

JoVE: Science Education
Mössbauer Spectroscopy
--Manuscript Draft--

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Overview

Mössbauer spectroscopy is a bulk characterization technique that examines the nuclear excitation of an atom by gamma rays in the solid state. The resulting Mössbauer spectrum provides information about the oxidation state, spin state, and electronic environment around the target atom, which, in combination, gives evidence about electronic structure and ligands arrangement (geometry) of the molecule. In this video, we will learn about the basic principles of Mössbauer spectroscopy and collect a zero field ^{57}Fe Mössbauer spectrum of ferrocene.

Commented [HK1]: What is the significance of this information obtained?

Commented [PTM2R1]: I'm not really sure what you mean by significance. This is a characterization method (provides evidence of what you made).

Principles

Nuclear Spin Angular Momentum (I)

The nuclear spin (I) of an atom is defined as the total angular momentum of the nucleus. Common ground states The ground state nuclear spin for a given atom is dependent on the number of protons and neutrons in the nucleus and can be a half integer value (1/2, 3/2, 5/2, etc) or an integer value (1, 2, 3, etc). Nuclear spin excited states, $I + 1n$, where n is an integer value, exist and can be accessed if enough energy is applied to the nucleus.

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Experiment Instrument setup

The general instrument setup is shown in Figure 1. The source that generates gamma rays is connected to a driver, which continuously moves the source with respect to the sample (the necessity of this will be explained below). During the Mössbauer experiment, a The gamma rays then hit the solid sample, which is frequently suspended in an oil, is irradiated with gamma rays. Upon passing through the sample, the resulting transmitted radiation hits the detector, which measures the intensity of the beam upon interaction with the sample.

Gamma ray generation

The source used to generate the gamma rays for the experiment needs to be of the same isotope as the atoms in the sample that are absorbing the radiation. For example, for ^{57}Fe Mössbauer spectroscopy, a radioactive ^{57}Co source is utilized. ^{57}Co decays (half life = 272 days) to the excited state of ^{57}Fe , $I = 5/2$. The resulting excited state further decays to either the $I = 3/2$ excited state or to the $I = 1/2$ ground state. Relaxation from the $I = 3/2$ excited state of ^{57}Fe to the ground state produces a gamma ray of desired energy for the experiment. However, the energy of the generated gamma ray does not exactly match the energy required for a nuclear excitation of the atom in a given molecule. Returning to the example of ^{57}Fe , the energy levels of the $I = 1/2$ and $I = 3/2$ states change upon putting Fe within a molecule, where the oxidation and spin state of the metal as well as the ligand environment have an effect on the electron field gradient at Fe. Therefore, to tune the energy of the resulting gamma ray, the source is moved with respect to the sample during

Commented [HK3]: Will students be familiar with the excitation states so no further explanation is necessary?

Commented [PTM4R3]: At this level, they should be (since they learned about NMR already). But I've added a brief statement about Nuclear spin quantum numbers above.

the experiment using a driver (**Figure 1**). Therefore, the conventional “energy” unit in Mössbauer spectroscopy is mm/s.

Upon passing through the sample, the resulting transmitted radiation hits the detector, which measures the intensity of the beam upon interaction with the sample.

What does a typical Mössbauer spectrum look like?

In a Mössbauer spectrum, the percent transmission (dips in % transmission, - or the location of a peak - indicates gamma rays were absorbed at that energy) detected is plotted against the energy of the transition (mm/s). A typical spectrum is shown in Figure 2. The two peaks together are considered a single quadrupole doublet, which is the result of where there are three two of the three types of observable nuclear interactions in a Mössbauer spectrum are shown.

1. The isomer shift (or chemical shift, δ , mm/s) is a measure of nuclear resonance energy and is related to the oxidation state of the atom. In Figure 2, the isomer shift is the energy value half way between the peaks in the spectrum. Table 1 includes the typical ranges of isomer shifts for given oxidation states and spin states of Fe.

Table 1. Some typical ranges of isomer shifts for Fe containing compounds.¹

Oxidation state	Spin state (S)	Isomer shift range (mm/s)
Fe(II)	0	-0.3 to 0.4
Fe(II)	2	0.75 to 1.5
Fe(III)	1/2	-0.2 to 0.4
Fe(III)	5/2	0.2 to 0.55

2. The quadrupole splitting (ΔE_Q , mm/s) is a measure of how the electric field gradient around the atom affects the nuclear energy levels of the atom. Like the isomer shift, ΔE_Q provides information about the oxidation state. The spin state and the symmetry of the electron density around the atom (placement of ligands around a metal) will also affect the observed ΔE_Q . In Figure 2, the quadrupole splitting is the energy difference in mm/s between the two peaks in the spectrum.

~~Finally, hyperfine splitting (or Zeeman splitting) can also be observed in the presence of an internal or external magnetic field.~~

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Isomer shift and quadrupole splitting – what nuclear transitions do these values represent?

Here, we will consider the nuclear spin transitions for an Fe atom ($I = 1/2$ ground state). The isomer shift is directly related to the electron transition in the s orbital of the atom from the $I = 1/2$ to an excited state (**Figure 23**). If the surrounding electric field gradient is non-spherical, due to either a non-spherical electronic charge or asymmetric ligand arrangement, the nuclear energy level splits (**Figure 23**) i.e. the $I = 3/2$ excited state splits into two m_I states $\pm 1/2$ and $\pm 3/2$. As a result, both nuclear transitions are observed in the Mössbauer spectrum and the distance between the two resulting peaks is called the

quadrupole splitting. The quadrupole splitting value is therefore a measure of the effect on the nuclear energy levels with the electric field gradient around the atom.

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Fe(III)	5/2	0.2 to 0.55

Hyperfine splitting

Hyperfine splitting (or Zeeman splitting) can also be observed in the presence of an internal or external magnetic field. In the presence of a magnetic field, each nuclear energy level, I , splits into $2I + 1$ sub-states. For example, in an applied magnetic field the nuclear energy level $I = 3/2$ would split into 4 non-degenerate states including $3/2$, $1/2$, $-1/2$ and $-3/2$, with 6 allowed transitions (**Figure 23**).

Procedure

1. Preparation of the sample.

- 1.1. Weigh 100 mg of ferrocene in a delrine Mössbauer cup.
- 1.2. Add several drops of paratone oil to the sample. Using a spatula, mix the sample and the oil into a uniform paste.
- 1.3. Freeze the sample in liquid nitrogen.

2. Mounting the sample.

~~3.2.~~ Turn off the vacuum pump connected to the Mössbauer instrument.

~~3.1.2.1.~~ Refill/Fill the sample chamber with He gas.

~~3.2.2.2.~~ Unscrew the sample rod from the instrument and remove the sample rod.

~~3.3.2.3.~~ While mounting the sample, close the sample chamber with a cap and secure with screws.

~~3.4.2.4.~~ Load the Mössbauer cup into the sample holder at the end of the rod.

~~3.5.2.5.~~ Tighten the screw to secure the cup in the sample holder.

~~3.6.2.6.~~ Dust off any ice that forms before freezing the end of the sample rod in liquid nitrogen.

Commented [HK5]: I am slightly confused by the second part of Figure 2, representing %transmission and velocity. Is this mentioned in the principles discussing ΔE_Q ?

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3.7.2.7. With He flowing through the sample chamber, unscrew and remove the cap, and insert the sample rod.

3.8.2.8. Secure the rod to the instrument with the screws.

2.9. Turn off the He and pull vacuum on the sample chamber.

3.9.2.10. Turn off the vacuum and refill the sample chamber slightly with He to enable thermal exchange between the sample and the cold head of the instrument via the He gas.

4.3. Data collection and workup.

4.1.3.1. Open the Mössbauer data collection software. Here we use W302 by Science Engineering & Education (SEE) Co.

4.2.3.2. The first screen will show the total count of gamma rays hitting the detector at a range of energies. Select the peak that includes the energy value 14.4 keV and 2 keV escape peak. ~~Select the peak that includes the energy value 14.4 keV.~~

4.3. Hit the "Send Windowss" button, to begin data collection.

3.3. This will send the data to the W302 software (SEE Co).

3.4. Open the W302 program. Select the desired source velocity (0-12 mm/s). Hit "clear channel" to begin a new data collection.

After the desired resolution is reached, fit the data with a suitable program. Here we use WMOSS by SEE Co. The fit provides the values for isomer shift and quadrupole splitting (if a doublet is present).

4.4. ~~Determine the isomer shift of the signal and quadrupole splitting if a doublet is present.~~

Representative Results

Zero field ^{57}Fe Mössbauer of ferrocene at 5 K.

The isomer shift at 0.06 mm/s ~~is consistent with an~~ falls in the range one would expect for a Fe(II) , $S = 0$ complex (Table 1).

Summary

Here, we learned about the basic principles of Mössbauer spectroscopy, including details on the experimental setup, the gamma ray source, and information that you can gather from a Mössbauer spectrum. We collected the zero field ^{57}Fe Mössbauer spectrum of ferrocene.

Applications

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Commented [HK9]: Do you determine it using a software?

Commented [HK10]: Is there more you could tell in regards of the spectra. For someone who has not seen data and values for such an experiment, what should the person be looking at? What does the isomer shift at 0.06 mm/s tell us? A guided, brief discussion of the zero field spectrum would be helpful.

Commented [PTM11R10]: Hopefully my discussion above has cleared this up.

Commented [PTM12]: Data will be provided on day of filming

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Mössbauer spectroscopy is a powerful technique that provides information about the electronic field gradient around an atom. While there are numerous Mössbauer active atoms, only elements with a suitable gamma ray source (long-lived and low-lying excited nuclear energy state) can take advantage of this technique. The most commonly studied atom using the technique is ^{57}Fe , which is used to characterize inorganic/organometallic molecular species, bioinorganic molecules, and minerals. For example, Mössbauer spectroscopy has been used extensively to study iron-sulfur (Fe/S) clusters found in metalloproteins.³ Fe/S clusters are involved in a variety of functions, ranging from electron transport to catalysis. ^{57}Fe Mössbauer spectroscopy has helped elucidate valuable information about Fe/S clusters in proteins, including, but not limited to, the number of unique iron centers present in a Fe/S cluster as well as the oxidation state and spin state of those irons. ~~While technically any atom can be studied using Mössbauer spectroscopy, o~~

~~Atoms that are suitable for Mössbauer spectroscopy. Additionally, only elements with a suitable gamma ray source (long-lived and low-lying excited nuclear energy state) can take advantage of this technique.~~

Legend

Figure 1. General instrumentation setup.

Figure 2. A typical Mössbauer spectrum is plotted with velocity (energy) along the x axis and % transmission along the y axis. Here we see a single quadrupole doublet, with isomer shift, δ , and quadrupole splitting, ΔE_Q .

Figure 23. Observable nuclear interactions in a ^{57}Fe Mössbauer spectrum including isomer shift, quadrupole splitting, and hyperfine splitting in the presence of a magnetic field.

¹ Brent Fultz, "Mössbauer Spectrometry", in *Characterization of Materials*. Elton Kaufmann, Editor (John Wiley, New York, 2011).

² Brent Fultz, "Mössbauer Spectrometry", in *Characterization of Materials*. Elton Kaufmann, Editor (John Wiley, New York, 2011).

³ Pandelia, M.-E.; Lanz, N.; Booker, S.; Krebs, C. Mössbauer spectroscopy of Fe/S proteins *Biochim. Biophys. Acta* **2015**, *1853*, 1395–1405.

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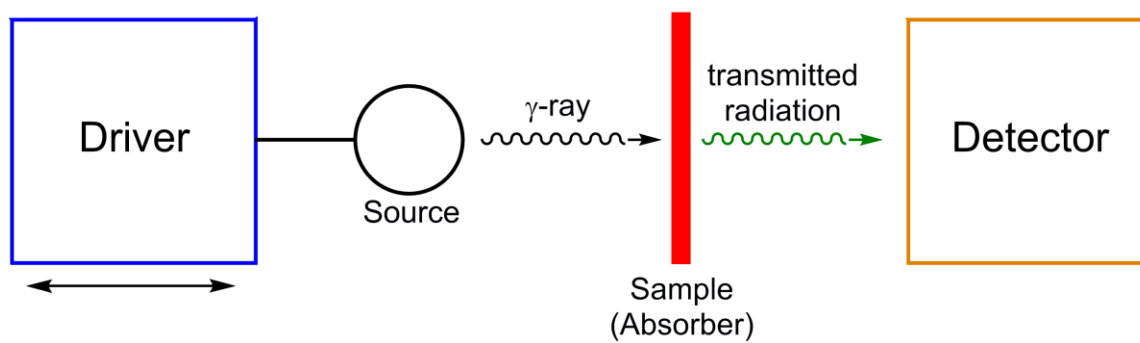


Figure 1.

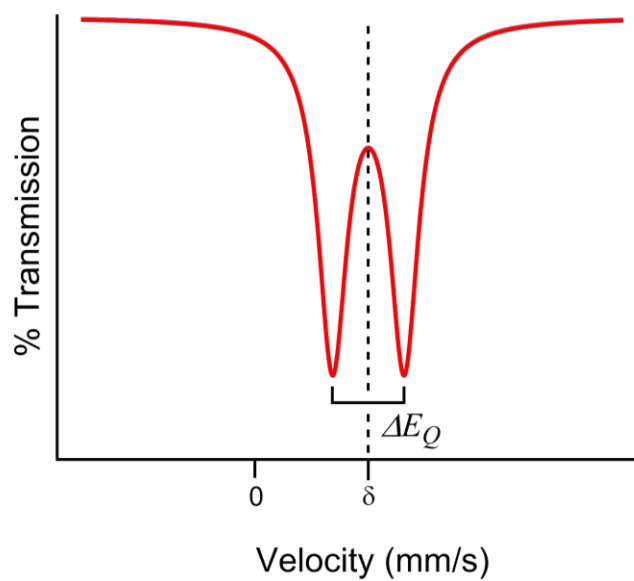


Figure 2.

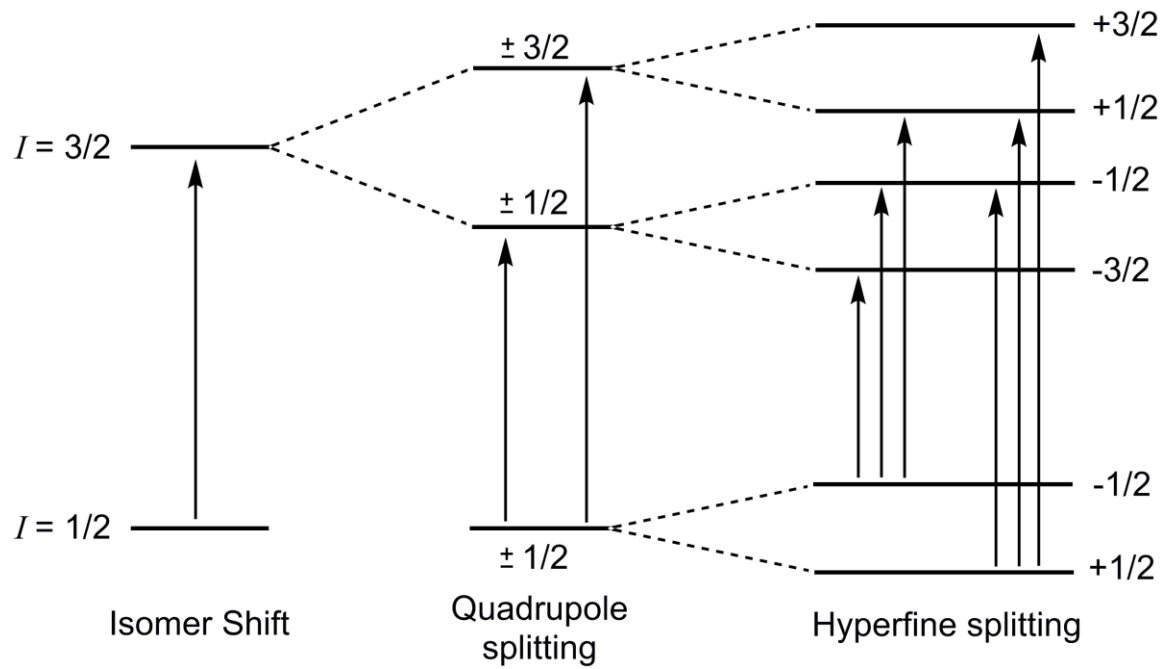


Figure 3.