SWAMI DAYANANDA COLLEGE OF ARTS & SCIENCE

(Affiliated to Bharathidasan University, Tiruchirappalli-620024)

MANJAKKUDI-612610, TIRUVARUR-(DT).

DEPARTMENT OF CHEMISTRY

ORGANIC CHEMISTRY- II

Dr.G.MARIMUTHU

Unit- V ORGANIC SPECTROSCOPY

INTRODUCTION

Analytical techniques or spectroscopy is one of the most powerful tools available for the study of atomic and molecular structure and is used in the analysis of most of the samples.

Spectroscopy deals with the study of interaction of electromagnetic radiation with the matter. During such interaction energy is either absorbed or released by the matter. The measurement of this radiation frequency is made using spectroscopy.

TYPES OF SPECTROSCOPY

The study of spectroscopy can be carried out under the following types

1. Atomic spectroscopy

2. Molecular spectroscopy

1. Atomic Spectroscopy

It deals with the interaction of the electromagnetic radiation with atoms during which the atoms absorb radiation and gets excited from the ground state electronic energy level to another.

2. Molecular Spectroscopy

It deals with the interaction of electromagnetic radiation with molecules. This results in transition between vibrational and electronic energy levels.

Difference between molecular and atomic spectra

Atomic Spectra	**Molecular Spectra**
1. It occurs from the interaction of atoms + electromagnetic radiation	1. It occurs from the interaction of molecules + electromagnetic radiation.

2. Atomic spectra is a line spectra	2. Molecular spectra is a complicated spectra.
3. It is due to electronic transition in an element.	3. It is due to vibrational, rotational and electronic transition in a molecule.

SPECTRUM

How does a spectrum arise?

1. Absorption spectrum

Consider a molecule having only two energy levels E1 and E2 as shown in fig 5.1.

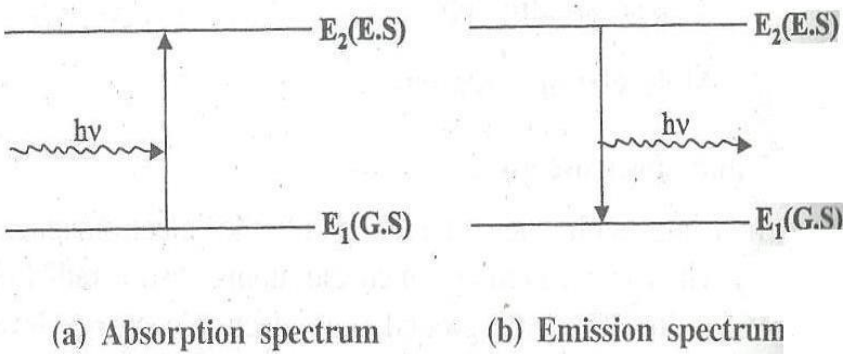


Fig 5.1

When a beam of electromagnetic radiation is allowed to fall out on a molecule in the ground state, the molecule absorbs ohoton of energy hν and undergoes a transition from the lower energy level to the higher energy level. The measurement of this decrease in the intensity of radiation is the basis of absorption spectroscopy. The spectrum thus obtained is called **absorption spectroscopy.** (Fig 5.1 a)

2. Emission spectrum

If the molecule comes down from the excited state to the ground state with emission of photons of energy hν, the spectrum is called **emission spectrum.** (Fig 5.1 b)

5.1 VISIBLE AND ULTRA VIOLET (UV) SPECTROSCOPY

Principle

Visible and Ultraviolet (UV) spectrum arises from the transition of valency electrons within a molecule or ion from a lower electronic energy level (ground state E_0) to higher electronic energy level (excited state E_1). This transition occurs to the absorption of UV (wavelength 100-400 nm) or visible (wavelength 400-750 nm) region of the electronic spectrum by a molecule (or) ion.

The actual amount of energy required depends on the difference in energy between the ground state and the excited of the electrons.

$$\mathbf{E_1 - E_0 = h\upsilon}$$

Types of electrons involved in organic molecule

The energy absorbed by an organic molecule involves transition of valency electrons. The following 3 types of electrons are involved in the transition.

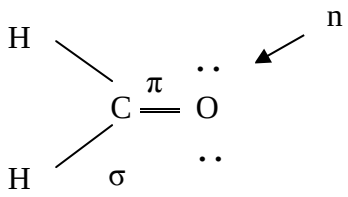
S.No	Electrons	Examples	Energy required to excite electrons	Present in
1.	σ-electrons	Saturated long chain hydrocarbons. (Paraffins) $(CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3)$		
2.	π-electrons	Unsaturated hydrocarbons like trienes & aromatic compounds.	UV (or) visible light	Double bond & triple bonds (unsaturated bond)

3.	n-electrons	Organic compounds containing N, O (or) halogens	UV radiation	Unshared (or) non bonded electrons.

Thus the unsaturated hydrocarbons and compounds containing N, O, S may absorb visible (or) UV radiations.

Example

The 3 types of electrons are shown in the molecule (HCHO).



Energy level diagram

Energy absorbed in the visible and UV region by a molecule causes transitions of valence electrons in the molecule. These transitions are $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$

The energy level diagram for a molecule is shown in fig 8.8. The energy values for different transitions are in the following order.

$$n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* << \sigma \rightarrow \sigma^*$$

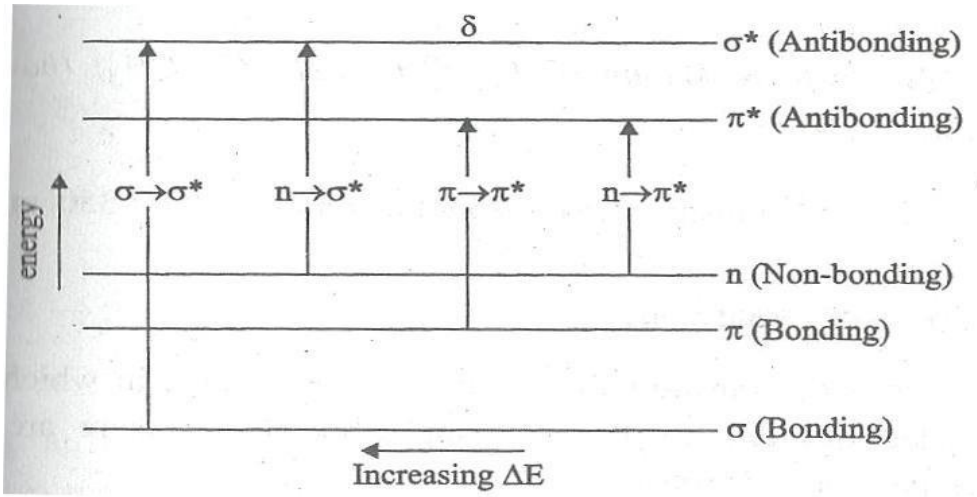
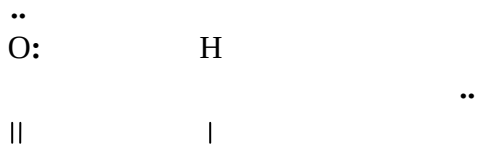


Fig 5.8 Energy level diagram

Types of transitions involved in organic molecules

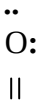
1. n → π* transitions n π* transitions are shown by unsaturated molecules containing hetero atoms like N, O & S. It occurs due to the transition of non-bonding lone pair of electrons to the anti-bonding orbitals. This transition shows a weak band, and occurs in longer wavelength with low intensity.

Example



(i) Aldehyde & ketone (CH_3-C-CH_3 & CH_3-C=O:) (having no C=C & C≡C bond)

n → π* transition occurs in the range of 270-300 nm.



(ii) Aldehyde & ketone (CH_3-CH=CH-C-CH_3) (having double bond).

n → π* transition occurs in the range of 300-350 nm.

2. σ → σ* transitions

σ → σ* transitions occur in the compounds, in which all the electrons are involved in single bonds and there are no lone pair of electrons.

The energy required for σ → σ* transition is very large. The absorption band occurs in the far UV region (120-136 nm).

Example

Saturated hydrocarbons

(CH_4, CH_3-CH_3, CH_3-CH_2-CH_3, etc.

(i) CH_4: For σ → σ* ; λ_{max} = 121.9 nm.

(ii) CH_3-CH_3: For σ → σ* ; λ_{max} =135 nm.

3. n → σ* transitions n σ* transitions occur in the saturated compounds containing lone pair (non-bonding) of electrons in addition to σ σ* transitions. The energy required

for an n σ^* transition is less than that required for a σ σ^* transition. This absorption band occurs at longer wavelength in the near UV region (180-200 nm).

Example $(CH_3)_3N$

For n $\longrightarrow \sigma^*$; λ_{max} = 227 nm and for σ $\longrightarrow \sigma^*$; λ_{max} = 99 nm.

4. π $\longrightarrow$ π* transitions π π^* transitions occur due to transition of an electron from a bonding π orbital to an anti-bonding π^* orbital. These transitions can occur in any molecule having a π electron system.

Selection rule determines whether transitions to a particular π^* orbital is allowed or forbidden.

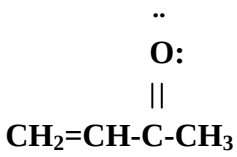
Example

1. *UV spectrum of ethylene*

It shows ***intense band*** at 174 nm and ***weak band*** at 200 nm. Both are due to π π^* transitions. According to selection rule, the intense band at 174 nm is due to allowed transition.

Alkyl substitution of the olefins moves the absorption to a longer wavelength. This is known as bathochromic effect or red shift. This effect increases with increase of alkyl group.

2. *UV spectrum of unsaturated ketone*

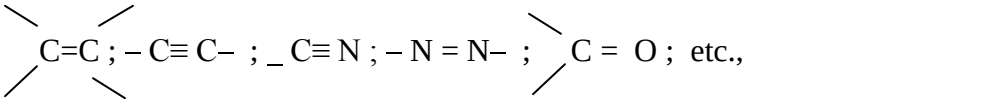


It shows that the low density band at 324 nm is due to n π^* transition, and high intensity band at 219 nm is due to π π^* transition.

Important terms used in UV- visible spectroscopy

1. Chromophores (Colour producing groups)

The presence of one or more unsaturated linkages (π-electrons) in a compound is responsible for the colour of the compound. These linkages are referred to as chromophores. **Example**



Chromophores undergo $\pi \longrightarrow \pi^*$ transitions in the short wavelength regions of UV-radiations.

2. Auxochrome (Colour intensifying groups)

It refers to an atom or a group of atoms which does not give rise to absorption band on its own, but when conjugate to chromophore will case a red shift.

Example: – OH, – NH_2, – Cl, –Br,– I, etc.,

3. Some important definitions related to change in wavelength and intensity

1.	**Bathochromic shift (red shift)**	Shift to higher wavelength (lower frequencies).
2.	**Hypsochromic shift (blue shift)**	Shift to lower wavelength (higher frequencies).
3.	**Hyperhromic effect**	An increase in intensity.
4.	**Hypochromic effect**	A decrease in intensity.

Illustration

In chloroethylene, CH_2=CHCl,

C=C is a chromophore.

Cl is an auxochrome.

Substitution of a hydrogen atom in ethylene by a halogen atom causes a bathchromic shift and a hyperchromic effect.

4. Difference between Chromophore and Auxochrome

S.No	**Chromophore**	**Auxochrome**
1.	This group is responsible for the colour of the compound.	It does not impact colour, but when conjugate to

		chromophore produce colour.
2.	It does not form salt.	It forms salt.
3.	It contains at least one multiple bond.	It contains lone pair of electrons.
4.	**Example:** —NO_2, — NO,— N=N	**Example:** — OH,— NH_2,— NR_2

Woodward–Fieser Rules for Diene :

Ø Woodward (1941) predicted λmax values only for the lowest energy

Transition (π è π*) from HOMO to LUMO. Woodward's rules, named after Robert Burns Woodward and also known as Woodward–Fieser rules (for Louis Fieser) are several sets of empirically derived rules which attempt to predict the wavelength of the absorption maximum (λmax) in an ultraviolet–visible spectrum of a given compound. Inputs used in the calculation are the type of chromophores present, the auxochromes (substituents on the chromophores, and solvent.Examples are conjugated carbonyl compounds, conjugated dienes,and polyenes.

Implementation:

One set of Woodward–Fieser rules for dienes is outlined in table 1. A diene is either homoannular with both double bonds contained in one ring or heteroannular with two double bonds distributed between two rings.

Structural feature:

Base values: Ø Base value for an unsubstituted, conjugated, acyclic or

Heteroannular diene 214 nm

Ø Base value for an unsubstituted, conjugated, homoannular diene 253 nm

Increments for: Each extra double bonds in conjugation + 30 nm

Exocyclic double bond (effect is two fold if the bond is exocyclic to Two rings) + 5 nm

Substituent effect:

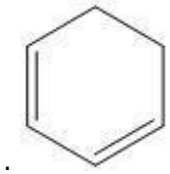
A. **-OCOR or –OCOAr + 0 nm**
B. **Simple alkyl substituents or ring residue + 5 nm**
C. **Halogen (-Cl, -Br) + 5 nm**
D. **OR (R=Alkyl) + 6 nm**
E. **SR (R=Alkyl) + 30 nm**
F. **NR2 (R=Alkyl) + 60**

WOODWARD- FIESER RULES:

Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the ***Base value or Parent value***. The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as –Cl, -Br etc are added to the basic value to obtain λ_{max} for a particular compound.

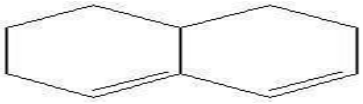
I) CONJUGATED DIENE CORRELATIONS:

a) Homoannular Diene:- Cyclic diene having conjugated double bonds in same ring

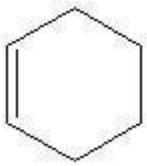


.

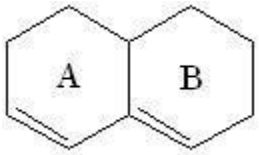
b) Heteroannular Diene:- Cyclic diene having conjugated double bonds in different rings.



© Endocyclic double bond:- Double bond present in a ring



d) Exocyclic double bond: - Double bond in which one of the doubly bonded atoms is a part of a ring system.



Here Ring A has one exocyclic and endocyclic double bond. Ring B has only one endocyclic double bond.

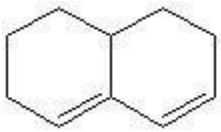
PARENT VALUES AND INCREMENTS FOR DIFFERENT SUBSTITUENTS/GROUPS:

I) CONJUGATED DIENE CORRELATIONS:

i) Base value for homoannular diene = 253 nm ii) Base value for heteroannular diene = 214 nm iii) Alkyl substituent or Ring residue attached to the parent diene = 5 nm

iv) Double bond extending conjugation = 30 nm v) Exocyclic double bonds = 5 nm vi) Polar groups: a) -OAc = 0 nm b) -OAlkyl = 6 nm , c) -Cl, -Br = 5 nm

Eg:



Base value = 214 nm
Ring residue = 3 x 5 = 15 nm

Exocyclic double bond = 1 x 5 = 5 nm
λ_{max} = 214 + 15 + 5 = 234 nm

Components of UV spectrometer:

The various components of a visible UV spectrometer are as follows.

1. Radiation Source:

In visible - UV spectrometers, the most commonly used radiation sources are hydrogen (Or) deuterium lamps.

Requirements of a radiation source

(a) It must be stable and supply continuous radiation.

(b) It must be of sufficient intensity.

2. Monochromators

The monochromator is used to disperse the radiation according to the wavelength. The essential elements of a monochromator are an entrance slit, a dispersing element and an exit slit. The dispersing element may be a prism or grating (or) a filter.

3. Cells (sample cell and reference cell)

The cells, containing samples or reference for analysis, should fulfill the following conditions.

(i) They must be uniform in construction.

(ii) The material of construction should be inert to solvents.

(iii) They must transmit the light of the wavelength used.

4. Detectors

There are three common types of detectors used in visible UV spectrophotometers. They are Barrier layer cell, Photomultiplier tube Photocell. The detector converts the radiation, falling on which current. The current is directly proportional to the concentration of the solution.

5. Recording system

The signal from the detector is finally received by recording system. The recording is done by recorder pen.

Working of visible and UV spectrophotometer

The radiation from the source is allowed to pass through the monochromator unit. The monochromator allows a narrow range of wavelength to pass through an exit slit. The beam of radiation coming out of the monochromator is split into two equal beams. One-half of the beams (the sample beam) is directed to pass through a transparent cell containing a solution of the compound to be analysed. The other half (reference beam) is directed to pass through an identical cell that contains only the solvent. The instrument is designed in such a way that it can compare the intensities of the two beams.

If the compound absorbs light at a particular wavelength, then intensity of the sample beam (I) will be less than that of the reference beam (I_0) The Instrument gives output graph, which is a plot of wavelength Vs absorbance of the light. This graph is known as an absorption spectrum.

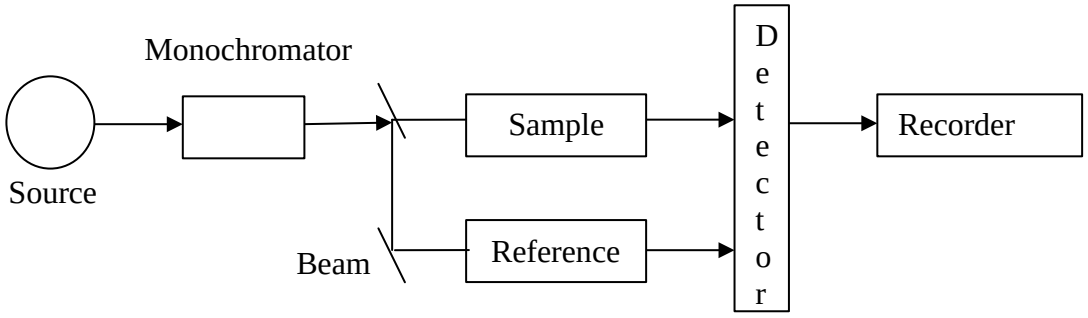


Fig. 1 Block diagram of visible UV spectrophotometer Applications

1. Predicting relationship between different groups

UV spectroscopy is not useful in the detection of individual functional groups, but it is used in predicting the relation between different groups i.e.,

(i) Between two or more C-C multiple bonds (= (or) = bonds).

(ii) Between C – C and C – C double bonds.

(iii) Between C –C double bonds and aromatic benzene ring.

Thus the structure of several vitamins and steric hindrance of the molecule can be determined using UV spectroscopy.

2. **Qualitative analysis**

UV absorption spectroscopy is used for characterizing and identification of aromatic compounds and conjugated olefins by comparing the UV absorption spectrum of the sample with the same of known compounds available in reference books.

3. **Detection of impurities**

UV absorption spectroscopy is the best for method detecting impurities in organic compounds, because

(i) The bands due to impurities are very intense.

(ii) Saturated compounds have little absorption band and unsaturated compounds have strong absorption band.

4. **Quantitative analysis**

Determination of substances: UV absorption spectroscopy is used for the quantitative determination of compounds, which absorbs UV light. This determination is based on Beer's law.

$$\mathbf{A = - \log T = \log I_O/I = \epsilon Cx}$$

where, ϵ= Molar extinction coefficient (constant)

C = Concentration

x = Length of the cell.

First, absorbance (optical densities) of the different solutions of known concentrations is measured. Then the graph is plotted between absorbance vs concentration (calibration curve). A straight line is obtained.

Then absorbance of unknown solution is measured. From the graph the concentration of unknown substance is found out.

5. Determination of molecular weight

Molecular weight of a compound can be determined if it can be converted into a suitable derivative, which gives an absorption band.

6. Dissociation constants of Acids and Bases

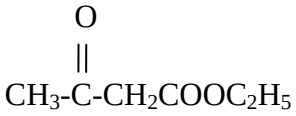
The dissociation constant (Pk_a) of an acid (HA) can be determined by determining the ratio of [HA] /[A] specrophotometrically from the graph plotted between absorbance vs wavelength at different pH va1ues. This value are substituted in the equation

$$\mathbf{Pk_a = pH + \log [HA] / [A]}$$

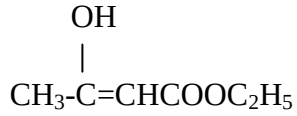
7. Study of tautomeric equilibrium

The percentage of various keto and enol forms present in a tautomeric equilibrium can be measured by the strength of the respective absorption bands using UV spectrometry.

Example: Ethylacetoacetate



Keto form; λ_{max}=275nm;



Enol form; λ_{max}=244nm

8. Studying kinetics of chemical reactions

Kinetics of chemical reactions can be studied using UV spectroscopy by following the change in concentration of a product or a reactant with time during the reaction.

9. Determination of calcium in blood stream

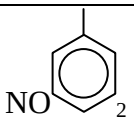
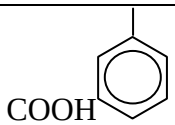
Calcium in the blood can be determined by converting the 'Ca' present in 1ml of the serum as its oxalate and re-dissolving it in H_2SO_4 and treating it with dilute ceric sulphate solution. The absorption of the solution is measured at 315 nm. Thus the amount of 'Ca' present in the blood serum can be calculated.

Problems based on visible-UV spectroscopy Problem 1

Which of the following compounds absorbs UV radiation? Heptane, benzene, butadiene,water, heptene, chlorohexane, ethanol, n-butylamine, acetone, ethylene, nitrobenzene, benzoic acid.

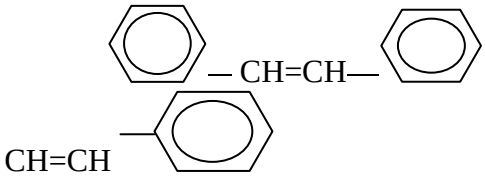
Solution

S.No	Name	Structure	Type of transition
1.	Heptane	CH_3-$(CH_2)_5$-CH_3	$\sigma \rightarrow \sigma^*$ transition(No absorption, need very high energy)
2.	Benzene		$\pi \rightarrow \pi^*$ transition
3.	Butadiene	CH_2=CH-CH=CH_2	$\pi \rightarrow \pi^*$ transition
4.	Water	H_2O	$\sigma \rightarrow \sigma^*$ transition
5.	Heptene	CH_3-$(CH_2)_4$-CH=CH_2	$\pi \rightarrow \pi^*$ transition
6.	Chlorohexane	Cl-$(CH_2)_5$-CH_3	No absorption in UV region

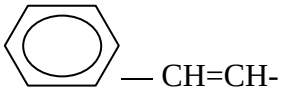
7.	Ethanol	CH_3-CH_2-OH	No absorption in UV region
8.	n-Butylamine	CH_3-CH_2-CH_2-CH_2-NH_2	No absorption in UV region
9.	Acetone	O ‖ CH_3-C-CH_3	$\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transition
10.	Ethylene	CH_2=CH_2	$\pi \rightarrow \pi^*$ transition
11.	Nitrobenzene		$\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transition
12.	Benzoic acid		$\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transition

Problem 2

Which will have greater λ_{max} value?



I

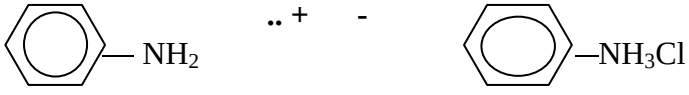


II Solution

Greater the extent of conjugation, greater will be the value of λ_{max} in the UV spectrum. Hence, the compound II (having more double bond) have greater λ_{max} value than that of compound I.

Problem 3

Which will have greater λ_{max}?



I **II**

Solution:

As the lone pair of electrons on nitrogen atom, is available for conjugation with aromatic ring in compound I, it shows greater λ_{max} value. But, in compound II no lone pair of electrons are available and hence no conjugation, so the compound II shows lesser λ_{max} value.

Problem 4

Select the compounds, which will absorb UV radiations. (a)1,3 butadiene, (b)cyclobutane, (c)nitrobenzene,(d) chlorobenzene,(e) n–hexane, (f) 1,3 cyclohexadiene

Solution

S.No	Compound	Structure	UV radiation
(a)	1,3 Butadiene	CH_2=CH-CH=CH_2	Absorb UV radiation
(b)	Cyclobutane		NO UV absorption
(c)	Nitrobenzene	NO_2 	Absorb UV radiation
(d)	Chlorobenzene	Cl 	Absorb UV radiation
(e)	Hexane	CH_3-(CH_2)$_4$-CH_3	NO UV absorption
(f)	1,3 Cyclohexadiene		Absorb UV radiation

Compound a,c,d,f absorb UV radiation due to the presence of double bonds.

Problem 5

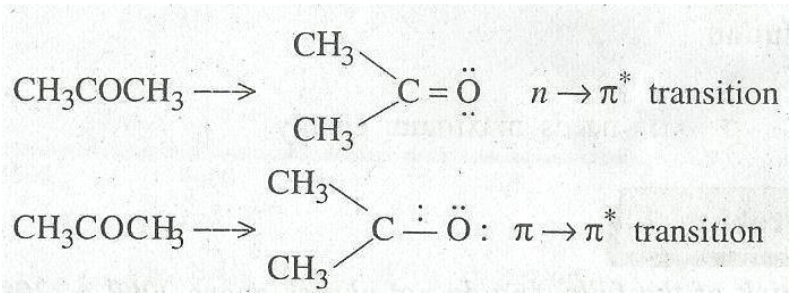
UV spectrum of acetone (CH_3COCH_3) shows two peaks at λ_{max}– 189 nm and λ_{max}=273 nm. Identify the electronic transitions for each peak.

Solution

1. Higher wavelength, have less energy, show n $\longrightarrow$ π transition (λ_{max}=273 nm).
2. Lower wavelength, have high energy, show $\pi \longrightarrow \pi^*$ transition (λ_{max}=189 nm).

We know that

$\pi \rightarrow \pi^*$ > $n \rightarrow \pi^*$



Problem 6

A compound which exhibits absorption peaks at 190nm and 300nm. What type of absorption is associated with each absorption?

Solution

(i) The peak exhibits absorption at 190 nm is due to $\sigma \rightarrow \sigma^*$ transition. (ii)

The peak exhibits absorption at 300 nm is due to $\pi \rightarrow \pi^*$ transition.

Problem 7

Acetaldehyde (CH_3CHO) has absorption peaks at 160, 180, 299 nm. which type of absorption is responsible for each of these absorption?

Solution

The peak at 160 nm is due to $\pi \rightarrow \pi^*$ transition. The

peak at 180 nm is due to $n \rightarrow \sigma^*$ transition.

The peak at 299 nm is due to $n \rightarrow \pi^*$ transition.

Problem 8

Which of the following needs maximum energy?

σ $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$ $\pi \rightarrow \pi^*$ **Solution** σ σ^*

needs maximum energy.

$\rightarrow$

Problem 9

Which of the following do not absorb 2000A^0(200nm)?n-propyl alcohol, benzene, diethyl ether, methylvinyl ketone, methyl alcohol.

Solution

In UV region i.e., above 2000A^0 (200nm) no absorption occurs in he following compounds.

n-propyl alcohol (CH_3-CH_2-CH_2-OH) diethyl ether (C_2H_5-O-C_2H_5) methyl alcohol (CH_3OH)

The reason for which is due to absence of double bonds.

5.2 INFRARED SPECTROSCOPY

Principle

IR spectra is produced by the absorption of energy by a molecule in the infrared region and the transition occur between vibrational levels. So, IR spectroscopy is also known as vinbrational spectroscopy.

Range of Infrared Radiation

The range in the electromagnetic spectrum extending from 12500 to 50 cm^{-1}(0.8 to 200μ) is commonly referred to as infrared. This region is further divided into three sub regions.

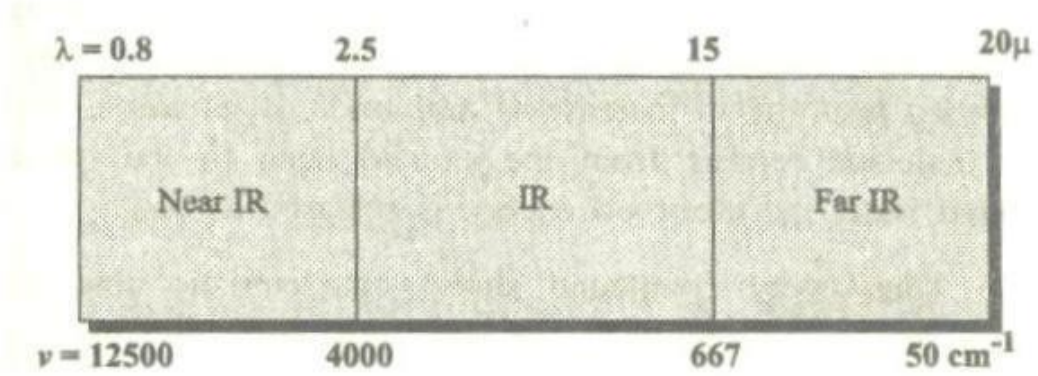


Fig 5.10 Range of IR radiation

(i) ***Near infrared:*** The region is from 12500 to 4000 cm^{-1}.

(ii) ***Infrared (or) ordinary IR:*** The region is from 4000 to 667 cm^{-1}.

(iii) ***Far infrared:*** The region is from 667 to 50 cm^{-1}.

(iv) ***Source of IR:*** Electrically heated rod of rare earth oxides.

Molecular vibrations and Origin of IR Spectrum

Since atoms in a molecule are continuously vibrating molecules are also vibrating. There are two kinds of fundamental vibrations in a molecule.

1. **Stretching vibrations**: During stretching the distance between two atoms decrease or increase, but bond angle remains unaltered.
2. **Bending (or) deformation vibrations**: During bending bond angles increases and decreases but bond distance remains unaltered.

Vibrational changes depend on the masses of the atoms and their spatial arrangement in the molecule. When IR light of the same frequency is incident on the molecule, energy is absorbed resulting in increase of amplitude of vibration. When the molecule returns from the excited ate to the original ground state, the absorbed energy is released as heat.

Thus every compound shows characteristic absorption bands in the IR region of the spectrum. Different functional groups produce easily recognizable band at definite positions in the IR spectral range (12500 to 50 cm^{-1}).

Fingerprint region

The vibrational spectral (IR spectra) region at 1400-700 cm^{-1} gives very rich and intense absorption bands. This region is termed as **fingerprint region**. The region 4000-1430 cm^{-1} is known as **Group frequency region**.

Uses of fingerprint region

(i) IR spectra are often characterized as molecular finger prints, which detect the presence of functional groups.

(ii) Fingerprint region group is also used to identify and characterize the molecule just as a fingerprint can be used to identify a person.

Types of stretching and bending vibrations

The number of fundamental (or0 normal vibrational modes of a molecule can be calculated as follows.

1. For non-linear molecule

A non-linear molecule containing 'n' atoms has (3n-6) fundamental vibrational modes.

Example

(i) CH_4 ⟶ (3 X 5-6) = 9 fundamental vibrational modes.

(ii) C_6H_6 ⟶ (3 X 12-6) = 30 fundamental vibrational modes.

2. For linear molecules

A linear molecule containing 'n' atoms has (3n-5) fundamental vibrational modes. **Example**

CO_2 ⟶ (3 X 3 – 5) = 4 fundamental vibrational modes.

Illustrations

1. Water

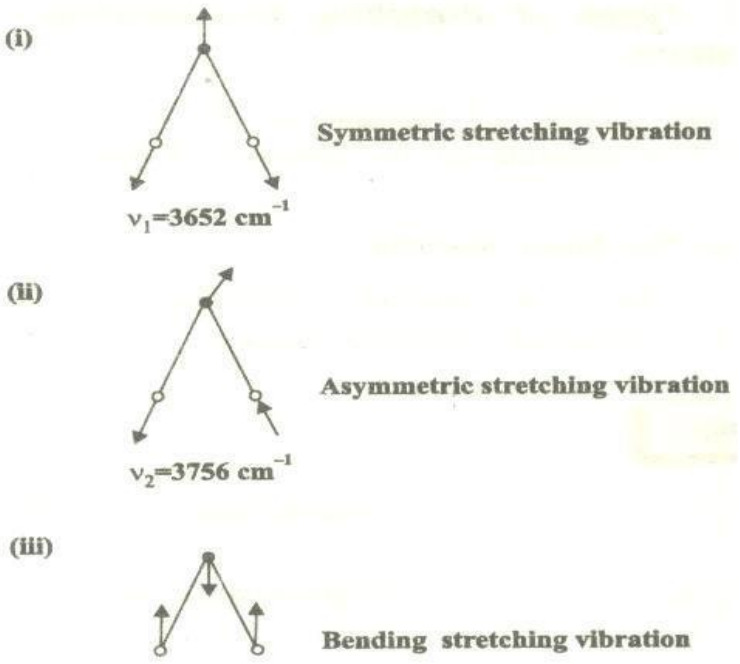


Fig 5.11 Vibrational modes of H_2O

Water is a bend (non-linear) tri atomic molecule, and has 3n-6 (3 x 3 -6) = 3 fundamental vibrational modes. These modes and their corresponding frequencies are shown above (Fig 5.11).

In general stretching frequencies are much higher than bending frequencies. This is because, more energy is required to stretch a bond than to bend it. All the above 3 vibrations are said to be active (change in dipole moment during the vibration) in the IR region and the IR spectrum of water exhibits 3 absorption bands at 1596, 3562 and 3756 cm^{-1} corresponding to the bending, symmetric stretching and the asymmetric stretching vibration respectively.

Thus, for a vibration to be active in IR, the dipole moment of the molecule must change.

2. Carbon dioxide

Carbon dioxide is a linear triatomic molecule, and has 3n-5 (3 x 3 – 5) = 4 fundamental vibrational modes. These modes and corresponding frequencies are shown (Fig 5.12).

Of the four normal modes of vibration of CO_2, only the asymmetric stretching and bending vibrations i.e., (ii), (iii) and (iv) involve change in dipole moment (all are IR active).

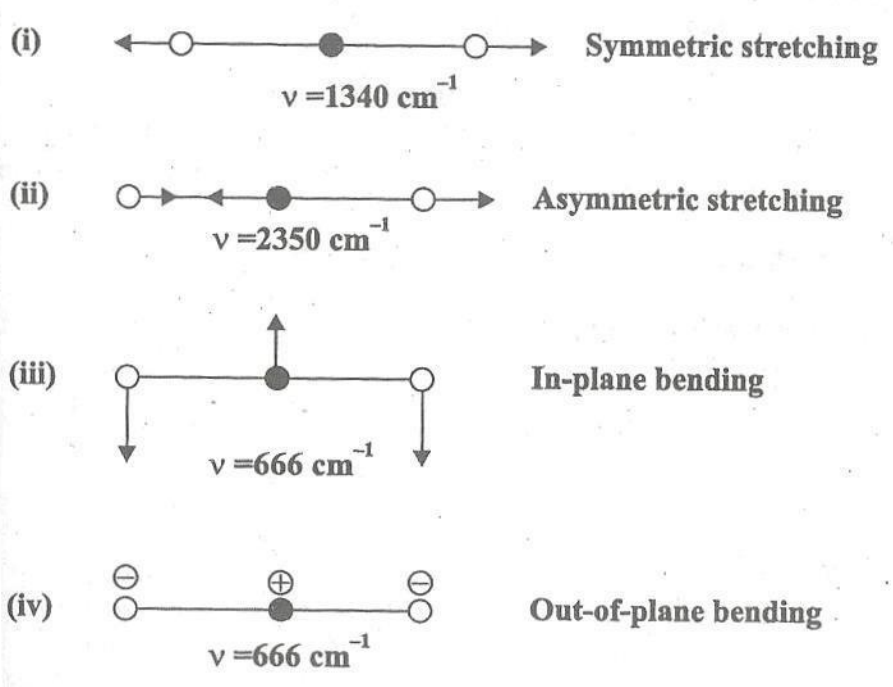


Fig 5.12 Vibrational modes of CO_2

But the symmetric stretching vibration i.e., (i) does not involve any change in the dipole moment (IR inactive).

(N***ote:*** + and – signs indicate the motion of the corresponding atom, above and below the plane of the paper respectively).

Thus, though there are three active vibrations, two of them ((iii) and (iv)) have the same frequency, so the IR spectrum of CO_2 exhibits only two bands i.e., one at 666 cm^{-1} and another at 2350 cm^{-1}.

Group frequencies (Tri atomic group)

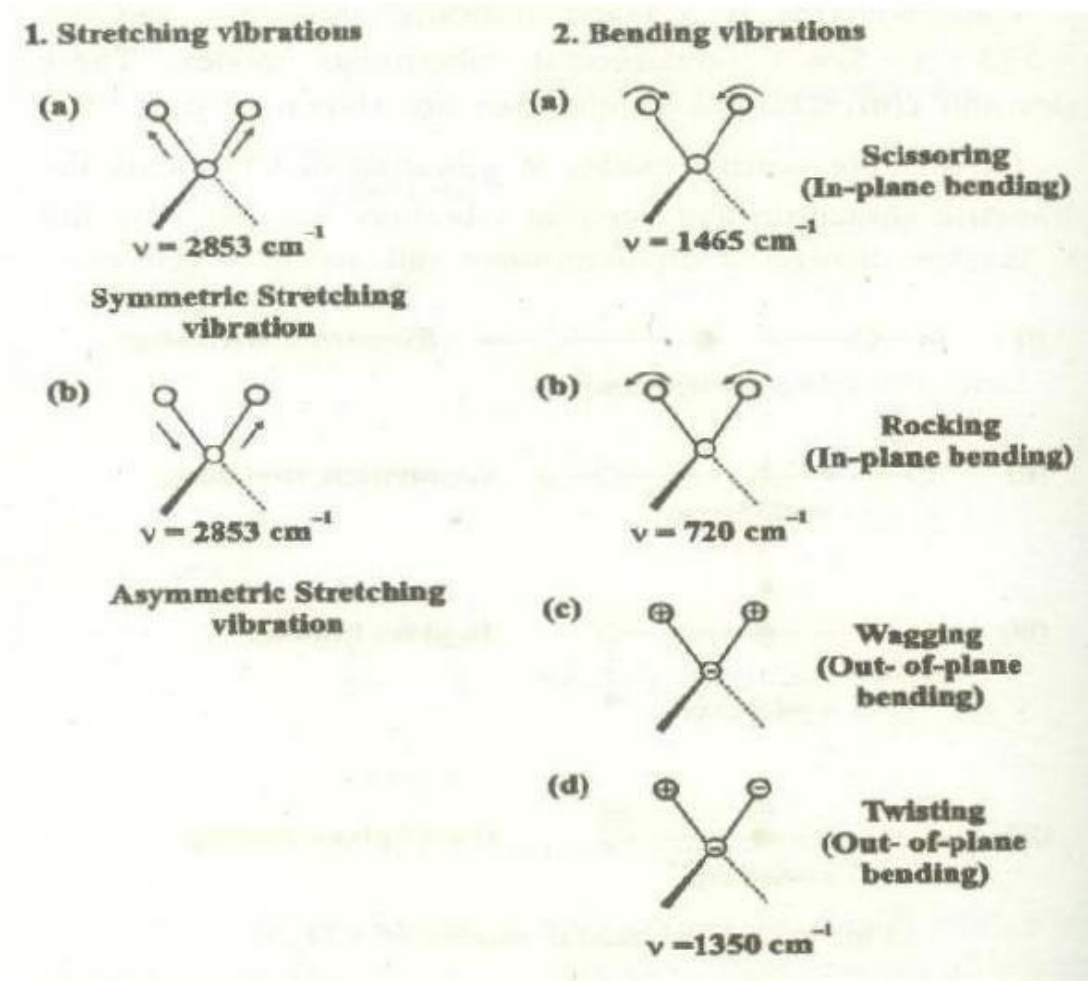


Fig 2.Various kinds of vibrations

Of the symmetrical triatomic functional group such as CH_2, $-NH_2$, $-\overset{\overset{O}{||}}{C}-O^-$, the methylene has got six characteristic vibrations. These vibrations and their frequencies are shown in Fig. 2

Instrumentation

I. Components 1. Radiation source

The main sources of IR radiation are

(a) Nichrome wire.

(b) Nernst glower, which is a filament containing oxides of Zr,Th,Ce, held together with a binder.

(c) When they are heated electrically at 1200 to 2000˚C, they glow and produce IR radiation.

2. Monochromator

It allows the light of the required wave length to pass through, but absorbs the light of other wavelength.

3. Sample cell

The cell, holding the test sample, must be transparent to IR radiation.

4. Detector

IR detectors generally convert thermal radiant energy into electrical energy. There are so many detectors, of which the followings are important.

(a) Photoconductivity cell.

(b) Thermocouple

(c) Pyroelectric detectors

5. Recorder

The recorder records the signal coming out from the detector.

II. Working of IR Spectrophotometer

The radiation emitted by the source is split into two identical beams having equal intensity. One of the beams passes through the sample and the other through the reference sample.

When the sample cell contains the sample, the half-beam travelling through it becomes less intense. When the two half beams (one coming from the reference and the other from the sample) recombine, they produce an oscillating signal, which is measured by the detector. The signal from the detector is passed to the recording unit and recorded.

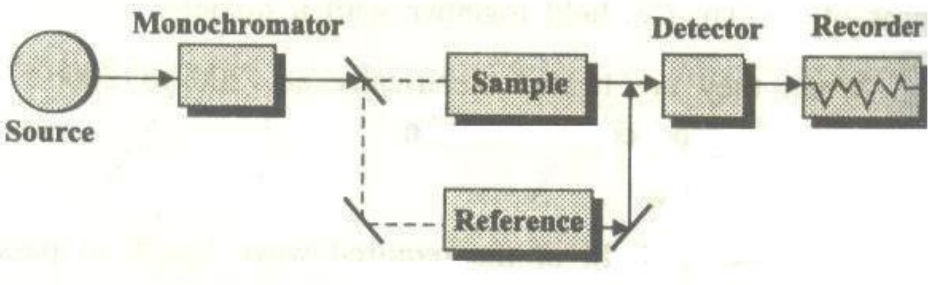


Fig 4 Block diagram of double beam IR spectrophotometer

Applications of IR spectroscopy

1. Identity of the compound can be established

The IR spectrum of the compound is compared with that of known compounds. From the resemblance of the two spectra, the nature of the compound can be established. This is because a particular group of atoms gives a characteristic absorption band in the IR spectrum.

Example

IR spectra of both benzaldehyde (C_6H_5-C=O) and phenylmethylketone (C_6H_5-C-CH_3) show a sharp absorption peak at 1700 cm^{-1}. This indicated the presence of C=O group in both the compounds.

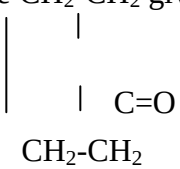
2. Detection of functional group

In a given environment, a certain functional group will absorb IR energy of very nearly the same wave length in all molecules.

Example

(i) Acetone (CH_3-C-CH_3) and diethylketone (C_2H_5-C-C_2H_5) give absorption peak at the **same place.**

(ii) But, acetic acid (CH_3COOH) and cyclobutanone CH_2-CH_2 give absorption peaks at **different places**.



3. Testing purity of a sample

Pure sample will give a sharp and well resolved absorption band. But impure sample will give a broad and poorly resolved absorption band. Thus by comparison with IR spectra of pure compound, presence of impurity can be detected.

4. Study of progress of a chemical reaction

The progress of a chemical reaction can be easily followed by examining the IR spectrum of test solution at different time intervals.

Example

(i) Progress of oxidation of secondary alcohol to ketone is studied by getting IR spectra of

test solutions at different time intervals.

The secondary alcohol absorbs at 2.8μ (~3570 cm^{-1}) due to O-H stretching. As the reaction proceeds this band slowly disappears and a new band near 5. 8μ (~1725 cm^{-1}) due to C=O stretching appears.

(ii) Similarly, the progress of any chromatographic separations can be readily monitored by examining the IR spectra of the selected fractions.

5. Determination of shape or symmetry of a molecule.

Whether the molecule is linear (or) non-linear (bend molecule) can be found out by IR spectra.

Example: IR spectra of NO_2 gives three peaks at 750, 1323 and 1616 cm^{-1}.

According to the following calculations,

(i) For non-linear molecule = (3n-6) = 3 peaks.

(ii) For linear molecule = (3n-5) = 4 peaks.

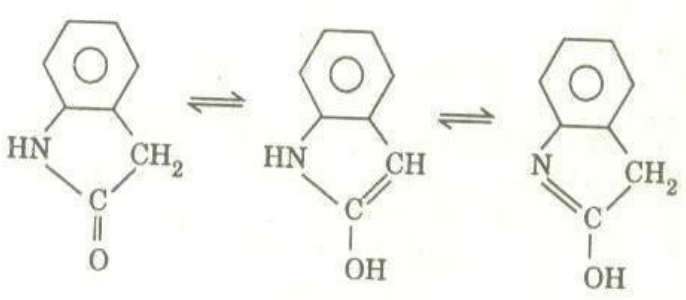
Since the spectra shows only 3 peaks, it is confirmed that NO_2 molecule is a non-linear (bend).

6. To study tautomerism

Tautomeric equilibrium can be studied with the help of IR spectroscopy.

Example

The common systems such as keto-enol, lacto-lactum and mercapto-thioamide, contain a grorup like C=O, -OH, -NH (or) C=S. These groups show a characteristic absorption band in the IR spectrum, which enable us to find at which form predominates in the equilibrium.



7. Industrial applications

(a) *Determination of structure of chemical products*

During the polymerization, the bulk polymer structure can be determined using IR spectra.

(b) *Determination of molecular weight*

Molecular weight of a compound can be determined by measuring end group concentrations, using IR spectroscopy.

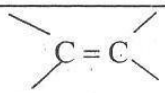
(c) *Crystallinity*

The physical structure like crystallinity can be studied through changes in IR spectra. Example

The absorption band at 934 cm^{-1} is for crystalline nylon 6:6.

The absorption band at 1238 $cm^{-1}$is for amorphous nylon 6:6.

IR positions f Various Band Vibrations

Band for the group	Type of molecule	Wavelength (μm)	Frequency cm^{-1}
	(in alkanes)	3.38 – 3.51	2850 – 2960
	(in alkenes)	3.22 – 3.32	3010 – 3100
≡ C – H	(in alkynes)	3.03	3300
Ar – C – H	(aromatic ring)	3.22 – 3.33	3010 – 3100
	(C – H bond in aldehydes	3.47 – 3.77	2650 – 2880
	(C – C bond in alkenes)	6.66 – 16.66	600 – 1500
	(C = C bond in alkenes	5.95 – 6.2	1620 – 1680
– C ≡ C –	(C ≡ C in alkynes)	4.42 – 4.76	2100 – 2660
– C = C –	(C = C in aromatic rings)	6.25 – 6.66	1500 – 1600
	(C – O bond in alcohol, ether etc.)	7.7 – 10	1000 – 1300
	(C = O in aldehydes, ketones etc.)	5.68 – 5.95	1680 – 1760
– O – H	(O – H in alcohols, phenols etc.)	2.74 – 2.78	3600 – 3650

Band for the group	Type of molecule	Wavelength (μm)	Frequency cm^{-1}
– O – H	Hydrogen bonded alcohols, phenols.	2.94 – 3.11	3200 – 3400
– O – H	O – H in hydrogen bonded carboxylic acids.	3.33 – 4.0	2500 – 3000
– N – H	(N – H in amines)	2.86 – 3.03	3300 – 3500
– C – N –	(N – H in amines)	7.36 – 8.49	1130 – 1360
– C ≡ N	(C ≡ N in nitrites)	4.42 – 4.52	2230 – 2260
$-NO_2$	(nitro compounds)	6.5 – 7.5	1345 – 1385

Problems based on IR spectroscopy Problem 1

How does the IR spectrum of the following pairs of compounds differ

(i)Acetone and ethanol

(ii)Acetic acid and methanol

Solution

(i) Acetone will show absorption band at 1710 cm^{-1} because of C=O stretching. Ethanol will

show absorption band at 3200-3600 cm^{-1} because of hydrogen bonded –OH.

(ii) Acetic acid shows absorption band at 1700-1725 cm^{-1} because of C=O group, while the

band at 2500-3000 cm^{-1} is due to hydrogen bonded –OH. Methanol will show desorption band just like ethanol as given in (i).

Problem 2

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

(i) CH_3CH_2OH and CH_3OCH_3

(ii) $CH_3CH_2C(=O)CH_3$ and $CH_2=CH-CH_2-O-CH_3$ **(iii)**  **and** 

(iv) $ClCH_2CH_2CH_2COOH$ and $CH_3OCH_2CH_2COCl$

Solution

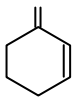
(i) CH_3CH_2OH will show absorption band at 3200-3650 cm^{-1} due to hydrogen bond.

Alkyl ether (CH_3COCH_3) will show absorption band at 1100 cm^{-1}.

(ii) $CH_3CH_2COCH_3$ will show absorption band at 1725-1705 cm^{-1} due to saturated butane.

$CH_2=CH-CH_2OCH_3$ will show absorption bands at 3040-3010 cm^{-1} due to alkyl ether.

(iii)  is cyclic keto compound and shows absorption band at 1725-1705 cm^{-1}.

 is α, β-unsaturated keto compound and shows absorption band at about 40 cm^{-1}.

(iv) $ClCH_2CH_2CH_2COOH$ is a saturated acid and shows absorption band at 800 cm^{-1}.

$CH_3OCH_2CH_2COCl$ shows absorption band at 1100 cm^{-1} due to alkyl ether and at 1795 cm^{-1} due to alkyl chloride.

Problem 3

Identify the unknown organic compound, if it shows IR peaks at 3000 cm^{-1},1600 cm^{-1}, 1050 cm^{-1}, 900 cm^{-1}, 750 cm^{-1} and 600 cm^{-1}.

Solution

(i) The peaks at 300 cm^{-1} and 1600 cm^{-1} indiacted the presence of CH_3 group.

(ii) A peak at 1600 cm^{-1} showed C=O group. One peak at 750-680 cm^{-1} showed CH group.

(iii) CH stretching at 300 cm^{-1}, CO stretching at 1600 cm^{-1}, C-C stretching at 1050 cm^{-1}, CH bending at 750 cm^{-1}. Hence the compound was

$CH_3COCH(CH_3)_2$.

Problem 4

Which of the following molecule will show IR spectrum and why?

$$H_2, HCl, CH_4, CO_2, H_2O_2.$$

Solution

All the molecule will show IR spectrum except H_2. Because $H_2$is non-polar molecule.

Problem 5

How many normal modes of vibration are possible in the linear molecule ethane (C_2H_5) and in the non-linear molecule C_6H_6.

Solution

(i) For linear molecule, number of modes of vibration may be calculated from 3n-5.

CH_3-CH_3 ; n = 8 ; 3 X 8 – 5 = 24 – 5

= 19 modes of vibration.

(ii) For non-linear molecule, number of modes of vibration may be calculated form 3n-6.

; n = 12 ; 3 X 12 – 6 = 36 – 6= 30 modes of vibration.

Problem 6

Predict the number of fundamental modes of vibration of HCl.

Solution

HCl is a linear molecule. Number of fundamental modes of vibration may be calculated from 3n - 5.

H-Cl ; n = 2 ; 3 x 2 – 5 = 6 – 5

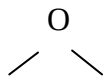
= 1 fundamental modes of vibration.

Problem 7

How many fundamental vibrational modes would you expect in the IR spectrum of water (H_2O)

Solution

H_2O is a bent molecule and the number of fundamental vibrational modes may be calculated from 3n – 6.



; n = 3 ; 3 x 3 – 6 = 9 – 6

= 3 fundamental modes of vibration.

5.3 NMR SPECTROSCOPY

What is NMR Spectroscopy?

NMR Spectroscopy is abbreviated as Nuclear Magnetic Resonance spectroscopy.

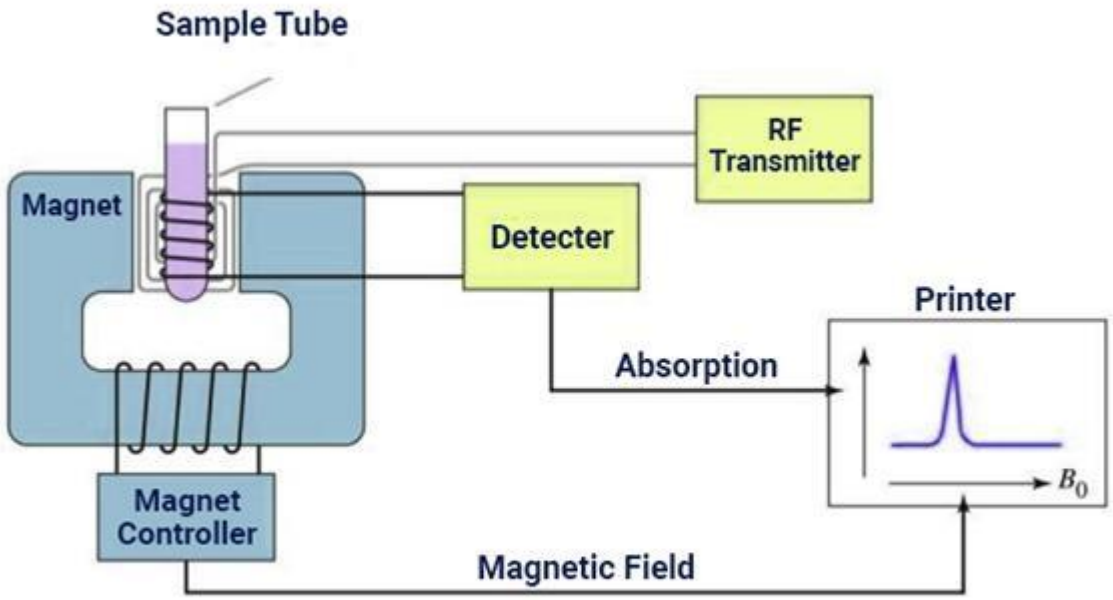
Nuclear magnetic resonance (NMR) spectroscopy is the study of molecules by recording the interaction of radiofrequency (Rf) electromagnetic radiations with the nuclei of molecules placed in a strong magnetic field.

Zeeman first observed the strange behavior of certain nuclei when subjected to a strong magnetic field at the end of the nineteenth century, but the practical use of the so-called "Zeeman effect" was only made in the 1950s when NMR spectrometers became commercially available.

It is a research technique thexploits the magnetic properties of certain atomic nuclei. The NMR spectroscopy determines the physical and chemical properties of atoms or molecules.

5.10 NMR Spectroscopy Working

i. The NMR spectroscopy determines the physical and chemical properties of atoms or molecules.



It relies on the phenomenon of nuclear magnetic resonance and provides detailed information about the structure, dynamics, reaction state, and chemical environment of molecules.

NMR Spectroscopy Principle

- All nuclei are electrically charged and many have spin.
- Transfer of energy is possible from base energy to higher energy levels when an external magnetic field is applied.
- The transfer of energy occurs at a wavelength that coincides with the radio frequency.
- Also, energy is emitted at the same frequency when the spin comes back to its base level.
- Therefore, by measuring the signal which matches this transfer the processing of the NMR spectrum for the concerned nucleus is yield.

NMR Spectroscopy Working

- Place the sample in a magnetic field.
- Excite the nuclei sample into nuclear magnetic resonance with the help of radio waves to produce NMR signals.
- These NMR signals are detected with sensitive radio receivers.
- The resonance frequency of an atom in a molecule is changed by the intramolecular magnetic field surrounding it.
- This gives details of a molecule's individual functional groups and its electronic structure.
- Nuclear magnetic resonance spectroscopy is a conclusive method of identifying monomolecular organic compounds.
- This method provides details of the reaction state, structure, chemical environment and dynamics of a molecule.

NMR Spectroscopy Instrumentation

This instrument consists of nine major parts. They are discussed below:

- **Sample holder –** It is a glass tube which is 8.5 cm long and 0.3 cm in diameter.
- **Magnetic coils –** Magnetic coil generates magnetic field whenever current flows through it • **Permanent magnet –** It helps in providing a homogenous magnetic field at 60 – 100 MHZ
- **Sweep generator –** Modifies the strength of the magnetic field which is already applied.
- **Radiofrequency transmitter –** It produces a powerful but short pulse of the radio waves.
- **Radiofrequency –** It helps in detecting receiver radio frequencies.
- **RF detector –** It helps in determining unabsorbed radio frequencies**.**
- **Recorder –** It records the NMR signals which are received by the RF detector.
- **Readout system –** A computer that records the data.

NMR Spectroscopy Techniques

1. Resonant Frequency

It refers to the energy of the absorption, and the intensity of the signal that is proportional to the strength of the magnetic field. NMR active nuclei absorb electromagnetic radiation at a frequency characteristic of the isotope when placed in a magnetic field.

2. Acquisition of Spectra

Upon excitation of the sample with a radiofrequency pulse, a nuclear magnetic resonance response is obtained. It is a very weak signal and requires sensitive radio receivers to pick up.

3. Chemical Shift

A spinning charge generates a magnetic field that results in a magnetic moment proportional to the spin. In the presence of an external magnetic field, two spin states exist; one spin up and one spin down, where one aligns with the magnetic field and the other opposes it.

NMR Spectroscopy Applications

1. NMR spectroscopy is a Spectroscopy technique used by chemists and biochemists to investigate the properties of organic molecules, although it is applicable to any kind of sample that contains nuclei possessing spin.
2. For example, the NMR can quantitatively analyze mixtures containing known compounds. NMR can either be used to match against spectral libraries or to infer the basic structure directly for unknown compounds.
3. Once the basic structure is known, NMR can be used to determine molecular conformation in solutions as well as in studying physical properties at the molecular level such as conformational exchange, phase changes, solubility, and diffusion.

Frequently Asked Questions

What is NMR in organic chemistry?

Since the fields are special or highly characteristic of individual compounds, the definitive method for identifying monomolecular organic compounds is NMR spectroscopy in modern organic chemistry practice. Similarly, to classify proteins and other complex molecules, biochemists use NMR.

What is proton NMR used for?

Proton nuclear magnetic resonance is the application in NMR spectroscopy of nuclear magnetic resonance to hydrogen-1 nuclei in a substance's molecules to determine the structure of its molecules.

What does resonance mean in NMR?

Though hydrogen nuclei are always precessing, nuclear magnetic resonance (NMR) is not continuously undergoing. Magnetic resonance occurs when external energy is applied above the Larmor (resonance) frequency into a nuclear spin device.

How is NMR used in medicine?

It is used by chemists to establish the molecular identity and structure. MRI, a multidimensional NMR imaging technique, is used by medical practitioners for diagnostic purposes.

How is NMR used in MRI?

Nuclear magnetic resonance imaging (NMR) is medical technology. In other NMR techniques such as NMR spectroscopy, NMR can also be used for imaging.

NMR Instrumentation

Place the sample in a magnetic field.

Excite the nuclei sample into nuclear magnetic resonance with the help of radio waves to produce NMR signals.

These NMR signals are detected with sensitive radio receivers.

The resonance frequency of an atom in a molecule is changed by the intramolecular magnetic field surrounding it.

This gives details of a molecule's individual functional groups and its electronic structure.

Nuclear magnetic resonance spectroscopy is a conclusive method of identifying monomolecular organic compounds.

This method provides details of the reaction state, structure, chemical environment and dynamics of a molecule.

NMR Spectroscopy Instrumentation

This instrument consists of nine major parts. They are discussed below:

Sample holder – It is a glass tube which is 8.5 cm long and 0.3 cm in diameter.

Magnetic coils – Magnetic coil generates magnetic field whenever current flows through it

Permanent magnet – It helps in providing a homogenous magnetic field at 60 – 100 MHZ Sweep

generator – Modifies the strength of the magnetic field which is already applied.

Radiofrequency transmitter – It produces a powerful but short pulse of the radio waves.

Radiofrequency – It helps in detecting receiver radio frequencies.

RF detector – It helps in determining unabsorbed radio frequencies.

Recorder – It records the NMR signals which are received by the RF detector.

Readout system – A computer that records the data.

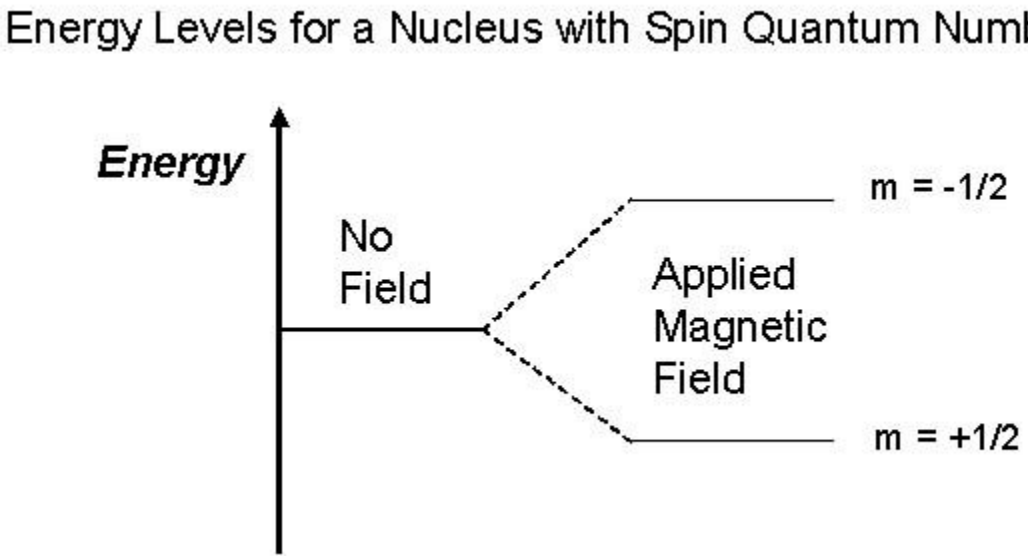
PRINCIPLES OF NMR:

Nuclear magnetic resonance spectroscopy (NMR) was first developed in 1946 by research groups at Stanford and M.I.T., in the USA. The radar technology developed during World War II made many of the electronic aspects of the NMR spectrometer possible. With the newly developed hardware physicists and chemists began to apply the technology to chemistry and physics problems. Over the next 50 years NMR developed into the premier organic spectroscopy available to chemists to determine the detailed chemical structure of the chemicals they were synthesizing. Another wellknown product of NMR technology has been the Magnetic Resonance Imager (MRI), which is utilized extensively in the medical radiology field to obtain image slices of soft tissues in the human body. In recent years, NMR has moved out of the research laboratory and into the on-line process analyzer market. This has been made possible by the production of stable permanent magnet technologies that allow high-resolution ^{1}H NMR spectra to be obtained in a process environment.

The NMR phenomenon is based on the fact that nuclei of atoms have magnetic properties that can be utilized to yield chemical information. Quantum mechanically subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as ^{12}C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in many atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows:

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

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



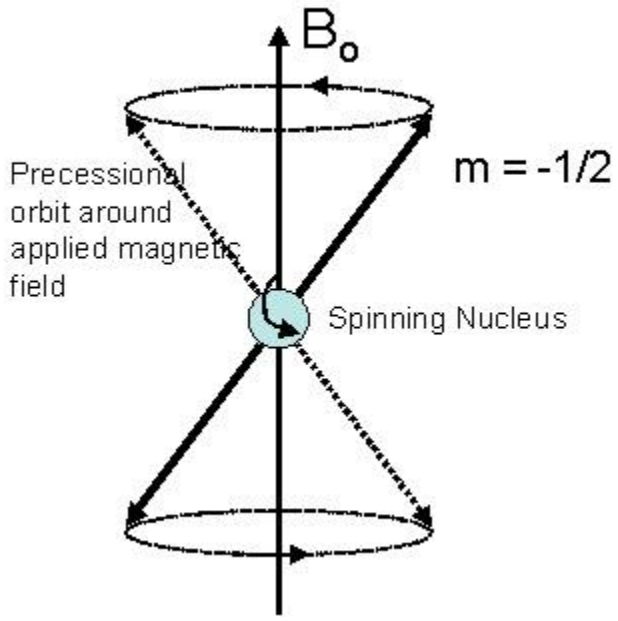
In quantum mechanical terms, the nuclear magnetic moment of a nucleus can align with an externally applied magnetic field of strength **Bo** in only 2I+1 ways, either with or against the applied field **Bo**. For a single nucleus with I=1/2 and positive g, only one transition is possible (D I=1, a single quantum transition) between the two energy levels The energetically preferred orientation has the magnetic moment aligned parallel with the applied field (spin m=+1/2) and is often given the notation a, whereas the higher energy anti-parallel orientation (spin m=-1/2) is referred to as b. The rotational axis of the spinning nucleus cannot be orientated exactly parallel (or anti-parallel) with the direction of the applied field **Bo** (defined in our coordinate system as about the *z* axis) but must precess (motion similar to a gyroscope) about this field at an angle, with an angular velocity given by the expression:

$w_o = g\mathbf{Bo}$

Where w_o is the precession rate called the Larmor frequency. The constant g is called the magnetogyric ratio and relates the magnetic moment m and the spin number I for any specific nucleus:

g = 2pm/hI

Each nucleus has a characteristic value of g, which is defined as a constant of proportionality between the nuclear angular momentum and magnetic moment. For a proton, g = 2.674×10^4 $gauss^{-1}$ sec^{-1}. This precession process generates an electric field with frequency w_o. If we irradiate the sample with radio waves (MHz) the proton can absorb the energy and be promoted to the less favorable higher energy state. This absorption is called resonance because the frequency of the applied radiation and the precession coincide or resonate.

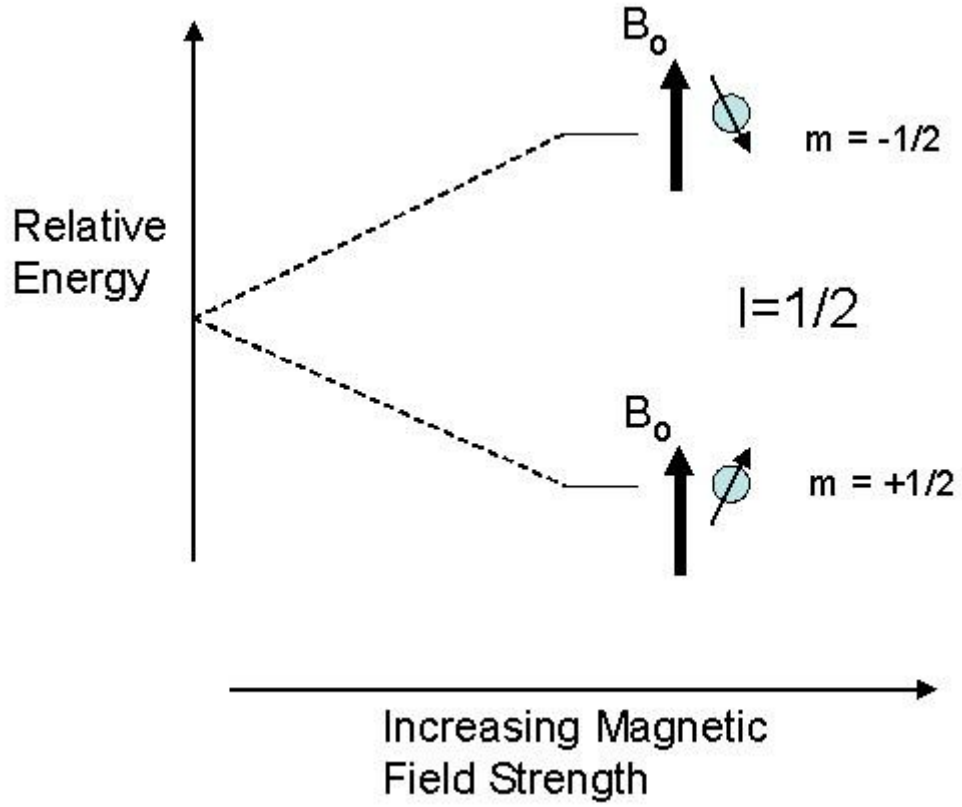


We can calculate the resonance frequencies for different applied field ($\mathbf{B}_o$) strengths (in Gauss):

The field strength of a magnet is usually reported at the resonance frequency for a *proton*. Therefore, for different nuclei with different gyromagnetic ratios, different frequencies must be applied in order to achieve resonance.

NMR Energies

The orientations a magnetic nucleus can take against an external magnetic are not of equal energy. Spin states which are oriented parallel to the external field are lower in energy than in the absence of an external field. In contrast, spin states whose orientations oppose the external field are higher in energy than in the absence of an external field.



Where an energy separation exists there is a possibility to induce a transition between the various spin states. By irradiating the nucleus with electromagnetic radiation of the correct energy (as determined by its frequency), a nucleus with a low energy orientation can be induced to “jump” to a higher energy orientation. The absorption of energy during this transition forms the basis of the NMR method. Other spectroscopic methods, such as IR and UV/Visible, also rely on the absorption of energy during a transition although the nature and energies of the transitions vary widely.

When discussing NMR you will find that spin state energy separations are often characterized by the frequency required to induce a transition between the states. While frequency is not a measure of energy, the simple relationship E=hu (where E=energy, h=Planks constant, and u=frequency) makes this substitution understandable. The

statement “the transition (peak) shifted to higher frequencies” should be read as “the energy separation increased”.

In quantum mechanical terms, the nuclear magnetic moment of a nucleus can align with an externally applied magnetic field of strength Bo in only 2I+1 ways, either with or against the applied field Bo. For a single nucleus with I=1/2 and positive g, only one transition is possible (D I=1, a single quantum transition) between the two energy levels The energetically preferred orientation has the magnetic moment aligned parallel with the applied field (spin m=+1/2) and is often given the notation a, whereas the higher energy anti-parallel orientation (spin m=-1/2) is referred to as b. The rotational axis of the spinning nucleus cannot be orientated exactly parallel (or anti-parallel) with the direction of the applied field Bo (defined in our coordinate system as about the z axis) but must precess (motion similar to a gyroscope) about this field at an angle, with an angular velocity given by the expression:

$$Wo = gBo$$

Where wo is the precession rate called the Larmor frequency. The constant g is called the magnetogyric ratio and relates the magnetic moment m and the spin number I for any specific nucleus:

$$G = 2pm/hI$$

Each nucleus has a characteristic value of g, which is defined as a constant of proportionality between the nuclear angular momentum and magnetic moment. For a proton, g = 2.674×104 gauss-1 sec-1. This precession process generates an electric field with frequency wo. If we irradiate the sample with radio waves (MHz) the proton can absorb the energy and be promoted to the less favorable higher energy state. This absorption is called resonance because the frequency of the applied radiation and the precession coincide or resonate.

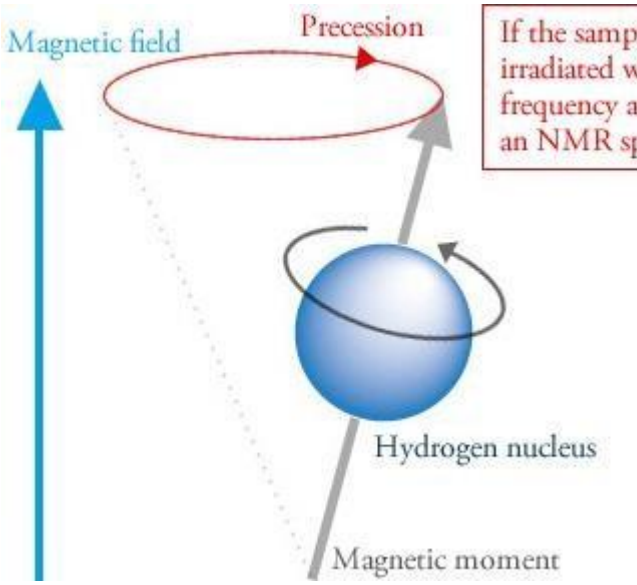
NMR Energies

The orientations a magnetic nucleus can take against an external magnetic are not of equal energy. Spin states which are oriented parallel to the external field are lower in energy than in the absence of an external field. In contrast, spin states whose orientations oppose the external field are higher in energy than in the absence of an external field.

Where an energy separation exists there is a possibility to induce a transition between the various spin states. By irradiating the nucleus with electromagnetic radiation of the correct energy (as determined by its frequency), a nucleus with a low energy orientation can be induced to "jump" to a higher energy orientation. The absorption of energy during this transition forms the basis of the NMR method. Other spectroscopic methods, such as IR and UV/Visible, also rely on the absorption of energy during a transition although the nature and energies of the transitions vary widely.

When discussing NMR you will find that spin state energy separations are often characterized by the frequency required to induce a transition between the states. While frequency is not a measure of energy, the simple relationship $E=h\upsilon$ (where E=energy, h=Planks constant, and υ=frequency) makes this substitution understandable. The statement "the transition (peak) shifted to higher frequencies" should be read as "the energy separation increased".

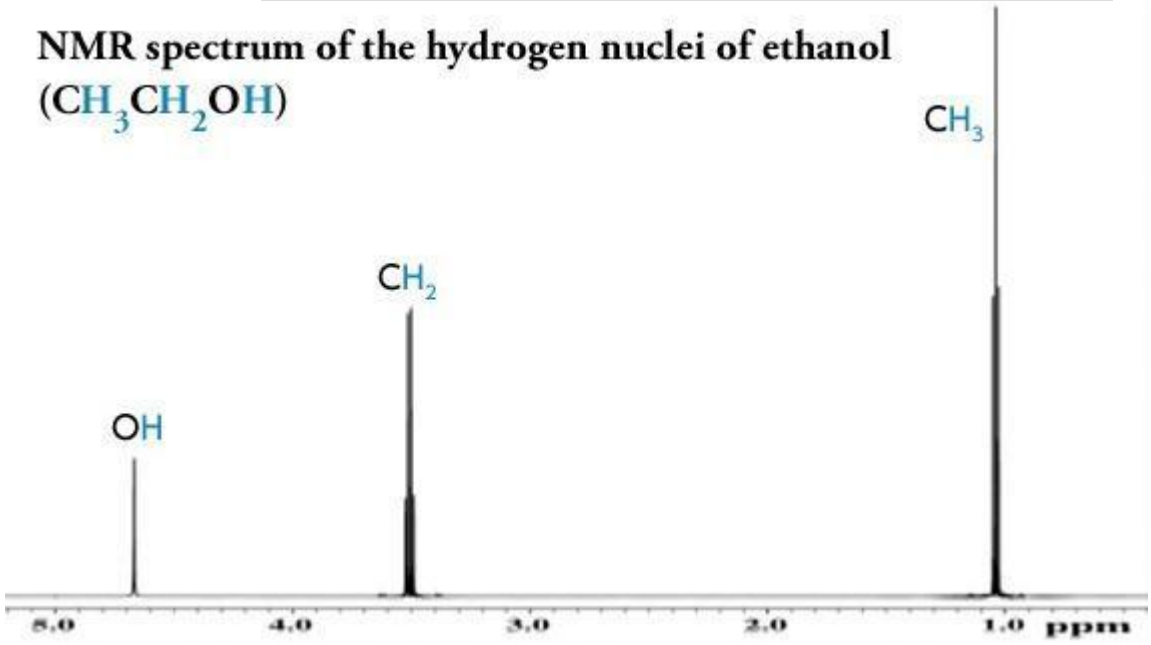
When a nucleus that possesses a magnetic moment (such as a hydrogen nucleus ^{1}H, or carbon nucleus ^{13}C) is placed in a strong magnetic field, it will begin to precess, like a spinning top.



Hydrogen type	Chemical shift (ppm)
$RC\underline{H}_3$	0.9 - 1.0
$RC\underline{H}_2R$	1.2 - 1.7
$R_3C\underline{H}$	1.5 – 2.0
	2.0 – 2.3
	1.5 – 1.8
$RN\underline{H}_2$	1 - 3
$ArC\underline{H}_3$	2.2 – 2.4
	2.3 – 3.0

ROC<u>H</u>$_3$	3.7 – 3.9
	3.7 – 3.9
RO<u>H</u>	1 - 5
	3.7 – 6.5
	5 - 9
Ar<u>H</u>	6.0 – 8.7

	9.5 – 10.0
	10 - 13



What we can learn from NMR spectra

- Chemical shift: Information about the composition of atomic groups within the molecule.
- Spin-Spin coupling constant: Information about adjacent atoms.
- Relaxation time: Information on molecular dynamics.
- Signal intensity: Quantitative information, e.g. atomic ratios within a molecule that can be helpful in determining the molecular structure, and proportions of different compounds in a mixture.

Chemical Shifts

Chemical shift is associated with the Larmor frequency of a nuclear spin to its chemical environment. Tetramethylsilan[TMS;$(CH_3)_4Si$] is generally used for standard to determine chemical shift of compounds: δ_{TMS}=0ppm. In other words, frequencies for chemicals are measured for a ^1H or ^{13}C nucleus of a sample from the ^1H or ^{13}C resonance of TMS. It is important to understand trend of chemical shift in terms of NMR interpretation. The proton NMR chemical shift is affect by nearness to electronegative atoms (O, N, halogen.) and unsaturated groups (C=C,C=O, aromatic). Electronegative groups move to the down field (left; increase in ppm). Unsaturated groups shift to downfield (left) when affecting nucleus is in the plane of the unsaturation, but reverse shift takes place in the regions above and below this plane. ^1H chemical shift play a role in identifying many functional groups.

1H chemical shift ranges for organic compounds

Chemical shift values are in parts per million (ppm) relative to tetramethylsilane.

Hydrogen type	Chemical shift (ppm)
RCH_3	0.9 - 1.0
RCH_2R	1.2 - 1.7
R_3CH	1.5 – 2.0
	2.0 – 2.3
	1.5 – 1.8
RNH_2	1 - 3
$ArCH_3$	2.2 – 2.4
	2.3 – 3.0
$ROCH_3$	3.7 – 3.9
	3.7 – 3.9
ROH	1 - 5
	3.7 – 6.5

	5 - 9
ArH	6.0 – 8.7
	9.5 – 10.0
	10 - 13

Factors affecting the Chemical shift :

Some atomic nuclei possess a magnetic moment (nuclear spin), which gives rise to different energy levels and resonance frequencies in a magnetic field. The total magnetic field experienced by a nucleus includes local magnetic fields induced by currents of electrons in the molecular orbitals (note that electrons have a magnetic moment themselves). The electron distribution of the same type of nucleus (e.g. $_{1}H$, $_{13}C$, $_{15}N$) usually varies according to the local geometry (binding partners, bond lengths, angles between bonds, and so on), and with it the local magnetic field at each nucleus. This is reflected in the spin energy levels (and resonance frequencies). The variations of nuclear magnetic resonance frequencies of the same kind of nucleus, due to variations in the electron distribution, is called the chemical shift. The size of the chemical shift is given with respect to a reference frequency or reference sample (see also chemical shift referencing), usually a molecule with a barely distorted electron distribution. Operating frequency.

The operating (or Larmor) frequency ω_0 of a magnet is calculated from the Larmor equation.

where B_0 is the actual strength of the magnet in units like Teslas or Gauss, and γ is the gyromagnetic ratio of the nucleus being tested which is in turn calculated from its magnetic moment μ and spin number I with the nuclear magneton μ_N and the Planck constant h:[*citation needed*]

Thus for example, the proton operating frequency for a 1 T magnet is calculated as:

MRI scanners are often referred to by their field strengths B_0 (eg "a 7 T scanner"), whereas NMR spectrometers are commonly referred to by the corresponding proton Larmor frequency (eg "a 300 MHz spectrometer", which has a B_0 of 7 T). While chemical shift is referenced in order that the units are equivalent across different field strengths, the actual frequency separation in Hertz scales with field strength (B_0). As a result, the difference of chemical shift between two signals (ppm) represents a larger number of Hertz on machines that have larger B_0 and therefore the signals are less likely to be overlapping in the resulting spectrum. This increased resolution is a significant advantage for analysis. (Larger field machines are also favoured on account of having intrinsically higher signal arising from the Boltzmann distribution of magnetic spin states.) Chemical shift referencing

Chemical shift δ is usually expressed in parts per million (ppm) by frequency, because it is calculated from:

where ν_{sample} is the absolute resonance frequency of the sample, ν_{res} is the spectrometer frequency and ν_{ref} is the absolute resonance frequency of a standard reference compound, measured in the same applied magnetic field B_0. Since the numerator is usually expressed in hertz, and the denominator in megahertz, δ is expressed in ppm.
The detected frequencies (in Hz) for $_{1}H$, $_{13}C$, and $_{29}Si$ nuclei are usually referenced against TMS (tetramethylsilane), TSP (Trimethylsilylpropanoic acid), or DSS, which by the definition above have a chemical shift of zero if chosen as the reference. Other standard materials are used for setting the chemical shift for other nuclei.

Thus, an NMR signal observed at a frequency 300 Hz higher than the signal from TMS, where the TMS resonance frequency is 300 MHz, has a chemical shift of:

Although the absolute resonance frequency depends on the applied magnetic field, the chemical shift is independent of external magnetic field strength. On the other hand, the resolution of NMR will increase with applied magnetic field.

Referencing Methods

Practically speaking, diverse methods may be used to reference chemical shifts in an NMR experiment, which can be subdivided into *indirect* and *direct* referencing methods. Indirect referencing uses a channel other than the one of interest to adjust chemical shift scale correctly, i.e. the solvent signal in the deuterium (lock) channel can be used to reference the a $_{1}H$ NMR spectrum. Both indirect and direct referencing can be done as three different procedures:

1. "**Internal referencing**, where the reference compound is added directly to the system under study." In this common practice, users adjust residual solvent signals of $_{1}H$ or $_{13}C$ NMR spectra with calibrated spectral tables. If substances other than the solvent itself are

used for internal referencing, the sample has to be combined with the reference compound, which may affect the chemical shifts.

2. "**External referencing**, involving sample and reference contained separately in coaxial cylindrical tubes." With this procedure, the reference signal is still visible in the spectrum of interest, although the reference and the sample are physically separated by a glass wall. Magnetic susceptibility differences between the sample and the reference phase need to corrected theoretically which lowers the practicality of this procedure.
3. "**Substitution method**: The use of separate cylindrical tubes for the sample and the reference compound, with (in principle) spectra recorded individually for each." Similar to external referencing, this method allows referencing without sample contamination. If field/frequency locking via the ^{2}H signal of the deutarated solvent is used and the solvents of reference and analyte are the same, the use of this methods is straightforward. Problems may arise if different solvents are used for the reference compound and the sample as (just like for external referencing) magnetic susceptibility differences need to be corrected theoretically. If this method is used without field/frequency locking, shimming procedures between the sample and the reference need to be avoided as they change the applied magnetic field (and thereby influence the chemical shift).

Modern NMR spectrometers commonly make use of the absolute scale, which defines the ^{1}H signal of TMS as 0 ppm in proton NMR and the center frequencies of all other nuclei as percentage of the TMS resonance frequency:

The use of the deuterium (lock) channel, so the ^{2}H signal of the deuterated solvent, and the Ξ value of the absolute scale is a form of internal referencing and is particularly useful in heteronuclear NMR spectroscopy as local reference compounds may not be always be available or easily used (i.e. liquid NH_3 for ^{15}N NMR spectroscopy). This system, however, relies on accurately determined ^{2}H NMR chemical shifts enlisted in the spectrometer software and correctly determined Ξ values by IUPAC. A recent study for ^{19}F NMR spectroscopy revealed that the use of the absolute scale and lock-based internal referencing led to errors in chemical shifts. These may be negated by inclusion of calibrated reference compounds. The induced magnetic field.

The electrons around a nucleus will circulate in a magnetic field and create a secondary induced magnetic field. This field opposes the applied field as stipulated by Lenz's law and atoms with higher induced fields (i.e., higher electron density) are therefore called *shielded*, relative to those with lower electron density. The chemical milieu of an atom can influence its electron density through the polar effect. Electrondonating alkyl groups, for example, lead to increased shielding while electron-withdrawing substituents such as nitro groups lead to *deshielding* of the nucleus. Not only substituents cause local induced fields. Bonding electrons can also lead to shielding and deshielding effects. A striking example of this is the pi bonds in benzene. Circular current through the hyperconjugated system causes a shielding effect at the molecule's center and a deshielding effect at its edges. Trends in chemical shift are explained based on the degree of shielding or deshielding.

Nuclei are found to resonate in a wide range to the left (or more rare to the right) of the internal standard. When a signal is found with a higher chemical shift:

- the applied effective magnetic field is lower, if the resonance frequency is fixed (as in old traditional CW spectrometers)
- the frequency is higher, when the applied magnetic field is static (normal case in FT spectrometers)
- the nucleus is more deshielded
- the signal or shift is **downfield** or at **low field** or paramagnetic

Conversely a lower chemical shift is called a **diamagnetic shift**, and is **upfield** and more shielded.

Diamagnetic shielding

In real molecules protons are surrounded by a cloud of charge due to adjacent bonds and atoms. In an applied magnetic field ($\mathbf{B}_0$) electrons circulate and produce an induced field ($\mathbf{B}_i$) which opposes the applied field. The effective field at the nucleus will be $\mathbf{B} = \mathbf{B}_0 - \mathbf{B}_i$. The nucleus is said to be experiencing a diamagnetic shielding.

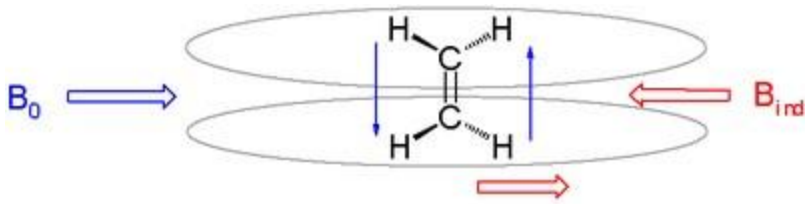
Factors causing chemical shifts

Important factors influencing chemical shift are electron density, electronegativity of neighboring groups and anisotropic induced magnetic field effects.

Electron density shields a nucleus from the external field. For example, in proton NMR the electron-poor tropylium ion has its protons downfield at 9.17 ppm, those of the electronrich cyclooctatetraenyl anion move upfield to 6.75 ppm and its dianion even more upfield to 5.56 ppm.

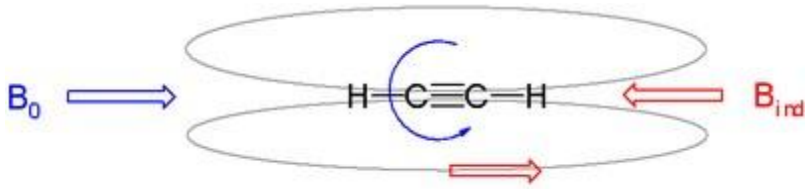
A nucleus in the vicinity of an electronegative atom experiences reduced electron density and the nucleus is therefore deshielded. In proton NMR of methyl halides (CH_3X) the chemical shift of the methyl protons increase in the order I < Br < Cl < F from 2.16 ppm to 4.26 ppm reflecting this trend. In carbon NMR the chemical shift of the carbon nuclei increase in the same order from around −10 ppm to 70 ppm. Also when the electronegative atom is removed further away the effect diminishes until it can be observed no longer.

Anisotropic induced magnetic field effects are the result of a local induced magnetic field experienced by a nucleus resulting from circulating electrons that can either be paramagnetic when it is parallel to the applied field or diamagnetic when it is opposed to it. It is observed in alkenes where the double bond is oriented perpendicular to the external field with pi electrons likewise circulating at right angles. The induced magnetic field lines are parallel to the external field at the location of the alkene protons which therefore shift downfield to a 4.5 ppm to 7.5 ppm range. The three-dimensional space where a diamagnetic shift is called the shielding zone with a cone-like shape aligned with the external field.



Induced magnetic field of alkenes in external magnetic fields, field lines in grey.

The protons in aromatic compounds are shifted downfield even further with a signal for benzene at 7.73 ppm as a consequence of a diamagnetic ring current.
Alkyne protons by contrast resonate at high field in a 2–3 ppm range. For alkynes the most effective orientation is the external field in parallel with electrons circulation around the triple bond. In this way the acetylenic protons are located in the cone-shaped shielding zone hence the upfield shift.



Induced magnetic field of alkynes in external magnetic fields, field lines in grey.

Magnetic properties of most common nuclei.

$_{1}H$ and $_{13}C$ are not the only nuclei susceptible to NMR experiments. A number of different nuclei can also be detected, although the use of such techniques is generally rare due to small relative sensitivities in NMR experiments (compared to $_{1}H$) of the nuclei in question, the other factor for rare use being their slender representation in nature and organic compounds.
$_{1}H$, $_{13}C$, $_{15}N$, $_{19}F$ and $_{31}P$ are the five nuclei that have the greatest importance in NMR experiments:

- $_{1}H$ because of high sensitivity and vast occurrence in organic compounds
- $_{13}C$ because of being the key component of all organic compounds despite occurring at a low abundance (1.1%) compared to the major isotope of carbon $_{12}C$, which has a spin of 0 and therefore is NMR-inactive.
- $_{15}N$ because of being a key component of important biomolecules such as proteins and DNA
- $_{19}F$ because of high relative sensitivity
- $_{31}P$ because of frequent occurrence in organic compounds and moderate relative sensitivity

Chemical Shift Manipulation

In general, the associated increased signal-to-noise and resolution has driven a move towards increasingly high field strengths. In limited cases, however, lower fields are preferred; examples are for systems in chemical exchange, where the speed of the exchange relative to the NMR experiment can cause additional and confounding linewidth

broadening. Similarly, while avoidance of second order coupling is generally preferred, this information can be useful for elucidation of chemical structures. Using refocussing pulses placed between recording of successive points of the Free Induction Decay, in an analogous fashion to the Spin Echo technique in MRI, the chemical shift evolution can be scaled to provide apparent low-field spectra on a high-field spectrometer. In a similar fashion, it is possible to upscale the effect of J-coupling relative to the chemical shift using pulse sequences that include additional J-coupling evolution periods interspersed with conventional spin evolutions.

Chemical Shifts

The NMR spectra is displayed as a plot of the applied radio frequency versus the absorption. The applied frequency increases from left to right, thus the left side of the plot is the low field, downfield or deshielded side and the right side of the plot is the high field, upfield or shielded side (see the figure below). The concept of shielding will be explained shortly.

The position on the plot at which the nuclei absorbs is called the **chemical shift**. Since this has an arbitrary value a standard reference point must be used. The two most common standards are TMS (tetramethylsilane, $(Si(CH_3)_4)$ which has been assigned a chemical shift of zero, and $CDCl_3$ (deuterochloroform) which has a chemical shift of 7.26 for ^1H NMR and 77 for ^{13}C NMR.

The scale is commonly expressed as parts per million (ppm) which is independent of the spectrometer frequency. The scale is the **delta (δ) scale**.

$$\delta = \frac{\text{frequency of signal - frequency of standard}}{\text{spectrometer frequency}} \times 10^6$$

The range at which most NMR absorptions occur is quite narrow. Almost all ^1H absorptions occur downfield within 10 ppm of TMS. For ^{13}C NMR almost all absorptions occurs within 220 ppm downfield of the C atom in TMS.

Shielding in NMR

Structural features of the molecule will have an effect on the exact magnitude of the magnetic field experienced by a particular nucleus. This means that H atoms which have different chemical environments will have different chemical shifts. This is what makes NMR so useful for structure determination in organic chemistry. There are three main features that will affect the shielding of the nucleus, electronegativity, magnetic anisotropy of π systems and hydrogen bonding.

Electronegativity

The electrons that surround the nucleus are in motion so they created their own electromagnetic field. This field opposes the the applied magnetic field and so reduces the field experienced by

the nucleus. Thus the electrons are said to **shield** the nucleus. Since the magnetic field experienced at the nucleus defines the energy difference between spin states it also defines what the chemical shift will be for that nucleus. Electron with-drawing groups can decrease the electron density at the nucleus, deshielding the nucleus and result in a larger chemical shift. Compare the data in the table below.

Compound, CH_3X	**CH_3F**	**CH_3OH**	**CH_3Cl**	**CH_3Br**	**CH_3I**	**CH_4**	**$(CH_3)_4Si$**
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ (ppm)	4.26	3.4	3.05	2.68	2.16	0.23	0

As can be seen from the data, as the electronegativity of X increases the chemical shift, δ increases. This is an effect of the halide atom pulling the electron density away from the methyl group. This exposes the nuclei of both the C and H atoms, "deshielding" the nuclei and shifting the peak downfield.

The effects are cumulative so the presence of more electron withdrawing groups will produce a greater deshielding and therefore a larger chemical shift, *i.e.*

Compound	**CH_4**	**CH_3Cl**	**CH_2Cl_2**	**$CHCl_3$**
δ (ppm)	0.23	3.05	5.30	7.27

These **inductive effects** are not only felt by the immediately adjacent atoms, but the deshielding can occur further down the chain, *i.e.*

NMR signal	$-CH_2-CH_2-CH_2Br$
δ (ppm)	1.25 1.69 3.30

Magnetic Anisotropy: π Electron Effects

The π electrons in a compound, when placed in a magnetic field, will move and generate their own magnetic field. The new magnetic field will have an effect on the shielding of atoms within the field. The best example of this is benzene (see the figure below).

This effect is common for any atoms near a π bond, *i.e.*

Proton Type	Effect	Chemical shift (ppm)
C_6H_5-H	highly deshielded	6.5 - 8
C=C-H	deshielded	4.5 - 6
C≡C-H	shielded*	~2.5
O=C-H	very highly deshielded	9 - 10

* the acetylene H is shielded due to its location relative to the π system

Hydrogen Bonding

Protons that are involved in hydrogen bonding (*i.e.*-OH or -NH) are usually observed over a wide range of chemical shifts. This is due to the deshielding that occurs in the hydrogen bond. Since hydrogen bonds are dynamic, constantly forming, breaking and forming again, there will be a wide range of hydrogen bonds strengths and consequently a wide range of deshielding. This as well as solvation effects, acidity, concentration and temperature make it very difficult to predict the chemical shifts for these atoms.

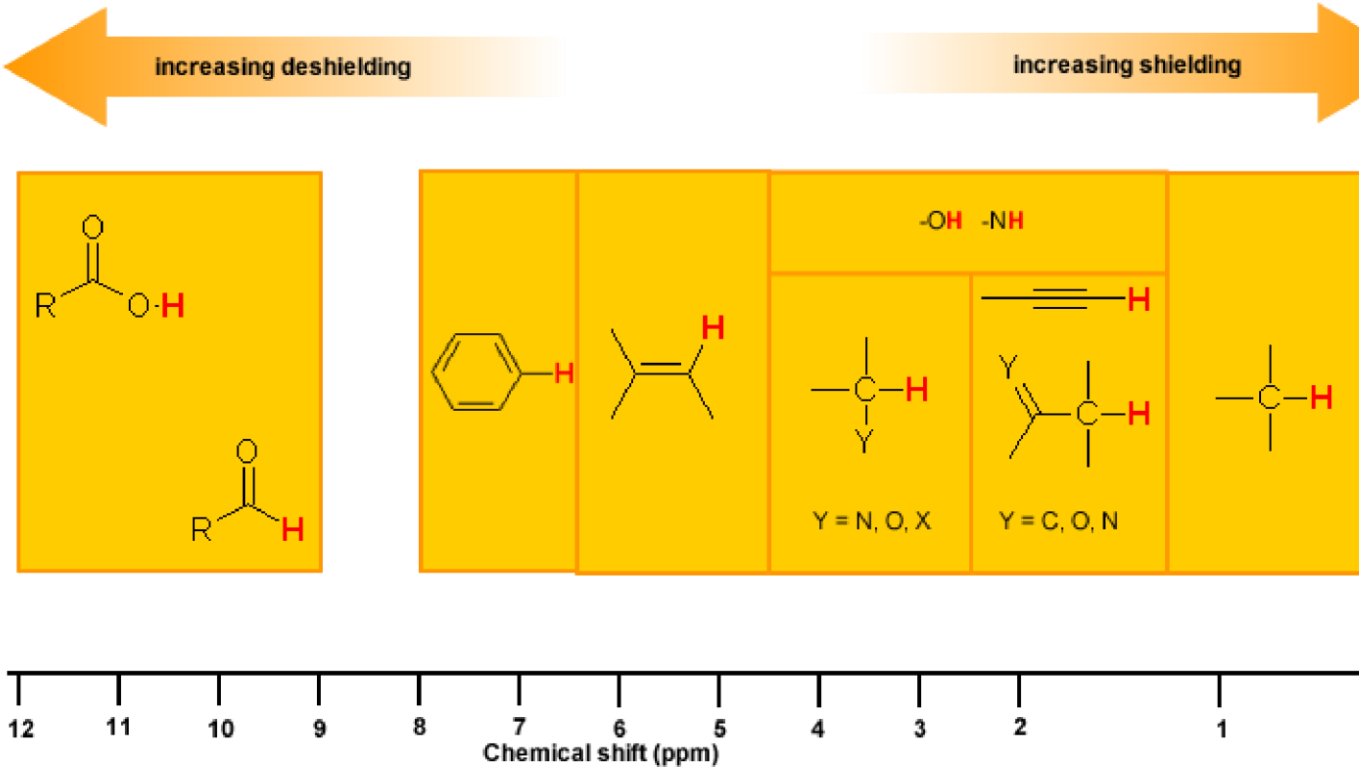
Experimentally -OH and -NH can be identified by carrying out a simple D_2O exchange experiment since these protons are exchangeable.

- run the normal H-NMR experiment on your sample
- add a few drops of D_2O
- re-run the H-NMR experiment
- compare the two spectra and look for peaks that have "disappeared"

Chemical

—

Spin-Spin coupling in NMR

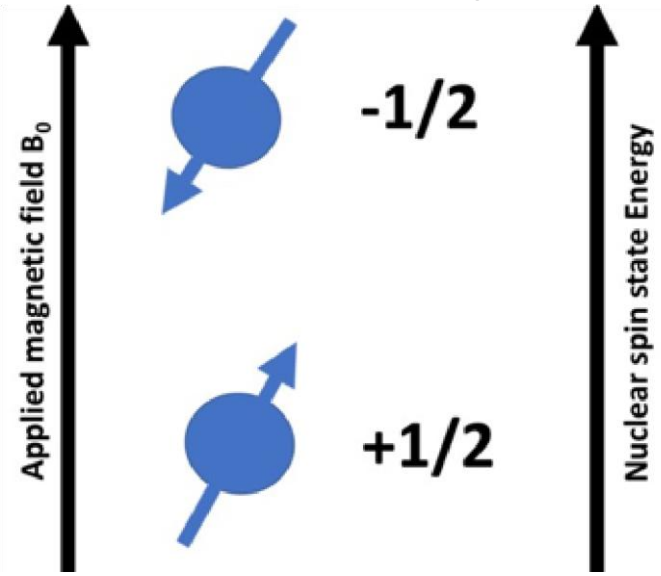


The structure of a molecule can be predicted using NMR spectroscopy. However, the interpreSINGof the signals in an NMR spectrum relies on several factors. One of the factors affecting the location of the peaks in an NMR spectrum is Chemical shift. The location of the peaks is important in discovering how many protons there are in a molecule, as well as other information about the surrounding electronic environment. In addition to knowing where the peaks are, on the chemical shift scale, and what influences the delta value, one must also consider the fact that the peaks in an NMR spectrum are not always a singlet. In fact, the interactions between different types of protons present in the

molecule cause a single peak on an NMR spectrum to split into doublet, triplet, or multiplet, a phenomenon known as the spin-spin coupling. There could also be other complex peak splitting patterns. The spin-spin coupling phenomenon, at its core, involves spinning nuclei.

The nuclear magnetic spin

A nucleus that has an odd number of protons spins along its axis. A proton has two possible spin states +1/2 or -1/2. In the absence of a magnetic field, these spins are quite random. In the presence of an external magnetic field, there is a tendency of the nuclei to align either with or against the magnetic field. The spins which are **aligned with** the external magnetic field have a **lower energy** state than the ones aligned against the magnetic field. The spin states and the energy levels are shown in the diagram below:



Depending on the orientation of the spins, the effective magnetic field on the proton would either increase or decrease by a small factor.
The applied magnetic field is denoted by B_0
The induced magnetic field is denoted by B_i
The effective magnetic field experienced by the proton
$B_{eff} = B_0 - B_i$

At the core of the molecule, these spinning nuclei ultimately give rise to the phenomenon of coupling in NMR spectrum.

Spin-spin coupling between spinning nuclei.

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

Peak splitting in NMR spectroscopy

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

$2nI + 1$

n= Number of neighboring protons

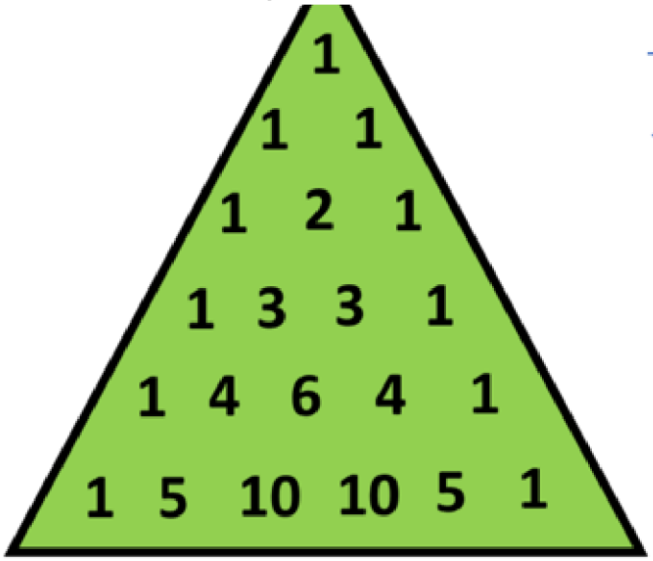
I= spin number of protons

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

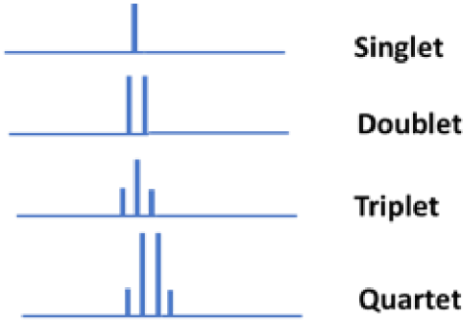
The other relevant information which comes along with knowing the number of peaks is the intensity of the peaks (which is seen as the height of the peaks). As a general rule, the height of the peaks or in other words, the relative intensities of the peaks can be determined by using Pascal's triangle.

Pascal's triangle

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



Pascal's triangle



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

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

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

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

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

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

CH_3CH_2Cl (Ethyl chloride)

Let us calculate the multiplicity for the hydrogen atoms.

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

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

I=1/2

After applying the formula,

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

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

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

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

Factors influencing peak split in NMR spectrum due to spin-spin coupling

We have seen earlier that the nuclei have a property known as spin. The spinning hydrogen nuclei in a molecule will interact with each other and cause the signal in the NMR peak to split. The separation distance between two adjacent peaks, as a result of the spin-spin interaction in a multiplet, is constant and is known as coupling constant (denoted by the letter J).

The value of the coupling constant depends on the following factors:

1. **Distance between the protons**

The distance between the hydrogen atoms in a molecule is an important determinant in the value of J constant. If the hydrogen atoms

involved in the coupling are closer to each other, these give rise to a greater value of J constant than if these atoms are further apart.

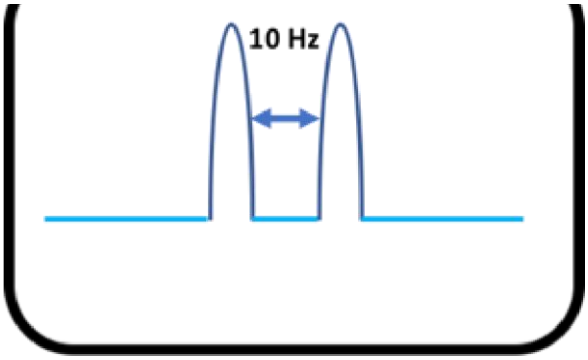
2. **The orientation of the coupled protons**

The orientation or angle of the protons with respect to each other is equally important. The value of J constant is greater in molecules, where the H atoms are in the cis conformation. Conversely, it is less when the H atoms are in the trans conformation.

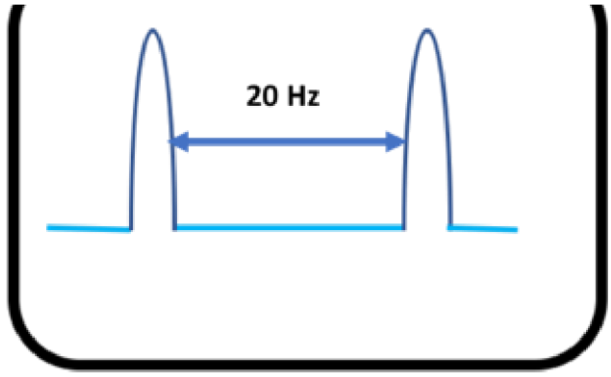
A curious case of singlets and doublets

Let us look at the interesting case of determining if the two adjacent peaks are doublets or actually made up of 2 singlets.

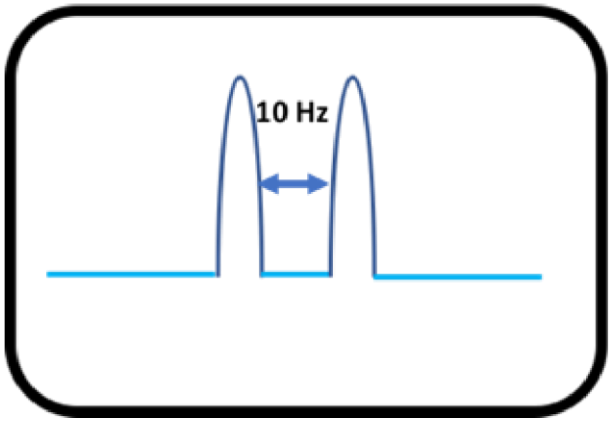
If we, for example, observe peaks in the molecule which are exactly 10 Hz apart and look indistinguishable from each other, it is very hard to decide if they are singlets or doublet. **Singlet/Doublet?**



In order to know whether the peaks are a doublet, we would increase the applied magnetic field. Now, because the coupling constant (J) is **constant** between the adjacent peaks, the doublet peaks would be **unaffected** by the change of magnetic field. On the other hand, if the peaks were made of two singlets, then, the individual peaks would shift further apart on the chemical shift scale as shown below:



Singlet



Doublet

In the above example, if the peaks are doublets then the value of the coupling constant remains 10 Hz.

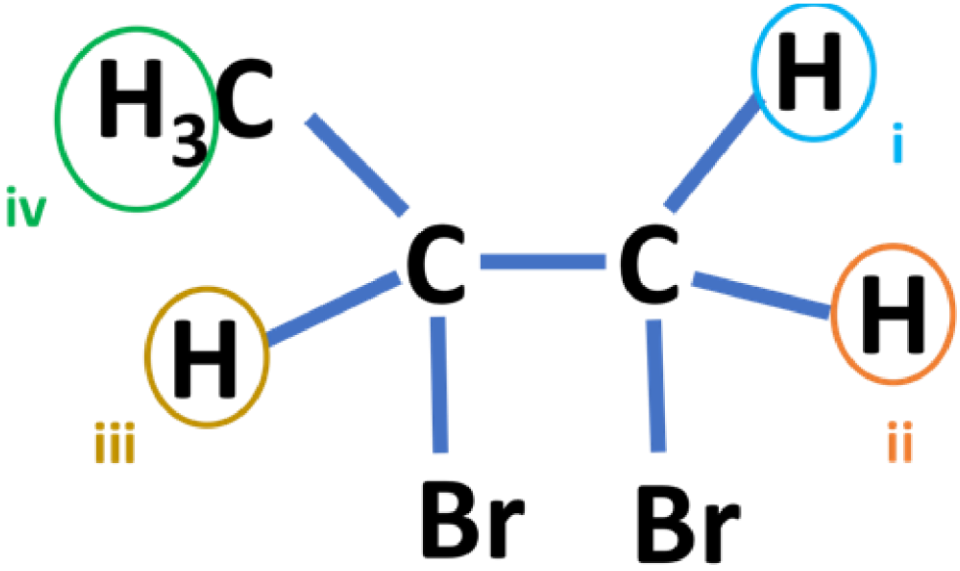
Unit of Coupling constant

The unit of a coupling constant is Hz and it is also referred as Cycles per second (CPS). The value of the coupling constant could be either positive or negative. The value of the coupling constant is a measure of interaction between neighboring protons. When two spinning nuclei are in the opposite orientation then the energy is lower and the value of the constant is positive. However, if the spinning nuclei are in the same orientation, then, the energy is higher and the value of the constant is negative. The spacing between the split lines or the J constant between coupling protons is of the same magnitude. The J constant can be used for distinguishing, e.g., between two singlets and one doublet or two doublet and one quartet. There is no effect of the external magnetic field on the coupling constant.

Different types of couplings and their effects on the coupling constant

Geminal coupling: The term Geminal means that 2 atoms or functional groups are bound to the same carbon atom. The geminal or

2-bond coupling constant is denoted by $_2J$. This also denotes that there are 2 bonds between the hydrogens being coupled. In some cases, two hydrogen atoms can be attached to the same carbon atom but can be in a completely different electronic environment which give rise to different chemical shifts. These protons are known as Geminal protons. Let us look at the molecule below:



According to the definition of Geminal protons, the protons i and ii are geminal protons, as they are attached to the same carbon atom, however, their electronic environments are different. The coupling constant value will also depend on the angle between protons i and ii. The coupling constant will increase with the electronegativity of the groups.

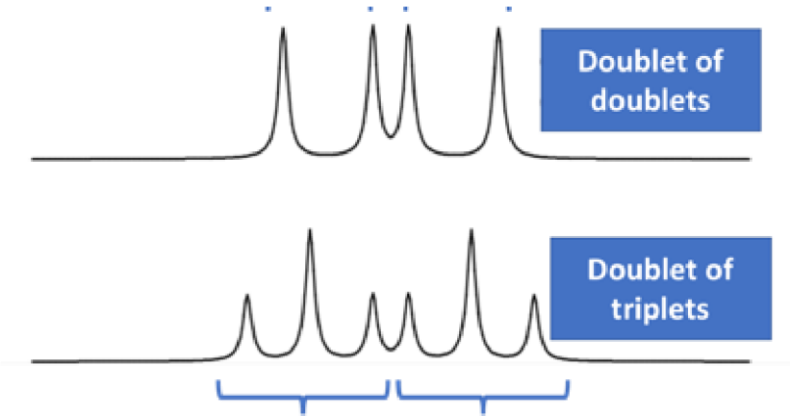
Vicinal Coupling: Vicinal protons are those which are separated by three bonds. In the molecule shown above, ii and iii are vicinal protons. The vicinal or 3 bond coupling constants is denoted by $_3J$. The hydrogen atoms are on the adjacent carbon atoms in vicinal coupling.

Long range coupling: If the distance between two protons is more than 3 covalent bonds, then, the phenomenon of coupling does not come into play. However, there would be some coupling if there are unsaturated or fluoro compounds present in the vicinity of the protons. Such type of coupling can only be observed using a very sensitive and

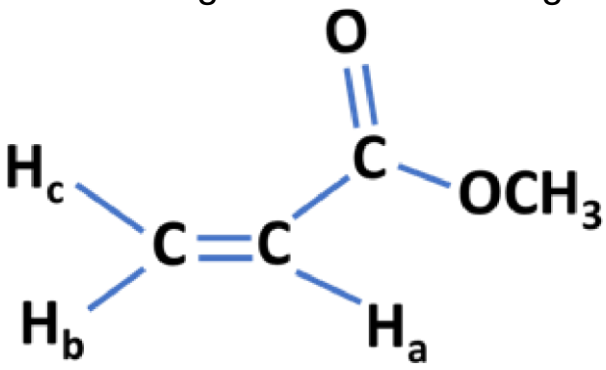
high-resolution NMR spectrophotometer (e.g. the 600 MHz Bruker Avance Spectrometer).

Complex splitting patterns on NMR spectrum

The NMR spectrum can sometimes have more complex splitting patterns than the simpler couplings involving equivalent coupling constants (such as doublet, triplet, quartet, quintet etc.). It may sometimes happen that each peak in a doublet (in an NMR spectrum) is further split into another peak. Such cases happen when a hydrogen atom is influenced by 2 adjacent non-equivalent hydrogen atoms. These complex patterns manifest as doublet of doublets, doublet of triplets, triplet of doublets etc.



Let us investigate this effect using a molecule named methyl acrylate



The protons H_a and H_b are coupled and would give rise to a doublet. The proton H_c is a non-equivalent proton and this would give rise to further splitting into a doublet of doublets. It is important to note that H_c is

coupled to both H_a and H_b but having different coupling constants. This is why each line in the doublet would further split into another doublet.

Conclusion

The resonating protons in a molecule are depicted as a series of peaks in the NMR spectrum. This physical interaction between the spinning nuclei is much more complex. The nature of the peaks and the position on the chemical shift scale is dependent on the electronic environment and the phenomenon of spin-spin coupling comes into play. The peaks are further split due to factors such as bonds and bond angles. The phenomenon of spin-spin coupling and the resulting coupling constant provides additional information which is very useful in elucidating the structure of the molecule under study. Since this coupling constant, by definition, is a fixed value for the interacting nuclei, it does not change on different NMR machines. Although the coupling is independent of the applied magnetic field, it does diminish with an increase in the number of bonds between the interacting nuclei.

High Resolution Proton NMR Spectra

This page describes how you interpretation high resolution nuclear magnetic resonance (NMR) spectra. It assumes that you have already read the background page on NMR so that you understand what an NMR spectrum looks like and the use of the term "chemical shift". It also assumes that you know how to interpret simple low resolution spectra.

The difference between high and low resolution spectra

What a low resolution NMR spectrum tells you

- The number of peaks tells you the number of different environments the hydrogen atoms are in.
- The ratio of the areas under the peaks tells you the ratio of the numbers of hydrogen atoms in each of these environments.
- The chemical shifts give you important information about the sort of environment the hydrogen atoms are in.

High resolution NMR spectra

In a high resolution spectrum, you find that many of what looked like single peaks in the low resolution spectrum are split into clusters of peaks.

1 peak		a singlet
2 peaks in the cluster	a doublet	
3 peaks in the cluster		a triplet
4 peaks in the cluster		a quartet

You can get exactly the same information from a high resolution spectrum as from a low resolution one - you simply treat each cluster of peaks as if it were a single one in a low resolution spectrum. But in addition, the amount of splitting of the peaks gives you important extra information.

Interpreting a high resolution spectrum

The n+1 rule

The amount of splitting tells you about the number of hydrogens attached to the carbon atom or atoms next door to the one you are currently interested in. The number of sub-peaks in a cluster is one more than the number of hydrogens attached to the next door carbon(s). So - on the assumption that there is only one carbon atom with hydrogens on next door to the carbon we're interested in.

singlet		next door to carbon with no hydrogens attached
doublet	next door to a CH group	

triplet		next door to a CH_2 group
quartet		next door to a CH group

Using the n+1 rule

What information can you get from this NMR spectrum?

Assume that you know that the compound above has the molecular formula $C_4H_8O_2$.

Treating this as a low resolution spectrum to start with, there are three clusters of peaks and so three different environments for the hydrogens. The hydrogens in those three environments are in the ratio 2:3:3. Since there are 8 hydrogens altogether, this represents a CH_2 group and two CH_3 groups. What about the splitting?

- The CH_2 group at about 4.1 ppm is a quartet. That tells you that it is next door to a carbon with three hydrogens attached - a CH_3 group.
- The CH_3 group at about 1.3 ppm is a triplet. That must be next door to a CH_2 group. This combination of these two clusters of peaks - one a quartet and the other a triplet - is typical of an ethyl group, CH_3CH_2. It is very common.
- Finally, the CH_3 group at about 2.0 ppm is a singlet. That means that the carbon next door doesn't have any hydrogens attached.

So what is this compound? You would also use chemical shift data to help to identify the environment each group was in, and eventually you would come up with:

Alcohols

Where is the -O-H peak? This is very confusing! Different sources quote totally different chemical shifts for the hydrogen atom in the -OH group in alcohols - often inconsistently.

For example:

- The Nuffield Data Book quotes 2.0 - 4.0, but the Nuffield text book shows a peak at about 5.4.
- The OCR Data Sheet for use in their exams quotes 3.5 - 5.5.

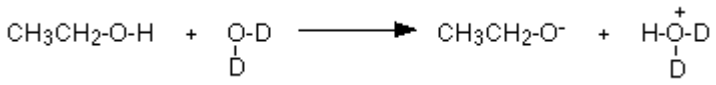
- A reliable degree level organic chemistry text book quotes1.0 - 5.0, but then shows an NMR spectrum for ethanol with a peak at about 6.1.
- The SDBS database (used throughout this site) gives the -OH peak in ethanol at about 2.6.

The problem seems to be that the position of the -OH peak varies dramatically depending on the conditions - for example, what solvent is used, the concentration, and the purity of the alcohol - especially on whether or not it is totally dry.

A clever way of picking out the -OH peak

If you measure an NMR spectrum for an alcohol like ethanol, and then add a few drops of deuterium oxide, D_2O, to the solution, allow it to settle and then re-measure the spectrum, the -OH peak disappears! By comparing the two spectra, you can tell immediately which peak was due to the OH group.

The reason for the loss of the peak lies in the interaction between the deuterium oxide and the alcohol. All alcohols, such as ethanol, are very, very slightly acidic. The hydrogen on the -OH group transfers to one of the lone pairs on the oxygen of the water molecule. The fact that here we've got "heavy water" makes no difference to that.



The negative ion formed is most likely to bump into a simple deuterium oxide molecule to regenerate the alcohol - except that now the -OH group has turned into an -OD group.

Deuterium atoms don't produce peaks in the same region of an NMR spectrum as ordinary hydrogen atoms, and so the peak disappears.

You might wonder what happens to the positive ion in the first equation and the OD^- in the second one. These get lost into the normal equilibrium which exists wherever you have water molecules - heavy or otherwise.

The lack of splitting with -OH groups

Unless the alcohol is absolutely free of any water, the hydrogen on the -OH group and any hydrogens on the next door carbon don't interact to produce any splitting. The -OH peak is a singlet and you don't have to worry about its effect on the next door hydrogThe left-hand cluster of peaks is due to the CH_2 group. It is a quartet because of the 3 hydrogens on the next door CH_3 group. You can ignore the effect of the -OH hydrogen. Similarly, the -OH peak in the middle of the spectrum is a singlet. It hasn't turned into a triplet because of the influence of the CH_2 group.

Equivalent hydrogen atoms

Hydrogen atoms attached to the same carbon atom are said to be equivalent. Equivalent hydrogen atoms have no effect on each other - so that one hydrogen atom in a CH_2 group doesn't cause any splitting in the spectrum of the other one.

But hydrogen atoms on neighboring carbon atoms can also be equivalent if they are in exactly

the same environment. For example:

These four hydrogens are all exactly equivalent. You would get a single peak with no splitting at all. You only have to change the molecule very slightly for this no longer to be true.

Because the molecule now contains different atoms at each end, the hydrogens are no longer all in the same environment. This compound would give two separate peaks on a low resolution NMR spectrum. The high resolution spectrum would show that both peaks subdivided into triplets – because each is next door to a differently placed CH_2 group.

NMR SPECTRUM OF SIMPLE ORGANIC MOLECULES

1.**Ethanol**(**Pure**) : **CH3-CH2-OH**

A B C

Number of equivalent sets of protons : Three Number of groups of peaks : Three

Splitting :

(A)Methyl protons: They have an adjacent methylene group with two equivalent protons. So the methyl NMR signal will be split in to three. The intensity ratio will be 1:2:1

(B)Methylene protons: They have two different groups on either side. So according to spin -spin coupling, the methylene NMR signal will be split in to eight. [(nA+1) nC+1) =4×2=8].the intensity ratio will be 1:7:21:35:35:21:7:1.

(C) Hydroxyl proton: It has an adjacent methylene group with two equivalent protons. So the OH group NMR signal will be split in to three. The ratio area will be 1:2:1

2.Acidified Ethanol : CH3-CH2-OH

A B C

Number of equivalent sets of protons : Three Number of groups of peaks : Three Splitting :

Splitting: (A)Methyl protons: They have an adjacent methylene group with two equivalent protons. So the methyl NMR signal will be split in to three. The intensity ratio will be 1:2:1

(B)Methylene protons: They have two different groups on either side. But in this case,there is no spin- spin interaction between OH proton and CH2 protons because H ion of the acid induces the exchange of protons between above two groups So lifetime of an OH proton in any given conformation becomes too short to permit the interaction. So only CH3 protons interact with CH2 protons, due to spin -spin coupling, the methylene NMR signal will be split in to four

(C) Hydroxyl proton: It has an adjacent methylene group with two equivalent protons , but as above reason in (b) ,no interaction between two groups, the OH group NMR signal will be only one.

3. n-Propyl bromide : **CH3-CH2-CH2Br**

A B C

Number of equivalent sets of protons : Three Number of groups of peaks : Three

Splitting :

(A)protons: They have an adjacent methylene group with two equivalent protons. So the methyl NMR signal will be split in to three. The intensity ratio will be 1:2:1

(B)Methylene protons[CH2 B]: They have two different groups on either side. So according to spin -spin coupling, the methylene NMR signal will be split in to eight. [(nA+1) nC+1) =4×3=12].the intensity ratio will be in the ratio of the coefficients of the terms of (r+1)12

(C) Methylene protons[CH2 C]: It has an adjacent methylene group with two equivalent protons. So it's NMR signal will be split in to three. The ratio area will be 1:

4. Isopropyl bromide(2-Bromo propane) : CH3-CHBr-CH3

A B A

Number of equivalent sets of protons : Two Number of groups of peaks : Two

Splitting :

(A)Methyl protons: Both methyl groups have identical environments. So they give only one peak. These have an adjacent methine group with one proton.So the methyl NMR signal will be split in to two. The intensity ratio will be 1:1

(B)Methine protons : It has two iidentical methyl groups on either side with a total of six protons. So the methine NMR signal will be split in to seven.The intensity ratio will be 1:6:15:20:15:6:1 .

Dr. G. MARIMUTHU

Assistant Professor of Chemistry

Department of Chemistry

Swami Dayananda College of Arts and Science

Manjakkudi-612610, Thiruvarur-Dt.