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Basic Requirements of IR spectroscopy :-

(1) Correct wavelength of frequency – Molecule absorbs radiation only when the natural frequency of vibration of some part of molecule i.e atoms or groups is the same frequency as the freq. of the incident radiation. for eg., HCl molecule & have freq. 8.7×10^{13} sec^{-1} & wave no. 2890 cm^{-1} when IR radiation is passed thru a sample of HCl molecule & the transmitted radiation is analysed by IR spectrometer have been obs. that the freq. (8.7×10^{13}) is absorbed and remaining frequency are transmitted so 8.7×10^{13} sec^{-1} is the characteristic freq of HCl molecule.

(2) Change in Dipole Moment → Another condition for molecule to absorb IR radiation. A molecule can absorb IR radiation when absorption posses a change in dipole moment. ~~tttt~~ A molecule is said to be electric dipole when a +ve & -ve charge exist on its component atom. When a mol. having electric dipole is kept in electric field. Then exerts forces on the electric charges of the molecule. This leads to the or tree in the separation & when this charge atom vibrates the absorbs IR radiation from radiation source. The symmetrical molecule O_2 & N_2 don't possess electric dipole ∴ can't excited from IR radiation so didnot give IR absorption spectra.

$E = E_{vib} + E_{rot} + E_{elec} + E_{spin} + E_{nuclear}$

The assumption of Born Oppenheimer Approximation considers separability nuclear & electronic motion. The exchange of energy b/w a molecule & electromagnetic field occurs ie $h\nu = E$, E - diff. b/w initial & final quantised state.

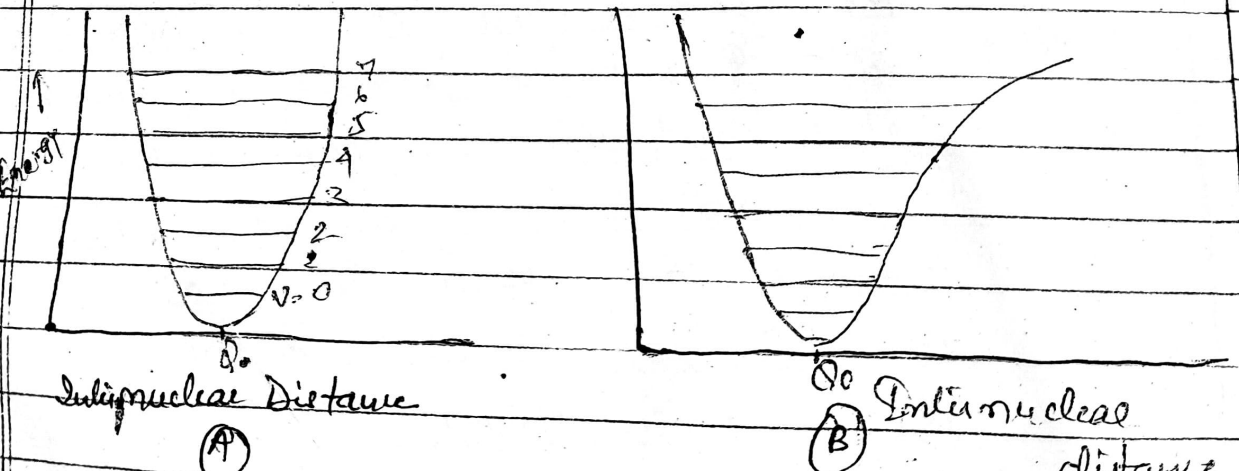
In terms of energy:-

$$\nu = \frac{c}{\lambda} \quad \frac{cm/sec}{cm} = Hz \qquad \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = cm^{-1}.$$

IR absorption covers the range $200 - 400\ cm^{-1}$.

Absorption spectra shud be used when peak ratio or conc^n information is desired. (eg. in kinetics, where the or the in conc^n is desired). The other imp. aspects of the IR and Raman Spectroscopy is that time scale of measurement amounts to the time it takes for a vibration. ($0.1\ sec^{-1}$)

Rapidly isomerising sps show distinct vibration spectra in contrast to slower techniques such as NMR spectroscopy



This plot depicts the total energy of molecule varies as the internuclear dist varies many from Internuclear values Re, Re. In simplest approximation the bond assume to behave as a spring. In

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polyatomic molecule nuclear motion is complex & assume that the vib^n motion along the co-ordinate of describes as a spring like force. Then restoring force F is given by Hookes Law.

$$F = k(Q_0 - Q)$$

By Integration the energy E is given by

$$E = \frac{1}{2} k (Q_0 - Q)^2$$

The nuclei are emitted to move on this parabolic potential surface & the soln of shroedinger wave eq^n yields the quantised vibrational energy levels. with energy

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

v = vibrational quantum no. 0, 1, 2...

freq. of vibration ν is given by

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

k = bond force constt.

μ = reduced mass of 2 mol of mass m_1 & m_2.

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

So, the harmonic oscillators description provides useful information for real molecules.

	$\bar{\nu}$	k (Newton/Å)	D (kcal/mol)
F_2	892	4.45	37
Cl_2	546	3.19	58
Br_2	319	2.46	46
I_2	215	1.76	36

Modes of vibrations in the molecule :- (Polyatomic molecules).

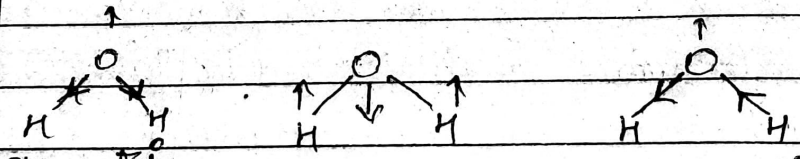
Linear molecules and non-linear molecules -

3N degrees of freedom in 3D space.

Consider a molecule containing N atoms, most of the masses resides in the nuclei, the translational + rotational + vibrational motion of the molecule. If there are N nuclei, then each molecule possess 3N degrees of freedom in 3D space. Three coordinates describes translational motion of the centre of the mass & three more degrees of freedom describes rotation around the centre of mass. The remaining 3N-6 degrees of freedom & 3N-5 for linear describes vibrations.

→ H_2O — Non linear 3N-6 3×3-6 = 3

symmetric, Asymmetric, bending



symmetric stretch ν_1 (3651 cm^{-1})

symmetric bending ν_2 (1595 cm^{-1})

asymmetric stretch ν_3 (3755 cm^{-1})

Symmetric stretching freq. is labelled as ν_1

bending " " " ν_2

Asymmetric stretching " " " ν_3

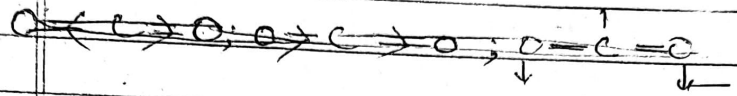
The values for the three freq for water are

$\nu_1 = 3651.7\ cm^{-1}$ $\nu_2 = 1595\ cm^{-1}$ $\nu_3 = 3755\ cm^{-1}$

Hence, the bending freq is lower than the stretching freq & it is easier to stretch a

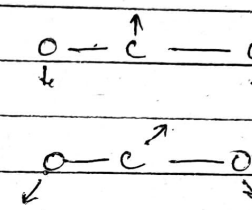
molecule symmetrically than to stretch it asymmetrically. So, the symmetric stretching freq. is lower than the asymm. stretching frequency.

$O=C=O$ $(3\times3-5) = 4$ vibrations



ν_1 $O \rightarrow C \leftarrow O$ $1340\,cm^{-1}$

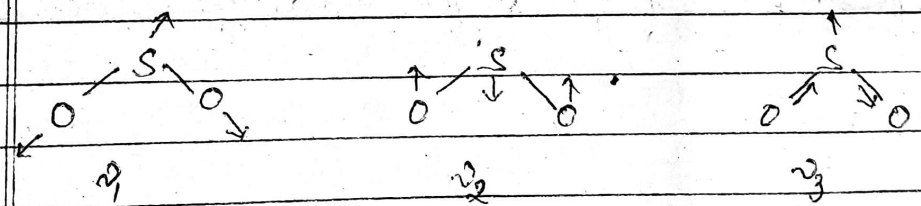
ν_3 $O \leftarrow C \rightarrow O$ $2349\,cm^{-1}$



ν_2, ν_4 degenerate $667\,cm^{-1}$.

The linear CO_2 molecule has 4 fundamental vibrational frequencies. Of the four fundamental vibrational of CO_2 2 has same freq & said to be degenerate. Symm stretching freq, is not observed in CO_2 since no change in dipole moment.

SO_2 — $3N-6 = 9-6 = 3$



ν_1 ν_2 ν_3

$\nu(cm^{-1})$	Assignment.	
519	ν_2.	
606	$\nu_1 - \nu_2 \longrightarrow$	combination bands.
1151	ν_1	
1361	ν_3	
1871	$\nu_2 + \nu_3 \longrightarrow$	
2305	$2\nu_1$	
2499	$\nu_1 + \nu_3 \longrightarrow$	

SO_2 have 3 normal modes of vibration from (3N-6) But the spectral data shows that possesses more than three bands. The three bands ν_1, ν_2 & ν_3 are the fundamental vibrations & are at 1151, 519 & 1361 cm^{-1} respectively. The highest freq. the totally symm. vibration is ν_1. The 2nd-highest totally " " is ν_2 The symm vib^n all been assigned. The highest frequency asymm. vib^n is counted next & the other remaining asymm vib^n in order of ↓ing frequencies. The ν_1 is s_2 is described as symmetric stretch ν_3 - asymm. stretch & ν_2 - bending mode. The other absorp^n freq. is obs. in IR spectra. The overtone of ν_1 occurs at $2\nu_1$. The bands at 1871, 2499 cm^{-1} are combination bands the 606 cm^{-1} is the diff. band & involves the transition from state in & the ν_2 mode is excited to that in & ν_1 mode is excited.

Detection of Hydrogen Bonding:- Stretching & bending freq of OH & NH is very sensitive to H Bonding when it is present in the compd. The stretching freq of free OH and NH grp occurs at - —OH → 3650 cm^{-1} & —NH → 3400 cm^{-1}.

When the H Bg takes place absorpth freq drops to lower value & band becomes less intense & broader. HB in compd depends upon its physical state, max^m in solid state & least in gaseous state. And HB also depends upon when compd is dissolved in inert solvent - There is less in —OH stretching freq. in certain H Bonded compounds going

from liquid to gaseous state.

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	Gas Phase. (cm^{-1})	Liquid phase (cm^{-1})
Water	3756	3153
Methanol	3682	3356
Formic acid	3570	3080
Acetic acid	3657	2128

If HB is intermolecular for eg o-nitrophenol the position & width of the band is independent of concentration, but in intermolecular HB eg H_2O, carboxylic acid ↑es as the conc. ↑es. c causes the absorption band to become sharper & to move to higher frequency. Therefore it is possible to distinguish between the two types of HB. by observing the effect of concentration on the IR spectrum.

The formation of the eqm b/w monomeric & polymeric sps. is also obtained by IR spectrum of an intermolecularly HBonded compd in an inert solvent at diff. conc.

Fermi Resonance: Coupling of two fundamental vibrational modes, we produce two new modes of vibration, higher & lower than that observed when Fulfraction can occur b/w two fundamental vibration i.e. overtone or combination vibration. Such interaction is k/a Fermi Resonance. for eg fermi reso. afforded by the observed spectrum of CO_2 the symmetrical stretching band of CO_2 occurs in Raman spectrum near 1340 cm^{-1} Actually 2 bands observed. One at 1285 cm^{-1}

and other at 1388 cm^{-1}. This splitting results from coupling b/w the fundamental CO stretching vibration at 1340 cm^{-1} & the first overtone of the bending vibration. The fundamental bending vib^{n} occurs near 666 cm^{-1}. The first overtone near 1334 cm^{-1}. So fermi resonance is a common phenomena in IR & Raman spectra. It requires that the vibrational level of the same symmetry type and interacting groups be located in the molecule. So, the mechanical coupling is appreciable.
Eg. doublet appearance of CO stretch of cyclopentanone under sufficient resolution condition.

Force Constant :→

$$\Delta E = \left(\frac{1}{2\pi}\right)\left(\frac{k}{\mu}\right)^{1/2} \quad \text{--- (1)}$$

k = force const.

The difference in energy b/w ΔE two adjacent level E_v & E_{v+1} is given by this eq^{n} for harmonic oscillator. k is the stretching force const. μ is the reduced mass for a diatomic molecule. The relationship b/w energy & frequency.

$$\Delta E = h\nu = hc\bar{\nu}$$

ν = freq
$\bar{\nu}$ = wave no.

for eg. in HCl molecule the absorption of IR radiation at 2890 cm^{-1} corresponds to the transition from ground state to 1st vibrational state & this excited state corresponds to greater amplitude & freq. for stretching of HCl bond converting it to energy by eq (1). Since all quantities are known, so we get

$k = 4.84 \times 10^5$ dyne/cm.

Force constt for some diatomic molecules

	$\bar{\nu}$ (cm^{-1})	K (dyne/cm)
HF	3958	8.8×10^5
HCl	2885	4.8×10^5
HBr	2559	3.8×10^5
HI	2230	2.9×10^5
B_2	892	1.5×10^5
Cl_2	557	3.2×10^5
CO	2143.	18.7×10^5
NO	1876	15.5×10^5.

→ No correlation b/w bond dissociation energy & force constant.

$-\overset{\backslash}{C}-\overset{\backslash}{C}-$	4.5×10^5
$C-C\equiv$	5.2×10^5
$>C'=C<$	9.6×10^5
$>C=O$	12.1×10^5
$-C\equiv N$	17.73×10^5
$\equiv CH$	5.9×10^5

- The triple bond has stretching force constt of order $13-14 \times 10^5$; double bond of order $8-12 \times 10^5$ and single bond of order 8×10^5 times.
- The force constt for bending mode are less than stretching mode.
- The reduced mass is imp. for determining the freq. of vibration. for eg. if H-bonded is replaced by D. then there will be negligible change but appreciable change in