Atomic and Molecular Physics
Prof. Amal Kumar Das
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture - 53
Electronic structure of molecules

So, you are discussing about the electronic structure of molecule or basically electronic spectra ok.

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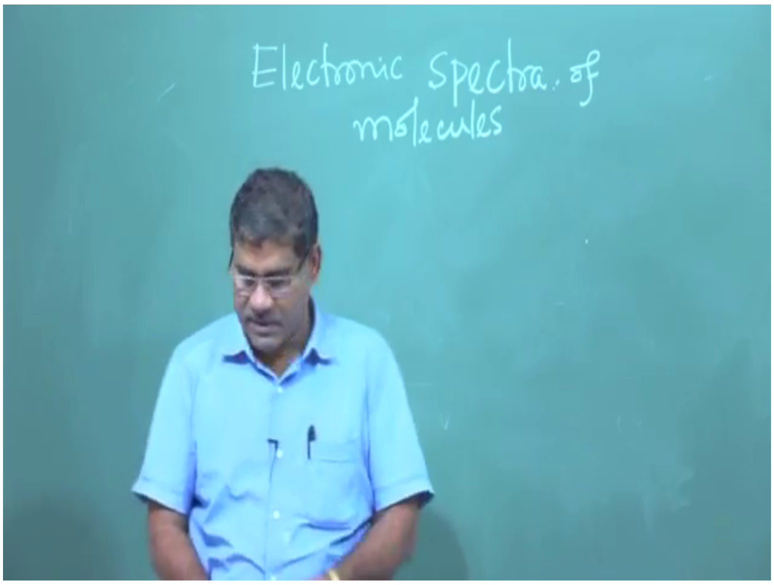

So, what we have seen this I will just show you here.

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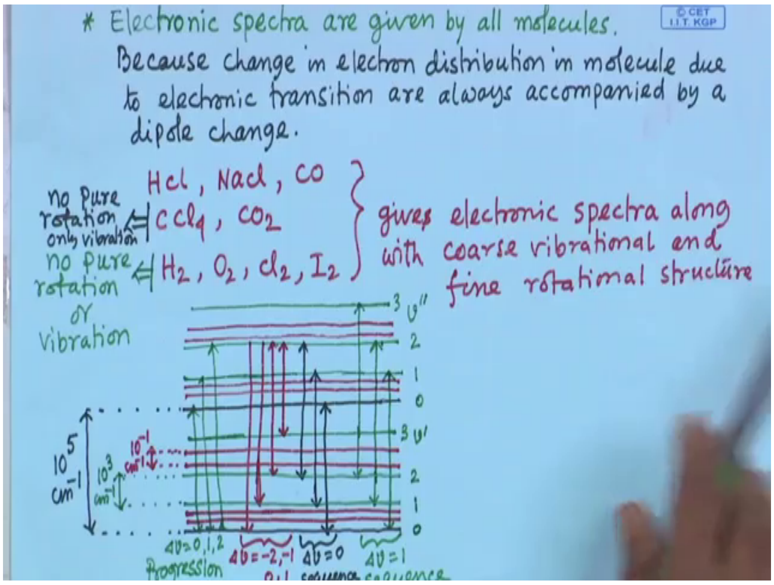

* Electronic spectra are given by all molecules.
Because change in electron distribution in molecule due to electronic transition are always accompanied by a dipole change.

HCl, $NaCl$, CO
CCl_4, CO_2
H_2, O_2, Cl_2, I_2
} gives electronic spectra along with coarse vibrational and fine rotational structure

So, here this we have seen that any molecules show these electronic structure, electronic spectra; although this some of the molecules which are which are not having permanent dipole moment. So, they do not show the rotational spectra as well as vibrational spectra, that is microwaved spectra or this infrared spectra.

But in case of electronic spectra, so these all molecules, which shows the rotational or vibrational spectra, they also shows these electronic spectra as well as well as they these other molecules like CCl 4, carbon dioxide, hydrogen, molecule oxygen, molecule chlorine, iodine. So, they also shows the electronic spectra, although they do not show any pure rotational or vibrational spectra ok.

So,. So, this in electronic spectra, basically it has coarse structure as well as fine structures. Coarse structure it is related with the vibration of the molecules, and fine structure it is related with the rotation of the molecules. So, if we consider just one electronic state and in that electronic states, there are vibrational energy level. So, this black 1 here this is the electronic state and this next black one.

So, this is the another electronic state, excited state may be. So, these different is 10 to the power 5 centimetre inverse and now or with each electronic state, there are vibrational state. So, this wheel lines; so, this I have written here this v dash vibrational quantum number. So, this v dash equal to 0, 1, 2, 3 ok. So, this is the lowest energy state, electric energy state and in that state these are vibrational energy level. So, similarly for higher electronic state, they are this vibrational energy level is v double dash 0, 1, 2, 3 this is the associated with e.

Now, each vibrational level again it has fine structure means rotational due to rotation, they are again finer energy level. So, I have drawn here with red line ok. So, now, if we just neglect the fine structure for the time being, if we just consider the vibrational structure. So, that is called basically coarse vibrational structure the electronic structure. So, in that case so, here this selection rules it is the del v equal to 0 plus minus 1 plus minus 2 etcetera it is the all are allowed all transitions are allowed.

So, now two types of spectra coarse vibrational electronic spectra is observed. So, one is called progression, another is called sequence. So, for progression this higher here we have we have shown this del v equal to 0. So, here to here this transition del v equal to 1. So, here to next vibrational level ok. So, similarly to from v dash equal to 0 to v dash v double dash equal to 2.

So, this is the progression similarly this another set we have shown here del v equal to minus 2 minus 1, 0, 1. So, this transition so, these also called progression. Other one is called sequence. So, maintaining this del v equal to 1 or del v equal to 0. So, this is del v equal to 0 for this these are the transition that all are follows that del v equal to 0. So, this type of spectra is called sequence; similarly del v equal to 1 another sets of spectra. So, these are these are the example of progression and sequence ok.

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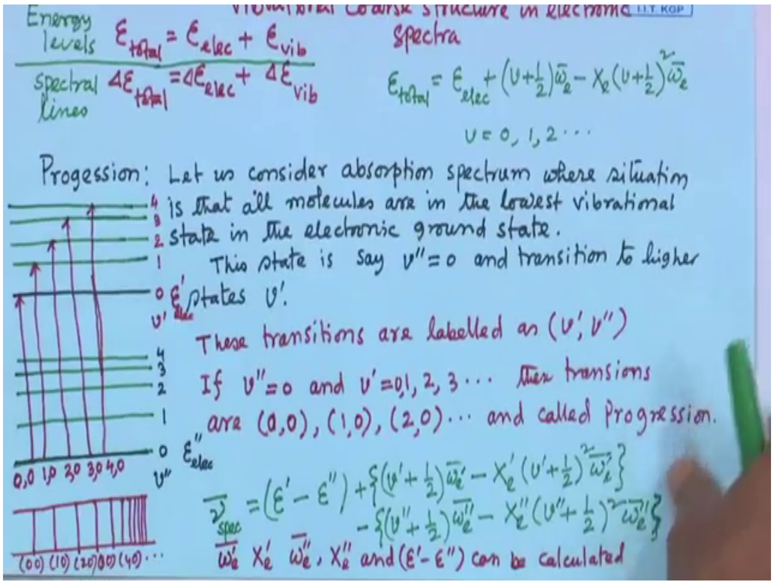

Coarse structure in electronic Spectra

Energy levels $\varepsilon_{total} = \varepsilon_{elec} + \varepsilon_{vib}$

Spectral lines $\Delta\varepsilon_{total} = \Delta\varepsilon_{elec} + \Delta\varepsilon_{vib}$

$\varepsilon_{total} = \varepsilon_{elec} + (v+\frac{1}{2})\bar{\omega}_e - x_e(v+\frac{1}{2})^2\bar{\omega}_e$

$v = 0, 1, 2 \cdots$

Progession: Let us consider absorption spectrum where situation is that all molecules are in the lowest vibrational state in the electronic ground state.

This state is say $v''=0$ and transition to higher states v'.

These transitions are labelled as (v', v'')

If $v''=0$ and $v'=0, 1, 2, 3 \cdots$ then transions are $(0,0), (1,0), (2,0) \cdots$ and called Progression.

$$\bar{\nu}_{spec} = (\varepsilon' - \varepsilon'') + \{(v'+\frac{1}{2})\bar{\omega}_e' - x_e'(v'+\frac{1}{2})^2\bar{\omega}_e'\} - \{(v''+\frac{1}{2})\bar{\omega}_e'' - x_e''(v''+\frac{1}{2})^2\bar{\omega}_e''\}$$

$\bar{\omega}_e'$ x_e' $\bar{\omega}_e''$, x_e'' and $(\varepsilon' - \varepsilon'')$ can be calculated

Now, if I. So, that if we consider the progression. So, they are they are basically these transition between the vibrational energy levels associated with different electronic level. So, E dash E double dash similarly here vibration v dash and v double dash. So, in case of progression. So, these; so, it this transition and these lines are basically it is it is called by this level v dash, v double dash.

So, transition from v double dash 0 to v dash 0. So, its 0 0 line, similarly 0 0 line, similarly here is 0 to 1. So, v dash is 1 v double dash is zero. So, 1 0 line, 2 0 line 3 0 line. So, these are the these transitions are lebelled with v dash v double dash. So, what are the what are the wave wave number for these each energy level. So, that one can find out just E total that is, E electronics plus vibrational energy level. So, E electronics and then vibrational energy levels for different value of v vibrational quantum number v equal to 0, 1, 2, 3 etcetera ok.

So, now transition from one electronic state to another electronic state and then one electronic state where this molecule is in a particular vibrational level, and then it is going to the another electronic state, but different vibrational level at different vibrational level. So, what will be the energy or wave number of these spectral lines? So, that one can calculate. So, this wave number of the spectral lines will be, energy difference of the electronic state E dash minus E double dash; plus now here is from v dash to v double dash. So, here this vibration energy so, that from electronic state E dash. So, if that is v dash is the vibrational quantum number.

So, this energy minus that the v double dash in that vibrational level, whatever the energy. So, if you just take the difference of these two as well as here already we have taken electron difference in electronic state. So, this will be the ah wave number of the spectral lines and basically in spectroscopy, one can see this type of coarse vibrational coarse structures in electronic spectra and one can measure the wavelength or wave number of this frequency from spectroscopy for each lines ok. And then basically one can determine the frequency the this omega e dash, omega e double dash for ground state as well as excited state; anharmonicity constant X e dash X e double dash as well as this electronic energy difference also or can be calculated using this expression ok.

So, now question is here, here whatever the spectral lines I am showing and here you can see these spectral lines basically their separation are decreasing with higher with quantum number vibrational quantum number. This is one observation and second observation is that, intensity of all lines are not same ok. So, now, we will concentrate this why the intensity are not same for all are lines. So, why it is different and how it varies. So, in that we would like to see and that is basically intensity of vibrational electronic spectra.

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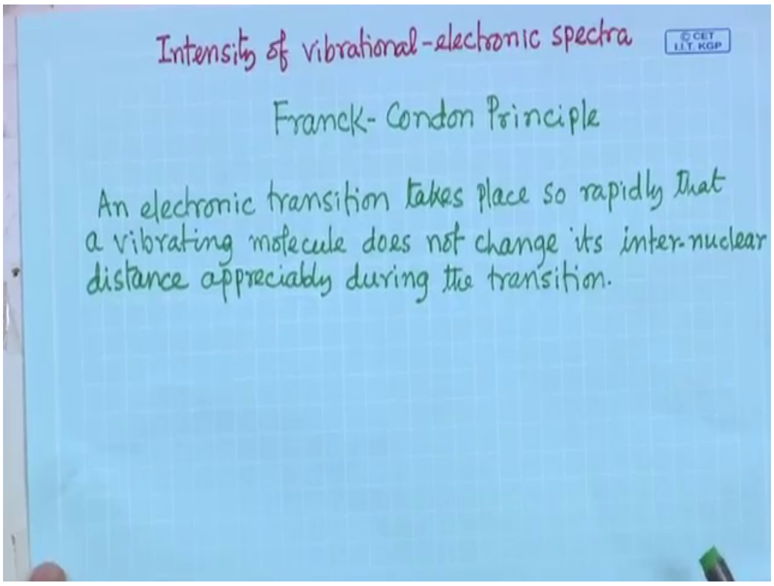

Intensity of vibrational-electronic spectra

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Franck- Condon Principle

An electronic transition takes place so rapidly that a vibrating molecule does not change its inter-nuclear distance appreciably during the transition.

So, there is as already I have mentioned that Franck Condon principle generally tells about the intensity of vibrational electronic spectra. So, what is that Franck Cardon principle? Is telling that an electronic transition takes place so rapidly, that a vibrating molecules molecule does not change its inter nuclear or distance appreciably during the transition. So, actually this molecule is all the time this its if it is diatomic molecules. So, these two atoms are vibrating and they are in different vibrational energy level, now they are in different vibrational level means, their separation are different ok.

So, with time their separation changes now, now during the transition from one electronic state to the another electronic state. So, this transition is so rapid that this during the transition, one can assume or consider that the molecular that atomic separation, inter nuclear distance will not change during this transition ok. So, that is the Franck Cardon principle.

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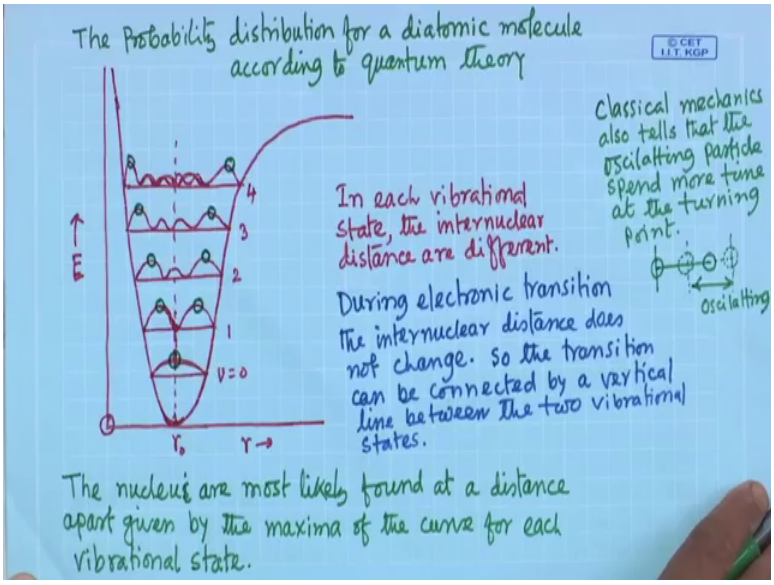
The Probability distribution for a diatomic molecule according to quantum theory

In each vibrational state, the internuclear distance are different.

During electronic transition The internuclear distance does not change. So the transition can be connected by a vertical line between The two vibrational states.

Classical mechanics also tells that the oscilatting particle spend more time at the turning point.

The nucleus are most likely found at a distance apart given by the maxima of the curve for each vibrational state.

So, now, from this to understand this principle basically one has to understand that if it is telling that this transition, this transition actually can be represented by the by the particle lines. So, what is the meaning of that so, that I will tell, but here let us understand that the probability distribution for a diatomic molecule according to quantum theory ok. Probably distribution for a diatomic molecule, harmonic oscillator in case of harmonic oscillator you know that this is the variation of the potential energy this is the most potential curve most potential curve, now it has different states it has different states different energy levels ok.

Now, what is the probability of finding molecules in different states and yeah. So, that depends on basically. So, this curve has come how it is it has come that I have discussed. So, one can consider this one atom is fixed here now another atom is vibrating another atom is vibrating. So, depending on the distance depending on the distance of the another atom. So, they are in different energy levels ok.

So, now what is the probability of finding the molecules in here? So, here it is shown that, this probability from quantum mechanics this at ground state this probability of finding particle it is it is a probability curve is like this psi square basically, it is like this for v equal to 2 first excited state. So, probability is like this second probability like this. So, from here one can see that the probability is shifting towards the at the end of the curve when we are going towards the higher vibrational quantum number ok. So, for lower quantum number so, its probabilities is its in middle, v equal to 0 it is for highest priorities here now this probability is shifted is going towards the end of this on the of this vibrational curve. So, end of this vibrational curve what does it mean? There basically is the turning point of the of the oscillator. So, in classical mechanics also tells that, the oscillating particle spend more time at the turning point ok.

So, one atom is fixed here and another atom is its say its these the equilibrium position now it is vibrating. Now this is the turning it is going and dealing turning point source more time spending at the end at the turning point more time spending at the turning point so; that means, at the turning point means here at the end of this of this curve here the curve. So, the probability will be maximum.

So, classically as well as quantum mechanically, we can say this is the probability distribution of the of the of the molecules or to find out the molecules this is the probability distribution now during. So, in each vibrational state the inter nuclear distance are different right. So, in each vibrational state the inter nuclear distance are different ok. Now during electronic transition the inter nuclear distance does not change ok, that is why that is what franck condon principle ok. So, the transition can be connected by a vertical line between the two vibrational state ok. So,. So, basically that if we consider. So, this so molecule it is in a in a particular state vibrational state.

Now, during electronic state during electronic transition. So, this molecule maybe in another vibrational state or it can be in same vibrational state. So, if we if we consider this curve for one one electronic state and corresponding vibrational state, and if we take similar another curve and there if we show the vibration different vibrational level ok. So, during electronic transition they are not changing the inter atomic distance so; that means, this is for one another if we consider.

So, now, the distance are not changing, if we construct that one. So, considering they are in the same configuration. So, we can just draw vertical lines to show the transition. So, in that case one has to consider that in ground state where is the maximum probability. So, it is going to the next excited state, there it will go in that state where the probabilities maximum ok.

So, in space basically here itself considering the connecting the maximum probability of this of this lower electronic state to the higher electronic state means, they are corresponding vibrational states at lower in a lower lower electronic state there are vibrational level it was in a particular vibrational level, now it is excited state electronic state, now their vibrational levels are there. So, in which vibrational level it will go so, that we can connect with the vertical line, basically connecting the maximum probability of this of vibrational level of this ground state and the excited state. So, that that is what the meaning of these Franck Condon principle, and that I will show you.

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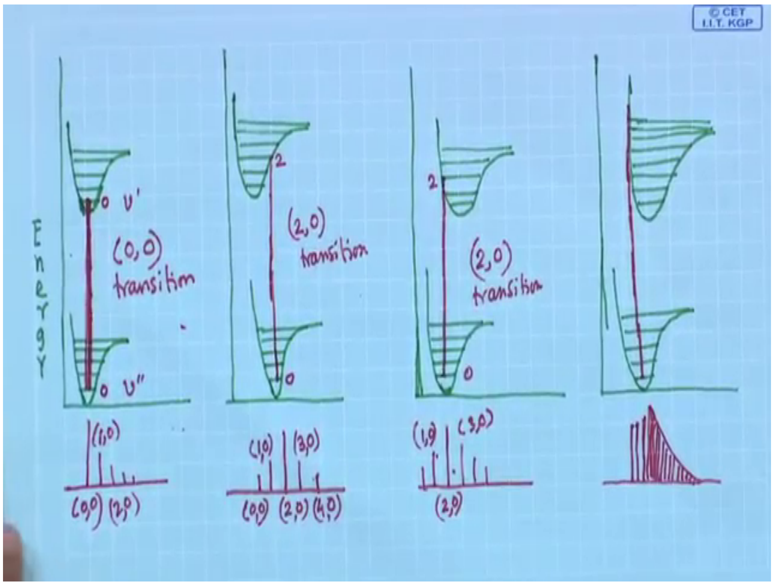

So, here we have considered this four configuration. So, here this is one one electronic state and they are corresponding vibrational states and this is another excited state electronic state and their corresponding vibrational state.

Now, during change during transition electric transition as this vibrational there will not be change of electronic this inter nuclear distance. So, if we consider this was the position of this vibrational state at lower electronic state and the higher electronic state. So, now, this. So, and we are considering that these molecules we have molecules are at the ground state ground vibrational state.

So, this here v double dash equal to 0. Now from here if I draw a vertical lines. So, here we have to see here the why it will cut. So, it will cut, we have to draw we have to choose this vertical line such a way that it will connect the connect the connect the maximum probability of the molecules in that vibrational level ok.

So, here is it is in the middle maximum probability, now from middle if I draw a vertical line. So, now, it is going to the middle of this of this vibrational level ok. So, there v dash equal to 0. So, these stuck this. So, this will be the possible transition maximum possibility between of this transition for this configuration of the vibrational states ok. So, these are called 0 0 transition ok.

Now in this case this 0 0 that that is the maximum probability of transition. So, there is intensity of these lines will be maximum and then this from 0 to from 0 to 1 you see if I draw this lines here. So, I have shown the probability of the here you can see this probability if we draw this way this probability at the middle is really small ok.

So, because it is shifted towards the n so, but there are some probability. So, you will get line spectral lines you will get spectral lines, but intensity will decrease. So, intensity you will decrease for 1 0 and then further decrease for 2 0 etcetera ok. So, in this case in this configuration you one will get the distribution of the intensity like this. So, here 0 0 line will be the will have the maximum intensity. Similarly if this is the situation during electric transition ok.

So, this ah ground state ground electronic state and this excited electronic state during this electronic transition this was the configuration of the vibrational state. So, so we consider that there will not be any change in vibrational in atomic nuclear distance inter nuclear distance. So, here now starting from the 0 if we draw the vertical lines. So, it is going, it is cutting this at the at this v dash equal to 2 ok. So, these will. So, this is the maximum probability and here the maximum probability at the v equal to 2. So, this basically will have the maximum probability of transition. So, 2, 0 lines will have the maximum intensity 2, 0 lines will have the maximum intensity 1, 0 will be the lower 0 0 will be the even lower ok.

So, here 0 0 was the maximum probability ok. So, intensity was the maximum and now here 2 0 will be the maximum intensity ok. So, so here we have shown here also in this case also if this is the configuration of vibrational states in ground electronic state and the higher electronic state. So, there if transition occurs in this condition situation so, you will get also this to 0 highest intensity ok.

Now, this is extreme case if their vibrational state is like this. So, here only this transition probability will be maximum here. So, this basically I think these the very high v dash value vibrational quantum number v dash this is a high v dash value and this basically it is close to the continuum. So, after that; so, all the whatever will give it is a continuum line you will get because separation between the vibrational energy levels at higher v you know it is very its tends to 0 ok.

So, this spectral lines the whatever will get. So, that is it will it will basically the continuum spectra and they are continuous spectra intensity here it is maximum and then its for other transitions its the just decay and for other transition close to these other transition close to these continuum lines or higher maximum intensity we observe. So, other few lines you may get, but they will have the reduced intensity ok.

So, these the this is the way one use the Franck Condon principle to explain the distribution of the intensity of the spectral lines, basically vibrational spectral lines. So, that is the coarse structures vibrational coarse structures of the electronic spectra. So, one has to really try to understand this Franck Conadon principle, and I think I try to explain, but you should think over it and try to try to be clear of this principle because its it is not very it is not very tough, but it is one has to realize and I think one has to understand the probability of the molecule staying in different vibrational states.

So, this from quantum mechanically we have shown that probabilities is at the ah close to the close to the curve close to the curve at different at higher basically higher vibrational states, this probabilities maximum at the close to the curve and that is nothing, but the turning point. So, classically one can think that at the turning point the probability of the molecules in that in the vibrational level is its maximum because it is spend it takes more time to turn ok. So, more time it will spend there ok. So, I think I will stop here I will continue in next class.

Thank you.