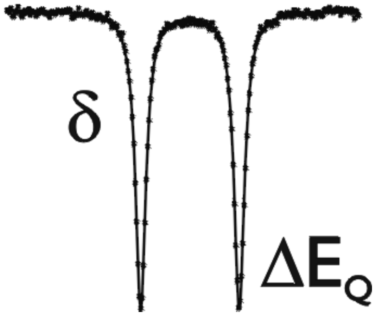
5th Penn State Bioinorganic Workshop
June 1 – 6, 2018

Mössbauer Spectroscopy



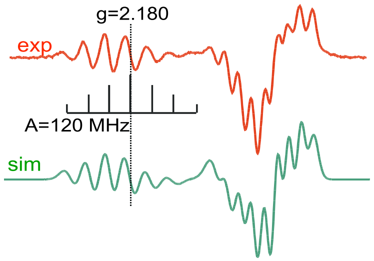
Eckhard Bill

Max Planck Institute for
Chemical Energy Conversion
Mülheim /Ruhr

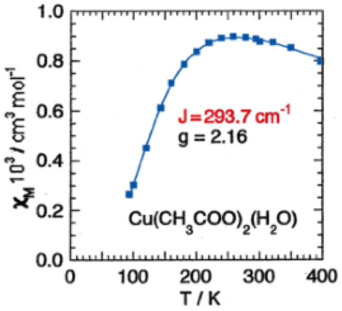
ebill@ gwdg.de

Inorganic Spectroscopy Toolbox

Electron-Paramagnetic Resonance (EPR)



Magnetic Suceptibility



Ligand field theory

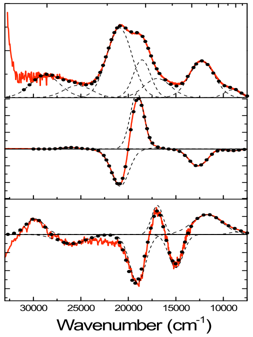
Spin Hamiltonian

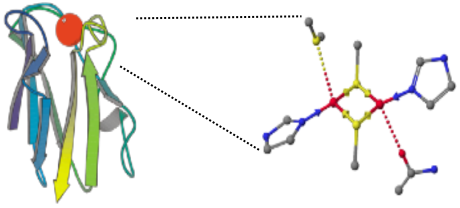
Quantum Chemistry

⇕

Structure/Function

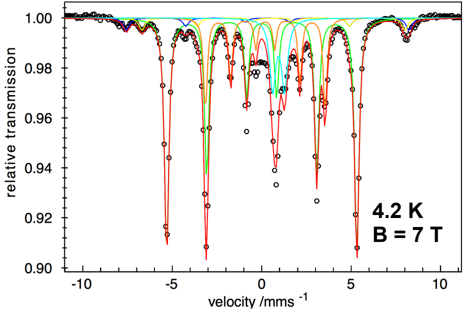
Magnetic Circular Dichromism (MCD)





IR, Raman, …

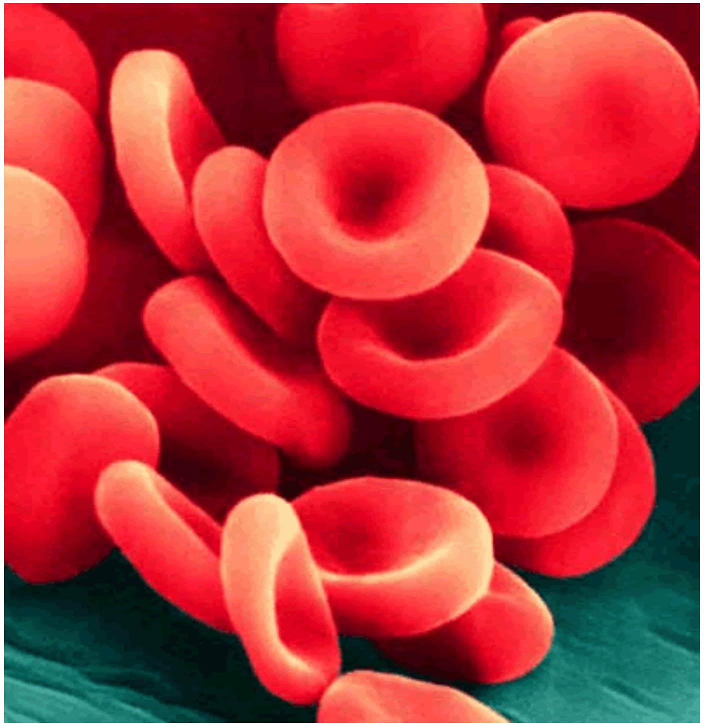
^{57}Fe- Mössbauer Spectroscopy

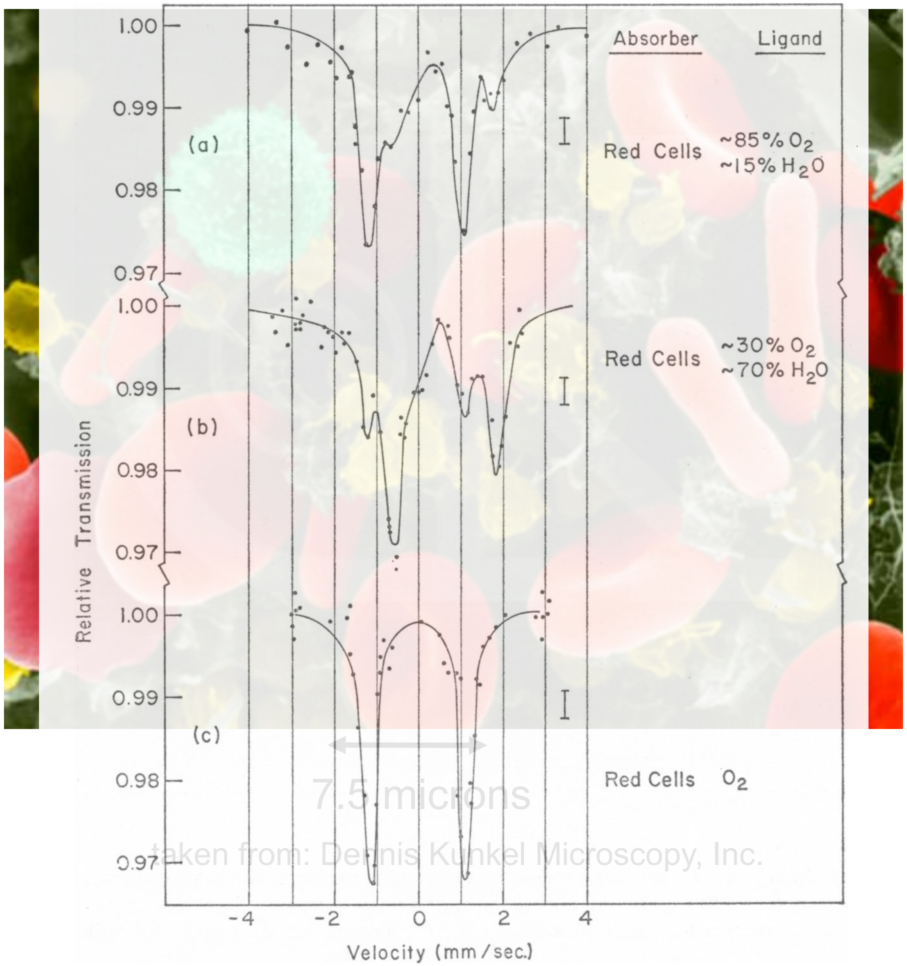


=> X-ray spectroscopy

Mössbauer Spectroscopy and Iron …

Hemoglobin / Myoglobin





7.5 microns

taken from: Dennis Kunkel Microscopy, Inc.

MOSSBAUER EFFECT IN HEMOGLOBIN AND SOME IRON-CONTAINING BIOLOGICAL COMPOUNDS

U. Gonser, R. W. Grant, Biophys. J. (1965)

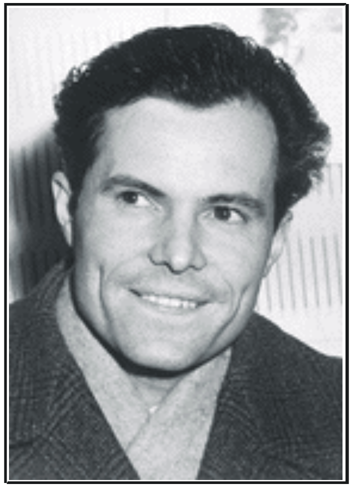
“Recoilless Nuclear Resonance Absorption of γ- Radiation”

or

Mössbauer Spectroscopy

named after

Rudolf Ludwig Mößbauer,
(January 31, 1929 -
September 14, 2011)



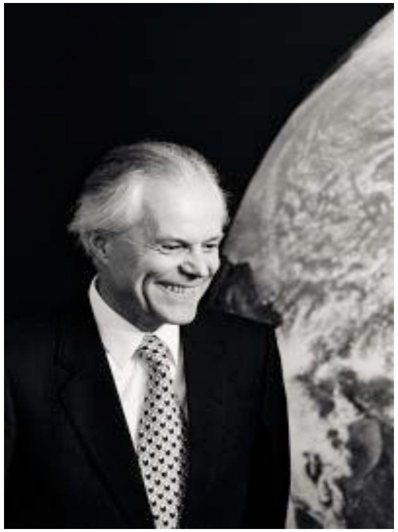


Foto: REGIERUNGonline
Rudolf Mößbauer

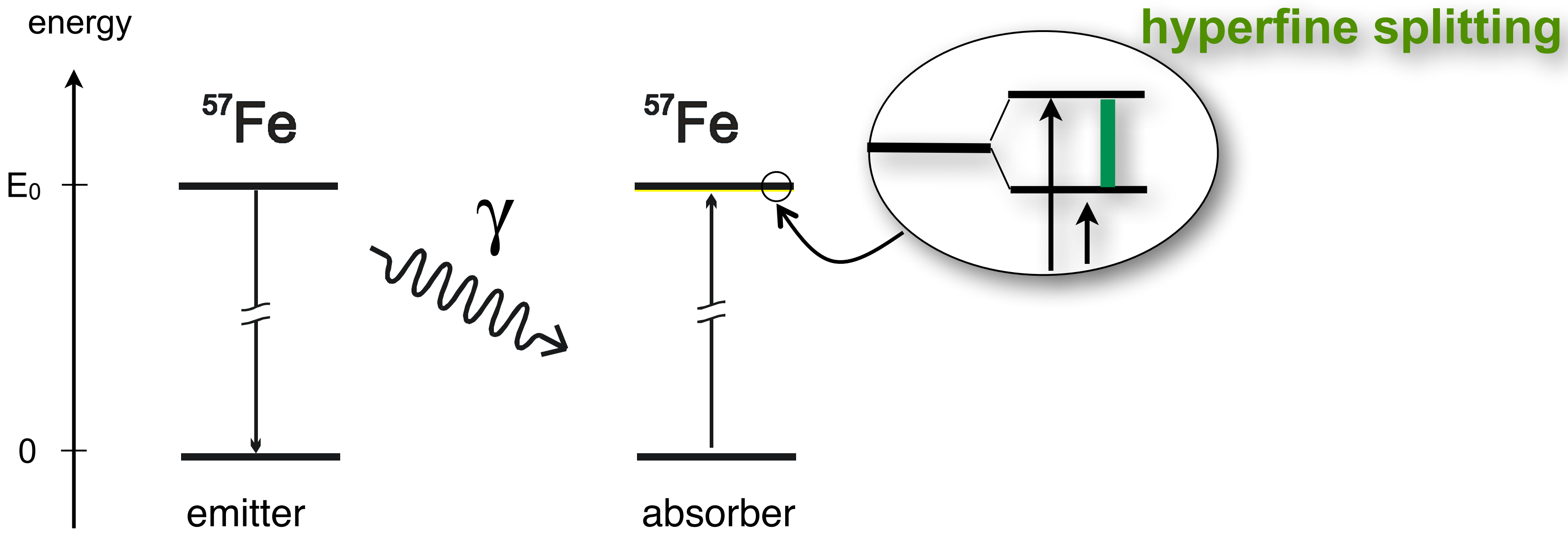
1955-1958: PhD study TU Munich (Prof. Maier-Leibnitz)

1958: first report in: *Zeitschrift für Physik* **1958**, *151*, 124

☞ Naturwissenschaften, **1958**, 22, 538

1961: **Nobel-Prize in Physics** (together with R. Hofstadter)

Nuclear γ-Resonance

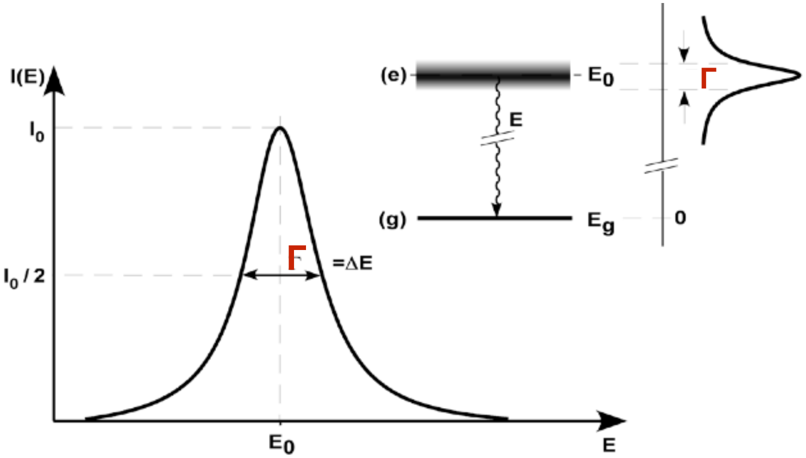


Nuclear energy levels are extremely sharp !

⇒ Measurements of Hyperfine Interaction

All following explanations and examples are given for the most important Mössbauer nuclide ^{57}Fe.

Narrow Natural Line Widths



Lorentzian

Finite lifetime of the excited state:

$$\Gamma \cdot \tau \geq \hbar$$

nuclear mean lifetime, $\tau = t_{1/2} / \ln 2$

line width

^{57}Fe:

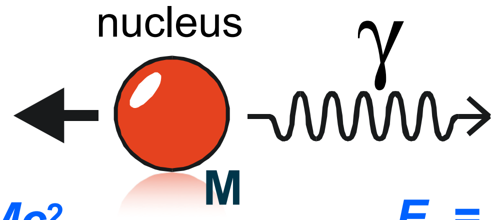
E_0 = 14.4 keV

τ = 143 ns

Γ = 4.6 neV

Problem:

Recoil Prohobits γ-Resonance in 'Free' Atoms



recoil energy: $E_R = E_0^2 / 2Mc^2$

$E_\gamma = E_{nuc} - E_R$

^{57}Fe:

$E_0 = 14.4$ keV

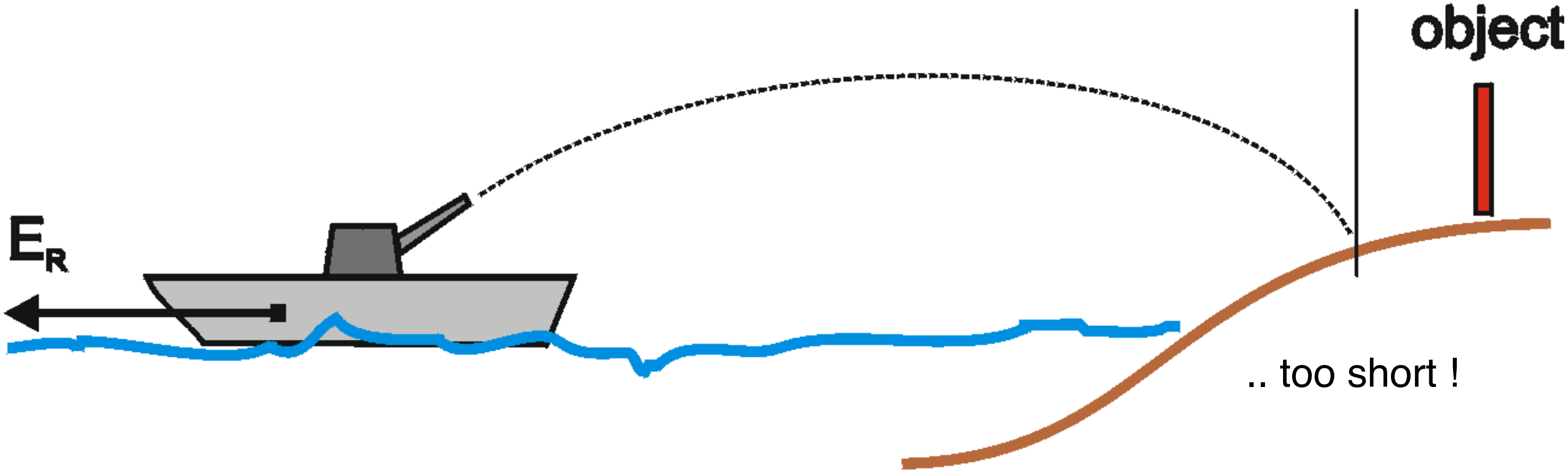
$\Gamma = 4.6$ neV (width)

$E_R = 2$ meV

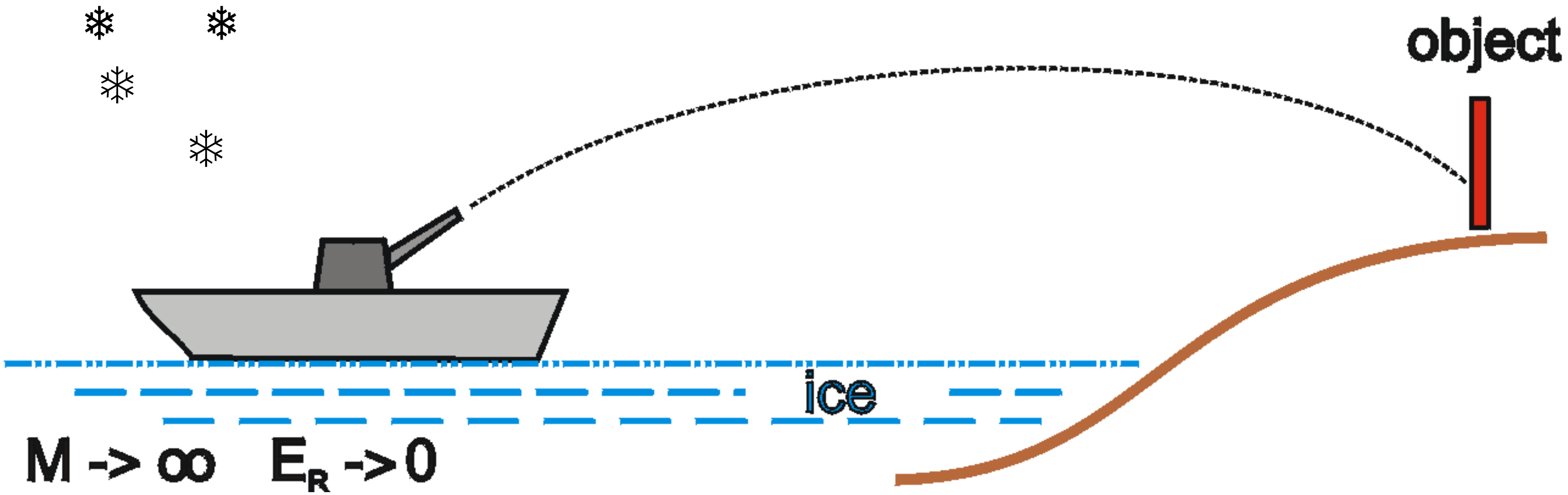
High-energy photons cannot be re-absorbed !

=> Nuclear γ-Resonance cannot be observed with gases and liquids !

Recoil in ‚free‘ atoms

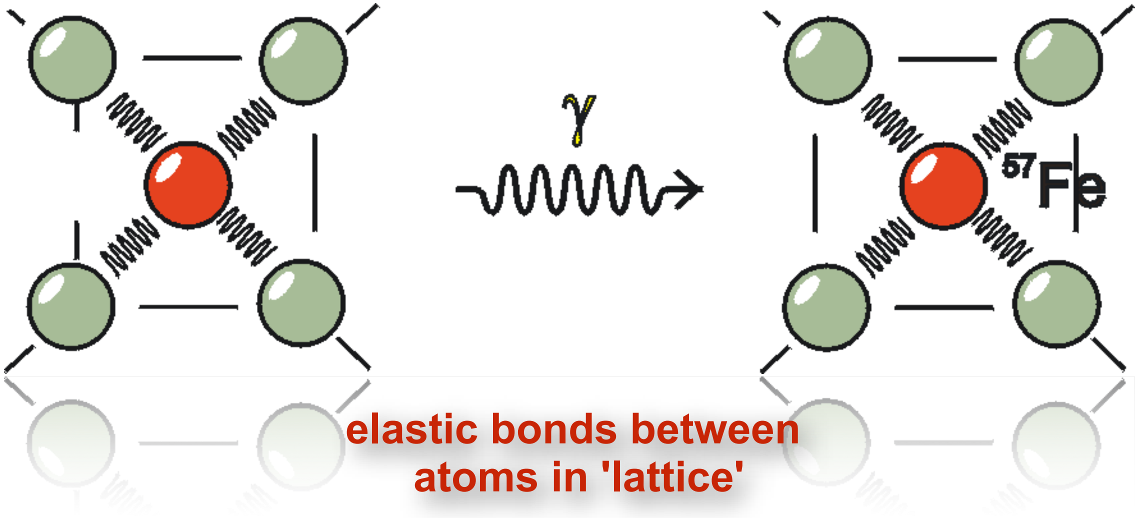


no recoil in solid material



$M \to \infty$ $E_R \to 0$

Recoilless Emission and Absorption of γ-rays in Solid State



elastic bonds between atoms in 'lattice'

mass is huge; **$M \to \infty$** ⇒ .. **no Recoil !**

proper theory: finite probability for **$E_R = 0$** (Mössbauer Effect)

⟶ ***f*** **- factor** (Debye-Waller / Lamb-Mössbauer factor)

Lamb-Mössbauer / Debye-Waller Factor

(Mössbauer Intensity)

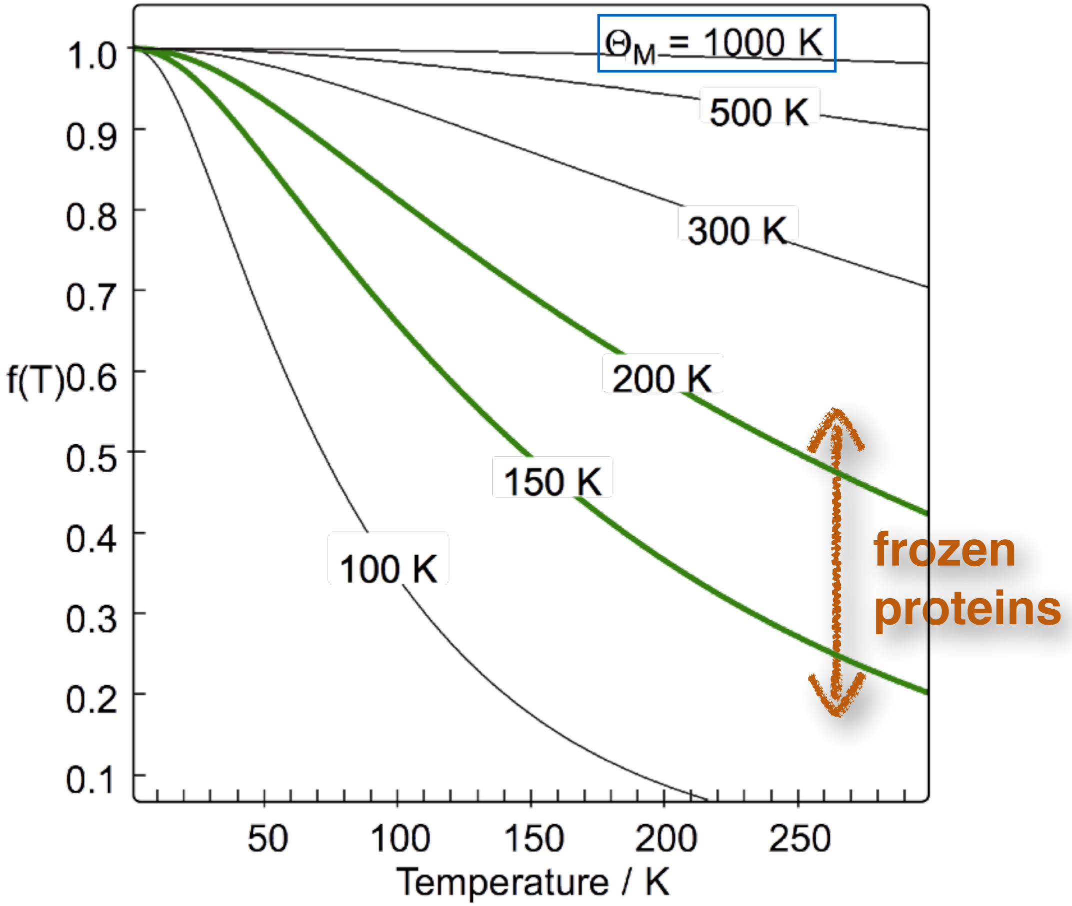
$$\boxed{f = \exp\left[- \langle x^2 \rangle E_\gamma^2 / (\hbar c)^2\right]}$$

mean-square-displacement

Debye model:

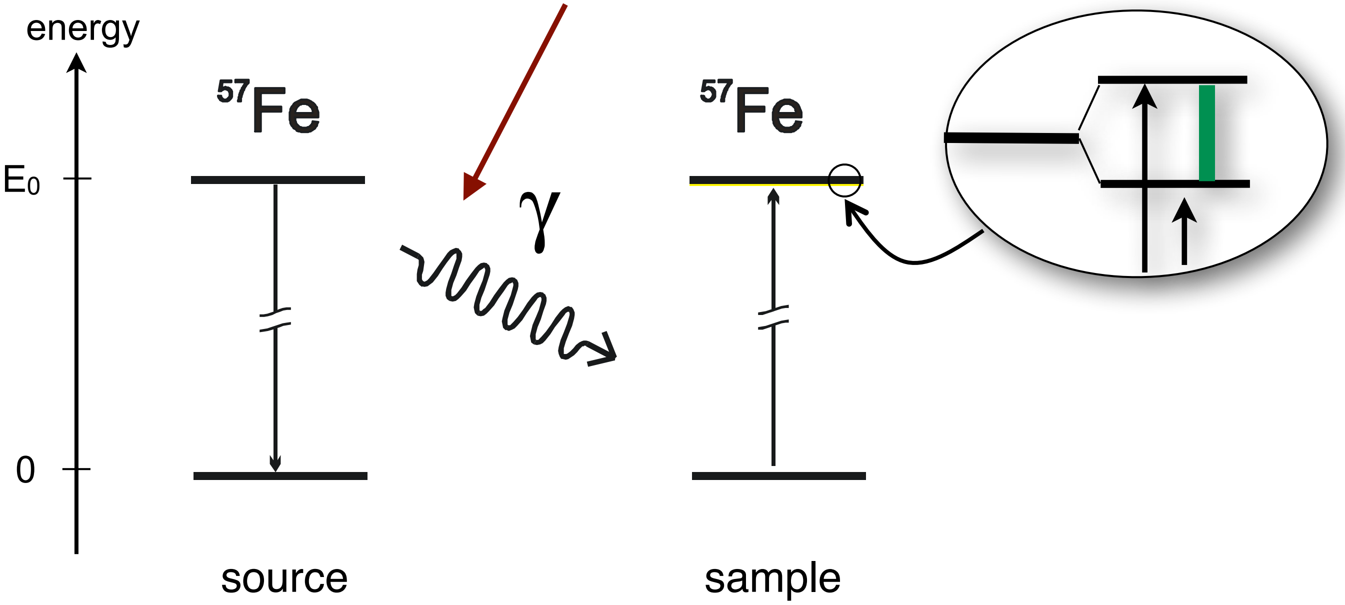
$$f(T) = \exp\left[\frac{-3E_\lambda^2}{k_B \Theta_D M c^2}\left\{\frac{1}{4} + \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\Theta/T} \frac{x}{e^x - 1}\,dx\right\}\right]$$

Θ_M: Debye Temperature

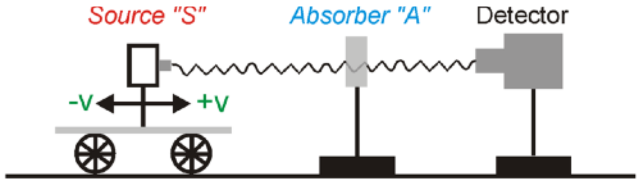


... how to do Mössbauer spectroscopy (i.e. sweep the energy) ??

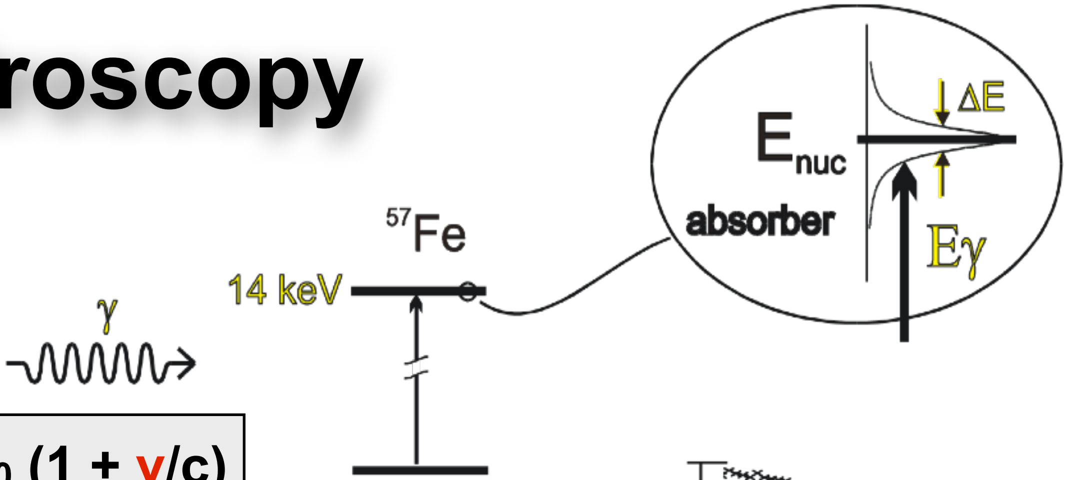
monochromatic light



⇒ manipulate photons during emission by Doppler Effect !!



Spectroscopy

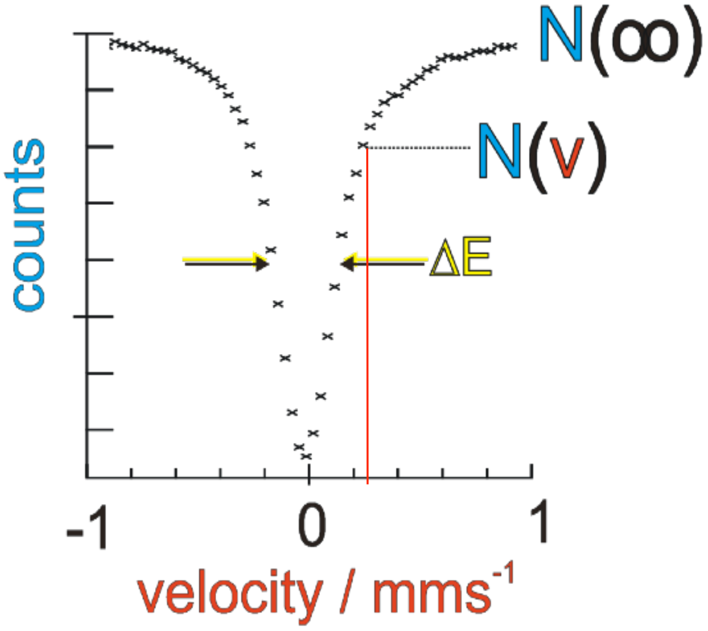


$$E_\gamma = E_0 \, (1 + v/c)$$

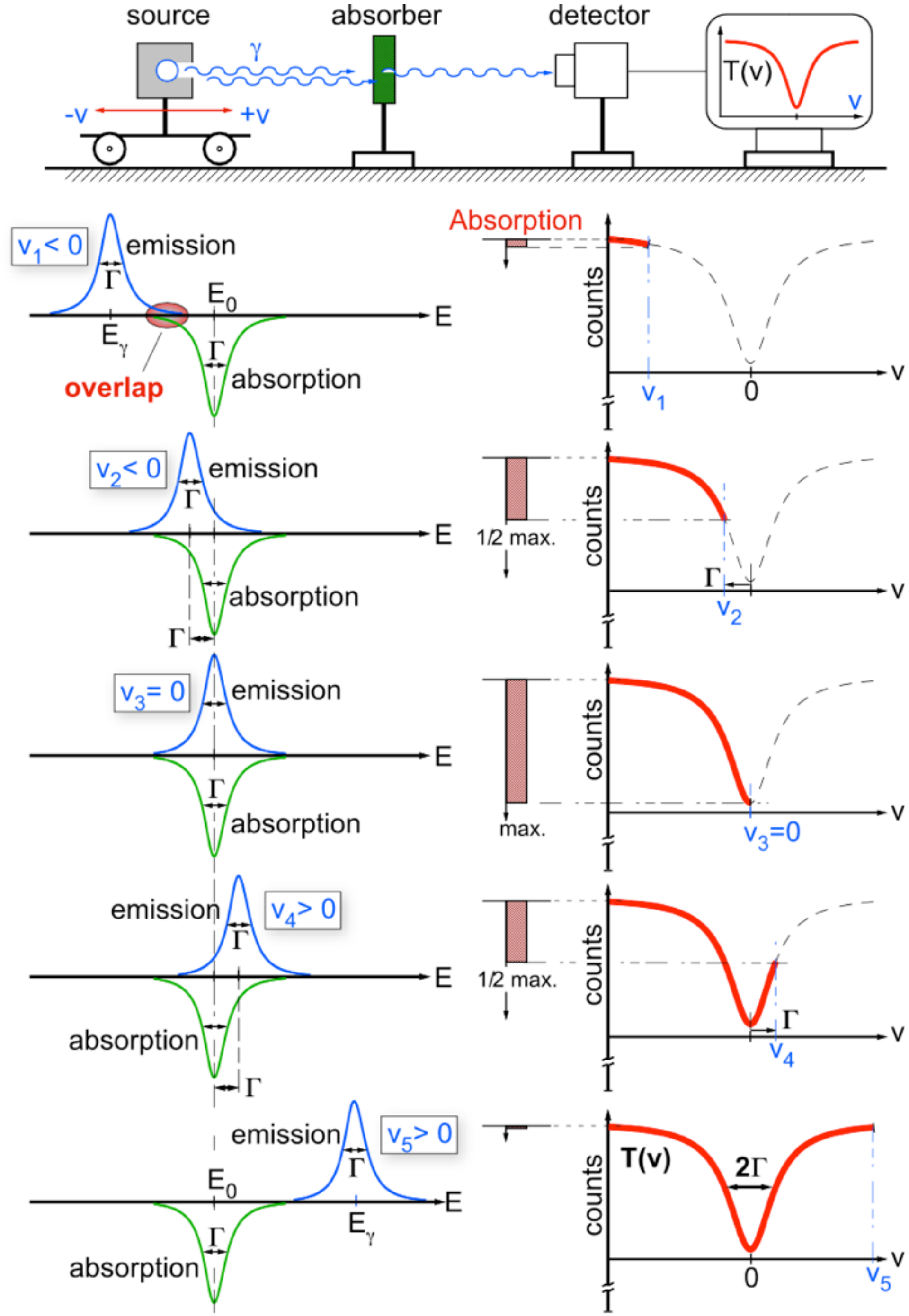
energy modulation

by Doppler effect

Christian Andreas Doppler (1803-1853)



The Mössbauer Experiment



Spectrum of a so-called *thin absorber:*

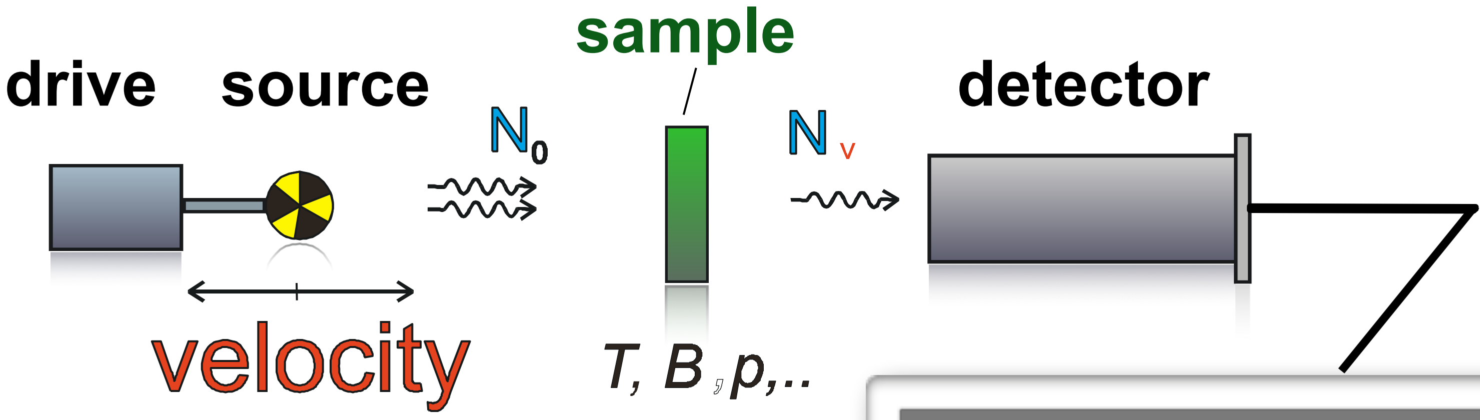
Lorentzian with Γ_{exp} **= 2Γ** (full-width at half maximum, fwhm, is twice the natural line width of emission and absorption)

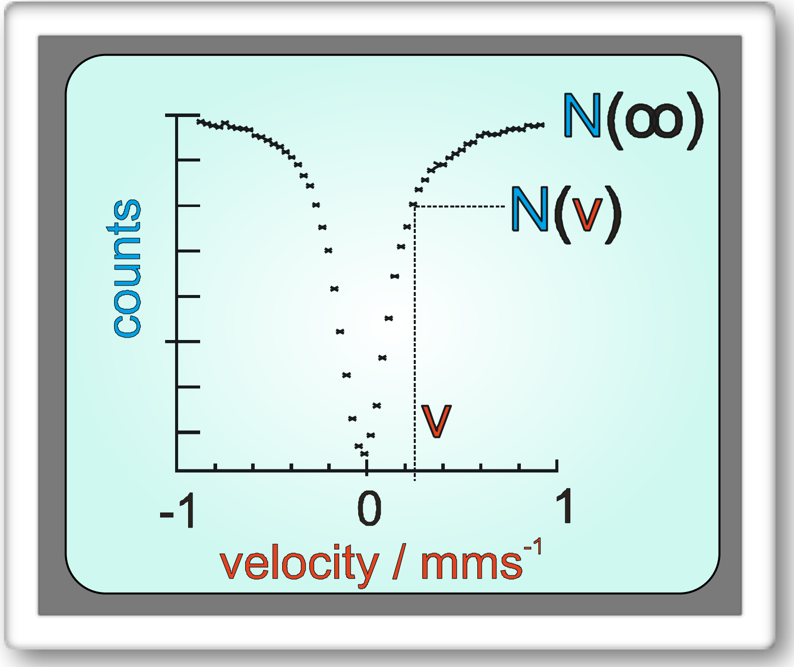
Counts in spectrum:

$$\boxed{\frac{C(\infty)-C(v)}{C(\infty)} = f_s \frac{t}{2} \frac{\Gamma^2}{\left[E_0(v/c)-\Delta E\right]^2+\Gamma^2}}$$

Lamb-Mößbauer factor f_S and effective thickness t, see later

The Mössbauer Spectrometer





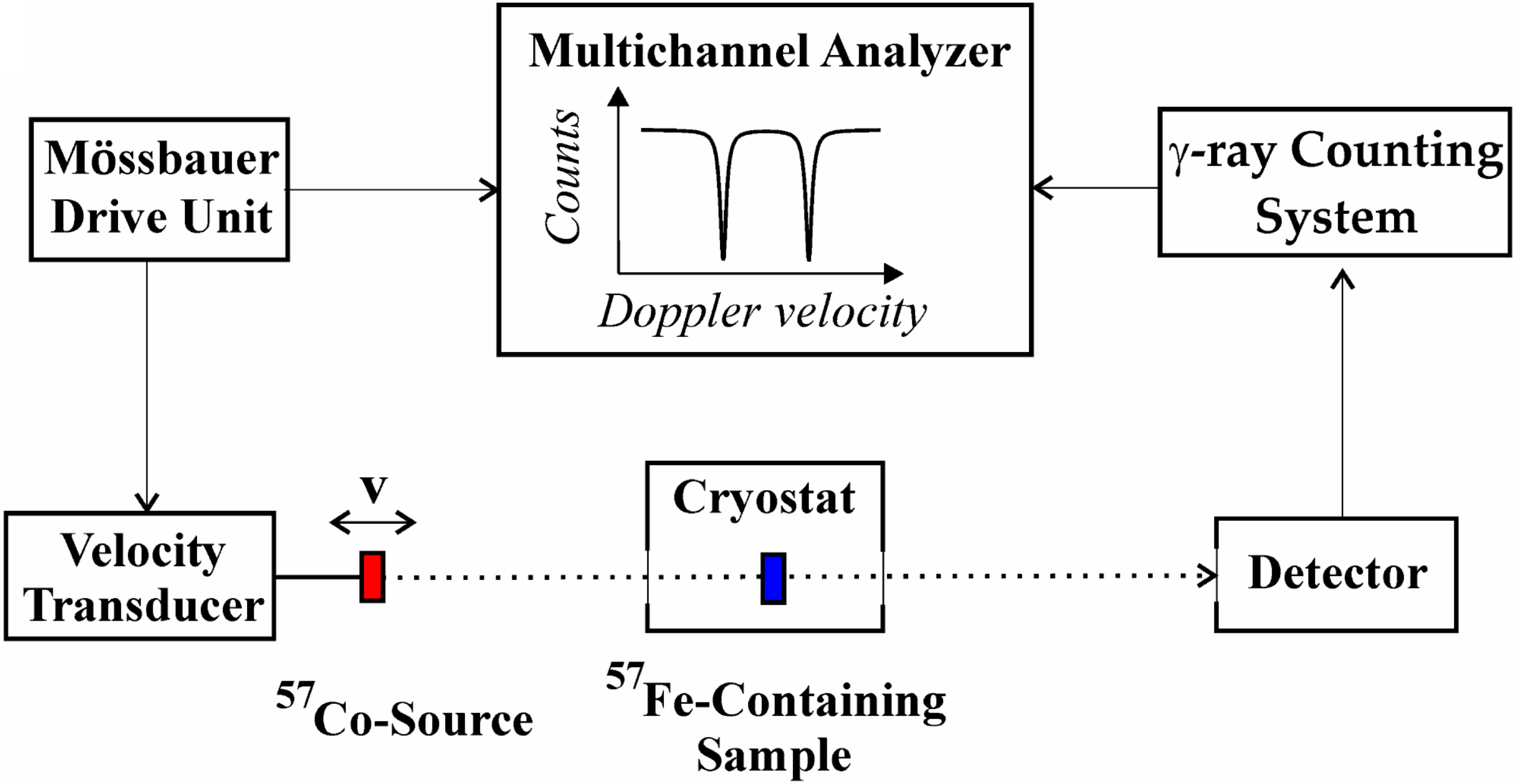
(^{57}Fe: 1 mm s^{-1} = $4.8*10^{-8}$ eV)

= 11.6 MHz

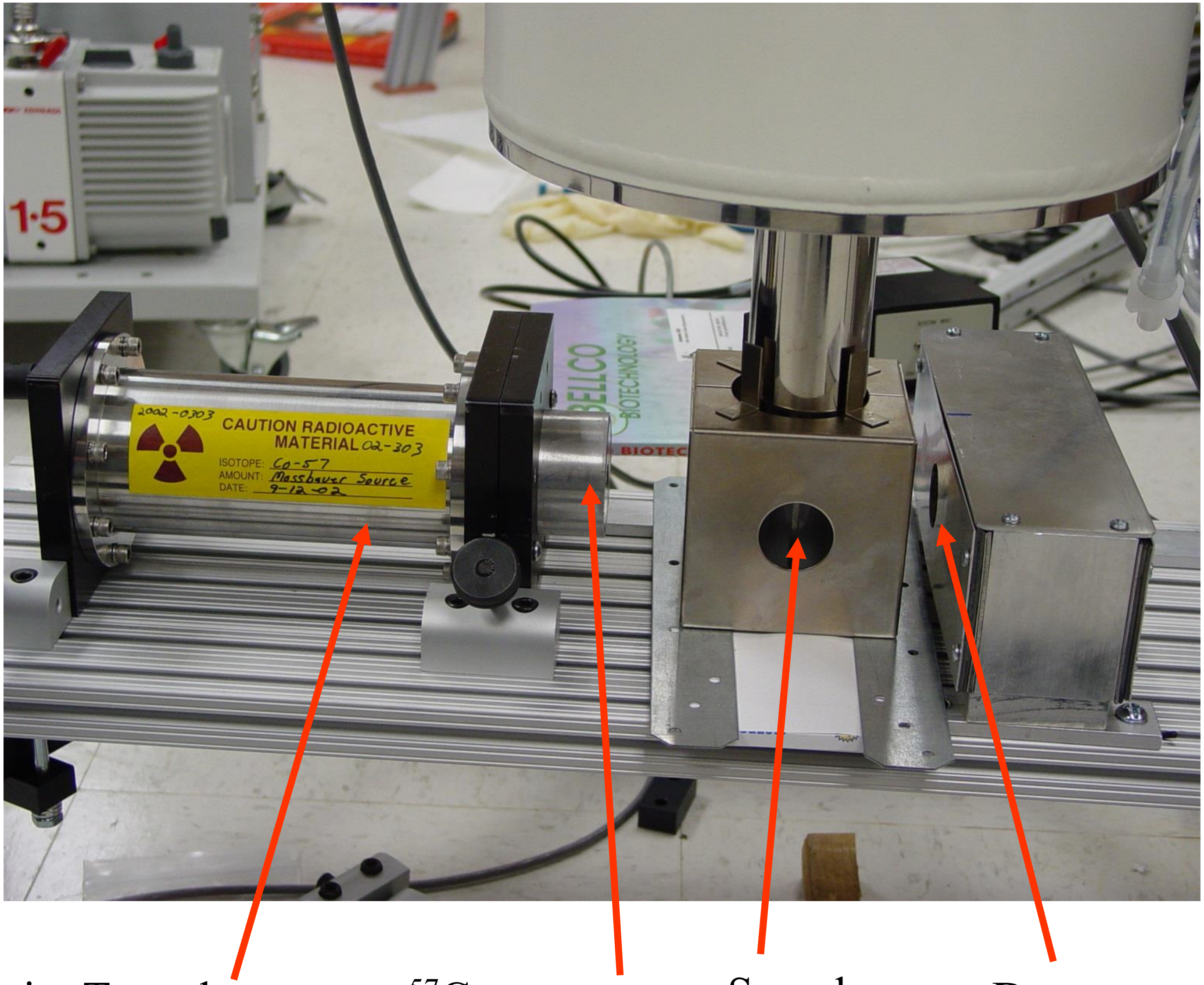
= $3.9 \cdot 10^{-4}$ cm^{-1}

≙ 5.6 K

Experimental Setup

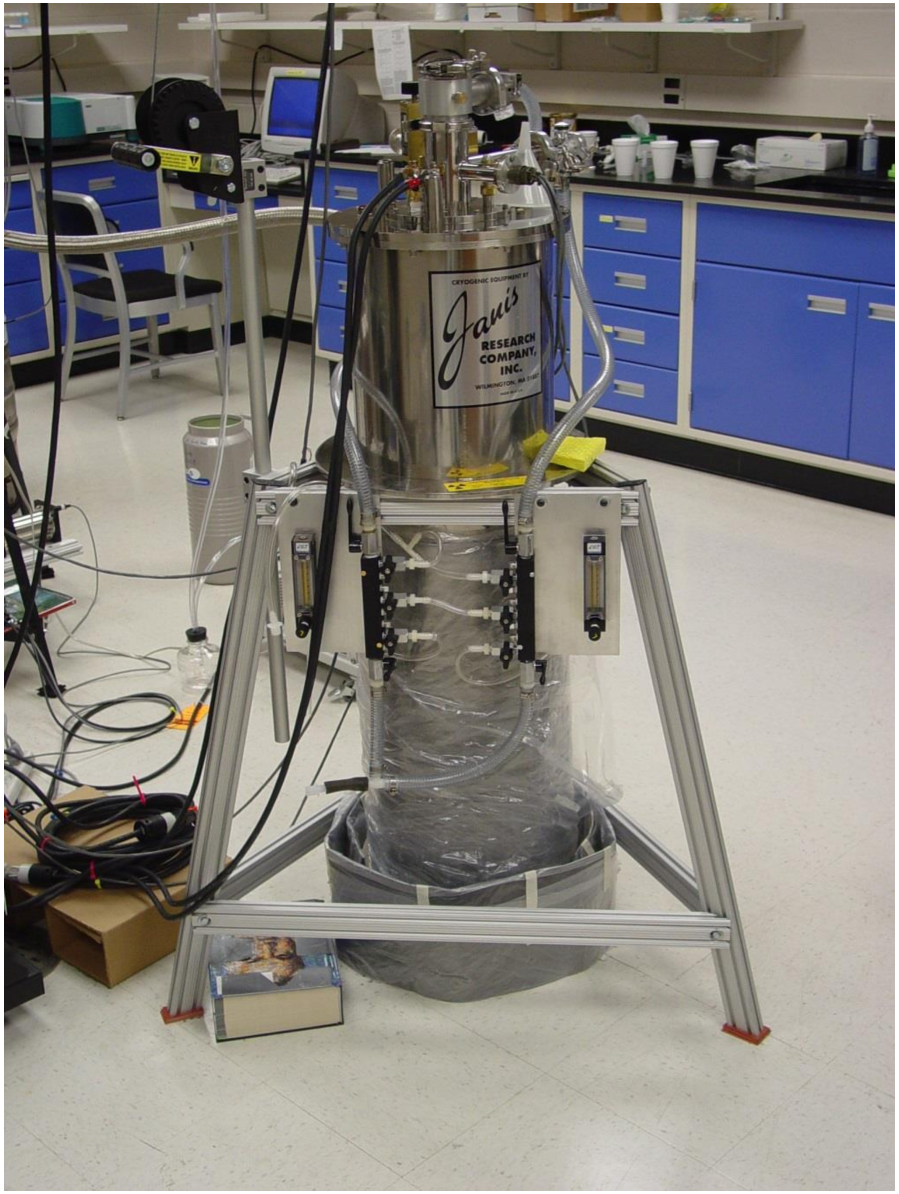


Spectrometer with Cryostat (low magnetic field possible)

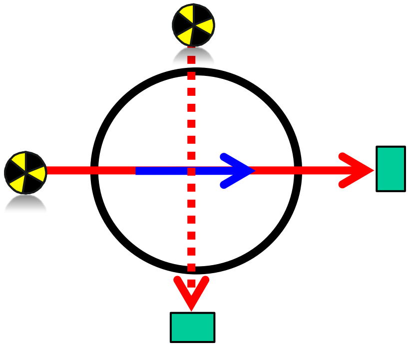


Velocity Transducer ^{57}Co source Sample Detector

High-Field Mössbauer spectrometer

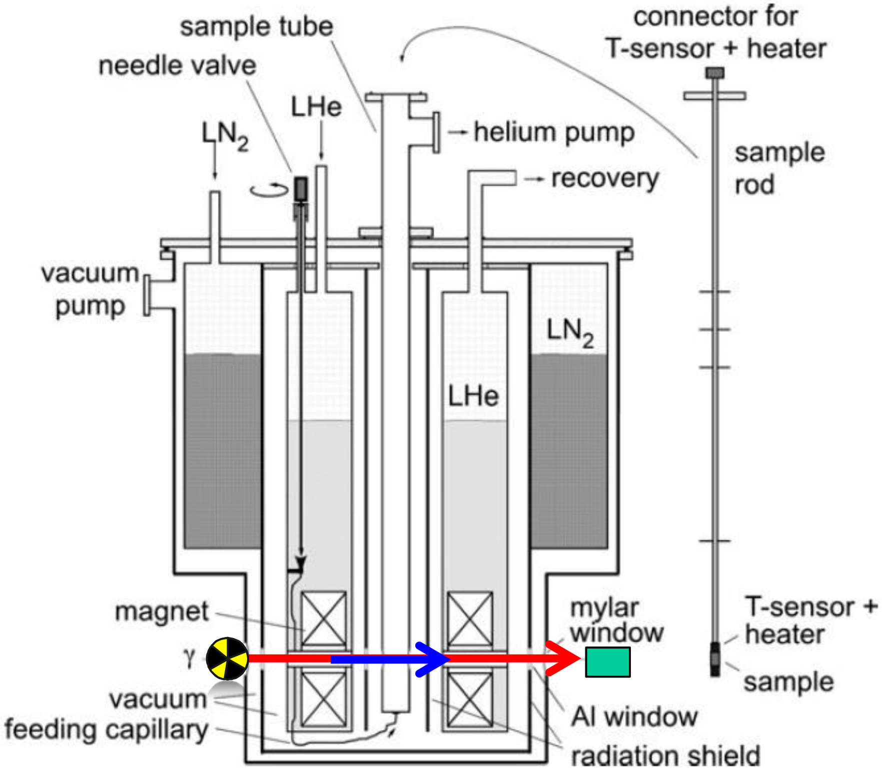


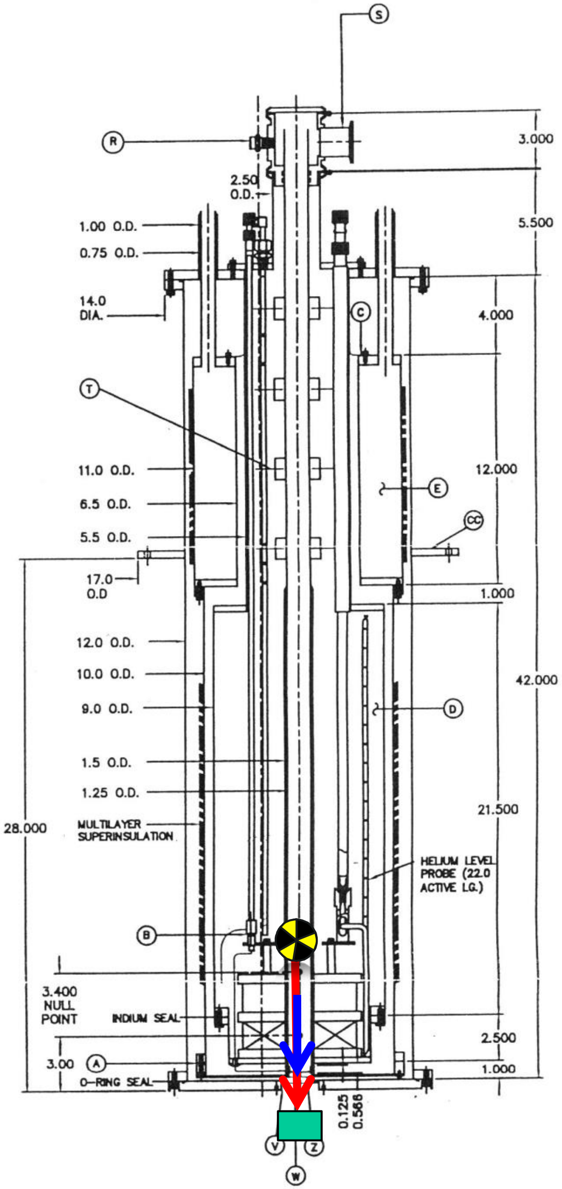
High-Field Mössbauer spectrometer



Magnetic field

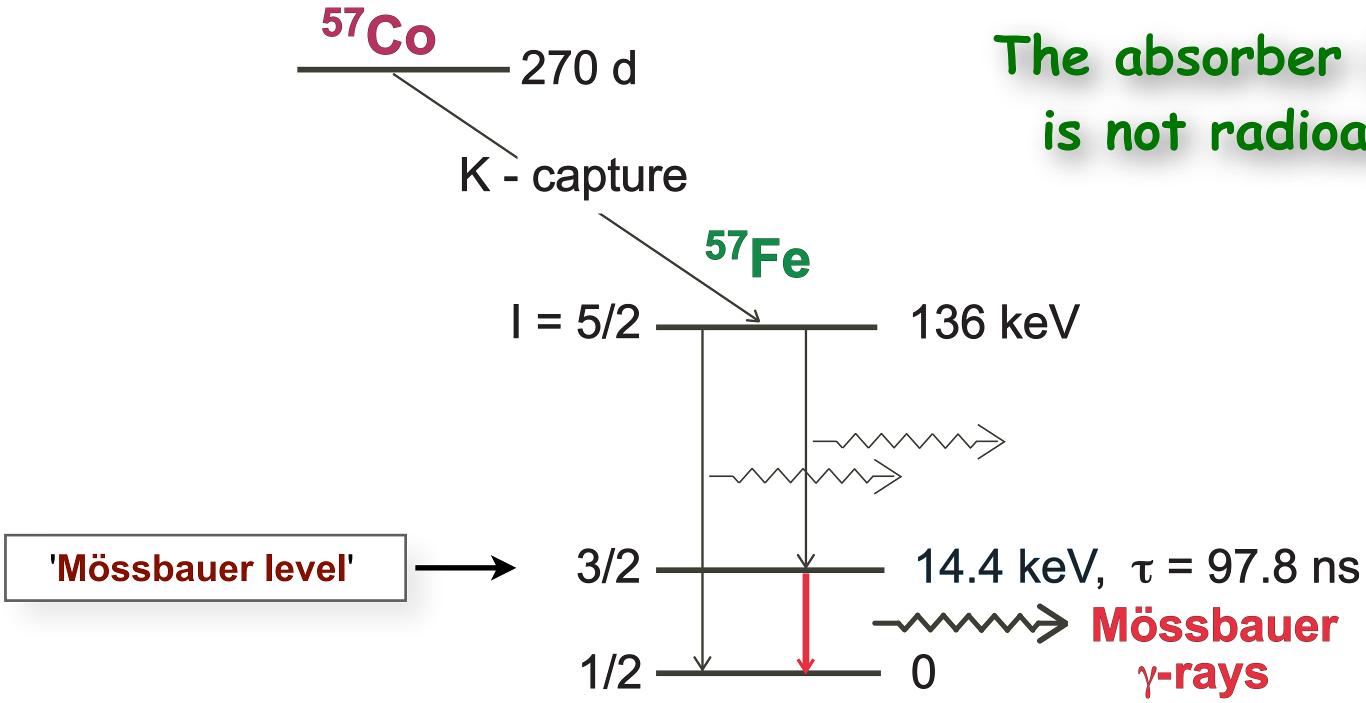
γ-beam





The Mössbauer γ-Source

The absorber (sample) is not radioactive !



^{57}Co

270 d

K - capture

^{57}Fe

I = 5/2 — 136 keV

3/2 — 14.4 keV, τ = 97.8 ns

1/2 — 0

'Mössbauer level' →

Mössbauer γ-rays

⇒ detector electronics needed to reject ‚non-resonant‘ pulses

What makes up a good Mössbauer Isotope ?

- **low energy of the Mössbauer level**
  suitable range: 5 keV $\leq E_\gamma \leq$ 180 keV
  $\leq$ 5 keV: non-resonance absorption dominates
  $\geq$ 180 keV: recoil energy $E_R = E_\gamma^2/2mc^2$ too large

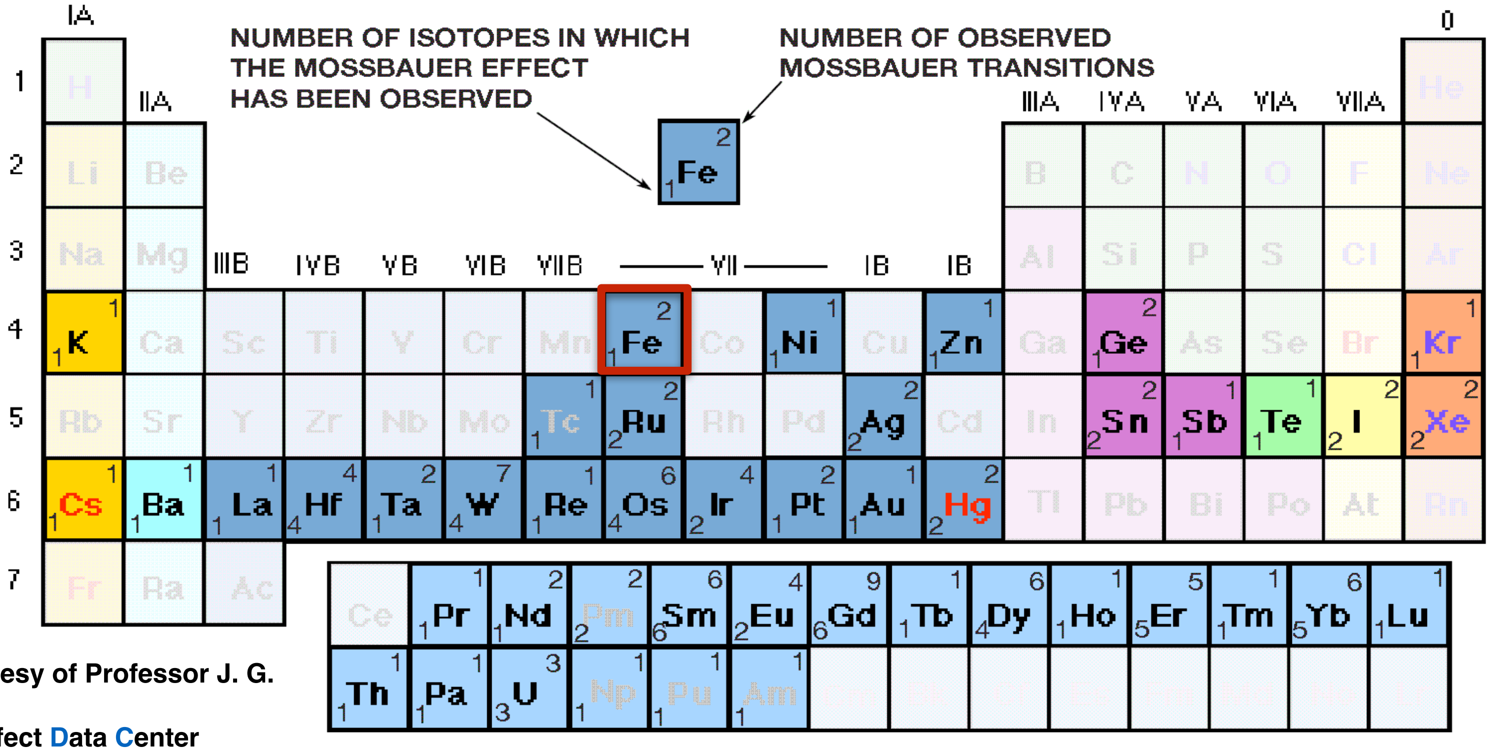
- **long life time** (sharp lines)

- reasonable **source** available

- suitable **nuclear spin** states

- strong **hyperfine coupling** constants

Mössbauer Active Elements



	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII			IB	IB	IIIA	IVA	VA	VIA	VIIA	0
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	${}_{1}\mathrm{K}^{1}$	Ca	Sc	Ti	V	Cr	Mn	${}_{1}\mathrm{Fe}^{2}$	Co	${}_{1}\mathrm{Ni}^{1}$	Cu	${}_{1}\mathrm{Zn}^{1}$	Ga	${}_{1}\mathrm{Ge}^{2}$	As	Se	Br	${}_{1}\mathrm{Kr}^{1}$
5	Rb	Sr	Y	Zr	Nb	Mo	${}_{1}\mathrm{Tc}^{1}$	${}_{2}\mathrm{Ru}^{2}$	Rh	Pd	${}_{2}\mathrm{Ag}^{2}$	Cd	In	${}_{2}\mathrm{Sn}^{2}$	${}_{1}\mathrm{Sb}^{1}$	${}_{1}\mathrm{Te}^{1}$	${}_{2}\mathrm{I}^{2}$	${}_{2}\mathrm{Xe}^{2}$
6	${}_{1}\mathrm{Cs}^{1}$	${}_{1}\mathrm{Ba}^{1}$	${}_{1}\mathrm{La}^{1}$	${}_{4}\mathrm{Hf}^{4}$	${}_{1}\mathrm{Ta}^{2}$	${}_{4}\mathrm{W}^{7}$	${}_{1}\mathrm{Re}^{1}$	${}_{4}\mathrm{Os}^{6}$	${}_{2}\mathrm{Ir}^{4}$	${}_{1}\mathrm{Pt}^{2}$	${}_{1}\mathrm{Au}^{1}$	${}_{2}\mathrm{Hg}^{2}$	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac															

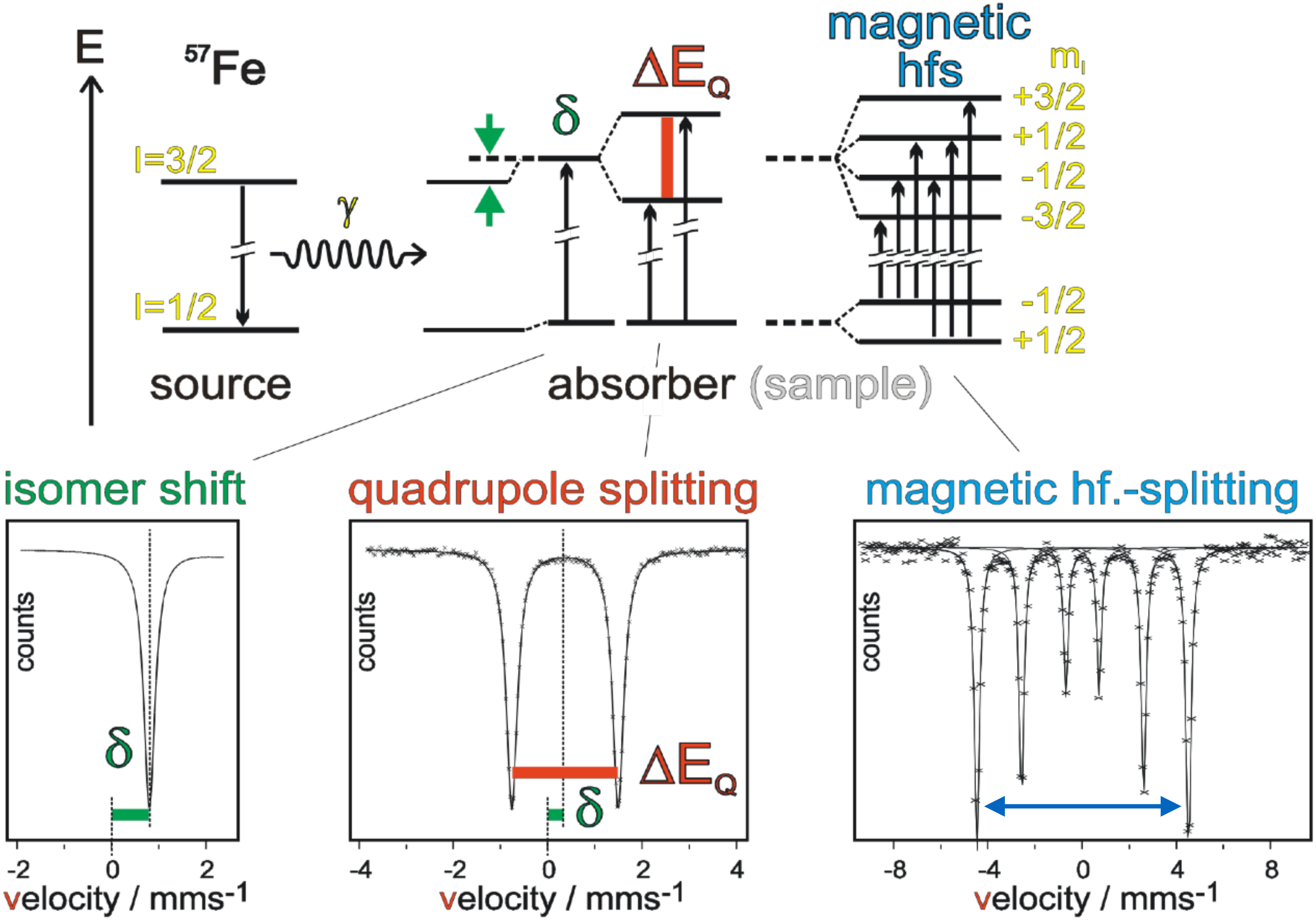
Ce	${}_{1}\mathrm{Pr}^{1}$	${}_{1}\mathrm{Nd}^{2}$	${}_{2}\mathrm{Pm}^{2}$	${}_{6}\mathrm{Sm}^{6}$	${}_{2}\mathrm{Eu}^{4}$	${}_{6}\mathrm{Gd}^{9}$	${}_{1}\mathrm{Tb}^{1}$	${}_{4}\mathrm{Dy}^{6}$	${}_{1}\mathrm{Ho}^{1}$	${}_{5}\mathrm{Er}^{5}$	${}_{1}\mathrm{Tm}^{1}$	${}_{5}\mathrm{Yb}^{6}$	${}_{1}\mathrm{Lu}^{1}$
${}_{1}\mathrm{Th}^{1}$	${}_{1}\mathrm{Pa}^{1}$	${}_{3}\mathrm{U}^{3}$	${}_{1}\mathrm{Np}^{1}$	${}_{1}\mathrm{Pu}^{1}$	${}_{1}\mathrm{Am}^{1}$	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Table by courtesy of Professor J. G. Stevens,
Mössbauer **E**ffect **D**ata **C**enter

^{57}**Fe** is by far the best !

More properties of Mössbauer nuclei online from MEDC: http://www.medc.dicp.ac.cn/Resources.php

^{57}Fe - Hyperfine Interactions



The Mössbauer Parameters:

Isomer shift (δ) ➞ charge density at ^{57}Fe

Quadrupole splitting (ΔE_Q) ➞ charge asymmetry

Magnetic hyperfine coupling ➞ electronic spin density

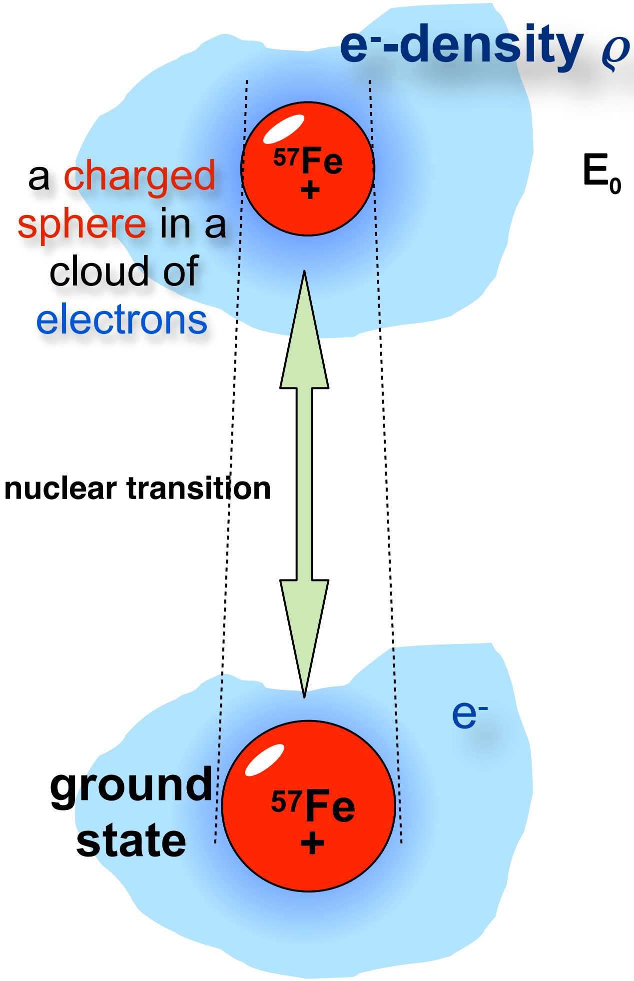
valence state, symmetry, ligands, covalency, ...

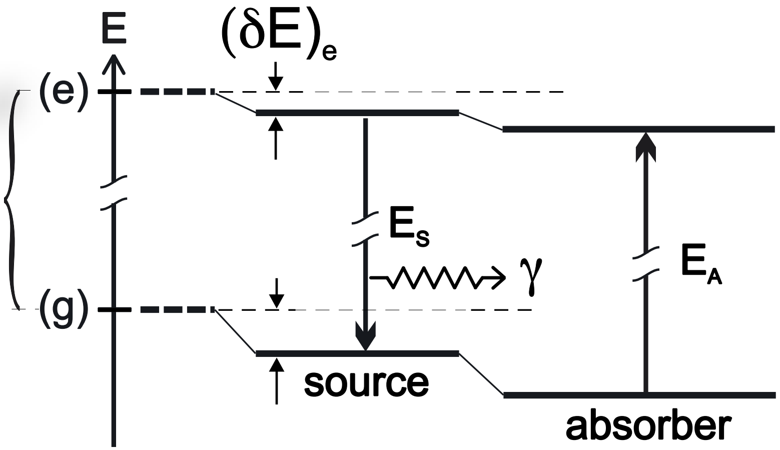
'chemical information'

The technique:

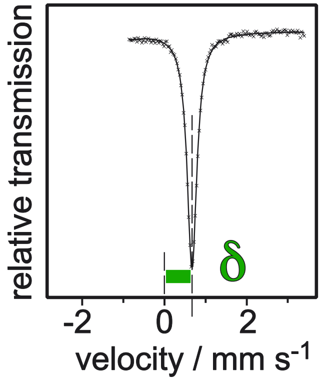
- is highly selective (only iron is detected; any iron is detected)
- yields 'local' information

Mössbauer Isomer Shift





isomer shift



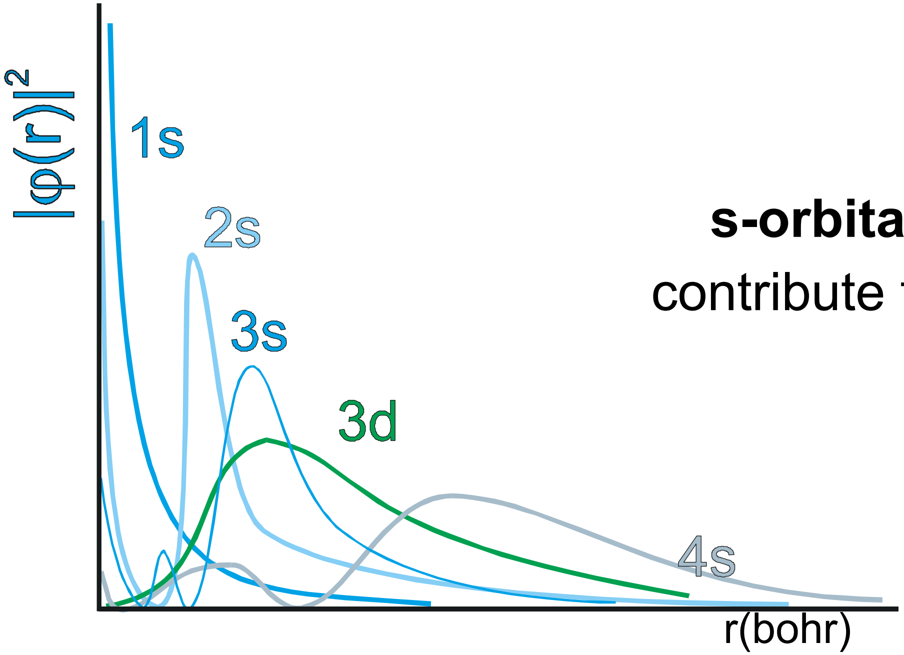
$$\delta = \frac{4\pi}{5} Z\left[\rho(0)_A - \rho(0)_S\right] \cdot R^2 \left(\frac{\Delta R}{R}\right)$$

Electron Charge Density ρ(0)

$$\boxed{\boldsymbol{\delta} = \alpha \{\boldsymbol{\rho(0)} - \text{const.}\}}$$

charge density at nucleus: $\boxed{\rho(0) = e|\varphi(0)|^2}$

nuclear properties; for ^{57}Fe: α = -0.2

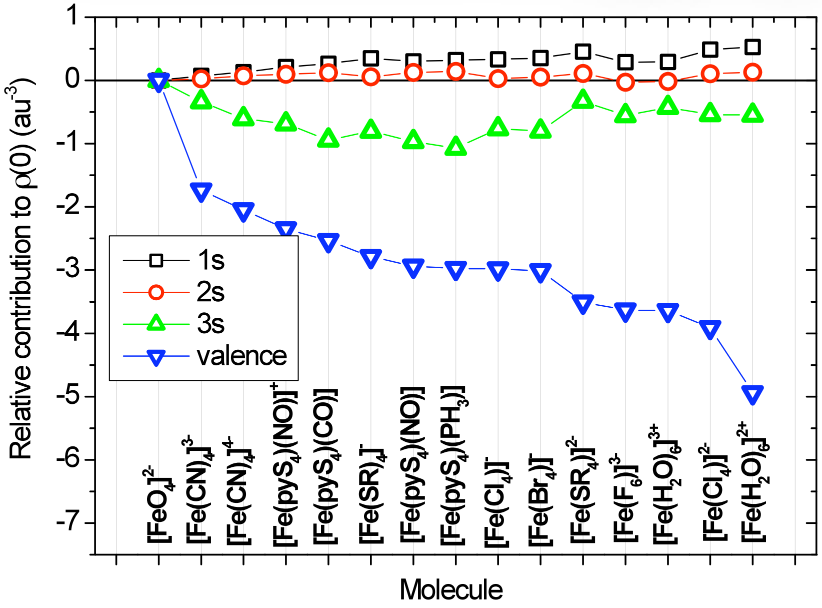


s-orbitals only

contribute to **φ(0)**

Isomer Shifts from MO-Theory

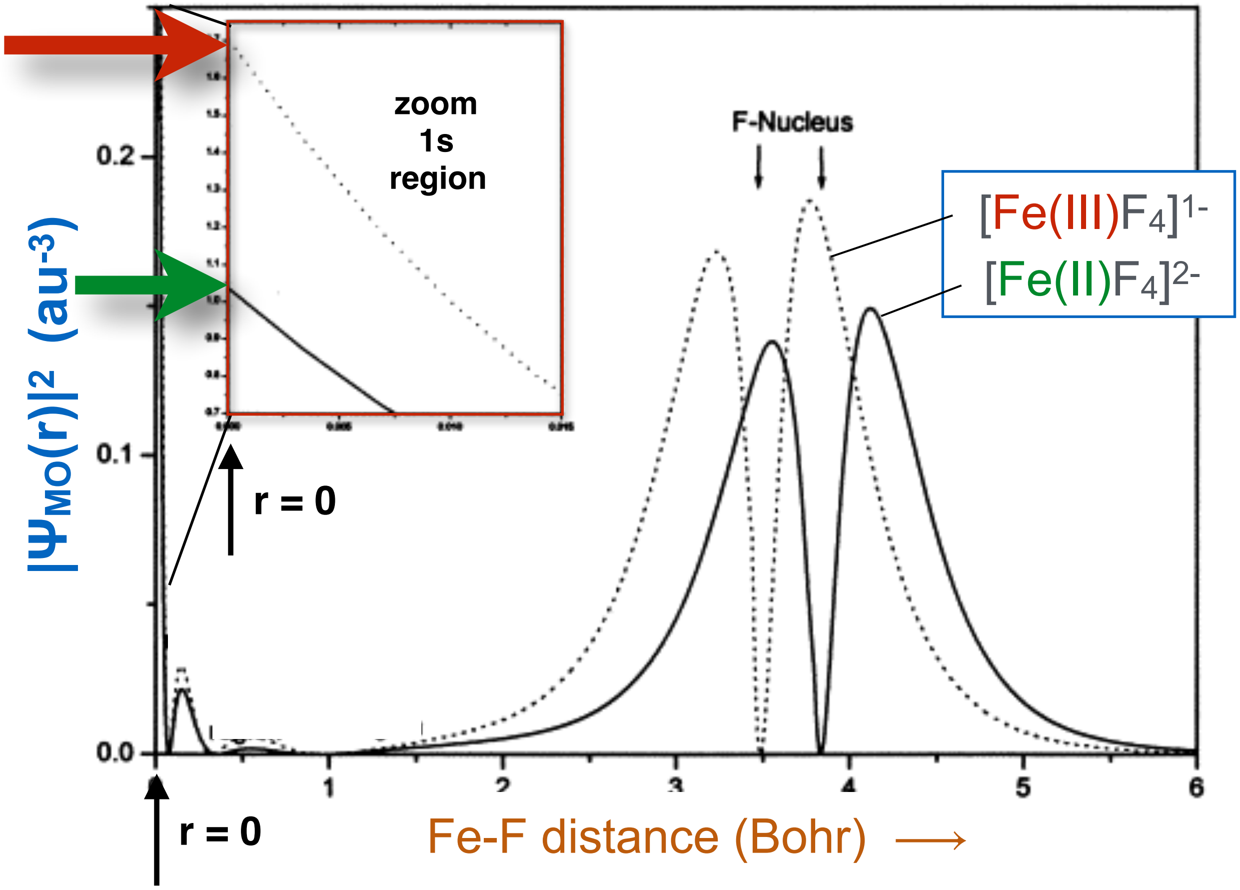
Variations of $|\varphi(o)|^2$



F. Neese, (2002)
Inorg. Chim. Acta **337C**,
181.

Variation of $|\varphi(o)|^2$ arises mostly from 4s contribution !

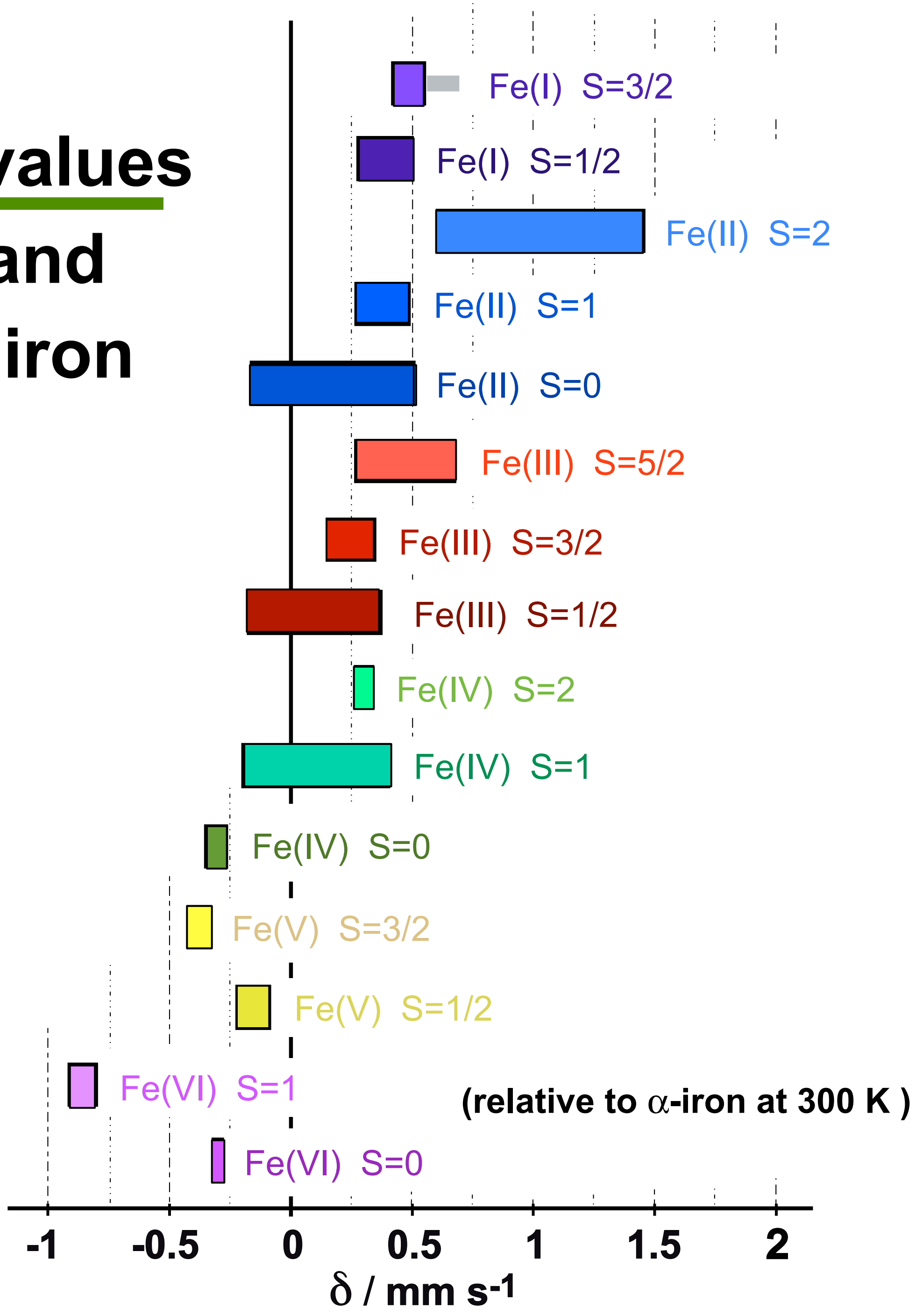
Isomer Shifts correlate best with Bond Length



F. Neese, (2002)
Inorg. Chim. Acta **337C**, 181.

shorter bonds: - increase 4s-Population
- compress of (all) s-orbitals
-> increase $|\varphi_{MO}(0)|^2$!

Typical isomer shift values for various spin- and oxidation states of iron



(adapted from Gütlich, Bill,Trautwein *Mössbauer Spectroscopy and Transition Metal Chemistry*, Springer 2011)

Mössbauer Isomer Shift Correlations

Oxidation State	**- number of 3d <u>valence electrons</u> at the iron** (δ increases with 3d population ⟶ longer bonds)
Coordination Number	**- lower coordination ⟶ shorter bonds** δ(4-coordination) < δ(6-coordination), …
Spin State	**- low-spin shows shorter bonds than high-spin** (lower δ for low-spin than for high-spin …)
Nature of Ligands	**- higher <u>covalency</u> ⟶ shorter chemical bonds** (δ decreases with higher covalency; δ(sulfur ligands) < δ(nitrogen ligands) …) **electronegativity, backbonding, s/p/d – hybridization, ...**

Mössbauer Isomer Shift Correlations

Some examples of high-spin Iron(II), and low-spin ...:

compound	ligands	δ (80 K)
Fe(II)CO$_3$ / siderite	6 O	1.36 mm/s
Fe(II)(NH$_3$)$_6$]$^{2+}$	6 N	1.12 mm/s
Fe(II)Cl$_2$	6 Cl	1.10 mm/s
[Fe(II)Cl$_4$]$^-$	4 Cl	0.9 mm/s
[Fe(II)(S-R)$_4$]$^{2-}$	4 S	0.7 mm/s

... δ correlates with bond lengths.

[Fe(II)(CN)$_6$]$^{4-}$	6 CN	-0.02 mm/s
[Fe(III)(CN)$_6$]$^{3-}$	6 CN	-0.08 mm/s

⇠very
⇠similar
??

Limitation of Isomer Shift Correlations:

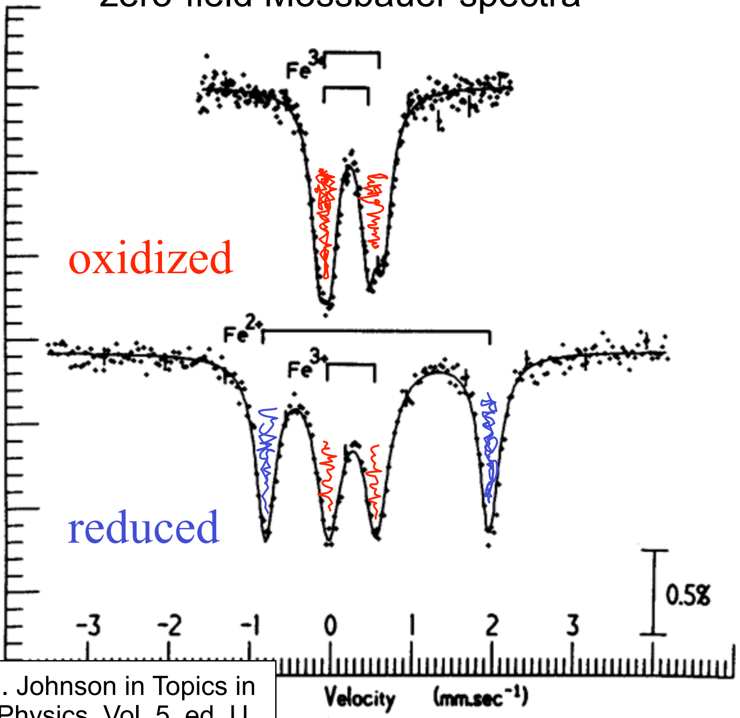
δ/valence correlation fades for low-valent and low-spin compounds !

⇒ explanation:

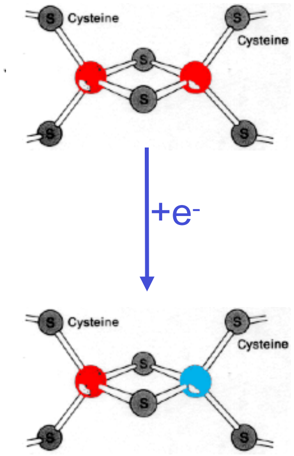
Change in ***back-donation*** compensates changes in valence orbitals.
(.. invariance holds also for bond distances of these compounds ;-)).

[2Fe-2S]$^{1+/2+}$ cluster from plant-type ferredoxins, Rieske-center, ...

zero-field Mössbauer spectra



C.E. Johnson in Topics in Applied Physics, Vol. 5, ed. U. Gonser, Springer 1975)



typical isomer shifts for Fe(III) and Fe(II) in 4S-coordination

	δ[mm/s]	ΔE_Q [mm/s]
oxidized	**0.27**	0.65
reduced	0.25	0.64
	0.54	3.0

Temperature Dependence of Isomer Shifts

Main origin: Second-order Doppler shift (**SOD**)

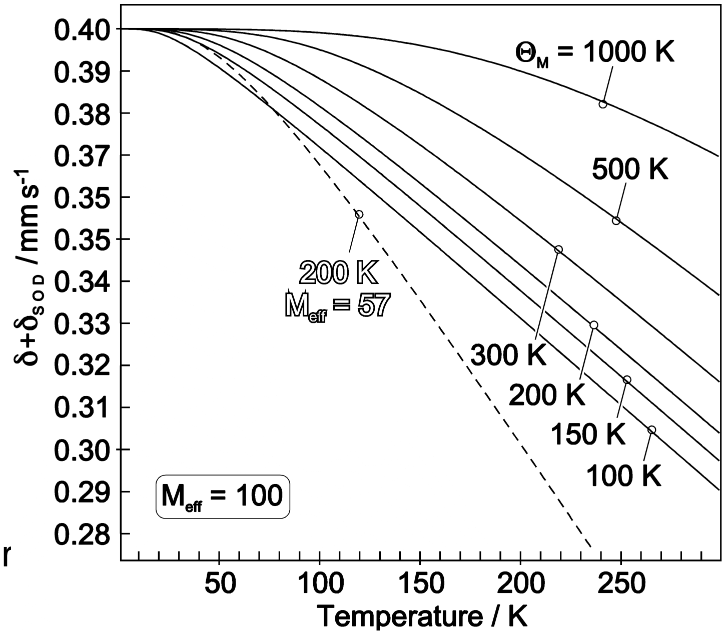
$$\delta_{\text{exp}} = \delta + \delta_{\text{SOD}}$$

a relativistic effect, depending on the **mean-squared velocity $<v^2>$** of nuclei

$$\boxed{\delta_{SOD} = -E_\gamma \frac{<v^2>}{2c^2}}$$

In the **Debye model** for lattice vibrations:

$$\boxed{\delta_{SOD} = -\frac{9 k_B E_\gamma}{16 M_{eff} c^2}\left(\Theta_M + 8T\left(\frac{T}{\Theta_M}\right)^3 \int_0^{\Theta_M/T} \frac{x^3}{e^x - 1}\,dx\right)}$$



… higher temperature

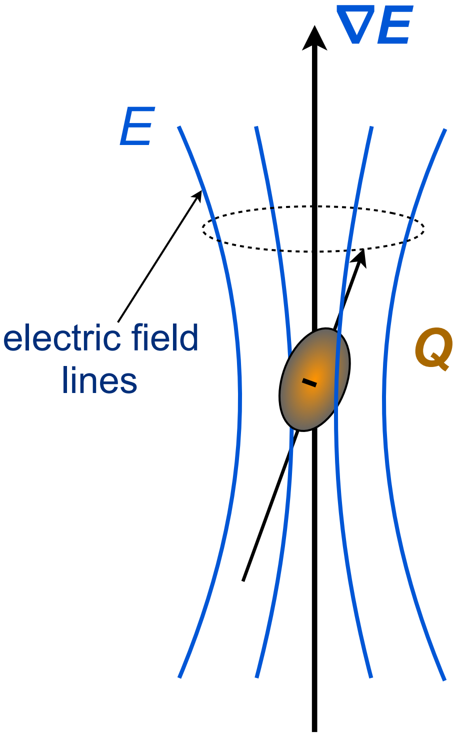
→ lower δ_{exp} !

Θ_M: Debye/Mössbauer temperature

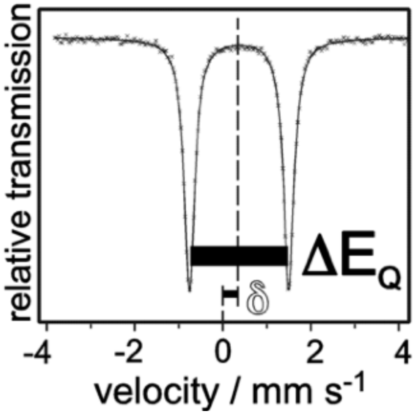
M_{eff}: effective mass of the nucleus

Electric Quadrupole Splitting

Nuclei with *I* > 1/2 have an
electric quadrupole moment *Q*,
which has 'rotational energy' in an
electric field gradient ∇*E* (efg).

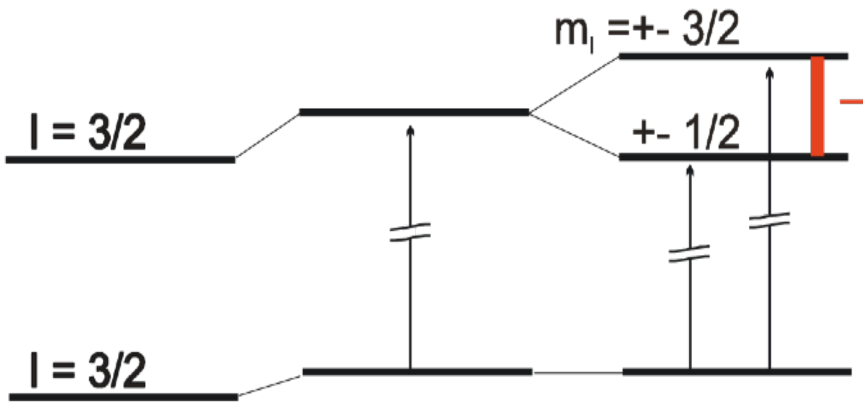


⇒ can be described in terms of **nuclear spin *I***

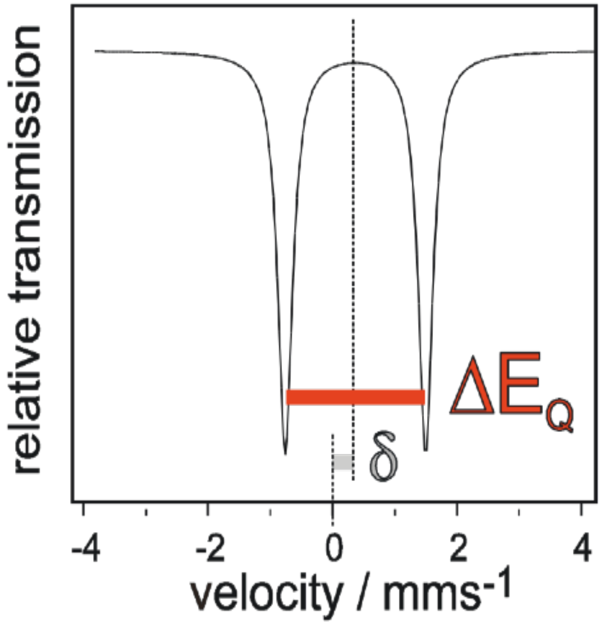


Electric Quadrupole Splitting

(described in terms of nuclear spin **I**)



$$\Delta E_Q = eQV_{zz} / 2\sqrt{(1+ \eta^2/3)}$$

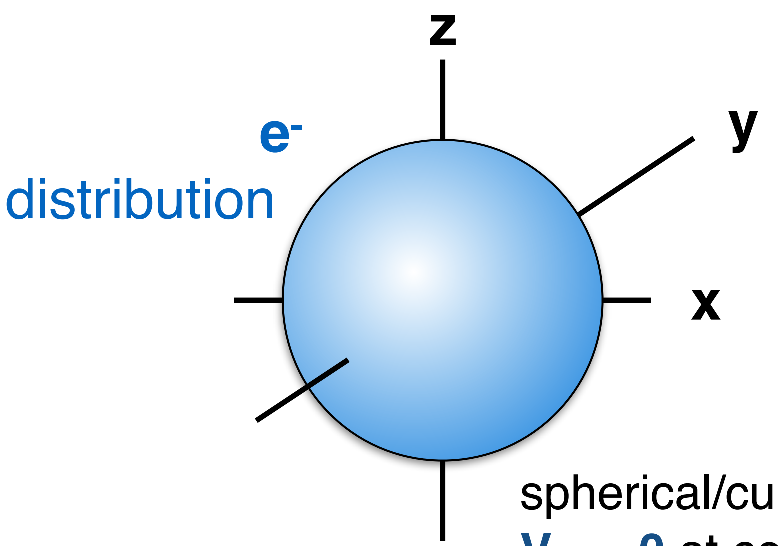


Q: nuclear quadrupole moment

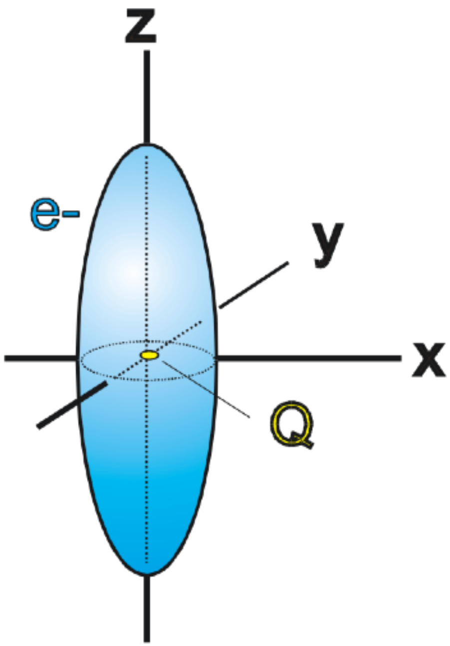
V_{zz}: **main component** of the **efg** (electric field gradient)

η: **asymmetry parameter**

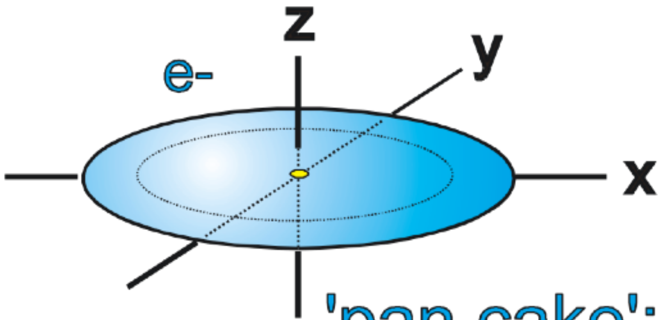
Electric Charge Distribution and the EFG-Tensor



spherical/cubic:
$V_{zz} = 0$ at center



'cigar' - shaped:
$V_{zz} < 0$



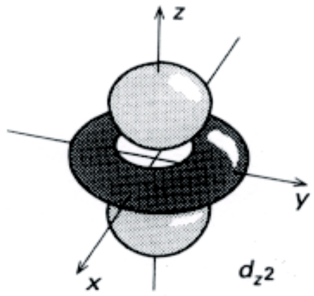
'pan cake': $V_{zz} > 0$

$\eta = 0$
(axial symmetry)

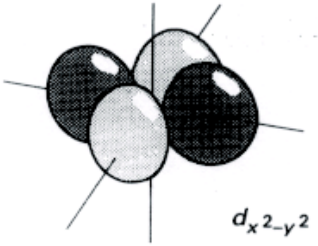
Valence Contribution to the Electric Field Gradient

- asymmetry in the valence shell → efg_{val}

e_g - orbitals



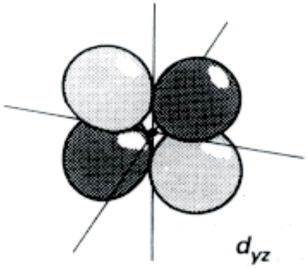
$V_{zz} < 0$



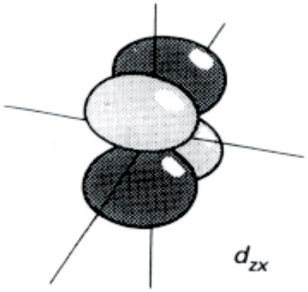
$V_{zz} > 0$

An electron in a pure d orbital would yield efg_{val} according to $\Delta E_Q \approx -4.2$ mm/s

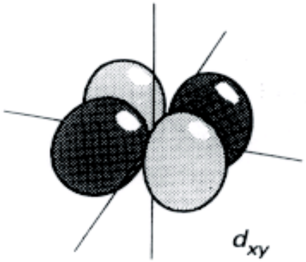
t_{2g} - orbitals



$V_{zz} < 0$



$V_{zz} < 0$



$V_{zz} > 0$

Expectation values of **efg$_{val}$**

$(V_{ii})_{val}/e\langle r^{-3}\rangle$ for *d*-electrons

orbital	V_{xx}	V_{yy}	$\mathbf{V_{zz}}$	η
d_{x2-y2}	-2/7	-2/7	**4/7**	0
d_{z2}	+2/7	+2/7	**-4/7**	0
d_{xy}	-2/7	-2/7	**+4/7**	0
d_{xz}	-2/7	+4/7	**-2/7**	+3
d_{yz}	+4/7	-2/7	**-2/7**	-3

to convert V_{ii} in ΔE_Q multiply by 4.2 mms^{-1}/ 4/7 e <r-3>
(for $\langle r^{-3}\rangle = 5a_0^{-3}$, Q=0.15b)

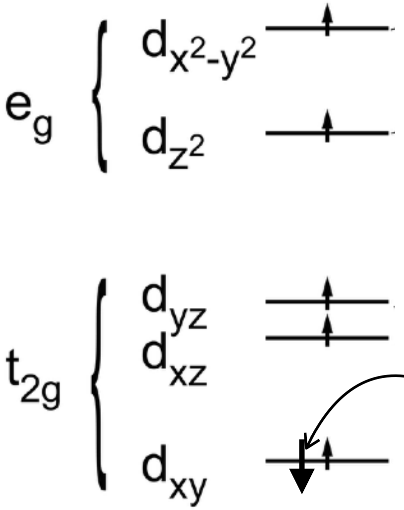
(Gütlich, Bill, Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry, Springer 2011*)

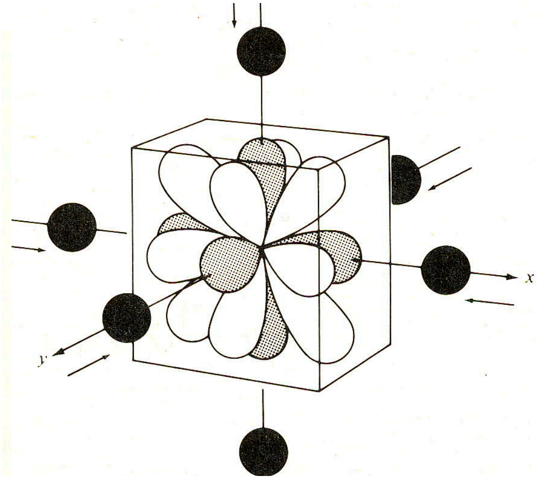
for a general 3d^n configuration:

add up the individual contributions for all d-electrons

example: **Fe(III) high-spin**

$^6A_1$





five d-orbitals

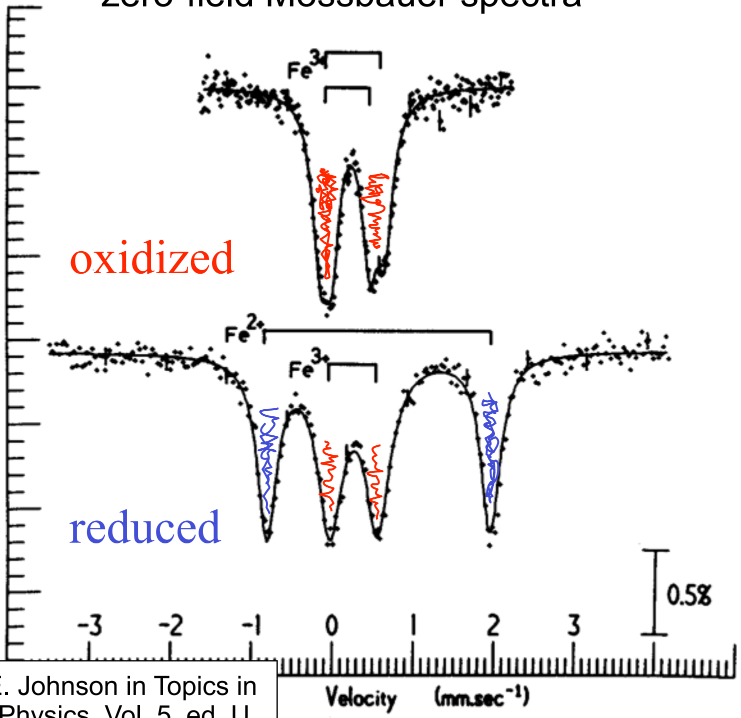
$efg_{val} = 0$

$\Delta E_Q \simeq 0$

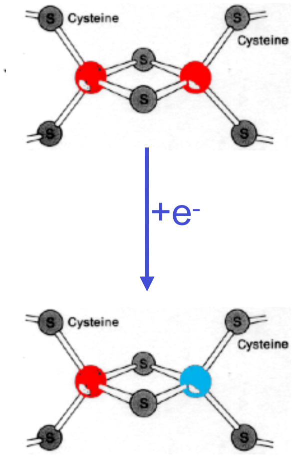
one electron more in **Fe(II)** will change the situation: $\Delta E_Q = 2 - 4$ mm/s

$[2Fe\text{-}2S]^{1+/2+}$ cluster from plant-type ferredoxins, Rieske-center, ...

zero-field Mössbauer spectra



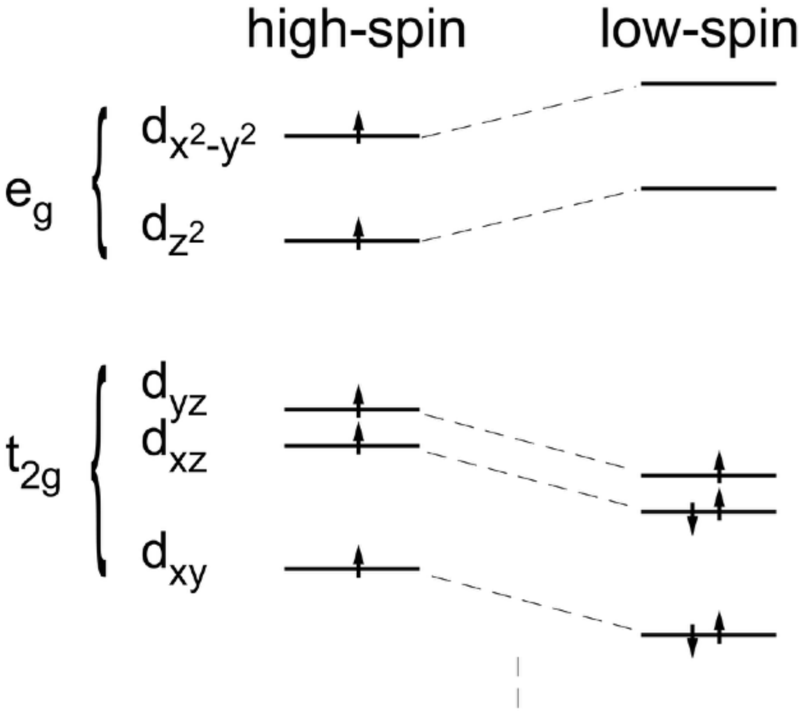
C.E. Johnson in Topics in Applied Physics, Vol. 5, ed. U. Gonser, Springer 1975)



typical quadrupole splitting for Fe(III) and Fe(II) in 4S-coordination

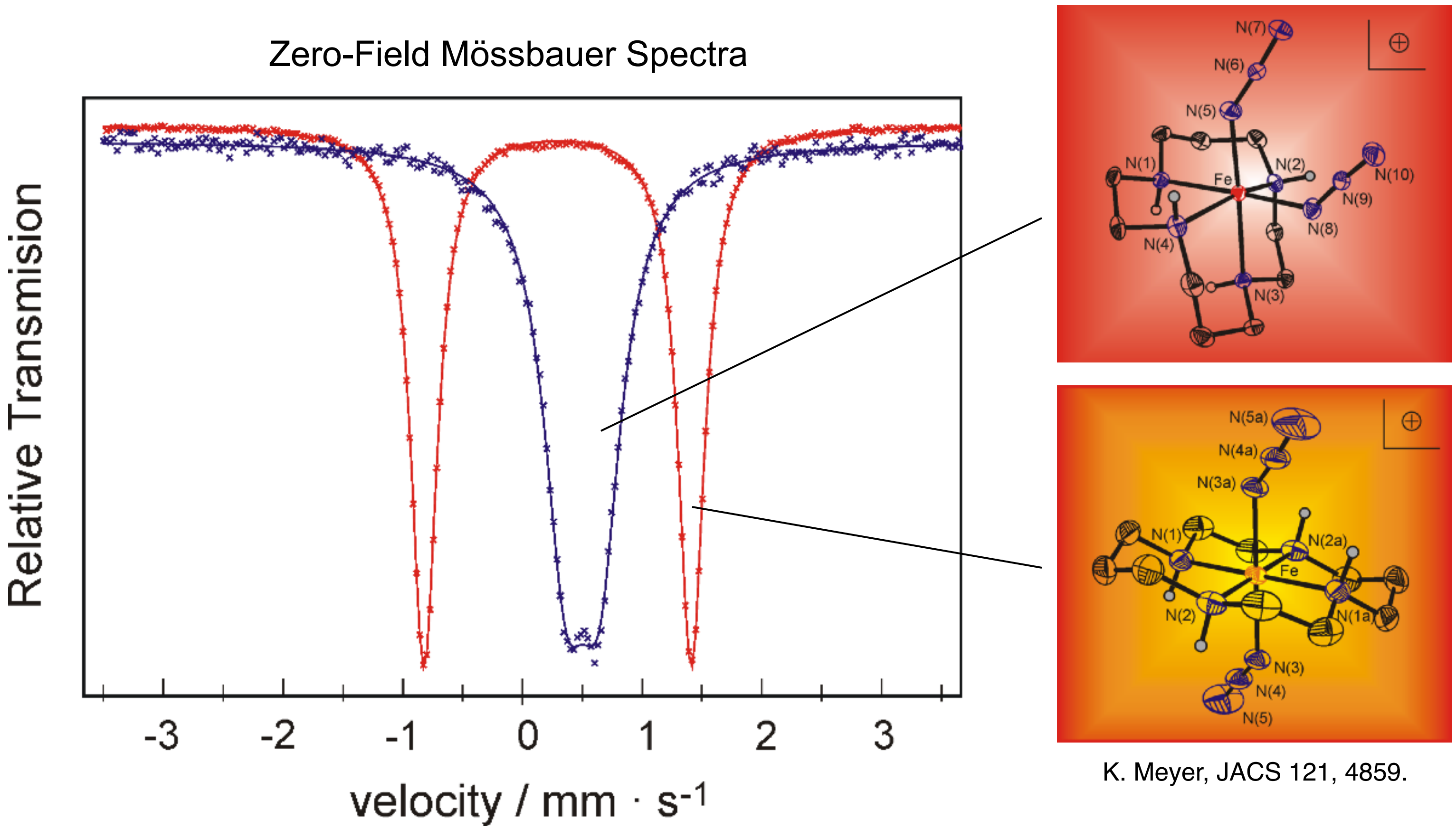
	δ[mm/s]	ΔE_Q [mm/s]
oxidized	0.27	**0.65**
reduced	0.25	0.64
	0.54	**3.0**

example: **Fe(III), distorted-octahedral**



EFG$_{val}$ ≈ 0 ≈ +4 mm s^{-1} **(large)**

example: two Iron(III) Cyclam Complexes


Zero-Field Mössbauer Spectra

K. Meyer, JACS 121, 4859.

	δ / mm/s	ΔE_Q / mm/s
cis–$[(\mathrm{cyclam})\mathrm{Fe(III)}(N_3)_2]^+$	0.49	0.29
trans–$[(\mathrm{cyclam})\mathrm{Fe(III)}(N_3)_2]^+$	0.29	2.24

Typical values of δ and ΔE_Q for biological samples

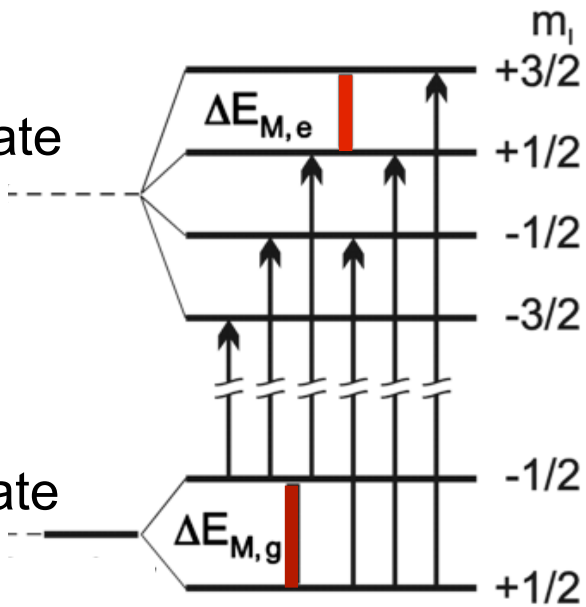
Oxidation state	Spin state	Ligands	δ (mm/s)	ΔE_Q (mm/s)
Fe(II)	$S = 2$	heme	0.85 - 1.0	1.5 - 3.0
		Fe-(O/N)	1.1 - 1.3	2.0 - 3.2
		Fe/S	0.60 - 0.70	2.0 - 3.0
	$S = 0$	heme	0.30 - 0.45	< 1.5
Fe(III)	$S = 5/2$	heme	0.35 – 0.45	0.5 – 1.5
		Fe-(O/N)	0.40 – 0.60	0.5 – 1.5
		Fe/S	0.20 – 0.35	< 1.0
	$S = 3/2$	heme	0.30 – 0.40	3.0 – 3.6
	$S = 1/2$	heme	0.15 – 0.25	1.5 – 2.5
		Fe-(O/N)	0.10 – 0.25	2.0 – 3.0
Fe(IV)	$S = 2$	Fe-(O/N)	0.0 – 0.35	0.5 – 1.5
	$S = 1$	heme	0.0 – 0.10	1.0 – 2.0
		Fe-(O/N)	-0.20 – 0.10	0.5 – 4.3

Adapted from E. Münck, *Physical Methods in Bioinorganic Chemistry*, L. Que, Jr. (ed) 2000

Magnetic Mössbauer Spectra

^{57}Fe

excited state
I = 3/2



μ_e = -0.155 μ_N

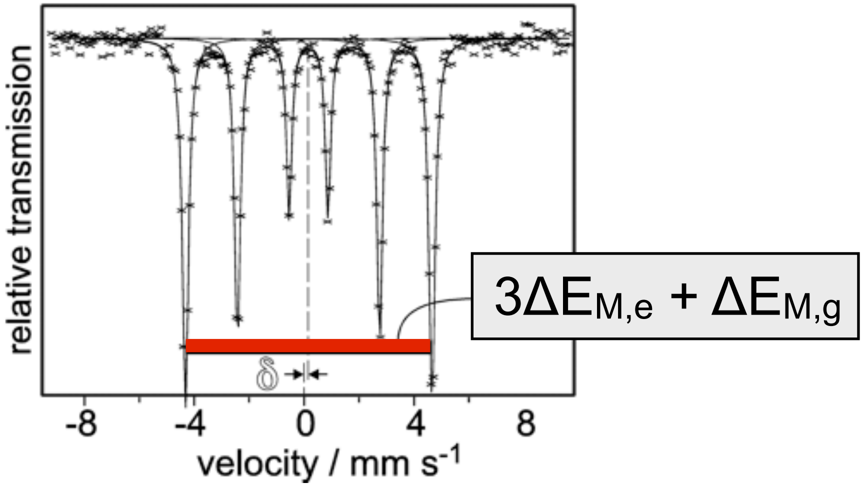
ground state
I = 1/2

μ_g = +0.09 μ_N

$$\hat{H}_M = -g_N \mu_N \hat{\boldsymbol{I}} \cdot \boldsymbol{B}$$

Δm_I = 0, ±1 selection rule

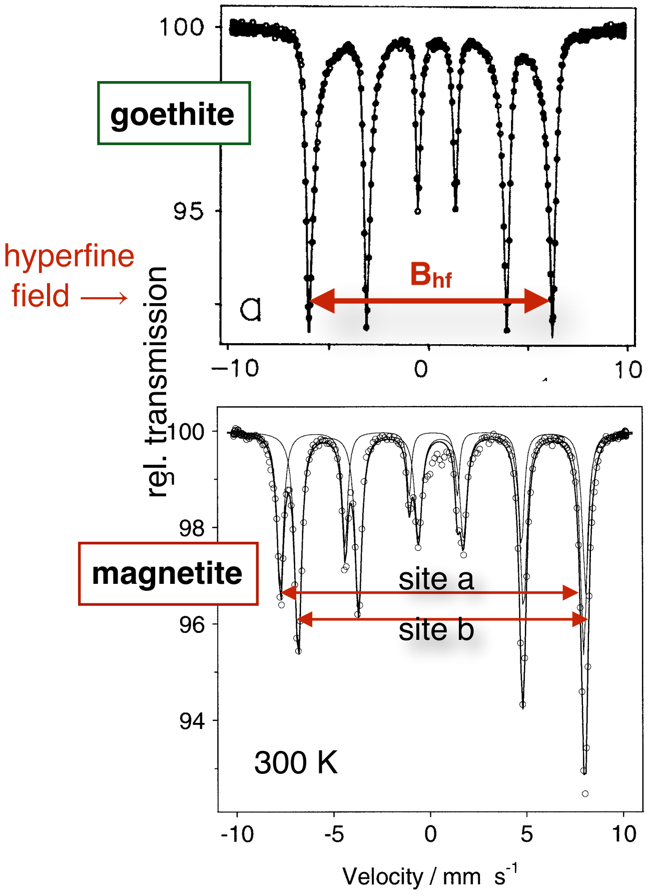
⇒ six-line spectrum



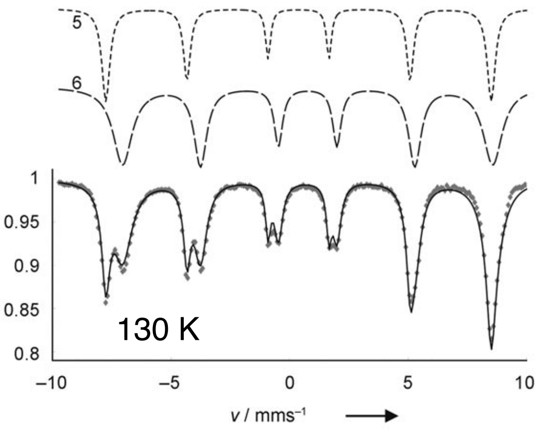
$3\Delta E_{M,e} + \Delta E_{M,g}$

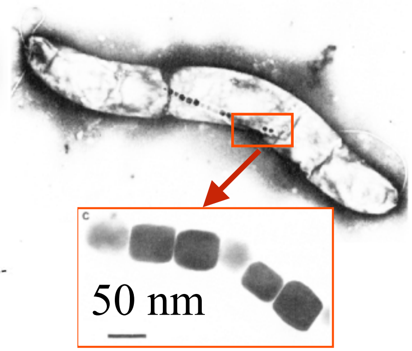
Magnetic Mössbauer Spectra

- examples -



magnetotactic bacteria





D. Faivre,…,B.Matzanke
Angew. Chem. 46, 2007
(*Magnetospirillum gryphiswaldense*)

- **biomagnetic compass** -
(Frankel, Papaefthymiou, 1983)

	B_{hf}	δ (295 K)
goethite (α-FeO(OH))	38 T	0.37 mm/s
magnetite (Fe_3O_4)	49 T (a) 46 T (b)	0.26 mm/s 0.67 mm/s

M. Cornell, U. Schwertmann
The Iron Oxides
Wiley Online Lib., Open Access

Combined Electric and Magnetic Hyperfine Interaction ?

isomer shift is just additive, ⟶ 'easy'

$$\boxed{\hat{H} = \delta E + \hat{H}_Q + \hat{H}_M}$$

combined quadrupole and Zeeman interaction is difficult in general

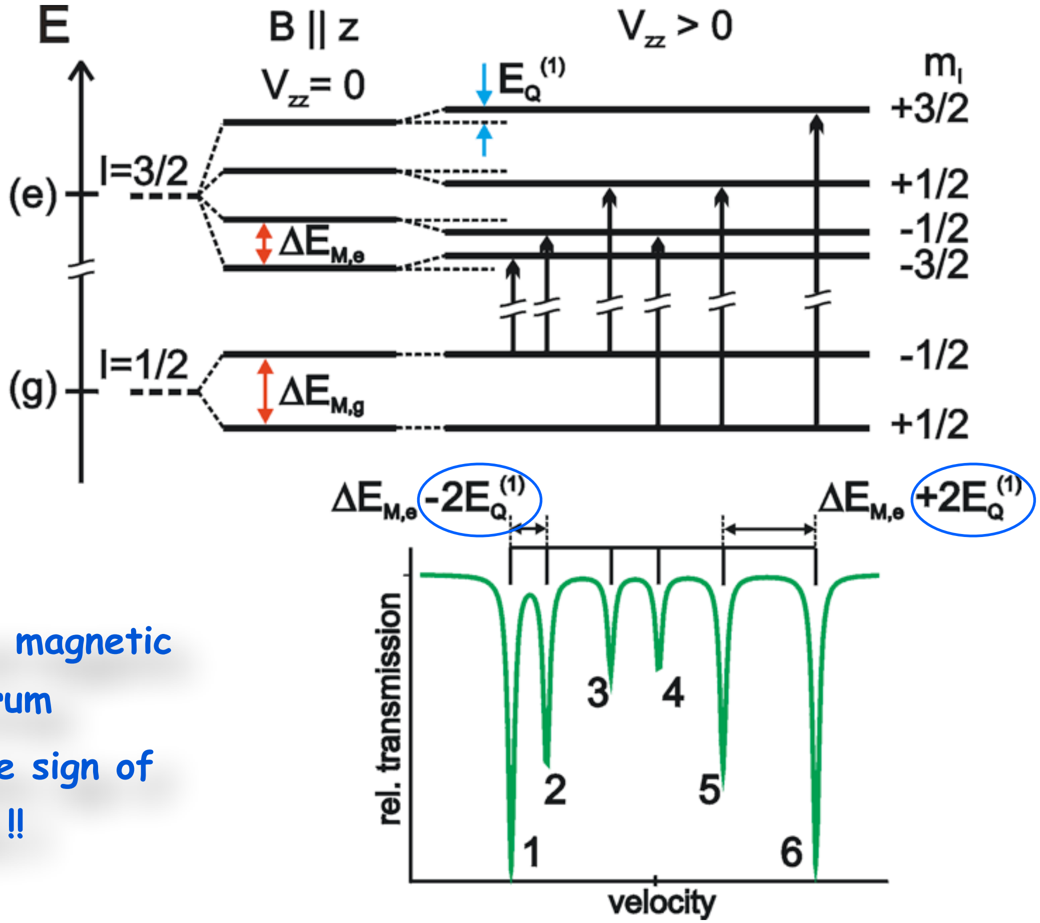
→ numerical diagonalization, …

Combined Electric and Magnetic Hyperfine Interaction (1)

^{57}Fe

special case 1:

$\mu_N B >> eQV_{zz}$



⇒ perturbed magnetic spectrum

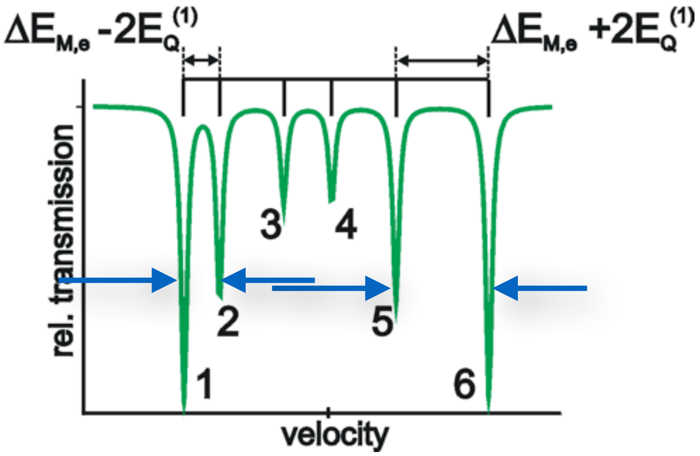
⇒ determine sign of EFG !!

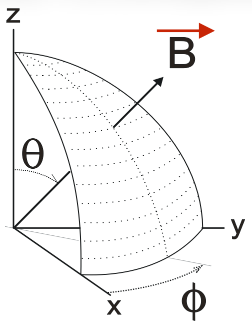
Such a sharp spectrum is observed only for fixed angles of *B* and *EFG,* as expected for magnetic materials, like Fe_3O_4, Fe_2O_3, metal alloys, nano-particles ...!!

Angular Dependence of Perturbed Magnetic Spectra

1st order: only V_{ij} component along $\vec{\mathbf{B}}$ is effective !

'high-field' condition: $\mu_N B \gg eQV_{zz}$





polar angles θ, Φ

The EFG is a **traceless tensor**:

$$\boxed{V_{xx} + V_{yy} + V_{zz} = 0}$$

(⟶ V_{xx}, V_{yy} negative if V_{zz} positive)

nuclear energies:

$$E_{M,Q}(I = 3/2, m_I)^{(1)} = -g_N B m_I + E_Q(m_I, \theta, \phi)^{(1)}$$

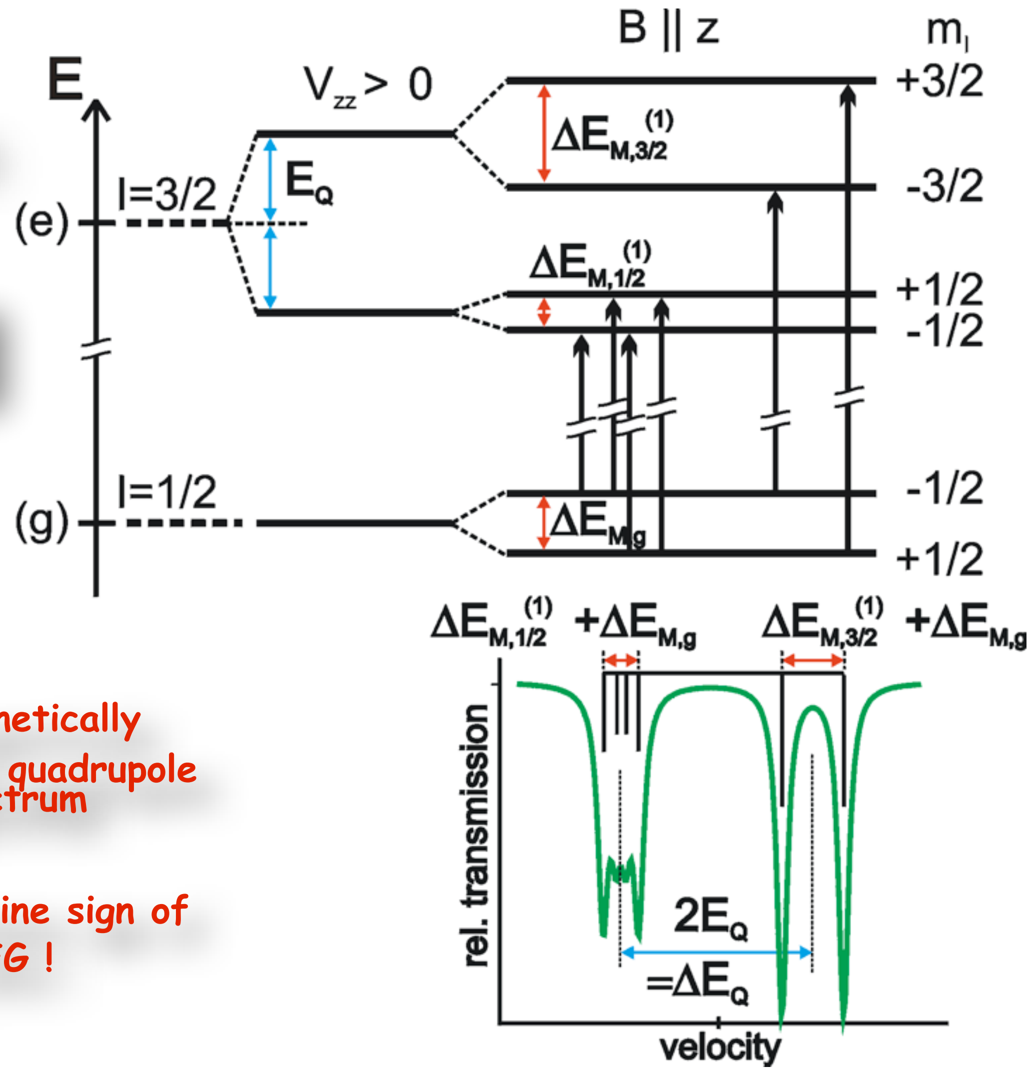
⇒ $E_Q^{(1)}$ can be positive or negative, depending on (θ,Φ) !

Combined Electric and Magnetic Hyperfine Interaction (2)

^{57}Fe

special case 2:

$$\boxed{eQV_{zz} \gg \mu_N B}$$



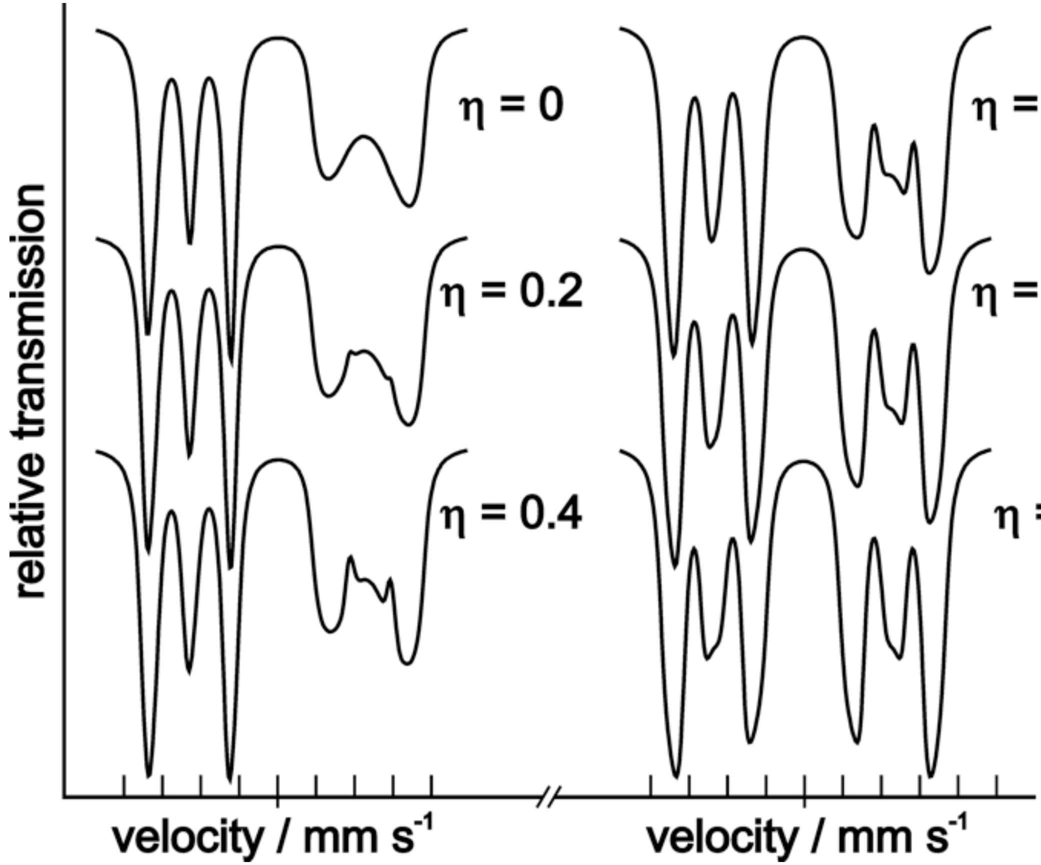
⇒ magnetically perturbed quadrupole spectrum

⇒ determine sign of EFG !

Combined Hyperfine Interaction (2)

-Powder Simulations -

add x,y direction step in-between !!!



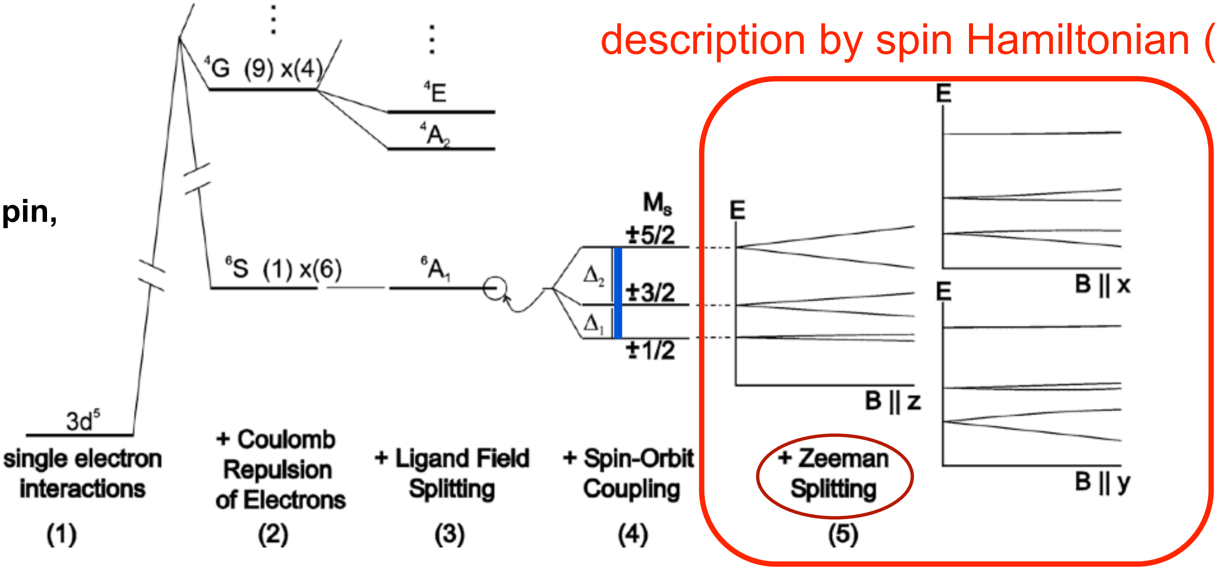
In 'weak-field' condition, $\mu_N B \ll eQV_{zz}$,
the sign of V_{zz} and the asymmetry parameter η can be determined
from a powder spectrum!

^{57}Fe-Mössbauer Spectra of Paramagnetic Systems

- Spin Hamiltonian Formalism -

Topic: Describe a *paramagnetic* ion by ***ligand field theory***

example:
Fe(III) high-spin,
S = 5/2

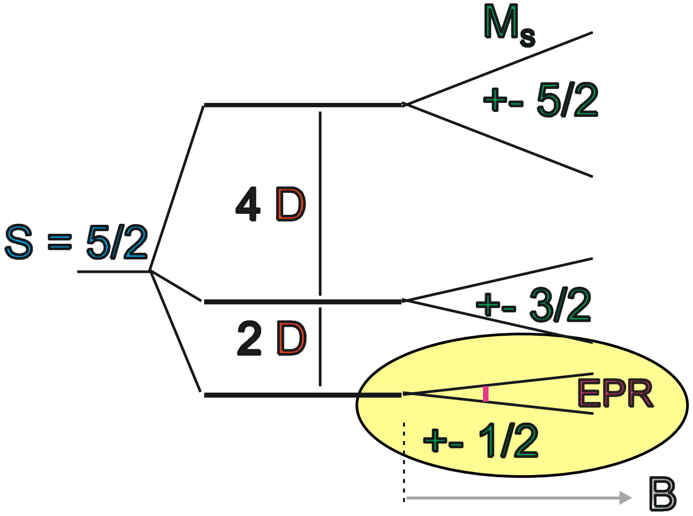


description by spin Hamiltonian (SH)

Electrostatic interactions and spin-orbit coupling in increasing order 1-4

⇒ explains **zero-field splitting** (Δ_1, Δ_2) and **anisotropic g-values** of the **ground state** (non degenerate)

example: Splitting into Kramers Doublets



every magnetic sublevel (*i*), m_S = -S, .., S

- exhibits a spin **expectation value** $<\vec{S}>_i$

  $(<\vec{S}>_i \propto \vec{\mu}_i, \ \propto \partial E_i/\partial B)$

- can be calculated from SH $\widehat{H}_S$
- yields an internal field $\vec{B}^{int}$

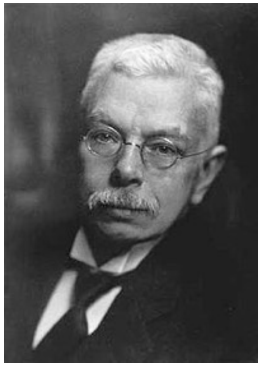
Hendrik Anthony Kramers
Ph.D Leiden, 1916

⟹ every m_S levels contributes its own Mössbauer subspectrum !

(in so-called slow relaxation)

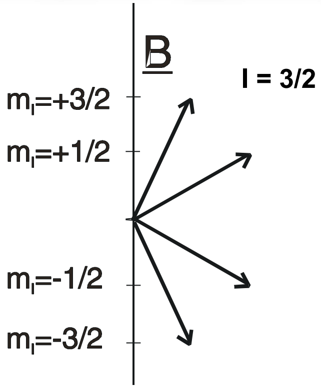
(revisited)

The Nuclear Zeeman Effect



Pieter Zeeman
Netherlands, 1865-1943

$$\boxed{\hat{H}_M = -g_N \mu_N \hat{I} \cdot B}$$

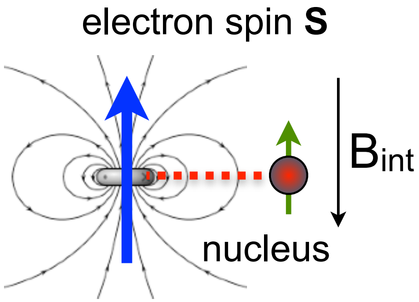


μ_N **nuclear magneton**
g_N **nuclear g-factor**
$\hat{I}$ **nuclear spin operator**

B: effective field at the nucleus

B_{appl}: applied field + B_{int} : internal field

$$\boxed{B = B_{appl} + B_{int}}$$



three contributions: Fermi-contact $B_{contact}$, dipole B_{dipole}, and orbital contribution, B_{orbit}.

$$\boxed{B_{int} = B_{contact} + B_{dipole} + B_{orbit}}$$

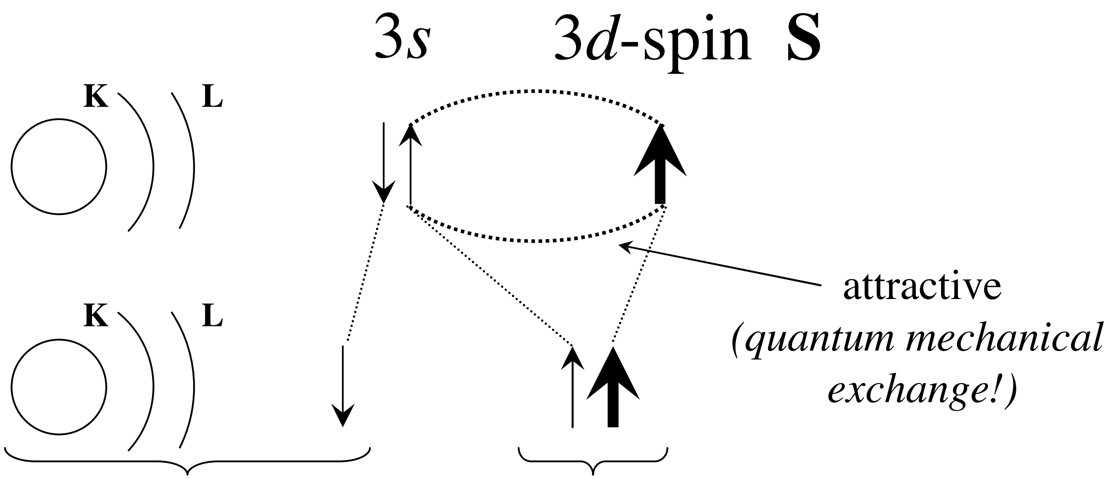
(B_{int} depends on <S> and A value)

The Internal Field at the Nucleus

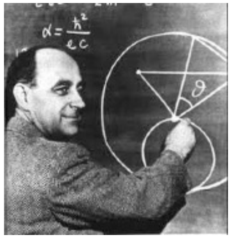
$$\boxed{\boldsymbol{B}_{\text{int}} = \boldsymbol{B}_{\text{contact}} + \boldsymbol{B}_{\text{dipole}} + \boldsymbol{B}_{\text{orbit}}}$$

a.) **Fermi - Contact Contribution**, → $\boldsymbol{B}_{\text{contact}}$

Exchange interaction affords polarisation of the filled inner s-shells.



attractive
(quantum mechanical exchange!)



Enrico Fermi, 1901-1954

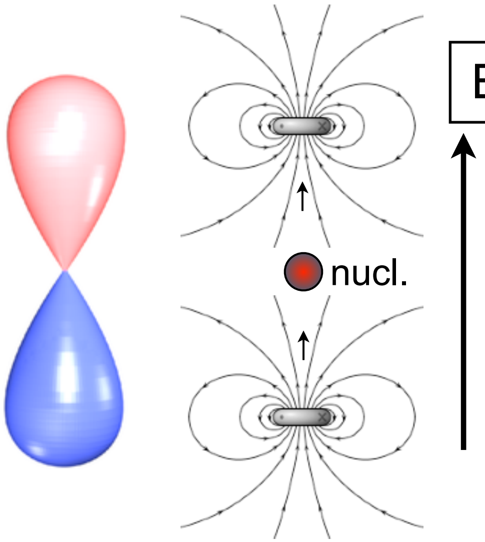
(different radial distribution of spin-up and spin-down electrons)

- in general the largest contribution to $\boldsymbol{B}_{\text{int}}$

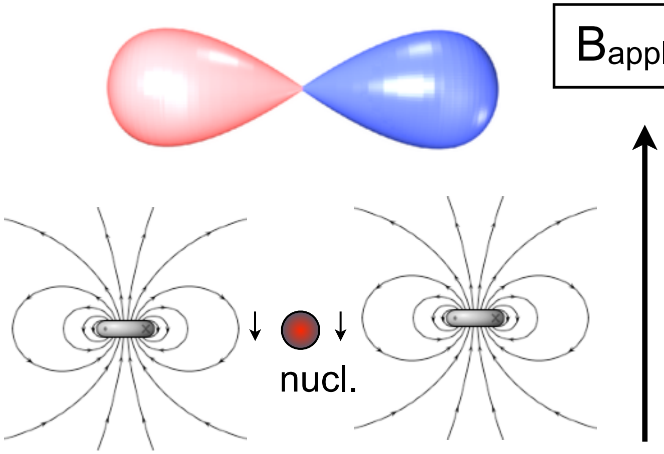
- isotropic, negative sign ! $(|\Psi(0)|^2_\downarrow > |\Psi(0)|^2_\uparrow)$

b.) **Dipole - Contribution**, → $\boldsymbol{B}_{\text{dipole}}$

Arises from **non-spherical distribution** of the electronic spin density.



$B_{\text{appl}} \parallel z$



$B_{\text{appl}} \perp z$

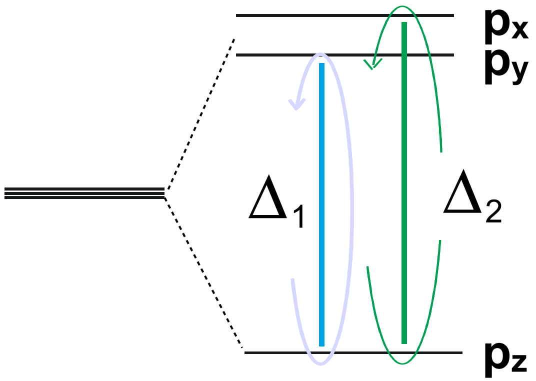
$$\boxed{B_{\text{int}} = B_{\text{appl}} + B_{\text{dipole}}}$$

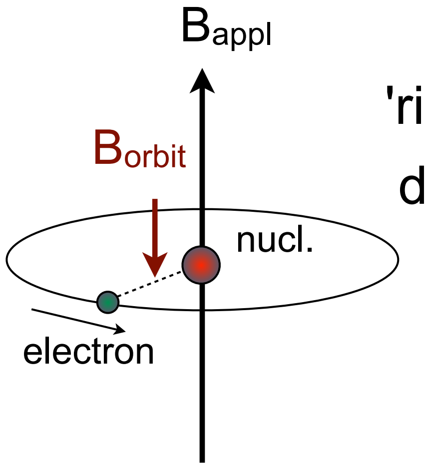
$$\boxed{B_{\text{int}} = B_{\text{appl}} - B_{\text{dipole}}}$$

$$\boxed{\boldsymbol{B}_{\text{dipole}} = -A\langle \boldsymbol{S} \rangle}$$

c.) **Orbital - Contribution**, → $\boldsymbol{B}_{\text{orbit}}$

Arises from **non-quenched orbital momentum** of the electronic state due to spin-orbit coupling (**SOC**).



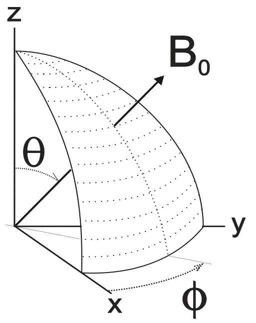


'ring' current depends on direction of B_{appl}, due to different SOC for different orbitals

level mixing by SOC induces some orbital momentum → g ≠ 2.002..

$$\boldsymbol{B}_{\text{orbit}} = -2\mu_B\langle r^{-3}\rangle\langle \boldsymbol{L}\rangle$$

Spin Hamiltonian Simulation for ^{57}Fe Nuclei



Numerical solution:

```
select applied field $B$, and orientation $\theta,\Phi$

solve $\widehat{H}_s$ and find $\langle S\rangle_i$,  i=1, .., 2S+1

for all $|i\rangle$:
use total field:  $B^{total} = B + B^{int}_i$, Boltzmann factor $p_i$ for $|i\rangle$

solve $\widehat{H}_{nuc}$ for I=1/2 and I=3/2 (with $H_Q$)

for all nuclear energies: find transitions
     - weight subspectrum with pi
return

return
```

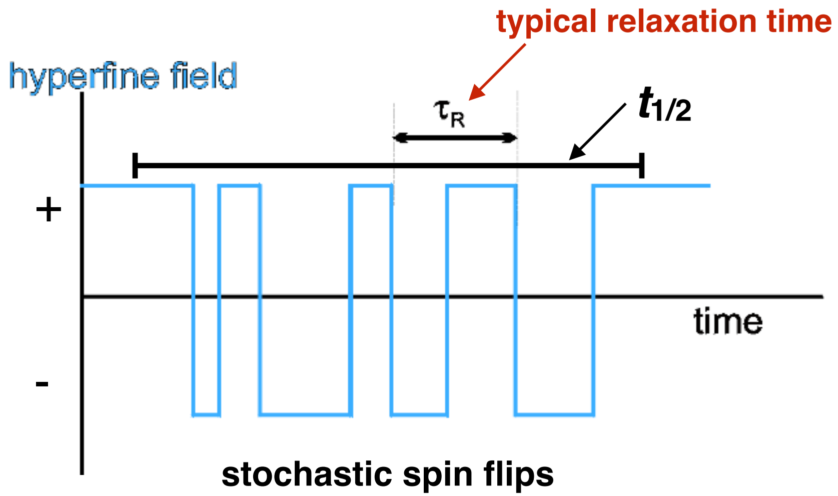
⇒ **slow electronic spin relaxation**:

every m_s-level contributes own internal field + subspectrum (Boltzmann weighted)

Spin Relaxation and Mössbauer Line Shapes

the Mössbauer nucleus has a built-in clock:

life time of the excited state: $t_{1/2}$ **= 98 ns** (also ~ nuclear Larmor frequency)



stochastic spin flips

sharp lines for:

-**slow relaxation:** $\tau_R \gg t_{1/2,\,\mathrm{nuc}}$

-**fast relaxation:** $\tau_R \ll t_{1/2,\,\mathrm{nuc}}$

(otherwise **intermediate relaxation** generates complicated 'coalescence' lines)

fast relaxation→ thermal average of <S>$_i$ expectation values

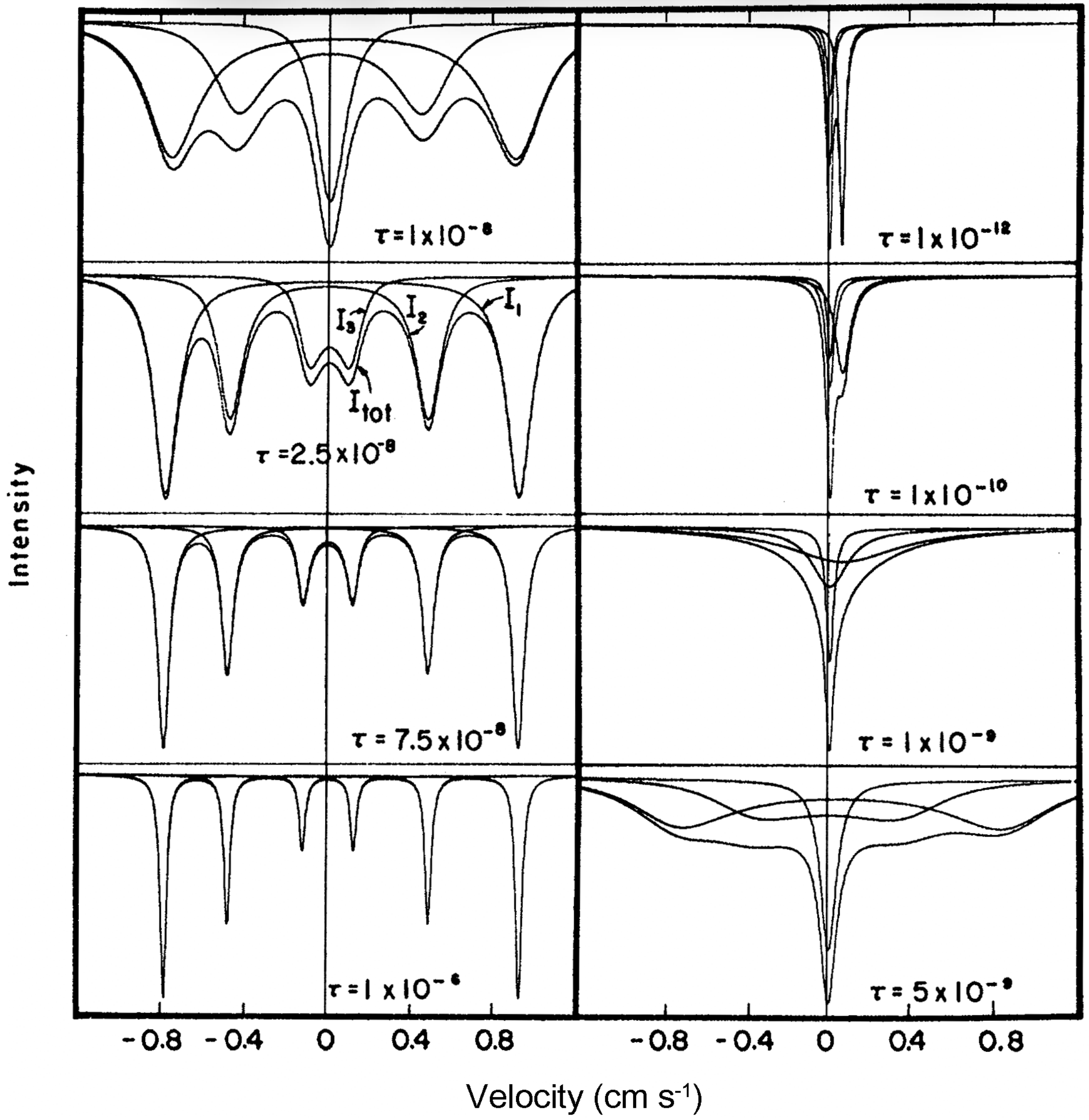
$$\boxed{<\vec{S}>_T \; = \; \sum_i <\vec{S}>_i \exp(-E_i/kT) \Big/ \sum_j \exp(-E_j/kT)}$$

generates **one** internal field

⇒ quadrupole spectra

at high T, low B

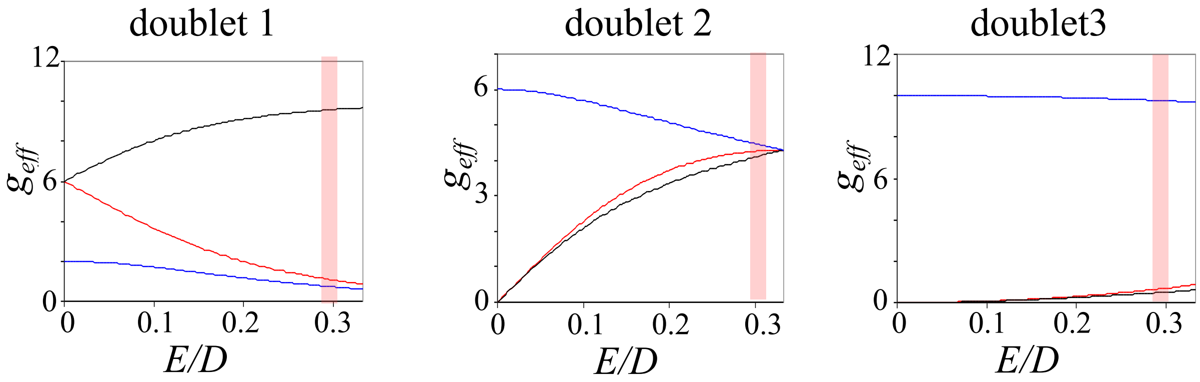
Theoretical ^{57}Fe Mössbauer relaxation spectra for a flipping hyperfine field ± 55 T.

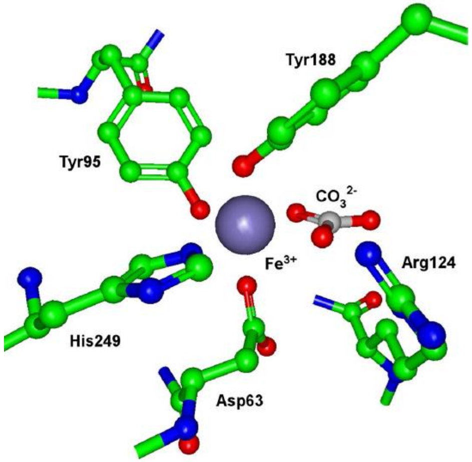


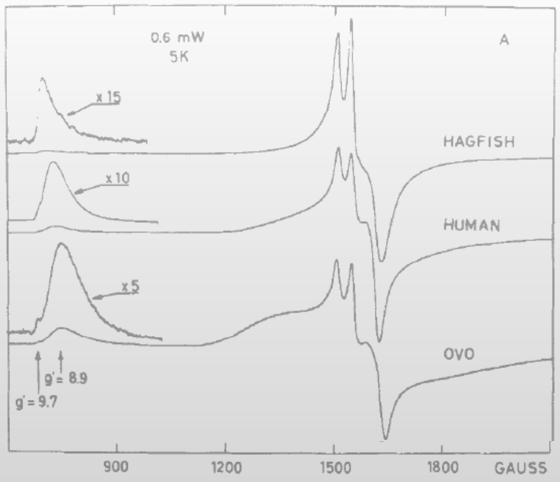
H.H. Wickman, M.P. Klein and D.A. Shirley, Phys. Rev. 152, 345-357 (1966)

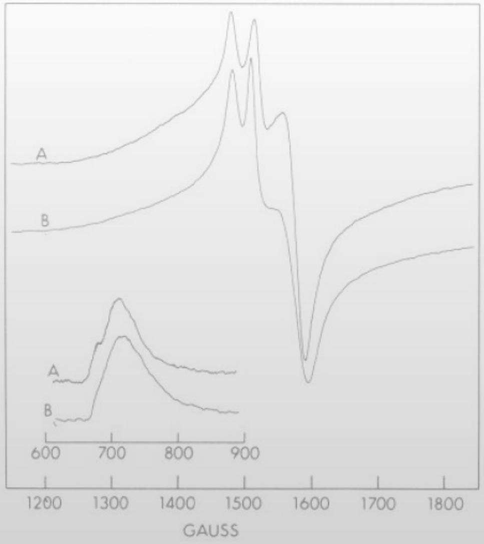
example: **The high-spin Fe(III) site in transferrin (S = 5/2)**

EPR





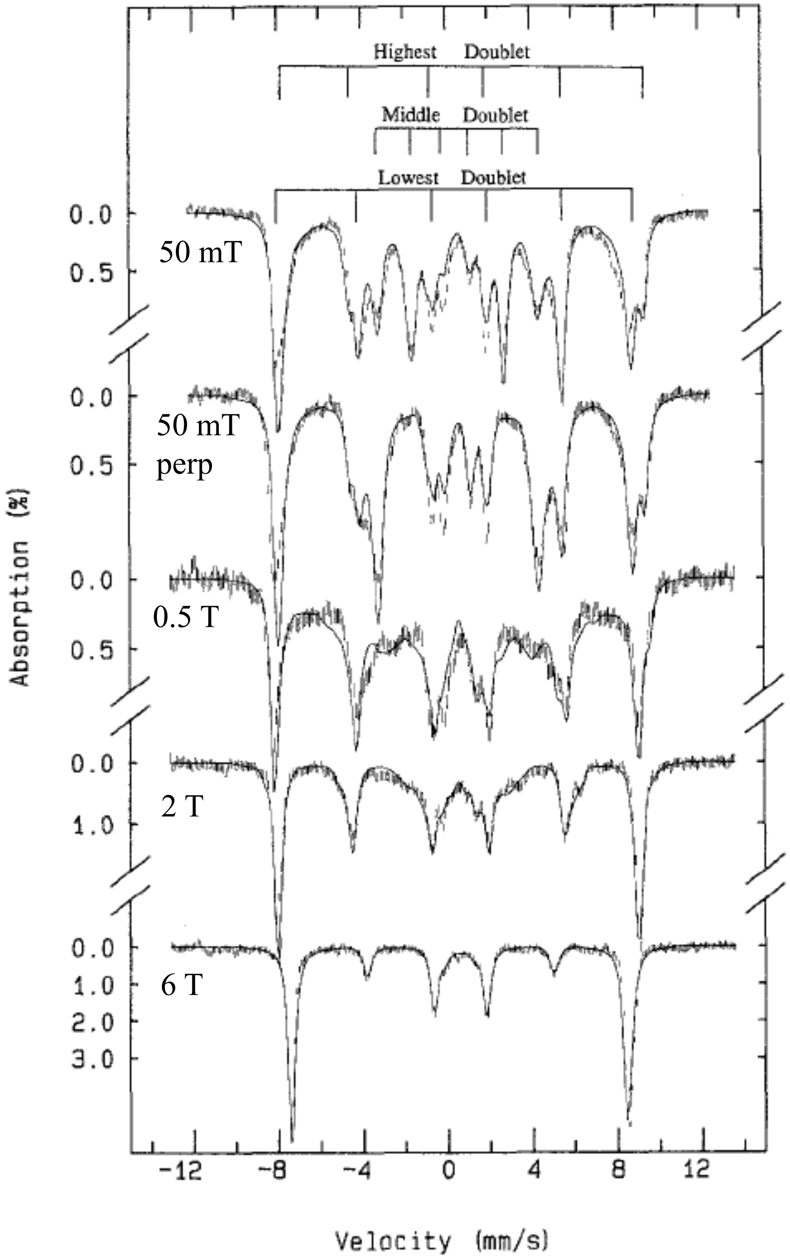




⇒ E/D ~ 0.3

(adapted from C. Krebs)

The high-spin Fe(III) site in transferrin (S = 5/2)



$D = 0.25\ \mathrm{cm}^{-1}$

$E/D = 0.3$

$g = 2.0$

$\delta = 0.54\ \mathrm{mm/s}$

$\Delta E_Q = 0.30\ \mathrm{mm/s}$

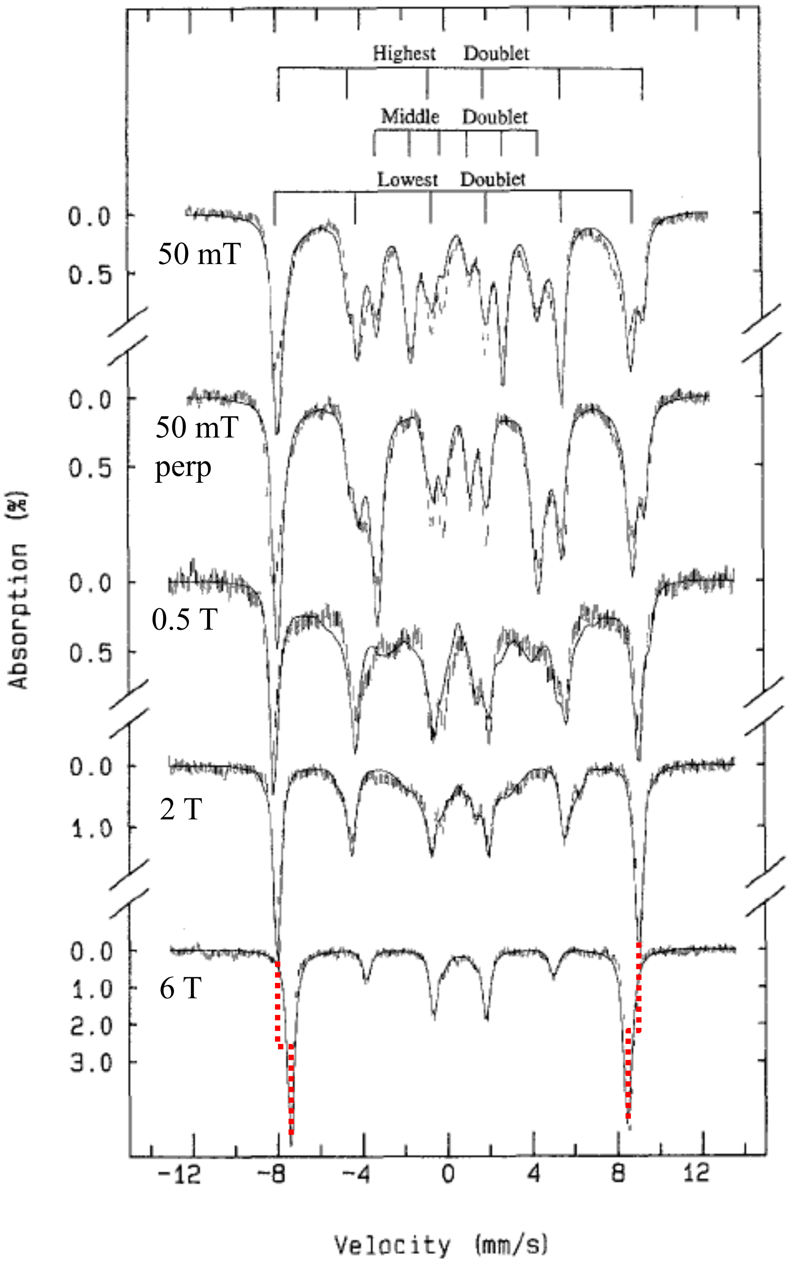
$\eta = 1.0$

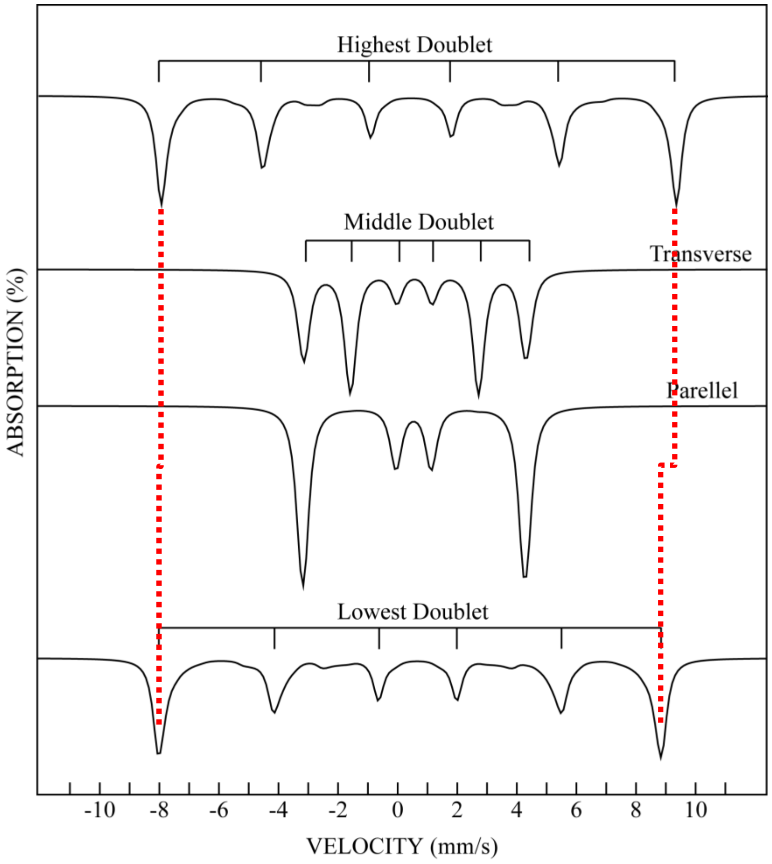
$\mathbf{A}/g_n\beta_n = (-22.3, -21.9, -22.3)\ \mathrm{T}$

(slow relaxation)

Kretchmar, et al. Biol. Metals 1988 (1) 26

The high-spin Fe(III) site in transferrin (S = 5/2)





Kretchmar, et al. Biol. Metals 1988 (1) 26

Some Mössbauer Books and Articles:

'*Mössbauer Spectroscopy*' by N.N. Greenwood and T.C. Gibb, Chapman and Hall Ltd. London, 1976

'*Mössbauer Spectroscopy Applied to Inorganic Chemistry*', Vol. 2,3, ed. G.J. Long,
Series *Modern Inorganic Chemistry*, ed. J.P. Fackler, jr, Plenum Press New York and London, 1987

'*Mössbauer Spectroscopy of Iron Proteins*' by P. G. Debrunner, in 'Biological Magnetic Resonance, Vol. 13, *EMR of Paramagnetic Molecules* (ed. L.J. Berliner, J. Reuben), pp. 59 - 102

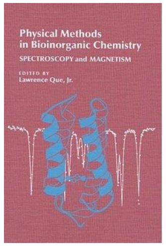
'*Iron-Containing Proteins and Related Analogs - Complementary Mössbauer, EPR and Magnetic Susceptibility Studies*' by A.X. Trautwein, E. Bill, E.L. Bominaar, H. Winkler, Structure and Bonding **78**, 1-96 (1991)

'*Structure and dynamics of biomolecules studied by Mössbauer spectroscopy*' by V. Schünemann and H. Winkler (2000) , Reports on Progress in Physics **63**(3): 263-353.

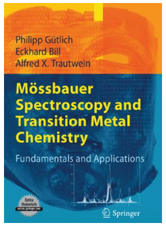
P. Gütlich, J. Ensling, Mössbauer Spectroscopy, in Inorganic Electronic Structure and Spectroscopy, Vol. I, Methodology, (eds. E. I. Solomon, A.B.P. Lever), pp. 161-212, J. Wiley&sons, New York, 1999

E. Bill in 'Practical Approaches to Biological Inorganic Chemistry' (R.R. Crichton R. Louro eds.), Elsevier, 2013

E. Münck in 'Physical Methods in Bioinorganic Chemistry' (Ed. L.Que), University Science Books,Sausalito, 2000



'*Mössbauer Spectroscopy and Transition Metal Chemistry*' by P. Gütlich, E. Bill, A. X. Trautwein, Springer, 2011



Applications of Mössbauer Spectroscopy

in (bio)inorganic chemistry mostly ^{57}**Fe** spectroscopy

✓ identification of (unknown) iron centers

✓ detection of local structural properties

(symmetry perturbations, ligand/substrate binding, ..)

✓ **characterization of the electronic structure**

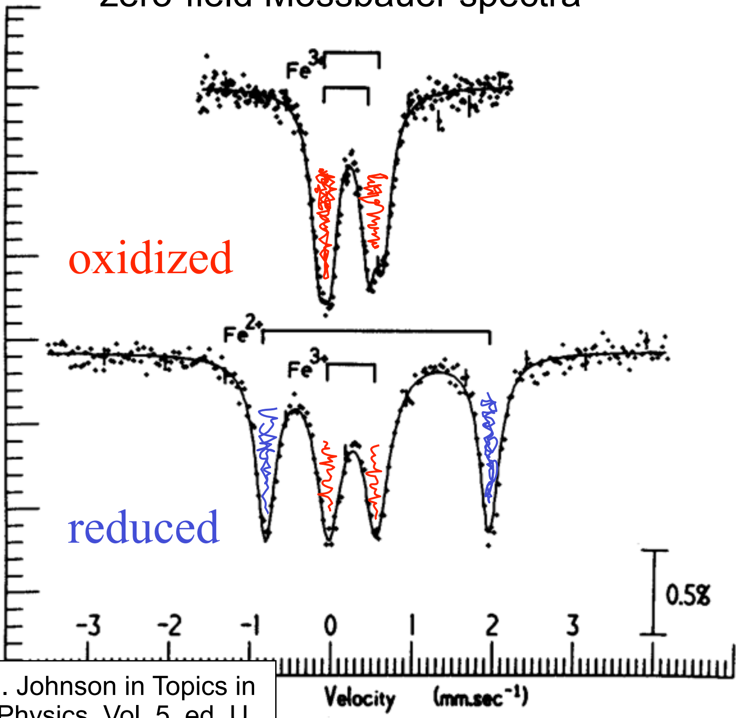
(valence, covalency, delocalization, spin coupling ...)

✓ probing of catalytic intermediates, 'local' redox steps, ...

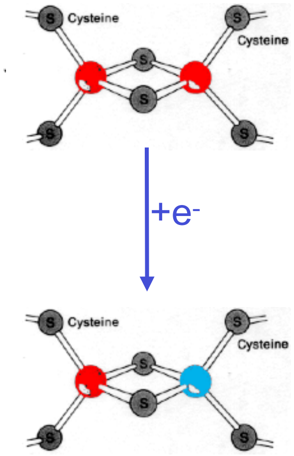
⇒ study model compounds, series, variations ...

[2Fe-2S]$^{1+/2+}$ cluster from plant-type ferredoxins, Rieske-center, ...

zero-field Mössbauer spectra



C.E. Johnson in Topics in Applied Physics, Vol. 5, ed. U. Gonser, Springer 1975)



Mössbauer spectra show reduction of a *single* iron ion

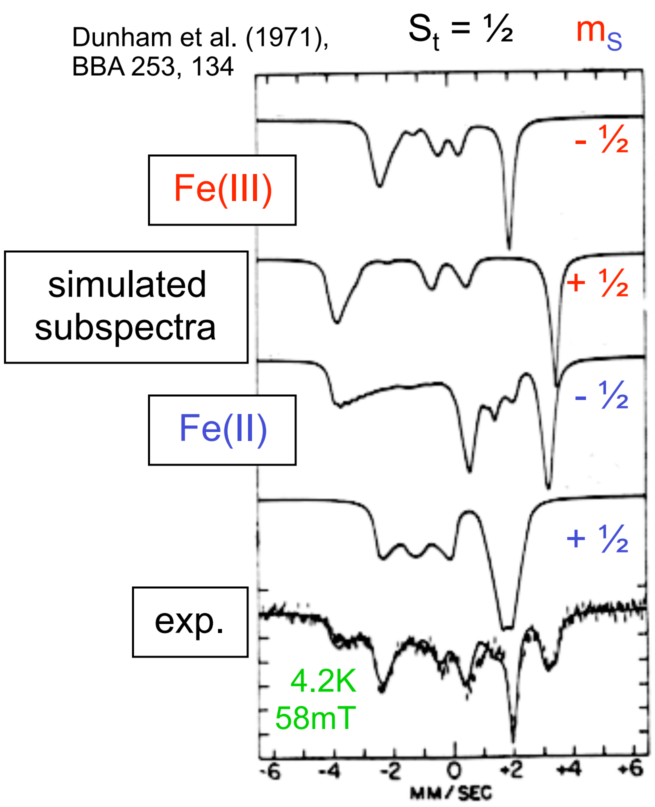
typical values for Fe(III) and Fe(II) in 4S-coordination

	δ[mm/s]	ΔE_Q [mm/s]
oxidized	0.27	0.65
reduced	0.25	0.64
	0.54	3.0

localized valences are unique for 2Fe-2S centers

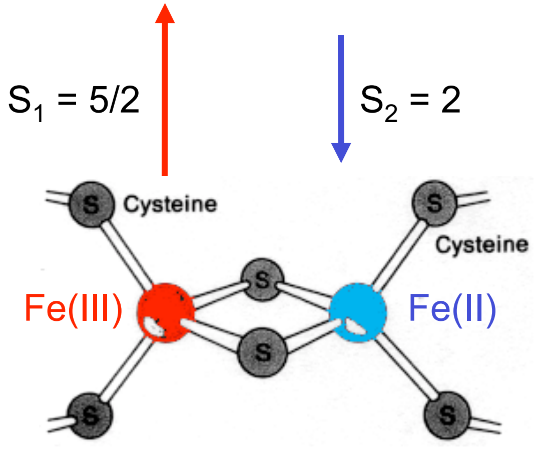
an example of paramagnetic ^{57}Fe Mössbauer spectra ...

spin-coupled [2Fe-2S]$^{1+}$ centers

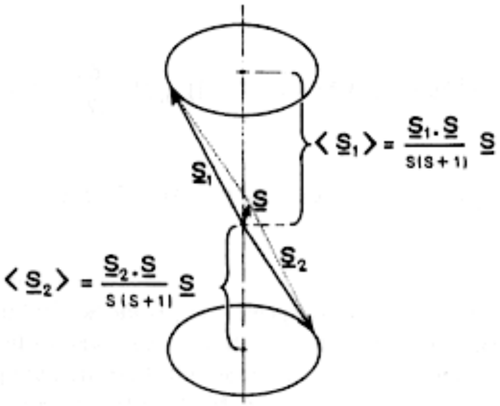


Dunham et al. (1971), BBA 253, 134

different applied fields help to probe the 'orientation' of the local efg- and A-tensors and zfs !



exchange interaction



$$\langle S_1 \rangle = \frac{S_1 \cdot S}{S(S+1)} S$$

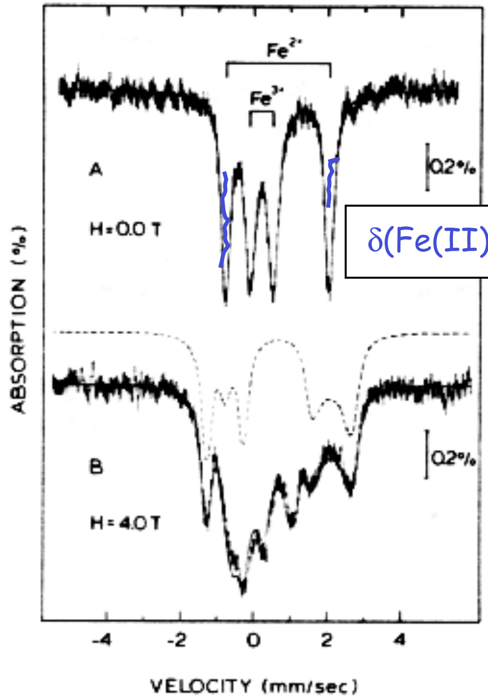
$$\langle S_2 \rangle = \frac{S_2 \cdot S}{S(S+1)} S$$

spin coupling scheme for total spin **S_t = ½** ground state

The Rieske 2Fe-2S Center

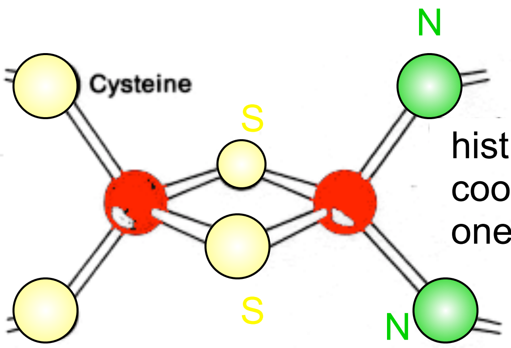
from *bc*$_1$ complex of the respiratory chain

J. Fee, E. Münck et al. (1984), JBC 259, 124

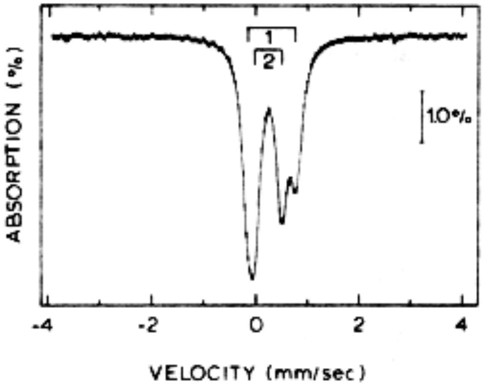


δ(Fe(II) = 0.74 mm/s

(vs. 0.54 mm/s)



histidine coordination on one side

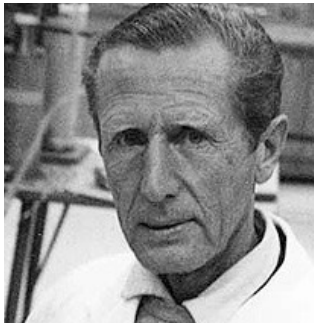


applied-field Mössbauer spectra show reduction of the histidine-coordinated iron

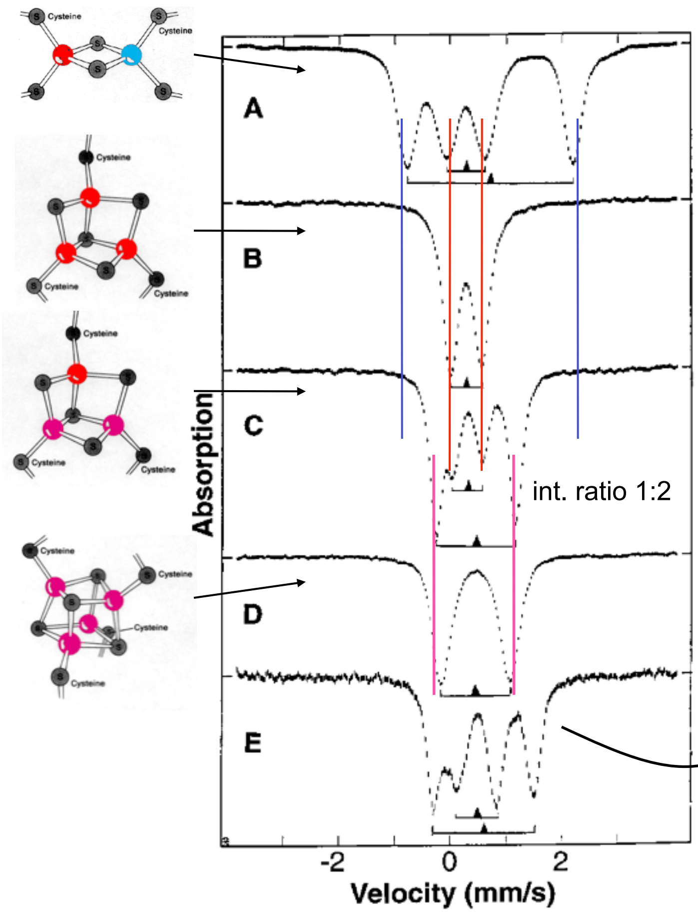
oxidized centers show slightly different iron sites

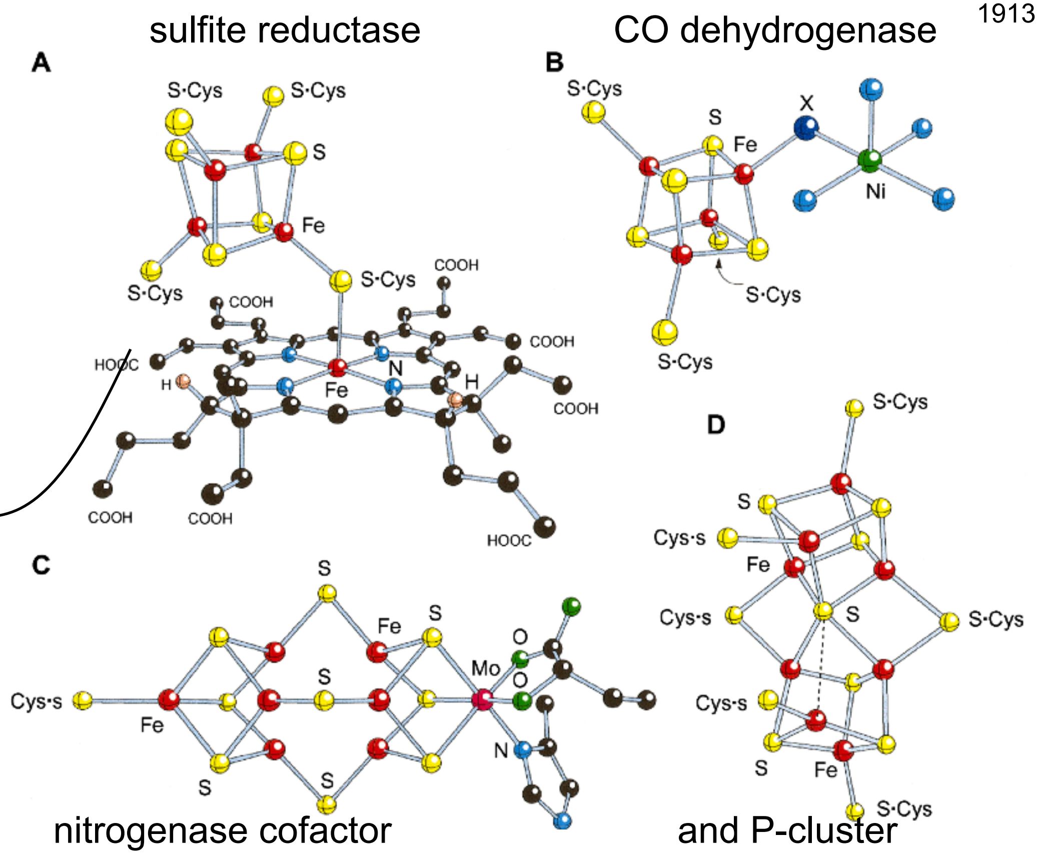
more Fe-S clusters ...

H. Beinert et al. (1997), Science, 277



H. Beinert, 1913 - 2007





sulfite reductase

CO dehydrogenase

nitrogenase cofactor

and P-cluster

valence delocalization in 3Fe-4S and 4Fe-4S clusters

typical values for the zero-field Mössbauer parameters of the 'basic' iron sulfur clusters

cluster	δ [mm/s] (at 4.2 K)	ΔE_Q [mm/s]
[1Fe]$^{3+}$	0.32	0.5
[1Fe]$^{2+}$	0.70	3.25
[2Fe-2S]$^{2+}$	0.27	0.65
[2Fe-2S]$^{1+}$ (a)	0.25 0.54	0.64 3.0
[3Fe-4S]$^{1+}$	0.24-0.27	0.54 – 0.71
[3Fe-4S]$^{0+}$ (b)	0.46 0.30	1.47 0.47
[4Fe-4S]$^{3+}$	0.40 0.29	1.03 0.88
[4Fe-4S]$^{2+}$	0.37 – 0.46	1.25 – 1.46
[4Fe-4S]$^{1+}$	0.50 0.58	1.32 1.89

(a) two subspectra 1:1
(b) two subsepctra 2:1