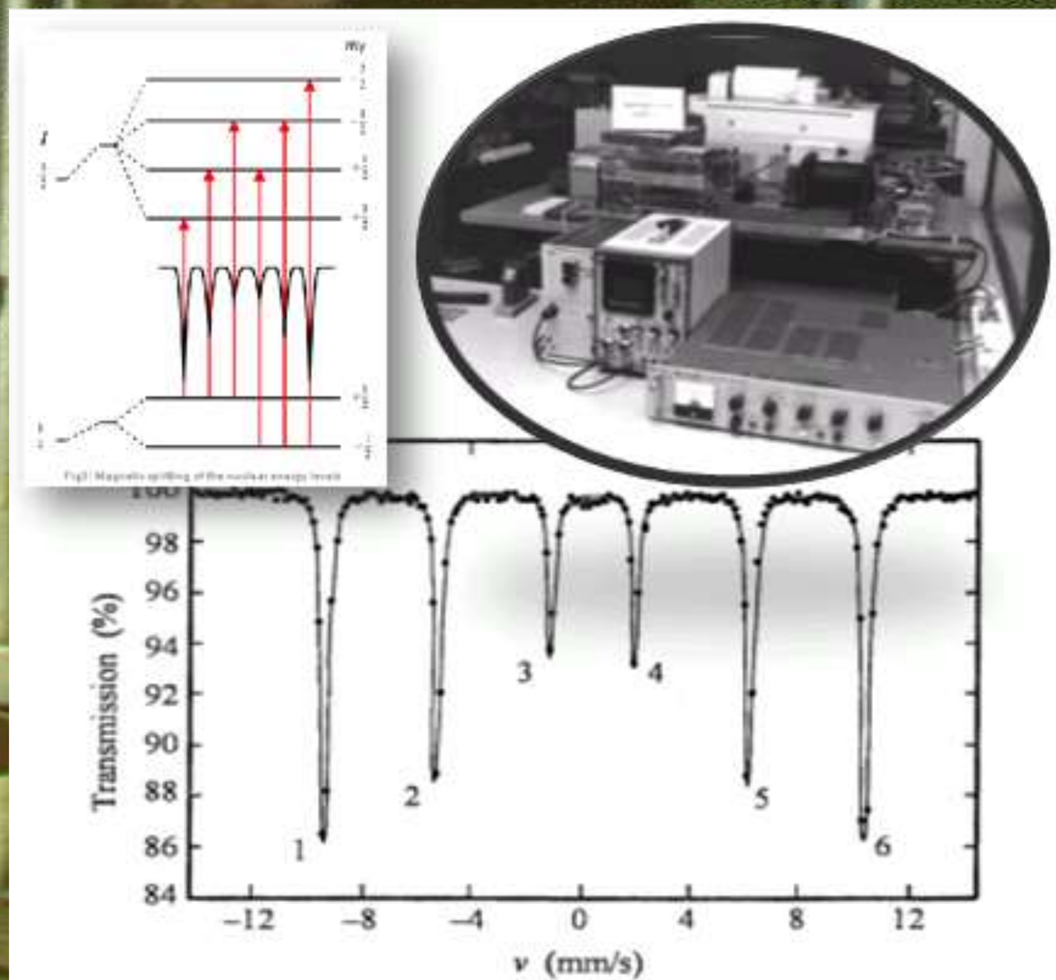
Mőβbauer Spectroscopy II



Agenda: ANSEL Mössbauer Experiment

Mößbauer (Mössbauer) Spectroscopy with proportional counters:

Ultra-high-precision photon energy measurement:
Precision scanning resonant-absorption spectroscopy
with doppler-shifted photon energy, using gas amplification counters.

- Gas amplification counters, proportional counters, electronics.

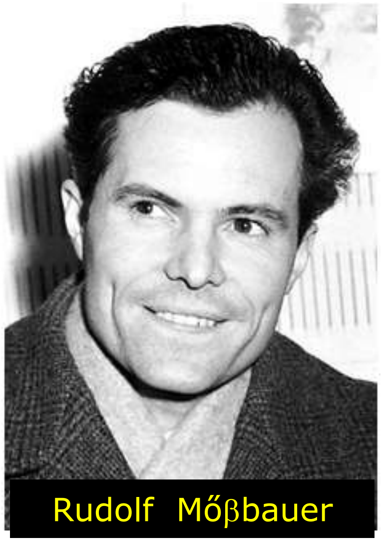
- Mössbauer Principles:

  Resonant γ absorption.
  Recoil effects in γ emission and absorption,
  Recoilless γ absorption by macroscopic samples,

- Determination of electric and magnetic HF interactions in various chemical Fe compounds

Reading Assignments:
(Knoll, LN): X ray spectroscopy with proportional counters (PC),
E_γ-dependent absorption coefficients, gas amplification counters,
Response of proportional counters to γ - and X rays, spurious peaks.

The Mőβbauer Effect



1961 Nobel Prize in Physics.

Discovered (1958) recoilless nuclear fluorescence of gamma rays in ^{191}Ir.

Famous application: proof of red shift of gamma radiation in the gravitational field of the earth (Robert Pound and Glen Rebka);
Pound–Rebka experiment was one of the first experimental precision tests of Albert Einstein's theory of general relativity.

Long-term importance:

Use of Mössbauer effect in
"Mössbauer spectroscopy" testing solid-state and chemical environments via electric and magnetic hyperfine interactions between atomic electrons and nuclear charge and magnetization distributions.

Nuclear Resonance Photo Absorption

Absorption of radiation= competition of various interactions between photons and microscopic structure (atomic, nuclear) of material →

absorbance = sum of statistical probabilities per constituent.

Mass absorption coefficient (photons): $\boxed{\mu\left(E_\gamma\right)=\sum_n \mu_n\left(E_\gamma\right)}$

^{57}Co

Nuclear
Resonance Absorption

$\mu_\nu(E_\gamma)=\mu_{res}(E_\gamma)$

Breit – Wigner Resonance

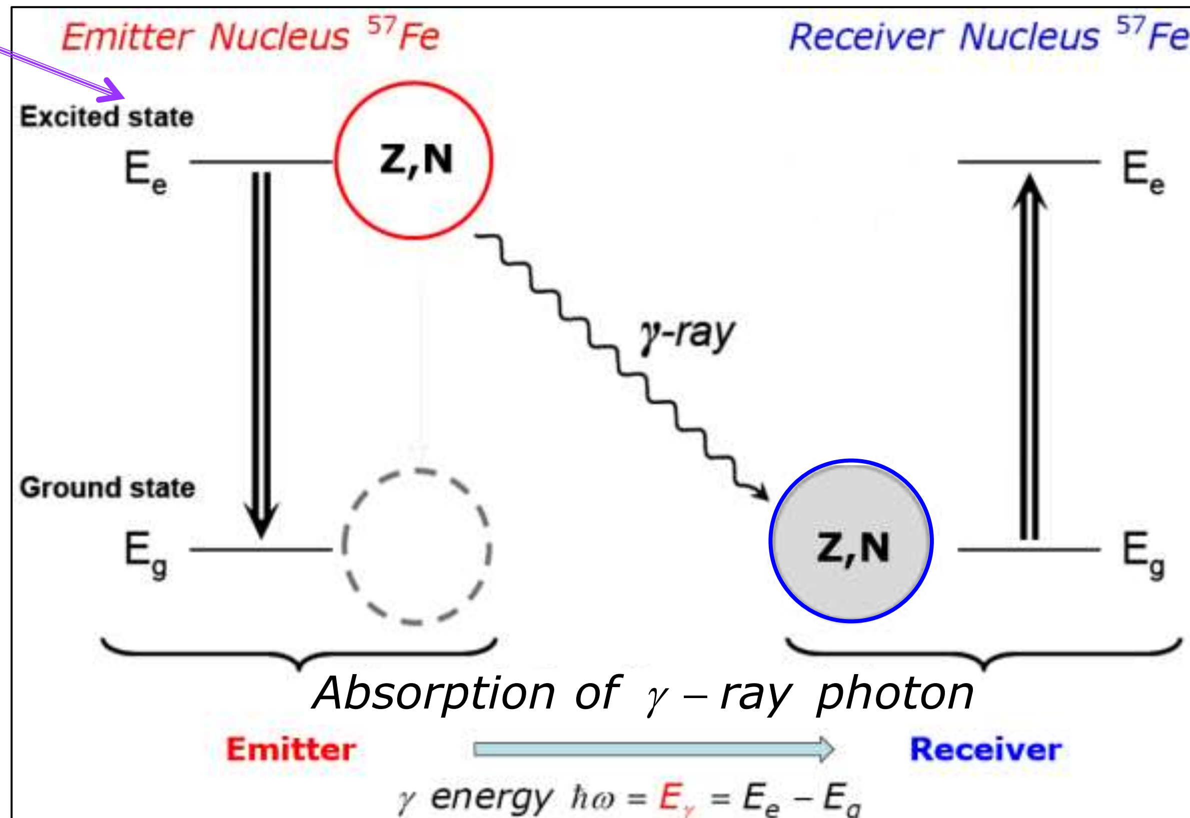
$$\mu_{res}(E_\gamma)\propto\frac{(\Gamma_e/2)^2}{(\Gamma_e/2)^2+\left(E_\gamma-E_e\right)^2}$$

Resonance parameters E_e,Γ_e

Free nucleus:

Recoil effects

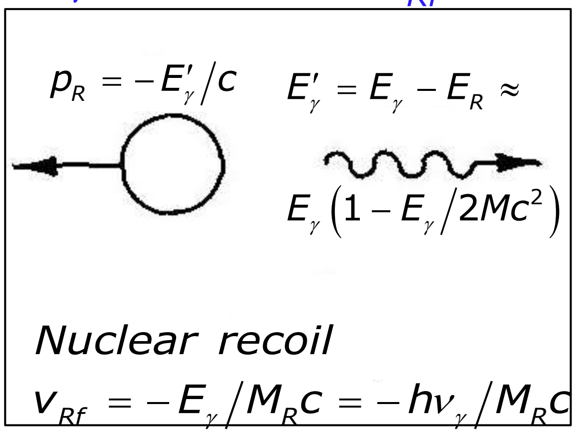
$$E_\gamma\neq E_e-E_g$$



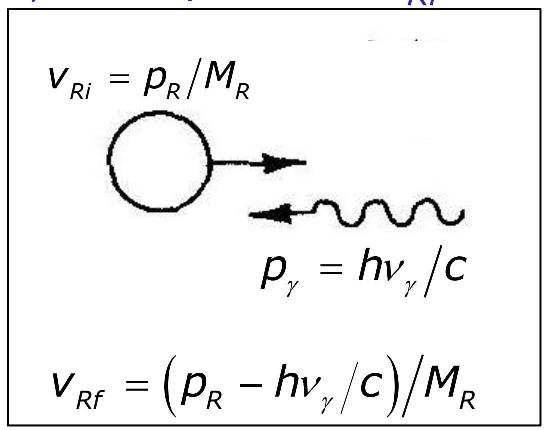
Spectroscopy Challenge: Doppler Shifted γ Energy

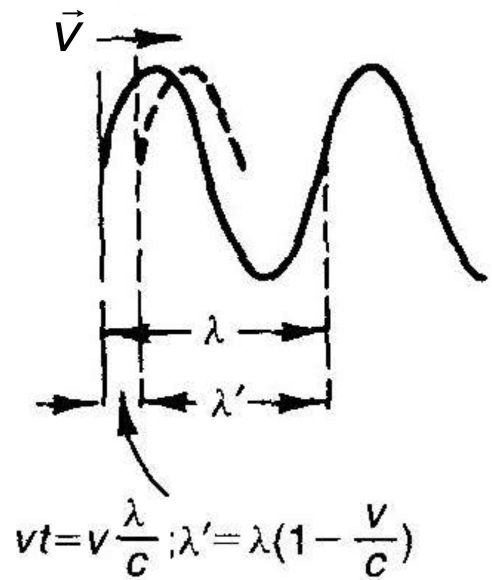
Emission and absorption of γ-rays by nuclei in motion (υ thermal lattice vibrations, recoil effects due to γ emission) → **Doppler effect** both in emission and absorption.
→ γ emission or absorption energy is different from
Nominal transition energy $h\nu_{if} = (E_i - E_f)$ (photon and nuclear recoil) $E_\gamma(\upsilon) \neq E_i - E_f$

γ *emission* @ $v_{Ri} = 0$



γ *absorption* @ $v_{Ri} \neq 0$





Observer Lab velocity v
$\rightarrow \lambda$ *red(blue) shift*

Typical Lab recoil velocities $\upsilon_R \sim \left(10^3 - 10^5\right) cm/s$

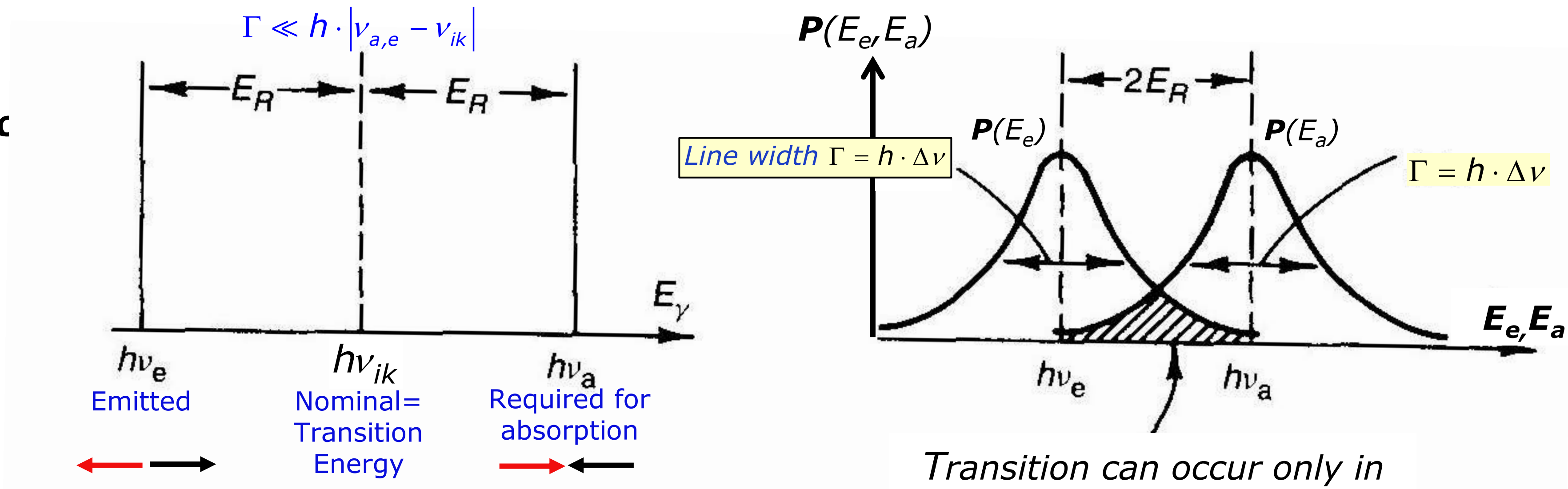
$$\text{Doppler Shift}: E_\gamma(\upsilon) \approx h\nu_{ik} \cdot \left(1 \pm \upsilon/c\right)$$

$\pm$ *sign* : ν *blue or red shift*

Emission/Absorption of γ-Rays in Thermal Environment

Quantum Effect: System absorbs electromagnetic radiation strongly if γ energy $h\nu$ equals a system energy level difference: $h\nu_{ik} = (E_i - E_k)$. For absorption, the lower level *(i, k)* must be occupied, the other empty.

→ **Use for scanning level scheme *{E_n}***



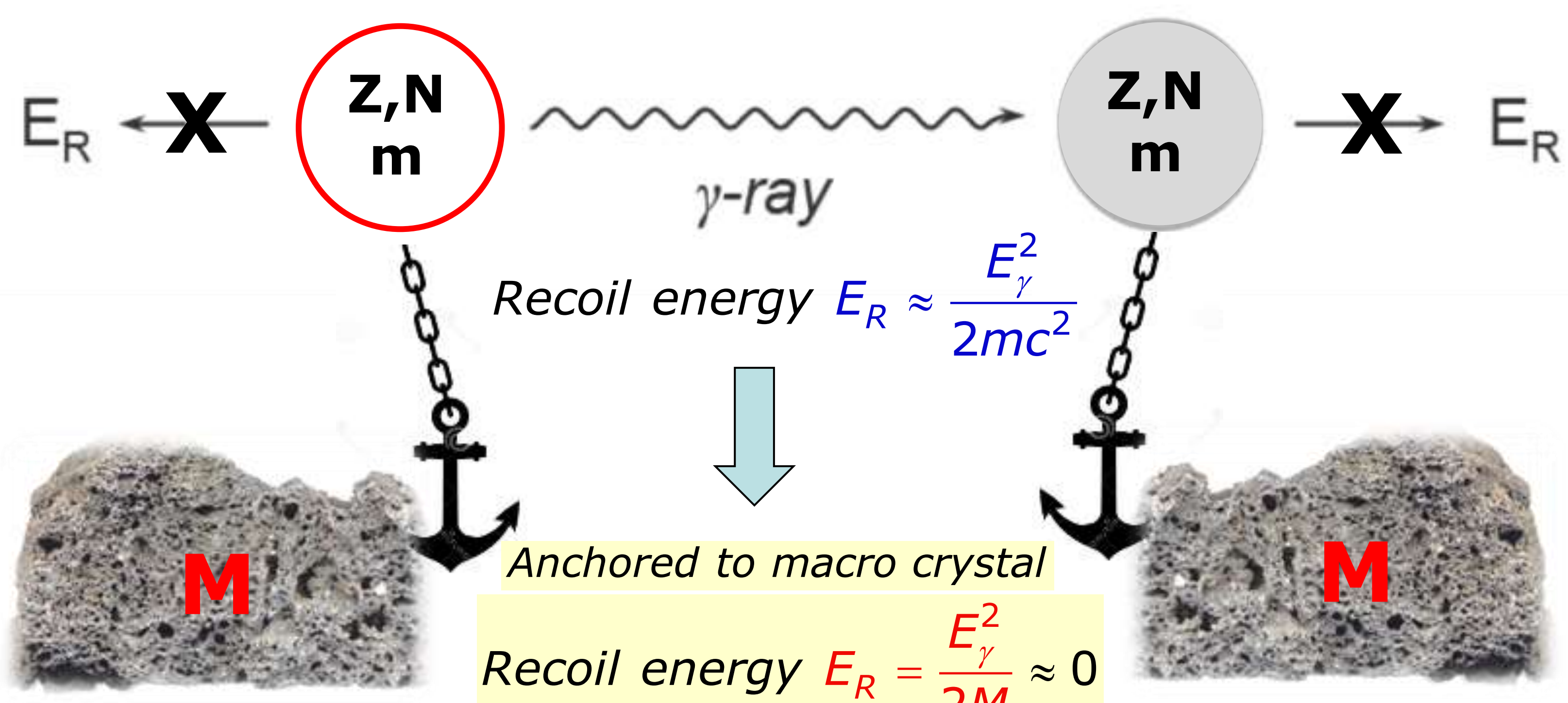
Transition can occur only in overlap region

Quantum Effect ➔ Coherent line broadening.
Normal environment $T \neq 0$ →
Thermal motion of nuclei → Incoherent line broadening.
Velocity distributions of emitters and absorbers lead to broad line shapes, wash out resonance requirement, broader with increasing T.

Recoilless Emission/Absorption

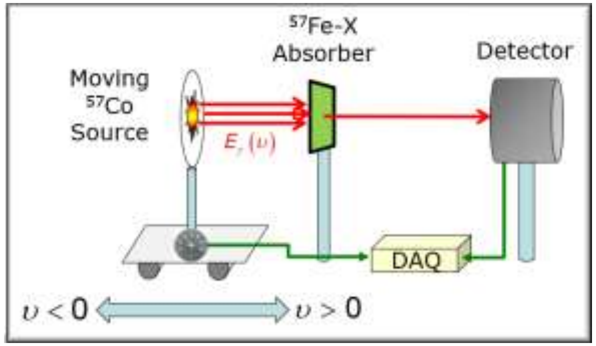
Momentum-energy transfer to nucleus (mass *m*) changes effective γ energy → Loss of resonance condition

Emitter Nucleus ^{57}Fe *Receiver Nucleus* ^{57}Fe



Momentum-energy transfer to nucleus embedded in macro crystal lattice is negligible → Resonance condition retained → Allows for precision absorption/emission spectroscopy!

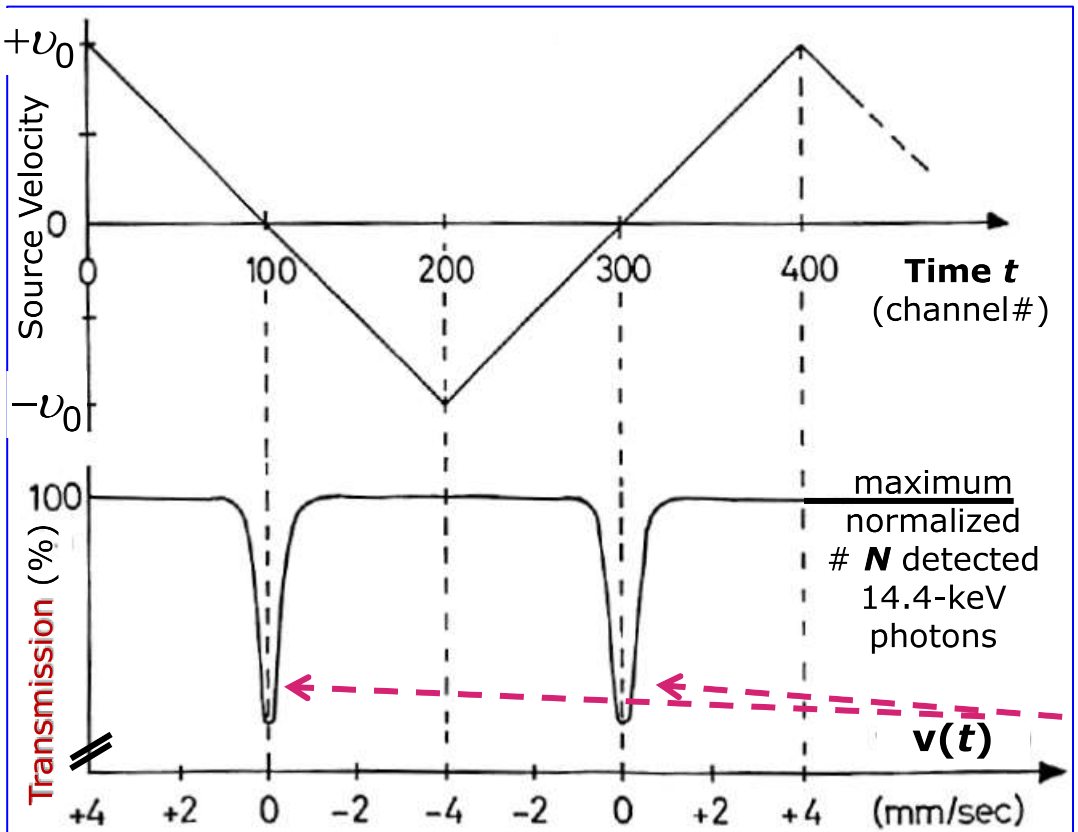
Precision Absorption Spectroscopy



$$\boxed{Tunable\ E_\gamma(\upsilon) = 14.4(1 \pm \upsilon/c)\,keV}$$

Lower transmission for $E_\gamma(\upsilon) = E(\langle^{57}Fe\rangle)$

Calibration $\langle^{57}Fe\rangle \equiv {}^{57}Fe$ *in Fe absorber lattice*



Example:
Identical crystal lattices of source & absorber
and *linear velocity* drive.
No external/crystal fields

$$\upsilon(t) = \upsilon_0 \cdot (t_0 \pm t);\ linear$$
$$t \in [nT, (n+1)T]$$
$$\rightarrow dN/dt \propto dN/d\upsilon$$

Maximum (resonant)
no – field absorption at
$E(\langle^{57}Fe\rangle) = E_\gamma(\upsilon = 0)$

W. Udo Schröder, 2024

Mőβbauer Spectroscopy Applications

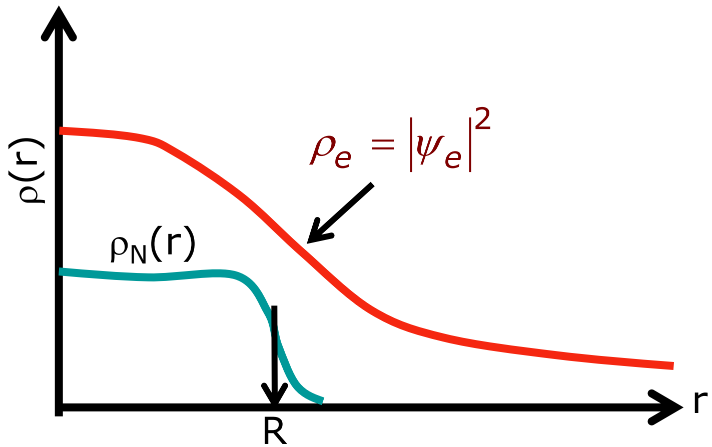
Precise level energy scan, resolution $\Delta E \sim 10^{-10}$ eV

→ Investigate small perturbations of nuclear level energies due to interactions between

- ❑ Nuclear charge distributions and electronic density distributions in molecules, solid lattices
  → chemical shifts, electrostatic hyperfine interactions;

- ❑ Nuclear spins and magnetic moments with external magnetic fields, man-made or in lattices
  →spin and g-factor determinations, magnetic hyperfine interactions.

Isomer (Chemical) Shift of Atomic States



Perturbation theory calculation of nuclear energy level, perturbation = H' due to interaction of ρ(r) with electrons ψ(r)

$$H'(r) = V(r<R) - V_0(r) = \textit{interaction}$$

$$\delta E_e = \langle \psi_e | H' | \psi_e \rangle \equiv \int \psi_e^*(r) H'(r) \psi_e(r) d^3 r$$

$$\delta E_e = \frac{1}{10\varepsilon_0} Z e^2 R_n^2 |\psi_e(0)|^2$$ Nuclear state (n=0,1,..)

$$\Delta E = \frac{1}{10\varepsilon_0} Z e^2 |\psi_e(0)|^2 \left(R_1^2 - R_0^2\right)$$ Difference between 2 states

$$\Delta E_{isomer} = \Delta E_{absorb} - \Delta E_{source} =$$

$$= \frac{1}{10\varepsilon_0} Z e^2 \left(R_1^2 - R_0^2\right)\left[\left|\psi_e^{absorb}(0)\right|^2 - \left|\psi_e^{source}(0)\right|^2\right]$$

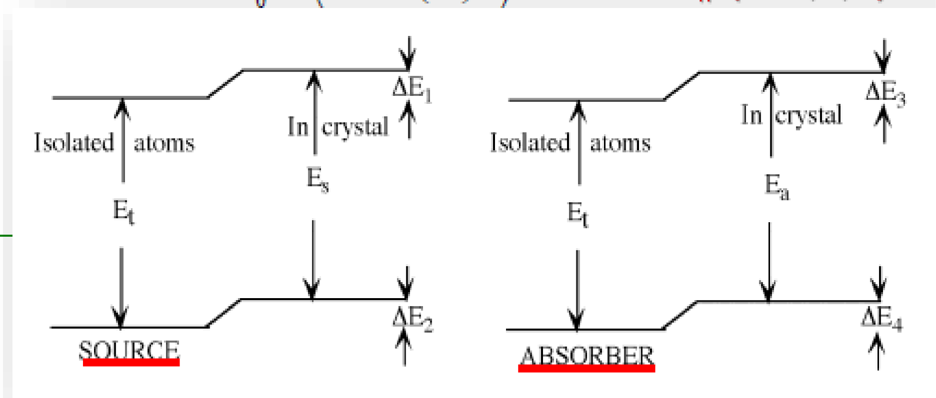
Coulomb potential for spatially extended nucleus → depends on R

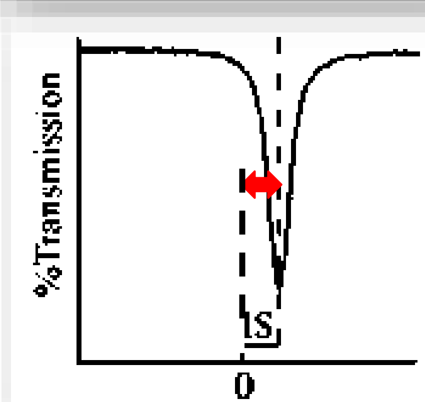
Point → finite size→ *Perturbation* $H'(r) = V(r) - V_0(r)$

$$V_0 = \frac{1}{4\pi\varepsilon_0}\frac{Ze}{r} \quad \text{for } r \geq R_n$$

$$V(r<R) = \frac{Ze}{4\pi\varepsilon_0}\frac{1}{R}\left(\frac{3}{2} - \frac{1}{2}\left(\frac{r}{R}\right)^2\right)$$

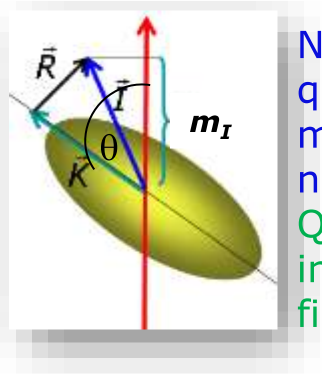
Finite Size nuclear states Radii $R=R_n$ (n=0,1,..)



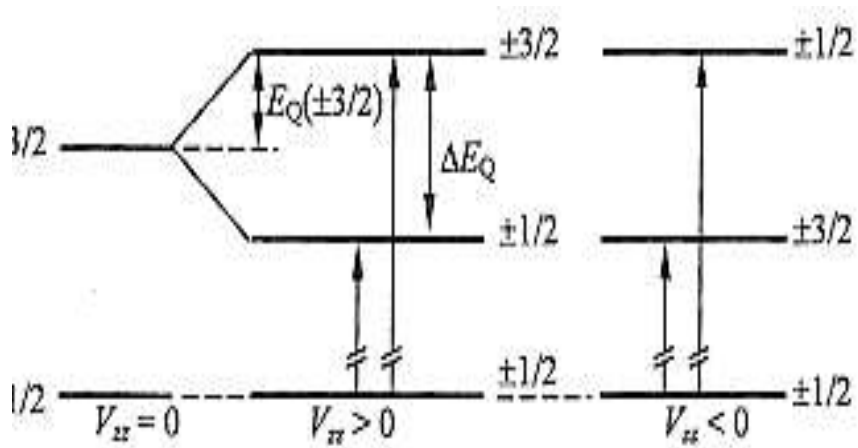


Transmission of γ-rays through absorber depends on source velocity
→ scan with $T=T(v)$

Electric Quadrupole Hyperfine Interaction in Atoms



Nuclear electric quadrupole moment eQ measures deviation of nucleus from sphere. Q_{eff}(I) can be aligned via interactions of external fields (spin I alignment).



Electric Field Gradient $\boldsymbol{V_{zz}}$

Energy shift depends on orientation of Q (i.e., I) with respect to crystal field gradient. Q_{eff} = Q′= 0 for I = 0,1/2

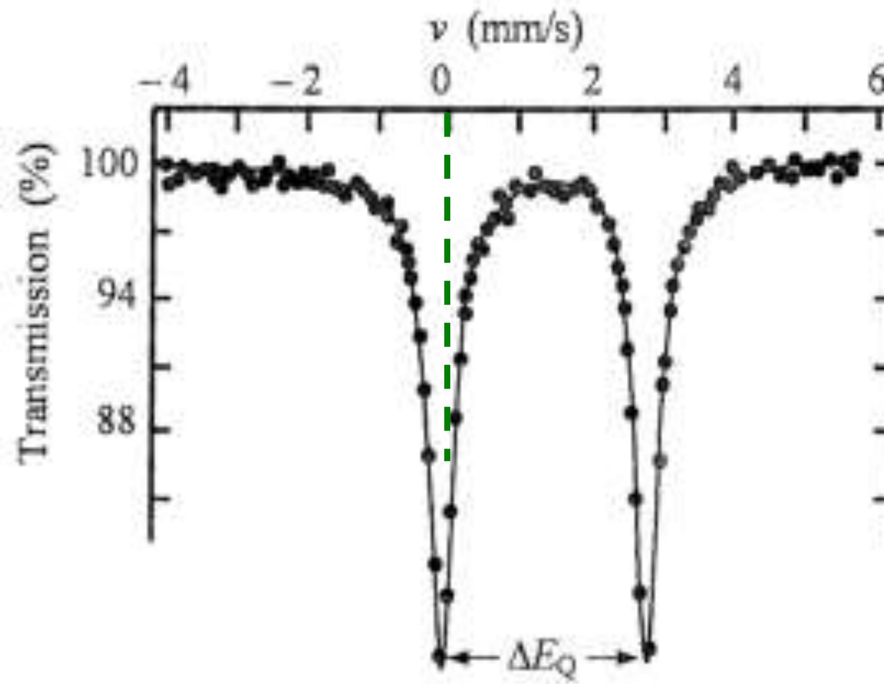
$$eQ=\int \rho(r)\, r^2\, (3\cos^2\theta-1)\, d^3r$$

$$E_Q=\frac{1}{4}eQ'\left(\frac{3}{2}\cos^2\theta-\frac{1}{2}\right)\left(\frac{\partial^2 V_{ext}}{\partial z^2}\right)_{z=0}$$

Orientation (I, m_I) dependent quadrupole shift

$$E_Q=eQ\,\frac{3m_I^2-I(I+1)}{4\,I(2I-1)}\left(\frac{\partial^2 V_{ext}}{\partial z^2}\right)_{z=0}$$

$\boldsymbol{V_{zz}}$



W. Udo Schröder, 2024

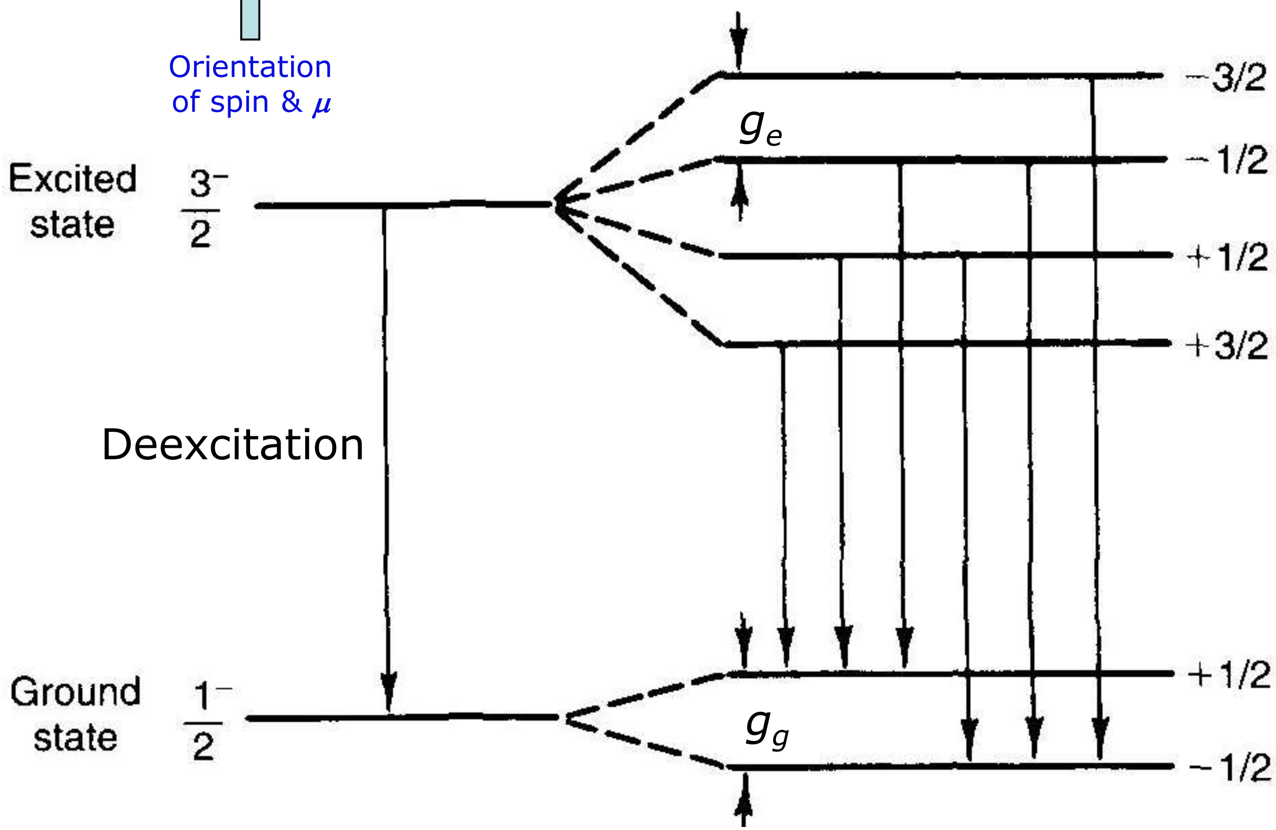
Magnetic Hyperfine Splitting in Atoms

Nuclear magneton $\boldsymbol{\mu_N}$ = 5.05078324(13)×10^{-27} J/T

$$\Delta E_n = -\vec{\mu}\cdot\vec{B} = -m_I g_n \mu_N B_z$$

Orientation of spin & μ

Nuclear magnetic moment μ oriented || to spin I, can be aligned w/r to magnetic field B. ***g_N*** = gyro-magnetic ratio: different for different nuclear states → structure information!



Hyperfine structure splitting of the nuclear energy levels of ^{57}Fe. (a) When stainless steel is used, the levels are not split. (b) In ordinary iron, however, both levels are split, giving rise to a hyperfine structure with six components.

Ferro-Magnetic HF Interaction

$$\delta E_i^{exp} = E_\gamma\left(1+\frac{\upsilon_1}{c}\right) \quad \textit{scan}$$

$$HF: E_{\vec{\mu}} = -\vec{\mu}\cdot\vec{B} = -m_I\cdot\left(g\cdot\mu_N\right)_I\cdot\left|\vec{B}\right|$$

$$Nuclear\ \ states\ \ \mu_{g,e} = +\left(I\cdot g\right)_{g,e}\mu_N$$

$g_{e,g}$ = gyro-magnetic ratios

μ_N = Bohr Magneton (unit)

$$\delta E_{\Delta\mu_{ij}} = -\left(g_e m_i - g_g m_j\right)\mu_N B$$

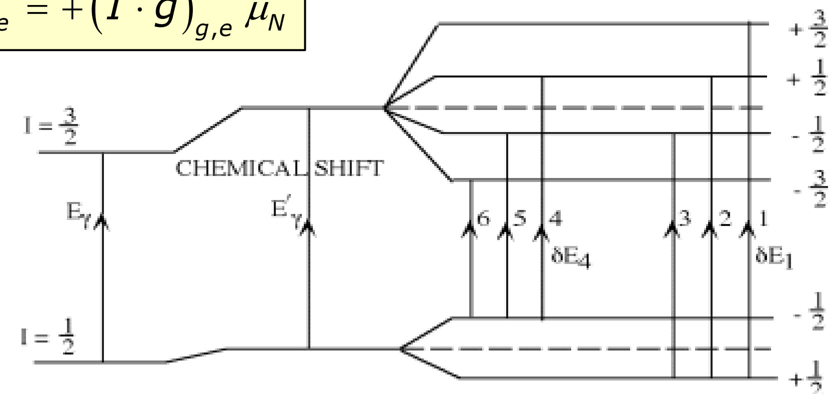
Chemical Shift IS

$$\begin{aligned}\delta E_1 &= E'_\gamma - (3/2g_e - 1/2g_g)\mu_N B\\ &= E'_\gamma - (\mu_e - \mu_g)B\end{aligned}$$

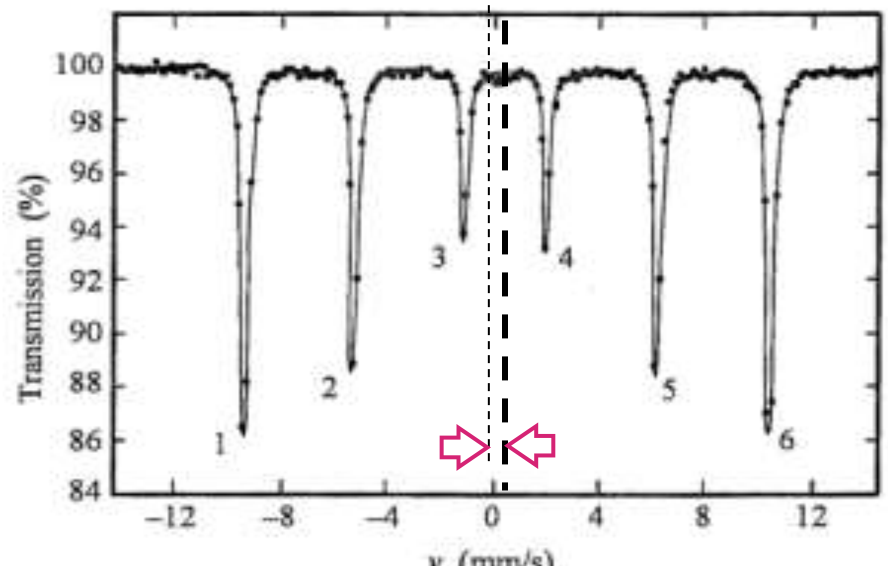
$$\begin{aligned}
E_\gamma\left(1+\frac{v_1}{c}\right) &= E'_\gamma - (\mu_e - \mu_g)B\\
E_\gamma\left(1+\frac{v_2}{c}\right) &= E'_\gamma - (\mu_e/3 - \mu_g)B\\
E_\gamma\left(1+\frac{v_3}{c}\right) &= E'_\gamma - (-\mu_e/3 - \mu_g)B\\
E_\gamma\left(1+\frac{v_4}{c}\right) &= E'_\gamma - (\mu_e/3 + \mu_g)B\\
E_\gamma\left(1+\frac{v_5}{c}\right) &= E'_\gamma - (-\mu_e + \mu_g)B\\
E_\gamma\left(1+\frac{v_6}{c}\right) &= E'_\gamma - (-\mu_e - \mu_g)B
\end{aligned}$$

$$(v_1 - v_2)\frac{E_\gamma}{c} = -\frac{2}{3}\mu_e B$$

$$(v_2 - v_4)\frac{E_\gamma}{c} = 2\mu_g B \quad \Rightarrow \quad \frac{v_1 - v_2}{v_2 - v_4} = \frac{-\mu_e}{3\mu_g}$$



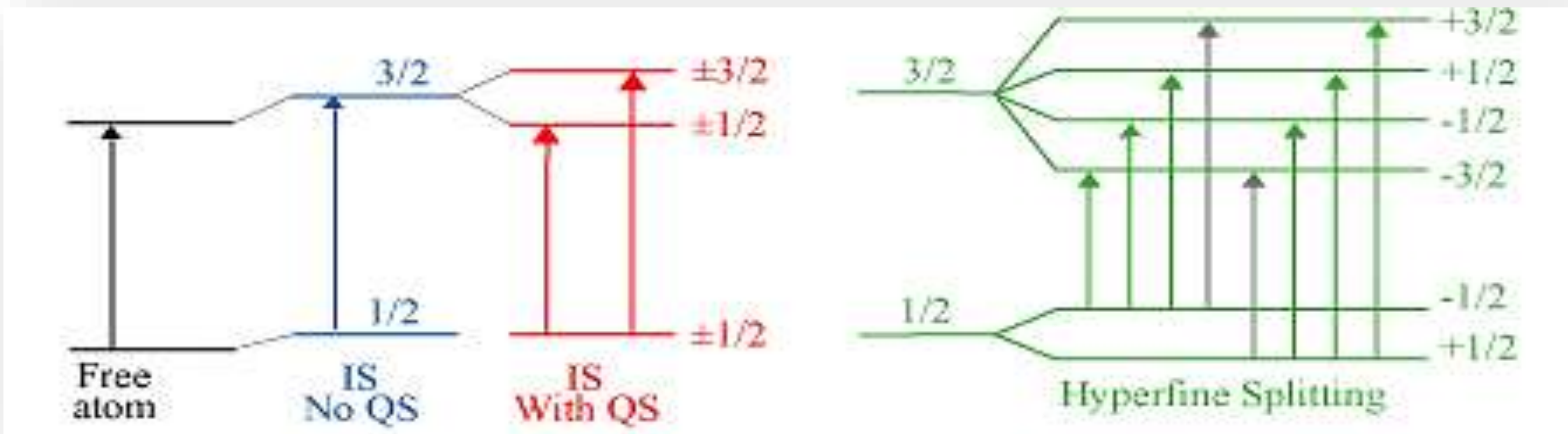
Ferromagnetic Fe absorber→ observe magnetic HF



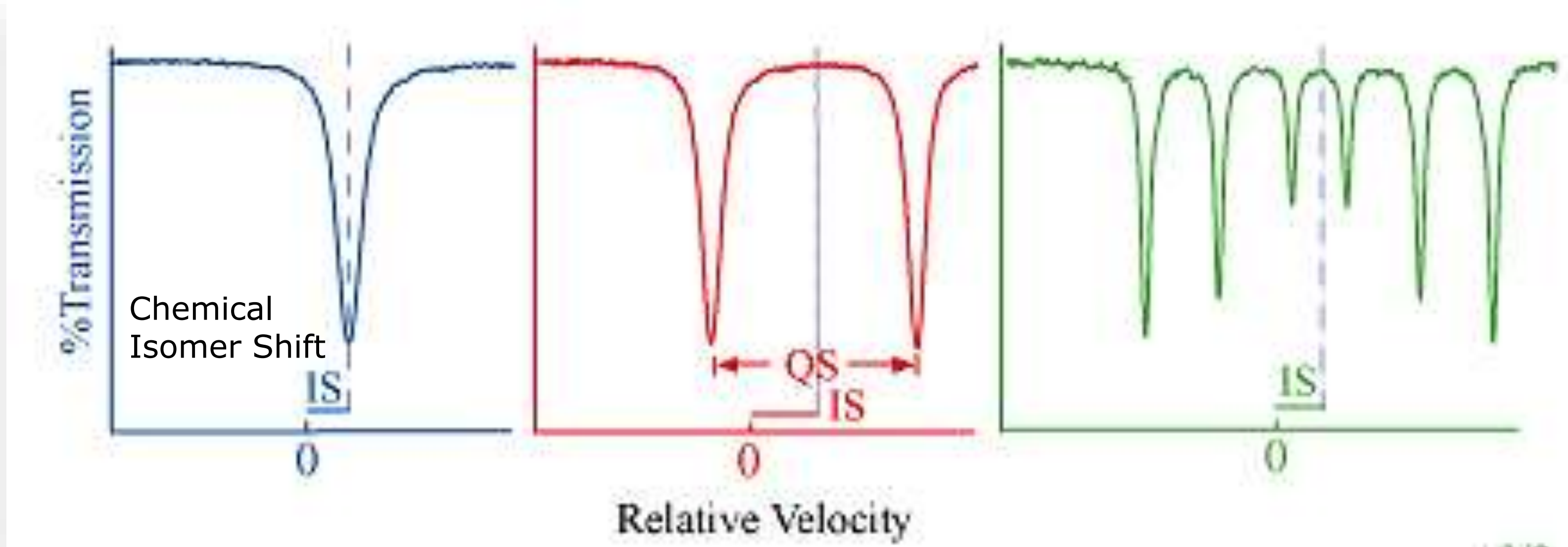
Velocity $v=-v_1 < 0$ source moving towards absorber

Electric + Magnetic HF Interactions

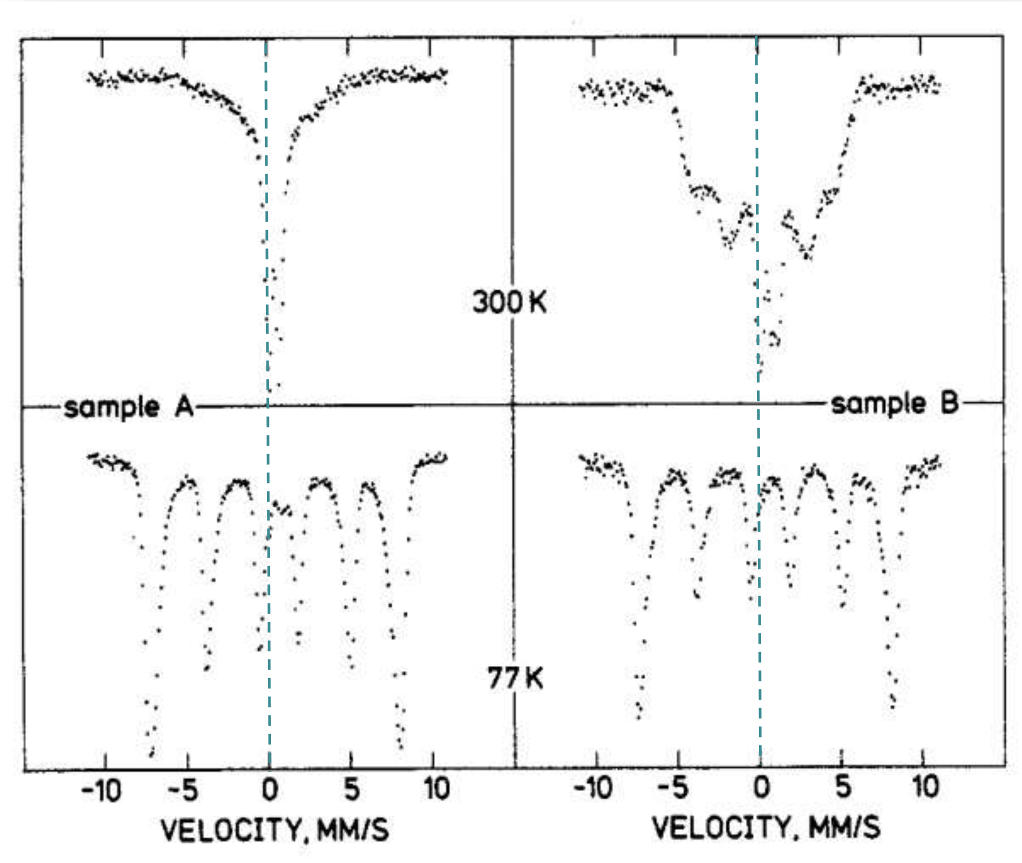
Isomer-shifted Fe hyperfine level scheme and allowed E1 transitions



Mössbauer velocity absorption spectra are shifted against zero and split



Applications in Chemistry/Material Science



Simulation of chemical reaction in Martian (oxygen-free) environment.

Precipitation of Fe in water under influence of UV light:

Intense Hg lamp at distance d from quartz flask
with Fe^{2+} solution d=5cm (A) or d=10cm (B) → Factor 4 in UV intensity

Moessbauer parameters at liquid-nitrogen temperature (77 K) of the photooxidized precipitation samples A and B, compared to natural FeOOH

→ α-FeOOH precipitates (B has larger particles, strong B field at 300K)

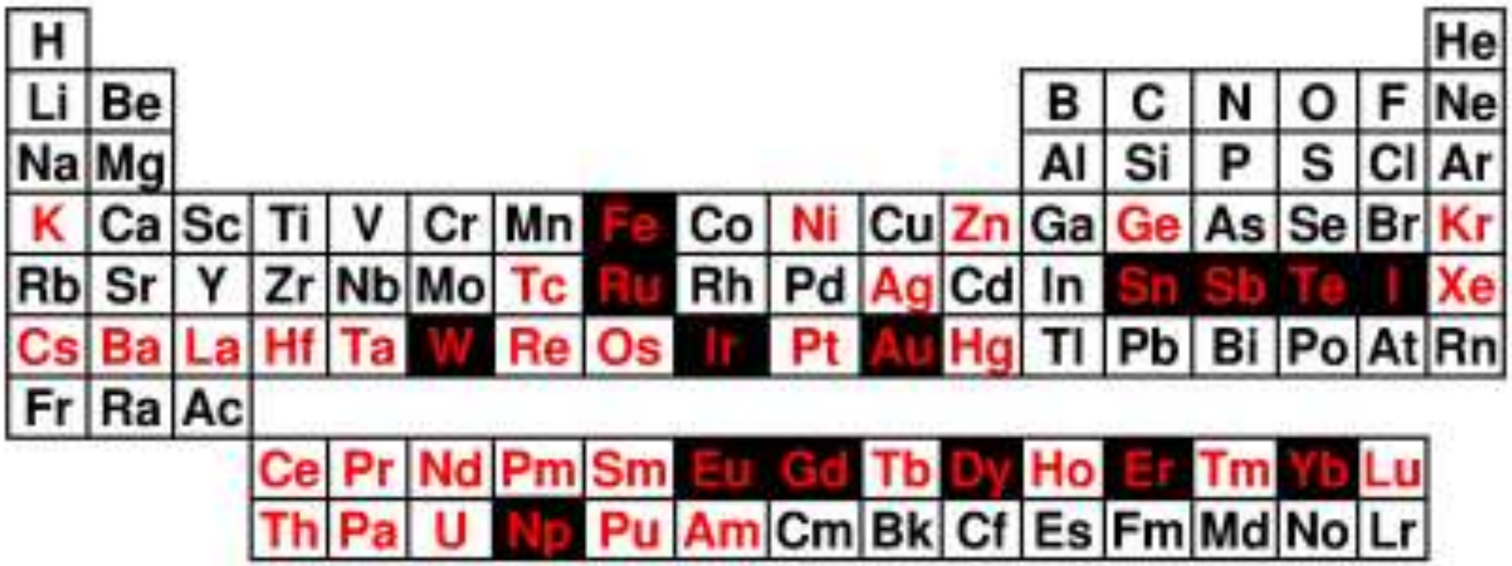
		δ (mm s^{-1})	Δ (mm s^{-1})	H (kG)
Photooxidized Fe^{3+}	sample A	0.39	−0.15	477
	sample B	0.38	−0.11	483
Natural FeOOH	α-FeOOH	0.39	−0.13	487
	γ-FeOOH	0.49	0.54	0

δ: isomer shift, relative to Fe metal
Δ: quadrupole splitting
H: magnetic hyperfine field

Other Möβbauer Cases

^{57}Fe is by far the most common isotope used in Möβbauer experiments.

Isotopes of other elements also frequently studied: ^{129}I, ^{119}Sn, ^{121}Sb



Elements of the periodic table which have known Mössbauer isotopes (shown in red font).

The End