

Interpretative Spectroscopy
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Lecture 49
Introduction to Mössbauer Spectroscopy

Hello everyone, I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. Today, let us look into briefly about Mössbauer Spectroscopy. So, let me begin with some background to Mössbauer Spectroscopy. Wide variety of chemical problems associated with synthesis, characterization and elucidation of structure involve a spectroscopic study, intense spectroscopic study to accumulate evidences in support of molecules that are generated in the laboratory. That means, basically when we make a molecule, to know whether we have made the same molecule, we anticipated or something else we got, or some byproducts and all those things to understand in a proper way, we involve spectroscopic studies. In most of the spectroscopic studies, what we do is, we observe lines or bands as we see in case of IR, UV visible, NMR, ESR and mass spectrometry which involve some sort of excitation or transitions and absorptions or emission of appropriate energy taken from the electromagnetic radiation or involving electromagnetic radiation of different wavelength and different frequency depending upon the energy required for such transitions.

For this purpose, a quantum source with a broad or nearly flat response over a range of energies, a global or incandescent light were used earlier or by scanning a wide range of energies through a continuously variable window, varying magnetic or electric fields in case of NMR, ESR or mass spectrometry. So, only in fluorescence, fluorescence resonance spectroscopy I am referring to a narrow band of energies emitted by a quantum source exactly matches the transition energy in an absorber material. Because of the considerable success resonance spectroscopy achieved in optics and atomic physics, a number of attempts were made by scientists soon after the discovery of gamma -radiation to extend its utility in fluorescence spectroscopy to nuclear transitions. Most of these early

experiments either were inconclusive or led to resonance absorptions which were so small and questionable.

The reason for these failures was mainly the line width of the transition as compared to the recoil energy suffered by the source and the absorber as a result of the transition. The width Γ of a spectral line emitted by a source is related to the mean lifetime τ of the excited state from which the transition to the ground state originates by the uncertainty principle, $\Gamma\tau = h$

That means this one will be equal to 6.58×10^{-16} over τ (6.58 x 10⁻¹⁶/τ) in seconds electron volts. In optical transitions, where τ equal to 10 raised to minus 10 ($\tau = 10^{-10}$) seconds or τ is approximately equal to 7 into 10 raised to minus 6 ($\tau = 7 \times 10^{-6}$) electron volts.

In the case of fluorescence excitation τ may be several seconds in which case Γ is less than 10^{-16} (10⁻¹⁶) electron volts. When a nucleus undergoes a transition from state E_e to the excited state to the E_g ground state by the emission of a photon, the conservation of momentum requires that the momentum of the atom p_M , recoiling in one direction is just equal and opposite to the momentum of the photon p_γ emitted in the opposite direction. The kinetic energy of the recoiling atom is E_R , so, that for an atom of mass M and velocity

$$E_R = \frac{1}{2} Mv^2 = \frac{p_M^2}{2M}$$

Moreover, the momentum of a photon of zero rest mass is related to the energy by

$$E = p_\gamma c$$

so that

$$p_\gamma^2 = \frac{E_\gamma^2}{c^2}$$

Since the two momenta must be equal, it follows that

$$E_R = \frac{E_\gamma^2}{2Mc^2}$$

Mössbauer spectroscopy is a versatile technique used to study nuclear structure with absorption and re-emission of gamma rays, a part of the electromagnetic spectrum.

The technique uses a combination of Mössbauer effect and Doppler effect or Doppler shift to probe the hyperfine transition between the excited and ground states of the nucleus. Mössbauer spectroscopy requires the use of solids or crystals which have a probability to absorb the photon in a recoilless manner. Many isotopes exhibit Mössbauer characteristics, but the most commonly studied isotope is ^{57}Fe .

Mössbauer spectroscopy is named after Rudolf L. Mössbauer. Mössbauer obtained a bachelors in physics from the Technical University of Munich, Germany and started doctoral work in 1955. Meanwhile he was working as an assistant lecturer in the institute for mathematics and in 1958 he obtained his doctoral degree and during that time he showed experimental evidence for recoilless resonance absorption in the nucleus which became popularly known as Mössbauer effect. In 1961 Mössbauer was awarded the Nobel prize in physics and he became the professor of physics at California institute of technology.

This is a typical Mössbauer spectrum which shows gamma energy is emitted. This is recoilless emission and this is resonance absorption and this is gamma radiation. It is the ground state and this is the excited state of nucleus.

The recoil energy associated with absorption or emission of a photon can be described by the conservation of momentum.

$$P_R = P_\gamma$$
$$P_R^2 = P_\gamma^2$$
$$2ME_R = \frac{E_\gamma^2}{c^2}$$
$$E_R = \frac{E_\gamma^2}{2Mc^2}$$

The recoil energy is inversely related to the mass of the system. For a gas, the mass of the single nucleus is small compared to a solid. The solid or crystal absorbs the energy as

phonons, quantized vibration states of the solid, but there is a probability that no phonons are created and the whole lattice acts as the mass, resulting in a recoilless emission of gamma ray.

The new radiation is at proper energy to excite the next ground state nucleus. The probability of recoilless events increases with decreasing transition energy.

Now, what is the Doppler effect? Doppler shift describes the change in frequency due to a moving source and a moving observer.

For example, it is given here

$$f = \left(\frac{v + v_r}{v + v_s} \right) f_0$$

$$f = \left(\frac{c}{c + c_s} \right) f_0$$

The Doppler shift describes the change in frequency due to a moving source and a moving observer.

f is the frequency measured at the observer,

v is the velocity of the wave in this case

C is the speed of light

v_r is the velocity of the observer,

v_s is the velocity of the source which is positive when

heading away from the observer, and f_0 is the initial frequency.

In case where the source is moving towards the stationary observer the perceived In the case where the source is moving towards a stationary observer the perceived frequency is higher. For the opposite situation where the source travels away from the observer frequencies recorded at the observer will be of lower compared to the initial wave. The energy of a photon is related to the product of Planck's constant and the frequency of the electromagnetic radiation. Thus, for increasing frequencies the corresponding energy also

increase, and the same is true in the reverse case where frequencies decrease and therefore energy decreases.

$$E_R = \frac{hc}{\lambda} = h\nu$$

This is the equation. Of course, generally we use all energy calculations between the ground state and the excited state.

The energy differences between the hyperfine states are minimal and the energy variation is achieved by moving the source towards and away from the sample in an oscillating manner, at a velocity of a few millimeters per second. The transmittance is then plotted against the velocity of the source and a peak is seen at the energy corresponding to the resonance energy.

The most common isotopes studied using Mössbauer spectroscopy is ^{57}Fe , but many other isotopes also have displayed Mössbauer spectrum. Two criteria should be satisfied i) The excited state is of very low energy resulting in a small change in energy between ground and excited states. This is because gamma rays at higher energy are not absorbed in a recoil free manner, meaning resonance only occurs for gamma rays of low energy. The resolution of mass spectroscopy depends upon the lifetime of the excited state. Longer the excited state last, the better the image.

Both the conditions are met by ^{57}Fe that is the reason it is very popular, well studied and used extensively in Mössbauer spectroscopy.

Is it possible to do similar studies with other elements in the periodic table? Yes, there are quite a few elements we can study using Mössbauer techniques. Elements marked in red color can be used for Mössbauer spectroscopy.

Let us discuss about the hyperfine interactions in Mössbauer spectroscopy. Mössbauer spectroscopy as a probe that gives insight into the structural elements of the nucleus such

as isomer shift, quadrupole interactions and magnetic splitting. Mössbauer spectra are capable of revealing all these effects.

What is isomer shift? An isomeric shift occurs when nonidentical atoms play the role of source and absorber, thus the radius of the source, is different that of the absorber, and the same holds that the electron density of each species is different. The Coulombic interactions affects the ground and excited state differently leading to a energy difference that is not the same for the two species. This is best illustrated with the equation shown below:

$$\delta = E_A - E_S = \frac{2}{3} nZe^2(\rho_A - \rho_S)(R_{cs}^2 - R_{gs}^2)$$

Delta is the change in energy necessary to excite the absorber, which is seen as a shift from the Doppler speed 0 to V_1 . The isomer shift depends directly on the s-electrons as they are very close to the nucleus, and can be influenced by shielding of *p* *d* and *f* electrons. From the measured delta shift there is information about the valence state of the absorbing atom. The energy level diagram per shift shows the change in the source velocity due to different sources used here. The shift may be either positive or it can be negative.

Now let us look into quadrupole interaction. The Hamiltonian for quadrupole interaction using again ^{57}Fe nuclear excited state is given in this equation, you can see here.

$$H_Q = \frac{eQV_{zz}}{12} [3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)]$$

The nuclear excited states are split into two degenerated doublets in the absence of magnetic interactions. For the asymmetry parameter, doublets are labeled with magnetic quantum numbers; with doublet having higher energy. The energy difference between the doublets is given by this equation here.

$$\Delta EQ = \frac{eQV_{zz}}{2} \sqrt{1 + \frac{\eta^2}{3}}$$

The energy diagram corresponding spectrum is also shown here. This is the energy diagram. First you can see here, isomer shift is there and then quadrupole splitting is there. You can see two lines, one is here, one is here, and one is positive, one is negative. The magnetic splitting is seen in Mössbauer spectroscopy is due to the nuclear spin moment undergoing dipolar interactions with a magnetic field

$$E(m_I) = -g_n \beta_n B_{\text{eff}} m_I$$

g_n = nuclear g-factor

β_n = nuclear magneton.

In the absence of quadrupole interactions, the Hamiltonian splits into equally spaced energy levels

.

On either side you can see, for example, a typical ground state to excited state I equal to 3 by 2 (3/2) again ^{57}Fe , this is isomer shift and then you can see here this is split into minus half (-1/2) and plus half (+1/2), and then here 3 by 2 (3/2) is split into 3 by 2 (3/2), half (1/2), minus half (-1/2) and minus 3 by 2 (-3/2). As a result, we see 6 transitions and you can see they are equally spaced from here 0 3 and 3 here symmetrically.

The allowed gamma stimulated transitions of nuclear excitation follows the magnetic dipolar transition selection rule: $\Delta I = \underline{\pm 1}$ and $\Delta m_I = \underline{0, \pm 1}$.

I = magnetic quantum number and the direction of β defines the nuclear quantization axis. If we assume g and A are isotropic where $g_x = g_y = g_z$ and B is actually a combination of the applied and internal magnetic fields.

Then this equation will be $H = g\beta S \cdot B + AS \cdot I - g_n \beta_n B \cdot I$

The electronic Zeeman term is far larger than the nuclear Zeeman term, meaning the electronic term dominates the equation. So, S is approximately calculated in this fashion will be equal to

$$(S_z) = m_s = \pm 1/2 \quad \text{and} \quad (S_x) = (S_y) \approx 0$$

$$H_n = A(S) \cdot I - g_n \beta_n B \cdot I$$

$$(S_z) = m_s = \pm 1/2 \quad \text{and} \quad (S_x) = (S_y) \approx 0$$

$$H_n = A(S) \cdot I - g_n \beta_n B \cdot I$$

Removing $-g_n \beta_n B$ followed by I leaves

$$H_n = -g_n \beta_n \left(-\frac{A(S)}{g_n \beta_n} + B \right) I$$

Substituting the internal magnetic field with $B_{int} = -\frac{A(S)}{g_n \beta_n}$

results in a combined magnetic field term involving both the applied magnetic field and the internal magnetic field

$$H_n = -g_n \beta_n (B_{int} + B) I$$

which is simplified by using the effective magnetic field B_{eff} .

$$H_n = -g_n \beta_n B_{eff} \cdot I$$

Now, a different form of molecular excitation is that of changes in the energies of the atomic nuclei. In general, enormous energies are involved and such excitations will not be of interest to the study of organic molecules unless the atomic energy levels are detectably influenced by the chemical surroundings of the nuclei.

Usually this is not so, but there is one form of nuclear spectroscopy, known as Mössbauer spectroscopy which is capable of giving chemical information. The technique would be used widely if there are more nuclei with the proper nuclear properties. For organic chemistry probably the most important available nucleus is the iron nuclide and in many biological systems we have ^{57}Fe which constitute 2.2 percent of the natural mixture of iron isotopes.

Iron occurs in many biologically important substances, such as hemoglobin, myoglobin, cytochromes, the iron storage substance ferritin, and so on, and there are a number of other types of stable organoiron compounds including ferrocene, cyclobutadiene iron tricarbonyl, and cyclooctatetraene iron tricarbonyl.

These compounds present unusually difficult problems in how to formulate the bonding between carbon and iron, but important information has been obtained for substances by Mössbauer spectroscopy.

The essence of the Mössbauer technique as applied to Fe^{57} follows. A radioactive Co^{57} nucleus captures an electron and is converted to an excited Fe^{57} nucleus, which then emits a γ ray and becomes an ordinary Fe^{57} nucleus.

If the excited Fe^{57} nucleus is in a rigid material so that there is no recoil motion associated with the emission of the γ ray, then this ray is extraordinarily monochromatic (has a very small $\Delta\nu$) even though of great energy ($14.4 \text{ KeV} = 3.3 \times 10^5 \text{ kcal mol}^{-1}$).

When such a γ ray passes through a sample containing Fe^{57} atoms (also held rigidly), the γ ray can be absorbed to produce another excited Fe^{57} nucleus.

The chemical environment of the iron atoms can change the wavelength at which this absorption occurs.

The problem is how to vary the wavelength of the γ rays to match the nuclear absorption frequency. The way this is done is almost unbelievably simple - move the sample back and forth a few mm sec^{-1} in the path of the γ rays and measure the velocities at which absorption takes place.

The velocity of light is $3 \times 10^{11} \text{ mm sec}^{-1}$.

Therefore, a Doppler effect of 1 mm sec^{-1} corresponds to a difference of only one part in 3×10^{11} .

However, the selectivity of the recoilless γ rays emitted from excited Fe^{57} nuclei is on the order of one part in 5×10^{13} (equivalent to about a 7-cm variation in the distance from the earth to the sun!).

A Mössbauer spectrum that has helped to corroborate the structure of cyclooctatetraene iron tricarbonyl is shown here

The separation of the two absorption peaks corresponds to a sample Doppler velocity of 1.23 mm sec^{-1} .

This Doppler effect means that there is the very small energy difference of $1.4 \times 10^{-6} \text{ kcal mol}^{-1}$ in the two transitions shown.

So, this is a typical Mössbauer spectrum of cyclooctatetraene tricarbonyl complex.

For example, among the following those can act as Mössbauer nuclei are ^{129}I , ^{57}Co , ^{57}Fe and ^{121}Sb . In these cases, also, Mössbauer spectroscopy can be used as a tool to understand their nuclei structures. So, let me stop here. Thank you.