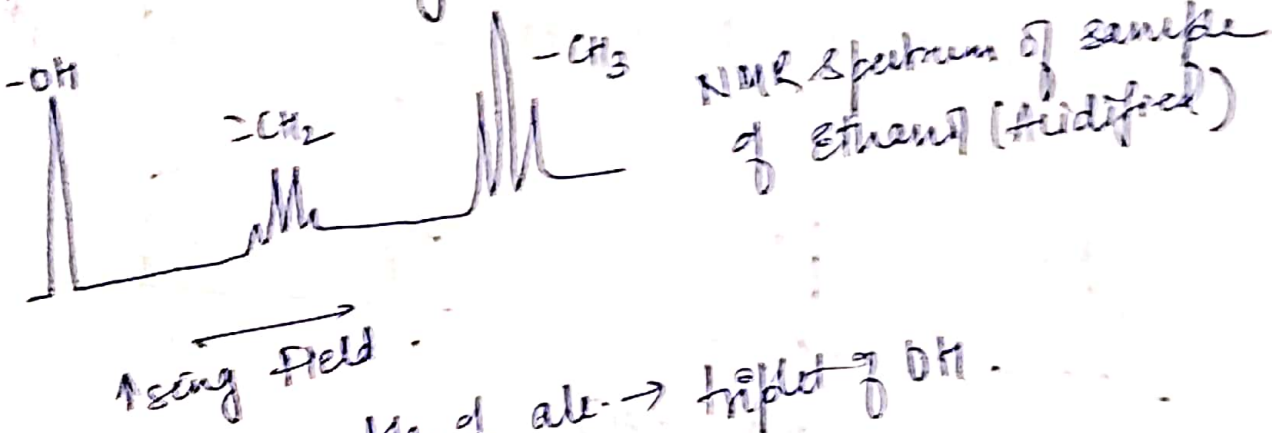
Spin-Spin Splitting

Magnitude of spin-spin coupling const. (J) — Unit cps
Field independent.

Eg → Ethyl Alc.

$CH_3 - CH_2 - OH$.

Triplet — Quartet — Triplet (Expected)
(Singlet → We get)



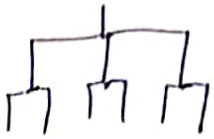
NMR Spectrum of sample of Ethanol (Modified)

For very pure sample of alc. → triplet of OH.
(without any basic / acidic impurities)

Reason → Any acidic / basic impurity catalyzes a rapid exchange among the hydroxyl groups. This rapid proton exchange occurs at such a rate that in short time interval many different protons occupy a site on the oxygen and only the average of their nuclear spin is seen in the methylene proton spectrum. An average peak devoid of fine structure from O-H splitting is obtained.

Eg → HPF_2

^{31}P → Case I →

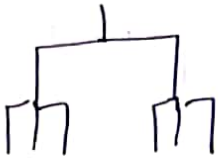


Splitting due to F = 2 × 2 × 1/2 + 1 = 3.

" " " H = 1 × 2 × 1/2 + 1 = 2

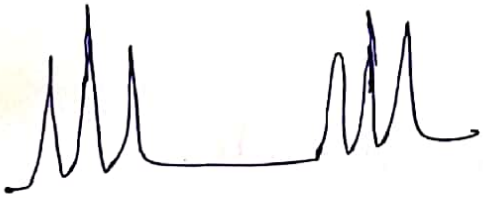
$J_{P-F} > J_{P-H}$

Case II →



Splitting due to H = 2 × 1 × 1/2 + 1 = 2

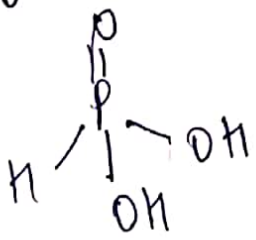
" " F = 2 × 2 × 1/2 + 1 = 3

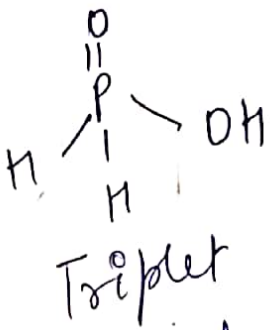


$J_{P-H} > J_{P-F}$

Eg → $HPO(OH)_2$ $H_2PO(OH)$.

^{31}P NMR.





doublet Triplet

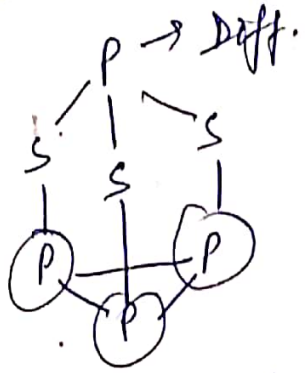
OH doesn't couple with P because —

1. Coupling of hydroxyl protons with P is either too small to be resolved
2. Or because of fast proton exchange reaction.

Eg → $FPO(OH)_2$ $F_2PO(OH)$

Doublet Triplet.

Eg → P_4S_3



^{31}P NMR →

Since 2 diff P.

~~Doublet~~ 2 peaks

Eg. protons

Doublet : Quadruplet

3 : 1

Eg → BrF_5

Structure → Symmetrical tetragonal pyramidal

2 types of F

Doublet : Quintet

4 : 1

Eg → Equimolar soln of TiF_6^{2-} & TiF_4 in ethanol

Gives – $[TiF_5(HOC_2H_5)]^-$ Oct.

2 types of F.

Doublet : Quintet

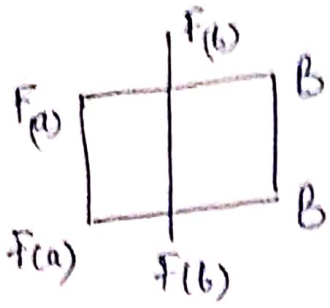
4 : 1

Eg → Ammonia in Water → 1 peak.

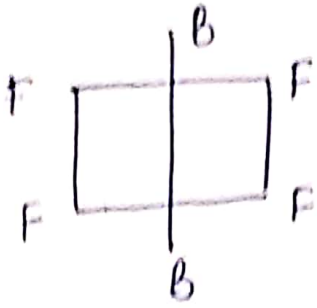
Rapid proton exchange reaction with water.

Spin-spin splitting also disappears if the ion exchange is fast enough, because the NMR spectrophotometer detects only the average spin state of the nucleus during the splitting.

Eg → $TiF_4 \cdot 2B$ B → Donor molecule



cis
(-30°C)
two triplets of equal intensity



Trans
(0°C)
Single Peak

Reason → at 0°C → Rapid dissociation reaction occurs.

$$TiF_4 \cdot 2B \rightleftharpoons TiF_4B + B.$$

But at low temp. this reaction is slowed down so that non equivalent ~~proto~~ nuclei can be detected by NMR.

Note: → Hence, structure determination should be done both at low & high temp.

Nuclear Quadrupole Relaxation →

No splitting / Single peak → Rapid exchange reactions
→ Rapid relaxation → Mainly due to Nuclear Quadrupole Relaxation.

↓

One broad peak

↓

Sometimes signal cannot be distinguished from background

Reason → for $I > 1$, → These nuclei are very effectively relaxed by the fluctuating E.F gradient which arrises from the thermal motion of the polar solvent and soluti molecules.

Eg → $^{14}NH_3$ (N^{14}, $I = 1$) three broad signals Due to Quadrupole Relaxation (No fine struc)

$^{13}NH_3$ (N^{13}, $I = 1/2$) Sharp doublet

Applications involving Magnitude of coupling const.

C^{13} Nucleus — H (Directly Bonded)

Hamiltonian eqn. describing the interaction → Fermi contact term → Dominates

Fermi Contact Term → Measure of probability of the bonding pair of electrons existing at both nuclei.

Used where electron spin polarization by the nuclei is the principal coupling mechanism.

Greater e⁻ density at both nuclei → greater interaction of nuclear moments with bonding e⁻ → Greater interaction with each other through e⁻ spin polarization.

S orbital → finite probability at nucleus

P, d → have nodes (zero prob.) at the nucleus.

Hence, Fermi contact term → measure of s character of the bond of two nuclei.

$\delta = \frac{\nu_s - \nu_R}{\nu_0}$ ν_s - Resonance frq: of sample

ν_R - " " " Reference.

$\delta = \frac{\Delta}{\nu_0}$ $\Delta = \nu_s - \nu_R$

$\nu_0 \rightarrow$ mc sec^{-1} (mega cycle per second)

cps (cycles per sec)

Usually decrease. $\delta = \frac{\Delta \times 10^6}{\text{fixed frq. of probe } (\nu_0)}$

ppm.

Usually Δ = -ve.

Hence, we use $\boxed{\tau = 10 + \delta}$ $\uparrow\tau \rightarrow$ More shielding

Chemical Exchange & Other Factors Affecting Line Width

$W \propto \frac{1}{t}$

W = Natural width of a spectral line

t = Av. time the system spends in excited state.

Acc. to uncertainty principle —

$\Delta E \cdot \Delta t \sim h$.

When life time becomes very small ($\Delta t \sim$ v. small)

ΔE ↑ses.

When $\Delta E \rightarrow$ large $\rightarrow$ Wide range of frequencies absorbed in transition resulting in broad line.

Natural Width < Spin-lattice
Spin-Spin Relaxation process.