LESSON-I MAGNETIC METHODS

Objectives: - Introduction – Gouy's methods – Faraday method – Applications to inorganic compounds.

3.1.i) Introduction

The electronic structure of the atoms and molecules contribute to their magnetic properties. When a substance is placed in an external magnetic field, there is an induced circulation of electrons producing a net of magnetic moment either aligned with or opposed to the applied magnetic field. Materials containing paired electrons orient in opposition to the applied field (Fig. 3.1.b) are classified as **diamagnetic**. Diamagnetism is an universal property of matter, since most of the compounds contain some paired electrons. Diamagnetic property is independent of temperature. Bismuth, antimony, copper, water, alcohol and hydrogen are some of the typical diamagnetic materials.

If the samples contain unpaired electrons, they align with the applied magnetic field,(Fig. 3.1.c) and said to be **paramagnetic.** The spin and orbital motion of electrons give rise to permanent molecular magnetic moments that tend to align themselves with the applied magnetic field. Since the paramagnetic moment arising from unpaired electrons is much larger than the diamagnetic moment arising from the paired electrons, it cancels any repulsion from the paired electrons in a sample. Thus even if a sample contains only one unpaired electron in a molecule it will cause a net attraction into a magnetic field. Aluminium, manganese, oxygen, platinum are a few typical materials that exhibit paramagnetism.

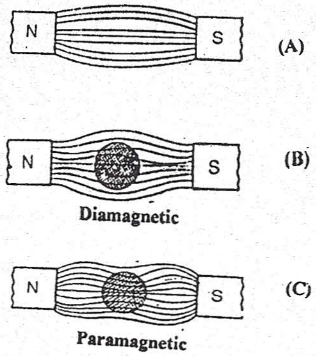

Fig 3.1 Behaviour substances in the applied external magnetic field.

The paramagnetic effect can be observed only in the presence of an externally applied magnetic field. When the external magnetic field is removed, the thermal motion of the molecules randomizes the individual molecular moments and the bulk sample has no overall moment. When the external magnetic field is present, it overcomes the thermal motion of the molecules and force the molecules to orient (Fig. 3.2a). Because of this if the temperature is increased, the paramagnetic property decrease in magnitude. In other words, paramagnetic property is inversely proportional to absolute temperature.

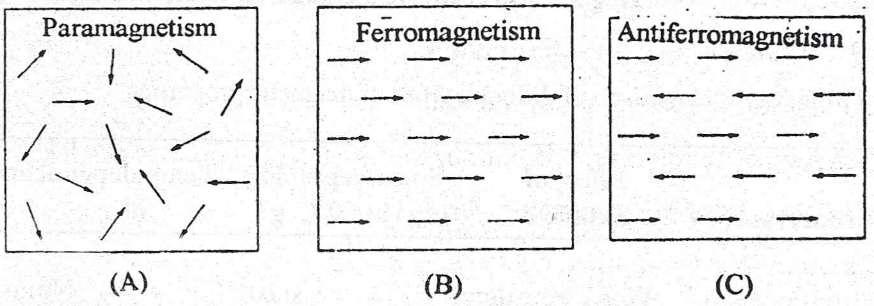

Fig. 3.2 Diagrammatic representations of magnetic dipole arrangements in A) Paramagnetic B) Ferromagnetic and C) Antiferromagnetic materials

There are a few substances such as iron, nickel, cobalt and their alloys which are attracted by the magnets and can also be magnetized. These are called **ferromagnetic** materials. They show all the properties of paramagnetic substances to a much greater degree. If the interacting magnetic moments on neighbouring atoms tend to form a parallel alignment, the substance is said to be ferromagnetic (Fig.3.2b). If on the other hand they tend to form antiparallel arrangement of the coupled spins, they are said to be **antiferromagnetic** (Fig. 3.2c). The effect of temperature on paramagnetic material is given by $\chi_M = K/T$. This expression is known as **Curie's law**. Materials that exhibit magnetic exchange, i.e., from one type to another, there will be some temperature below which magnetic exchange dominates, this temperature is called Critical Temperature (T_C) or **Curie's temperature**. for ferromagnetic materials and **Neel temperature (T_N)** for antiferromagnetic materials. Fig.3.3. gives the effect of temperature on different types of magnetic materials. Table 3.1. gives the comparison of magnetic properties of different types of materials:

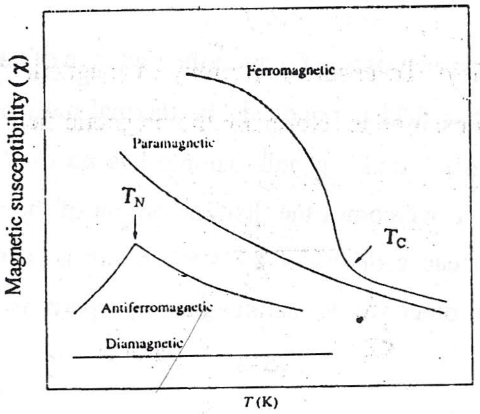

Fig.3.3 Effect of Temperature on different magnetic properties if materials.

Table 3.1 Comparison of different types of magnetic properties.

Property	Effect of Extl.field	Sp.susceptibility (χ) at 20°C g^{-1}	Temp.dependence of χ	Field dependence of χ
Diamagnetism	Weak repulsion	-1 x 10^{-6}	None	None
Paramagnetism	Moderate attraction	100x10^{-6}	1/T	None
Ferromagnetism	Very strong attraction	1 x 10^{-2}	Complex	Dependent
Antiferromagnetism.	Weak attraction	10^{-7} to 10^{-5}	Complex	Dependent

3.1.ii) Gouy's method

It was devised by French scientist Gouy in 1889. It is based on the principle that the magnetic field exerted on the sample when it is placed in an external magnetic field varies directly with its mass (i.e., the difference in mass in the presence and absence of magnetic field).

The Gouy's apparatus (Fig. 3.4.) consist of a microbalance and a magnetic source. The sample in the form of a long cylinder or packed in a cylindrical tube is suspended from one arm of the microbalance in such a way its lower end lies in a string magnetic field, whereas its upper end is in the region of negligible magnetic field. The axis of the cylindrical tube is at right angle to the magnetic field. To ensure uniformity in magnetic field, the two poles of the magnets are placed very close to each other. Normally the magnetic field strength used vary from 5000 to 15000 oersteds.

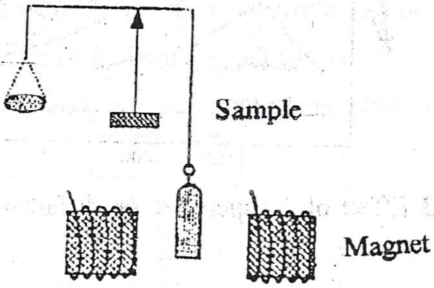

Fig.3.4 Schematic representation of Gouy's method of magnetic Susptibility measurements

The magnetic field experienced by the sample along its length is given by

$$F = \tfrac{1}{2} (K_1 - K_2) (H_1^2 - H_2^2) A \qquad \text{---(3.1)}$$

K_1, K_2 are volume susceptibility of the sample and atmosphere, H_1, H_2 are maximum and minimum fields that the sample experience along its length. A is the cross sectional area of the sample.

In practice the H_2 is made negligible. The K_2 is also made negligible by maintaining an atmosphere of hydrogen or nitrogen. Under this condition the equation 3.1.1. is reduced to

$$F = \tfrac{1}{2} K_1 H_1^2 A = g \Delta w \qquad \text{---(3.2)}$$

where 'g' is the gravitational constant, Δw is the apparent change in weight of the body. In short the weight of the sample is measured in the presence and absence of the magnetic field (W_1 and W_2) from which the 'w' is arrived at.

Metals and alloys are cast or machined into the required cylindrical size and used directly. Powdered samples are packed into a cylindrical glass tube which is generally diamagnetic. It is usual practice to make corrections for the susceptibility of the glass tube. To obtain better accuracy uniform packing must be ensured. Pure liquids and liquid samples are used in glass tubes. Gouy's method is not suitable for gases though some measurements are made on oxygen and other gases/vapours.

The major limitations are, large size samples are required and packing must be done carefully to ensure uniform cross section.

3.1.iii) Faraday Method

In the Faraday's apparatus the magnetic poles are carefully shaped (Fig. 3.5.) so that the value of $H_o(\delta H/\delta \chi)$ is constant over the region that is occupied by the sample. The methodology involved in Faraday method is similar to that of the Gouy's method but for the distinct advantages over the Gouy's method. The sample size is normally in the range of milligrams. The specific magnetic susceptibility is obtained directly unlike the Gouy's method where we get volume susceptibility from which the specific susceptibility to be arrived at involving density which in turn depends on packing of samples.

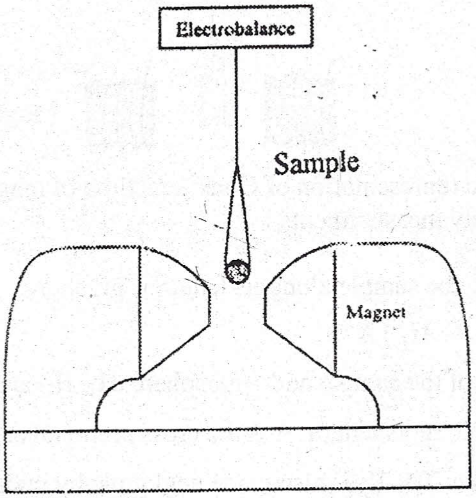

Fig.3.5 Schematic representation of Faraday's method of Magnetic susceptibility measurements

The sample experiencing force f along x I due to field gradient is given by

$$F = (mH_o)\,\delta H / \delta\chi \qquad \text{---(3.3)}$$

The force is measured by weighing the sample both in the field and out of the field and the difference between the two weights is equal to f. In practice it is simplified by the use of a standard reference material (S) such as $Hg[Co(SCN)_4]$ ($\chi = 16.44 \times 10^{-6}\ cm^3 mol^{-1}$) with that of unknown (U) under the same magnetic field and gradient. Thus we have,

$$f_S / m_S \chi_S = f_u / m_U \chi_U \qquad \text{---(3.4)}$$

solving this equation the susceptibility of unknown is obtained.

$$\chi_U = \frac{f_U\, m_S \chi_S}{f_S\, m_U} \qquad \text{---(3.5)}$$

The molar susceptibility of the sample χ M is obtained by multiplying with its molecular weight. From the experimental value of the number of unpaired electrons present in the molecule are arrived at. Though the paramagnetic moment originates from the spin and orbital motions of unpaired electrons of the substance, there are three possible modes of coupling between these components viz., spin-spin, orbital -orbital and spin-orbital interactions. One or more of these contribute to the paramagnetic property. Thus for transition elements spin only values are important whereas for lanthanides and actinides all the three contribute.

3.1.iv) Applications

A) Structure of molecules and simple compounds

Simple molecules like NO, NO_2 and ClO_2 containing an odd electron exhibit paramagnetism under normal conditions. Whereas in the condensed phases NO and NO_2 are diamagnetic consequent on electron pairing and formation of dimeric molecules.

Hydrophosphoric acid, H_2PO_3 supposed to be parmagnetic is actually diamagnetic. This suggests that the correct formula is $H_4P_2O_6$ with all the electrons paired. Similarly dithionates are derivatives of $H_2S_2O_4$ rather than HSO_2 and mercurous chloride to be written as Hg_2Cl_2 rather than HgCl.

Magnetic susceptibility measurements of oxygen in liquid and gaseous state give a value of 2.8 BM suggesting the presence of two unpaired electrons occupying two equivalent orbitals and strongly paramagnetic than the odd electron molecules such as NO, NO_2 and ClO_2. S_2 molecules in the vapour state are also paramagnetic suggesting that its structure is similar to oxygen molecule.

Cupric acetate monohydrate $Cu(CH_3COO)_2\ H_2O$ is expected to be paramagnetic corresponding to one unpaired electron. The observed diamagnetic property suggests that it exists as a dimmer $Cu_2(CH_3COO)_4\ 2H_2O$. X-ray studies of the compound showed the formation of metal –metal bond (2.64 A) consequent on electron pairing and becoming diamagnetic. Similarly $Fe_2(CO)_9$ and $Co_2(CO)_8$ expected to be paramagnetic are diamagnetic suggesting bonding between two metal atoms.

The experimental and calculated values of magnetic moments of a few typical compounds are given in Table 3.2. There is fairly good agreement between the experimental and calculated values. Deviations from certain cases arise from orbital contributions.

Table 3.2. Experimental and calculated magnetic moments of certain compounds.

No.of unpaired Electrons	Compound	Ground state	Experimental μeff	Calculated [n(n+2)]1/2
1	$CsTi(SO_4)_2.12H_2O$	$^2T_{2g}$	1.8	1.73
	$K_4Mn(CN)_6$, $3H_2O$	$^2T_{2g}$	1.8	1.73
	$K_2PbCo(NO_2)_6$	^2E_g	1.8	1.73
	$(NH_4)_2\ Cu(SO_4)_2.6H_2O$	^2E_g	1.9	1.73
	$(NH_4)_2V\ (SO_4)_2.\ 12H_2O$	$^3T_{1g}$	2.7	2.83
2	$Cr(dipy_3Br_2.\ 4H_2O$	$^3T_{1g}$	3.3	2.83
	$(NH_4)_2\ Ni(SO_4)_2.\ 6H_2O$	$^3A_{2g}$	3.2	2. 83
	$K\ Cr(SO_4)_2$ 12H2O	$^4A_{2g}$	3.8	3.88
3	$(NH_4)_2Co(SO_2)_2.\ 6H_2O$	$^4T_{1g}$	5.1	3.88
	$Cr_2(SO_4)_3.\ 6H_2O$	^5E_g	4.8	4.90
4	$(NH_4)_2\ Fe(SO_4)_2\ .\ 6H_2O$	$^5T_{2g}$	5.5	4.90
5	$K_2Mn(SO_4)_2.\ 6H_2O$	$^6A_{1g}$	5.9	5.92

The volume magnetic susceptibility of oxygen is 100 to 1000 times greater than that of other gases except, NO, NO_2, ClO2. Hence it can form a method for the determination of oxygen in air or gases in the absence of above mentioned gases.

B) Transition metals, Lanthanides and actinides

The paramagnetic moments of first row transition elements resulting in high spin and low spin complexes are given in Table 3.3. The paramagnetic moments of lanthanides are given in Table 3.4. In complexes the ligand field effect is small because the 4f orbital lie inside and do not effectively interact with the ligands.

Table 3. 3. Magnetic properties of some complexes of first row transition metals@

		High spin complexes			Low spin complexes		
Central Metal	No.of d electrons	No.of unpaired electrons	μ(expt) BM	μ(calc)* BM	No.of unpaired electrons	μ(expt) BM	μ(calc)* BM
Ti^{3+}	1	1	1.73	1.73	--	--	--
V^{4+}	1	1	1.68-1.78	1.73	--	--	--
V^{3+}	2	2	2.75-2.85	2.83	--	--	--
V^{2+}	3	3	3.80-3.90	3.88	--	--	--
Cr^{3+}	3	3	3.70-3.90	3.88	--	--	--
Mn^{4+}	3	3	3.8 – 4.0	3.89	--	--	--
Cr^{2+}	4	4	4.75-4.90	4.90	2	3.20-3.30	2.83
Mn^{3+}	4	4	4.90-5.00	4.90	2	3.18	2.83
Mn^{2+}	5	5	5.65-6.10	5.92	1	1.80-2.10	1.73
Fe^{3+}	5	5	5.70-6.0	5.92	1	2.0-2.50	1.73
Fe^{2+}	6	4	5.10-5.70	4.90	0	--	--
Co^{3+}	6	4	---	4.90	0	--	--
Co^{2+}	7	3	4.30-5.20	3.88	1	1.8	1.73
Ni^{3+}	7	3	---	3.88	1	1.8.- 2.0	1.73
Ni^{2+}	8	2	2.80-3.50	2.83	--	--	--
Cu^{2+}	9	1	1.70-2.20	1.73	--	--	--

@ Burger,K., Coordination Chemistry, Experimental Methods, Buttterworth, London 1973

*spin only value

Table3. 4. Magnetic properties of some compounds of the lanthanide metals*

Central Metal	No.of f electrons	Ground state	Compound	μ(expt) BM	μ(calc)@ BM
Ce^{3+}	1	$^2F_{5/2}$	$Ce_2Mg_3(NO_3)$6.24H2O	2.28	2.54
Pr^{3+}	2	$^3H_4$	Pr2(SO4)3.8H2O	3.40	3.58
Nd^{3+}	3	$^4I_{9/2}$	Nd2(SO4)3.8H2O	3.50	3.62
Sm^{3+}	5	$^6H_{5/2}$	Sm2(SO4)3.8H2O	1.58	1.6#
Eu^{3+}	6	$^7F_0$	Eu2(SO4)3.8H2O	3.42	3.61#
Sm^{2+}	6	$^7F_0$	SmBr2	3.57	3.61#
Gd^{3+}	7	$^8S_{3/2}$	Gd2(SO4)3.8H2O	7.91	7.94
Eu^{2+}	7	$^8S_{3/2}$	EuCl2	7.91	7.94
Tb^{3+}	8	$^7F_6$	Tb2(SO4)3.8H2O	9.50	9.72
Dy^{3+}	9	$^6H_{15/2}$	Dy2(SO4)3.8H2O	10.4	10.63
Ho^{3+}	10	$^5I8$	Ho2(SO4)3.8H2O	10.4	10.60
Er^{3+}	11	$^4I_{15/2}$	Er2(SO4)3.8H2O	9.4	9.57
Tm^{3+}	12	$^3H_6$	Tm2(SO4)3.8H2O	7.1	7.63
Yb^{3+}	13	$^2F_{7/2}$	Yb2(SO4)3.8H2O	4.86	4.50

* Figgs,B.N In Comprehensive coordination Chemistry, Wilkinson, G.,

et.al.,Pergamon, N,Y., 1987, vol.1. p.261.
@ g[J(j+1)]1/2 exept where noted.
# calculation includes effects of mixing of ground and higher energy terms.

The magnetic properties of actinides are quite complex. In the case of first row transition elements the effect is mainly based on spin only formula (i.e., the ligand field is large compared to spin-orbit coupling). For lanthanides the spin-orbit coupling is large compared to ligand field effects, whereas in actinides the 5f electrons interact much more with the ligands than 4f electrons of lanthanides. Consequently the spin-orbit coupling and ligand field effects are comparable in magnitude.

C) Metal complexes

$[Fe(CN)_6]^{3-}$The metal complexes have partially filled d/f orbitals depending on its oxidation state, electron configuration and co-ordination number of central metal ion. Magnetic moment measurements can be used a tool to know the oxidation state of metal atom, type of bonding involved and stereochemistry of metal complexes.

In metal complexes, not only the electrons spin and orbitals of central metal atom but also the field arising the co-ordinated ligands is equally important in the distribution of electrons in different orbitals, structure and orientation of molecules. The electron occupancy for possible ground states of a^4, d^5, d^6, d^7 ions in octahedral field is given in Fig. 3.6 resulting in high and low spin complexes.

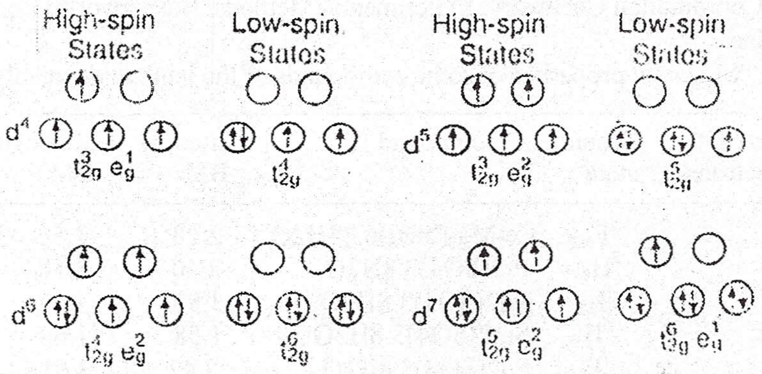

Fig.3.6 Electron occupancy diagrams for possible ground states of a^4,d^5,d^6 and d^7 ions octahedral fields.

Table 3.5. gives the relationship with the number of electrons, effective magnetic moment and molar magnetic susceptibility. Determination of molar magnetic susceptibilities will give an indication on the number of unpaired electrons present in an ion or molecule of study. Thus the values 5.9 and 4.9 BM for Fe^{3+} and Fe^{2+} suggest the presence of five and four unpaired electrons respectively. Similarly, cuprous and cupric ion can be distinguished, because the cupric form is paramagnetic (d^9)

Whereas cuprous (d^{10}) is diamagnetic. Nitroprusides were earlier presumed to contain tri-positive iron coordinated to five CN groups and one NO molecule in $[Fe(CN)_5NO]^{2-}$ and should have evinced paramagnetism due to d^2sp^3 hybridization. But they are all diamagnetic, consequent on the transfer to odd electron from NO to iron and its co-ordination to iron, thereby the oxidation state of iron is 2+ in the complex molecule.

Table 3.5 Effective magnetic moment and molar magnetic susceptibilities.

Number of unpaired electrons	μeff BM	χM (10-6)
1	1.72	1260
2	2.83	3350
3	3.88	6293
4	4.90	10130
5	5.91	14700

D) Bond type:

Measurement of magnetic moments can be used as a tool to differentiate the type of complexes formed by transition metal ions which normally contain a number of un-paired electrons. This can be illustrated in the formation of cyanide complexes of iron, (Fig.3.7) such as ferricyanide $[Fe(CN)_6]^{3-}$ and ferrocyanide $[Fe(CN)_6]^{4-}$ Thus the five unpaired electrons in Fe^{3+} (Fig.3.7B) gives a value of 5.92 BM while that of $Fe(CN)_6]^{3-}$ gives a value of 2.3BM suggesting much less unpaired electrons. This is because on complex formation, the d-electrons of iron undergo pairing as shown in Fig. 3. 7C and the resultant complex contain only one un-paired electron, The bonding involved d^2sp^3 hybridization wherein the six cyanide ligands form a co-ordinated linkage with the central metal ion, iron. In the case of ferrocyanide $[Fe(CN)_6]^{4-}$, there is one more electron than in the ferricyanide, which pairs with un-pairedd-electron and give the structure Fig.3.1.7./D. As there is no unpaired electron, it is diamagnetic, though the type of bonding is same ie., d^2sp^3 hybridizaation. These complexes also known as **inner-orbital complexes**, because d-orbitals involved in the bonding process are in the lower shell than the s and p-orbitals.

$Co(NH_3)_6^{3+}$, $Mn(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Cr(CN)_6^{4-}$ complexes evince structures similar to that of ferri- and ferro-cyanides.

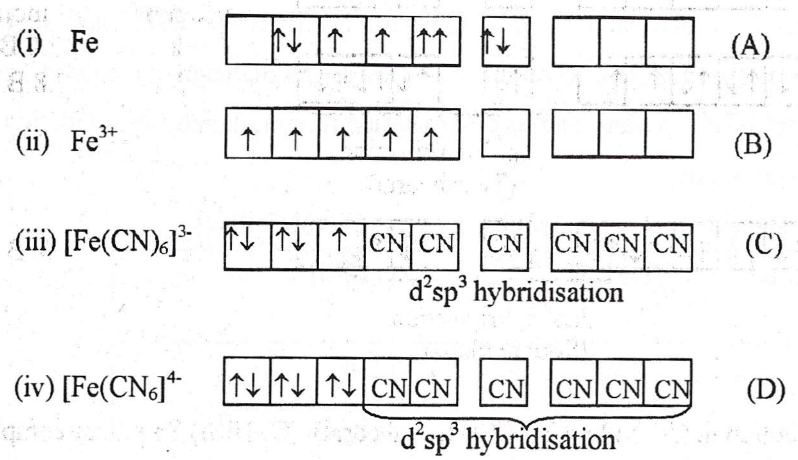

Fig.3.7 Electron distribution in (A) Fe (B) Fe^{3+} (C) Ferrocyanide and (D) Ferrocyanide

Ferricfluoride ion, $[FeF_6]^{3-}$ also forms an octahedral complex similar to that of ferri-and ferrocyanide ions. But its magnetic moment value is of 6 corresponding to five un-paired electrons. It is because the outer d-orbitals are involved in the bonding process, (sp^3d^2) rather than the inner d-orbitals. (Fig. 3.1.8). This type of complexes are called **outer orbital complexes.** CoF_6^{3-}, $Fe(NH_3)_6^{2+}$, $Cu(NH_3)_6^{+}$ also form similar outer orbital complexes.

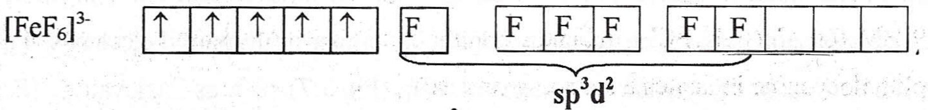

Fig 3.8. Electron distribution in $[FeF_6]^{3-}$ resulting in an outer orbital complex.

E) Stereochemistry

Magnetic measurements can also be used for the study of stereochemistry of transition metal complexes. For instance, the divalent nickel which contains two unpaired electrons in its 3d orbitals (Fig 3.9A), co-ordinate with four ligands in two different ways to form stereochemically different structures. Thus on sp^3 hybridization, the bonds are tetrahedrally arranged, the two electrons in the 3d orbitals remain unpaired (Fig.3.9B) and evince paramagnetism. Whereas on dsp^2 hybridization, it forms a square planar complex

wherein all the 3d electrons are paired(Fig.3.9C) and the molecule exhibit diamagnetism. The striking difference in magnetic properties forms an effective tool to know how the ligands are arranged around the metal atom. $Ni(NH_3)_4SO_4$, $Ni(N_2H_4)_2SO_4$ and nickel bisacetylacetonate form tetrahedral structure. $K_2Ni(CN)_4$, nickel glyoxime, nickel phthalocyanine form planar complexes.

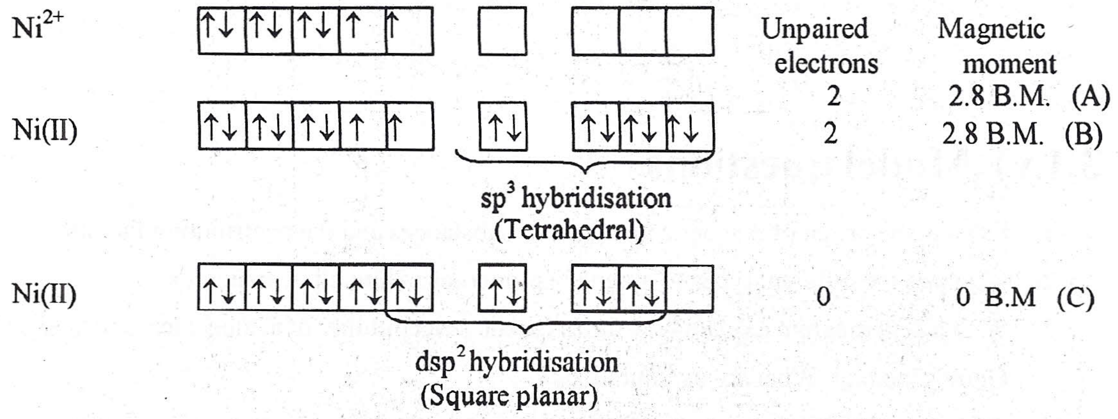

Fig 3.9 Electron distribution in (A) Ni2+ (B) Ni(II) (tetrahedral) (C) Ni(II) Sq.planar complexes

Similar to nickel, the divalent cobalt having three unpaired electrons (Fig.3.1.10A) form tetrahedral (sp^3) and square planar (dsp^2) complexes with different ligands.. In the case of tetrahedral complex only s and p orbitals are involved in bonding and the three electrons in the d-orbitals remain unpaired as in the of free Co^{2+} (Fig.3.1.10B) and show a magnetic moment of about 3.9 BM. In the case of square planar complex,

one of the d-orbitals is involved in bonding, consequently pairing of electrons take place and only one electron remain un-paired (Fig.3.1.10C) and show a magnetic moment of 1.7. Thus the magnetic moment of 3.9 BM for Co(N$_2$H$_4$)$_2$Cl$_2$ indicates a tetrahedral structure whilst a moment of 1.7 BM for cobaltous phthalocyanine indicates a square planar structure.

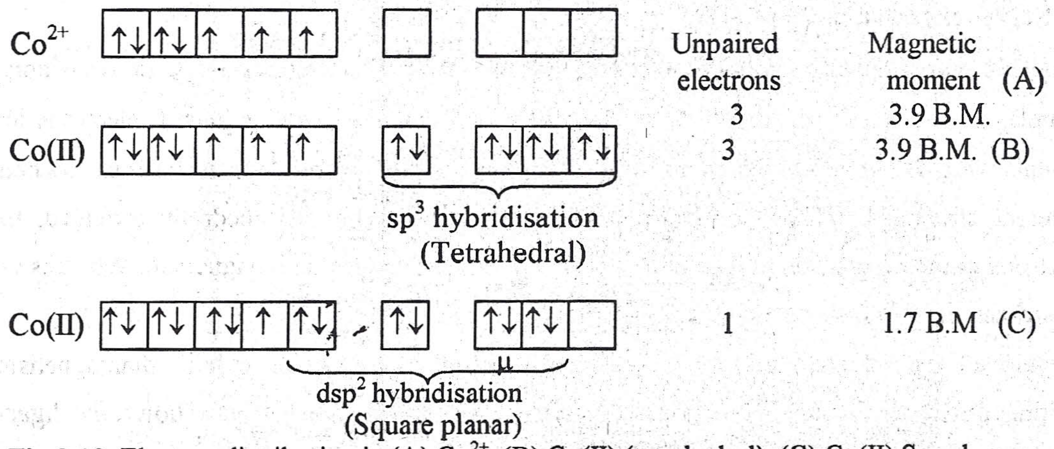

Fig 3.10. Electron distribution in (A) Co^{2+} (B) Co(II) (tetrahedral) (C) Co(II) Sq. planar complexes.

3.1.v) .Model questions

1. Explain the origin of magnetic moments of substances and the contributing factors.
2. What are the different types of magnetic properties exhibited by materials?
3. With a neat diagram explain how the magnetic susceptibility of a substance is measured by Guoy's method. What are its limitations?
4. With a suitable diagram explain the Faraday method of determination of magnetic susceptibility. What are its advantages over the Gouy's method?
5. Illustrate the applications of magnetic measurements in the following: (i) Simple molecules (ii) dimeric compounds (iii) structure of simple molecules (iv) high spin and low spin complexes (v) Structure of metal complexes (vi) stereochemicy of molecules.

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2. Advanced Inorganic Chemistry, Cotton and Wilkinson.
3. Advanced Inorganic Chemistry, Gurdeep Raj., Vol.-II Goel Pub. House (2002).

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LESSON-II. NMR SPECTROSCOPY

Objectives:- Introduction – Principle – Basic Instrumentation – Chemical shifts – Spin-Spin coupling - Applications.

3.2.i). Introduction

In molecules, the electronic energy levels are quantized. With the help of UV-visible, IR, Raman and rotational spectroscopy we study the electronic, vibrational and rotational transition of electrons in the molecules and arrive at the molecular structure. This process involves absorption at specific radiations of appropriate energy and transition of electrons in the quantized energy levels. Similar to this, the energy levels of nucleus are quantized and degenerate under normal conditions. However, the degeneracy is removed and the energy levels are split under the influence of external magnetic field. The resultant spin of the nucleus can absorb energy in the radiofrequency region and result an absorption spectrum. Such a spectrum is called **Nuclear Magnetic Resonance Spectrum.** From this we can derive information on the type of bonding involved and the structure of molecules, etc.

3.2.ii). Principle

Atoms in molecules have a nucleus at the center with electrons occupying the extranuclear space. With the components of nucleus, namely protons and neutrons, the nuclei are positively charged, but in addition some of them have the property of spinning. The spin is characteristic of nuclei and defined by spin angular momentum quantum number. It is the vector sum of the individual spin angular momentum of the neutron and protons. If the nucleus has a spin angular momentum $I \neq 0$, it corresponds to a spinning positive charge and possess a magnetic moment, μ. Nuclei having even number of protons and neutrons have $I = 0$ (Eg. ^{4}He, ^{12}C, ^{16}O, etc.,) and are spherical and non-spinning. Nuclei having odd values for the sum of protons and neutrons have half integral values $I = \frac{1}{2}$ (Eg. ^{1}H, ^{15}N, ^{11}B, ^{19}F ^{31}P, etc.,) constitute a spherical spinning nucleus. Such a nuclei can be considered as a bar magnet and spinning on its axis. Its interaction with the external magnetic field produces torque. This causes the magnetic moment of the nuclei to precess about the applied field. The angular frequency of precision is refereed as Larmor frequency (ω),whose magnitude depends on field strength applied (H_0) and the spin angular momentum.

9)

$$\omega = \gamma H_0$$

where γ is gyromagnetic ratio which is a constant for a given nuclei. It represents the ratio of the nuclear magnetic moment to the nuclear angular momentum. Such nuclei precess in a strong homogeneous magnetic field. Energy comparable to it (ΔE) is imposed with a radiofrequency transmitter. When the applied frequency is equal to Larmor frequency the two are said to be in resonance and the energy can be transferred to and from and absorption takes place. The absorption is measured with the help of a detector, processed and recorded.

3.2.iii). Basic instrumentation

The NMR spectrometer is schematically presented in **Fig.3.11**. The basic components are magnet, radio frequency source, detection system and a recording device. The magnetic field is generally varied from 0 – 23,000 gauss. Homogenicity of the magnetic field is critical and must be maintained 1 part in 60 million. A small amount of the sample is dissolved in a suitable solvent and taken in a glass tube (0.5 mm dia and 15 cm. Long) is placed between the poles of magnet. The sample tube is rotated to ensure uniform magnetic field on all the nuclei of the sample.

Crystal oscillators are used to obtain the desired radiofrequency. Suitable radiofrequency is applied, the nuclei absorb the energy, which is detected and recorded. For absorption of energy by the nuclei, the energy of the radiofrequency source should match with that of the nuclei. This is achieved by (i) either keeping the frequency constant and varying the magnetic field strength (ii) or keeping the magnetic field strength constant and varying the radiofrequency and record the resonance position. .In most of the instruments the frequency source is fixed and the magnetic field is varied till the resonance condition is reached. Since most of the compounds contain proton, the solvents used must be free from protons, such as CCl_4, $CDCl_3$, C_6D_6, D_2O, $(CD_3)_2SO$, CS_2, etc.

There are two types of NMR, viz., continuous wave method or pulse method (Fourier Transform method). The instruments range from 60 to 600 MHz, type depending on its resolving power. High resolution NMR is used to resolve fine structures.

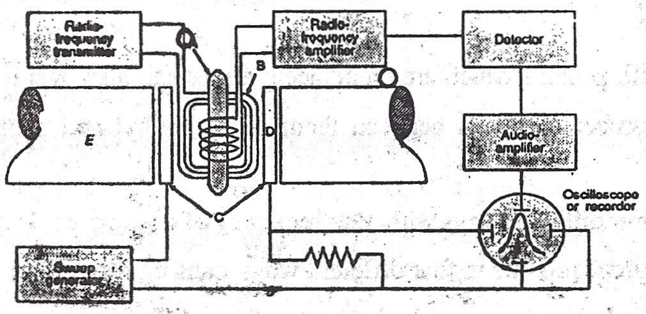


Fig 3.11 NMR spectrometer.

3.2.iv). Chemical shifts

Accurate measurement of H_N (unknown nuclei) and H_0 is difficult. Hence a reference material is employed. Thus,

$$H_S - H_R = H_0 (\sigma_R - \sigma_S)$$

where subscript S and R correspond to sample and reference material, while σ is the screening constant. In other words,

$$\sigma_R - \sigma_S = H_S - H_R / H_R = \delta \quad \text{(Chemical shift)}$$

Positive value of σ means that the nuclei are shielded by the electronic environment, while the negative σ corresponds to deshielding of the nucleus. Thus if a same nucleus is under different chemical environment, (i.e., different electron density) resonate at different values of applied field. These values are characteristic and can be used to identify the various types of chemical environment in which the nucleus is present. Since the shift in position of resonance is due to difference in chemical environment, it is called **Chemical Shift** (δ). The shift in field or frequency is nearly 10^6 times smaller than the measuring field or frequency, the value is therefore multiplied by 10^6 and expressed in terms of ppm.

Since we cannot measure the resonance of bare nuclei, a reference material, such as tetramethyl silane, $(CH_3)_4Si$ (TMS) is used. The TMS contains 12 protons, all of which are chemically equivalent, highly shielded and gives a strong NMR signal at higher field., compared to most of the organic compounds. The NMR spectrum of ethanol having protons under three different chemical environ ment, (the least shielded -OH proton, more shielded $-CH_2$ protons and most shielded $-CH_3$ protons) is presented in **Fig. 3.12**. in comparison with the reference material TMS. The least shielded protons appear in the lower field strength compared to TMS.

3.2.v). Spin-spin coupling

Apart from the phenomenon of chemical shift, protons which are on adjacent atoms can also interact with each other depending on the nature and number of bonds between them. Thus methyl and methylene protons can orient in the following manner:

The spin of methyl protons can orient in four different ways with the frequency of occurrence 1: 3 : 3: 1 and interact with the neighbouring methylene protons in four different ways, causing four peaks in the intensity ratio 1 : 3 : 3 : 1. Similarly the methylene protons which orient in three different ways will

Methyl protons

	Spin quantum number (I)	Frequency of occurrence/ Intensity
↑↑↑	+ 3/2	1
↑↑↓ ↑↓↑ ↓↑↑	+ 1/2	3
↓↓↑ ↓↑↓ ↑↓↓	- 1/2	3
↓↓↓	- 3/2	1

Methylene protons

	Spin quantum number (I)	Frequency of occurrence/ Intensity
↑↑	+ 1	1
↑↓ ↓↑	0	2
↓↓	- 1	1

interact with the methyl protons in three different ways causing three peaks in the intensity ratio 1 : 2 : 1, vide **Fig.3.12.** The influence of -CH_2 protons on –OH proton would have caused a triplet. But due to rapid exchange spin-spin coupling was not observed and only a single peak is observed. The fine structure or splitting of lines is due to coupling between the neighbouring group protons. This process is called spin-spin coupling and gives rise to fine structure of the molecules. Spin-spin coupling range between few Hz to tens of Hz depending on the hybridization of the bonds involved and the number of bonds intervening the two coupled nuclei under consideration. Thus in ^1H – NMR spectrum, n equivalent protons will split a signal into n + 1 lines.

3.2.vi). NMR of nuclei other than protons

Apart from proton there are more than 200 isotopes have magnetic moments and can be studied by NMR. ^{13}C, ^{15}N, ^{17}O, ^{19}F, ^{31}P and ^{11}B are some of the most important nuclei in the field of study of complex molecules. ^{19}F, ^{31}P are abundant in this state. Their spectra can be analysed in terms of their characteristic chemical shifts and spin-spin coupling to the neighbouring nuclei, in the same way as protons. The natural abundance of ^{13}C is 1.1% and studied by high resolution NMR. Unlike proton NMR, 13C NMR gives information on the skeletal structure of hydrocarbons.

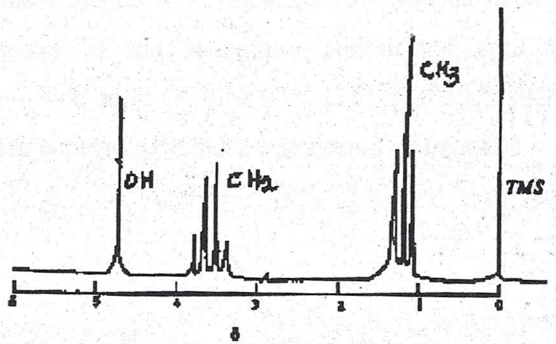


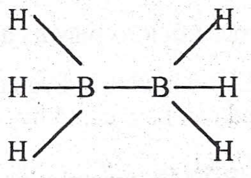
Fig .3.12. Hyperfine NMR spectrum of ethanol.

3.2.vii). Applications

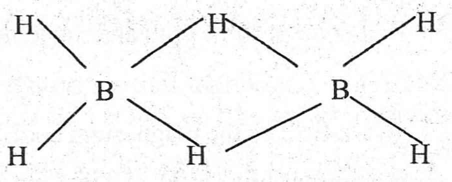
NMR spectroscopy is extensively used for the study of structure of organic molecules and their reaction mechanism and related properties. The following illustrate the application of NMR in the study of inorganic compounds, their bonding and structures, their reactions, reaction mechanisms, etc.

A). Hydrogen bonding: For -OH group, the shift is concentration and temperature dependent. In pure ethanol, it appears in the down field. In CCl_4 the chemical shift is varied to about 5 ppm from concentrated to dilute solution, and when extrapolated to infinite dilution the -OH proton appear in the higher field than methyl proton in contrast to ethanol spectrum. This change is due to hydrogen bonding variation as there is more hydrogen bonding in concentrated solution than in dilute solution. This effect reduced the screening of proton causing a shift to lower field. This effect is used to verify the existence of steric effects in hydrogen bonding and also to verify the inter- and intra-molecular hydrogen bonding.

B). Structure of B_2H_6: NMR spectrum of diborane gives two groups of resonance lines for the protons.



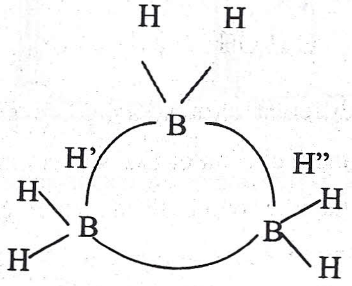
Structure (a)



Structure (b)

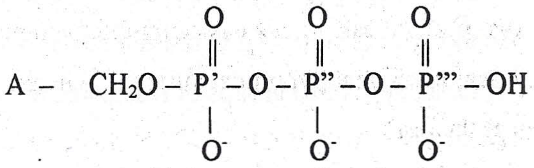
The structure (a) contains two equivalent BH_3 units and expected to give a single resonance line. Whereas the structure (b) has two bridged protons for four terminal protons and is expected to give two different resonance lines. Structure (b) is confirmed by NMR studies.

C). Structure of $B_3H_8^-$: ^{11}B NMR spectrum of $B_3H_8^-$ gives a nonent resulting from three equivalent borons and eight equivalent protons. The mobile protons, H’ and H” exchange fast with the bonded protons, thereby all the eight protons are bonded equally with the three boron atoms. The equivalence of eight protons suggest that there is a fast intra-molecular exchange of protons in the molecule.



D). ^{13}C spectra of CO_2 in water: Carbon dioxide dissolves in water to form, CO_2(sol), H_2CO_3, HCO_3^- and CO_3^{2-}. Four different ^{13}C NMR signals would result if all the forms are stable. Only two peaks appear on the spectrum, one corresponding to dissolved carbon dioxide and other due to all the remaning species. Single peak for the species, H_2CO_3, HCO_3^-, CO_3^{2-} suggests that there is a rapid exchange among the species. Since half life of the reaction, $CO_2 + H_2O \rightarrow H_2CO_3$ is about 20 sec., a separate peak is obtained for dissolved carbon dioxide.

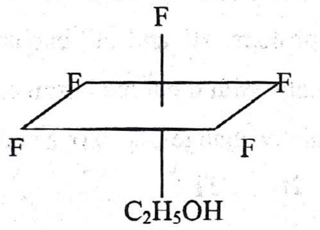
E). Adinosine triphosphate (ATP) , a triply charged anion plays a vital role in carbohydrate metabolism and in energy storage and release in the body.



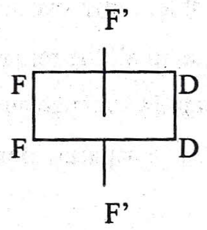
$$\mathrm{A-\ CH_2O-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P'}}-O-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P''}}-O-\underset{\underset{O^-}{|}}{\overset{\overset{O}{\|}}{P'''}}-OH}$$

ATP in aqueous environment gives 3 sets of peaks corresponding to 3 phosphorus atoms: P” a triplet around 23 ppm, P’ a doublet at 14 ppm and the terminal p’’’ at 11 ppm. Magnesium ions play a part in the metabolic role of ATP. Magnesium forms a complex with the ionic part of ATP which is indicated by the chemical shift to down field as the magnesium concentration is increased.

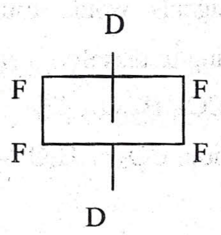
F). Equimolar concentrations (1: 1) of TiF_6^{2-} and TiF_4 in ethanol gives ^{19}F NMR spectrum consisting of 2 peaks with intensity ratio 4 : 1 (doublet and quintuplet respectively) constituting an octahedrally co-ordinated titanium of the structure $[TiF_5(C_2H_5OH)]^-$ wherein four F^- occupy the planar position and the fifth F^- the apex at right angles to the plane and the solvent molecule ethanol at the sixth position. Thus it constitutes two sets of fluorine atoms in the molecule resulting the above mentioned spectrum.



In donor (D) solvents TiF_4 shows different structures that are temperature dependent. Thus at –30 °C it assumes a octahedral structure with the inclusion of two solvent molecules, wherein two F^- and 2 solvent molecules occupy one plane, while the other two F^- lie at right angles to it. Hence it gives rise to 2 triplet peaks of equal intensity corresponding to 2 sets of non-equivalent F atoms. However at 0 °C, it gives a single peak consequent on fast exchange and resulting an octahedral structure but with all the four F lying in one plane and the two solvent molecules at the apex of octahedra.

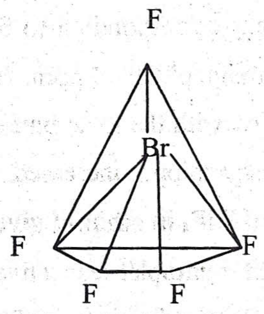


Cis form at –30 °C
(2 triplet peaks)

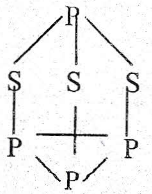


Trans form at 0 °C
(single peak)

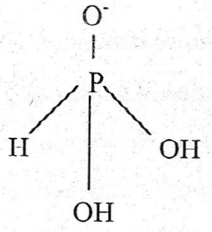
G). Fluorine resonance of **BrF_5** gives rise to two peaks. Peak 1, a weak quintuplet and peak 2 an intense doublet in the ratio 1:4. This suggests symmetrical tetragonal pyramidal structure wherein the Br is at the center, four F atom at the base and one F atom at the peak.



H). **^{31}P** resonance in **P_4S_3** cause 2 peaks with intensity ratio 3:1 (doublet and quintuplet respectively) suggesting a structure containing 3 equivalent P and one non-equivalent P.

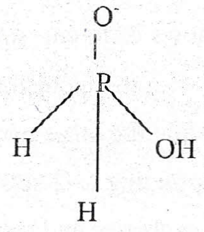


The phosphorus resonance results the following in the phosphorus compounds:



HPO (OH)$_2$

Doublet



H$_2$PO (OH)

Triplet

The coupling of hydroxyl protons with P is either too small to be resolved as they are far removed or does not happen due to fast proton exchange reaction.

Similar results were observed with FPO(OH)$_2$ and F$_2$PO(OH) as the Fluorides are attached to P in place of H.

I). Rhodium complex: H Rh(CN)$_5^{3-}$ gives a doublet at 15.6 ppm on the high field side of water. The splitting and shift established the existence of bond between Rh and H.

J). Poly acids: The structure and NMR spectrum of W$_6$O$_{19}^{2-}$ are presented in **Fig. 3.13a.** There are 12 bridging oxygen atoms (B), one encapsulated oxygen (A) and one terminal oxygen (C) in the unit molecule of W$_6$O$_{19}^{2-}$ giving the NMR signal in accordance with it. The organometallic derivative of the above [(Cp)Ti W$_5$O$_{18}$]$^{3-}$ contains six different kinds oxygen atoms, A, B, C, D, E and F (**Fig. 3.13b).** . In comparison with that of W$_6$O$_{19}^{2-}$, reasonable assignment can be made for the appearance of NMR signal. Thus E and F corresponds to terminal oxygens, A - encapsulated oxygen, C and B - bridging oxygens and D – the remaining oxygens.

K). Study of fluxional molecules: Temperature dependent inter-conversion process of fluxional molecules are easily followed on NMR time scale as a function of temperature. The proton NMR spectra of (η^1-C$_5$H$_5$)$_2$(η^5C$_5$H$_5$)$_2$Ti from 62°C to –27°C (**Fig.3.14.)** illustrates these phenomena. The crystal structure of the molecule (η^1-C$_5$H$_5$)$_2$(η^5C$_5$H$_5$)$_2$Ti show two monohapto and two pentahapto cyclopentadienyl rings. In keeping with this, two separate resonance lines were obtained at lower

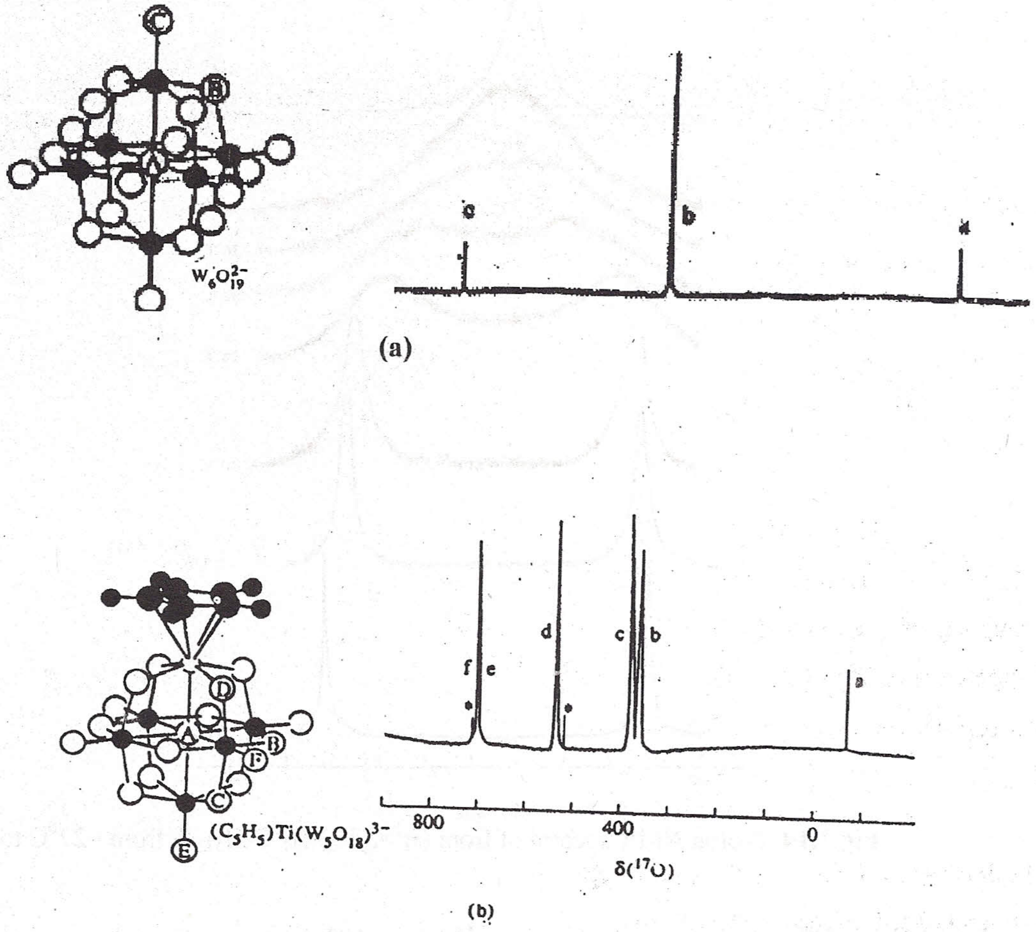


Fig 3.13 Structure and ^{17}O NMR spectrum of (a) $[W_6O_{19}]^{2-}$ and (b) $[(C_5H_5)Ti(W_5O_{18})]^{3+}$

temperature for the two types of Cp rings at lower temperatures that gradually broadens and forms a single peak due to inter-conversion as the temperature is increased from - 270C to 62°C.

L). Allyls and allenes also show fluxional process. For the π complex formed between tetramethyl allene and tetracarbonyl iron **(Fig. 3.15.)** the Proton NMR spectrum below –60°C show three peaks in the ratio 1: 1: 2 corresponding to three cis hydrogen atoms, three trans hydrogen atoms and six hydrogen atoms in a plane perpendicular to the carbon – iron bond. As the temperature is increased the spectrum collapse to a single line for the average environment of 12 hydrogens, due to the migration of iron over the allene π system.

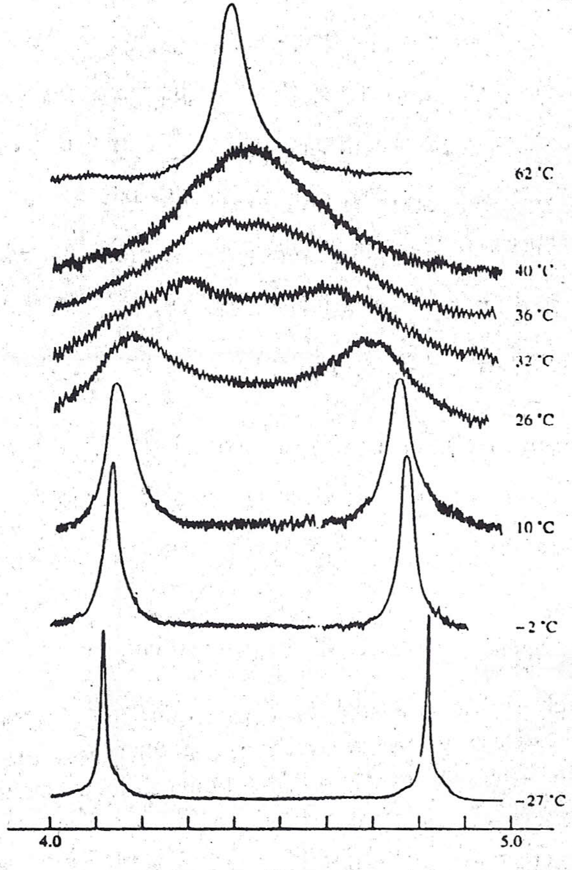


Fig.3.14 Proton NMR spectra of from (η^1-C_5H_5)$_2$($\eta^5C_5H_5$)$_2$Ti from –27°C to + 62°C.

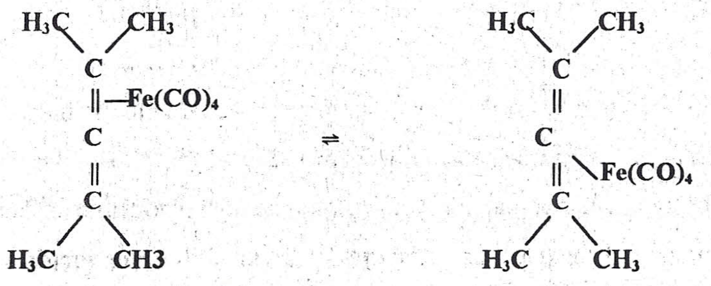


Fig.3.15 Migration of iron in tetracarbonyltetramethylalleneiron (0)

M). Orgnometallic clusters: In organometallic clusters, the ligands appear to move over the surface of the metal frame work. For example in triosmium complex, $Os_3(CO)_{10}$ ($\mu_3 - \eta^2$–CH_3CH_2 C ≡ CCH_2CH_3) the allene move over surface metal triangle **(Fig. 3.16.)** at higher temperature but remain fixed at lower temperature. The proton NMR spectrum of this complex is presented in **Fig. 3.17.** At –65 °C we get 2 equivalent ABX_3 spin systems. With increasing temperature, the multiplet signals broaden and form a single quartet due to free movement of alkyne.

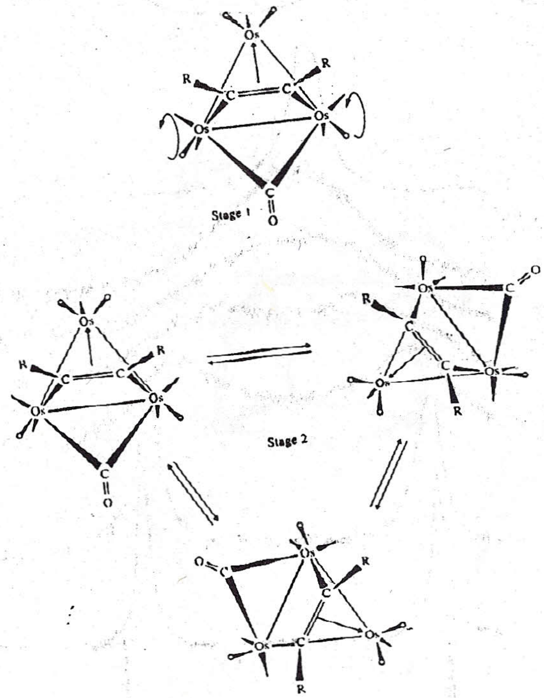


Fig.3.16. Fluxional behavior of $Os_3(CO)10$ (μ_3-η^2-$CH_3CH_2C \equiv CH_2CH_3$). In stage 1, terminal carbonyl groups are exchanging. In stage 2, the alkyne ligand moves about the triosmium surface while carbonyl shifts to remain tans to it.

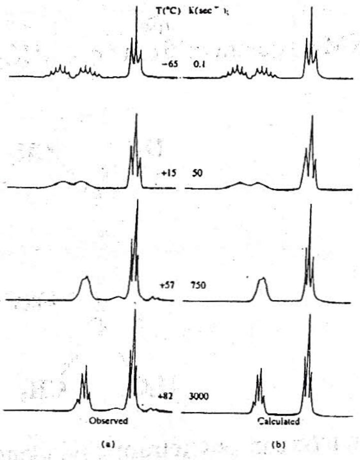


Fig. 3.17 Observed (a) and simulated (b) proton NMR spectra at different temperatures. For $Os_3(CO)_{10}$ (μ_3-η^2-$CH_3CH_2 = CCH_2CH_3$)

N). Polynuclear metal system: $[(CH_3C_5H_4)_4Ru_4S_4]^{2+}$ consist of a distorted cuane-like structure with three Ru-Ru bonds in the crystalline state **(Fig. 3.18).** At low temperature, two lines of equal intensity for the methyl protons and eight lines for the cyclopentadienyl ring protons are obtained, **Fig.319.** The methyl and ring protons resonance over over the temperature –43 °C to +70 °C and the complex undergo a dynamic process involving metal-metal bond.. The single peak form at higher temperature is attributed to the Ru-Ru bond mobility.

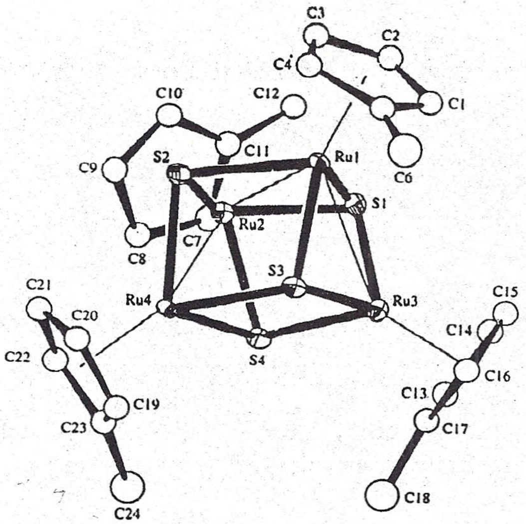


Fig.3.18 Structure of $[(CH_3C_5H_4)_4Ru_2S_4]^{2+}$

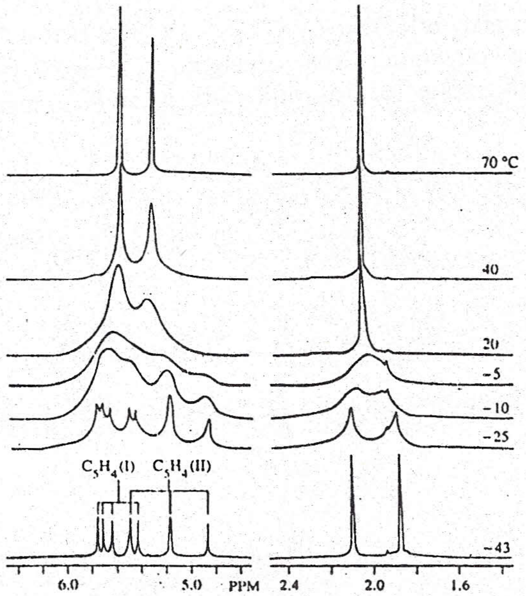


Fig.3.19. NMR spectra of $[(CH_3C_5H_4)_4RuS_4]^{2+}$

O). Nonrigidity of molecules: NMR spectroscopy is conveniently used to study the stereochemial non-rigidity of molecules such as cyclopentadienyl diironcomplex containing bridging vinylcarbyne(**Fig. 320.**). Three distinct rotational motions involving the bridging ligands (i) rotation of the entire vinylcarbyne ligand (44.3 kJ mol^{-1}.) (ii) rotation of dimethylamino group (45.6 kJ mol^{-1}. and (iii) rotation of aryl group (54.3.kJ mol^{-1}.) were established by NMR studies.

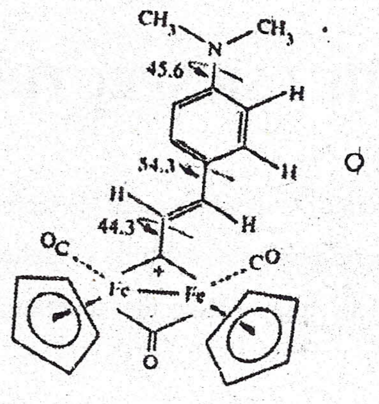


Fig.3.20. Energy barriers for the three separate types of rotational motion involving a bridging vinyl carbine ligand.

3.2.viii). Model questions

1. Explain the basic principle involved in NMR spectroscopy.
2. With suitable diagram, explain how NMR spectrum is recorded.
3. What is Chemical shift?
4. What is spin-spin coupling? Illustrate its importance in the study of fine structure of molecules.
5. With suitable example explain how the NMR study is useful in the following: in inorganic chemistry: (i) Simple compounds (ii) Molecular structure (iii) fluxional molecules (iv) organometallic complexes v) allyls and allenes.

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2. Fundamentals of Molecular Spectroscopy, Banwell, TataMcGrawhill (1979)
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4. Advanced Inorganic Chemistry, Gurdeep Raj., Vol.-II Goel Pub. House (2002).

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LESSON - III. ESR SPECTROSCOPY

Objectives :- Introduction - Principle - Significance of 'g' factor - Basic Instrumentation - Presentation of spectra-Hyperfine splitting - Applications - Simple compounds - Metal complexes - Anisotropy - Molecular tumbling.

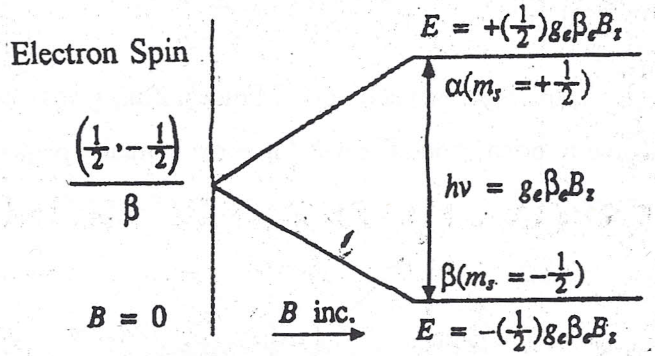
3.3.i). Introduction

Similar to that of ^{1}H nucleus, which possess spin and hence the magnetic moment, the electron with its spin is paramagnetic and possesses a magnetic moment. Like the proton, the electron precess in an applied magnetic field and undergo transitions between the spin states, and absorb energy in the microwave region. Measurement of electron spin transitions is the basis of Electron Spin Resonance Spectroscopy. It is also called as Electron Paramagnetic Resonance (EPR) Spectroscopy and Electron Magnetic Resonance (EMR) Spectroscopy. The magnetic moment of unpaired electron is about 1000 times greater than that of proton, hence the ESR signal is much more sensitive than NMR signal. Substances with unpaired electrons may arise either naturally or produced artificially. Thus the molecules NO, O_2 and NO_2 and ions of transition metals and their complexes come under the first category. They are stable and easily studied by ESR. Unstable free radicals, or radical ions may be formed as intermediates in chemical reactions or by irradiation with UV, X-ray and nuclear particles. Particles with life time of about 10^{-6} Sec. can be studied by ESR.

3.3.ii). Principle

It is an absorption spectroscopy in which the microwave frequency is absorbed by molecules possessing electrons with unpaired spins ($s = ½$), similar to that of nuclear spin absorbing in the radio frequency region in NMR. The spin angular momentum quantum number $m_s = \pm ½$ is doubly degenerate in the absence of magnetic field. When an external magnetic field is applied, the degeneracy is resolved to give rise to low and high energy states, **(Fig.3.21).** The energy of transition is given by

$$E = h\nu = g \beta H_o .$$



Fif. 3.21. Splitting of energy levels of electron spin in the presence of an applied external magnetic field.

where, h – Planck's constant, ν -frequency of radiation, β - Bohr magneton, H_o - the field strength, g- spectroscopic splitting factor. If the system under the above condition is subjected to a radiation of appropriate frequency (resonant energy), the electron absorbs the energy and move from lower energy orientation to higher energy orientation. Generally the source frequency is fixed and the magnetic field strength is varied and the ESR spectrum is recorded in first derivative mode.

The resonant position is referred to as the 'g' value and it is directly determined by the separation of energy levels of the system under study. The variation of 'g' value is interpreted in terms of spin-orbit interactions The resonance frequency of free electron is 9500 Mhz or 9.51×10^9 Hz.

3.3.iii). Significance of 'g' factor

Every paramagnetic substance is characterized by a unique **'g' value** similar to that of chemical shift value in NMR. The g-factor is a variable quantity and for free electron it is 2.00232. In many free radicals the g-value is close to that of free electron, whereas in metal ions it is greatly different from that of free electron. The magnitude of g-value depends on the orientation of the molecule containing the unpaired electron with respect to the magnetic field. In solution and in gas phase the g-value is averaged over all orientations due to free motion of the molecules, whereas in crystals, the movement is restricted hence orientation is an important factor.. In isotropic systems, directional properties are not encountered. Whereas in anisotropic systems, directional properties play an important role and give different g-values, g_{xx}, g_{yy}, g_{zz} and refereed as g_{11} (g parallel) or $g_\perp$ (g perpendicular) **(Fig. 3.22.)**. In general the g value is measured along the axis of symmetry 'a' and

represented as g_{11} and are designated as g_{zz}. The other two g-values are along the other two principal axes perpendicular to g are called as $g_\perp$ and designated as g_{xx} and g_{yy} . For many crystalline substances, the g-value varies with the orientation of the crystal with respect to the applied magnetic field. Thus the dilute solution of CoF_2 in ZnF_2 gives three values, $g_x = 2.6$, $g_y = 6.05$ and $g_z = 4.1$ due to orientation of crystal in three mutually perpendicular directions with respect to the applied field.

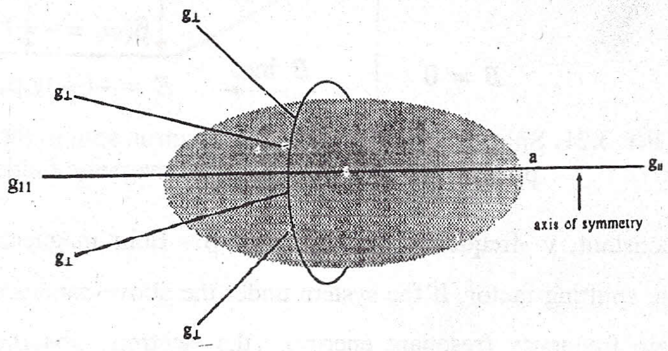


Fig.3.22. Directional properties of anisotropic system.

The **magnitude of splitting** (Coupling constant) depends on (i) ratio of nuclear magnetic moment to the nuclear spin (ii) electron spin density in the immediate vicinity of the molecule and (iii) anisotropic effect In short the chemical environment largely influence the g-value, thereby we come to know about the molecular structure, etc., through ESR spectral studies. The **Table 3.6** illustrates how g-values vary with the nature of the molecules.

Table 3.6. g-values for representative radicals

Free electron	2.00232	$B_{12}Cl_{11}$	2.011
$CH_3^{\cdot}$	2.00255	Fe^{2+} in ZnO	2.0060
$C_2H_5^{\cdot}$	2.00260	Fe^{2+} in MgO	3.4277
$CH_2{=}CH^{\cdot}$	2.00220	Co^{2+} in $ZnSO_4 . 7H_2O$	6.90
$CH_2{=}CHCH_2^{\cdot}$	2.00254	Electron in NH_3	2.0012
$C_6H_5C(CH_3)_2\text{-}O\text{-}O^{\cdot}$	2.015		
$[(CH_3)_2C]_2N^{+}-O^{-}$	2.0058		
$[C6H6]^{\cdot -}$	3.75		

3.3.iv). Basic Instrumentation

The salient features of ESR spectrometer are presented in **Fig. 3. 23.** The **sample** is generally held in a small glass / quartz tube of about 5 mm OD positioned between the poles of permanent magnets. About 0.4 ml of liquid sample is held in the tube. Micro tubes for smaller samples are also available. The **sample probe** holds the energy sweep source and the detector, with facility to rotate the sample at about 4000 rpm in order to average out the effects of inhomogenity in the field and to get sharper lines and better resolution.

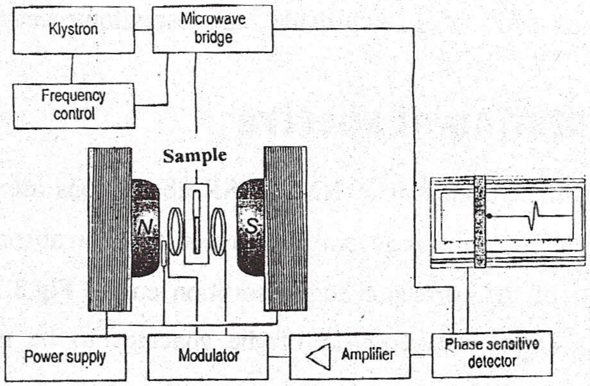


Fig.3.23. Schematic diagram of a continuous wave ESR spectrometer.

Frequency source is a Klystron tube that produces the microwave, energy corresponding to energy of transition of the electron spin. Klystron is an electronic oscillator from which a beam of electrons is pulsed between a cathode and reflector. The oscillating output is transmitted to a wave guide, which in turn transmits the microwave radiation to the sample. Normally a fixed oscillator of 60, 90, 100 MHz is used and its output is plane polarized.

Magnet: The magnetic field used must be homogeneous and reproducible. NMR instruments make use of three kinds of magnets (i) permanent magnet (ii) electromagnet and (iii) super conducting magnets to obtain the required resolution and sensitivity. 60 MHz instrument makes use of 1.4. T **permanent magnet** weighing about 350 Kg. Installation of the magnet is simple and the running cost is zero. **Electromagnets** are used for magnetic field strength up to 2.35 T (100 MHz instrument) and weigh nearly 1000 Kg. This requires water cooling to maintain the temperature plus other operating costs and maintenance. **Super-conducting magnets:** Provide magnetic field strength of 14 T (600 MHz instrument) and give rise to high resolution spectrum. The magnets are immersed in liquid helium (4 °K) (i.e., -269 °C). Compared to permanent and electromagnets, the weight of a super-conducting magnet is much less (about 250 Kg) and power consumption is almost zero. However, the principal running cost is liquid helium.

Detector: The detector coil is positioned at the sample at 90° with respect to the frequency source employed. Two types of detectors are used. (i) Cross coil collectors based on nuclear induction and (ii) single coil collectors based on nuclear absorption. In the single coil method, the microwave source and detector form a single coil with a variable capacitor. Apart from the above basic components, control systems, signal amplifier, processor, storage devices, display devices form the part of the instrument. The pulse or Fourier Transform (FT) ESR spectrometer, make use of pulse microwave source and provide high resolution spectra..

3.3.v). Presentation of spectra

ESR spectra look different from that of NMR. ESR absorptions are broad compared to NMR absorption .spectra. The spectrum is generally not recorded as an absorption spectrum but as first order derivative(slope) of the corresponding absorption curve, **Fig.3.24** The first derivative spectra helps more accurate measurement of the spacings to be made. Use of oscillating magnetic field directly display the spectrum in the derivative mode.

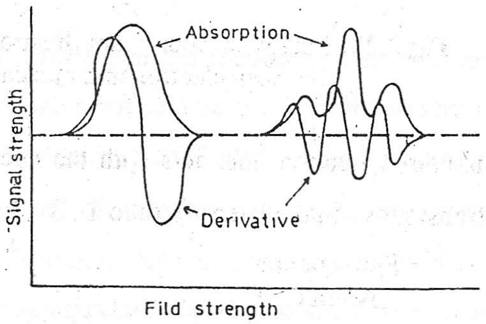


Fig.3.24. Presentation of ESR absorption spectrum in the first derivative mode.

3.3.vi). Hyperfine splitting

ESR causes two kinds of multiple structures. Thus **fine structure** by crystals containing more than one unpaired electron (electron spin – electron spin coupling) and **hyperfine structure** when an unpaired electron can get closer to a nucleus that contains resultant nuclear spin (electron- nuclear spin coupling). In other words, the interaction of magnetic moment of unpaired electron with that of the surrounding nuclear magnetic moment gives rise to hyperfine structure. The coupling is similar to that of nuclear spin discussed in NMR, however electron-nucleus coupling is much larger (MHz) compared to nucleus-nucleus coupling (kHz). It is because, the electron can approach the nucleus very closely and the electron's magnetic dipole is about 1000 times larger than that of a nucleus. The interaction of an unpaired electron with a nuclear spin (i) ½ will give rise to a doublet, **(Fig.3.25.).** (ii)more than ½ will give rise to family tree. Unlike the nuclear spin, the unpaired electron is not confined to one nucleus but moves over several bonds (delocalized) spending only part of the time at any one nucleus. In other words the electron density is varied over the molecule.

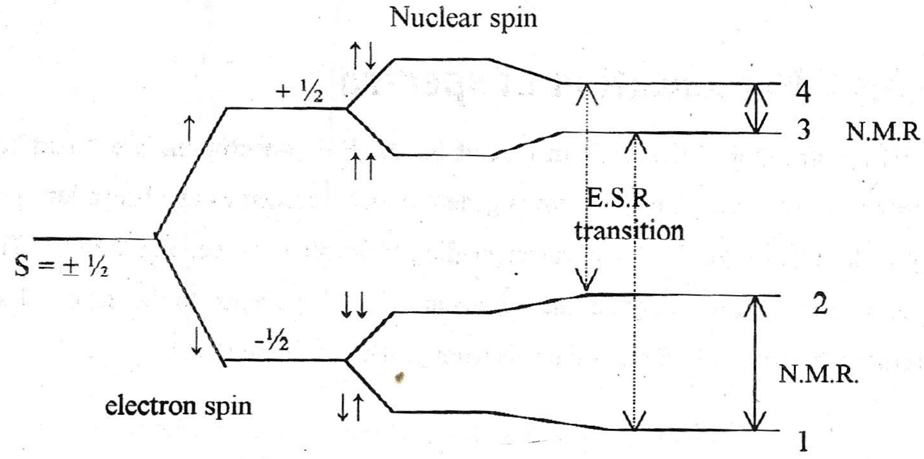
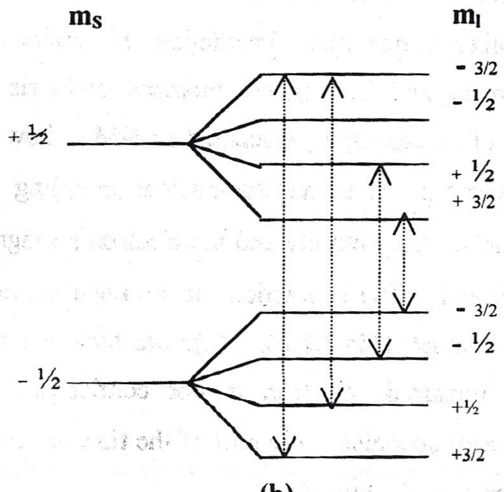


Fig.3.25. Energy level diagram illustrating the coupling between electron and nuclear spins.

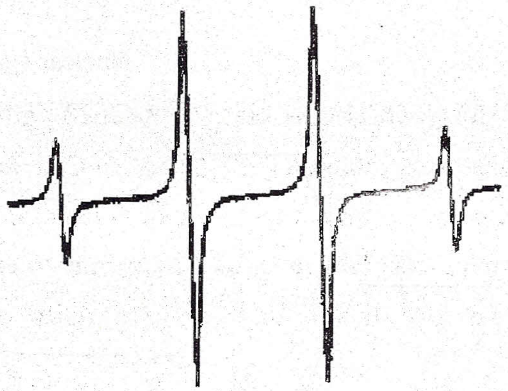
Thus in **methyl radical**, the unpaired electron, interacts with the nuclear spins of three protons and gives rise to a quartet (4 transitions) in the intensity ratio 1 : 3 : 3: 1 **(Fig. 3.26.).**

Methyl protons currence	Spin quantum Number (I)	Frequency of Intensity
↑↑↑	+ 3/2	1
↑↑↓ ↑↓↑ ↓↑↑	+ ½	3
↓↓↑ ↓↑↓ ↑↓↓	- ½	3
↓↓↓	- 3/2	

(a)



(b)



(c)

Fig.3.26. (a) Possible orientation of nuclear spins of methyl radical and the frequency of occurrence.
(b) Interactions of electron spin with nuclear spins of methyl radical.
(c) Resultant ESR spectrum of methyl radical.

Similarly in **benzene radical**, the interaction of one unpaired electron with the nucleus, six equivalent protons give rise to seven hyperfine lines in the ratio 1:2:3:4:3:2:1 **(Fig.3.27)** and **naphthalene radical**, the interaction of unpaired electron with eight equivalent proton nucleus gives rise to 9 lines in the ration of 1:2:3:4:5:4:3:2:1. The appearance of seven equally spaced lines in the benzene radical is a proof that all the hydrogens are equivalent and the unpaired electron couples/interacts equally with all the hydrogens. The electron spin density is directly proportional to the observed hyperfine splitting constant a_H (3.75G).

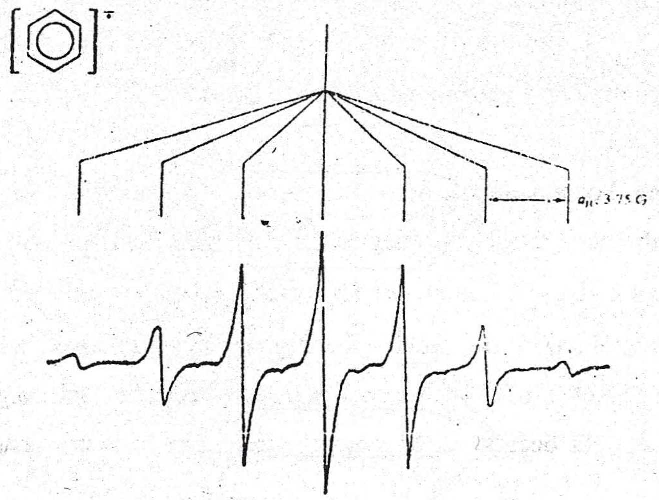


Fig.3.27. The ESR spectrum of benzene radical ion showing hyperfine lines for equal coupling with six protons.

The ESR spectrum of $CH_3CHCOCH_2CH_3$ radical **(Fig.3.28.)** gives various hyperfine splittings that correspond to coupling with protons of CH_3, CH and CH_2 in order of decreasing a_H values. The γ-CH_3 group (terminal) is too distant to contribute further splitting. **Fine Structure** occurs only in substances with more than one unpaired electron due to electron-electron coupling. This type of spectra normally occur only in crystals and particularly compounds containing complex ions.

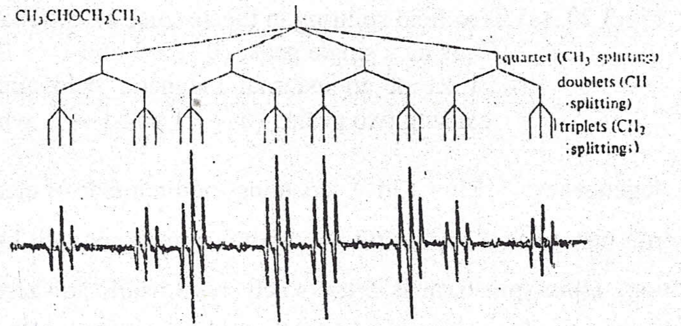


Fig.3.28. ESR spectrum of diethyl ether radical.

A. Splitting in the absence of magnetic field: When a metal ion is placed in a crystal field, the degeneracy of d-orbitals will be resolved by electrostatic interactions. Thus the spin levels are split even in the absence of a magnetic field. This phenomena is called **zero field splitting. If** the species contain odd number of unpaired electrons, the spin degeneracy of every level is doubly degenerate. This is known as **Kramer's degeneracy.** For even number of electrons the spin degeneracy may be removed entirely by the crystal field.

B. Zero field splitting: For a molecule or ion containing 2 unpaired electron $S = 1$, and $m_S = -1, 0, +1$. In the absence of external magnetic field, zero field splitting cause two possible transitions $0 \rightarrow +1$ and $-1 \rightarrow 0$, which are degenerate and we get only one **ESR** signal. But in the presence of external magnetic field , the degeneracy is resolved and we get 2 peaks **(Fig.3.29.).** Thus in Nickel ($3d^8$, $4s^2$) with 2 unpaired electrons, splitting of the ground state, ($^3A_{2g}$) in an octahedral field occurs. In general when spin-orbit coupling is large zero field splitting occurs.

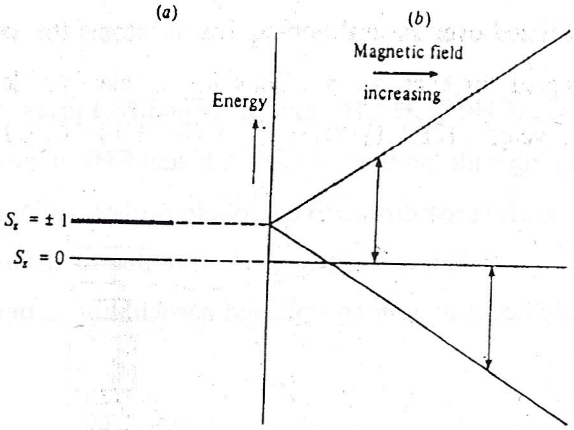


Fig.3.29. (a) Zero field splitting in the absence of external magnetic field Causing a single peak, (0→ + 1 and -1→ 0, that are degenerate)
(b) Effect of an external magnetic field applied and allowed transitions causing two peaks, (0→ +1 and 1→ 0, where degenerach is removed)

C). Kramer' degeneracy: Mn^{2+} ($3d^5$) contains odd number of electrons. It has spherically symmetric electron distribution so that the ^6s ground state is not split by the crystal field. This on zero field splitting (spin-spin term is often solely responsible for zero field splitting). produce three doubly degenerate spin states **(Fig.3.30)**, $m_S = \pm 5/2, \pm 3/2$ and $\pm 1/2$. In the presence of an external magnetic field, each of the above split into 2 singlets resulting 6 levels of 5 transitions (peaks).

-5/2 → -3/2
-3/2 → -1/2
-1/2 → +1/2
+1/2 → +3/2
+3/2 → +5/2

Further, the effect of Mn(II) nuclear spin (I=5/2) cause six hyperfine splitting with varying intensities (greatest intensity for the central line and smallest intensity for the outermost lines).

Rules governing first order hyperfine splitting:

1. If an odd electron is delocalized over n-equivalent protons, a total of n + 1 lines (2n I + 1) will appear in the spectrum.
2. If a radical contains n-nonequivalent protons onto which the odd electron is delocalized, it will give rise to 2^n lines corresponding to 2 spin state ($m_I = \pm ½$) for n-protons.
3. If an odd electron is delocalized over two sets of non-equivalent protons it will give rise to ($2n\ I_x + 1$) ($2m\ I_y + 1$) lines. Thus for 2 sets of 4 equivalent protons it will give rise to 25 lines.

4. If an electron is delocalized over several non-equivalent atoms the expected peaks are the product of the number expected for each atom. Thus for an electron deloclised over 2 non-equivalent nuclei with $I = 1$, we get , $(2I_x + 1)(2I_y + 1) = (2 \times 1 + 1)(2 \times 1 + 1) = 9$ lines.

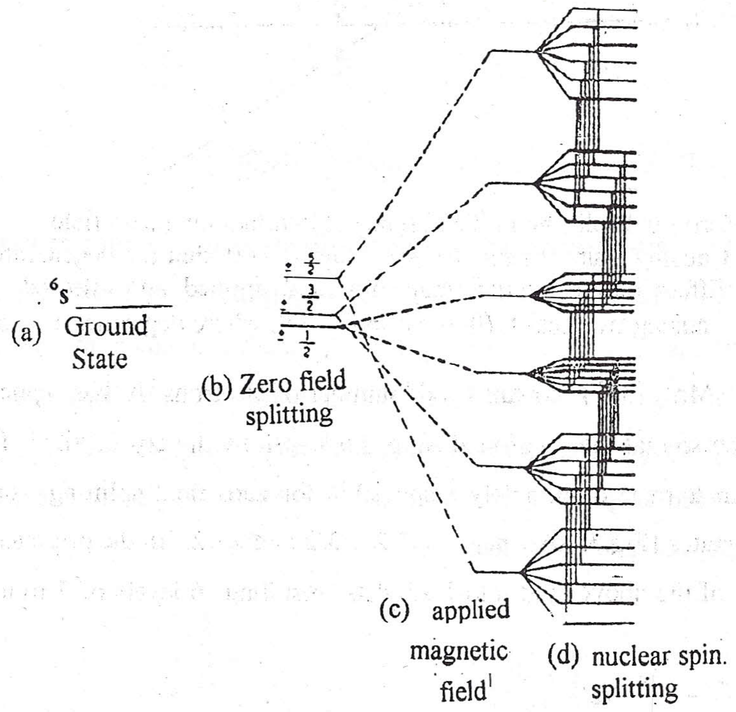


Fig.3.30. Splitting pattern in the octahedral Mn(II) complex. (a) Ground state (b) Zero field splitting (c) Splitting by applied magnetic field and (d) Splitting by nuclear spin.

3.3.vii). Applications

The following are a few typical applications of ESR spectroscopy in the study of inorganic chemistry.

A. Simple compounds

The aqueous solution of potassium peroxylamino disulphonate, $K2ON(SO_3)_2$ gives rise to 3 ESR signals. This arise from the interaction of odd electron of the ionic species, $\mathbf{ON(SO_3)_2^{2-}}$, with nuclear magnetic moment of ^{14}N nucleus ($I = 1$) giving rise to three ESR signals $(2nI + 1 = 2 \times 1 \times 1 + 1 = 3)$ **(Fig.3.31.)**.

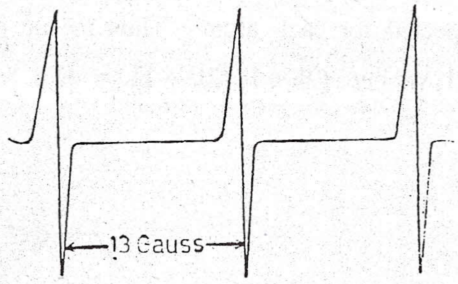


Fig.3.31. ESR spectrum of an aqueous $ON(SO_3)_2^{2-}$ ion.

ESR spectrum of **hydrogen atoms trapped in calcium fluoride** is presented in **Fig. 3.32.** In CaF_2 crystal structure, there are holes bounded by cubic arrangements of fluoride ions that can accommodate hydrogen atoms. The spectrum consist of two main resonance lines corresponding to proton splitting (2x 1 x ½ + 1 = 2). Each of these consists of nine hyperfine lines. The secondary splitting arise from the interaction of eight equivalent fluorine nuclei (I = ½). The above spectrum was recorded keeping the magnetic field parallel to the cubic edge, so that the eight fluorine nuclei are magnetically equivalent.

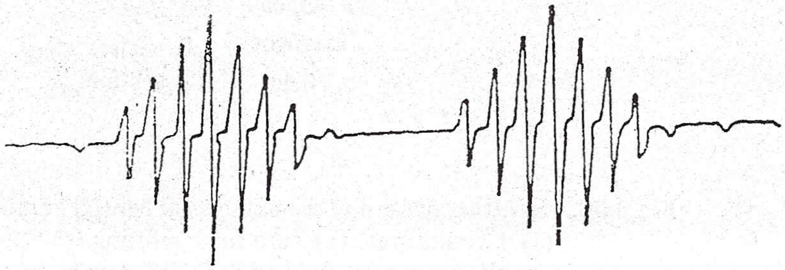


Fig.3.32. ESR spectrum of H trapped in CaF_2 crystal.

ESR spectra of **anhydrous $FeCl_3$ and $FeCl_3.6H_2O$** are different from each other. This suggests that different types of bondings present in these compounds due to the absence and presence of water molecules in the crystal structure.

ESR spectrum is extremely sensitive to very small amounts of paramagnetic materials. ESR study of S_8 molecules do not cause any spectrum, because it is diamagnetic. But when it is heated, the diamagnetic **S_8 ring** cleaves to produce high molecular weight S_x chains with one unpaired electron at each end. The area under the ESR curve is proportional to the number of unpaired electrons. By adding known concentration of radical ion of diphenylpicrylhydroxyl

(DPPH) radical, and from the area of the curve, the total number of radicals are derived, since the total number of sulphur used is also known. Thus the radical concentration at 300 ^{0}C was 1.1. x 10^{-3}M, and average chain length at 171 ^{0}C was 1.5 x 10^6 atoms. The heat of dissociation of S – S bond was found to be 33.4 k cal mole^{-1}.

ESR spectrum of **$IrCl_6^{2-}$** has got the I value of 3/2. It gives rise to a quartet of peaks due to splitting of iridium nucleus. Each of these peaks contain hyperfine structure resulting from electron delocalization onto chlorine atoms.

Radicals generated with high energy radiation, O_2^-, ClO, ClO2, PO_3^{2-}, SO_3^-, ClO_3 are among the many interesting radicals produced and studied by this technique.

B. Metal complexes:

i). Bis-salicylaldimine copper(II) complex: In this complex Copper **(Fig.3.33.a.)** with d^9 configuration has got an odd electron that is delocalized over the complex. ^{63}Cu nuclei with I = 3/2 on coupling with one unpaired electron present in the molecule would cause four main groups of peaks, **Fig.3.33.b.**

$$(2nI + 1) \quad = \quad (2 \times 1 \times 3/2 + 1) \quad = \quad 4 \text{ major peaks.}$$

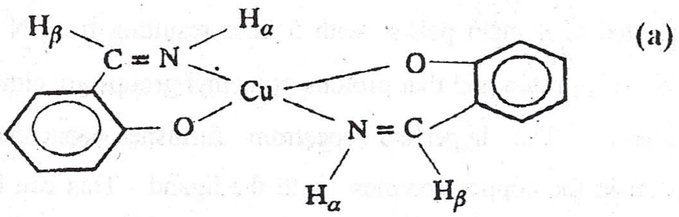
Hyperfine line for each main peak consists of 11 peaks in the intensity ratio, **(Fig.3.33.c.)**

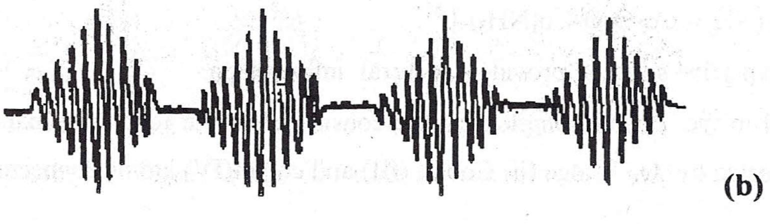
1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1

resulting from the splitting of 2 equivalent N and 2 equivalent H.

$$(2n_N I_N + 1) \; (2n_H I_H + 1) = (2 \times 2 \times 1 + 1) \; (2 \times 2 \times ½ + 1) = 5 \times 3 = 15$$

hyperfine lines.





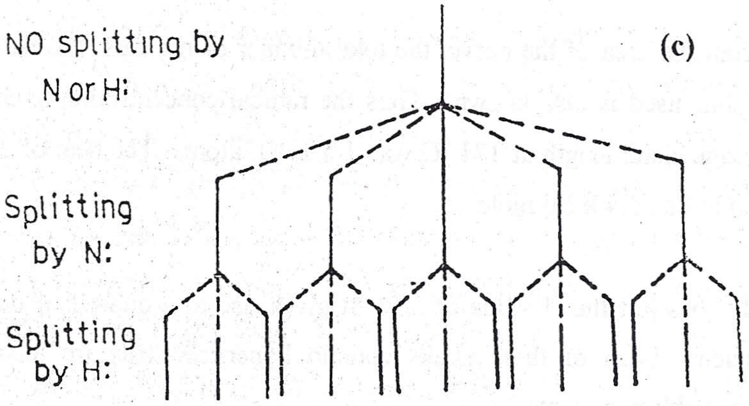
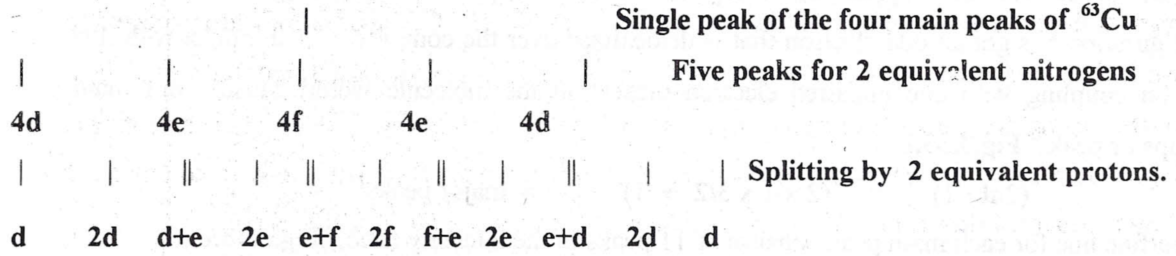


Fig.3.33. (a) ESR spectrum of bis salicylaldimine copper(II) complex. Structure of complex (b) Four major peaks arising ^{63}Cu nuclei. (c) Resultant hyperfine lines.

The actual spectrum consists of 11 hyperfine lines in each of the four major peaks consequent on overlap of some of the peaks, as depicted below:



1 : 2 : 3 : 4 : 5 : 6 : 5 : 4 : 3 : 2 : 1 **(Intensity ratio of hyperfine lines)**

(Line intensity : d = 1; e = 2; f = 3 .)

Deutration of N - H_α groups produced an identical spectrum. When H_β was replaced by methyl groups ESR spectrum consisted of 4 main peaks with 5 lines resulting from N splitting only. The hyperfine splitting of N – H_α proton and that protons of methyl groups are either too small to be detected or non-existent. The hyperfine spectrum furnishes conclusive proof of delocalization of odd electron in the copper complex onto the ligand. This can be considered as a sort of covalence in the metal-ligand interaction.

ii). Cobalt complex: $[(NH_3)_5.Co\text{-}O\text{-}O\text{-}Co(NH_3)_5]^{5+}$.

The spin density and hyperfine splitting provide structural information.

The bonding involved in the cobalt complex can be considered in the following manner: (i) 2 cobalt (III)atoms connected by O_2^- bridge (ii) Cobalt (III) and cobalt(IV) atoms connected by peroxy, O_2^{2-} bridge. (iii) 2 equivalent cobalt atoms due to equivalent interaction of one unpaired electron with both the cobalt atoms. (iv) Interaction of electron with both the cobalt atoms but more with one than the other. ESR signal would result single line for structure (i), 8 lines for the structure(ii), 15 lines for structure (iii) and 64 lines for structure (iv) proposed. The ESR actually consisted of 15 lines supporting structure (iii) proposed and eliminating the structure (ii) and (iv). When the hyperfine interaction constant is compared with that of other cobalt complexes, it is found to be low in this complex. This indicated that there is appreciable contribution from structure (i), because this removes electron density from cobalt atoms and thereby decrease the hyperfine constant.

C). Anisotropy

ESR spectrum of $CuSiF_6 . 6H_2O$ on diluted with diamagnetic $ZnSiF_6.6H_2O$ at 90 ^{0}K showed only one band with partly resolved hyperfine line and a nearly isotropic 'g' value. Three tetragonal distortions of (with mutually perpendicular axes) of $Cu(H_2O)_6 . SiF_6$ are expected to cause 3 ESR transitions. Since only one signal was observed, it is proposed that the crystal field resonate among the three distortions. When the temperature is lowered, it becomes anisotropic and give rise to 3 sets of lines, corresponding to three different copper ions distorted by 3 different tetragonal distortions. The transition takes place between 50 ^{0} and 12 ^{0}K.
$(CuMg)_3 La_2(NO_3)_{12}. 24 D_2O$ and $(ZnCu)(BrO_3)_2 . 6 H_2O$ behave similarly at transition temperatures, 33^0 – 45 ^{0}K and <7 ^{0}K respectively.

Tris-complexes of Cu(II) with 2,2' dipyridine and 1,10-phenanthroline also show resonating crystal field at elevated temperature.
The **ESR spectrum of NO_2** in argon matrix gives rise to 3 lines of nitrogen hyperfine interaction with variable widths indicating anisotropy in both 'g' and hyperfine splitting. ($g_{\parallel} = 1.9920$, $g_{\perp} = 2.0033$). It is inferred from the ESR spectrum and other data that NO_2 molecule has axial symmetry in argon matrix, about an axis which is perpendicular to the molecular symmetry axis.

D). Molecular tumbling

In solution, the molecular motion leads to simplification of spectra due to averaging of anisotropic interactions to zero and resulting an isotropic spectrum. When molecular tumbling leads to incomplete averaging, because of high viscosity of of medium, variations are observed in the line width of the hyperfine lines. Thus ESR spectrum of vanadyl acetylacetonate dissolved in 1:1 toluene : chloroform at room temperature result in asymmetric line broadening **(Fig.3.34.).** Asymmetric line broadening is commonly observed for aminoxyl radicals and used for spin label and spin probe studies.

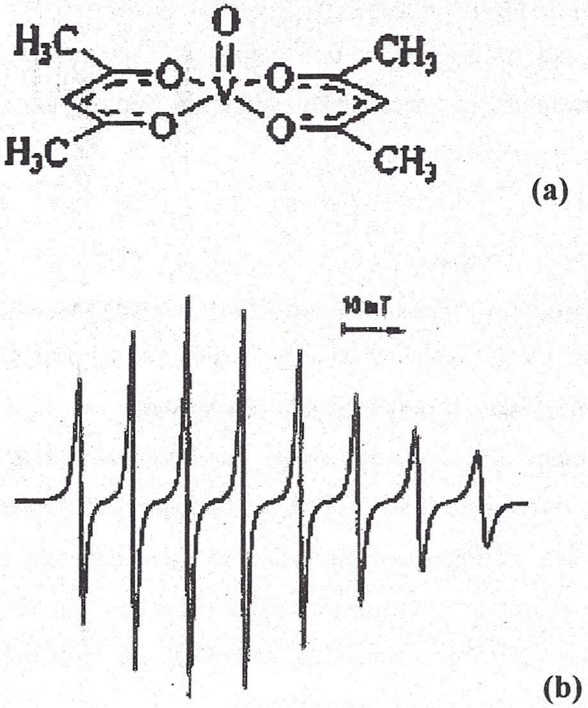


Fig.3.34 (a) Symmetrical structure of vanadyl acetylacetonate
(b) ESR spectrum (asymmetric line broadening) in 1:1 toluene : chloroform.

3.3.viii).Model questions:

1. How the ESR spectroscopy is different from NMR spectroscopy?
2. Explain the principle involved in ESR spectroscopy.
3. What is ‘g’ factor? What are factors that influence ‘g’ value? How it is useful in the study of structure of molecules?
4. Sketch the schematic diagram of ESR spectrometer and explain the function of basic components.
5. How the ESR spectrum is generally presented? Give reasons.
6. Illustrate with an example how the hyperfine spectrum arise in ESR.

7. What is zero field splitting and Kramer's degeneracy? Explain with a suitable example.
8. Illustrate application of ESR in the study of simple inorganic compounds.
9. With a suitable example explain how ESR spectroscopy is useful in the study metal complexes and the nature of bonding involved in them.
10. What is molecular tumbling? Explain with an example.

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5. Advanced Inorganic Chemistry, Gurdeep Raj., Vol.-II Goel Pub. House (2002).

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LESSON –IV MASS SPECTROSCOPY

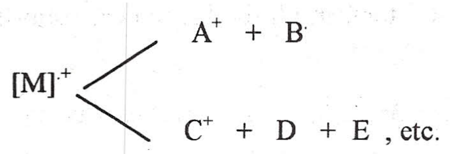
Objectives:- Principle – Instrumentation – General rules governing fragmentation – Applications - Interpretation of spectra of metal compounds – Identification of metal compounds.

3.4.i). Principle

Mass spectrometry is based on the principle which is different from that underlying in various forms of other spectroscopy. In mass spectrometry the sample is bombarded with high energy electrons which knock of an electron from the sample leading to a positively charged radical ion, $[M]^{+\cdot}$.

$$M + e^- \text{ (electron)} \text{ ---------}\rightarrow [M]^{+\cdot} + 2e^- \qquad \text{---(3.6)}$$

The radical ion being highly energetic, may fragment further yielding smaller fragments as shown below



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.The radical ion(s) and other **fragments formed** are separated according to their **m/z ratio** (where 'm' is the mass of the fragment and 'z' is the charge on the ion). The record of m/z values of these species versus their relative abundance gives the mass spectrum of the sample. In addition to the positive ions, which are generally very high in number, a few negative ions are also formed that are insignificant for general mass spectrometry. In the mass spectrum, each of the mass peak is associated a large number of smaller mass peaks. This arise from the natural isotopic abundance of the element.

Mass spectrometry is an important and precise analytical technique with which one can determine the molecular mass, isotopic masses, isomeric species, and structure and reaction mechanism with ease. Mass spectrometry is considered as a complementary technique as it provides additional information on the structure of atoms and molecules obtained by other spectroscopic techniques.

3.4.ii). Instrumentation

The salient features of a typical mass spectrometer is shown in **Fig.3.35**. It consists of sample inlet system, ionization chamber and ion source, mass analyzer, collector/ detector, signal processor/amplifier and read out. A small amount of the sample in micromole introduced into the sample inlet system is converted into gaseous ions by volatilizing liquid or solid samples. The ion source converts the sample into ions by bombardment with electrons, ions, molecules or photons. In certain other instances ionization is also brought about by thermal or electrical energy. In many instruments, the sample inlet system and the ion source are combined to form a single unit. The ionized sample is accelerated into the mass analyzer, where the ions are separated based upon mass-charge ratio (m/z ratio). **Dempster's** first mass analyzer **(Fig.3.36.)** is a single focusing instrument in which the positive ions were deflected through 180^0 in a magnetic field The ions of given m/z values will follow a particular path of radius 'r' . The ions of various m/z values are transmitted to the collector slit either by varying the magnetic field (B) at constant potential V (Magnetic scanning) or by varying V at constant B (Voltage scanning). The detector converts the beam of ions into an electrical signal and stored in the memory of a computer and displayed or recorded in a variety of ways. The characteristic feature of a mass spectrometer is that it requires an elaborate vacuum system (10^{-4} to 10^{-8} torr) in all the instrument components except the signal processor and ready out.

Ionization of molecule is an important process, as it imposes energy on the molecule and influence the formation of fragmentation products, though it is governed by the structural features of the molecule. In **electron ionization method**, the sample vapour is bombarded with high energy electron (about 1.12×10^{-17} J). A very low pressure is maintained in the ionization chamber, so that collision between ions and unionized atoms or molecules are at a minimum level. The electron ionization is useful for the study of molecular ion and fragmented ions.

In **chemical ionization method**, a reagent (such as CH_4 or NH_3) is passed into the ionizing chamber, where it ionizes, fragments and collided with neutral molecules to yield CH_5^+ or NH_4^+ ions. These reagent ions protonate the sample to yield MH^+ ions which are one unit higher in mass than the parent molecule. This method is highly useful for the determination of molecular mass of the compound as it undergoes very little fragmentation unlike the electron ionization method.

The ions generated are then passed through the accelerating plates, where the positively charged ions get accelerated, while negative ions and neutral particles are continuously removed. The accelerated positive ions is made pass through a magnetic analyzer which reflects them along a

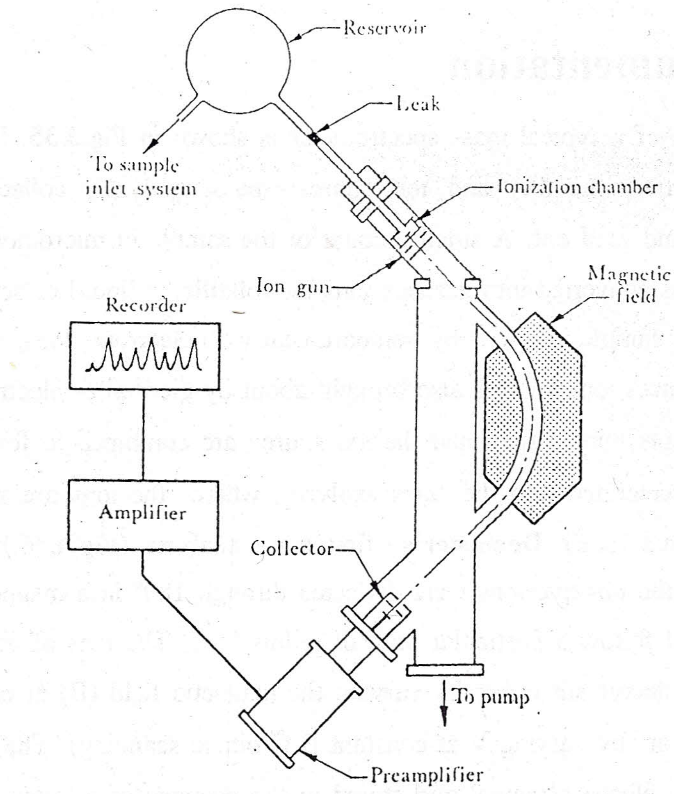


Fig.3.35. Schematic diagram of a typical single focusing mass spectrometer.

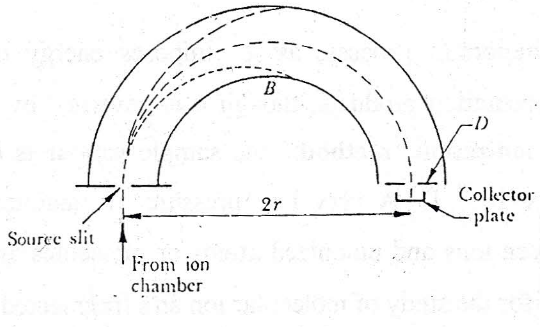


Fig.3.36. Schematic diagram of Dempster mass spectrometer.

curved path. By varying the magnetic field, ions of different masses are separated and detected/recorded.

Field ionization : In this method powerful electric field (10^9 to 10^{10} V m^{-1})is used to promote ionization. The ionization of the molecule occurs by migration of an electron to the anode and it is based on quantum mechanical tunneling effect. In this process, the quantity of excess energy imparted to the molecular ion is usually small. Therefore the molecular weight or molecular formula information can be acquired with ease.

Mass Analysis: Following the Dempster's instrument, 90^0 sector single focusing instruments either in direction or velocity were developed. The resolving power of this type of instruments are limited by the spread of translational energies of the ions leaving the source. This problem can be overcome by passing the ions through an electric field prior to magnetic field. Instruments based on this phenomena are called double focusing mass spectrometers, because the ions are focused twice, i.e., in direction and in energy. **Fig. 3.37** depicts the high resolution **double focusing** mass spectrometer. In addition to the basic features, it consists of an electrostatic analyser which carries out the preliminary focusing and pass the ions through the magnetic analyzer. The direct probe inlet allows the solids and non-volatile liquids to be introduced into the ionizing region and their analysis. The resolving power of this instrument is much higher than that of single focusing instruments.

Time-of-Flight mass spectrometer: The Time-of-Flight mass spectrometer **(Fig.3.38)** is based on the principle that ions of different masses accelerated to a uniform kinetic energy, have different velocities, and hence different times of flight over a given distance. The most common type of Time-of-Flight mass spectrometer uses a pulsed ion source with a voltage pulse on grid A to extract the ion from the source. A potential gradient in between A and B accelerates the ions to uniform kinetic energy and into the field-free flight tube. The ions are separated in time according to their m/z values, on arrival at the repeller grid C and are collected at D. The differences in arrival time should be about 10^{-7} sec for successive masses to get good resolution of mass spectrum.

Ion-cyclotron resonance mass spectrometer: it is a powerful technique for investigating ion-molecule reactions and useful for the determination of structures in the gas phase. The block diagram of Ion-cyclotron resonance mass spectrometer (ICR) is shown in **Fig.3.39.** The ions are generated by electron impact in a uniform magnetic field (perpendicular to the plane of the paper) and restricted to a circular path perpendicular to the direction of magnetic field. The angular frequency ω_c of this motion is independent of velocity of the ions and given by $\omega_c = z\,eB/m$. The angular frequency, ω_c, which depends on m/z value, is known as cyclotron resonance frequency. An alternating electric field of radiofrequency, ω_1 is applied normal to the magnetic field B, an ion will absorb energy if $\omega_c = \omega_1$. The ions are made to pass through the analyzer A, to the collector C, by applying a small static electric field. Then the mass spectrum is obtained by fixing ω_1 and scanning the magnetic field so that the ions of different m/z values are satisfied.

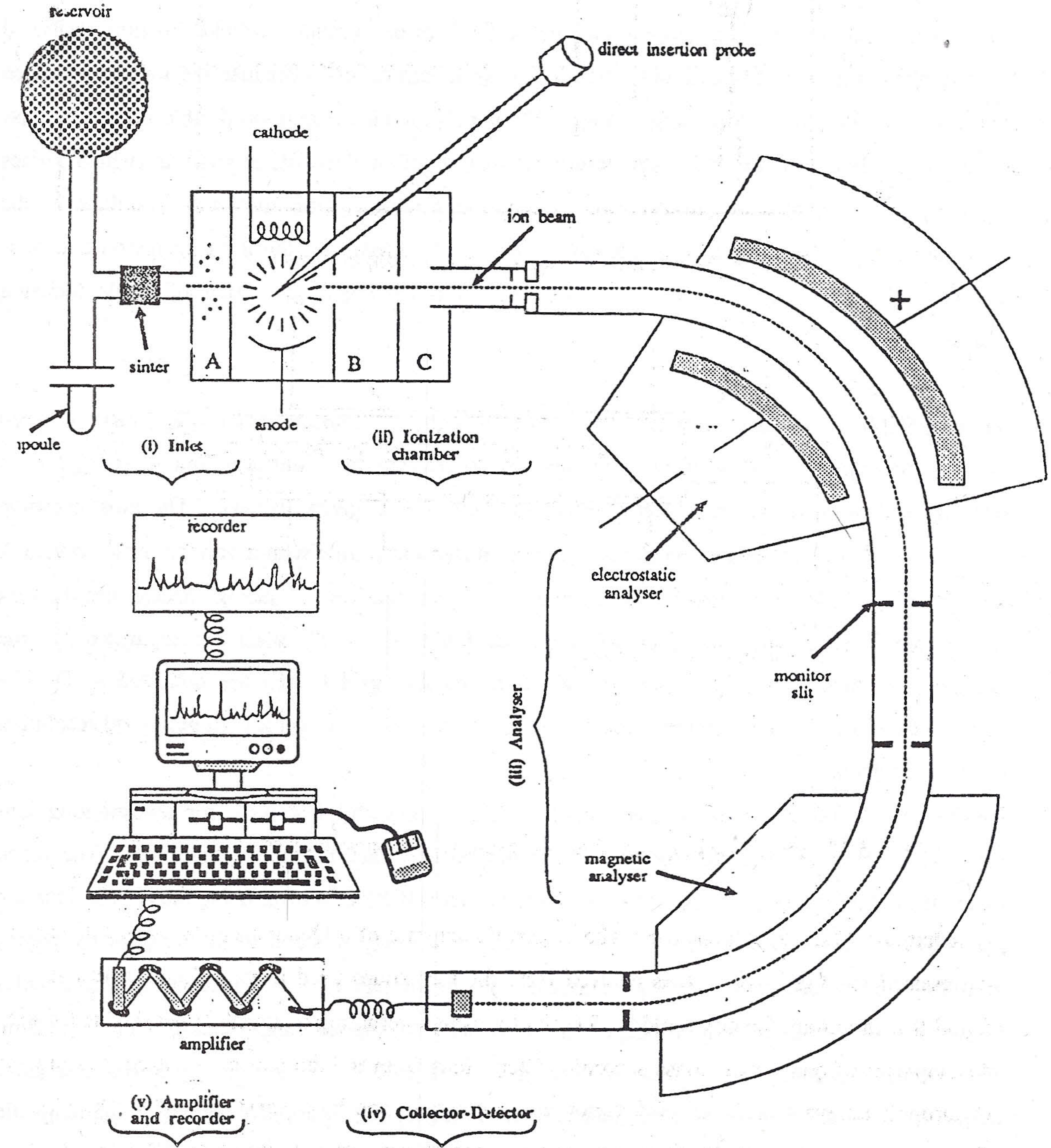


Fig.3.37. Schematic diagram of a high resolution double focusing mass spectrometer.

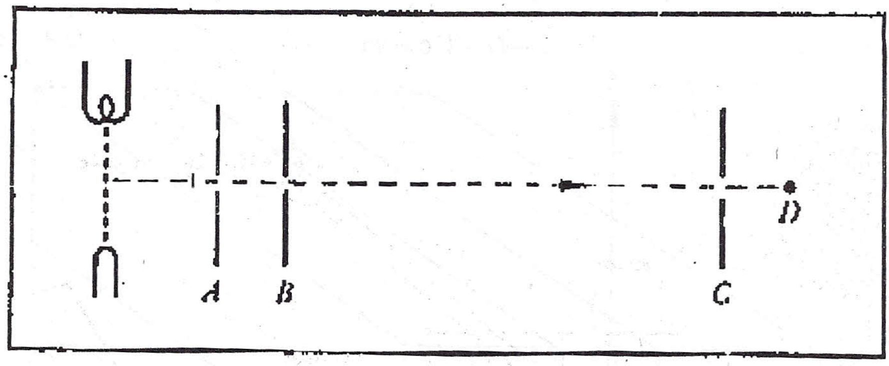


Fig.3.38. Schematic diagram of a time-of-flight mass spectrometer.

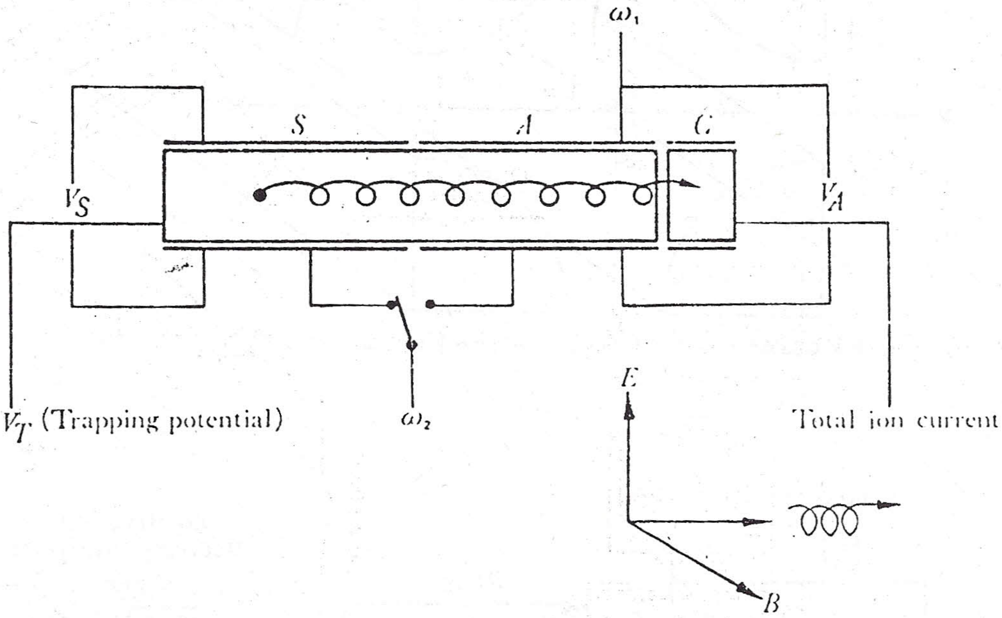


Fig.3.39. Schematic diagram of an ion-cyclotron resonance mass spectrometer.

Quadrupole Mass Spectrometer : The schematic diagram of a Quadrupole Mass Spectrometer is represented in **Fig. 3.40.** It is evolved from the techniques used in particle acceleration. It is found that the proton beams could be focused by using alternating quadrupole fields, this led to the development of quadrupole mass separator/filter. Ions from the ion source is introduced into the quadrupole analyzer along the x-direction and are acted upon by a variable field in the yz plane. For a given set of voltages, frequency and rod separation, the ion trajectory remains within the bounds of the electrode. This enables the ions having same nominal m/z values to be transmitted through the narrow passage, while the other m/z species undergo unstable osciallations and are removed in the y and z directions. The mass spectrum is scanned by varying the amplitude of V

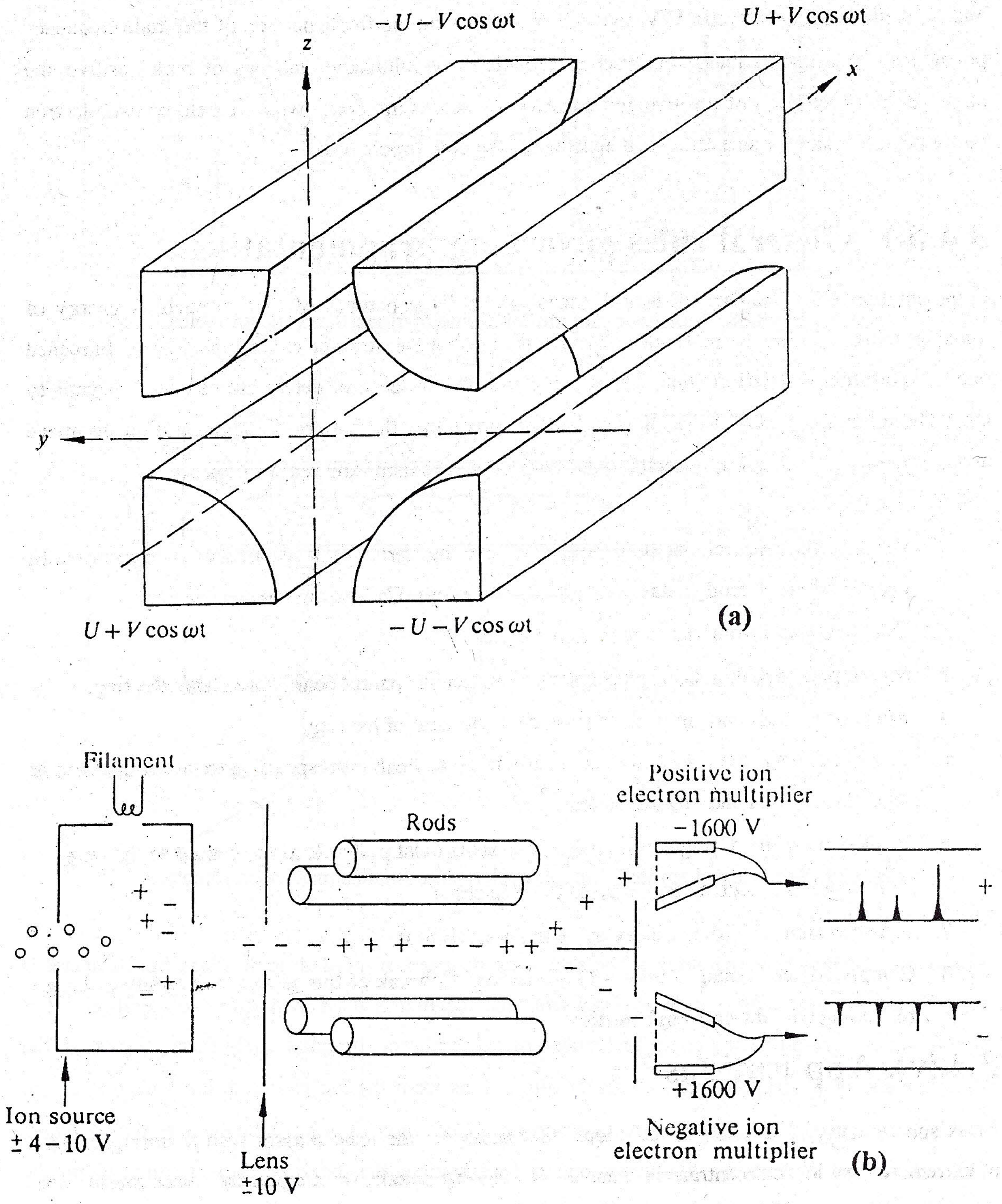


Fig.3.40.(a) Electrode arrangement for quadrupole mass filter.
(b) Schematic diagram of a quadrupole mass spectrometer.

and U, while keeping the ratio U/V constant or by varying the frequency, ω of the radiofrequency potential. Quadrupole mass analyzer is capable of simultaneous analysis of both positive and negative ions. Detection of positive and negative ion beams are done with the help of two electron multipliers kept side by side at the exit aperture of the quadrupole rods.

3.4.iii). General rules governing fragmentation

Fragmentation of molecular ion is influenced by a large number of factors such as energy of ionizing source, nature of molecules whether it is a simple straight chain molecule or branched one, unsaturation, its location and degree , ring system, presence of hetero atoms, electronegativity etc. The following general rules hold good for predicting the pattern of fragmentation to arrive at the structure of molecules, understand the reaction mechanisms and rearrangements.

1. Cleavage is favoured at branched carbon atoms, tertiary > secondary > primary with positive charge tend to stay with branched carbon (Carbonium ion)
2. Double bonds favour cleavage β to the bond
3. Strong parent peak indicate ring system, stronger the parent peak more stable, the ring.
4. Ring compounds contain peak at mass characteristic of the ring.
5. Saturated rings lose side chains at α carbon atom. Peak corresponding to two ring atoms is much larger than one ring atoms loss.
6. In alkyl substituted ring compounds, cleavage is most probable at the bond β to the ring, if the ring has a double bond, next to the side chain.
7. A hetero atom will induce cleavage at the bond β to it.
8. Compounds containing > C = O group tend to break at this group with positive charge remaining with the carbonyl portion.

3.4.iv). Applications

Mass spectrometry is a versatile technique that measures the ionic masses with utmost precision at extremely very low concentrations. Just as the zig-zag puzzle, the fragmented ionic masses can be reorganized to arrive the structure of the ~~molecules, understand~~ the reaction pathways, etc. Primarily mass spectrometry is extensively used by organic chemists for the study of organic compounds, including high molecular weight polymeric species. As far as inorganic chemistry is concerned, the mass spectrometry is useful for the evaluation of atomic masses of the elements, their isotopes and their abundances. Apart from this, metals form carbonyls, nitrosyls, complexes/chelates with a vast number of organic molecules. Mass spectrometry is quite useful for the study of metal complexes and arrive at the molecular structure, reaction mechanism and properties of metal complexes. Apart from the above, mass spectrometry finds considerable use in determining the concentrations of the elements in diverse materials such as semiconductors, minerals, particulate atmospheric pollutants, lunar rocks, forensic samples and fossil fuels.

3.4.v). Interpretation of spectra of metal compounds

The mass spectrum is generally presented in the form of a bar graph, in which m/z values are plotted horizontally and the relative ion abundances vertically. The bar graph of 70 eV mass spectrum of n-decane is presented in **Fig. 3.41.** Fragmentation of hydrocarbon chain at different locations and the resultant mass species and their relative abundance are depicted pictorially. The most abundant ion is arbitrarily assigned an abundance of 100% and is called the **base peak.** In this case mass number 57 is the most abundant ionic species, while the mass number 142 correspond to **molecular ion .** In cases where the molecular ion peak is more abundant, it also form the base peak.

The fragmentation pattern of molecules is dependant on the energy of the electron source used. Thus the mass spectrum of di-n-dodecylether at 70 eV and 12 eV presented in **Fig.3.42.. a** and **b** illustrates this phenomena. In the 12 eV spectrum only the ions of lowest appearance energy are generated by the reaction, whereas in the 70 eV spectrum, the molecule is extensively fragmented to form large proportion of lower ionic species/masses. In other words the fragmentation of compounds depend on the energy of the source used for the ionization of molecules. In addition, in the case aromatic/ring compounds, the ring structure is less prone to cleavage while the agmentation is favoured at the chain/side chain. Consequently, the mass peak is more predominant than the fragmented peaks. **Organometallic compounds: Fig.3.43.** represents the 70 eV mass spectrum of tetramethyl tin and its characteristic isotopic pattern. Tin has got ten naturally occurring stable isotopes. The molecular ion is observed at mass number 180. Successive loss of methyl groups are indicated by different mass numbers and also the formation of tin hydrides. The isotopic abundance of tin is indicated by the multiple peaks at each of the fragmented products.

Similarly the molecular ion of $Re(CO)_5Cl$ result in isotopic abundances, as the naturally occurring isotopes, ^{185}Re and ^{187}Re (37.07% and 62.93% respectively) and also the chlorine ^{35}Cl and ^{37}Cl

(75.53% and 24.47% respectively). Similar to this the peak distribution of molecular ion of л $C_5H_5(CO)_3MoGeEt_3$ vary from mass numbers 398 to 412.

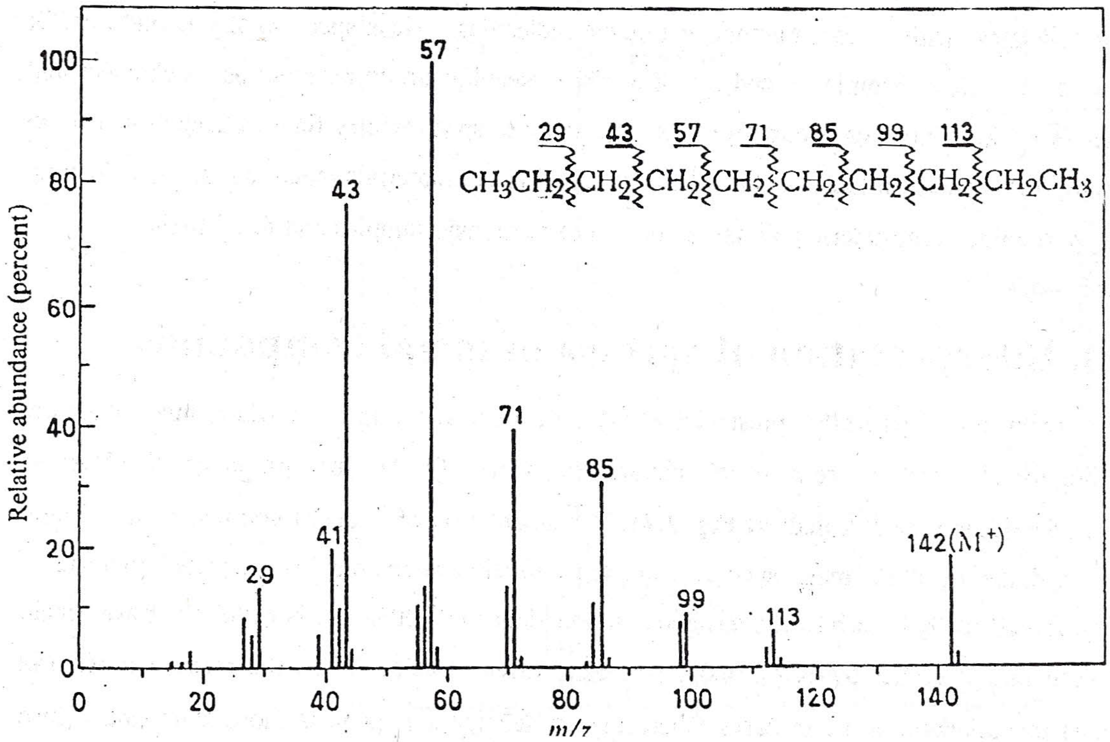
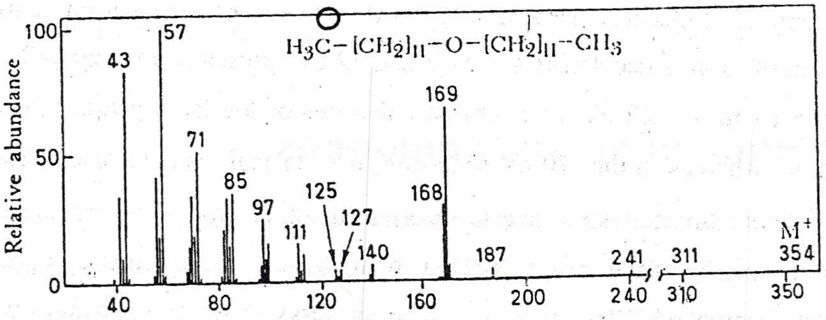
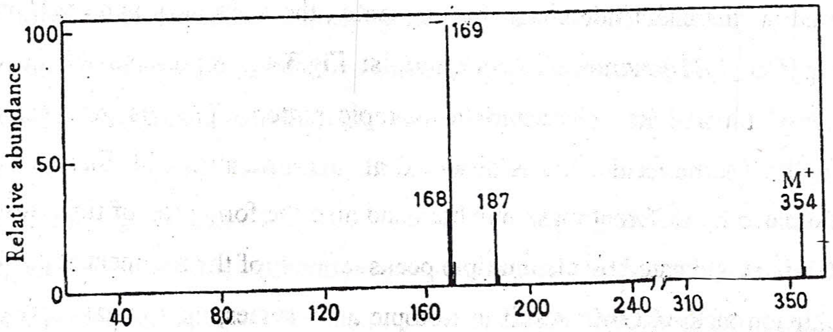


Fig.3.41. Mass spectrum of n-decane depicting the fragmentation pattern (70eV)



(*a*) 70 eV



(*b*) 12 eV

Fig.3.42. Comparison of mass spectrum of di-n-dodecylether at (a) 70eV and (b) 12eV.

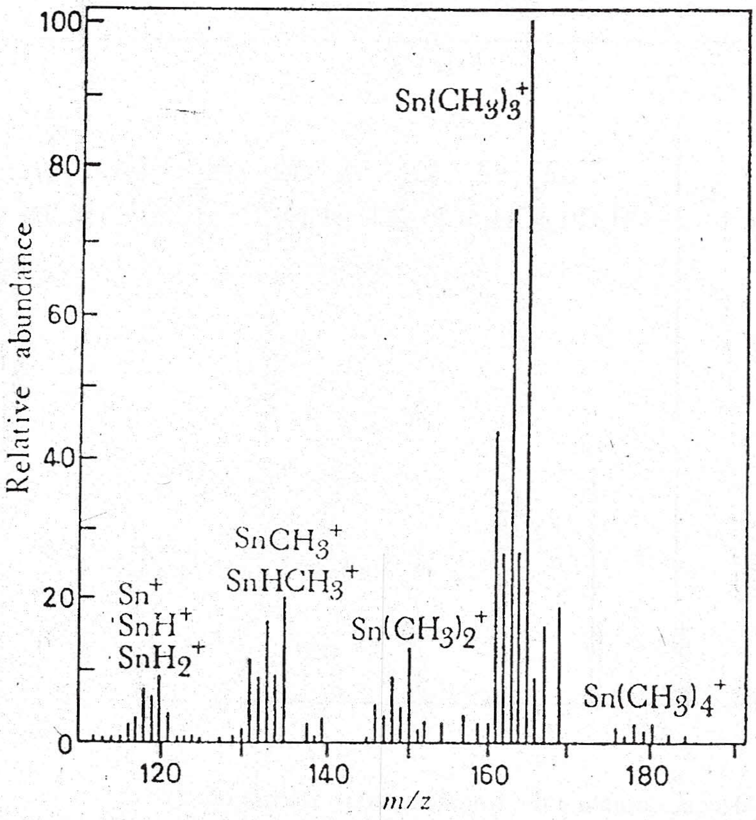


Fig.3.43. Mass spectrum of multi-isotopic species, tetramethyl tin at 70 eV.

3.4.vi). Identification of metal compounds

Fragmentation pattern: The mass spectrum of iron **pentacarbonyl** is presented in **Fig.3.44.** The molecular ion gives a peak at mass number 196. The ligand (carbonyl) in the molecular ion, is lost in sequence causing peaks for $Fe(CO)_n^+$ (n = 0 to 5), wherein Fe^+ and $FeCO^+$ are in major fractions of the fragmentation process. Similar to this molybdenum pentacarbonyl [$Mo(CO)_6$] result in a mass spectrum (**Fig. 3.45.**) corresponding to successive loss of carbonyl group (mass Nos. 238, 210, 182, 154, 126, and 98) in addition to molecular ion peak (mass No. 266) and carbonyl peak (mass No.28). In the case of complexes containing **mixed ligands**, for example, nitrosyl and carbonyl complexes, the CO groups are more readily lost than NO groups in ionic decompositions, **Fig.3.46.**. This is because of the greater electron donating ability of NO compared to CO ligand. Similarly, the stronger electron donating constituent, $P(OEt)_3$ is introduced into the nitrosyl carbonyl complexes, the metal preferentially retains $P(OEt)_3$ ligand due to stronger metal ligand bond.

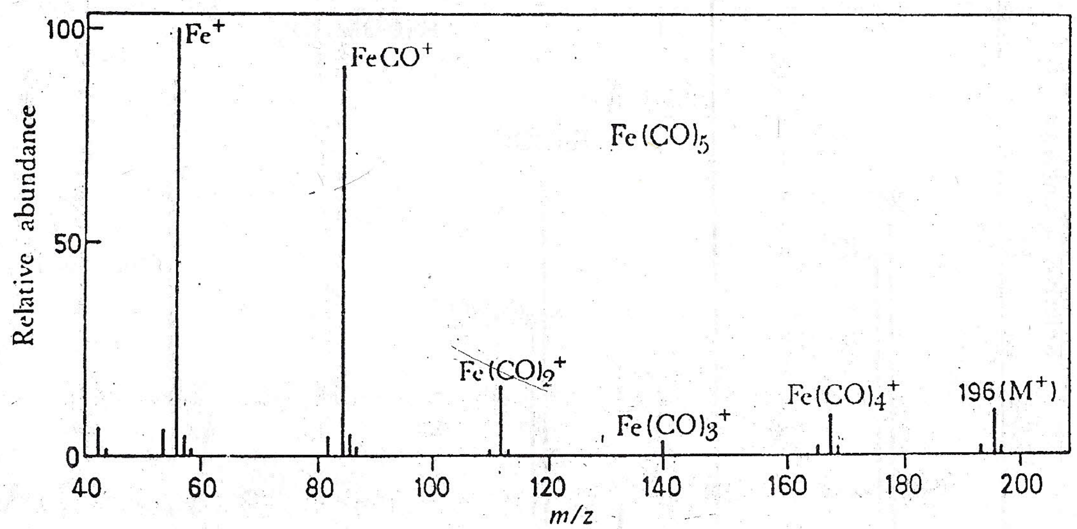


Fig.3.44. Mass spectrum of iron pentacarbonyl, indicating stepwise loss of ligand.

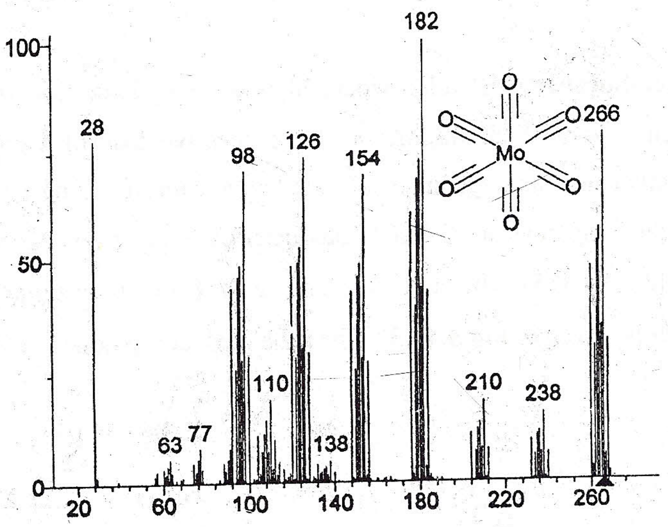


Fig. 3.45. Mass spectrum of molybdenum hexacarbonyl. Formula C_6MoO_6

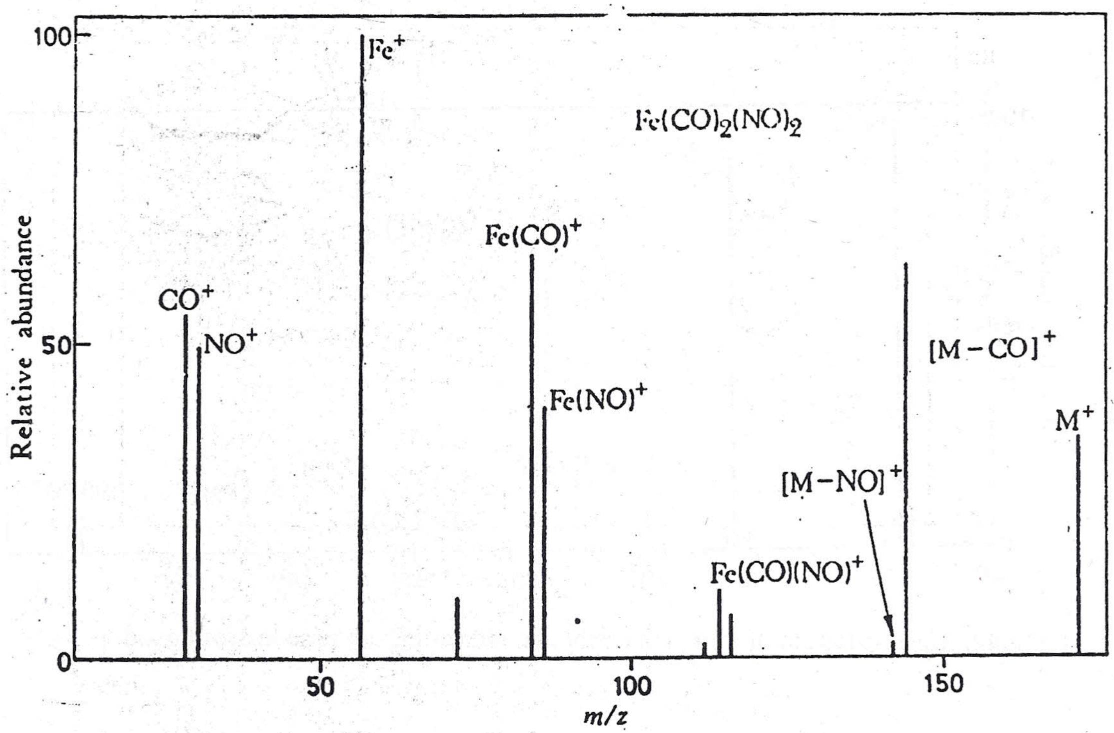
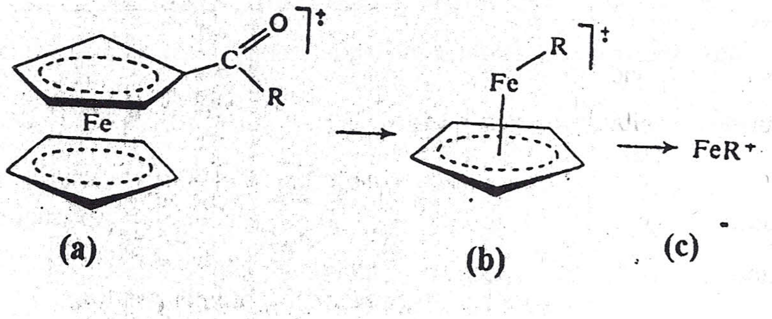


Fig.3.46. Mass spectrum of nitrosyl carbonyl complexes of iron.

Highly thermally stable **metallocenes** [$M(C_5H_5)_2$ where M is a metal) have low ionization energies and yield abundant molecular ion which fragments by successive loss of C_5H_5 units. A large number of substituted matallocenes undergo unusual rearrangements involving organic side chain. Thus in the case of ferrocene, ejection of C_5H_4CO has been observed from the molecular ion (a) followed by further elimination of C_5H_5 (b) and resulting FeR^+ (c) . The resultant mass spectrum of $C_5H_5 - Fe - C_5H_4COOH$ is given in **Fig.3.4.13**. The base peak corresponds to M = 138.



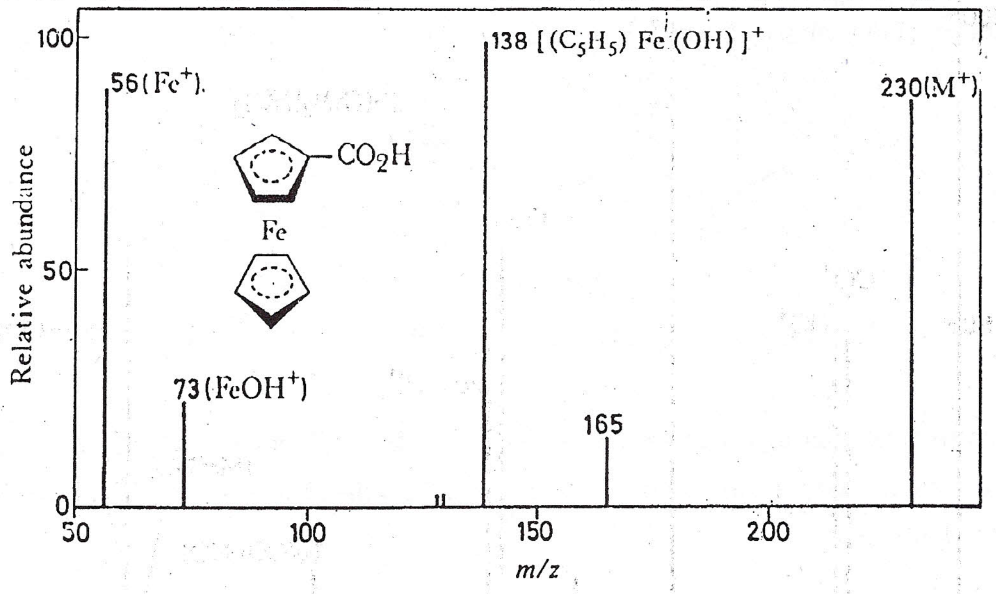
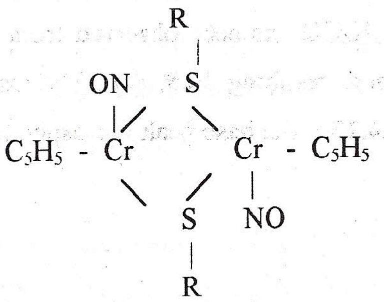


Fig.3.47. Mass spectrum of ferrocene undergoing rearrangement.

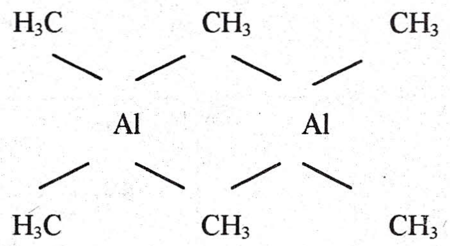
Migration of ligands: It is also known as group migration or skeletal rearrangement. Migration of ligand is most commonly observed in the breakdown of organometallic ions. The binuclear complex of chromium given below illustrates this point.



The presence of an ion at m/z =182 in the mass spectrum corresponding to $Cr(C_5H_5)_2^+$ suggests the migration of C_5H_5 from one nuclei to the other on fragmentation. The binuclear metal nitrosyls with sulphur bridges exhibit this phenomena.

Polymers : Mass spectrometry is useful for the detection of dimeric or polymeric species in organometallic compounds. Thus the mass spectrum of aluminum alkyls, Me_3Al, Me_2AlH,

Et_2AlH and Et_2AlOEt have all revealed the presence of dimers and trimers at low source temperatures. For example, the highest mass ion



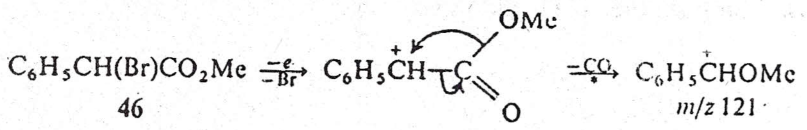
in the spectrum of trimethyl aluminum corresponds to $Me_5Al_2^+$ and carried 3% of the total ion current at a source temperature of 50 °C . This arises from the elimination of methyl radical from the ionized dimeric species.

Skeletal rearrangement: Group migrations are quite common in the mass spectra of organometallics. It is also commonly called as skeletal rearrangements. Though it is less common in ordinary organic compounds, it does occur. Group migration is normally initiated by the generates an isomerised molecular ion or fragment ion. For example

$$A^+ - B - C \rightarrow C - A - B^+ \rightarrow C - A^+ + B$$

This is illustrated in the mass spectrum of methyl alpha-bromopheylacetate , **Fig. 3.48,** where the M^+ - Br undergoes loss of CO in one step process with associated methoxyl migration to the carbonium ion center. This type of rearrangements, generates units which are not present in the original molecule and on many occasions may lead to incorrect structural conclusions arrived at from a mass spectrum. One has to exercise utmost care in interpreting the mass spectrum.

Metal complexes: The mass spectrum of acetylacetonate complex of iron(III) is given in **Fig.3.49**. It gives a base peak at m/z = 43 corresponding to C_2H_3O (CH_3CO) fragment. $C_{10}H_{14}FeO_4$ at mass number 254 corresponding to a bis complex of iron and for the fragmented ligand , $C_5H_5O_2H$ at mass number 100 , $C_4H_4O_2^+H$ at mass number 85, CH_3CO at mass number 43 and for oxygen at mass number 16. The absence of molecular ion peak at 353 suggests its unstable nature under the conditions and the formation of other fragments consequent on rearrangements.



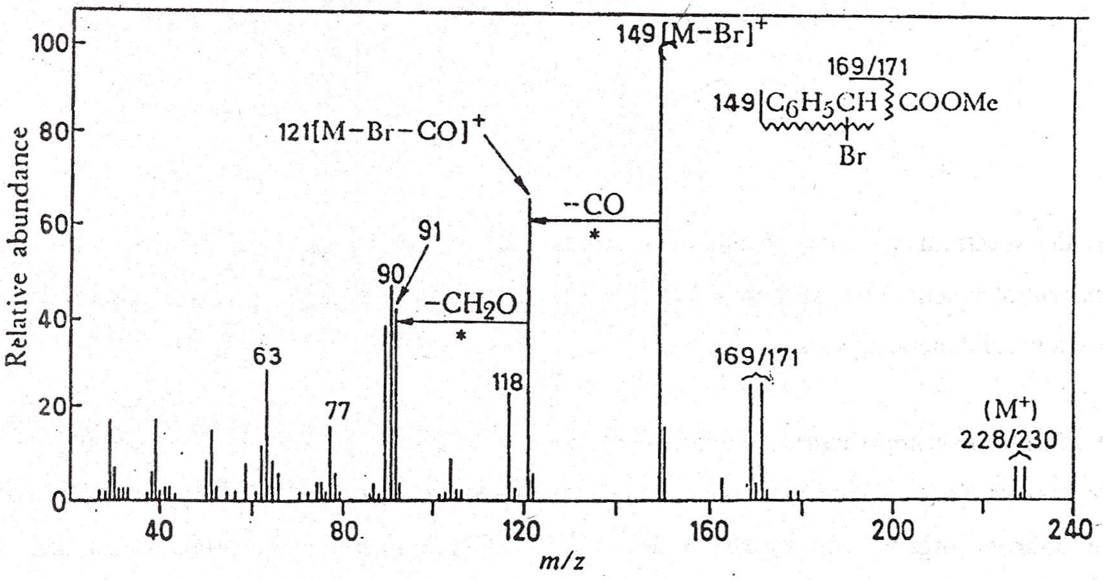


Fig.3.48. Mass spectrum indicating skeletal rearrangement in a molecule/complex.

The mass spectrum of Copper 8-hydroxyquinolate complex **(Fig.3.50)** cause molecular ion peak at mass number 351, and the base peak at mass number 207 corresponding to the fragment, C_9H_6CuNO and for the fragmented ligand, $C_9H_6N^+HO$ at 145. Copper peak in the region of mass number 63. The presence of other peaks arise from further fragmentation of ring structure and the resultant products.

The mass spectrum of Nickel bis-(.eta.3-2. propenyl) and cobalt cyclopentadienyl-dithiolene are presented in **Fig.3.51** and **Fig.3.52** respectively for the practice of reader for identification and interpretation of fragmented products and for comments.

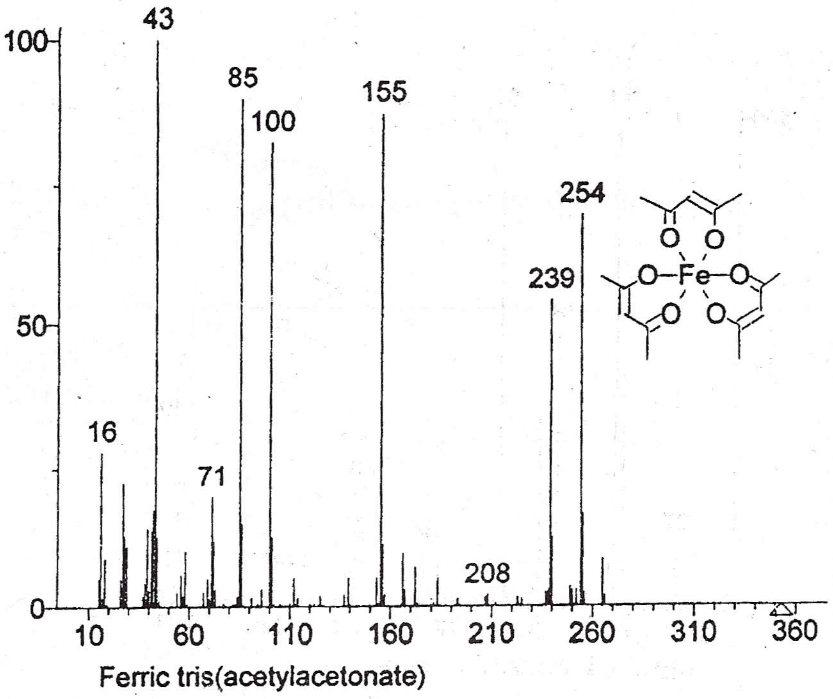


Fig.3.49. Mass spectrum of ferric tris (acetylacetonate). Formula: $C_{15}H_{21}FeO_6$

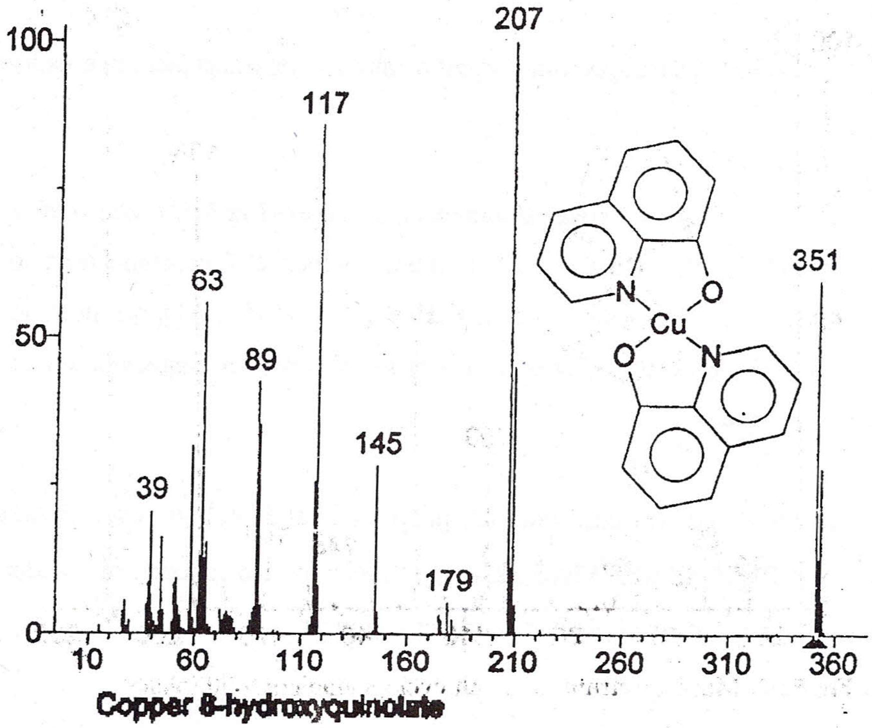
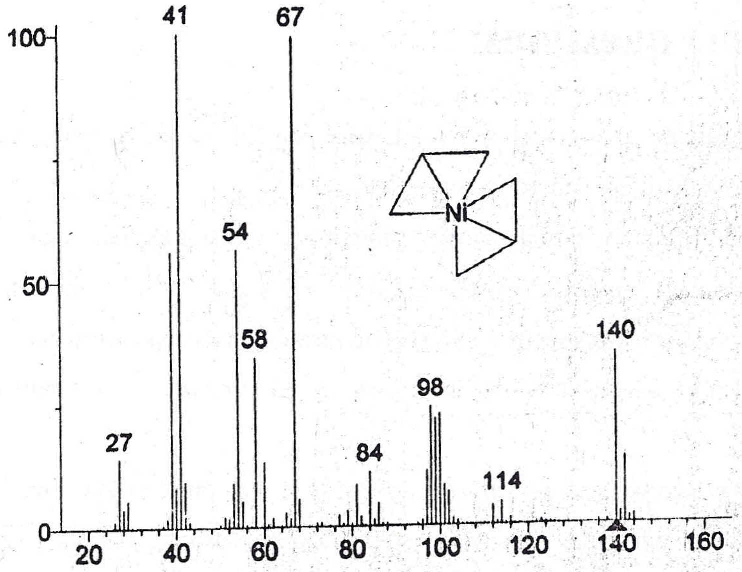


Fig.3.50. Mass spectrum of copper 8- hydroxyquinoline. Formula: $C_{18}H_{12}CuN_2O_2$.



Nickel, bis(.eta.3-2-propenyl)-

Formula: $C_8H_{10}Ni$

Fig.3.51. Mass spectrum of Nickel bis-(.eta.3.2 propenyl). Formula $C_6H_{10}Ni$.

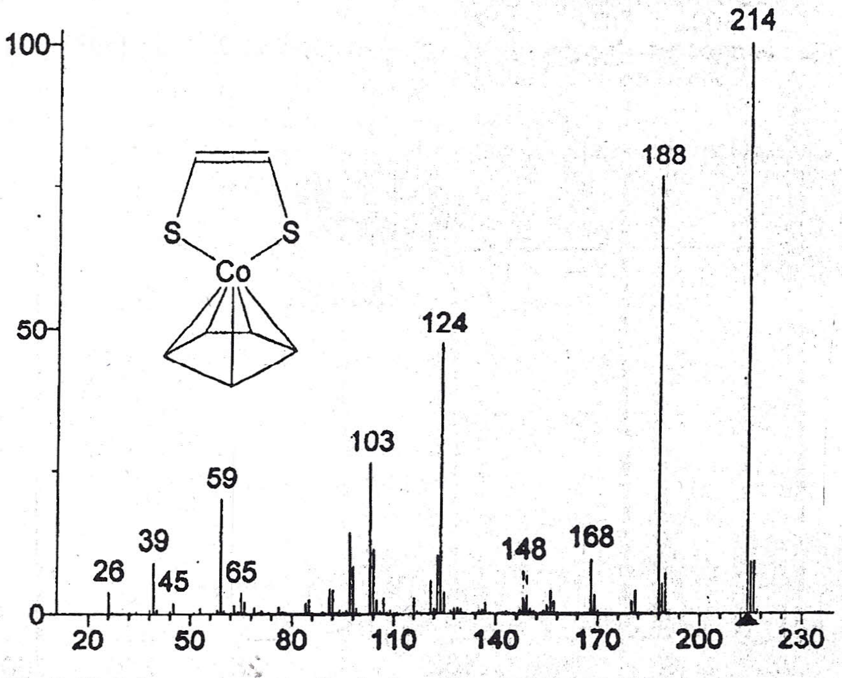


Fig.3.52. Mass spectrum of cobalt cyclopentadienyl-dithiolene.

3.4.vii). Model questions:

1. Sketch the schematic diagram of (a) single focusing (b) double focusing mass pectrometer and explain how the mass spectrum is obtained.
2. What are the different ionization sources commonly used and explain their relative merits.
3. Explain the principle involved in the following: (i) Time-of-flight mass spectrometer. (ii) Cyclotron resonance mass spectrometer (iii) quadrupole mass spectrometer.
4. Give an account on general rules governing fragmentation of molecules in mass spectrometry.
5. Illustrate how ionization energy influence the mass spectrum of a molecule.
6. Illustrate how the mass spectrometry is useful in the study of (i) metal carbonyls,(ii) metal complexes, (iii) polymers and (iv) tin-alkyls.

References:

1. Mass spectrometry , I. Howe, D.H. Williams and R.D. Bowen, 2nd Ed., (1981), McGraw-Hill Inc.
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