Course Outline

1. Symmetry, Group Theory, and Electronic Structure

2. Ground State Spectroscopic Methods

2.1 Nuclear Magnetic Resonance

2.2 Electron Paramagnetic Resonance

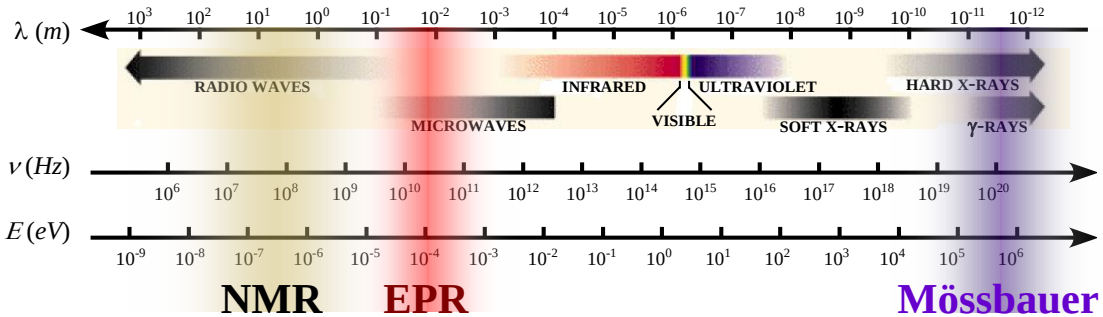
2.3 Mössbauer Spectroscopy

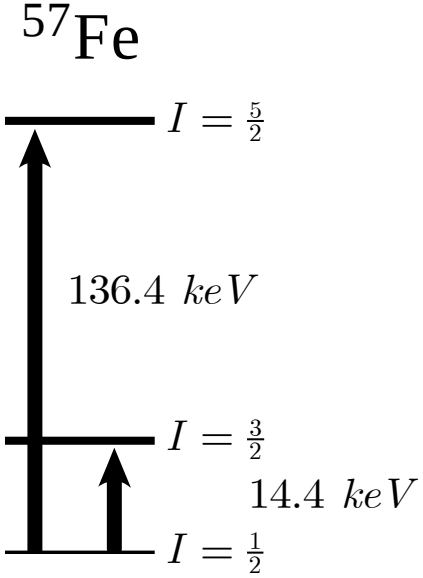
3. Excited State Spectroscopic Methods

4. Other Physical Methods

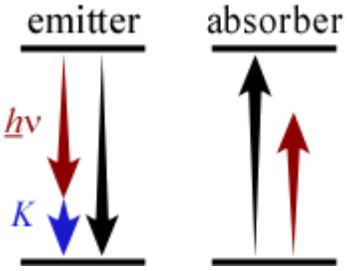
Fundamentals of Mössbauer Spectroscopy

- atoms have *nuclear energy states*
  - different possible 'arrangement' of nuclear particles will yield different angular momentum states – *e.g.* ^{57}Fe
  - just like *electronic states – singlets/triplets, HS/LS complexes*
  - transitions between these states require γ-rays



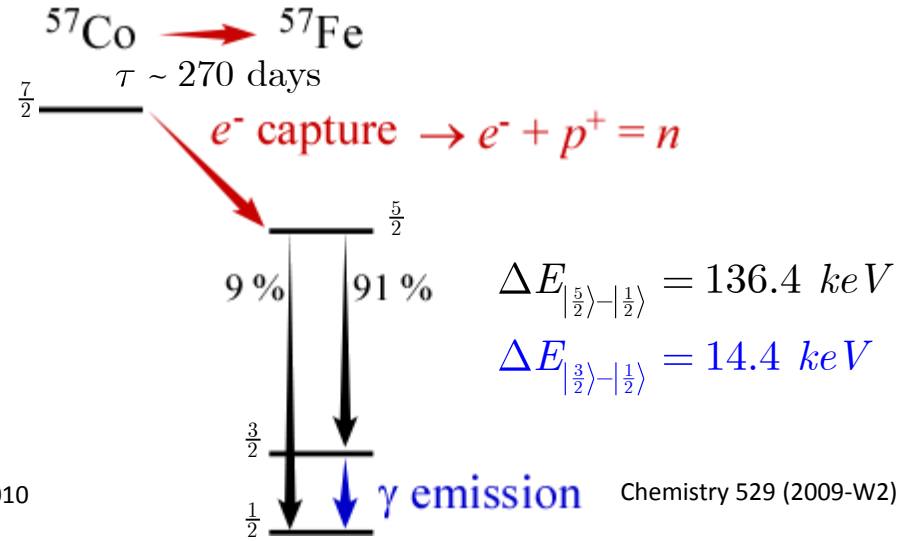


- resonant absorption/emission of γ-radiation should be possible...
  - but gas phase experiments did not work
  - freely moving atoms lose energy through *recoil* → kinetic energy (*K*)
  - *Mössbauer* thought it should work in solids → no loss due to recoil



Sources of γ-radiation

- to do spectroscopy – we need a *tunable* source of γ-radiation
- but there are few ways to generate γ-radiation
  - γ-emission of radioactive nuclei (not directly tunable)
  - electron accelerators/synchrotron sources (still very new)
- use radioactive source of appropriate atom, which emits radiation at ~ the correct energy (*e.g.* ^{57}Fe)



$$\Delta E_{|\frac{5}{2}\rangle - |\frac{1}{2}\rangle} = 136.4\ keV$$

$$\Delta E_{|\frac{3}{2}\rangle - |\frac{1}{2}\rangle} = 14.4\ keV$$

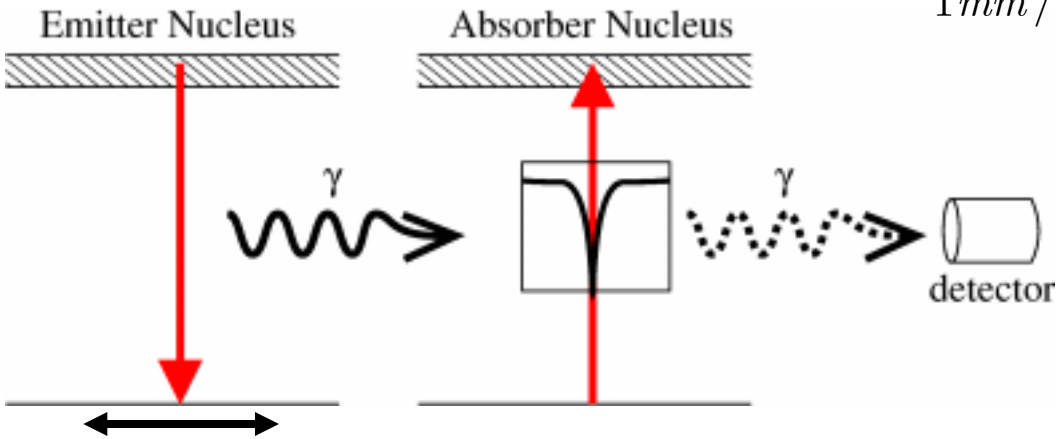
but energy of source is constant...
how do we change this?

Important: needed energy shifts are *very* small

use *Doppler Effect* → move the source

$$\Delta E_{Doppler} = \frac{\nu}{c} E_{\gamma}$$

The Mössbauer Experiment



Move emitter to change E_γ

$$1\,mm/s \sim 4.8\times10^{-8}\,eV$$
$$\sim \underbrace{11.6\,MHz}_{NMR\ \text{range!}} \sim 4\times10^{-4}\,cm^{-1}$$

for $^{57}Fe \Rightarrow$ energy shift from $1\,mm/s$ Doppler is $0.003\,ppb$

'Spectrum' is normally given in transmission mode:

negative spectrum like IR

- on which elements has this been done?
  - experiments have been successful on atoms in red

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	Lr	

Nuclear parameters for selected Mössbauer isotopes

Isotope	E_γ/keV	Γ_r/(mm s^{-1}) = 2 Γ_{nat}	I_g	I_e	α	Natural abundance %	Nuclear decay*
^{57}Fe	14.41	0.192	1/2–	3/2–	8.17	2.17	^{57}Co(EC 270 d)
^{61}Ni	67.40	0.78	3/2–	5/2–	0.12	1.25	^{61}Co(β⁻99 m)
^{119}Sn	23.87	0.626	1/2+	3/2+	5.12	8.58	^{119m}Sn(IT 50 d)
^{121}Sb	37.15	2.1	5/2+	7/2+	~10	57.25	^{121m}Sn(β⁻76 y)
^{125}Te	35.48	5.02	1/2+	3/2+	12.7	6.99	^{125}I(EC 60d)
^{127}I	57.60	2.54	5/2+	7/2+	3.70	100	^{127m}Te (β⁻109 d)
^{129}I	27.72	0.59	7/2+	5/2+	5.3	nil	^{129m}Te (β⁻33 d)
^{149}Sm	22.5	1.60	7/2–	5/2–	~12	13.9	^{149}Eu(EC 106 d)
^{151}Eu	21.6	1.44	5/2+	7/2+	29	47.8	^{151}Gd(EC 120 d)
^{161}Dy	25.65	0.37	5/2+	5/2–	~2.5	18.88	^{161}Tb(β⁻6.9 d)
^{193}Ir	73.0	0.60	3/2+	1/2+	~6	61.5	^{193}Os(β⁻31 h)
^{197}Au	77.34	1.87	3/2+	1/2+	4.0	100	^{197}Pt(β⁻18 h)
^{237}Np	59.54	0.067	5/2+	5/2–	1.06	nil	^{241}Am(α458 y)

*EC = electron capture, β⁻ = beta-decay, IT = isomeric transition, α – alpha-decay

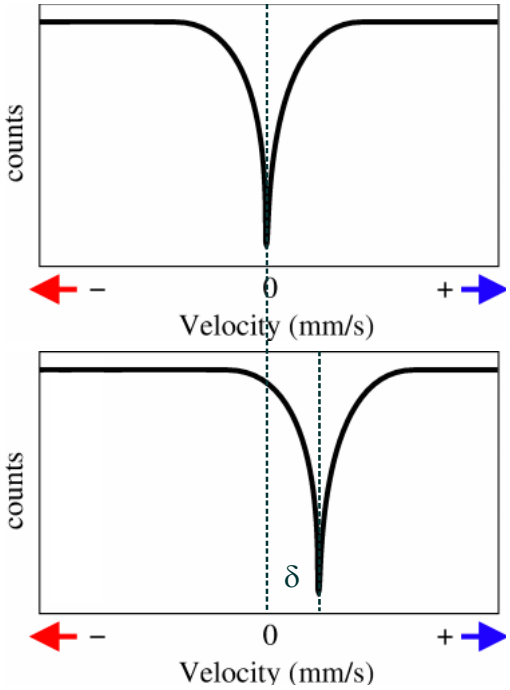
Basic Principles

- spectrum will give *relative energy* of absorber nuclear transitions
- if sample = source (^{57}Fe atom in source ^{57}Co lattice)
  - single transition at $\nu = 0$
- if sample is different from source
  - transition may not occur at same energy
  - isomer shift (δ) gives ΔE from ^{57}Fe atom reference

$$\delta = E_A - E_S$$

  - *note:* δ is ***very*** small relative to actual transition energy

$$1\,mm/s \sim 4.8 \times 10^{-8}\,eV \quad vs. \quad 14400\,eV$$



Contributions to Mössbauer Isomer Shift (δ)

- very similar to NMR chemical shifts...
- difference in electron density at the nucleus relative to source

$$\delta = k\ \langle \psi_A^n\ 0\ |\psi_A^n\ 0\rangle - \langle \psi_S^n\ 0\ |\psi_S^n\ 0\rangle$$
$$= E_A - E_S$$

Standard reference for ^{57}Fe:
α-Fe

  - *shielding/deshielding* of nuclear charge = change in energy levels
  - can only come from electron density in *s* orbitals
  - a.k.a. *electric monopole interaction*

- $\langle \psi_A^n\ 0\ |\psi_A^n\ 0\rangle$ is controlled by several factors:
  - total electron density of the ion
  - electronic spin state
  - metal-ligand delocalization

$$\underset{\mathrm{Fe^{II}}(3d^6)}{\langle \psi_{\mathrm{Fe^{II}}}^n\ 0\ |\psi_{\mathrm{Fe^{II}}}^n\ 0\rangle} < \underset{\mathrm{Fe^{III}}(3d^5)}{\langle \psi_{\mathrm{Fe^{III}}}^n\ 0\ |\psi_{\mathrm{Fe^{III}}}^n\ 0\rangle}$$

greater shielding in Fe^{II} delocalizes electron cloud...

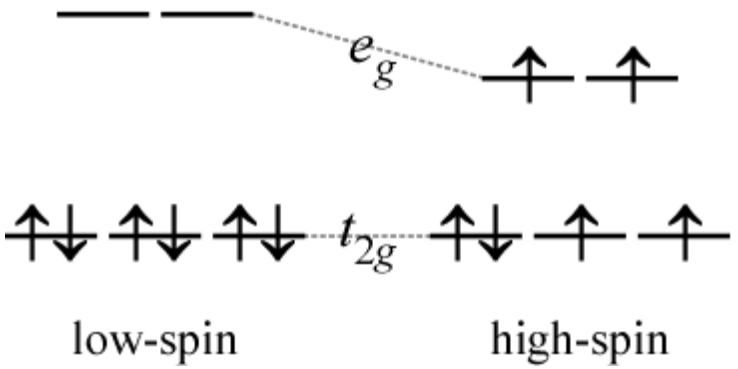
$$\delta_{\mathrm{Fe^{II}}} > \delta_{\mathrm{Fe^{III}}}$$

2.3 Mössbauer Spectroscopy

- spin state can have important impact on δ
  - due to differences in shielding of Fe 3*s* and 4*s* orbitals by 3*d* orbitals in different spin states

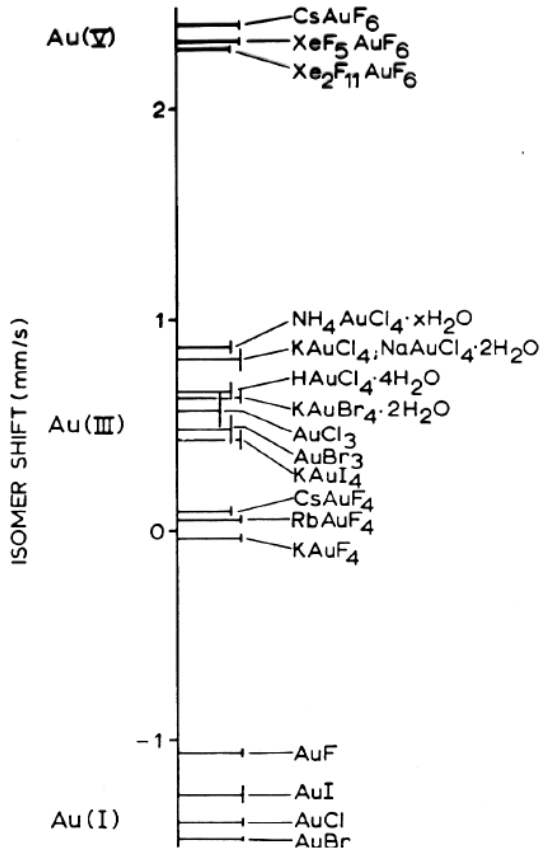
Hemes	*δ*
HS Fe^{II}	+0.75-0.85 *mm/s*
LS Fe^{II}	+0.18-0.43 *mm/s*
HS Fe^{III}	+0.35-0.40 *mm/s*
LS Fe^{III}	+0.15-0.35 *mm/s*

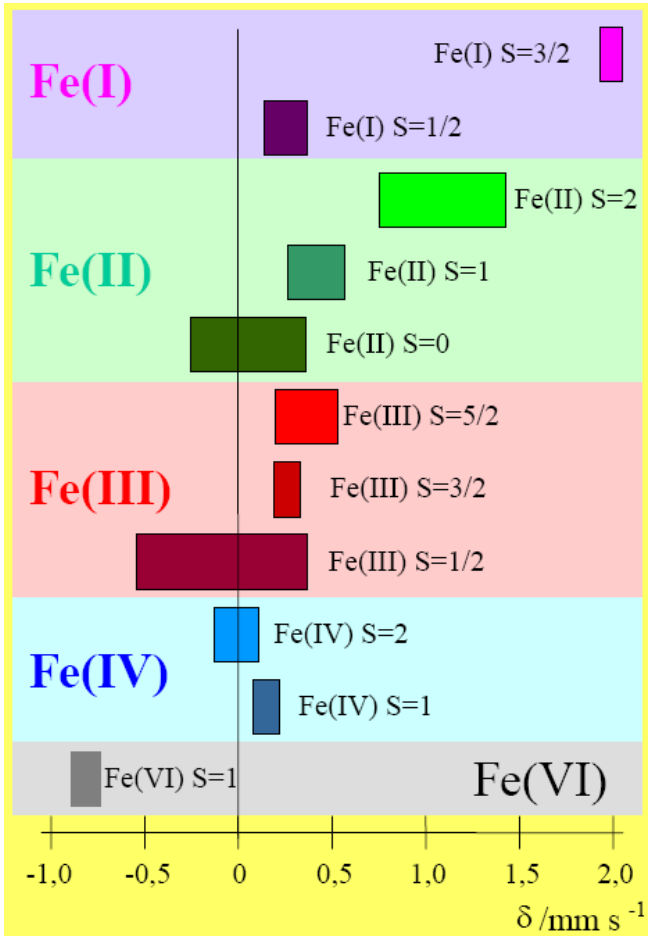
- shielding depends on population distribution of electrons in 3*d* orbitals
  - more shielding from low-spin case
  - effect of shielding will always be *isotropic*
  - t_{2g} orbitals are more metallic (less covalent)
  - 3*d* delocalization is greater for HS config
  - shielding will be less effective in HS case



2.3 Mössbauer Spectroscopy

Isomer shift ranges…





Electric Quadrupole Interaction

- states with $I > ½$ will have *nuclear quadrupole moment* (Q)
- for ^{57}Fe, $I = 3/2$ state has Q

$$\hat{\mathcal{H}}_Q \propto eQ\vec{V}\cdot\hat{I}$$

where $Q \equiv$ nuclear quadrupole moment
$\hat{I} \equiv$ nuclear spin operator
$\vec{V} \equiv$ electric field vector

  - interacts with *electric field gradient*
  - nucleus not spherical

$$\Delta = \Delta E_Q = \frac{eQ}{2}\vec{V}_{zz}\sqrt{1+\frac{\eta^2}{3}}$$

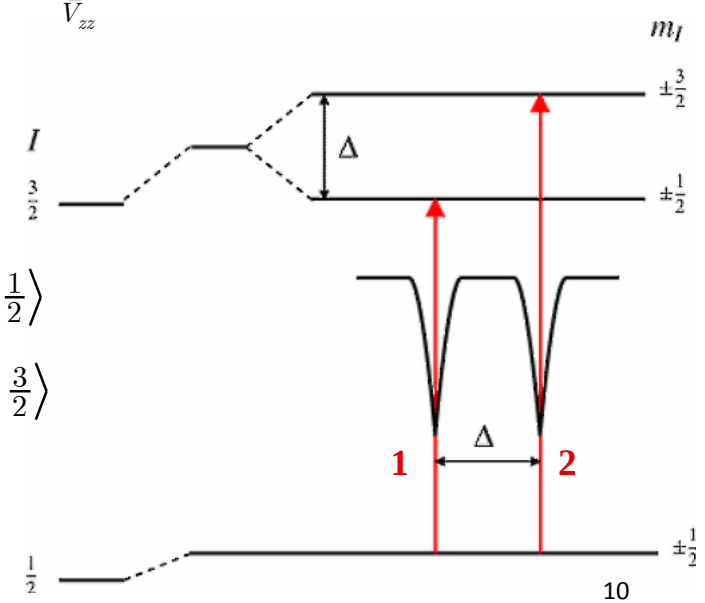
$$\eta = \frac{\vec{V}_{xx}-\vec{V}_{yy}}{\vec{V}_{zz}}$$

$\vec{V}_{ii}$ are the principal components of electric field gradient

  - splits excited state levels
    - does this remind you of something?
    - loss of cubic symmetry → ZFS
  - allowed transitions ($\Delta m_I = \pm 1$)

$$1 \Rightarrow \left|\tfrac{1}{2},+\tfrac{1}{2}\right\rangle \rightarrow \left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle \text{ and } \left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \rightarrow \left|\tfrac{3}{2},+\tfrac{1}{2}\right\rangle$$

$$2 \Rightarrow \left|\tfrac{1}{2},+\tfrac{1}{2}\right\rangle \rightarrow \left|\tfrac{3}{2},+\tfrac{3}{2}\right\rangle \text{ and } \left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \rightarrow \left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle$$

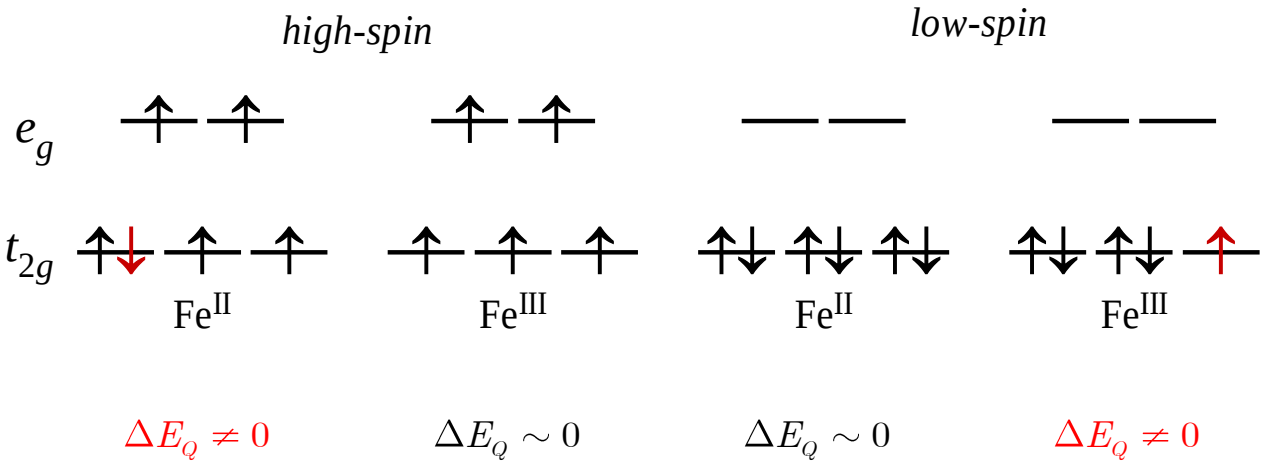


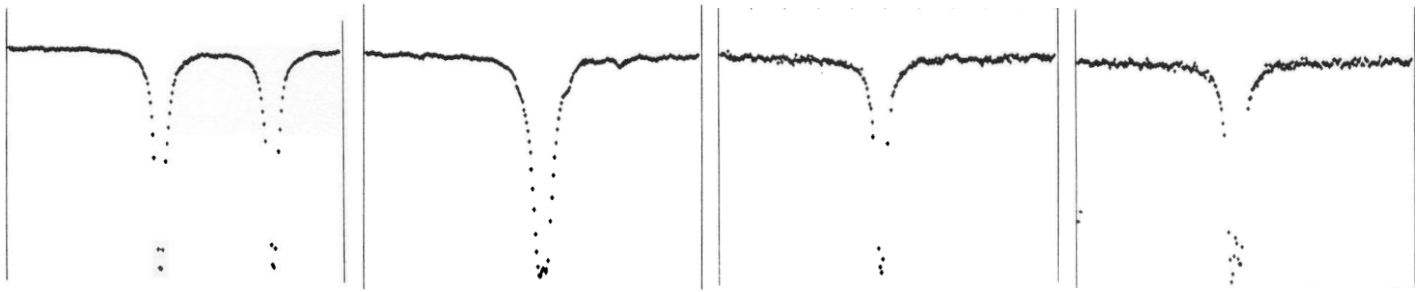
2.3 Mössbauer Spectroscopy

- if electronic distribution has cubic symmetry ($x = y = z$)
  - the nuclear quadrupole moment vanishes (*no electric field*, V, at nucleus)
  - therefore no quadrupole splitting
- therefore must have asymmetric electron distribution for quadrupolar splitting
  - asymmetry in electronic distribution also suggests that quadrupolar coupling should be anisotropic

Isotope	IS standard	Oxidation state	IS range ($mm\ s^{-1}$)	QS(QCC) range ($mm\ s^{-1}$)	
^{57}Fe	Iron metal[a]	Iron(0)	−0.2 to −0.1	0.3 to 2.6	
		Iron(II) —HS[b]	+0.6 to +1.7	1.0 to 4.5	$3d^6$
		LS	−0.2 to +0.4	0.0 to 2.0	
		Iron(III)—HS	+0.1 to +0.5	0.0 to 0.7	$3d^5$
		—LS	−0.1 to +0.5	0.0 to 1.5	
		Iron(IV)—HS	−0.2 to +0.2	0.0 to 1.0	$3d^4$
		—LS	+0.1 to +0.2	1.5 to 2.5	

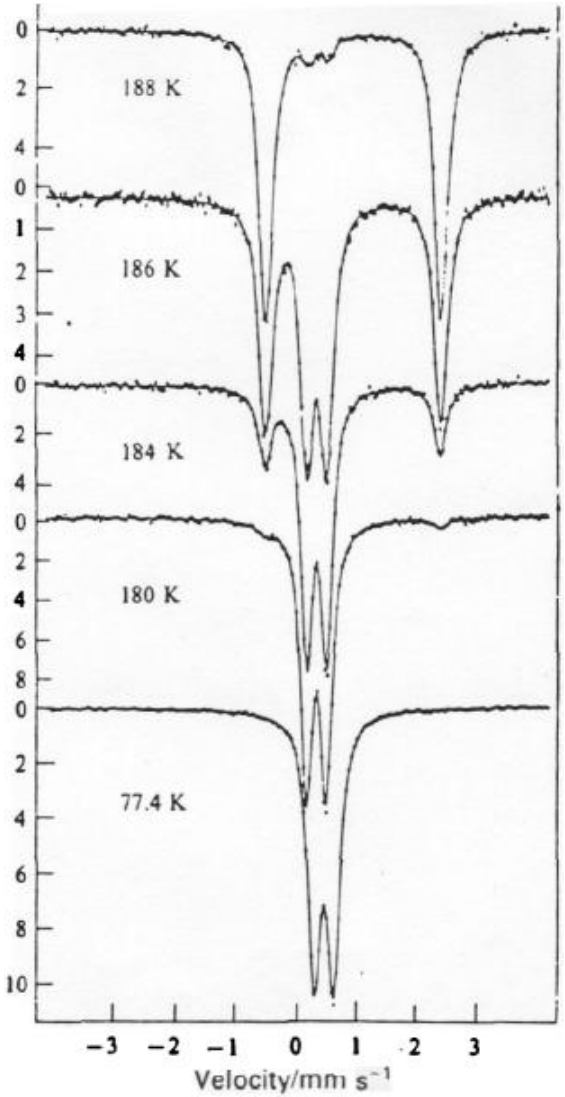
2.3 Mössbauer Spectroscopy





$FeSO_4 \cdot 7H_2O$ $Fe_2(SO_4)_3$ $K_4Fe(CN)_6 \cdot 3H_2O$ $K_3Fe(CN)_6$

2.3 Mössbauer Spectroscopy



$[\mathrm{Fe(NCS)_2(phen)_2}] \rightarrow \mathrm{HS}\ 3d^6$

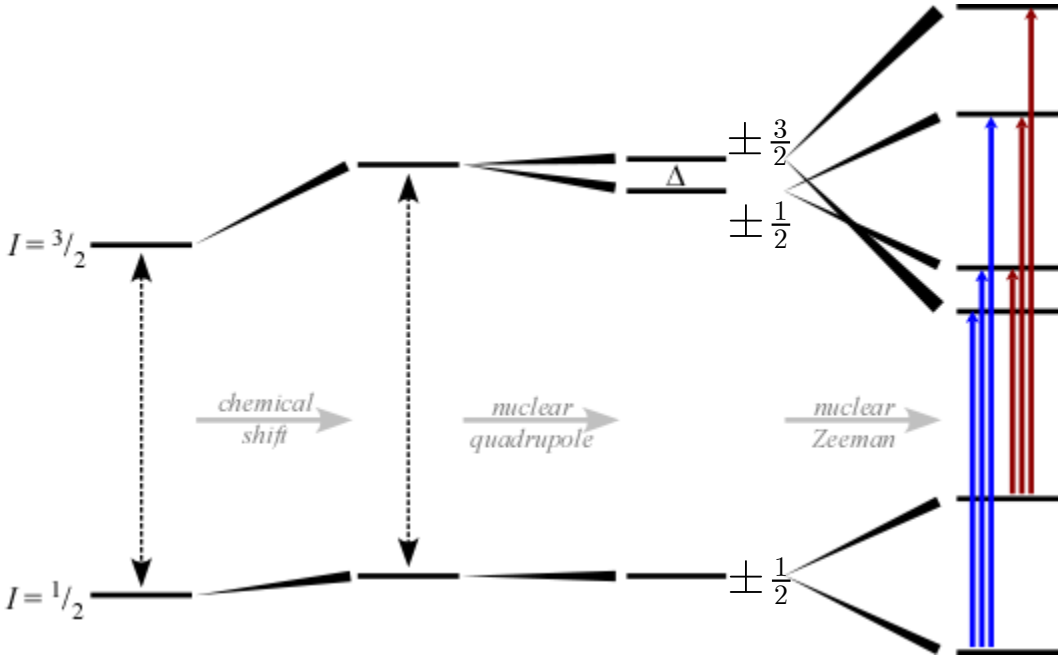
$[\mathrm{Fe(NCS)_2(phen)_2}] \rightarrow \mathrm{LS}\ 3d^6$

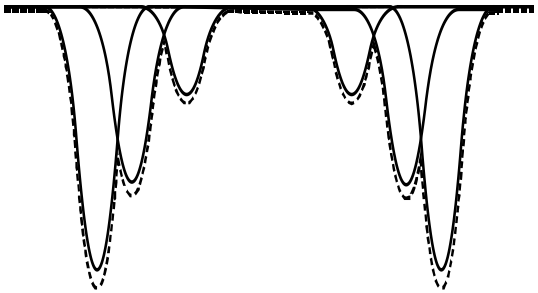
spin equilibrium system:

$T_{\Delta S} \sim 185K$

Effect of Magnetic Field on Mössbauer Spectra

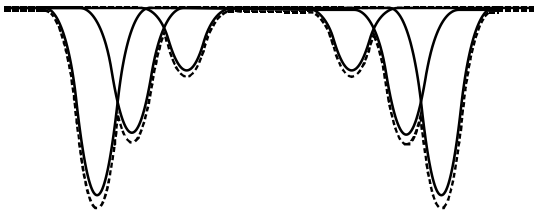
- the nuclear spin states will split - nuclear Zeeman splitting!
  - changes energy level diagram, increases number of observable transitions
  - if quadrupolar splitting can occur → anisotropy in the magnetic Mössbauer
  - if there is an electronic spin as well → hyperfine coupling as well





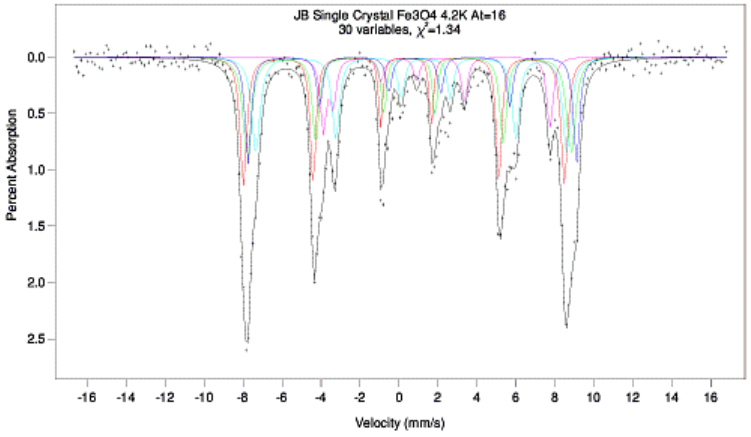
intensity pattern is 3:2:1:1:2:3
for powder samples

2.3 Mössbauer Spectroscopy

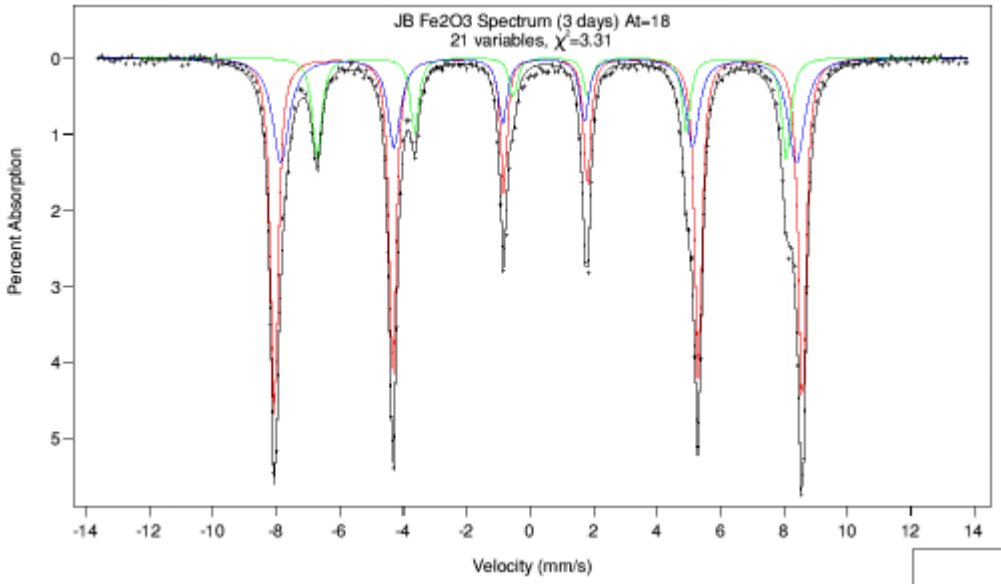


intensity pattern is 3:2:1:1:2:3 for powder samples

m_2	$-m_1$	m	C^2	Θ
+3/2	+1/2	1	3	$1 + \cos 2\Theta$
+1/2	+1/2	0	2	$2 \sin 2\Theta$
-1/2	+1/2	-1	1	$1 + \cos 2\Theta$
-3/2	+1/2	-2	0	0
+3/2	-1/2	2	0	0
+1/2	-1/2	1	1	$1 + \cos 2\Theta$
-1/2	-1/2	0	2	$2 \sin 2\Theta$
-3/2	-1/2	-1	3	$1 + \cos 2\Theta$

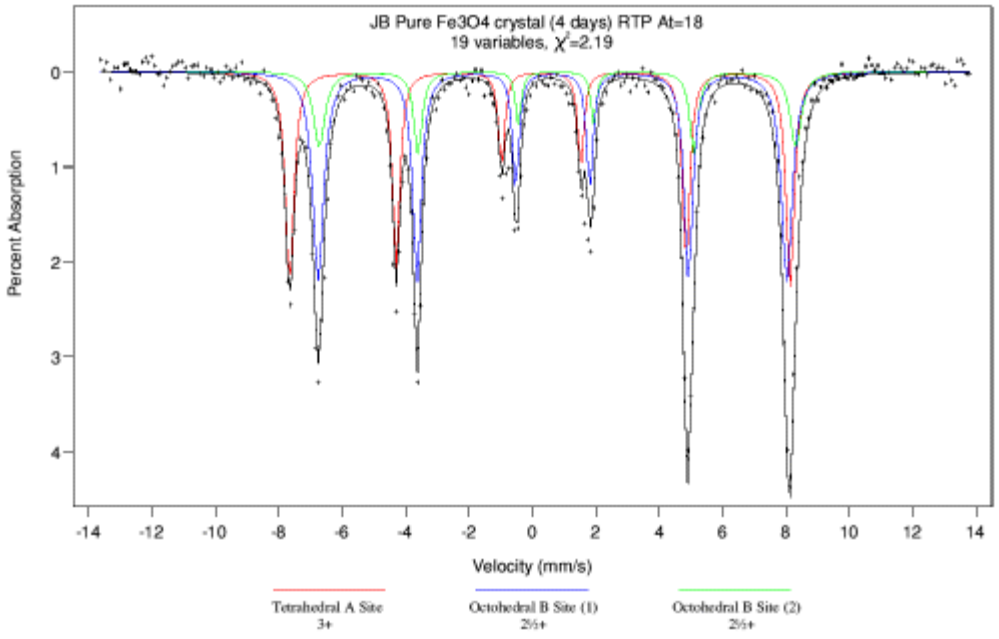


2.3 Mössbauer Spectroscopy



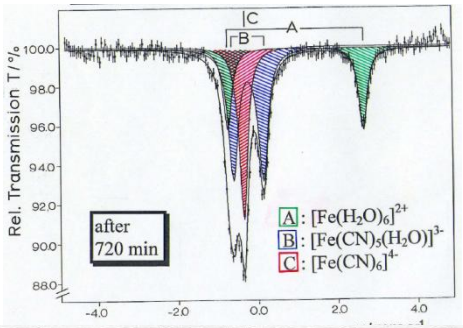
Fe_2O_3

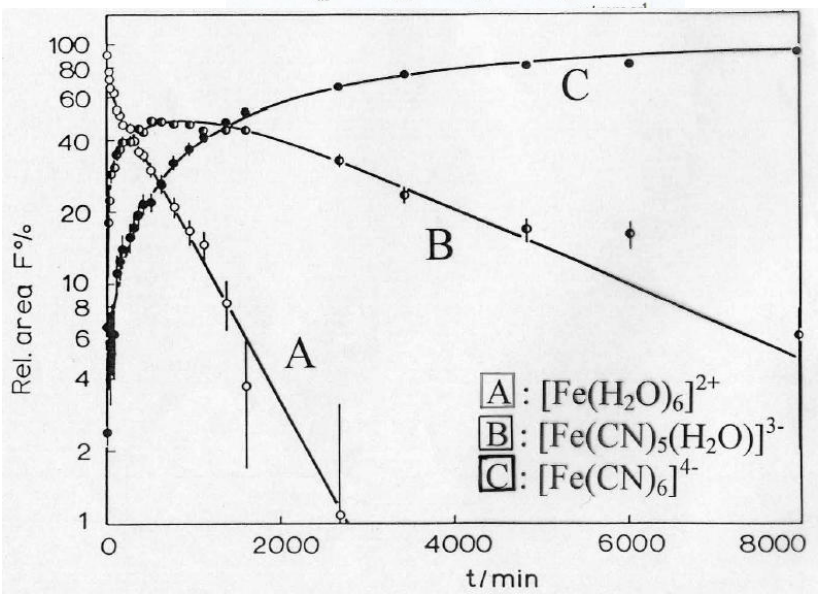
Fe_3O_4

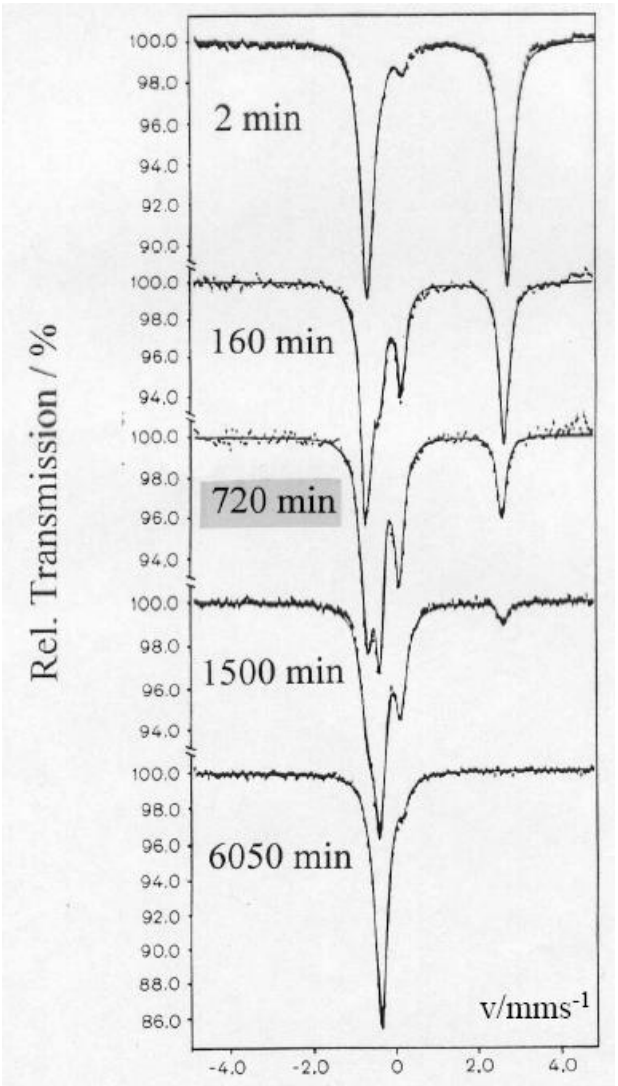


Following ligand exchange reactions

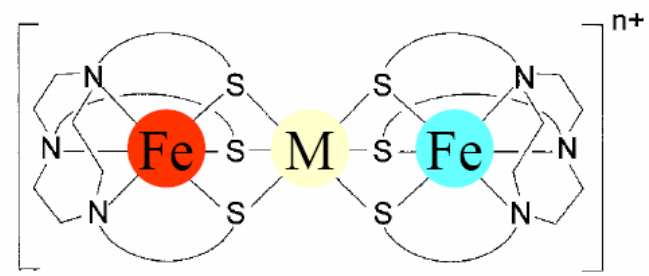
- $FeSO_4 \cdot 7H_2O$ + 6KCN (at 5degC)





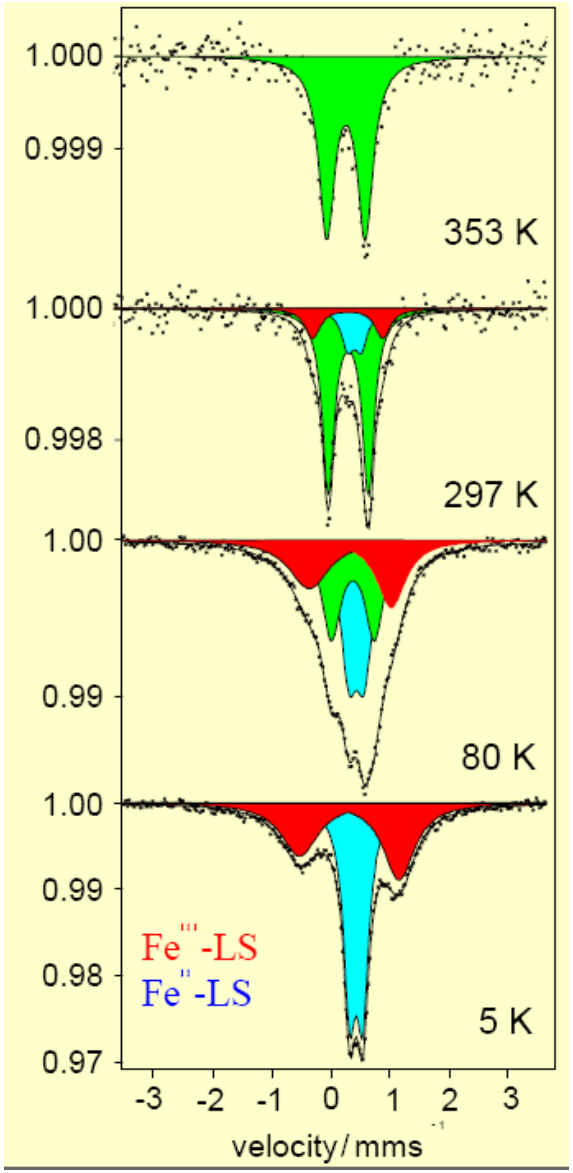


Valence fluctuations in mixed-valence complexes…



$[LFe^{III}Co^{III}Fe^{II}L]^{2+}$

$k \sim 10^7\ s^{-1}$



Overall View of Mössbauer Spectroscopy