Circular Dichroism and Mossbauer Spectroscopy for Chemists
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Lecture – 45
Mossbauer Spectroscopy: Quadrupolar Splitting – I

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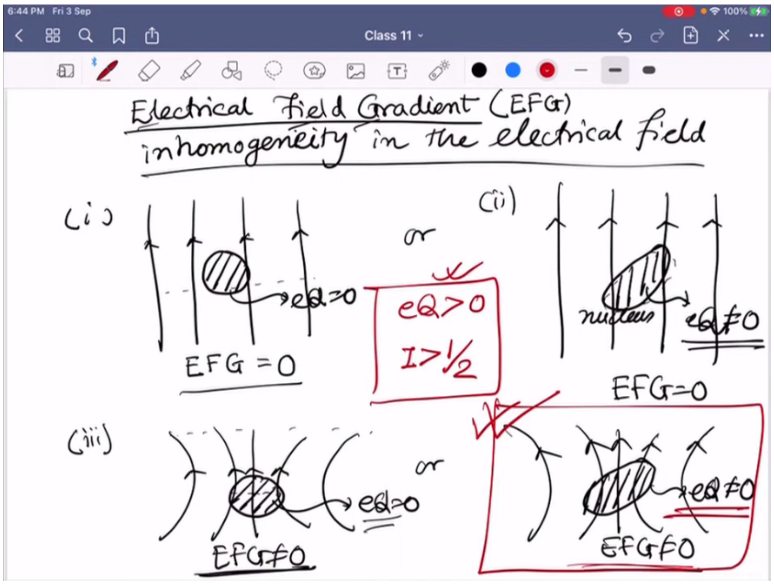

Electrical Field Gradient (EFG)
inhomogeneity in the electrical field

So, now the actual factor that is going to affect over here is known as electrical field gradient. What is an electrical field gradient? A very rough term or very overview term what we can say it is nothing, but the inhomogeneity in the electrical field; electrical field coming from where from the s electron density penetrating the nucleus and that one is going to interact with your nucleus.

And if you have a quadrupolar moment and if you have an inhomogenous electrical field only then you are going to see the effect of the non spherical field. So, let us come into that what are the pictures I can have. First say my field is homogenous anywhere, any direction you go your field is homogenous that is how it looks like, does not matter where you put your system you are going to see the similar field.

So, over there the electrical field gradient or the difference in the electrical field with respect to the direction or the position is not present. So, we said EFG short form for electric field gradient is going to be 0. So, if you have electrical field gradient 0 then if you put a spherical field or if you put a non-spherical nucleus it does not really matter because your electrical field gradient is already 0.

So, even if you have a quadrupolar moment active system it is given by $eQ \neq 0$ a non spherical nucleus and I am putting into a very homogenous electrical field it is not going to be effected because you are not having electrical field change with respect to the difference of the presence of the quadrupolar moment and over here the quadrupolar moment is already 0, electric field gradient is 0 so nothing matter.

So, either two cases you are not going to see any difference. Now, what happens a field is inhomogenous. So, now you can see over here you have a larger electron density over here it is lower electron density it is a inhomogenous field. So, my EFG is not equal to 0 I am drawing two fields like this and now you can imagine what are the different things you can change you can put a spherical nucleus $eQ = 0$.

Although, the electrical field gradient is non zero because the nucleus is not creating any quadrupolar moment you are not going to see any effect on the nuclear states in this condition. However, if now your nucleus is a non-spherical 1 and you have a non zero value of quadrupolar moment your electric field gradient is also there it is inhomogenous. In this particular condition you are going to see some effect of it in the transition of the adjusted transition of the system only when your system is giving some quadrupolar moment that means you have to have a non-spherical nuclei.

Non spherical nuclei is only possible if $I > ½$ only then your quadrupolar moment would be active that is the condition and your electric field gradient should be also active that means you should have an electron density around the nucleus which is inhomogenous and that is very easy to find. How? Let us take a look into that, but before going there let us try to find out what is the effect of that?

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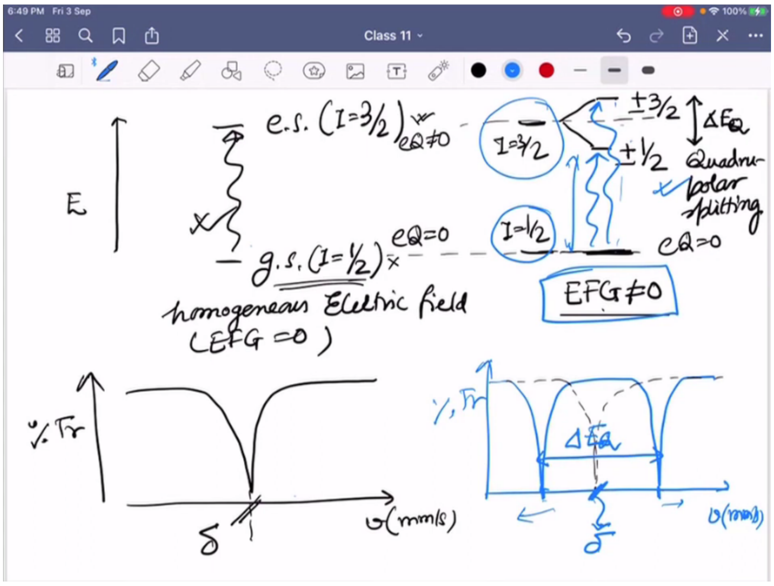

If I have a system which is having a electric field gradient positive non zero and quadrupolar moment non zero system. So, first ^{57}Fe system I have a ground state of I = ½ an excited state of I = $\frac{3}{2}$. Now, say in this condition this ground state can it be active for quadrupolar moment? The answer is no because I = 0 and I = ½ they are spherical system so it cannot create eQ. This one can create a quadrupolar moment.

But now say I am putting it in a homogenous electric field that means EFG = 0. So, then what I am going to see only one bent in the terms of Mossbauer spectroscopy I am going to see a bent like this, this is the %T, this is v = mm/s wherever it is cutting that is the δ value isomer shift that is how it looks like that is what we study.

Now say the same system I am talking about, but now say I am taking a system where the electric field gradient does exist it is a in homogenous field. So, if you have a system where you have a quadrupolar moment that will be very effective. So, I = ½ it is eQ = 0 so there is no effect of that so does not matter. So, this is electric field gradient non-zero, but your quadrupole moment is 0.

So, it is a classic case of this one. So, you are not going to see any effect. However, I = $\frac{3}{2}$ so it is I > ½ so it is a non spherical system and you also have a electric field gradient present. So, the system I want to look into. Over here what will happen that will split up in two different system. One will be $-+$ ½ , one will be $-+$ $\frac{3}{2}$ and what will be the difference?

It is known as δeQ or quadrupolar splitting. This is known as quadrupolar splitting because that is generated from quadrupolar moment and previously you are going to have only one signal now what you are going to see two signals and you can very easily see the energy gap between these two will be nothing, but an average of the previous value. So, previously you are seeing a value like this.

Right now what I am going to see is the following two signals. One from the lower energy, one from the higher energy; lower energy means lower side v higher energy means higher side v and if you take an average of that; that will be the original value without any splitting. So, I am not exactly drawing in the middle of it. So, that is how it is going to look like. So, this blue line is the one you are going to see.

And the difference you are going to get it at two different positions if you take an average of that wherever the average value would be the delta value or isomer shift and the difference between these two it will the δeQ or quadrupolar splitting. So, that is the two terms you are always going to find in a Mossbauer spectroscopy. The quadrupolar splitting and isomer shift.

Isomer shift will be always there quadrupolar shift depends on the condition only if you have a electric field gradient non-zero only then it will be valid and for I = ½ and I = $\frac{3}{2}$ the ground state of the ^{57}Fe cannot shift, the excited state can split that will depend whether you have an electric field gradient present or not. Any questions up to here? If not we will go to the next part.

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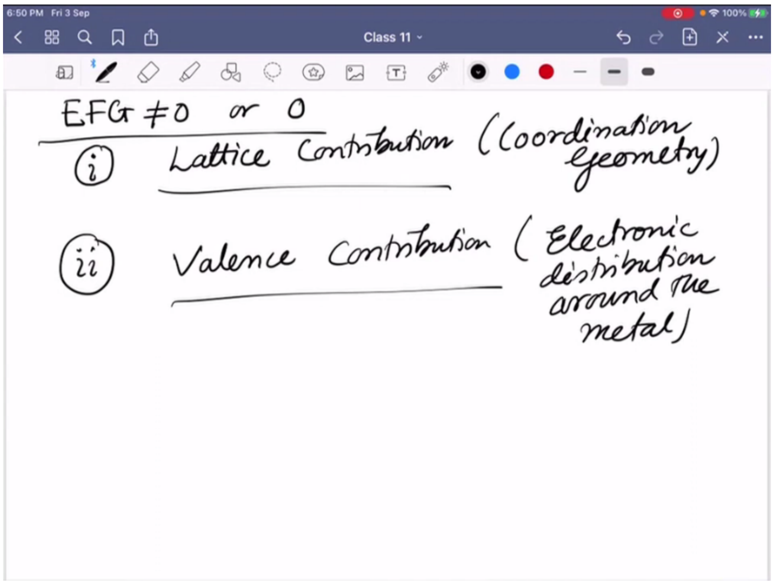

EFG ≠ 0 or 0

(i) Lattice Contribution (Coordination geometry)

(ii) Valence Contribution (Electronic distribution around the metal)

How do I find out my electric field gradient is non-zero or 0 because that is going to be the only important factor in controlling that and this is given by only the coordinate side by two different system one is called the lattice contribution which is nothing, but with respect to the coordination geometry and second thing is known as the valance contribution which is coming from the electronic distribution around the metal centre.

So, these are the things which are going to say whether you are going to have a electric field gradient present or not. It is always better to understand with an example. So, let us look into an example.

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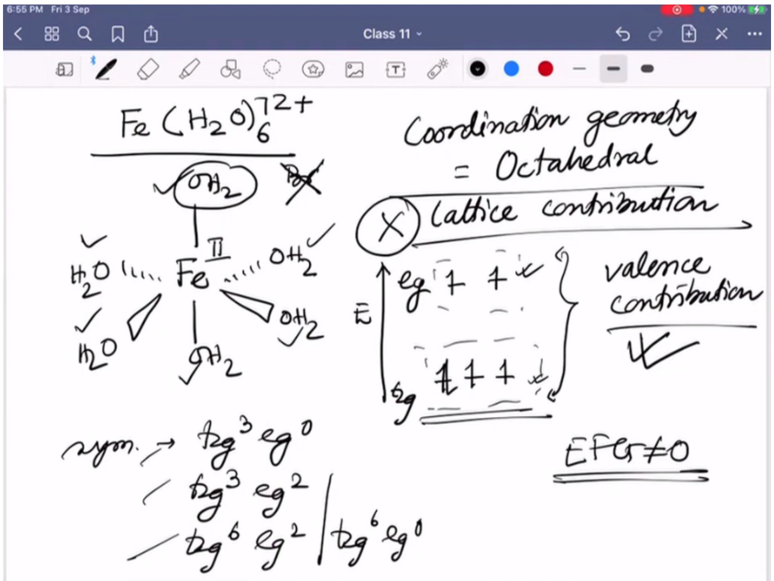

So, the example I am taking is the following Fe with 6 water molecules Fe is in + 2 oxidation state. So, I am taking this iron it has 6 coordination and all of them are water molecule. So, the first thing we are going to look into about the coordination geometry. The coordination geometry in this system you can see it is perfectly octahedral system. So, if it is a perfect octahedral system do you expect that just because of the coordination it is going to create any difference in the electronic field around the iron all are 6 water molecules.

So, all should be same so it should not be showing any electronic distribution difference. What I mean to say if instead of this one of the water molecules over here if I put a Br^-. Now, I create a asymmetry in the system. Now, it will create a electronic distribution inhomogeneity and at that condition it will be contributing which is known as the lattice contribution.

However, at this moment if you do not have that Br^- if you have all 6 water molecules you should not see any effect. However, what is the electronic distribution? It is a Fe^{+2} systems so that means 6 d-electrons, it is a octahedral system. So, it is going to have t_{2g} and e_g the electronic configuration I am drawing 6 d electrons. The first 3 goes over here where the fourth one goes? That depends on whether it is a high spin or low spin.

Now water molecule group 16 σ doner, Π doner it is going to be weak field ligand that means it is a high spin system. So, the fourth electron will go there, fifth here, sixth one here. So, now the electronic distribution is it symmetry? Symmetric electronic distribution means if you have a $t_{2g}^3e_g^0$ it is a symmetric electronic distribution. If you have $t_{2g}^3e_g^2$ it is symmetric electronic distribution.

If you have $t_{2g}^6e_g^2$ symmetric electronic distribution, if you have $t_{2g}^6e_g^0$ is 0 for low spin complexes that is symmetric electronic distribution, but this one is not e_g is fine, but t_{2g} case not all the orbitals have similar electron density. So, that means it has some inhomogeneity such a kind of electronic inhomogeneity coming from the electronic distribution it is known as the valance contribution.

So, over here in this case of iron water molecule what do you expect? There should be valance contribution and there should not be any lattice contribution for the first **(()) (14:42)** believe. So, that means there should be an electric field gradient present because as we said electric gradient has two contribution valance or lattice; lattice means simply look into the coordinate side see if it is symmetric or not.

If it is square planar geometry four of them same symmetric, octahedral all 6 of them are same symmetric, linear two of the ligands are same symmetric, but if it is not if we have different ligands on either end then it is asymmetric. Valance electron contribution is coming from the electron density distribution either the t_{2g} or e_g should have same number of electron only then you can have a valance electron contribution for tetrahedral also you can think about the similar way.

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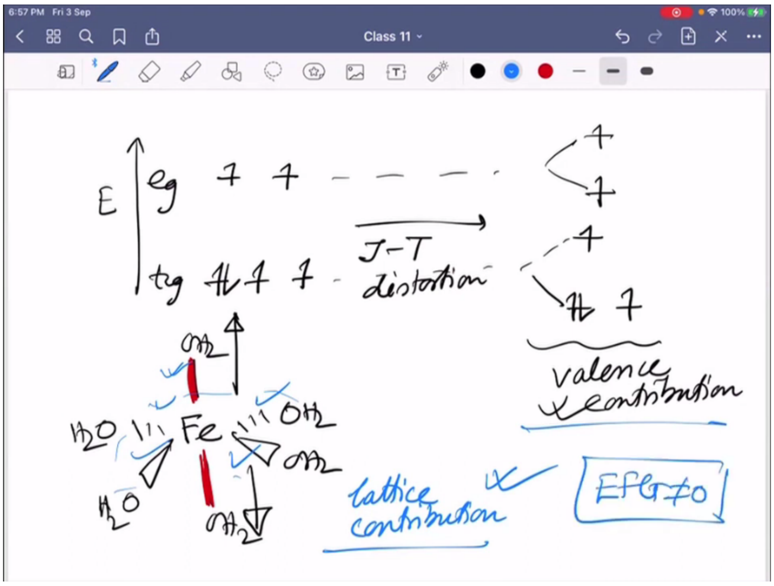

Now, in this particular case of Fe system the system is not run over here because what I said it is a $t_{2g}^4e_g^2$system and then with this particular electronic configuration one thing can happen which is known as Jahn-Teller distortion. So, what will happen in Jahn-Teller distortion? These orbitals will split up. So, the valance shell is still fine it is still inhomogenous. So, valence contribution will be still here so nothing change over there after the Jahn-Teller distortion, but what is happening in the coordinate side?

Previously all of them has 6 water molecules and all of them are like this, but now two of them will move out that is the Jahn-Teller distortion. So, say this two the red one will have now different bond distance compared to this one. So, altogether previously you have a perfect octahedral. Now after Jahn-Teller distortion you do not have it. So, these two are different than compared to the equatorial one the axial points are different.

So, now your coordination side is also not totally symmetric. So, now you are also going to have some lattice contribution due to the Jahn-Teller distortion and both those things will happen in the same time. So, it will have a very strong electric field gradient present a non zero electric field gradient and that is why what will happen.

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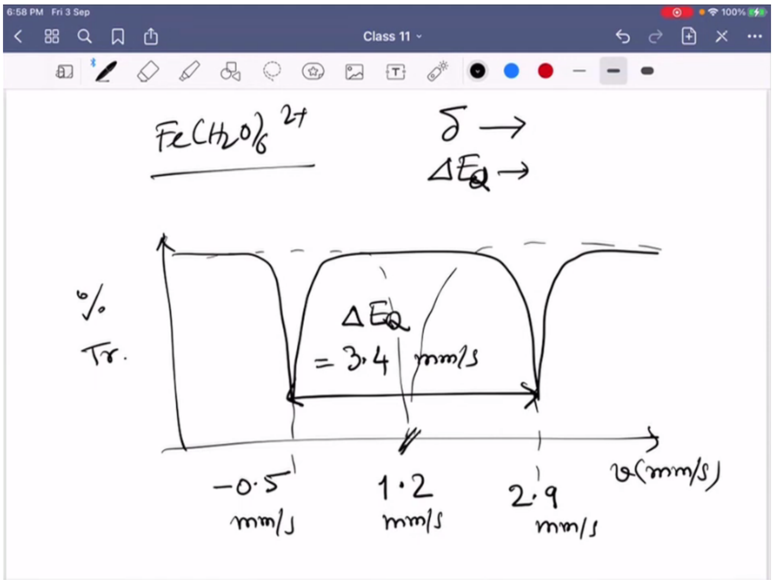

For this $[Fe(H_2O)_6]^{2+}$ where we say it has going to be have a δ value and it is going to have a non-zero quadrupolar splitting value and what you are going to see is the following like this two values plotted in velocity y axis is %T. These values experimentally found at – 0.5 mm/s and 2.9 mm/s. So, what should be the δ value average of them.

Average it out it will come out at 1.2 mm/s and what is the δeQ difference between these two that is nothing, but 3.4 mm/s. So, that is how you figure it out what is the isomeric shift and what is the quadrupolar splitting. So, I take two minutes extra today so I will stop over here.