Mössbauer Spectroscopy

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Rudolf Ludwig Mössbauer, born in 1929, is a German physicist who first investigated the recoil-less nuclear absorption of gamma ray photons from 1955 to 1958. He won the Nobel Prize in 1961.

All regions of the electromagnetic spectrum can be used in some spectroscopic technique, even the very high-energy region called *gamma radiation.* For starters, let us remind ourselves of the characteristics of gamma radiation. Although limits vary, gamma radiation is the part of the spectrum whose wavelengths are less than 1×10^{-9} m (< 10 Å) and whose frequencies are greater than 10^{17} s^{-1}. Energies of individual photons are greater than 6×10^{-17} J, which may be small to us but is large at the atomic and molecular level — it's enough energy to break almost 100 C-H chemical bonds! At such energies, the electron volt (eV) unit is useful. One eV equals 1.602×10^{-19} J, so gamma ray photons have energies of about 400 eV and higher, even in the kiloelectron volt (keV) or megaelectron volt (MeV) ranges. Gamma rays are usually emitted by atomic nuclei undergoing radioactive decay. Why can't we use these gamma rays to do nuclear spectroscopy?

We can. Recall that nuclei have a net spin indicated by the quantum number I, just like electrons have spin indicated by the quantum number S. Just as electrons have $2S + 1$ orientations of spin (referred to as m_S and with values of $+\frac{1}{2}$ and $-\frac{1}{2}$), there are $2I + 1$ orientations of nuclear spin that have different energies. A nucleus in the ground spin state can absorb energy from a photon and go to an excited spin state. *Voilà* — spectroscopy!

The potential problem is that it's rather difficult to find and control a broadband source of gamma radiation. It's easy to generate broadband UV or visible or infrared light, pass it through a monochromator or interferometer, then through a sample, and then to a detector — which is how classic spectroscopy is typically done. Most matter is relatively transparent to gamma radiation, so it's difficult to manipulate with lenses and mirrors.

A different tactic is used for gamma rays. Under certain circumstances, nuclei in excited states can be produced. These nuclei will de-excite and, in the process, give off a gamma ray photon. In doing so, these nuclei will be acting as the source, and the gamma rays given off can be used to probe nuclei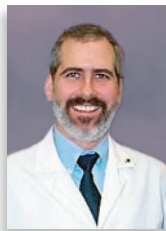 of the same isotope (which will have the same energy levels and should absorb that particular emitted photon). There is one potential problem with this: nuclear recoil. Because photons have momentum, as a gamma ray photon is emitted in one direction, the nucleus recoils in the opposite direction, and the energy of the photon is not equal to the energy difference between the excited and ground states; it is slightly less:

$$E \text{ (photon)} = \Delta E - R$$

where ΔE is the difference in the nuclear energy levels and R is the recoil energy of the nucleus. The energy of the emitted photon may not be the correct energy to be absorbed by the second nucleus.

And then there's the problem of creating the initial excited nucleus in the first place. How do we do that?

Let's focus on the second thing first. A source nucleus is the daughter isotope of some nuclear decay process. For example, ^{57}Co decays via electron capture to ^{57}Fe with a half-life of 270 days. The ^{57}Fe atom produced has its nucleus in an excited state (in which $I = \frac{5}{2}$) that quickly decays to the $I = \frac{3}{2}$ spin state. This state is rather long-lived ($\sim 10^{-7}$ s), but does eventually decay to the lowest-
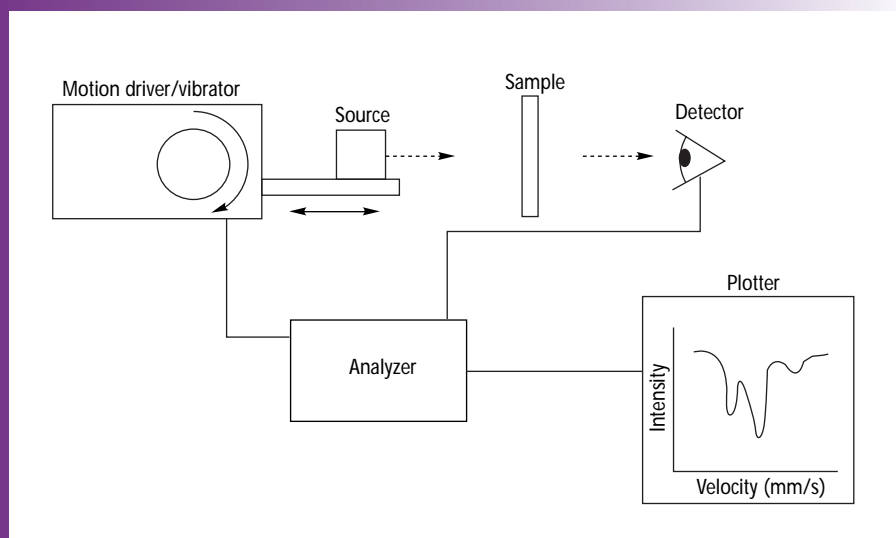
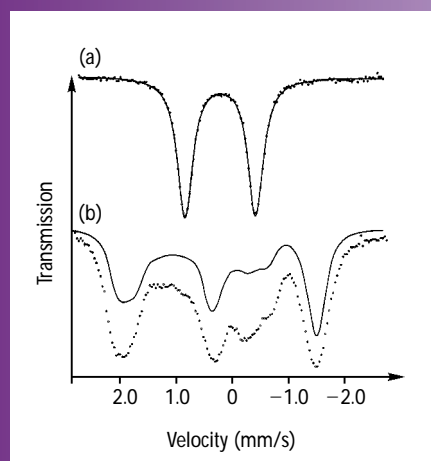**Figure 1.** Diagram of a simple Mössbauer spectrometer.

Figure 2. Mössbauer spectra of (Et$_4$N) [Fe$_4$S$_4$(SCH$_2$Ph)$_4$]. (a) No magnetic field, $T = 1.5$ K. (b) Magnetic field = 8 tesla, $T = 4.7$ K. (Reprinted with permission from reference 1. Copyright by the American Chemical Society.)

energy $I = \frac{1}{2}$ spin state. As a consequence of the rather long lifetime of the $I = \frac{3}{2}$ state, however, the linewidth of the final gamma ray emission — which has an energy of about 14.4 keV — is very narrow: about 5×10^{-9} eV, more than 12 orders of magnitude smaller than the absolute energy. This very narrow emission can be a very effective probe for other iron atoms.

We still have the problem of recoil, however. Recoil will shift the energy of the emitted gamma ray photon out of range of resonance with other iron nuclei (which is required for absorption to occur). There are two ways to minimize recoil, however. The first is to use a solid sample, obviously. The second is to cool the sample down to low temperatures (that is, cryogenic temperatures; typically, using liquid helium) so that the individual atoms cannot recoil. At low enough temperatures, the quantized vibrations of the crystal lattice require that recoil energy be distributed throughout the entire lattice, not just the nucleus emitting the photon. Thus, there are ways of maximizing recoilless emission of gamma ray photons.

Now that we have a source of photons relatively unaffected by recoil, are we ready to have them absorbed by a sample? Yes, but the sample may not actually absorb. That's because the nuclear energy levels are very slightly affected by the electronic environment. The distribution of energies of the emitted photons is very small, recall — 5×10^{-9} eV. Even tiny differences in chemical environment are enough to shift the second nucleus's energy levels out of resonance. This is referred to as the *isomer shift* (also called *chemical shift*).

However, nuclear energy levels are not strongly affected by the outer environment — only as a consequence of the extremely narrow linewidth of the emitted gamma rays are the nuclear energy levels out of resonance. They can be brought back into resonance very easily, by inducing a red or blue shift between the emitter and potential absorber. Recall that photons, like sound, experience a Doppler shift if the source and receiver are moving with respect to each other, the amount of the shift being predicted by relativity. Therefore, by moving the emitting nucleus and the target nucleus back and forth with respect to each other, at some velocity the gamma ray photon will have the same energy as the energy difference in the absorbing nucleus and will be absorbed. A plot of gamma ray photon intensity versus velocity results in a spectrum. This constitutes Mössbauer spectroscopy. Because of the narrow linewidth of the source photons, different chemical environments of iron atoms can be discerned, allowing an experimenter to discriminate between different oxidation states and bonding arrangements in unknown samples. The back-and-forth velocities involved aren't very large: several millimeters per second is sufficient.

As you can guess by the description of the process, Mössbauer spectra aren't possible for all nuclei. The emitted gamma ray photon should be relatively low in energy, so recoil affects are not large to begin with. Not all gamma ray emissions are so narrow in linewidth — nuclei can absorb these photons, but any ability to discriminate between chemical environments is lost. The nucleus must also have a fairly large cross section for absorption to maximize the signal-to-noise ratio. Common nuclei used are ^{57}Fe, ^{119}Sn, and ^{191}Ir, with the iron isotope being the most popular (understandably). Figure 1 shows a diagram of a typical Mössbauer spectrometer.

Because magnetic fields split the $2I + 1$ degeneracy of spin states, magnetic Mössbauer spectra show additional details, as does the presence of quadrupole interactions (that is, the presence of nonsymmetric electric fields). Figure 2 shows Mössbauer and magnetic Mössbauer spectra of an iron–sulfur cluster. The extremes of the x-axis are less than 3 mm/s — it doesn't take much of a Doppler shift to bring the

iron nuclei back into resonance with the emitted gamma ray photons.

Interested readers are directed to the "Suggested Reading" section for more detailed information about this fascinating form of spectroscopy.

Reference

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Suggested Reading

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