COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
UNIVERSITY GRANTS COMMISSION

CHEMICAL SCIENCES   **CODE:01**

1.11. Characterization of inorganic compounds by spectroscopic method

At a glance

IR Spectroscopy, Raman Spectroscopy, NMR Spectroscopy, EPR Spectroscopy, NQR Spectroscopy, Mass Spectrometry, Electron Spectroscopy

Key Statements

Basic Key statements: IR Spectroscopy (1.11.1), IR active and IR inactive vibrations (1.11.2), Raman spectroscopy 91.11.5), NMR spectroscopy (1.11.7), EPR (1.11.9), Principle of Mossbauer Effect (1.11.20), Natural Line width in Mossbauer spectroscopy (2.11.21), Nuclear quadrupole resonance (NQR) spectroscopy (1.11.23), Basic principle of NQR (1.11.24), Quadrupole nuclei (1.11.25), Mass spectrometry (1.11.32), Photoelectron spectra (PES) (1.11.37),

Standard Key statements: Factors affecting the metal ligand vibrations (1.11.3), Basic equation in EPR (1.11.10), Back‐Goudsmit Effect (1.11.13), Magnetic Hyperfine splitting in Mossbauer spectroscopy (2.11.22), Factors affecting NQR (1.11.28),

Advance Key statements: Applications of Raman spectroscopy for inorganic chemistry (1.11.6), Splitting of spectral lines in presence of third body in EPR spectroscopy (1.11.15), Electric field gradient (1.11.26), Even electron rule and meta stable peak in Mass spectrometry (1.11.33/34), Types of PES (1.11.40)

IR spectroscopy

1.11.1. Infrared (IR) spectroscopy: IR spectroscopy is the spectroscopy which deals with the infrared region of the electromagnetic spectrum and it is observe the vibration of bonds that is with a longer wave length and lower frequency than visible light. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

- It provides a fingerprint for molecular bonding. Fingerprint is a set of specific absorption for a given bonding arrangement and geometry.

1.11.2. IR active and IR inactive vibrations: Not all molecular vibrations absorb IR radiation.

- A chemical bond which is polarized has a dipole moment.
- An electric field will interact with the polar Bond, causing it either stretch or compress.
- An electromagnetic wave has a rapidly reversing electric field. So, this radiation rapidly compresses and stretches the polar Bond.
- If the frequency of the stretching and compression is at the frequency of the molecules natural rate of hydration, then the energy may be absorbed.
- The condition for obtaining IR spectra is that the dipole moment of the molecule mass change when the atoms are displaced due to vibration.

1.11.3. Factors affecting the metal ligand vibrations:

- Greater the mass of the metal and higher the coordination number of the metal, smaller is the frequency of vibration. Increase in coordination number decreases the M-L stretching frequency.
- With increasing the oxidation state of the metal the frequency of vibration also increases.
- With increasing the basicity of the ligand, the frequency for the Sigma bonding increases.
- Higher the ligand field stabilization energy, higher the frequency of vibration.
- Bridging ligands have lower frequency than non bridging ligands.

Species	Range (cm^{-1})
CH	2900-3200
OH	3400-3600
CN^-	2000-2200
NO	1675-1870
O^{2-}	920-1120
O_2^{2-}	800-900
Metal-metal bond	120-400

1.11.4.
IR can determine whether the Thiocyanate ion, NCS^-, is bonded in a metal complex via the nitrogen atom or via the sulphur atom. The stretching frequency of CN generally occurs at a lower frequency in the N-bonded isomer than in the S-bonded. For nitrogen coordinated complex the region is 780-760 cm-1. For Sulphur bonded complexes the region is 690-720 cm-1. NCS bond at 450 to 440 cm^{-1} for N-bonded isomer and 400-440 cm^{-1} for S-bonded isomer.

Raman Spectroscopy

1.11.5. **Raman spectroscopy:** It is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with example. Raman spectroscopy can be used to study solid liquid and gaseous samples.

- Raman activity of any molecule depends on the polarizability of the molecule.
- Homonuclear diatomic molecules (N_2, O_2, Cl_2) are often how to be active in Raman spectra.
- Water can be used as a solvent in Raman spectra.
- Three Raman lines are observed in the spectrum of scattered light. One line at the frequency of incident light corresponding to Rayleigh scattering. If the scattered light will have the same frequency as the incident light, is known as **Rayleigh scattering.**

  Second line will be at lower frequency than the incident light. This line of lower frequency is known as **Stokes line.**

  Third line will be at higher frequency than the incident line, it is called **Anti-stokes line.**

  The frequency of light undergoing Raman effect is

  $V = V_{ex} \pm V_m$.

  $V = V_{ex}$ ($\Delta V = 0$) $\rightarrow$ Rayleigh scattering

  $V = V_{ex} - V_m$ ($\Delta V < 0$) $\rightarrow$ Stokes line

  $V = V_{ex} + V_m$ ($\Delta V > 0$) $\rightarrow$ Anti Stokes line

1.11.6. **Applications of Raman spectroscopy for inorganic chemistry:**
The vibrational Raman spectrum has been used to distinguish between linear (CS_2, HF_2^-, NO_2^+, N_3^-, BO_2^-, $ZnCl_2$) and bent (H_2O, H_2S, H_2Se, NO_2, OF_2, NO_2^-, UO_2^{2-}) structures.

- In H_2O, three fundamental vibrations in a non linear triatomic molecule are expected to be active both in IR and Raman. Since this is so for H_2O, it has a bent structure like SO_2 and D_2O.
- In Raman spectrum HCN exhibit 2 lines at 2062 cm^{-1} and 2094 cm^{-1} for two isomers HCN and HNC.
- Raman spectra confirmed the structure of N_2O as N-N-O.

- Totally symmetric vibrations of tetrahedral complexes ($ZnCl_4^{2-}$, $CdCl_4^{2-}$, $HgCl_4^{2-}$, etc) and the octahedral complexes (SiF_6^{2-}, SF_6^{-}, PF_6, UF_6) are IR active due to only the bond length change during the vibration. But the same vibration gives rise to intense lines in the Raman spectra. Tetrahedral structure for OsO_4, CrO_4^{2-}, MoO_4^{2-} and WO_4^{2-} while pyramid structure for ClO_3^{-}, BrO_3^{-} has been confirmed by Raman spectra.

NMR Spectroscopy

1.11.7. **NMR spectroscopy:** In nuclear magnetic resonance spectroscopy radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule. The magnetic energy levels are created by keeping the nucleus in magnetic level.

All atomic nuclei possess nuclear spin, I, which may be integral (i.e., 1, 2, 3,…) or half-integral (i.e., 1/2, 3/2, 5/2,7/2,….). The proton and the neutron is has spin ½. The angular momentum associated with a nuclear spin is given by $[I(I + 1)]^{1/2}(h/2\pi)$

The following rules are helpful in predicting the nuclear spin:

- If the mass number A is odd, nuclear spin I is half integral. 10 in the case of ^1H, ^{15}N, ^{19}F, ^{31}P, I = 1/2 and in the case of ^{11}B, I = 3/2.
- If the mass number A and the atomic number Z are both even, spin is zero. Thus, in the case of $_2He^4$, $_8O^{16}$, I = 0.
- If the mass number A is even but the atomic number Z is odd, the spin is integral. Thus, the spin of $_1H^2$ and $_7N^{14}$ is 1 while that of $_5B^{10}$ is 3.
- **The nuclei having spins more than 1:**
  3/2 spin nuclei $\rightarrow$ $_5B^{11}$, $_{17}Cl^{35}$, $_{17}Cl^{37}$, $_{19}K^{39}$, $_{19}K^{41}$, $_{24}Cr^{53}$, $_{28}Ni^{61}$, $_{29}Cu^{63}$, $_{29}Cu^{65}$, $_{29}Br^{79}$, $_{35}Br^{81}$.
  5/2 spin nuclei $\rightarrow$ $_8O^{17}$, $_{12}Mg^{25}$, $_{13}Al^{27}$, $_{22}Ti^{47}$, $_{25}Mn^{55}$, $_{30}Zn^{67}$, $_{42}Mo97$, $_{44}Ru^{101}$, $_{46}Pd_{105}$.
  7/2 spin nuclei $\rightarrow$ $_{20}Ca^{43}$, $_{21}Sc^{45}$, $_{22}Ti^{49}$, $_{23}V^{51}$.

1.11.8. NMR frequency of a bare proton (or a bare nucleus with I = ½) is given by, $\nu = \dfrac{\Delta E}{h} = \dfrac{g_N \mu_N B_z}{h}$

$$\boxed{\text{EPR}}$$

1.11.9. Electron Paramagnetic Resonance (EPR), sometimes referred to as Electron Spin Resonance (ESR), is a widely accepted spectroscopic technique in various research fields. The resonance occurs between the spin of the unpaired electron and the electromagnetic field under a static magnetic field. This technique is used to study paramagnetic centers on various oxide surfaces, which are frequently encountered in heterogeneous catalysis. The observed paramagnetic centers include surface defects, inorganic or organic radicals, metal cations or supported metal complexes and clusters. Each of these paramagnetic species will produce a characteristic EPR signature. Diamagnetic oxide materials can also be studied using suitable paramagnetic probes, including nitroxides and transition metal ions.

1.11.10. **Basic equation:**
Let us start with ground state $^2S_{1/2}$ of hydrogen atom having single electron. Here, $L = 0$, $S = ½$, and $J = ½$. Under the magnetic field this level splits into two energy levels, essentially due to the spin projection $m_s = ½$ and $m_s = -½$ because $m_L = 0$. The splitting energy due to the magnetic field is $E_{mag} = g_J \mu_B B_z$ as shown in following figure.
The value of $g_J = 2$.
The transition between this level is governed by the magnetic dipole selection rule $\Delta l = 0$, $\Delta S = \pm 1$. This transition changes the spin projection by ± 1.
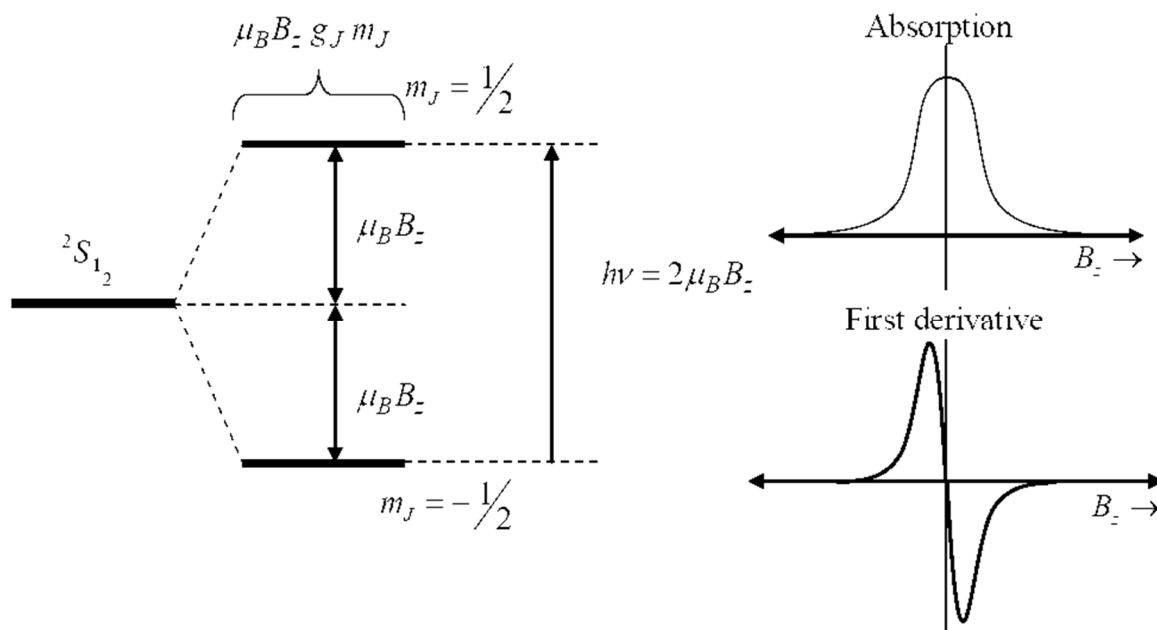
Since

$$h\nu = g_s\mu_B B_z = 2\mu_B B_z$$

Here, $g_J = g$, because $L = 0$

$$h\nu = g_s\mu_B B_z = 2\mu_B$$

$$\frac{\nu}{B_z} = \frac{2\mu_B}{h} = 2.8 MHz/gauss$$

It can be seen that the frequency required for the transition to occur is about 2.8 Hz per Gauss of applied field. This means that for the magnetic field usually employed in the laboratory, the radiation required belongs to the microwave region. When the magnetic field used is about 3400 Gauss, the corresponding applied frequency required is in the microwave region of the electromagnetic spectrum (~9 to 10 GHz). This corresponds to a wavelength of about 3.4 cm and is known as the X - band frequency.

1.11.11. **Instrumentation:**
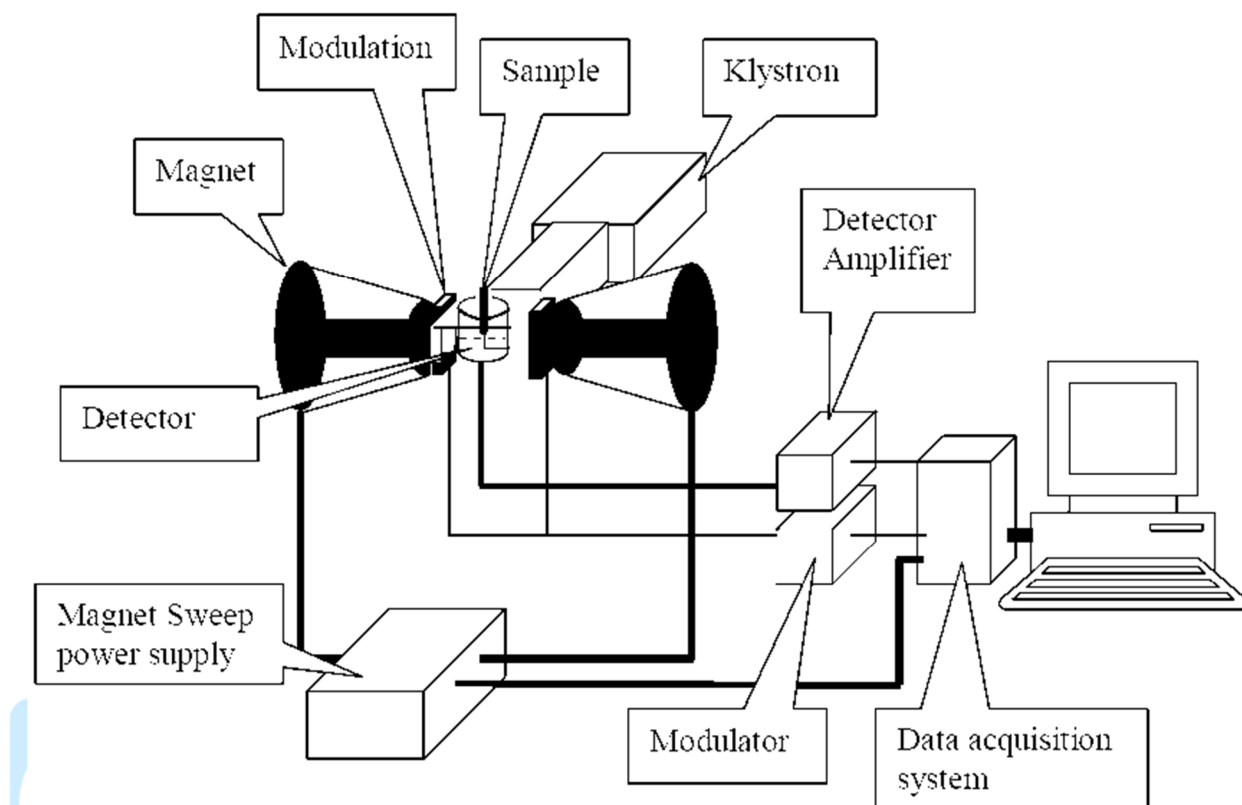
1.11.12. **Population:**

The ratio of the electron population in the $m_J = 1/2$ state $n_{1/2}$ to the $m_J = -1/2$ state $n_{-1/2}$ at a given temperature is given by $\frac{n_{+1/2}}{n_{-1/2}} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{g_J \mu_B B_z}{kT}}$

To improve the sensitivity of the measurement, either B_z increases or temperature decreases.

For common EPR experiments one of the frequency is selected for microwave radiation

Band	v_0 (MHz)	λ (cm)	B_z (Gauss)
X	9,500	3	3,400
K	36,000	0.8	13,000

For resonance condition, instead of varying ν_0, the magnetic field is varied.

At resonance condition, the absorption takes place. So the graph obtained is the absorption versus the magnetic field.

To measure the value of the magnetic field correctly, the first derivative of the absorption curve is recorded, as shown in the figure.
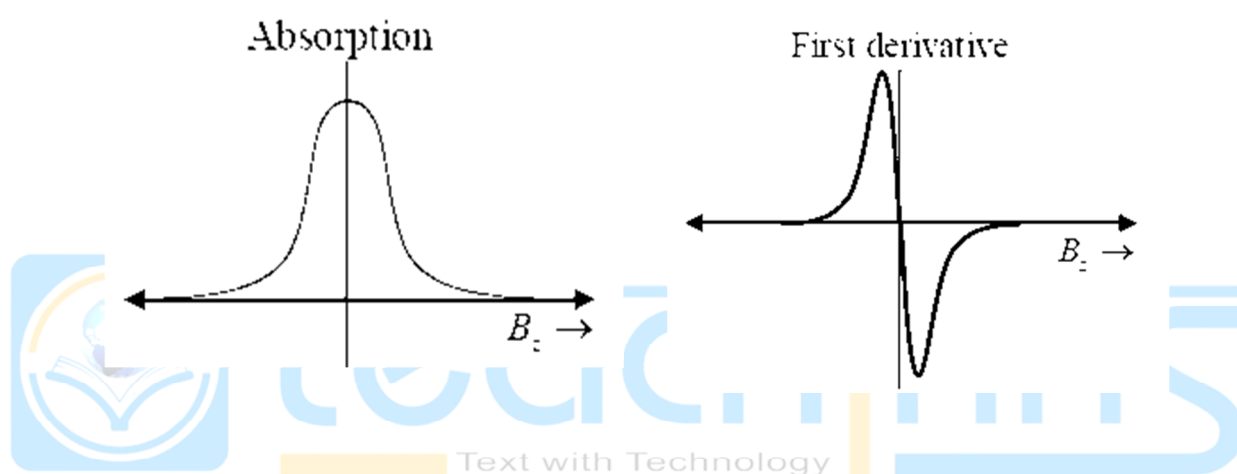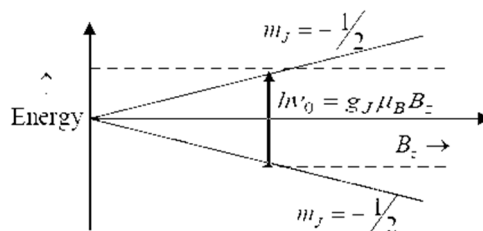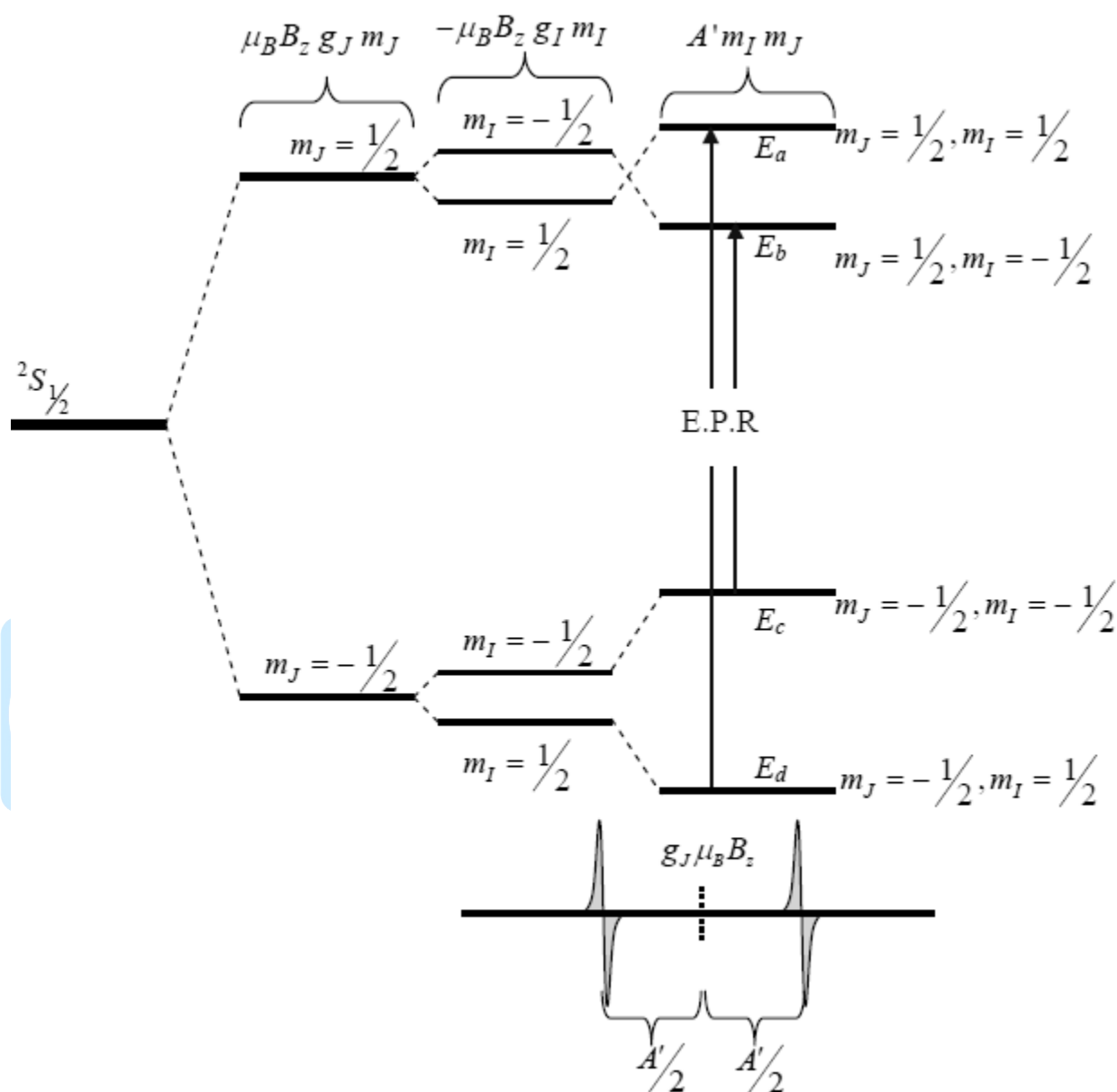

1.11.13. Back – Goudsmit Effect:

Now we will consider the interaction of electron magnetic moment and the nuclear spin. As discussed in the previous lecture, the interaction energy (Back-Goudsmit Effect) is

$$(m_J g_j - m_I g_I)\mu_B B_z + A' m_I m_J$$

when the magnetic field strength is higher than the hyperfine interaction. Using this relation, we see that the electron Zeeman levels split further into four levels due to the nuclear spin.

$$\mu_B B_z \, g_J \, m_J \qquad -\mu_B B_z \, g_I \, m_I \qquad A' m_I \, m_J$$

$^2S_{1/2}$

$m_J = \frac{1}{2}$

$m_I = -\frac{1}{2}$

$m_I = \frac{1}{2}$

$E_a \qquad m_J = \frac{1}{2}, m_I = \frac{1}{2}$

$E_b \qquad m_J = \frac{1}{2}, m_I = -\frac{1}{2}$

E.P.R

$m_J = -\frac{1}{2}$

$m_I = -\frac{1}{2}$

$m_I = \frac{1}{2}$

$E_c \qquad m_J = -\frac{1}{2}, m_I = -\frac{1}{2}$

$E_d \qquad m_J = -\frac{1}{2}, m_I = \frac{1}{2}$

$g_J \mu_B B_z$

$\frac{A'}{2} \qquad \frac{A'}{2}$

The E.P.R Selection rule : $\Delta m_J = \pm 1$, $\Delta m_I = 0$.
The reason for this is that these transitions are magnetic dipole transitions of electron where the m_J changes by 1. But this cannot change the nuclear spin simultaneously. So the mI will be unchanged during the transition. Applying this E.S.R. selection rule two transitions are observed.

1.11.14. **Energies of substiuents:**

We calculate now the energies of these levels and see the energies of these two transitions. Substituting the value of and in proper equation, we get $m_J = \pm \ 1/2$; $m_I = \pm 1/2$

$$E_a = \frac{1}{2}g_J\mu_B B_z - g_I\mu_B B_z + \frac{A'}{4} \qquad m_J = \frac{1}{2}, m_I = \frac{1}{2}$$

$$E_b = \frac{1}{2}g_J\mu_B B_z + g_I\mu_B B_z - \frac{A'}{4} \qquad m_J = \frac{1}{2}, m_I = -\frac{1}{2}$$

$$E_c = -\frac{1}{2}g_J\mu_B B_z + g_I\mu_B B_z + \frac{A'}{4} \qquad m_J = -\frac{1}{2}, m_I = -\frac{1}{2}$$

$$E_d = -\frac{1}{2}g_J\mu_B B_z - g_I\mu_B B_z - \frac{A'}{4} \qquad m_J = -\frac{1}{2}, m_I = \frac{1}{2}$$

And the two transition energies are

$$v_1 = E_a \leftarrow E_d = g_J\mu_B B_z + \frac{A'}{2}$$

$$v_2 = E_b \leftarrow E_c = g_J\mu_B B_z - \frac{A'}{2}$$

So these two transitions are separated by the hyperfine constant between them. This is a direct measure of the Fermi contact term (*AF*) for the hydrogen atom discussed in previous lectures. *A'*

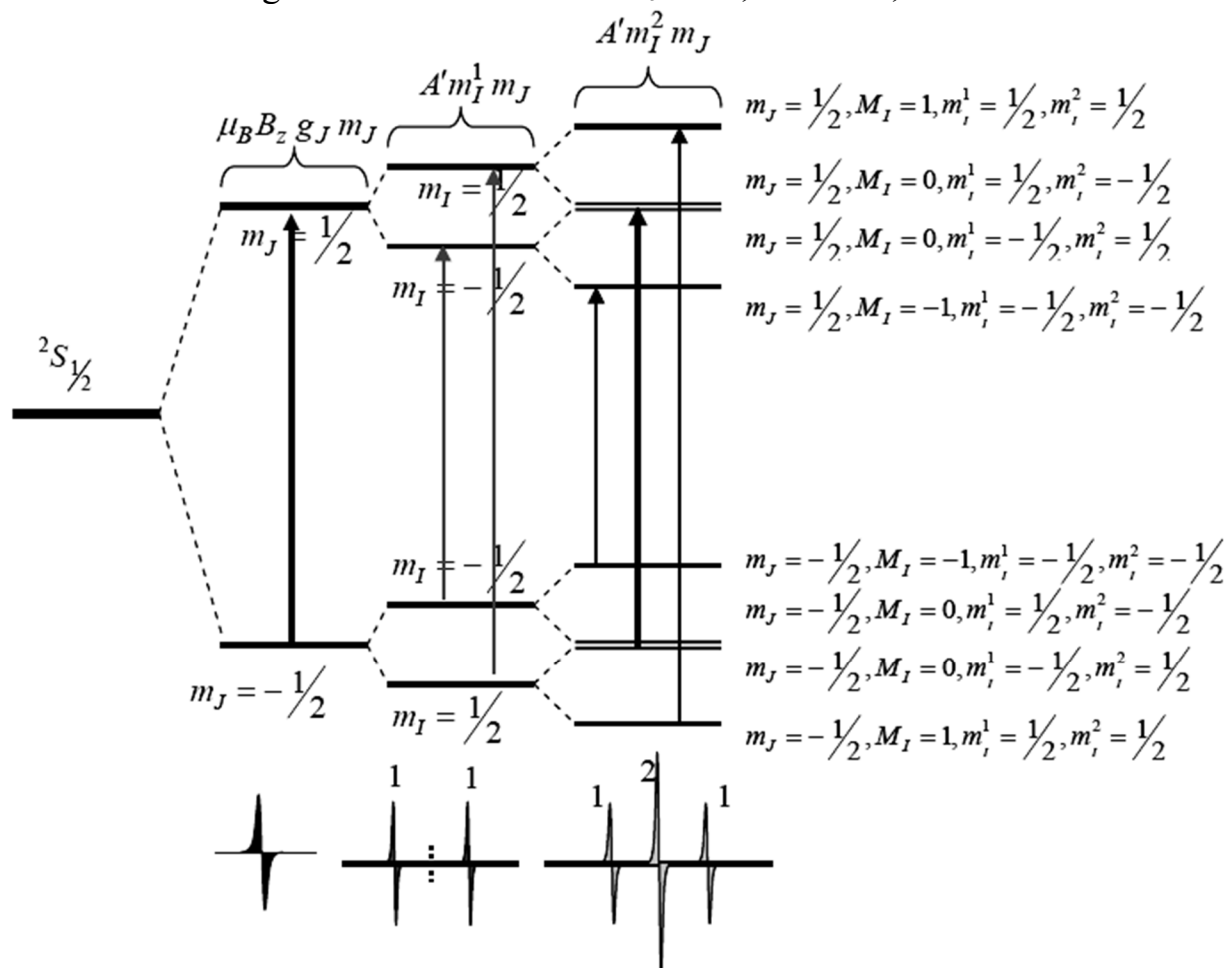The intensity of both the transitions will be equal as shown in above figure.

Note:

Since in the transition energy expression $g_I\mu_B B_z$ does not appear, from now on we will drop this term for the discussion as well as we will not include it in the diagram.

1.11.15. Splitting of spectral lines in presence of third body:

Let us consider that the electron is interacting with two similar protons with $I = \frac{1}{2}$ and $\frac{1}{2}$. According to coupling of angular momenta, we have the value of coupled $I = 1$, 0 and the value of $m_I = 1$, 0, -1.

As shown in above figure, each electron Zeeman level splits into three levels. Using E.S.R selection rule $\Delta m_J = \pm 1$, $\Delta m^1_I = 0$, $\Delta m^2_I = 0$ there will

$$A' m_I^2 m_J$$

$$A' m_I^1 m_J$$

$$\mu_B B_z g_J m_J$$

$$m_J = \frac{1}{2}$$

$$m_I = \frac{1}{2}$$

$$m_I = -\frac{1}{2}$$

$$^2S_{\frac{1}{2}}$$

$$m_J = -\frac{1}{2}$$

$$m_I = -\frac{1}{2}$$

$$m_I = \frac{1}{2}$$

$$m_J = \frac{1}{2}, M_I = 1, m^1_I = \frac{1}{2}, m^2_I = \frac{1}{2}$$

$$m_J = \frac{1}{2}, M_I = 0, m^1_I = \frac{1}{2}, m^2_I = -\frac{1}{2}$$

$$m_J = \frac{1}{2}, M_I = 0, m^1_I = -\frac{1}{2}, m^2_I = \frac{1}{2}$$

$$m_J = \frac{1}{2}, M_I = -1, m^1_I = -\frac{1}{2}, m^2_I = -\frac{1}{2}$$

$$m_J = -\frac{1}{2}, M_I = -1, m^1_I = -\frac{1}{2}, m^2_I = -\frac{1}{2}$$

$$m_J = -\frac{1}{2}, M_I = 0, m^1_I = \frac{1}{2}, m^2_I = -\frac{1}{2}$$

$$m_J = -\frac{1}{2}, M_I = 0, m^1_I = -\frac{1}{2}, m^2_I = \frac{1}{2}$$

$$m_J = -\frac{1}{2}, M_I = 1, m^1_I = \frac{1}{2}, m^2_I = \frac{1}{2}$$

be three transitions. The separation between the two transitions is A'. The intensity ratio is 1:2:1, because the middle line is consisting of two transitions as shown in figure

1.11.16. **Application:**

Here we will focus some applications of E.S.R

A. Structural determination of radicals.

Methyl radical -$\cdot CH_3$ has three equivalent $\cdot C$ - H bonds. This provides four lines. The splitting between the lines is 25 Gauss.

The structure can be planar or tetrahedral.

For most planar aromatic radicals, the value of A' is 25 Gauss.

The theoretical value of the splitting in planar form is ~ 41 Gauss

The theoretical value of the splitting in tetrahedral form is ~ 300 Gauss.

Therefore, the structure of the methyl radical is planar.

B. Benzoquinone anion radical:

Four identical $\cdot C$ - H bonds provide five lines.

1 proton – splits into 2 lines 1:1

2 protons split into 3 lines 1:2:1

3 protons split into 4 lines 1:3:3:1

4 protons split into 5 lines 1:4:6:4:1
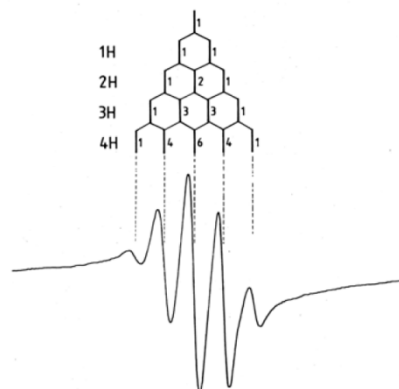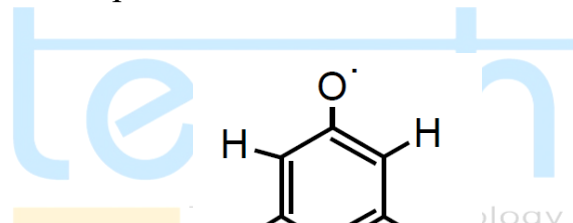
1.11.17. **E.S.R for solid sample:**

In crystal, the crystal field can interact strongly with $\vec{L}$ and splits into 2L+1 sublevels. Each of these sublevels further split into 2S+1 sublevels when the external magnetic field is applied. The magnetic dipole selection rule

$$\Delta m_J = \pm 1$$

In another case, the spin degeneracy is removed in the crystal when weak spin orbit coupling is present. In this case the spin degeneracy is removed without external magnetic field.
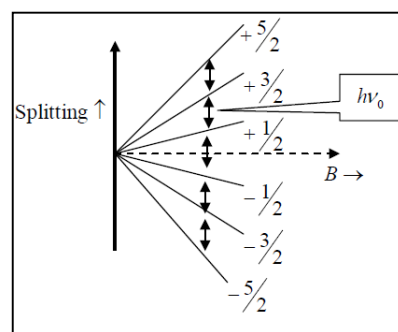
1.11.18. For Mn^{+2}:

For Mn^{2+}, spin orbit coupling is zero. On applying magnetic field the ground state ($^6S_{5/2}$) splits into $\left(2 \times \frac{5}{2} + 1 = 6\right)$ levels. Since the separation between the sublevels is same, all the resonance occurs at the same frequency.

1.11.19. For Cr^{3+}:

In case of Cr^{3+}, spin degeneracy is removed by crystal field, and the sublevels are not equally placed. So the resonances occur at different frequencies.

Further, if the paramagnetic ion has nuclear spin, each sublevel will further split and the separation between the splitted sublevels provides information of the hyperfine constant.
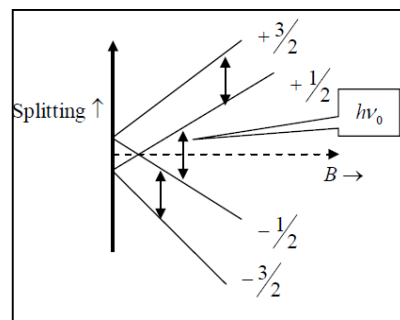
Mossbauer Spectroscopy

1.11.20. Principle of Mossbauer Effect:

An excited nucleus comes to its ground state by emission of γ-ray, the emitted γ-ray can be sensed or absorbed by another identical nucleus in the ground state and the process is called as resonance. Similar process is well known in optical resonance, the difference is only in the order of energy.

emission and absorption process of γ rays.
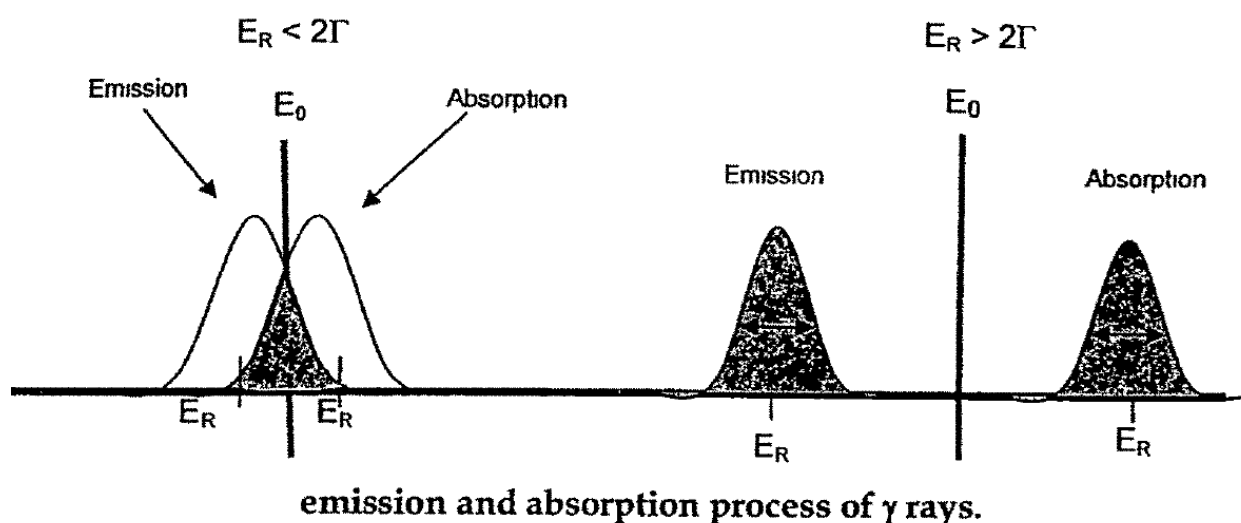
In optical process the energy of electromagnetic radiation is of the order of KeV, where as γ coming from nucleus has energy thousand times greater. During emission-absorption process there is a recoil energy involved in order to conserve linear momentum. They emission process will provide more recoil than in the case of optical radiation. The energy of the emitted γ radiation will differ from transition energy by an amount equal to Er. Hence the resonance probability for γ ray is less than the optical radiation. For resonance absorption the incoming photon must provide energy equal to the transition energy. R. L. Mossbauer successfully demonstrated the feasibility of observing the y resonance fluorescence.

The kinetic energy associated with recoil is

$$E_r = \frac{E_0^2}{2mc^2}$$

Where Eo is the energy of the nuclear transition, m is mass of atom, c is velocity of light, Eris the recoil energy of the atom.

Thus, the energy of emitted γ ray

$$E_\gamma = E_0 - E_r$$

Similarly in absorption process the photon should have energy

$$E_\gamma' = E_0 - E_r$$

Due to Doppler broadening the width of the emission and absorption lines becomes

$$\Delta = 2(E_r K_B T)^{1/2}$$

Where K_B is the Boltzman's constant, T is the absolute temperature of source and absorber.

In Debye model of lattice vibration, recoil free fraction is given by

$$f = exp\left[\frac{-6E_R T}{K_B \theta_D}\right]$$

Above equation shows that the favorable conditions for Mossbauer resonance is

1) low recoil energy.

2) Low temperature.

3) High Debye Temperature θ_D.

1.11.21. **Natural Line width:**

The nuclear level with finite mean life time can have uncertainty in its energy given by the equation $\Gamma = \dfrac{\hbar}{\tau_N}$. Γ is called natural line width. The frequency spectrum of the emitted γ ray has a Lorentzian distribution centered at coo and half width is $\Gamma/\hbar$. The Intensity distribution of radiation at frequency ω is written as

$$I(\omega) = \frac{I_0}{1 + [(\omega - \omega_0)2\hbar/\Gamma]^2}$$

Intensity distribution of the emitted γ ray in decay process
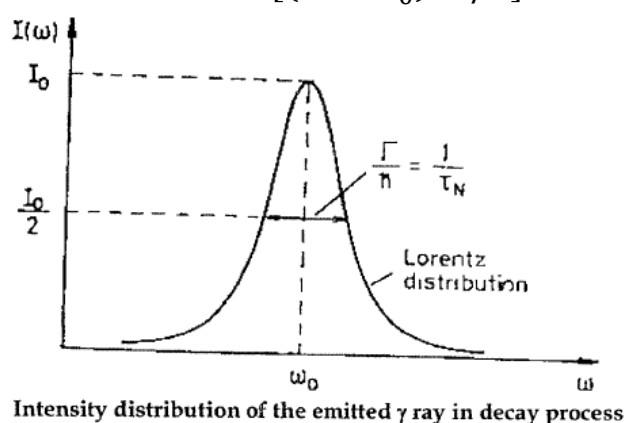
1.11.22. **Magnetic Hyperfine splitting:**

The presence of a magnetic field H at the nucleus of the Mossbauer active isotope will produce a splitting of nuclear levels through magnetic Dipole interaction, this is called nuclear Zeeman effect. The nucleus with spin I and magnetic moment p in the presence of magnetic field H experiences a torque due to which the moment tries to align with the field. The interaction energy associated with it is given by Hamiltonian

$$H_M = -g\mu_N H I_z$$

Where g is the nuclear lande factor, gN is nuclear magnetic moment and lz is the z component of I in the direction of H.

The Magnetic Hyperfine field H exists at the nucleus can be written as

$$H = H_0 - DM + \frac{4}{3\Pi}M + H_S + H_L + H_D$$

Where H_0 is the externally applied field, H_S is the interaction between electron spin density and the nucleus (Fermi contact term), H_L is contribution arising from orbital magnetic moment and H_D is dipole interaction of the nucleus with spin moment. Fig shows schematic diagram of magnetic Hyperfine splitting of Fe^{57}.
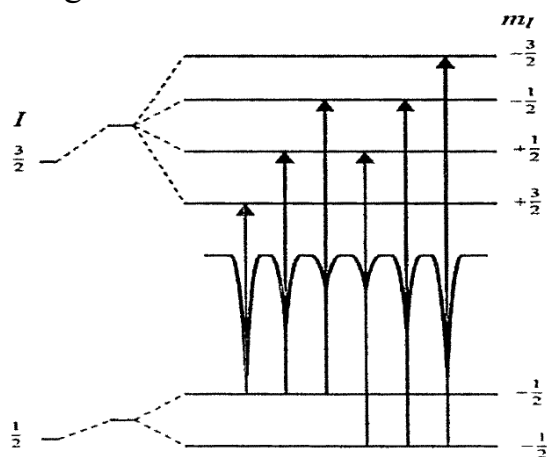
Magnetic Hyperfine splitting of Fe^{57}

NQR

1.11.23. **Nuclear quadrupole resonance (NQR) spectroscopy:** A concept of NQR is almost similar with NMR only differ from the magnetic field interaction. Hair it is basically **zero field NMR.**

From this β spectroscopy we can obtain whether a compound is ionic or covalent, not only that present of H-bonding can be known with the help of NQR.

1.11.24. **Basic principle of NQR:** There is an interaction between the induced dipole moment within the quadrupole nuclei ($I > 1/2$) with the asymmetric charge distribution followed by induced electric field gradient. Such kind of interaction split the m_I level into $(2I + 1)$ without the application of radio frequency. Zero point energy is the key factor for creative inducing dipole moment within the molecule.

1.11.25. **Quadrupole nuclei:** It is one where a value of I is greater than ½ and here asymmetrical charge distribution gives rise to elliptical or egg shaped compound.

1.11.26. **Electric field gradient:** It is the negative value of -dV/dx

Where,

V = the potential

X = the direction

Basically it is a tensor quantity

$$\begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yz} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix}$$

It is basically three types-

- **Spherical:**
  Vxx = Vyy = Vzz = 0 (EFG = 0)

- **Axial:**
  Vxx = Vyy ≠ Vzz = 0 (EFG ≠ 0), η = 0.
  η = asymmetrical parameter

- **Non axial:**
 Vxx ≠ Vyy ≠ Vzz = 0 (EFG ≠ 0), η ≠ 0.

1.11.27. **Condition for NQR:**
- I > 1/2
- Asymmetrical dipole moment must present i.e., electrical field gradient (EFG) ≠ 0.
- Sample nature should be solid.
- Sample should be diamagnetic in nature

1.11.28. **Factors affecting NQR:**
- **Orbital nature:** In between s, p, d, f orbital, the contribution of s orbital in EFG is zero. So, any electronic contribution is negligible for s orbital w.r.to NQR. But p, d, f orbitals not spherical in nature. They contribute some electric field gradient in NQR but among them p orbital contribution is maximum due to the closest distance w.r.to the nucleus i.e., the asymmetrical charge distribution will be the maximum for p orbital. But as the radial distance of d, f orbital is higher so, the asymmetric charge distribution is less.
  Not only that the orbitals which belongs to nearest noble gas configuration have no EFG.

- **Nature of the sample:** Sample should be solid in nature so that there must be some EFG. But in case of gaseous or liquid sample due to their higher randomness and orientation equally in the x, y, z axis. So, the average EFG is assumed to be zero. So, splitting is obtained for liquid or gaseous sample in NQR.

- **Magnetic character of the sample:** Excited state lifetime i.e., the Δt is the key factor for the present cases. If the relaxation process is faster i.e., the Δt is minimum then using HUP the peak width will be broaden $\left(\Delta\nu \propto \frac{1}{\Delta t}\right)$. This indicates that the paramagnetic species containing an unpaired electron causes rapid relaxation due to the unstable nature leading to broadening of peak in NQR. So, diamagnetic sample is preferred to obtain sharp peak.

- **Natural abundance:** Higher the natural abundance higher will be the peak intensity.
  $NaCl^{35}$, $NaCl^{37}$
  $Cl^{35} \rightarrow 75\%$, $Cl^{37} \rightarrow 25\%$
  $EFG_{Cl}^{35} \gg EFG_{Cl}^{37}$
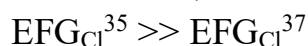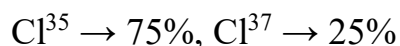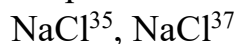
- **Bond nature:**
  EFG is more for covalent compound.
  EFG is less for ionic compounds.
  Knowing the value of EFG in NQR degree of covalency or percentage of ionic character can be easily known.
  H-F < H-Cl < H-Br < H-I → NQR peak intensity.
  NaCl < NaBr
  Higher the ionic character lower will be the EFG or vice versa for covalent character.
- **Effect of H-bonding:** H-bonding increases the ionic character of the compound. So the magnitude of EFG will be increased.
- **Effect of resonance:** Conjugation may decrease or increase EFG in NQR depending on the charge separation.
- **Effect of temperature:** With the increase of temperature relaxation time will decrease as a result. So Δv will increase i.e., peak will be broaden.

1.11.29.

NQR	NMR
No induced magnetic field i.e., zero radiation.	Magnetic radiation is used.
$I > \frac{1}{2}$	$I = \frac{1}{2}$ or other i.e., $I \neq 0$

1.11.30. **Note:**

- All nuclei having integral and half integral ($I = 1, 3/2, 2, 5/2, 3, 7/2$) possess nuclear electric quadrupole moments, designated as eQ (or simply as Q) where, e is the electronic charge, Q is a measure of the deviation of nuclear charge from spherical symmetry.

  $Q = \int \rho r^2 (3\cos^2\theta - 1) dr$

  Where, ρ is the nuclear charge density

  r = the distance from the origin to the element dr

  θ = the angle between r and spin axis.

  The quadrupole moment Q(or eQ) interact with electric field gradient designated as q (or eq), created at the quadrupolar nucleus by the acid battery charge distribution arising from the extranuclear electrons all the non bonding electrons in the molecule which the nucleusforms a part. **The product of eQ and eq i.e., e²Qq is called nuclear quadrupole coupling constant, also sometimes designated as QCC.**

- NQR is observed for nuclei with $I \geq 1$. When $I < 1$, the nuclei do not possess eQ so that there is no nuclear quadrupole interaction with eq.

- The quantities e²Qq, q and η are three most important quantities in NQR. **Eta** is a measure of the non-symmetry of the EFG.

- $Em_I = e^2Qq/4I(2I - 1) [3m_I^2 - I(I+1)]$

  $m_I = -I, -I + 1…, + I$ = is the component of the nuclear spin I the axis of quantization.

  m_I^2 is involves in the energy expression, hence the NQR energy levels are **doubly degenerate.**

  The selection rule for the NQR transitions is $\Delta m_I = \pm 1$.

- Due to the strong temperature dependence of the NQR frequency, it can be used as a precise temperature sensor with resolution on the order of 10^{-4} °C.

1.11.31. $_5B^{11}$:

$I = 3/2$

$m_I = -3/2, -1/2, 1/2, 3/2$

Because of the $m^2{}_I$ term in the energy expression, the NQR interaction splits the $I = 3/2$ level into two doubly-degenerate pairs of sublevel, $m_I = \pm 1/2$ and $m_I = \pm 3/2$.
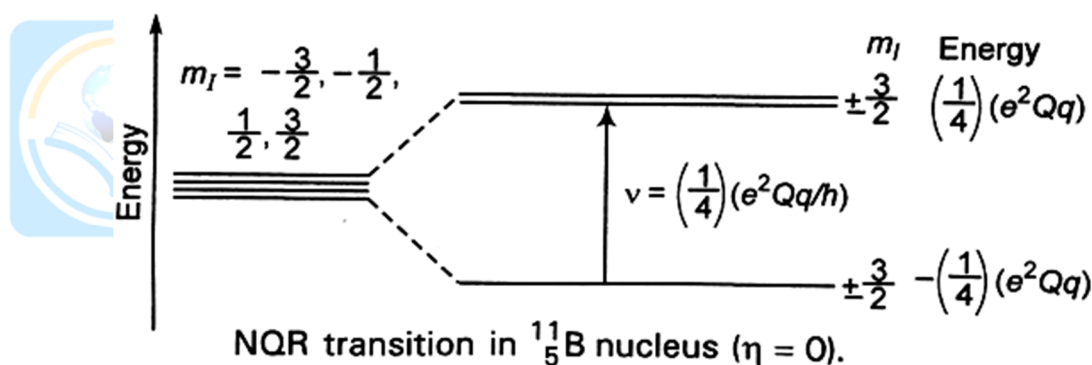
Thus, $I = 3/2 \rightarrow \pm 1/2, \pm 3/2$.

Substituting these values of m_I in the energy expression we obtain,

$E_{\pm 1/2} = -\left(\dfrac{1}{4}\right)(e^2Qq)$ and $E_{\pm 3/2} = \left(\dfrac{1}{4}\right)(e^2Qq)$.

The selection rule gives only one NQR frequency.

$\nu\ (\pm 1/2 \leftrightarrow \pm 3/2) = (E_{+-3/2} - E_{+-\frac{1}{2}})/h = (\tfrac{1}{2})(e^2Qq/h)$

NQR transition in $^{11}_{5}B$ nucleus ($\eta = 0$).

Mass Spectrometry (MS)

1.11.32. **Mass spectrometry:** It is the most accurate method for determining the molecular mass of the compound and its elemental composition. In this technique, molecules are bombarded with a beam of energetic electrons. The molecules are ionized and broken up into many fragments, sum of all positive ions. Each kind of ion has a particular ratio of mass to charge i.e., m/e ratio. For most ions the charge is one and thus, m/e ratio is simply the molecular mass of the ion.

1.11.33. **Even electron rule:**

Even electron species never break down into the odd electron species.

Even electron species $\rightarrow$ neutral molecule and cation.

Odd electron species $\rightarrow$ radical and radical cation.

1.11.34. **Meta stable peak:** Meta stable peak is equal to square of the m/e value of daughter peak divided by m/e value of the parent. For particular fragmentation $m_1 \rightarrow m_2$, the position of meta stable peak is $m^* = \frac{m_2^2}{m_1}$.

1.11.35. **Molecular ion peak and relative intensity ratio:**

In case of chloro or bromo compounds, isotopes peaks are also formed along with the molecular ion peak. In case of bromo compounds, M^+ and $(M^+ + 2)$ peaks are formed in the intensity ratio 1:1. In case of chloro compounds, M^+ and $(M^+ + 2)$ peaks are formed in the intensity ratio 1:3.

Any compound containing 'n' number of Cl or Br atom:

Molecular peak = $(n + 1)$

Relative intensity = $(A + B)^n$

Where, n = number of halogen atom.

A,B = abundance of nature between two adjacent Cl or Br atom peak difference must be 2.

$C_3H_6Br_2$:

Molecular ion peak = $(2 + 1) = 3$

Relative intensity ratio = $(1 + 1)^2 = 1^2 + 2.1.1 + 1^2 = 1 + 2 + 1 \rightarrow 1:2:1$

$C_6H_4Cl_2$:

Molecular ion peak = $(2 + 1) = 3$

Relative intensity ratio = $(3 + 1)^2 = 3^2 + 2.3.1 + 1^2 \rightarrow 9:6:1$

Electron Spectroscopy

1.11.36. **Electron spectroscopy:** It is an analytical technique to study the electronic structure and its dynamics in atoms and molecules.

1.11.37. **Photoelectron spectra (PES):** PES spectroscopy measures the electron count by the ejection of electrons by the bombardment of monochromatic photons from the surface of atom or molecule and thereby it is very much effective for knowing the exact electronic structure with respect to surface balk of the system.

It is basically a kind of light absorption or emission or scattering of electromagnetic radiation from the surface of the compound.

This phenomenon is almost similar to the photoelectric effect.

1.11.38. **Condition:** It is not necessary to take place the electron injection from the metal surface when the frequency of monochromatic photon just equal or less than frequency. But it happens when a sufficient amount of frequency will exceed the range so that the excess energy converted to kinetic energy and thereby it will exceed the value of work function.

Here, $h\nu = IP + \frac{1}{2}mV^2$ (for gaseous state).

1.11.39. **Application:**

- Not only the surface but the structure of bulk of an atom or molecule can be known from the concept of PES. Hair the amount of electron ejection per unit time is plotted as a function of either KE or IP. Monochromatic photons used particularly to avoid unwanted spectra from different frequency of source.

- To eliminate broadening nature of the spectrum monochromatic light should be used.

1.11.40. **Types of PES:**

- UPS → ultraviolet photoelectric spectra
  Here electron ejection takes place from the surface i.e., from the valence shell orbital by the bombardment of monochromatic UV visible Ray (He-lamp, Na-lamp → source). Only the structure of surface can be measured by such UPS.

- XPS → x-ray photoelectron spectra
  Here soft X-ray as a monochromatic source is used to find out the inner structure or bulk of the structure from the electronic injection of core levelled orbital.

- AES→ Auger electron spectra
  Here monochromatic photon having a sufficient kinetic energy is used to eject electron from the core orbital firstly, giving rise to A+ + $h\nu \rightarrow A^+ + e^-$. Then relaxation process will happen to maintain the electron deficiency within the core orbital from jumping down the electron from the next higher level orbital. In such a way, the excess release energy having $K.E > \phi$ will eject another electrons from the loosely bound valence orbital of the system giving rise to $A^+ \rightarrow A^{2+} + e^-$.

  For such cases the surface and the back of the structure can simultaneously measured.
  Selection rule followed here,
  $\Delta L = 0$; $\Delta J = 0$; $\Delta S = 0$

- XRP→ X-ray fluorescence photoelectron spectra.
  Here, monochromatic X-ray source (heated W lamp) is used for the ejection of electron from the core level and to fulfill the vacancy in the core level from the higher orbital will jump down why the emission of particular frequency which is not sufficient enough for the electronic transition from the surface.
  In such process find structure of bulk of a system can be measured.
  Here selection rule obey;
  $\Delta L = \pm 1$; $\Delta J = \pm 1, 0$; $\Delta S = 0$

1.11.41. Alkali metal like Na, K etc. gives very easy photoelectron transition as the IP or binding energy for such system is very low. So, such PES is very much effective for the alkali metal related species using minimum energy.

NET JUNE 2016

Q. Identify correct statements for the EPR spectrum of VO(acac)$_2$ [with square pyramidal geometry at vanadium] at 77K [I(^{51}V) = 7/2].

(A) It has two g values

(B) It has 8 lines only

(C) It has one g value

(D) It has two patterns of 8 lines each.

(a) A and D   (b) A and C   (c) B and C   (d) B and D

Ans. For the molecule, we have, $g_x = g_y \neq g_z$

For Vanadium, $I = \dfrac{7}{2}, (2NI + 1) = 8$

Correct option is (a).

Q. The numbers of lines shown by the BH$_3$ part of the molecule Ph$_3$P, ^{11}BH$_3$ in the ^{1}H and ^{11}B NMR spectra are, respectively [I(^{11}B) = 3/2; I(^{31}P) = ½]

(a) 8 and 8   (b) 4 and 8   (c) 3 and 6   (d) 6 and 3

Ans. ^{1}H-NMR, $(2N_1 + 1)(2N_2 + 1) = 8$

^{11}B-NMR, $(2N_1 + 1)(2N_2 + 1) = 8$

Correct option is (a).

Q. To record Mössbauer spectrum of Fe containing samples, a source 'X' is used. X after a nuclear transformation (Y), gives γ-radiation used in Mössbauer spectroscopy.

(a) ^{57}Fe, β-emission

(b) ^{57}Fe, β-emission

c) ^{57}Co, electron capture

(d) ^{57}Fe, electron capture

Ans.
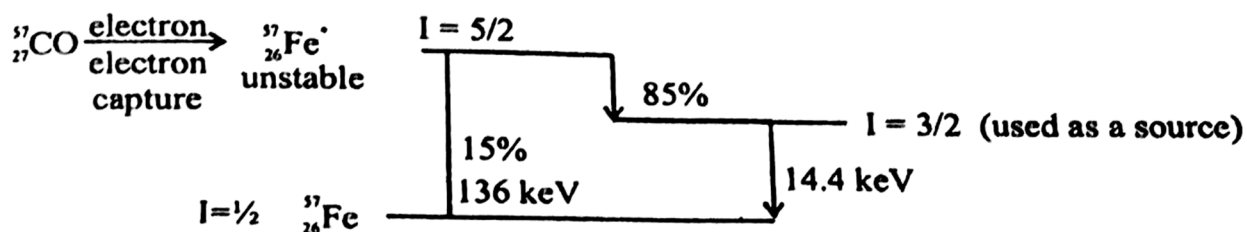
Correct option is (c)

Q. In an NMR spectrometer containing a 2.5T magnet, Larmor precession frequency of ^{1}H is 100 M*Hz*. The radiofrequency used in this spectrometer has an associated magnetic field strength of 2.5×10^{-4}T. The duration of a 90º pulse in this instrument is

(a) 25×10^{-6} s   (b) 50×10^{-6}s   (c) 25×10^{-5}s   (d) 50×10^{-5}s

Ans.

$RF_{field} = 2.5 \times 10^{-4}T= 2.5 \times 10^{-4} \times 42.57$MHz $= 10642.5$MHz.

Pulse duration $= \dfrac{1}{1064.5 \times 5} = \dfrac{1}{42570} = 23.5 \times 10^{-6}$ s

Correct option is (a).

NET DEC 2016

**Q.** The primary analytical method (not using a reference) is

(a) inductively coupled plasma emission spectrometry

(b) energy dispersive X-ray fluorescence spectrometry

(c) anodic stripping voltammetry

(d) isotopic dilution mass spectrometry

Ans. Primary analytical method is isotopic dilution mass spectroscopy (not using a reference).

Correct option is (d).

Q. For complex A, deuteration of NH protons does not alter the EPR spectrum. The number of hyperfine lines expected in the EPR $\left[I(^{63}Cu) = \frac{3}{2}\right]$ of A is
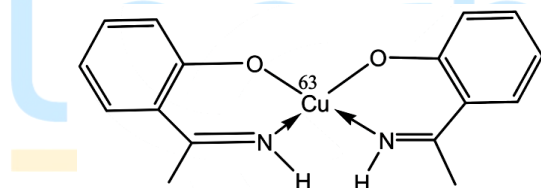
(a) 20   (b) 12   (c) 60   (d) 36

Ans. No of hyperfine line $= (2NI_1 + 1)(2NI_2 + 1) = 4 \times 5 = 20$

Correct option is (a).

Q. Number of lines in the ^{19}F-NMR spectrum of $F_2C(Br)$–$C(Br)Cl_2$ at –120ºC assuming it a mixture of static conformations given below, are
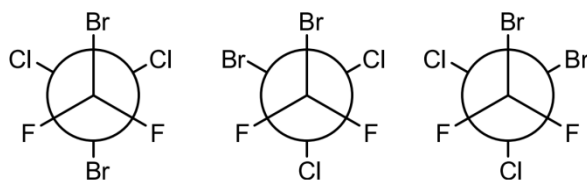
(a) one   (b) two   (c) four   (d) five

Ans.

Among the given isomers, II and III are enantiomers, for that, $(2NI_F + 1) = 3$; and for I, $(2NI_F + 1) = 2$.

So total splitting will be 3+2 = 5

Correct option is (d)

Q. In a 200 MHz NMR spectrometer, a molecule shows two doublets separated by 2 ppm. The observed coupling constant is 10 Hz. The separation between these two signals and the coupling constant in a 600 MHz spectrometer will be, respectively

(a) 600 Hz and 30 Hz   (b) 1200 Hz and 30 Hz

(c) 600 Hz and 10 Hz   (d) 1200 Hz and 10 Hz

Ans.

As we know, the coupling constant value is a machine independent parameter.

So, 2ppm in 600MHz will be, 600×2=1200MHz.

Correct option is (d).

Q. If the energies of a bare proton aligned along and against an external static magnetic field (B_Z) are $-\dfrac{\hbar\gamma B_z}{2}$ and $+\dfrac{\hbar\gamma B_z}{2}$, respectively, then the ratio of probabilities of finding the proton along and against the magnetic field is

(a) $e^{-\frac{\hbar\gamma B_z}{4k_B T}}$ (b) $e^{-\frac{\hbar\gamma B_z}{2k_B T}}$ (c) $e^{\frac{\hbar\gamma B_z}{2k_B T}}$ (d) $e^{\frac{\hbar\gamma B_z}{k_B T}}$

Ans.

$$E_{along} = -\frac{kTB_z}{2}; \text{ and } E_{ground} = \frac{kTB_z}{2}$$

Now, $\dfrac{\left(\frac{n}{N}\right)_{along}}{\left(\frac{n}{N}\right)_{ground}} = \dfrac{e^{-\frac{E_{along}}{kT}}}{e^{\frac{E_{ground}}{kT}}} = \dfrac{+\frac{\hbar\gamma B_z}{2kT}}{-\frac{\hbar\gamma B_z}{2kT}} = e^{\frac{\hbar\gamma B_z}{k_B T}}$
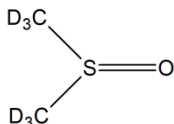
Correct option is (d).

NET JUNE 2017

Q. ^{13}C-NMR spectrum of DMSO-d^6 as δ 39.7 ppm gives a signal at a

(a) singlet   (b) triplet   (c) quintet   (d) septet

Ans.

Multiplicity $= (2nI + 1) = (2 \times 3 \times 1) + 1 = 7$

Correct option is (d).

Q. (R_3Ge)$_2$ on photolysis gives a radical which shows ESR spectrum. The ESR signals carrying the signature of ^{73}Ge(I=9/2) are in terms of

(a) Nine lines   (b) Ten lines   (c) Two lines   (d) One line

Ans.

Multiplicity $= (2nI + 1) = 10$; **Correct option is (b)**

Q. Mass fragment of $[IrCl]^+$ in mass spectrometry shows three mass peaks at m/z = 226, 228, and 230. Given that natural abundances of ^{191}Ir, ^{193}Ir, ^{35}Cl and ^{37}Cl are 37%, 63%, 76%, and 24% respectively, the intensities of the mass peaks are in the order

(a) 49.5:100:26.6   (b) 100:49.5:26.6   (c) 26.6:100:49.5   (d) 26.6:49.5:100

Ans.

$$^{191}Ir \quad : \quad ^{191}Ir \quad + \quad ^{35}Cl \quad : \quad ^{37}Cl$$

(Natural   37% : 63% + 76% : 24%

abundance) x y a b

$(3.7x + 6.3y)^1 (7.6a + 2.4b)^1$

$= 28.12 \dfrac{xa}{M} + 47.88 \dfrac{ya}{M+2} + 8.88 \dfrac{xb}{M+2} + 15.12 (M + 4)$

$= 49.5M + 100(M + 2) + 26.6(M + 4)$

So we have, $M : (M + 2) : (M + 4) = 49.5 : 100 : 26.6$
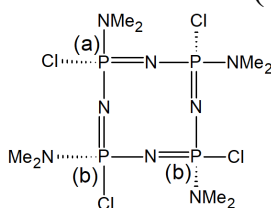
Correct option is (a).

Q. The $^{31}P\{^1H\}$ NMR spectrum of 2,2,6,6-$N_4P_4Cl_4(NMe_2)_4$ is expected to show

(a) two triplets   (b) two doublets

(c) one doublet and one triplet   (d) one quartet and one doublet

Ans.

$^{31}P\{^1H_a\} \rightarrow (2nI + 1) = 3$

$^{31}P\{^1H_b\} \rightarrow (2nI + 1) = 3$
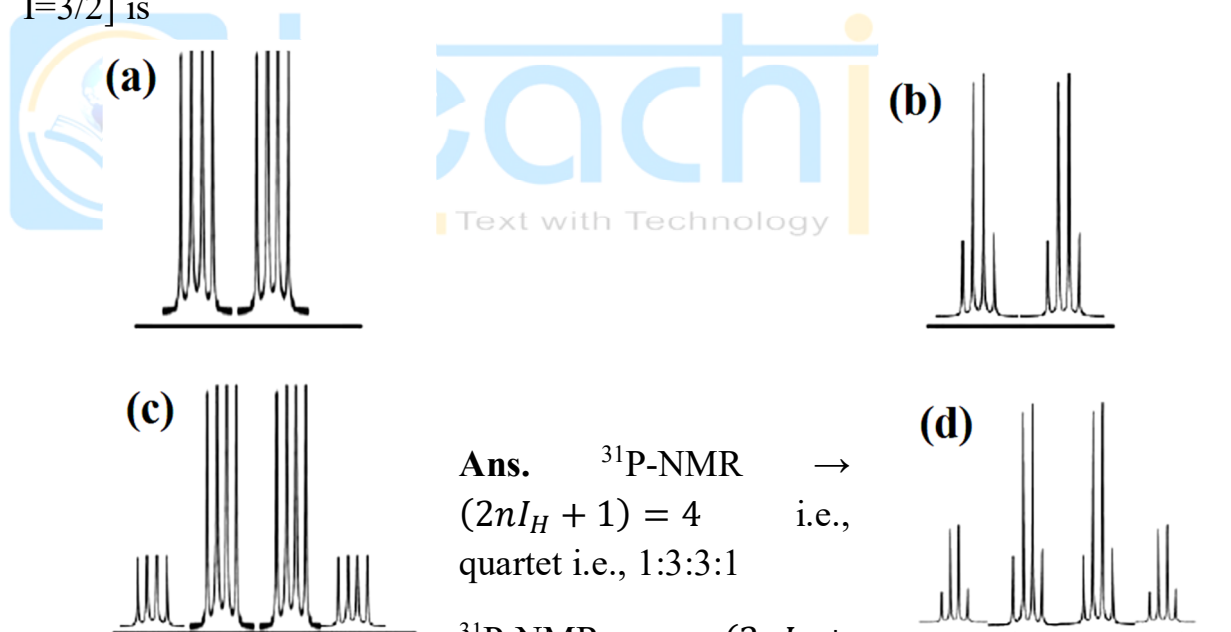
Correct option is (a).

NET DEC 2017

Q. Mismatch among the following is

(a) Sharp transition and fluorescence in lanthanides

(b) Broad bands and d-d transitions

(c) Very high spin-orbital coupling and transition elements

(d) Charge transfer and molar absorptivity of the order of 10^4 L.mol^{-1}.cm^{-1}.

Ans. Spin – orbit coupling is larger for heavier atoms and very small for lighter atoms.

Correct option is (c).

Q. Assuming $^1J_{PH} > {}^1J_{PB}$, the expected ^{31}P-NMR spectrum of H_3P:$^{11}BCl_3$ [for ^{11}B, I=3/2] is

(a)

(b)

(c)

(d)

Ans. ^{31}P-NMR → $(2nI_H + 1) = 4$ i.e., quartet i.e., 1:3:3:1

^{31}P-NMR → $(2nI_B + 1) = 4$ i.e., quartet i.e., 1:1:1:1

Correct option is (c).

Q. The g-factors of ^{1}H and ^{13}C are 5.6 and 1.4 respectively. For the same value of the magnetic field strength, if the ^{1}H resonates at 600 MHz, the ^{13}C would resonate at

(a) 2400 MHz   (b) 600 MHz   (c) 150 MHz   (d) 38 MHz

Ans. $\Delta E = h\nu = g\beta B_0$ i.e., $\nu \propto g$

So, $\dfrac{\nu_H}{\nu_C} = \dfrac{g_H}{g_C} \Rightarrow \nu_C = \dfrac{600}{4} = 150 MHz$

Correct option is (c).

NET JUNE 2018

Q. Mass spectrum of a compound shows an [M+2] ion peak that is about 4% of M^+, this indicates that the compound has one

(a) Fluorine   (b) Sulfur   (c) Bromine   (d) Chlorine

Ans. Natural abundance of S atom in, ^{32}S = 100%, ^{33}S = 0.79%, ^{34}S = 4.4%.

$M^+ = \dfrac{100}{100+0.79+4.4} = 0.95$

$[M + 2]$ peak $= \dfrac{0.042}{100+0.79+4.43} = 0.042$

% of [M+2]$= \dfrac{0.042}{0.95} \times 100 = 4.4\% \approx 4\%$

Correct option is (b).

Q. The number of lines in EPR spectrum of CD_3 ($I_D = 1$) is

(a) 3   (b) 5   (c) 7   (d) 9

Ans. $(2nI + 1) = 7$

Correct option is (c).