Subject: **Chemistry**

Semester: **IV**

Paper: **CEM-401**

Topic: **Mössbauer Spectroscopy**

Reference books:

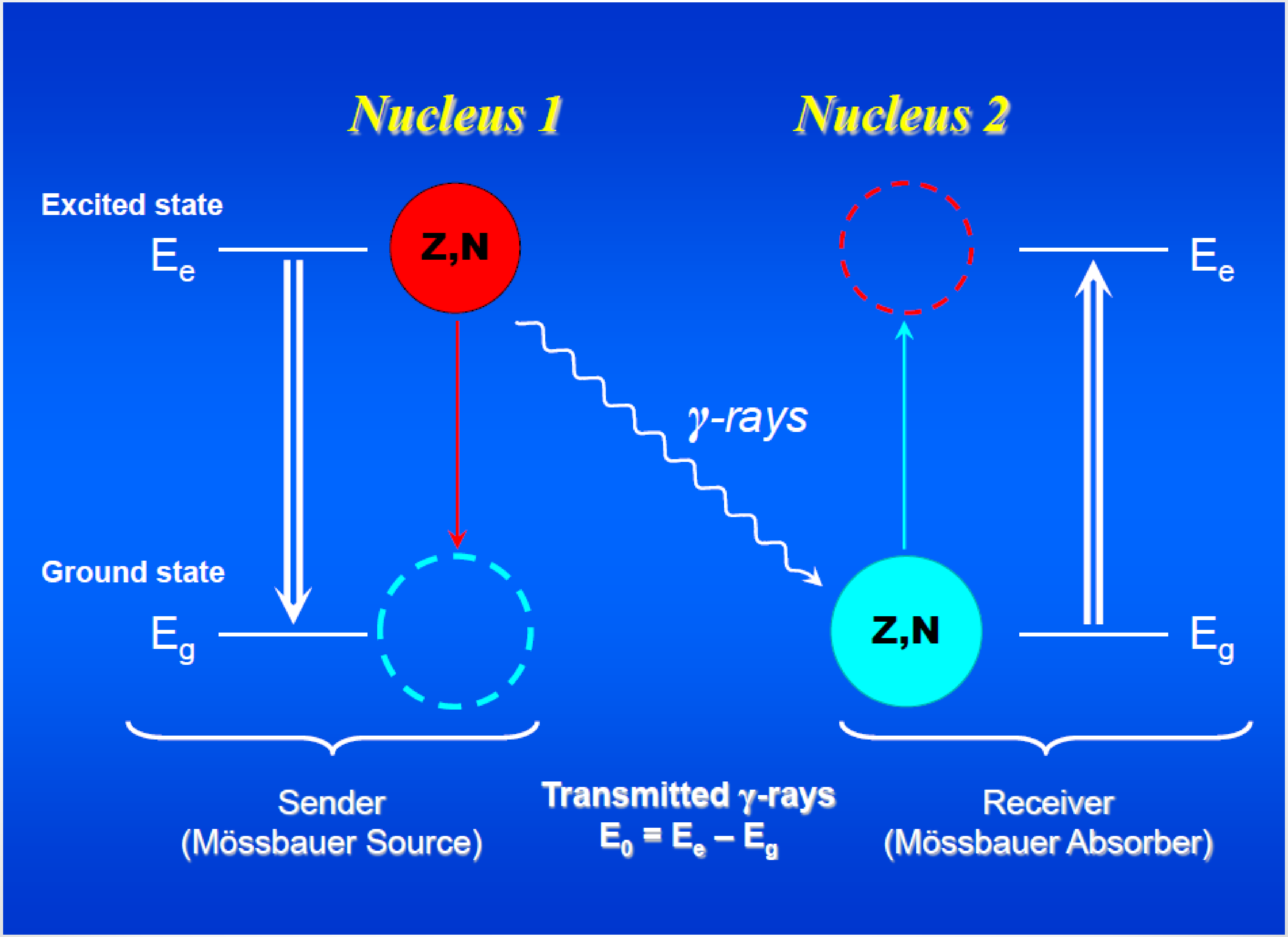
1) Mössbauer Spectroscopy and Transition Metal Chemistry -
Philipp Gütlich, Eckhard Bill, Alfred X. Trautwein
(Springer)

(2) Physical Methods for Chemists (Second Edition) –
Russell S. Drago

Mössbauer spectroscopy

Mössbauer spectroscopy abbrivated as MB spectroscopy, involves nuclear transition that results from the absorption of γ-rays by the sample. The transition is characterized by a change of nuclear spin quantum number, I. The conditions for absorption depend upon the electron density about the nucleus, and the number of peaks obtained is related to the symmetry of the compound. As a result structural information can be obtained.

Nuclear γ-Resonance



Sender
(Mössbauer Source)

Transmitted γ-rays
$E_0 = E_e - E_g$

Receiver
(Mössbauer Absorber)

Mössbauer Nuclides

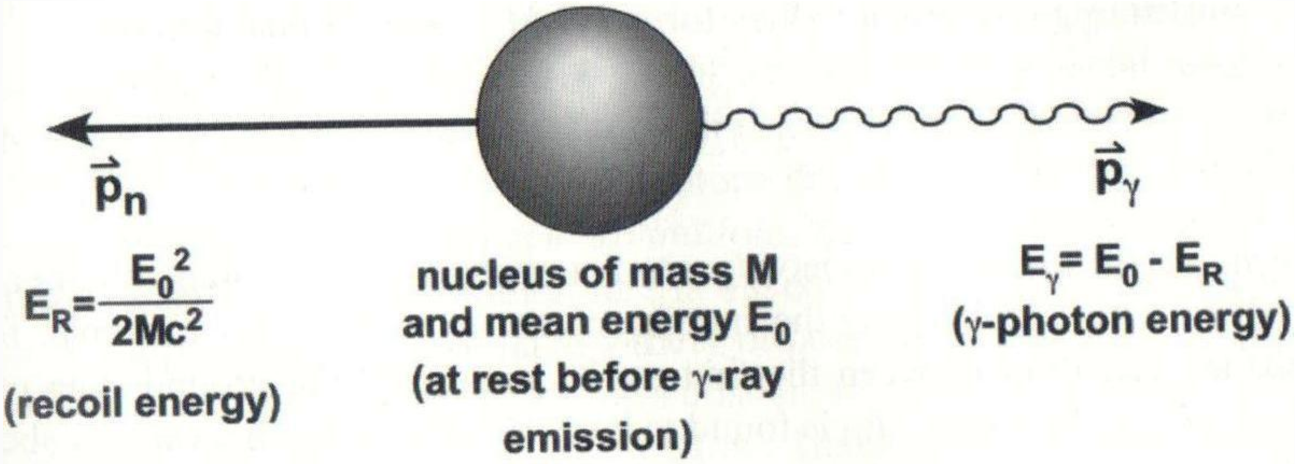
All the γ-emitters are not suitable for Mössbauer study. The nuclides should possess the following characteristics.

- ➢The energy of γ-radiation should be in the range of 10-200 keV.
- ➢Half-life of the parent nuclide generating the γ-emitter nuclide should be of the order of a year so that the same source with reasonably constant activity may be made available for a series of experiments.
- ➢The γ-emission half-life of the excited source should be within the limits 10^{-6} s to 10^{-10} s.
- ➢The conversion coefficient should be as low as possible so that most decays are via γ-emission.
- ➢The absorber nuclide should be present in high isotopic abundance. Samples enriched in the relevant isotopes are sometimes used in those cases where higher sensitivity needed.

Recoil Energy loss in free atoms

Mass of nucleus = M

Nucleus moves with the velocity *v* in a direction opposite to that of the γ-ray propagation vector.



Recoil energy $E_R = (1/2)Mv^2$ ……………………..(i)

Momentum conservation $P_n = -P_\gamma$ …………………(ii)

The momentum of P_γ of the (mass less) photon is given by its quantum energy:

$P_\gamma = -E_\gamma / c$ …………………………..(iii) (c = velocity of light)

$E_\gamma = E_0 - E_R$ ………………………(iv)

Because of the large mass of the nucleus and the low velocity involved, we may use nonrelativistic approximation

$E_R = (1/2)Mv^2$ ……………………….(v)

$= (Mv)^2/2M$

$= P_n^2/2M$

$= E_\gamma^2/2Mc^2$ ……………………(vi)

Since E_R is very small compared to E_0, it is reasonable to assume that $E_\gamma \approx E_0$, therefore

$E_R = E_0^2/2Mc^2$

By substituting numerical values for c and $M = m_{n/m} \times A$

We get $E_R = 5.53 \times 10^{-4} (E_0^2/A)$ eV

where $m_{n/m}$ is the mass of a nucleon (proton or neutron), A is the mass number of the Mössbauer isotope , and E_0 is the transition energy in keV.

E_R for Mössbauer transition between the first excited state and ground state of ^{57}Fe

$E_0 = E_e - E_g = 14.4$ keV

$E_R = 1.95 \times 10^{-3}$ eV

This value is about six orders of magnitude larger than natural width ($\Gamma = 4.55 \times 10^{-9}$ eV)

Energy shift of the emission line and absorption line due to recoil effect

The recoil effect causes an energy shift of the emission line from E_0 to smaller energies by an amount E_R , whereby γ-photon carries an energy only

$E_\gamma = E_0 - E_R$

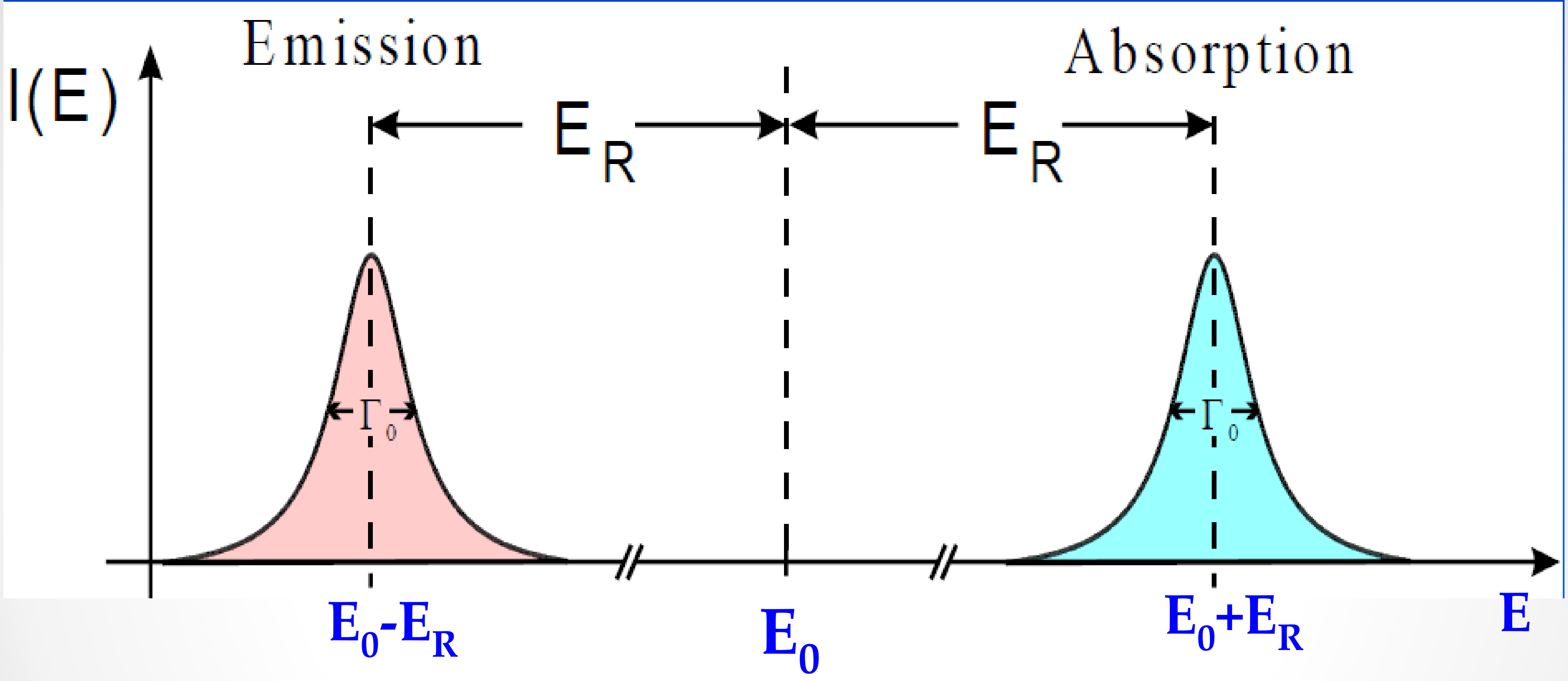
However, a recoil effect also occurs in the absorption process so that the photon, in order to be absorbed by the nucleus, requires the total energy

$E_\gamma = E_0+E_R$ to make up for the transition from the ground to the excited state and the recoil effect (for which P_n and P_γ will have same direction).

Hence, nuclear resonance absorption of γ-photons (the Mössbauer effect) is not possible between free atoms (at rest) because of the energy loss by recoil.

The deficiency in γ-energy is two times the recoil energy, $2E_R$, which in the case of ^{57}Fe is about 10^6 times larger than the natural line width Γ of the nuclear levels involved.

Recoil Effect

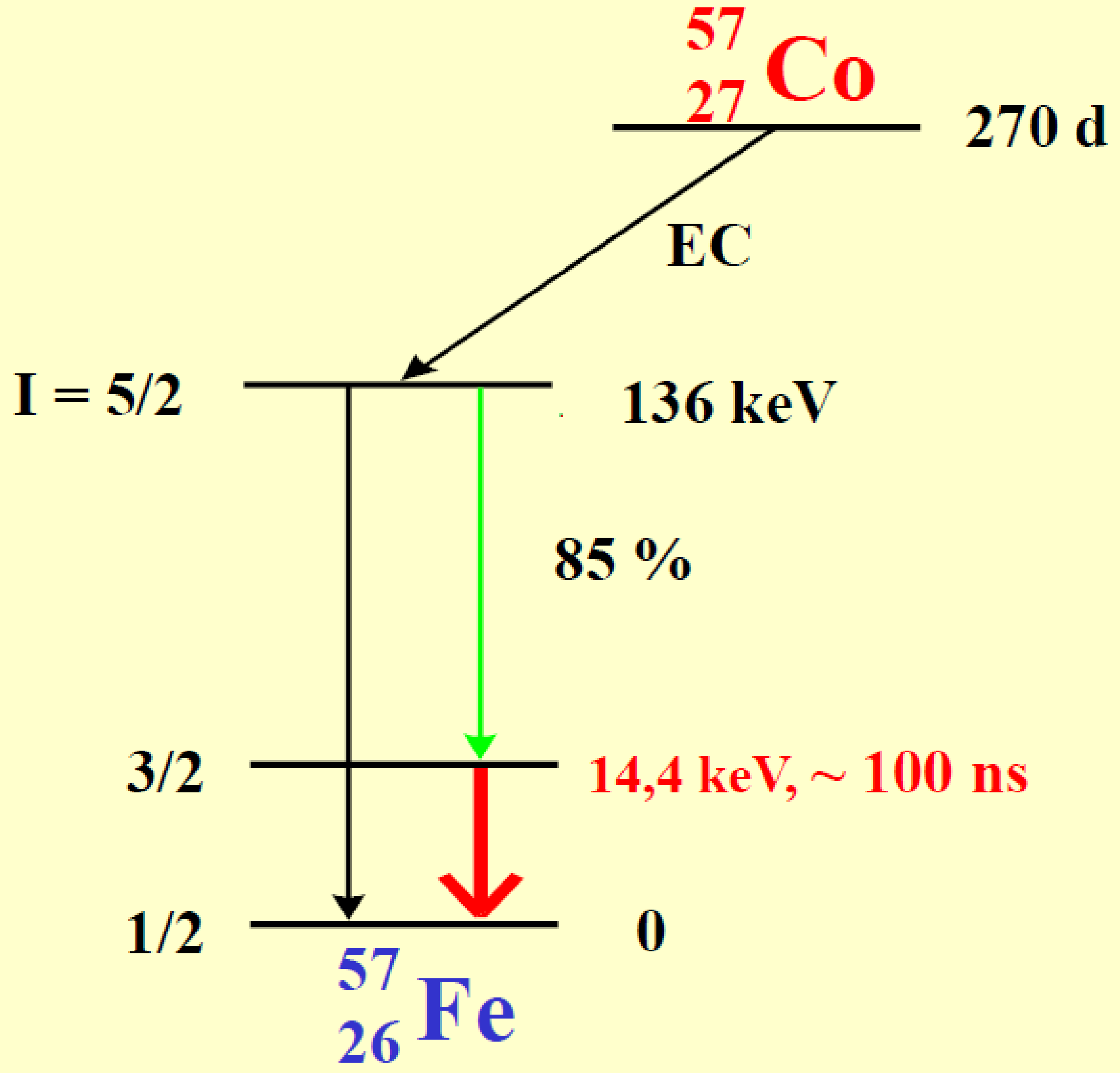


$$E_R = E_0^2/2Mc^2$$

For ^{57}Fe: $E_R = 1.95 \times 10^{-3}$ eV

$\Gamma = 4.55 \times 10^{-9}$ eV

Nuclear Decay Scheme for ^{57}Fe Mössbauer Resonance



Radioactive ^{57}Co with 270 days halflife, which may be generated in a cyclotron and diffused into a noble metal like rhodium, serves as the gamma radiation source for ^{57}Fe Mössbauer spectroscopy. 57Co decays by electron capture (EC from K-shell, thereby reducing the proton number, from 27 to 26 corresponding to ^{57}Fe) and initially populates the 136 keV nuclear level of ^{57}Fe with nuclear spin quantum number I = 5/2. This excited state decays after ca. 10 ns and populates, with 85 % probability the 14.4 keV level by emitting 122 keV gamma quanta, with 15 % probability the 136 keV level decays directly to the ground state of ^{57}Fe. The 14.4 keV nuclear state has a halflife of ca. 100 ns. Both the halflife and the emitted gamma quanta of 14.4 keV energy are ideally suited for ^{57}Fe Mössbauer spectroscopy. I = 3/2 and I = 1/2 are the nuclear spin quantum numbers of the excited state (14.4 keV) and the ground state, respectively. The internal conversion coefficient α (= the number of ejected K-shell electrons for each γ-quantum interacting with the K-shell) is 9.7.

Hyperfine Interactions between Nuclei and Electrons and Mössbauer Parameters

- ➢**Electric Monopole Interaction**

  →**Isomer Shift δ**

- ➢**Electric Quadrupole Interaction**

  →**Quadrupole Splitting ΔE_Q**

- ➢**Magnetic Dipole Interaction**

  →**Magnetic Splitting ΔE_M**

➢Electric Monopole Interaction → Isomer Shift δ

Electric monopole interaction between protons of the nucleus and electrons (mainly s-electrons) penetrating the nuclear field. The observable Mössbauer parameter is the “isomer shift δ”. Isomer shift values give information on the oxidation state, spin state, and bonding properties such as covalency and electronegativity.

➢Electric Quadrupole Interaction

→ Quadrupole Splitting ΔE_Q

Electric quadrupole interaction between the nuclear quadrupole moment and an inhomogeneous electric field at the nucleus. The observable Mössbauer parameter is the "**quadrupole splitting ΔE_Q**". The information derived from the quadrupole splitting refers to oxidation state, spin state and site symmetry.

➢Magnetic Dipole Interaction

→Magnetic Splitting ΔE_M

Magnetic dipole interaction between the nuclear magnetic dipole moment and a magnetic field at the nucleus. The observable Mössbauer parameter is the "**magnetic splitting ΔE_M**". This quantity gives information on the magnetic properties of the material under study.

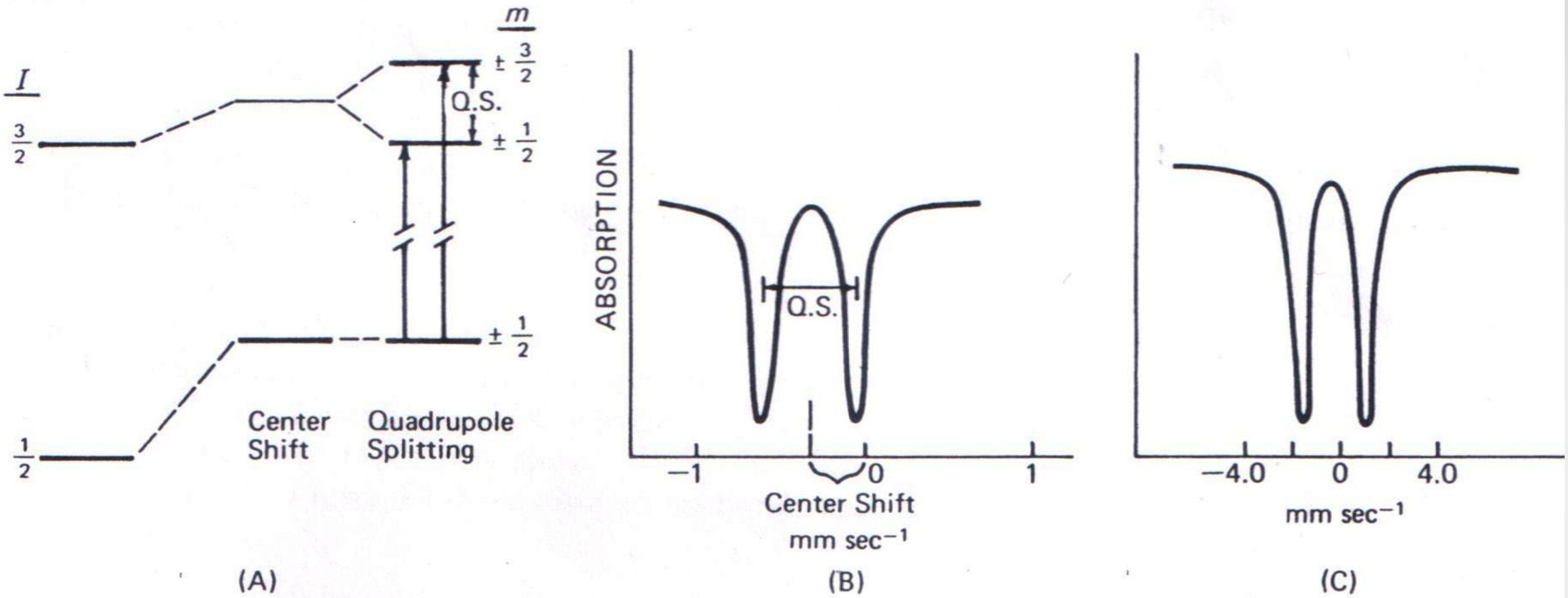
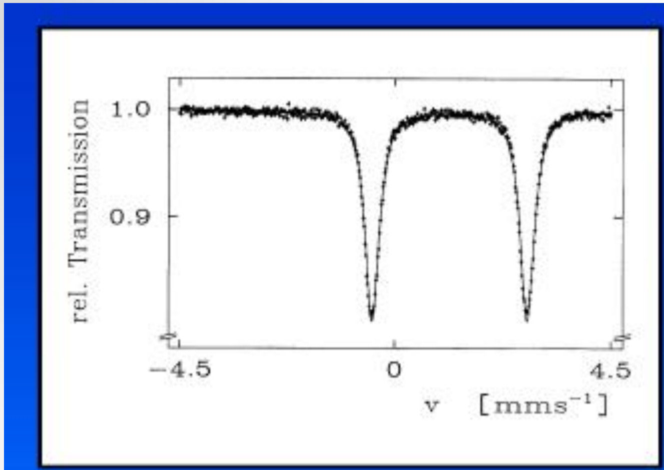


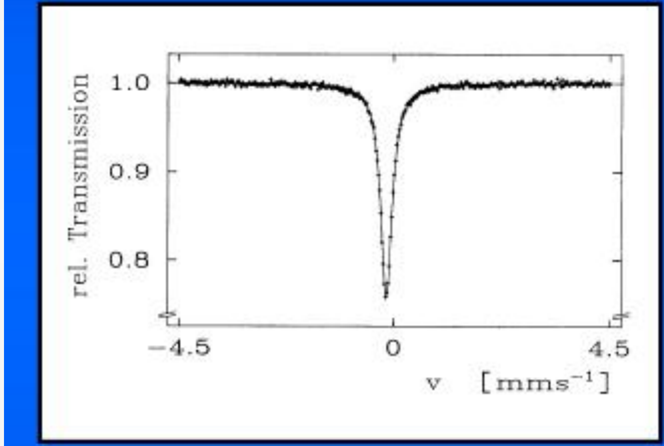
FIGURE 15–4 The influence of a non-cubic electronic environment on (A) the nuclear energy states of ^{57}Fe and (B) the Mössbauer spectrum. (C) The iron MB spectrum of Fe(CO)$_5$ at liquid N$_2$ temperature.(9)



$FeSO_4 \cdot 7H_2O$

$[Fe(H_2O)_6]^{2+}$

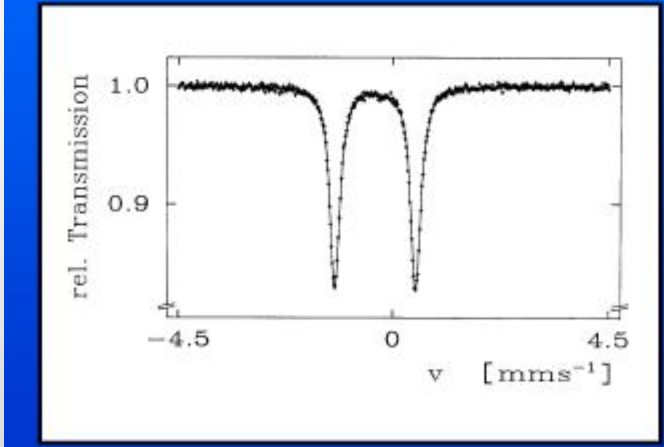
Fe(II)-HS, S=2



$K_4[Fe(CN)_6]$

Fe(II)-LS, S=0

cubic



$Na_2[Fe(CN)_5NO]$

Fe(II)-LS, S=0

tetragonal

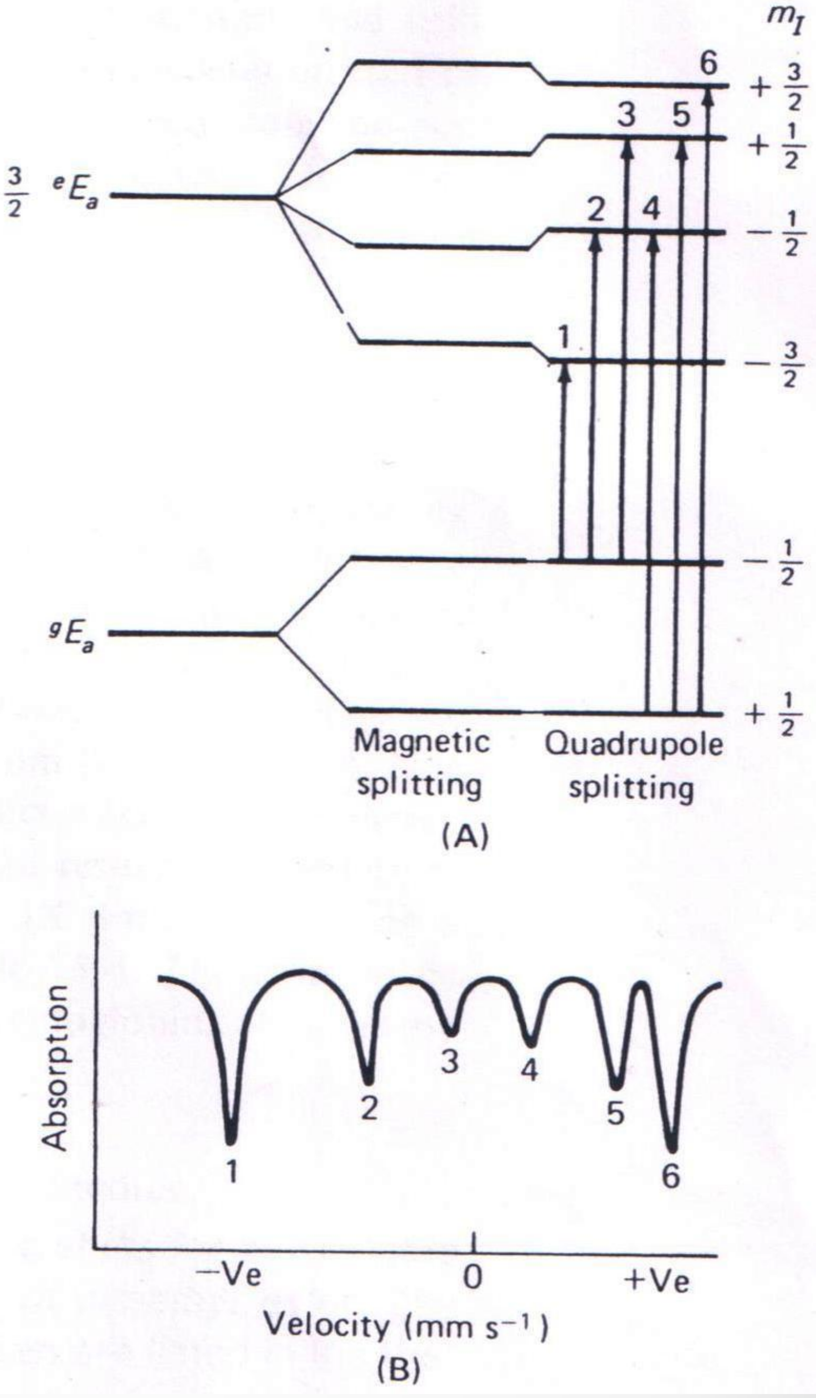


FIGURE 15-5
Magnetic and quadrupole splitting in a ferromagnetic ^{57}Fe compound. (A) Energy level diagram. (B) Expected Mössbauer spectrum.