Bio-Physical Chemistry

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Lecture - 36

Spectroscopy : The Franck Condon Principle

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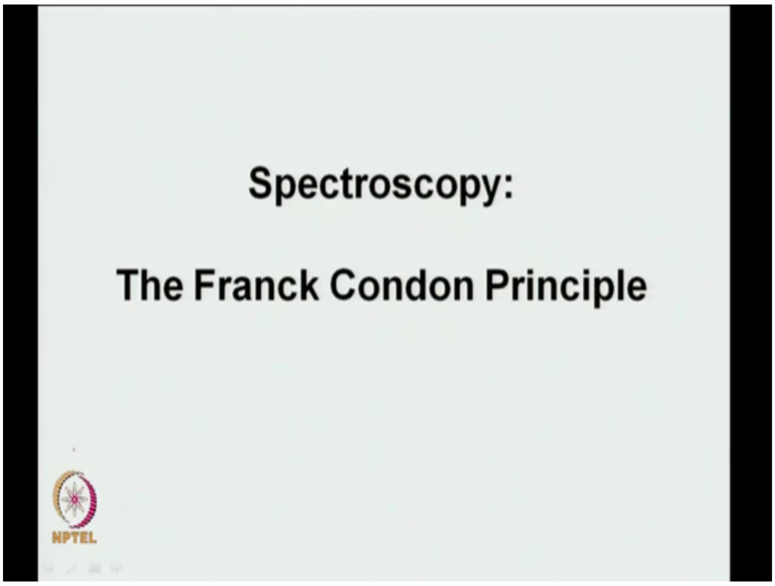

Spectroscopy:

The Franck Condon Principle

We will carry on with a discussion on Spectroscopy the one we started last time. So, in the last class we looked at a very basic you know a set of very basic constants which are Einstein's coefficients a and b where a resembles or a represents the spontaneous emission and b corresponds to the stimulated one right. So, absorption can only be stimulated because only if you have light will or if you have energy density coming in will the molecule absorb and go up to the excited state.

So, absorption has no counterpart or no similar counterpart as stimulated or spontaneous emission right. So, there is nothing as spontaneous absorption. Absorption is always based on absorption of light. On the contrary there are two ways that molecules can come down. One is stimulated; that means, the light you are shining itself stimulates the transition from the upper state to the lower state and the other one is spontaneous. It means you do not need any energy density the molecule itself comes down right.

And then we went on to see that based on certain derivation taking equilibrium Boltzmann population into consideration that there was a ratio a to 1 over b to 1 right.

And we saw that this was proportional to nu cubed and then and thus we said that the higher the frequency; that means, the higher the energy lower the wavelength the higher is the probability of having spontaneous emission over stimulated emission. And that is why because lasers are based on the principles stimulated emission, it is so hard to get lasers which lays in the UV just because of this right this you cannot avoid.

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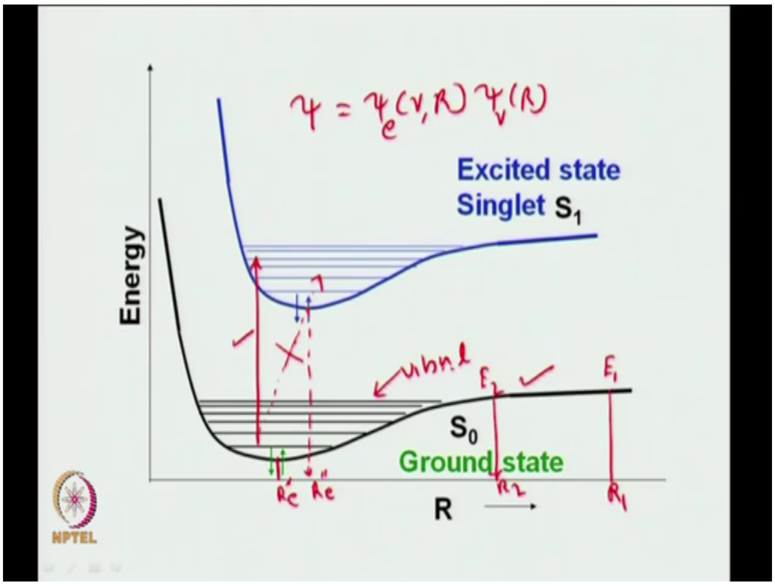

So, based on this then we moved forward and started discussing another aspect which is very fundamental to spectroscopy which is Franck Condon. Now, we are talking about electronic spectroscopy out here. So, this is what we said. So, if you are given you see all these things were written in last class.

If you are given 2 electronic states one is S 0 which is the ground electronic state right singlet the other one is S 1 the excited singlet electronic state. Now, these are just examples right. These are just there can be many other states out there too.

So, but let us start with the very simplest one ok. Transition is always vertical in nature right. This is what we are looking at of vertical transition. This one the crossed one is a slanting transition. It should not be having any slope; the basic premise behind this being that electrons are much lighter than what your nuclei.

So, when you are having a vertical transition during the vertical transition your R is not changing where R is what? The inter nuclei distance; that means, even before the nuclei can respond to that perturbation your electrons have already moved to the higher state that is why a transition is always vertical. That is why it is called a vertical transition.

Now, this has many consequences you will see as we go on discussing. But, you know there is also a fundamental issue, but before going there just to make the point along with the electronic states which are S 0 and the S 1 the bold line which are the electronic states you also have these lines right these lines going across the electronic states. These are the vibrational states as shown out here.

So, you will be having vibrational states for the ground electronic state, vibrational states for the excited electronic state. And whatever electronic state you consider every electronic state would be associated with a set of vibration levels and then obviously, the vibration levels will also be having rotation level right all those things.

But here we are mainly concerned about electronic and vibrational. Now, so you can understand one thing that if I am going to do an electronic transition; that means, if I am going to do a transition from S 0 to S 1 now just keep these in keep this thing in mind if I am going to do a transition from S 0 to S 1 I am not only going to change my electron excited state going from S 0 to S 1.

But along with that I also have depending upon how my nuclear geometry changes I will show that to you later. I will also have a probability of finite probability of populating vibration levels or higher vibration levels in your excited electronic state right, because in the low electronic state you have v is equal to many right can v be 0.

The quantum number v cannot be 0 the quantum v cannot be 0 it can be 0 right. So, the quantum v can be 0. So, you can have 0 to n for S 0 you can have also 0 to n for S 1 0 to n for

S 2 and so on because each electronic state is associated with a set of vibration energy levels. So, that is why that is why I hope you have come across this word.

There are certain group of transitions known as vibronic transitions. So, vibronic transitions if you split the word it would refer to vibration that is where the vibr comes from and onic comes from electronic. So, vibronic means a combined vibration and electronic transition. So, you keep this in mind we will come across this very soon.

Now, the fundamental thing that, I was talking about ok. You are given a set of electronic states S 0 and S 1 and you are asked this question. The question you are asked is what is the transition probability. What is the transition probability of this compound making a transition from S 0 to S 1? How would you figure that out or on what quantum mechanical parameters should it depend ok?

Now, this can be derived. What we will do is we will actually go through the derivation and you will see how fundamental it is to spectroscopy special electronic spectroscopy. And, what are the different components that come out and why it is called a vibronic transition not only an electronic transition ok.

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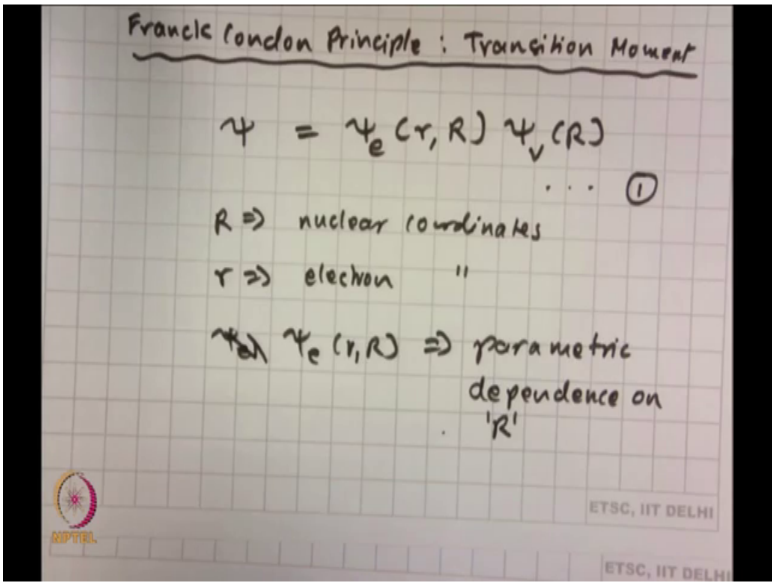

Franck Condon Principle : Transition Moment

$$\psi = \psi_e(r, R)\,\psi_v(R) \quad \ldots ①$$

$R \Rightarrow$ nuclear coordinates

$r \Rightarrow$ electron "

~~ψel~~ $\psi_e(r, R) \Rightarrow$ parametric dependence on 'R'

So, let us look at that. So, what we are going do now is we are again going to look at Franck Condon Principle and here we are going to introduce something known as transition moment. So, as you can understand the transition moment the transition comes from the transition from one state to the other state right and where does a moment come from. Where did you heard this moment before.

Student: (Refer Time: 07:21).

The moment comes from the dipole moment right. So, it must be so there must be a combination of this transition along with a change in electron density or electron distribution. You know that is what would give rise to a change in your moment. So, that is why it is called a transition moment ok. Now, where do we start from we again start from the bond Oppenheimer’s principle.

So, what we say is your electro or your total combined wave function psi is given by psi electronic. So, the electronic is referred to as e r comma R times psi vibrational this you can also write a psi nuclear which is n depending on R and this is equation 1. So, what is big R? Big R corresponds to what the inter nuclear distance; that means, the nuclear coordinates r corresponds to what the.

Student: (Refer Time: 08:20).

Electron coordinates right. So, big R corresponds to the nuclear coordinates and small r corresponds to the electron coordinates. So, what you can realize is if you split it up into 2 the vibrational part depends only on what? The vibrational part depends only on what?

Student: The nuclear (Refer Time: Refer Time: 08:49).

The nuclear coordinates R right and this you know why. Because when you are talking when you are talking about a potential you do half k x squared, what is x? x is essentially how much you are shifting from your equilibrium position r ok. It is x is essentially extension or compression whichever you look at it. Now, the electronic. However, depends on 2 coordinates one is the small r which is it is the coordinates as defined by itself by it is own position and the other is defined by the nuclear coordinates too.

It is obviously understood that when the electrons move the nuclear would not be moving they would be following, but still the nuclei would be moving; that means, your I mean your transition is also accompanied by a vibration right that is what it means and the moment you have a vibration; that means, your nuclear coordinates are also changing right.

So, this type of dependence; so, this type of dependence; that means, psi electronic; so, sorry let me write psi electronic r, R this is referred to as a parametric dependence on R. It is a parametric dependence on R. The parametric dependence on R again means that for each and every R whatever R values are which will help you give rise to a plot, you solve your electronic Schrodinger equation and you get psi electronic you get e electronic and then you get the energy curve this is referred to as parametric dependence.

So, this is a starting point right. Now this is a starting point. So, what we have done is we have said that these two motions being independent they can be decoupled from each other, but keeping in mind that the electron motion is still being governed not only by its own coordinates, but also by the nuclear coordinates ok.

So, where do we go from here? See it is like this when you do quantum mechanics there is one very important thing you always talk about it is an operator. What is the operator do? What the operate does is if you operate on a certain wave function with this operator you will be able to do a certain action or a certain transformation right ok.

It is like matrix operations. So, similarly if you would like to do a transition you have to be able to operate on the molecule by an operator the molecule being a quantum mechanical system by an operator and only after you do this operation will it make a transition.

So, then you can understand what is going to happen is if you are going to find if you are going to find a probability which is related to this probability of transition; that means, to what extent the transition would be taking place you would be actually solving what? You would be actually solving what? You will be actually solving something which corresponds to an expectation value where the expectation value involves two things two major things.

One is the ground electronic wave function, the other one is the excited electronic wave function with an operator sandwiched between these two because the operator makes this transition happen as simple as. That you know that is why quantum mechanics expectation values are so important.

See if you are going for a position what do you do. You take the position operator and sandwiched in between the two wave functions the same thing you do here. So, then our attention now shifts to what is my operator ok. To think about it is very simple. When you are doing a transition, when you are doing a transition what is essentially happening. You are shifting electrons from one place to the other place from one orbital to the other orbital.

Essentially what you are doing is you are giving rise to a change in the charge distribution. Whenever you have a change in the charge distribution this would be accompanied by a change in some sort of dipole moment, but this dipole moment is changing during a transition ok.

Hence, it is referred to as a transition dipole moment or a transition moment that is why it is called a transition moment or a transition dipole moment as was written on the title of the previous sheet ok.

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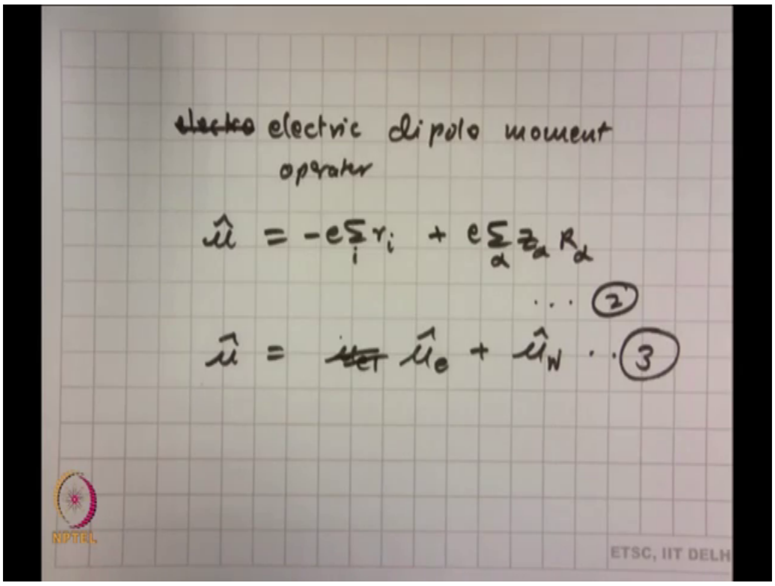

~~electro~~ electric dipolo moment operator

$$\hat{\mu} = -e\sum_i r_i + e\sum_\alpha Z_\alpha R_\alpha \quad \ldots ②$$

$$\hat{\mu} = \hat{\mu}_e + \hat{\mu}_N \quad \ldots ③$$

So, then if it is the dipole moment we should be considered about what we can write is the electronic rather the electric dipole moment operator can be written as mu with the hat on top being the operator is equal to minus e sigma i r i the small r referring to the coordinates of the electrons e being the charge plus e sigma alpha Z alpha R alpha ok.

So, this is equation number 2. So, see this can be further simplified as mu is equal to mu electronic. I always right here sorry mu electronic plus mu nuclear 3. So, that means, your dipole moment has contributions from two things. One is because of the electron movement and the other is because of the movement of the nuclei ok. So, if you would ever try to actually calculate something like this you would introduce this a dipole moment electric dipole moment operator.

Now, what do we do? Because this is the operator this operator is the one which brings about the transition, we take this and we sandwich it between the 2 wave functions we are concerned. One wave function belongs to S 0 say the ground state and the other wave function belongs to the excited state right as simple as that.

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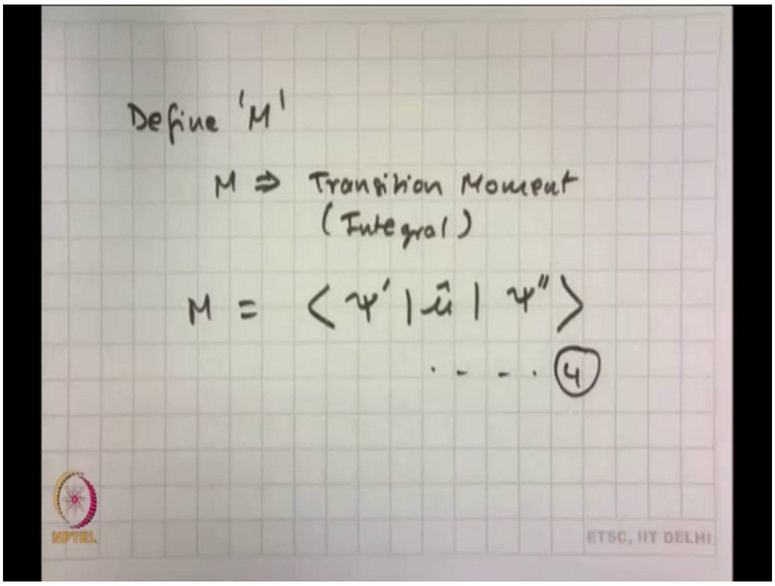

Define 'M'

M ⇒ Transition Moment (Integral)

$$M = \langle \psi' | \hat{\mu} | \psi'' \rangle \quad \ldots\ldots ④$$

So, then what we define is we define something we define something known as M. This M is referred to as the transition moment the M is referred to as the transition moment and we get the transition one by solving an integral ok. What is an integral? So, therefore, M is in your direct notation M in your direct notation is given by psi mu psi. So, what is mu? Mu is the operator right which brings about this change. After doing the operation you have this change from the ground state to the excited state.

What are these 2 psis? One psi say it is double prime belongs to the ground state and after you take the operator operate on the ground state where do you go? You go to the excited state and that psi is referred to as psi prime ok. That psi is referred to as psi prime. So, this you can see is an integral in direct notation.

I am sure you have done this in quantum mechanics right. The direct the direct Brownian cat notations right M is referred to as the transition moment and it is also referred to as integral because this is an integral essentially what you are solving. Finally, you get a certain value which is the transition moment ok.

So, this guys let me tell you if you are doing electronic spectroscopy this is something you will always have to deal with and this is one finally, what defines your absorption spectrum your florescence spectrum whatever you see it comes from here because it is an overlap of 2 wave functions.

If you are doing an absorption it is an overlap between. See if you are going to have an absorption then it is an overlap between your ground state and the excited state. If you are going to have an emission what will happen it is an overlap between your excited state and the ground state.

But it does not matter. Whenever you are having any transition what is going to happen is your electrons going to move faster and the nuclei are going to follow it that is essential always what happens. So now, this being the most important thing; so, this would be equation number 4 we need to solve it ok.

But, you will see the solution is not that bad to get to the final expression that is what I mean. What we do now is because we know that psi prime and psi double prime can both be split into what? The electronic and the nuclear components of the electronic in the vibration counterparts right then we expand this integral.

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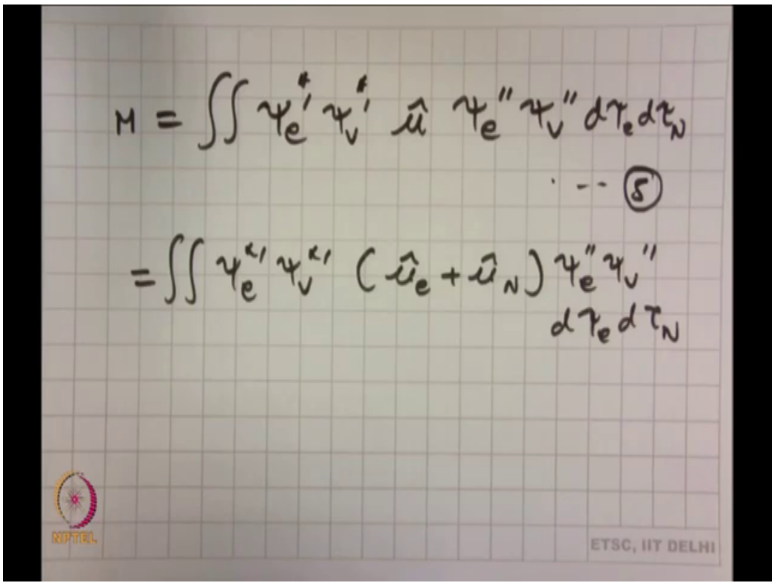

$$M = \iint \psi_e'^{*} \psi_v'^{*} \hat{\mu} \, \psi_e'' \psi_v'' \, d\tau_e \, d\tau_N \quad \cdots ⑤$$

$$= \iint \psi_e'^{*} \psi_v'^{*} (\hat{\mu}_e + \hat{\mu}_N) \psi_e'' \psi_v'' \, d\tau_e \, d\tau_N$$

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So, what we say is now therefore, M based on our discussion is equal to. I will tell you why I am giving a double integral is equal to this. What do you have? The psi prime; the psi prime can be written as psi e prime and because this is on this side it comes with a star psi v prime star it is like psi star h psi do you remember that. When you would do an expectation value psi star or h psi essentially that is what I am doing.

I am doing psis psi prime star then the operator then psi double prime your operator was mu. So, I write mu out here times psi e psi v is double prime double prime being the ground state ok. Then what do you have is you will be having your volume elements, but how many volume elements would you will be having here? How many volume elements you will be having? What are the coordinates involved?

Student: 6 volume elements.

Good, you will be having 6 volume elements that is true. So, essentially I can say without splitting each volume elements into 3, but volume element will be having 2 though individual will be having 6 right. So, volume elements there will be having 2 volume elements. One volume element will be defined by the coordinates of the electron the other volume element will be define by the coordinates of the.

Student: Nucleus.

Nucleus. So, I would be having d tau e then d tau N. So, this would be equation number 5 ok. With the thing remember that psi electronic depends upon small r and big R psi vibrational depends only on big R right. So, then we go to the next step.

What we now do is we split we split this by doing psi e star psi v star then mu can be written as what now. Mu has two components right; one is mu electronic the other one is mu nuclear did I write mu N or mu v. I write mu N good then psi e psi v d tau e d tau N. So, hence you will be solving essentially 2 integrals ok. One which would be having only the mu electronic as the operator the other one would be having the mu nuclear as the operator ok.

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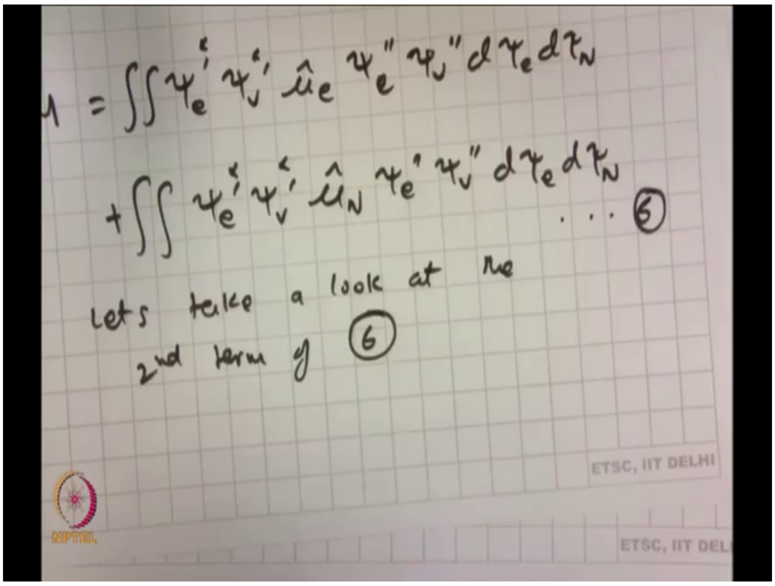

$$= \iint \psi_e'^{*} \psi_v'^{*} \hat{\mu}_e \psi_e'' \psi_v'' \, d\tau_e \, d\tau_N$$

$$+ \iint \psi_e'^{*} \psi_v'^{*} \hat{\mu}_N \psi_e' \psi_v'' \, d\tau_e \, d\tau_N \quad \ldots ⑥$$

lets take a look at the 2nd term of ⑥

Let us do that quick. So, this can be split into 2. So, I can write psi electronic star psi v prime star then I can write mu e psi e double prime psi v double prime d tau e d tau N plus. Now, I will bringing the mu nuclear psi v prime star mu nuclear psi e psi v double prime d tau e d tau N.

So, that means, your transition moment is now a sum of 2 very generalized integrals. One which has mu e and the other one which has mu N ok. Now, if it is mu e which wave functions are going to be affected? See it is the electronic dipole moment. So, which wave functions would be going to be affected?

Student: Psi.

Psi electronic good. If it is mu N, which wave function is going to be affected? Psi vibration which is psi N essential right ok. So, you have to keep that in mind. Now, let us look; let us look at the second integral. Let us take a look at the. So, let this be equation number 6 at the second term of equation 6. Let us look at the second term of equation 6 let us see what we have.

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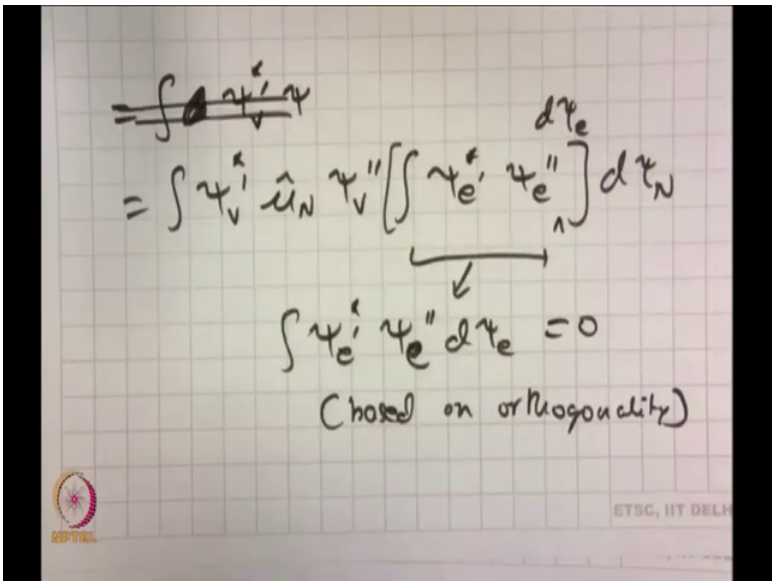

~~$= \int \psi_v'^{*} \psi$~~

$$= \int \psi_v'^{*} \hat{\mu}_N \psi_v'' \left[\underbrace{\int \psi_e'^{*} \psi_e'' \, d\tau_e}_{\swarrow} \right] d\tau_N$$

$$\int \psi_e'^{*} \psi_e'' \, d\tau_e = 0$$

(based on orthogonality)

So, the second term can be written like this. Sorry, psi v prime star psi v prime star ok. Let me write it again this one psi v prime star then I have mu N and psi v double prime ok. I have another integral. I should not be forgetting that integral which is psi e prime star psi e double prime. Let me put this in a large brackets. Here, I will be having d tau e then I will be having d tau N. Is it with you?

How I have written it what I have done is I have just separated out the nuclear component from the electronic component keeping in mind that mu N will only be sandwiched between which ones the psi Ns I have which is essentially this psi Vs. You will be having an integral which will be having psi e prime star psi e double prime with d tau e.

Because that is the integral with electronic coordinates and because your integral electronic integral also depends upon the nuclear coordinates that is why I have d tau N at the very last ok. Because d tau N is like a father figure for everyone you know everything depends upon d tau N ok. Now, guys tell me what is the value of this integral. The answer is very simple.

Student: 1.

1 ok. What is the other binary digit?

Student: 0.

Very good. So, at least he pointed us to the answer right ok. It is not 1 it is 0, why? Tell me why you said 1? You can tell me why it is 0?

Student: Orthogonal.

Which one is orthogonal right which one is orthogonal?

Student: The second one.

The second integral is orthogonal the second integral satisfies orthogonality do you understand that. So, look at this one. So, if you look at this one which is psi e prime star psi e double prime d tau e. Would this be would not this be equal to 0, would not this be equal to 0? For example, let us say this you taking you are taking a particle in a box take the simple simplest example particle in a box right. How many wave functions do you have? Say you start from N is equal to 1 you cannot go to N is equal to 0 particle in a box.

Say you have psi 1 you have psi 2 you have psi 3 and so on. If you take an integral between psi 1 and psi 2 what would it give you psi 1 and psi 2 would always go to 0 because orthogonality right. Because they are what their energy functions of the same operator which is the Hamiltonian ok.

Here too the psi electronic double prime and psi electronic prime they are wave functions of what? The Hamiltonian the electronic Hamiltonian of whatever system you are considering, hence they would be orthogonal.

So, therefore, this is equal to 0 based on orthogonality ok. This would be equal to 0 based on orthogonality. Is this clear to you why it is orthogonal? Because if you would be solving hydrogen say you are solving a simplest 1 say you are solving say hydrogen atom ok.

You will be having these different quantum numbers N 1 2 3 4 right, but if you would take psi N equal to 1 psi N equal to 2 right if you do an integral what will you get you will get 0. But, then where do they come from? They come from solution of a single Schrodinger equation where h is always defined for you.

So, they belong that is what; that is what an orthogonal normal set is right. An orthonormal set is formed from that set of wave functions which coming from the same operator and here these 2 belong to the same operator which is a h electron that is why they are orthogonal to each other good. So, that is that means, the equation or the expression is already simplified for us.

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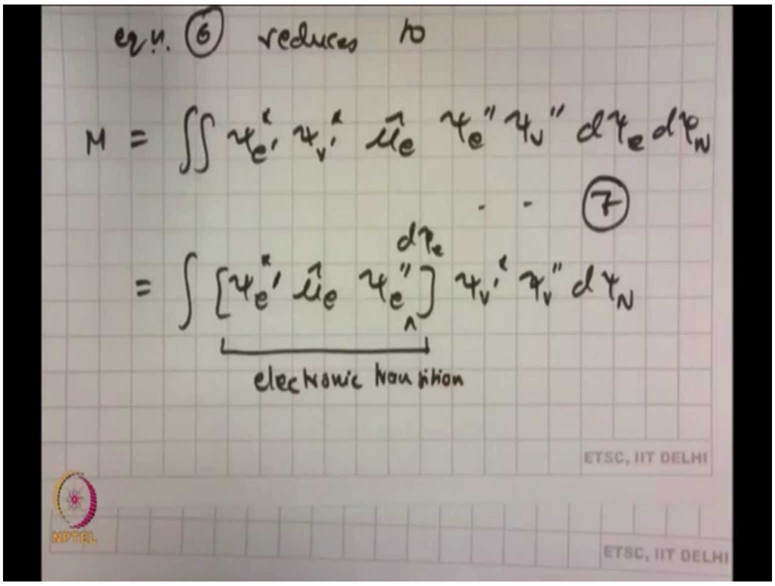

eqn. ⑥ reduces to

$$M = \iint \psi_{e'}^{*} \psi_{v'}^{*} \hat{\mu}_e \psi_{e''} \psi_{v''} \, d\tau_e \, d\tau_N \quad \text{- -} \ ⑦$$

$$= \int \underbrace{\left[\psi_{e'}^{*} \hat{\mu}_e \psi_{e}'' \, d\tau_e\right]}_{\text{electronic transition}} \psi_{v'}^{*} \psi_{v}'' \, d\tau_N$$

So, what is equation 6 reduced to now. Therefore, equation 6 reduces to M equal to I can write psi electronic star psi v star mu e psi electronic double primes psi v double prime d tau e and d tau N. Let this be 7. So, this is the one I would be focusing on now because the other one is of no consequence to us right ok. Now, here too guys here too I can split it into kind of I can bunch it into 2 you know groups. What are the groups? So, this would be equal to I can write.

So, I can write psi e prime then I can write mu e this is star psi e double prime like this I always forget the volume element which is d tau e then psi v star psi v double prime t tau N ok. I have already clumped into 2 I have already clumped into 2 right ok. So, this represents what? This represents what?

This represents an electronic transition. This represents an electronic transition between 2 states psi e double prime which is the ground state psi e single prime which is the excited state right. I should not be writing psi double prime. Well, psi double prime is essentially means the ground state, but just keep that in mind ok. Double prime is the ground state then mu e.

So, you take your dipole moment operator mu electronic you operate on the ground state psi double prime where do you end up in where do you end up. You end up in psi e single prime. So, this is your electronic transition this is your electronic transition; this is your electronic transition.

Now, what am I left with I am left with 2 vibrational wave functions. One vibrational wave function belongs to the electronic ground state the other vibration wave function belongs to the electronic excited state. Now, tell me this is an overlap actually, but tell me would this be 0 or not?

Hey, if this is 0 you know the answer is not 0 right because everything goes to 0 there would be no transition no spectroscopy we are not be talking about this right. So, you can safely now say that the answer is?

Student: 1.

Hold on.

Not so quick that the answer is not 0.

Right, the answer is not 0. Now, tell me why is it not 0? Why was the previous one 0? Why is this not 0?

Student: There is a (Refer Time: 30:06) co-relateing term.

There is a.

Student: Co-relating term between the excited state or ground state.

Well, I mean this is an overlap term we are looking at. This is an overlap integral you are looking at. Why is it not 0? The the other one was also an overlapping in that sense, why is this not 0? Why was the previous one 0? What is the difference?

Student: Operator.

Operator right operator you are in the right direction. Is the operator same or not? Hey listen when you are doing the electronic when we are solving for the electronic you are solving with only one Hamiltonian right. When you go to vibration what happens. When you go to vibration you not only have your kinetic part you also have a potential energy part half k x squared right.

Now, think about this when you are; when you are doing a transition in most of the cases what would happen is you would give rise to a change in bond order possibly in most of the case bond order even you are shifting in distance; that means, there would be a shift in the equilibrium geometry.

Well, it does not matter. The point is if your bond order is changing; that means, a force constant is changing what is the potential for a harmonic oscillator half k x squared ok. But that k x squared k is defined for each and every electronic state. So, that means, if you have the ground electronic state your k would be k ground. If you have an excited electronic say your k would be k excited and in most of the cases is k excited would not be equal not be the same as k ground otherwise you will not be observing any change at all.

So, that means, when you are going when you are solving for these 2 vibrational levels your Hamiltonian has already changed and please remember now they do not form an orthonormal set anymore because your Hamiltonian is changed. Is this clear or not? It is not clear.

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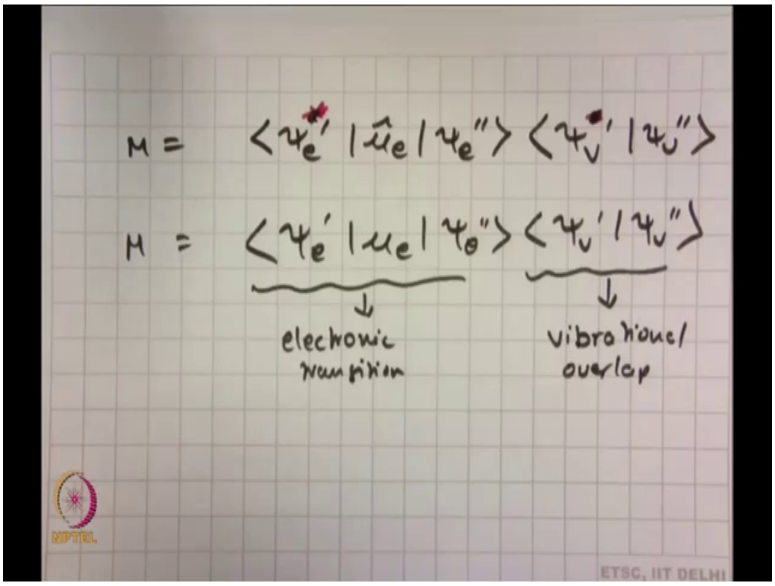

$$M = \langle \psi_e^{*\prime} | \hat{\mu}_e | \psi_e'' \rangle \langle \psi_v^{*\prime} | \psi_v'' \rangle$$

$$M = \underbrace{\langle \psi_e' | \mu_e | \psi_e'' \rangle}_{\text{electronic transition}} \underbrace{\langle \psi_v' | \psi_v'' \rangle}_{\text{vibrational/ overlap}}$$

So, let me write this and I will explain. So, going forward then M the going forward then M can be written as this can be generalized as this I can write it as psi e mu electronic. So, this is e means electronic psi e right double prime then I can write psi v prime sorry just making a mess of it anyway sorry.

So, do not write this star here please remove the star rewrite again psi v double prime. So, this is essentially is psi e prime mu e psi e double prime psi v prime psi v double prime ok. So, this is what your M is. This is your electronic transition as I wrote last time. This is referred to as vibrational overlap this is referred to as vibrational overlap right. It is overlap between two vibrational wave functions.

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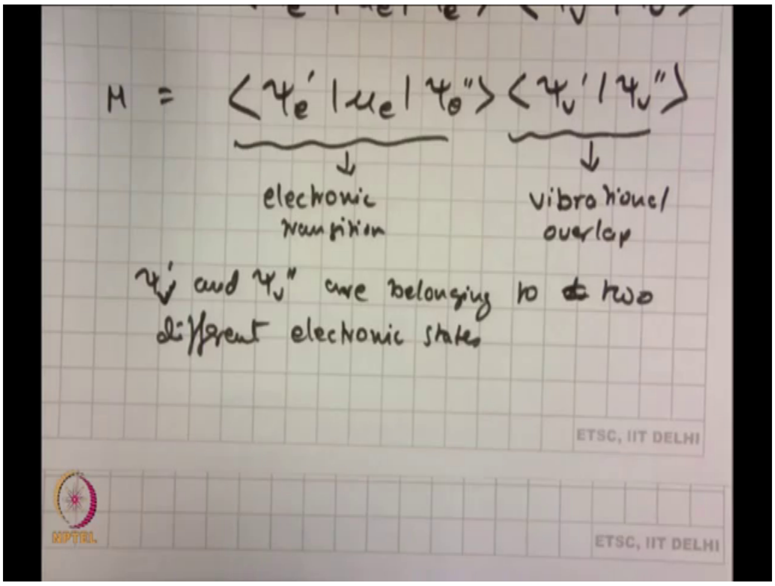

$$M = \underbrace{\langle \psi_e' | \mu_e | \psi_e'' \rangle}_{\downarrow \text{ electronic transition}} \underbrace{\langle \psi_v' | \psi_v'' \rangle}_{\downarrow \text{ vibrational overlap}}$$

ψ_v' and ψ_v'' are belonging to two different electronic states

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So, coming back to our discussion; coming back to our discussion. Psi v prime and psi v double prime are belonging to two different electronic states are belonging to two different electronic states first keep that in mind. Now, if that is so; if that is so think about this. We were briefly discussed in this last class.

If you take ethene right or ethylene what you would do is, you would do an excitation; that means, your homo which is highest occupied molecular orbital is filled with 2 pi electrons right. You do make a transition from homo to lumo what happens is you have 1 electron in antibonding orbital essentially if you go by molecular orbital theory.

Initially a bond order was what 2. Now, when you go to the excited state what is your bond order? 1 right. Because the bond order is 1 you know if you would ever want to do a cis trans isomerization on substitute ethylenes you do an excitation and because then the bond order is 1 it will just move around the bond and then when it relax you might get an equilibrium between cis and trans depending upon what you start with right.

Now, that is the way of doing an isomerization, but anyway the idea was this. Your Hamiltonian for harmonic oscillator is what? It has a kinetic energy term and it has a potential energy term.

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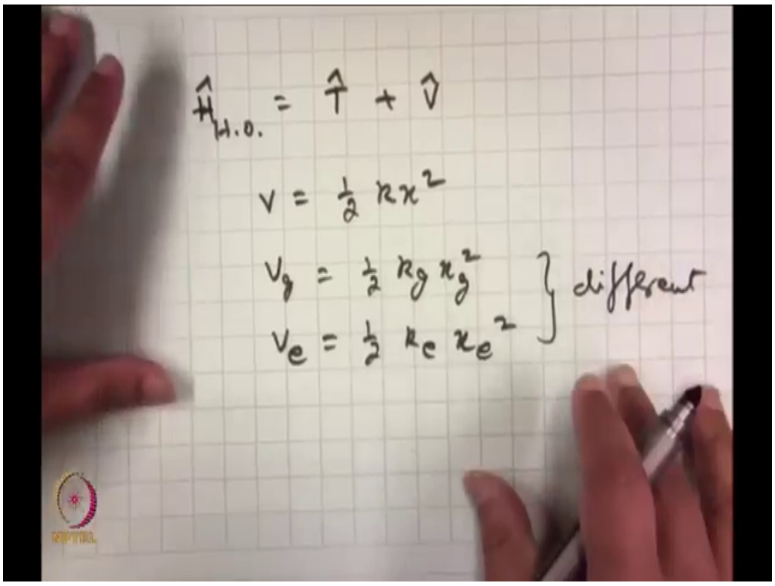

$$\hat{H}_{H.O.} = \hat{T} + \hat{V}$$

$$V = \frac{1}{2} k x^2$$

$$\left.\begin{aligned} V_g &= \frac{1}{2} k_g x_g^2 \\ V_e &= \frac{1}{2} k_e x_e^2 \end{aligned}\right\} \text{different}$$

So, for a harmonic oscillator for Hamiltonian of a harmonic oscillator HO a harmonic oscillator would be given by a kinetic energy term and a potential energy term. Now, if you are considering a linear; that means, a harmonic oscillator in 1 dimension say x what is v equal to half k x square, where x is the amount of change you do from the equilibrium position right ok.

Now, tell me this. If I am doing an ethylene right if I am doing an ethylene transition 1 electron goes to the anti-bonding in the ground state v ground would be half k ground x square right ok.

Let this be x g v excited would be half k excited x e squared. Now, this you should be able to recognize because this is a fundamental importance. The moment you make a change from a double bond to a single bond is not your first constants changing. It has to change right because you look at the ir frequency c double bond c single bond c all these frequencies come at different places one bond is stronger than the other bond.

So, that means, if you are making a change from double bond to a single bond would not k change to. Now, the moment k changes because your k is intrinsically involved in the Hamiltonian is not your Hamiltonian changing to. Do you understand that or not?

Because your potential is now changing because you have moved from one potential energy well to another potential energy well. Now, because your Hamilton has changed no longer are they orthogonal because they do not belong to the same Hamiltonian. That was how you define an orthonormal set if you go back to your postulates ok.

So, that is why psi v times psi v prime time psi v double prime in general is never 0. Only in certain cases now you can tell me when can it be 0? It can be 0 only when the potential energy in the upper excited state looks very similar to the potential energy in the ground state.

Only in that case would there will be no vibrational overlap essentially that is what you are saying that means, this one would be almost gone ok. So, then what we can write down is based on this discussion so that means, these are different.

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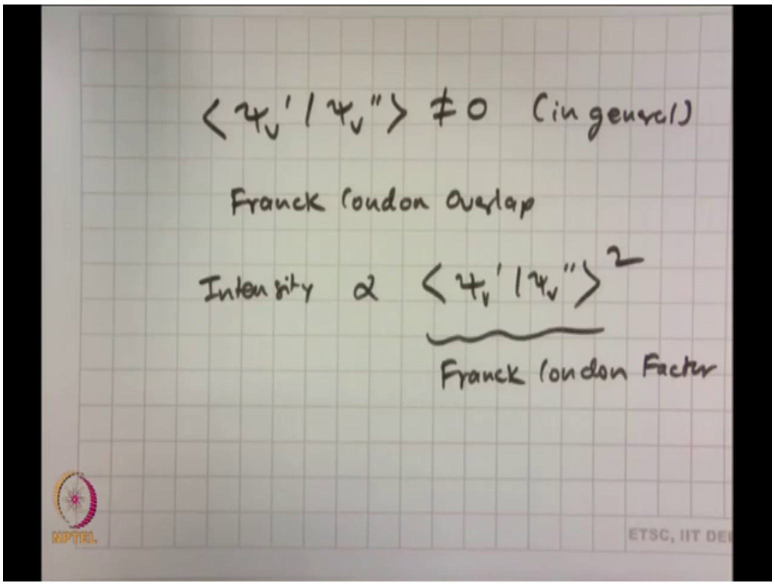

$$\langle \psi_v' | \psi_v'' \rangle \neq 0 \text{ (in general)}$$

Franck Condon Overlap

$$\text{Intensity} \propto \underbrace{\langle \psi_v' | \psi_v'' \rangle^2}_{\text{Franck Condon Factor}}$$

So, based on this what we can write down now is psi v prime psi v double prime is not equal to 0 in general. So, this guy again was referred to a overlap integral it is called the Franck Condon overlap it is referred to as the Franck Condon overlap it is referred to as a Franck Condon overlap,

And the intensity of a transition whatever intensity of a transition you see is essentially proportional to the square of this is essentially proportional to the squared of this. So, for example, the intensity is proportional to psi v prime psi v double prime squared and this square is called Franck Condon Factor.

This is called Franck Condon Factor. So, Franck Condon factor is just the square of your Franck Condon integral or overlap integral right that is the essentially word means. So, what we just saw is that if you would ever want to know on what the intensity of a transition would depend it would depend upon this the square of this Franck Condon overlap. So, instead of dealing with the square it is easier for us to just deal with the overlap ok. We just then we will square it later right ok.

So, again having said this; having said this what would the equation number be for this one. So, what was the last equation? M I did not keep an equation here. So, if for 7 this one would be 8 is it. If this one is 8, then I can say this one is 9 ok. Now, guys coming back to what we had derived before this N has 2 parts; one is your electronic transition and the other one is a vibrational overlap.

Now, do you; now do you realize why it is called a vibronic transition. It is called a vibronic transition because when you derive the expression for M it is just not either vibration or not only electronic it is what?

It has the electronic transition moment integral times what the vibrational overlap and these 2 give rise to a transition which is referred to as a vibronic transition; that means, whenever you are doing an electronic transition you will also have possible vibrational overlap and that is vibration transitions would be ocurring too. Is it clear? What do you mean by vibration vibronic transition?

So, you would see so that is why you would see vibronic vibrations give rise to mixing of states. So, you would see that there are many transitions which are not allowed, but because of mixing they actually get allowed. You have you guys have all read a lot of you know these spectroscopic these things like laporte forbidden and all these things right ok. This is essentially come from here.

Even if some transition is forbidden you would see there is you know a little evidence of the transition occurring still and because of these mixing of wave functions you know that is where it comes from, but anyway.

So, that is not a point of discussion right now. So, again this M is a transition moment integral. This is what defines the probability of a transition. The probability is essentially the number of molecules which would end up there in the excited state and then the number of molecules would easily transformed to what the intensity you know the intensity of your transition essentially and hence intensity is proportional to your Franck Condon overlap squared.

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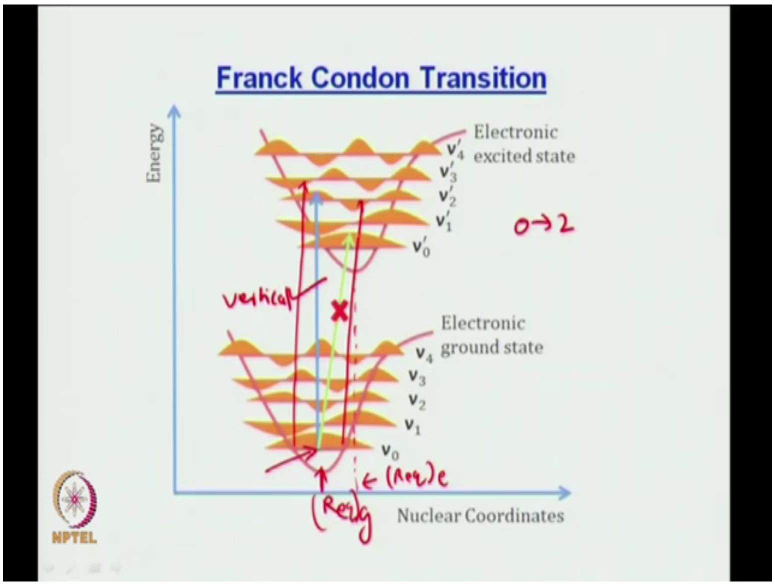

Franck Condon Transition

So, now coming back to see some of these effects on the slides; so, let us look at this; so, this was a Franck Condon transition ok. So, this was a Franck Condon transition as I said I will always go with a vertical transition. So, this is the vertical and I would never go for this I can never have a change in nuclear coordinate. Now, what you can see here is see this is very important. You look at the blue one right you look at the blue one.

In the ground electronic state you have vibration levels. So, v 0 v 1 v 2 in the excited transition you also have vibrational levels you have to have right. Now, if you are talking about the ground electronic state which vibration level would be most populated? It would be v 0 ok.

So based on room temperature based on thermal energy, based on Boltzmann population most of the molecules the major share of the molecules would be in v 0; that means, whatever transition you are looking at from the ground state would essentially happen from where? Would essentially happen from v is equal to 0 good.

Now, if you look at the wave function where does it max? The wave function max is in the middle right. So, then if it is the middle of the well I mean this is your well if it is the middle of the well then the transition the maximum probability of the transition would be occurring from the middle. So, that is why you see this is occurring from the middle. Now, because the transition is vertical this would not care what has happened in the excited state. It will just go up vertically straight [FL] fine.

So, now it goes up vertically straight. Now, what do you see is when you go and look at the excited electronic state is the excited electronic state same or different from that of the ground state. In what way is it different tell me? There is a difference in what way is it different? Tell me the most obvious way it is different. What has happened?

Student: The nuclear coordinate (Refer Time: 44:03).

The nuclear coordinated has changed; that means, if this is your; if this is your R equilibrium for the ground state; that means, for the ground state the R equilibrium for the excited state has not changed? So, this is R equilibrium for the excited state has not that changed; that means, what has happened; that means, the average distance or the equilibrium distance between the 2 nucleus is increased in the excited state.

Now, that is what we were talking about in the case of ethylene right if you would make it from a double bond to single bond obviously, it is length would increase; that means, the distance between the nucleus the 2 nuclear would increase the 2 atoms right. Now, the moment you have it shifted what has happened is the R equilibrium of the excited state is no longer on top of the R equilibrium on the ground state. Because if this is your R equilibrium of the ground state based on this it has already shifted here.

Now, because it has shifted here you see will it do a vertical transition where is the maximum overlap of this transition occurring; that means, in the ground state it is v is equal to 0 which state is it overlapping maximum?

The third one which is v 2 right so; that means, you can see the vibrational overlap which is the maximum which is going to give you the maximum intensity, which is going to give you the maximum intensity is the transition from 0 to 2 where 0 is the v 0 of the ground state electronic state and 2 is the vibration level with quantum number 2 of the excited electronic state ok.

Now, keep this in mind we are talking about the vibrational overlap this is what your Franck Condon overlap is. Because your overlap is essentially what? Psi v prime psi v double prime you know that is what you are looking at right. So, 0 to 2 would be giving you the maximum intensity in your transition.

Now, tell me would this be the only transition that is happening. First of all remember all the transitions have to start from v is equal to 0 level you have no other choice. Even if you have smaller transitions up there they would be very much of massed you have heard of something in vibration spectroscopy known as hot bands right. So, hot bands you know how hot bands come from so that means, if higher excited states.

Student: (Refer Time: 46:28).

Are populated right, but anyway without going there tell me what are the other or would there be other transitions possible in between the vibration levels. If they would be possible why would they be possible tell me?

See this is not the only transition try to keep that in mind telling you the answer this is not the only transition. If you look at a wave function a wave function is just not peaking at one point it is peaking at one point, but a wave function is it is like this it is and it is encompassing the whole place like this right.

So, this is your wave function. So, this is how your wave function goes along with the tunnelling parameters and all these things right. So, that means, if I am having electron density here if I am going to do the probability density then I will also be having electron density here; that means, I can also make a transition from here right.

How do I draw? I can also make a transition from here I can also make a transition from here so on right. So, you will see in the later slides what happens is you do not just get 0 to 2 because of this band; because of this band you will be getting multiple transitions right. It is just not one transition. Now, what are these transitions ok?

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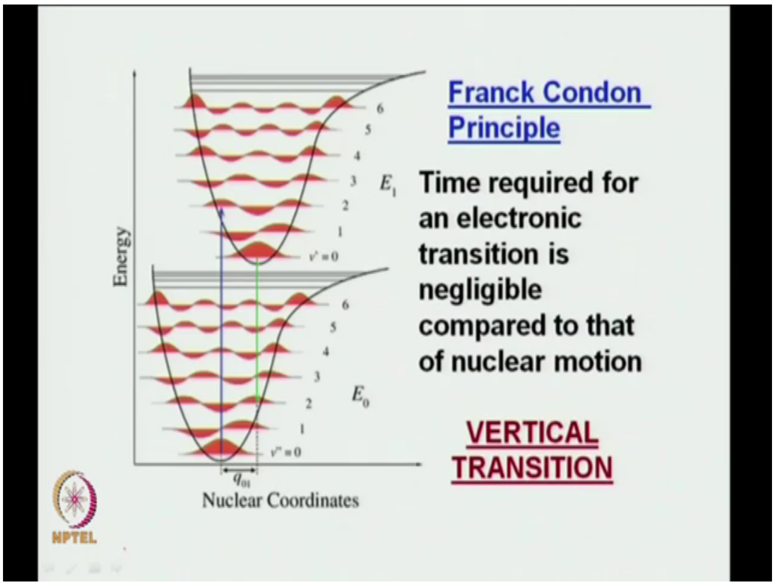

Franck Condon Principle

Time required for an electronic transition is negligible compared to that of nuclear motion

VERTICAL TRANSITION

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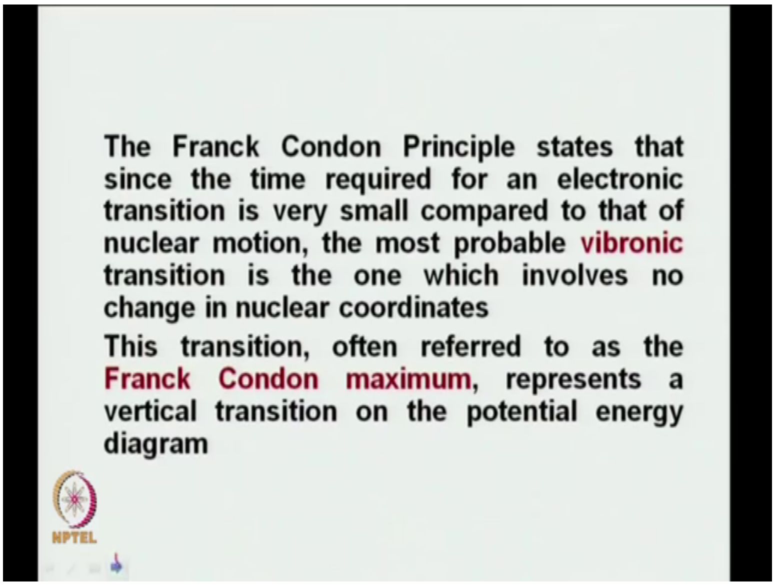

The Franck Condon Principle states that since the time required for an electronic transition is very small compared to that of nuclear motion, the most probable **vibronic** transition is the one which involves no change in nuclear coordinates

This transition, often referred to as the **Franck Condon maximum**, represents a vertical transition on the potential energy diagram

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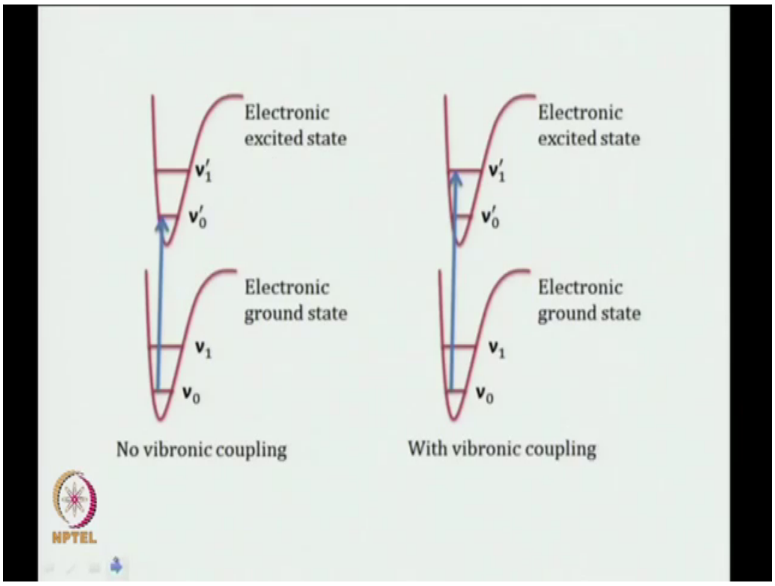

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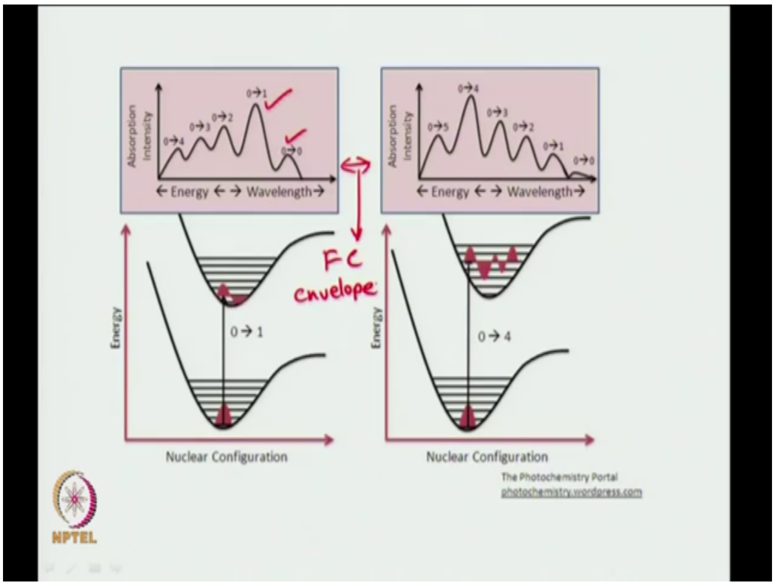

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Let us just avoid this right now go to the transition and let look at it here. This is what I was talking about. So, look at this. On the left panel, you have a nuclear configuration. In this nuclear configuration, you have a 0 to 1 transition. The 0 to 1 transition is your highest the 0 to 1 transition means from v is equal to 0 in the ground state to v is equal to 1 in the excited state right.

Now, this is your absorption intensity; that means, the intensity of a transition the intensity of a transition. Now, look at this 0 to 1. You can see has the maximum intensity because that is the most probability transition that is happening. What is it defined by? It is defined by the overlap of a vibrational wave function the Franck Condon overlap. The higher is the value the higher is the.

Student: (Refer Time: 48:41).

Intensity. Now, because of this band it is not. So, because of this band; because of this band the other transitions like 0 to 4, 0 to 3, 0 to 2 would also be there; that means, if 0 from 0 to v is equal to 3 from v is equal to 0 to v is equal to 4 and so on. But, because here the vibration is not as high the extent of the rather vibration overlap is not as high as that for which one 0 to 1 hence their intensities would be lower.

Now, the 0 to 0 transition you can see this is the 0 to 0 transition we can see this 0 to 0 transition what is the 0 to 0 transition mean to you? A 0 to 0 transition means you are going from v is equal to 0 in the ground state to v is equal to 0 in the excited state. Now, this 0 to 0 transition is referred to as a purely electronic transition this 0 to 0 transition was 0 to 0 traction is referred to as a purely electronic transition.

Do you know why? Why? Because, in the electronic ground state your molecules are populated in the v is equal to 0. In the vibrational state rather in the excited state the molecules are also there in the 0 level. See if you are doing a 0 to 0 the molecules have to be in the 0 vibrational level right.

There is no other way they have to be in the 0 vibration level; that means, you are making from 0 to 0. No other vibration level in the excited state is involved in that transition corresponding to that wavelength or that frequency and it is referred to as a purely electronic transition.

Now, similarly look at this. Let us next look at the right panel. See in the right panel what has happened is the R equilibrium has shifted a lot. Because the R equilibrium has shifted a lot as opposed to the previous case where 0 to 1 was a maximum transition in this case it is no longer 0 to 1.

What is the maximum density? It is not 0 to 4. If it is 0 to 4 again simply because the wave function of your fourth vibrational state in the excited state has the maximum overlap with the wavefunction of your v is equal to 0 in the ground state and that is why it has a maximum intensity out there again as simple as that. But, again because if you have a band and hence you would be looking at an envelope of transitions.

So, this guys whatever this you are looking at. These 2 this is referred to as a Franck Condon envelope this is referred to as Franck Condon envelope. Franck Condon Franck Condon means it is a vertical transition why is it envelope? Envelope means it is just not one transition it is encompassing or it is enveloping under the shed a series of transitions 0 to 1, 0 to 2, 0 to 3, 0 to 4 and which one will be having the maximum intensity would be defined by the overlap integral essentially that is how it goes right.

So, this is also referred to as you know vibronic overlap or rather vibronic envelope rather or Franck Condon envelope and this is often seen this is often seen if you would take absorption spectra specially of well organic molecules if you take absoption spectra you would you would often see bands coming up like this which are referred to as a vibronic bands.

And a vibronic bands just tell you that I have or you have excitations to higher vibrational levels in the excited state starting from the ground state vibrational level of your ground state of a ground electronic state.

So, just to wrap this up; so, I have talked about the vertical transition. So, again the Franck Condon Principle states that since the time required for an electronic transition is very small compared to that of nuclear motion the most probable vibronic transition is the one which involves no change in nuclear coordinates that we know.

Next this transition often referred to as the Franck Condon maximum represents a vertical transition on your potential energy diagram. This we have seen. Now, what does this say? Look at the left panel it says no vibronic coupling. Why does it say no vibronic coupling?

Now, look at this what has happened is; what has happened is your R is equal to 0 rather your R equilibrium in the ground state and your R equilibrium in the excited state are very similar can you see.

So, this one and this one they are almost at the same R; that means, your equilibrium distance is not shifted between the nucleic. Because it has not shifted guys because it has not shifted because it has not shifted so v is equal to 0 level would be right on top of v is equal to 0 level. So, v is equal to 0 in the grounds in the excited state would be right on top of v is equal to 0 ground.

So, which one would be having the maximum overlap anyway? The 0 to 0 transition and because it is 0 to 0 transition if you as I said if you are talking about any electronic state your molecules would not be having a choice, but to stay in this v is equal to 0 state. So, that means, this is not involving any higher vibrational levels and hence it called a pure electronic transition no vibrational levels involved that is what a 0 to 0 is ok.

So, now you can understand how do you get vibrational bands, how do you get vibronic bands. So, if you go to the next one what has happened is now it is no longer the R equilibrium is no longer the same in the ground and excited state shifted and the moment you shift the transition remaining a vertical transition it will still go up, but it will overlap with another v in the excited state.

So, say in this case it is v is equal to 1 and because you are having a change in the vibrational condon number say from 0 to 1 these being of two different electronic states here you are having vibronic coupling ok; that means, this is a vibronic transition where you not only having electronic transition.

Electronic transition means that you are going from S 0 to S 1 or ground electronic state to excited electronic state that itself is an electronic transition. Not only that, but also when you moving the electronic electronically excited state you are occupying higher vibrational levels of the electronic state right and that is why it is called a vibronic transition ok.

So, we will stop here. So, this is essentially what your absorption spectroscopy is all about in terms of the theory. If you are talking about fluorescence, which we will do in the next class. Fluorescence is just a reverse of this. See you would see if you are getting an absorption overlap for the your overlap in the absorption you are going to get a similar overlap in the fluorescence because those are the ones which are going to come down vertically too right giving rise to something known as mirror image symmetry.

So, and after that we will move on to Lambert Beer law look at some issues and absorbance and try to move into fluorescence ok.

So, that is it for today.