues: | | 10 nm |
| $\beta$-Alkyl groups or ring residues: | 2 x 12 = | <u>24 nm</u> |
| Calculated: | | 249 nm |
| Observed: | | 249 nm |
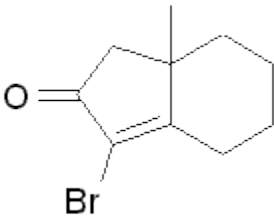
**Example 2:**



| Five-membered ring parent enone: | | 202 nm |
|---|---|---|
| β-Alkyl groups or ring residues: | 2 x 12 = | 24 nm |
| Exocyclic double bond: | | 5 nm |
| Calculated: | | 231 nm |
| Observed: | | 226 nm |
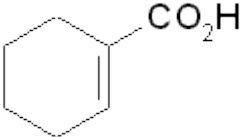
**Example 3:**



| Six-membered ring or alicyclic parent enone: | | 215 nm |
|---|---|---|
| Extended conjugation: | | 30 nm |
| Homocyclic diene component: | | 39 nm |
| δ-Alkyl groups or ring residues: | | 18 nm |
| Calculated: | | 302 nm |
| Observed: | | 300 nm |
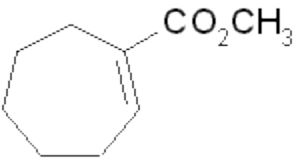
**Example 4:**



| Five-membered ring parent enone: | | 202 nm |
|---|---|---|
| $\alpha$-Br: | | 25 nm |
| $\beta$-Alkyl groups or ring residues: | 2 x 12 = | 24 nm |
| Exocyclic double bond: | | <u>5 nm</u> |
| Calculated: | | 256 nm |
| Observed: | | 251 nm |
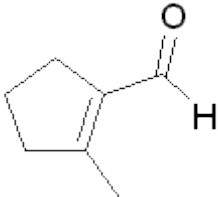
**Example 5:**



| Carboxylic acid: | | 195 nm |
|---|---|---|
| $\alpha$-Alkyl groups or ring residues: | | 10 nm |
| $\beta$-Alkyl groups or ring residues: | | <u>12 nm</u> |
| Calculated: | | 217 nm |
| Observed: | | 217 nm |
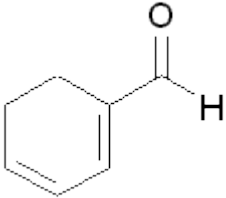
**Example 6:**



| Ester: | | 195 nm |
|---|---|---|
| $\alpha$-Alkyl groups or ring residues: | | 10 nm |
| $\beta$-Alkyl groups or ring residues: | | 12 nm |
| Endocyclic double bond in 7-membered ring: | | <u>5 nm</u> |
| Calculated: | | 222 nm |
| Observed: | | 222 nm |

**Example 7:**



| Aldehyde: | | 208 nm |
|---|---|---|
| $\alpha$-Alkyl groups or ring residues: | | 10 nm |
| $\beta$-Alkyl groups or ring residues: | 2 x 12 = | <u>24 nm</u> |
| Calculated: | | 242 nm |
| Observed: | | 242 nm |

**Example 8:**



| Aldehyde: | | 208 nm |
|---|---|---|
| Extended conjugation: | | 30 nm |
| Homodiene component: | | 39 nm |
| $\alpha$-Alkyl groups or ring residues: | | 10 nm |
| $\delta$-Alkyl groups or ring residues: | | <u>18 nm</u> |
| Calculated: | | 304 nm |
| Observed: | | 302 nm |

(OR)

(b). How will you distinguish between the following pairs on the basis of IR spectroscopy?

    (i)      Fundamental vibrations and overtones.

Combination bands, overtones, and Fermi resonances are used to help explain and assign peaks in vibrational spectra that do not correspond with known fundamental vibrations. Combination bands and overtones generally have lower intensities than the fundamentals, and Fermi resonance causes a spilt and shift in intensity of peaks with similar energies and identical symmetries.

Fundamental vibrational frequencies of a molecule corresponds to transition from $v=0$ to $v=1$. For a non-linear molecule there will by 3N-6 (where N is the number of atoms) number

vibrations. The same holds true for linear molecules, however the equations 3N-5 is used, because a linear molecule has one less rotational degrees of freedom. (For a more detailed

explanation see: Normal Modes). Figure 1 shows a diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers $v$ represent the potenital energy for the harmonic (quadratic) oscillator. The transition $0\to10\to1$ is fundamental,

transitions $0{\to}n$ $0{\to}n$ $(n{>}1)$ are called overtones, and transitions $1{\to}n$ $1{\to}n$ $(n{<}1)$ are called hot transitions (hot bands).
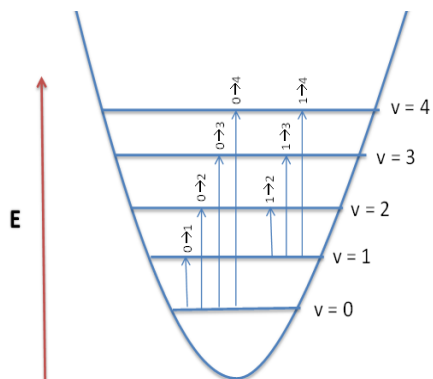


*Figure 1: Potential energy diagram for a vibrating diatomic molecule.*

(ii)    Fermi resonance and overtones

Fermi resonance results in the splitting of two vibrational bands that have nearly the same energy and symmetry in both IR and Raman spectroscopies. The two bands are usually a fundamental vibration and either an overtone or combination band. The wavefunctions for the two resonant vibrations mix according to the harmonic oscillator approximation, and the result is a shift in frequency and a change in intensity in the spectrum. As a result, two strong bands are observed in the spectrum, instead of the expected strong and weak bands. It is not possible to determine the contribution from each vibration because of the resulting mixed wave function.

Overtones occur when a vibrational mode is excited from $v{=}0$ $v{=}0$ to $v{=}2$ $v{=}2$, which is called the first overtone, or $v{=}0$ $v{=}0$ to $v{=}3$ $v{=}3$, the second overtone. The fundamental transitions, $v{=}\pm1$, are the most commonly occurring, and the probability of overtones rapid decreases as $v{=}\pm n$ $v{=}\pm n$ increases. Based on the harmonic oscillator approximation, the energy of the overtone transition will be about n times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

(iii)    Intermolecular and intramolecular hydrogen bonding.

Intramolecular H-Bonding, Intermolecular H-Bonding only occurs if the two molecules are in vicinity (Closer to each other). Let us consider the case of ortho and para nitrophenol. The ortho isomer will have intramolecuar H-bond whereas the para isomer will have intermolecular H-bond.

o-nitrophenol
Intramolecular

p-nitrophenol
Intermolecular
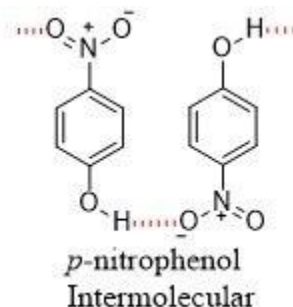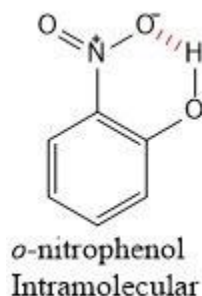
Initially if you record an IR spectum of the two compounds they will appear almost identical. To distinguish between the two you need to disrupt the H-bonding in either of the two which will lead to a change in the IR stretching frequency of the OH group. Since it is not easy to disrupt an intramolecular H-Bond you should focus on the intermolecular H-Bond. Forcing solvent molecules between the two molecules usually does the job (*i.e* remove them from each others vicinity). If you prepare a dilute solution of the para nitrophenol in a solvent (CCl4, aprotic and non oxygenated) the intermolecular H-bonding breaks leading to a change in the IR spectra. On the other hand the IR spectra of ortho nitrophenol remains unchanged in dilute solutions as the dilution does not disrupt the intramolecular H-Bonding.

26.(a). Describe with examples the various factors which affect the magnitude of the chemical shift in NMR spectra.

*Influencing factors on chemical shifts*

*Electronegativity*

Electronegative atoms present in molecules tend to draw the electron density towards themselves and deshield the nucleus. An increase in electronegativity of the surrounding groups will result in decrease of the electron density and lead to an increase in chemical shift value due to the shielding of the nucleus.

*Anisotropy*

Anisotropy refers to the property of the molecule where a part of the molecule opposes the applied field and the other part reinforces the applied field. Chemical shifts are dependent on the orientation of neighbouring bonds in particular the $\pi$ bonds. Examples of nucleus showing chemical shifts due to $\pi$ bonds are aromatics, alkenes and alkynes. Such anisotropic shifts are useful in characterizing the presence of aromatics or other conjugated structures in molecules.

*Hydrogen bonding*

Hydrogen bonding results from the presence of electronegative atoms in neighbourhood of protons .The resulting deshielding leads to higher values of chemical shifts. This confirms the presence of hydrogen bonding in the molecules.

Chemical shifts of NMR active protons and other nuclei serve to provide a wealth of structural information on molecules.

(OR)

(b). Explain the applications of IR spectroscopy in organic compounds?

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and dynamic measurement. It is also used in forensic analysis in both criminal and civil cases, enabling identification of polymer degradation for example.

The instruments are now small, and can be transported, even for use in field trials. With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment). Some instruments will also automatically tell you what substance is being measured from a store of thousands of reference spectra held in storage.

By measuring at a specific frequency over time, changes in the character or quantity of a particular bond can be measured. This is especially useful in measuring the degree of polymerization in polymer manufacture. Modern research instruments can take infrared measurements across the whole range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.

Infrared spectroscopy has been highly successful for applications in both organic and inorganic chemistry. Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics: for example, infrared spectroscopy can be applied to semiconductors like silicon, gallium arsenide, gallium nitride, zinc selenide, amorphous silicon, silicon nitride, etc.

Reg. No...............

[17CHP104]

## KARPAGAM ACADEMY OF HIGHER EDUCATION
(For the candidates admitted from 2017 & onwards)
### COIMBATORE-21
### DEPARTMENT OF CHEMISTRY
### MSC DEGREE EXAMINATION-NOVEMBER-2017
### ORGANIC AND INORGANIC SPECTROSCOPY
### INTERNAL TEST-II

DATE:                                     SUBJECT CODE: 17CHP104

TIME: 2.00 HRS                            TOTAL: 50 MARKS

### PART-A (20x1=20 MARKS)
### ANSWER ALL THE QUESTIONS

1. What is precessional motion?
   a) top moves around the vertical        b)moves away the horizontal
   c) top moves away from the vertical     d)moves around the horizontal

2. The gyromagnetic ratio is
   a) 2 pi M/Hi        b) 2C pi M/hI        c) hI/2 pi M        d) hI/ 2C pi M.

3. What is flipping?
   a) Energy transfer within the molecule        b) Energy transfer outside the molecule
   c) Energy transfer from one energy            d) No energy has been transfer

4. Acetone gives
   a) One signal NMR        b) Two signal NMR        c) Three signal NMR
   d) Four signal NMR

5. The relative abundance of the metastable peak m*is often of the order or less compared to the abundance of parent ion
   a)$10^2$        b)$10^{-1}$        c)$10^{-3}$        d)$10^{-5}$

6. Conjugated olefins show ------intense molecular ion peak as compared to the corresponding non-conjugated olefins
   a)less        b)more        c)same        d)poor

7. Double focusing mass spectrometers are capable of attaining much------resolving power than single focusing instruments
   a)higher        b)lower        c)same        d)poor

8. In Mass spectroscopy, molecules are bombarded with a beam of energetic
   a) Neutrons        b) Positrons        c) Electrons        d) Nucleons

9. The intensity of the base peak is taken as
   a) 80        b) 100        c) 87        d) 57

10. The energy required for removing one electron from the neutral parent molecule is usually
    a) 10ev        b) 30ev        c) 70ev        d) 15ev

11. The energy required for the fragmentation of parent ion is
    a) 40ev        b) 100ev        c) 80ev        d) 70ev

12. The energies of the emitted γ-ray is
    a) 10 to 150 kev        b) 10 to 100 kev        c)10 to 200 kev        c 10 to 175 kev

13. The Mossbauer Effect is based on
    a) Electromagnetic radiation        b) Recoil momentum        c) Recoil energy of the nucleus
    d) Radioactive source

14. Most commonly used isotopes in Mossbauer spectroscopy is
    a) $U^{235}$        b) $Sn^{119}$        c) $I^{131}$        d) $Fe^{35}$

15. Isomer shift is denoted by
    a) δ        b) γ        c) λ        d) η

16. Quadrupole interaction is related to
    a)S-electron density        b)nuclear energy level        c)symmetry of electron cloud
    d)Selection rule

17. Isomer shift is related to
    a)S-electron density        b)nuclear energy level        c)symmetry of electron cloud
    d)Selection rule

18. Example for ferromagnetic and antiferro magnetic substance
    a)Co and Cu        b)Mn and Cr        c)Ni and I        d)Fe and Mn

19. The shift of the resonance curve from zero velocity is termed as
    a)quadrupole interaction        b)nuclear-zeeman spliting        c)Doppler shift
    d)isomer shift

20. Mossbauer data for a large number of biochemical's have actually been compiled by Bhide in...........
    a) 1973        b) 1975        c) 1985        d) 978

Reg. No………………. [17CHP104]

**KARPAGAM ACADEMY OF HIGHER EDUCATION**
**(For the candidates admitted from 2017 & onwards)**
**COIMBATORE-21**
**DEPARTMENT OF CHEMISTRY**
**MSC DEGREE EXAMINATION-NOVEMBER-2017**
**ORGANIC AND INORGANIC SPECTROSCOPY**
**INTERNAL TEST-II**

DATE: SUBJECT CODE: 17CHP104

**TIME: 2.00 HRS** **TOTAL: 50 MARKS**

**PART-A (20x1=20 MARKS)**

**ANSWER ALL THE QUESTIONS**

**Answer Key**

**1.** a) top moves around the vertical

**2.** a) 2 pi M/Hi

**3.** a) Energy transfer within the molecule

**4.** a) One signal NMR

**5.** a)$10^{-2}$

**6.** a)less

**7.** b)lower

**8.** c) Electrons

**9.** b) 100

**10.** a) 10ev

**11.** d) 70ev

**12.** b) 10 to 100 kev

**13.** c) Recoil energy of the nucleus

**14.** b) $Sn^{119}$

**15.** a) δ

**16.** c)symmetry of electron cloud

**17.** a)S-electron density

**18.** b)Mn and Cr

**19.** d)isomer shift

**20.** a) 1973


<center>

**PART-B (3X2=6 MARKS)**

**ANSWER ALL THE QUESTIONS**

</center>


21. Why is TMS used as a standard reference in NMR spectroscopy?

TMS has 12 protons which are all equivalent and four carbons, which are also all equivalent. This means that it gives a single, strong signal in the spectrum, which turns out to be outside the range of most other signals, especially from organic compounds.

Although the chemical shift scales are still zeroed at the TMS peak, most spectra are now calibrated against the residual solvent peak. Typically, deuterated solvents such as $CDCl_3CDClX_3$ and DMSODMSO-$d_6dX_6$ are used and these contain a very small amount of undeuterated, or partially deuterated, solvent which produces a peak in hydrogen NMR. In carbon NMR the solvent peak is recognised by its splitting pattern, which is a triplet for $CDCl_3CDClX_3$ and a heptet for DMSODMSO-$d_6dX_6$ and the fact that it always comes at exactly the same place.


22. Write a brief note on the molecular ion peak or the parent ion?

When the vaporised organic sample passes into the ionisation chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the ***molecular ion***

The molecular ion is often given the symbol $\mathbf{M^+}$ or **M⁺** - the dot in this second version represents the fact that somewhere in the ion there will be a single unpaired electron. That's one half of what was originally a pair of electrons - the other half is the electron which was removed in the ionisation process.

The molecular ions tend to be unstable and some of them break into smaller fragments. These fragments produce the familiar stick diagram. Fragmentation is irrelevant to what we are talking about on this page - all we're interested in is the molecular ion.

23. Explain isomer shift.

The shift of the resonance curve from zero velocity is termed as isomer shift.

<center>

**PART-C (3X8=24 MARKS)**

</center>

24. a. (i). Explain first order and non first order NMR spectra with examples.

## First-order splitting pattern

The chemical shift difference in Hertz between coupled protons in Hertz is much larger

than the JJ coupling constant:

$$\Delta vJ \geq 8 \Delta vJ \geq 8$$

Where $\Delta v \Delta v$ is the difference of chemical shift. In other word, the proton is only coupled to other protons that are far away in chemical shift. The spectrum is called *first-order*

*spectrum*. The splitting pattern depends on the magnetic field. The second-order splitting at the lower field can be resolved into first-order splitting pattern at the high field. The first-order splitting pattern is allowed to multiplicity rule (N+1) and Pascal's triangle to determine splitting pattern and intensity distribution.

Example

The note is that structure system is $A_3M_2X_2$. $H_a$ and $H_x$ has the triplet pattern by Hm because of N+1 rule. The signal of Hm is split into six peaks by $H_x$ and $H_a$ (Fig.3) The First order pattern easily is predicted due to separation with equal splitting pattern.
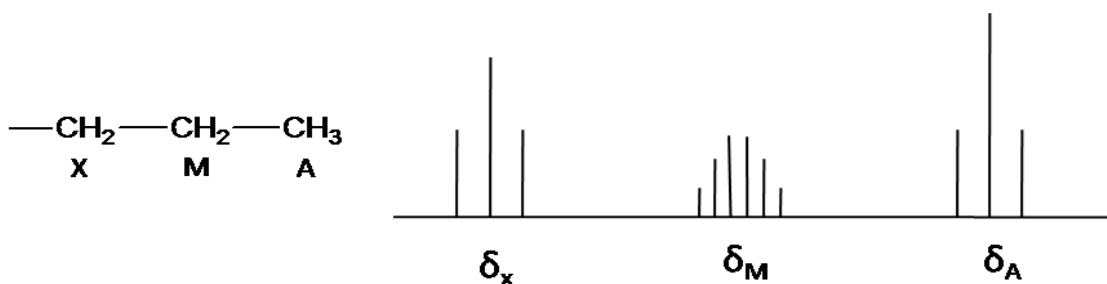


**Figure 3**: An example of splitting pattern

## High-order splitting pattern

High-order splitting pattern takes place when chemical shift difference in hertz is much less or the same that order of magnitude as the j coupling.

$$\frac{\Delta v}{J} \leq 8$$

The second order pattern is observed as leaning of a classical pattern.: the inner peaks are taller and the outer peaks are shorter in case of AB system(Fig 4). This is called the "roof effect."
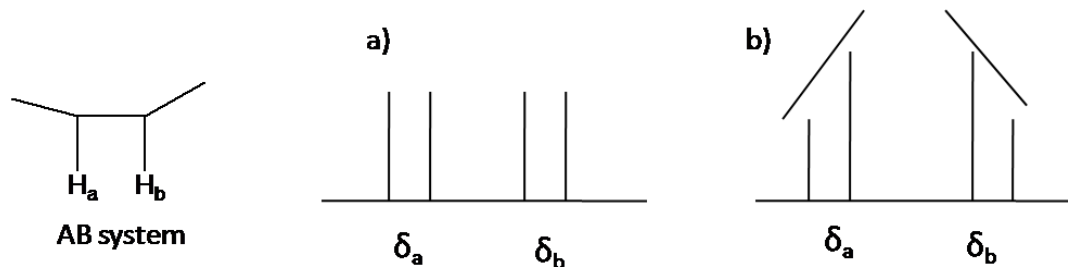


Fig 4. a) first-order pattern and b) second-order pattern of AB system

Here is other system as an example: $A_2B_2$ (Fig 5). The two triplet incline toward each other. Outer lines of the triplet are less than 1in relative area and the inner lines are more than 1. The center lines have relative area 2.
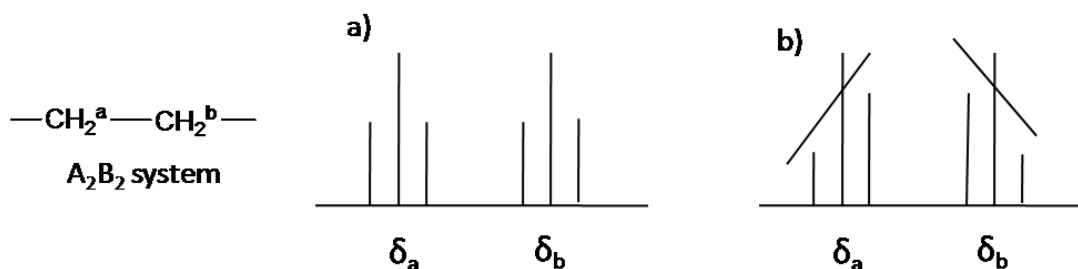


Fig 5. a) first-order pattern and b) second-order pattern of $A_2B_2$ system

(ii). Explain (a) geminal coupling (b) vicinal coupling (c) Long range coupling

*Geminal proton-proton coupling ($^2J_{HH}$)*
Germinal coupling generates through two bonds (Fig 6). Two proton having geminal coupling are not chemically equivalent. This coupling ranges from -20 to 40 Hz. $^2J_{HH}$depends on hybridization of carbon atom and the bond angle and the substituent such as electronegative atoms. When S-character is increased, Geminal coupling constant is increased : $^2J_{sp1} > ^2J_{sp2} > ^2J_{sp3}$ The bond angle(HCH) gives rise to change $^2J_{HH}$ value and depend on the strain of the ring in the cyclic systems. Geminal coupling constant determines ring size. When bond angle is decreased, ring size is decreased so that geminal coupling constant is more positive. If a atom is replace to an electronegative atom, Geminal coupling constant move to positive value.

Vicinal proton-proton coupling ($^3J_{HH}$)

Vicinal coupling occurs though three bonds. The Vicinal coupling is the most useful information of dihedral angle, leading to stereochemistry and conformation of molecules. Vicinal coupling constant always has the positive value and is affected by the dihedral angle (?;HCCH), the valence angle (?; HCC), the bond length of carbon-carbon, and the effects of electronegative atoms. Vicinal coupling constant depending on the dihedral angle (Fig 8) is given by the Karplus equation.

$$^3J = 7.0 - 0.5cos\phi + 4.5cos^2\phi$$

When ? is the $90^o$, vicinal coupling constant is zero. In addition, vicinal coupling constant ranges from 8 to 10 Hz at the and ?=$180^o$, where ?=$0^o$ and ?=$180^o$ means that the coupled protons have cis and trans configuration, respectively.

The valence angle also causes change of $^3J_{HH}$ value. Valence angle is related with ring size. Typically, when the valence angle decreases, the coupling constant reduces. The distance between the carbons atoms gives influences to vicinal coupling constant

The coupling constant increases with the decrease of bond length. Electronegative atoms affect vicinal coupling constants so that electronegative atoms decrease the vicinal coupling constants.

(OR)

b.(i). What are lathaninde shift reagents and chemical shift reagents?

NMR shift reagent

The original application of Eu(fod)$_3$ was for analyzing diastereomeric compounds in NMR spectroscopy. As is typical in paramagnetic NMR spectroscopy, the paramagnetic compound induces additional chemical shift in the protons near any Lewis basic site to which it binds in a molecule. This change helps resolve closely spaced signals by separating the ones from these hydrogens away from others that are not near basic sites but whose normal chemical shift is similar. Only small amounts of shift reagents are used, because otherwise the paramagnetism of the reagent shortens the spin-lattice relaxation times of the nuclei, which causes uncertainty broadening and loss of resolution. The availability of higher magnetic field spectrometers have lowered the demand for NMR shift reagents.

The original shift reagent was Eu(DPM)$_3$, developed by Hinckley. Its structure is similar to EuFOD, but with *tert*-butyl groups in place of heptafluoropropyl substituents. That is, DPM$^-$ is the conjugate base derived from dipivaloylmethane, also known as 2,2,6,6-tetramethylheptane-3,5-dione. The ligand fod$^-$ is more lipophilic and by virtue of the perfluoralkyl substituent, its complexes are more Lewis acidic than those derived from DPM$^-$.

Lewis acid

Eu(fod)$_3$ serves as a Lewis acid catalyst in organic synthesis including stereoselective Diels-Alder and aldol addition reactions. For example, Eu(fod)$_3$ catalyzes the cyclocondensations of substituted dienes with aromatic and aliphatic aldehydes to yield dihydropyrans, with high selectivity for the *endo* product.

(ii). Explain that spin-spin coupling and spin-spin splitting are resonance phenomenon
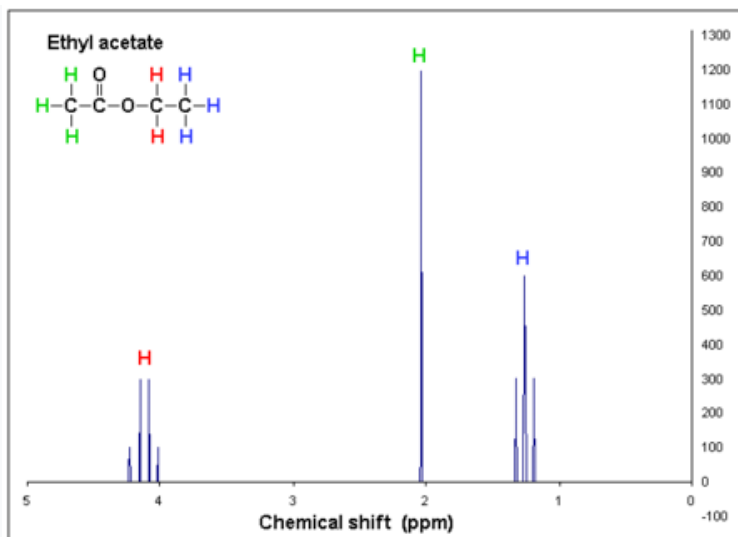


Example $^1$H NMR spectrum (1-dimensional) of ethyl acetate plotted as signal intensity vs. chemical shift. There are three different types of H atoms in ethyl acetate regarding NMR. The hydrogens (H) on the CH$_3$COO- (acetate) group are not coupling with the other H atoms and appear as a singlet, but the -CH$_2$- and -CH$_3$ hydrogens of the ethyl group (-CH$_2$CH$_3$) are coupling with each other, resulting in a quartet and triplet respectively.

In addition to chemical shift, NMR spectra allow structural assignments by virtue of spin-spin coupling (and integrated intensities). Because nuclei themselves possess a small magnetic field, they influence each other, changing the energy and hence frequency of nearby nuclei as they resonate—this is known as spin-spin coupling. The most important type in basic NMR is *scalar coupling*. This interaction between two nuclei occurs through chemical bonds, and can typically be seen up to three bonds away.
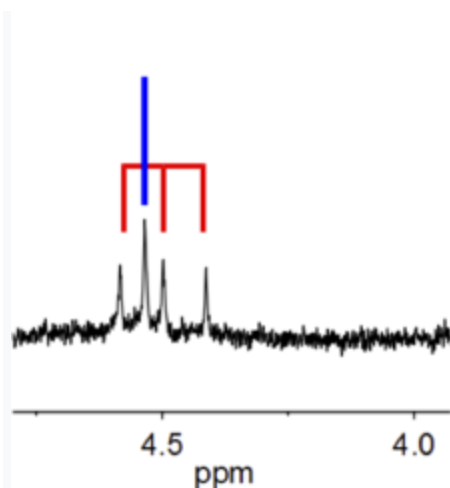
H NMR spectrum of a solution of HD (labeled with red bars) and $H_2$(blue bar). The 1:1:1 triplet for HD arises from heteronuclear (different isotopes) coupling.

The effect of scalar coupling can be understood by examination of a proton which has a signal at 1 ppm. This proton is in a hypothetical molecule where three bonds away exists another proton (in a CH-CH group for instance), the neighbouring group (a magnetic field) causes the signal at 1 ppm to split into two, with one peak being a few hertz higher than 1 ppm and the other peak being the same number of hertz lower than 1 ppm. These peaks each have half the area of the former singletpeak. The magnitude of this splitting (difference in frequency between peaks) is known as the coupling constant. A typical coupling constant value would be 7 Hz.

The coupling constant is independent of magnetic field strength because it is caused by the magnetic field of another nucleus, not the spectrometer magnet. Therefore, it is quoted in hertz(frequency) and not ppm (chemical shift).

In another molecule a proton resonates at 2.5 ppm and that proton would also be split into two by the proton at 1 ppm. Because the magnitude of interaction is the same the splitting would have the same coupling constant 7 Hz apart. The spectrum would have two signals, each being a doublet. Each doublet will have the same area because both doublets are produced by one proton each.

The two doublets at 1 ppm and 2.5 ppm from the fictional molecule CH-CH are now changed into $CH_2$-CH:

- The total area of the 1 ppm $CH_2$ peak will be twice that of the 2.5 ppm CH peak.
- The $CH_2$ peak will be split into a doublet by the CH peak—with one peak at 1 ppm + 3.5 Hz and one at 1 ppm - 3.5 Hz (total splitting or coupling constant is 7 Hz).

In consequence the CH peak at 2.5 ppm will be split *twice* by each proton from the $CH_2$. The first proton will split the peak into two equal intensities and will go from one peak at 2.5 ppm to two peaks, one at 2.5 ppm + 3.5 Hz and the other at 2.5 ppm - 3.5 Hz—each having equal intensities. However these will be split again by the second proton. The frequencies will change accordingly:

- The 2.5 ppm + 3.5 Hz signal will be split into 2.5 ppm + 7 Hz and 2.5 ppm

- The 2.5 ppm - 3.5 Hz signal will be split into 2.5 ppm and 2.5 ppm - 7 Hz

The net result is not a signal consisting of 4 peaks but three: one signal at 7 Hz above 2.5 ppm, two signals occur at 2.5 ppm, and a final one at 7 Hz below 2.5 ppm. The ratio of height between them is 1:2:1. This is known as a triplet and is an indicator that the proton is three-bonds from a $CH_2$ group.

This can be extended to any $CH_n$ group. When the $CH_2$-CH group is changed to $CH_3$-$CH_2$, keeping the chemical shift and coupling constants identical, the following changes are observed:

- The relative areas between the $CH_3$ and $CH_2$ subunits will be 3:2.
- The $CH_3$ is coupled to two protons into a 1:2:1 triplet around 1 ppm.
- The $CH_2$ is coupled to *three* protons.

Something split by three identical protons takes a shape known as a quartet, each peak having relative intensities of 1:3:3:1.

A peak is split by $n$ identical protons into components whose sizes are in the ratio of the $n$th row of Pascal's triangle:

```
n
0  singlet                    1
1  doublet                  1  1
2  triplet                1  2  1
3  quartet              1  3  3  1
4  quintet            1  4  6  4  1
5  sextet           1  5 10 10  5  1
6  septet         1  6 15 20 15  6  1
7  octet        1  7 21 35 35  21 7  1
8  nonet      1  8 28 56 70 56  28 8  1
```

Because the $n$th row has $n+1$ components, this type of splitting is said to follow the "$n+1$ rule": a proton with $n$ neighbors appears as a cluster of $n+1$ peaks.

With 2-methylpropane, $(CH_3)_3CH$, as another example: the CH proton is attached to three identical methyl groups containing a total of 9 identical protons. The C-H signal in the spectrum would be split into ten peaks according to the $(n + 1)$ rule of multiplicity. Below are NMR signals corresponding to several simple multiplets of this type. Note that the outer lines of the nonet (which are only 1/8 as high as those of the second peak) can barely be seen, giving a superficial resemblance to a septet.



triplet n = 2    quartet n = 3    pentet n = 4    sextet n = 5    nonet n = 8
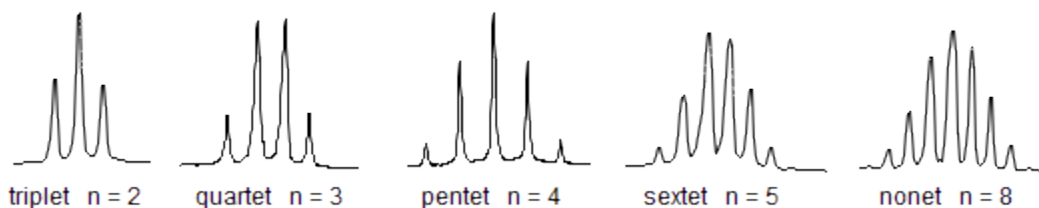
When a proton is coupled to two different protons, then the coupling constants are likely to be different, and instead of a triplet, a doublet of doublets will be seen. Similarly, if a proton is coupled to two other protons of one type, and a third of another type with a different, smaller coupling constant, then a triplet of doublets is seen. In the example below, the triplet coupling constant is larger than the doublet one. By convention the pattern created by the largest coupling constant is indicated first and the splitting patterns of smaller constants are named in turn. In the case below it would be erroneous to refer to the quartet of triplets as a triplet of quartets. The analysis of such multiplets (which can be much more complicated than the ones shown here) provides important clues to the structure of the molecule being studied.



Doublet of doublets          Triplet of doublets          Quartet of triplets
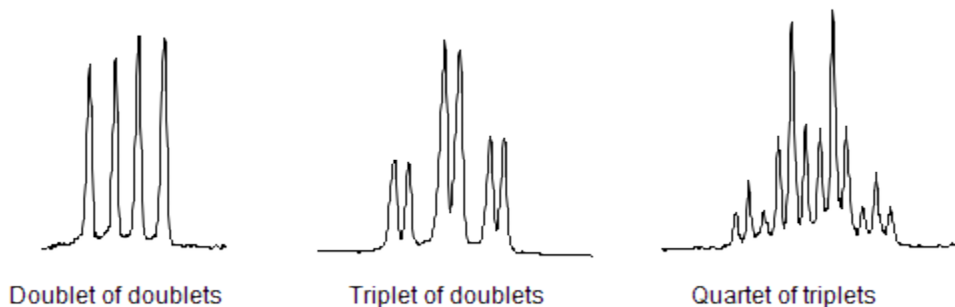
The simple rules for the spin-spin splitting of NMR signals described above apply only if the chemical shifts of the coupling partners are substantially larger than the coupling constant between them. Otherwise there may be more peaks, and the intensities of the individual peaks will be distorted (second-order effects).

25. a. Write notes on

(i). Metastable peaks

The term metastable has been applied to those ions in a mass spectrometer that have just sufficient energy to fragment some time after leaving the ion source but before arriving at the detector. The excess of internal energy imparted to these ions during ionization is sufficient to give them a rate of decomposition such that the latter occurs during the ion *flight-time*. The product ions from such in-flight fragmentation have less than the full kinetic energy originally imparted to the precursor metastable ion when it left the ion source because the initially imparted momentum must be shared between the products of decomposition. As one of these products is itself an ion that is necessarily of smaller mass than its precursor metastable species, it follows that the product ion must have less momentum than the precursor. It is this reduced momentum that leads to the products of metastable ions having an *apparent* mass different from the corresponding normal product ions formed *in the ion source*. The difference is explained more fully below.

To understand the origin and decomposition of metastable ions, it is convenient to consider electron ionization in a conventional double-focussing, magnetic-sector mass spectrometer as depicted in figure 8.1. For a mass spectrometric fragmentation reaction in which an ion $M^+$ of mass $m_1$ yields a fragment ion $A^+$ of mass $m_2$ and a neutral particle N, equation holds:

$$M^+ \rightarrow A^+ + N$$
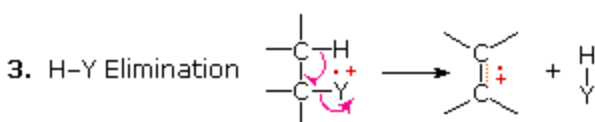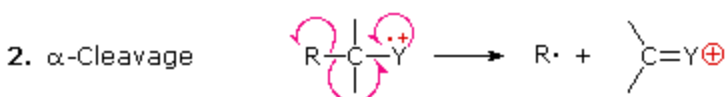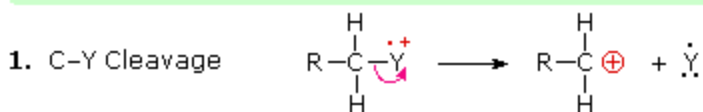$$(m_1/z) \quad (m_2/z) \quad (m_1-m_2)$$
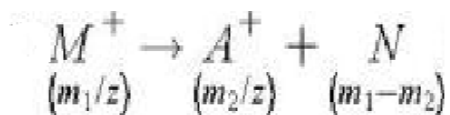
(ii). Relative abundance of the parent and the fragment ions

The fragmentation of molecular ions into an assortment of fragment ions is a mixed blessing. The nature of the fragments often provides a clue to the molecular structure, but if the molecular ion has a lifetime of less than a few microseconds it will not survive long enough to be observed. Without a molecular ion peak as a reference, the difficulty of interpreting a mass spectrum increases markedly. Fortunately, most organic compounds give mass spectra that include a molecular ion, and those that do not often respond successfully to the use of milder ionization conditions. Among simple organic compounds, the most stable molecular ions are those from aromatic rings, other conjugated pi-electron systems and cycloalkanes. Alcohols, ethers and highly branched alkanes generally show the greatest tendency toward fragmentation.

The mass spectrum of dodecane on the right illustrates the behavior of an unbranched alkane. Since there are no heteroatoms in this molecule, there are no non-bonding valence shell electrons. Consequently, the radical cation character of the molecular ion (m/z = 170) is delocalized over all the covalent bonds. Fragmentation of C-C bonds occurs because they are usually weaker than C-H bonds, and this produces a mixture of alkyl radicals and alkyl carbocations. The positive charge commonly resides on the smaller fragment, so we see a homologous series of hexyl (m/z = 85), pentyl (m/z = 71), butyl (m/z = 57), propyl (m/z = 43), ethyl (m/z = 29) and methyl (m/z = 15) cations. These are accompanied by a set of corresponding alkenyl carbocations (e.g. m/z = 55, 41 &27) formed by loss of 2 H. All of the significant fragment ions in this spectrum are even-electron ions. In most alkane spectra the propyl and butyl ions are the most abundant.

The presence of a functional group, particularly one having a heteroatom Y with non-bonding valence electrons (Y = N, O, S, X etc.), can dramatically alter the fragmentation pattern of a compound. This influence is thought to occur because of a "localization" of the radical cation component of the molecular ion on the heteroatom. After all, it is easier to remove (ionize) a non-bonding electron than one that is part of a covalent bond. By localizing the reactive moiety, certain fragmentation processes will be favored. These are summarized in the following diagram, where the green shaded box at the top displays examples of such "localized" molecular ions. The first two fragmentation paths lead to even-electron ions, and the elimination (path #3) gives an odd-electron ion. Note the use of different curved arrows to show single electron shifts compared with electron pair shifts.

molecular ions $[M^{+\bullet}]$ ≡ R–$\overset{\bullet+}{\underset{\bullet\bullet}{\ddot{C}l}}$: or R–$\overset{\bullet+}{\underset{\bullet\bullet}{\ddot{O}}}$-R' or R–$\overset{\bullet+}{N}R'_2$ or $R_2C=\overset{\bullet+}{\underset{\bullet\bullet}{\ddot{O}}}$

**1. C–Y Cleavage**

**2. α-Cleavage**

**3. H–Y Elimination**

The charge distributions shown above are common, but for each cleavage process the charge may sometimes be carried by the other (neutral) species, and both fragment ions are observed. Of the three cleavage reactions described here, the alpha-cleavage is generally favored for nitrogen, oxygen and sulfur compounds. Indeed, in the previously displayed spectra of 4-methyl-3-pentene-2-one and N,N-diethylmethylamine the major fragment ions come from alpha-cleavages. Further examples of functional group influence on fragmentation are provided by a selection of compounds that may be examined by clicking the left button below. Useful tables of common fragment ions and neutral species may be viewed by clicking the right button.

(OR)

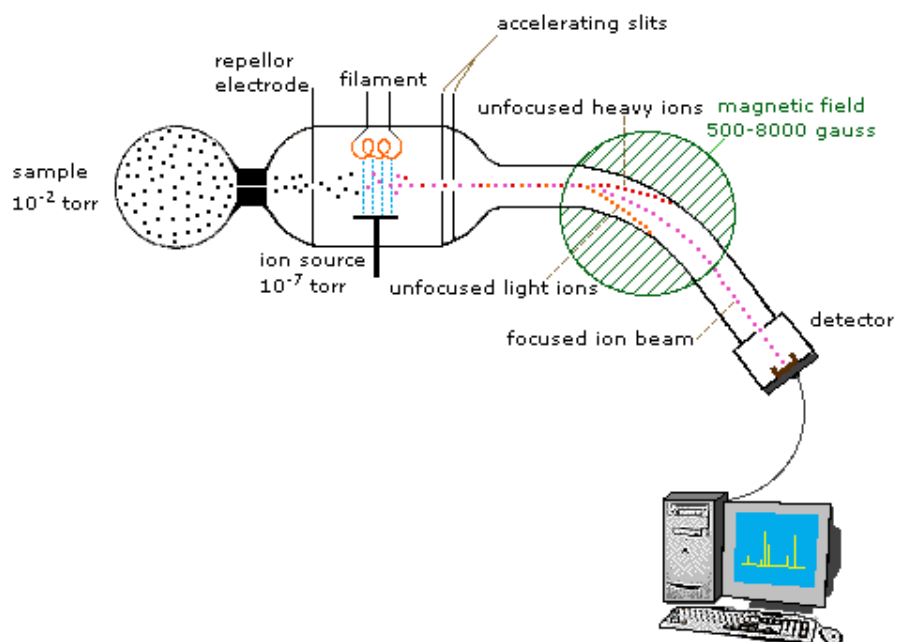b.(i). Explain the instrumentation of mass spectroscopy.

The Mass Spectrometer
        In order to measure the characteristics of individual molecules, a mass spectrometer converts them to ions so that they can be moved about and manipulated by external electric and magnetic fields. The three essential functions of a mass spectrometer, and the associated components, are:

1. A small sample is ionized, usually to cations by loss of an electron.  Ion Source
2. The ions are sorted and separated according to their mass and charge.   The Mass Analyzer
3. The separated ions are then measured, and the results displayed on a chart.   The Detector

Because ions are very reactive and short-lived, their formation and manipulation must be conducted in a vacuum. Atmospheric pressure is around 760 torr (mm of mercury). The pressure under which ions may be handled is roughly $10^{-5}$ to $10^{-8}$ torr (less than a billionth of an atmosphere). Each of the three tasks listed above may be accomplished in different ways. In one common procedure, ionization is effected by a high energy beam of electrons, and ion separation is achieved by accelerating and focusing the ions in a beam, which is then bent by an external

magnetic field. The ions are then detected electronically and the resulting information is stored and analyzed in a computer. A mass spectrometer operating in this fashion is outlined in the following diagram. The heart of the spectrometer is the ion source. Here molecules of the sample (black dots) are bombarded by electrons (light blue lines) issuing from a heated filament. This is called an **EI** (electron-impact) source. Gases and volatile liquid samples are allowed to leak into the ion source from a reservoir (as shown). Non-volatile solids and liquids may be introduced directly. Cations formed by the electron bombardment (red dots) are pushed away by a charged repeller plate (anions are attracted to it), and accelerated toward other electrodes, having slits through which the ions pass as a beam. Some of these ions fragment into smaller cations and neutral fragments. A perpendicular magnetic field deflects the ion beam in an arc whose radius is inversely proportional to the mass of each ion. Lighter ions are deflected more than heavier ions. By varying the strength of the magnetic field, ions of different mass can be focused progressively on a detector fixed at the end of a curved tube (also under a high vacuum).



When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** (colored red in the following diagram). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller **fragment ions** (colored pink and orange). The molecular ion is a radical cation, but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral

fragment. An animated display of this ionization process will appear if you click on the ion source of the mass spectrometer diagram.



$$M: + e \longrightarrow 2e + M^{+} \nearrow M^{+}_{\cdot} + F^{*} \text{ neutral fragment}$$
$$\searrow M^{+} + F^{*} \text{ neutral fragment}$$

26. a. How would you distinguish between ethylamine and triethylamine on the basis of mass spectroscopy?

The presence of nitrogen in an amine can be detected by its odd molecular weight and the even fragments that it produces .Often times the presence of the molecular ion in longer straight chain amines is not detectable. In these cases, chemical ionization techniques are often used in determining the molecular mass in order to determine the presence of nitrogen.

The base peak in most amines results from the cleavage of the β bond. The loss of the largest branch (R") is preferred because the larger alkyl fragment stabilizes the produced radical.
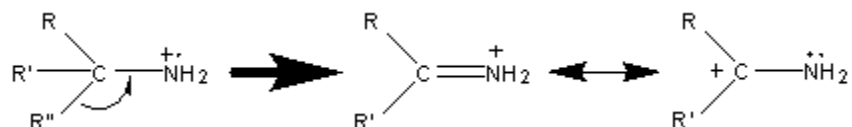


Like alcohols, if α carbon is bonded to a hydrogen atom, a [M − H] peak is usually visible. In primary amines with an unbranched α carbon, cleavage of the β bond produces a peak at $m/z$ 30. This peak is not conclusive proof of a primary amine because secondary and tertiary amines undergo a rearrangement similar to that of alcohols.
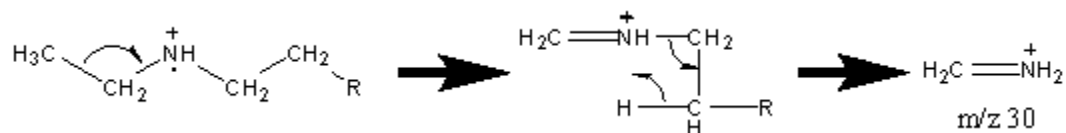


Amines also produce even fragments caused by the cleavage of C − C bonds farther away from the functional group. The fragment containing the nitrogen group usually retains the charge resulting peaks characterized by $C_nH_{2n+2}N$ spaced at 14 units. There is also the less prevalent hydrocarbon pattern of $C_nH_{2n+1}$, $C_nH_{2n}$, and $C_nH_{2n-1}$.

Fragmentation of Three Amines - The mass spectrum is easily recognized as an amine due to its odd molecular ion and the presence of even fragments. The base peak in each spectrum, due to β cleavage distinguishes between the primary, secondary, and tertiary amine. Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

(OR)

b. Explain the instrumentation of mossbauer spectroscopy.
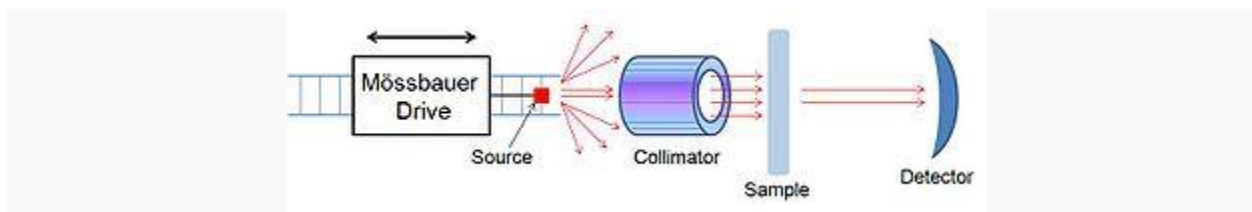


A schematic view of mössbauer spectrometer

A Mössbauer spectrometer is a device that performs Mössbauer spectroscopy, or a device that uses the Mössbauer effect to determine the chemical environment of Mössbauer nuclei present in the sample. It is formed by three main parts; a source that moves back and forth to generate a Doppler effect, a collimator that filters out non-parallel gamma rays and a detector.

A miniature Mössbauer Spectrometer, named (MB) MIMOS II, was used by the two rovers in NASA's Mars Exploration Rover missions.

$^{57}$Fe Mossbauer spectrocopy
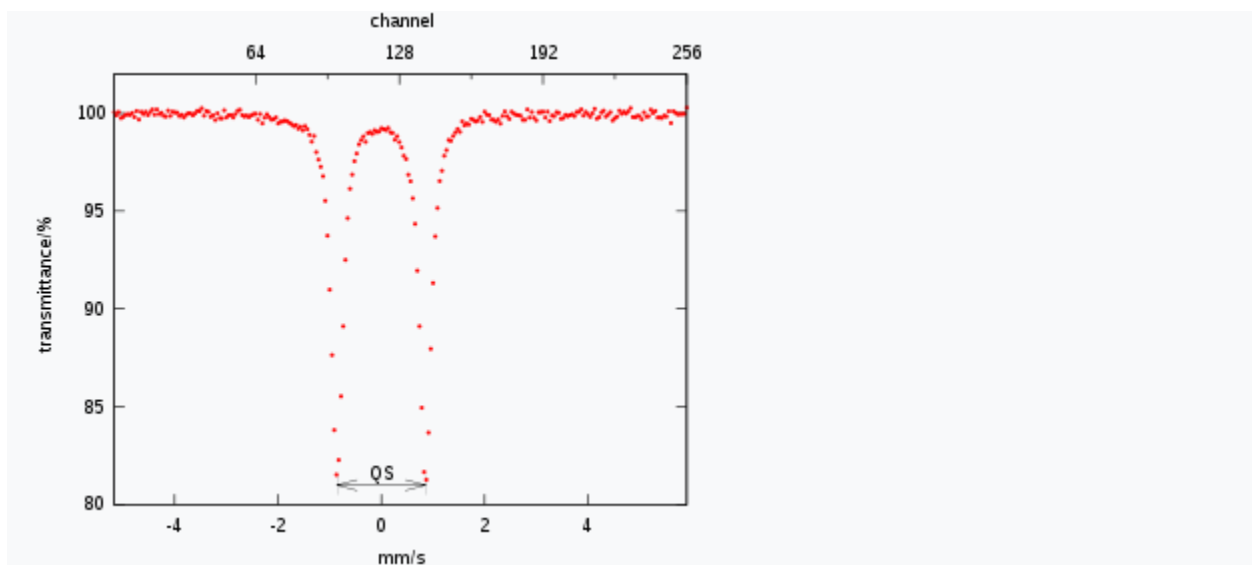


Sodium nitroprusside is a common reference material

The chemical isomer shift and quadrupole splitting are generally evaluated with respect to a reference material. For example, in iron compounds, the Mössbauer parameters were evaluated using iron foil (thickness less than 40 micrometers). The centroid of the six lines spectrum from metallic iron foil is −0.1 mm/s (for Co/Rh source). All shifts in other iron compounds are computed relative to this −0.10 mm/s (at room temperature), i.e., in this case isomer shifts are relative to Co/Rh source. In other words, the centre point of the Mössbauer spectrum is zero. The shift values may also be reported relative to 0.0 mm/s, here shifts are relative to the iron foil.

To calculate outer line distance from six line iron spectrum:

$$V = \frac{CB\text{int}\,\mu N}{E\gamma}(3g^e n + g n)$$

where $c$ is the speed of light, $B_{int}$ is the internal magnetic field of the metallic iron (33 T), $\mu_N$ is the nuclear magneton($3.1524512605 \times 10^{-8}$ eV/T), $E_\gamma$ is the excitation energy (14.412497(3) keV), $g_n$ is the ground state nuclear splitting factor (0.090604/($I$), where Isospin $I = \frac{1}{2}$) and $g*$ n is the excited state splitting factor of $^{57}$Fe (-0.15532/($I$), where $I = \frac{3}{2}$).

By substituting the above values one would get $V = 10.6258$ mm/s.

Other values are sometimes used to reflect different qualities of iron foils. In all cases any change in $V$ only affects the isomer shift and not the quadrupole splitting. As the IBAME, the authority for Mössbauer spectroscopy, does not specify a particular value, anything between 10.60 mm/s to 10.67 mm/s can be used. For this reason it is highly recommended to provide the isomer shift values with respect to the source used, mentioning the details of source (centre of gravity of the folded spectrum), instead with respect to iron foil.

## KARPAGAM UNIVERSITY
(Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2014 onwards)

### M.Sc. DEGREE EXAMINATION, NOVEMBER 2014
First Semester

#### CHEMISTRY

#### ORGANIC AND INORGANIC SPECTROSCOPY

Time: 3 hours          Maximum : 60 marks

### PART – A (10 x 2 = 20 Marks)
### Answer any TEN Questions

1. What is Lambertz-Beers law? What are its limitations?
2. What are chromophores and auxochromes. Give suitable example.
3. What is hypsochromic shift?
4. Whether carbon-di-oxide absorb infrared light? Justify.
5. Why frequencies are generally expressed in terms of wave numbers.
6. Write an equation for calculating the frequency of vibration of a diatomic molecule.
7. What is the chemical shift range for aromatic protons?
8. What is meant by deshielding effect?
9. Explain spin – spin coupling.
10. How NMR spectorscopy differ from other spectroscopic techniques.
11. What is meant by base peak in mass spectrum?
12. Explain what is meant by metastable peak in mass spectrometry
13. Write a note on Recoil –free energy.
14. Define Isomer shift. Give suitable example.
15. Explain the characteristics of Mossbauer nuclides.

### PART B (5 X 8= 40 Marks)
### Answer ALL the Questions

16. a. i. Write the expected infrared peaks for the following compounds.
    (a) Acetamide   (b) Benzophenone
  ii. Discuss the features of the infrared spectra could help in distinguishing the following pairs. $H_2N\ CH_2C_6\ H_4\ COCl$ and $H_2\ N\ C_6\ H_4\ CH_2\ COCl$
    Or

  b. i. Obtain the selection rules for linear molecules, symmetric top molecules, asymmetric molecules for IR spectrum.
    ii. Discuss briefly about the techniques employed for preparing solid samples in IR spectrum.

17. a. Describe with examples the various factors which affect the magnitude of the chemical shift in NMR spectra.
    Or
  b. What is double resonance and spin tickling? How these are helpful in simplifying the spectra?

18. a. Explain the following rearrangements in the mass spectra
    i. McLafferty rearrangement    ii. Retero – Diels order rearrangement
    Or
  b. Describe some important features of the mass spectra of
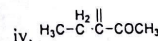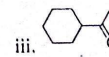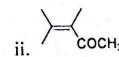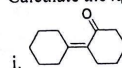    i. Alcohols    ii. Ketones   iii. Acids

19. a. What is Mossbauer effect? Explain the principle and theory of Mossbauer Spectroscopy
    Or
  b. Explain the Zero field splitting and Kramer degeneracy.

20. **Compulsory :** -

Calculate the $\lambda_{max}$ of the following compounds.

i.     ii.     iii. 

iv. $H_3C-\overset{H_2}{C}-\overset{\|}{C}-COCH_3$

-------------

Reg. No..................................

[15CHP104]

# KARPAGAM UNIVERSITY
Karpagam Academy of Higher Education
(Established Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2015 onwards)

## M.Sc., DEGREE EXAMINATION, NOVEMBER 2015
First Semester

### CHEMISTRY

### ORGANIC AND INORGANIC SPECTROSCOPY

Time: 3 hours                                      Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)
(Question Nos. 1 to 20 Online Examinations)

(Part - B & C  2 ½ Hours)

PART B (5 x 6 = 30 Marks)
Answer ALL the Questions

21. a. (i) Explain the description of double beam UV spectrophotometer.
    (ii) How will you determine the structure of $\alpha$, $\beta$ – unsaturated compounds and conjugated dienes by UV spectroscopy?
                                    Or
    b. (i) Explain the various applications of UV spectroscopy.
    (ii) Explain the absorption laws in detail.

22. a. (i) Explain the following effects on vibrational frequency shift in IR spectrum.
        1. Coupled vibration    2. Field effect and Bond angle
    (ii) What is the effect of ring size on carbonyl absorption in case of cycloketones
                                    Or
    b. How will you distinguish between the following pairs on the basis of IR spectroscopy.
        i. Fundamental vibrations and overtones.
        ii. Fermi resonamce and overtones
        iii. Inplane bending and out of plane bending virbrations
        iv. Inter and intramolecular hydrogen bonding.

23. a. Describe $^{13}C$ NMR spectroscopy. What are the advantages of it over proton magnetic resonance spectroscopy?
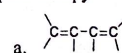                                    Or
    b. (i) Explain
        (1) Qualitative analysis  (2) Quantitative analysis using NMR spectra
    (ii) Explain heteronuclear coupling with examples

24. a. (i) What are the factors influencing the fragmentaiton process
    (ii) What are the factors governing the reaction pathways in mass spectroscopy. Explain any two.
                                    Or
    b. (i) Write brief notes on isotropic and anisotropic system
    (ii) Explain the factors affecting the magnitude of the g-value.

25. (a) How will you detect the following types of compounds by infra-red spectroscopy?

    a. $\begin{array}{c}\diagdown\\ \diagup\end{array}C=C-C=C\begin{array}{c}\diagup\\ \diagdown\end{array}$    b. $\begin{array}{c}H\\ \diagdown\\ \diagup\end{array}C=C\begin{array}{c}\diagup\\ \diagdown\\ H\end{array}$    c. $\begin{array}{c}H\\ \diagdown\\ \diagup\end{array}C=C\begin{array}{c}H\\ \diagup\\ \diagdown\end{array}$

                                    Or
    (b) Discuss in detail the various factors that influence the vibrational frequency of a particular group. Give examples

### PART C (1 x 10 = 10 Marks)
(Compulsory)

26. (a) Write the expected IR peaks for the following compounds:
        (i) p-nitro phenol (ii) p-nitrobenzoic acid (iii)acetic anhydride
    (b) An organic compound (a) with molecular formula $C_3H_7NO$ gives absorption peak in the regions 3413 (m),3236 (m),3030-2899 (m), 1667 (s),1634(s), and 1460 cm$^{-1}$ (s). Give its possible structure.

-----------------

Reg. No.............................

[16CHP104]

# KARPAGAM UNIVERSITY
Karpagam Academy of Higher Education
(Established Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2016 onwards)

## M.Sc., DEGREE EXAMINATION, NOVEMBER 2016
First Semester

### CHEMISTRY

### ORGANIC AND INORGANIC SPECTROSCOPY

Time: 3 hours                                    Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)
(Question Nos. 1 to 20 Online Examinations)

(Part - B & C 2 ½ Hours)

PART B (5 x 6 = 30 Marks)
Answer ALL the Questions

21. a) Explain the various types of electronic transitions in UV spectrum.

Or

b) Choosing appropriate example show how woodward rule is useful in determining the $\lambda_{max}$ for conjugated dienes and $\alpha, \beta$ – unsaturated carbonyl compounds.

22. a) Give a detailed account on simple harmonic oscillator.

Or

b) Explain how hydrogen bond, Inductive and mesomeric effects affect the vibrational frequencies .

23. a) Choosing appropriate examples explain spin- spin coupling.

Or

b) Describe off resonance decoupling.

24. a) What is meant by Double McLafferty rearrangement? Explain with suitable examples.

Or

b) i) How are $\alpha$ and $\beta$-Ionones differentiated using mass spectra?

ii) Describe fragmentation associated with amines and halides.

25. a) Illustrate principle involved in Mossbauer spectroscopy.

Or

b) An organic compound with MF $C_5H_{10}O_2$ shows the following spectral data:
IR: 3082-2860 cm$^{-1}$(m), 1825 cm$^{-1}$,1735 cm$^{-1}$ and 1455 cm$^{-1}$;
PMR: triplet $\delta$=1.7(6H) and quartet $\delta$=2.3(4H).
Deduce the structure of the compound.

### PART C (1 x 10 = 10 Marks)
(Compulsory)

26. i. Give the Position of the important IR absorption frequencies for the following compound

(i) Toluene   (ii) Acetic acid   (iii) Ethyl alcohol   (iv) Methyl vinyl ketone

ii. Assign a suitable structure consistent with the following spectral data:
Molecular formula : $C_{10}H_{12}O_2$
IR                        : 1740 cm$^{-1}$
NMR                   : triplet $\delta$ = 1.2(3H), Singlet $\delta$ = 3.5 (2H);
                             Quartet $\delta$ = 4.1 (2H); Multiplet $\delta$ = 7.3 (5H)

—————

1                                                    2