M.Sc Inorganic Chemistry (Special-III) Elective Paper-1

Semester-IV

UNIVERSITY OF DELHI
निष्ठा धृतिः सत्यम्

Course Title: Spectral Techniques in Inorganic Chemistry

Paper Code: 4101-A

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Inorganic Group I and II

Mössbauer Spectroscopy

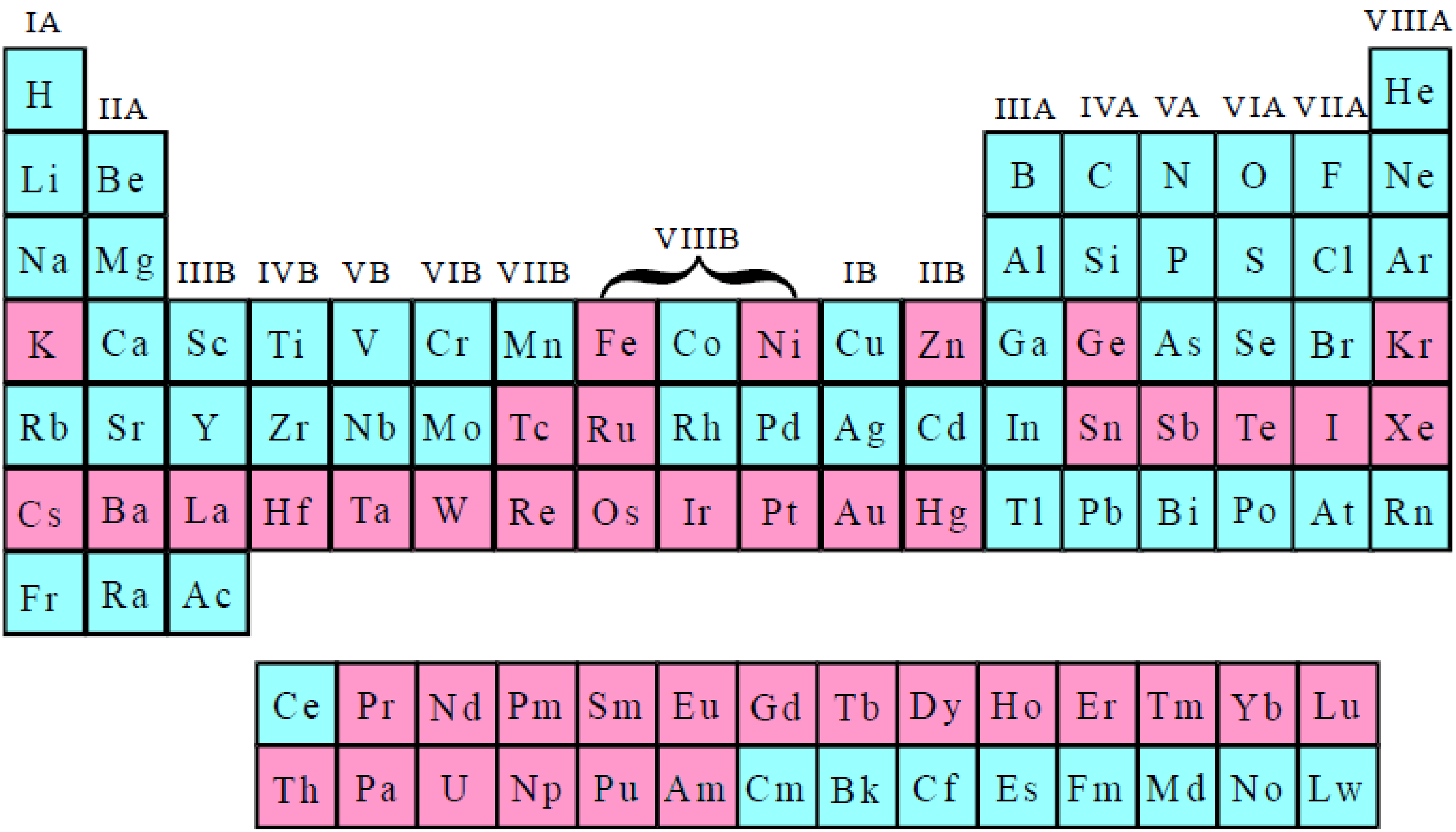
Rudolf L. MÖSSBAUER

discovers the "Recoilless Nuclear Resonance Absorption of γ-Radiation" in1958 and receives the Nobel Prize in 1961

R.L. Mössbauer made his first observation of recoilless nuclear resonant absorption in ^{191}Ir!

R.L. Mössbauer,
Z. Physik, 1958, 151, 124.
R.L. Mössbauer,
Naturwissenschaften, 1958, 45, 538

Mössbauer Active Elements



IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

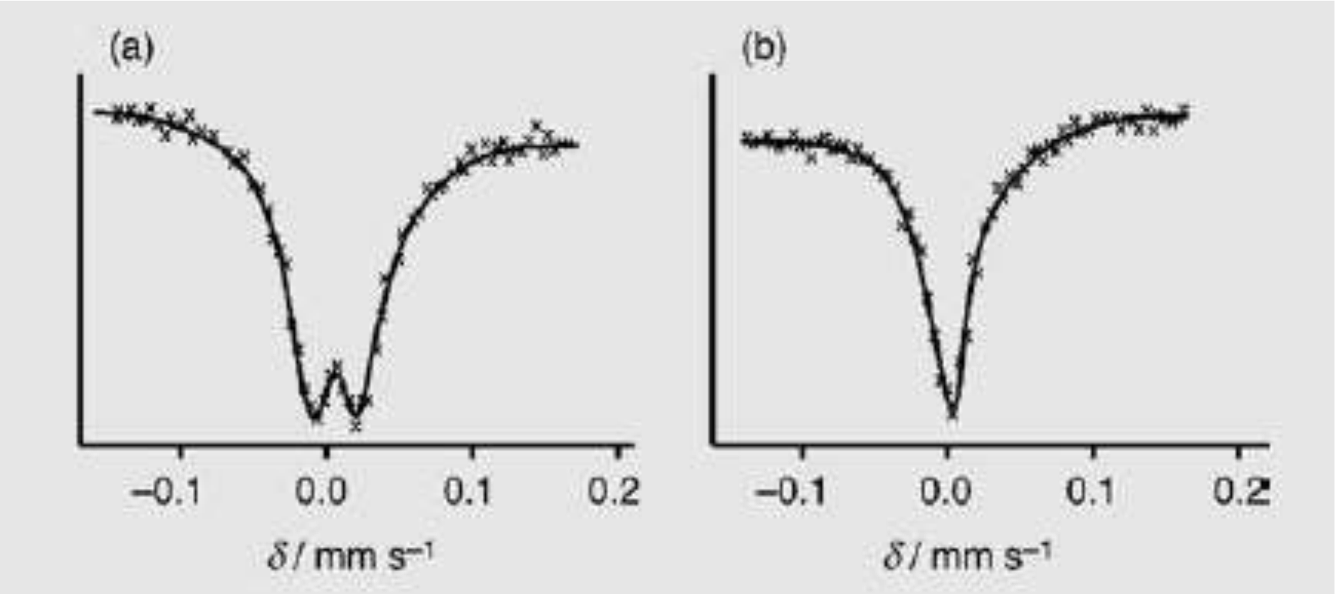
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Periodic table of the elements. Marked in red are the elements (more than 40) for which the Mössbauer effect has been observed. The most prominent Mössbauer nuclide is ^{57}Fe. More than 90 % of the nearby 50000 publications which have appeared so far refer to ^{57}Fe isotope.

- Nuclides suitable for Mössbauer (MB) spectroscopy should possess excited nuclear states with lifetimes in the range of ca. 10^{-6} to ca. 10^{-11} s, and transition energies between ca. 5 and 180 keV.
- The Mössbauer effect has been detected with a total of nearly 90 γ-ray transitions in 72 isotopes of 42 different elements.
- Due to several criteria (suitable lifetime of nuclear excited state, transition energy, easy accessibility and handling) only ca. twenty elements can be studied by Mössbauer spectroscopy, e.g. iron, tin, antimony, tellurium, iodine, gold, nickel, ruthenium, iridium, tungsten, krypton, xenon, many of the rare earth elements, neptunium.

Application of Mössbauer Spectroscopy in Structure Determination

Q. The following two ^{57}Fe Mössbauer spectra belong to the red and yellow hexacyanoferrates $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$. Which is which?

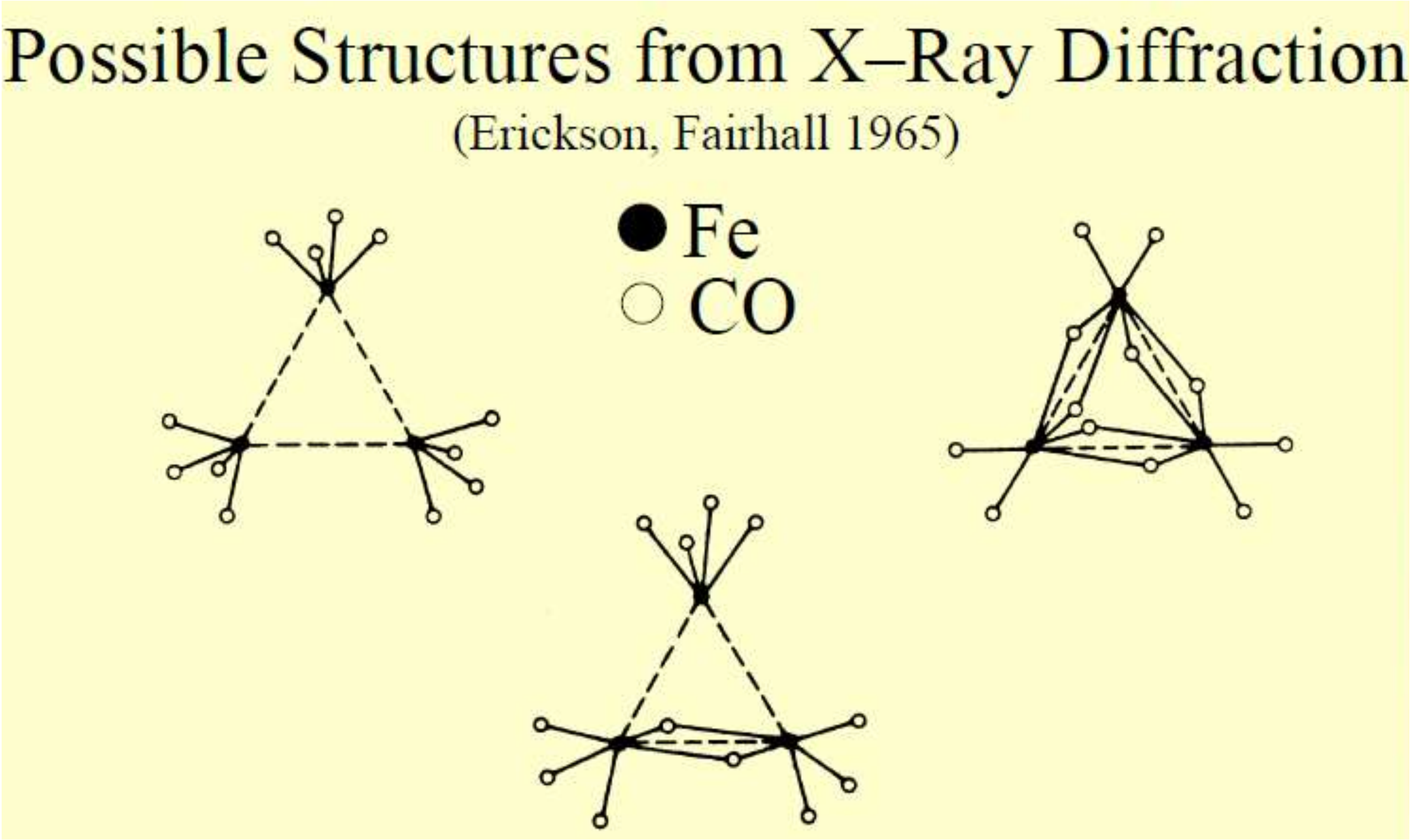


Ans. (a) corresponds to $K_3[Fe(CN)_6]$ and (b) corresponds to $K_4[Fe(CN)_6]$. The splitting is due to the less symmetric asymmetric distribution of electron density in the d^5 system for Fe(III) and consequently to an $EFG_{\text{val}} \neq 0$ in comparison to the symmetric electron density distribution of the diamagnetic low-spin Fe(II) ion.

MB Spectrum of [$Fe_3(CO)_{12}$]

- The structure of $Fe_3(CO)_{12}$ deduced from its MB spectrum was at odds with infrared results and a preliminary x-ray study.
- In 1965 Erickson and Fairhall suggested, on the basis of single crystal X-ray diffraction, three possible molecular structures for $Fe_3(CO)_{12}$. (next slide)
- The MB indicated more than one type of iron, as shown in Fig. A (slide # 8) . The outer two lines are assigned to one type of iron and the inner two to a second type.
- In general, the areas are roughly proportional to the number of a particular type of iron present.
- A definitive crystal structure study has supported the structure shown in Fig. B which was predicted from the Mössbauer results.
- The spectra of $Fe(II)X_2(CO)_2P_2$ (where X = Cl**,** Br, and I**,** and P = phosphines and phosphites) have been interpreted in terms of the five different isomers that exist.

$Fe_3(CO)_{12}$

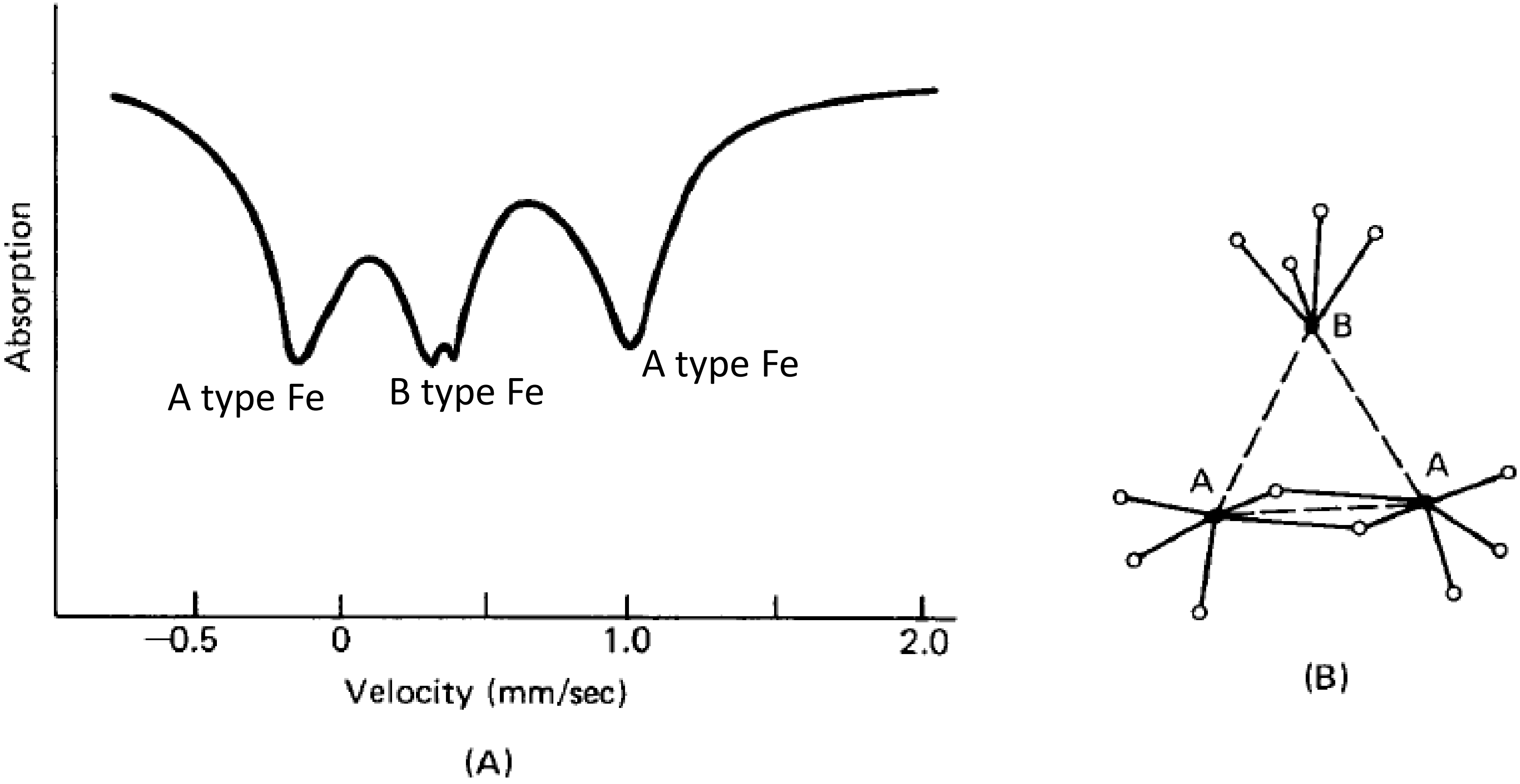


Possible Structures from X–Ray Diffraction

(Erickson, Fairhall 1965)

● Fe

○ CO



(A)

(B)

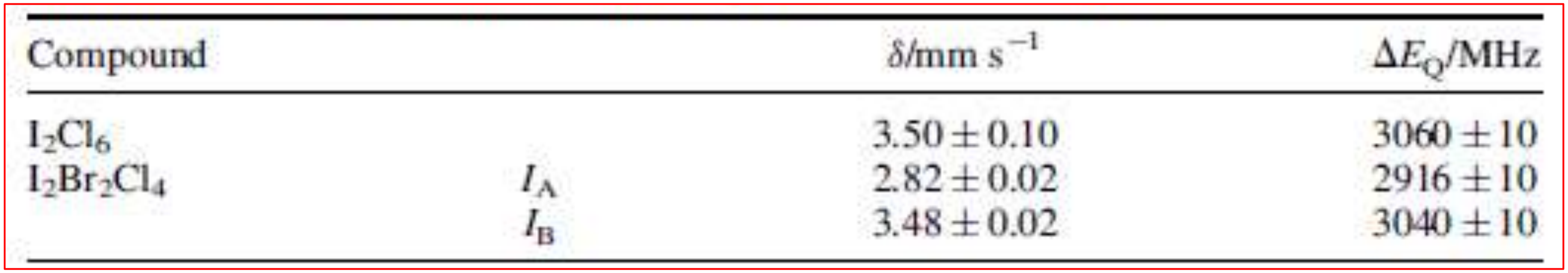
Figure: The Mössbauer spectrum (A) and structure (B) of $Fe_3(CO)_{12}$

Structure Determination of Interhalogen Compound $I_2Br_2Cl_4$

- The compound $I_2Br_2Cl_4$ was prepared by oxidizing NaI with $KBrO_3$ followed by Cl_2 gas.
- Its structure seems likely to be related to that of I_2Cl_6, which is made from NaI and Cl_2 without treatment by $KBrO_3$.
- I_2Cl_6 is known to be a planar molecule with a symmetrical Cl-bridged structure (6.IIa). However, there are several possible structures for $I_2Br_2Cl_4$ even within this geometric framework.
- The two Br atoms could both be bridging (6.IIb), or both terminal but on different I atoms (6.IIc and 6.IId), or both terminal but on the same I atom (6.IIe), or one bridging and one terminal (6.IIf and 6.IIg).
- The answer was found by Mossbauer spectroscopy. The parameters from the ^{129}I spectrum are given in Table.

- In the spectrum of I_2Cl_6 there was one set of lines, but in that for $I_2Br_2Cl_4$ there were two sets of lines. From this, we can conclude that there are non-equivalent iodine atoms.

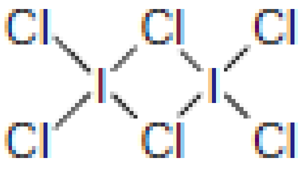
Table. Mössbauer parameters for I_2Cl_6 and $I_2Br_2Cl_4$.



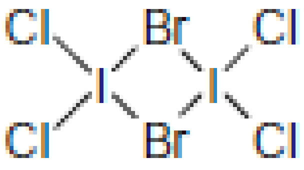
Compound		δ/mm s^{-1}	ΔE_Q/MHz
I_2Cl_6		3.50 ± 0.10	3060 ± 10
$I_2Br_2Cl_4$	I_A	2.82 ± 0.02	2916 ± 10
	I_B	3.48 ± 0.02	3040 ± 10

- This means that if the molecule has a single structure the two iodine atoms cannot be equivalent, and so structures 6.IIb, 6.IIc and 6.IId are already ruled out.
- The isomer shift *δ* and quadrupole coupling constant ΔE_Q for one of the iodine atoms are close to those found for I_2Cl_6 (Table); this implies that one of the iodine atoms in $I_2Br_2Cl_4$ is in much the same environment as are the two in I_2Cl_6 – that is, bound to two terminal and two bridging Cl atoms.

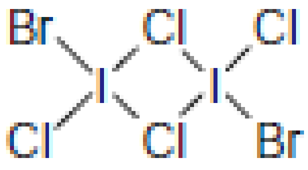
- In structure 6.IIe, one of the iodine atoms satisfies this condition, but in structure 6.IIf and 6.IIg neither does, for both are bound to at least one bromine atom. Hence the correct structure must be 6.IIe.



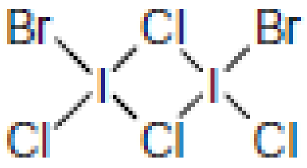
6.IIa



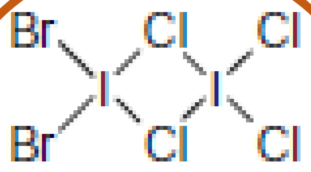
6.IIb



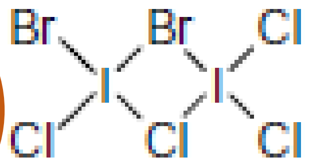
6.IIc



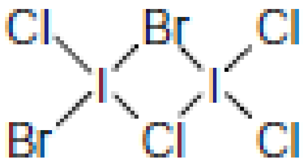
6.IId



6.IIe

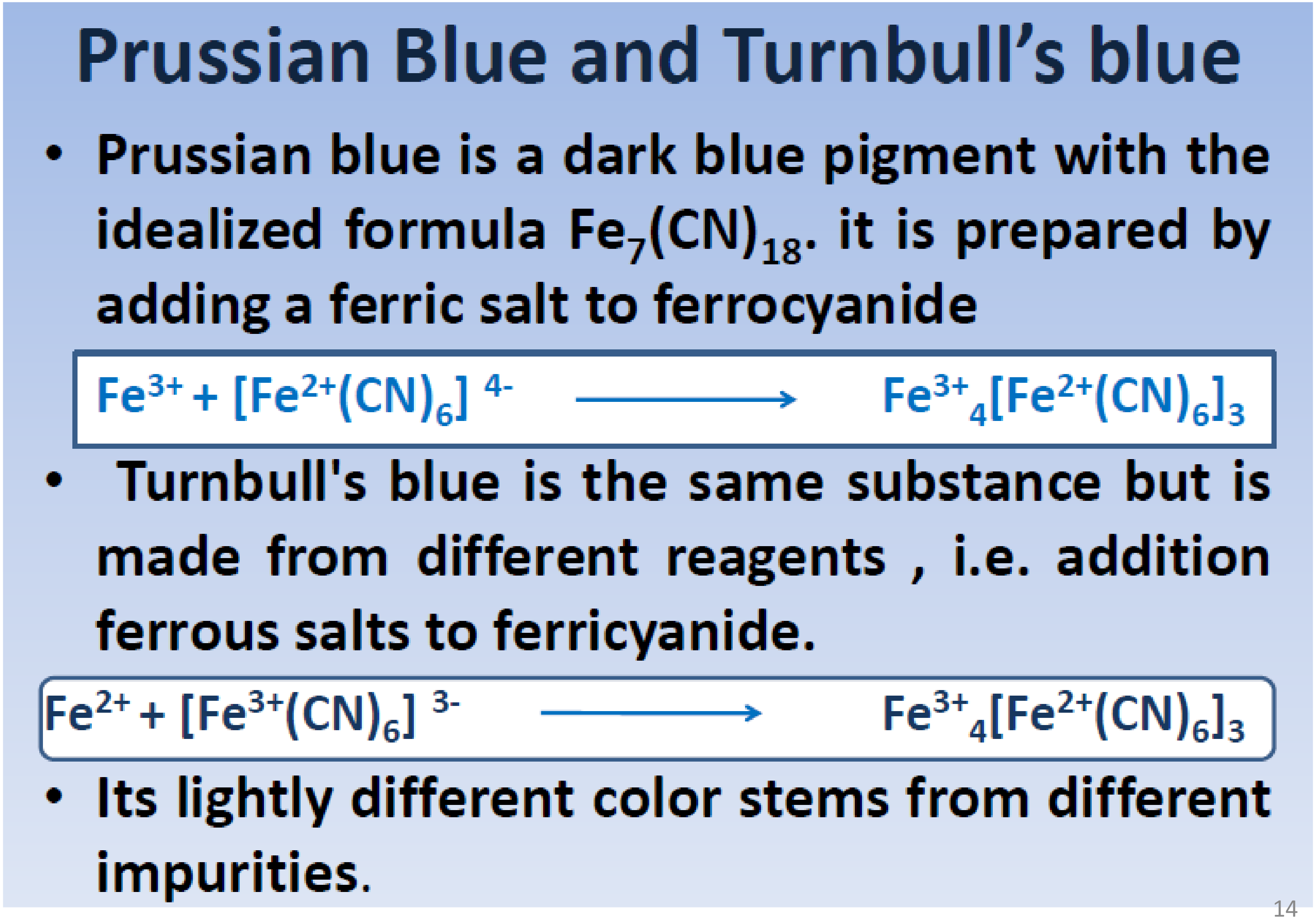


6.IIf



6.IIg

Study of Prussian Blue and Turnbull’s Blue using MB Spectroscopy



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

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

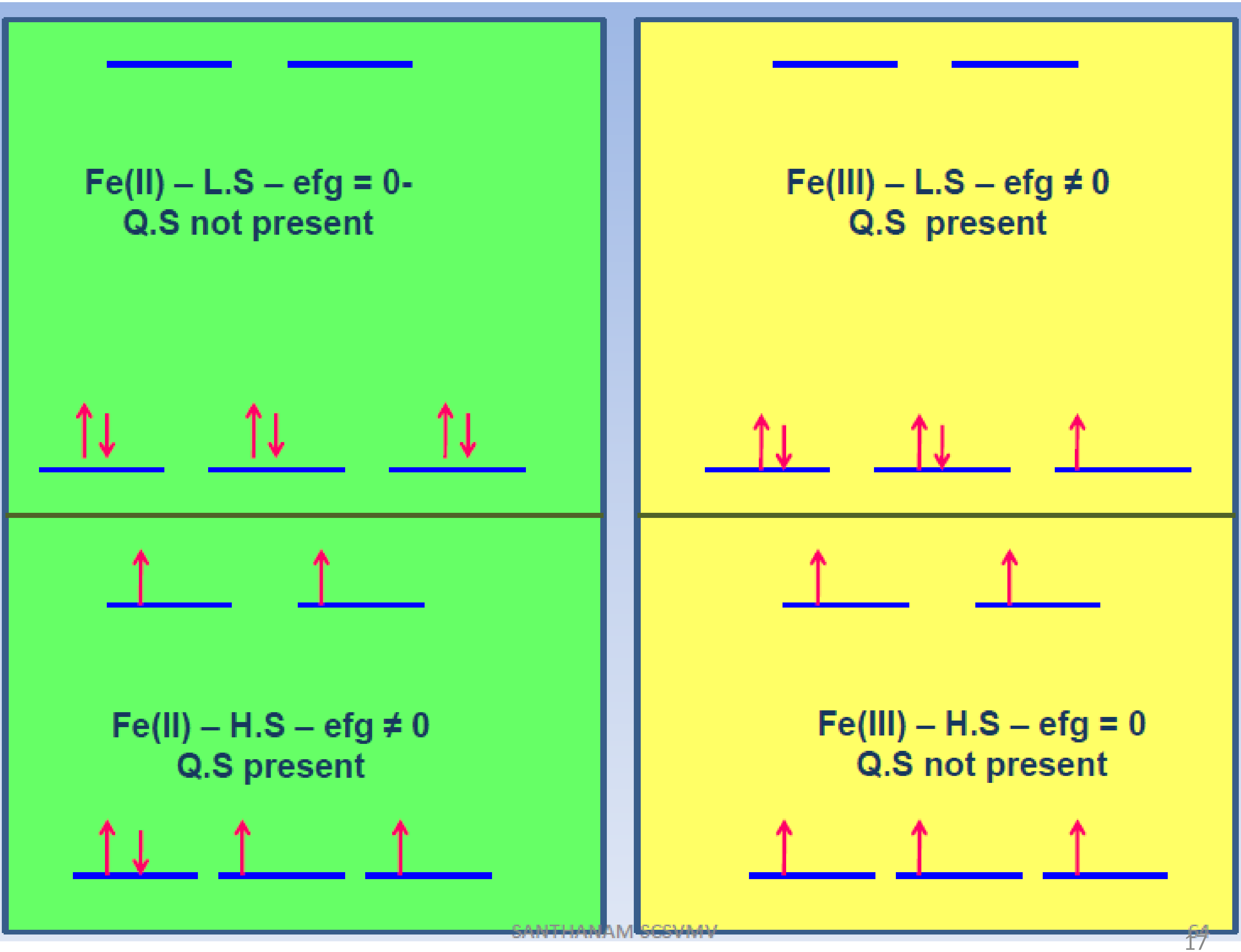
- Turnbull's blue is the same substance but is made from different reagents , i.e. addition ferrous salts to ferricyanide.

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

- 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(II) and a quadruple doublet for Fe(III) were which confirmed Prussian blue and Turnbull's blue are identical**



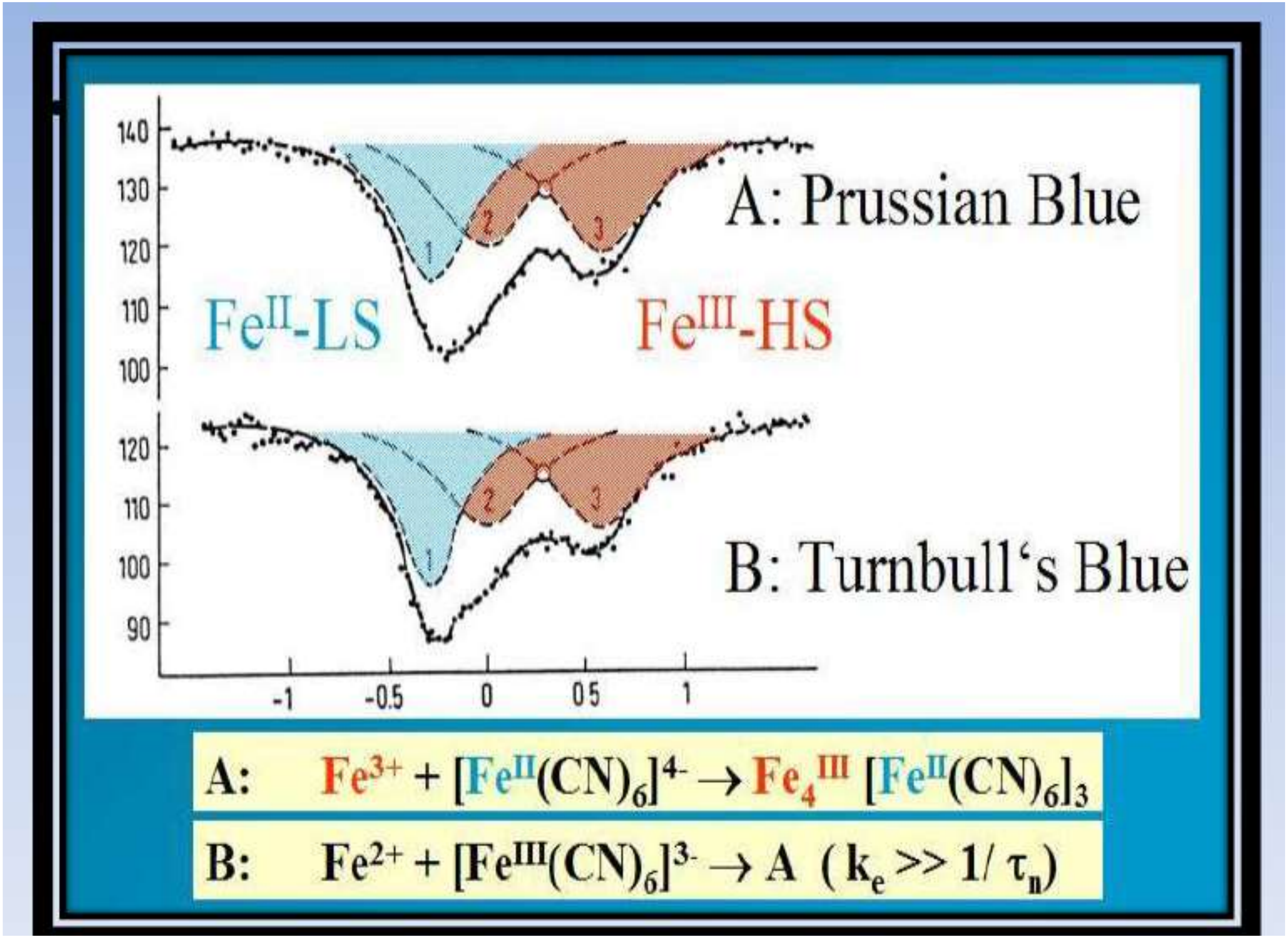
Fe(II) – L.S – efg = 0-
Q.S not present

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

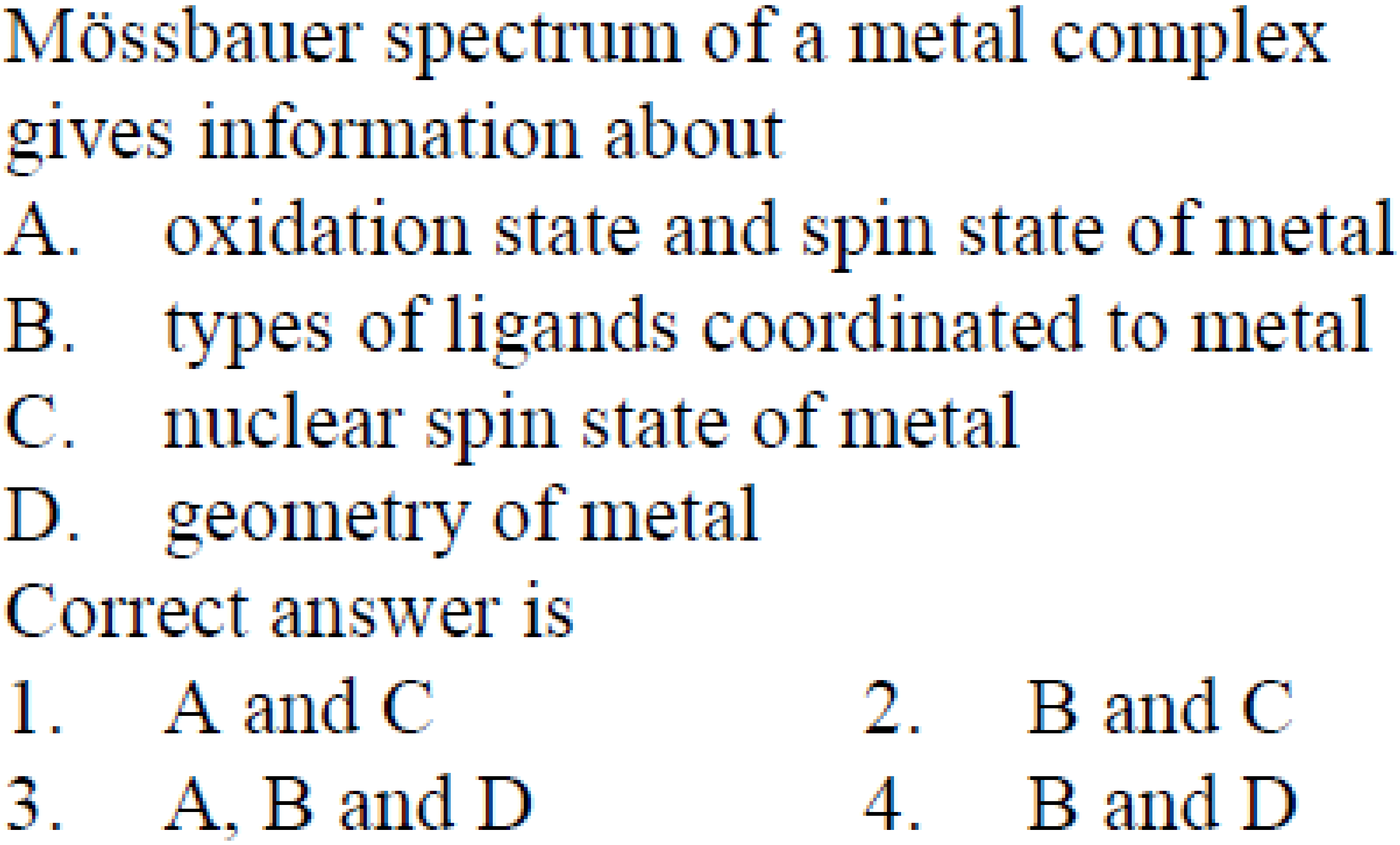
- The Fe(II) centers, which are low spin, are surrounded by six carbon ligands in an octahedral configuration.
- The Fe(III) centers, which are high spin, are octahedrally surrounded on average by 4.5 nitrogen atoms and 1.5 oxygen atoms (the oxygen from the six coordinated water molecules).
- This introduces 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: $Fe^{2+} + [Fe^{III}(CN)_6]^{3-} \rightarrow A\ \ (k_e >> 1/\tau_n)$

Q



Mössbauer spectrum of a metal complex gives information about

A. oxidation state and spin state of metal

B. types of ligands coordinated to metal

C. nuclear spin state of metal

D. geometry of metal

Correct answer is

1. A and C
2. B and C
3. A, B and D
4. B and D

Answer 3

Recommended Texts:

1. Kettle. S. F. A. Physical Inorganic Chemistry: A Coordination Chemistry Approach, Springer, Berlin, Heidelberg (1996).
2. Drago, Russell S. Physical Methods for Chemists 2^{ed}. East West Press Pvt. Ltd. (2016).