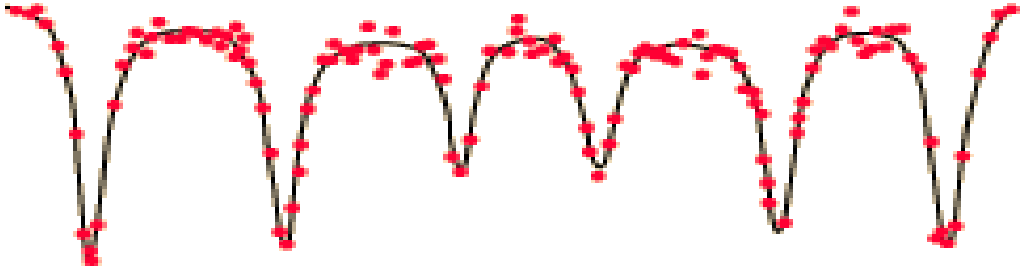
Mossbauer Effect and Spectroscopy



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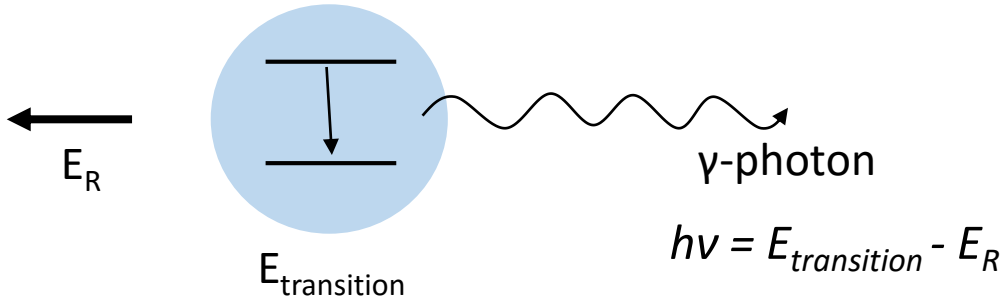
Emission



Photon does not carry the full transition energy

Conservation of momentum → **Energy loss in the form of recoil of the source atom**

Higher the energy of transition, the greater the photon energy ($h\nu$) and hence, its momentum ($h\nu/c$)

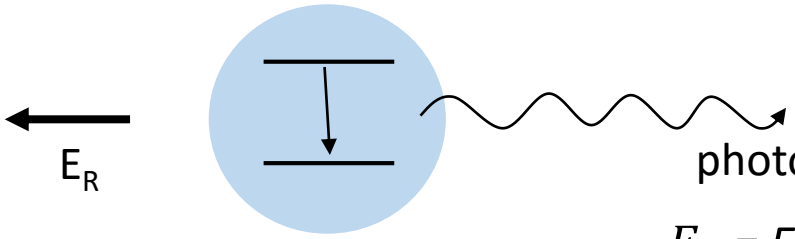
↓

Higher is the energy loss to the recoil

$$h\nu = E_{transition} - E_R$$

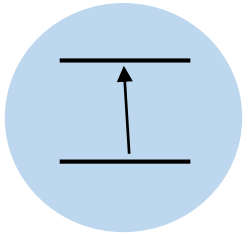
Actual energy of the emitted photon.

Emission



$E_\gamma = E_{transition} - E_R$

Absorption



$E_\gamma{}' = E_{transition} + E_R$

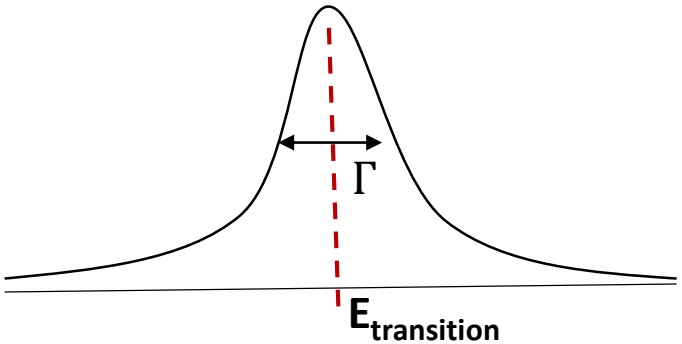
Thus, there is an energy mismatch of $2E_R$.

Is absorption possible?

It depends on the **lifetime of the excited state** and **recoil energy**.

Natural energy width $\Gamma = \frac{1}{T}$

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



Condition for absorption

$\boldsymbol{\Gamma > 2E_R}$

Atomic transitions

$E_{transition}$ = few eV (in visible region)

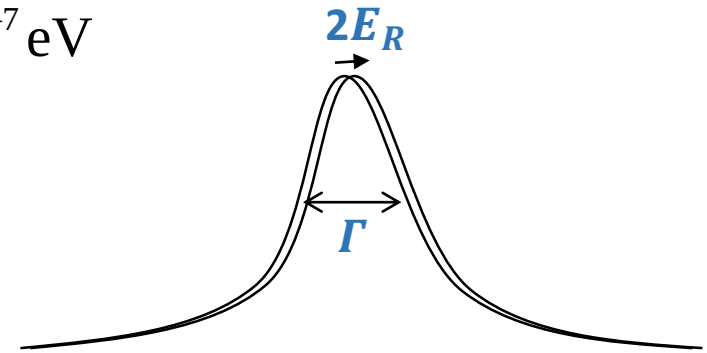
m_a = atomic mass = *A* x 1000MeV (*A* is atomic number)

$$E_R = \frac{(1 \to 10eV)^2}{(10 \to 100)1000MeV} = \quad 10^{-12} - 10^{-10}\text{eV}$$

For atomic transitions, the typical lifetime is $\sim 10^{-8}$ sec

The energy uncertainty $\Gamma = 10^{-7}$ eV

$$\boldsymbol{\Gamma >> 2E_R}$$



Thus, recoil does not affect the absorption

Nuclear transitions

$E_{transition}$ = few MeV (for γ-emission)

m_a = atomic mass = *A* x 1000MeV (*A* is atomic number)

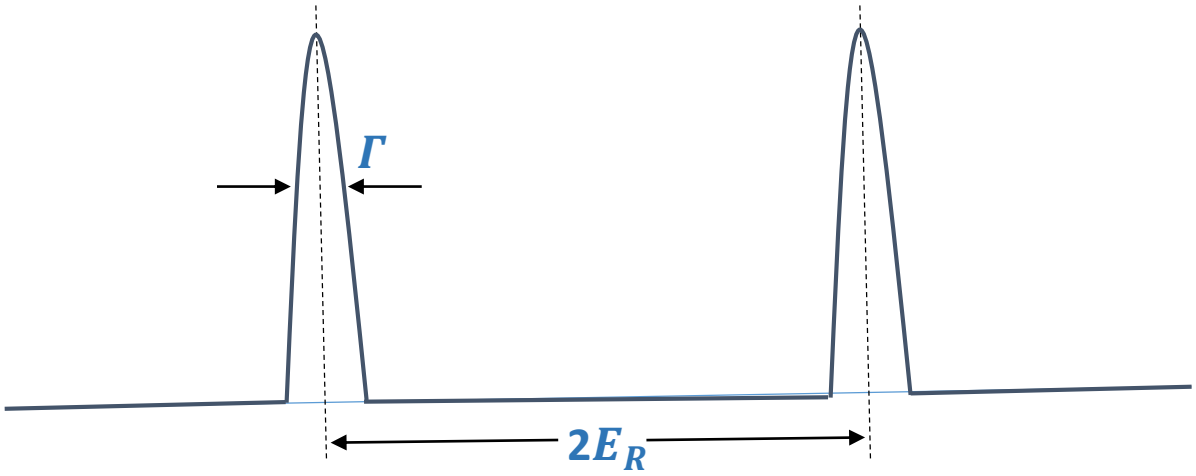
$$E_R = \frac{(0.1 \to 10 MeV)^2}{(10 \to 100)1000 MeV} = \; 0.1 - 10^4 \text{ eV}$$

For atomic transitions, the typical lifetime is $\sim 10^{-10}$ sec

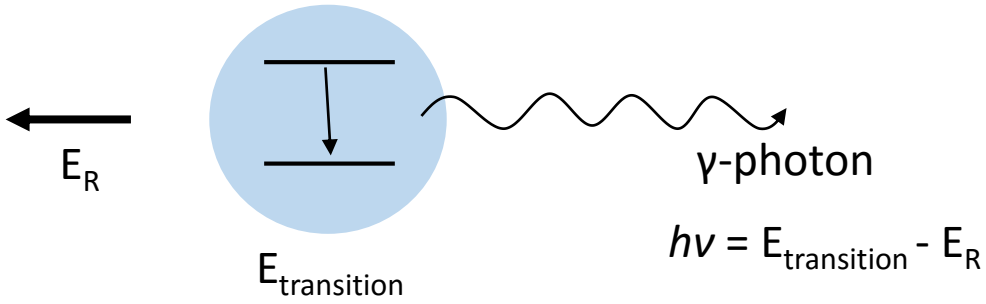
The energy uncertainty $\Gamma = 10^{-5}$ eV

$$\boldsymbol{\Gamma << 2E_R}$$

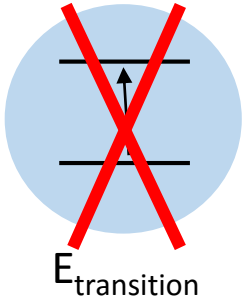
Magnitude of recoil in a free atom is much larger than the natural linewidth.



Emission



Absorption



Resonance Fluorescence in a free-standing nucleus is impossible

Iridium 191

Transition energy ($h\nu$) = 129 keV)
Recoil velocity on emission of a γ-photon emission (v) = 202 m/s
Actual energy of the emitted γ-photon ($h\nu'$) = 128.999912874 keV

Energy difference $\Delta E = 8.71 \times 10^{-5}$ keV

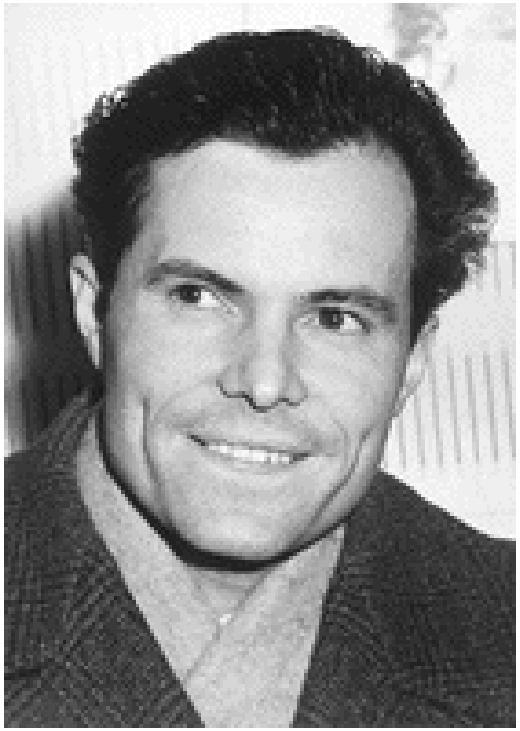
Natural linewidth $\Gamma = 3.22 \times 10^{-8}$ keV

$\Delta E \gg \Gamma \rightarrow$ Transition not possible

Resonance fluorescence in a gas in visible region (atomic transitions) is readily observed. This is not true for nuclear transitions in a gas.

Mossbauer Effect

Recoil-less emission and re-absorption



In 1958, Rudolf Mossbauer, a German physicist demonstrated recoil-less emission and resonant absorption of γ-radiation.

Mossbauer's Scheme

Embed the emitting and absorbing nuclei in crystals and cool them down

↓

Nuclei tightly held in place

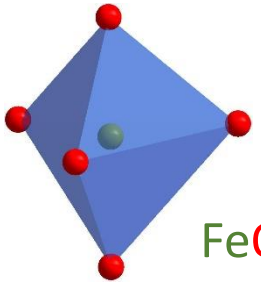
↓

Negligible momentum transfer during emission due to much larger mass (virtually stationary)

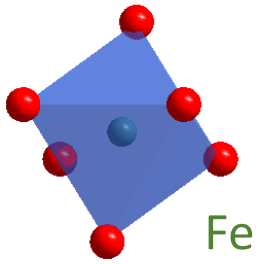
↓

Resonant absorption ***IF*** the absorber nucleus is in the same state as the source nucleus.

What if the source and the absorber are not in identical environment?



FeO_5



FeO_6

Fe^{3+} nuclei are placed in different environments

↓

Shift in nuclear transition energies

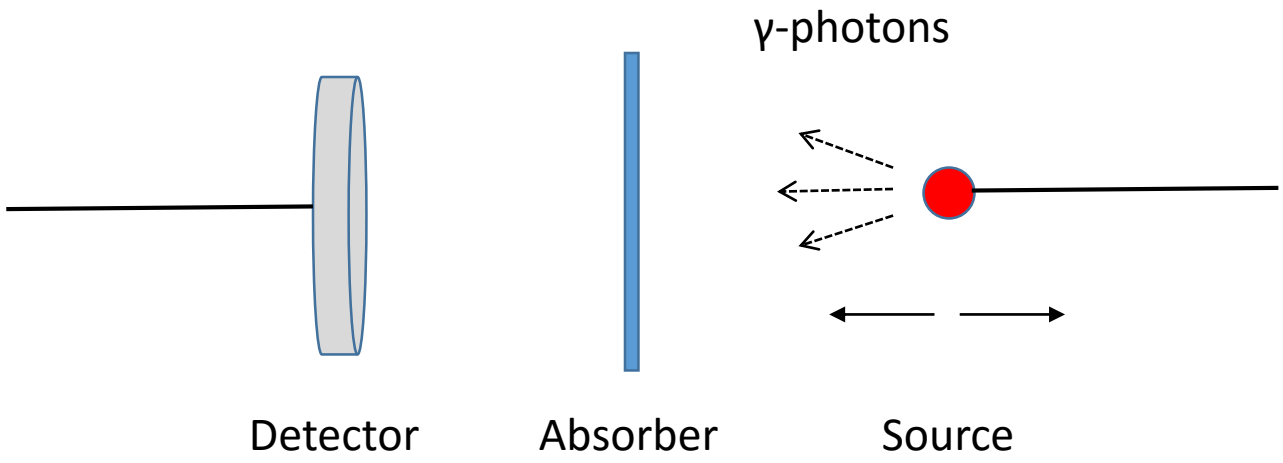
↓

These *signature* shifts can experimentally determined using **Mossbauer effect** and **Doppler effect**

Mossbauer Spectroscopy

What if the source and the absorber are not in identical environment?

Mossbauer Spectroscopy



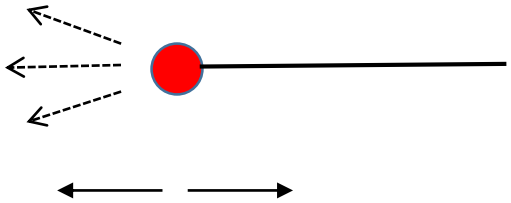
Absorber consists of atoms whose spectra is to be studied is embedded in a crystal.

Source consists of identical (radioactive) atoms that emit γ-photons and is back and forth with variable speeds.

Detector collects γ-photons and records dips in intensity corresponding to resonant absorptions.

Moving the source introduces Doppler shift in the emitted photons

$$h\nu_{observed} = h\nu_{source}\sqrt{\frac{1+\mathrm{v}/c}{1-\mathrm{v}/c}}$$



If v/c <<1 this simplifies to

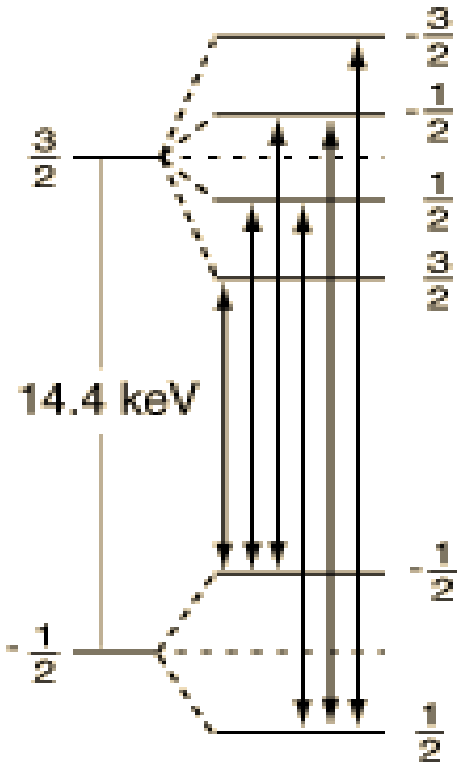
$$h\nu_o \approx h\nu_s(1 \pm \mathrm{v}/c)$$

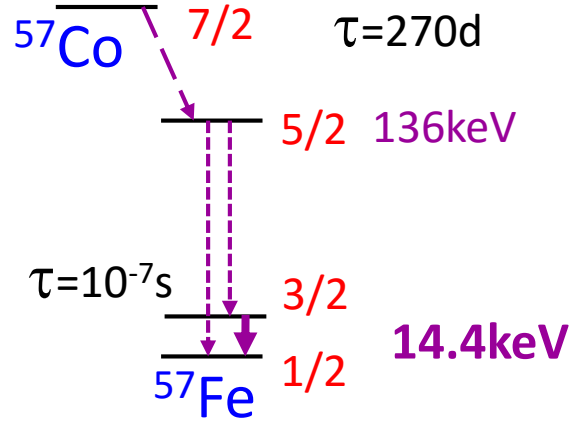
Source of continuous energy over a small range about a central frequency

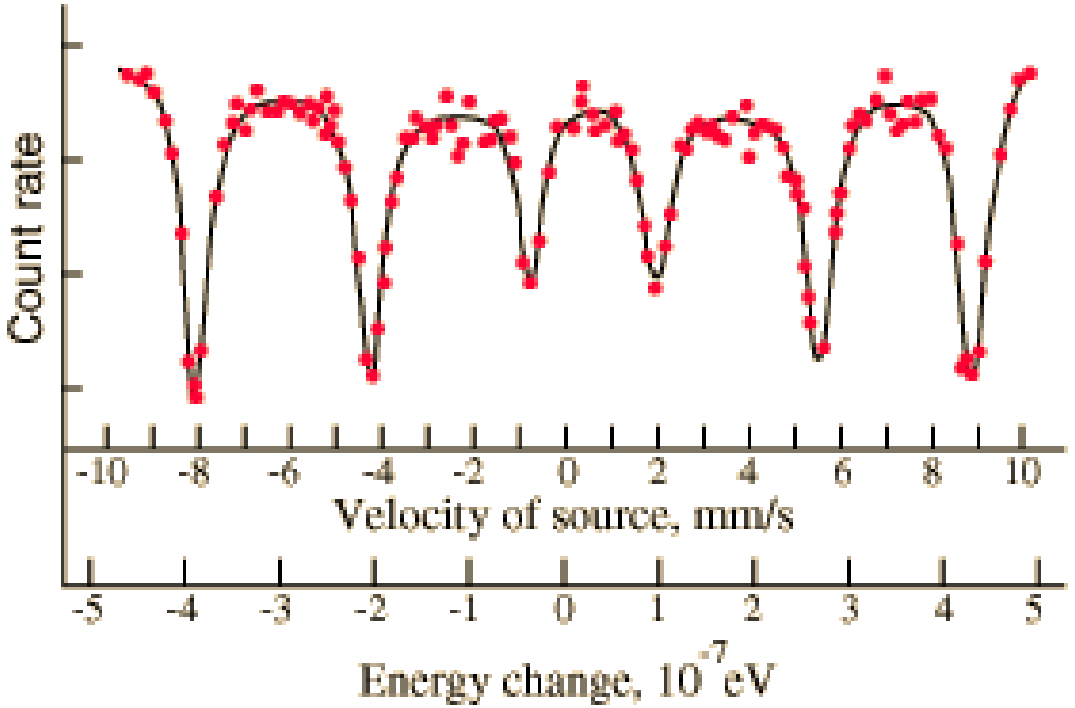
Suitable for probing nuclear transition energies
which are very closely spaced

Nuclear Zeeman effect

Mössbauer effect in ^{57}Fe







Note that the splittings are 11 orders of magnitude smaller than the nuclear transition energy!

O. C. Kistmer and A. W. Sunyar, Physical Review Letters, 4, 412(1960).

Chemical information in Mossbauer Spectra

Spectra reveal splittings of nuclear levels, determined by the electronic environment

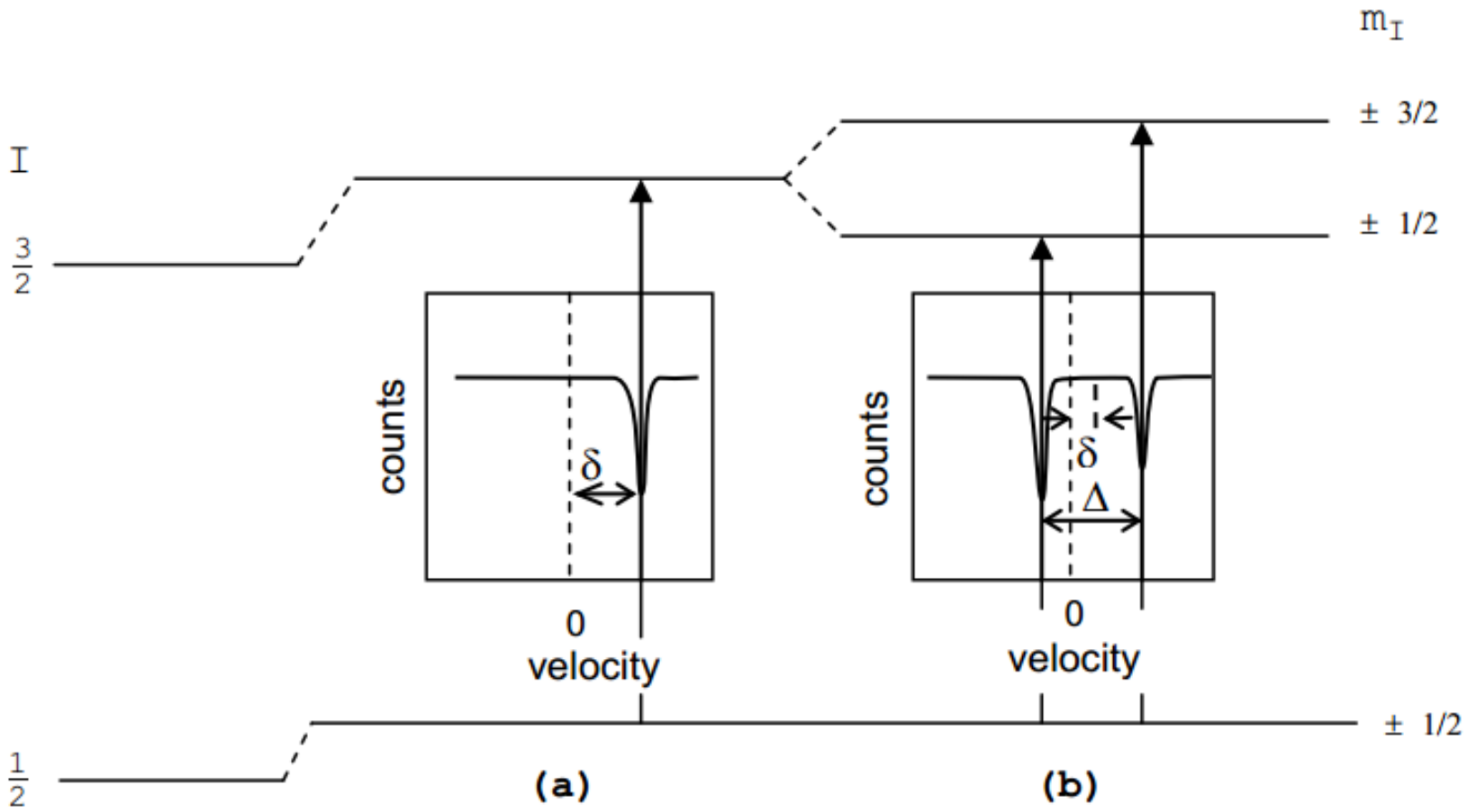
- ***Isomer shift***: Interaction of the nuclear charge distribution with the electron cloud surrounding the nuclei in both the absorber and source.

Information about position of the centroid of the line, oxidation state, covalency of the bondings

- ***Quadrupole splitting***: Interaction of the nuclear electric quadrupole moment with the EFG (electric field gradient) and the nucleus

Multiple assymetry in the electronic environment, chemical spin state, strength of ligand field

- ***Magnetic splitting*** (Zeeman or Dipole interaction): Interaction of the nuclear magnetic dipole moment with the external applied magnetic field on the nucleus.



Effect of a) Isomer shift, and b) Quadrupole splitting on nuclear energy levels of ^{57}Fe

Criteria for observing Mossbauer Effect are:

1.

Thank you!