Fundamentals of Spectroscopy

Dr. Sayan Bagchi
Physics and Materials Chemistry Division, NCL PUNE
Dr. Anirban Hazra
Department of Chemistry
Indian Institute of Science Education and Research – Pune

Lecture – 59
Electronic Spectroscopy – 3

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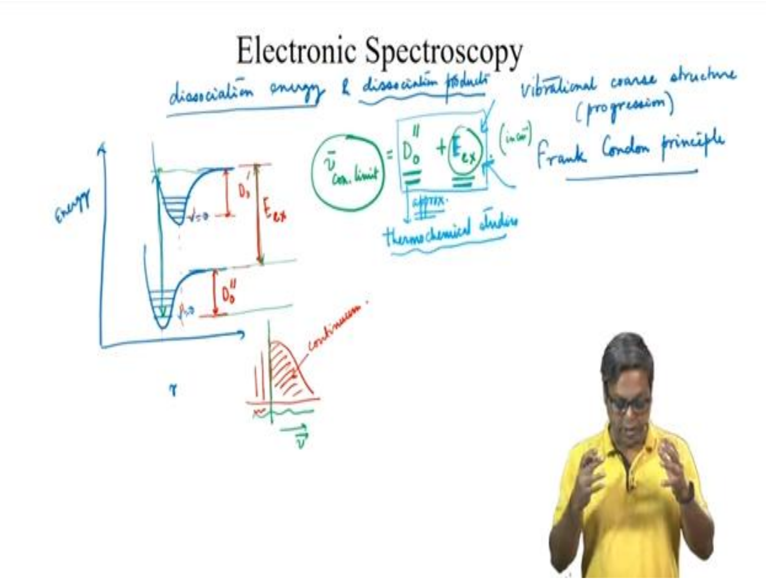

Electronic Spectroscopy

Hello all, welcome to the lecture. In the last lecture, we looked into the vibrational coarse structure, which is also known as progression because the V prime increases by 1 and we have new, broader diffuse score structure which are known as progression. We also looked into the Frank Condon principle. So while looking into the different possibilities based on the separation of the internuclear distances between the ground state and the excited electronic state, we mentioned about the dissociation energy. So in today's lecture, we would focus on dissociation, energy and dissociation products.

So there are two ways in which the electronic excitation can lead to dissociation. So now let us look into the first possibility which we have discussed in the last lecture. So what we saw is that this is our energy axis, and this is where we are plotting the internuclear distance. So this is our ground electronic state, which mimics our most potential. So this is V = 0 and from here there is a transition, and these are the other vibrational levels like 1, 2, 3. And this is our excited electronic state.

So because of Frank Condon factor, it goes vertically up to some high value a V. So this is my V = 0 the excited state. And these are the other V levels. And this is where the dissociation should occur in the excited state. And this is where the dissociation should occur in the ground state. So this is a case where the internuclear distance of the excited state is considerably greater than that in that ground state.

And here we write D0 double prime and this is our D0 prime. So this D0 double prime and the D0 prime are the dissociation energies from V double prime = 0 to V prime = 0. So we can see the dissociation products from the upper state is greater by an amount of E excitation. That is the excitation energy than that of the dissociation products of the lower state. So in the last lecture we saw that the electronic spectrum in such a case consists of a few quantized transitions, which is followed by a continuum.

So this is the electronic spectrum these are the quantized transitions, and this is the continuum. So the lower wave number limit, that means this one. So if I put a different color, so this is a lower wave number limit of the continuum because the wave number or the energy increases to the right. So the lower wave number limit of this continuum represent that sufficient energy to cause dissociation. But normal we can think that the dissociated products separate with virtually zero kinetic energy.

So we can write this nu bar the continuum limit equal to D0 double prime + E excitation and let us this is in wave numbers. So what does it mean? So the continuum limit is here. So if I think about a transition, the energy difference, this is the continuum limit, and this is nothing but that D0 double prime plus the energy of excitation. So thus, if we know the energy of excitation, we can measure the D0 double prime. That is the dissociation energy for the ground electronic state.

In other words, all we can get from directly from spectroscopy or this spectrum is this nu bar at the continuum limit. So we need to separate D0 double prime and E excitation into two components. The question is how can we do that? The thermochemical studies often provide an approximate value of D0 double prime.

So approximate value of D0 double prime can be obtained from thermochemical studies and a spectroscopy can provide this accurate estimate of this total part that is nu bar continuum limit that means if we can get an approximate idea of D0 double prime from thermochemical chemical studies and then accurate estimate of this D0 double prime plus energy of excitation from spectroscopy. What we get from spectroscopy is a rough idea of this E excitation or the excitation energy.

So when spectrum of Atomics products, because due to dissociation, atomic products are formed. So when the spectrum of academic products are studied, mostly one value of excitation energy correspond to this E excitation. So thus E excitation can be measured accurately by studying the atomic products and once we get this E excitation then we can find the precise value of D0.

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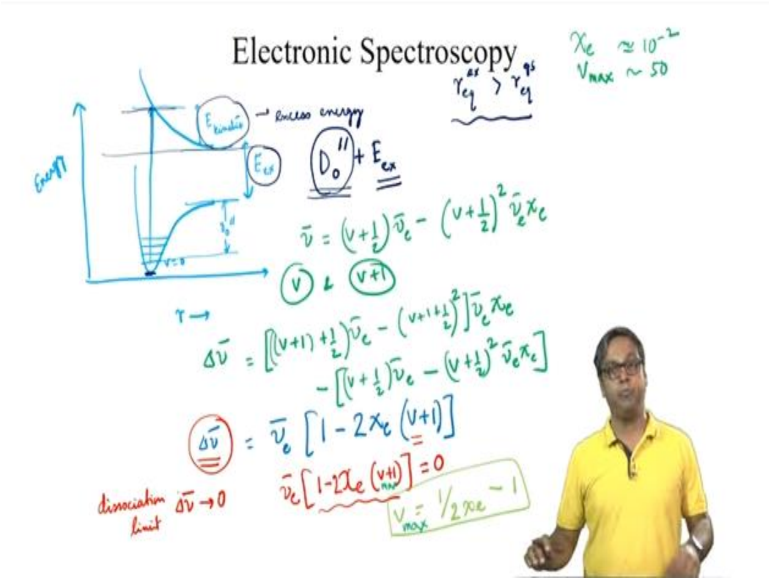

So now let us look into the second way which can to dissociation. So we will draw the second diagram. Now again energy is on the Y axis and the internuclear distance R is on the X axis. So the difference from what we saw in the last diagram or the last energy diagram and this diagram is the excited state is totally unstable. So this is again my V = 0 and these are the other vibrational states.

So we have a vertical transition it goes to the excited state? So this is my dissociation limit, and this is my dissociation energy that is D0 double prime for the ground state and we can say this part is the kinetic energy of the products and this part is the E of excitation. So now we have this figure in front of us. So we can say in this case, as I had mentioned, the upper state is unstable and how do you know that? Because there is no minimum in the energy curve.

For example, the ground state has a minimum here, but if you see the upper state, the energy is continuously decreasing. So there is no minimum that means as soon as the molecule is excited, the molecule dissociates into products with the total excitation energy ex and this products fly apart with the kinetic energy which is given by E kinetic which represents the excess energy in the final state that is the excited state.

That means the energy above that is needed to dissociate the molecules. That means this much energy was needed to dissociate the molecule, but we have provided more energy. So this is the excess energy which comes out in terms of kinetic energy and since this kinetic energy is not quantized, the whole spectrum of this system will exhibit a continuum. So in the previous case we saw few quantized, quantized transitions and then the continuum. In this particular case, because the kinetic energy is not quantized everything will be a continuum.

And the lower limit of this continuum will be again D0 double prime plus the energy of excitation. So, as we have discussed before, if this energy of excitation can be found out accurately, this D0 double prime or the dissociation energy in the ground electronic state can be accurately obtained. So in many electronic spectra, this continuum does not appear at all as the internuclear distances in the upper and the lower states are such that the transitions near the dissociation limit, are negligibly favorable.

So what this means is that the R equilibrium of the excited state might be slightly greater than the R equilibrium of the ground state. However, the difference or the separation is not huge. And because it is not huge, then the transition does not take it to the dissociation limit. So that is the reason the transitions near the dissociation limit are negligibly favorable. But it is still possible to derive our value of the dissociation energy.

Because as you can understand, we are interested to find the dissociation energy of the ground electronic state that is this D0 double prime and we can derive a value for this dissociation energy by noting how the vibrational lines convert. So we can write, and we have seen this in vibrational spectroscopy. So we will write the same equation. This nu bar in if we consider an harmonicity is given by V + half nu bar E – V + half square nu bar E hi E, where hi E is the harmonicity constant.

So thus the separation between any 2 consecutive levels. So let us say we have 2 levels; one is V and the other is V + 1. So we can write this delta nu bar will be V + 1 + half nu bar E – V + 1 + half square nu bar E hi E -. What we had for V that is V + half nu bar E – V + half square nu bar E hi E.

So if we do the simplification and the subtraction, what we get here is this delta nu bar. We can write this as new bar E times 1 - 2 hi E times V +1. In other words, this equation means that this delta nu bar or the change in energy is linearly proportional to V. That is the vibrational quantum number. So those we can see that the separation that is delta nu bar decreases linearly with increase in V. So at the dissociation limit, this energy gap tends to 0 or nu bar E times.

In other words, I can write at the dissociation limit this delta nu bar tends to 0 or nu bar E times 1 - 2 hi E V + 1 this equals 0. So now that means this equals 0 and if we simplify that, what we get is V = 1 / 2 – hi E – 1. Now one thing we should remember, because we have reached the dissociation limit, we can replace this V with V max. So this is my V max and because roughly this hi E or the harmonicity is in the order of 10 to the power – 2. That means the V max or the maximum possible vibrational level before we reached the dissociation limit is about 50.

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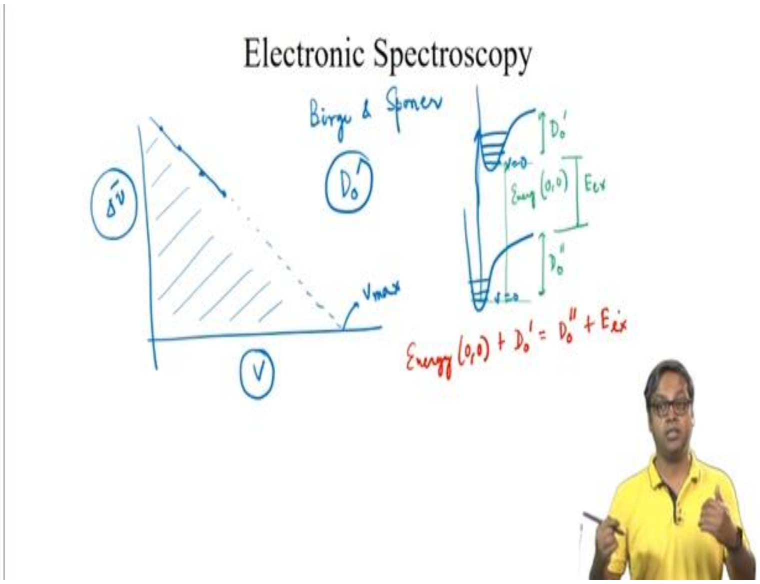

Electronic Spectroscopy

So if you plot the separation of the energy between vibrational transitions, so let us say delta nu bar as we see in the electronic spectrum against the vibrational quantum number, that is V we will get a graph. So we will get some points here. So initially the graph would look quite linear and this linear graph can be extrapolated to 0 to obtain the V max. So the dissociation energy actually can be obtained by considering the area under this curve. That is the area under the graph of delta nu bar versus V and such a linear extrapolation was first suggested by Birge and Sponer.

So this Birge and Sponer extrapolation actually provides D0 prime. That means it provides the dissociation energy of the excited electronic state. Now if you draw the energy level diagrams of the ground or the excited state again, and this is my V = 0. So we have here some vertical transition. So this should be vertical my drawing is not that good, but so these are the different vibrational levels.

So we can see this difference is the we can say the energy for the 0, 0 transition. And this is my D0 double prime. This is my D0 single prime and this is my energy of excitation. So from this diagram we can see that we can write this energy of the 0, 0 transition plus this D0 prime = D0 double prime plus energy of the excitation or the excitation energy. So this way we can find the D0 double prime or which is a dissociation energy of the ground state if we have some idea about the 0, 0 transition or the 0, 0 energy involved in those 0, 0 transition. So now after discussing this dissociation energy.

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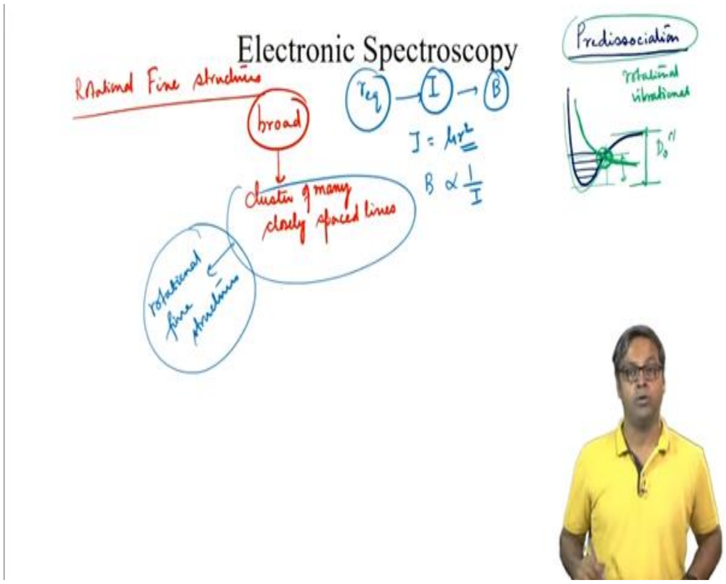

Electronic Spectroscopy

We will briefly discuss the rotational fine structures. So we will discuss this rotational fine structures, which are found is electronic vibrational transitions. However, we will not get into the greater details of this rotational fine structures. So normally, as we have mentioned in the last lecture, the electronic spectrum of a diatomic molecule consists of one or more series of convergent lines and this constitutes the vibrational core structure for each electronic transition. And each of these lines is observed to be broad or diffuse.

So this broad or diffuse line is observed when the resolution is low. However, if we have a high resolution (()) (22:37) or in other words, if the resolution is high, each of these broad lines. So the broad lines actually appears as a cluster of many very closely spaced lines. So they appear as cluster of many closely spaced lines. So these are known as the rotational fine structures. So we have talked about this rotational fine structures during the rotational vibrational spectroscopy.

So we discussed this rotational vibrational spectroscopy and there we mentioned about this rotational fine structures. And there we mentioned that the difference between the B values. So B values B is the rotational constant. So the difference between the B values in different vibrational states are very small. However, this is not true in case of electronic spectroscopy, as the equilibrium distances between the lower and the upper States may differ considerably.

So that means R equilibrium differs that means the moment of inertia that differs. And that means the rotational constant or the B value in the two states will also be different. So we can say, or we cannot see beforehand which of the two B values that is the B value of the ground state or the B value of the excited state will be greater. Quite often the electron is one of those forming the bond between the nuclei and if that is so the bond in the upper state will be weaker or longer.

And if the bond is weaker then I which is given by mu r square, so this is the bond length. So the moment of inertia increases because the bond is weaker, and the bond length increases and because B or the rotational constant is inversely proportional to I then as the moment of inertia I increases B decreases. So however we will not get into the details of the structure or the structure or the fine structure that we get in this electronic spectrum.

We would end this discussion on this diatomic molecules with something known as Predissociation. So we have talked about dissociation. Now the question is what is predissociation. So let me draw a figure so this is my ground state these are my different vibrational levels and let us say let me use a different color. So this is my excited state, which is unstable. So if the potential energy of a diatomic molecule is crossed by a curve of a repulsive state.

So this is the repulsive state and it crosses the potential energy of a diatomic molecule. Then it, creates a region of diffuses in the spectrum and when the inter-nuclear distance and the energy of the molecule in the ground state is actually near this crossing point. So there is a probability that the molecule transferred from this ground state to this repulsive state that means from the lower to the upper curve to dissociate and this has the effect of broadening both the rotational and the vibrational levels in the region of the spectrum.

So this effect is actually referred to as predissociation because we know this is the dissociation energy of the ground state, but it can dissociate here, which is much lower than the D0 double prime. So we can see the molecule and dissociate at a lower energy than the dissociation limit and this process is known as Predissociation. So this brings us to the end of this lecture. So in the next lecture, we will look into the electronic spectroscopy of more complex molecules. For example, will not look into diatomic molecules, but we will talk about polyatomic molecules.