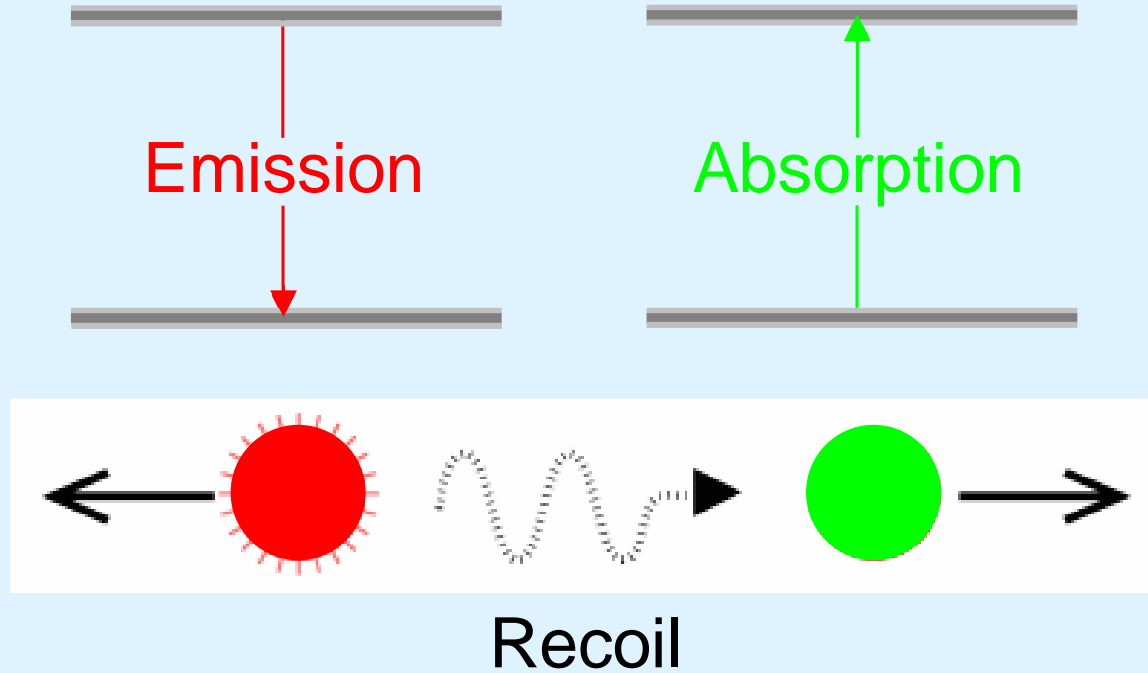


MOSSBAUER SPECTROSCOPY

Submitted by:
Kanica Sharma

Basic principles of Mössbauer spectroscopy

Free **emitting** and **absorbing** atoms

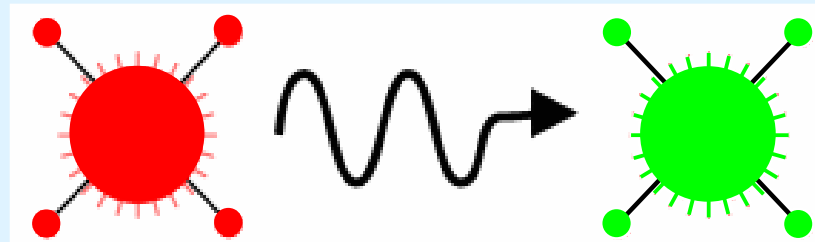


Energy of recoil $\rightarrow E_R = \frac{E_\gamma^2}{2mc^2}$

E_γ ← γ -ray energy

$2mc^2$ ← Mass of atom

Emitting and absorbing atoms fixed in a lattice



No recoil

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

Mass of particle

Sample preparation

- Low resonance absorption conditional for Mössbauer spectroscopy
- → solid sample can distribute recoil energy in the crystal lattice

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

- Energy levels in atom are quantized
- limited probability f of absorbing a γ -quant without accompanying phonon transition = recoilless absorption is given by the Lamb-Mössbauerfactor

$$f = \exp \left[-\frac{6E_R}{k\theta_D} \left\{ \frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x dx}{e^x - 1} \right\} \right]$$

- → recoilless emission and absorption favoured at deep temperatures

Common samples for Mössbauer spectroscopy

Periodic table of Mössbauer active elements																		
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	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus		Uuo
		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	Lr			
Mössbauer-active elements						Gammy-ray sources						Unsuitable for Mössbauer						

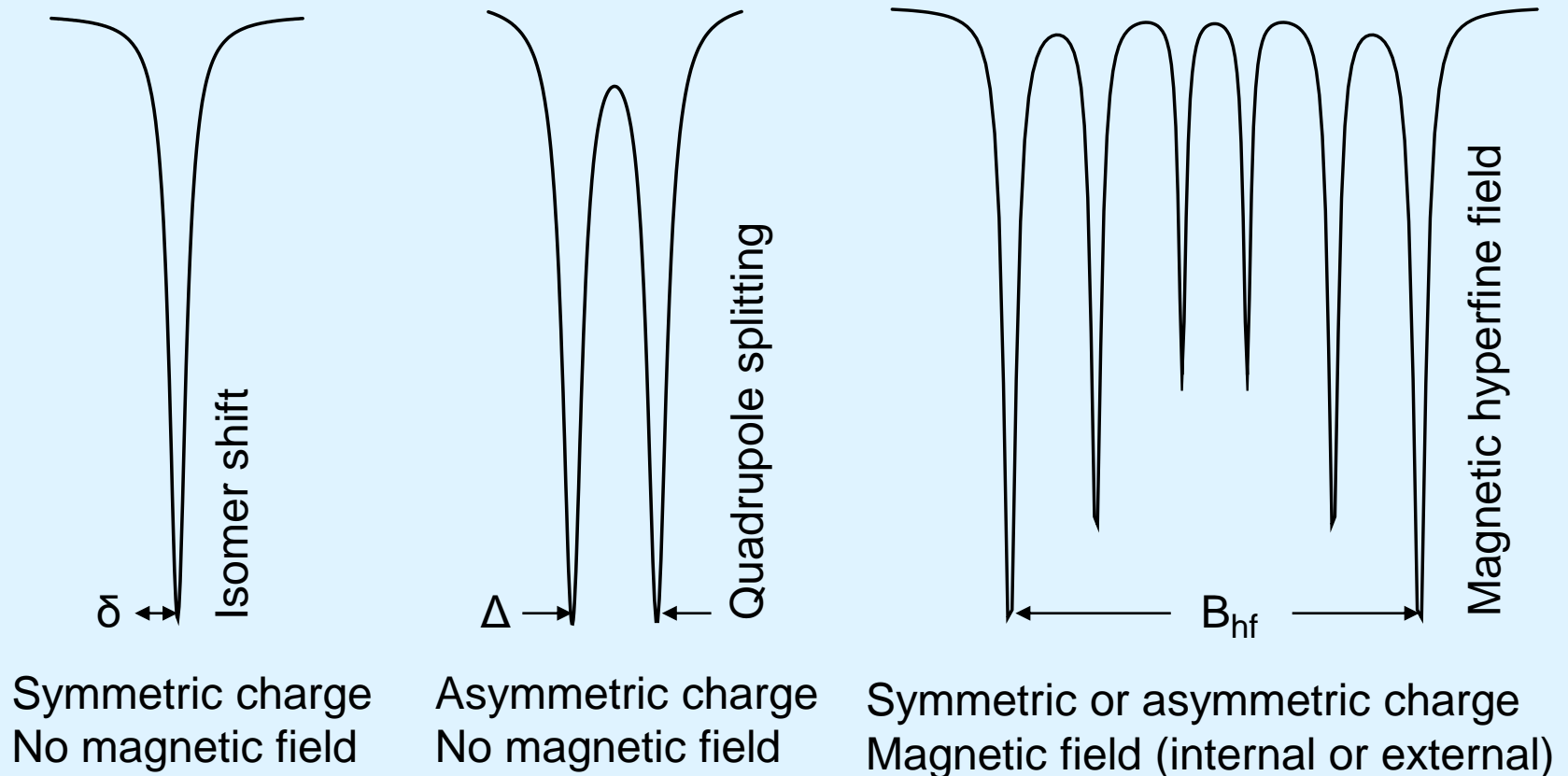
Important factors:

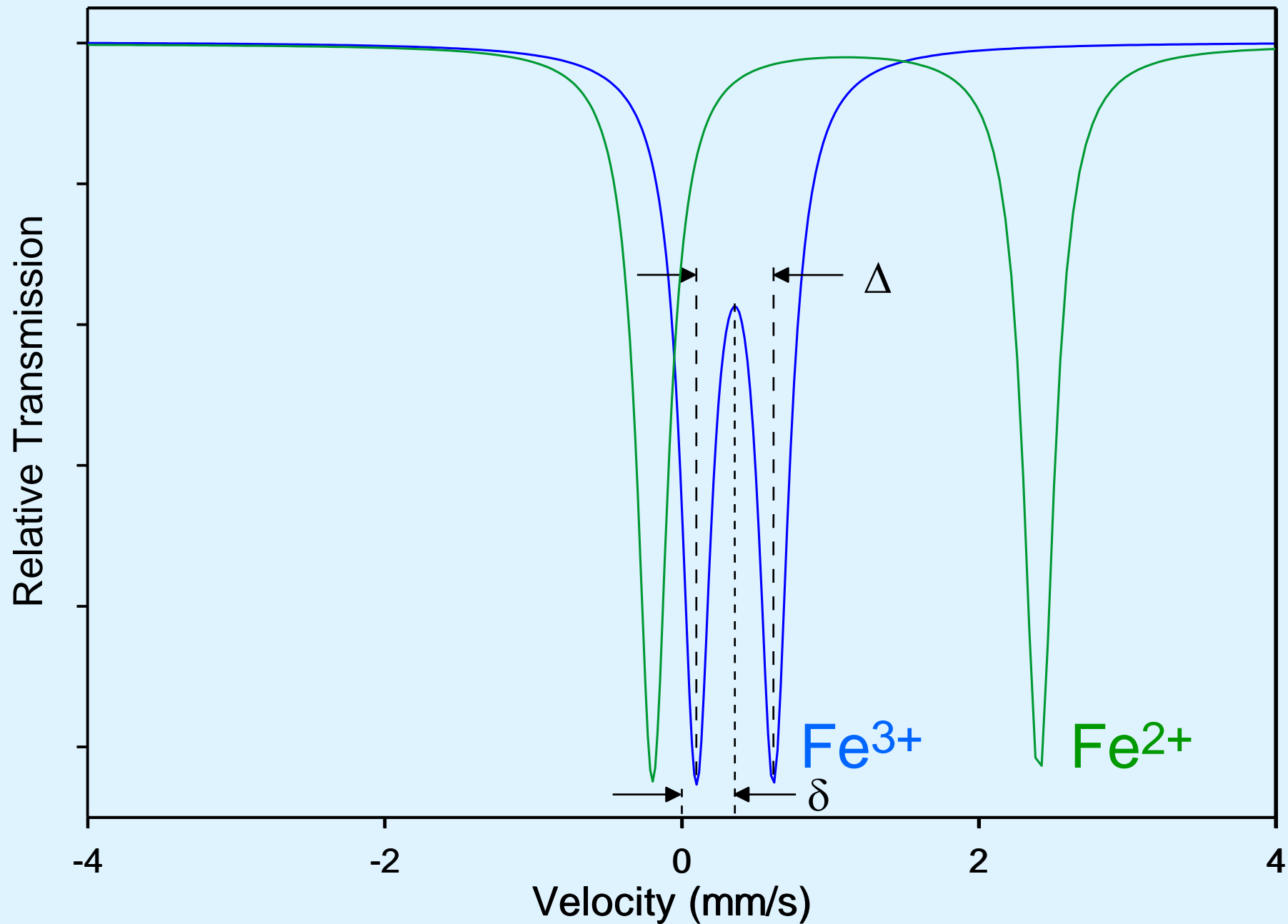
- Suitable half-life time of the parent isotope
- Low gamma-ray energy to gain sufficient signal-to-noise ratio

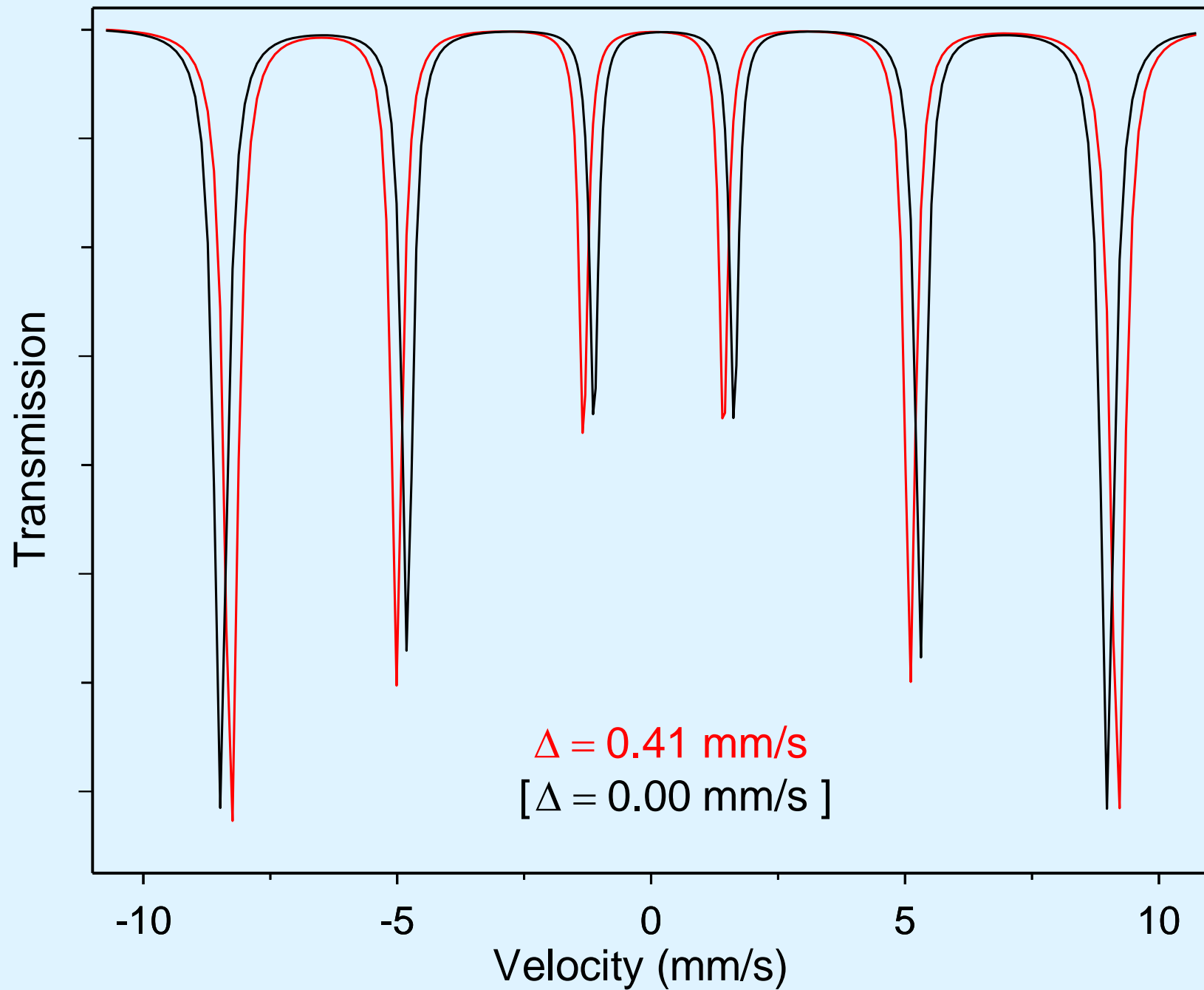
Most frequently used isotopes are: ^{57}Fe , ^{119}Sn , ^{121}Sb and ^{129}I

Appearance of Mössbauer spectra

Depending on the local environments of the Fe atoms and the magnetic properties, Mössbauer spectra of iron oxides can consist of a singlet, a doublet, or a sextet.

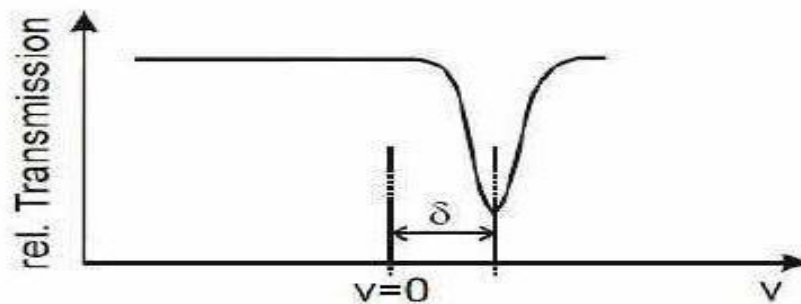
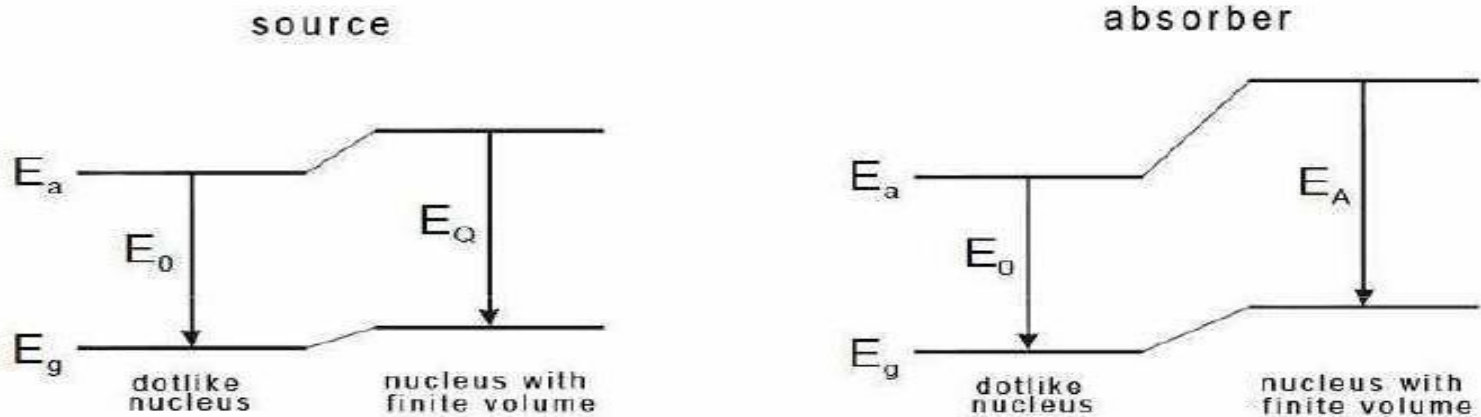






Isomer Shift

A parameter in Mössbauer-spectroscopy



Isomer Shift

Reasons for isomer shift:

- electron density at the nucleus is different for ground and excited state
- unlike coulomb interactions

Measurement of electron density at the nucleus

Information about:

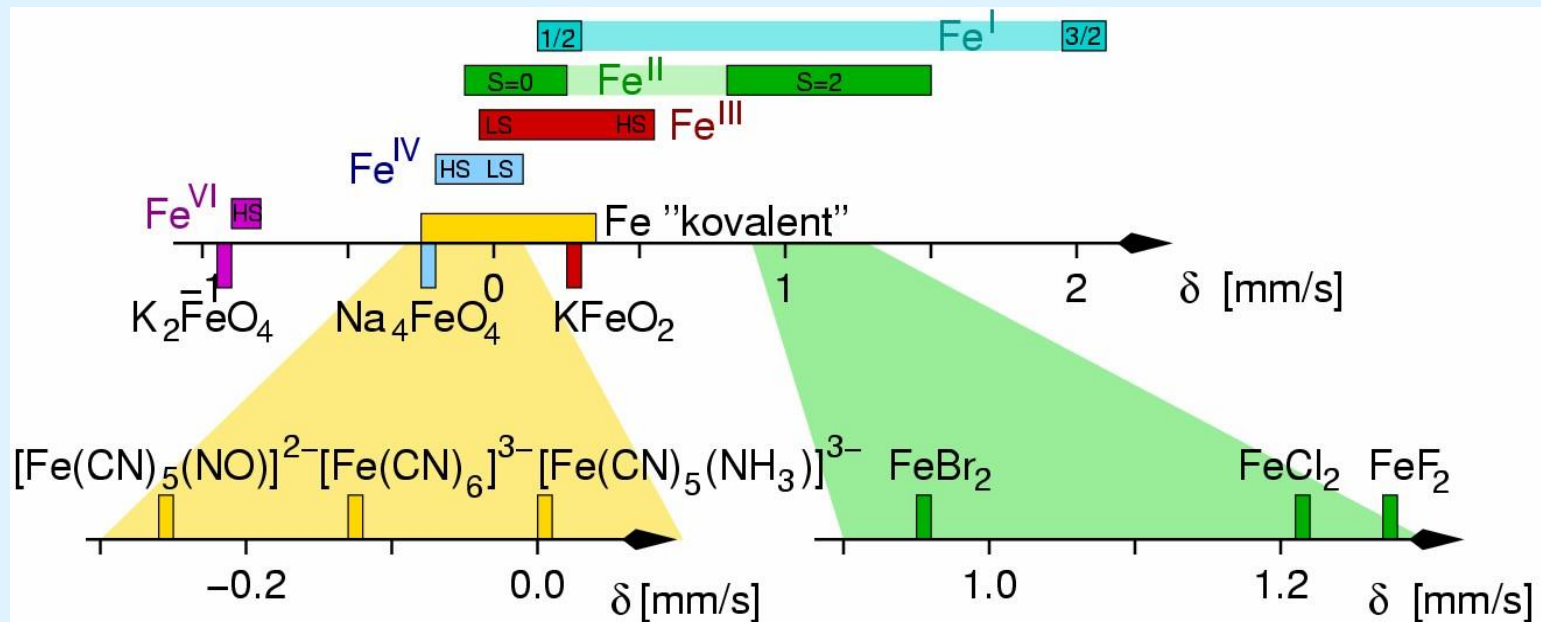
- Oxidation state of the Mössbauer atom.
- Bonding properties in case of coordination compounds (covalency)
- Delocalization of d-electrons due to back-bonding or shielding-effects of s-electrons
- Electronegativity of ligands

Isomer Shift

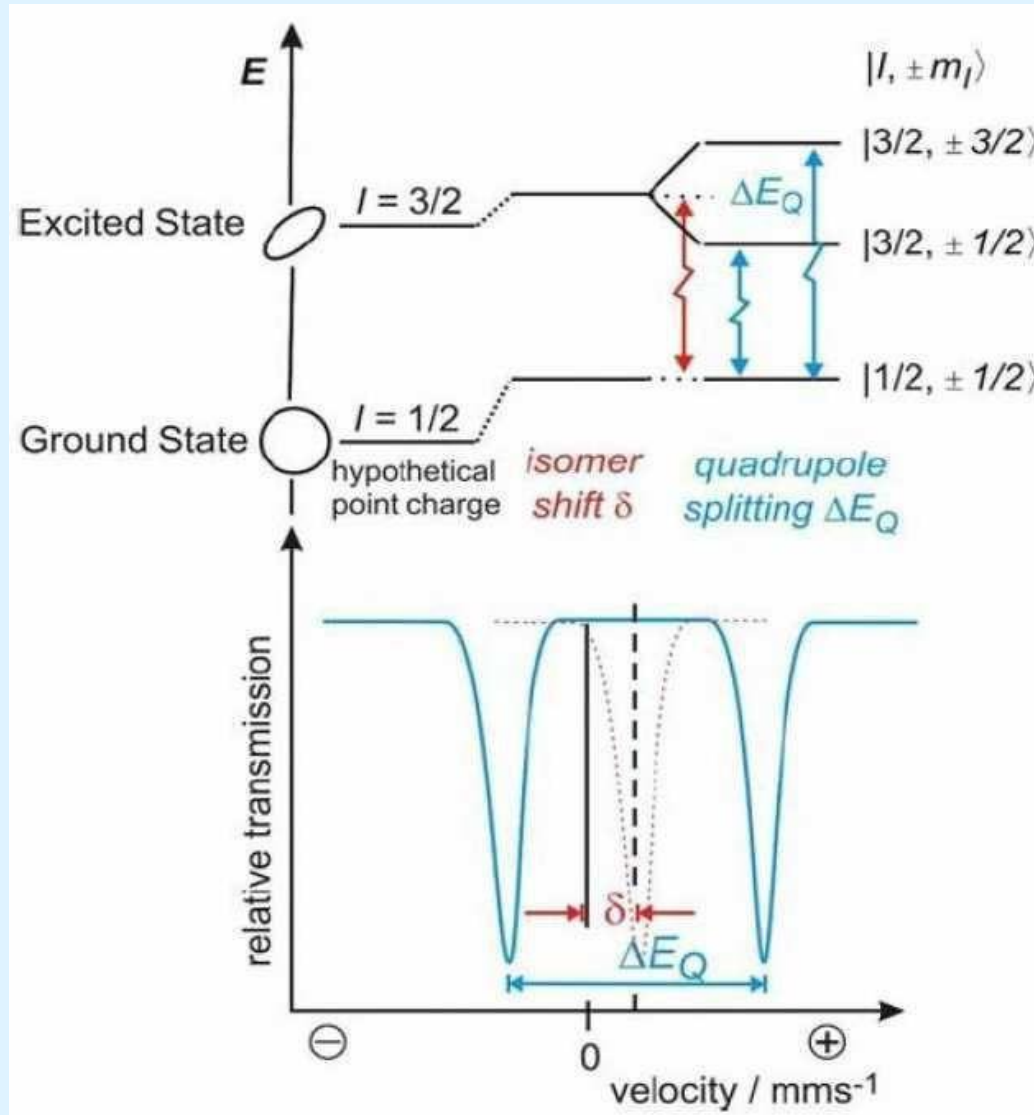
keep in mind: Due to many possibilities affecting isomer shift there can't be any absolute value for δ – but you can tell about trends!

Example: ^{57}Fe -Mössbauer with $(\delta R/R)$ being negative

"The higher the oxidation state the lower is the isomer-shift!"



Quadrupole Splitting

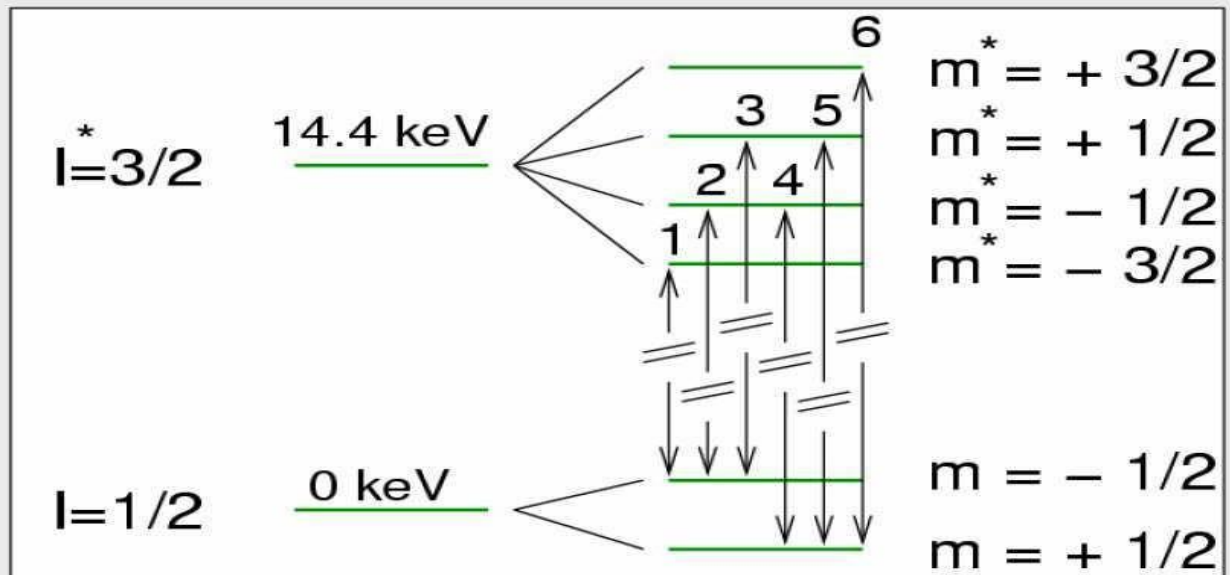
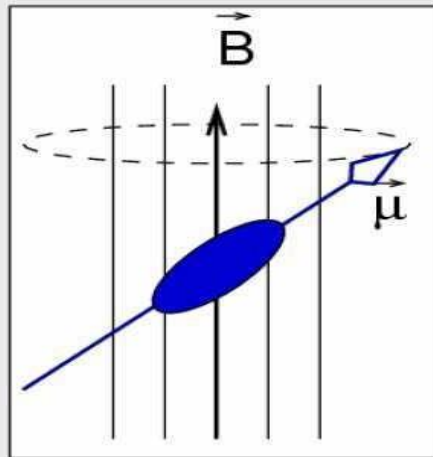


Magnetic Dipole Interactions

Interaction of Dipole and magnetic field:
 Magnetic moment (l) with internal magnetic field
 gives $m_l = 2l + 1$

→ for $l=1/2$ ---> $m_l = +1/2, -1/2$

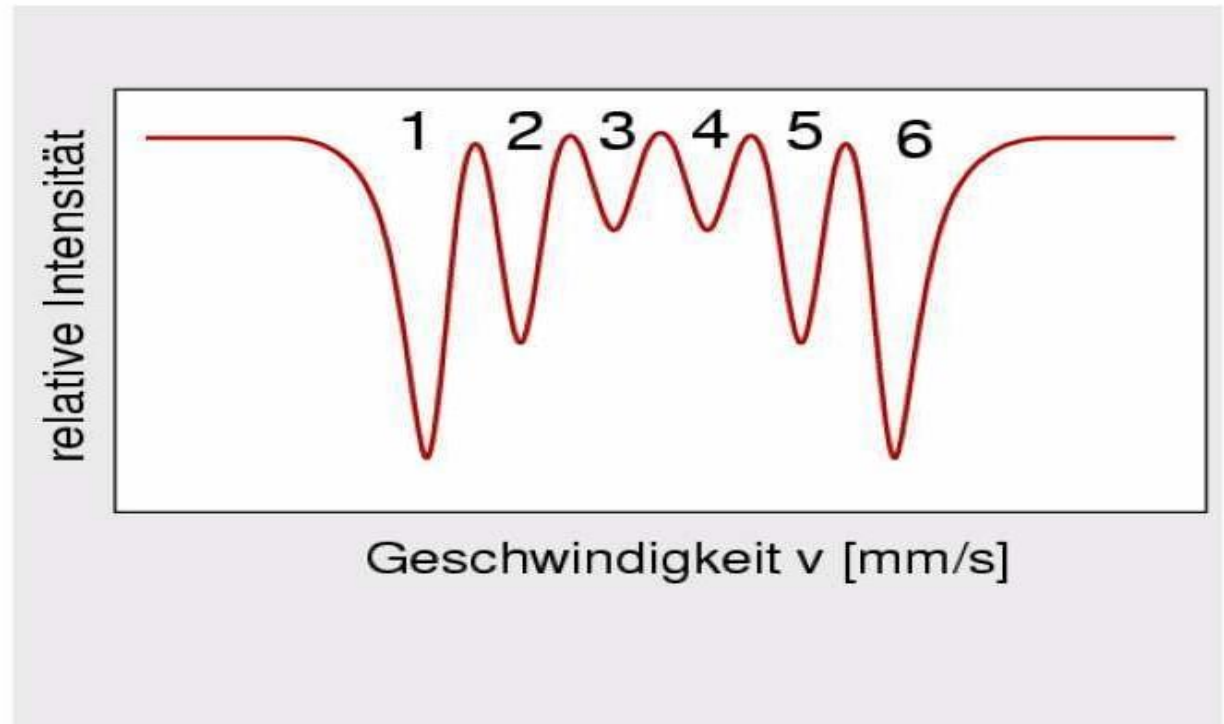
→ for $l=3/2$ ---> $m_l = +3/2, +1/2, -1/2, -3/2$



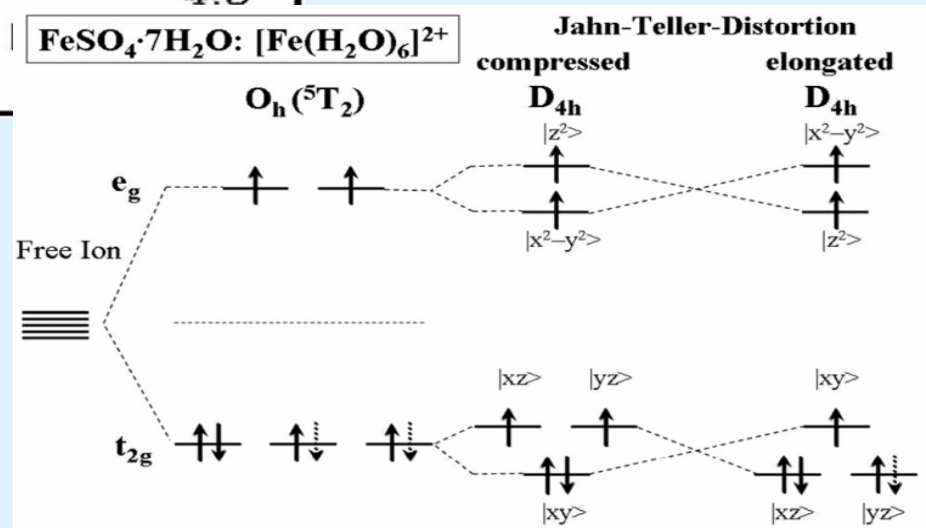
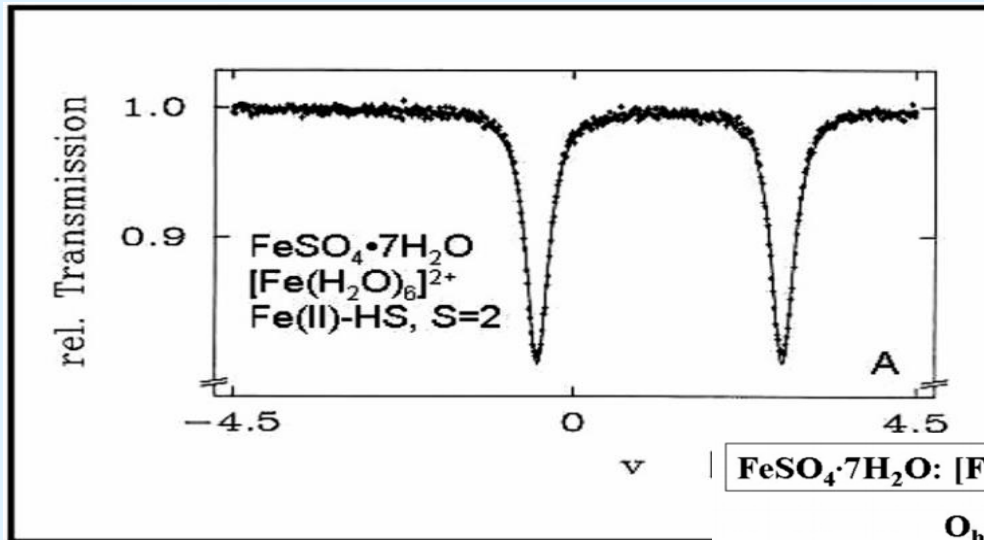
Magnetic Dipole Interactions

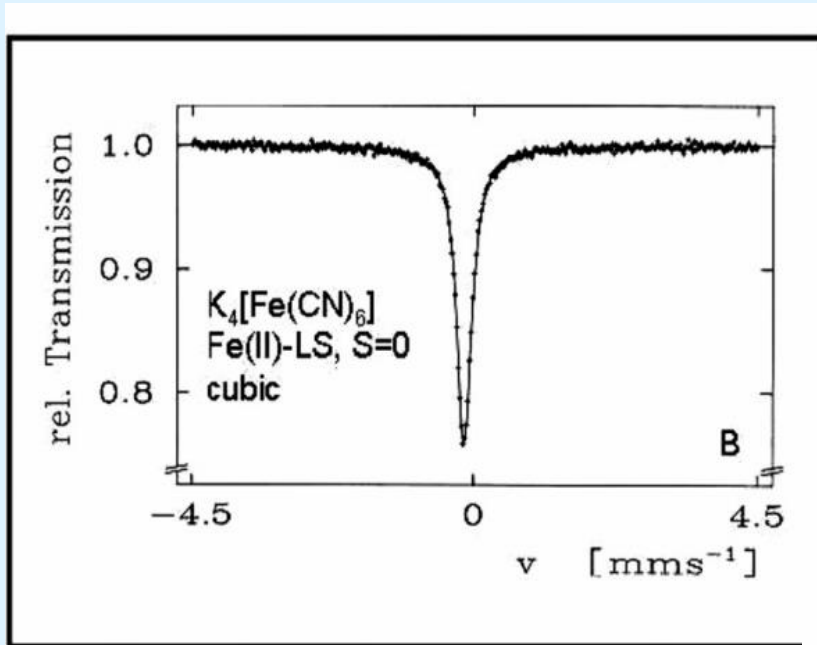
For transitions between $I=1/2$ and $I=3/2$

- 6 possible crossovers
- 6 lines in spectrum

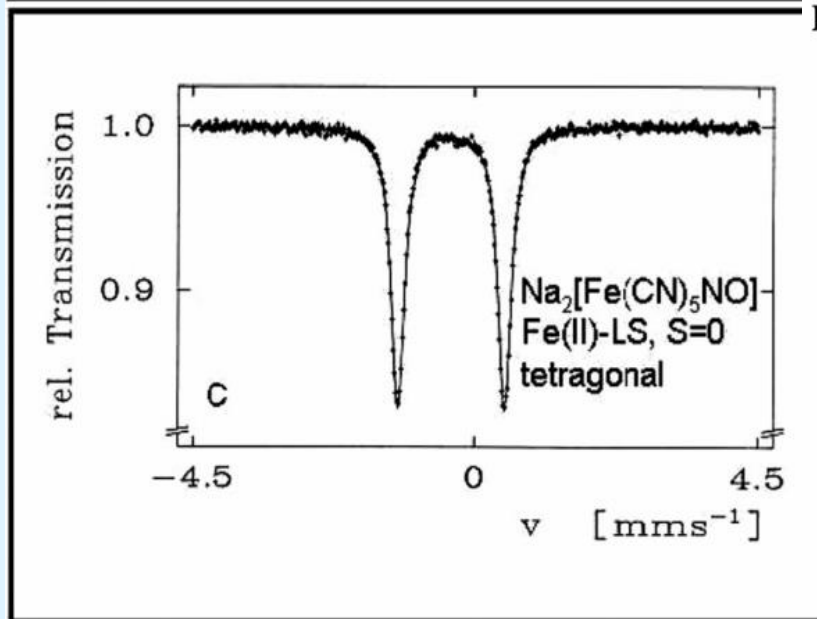


Comparison of ^{57}Fe (II) Mössbauer spectra

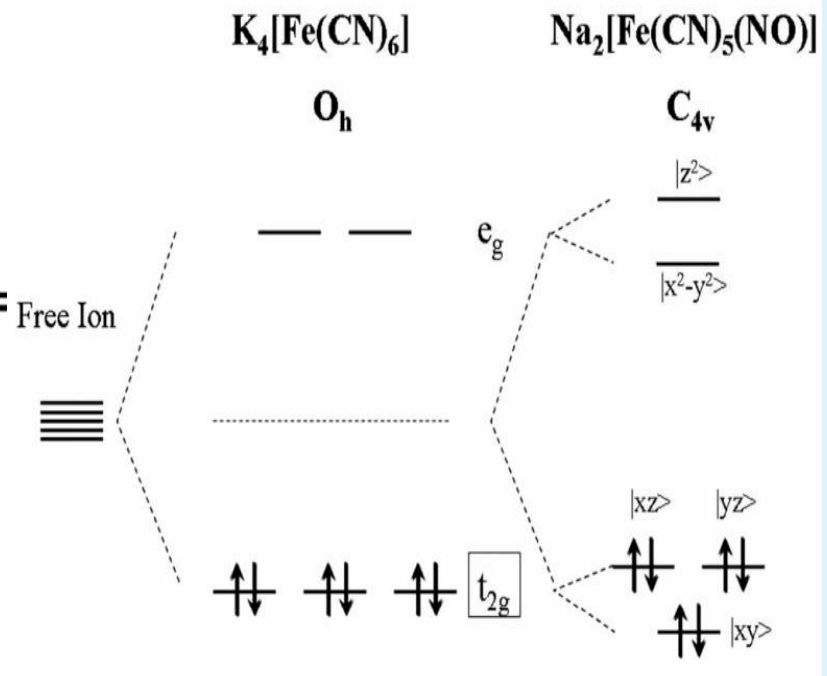




$\tilde{\infty} O_h$ symmetry $\tilde{\infty}$ **no** quadrupole splitting



$\tilde{\infty} C_{4v}$ symmetry $\tilde{\infty}$ significant quadrupole splitting



Strengths and weaknesses of ^{57}Fe Mössbauer spectroscopy

Strengths

- Sensitive only to ^{57}Fe (no matrix effects)
- Sensitive to oxidation state
- Allows distinction of magnetic phases
- Very sensitive towards magnetic phases
- Non-destructive
- Resolution limited by uncertainty principle

Weaknesses

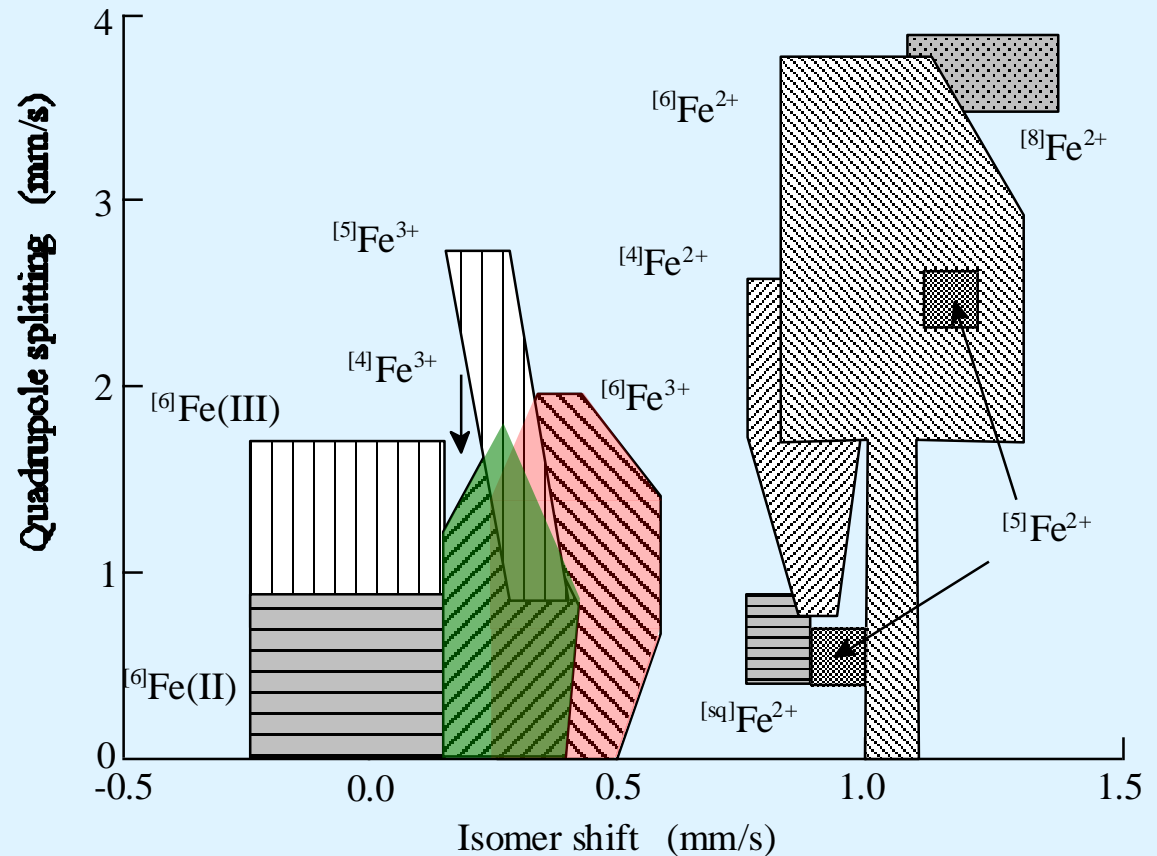
- Sensitive only to ^{57}Fe (“sees” only ^{57}Fe)
- Coordination ? to \pm
- Paramagnetic phase data often ambiguous
- Diamagnetic element substitution & relaxation
- Slow
- If possible, use other techniques as well

Often a combination of Mössbauer spectroscopy with other techniques can help solve problems that cannot be resolved using Mössbauer spectroscopy alone.

Use of Mössbauer spectroscopy as a “fingerprinting” technique

Isomer shifts and quadrupole splittings of Fe-bearing phases vary systematically as a function of Fe oxidation, Fe spin states, and Fe coordination.

Knowledge of the Mössbauer parameters can therefore be used to “fingerprint” an unknown phase.



THANK YOU!!!