

# Mössbauer Spectroscopy & Learning Objectives

- **Title:**

Mössbauer Spectroscopy in Inorganic Chemistry

- **Objectives:**

1. Understand the Mössbauer Effect (recoilless emission and absorption).
2. Interpret the isomer shift ( $\delta$ ) and its relation to oxidation states.
3. Analyze quadrupole splitting ( $\Delta E_Q$ ) and magnetic hyperfine splitting.

# The Physical Principle — The Mössbauer Effect

## The Challenge:

Normally, when a nucleus emits a gamma photon, it recoils (like a gun), losing energy and preventing resonance.

- **The Solution:**

In a solid lattice, the nucleus is rigidly bound, allowing recoilless emission and absorption.

- **Source & Sample:**

Typically uses a radioactive  $^{57}\text{Co}$  source that decays into an excited state of  $^{57}\text{Fe}$ .

# Instrumentation & The Doppler Effect

## Mechanism:

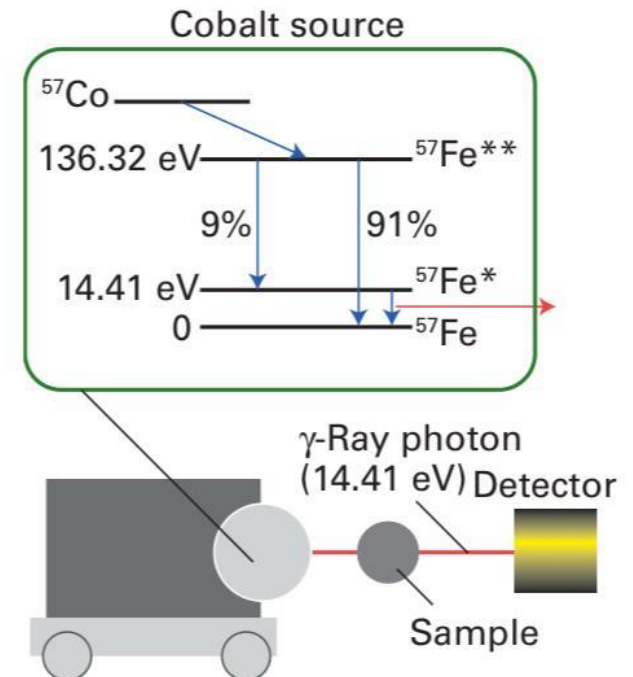
To achieve resonance, the source is moved back and forth at very small velocities (mm/s).

- **The Doppler Shift:**

This movement slightly changes the energy of the  $\gamma$ -ray "Doppler Effect " until it matches the energy levels of the sample.

- **The Spectrum:**

A plot of transmission intensity versus the velocity of the source.



# The Isomer Shift ( $\delta$ )

- **Definition:**

The distance the peak moves from the center. It depends entirely on the density of electrons around the nucleus, and it is the best way to distinguish between ferrous, ferric, and tetravalent iron in complexes.

- **Physical Origin:**

- I. Caused by the s-electron density at the nucleus.
- II. So, Since the nucleus is surrounded by these electrons, the size of the nucleus interacts with the density of these electrons.
- III. Any change in the chemical environment (such as losing or gaining electrons) changes the density of s electrons at the nucleus, leading to a change in energy levels and the appearance of this shift.

- **Diagnostic Value:**

Highly sensitive to the oxidation state, allowing distinction between  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Fe}^{4+}$ . So, as the oxidation state increases, the number of d electrons decreases. Since d electrons shield s electrons from the nucleus, a deficiency of d electrons leads to an increase in the density of s electrons at the nucleus, which changes the value of  $\delta$ .

# Quadrupole Splitting ( $\Delta E_Q$ )

- **Requirement:**

Occurs if the nucleus has a non-spherical charge distribution ( $I > 1/2$ ) if spherical then  $I = 1/2$  so this nucleus is not affected by the surrounding electric field .

- I. **EFG “electric field gradient “** measures the asymmetry in the charge distribution around the nucleus.
- II. Perfect symmetry: If iron is surrounded by six completely identical ligands (ideal octahedron), the electric field is uniform (**EFG = 0**), and only one peak appears.
- III. Asymmetry: If one ligand is replaced, or there is a distortion in shape (Distortion), a gradient in the electric field arises **EFG**. This gradient presses on the oval—like (non-spherical) nucleus and causes its energy levels to split.

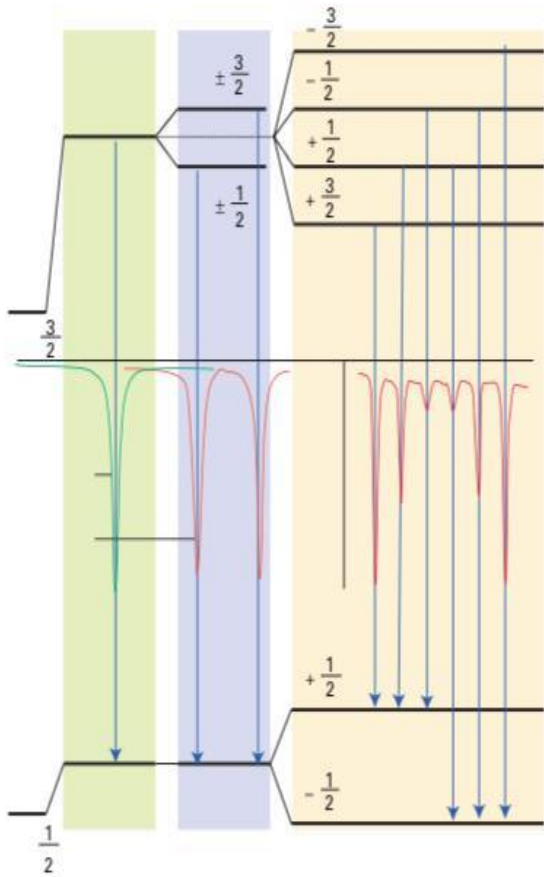
- **Effect:**

The single peak splits into two lines (a doublet) due to interaction with an electric field gradient (EFG). So, A singlet transforms into a doublet. The distance between these two peaks is the value of  $\Delta E_Q$ . The more the complex is 'distorted' and asymmetric, the greater this distance of  $\Delta E_Q$ .

- **Insight:**

Provides information about the symmetry and distortion of the coordination environment.

# Quadrupole Splitting ( $\Delta E_Q$ )



Spectrum Shape	Physical Origin	Information Provided	Chemical Example	
Green Region	Singlet (Single Peak)	s-electron density only (Isomer Shift $\delta$ )	Oxidation state (e.g., $\text{Fe}^{2+}$ ) and a highly symmetric environment	$\text{K}_4[\text{Fe}(\text{CN})_6]$
Purple Region	Doublet (Two Peaks)	Electric Field Gradient (EFG) + $\delta$	Symmetry and distortion (confirms non-equivalent ligands)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Yellow Region	Sextet (Six Peaks)	Magnetic field effect (Hyperfine splitting)	Magnetic properties (e.g., ferromagnetism, magnetic ordering)	$\text{Fe}_2\text{O}_3$ (Rust)

# Magnetic Hyperfine Splitting (The Sextet)

- **The Effect:**

When an internal or external magnetic field is present, the nuclear energy levels split further.

- **Observation:**

Instead of one or two lines, the spectrum splits into six lines (a sextet).

- **Significance:**

Used to study ferromagnetic materials and the internal magnetic environment of iron atoms.

# Distinguishing Oxidation States of Iron

- **Fe(II) vs. Fe(III):**

High-spin  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  show very different isomer shifts ( $\delta$ ).

- **Range:**

$\text{Fe}^{2+}$  typically exhibits a higher (more positive)  $\delta$  value than  $\text{Fe}^{3+}$ .

- **Covalency:**

As metal–ligand bonding becomes more covalent, the isomer shift decreases. “with higher (more positive)  $\delta$  value than  $\text{Fe}^{3+}$ .”

# High Spin vs. Low Spin Configurations

- **Electronic Effect:**

The s-electron density at the nucleus is shielded differently by d-electrons.

- **Spectral Change:**

High-spin complexes show much larger quadrupole splitting ( $\Delta EQ$ ) due to asymmetric electron distribution.

- **Spin Crossover:**

Mössbauer spectroscopy can track changes in spin state with temperature or pressure.

# Application in Bio-inorganic Chemistry

- **Heme Proteins:**

Used to study the iron center in hemoglobin and myoglobin.

- **Enzymes:**

Identifying active sites in nitrogenase and iron–sulfur clusters.

- **Sensitivity:**

Selectively detects iron in complex biological systems without interference.

# Mixed-Valence Compounds

- **The System:**

Compounds containing both Fe(II) and Fe(III) in the same lattice (e.g., Prussian Blue).

- **Timescale:**

Mössbauer spectroscopy is very fast ( $10^{-7}$  s), allowing observation of individual iron sites. Therefore, The Mössbauer time is very short ( $10^{-7}$  seconds). This means it is "very fast" in shooting And capturing Electrons moving between iron atoms ( $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ ). This is called electron exchange And captured in Mossbaure Spectroscopy.

- **Mapping:**

Directly measures the ratio of different iron oxidation states.

# Quadrupole Splitting and Geometry (Figure 8.30)

- **EFG Origin:**

The electric field gradient arises from both ligands and valence electrons.

- **Symmetry Probe:**

Perfect cubic or octahedral symmetry results in zero quadrupole splitting ( $\Delta E_Q = 0$ ).

- **Distortion:**

Any deviation from symmetry produces a doublet.

# Other Mössbauer Nuclei

- **Beyond Iron:**

While  $^{57}\text{Fe}$  is the most common Mössbauer nucleus, others include  $^{119}\text{Sn}$ ,  $^{121}\text{Sb}$ , and  $^{197}\text{Au}$ .

- **Tin ( $^{119}\text{Sn}$ ):**

Widely used in organometallic chemistry to study tin-containing catalysts.

- **Gold ( $^{197}\text{Au}$ ):**

Used to characterize gold clusters and nanoparticles.

# Sample Preparation for Mössbauer

- **State:**

The sample must be solid (powder, crystal, or frozen solution).

- **Concentration:**

Requires a specific thickness to ensure optimal absorption of  $\gamma$ -rays.

- **Temperature Control:**

Often performed at low temperatures to increase the recoilless fraction.

# The Isomer Shift and Electron Density

- **s-Electrons:**

Only s-electrons have a non-zero probability at the nucleus.

- **Shielding:**

d-Electrons shield the s-electrons from the nucleus.

- **Direct Link:**

Changing the d-electron count (oxidation or reduction) directly shifts the spectrum.

# Comparison with NMR and EPR

- **NMR:**

Best for detailed structural mapping of light atoms.

- **EPR:**

Ideal for identifying radicals and unpaired electrons.

- **Mössbauer:**

Superior for determining oxidation and spin states of specific metals in solids.

# Zero-Field Splitting in Mössbauer

- **Interaction:**

Electron interactions affect nuclear energy levels even without an external magnetic field.

- **Spectrum Profile:**

Leads to broadening or complex splitting patterns.

- **Information:**

Provides details about the electronic ground state.



# Summary of Parameters

- **Isomer Shift ( $\delta$ ):**

Oxidation state and s-electron density.

- **Quadrupole Splitting ( $\Delta EQ$ ):**

Symmetry and electric field gradient.

- **Hyperfine Splitting:**

Magnetic environment.

# References & Self-Assessment

- **Core Reading:**

Atkins, *Inorganic Chemistry* (Physical Techniques Chapter).

- **Problem:**

Explain why a high-spin  $\text{Fe}^{2+}$  complex shows a larger quadrupole splitting than a high-spin  $\text{Fe}^{3+}$  complex.