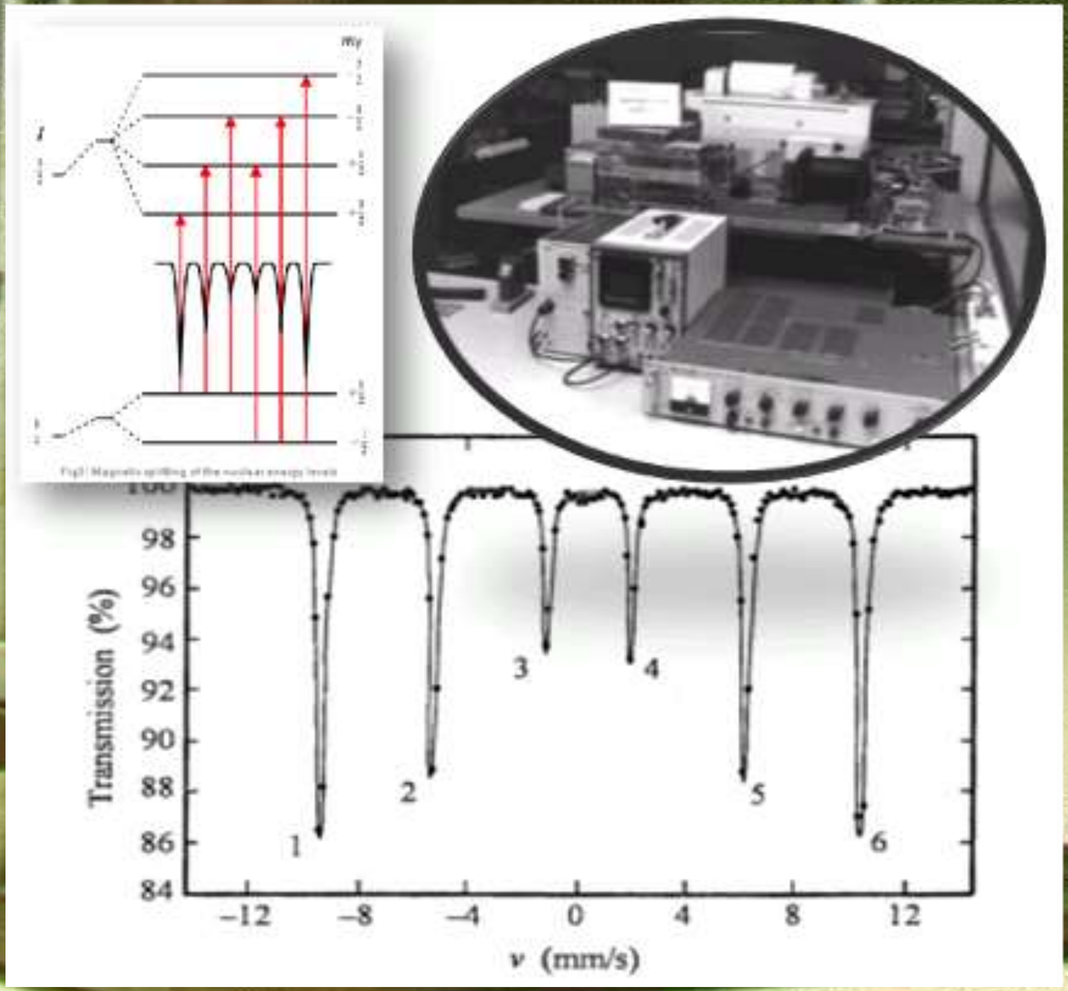
Mőßbauer Spectroscopy II



Agenda: ANSEL Mössbauer Experiment

Möβbauer (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.

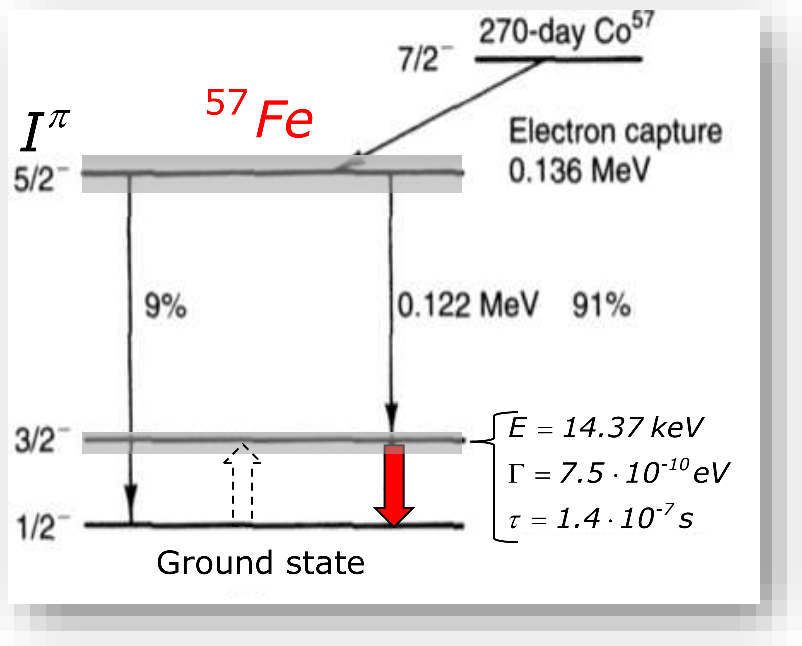
- Mössbauer Principles:

  Resonant γ absorption (=part of μ_{total}).
  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.

Precision Absorption Spectroscopy with ^{57}Fe



^{57}Co source emits 14.4 – keV γ – rays

Measure scanning resonance absorption

with Doppler – tunable γ – ray energies

→ chemical compounds $^{57}Fe - X(t)$

$$\text{"Tunable"}\ \ \gamma - rays$$

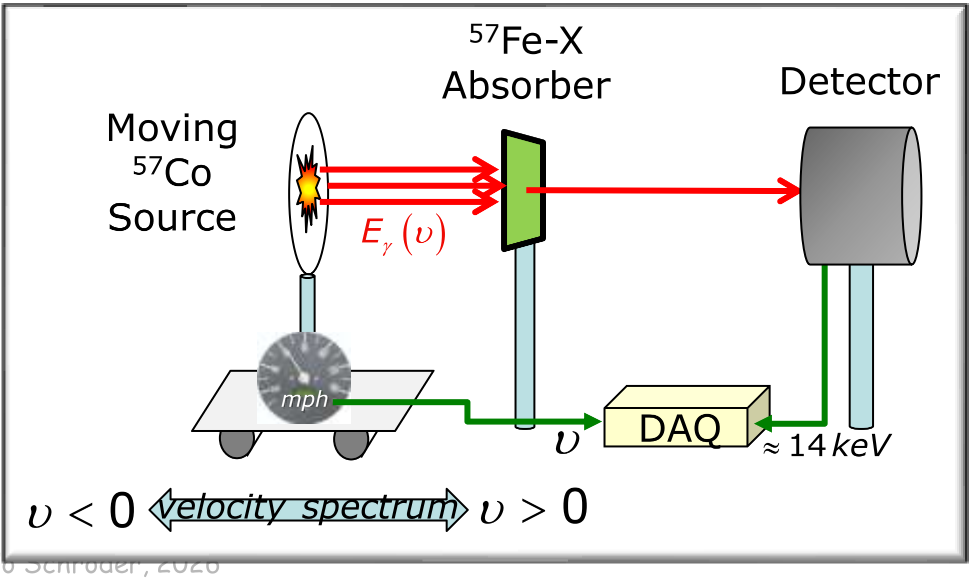
$$E_{\gamma}(\upsilon) \approx 14.4\left(1 \pm \upsilon/c\right) keV$$

^{57}Co γ – source

moving with velocity υ

emits precisely controlled

Doppler – shifted $E_{\gamma}(\upsilon)$

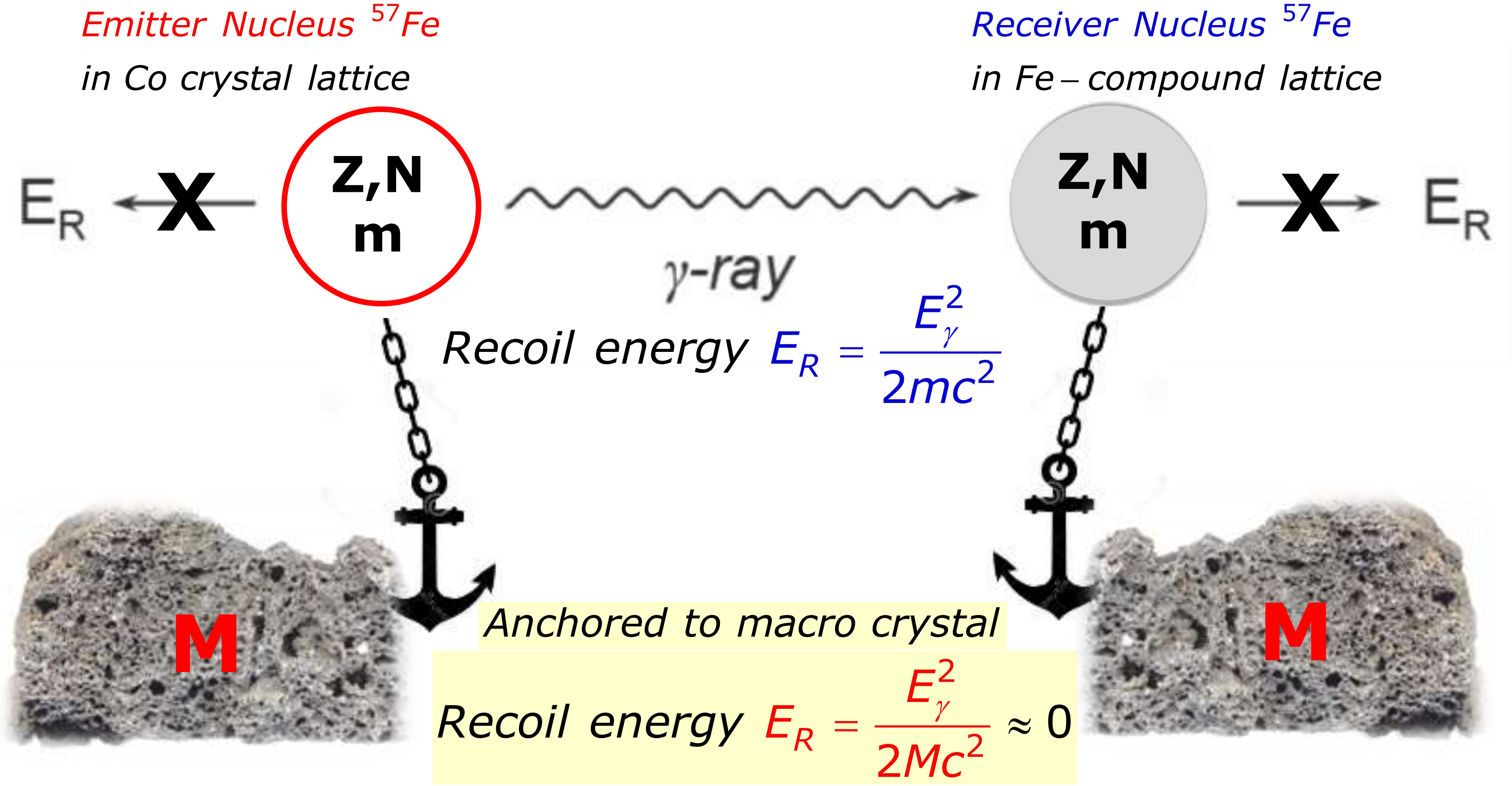


$$Resolving\ \ power\ \ \Gamma/E_{\gamma} = 3 \cdot 10^{-13}$$

$$\gamma\ \ detectors: \Gamma_{FWHM}/E_{\gamma} \sim 10^{-3} - 10^{-2}$$

Recoilless Emission/Absorption

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



Emitter Nucleus ^{57}Fe *in Co crystal lattice*

Receiver Nucleus ^{57}Fe *in Fe – compound lattice*

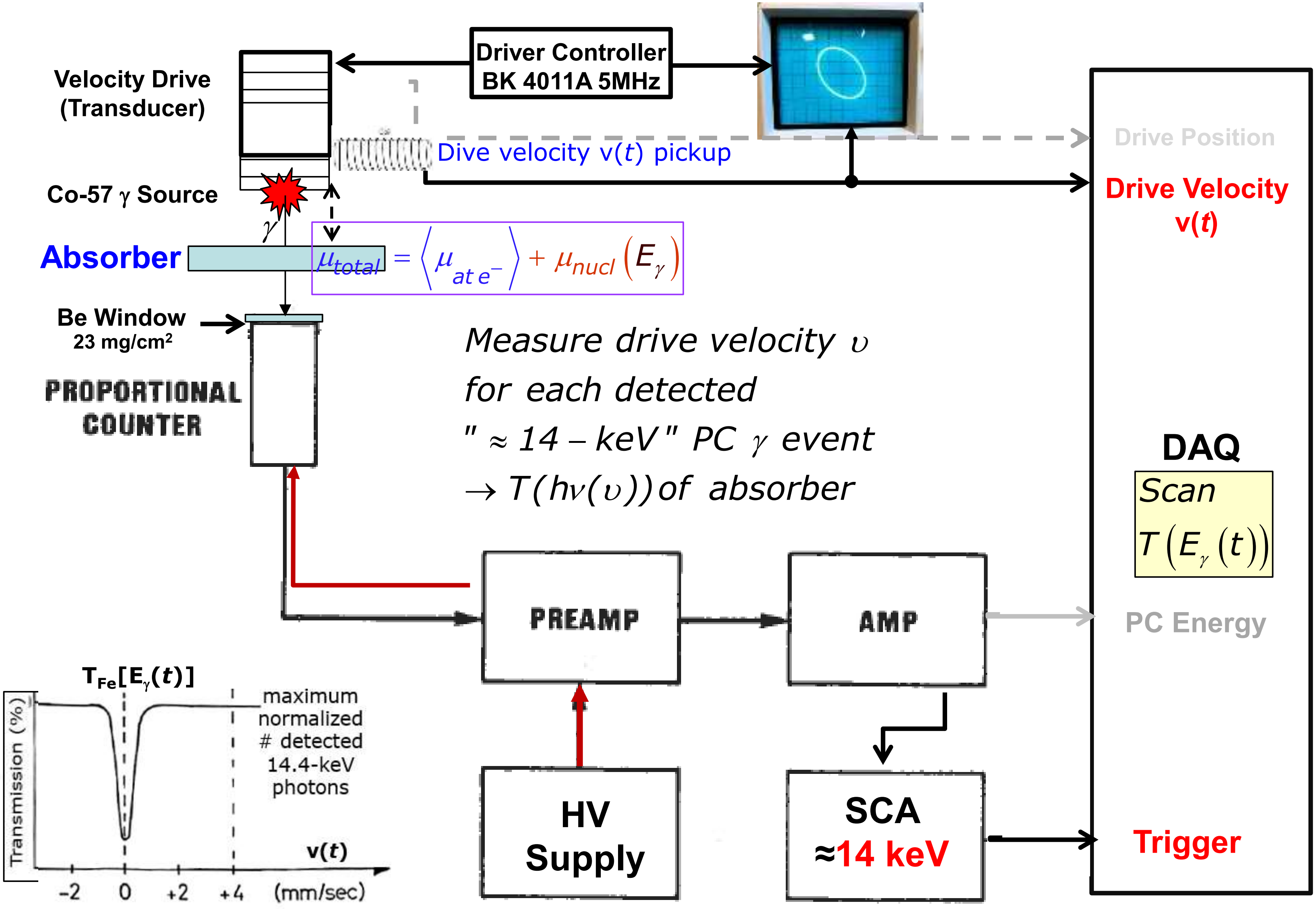
$$\text{Recoil energy } E_R = \frac{E_\gamma^2}{2mc^2}$$

Anchored to macro crystal

$$\text{Recoil energy } E_R = \frac{E_\gamma^2}{2Mc^2} \approx 0$$

Momentum-energy transfer to nucleus embedded in macro crystal lattice is negligible → Resonance condition fulfilled

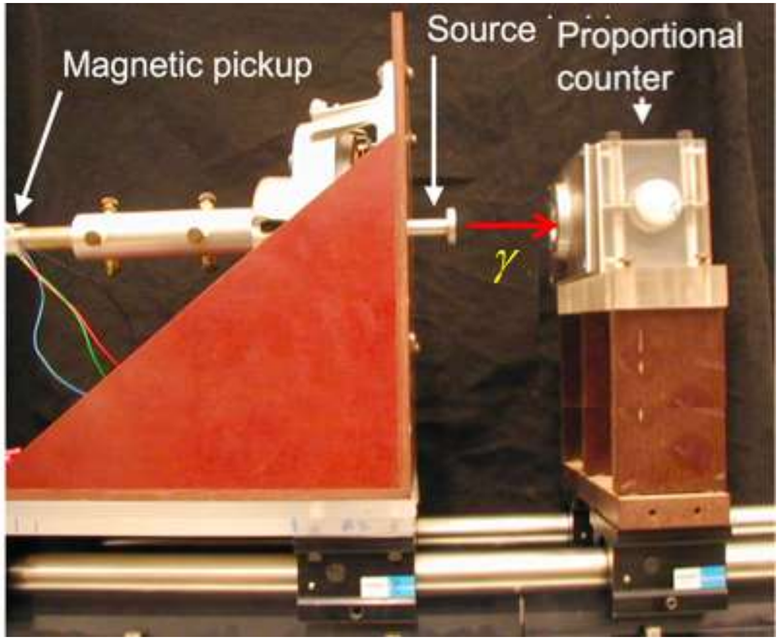
Mőβbauer Transmission Scan: DAQ Setup



$$\mu_{total} = \left\langle \mu_{at\,e^-} \right\rangle + \mu_{nucl}\left(E_\gamma\right)$$

Measure drive velocity υ
for each detected
$"\approx 14-keV"$ PC γ event
$\rightarrow T(h\nu(\upsilon))$ of absorber

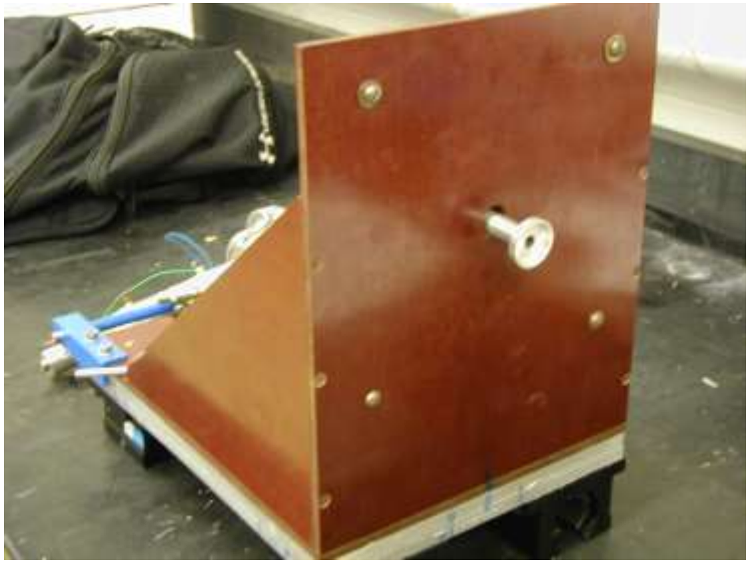
ANSEL Mőssbauer Drive/Setup

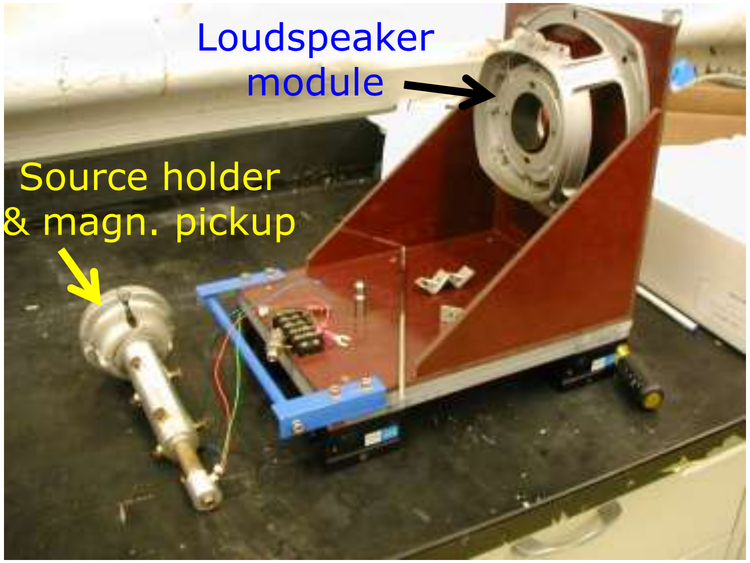


ANSEL drive has non-linear, sinus-type velocity profile defined by function generator controlling electro-magnet

$$\boxed{\begin{array}{l}\upsilon(t) = \upsilon_0 \sin(2\pi t/T) \rightarrow dN/dt \cancel{\propto} dN/d\upsilon \\ \textit{Velocity signal } 1\,mm/s \hat{=} 16\,mV\end{array}}$$

Drive velocity profile is highly stable and precise. Auto-correction via electronic feedback to function generator from magnetic induction pickup.





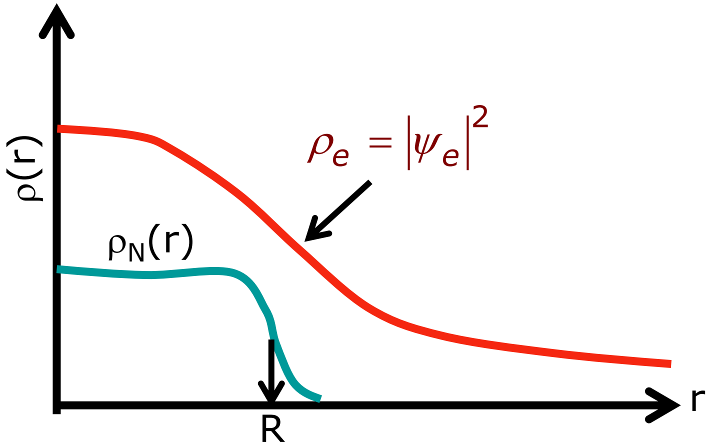
Mőβbauer Spectroscopy Applications

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 electronic or external magnetic fields, in lattices (spin and *g*-factor determinations, magnetic hyperfine interactions)
- Other applications (chemistry, material science)

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)

1^{st} PT : $H'(r) = V(r < R) - V_0(r)$ =: *interaction*

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

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

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

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

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

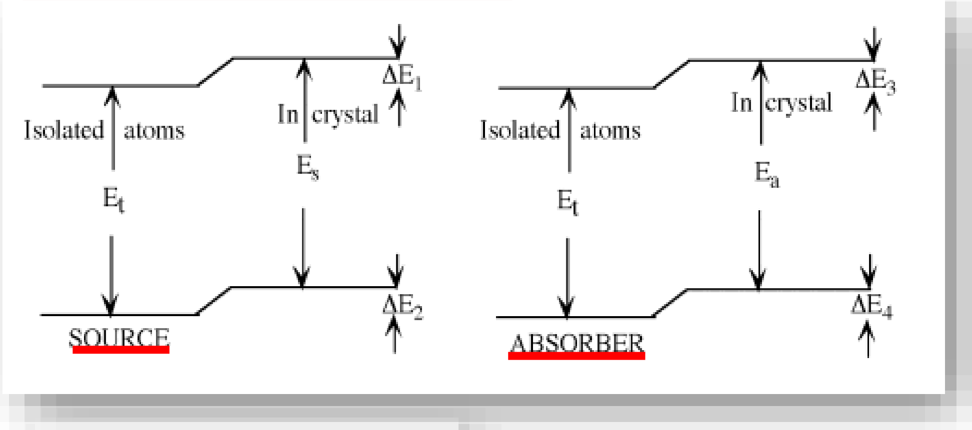
Coulomb potential for spatially extended nucleus → depends on R

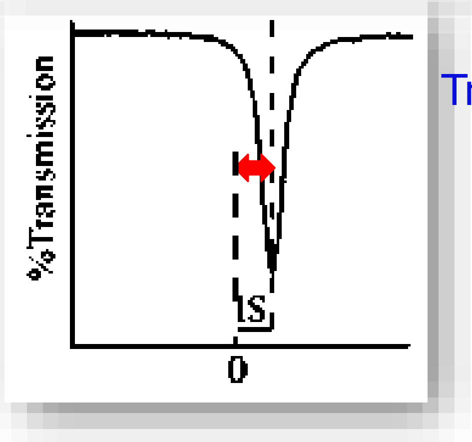
Point → finite size→ *Perturbation* $H'(r) = V(r) - V_0(r)$

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

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

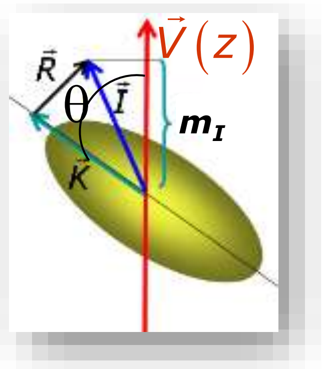
Finite Size nuclear states Radii $R=R_n$ (n=0,1,..)



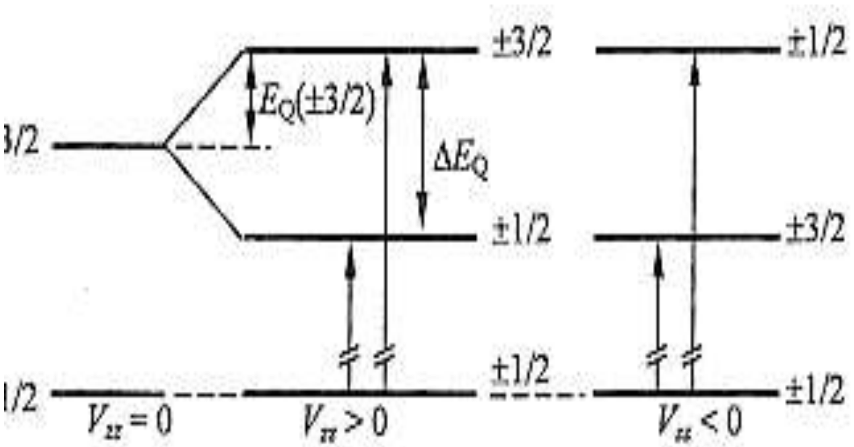


Transmission of γ-ray through absorber depends on source velocity → scan with *T*=*T*(v)

Electric Quadrupole *Hyperfine Interaction* in Atoms



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



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

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

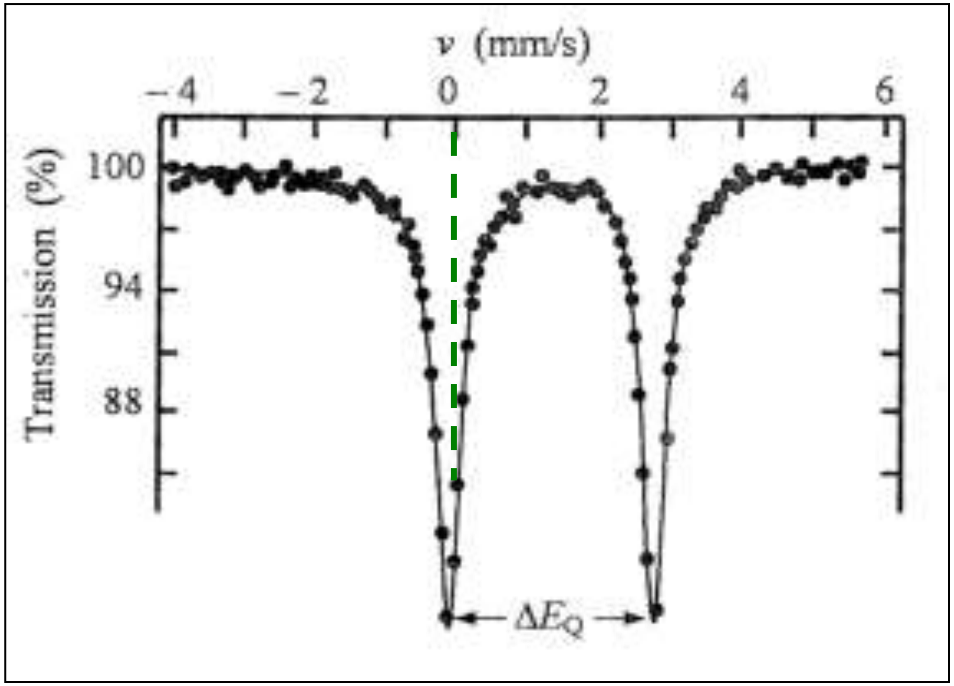
V_{zz}

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

Orientation dependent

$$\Downarrow \quad I > (1/2)\hbar$$

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



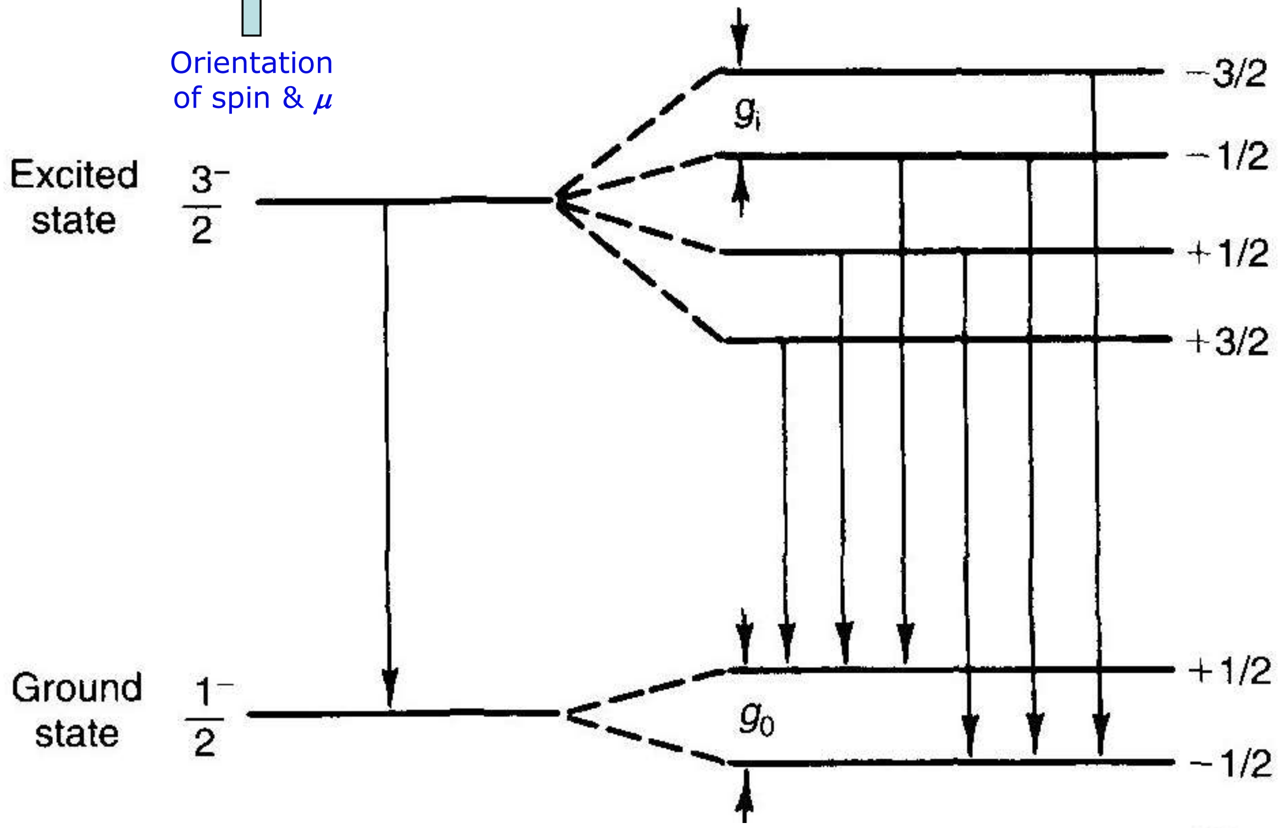
Magnetic Hyperfine Splitting in Atoms

Nuclear magneton μ_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

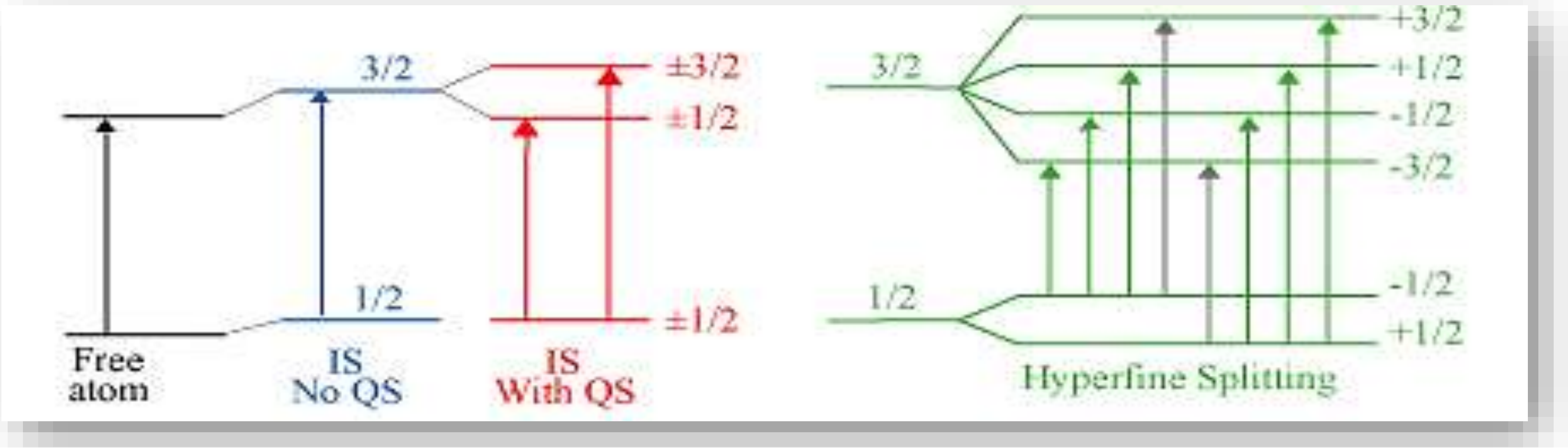
Nuclear magnetic moment μ oriented || to spin I, can be aligned w/r to magnetic field B. ***g_N*** = gyro-magnetic ratio: different for different nuclear states → structure information!



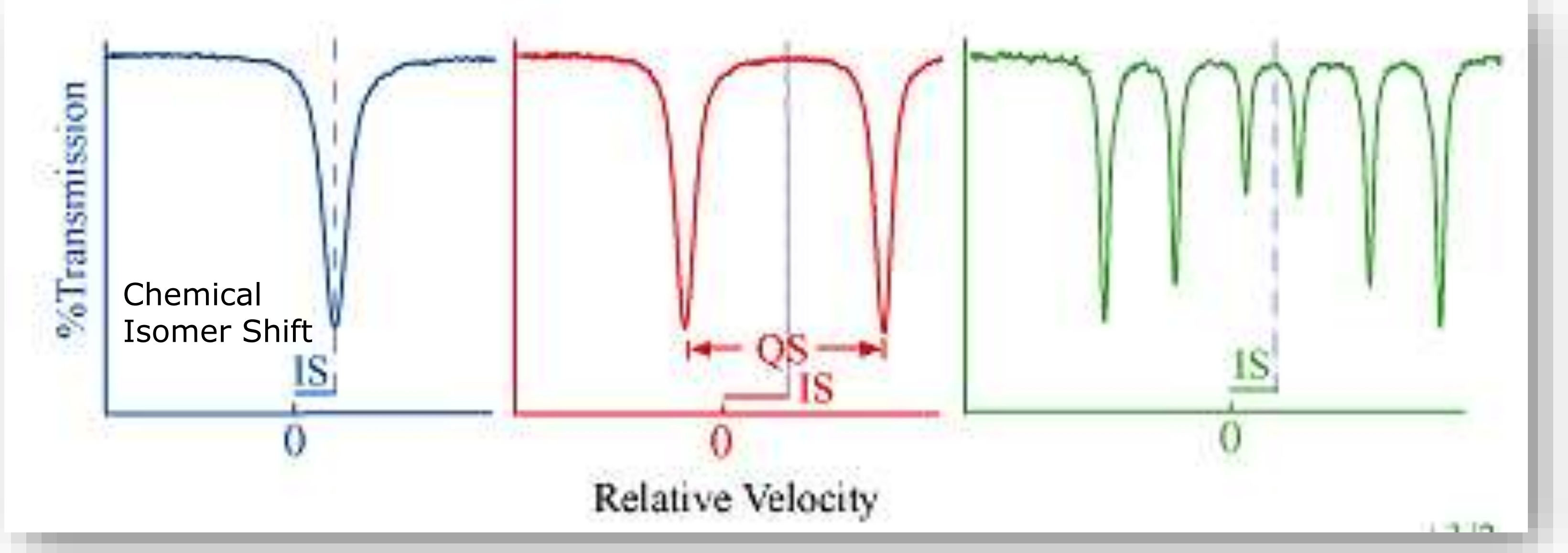
Hyperfine structure splitting of the nuclear energy levels of ^{57}Fe. (a) When stainless steel is used, the levels are not split. (b) In ordinary iron, however, both levels are split, giving rise to a hyperfine structure with six components.

Electric + Magnetic HF Interactions

Isomer-shifted Fe hyperfine level scheme and allowed E1 transitions



Mössbauer velocity absorption spectra are shifted against zero and split



Magnetic **HF** Interaction from MB Spectroscopy

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

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

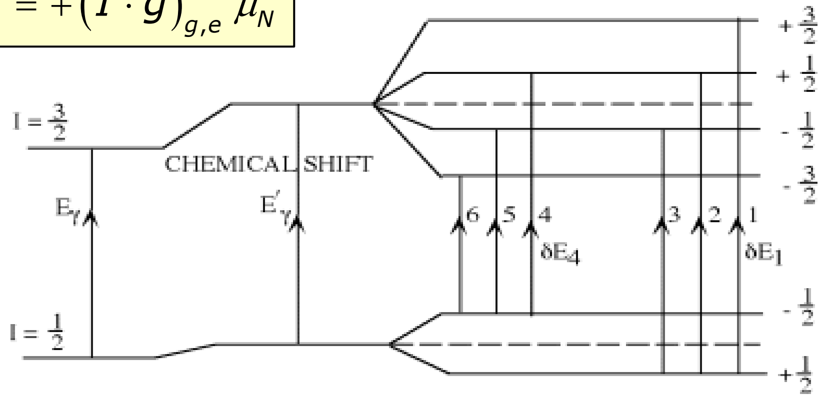
Nuclear states $\mu_{g,e} = +\left(I\cdot g\right)_{g,e}\,\mu_N$

$g_{e,g}$ = 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

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

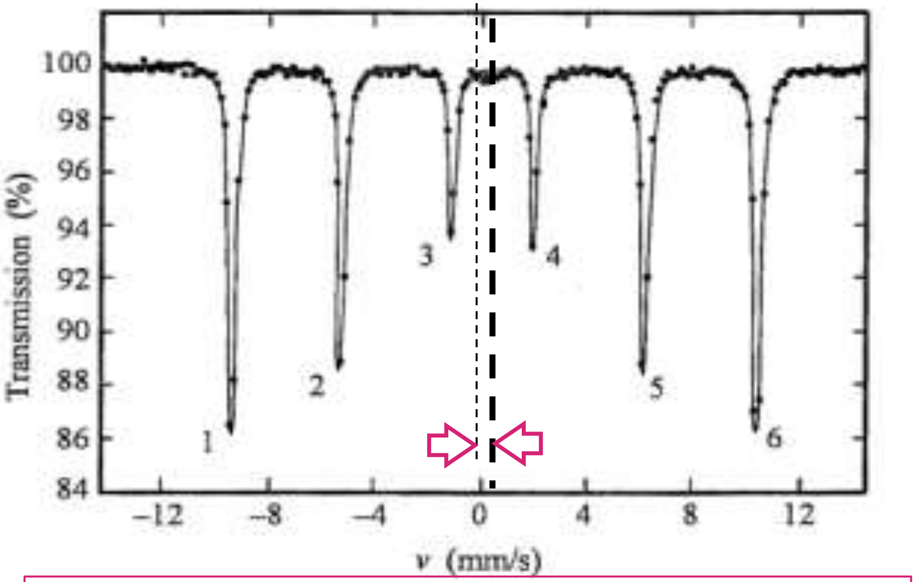


$$\begin{aligned}
E_\gamma\left(1+\frac{v_1}{c}\right) &= E'_\gamma - (\mu_e - \mu_g)B\\
E_\gamma\left(1+\frac{v_2}{c}\right) &= E'_\gamma - (\mu_e/3 - \mu_g)B\\
E_\gamma\left(1+\frac{v_3}{c}\right) &= E'_\gamma - (-\mu_e/3 - \mu_g)B\\
E_\gamma\left(1+\frac{v_4}{c}\right) &= E'_\gamma - (\mu_e/3 + \mu_g)B\\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

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

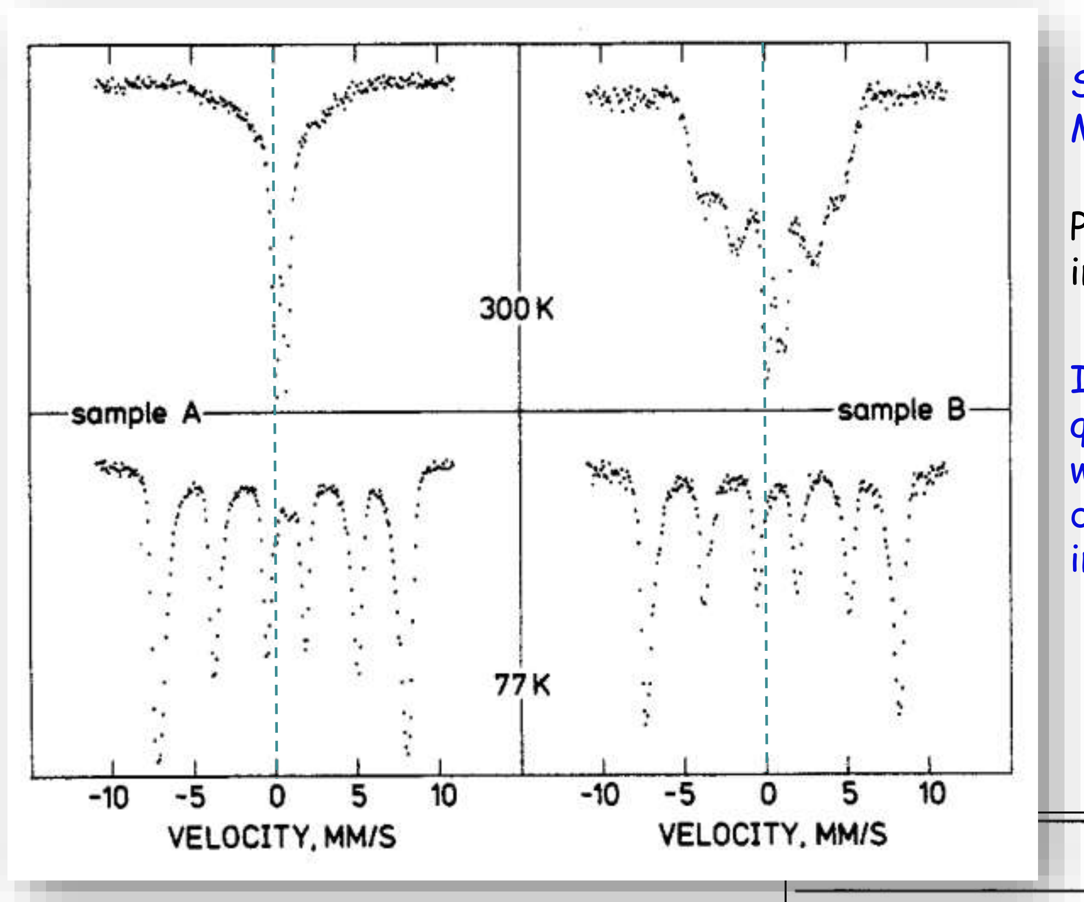
$$(v_2 - v_4)\frac{E_\gamma}{c} = 2\mu_g B \Longrightarrow \frac{v_1 - v_2}{v_2 - v_4} = \frac{-\mu_e}{3\mu_g}$$

Ferromagnetic Fe absorber→ observe magnetic HF



Velocity v=-v_1 < 0 source moving towards absorber

Applications in Chemistry/Material Science



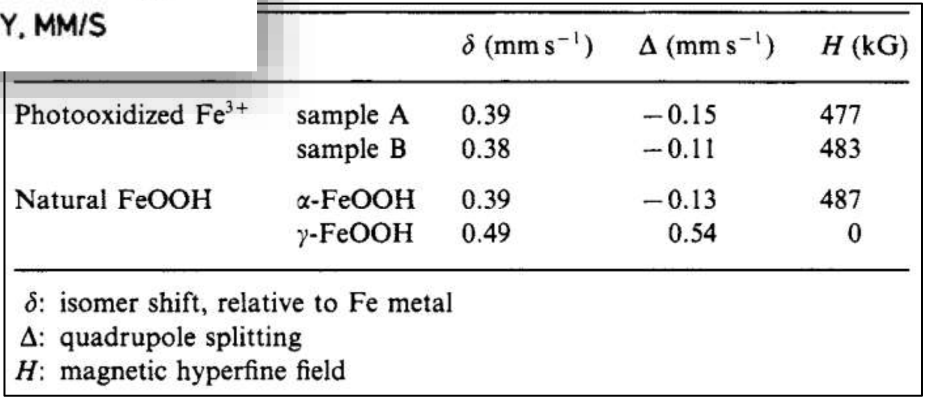
Simulation of chemical reaction in Martian (oxygen-free) environment.

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 photo-oxidized precipitation samples A and B, compared to natural FeOOH

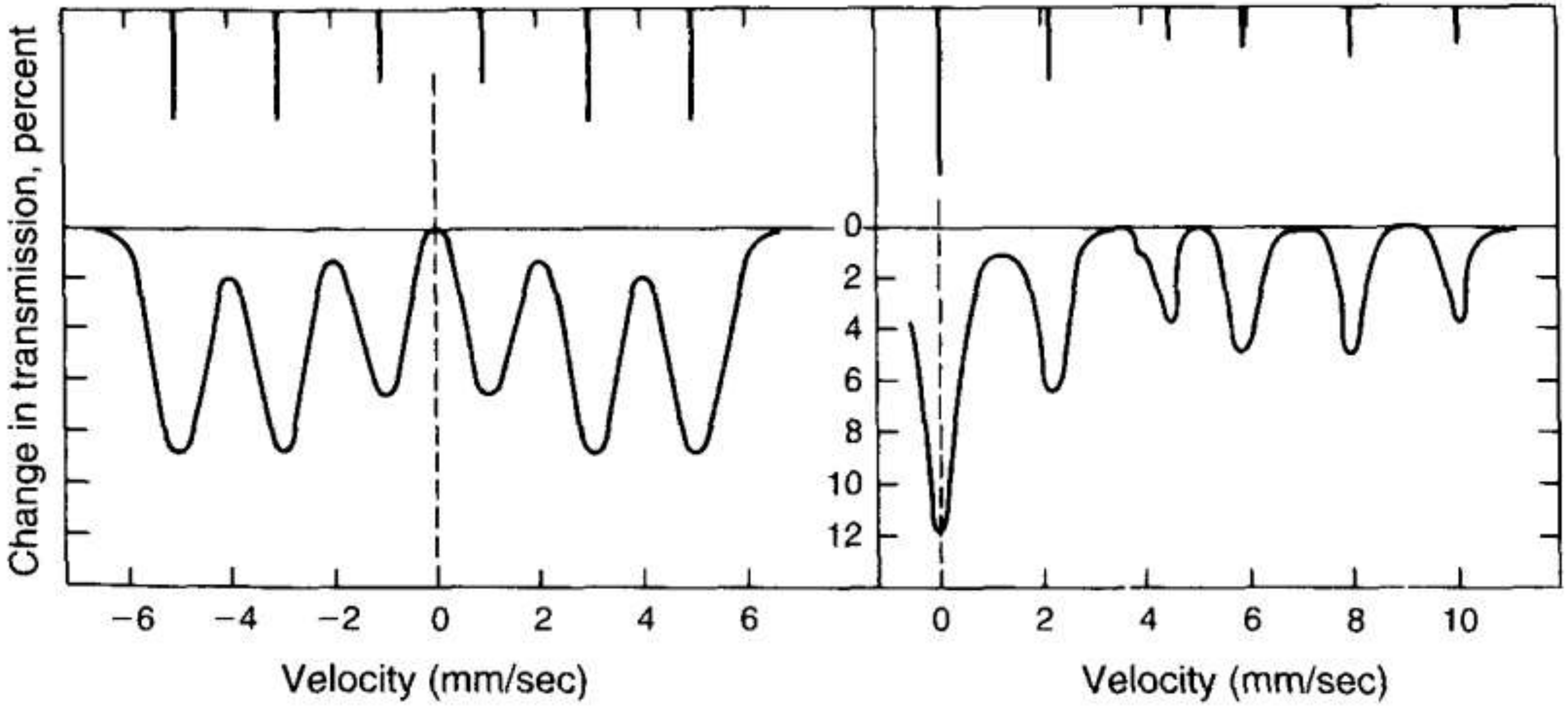
→ α-FeOOH precipitates (B has larger particles, strong B field at 300K)



		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

Probing Ordinary Iron

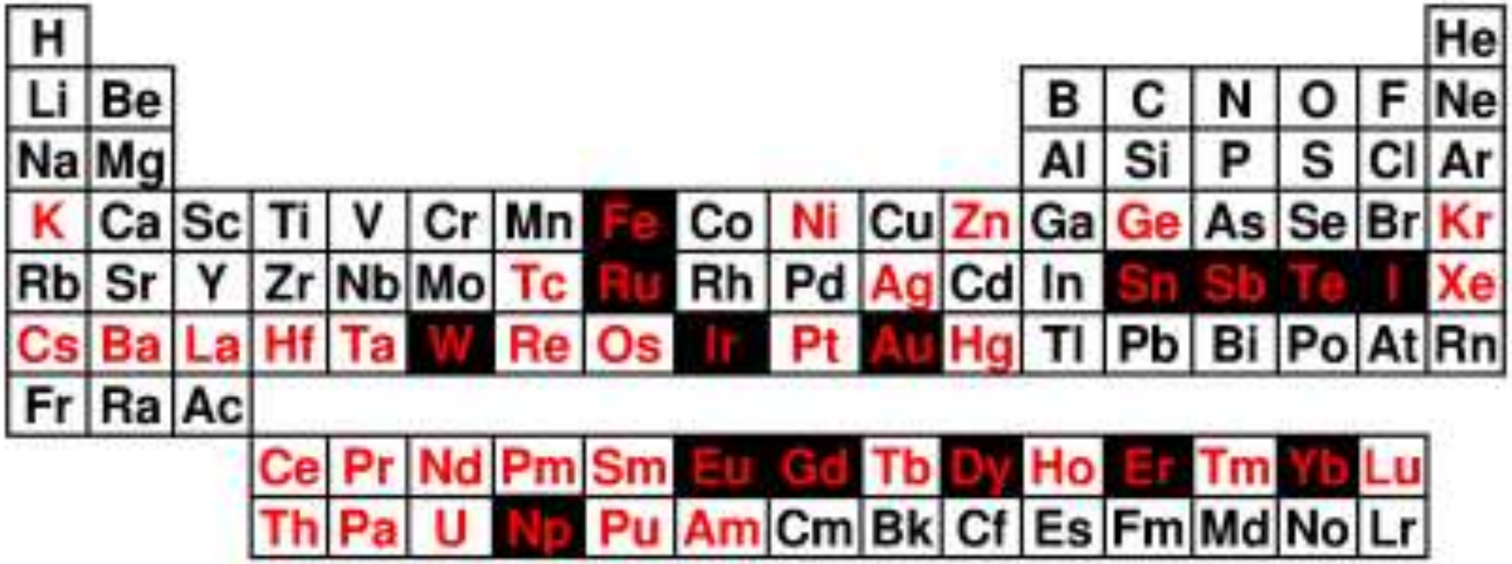


The expected pattern of the Mössbauer line when splitting of the levels takes place. (a) Either the source or absorber is split; note that the Mössbauer line is split into six components and no absorption takes place for zero velocity. (b) When both source and absorber are split a complicated pattern results with maximum absorption at zero velocity.

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



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	

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

End
Mőssbauer Experiment