

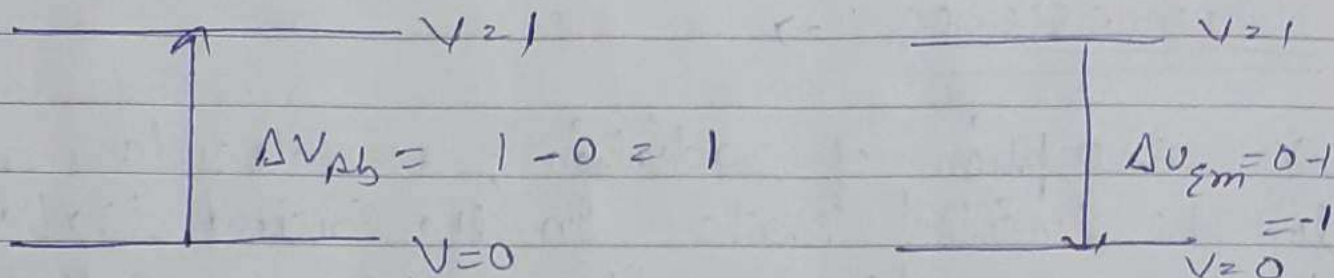
Q. what are the applications of ~~electronic~~ Spectroscopy & Selection Rules?

Ans. 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 following transitions are

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

$\Delta v = +1$ for Absorption

$\Delta v = -1$ 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

s \rightarrow p $\Delta l = 1 - 0 = 1 = \text{allowed}$

p \rightarrow d $\Delta l = 2 - 1 = 1 = \text{allowed}$

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

But for s \rightarrow d (not allowed)

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

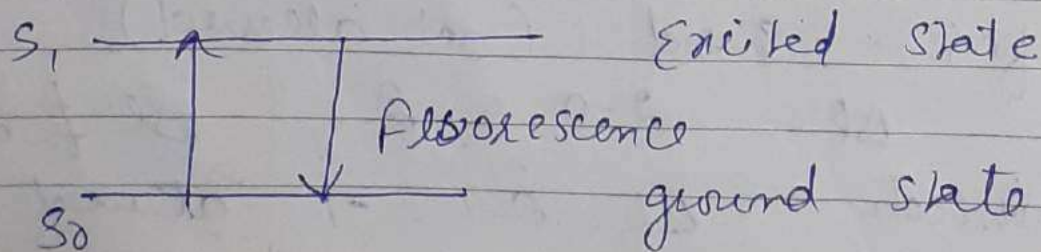
For Emission $\Delta l = 0 - 1 = -1$ allowed

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 show 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.



Exp The Substances like chlorophyll, Fluorospare (CaF_2), Uranyl sulphate, Anthracene, Naphthalene, mercury vapours
Fluorospare - 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 fluorescence emission.
- 4) The Quantity of a dye is found out with spectrofluorometer.
- 5) Fluorescence microscopy of tissues cells or subcellular structures can be

- accomplished by labeling an antibody with fluorophore and allowing to find out its target antigen within sample
6. Fluorescence lifetime imaging microscopy can be used to detect biomolecular interactions
 7. ~~and~~ 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. ~~Q~~ Near IR Region - 12500 - 4000 cm^{-1}
Middle IR Region - 4000 - 667 cm^{-1}
Far IR Region - 667 - 50 cm^{-1}
most important region lies in between 4000 - 667 cm^{-1} .

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

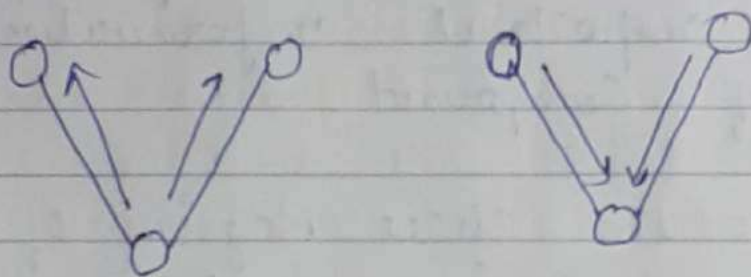
Ans. Molecular vibrations are of two types

- 1) stretching vibrations
- 2) bending vibrations

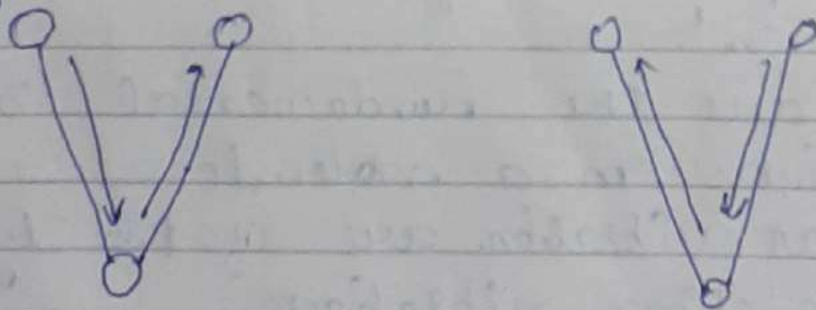
1) stretching vibrations - In this position of atoms change results in change in

Bond length. Stretching vibrations are of types (two)

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



2.) Asymmetric stretching \rightarrow In this one is moving towards and one is moving away from the central atom.

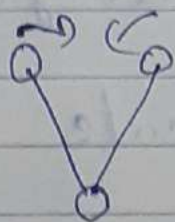


2.) Bending Vibrations

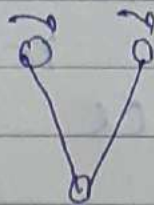
In this change in position of atoms results in change in bond angle.

Types

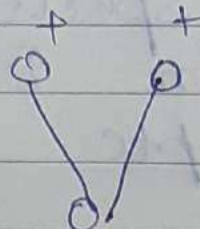
- 1) Scissoring \rightarrow when two atoms approach each other
- 2) ~~Rocking~~ Rocking - when two atoms move in the same direction.
- 3) Wagging \rightarrow Direction of two atom is either up or down
- 4) Twisting \rightarrow Direction of one atom is up and second is down



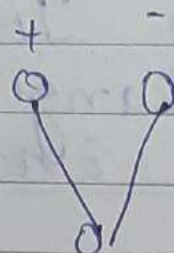
Scissoring



Rocking



wagging



twisting

More energy is Req. 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

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

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

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

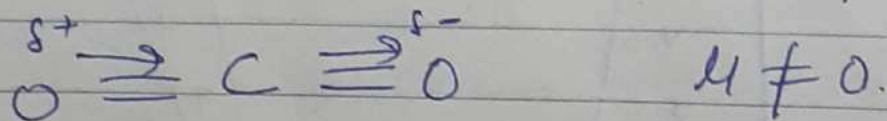
IR Active :- which shows IR spectra

IR Inactive :- which ~~shows~~ 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 ~~can~~ molecule consisting of two atoms joined by a bond vibrates as a one dimensional simple harmonic oscillator.

Acc to Hooke's law.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{--- (1)}$$

μ = Reduced mass

ν = Vib. frequency k = Force constant

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

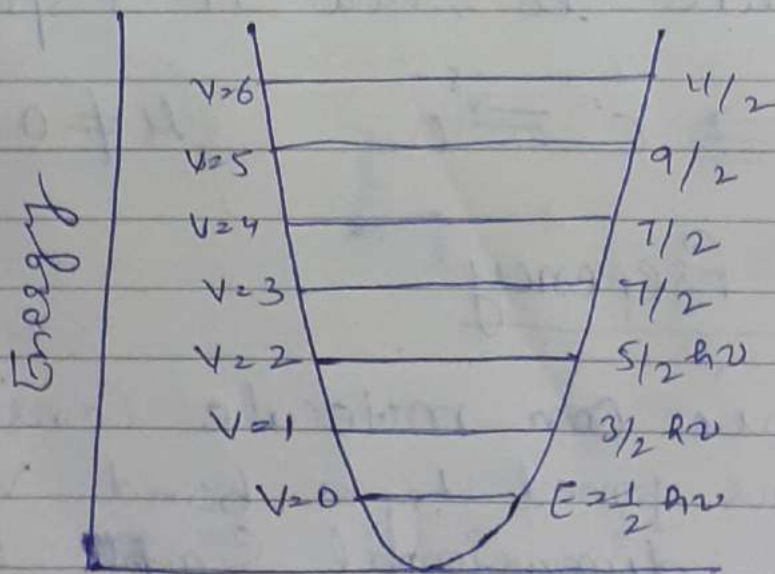
So from equation (1)

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

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

Vibrational Energy

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



Internuclear distance

Vib. energy levels

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

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

"The Degree 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.

$$3N = \text{Vibrational degrees of freedom} + \text{Rotational degrees of freedom} + \text{Translational degree of freedom}$$

For Linear Molecule

(2)

Translational Degrees of Freedom = 3

Rotational Degree of freedom = 2

Equation (2) becomes

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

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

Exp BeF_2 , CO_2

For Non Linear Molecule

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

Exp BF_3 , NH_3 , H_2O

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 $\text{C}=\text{C}$, $\text{C}=\text{O}$, $\text{C}=\text{N}$
- (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 Infra-red Spectra lies between $4000 - 600 \text{ cm}^{-1}$. The Region $4000 - 1500 \text{ cm}^{-1}$ is called functional group region, as functional groups 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.

