Advanced Chemical Thermodynamics and Kinetics

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Lecture - 19
Advanced topic in chemical kinetics – I

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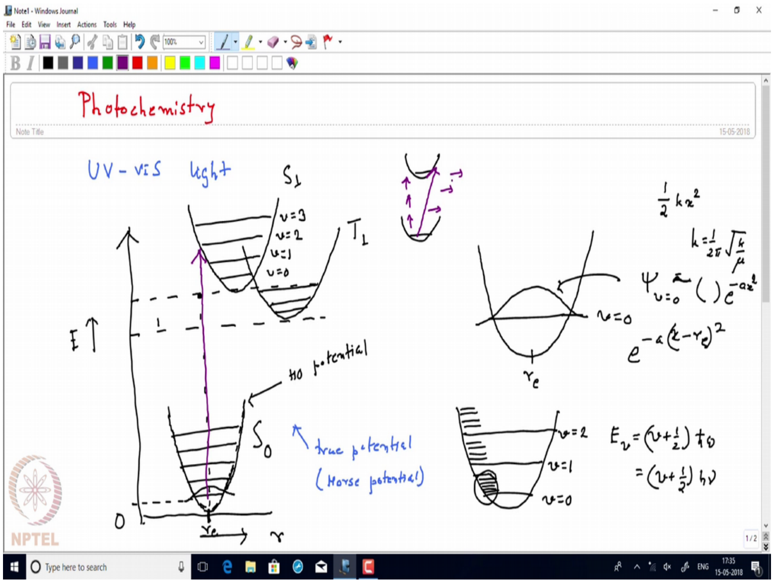

Hello everyone. So, in this lecture, we will discuss about photo chemistry or the basic aspects of the photo physics of an molecule. So, we call it as photo chemistry. Now, as the name suggests, so this photo chemistry means, what is the chemistry, which is induced by photon or light. And photo chemistry is the (Refer Time: 00:45) process, and will only discuss very fundamental aspects of photo chemistry like what are the how we define phenomenologically the different processes that are involved in photochemistry.

Now, when you talk about photo chemistry, I usually, I mean referred to photo chemistry that happens in the ultraviolet and visible range. So, we are calling photo chemistry by the ultraviolet and visible light. There can be infrared photo chemistry; we will come back to it at the very end. Now, UV and visible means, actually here the electronic states of the molecules are get excited. And many processes actually happen, and we will just review those processes one by one. Now, that is the first aspect. And the second aspect is that one thing, we have to I mean you have to know is that the basic fundamental aspects of molecular quantum mechanics, like what are the energy levels of the molecule. Like any molecular energy level can be partitioned as electronic, then vibrational, then rotational, and translational energy levels.

Now, translational energy levels, we are not going to discuss, because, we are only going to discuss, how the internal energy levels are populated for this discussion. Even rotational energy levels also, I am not going to discuss. So, what we are going to discuss is right now is that all of you know that suppose, if I take if I want to represent the potential of an of a bond chemical bond, and it is a ground electronic state. So, the potential looks like something like this. So, this is an called an un harmonic potential. And we discussed it in we have discussed most likely or we will be discussing it many times.

Now, let me draw it a little bit more clearly, so we will use a different color. So, what I am showing here is harmonic potential well. And on top of it, I am showing the real potential felt by a molecule. Now, as you can see at the very close to zero level. Zero level in the sense close to the ground electronic level. The energy levels or the potential, actually looks like or can be approximated as a harmonic potential.

So, this is the harmonic oscillator potential, and this is the true potential, true potential, which I mean can be to an very good approximation, can be approximated by the Morse potential. So, Morse potential is in analytical form of anharmonic potential or you can actually have the harmonic potential. And then, you can actually expand it in terms of non-linear terms as we do in Taylor expansion.

Now, suppose this axis is my energy axis; this vertical axis; so, the energy varies according to along this axis. And this axis is nothing but the say bond length a typical bond length. So, here I have the equilibrium bond length. Now, we have many energy levels. Let us talk let us approximate, it as a harmonic oscillator. Although at a very high energy level those to the dissociation cannot make that approximation, but just for the sake of argument, let us think that we are approximating, it to be an harmonic oscillator.

Now, as you can see in the graph, this is basically the ground electronic state. And suppose, this energy is zero here, that is the zero of energy that is the reference zero of energy. And then, you know that the molecule should have a minimum energy, which is equivalent to its zero point vibrational energy. And each vibration like, if I kind of zoom it here, so I have a harmonic oscillator like this. Suppose, this is the zero point energy;

this is the v equal to 1 energy; this v equal to 2 energy. So this is v equal to 0; this is v equal to 1; this is v equal to 2; where v is the vibrational quantum number.

And the energy levels are at the energy expression is v plus half h bar omega or you could write it in terms of the, so omega is the angular frequency or you can write it as a circular frequency. So, then actually we write it as h new. And then each the each of this vibrational level will be will have actually many many rotational manifold that, so that we are not showing, and each rotational manifold may also have degeneracies, actually they have degeneracies.

So, all these finer energy level structures, we are not considering right now. And similarly, if it is confined in a in a suppose these molecules are in a gas phase, and they are confined in a in a container. So, then we know that for a particle in a confined box. We also have energy levels quantized, energy levels for translational motion. So, this rotational levels will also further be have, each rotational level will have a further translational manifold, but those things we are not discussing right now.

Now, we will restrict ourselves with electronic energy levels with a vibrational manifold. Now, there is a Boltzmann distribution law, and in the Boltzmann distribution law, you know that if I calculate how many molecules are sitting at the ground electronic state and the ground vibrational state, you will find that most of the molecules are at room temperature will sit in the ground vibrational level.

Now, I have shown here, as like I have drawn a curve like this. Now, what is this curve, so this is my potential, and this is v equal to 0. And I have drawn a curve like this. Now, this is nothing but the v equal to 0 wave function. So, as you know that these wave functions are basically solution of the Schrodinger equation; If you use the potential in the time dependent Schrodinger equation to be just the harmonic potential one dimensional harmonic potential, which is half k x square.

If I use that then and k again k is basically, 1 over 2 pi root k by mu. So, if write all these equations, so then you will see that these wave function will be of the form of a Gaussian wave function. So, it will it will go as an with some constant, which is that the normalization constant. And then it will be something like e to the power minus a x square. So, this is a Gaussian function. And in to be more specific precise, it will be e to the power of minus a x minus r equilibrium square. So, r equilibrium is the center. So, the Gaussian is centered around the equilibrium position, and this is basically the wave function.

Now, for an excited state, as you can think excited electronic state, where will be the potential energy well will located. Suppose, this is the excited electronic energy levels this is the 0. I mean minimum energy for the excited electronic energy level. Now, the question is the question is how the potential well will be placed with respect to the ground state potential well. Now, you know that there are two interesting thing that do we often get. students often get confused.

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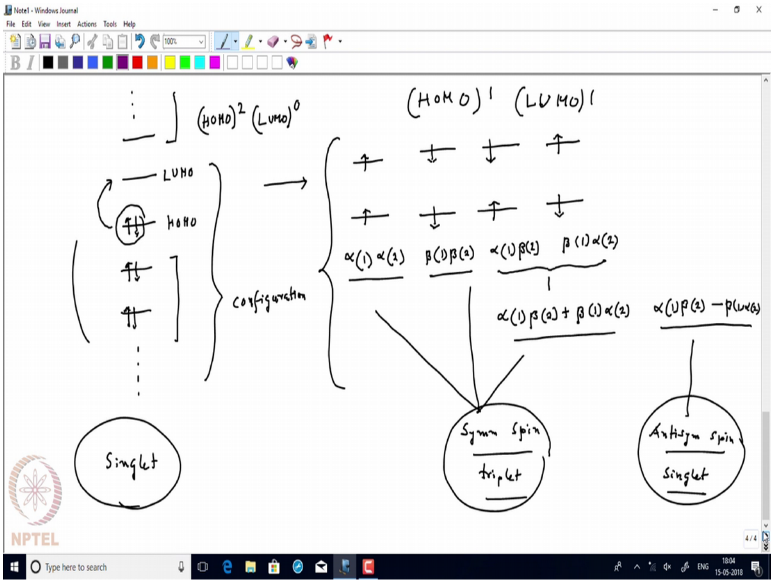

Suppose, I have in a molecular energy level, I am showing like this. And suppose I have energy levels, so how do you get this molecular energy levels, you solve the Schrodinger equation. And you get some molecular energy levels. Now, the question is this level we call it as homo, because it is the highest occupied molecular orbital. And this level I call as lumo, the lowest unoccupied molecular orbital. Now, suppose we are exciting this molecule meaning, I am pulling one electron to this level. And if I do that only with respect to the homo and lumo, because all other energy levels will be unperturbed.

So, there are energy levels these are called coordinate electrons. And there are also high unoccupied energy levels that we are not writing. So, we are only consent focusing our self on the homo and lumo. Now, the configuration will be like this. Now, you have an interesting situation here, depending on the spin. Because, as you can see the way I have drawn it, this is just one of the possibilities. The both spins can be up, one spin can be up, one spin can be down. In the ground state, as you see that the both spins have to be paired up because of the Pauli Exclusion Principle. And then I can have one up one, so both can be down.

Let us draw it first. So, both can be up; both can be down; one can be up; one can be down. And similarly the other possibility that of the up down, it is the down up. Now, electrons being fermions are indistinguishable. So, you cannot distinguish, which one is up and which one is down. So, when you write the wave function for all of them, what you do is that suppose I call the up spins as alpha. So, for this state the total the spin, but the spin state can be represent as a alpha 1 and alpha 2. So, electron 1 is in alpha state, electron 2 is also in alpha state. Similarly, the down spin if I represent as beta, so it will be beta 1, beta 2. And then this one is nothing but alpha 1, beta 2. And this one is nothing but beta 1, alpha 2.

Now, this is an unique configuration. In the sense that if I exchange the electrons like, if I put alpha 2 and alpha 1, that is exactly equal to alpha 1 into alpha 2. So, back after exchange of the two electrons, so the sign of the wave function is not changing, which means actually this is a symmetrical function. This is also symmetric.

But, here you cannot say whether it is a symmetric or anti-symmetric, because these wave functions I mean electrons are indistinguishable. You cannot say that, which one is up or which one is down. Now, for that actually we take a linear combination of these wave functions. And we write it in the way that I will if I take linear combination, I will have two possibilities beta 1, alpha 2. And also another possibility alpha 1, beta 2 minus beta 1, alpha 2. Now, this is the symmetric combination.

Now, as you can see that if I exchange 1 and 2 labeling, so it will be alpha 2, beta 1 plus beta 2, alpha 1. But, that is exactly equivalent to the original configuration. However, if I change electron 1 and 2 here, so I will have originally the wave function is alpha 1, beta 2 minus beta 1, alpha 2. And that time it will become alpha 2, beta 1 minus beta 2 alpha 1, which is negative of the original wave function. So, this is an anti-symmetric combination. So, these three are basically symmetric spin part, and this is basically the anti-symmetric spin part. And this three symmetric spin part, actually form a triplet, and that is the triplet state of the molecule. And this forms a singlet state in the molecule.

However, the interesting thing here is that when the molecule was in I mean all electrons are paired, so this configuration has to be a singlet, because all electrons are paired up. So, what I am saying here, right now there is something called electronic configuration of the molecule, which I have drawn here. Like I have energy levels, and what are the electronic configuration of the molecule. It is just like the atomic configuration, you have done in your high school. Like say for example, if I ask you what is the atomic configuration for lithium, so you say that 1 s 2, 2 s 1. So, 2 electrons are in 1 s, and then 1 unpaired electron in 2 s.

So, similar way molecules also have energy levels. And we have special nomenclature for them for them, and if I filling the electrons in the molecule in a similar way from lower energy orbitals first, and then the higher energy orbitals molecular orbitals in this case, not atomic orbitals, then we will get an energy and then we will get an electronic configuration.

Now, moment I promote an electron in the excited state, I actually have four different possibilities. And this four for the same configuration. And the configuration is one electron in a homo, and one electron in lumo. So, we call this kind of configurations together as homo minus, so basically homo has one electron, and in the same token like we do for atomic orbitals. So, it is nothing but homo 1 and lumo 1. And here it is nothing but homo 2 and lumo 0.

So, you promoted one electron to the lumo, but as you see that this actually corresponds to two different electronic states. So, this is basically configuration say particular configuration that forms a state, which is a singlet state. So, the ground state we said is this state is a singlet state. So, what we are representing here is basically state of the molecule. Now, every state of the molecule also will have some energy level. In the sense that now it is a singlet electronic state, and this singlet electronic state has now vibrational manifold.

Now, excited electronic state means, actually we promoted one electron to the homo and lumo. According to the electronic configuration, which is this configuration, but I can actually have four configurations. And these four configurations according to Schrodinger equation. They also have the same energy, because Schrodinger equation does not take into account of the spin energy. So, they are the same kind of orbital energies, and there they are also degenerate. But, in reality these something called Hund's rule. And Hund's rule shows that the triplet will be more stable than the singlet.

So, we will have basically two energy levels, where one is one will be say a singlet, and one will be say the triplet energy level. And each energy level will again have some vibrational manifold. Now, the question is if you think in this way what happened, when we got the way we actually had an excited state is something like this, I had an I have an homo. And then I promoted one electron, so where I am promoting the electron.

Now, usually up to homo these are actually called bonding orbitals. And the lumo is usually the anti-bonding orbital. So, once I am promoting one electron from the homo, to the one electron to the lumo. I my bond order actually decreases meaning I am having one electron in the anti-bonding orbital. So, the total bond order, which is defined as number of bonding electrons number minus number of anti-bonding electrons divided by 2 that is smaller number.

So, what is happening if I have actually one electron in anti-bonding orbital, and my bond order is decreasing. The bond lengths must increase the equilibrium bond length there is nothing called the fixed bond length. Because, there is an equilibrium bond length, and this is vibrating always, so that is why we have all these amplitudes of vibration. And that is why around the equilibrium position, I have a harmonic potential.

If I excite more the bond will vibrate with more amplitude, however keep in mind these wells correspond to a particular frequency. Because, it is a harmonic oscillator with a particular frequency. So, once I am going up and up the frequency does not change, only thing changes is the amplitude of the vibration. Now, so by that token I will have a singlet state, this singlet state equilibrium bond length will be actually shifted it has to be shifted, why because the singlet state actually corresponds to electronic configuration, where one lumo was promoted.

So, the potential well will be situated somewhere here. And it will have it is own energy level zero point energy level. And all this excited energy level v equal to 0; v equal to 1; v equal to 2; v equal to 3 something like that. Similarly, with the same argument there will be a triplet state also, but usually in the triplet you have more extension of the equilibrium bond length. And a triplet will be somewhere situated here. And these are suppose the triplet energy levels. Now, so this is the excited singlet and this is the excited triplet, but it is the first triplet that we see and this one was the singlet.

Let me, actually remove the dotted line or actually we can remove the blue curve totally. And we can approximate it to be the harmonic oscillator. And this curve, which was the ground state vibrational potential. So, this correspond to ground electronic state, which is also singlet. So, usually call it as S 0, because it is the ground state. We call it as S 1 state, it is the first excited singlet state. And we call it as T 1 state, because it is correspond to the triplet of the ground state. You can have triplet state also in the ground state, if we have an unpaired electron, otherwise you cannot have an sorry two unpaired electrons, otherwise you cannot have a triplet. If I have a one unpaired electron in the ground state, so then I will have a doublet, because the spin multiplicity goes as 2 S plus 1, so I will have a doublet state there.

Now, let us think that I have a molecule, where all electrons are paired, which actually happens with most of the chromophores, I mean chromophore means actually it is a it is a molecule or it is a part of the molecule that actually absorbs light in this UV visible range. Now, let us talk about a transition, which kind of transition let us say electronic transition. Now, what do we mean by an electronic transition I mean I mean, how do define an electronic transition. Now, when a photon gets absorbed, a photon of say ultraviolet and visible energy, so it is absorbed, and then the molecule is promoted from the ground state to the excited electronic state.

Now, this process happens very quickly in the sense that when these electronics transition happens, it happens so fast that the molecular vibrations are like kind of much slower than compared to this transition. In the sense that you can think that every bond is vibrating like this, but so that molecule was in ground electronic state, and suppose it was in a zero point vibration. Because, as I said most of the molecules will be residing at the ground vibrational level, and it is vibrating.

Now, when I am exciting it during that excitation, since electronic excitations are fast. Now, we can think it in loosely in that way that electrons mass is much much smaller than the reduced mass of vibration of a particular bond. So, you can think that just like, you had this analogy of apple, and earth that when apple falls on the earth the force acting between them is the same. So, apple is attracting earth, earth is also attracting apple. But, the there is a huge difference in the mass. So, the acceleration for the apple is more. And you see practically that the apple falls it do not see the (Refer Time: 22:05) earth, actually moving towards the apple. So, it is the same analogy.

And the when the electrons move during an electronic transition, they are so light that their transition is extremely fast. And by that time scale the vibration there is no change in the vibrational coordinate. So, you can think that electronic transitions in this diagram, because the X axis is a vibrational motion coordinate. Because, it is bond a change in the bond length, when that transition happens a transition will be vertical. Vertical, in the sense that I am not changing my position, when I am doing the electronic transition, so any electronic transition in this diagram, and show it as a vertical crunch.

So, let me just draw a logical arrow. So, this is basically how we represent an electronic transition. If there was bond a change in bond length, suppose I had something like this. And I am starting from here, and if during the transition, I am having a change in bond length. So, then I can represent it like tilted arrow, because, as I am exciting up and up, and I am also shifting in this coordinate. But, yeah so it is it is not it does not make sense, so we could not make this approximation here. So, what we see here is electronic transitions are extremely fast.

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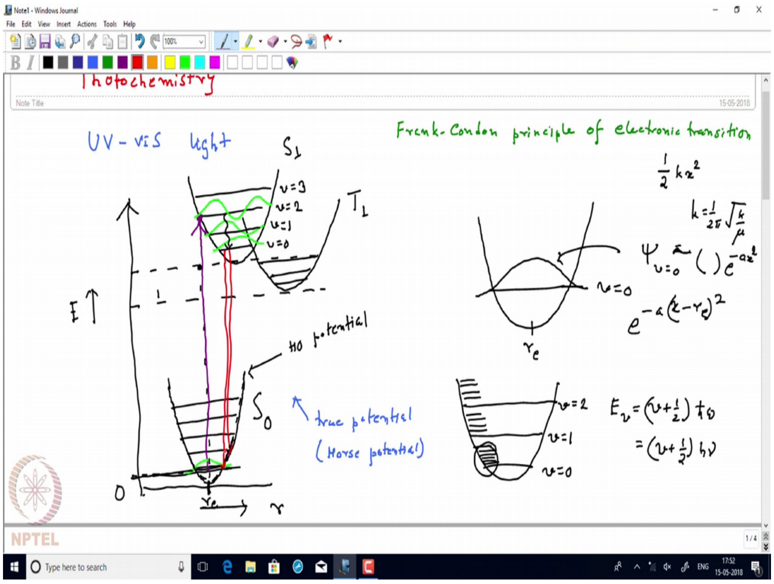

And then, we also say that this is a vertical transition. So, this has this has a name and this principle is mostly, you know what is the name of this principle. This principle is known as Frank Condon principle. So, this is known as Frank Condon principle of electronic transition or for electronic transition. So, it says that during the electronic transition, the vibrational motion will be fixed. And on this diagram, I can actually show the electronic transition sorry vibrational motion specifically frozen that there is no vibrational motion, during the electronic transition.

Now, what there is an alternative description, why actually the this arrow the way I have drawn it as you can see here. The point end point of the arrow is actually ending up here. So, this is a very important thing. Now, think about how the vibrational wave functions look like for an harmonic oscillator. So, let me actually use some other color.

So, as I said that ground vibrational ground vibrational wave function that looks like more or less as a not more or less it for a harmonic oscillator, it will be a Gaussian. So, here also to have a it will be a Gaussian. The excited vibration will actually look like something like this, because it has a node. The third one will look like something like this. So, what is happening here, when I am exciting and electron I am doing an electronic transition, since the upper well are the upper potential well they shifted. I cannot have the 0 0 transition to be the most predominant transition.

Let me actually give you a mathematical expansion for that, so the mathematical expansion is something like this. Suppose we have electronic transition and any transition, what we say here is that there is a transition dipole that is involved. Now what is the transition dipole, now transition dipole we kind of discussed earlier. And as opposed to a permanent dipole, and we said that there is kind of induced dipole, which is induced by the electromagnetic field or the electric field of light, and that induced dipole causes a transition.

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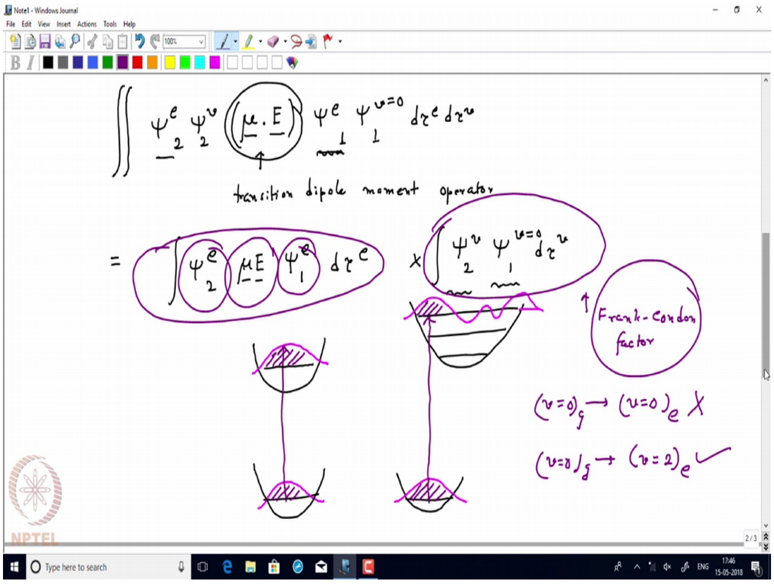

$$\iint \psi_2^e \psi_2^v \boxed{(\underline{\mu}\cdot\underline{E})} \psi_1^e \psi_1^{v=0} \, d\tau^e d\tau^v$$

transition dipole moment operator

$$= \int \psi_2^e \, \underline{\mu}\underline{E} \, \psi_1^e \, d\tau^e \times \int \psi_2^v \psi_1^{v=0} \, d\tau^v$$

Frank-Condon factor

$(v=0)_g \rightarrow (v=0)_e$ ✗

$(v=0)_g \rightarrow (v=2)_e$ ✓

Now, remember that I can write the total wave function as a product of say electronic wave function times the vibrational wave function. And suppose I am doing a transition from the ground state to the first excited state. Let me actually write this name electronic and vibrational in the end the suffix, electronic and this is vibrational, electronic and this is a vibrational. And suppose I am going from the ground electronic state, which is corresponding to sigh 1, and then I will end up in sigh 2.

So, there is something called transition moment integral. It is nothing but a dipole operator again it is it is a transition dipole operator that actually acts between these two wave functions. So, basically it couples the ground state with the excited state. Now, the ground state is so what is the ground state, ground state is basically and wave function that has an energy this. So, it has an elect electronic contribution as well as vibration as well as rotation, and translation that we are not considering.

So, a right now we are just writing it as a product of electronic and vibrational. And this dipole moment actually, which is vector quantity. And this mu dot E. E is the electric field is actually known as a transition dipole operator. Transition dipole moment or transition moment sometimes it is called. And this is of course an operator, because it is operating on the wave function. And then what we have to do we have to basically integrate over all possible coordinate. All possible electronic coordinate, let us say I am calling it as a d tau electronic, and all possible vibrational coordinate. So, it is it is basically a double integral.

Now, what you see here, this transition moment actually acts on the electronic transition. Because, we are not talking about a vibrational transition that actually falls in the infrared, because we shown you like UV visible light; so, it actually couples the electronic part of my wave function. So, this operator acts only on the sigh electronic part, this part it acts. So, I can actually separate out the integral, and what I can write is that this integral is nothing but electronic coupling mediated via this mu dot E, and between the ground electronic state, and the excited electronic state.

So, basically it is an electronic part of those two states. And then I have multiplied by vibrational integral, but which is just an overlap integral between the ground electronic states vibrational part and excited electronic states vibrational part. Now, ground electronic state vibrational part how it look like, it was basically all at v equal to 0, because ground state was always v equal to 0, because it started from v equal to 0 in the ground state.

And then in the excited state I can actually end up in some other state, but that will depend on the how I am positioned in the excited state meaning, it my wells vibrational wells are exactly top of each other something like this. Then you can see since the electronic transitions are vertical. Then I have a good chance that this and this will overlap, because I have a Gaussian here, and another Gaussian here. And then, if I think mentally that I am considering the overlap integral of these two Gaussians without moving my X axis, because, everything is frozen then actually I will have a good overlap between this two wave function.

Then the zero-zero transition will be maximum, but this is not the case. Why, because the in the excited state I already told the well has been shifted. It looks like something like this. So, what will happen I will start from v equal to 0, but I am trying to end up. Since, it has been shifted with some excited state wave function that has some amplitude of vibration at the corner. Because, if you remember that when I am exciting vertically, I am ending up in a corner, so that I will have some vibrational amplitude overlap, which is given by this Frank Condon factor. So, this is known as basically this vibrational-vibrational overlap is known as Frank Condon factor.

So, the electronic transition actually the strength of the electronic transition will depend on two things will depend it will depend on this particular Frank Condon factor, that it depends on any other factors also. But, right now will discussing only one thing that since the electronic transitions are vertical, and since the excited potential is actually shifted. Because, of the increasing bond length in the excited electronic configuration. And this excited electronic state represents this configuration among many other states.

So, in order to have a maximum vibrational-vibrational overlap, this will end up in some other electronic I mean the transition will be maximum for not for v equal to 0 in the ground state to v equal to 0 in the excited state. But, it will be maximum for say v equal to 0 in the ground state to some v equal to I did not know that way I have drawn it as it is v equal to 2 in the excited states, so which means, I will have a more Frank Condon factor for this state than this state.

So, this transition will be more stronger. Now, how this transitions will look like, so that we are going to draw. But, before that let us actually have a quick discussion on this part. So, as you can see here that we have a dipole operator here. And this dipole operator, we had already discussed that it goes as X, and so it goes as just a linear term. And then, so we discussed that whether if the what are the parity rule for a dipole operator, like this two wave functions should have opposite parity, otherwise this moment will be 0.

So, this part whether the parities are odd and even or even and odd something like that; so, it dictates whether the transition moment is zero or not, but he does not talk anything about how the whether it is if it is actually allowed transition how strong it will be, so that is I mean mostly controlled by this Frank Condon factor. And that basically talks about what is the overlap integral between the ground vibrational state, and some other vibrational state in the excited manifold.

Now, as you can see that the spectrum will have many different features that we are going to discuss right now. So, I will have an absorption spectrum corresponding to this electronic transition the way I have drawn it. And the absorption spectrum will be something like that that I am going from say v equal to 0 to v equal to all these states in the excited state. And one of them will be maximum, which is not actually v equal to 0.

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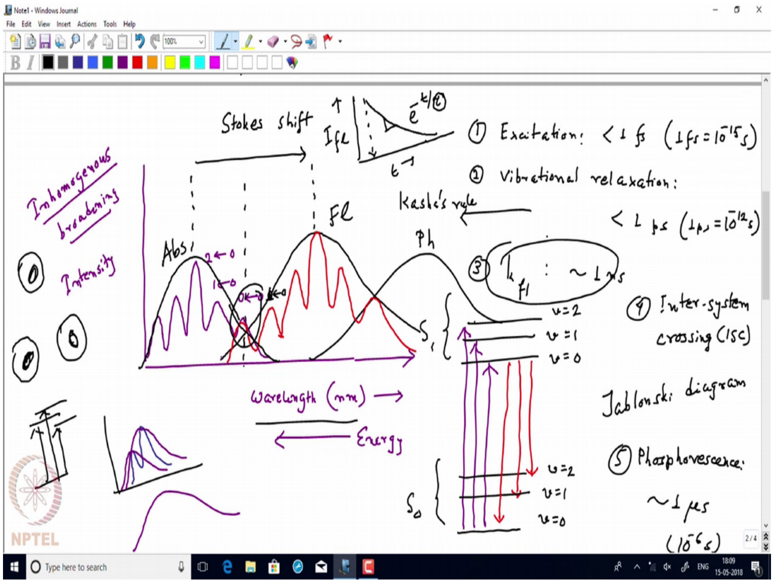

So, if I plot the absorption spectrum along this direction, so I will have v equal to so, suppose an plotting the intensity versus wavelength. A wavelength usually we denote in nanometer. So, the energy actually goes in this direction. So, this the inverse of energy. Now, and wavelength is increasing in this direction. Now, suppose these corresponds to my v equal to 0, 0 transition. So, we call write it as 0, 0 some textbook, actually write the final state in the first. So, they write it like this 0, 0 transition. But, the 0, 0 transition will be weaker than say 0, 1 transition. And that will weaker than suppose I I the way I have drawn it that the 0 sorry this is this should be written like this it will be 1, 0. So, this is the strongest transition.

So, the vibrational spectrum will look like a structured spectrum overall. So, it will have a structure like this. And as I see that in this structure will have basically kind of it is a very characteristic vibrational spectrum for the molecule that we have drawn. Now, you think about what will be the emissions spectrum or the fluorescence for this molecule. Now, once the molecule is excited, which is a very fast process, then the population will relax. And it will relax first vibrationaly, and that is known as a vibrational relaxation. And this vibrational relaxation is usually fast. So, within a time scale of one picosecond are so all the molecules actually come to the 0 vibrational level of the excited electronic state.

So, in the fate of the excited molecule, if we consider first thing will be first thing was basically our excitation, and that was extremely fast. If you asked what is the time scale actually, it is less than one frame to second. And one frame to second means actually 10 to the power of minus 15 second. And then the second thing is that fine it had an excitation. And the pattern will look like, it will be according to the Frank Condon overlap.

And we said that everything is starting from v equal to 0, but some v, which is not equal to 0, some higher v will have the maximum Frank Condon overlap. And for that we have a particular structure in the vibrational a vibrational electronic spectrum, which has a vibrational manifold. So, this is actually electronic spectrum, this falls in the every visible range. And then there will be a vibrational relaxation, and this vibrational relaxation is it usually competes within say 1 to 10 picosecond. And it is extremely fast, so again one picosecond is 10 to the power minus 12 second.

Now, then it says that all the emission will start from this v equal to 0 in the excited state. Now, this assumption that this vibrational relaxation will be fast; then this state say for example, v equal to 2 can actually radioactively emit to the ground state. But, that probability will be very low, because most of the population actually quickly leaves that v equal to 2, it comes to be equal to 1; it quickly leaves v equal to 1, it comes to v equal to 0, and there it stays for a while and from there it emits. So, we call this vibrational relaxation extremely fast, and everything arising from this v equal to 0, this has rule. And this is known as Kasha's rule. This is after, Michael kasha, who basically described this phenomenon in this way that this approximation that vibrational relaxation are fast, which is a fairly good approximation.

So, now this v equal to 0 state starts emitting, and it can start relaxing. And then, it can relax by say radiative relaxation, where actually this state emits and comes back to all these states, which are in the ground state. So, now you can think that there will be emission, which is exactly like an absorption from v equal to 0 to 0, which means actually just like our emission just like our absorption the emission will also be structured. But, this time I will have a 0 to 0 emission, but then I will have a 0 to 1 emission, I will have a 0 to 2 emission something like that. I have a 0 to 3 emission, now these 0 is in the excited state, and then it is coming back to the ground state.

And we will have a similar structure in the emission spectrum also. So, overall the emission spectrum will also look like something like this. It will also have a structure like this. And so we say that this absorption and emission spectrum looks like a mirror image, in the sense the 0, 0 transition as you can see here. Actually, overlaps very nicely because this is practically the same energy transition. And then you have 0 to 1 for the excited state, let me just write it like this. So, this transitions both are 0, 0 absorption and emission. So, this transition will be 0 in the vibrational sorry, 1 in the vibrational state say for example, and 0 in the excited electronic state. Now, this is the emission spectrum or the fluorescence spectrum.

Now, apart from fluorescence the molecule will also relax via non-radiative relaxation. Now, how this non-radiative relaxation happens, this non-radiative relaxation is basically, it can happen due to many process. Now, if it happens in the corner space, it can actually exchange energy with the surrounding and then through collision and many other process. And then it can quickly relax the energy as a thermal energy. And so the aim of the excited state processes will have both the radiative relaxation or basically the fluorescence. And the fluorescence life time the time it takes for to come back to the from the excited state is typically on the order of one nanosecond, whereas this non-radiative relaxation will be on the order of say it is a it is a fraction of nanosecond, it will be it will be less than a nanosecond.

Now, usually when you measure the fluorescence lifetime, you actually measured both the radiative and non-radiative lifetime together that is known as fluorescence lifetime. What is fluorescence lifetime, suppose I have an excited state, let me actually draw this diagram once again, so what I have drawn here, in the preceding page. I am trying to draw once again v equal to 0; v equal to 1; v equal to 2; v equal to 3; v equal to sorry this were all in the excited state energy level of S 1 level v equal to 0; v equal to 1; v equal to 2 something like that. And this all these levels where from S 0 level. All these levels of from S 1 level and then we had vertical transition arising from v equal to say 0 to 2, 0 to 1, 0 to 0, because everything actually starts from here. And then there is a rapid relaxation to v equal to 0.

So, when you start the emission, we start from v equal to 0 in the excited state. And as we can see that this 0, 0 transitions are basically the same transitions, like naturally draw this more precisely. And then we have all this energy, all this emission to the all other levels something like this. So, as you can see this 0, 0 transitions are basically the common transition in the absorption as well as in the fluorescence. And then I have kind of mirror image relationship, I have higher line absorbing states, and then there is a lower line thing. And then as you can see there is a shift in absorption and emission. This shift what this shift is coming from usually, you will see I mean this kind of nice structured spectrum, you will see only in gas phase.

Usually, in condense phase you do not see this kind of absorption and emission. Because, and particularly for two reasons, I will come to that. And you will see a structure less feature. And then you will see some absorption maximum, and some emission maximum. And that difference you call this as Stokes shift. Because, Gabriel stokes first talks about this shift, when DT is a classic experiments on fluorescence and this stoke shift also the term the same time also used for roman transitions.

There also we talked about difference between absorption and emission. And how much is the red shift in frequency, because if you see that this is actually a length scale, so we are going from the blue side to the red side. So, this is known as the Stoke shift, maybe I should draw the arrow like this. And so there is a characteristic shift from the absorption from I mean in the fluorescence spectrum from with respect to the absorption. And this extra energy shift means, actually extra energy has gone somewhere, this has been adjusted by that vibrational relaxation. And all other non-negative processes, because everything will come back again to the ground state. And due to this vibrational relaxation, that extra energy has been you can be a can be accounted for.

Now, this type of diagram were actually, we show the energy levels. And we show it as a vertical transitions, and about the singlet energy levels as well as the triplet energy levels. This is known as Jablonski diagram. But, the way we drawn it with the potential well it is a modified day Jablonski diagram. Now, the excited molecule can actually come from the excited singlet state to the excited ground state back to the ground state. But, there can be an interesting process this molecule are the population can also go our cross to the triplet state.

I know that this is basically a spinning forbidden process, because I am going from the singlet to the triplet. And this process is known as inter-system crossing, because ISC. Now, this ISC happens because of spin orbit coupling, and molecules in the excited they are singlet state. Actually, due to ISC goes to the excited triplet state, and then the excited triplet state can also emit radiatively and non-rediatively.

Now, you can see that when it emits, we have a problem here. Then the problem here is that it is actually emitting from the triplet state to the singlet state. And that emission, we call it as phosphorescence. And it has a huge long lifetime, because it is coming from the triplet state to the singlet state, and which is spin forbidden, and that we call as phosphorescence. So, this phosphorescence usually is long, and the typical time scales are on the order of one microsecond, which is 10 to the power minus 6 second 1 microsecond. So, thus we see that we can actually explain the several photo physical processes extremely, phenomenologically.

So, I will just give you a quick overview of what we have a quick summary about what you have discussed so far. So, before that I will just quickly explain, why these structures usually If you take a fluorophore in the gas phase, you will have nice vibrational features in the electronic absorption. But, you not see the same thing in Condon space. The reason is usually, textbook write that the molecules have many energy levels. And that is why you have a congested spectrum, and that is why all the lines there many lines. And it will be structure less, which is not very true.

Because, if you take even a fairly large molecule in gas phase, you will see some structure; and you can actually make those structures go far apart, because if you apply a electric field or magnetic field depending on the nature of those states. You can actually shift the energy levels by stark effect or Zeeman effect. And thereby actually, you can actually get a high resolution spectrum or actually the lines are for separated. And once you have these molecules this, which has a structure in the gas phase a small molecule or a large molecule, whatever it is.

In Condon space, you have a very interesting thing. And the interesting thing is that every, like suppose one molecule is there, and there is one particular transition corresponds to that molecule, which has a corresponding absorption in the spectrum. Now, what will happen one molecule, suppose I am showing this as a one molecule, and this as another molecule, this is another molecule. Now, the local environment around this molecule, will be very different than a local environment around the other molecule, meaning and there are solvent molecules around.

And the solvent molecules are actually dynamically changing their position. And they always interact with the molecules. And, so the molecular energies are shifted or perturbed. And as a matter of fact for one molecule, we might see this energy level. For the second molecule, you might see the energy level is little bit up. For the third molecule, might see that energy level is little bit down. So, these molecules although they are identical molecules. The local environments are so different, that is why their absorption becomes little bit broad.

Now, you can see I had one transition here. I had a let me just draw it in some with some other color. So, suppose I had two transitions to begin with, which are very nicely resolved transitions in the gas phase. Let me draw it like this. So, I have a transition, like this in the say in the gas phase. And this transition each of this transition, now the problem is that in Condon space, each will be now broadened, due to this local different different local environment of the molecules.

So as a result, you will see a very structure less band for these two things, where actually you cannot distinguish like are this individual absorptions are now so broad that they are they are kind of hiding in the in that absorption spectrum. So, the line shade actually becomes a broaden. And this kind of broadening mechanism is called inhomogeneous broadening. In the sense that in your sample the one you have different structures of the local environment, and which is pretty much inhomogeneous, because there is no homogeneity or there is no particular unique solvent structure around it, and that is why it is called inhomogeneous broadening or sometimes it is called as static broadening. I cannot explain you here why it is called as static broadening as offers to the dynamic broadening or so called inhomogeneous homogeneous broadening. So, those are beyond our discussion.

Now, let me just summarize what we have told, and we have actually talked about that electronic transitions here. And first thing, first you should remember that number one there is an electronic configuration for molecules, just like electronic configuration of atoms. And then one electronic configuration may correspond to one or several electronic states. Like all period of configuration has a unique state, which is the singlet state.

But, if I have two electrons in two orbitals, I have four possibilities, because one electron in one or the first orbital can have upper down spin. The second one for each of this up or down spin can also exist in a up and down spin. So, I will have two into two or four combinations. And those for four combinations are after we do the symmetric and anti-symmetric, I mean combinations can be grouped into three plus one. And those three we call as singlet, which is symmetric spin combination. And the one will call it as a singlet, which is the anti-symmetric combination.

So, I will have a singlet state and as a triplet state. But, usually the triplet is lowering energy than the singlet state the way we have drawn it. This is the excited strip triplet. This is the excited singlet. And this is the ground singlet. Now, what happens is that when I have an electronic transition, the electronic transitions are fast. And then also the excited well is little bit shifted because of the change in bond length. So, usually the vibrational overlap or the Frank Condon factor will be maximum for some vibrational level of the excited electronic state other than v equal to zero.

So, we will have a maxima, which is slightly shifted than the 0, 0 transition. And then what happens is that right of this transition, all the population actually comes back to the ground elect ground vibrational level of the excited electronic state from there it starts emitting. Now, it can rediatively on non-rediatively emit back to the ground singlet state, that will give you the radiative emission will give you structure in the fluorescence spectrum in the same token like, we had the absorption.

And then, it can also go to the triplet state via a process, which is a non-radiative process, which is known as inter-system crossing, which actually arises as a result of spin orbit coupling. And then from that the molecules can also emit back to the ground electronic state. But, since now the ground electronic state has a singlet state there is a spin it is a spin forbidden. So, the transition lifetime will be increased. And this radiative lifetime is usually falls in the order of microseconds that we call as phosphorescence.

As you can see that energy wise, like I excited and then there is a vibrational relaxation, then I fluoresce, and or I can actually go to the triplet state, which is even more down, and then I phosphor do the phosphorescence. So, the phosphorescence wavelengths will be even more red shifted than the fluorescence wavelength. So, I will have a phosphorescent spectrum. So, this is basically the absorption spectrum, this is the fluorescence spectrum, and this is the phosphorescent spectrum.

And phosphorescence is a longer life time component. Sometimes actually you might have the fluorescence having a longer life time component. Sometimes what happens, actually it comes to the v equal to 0. But, it actually goes to another state, which is lying nearby, because the way I have drawn, it is basically a few distinct states. But, in reality actually there will be many different electronic states lying around.

And then when I have that situation, then what will happen actually, now that population can go to some other state. And then it can come back later and emit that will increase the fluorescence lifetime it is called delayed fluorescence. Now, then if it is delayed fluorescence, you cannot distinguish just by measuring the lifetime, whether it is coming from the singlet state, whether it is a fluorescence or it is coming from the triplet state, whether it is the phosphorescence.

Now, to check that you can actually do this experiment in a magnetic field or static electric field and since the singlet actually does not split into further energy levels. So, its energy will not change, but every triplet will now split into three in the in the presence of magnetic or static electric field. So, every line in the phosphorescent spectrum will now split into three. So, the splitting is a characteristic feature of phosphorescent spectrum not a fluorescence spectrum. And if you have a longer lifetime emission, you can actually cross check that whether it is the fluorescence or phosphorescence.

And we talked about fluorescence lifetime, and we did not tell what exactly it corresponds to so, usually when you measure the fluorescence emission from an excited state, you will get a suppose I am talking about the intensity of fluorescence versus time. And then, you will see that suppose I excite it here, and immediately after excitation you will start seeing the emission, which actually decays over time. And this, you can actually fit to multi exponential. Suppose if I fit it with an single exponential, you will find it goes like e to the power minus t by tau. This tau is the fluorescence lifetime.

So, the fluorescence lifetime, which I told about here that it is about one nanosecond. This is nothing but the time constant of the exponential decay, similarly the phosphorescence lifetime is also the time constant of the exponential decay. So, this is an overview, again of how what are the effects of the excited molecule in terms of we explained it in terms in a jablonski diagram. And we also talked about the Franklin factor or how it arises, because the coupling here is the electronic coupling.

And keep in mind that there are two distinct things. One is electronic state, on is electronic configuration, do not get confused between the electronic configuration and the states. Configurations can corresponds to multiple electronic states. And then we also talked about the characteristic absorption, how the absorption and emission spectrum will look like, what the mirror image relationship comes from. And how basically the fluorescence and the phosphorescence spectrum, fluorescence absorption and the fluorescence spectrum are look like the mirror image to each other.

So, we will stop our discussion here on a photo chemistry. And then, we will discuss about few reactions, which are photo chemically, which occur in nature photo chemically. And those there are many examples of photochemical reactions, like say photosynthesis or vision like the way I you are watching me, like light is falling on you on your eye. And there is a interesting photo chemistry, there is a protein called retinal. And then there is it is rhodopsin protein, and the protein names is rhodopsin.

And there is a chromophore, which is known as retinal. And there is a double bond there are many double bonds inside this chromophore. And then around a particular double bond there cis-trans isomerization happens. And after absorption of the photon, and this systems isomerization leads to a structural change of the chromophore. And then the protein also makes a change the protein actually folding a different way.

And that actually opens up this proteins, actually sit in your cell membrane of your cell, and that actually opens up some ion channels in your membrane. And some protons, actually come in and out that creates a I mean potential difference, and that creates a stimuli or the electrical impulse. And that actually propagates through the nerve cells, and then your brain registers the signal and it says ok, so fine I have seen a photon. Now, you see a photon and you see a photon of different colors. And then actually construct a image, what you were seeing and that is how it works.

So, everything behind photo efficient is nothing but a very fundamental photo chemistry and some subsequent downstream biological reactions or biological response. Similarly, photosynthesis one of the thing were actually the light energy is absorbed by chlorophylls, and subsequently transferred to a reaction center, where you have a charge separation. And then you oxidize water to oxygen, and as a by product to get oxygen.

And you reduce some coenzymes, and those coenzymes further reduce actually carbon dioxide to make food.

So, again photosynthesis the first part, the light harvesting part is nothing but very interesting photo chemistry. But, we will be talking about not photosynthesis or this the vision chemistry. We will be talking about the photo chemistry of the atmosphere, like what happens when the atmospheric molecules absorb light. And how what are their interesting rates, what are the photochemical rate constants, and how basically will be particularly talking about the ozone chemistry, how the ozone layer actually protects us from the harmful ultraviolet radiation that we will also be talking.

So, we will be talking about two different things. One is combustion chemistry, and the one is photochemical reactions, which is the environmental chemistry, atmospheric chemistry we call it, so that falls under the under the big subject, which is known as photo chemistry. So, we will be discussing it when I mean, in terms of the kinetics of those processes.

Thank you.