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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – I – INTRODUCTION TO SPECTROSCOPY – SCY1612

Introduction

Spectroscopy is the branch of science dealing with the study of interaction of electromagnetic radiation with matter like atoms and molecules. The interaction of EMR with matter gives rise to two types of spectra namely atomic spectra and molecular spectra.

Atomic spectrum arises from the transition of electrons from one energy level to another due to changes of energy in the atom.

Molecular spectrum involves transition of electrons between rotational and vibrational energy levels in addition to electronic transition. Therefore molecular spectrum is much more complicated than the atomic spectrum.

Molecular Spectroscopy provides a clear image of how diatomic and polyatomic molecules interact by looking at the Frequency, Wavelength, Wave number, Energy, and molecular process also provides most useful information regarding the shape and size of molecules, the bond angles, bond lengths, strength of bonds and bond dissociation energies.

Hence molecular spectroscopy is of great use in determining the structure and constitution of compounds.

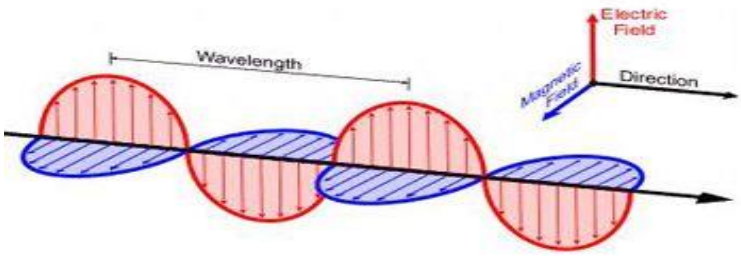
Electromagnetic Radiations (EMR)

EM radiation is created when a subatomic particle, such as an electron, is accelerated by an electric field. The movement produces oscillating electric and magnetic fields, which travel at right angles to each other in a bundle of light energy called a photon. Photons travel as harmonic waves at the fastest speed possible in the universe: 186,282 miles per second (299,792,458 meters per second) in a vacuum, also known as the speed of light.

The EM waves are characterized by frequency, wavelength, wave number and energy.

Electromagnetic (EM) radiation is a form of energy that is all around us and takes many forms, such as radio waves, microwaves, X-rays and gamma rays.

Visible light is only a small portion of the EM spectrum, which contains a broad range of electromagnetic wavelengths.



Electromagnetic waves are formed when an electric field (shown in red arrows) couples with a magnetic field (shown in blue arrows). Magnetic and electric fields of an electromagnetic wave are perpendicular to each other and to the direction of the wave.

The four main electromagnetic interactions:

The force of attraction or repulsion between electric charges is inversely proportional to the square of the distance between them.

Magnetic poles come in pairs that attract and repel each other, similar to that of electrical charges.

An electric current in a wire produces a magnetic field, the direction of which depends on the direction of the current.

A moving electric field produces a magnetic field, and vice versa.

Characterization of EMR

Wavelength (λ) : It is the distance between two consecutive peaks of a wave (crests). Unit = m.

Frequency (√): It is the number of waves that are formed in a given length of time. Unit = number of wave cycles per second or hertz (Hz).

A short wavelength means that the frequency will be higher and a longer wavelength has a lower frequency.

Wavenumber ($\bar{\upsilon}$): It is the number of waves per unit distance. Unit = cm^{-1} $\bar{\upsilon} = 1/\lambda$

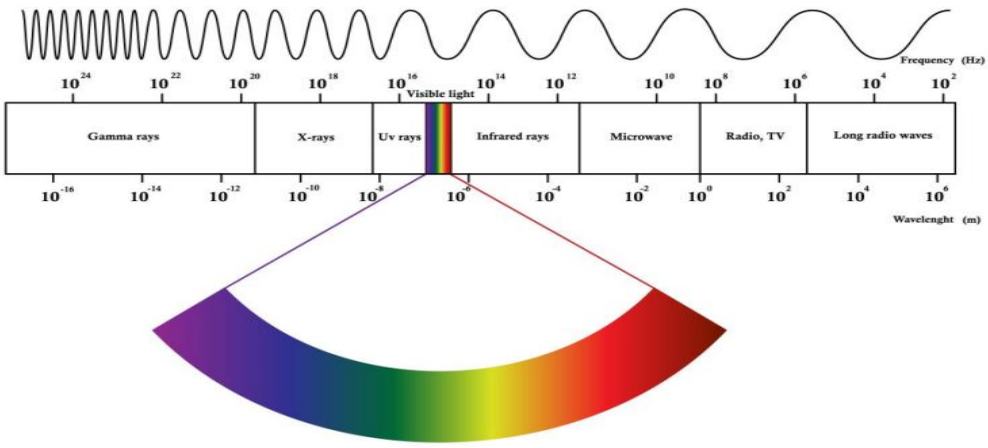
Energy of EMR (E): Electromagnetic radiations consists of particles having small packets of energies called quanta or photons. Photons possess the characteristic of wave and travel with the speed of light. The amount of energy corresponding to one photon is expressed by Planck's equation as

$E = h\nu$ or $E = \frac{hc}{\lambda}$

where h = Planck's constant (6.62×10^{-34} Js)

ν - frequency in Hz

λ - wavelength in cm/m.



Energy (E) = hc/λ

E = hν̄

E = hc$\bar{\upsilon}$

Interaction of EMR with matter

EMR interacts with matter only when the matter has some electric and magnetic effect and are influenced by the electric and magnetic components of the EM radiation.

The net change in the electric/magnetic dipole moment in the molecule or nuclear spin, interact with the magnetic/electrical component of the EMR by either absorption or emission of the EMR.

Total energy of molecules = Translational + rotational + vibrational + electronic

Absorption or emission of EMR causes a change in any of these types of energies.

In molecular spectroscopy, we measure the change in these energy states.

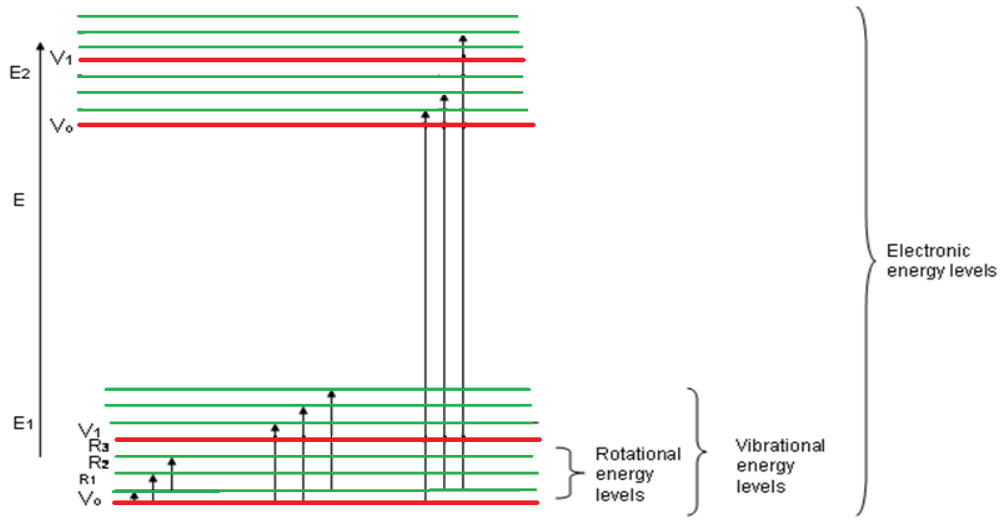
Translational energy – It is due to the overall movement of the molecule. Energy levels are not quantized . Hence no spectroscopy.

Rotational energy – It is due to spinning of molecules about the axis passing through the centre of gravity - Rotational Levels are quantized – **Rotational spectroscopy (Microwave spectroscopy)**

Vibrational energy – It is due to vibrations in molecules – Vibrational Levels are Quantized – **IR Spectroscopy (Vibrational spectroscopy)**

Electronic energy – Consists of electronic levels which are quantized – **UV/visible spectroscopy (Electronic spectroscopy)**

If E is the total energy of a molecule, it can be expressed as the sum of translational, rotational, vibrational and electronic contributions. $E = E_{trans} + E_{rot} + E_{vib} + E_{elec}$



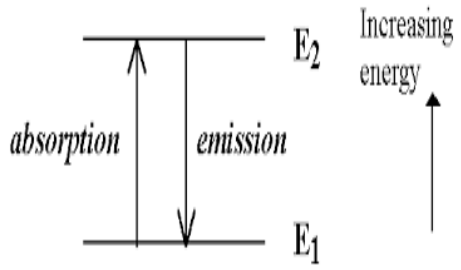
Spectra

Molecular spectra result from either the absorption or the emission of electromagnetic radiation as molecules undergo changes from one quantized energy state to another.

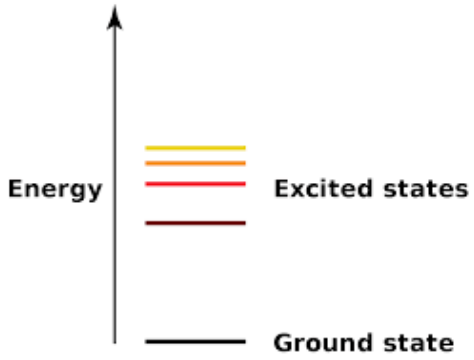
- The electrons in a molecule possess kinetic energy due to their motions and potential energy arising from their attraction by the positive nuclei and their mutual repulsion. These two energy factors, along with the potential energy due to the mutual electrostatic repulsion of the positive nuclei, constitute the electronic energy of a molecule.
- Molecules are not rigid structures, and the motion of the nuclei within the molecular framework gives rise to **vibrational energy levels**.
- In the gas phase, where they are widely separated relative to their size, molecules can undergo free rotation and as a result possess quantized amounts of **rotational energy**.
- In theory, the translational energy of molecules through space is also quantized, but in practice the quantum effects are so small that they are not observable, and the motion appears continuous.

- The interaction of electromagnetic radiation with these molecular energy levels constitutes the basis for Electronic, IR and Microwave spectroscopy.

Absorption and Emission Spectra

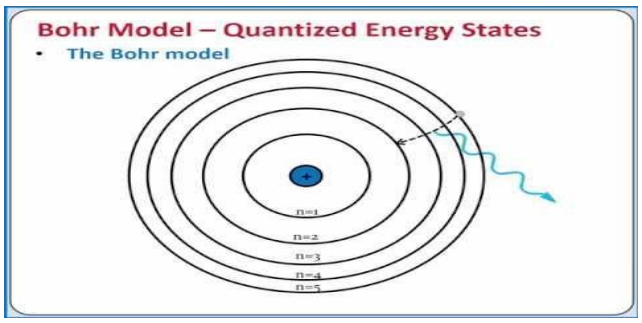


Absorption of electromagnetic radiation by compounds gives absorption spectrum and spectrum obtained by the emission of absorbed radiation is called emission spectrum.



Ground level/state is the lowest energy state. Higher energy levels/states are called excited states.

QUANTIZATION OF ENERGY LEVELS



Relative Population : Boltzmann Distribution Formula

Relative population in different energy levels is given by N_2/N_1

N_2 = number of molecules in the higher energy state E_2

N_1 = number of molecules in the lower energy state E_1

$$\mathbf{N_2/N_1 = e^{-(E2 - E1)/kT}}$$

k = Boltzmann constant, T = temperature

.

Thermodynamic equilibrium condition: $N_1 > N_2$; There is observed absorbance of electromagnetic radiation

For emission spectra : $N_2 > N_1$; There is population inversion

Saturation condition : $N_1 = N_2$; There is no absorption or emission of radiation

Selection Rule in Spectroscopy

Selection rules describe the allowed transitions between energy states in quantum systems. They are determined by which final states are accessible given an initial state and perturbing potential.

Atomic and molecular species contain a very large number of states in which energy can be distributed, although generally only the states lying lowest in energy will be thermally populated.

If electromagnetic radiation could effectively stimulate transitions between any one of these states, atomic and molecular spectra would be complex.

Selection rules, limit the possible transitions and render these spectra amenable to analysis.

Some transitions are “allowed” by the selection rules, while others are “forbidden”.

- The selection rules may differ according to the technique used to observe the transition.
- In quantum mechanics the basis for a spectroscopic selection rule is the value of the *transition moment integral*

$$\int \psi_1^* \mu \psi_2 d\tau$$

- where Ψ1 and Ψ2 are the wave functions of the two states, "state 1" and "state 2", involved in the transition, and μ is the transition moment operator. This integral represents the propagator (and thus the probability) of the transition between states 1 and 2; if the value of this integral is *zero* then the transition is “forbidden".
- In practice, to determine a selection rule the integral itself does not need to be calculated: It is sufficient to determine the symmetry of the *transition moment function.* If the transition moment function is symmetric over all of the totally symmetric representation of the point group to which the atom or molecule belongs, then the integral's value is (in general) *not* zero and the transition *is* allowed. Otherwise, the transition is “forbidden”.
- The transition moment integral is zero if the *transition moment function,* is anti-symmetric or odd.

Width of Spectral lines

Spectral lines are broadened because of two reasons:

1. Energy levels are not sharp.
2. Atoms are moving relative to observer.

Three mechanisms determine the line profile –

1. Quantum mechanical uncertainty in the energy E of levels with finite lifetimes. Determines the natural width of a line (generally very small).
2. Collisional broadening: Collisions reduce the effective lifetime of a state, leading to broader lines. High pressure gives more collisions (eg stars).
3. Doppler or thermal broadening, due to the thermal (or large-scale turbulent) motion of individual atoms in the gas relative to the observer.

Signal-to-Noise Ratio (SNR)

The ability of the spectrometer to make accurate measurements depends on the quality of the signal obtained from the detector and the subsequent electrical circuits. The signal-to-noise ratio (SNR) provides a measure of the signal quality. The SNR compares the average power available in

the signal to the average power contained in the noise, which includes any signal from sources other than the target signal source. In a spectrometer, the desired signal consists of the optical power at a given wavelength directed by the diffraction grating (and by the DMD, in a DLP-based system) to the detector. The noise signal arises from a number of sources, both electrical and optical.

In order to improve the SNR in a spectrometer, the design choices must increase the power in the measurement signal while at the same time minimize the noise sources as much as possible.

- Thermal energy provided by ambient heating generates the additional carriers that contribute to the noise current.
- Additional electronic noise, sometimes referred to as the readout noise, arises from the circuitry directly behind the detector that provides the initial filtering and scaling of the signal.
- Fixed pattern noise arises from the variation in the response to incident light of the detectors in a detector array. The variation originates primarily from differences in quantum efficiency caused by differences in the aperture area and the thickness of the detectors that occurred during fabrication. Only spectrometers employing a linear detector array for discriminating between wavelengths suffers from this source of noise.

Improving SNR

Several methods of spectrometer design and measurement, based on the nature of the noise sources, can improve the SNR of the spectrometer and lead to higher quality measurements.

- The use of holographic gratings, which have much fewer imperfections than ruled gratings, can reduce the stray light generated by the optical system. For this reason, holographic gratings are commonly used in UV spectrometers that suffer signal losses in the optical system due to absorption and are thus more susceptible to noise from stray light.
- A thermo-electric cooler (TEC) attached to any detector reduces the effective temperature of the detector and thus can reduce the impact of on the SNR.

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2. Kalsi P. S., Stereochemistry, 3rd Edition, New Age International Publishers, 1995.

Question Bank

Part A

1. What is electromagnetic radiation?

2. Mention the important characteristics of electromagnetic radiation.

3. Define wavelength, frequency and wavenumber.

4. Give the equation relating energy and frequency of EMR.

5. Relate energy and wavelength of EMR.

6. What are the different quantized energy levels?

7. Compare absorption and emission spectra.

8. What is SNR in spectroscopic techniques?

9. List out the important conditions for spectral line broadening.

10. Give any two methods of improving SNR.

11. Give the expression for Boltzmann Distribution Law.

Part B

1. Explain EMR and how are they characterized?

2. Elaborate on energy level quantization and the different spectroscopic method of analysis.

3. Write short note on Boltzmann Distribution Law and give its significance.

4. Discuss the signal to noise ratio related to spectroscopy.

5. Explain the various factors causing spectral line broadening.

6. Elaborate on selection rule in spectroscopic method of analysis.

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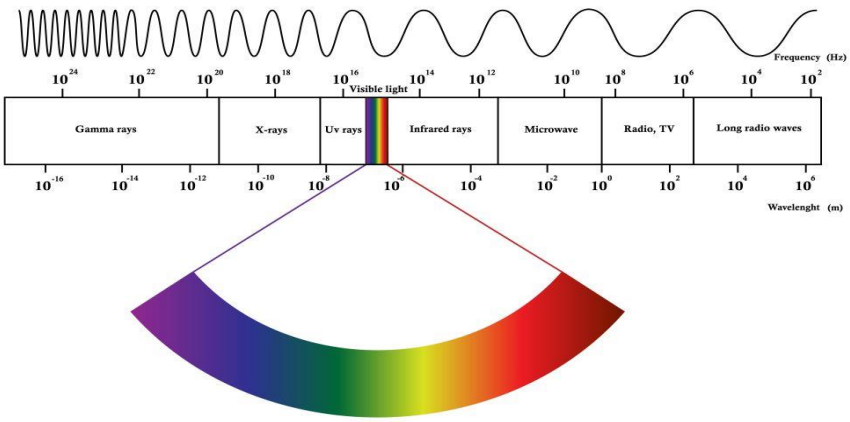
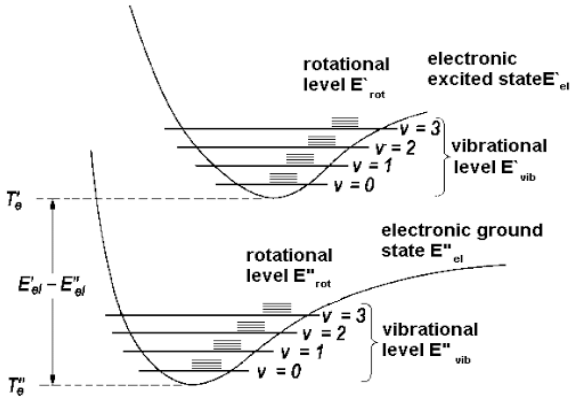
UNIT – II –UV-VISIBLE SPECTROSCOPY – SCY1612

Electromagnetic Spectrum– UV-Visible range



The UV-Visible range in the electromagnetic spectrum is from 200 – 800nm. The range 200 – 400 nm is the UV range and from 400 – 800 nm is the Visible range.

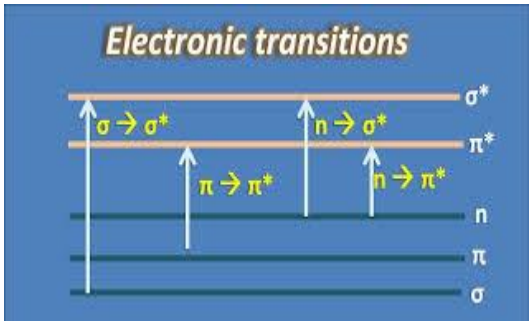


The electronic transitions are accompanied by vibrational and rotational transitions. Therefore the electronic absorption bands are broad in the spectrum.

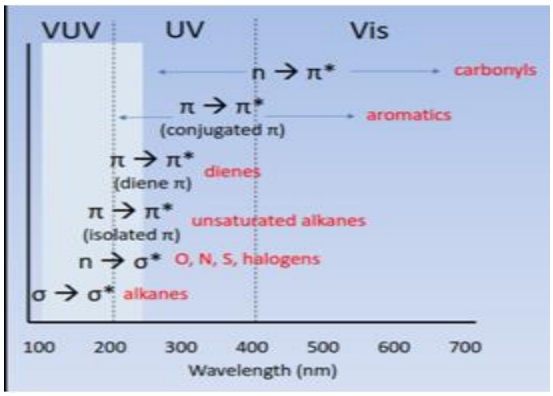
Characteristics of electronic transitions

- Electronic transitions are appeared as broad bands due to the accompanying vibrational and rotational transitions.
- During electronic transition there should be change in the dipole moment of the molecule (i.e. Ground state and Excited state dipole moment should not be the same)
- During electronic transition change in angular momentum should be zero or +/- 1

Types of Electronic Transitions



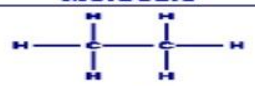
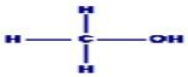
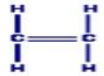
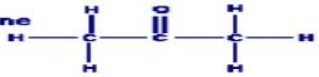
Examples of molecules exhibiting various electronic transitions



Types of electronic transitions

- σ → σ * transition: The energy required for this transition is high (i.e. very short wavelengths; 150nm). The saturated alkanes will undergo this type of transition.
- n → σ * transition: The saturated hydrocarbons attached to hetero atoms will undergo this type of transition. Example: Alcohols, amines, ether and water. The energy required for this transition is 180-190 nm.
- π → π * transition: The unsaturated hydrocarbons, carbonyl compounds, cyanides and azo compounds will undergo this type of transition around 250 nm. Ex: Alkenes, Alkynes, Aldehyde and Ketone. The energy required for this transition is very low (i.e. very longer wavelengths).
- n → π * transition: The carbonyl compounds will undergo this type of transition around 275 nm. Ex: Aldehydes, Ketone and cyanide.

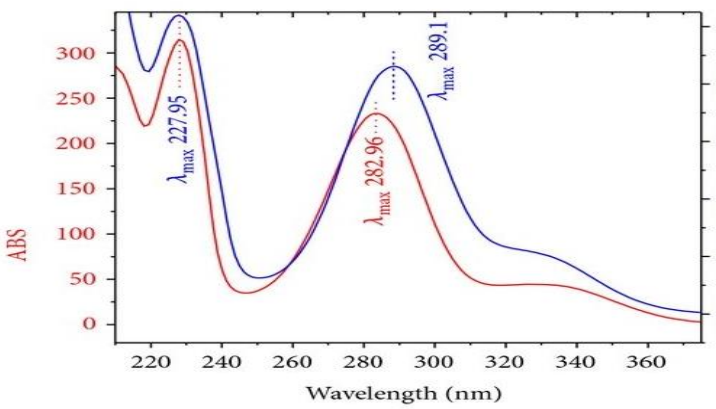
Table illustrates the type of transition and the resulting maximum wavelength.

Molecule	Transition	λ_{max} (nm)
Ethane 	$\sigma \rightarrow \sigma^*$	135
Methanol 	$\sigma \rightarrow \sigma^*$ $\eta \rightarrow \sigma^*$	150 183
Ethylene 	$\pi \rightarrow \pi^*$	175
Benzene 	$\pi \rightarrow \pi^*$	254
Acetone 	$\eta \rightarrow \pi^*$	290

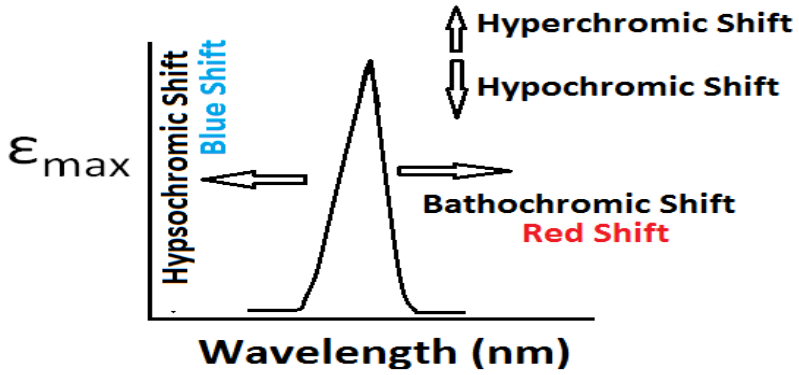
Differences between $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions

S.No.	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
1	Allowed transition	Forbidden transition
2	High energy transition	Lower energy transition
3	Molar extinction coefficient (ε) value lies between 100 to 10000	Molar extinction coefficient (ε) value is < 100
4	More intense than $n \rightarrow \pi^*$	More intense than $\pi \rightarrow \pi^*$

λ_{max} is the wavelength corresponding to maximum absorbance and ε_{max} is the molar absorption coefficient which is a constant for a particular molecule and proves the identity of the molecule.

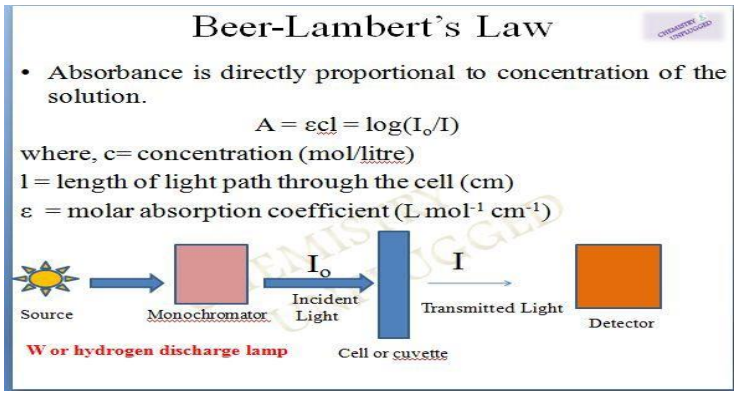


Effect of Substitutents on Absorption Spectra



- Bathochromic shift :- Absorption maximum of a compound shift to longer wavelength, it is known as Bathochromic shift or red shift.
- Hypsochromic shift:- Absorption maximum of a compound shifts to a shorter wavelength it is called a Hypsochromic shift or Blue shift.
- Hyperchromic shift :- Intensity of the absorption band increases.
- Hypochromic shift :- Intensity of the absorption band decreases.

UV-Visible spectroscopy – Instrumentation



A spectrophotometer is an instrument which uses monochromatic light. It measures the absorbance of various solutions at different wavelenths. This instrument scans the entire UV-visible regions.

In a double beam spectrophotometer, radiation from hydrogen lamp or tungsten lamp enters the monochromator, which produces very narrow band widths. The beam is then passed through a

reference cell and the sample cell by means of rotating mirrors. The photomultiplier tube is used as a detector which receives alternate pulses of radiation from the reference and sample beam.

Sources: Commonly used sources of UV radiation are the hydrogen lamp and the deuterium lamp. Tungsten filament lamp is used for the visible range.

Filters and Monochromators: Tinted glass filters are used to produce monochromatic radiations. Filters resolve polychromatic light into a relatively wide bandwidth to produce monochromatic radiations. Monochromator is a device which resolves polychromatic radiation into its individual wavelength and isolates them into very narrow bands.

Prism: A prism disperses polychromatic light from a source into its constituent wavelengths. Cornu quartz and littro prisms are used. Glass prisms are used for visible range while silica, fused silica or quartz prisms are used for the UV range.

Sample Holder (Cells / Cuvette) : The sample container should be transparent to the UV-visible radiation. Cuvettes are made ordinary glass or quartz. Fused silica cells are used for the UV range. The path length of these cuvettes is usually 1 cm.

Solvents: A solvent is selected in such a way that it does not absorb in the UV-visible range. The solvents that are frequently used are water, methanol, ethanol, hexane, chloroform etc.

Detectors: The commonly used detectors are photocells, phototubes and photomultiplier tubes.

Amplification and Read out: The transmitted radiation is converted into electrical signal and the electrical signals are interpreted using ammeters, amplifiers and potentiometers.

Mathematical Derivation of Beer- Lambert's Law:

When a beam of monochromatic radiation passes through a transparent absorbing medium, the rate of decrease of intensity of radiation with the thickness of the absorbing medium is proportional to the intensity of the incident radiation and concentration of the medium.

$$-\frac{dI}{dx} \alpha\ cI$$

where $-\frac{dI}{dx}$ = decrease of intensity of radiation with the thickness of the absorbing medium

c = concentration of the absorbing medium

dI = Change in intensity of incident light (range is from I_0 to I)

dx = Change in thickness of medium (range is from 0 to b)

$$-\frac{dI}{I} = \varepsilon c dx$$

$\varepsilon = \text{Molar extintion coefficient}$

$$-\frac{dI}{I} = c dx$$

$$\int_{I_o}^{I} \frac{dI}{I} = -\int_{x=0}^{x=b} \varepsilon c dx$$

$$\log[I]_{I_o}^{I} = -\varepsilon c[x]_0^b$$

$$\log I - \log I_o = -\varepsilon bc$$

$$\log \frac{I}{I_o} = -\varepsilon bc$$

$T = -\varepsilon bc$, $T = \text{Transmittance}$

$$\log \frac{I_o}{I} = \varepsilon bc$$

$A = \varepsilon bc$, A = Absorbance or Optical density

Transmittance (T) : It is the fraction of the incident light that is transmitted by a sample. $T = I/I_o$

Absorbance (A) : It is the negative logarithm to the base 10 of the transmittance of the solution.

$A = -\log T$ (no unit)

Molar absorptivity (ε): It the absorbance of a one molar solution placed in a cell of one cm path length. $A = \varepsilon bc$ (unit = $dm^3mol^{-1}cm^{-1}$)

Chromophore

It is a covalently unsaturated group which is responsible for absorption of UV or visible radiation and may or may not have an impact on the colour to the compound.

A compound which contains chromophore it is called chromogen. In unsaturated linkage such as –C=C-,-N=N-, the π electron are loosely bound. These loosely bound electron required less energy for electronic transition and the absorption band occur in near UV region.

Example: Acetylene possess -C=C- in structure its λ_{max} is 175-180 nm.

Auxochrome

It is saturated and unsaturated group which consists of one or more pair of non-bonded electron. This group when attached to a Chromophore help in altering the wavelength by increasing the intensity of absorption and increases λ_{max}.

Examples of Auxochrome are: -OH, $-NH_2$, -OR etc.

Problems and Solutions

Problem 1

If the transmittance of a solution is 19%, what is its absorbance or optical density?

Solution

%T = 19.4

T = 0.194

Absorbance = - log T

= log 1/T

= 0.712

Problem 2

A solution of a transmittance of 20% when taken in a cell of 2.5cm thickness. Calculate its concentration if the molar absorption coefficient is 12,000 $dm^2mol^{-1}cm^{-1}$

Solution:

$\log 1/T = \varepsilon bc$ $T = I/I_o$

%T = 20, T = 0.2, b = 2.5 cm $\log T = \log I/I_o$

$\varepsilon = 12000\ dm^3mol^{-1}cm^{-1}$ $-\log T = \log I_o/I$

log 1/0.2 = 12000 x2.5xc - log T = εbc

c = 2.33 x 10^{-5} mol dm^{-3}

Problem 3: A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution given that ε = 6000 $dm^3mol^{-1}cm^{-1}$

Log 1/T = εbc

%T = 40 , T = 0.4 , b = 2 cm

Log 1/0.4 = 6000 x 2 x c

C = 3.31x10^{-5} mol/dm^3

Problem 4: The transmittance of a 2x10^{-4} M solution of a substance was found to be 76.2% at a wavelength of 360nm, when placed in a cell of 1 cm length. Calculate A and ε.

%T = 76.2 , T = 0.762

A = -log T or A = log 1/T

A = log 1/0.762 = 0.118

A = εbc or ε = A/bc

ε = 0.118/1 x 2x10^{-4}

ε = 0.059 x10^4 $dm^3mol^{-1}cm^{-1}$

Problem 5: The molar extinction coefficient of a solute is 1.4x10^4 $dm^3mol^{-1}cm^{-1}$. If a solution of a substance has an absorbance of 0.85, in a cell of 1cm path length, calculate T and c of the solution.

Log 1/T = A = 0.85

1/T = 7.0794

T = 0.1412

A = εbc

c = A/εb

c = 0.85/1x1.4x10^4

c = 6.07x10^{-5} M

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2. Willard H. H., Merritt Jr. L. L., Dean J. A., and Settle Jr. A. F., Instrumental methods of analysis, 6th Edition, Van Nostrand, 1981.

Question Bank

Part A

1. What is electronic spectroscopy?

2. Mention the different types of electronic transitions in UV-visible spectroscopy.

3. Differentiate chromophore and auxochrome.

4. Write on solvent selection in electronic spectroscopy.

5. Give the important parts of an UV-visible spectrophotometer.

6. Write the principle behind UV-visible spectroscopy.

7. What are the limitations of electronic spectroscopy?

8. What is Beer-Lambert's Law?

9. Compare bathochromic and hypsochromic shifts.

10. Differentiate hyperchromic and hypochromic shifts.

11. Give one example of a molecule showing $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions.

12. Differentiate $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in electronic spectroscopy.

13. Define λ_{max} and ε_{max} in electronic spectroscopy.

Part B

1. Write short on the different types of electronic transitions in molecules.

2. Explain the instrumentation of UV-visible spectroscopy in a block diagram

3. Derive the expression for Beer – Lambert's Law.

4. Explain the effect of substituents on λ_{max} and ε_{max} values in electronic spectroscopy.

5. Discuss the effect of chromophoric and auxochromic groups in molecules.

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DEPARTMENT OF CHEMISTRY

UNIT – III –IR AND RAMAN SPECTROSCOPY– SCY1612

VIBRATIONAL SPECTROSCOPY (IR spectroscopy)

Vibrational spectroscopy is due to the interaction of matter with the Infra red region of the electromagnetic spectrum.

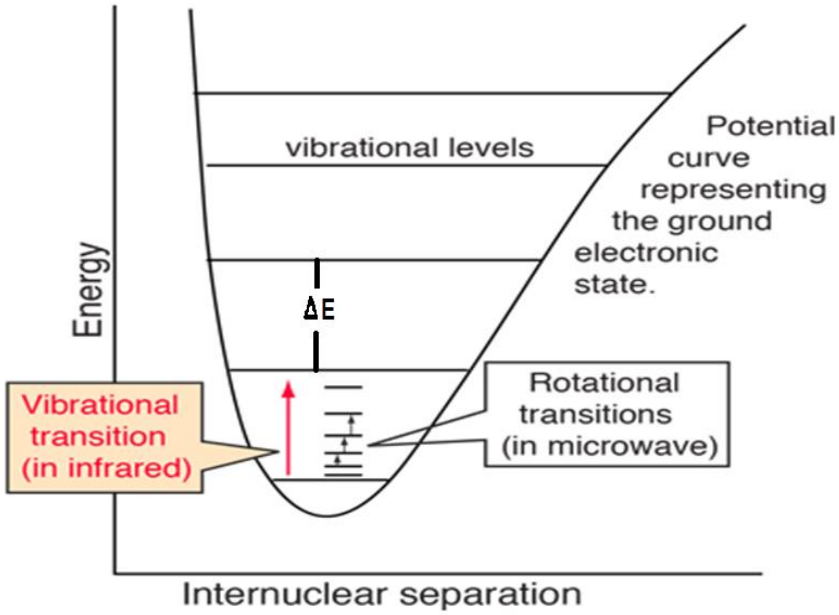
Spectral Range of IR Radiation:

- Near IR: 12000 cm^{-1} to 4000 cm^{-1}
- MID IR: 4000 cm^{-1} to 620 cm^{-1}
- Far IR: 300 cm^{-1} to 10 cm^{-1}

The mid IR region is used for the sample analysis in IR spectroscopy.

Quantum Approach

Irradiation of sample with IR radiation brings about vibrational changes in molecules. The transition of molecule is from lower vibrational energy level to higher vibrational energy level. The transition is induced by absorption of photon of the IR radiation of appropriate frequency, which matches with energy gap between the two levels.



IR absorption by molecules happens only when there is a change in the dipole moment of the molecule.

Dipole Moment (μ) = Charge (Q) * distance of separation (r)

Measured in Debye units denoted by 'D'.

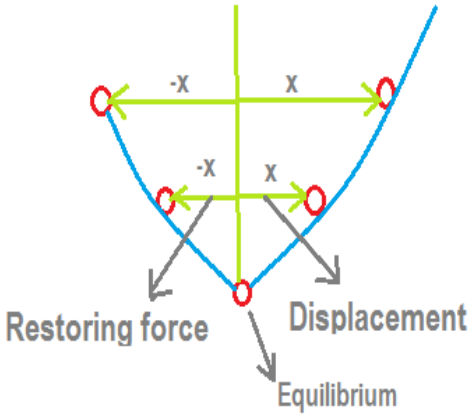
1 D = 3.33564 × 10^{-30} Cm, where C is Coulomb and m is meter.

The bond dipole moment that arises in a chemical bond between two atoms of different electronegativities can be expressed as follows:

$$\mu = \delta.d$$

where μ is the bond dipole moment, δ is the magnitude of the partial charges δ^+ and δ^-,

and d is the internuclear distance between δ^+ and δ^-.



The bond between the atoms is considered as a spring which can undergo stretching and bending vibrations. During vibration, there is a change in the dipole moment of the molecule as a result of the change in the distance between the atoms. When an atom in a molecule is stretched over a certain distance keeping the other atom stationary, the atom gets displaced from its equilibrium position by distance "x" . To attain equilibrium, the atom tries to move back to the original position, by applying a restoring force which is equal the displaced distance but will be in the opposite direction and has a negative value. According to Hook's Law:

-restoring force α x

-F α x

-F = kx k = force constant

Harmonic Oscillator – vibrating pendulum

ω_{osc} = vibrational frequency = $\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

$$\overline{\omega}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

VIBRATIONS OF POLYATOMIC MOLECULES

Degrees of freedom:

The number of degrees of freedom is equal to the sum of coordinates necessary to locate all the atoms of a molecule in space. Each atom has three degrees of freedom corresponding to the three Cartesian coordinates (X, Y, Z) which is necessary to describe its position on relative to other atoms in a molecule.

The total number of degrees of freedom in a molecule containing N-atoms is equal to 3N which includes rotational, vibrational and translation degrees of freedom.

Total number of degrees of freedom (3N) = Translational + Vibrational + Rotational

The number of degrees of freedom for H atom = 3

The number of degrees of freedom for Methane (CH_4) molecule = 3N = 3x5 = 15

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

Vibrational Degrees of freedom for Linear molecule

Total degrees of freedom for a polyatomic molecule = Translational + Rotational + Vibrational

3N = 3 + 2 + Vibrational

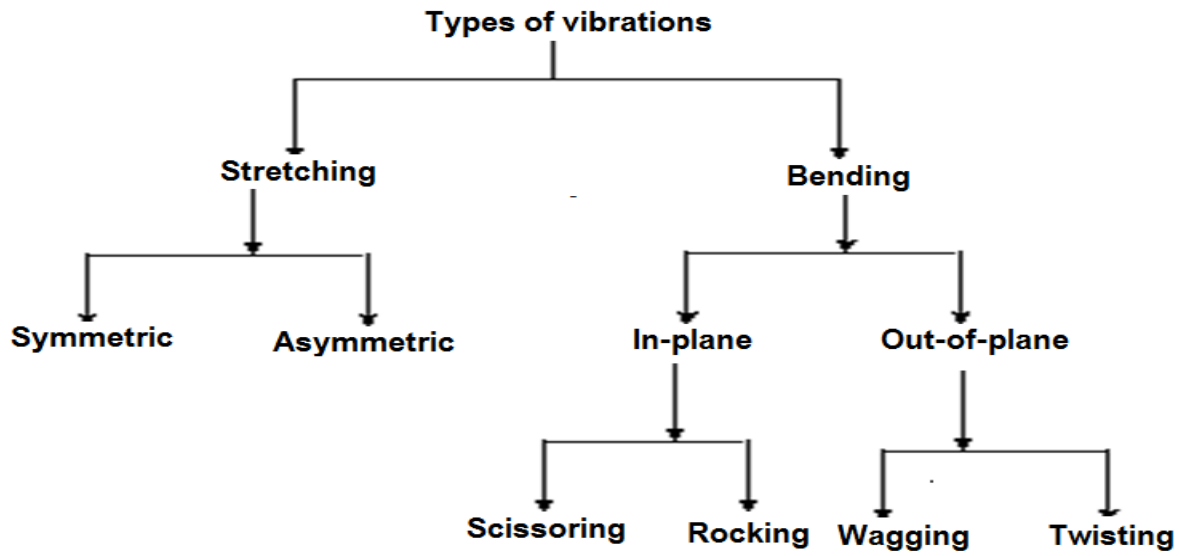
- Vibrational Degrees of freedom = 3N-5
- For example: CO_2, CO, HCl, Acetylene
- Vibrational Degrees of freedom for CO = 3N-5 = 1
- Vibrational Degrees of freedom for C_2H_2 = 3N-5 = 7
- Vibrational Degrees of freedom for CO_2 = 3N-5 = 4

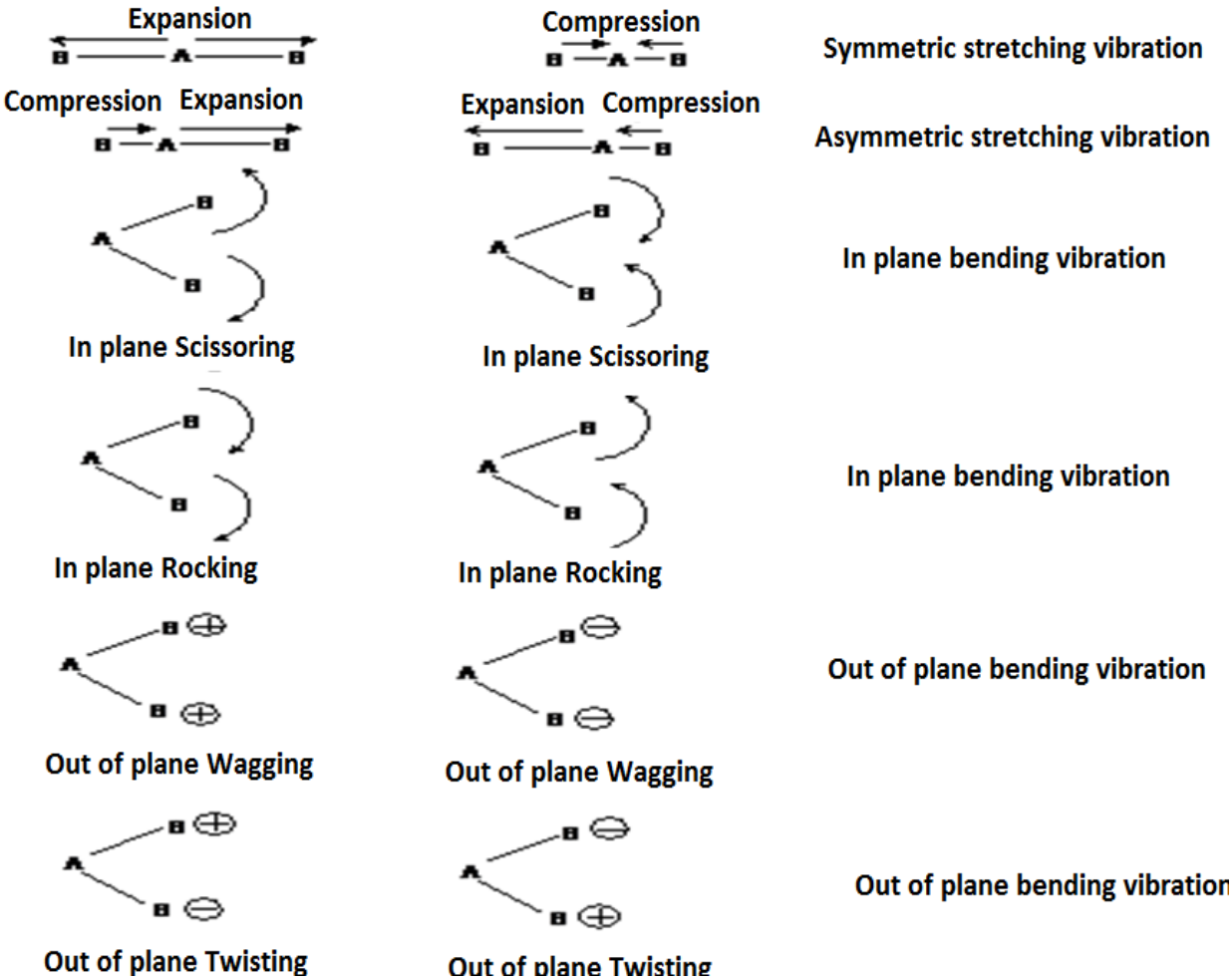
Degrees of freedom of vibration for Non-linear molecule

Total degrees of freedom for polyatomic molecule = Translational + Rotational + Vibrational
3N = 3 + 3 + Vibrational
Vibrational Degrees of freedom = 3N-6
Vibrational Degrees of freedom for H_2O = 3N-6 = 3
Vibrational Degrees of freedom for CH_4 = 3N-6 = 9
Vibrational Degrees of freedom for NH_3 = 3N-6 = 6
Vibrational Degrees of freedom for C_6H_6 = 3N-6 = 30

Types of Vibrations

Vibration is periodic displacement of atoms or nuclei from their equilibrium position.





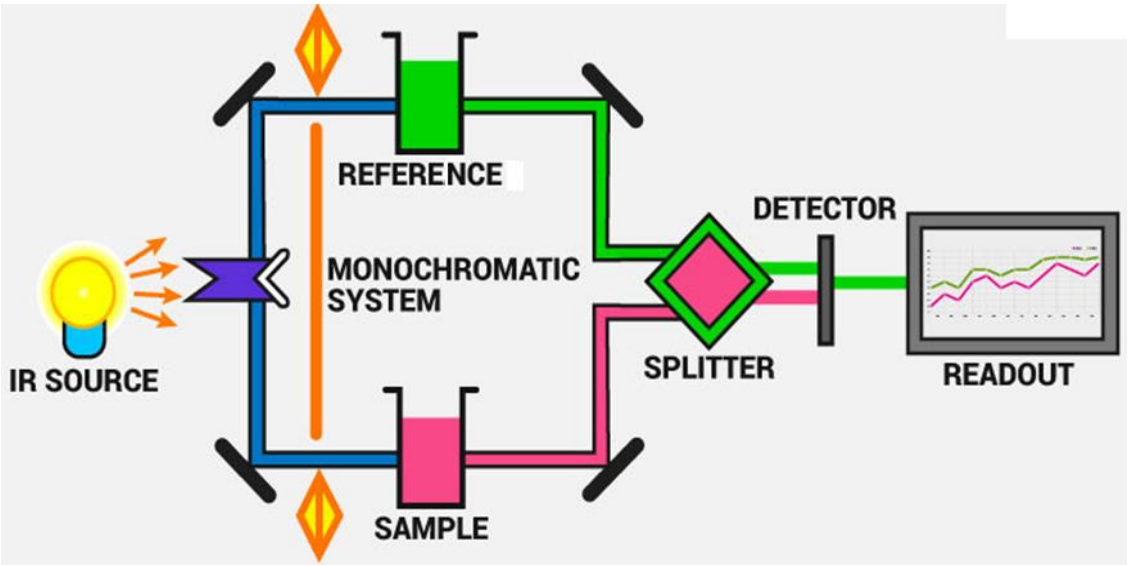
Regions of the Infrared spectrum

- Most of the bands that indicate what functional group is present are found in the region from 4000 cm^{-1} to 1300 cm^{-1}. Their bands can be identified and used to determine the functional group of an unknown compound.
- Bands that are unique to each molecule, similar to a fingerprint, are found in the fingerprint region, from 1300 cm^{-1} to 400 cm^{-1}. These bands are only used to compare the spectra of one compound to another.

IR – Sampling Techniques

- The samples used in IR spectroscopy can be either in the solid, liquid, or gaseous state.
- Solid samples can be prepared by crushing the sample with a mulling agent (KBr) which has an oily texture. A thin layer of this mull can now be applied on a salt plate to be measured.
- Liquid samples are generally kept between two salt (NaCl) plates and measured since the plates are transparent to IR light. Salt plates can be made up of sodium chloride, calcium fluoride, or even potassium bromide.
- Since the concentration of gaseous samples can be in parts per million, the sample cell must have a relatively long pathlength, i.e. light must travel for a relatively long distance in the sample cell.
- Thus, samples of multiple physical states can be used in Infrared Spectroscopy.

IR Spectroscopy – Instrumentation



- A beam of IR light from the source (Nernst Glower / Globar) is split into two and passed through the reference and the sample respectively.

- Now, both of these beams are reflected to pass through a splitter and then through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector.

Vibrational Frequencies

Bond	Stretching frequency (cm^{-1})	Intensity
O-H (alcohol)	3200-3650	Medium, broad
O-H (carboxylic acid)	2500-3300	Strong, broad
N-H	3100-3550	Medium
C-H (alkane)	2850-3000	Medium
C-H (alkene)	3000-3100	Medium to strong
C-H (alkyne)	3300	Weak to medium
C≡C	2100-2250	Weak
C=C	1600-1680	Weak to medium
C=O (aldehyde/ketone)	1630-1820	Strong
C=O (ester)	1735-1800	Strong
C=O (carboxylic acid)	1700-1725	Strong
C-O	1000-1250	Strong

Selection rules for Infrared transitions

For a particular vibration to be infrared active there must be a change in the dipole moment of the molecule during the vibration. In other words transition dipole moment must not be zero.

Homonuclear diatomic molecules are inactive in the infrared spectrum. They do not have a dipole moment and during the vibration also the dipole moment is zero. eg: H_2, O_2, N_2 etc.

Heteronuclear diatomic molecules such as CO, NO are active in IR.

Symmetrical polyatomic molecules such as CO_2, the symmetric stretching vibration is infrared inactive where as the asymmetric stretching vibration is IR active $\Delta v = \pm 1$, transition can take place between Adjacent vibrational levels, 0 to 1, 1 to 2 etc.

- IR spectrum shows bands rather than line spectrum due to coupling of various rotational transitions within a given vibrational transition. IR spectrum is generally complex and contains many bands in addition to the ones corresponding to fundamental vibrational transitions

- Overtones: Bands corresponding to integral multiple of fundamental vibration. They are due to transition from ground state to higher vibrational states. They are very weak bands. An absorption band at 1050 cm^{-1} may well have an accompanying band at 2100 (2 ν) and 3150 (3 ν) cm^{-1}.

- Combination bands: Two vibrational frequencies in a molecule couple to give a new frequency within the molecule. This band is a sum of the two interacting bands.
- Difference bands: Similar to combination bands. The observed frequency is the difference between the two interacting frequencies.
- Fermi resonance: When a fundamental vibration couples with overtone or combination Band, the coupled vibration is called a Fermi resonance.

Raman Spectroscopy

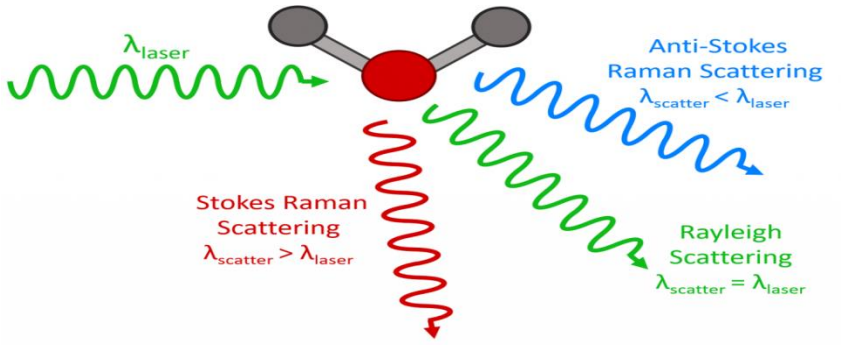
Raman spectroscopy is an analytical technique where scattered light is used to measure the vibrational energy modes of a sample. It is named after the Indian physicist C. V. Raman who, together with his research partner K. S. Krishnan, was the first to observe Raman scattering in 1928.

Raman spectroscopy can provide both chemical and structural information, as well as the identification of substances through their characteristic Raman 'fingerprint'. Raman spectroscopy extracts this information through the detection of Raman scattering from the sample.

Raman Scattering

When light is scattered by molecule, the oscillating electromagnetic field of a photon induces a polarisation of the molecular electron cloud which leaves the molecule in a higher energy state with the energy of the photon transferred to the molecule. This can be considered as the formation of a very short-lived complex between the photon and molecule which is commonly called the virtual state of the molecule.

The virtual state is not stable and the photon is re-emitted almost immediately, as scattered light.



Rayleigh scattering

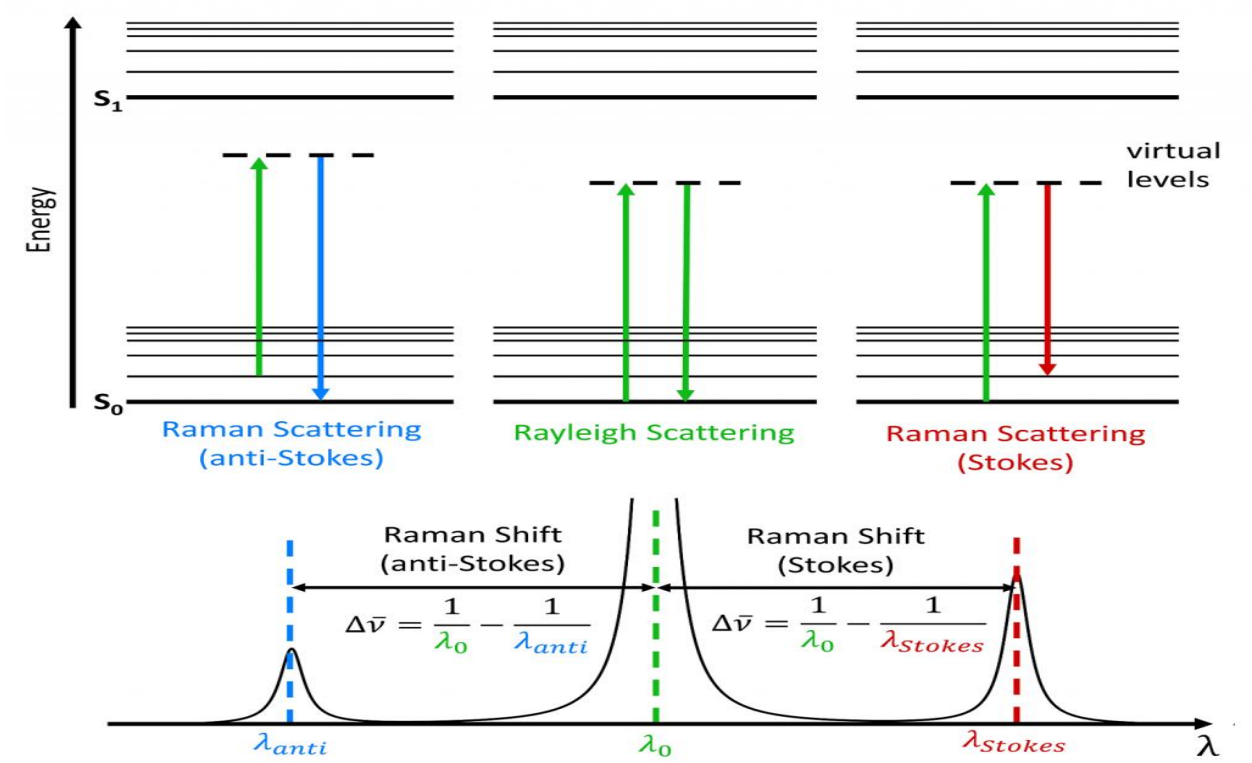
In the vast majority of scattering events, the energy of the molecule is unchanged after its interaction with the photon; and the energy, and therefore the wavelength, of the scattered photon is equal to that of the incident photon. This is called elastic (energy of scattering particle is conserved) or Rayleigh scattering and is the dominant process.

Stokes and Antistokes lines

In a much rarer event (approximately 1 in 10 million photons) Raman scattering occurs, which is an inelastic scattering process with a transfer of energy between the molecule and scattered photon. If the molecule gains energy from the photon during the scattering (excited to a higher vibrational level) then the

scattered photon loses energy and its wavelength increases which is called Stokes Raman scattering (after G. G. Stokes). Inversely, if the molecule loses energy by relaxing to a lower vibrational level the scattered photon gains the corresponding energy and its wavelength decreases; which is called Anti-Stokes Raman scattering.

Quantum mechanically Stokes and Anti-Stokes are equally likely processes. However, with an ensemble of molecules, the majority of molecules will be in the ground vibrational level (Boltzmann distribution) and Stokes scatter is the statistically more probable process. As a result, the Stokes Raman scatter is always more intense than the anti-Stokes and for this reason, it is nearly always the Stokes Raman scatter that is measured in Raman spectroscopy.



Differences between IR and Raman methods

RAMAN	**IR**
It is due to the scattering of light by the vibrating molecules.	It is the result of absorption of light by vibrating molecules.
The vibration is Raman active if it causes a change in polarisability.	Vibration is IR active if there is change in dipole moment.
The molecule need not possess a permanent dipole moment.	The vibration concerned should have a change in dipole moment due to that vibration.
Water can be used as a solvent.	Water cannot be used due to its intense absorption of IR.
Sample preparation is not very elaborate, it can be in any state.	Sample preparation is elaborate Gaseous samples can rarely be used.
Gives an indication of covalent character in the	Gives an indication of ionic character in the

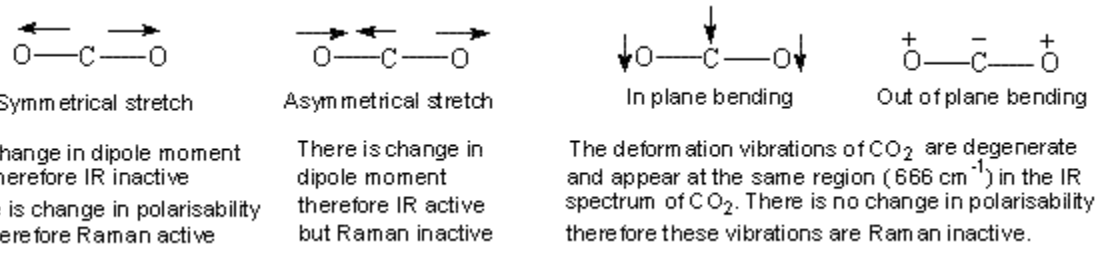
molecule.	molecule.
Cost of instrumentation is very high	Comparatively inexpensive.

Mutual Exclusion Principle

In molecules with a center of symmetry it is observed that vibrations that are Raman active are IR inactive and vice-versa, this is called the Principle of mutual exclusion (eg: CO_2). In molecules with different elements of symmetry, certain bands may be active in IR, Raman, both or neither. For a complex molecule that has no symmetry except identity element, all of the normal modes are active in both IR and Raman. In both types the neighbouring strong bands may obscure weak bands, while others may be intrinsically too weak to be observed even if they are theoretically "allowed".

In general the strong bands in the IR spectrum of a compound corresponds to weak bands in the Raman and vice versa. This complimentary nature is due to the electrical characteristic of the vibration. If a bond is strongly polarised, a small change in its length such as that occurs during a vibration, will have only a small additional effect on polarisation. Vibrations involving polar bonds (C-O , N-O , O-H) are therefore, comparatively weak Raman scatterers. Such polarised bonds, however, carry their charges during the vibrational motion, (unless neutralised by symmetry factors), which results in a large net dipole moment change and produce strong IR absorption band. Conversely, relatively neutral bonds (C-C , C-H , C=C) suffer large changes in polarisability during a vibration. But the dipole moment is not similarly affected and vibrations that predominantly involve this type of bond are strong Raman scatterers but weak in the IR.

In molecules having inversion center, none of the normal modes of vibrations will be both Raman and IR active. This is known as "mutual exclusion principle". A simple molecule which obeys this principle is CO_2. Carbondioxide has an inversion center or center of symmetry. The following are its normal modes of vibrations. The IR and Raman active modes are indicated below each type of vibration.



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2. Skoog D. A., West D. M., Holler f. J., and Crouch S. R., Fundamentals of Analytical Chemistry, 9th Edition, Wadsworth Publishing Co. Inc., 2012

Question Bank

Part A

1. Mention the use of IR radiation in vibrational spectroscopy.

2. Write the important conditions for IR absorption by molecules.

3. Calculate the number of vibrational degree of freedom in CO_2, H_2O molecules

4. Give the expression relating forcr constant and wavenumber used in IR spectroscopy.

5. Differentiate functional and finger print regions in vibrational spectroscopy.

6. What is Rayleigh scattering?

7. What is Raman scattering?

8. Compare stokes and antistokes lines in IR spectroscopy.

9. What is mutual exclusion principle?

10. Compare Raman and IR spectroscopic techniques.

Part B

1. Discuss the different types of vibrational transitions.

2. Explain the instrumentation of IR spectroscopy with a neat block diagram.

3. Elaborate on the structural determination of molecules by Raman spectroscopy.

4. Write short note on mutual exclusion principle.

5 .Compare and contrast IR and Raman spectroscopic methods of analysis.

6. Write briefly on the selection rule in IR spectroscopy.

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DEPARTMENT OF CHEMISTRY

UNIT – IV– NMR SPECTROSCOPY – SCY1612

Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy takes advantage of the magnetic properties of certain nuclei and records the absorption of energy between quantized nuclear energy levels. In an NMR experiment, the spectrometer is tuned to the frequency of a *particular* nucleus and the spectrum reveals all such nuclei in the molecule being investigated. It is thus a very powerful technique, the closest analogy being a powerful microscope that allows the chemist to "see" the structure of molecules in solution.

Theory

NMR is possible owing to the magnetic properties of certain nuclei. In addition to charge and mass, which all nuclei have, various nuclei also possess a property called *nuclear spin*, which means that they behave as if they were spinning. Since nuclei have a charge, they generate a magnetic field with an associated *magnetic moment*.

There are useful empirical rules relating mass number, atomic number (Z) and *nuclear spin quantum number* (I):

Mass Number	Z	I
even	even	0
odd	even or odd	$^1/_2$, $^3/_2$, $^5/_2$, ...
even	odd	1, 2, 3, ...

Since NMR depends on the existence of a nuclear spin, nuclei with I = 0 have no NMR spectrum (*e.g.*, ^{12}C, ^{16}O, ^{18}O). From standpoint of generating NMR spectra, the most important class of nuclei are those with I = $^1/_2$. Nuclei with I >$^1/_2$ (*e.g.*, ^{11}B, I = $^3/_2$; ^{14}N, I = 1) have *quadrupole moments*, a non-spherical distribution of nuclear charge, which results in broad absorption lines and makes observation of spectra more difficult. The quadrupole moment can even affect the lineshape of neighbouring nuclei. For example, resonances of protons bonded to nitrogen or boron atoms are generally broad in ^{1}H NMR spectra. We shall thus be primarily concerned with nuclei where I = $^1/_2$, but the effect that quadrupolar nuclei can have on the NMR spectra of I = $^1/_2$ nuclei should be remembered. A listing of isotopes with I = $^1/_2$ is provided in Table 1.

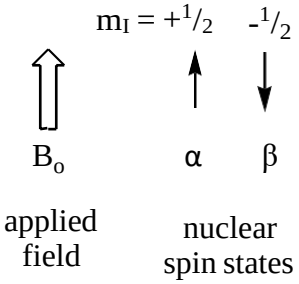
Table 1: Natural abundances of isotopes with I = $^1/_2$.

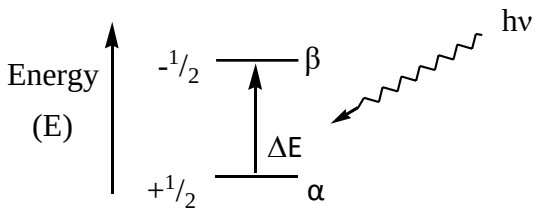
Isotope	Natural Abundance (%)	Isotope	Natural Abundance (%)	Isotope	Natural Abundance (%)
^{1}H	100	^{107}Ag	51.35	^{129}Xe	26.44
^{13}C	1.108	^{109}Ag	48.65	^{169}Tm	100

^{15}N	0.365	^{111}Cd	12.75	^{183}W	14.4
^{19}F	100	^{113}Cd	12.26	^{187}Os	1.64
^{29}Si	4.71	^{115}Sn	0.34	^{195}Pt	33.8
^{31}P	100	^{117}Sn	7.57	^{199}Hg	16.84
^{57}Fe	2.17	^{119}Sn	8.58	^{203}Tl	29.50
^{77}Se	7.58	^{123}Te	0.87	^{205}Tl	70.50
^{89}Y	100	^{125}Te	6.99	^{207}Pb	21.7
^{103}Rh	100				

In an NMR experiment, the sample is placed in a strong magnetic field, B_o. Since the spins of the magnetic nuclei are quantized, they can have only certain well-defined values. If we have nuclei with $I = {}^1/_2$ (*e.g.*, ^1H, ^{31}P), the spins can orient only in two directions: either with ($m_I = +{}^1/_2$, α) or against ($m_I = -{}^1/_2$, β) the applied field. NMR transitions are allowed for cases where $\Delta m_I = \pm 1$. There is an energy difference, ΔE, between the two states, and this is given by

$\Delta E = h\nu = (h/2\pi\gamma) B_o$ or $\nu = (1/2\pi\gamma) B_o$





where h is Planck's constant, γ is the gyromagnetic ratio (a constant characteristic of each nucleus)*, and B_o is the applied magnetic field. When the energy of the incoming radiation matches (is in *resonance* with) the energy difference between the spin states, energy is absorbed and the nucleus is promoted from the lower $+^1/_2$ to the higher $-^1/_2$ spin state. Since the sign of m_I changes, this is sometimes referred to as a "spin flip". NMR transitions occur in the *radio frequency* (rf) range of the electromagnetic spectrum. The absorption of rf energy is electronically detected and is displayed as an NMR spectrum.

The above equation is very important since it shows that ΔE depends only on γ and B_o. The gyromagnetic ratio, γ, is an intrinsic property of the magnetic nucleus. Therefore, each type of nucleus has a distinct and characteristic value of γ. Accordingly, the NMR experiment must be tuned for a *specific nucleus* and one must record a *different* NMR spectrum for each NMR active nucleus of interest. Conversely, you do not have to worry about observing signals from different nuclei on the same NMR spectrum. In order to gather all NMR knowledge about a molecule such as PH_3, we would record two different NMR spectra - a ^1H NMR spectrum to observe the ^1H nuclei and a ^{31}P NMR spectrum to observe the ^{31}P nucleus. We would not observe the ^{31}P nucleus in a ^1H NMR spectrum and *vice-versa*.

The above equation also reveals that ΔE is directly proportional to B_o, the external magnetic field. The higher the external field, the greater is the energy separation between the α ($m_I = +^1/_2$) and β ($m_I = -^1/_2$) spin states. Recalling that E = hν, another way of saying this is that the *resonance frequency* of the nucleus increases with increasing B_o since if E increases, so does ν. This is shown in the following table.

B_o	Resonance Frequency (ν, MHz)				
(tesla)‡	^1H	^{13}C	^{11}B	^{19}F	^{31}P
2.35	100	25.2	32.1	94.1	40.5
4.70	200	50.4	64.2	188.2	81.0

‡a *tesla* is a unit describing magnetic field strength

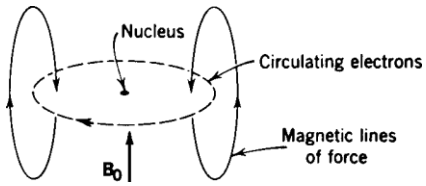
.

Note that *all $I = {}^1/_2$ nuclei behave according to the same theoretical principles* - although ^{1}H NMR spectroscopy is the most commonly practiced, ^{19}F and ^{31}P NMR spectra are generated in exactly the same way as a ^{1}H NMR spectrum. The main difference between the different $I = {}^1/_2$ nuclei is that the resonance frequency is changed when recording the spectrum.

Chemical Shift

The resonance frequency is determined only by γ and B_o, therefore, all atoms of a given nucleus in a molecule (*e.g.*, all ^{1}H nuclei) should resonate at the same frequency. If this were the case, the only thing NMR could tell us is whether a molecule contains NMR active nuclei (^{1}H, ^{31}P, ^{13}C, etc.). Fortunately, the frequency of the NMR absorptions of a given nucleus also depends on the *chemical environment* of the nucleus. The variation of the resonance frequency with chemical environment is termed the *chemical shift*, and herein lies the power of the NMR method.

The origin of the chemical shift can be traced to the electrons surrounding the nucleus, and the interaction of the electron cloud with the applied field, B_o. The reason for this is that circulating electrons also generate a magnetic field that orients itself in the *opposite direction* to the applied field.



The actual field (B_{local}) "felt" by a nucleus is thus *less* than B_o, and the ability of the electrons to alter the field felt at the nucleus can be expressed by θ, the *shielding constant.*

$$B_{local} = B_o (1-\theta)$$

Nuclei are said to be *shielded* or *deshielded* depending on the presence or absence of electron density surrounding them. For example, the introduction of an *electron withdrawing group* (*e.g.*, halogen, O, etc.) will reduce the electron density around a nucleus (*deshielding*; δ is small) and the resonance frequency will increase. Conversely, an *electron donating substituent* (*e.g.*, CH_x, SiH_x) will cause increased *shielding* (δ is large) and lower the resonance frequency.

In reporting chemical shifts, one could use absolute field or absolute frequency, but this would be cumbersome and would result in the chemical shift being dependent upon the applied field. A simpler scale for chemical shifts has been devised. Chemical shifts (δ) are expressed in units of parts per million (ppm) of the spectrometer frequency with respect to a *reference material* whose position is arbitrarily assigned a value of 0.0 ppm.

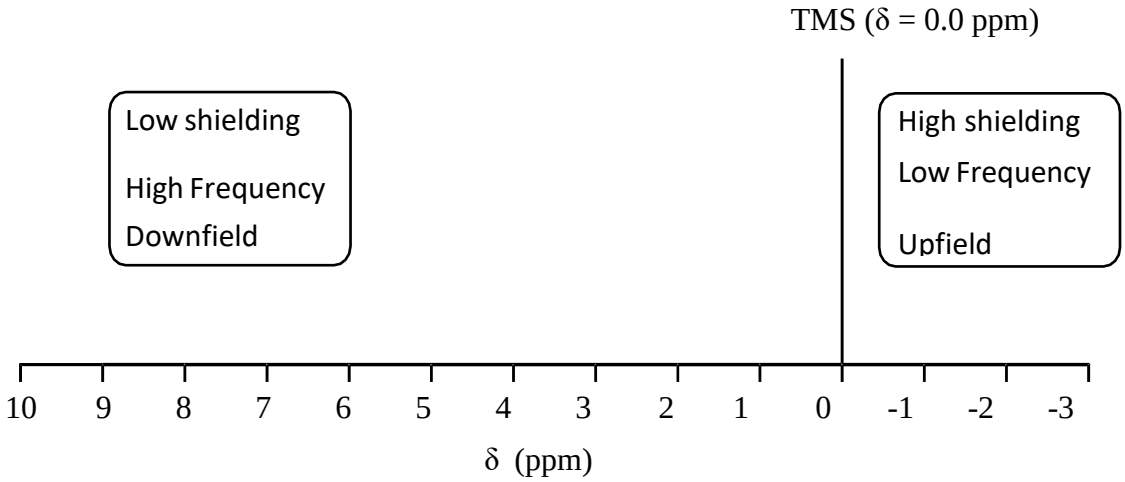
$$\delta = \frac{\text{frequency of signal - frequency of standard}}{\text{spectrometer frequency}} \times 10^6$$

When expressed in such dimensionless units (δ in ppm), the chemical shifts are *invariant of the frequency of the spectrometer* and can be used as molecular parameters. For example, 1.0 ppm at 60 MHz is equal to a separation of 60 Hz, and at 200 MHz, 1.0 ppm equals 200 Hz. Thus, the same two resonances that are separated by 1 ppm at 60 MHz are still 1 ppm apart at 200 MHz, because δ = 60 Hz/60 MHz = 200 Hz/200 MHz = 1 ppm. Therefore, if the *same sample* is run at two different spectrometer frequencies, the chemical shifts of the resonances will be *identical*. Naturally, this statement is only true if the same reference material is used for each spectrum. Different references are used for different nuclei. The most widely accepted reference for ^{1}H and ^{13}C NMR is tetramethylsilane ($Si(CH_3)_4$ = TMS). For ^{11}B NMR, $F_3B{\bullet}OEt_2$ is commonly used, as are $CFCl_3$ for ^{19}F NMR and 85% H_3PO_4 for ^{31}P NMR spectroscopy.

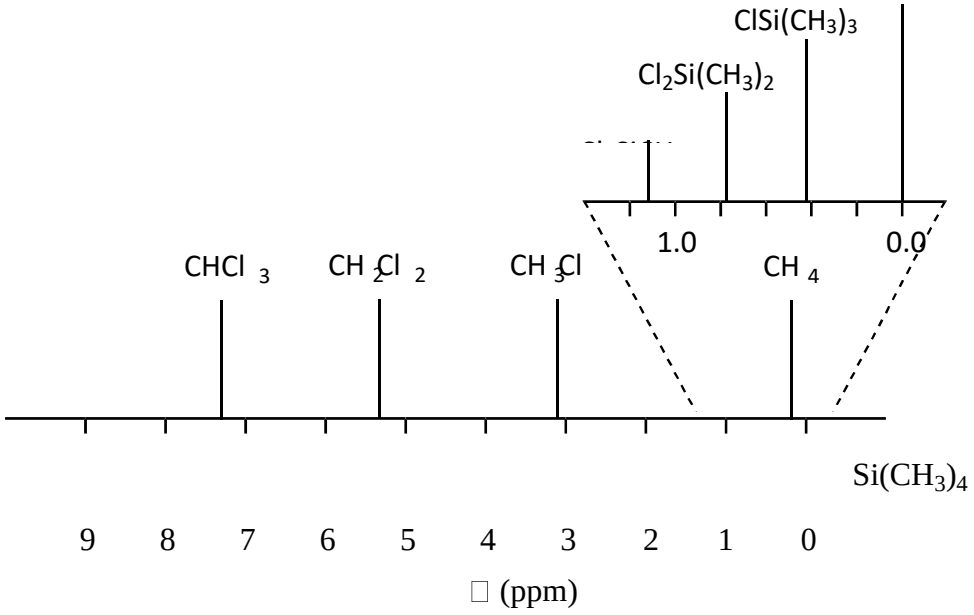
In the past, NMR spectra were obtained by varying the applied field and measuring the chemical shift as a function of the field strength. This gave rise to the terminology of a *downfield shift* for nuclei that were *deshielded* (as they required a lower applied field to bring the nucleus into resonance) and *upfield shift* for *shielded* nuclei. For example, one would say that a resonance at δ 8.0 ppm is downfield of one at δ 2.0 ppm, and conversely that the signal at δ 2.0 ppm was upfield of the signal at δ 8.0 ppm.

More modern NMR spectrometers generate spectra by varying the frequency, γ, while keeping the magnetic field strength, B_o, constant. Nevertheless, the upfield/downfield terminology remains in common use. Unfortunately, this results in the confusing situation that δ is *positive* in the *downfield* direction (to the left of the standard on spectra) where *resonance*

frequencies are higher. Resonances that are *upfield* of the reference appear at *lower frequencies* and have *negative* δ values.



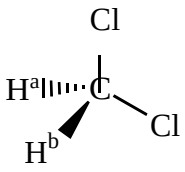
The concept of chemical shift is illustrated in Figure 8. As the hydrogens of methane are increasingly substituted by electron withdrawing chlorine atoms, the chemical shift of the remaining hydrogens shifts further *downfield* as the hydrogens become increasingly *deshielded*. Substitution of the methyl groups of tetramethylsilane (TMS) by chlorine has similar, but far less dramatic, results. In this case, the electron withdrawing chlorine atoms are separated from the hydrogens by carbon and silicon, resulting in less significant deshielding of the ^{1}H nuclei.



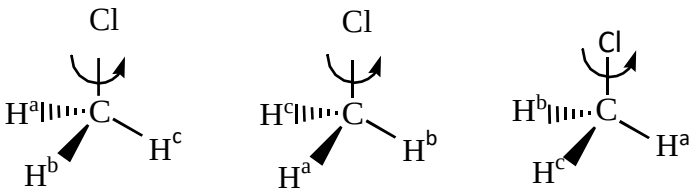
^{1}H NMR Spectra of CH_xCl_y and $Cl_ySi(CH_3)_x$.

One important consequence of chemical shift is that each *chemically different* type of NMR-active nucleus in a molecule will give rise to *its own signal* in an NMR spectrum. Nuclei

are thus referred to as *chemically equivalent* or *chemically inequivalent* in determining how many signals will be observed in an NMR spectrum. For example, both CH_3Cl and CH_2Cl_2 provided one resonance each in the ^1H NMR spectrum in the figure. From this, we can infer that the individual hydrogens in each of these molecules are *chemically equivalent*. From the viewpoint of chemical structure, the reason for this is that hydrogens are related by symmetry elements (reflection through a mirror plane or rotation about an axis) and are thus identical.



mirror in the plane of the page renders $H^a = H^b$



three-fold rotation axis demonstrates $H^a = H^b = H^c$

Sometimes, determining chemical equivalence or inequivalence is straightforward. The methyl hydrogens in ethanol (CH_3CH_2OH) are different from the methylene hydrogens and that both of these are different than the hydroxyl hydrogen; we would thus anticipate three signals in the ^1H NMR spectrum. Upon further reflection though, why should the hydrogens of the methyl group all be equivalent? The answer is simple when it is recognized that methyl groups rotate freely and rapidly, with the result that each hydrogen experiences the same overall chemical shift as it completes one rotation, a situation analogous to CH_3Cl described above. Therefore, all methyl groups generally give rise to one signal in ^1H NMR spectra. This concept can generally be applied to analogous groups such as *tert*-butyl, $C(CH_3)_3$, trimethylsilyl, $Si(CH_3)_3$, and trifluoromethyl, CF_3 (in ^{19}F NMR spectra).

The most general method of determining whether nuclei are chemically equivalent to other nuclei in a molecule is to determine whether they are in the same environment, and whether one nucleus can be related to the other through a symmetry transformation such as rotation or reflection through a mirror plane. Some examples are provided below for illustration.

$CH_3CH_2—O—CH_2CH_3$

The CH_2 groups are equivalent and the CH_3 groups are equivalent. 2 signals in either the ^1H or ^{13}C NMR spectra

$CH_3CH_2—O—CH_3$

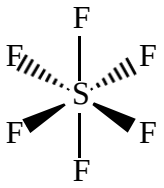
The CH_3 groups are inequivalent. 3 signals in either the ^1H or ^{13}C NMR spectra

$CH_3CH_2CH_2Cl$

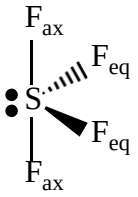
The CH_2 groups are inequivalent. 3 signals in either the ^1H or ^{13}C NMR spectra

$ClCH_2CH_2CH_2CH_2Cl$

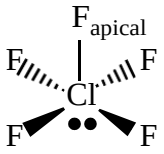
There are two distinct sets of CH_2 groups. 2 signals in either the ^1H or ^{13}C NMR spectra



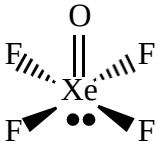
SF_6 is a highly symmetrical octahedral molecule. 1 signal in the ^{19}F NMR spectrum



The axial (ax) and equatorial (eq) fluorines are chemically inequivalent 2 signals in the ^{19}F NMR spectrum



The apical fluorine is chemically distinct from the four fluorines in the square base 2 signals in the ^{19}F NMR spectrum



The four fluorine nuclei in the square base are chemically equivalent 1 signal in the ^{19}F NMR spectrum

Integration

The area under each NMR absorption peak can be electronically *integrated* to determine the *relative number of nuclei* responsible for each peak. The integral of each peak can be provided numerically, and is often accompanied by a line that represents the integration graphically. Intensities of signals can be compared within a particular NMR spectrum only. For example, ^{1}H intensities cannot be compared to those of ^{19}F or ^{31}P nuclei. It is important to note that the integration of a peak is a relative number and does not give the *absolute number* of nuclei that cause the signal. Thus, the ^{1}H NMR spectrum of $H_3C–SiH_3$ will show two peaks in a 1:1 ratio, as will the ^{1}H NMR spectrum of $(H_3C)_3C– Si(CH_3)_3$. This is simply because the ratios 3:3 = 9:9 = 1:1. Nonetheless, the integrated intensities of the signals in an NMR spectrum are a vital piece of the puzzle.

The concept of integration, and also that of chemical shift, is illustrated by Figure 9. Determining integration ratios is an exercise in finding the greatest common divisor for the series of peaks (the largest whole number divisor that will produce a whole number ratio). In the above example, this value is either 1.4 cm or 9.9 integration units. It should be remembered that integration is a measurement that is subject to error; it is common for the error in integrated intensity to approach 5 - 10 %. The ratio of the integrated peak intensities is 1:3 = 3:9, allowing us to assign the resonance at δ 3.21 to the methyl group and that at δ 1.20 to the $(CH_3)_3C$ group. It is important to note that the hydrogens of the $(CH_3)_3C$ group are more *shielded* than the CH_3

group. This occurs because the CH_3 group is directly adjacent to the electron withdrawing oxygen, but the corresponding methyl protons in the $(CH_3)_3C$ group are separated from oxygen by a second intervening carbon center.

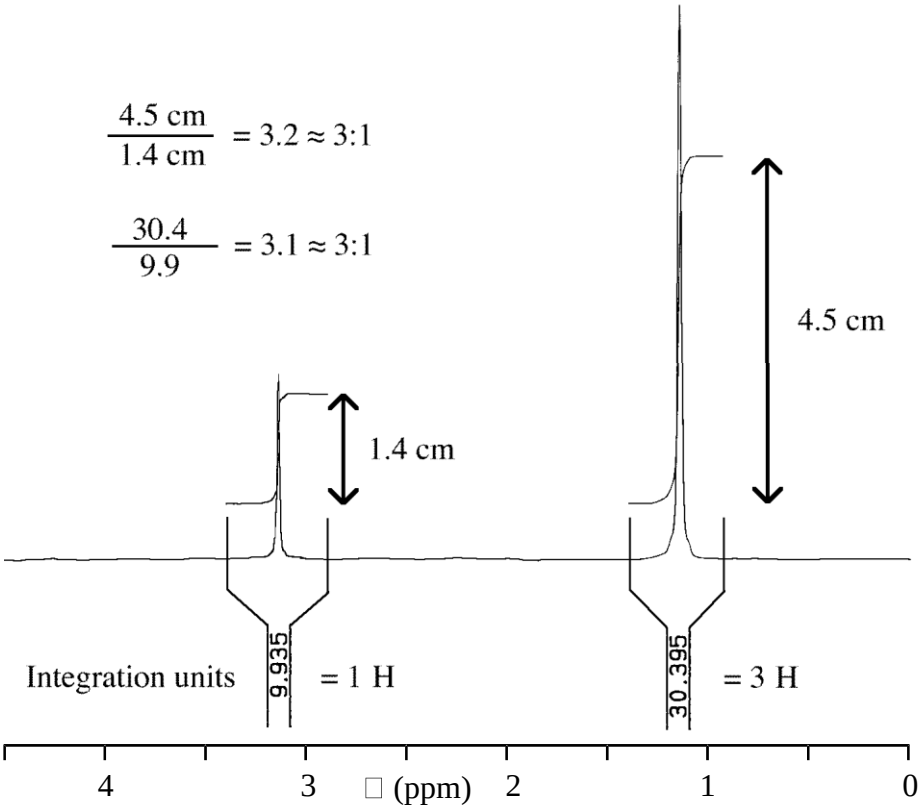


Figure 1. ^1H NMR Spectrum of $CH_3OC(CH_3)_3$.

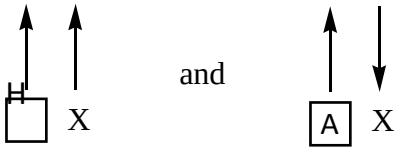
At this stage, we can begin to appreciate how NMR resembles a molecular microscope. For example, at one frequency we could "see" the various protons, while the carbons, fluorines, phosphorus, and even certain metal nuclei could be observed at other frequencies. Within one spectrum, we can make use of the position (*chemical shift*) and *integrated intensity* of the different signals to assign particular molecular fragments responsible for them, and to build up a model of the molecule. There is one more aspect of NMR that is extremely helpful in determining how to connect the parts together.

Spin-Spin Splitting (Coupling)

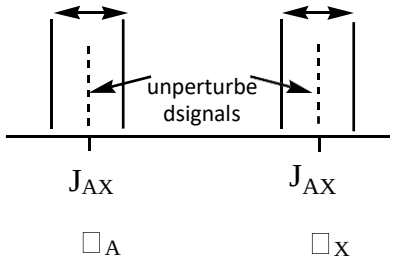
The appearance of a resonance may be very different when there are other *neighbouring* magnetic nuclei. The reason for this is that the nucleus under observation will interact with the magnetic spins of the different neighbouring nuclei.

The simplest case is that of two protons having significantly different chemical shifts (designated A and X). Considering chemical shift and integration only, we could represent the spectrum as:

Both protons have a spin of $^1/_2$, and both can exist in the $+^1/_2$ and $-^1/_2$ spin states. Now, it turns out that the magnetic environment of H_A is slightly different when H_X is in the $+^1/_2$ state than when it is in the $-^1/_2$ state. This can be represented pictorially with arrows (pointing either up or down) representing the two spin states of H_X.

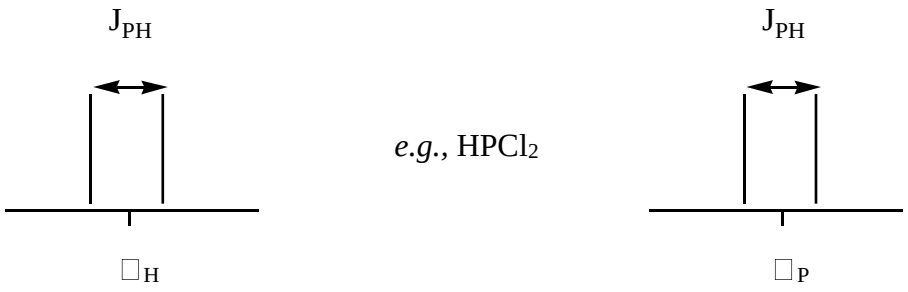


As a result, H_A will split into two lines, each half the intensity of the unperturbed signal. Similarly, H_A will influence H_X which becomes a *doublet* also. The *splitting*, or *coupling*, is symmetrical about the unperturbed resonances H_A and H_X, and is described by the means of a *coupling constant*, J_{AX}, which has units of Hz.



Note that the magnitude of J_{AX} is *identical* at both signals - coupled nuclei must share the *same* coupling constant.

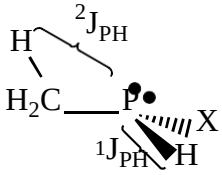
In a similar way, the resonance of a proton attached to phosphorus will be a doublet, since the phosphorus nucleus has I = $^1/_2$ and may be in the $+^1/_2$ or $-^1/_2$ state. However, the key distinction here is that we are dealing with two different nuclei, and thus two different NMR spectra. *Each* NMR spectrum (^{1}H and ^{31}P) will show *one doublet* with a J_{PH} coupling constant that is identical in magnitude. Recall that we cannot "see" a ^{31}P nucleus in a ^{1}H NMR spectrum and vice-versa. Nonetheless, the splitting of the peaks into doublets in each spectrum tells us that the ^{1}H and ^{31}P nuclei are interacting.



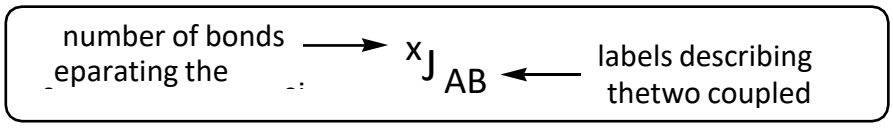
^{1}H NMR Spectrum ^{31}P NMR Spectrum

To review, the influence of the neighbouring spins is called *spin-spin coupling* and NMR peaks are split into *multiplets* as a result. The separation between the two peaks is called the *coupling constant*, J, which is expressed in Hz. Spin-spin coupling has the following characteristics:

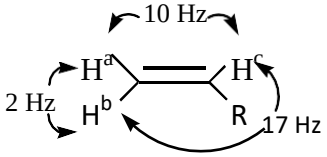
- the *magnitude* of J measures how strongly the nuclear spins interact with each other.
- coupling is normally a through-bond interaction, and is proportional to the product of the gyromagnetic ratios of the coupled nuclei. For example, $^1J_{CH}$ = 124 Hz for ^{1}H-^{13}C coupling in CH_4, and $^1J_{SnH}$ = 1931 Hz for ^{119}Sn-H coupling in SnH_4. This happens because δ (^{119}Sn) is much larger than δ (^{13}C).
- since coupling occurs through chemical bonds, the magnitude of J normally falls off rapidly as the number of intervening bonds increases. *e.g.*, $^1J_{PH}$ ~700; $^2J_{PH}$ ~20 Hz in



Coupling constants are thus labeled to show the *types of nuclei* and the *number of bonds separating the nuclei* that give rise to spin-spin splitting.



- since spin-spin coupling is a through-bond interaction, it is sensitive to the orientation of the bonds between two interacting nuclei. *This is particularly important for two-bond coupling constants.* The influence of the orientation of the two coupled nuclei can occasionally render $^2J < {}^3J$. For example,



$^2J_{H^aH^b} << {}^3J_{H^aH^c} < {}^3J_{H^bH^c}$

^1J is *not* affected by the orientation of the coupled nuclei, so it is generally true that ^1J >> ^2J or ^3J, but it is *not* always true that $^2J > {}^3J$.

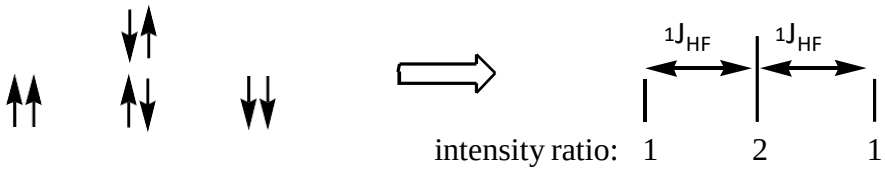
- spin-spin interactions are *independent of the strength of the applied field*. The spacing (in Hz) between lines at two different field strengths *will be the same if it is due to coupling*, but will be proportional to the field strength if it is due to a difference in chemical shift.

Table 2: Typical Coupling Constant Ranges (in Hz)

	Coupled Nuclei (AB in $^xJ_{AB}$)			
x	HH	CH	PH[b]	PC[b]
1	–	115 - 250	630 - 710	120 - 180
2[a]	2 - 30	5 - 60	7 - 13	5 - 40
3	2 - 17	2 - 20	6 - 11	5 - 11
4	–	–	0 - 1	–

[a]Two bond couplings are particularly sensitive to the geometrical arrangement of the nuclei, which in some cases may render $^2J_{AB} < {}^3J_{AB}$. [b]Restricted to acyclic compounds.

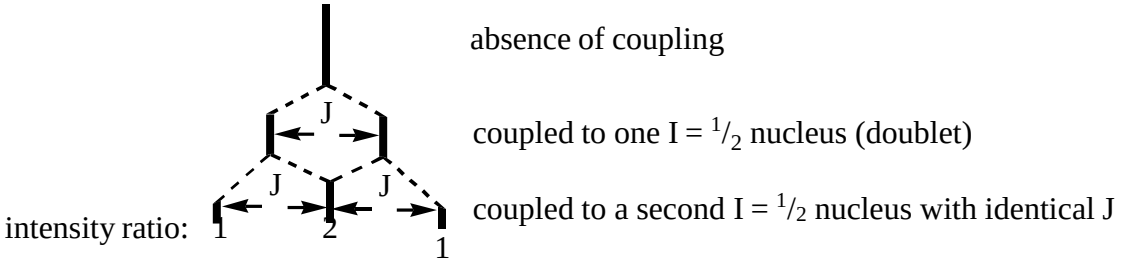
Cases involving more than two nuclei with I = $^1/_2$ are direct extensions of the above. However, because there are more nuclear spins interacting, the *pattern* of lines observed in the NMR spectrum becomes more complicated. For example, let's consider the ^{1}H NMR spectrum of the HF_2^- anion (*i.e.*, [F--H--F]$^-$). We are observing the ^{1}H nucleus, but it is coupled to two chemically equivalent ^{19}F (I = $^1/_2$) nuclei. There are four ways that we can arrange the nuclear spins of the two fluorine nuclei, but only three different energy states are created, as is explained below:



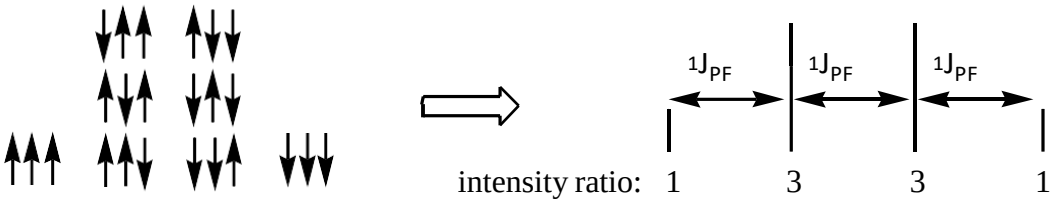
Extending what we learned about the generation of a doublet, we can clearly see that the ^{1}H environment where both ^{19}F spins are "up" is different from that where both ^{19}F spins are "down". However, we can also arrange things so that one ^{19}F spin is "up" and the other is "down". The latter case is *degenerate*; that is, there is more than one way of accomplishing an "up/down" arrangement of nuclei, but each "up/down" arrangement has the same energy. As a result, a pattern of three peaks (or *triplet*) with an intensity pattern of 1:2:1 is generated as shown above. It is important to note that each line in the triplet is separated by the same $^1J_{HF}$ coupling

constant. As we would expect, the ^{19}F NMR spectrum of HF_2^- would show a doublet because the fluorine nuclei are chemically equivalent and couple to one ^1H nucleus.

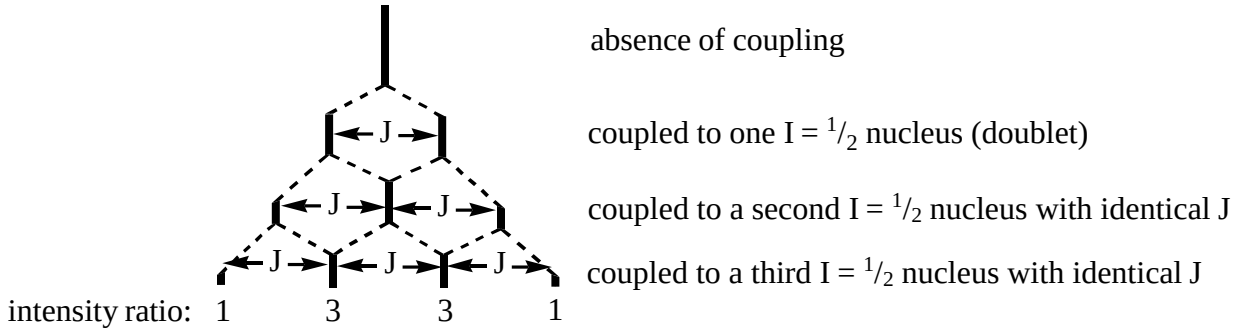
Another way of looking at this is to begin with a singlet for the ^1H nucleus and then couple each ^{19}F nucleus one step at a time. The coupling of the first ^{19}F nucleus generates a doublet. When each line in this doublet is *split again* into a doublet, they overlap identically at the center of the signal, generating a single line of intensity two relative to each outer line of intensity one:



When a similar exercise is undertaken for the ^{31}P NMR spectrum of PF_3, the nuclear spins of the three equivalent ^{19}F nuclei can be arranged in four ways to generate a *quartet*

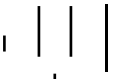
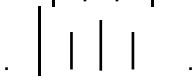


or we can split a singlet into doublets three times to accomplish the same transformation:



In this case, when each line at the triplet stage is split again into doublets, the intensity of the overlapping peaks is not identical; a signal of relative intensity two (from the middle peak) overlaps with a signal of intensity one (from the outer peak) to create a peak of intensity three.

Fortunately, the pattern of peaks generated by the interaction of $I = {}^1/_2$ nuclei can be easily generated by remembering that *one nucleus is split by (n) equivalent nuclei into (n+1) peaks*, each separated by the coupling constant, ${}^xJ_{AB}$. The number of peaks is referred to as the *multiplicity*. The intensity pattern is a direct consequence of the number of combinations of the various nuclear spins that are possible and is described by a series of binomial coefficients. In practice, it is easiest to determine the intensity pattern by use of a mnemonic device such as Pascal's triangle.

n	*n*+1	Intensity	Multiplicity	Pattern	Example
0	1	1	singlet (s)		$C\boldsymbol{H}_4$
1	2	1 : 1	doublet (d)		$(C\boldsymbol{H}_3)_2CHCl$
2	3	1 : 2 : 1	triplet (t)		$C\boldsymbol{H}_3CH_2Cl$
3	4	1 : 3 : 3 : 1	quartet (q)		$CH_3C\boldsymbol{H}_2Cl$
4	5	1 : 4 : 6 : 4 : 1	quintet		$^{29}\boldsymbol{Si}F_4$
5	6	1 : 5 : 10 : 10 : 5 : 1	sextet		$\boldsymbol{P}F_5$
6	7	1 : 6 : 15 : 20 : 15 : 6 : 1	septet		$(CH_3)_2C\boldsymbol{H}Cl$
			etc.		

The phenomenon of spin-spin coupling and its effect on the appearance and interpretation of NMR spectra is best described by example, several of which appear on the following pages.

Analyzing NMR Spectra and Reporting Results

NMR spectra contain a wealth of information and must be analyzed in a methodical way. Much like a jig-saw puzzle, all of the pieces (*i.e.*, chemical shift, integration, multiplicity, and coupling constants) must fit together properly. As with a puzzle, you may find that your initial conclusion is incorrect because several “pieces” are out of place. It is important to approach the problem in a creative way and investigate alternate solutions. The most straightforward method for analyzing NMR spectra is:

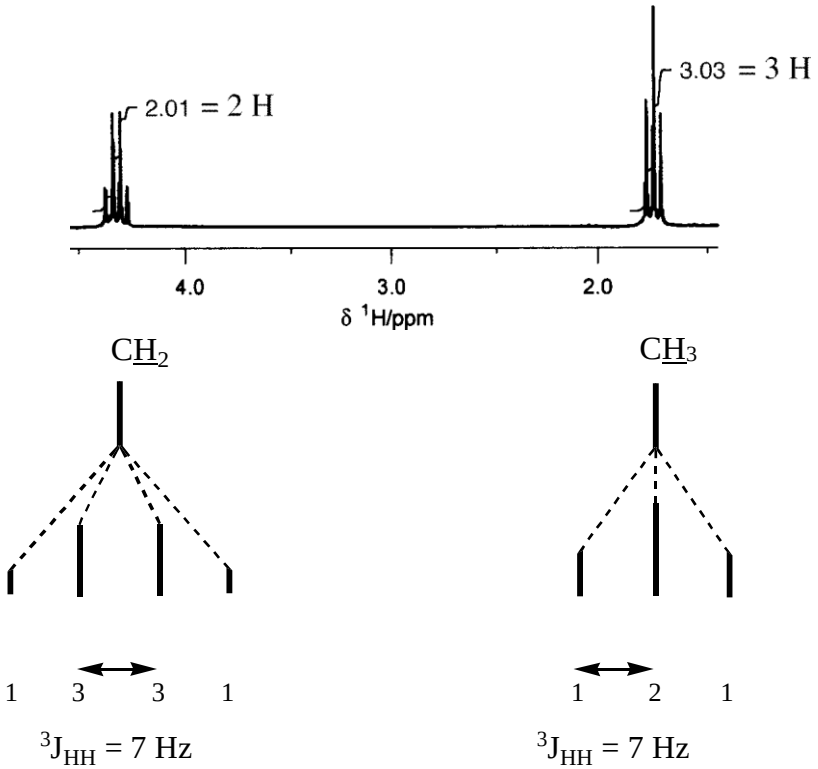
1) identify signals by chemical shift and determine their relative integration
2) identify the multiplicity of the peaks and calculate coupling constants.

Many students are tempted to “leap in” and attempt to analyze coupling patterns first, but the coupling pattern may not correlate if the integration ratio of the coupled multiplets has not already been deduced. Above all else, remember to double-check that the assignments make sense. It is often a good practice to use your results to generate a simple stick-diagram of the

NMR spectrum. If the stick-diagram matches the actual spectrum exactly, then you have correctly analyzed the NMR spectrum.

Chemical shifts should generally be reported to two decimal places. Multiplicities may be written out (*e.g.*, "triplet") or expressed in terms of common abbreviations (*e.g.*, "t"). Coupling constants are commonly reported as whole numbers, but may be expressed to one decimal place if the spectrum is of sufficiently high resolution. The coupling constants should be properly labeled (*i.e.*, $^{x}J_{AB}$) to show the nuclei that are coupled; if there is more than one NMR active isotope for a nucleus (*e.g.*, $^{117}Sn/^{119}Sn$), it should be clearly defined which is involved in the coupling interaction you are describing.

Example : ^{1}H NMR spectrum of $(CH_3CH_2O)_4Si$.



1. On the basis of chemical shift and integration, a CH_2 signal of intensity two appears downfield of a CH_3 signal of intensity three.
2. The CH_3 signal will be split into a triplet by interaction with the two equivalent methylene protons (n = 2 and thus n+1 = 3). The CH_2 signal is split into quartet by the three equivalent CH_3 protons (n = 3 and thus n+1 = 4).
3. The spacing is $^{3}J_{HH}$ = 7 Hz, and is the same in both regions.
4. The relative peak heights in the methyl triplet will be 1 : 2 : 1 and will be 1 : 3 : 3 : 1 for the methylene quartet. Recalling the overall integration, the methyl absorption must be $^{3}/_{2}$ as intense as methylene absorption as the total signal intensity is proportional to the number of nuclei; the integration ratio is 3.03÷2.01 ~ $^{3}/_{2}$.

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Question Bank

Part A

1. What type of EMR is used in NMR. Why?
2. Differentiate shielding and deshielding in NMR.
3. Mention the use of chemical shift in NMR.
4. Define spin-spin coupling in NMR spectroscopy.
5. Give the significance of splitting of signals in NMR.
6. Relate the effect of spin quantum number in NMR spectroscopy.
7. What is spin flip in NMR spectroscopy?
8. What is shielding constant and bring out its role in NMR spectroscopy.
9. What is the principle of NMR spectroscopy?

Part B

1. Discuss shielding and deshielding effects in NMR spectroscopy.
2. Explain chemical shift in NMR.
3. Elaborate on spin spin coupling in NMR with examples.
4. Explain the role of reference compounds in NMR.
5. Explain the significance of sin quantum number values in NMR spectroscopy.

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – V– MASS SPECTROMETRY – SCY1612

Mass spectrometry is an analytical tool useful for measuring the **mass-to-charge ratio** (*m/z*) of one or more molecules present in a sample.

These measurements can be used to calculate the **exact molecular weight** of the sample components.

Mass spectrometers can be used to identify unknown compounds via molecular weight determination, to quantify known compounds, and to determine structure and chemical properties of molecules.

Mass spectrometer consists of at least these three components:

- Ionization Source
- Mass Analyzer
- Ion Detection System

1. The Ionization Source

Molecules are converted to **gas-phase ions** so that they can be moved about and manipulated by external electric and magnetic fields.

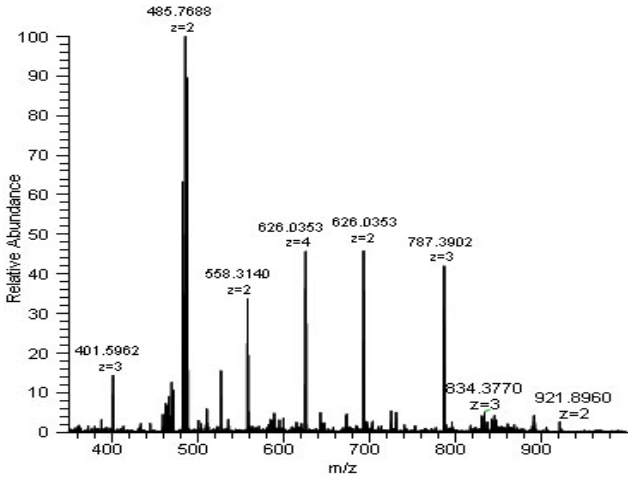
2. The Mass Analyzer

Once ionized, the ions are sorted and separated according to **mass-to-charge** (*m/z*) ratios.

3. Ion Detection System

The separated ions are then measured and sent to a data system where the *m/z* ratios are stored together along with their relative abundance.

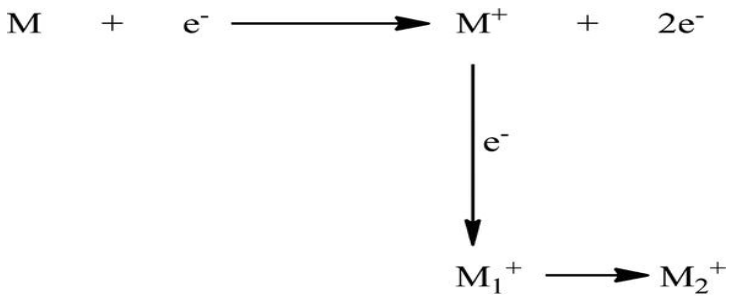
A **mass spectrum** is simply the *m/z* ratios of the ions present in a sample plotted against their intensities. Each peak in a mass spectrum shows a component of unique *m/z* in the sample, and heights of the peaks gives the relative abundance of the various components in the sample. A mass spectrum of a sample is given below:



Principle

The mass spectroscopy is based on the positive ion generation. In electron impact ionization technique, the sample under investigation is converted into vapor phase and bombarded with electrons having energy sufficient to knock out one electron from it (>10 eV) to produce a positively charged ion called molecular ion or parent ion which is denoted by M^+.

Positively charged molecule M^+ is often unstable, and with increase in energy (10–70 eV) according to bond strength, they break into fragments called fragment or daughter ion which is denoted by M^{+1}. Ions formed are separated in analyzer under the influence of electric and magnetic field and are recorded by the detector to give rise a mass spectrum.



Where,

M^+ = molecular ion

M_1^+ and M_2^+= Fragment ions

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

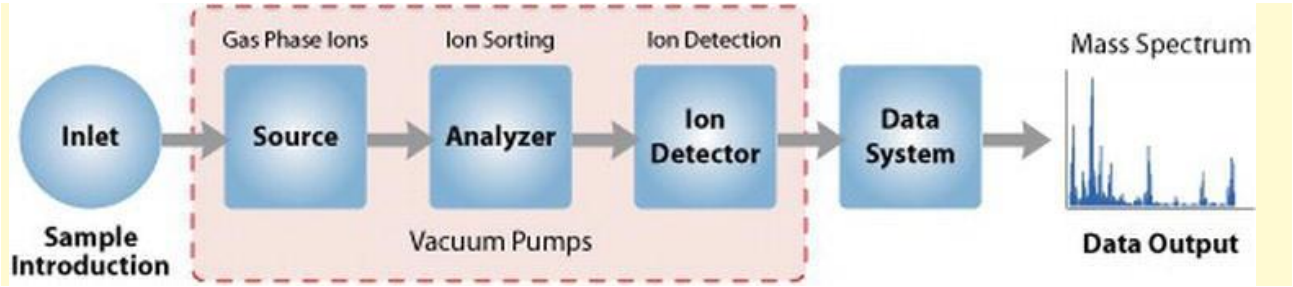
A mass spectrum will usually be presented as a vertical bar graph, in which each bar represents an ion having a specific mass-to-charge ratio (m/z) and the length of the bar indicates the relative abundance of the ion. The most intense ion is assigned an abundance of 100, and it is referred to as the **base peak**. Most of the ions formed in a mass spectrometer have a single charge, so the m/z value is equivalent to mass itself. Modern mass spectrometers easily distinguish (resolve) ions differing by only a single atomic mass unit (amu), and thus provide completely accurate values for the molecular mass of a compound. The highest-mass ion in a spectrum is normally considered to be the molecular ion, and lower-mass ions are fragments from the molecular ion, assuming the sample is a single pure compound.

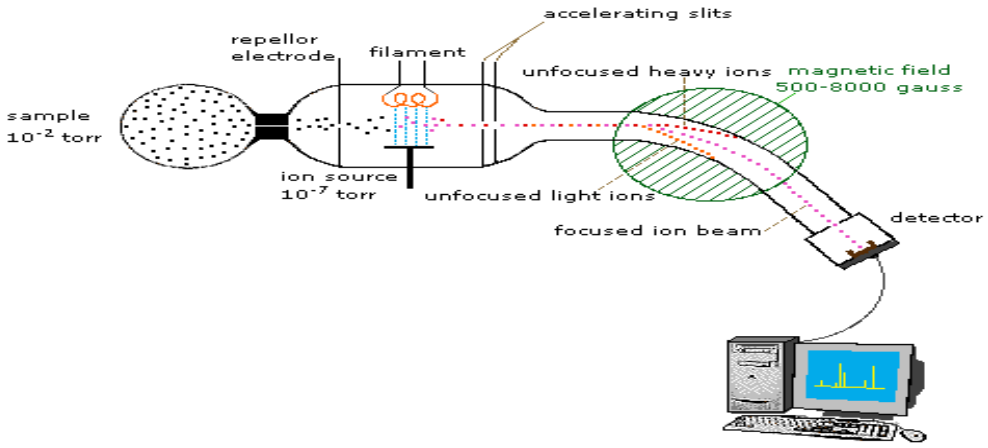
Components of mass spectrometer

Mass spectrometer mainly consists of following components:

1. Inlet system
2. Ion generation chamber
3. Analyzer tube
4. Ion collector
5. Data collection system

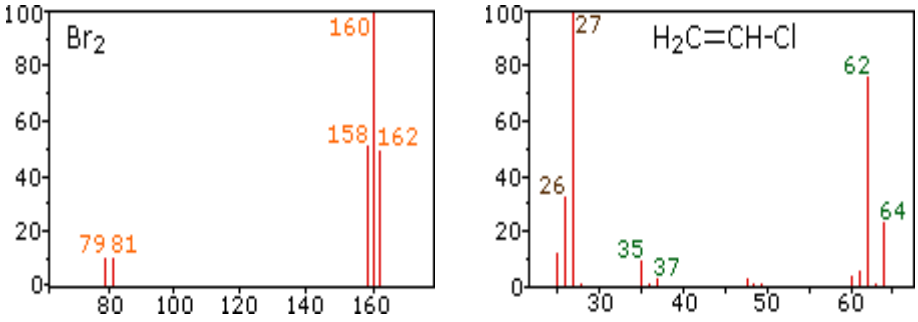
The inlet system transfers the gaseous form of sample into the vacuum of the ion generation chamber of mass spectrometer. In the ion generation chamber, neutral sample molecules are ionized and then accelerated into the mass analyzer tube. The mass analyzer tube is the most important part on which a range of the mass spectrometer depends. This segment separates generated ions, either in space or in time, according to their mass-to-charge ratio (m/z). Once the ions are separated, they are collected and detected in ion collector chamber. Then, the signal is transferred to a data collection system for data investigation. The high vacuum is applied between the ion generation chamber, analyzer tube and ion collector. The vacuum system is maintaining the low pressure which minimizes the chances of ion-molecule reaction, scattering and neutralization of the ions. Components of a mass spectrometer are shown in the figure given below.





Isotopes

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



Metastable ions

Metastable ions are those that dissociate en route from an ion source, through a mass analyser to an ion detection device. The term metastable refers only to ions that are able to fragment in flight by virtue of internal energy that they acquired within the ion source, not after acceleration there from,

nor by collisions with a target gas, nor by radiative excitation as they traverse the apparatus. They are thus unimolecular dissociations.

The ions resulting from decomposition between the source region and magnetic analyzer are called as metastable ions. These appear as broad peaks called metastable ion peaks.

Characteristics of metastable peaks are:

1. These peaks are much broader, that is, they spread over several mass units.

2. These peaks appear in the mass spectrum usually at non-integral m/e values.

3. These peaks are of relatively low abundance or low intensity

4. The metastable ions can be detected by a double focussing mass spectrometer.

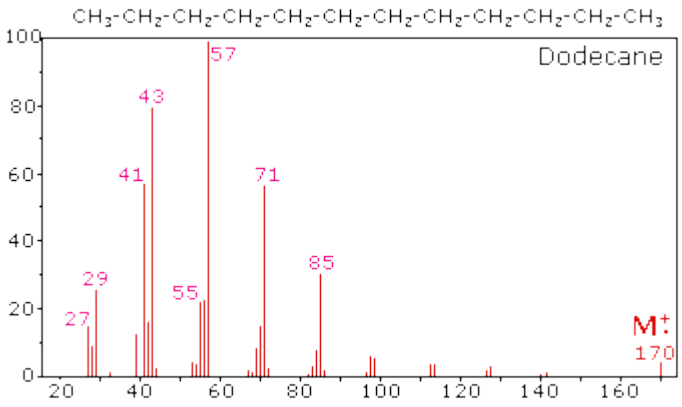
Metastable peaks in the mass spectrum greatly contribute in structure ellucidation

Fragmentation patterns

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

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

The presence of a functional group, particularly one having a heteroatom Y with non-bonding valence electrons (Y = N, O, S, X etc.), can dramatically alter the fragmentation pattern of a compound.



The Nitrogen Rule

If the molecular mass of an unknown compound to the nearest integer value is an odd number, the compound contains an odd number of nitrogens in its molecular formula. Correspondingly, if the molecular mass is an even number, the compound contains zero or an even number of nitrogens in its molecular formula. This rule, illustrated below, results from nitrogen having a valence of three and an even atomic mass. Consistent with the nitrogen rule, a correct molecular formula for a molecule with an odd molecular mass in the nearest integer value will have the sum of the number of hydrogens plus halides as an odd number. Correspondingly, a correct molecular formula for a molecule with an even molecular mass will have the sum of the number of hydrogens plus halides as an even number.

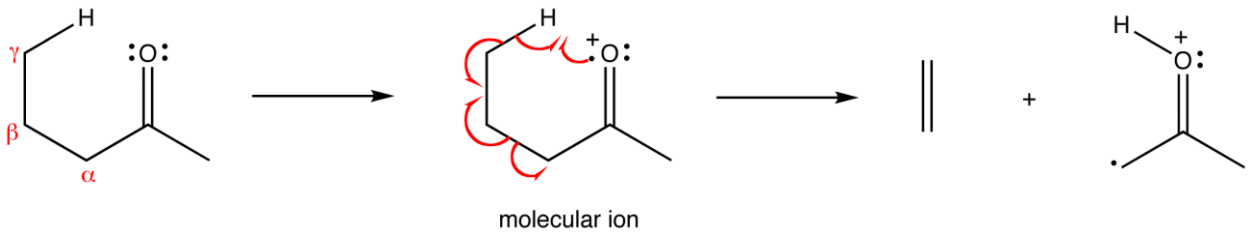
Examples

The molecular ion for aminoethane (ethylamine), $[CH_3CH_2NH_2]^+$, is m/z=45 amu, an odd number; the number of hydrogens is five, also an odd number.

The molecular ion for 1,2-diaminoethane, $[NH_2CH_2CH_2NH_2]^+$, is m/z= 60 amu, an even number; the number of hydrogens is eight, also an even number.

McLafferty rearrangement

McLafferty rearrangement is a characteristic fragmentation of the molecular ion of a carbonyl compound containing at least one gamma hydrogen, eg:



Applications

1. Phytochemical analysis

Mass spectroscopy is widely employed in phytochemical analysis due to its capability to identify and measure metabolites having very low molecular weight at very low concentration ranges below nanogram per milliliter (ng/mL). Therefore, it is considered as trace analysis methodology.

2. Structure elucidation

Mass spectroscopy has major use in structure elucidation of compounds. Mass spectrum is produced in the form of bar graph which is interpreted by using the following peaks: Base peak, Molecular ion peak, fragment ion peak, metastable ion peak.

3. Peptide and protein sequence/structure analysis

Mass spectroscopy has an important application in analysis of sequence of amino acids in proteins and peptides, that is, analysis of structure of proteins and peptides, and this is employed increasingly. This can be performed by stepwise hydrolysis accompanied with chromatography.

4. Clinical studies

Greater degree of sensitivity is required when analyte quantity is too low and mass spectroscopy due to its higher sensitivity marks a valuable place in clinical analysis.

5. Pharmaceutical analysis

Mass spectroscopy now becomes an irreplaceable tool in all types of drug discoveries due to its high sensitivity, speed, versatility and selectivity.

6. Forensic applications

In forensic study, sample is in minute quantity; therefore, high sensitivity is required for analysis. Mass spectroscopy coupled with gas chromatography emerged as an indispensable tool in forensic field as well as LC–MS has also wide utility in forensic study. In forensic studies, the use of mass spectroscopy is becoming significant because of increase in the demand to investigate use of illegal drugs through analyzing body fluids and tissues.

References

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3. Skoog D. A., West D. M., Holler f. J., and Crouch S. R., Fundamentals of Analytical Chemistry, 9th Edition, Wadsworth Publishing Co. Inc., 2012

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Question Bank

Part A

1. What is a molecular ion peak?
2. What are metastable ions?
3. What is m/z value in mass spectrometry?
4. Give the principle of mass spectrometry.
5. Compare molecular ion and base peak in mass spectrometry.
6. Write short note on nitrogen rule.
7. What is Mclafferty rearrangement?
8. List out the applications of mass spectrometry.

Part B

1. Explain the instrumentation of mass spectrometry with a neat block diagram.
2. Discuss nitrogen rule in mass spectrometry.
3. Elaborate on fragmentation pattern in mass spectrometry quoting an example.
4. Discuss the formation of molecular ion and base peaks in mass spectrometry.
5. Explain Mclafferty reaarangement with examples in mass spectrometry.