Optical Spectroscopy and Microscopy

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Module No # 05
Lecture No # 24
Fundamentals of optical measurements and instrumentation

Hello welcome to the series of lectures on optical spectroscopy and microscopy so far what we have in the last lecture what we have been looking at is that the predictability of a transition happening or occurring or more precisely predictability of transition not occurring given to states is that how can we do that i mean how can we rule out a given transition cannot happen is there any way we can do that.

And in fact this came out as a direct consequence of trying to understand if in any way we can simplify and estimate whether given transition will happen or not it turned out that when we wrote down and under special circumstances where you have a definite parity of this wave function. You can actually talk about a transition not happening while you really cannot say whether the transition will happen or not.

But what do you can actually say is that a transition cannot happen which if it is if you can look at the parity and then it does not meet the parity demand we can boldly say that “hey look this transition cannot happen”. So now the to the end of the towards the end of the lecture I told you that the there are photo physical processes which we can actually look into in a little bit more detail and then say okay why I mean will this photo physical process happens will this transition happens.

If it have to happen under what condition can I happen that investigation can be done just by looking at simply parity analysis without really having to know too much about the exact nature of the wave function that we are actually talking about that is very powerful right. Because you really do not have to calculate the way function at all but you just directly go head and say “hey look I am going to look at the parity of this and then analyze this and then say this” okay.

The example be that I am going to talk about the physical process that i am going to be talking about is called as phosphorescence's it is a similar to the fluorescence in that it is a radiative process where the molecular emanates from the electronically excited state and then it when while it is dropping down to the ground state it comes through emitting a light radiation. However this is the state the excited state from which it is starting is not the same state of that of the fluorescence states right.

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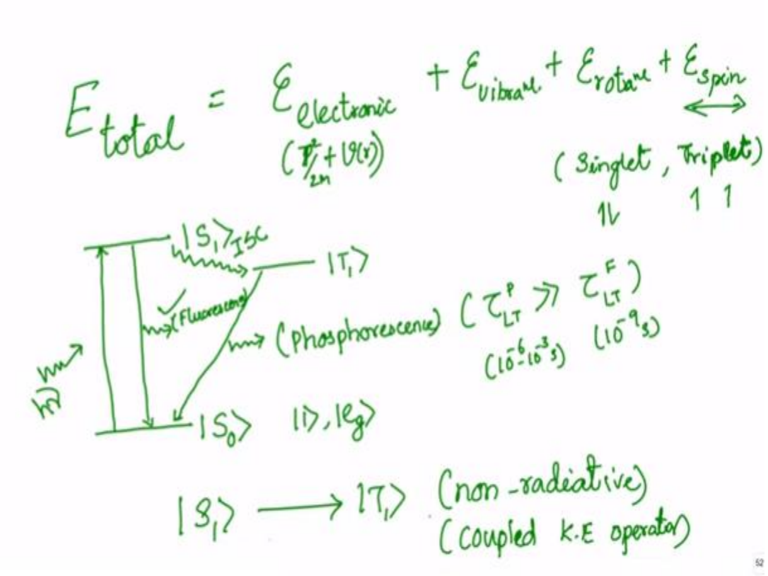

$$E_{total} = \mathcal{E}_{electronic} + \mathcal{E}_{vibrat^{nl}} + \mathcal{E}_{rotat^{nl}} + \mathcal{E}_{spin}$$

$$\left(\frac{p^2}{2m} + V(r)\right)$$

$$|S_1\rangle \longrightarrow |T_1\rangle$$ (non-radiative) (Coupled K.E operator)

You remember when we wrote the expression for total energy of the system in this case we are talking about the electron we have many terms and the so the energy electronic energy or E total okay can be written as E electronic which had a kinetic energy term we called v square over 2m coming from the Hamiltonian right directly and the potential energy term like right this is coming because of the distribution of the charge about inside the molecule per se right.

And then the nuclear location and so on and so forth and then we had E vibrational E rotational plus E spin there is nuclear spin and then electron spin. So I am here since I am talking about an energy associated with the electron being in a given state. So and then we are talking about the electrons spin themselves. Now based on this when you actually go ahead and estimate the electronic energy you have the possibility of the system existing in 2 kinds of spin states I mean many but at least are dominant ones that we are interested in or 2 one is called as a singlet state and the other is called as a triplet state okay.

Now this are direct consequence of the I mean you can think of this as just the way how every energy the electronic energy vibrational energy and rotational energy are quantized in form of discrete states you are thinking you are talking about spin electron spin energy is also quantized in terms of distinct states and one being the singlet state and then the other being the triple state. So you would also typically come across this description of the single in the singlet state the electrons are paired and triplets I mean this half errors represents the electron and then the direction of the arrow represents the spin and then the triplet it is unpaired.

While it is a it may be convenient and it helps you to keep track of what is happening it is a more general and it is a to think in terms of these states representing different quantal states of the electron spin energy and then not necessarily having to attribute to this is convenient I mean it is not only convenient it is a it is more accurate alright. So I mean if not it is I am not saying by any means that if you were to think of this and then it is completely wrong no that is not the idea.

But sometimes there will be states of the electronic spin where you will see that neither here nor there and then what do we do and how do we think about this. Again if you still can go ahead and calculate and it gets very complicated. So there instead if where to think of this as one discrete state then that is all we need I mean it is just one other way of quantizing the available energy for electron so associating with this spin okay good.

So now what of course it so then if you have this then you can think of the states being a ground state of for pretty much every single molecule the ground state is a singlet state there is only one exception and the exception being oxygen with where the ground state is a triplet state oxygen molecule as a triplet ground state but the otherwise everybody is singlet. So we can think off the singlet state the singlet starts with S so let us call it as s and then starts it state the first state ground state.

So let us call that as S0 okay so this is just like is extreme I mean is exactly similar to what we have done either we represented this as 1 or Eg right basically the same Eigenket but we are now explicitly saying that there we are going to take into account the spin of this and the going to name them if it is happen to be the singlet S0 okay. And then we also going; to talk about an excited state again a singlet okay.

But since it is excited just the way we go from 1 to 2 g to k we go from 0 to 1 S1 now what you can actually do is that we can ask where in this energy scale does the triplet and energy triplet excited state come maybe know that the ground state does not exist right. So naturally that excited state that can be a triplet state and if there is a triplet state where would it fall. It turns out they are of lower energy for a good reasons because there is some exchange term and all that stuff but for our purposes we can think of all we need to know is that they will call little lower than that singlet state okay.

So we have this representation right similar the one that I have drawn before right ground state E1, E2 or E1 and E2 okay. Now except the both of them are the exited electronic state one has a singlet spin other as the character on so that triplets spin. Now we know the absorption takes place from ground state to the singlet excited state. So since the rate of transition is symmetric about whether the transition is happening from 0 to 1 or 1 to 0 the fact that you can have a molecule observe the light radiation and go from ground state to the excited state would tell you that it can actually come back alright by emitting the parity should be I mean the parity argument should not matter right.

I mean the integral does not care whether you have Psy f times Psy i or Psy I times Psy f right we all we need to know is that the what is the net output of this product if it is going to be odd then that odd output is going to combine with an odd operator giving rise to an even function and on the other hand if it happens to be even then it is going to combine with an odd operator to given an odd function that is all we need to know when we are going to integrate that over and that has its unique property.

So we all we need to know is whether the nature of the product and we are not worried about the order in which we are multiplying this 2. So which means you being able to see the upward transition means you should also be able to see this alright coming out by emitting a light photon good that is fine. Now on the other hand it turns out that you hardly ever be able to cause this excitation of the singlet state from the singlet ground state to the triplet state using a light radiation okay.

The but somehow let us say if you do take the molecule to the excited state S1 or somehow you populate the molecule to the triplet state then you wait what do you see is that in some of the molecules they do come back down to the ground excited state by emitted a light radiation though with much larger life time okay. And this is I am talking about phosphorescence I mean this process of the i mean the molecule coming from the excited triplet state to the ground singlet state by emitting a light radiation is called as phosphorescence and I am going to this called as phosphorescence and the life time right.

Remember we when we talked about spontaneous emission of the molecule from the singlet excited state to the ground state and there is a rate constant associate with this which is independent of the presence or which is independent of the presence of the incident light. So that is why we call it as spontaneous emission it came out because of the +1 term you in our second conversation analysis.

And similarly somehow if you were to take the molecule and leave it to the triplet state the molecule does come back down to the singlet state by emitting the phosphorous I mean emitting the light radiation we call that as phosphorescence just the way we call this as fluorescence. However the life time right the time that the molecule stays on an average on the excited state before it comes back down to the ground state for this process okay.

So life time for phosphorescence is much greater then the life time for fluorescence okay this is of the order of 10 to the power -9 seconds while this the fastest is the of actually not even microsecond 100 microsecond but typically of the order of milliseconds. So giving the clue that the rate is extremely slow right because the time it is life time is high which means that the rate of probability is coming down is low are indicating to the fact that since the reverse sounds good right meaning that the transition is symmetric right.

So indicating to the so the fact that you may not be able to directly take the molecule from the ground singlet state to the triplet state at all. Now if that being the case then how do we even populate the molecule at that triplet state so it turns out that once you excite the molecule to the singlet state while the molecule is staying there in the singlet excited state for about nano seconds.

Some of them can go into a special kind of processes called as inter system crossing it is called inter system crossing because the system here refers to the spin system this is a singlet spin system to the triplet sync system is the energy system they are 2 different potential energy lands scape right. So you are going from one to the other when that is happening then you call it as inter system crossing and this happens in a non radiative way.

And when it does so I am going to remove this fluorescence I am writing here just to make sure that we do not miss fluorescence well this inter system crossing and then they can actually come and then stay there for a quite a good amount of time before they actually come back to the ground state emitting the phosphorescence. The question is then we know that this process is happening right the process from the ground singlet state to the first excited state singlet state again can happen the transition can happen by absorbing the light radiation it is new.

So is it possible to for you to take the molecule from this S1 state to the triplet state in the presence of light. It turns out if you actually look at the parity argument then it is very revealing and interesting first thing is that it turns out that by no means you would be able to make this transition from S1 to t okay. The dipole moment operator are does not couple with the spin way function. So that is that the integral if you had to write down for each of this the integral would be then size spin of singlet to dot I spin of triplet d tau.

Because there is no I mean the dipole moment operator does not come into picture because it does not couple these 2 spins. As a result that integral goes to 0 because they are I mean they are orthogonal functions in some sense. And so then because it is not been operated by any operator so it the integral vanishes as a result what you have is no transition you predict there is no transition.

So that transition cannot happen it does not happen and if it does not happen then the question is what can we say about the parity of the states between t1 and S0. Since they are not normally radiatively coupled it turns out that the parity between the S0 and t1 okay. We can make some prediction about that parity and then say why it is of very low probability how do we go about doing this?

So we go about doing this by first recognizing since the S1 to t1 transition right is non-radiative and coupled by mediated by collisions okay. So the coupled by kinetic energy operator okay so what does it tell us so the kinetic energy operator what we can actually do is now we can actually go ahead and write down the rate of transition for this transition right rate of the process for this transition.

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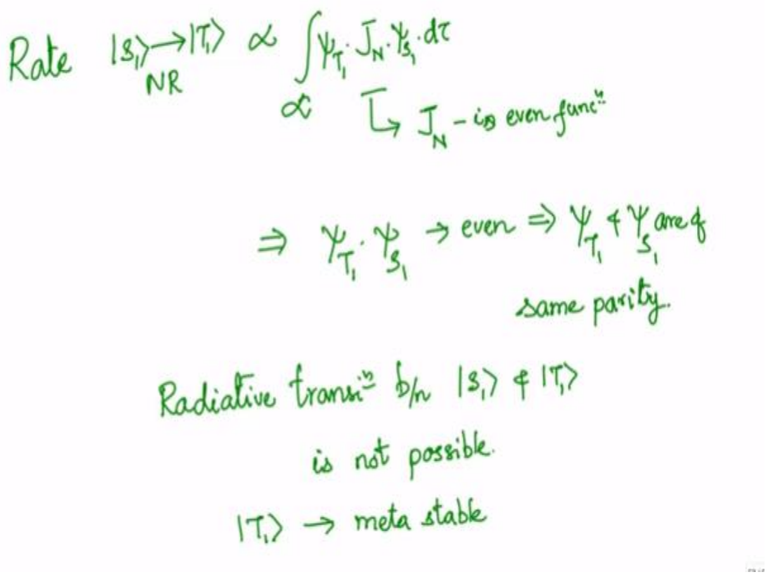

Rate $|S_1\rangle \xrightarrow[NR]{} |T_1\rangle \propto \int \psi_{T_1} \cdot J_N \cdot \psi_{S_1} \cdot d\tau$

$\propto$ ↳ J_N – is even funcⁿ

$\Rightarrow \psi_{T_1} \cdot \psi_{S_1} \rightarrow$ even $\Rightarrow \psi_{T_1}$ & ψ_{S_1} are of same parity.

Radiative transⁿ b/n $|S_1\rangle$ & $|T_1\rangle$ is not possible.

$|T_1\rangle \rightarrow$ meta stable

So rate of S1 to t1 non radiative is given by the let us write down the kinetic energy operator as J it is basically the nuclear and S1 d tau. So again it is over the entire space so it is minus infinity to plus infinity so you can adjust the I mean just going to see it is integrated over all space it is infinity okay. So this being the case we can actually investigate we can investigate the parity again here right.

Now unlike the r the kinetic energy operator Jn is an even function okay alright you can easily see why it is because it is given as P square by 2m and anyway so that is the we can go ahead and work it out does a small takeoff assignment yJn is actually an even function and if you do that what it tells you is that since Jn is an even function and we know that these non radiative transitions between the singlet state and to the triplet state happen.

Then they do couple they do really ahh couple so in which case you can say that the Phy T and Psy S are need to be of same parity this would because this is an even function. So we want for this integral to not go to 0 to be non-vanishing we would like we would want to have I mean this will be case only if this product right this product is even if it is happen to be odd then the whole thing becomes hard and then you are going to have a 0 for the transition right yes we can we know from here right.

If it will become equal to 0 if it becomes odd okay where is that yeah the whole integral become 0 for f of t being odd and for f of this integral should not wanted to have a possibility of becoming I mean not being 0 then it has to be even. So if it has to be even for a Jn to be even then this product should be even which would imply from our table right from our little table that we have drawn. So if it have to be even it will it implies that the F1 and F2 right F final and F initial as to be same parity odd and odd or even and even nowhere else would you have then to be even.

So that means that Psy T1 and Psy S1 are of same parity alright that is good so we know the nature of the parity if it is defined for this molecules then we know that the S1 and T1 need to be same parity okay. So that immediately tells you that the radiative transition right the between S1 and T1 yeah is not possible at all right. Because S1 and T1 are of same parity which means if you are the wanting the take the molecule from the singlet to the triplet state in presence of the light that is simple not possible.

And of course it also makes the prediction that if rest everything being fine is it possible for the molecule from the parity arguments for the transition from the triplet state down to the singlet state the answer is yes it can because the parity of the triple state it just similar to the S1and since we know that S1 is S0 is possible is allowed in parity terms it would be allowed in terms of the t1 to S0 however what is stopping it from doing this transition is that the operator are does not coupled with the change in the spin state so that actually makes it really probable.

Or in other words the state T1 you can call as meta stable okay once it goes the molecule tends to stay there for longer time because it does not have easy way of actually coming back from the T1 and S0. Now you can ask hey you told that S1 to T1 actually the transition the happen through the kinetic energy operator. So the why not T1 to S0 are happened through the same way and then the molecule do not stay there for a longer period it is just come back in which case you will not see the phosphorescence taking I mean you will not see that the molecule staying there for that longer period of time.

When the phosphorous and sustaining for that long will not happen where the answer to that is that you see the rate of the transition we are looking of one of the term here which is that the matrix element square okay. And there we also looked at there is if you look at the Fermi golden rule we equated the energy separation which is the omega Key G term to the interaction energy right.

So they need of the same scale and if they are not of same scale the resonance does not happen and if the resonance does not happen that the as I go further from the resonance you know that the rate of the transition falls down really badly right we wrote down the if you remember the original rate expression it goes as sin square of this off resonance by the off resonance itself so science it does fall down quite rapidly as falls down as sin square.

So sin square by I mean it actually falls down as sync function is it is a sin x/x so it is a square of that I mean that is what we have written so as a result you need to have the interaction happening I mean the interaction energy to be of the order of or close to that of the energy level separation and it turns out that is the case for the transitions involving S1 T1 because they are reasonably closely spaced in energy while T1 to S0 they are not they have much further apart.

As a result the they are off resonance quite heavily off resonance so that terms pulls the total rate down as a result leaving the molecule in the triplet state for a longer period of time. And hence you have the phosphorescence prevailing for a longer period of time. So now that is another example of how we can write down I mean or we did write down the expression for the rate of the transition and then teasing hem in part by part and then utilizing it to the very core and then understanding very various different physical processes.

First we looked at the anisotropy where the coupling is between the unit vector pointing towards the electric field of the or the polarization vector or we call that as polarization vector for the photon and how it is oriented towards or oriented with the I mean dipole moment transition dipole moment itself then that is a and how that gives rise to preferential excitement and then so on and so forth we can actually go ahead and predict what is the maximum possible anisotropy from the ground basics right.

If our treatment of this whole system as not be correct and our understanding is not correct you will not be able to get such tight prediction about an experimental observation and hence so forth. And then give you here an example of how looking at the matrix element and then it is correspondence to the integral and we can actually define something called as parity and using the parity we can predict which of the transitions might happen and which for sure cannot happen.

Using that we said if there were to be triplet state we could actually sitting just sitting I mean sitting down with the pen and paper we can predict if there were to be at triplet state and of with the certain property of the spins we know that they have to be metastable okay with that i would like to end this class and then the next class we will go further and then see how the various vibronic energy levels can be abstracted into a simpler energy level diagram and the usefulness of that and what the rules are for drawing such diagrams.

And from there we will make some prediction and interesting useful properties and properties basically how about their emission process itself okay I will see you in the next class.