Fundamentals of Spectroscopy

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Lecture – 58
Electronic Spectroscopy - 2

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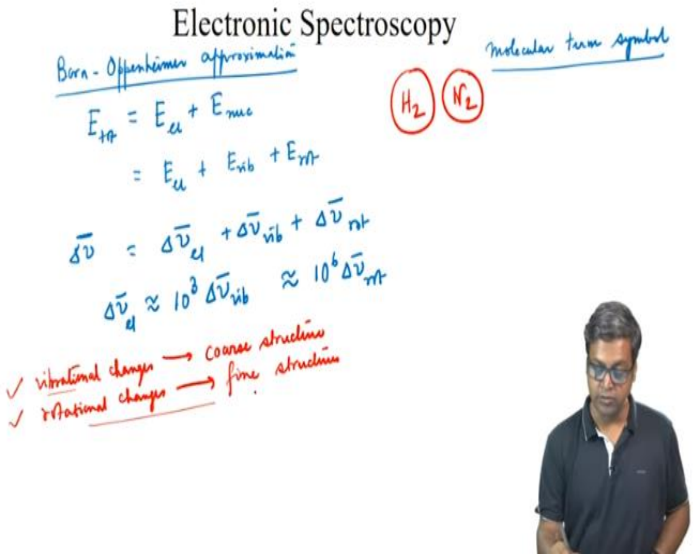

Electronic Spectroscopy

Born - Oppenheimer approximation

molecular term symbol

H_2 N_2

$E_{tot} = E_{el} + E_{nuc}$

$= E_{el} + E_{vib} + E_{rot}$

$\delta\bar{\nu} = \Delta\bar{\nu}_{el} + \Delta\bar{\nu}_{vib} + \Delta\bar{\nu}_{rot}$

$\Delta\bar{\nu}_{el} \approx 10^3 \Delta\bar{\nu}_{vib} \approx 10^6 \Delta\bar{\nu}_{rot}$

✓ vibrational changes → coarse structure
✓ rotational changes → fine structure

Hello welcome to the lecture in the last lecture we discussed about the molecular term symbol. So in today's lecture we will start with Born-Oppenheimer approximation. So we have talked about Born-Oppenheimer approximation before in previous modules and this approximation can be used as the first approach to the electronic spectra of diatomic molecules. So as we have seen before we can write this E total that is the total energy, we can write it as E electronic + E nuclear and further we can write this as E electronic + E vibrational + rotation.

So this implies that electronic vibrational and rotational energies of a molecule are completely independent of one another. So this approximation is not fully valid however in wave numbers unit we can write the difference in energy that is delta nu bar = delta nu bar electronic + delta nu bar vibrational + delta nu bar rotation. So the approximate order of these changes or we can write delta nu bar is approximately equals to 10 to the power 3 delta nu bar so this is electronic this is vibrational, or we can write approximately equal to 10 to the power 6 delta nu bar rotation.

So thus we can see that this vibrational changes will produce something. So the vibrational changes will produce something which is known as the course structure in the electronic spectrum or in the spectra involving electronic transitions and we should also note that the rotational changes will also affect the spectra of electronic transitions and it will give rise to fine structures.

So we should note here that whereas pure rotational spectra are shown only by molecules possessing a permanent dipole moment and pure vibrational spectra are shown only by molecules where there is a change in the dipole moment during the motion and we have discussed about this pure rotational spectra and pure vibrational spectra in detail when we are discussing the modules on rotational spectroscopy and vibrational spectroscopy.

However, the electronic spectra are given by all molecules since changes in electron distribution in a molecule always is accompanied by a dipole change. So thus for homonuclear molecule so molecules like hydrogen or nitrogen for these homonuclear diatomic molecules which show no rotation or no vibrational rotational spectra do give electronic spectrum and show vibrational and rotational structure in their spectra.

And from these vibrational rotational structures, we can find the bond vibration frequencies or the rotational constants and so for now we will ignore the rotational fine structures and we will only focus on the appearance of this vibrational core structure in the electronic spectra.

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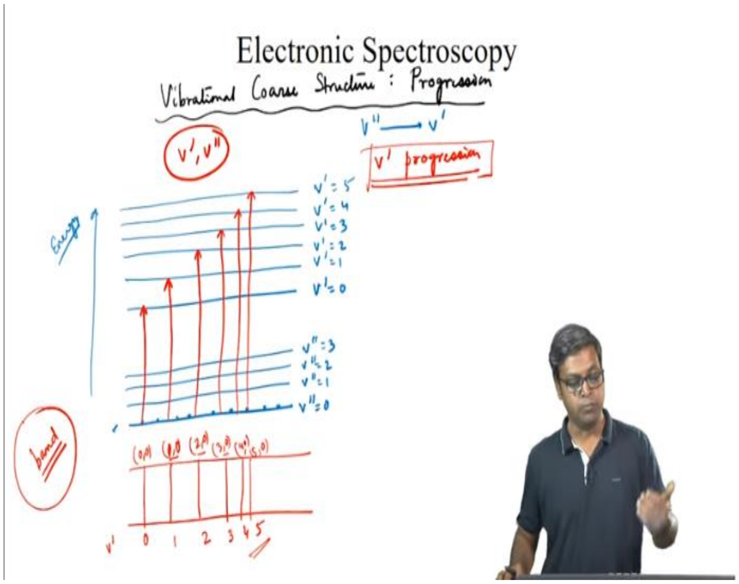

So now let us talk about the vibrational coarse structure which is also known as progression. So here we draw a figure which shows the energy levels of two different electronic states. So this is one electronic state, and this is the other electronic state. So this is the ground electronic state, but it has different vibrational levels. So we can draw the different vibrational levels and here also we have different vibrational levels.

So let us draw this different vibrational levels. So here we can write V double prime = 0 where the double prime means the lower state or state with lower energy and here, we can write V prime = 0 but the single prime means it is the upper state. So we can write right V double prime = 1 V double prime = 2 , V double prime = 3 here, here we can write it V prime = 1, V prime = 2 , V prime = 3, V prime = 4, V prime = 5.

So though it is not absolutely clear the way I have drawn it but what I try to draw is that as you go up in energy the spacing between this vibrational states, they decrease due to anharmonicity. So there is no selection rule for the vibrational quantum number V when a molecule undergoes an electronic transition that means every transition from any value of V double prime to any value of V single prime has some probability and many spectral lines are therefore expected.

So the situation is simplified if we think that the absorption spectrum starts from the electronic ground state and in such a case all the molecules will be at V double prime = 0. So we can draw the different transitions that can be observed we can have a V double prime = 0 to V prime = 0 transition then we can have a 0 to 1 transition then we can have 0 to 2, 0 to 3, 0 to 4, 0 to 5 and so on.

So if I now try to draw the position of the frequencies that are observed in the spectrum. So this I will write 0,0 this as 0,1 or 1,0 this as 2,0 3,0 4,0 5,0. So the vibronic transitions that is between different vibrational levels the electronic transition, so they are called the vibronic transitions so these vibronic transitions are conveniently labeled as V single prime, V double prime. So that is why I have labeled here 1, 0 2, 0 3, 0 and so on.

So and such a set of transitions because we see here, we can have a set of transitions. So such a set of transitions is called a band and under low resolution each line in this set or inch line in this band appears somewhat broad and different. In particular this is called the V progression, or we can think about V prime progression as V prime increases by 1 or unity for each line in the set. So we have V prime equals.

So if you put the V prime values this is 0, 1, 2, 3, 4, 5. So the V prime increases by 1 and that is why it is called a V prime progression and the band kind of crowd together more closely at higher frequencies and this is due to the anharmonicity of the upper state. So this anharmonicity causes the excited vibrational levels to converge and the molecule normally may have many excited electronic energy levels and each transition from the ground state to an excited state is accompanied by a band spectrum. So now because we talked about this vibrational coarse structure.

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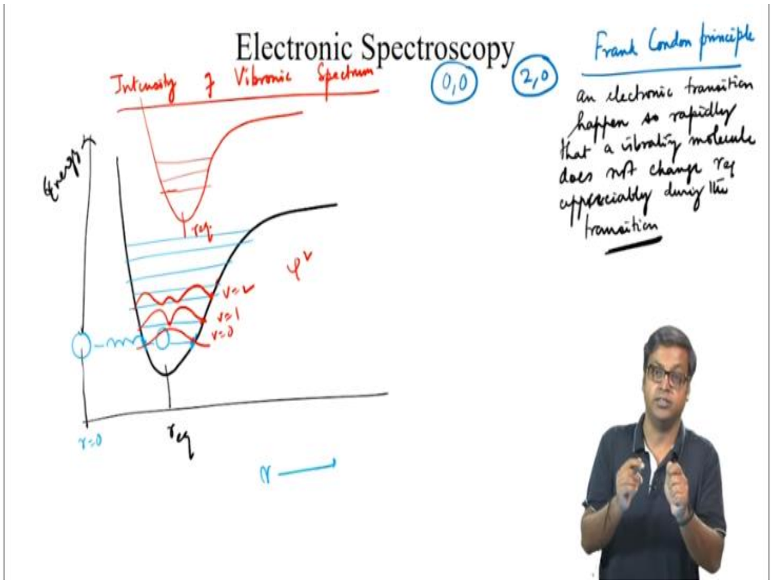

Electronic Spectroscopy

Frank Condon principle

an electronic transition happen so rapidly that a vibrating molecule does not change r_{eq} appreciably during the transition

Let us go into more details and look into the intensity of the vibronic spectrum. So although quantum mechanics imposes no restrictions on the change in the vibrational quantum number that means it can go from V double prime to any value of V prime during an electronic transition the vibrational lines are not all observed to be of the same intensity and for example in some spectra we find 0, 0 line to be the more intense and in some other spectrum we might find the 2, 0 line to be the strongest or it can be any other value of V Prime in some other cases only a few vibration lines unobserved which is followed by a continuum.

So all the spectra that means the intensity which line would have the highest or the strongest intensity whether we should get a continuum or not. So all these spectra can be understood in terms of something known as Frank Condon principle so what is this Frank Condon principle. So this Frank Condon principle states that an electronic transition happens so rapidly that a vibrating molecule that vibrating molecule does not change the inter nuclear distance that is our equilibrium appreciably during the transition.

So this means it happened so fast that the vibrating molecule does not really change the R equilibrium or the internuclear distance during the transition. So we have seen before how the energy of a diatomic molecule varies with the in the nuclear distance. So this is given where Morse potential. So we have energy here on the y axis and we have the internuclear distance and this is my R equilibrium.

So for a diatomic molecule we can think that one atom is fixed at R = 0 and the other atom is oscillating between the limits of the curve that means it is going back and forth within the limits of the curve. So the classical theory suggests that this oscillating atom would spend most of the time on the curve at the turning point this is because at this walls or the curve it is spending most of the time because it is moving slow there.

However, if you think from the quantum theory the quantum theory suggests that the same is true for high values of V. So we have these different values of V and whatever the classical theory such as the quantum theory suggests that the same is true for high value V however for V = 0 the atom is most likely to be found at the center of its motion. In other words as V increases the probable positions approach the curve and the classical and the quantum pictures they merge.

So we now draw the probability distribution in each state. So if you draw the probability distribution so it looks like this so this is V = 0, V = 1 let us say this is V = 2 and so on and so forth and this actually shows the variation in psi square where psi is the vibrational wave function. So if a diatomic molecule undergoes transition to the upper state such that the excited molecule is stable with respect to the dissociation into the respective atoms then we can also represent the upper state by a similar Morse potential.

So we can think the excited state is another similar Morse potential however to start with we do not know if the R equilibrium of the excited state is the same as the R equilibrium of the ground state and the differences in the R equilibrium of the excited state curve can actually give rise to multiple opportunities.

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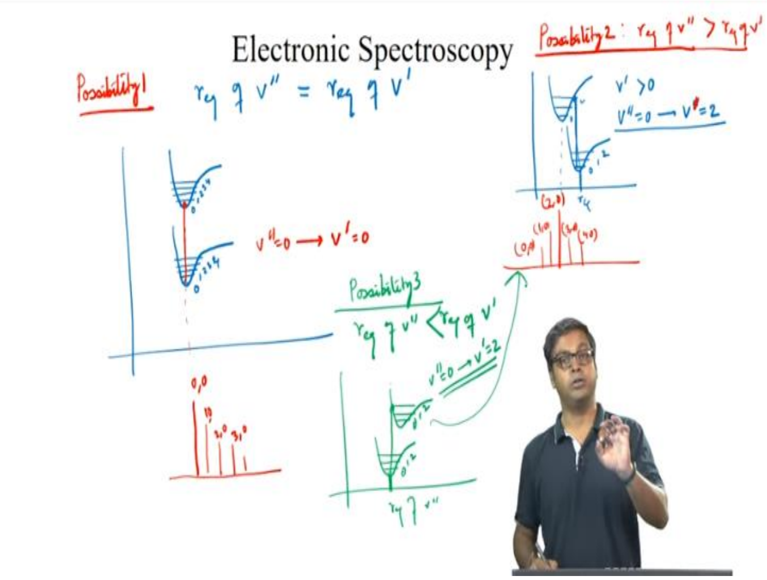

So let us look into four different opportunities or the four different possibilities now. So let us say we have possibility 1 so what is this possibility this is where we have the R equilibrium of the V double prime = R equilibrium of V single prime that means if I draw the energy diagram again. So this is my excited state this is my ground state, so this is 1, 2, 3, 0, 4 let us say this 0, 1, 2, 3, 4 and the R equilibrium are actually on top of one another.

So the Frank Condon principle such as that a transition will occur vertically because now it was in a V = 0 the ground state it will occur vertically because the internuclear distance does not change. So if the molecule was at V double prime = 0 of the electronic ground state then the most probable transition is V double prime = 0 to V single prime = 0. So the strongest spectral line will be the 0, 0 line.

But quantum mechanics such as probability of finding an oscillating atom is greatest at R equilibrium = 0 for V = 0 but quantum mechanics also allows some chance of the atom being away from R equilibrium. Hence there are more lines there are lines like 1, 0 2, 0 3, 0 etc but the intensity of this line is rapidly diminish as the value of V prime increases. So now let us look into the next possibility there is a possibility 2. The possibility 2 is R equilibrium of V double prime is actually greater than R equilibrium of V single prime.

What does that mean? That means if we draw this diagram and this is my ground state, and this is my R equilibrium of the ground state then this is greater than that of the R equilibrium at V single prime. So what that does mean this means the V single prime comes here that is this is the R equilibrium of V single prime. So now let us put this 0, 1, 2 let us also put here 0, 1, 2. So we see that a vertical transition would lead to V prime not = 0 but to a value of V prime which is greater than 0 and based on what I have drawn here is more likely the transition is V double prime = 0 to V double prime = 2.

So the transition that would occur to other values of V prime are less likely and most likely the strongest line will get from V double prime = 0 to V single prime = 2 and so the spectrum will have the strongest line at 2, 0 and weaker lines otherwise 0, 0 1, 0 this is 3, 0 4, 0. So the strongest will come from 2, 0. So now let us think about possibility 3 the possibility 3 does the reverse that is R equilibrium of V double prime is smaller than R equilibrium of V single prime.

So now if we draw the energy level diagram. So this is my ground state, so this is the R equilibrium of V double prime. So this is less than R equilibrium of V single prime. So this is my V single prime this is my V double prime. So the transition let us say will happen 0, 1, 2 0, 1, 2. So the most favorable transition is V double prime = 0 to V single prime = 2. So though this is a different possibility this possibility would give rise to a very similar spectrum what we saw for the possibility 2.

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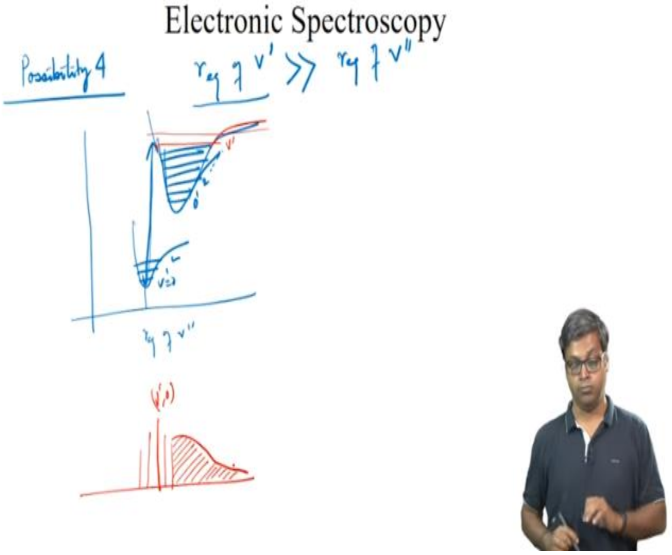

Now let us talk about the final possibility that is the possibility 4 and in this case the R equilibrium of let us say V single prime is much greater than R equilibrium of V double prime. So if I want to draw this this is my ground state this is the R equilibrium of V double prime what the R equilibrium of this single prime is much greater. So let us say is much greater so this diagram is not great however we have transitions here V = 0, 1, 2 and here at 0, 1, 2 etc.

So here the separation between the R equilibrium value of the upper and the lower state is considerably greater. So the final level to which this transition takes place is a much high value or higher value of V and we can see this value is very close to the dissociation limit. So further transition can now occur to states where the excited molecule has energy in excess of its own dissociation energy.

For such states the molecule will dissociate without any vibration and since the atoms formed due to the dissociation can take up any value of the kinetic energy the transitions are not quantized but results in a continuum. So what does this mean this means we will have some strongest line which corresponds to this V prime. So we will write V prime 0 and we have some other lines but if I go little higher up at some point it will be above the dissociation energy.

And in this case, we will not have discrete lines, but it will lead to a continuum. So we discussed these four possibilities based on the difference or the separation in R equilibrium of the lower state and the upper state. So this brings us to the end of this lecture, and we will discuss the dissociation energy in details in the next lecture.