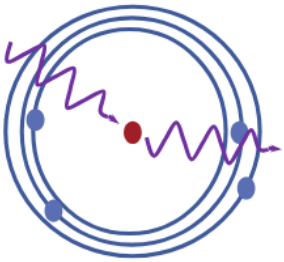
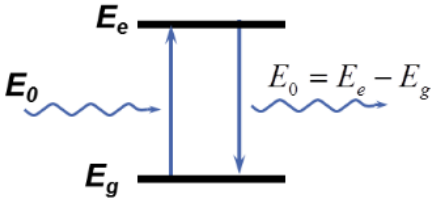
The Mössbauer effect

Resonant scattering of light from the atomic shell:

A beam of yellow light irradiates a vapour of sodium atoms. Upon de-excitation yellow light with the same wavelength as the incoming light is emitted in **4π** geometry, i.e. **resonance fluorescence**.



γ-rays



Conservation of momentum and energy (emission):

$$Mv_x = \frac{E_\gamma}{c} + M(v_x - v_R)$$

nucleus mass; recoil velocity

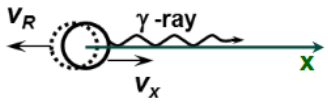
nucleus is excited before!

$$E_e + \frac{1}{2}Mv_x^2 = E_g + E_\gamma + \frac{1}{2}M(v_x - v_R)^2$$

$$E_\gamma = (E_e - E_g) - \frac{1}{2}Mv_R^2 + Mv_x v_R = E_0 - E_R + E_D$$

This process should be observed in the atomic nucleus but it is challenging !!! Why ?

W. Kuh, Phil. Mag. 8, 625 (1929)



Doppler shift energy:

$$E_D = Mv_x v_R = \frac{v_x}{c}E_\gamma$$

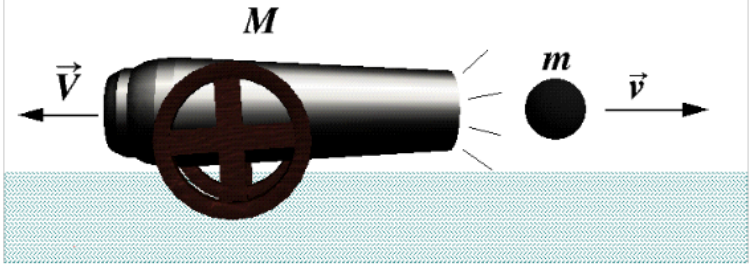
Recoil energy:

$$E_R = \frac{1}{2}Mv_R^2 = \frac{E_\gamma^2}{2Mc^2}$$

The Mössbauer effect

Recoil effect

v_x=0 → E_D=0 : The spectrum is shifted from E_0 by E_R and has FWHM ≈ Γ



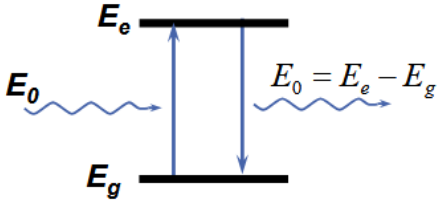
Nucleus of ^{57}Fe:

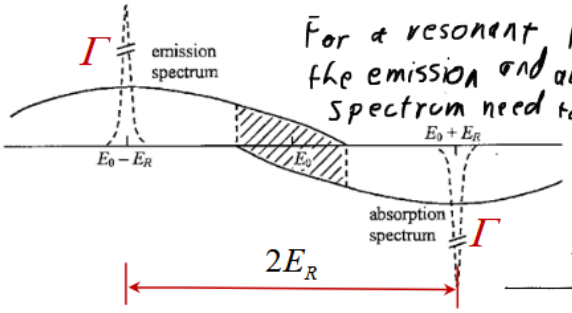
E_0 = 14.413 keV

huge → ***τ = 141.1 ns;***

extremely narrow → ***Γ = 4.66 neV***

$$\Gamma\tau \geq \hbar/2$$





For a resonant process, the emission and absorption spectrum need to overlap!

(- not the case here

$$E_R = \frac{1}{2}Mv_R^2 = \frac{E_\gamma^2}{2Mc^2} \cong 2meV$$

Condition for resonant process: $\Gamma/2E_R > 1$

A comparision of the parameters of the atomic and nuclear levels

	E_γ(eV)	Γ_n (eV)	E_R (eV)	$\Gamma_n/2E_R$
^{57}Fe nucleus	14.4×10^3	4.65×10^{-9}	1.95×10^{-3}	1.2×10^{-6} (not resonant)
Na atom (D-lines)	2.1	4.39×10^{-8}	1.0×10^{-10}	2.2×10^{2} (resonant)

Recoil and Doppler effects

$v_x \neq 0 \rightarrow E_D \neq 0$: The spectrum is shifted from E_0 by E_R and has FWHM >> Γ

$$E_\gamma = (E_e - E_g) - \frac{1}{2}Mv_R^2 + Mv_x v_R = E_0 - E_R + E_D$$

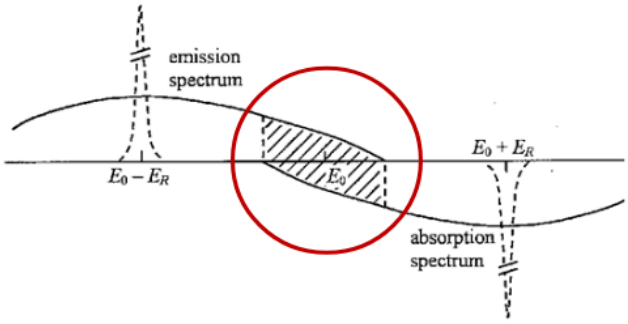
if these cancel! Then $E_\gamma = E_0$

Recoil energy:

$$E_R = \frac{1}{2}Mv_R^2 = \frac{E_\gamma^2}{2Mc^2} \cong 2meV$$

Doppler shift energy:

$$E_D = Mv_x v_R = \frac{v_x}{c}E_\gamma$$



The thermal random motion of free atoms results in broad velocity distribution of v_x described by the Maxwell distribution:

$$p(v_x)\,dv_x = \left(\frac{M}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{M}{2k_B T}v_x^2\right) dv_x$$

k_B is the Boltzmann constant, T – the absolute temperature

This is known as a Doppler broadening with a width:

$$2(2k_B T \ln 2/M)^{1/2}$$

Therefore the width of the emission line is:

$$\Delta E_D = Mv_R\left(2\sqrt{\frac{2k_B T \ln 2}{M}}\right) = 4\sqrt{E_R k_B T \ln 2}.$$

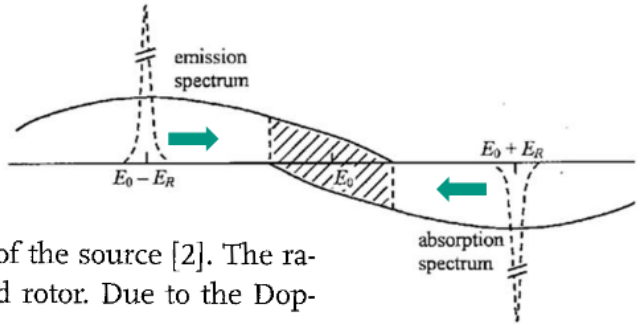
For ^{57}Fe at 300K the ΔE_D=24 meV > $2E_R$=4 meV
→ a small overlap between emission and absorption spectra
→ non zero probability for a resonant process

$\Delta E_D/2E_R$=6

The Mössbauer effect

How to compensate the recoil?

$$E_\gamma = (E_e - E_g) - \frac{1}{2}Mv_R^2 + Mv_x v_R = E_0 - E_R + E_D$$



The first experiment made use of mechanical motion of the source [2]. The radioactive source was mounted on the tip of a high-speed rotor. Due to the Doppler effect, the γ-rays acquired an additional energy ΔE,

$$\Delta E = \frac{v}{c}E_\gamma. \quad \rightarrow \quad (v/c)E_\gamma = 2E_R \ (\text{for } ^{57}\text{Fe},\ v = 81\ \text{m s}^{-1}) \approx 292\ \text{km/h})$$

Two problems: (i) very low count-rate; (2) poor stability of the setup due to enormous speed

$$\Delta E_D = Mv_R\left(2\sqrt{\frac{2k_B T \ln 2}{M}}\right) = 4\sqrt{E_R k_B T \ln 2}.$$

The second experiment used the fact that the Doppler broadening is increased by raising the temperature. As a result the overlapping arrea, i.e. probability for resonant process increases.

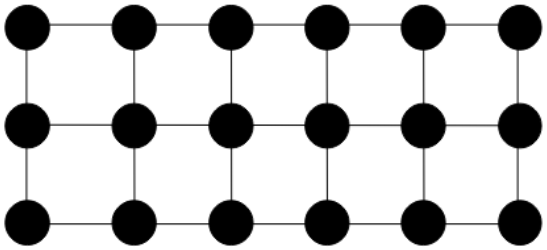
By both methods the nuclear resonant absorption has been observed before 1954.
The spectrum was shifted due to recoil and broadened due to thermal motion.

How to compensate the recoil? – new idea

In a crystal lattice the atoms are held in equilibrium positions by strong chemical bonds (≈10 eV).
For 129 keV (Γ = 6.5 neV) transition in free ^{191}Ir nucleus E_R=4.7x10^{-2} eV.
From the classical mechanics point of view it follows that when an atom is bound in a lattice, the nucleus will not recoil alone, rather than the entire crystal lattice recoils (≈10^{18} atoms):

$$E_R = \frac{E_\gamma^2}{2Mc^2} \cong 10^{-20} eV \rightarrow \Gamma / 2E_R > 1$$

i.e. $E_\gamma \approx E_0$ which corresponds to a recoilless resonant process.



The nucleus does not recoil alone.

Instead the recoil is taken up by the entire crystal lattice (~ 10^{18} atoms).

($M \rightarrow \infty$, $E_R \rightarrow 0$), i.e. recoilles resonant absorption.

Experimental setup

process.

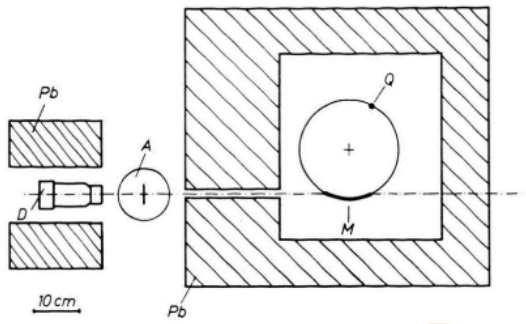


Abb. 2. Versuchsgeometrie. A Absorber-Kryostat; Q rotierender Kryostat mit Quelle; D Szintillationsdetektor. M ist der bei der Messung ausgenützte Teil des Rotationskreises der Quelle.

The Mössbauer effect

How to compensate the recoil? – new idea

Instead of heating the sample to broaden the absorption and emission lines Rudolf Mössbauer cooled the sample to 88 K. The aim was to make the crystal lattice even more rigid.

$\Delta E/E = 5.0 \times 10^{-11}$

This unreachable before energy resolution offered fundamentally new research opportunities.

R.L. Mössbauer,
Z. Physik, ***151****,124 (1958)*
Naturwissenschaften 45, 538, (1958)
*Z. Naturforsch.****14a****, 211 (1959)*

Nuclear recoilless (recoil-free) absorption in ^{191}Ir

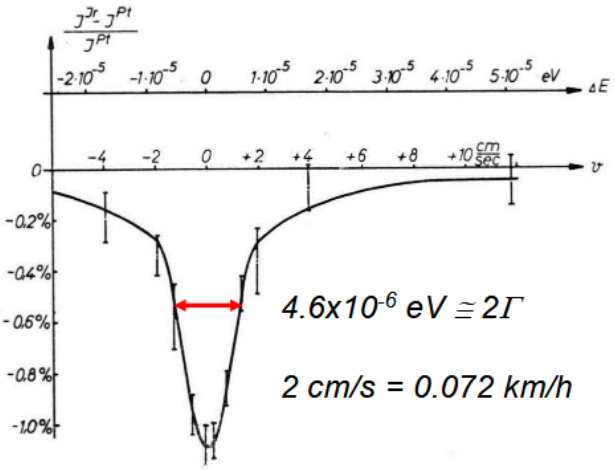


Abb. 3. Relatives Intensitätsverhältnis $(I^{Ir}-I^{Pt})/I^{Pt}$ der hinter Iridium- bzw. Platinabsorbern gemessenen γ-Strahlung als Funktion der Geschwindigkeit der Quelle relativ zu den Absorbern. $E=(v/c)\cdot E_0$ ist die Energieverschiebung der 129 keV-Quanten relativ zu den ruhenden Absorbern. Als Strahlungsquelle diente eine 65 mCurie starke Osmiumquelle, deren Zerfallsspektrum die 129 keV-Linie in Ir^{191} enthält.

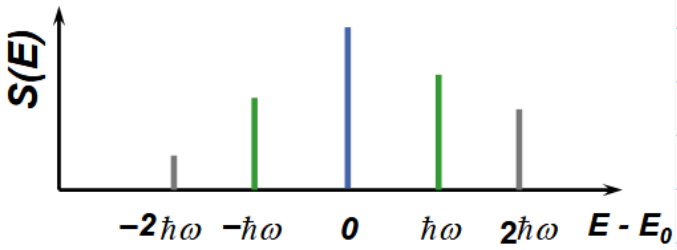
The Mössbauer effect

Atoms bound in a crystal lattice, **but** they vibrate about an equilibrium position.
The lattice vibrations, i.e. phonons, are quantized:

$$E_P = \hbar\omega$$

The photon can exchange energy with the lattice, by creating or anihilating of phonons.

Einstein model of a solid



The recoil resonant absorption takes place if: $E_R \ll \hbar\omega$

cool it! or lower energies

The probability for recoiless process is given by the Lamb-Mössbauer factor : $f = e^{-k^2\langle x^2\rangle}$

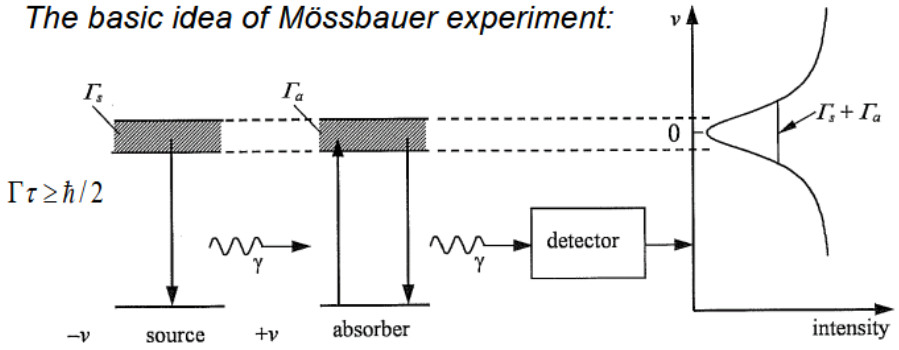
$\langle x^2 \rangle$ - the mean-square displacement of the nucleus along the direction of the wave vector

$k = 2\pi/\lambda$ - the wave vector of the photons

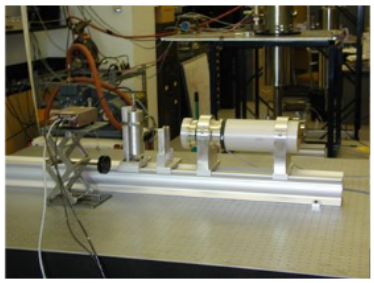
Mössbauer spectroscopy

Mößbauer spectrum-shape and intensity

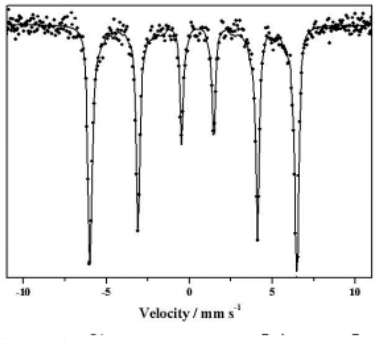
The basic idea of Mössbauer experiment:



Laboratory setup:

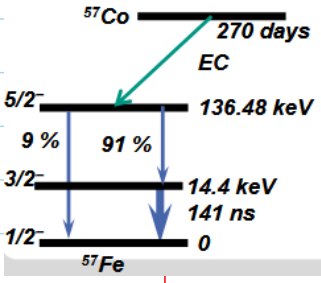


Mössbauer spectrum of ^{57}Fe

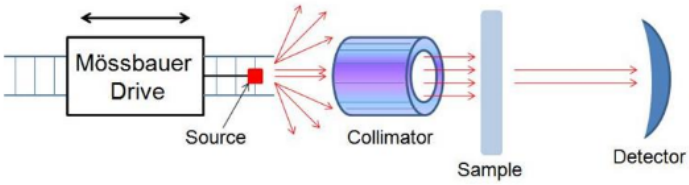


for ^{57}Fe, $E_\gamma/c = 4.8075 \times 10^{-8}$ eV mm^{-1} s

Radioactive source:

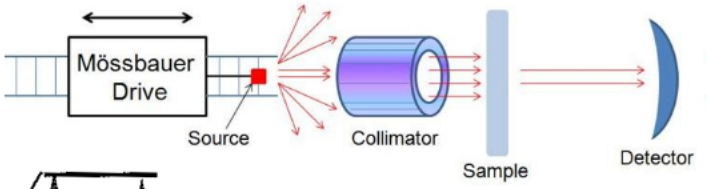


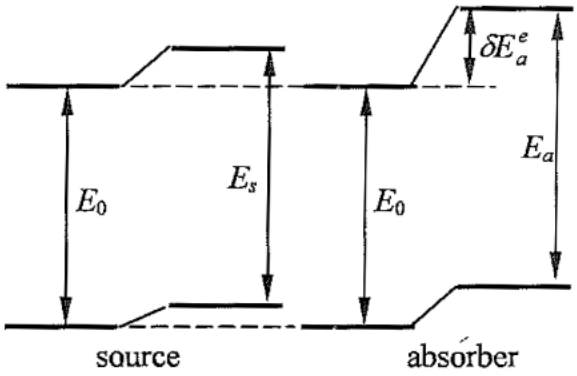
A scheme of the setup



Mössbauer spectroscopy

Isomer shift



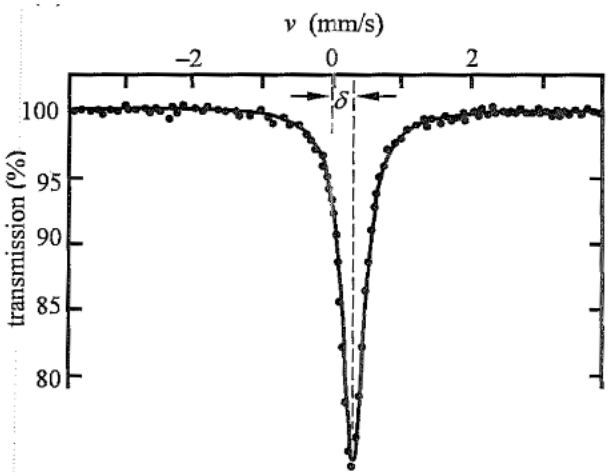


Energy shift of the nuclear levels in the source and absorber

$$\delta = \frac{4\pi}{5} z S'(z) e R^2 \left(\frac{\Delta R}{R}\right) \Delta\rho(0) = \alpha \Delta\rho(0)$$

nucleus shell

$$\Delta R = R_e - R_g \quad R = (R_e + R_g)/2$$



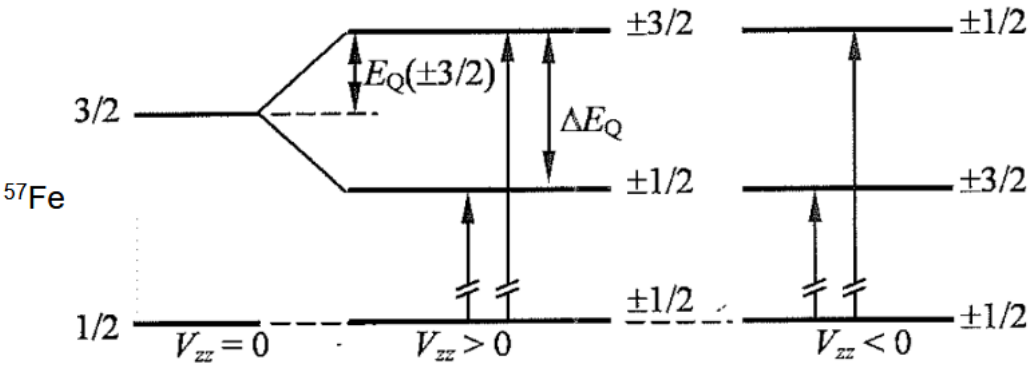
Mössbauer absorption spectrum in case of single-line and isomer shift δ.

Quadrupole splitting

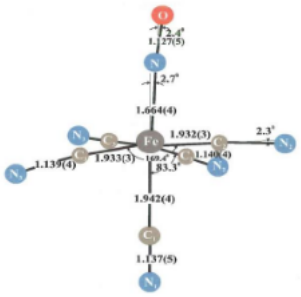
The eigenvalues of this Hamiltonian are:

$$E_Q = \frac{eQV_{zz}}{4I(2I-1)}[3m^2 - I(I+1)]\left(1+\frac{\eta^2}{3}\right)^{1/2}$$ with $m = I, I-1, \ldots -I$

Each level is double generated to the magnetic quantum number m ($E_Q \approx m^2$)



Nitropruside anion: $Fe(CN)_5NO$



The ground state has a spin 1/2 corresponding to Q=0, therefore it does not split.

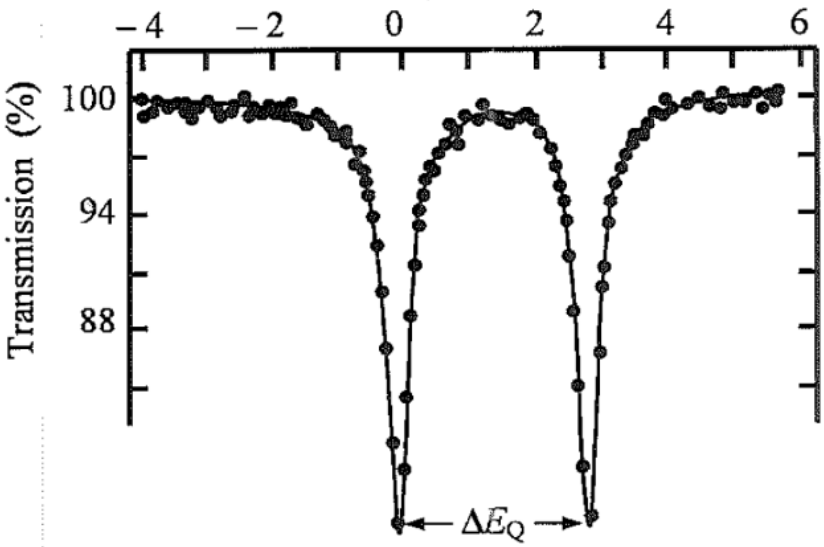
Mössbauer spectroscopy

Quadrupole splitting

The energy difference between the two sublevels is given by:

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

by changing velocity, we can excite different transitions!



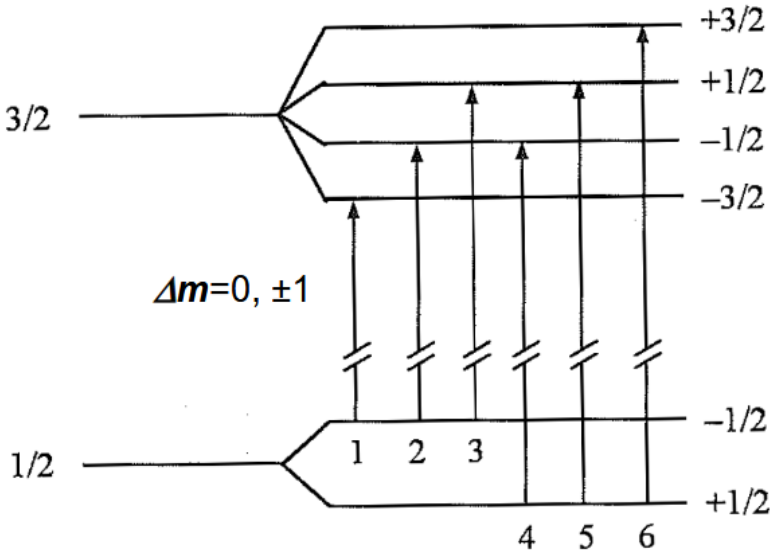
The measured quantity is a product between the nuclear (Q) and crystal lattice (V_{zz}, η) parameters.

Mössbauer absorption spectrum in case of quadrupole splitting.

Magnetic dipole interaction

The magnetic hyperfine interaction arises from the interaction between the nuclear magnetic moment μ and the magnetic field $\boldsymbol{B}$ at the nucleus produced by the surrounding electrons or ions. This interaction lifts the degeneracy of the energy level of the nucleus with a spin $\boldsymbol{I}$ and it splits to (2I+1) sublevels.

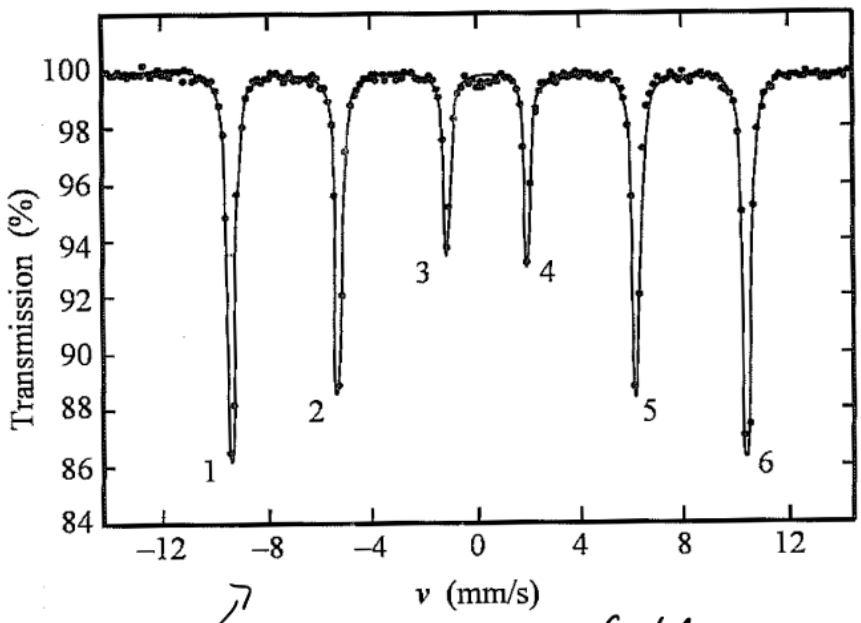
This splitting is known as the nuclear Zeeman effect.
Similar hyperfine splitting in the atomic levels, i.e. Zeeman effect has been observed by optical spectroscopy long time ago. Before the Mössbauer effect, however, the nuclear Zeeman effect was not observable due to the lack of the needed energy resolution.



Nuclear Zeeman splitting of the ground and the first excited state in ^{57}Fe

Mössbauer spectroscopy

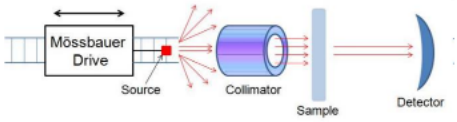
Magnetic dipole interaction



local Probe for magnetic field acting at the sample

Mössbauer spectrum corresponding to the nuclear Zeeman splitting in ^{57}Fe

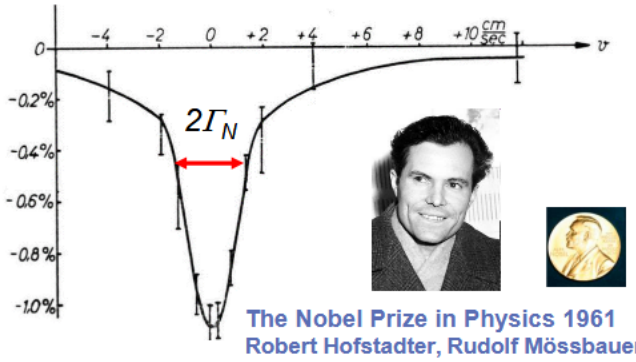
Mössbauer spectroscopy



Summary

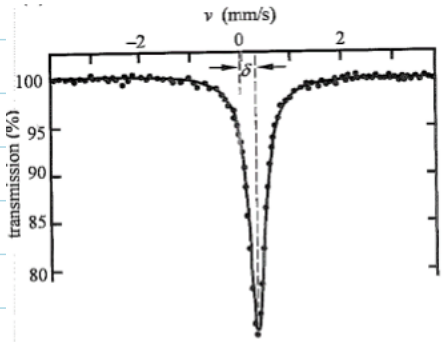
The Mössbauer effect: resonant, recoilless absorption/emission of gamma-rays from the nucleus. The basis of a hyperfine spectroscopy with an energy resolution limited by the natural linewidth of the excited nuclear level.

Information on:
chemical bond, oxidation state, spin state, electronegativity of the ligands, coordination number, electric field gradient (sign & direction), magnetic field (sign & direction).
The information is very useful for verification of various theoretical models, DFT & quantum chemical calculations.

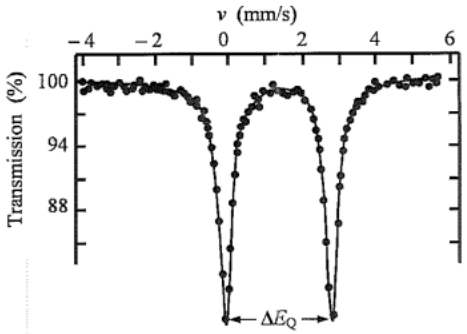


The Nobel Prize in Physics 1961
Robert Hofstadter, Rudolf Mössbauer

Isomer shift



Quadrupole splitting



Magnetic splitting