Atomic and Molecular Physics

Prof. Amal Kumar Das
Department of Physics
Indian Institute of Technology Kharagpur

Lecture - 52
Electronic spectra of a molecule (Contd.)

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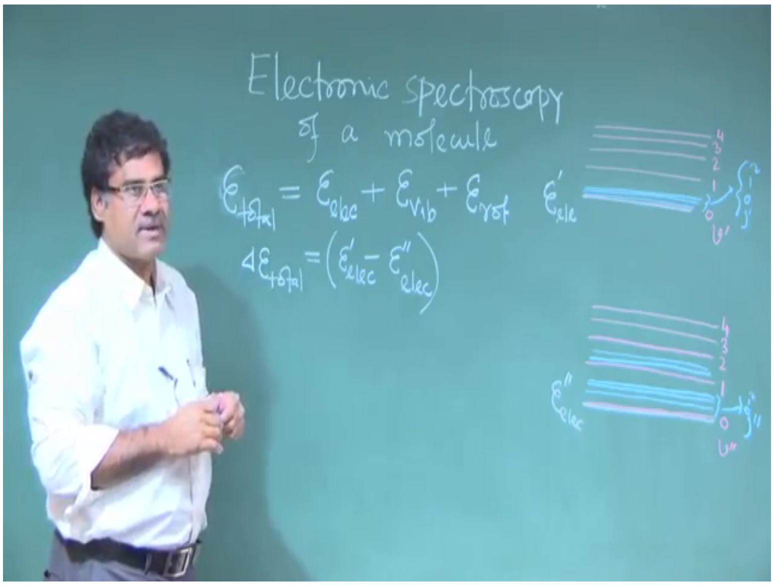

So, Electronic Spectroscopy of a molecule they are basically as we have seen this total energy E total or let us write in terms of centimetre inverse E total equal to E energy of electronic energy level plus vibrational energy level energy of the vibration, vibration and energy due to the rotation ok.

So, this will be the states of molecules this will the states of molecules, where this electronic energy levels are accompanied with the vibrational and rotational energy levels ok.

So, for a particular state it will give the energy of the state as a sum of this individual energy of electronic vibrational and rotational ok. So, now when there will be transition from one state to the another state. So now, one has to one has to remember that electronic transition from one state to another state. So, one state means here electrons or molecules in a in a state where it is electronic state vibrational state and rotational state is defined. Now from this state it is going to the another state. So, another electronic state another in that electronic states another vibrational state in that vibrational state another rotational states are there ok.

So, transition between two electronic energy level; for a particular these two energy levels ok. So, this so this energy, so now these molecules so it has come from one energy level to the another energy level. So, if it is so their energy difference will be energy difference or energy of the spectral lines will be. So, del epsilon is total of the spectral lines equal to. So, if we take that these energy levels their transition between these two energy levels. So, if we take this electronic it is in a electronic state is E double dash and transition from this state to another electronic state it is E dash E electronic E dash ok.

So, they are energy separation this energy separation will be I can write E electronic dash minus E electronic double dash ok. So, this energy separation now each electronic state it will have this vibration due to vibration; it will have vibrational states and that vibrational states if I draw with other colour. So, this so this will be one, the second one is this third one is this because, this vibrational energy level what we have seen that we that is basically vibration.

So, let me draw so this is the vibrational energy level and here this for these electronic states these vibrational energy levels are like this ok. So, here so if we give these states b double dash that will be this is 0, this is 1, 2, 3, 4 similarly this in this electronic state. So, if we vibrational state if we write V dash, so V dash it will be I think it is 0, 1, 2 3, 4, 5 etc right so.

So, now between this so transition from this electronic state to this electronic state, now is transition from which vibrational state to the, which vibrational state here. So, that also one has to see and then each vibration energy level again it is a shaded with the, with the with the rotational energy levels so this their energy are small. So, each one will be again so they are spacing decrease basically their spacing decrease.

So, each one will be yes each vibrational level will be shaded with the with the rotational energy level. So, this one can write g double dash equal to say 0, 1, 2 etc ok. Similarly here also there will be rotational energy level there will rotational energy level. So, here j dash 1 can write j dash that 0, 1, 2, 3 etc ok.

So, this basically it is here this basically it is here right. So, your energy so seems so here let us see first this only considering the vibration energy neglecting these rotational energy separation.

So, that is why if we tell that so let us see these electronic spectra that is a basically electronic spectra, this coarse structure of electronic spectra or vibrational coarse structure of electronic spectra. So, now we are seeing the basically core structure vibrational coarse structure vibrational coarse structure yes.

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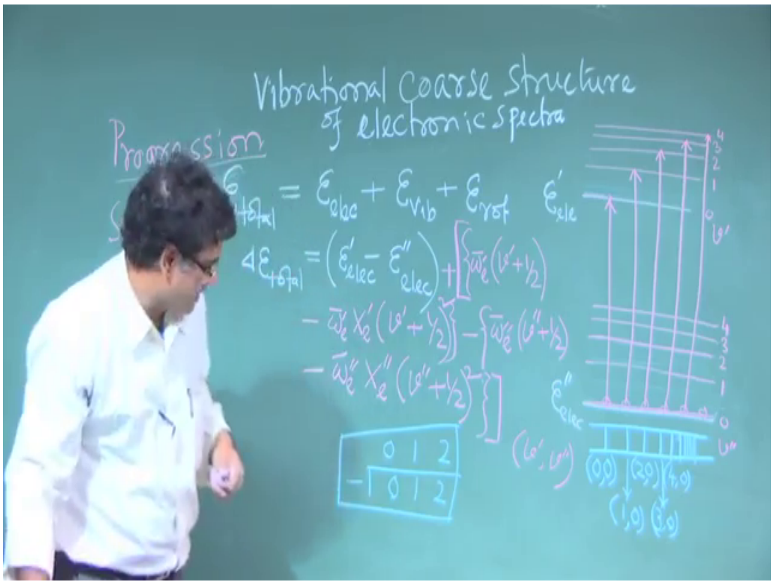

So, this vibrational of electronic spectra basically vibrational coarse structure electronic spectra electronic spectra and then later on we will see this rotational fine structure of electric spectra. So, at the moment we are neglecting this rotational fine structure, so that means say this is we are not considering these energy levels we are not considering this energy level.

So, in this case this total energy it is basically this plus I think I can use this another colour, so this energy so here you will see this for vibrational energy that is omega E bar V plus half, so here we will write V dash. So, V dash here also we write omega E dash this minus not yes minus. So, I can write basically this minus of minus of omega E dash E dash V dash plus half ok, then close second bracket ok.

So, this is the vibrational energy say in one of them V equal to 0, 1, 2, 3, now it is going from here to here. So, minus minus of omega E this double dash V double dash plus half minus omega E double dash bar chi E double dash V double dash plus half, I think this is square I think this one is square hopefully this yes I think.

So, yes V plus half square I guess yes it is square I think this one is square this one is square, so here also this is square ok. So, then so this change will be basically this change will be basically due to the vibration ok. So, send this rotational part we have neglected for this for this for this case and you can tell that this the energy of the spectral lines and if you consider the this selection rule del V selection rule is del V this change is, now it is not in same electronic state you know. So, it is one electronic state to the another electronic state, so del V basically V dash minus V double dash ok.

So, that will be say 0 plus minus 1 plus minus 2 etc ok. So, if you consider the transition, now in really the spectral lines 2 types of spectral lines which tell that one is absorption spectral lines another is emission spectra lines. So, there are some advantage considering the absorption spectral lines 1 advantage is that, that I can consider that this before transition the system the molecular system it is at a ground state lowest energy level state, it is in lowest energy level of electronic energy as well as vibration energy. So, we can consider this initially molecules are in this energy in this energy right.

Now, if you put light on it or if we excite it, so it will go from here to the higher energy state ok. So, this spectral lines we will we will see that it is two ways we define them one is progression one is progression another is one is progression and another is called sequence another is called sequence ok.

So, what is progression, progression is basically if all if this transition starts from here, so this is the ground state if transition starts from here V double dash equal to 0 and it is going and it is going to here V double V dash equal to 0 then V dash equal to 1 V dash equal to 2 V dash equal to 3 V dash equal to 4. If it is it is transition is like this then we label this these spectral lines we label the spectral lines by using V dash V double dash.

That means these spectral lines whatever the spectral lines we will see say let me just the spectral lines we will see this these spectral lines here, the spectral lines yes here ok, I think it should be closer it should be closer. So, like this we will see spectral lines, so these spectral lines here we I think I will remove this, then this will be labelled using this

0 0 0 0 this will be labelled as a as a 1 0 this is 2 0, this is 3 0 then this is 4 0. So, this way these spectral lines are labelled and this is called this progression spectral lines, this vibrational coarse structure whatever it is this type of spectral lines this is called progression because, here you can see this V dash it is in progression because this 0, 1, 2, 3, 4, so it is increased by 1 ok.

So, that is why it is called this displaced spectral lines are called progressive spectral lines and another type as I as I told that it is called sequence it is called sequence sequence. So, basically it is a it is like this so here to here then here to here then here to here then here to this is as a sequence. So, 0 to 0 to 0 1 to yes 1 to 0 1 to 2 to 0, 3 to 0 4 to 0 like this or this yes, I think these difference this is coming as a I think this is it is a sequence the difference it will be it will be like this either 0 1 2 or minus 1 0 1 2 ok.

So, these are the as if it is following the sequence sequence ok. So, this del V here it is I think I will I will tell you this I think let us finish this, I have to I think let me finish this progressive 1 later on I will tell about this sequence on because, I have to I have to draw this spectral line separately then it will be easy to understand.

So, now here what I have shown you these spectral lines there are many spectral lines and their separation are decreasing their separation are decreasing right. Now, question is that here whatever the spectral lines you are seeing whether we will what will be the what about the intensity of the spectral lines, all spectral lines are same intense or there are some spectral lines only we can see all spectral lines you cannot see.

So, let us see what about the intensity of the spectral line. So, this intensity of the spectral lines in case of sequence in this case what will be the intensity of the spectral lines, intensity of the spectral lines vibrational coarse structure of course. So, in this case what is the intensity of intensity of spectral lines or spectra yeah intensity of spectra whatever we have seen here spectra whatever the intensity of that one.

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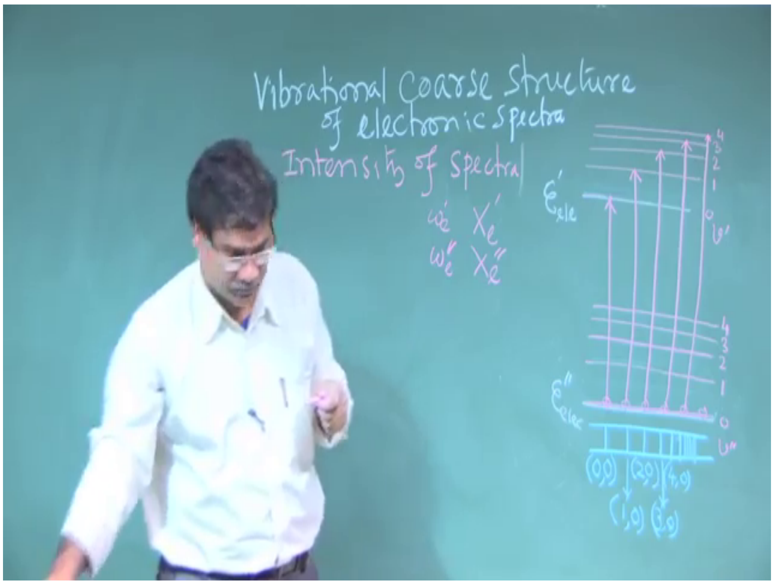

Now, intensity it is so intensity means the transition probability right. So, here if all atoms or molecules are in this state have down state ok, now when there will be electronic transition ok. So, now molecule so from these state from this electronic state it will go to the another electronic state ok. So, then it is a it is in a different situation right, it is in a different situation x omega we have seen that I have written this omega E and k e X e that harmonicity constant.

So, we have written dash also we have written double dash; so that means. So, in this state in this electronic states there is vibrational frequency and there a anharmonicity; So, there for in this state whatever vibrational frequency and anharmonicity constant, so that will be different in this another electronic state ok.

So, that will be different in another electronic state so; that means, it is vibration states will be affected say it is. So, it will it will be different vibrational states sets of vibrational energy levels ok. Now so from here when from this electronic step it is in a particular vibrational state, now what is the probability to go from here to there?

So, this is the electronic state that is fixed now what is the probability to go in these vibrational energy state or these vibrational state or the other vibrational states ok. So, what is the probability so that will decide the intensity of the of the spectral light because here all are say more than we considered that is why we consider the absorption spectra lines. So, in that case one can easily assume that all molecules are in a lower lowest energy state either electronic or this vibrational.

Now, from here it is going to the another electronic state, when it will go in another electronic state it will be in different vibrational configuration; that means, it is vibrating 2 molecules 2 atoms in a in a in a molecule they are vibrating. So, energy levels of this vibration it depends on the separation of these 2 atoms right. So, separation is changing their energy are changing, so they are in different and they will be in different energy states ok.

So, when it is here as if vibrational, so they are vibrational state they are in equilibrium distance because it is V double dash equal to 0. So, they are in equilibrium distance ok, so that is the vibrational state in this electronic state electronic double dash now from here it is going to the another electronic state E dash E electronic dash that is fine.

Now, when it is going to E electronic dash in that electronic state, what is the what will be the vibrational state of when it is in this electronic state, what will be the vibrational state means what will be the separation of these 2 atom in the molecule ok.

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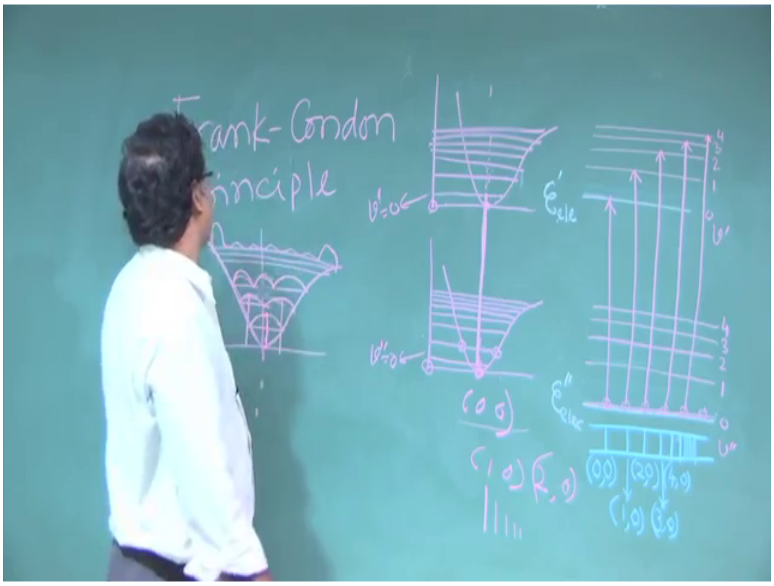

So, that means here I can so here we can tell that this their. So, 1 molecule 1 atom is say fixed ok. So, when they are separation is changing, so their energy will change energy will change right. So, this is the equilibrium energy. So, from here it is changing like this and from here it is changing like this ok.

So, this is the separation corresponds to this vibrational level now if separation is this. So, now separation is changing so other 1 is it is vibrating right when it is energy will be same ok, in this state from equilibrium it is vibrating. So, it is this the energy this is the energy states energy level.

So, this it is the different energy level is a different energy level right, now similarly here when it is in these electronic state just electronic transition then exactly at that time what is it is vibrational state ok. So, I think I need the space. So, in this case so if we consider see in this electronic state it is if I consider that x so that we have to consider it can be in any states, but I do not know it can be in any states ok.

So, if I consider that after this transition here it has come here, so electron this vibrational state in this electronic state is this V dash equal to 0 ok. So, if so then again if you draw this I think I should go along the symmetry ok. So, actually I have drawn here this on this for 0 state energy is not 0, so that is our (Refer Time: 29:12) we energy of this yeah it is here energy is here basically ok, when atom is here in this molecule. So, it is energy state is this ok. So, that is the V equal to 0 that is V equal to 0 V double dash equal to 0. So, this yeah then 1 2 3, so here it is V dash equal to this 1 is V dash equal to 0 ok.

So, now if we consider that these will be the energy state vibration energy state in this electronic state, if we consider then there will be all transitions as if the way I have told this all conditions are possible, but here Franck-Condon. So, this there is a principle is called Franck-Condon; principle Franck-Condon principle, what it is telling, it is telling that this one may tell that it is it is initial state now from initial state it is going to the excited state.

So, it so during transition electronic transition and this vibration all the time it is changing right, all the time this vibration this position of the that is why it is vibration, this vibration this molecule atomic distance between these 2 molecules is basically changing type so.

So, transition from this electronic state to another electronic state, in case of absorption spectra it is fine all the molecules are in this lowest vibrational state. Now, in during transition after transition it can go it, so this vibrational state of this excited electronic state excited electronic state these vibrations vibration state. So, it is all the time it is vibrating.

So, during transition so these vibrational state these vibrational state can be this one because, all the time it is changing all the time it is changing it can be any one of them right. So, it can go from this transition vibrational transition it can be from here to here, it can be from here to here it can be from here to here that is how we have we have done drawn like this ok.

So, but this principle is telling it is considering that electronic transition is so fast, compared to the vibrational transition compared to the vibrational transition ok. So, one can consider that one can consider that this during this electric transition whatever the molecular vibrational state here and here during this electron transition, so it will see that that state only ok.

So, another state to change to the another state vibrational state whatever the time it is taking. So, before that time before this that time is higher than that this just sudden transition electronic transition, it is so fast this transition will not see change of the vibrational change ok.

So, as if whatever it will during transition electron whatever it is here. So, whatever the position of the vibrational state it will see that one and it will go there ok. Now, if this is the situation during electronic transition, now it is telling one can tell that this what is the probability here. So, a special probability if we consider this first for harmonic oscillator, if you if you draw the wave function or probability function it varies it varies like this I think this.

So, for 0 point so this wave function is like this for next one this probability sorry you know the wave function is like this, in this wave function is like this the second next one wave function will be like this now priorities high square. So, probability will be like this yes probability will be like this probability will be like this. So, here yeah probability will be like this ok.

So, what is the probability what so this in it is telling that this molecule this it states is here at these distance and here this for it to stay at this distance at this distance this is the highest probability this is the highest probability and here if you go higher and higher you will see, so this probability will not be I think it is smaller ok.

So, you will see this if you go higher and higher vibrational level you will see this probabilities is shifting towards the edge. So, at the edge of this curve at the edge of this curve the probability will be maximum and that is the classic issue from quantum mechanics you can say like this and classically you can say that you see this it is oscillating vibrating right ok.

So, in turning point it will spend more time because, it is going and then coming back it is going and then from here coming back. So, turning point this molecule atom will spend more time oscillator will spend more time. So, to find the oscillator at this position is maximum and that is what. So, it is going towards classical concept for higher vibrational level. So, initially it is in middle highest probability and then this probability shifting towards the towards the edge towards the turning point.

So, if you consider this probability so in this case here is the highest probability and if this is the position of this excited state. So, these lines so transition between these two transition between these two. So, 0 0 that will be maximum transition from here to here to another you see here, if we go this way so it will see this as if this vibrational state it like this.

So, here going there it is probability is less as for here probability less in middle or other energy level this probability will be less ok; that means, it will go, but probability less. So, the intensity this of other lines 1 0 2 0 this probability will be less than intensity will be less.

So, this will be most intense line and in this case that is why 1 can tell that these the intensity of 0 0 spectral line and the intensity will decrease will decrease for another ok. So, this is far as what this Franck-Condon principle. So, these are intensity value. So, this one state I have shown you. So, if it is so I think I will continue the discussion it will take some time.

So, here I have consider one situation, so if situation is different see if when this electron transitions is there. So, atomic this position in this excited state or vibrational that distance is not this one, it is different either higher or lower. So, considering that 1 what will be the transition probability. So, in that case we will see this not 0 0 it may be 2 0 may be this intense line ok, so I think we need to discuss more.

So, I will continue next class.

Thank you.