Concepts of chemistry for engineering
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Lecture 46
Electronic Spectroscopy - III

We are discussing absorption spectrum. And as is not very common in our course, we start with the same kind of opening slide that is the last lecture, but now perhaps you understand it a little better.

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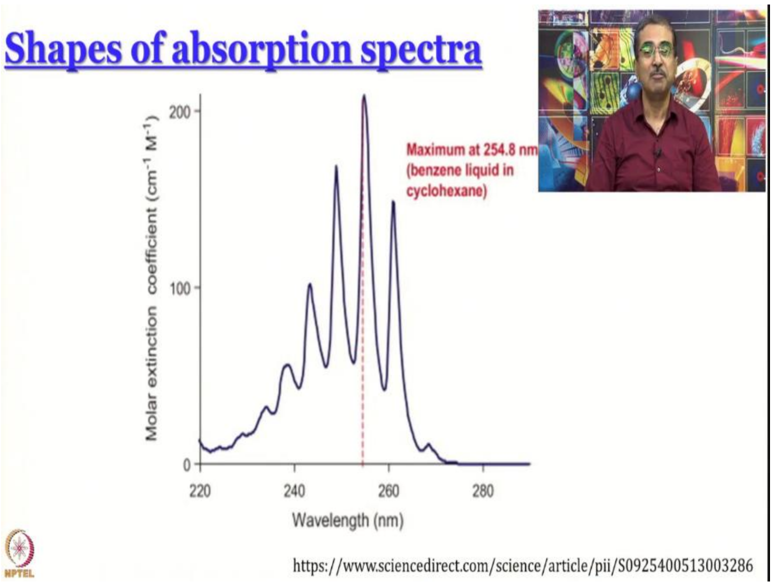

Shapes of absorption spectra

https://www.sciencedirect.com/science/article/pii/S0925400513003286

Here is an absorption spectrum of benzene dissolved in cyclohexane. Now, you know what is molar extinction coefficient and why the unit is centimeter inverse per molar. Now, you know why the x axis is in wavelength rather than in electron volt or something like that. And now, you can sort of guess that this structure comes because these are vibronic transitions.

And these different heights or different values of molar extinction coefficient for different wavelength tells us that the probability of these vibronic transitions are not all the same. So, this entire spectrum is of the very well-known benzenoid band that is available in all organic well aromatic organic molecules. It shows up nicely if the solvent is non-aromatic but nonpolar also.

Now, what we are going to learn is why is it that this third band is most intense, why not the first band, when will the first band become most intense, because, if you remember, we had shown a spectrum of some of the compound earlier the first lowest energy band was the most intense band. That depends on the relative values of the bond length in the ground and the excited states.

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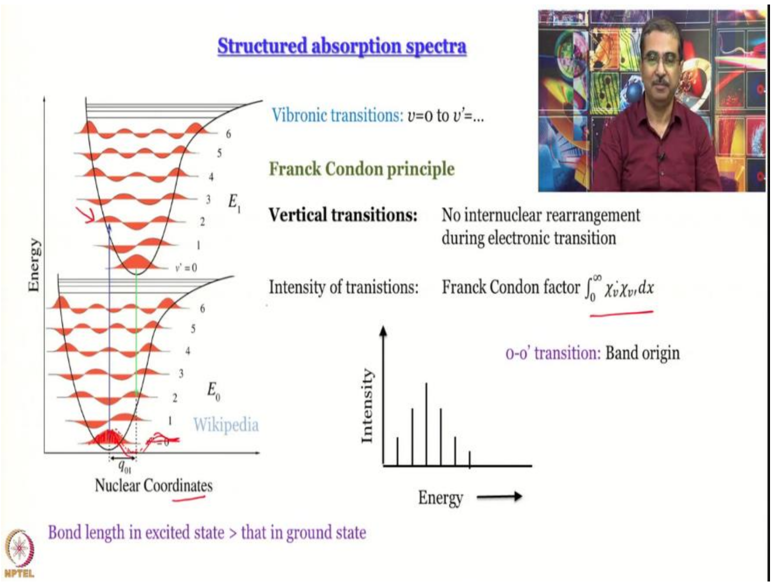

Structured absorption spectra

Vibronic transitions: υ=0 to υ'=...

Franck Condon principle

Vertical transitions: No internuclear rearrangement during electronic transition

Intensity of tranistions: Franck Condon factor $\int_0^\infty \chi_{\upsilon}^{\cdot} \chi_{\upsilon'} dx$

0-0' transition: Band origin

Bond length in excited state > that in ground state

Now, see I have taken this figure from Wikipedia and I have done a little bit of surgery, I have cut the top part and I have moved it around. So, please neglect this blue vertical arrow wherever it comes, I have drawn my own arrow wherever required. Now structured absorption spectra like the one that you have seen arise out of vibronic transitions v=0 to $v^{/}$= 0, 1, 2, 3 whatever.

This is governed by something called Franck Condon principle. There are two things to understand about Franck Condon principle. Actually, Franck Condon principle started with a classical formulation and it essentially said that the transitions are all vertical, what is the meaning of that, in this diagram, y axis is energy x axis is nuclear coordinate, very easy to understand if you are talking about diatomic molecules, it is simply inter nuclear separation.

So, when it is vertical what it means is that, when there is a transition between two electronic states, there is no change in inter nuclear separation. So, no inter nuclear rearrangement takes place during electronic transition. This is the classic formulation of Franck Condon principle. And the quantum formulation is that the intensity of transition is governed by Franck Condon factor, which is integral of $\chi_v^{/}\ \chi_v$, what are this $\chi_v^{/}\ \chi_v$. Well, these are the vibrational wave functions. Energy is a quantized, vibrational quantum numbers range from 0 to whatever, 0, 1, 2, 3 so on and so forth. And what we are showing here is an harmonic oscillator, this is essentially the kind of potential energy surface you get for an actual diatomic molecule. So, the energy gaps keep decreasing, decreasing, decreasing, until here they become a continuum and this is where if you promote the molecule from here to here, then the bond is going to break.

Another point to note is that there is a minimum nonzero value of energy corresponding to v equal to 0. This is called zero-point energy, for our course it is sufficient if you know this will not go into further discussion. Coming back to wave functions. The v equal to 0 wave function is essentially a Gaussian.

Higher wave functions are this Gaussian multiplied by what are called Hermite polynomials, forms of which we do not need to know at this point, but this is what they look like. So, for v equal to 0, there is no node, for v equal to 1 there is a node at the center, for v equal to 2, there are two nodes equally spaced from the center, for v equal to 3, there are 1, 2, 3 nodes, the middle one is at the center, and so on and so forth.

As you go higher up, the number of nodes increases pretty much like your particle in a box problem. But these wave functions are not sin functions. And also, these wave functions go a little beyond this potential energy surface because you might remember our discussion of how quantization arises out of boundary conditions, boundary conditions for these wave functions is that they have to vanish at internuclear separation of infinity and minus infinity, that is why it is okay if they go beyond the potential energy surface.

Now, Franck Condon factor means the integral of the product of the vibrational wave function from which the transition originates and the vibrational wave function of the level to which the transition goes. So, essentially it is a numerical integration we will see how it is. So, now, let us say this is the excited state of the molecule, diatomic molecule let us say.

So, essentially this kind of diagram means, what does this minimum indicate, the minimum indicates equilibrium bond length. So, in this situation bond length in the excited state is greater than that in the ground state, that is what we are discussing right now, we will discuss other situations when they are equal or when the excited state bond length is smaller than the ground state bonding also. But let us see what this means.

So, this is the wave function of the target state. Let me just draw it here this is what it is, something like this, it goes up or something like this. So, what is this Franck Condon factor, it is this function multiplied by this function, this function multiplied by this function for a given value of nuclear coordinate and then you add them up. So, essentially you multiply the two plots and find the area under the curve, this is how you can find out Franck Condon factor.

Another thing to remember is that all upward transitions start for nuclear coordinate equal to equilibrium bond length because for v equal to 0, that is where the maximum is. So, this is where the maximum of ψ is, that is why $\psi\psi^{*}$ is maximum and dx is equal everywhere. So, the maximum probability of finding this wave function is at the equilibrium bond length for v equal to 0.

So, all transitions start for at the center of this wave function and we have vibration. So, this is where it is going to go. So, what do we see? If we work out the Franck Condon factors of all other wave functions, the Franck Condon factor will be maximum for $v^{/}$ equal to 2. So, now, what will the spectrum look like? I am plotting against energy. So, not wavelength energy please remember.

So, let us say this is $00^{/}$ transition, it will have some intensity some absorbance. The next one will actually have a little more because if you work out Franck Condon factor will be greater for $02^{/}$, $01^{/}$ transition. For $02^{/}$, it will be maximum. For $03^{/}$, it will fall again and it will keep decreasing. So, it is going to go through a maximum. If you remember the absorption spectrum of benzene, it does go through a maximum because this is what the situation is like for benzene.

Of course, benzene is not a diatomic molecule, it is a polyatomic molecule. So, the nuclear coordinate there is not simply an inter nuclear separation, it is something else, we do not need to get into that now. Next, $00^{/}$ transition, there is a name for it, it is called the band origin. What is the meaning of band origin? Suppose, there is no vibronic structure, if it is a pure electronic transition then the only transition you would see is $00^{/}$.

So, that is called the band origin that is the smallest energy vibronic band that you can hope to observe. In a situation like this many times what happens is that the intensity of the band origin is so small that you do not even see it. So, finding the band origin may be a non-trivial problem depending on what kind of a system we are handling.

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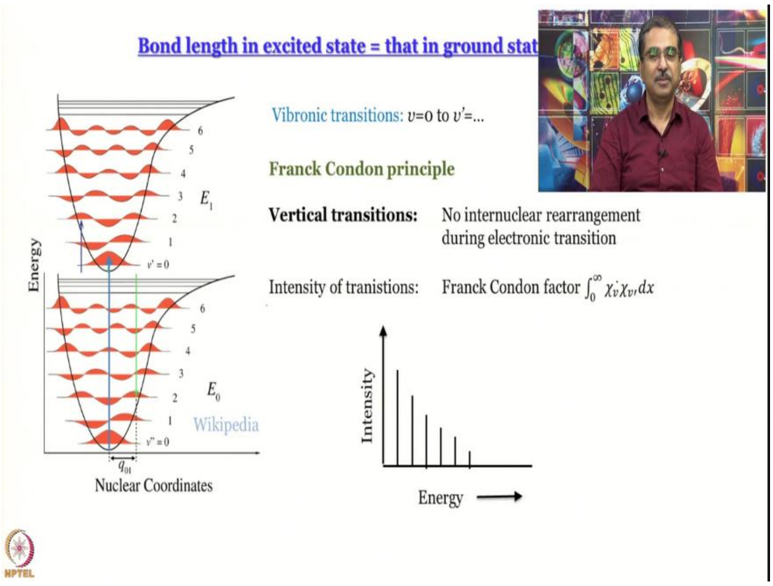


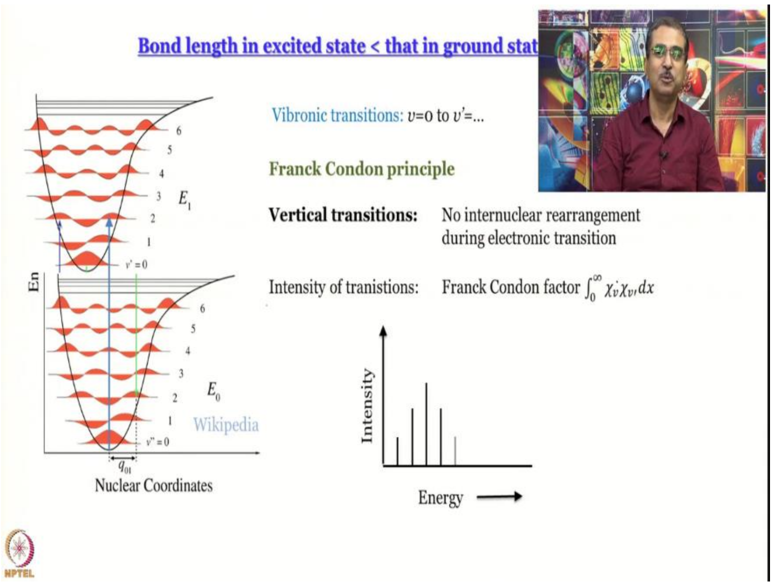
Bond length in excited state = that in ground stat

Vibronic transitions: υ=0 to υ'=...

Franck Condon principle

Vertical transitions: No internuclear rearrangement during electronic transition

Intensity of tranistions: Franck Condon factor $\int_0^\infty \chi_{\upsilon}^{*}\chi_{\upsilon'}dx$



Bond length in excited state < that in ground stat

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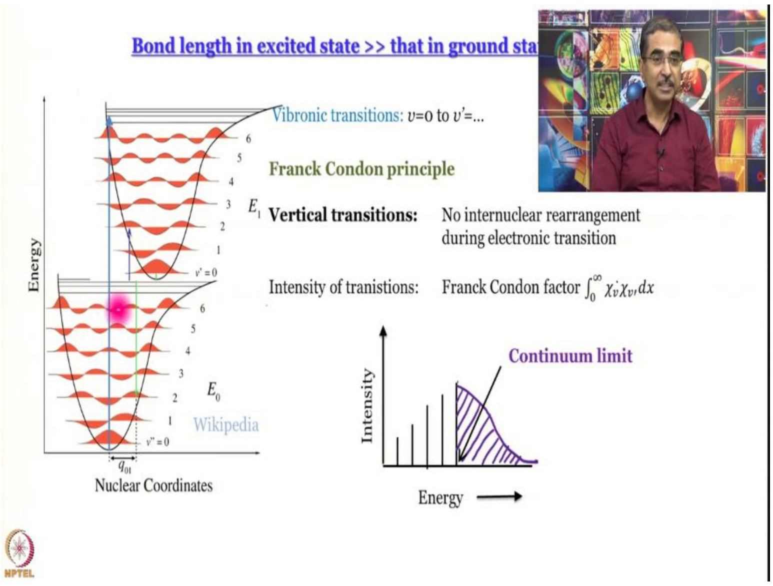

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Now, let us go to the situation where the bond length in excited state is equal to that in the ground state. Now, obviously, the transition that will be most intense, the transition that will have the largest Franck Condon factor is $00^{/}$ transition, please neglect this small blue arrow I have told you why that has arisen. So, Franck Condon factor will be largest for $00^{/}$ transition. So, what will the spectrum be like?

As you go higher up in the energy, the vibronic lines become smaller and smaller and smaller in intensity. This is the situation in I think naphthacene that is a spectrum we are seen in the previous module. What happens is the bond length in the excited state is smaller than in the ground state.

Well then again, the same thing happens as what happens in the situation where bond length is in the excited state is greater than that in the ground state. Because once again, Franck Condon factor would be maximum for $02^{/}$ transition, it would fall off both ways. So, the spectrum would go through a maximum.

And sometimes the bond length, the excited state may be very, very, very much larger than that of the ground state. With the limit that the bond length in the excited state may be infinity, which means you will not even see this minimum anywhere, it will just keep decreasing, decreasing, decreasing as you increase the nuclear coordinates. We will come to that also.

But before that, if the bond length in excited state is much greater than in ground state, then the Franck Condon factor is going to be maximum for some very high energy vibrational level which can be in this continuum range. So now, what will happen, $00^{/}$ transition will have some very, very smaller intensity, $01^{/}$ will have little more, $02^{/}$ will have a little more, it will keep going like this, until you reach this level, after which what will happen is that the molecule is fragmented, so it can have any energy.

So suddenly, after a certain level, you are going to get not discrete structure anymore, but rather a continuum. So that continuum, so this wavelength, energy at which the continuum sets in is called the continuum limit. It can be related to many other things, which we are not going to discuss today, whoever is interested, please read this from one of these textbooks. Banwell is a good textbook for this.

But you are going to have this, lower energy will have structure at higher energy after a certain limit, you are going to have a continuum. This is the signature that the molecule is dissociating by a transition and a transition to a bound state. Photoelectron spectroscopy is something that was known when you give the x-ray or something the electron is expelled, so provide ionization energy.

Here we are not providing ionization energy, is a much lower energy photon than the ionization energy. Yet, one can make the molecule dissociate. And this was a question from which Frank and Condon started working out their principle. So, what we learn is that even by a relatively low energy photon, one can bring about dissociation of a diatomic molecule, also polyatomic molecule, but that is more complicated.

Let us stick to diatomic molecules at the moment, one can bring about dissociation by transition to a state, that energy state that goes from minimum provided the energy takes it to a continuum. That is the first important thing.

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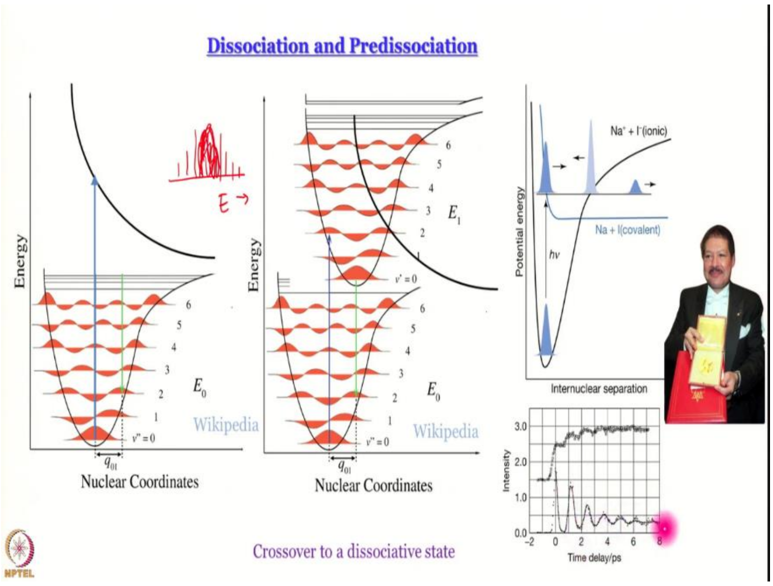

Dissociation and Predissociation

Crossover to a dissociative state

Next, now, we can think of that other extreme we are talking about. If the bond length is so large, that it is close to infinity, then we will never reach a minimum. Then the excited state is going to look like this, it will be a, it will just fall off exponentially asymptotically. And there will be no vibration energy level associated with it because it is an unbound state. In this case, so I hope this reminds you of the energy of antibonding orbitals, for example.

So, in this case, what will happen is that your spectrum is going to be a continuum all the way, there will be no structure, you are going to have a transition to a dissociative state, this is called a dissociative state, it does not go through a minimum, so you can cause a disassociation even without providing ionization energy. And there is another very interesting phenomenon called predissociation.

Let us say, our transition stages are like, sorry, energy levels are like this, the bond lengths are different, but not so different, that you can cause dissociation unless you provide this much of energy. However, many times what happens is that energy levels cross, these potential energy surfaces cross. And crossing can be of two types adiabatic and diabatic, that is another important topic.

But without getting into that, let us say that this excited state that goes to a minimum crosses another excited state which is dissociated, then what will happen, excite to higher energy levels, you are going to get lines in the spectrum, excite to lower energy levels, you will get lines, excite to energy levels close to say 2 here, then there can be a crossover from the bound energy state to a dissociative energy state and that is where you will get a continuum.

So, the spectrum will be something like this. You have lines at low energy, you have lines at high energy, and in the middle, you have this kind of a continuum. This is a signature of predissociation. So, this is what we wanted to discuss about spectroscopy. But before closing, I would like to point out a very elegant and very important experiment that has been performed by considering this phenomenon that you can bring about dissociation by excitation by UV visible light and potential energy surfaces can cross.

And that example is something that we encounter every day in labs, sodium, we know flame test, why is it that we get yellow flame for sodium, you take an iron Na^+I^- , but you get the characteristic spectrum of sodium atom. That is because this here, this figure is from Atkins physical chemistry book, but I will show you the original work. So, $Na^+ + I^-$ the ionic state goes to a minimum, Na+I (covalent) state is dissociative.

However, these two energy states cross and if you excite you can access you can have a situation like this, you excite regular Na^+I^- given the right energy, you can do a transition to this dissociative Na+I (covalent). So, that is your neutral sodium atom. By photoexcitation you can make this NaI dissociate. This experiment which was already known was performed by using short pulse high intensity lasers.

When I say high intensity short pulse, I mean lasers that are on for a few femto second and this is a seminal work done by Professor Ahmed Zewail and his group for which he got Nobel Prize in 1999. Here you see Zewail with his Nobel Prize. And what they did was that they excited this and we will not get into the technique, but let us just believe me when I say that they could work out the time evolution of the population of Na^+ and time evolution of population of Na.

So, Na plus is reactant, Na is product. What would happen? The moment you trigger the reaction by a pulse of light, then over time, sodium gets depleted and Na^+ gets formed. So, population of Na^+ would increase or I^- for that matter. And population of Na or I for that matter would decrease, without going into experimental detail, that is what was observed.

The top curve where you see a rise that is a measure of the time evolution of population of the neutral state, the neutral NaI. The bottom one is a decay, that is for the Na^+I^- situation. Note the x axis, x axis is time and time is in picosecond and femtosecond. If you look at this curve, it gets saturated in about 2 or 3 picosecond. So, if you fit this curve, you get a time constant of some 200 femtosecond or so.

So, the reason why this was a Nobel Prize winning work was that this was, this is the first experiment that determine how much time does it take to break a bond, and the answer was something like 200 femtosecond or so. Not only that, this experiment was what Zewail call a snapshot of the bond breaking, does not just tell us how much time it takes, it tells us how it happens.

Actually, I would prefer a video recording of one breaking. You see, we said that this tells us how the population grows of the covalent bond. It does not grow smoothly, does it? There are oscillations in the signal. And the oscillations are much more prominent for Na^+I^-. What are these oscillations? See it goes down, that means there is a decay, then it forms again, to some extent.

Then it goes down forms again to some extent and then gradually it goes away. It is like a damped oscillation. What is happening here? What is happening is you have Na^+I^- minus, they are together, give the laser pulse, they start breaking, do not break completely come back, start breaking this time they go a little further, come back, start breaking, and after 3 or 4 oscillations, they dissociate completely.

So, this is how a bond breaks. And so, what we are saying is that not only can you say whether it is a n pi star transition, not only can you determine the concentration of the solute, not only can you say fingerprint a molecule using electronic spectroscopy, but you can also by using advanced laser spectroscopic technique, try to get an intricate idea about dynamics.

And this becomes even more so, when we look at not only just absorption, but also, we start worrying about what happens after absorption. By light absorption, we have created a molecule in its excited state. Then what happens? Does the molecule just calm down, while coming down? How does it emit the excess energy, in the form of heat or light? Can it do some reaction in the excited state that it cannot do in the groundstate this, these are questions that we will touch upon very briefly in the next module.