①

Effect of Quadrupolar nuclei on the ^1H-NMR Spectra
(^2H, ^{10}B, ^{11}B)

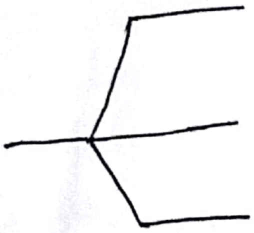
⇒ quadrupolar nucleus is one that has a quantum spin number greater tha ½, lower symmetry.

⇒ NMR signals are wider (or) broad, due to relaxation, line-width increase

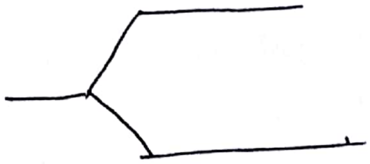
⇒ ^2H → small line-width factor 0.41 fm^4 with quadrupole moment of 0.286 fm^2, line with of HOD is 1.7 Hz

spin→1

^2H



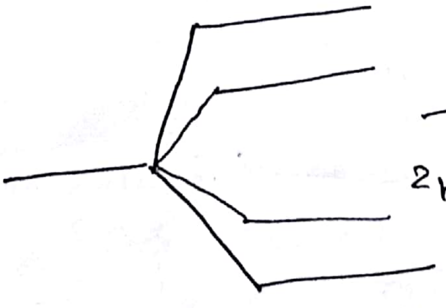
^1H spin→½



[Nuclear quadrupole moment Q is a measure of the charge distribution in the nucleus]

$$Q = \frac{1}{e}\int r^2\left(3\cos^2\theta - 1\right)\rho(r)\,d\tau$$

$\rho(r)$ charge density



spin→ 3/2 ^{11}B

Eg spin $10^{-28}\,m^2$

^2H 2.73×10^{-3}

$Q = 0$ $I = 0$ or ½
nuclei spherical 's'

$I \geq 1$ $\left.\begin{matrix} Q > 0 \\ Q < 0 \end{matrix}\right\}$ non-spherical 'p', 'd'

The spherical rotation, the width is a function of the nuclear quadrupole moment & correlation time τ_c

$$\frac{1}{T_1} = \frac{3}{40}\cdot\frac{2I+3}{I^2(2I-1)}\left(1+\frac{1}{3}\eta^2\right)\left(\frac{e^2qQ}{\hbar}\right)^2\tau_c$$

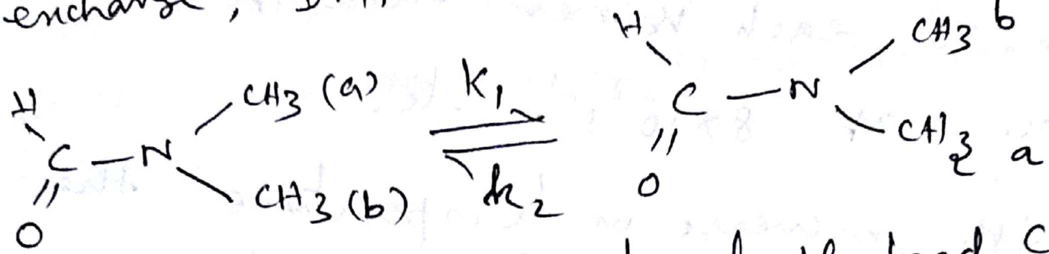
the NQE on the relaxation process dominates the line width and since this effect is intramolecular. one rotational contribution to T_1 is important.

r. K. RAJASEKAR, M.Sc.,M.Phil.,B.Ed.,Ph.D.
Asst. Professor & Research Advisor
G & Research Department of Chemistry
Govt. Arts College, Ariyalur-621 713

System with chemical exchange

⇒ Time-dependent process affect the spectra e.the spectra is modified if the magnetic nuclei exchanged b/t Intra & Inter,

⇒ Example of Proton exchange, DMF

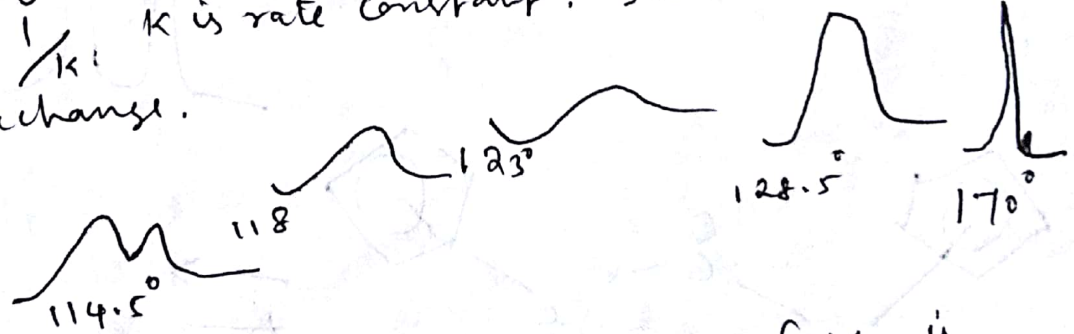


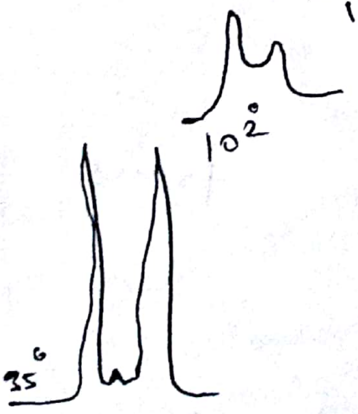
→ the molecule is planar due to double bond character of the C–N bond. At RT, the internal rotation about the C–N bond is slow & ^1H-spectrum shows two equally intense resonance from the methyl group cis & trans to the C=O bond at 2.84 & 3.00 ppm.

⇒ the Coupling b/t two $-CH_3$ proton is small.

⇒ At high T, the dimethyl group flips at appreciable rate

⇒ The resonance frequency of $-CH_3$ changes from ν_{cis} to ν_{tra} and back again with an average time b/t the jumbs of $\tau = 1/k$. k is rate constant. such process is known as chemical exchange.





A process is slow or fast is determined by the exchange rate constant k related to the difference b/t resonance frequency δν of the exchanging nuclei.

Eq. 2

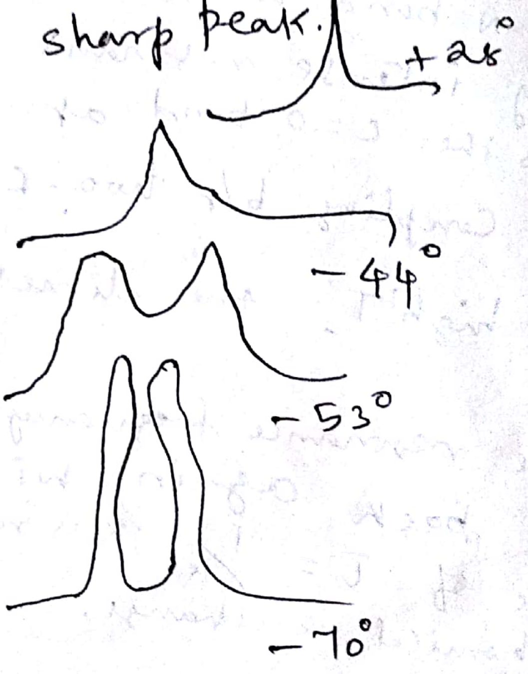
bis(cyclopentadienyl)tetracarbonyl)di-iron (0),

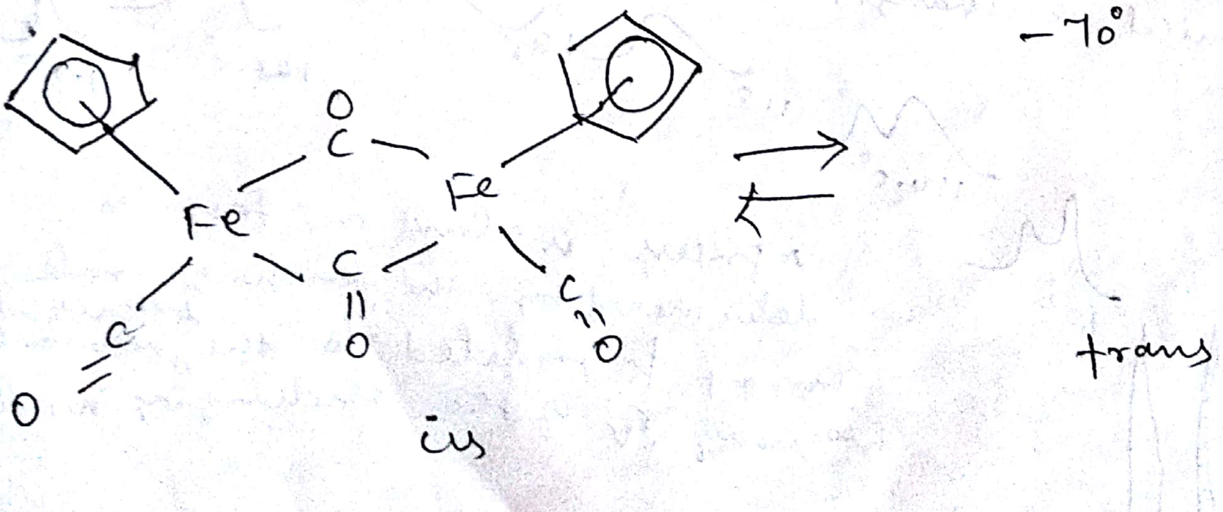
$(\eta^2 - C_5H_5)_2Fe_2(CO)_4$

⇒ At -70° each isomer exhibits its own proton resonance at $8\times10^{-2}s^{-1}$ rate.

⇒ with increase in temperature the signals broaden and merge into a broad peak at -44°.

⇒ at room T, the rate of interconversion is higher $4\times10^{3}s^{-1}$ which gives sharp peak.





3n -305

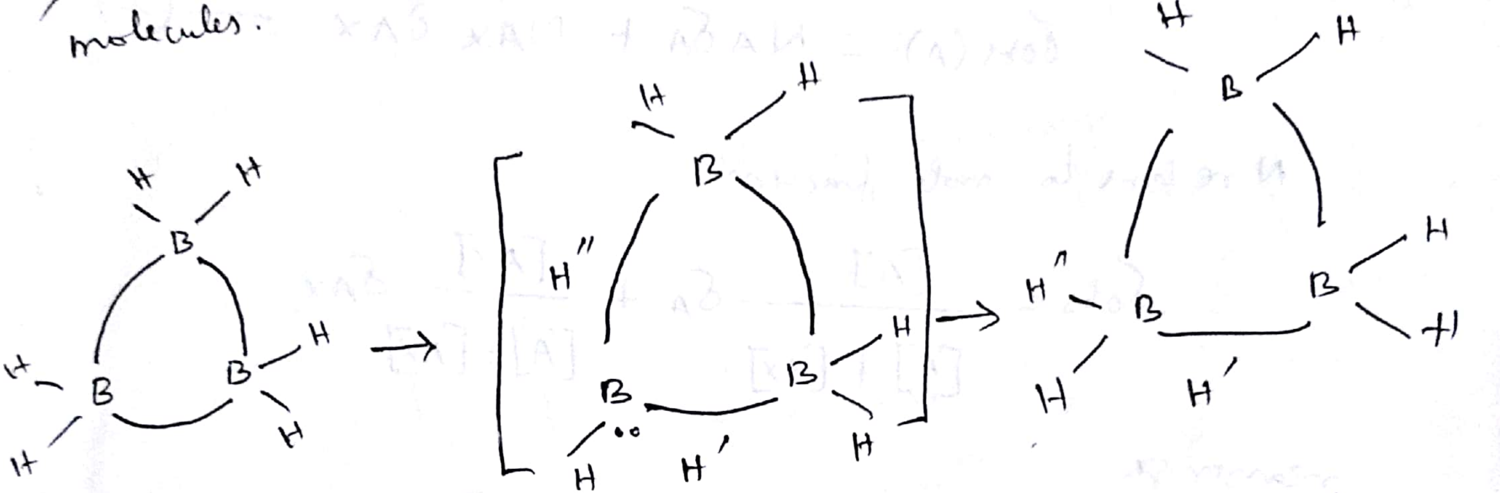
Fluxional behaviour of molecules (or)

Intra molecular exchange

⇒ $B_3H_8^-$; intra molecular hydrogen exchange. mechanism

→ ^{11}B spectrum is a nonet, splitting of 3 equivalent borons by eight equivalent protons.

⇒ J_{B-H} is a time average of all the B–H couplings in the molecules.



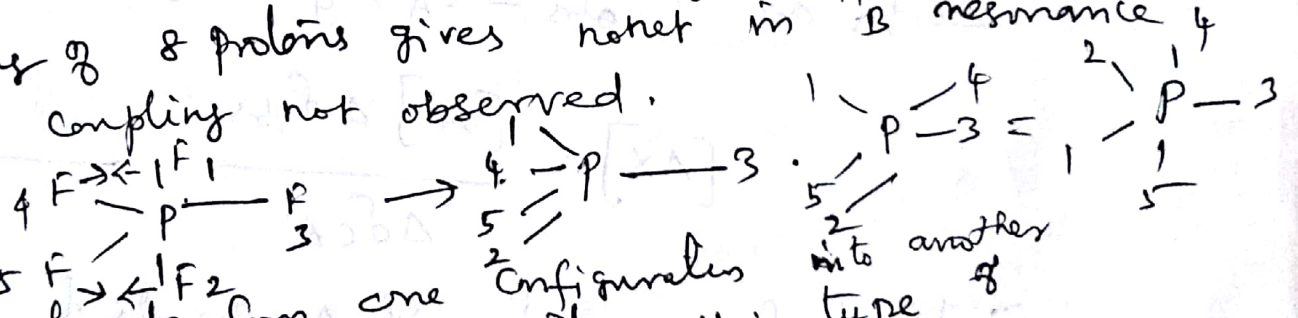
* a single boron resonance signal result if exchange made all protons equivalent.

$Fe(CO)_5$

* Coupling of 8 protons gives nonet in ^{11}B resonance

* Strong coupling not observed.

Eg-2



→ The molecule from one configuration into another of chemically equivalent configuration, this type by intramolecular rearrangement stereochemical non-regidity is called fluxional behaviour.

→ Trigonal bipyramidal XY_5 type molecules shows fluxional.

→ PF_5 ^{19}F spectrum was found to be a 1:1 doublet, all the 5 fluorine are equivalent.

→ signal split by ^{31}P nucleus.

→ Berry mechanisms TBP → square pyramide → Trigonal b P

(b)

Evaluation of thermodynamics parameters in simple Systems

$$A + X \rightleftharpoons AX \quad \text{—} ①$$

resonance will be a mole
chemical shift of A or X
the resonance A or X in the
fraction weighted average of
AX

$$\delta_{obs}(A) = N_A \delta_A + N_{AX} \delta_{AX} \quad \text{—} ②$$

N refers to mole fraction.

$$\delta_{obs} = \frac{[A]}{[A]+[AX]} \delta_A + \frac{[AX]}{[A]+[AX]} \delta_{AX}$$

rearrange

$$[A](\delta_{obs} - \delta_A) + [AX](\delta_{obs} - \delta_A) = [AX](\delta_{AX} - \delta_A)$$

$\Delta\delta_{obs}$ as $(\delta_{obs} - \delta_A)$ & $\Delta\delta_{CA}$ as $(\delta_{AX} - \delta_A)$

$$[AX] = \frac{[A^\circ]\,\Delta\delta_{obs}}{\Delta\delta_{CA}} \quad \text{—} ③$$

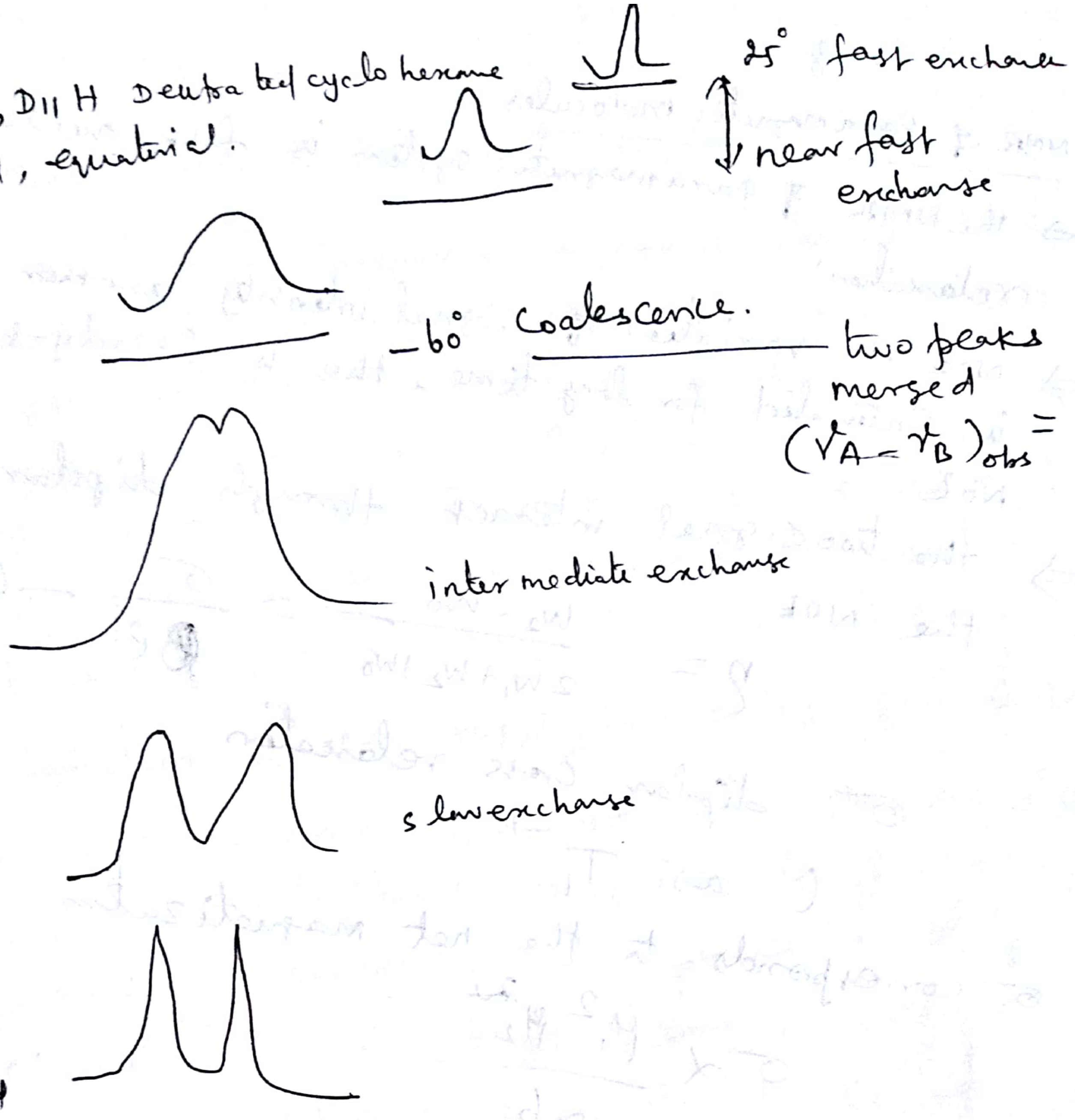
$[A^\circ]$ initial concentration of A equals to $[A]+[AX]$

substituting in eq ③

$$K = \frac{[AX]}{([A^\circ] - [AX])([X^\circ] - [AX])}$$

$$K = \frac{\Delta\delta_{obs}}{(\Delta\delta_{CA} - \Delta\delta_{obs})\left([X^\circ - \frac{\Delta\delta_{obs}[A^\circ]}{\Delta\delta_{CA}}\right)}$$

Eg $C_6D_{11}H$ Deuterated cyclohexane
axial, equatorial.



NMR of Paramagnetic molecules

⇒ the NMR of paramagnetic system is fast nuclear relaxation

⇒ NOE → variation of signal intensity another signal is saturated for long time, this is Steady-state NOE

⇒ the two signal interact through dipolar coupling

the NOE

$$\eta = \frac{W_2 - W_0}{2W_1 + W_2 + W_0} = \frac{\sigma}{\rho} \quad — ①$$

σ dipolar cross relaxation

ρ as T_1^{-1}

σ corresponds to the net magnetization

$$\sigma \propto \frac{\mu_1^2 \mu_2^2}{r^6}$$

$\mu_1 \mu_2$ → nuclear magnetic moment

r – distance

Paramagnetic molecules larg ρ values η is small

For proton in ortho positing ~~para~~ aromatic or geminal in a CH_2 moiety → the ρ is $10^2 \, sec^{-1}$

η is 1 to 5%.

→ magnetic field's high τ_c is large

so, paramagnetic metalloproteins applicable by NOE

Isotropic shifts

Contact shift (NMR of Paramagnetic Complexes)

⇒ NMR of para magnetic Compounds cannot be obtained because of unpaired $\bar{e}$s broadens the Spectrum by both dipolar and $\bar{e}$ spin-nuclear spin Coupling mechanisms.

⇒ paramagnetic state has a very short life time two spin States of the $\bar{e}$ and a single peak is observed, spin relaxation is intermediate shortening T_2 and Causing broadening.

⇒ $\bar{E}$ relaxation is very rapid, broadening is minimized The major effect on the spectrum from the presence of unpaired $\bar{e}$ is to change the magnetic field by the magnetic nucleus. This Causes a very large chemical shift (3000 to 5000 cps) of the resonance in the NMR Spectrum. This is Called contact NMR shift.

contact shift $\Delta\nu/\nu$ and electron spin-nuclear spin Coupling Constant A_N derived from

$$\frac{\Delta H}{H} = \frac{\Delta\nu}{\nu} = -2A_N \frac{\gamma_e}{\gamma_N} \frac{g\beta I(I+1)\,S(S+1)}{9kT}$$

For proton magnetic resonance

$$\frac{\Delta H}{H} = \frac{\Delta\nu}{\nu} = -\frac{1}{6} A_N \frac{\gamma_e}{\gamma_N} \frac{g\beta S(S+1)}{kT}$$

γ_e – gyromagnetic ratio for the $\bar{e}$

γ_N → " " for magnetic nucleus.

I - nucleur spin, S - $\bar{e}$ spin multiplicity

ΔH is H complex $- H$ ligand

$\Delta \gamma = \gamma$ complex $- \gamma$ ligand

β - Bhor magneton

$g \rightarrow$ ratio of magnetic moment to the total angular momentum of the $\bar{e}$

the Contact shift is to lower fields A_N is +ve
higher fields A_N is negative

$$\frac{1}{T_s} \gg A_N \quad \text{or} \quad \frac{1}{T_e} \gg A_N$$

T_s - $\bar{e}$ relaxation time

$T_e \rightarrow$ chemical exchange time

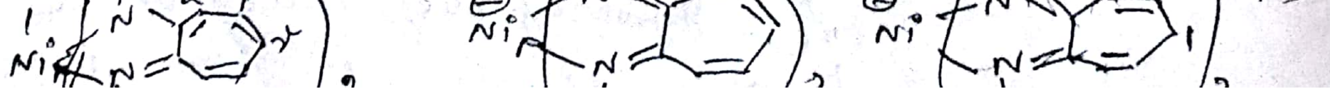
$A_N \rightarrow$ Contact interaction Constant.

⇒ Paramagnetic first transition metal ions have short $\bar{e}$ spin life time or fast ligand exchange rates to allow NMR Studies to be made on their Complexes.

⇒ bonding obtained by A_N

⇒ unpaired $\bar{e}$ in the metal ions transferred to the ligand through the formation of Covalent bond.
(CT mechanisms)

eg Nickel(II) aminotroponeimineate



Pseudocontact Shift

⇒ The spinning Para magnetic ions generates magnetic vector through space and creates Secondary-field around the protons
The shift ~~is~~ Caused is known as pseudo Contact shift

⇒ It is Predominates in the lanthanides ions

⇒ For lanthanides characterized by large spin-orbit effects so both the spin and orbital angular momenta are Coupled strongly which means the orbital angular momentum m_l interact differently with Spin angular momentum m_s

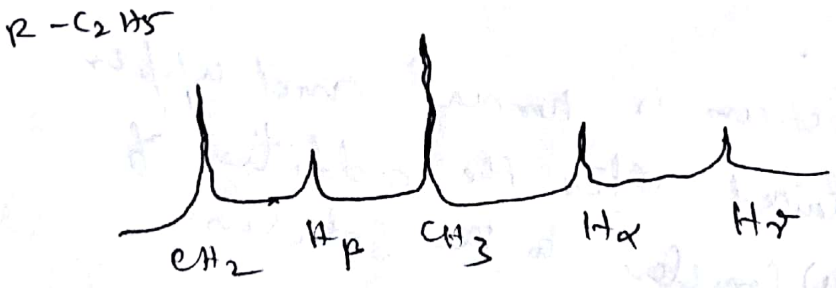
total angular momentum $m_j = m_l + m_s$

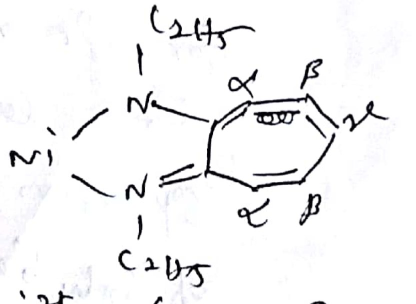
m_j identify a j multiplent

m_l & m_s related to l and s.

eg. Ce^{3+} one $\bar{e}$ in f orbital $s = 1/2$ combine with $L = 3$ to give both $J = 3 + 1/2 = 7/2$ and $3 - 1/2 = 5/$

⇒ f orbitals not involved in covalent bonding with donor atoms.





Ni^{2+} N,N' diethyl amino tropo

Shift reagents

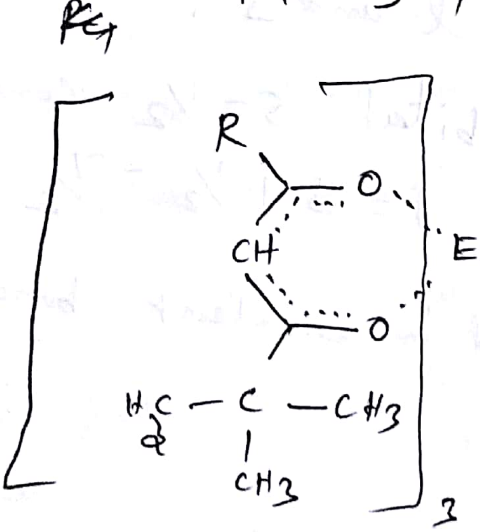
→ Rare earth tris-chelates of β-diketones having general formula Ln (R_1 COCHCOR$_2$) wher Ln is paramagnetic Lanthanide ion are known as shift reagent.

→ Ln generaly used Eu, Pr, Dy, Yb
Eu, Pr most common.

→ two ligands dipivaloylmethane dpm $R_1COCHCOR_2$ ($R_1 = R_2 =$ t-Bu) and fluorinated chelate 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, fod

$(CH_3)_3CC(O)CHC(O)CF_2CF_2CF_3$

$R_1 = C_3F_7$, $R_2 \rightarrow$ t-Bu

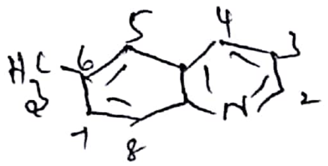


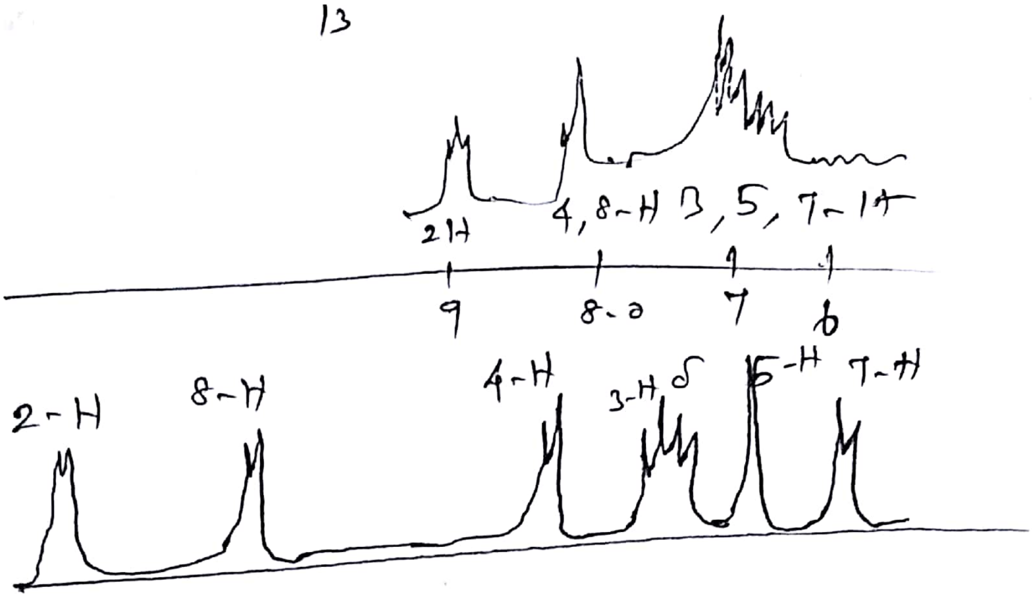
R = t-butyl, Eu(dpm)$_3$

R = $CF_2CF_2CF_3$ Eu(fod)$_3$

→ downfield shift two europium but upfield for Pr reagent.

eg lower spectrum is normal and upper spectrum was obtained after the addition of of soluble Eu(III) complex to the solution.





⇒ geometry of the molecules in solution

⇒ simplify the second-order spectra

⇒ optical purity of the enantiomeric mixture.