MÖSSBAUER SPECTROSCOPY

PRINCIPLES AND APPLICATIONS

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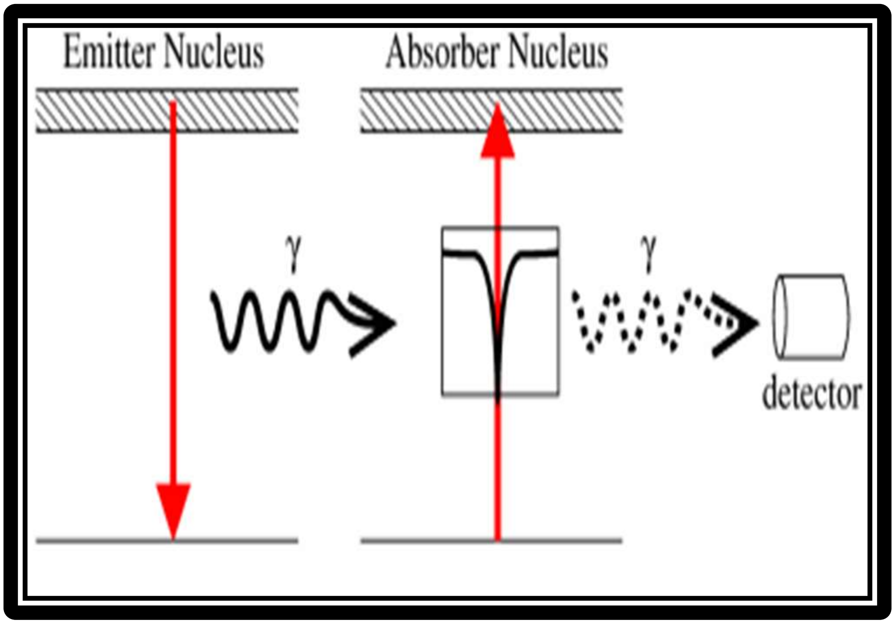
MOSSBAUER SPECTROSCOPY

- **Also known as Nuclear Gamma Resonance Spectroscopy.**
- **In this method nucleus absorbs an gamma ray photon and undergoes transition.**
- **First the concept of ϒ photon resonant absorption was suggested by Kuhn-1929**
- **First observed by Mossbauer in 1958**
- **Awarded Nobel prize for this work**



Why it is difficult?

- The only suitable source of ϒ radiation is the excited nuclei of the same isotope in the course of radioactive decay.
- No way of tuning the energy of the emitted ϒ photon.
- The energies involved are much higher and in the order of keV.
- Recoil effect

What is recoil?

- When ever a high energy particle/projectile is released from a body at rest, the releasing body feels a back-kick i.e. it is pushed backwards, which is called recoil effect.
- This is true for absorption of high energy particles also.
- The recoil happens to conserve the momentum.

Recoil continued…

- **When a gaseous atom or molecule emits a quantum of energy E , the emitted quantum will always have the momentum E/C**

Where C – is the velocity of light

- **To conserve momentum the emitter recoils with momentum P which is equal and in opposite direction.**

$$P = M.V_R = -E/C$$

where V_R recoil velocity

- sign shows that its direction is opposite

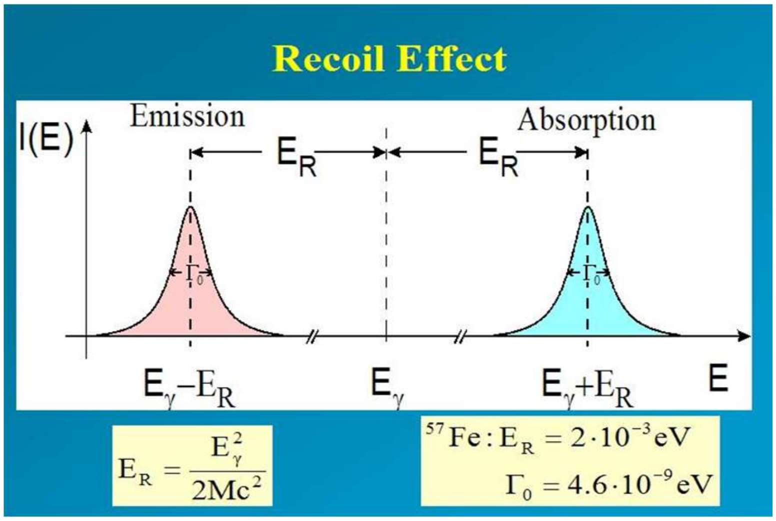
$$E_R = P^2/2m = E^2/2MC^2$$

$$= (E_t-E_R)^2/2MC^2 \approx E_t/2MC^2$$

Since E_R is small

- If M increases the recoil energy can be still lower. So the source and the absorber are fixed on a larger lattice to increase mass

What happens because of recoil effect ?

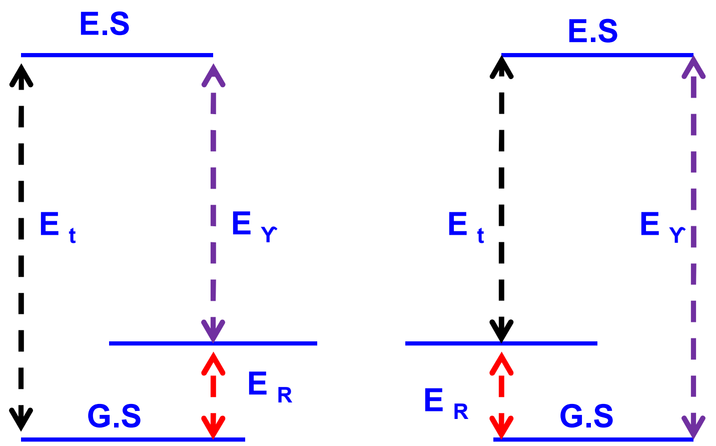


Recoil Effect

$$E_R = \frac{E_\gamma^2}{2Mc^2}$$

$$^{57}Fe: E_R = 2 \cdot 10^{-3} eV$$

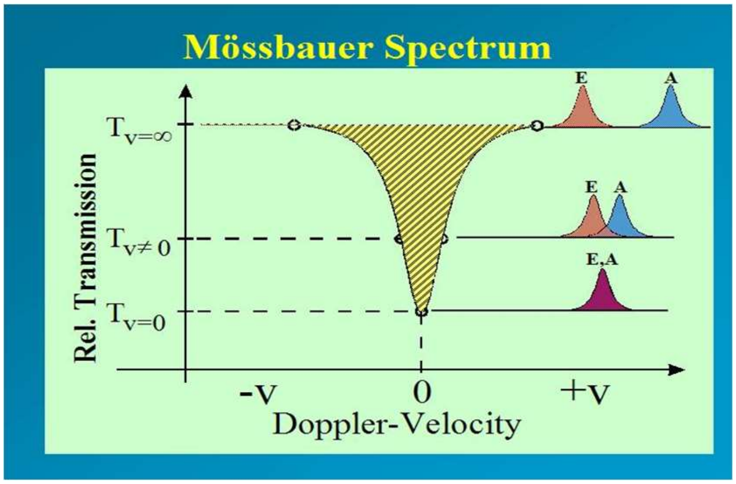
$$\Gamma_0 = 4.6 \cdot 10^{-9} eV$$



Emission [$E\gamma = E_t - E_R$]

Absorption [$E\gamma = E_t + E_R$]

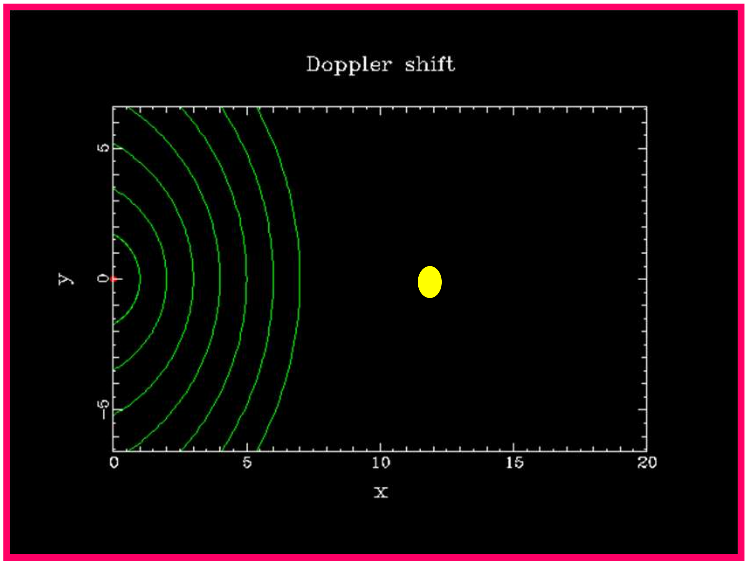
Why recording MB spectrum is difficult?



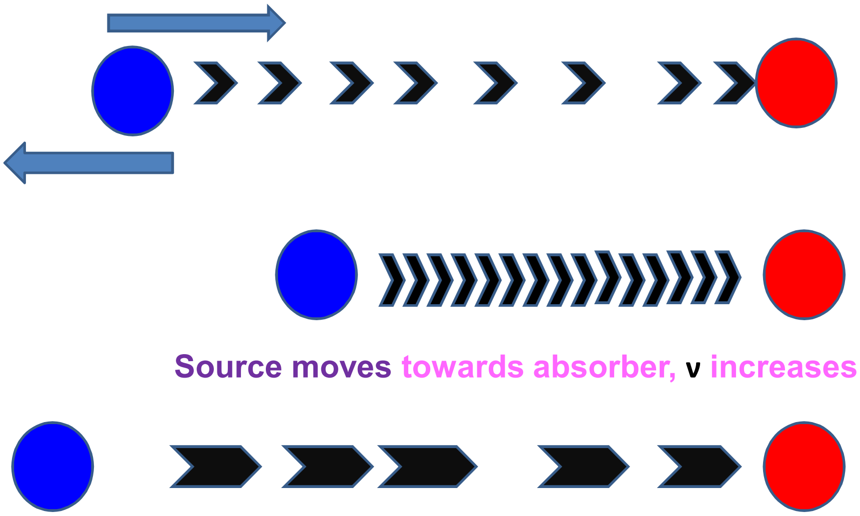
What is there in X axis? λ or ν or E?

- It is already known that, for spectroscopic technique we need a monochromatic radiation.
- But gamma rays are coming out because of the energy difference between the nuclear levels.
- We cannot alter it, to change the gamma photon’s energy.
- So we use Doppler effect to change the energy of the photon.

Doppler Effect



Tuning the energy by using Doppler Effect

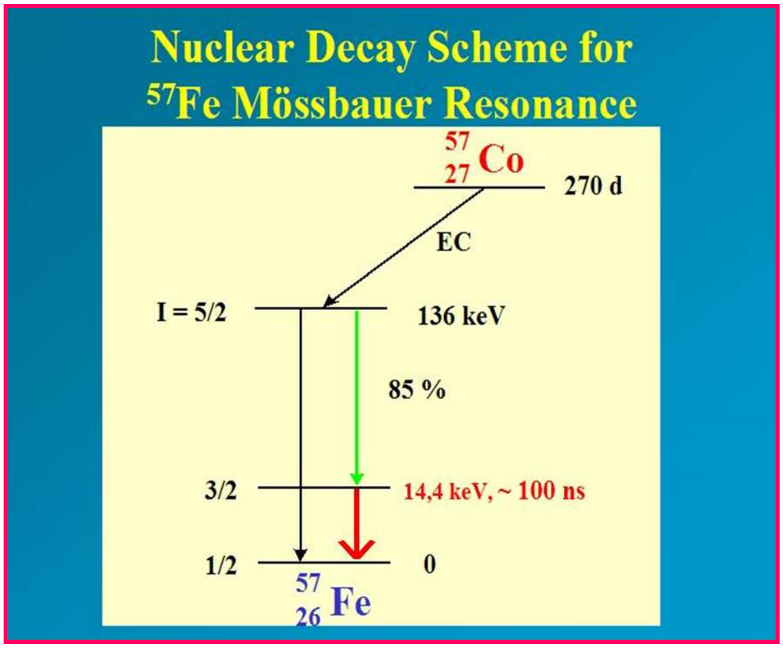


Source moves towards absorber, ν increases

Source moves away from absorber, ν decreases

Mössbauer Effect

- Recoilless Nuclear Resonance Absorption of gamma-Radiation.
- The Mössbauer Effect has been observed for about 100 nuclear transitions in some 80 nuclides in nearly fifty elements.
- Not all of these transitions are suitable for actual exploitation.
- valuable contributions to the physical, chemical, biological- and earth sciences



Nuclear Decay Scheme for ^{57}Fe Mössbauer Resonance

Conditions for MB spectra

- The energy of nuclear transition must be large enough to give, useful ϒ ray photon ; but not large enough to cause recoil effect.
- The energy of the ϒ ray photon must be in the range of 10 – 150keV.
- A substantial amount of the nuclear decay must be with ϒ ray emission.

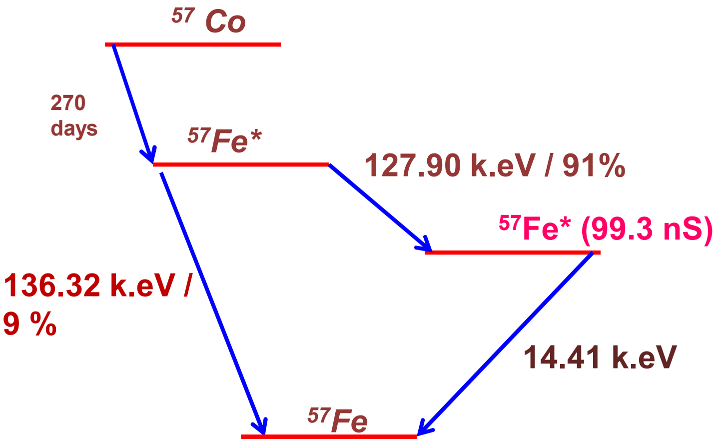
…..Conditions continued….

- The lifetime of the excited state must be long enough give a reasonably broad emission range. Since, extremely narrow lines are not useful (τ must be 001 – 100 nS)
- The excited state of the emitter should be having a long-lived precursor, and easy to handle.

…..Conditions continued….

- The ground state of the isotope should be stable. Its natural abundance should be high or at least the enrichment of that isotope should be easy.
- The cross section of for absorption should be high.

Why Fe is the most studied?



^{57} Co

270
days

^{57}Fe*

127.90 k.eV / 91%

^{57}Fe* (99.3 nS)

136.32 k.eV /
9 %

14.41 k.eV

^{57}Fe

Why Fe is the most studied?

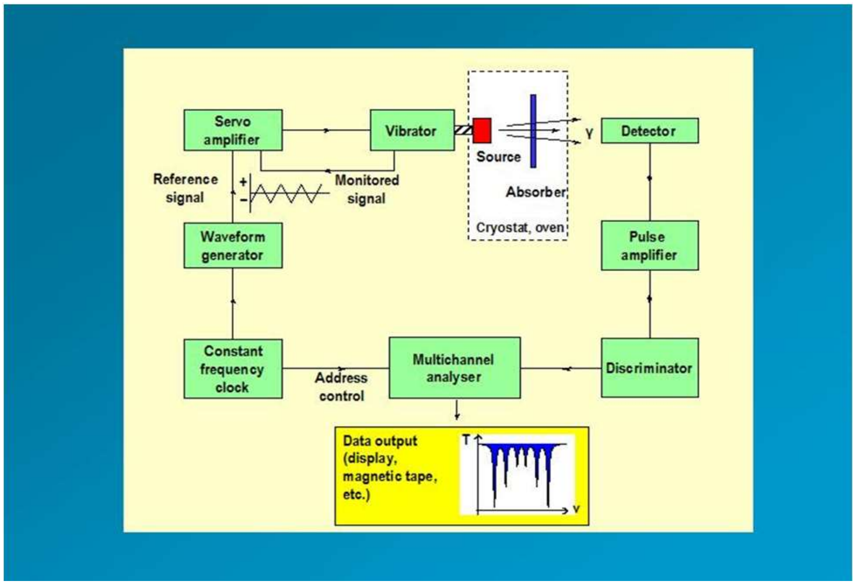
- The precursor of ^{57}Fe is ^{57}Co which decays to ^{57}Fe* with a half life of 270 days (highly stable precursor)
- 9% of ^{57}Fe* decays to ground state directly with emission of ϒ photon of energy 136.32 keV.
- 91% of ^{57}Fe* decays to another excited state with emission of 121.91 keV energy

- The lower excited state is having a life time of 99.3nS (more stable)
- This decays to ground state with emission of 14.41 keV.
- This transition satisfies all the conditions for MB spectra except 2nd condition.
- But it is compensated by larger absorption cross section.
- Other elements that can be studied- are ^{119}Sn, ^{121}Sb, ^{125}Te, ^{129}I, ^{129}Xe and ^{197}Au

Recording the MB spectrum

- Usually the standard emitter is used as the source.
- Sample under investigation is the absorber.
- Both the sample and absorber are embedded on a crystal lattice to minimize the recoil effect.

INSTRUMENTATION



- Identical source and absorber material; maximum overlap occurs at zero Doppler velocity.
- The source for ^{57}Fe spectroscopy is commercially available ^{57}Co/Rh, is mounted on the shaft of a ***vibrator***.
- source is generally kept at room temperature.
- Absorber (sample under study) may be cooled down to liquid nitrogen or liquid helium temperatures in a cryostat, or for controlled heating in an oven.

- γ-rays are detected by a scintillation counter, gas proportional counter or a semi-conductor detector.
- A *constant frequency clock* synchronises a voltage waveform which serves as a reference signal to the servo-amplifier controlling the electro-mechanical vibrator.

- The difference between the monitored signal and the reference signal is amplified and drives the vibrator at the same frequency (typically 50 s^{-1}) as the channel address advance.
- Each channel corresponds to a certain relative velocity and is held open for a fixed time interval depending on the frequency and number of channels used.

- The incoming γ-counts are collected in their corresponding channels during the sequential accessing e.g. 50 times per second, until satisfactory resolution is reached.
- The cryostat can be furnished with a super-conducting solenoid for measuring the sample in an applied magnetic field.
- It is also possible to mount a pressure cell inside the cryostat for studying the sample properties under pressure.

ISOMER SHIFT / CENTRE SHIFT / CHEMICAL SHIFT

- The E_t value is affected by the interaction between the nucleus and the e^-s present around it.
- This arises because of the different sizes of nucleus in ground and excited states.
- The change in nuclear radius when going from g.s to e.s is ΔR
- Z is the atomic number

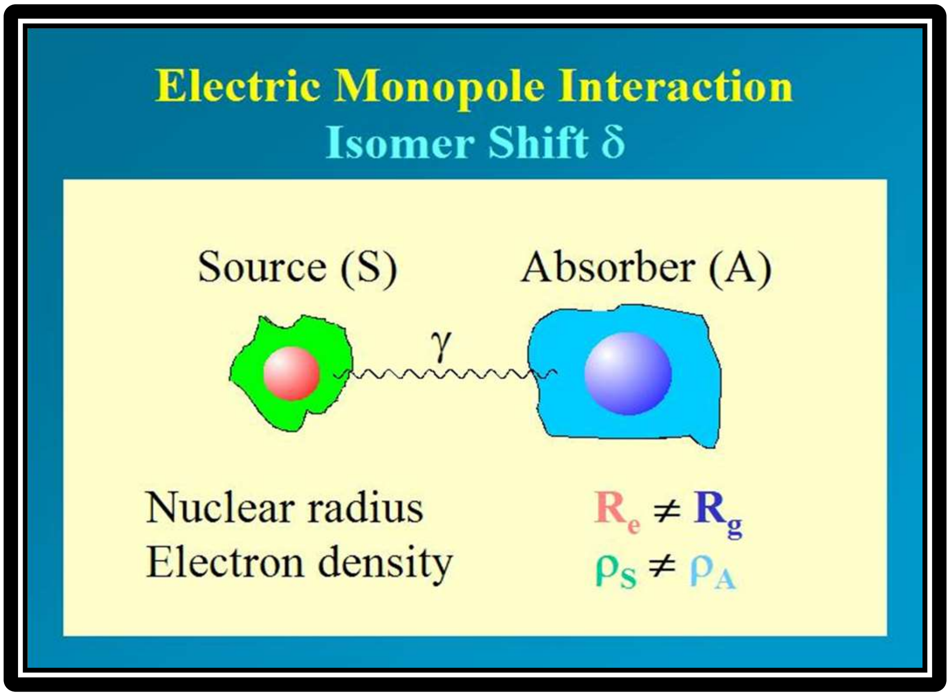
Isomer shift

- The change in electrostatic energy on decay is given by (chemical shift / Isomer shift)

$$\delta = (\varepsilon_0/5)\,(Ze^2R^2)(\Delta\, R/R)[|\psi_s(abs)|^2 - |\psi_s(source)|^2]$$

where

ε_0	– Permittivity of free space
Z	- atomic number of the nucleus
e	- electronic charge
ψ_s(abs)	- s orbital wave function of absorber
ψ_s(source)	- s orbital wave function of source



Electric Monopole Interaction

Isomer Shift δ

Nuclear radius $R_e \neq R_g$

Electron density $\rho_S \neq \rho_A$

- Since s electron wave functions have their maxima at the nucleus, s electron density affects the isomer shift to a great extent.
- But changes in p & d orbital occupancies affect the s electron through screening hence have a smaller effect on isomer shift.
- When ΔR/R is positive the isomer shift is also positive and negative ΔR/R reflected as negative shift

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- Isomer shift is related to the oxidation state of the metal.
- In ^{119}Sn MB spectra Sn(II) shows a positive shift (ΔR/R) w.r.to Sn where as for Sn(IV) it is negative

s - electron density decreased so negative shift

Species	configuration	ΔR/R	δ
Sn(IV)	$5s^0 5p^0$	- ive	-ive
Sn	$5s^2 5p^2$	0	0
Sn(II)	$5S^2 5p^0$	+ive	+ive

s - electron density increased – p screening not present, so positive shift

- In ^{119}Sn compounds, the shift values depend on the ligands present and the coordination number of tin.
- The isomer shift values are useful in characterizing tin derivatives.
- Many Sn compounds appear to contain Sn(II) from the formulae but on analyzing with MB spectra Sn(IV) is present in them.

- Many of them are polymeric and contain Sn(IV).
- Generally Sn(II) compounds show shift > than 2.1 mmS^{-1} and Sn(IV) show shift < 2.1 mmS^{-1} (With relative to SnO_2)
- The point of changeover is a dispute but shifts less than 2 are for Sn(IV) and above 2.5 are clearly for Sn(II)

Organotin compounds

- The isomer shift of $(SnPh_2)_n$ is 1.5 mm/S clearly showing the presence of Sn(IV).
- A similar formula $Sn(C_5H_3)_2$ is having a monomeric structure in the solid state and shows a shift of 3.74 mm/S.

Chemical shift values for Fe compounds

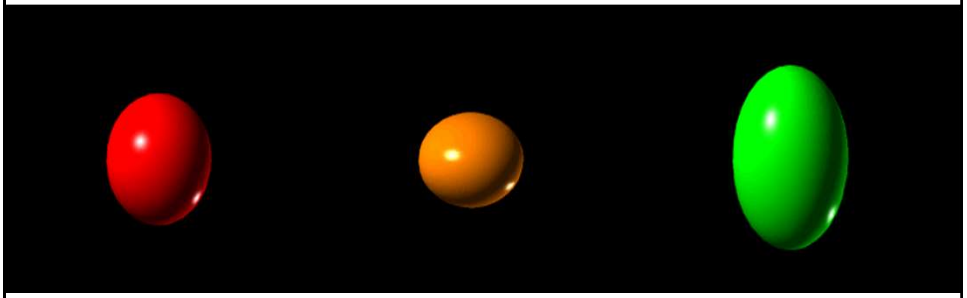
- Fe isomer shift cannot be used for determining the O.S of Fe in a molecule.
- Fe O.S from 0 to 4, often differ in unit charge only.
- The electrons involved are from d orbital. So effect on the s electrons is smaller.
- Varying spin states(which depends on the ligands present) also affect the shift value.

- **Anyway some useful correlations had been drawn.**
- **Fe-porphyrin complexes are very important biologically.**
- **Fe can be present in +2 or +3 state in them.**
- **The complexes can be easily reduced. The electron may be to the Fe or to the ligand. In that ambiguous case MB spectra is useful in determining the O.S**

- **Even though assignment of O.S is often possible, in some cases like ^{197}Au many oxidation states show shift values considerably overlapping.**
- **In that case, MB spectrum can only be used as a supporting evidence and cannot be used for ascertaining the oxidation state.**
- **In addition, the isomer shifts are with relative to a standard only. Different studies have used different standards. So it is important to mention which standard was used. For ^{57}Fe – $[Fe(CN)_5NO]$,^{119}Sn-SnO_2**

Electric Quadruple Interactions

- Nuclei in states with an angular momentum quantum number I>1/2 have a non-spherical charge distribution. This produces a nuclear quadruple moment.
- In the presence of an asymmetrical electric field (produced by an asymmetric electronic charge distribution or ligand arrangement) this splits the nuclear energy levels.
- The charge distribution is characterized by a single quantity called the Electric Field Gradient (EFG).

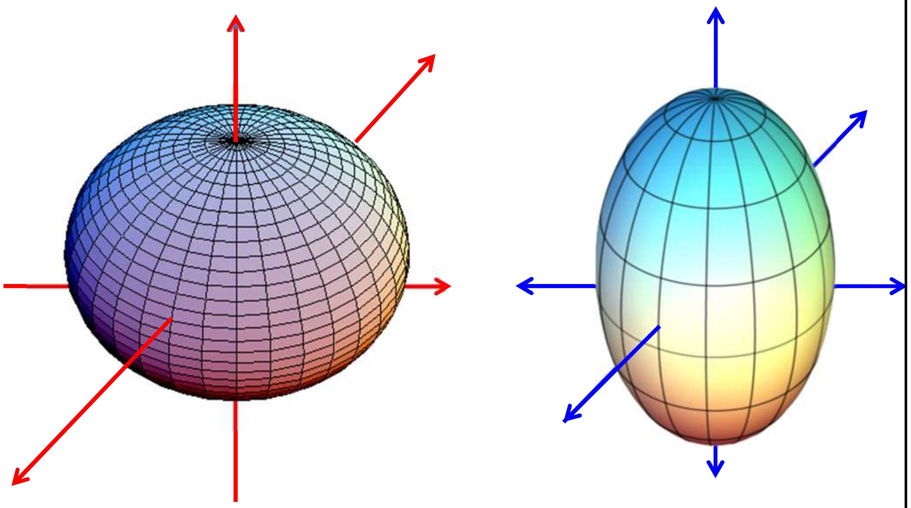


SPHERICAL Q IS 0

OBLATE Q IS -IVE

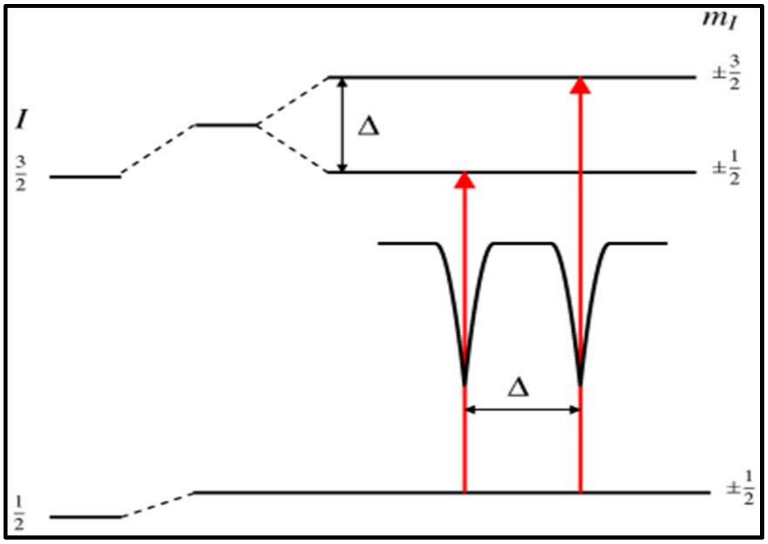
PROLATE Q IS +IVE

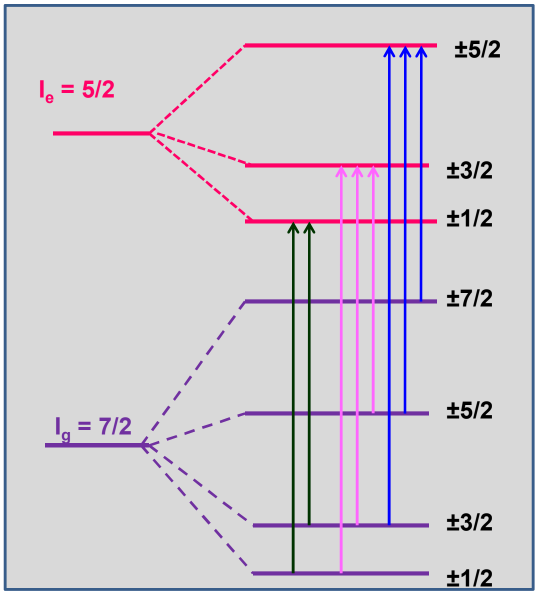
Oblate and Prolate nuclei



- In the case of an isotope with a I=3/2 excited state, such as ^{57}Fe or ^{119}Sn, the excited state is split into two sub states $m_I=\pm 1/2$ and $m_I=\pm 3/2$.
- This gives a two line spectrum or 'doublet'.
- The magnitude of splitting, Delta, is related to the nuclear quadrupole moment, Q, and the principle component of the EFG, V_{zz}, by the relation $\Delta = eQV_{zz}/2$

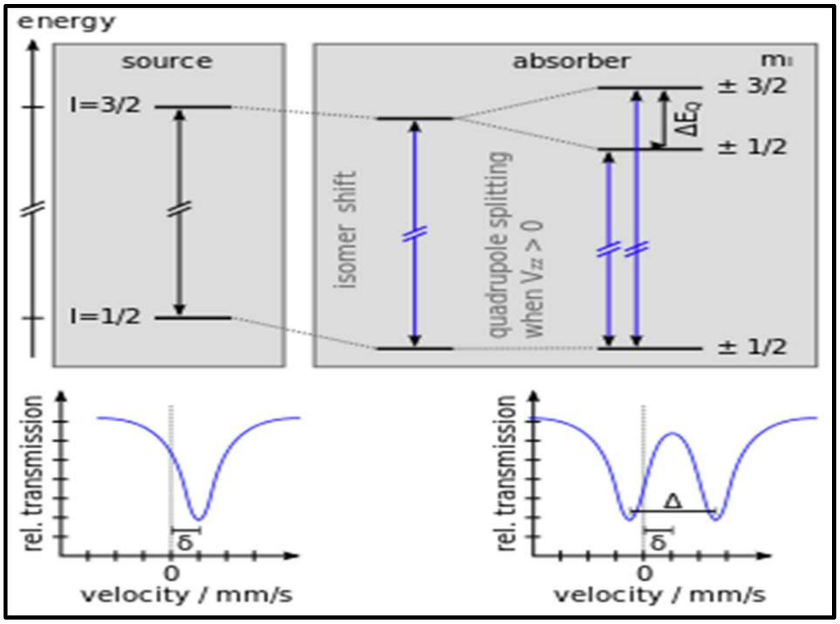
Quadruple Splitting for ^{57}Fe and ^{119}Sn





Selection Rule for MB spectra

$m_I = 0, \pm 1$



Informations from quadruple splitting

- Appearance of quadruple splitting shows the presence of *efg* at the nucleus.
- The efg may be created by the ligand field or by the electron distribution aroung the nucleus.
- Single crystal or application of magnetic field gives more information.
- If a nucleus with symmetric electron distribution is in an O_h field, efg is not expected.

Stereochemical activity of lone pair

- Consider Te(IV) compounds with six ligands
- If the lone pair of electron of Te is stereochemically active , it will occupy one vertex of a pentagonal bipyramide(*pbp*)
- This will create an efg at the nucleus, resulting in q.s
- But no q.s in these class of compounds.
- So the lone pair is stereochemically inactive
- It occupies the 5s orbital

- Structures of the TeX_4Y^{2-} had not been crystallographically studied.
- The MB spectra of those species shoe no q.S, but this is not a conclusive evidence for absence of efg at nucleus.
- The efg may not be enough to cause q.s.
- But inCsIF6 substantial q.s shows the stereochemical activity of lone pair.

Magnetic interactions

- :In the presence of a magnetic field the nuclear spin moment experiences a dipolar interaction with the magnetic field ie Zeeman splitting
- There are many sources of magnetic fields that can be experienced by the nucleus.
- The total effective magnetic field at the nucleus, B_{eff} is given by

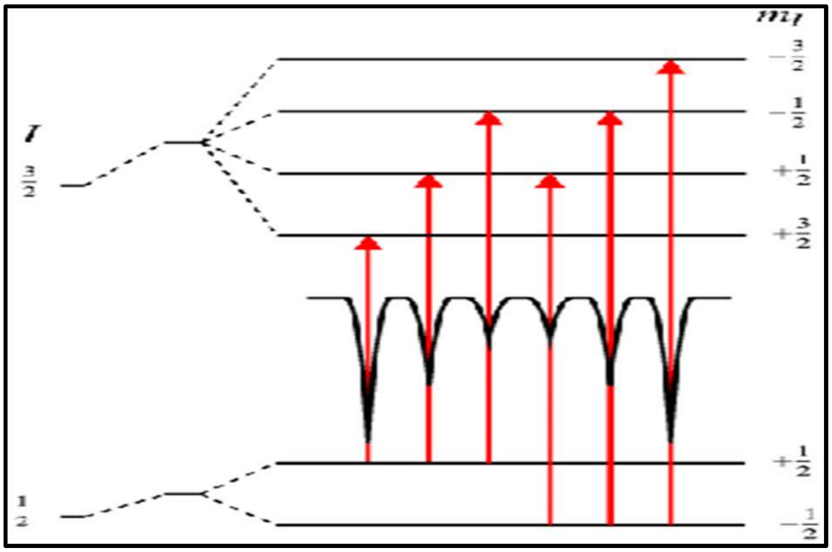
$$B_{eff} = (B_{contact} + B_{orbital} + B_{dipolar}) + B_{applied}$$

- The first three terms being due to the atom's own partially filled electron shells.
- $B_{contact}$ is due to the spin on those electrons polarising the spin density at the nucleus
- $B_{orbital}$ is due to the orbital moment on those electrons, and $B_{dipolar}$is the dipolar field due to the spin of those electrons.

Energy of the nuclear levels $E_m = -g\mu_N B m_I$

- **This magnetic field splits nuclear levels with a spin of I into (2I+1) substates.**
- **Transitions between the excited state and ground state can only occur where m_I changes by 0 or 1.**
- **This gives six possible transitions for a 3/2 to 1/2 transition, giving a sextet , with the line spacing being proportional to B_{eff}.**

Effect of magnetic field on ^{57}Fe



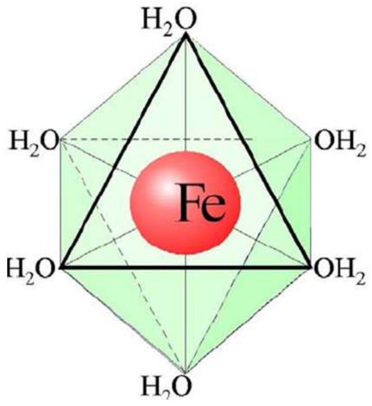
- The line positions are related to the splitting of the energy levels, but the line *intensities* are related to the angle between the Mössbauer gamma-ray and the nuclear spin moment.
- The outer, middle and inner line intensities are related by:

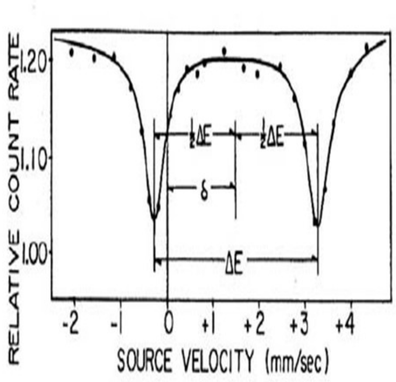
$$3 : (4\sin^2\theta)/(1+\cos^2\theta) : 1$$

- Outer and inner lines are always in the same proportion.
- The middle lines can vary in relative intensity between 0 and 4 depending upon the angle the nuclear spin moments make to the gamma-ray.
- In polycrystalline samples with no applied field this value averages to 2,
- But in single crystals or under applied fields the relative line intensities can give information about moment orientation and magnetic ordering.

APPLICATIONS
OF
MOSSBAUER SPECTRA

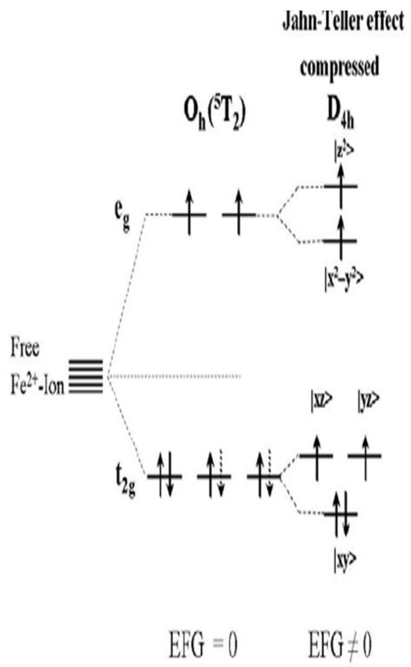
Spectra of spin free Fe(II) – $FeSO_4.7H_2O$





- From the crystallographic data it was initially concluded that $FeSO_4.7H_2O$ is having a perfect O_h symmetry, with six H_2O on each vertex.
- But the MB spectrum recorded showed a large quadruple splitting, which is not possible in a regular O_h symmetry. (for perfect O_h field *efg* is zero)

- Fe(II) is a d^6 system.
- In weak field created by H_2O, an orbitally degenerate system results.
- This under goes J-T distortion (Z_{in})to remove the degeneracy and forms a tetragonal field.
- This creates an *efg* at the nucleus and hence quadruple splitting.
- The structure assigned is an distorted O_h with all angles 90^o and $x \neq y \neq z$



Ligand field splitting of $^5T_2$ ground state in O_h symmetry and Jahn-Teller effect leading to a compressed octahedron with D_{4h} symmetry for $[Fe(H_2O)_6]^{2+}$.

Prussian Blue and Turnbull's blue

- **Prussian blue is a dark blue pigment with the idealized formula $Fe_7(CN)_{18}$. it is prepared by adding a ferric salt to ferrocyanide**

$$Fe^{3+} + [Fe^{2+}(CN)_6]^{4-} \longrightarrow Fe^{3+}_4[Fe^{2+}(CN)_6]_3$$

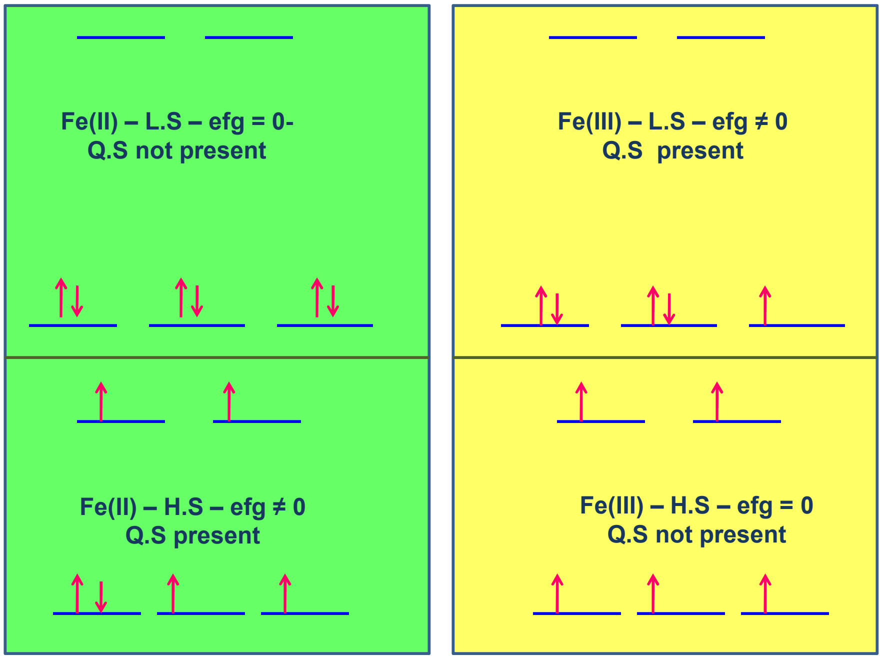
- **Turnbull's blue is the same substance but is made from different reagents , i.e. addition ferrous salts to ferricyanide.**

$$Fe^{2+} + [Fe^{3+}(CN)_6]^{3-} \longrightarrow Fe^{3+}_4[Fe^{2+}(CN)_6]_3$$

- **Its lightly different color stems from different impurities.**

- **For a long time one had considered them as chemically different compounds.**
- **Prussian Blue with $[Fe^{II}(CN)_6]^{4-}$ anions and Turnbull's Blue with $[Fe^{III}(CN)_6]^{3-}$ anions, according to the different way of preparing them.**
- **However, the Mössbauer spectra recorded by Fluck et al., were nearly identical for both PB and TB showing only the presence of $[Fe^{II}(CN)_6]^{4-}$ and Fe^{3+} in the high spin state.**

- **This could be confirmed by use of $K_4[Fe^{II}(CN)_6]$ and $K_3[Fe^{III}(CN)_6]$ as reference compounds.**
- **Immediately after adding a solution of Fe^{2+} to a solution of $[Fe^{III}(CN)_6]^{3-}$ a rapid electron transfer takes place from Fe^{2+} to the anion $[Fe^{III}(CN)_6]^{3-}$ with subsequent precipitation of the same material .**
- **A singlet for Fe(III) and a quadruple doublet for Fe(II) were which confirmed Prussian blue and Turnbull's blue are identical**



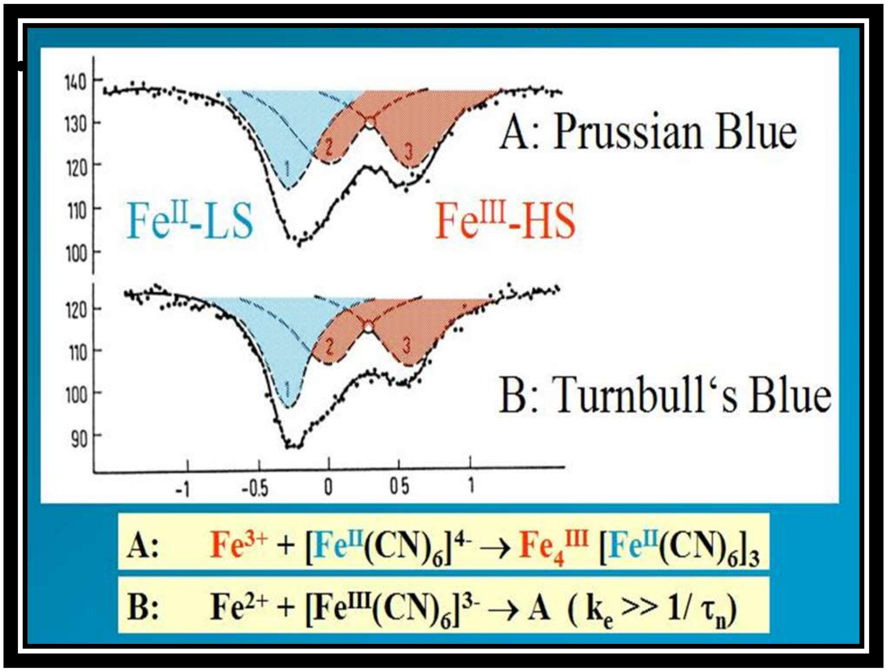
Fe(II) – L.S – efg = 0-
Q.S not present

Fe(III) – L.S – efg ≠ 0
Q.S present

Fe(II) – H.S – efg ≠ 0
Q.S present

Fe(III) – H.S – efg = 0
Q.S not present

- The Fe(II) centers, which are low spin, are surrounded by six carbon ligands in an octahedral configuration.
- The Fe(III) centers, which are high spin, are octahedrally surrounded on average by 4.5 nitrogen atoms and 1.5 oxygen atoms (the oxygen from the six coordinated water molecules).
- This introduces an efg at Fe(III) nucleus and hence Q.S

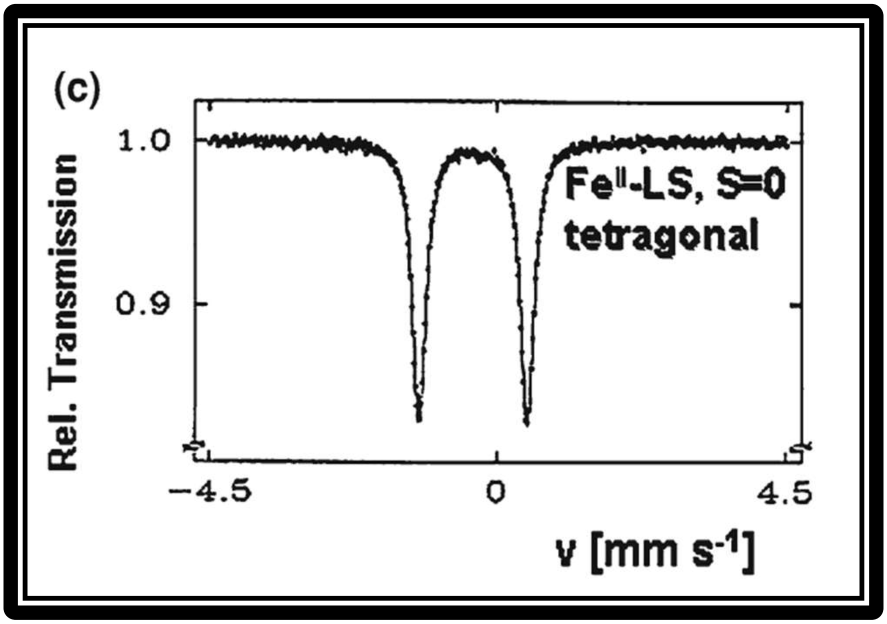


A: $Fe^{3+} + [Fe^{II}(CN)_6]^{4-} \rightarrow Fe_4^{III}[Fe^{II}(CN)_6]_3$

B: $Fe^{2+} + [Fe^{III}(CN)_6]^{3-} \rightarrow A \; (k_e >> 1/\tau_n)$

Sodium nitroprusside – $Na_2[Fe(CN)_5(NO)]$

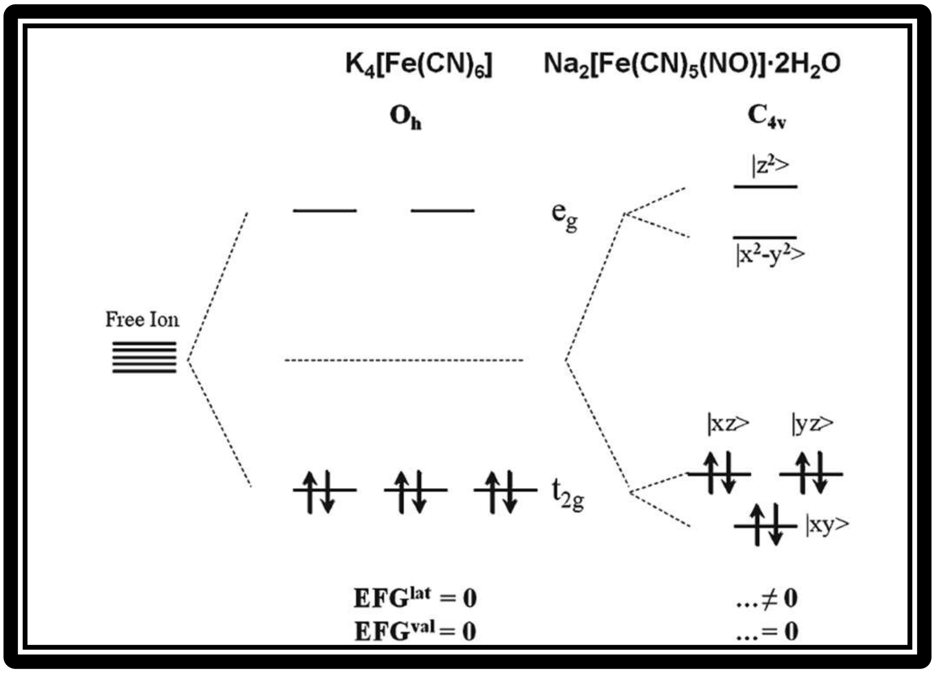
- **The O.S of Fe in nitroprusside was a matter of controversy for a long time.**
- **Initially it was assumed that it contained Fe(II) and NO^+ since it was diamagnetic. [Fe(II)-d^6; Fe(III) –d^5]**
- **But the MB spectrum of the sample showed a doublet with δ = -0.165 mm/S**
- **This value is too negative for a Fe(II) complex.**



- **This suggests that the Fe may be in Fe(IV) state.**
- **The magnetism and MB spectrum are in consistent with the structure which has an extensive π-bonding with $^+$NO ligand .**
- **The t_2g orbitals of Fe and the p-orbital of N present in $^+$NO containing the odd e-, to form a π-bond**

- The Fe(II) is transferring the e^-s form filled t_2g level to the vacant π- antibonding orbital of NO.
- This makes the shift value to approach Fe(IV) values.
- Now because of this the shielding of s-e^- by the d e^-s decreases and hence the shift becomes more.
- This is supported by the decrease in N-O stretching frequency in IR, since the anti bonding level is filled.

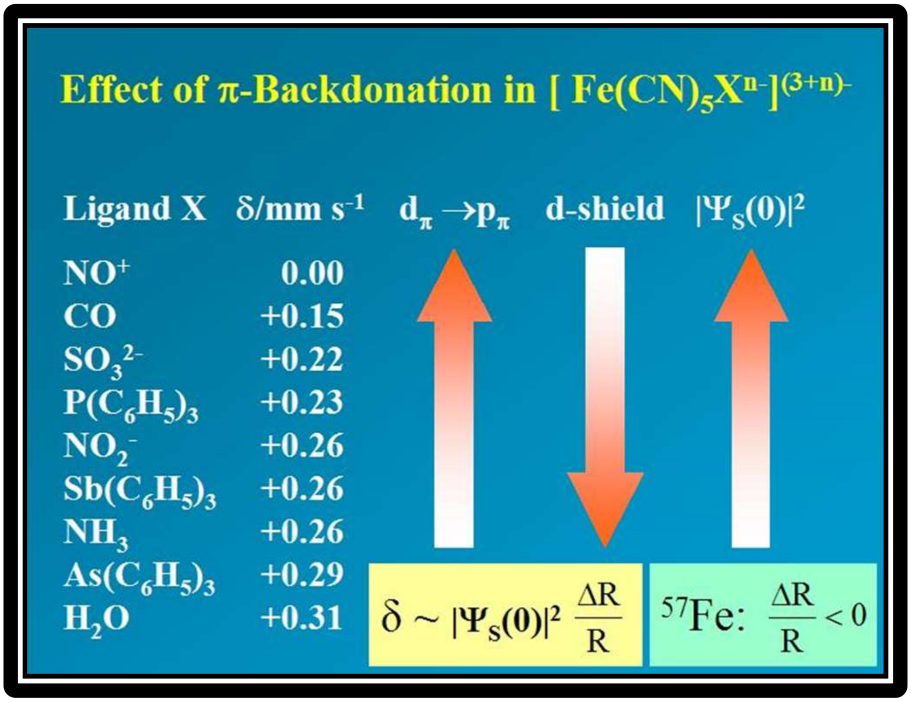
- $K_4[Fe(CN)_6]$ is a $3d^6$ LS complex with O_h symmetry, where all six electrons are accommodated in the three t_{2g} orbitals.
- Both contributions $(EFG)_{val}$ and $(EFG)_{lat}$ vanish; there is no quadrupolar interaction.
- $Na_2[Fe(CN)_5NO]2H_2O$ has C_{4v} symmetry with d-orbital splitting as shown.



- Its LS behavior requires that all six electrons are accommodated in the lowest three orbitals arising from the tetragonal splitting of the former cubic t2g (Oh) subgroup.
- $(EFG)_{val}$ is still zero, but $(EFG)_{lat} \neq 0$ arises from the ligand replacement in the iron coordination sphere.

- The isomer shift data for the pentacyano complexes of iron(II) with a different sixth ligand X.
- Normalizing the isomer shifts to that of the pentacyanonitrosylferrate complex as zero point
- The ordering expresses the varying effects of *d_π-p_π back donation* for the different sixth ligand X.
- The isomer shift values become more positive on going from NO^+ to H_2O

- *d_π-p_π backdonation* decreases causing an increasing d-electron density residing near the iron centre.
- Stronger shielding of s-electrons by d-electrons, which finally creates lower s-electron density at the nucleus.
- The nuclear factor $\Delta R/R$ is negative for ^{57}Fe explains the increasingly positive isomer shift values in the given sequence from NO^+ to H_2O



Effect of π-Backdonation in $[\text{Fe(CN)}_5\text{X}^{n-}]^{(3+n)-}$

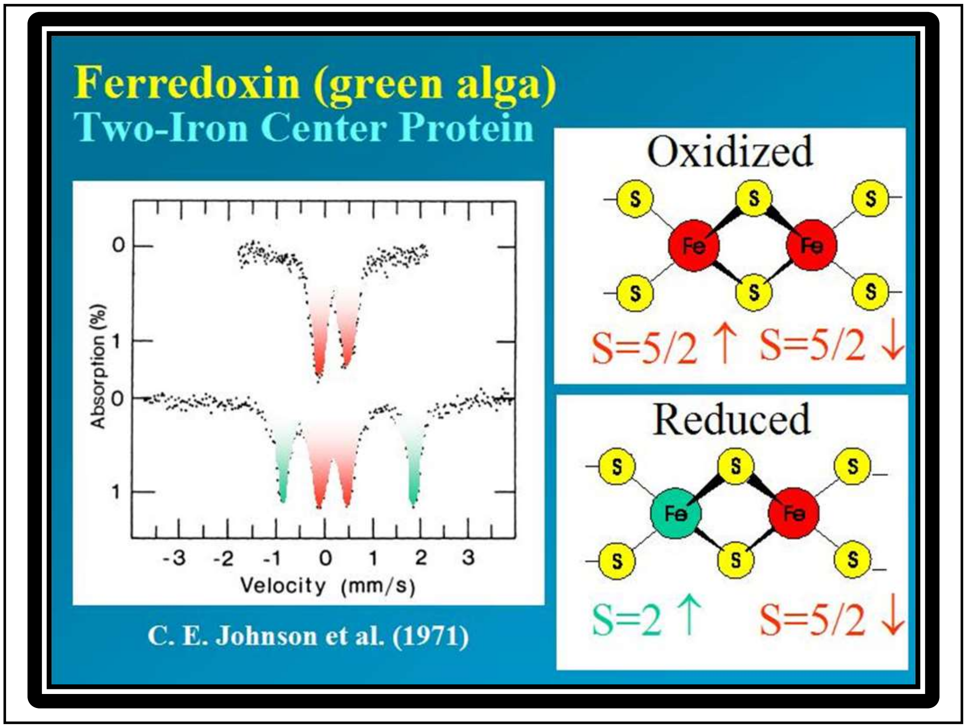
Ligand X	δ/mm s^{-1}	$d_\pi \rightarrow p_\pi$	d-shield	$\lvert\Psi_S(0)\rvert^2$
NO^+	0.00	↑	↓	↑
CO	+0.15			
SO_3^{2-}	+0.22			
$P(C_6H_5)_3$	+0.23			
NO_2^-	+0.26			
$Sb(C_6H_5)_3$	+0.26			
NH_3	+0.26			
$As(C_6H_5)_3$	+0.29			
H_2O	+0.31			

$$\delta \sim \lvert\Psi_S(0)\rvert^2 \frac{\Delta R}{R}$$

$$^{57}\text{Fe}: \frac{\Delta R}{R} < 0$$

Ferredoxin

- Study of ferredoxin, a Fe-S protein, which assists in *in-vivo* e^- transfer reactions
- The two-iron centres are not equivalent in the reduced form.
- The oxidized form with two Fe(III)-high spin centres can be distinguished from the reduced form with one Fe(III)-high spin centre and one Fe(II)-high spin centre only by using MB spectrum



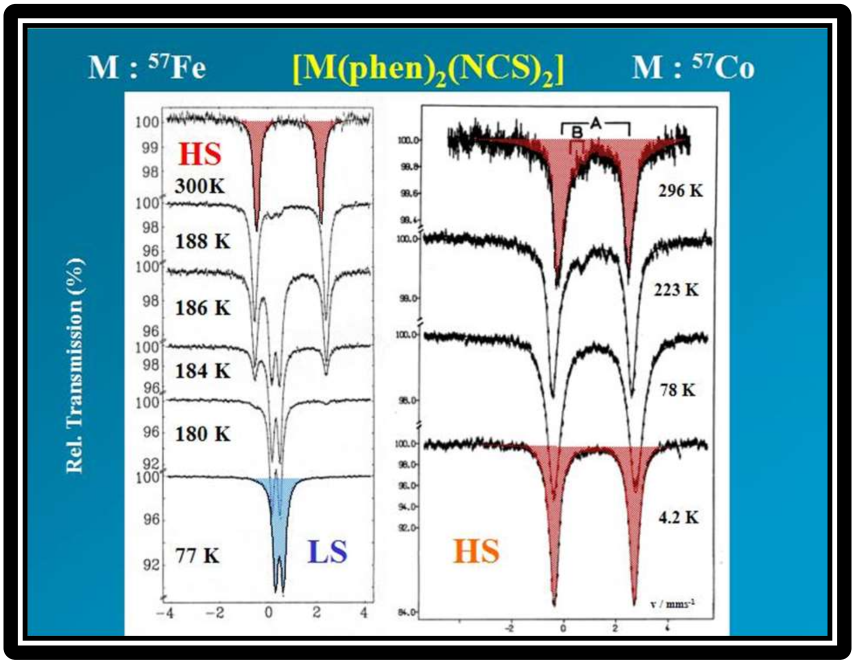
Ferredoxin (green alga)

Two-Iron Center Protein

C. E. Johnson et al. (1971)

Study of thermal spin-cross over

- Many coordination compounds possessing intermediate ligand field strengths show thermal spin crossover. [i.e. HS <--> LS]
- [Fe(phen)$_2$(NCS)$_2$] undergoes thermal spin transition .
- The main result is that in the temperature region, where the MAS spectra reflect the transition to the LS state, the MES spectra still show the typical HS signals arising from excited ligand field states



M : ^{57}Fe [M(phen)$_2$(NCS)$_2$] M : ^{57}Co