Mössbauer Spectroscopy

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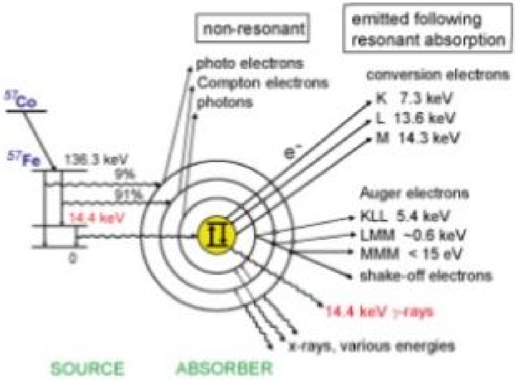
Photon absorption by atoms

Nucleus can undergo transitions between quantum states like electrons in an atom.

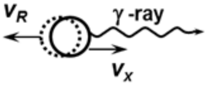


Credit: University of Cyprus [5]

Figure: Absorption of photons by an atom

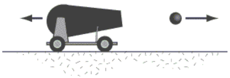
Absorption and emission of γ-rays

Nucleus releases γ-ray with transition energy E_0. γ doesn't carry full energy ($E_\gamma \neq E_0$), part is lost to recoil (momentum conservation).



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Nucleus recoil (γ-ray emission)



Credit: St. Mary's H.S. Physics [6]

Figure: Gun recoil

Momentum/energy conservation

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

v_x, v_R initial/recoil velocity

E_g, E_e ground/excited state energy

Gamma Decay

Energy of γ-ray

$$E_\gamma = E_0 - E_R + E_D, \quad \underbrace{E_R = \frac{1}{2}Mv_R^2 = \frac{E_\gamma^2}{2Mc^2}}_{\text{recoil energy}}, \quad \underbrace{E_D = Mv_x v_R = \frac{v_x}{c}E_\gamma}_{\text{Doppler energy shift}}$$

$E_0 = E_e - E_g$ energy difference between excited and ground state

Energy-time uncertainty

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

Example for $^{57}\mathrm{Fe}$

$$E_0 = 14.4\,\mathrm{keV}$$
$$\tau = 141.1\,\mathrm{ns}$$
$$\Gamma_n = 4.66x10^{-9}\,\mathrm{eV}$$

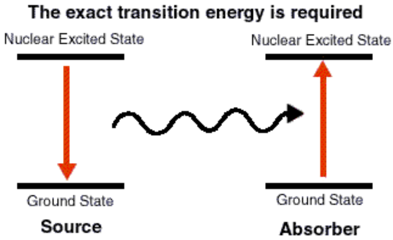
Natural line width Γ_n

Stability of an energy level:

$$\Gamma_n \tau \geq \hbar/2$$

τ energy level lifetime (typically $10^{-10}\,\mathrm{s}$ for nuclear transitions)

Nuclear resonant absorption



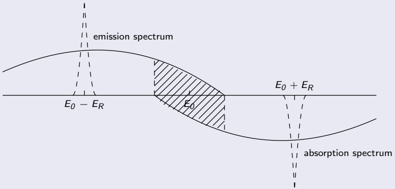
Credit: Georgia State University [2]

Energy needed for absorption

$$
\begin{aligned}
E_\gamma^{abs.} &= E_0 + 2 \cdot E_R \\
&= E_0 + \frac{E_\gamma^2}{Mc^2}
\end{aligned}
$$

Nuclear resonant absorption

$v_x = 0 \Rightarrow E_D = 0$



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Emission and absorption γ-ray spectra with recoil [9]

Spectrum (dashed line)

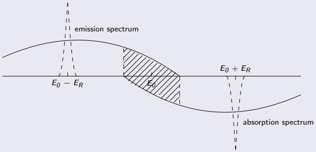
- sharp peaks centered
- full-width at half-maximum (FWHM) $\approx \Gamma_n$

Resonant absorption condition

$$\frac{\Gamma_n}{2E_R} > 1$$

Nuclear resonant absorption

$v_x \neq 0 \Rightarrow E_D \neq 0$



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Emission and absorption γ-ray spectra with recoil [9]

Spectrum

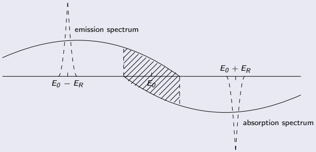
- $FWHM \gg \Gamma$
- thermal random motion of atoms (Maxwell distribution of v_x):

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

- width of Doppler broadening $\Delta E_D = 4\sqrt{E_R k_B T \ln 2}$

Nuclear resonant absorption

$v_x \neq 0 \Rightarrow E_D \neq 0$



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Emission and absorption γ-ray spectra with recoil [9]

Example for $^{57}\mathrm{Fe}$

At $T = 300\,\mathrm{K}$, $\Delta E_D = 24\,\mathrm{meV} > 2E_R = 4\,\mathrm{meV}$

$\rightarrow$ small overlap between emission and absorption spectra

$\rightarrow$ non-zero probability for a resonant process

Shifting due to recoil, broadening due to thermal motion spectrum

Compensating for recoil energy

1. Mechanical motion of the source
   - source mounted on tip of high-speed rotor
   - γ-rays gained extra energy

$$\Delta E = \frac{v}{c} E_\gamma \quad \Rightarrow \quad \frac{v}{c} E_\gamma = 2E_R$$

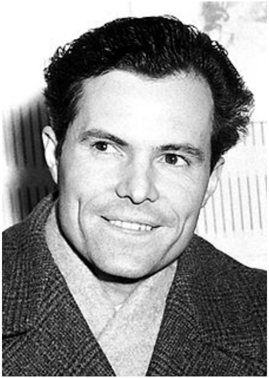
$$(\text{for } ^{57}\mathrm{Fe},\ v = 81\,\mathrm{m/s} \approx 292\,\mathrm{km/h})$$

2. Doppler broadening
   - temperature increase $\Rightarrow$ overlapping emission and absorption spectra

Limitations

1. low count rate: γ-rays usable for very short periods
2. maximum speed of mechanical rotor
3. recoil still present

Discovery



Credit: Wikipedia [12]

Figure: Rudolph Mössbauer

Born: January 31, 1929 (Munich)
Died: September 14, 2011 (Grünwald)

1958 PhD on *recoilless nuclear fluorescence of gamma rays in* $^{191}\mathrm{Ir}$

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

1961 Nobel Prize in Physics

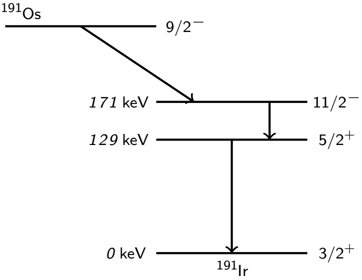
"for his researches concerning the resonance absorption of gamma radiation and his discovery in this connection of the effect which bears his name"

Discovery

Mössbauer Experiment

- source nuclei $^{191}\mathrm{Os}$, absorber nuclei $^{191}\mathrm{Ir}$, both heated at $88\,\mathrm{K}$
- both source and absorber rigidly bound in crystal latices

$\Rightarrow$ resonant absorption



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Decay scheme of ^{191}Os [9]

Classical Explanation

- atom held by $10\,\mathrm{eV}$ chemical bond energy in crystal lattice
- recoil energy for $129\,\mathrm{keV}$ photon in $^{191}\mathrm{Ir}$: $4.7\mathrm{x}10^{-2}eV$

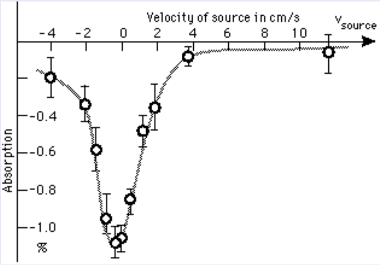
$\Rightarrow$ recoil $\ll$ chemical bond energy

$\Rightarrow$ entire lattice recoils ($\approx N_A$):

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

Mössbauer Effect

Spectrum



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Resonance absorption curve of the 129 keV γ-rays by $^{191}\mathrm{Ir}$ [8]

- width $\Delta E = 4.6 \text{x} 10^{-6}\,\mathrm{eV}$
- very high energy resolution $\frac{\Delta E}{E} = 3.5 \text{x} 10^{-11}$
- $\Delta E \approx 2 \cdot \Gamma_N$
- Doppler effect modulates γ-ray energy to small energy range $E_\gamma(1 \pm v/c)$

$\Rightarrow$ *new* opportunities for research (i.e. Zeeman effect first observed using the Mössbauer effect)

Mössbauer Effect

Einstein Solid

Assumptions:

- lattice atoms are independent quantum harmonic oscillators
- same-frequency oscillation of atoms (unlike Debye model)

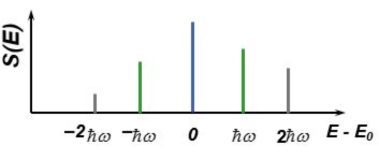


Figure: Einstein model of a solid

Derivation of the effect

- atoms bound in crystal lattice and vibrate about equilibrium position
- lattice vibrations are quantized: $E_p = \hbar\omega$
- photons exchange energy with lattice by creating/annihilating phonons

Mössbauer effect

Lamb-Mössbauer (recoilless) factor

- Condition for recoilless resonant absorption: $E_R \ll \hbar\omega$
- Probability for resonant absorption:

$$f = e^{-k^2 \langle x^2 \rangle}$$

$\langle x^2 \rangle$ mean square diplacement of nucleus in direction of wave vector

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

Implications

- Low probability for resonant absorption in liquids (large $\langle x^2 \rangle$)
- High probability for small k (i.e. low-energy photons)

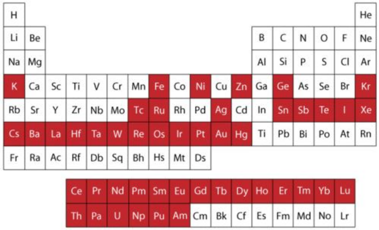
Mössbauer Active Elements

$\approx$ 40 elements suitable for Mössbauer spectroscopy

Requirements towards Mössbauer isotopes

Excited states with

- low energies $\Rightarrow$ recoil-free absorption
- long lifetimes $\Rightarrow$ high resolution



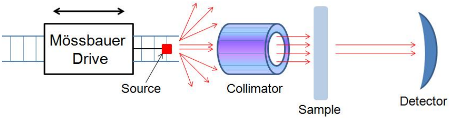
Credit: Chemistry LibreTexts [4]

Figure: Mössbauer active elements

Mössbauer spectrometer

Construction

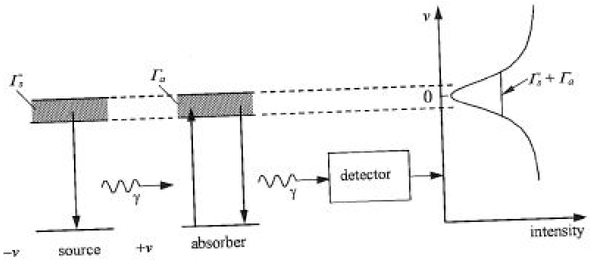
- **Mössbauer Drive:** moving part which generates the Doppler effect
- **Collimator:** filters out non-parallel γ-rays
- **Detector**



Credit: Wikipedia [11]

Figure: Schematic view of Mössbauer spectrometer

Mössbauer spectrum



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Measuring a Mössbauer spectrum

- minimum linewidth $\Gamma_s + \Gamma_a$
- energy axis labelled using v_x (source velocity in mms^{-1})
- energy value obtained by multiplying v_x with E_γ/c (i.e. $^{57}\mathrm{Fe}$: $4.8075x10^{-8}\,\mathrm{eV\,mm^{-1}\,s}$)

Hyperfine interactions

Definition

Interactions between nucleus and electromagnetic fields produced by surrounding electrons, atoms or ions. They are very weak interactions.

Types

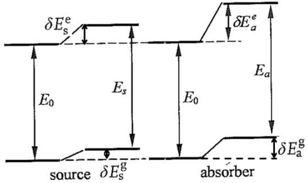
- **Isomer shift δ:** electric monopole interaction
- **Quadrupole splitting:** electric quadrupole interaction
- **Zeeman splitting:** magnetic dipole interaction

Isomer Shift

Definition

$$\delta E = \frac{2\pi}{3} z e^2 |\psi(0)|^2 \langle r^2 \rangle$$

Nuclear energy levels shift δE



Credit: Yi-Long Chen: Mössbauer Effect [9]

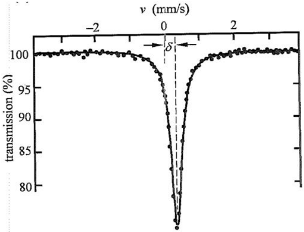
Figure: Shift of nuclear energy levels due to electric monopole interaction

Energy of emitted γ-ray:

$$E_s = E_0 + \delta E_s^e - \delta E_s^g$$

Condition for resonant recoilless absorption:

$$E_a = E_0 + \delta E_a^e - \delta E_a^g$$



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Typical Mössbauer spectrum in the presence of an isomer shift

Isomer Shift

Provides information on

- electronic structure
  1. inner **s** electrons of the Mössbauer atom
  2. valence electrons in outer shells
  3. valence electrons of ligands
- type of chemical bond (covalent, metallic etc.)
- oxidation state
- spin state
- electronegativity of the ligands
- coordination number

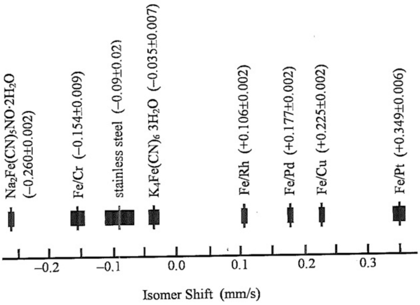
Isomer Shift Calibration

Isomer shift δ is measured with respect to that of a reference absorber (source and absorber in different chemical environments):

$$\delta = \delta_0 - \delta_{ref}$$

δ_0 measured isomer shift

δ_{ref} isomer shift of reference absorber



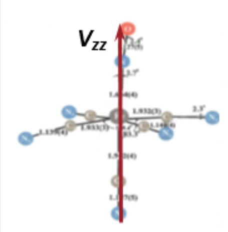
Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Isomer shifts of several reference absorbers

Quadrupole Splitting

Why it happens?

1. nucleus with an electric quadrupole moment experiences non-uniform electric field (electric field gradient, EFG)
2. nuclear charge distribution has non-spherical symmetry if nucleus has spin quantum number $I > 1/2$ and non-zero electric quadrupole moment

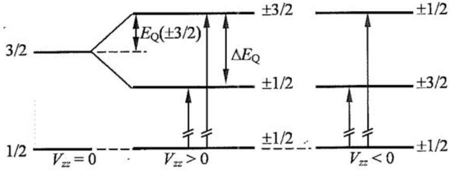


Credit: V. Rusanov et al (2003) [10]

Quadrupole Splitting

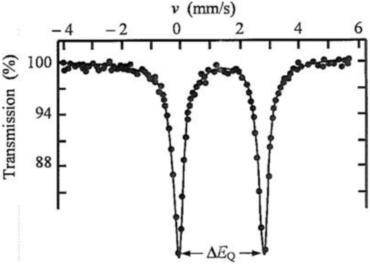
V_{zz} is the electric field gradient due to total electron density plus all nuclear charges. Separation between the lines:

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



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Split $^{57}\mathrm{Fe}$ energy levels by quadrupole interaction



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Quadrupole splitting Mössbauer spectrum

Zeeman Splitting

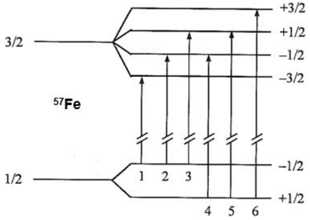
Definition

The nuclear magnetic moment μ and the magnetic field $\vec{B}$ at the nucleus cause the magnetic hyperfine interaction.

Details

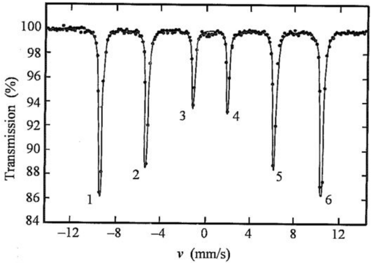
1. magnetic field is produced by surrounding electrons/ions
2. degeneracy of $\vec{I}$ level is lifted
3. level is split into $(2I + 1)$ sublevels (Zeeman Splitting)

Zeeman Splitting



Credit: Yi-Long Chen: Mössbauer Effect [9]

Figure: Magnetic splittings of the $^{57}\mathrm{Fe}$ nuclear energy levels



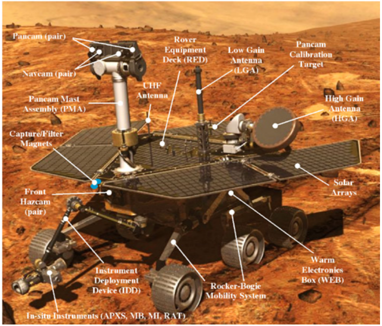
Credit: Yi-Long Chen: Mössbauer Effect [9]

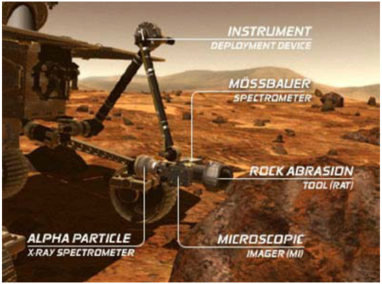
Figure: Mössbauer spectrum of $\mathrm{FeF_3}$ with a sextet due to magnetic

- M1-magnetic dipole γ transition in $^{57}\mathrm{Fe}$
- selection rule $\Delta m = \pm 1, 0$
- 6 allowed sublevel transitions

Applications

Mars Exploration Rover "Spirit" and "Opportunity" Missions studying iron-containing minerals



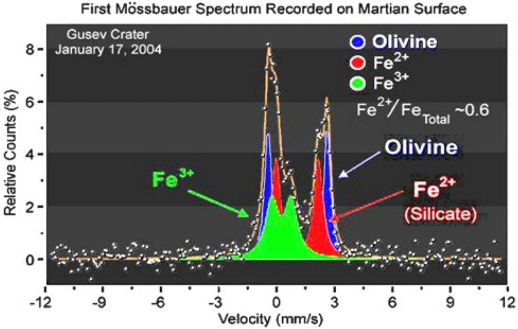


Credit: exploratorium.edu, thetimenow.com/astronomy [1] [7]

Figure: Mars Exploration Rover

Applications

Mars Exploration Rover "Spirit" and "Opportunity" Missions studying iron-containing minerals



Credit: mossbauer.info [3]

Conclusion

- Mössbauer spectroscopy offers the highest-possible energy resolutions limited only by nature
- Simple experimental setup makes it very accessible
- Widespread in many labs with applications in these fields:
  - **Physics and chemistry:** study of electronic, magnetic and structural properties of materials, chemical environment of nuclei, chemical reactions, molecular structure
  - **Biology:** hemoglobin and protein structure analysis
  - **Mineralogy and metallurgy:** analysis of metal and mineral samples

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