Biophotonics
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Lecture 9
Molecular Materials

Welcome back, so we shall continue our discussion on light matter interaction, here we are going to particularly look at matter which we call as molecular matter or molecular material.

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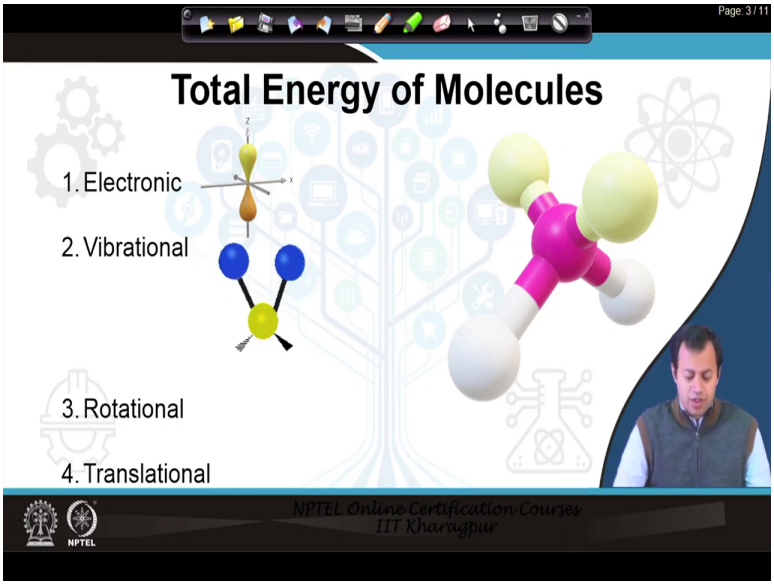

So, before we discuss this molecule matter we need to understand what we in what different ways energy light is a form of energy you can say, light can be interacting with the molecules. So, there are four different ways in which the energy of molecules can be divided and thereby light can interact per say with at least few of them.

There is electronic energy of molecule electronic energy simply means that you supply energy to the molecule that energy allows the electrons present in the molecules to move from lower level to upper level, that is simply what electronic energy means. Vibrational means you supply some amount of energy to the molecule and this complex molecule will have some sort of vibration like use like you are seeing in the gif see this is called scissoring there are several other of these vibrational moments anti-symmetric stretching or rocking or different ways in all these

molecules can move independently of one another upon excitement by light. There are rotational and translational, rotational is mostly stereoisomers where there is a chirality where these molecules are not exactly mirror image to one another and translational is simply when you supply energy to a molecule and the phase of the molecule changes.

So, consider you are boiling water, so it is converting it to steam, ice to water to steam all three different phases of matter all three different phases of molecule it is not actually quantized. So, this is the four different ways in which you can classify the overall total energy of molecules and thereby you can supply external energy into it to give it rotationally simply when you are rotating at a particular symmetry different from vibration. For bio photonics purpose we strictly stick to electronic and vibration translational we it is not even quantized we are not going to discuss that, rotational we may discuss this at the end.

But, for the time being for all intent and purpose your life will be very easy if you stick to electronic and vibration that are the different types of energy of a molecule that we are going to deal with for a couple of more chapters if and when rotational energy comes I will bring it in for this lecture at least, let us discuss electronic and vibration electronic energy where electrons are involved vibrational energy where the whole molecule or the whole atom is involved there is this thing called vibranic energy vibranic where both of them are involved because, obviously when you are supplying huge amount of energy different types of energy different types of wavelength not just one wave.

But, multiple wavelength you are agitating both the molecule per say as well as the electrons that are present inside those molecules.

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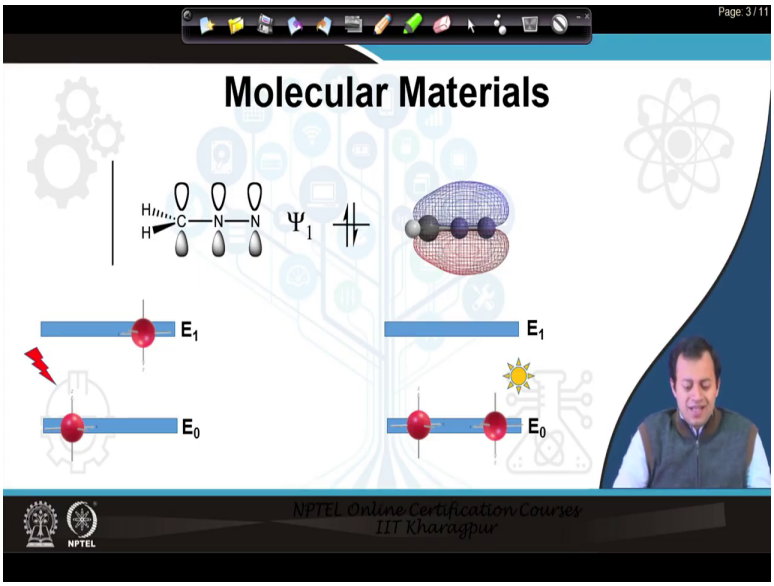

So, let us go through it so, molecular materials we know pretty well we have discussed this image that the atoms the quant the discrete level of the orbitals of the atoms overlap you have different types of bonds and overall the atomic orbitals merge together overlap together and we form hybridized orbitals molecular orbitals we have known this molecular materials that is organic materials per say biological materials you can discuss mostly deal with saturated materials or conjugated materials.

So, molecular materials can be divided into saturated materials and conjugated materials, saturated materials in which a chain type of molecular chain is formed where they are very-very strongly bonded with one another, huge amount of energy is required and that energy only displaces the electrons per say the atoms are very-very rigidly bonded and it is basically like your transparent plastics any energy lower than wavelength of ultraviolet is simply pass through it, simply transmitted through it ultraviolet only are able to generate some amount of reaction to it saturated molecule saturated materials are the plexiglasses polymethyl methacrylate they are for all intended purpose as even stronger than glass and as transparent as glass.

We are not going to discuss about that we are mostly discussing about the conjugated materials the conjugated molecular materials what conjugated molecular materials are this is a perfect example of a conjugated materials where the molecules in themselves carbon, hydrogen and nitrogen in themselves are very strongly covalently bond.

So, a molecule is formed with set of atoms and these atoms are very strongly joined together as a molecule but this set of molecule is very weakly joined with another set of molecule understand this is, this is the fundamental difference between saturated and conjugated, saturated every atom every molecule is very strongly bond with one another and thereby this is a very-very strong chain tensile strength all those things increase just look at windshield of your car you know the first windshield that you have that is not made up of glass that is actually made up of polymethyl methacrylate PMMA.

But, conjugated materials are very soft conjugated materials are very soft because, though the individual molecules are very strongly covalently attached each molecule is attached with another molecule with the weakest chemical force the van der waals forces, van der waals forces are happening because, of the random fluctuation of the electron cloud and they rapidly fall with distances.

So, molecular materials especially conjugated molecular materials are very-very soft to touch very soft bond and they have a low melting point take any organic compound look at yourself how much heat different part of your body can sustain, how soft it is and thereby understand that what I mean by biological materials which are conjugated. However, remember this fact that individual molecules are quite strong individual molecules are quite strong perhaps one of the reason why when we go below few molecules couple of molecules it is very difficult to affect them destroy them and get rid of them.

If, they are causing any problem to your health and safety but, anyways let us, discuss little bit more about these conjugated molecular materials. So, they contain if we the idea here is that if we understand individual molecules we will be more or less able to understand the whole material because, whole material is overall made up of loosely connected molecules van der wall connected molecules.

So, if we understand the optical property of molecule we can simply average it out and thereby determine the overall property. So, when we are talking about individual molecules as I discussed each atom of this individual molecule have its own orbitals where the electrons are probably found and when they come together to form a bond their atomic orbitals overlap and you have a ground state and I have a higher energy state.

So, the idea that I have discussed you already know that when we supply some amount of energy some amount of energy has been supplied one of the electron moves from lower level to the upper level, whenever some amount of and this is absorption as we discussed whenever this electron at the upper level after spontaneous emission comes back to the original level photon may or may not be emitted. Remember, previous lecture may or may not be simply emitted.

So, that is overall thing life is good life is fine we have understood.

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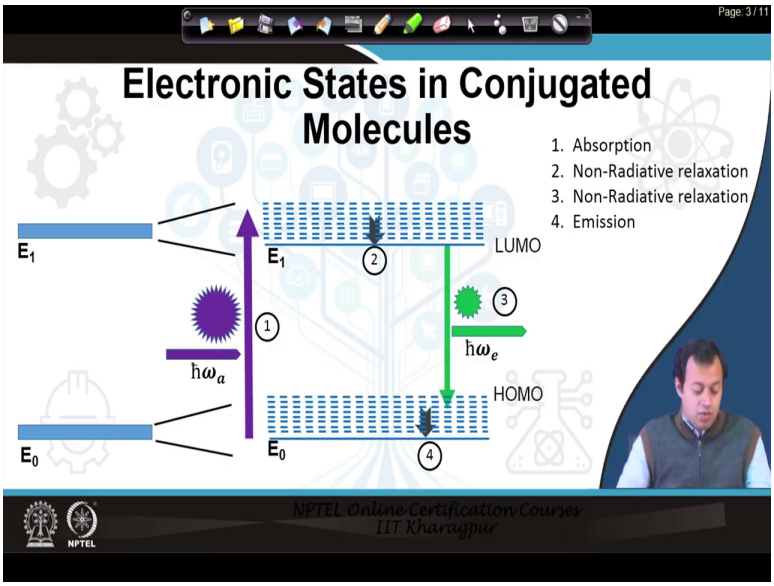

Turns out there is little bit more complication to that, you see when we talking about the electronic states in conjugated molecules it not just we are talking about one energy band or two energy band what exactly are these energy bands per say turns out that each of these energy bands contain huge numbers of individual molecular orbitals, what do I mean? I mean that you have a particular molecule that particular molecule have molecular orbital then you have another molecule coming closer to it another molecule coming closer to it and as such infinite number of molecules have joined together weekly.

So, but they have come very-very close with respect to one another when they have some that close with respect to one another their molecular orbitals starts overlapping. However when I talk about overlapping here is needs to be understood that throughout the bulk material throughout though the molecules are very similar in fact same with one another all the molecular

orbitals cannot simply collapse into one single molecular orbital, understand this point there is a molecule there is a molecular orbital where the electrons of the entire molecule moves, you bring in another molecule towards it another molecule towards it another molecule.

So, all of their molecular orbitals will overlap but it will still have a minor difference between one another it cannot combine into one single molecular orbital, why? Because then it will violate the Pauli's exclusion principle remember we cannot have one single orbital for these n number of electrons moving around you have to have some amount of difference.

So, thereby if you are looking into a band that is the reason why we call them band all these individual molecular orbitals of individual molecules come together they have very similar energy level though they are nominally discrete and they merge together to form instead of one single energy state one single molecular orbital they form a band consider this as a highway very small number of streets large number of small streets are merging together to form a highway a highway is one total single thing.

But, it has lanes but, it has different lanes you can transfer from one lane to another lane easily you can transfer from one lane to another lane easily if this is your upper level this is your lower level within the upper level you can transfer very easily between lanes within the lower level also you can transfer very easily between individual lanes.

But, transferring from upper level to lower level is difficult and how this has happened this has happened this highway different lanes have formed how highway has formed because, of the merging of individual very small streets large number of narrow streets have combined together to form a bond form a band, they still have discrete energy value the discretion is never going anywhere there are individuals levels no E1 has not been divided into E1.1, E1.2 they are still discrete they are still whole number.

But, E1 actually is a proper total band which covers an entire range of energy say five electron volt to six five electron volt to ten electron volt say I am just using very-very metaphorically not to take literally and five electron volt to ten electron volt you have individual lens, individual paths where electron can exist. Now if , electrons can exist in any of these individual orbitals it is very easy for them to move around up to down without much of a problem, it's like you are

driving a car in the lane of a highway and you can simply change the lane in a particular direction of the highway.

But, if you have to change the highway altogether you have to go through the you have to take some measures. So, the lowest value of the, sorry the highest value of the ground state is the minimum energy we call it HOMO which stands for highest occupied molecular orbital this is the highest occupied molecular orbital and LUMO stands for lowest unoccupied molecular orbital this is for the excited state E_0 is the ground state E_1 is the excited state the minimum of excited state is LUMO lowest unoccupied molecular orbital.

Because, when in ground state normal cases this E_1 is completely unoccupied though there are several births, several seats available but, there are not enough passengers, passengers meaning electrons and HOMO stands for highest occupied energy level ground state where there are also several levels in this several levels usually electron tend to occupy the lowest sheet.

But, if we are discussing about the gap between E_0 and E_1 we actually are looking for the gap between highest occupied molecular orbital this is the highest energy you can get in a ground state HOMO is the highest energy and electron can get in ground state where LUMO is the lowest energy an electron can get in excited state the gap between LUMO and HOMO electronics engineer students will laugh at it, can be considered as band gap electronics engineers people who deal with semiconductors these days considered this as balance band and conduction band.

I could see that you figured it out HOMO and LUMO stands for valence band and conduction band, why the change of the name? Well, HOMO and LUMO is mostly to do with chemistry organic, chemistry organic people or the chemistry people usually like to deal with you know molecular orbitals whereas I am an electronics engineer we discuss more about valence band and conduction band.

But, remember valence band and conduction band is specifically to semiconductors HOMO and LUMO is this vast array of insulators organic compounds per say. So, now remember previously we were discussing simply changing an electron moving an electron from upstairs to downstairs

to upstairs moving it up turns out there are various rooms both downstairs as well as various room in upstairs.

So, now we have to be bit more specific it is not simply we are taking the stair moving from below to up we now need to understand which part of below part of ground state you are moving to I am giving you the analogy consider a house which has two stores you take the stair to go from lower level to upper level but, here I am becoming more specific and I am saying that how much energy you to go from which specific room of the ground floor to go to which specific room of the first floor this is my simple analogy you can laugh as it as you want.

So, usually when we supply some amount of external energy here we are giving say a particular frequency of light which matches with the absorption frequency light moves from electron can move from a specific level inside that E_0 a specific room of the ground floor to a specific room of the first floor.

Now, it has move to a specific room of the first floor specific room of the higher energy level. It can move within different rooms at first floor, it is like again another analogy once you have come to a highway you can change the lanes within that same highway five lane highway you can change just simply moving.

So, it can simply move back to the LUMO position everything wants to return to the lowest energy state available you have excited electron from low energy to high energy but, high energy is divided into several subsection some of them are higher some of them are lower, it can therefore tend to move back to the lowest unoccupied molecular orbital if, it is occupied it cannot move like anything else.

And then from the lowest occupied molecular orbital it can return to the original HOMO that is highest occupied molecular orbital that is the ground state resulting in an emission of photon resulting in an emission of photon from the HOMO state highest part of the ground state it can simply again come back to the lowest LOMO lowest occupied molecular orbital.

What does that mean? Electronics engineers will simply think that I am overly complicated things previously electronics engineers simply thought about moving electron from valence band to conduction band and current will flow it is bit more complicated in case of conjugated

molecules, conjugated molecules have sub-bands, conjugated molecules have large number of these sub bands orbitals molecular orbitals within each band.

So, it becomes complicated and it is not straight forward I go from lower energy to higher energy and higher energy to lower energy if, that would have been case whatever has been consumed whatever photon has excited will be emitted, but this is not the case here whatever photon has been absorbed given by this particular frequency a part of it is lost while traveling inside the higher energy band, understand this in conjugated molecules the absorption photon and the emitted photon are of different energies, different frequencies almost well a majority of cases the emitted photon is at lower energy lower frequency than the absorbed photon yes.

Because, the electrons that the been excited by the photon has spent some of its energy roaming which within the higher energy level roaming within the lower energy level this is the primary difference between the valence band conduction band theory of semiconductors with respect to the electronic state in conjugated molecules.

Now, here the different phenomenon that happens are one and three are quite straight forward absorption and emission is happening to one and four absorption and emission two and three are non-radiative relaxation, what does this mean? This is again that photon thing which I said.

So, once the electron is in an upper level and it has to move somewhere below in the upper level itself it can lose energy in the form of heat or it can lose energy in the form of vibration it needs to lose energy that is its nature it has to somehow dissipate its energy within a band the electrons can lose energy without emitting any photon it can lose energy by simply dissipating it as heat or some kind of a vibration.

This is the fundamental difference between semiconductor based conduction band valence band transfer of electrons or electrons charge carriers and organic compound based trans carriers where the energy band is quite thick and they each contain sub band consider these are different rooms of first floor and different rooms of second floor or different rooms of ground floor and different rooms of first floor Americans will consider the ground floor as first floor.

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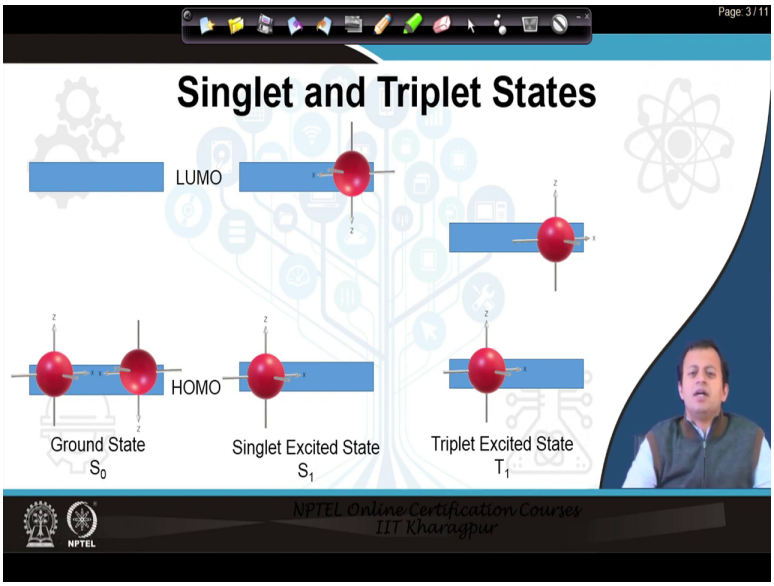

So, there are three major states that are available here probably I should have discussed this at the fluorescence part but, let us understand this nevertheless because, this will set up the tone for my next class. So you have a ground state where electrons are present at different levels the electrons have to be spin paired here we are discussing about spin.

Spin is another fundamental property of sub atomic particles specifically electron apart from mass and charge electrons also poses spin remember spin quantum number from your I think high school physics everybody has gone through all those different quantum numbers the last one is spin quantum number the spin quantum number spin is one of the two angular momentums the other being orbital annular momentums this.

So, the spin so for since paul is exclusion principle no two electron will have the same all four quantum numbers in the same atom. So, at the same orbital the electron have you know anti parallel how to do it here antiparallel spin. So, when you excite say one of the electron to move from HOMO to LUMOs state it goes this particular position it is still paired previously it was like this I will go to the green background here blue background.

Now, it has moved like this, this is excited but still anti parallel to one another that is called the singlet excited state ground state is also anti parallel there are spin paired but, when an electron has moved to the LUMO level from HOMO to the LUMO level the spin are opposite to one another see this is facing up this is facing down this is called a singlet excited state.

It can immediately return back to its original position giving some amount of photon out and this is a very-very fast phenomenon. However, there are certain anomalies, anomalies aberrations that happen when you have the same spin appearing at a LUMO level strictly not LUMO below LUMO and this is called triplet excited state and this is aberration this is an anomaly this has the exact same spin as this as this electron, why am I talking about this because, unless this return to its original position just like that it will be violating the spin rule this can very strongly return back to its original position and it will be in a ground state.

But this cannot meaning if you have been able to excite an electron from lower level to higher level at higher level somehow you have been able to turn its spin it will have difficulty returning back home it will have difficulty in returning to the ground state what do you think could be the manifestation of such an anomaly where it would like to dissipate the energy that is its nature.

But, simply cannot because it is not allowed back home because of its bad spin this overall diagram can be considered as a rough version of Jablonski diagram, this is the basic of fluorescence and phosphorescence we will be discussing fluorescence and phosphorous in coming chapters this when the spin is paired the spin is opposite and it returns very easily to its ground state by emitting a photon is gives rise to fluorescence you hit light electron moves up then electrons comes about gives out some amount of electron this is phosphorus where after hitting it with light you have switched off the light.

But, it will keep on glowing it has to dissipate it somehow you might think of dissipating it as phonon but phonon is also out of reach for this particular case because of the spin. So, you might have seen those previously we used to call radium watches which glows in the dark that actually uses phosphorescence anyways.

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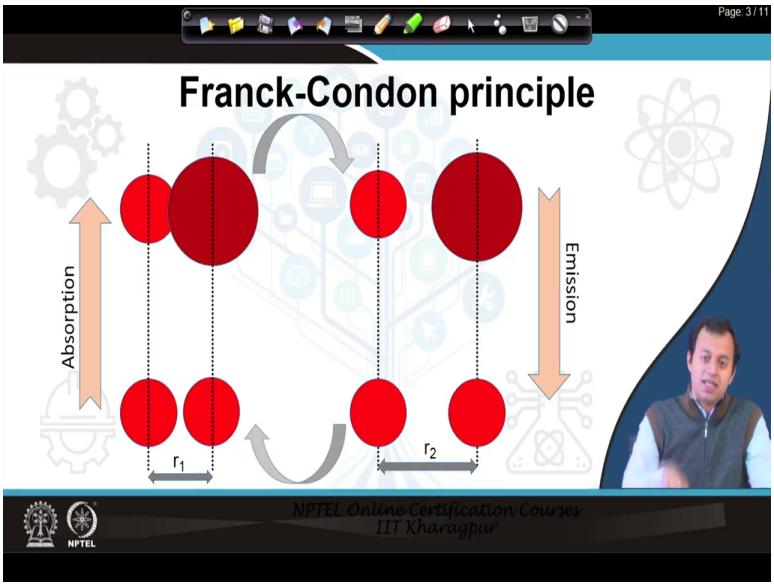

We will discuss phosphorescence at a later stage but, let us discuss what actually happens when we excite particular electrons in specific molecules. So, we have two nucleuses they are separated by a distance r1 you have a molecule made up of two atoms very-very simply hydrogen atoms hydrogen 1, hydrogen 2 hydrogen identical atoms they have formed the diatomic molecule H_2 and they are like this they have a separated distance between their nucleus their nucleus are separated by a distance of r1. Frank Condon principle states that if you are exciting these atoms with energy light.

For example, since we are discussing with light the time taken for electron to move electron to get excited is much smaller because, it is so light than the entire nucleus because the nucleus is heavy you might think this is common sense but there is a manifestation for that there is a very-very strong manifestation to that and that is described in this Frank Condon principle which we are going to see how they help us emitting of light.

So, again you have two diatomic molecules well a diatomic molecule hydrogen and hydrogen separated by a distance r1 you have now, excited just one of them just one atom of them with an energy with some amount of light. So, what will happen the electron of one of the hydrogen atom will go to the next level will go to the higher energy level.

So, if it has moved to higher energy level it has gone to the next quanta the next level would not the size of the diameter of the mole atom increased previously you have nucleus and you have the electron cloud around it. Now, the electron cloud has gone to the next level so, overall the diameter has changed of the individual atom but since it takes nucleus more amount of time to move they have not separated per say they are still in this particular case where the electron cloud of one is now almost overlapping a certain section of the electron cloud of the other.

Remember we have only supplied energy only supplied light to one specific atom this has been touched this remains untouched this has been touched energy has come its electron has moved to upper level, eight electron has moved to upper level and thereby this has swollen up this atom has swollen up and this electron cloud is now almost overlapping a portion of the original atoms electron cloud.

So, what will happen if two electrons or since it is hydrogen there are two electrons are overlapping one another there will be a force of repulsion between them will be a force of repulsion between them resulting in some kind of a separation this will force there will be mutual repulsion between the electrons which were overlapping each other to you know separate they have now separated.

Now, they have separated it took some amount of time because it is not instantaneous the electron has moved but, the nucleus is still there but now one more force the repulsive force between the two electron clouds have come back and it has separated it through after sometime because of spontaneous emission this will lose the photon and comes back to its original position by emitting a light however the nucleus has still not moved.

Because, nucleus is heavy nucleus takes time to move thereby the inter-nucleus distance have now moved from r1 to r2 though the excited state has gone away though the excited state has gone away yet the separation distance between the diatomic molecule are different than it was in the original position.

Now, obviously in this particular case after some time the restoring force will come into effect and it will revert back to its original position, why is this important? Frank Condon principle allows us gives us time because electron and nucleus moves at different timing this and this are the intermediary phases these are the phases that happens in between absorption and emission and all of them has manifestation when we are trying to identify mark my words this is very important when we are trying to identify, trying to sense trying to detect a very-very specific molecule.

Different molecules will have different r1 and r2 different time where it can stay at r1 different time it takes to go to r2 different time it takes from r2 to relax back to r1 these are the characteristic feature of individual molecules if we can identify this telltale signs, what is r1 how long it stays in r1 after absorption, how long it stays in r2 after emission, how long it takes it from coming from r2 to r1 after relaxation.

If you can identify all of these structures they are very-very specific to specific molecules we can somehow get closer in detecting what are the molecules trust me this happens this is a requirement when it comes into conjugated molecular materials when we are dealing with a hugely complicated compound think about chloroform think about DNA, think about RNA, how may think about a virus, think about a cell what are the different molecules that are available that makes up this entire human biological cell.

And if you want to identify each and every individual molecule that makes up this entire cell entire virus entire RNA you have to start from somewhere might well it be this is not only one but, the significance I am telling you the point that I am making here is that Frank Condon principle will be useful when you are going to understand the emission and the absorption part as well as perhaps in identifying detecting tagging a particular molecule.

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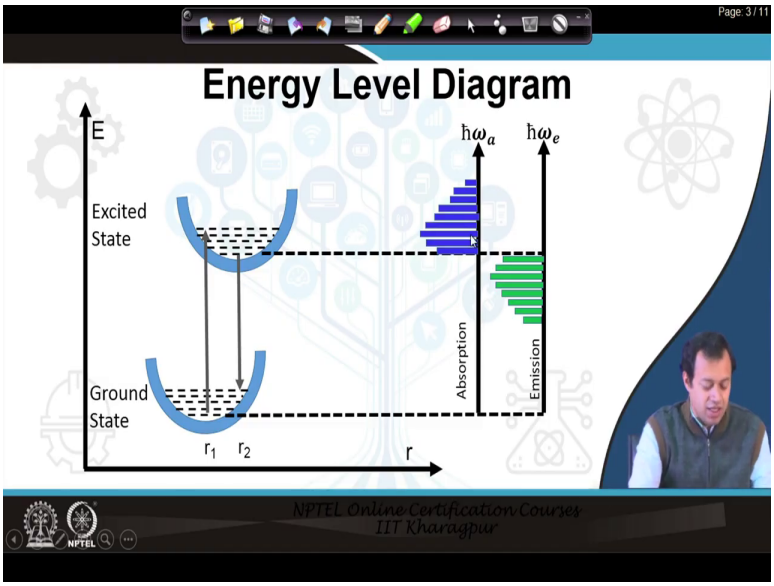

So, the energy level diagram in terms of r1 r2 and the excited state ground state can be considered it like this, this is I am repeating it do not worry about why I have made it bend previously I was making straight lines but you understand that energy bands cannot be simply straight flat away they cannot also be bow shaped like this but this is something to do with e k diagram energy versus momentum diagram any physics text book will tell you why this is bend or why this is a representation.

So, excited states once again has several sub atomic sub orbitals ground state have several sub orbitals depending on what kind of frequency of light being absorbed and where the electron is going from the lowest of ground state to the highest of excited state or something intermediate you get different bands of frequencies that it can absorb. See that is what I am saying since you have a very thick band depending on whether this electron is going here or here different levels different photons are getting absorbed.

And quite similarly, when you have emission depending on from which excited state suborbital the electron is falling onto the ground state sub orbital give rise to different values of emission. Usually this is at higher frequency it losses some amount of it by non-radiative decay non radiative emission and similarly when it has reached to the ground state it also loses some amount of energy in non-radiated emission depending on where exactly in the ground state it is

coming from which particular excited state suborbital we have different bands of emission they can usually merge together.

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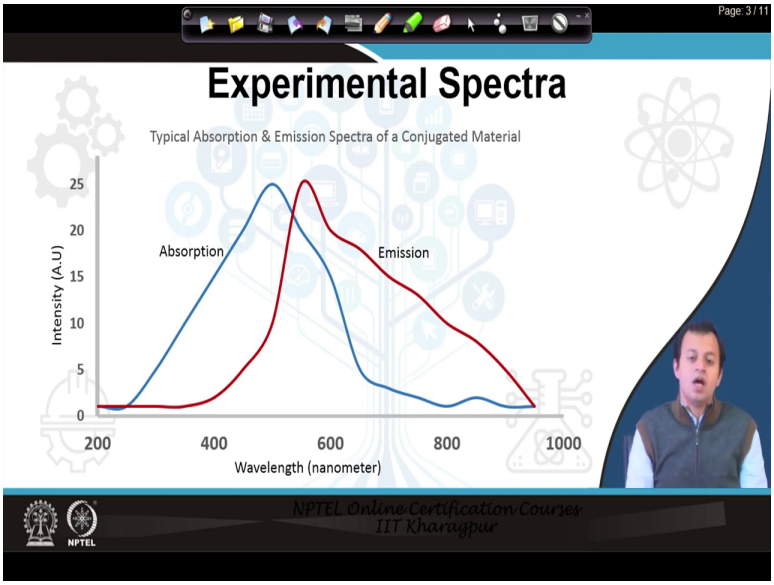

And in experimental spectra you get something like a very-very flat band. So, absorption is from this to this region emission is from this to this region, you can ask yourself this question what happens in this region where absorption and emission spectra are overlapping this is a typical absorption spectra of conjugated material spectra simply means wavelength which is frequency which gives rise to energy and the intensity as in how much is absorbed and how much it is emitted.

So, you can see around 500 the absorption of this conjugated material is very high 500 is where any light any electron will move from lower level to upper level and it start emitting at 600 nanometers and then the emission rate starts working. Basically what I am telling you is that unlike silicon or any other semiconductor material per say the overall moral of the story is there are several sub-bands, there are several orbitals molecular orbitals inside each single band.

And depending on which position of the band the electron is jumping to which position of the ground state you get an emission. Usually we send a bunch of photons and we get a bunch of photon emitted they are at different wavelength from another some of them may overlap some of them will not overlap.

A significant use of that is in fluorescence microscopy where we add fluorophores to certain areas of cell or viruses subcellular parts DNA etc we bombard them with a high frequency laser say blue laser, ultraviolet laser and it start emitting light in green or in red part of the visible spectrum thereby we can see it thereby we can observe where this light is emitting form and from our microscope we can observe what exactly is going on

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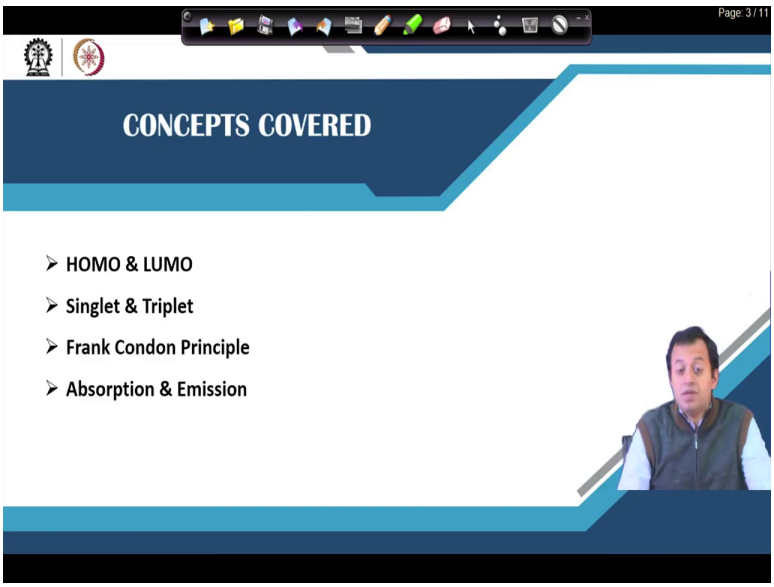

Next class, I will be discussing about fluorescence how it has revolutionized biology per say here in fluorescence you will see the first glimpse of biophotonics or what biophotonics can actually achieve.

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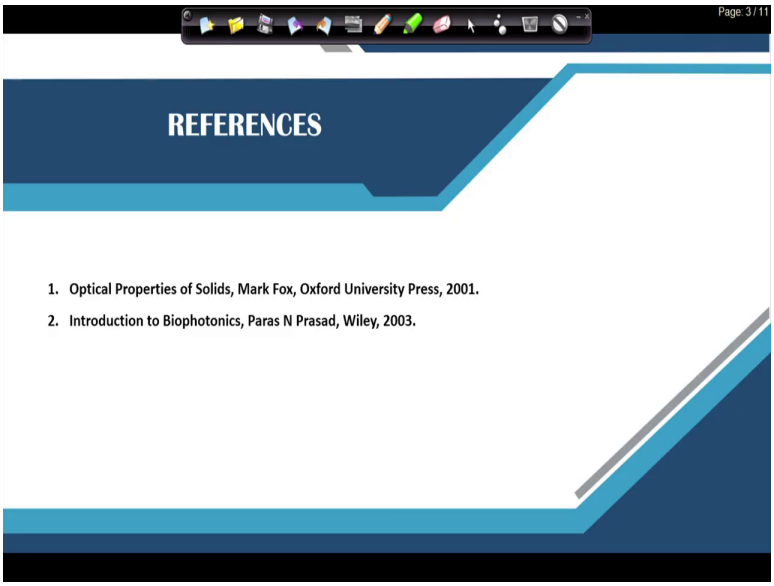

So, the concept covers here are again HOMO and LUMO singleton triplet absorption emission along with Frank Condon principle and please go through the optical properties of solid book it is a very-very interesting book very nicely written and you can start from any level to understand it not very much math's intense, so even medical students or anybody who dislike math's can simply go through it understanding the basic of light matter interaction and as always introduction to biophotonics by professor Prasad had been my companion throughout.

So, thank you very much, next class will be just fluorescence and I will finish the revision of light matter interaction, please write your comments below I will try to modify my lecture accordingly, thank you very much.