

Optical Spectroscopy and Microscopy
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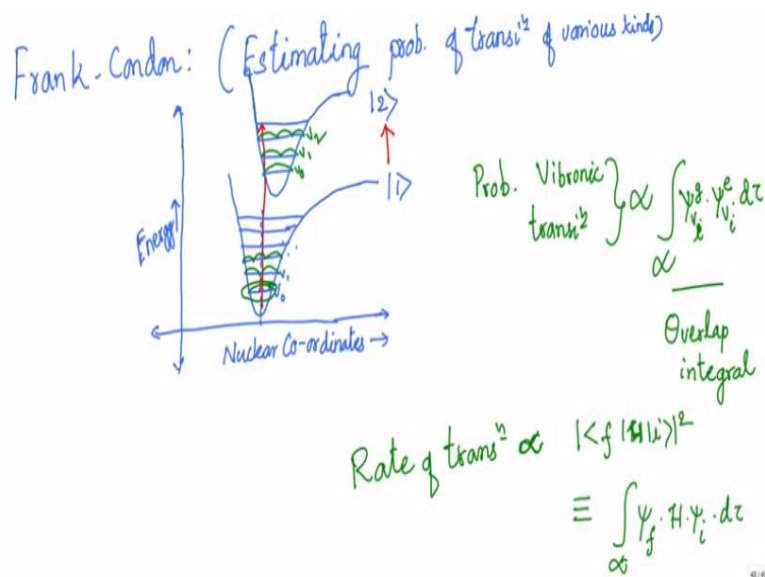
Module No # 05
Lecture No # 23
Fundamentals of optical measurements and instrumentation

Hello and welcome to the lecture series on optical spectroscopy and microscopy so far what we have seen is that how the fluorescence's originates from the basic principle of quantum mechanic's we can actually treat the light as well as the matter in terms of quantized particles and then when we do that the interaction of the light with the matter and when we describe in the full quantized picture. This spontaneous emission comes out naturally and then we said that the fluorescence's.

And we extended that to complex substances like complex molecules and we when go into the complex molecules what we said is that the first thing we notice is that the energy itself is composed various different components and thanks to Borne and Oppenheimer Max Bond and Robert Oppenheimer what we could say is that these energy can in turn be written as sum of individual energy you can approximate it to the that way.

Basically it is a saying that each of them are behaving independently on their own I mean electrons are doing whatever I mean energy associated with the electron is different I mean it is not coupled that is a mean point of that released to the approximation and a direct consequence of that when we are looking at spectrum is that instead we seeing all sides I mean instead of we having to worry about estimating the transition ranging from very complex vibronic structure of the molecule we can actually now allows you to predict where I mean how the transition is going to happen right that what Franck and Condon did.

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And all they said is that if you remember in a class we saw that the energy if you are plot the potential energy of the molecule to plot in terms of the nuclear coordinates and then we were talking about 2 electronic energy states the state 1 and state 2 and if you are talking about transition between them. So you can think of transitions any of this ground vibrational level to the excited state vibrational level of course we can come back and argue that okay let us go ahead and estimate how much of the population present in vibration versus the first vibration of the electronic state and so on and so forth.

What it turns out is that if we do that the dominant population is at the ground vibrational level as with the because the energy the gap is considerably high and so you are thinking about I mean it is definitely much I mean it is definitely larger than the electronic energy state the excited state population however what we do see is that still a larger fraction is present at the ground state okay.

So then the question is then from the ground state which vibrational state of the higher electronic state can the molecule reach on the transition and for that Franck and Condon said which I said is the direct consequence of the Born Oppenheimer approximation they said that the transition that happen due to like matter interaction they are vertical in nature in this diagram that is to say that then during this light mediated transition the nucleus I mean electrons when they are going from ground state to excited state then nucleus does not have enough time to reorganize themselves I mean before that the electron jumps in which that is essentially the case.

That is why the line is straight the nuclear coordinates do not change at all it is only the energy of the electronics state goes up okay that is why it is straight and parallel to the energy axis. But then still it can land in V_0 of the excited state V_1 of the excited state or V_0 , V_1 or V_2 of the excited state. Now how do we estimate where exactly it will land on? So for that they said okay now look at the wave function of this states or in fact the square of the I mean modulus square of the wave function themselves the probability amplitude.

Now if you see that the probability of locating molecule with V_0 energy at the electronic excited state and having a nuclear coordinate around this is almost negligible it is close to 0 like that because these green dark green lines actually represent that probability. Now you can actually go ahead and ask how was how is this probability changing as we go up in the vibration vibronic state.

In this particular case where I have drawn as we see that the among the 3 states V_2 seem to be having the higher probability right because that it is reaching at a place where it is further from the mean position. So the means the blue line represent the 0 and they are going up and then coming back on. So when we add up all this areas and it will corresponds to one which means a there is a small but still pretty considerable probability of locating the molecule with this nuclear distance and energy corresponding to V_t .

So here from Condon principle we predict the molecules to starts from the vibrational state and reaches to that V_2 state. Now that is nicely summarized in the expression which is the probability of vibronic transition is directly proportional to integral this integral over the space we can call that as infinity over the entire space is not $dt d\tau$ we can I mean it is a space you are integrating it over the space.

So the if you do that and this is also it is called as the overlap integral if the overlap is high your probability I mean your probability is high as a result the intensity of that particular transition is going to be high. Now that allows you to predict the absorption band of this molecules or the excitation band of this molecules. So that is fantastic and it is good point actually to introduce a correspondence between what we have been taking about as the matrix element which as basically whenever we are trying to estimate the rate of a transition process and we go ahead and

write down that the rate of transition is directly proportional to modulus square of the matrix element right.

So that is this matrix element that is exactly what that is what we have seen in our time dependent perturbation theory and all throughout it does not a matter basic rational does not change so that we can actually look at that. So now this is writing down in terms of the bra and ket vector now often it is convenient to have a corresponding expression in terms of integral so because the final and the initial eigenkets so to speak or energy eigenkets are basically the wave functions of the molecules that we are talking about.

And so this can be solved and obtained for given a structure of the molecule so since they are mathematically describable functions it is nice to know AA I would be nice to establish a corresponding between this and then a calculable mathematically calculable operation and that we can actually the I am going to write down is this matrix elements is equivalent to the integral alpha final the wave function let us call that as a corresponding to the final state.

The operator will just present in the matrix element times Psi I integrated over r space okay now this is I mean moment you write down like this immediately it gives you I mean there are quite a few usefulness that comes in ranging from often we are wanting to know.

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$$\int_{-\infty}^{\infty} (f(\tau)) \cdot d\tau, \quad f(\tau) \text{ - symmetric}$$

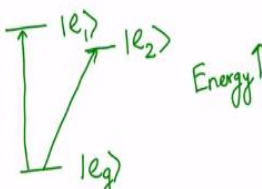
↓
odd parity / even parity

$$f(-\tau) = -f(\tau) \rightarrow \text{odd func}^n$$

$$f(-\tau) = f(\tau) \rightarrow \text{even func}^n$$

$$\int_{-\infty}^{\infty} f(\tau) \cdot d\tau = \int_{-\infty}^0 f(\tau) \cdot d\tau + \int_0^{\infty} f(\tau) \cdot d\tau$$

$$= -\int_0^{\infty} f(-\tau) \cdot d\tau + \int_0^{\infty} f(\tau) \cdot d\tau$$



If let us say there is an electronic state okay eg, e_1 , e_i whichever we would like to call it has or you can take it and then there are let us say 2 available closely spaced electronic states electronic excited states right. So now the transition there are 2 transitions that are possible transition number 1 transition number 2 like that and our energy axis in this direction. So now I am often we would like to know which of these transitions would happen or dominate 1 and even more basic would both these transition be happening at all okay.

So I mean what do you mean by that it is possible that the molecule I mean is it possible for us to predict if eg to e_1 is possible while eg to e_2 is not possible or vice versa are neither of them are possible things like that. And it turns out the at least in some of the cases it is possible thanks to the corresponding I mean correspondence that exist between the integral representations on the direct invitation that we wrote.

So if you look at this now this integral so here what we are actually doing is we are integrating over the all space. So basically it is an integral it is going from minus infinity to plus infinity estimated over all space. So now we can make some prediction about the integral the value of the integral depending on the nature of the function that is going to go inside like for example.

Let us say if you are going to put in sum f of x right I mean f of τ okay so now I am going to be talking about 2 different I mean kind of functions a special kind of functions to start with first where these functions are symmetric or typically this is the case when you have the underlying molecule the wave function were to be describing an underlying molecule which is symmetric. If they are symmetric and FFT10 FF function then to be symmetric tend to be not necessary always but tend to be symmetric.

And they are set to have something called as a parity okay now what is it we are going to define it? So they are sent to tend to have 1 of the 2 kinds of parity only we call it as parity or even parity it is also known as odd functions or an even function. If f of minus τ equals minus f of τ then we call this as odd function on the other hand is equal to f of τ right the sign does not matter then we call that as even function are function with even parity.

Now why we are talking about this now let us say look into let us look at this little bit more i mean in the context of this integral right minus infinity to plus infinity integral for estimating the

rate of the transitions right. So now if the functions were to be of one of these 2 parity then we can actually predict without having to exactly calculate without having to really work out the integral before even working of the integral we can actually predict whether these integral will have a finite value or not now do we do that.

So now let us take this function minus infinity to plus infinity f of τ $d\tau$ and we will write it down it is defined in an interval right minus infinity to plus infinity. We can actually split it up and write it down in as minus infinity to plus infinity f of τ $d\tau$ equals minus infinity to 0 f of τ $d\tau$ plus 0 to infinity and f of τ $d\tau$. Now we can actually for this integral we can actually make a little variable transformation so where we say that τ I mean the τ this τ equal to minus τ I mean is let us say τ I mean since it is a it variable of integration you can actually it is an naming is pretty much arbitrary.

So if you do this transformation then what you have is that you can write it as when the τ become minus τ this whole integral becomes infinity to 0 minus $d\tau$ is equal to minus τ so $d\tau$ equal to minus let us call that as τ prime okay. So avoid any confusion then we have here no transformation so we just retain this as f of τ $d\tau$. Now again I am this limit goes from infinity to 0 so the it is actually the if I reverse the direction so it will be another negative sign.

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$$\begin{aligned}
 &= + \int_0^{\infty} f(-\tau) \cdot d\tau + \int_0^{\infty} f(\tau) \cdot d\tau \\
 &= 0 \quad \text{for } f(\tau) \text{ being odd} \\
 &= 2 \int_0^{\infty} f(\tau) \cdot d\tau \quad \text{for } f(\tau) \text{ being even.}
 \end{aligned}$$

Rate of electronic transition } $|\langle f | \hat{r} | i \rangle|^2 = \int_{-\infty}^{\infty} \psi_f^* \cdot \hat{r} \cdot \psi_i \cdot d\tau$

\downarrow
displacement vector.

$r \rightarrow$ odd func.

So we could actually write it as plus and infinity 0 to infinity now we have 2 of this terms so why do not we actually separately write it n the next page which is equal to minus of minus because

τ prime becomes plus and 0 to infinity f of minus τ $d\tau$ plus 0 to infinity f of τ $d\tau$. Now you can see for I mean d prime right so since it is a variable of I mean it is an it is going to be integrated out so then you can see that for odd functions alright this guy will cancel out okay.

So because this is equal to 0 may be I can write down here this whole expression becomes equal to 0 for f of τ being odd while equal to 2 times this integral for being even so what do we learn from here? What we learn is that if we know that the parity of f of τ is odd to start with then for sure that transition may not I mean that transition does not exist because the integral goes to 0 the probability of the goes to 0 that there are probability of transition goes to 0 which means the rate and the probability goes to 0.

So you do not see the transition only however if it is being even then there is a chance that it might exist okay it is still a chance because when you work out this integral right that may still turn out to be 0 it turns out to be 0 to infinity when you integrate the function f of τ dot $d\tau$ if it integrate over an then it turns out to be 0 you would still have a change of that being equal to 0. However this does not I mean what it allows you to do is that it allows you to rule out certain transition B as being not allowed or in probable transition okay.

So the bottom line is in order for us to know if a given transition is allowed or not allowed then all that we need to look for is I mean if a given transition is could be allowed right please note that it is only could be allowed then all we need to do is that we need to know if f of τ is odd parity or of even parity okay. So now let us see that it is a it simplifies lot of math tremendously like for example we were talking about transition occurring between electronic states alright.

So the transition of rate of that process again let us write now here i am going to specifically introduce dipole moment operator and then write down the matrix element. So rate of transition I mean electronic transition I should say it is modulus square of the square of the final stage and the operator that we are actually looking for is the dipole moment operator are initial state square and then the integral correspondence you make use of is basically minus infinity to plus infinity are infinity I mean over all space.

I am going to write it as $\Psi_f \cdot r \cdot \Psi_i$ $d\tau$ now here it allows you to make some prediction because you see the r the it is just a radial vector right the radial displacement vector right r is

basically the sorry not the radial it is displacement vector in a from our dipole moment operator it is actually. So here the r is an odd function okay if you replace r by minus r it is a it is not equal it is actually a minus of r so it is r is in odd function I as definite parity.

And we know that when we were multiplying a functions of different parity then we have a predictable relation which is I mean again if you this is a common 2 table that we all know but I am going to state it.

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Rate \bar{e} transⁱ = $\int_{-\infty}^{\infty} \psi_f^* \hat{r} \psi_i \cdot d\tau \neq 0 \Rightarrow () \rightarrow \text{even}$

odd

i/f_2	odd	even
odd	even	odd
even	odd	even

$\psi_f \cdot \psi_i \rightarrow \text{odd} \Rightarrow \psi_f \neq \psi_i$ need to be of opp. parity.

$|g\rangle \neq |e_1\rangle$ parity relaⁿ

$|g\rangle \neq |e_2\rangle$ "

opp. ✓

same (x)

If you have a odd function you multiply with an odd function the resultant that you will have would be even on the other hand. So why do not we write it in proper tabular form so this is my function 1 slash function 2 is on the top and if the top functions happens to be odd it can be also even and that can be multiplied with either f_1 being odd or f_1 being even right. So we would like to know what their product is going to be right.

So odd and odd gives you an even odd times even gives you odd function and similarly this is the case and even times even is even okay. Now given this what can we say about this transition odd is a odd function and we also know the truth table kind of. So now the rate of electronic transition then when we write it is actually minus infinity to plus infinity and final r initial d tau. Since this is odd for this integral to be not equal to 0 possibility that being not equal to 0 then this product right I mean $\psi_f \psi_i$ this need to be I mean the whole integral we would like for it to non be non-vanishing we want that whole integral need to be even right.

And if this whole integral needs to be even we want this to be not equal to 0 implies this integral is even I mean the result of this integral is even. This is even so now I mean the whole function is even which means and then we know that it has 3 terms of which one of them is odd which naturally means the product of the resultant to Ψ_f and Ψ_i need to be odd which means which would imply Ψ_f and Ψ_i cannot be of same parity right.

Because if you have them to be of same parity which is odd and odd or even and even being 2 possibilities you see that they end up having even parity and the even parity when multiplied with odd which is odd then will give rise to 0 transition dipole moment I mean the rate of transition. So then that is not that transition is not going to happen so that immediately leaves us with the possibility the Ψ_f and Ψ_i need to be of opposite parity.

So then let us go back to our original question if we have a ground state and states e_1 and state e_2 and we are going to ask alright if there are this possibility then which of them is going to dominate clearly what it tells first thing it tells you is that go ahead and ask if there is definite parity. If it is definite parity then can you please can we look at the relationship between the ground state and the excited state parities okay.

And ration if they are opposite only then we have transition if they are same no transition now that is the very direct prediction of whether I given transition is going to happen or not even more interestingly. Suppose experimentally if you see that there is a transition that is happening between ground state and the state e_1 or let us say state e_2 here and e_1 here we are ordering according to the energy and state e_1 here.

So then what we can actually go ahead and say if we see both these transition happening we can clearly say that this transition is highly unlikely because we know g and e_2 is by the fact by the virtue of the transition happening from ground state to the e_2 and ground state to the e_1 we know that the parity between ground state and the e_1 and ground state and the e_2 needs to be of opposite parties with respect to each other.

And since ground state is common then what it means is that the e_2 and e_1 will be of same parity as a result the transition between e_1 and e_2 cannot happen that is extremely useful. If you have a

complex system to rule out such transitions is very handy and in fact we will see the usefulness of such a system and make some prediction about it in the next class about a photo physical process called phosphorescence's and then see what we can make out from there alright thank you.