Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 53
Mossbauer Spectroscopy: Effect of Ligands - II

Hello and welcome to this new segment of CD Spectroscopy and Mossbauer Spectroscopy for Chemist. My name is Arnab Dutta and I am an Associate Professor in the Department of Chemistry IIT Bombay. So, we are now looking into the applications of Mossbauer spectroscopy. So, so far we have covered how the ligand and it is properties, can regulate where the isomer shift of a Mossbauer Spectra will come up.

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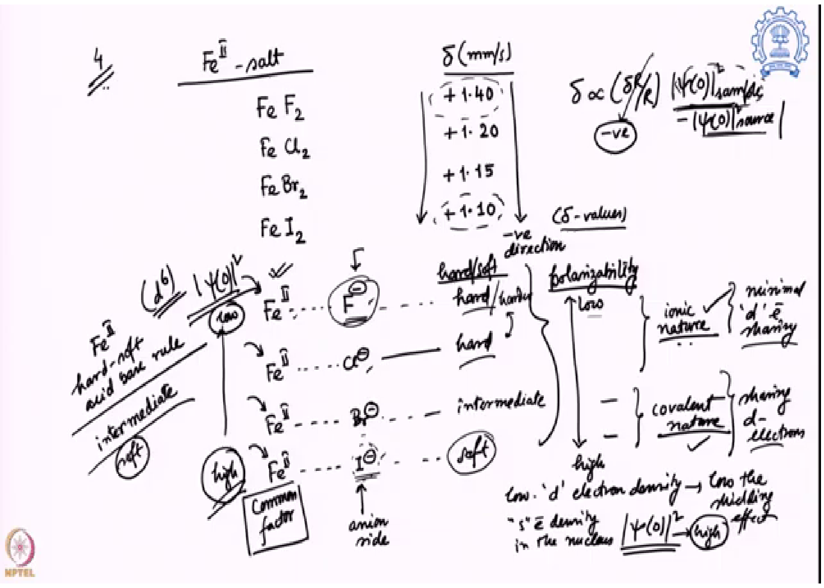

So, today we are going to take one more example and we are taking this example of a Fe(II) salt. However, there are different ligands bound to it FeF_2, $FeCl_2$, $FeBr_2$ and FeI_2. And if I look into the δ value for the salts, they are as following 1.40 for FeF_2, 1.20 for $FeCl_2$, for the $FeBr_2$ for 1.15 and for FeI_2 it is 1.10. So, you can see as we move from the fluoride to iodide.

We are slowly moving towards the more negative direction of δ values. Now, the question is why? So, for that we want to take a look into the structure of these particular complexes and over here we are looking Fe(II) sample this interacting with F^-, Fe(II) of them and this interaction and it is properties, are going to control. How the d-electron density and the resultant acid refund density is going to change?

And how it will affect the Mossbauer spectroscopy parameter the isomer shift. So now, if we look into all the system, FeF_2, $FeCl_2$, $FeBr_2$ and lastly FeI_2. And over here, you can see all of them the common factor is the Fe^{+2}. So, obviously the difference you are seeing is not for iron because it is remaining the same. The difference is happening, what is there on the anion side?

So that is creating the problem, I should say the differentiating factor is the anion now how we can explain that. So, if I look so, this iron and this anionic interaction, iron is remaining constant all over the changing factor is over here, how it is changing? So, Fe^{+2} if I want to talk Fe^{+2} in terms of hard-soft acid-base rule, it is more actually, on the intermediate side. That means it is actually, staying more on the softer side, soft in nature compared to Fe^{+3}.

Whereas what will happen? If I talk about hard soft system for these anions F^- are actually, hard, Cl^- is also hard, Br^- is something in the intermediate and I^- is a soft in nature. So, what is that particular factor? That defines whether it says hard and soft? It is the polarizability all of them has a charge of -1. So, charge density is going to be the important factor.

All of them has a charge of -1 but F^- is a very small ion, so, it controls it is charge very strongly. So, it is very difficult to change the electronic distribution around the F^- so that we can change the charge distribution. So, it is very difficult to do that so, they are less polarizable and in that case hard. So, this is the polarizability factor would come into that is with hard. Cl^-, on the other hand, is very much similar but this size is a little bit larger than F^-.

So, over here it will still be hard but the hard nature between F^- and Cl^-. F^- will be harder compared to Cl^-, whereas at Br^-side the size is increasing further. So that will be slowly moving to the soft nature and I^- is the largest of all charged steel same -1. So, because it is a large size and same charge, it is much easier to control the charge density and even change it alter it.

So that is why the polarizability is on the higher side, as we go down over there and on the lower side on the top of the group. So, they belong to all in group 17, I^- is the highest polarizable molecule. So, it will be the soft in nature or softest in nature among these species. F^-, on the other hand is the lowest polarizable and it will be the hardest among all the system. Now, Fe (II) it is interacting with all of them.

I am not going into which will be more stable or not that depends on the stability between the hard and hard of interaction but I am trying to understand how the electron density is moving around? So, when it is a softer nature, $FeBr_2$ and FeI_2 they will be more on covalent nature because they are in software in nature, so, they will be much more interested to share the electron density among them.

Whereas Cl^- and Br^- there will be more ionic nature, so, the ions would like to keep their charge and electronicity more closer to themselves, rather than sharing it. So that is defined over there this ionic, this is in covalent nature and if it is ionic in nature, this FeF_2 and $FeCl_2$. What will happen? The Fe is going to keep it is d-electrons to itself, whereas in covalent nature d-electrons will be shared.

And over here it is minimal shearing because all of them are Fe^{+2}. So, it is having 6-d electrons to start with all these 6 electrons more or less remain, as it is for the case of FeF_2 and. $FeBr_2$ and FeI_2 it is going to be sharing the electron density with the anions, Br^- are I^-. And over here when it starts sharing if I lose s-electron density, it will be lowering the d-electron density.

So, it will lower the shielding effect again if I have a low shielding effect what is going to happen? My s-electron density in the nucleus is going to affected which is nothing but Ψ_o^2. It is going to be a high value when there is low shielding effect. So, Ψ_o^2 value how it is going to differ? It will be the highest for this FeI_2 because most of the d-electron is moving out as much as possible, s-electrons are not feeling any shielding effect.

It has all the chances to go in the nucleus and Ψ_o^2 will be high but it is going to be lowered on FeF_2 case because most of the d-electrons are staying as it is there. And as we know, δ value is again depending on $\frac{\delta R}{R}$ and $|\Psi_o^2| sample - |\Psi_o^2| source$. And over here you can see the $\frac{\delta R}{R} = -ve$ value because ^{57}Fe actually shrinks down in size when it goes to the higher excited site. $I = 3/2$.

So, this is negative and these values constant. I am using the same source, the sample value higher the value it will multiply the negative number and it will go towards the negative region and that is what is actually, happening over there because $|\Psi_o^2|sample$, as you figure it out, is high for the I$^-$, so, it is multiplied by the negative number and that is why it is having a lower value on the negative side.

On the F$^-$ case, it is on the most positive side that it can be because it has the lowest $|\Psi_o^2|$ so, even if it is multiplied with the negative number, it is actually, most on the positive side. And that is what is actually, happening over here the difference we are seeing, it is mostly generating from the s electron density how much it can be there on the electron which is connected to the shielding effect which in turn is connected to the d-electron availability on the iron.

And that d-electron availability of the iron is controlled by the ionic or covalent nature of the complexes. Over here, I$^-$ being a soft nature, ligand it try to bind with Fe^{2+} but strongly doing a covalent bond and moving the electron density out of the iron and that is why, in case of I$^-$, we see that it shifted towards the relatively negative side from 1.4 to 1.1.

Again, it is not the absolute negative value we are discussing. We are discussing about which particular direction this is actually, moving out. So, with that particular example, we would like to stop for this particular segment, where we have explained how we can take a look into the covalent and ionic nature of the ligand and the molecule to figure it out. What will be the isometric shift for the Mossbauer spectroscopy?

And over here, this also shows us that how we can use the Mossbauer spectroscopy to figuring out whether my molecule is having a covalent nature or ionic nature during the bond formation. So, with that we would like to conclude over here. Thank you. Thank you very much.