

**Interpretative Spectroscopy**  
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**Lecture 50**

**More discussion, problems, and solutions (Mös)**

I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. So, let us continue discussion on Mössbauer spectroscopy today. Of course, you all know what is Mössbauer effect. Mössbauer effect is the emission and resonant absorption of nuclear  $\gamma$  rays under conditions such that the nuclei have negligible recoiling velocities when  $\gamma$ -rays are emitted or absorbed. This is only achieved by working with solid samples in which the nuclei are held rigidly in a crystal lattice. The energy and the frequency of the  $\gamma$ -radiation involved corresponds to the transition between the ground state and the short lived excited state of the nuclei concerned.

So, we saw nuclear transitions, spin transitions, spin flipping in case of NMR, electron transition in case of UV visible and electron spin excitation in case of EPR. Now, we are looking into nuclear transitions in case of Mössbauer.

Properties of selected nuclei which can be observed or studied using Mössbauer spectroscopy are shown here:  $^{57}\text{Fe}$ ,  $^{119}\text{Sn}$ ,  $^{99}\text{Ru}$ ,  $^{197}\text{Au}$  and their natural abundance, ground and excited spin state and radioisotope source are included in the list here

Radio isotope source we use in case of  $^{57}\text{Fe}$  is  $^{57}\text{Co}$  in case of tin is meta stable  $^{199}\text{Sn}$ ,  $^{99}\text{Rh}$  in case of  $^{99}\text{Ru}$  and then in case of  $^{197}\text{Au}$  it is  $^{197}\text{Pt}$ .

$^{57}\text{Fe}$  Mössbauer spectroscopy illustrates very nicely the Mössbauer effect.

Basic apparatus consists of a radioactive source, a solid absorber with the  $^{57}\text{Fe}$  containing sample and a  $\gamma$ -ray detector.

For  $^{57}\text{Fe}$  samples, the radioactive source is  $^{57}\text{Co}$  which is incorporated into stainless steel; the  $^{57}\text{Co}$  source decays by capture of an extra-nuclear electron to give the excited state of  $^{57}\text{Fe}$  which emits  $\gamma$ -radiation as it decays to its ground state.

If  $^{57}\text{Fe}$  is present in the same form in both source and absorber, resonant absorption occurs and no radiation is transmitted.

However, if the  $^{57}\text{Fe}$  in the source and the absorber is present in two different forms, absorption does not occur and  $\gamma$ -radiation reaches the detector.

Moving the source at different velocities towards or away from the  $^{57}\text{Fe}$  absorber has the effect of varying the energy of the  $\gamma$ -radiation (i.e. by the Doppler effect).

The velocity of movement required to bring about maximum absorption relative to stainless steel (defined as an arbitrary zero for iron) is called the isomer shift of  $^{57}\text{Fe}$  in the sample, with units of  $\text{mm s}^{-1}$ .

The time scale for Mössbauer spectroscopy is  $10^{-18}$  s

### **What structural information one can get from isomer shift data?**

The isomer shift gives a measure of the electron density on the  $^{57}\text{Fe}$  center, and isomer shift values can be used to determine the oxidation state of the Fe atom. Similarly, in  $^{197}\text{Au}$  Mössbauer spectroscopy, isomer shifts can be used to distinguish between  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}$ . Three specific examples are chosen here from iron chemistry.

1. In the cation  $[\text{Fe}(\text{NH}_3)_5(\text{NO})]^{2+}$  there is an ambiguity in describing the bonding, since in some instances, it has been described  $[\text{NO}]^+$  bound to an  $\text{Fe}^{\text{I}}$  centre. Results of  $^{57}\text{Fe}$  Mössbauer spectroscopy have revealed that the correct description is that of an  $[\text{NO}]^-$  ligand bound to an  $\text{Fe}^{\text{III}}$  center.

The iron centers in  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  are in +2 and +3 states; however, the closeness of the isomer shifts for these species suggests that the actual oxidation states are similar and this may be interpreted in terms of the extra electron in  $[\text{Fe}(\text{CN})_6]^{4-}$  being delocalized on the cyano ligands rather than the iron centre.

3. Differences in isomer shifts can be used to distinguish between different iron environments in the same molecule: the existence of two signals in the **Mössbauer** spectrum of  $\text{Fe}_3(\text{CO})_{12}$  provided the first evidence for the presence of two types of iron atoms in the solid-state structure as confirmed by X-ray diffraction methods.

So, this we should remember. Two iron atoms here have two bridging carbonyls, and the one on the top of this triangular planar geometry do not have any bridging. So, that means strictly speaking there are two types of iron centers. This can be distinguished, no doubt from x ray crystallography, but **Mössbauer** spectroscopy also shows two signals in 2 to 1 (2:1) ratio suggesting that there are two different types of iron environments in the molecule of  $\text{Fe}_3(\text{CO})_{12}$ .

This will show you the region of electromagnetic radiation that is used in **Mössbauer** spectroscopy, we use gamma rays. Then this is a typical layout of a **Mössbauer** spectrometer. Here the cobalt source is there as I mentioned  $^{57}\text{Co}$  is considered. The speed of the carriage is adjusted until the Doppler-shifted frequency of the emitted gamma ray matches the corresponding nuclear transition in the sample.

The inset shows the nuclear transition responsible for the emission of the gamma-ray.

The effect of an electric field gradient and a magnetic field on the energy levels involved in the **Mössbauer** technique for iron sample is shown here. The derived spectra shown depicts the origin of the isomer shift, quadrupole coupling and magnetic hyperfine coupling, but no quadrupole splitting.

The spectrum of (ii)  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ , octahedral low spin  $d^6$ , is representative of a highly symmetric environment and shows a single peak with an isomer shift.

The spectrum of (iii)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $d^6$  in a nonsymmetric environment, shows quadrupolar splitting.

Here is a question: The isomer shifts of  $\text{Fe}^{\text{II}}$  compounds relative to metallic iron,  $\text{Fe}^0$ , are generally in the range 1 to 1.5  $\text{mm s}^{-1}$ , whereas isomer shifts for  $\text{Fe}^{\text{III}}$  compounds lie in the

range 0.2 to 0.5 mm s<sup>-1</sup>. Explain these values in terms of the electronic configurations of Fe<sup>0</sup>, Fe<sup>II</sup> and Fe<sup>III</sup>.

The outermost electron configurations of Fe<sup>0</sup>, Fe<sup>II</sup> and Fe<sup>III</sup> are 4s<sup>2</sup>3d<sup>6</sup>, 3d<sup>6</sup>, and 3d<sup>5</sup>, respectively. The *s*-electron density at the nucleus is reduced in Fe<sup>II</sup> compared with Fe<sup>0</sup>, producing a large positive isomer shift.

When a 3d electron is removed to produce Fe<sup>III</sup> from Fe<sup>II</sup> there is a small increase in *s*-electron density at the nucleus (as the 3d electrons partly screen the nucleus from the inner *s* electrons) and the isomer shift becomes less positive.

Q2. Variable temperature <sup>57</sup>Fe Mössbauer spectra for [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>] are shown below. Using the data such as isomer shift, quadrupole splitting data provided in the 300K and 77K spectra and the magnetic susceptibility data, explain the VT behaviour.

Two NCS thiocyanate and two phenanthroline bidentate ligands are there and iron is in octahedral geometry. <sup>57</sup>Fe Mössbauer spectra shown here. Variable temperature starting from 77 k to 300 k. Using the data such as isomer shift a quadrupole splitting data provided in the 300 k and 77 k spectra and the magnetic susceptibility data explain the variable temperature behavior is the question.

So now, <sup>57</sup>Fe Mössbauer spectra indicate the significant changes in the iron environment with temperature

<sup>57</sup>Fe Mössbauer spectra indicate the significant changes in the iron environment at ~185 K in the given complex.

The magnetic data indicate high-spin nature of the complex at RT and low-spin at low temperature.

It is d<sup>6</sup> system showing spin-crossover. Isomer shift and quadrupole splitting parameters for the high-spin and low-spin isomers.

Another question here

$^{57}\text{Fe}$  Mössbauer spectra for  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  octahedral spin-crossover complexes recorded at different temperatures are given below. Determine the isomer shift and quadrupole splitting for each spectrum, and use these to assign the spectra to the iron oxidation state and spin state.  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ .

$^{57}\text{Fe}$  Mössbauer spectroscopy is a very powerful way of identifying the oxidation and spin states of iron complexes

So, here  $^{57}\text{Fe}$  Mössbauer spectroscopy is again a powerful way of identifying the oxidation and spin states of iron complexes that we saw in case of iron 0 iron 2 iron 3 complexes.

If you just look into the data given for  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  octahedral spin-cross over complexes, the isomer shift is expected to move to more negative values as the access state changes from iron 2 to iron 3.

The isomer shift is expected to move to more negative values as the oxidation state changes from  $\text{Fe}^{\text{II}}$  to  $\text{Fe}^{\text{III}}$ .

However, apart from the  $0.85 \text{ mm s}^{-1}$  value for the 383 K, the other values are reasonably similar and indicate that the left hand spectra are probably from  $\text{Fe}^{\text{II}}$  complexes, the  $\delta$  values alone are not always sufficiently diagnostic. Octahedral high-spin  $\text{Fe}^{\text{II}}$  has a  $^5\text{T}_{2\text{g}}$  ground term, low-spin  $\text{Fe}^{\text{II}}$  has a  $^1\text{A}_{1\text{g}}$  ground term, high-spin  $\text{Fe}^{\text{III}}$  has a  $^6\text{A}_{1\text{g}}$  ground term and low-spin  $\text{Fe}^{\text{III}}$  has a  $^2\text{T}_{2\text{g}}$  ground term.

Therefore, electronically induced EFGs are predicted for high-spin  $\text{Fe}^{\text{II}}$  and low-spin  $\text{Fe}^{\text{III}}$ . As significant  $\Delta E_{\text{Q}}$  values are observed at high-temperature in the left-hand spectra and at low-temperature for the right-hand spectra, this confirms that the left-hand spectra are from an  $\text{Fe}^{\text{II}}$  complex, and the right-hand spectra from an  $\text{Fe}^{\text{III}}$  complex.

### Another Question

The  $^{57}\text{Fe}$  **Mössbauer** spectra and structures of some iron carbonyls are shown here. Assign the spectra to the correct structure.

Spectra are given here and also some structures are given. We have to assign the spectra to the corresponding structures.

The isomer shift,  $\delta$ , for each spectrum is close to zero, and does not vary much between the three carbonyl compounds as all have  $\text{Fe}^0$ . However, there are marked differences in the quadrupole splitting,  $\Delta E_Q$ , observed in the three spectra, and this is related to the different **electric field gradient** (EFGs) at the iron nucleus. In this case, the greatest contribution to the EFG comes from structural/geometric effects, rather than electronic ones

In  $[\text{Fe}(\text{CO})_5]$  with Fe is in TBP environment, and the electric field has axial symmetry, which is different in the  $z$  direction, compared to that in the  $x$  and  $y$  directions, which are the same.

Therefore, there will be an appreciable EFG, and hence  $\Delta E_Q$ , observed in the spectrum of  $[\text{Fe}(\text{CO})_5]$ . In  $[\text{Fe}_2(\text{CO})_9]$  there are two equivalent iron atoms so there will be one multiplet.

As each is in an approximately octahedral configuration, the EFG and  $\Delta E_Q$  will be smaller than in  $[\text{Fe}(\text{CO})_5]$ .

In  $[\text{Fe}_3(\text{CO})_{12}]$ , there are two different iron environments, so two multiplets are expected, one from the iron at the top of the triangle, and one from the bottom of the triangle, and as these are in a 1:2 ratio, this will be reflected in the peak intensities.

The iron on TOP is in a more symmetric and almost regular octahedral environment, with no bridging carbonyl ligands, whereas the two iron atoms at the bottom have a mix of both terminal and bridging carbonyls. On this basis a widely spaced quadrupole doublet with twice the intensity of a narrowly spaced quadrupole doublet is expected. Spectrum (a) with a large  $\Delta E_Q$  is assigned to  $[\text{Fe}(\text{CO})_5]$ , spectrum (b) with a small  $\Delta E_Q$  is assigned to  $[\text{Fe}_2(\text{CO})_9]$ , and spectrum(c) with two multiplets is assigned to  $[\text{Fe}_3(\text{CO})_{12}]$ .

<sup>57</sup>Fe Mössbauer experiments were the first to identify the structure of  $\text{Fe}_3(\text{CO})_{12}$ .

So, now one more question here

2-Acetylpyridinethiosemicarbazone can act as a tridentate ligand either in its neutral thione state (HATP), or after deprotonation of the thiol tautomer to give ATP<sup>-</sup>. This forms complexes, [Fe<sup>II</sup>(HAPT)<sub>2</sub>]Cl<sub>2</sub>, and [Fe<sup>III</sup>(APT)(HAPT)]Cl<sub>2</sub>. Use the isomer shift and quadrupole splitting data in the <sup>57</sup>Fe Mössbauer spectra shown to identify the oxidation states and spin states and hence assign the spectra to the [Fe(HAPT)<sub>2</sub>]Cl<sub>2</sub> and [Fe(APT)(HAPT)]Cl<sub>2</sub> complexes.

For <sup>57</sup>Fe Mössbauer spectra the isomer shift is expected to be at lower values for Fe<sup>III</sup> than Fe<sup>II</sup>. On this basis, the spectrum (a) is assigned to Fe<sup>III</sup> with  $\delta = 0.065 \text{ mm s}^{-1}$  and spectrum (b) with  $\delta = 0.264 \text{ mm s}^{-1}$  to Fe<sup>II</sup>.

The quadrupole splitting,  $\Delta E_Q$ , can be used to identify the spin state using the same methodology as in Fe<sub>3</sub>(CO)<sub>12</sub> as these complexes are also six coordinate, therefore the structural EFG is likely to be small, and the EFG to be dominated by electronic effects.

Octahedral high-spin Fe<sup>II</sup> has a <sup>5</sup>T<sub>2g</sub> ground term,

Octahedral low-spin Fe<sup>II</sup> has a <sup>1</sup>A<sub>1g</sub> ground term,

Octahedral high-spin Fe<sup>III</sup> has a <sup>6</sup>A<sub>1g</sub> ground term

Octahedral low-spin Fe<sup>III</sup> has a <sup>2</sup>T<sub>2g</sub> ground term.

Therefore, electronically induced EFGs and hence appreciable  $\Delta E_Q$  values are predicted for high-spin Fe<sup>II</sup> and low-spin Fe<sup>III</sup>, with small EFGs and  $\Delta E_Q$  values for low-spin Fe<sup>II</sup> and high-spin Fe<sup>III</sup>.

The  $\Delta E_Q$  value in spectrum (a) is  $2.430 \text{ mm s}^{-1}$  and that in spectrum (b) is  $0.537 \text{ mm s}^{-1}$ . Using this information, in conjunction with the isomer shift data, we can assign spectrum (a) to the low-spin Fe<sup>III</sup> complex [Fe(APT)(HAPT)]Cl<sub>2</sub> and spectrum (b) to the low-spin Fe<sup>II</sup> complex [Fe(HAPT)<sub>2</sub>]Cl<sub>2</sub>.

(This is a good example where a large quadrupole doublet does not automatically imply high-spin Fe<sup>II</sup>.)

Another question

Ferredoxins are iron-sulfur proteins that mediate electron transfer in a variety of metabolic reactions. Electron transfer is accompanied by iron redox chemistry in the Fe<sub>2</sub>S<sub>2</sub> core. The <sup>57</sup>Fe Mössbauer spectra of the oxidized and reduced forms of *Scenedesmus* ferredoxin are shown in the Figure. Use these data to account for the electronic and magnetic behavior of ferredoxin in its oxidized and reduced form.

Figure shows the structure of the Fe<sub>2</sub>S<sub>2</sub> core and the <sup>57</sup>Fe **Mössbauer** spectra of the oxidized and reduced forms of *Scenedesmus* ferredoxin.

Therefore, the <sup>57</sup>Fe **Mössbauer** spectra show convincingly the difference between the oxidised form of ferredoxin with two Fe<sup>III</sup> centres and the reduced form with one Fe<sup>III</sup> and one Fe<sup>II</sup> centre

Taken from: Structure of Fe<sub>2</sub>S<sub>2</sub> core of ferredoxins and <sup>57</sup>Fe **Mössbauer** spectra of *Scenedesmus* ferredoxin at 195 K (data from C. E. Johnson, *J. Appl. Phys.*, 42, 1325 (1971) and K. K. Rao, R. Cammack, D. O. Hall and C. E. Johnson., *Biochem. J.*, 122, 257 (1971))

In the oxidized version, there is a simple quadrupole doublet ( $\delta = +0.20 \text{ mm s}^{-1}$ ,  $\Delta E_Q = 0.60 \text{ mm s}^{-1}$ ), but on reduction this is replaced by a pair of quadrupole doublets.

In the oxidized form, both iron atoms in the Fe<sub>2</sub>S<sub>2</sub> core are tetrahedral high-spin Fe<sup>III</sup>, therefore each Fe is expected to have a <sup>6</sup>A ground term giving rise to a small or negligible valence EFG and hence small  $\Delta E_Q$ .

As the iron atoms are strongly antiferromagnetically coupled by both exchange and superexchange mechanisms through the sulfur atoms, the ground state is in fact a spin singlet.

In the reduced form, there is a central quadrupole doublet at  $+0.22 \text{ mm s}^{-1}$ , with  $\Delta E_Q = 0.59 \text{ mm s}^{-1}$ , both of which are very similar to those in the spectrum of the oxidized form. In addition, there is a second quadrupole doublet at  $+0.56 \text{ mm s}^{-1}$ , with  $\Delta E_Q = 2.75 \text{ mm s}^{-1}$ . The increase in isomer shift is consistent with this quadrupole doublet belonging to  $\text{Fe}^{\text{II}}$ . The large quadrupole splitting is consistent with a large EFG caused by the non-cubic electron density in tetrahedral high-spin  $\text{Fe}^{\text{II}}$  which has a  ${}^5\text{E}$  ground term. Therefore, in the reduced form there is one tetrahedral high-spin  $\text{Fe}^{\text{III}}$  with a  ${}^6\text{A}$  term giving rise to a small  $\Delta E_Q$  and a tetrahedral high-spin  $\text{Fe}^{\text{II}}$  with a  ${}^5\text{E}$  term, giving rise to a large  $\Delta E_Q$ , but as these are also antiferromagnetically coupled, overall it is a spin doublet system.

I think I should stop here. Maybe in my next lecture I will be talking more about problems. As I had mentioned, I will be solving problems on almost all spectroscopic aspects and I am sure you are going to enjoy these problems.

So, until then have an excellent time. Thank you so much.