NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 402

COURSE TITLE: THEORY OF MOLECULAR SPECTROSCOPY

CHM 402

THEORY OF MOLECULAR SPECTROSCOPY

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INTRODUCTION

Spectroscopy originates from the word ‘spectrum’ which was first applied by Isaac Newton during his optics experiments (1666-1672). He passed white light through a prism and the emergent rays revealed a rainbow of colours which he called a ‘spectrum’. In 1800’s Joseph von Fraunhofer made advances in employing spectroscopy as a quantitative tool for chemical research.

The electrons in atoms exist in quantized states. When electromagnetic radiation interact with atoms or molecules, they become excited, absorb electromagnetic radiation thereby causing a transition from a lower quantum level to a higher quantum level. On the other hand, if transition occurs from a higher energy level to a lower energy level, emission of excess radiation takes place.

Wavelength is an important factor in molecular spectroscopy, as electromagnetic radiation of different wavelengths excite different modes of molecular motions. Ultraviolet or visible light is used to promote electrons to higher orbitals, infrared radiation excite molecular vibrations, while microwaves excite molecular rotations.

The absorption of molecules is shown as narrow lines (spectrum). This absorption is characteristic of the molecule and depends on temperature and pressure. In the infrared and microwave regions these lines results from rotations which are quantized at shorter wavelength, the quantized rotations, vibrations and electronic transitions give rise to similar lines.

Raman scattering which is the inelastic scattering of monochromatic light gives information about the vibrational mode in a molecule.

In Nuclear Magnetic Resonance Spectroscopy, certain odd electron nuclei such ^{1}H and ^{13}C absorb radiofrequency radiation in the presence of a magnetic field. Nuclear rather than electronic transitions take place. The technique is used to determine the carbon-hydrogen framework of a molecule which is helpful in molecular structure determination.

Mössbauer effect involves emission and absorption of gamma rays by a nucleus without loss of energy due to recoil. This technique has been used to monitor small changes in oxidation states, as well as to observe the second order transverse Doppler Effect.

COURSE DESCRIPTION

Theory of Molecular Spectroscopy (CHM 402) explores the behavior of molecules in the presence of radiation. Generally, in treating various spectroscopic methods the underlying principle of spectroscopy which involves changes in motion of molecules as a result of interaction with one form of radiation or another is employed.

WHAT YOU WILL LEARN IN THIS COURSE

In this course you will learn about the types of changes which occur when molecules absorb radiation as well as the qualitative expression of the energy term. You will learn the quantum mechanical approach to estimating the energy. You will also learn the principles, applications and instrumentations of infrared, uv/visible, nuclear magnetic resonance, electron spin nuclear quadrople and Mössbauer spectroscopy

COURSE AIMS

The aim of this course is to expose the learner to the various forms of spectroscopy including ways of estimating their energy involvement and spectral forms.

COURSE OBJECTIVES

By the end of the course, the learner should be able to:

- Express the energy of rotation and vibration of a molecule in the quantum mechanical sense using the Schrödinger equation.
- Explain the theories of spectroscopy involving rotation, vibration and electronic transition; their instrumentations and applications
- Calculate the maximum wavelength of absorption for conjugated dienes and polyenes.
- Explain the principles of spectroscopy involving the nuclei of atoms, their applications, instrumentation and spectral interpretation.
- Differentiate between these nuclear methods.

WORKING THROUGH THIS COURSE

This course material is divided into three modules and subdivided into a total of seven units. At the end of each unit there are tutor marked assignments which serve as the continuous assessment for the course.

COURSE MATERIALS

For this course, you will be provided with the following:

1. Course Guide
2. Study units.

STUDY UNITS

Module 1

Unit 1 Quantum Theory of Rotation

Unit 2 Quantum Theory of Vibration

Unit 3 Infrared and Raman Spectroscopy

Module2

Unit 1 Ultraviolet-violet Spectroscopy

Unit 2 Absorbance and Transmittance

Module 3

Unit 1 Nuclear Magnetic Resonance Spectroscopy

Unit 2 Carbon NMR Spectroscopy and Electron Spin Resonance

Unit 3 Nuclear Quadrupole and Mössbauer effect.

TEXTBOOKS AND REFERENCES

Atkins, P.W. and Paula, J. (2006).*Physical Chemistry* 8th edition. New York. W.H.

Freeman, pp. 291 and 453.

Skoog, D. A. and Holler,F. J. (2007) *Principles of Instrumental Analysis* 6th edition.

Belmont,C.A. Thompson Higher Education.Pp 169-173

Pozar, David M (1993) *MicrowaveEngineering*. Addison-Wesley publishing company

Barton, F.E. (2002) *Theories and Principles of Near infrared spectroscopy*.Europe

Hollas ,J.M(1996) *Modern Spectroscopy* 3rd edition. John Wiley. P.21

Nava , C.R.(2005) *Mössbauer effect in ion-57 Hyperphysics*. Georgia State University.

Dudley, H. and Ian, F.(2008) *Sectroscopic Methods in Organic Chemistry*. McGraw-Hill

ASSESSMENT

At the end of each unit there are a number of Teacher Marked Assignments , these TMAs are used for the continuous assessment which carries 30% of the total assessment for the course while the end of semester examination carries 70%. It is important that you effectively study this course material as well as the exercises and endeavour to attend tutorial classes and group study sessions.

SUMMARY

CHM 402 is designed to explore the principles underlying the spectroscopy of molecules. The theory of rotation and vibration include the quantum mechanical treatment by employing the Schrödinger equation. The course entails the applications of different forms of spectroscopy .

MODULE 1

UNIT 1 QUANTUM THEORY OF ROTATION

CONTENTS

1.0 INTRODUCTION

Rotational energy levels are very closely spaced such that low-energy radiation such as that produced by radio transmitters which have operational frequencies in the microwave region of the spectrum are capable of causing excitation in the rotational energies of the molecule. Conversely, electronic and vibrational energy levels are widely spaced and higher energies are required to cause their transitions. Absorption of microwave by molecules in the gas phase is characterized as essentially pure "rotational spectra".

Absorption band spectrum of rotating a molecule is dependent on the configuration of the molecule, whether linear, spherical, symmetric or asymmetric. The band spectrum of any molecule can be calculated from its moments of inertia. Comparing the theoretical band with the experimentally obtained band makes it possible to determine characteristics such as bond lengths, bond angles and molecular configurations which depend on the spacings of rotational energy levels.

2.0 OBJECTIVES

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

1. State Born-Oppenheimer approximation in solving Schrödinger equation.

2. Describe the model for a rotating molecule.

3. Derive the quantized energy of rotation of a molecule.

4. Transform energy level transitions to corresponding rotational spectrum.

5. Explain the theory of microwave spectroscopy.

6. Distinguish molecules based on their rotational symmetry.

7. Describe the operation of a radiospectroscope.

3.0 MAIN CONTENT

3.1 The Electromagnetic Spectrum

The electromagnetic radiation used in spectroscopic analysis of organic compounds span a wide range of wavelengths or frequencies ranging from radio waves 600-200 m to gamma rays $<10^{-12}$m wavelength units. (See figure 1.0 and table 1.0). The energies increase correspondingly.

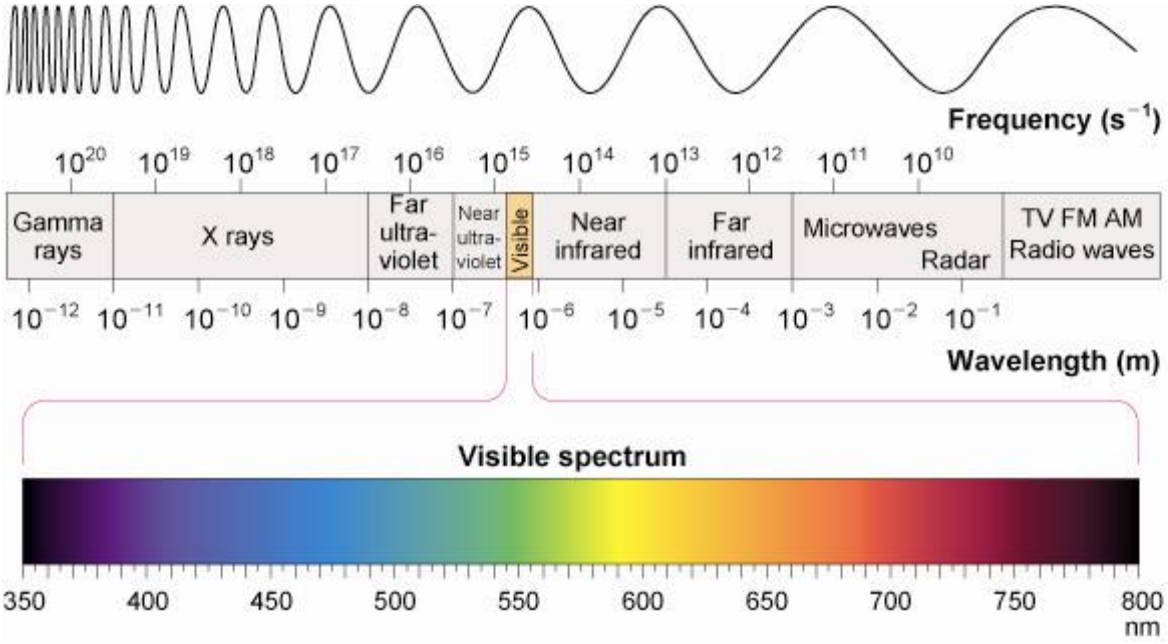


Figure 1.1 The electromagnetic spectrum Source: www.oneonta.edu/../ chapter06.pdf

Table 1.1 Important spectroscopic methods used for analysis of structure of organic molecules.

Spectroscopic Method	**Energy range of absorbed radiation in cm^{-1}**	**Type of excitation produced by absorbed radiation**	**Information obtained.**
Nuclear magnetic resonance (nmr)	10^{-4} to 10^{-2}	Changes in orientations of nuclear spin in a magnetic field.	Chemical shifts and coupling constants
Electron spin resonance (esr)	10^{-2} to 1	Excitation of unpaired electron-spin orientations in a	Electron distribution in radicals, electron-transfer reactions.

		magnetic field	
Microwave	1 to 100	Rotational excitation	Spacings of rotational energy levels; bond distances and bond angles.
Infrared (ir)	100 to 10,000	Rotational-vibrational excitation	Rotational and vibrational energy levels of molecules
Raman	100 to 4,000	Rotational-vibrational excitation	Rotational and vibrational levels of molecules.
Visible	5,000 to 25,000	Electronic excitation with vibrational-rotational changes.	Electronic energy levels of molecules.
Ultraviolet	25,000 to 50,000	Electronic excitation with vibrational-rotational changes.	Electronic energy levels of molecules.
Mössbauer	10^7 to 10^9	Excitation of atomic nuclei	Electric-field gradients at the nucleus produced by difference in bond types

Mass spectrometry	Excitation produced by electrons with energies of about $10^5 cm^{-1}$	Molecular ionization and fragmentation	Molecular weights; modes of fragmentation.

3.2 Born—Oppenheimer Approximation.

Quantum mechanical model of the electronic structure of a molecule involves solving the Schrödinger equation, $H\psi = E\psi$. THE Hamiltonian operator, H depends on the kinetic and potential energies of the nucleus. The wave function ψ, gives information about the probability of finding electrons in differerent positions in the molecule. The energy, E ,is the energies of the electrons which are useful in interpreting electronic spectroscopy.

Solving the Schrödinger equation is done by making approximations. One such approximation is the Born-Oppenheimer approximation.

Born- Oppenheimer approximation states that the motion of the electron is independent of the motion of the nucleus. Thus the energies of the two can be calculated separately. This approximation is based on the large difference in the mass of nuclei compared to the electrons, hence the assumption that the nucleus is so heavy that its motion can be ignored whereas the electrons possess kinetic energy and can move quickly.

$$H_{\mathrm{tot}} \propto (T_{\mathrm{n}}) + T_{\mathrm{e}} + V_{\mathrm{ne}} + V_{\mathrm{n}} + V_{\mathrm{e}}$$

Where T is kinetic energy; V is potential energy.

T_n, the kinetic energy of the nucleus is not included.

$$\psi_{molecule(\dot{r}i\,,\dot{R}j)} = \psi_{electrons(\dot{r}i\,,\dot{R}j)}\,\psi_{nuclei\,(\dot{R}j)}$$

It is assumed that electronic wavefunction depends upon the position of the nucleus rather than their velocities this is because the motion of the nucleus is so much slow compared to the motion of the electrons, hence the nucleus is assumed to be static.

Based on the approximation, molecular wavefunctions are given in terms of both positions of electrons and positions of nuclei. Electronic positions is given by r_i and positions of the nuclei is R_j.

3.3 Model for a Rotating Molecule:

Rotating molecules are considered to be rigid rotors.
The moment of inertia for a rotating atom is given by:

$$I = \sum_{i} m_i r_i^2$$

In the Fig. 1.1 below, atom "B" have three identical atoms bonded to it, atom "C" have three different atoms bonded to it. Rotation is about the three axes I_a, I_b, I_c.The moment of inertia about their internuclear axis is zero.

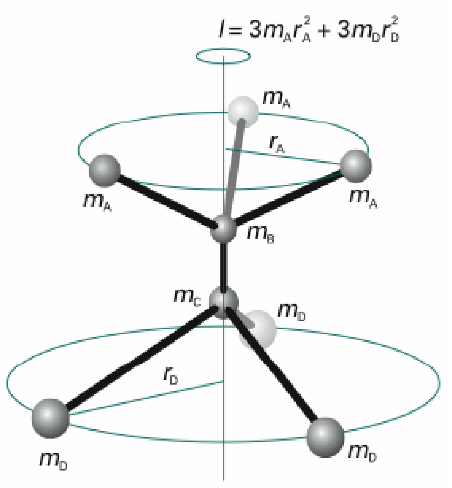


Figure 1.2 model of rigid rotors

Source: https://www.google.com.ng/images.slideplayer.com

$$I = 3m_A r_A^2 + 3m_D r_D^2$$

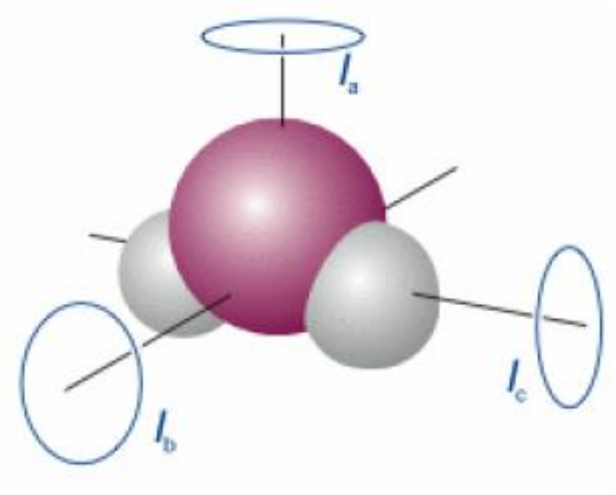


Figure 1.3 a rigid rotor rotating about 3 axes.

Source: https://www.google.com.ng/pbworks.com

3.4 Quantized Rotational Energy

Refer to figure 1.2. According to classical mechanics, the energy of a rotating body is given by the expression

$E_a=\frac{1}{2I_a w_a^2}$Where $w_a$is the angular velocity in radians/sec.

Energy for rotation about the three axes is given by:

$$E = \frac{1}{2I_a w_a^2} + \frac{1}{2I_b w_b^2} + \frac{1}{2I_c w_c^2}$$

$J = I$, where J is rotational energy level, and w represents the angular momentum.

$I$is the moment of inertia.

$$E = \frac{J^2}{2I_a} + \frac{J^2}{2I_b} + \frac{J^2}{2I_c}$$

Based on the principles of quantum mechanics, angular momentum is quantized, hence,

$J = \sqrt{(J+I)\hbar^2}$, J = 0,1,2,...,

Therefore, $E_J = J(J+I)\hbar/2I), J = 0,1,2 ...,$

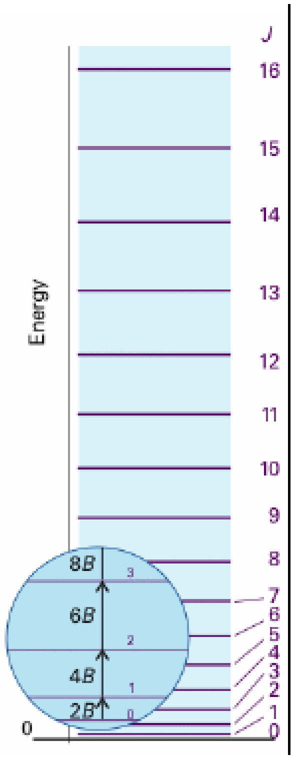


Figure 1.4 Rotational constants in quantized rotational levels.

Source: slideplayer.com PY3P05 Lecture 14.

The quantized rotational energy levels is expressed in terms of rotational constant , B, as

$$E_{rot.} = \frac{\hbar^2}{2I}J(J+1) = \frac{h}{8\pi^2}\frac{J(J+1)}{I} \equiv hc\vec{B}J(J+1)$$

$$\vec{B} = \frac{h}{8\pi^2 cI}$$

Or $\vec{B} = \frac{\hbar^2}{2Ihc}$

Therefore, the energy of a rigid rotor in wavenumber units is F(J) =BJ(J+1) cm^{-1},

the separation of adjacent rotational energy levels is F(J) –F (J-1) =2BJ

Integral values taken by rotational quantum number are , $J = 0, 1, 2\dots$ (see figure 1.3). If J = 0,

the molecule is non-rotating, then $F(J) = 0$. the levels of the energy in a rigid rotor increases as $\propto J^2$. Every level has a fold degeneracy of $(2J + 1)$.

The spectrum of the rigid rotor consists of a series of equidistant lines with a separation $2B$.Using observed rotational spectra the rotational constant B can easily be determined empirically.

3.5 Rotational Spectra.

In the selection rule for rotational transition only molecules possessing angular momentum $\Delta J \pm 1$ are allowed for transition.

Figure 1.4 below level shows rotational energy and the corresponding rotational spectrum for a linear rotor in which the intensity of each line in the spectrum is a reflection of the population of the initial level in each line.

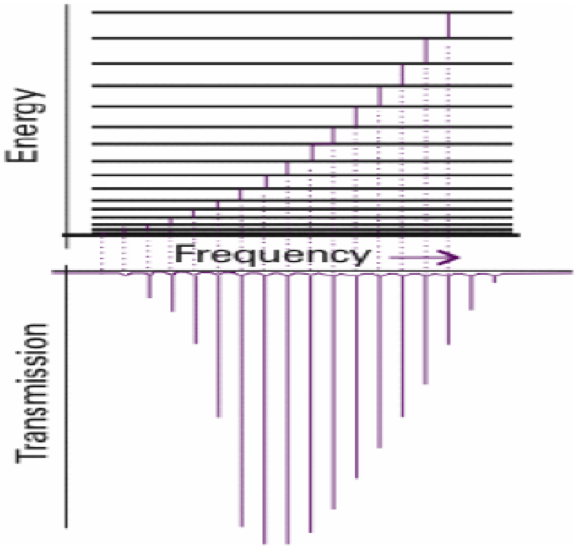


Figure 1.5 Rotational energy and the corresponding rotational spectrum for a linear rotor.

Source: slideplayer.com PY3P05 Lecture 14.

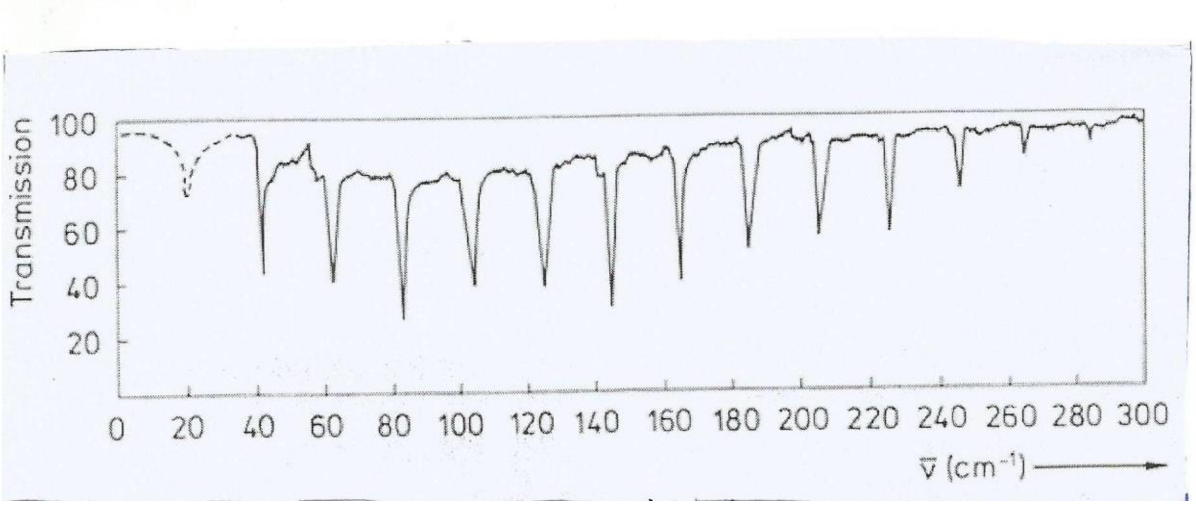


Figure 1.6 Rotational spectrum of HCl source: Haken& Wolf(2006)

3.6 Theory of Microwave Spectroscopy

When microwave radiation interacts with a molecule, the molecule absorbs energy in the form of photons. Because the molecules absorb energy there will be transition between energy states in the molecule. Only molecules possessing changing permanent dipole moment during their rotation can result in such transitions. As the molecule rotate its change in dipole moment causes the oscillating electric field of the photons to impart a torque on the molecule at an axis perpendicular to the dipole of the molecule, which also passes through the of the molecule’s centre of mass.

In microwave rotational spectroscopy, microwave radiation interacts with electric dipole of the molecule leading to excitation of the molecule and transitions between rotational states of the molecule. This rotational spectroscopy uses the radiation in microwave region to measure the rotational transition energies for gas phase molecules.

Scientists employ rotational spectroscopy in the microwave region to study the pure rotational transitions of molecules. Photons in the microwave region bring about transitions in the rotational energy levels which are quantized . For microwave spectroscopy, sample must be in the gaseous phase. Rotations are hindered due to intermolecular interactions in both liquid and solid phases.

Microwave spectroscopy is absorption spectroscopy with high resolution of rotational transitions of gas phase molecules. The energies of microwaves range between 300MHz and 300 GHz.

3.7 Rotational Symmetry of Molecules

There are five categories of microwave active molecules, viz: diatomic, linear, spherical top, symmetric top and asymmetric top. This categorization is based on the molecular shape and inertia of molecule with respect to 3 orthogonal rotational axes.

3.7.1 Diatomic Molecules:

diatomic molecules are modeled as rigid rotors, in which two masses are attached to each other at a fixed distance.

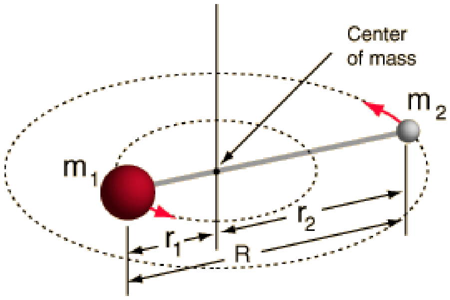


Figure 1.7 Rigid rotors, model of diatomic molecules.

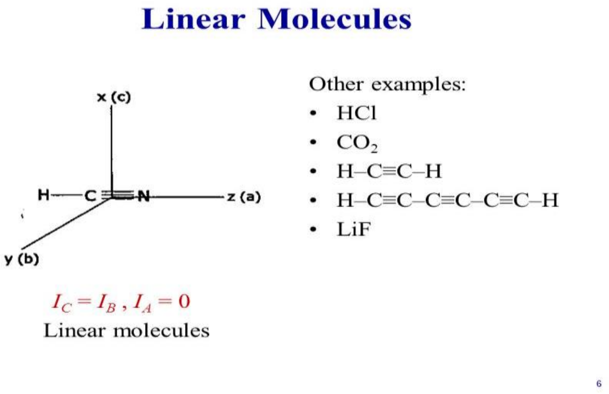
https://www.google.com.ng/hyperphysics

The molecule has an inertia (I) which is equal to the product of square of the distance between the two masses and the reduced mass of the rigid rotor.

$$I = \mu r^2 \quad \text{Where } \mu\ is\ reduced\ mass\ = m_1 m_2 / m_1 + m_2$$

3.7.2 Linear Molecules:

Linear rotors have one moment of inertia equal to zero (e.g. H_2O).
Linear molecules are similar to diatomic molecules in terms of rotations, but a linear molecule has the rotor. The inertia is the sum of the distance between each mass and the centre of mass of the rotor multiplied by square of the difference between them.



Linear Molecules

Other examples:
- HCl
- CO_2
- H–C≡C–H
- H–C≡C–C≡C–C≡C–H
- LiF

$I_C = I_B , I_A = 0$
Linear molecules

6

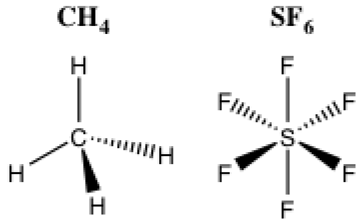
Source: https://www.google.com.ng/imgress

$$I \ = \sum j \ = 1nmjr^2 j$$

mj represents the mass of the jth mass on the rotor, and r_j represents the distance between the jth mass and the centre of mass of the rotor.

3.7.3 Spherical Tops:

Molecules with spherical tops have equal rotations in three orthogonal rotatations .i.e Spherical rotors have equal moments of inertia (e.g., CH4, SF6).
Because the molecules are symmetrical they have no dipole therefore do not give microwave rotational spectrum.



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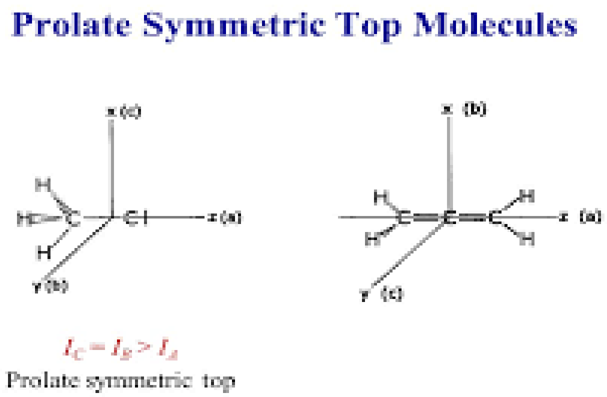
3.7.4 Symmetrical Tops:

Symmetrical top molecules have two rotational axes having equivalent inertia and one rotational axis having a different inertia. i.e. Symmetrical rotors have two equal moments of inertial (e.g., NH_3).
There are two categories of symmetrical top molecules: **oblate symmetrical top** in which the inertia of the two rotational axes with equivalent inertia is less than the inertia of the unique rotational axis for example benzene and BF_3. **Prolate symmetrical top** has inertia of the two equivalent rotational axes greater than the inertia of the unique rotational axis, for example CH_3Cl, C_3H_4 and NH_3.



3.7.5 Asymmetric rotors

Asymmetric rotors have three different moments of inertia. Examples of asymmetric rotors include water and ethanol.

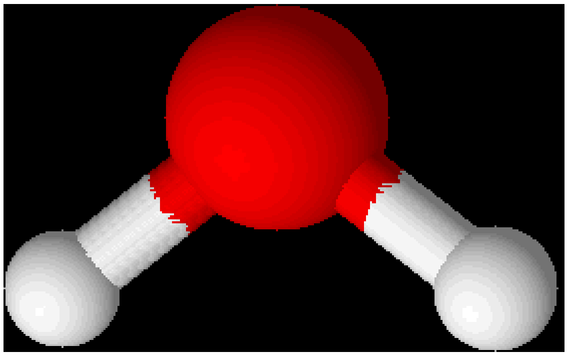


Figure 1.8   3D image of water molecule (an asymmetric rotor).

3.8 Operation of a Radiospectroscope

A radiospectroscope is used to obtain band spectra of molecules. In a radiospectroscope, a microwave generator passes wave through a wave guide filled with the gaseous sample. The emanating waves strike a detector. The signal from the detector is recorded for example on an osciliograph. The signal detected is proportional to the microwave field absorbed in the wave guide by the gaseous sample. The resonance frequency V and the absorption intensity are determined simply by changing the frequency of the microwave generator. Sometimes cavity resonators are used in place of wave guide cell. Though cavity resonators have higher quality factors, they operate within narrow band range, for example, a separate resonator must be used for almost spectral line.

The sensitivity of radio spectroscope is increased by modulation of the line intensity through electric or magnetic field. Modulation which takes place as a result of line splitting in the electric field is known as the “stark effect”. Modulation resulting from influence of magnetic field is called the “ Zeeman

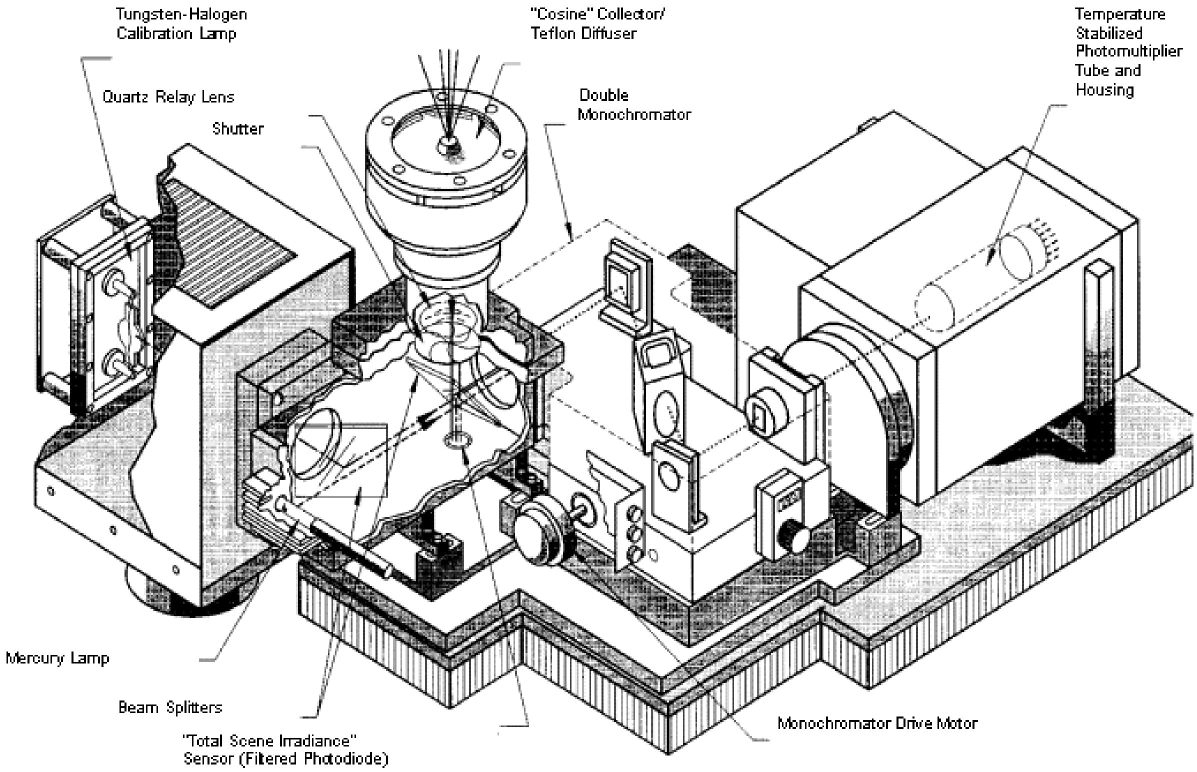


Figure 1.9 Parts of a radiospectrometer

Source: https://www.esrl.noaa.gov

Figure 1.9 Picture of a spectroradiometer

Source: https://www.ci-systems.com%2FSR-5000N-Spectroradiomete**r**

4.0 CONCLUSION

Rotational spectroscopy arises from absorption of microwave photons by rotating molecules. These molecular rotations are quantized. Rotational energy levels are very closely spaced, compared with vibrational and electronic transitions. Microwave active molecules are in five categories, which include diatomic, linear, spherical top, symmetric top and asymmetric top.

5.0 SUMMARY

Born-Oppenheimer approximation is made in solving the Schrödinger equation which is involved in the quantum mechanical treatment of a molecule. The quantized rotational energy level is expressed in terms of rotational constant, B. The selection rule for rotational transition is that molecules having $\Delta J \pm 1$ angular momentum are allowed for transition.

6.0 Tutor-Marked Assignment.

1. Write the applications of the different sections of the electromagnetic spectrum in spectroscopy

2. Write the expression for moment of inertia of a rotating atom.

3. Discuss the Born-Oppenheimer approximation in solving the Schrödinger equation.

4. Why are rotating molecules considered as rigid rotors?

5. From classical mechanics, derive the equation for rotational energy of a molecule.

6. Explain the principle of microwave spectroscopy.

6. Why is low energy radiation such as in the radiofrequency range capable of causing rotational excitation in a molecule.

7. In what way do scientists employ rotational spectroscopy?

8. Why is it necessary for sample to be in the gaseous state before being used in microwave spectroscopy?

9. Discuss the five categories of microwave active molecules.

10. What is a radioscope?

11. Describe the operation of a radioscope

7.0 REFERENCES/FURTHER READING

Ricaud, P.;Baron, P; de la Noëj. (2004) Quality Assessment of Ground Based Microwave Measurements of chlorine monoxide, ozone and nitrogen dioxide from the UDSC radiometer at the plateau de Bading.

UNIT 2 QUANTUM THEORY OF VIBRATION

CONTENTS

1.0 Introduction

Molecular vibration occurs due to periodic motion of a molecule that experiences constant translational motion. The frequency associated with the periodic motion ranges from approximately 10^4 to less than 10^{-6}cm^{-1} energy which is equivalent to 10^3 to greater than 10^{13}nm wavelength.

Vibrational states of a molecule can be measured directly through infrared spectroscopy, which involves an amount of energy equivalent to the infrared region of the electromagnetic spectrum causing vibrational transitions in the molecule. Raman spectroscopy is another technique for measuring molecular vibrational states. Raman technique uses light in the visible region to directly measure vibrational frequencies.

Vibrational excitation can occur simultaneously with electronic excitation, which is called vibronic transition. Vibrational fine structure in electronic transitions, especially in gaseous molecules is the result of the above type of excitation. Also, simultaneous excitation of a vibration and rotation results in vibration-rotation spectra.

2.0 OBJECTIVES

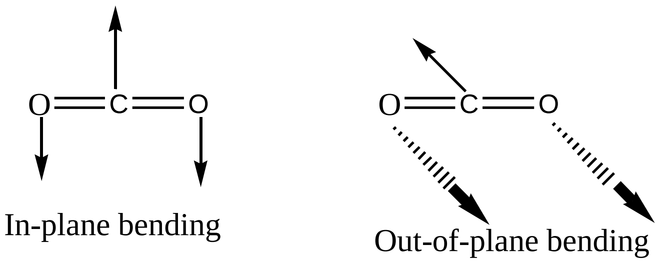
At the end of this unit you should be able to

- Explain the principle of molecular vibration.
- State the modes of vibration of poly atomic molecules.
- Derive the energy of a vibrating molecule with respect to classical mechanics.
- State the energy of a vibrating molecule in quantum mechanics.
- Describe the two models of a vibrating molecule.
- Explain vibronic transitions in a molecule.
- Write the energy expression for a vibration-rotation.
- State the selection rule for vibration-rotation
- Sketch a spectrum for the vibration-rotation transitions in a diatomic molecule, showing P branch, Q branch and R branch.

3.0 MAIN CONTENT

3.1 Modes of Vibration of Polyatomic Molecules

A polyatomic molecule possessing n atoms has equivalent 3n-6 normal modes of vibration; in which n-1 are stretching vibrations and 2n-5 are bending vibrations. A linear molecule like CO_2, has 3n-5 or 4 modes of vibrations (as rotation about its axis is not possible), two of such vibrations are stretching and other two are bending. The two bending modes (in-plane and out-of-plane bending) are equivalent, because the direction of bending of the molecule is immaterial.



In-plane bending

Out-of-plane bending

Figure 2.1 Bending vibration modes of CO_2

Equivalent modes of vibrations are degenerate. Stretching vibrations of CO_2 is illustrated below:

Figure 2.2 Stretching vibration modes of CO_2

An unsymmetrical diatomic molecule for example HCl has only one mode of vibration, namely stretching vibration. However, symmetrical molecules like N_2, O_2, Cl_2, etc. do not absorb in the infrared region of the spectrum because the vibration will be electrically neutral.

Although, polyatomic molecules vibrate in modes which are independent of each other, there is a simultaneous vibration of the different bonds in the molecule.

3.2 Classical Mechanics of Vibration

When a molecule absorbs a quantum of energy, it becomes excited. The vibrational energy is given by $E = hv$, where *h* is Planck's constant, and v is vibrational frequency.

Excitation of a fundamental vibration occurs when a molecule in its ground state absorbs one quantum of energy. The first overtone is excited when a molecule absorbs two quanta and so on to higher overtones.

3.3 Harmonic Oscillator

In a normal vibration the motion can be approximated to a simple harmonic motion, in which the vibrational energy is a quadratic function of the atomic displacements, and the frequency of the first overtone is two times that of the fundamental.

The simplest model for vibrating molecule is two atoms connected with a spring. We assume that the molecule is non-rotating.

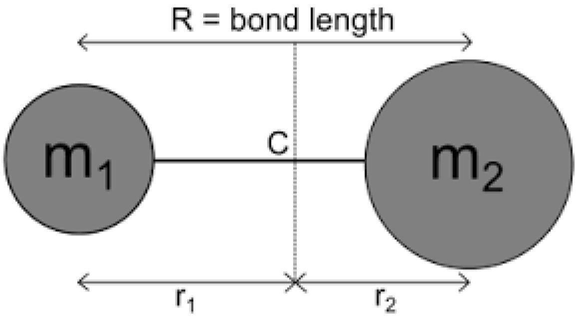


Figure 2.3 model for vibrating molecule (Harmonic Oscillator)

https://www.wikiversity.org

In a diatomic molecule such as HCl, the vibration of a molecule can be viewed as corresponding to that of a spring which is in a simple harmonic motion. The harmonic approximation obeys Hooke's law which states that the force applied to extend the spring is proportional to the extension.

In applying Hooke's law, F is a restoring force which the spring exerts on a body pulling it. Usually the restoring force (reaction) acts in opposite direction to the extension (displacement).

$F \propto -x$

$F = -kx$

Where k, the proportionality constant is known as the force constant.

From Newton's second law of motion,

$F = ma$

Where F = sum of forces acting on a body

m = mass of the body

a = acceleration (displacement/time^2).

the force acting on the mass is given by:

$F=\mu\frac{d^2x}{dt^2} = -kx$ where: $\mu = \frac{m_1 m_2}{m_1+m_2}$, the reduced mass.

x is the distance from the equilibrium position.

$x = x_0 \sin〖(2\pi v\ t+ \phi)〗$, where x_0 is the amplitude of the vibration

The frequency of vibration is given by $v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

The force is related to the potential energy, V,

Therefore, $V = \frac{1}{2}kx^2$

The total vibrational energy is

$$E = \frac{p^2}{2\mu} + \frac{\mathrm{kx}^2}{2}$$

3.4 Quantum Mechanics of Vibration

The quantum mechanical treatment of the total vibrational energy of the molecule is given by:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\Psi}{dx^2} + \frac{1}{2}kx^2\Psi = E\Psi$$

$E_v =(V+1/2)\hbar w$

v is the vibrational quantum number while V is the harmonic frequency.

Where $w = \sqrt{k/\mu}$, v= 0,1,2,…, n

Generally, the vibrational energy is written as:

$$G(v) = (V + {}^{1}/_{2})w$$

For the lowest vibrational energy state, v_o=0, the energy is at zero. The selection rule $\Delta v \pm\ 1$ applies for harmonic oscillator only, but not for anharmonic oscillator.

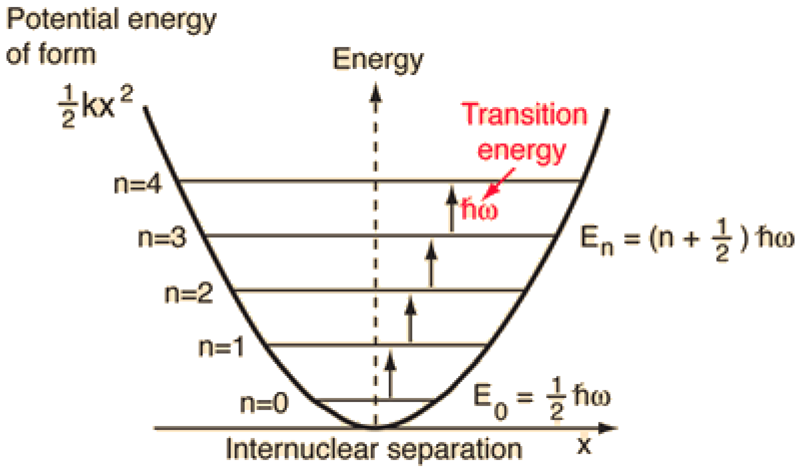


Figure 2.4 A harmonic oscillator represented by a parabola.

Source: https://www.google.com.ng/hyperphysics.phy-astr.edu

The potential energy curve shows that the restoring force increases infinitely as the distance from the equilibrium position increases.

3.5 Anharmonic Oscillator

The potential energy curve of a harmonic oscillator does not apply to molecules that are so far apart as to reach dissociation point i.e, attractive force between the atoms is zero as in the case of real molecules in which the potential energy is constant with respect to the total energy of the separated atoms.

A better model called a Morse potential is employed , which is an anharmonic oscillator.

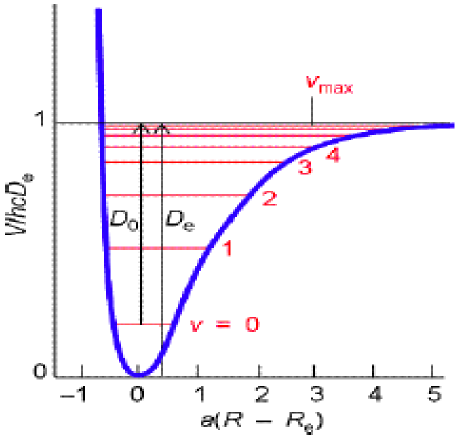


Figure 2.5 An Anharmonic Oscillator
Source: slideplayer.com PY3P05 Lecture 14.

$$V = h_c D_e (1 - \mathrm{e}^{-\mathrm{a}}\,(\mathrm{R} - \mathrm{R_e}))^2$$

Where D_e is the is the dissociation energy.

a is characteristic of the molecule,

$$a = \sqrt{\frac{\mu\, w^2}{2 h_c D_e}}$$

The vibrational energy for anharmonic oscillator is given as

$$G(v) = w_e\left(v + {}^1\!/_2\right) - w_e x_e\,(v + {}^1\!/_2)^2 \; + \; w_e y_e\,(v + {}^1\!/_2)^3 + \ldots +$$

w_e ,$w_e x_e w_e y_e$ are vibrational equilibrium constants which depend on the molecule’s electronic configuration.

The anharmonicity constant ,

$$x_e = \frac{a^2\hbar}{2\mu w}$$

For anharmonic oscillation, the electric dipole selection rule Δv is not restricted, i.e Δv =± 1,± 2, ± 3, ± ...,

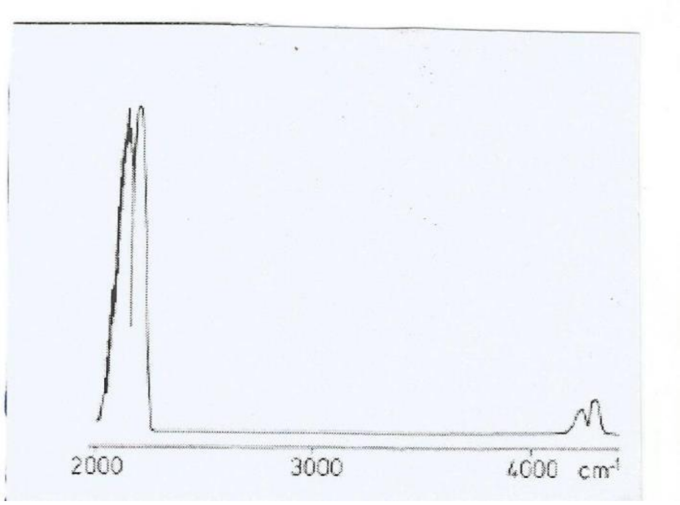


Figure 2.6 Vibarational spectrum of CO in the gas phase, showing fundamental vibration at 2143 cm^{-1} and first harmonic at 4260cm^{-1}.The resolution of the spectrum is low.

Source: Haken & Wolf (2006)

3.6 Vibration-Rotation

Real molecules experience vibration and rotational motions simultaneously. The best model for this is a vibrating rotor.

$$S(V,J) = G(V) + F(J)$$

$$S(V,J) = (V + {}^{1}/_{2})w_e + BJ(J+1) .$$

The selection rules for vibration-rotation are obtained by combining selection rule for rotation $\Delta J = \pm 1$ and selection rule for vibration $\Delta v = \pm 1$.

Transitions with $\Delta J = -1$ are called the P branch, transitions with $\Delta J = +1$ are called the R branch.

Transitions with $\Delta J = 0$ are called Q branch.

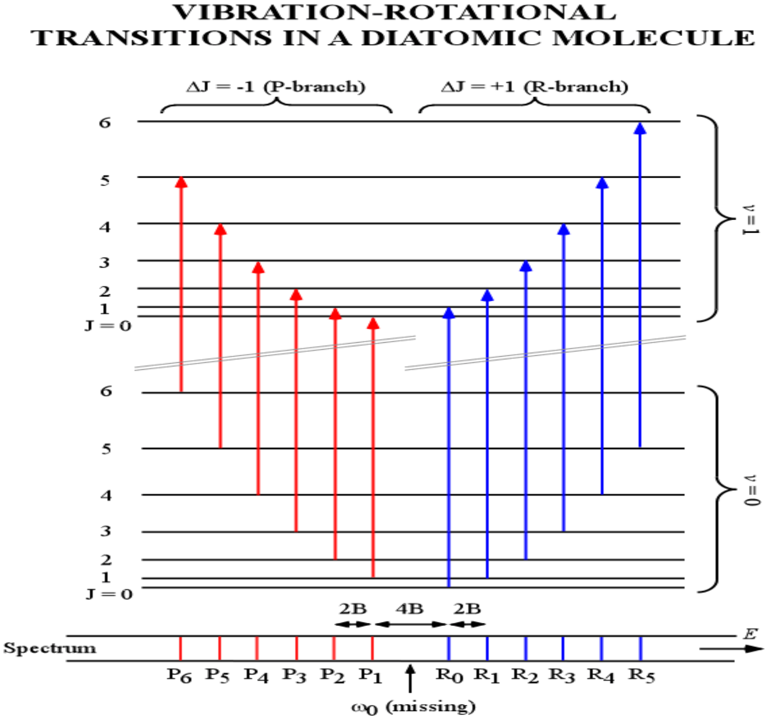


Figure 2.7 Vibration – rotational transitions in a diatomic molecule. Source: slideplayer.com PY3P05 Lecture 14.

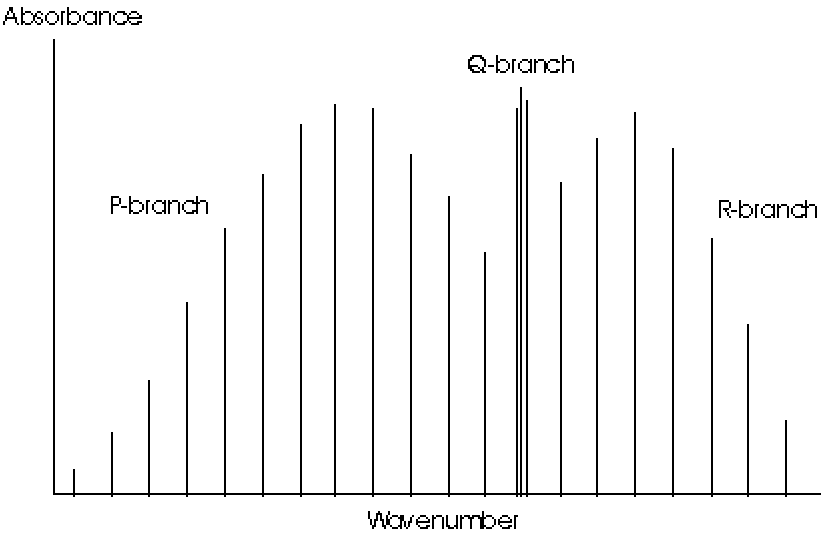


Fig. 2.8 Vibration-Rotational transitions in a diatomic molecule

Source: https://www.everyscience.com

4.0 CONCLUSION

Vibrating molecules are best modeled as anharmonic oscillator, in which a Morse potential is employed in calculating vibrational energy.Howevever, real molecules experience vibration and rotation simultaneously. Hence, the total energy involves vibration and rotation terms.

5.0 SUMMARY

When a molecule absorbs a quantum of energy it becomes excited, the vibrational energy can be estimated by $E = hv$, where $h\ is\ Planck's constant.\ and\ v\ is\ vibrational\ frequency.$

The techniques for measuring molecular vibration include infrared and Raman spectroscopy. Whereas IR involves absorption of light in the infrared region, Raman involves scattering of light in the visible, near infrared or near ultraviolet region by a molecule.

Vibronic transitions occur when electronic transitions occur simultaneously with vibrational transition.

The selection rules for vibration-rotation are $\Delta J = \pm 1$ and $\Delta v = \pm 1$.Transitions with $\Delta J = -1$ are called the P branch, transitions with $\Delta J = +1$ are called the R branch. Transitions with $\Delta J = 0$ are called Q branch.

6.0 TUTOR MARKED ASSIGNMMENT.

1. What is responsible for molecular vibration?
2. Explain the model for a vibrating molecule.
3. What are the selection rules for harmonic and anharmonic oscillation.
4. Name two techniques used for measuring the vibrational states of a molecule.
5. Explain vibronic transition.
6. Give the expression for the energy of a vibrating rotor.
7. State the selection rules for rotation and vibration.
8. Sketch a spectrum for the vibration-rotation transitions in a diatomic molecule, showing P branch, Q branch and R branch.

7.0 REFERENCES AND FURTHER READING.

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UNIT 3 INFRARED AND RAMAN SPECTROSCOPY

CONTENTS

1.0 Introduction

2.0 Objectives

3.0 Main Content

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- 3.2 Molecular Vibrational Energy-The Infra Red Region
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- 3.2.2 Instrumentation of Infrared Spectroscopy
- 3.2.2.1 Continous Wave Spectrometers
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- 3.2.3.1 Liquid Samples:
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- 3.2.4 The Fingerprint Region
- 3.3 Raman spectroscopy:
- 3.3.1 Theory of Raman Scattering

1.0 INTRODUCTION

The infra-red region of the of electromagnetic spectrum spans 1400-10cm^{-1} (0.71-1000μm). It is divided into three regions: near IR (14000-4000cm^{-1}) mid-IR (4000-400cm^{-1}) and far – IR (400-10cm^{-1}). The near IR (higher energy 14000-4000cm^{-1}) can excite overtone or harmonic vibrations. The mid IR (4000-400cm^{-1}) is used to study fundamental vibrations and associated rotational-vibrational structure. The far infra-red close to microwave region, has low energy and may be useful for rotational spectroscopy. The mid IR range (4000-400cm^{-1}) is the most useful for analysis in organic chemistry. When a molecule absorbs electromagnetic radiation in the infra-red region, the energy of the radiation causes vibrational and rotational changes in the molecule.

Raman spectroscopy discovered in 1928 by C.V. Raman and K.S. Krishnan is another technique employed to observe vibrational, rotational modes in a system. Its principle is based on inelastic scattering or Raman scattering of monochromatic light from a laser source in the visible, near infrared or near ultraviolet region by a molecule.

2.0 OBJECTIVES

At the end of this unit you should be able to

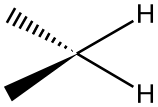
- Describe the models for stretching and bending vibrations molecules
- Describe the instrumentation and sample preparation for IR
- Explain the theory of Raman spectroscopy
- Distinguish between elastic and inelastic scattering
- Classify different types of inelastic scattering
- Describe the instrumentation of Raman spectroscopy
- Classify molecules as infrared or Raman active
- State the advantages of Raman spectroscopy
- Compare Raman with IR spectroscopy

3.0 MAIN CONTENT

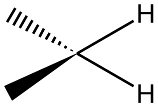
3.1 Types of Stretching and Bending Vibrations

The bonds holding atoms together in the molecule undergo stretching or bending motions. These bonds are like springs while the atoms are like small masses attached to both ends of the spring.

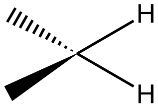
Figure 2 below shows the different between stretching and bending (deformation) vibrations of Methylene (-CH_2).



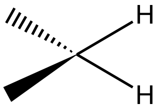
Symmetric stretching ($2850cm^{-1}$)



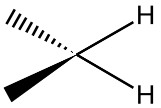
Symmetric stretching ($2850cm^{-1}$)



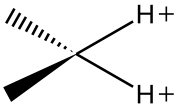
Asymmetric stretching ($2925cm^{-1}$)



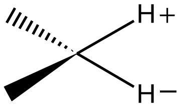
Scissoring (in-plane bending) $1460cm^{-1}$



Rocking (in-plane bending) $750cm^{-1}$



Wagging (out-of-plane bending) 1350-$1150cm^{-1}$



Twisting (out-of-plane bending) 1350-$1150cm^{-1}$

Fig 3.1 Normal modes of -CH_2 vibration

3.2 Molecular Vibrational Energy-The Infra Red Region

Each bond in a molecule has a characteristic frequency of vibration. Stretching vibration occurs at higher frequency than the bending vibration in the bond. When the frequency at which a bond is vibrating is equivalent to the infra-red radiation interacting with the bond, the bond will absorb the radiation. Different bonds in a molecule absorb at different frequencies. A bond absorbs IR when the vibration of the bond gives rise to change in the bond dipole moment. The intensity of absorption depends on the magnitude of change in dipole moment of bond arising from bond vibration.

In the nineteenth century, Sir William Herschel discovered the infra red region of the electromagnetic spectrum. The word infra red means “beneath the red”. Which include region of the electromagnetic spectrum spanning 10^3 to 10^6 nm.

When a molecule absorbs IR radiation it is promoted to a level of higher vibrational energy. The energy for this transition is quantized and is given as

$$\Delta E = hv$$

ΔE is the difference in energy between the two vibrational levels,

H is planck’s constant, (6.6×10^{-34} Joules per sec.)

v is frequency of radiation (in Hz).

$v = c/\lambda$ where c is the speed of light ($3 \times 10^8 ms^{-1}$),

λ is wavelength of vibration (in meter).

$$\Delta E = hv = hc/\lambda$$

i.e energy is directly proportional to frequency and inversely proportional to wavelength.

Wavenumber $\tilde{v} = 1/\lambda x\ (1000)\ (\mu m)$

3.2.1 Expressing IR Absorption

The positions of absorbtion bands in an IR spectrum are stated by wave numbers ($\bar{v}$ in cm^{-1}). The wave numbers are proportional to the vibrational energy.

Absorption of IR may be expressed in two ways (i) Transmittance (ii) Absorbance (A)

(i) $$Transmittance(T) = \frac{Amount\ of\ radiation\ transmitted\ by\ sample}{Amount\ of\ radiation\ incident\ on\ sample}$$

(ii) $$Absorbance\,(A) = \log_{10}(^{1}/_{T})$$

3.2.2 Instrumentation of Infrared Spectroscopy

3.2.2.1 Continous Wave Spectrometers

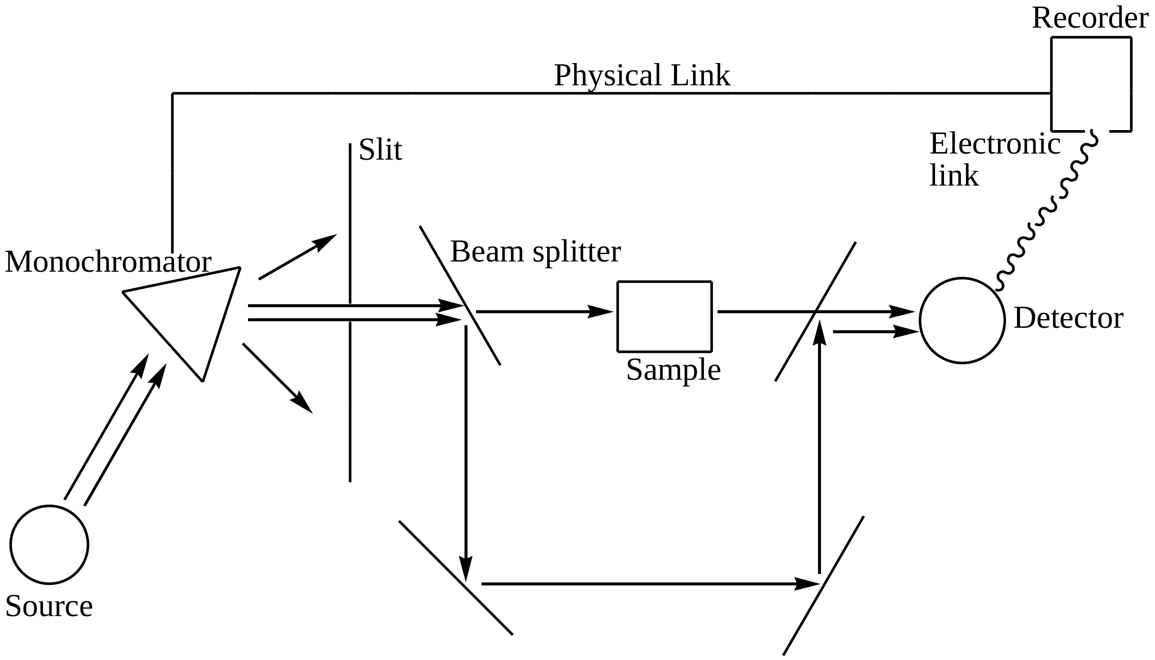


Figure 3.2 Schematic diagram of a Continous Wave Spectrometer

A source of light whose energy is in the IR region of the electromagnetic spectrum.

A monochromator which can be either a salt prism or a grating. The monochromator seperates the radiation from the source into different wavelengths. The wavelengths that shine through the sample is selected by the slit.

In double beam instrument, a beam splitter separates the incident beam into two. One part passes into the sample and the second part goes into the reference. The sample absorbs infrared radiation, the radiation passing through the sample is detected. The detector sends electrical signals to a recorder. In double beam instrument the absorption energy of the sample is compared with the reference. Energy is recorded as a function of frequency or wavelength.

The classical infrared spectrometer described above have some limitations. The amount of signal resulting from a resolution is limited by the monochromator/slit. The slit has to be narrowed to get a higher resolution. Secondly, there is need for repetitive calibration of the instrument because the connection of the positions of the monochromator and recorder can get out of alignment. Thirdly, multiple scans cannot be run to give rise to signal-to-noise-ratios.

3.2.2.2 Fourier Transform Spectrometer

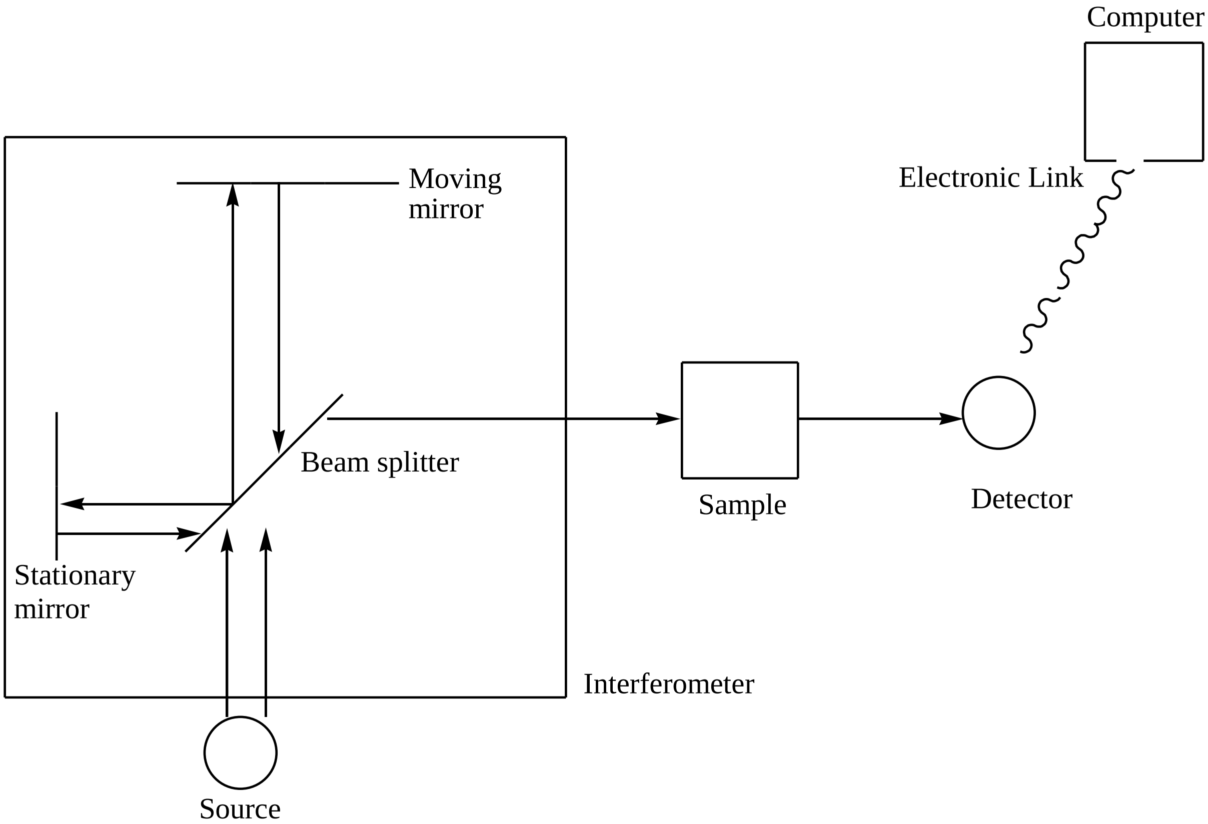


Figure 3.3 A FTIR spectrophotometer consisting of radiation source, a Michelson Interferometer and a detector.

The Fourier-Transform IR technique uses the possibilities of modern computer technology for the storage and processing of large amounts of data. The basic principle is the simultaneous collection of data at all frequencies in the IR spectrum, thus eliminating the time required for scanning through the different frequencies. This is done with the use of an interferometer to convert the intense, multifrequency IR radiation, which is constant with time, into interferogram, which is not a function of the frequency, but of time (i.e conversion from a frequency domain into a time domain. The interferogram is then converted back to the spectrum.

Energy from the source is sent through the interferometer into the sample. The IR source is a Nernst filament heated to 2000^{o}C. The interferometer replaces the monochromator in the classical spectrophotometer. The light from the source is guided into the interferometer. The light passes through a beam splitter which splits it at right angles into two beams of equal energy. One beam goes to a stationary mirror and reflected back to the beam splitter. The other beam is reflected to a moving mirror. Due to motion of one of the mirrors, one of the beams travels at a longer optical distance than the other beam. When the two beams meet again at the beam splitter, the difference in path lengths give rise to constructive and destructive interferences.

Constructive interference takes place when all beams meeting at the beam splitter are in phase, leading to beam of high intensity. Conversely, if the beams are out of phase destructive interference occurs with a beam of low intensity.

As the recombined beams pass through the sample, the sample absorbs the different wavelengths from the interferogram. A plot of light intensity against optical path difference gives an interferogram which is Fourier-transformed from a time domain to frequency domain. This transformation gives the IR spectrum. A laser beam is provided in the instrument to serve as a reference standard for the operation of the instrument

Fourier Transform is a mathematical function which is used to convert an intensity vs time spectrum into intensity vs Frequency spectrum.

The fourier transform function:

$$A(r) = \Sigma X\,(K)\,exp\,(-2\pi\,(irk)/N)$$

$A(r)$is the frequency domain point

$X\ (K)$is the time domain point

N is number of points in spectrum.

3.2.3 Preparation of sample for FT-IR

3.2.3.1 Liquid Samples:

To obtain the spectra of liquid samples, thin film of the liquid is placed between polished KBr plates. NaCl plates can also be used. These materials are transparent in the infra-red spectrum. The plates are placed in the sample holder, then positioned in the path of IR light. The salt pellets being soluble in water must be protected from moisture. They should be picked up by the edges with gloves so that moisture from your fingers will not mar the polished surface. At the end of the operation, the windows are gently wiped with a tissue, then washed first with methylene chloride then ethanol. Afterwards polish the window surface.

3.2.3.2 Solid Sample:

Solid sample for IR measurement may be prepared in three ways: as a pellet, a mull or a solution.

To make a pellet, grind about 3 mg of the sample with about 300 mg dry KBr powder or NaCl using a clean dry agate mortar and pestle. Mix and press the mixture into a transparent pellet in a small die under pressure.

A mull is made by grinding 5 mg of the sample, a drop of Nujol is added as the mulling agent. (Nujol is purified mineral oil) place the mixture of ground sample and Nujol between salt plates as a thin film. Determine the IR of the thin film. Because the mulling agent Nujol is a saturated hydrocarbon, bands will be visible at 2950-2800, 1465, 1450 and 1380-1370cm^{-1} which are typical bands for saturated hydrocarbons. To eliminate these bands in the spectrum, Nujol prevents decomposition of the sample during IR, measurement of the sample effort is made not to saturate the sample with nujol to prevent domination of the Nujol bands in the spectrum, making it difficult to observe the peaks of the substance being measured.

3.2.3.3 Gaseous Samples

To determine IR spectrum of a gaseous sample, the sample is put in an evacuated cylindrical cells which is made of glass or metal, but having IR transparent materials as windows at two ends, such as KBr or NaCl. The path length of the cell is a few centimeters to several meters (normally 10 cm). The evacuation and filling of the cell are made possible by inlet and outlet ports which are controlled by values.

Gas phase spectra molecules show two special features:

(i) Rotational fine structure is observable for certain small molecules due to excitation of the rotational states of the molecule simultaneously with the Vibrational excitation.

(ii) Some bands which are strong in the condensed phase, and get their intensity from intermolecular interactions are weak in gaseous samples since the molecules are isolated.

Table 3 .1 Some characteristics infrared absorption frequencies

Functional group	**Type of vibration**	**Characteristic Absorption Frequencies (cm^{-1})**	**intensity**
Alkane			
C-H	Stretching	2850-3000	Strong
-CH	Bending	1350-1480	Variable
Alkene			

=C-H	Stretching	3010-3100	Medium
=C-H	Bending	675-1000	Strong
C=C	Stretching	1620-1680	Variable
Alkylhalide			
C-F	Stretching	1000-1400	Strong
C-Cl	Stretching	600-800	Strong
C-Br	Stretching	500-600	Strong
C-I	Stretching	500	Strong
Alkyne			Strong, Sharp, Variable Absent In Symmetric Alkynes
C-H	Stretching	3300	
—C≡C—	Stretching	2100-2260	
Aromatic			
C-H	Stretching	3000-3100	Medium
C=C	Stretching	1400-1600	Medium-weak multiple bands
C-H out of plane bending patterns are useful for distinguishing ring substitution patterns,		690 750	Mono-substitution Ortho-disubstitution

as follows		690 and 780 800-850	Meta-disubstitution Para-disubstitution
Alcohol/Phenols O-H O-H C-O	Stretching (hydrogen-bonded) Stretching (free) Stretching	3200-3600 3500-3700 1000-1250	Strong, broad Strong sharp Strong
Amines N-H N-H C-N	Stretching Bending Stretching	3300-3500 1600 1080-1360	Medium (primary amines have two bands, secondary amines have one band weak) Medium Medium-weak
Nitro N-O	Stretching	1500-1600 and 1300-1390	Strong two bands
Nitriles $C\equiv N$	Stretching	2250, conjugation shifts the absorption to lower	Medium

		frequencies	
Carbonyl groups.			
C=O	Stretching	1670-1820 (conjugation shifts absorption to lower frequencies	Strong
Aldehyde			
C=O	Stretching	1720-1740	Strong , medium, two peaks
=C-H	Stretching	2820-2850 and 2720-2750	
Ketone			
Acyclic	Stretching	1750-1725	Strong
Cyclic	Stretching	3-membered 1850	
		4-membered 1780	Strong
		5-membered 1745	
		6-membered 1715	
		7-membered 1705	
α, β-unsaturated	Stretching	1665-1685	Strong
Arylketones	Stretching	1680-1700	Strong

Acid			
C=O	Stretching	1700-1725	Strong
O-H	Stretching	2500-3300	Strong, very broad
C-O	Stretching	1210-1320	Strong
Anhydride			
C=O	Stretching	1800-1830 and 1740-1775	Two bands
Ester			
C=O	Stretching	1735-1750	Strong
C-O	Stretching	1000-1300	Two bands or more
Amide			
C=O	Stretching	1640-1690	Strong
N-H	Stretching	3100-3500	Unsubstituted, have two bands
N-H	Bending	1550-1640	
Acid Chloride			
C=O	Stretching	1800	
Ether			
		1000-1300 (1070-	

C-O	Stretching	1150)	Strong

3.2.4 The Fingerprint Region

The region of the infra-red having absorption bands between 1250 and 675cm^{-1} consist of complicated absorptions due to complex vibration and rotational energy changes within the molecules. This region is called the fingerprint region.

The fingerprint region is complex and does not permit a complete analysis of an entire spectrum. This region is not useful in identifying individual bonds/ functional groups because each absorption band in this region often overlap with other bands. Rather, the finger print region is used to distinguish two compounds having isomeric relationship , both compounds having similar vibrational peaks in the main regions of their IR spectra.

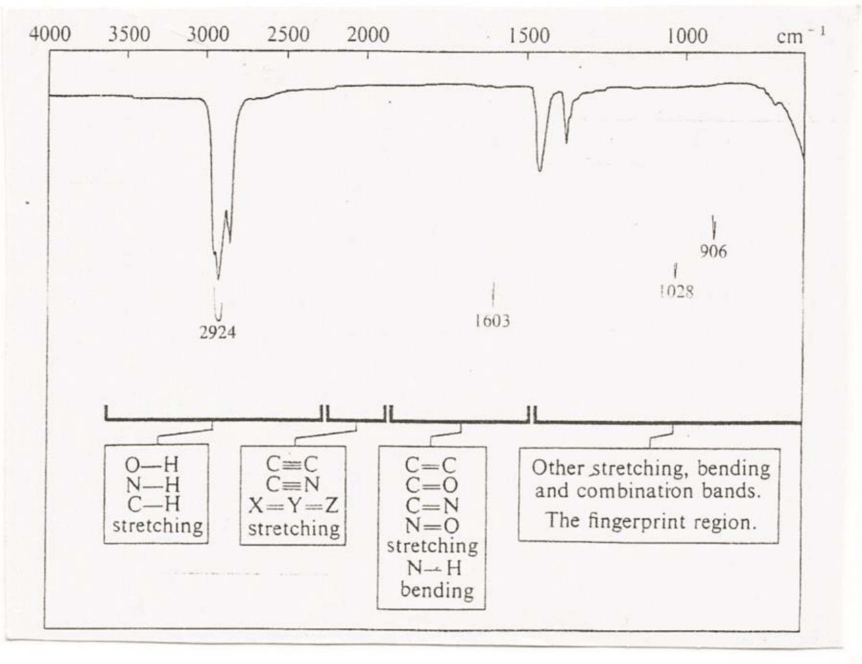


Figure 3.4 Common regions of the IR spectrum. Source: Spectroscopic Methods in Organic Chemistry, 2nd Edition, by D.H. Williams and I. Fleming.

Comparing the infrared spectra of propan-1-ol and propan-2-ol, it will be observed that the spectra of the two compounds have similar absorption bands in the region 4000 to 1250cm^{-1}, but differ in the 1250 to 675cm^{-1} region.

The fingerprint region is useful for correlating spectra. If the infra-red spectra of two samples are identical in the frequencies ranging from 3600 to 675cm^{-1} there is very high probability that both samples are of the same compound.

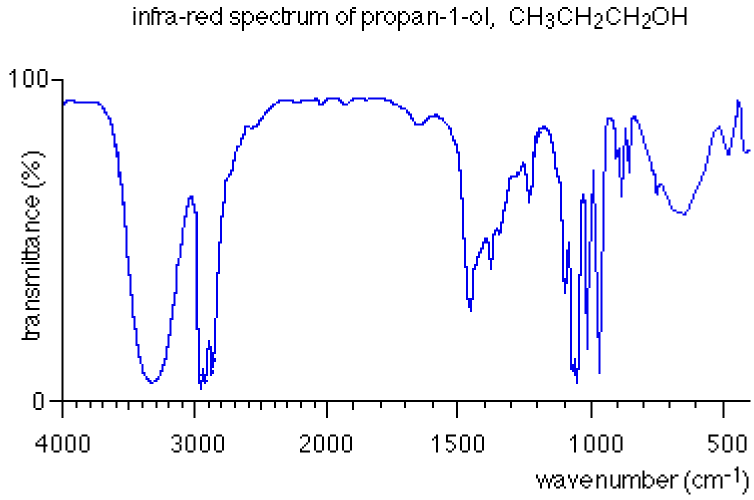


Figure 3.5 IR spectra of propan-1-ol. Source: www.chemguide.co.uk

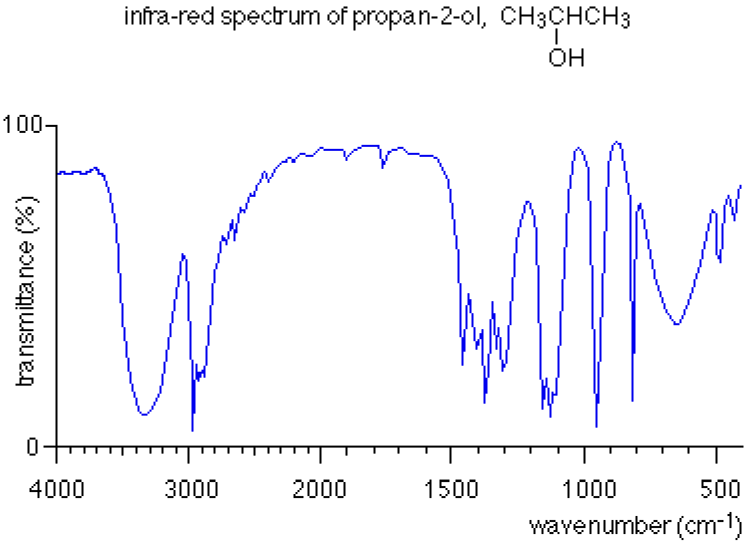


Figure 3.6 IR spectra of propan-2-ol. Source: www.chemguide.co.uk

3.3 Raman spectroscopy

3.3.1 Theory of Raman Scattering

When a molecule experiencing vibration and rotation absorbs photons, the light is emitted (scattered) elastically or inelastically. The inelastic scattering is the Raman effect. Chemist are concerned with vibrational Raman effect.

The light from the laser source falls on a molecule experiencing vibration or other form of excitation, the energy of the laser is shifted up or down. Information from the energy shift determines the modes of vibration in the system.

In the experimental arrangement for Raman spectroscopy, a laser which is a source of monochromatic light falls on a molecule in a state of vibration or rotation, changes occur in the molecular vibration and rotation before the light is emitted or scattered.

The changes in the rotational and vibrational energy lead to changes in wavelength of the incident light which are observed as lines falling above and below the wavelength of the incident light. The positions of these lines in Raman spectra are in wave numbers

3.3.2 Elastic and Inelastic scattering

3.3.2.1 Rayleigh scattering

Rayleigh scattering occurs when photon is absorbed to a higher level known as the vitual level and instantaneously emitted (scattered) to the initial level. This is an elastic scattering.

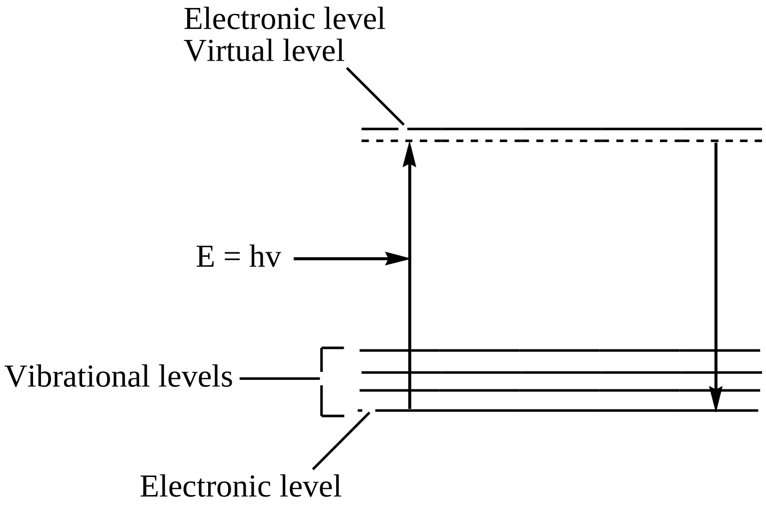


Fig.... Rayleigh Scattering

Figure 3.7 Rayleigh Scattering

3.3.2.2 Stokes – Raman Scattering

In stokes – Raman scattering the emitted photon possess a lower energy and frequency than the absorbed photons. The photons in this case are inelasticlly scattered, some of the energy of the photons are transferred to the molecule.

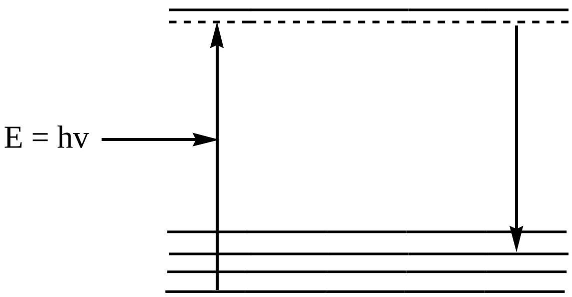


Fig.... Stokes-Raman Scattering

Figure 3.8 Stokes-Raman scattering

3.3.2.3 Anti – stokes Scattering

When the emitted photons possess higher energy than the absorbed photons, anti-strokes scattering occurs. This is less likely to take place at room temperature because at room temperature electrons would not occupy an excited level rather they would prefer the ground state.

The stokes and anti-stokes scattering are called Raman scattering which provides the rotational and vibration information needed for Raman spectroscopy.

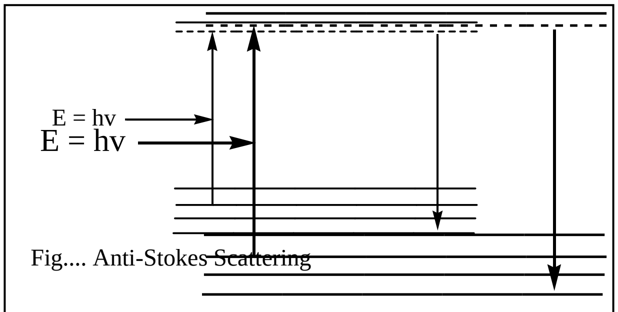


Fig.... Anti-Stokes Scattering

figure 3.9 Anti-Stokes scattering

The Rayleigh scattering is of the strongest intensity followed by stokes. Antistokes is the weakest.

The main challenge of Raman spectroscopy is to reduce the intensity of Rayleigh scattering. This is achieved by using multiple monochromators to filter out the unwanted wave and allow the needed wave range i.e. stokes and antistokes.

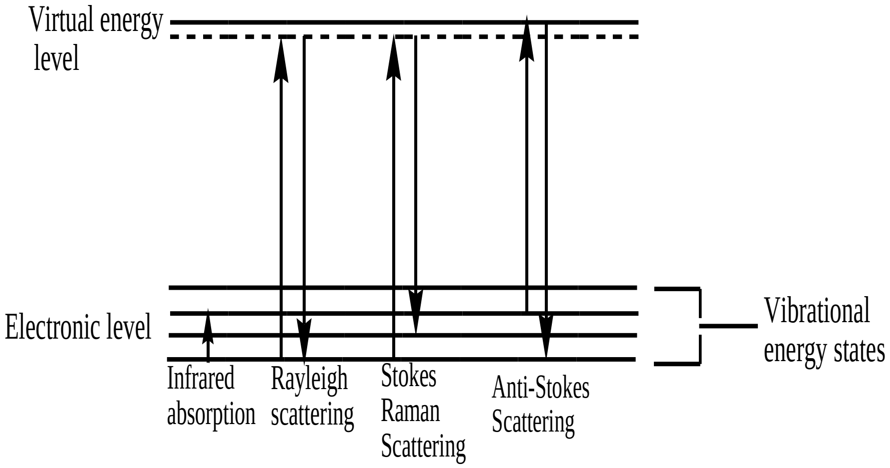


Figure 3.91 infra-red and Raman scattering.

Raman Spectroscopy provides a fingerprint which is used to identify a molecule

Raman spectroscopy gives complementary information to infra-red spectroscopy, but the spectra are not identical. Electrically symmetrical molecules do not absorb infra-red radiation therefore symmetrical molecules such as H_2O_2 and $CH_2=CH_2$are infrared inactive , but such molecules have absorptions which are strongly observed in the Raman Spectrum

3.3.3 Advantages of Raman Spectroscopy

1. Gives information about the chemical composition and structures of materials Raman spectroscopy, gives information about the atoms and their arrangement in the substance. For example, both graphite and diamond contain carbon atoms, but give different information in their respective Raman spectra.
2. Sample Preparation not necessary: If only an optical microscope can be focused on the region of analytical interest, a Raman microscope can be used to collect its Raman Spectrum.
3. Non-destructive: Sample analysis can be done several times without damage of the sample.
4. Analysis is Possible through transparent container and windows: Raman information can be got when the sample is in a transparent container such as a vial or capillary tube, or if the sample is contained in a cell with a viewing window.
5. Sensitive to subtle differences in structure of material: Raman spectroscopy is used to detect the small changes arising from chemistry and molecular structure due to arrangement of atoms within the molecular environment.
6. Sample can be analyzed in water: Sample can be analyzed in aqueous solutions for example suspensions and biochemical samples. Processes such as extraction or drying which are time consuming and may change the chemistry of the sample are not necessary.
7. Variable sample sizes can be analyzed: Good Raman microscopes are capable of allowing different amount of sample, ranging from very minute to large amounts.
8. It can be used for almost all material: apart from pure metals which reflect light, Raman spectroscopy can be used on almost all other materials, because of their ability to Raman scatter.

9. Raman spectroscopy uses light: It is easy to manipulate light in the course of Raman spectroscopy. A powerful microscope fitted to the spectrometer will enable analysis of particles in the micrometer range.

Data from Raman spectroscopy can be analyzed via fibre optics to a remote station.

3.3.4 Comparing Raman with Infra-red Spectroscopy.

1. Their main difference is based on the molecular transitions occurring in each case: In Raman spectroscopy there is change in the polarizability in the molecule during vibration. Change in molecular polarizability is change in position of electron cloud of the molecule. In infrared spectroscopy there must be change in molecular dipole moment. For example in a symmetrical molecule such as O_2 there is no change in dipole moment hence shows no observable infrared absorption. However, molecules having strong dipole moment have low polarizability.
2. Excitation Wavelength: Raman spectroscopy employs a monochromatic laser or beam whose wavelength is in the visible, near-infrared or near ultraviolet range. The wavelength used in the IR is in the infra-red region.
3. The resulting spectra: The spectrum of IR show lines corresponding to absorptions (or transmittance) of photons by the sample. Whereas Raman spectra show scattered light which comprise elastically scattered (Rayleigh) line and inelastic (Stokes and Anti-stokes) scattered light. The anti-stokes line is weak and not easily detected.
4. Cost: Raman spectroscopy instrument are more expensive than infrared equipment. The higher cost of Raman spectrophotometers is because they require highly stable laser sources.

3.3.5 Instrumentation of Raman Spectrometer

The main components of a Raman spectrophotometer consists of the following:

1. Monochromatic light source: Typically laser source which transmit light in the wavelength of ultraviolet, visible or near infrared.
2. Arrangement of optical components lenses and mirror which focuses the light on the sample and collect the scattered light.
3. A spectrometer.
4. A detector

Notch filters are used to filter the Rayleigh line before the scattered light enters the spectrometer and detector.

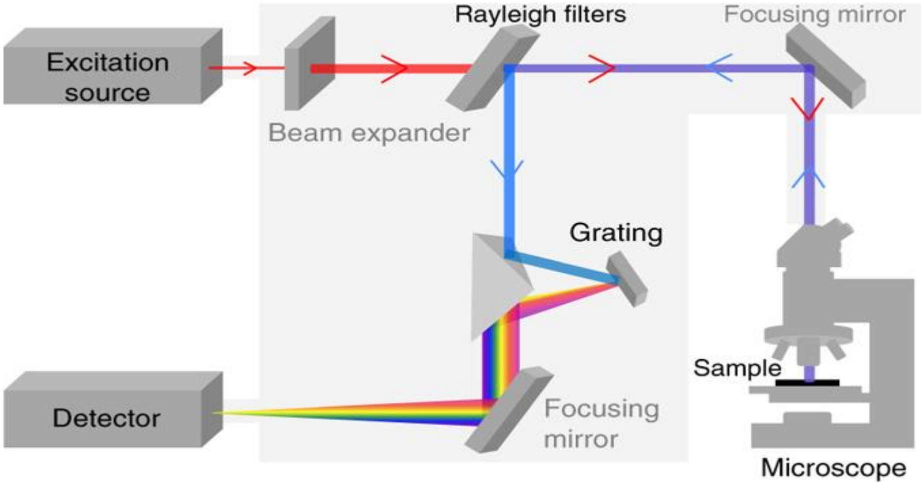


Figure 3.92 instrumentation for Raman spectrometer.

Source: https://www.nature.com

4.0 CONCLUSION.

The frequencies of stretching and bending vibration of a molecule are used in the identification of the functional groups present. When a molecule absorbs electromagnetic radiation in the IR region the energy of radiation causes vibrational and rotational changes in the molecule.

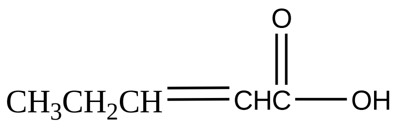
Both IR and Raman technique are employed in the identification of functional groups in the molecule. Raman spectroscopy involves scattering of monochromatic light by a vibrating molecule which gives information about its mode of vibration. Raman spectroscopy depends on change in polarizability in the molecule during vibration, whereas in infrared spectroscopy there must be change in molecular dipole moment.

5.0 SUMMARY

The normal modes of vibration of a molecule can be classified into stretching and bending types. The infrared region of the spectrum is divided into near, mid and far IR. The mid IR is the spectroscopically more useful of the three, it is used to study fundamental vibrations and associated rotational vibrational structure. Though each functional group has a unique frequency of absorption band in the 4000-1250 cm^{-1} range, the fingerprint region in the 1250-675cm^{-1} is useful for distinguishing molecules which may have similar spectra in the main region. In the instrumentation for IR, a Fourier transform spectrophotometer is employed to overcome the limitations of the classical spectrophotometer. Raman spectroscopy is based on inelastic scattering of light in the near IR and near UV region.

Solved Problems

1. Predict the positions of absorptions of in the IR spectrum of:



$CH_3CH_2CH{=}CH\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$

Solution :

-OH 3000cm^{-1} broad

=CH 3100-3000cm^{-1}

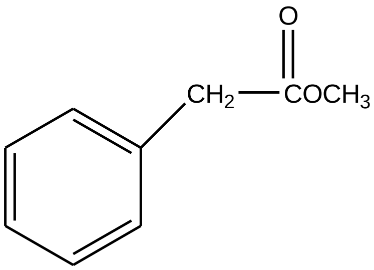
-CH 3000-2850cm^{-1}

C=O 1725-1700cm^{-1}

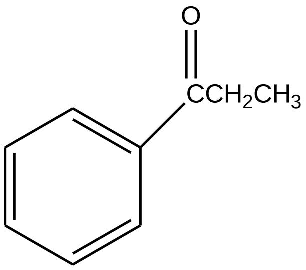
C=C 1660-1640

2. Use IR absorption bands to distinguish between the two compounds below

Predict the IR absorption peaks in the compounds below:



A



B

Solution:

A (Ester)

C=O 1740cm^{-1}

C-O 1300-1000cm^{-1}

B (Ketone)

C=O 1715cm^{-1} (-20 to -40)

=1695 to 1675cm^{-1}

6.0 Tutor Marked Assignment

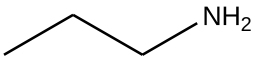
1. Explain the basic principle of infrared spectroscopy.

2. Describe (i) Continous wave spectrometer (ii) Fourier-Transform spectrometer.

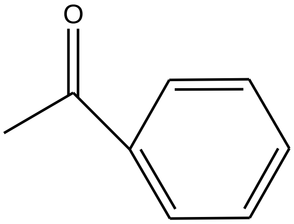
3. Explain the preparation of different samples for IR spectroscopy

4.

a



b



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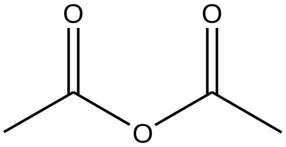

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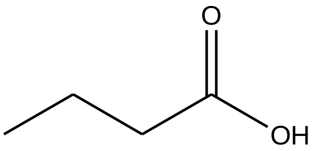

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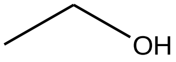

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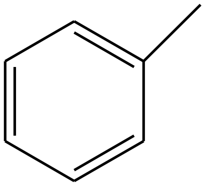

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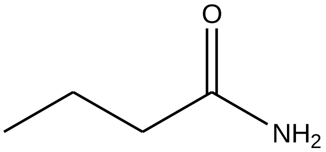

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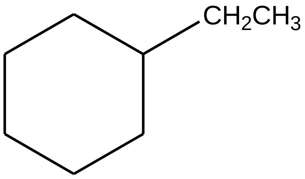


5. Draw the structures of two isomers of C_3H_6O which have the following IR absorption peaks.

a. 3100, 2900, 1650, 1100cm^{-1}

b. 2900 and 1715cm^{-1}

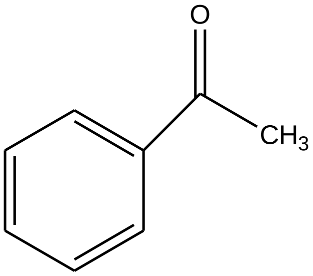
6. Use IR spectroscopy to distinguish between the following pairs of isomers:

a. $CH_3CH_2CH_2C\equiv N$ and $CH_3C\equiv CCH_2NH_2$

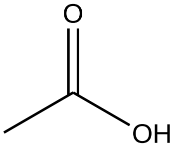
b. $CH_3CH_2COCH_3$ and $CH_3CH_2CH_2CHO$

7. Sketch the IR spectrum of

a.



b.



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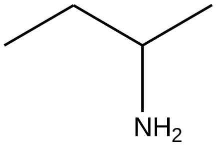

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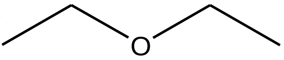

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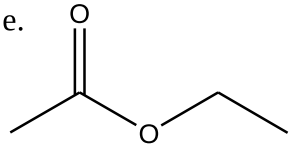


8. Explain the principle of Raman spectroscopy.

9. Classify the following molecules as infrared or Raman active

(a) CO_2 (b) CO (c) $CH_2 = CH_2$ (d) $(CH_3)_2$ (e) $CH_3CH = CHCH_3$ (f) O_2

9. Write brief notes on

(i) Elastic scattering (ii) Inelastic scattering

10. What are the advantages of Raman spectroscopy?

11. Compare Raman with IR spectroscopy.

12. Describe the instrumentation for Raman spectroscopy.

7.0 Reference/ Further Readiing

Chemguidewww.chemguide.co.uk/analysis/ir/fin...

Workman, J. (1998). *Applied Spectroscopy: A Compact Reference for Practitioners*. San Diego: Academic Press.

Atkins, P.W. & Friedman, R. (2008).*Quanta, Matter and Change: A Molecular Approach to Physical Change*. Oxford: Oxford University Press.

MODULE 2

UNIT 1 ULTRA VIOLET – VISIBLE (UV-VIS) SPECTROSCOPY

CONTENTS

1.0 INTRODUCTION

The Ultra violet - visible range of the electromagnetic spectrum, (200-400nm) and (400-800nm) cause electronic transitions. When a molecule absorbs UV-visible light one of its electrons jumps from a lower energy to a higher energy molecular orbital.

The HOMO of the ground state and the LUMO of the excited state are involved in the excitation.

2.0 OBJECTIVES

At the end of this unit, you will be able to

- Draw the energy diagram showing electron transitions.
- State the allowed and forbidden transitions.
- State the applications of UV-visible spectroscopy.
- Define important concepts in UV-visible spectroscopy.
- Explain effect of solvent on absorption maxima.
- Describe the instrumentation for UV-visible spectroscopy.

3.0 MAIN CONTENT

3.1 Energy Diagram of Electronic Transitions

The electronic transitions which are possible include: p-p*, n-p*, s-s*, and n-s* and illustration below is a hypothetical energy diagram.

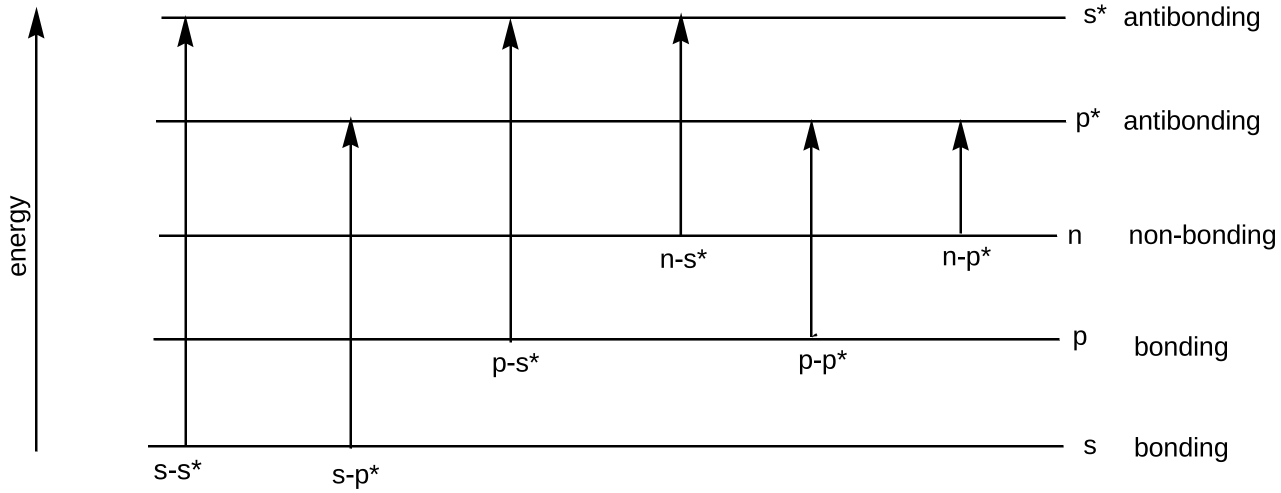


Figure 2.1 Types of electronic transition.

The s-s* absorption transition required wavelength which is beyond the UV-visible range. However, only p-p* and n-p* transitions are observable in the UV-visible region. These transitions are quantized. According to selection rules which are based on orbital symmetry of quantum theory, s-s* and p-p* are allowed transition, n-s* and n- p*.are forbidden. Although certain forbidden transitions can occur, but their probability and intensity of peaks are lower than those for allowed transitions.

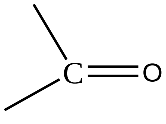
3.2 Applications

UV-visible spectroscopy is used as a routine tool for quantitative analysis of highly conjugated organic molecules biological macromolecules and transition metal ions. Analysis can be done mostly in solutions. Solid and gaseous samples may also be analyzed.

3.3 Important Definitions

3.3.1 Chromophores

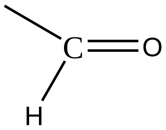
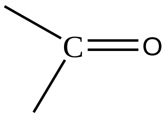
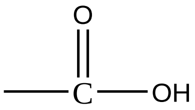
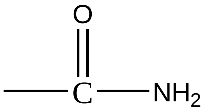
Chromophores is the system which contains the electrons responsible for absorption of UV-Vis radiation. The presence of non bonding electrons and loosely bound electrons as in π and n molecular orbitals are responsible for these absorption. The wave length and intensities of these absorption are recorded using a spectrophotometer.

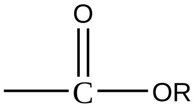
Most simple unconjugated chromophores are of little significance due to their short wavelength and high energy. However, one simple unconjugated chromophore is the ketone  very weak, n-p* transition at 300nm which is used in optical rotatory dispersion. This absorption bond result from excitation of one of the lone pair of elevtrons (n) on the oxygen to the lowest anti bonding obital (p*) of the carbonyl.

Important chromophores are those possessing a system of conjugated double bonds. Long conjugated polyene system like carotene exhibit strong absorptions, this is quite manifest in its colour in the visible region. Generally, longer conjugated systems give more obvious absorptions because they have longer wave length of absorption maxima.

The solvents used to make solutions for this determination are water if the compound is soluble in water or ethanol for compounds soluble in organic solvents. Ethanol is preferred because other organic solvent absorb strongly, but ethanol show weak absorption.

Table 2.0 Some common chromophores

Chromophore	**Type of excitation**	**λmax (nm)**	**ξ**	**Solvent**
Alkene C=C	*p*- *p* *	177	13,000	n-Heptane
Alkyne $C\equiv C$	*p* - *p* *	180	10,000	n-Heptane
Aldehyde 	*p* - *p* *	180	10,000	n-Hexane
	n- *p* *	290	15	
Ketone 	*p* - *p* *	186	10,000	n-Hexane
	n- *p* *	280	16	
Carboxylic acid  $-C(=O)-OH$	n- *p**	204	41	Ethanol
Amide  $-C(=O)-NH_2$	n- *p**	220	63	Water
Ester	n- *p* *	210	50	Gas

 $-C(=O)-OR$				
Nitro N=O	*p* - *p* *	200	5000	Ethanol
	n- *p* *	275	17	

3.3.2 Auxochrome:

An auxochrome is a group which when substituted on a chromophore shifts the absortion maximum to longer wavelength. For example an isolated double bond (C=C) absorbs at 190nm. When nitrogen is bonded to it to give an eneamine, the conjugation on the nitrogen atom shifts the absorption maxima to 230nm. The nitrogen substituent which causes this shift to higher wavelength is the auxochrome. Therefore, an auxochrome extends a chromophore to give a new auxochrome.

Examples of auxochromes are hydroxyl group (- OH), amino group (- NH_2) and aldehyde group (- CHO)

3.3.3 Bathochromic Shift (Red Shift):

A bathochromic shift is a shift of absorption maximum to a longer wavelength. Bathochromic shift can result from the presence of an auxochrome on the chromophore or a change of medium.

3.3.4 Hypsochromic Shift (Blue Shift):

A hypsochromic shift or blue shift is a shift of absorption maximum to a shorter wavelength. This may be caused by either a change of medium or removed of conjugation of the chromophore. For example in aniline, there is conjugation of the lone pair of electron on nitrogen with the π-system of benzene, and aniline absorbs at 230nm. In acid medium, aniline is protonated and the conjugation between nitrogen lone pair electron and benzene ring is disrupted, the absorption maximum will now be at 203nm which is identical to that of benzene.

3.3.5 Hyperchromic Shift:

This is an increase in absorbance (absorption intensity). A or molar extinction coefficient, ξ of an absorption band. The term describes an increase in intensity

3.3.6 Hypochromic Shift:

This is a decrease in absorbance, A or molar absorptivity. It means a decrease in intensity.

3.4 Effect of Solvent on Absorption Maxima

The nature of solvent affects the absorption of molecules in the UV-visible region. For molecules experiencing p-p* transition, electrons in the molecule as well as the solvent reorganize giving an excited state which is polar compared with the ground state. The resulting dipole-dipole interaction which occurs between the molecule and the solvent (if polar) will cause the excited state to be in a state of lower energy than the ground state. Thus using ethanol solution will make absorption to occur at a longer wavelength maxima (red shift of about 10 to 20nm) compared to using hexane as solvent.

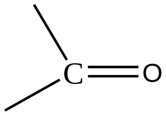
In n-p* transition such as in , n-p* transition of electrons, the effect of solvent is reverse of the p-p* solution. Energy increase (shorter wavelength) results from lesser ability of the solvent to hydrogen bond to the excited carbonyl. For example acetone absorb at 279nm in hexane, but 264.5nm in water. This shift to lower wavelength is known as blue shift. Generally, type of transition and polarity of solvent affect absorption maxima of organic molecules. pH also affect absorption bands of organic compounds. For example the absorption maxima of tyrosine as well as its molar coefficient extinction, coefficient increase when pH of the solution increases from 6 to 13.

Table 2.1 Solvents used in UV-visible spectroscopy and their minimum wavelength of absorption.

solvent	Min. wavelength of absorbance
Acetonitrile	200
Water	191
Cyclohexane	195
Hexane	201
Methanol	203
Ethanol	204
Ether	215

Dichloromethane	220
Trichloromethane	237
Tetrachloromethane	257

3.5 Instrumentation of UV/Visible Spectrometer

The instrument used in UV/Vis spectroscopy is a UV/Vis spectrophotometer. Example is Beckman DU640 model.

A spectrophotometer is made up of the following basic components.

1. Source of UV-visible radiation
2. Filter or monochromator
3. Sample cells
4. Detector.

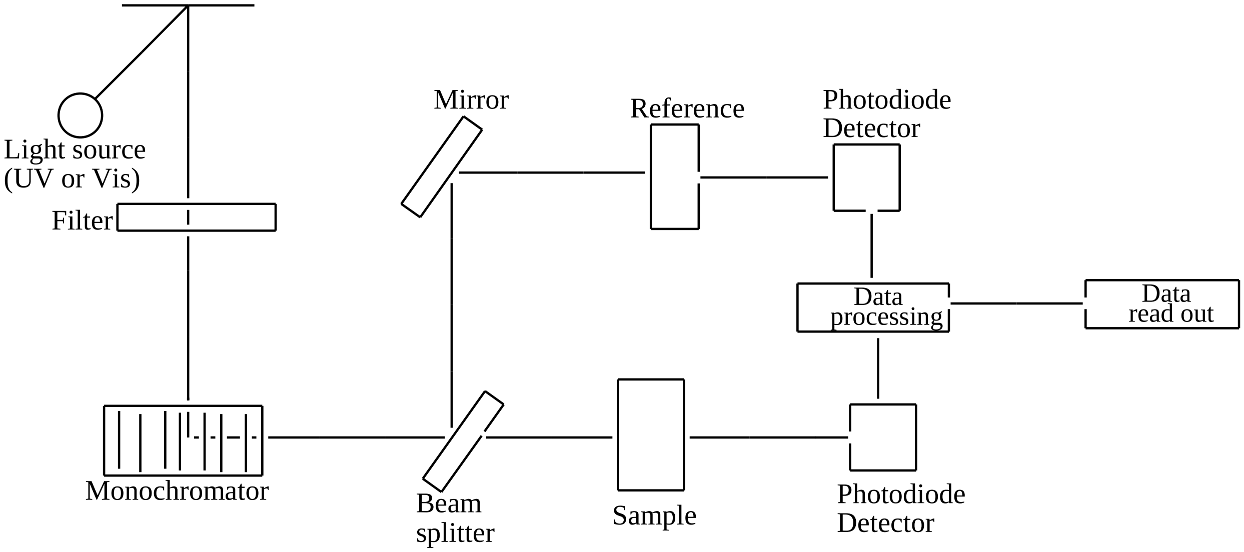
3.4.1 Source of Radiation

Deuterium or hydrogen lamps are used as radiasources capable of producing light in the range 160-375nm for UV radiation. Other radiation sources for UV are Tungsten, lamp, xenon discharge lamp and mercury arc lamp. Sources for visible radiation are Tungsten lamp, mercury vapour lamp and carbonate lamp. However tungsten filament provides light from 320-2500nm for visible region.

Radiation from the source enters the monochromator through the slit. The radiation is collimated and then strikes the diffraction grating or prism which split the beam into its component wavelengths. By rotating a chopper light of a particular wave leaves the monochromator and is directed towards the sample cell/container.

The container holding the sample is also called the cell. The cell should be transparent to the region of wavelength of measurement. Rectangular curettes made of quarts are used which are transparent in the 350-2000nm and 1cm thick.

Radiation emerging from both the sample and reference cells are detected using photosensitive detectors such as photovoltaic cell, photomultiplier tube or photoemissive tube.



Schematic diagram of a double beam UV-Visible spectrophotometer.

Fig. 2.2 Schematic diagram of a double beam UV-Visible spectrophotometer.

Intensity of light incident on a sample is denoted as I_o while the intensity of light passing through the sample is I.

The ratio $I/I_o$is called the transmittance T. Transmittance is usually expressed as percentage transmittance (%T). Absorbance is related to transmittance:

A = -log (%T/100%)

4.0 CONCLUSION

UV-visible spectroscopy is an important tool for quantitative analysis of organic molecules. It is caused by electronic excitation in molecules when they interact with UV-visible radiation. Organic compounds that can be analysed by UV-visible spectroscopy are those having highly conjugated systems.

5.0 SUMMARY

UV-visible excitation involves LUMO and HOMO excitation. The electrons responsible for absorption of uv-visible radiation are called chromophores. Substitution on the chromophores shifts the position of absorption maximum. The nature of solvent affects the absorption of molecules, thus for *p* - *p** transition, polar solvent will make absorption to occur at a longer wavelength, than using non-polar solvent, and vice-versa for n- *p* *.

6.0 TUTOR MARKED ASSIGNMENT

1(a) Sketch an energy diagram to illustrate possible electronic transitions.

(b) State the transitions that are allowed. (c) state the forbidden transitions.

2. Define the following: (i) Chromophore

(ii) Auxochrome

(iii) Bathochromic Shift

(iv) Hypsochromic Shift

(v) Hyperchromic shift

(vi) Hypochromic Shift

3. Briefly describe the instrumentation of a UV-visible spectrophotometer

4. Explain the influence of nature of solvent in uv-visible absorption

7.0 Reference/ Further Readiing

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media.rsc.org/Modern%2520chemical%2…

www.molecularinfo.com/MTM/UV.pdf

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UNIT 2 ABSORBANCE AND TRANSMITTANCE

Contents

1.0 INTRODUCTION

The more there are molecules absorbing light of a particular wavelength, the greater the extent to which the molecules absorb light and higher the intensity of the peak in absorption spectrum. If few molecules are absorbing radiation, the extent of light absorption will be less, leading to lower peak intensity. This is the basis of Beer-Lambert Law.

2.0 OBJECTIVES

At the end of this unit, you will be able to

- State Beer-Lambert law.
- Derive Beer-Lambert law expression.
- Solve calculations involving Beer-Lambert law.
- Explain the effect of conjugation on λ_{max}
- Use Wood Ward Feiserrules to calculate $\lambda_{max}$of dienes and polyenes.

3.0 CONTENT

3.1 Beer-Lambert Law

Beer-Lambert law states that absorbance, A is directly proportional to the concentration, C of absorbing molecules and the path length, l of the radiation passing through the sample.

The concentration is measured in $moldm^{-3}$ and path length l is in cm.

Intensity of light incident on a sample is denoted as I_o, while the intensity of light emerging from the sample is I. ξ is the molar extinction coefficient. The unit of molar absorptivity is $dm^3cm^{-1}mol^{-1}$. ξ indicates the wavelength at which measurement is made.

Transmittance = I/I_o.

$Log_{10}\ I_o/I = \xi.l.C$

Absorbance or optical density, $A= log_{10}\ (I_o/I)$

$A=log_{10}\ (I_o/I) = \xi.C.l$

The UV-visible absorption of a sample is presented as a plot of absorbance (or transmittance)

against wavelength. The concentration of an absorbing solution can be calculated using information from molar absorptivity and absorbance at a given wavelength.

Solved calculation problems:

Problem 1

Calculate the concentration of a solution of a compound with molar absorptivity constant of $15000M^{-1}dm^{3}cm^{-1}$ and absorbance of 0.72 at λ_{max}465nm with a path length of 1.1cm?

Solution:

Using Beer-Lamberts law, $A = \xi_{\lambda}cl$

Thus, $c = (A/\xi_{465})l$

$= 0.75/1.5x10^{4}M^{-1}dm^{3}cm^{-1}x1.1cm$

$= 0.45x10^{-4}M.dm^{-3}$

Problem 2

A solution with concentration of 0.15M is measured to have an absorbance of 0.56. Another solution of the same compound measured under the same condition has an absorbance of 0.42. What is its concentration?

Solution:

From Beer’s law, absorbance is directly proportional to concentration. In other words, the ratio of concentration is proportional to the ratio of absorbance.

C_1 = 0.5M

A_1 = 0.56

C_2= ?

A_2 = 0.42

$C_1/C_2 = A_1/A_2$

$C_2 = C_1 \times (A_2/A_1)$

= 0.15M x (0.42/0.56)

= 0.11M

Problem 3:

From the Table below, what is the concentration of a 1.00 cm (path length) sample that has an absorbance of 0.82

Concentration (M)	Absorbance
0.10	0.14
0.20	0.35
0.30	0.46
0.40	0.60

Solution:

First, plot the graph of absorbance against concentration.

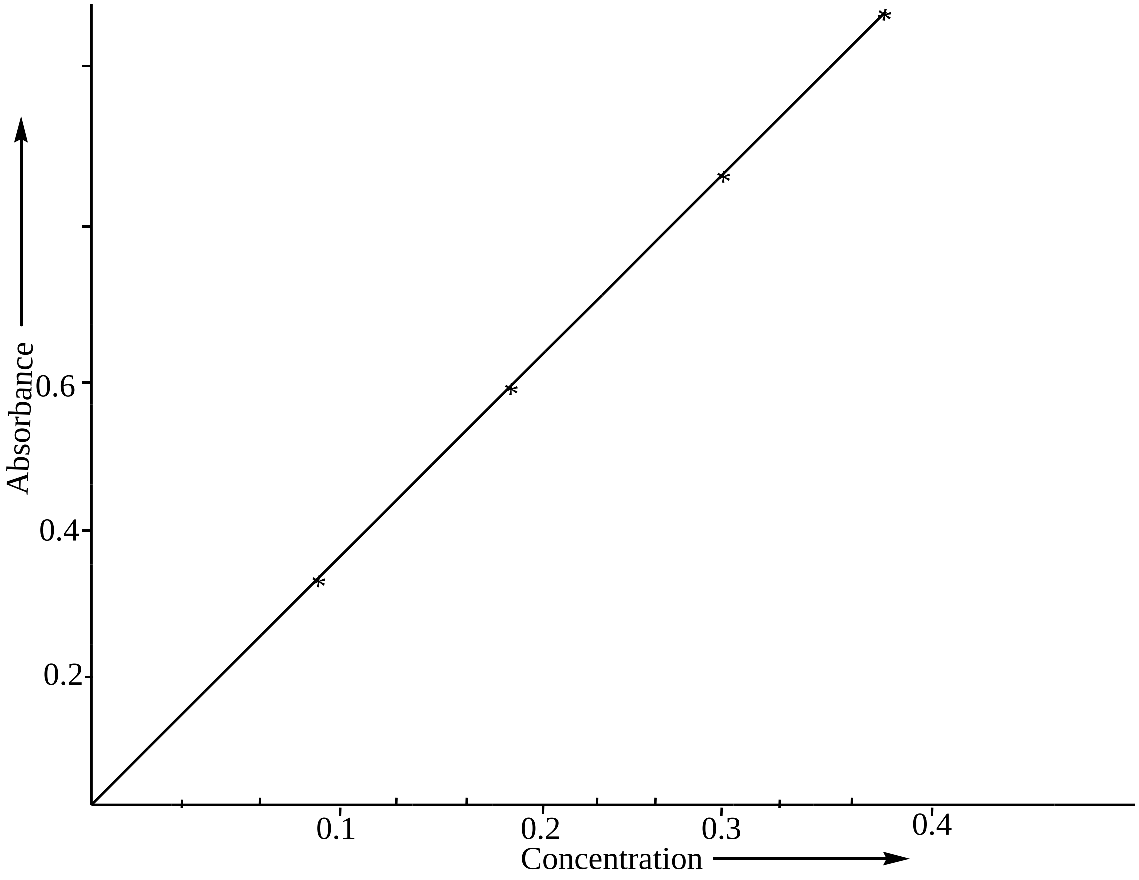
Then calculate the concentration for the solution thus:

$$concentration = \frac{Absorbance}{Slope}$$

The slope of the line of best-fit in this case is the product of molar absorptivity and the path length. i.e slope=ξ.l

A = ξ.l.C.

C = A/ξ.l



3.2 Effect of Conjugation on λ_{max}

The UV visible range of the electromagnetic spectrum, (200-400nm) and (400-800nm) cause electronic transitions i.e when a molecule absorbs UV-visible light. One of its electrons jumps from a lower energy to a higher energy molecular orbital.

In H_2, its molecular orbitals picture consists of one bonding (s) MO, and a higher energy (s*) antibonding MO. the lower- energy bonding MO is the HOMO (Highest Occupied Molecular Orbital). The anti bonding MO orbital of higher energy, is the LUMO (Lowest Unfilled Molecular Orbital).

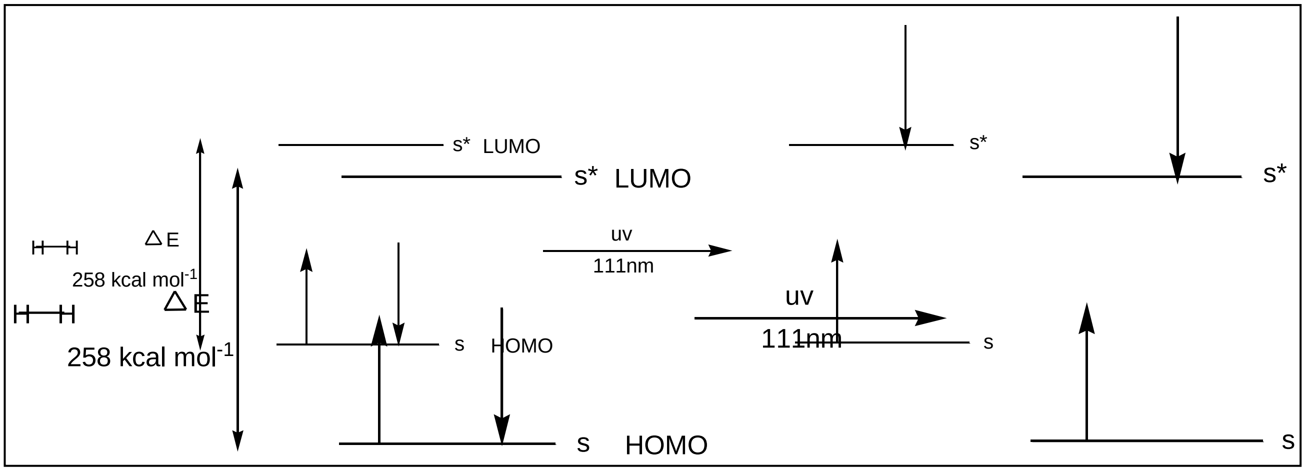


Fig.2.3 Electronic transitions in Hydrogen molecule

If the molecule absorbs light of wavelength equal to ΔE, the energy promotes one electrons from the HOMO to the LUMO i.e. from s to s*. The energy for this transition is 258 Kcalmol^{-1} which is equivalent to 111 nm.

When C=C having double bond such as ethene absorbs light it undergoes a p-p* transition. p-p* energy are narrower than s-s* Energy gaps (i.e longer wavelength) ethene absorbs at 165nm.

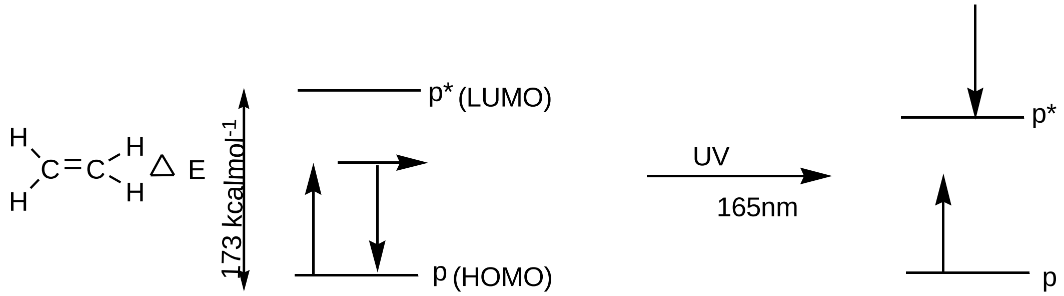
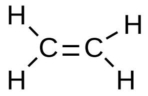


Fig. 2.4 Electronic transitions in ethene

The electronic transitions of both H_2 and  are too energetic (too short wavelength) to be recorded in UV spectrophotometer.

UV-vis spectroscopy is useful for conjugated pi systems. In these systems, the energy gap or transition is smaller than isolated system, thus absorbing at longer wavelengths.

In the MO of 1,3-butadiene, (the simplest conjugated system)

There are four pi MO's resulting from combining the four $2p_z$ atomic orbitals, two lower bonding orbitals and two higher anti-bonding orbitals.

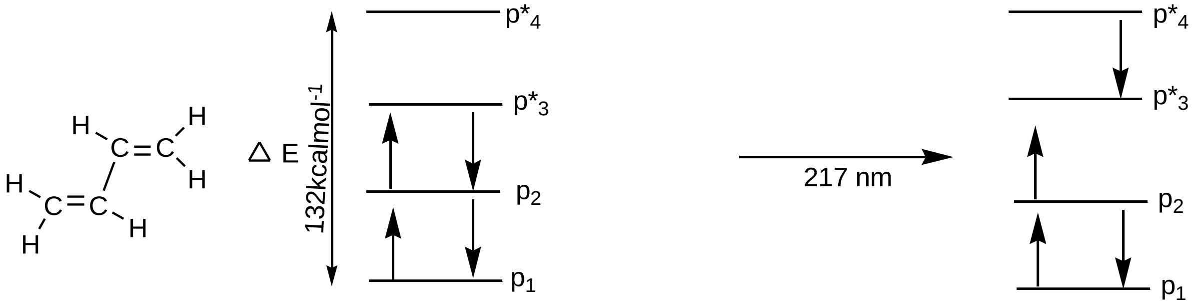


Fig. 2.5 Electronic transitions in 1,3-butadiene

Comparing the MO of ethane with 1,3 – butadiene the HOMO-LUMO energy gap is smaller (longer wavelength). Hence, 1,3-butadiene absorb UV light with a wavelength of 217nm.

With increasing conjugation of Pi system, the energy gap p-p* for transition becomes more narrow and longer wavelength. In 1,3,5-hexatriene p-p* transition occurs at 258nm, equivalent to ΔE of 111Kcal/mol.

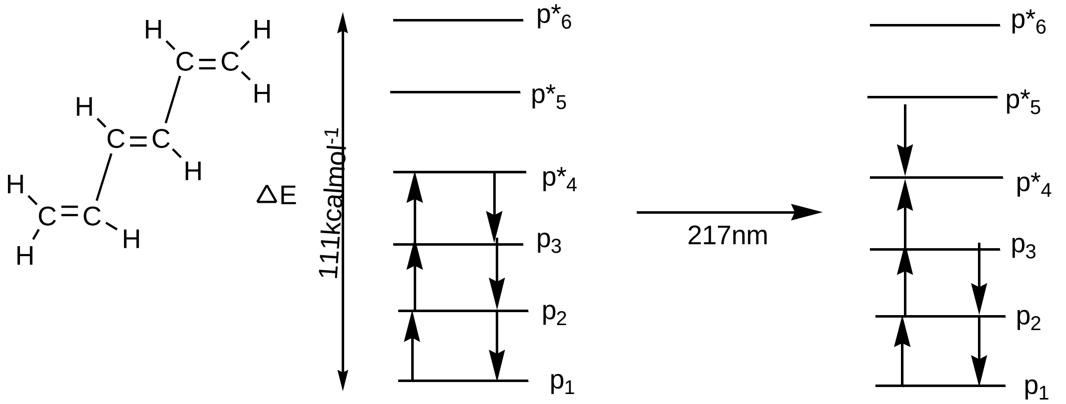
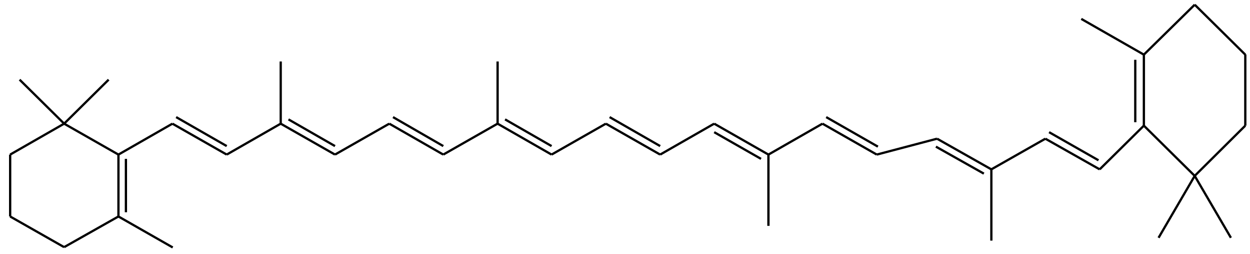


Fig. 2.6 Electronic transitions in 1,3 – butadiene

In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather than the UV region. Beta-carotene with 11 conjugated double bonds, absorb light with wavelength in the blue region of the visible spectrum while allowing other visible wavelengths mainly those in the red-yellow region to be transmitted. Thus carrots are orange in colour



β-carotene

The conjugated pi system in 4- methyl-3-penten-2-one gives strong absorbance at 236nm due to p-p* transition and at 314nm due to n-p* transition.

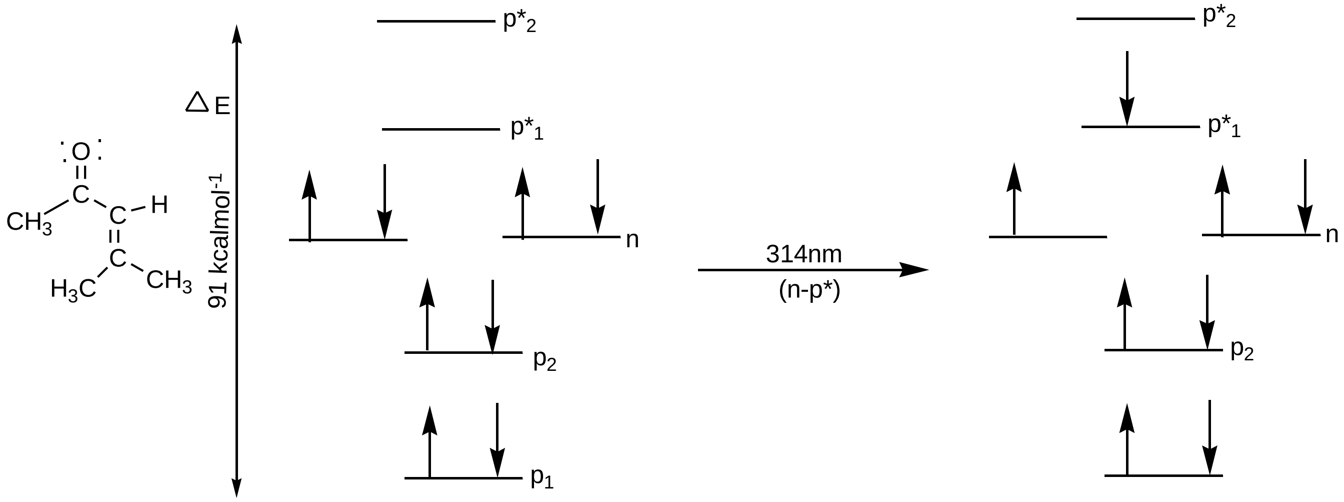
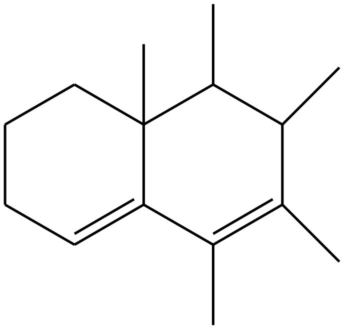


Fig. 2.7 Electronic transitions in 4- methyl-3-penten-2-one

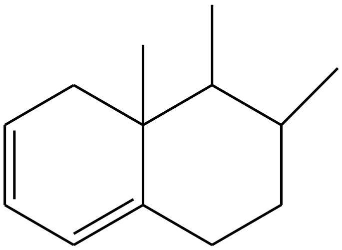
In this n-p* transition, the non-bonding n MOs are higher in energy than the highest p-orbital, so the energy gap for n-p* transition is smaller than p-p* transition, thus the n-p* occurs at longer wavelength generally, n-p* transition are weaker than p-p* transitions.

3.3 Woodward-Feiser Rules

Rules for conjugated Dienes and Polyenes



Heteroannular diene
Trans form



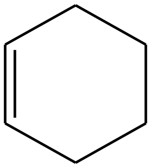
Homoannula diene
Cis form

Heteroannular diene	Homoannular diene
Parent Heteroannulardiene (or open chain)	214nm
Parent Homoannulardiene	253nm
Alkyl substituent or ring residue	+ 5
Exocyclic double bond	+ 5
Double bond extending conjugation	+ 30

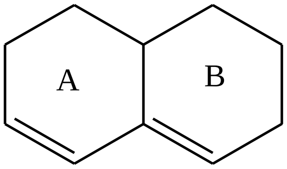
Ethanol is usually used changing solvent has no appreciable effects on the λmax value.

Polar groups	- OAC (acetate)	0nm
	- OAalkyl(ether)	6nm
	- Cl, - Br	5nm

Endocyclic double bond is a doube bond present in a ring:



Exocyclic double bond : is a double which is part of a ring system



Ring A has one exocylic double bond and one endocyclic double bond. Ring B has no exocyclic double bond, but has one endocyclic double bond.

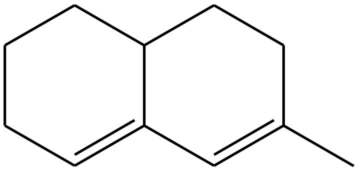
Value for homoannular diene	253nm
Value for hetroannular diene	214nm
Alkyl substituent or ring residue attached to the parent diene	5nm

Double bond extending conjugation	30nm
Exocyclic double bonds	5nm
OAC (Acetate groups)	0
-O-R(ether)	6

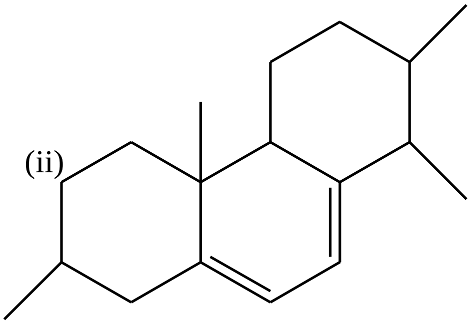
Solved Problems :

1. Calculate the absorption maximum of the compounds below:

(i)

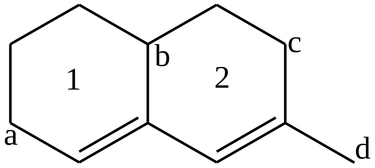


(ii)



Solution

(i)



		nm
Heteroannular diene		214
Alkyl substituent	4 X 5	= +20

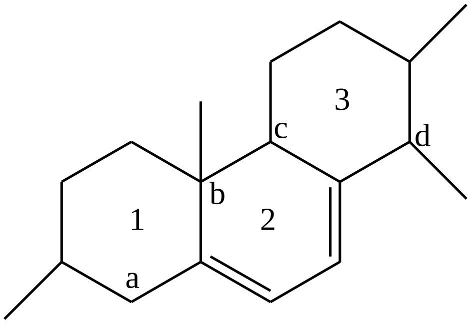
Exocyclic double bond	= +5
Total	239nm

Explanations: The base skeleton is a heteroannulardiene, hence 214nm.

The parent diene has 4 alkyl groups, labeled a, b, c, d i.e 4 X 5nm = +20nm

The double bond in ring 1 is exocyclic to ring 2 = 5nm

(ii)



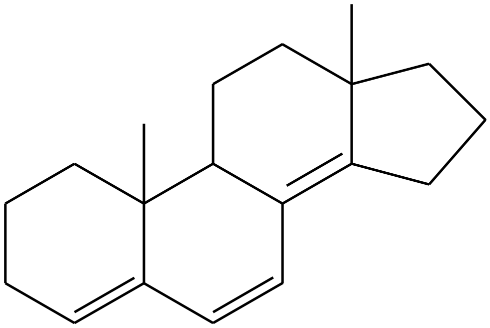
		nm
Homoannulardiene		253
Alkyl substituents	4 X 5	+ 20
Exocyclic double bond	2 x 5	+ 10
Total		283nm

Explanation :

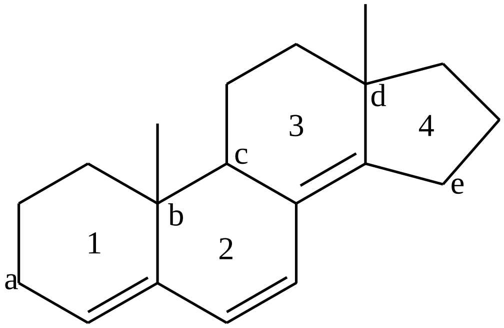
The skeleton is a homoannular diene (i.e two double bonds in one ring) = 253nm. It has 4 alkyl substituents labeled a,b,c,d (4 X 5) = 20nm

The double bond on the left in ring 2 is exocyclic to ring 1, and the double bond on the right in the same ring 2 is exocyclic to ring 3 i.e 2 X 5 = 10nm.

1. Calculate the λmax for



Solution:



		nm
Hetero annular diene		214
Alkyl substituent or ring residue		
(Labeled a,b,c,d and e)	5 X 5	+25
Exocyclic double bond	3 X 5	+15
Double bond extending conjugation		+30

Total calculated	284nm
Observed	283nm

4.0 CONCLUSION

UV- visible spectroscopy is useful in the quantitative analysis of molecules having conjugated pi electron systems. Concentration of dilute solution of such conjugated molecules absorbing UV-visible light can be calculated using the molar absorptivity at a given wavelength.

5.0 SUMMARY

Applying Beer-Lambert law, concentration of a dilute solution absorbing UV-visible light can be calculated using the molar absorptivity at a given wavelength. The HOMO-LUMO energy gap decreases as conjugation increases in molecules, hence the more conjugated molecules have narrower energy gaps and lower wavelength. The maximum wavelength of absorption of conjugated molecules can be calculated using the WoodWardFeiser rules.

6.0 TUTOR MARKED ASSIGNMENT

1. Calculate the molar absorbitvity of a solution containing 4.2×10^{-2} $moldm^{-3}$ absorbance 0.92 at max = 310nm.

2. A solution containing 2.5×10^{-4} $moldm^{-3}$ had absorbance value of 1.26 at λ_{max} = 250 when a cell with path length of 1cm was used. Calculate its molar absorptivity constant

3. A solution gave absorbance value of 0.0206 at maximum wavelength of 530nm, with molar extinction coefficient of 40,000 $mol^{-1}dm^3cm^{-1}$ when 1cm cell was used during measurement. Calculate the concentration of the solution.

4.(a) Calculate the concentration in $Moldm^{-3}$ a compound which gives an absorbance of 1.3 in ethanol at max 530nm and 1.0cm path length

(b) Calculate the concentration in gdm^{-3} the solution given above it the compound has a molecular weight of $260gmol^{-1}$

5. The following data were obtained for $CuSO_4.5H_2O$ solutions at a wavelength of 650nm

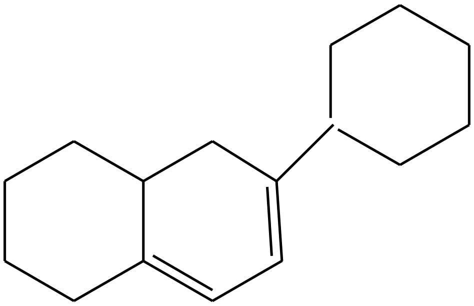
Conc. (M)	Absorbance
0.000	0.000
0.0100	0.110
0.0200	0.200
0.0400	0.450
0.0800	0.920

(a) Plot a graph of absorbance (y-axis) against concentration (x-axis). Using the above data, get the best straight line and the slope of this line.

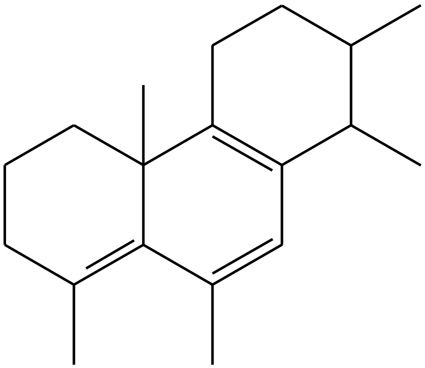
(b) from the graph, determine the molarity of copper (II) tetraoxosulphate (VI) pentahydrate solution whose absorbance is 0.170 at 650 nm.

6.Calculate λ_{max} of each compound given below:

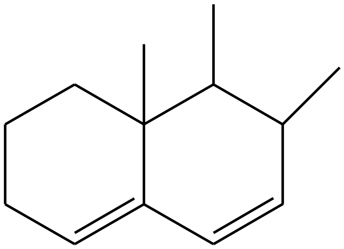
(i)



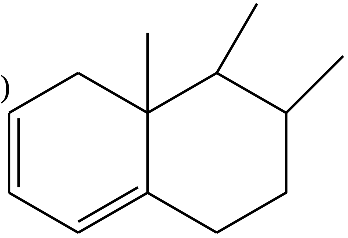
(ii)



(iii)



(iv)



MODULE 3

UNIT 1 ^{1}H NUCLEAR MAGNETIC RESONANCE AND ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTROSSOPY

Contents

1.0 Introduction

Nuclear Magnetic Resonance (NMR) employs the magnetic properties of nuclei to study the structure of molecules. The Nuclei usually considered are ^{1}H, ^{13}C, ^{19}F etc.

In a nucleus containing unpaired protons and neutrons the charged nucleus spin round. Because of its charge, it generates a magnetic field. The spinning axis is the axis of the field.

If an external magnetic is applied, the protons would align themselves either parallel (in the same direction with the magnetic field) which is a stable orientation, or anti-parallel (in opposite direction with the magnetic field) which is an unstable orientation and of higher energy.

The energy difference between the stable and unstable orientation is small. At ordinary temperature, most nuclei exist in the unstable antiparallel orientation. A nucleus whose spin is not aligned exactly parallel with the magnetic field precess in such a way that the rotational axis is at right angle to the applied magnetic field.

From quantum mechanics, the frequency of precession is equal to the frequency required to change the orientation of the nucleus from parallel to anti parallel orientation, i.e to cause a “flip”.

Among the isotopes of carbon, carbon-13 has magnetic properties, because it has an odd mass number and is capable of giving rise to NMR signal, it has spin quantum number $I = ½$ and detectable by NMR.

Carbon-13 makes up 1.1% of naturally occurring carbon. This natural abundance is high enough to make ^{13}C useful in determination of structure of molecules. Because of the low natural abundance of ^{13}C, it is about 6000 times more difficult to observe ^{13}C resonance than proton resonance.

2.0 Objectives

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

- Explain the principle of NMR spectroscopy.
- Describe the operation of an NMR spectrometer.
- Discuss factors affecting chemical shift.
- Employ the information from NMR spectra to propose the structure a simple organic compounds.
- Draw NMR spectra of simple organic compounds.

3.0 CONTENT

3.1 Principle of NMR

When radiofrequency energy irradiates a precessing nucleus whose precessing frequency is equal to the radio- frequency, the system will be said to be in resonance and transition occur from parallel to anti-parallel orientation. The absorption of energy that occurs can be detected by a radiofrequency receiver and recorded.

This resonance energy which causes the transition can be expressed by the following equation

$$Energy = hv = 2\mu H$$

h is planck's constant , v is frequency of electromagnetic radiation (radiofrequency)

H is static magnetic field strength.

μ is the magnetic moment of the nucleus

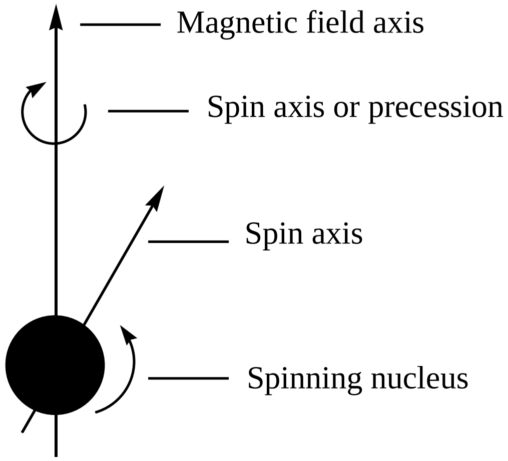


Fig. 3.1 A precessing nucleus in a magnetic field.

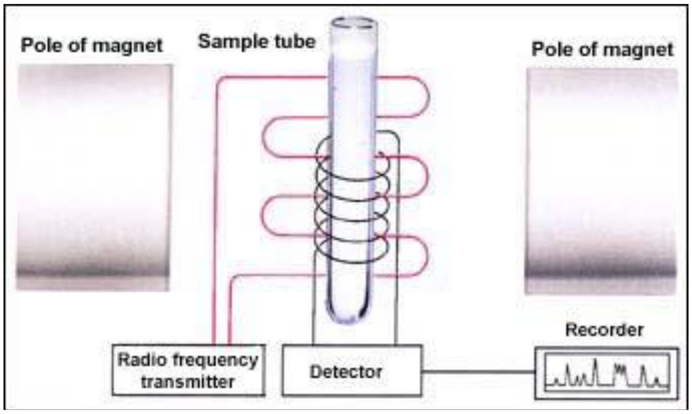


Fig. 3.2 An NMR spectrometer

http://www.brookscole.com/chemistry_d/templates/student_resources/shared_resources/act/photochem/electro6.html

A solution of the sample contained in a small glass tube is placed between the poles of a magnet. The glass tube spins in that environment. The sample is irradiated with radiofrequency through the antenna coils from a radiofrequency source.

The sample absorbs the radiofrequency energy, the absorbed rf energy is emitted via receiver coil which surrounds the sample tube the emitted rf energy is detected and recorder by electronic devices and computer.

Resonance between the nucleus and the rotating magnetic field can be achieved either by varying the magnetic fields strength at constant radiofrequency or sweeping (varying) radiofrequency while the extent magnetic field is constant.

The different resonance signals give rise to a spectrum. Different resonance signals are observed for each of the different types of proton. Different signals arise because different protons exist in different chemical environments. The electrons in the bonds between hydrogen and other atoms in the molecules such, as H-C, H-O, and H-N screen the neighbouring hydrogen nucleus, altering the effective magnetic field at the nucleus. Therefore protons are shielded to different extent according to their chemical environment. Hence different protons resonate at different frequencies.

3.2 Information from NMR Spectra

The utility of the spectra of protons lies in the three basic information which are important in characterizing/identifying a compound: (1) signal strength or peak areas (2) chemical shifts (3) spin-spin splitting.

3.2.1 Signal Strength or Peak Area

The number of identical protons in a compound is obvious from the signal strength or area occupied by each peak which is measured by electronic integration. This is directly proportional to the number of protons which produces the signal.

3.2.1.1 Chemical Shift

This is the position of a peak in the spectrum relative to TMS. Since protons in different chemical environments show resonance at different positions, there is need for a standard of measurement for chemical shifts. Tetramethylsilane TMS is used as a reference compound. TMS, $(CH_3)_4Si$ has 12 chemically and magnetically equivalent protons, and its resonance position is arbitrarily designated as zero. A small quantity of TMS in $CDCl_3$ or CCl_4 is used as an internal standard.

3.2.1.1.1 Measurement of Chemical shift

Chemical shift of different protons are expressed in δ(delta) on a scale, with TMS having $\delta=0$. Other protons have δ in parts per million (ppm) downfield (to the right) of TMS

Generally, chemical shift of a resonance is expressed as

$$\delta = \frac{v_s - v_{TMS}}{Operating\ frequency\ of\ spectrometer} \quad X\ 10^6\, ppm$$

v_s= frequency of signal

$0\ ppm$= frequency of reference

τ may also be used as a chemical shift parameter.

$\tau = 10 - \delta\ ppm$

3.2.1.2 Factors Influencing Chemical Shift

The factors which influence chemical shift in dilute solution are classified under intramolecular and intermolecular.

3.2.1.2.1 Intramolecular Factors

3.2.1.2.1.1 Shielding and Deshielding (Inductive Effects by Electronegative Groups)

The chemical environment of a proton influences its chemical shifts. If the proton has electrons around it, it will be screened from the effect the external magnetic field. Electrons surrounding the nucleus circulate to cause a secondary magnetic field which opposes the applied field B_o in the nucleus region. This reduces the field experienced at the nucleus, thereby requiring higher B_o field for resonance to occur. The protons in the nucleus are said to be shielded by the electrons, hence resonance occurs at higher field strength to the right side of the spectrum.

On the other hand, if the atoms attached to the proton withdraw electrons from around it, the atom has reduced electron density around it due to inductive effect caused by attached electronegative atom. The secondary field caused by circulating surrounding electrons is decreased. The nucleus therefore requires a lower applied field for resonance to occur, i.e. resonance occurs relatively to the left of the spectrum. The proton will be deshielded and show a signal at lower field. Generally, electronegative atoms attached to protons exert a deshielding effect and results to a downfield shift.

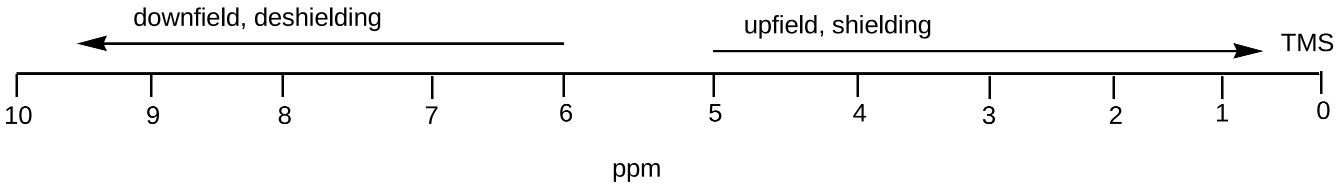


Figure 3.3 Chemical shifts scale showing upfield and downfield shifts.

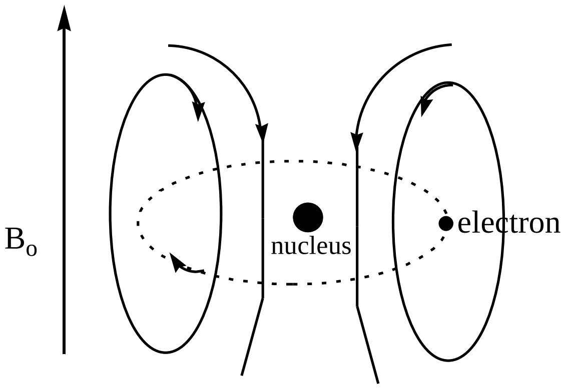
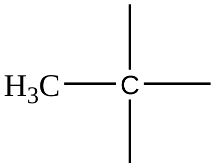
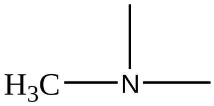


Figure 3.4 Shielding and deshielding of a nucleus by electrons in its vicinity. B_o represents the applied magnetic field.

Table 3.1 Deshielding effects of methyl protons attached to groups with different electronegativities.

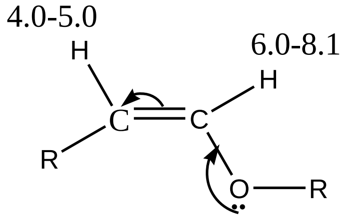
Structural Unit	Chemical Shift
 H_3C-C-	0.9
 H_3C-N-	2.3
H_3C-O-	3.3

3.2.1.2.1.2 Anisotropy

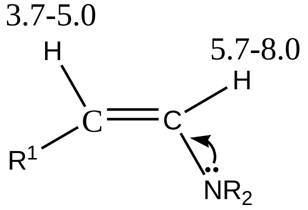
In many molecules containing pi electrons like ethylene double bond, carbonyl or benzene ring, the applied magnetic field induce circulation of these electrons which lead to secondary fields that affects the nearby nuclei. This secondary field may be stronger in one direction of the molecule.

The double bond in ethylene makes their proton to resonate at 4.5-6.5 ppm, this is due to the high electron density at the nucleus, shielding the nucleus, causing an upfield resonance peak towards TMS.

In enols, enolethers or ene amines shown below, polarization occurs such that the alkenes draws electrons from the lone pair of electron on the heteroatom. Their α-protons are deshielded by electronegativity of the heteroatom. But their β-protons are shielded by electrons, hence resonate at lower δ value (up field) relative to the α-protons.

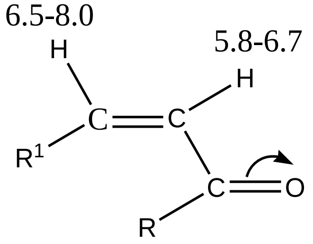


R=H (enol), R=R (enolether)



eneamine

In α-β-unsaturated ketones. The polarization takes place in a reverse manner, the effect is opposite compared to that mentioned above. The α-protons are shielded and the β-protons are deshielded.



Anisotropy in Benzene:

The protons of a benzene ring are observed at δ 7.27, they are deshielded by 1.5 to 2.0ppm relative to ethylene protons. The increase deshielding is due to ring current which occurs in aromatic compounds. When benzene molecule is in a magnetic field, the pi electron cloud above and below the plane circulate causing an induced ring current (a secondary field) generating an opposing field at the centre of the ring and reinforcing the applied field outside the ring at the aromatic protons. Thus the inner protons are shielded while the outer protons are deshielded.

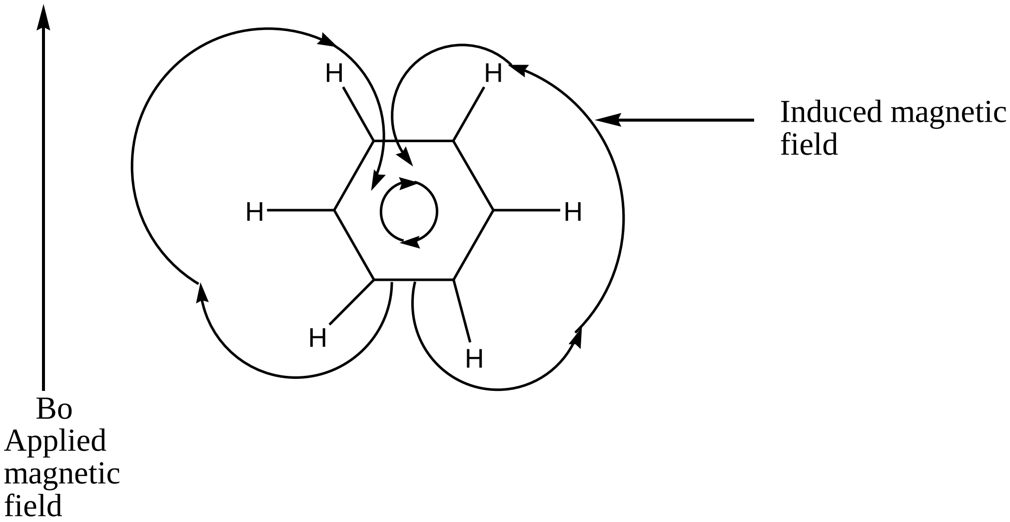
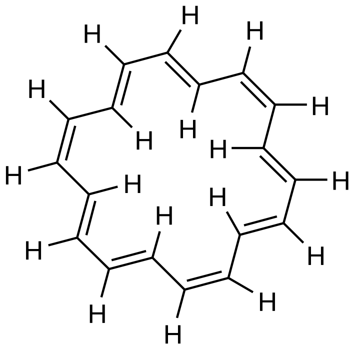


Fig.3.5 Anisotropy in benzene

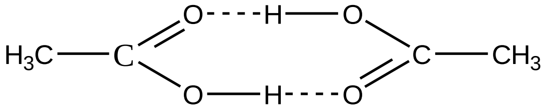
Similarly, in annulene which is also an aromatic system with 14π electrons system (4n+2)π, where n = 4, ring current bring about deshielding of the outside protons and shielding of the inner protons. The outside protons resonate at 8.9 ppm and the inner protons at -1.8ppm (to the left of TMS).



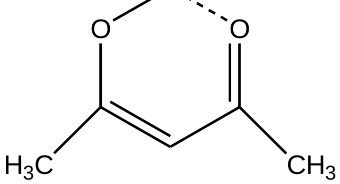
3.2.1.2.2 Intermolecular Factors Influencing Chemical Shift.

3.2.1.2.2.1 Hydrogen Bonding:

Hydrogen bonds are formed in compounds containing OH, NH and SH groups. The hydrogen bonds are due to those groups. Generally, hydrogen bonding causes deshielding, hence downfield. OH groups in hydrogen bonded carboxylic acids resonate at very low fields (9-13ppm)



In intramolecular hydrogen bonded molecules –OH protons also show very low field resonance in the enol form of acetylacetone, the OH protons resonate at 15.4ppm.



3.2.1.2.2.2 Temperature:

Temperature normally has no influence on C-H protons. However, O-H, N-H and SH protons which involve in hydrogen bonding are subject to temperature effect. Such protons are shifted to high fields as temperature increases. The shifts to high field are as a result of breaking hydrogen bonds.

3.2.1.2.2.3 Solvent:

The usual solvents for NMR spectroscopy include $CDCl_3$, CCl_4, d_6-acetone, d_4-methanol, D_6-DMSO. If CCl_4 is used instead of $CDCl_3$, the change in chemical shift is small. However, if a more polar solvent is used such as d_6-acetone there will be an appreciable change in chemical shift up to ± 1ppm.

Deuterated solvents are used in order to prevent protons in the solvent appearing in the spectrum.

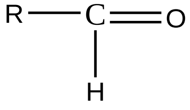
3.2.1.2.2.4 Chemical Exchange:

Protons bonded to electronegative atoms undergo rapid exchange of proton at a rate that may be difficult for the frequency of the system to detect. This is why OH, NH and SH appear as singlets, despite the number of adjacent protons. This problem is overcome by mixing a little heavy water D_2O with the solvent, ($CDCl_3$) used for the experiment. This is called deuterium exchange.

The protons are replaced with deuterium and their signals disappear from the spectrum.

Table 3.2 Characteristic ^{1}H NMR Chemical Shifts of Protons

Type of proton		**Chemical Shift**

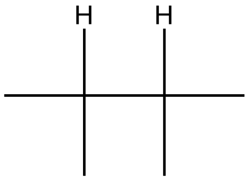
Methane	CH_4	0.2
Methyl (primary)	RCH_3	0.9
Methylene (secondary)	R_2CH_2	1.3
Methine (tertiary)	R_3CH	1.5
Vinylic	$C=C-H$	4.6 - 5.9
Acetylenic	$H-C\equiv C$	2 – 3
Aromatic	Ar-H	6 - 8.5
Benzylic	Ar-C-H	2.2 – 3
Allylic	$C=C-CH_3$	1.7
Fluorides	RCH_2-F	4 – 4.5
Chlorides	RCH_2-Cl	3 – 4
Bromides	RCH_2-Br	2.5 -4
Iodides	RCH_2-I	2 – 4
Alcohols	H-C-OH	3.4 – 4
Ethers	H-C-OR	3.3 – 4
Esters	RCOO-C-H	3.7 – 4.1
Esters	H-C-OOR	2 – 2.2
Acids	H-C-OOH	2 – 2.6
Carbonyl compounds	H-C-C=O	2 – 2.7
Aldehydic	 $R-\underset{\mid \atop H}{C}=O$	9 – 10
Hydroxylic	R-C-OH	1 – 5.5
Phenolic	Ar-OH	4 – 12
Enolic	C=C-OH	15 – 17
Carboxylic	RCOOH	10.5 – 12

Amino	RNH_2	1 – 5

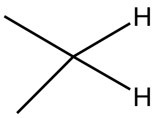
3.2.2 Spin-spin Coupling

Adjacent protons which are linked by a common saturated bond experience coupling. This arises because the local field experienced by a proton depends on the magnetic field operating in the neighbouring protons.

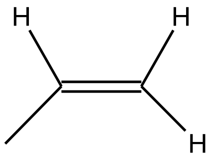
3.2.3 Coupling Constant (J): The spacing in the lines is called the coupling constant, J. Coupling constant is used to quantify the spin-spin coupling effect of neighbouring protons. J is simply the difference in Hz between two neighbouring peaks. Coupling constant is used in identifying the coupling relationship between neighbouring protons. Coupling constant for sp^3 hybridized carbons range from 6-8Hz for sp^2, it can range from 0 (no coupling) to 18Hz, depending on the arrangement of the bonds.



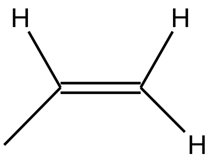
^3J=6-8Hz



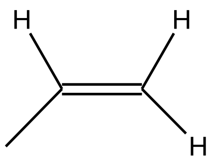
^2J = 12 - 15 Hz



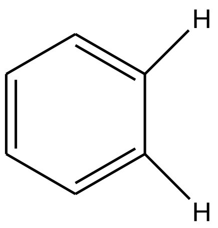
$^3J_{cis}$=7-11Hz



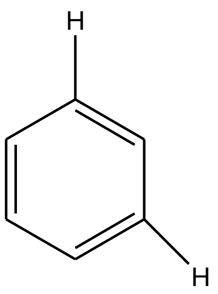
3J_{trans}=13-17Hz



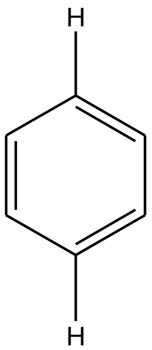
$^2J_{gem}$=0-3Hz



$^{3}J_{ortho}$=6-9Hz

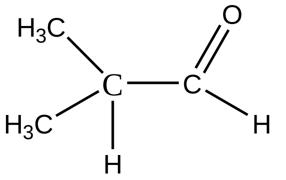


$^{4}J_{meta}$=1-3Hz



$^{5}J_{para}$=0-1Hz

The superscript indicates the number of bonds between the interacting (coupling) protons.



Aldehyde ^{3}J=2-3Hz

3.2.4 Spin-Spin Splitting

The signal for a proton having n identical adjacent protons is split into n+1 peaks. Where n is the number of neighbouring protons. Thus, in ethylchloride CH_3CH_2Cl, the $–CH_3$- protons are split into a triplet because its adjacent carbon ($-CH_2-$) bears two protons, i.e 2+1 = 3 lines (triplet). The $–CH_2$- is adjacent to carbon having three protons hence it is split into a quartet. Refer to fig. 3.4 below.

The ratio of the intensities of these peaks corresponds to the binomial coefficient, which can be arrived at using a Pascal's triangle.

1

1 1

1 2 1

1 3 3 1

1 4 6 4 1

1 5 10 10 5 1

Figure 3.6 Pascal triangle

Examples of NMR Spectra

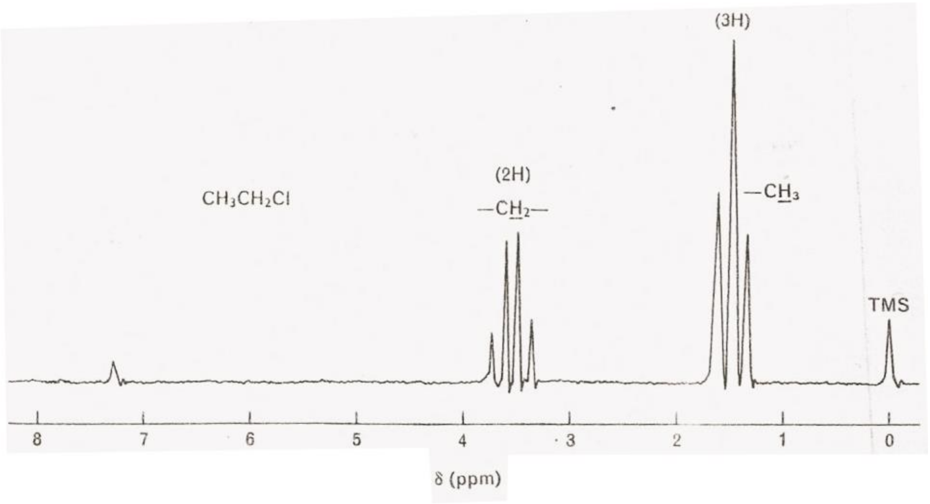


Figure 3.7 Proton NMR spectrum of ethylchloride.

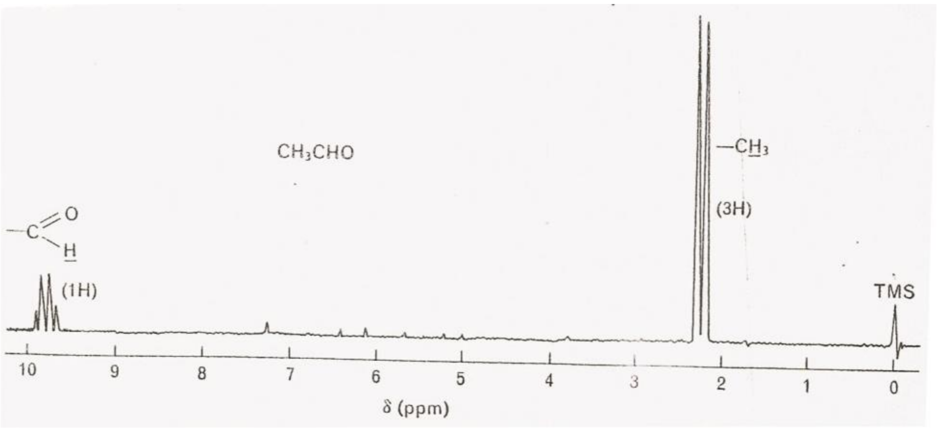


Fig. 3.8 ^{1}H NMR spectrum of ethanal

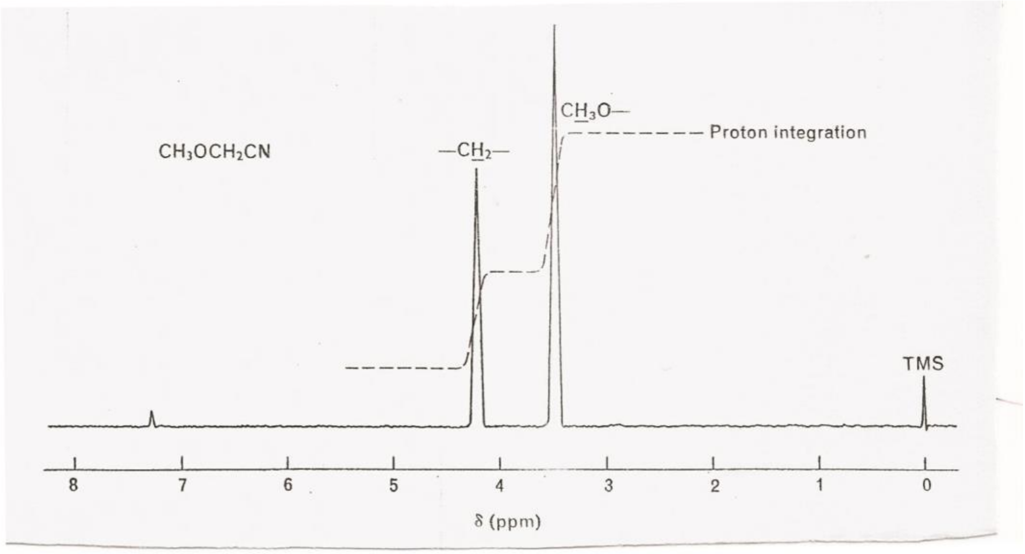


Fig. 3.9 ^{1}H NMR spectrum of methoxyacetonitrile

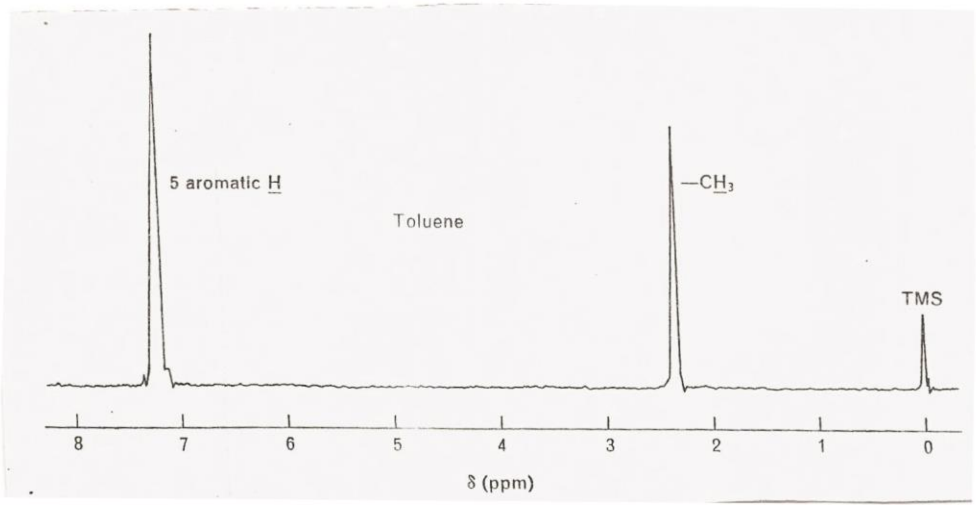


Fig. 3.91 ^{1}H NMR spectrum of toluene

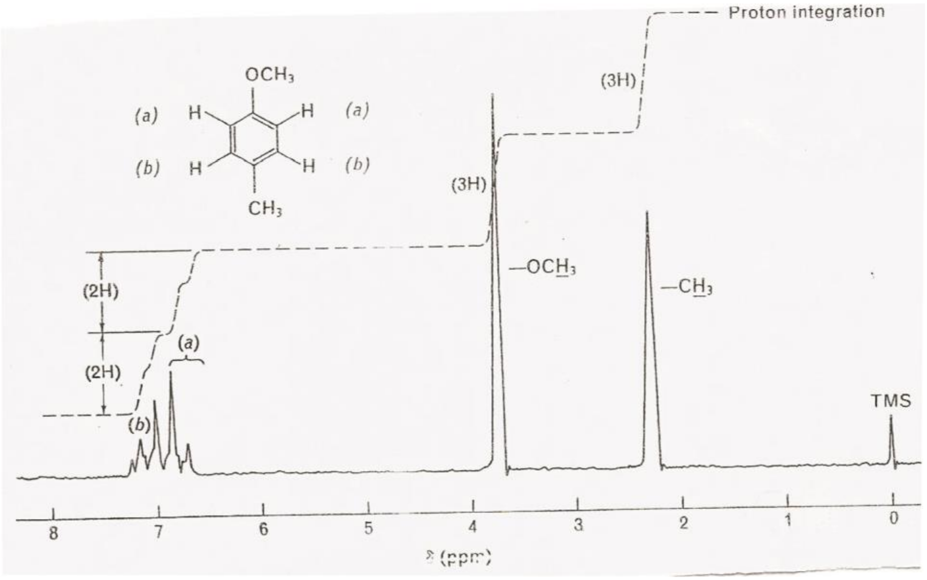


Fig. 3.92 ^{1}H NMR spectrum of methoxytoluene

Source: T.A. Geissman Principles of Organic Chemistry 4th Edition

3.3 ^{13}C NMR

Among the isotopes of carbon, carbon-13 have magnetic properties, because it has an odd mass number and is capable of giving rise to NMR signal. It has spin quantum number I = ½ and detectable by NMR.

Carbon-13 makes up 1.1% of naturally occurring carbon. This natural abundance is high enough to make ^{13}C useful in determination of structure of molecules. Because of the low natural abundance of ^{13}C, it is about 6000 times more difficult to observe ^{13}C resonance than proton resonance. Similar to ^{1}HNMR, ^{13}C chemical shifts are measured in parts per million downfield of TMS.

Chemical shifts for ^{13}C range from 0-200ppm relative to TMS, which is about 20 times the range for ^{1}H chemical shifts. The structural environment of a carbon influences its chemical shift. The chemical shift of a carbon is a function of its hybridization, the polar and steric effects of the substituents as well as ring current.

Unlike ^{1}HNMR which provides information concerning peak areas, chemical shifts, and splitting of peaks due to coupling of nuclei, ^{13}C NMR, does not provide information on peak area (integration). However, chemical shifts and splittings are the two features of ^{13}C NMR spectra.

^{13}Carbon easily exhibits coupling with nearby protons, .i.e. protons directly attached to a carbon. This results to splitting of signals. The resulting split signals are so complicated, signal to noise ratio is so low that ^{13}C NMR spectra are usually obtained under proton decoupling condition, in which each non-equivalent carbon is seen a single peak. The line intensities do not reflect the relative number of carbon atoms. However, what is usually observed is that in carbons without hydrogens such as C=O carbons, the intensity of the line will be less than those having hydrogens. For those carbons having hydrogens, the relative height of the peak is an estimate of the relative number of carbon.

Because an aromatic carbon atom which is attached to a substituent are not attached to hydrogen, such carbons appear with lower intensity than the other carbon atoms in that molecule, but they also appear with higher intensity than carbonyl carbons.

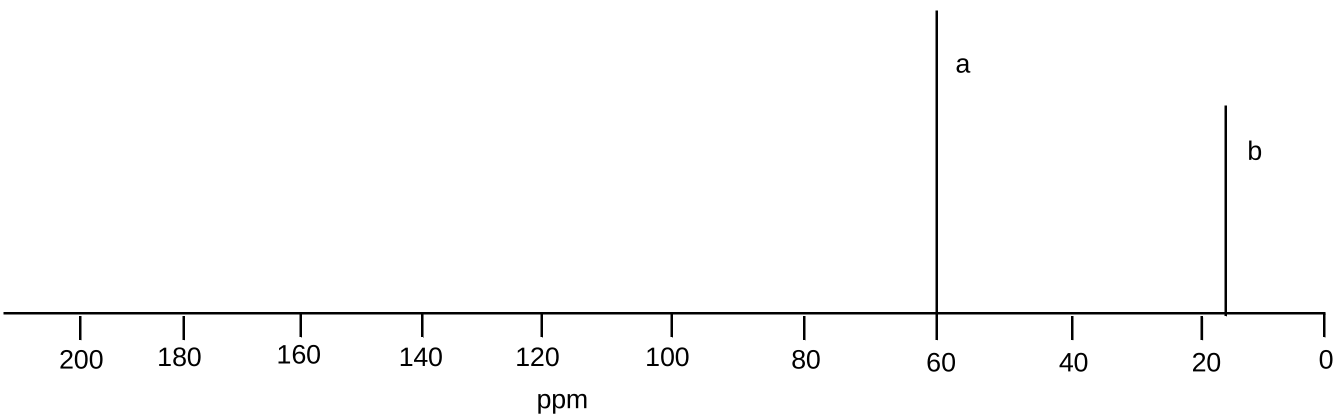
Table 3.3 ^{13}C chemical shifts

Types of Carbon	Chemical Shift
$R\underline{C}H_3$	10 – 15
$R_2\underline{C}H_2$	16 – 25
$\underline{C}H_3CO$-	20 – 50
$R_3\underline{C}H$	25 – 35
$R\underline{C}H_2NH_2$	30 – 65
$R\underline{C}H_2Cl$	30 – 60
$R\underline{C}H_2O$-	50 – 90
C=C (Alkenes)	115 – 140
C (in aromatic rings)	125 – 150
C=O (in acids and esters)	160 – 185
C=O (in aldehydes)	190 – 200
C=O (in ketones)	205 – 220
C-C	0 – 50
C-O	50 – 100

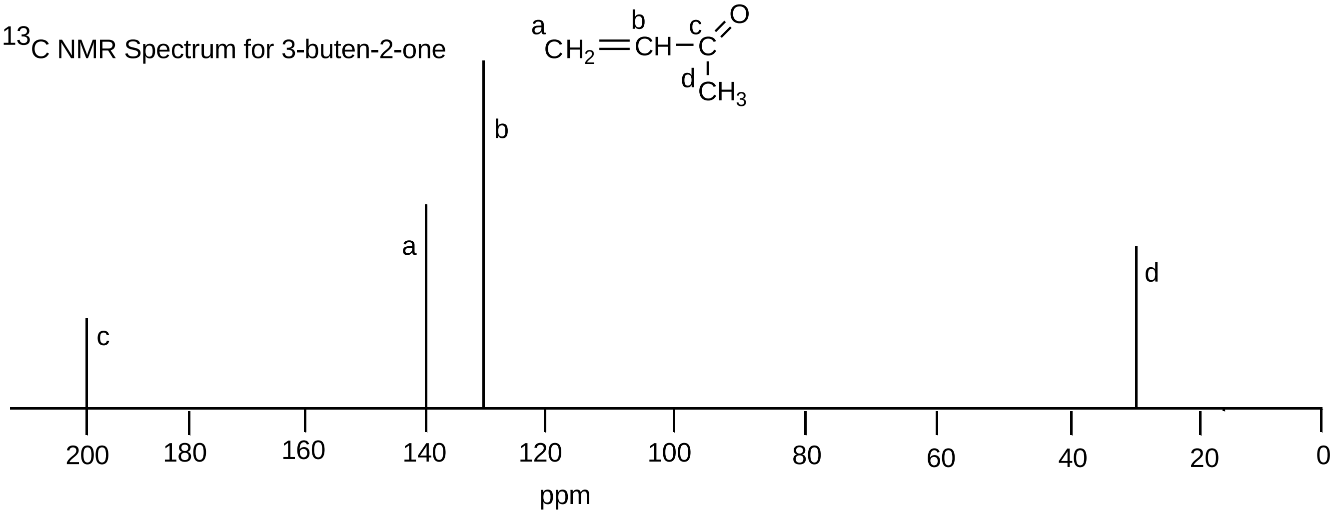
C=C	100 – 150
C=O	150 -200

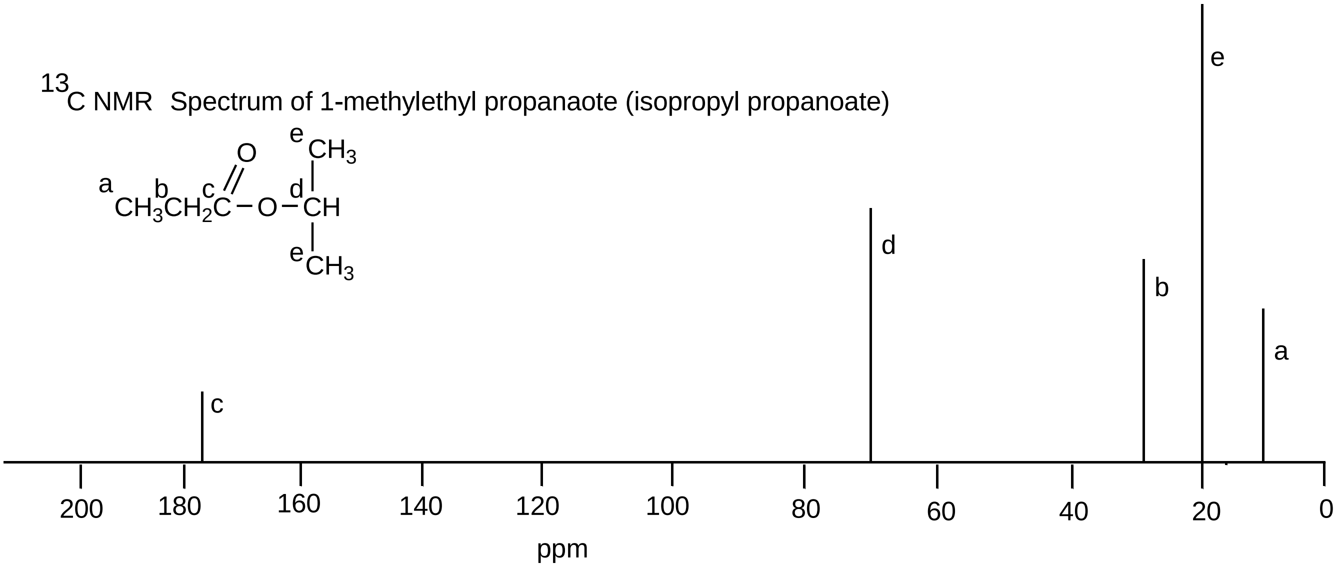
^{13}CNMR Spectrum for ethanol

$^{b}CH_3{}^{a}CH_2OH$



^{13}C NMR Spectrum for 3-buten-2-one





^{13}C NMR Spectrum of 1-methylethyl propanaote (isopropyl propanoate)

4.0 CONCLUSION

In proton NMR, three basic information, viz: signal strength, chemical shift and spin-spin splitting are applied in identifying a compound . However for ^{13}C , only chemical shift positions are important in decoupled spectra.

5.0 SUMMARY

Nuclei possessing odd number of protons or neutrons such as ^{1}H, ^{13}C, ^{15}N, ^{19}F e.t.c exhibit magnetic properties which is employed to study the structures of molecules. In an NMR spectrometer, by irradiating the sample being analysedwith radiofrequency energy, the resonance energy which causes transition can be determined. Employing a combination of chemical shift, peak area and spin-spin splitting, the structure of organic molecules can be established.

6.0 TUTOR MARKED ASSIGNMENT

Propose structures for each of the following NMR data.

1. (a) A compound with molecular formula $C_3H_5Cl_3$, showing two signals, a singlet at δ2.20ppm with 3H and another singlet at δ4.02ppm with 2H

   (b) A compound with molecular formula $C_{10}H_{13}Cl$, showing a singlet at δ3.07ppm, 2H and a singlet at δ7.27, 5H.

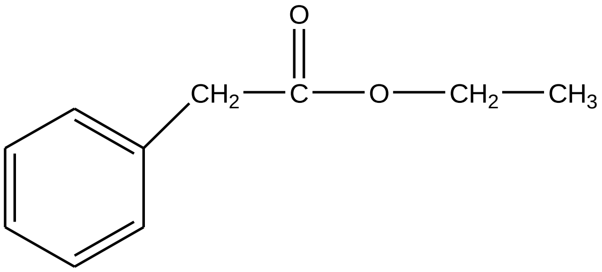
   (c) A compound with molecular formula $C_{10}H_{14}$, showing a doublet at δ0.88ppm, 6H, a multiplet at δ1.86ppm, 1H, a doublet at δ2.45, 2H and a singlet at δ7.12, 5H.

   (d) An unknown compound, C_9H_{12}, gave the following: Triplet at δ1.2ppm, (3H), singlet at δ 2.30ppm (3H), quartet at δ 2.60ppm, (2), singlet at 7.04ppm (4H)

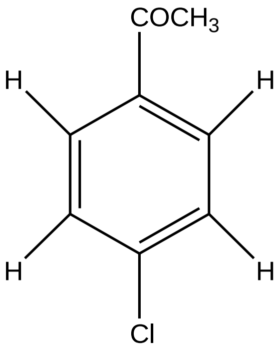
2. Draw the NMR spectrum of

a. $CH_3CH_2OCH_3$

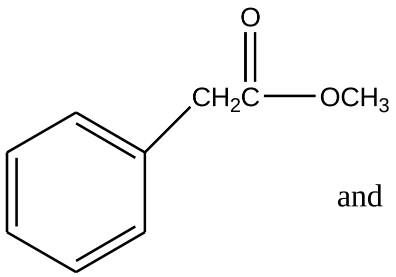
b.



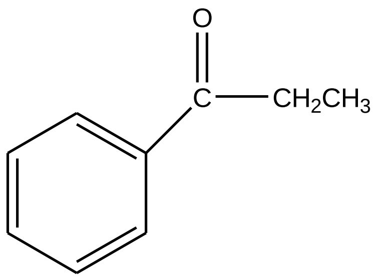
c.



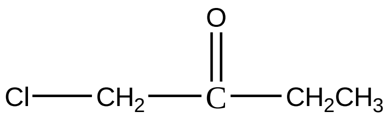
3. Explain how ^{1}HNMR spectroscopy could be used to distinguish between the two compounds below:



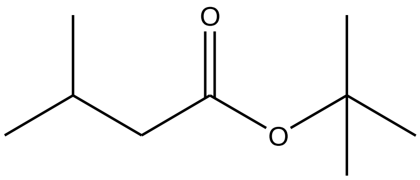
and



4. Predict the approximate chemical shift and multiplicity for each of the different hydrogens in the ^1H-NMR spectrum of :

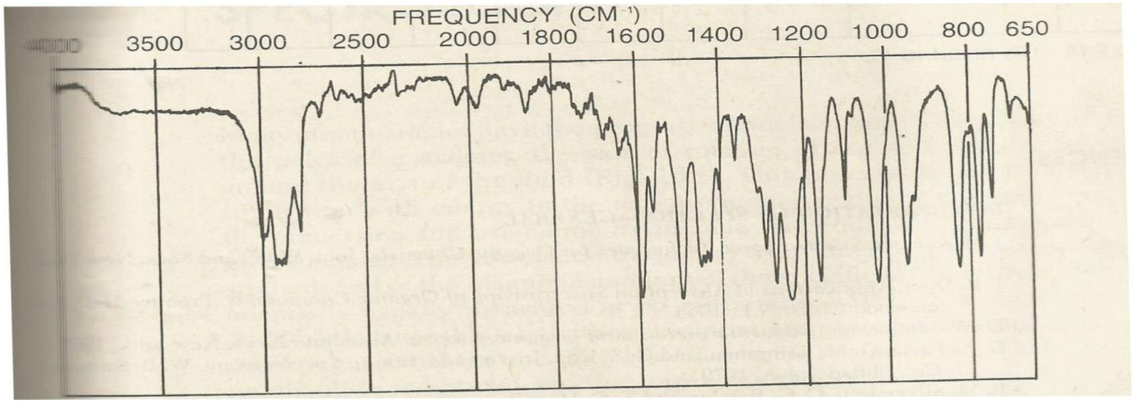
a. 

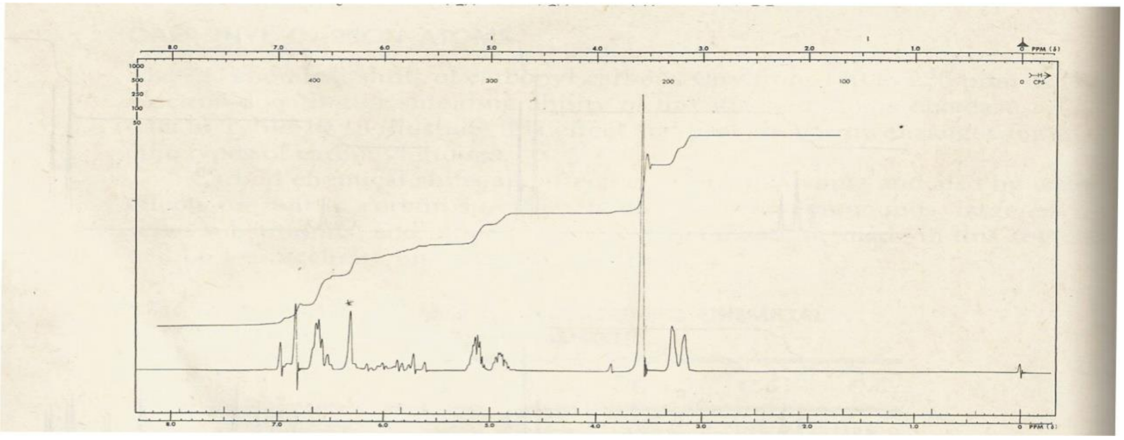
$$Cl-CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

b. 

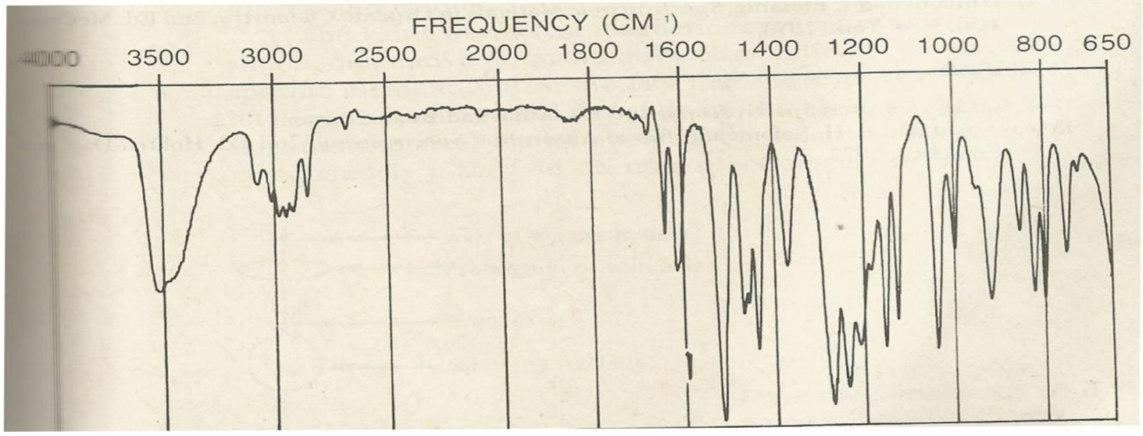
5. The infrared and nmr spectra of three compounds A($C_{10}H_{12}O$), B ($C_{10}H_{12}O_2$) and C ($C_{10}H_{12}O$) are given below:
(i) Give the their respective functional group
(ii) Write the structure of each compound.

Compound A




8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0 PPM (δ)
400
300
200
100
0 CPS

compound B


FREQUENCY (CM⁻¹)
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3500
3000
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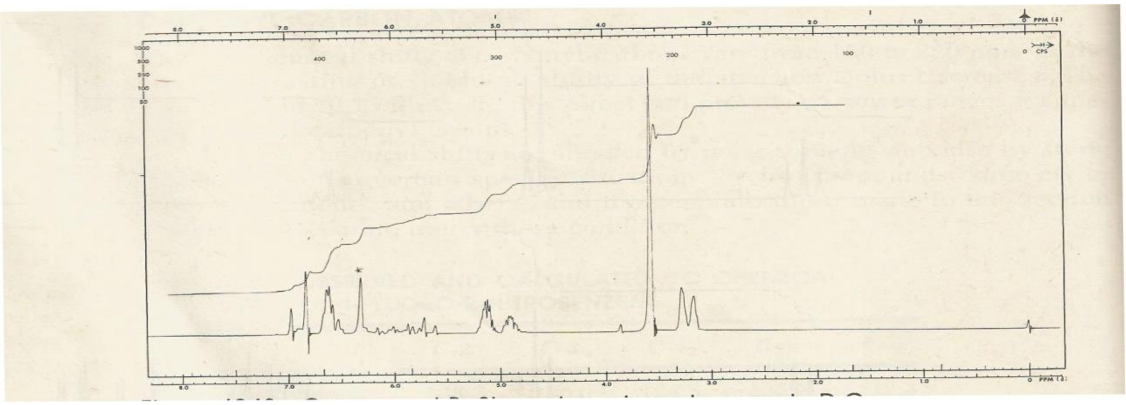
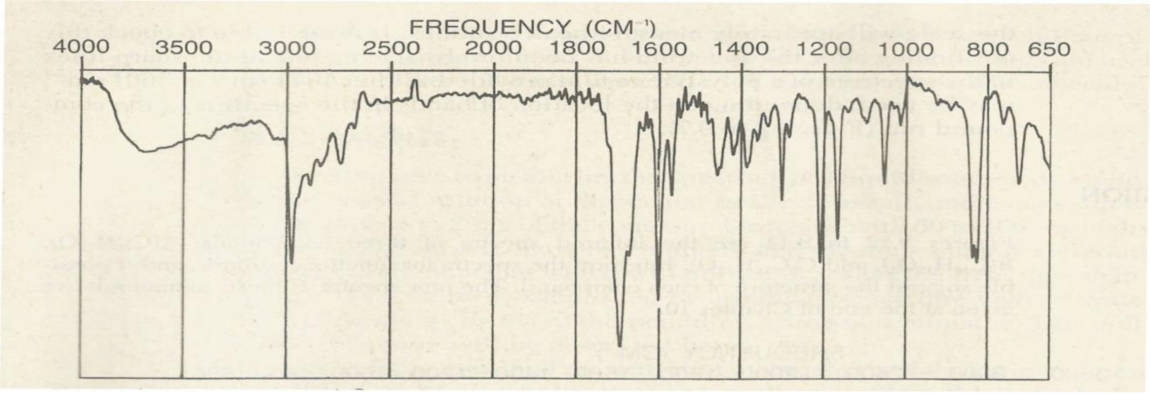
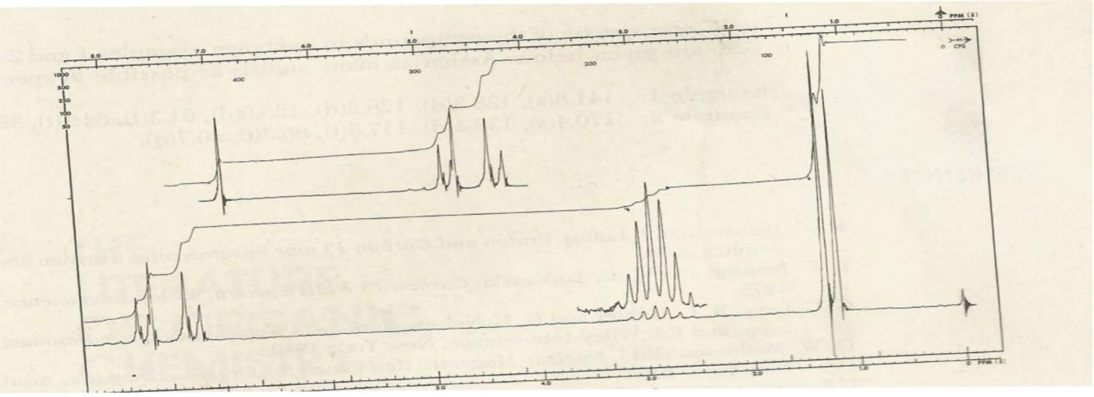
1200
1000
800
650



Compound C

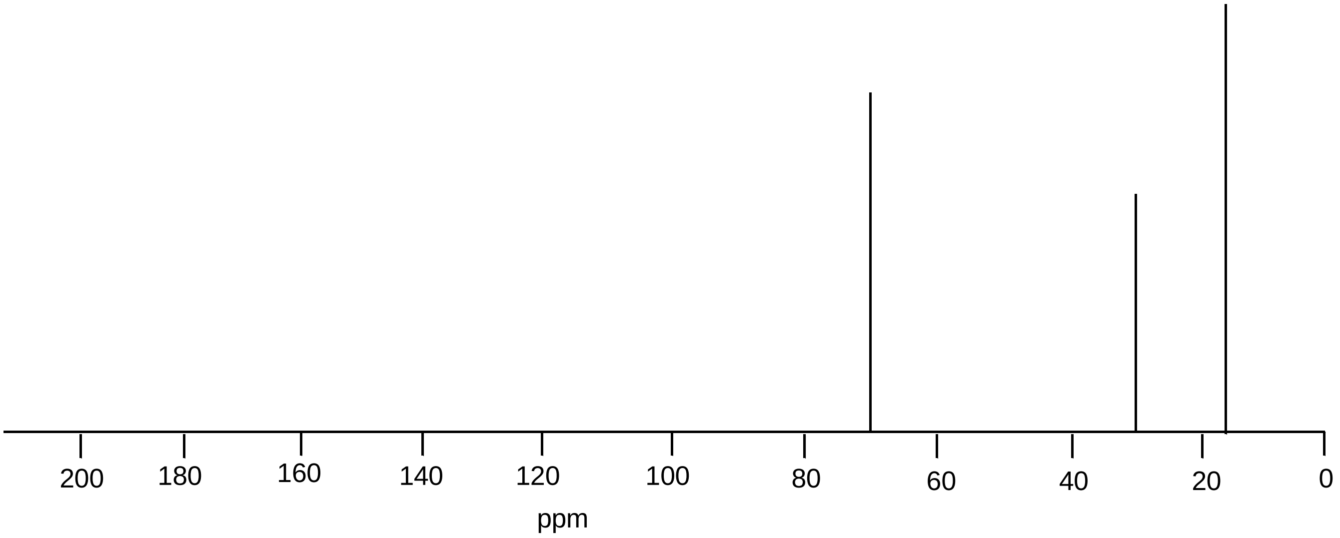




Source of spectra: Experimental Methods in Organic Cemistry, 3rd Edition, by James A. Moore, David L. Dalrymple and Oscar R. Rodig.

Exercises

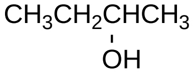
6. Given the ^{13}C NMR Spectrum below,



Which of the four alcohols with molecular formula $C_4H_{10}O$ matches the spectrum?

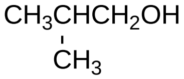
A. $CH_3CH_2CH_2CH_2OH$

B.



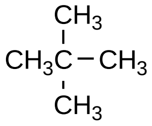
$CH_3CH_2\underset{OH}{CH}CH_3$

C.



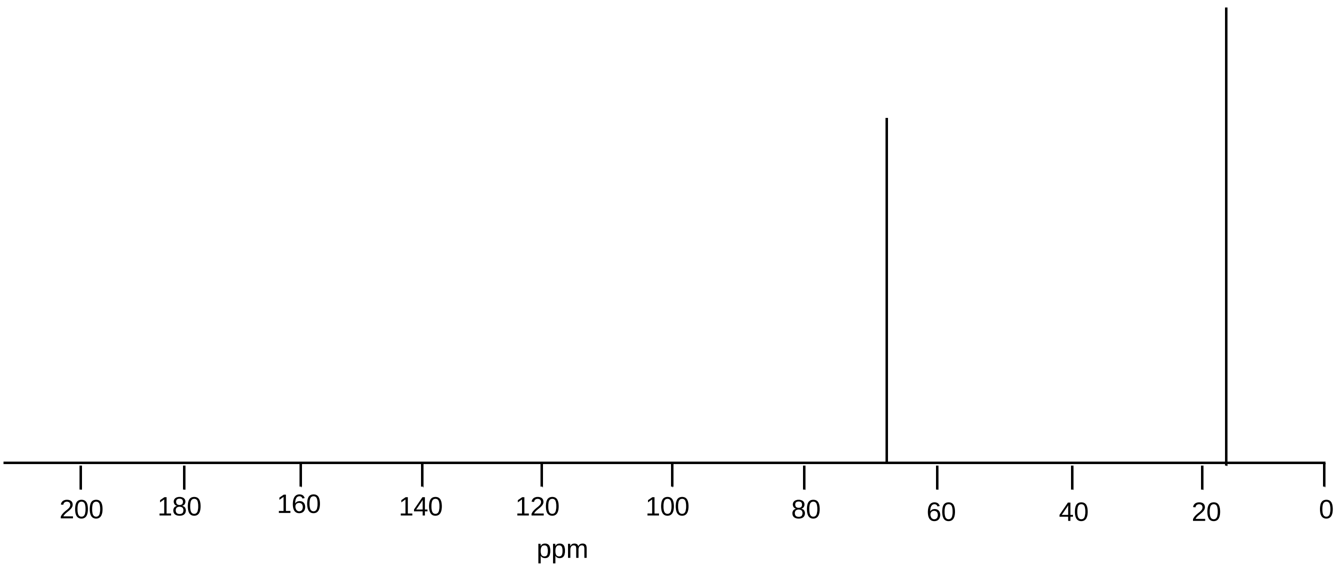
$CH_3\underset{CH_3}{CH}CH_2OH$

D.

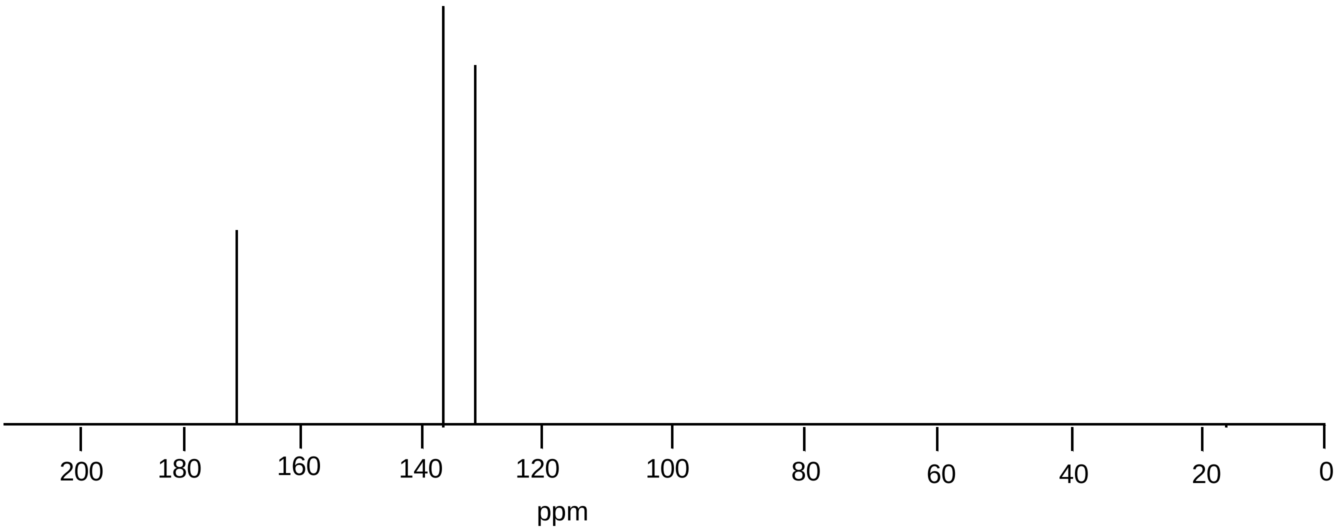


$CH_3\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

7. The ^{13}C spectrum of another isomer of $C_4H_{10}O$ which is not an alcohol is given below. Predict the structure.



8. Themolecular formular of a compound is $C_4H_6O_2$, predict the structure of the compound. The ^{13}C NMR Spectrum is given below:



UNIT 2 ELECTRON SPIN RESONANCE; NUCLEAR QUADRUPLE RESONANCE AND MÖSSBAUER EFFECT

Contents

7.0 Reference/ Further Reading.

1.0 INTRODUCTION

Nuclei having non-zero spin are resonance active. For NMR,$I = {}^{1}/_{2}$while NQR is resonance in nuclei with $> {}^{1}/_{2}$, where I is the spin of the nucleus. Resonance depends on the magnetic field which eliminates nuclear spin degeneracy. Subsequent application of radiofrequency leads to absorption of energy which can be detected. ESR or EPR (Electro Paramagnetic Resonance) is concerned with electronic spin, rather than nuclear spin. EPR can be detected in molecules or ions having unpaired spins. Mössbauer spectroscopy is a nuclear gamma ray resonance, in which nuclei absorb gamma rays. Few molecules are Mössbauer active such as ^{57}Fe . The chemical shifts given by Mössbauer are called isomer shifts. Because isomer shifts are sensitive to oxidation states and surrounding environment, Mössbauer spectroscopy is used to study species in biochemical systems.

2.0 OBJECTIVES

3.0 MAIN CONTENT

3.1 Theory of Electron Spin Resonance

Electron spin resonance ESR is also called Electron Paramagnetic resonance EPR. In electron spin resonance, microwave radiation (3-400GHz) interact with odd number electron species such as radicals, cations, anions which are present in a magnetic field.

The ESR theory and technique is similar to NMR in many ways, however the basic difference is that the manner of probing of electron spins properties in ESR is opposite that in NMR. ESR is used to study the kinetic and mechanism of radicals reactions in biological enzymes.

An odd pair of electron (or radical) with magnetic moment μ, has spin quantum number = ½ and magnetic quantum number Ms +1/2 and –1/2. If the electron is placed in an external magnetic field with strength is B_o, they can align itself in the magnetic field such that its magnetic moment can either be parallel (align with the field) or antiparallel (align against the field) i.e. Ms = -1/2 or +1/2 respectively to the magnetic field.

Each alignment has energy due to Zeeman effect.

$E = M_s g_e \mu_B B_o$

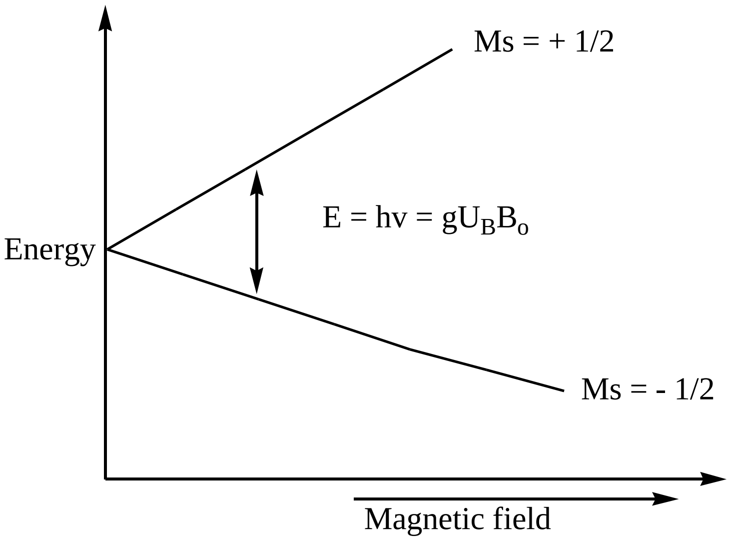
g_e is the g-factor for free electron, and its value is 2.0023,

μ_B is the Bohr magnetron.

The radiation absorbed changes the electron spin from the more stable alignment -1/2 to the less stable spin +1/2. The energy change E corresponds to the difference between the initial and final states

$E = g_e \mu_B B_o$

As the strength of the magnetic field increases, the energy level splitting increases. i.e. the magnetic field strength is directly proportional to the splitting of energy levels.



When an unpaired electron absorbs microwave photon, it can move to a higher enegy. However, it will emit photons when it moves to a lower energy. The energy absorbed or emitted:

E = hv

:. hv = $g_e\mu_B B_o$

3.1.1 Spectral Parameters

Because electrons are associated with more than one atom, an unpaired electron can change its angular momentum, thereby changing the g factor value. This is common in transition metal ion systems.

Interaction between the magnetic moment of a nuclei whose nuclear spin is non-zero and the unpaired electrons results in hyperfine coupling, which split the resonance signals of the ESR further into doublets, triplet, etc.

The shape of an ESR spectral line is determined by the interactions between an unpaired electron with its environment. Such information as rates of chemical reaction can be furnished by the shape of the spectral line.

3.1.2 Comparing EPR and NMR

1. EPR is concerned with the interaction between applied magnetic field, and unpaired electrons localized on a system of atoms and the applied magnetic field whereas in NMR resonance is based on interaction between individual nuclei and applied magnetic field.
2. In EPR, the microwave radiation (3-400GHz) is used, but in NMR, radio frequency radiation 300-1000MHz is used.
3. In EPR, the magnetic field is varied, while the frequency is held constant, whereas in NMR, the opposite is the case.
4. Because the microwave radiation used in EPR has a higher frequency than radio frequency used in NMR, EPR is about 1,000 times more sensity than NMR.
5. Electron spins have shorter relaxation time than nuclear spins, hence EPR is carried out at very low temperatures of between 2-10K which can be achieved in liquid lithium.

EPR was first discovered in 1945 by Zavaoisky by using it to study transition metal ions found in some salts. The technique was further developed due to advances in microwave and solid state technology after world war II. EPR though not as popular as NMR is presently used in biochemical study of enzymes, radiation chemistry, solid state physics and organic radicals.

However, both EPR and NMR are similar because both techniques absorption of radiation having the proper frequency to produce an absorption spectrum.

Both EPR and NMR are analogous in terms of origin of splitting which is due to coupling with spins of nuclei of nearly atoms.

3.1.3 Uses of ESR

ESR is used to detect the presence and concentration of free radicals, to study transition metals ions found in some salts and biochemical studies of enzymes.

3.2 Theory of Nuclear Quadropole Resonance

This method is related to Nuclear Magnetic Resonance (NMR). However, Nuclear Quadropole Resonance is detected in an environment without a magnetic field. Hence, it is called “zero field NMR”. NQR is caused by the interaction of the Electric Field Gradient (EFG) with the quadropole moment resulting from the distribution of the charge from the nucleus. The EFG operating on a nucleus depends on the valence electrons which is used in bonding with other close nuclei. Each substance has a unique frequency at which NQR occurs. This frequency is a product of the nuclear quadropole moment and the EFG. This product is the nuclear quadropole coupling constant for an isotope present in a substance. NQR occurs in the 1-1000MHz range.

In NMR, nuclear with unpaired electrons possessing spin (I) of ½, in a magnetic field has a dipole moment, the nuclei either align themselves parallel or antiparallel to the applied magnetic field. The magnetic field split their energies so that the nuclei can absorb radiation which corresponds to the difference between the ground state and excited state.

However, in NQR, also nuclei with spin $\geq$ 1 for example ^{14}N, ^{17}O, ^{35}Cl possess electric quadruple moment, hence electric field gradient is used to split their energies. The electric field gradient results from the valence electrons used in bonding with nearby nuclei.

The non uniform charge distribution gives rise to the quadropole moment. Therefore, interaction of the nuclear charge with an electric field gradient shift the allowed energy levels of the nucleus. In NMR, the nucleus absorbs radio frequency radiation of a particular frequency to become excited.

3.2.1 Application of Nuclear Quadropole Resonance

The applications of NQR include the detection of explosive and land mines. An explosive detector based on NQR principle consist of a source of radiofrequency radiation, a magnetic field coil and a detector to monitor response from the explosive in the material.

NQR can also be applied to real time measurement of the water/gas coming out of an oil well.

Because NQR frequency depends on temperature, it can be employed as a sensor for temperature.

3.3 Theory of Mössbauer Spectroscopy

In Mössbauer spectroscopy, a nucleus emits gamma rays which can be absorbed by a sample containing the nuclei of the same isotope. The source nuclei of gamma should be in a rigid material to prevent recoil motion of the γ (gamma) radiation.

Mössbauer spectroscopy is a very sensitive technique which can be applied to iron. The nucleus of ^{57}Co is radioactive and will undergo electron capture to become an excited nucleus of ^{57}Fe. Excited ^{57}Fe emits a γ-ray to become ^{57}Fe nucleus. The ^{57}Fe should be component of a rigid material which will guarantee a recoil free emission and absorptions of γ -rays.

If the environment of the atomic nuclei are identical, they will posses equal transition energy and absorption will occur. If the atomic nuclei are in different environment the wavelength at which absorption occurs changes. The wavelength of the gamma ray can be varied to bring the two nuclei into resonance by using the ‘Doppler effect – move the sample towards and away from the source of the gamma radiation, a few mms^{-1}, plotting the gamma ray intensity against the Doppler velocity gives the Mössbauer spectrum.

3.3.1 Information from Mössbauer Spectrum

Information about the chemical environment of a nucleus absorbing radiation is given by the number of peaks, the position of peaks and intensities of peaks. These information are useful in characterizing a sample.

3.3.2 Limitations of Mössbauer Spectroscopy

1. The number of gamma ray sources employed by Mössbauer spectroscopy is limited.
2. Sample must be solid to avoid recoil motion of the gamma ray emission.
3. The supply of radiation of the required intensity from the parent nucleus must be sustainable; therefore the half-life and decay rate of the parent nucleus must be sufficient.

3.3.3 Uses of Mössbauer Spectroscopy

1. Being a technique that is very sensitive even to small changes in the chemical environment of a nucleus, it can be used to detect changes in oxidation state, and the effect of ligands on an atom.

2. In geology, the technique is used to analyse the composition of minerals containing iron.
3. In bioinorganic chemistry, it has been used to study iron containing proteins and enzymes.

3.4 CONCLUSION

The methods involving electron spin resonance, nuclear quadropole resonance and Mössbauer spectroscopy each are related to nuclear magnetic resonance, because they are concerned with the interaction of the nuclei of atoms with radiation .

5.0 SUMMARY

In electron spin resonance, microwave radiation interacts with odd number electron species in a magnetic field. it is used to detect the presence and concentration of free radicals, to study transition metals ions found in some salts and biochemical studies of enzymes.

Nuclear Quadropole Resonance is detected in an environment without a magnetic field. NQR is applied in the detection of explosive and land mines and measurement of the water/gas coming out of an oil well.

In Mössbauer spectroscopy, a nucleus emits gamma rays which can be absorbed by a sample containing the nuclei of the same isotope. The source nuclei of gamma should be in a rigid material to prevent recoil motion of the γ (gamma) radiation.

it can be used to detect changes in oxidation state, and the effect of ligands on an atom.

6.0 TUTOR MARKED ASSIGNMENT

1. Briefly explain the principle of Mössbauer spectroscopy.
2. Why should the source nuclei of gamma radiation be in a rigid material?
3. What is the function of Doppler effect in Mössbauer spectroscopy?
4. How does the environment of nuclei influence absorption?
5. What information can be got from Mössbauer spectrum?
6. Outline the limitations of Mössbauer spectroscopy.
7. Outline the applications of Mössbauer spectroscopy.
8. Distinguish between NMR and NQR techniques.
9. Describe the operational principle of NQR.
10. In what areas are NQR applied ?
11. Compare the principles of EPR with NMR

7.0 REFERENCE/ FURTHER READING.

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