Ultrafast Optics and Spectroscopy
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Lecture – 29
Ultrafast Physical Chemistry: Photophysics and Photochemistry

Welcome to the module 11 of the course Ultrafast Optics and Spectroscopy. In this module we will go for Ultrafast Physical Chemistry involved in Photophysics and Photochemistry.

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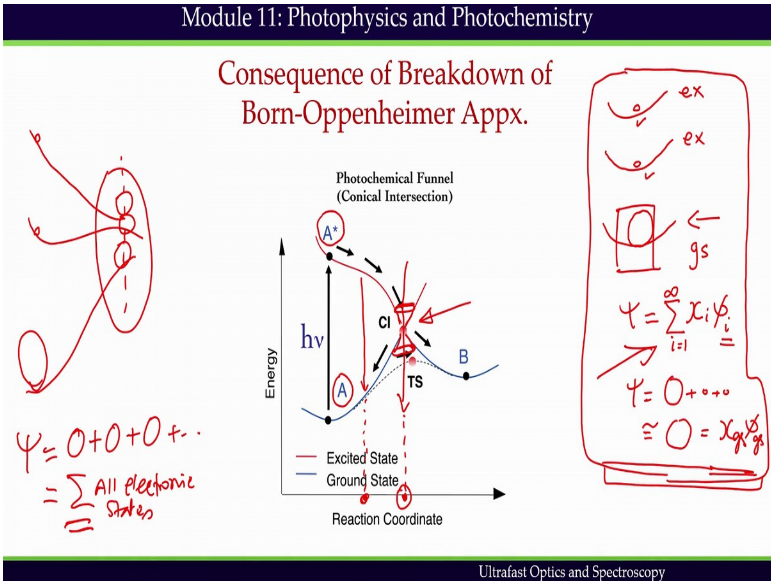

Module 11: Photophysics and Photochemistry

Consequence of Breakdown of Born-Oppenheimer Appx.

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The adiabatic Born Oppenheimer Approximation which separates electronic and nuclear motions in a molecule is the keystone to the visualization of chemical processes. This approximation enables us to picture molecules as a set of nuclei moving over a potential energy surface created by the faster moving electrons.

Despite it is central role in chemical theory breakdown of the adiabatic Born Oppenheimer approximation is particularly common in the photo chemistry and photo physics of polyatomic molecules for which a large number of energetically close lying electronic states and many degrees of freedom exist. Specific examples of the breakdown of Born Oppenheimer approximation include charge transfer, electronic quenching, spin forbidden, reactions, and nature's two important basic processes.

The initial radiation less energy transport step in photosynthesis and the cis trans isomerisation that initiates the process of vision. So, what does it mean by adiabatic Born Oppenheimer approximation, we have already seen that. So, what does it mean by adiabatic Born Oppenheimer approximation? We have let us say a number of electronically ground and excited states, so this is ground state and this is electronically excited states.

And if I think of how to represent the total wave function then according to Born expansion is going to be nuclear wave function as well multiplied by electronic wave function. And this i going from 1 to infinity, all the possible states we have to consider, so this is the total wave function and each i representing the electronic states. Now, if we are in the ground state then what might happen that I have a maximum contribution coming from the ground state.

And one can say that psi[Ψ] can be represented as this plus, this plus, this which is approximately can be written as this which means that I will be able to represent g s multiplied by phi g s ground state. So, one single product is perfectly fine for a situation where upper electronic states and lower electronic states are well separated. But this situation may not be valid when the when we extend this potential energy surface to a certain degree.

And in that case we see that different electronic states although here we have very little contribution from the upper electronic states, but in a this region we have almost equal contribution from different excited states. So, total wave function has to be represented then in that case like this way and will not be able to avoid this summation which we have seen here in the Born expansion. And the moment we do this summation we have to write down this summation is going to be all electronic states.

So, this only taking the product is nothing but adiabatic Born Oppenheimer approximation. Adiabatic Born Oppenheimer approximation assumes that most of the contribution is coming from one electronic state other electronic states are silent which means that I do not have much contribution from other electronic state to the total wave function.

However, there are places in the potential energy landscape where different electronic states can come closer. And we can have total wave function has to be then represented by the linear combination of different electronic states which are close line and in that case we have to use this summation. The moment we use this summation that breaks down Born Oppenheimer approximation.

Now, once we break down the Born Oppenheimer approximation what happens, we get an interesting feature in the potential energy landscape. And the feature is shown here by this conical intersection a crossing between potential energy surfaces different surfaces will cross each other. So, adiabatic Born Oppenheimer surface will never cross, but if you go beyond Born Oppenheimer approximation surfaces will start crossing.

The breakdown of Born Oppenheimer approximation leads to the formation of a conical intersection between electronic potential energy surfaces. A conical intersection is a point at which two adiabatic potential energy surfaces cross while an infinite variety of intersections are possible. Conical intersections can be usually distinguish from the nuclear coordinate dependence of the potential energy surfaces near the intersection.

If the potential energy depends linearly on the nuclear coordinate near the intersection the confluence is referred to as conical intersection is the local topography near the conical intersection looks like a double cone as illustrated here. So, one can think of this is near the conical intersections is just like double cone and this is called photochemical funnel.

Conical intersections are firmly established now to be the key features in the photo physical and photochemical processes of polyatomic molecules. They provide an efficient pathway for radiation less transition between electronic states. When a conical intersection is involved in a chemical or physical process the nuclei move on more than one adiabatic Born Oppenheimer potential energy surface.

This process is called non adiabatic process and the radiation list transition between electronic states through a conical intersection is called non adiabatic transition. The transition going through conical intersection is called non adiabatic transition. The probability of a non adiabatic transition is high if the nuclei encounter a conical decision at which point the two potential energy surfaces are energetically degenerate.

So, when we think about the photo excitation process here and shown here A is excited to A star electronically excited states and then it will evolve on the potential energy surface. But, there is a chance or probability having this transition at this point of nuclear coordinate, this nuclear coordinate corresponds to this point at this point. But the probability will be very low as compared to the probability here because they are degenerate at that point.

And I will let you know why it should be the probability would be high at this point of regime. In general a number of intrinsic issues are associated with non adiabatic chemistry and physics through conical intersections. All these issues can have significant influence on understanding molecular photo physics and photo chemistry on ultra fast time scale.

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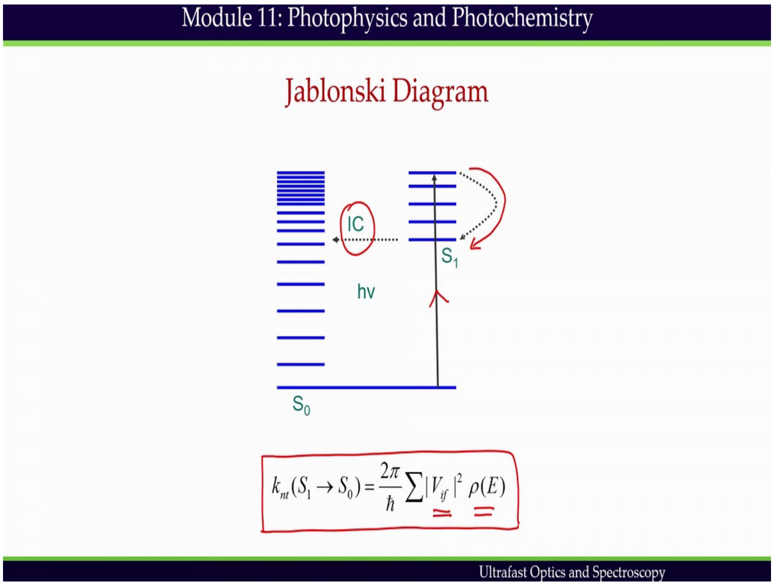

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Jablonski Diagram

$$\boxed{k_{nr}(S_1 \rightarrow S_0) = \frac{2\pi}{\hbar}\sum |V_{if}|^2 \rho(E)}$$

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Our early thinking about non adiabatic transitions between different electronic states was dominated by the application of Fermi's golden rule in the context of energy level diagrams as illustrated here. This kind of diagrams we have seen in our textbook before and this kind of diagram was used to explain different processes following photo excitation.

So, this vertical line represents the photo excitation that photo excitation can lead to first i v r to the coming back to the lowest ground state of the S 1 excited state. And then I can have internal conversion which is represented by IC from S 1 to S naught. And that internal conversion is nothing but a non adiabatic transition and the previously this kind of non adiabatic transition has been discussed in the picture of a Jablonski diagram.

And finally, the non adiabatic transition rate which is derived from Fermi's golden rule is given by this by this equation, where I and f refer to the initial. And final vibrational eigenstates on the S 1 and S naught adiabatic Born-Oppenheimer electronic potential energy surfaces respectively.

The matrix element V i f this matrix element V i f represents the electronic coupling between this adiabatic Born Oppenheimer states. Finally, the density of states of S naught at the given energy E is denoted as rho R, Fermi's golden rule is derived from perturbation theory and is valid as long as the coupling between electronic states are weak. Only detailed knowledge of the final vibrational eigenstates would allow one to extract any information about product branching ratios in the process following photo excitation.

This requires complete solution of the vibrational Schrodinger equation which is impractical for most polyatomic molecules. Therefore, direct quantitative use of Fermi's golden rule to describe non adiabatic processes of polyatomic molecules is practically impossible.

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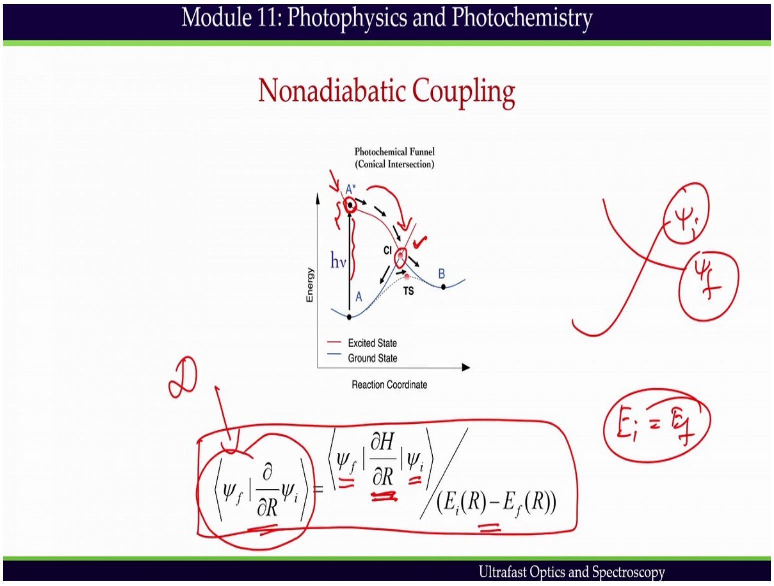

Module 11: Photophysics and Photochemistry

Nonadiabatic Coupling

$$\left\langle \psi_f \middle| \frac{\partial}{\partial R}\psi_i \right\rangle = \left\langle \psi_f \middle| \frac{\partial H}{\partial R} \middle| \psi_i \right\rangle \Big/ (E_i(R) - E_f(R))$$

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So, what is more realistic picture, which came up after Fermi's golden rule based Jablonski diagram the more realistic picture which is describing. The non adiabatic process is to include non adiabatic coupling term, which is discussed here. In order to describe the processes following photo excitation a more convenient theoretical framework should definitely go beyond the Born Oppenheimer approximation.

This allows non adiabatic transitions between different electronic states by introducing the terms neglected in adiabatic Born Oppenheimer approximation they are called. So, the moment we have taken that we have neglected that summation we have neglected many other terms which are not shown here through derivation, but many terms which are neglected.

And we have to now rethink of those neglected terms, they are mostly called non adiabatic coupling term which is given by this, what does it suggest? It suggests that this psi f and psi i$[\Psi_f,\Psi_i]$ are the electronic states of final and initial states. So, there are two states which are coupled with each other this is your final state this is your initial state. These are electronic states electronic states are getting coupled by nuclear coordinate or nuclear motion that is capital R representing the nuclear motion.

And this is the essence of non adiabatic coupling to electronic states are getting coupled due to nuclear motion capital R; this equation highlights that non adiabatic coupling term becomes infinite near a conical intersection which is a singular behaviour. Because, near conical intersection E i is going to be E f; so, coupling would be infinite that is when a conical intersection is present integrals over the nuclear coordinates involving non adiabatic coupling terms will be dominated by the geometry near the conical intersection nor by geometry near the f c point. (Please look at the slides for mathematical expresions)

So, f c point is the point where the initial photo excitation occurs which is the vertical excited state point and conical intersection point is here. So, what is the idea here? Is that because, the energy difference near the f c point would be very high that is why non adiabatic coupling curve would be very low and in that case one can neglect adiabatic coupling term in this regime in the f c regime.

But, the moment it is the system is evolving to the conical intersection point where I can have a maximum the contribution coming from the non adiabatic coupling term we have to consider this non adiabatic coupling term we cannot neglect it. And we cannot assume what would be the non adiabatic coupling at the conical intersection following an f c point geometry, we have to get the right geometry near the conical intersection and then predict what would be the non adiabatic coupling.

If the geometry corresponding to the conical intersection is quite different from that at the f c point; the form of the nuclear wave function and electronic coupling in the CI regime will be purely approximated by low order approximations around the f c point. This low order expansion of a potential energy surface around its f c point is often used to evaluate V i f in Fermi's golden rule.

Thus even if the even if the Fermi's golden rule is strictly valid the subsequent approximation used to evaluate V i f becomes questionable and quantitative application of the g r approach to the inner molecular photochemistry and photo physics is difficult. In many polyatomic molecules of photochemical interest the relevant conical intersections are in need far away from the f c point.

And the Fermi's golden rural approach with the usual approximation is not appropriate detail non adiabatic theory is more appropriate to describe non adiabatic processes. In general these electronic non adiabatic processes are mediated by conical intersection.

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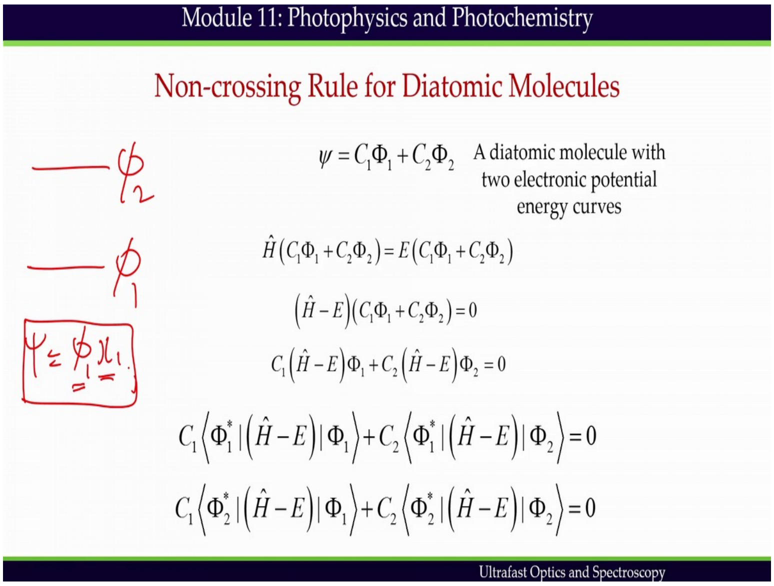

Module 11: Photophysics and Photochemistry

Non-crossing Rule for Diatomic Molecules

ϕ_2

ϕ_1

$\boxed{\Psi = \underline{\phi_1} \, \underline{\chi_1}}$

$\psi = C_1\Phi_1 + C_2\Phi_2$ A diatomic molecule with two electronic potential energy curves

$$\hat{H}(C_1\Phi_1 + C_2\Phi_2) = E(C_1\Phi_1 + C_2\Phi_2)$$

$$(\hat{H} - E)(C_1\Phi_1 + C_2\Phi_2) = 0$$

$$C_1(\hat{H} - E)\Phi_1 + C_2(\hat{H} - E)\Phi_2 = 0$$

$$C_1\left\langle \Phi_1^* | (\hat{H} - E) | \Phi_1 \right\rangle + C_2\left\langle \Phi_1^* | (\hat{H} - E) | \Phi_2 \right\rangle = 0$$

$$C_1\left\langle \Phi_2^* | (\hat{H} - E) | \Phi_1 \right\rangle + C_2\left\langle \Phi_2^* | (\hat{H} - E) | \Phi_2 \right\rangle = 0$$

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So, we will take a look at it in details, but in through the simple math if we have let us say two states; one is phi 1 another one is phi 2. There are two states we have and we will consider that our wave function has to be written. So, if we had two states under

Born Oppenheimer approximation we would have written psi equals phi 1 and chi 1; that is the nuclear wave function electronic wave function the product of nuclear wave function electronic wave function would represent the total wave function.

This is the Born Oppenheimer approximation, but we do not want to use Born Oppenheimer approximation. We want to use Born expansion which will be including the full non adiabatic theory.

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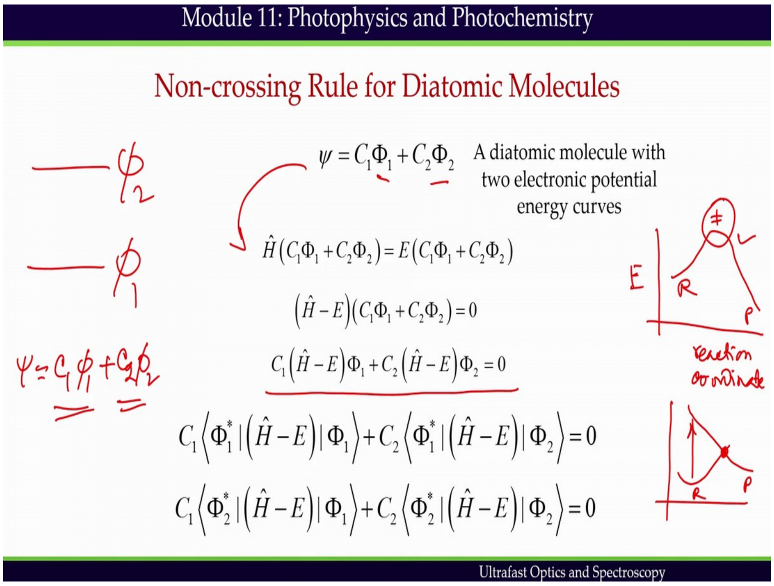

Module 11: Photophysics and Photochemistry

Non-crossing Rule for Diatomic Molecules

$$\psi = C_1\Phi_1 + C_2\Phi_2$$

A diatomic molecule with two electronic potential energy curves

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$$\underline{C_1(\hat{H}-E)\Phi_1 + C_2(\hat{H}-E)\Phi_2 = 0}$$

$$C_1\langle\Phi_1^*|(\hat{H}-E)|\Phi_1\rangle + C_2\langle\Phi_1^*|(\hat{H}-E)|\Phi_2\rangle = 0$$

$$C_1\langle\Phi_2^*|(\hat{H}-E)|\Phi_1\rangle + C_2\langle\Phi_2^*|(\hat{H}-E)|\Phi_2\rangle = 0$$

ϕ_2

ϕ_1

$\psi = C_1\phi_1 + C_2\phi_2$

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In that case psi has to be total wave function has to be represented as C 1, phi 1 expansion coefficient plus C 2 phi 2 both states we have to include together. In thermal reactions in general molecular structure associated with the transition state. So, we think about a transition state and we say this is energy versus reaction coordinate. And if they are going through the transition state this is reactant this is product when they are transforming from reactants to product they go through this transition state.

And generally thermal reactions are predicted with the help of the transition state. Similarly, in photochemical reaction, geometry associated with a conical intersection is often found to be related to the expected photo products. So, that is why if we want to find out ok, what is the photo what is the outcome of the photo excitation? Then, we have to think about the conical intersection and we have to we were and through this conical intersection only we will be able to predict what would be the photo product in a photo excitation photo excitation process.

For diatomic molecule, where only 1 degrees of freedom I have that is the bond distance electronic states with the same symmetry do not cross yielding a non crossing rule. So, what is the origin of this non crossing rule? We will go for it right now. To understand the non crossing rule, we will consider a diatomic molecule with two electronic potential energy curves mathematically two electronic states are represented by phi 1 and phi 2.

And we have two as I mentioned this is the Born expansion we have to take. So, the total wave function has to be represented by this way. So, we can insert this in the time independence Schrodinger equation H psi equals E psi and we will be able to rearrange this equation a little bit and we get this expression. Now what we have done? We have used; we have used ortho normalization condition to reduce this equation, this is often we use I will remind one more time previous in our previous modules, we have used this kind of condition to reduce quantum mechanical equation.

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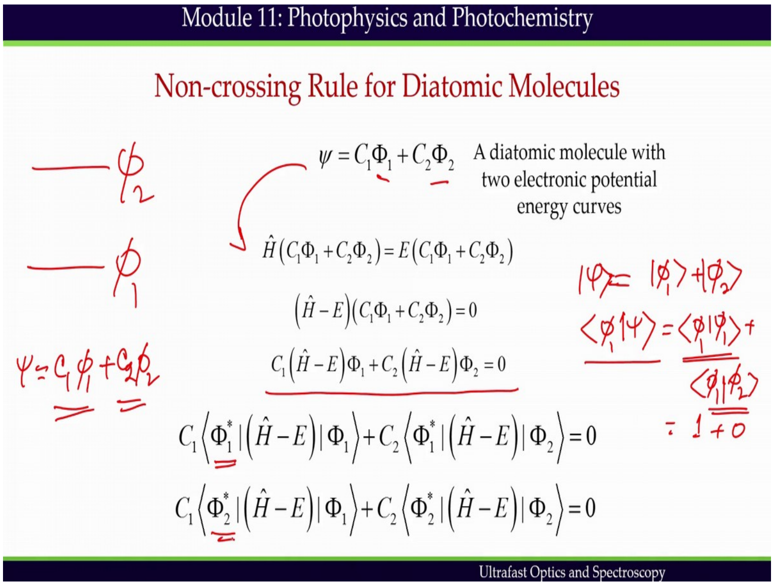

Module 11: Photophysics and Photochemistry

Non-crossing Rule for Diatomic Molecules

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$$(\hat{H} - E)(C_1\Phi_1 + C_2\Phi_2) = 0$$

$$\underline{C_1(\hat{H} - E)\Phi_1 + C_2(\hat{H} - E)\Phi_2 = 0}$$

$$C_1\langle\Phi_1^*|(\hat{H} - E)|\Phi_1\rangle + C_2\langle\Phi_1^*|(\hat{H} - E)|\Phi_2\rangle = 0$$

$$C_1\langle\Phi_2^*|(\hat{H} - E)|\Phi_1\rangle + C_2\langle\Phi_2^*|(\hat{H} - E)|\Phi_2\rangle = 0$$

ϕ_2

ϕ_1

$\psi = C_1\phi_1 + C_2\phi_2$

$|\psi\rangle = |\phi_1\rangle + |\phi_2\rangle$

$\langle\phi_1|\psi\rangle = \langle\phi_1|\phi_1\rangle + \langle\phi_1|\phi_2\rangle$

$= 1 + 0$

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So, let us say I have phi 1 plus phi 2 this kind of wave function. If I have this kind of wave function then I can multiply with phi 1 first phi 1 star. And if we multiply then what I get is phi 1 plus phi 1 phi 2 and this we know it is going to be 1 and this we know this is going to be 0. So, this is the way we can reduce this equation. <u>(Please look at the slides for mathematical expresion)</u>

So, in many occasions in quantum mechanics, we use this ortho normalization condition to reduce the equation further. So, here we are doing the same thing we are multiplying in this step we are multiplying with phi 1 star and the next step we are multiplying by phi 2 star.

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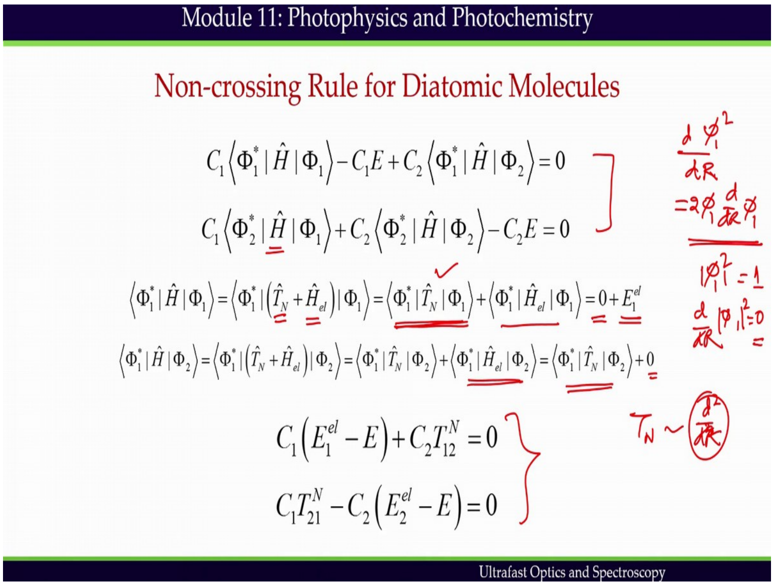

Module 11: Photophysics and Photochemistry

Non-crossing Rule for Diatomic Molecules

$$C_1\left\langle \Phi_1^* | \hat{H} | \Phi_1 \right\rangle - C_1 E + C_2 \left\langle \Phi_1^* | \hat{H} | \Phi_2 \right\rangle = 0$$

$$C_1\left\langle \Phi_2^* | \underline{\underline{\hat{H}}} | \Phi_1 \right\rangle + C_2 \left\langle \Phi_2^* | \hat{H} | \Phi_2 \right\rangle - C_2 E = 0$$

$$\left\langle \Phi_1^* | \hat{H} | \Phi_1 \right\rangle = \left\langle \Phi_1^* | \left(\underline{\underline{\hat{T}_N}} + \underline{\underline{\hat{H}_{el}}} \right) | \Phi_1 \right\rangle = \overset{\checkmark}{\underline{\underline{\left\langle \Phi_1^* | \hat{T}_N | \Phi_1 \right\rangle}}} + \underline{\left\langle \Phi_1^* | \hat{H}_{el} | \Phi_1 \right\rangle} = \underline{\underline{0}} + \underline{\underline{E_1^{el}}}$$

$$\left\langle \Phi_1^* | \hat{H} | \Phi_2 \right\rangle = \left\langle \Phi_1^* | \left(\hat{T}_N + \hat{H}_{el} \right) | \Phi_2 \right\rangle = \left\langle \Phi_1^* | \hat{T}_N | \Phi_2 \right\rangle + \underline{\underline{\left\langle \Phi_1^* | \hat{H}_{el} | \Phi_2 \right\rangle}} = \underline{\underline{\left\langle \Phi_1^* | \hat{T}_N | \Phi_2 \right\rangle}} + \underline{\underline{0}}$$

$$\left.\begin{aligned} C_1\left(E_1^{el} - E \right) + C_2 T_{12}^N &= 0 \\ C_1 T_{21}^N - C_2\left(E_2^{el} - E \right) &= 0 \end{aligned}\right\}$$

$$\frac{d\phi_1^2}{dR} = 2\phi_1 \frac{d}{dR}\phi_1$$

$$|\phi_1|^2 = 1$$

$$\frac{d}{dR}|\phi_1|^2 = 0$$

$$T_N \sim \boxed{\frac{d^2}{dR^2}}$$

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And if we reduce that further we get this expression and its easy to follow and then after this expression what we are going to write is that, we are we will decompose this total Hamiltonian into its kinetic component and electronic component we are separating it. The moment we do that then what we get is that, this integral becomes 0 and this integral gives me E 1 electronic energy this integral becomes 0.

Its because I have let us say phi 1 square d d R; if I have this then I will write 2 phi 1 d d R phi 1. And what I have is this phi 1 square is always going to be 1. So, phi 1 square if it is normalized then, its going to be always 1 that is why the first derivative with respect to R is always going to be is 0. So, finally, this expression is nothing but 0 and T N is nothing but d d R; is related to the derivative with respect to R. (Please look at the slides for mathematical expresion)

In fact, this is the second derivative. So, it is the second derivative, but if we consider the first derivatives already 0 second derivative is going to be 0 as well. So, this term should be always 0 similarly, here this term will be will also be 0; this term will also be 0 because here I have ortho normalization 0, but this term may not be 0. So, finally, we reduce all these equations to these two equations these two linear equations, which can be; which can be solved we can get a non trivial solution. (Please look at the slides for mathematical expresion)

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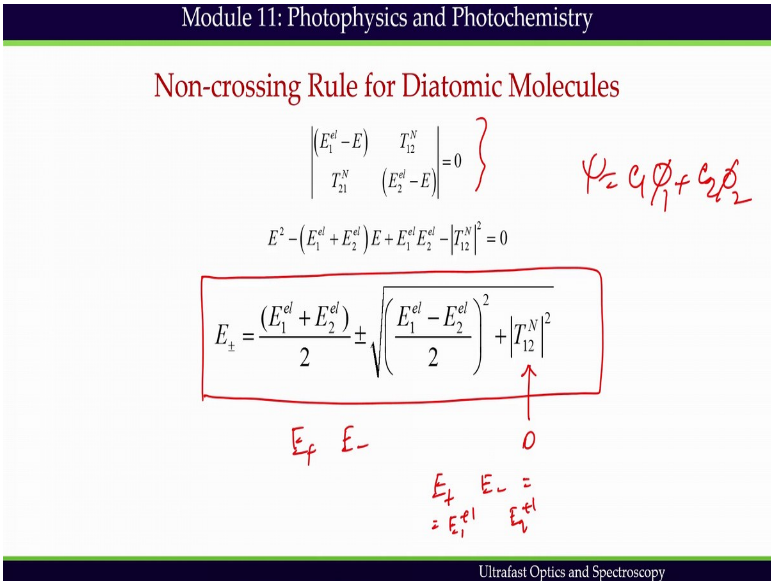

Module 11: Photophysics and Photochemistry

Non-crossing Rule for Diatomic Molecules

$$\left.\begin{vmatrix} (E_1^{el}-E) & T_{12}^N \\ T_{21}^N & (E_2^{el}-E) \end{vmatrix} = 0 \right\}$$

$$\psi = c_1\phi_1 + c_2\phi_2$$

$$E^2 - (E_1^{el}+E_2^{el})E + E_1^{el}E_2^{el} - |T_{12}^N|^2 = 0$$

$$\boxed{E_{\pm} = \frac{(E_1^{el}+E_2^{el})}{2} \pm \sqrt{\left(\frac{E_1^{el}-E_2^{el}}{2}\right)^2 + \underset{\uparrow \; 0}{|T_{12}^N|^2}}}$$

$E_+ \quad E_-$

$E_+ \quad E_- =$

$= E_1^{el} \quad E_2^{el}$

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For the secular equations we have the secular determinant to be 0 and if secular determinant is 0 then I have the final expression for E plus minus 1 there are two values of E we get. If we have expressed the total wave function as summation of c 1 phi 1 plus c 2 phi 2; this means that due to coupling of phi 1 and phi 2 electronic states via nuclear motion that is non adiabatic coupling we get the energies of two states as e plus. (Please look at the slides for mathematical expresion)

So, one state is going to be e plus and another state is going to be e minus in absence of non adiabatic coupling; that is if I make this to be 0, then what I get? I get always E plus and E minus is going to be always E 1 electronic energy and E 2 electronic energy always we are getting adiabatic states. (Please look at the slides for mathematical expresion)

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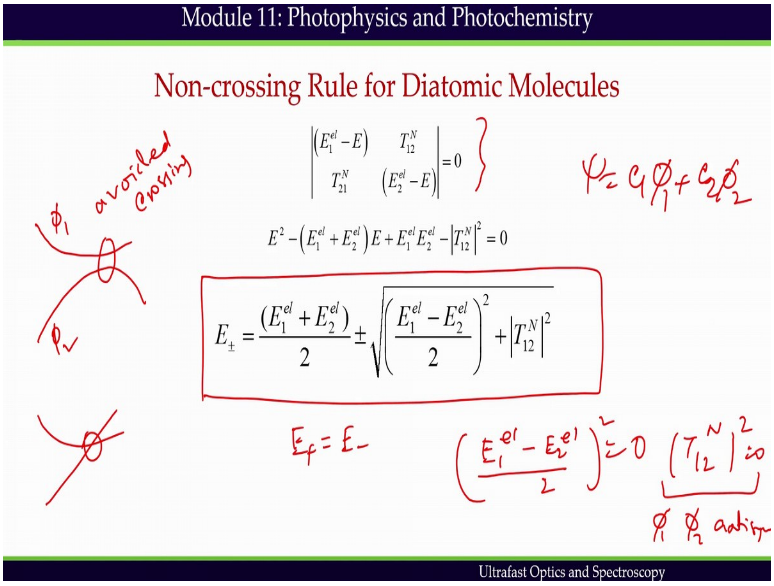

Module 11: Photophysics and Photochemistry

Non-crossing Rule for Diatomic Molecules

$$\begin{vmatrix} (E_1^{el}-E) & T_{12}^N \\ T_{21}^N & (E_2^{el}-E) \end{vmatrix} = 0$$

$$E^2-\left(E_1^{el}+E_2^{el}\right)E+E_1^{el}E_2^{el}-\left|T_{12}^N\right|^2=0$$

$$\boxed{E_\pm=\frac{(E_1^{el}+E_2^{el})}{2}\pm\sqrt{\left(\frac{E_1^{el}-E_2^{el}}{2}\right)^2+\left|T_{12}^N\right|^2}}$$

$\Psi = c_1\phi_1 + c_2\phi_2$

$E_+ = E_-$

$\left(\frac{E_1^{el}-E_2^{el}}{2}\right)^2 = 0$ $\underbrace{(T_{12}^N)^2 = 0}_{\phi_1\ \phi_2\ \text{antisym}}$

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But with what we are interested in; we are interested in knowing a point on the potential energy landscape, where I have E plus equals E minus. And in order to satisfy this condition I have to have two condition satisfying simultaneously. What are the conditions? The first condition is going to be E 1 electronic; E 1 electronic minus E 2 electronic divided by 2 square is 0 and then T 12 N 0 both we have to satisfy simultaneously. (Please look at the slides for mathematical expresion)

Now for diatomic molecule in which 1 nuclear content we have only variation we can change the potential energy surface. We can change the potential energy with the help of only one variable what is that variable? (Refer Time: 25:19) nuclear distance. So, for diatomic molecule with one inter nuclear distance fulfilling both conditions is extremely unlikely.

This occurs if the two adiabatic electronic states have the same symmetry if I have the same symmetry then TN is symmetric always. So, in order to vanish the integral phi 1 T N phi 2 if phi 1 and phi 2 have to be anti symmetric. So, for diatomic molecule this condition can be fulfilled if phi 1 and phi 2 are anti symmetric. Otherwise, they will not fulfil.

So, what happens if for diatomic molecule only 2 potential energy surfaces may approach each other and then they may not cross this is called avoided crossing. And this is this occurs when phi 1 and phi 2 symmetries are the same, but if there are symmetries are not same then they can cross each other. And if they are crossing each other then this crossing point is called conical intersection. For polyatomic molecules we have many degrees of freedom born angle born length many things and that is why because of the many degrees of freedom. We have we can very easily get this degeneracy because these two conditions can be fulfilled very easily.

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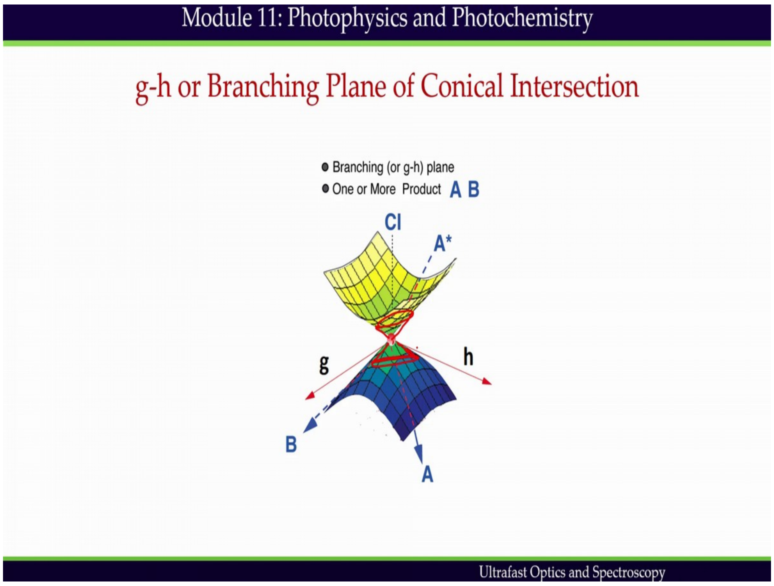

Module 11: Photophysics and Photochemistry

g-h or Branching Plane of Conical Intersection

- Branching (or g-h) plane
- One or More Product A B

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Near degeneracy the topography of the surfaces features a double cone, meeting at the point of degeneracy. Adiabatic energies varies linearly with coordinate near the conical intersection. The space, which uplifts that degeneracy is called branching space or g h plane; orthogonal to the branching plane is the intersection space in which the degeneracy is not lifted. Constructing conical intersection seam at each point of the seam there is a conical intersection.

Thus, at a conical intersection one can distinguish two directions g and h such that if one were to plot the energy. In the subspace of these two geometric variables the potential energy would have the form of a double cone in the region of the degeneracy shown here. Thus, the g h internal coordinates lifts the degeneracy linearly near the conical intersection which is shown here.

This two double cone present and this if we plot near the conical intersection if we plot the g h plane or if we plot the g h coordinate as a the energy as a function of g h coordinate then we get this double cone feature.

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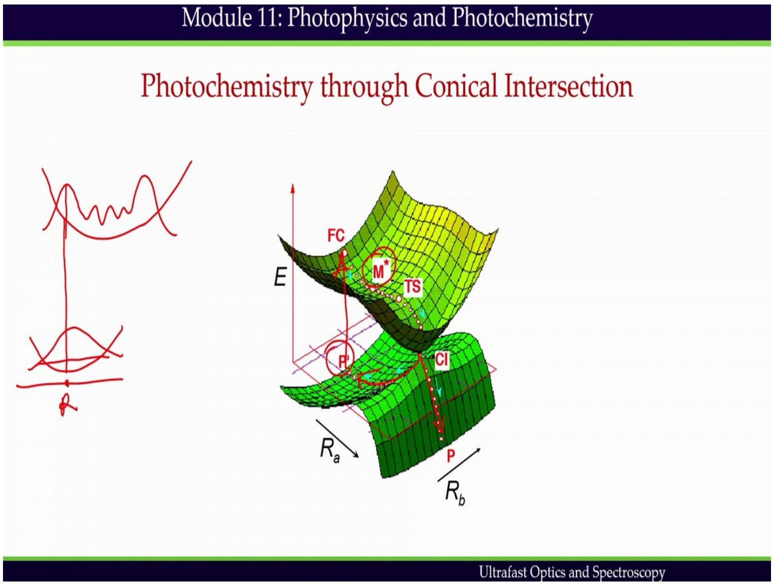

Module 11: Photophysics and Photochemistry

Photochemistry through Conical Intersection

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Conical intersections are also called photochemical funnels, provide pathways for ultra fast internal conversion or inter system crossing. Here a number of general phenomena of ultra fast non adiabatic dynamics through the conical intersections are discussed. Electronic excitation promotes a molecule from its ground to an electronically excited state. Here the nuclei in the electronic ground state are assumed to have their positions characterized by point P dash in the reaction coordinate.

So, this is my ground state P u dash electronic excitation takes place so fast that nuclei do not have enough time to move and that is why it is called vertical transition vertical excitation occurs. The quantum mechanical analogue of the classical Franck Condon rule is that the probability of nuclei making a transition from one potential energy surface to another is greatest for these places.

So, when I have a vertical transition we have to think about either we classical we can think of that nuclear does not move. So, I have this preserve this coordinate R and quantum mechanical version of this same idea is that I have the maximum overlap between the vibrational states which are undergoing the transition.

The nuclear configuration of the FC point of the upper excited state may differ quite significantly from the nearest potential energy minimum which is M star given here in the excited state potential energy surface. In a few tens femtoseconds the system slides down from FC to the neighbourhood of the M star. Transforming its potential energy into kinetic energy this occurs because of the force dvd r; on the nuclei due to the change in electronic configuration from S naught to S 1.

If M star is separated from conical intersection by a barrier as soon as the molecule during vibration overcomes the barrier. And the transition state by going over it or by tunnelling through it will be driven by the new force to the conical insulation attractor. And often it is going to be 100 percent probability of transition in the conical intersection at the conical intersection the molecule undergoes are non adiabatic or non radioactive transition to the ground state of the intersection of the potential surface.

If the relative momentum of the nuclei is large enough, the system slides down a long pathway towards P; the nearest minimum of the product, if the momentum is small the system may go back to the piece dash returning to the original molecules. So, at this point I can have two possibilities going back to the reactant side going to the product side.

The total energy of course, has to be conserved in a condensed phase environment the system finds a way to dissipate its energy transfer an excess of electronic energy into its own molecular vibration; rotational and translational degrees of freedom or to those of the neighbouring solvent molecules. Under gas phase isolated conditions; however, they excess electronic energy following unknown at every transition through a conical section is stored. In the vibration vibrational degrees of freedom on the ground electronic surface which can often cause molecular fragmentation or rearrangement.

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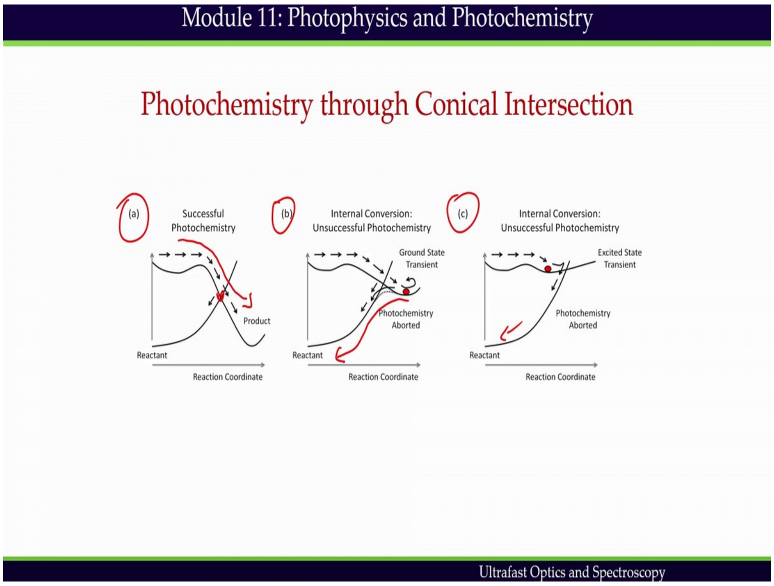

Module 11: Photophysics and Photochemistry

Photochemistry through Conical Intersection

Ultrafast Optics and Spectroscopy

Topographical structure or potential energy surfaces near a conical intersection may mediate. Either a non adiabatic photo physical process which is purely internal conversion or non adiabatic photochemical process; three basic types of photochemical reactions pathways are often found for organic chrome force they are shown here. Path a here by this path, we are showing that photo excitation can lead to successful photochemistry because of the feature of the conical intersection we have here. For which of finite percentage of absorbed photon energy is used to produce a different chemical species.

In path b if I have a feature like this then what might happen because of this photo product may come back to the reactant side and that can in introduce internal conversion only. And path c what we see here it can avoid photochemical reaction near the conical decision because it is directly coming back to the reactant side. So, what is the topographical feature of conical intersection and overall excited state pathways that controls the photo product or the internal conversion.

The development of femtosecond pulses laser has made it possible to make observations on transient species which have very short lifetime. With respect to the lifetime the transient species form near and avoided crossing or conical decision in photo induced processes may quite resemble an activated complex or transition state which we used in thermally activated processes.

We shall go over we shall go over now, the ultra fast relaxation dynamics through an avoided crossing for a well known example isolated gas phase sodium iodide system which exhibits covalent to ionic avoided crossing.

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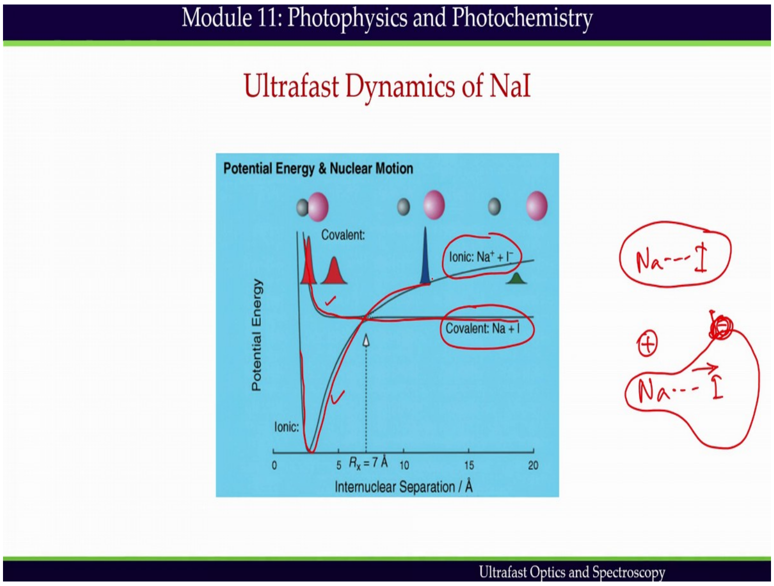

Module 11: Photophysics and Photochemistry

Ultrafast Dynamics of NaI

Ultrafast Optics and Spectroscopy

Here we have shown NaI, sodium iodide potential energy surfaces electronically ground. And first excited state of NaI molecule is described with two potential energy curves one is ionic the first ground state is ionic and excited electronic state is actually in covalent in nature.

When I say ionic N a I ionic means most of electron cloud is shared by iodine and covalent is attracted to a. So, when I say ionic most of the electron density is attracted towards I that is why it gets high minus and sodium plus and here covalent means its equally shared. The electron density is equally shared. So, this is the two different kind of bonding nature of bonding and both nature and extent of ionic contribution and extend of covalent contributions they all contribute to the overall bonding of any molecule.

N a I particularly is an example where ground state showing ionic potential and another excited state issuing covalent potential; both curves create an avoided crossing at an inter nuclear separation of approximately seven angstrom. In the ground state the NaI molecule exhibits ionic electronic character and the same molecule features covalent electronic character.

In the first electronically excited state; however, because of difference in ionization potential of Na and Na plus an electron affinity of I and I minus dissociation limit for Na plus and I minus is greater than that of Na plus I. So, this dissociation limit is higher than this dissociation limit. NaI is a hetero heteronuclear diatomic molecule, which does not possess a centre of symmetry. Hence, symmetry argument does not help to electronic potential energy curves to cross rendering avoided crossing.

Because of this avoided crossing, at inter nuclear distance approximately seven angstrom electronic electron harpooning occurs when the molecule is bound on the upper electronic state. This suggests that, electron is transferred from one atom to another during vibration on the upper excited curve as the electronic character changes from covalent to ionic in the bound upper curve.

However, if there is a non adiabatic transition from upper state to the lower state through the avoided crossing regime region which ultimately results in dissociation molecules does not need to. However, if there is a non adiabatic transition from upper state to the lower state through the avoided crossing then, molecule does not need to change the electronic character it is always covalent. So, basically the covalent curves after crossing looks like this an ionic curve after crossing looks like this.

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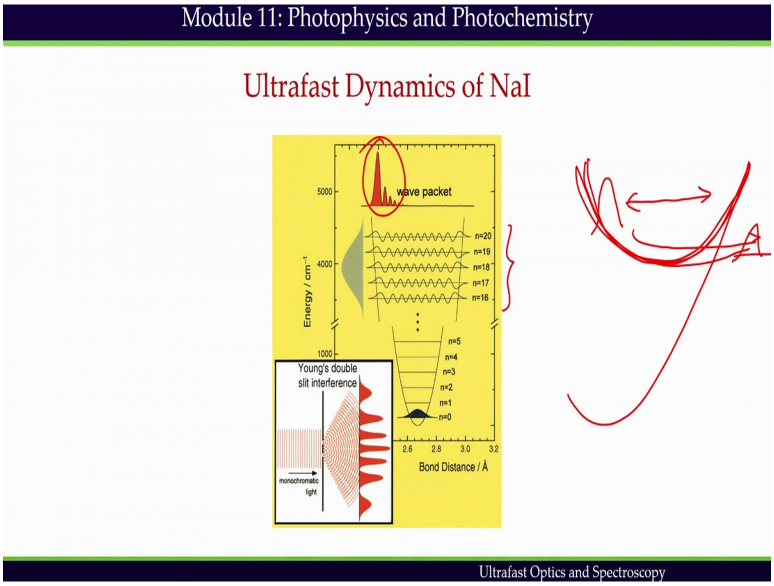
Module 11: Photophysics and Photochemistry

Ultrafast Dynamics of NaI

Ultrafast Optics and Spectroscopy

In the femtosecond pump probe spectroscopy the pump pulse at lambda 1, which is centre wavelength excites the molecule from ionic ground state to the covalent excited state. And because, we are using a broadband source which is a femtosecond pulse we are creating. We are exciting simultaneously many vibrational states in the upper excited state and which is creating the wave packet. We have shown previously what is the origin of the wave packet.

Consequently, electronically excited complex exists as a superposition of many vibrational states which renders a localized vibrational wave packet. There are two limiting possibilities now following electronic excitation the vibrational wave packet of the electronically excited NaI may get trapped on them adiabatic potential energies curve. So, I have the adiabatic potential energy curve and I can have this web packet which I have created it can be trapped.

And if it is trapped it is then going to vibe it going to oscillate within this adiabatic curve. Or there is another possibility, the vibrational wave packet may dissociates shown as the movement of wave packet towards the very long and (Refer Time: 39:23) reason. So, in that case wave packet may actually dissociate and it can actually propagate along this way through this non adiabatic transition only and they can have a dissociation.

These two possibilities should exhibit entirely different temporal behaviour and if there is a trapping, the details of the nature of the curves and the strength of non adiabatic coupling near the avoided crossing can be deciphered from femtosecond pump probe spectroscopy.

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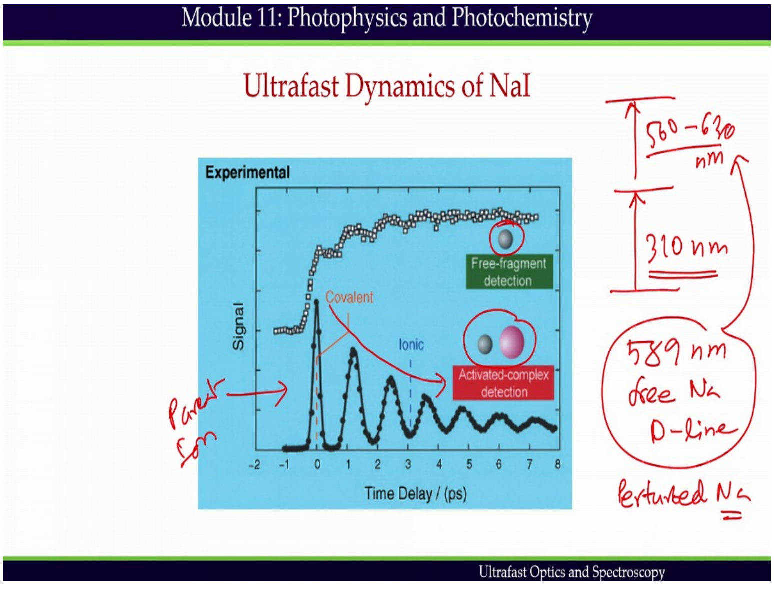

Module 11: Photophysics and Photochemistry

Ultrafast Dynamics of NaI

Ultrafast Optics and Spectroscopy

In the femtosecond pump probe spectroscopy, the dynamics of the vibrational wave packet is proved by a second probe pulse. Probe excitation essentially creates molecular ions with frequency that corresponds to absorption frequency of perturbed nm. So, I have now used pump probe, we have here pump probe spectroscopy. The pump is exciting the molecule to the excited state.

This experiment was performed by (Refer Time: 40:19) group and femtosecond pump pulse was selected at 310 nanometre. And the probe pulse was selected from the wavelength range of 560 to 630 nanometre. And here 310 nanometre is enough to excite NaI system to the electronically excited state. And we have to remember that 589 nanometre is only on resonance with free Na, D line sodium D line.

But, other probes like other than 589 nanometre all other wavelengths are off resonance with free sodium atom, but they are on resonance with perturbed sodium. So, weakly bound sodium species with so, iodine they are on resonance. And that is why we can actually look at the molecular ion or the fragment. The observed parent ion intensity this is the parent ion intensity this is parent ion intensity, as a function of pump probe delay time is plotted here which shows oscillatory behaviour that reoccurs in about 1.25 picosecond featuring the wave packet oscillation with about that period.

This period corresponds to a frequency of 27 wave number. The decline of intensity slow decline of intensity shows that the rate at which excited state species dissociates via non adiabatic jump from upper curve to the lower curve through the avoided crossing furthermore. The complex survives for about 10 oscillations and the oscillations are damped in 10 picosecond.

Therefore, the average probability of non adiabatic transition through the avoided crossing is estimated to be 0.1. Similar, probability of non adiabatic transition for NaI was also predicted by landau zener curve crossing calculations. For n a b r another system when we consider n a b r we see that the frequency of oscillation is found to be similar in magnitude.

However, severe damping is observed it be early survives one oscillation. Therefore, the result evidence is that the probability of non adiabatic transition through the avoided crossing for n a b r is more than that for NaI. This is consistent with the mass dependence of non adiabatic coupling term, large mass exhibits small non adiabatic coupling term resulting in slow non adiabatic transition through the crossing.

With this we have come to the end of this module. In this module we have discussed the origin of conical intersection consequences of conical intersection how to represent conical intersection. How to think about or how to predict photochemical behaviour of a molecule through conical intersection? And then we have given an example of ultra fast spectroscopy which has probed the dynamics of Na is system evolving through an avoided crossing. We will meet again for the next module.