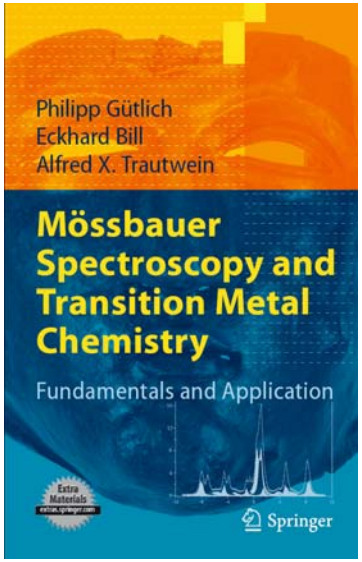
The Mössbauer effect

Resonance fluorescence of nuclear gamma transitions

Some recent Mössbauer literature



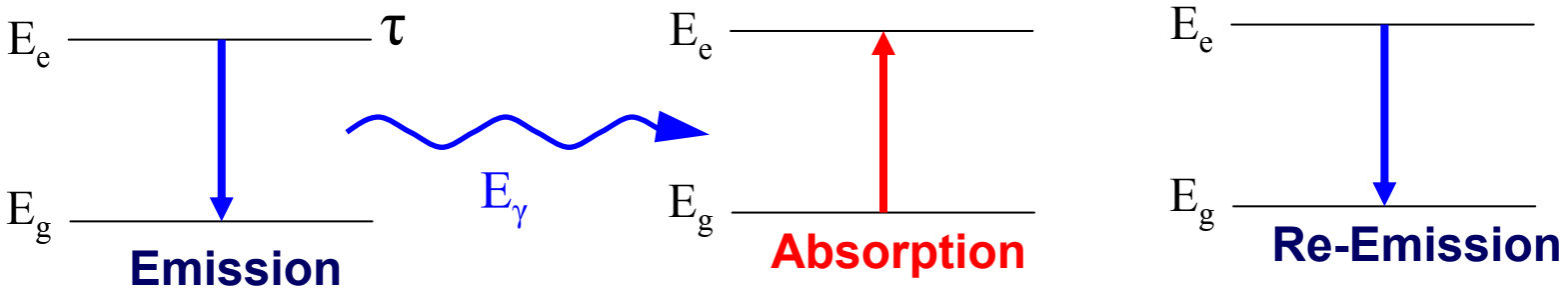
Philipp Gütlich
Mössbauer Spectroscopy – Principles and Applications

http://ak-guetlich.chemie.uni-mainz.de/Moessbauer_Lectures_web.pdf

Peter Blaha
Computation and interpretation of Mössbauer parameters from DFT based WIEN2k calculations for extended systems
http://publik.tuwien.ac.at/files/PubDat_195084.pdf

Resonance fluorescence

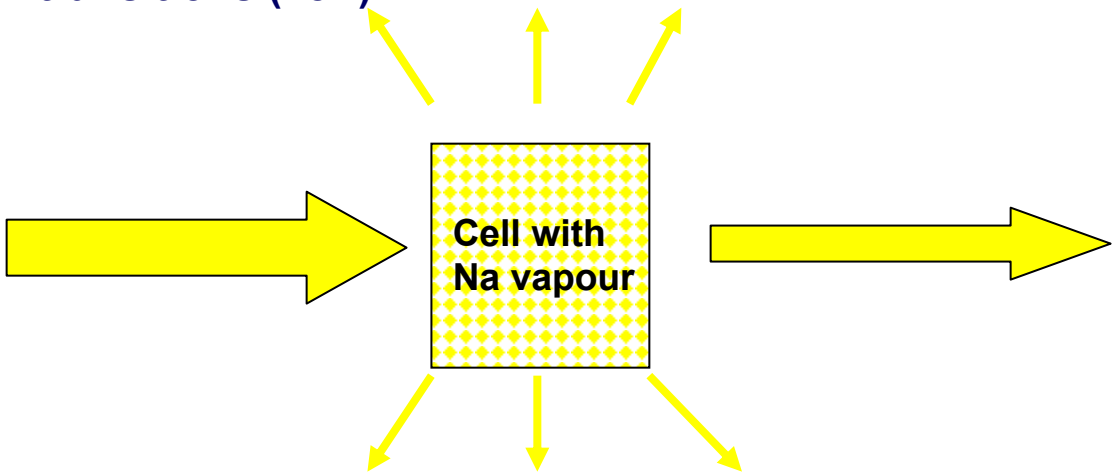
Absorption and isotropic Re-Emission



Resonance fluorescence is easily observed with optical transitions (eV)

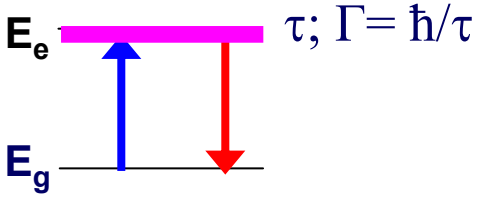
but usually not with nuclear transitions (keV)

Light from a Sodium-vapor lamp



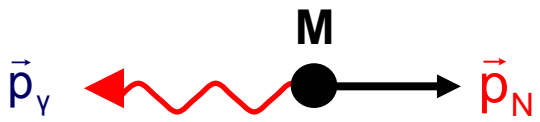
Energy- and Momentum Conservation of Photon-Emission and Absorption

$E_0 = E_e - E_g$



Γ = **natural line width** = $\hbar/\tau$
Heisenberg uncertainty relation

Momentum conservation



$$|p_\gamma| = |p_N| = \frac{h\nu}{c} = \frac{E_\gamma}{c} = M v \quad \rightarrow \quad v = \frac{E_\gamma}{Mc}$$

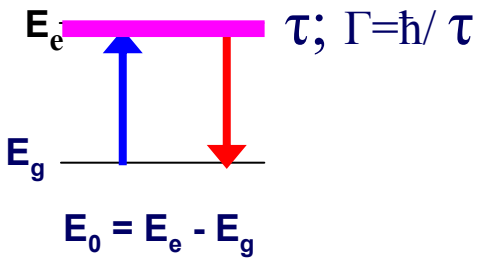
Recoil energy $R = \frac{M}{2} v^2 = \frac{E_\gamma^2}{2Mc^2}$

Emission: $E_\gamma < E_0$

Example ^{57}Fe:

$R \approx 2 \times 10^{-3}$ eV ~ $4 \times 10^5 \Gamma$

Energy- and Momentum Conservation of Photon-Emission and Absorption



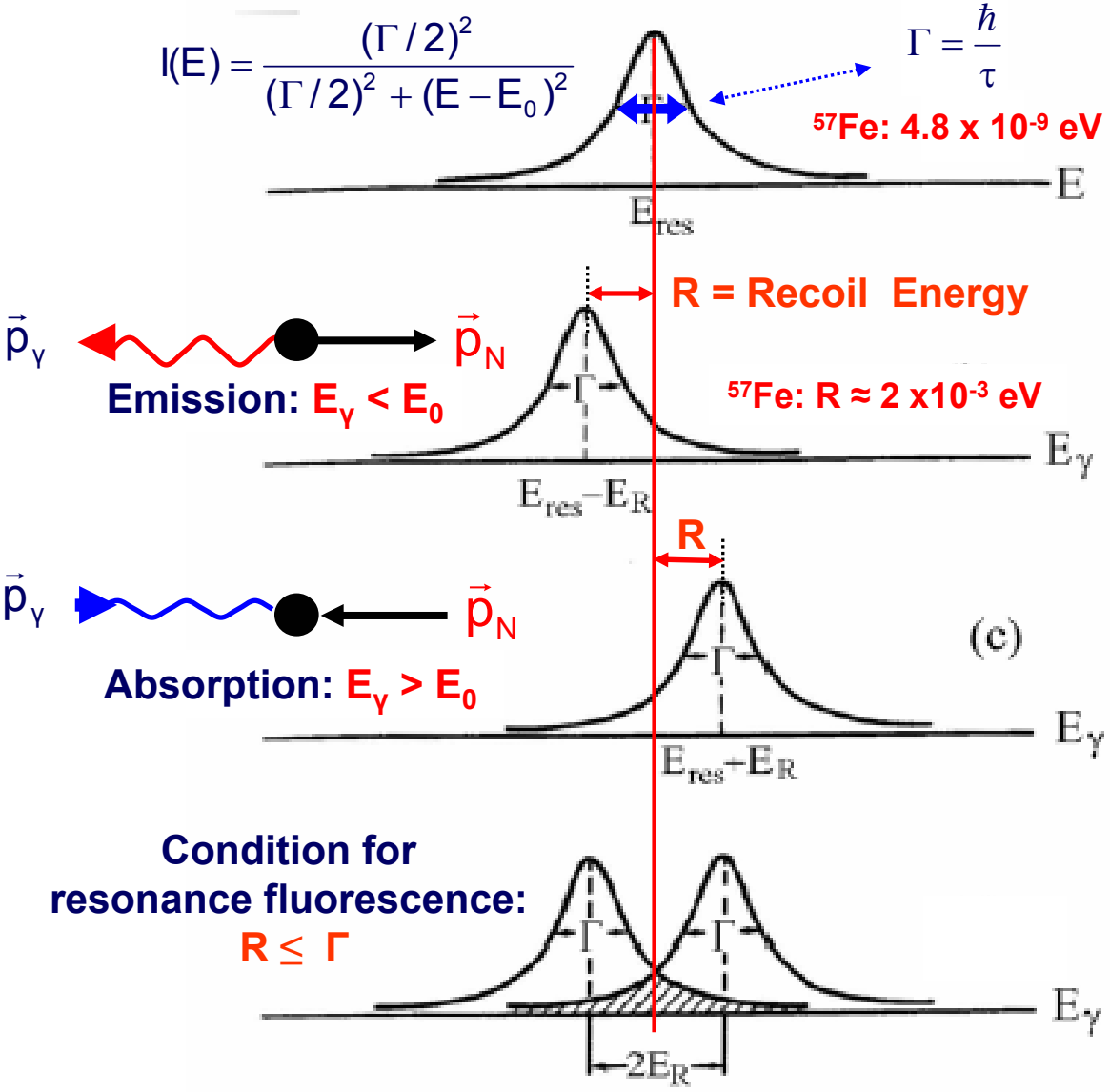
$$R = \frac{M}{2}v^2 = \frac{E_\gamma^2}{2Mc^2}$$

Line width

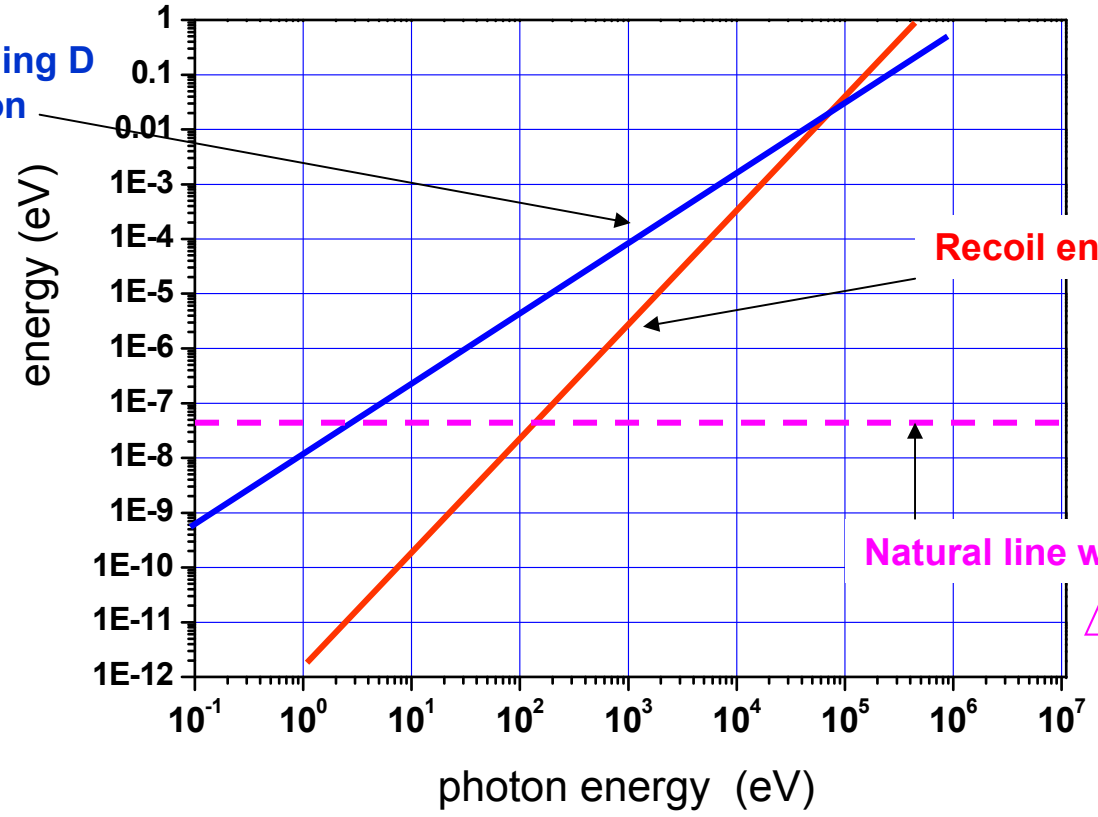
$$I(E) = \frac{(\Gamma/2)^2}{(\Gamma/2)^2 + (E - E_0)^2}$$

$$\Gamma = \frac{\hbar}{\tau}$$

^{57}Fe: 4.8 x 10^{-9} eV



Condition for Resonance Fluorescence



Optical transitions

$\Gamma \geq D, >> R$

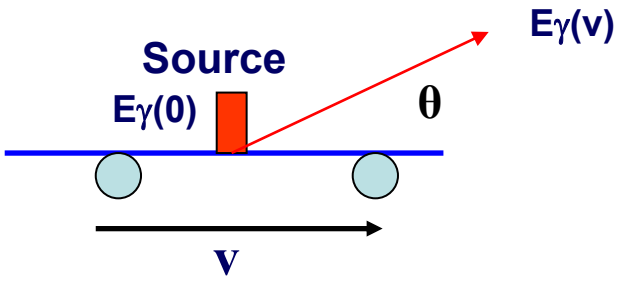
γ-ray transitions

$\Gamma << R,\ D$

Line shift using the Doppler effect

Doppler effect

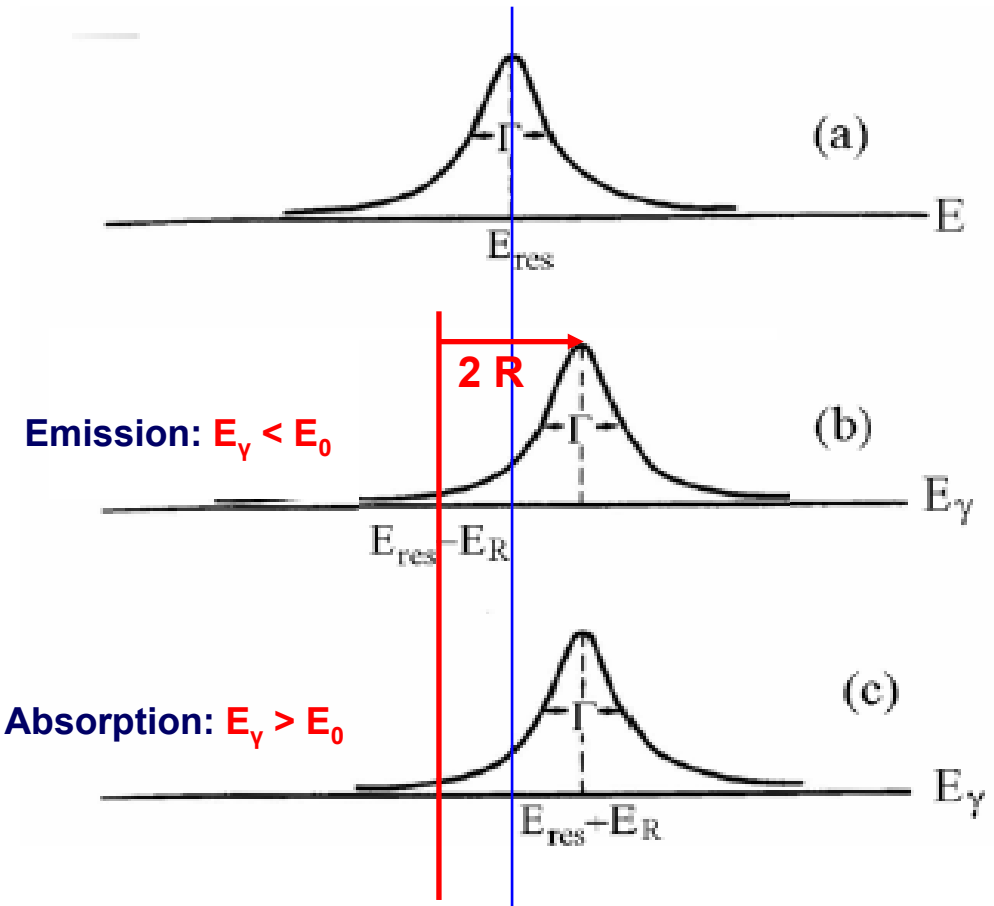
$$E_\gamma(v) = E_\gamma(0)\left(1 + \frac{v}{c}\cos\theta\right)$$



^{57}Fe: E_γ = 14.4 keV
2 R ≈ 4 x10^{-3} eV

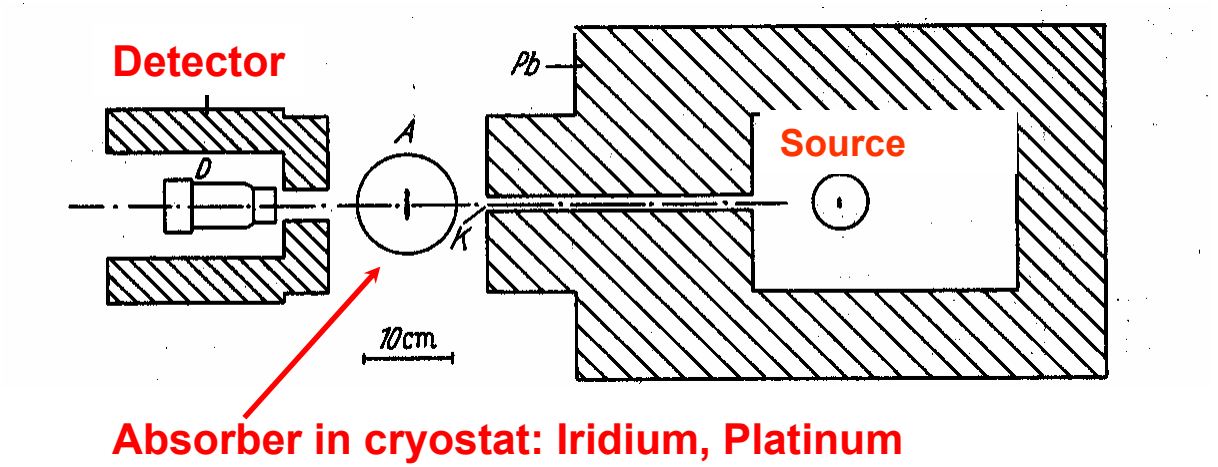
Velocity required to **force** resonance by moving the source

V_{res} ~ 100 m/s

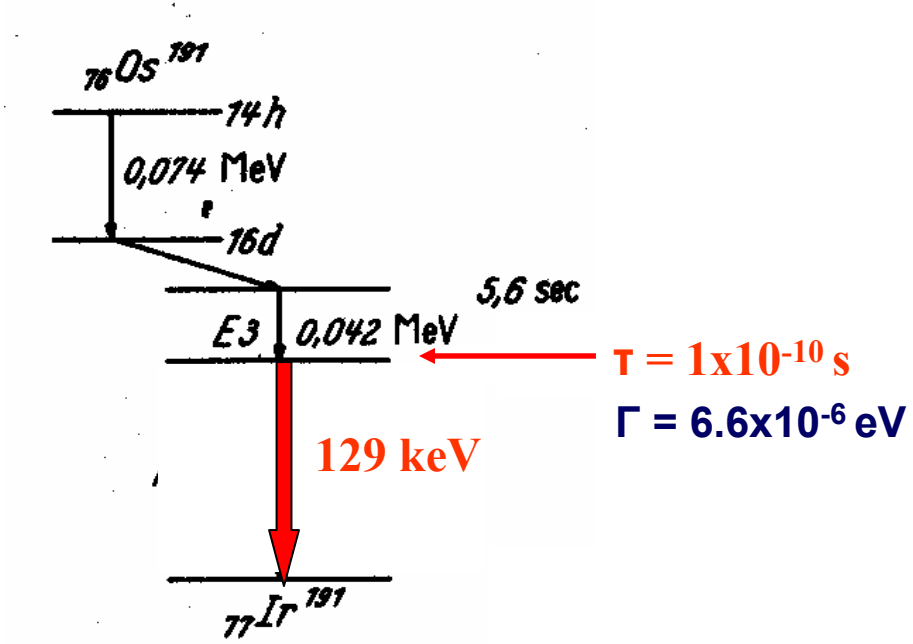


Mössbauers 1. Experiment

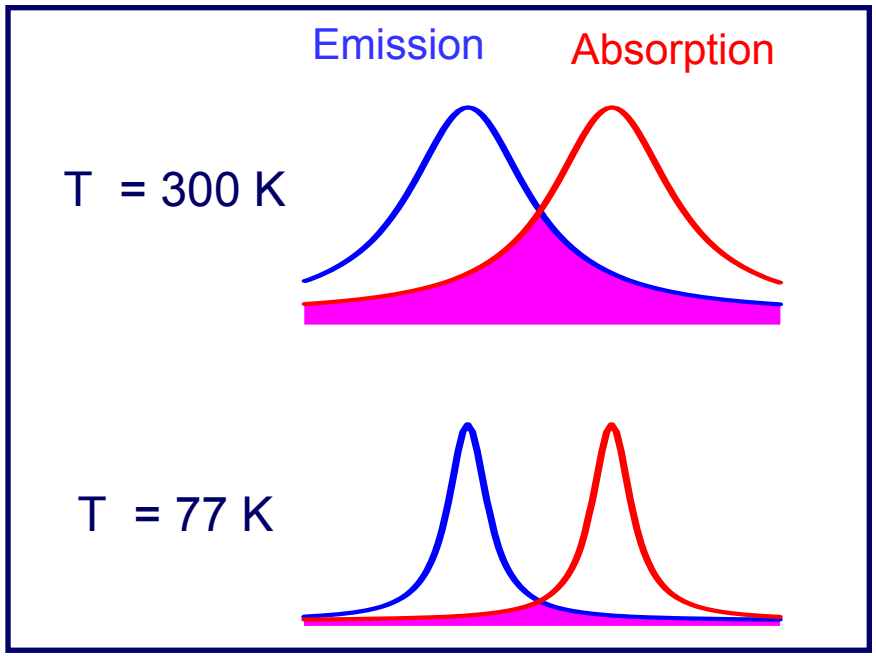
Experimental Set-up

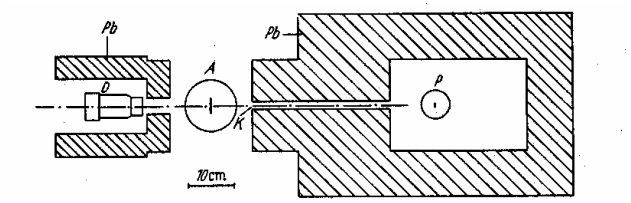


The radioactive source



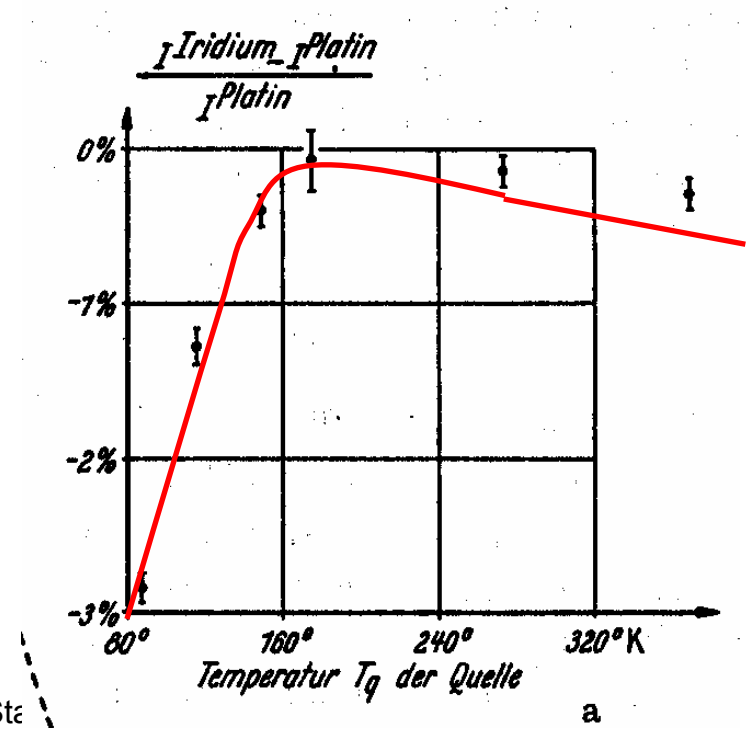
Absorption of the 129 keV-line as a function of absorber temperature





Surprising experimental result:

The absorption increases with decreasing temperature



Expectation

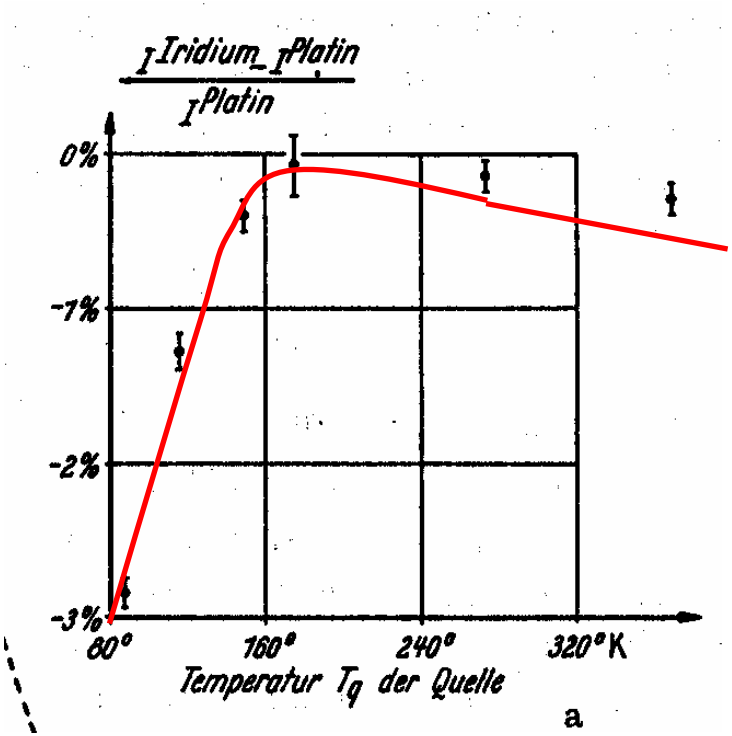
Slower thermal motion leads to narrower lines at lower temperatures

→ Less overlap

→ Less absorption

Result of the 1. Moessbauer experiment

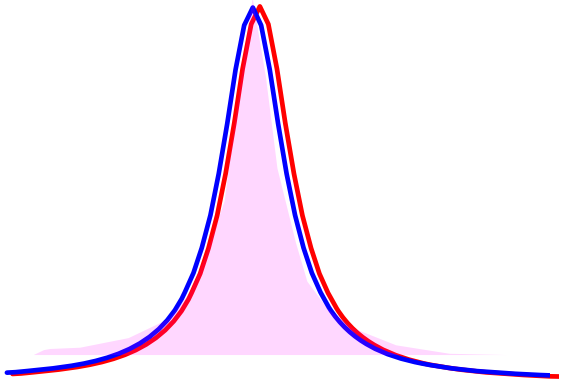
Absorption increases with decreasing temperature



Proposed explanation

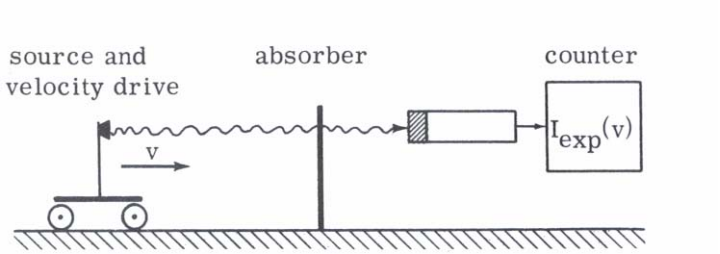
For some fraction of the Ir nuclei the emission- and the absorption line are NOT recoil-shifted relativ to each other:

- Recoil-free emission and absorption
- The recoil-free fraction of γ-quanta (Debye-Waller factor) increases with decreasing temperature

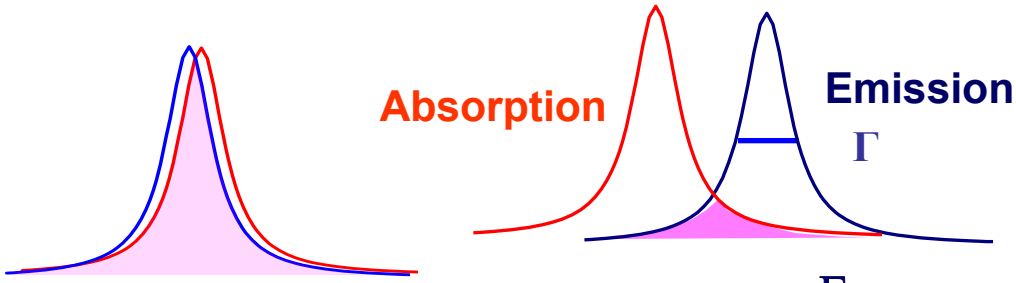


Mössbauers 2. Experiment

Test of the hypothesis of recoil-free emission and absorption



Destruction of the resonance fluorescence by moving the radioactive source

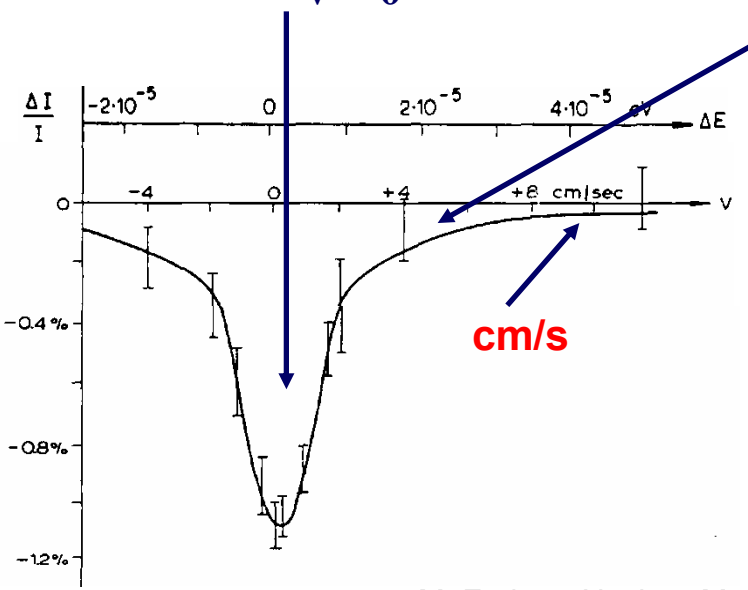


Doppler effect

$$E_\gamma(v) = E_\gamma(0)\left(1 + \frac{v}{c}\cos\theta\right)$$

$v \sim 0$

$$v \approx 2-3\,\frac{\Gamma \cdot c}{E_\gamma^0}$$



^{191}Ir:

E_γ = 129 keV

$\tau = 1 \times 10^{-10}$ s

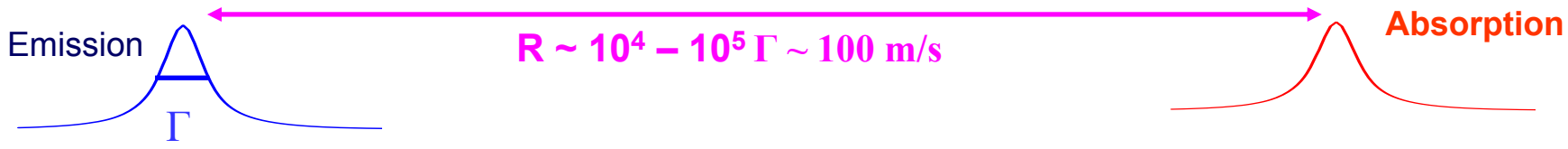
$\Gamma = 6.6 \times 10^{-6}$ eV

Energy resolution

$\Gamma / E\gamma \sim 5 \times 10^{-11}$

Recoil-free γ-emission in solids

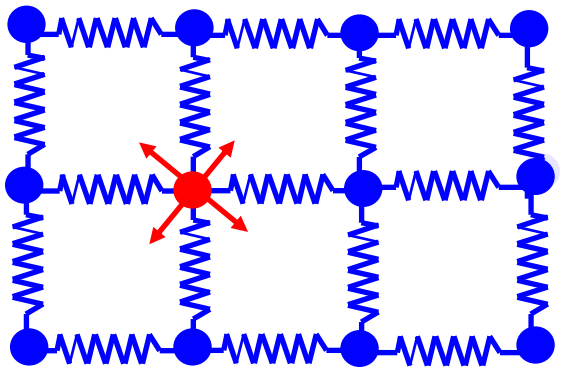
Free nuclei:

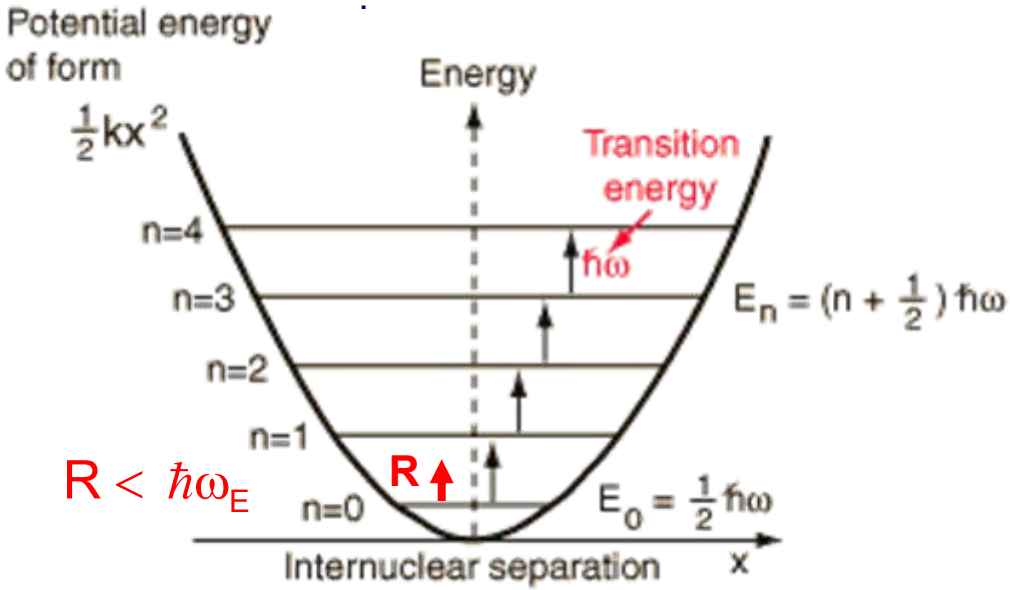


The recoil energy can only be dissipated as **kinetic energy** of the emitting/absorbing nuclei.

Nuclei in solids

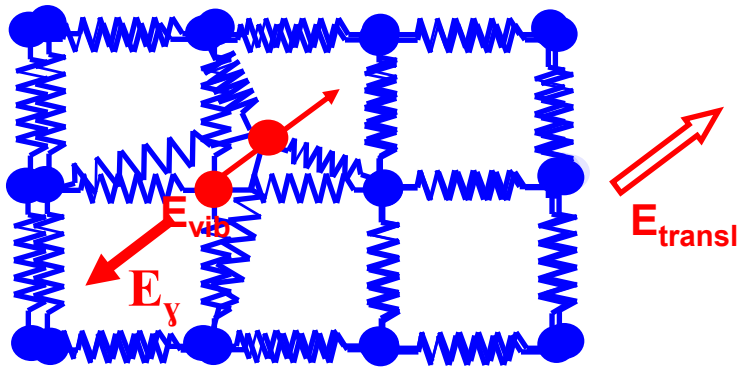
the atoms/nuclei are elastically bound to the lattice and oscillate around their equilibrium position





The energy of these lattice vibrations (phonons) is quantized.

Recoil-less γ-emission in solids - a consequence of quantized lattice vibrations



The recoil energy can be partitioned into a translational part E_{transl} and a vibrational part E_{vib}

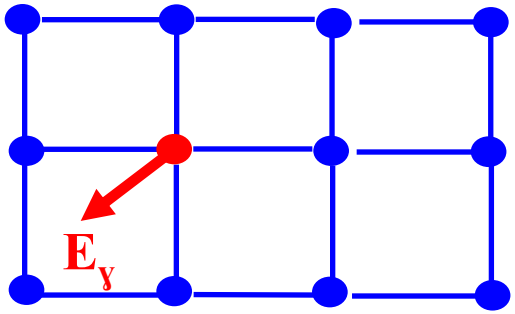
$$R = E_{transl} + E_{vib}$$

E_{vib} ~10^{-3} – 10^{-1} eV
R ~ 10^{-4} – 10^{-1} eV
Γ ~ 10^{-6} eV

The vibrational energy changes only by discrete amounts 0, ±ħω, ± 2ħω: **phonon transitions**

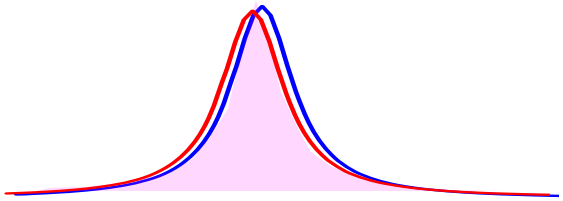
There is a finite probability that the gamma–emission does not **change the quantum state of the lattice.**

$$R = \frac{E_\gamma^2}{2\sum_n M_n c^2}$$



In the case of **a such zero-phonon transition, the nucleus is bound into a rigid lattice.** The entire crystal ($\sum_n M_n$) takes the recoil, the loss of energy of the emission- (and absorption-) γ-line is practically zero.

→ **Recoil-free emission and absorption**



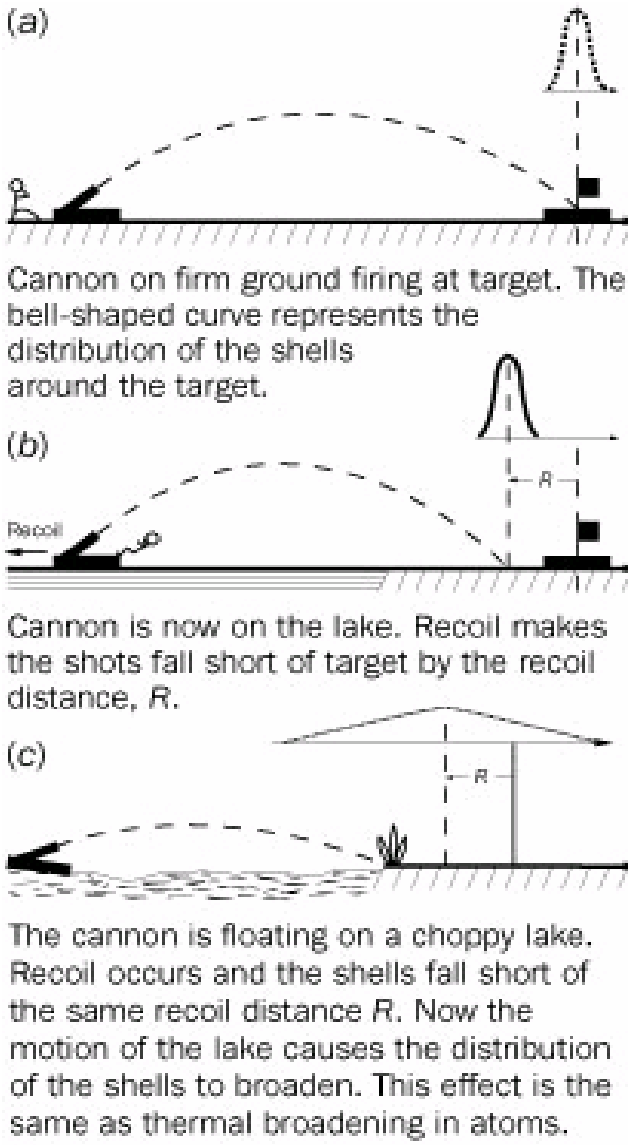
Mössbauer's analogy

Translation from Mössbauer´s thesis

This situation (is)...like a person throwing a stone from a boat.

The majority of the energy is submitted to the stone, but a small amount goes into the kinetic energy of the recoiling boat. During the summer time, the boat will simply pick up this recoil energy.

If, however, the person throws the stone during winter time, with the boat frozen into the lake, then practically all energy is going into the stone thrown and only a negligible amount is submitted to the boat. The entire lake will, thus, take up the recoil and this procedure occurs as recoilless process.

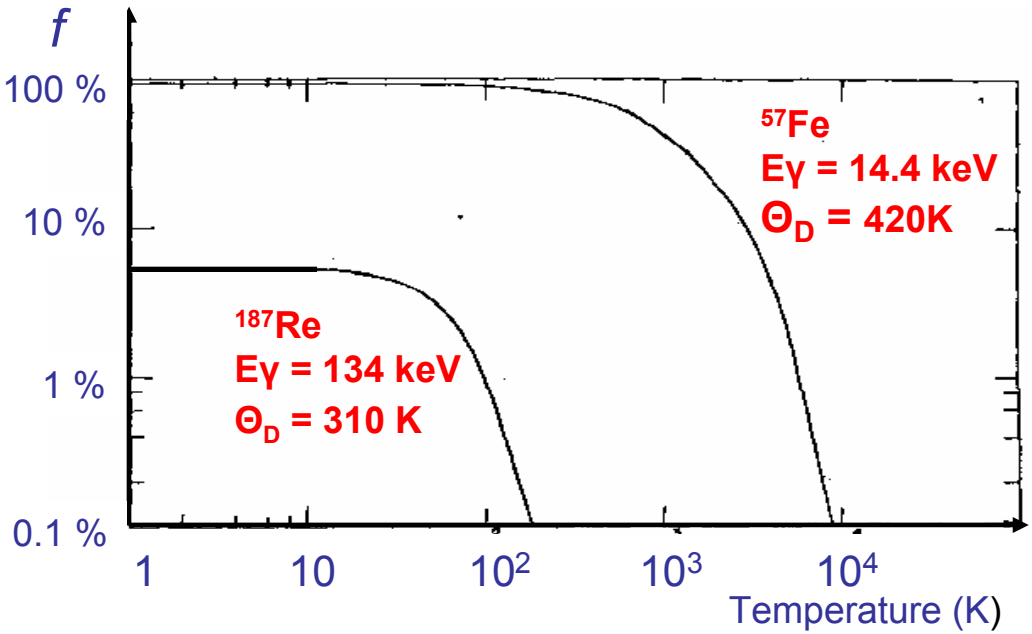


Debye-Waller-Factor – recoil-free fraction

$$f = \exp\left\{-\frac{6E_R}{k_B\Theta_D}\left[\frac{1}{4}+\left(\frac{T}{\Theta_D}\right)^2\int_0^{\Theta_D/T}\frac{z}{e^z-1}dz\right]\right\}$$

Θ_D = Debye temperature:

$$k_B\Theta_D = \hbar\omega_D$$



The recoil-free fraction *increases*

a) with **decreasing recoil energy E_R**

b) with **decreasing temperature T**

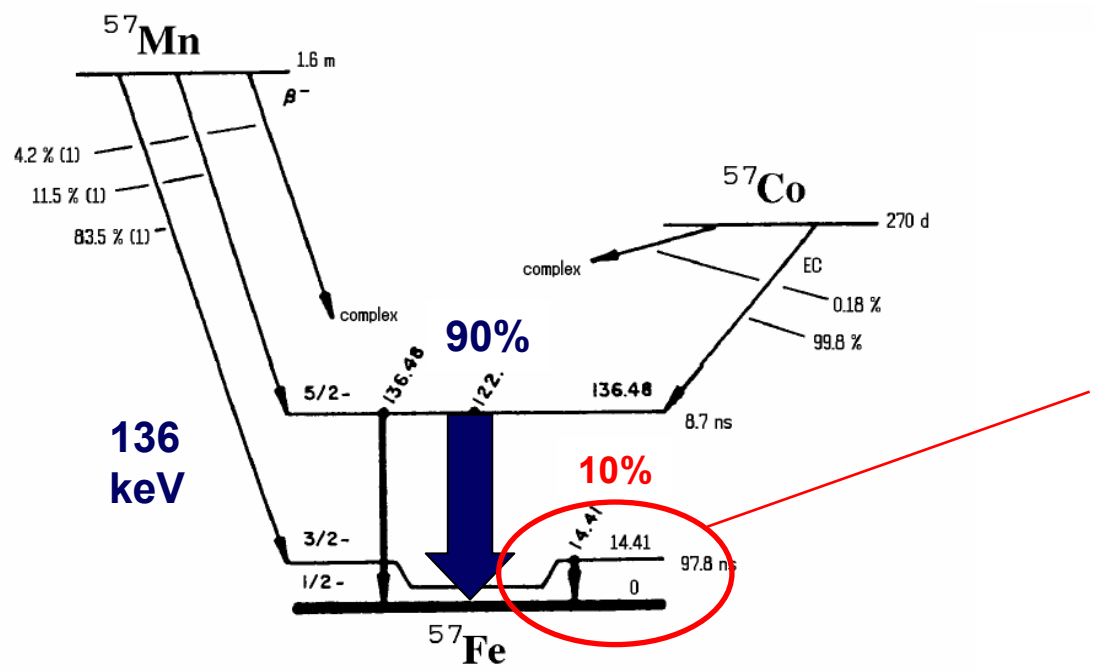
c) with **increasing Debye-temperature** (bondstrength)

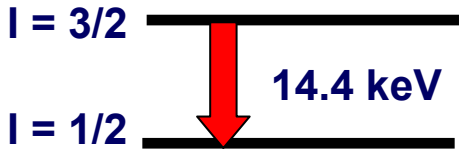
Mössbauer Elements

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	Lw

^{57}Fe – the most popular Mössbauer isotope





τ = 141 ns

Γ = 4.8 neV

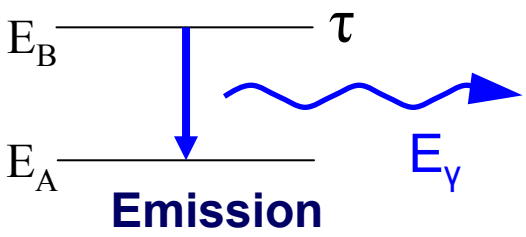
Energy resolution:

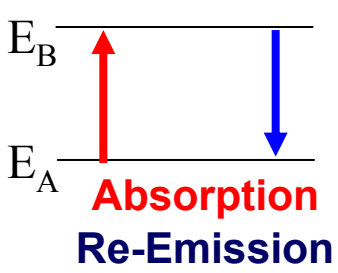
$\Gamma/E_\gamma = 3.3\ 10^{-13}$!!!

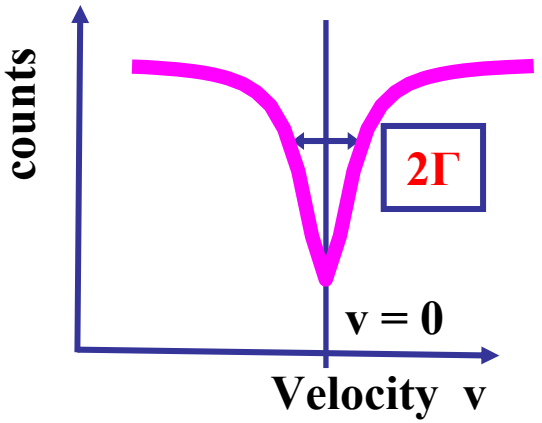
M. Forker, Nuclear Methods in Solid State Research, CBPF 2012

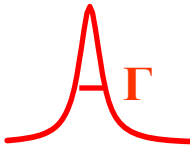
Mössbauer Geometries

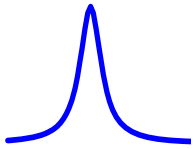
Transmission Geometry

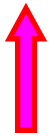






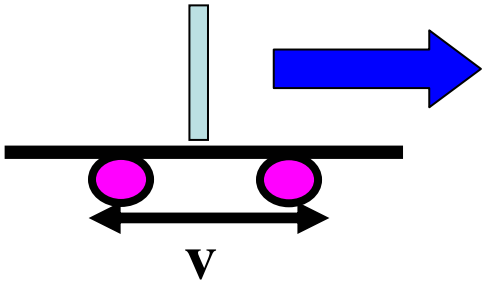


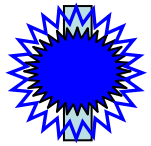




Source (CoRh)

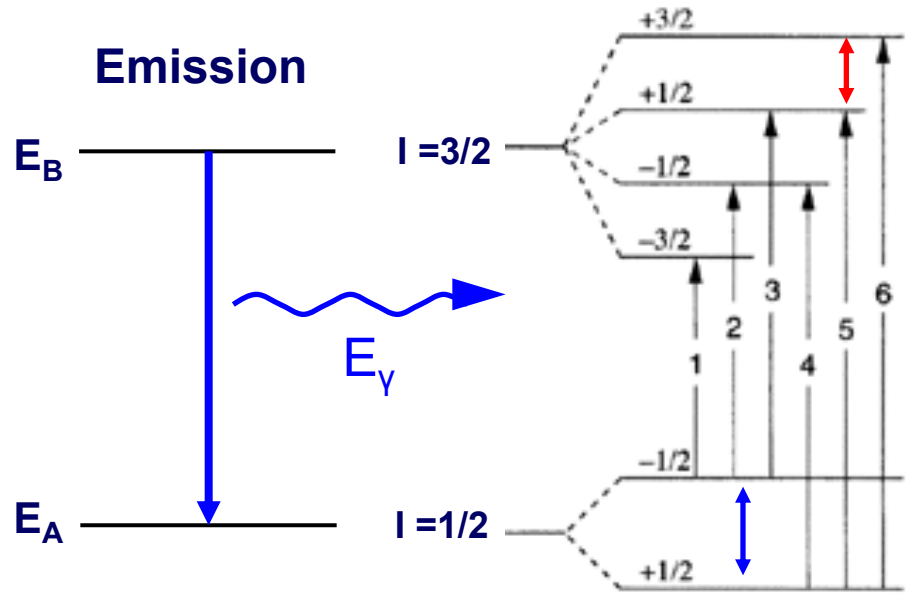
Absorber



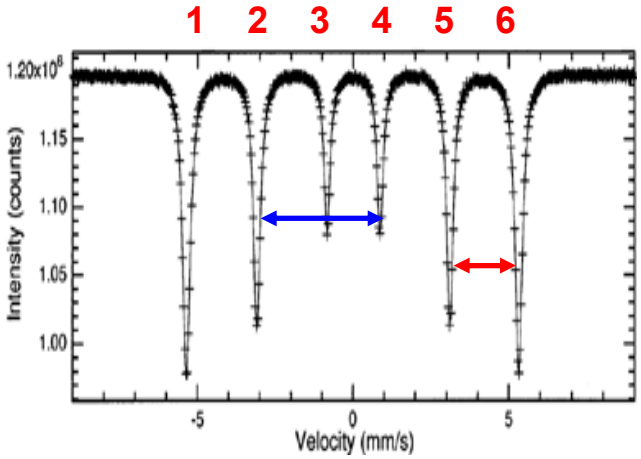


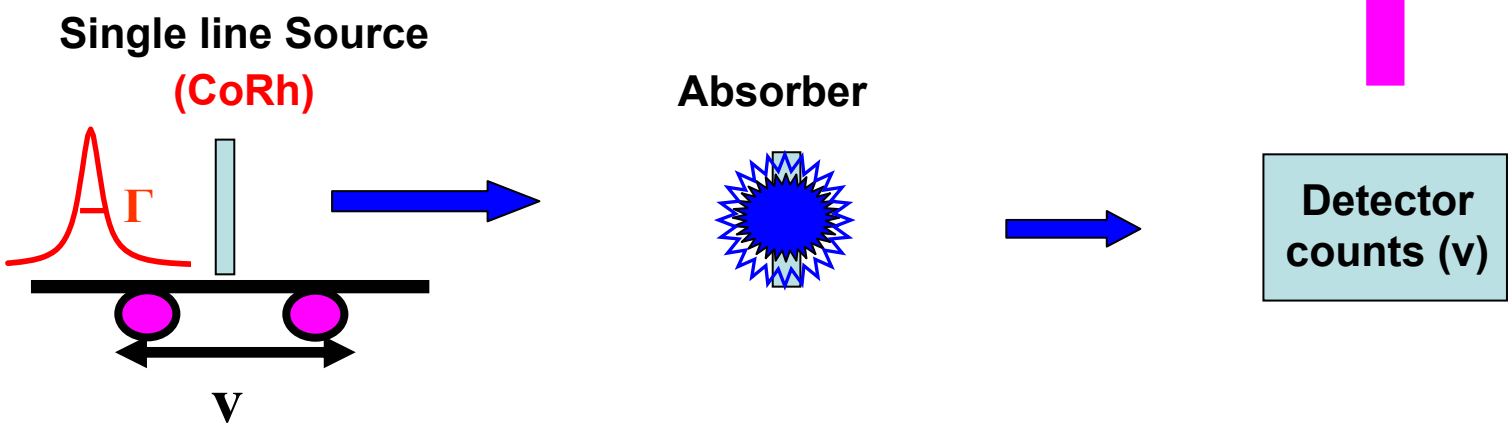
Detector counts (v)

Magnetically split absorber (bcc Fe) in Transmission Geometry

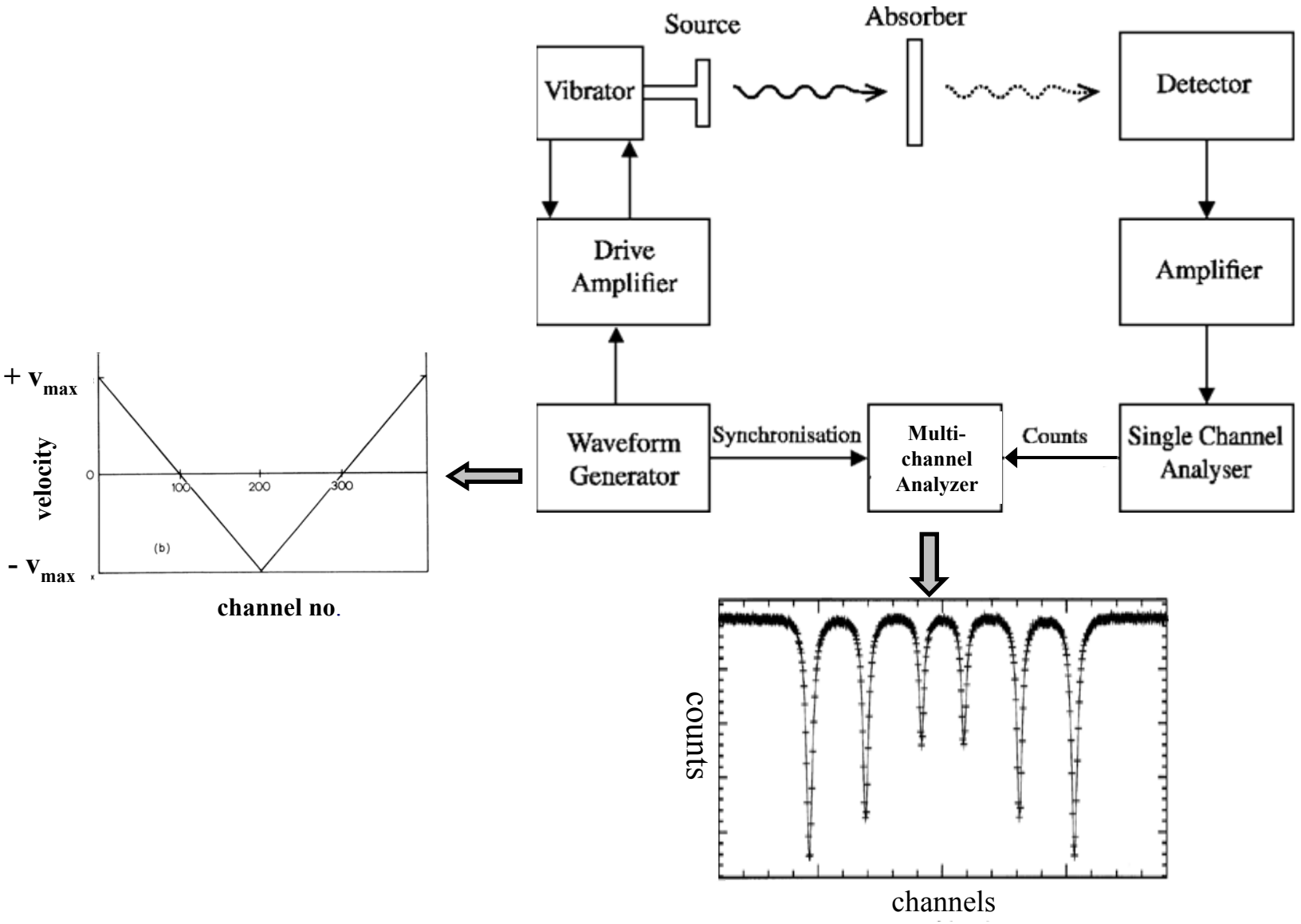


Selection rule $\Delta I = \pm 1$, $\Delta m_I = 0, \pm 1$ excludes 1/2→-3/2 and -1/2→3/2 transitions





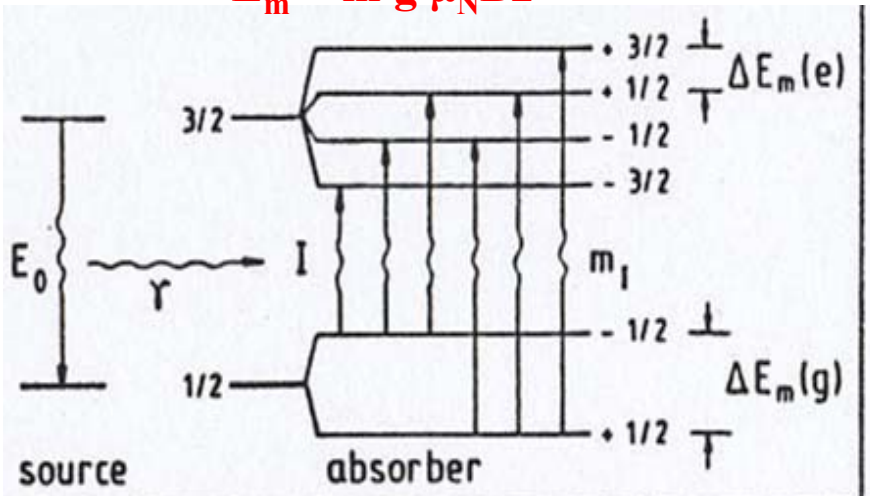
Mössbauer spectrometer schematic



Mössbauer spectra and hyperfine interactions

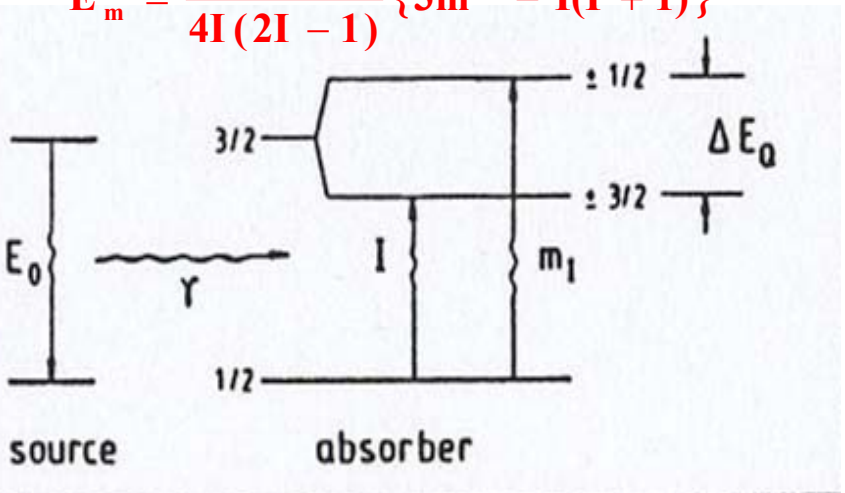
Magnetic interaction

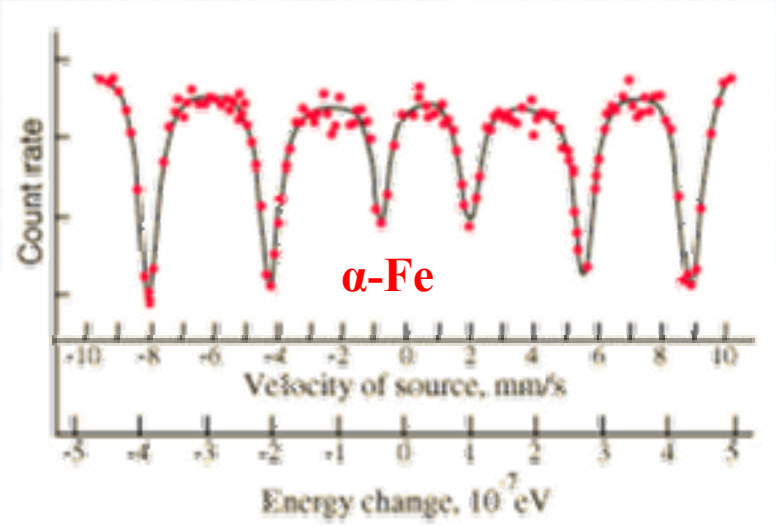
$$E_m = m\, g\, \mu_N B_z$$

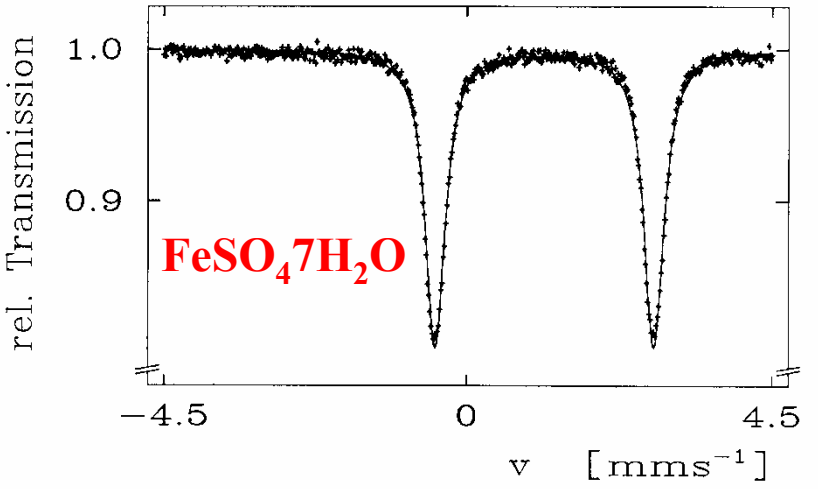


Quadrupole interaction

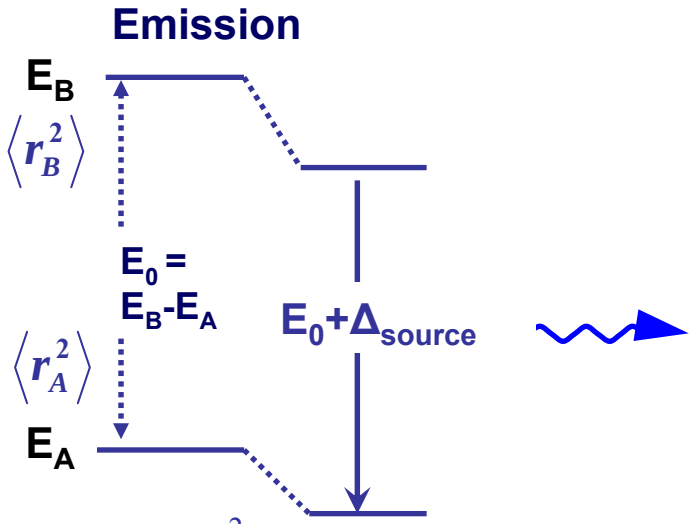
$$E_m^Q = \frac{eQV_{zz}}{4I(2I-1)}\{3m^2 - I(I+1)\}$$

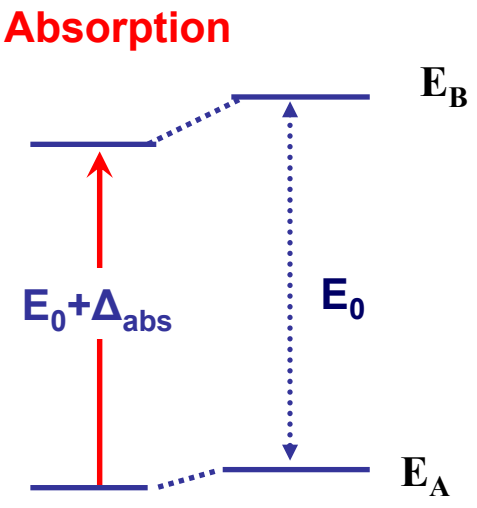


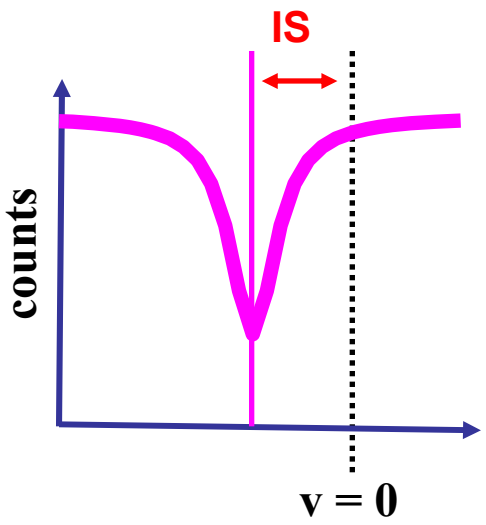




Isomer Shift in Mössbauer spectra







$$\Delta_{source} = \frac{Ze^2}{6\varepsilon_0}\left|\Psi(0)_{source}\right|^2\left\langle \Delta r^2 \right\rangle$$

$$\Delta_{abs} = \frac{Ze^2}{6\varepsilon_0}\left|\Psi(0)_{Abs}\right|^2\left\langle \Delta r^2 \right\rangle$$

$$IS = \frac{Ze^2}{6\varepsilon_0}\left\langle \left|\Psi_{source}(0)\right|^2 - \left|\Psi_{absorber}(0)\right|^2 \right\rangle (R_A^2 - R_B^2)$$

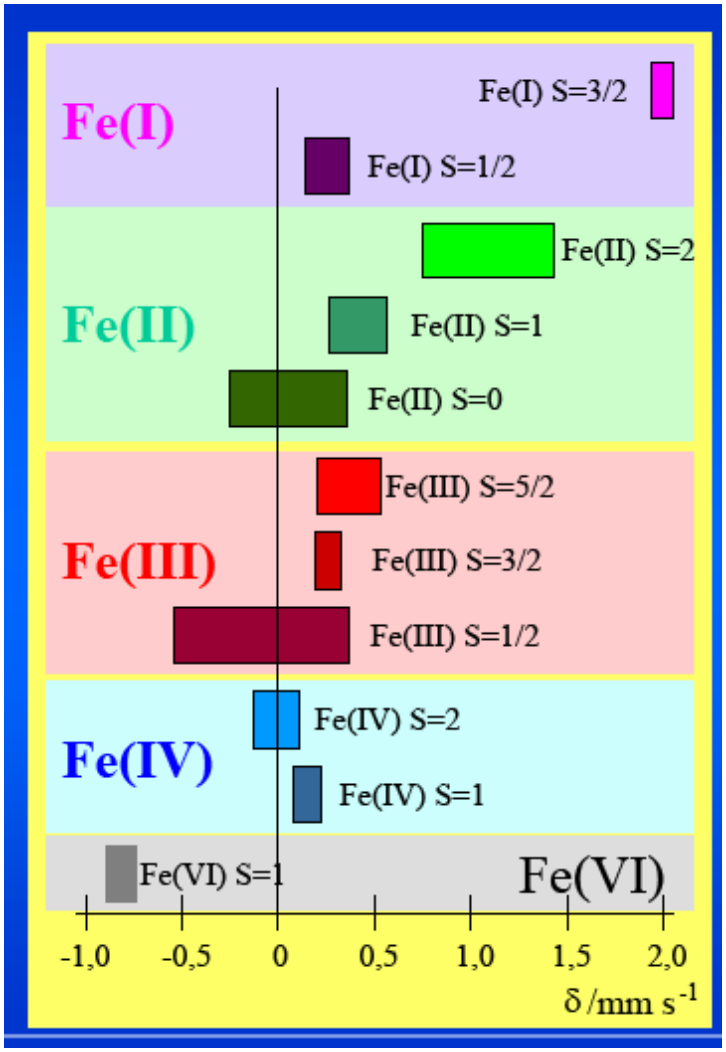
Isomer Shifts of Iron Compounds

$$IS = \frac{Ze^2}{6\varepsilon_0}\left\langle |\Psi_A(0)|^2 - |\Psi_S(0)|^2 \right\rangle (R_e^2 - R_g^2)$$

For ^{57}Fe : $(R_e^2 - R_g^2) < 0$

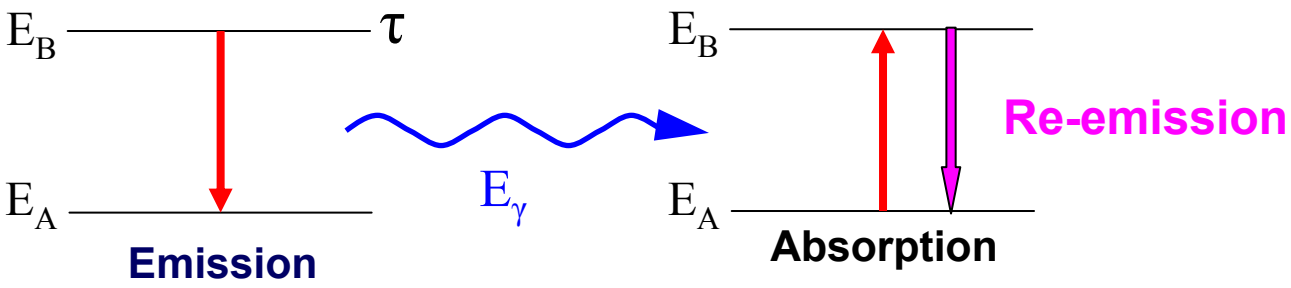
With the same source $(|\Psi(0)|_S^2 = \text{const.}$

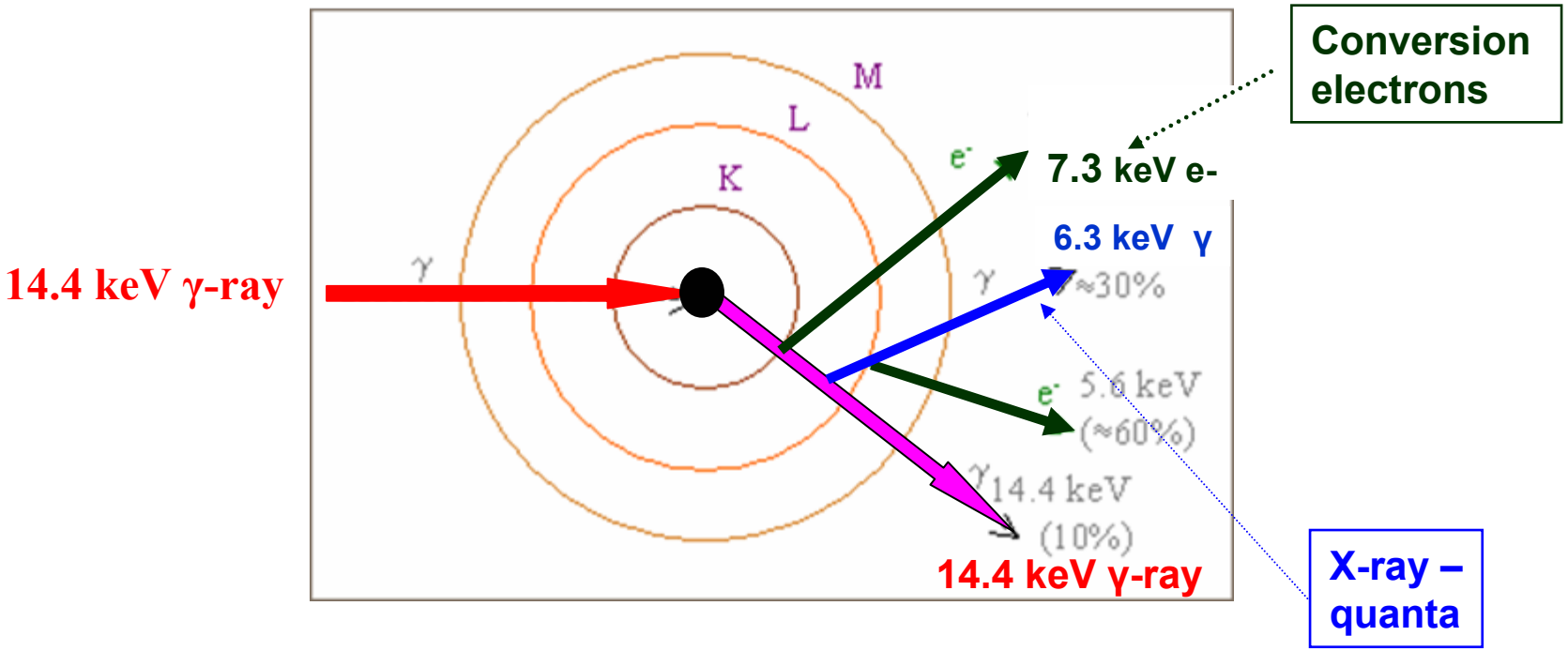
$$Shift\ \Delta = C\,|\Psi(0)|_A^2\,(R_e^2 - R_q^2)$$



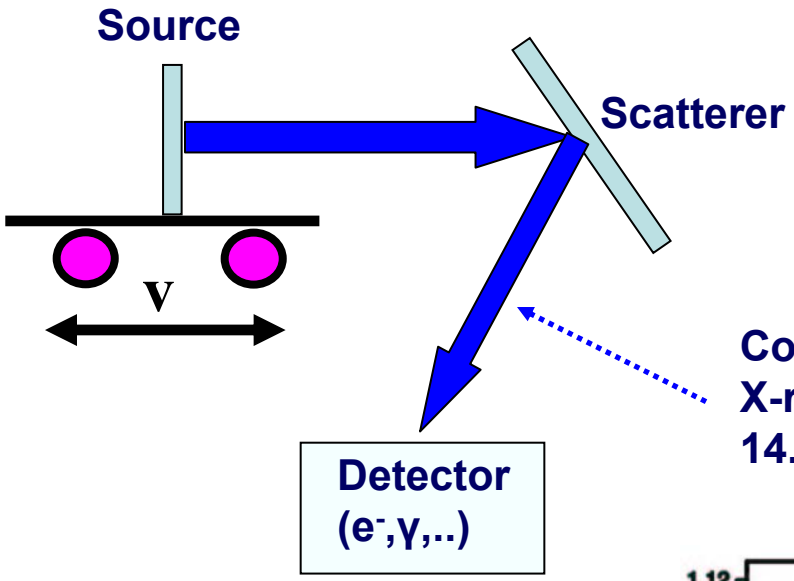
Increasing $|\Psi(0)|_A^2$

Re-emission processes with ^{57}Fe as example





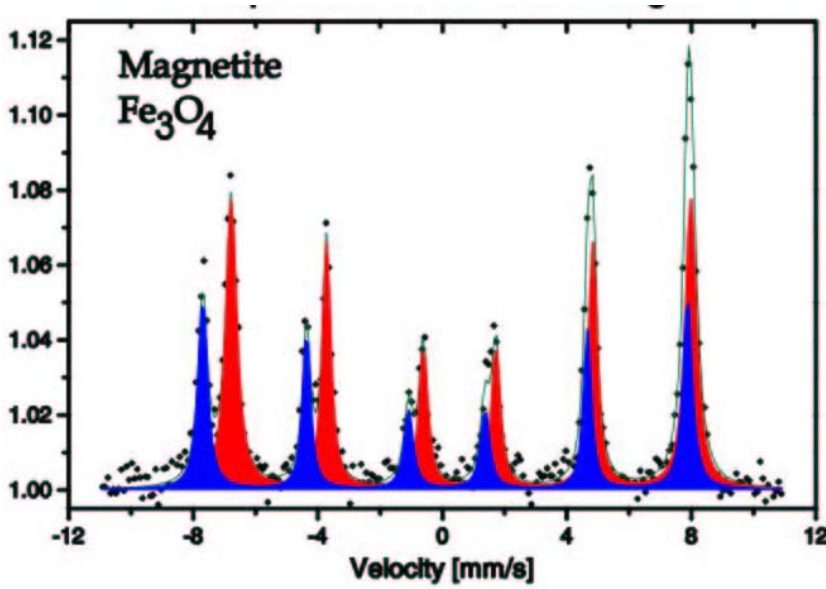
Backscattering Geometry



Conversion -electrons
X-ray -Quanta
14.4 keV γ-Quanten

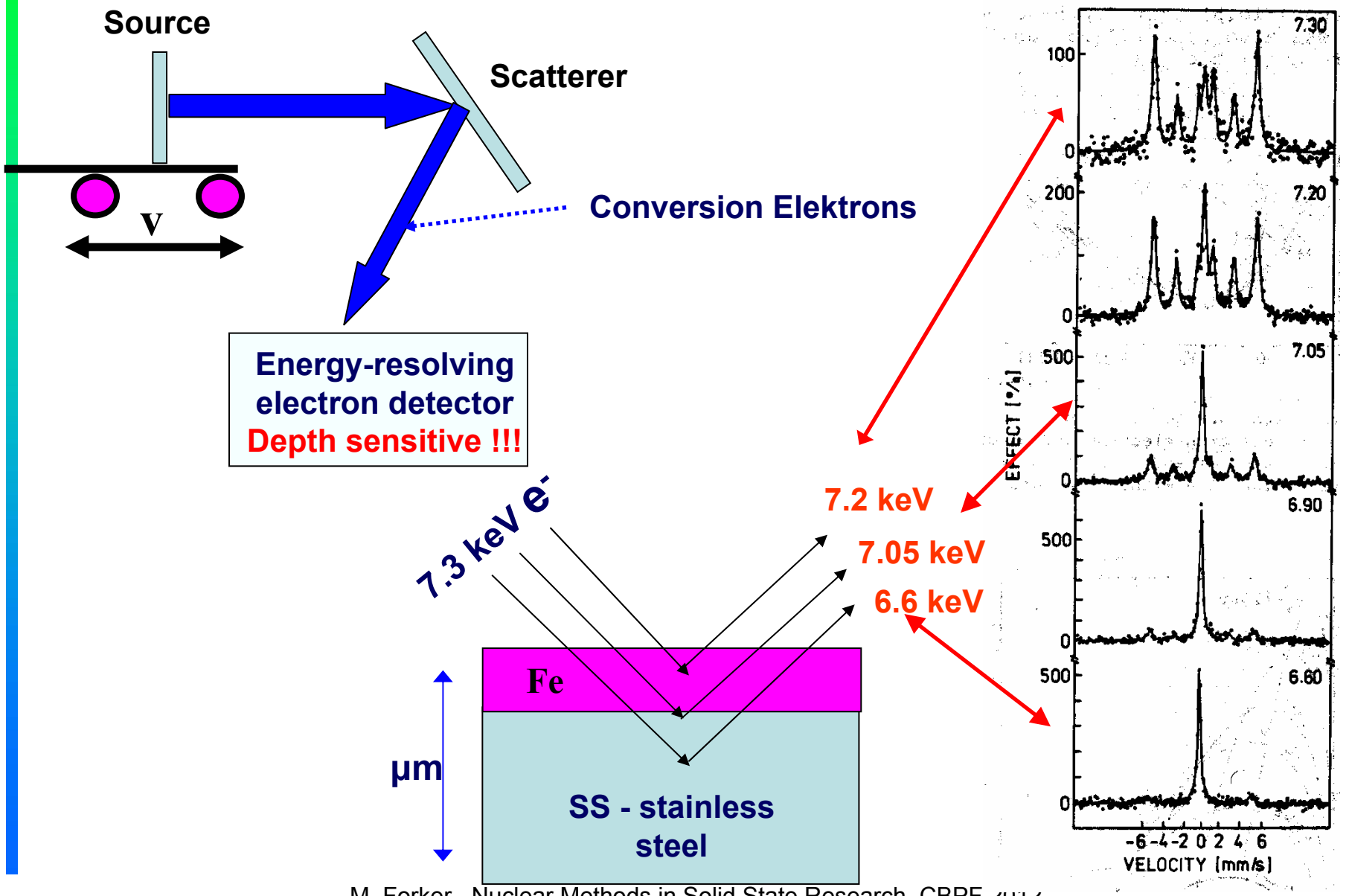
CEMS

Conversion Electron Moessbauer Spectroscopy



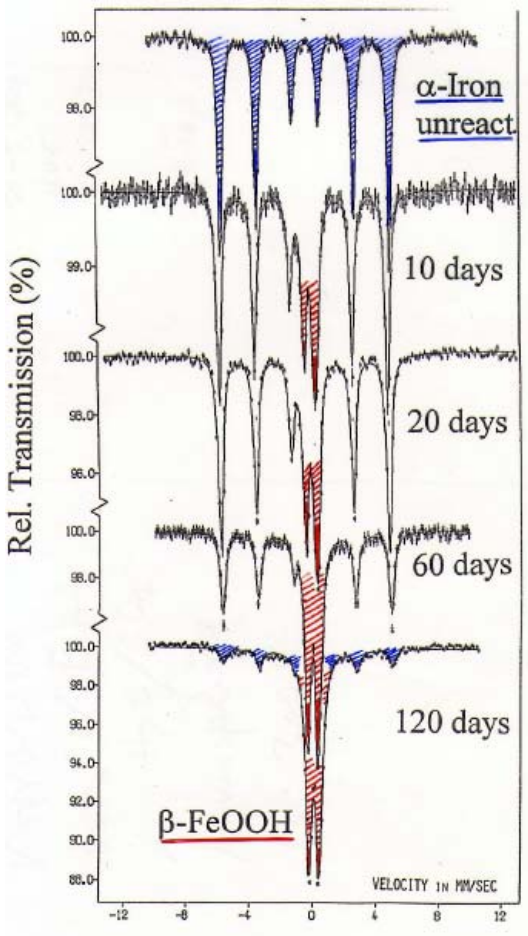
CEMS Spektrum von Magnetite (Fe_3O_4)

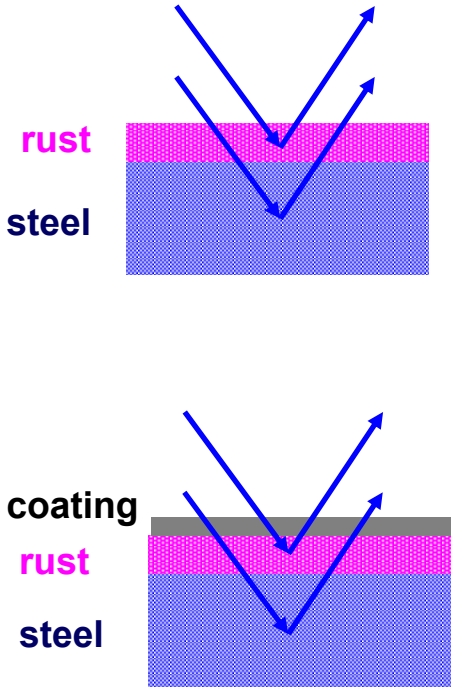
DCEMS : Differential Conversion Electron Mössbauer Spectroscopy



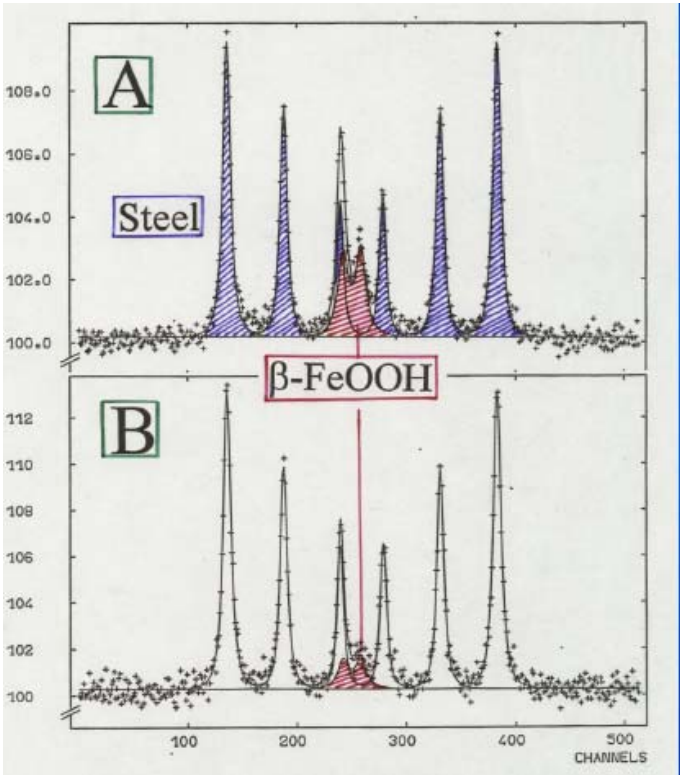
Industrial applications: Mössbauer study of corrosion

α-Fe foil in H_2O/SO_2 atmosphere





CEMS study of corrosion inhibition



Applications of Mössbauer Spectroscopy

HFI Parameter	Nuclear Physics	Solid State Physics	Chemistry
Isomerie-Shift	Nuclear Radii	Electron densities Electronic structure	Valencies
Magnetic HFI $\omega_L \propto (\mu \cdot B_{hf})$	Nuclear Moments	Magnetic Structures Relaxation phenomena	Properties of magnetic Ions Catalysis e.g. Fischer-Tropsch synthesis
Electric QWW $\omega_Q \propto (Q \cdot V_{zz})$ η		Charge distributions (strength, symmetry)	Ligand Symmetries Phase Identification
Debye-Waller Factor		Phonon specta	Anisotropic Ligands

SR

The Athena MIMOS II Mössbauer Spectrometer Investigation

G. Klingelhöfer[1], R.V. Morris[2], B. Bernhardt[1], D. Rodionov[1,3], P. A. de Souza Jr.[1,4], S. W. Squyres[5], J. Foh[1], E. Kankeleit[6], U. Bonnes[6], R. Gellert[1], Ch. Schröder [1], S. Linkin[3], E. Evlanov[3], B. Zubkov[3], and O. Prilutski[3]

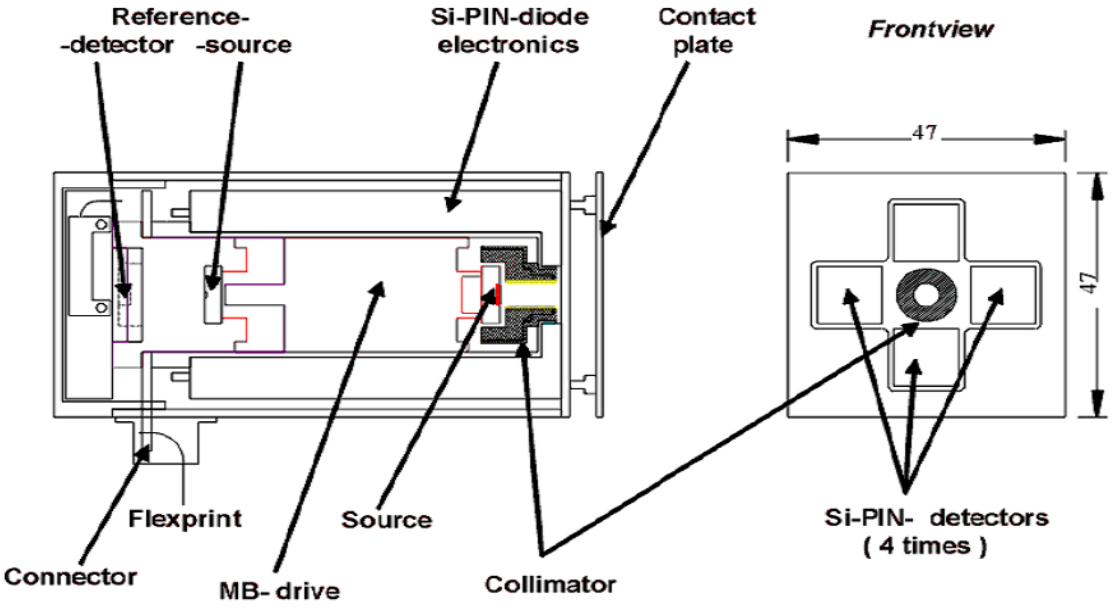
[1]Institut Inorg. & Analytical Chemistry, Johannes Gutenberg-University, 55099 Mainz, Germany
[2]NASA Johnson Space Center, Houston, TX 77058, USA
[3]Space Research Institut IKI, Moscow, Russia
[4]Pelletizing Department, Companhia Vale do Rio Doce, Vitoria, ES, Brazil
[5]Cornell University, Ithaca, NY 14853,USA
[6]Nuclear Physics Institut, Darmstadt University of Technology, 64289 Darmstadt, Germany

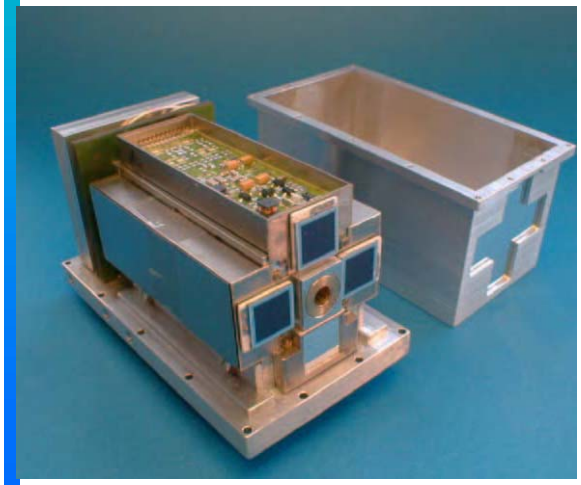
Athena = Scientific Program of Rover Mars Expedition - started in 2003

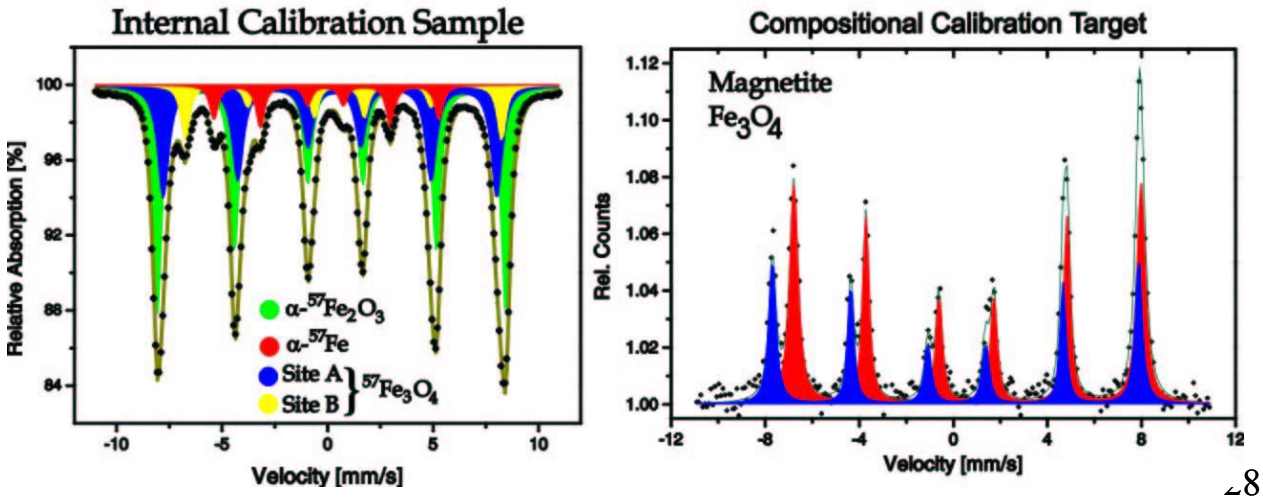
MIMOS = MIniaturized MOSsbauer Spectrometer

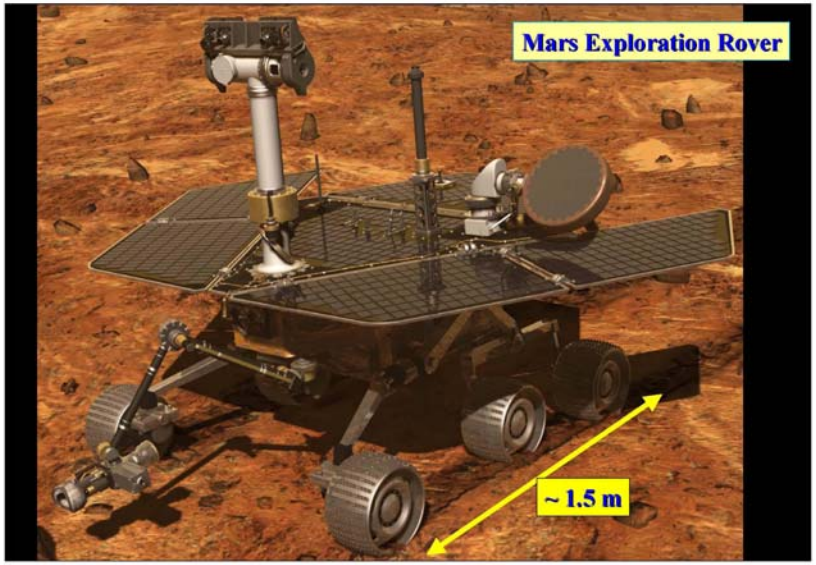
Backscattering geometry:does not require sample preparation !!!

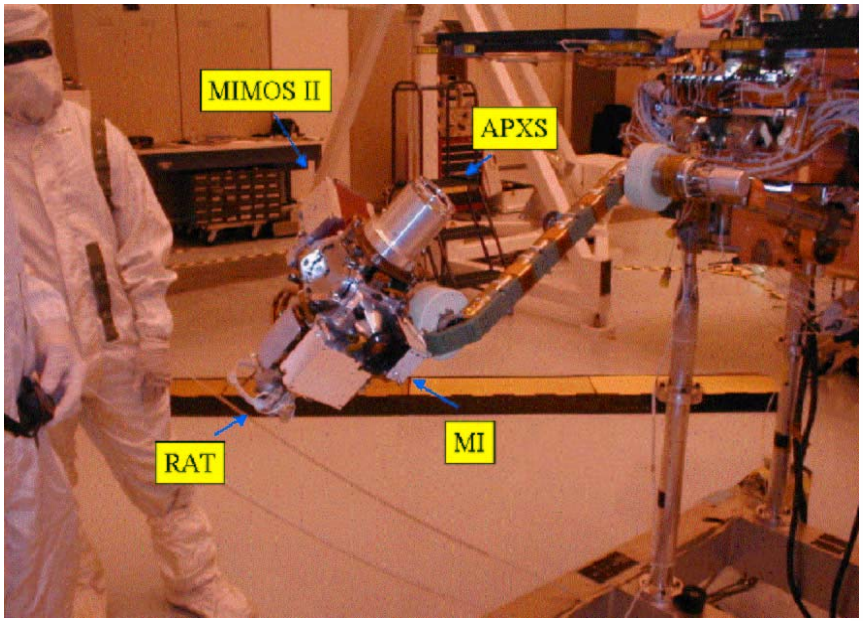
DESIGN of MIMOS II

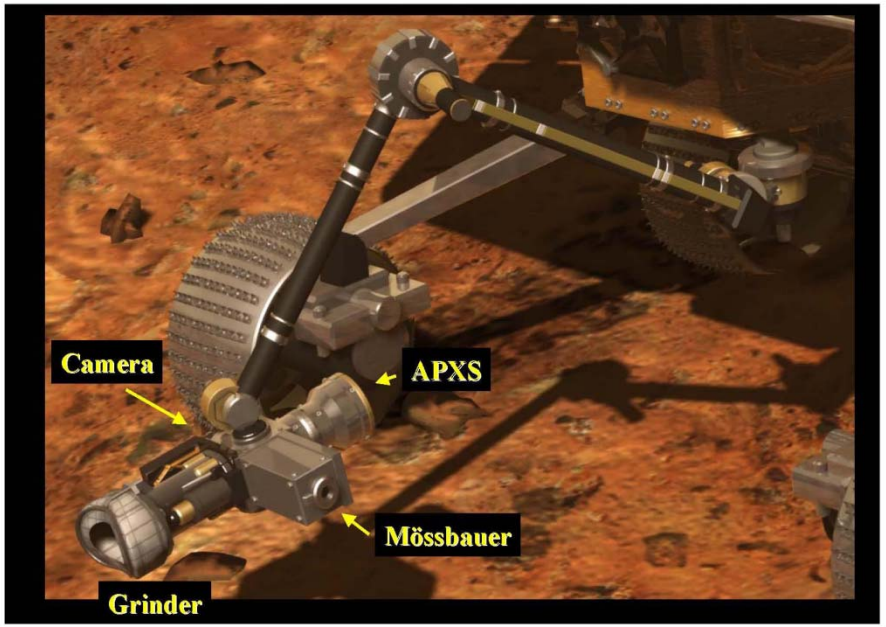







Mars Exploration Rover
~ 1.5 m


MIMOS II
APXS
RAT
MI


Camera
APXS
Mössbauer
Grinder

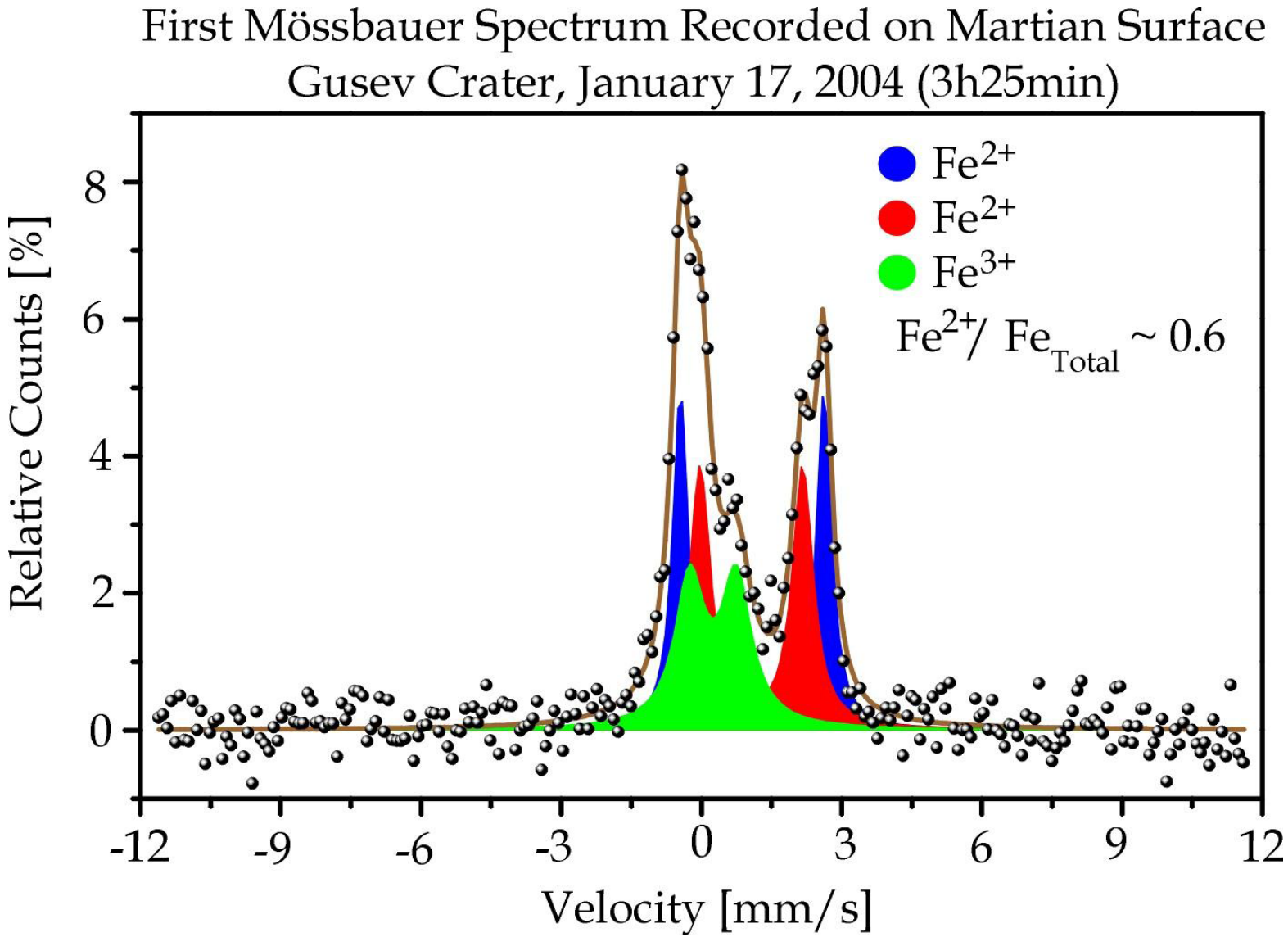
The scientific measurement objectives of the MIMOS II on Mars investigation

are to obtain **quantitative mineralogical analysis of Fe-bearing materials (**rock, soil, and dust) by

(1) the **mineralogical identification** of iron-bearing phases (e.g., oxides, silicates, sulfides, sulfates, and carbonates),

(2) the **quantitative measurement of the distribution of iron** among these iron-bearing phases (e.g., the relative proportions of iron in olivine, pyroxenes, ilmenite and magnetite in a basalt), and

(3) the quantitative measurement of the **distribution of iron among its oxidation states** (e.g., Fe2+, Fe3+, and Fe6+).


First Mössbauer Spectrum Recorded on Martian Surface
Gusev Crater, January 17, 2004 (3h25min)
Relative Counts [%]
Velocity [mm/s]
Fe2+
Fe2+
Fe3+
Fe2+/ FeTotal ~ 0.6
8
6
4
2
0
-12
-9
-6
-3
0
3
6
9
12

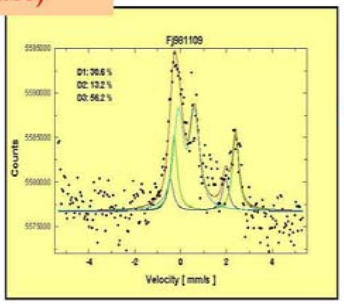
Terrestrial applications of MIMOS II

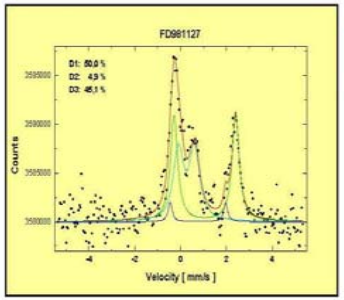
Monitoring of Iron Mineralogy and Oxidation States in the Field: the Green Rust Mineral

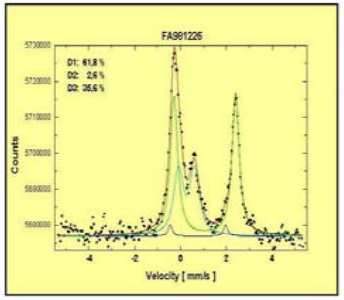
Electronics-box with digital board and positioning-mechanism.

- long tube with windows located in different depths.
- MIMOS II is moved within the tube to different depth.

Depth (with respect to surface)	Fe^{II}/Fe^{III}
69 cm	0,78
34 cm	1,22
9 cm	1,81

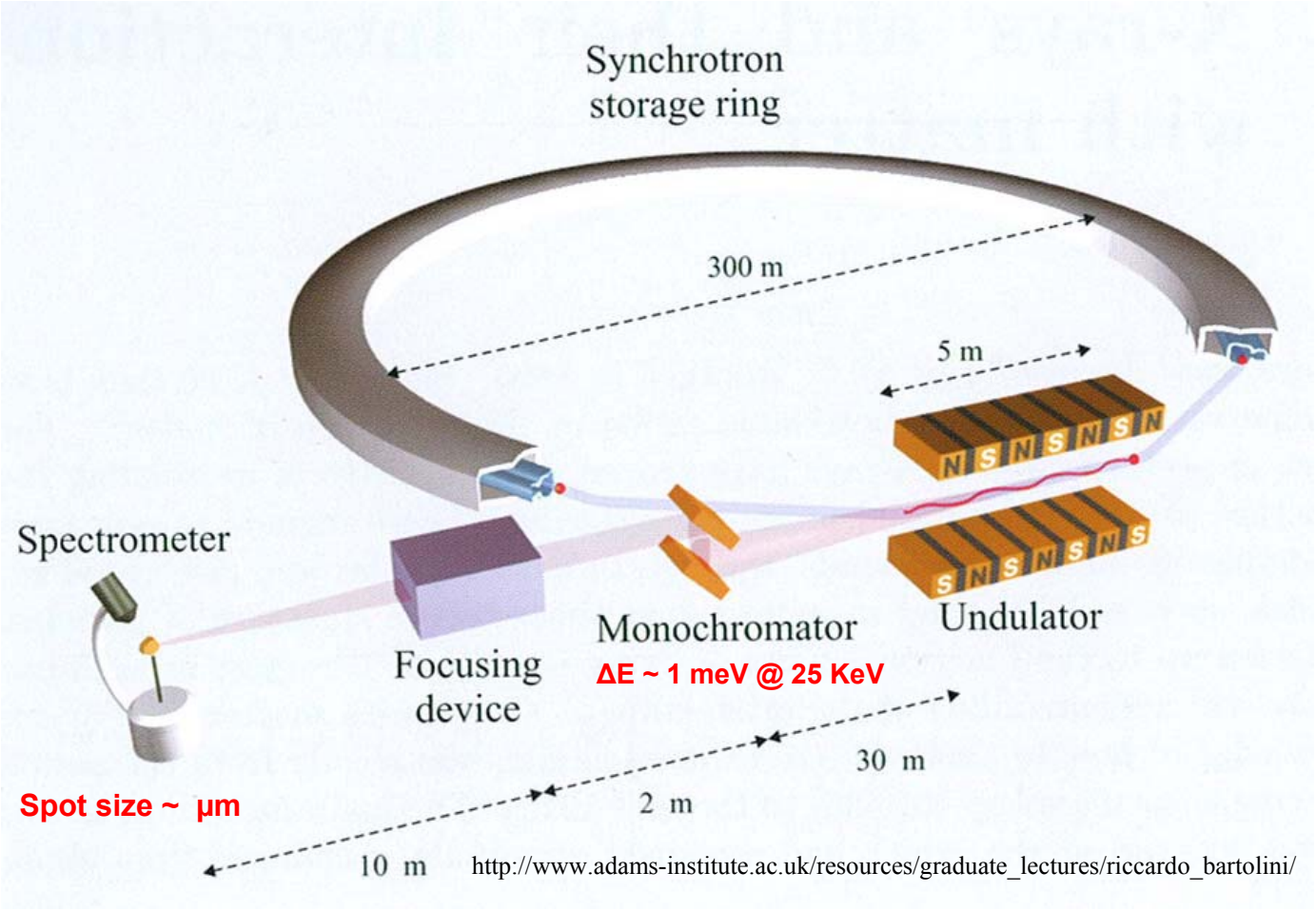






SR-based Mössbauer spectroscopy

SR: Synchrotron radiation: The electromagnetic radiation emitted when charged particles are accelerated radially. It is produced in the synchrotron radiation sources using **bending magnets, undulators and wigglers**



Properties of synchrotron radiation

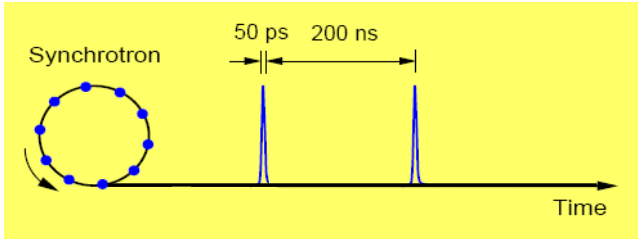
Broad Spectrum from microwaves to hard X-rays:
the users can select the wavelength required for their experiment.
Monochromators **ΔE ≥ 1 meV @ 25 KeV**

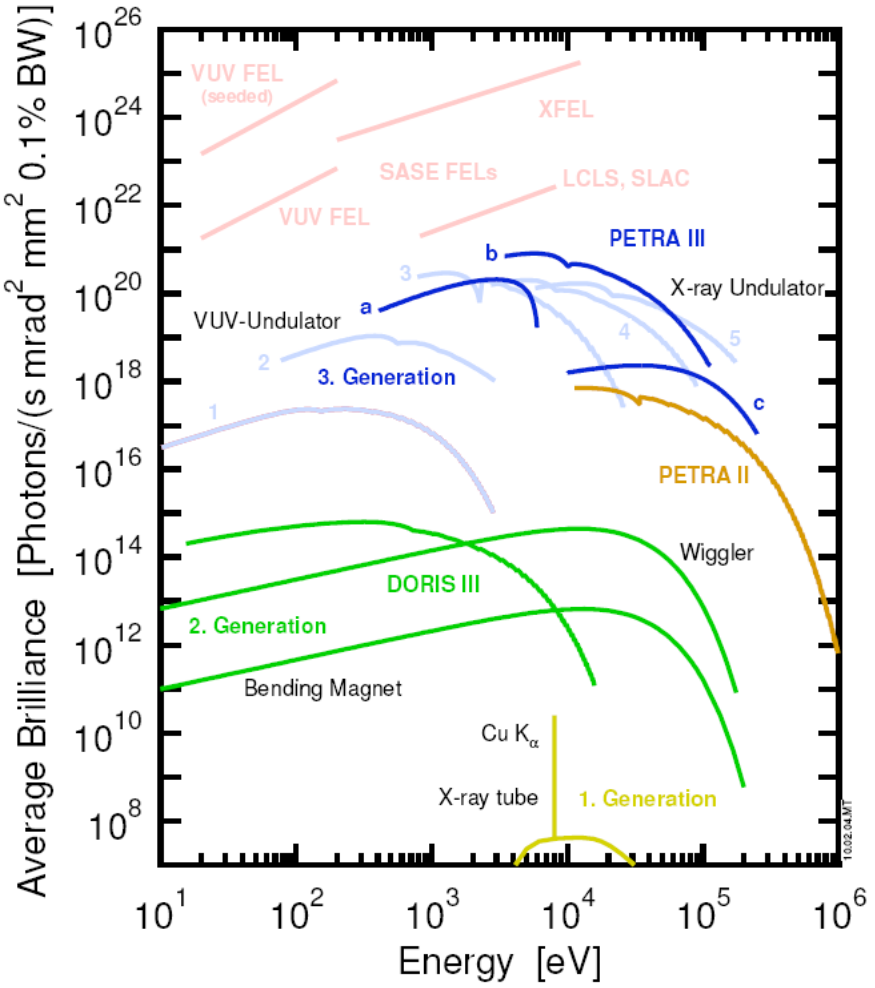
High Brilliance:
highly colliminated photon beam generated by a small divergence and small size source (spatial coherence)
Focussing of hard X-rays down to a spot size of < 100 nm has been demonstrated at ESRF

High Stability: submicron source stability

Polarizaton: both linear and circular

Pulsed Time Structure:
pulsed length down to tens of picoseconds
Pulse separation: 2 ns to 4 μs





2005: Worldwide about 40.000 scientists are using synchrotron radiation

SR Mössbauer spectroscopy – Nuclear resonant scattering

Conventional Mössbauer spectroscopy with radioactive sources is difficult when narrow , high intensity beams of γ-rays are needed for e.g. the study of **very small samples, ultrathin films samples and, under high pressures**

Synchrotron radiation is a very powerful instruments for such studies because of its properties: **Tunable energy, high brilliance, small beam size, small beam divergence and pulsed time structure**.

SR Mössbauer studies can be carried out in

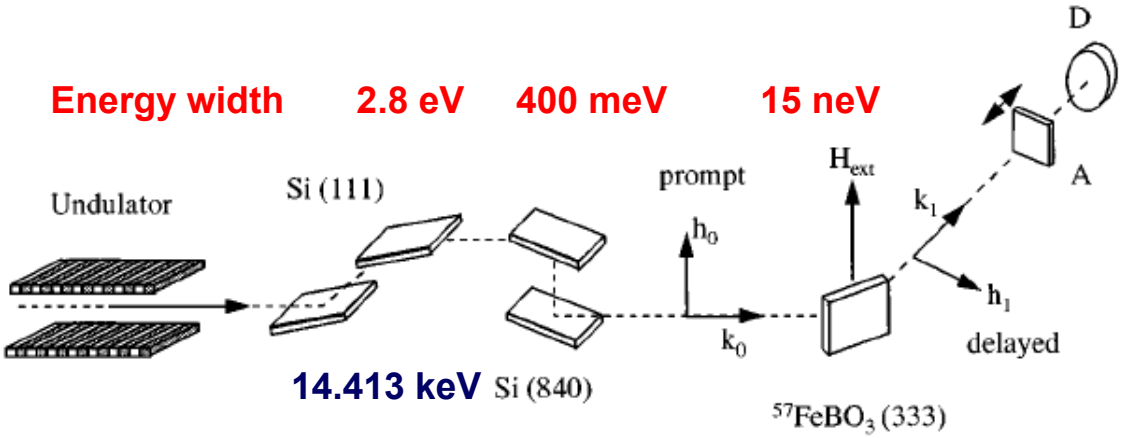
(i) the energy domain:
observation of the nuclear resonant scattering as a function of energy

(ii) The time domain:
Time differential observation of the scattered intensity

Presently, most of the nuclear resonant scattering studies are carried out in the time domain

SR Mössbauer spectroscopy in the energy domain

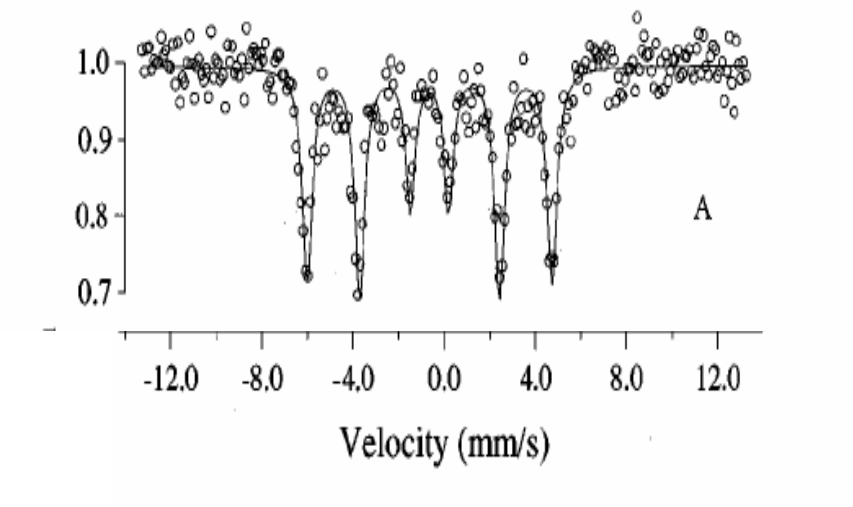
A ^{57}Fe Synchrotron Mössbauer Source G. V. Smirnov et al. PRB 55 (1997) 5811



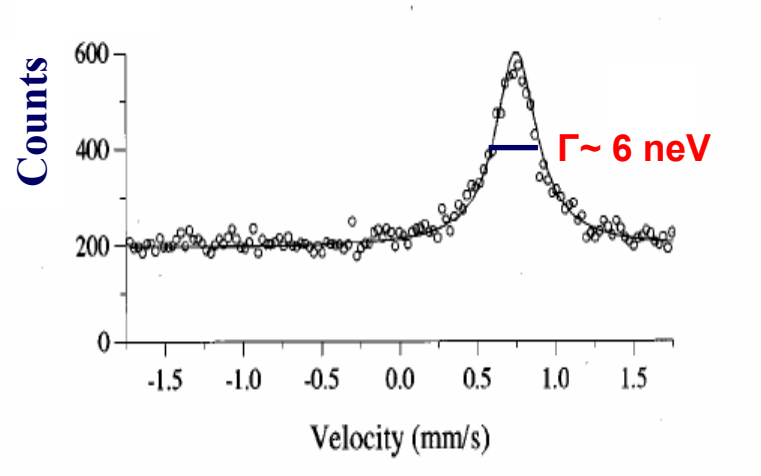
Si crystal monochromators

Nuclear Bragg diffraction

Absorber ^{57}Fe foil



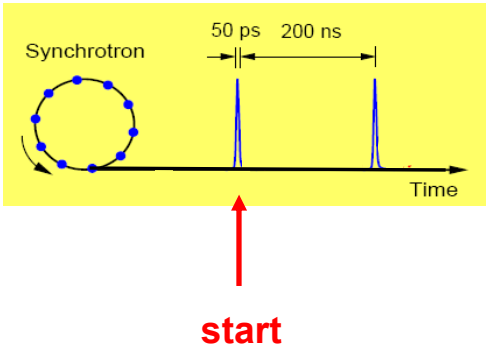
absorber of sodium nitroprusside

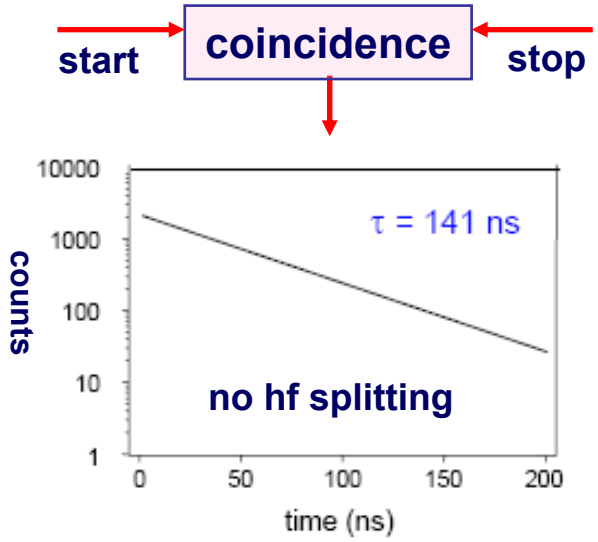


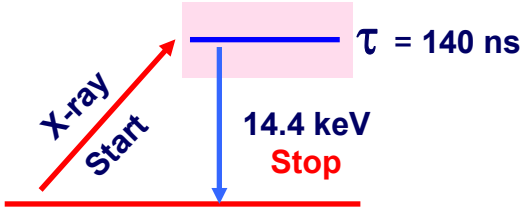
SR Mössbauer spectroscopy in the time domain

Time differential observation of nuclear resonance scattering

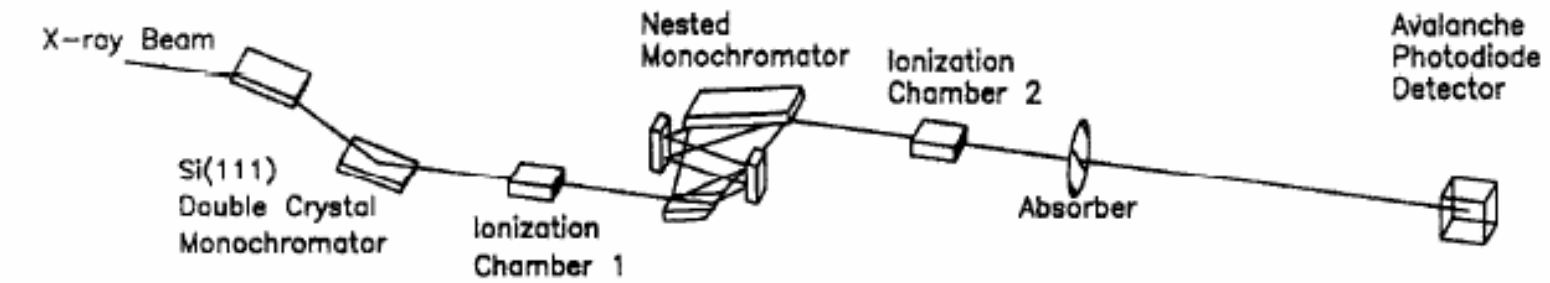
SR time structure





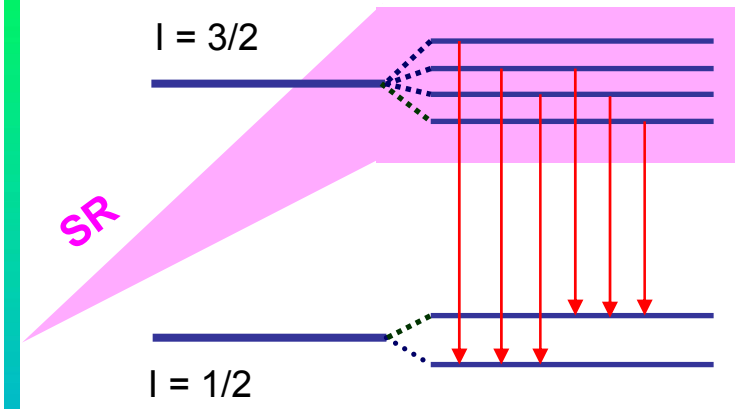


E.E. Alp et al.,
Nucl. Instr. Methods B 97 (1995) 526-529



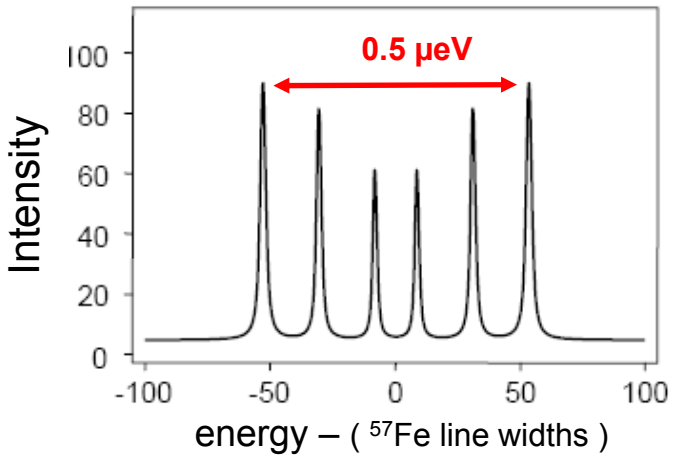
SR Mössbauer spectroscopy in the time domain

Time spectra in the presence of hyperfine interactions

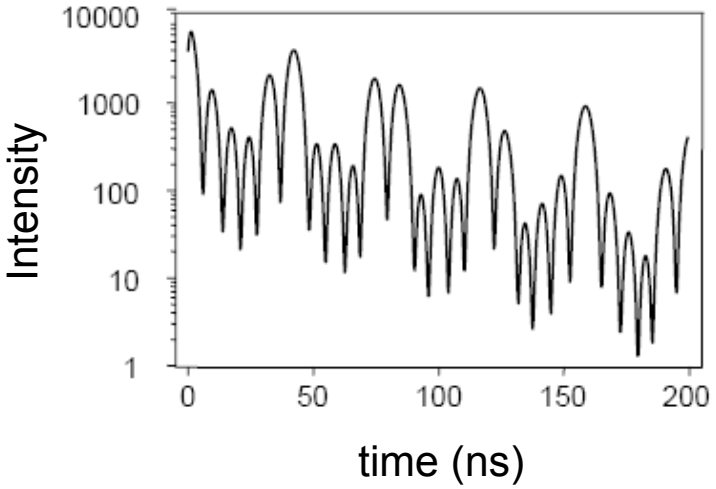


Simultaneous broad band excitation of all hyperfine levels results in **interference** between the different nuclear transitions and fast **quantum beats** in the time spectrum

Corresponding energy specrum

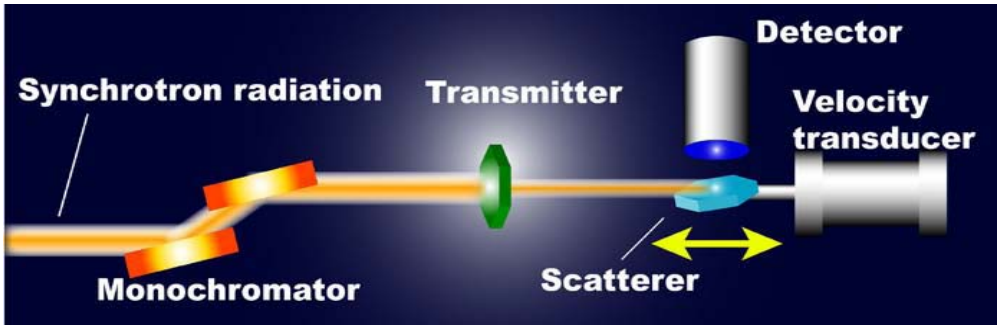


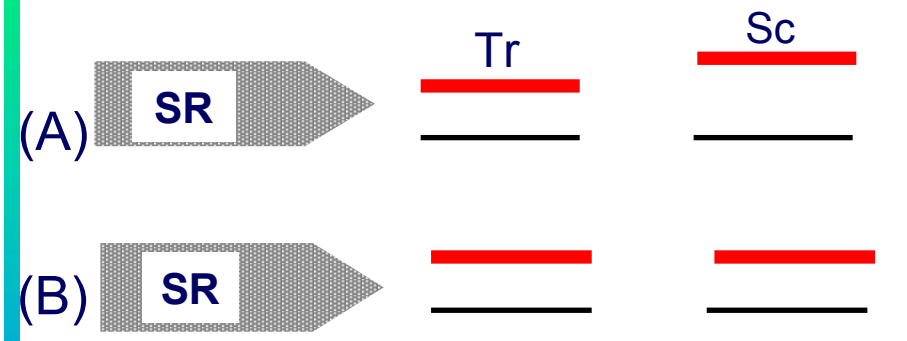
Time spectrum

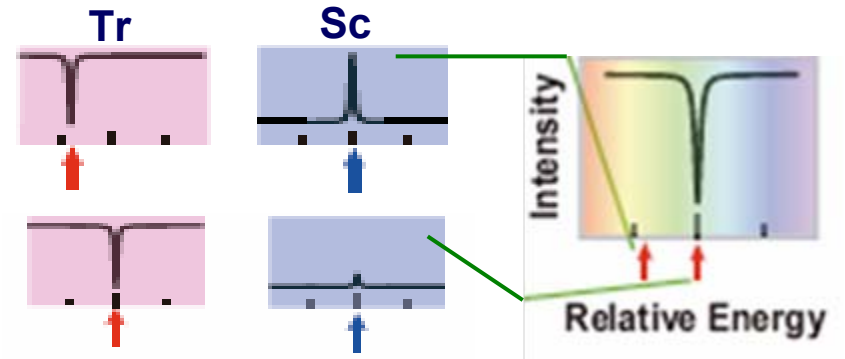


SR Mössbauer spectroscopy in the energy domain

M. Seto et al.
PRL 102, 217602 (2009)
Journal of Physics: Conference Series **217** (2010) 012002





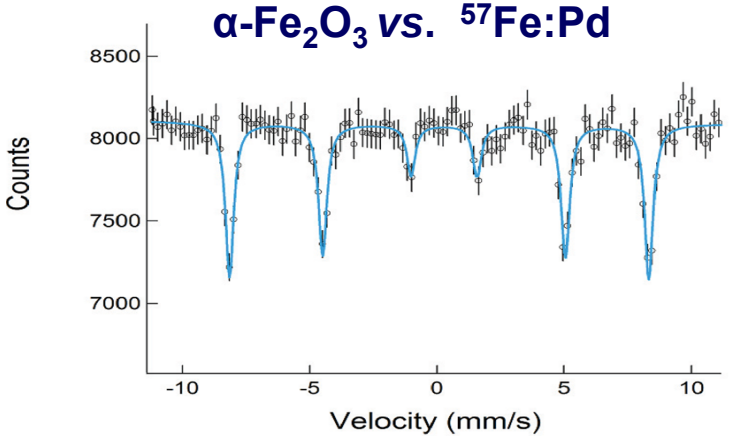


(A): Different resonance energies of transmitter E_0(Tr) and scatterer E_0(Sc), high transmission at the resonance E_0(Sc), strong scattered intensity at E_0(Sc)

(B): Equal resonance energies E_0(Tr) and E_0(Sc). Weak tranmission and minimum of the scattered intensity

The hyperfine pattern can therefore be sampled by relative motion of scatterer and transmitter

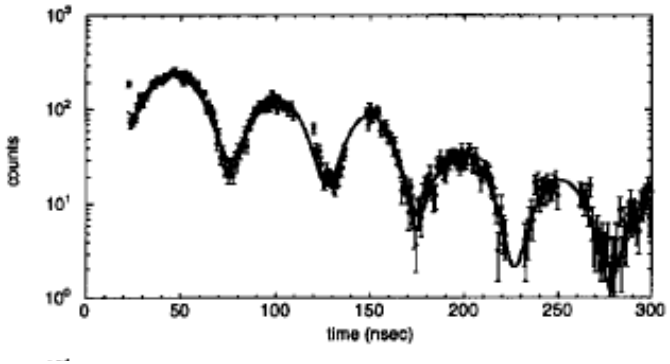
α-Fe_2O_3 *vs.* ^{57}Fe:Pd



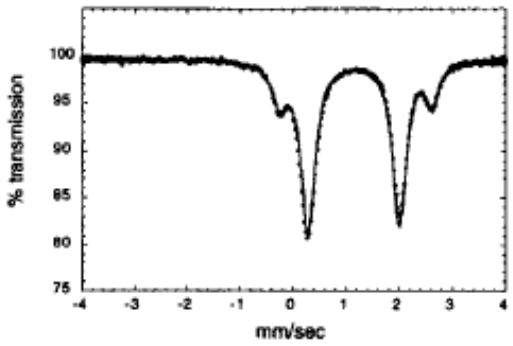
Comparison of Mössbauer spectra in the time- and the energy domain

Example: $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

Time domain
using Synchrotron radiation



Energy domain
Transmission spectrum
using a radioactive source



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Comparison of results obtained by synchrotron Mossbauer spectroscopy, SMS, and transmission Mossbauer spectroscopy experiments

Parameter	SMS	Transmission Mossbauer
Component 1		
Isomer shift [mm/s]	1.41 ± 0.02	1.36 ± 0.02
Quadrupole splitting [mm/s]	1.71 ± 0.008	1.73 ± 0.02
Relative weight	0.79 ± 0.06	0.88 ± 0.001
Component 2		
Isomer shift [mm/s]	1.41 ± 0.24	1.41 ± 0.02
Quadrupole splitting [mm/s]	2.83 ± 0.43	2.82 ± 0.02
Relative weight	0.21 ± 0.13	0.15 ± 0.003