Mössbauer Spectroscopy

a.k.a.: gamma ray nuclear absorption spectroscopy

I. Origin
II. Isomer Shifts
III. Quadrupole Splittings
IV. Magnetic Field Splittings
V. Uses & Applications
Mössbauer Pros & Cons

What Mössbauer can tell us:

- Oxidation state of metal (Fe or Sn only)
- Local structure/symmetry
- Comparison to known model compounds
- Information about electronic structure (via nuclear Zeeman)

Major disadvantages:

- Only $^{57}$Fe, $^{99}$Ru, $^{119}$Sn, and $^{191}$Ir are practical nuclear isotopes (due to availability/lifetime of radioisotope sources of $\gamma$-rays).
- Only at <10 K, in frozen solids or xstals.

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Mössbauer Spectroscopy Terms

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_\gamma$</td>
<td>keV</td>
<td>Mean Energy of $\gamma$-ray</td>
</tr>
<tr>
<td>$\Gamma_{exp}$</td>
<td>mm/s</td>
<td>Exp. Half-Height Width</td>
</tr>
<tr>
<td>$\Gamma_{n}$</td>
<td>mm/s</td>
<td>Natural line Width = $\frac{\Gamma_{exp}}{2}$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>mm/s</td>
<td>Isomer Shift; Displacement from Reference Pt.</td>
</tr>
<tr>
<td>$\Delta E_0$</td>
<td>mm/s</td>
<td>Hyperfine Splitting between nuclear Quadrupole Moment and Electric Field Gradient</td>
</tr>
<tr>
<td>$EFG$</td>
<td>3x3 matrix</td>
<td>$\nabla \cdot EFG$ - Tensor describing change in Electric Field</td>
</tr>
</tbody>
</table>
**Mössbauer Spectroscopy Terms**

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<thead>
<tr>
<th>Symbol</th>
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</thead>
<tbody>
<tr>
<td>$v_{zz}$</td>
<td>$g_{zz} = \frac{\partial I}{\partial x}$</td>
<td>$zz$ component of $\varepsilon$.</td>
</tr>
<tr>
<td>$\eta$</td>
<td></td>
<td>Asymmetry Parameter $\eta = \frac{v_{xx} - v_{yy}}{v_{xx}}$.</td>
</tr>
<tr>
<td>$Q$</td>
<td>barn ($10^{-24}$ cm$^2$)</td>
<td>Nuclear Quadrupole Moment describes spin/orbital charge distribution.</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>$cm^2$ barns</td>
<td>Cross Section for Absorption.</td>
</tr>
<tr>
<td>$f$</td>
<td></td>
<td>Fraction of all emitted (or absorbed) $\gamma$-rays which are Recoilless.</td>
</tr>
<tr>
<td>$R$</td>
<td></td>
<td>Change in Nuclear Radii from Ground to Excited State.</td>
</tr>
</tbody>
</table>

**Mössbauer Spectroscopy**

**$\gamma$-Ray Emission Energy Diagram**

- **Mössbauer Spin**
  - $\frac{7}{2}$
  - $\frac{9}{2}$
  - $\frac{11}{2}$
  - $\frac{13}{2}$

- **$\Delta E$**
  - $570$ keV
  - $1231$ keV
  - $198$ keV

- **State**
  - $^{57}$Co
  - $^{57}$Fe
  - $^{59}$Fe

- **Half-Life**
  - $2.70$ days
  - $10$ microsec
  - $100$ microsec
  - $\infty$
Mössbauer Spectroscopy

\[ E_f = E_r + D + R \]

\( E_r = 14.4 \text{ keV} \) for \( ^{57}\text{Fe} \)

\[ D = E_r \frac{v}{c} \]

\[ R = \frac{E_r^2}{2mc^2} \]

But: \( R \sim 10^{-3} \text{ ev} \) for \( m = 100 \text{ amu} \) (i.e., single metal atom)

So to tune the \( \gamma \)-ray by doppler shifting, \( D >> 2R \)

For \( D = 2R, \ v = 80 \text{ mph (40,000 mm/s)} \)

(typically 10 mm/s is practical limit)

Mössbauer Effect

- In solids, the entire crystallite can absorb the \( \gamma \)-ray photon’s momentum.

- This reduces \( R \sim 10^{10} \) to \( 10^{20} \) from that of an isolated molecule: “Recoilless transition”.

- The probability of Recoilless Transition decreases with increasing \( R \). i.e., is a function of \( \gamma \)-ray energy.

- Crudely, if \( R \) for the isolated molecule is less than the lattice vibrations (i.e., phonons, \( \sim 0.04 \text{ ev} = \sim 300 \text{ cm}^{-1} \)), then the loss of \( \gamma \)-ray energy by inelastic absorption (i.e., phonon excitation) will diminish, which increases the Recoilless events.
Mössbauer Effect and Recoil Energy

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$E_x$</th>
<th>$R$</th>
<th>Recoilless Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{57}$Fe</td>
<td>14.4 keV</td>
<td>$10^{-3}$ eV</td>
<td>Yes</td>
</tr>
<tr>
<td>$^{57}$Fe</td>
<td>800 keV</td>
<td>6 eV</td>
<td>No</td>
</tr>
</tbody>
</table>

Good for Mössbauer
No Mössbauer

MB possible only with $\gamma$-ray energies $< \sim 50$ keV

Mössbauer Spectrometer

Sample

Semiconductor Detector

X-ray forms $e^-$/hole pairs
decreasing resistivity momentarily ($10^{-8}$ sec)
allowing voltage pulse w/ current vs $E_x$
Counts x-ray photons at a time.
Mössbauer Linewidth

To see Mössbauer effect, linewidth must be < Doppler Shift in order to resolve anything.

\[ \Gamma_{\text{nat}} = \frac{k}{c} = 5 \times 10^{-9} \text{ eV} \approx 0.1 \text{ mm/s} \]

Typical drives provide \( \pm 5-10 \text{ mm/s} \)

Mössbauer Effect: Isomer Shifts

Source \( l=3/2 \) \( E_S \) \( E_A \) \( l=1/2 \) Isomer shift \( \delta \)

\( \delta = \text{isomer shift} \)

Absorption [%]

velocity [mm/s]

quadrupole splitting = \( \Delta E_Q \)
Mössbauer Effect: Isomer Shifts

For $^{57}\text{Fe}$, increasing s electron density produces more negative isomer shift ($\delta$).

But what controls s density?  

Shielding!

Shielding complicates interpretation:  
e.g., lowered d electron density increases s density at metal nucleus, thus making $\delta$ more negative.
Mössbauer Effect: Fe Spin States

Common spin states of mononuclear Fe complexes

- FeV $S=1/2$
- FeIV $S=1$
- FeIV $S=2$
- FeII $S=1/2$
- FeII $S=5/2$
- FeI $S=0$
- FeII $S=2$

Mössbauer Effect: Isomer Shifts

Isomer shift depends on

- Oxidation state
- Nature of Ligands
- Geometry
- Spin State
- Coordination Number
- Covalency
Mössbauer Effect: Isomer Shifts

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Isomer shift (vs Fe&lt;sup&gt;0&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Valence Organometallics</td>
<td>-4.2 to 0.5</td>
</tr>
<tr>
<td>II, ionic, H₂S (s=2)</td>
<td>1.0 to 1.5</td>
</tr>
<tr>
<td>II, covalent, C₂H₂S (s=0)</td>
<td>-0.3 to 0.45</td>
</tr>
<tr>
<td>II, ionic, H₂S²⁺ (s=3)</td>
<td>0.45 to 1.0</td>
</tr>
<tr>
<td>II, covalent, C₂H₂S²⁺ (s=½)</td>
<td>-0.2 to 0.0</td>
</tr>
</tbody>
</table>

Mössbauer Effect: Isomer Shifts

![Diagram showing isomer shifts for different oxidation states of iron](image)
Mössbauer Effect: Quadrupole Doublets

If electron density is non-cubic, then the $m_I$ values of the nucleus will be split:

For $\frac{1}{2} < I_n$, Kramer's Doublet Theorem applies ($\pm \frac{n}{2}$ remain degenerate). $\therefore I_n \neq \frac{1}{2}$ States

For integral $I_n$, all degeneracy goes $\therefore 2I_n + 1$ States

Mössbauer Effect: Inhomogeneous e- density

The inhomogeneity of electric field at the nucleus is expressed as a $3 \times 3$ tensor:

$$EFG = \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix}$$

Where $V_{xx} + V_{yy} + V_{zz} = 0$ (Laplace Eqn. Requirement)
Mössbauer Effect: Inhomogeneous e- density

There exists some choice of axes such that $\text{EFG} = \begin{bmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{bmatrix}$

We can express all info as $V_{zz}$ and $n \equiv \frac{V_{xx} - V_{yy}}{V_{zz}}$

where convention gives $|V_{zz}| > |V_{yy}| > |V_{xx}|$

$0 \leq |n| < 1$

ellipsoid

ICBST:

$\Delta E_Q = \frac{e^2 Q \sqrt{1 - (n^2)^2}}{2}$

for $I_\alpha = \frac{3}{2}$

$Q = \text{nuclear quad. moment}$

Chemical Origins of $\Delta E_Q$

Sign of $\Delta E_Q$

$I = 3/2$

$\Delta E_Q < 0$

$\pm 3/2$

$\pm 1/2$

$I = 3/2$

$\Delta E_Q > 0$

$\pm 3/2$

$\pm 1/2$

much smaller than the d2z2 orbital

Positive charge
Chemical Origins of $\Delta E_Q$

1) \( e^- \) in the Fe's orbitals
2) Charge Distribution of lattice ions (ligands)

\[ \text{e-density symmetric, no } \Delta E_p \text{ contribution} \]

1. L.S. Fe$^{\text{II}}$ and H.S. Fe$^{\text{III}}$ have no $\Delta E_p$ contribution
2. H.S. Fe$^{\text{II}}$ and L.S. Fe$^{\text{III}}$ do.

2) Asymmetric ligand distribution will cause small $\Delta E_p$ contribution \[ \Delta E_p = 36 \text{ mm/s} \]
Range of $\Delta E_Q$

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta E_Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Valence</td>
<td>$0 - 2.5^{\circ}$</td>
</tr>
<tr>
<td>Fe$^{II}$ H.S.</td>
<td>1.7 - 3.5</td>
</tr>
<tr>
<td>Fe$^{II}$ L.S.</td>
<td>0 - 2.0</td>
</tr>
<tr>
<td>Fe$^{III}$ H.S.</td>
<td>0 - 0.9</td>
</tr>
<tr>
<td>Fe$^{III}$ L.S.</td>
<td>0.3 - 2.5</td>
</tr>
</tbody>
</table>

* Depends heavily on Ligand Field Symmetry

Mössbauer Effect: Quadrupole Doublets

Absorption (arb. units) vs. Velocity (mm/s) for:
- $S=2$ Fe$^{II}$
- $S=0$ Fe$^{III}$
- $S=2$ Fe$^{II} = O$
- $S=1$ Fe$^{III} = O$
- $S=1/2$ Fe$^{III} = O$

Species:
- dioxygenase
- Cyt c
- Tau D J
- TPA ligand
- TAML ligand
### Isomer Shift vs. Quadrupole Doublets

**Fe Porphyrin Complexes**

- H.S. Fe(II)
- L.S. Fe(II)
- H.S. Fe(III)
- L.S. Fe(III)

### Chemical Correlation with Isomer Shifts

Fe$^{II}$ (CN)$_3$ L$^{-n}$

<table>
<thead>
<tr>
<th>L</th>
<th>Δ mm/s</th>
<th>Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>SO$_2^-$</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.31</td>
<td></td>
</tr>
</tbody>
</table>

\[
\delta \propto \Delta_0
\]

\[
\delta_{L \rightarrow M} \text{ directly increase } S_{M_{d_{0}}} \text{ e-density}
\]

\[
\pi_{M \rightarrow L} \text{ decrease } d_{M} \text{ e-density } \alpha \text{ indirectly}
\]

\[
\therefore \text{ cause } S_{M_{d_{0}}} \text{ e-density increase}
\]

For Fe$^{II}$ \( \delta R < 0 \) \( \Rightarrow (\uparrow \uparrow, \uparrow \downarrow) \)
Chemical Correlation with Isomer Shifts

\[ \text{Ru}^{II} (\text{NH}_3)_2 L^{n} \]

\[ \begin{array}{c|c}
L & \sigma \\
\hline
\text{NO} & -0.18 \\
\text{CO} & -0.34 \\
\text{SO}_2 & -0.61 \\
\text{N}_2 & -0.62 \\
\text{NH}_3 & -0.82 \\
\end{array} \]

Some as Fe(II) L but note:

For \( \text{Ru}^{II} \), \( \frac{\Delta R}{R} > 0 \Rightarrow (s \uparrow, \delta \downarrow) \)

---

Chemical Correlation with Isomer Shifts: Sn\textsuperscript{IV}

For \( \text{Sn}^{IV} \) transition, \( \frac{\Delta R}{R} > 0 \)

\( s \rightarrow 3s \) density \( \rightarrow 0 \)

\( \delta \rightarrow \) more negative

\( \downarrow \) as ligands become more \( \pi \) withdrawing (\( \sigma \))

\( 3s \) density \( \rightarrow 0 \) \& \( \delta \rightarrow \) more negative

(\( 3\psi, \delta \))
Mössbauer vs. Structure

The Spin Hamiltonian

\[ \hat{H} \Phi = \varepsilon \Phi \]

kinetic energy, \( e^- \) - nuclear attraction, \( e^- - e^- \) repulsion, nucl.-nucl. repulsion, ligand field

Nuclear Zeeman (NMR)

Electronic Zeeman (EPR)

Zero Field Splitting (ZFS) from spin-orbit coupling of angular mom.

Hyperfine Coupling of \( e^- \) & nuclear moments (NMR & EPR)
Mössbauer Effect: Magnetic Field Effect

Magnetic Dipole Splitting

$E_A$

$|m_s|$

$+3/2$

$+1/2$

$-1/2$

$-3/2$

$-1/2$

$+1/2$

Absorption [%] vs velocity [mm/s]