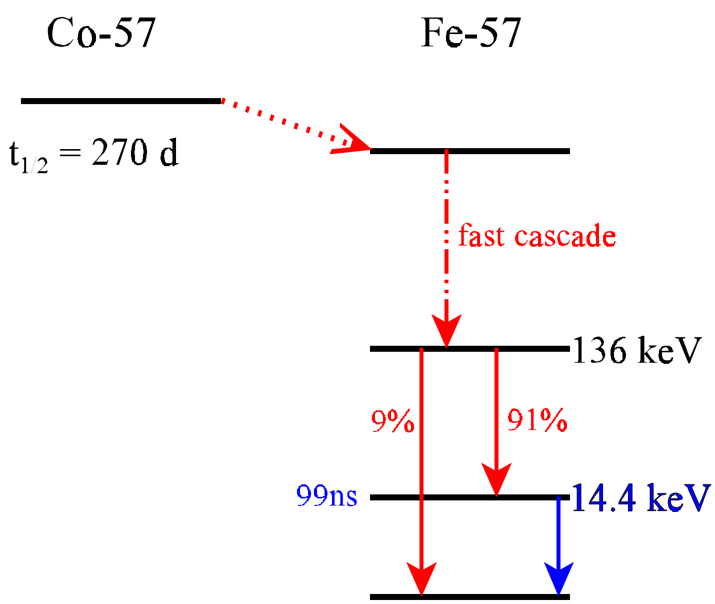
MÖSSBAUER SPECTROSCOPY

In the course of radioactive decay, product nuclei are produced in excited states. The excited nuclei decay to the ground state and emit γ-rays in the process. Mössbauer spectroscopy involves the resonant absorption of these γ-ray photons by corresponding nuclei in their ground states. Mössbauer's contribution (1957) was to demonstrate how this process could be achieved.



As an example, radioactive ^{57}Co (produced artificially in a linear accelerator) decays, with a half-life of 270 d, by K-electron capture to produce ^{57}Fe.

^{57}Fe is **NOT** radioactive but the nuclei are produced in highly excited states that rapidly decay to an excited state at 136 keV. This state decays to the ground state by two routes - 9% directly (emitting a 136-keV photon), and 91% to a relatively long-lived (99 ns!) state at 14.4 keV, which eventually emits a 14.4-keV photon and produces a stable ^{57}Fe nucleus (natural Fe contains 2% of this isotope).

From the Uncertainty Principle and the lifetime of the excited state we calculate the line-width of the emitted 14.4-keV photon as 4.7×10^{-9} eV.

When the photon is emitted the nucleus suffers a recoil with energy $E_r = E_\gamma^2/2Mc^2$ where M is the mass of the nucleus and c is the velocity of light.

E_r is typically of the order of 10^{-1} eV. The actual energy of the emitted γ-photon is therefore $E_\gamma - E_r$ (for ^{57}Fe, 14.4 keV - 0.1 eV). For that photon to be captured by another ground state ^{57}Fe nucleus the γ-photon should have an energy of 14.4 keV + 0.1 eV.

Mössbauer showed that when the nucleus is in a solid lattice the recoil energy can be transferred to the lattice vibrations. If the recoil energy is smaller than the lattice vibrational quanta, then the lattice as a whole absorbs the recoil, and the recoil energy becomes negligible. The extent to which this is true depends upon the "stiffness" of the lattice (better at lower temperatures for example) and is expressed as the "recoil-free fraction", f. Other things being equal, f becomes smaller as the energy of the γ-photon increases. ^{57}Fe, with a 14.4-keV photon, is one of the most favorable Mössbauer nuclei on this account . Other chemically-interesting MB nuclei include ^{99}Ru (90 keV), ^{119}Sn (23.9 keV), ^{121}Sb (37.2 keV), ^{129}I (27.7 keV), and ^{197}Au (77.3 keV).

The Experiment

The energies (wavelengths) of the γ-photons emitted from the Source (radioactive nuclide, e.g. ^{57}Co in stainless steel disc) are modulated by moving the source towards or away from the Absorber (sample containing the ground state product nuclide, e.g. ^{57}Fe).

With respect to the absorber the γ-photon energies are altered by the Doppler effect, $\Delta E = v_0/c)E\gamma$. For the 14.4-keV photon a relative velocity (v_0) of 1 mm/s changes the energy by 4.8×10^{-8} eV.

Mössbauer spectra show photons absorbed as a function of the relative velocity of the source and absorber. The position of a Mössbauer line is given in terms of a velocity.

1. The "Isomer" Shift (or "Center" Shift), δ

[Isomers, to nuclear physicists, are nuclei in different (ground, excited) states]

$$\delta = \text{constant} \cdot \left(\frac{\Delta R}{R}\right)\left[\left|\psi_s(\text{abs})\right|^2 - \left|\psi_s(\text{source})\right|^2\right]$$

where the ψ's are s-functions evaluated at the nucleus, and ΔR/R is the change in nuclear radius between the ground and excited states. For ^{119}Sn ΔR/R is a positive quantity.

Compound	δ/mm.s^{-1}
SnF_4	-0.47
SnO_2	0 (ref.)
$SnCl_4$	0.85
$SnBr_4$	1.15
SnI_4	1.55
$SnMe_4$	1.21
SnH_4	1.27
SnO	2.71
SnS	3.16
$SnSO_4$	3.90
$SnCl_2$	4.07

Note that δ for Sn(II) is greater than δ for Sn(IV).

For ^{57}Fe $\Delta R/R$ is negative

Relative isomer shifts for high-spin Fe compounds:

Fe^{II}	Fe^{III}	Fe^{IV}	Fe^{VI}
+1.4	+0.7	+0.2	-0.6 mm/s

least------------------------->greatest s-density (less shielding by d-electrons)

2. The Quadrupole Splitting, ΔE_Q

The ground- or excited state of the nucleus (or both) may have a quadrupole moment. If the nucleus experiences a nonzero electric field gradient, the energy levels are split as we have discussed in NQR spectroscopy.

Two (or more) MB transitions are seen.

For both ^{57}Fe and ^{119}Sn the ground state spins are 1/2 and the excited state spins are 3/2. In nonzero field gradients, two MB transitions are seen, centered on the isomer shift, δ.