

Q. what are the applications of Selection Rule?

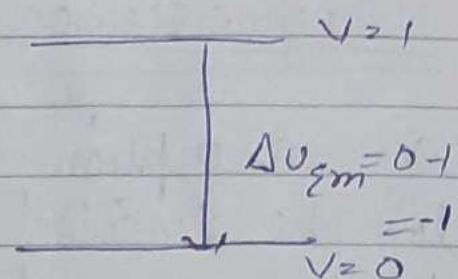
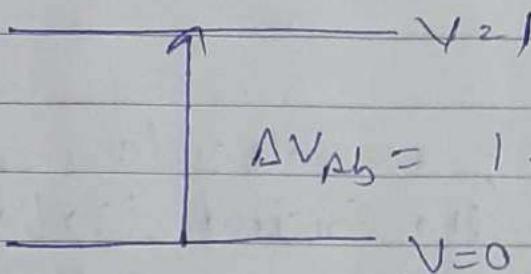
~~Spectroscopy~~ Selection Rule?

All Selection Rules are the set of restrictions imposed on Quantum numbers according to which some transitions are allowed and some are forbidden. Selection Rules for moving transitions are

1) For Vibrational Transition :- For this change in vibrational energy must be equal to ± 1 or $\Delta v = \pm 1$

$$\Delta v = +1 \text{ for Absorption}$$

$$\Delta v = -1 \text{ for Emission}$$



2) For Rotational Transition:- Selection Rule is $\Delta J = \pm 1$

$\Delta J = +1$ for Absorption

$\Delta J = -1$ for Emission

3) For Electronic Transitions - Selection

Rule is $\Delta l = \pm 1$

Values of l for S P d f

For Absorption

0	1	2	3
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$S \rightarrow P$ $\Delta l = 1 - 0 = 1$ = allowed

$P \rightarrow d$ $\Delta l = 2 - 1 = 1$ = allowed

$d \rightarrow f$ $\Delta l = 3 - 2 = 1$ = allowed

But for $S \rightarrow d$ (not allowed)

$\Delta l = 2 - 0 = 2$ $\Delta l \neq 2$

For Emission

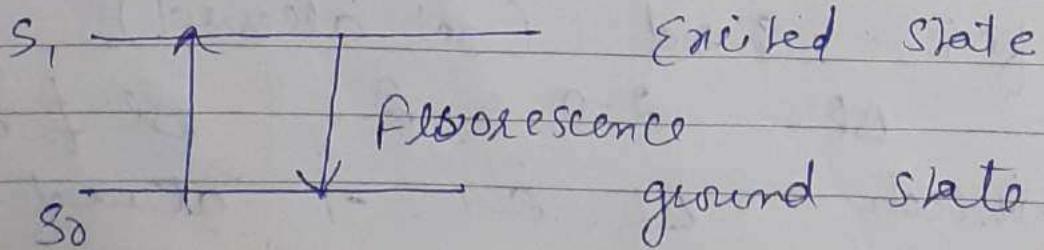
$\Delta l = 0 - 1 = -1$ allowed

Q. What is Fluorescence?

Fluorescence →

→ On absorption of radiation, a molecule goes to the excited state. In the excited state if the molecule loses its energy by collisions with other molecules, then the energy is emitted in the form of radiation it is known as fluorescence. The life time of the molecule in the excited state is 10^{-8} seconds.

→ The substances which shows fluorescence are known as fluorescent materials. The process of fluorescence starts immediately after the absorption and stops as soon as the light source has been removed. From singlet excited state to ground state the emission of radiations are in the form of fluorescence. Singlet state is unstable.



Expt The substances like chlorophyll, Fluorospar (CaF_2), Uranyl Sulphate, Anthracene, Naphthalene, mercury vapour
Fluorospar - Shows Blue light
Chlorophyll - Shows Red light

Q. What are the Applications of Fluorescence?

Ans. Applications of fluorescence is

- 1) The structure of proteins can be studied by measuring the closeness of fluorescent groups in the protein.
- 2) Fluorescent material is used in fluorescent microscopes and X-ray diagnosis.
- 3) Fluorescence in the life sciences is used generally as a non destructive way of tracking or analysis of biological molecules by means of fluorescent emission.
- 4) The quantity of a dye is found out with spectrophotometer.
- 5) Fluorescence microscopy of tissues cells or subcellular structures can be

accomplished by labeling an antibody with fluoresphore and allowing to find out its target antigen with in sample

6. Fluorescence lifetime imaging microscopy
Can be used to detect biomolecular interactions
7. ~~Biosensors~~ Biosensors are ~~used~~ being studied
Using fluorescence.

8. It is used in cell sorting techniques
in a body.

9. DNA detection is done using fluorescent material like Ethidium Bromide.

Vibrational/Rotational (IR) Spectroscopy

Q. What is Vibrational and Rotational Spectroscopy

Ans. It refers to the spectrum obtained due to vibrational transitions caused by absorption of IR Radiation by molecules.
It is also called vibrational spectroscopy as it involves the transition between the vibrational energy levels of molecules.

It is abbreviated as IR Spectroscopy.

- The IR radiations can induce both vibrational energy levels as well as between rotational energy levels. So it is also called Rotational - Vibrational Spectroscopy.
- It gives important information about Structure of Compound.

Q. What are the three Regions of IR

- Ans ~~Ans~~ Near IR Region - $12500 - 4000 \text{ cm}^{-1}$
Middle IR Region - $4000 - 667 \text{ cm}^{-1}$
Far IR Region - $667 - 50 \text{ cm}^{-1}$
most important Region lies in between $4000 - 667 \text{ cm}^{-1}$.

Q. What are the fundamental modes of vibrations in a molecule.

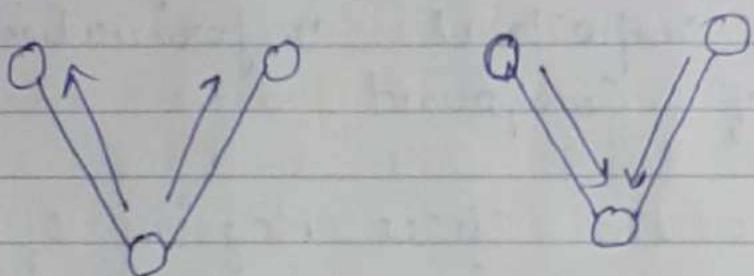
Ans Molecular vibration are of two types

- 1) Stretching vibrations
- 2) Bending vibrations

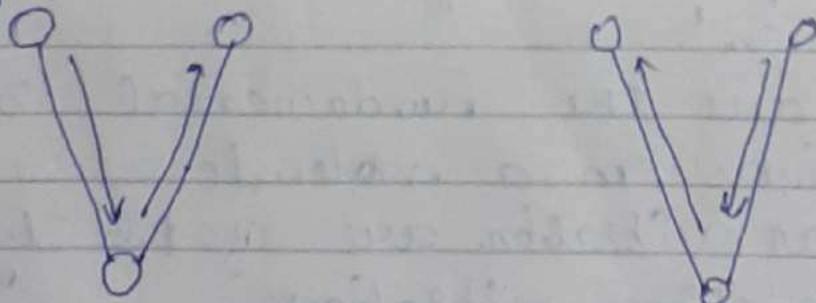
1) Stretching vibrations - In this position of atoms change results in change in

Bond length stretching vibrations are of types (two)

- 1) Symmetric stretching → In this movement of atoms with respect to particular atom in a molecule is in the same direction.



- 2.) Asymmetric Stretching → In this one is moving towards and one is moving away from the central atom.

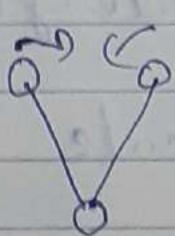


2) Bending Vibrations

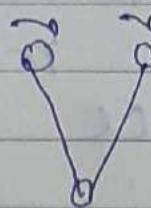
In this change in position of atoms results in change in bond angle.

Types

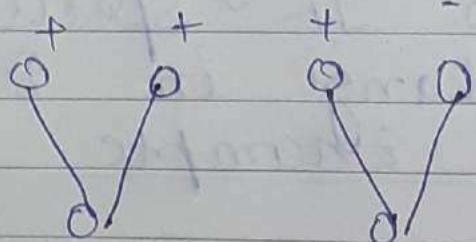
- 1) scissoring → when two atoms approach each other
- 2) Rocking Rocking - when two atoms move in the same direction.
- 3) Wagging → Direction of two atom is either up or down
- 4) Twisting → Direction of one atom is up and second is down



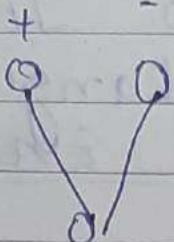
scissoring



Rocking



wagging



twisting

Mole energy is Rep. to Stretching a Bond than to Bend it. So Stretching occurs at higher frequency than bending

Q. what is the theory of IR spectra and what are IR active and IR inactive molecules

Ans:- To Record Vibrational Rotational Spectra, IR radiations must incident on molecule. Molecule will absorb the IR radiations if vibration results in change in dipole moment hence Only those molecules will show IR spectra which undergoes a change in Dipole moment.

for example HCl molecule

$$\text{Dipole moment } (\mu) = S \times d$$

$\text{H}^{\text{s}+} - \text{Cl}^{\text{s}-}$

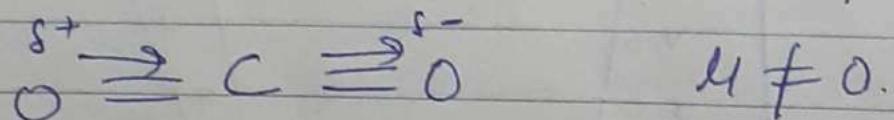
S refers to charge d is length
Dipole moment of HCl will undergo a change on the absorption of IR radiations.

IR Active :- which shows IR spectra
IR Inactive :- which ~~does~~ do not show IR Inactive.

Heterodiatomic molecules will show IR spectra like HCl, HBr, NO, and HI.

Q. CO_2 molecule will show IR spectra although it is having zero dipole moment. Why?

Ans In CO_2 molecule due to asymmetric stretching it is having a certain dipole moment which helps CO_2 molecule to show IR spectra.



Vibrational Frequency

A diatomic ~~molecule~~ molecule consisting of two atoms joined by a bond vibrates as a one dimensional simple harmonic oscillator.

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{Acc to Hook's law.}$$

v = Vib. frequency k = Force constant

μ = Reduced mass

$$v = \frac{c}{\lambda} = c\bar{v}$$

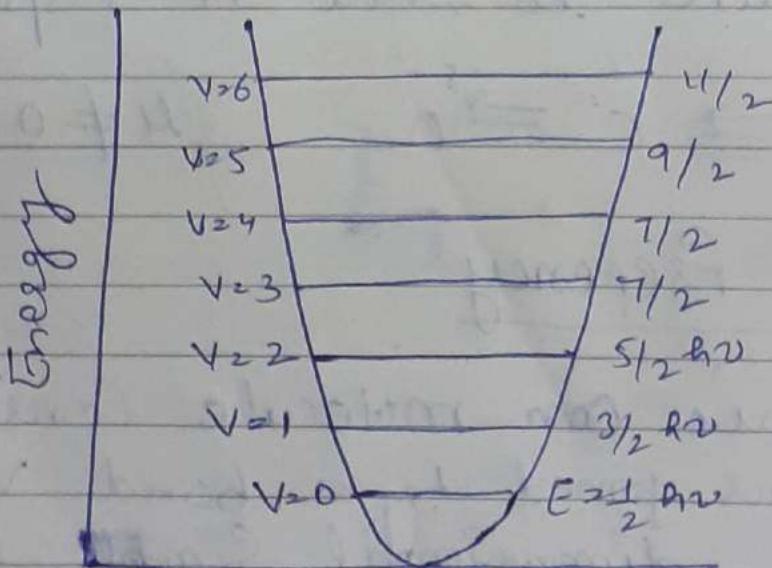
So from equation ①

$$c\bar{v} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{m}}$$

Vibrational Energy

$$E_{vib} = \left(v + \frac{1}{2}\right) \hbar v$$



Vib. energy levels

Model of Vibrations of Polyatomic Molecule (IR spectra of Polyatomic Molecules)

Vibrational signals of a polyatomic molecule depends on the degrees of freedom.

"The Degrees of Freedom" in a molecule is defined as the number of independent co-ordinates required to describe the position of the molecule completely.

For a single atom we have three co-ordinates $(x, y, z) = 3$

for N no. of atoms we have $3N$ degrees of freedom.

$$3N = \text{Vibrational} + \text{Rotational} + \text{Translational}$$

degrees of freedom degrees of freedom Translational degrees of freedom

For Linear Molecule — (2)

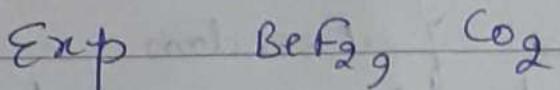
Translational Degrees of Freedom = 3

Rotational Degrees of freedom = 2

equation (2) Becomes

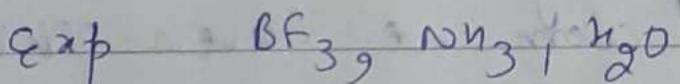
$$3N = 3 + 2 + \text{vibrational modes}$$

$$\text{vib modes} = 3N - 5$$



for Non Linear Molecule

$$\begin{aligned}\text{vib. modes} &= 3N - 3 - 3 && \text{Rotational degrees} \\ &= 3N - 6 && \text{of freedom} = 3\end{aligned}$$



Calculate vibrational modes in H_2O and BeF_2

for H_2O $N = 3$ (Non linear)

$$3N - 6 \quad 3(3) - 6 = 3$$

for BeF_2 $N = 3$ (Linear)

$$3N - 5 \quad 3(3) - 5 = 4$$

Regions of IR Signals

- (1) Hydrogen Stretching Vibrational Region :-
It lies in $2500 - 3700 \text{ cm}^{-1}$. It is showed by the stretching vibrations of bonds like O-H , C-H , N-H
- (2) Triple Bond Region :- Range is $2000 - 2500 \text{ cm}^{-1}$ Exp $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{N}$
- (3) Double Bond Region :- Range is $1600 - 2000 \text{ cm}^{-1}$
The IR signals are shown by stretching vibrations of C=C , C=O , C=N
- (4) Single Bond Region :- The Range is $500 - 1600 \text{ cm}^{-1}$
The IR Signals in this region are shown by stretching and bending vib. of single bonds. This Region is called Finger Print Region

Finger Print Region :-

Most useful Region of Infrared Spectra lies between $4000 - 600 \text{ cm}^{-1}$. The Region $4000 - 1500 \text{ cm}^{-1}$ is called functional group region. as functional group shows their spectra in this region.

The region below 1500 cm^{-1} is called finger print Region as in which the absorption bands occurs due to bending vibration and in this Region no two Compounds can have the same spectra.

functional group Region.

finger print
Region

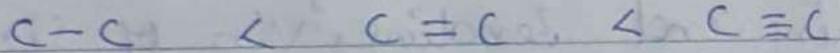
4000

frequency (cm^{-1}) 1500 cm^{-1}

600 cm^{-1}

factors affecting Vibrational frequency :

- 1) Force constant : vibrational frequency (~~is proportional~~ (\propto) directly depends on force constant according to 'Hooke's Law', for example:-

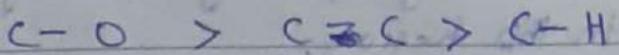


1200

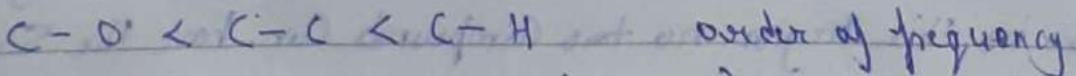
1650

2150 (frequency)

- 2) Reduced mass : Acc to hooks law reduced mass is inversely related to vibrational frequency. So higher the reduced mass lower the frequency.



order of reduced mass.



order of frequency
1100 1200 2960 ($\text{in } \text{cm}^{-1}$)