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II-M.Sc CHEMISTRY

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TITLE OF THE PAPER: PHYSICAL METHODS IN CHEMISTRY

UNIT – II

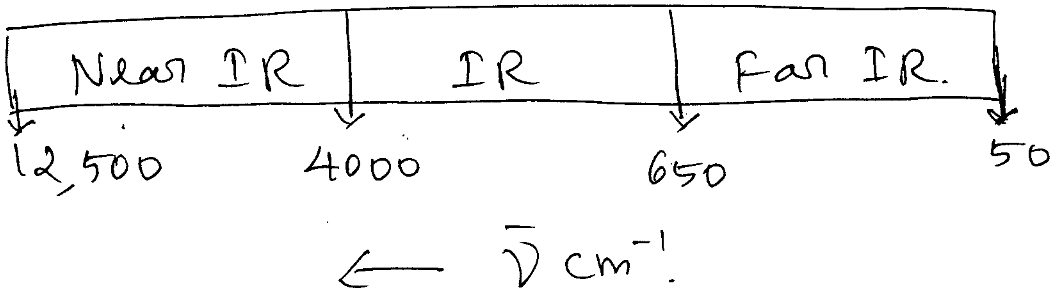
IR and Raman Spectroscopy

Combined uses of IR and Raman spectroscopy in the structural elucidation of simple molecules likeH2O, ClF3, NO3' ion, ClO3' ion, - effect of coordination on ligand vibrations- uses of group vibrations in in the structural elcidation of metal complexes of urea, thiourea, cyanide, thiocyanate, nitrate, sulphate, and dimethyl sulphoxid e- effect of isotopic substitution on the vibrational spectra of molecules- vib. Spectra of metal carbonyls with reference to the nature of bonding, geometry, nd number of C-O stretching vibrations- group theoretical treatment.-

S. Valar Selvan:

IR and Raman spectroscopy.

Electromagnetic radiation of Infra red region causes vibration of bonds between atoms in a molecule. There are two kinds of fundamental vibrations for molecules, stretching and bending. The essential requirement for a substance to exhibit IR spectroscopy is that there is a change in dipole moment of the molecule during vibrations. The intensity of an IR band depends upon the magnitude of change of dipole moment. The position of an IR band is specified in wave number $\bar{\nu}$ units. (frequency in reciprocal cm.)



Spectral range:

The vibrational transition involves more energy of the order of a few thousands of joules per mole. $E_{vib} > E_{rot}$. Since each vibrational transition is accompanied by changes in rotational energy levels also IR spectroscopy is termed vibrational-rotational spectroscopy.

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Conditions for a molecule to be IR active :-

The essential requirement for a substance to exhibit vibrational rotational spectroscopy is that the molecule must possess an oscillating dipole moment.

Examples:

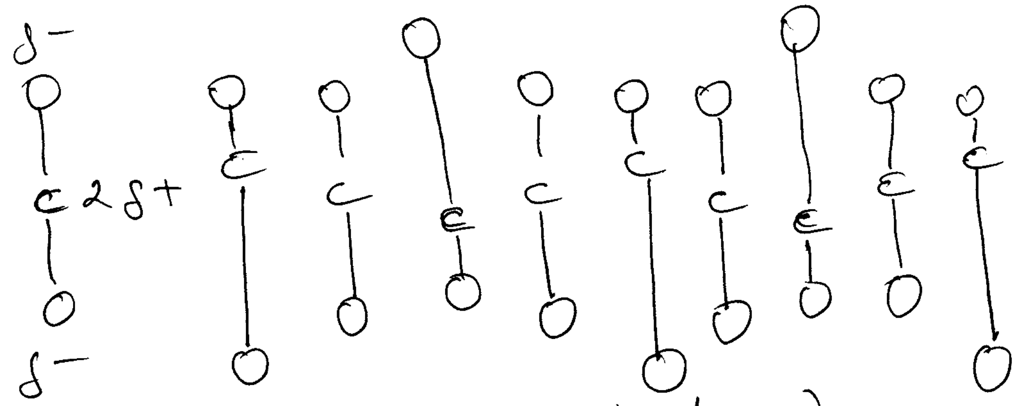
(1) Heteronuclear diatomic molecules e.g HD, HCl, HBr, HI, CO. and Non linear polyatomic molecules like H_2O, NH_3 etc are IR active

(2) Homo nuclear diatomic molecules like H_2, N_2, O_2 and Cl_2 that possess a zero dipole moment will not interact with IR Radiation.

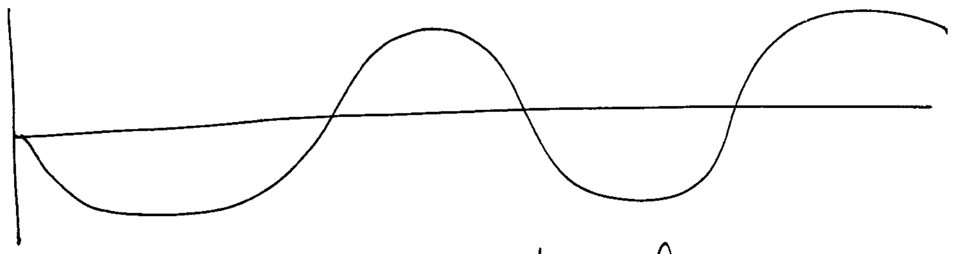
(3) Molecules like CO_2, CS_2, C_2H_4, CH_4 and N_2O have no dipole moment of their own. However certain modes of vibration of such molecules induce an oscillating dipole moment and make them IR active.

Origin of IR spectra :-

When a molecule undergoes asymmetric stretching or bending vibration, there is a periodic change in the dipole moment of the molecule due to alteration in bond length or bond angle The oscilating dipole moment thus produced is capable of interacting with the electric component of the electromagnetic radiation in the infra-red region which results in an intense IR band.



(Asymmetric stretching vibration.)



component of dipole.

Anharmonic oscillator:

Real molecules do not obey exactly the laws of simple harmonic motion. The harmonic oscillator predicts that the vibrational energy levels are equispaced. But experiments show that as V increases, the spacing goes on decreasing. Further for a harmonic oscillator, each mode of vibration would yield one band only. But actual investigation of the IR spectrum of molecules shows that there is one strong band (fundamental band) with one or two weak bands called overtones. Thus the vibrations of a diatomic molecule are anharmonic

Selection rule :-

Because of anharmonicity, the vibrational transitions are not confined to adjacent levels only, They may also occur between different levels so that

$$\Delta V = \pm 1, \pm 2, \pm 3 \ldots$$

Vibrational Spectrum :-

At room temperature all the molecules in a sample have the zero point energy and exist in V=0 state. Therefore, the vibrational transitions would originate from V=0 to V=1, V=0 to V=2, V=0 to V=3 and so on.

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For transitions,

$V=0$ to $V=1$, gives fundamental band.

$V=0$ to $V=2$, gives the first overtone band.

$V=0$ to $V=3$ gives the second overtone band.

Fermi resonance:-

When two vibrational modes in a mollecule have frequencies very close to each other, they resonate and exchange energy. This is known as Coupling. It may also happen that a fundamental vibration couples with the overtone of some other vibration. This type of Coupling is called fermi resonance. As a consequence of Fermi resonance the overtone band gains intensity at the expense of the fundamental band. Thus, the fundamental and overtone bands are of the same intensity.

Examples:- There are two strong bands at 1786 cm^{-1} and 1740 cm^{-1}. in the IR spectrum of benzoyl chloride. If it was known that the spectrum is of benzoyl chloride one would have concluded that the compound contains two carbonyl ~~compound~~. groups.

The stretching vibration of C=O (1625 cm^{-1}) and the first overtone of the bending vibration of C–Cl ($2 \times 800 = 1600\ cm^{-1}$) have frequencies close to each other. So they couple together strongly and give two bands of equal intensity.

Types of molecular vibrations:-

There are two types of fundamental vibrations for a molecule.

(i) Stretching

(ii) Bending.

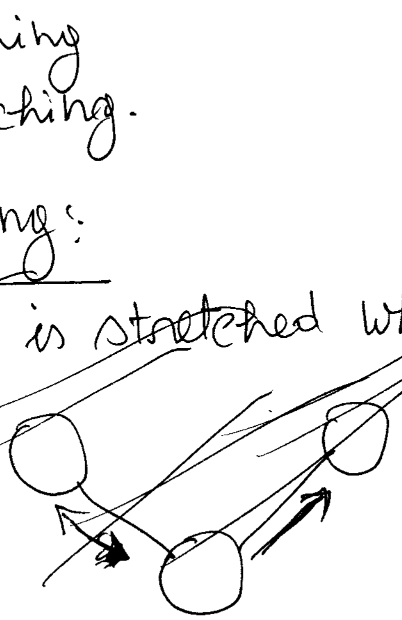
(i) **Stretching**:- This is a type of molecular vibration in which the distance between two atoms increases or decreases but the atoms remain in the same bond axis. i.e. stretching vibrations involve oscillations of atoms parallel to the bond axis. The stretching vibrations are classified as

(i) Symmetric stretching

(ii) Asymmetric stretching.

(i) **symmetric stretching**:

~~One of the bonds is stretched while the other is compressed.~~



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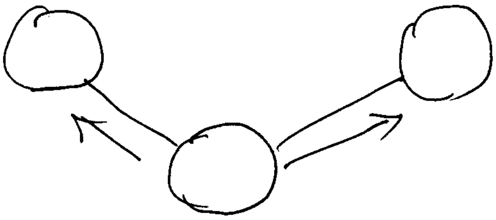
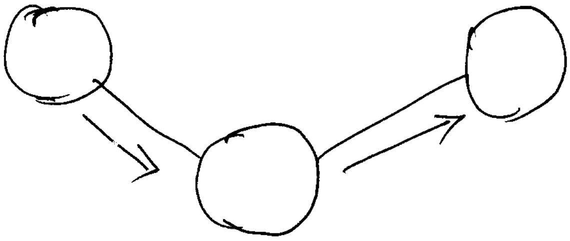
(i) Symmetric Stretching:- Both the bonds are either stretched or compressed.



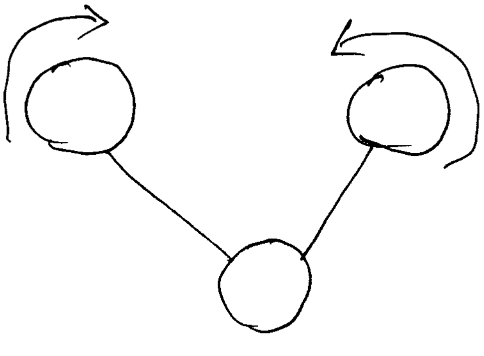
(ii) Asymmetric stretching:- One of the bonds is stretched while the other is compressed.



Bending:-

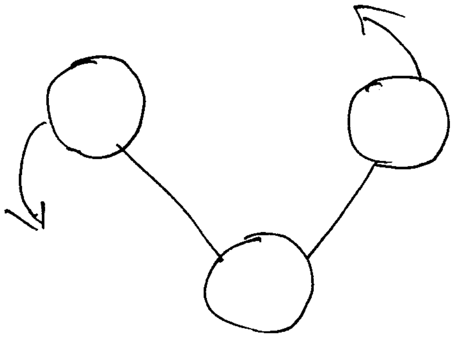
In this mode of vibration atoms move in and out of the bond axis plane. There are four types of Bending vibrations.

(i) Scissoring:- The two atoms move towards and away from each other in the same plane and there is a change in bond angle.

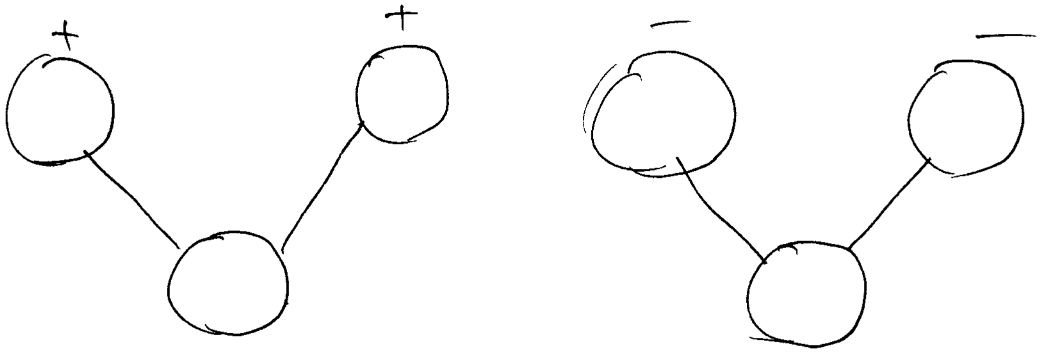


(ii) Rocking :-

The two atoms move in the same direction as also in the same plane.

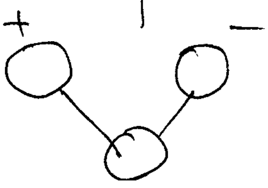


(iii) Wagging :- The two atoms move up and down the plane with respect to the central atom.



The + and − signs represent motion above and below the plane of paper respectively.

(iv) Twisting :- One of the atoms move up the plane and the other moves down the plane with respect to the central atom. There is a change in the angle between two planes in which the two atoms lie.



Raman Spectroscopy.

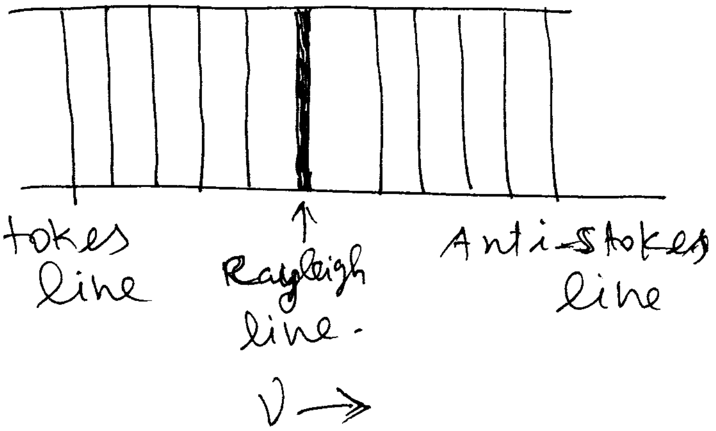
Raman effect :-

When a beam of monochromatic light is passed through a transparent substance a part of the light is scattered in all directions. Rayleigh observed the scattered light in a direction $\perp$ to the incident beam and found that the frequency of the scattered light is the same as that of the incident light. This is known as Rayleigh scattering. In 1928 sir. C.V. Raman Observed that the scattered light contains some additional radiations with frequencies lower or higher than that of the incident light This is called Raman scattering or Raman effect.

Raman spectrum :-

Raman scattering observed in the ~~f~~form of a spectrum is called Raman spectrum. It consists of an intense line with frequency equal to that of the incident light. This ~~intense~~ intense line is known as Rayleigh line. In addition there are lines on either side of the Rayleigh line called Raman lines.

The Raman lines of frequency lower than that of the incident beam are called Stokes lines. while those having higher frequency are referred to as anti-Stokes lines.



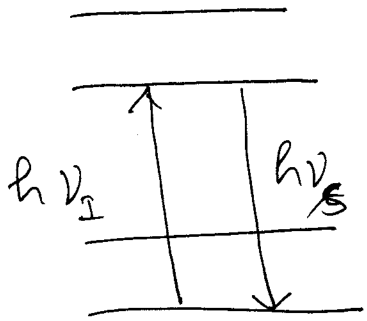
The separation or shift in frequency of these lines from the incident frequency is termed Raman frequency or Raman shift designated as $\Delta\nu$. For stokes lines, $\Delta\nu$ is +ve and for anti-stokes lines $\Delta\nu$ is -ve.

Theory of Raman effect:-

According to quantum mechanics Raman effect is the outcome of collisions between the light photons and the molecules of a substance.

The collisions may be elastic or inelastic. Depending upon the nature of collisions three types of interactions between the light photons and the molecule are possible.

case I: Suppose a molecule collides with a light photon at the ground state and gets excited. If the collision is elastic, there will be no exchange of energy and the excited molecule returns back to its original state emitting radiation with frequency equal to that of the incident light. This produces Rayleigh line.

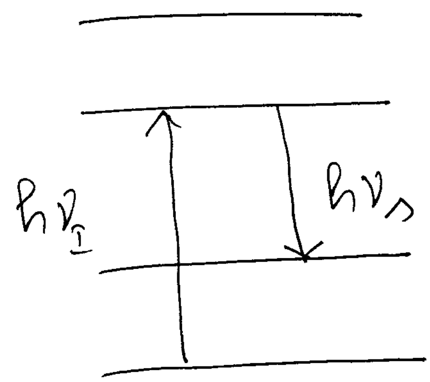


$$h\nu_I = h\nu_S \quad \text{or} \quad \nu_I = \nu_S$$

$$\therefore \Delta\nu = \nu_I - \nu_S = 0$$

case II: (Stokes lines)

When a molecule collides with a light photon at the ground state, it gets excited. If the collision is inelastic, exchange of energy between the photon and the molecule takes place. The excited molecule may return to one of its higher energy level, instead of returning to the ground state by emitting less energetic radiation. Here, the molecule gains energy from the photon and the frequency of the scattered radiation is less than that of the incident radiation. This accounts for the stokes lines

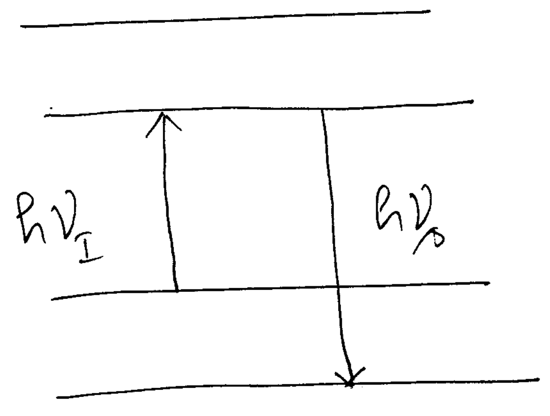


$h\nu_I > h\nu_s$ (or) $\nu_I > \nu_s$

$\therefore \Delta\nu = \nu_I - \nu_s = +ve$

Case III: Anti Stokes lines:

Some times, the molecules is in its higher energy level at the time of collisions. As a consequence of inelastic collision with the photon the molecule gets excited and returns to the ground state by emitting more energetic radiation. These radiations have frequencies higher than that of the incident light. This explains the origin of anti-stokes lines.



$h\nu_I < h\nu_s$

(or) $\nu_I < \nu_s$

$\therefore \Delta\nu = \nu_I - \nu_s = -ve$

condition for a molecule to be Raman active

When a molecule is placed in an electric field the positively charged nucleus and the negatively charged electrons are displaced from their normal positions. Now an induced dipole moment is set up in the molecule. The induced dipole moment μ depends on the magnitude of the field strength H.

$$\mu \propto H$$

$$\mu = \alpha H$$

where α is a constant called polarizability of the molecule.

The polarizability can be conveniently represented by drawing a polarizability ellipsoid. The polarizability changes with rotational or vibrational motion of the molecule. This change is reflected from the change in size or direction of the polarizability ellipsoid. In order to be Raman active, a molecular rotation or vibration must cause a change in the polarizability of the molecule.

Selection Rule. For Raman spectroscopy

$\Delta J = 0, \pm 1, \pm 2, \pm 3$

$\Delta V = 0, \pm 1, \pm 2, \pm 3$

Modes of vibration and change in polarizability.

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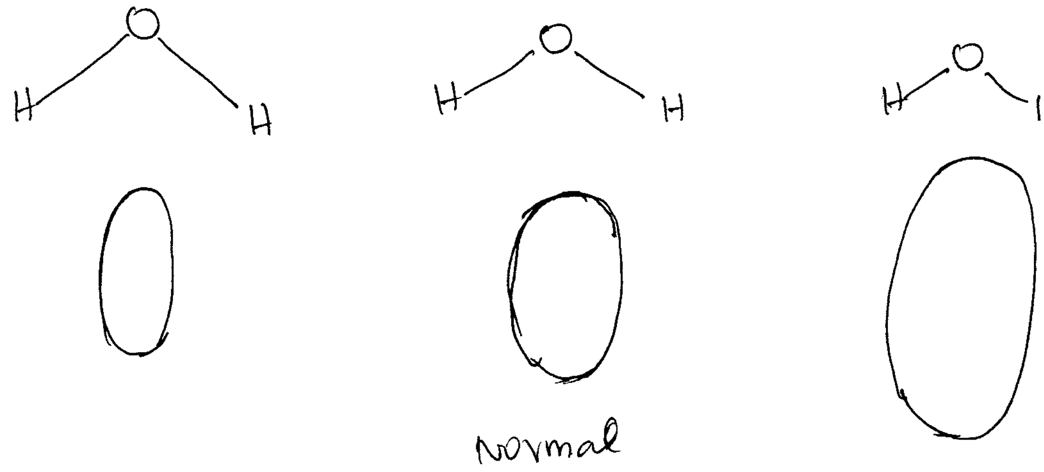
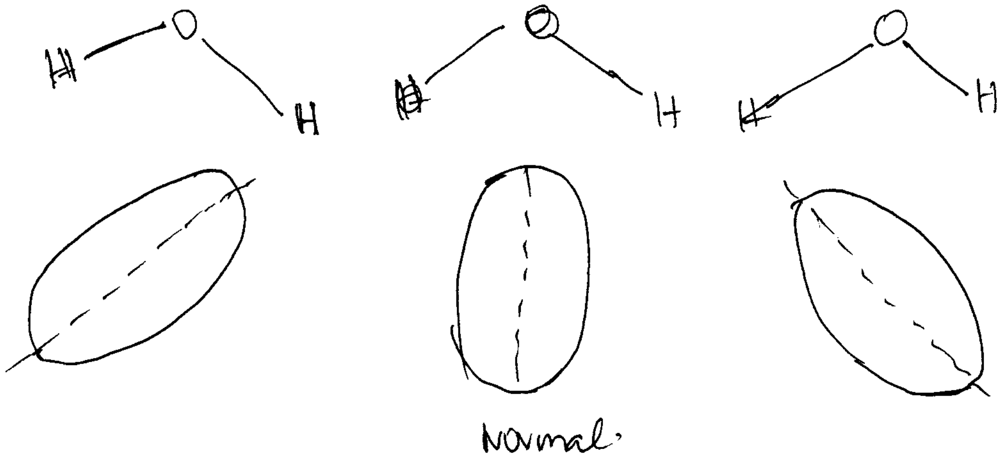
1. Non linear molecules (e.g H_2O)

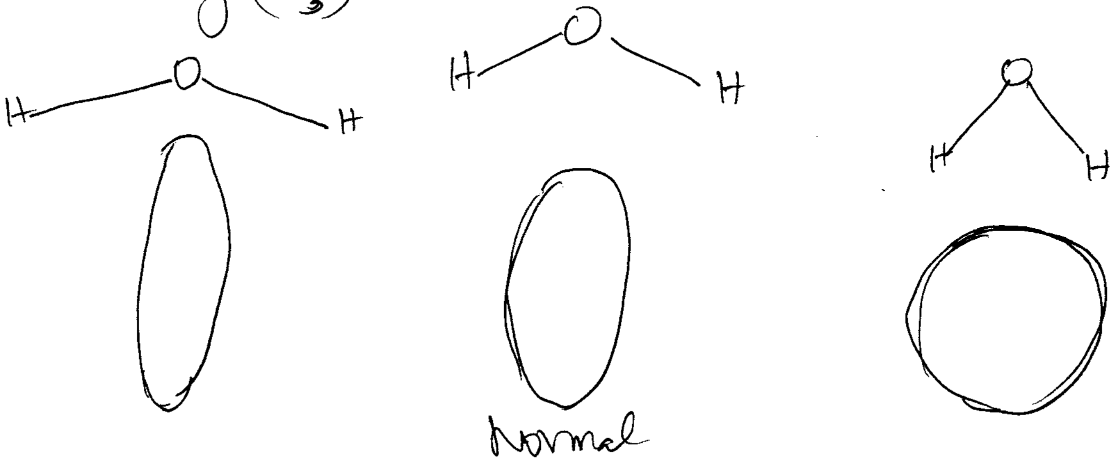
(a) sym. stretching (V_1)



(b) Asym. stretching (V_2)



(c) Bending (V_3)



(i) V_1 involves change in size of the ellipsoid

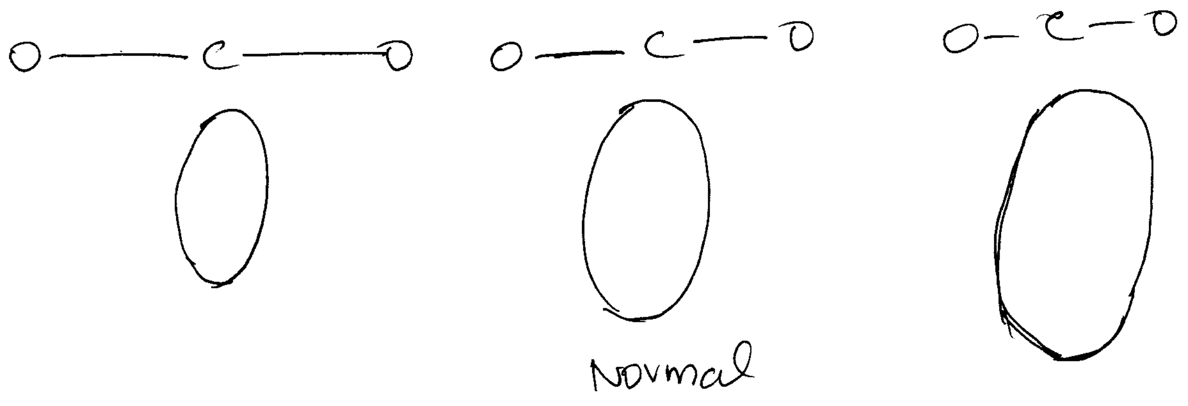
(ii) V_2 involves change in direction of the ellipsoid.

(iii) V_3 involves change in size and shape of the ellipsoid.

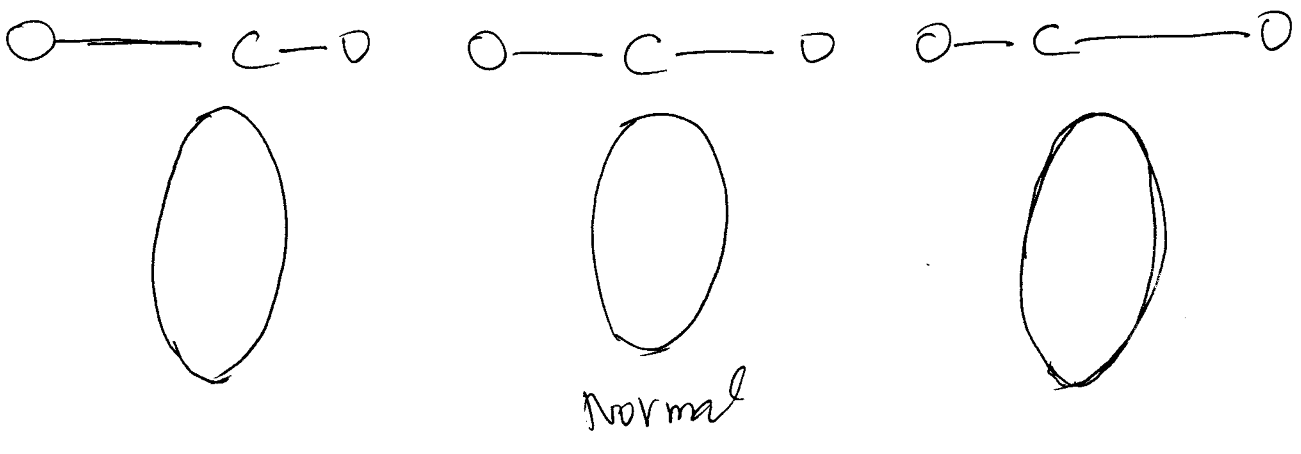
Thus all the three modes of vibration are Raman active.

2. Linear molecules(e.g. CO_2)

(a) Sym. stretching (V_1)

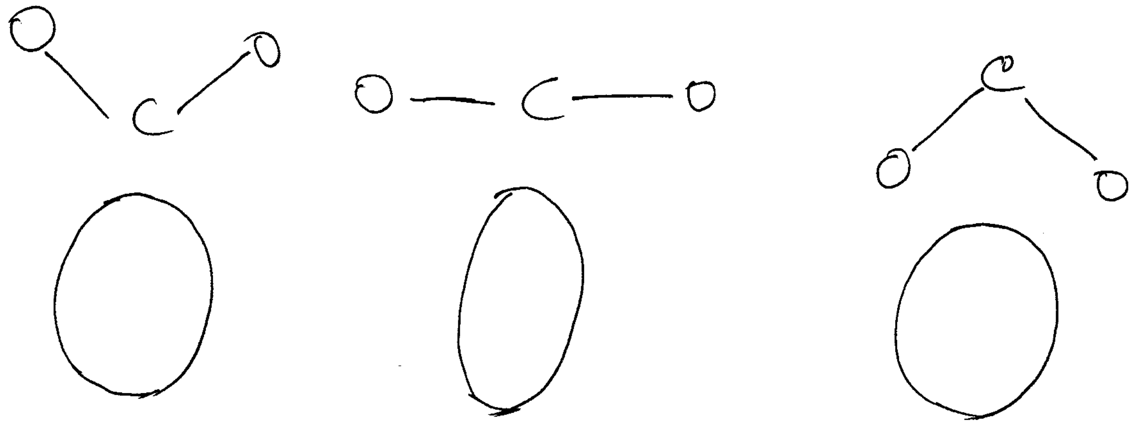


(b) Asym. stretching (V_2)



(16)

(c) Bending (V_3)



normal

(i) V_1 involves change in size of the ellipsoid

(ii) V_2 involves no change in the ellipsoid.

(iii) V_3 involves no change in the ellipsoid.

Thus, V_1 is Raman active and V_2 and V_3 are Raman inactive.

Comparative study of Raman spectra and IR spectra :-

Both IR and Raman spectra arise out of vibrational and rotational transitions in molecules. They give the same kind of informatio
i.e one is complimentary to the other.

Example (1) water molecule.

Mode of Vibration	IR activity	Raman activity
(i) Sym-stretching	Active	Active
(ii) Asym-Stretching	Active	Active
(iii) Sym_bending	Active	Active

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2. CO_2 molecule.

Mode of vibration	IR activity	Raman activity.
(i) sym- Stretching	Inactive	Active
(ii) Asym-Stretching	Active	Inactive
(iii) sym- bending	Active	Inactive

Rule of Mutual Exclusion:- This is a general rule which throws light on the molecular symmetry. According to the rule, if a molecule has a centre of symmetry, then Raman active vibrations are IR inactive and vice versa. If there is no centre of symmetry then some (not all) vibrations may be both Raman and IR active.

Illustrations:-

Carbon dioxide and Nitrous oxide molecules give rise to some no. of IR bands. They must therefore be linear. In the case of CO_2 molecule, the IR active vibrations are Raman inactive and the Raman active vibrations are IR inactive. This shows that CO_2 molecule has a centre of symmetry. However, all the vibrations of N_2O molecule are simultaneously IR and Raman active

Thus, the molecule is asymmetric and has no centre of symmetry. The structures are

O—C—O

N—N—O

Difference between Raman spectra and IR spectra

	Raman spectra	IR spectra.
1.	It is due to scattering of light by the vibrating molecules.	It is outcome of the absorption of light by the vibrating molecules.
2.	change in polarizability is the cause for Raman spectra.	change in dipole moment is the cause for IR spectra.
3.	Water can be used as a solvent	Water can not be used as a solvent since it is opaque to IR radiation.
4.	Vibrational frequencies of large molecules can be measured.	Vibrational frequencies of large molecules can not be measured.
5.	Concentrated solutions must be used.	Dilute solutions are preferred.
6.	Homonuclear diatomic molecules are active	Homonuclear diatomic molecules are inactive.
7.	For Raman spectra any source of light can be used.	only IR light is used.

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Combined uses of IR and Raman spectroscopy in the structural elucidation of simple molecules

Fundamental vibrations are given as follows:

(a) For non linear polyatomic molecules like H_2O.

Total no. of degrees of freedom = $3n$

No. of translational degrees of freedom = 3 (along x, y and z axes)

No. of rotational degrees of freedom = 3 (Rotation is resolved into three components about three ⊥ axes)

∴ No vibrational degrees of freedom = $3n - (3+3)$

$= 3n - 6$

(b) For Linear polyatomic molecules (e.g CO_2, N_2O)

Total no. of degrees of freedom = $3n$

No. of translational degrees of freedom = 3.

No. of ~~vibrational~~ Rotational degrees of freedom = 2

(~~There is no~~ energy of rotation about the bond axis ~~only~~ is negligible as rotational [illegible] is minimum) (only ⊥ axes are resolved).

∴ No. of vibrational degrees of freedom = $3n - (3+2)$

$= 3n - 5$

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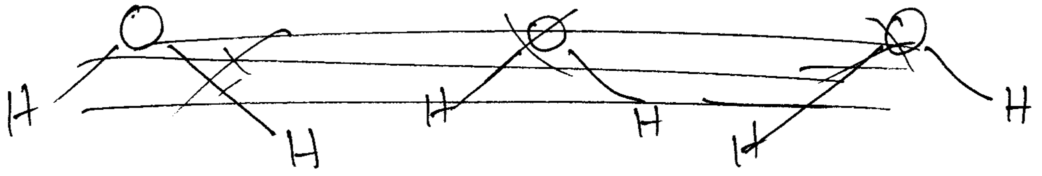
(i) H_2O:

$2A_1 + B_1$

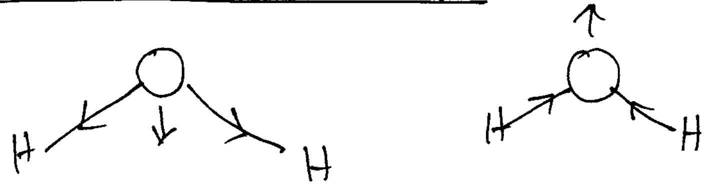
2 Symmetric
1 Asymmetric

By $(3n-6)$ rule

$3 \times 3 - 6 = 9 - 6 = 3$ fundamental modes of vibrations are observed.



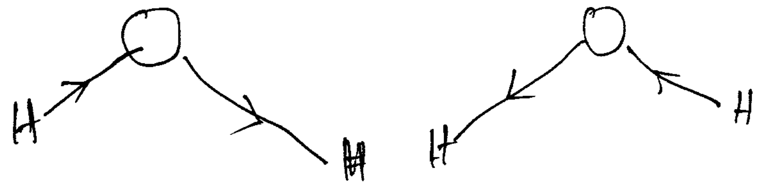
Symmetric stretching:



IR active
Raman active.

$\nu_1 = 3655\ cm^{-1}$

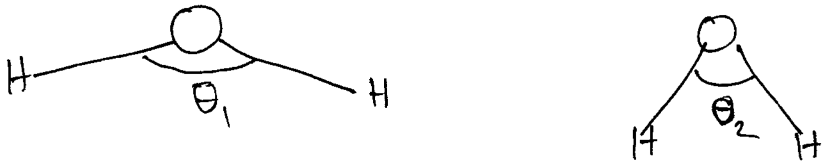
Asymmetric stretching



IR active
Raman active

$\nu_2 = 3756\ cm^{-1}$

Symmetric Bending:



IR active
Raman active.

$\theta_1 > \theta_2$.

$\nu_3 = 1595\ cm^{-1}$

As in the case of H_2O all fundamentals are both Raman and IR active, the molecule has no centre of symmetry according to mutual exclusion principle.

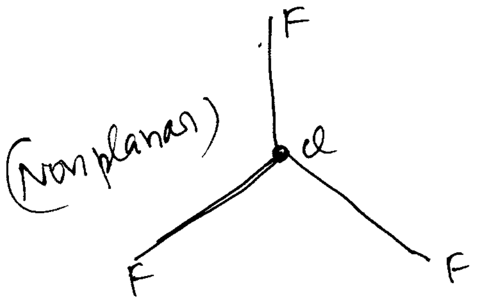
So It is concluded that water has bent structure.

(ii) ClF_3 :-

Six fundamentals are observed for this Compound. It established that the structure is non linear. since $(3n-6)$ ~~a~~ rule is satisfied.

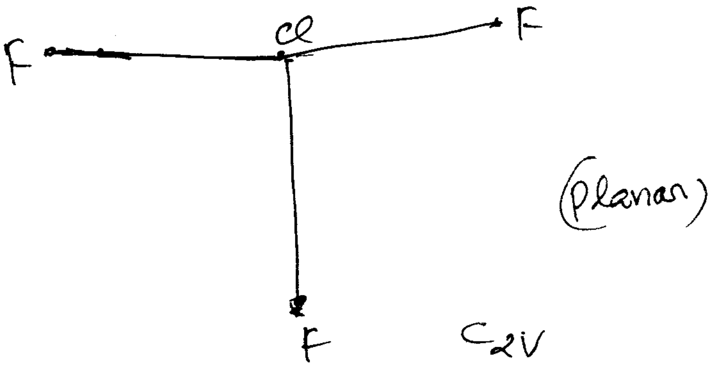
$3 \times 4 - 6 = 12 - 6 = 6$.

It is also observed that all ~~the~~ are IR and Raman active. It is finaly confirmed that ClF_3 has planar T-shaped structure. It fulfills the C_{2V} symmetry. Bond angle is nearly 90°.



(C_{3V})

(C_{3V} symmetry is ruled out)



(C_{2V} is confirmed)

(iii) NO_3^-

D_{3h} point group))

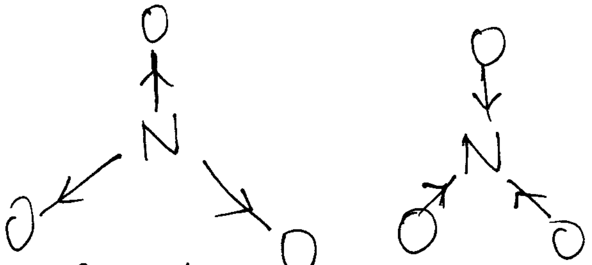
The IR and Raman spectra ~~compo~~ of this compound indicates that V_1 is Raman active but IR inactive and V_2 is IR active but Raman inactive. V_3 and V_4 are both Raman & IR active.

④

(trigonal planar

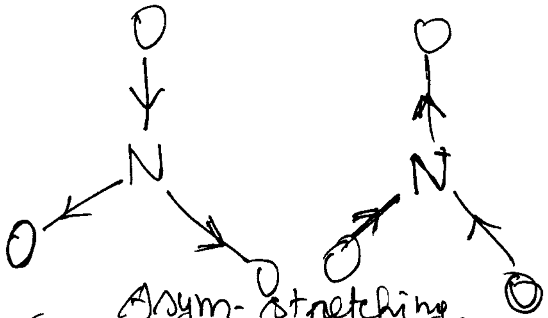
Therefore Asymmetrical planar structure is proposed.

mode.	Raman active (cm⁻¹)	IR active. (cm⁻¹)
V_1	1049	–
V_2	–	830
V_3	1355	1350
V_4	690	680



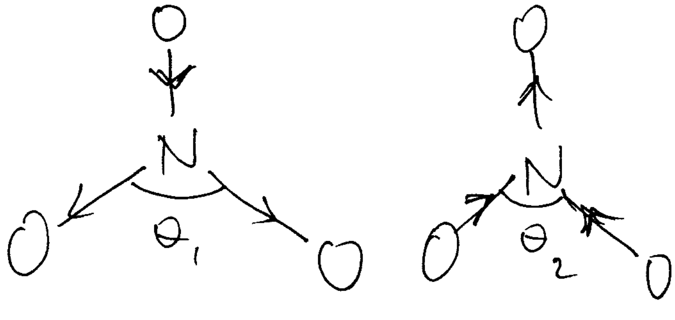
sym. stretching

(V_1) Raman active (IR inactive)



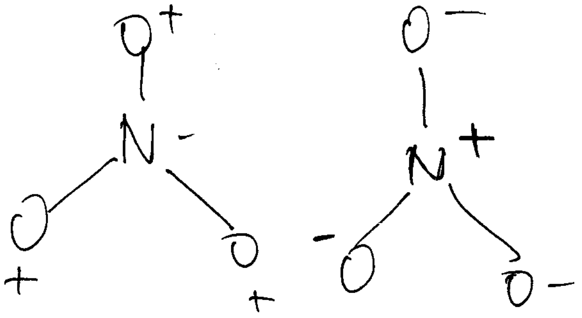
Asym- stretching.

(V_2) Raman Inactive (IR active)



$\theta_1 > \theta_2$.

(V_3) Symmetric Bending (Raman & IR active)



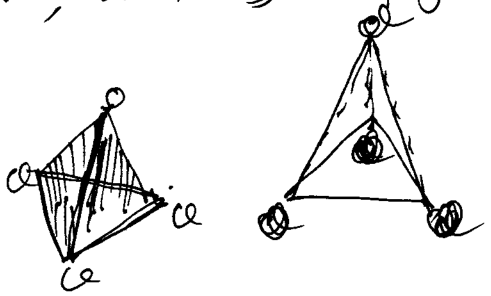
(V_4) Asymmetric Bending (Raman & IR active)

(iv) ClO_3^- :-

The following modes of vibrations are assigned for this compound.

Raman active (cm⁻¹)	IR active (cm⁻¹)	Assignment (cm⁻¹)
450	434	ν_4
610	624	ν_2
940	950	ν_3
982	994	ν_1

As all vibrations are both Raman and IR active, it has a pyramidal structure (Nonplanar)



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GROUP VIBRATIONAL Concept :-

Most of the functional groups absorb in a narrow region of the spectrum irrespective of the molecule contains the functional group.

For example, the carbonyl absorptions due to C–O stretching occur roughly in the region 1700 cm^{-1}. Because of mass, inductive and conjugative effects the position of the band varies slightly (± 150 cm^{-1}) similarly, $-CH_3$ group has five absorptions. Viz.

<u>stretching</u> :- $C-H_s$ and $C-H_{as}$ $\longrightarrow$ 3000–2860 cm^{-1}

<u>Bending</u> :- $C-H_s$ and $C-H_{as}$ $\longrightarrow$ 1470–1400 cm^{-1}

<u>Rocking</u> : $C-H_{rocking}$ $\longrightarrow$ 1200–800 cm^{-1}

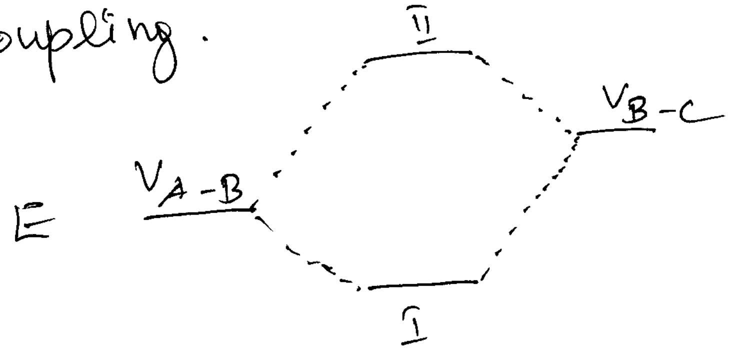
The concept of group vibrations implies that the vibrations of a particular group in a compound are relatively independent of the rest of the molecule. i.e. a molecule can be dissected into many independent groups. Many functional groups in unknown compounds have been identified by this assumption.

Limitations of the concept :-

The group vibration concept implies that the vibration of a particular group are independent of the remaining part of the molecule. During normal modes of vibration the centre of mass has to be retained. If the functional group has heavier atom, very little motion is required to maintain the centre of gravity. ~~But we~~ Here group vibration concept is applicable.

But when the atoms in a molecule are of smaller mass and are connected by ~~mass~~ bonds with similar force constants, the entire molecule will participate in the vibration. This simultaneous vibration of more than one group is called Coupling of group vibrational modes.

Two group vibrations of similar energies V_{A-B} and V_{B-C} couple to give vibrations I and II. The vibration I involves some motion of B–C bond and the vibration II some motion of A–B bond. When the frequencies of the two group vibrations are close together there will be extensive coupling.



For example:-

(1) In HCN, C–H and C–N vibrations couple. Therefore, the observed frequencies cannot be described as being pure C–H and C–N stretch. The presence of coupling in this molecule can be demonstrated by deuteriation.

	H–CN	D–C–N
$C-N_s$	2089	1906
$C-H_s$	3312	2629

The values explain that

(a) Dueteriation affects the C-N stretching frequency.

(b) C-D and C-N frequencies are very closer than V_{C-H} and V_{C-N}. Therefore, there is more extensive Coupling in DCN. ~~and~~

(c) Because of Coupling, expected decrease in V_{C-H} has not been observed on deuteriation (expected 3312/1.3 = 2540, observed = 2629 cm^{-1})

(2) In some cases the Coupling may occur if the vibrations are of same symmetry. e.g In acetylene $C-H_s$ and $C-C_s$ are of same symmetry. So they Couple. ~~B~~ But $C-H_{as}$ and $C-C_{as}$ are of different symmetry. So they do not Couple. Here the deuteriation effect is normal ($C-H_{as}$ = 3287 cm^{-1}) ($C-D_{as}$ = 2427.)

(3.) In compounds such as F_2CO, Cl_2CO and Br_2CO, the $V_{C-O(s)}$ are 1928, 1827, and 1828 cm^{-1} respectively. On the basis of electronegativity of halogen atoms the observed decrease can not be explained. The trend is explained due to Coupling of $C-F_1$ and $C-O_s$ vibrations as they are closer, thereby making the V_{C-O} higher than expected for an isolated CO. Since the size increases from F to Br the extent of Coupling and, hence the V_{C-O} decreases in the same order

(9.)

Factors that influence the vibrational spectra.

Factors:

(a) Rotational fine structures are also obtained for gaseous samples. Fine structures are not obtained in solution because collisions of molecules in the condensed phase occur before a rotation is completed.

(b) The number of absorption bands and frequencies of vibrations vary in different states.

(c) There are more bands in the liquid state than in the gaseous state of the substance. New bands below 300 cm^{-1} appear in the solid state spectrum.

Reasons:-

(i) Intermolecular forces:- The intermolecular forces existing in the solid and liquid states are stronger compared to that in the gaseous state. As a result slight shifts in frequencies are observed.

(ii) Lattice Vibrations:- The bands appearing around 300 cm^{-1} for the solid samples are due to the translational and torsional motions of the molecules in the lattice. Lattice vibrations form combination bands with intramolecular vibrations causing frequency shifts.

(iii) Vibrational Coupling :- If the unit cell contains more than one chemically equivalent molecule, the vibrations in the individual molecules couple with each other and this intermolecular coupling causes frequency shifts.

(iv) Site symmetry :- When a molecule is present in a crystal, the symmetry of the surroundings of the molecule in the unit cell determines the selection rules. i.e. bands forbidden in the gaseous state appear in the solid and degenerate vibrations in the gaseous state are split in the solid. For example, the IR spectrum and Raman spectra of $CaCO_3$ in calcite, where the CO_3^{2-} ion is in the site of D_3 symmetry, contain the following bands:

V_1 1087 (R), V_2 879 (I), V_3 1432 (I, R)

and V_4 710 (I, R).

The IR spectrum of $CaCO_3$ in Aragonite, where the site symmetry of carbonate is C_s, differs in that V_1 becomes IR active and V_3 and V_4 each split into two bands.

(v) H-bonding :- In hydrogen bonding solvents the shifts are due to specific solute-solvent interactions which cause changes in the electron distribution in the solute.

Effect of Coordination on ligand vibrations

When a ligand coordinates to a metal atom the electron density is changed which, in turn changes the bond length, bond angles and inter-atomic forces. Therefore, IR spectrum of coordinated ligand differs from that of free ligand. The differences are observed in (i) the band positions (ii) the relative intensity of bands and (iii) the nature of bands (single peak being split up into several bands). These changes are mainly due to [illegible] the effect of complex formation on the symmetry of the ligand and changes in the electronic structures and bonding characterestics of the ligand.

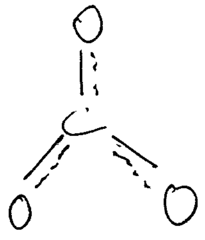
(1) Effect of complex formation on the symmetry of the ligands :

The equivalent bonds in a free ligand become non-equivalent on complex formation resulting in a change in the symmetry of the ligands. As a result, certain bands are split up and new bands are obtained in IR spectrum

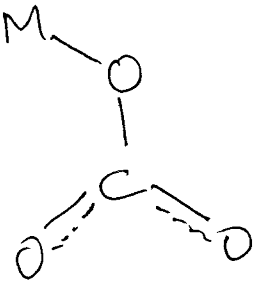
Example :-

1. CO_3^{2-}

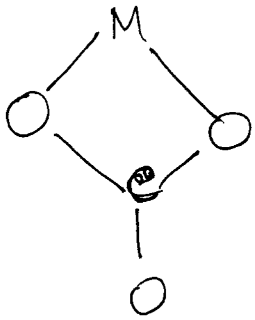
It is observed that the carbonate ion can Coordinate with a metal ion as a Unidentate or bidentate ligand. In the free ligand all the three C–O bonds are equivalent; only one IR band is observed. But on Coordination, two types of C–O bond result and as a result two bands are observed. The difference between the two kinds of C–O bond is much greater for bidentate Coordination than for Unidentate Coordination.



Free ion



Unidentate



Bidentate

e.g. for $[Co(NH_3)_5CO_3]Br$ (Pentamino carbonato cobalt III Bromido)

CO_3^{2-} is unidentate; bands are at 1373 and 1070 cm^{-1}; Difference = ~~330~~ 303 cm^{-1}.

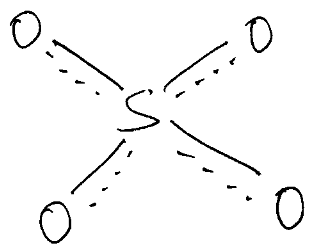
for $[Co(NH_3)_4CO_3]Br$

CO_3^{2-} is bidentate bands are at 1373 and 1030 cm^{-1}; Difference = 343 cm^{-1}

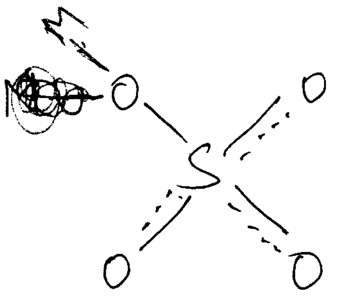
⑬

(2) SO_4^{2-}

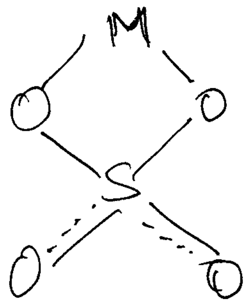
The free sulphate ion belongs to the high symmetry point group Td. Of the four fundamental vibrations, only V_3 and V_4 are infrared active. If the ion is coordinated to a metal, the symmetry is lowered which results in the splitting of the degenerate modes to give new bands in the IR spectrum corresponding to Raman active bands in the free ion.



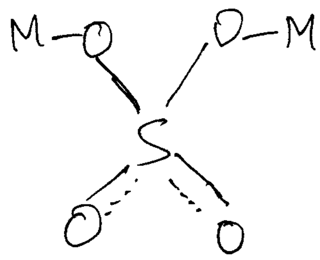
Free ion
Td
(Tetra hedral point group)



Unidentate complex
C_{3V}



Bidentate Complex
(C_{2V})



Bridged Bidentate Complex (C_{2V})

The lowering of symmetry is much more in bidendate and bridging coordinations than in unidendate coordination.

e.g: For $[Co(NH_3)_6]_2(SO_4)_3 \cdot 5H_2O$.

Free sulphate

Free sulphate ion shows two IR bands at 1104 (V_3) and 613 (V_4) cm^{-1}. (V_1 and V_2 are Inactive)

For $[Co(NH_3)_5SO_4]Br$.

Bidentate

SO_4 is bidentate (C_{2V}) shows six bands at 970, 438, 1032–1044, 1117–1143, 645 and 604 cm^{-1}.

Bridged

For bridged SO_4^{2-} (C_{2v}) the spectrum shows still more number of bands.

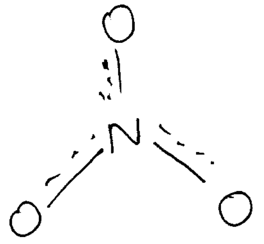
(3) NO_3^-

NO_3^- has mole resemblances with Carbonate (CO_3^{2-}) ion. The results obtained fol carbonato complexes are also applicable to nitrato Complex. It is observed that the infra-red spectra of Unidentate nitrato Complexes have C_{2v} symmetry. They show NO stretchings at 1530–1480 cm^{-1} (V_3) or 1290 – 1250 (V_1) and 1035–970 (V_2).

Fol example

$[Co(NH_3)_5(NO_3)]PtCl_4$ – unidendate (NO_3)
1481, 1269, and 1012 cm^{-1}.

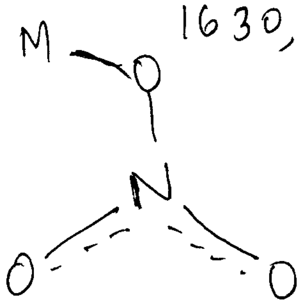
$Sn(NO_3)_4$ – bidentate (NO_3)
1630, 1255, 983 cm^{-1}



Free ion

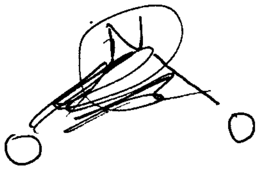
D_{3h}

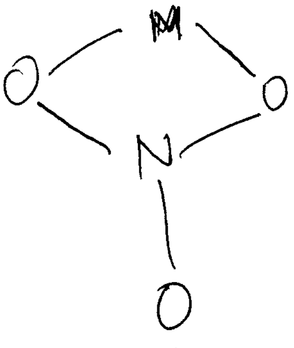
stretching mode IR Inactive



Uni dentate

C_{2v}





Bidentate

C_{2v}

⑮

(2) Effect of complex formation on the electronic environment of the ligands:

~~(i) cyanato complex~~:

(i) cyano(CN) complexes:

cyano complexes exhibit sharp C≡N stretching bands at 2200-2000 cm^{-1}. Some complexes exhibit band splitting in the crystalline state. Poly nuclear complexes give several bands. Hydrates exhibit spectra different from those of the anhydrates. The C≡N stretching frequencies of cyano complexes are generally higher than that of the free ion (2080 cm^{-1} for KCN)

free ion: $\overset{(-)}{:C}\equiv N:$ ⟷ $:C=\ddot{N}:^{(-)}$

Complex: $M-C\equiv N:$ ⟷ $\overset{+}{M}=C=\bar{\ddot{N}}:$

The C≡N stretching frequencies of cyano complexes depend upon (1) Electronegativity (2) the oxidation state (3) the coordination number of the metal.

The effect of electronegativity is seen in the frequency order $[Ni(CN)_4]^{2-} < [Pd(CN)_4]^{2-} < [Pt(CN)_4]^{2-}$. The effect of oxidation state is seen in the frequency order $[Ni(CN)_4]^{4-} < [Ni(CN)_4]^{2-}$ The effect of coordination number is seen in the frequency order $[Ag(CN)_4]^{3-} < [Ag(CN)_3]^{2-} < [Ag(CN)_2]^{-}$

examples: $K_3[Mn(CN)_6]$ - 2125 cm⁻¹.
$K_4[Mn(CN)_6]$ - 2060 cm⁻¹.
$K_5[Mn(CN)_6]$ - 2048.

(2) Thiocyanato Complexes:

The SCN group may coordinate to a metal through the nitrogen or the sulfur or both (M-NCS-M′). It is obervered that the CN stretching frequencies are generally lower in the M-NCS complexes than in the M-SCN complexes. The C-S stretching frequency is very useful in distinguishing these two isomer as their difference in frequencies.

For M-NCS 780-860 cm⁻¹. C-S p
For M-SCN 690-720 cm⁻¹. C-S p

The bending frequency is also different for these isomers.

For M-NCS. 450-490 cm⁻¹.
For M-SCN - 400-440 cm⁻¹.

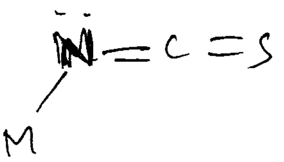
⑰

It is shown that the M–NCS group is linear or bent while the M–SCN group is always bent. This suggests that the following resonance structures are predominant.

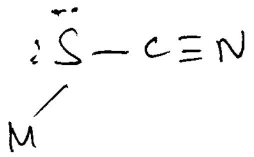
M–NCS group

$M-\overset{+}{N}\equiv C-S^-$

(or)



M–SCN group

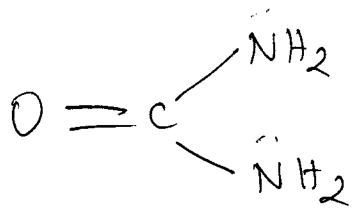


examples:–

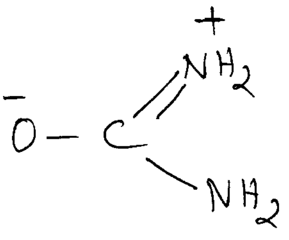
Thiocyanato complexes		Isothiocyanato complexes	
Complex	ν_{C-N} cm^{-1}	Complex	ν_{C-S} cm^{-1}
KSCN	748	$K_2[Co(NCS)_4]$	819
$K_2[Pt(SCN)_4]$	705	$K_2[Cr(NCS)_4]$	820
$K_2[Hg(SCN)_4]$	715	$Ca_2[Zn(NCS)_4]\cdot 4H_2O$	821, 826
$Zn[Hg(SCN)_4]$	786	$Hg_3[Cr(NCS)_4]_2$	801

(3) Urea:

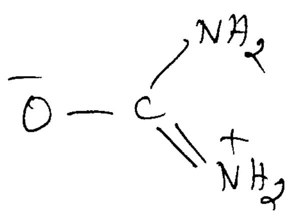
It is important to study the I.R spectra of Urea complexes whether coordination occurs through nitrogen or oxygen. The resonance structures of Urea is given as follows.



I



II



III

If Coordination occurs through nitrogen contributions of structures II and III will decrease. This results in an increase of the CO stretching frequency with a decrease of the CN stretching frequency. The NH stretching frequency may fall in the same range.

If Coordination occurs through oxygen the contributions of structure I will decrease. This may result in a decrease of the CO stretching frequency but no appreciable change in the NH stretching frequency.

The results showed that coordination occurs through nitrogen in the Pt (II) Complex, and through oxygen in the Cr(III) complex including Fe III, Zn II and Cu II.

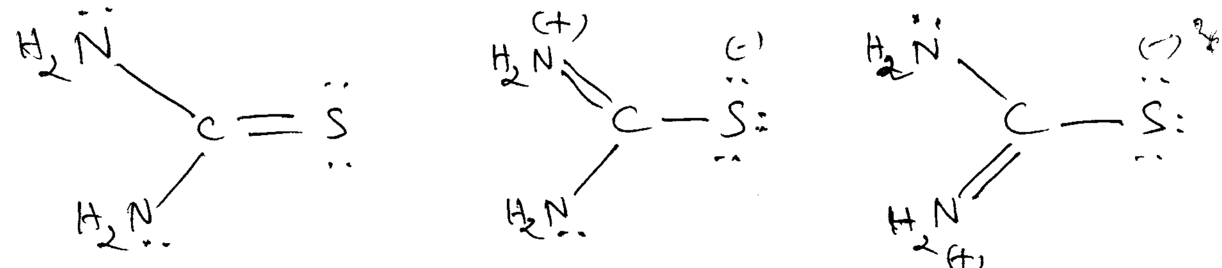
examples:

$[Pt(urea)_2Cl_2]$ ν (cm⁻¹)	Urea	$[Cr(urea)_4]Cl_3$	Predominant mode.
3390	3500	3440	(NH_2), free.
3290	3350	3230	
3130 3030		3190	(NH_2), bonded
1725	1683	1505	(C=O)
1395	1471	1505	(C−N)

(19)

(4) Thio urea Complexes:-

From the I.R studies on thio urea $[(NH_2)_2CS]$ complexes. it was observed that all the metals (Pt, Pd, eg-> Zn and Ni) form M-S bonds, since the CN stretching frequency increases and the CS stretching frequency decreases upon coordination without an appreciable change of the N-H stretching frequency. The resonance structures of thiourea is given as follows.



I II III

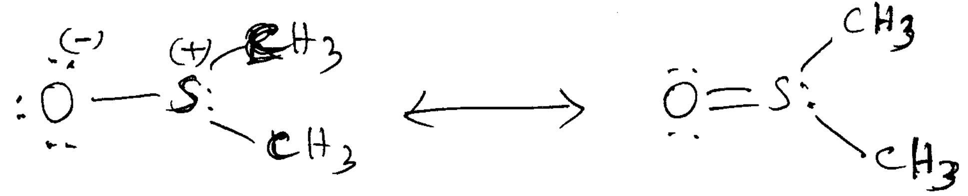
When thio urea coordinates through S to a metal ion, structures II and III are favoured and this decreases the V_{C-S} and increases the V_{C-N}. If it coordinates through N, then the nitrogen lone pair is involved (structure I is favoured) resulting in a decreased V_{C-N} and increased V_{C-S}

For thiourea V_{C-S} 730 cm^{-1}

When complexed with Mg(I), Co(II) ions, the value is shifted to lower frequencies indicating coordination through S-atom.

(5) Dimethyl sulphoxide :- (DMSO)

The resonance hybrid structures of dimethyl sulphoxide is given as follows:



I II

When DMSO coordinates through S-atom, the electron density is shifted from O to S and as a result S-O bond strength increases and ν_{S-O} increases. when DMSO coordinates through O atom, the electron density is shifted to metal atom and as as result S-O bond strength decreases and ν_{S-O} decreases.

examples:

DMSO → 1055 cm^{-1}

$SnCl_4 \cdot 2Me_2SO$,
$NiBr_2 \cdot 2Me_2SO$,
$CuBr_2 \cdot 2Me_2SO$
} (911-957 cm^{-1}. (Indicates DMSO has bonded through O-atom))

$PdCl_2 \cdot 2Me_2SO$,
$PtCl_3$ 2DMSO
} (1100 cm^{-1}. Indicate that DMSO has bonded through S-atom)

—X—

(21)

Effect of Isotopic substitution on the vibrational spectra of molecules :

As vibrational frequencies depend on the masses of moving atoms, substitution of an atom in a molecule by an isotope of different mass, will alter the frequencies of some modes. This can be very useful in assigning particular vibration if there is close range of frequencies.

H/D substitution :-

As Deuterium substitution leads to larger relative mass that results in decrease of vibrational frequencies. Thus all M-H stretching frequencies decrease by several hundreds of cm⁻¹. For example the IR spectrum of $[Co(CO)_4H]$ here the lowest frequency is due to deuterium substitution as given in the table

$Co(CO)_4H$	$Co(CO)_4D$	Assignment
2121	2120	ν_{CO}
2062	2058	
2043	2043	
1934	1396	$\nu(CoH),D$

All other higher frequencies are due to CO stretches. Thus out of 4 modes of frequencies which are initially in the closer range now become distinguished from the 4th one that is the lowest frequency which is due to Co-H stretch.

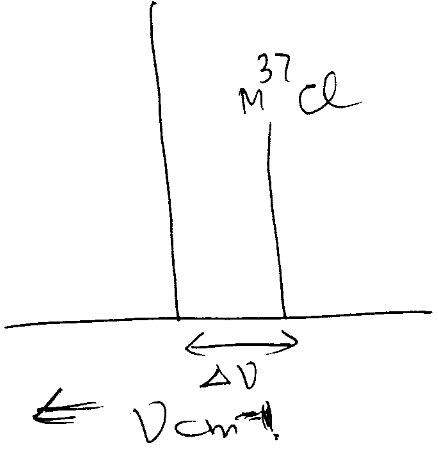
Heavy-atom isotope substitution:-

For atoms other than hydrogen, the relative changes in mass on isotopic substitutions are small and frequency shifts are less dramatic. But in very few cases, both naturally-occuring and artificial isotope mixture can ~~give~~ give useful information.

For an example the normal 3:1 mixture of chlorine isotopes leads to a characterestic isotope pattern ~~of~~ for a single M-Cl bond stretch with a stronger higher-frequency band due to ^{35}Cl and a weaker lower frequency band due to ^{37}Cl.

The relative shift is less than 0.5

$\Delta\nu/\nu < 0.5(\Delta m/m)$. It is readily resolvable if the bands are narrow.



Vibrational spectra of metal carbonyls

Metal carbonyls exhibit a variety of structures their structural elucidation by means of vibrational spectra has been a considerable interest. Metal carbonyls may be classified in to the following four groups.

(a) Mononuclear carbonyls:-

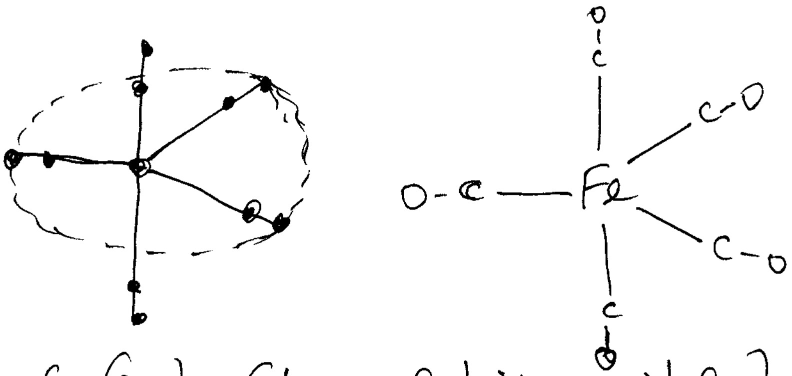
Their ~~stru~~ structures are very simple and they can be determined easily by vibrational spectrum. The following table shows the observed Co and Mc stretching frequencies of mononuclear carbonyls.

Compound	Symmetry	IR/Raman.	Observed ν_{CO}	observed ν_{MC}
BH_3CO	C_{3v}	IR	2165	691
$Ni(CO)_4$	T_d	IR	2057	422
		R	2121 2039	422 381
$[Co(CO)_4]^-$	T_d	R	1918 1883	532 439
$[Fe(CO)_4]^{2-}$	T_d	R	1788	550 464
$Fe(CO)_5$	D_{3h}	IR	2028 1994	472 430
		R	2114 2031 1984	492 414 377

24

The Co stretching frequency decreases remarkably in going from $Ni(Co)_4$ to $[Fe(Co)_4]^{2-}$. This is due to the back donation of electrons from the metal to the Co group in the same order of metals. As a result, the MC stretching frequency increases in the same order.

$Fe(Co)_5$ molecule is trigonal bipyramidal; Group theory predicts that there are two infrared active (A_2 and E') and three Raman active ($2A_1'$ and E') fundamentals for both the Co and FeC stretching frequency.



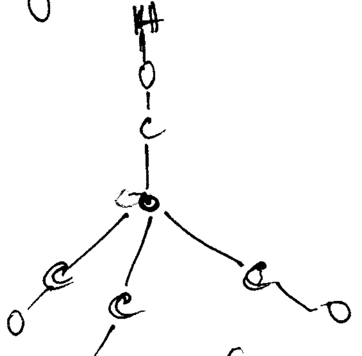
D_{3h}

$Fe(Co)_5$ (trigonal bipyramidal)

(b) Hydrocarbonyls :-

The infrared spectrum of $HCo(Co)_4$ exhibits one Co stretching band at 2049 cm^{-1} with a shoulder at 2066 cm^{-1}. It is in agreement with the following structure.

free OH → $\nu \simeq 3600\ cm^{-1}$

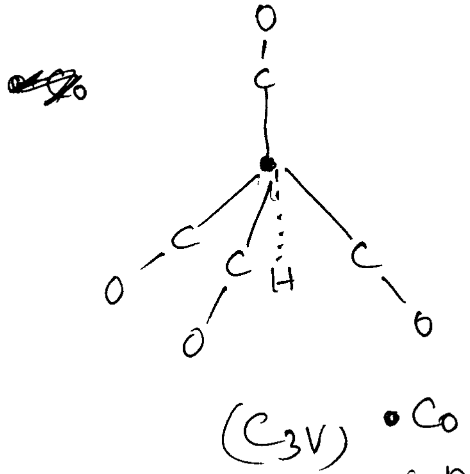


(C_3V)

However the O-H stretching frequency expected for this structure is not observed. So it is concluded that hydrogen

25

may be close enough to one or more oxygens to give ~~an~~ two infrared active CO stretching modes, but not bound strongly enough to produce an observable OH stretching band. So another structure was proposed as given below.



Here the hydrogen atom is on the three-fold axis and about 2Å away from the Co atom. The 1s orbital of hydrogen and 2pπ orbitals of carbon and oxygen overlapping occurs at a distance of 1·2Å from the Co atom. Finally it was assigned that a band at 1934 cm⁻¹ for Co-H stretching and the band at 704 cm⁻¹ for the Co-H bending mode.

Another hydro carbonyl $[HFe(CO)_4]^-$ has a similar structure as $HCo(CO)_4$. The IR spectrum of $HMn(CO)_5$ has shown that the structure ~~is~~ having C_{4v} symmetry.

The IR spectra of $HRe(CO)_5$ and $DRe(CO)_5$ have shown two bands at 1832 and 1318 cm⁻¹ for Re-H and Re-D stretching modes respectively. But it is difficult to propose a definite structure~~s~~ for it.

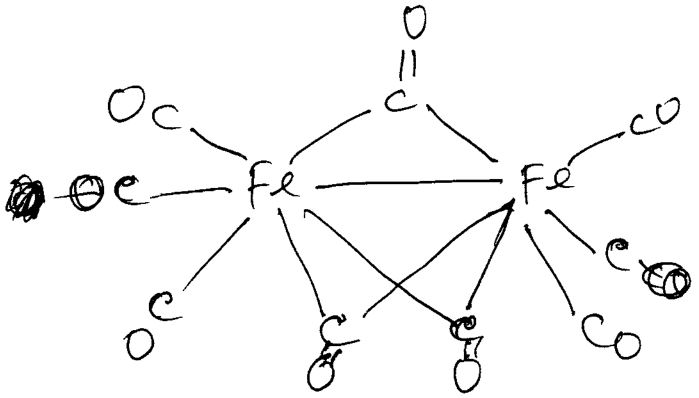
(B). Polynuclear carbonyls :-

Terminal and bridged carbonyls:-

Terminal carbonyls are relatively unchanged from free carbon monoxide (bond order ≃ 3). But bridged carbonyls are electronically much closer to carbonyl group of organic ketones (bond order ≃ 2).

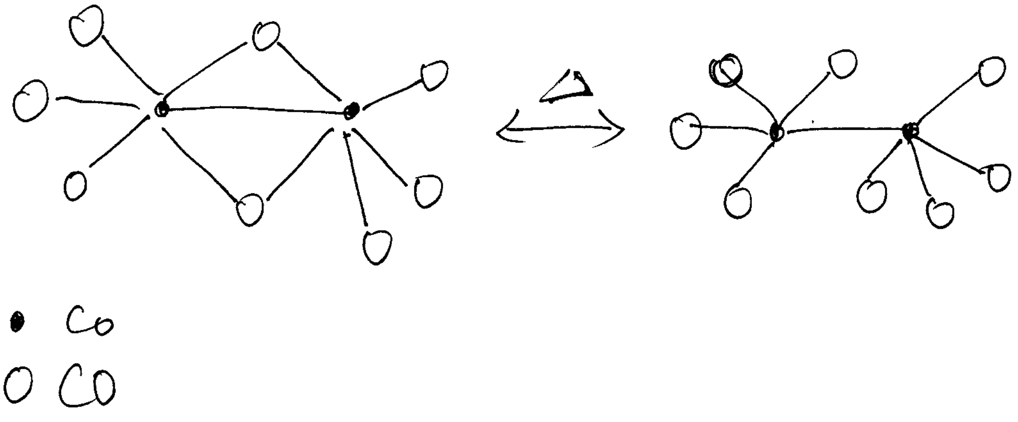
Free CO	ν_{C-O}	$2143\ cm^{-1}$.
Terminal CO	ν_{C-O}	$2000 \pm 100\ cm^{-1}$.
Bridged CO	ν_{C-O}	$1800 \pm 75\ cm^{-1}$

The IR spectrum of $Fe_2(CO)_9$ shows ν_{C-O} bands at 1828 and 2000 cm^{-1}. indicating the presence of both terminal and bridged CO groups.

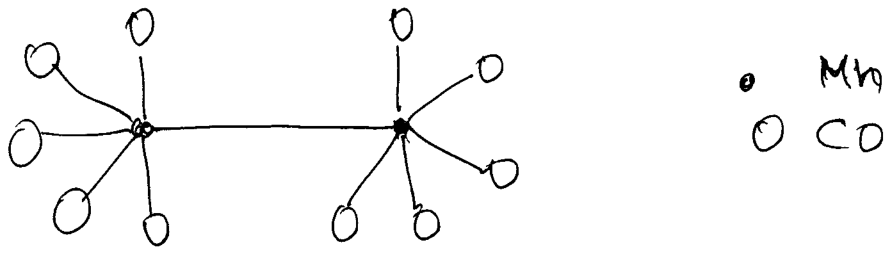


The IR spectrum of $Co_2(CO)_8$ shows bands at 2050 and 1860 cm^{-1}. establishing the presence of both terminal and bridged CO groups. When the spectrum is recorded at high temperatures, the ν_{C-O} band at 1860 cm^{-1} dissappears, and hence all

CO groups become terminals. In solution both forms exist in equilibrium.



The IR spectrum of $Mn_2(CO)_{10}$ contains no band in the region 1800 – 1900 cm^{-1}. thereby showing the absence of bridged CO.



cis and Trans carbonyls:

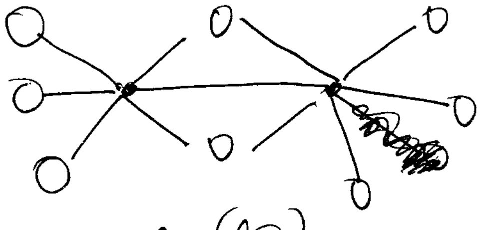
$[M(CO)_4L_2]$ Trans isomer (D_{4h}) has more symmetric structure and shows fewer IR bands but cis isomer (C_{2v}) has a lower symmetry and shows many bands. For example: $[Mo(CO)_4(P(OPh)_3)_2]$. The trans form has only one band at 1950 cm^{-1} and the cis form shows three bands at 2010, 1960, 1940 cm^{-1}.

(28)

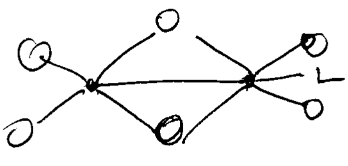
Substituted Metal carbonyls :

The CO stretching frequencies of a number of Pt(II) carbonyl complexes such as $Pt(CO)_2X_2$, $Pt_2(CO)_2X_4$ and $[Pt(CO)X_3]^-$ (where X = Cl, Br or I). The CO stretching frequency of the chloro complex was the highest and that of the iodo complex was the lowest in all series of halogeno compounds.

In another case the infrared spectrum of binuclear olefin-substituted Co carbonyl compounds of the type $Co_2(CO)_6L$ and $Co_2(CO)_4L_2$ where L is a diene. Appearance of bridging CO stretching bands suggests that the two bridging CO groups originally present in $Co_2(CO)_8$ are retained in these compounds.



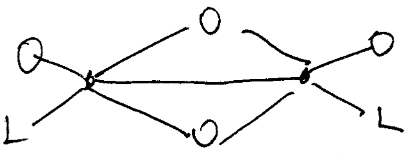
$Co_2(CO)_8$



$Co_2(CO)_6L$

L - Diene.

O - CO



$Co_2(CO)_4L_2$

— x —