* Selection Rules for ESR Spectra

The selection rule for Hyperfine transition in esr spectra is —

$$\Delta m_s = \pm 1 \quad \& \quad \Delta m_I = 0.$$

This selection rule may be interpreted by saying that the nuclear motion is much slower than the harmonic motion so that during the time electron changes its spin orientation, the nucleus, being heavier, has no time to reorient its spin so that $\Delta m_I = 0$.

* Hyperfine splitting :—

In ESR spectra these occurs interaction between electronic spin and nuclear spin. As a result ESR signals (curves) will splits. This interaction between electronic spin and nuclear spin leading to splitting of ESR signals is called Hyperfine splitting.
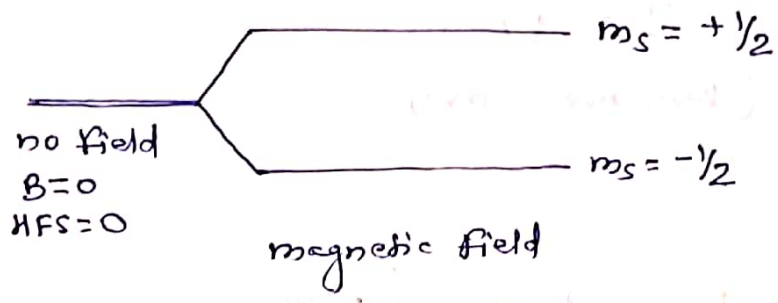
We know that the species containing unpaired electron must have nuclei and if those nuclei are magnetic in nature. The applied magnetic field due to electron spin will intract causing splitting of ESR signals. Thus, the number of splitting of the signal will depends upon the magnetic nuclei.
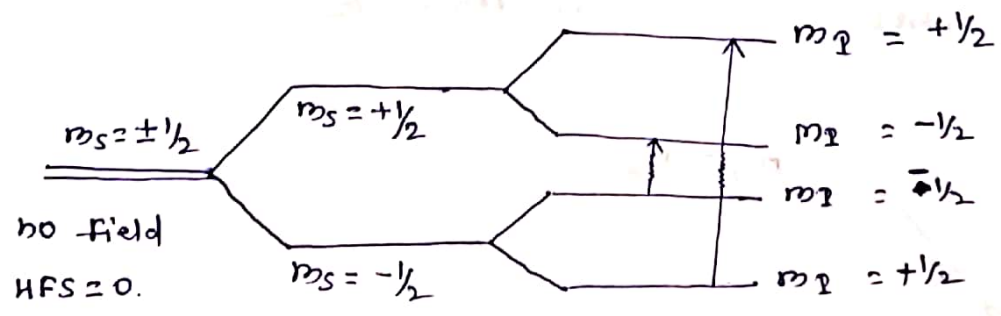
*. <u>Spectra of H-atom</u> ─x─

H-atom consists of one electron with electron spin $S = \pm\frac{1}{2}$ and it also contain a magnetic nucleus having $I = \pm\frac{1}{2}$.

When this H-atom is placed in a strong magnetic field these will be splitting into two electronic sub-levels.

(a) Due to $m_s = +\frac{1}{2}$ (higher energy levels)

(b) Due to $m_s = -\frac{1}{2}$ (lower energy levels)

Now, the magnetic nucleus of H-atom having $m_I = \pm\frac{1}{2}$ will intract with each electronic sub level giving rise to following four sub-energy levels due to hyber fine splitting.

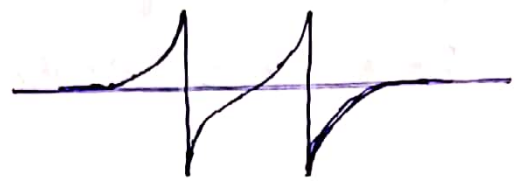

Thus, we get two ESR peaks in case of H-atom. These are equally spaced line & equally intense.

Intensity ratio :-

no. of H = 1.
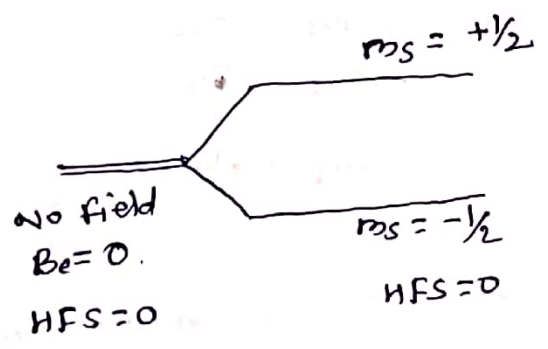
$(x+1)^{21}$ = $x+1$

= 1:1

Experimental Spectrum.

(1 : 1)

(Derivative curve)

* **Methyl free radical.** (·CH₃)

Methyl radical consists of one unpaired electron and three equivalent protons which have magnetic nuclei. When this species is placed in strong magnetic field due to splitting we get two electronic sub-levels.
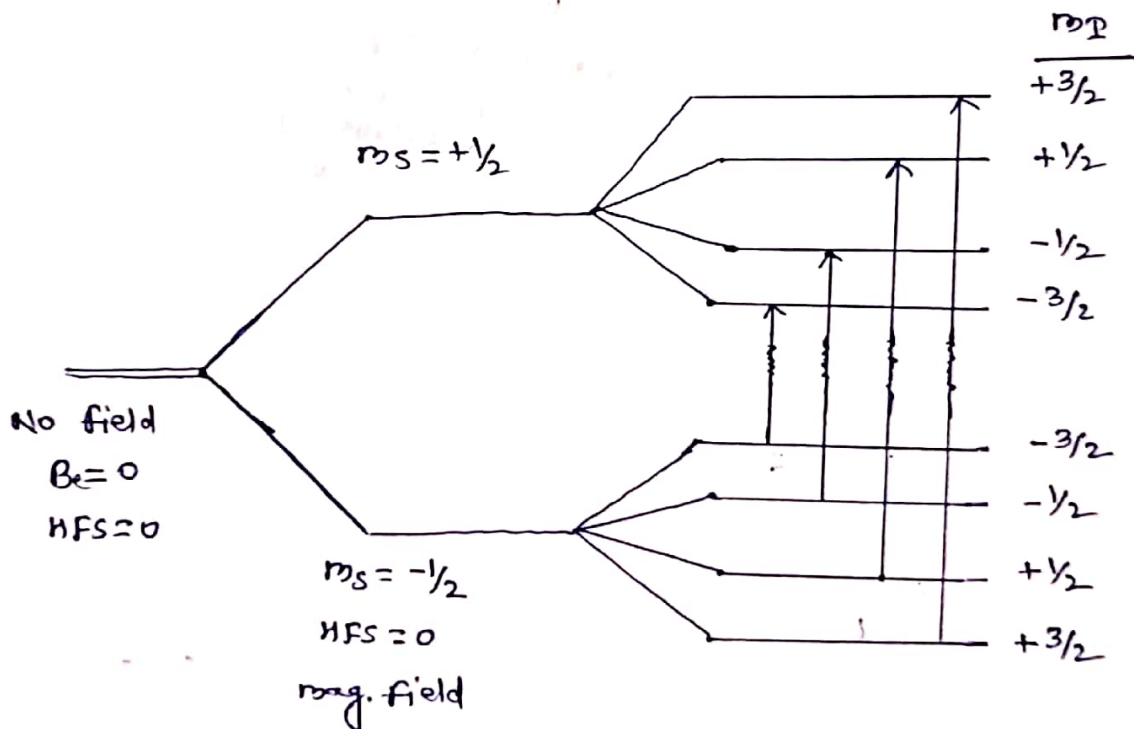
(a) One corresponding to $m_s = +\frac{1}{2}$

(b) other ,, ,, $m_s = -\frac{1}{2}$

$m_s = +\frac{1}{2}$

No field
Be= 0.

HFS=0

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

HFS=0

Now the three protons of methyl radical can have following fours different spin combinations having values $m_p = +3/2, +1/2, -1/2 \ \& \ -3/2$.

$$\uparrow\uparrow\uparrow \longrightarrow +3/2$$

$$\downarrow\downarrow\downarrow \longrightarrow -3/2$$

$$\uparrow\downarrow\uparrow \qquad \downarrow\uparrow\downarrow \qquad \uparrow\uparrow\downarrow \longrightarrow +1/2$$

$$\uparrow\downarrow\downarrow \qquad \downarrow\uparrow\downarrow \qquad \downarrow\downarrow\uparrow \longrightarrow -1/2$$

Therefore each electronic sub-levels will be influenced by four different types causing hyperfine splitting as shown below :-

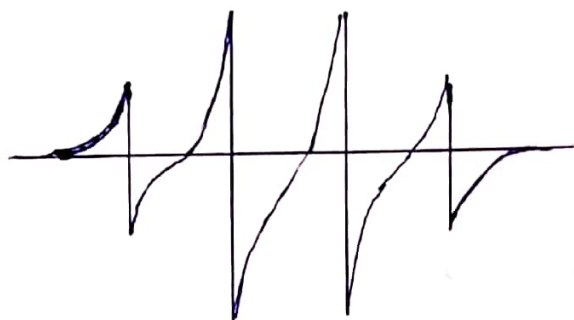Thus, we get four signals (Peaks) in ESR of methyl radical.

Intensity ratio :-
$H = 3$.

$$(x+1)^3 = x^3 + 3x^2 + 3x + 1$$

$$= 1:3:3:1.$$

Experimental spectrum :-

——————x——————

(1 : 3 : 3 : 1)

(Derivative Curve)

By
Dr. A.K. Gupta.
chemistry
(L.S. College.)