Fundamentals of Spectroscopy
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Lecture – 61
Electronic Spectroscopy - 5

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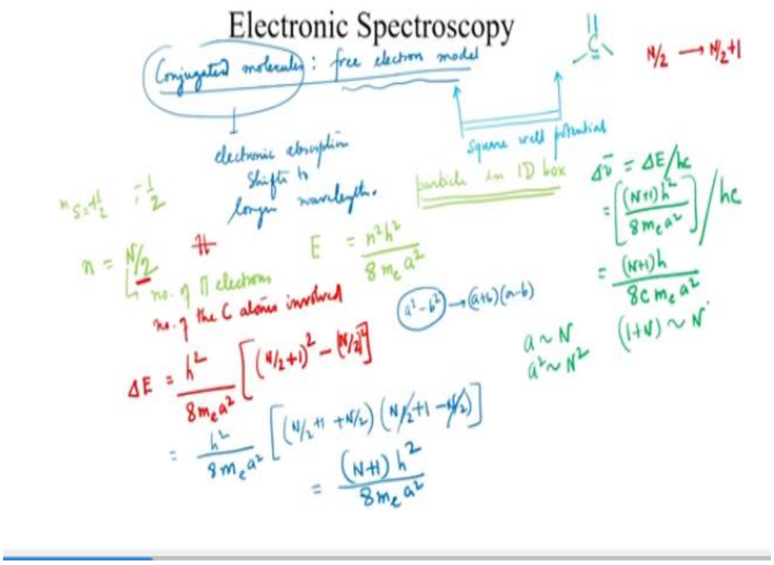

Electronic Spectroscopy

Hello all; welcome to the lecture, in today's lecture we will talk about conjugated molecules, so we will talk about conjugated molecules, the free electron model. So, for molecules with conjugated double bonds it is found that the electronic absorption band shifts to longer wavelengths, so for this conjugated molecules the electronic absorption shifts to longer wave lengths and the shift is longer as the number of conjugated double bonds increase.

So, these approximate quantitative calculations of the absorption frequencies may be made on the basis of the free electron model for the pi electron of these molecules. So, in a system of conjugated double bonds, each carbon atom has 3 sigma bonds and these 3 sigma bonds lie in a plane and this each sigma bond involves 1 outer electron of the carbon atom, however above and below the plane are the pi orbital systems.

So, each carbon atom contributes 1 electron to the pi system but these electrons are free to move the entire length of the series of the pi orbitals and are not localized at a given carbon atom, so we can say these pi electrons are delocalized and are not localized at the carbon atom. So, in this free electron model it is assumed that the pi system is a region of uniform potential and the potential energy rises sharply to infinity at the ends of the system.

So, if this is my conjugated system, so the potential energy rises sharply to infinity at the end, so this is like a square well potential, so thus the energy levels available to the pi electrons would be like those calculated for particle in 1 dimensional box, so we have learned about this particle in a box problem earlier in this course and the energy is given by n square h square by 8 me that is mass of the electron, a square where a is the length of the box.

And this is usually taken as the length of the chain between the terminal carbon atoms plus maybe a bond length or 2, so the pi electrons are assigned to the orbital, so that there are 2 in each level, so we can think about the spin is or ms is plus 1/2 and minus 1/2 and so when you are filling these orbitals we are starting from the lowest. So, for a completely conjugated hydrocarbon, the number of pi electrons is even.

And the quantum number of the highest field level, if you write the quantum number as n; n will be equal to n by 2, where n is the number of pi electrons or so, n is the number of pi electrons or we can say this is the number of the carbon atoms involved, so this is n by 2 because each orbital has 2 electrons. So, in the absorption process an electron is excited from the n by 2th level to the N by 2 + 1th level.

So, the energy difference that is delta E due to this transition can be written as; we can take common h square 8 me a square and then we will put n by 2 + 1 whole square - n by 2 whole square, so this actually is like in the form of a square - b square which is a + b times a – b, so we can write this as h square 8me a squared, then n by 2 + 1 + n by 2 times n by 2 + 1 - n by 2, so here n by 2, n by 2 cancels.

So, what we have here; we can write this as n + 1 h square by 8 me a squared, so this is in Joule, so if you want to find the absorption frequency in wave number, so we can write the delta nu bar which is given by delta E by hc, so we will divide; we will write this as N + 1 h squared divided by 8 me a squared divided by hc, so this gives n + 1 times h divided by 8 c me a square.

So, for linear molecules the size of the system that is a is proportional to N, so the absorption frequency will vary as 1 by n for large N, so this is because if a is proportional to N, then a square is proportional to N squared, so for large N; 1 + N we can write as N, so in the numerator we have N and in the denominator we have N square, so it varies as 1 by N for large values of N.

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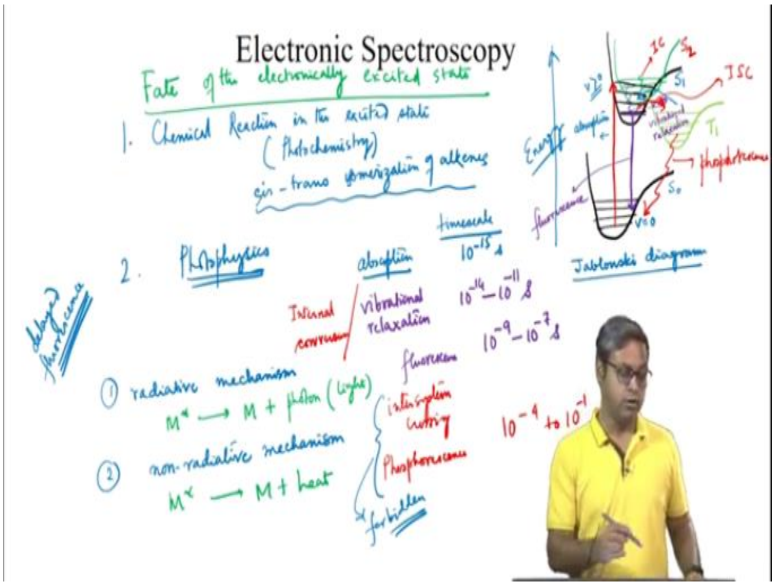

Electronic Spectroscopy

Fate of the electronically excited state

1. Chemical Reaction in the excited state
(Photochemistry)
cis - trans isomerization of alkenes

2. Photophysics

timescale

absorption 10^{-15} s

Internal conversion / vibrational relaxation $10^{-14}-10^{-11}$ s

fluorescence $10^{-9}-10^{-7}$ s

intersystem crossing

Phosphorescence 10^{-4} to 10^{-1}

forbidden

delayed fluorescence

① radiative mechanism
$M^* \longrightarrow M$ + photon (light)

② non-radiative mechanism
$M^* \longrightarrow M$ + heat

Jablonski diagram

So, now we would shift here and we would look into the fate of the electronically excited state, so we would look into what happens to the electronically excited state after the molecule is excited from the ground electronic state to the excited electronic state. So, we look into the fate of the electronically excited state. So, the molecule in the excited state can decay to the ground state in 2 different ways.

First of all, there can be a chemical reaction that can take place in the excited state, so there can be a chemical reaction in the excited state and this is known as photo chemistry. So, for example we can have this photochemical sis trans isomerization of alkenes that happen in the excited electronic state. So, this is an example of a photochemical reaction however, we would not discuss photo chemistry in this course rather we would focus on the other way that the molecule can decay to the ground state.

That is we will talk about the photo physics or the photo physical pathway, so let us try to understand the photo physical pathways. So to understand this, we will first draw a diagram or an energy diagram that illustrates the electronic states of a molecule and the transition between them, so let us say we have this ground electronic state, so this is the ground electronic state and this is the excited electronic state.

So, we have the transition from the ground to the excited electronic state, so first of all the diagram that we will draw here is known as the Jablonski diagram, so this diagram is basically a schematic energy diagram arranged with energy in the vertical axis or the y axis and so we have drawn this straight line and as you see we will also draw some curved lines, so this straight and the curved lines are the possible transitions that can occur from the exposure of a molecule to a particular wavelength.

So, the first transition that we have drawn is the absorption of a photon such that the molecule reaches the excited state, so this is the absorption process. So, as we have seen before this is a vertical transition and obeys the Franck-Condon principle, so thus the initial state shown in the diagram is v equals 0 of the ground electronic state and the ground electronic state is represented by s0.

So, the final state or the final value of v will depend on the separation of the inter nuclear distance between the ground and the excited state and we represent this by s1, so this absorption process might lead or most probably would lead to exciting the molecule to higher hydration levels that means, to some level where v is greater than 0 and this process, this absorption process happens really fast.

And the time scale is of the order, so we would put time scale here and the time scale for absorption is of the order of 10 to the power minus 15 seconds or we can say it has a femtosecond time scale. So, once the molecule is excited, there are multiple ways that the energy can be dissipated. The first is (()) (14:43) at what we know as the vibrational relaxation, so this is a vibrational relaxation, so this is a non radiative process.

And this vibrational relaxation is also a fast process that happens in 10 to the power minus 14 to 10 to the power minus 11 seconds, so the relaxation occurs between vibration levels such that the molecule is relaxed to the v equals 0 of the excited electronic state. So, if the vibrational energy level of the upper electronic level strongly overlap, so let us say we have another level and the vibrational levels strongly overlap.

So, then we can have a process which is known as internal conversion that means and this is based on this kasha's rule that when some molecule is excited, it can be excited let us say to s1, s2 or any other excited electronic state but after it is excited to any electronic state, it would actually come back to the lowest lying excited state. So, let us say if it is excited to s2, so this is known as IC or internal conversion.

That means from s2 it will come back to s1 first that is IC and then we will have vibrational relaxation which will bring it to the v equal 0 of s1, so mechanistically IC is identical to vr and also IC occurs in the same time scale as vr, so this internal conversion and the vibrational relaxation they have the same time scale that is 10 to the power minus 14 to 10 to the power minus 11 seconds.

So, now from the v equals 0 of the excited state that is s1 state, the molecule can decay to the ground state in 2 different ways. So, one way is through a radiative mechanism, in other words I can write that this excited molecule M star will give rise to M plus photon that is light, so this is the radiative mechanism. The other way it can come down is through a non radiative mechanism.

So, we can write here as this M star will give rise to M plus heat because it does not give rise to light it is called the non radiative mechanism, so these are mainly first order processes and in this lecture, we will mainly focus on the radiative mechanism. So, now let us say what we have; we have the molecule at v equals 0 of s1, so we can have a radiative transition that is from s1 to s0.

And if the internuclear distances are different as shown in this figure for s1 and s0, the final state due to transition, so this transition from s1 equals 0 to some value of v at a 0, this will come to some value of v, which is not equal to 0 or it does not come back directly because of this Franck-Condon principle to the v equals 0 of the ground electronic state and this process is known as fluorescence.

And this fluorescence has the time scale of 10 to the power minus 9 to 10 to the power minus 7 seconds, so other than fluorescence what can happen is that the molecule can actually dissipate the energy with something known as inter system crossing. So, let us say there is a low energy triplet state that is T1 is here, so there can be some crossover from this s1 to T1 and that process is known as ISC or inter system crossing.

So, this inter system crossing is basically a transition from an excited singlet step as shown here in this case to an excited triplet state and as we had discussed before in the module, this kind of transition is a forbidden transition because it does not obey the spin selection rule, so by coupling vibrational factors into the selection rules, these transitions become weakly allowed and this process is much, much lower than that of fluorescence.

So, this inter system crossing or ISC leads to several interesting routes with which this excited electronic state which is now the T1 can come back to a 0 or the ground electronic state. So, one such case is the phosphorescence, so when it directly comes from T1 to s0 and this is a relatively slow process but this is a radiative process, so phosphorescence is very slow, phosphorescence has the timescale of 10 to the power minus 4 to 10 to the power minus 1 second.

And as you remember these 2 cases; inter system crossing and phosphorescence these are forbidden, so another possibility is that there can be something which is known as delayed fluorescence that means, it can wait and come back to s1, so it is another example of inter system crossing but now it is going from the excited state triplet to the excited state singlet and after this ISC, we can have fluorescence.

But because it took the ISC triplet that is T1 and it came back to s1 and then the fluorescence happened, this is called delayed fluorescence because in this case, the fluorescence is delayed. So, this brings us to the end of today's lecture and now, we will solve few problems on this electronic spectroscopy.

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Problems and Solutions

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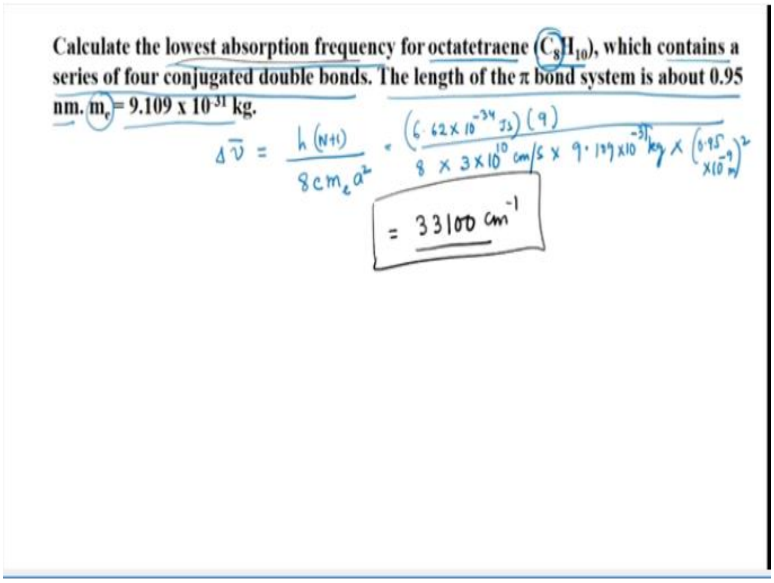

Calculate the lowest absorption frequency for octatetraene (C_8H_{10}), which contains a series of four conjugated double bonds. The length of the π bond system is about 0.95 nm. m_e = 9.109 x 10^{-31} kg.

$$\Delta\bar{\nu} = \frac{h(N+1)}{8cm_e a^2} = \frac{(6.62\times10^{-34}\,Js)(9)}{8\times3\times10^{10}\,cm/s\times9.109\times10^{-31}\,kg\times(0.95\times10^{-9}\,m)^2}$$

$$\boxed{=\underline{33100}\ cm^{-1}}$$

So, let us look into the first problem; so we have to calculate the lowest absorption frequency for octatetraene which is C8H10 and this molecule contains a series of 4 conjugated double bonds, so the length of the pi bond system is about 0.5 nanometer and the mass of the electron is given. So, as we discussed in the free electron model, delta nu bar is given by h times n + 1 times 8c me times a square.

So, if I put the values here, h is 6.62 times 10 to the power minus 34 joule second and n is 8 because there are 4 double bonds, so this is there are c is a c8, so n + 1 is 9 and then we divided by 8 times c that is 10 to the power 3 times 10 to the power 10 centimeter per second times me that is mass of electron that is 9.109 times 10 to the power minus 31 kilogram, then times we have a square, so that is 0.95 nanometer that is 0.95 times 10 to the power minus 9 meter square.

So, now if we take care of all the units and if we put the values and do the simplification what we get here is; 33100 wave numbers, so this is the answer, so the lowest absorption frequency for octatetraene is 33100 wave numbers.

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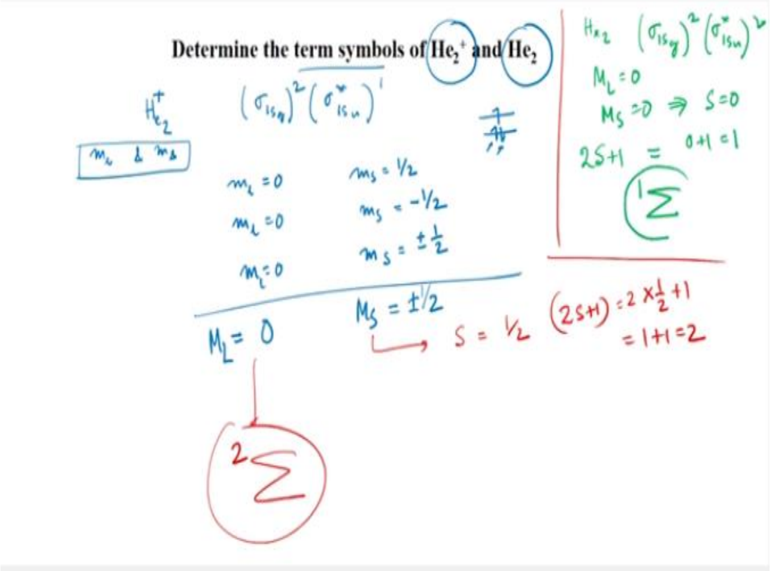

Determine the term symbols of He_2^+ and He_2

So, now let us look into the next problem; here we need to find the or determine the term symbols of 2 cases; one is He2 + and one is He2, so let us first write He2 +, so the electronic configuration is sigma 1 sg2 and sigma star 1 su1, so we need to consider the values of ml and ms for all 3 electrons. So, if we consider the ml and ms values for all 3 electrons, we can write; so this is a case like this.

So, we can write ml equals 0 because it is in the sigma orbital and let us say ms equals 1/2, second electron ml equals 0, so this is the second electron ms is opposite spin, so minus 1/2 and in the third electron case, ml is still equal 0 because it is still occupying the sigma orbital but the ms now can be either plus half 1/2 or minus 1/2 so now, if we add this ml we get ML that is 0 and what we get MS that is plus minus 1/2.

So, ML equals 0 immediately tells us this is a sigma state and MS equals plus minus 1/2 which means that S equals 1/2 that means spin multiplicity or 2S + 1 equals 2 times 1/2 + 1 that is 1 + 1 equals 2, so it is a (()) (28:49), so it is 2 sigma. Now, if you want to look into the

He2 case, so the electronic configuration of He2 is sigma 1 sg2 and sigma star 1 su2, so because now all the orbitals are paired.

So, we can write ML equals to 0 and also MS equals 0, so that means its spin multiplicity or 2S + 1, so MS equals 0 is means S equals 0, so 2S + 1 equals 0 + 1 equals 1, so it is a singlet state, so it is a singlet sigma state.