Pericyclic Reactions and Organic Photochemistry
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Module No. #06
Lecture No. #27
Introduction of Organic Photochemistry

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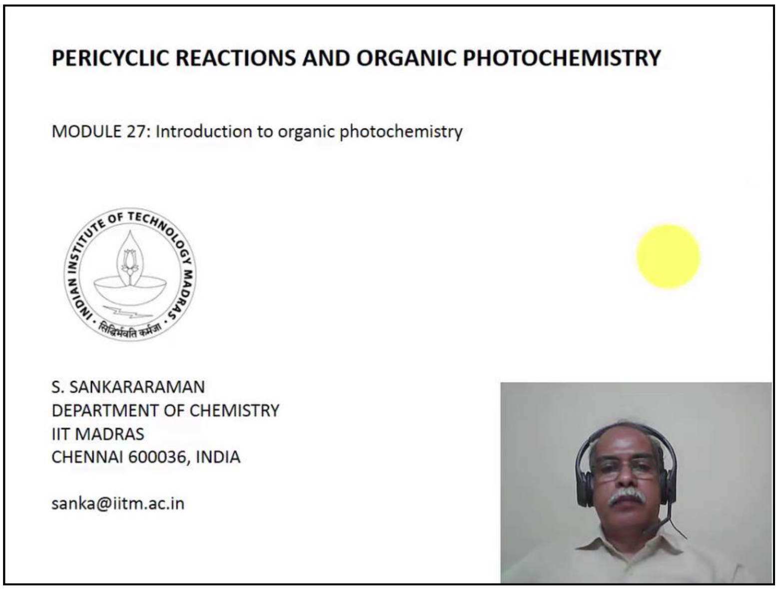

PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY

MODULE 27: Introduction to organic photochemistry

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Hello, welcome to the online course on, Pericyclic Reactions and Organic Photochemistry. We are in Module Twenty-Seven, of the Sixth Week. We are going to introduce the, Organic Photochemistry, from this Module onwards. Let us, in this particular Module, see some fundamental concepts related to, Photochemistry in general, specifically to Photochemistry of Organic molecules.

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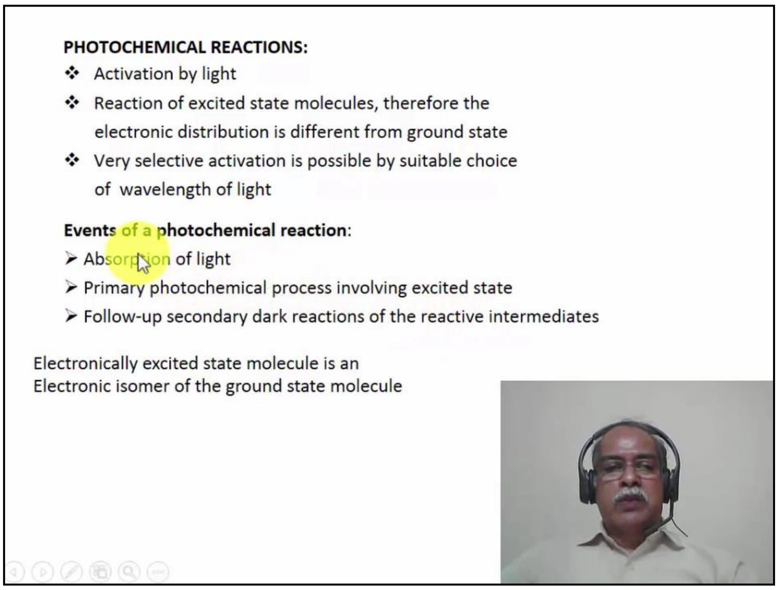

PHOTOCHEMICAL REACTIONS:

- ❖ Activation by light
- ❖ Reaction of excited state molecules, therefore the electronic distribution is different from ground state
- ❖ Very selective activation is possible by suitable choice of wavelength of light

Events of a photochemical reaction:

- ➢ Absorption of light
- ➢ Primary photochemical process involving excited state
- ➢ Follow-up secondary dark reactions of the reactive intermediates

Electronically excited state molecule is an
Electronic isomer of the ground state molecule

Photochemical reactions are essentially reactions, which are activated by Photon energy. In other words, the activation is by light. The energy associated with the Photon, is transferred on to the molecule, by an Electromagnetic radiation molecule, interaction kind of a process, that takes place. The reaction involved are, coming from the Excited state of the molecule. Therefore, the Electronic distribution, is different from the Ground state.

In other words, the molecules, that we are dealing with in the Excited state, are essentially Electronic isomer of the Ground state of the molecule. In fact, the Electronic configuration is what is different about the Excited state molecule, compared to the Ground state molecule. Unlike, the Thermal reaction, the Photochemical reactions can be extremely selective, in terms of the activation.

Because, by suitably choosing the wavelength of light, that corresponds to a particular species,

One can activate, that particular chemical species, without affecting the other chemical species, by light. So, the selection of wavelength, is extremely important for selective activation, of a particular molecule, in a mixture containing many starting materials. The events, that are taking place in the Photochemical reactions, are as follows. The first event has to be, the absorption of light. Without absorption of light, you cannot have a Photochemistry.

The primary Photochemical process, involving the Excited state. And then, the follow-up secondary reaction, which are actually dark reactions, arising out of reactive intermediates. So, these are at least, the three types of processes, that would take place in any Photochemical reaction. In this, we are not considering, the Photophysical processes. We will not pay much attention, to the Photophysical processes, in this module.

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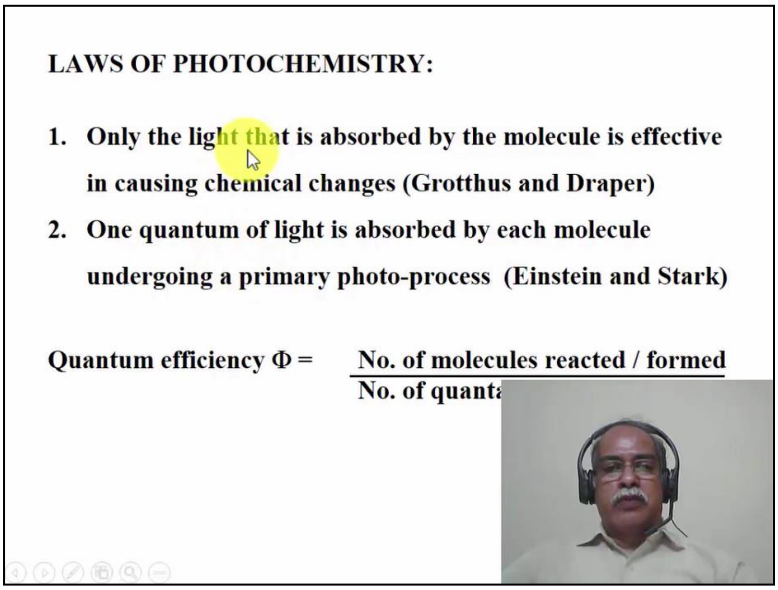

LAWS OF PHOTOCHEMISTRY:

1. **Only the light that is absorbed by the molecule is effective in causing chemical changes (Grotthus and Draper)**
2. **One quantum of light is absorbed by each molecule undergoing a primary photo-process (Einstein and Stark)**

Quantum efficiency $\Phi = \dfrac{\text{No. of molecules reacted / formed}}{\text{No. of quant}}$

We will consider the Photophysical process, in the later modules. Now, there are couple of laws of Photochemistry, which are essentially, common-sense kind of a law. The first law, is proposed by Grotthus and Draper. And, it states that, only light that is absorbed by a molecule, is effective in causing the chemical changes. This is fairly obvious. Because, if the Photon energy is not observed, then there is no Photochemical reaction.

But, the important aspect of this particular thing is that, one should choose the wavelength of light, that corresponds to, where the molecule absorbs. In other words, it is absolutely essential to first record, the UV-visible spectrum of the molecule, before Photochemistry can be attempted, for any kind of a molecule. So, already it is a common-sense kind of a thing, it is to be practiced properly.

In order to do Photochemical reaction, one need to first run the UV-visible spectrum, and find out, where the molecule absorbs the UV-visible spectrum, and use the wavelength, corresponding to a specific excitation wavelength, corresponding to the absorption of the molecule, in the UV-visible spectrum. Now the second law is proposed by, Einstein and Stark. One Quantum of light is absorbed by each molecule, undergoing a primary Photoprocess.

In other words, in order to produce an Excited state, at least one Photon has to be absorbed, one Quantum of light has to be observed. So, as a corollary of this particular law, one can state, what is Quantum efficiency. The Photochemical reactions, are characterized by Quantum efficiency, just like, you would characterize the, turn over frequency, and turnover numbers, in a catalytic process, for example, or the percentage yield in any Organic synthesis, which shows the efficiency of that particular process.

The Quantum efficiency is essentially, a ratio of the number of molecules reacted, or the number of molecules formed, divided by the number of Quanta of light, absorbed by the molecule. Ideally speaking, for every Quantum, that is a absorbed by the molecule, if it undergoes a Photochemical reaction, the Quantum efficiency will be one. Because, every Excited state molecule, produces one product molecule, or one reactant molecule is consumed, to give a product molecule, by one Quantum of absorption of light.

Then, the Quantum efficiency, because this ratio becomes one, the Quantum efficiency becomes one. Often times, the Excited state molecule, does not produce the product. Excited molecule gets deactivated, by several Photophysical processes, that can take place. So, the Quantum efficiency can be much less than one. The Quantum efficiency can also be greater than one, if the primary Quantum absorbed by the molecule, is producing a reactive intermediate, which is causing for example, some kind of a chain reaction.

So, Photochemical chain reaction, is the Quantum efficiency, can be much higher than one. So, Quantum efficiency, essentially depends upon, how effectively the Excited state molecule that is produced, is reacting in a Photochemical manner, to produce the product, or producer reactive intermediate, which will propagate the reaction, by a chain process, and so on. We will come back, to the Quantum efficiency of Photochemical process, at a later stage, with some examples. But, this is a general definition of the, Quantum efficiency of any Photochemical reaction.

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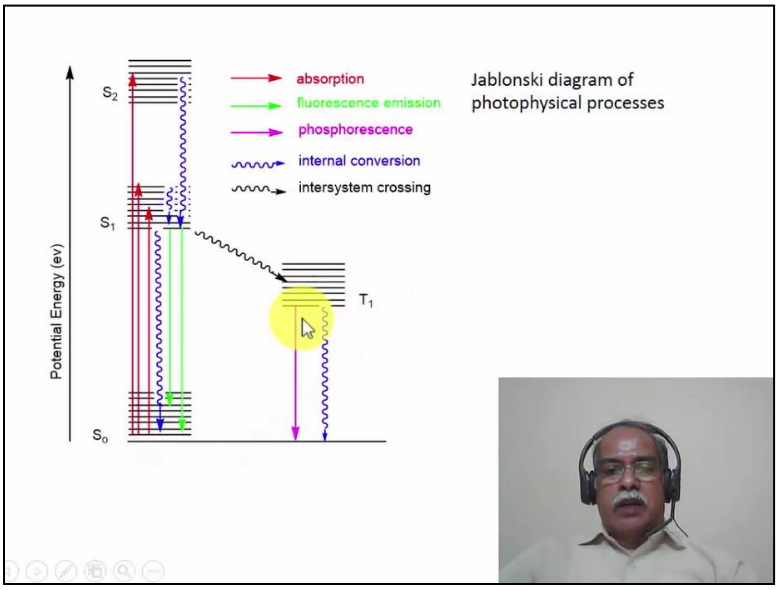

Jablonski diagram of photophysical processes

Now, in order to understand the Photophysical processes, Jablonski devised a diagram, which is represented in this particular picture. The Y-axis, is essentially a potential energy axis. The X-axis, does not have, any kind of a dimension or anything. It is not reaction coordinate, or it is not a Inter-Nuclear distance of any kind. Instead of drawing potential energy wells, to represent the various energy levels, he is simply adapted a flat diagram like this, to describe the processes, that are involved in the excitation process.

And, the excited molecules, undergoing various type of Photophysical processes. Now, all the molecules, Organic molecules, essentially stay in the ground vibrational state, of the Ground Electronic state. The S0 is the Ground Electronic state. And, the small lines, that are drawn here, in the ground Electronic level, is essentially the vibrational level, starting from Zeroth Vibrational level, First Vibrational level, Second Vibrational level, third, and so on, and so forth.

So, S0 and these lines, essentially represent the Ground Electronic state, with the vibrational structure, associated with the Ground Electronic state. S1 similarly, is the first Excited Singlet state. And, S2 corresponds to the, second Excited Singlet state. So, the S, essentially represents a Singlet state. And, the T, represents a Triplet state. So, essentially this is a first excited Triplet state, with the corresponding vibrational levels, that are shown here.

Now, the Red lines are essentially, the Electronic excitation from the ground vibrational, Zeroth Vibrational level, to the various vibrational levels, in the Excited state S1, as well as to S2. Now, any excitation to corresponding to the S2 level, will result in the immediate deactivation by Non-Radiative pathway, which is in internal conversion, resulting in the formation of the first Excited state, which is the S1 state.

So, the S2 state, rapidly decays back to the S1 state. And, the other Photophysical events, essentially take place from the S1 level. Suppose, if the molecule is excited, to the various vibrational levels of the S1 level, before it can undergo any other Photophysical processes, the excited vibrational levels will essentially come to, Zeroth Vibrational level of the Excited state, according to Kasha's rule. And, whatever the Photophysical events take place, essentially take place from the Zeroth Vibrational level, to the Ground state of the molecule.

What are the processes, that can take place, from the Zeroth Vibrational level of the Excited state, to the Ground state molecule? The first one is the wavy line, that is shown, which is an internal conversion. Which is nothing but, dissipation of the excess energy, that is present in the Excited state, to the surroundings, by means of heat. So, it is a Non-Radiative pathway kind of a process, is what is taking place.

The Radiative pathway, of course, is known as the Fluorescence, coming from the Zeroth Vibrational state of the, Higher Excited state of the, Singlet Excited state of the molecule, to the Ground state, to the various vibrational levels of the Ground state, which is a zero. So, the Green lines, that are shown here, are essentially Fluorescence emission lines. In addition to that, there is a possibility of the S1 state, undergoing decay to T1 state, which is an inter-system crossing.

This is a spin forbidden process. Essentially, it is a forbidden process, because there is a spin change, from Singlet to a Triplet state, in this particular system. Nevertheless, several molecules do undergo the intersystem crossing, by various mechanism. Once it comes to the excited Triplet state, from the excited Triplet state, it can either undergo an emissive transition, which is the Phosphorescence transition, which is shown in the Magenta color.

Or, it can undergo internal conversion, by means of Non-Radiative decay pathway, to the Ground state, which is a S0 state. So, the Jablonski diagram, essentially explains the various excitation processes, and the corresponding decay of the Excited state, Electronic state, molecule to the Ground state, by Radiative, as well as Non-Radiative processes. At this juncture, one should, now characterize these processes, by the time domain, that is involved in the system.

For the Electronic excitation to take place, it takes place in the Femtosecond, or Sub-Femtosecond time scale. And, for the Fluorescence lifetime, is essentially of the order of nanoseconds, 10^{-9} seconds. And, the Phosphorescence lifetime, is of the order of seconds, to several minutes, or even days, for example. So, this is a longest-lived species, in terms of the lifetime of the Phosphorescence state, or the T1 state. The reason, that is taking such a long time is because, the T1 to S0 transition, is also a spin forbidden transition. So, it takes place quite a long time, for the decay of the molecule, from the Triplet state to the Ground Singlet state, by means of either emissive or non-emissive process. Now, why are the lines drawn, in the vertical direction, in this particular way.

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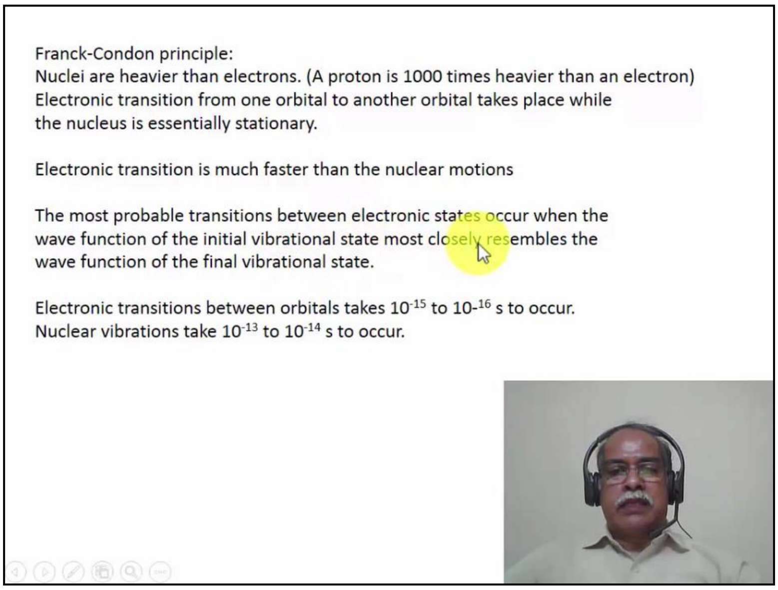

Franck-Condon principle:
Nuclei are heavier than electrons. (A proton is 1000 times heavier than an electron)
Electronic transition from one orbital to another orbital takes place while the nucleus is essentially stationary.

Electronic transition is much faster than the nuclear motions

The most probable transitions between electronic states occur when the wave function of the initial vibrational state most closely resembles the wave function of the final vibrational state.

Electronic transitions between orbitals takes 10^{-15} to 10^{-16} s to occur.
Nuclear vibrations take 10^{-13} to 10^{-14} s to occur.

This is essentially, because of the Franck Condon principle. What is a Franck Condon principle? It is a principle, which tells you the, relative kinetics of the Nuclear motion, versus the Electron excitation process, that is taking place, in a molecule. Now, the nuclei are heavier than Electrons. A Protons is about, 1000 times heavier than the, Electron. So, the Electronic transition from one orbital, to another orbital, takes place quickly, when the nucleus is essentially stationary.

In other words, there is no inter-Nuclear distance change, during the Electronic transition. Electronic transition is essentially, much faster than the Nuclear motion. In terms of time scale, if you look at, the Electronic transition takes place, in the Femtosecond time scale, 10^{-15} to 10^{-16} seconds, it takes place. Whereas, the Nuclear vibration, in other words, the Inter-Atomic distance changes take place, essentially in the Sub-Picosecond, which is 10^{-13} to 10^{-14}. In other words, it is at least two orders of magnitude slower than the, Electronic excitation is two orders of magnitude faster than the, Nuclear vibration, in terms of the time scale, that is involved in the system. You can also state the, Franck Condon principle, in another way. The most probable transition between Electronic states occur, when the wave function of the initial vibrational state, most closely resembles a wave function of the final vibrational state. This is something, we will see in the next diagram.

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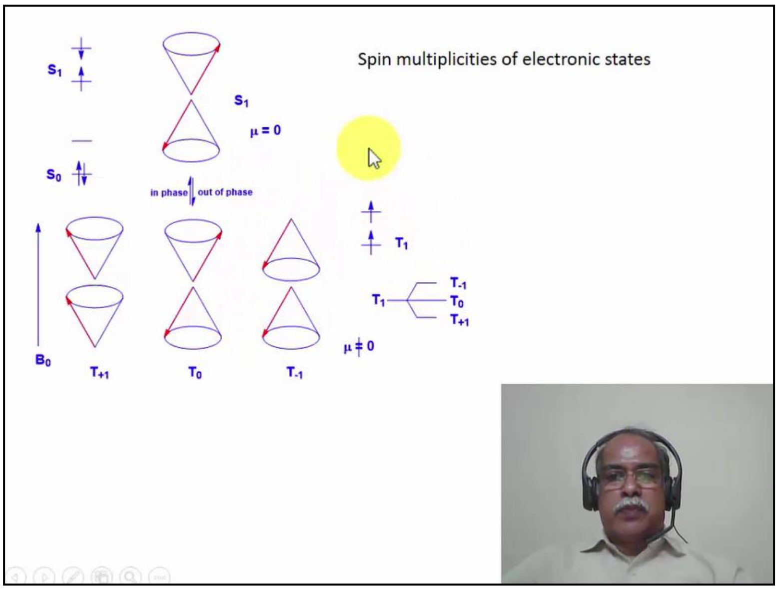

Spin multiplicities of electronic states

Now, what do we mean by Singlet state, and Triplet state. These are essentially, to deal with the Magnetic moment, or the spin orientation of the 2-Electrons, that are involved. Let us take the Ground state configuration, is like this, where S0 state, there are 2-Electrons. And, this is the lowest unoccupied molecular orbital. And, this is a highest occupied molecular orbital, of the molecule, let us say.

Now, during the Electronic excitation, without change in the spin, this is spin paired, and this Excited state also spin paired. If you look, not spin paired, but the spin orientations are in opposite direction, for example. This is the Singlet state. So, in other words, the multiplicity is retained, in going from the Singlet zero, to Singlet first Excited Singlet state of the Electronic transition, that is taking place. In order to go from the Excited Singlet state, to the Triplet state, which is shown here, there has to be a spin inversion.

As you can see here, this is downward to upward inversion, is what is taking place. What do we mean by, the orientation of the 2-Electrons? In the presence of an external Magnetic field, i can state that, it can exist, or only one, in the case of the Singlet state. Because, essentially the Magnetic moment is essentially zero, in this particular case. In the presence of an external applied Magnetic field, the 2-Electrons that are in opposite direction, essentially undergo precessional motion.

And, not only they undergo precessional motion in the same frequency, they are also in phase, in terms of cancelling the Magnetic moment vector, that is created by these two spinning Electron. So, essentially the overall Magnetic moment is, essentially equal to zero. Because, this is pointing in the, aligning with external Magnetic field, this is pointing opposed, to the external Magnetic field. So, the net Magnetic moment, essentially cancels each other, to give the net Magnetic moment of zero, in the S1 state.

So, there is only one state, that is possible, where the two spins are in opposite direction, and they are synchronous, in terms of their precessional motion, in the presence of an external Magnetic field. On the other-hand, when the two spins are parallel to the external Magnetic field, there are three possible orientation, that it can take place. The two spins, both of them can be parallel, with respect to the external Magnetic field.

This is one state, called the T+1 state. The 0, +1, and -1, are the three eigen values, to which the Magnetic orbital momentum can be, described in this molecule. The two spins can be pointing in the same direction, aligning with the external Magnetic field, or they could be pointing opposed to the external Magnetic field, which will have the highest energy.

Or, they can be pointing, one pointing up, and one pointing down, in this manner, this particular manner, essentially not cancelling the Magnetic moment vector, as in the case of Singlet state. Because, these two spins are précising in different frequencies, they are not in phase, with respect to each other, so, the Magnetic moment vector, in the direction opposing the external Magnetic field, and aligning with external Magnetic field, are not equal, in this particular case.

So, the net Magnetic moment, is still persisting, in this one. The Singlet to Triplet transition, essentially take place, when the two spins are in phase, or out of phase, with respect to the precessional motion, in the presence of an external Magnetic field. So, this essentially in a very qualitative manner, describes the spin multiplicity of Electronic states, in an Excited state, Singlet state, and Triplet state, of the molecules.

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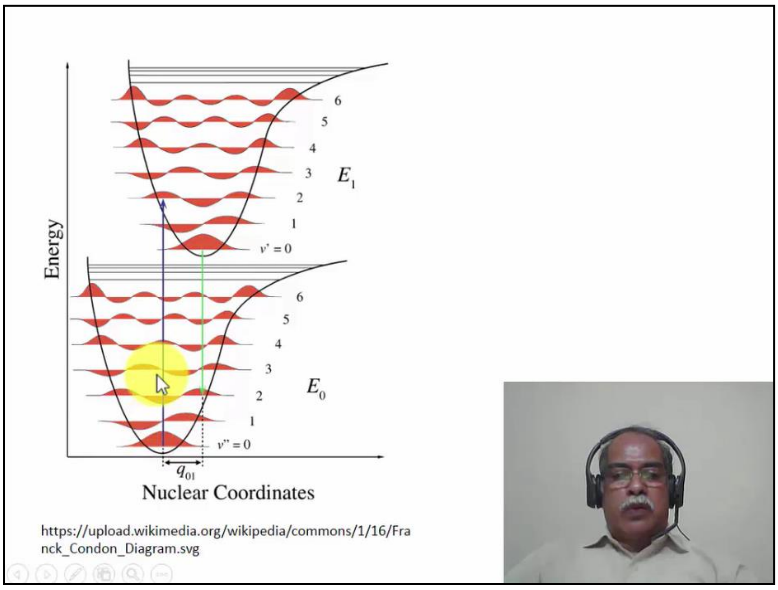

https://upload.wikimedia.org/wikipedia/commons/1/16/Franck_Condon_Diagram.svg

Now, this is a diagram, which essentially shows the potential energy diagram. You can see here, going from this position Inter-Nuclear, this is an X-axis, Inter-Nuclear distance here.

And, Y-axis is the potential energy. So, essentially during an Electronic transition, because of the Franck Condon principle, there is no change in the Inter-Nuclear distance. So, vertical lines are drawn for Electronic excitation, as well as the Fluorescence emission, in this particular case.

What this diagram shows, is the various vibrational levels of the Ground state, and the vibrational levels of the Excited state, and the density function, is what is plotted, in terms of the Electron density probability, is what is being plotted, in this particular instance. So, if an Electronic excitation is taking place, from the Zero-Vibrational state, of the Ground Electronic state, and ends up in the Second Vibrational state, of the Electronically Excited state.

You can see here, this is reaching the highest probability density, starting from the highest probability density. So, such a transition would be having, the maximum intensity in the absorption emission spectrum. Similarly, from this position also, from the highest probability density, it is coming back to the highest probability density in the, 0 to 2 transition, which is a emission transition. So, the excitation and the emission of, 0 to 2 transition, is the highest probability transition.

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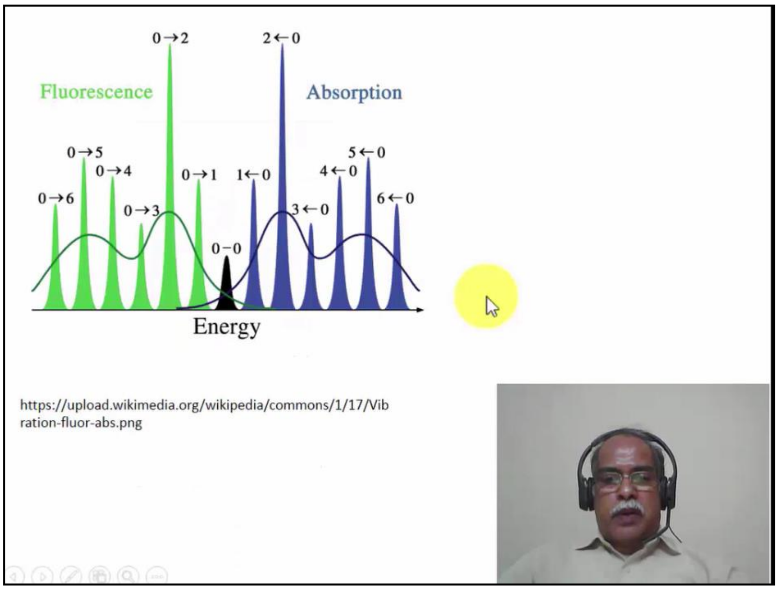

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So, that will have the maximum intensity of, Fluorescence emission and absorption, in terms of the intensities, that are directly proportional to the probability densities of the Electrons, in this diagram, that is shown here. One can also see here, this is a Fluorescence Emission spectrum, and this is an Absorption spectrum, drawn in the Blue. The Zero-Zero emissions are essentially, matching with each other.

And, the rest of the peaks are essentially, looking like mirror image, with respect to the Zero-Zero transition. In other words, if you look at the right-hand side, the Blue transitions are essentially, looking like a mirror image of the Green transitions, which are shown on the left-hand side of the molecules. What is the reason, we have a mirror image, with the overlap of the Zero-Zero transition?

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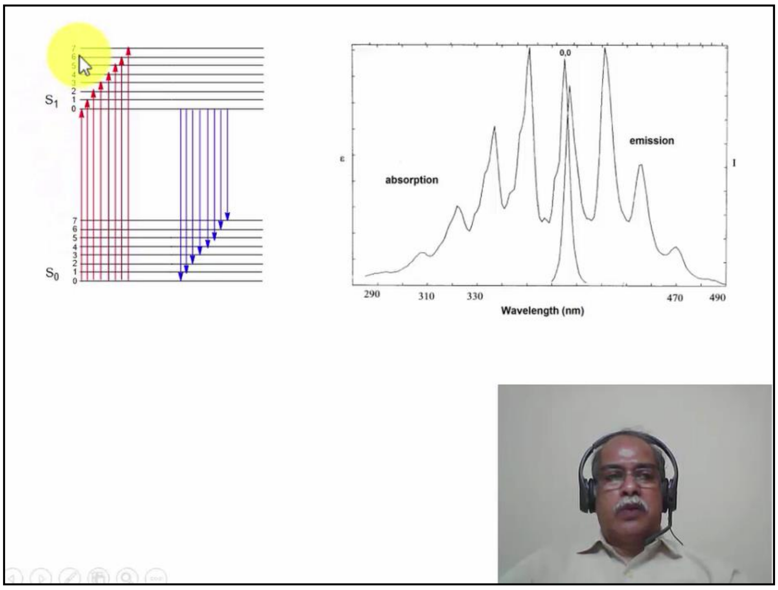

This is explained, in this particular diagram. This is a S0 state, with vibrational levels 0 to 7. And, this is S1 state, with vibrational levels 0 to 7. And, these are the excitation processes, where Electronic excitation take place. In other words, these are the absorption wavelengths of the excitation process, that is involved, going from the Ground state, to the Electronically Excited state molecule.

So that, this is a Zero-Zero excitation, and this is a 07 excitation. In between, you have 01, 02, 03, and so on, that is represented by the Red arrows, in showing here. Once the molecule reaches the Excited state, to the various vibrational level, one were according to Kasha's rule, they have to come back, to the zero-vibrational state of the Excited state. In other words, they have to come to this particular level, before they can undergo emission process.

This is because, these vibrational levels are so closely spaced, a Thermal deactivation process, in terms of internal conversion, can take place quite readily. And, that is what promotes the internal conversion, to come to the zero-vibrational state of the excited Electronic state. From the zero-vibrational state, now it can come to the Ground state, to the zero level, first level, or up to the seventh level, as indicated by the Blue arrows.

Now, if you look at this Zero-Zero transition, which is the excitation process, and this Zero-Zero transition, which is the emission process, these two Energy levels are essentially same, that is the reason. In the picture, the Zero-Zero levels are essentially matching, overlapping with each other. This is a spectrum of Anthracene. This is an Absorption spectrum, on the left-hand side, and the Emission spectrum, on the right-hand side, for example.

The Zero-Zero transition of the absorption, and the Zero-Zero transition of the emission, are nearly overlapping, with respect to each other. There can be some polarity, solvent polarity effect, and so on, which can shift the Zero-Zero band of the absorption, from the Zero-Zero bond of the emission, to various levels. This is called Stoke shift. In this case, very minimum amount of stroke shift is observed, because this is recorded essentially, in the Non-Polar solvent.

What is important, is the mirror image relationship, that one can see, very clearly of the Absorption spectrum, to the Emission spectrum. This is 00, this is 01, 02, 03, 04, 05, and so on, of the various vibrational fine structure. And, this vibrational fine structure, in the Absorption spectrum, corresponds to the Excited state vibrational fine structure. And because, it essentially coming from this process of excitation, to various vibrational level.

So, Absorption spectrum gives you information, about the excited Electronic state. Whereas, the Emission spectrum gives you information, regarding the vibrational levels of the Ground state. So, this is Zero-Zero of the Ground state, 01 of the Ground state, 02, 03, 04, and so on, of the Ground state vibrational level, is what is reflected in the Emission spectrum. So, this diagram essentially describes, the mirror-image relationship, explains a mirror image relationship.

It is also explains, the Stoke shift. If it is a very highly Polar solvent, specific solvation of the Excited state, or the Ground state, can essentially affect the upward transition, from the downward transition, which will result in large Stoke shift, in the case of highly Polar solvent, which can specifically solvate, either the Excited state, or the Ground state, depending upon the polarity of the Excited state, or the Ground state.

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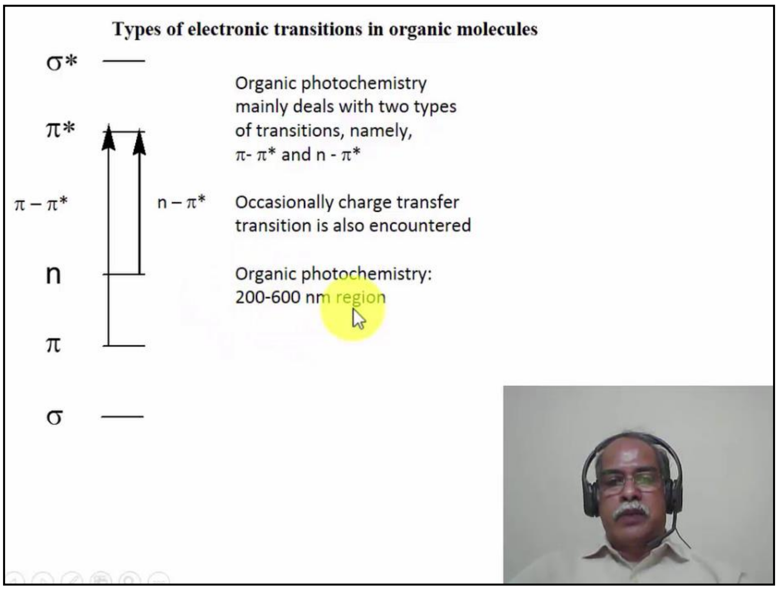

Types of electronic transitions in organic molecules

Organic photochemistry mainly deals with two types of transitions, namely, π- π* and n - π*

Occasionally charge transfer transition is also encountered

Organic photochemistry: 200-600 nm region

The type of Electronic transition in Organic molecule, essentially depends on, what kind of molecule, that we are dealing with. If it is a Saturated molecule, here you have only Sigma Electrons. Then, there is only a possibility of Sigma to Sigma transition, that is possible. Let us take the example of Methyl Iodide, the CI bond has the lowest energy absorption. So, if one excites CH3I, using a visible light, in fact, if you leave it in room light, Iodine is liberated, essentially because, Electronic excitation causes, the CI bond Sigma Electrons, to go to the Sigma-Star Electron.

Once the Electrons reach the Sigma-Star, the bond that is essentially zero, that would correspond to the dissociative state of the CH3I, and it releases CH3 Radical, and Iodine Radical. Iodine Radical, essentially dimerizes to give Iodine. So, such is the Photochemistry, that is occurring, because of the dissociative Sigma to Sigma-Star process, that is taking place in Saturated molecule. But, the most interesting Photochemistry essentially takes place, in Unsaturated compounds, such as Olefins, Ketones, and so on, which have PI Electrons, as well as Lone pair of Electron.

If you take Ethylene for example, it can undergo excitation, from PI to PI-Star level. And, this is a PI-PI-Star transition of the Olefin, or the Diene, or Aromatic compounds, for example, we talk about. On the other hand, if you take Acetone, which is a Ketone, it can undergo N to PI-Star excitation. The N to PI-Star excitation, is essentially happening in, Unsaturated Carbonyl compounds, Unsaturated Imines.

Those compounds, which have a Heteroatom, with the Lone pair of Electron, which corresponds to the N Electron in the molecule. In Saturated system like Ether, Sulfide, and so on, the N to Sigma-Star transition is also possible, because the Heteroatom in the Ether, or Sulfide, or a Phosphine, can essentially give the Electron, from the Non-bonded level, to the

Sigma-Star level. Again, a dissociative transfer of Electron, is what is taking place, during the excitation process.

Most of the cases, we are going to deal with, the PI-PI-Star, and the N-PI-Star transition, that is what, deals with most of Organic Photochemistry. Occasionally, Charge Transfer transition is also involved. We will discuss, the Charge Transfer transition, in a separate module. So, typically, these two transitions are taking place, in the spectral region of 200 Nanometer, to 600 Nanometer regions, which is a UV visible region of the Organic Photochemistry, where these two transitions are involved, in terms of their energies.

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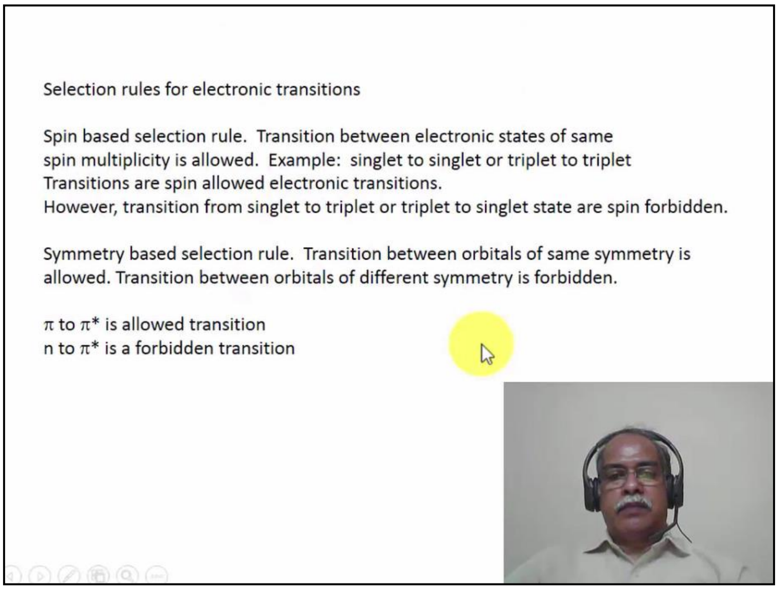

Selection rules for electronic transitions

Spin based selection rule. Transition between electronic states of same spin multiplicity is allowed. Example: singlet to singlet or triplet to triplet Transitions are spin allowed electronic transitions.
However, transition from singlet to triplet or triplet to singlet state are spin forbidden.

Symmetry based selection rule. Transition between orbitals of same symmetry is allowed. Transition between orbitals of different symmetry is forbidden.

π to π^* is allowed transition
n to π^* is a forbidden transition

Now, there are selection rules on the Electronic transition. There are two types of selection rule. One is based on the spin, which is called, the spin based selection rule. Transition between Electronic states, of the same spin multiplicity, is allowed. In other words, if you go from a Singlet state to a Singlet state, or from a Triplet state to a Triplet state, they are spin allowed transition state.

However, going from a Singlet state to a Triplet state, or the Triplet state to a Singlet state, are spin forbidden. This is what, i mentioned, when i talked about the intersystem crossing, from the Excited Singlet state to a Triplet state. There is a spin change, that is taking place. So, that is a forbidden transition, according to the spin selection rule. On the basis of symmetry selection rule, transition between orbitals of same symmetry, is allowed.

Whereas, transition between orbitals of different symmetry, is forbidden. So, this is something, we will deal with, a little later. Typically, in Olefinic compound, the PI to PI-Star transition, is an allowed transition. Whereas, Nth PI-Star transition, is a forbidden transition, because of the selection rules, that we talked about, in this particular slide.

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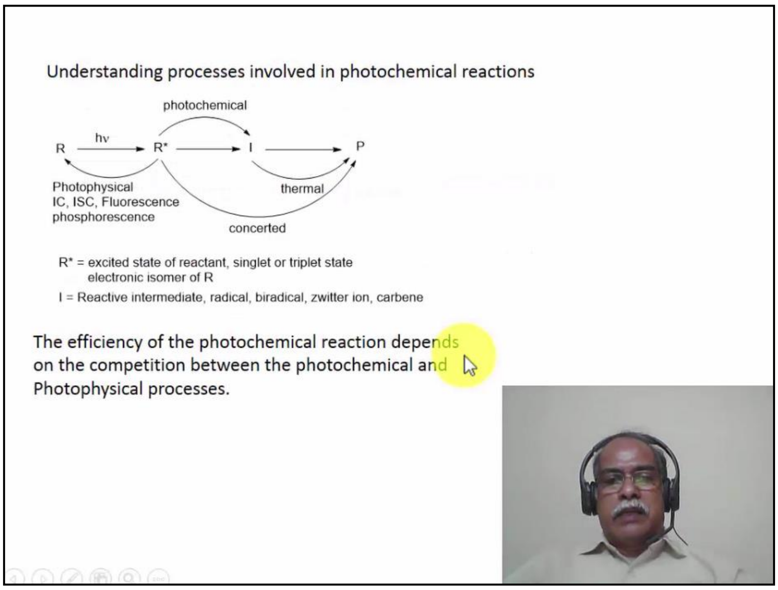

Understanding processes involved in photochemical reactions

R* = excited state of reactant, singlet or triplet state
electronic isomer of R

I = Reactive intermediate, radical, biradical, zwitter ion, carbene

The efficiency of the photochemical reaction depends on the competition between the photochemical and Photophysical processes.

Now, in order to understand the processes, that are involved in a Photochemical reaction, this diagram will help, quite significantly. Let us start, with the reactant R. It is undergoing, a photo excitation process, by means of absorption of a Proton, and it goes to an Excited state. So, R-Star is the Excited state of the molecule. From the Excited state molecule, it can go to an intermediate stage, which is a reactive intermediate, for example.

This is the primary Photochemical process, that can take place. In other words, the observed Photon energy, is now converted into chemical energy, in transforming the Excited state, Electronically Excited state molecule, to a reactive intermediate. This reactive intermediate, can be either a Radical, or it could be a Biradical, it could be Zwitter ion, it could even be a Carbene, and so on. So, there are several different types of a reactive intermediates, that can be found, from Electronically Excited state.

It is not necessary, the Electronically Excited state molecule, should always undergo unimolecular transformation. It can react with another molecule, which is in the Ground state, to produce this kind of reactive intermediates. This is a productive Photochemical step, that is involved, in converting the Photon energy, into some reactive species, which can further undergo, formation of the product. So, this is a subsequent Thermal reaction, is what is taking place, in converting the reactive intermediate, to the final product.

It is not necessary, that every reaction should undergo, via an intermediate formation. There are reactions, which the Excited state, directly undergoes to go to the product, in a unimolecular fashion, or in a bimolecular fashion, depending upon the kind of interaction, that exists in the transition state. And, these are called, Concerted processes. Remember, Concerted processes, or Photochemical processes are, where an Electronically Excited state molecule, directly goes to the product, without the involvement of any kind of an intermediate.

And, hence this arrow, corresponds to a Concerted process. Now, the energy wasting process, is a Photophysical process, which are internal conversion, inter system crossing, Fluorescence emission, and Phosphorescence emission. The former two, are the radiation less transition, whereas the latter two are, the Radiative transition, which are Photophysical processes. The Excited state, Electronically Excited state molecule, essentially loses the energy, goes back to the Ground state.

So, this is an energy wasting process. All the processes, which are Photophysical processes, are energy wasting. Whereas, the Photochemical processes are the one, that increases the Quantum efficiency of the overall Photochemical process. That is, therefore the efficiency of the Photochemical reaction, depends on the competition between the energy utilizing Photochemical step, to the energy wasting Photophysical steps, that are involved in this.

If, this is extremely active, in terms of the process that takes place, then the Quantum efficiency will be low. If this is going to be extremely efficient, then the Quantum efficiency will be very high, for the particular Photochemical reaction. So, this diagram essentially in a very simplistic manner, explains the processes, that are involved in a Photochemical step.

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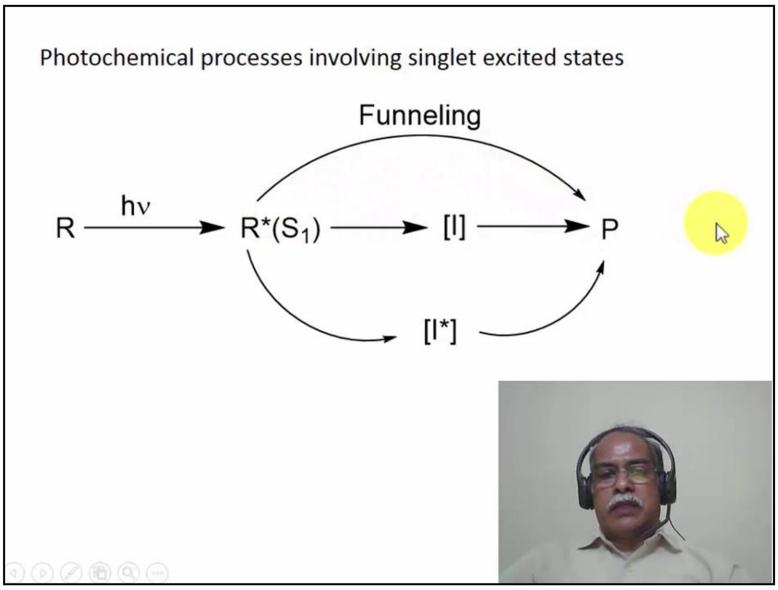

Photochemical processes involving singlet excited states

Now, within the processes, there are two types of process, that can take place. The excitation can be, either through a Singlet state. Once a Singlet Excited state is formed, it can go to a reactive intermediate, and then go to the product, as explained in the earlier slide. The reactive intermediate can be, again excited to a reactive intermediate, which is an excited intermediate, from which the product can be formed. This is a double Photon excitation process. Seldom, it is not a very common occurrence, that you have, this kind of a process, taking place.

Most Photochemical reactions, are directly arising from the primary photo excitation process, which results in the R-Star. R-Star, goes to an intermediate, and then goes to the product. Now, without going through an intermediate, there can be a funneling process, that can be taking place, where the Franck Condon minimum of the reactant molecule. In other words, the lowest energy point of the reactant potential energy surface, touches or crosses, the product

Potential energy surface, thereby converting the reactive intermediate to the product, which is a tunneling process, which is a funneling process actually, which is essentially equivalent to a Concerted kind of a process. Because, there are no reactive intermediates, formed in this particular step. So, this is a process, that involves the Electronically Excited Singlet state.

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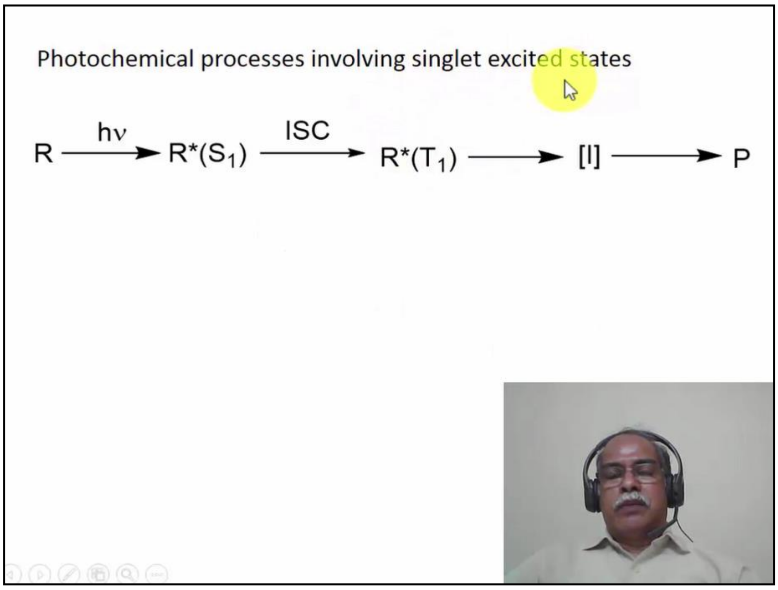

Photochemical processes involving singlet excited states

$$R \xrightarrow{h\nu} R^*(S_1) \xrightarrow{ISC} R^*(T_1) \longrightarrow [I] \longrightarrow P$$

One can also have, an Electronically Excited Triplet state, from which the reactive intermediate is formed. Once the Triplet state is formed, from the Singlet state, via the inter system crossing process. Depending upon, the efficiency of the inter system crossing, the Triplet Quantum efficiency, can be either very high or low, it depends on the inter system crossing efficiency,

From the Triplet state, the reactive intermediates can be formed. From the reactive intermediates, the products can be formed. So, this is a process, involving Triplet Excited state. There is a mistake here. This is not Singlet Excited state. This is a Singlet Excited state. Whereas, this is a Triplet Excited state process, that is taking place, in this case.

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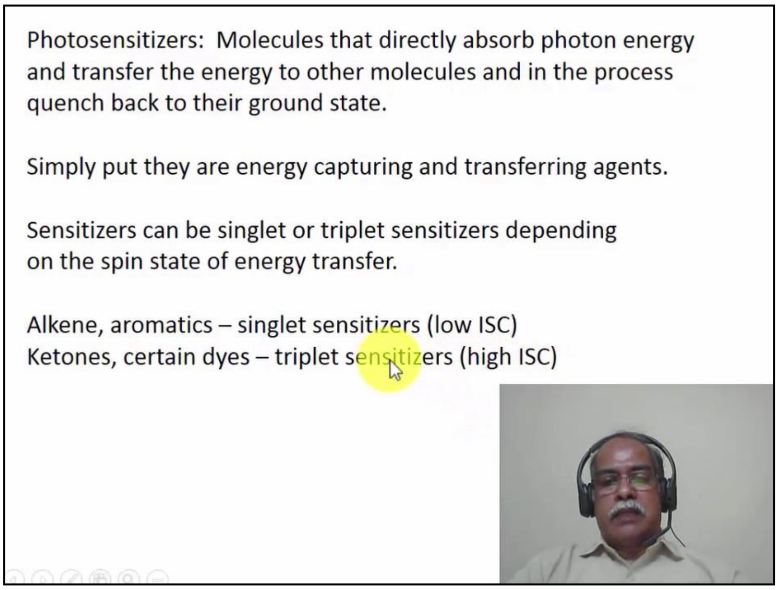

Photosensitizers: Molecules that directly absorb photon energy and transfer the energy to other molecules and in the process quench back to their ground state.

Simply put they are energy capturing and transferring agents.

Sensitizers can be singlet or triplet sensitizers depending on the spin state of energy transfer.

Alkene, aromatics – singlet sensitizers (low ISC)
Ketones, certain dyes – triplet sensitizers (high ISC)

Now, let us define, what are Photosensitizers. Photosensitizers are molecule, that directly absorb the Photon energy, and transfer the energy to another molecule, which is a starting material for the Photochemical reaction. And, in the process, the Photosensitizer essentially, quenches back to the Ground state of the Photosensitizer. In other words, this is purely an energy absorbing, and energy transmitting molecule. It does not undergo by itself, any Photochemical reaction. It is almost like a catalyst, except it is not catalyzing the reaction.

It is only promoting the transfer of energy, from the Photon energy, to the other molecule. Simply, put it is an energy capturing, and transferring agent. That is all, a Photosensitizer is all about. Photosensitizers can be, either a Singlet type of Sensitizer, or it can be Triplet type of Sensitizer, depending upon the spin state of the Sensitizer. Typically, Alkenes, and Aromatic systems, which are PI to PI-Star transition systems, will act as Singlet Sensitizer. In other words, their inter system crossing efficiency, is extremely low.

On the other hand, Ketones, and certain type of Dye molecules, like the Methylene Blue, Rhodamine, and so on, they undergo the N-PI-Star excitation. In some cases, because of the heavy Atom, they also undergo the intersystem crossing, with a high efficiency. And, these are typically, Triplet photosensitive. For example, Benzophenone, or Anthraquinone, they are all very good Triplet Sensitizers, because their inter system crossing efficiency, of the N-PI-Star state is very high. So, hence, they are the Triplet Sensitizers.

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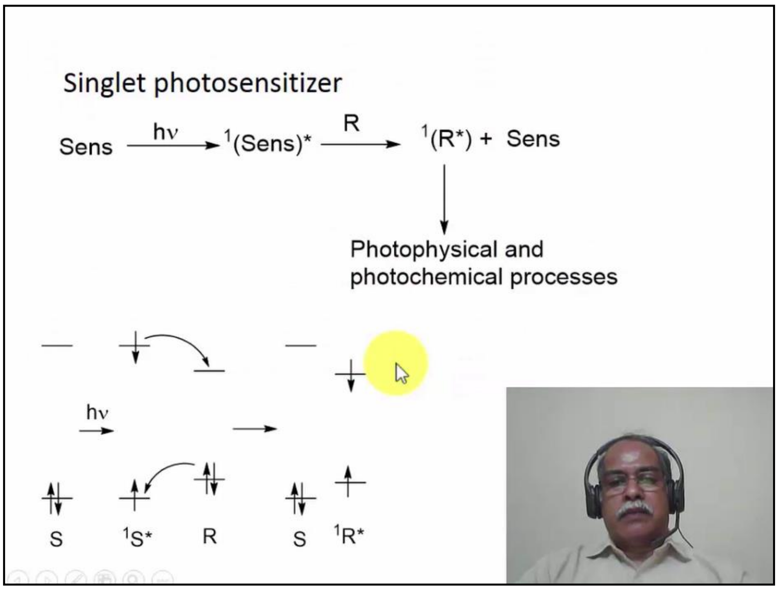

Singlet photosensitizer

$$\text{Sens} \xrightarrow{h\nu} {}^1(\text{Sens})^* \xrightarrow{R} {}^1(R^*) + \text{Sens}$$

Photophysical and photochemical processes

How does the Sensitizer work? Sensitizer, essentially absorbs the energy, goes to the first Excited Singlet state, which is an excited state of the Sensitizer. From the excited state of the Sensitizer, it interacts with the reactant molecule, transverse the energy, and in the process, the excited state reactant molecule is formed, and the Sensitizer is regenerated. Once the reactive Excited state of the reactant is formed. It can undergo, Photochemical, as well as Photophysical processes, as described in the earlier slides.

This is a diagram, which tries to explain, the relative energy requirements of the Sensitizer, and the reactive molecule. Let us say for example, this is the energy gap of the Ground Singlet state, and the Excited Singlet state, of the Sensitizer. Upon photo excitation, the Singlet to Singlet excitation takes place. This is the Electronic configuration, of the Singlet excited state of the Sensitizer. S stands for the Sensitizer, and Number 1, stands for the Singlet Excited state of the, the Number 1*, represents the Singlet Excited state of the Sensitizer.

Now, this is the Electronic energy levels, of the reactant molecule. You can see here, the reactant molecules have a lower energy, so that, it can receive this Electron, from this Higher Excited state. In other words, this is a transfer of energy, in terms of this Electron hopping onto this level, and one of this Electron hopping onto this particular level. These are all spontaneous processes, as you can see, going from Higher energy level, to the lower energy level.

So, when the Sensitizer comes in contact with the reactant molecule, is essentially transfers the energy. In the process, it regenerates the Sensitizer, and it results in the formation of the Excited state of the reactant. You can see here, by a simple Electron transfer processes, you can explain the transfer of the Singlet energy, from the Singlet Sensitizer, to the Singlet energy of the reactant, in forming the Singlet Excited state of the reactant, by means of a simple mechanism, like this.

So, this is a photo excitation process. This corresponds to, the energy transfer process, regenerating the Sensitizer molecule, and producing the Electronically excited reactant molecule, in this particular case.

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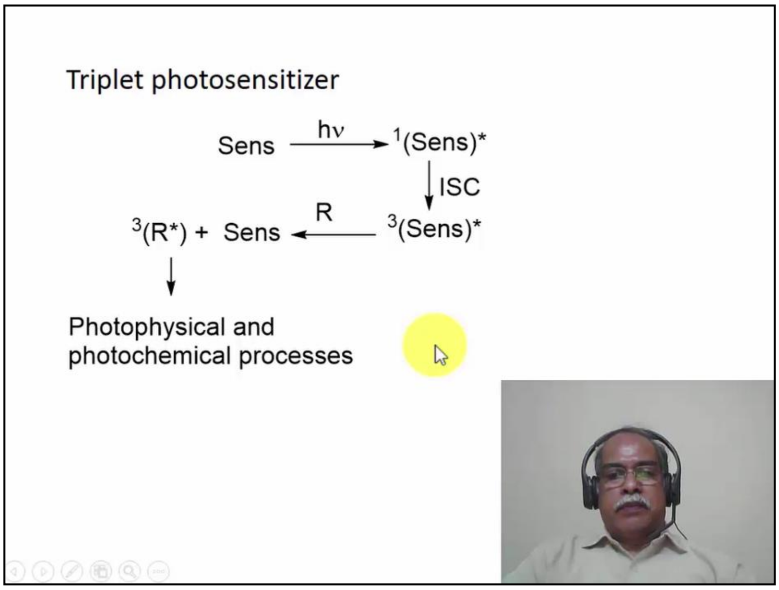

Triplet photosensitizer

$$\mathrm{Sens} \xrightarrow{h\nu} {}^1(\mathrm{Sens})^*$$

$${}^1(\mathrm{Sens})^* \xrightarrow{\mathrm{ISC}} {}^3(\mathrm{Sens})^*$$

$${}^3(\mathrm{Sens})^* \xrightarrow{\mathrm{R}} {}^3(\mathrm{R}^*) + \mathrm{Sens}$$

$${}^3(\mathrm{R}^*) \longrightarrow$$ Photophysical and photochemical processes

The same kind of a mechanism, can be applied for a Triplet Sensitizers also. The Sensitizer, undergoes excitation, to give the Singlet Excited state of the Sensitizer. High efficiency of intersystem crossing, in certain molecules produce the, Triplet Excited state of the Sensitizer molecule.

When, it encounters the R, which is a reactant, the reactant Triplet is produced, forming the Ground state of the Singlet Excited state. So, there is a spin conversion here. This is a spin forbidden process. This is a spin allowed process, going from a Triplet state, to a Triplet state. Once the Triplet state of the reactant is formed, it can undergo Photochemical, and Photophysical processes, as the case may be.

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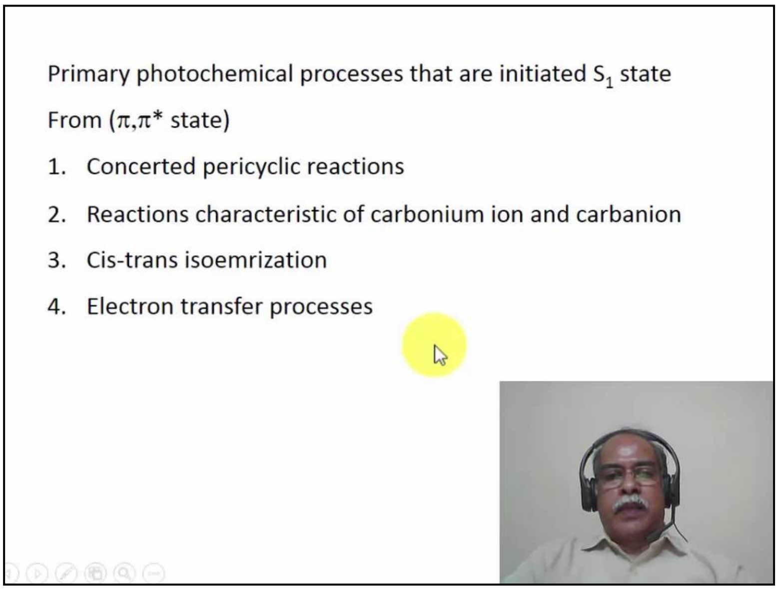

Primary photochemical processes that are initiated S_1 state

From (π,π^* state)

1. Concerted pericyclic reactions
2. Reactions characteristic of carbonium ion and carbanion
3. Cis-trans isoemrization
4. Electron transfer processes

Now, the primary Photochemical processes, that are typically initiated by Excited Singlet state, is from the PI-PI-Star state, is Concerted pericyclic reactions, like a 2+2 Cycloaddition reaction, for example. Reaction characteristic of Carbonium ion, and Carbanion, which are photo ionization processes, which takes place in the Singlet Excited state

Cis-Trans isomerization of the PI system, which also isomerization. There is a spelling m, should come before e. So, this is the Cis-Trans isomerization of Olefins, that can undergo, from the PI to PI-Star Excited state. They occur, from the Singlet Excited states. And, the Electron transfer process, can either take place from the Singlet Excited state, or Triplet Excited state.

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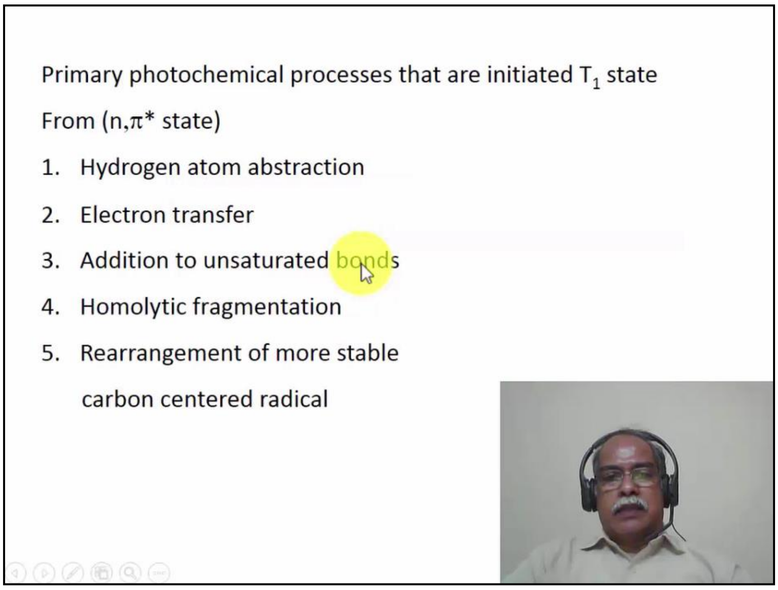

Primary photochemical processes that are initiated T_1 state

From (n,π^* state)

1. Hydrogen atom abstraction
2. Electron transfer
3. Addition to unsaturated bonds
4. Homolytic fragmentation
5. Rearrangement of more stable carbon centered radical

The primary Photophysical processes, or Chemical processes, that can be initiated from the Triplet Excited state. In other words, from typically, from an N-PI-Star Excited states, are

Hydrogen Atom abstraction, which will typically come from a Triplet N-PI-Star Excited state, Electron transfer processes, addition to Unsaturated bonds for example, Hemolytic fragmentation processes, Alpha cleavage, and so on, so forth. And, rearrangement of more stable, Carbon centered Radical.

This is something, we will see, during the course of the example. So, these are the processes, that can take place, from a Triplet Excited state of a molecule.

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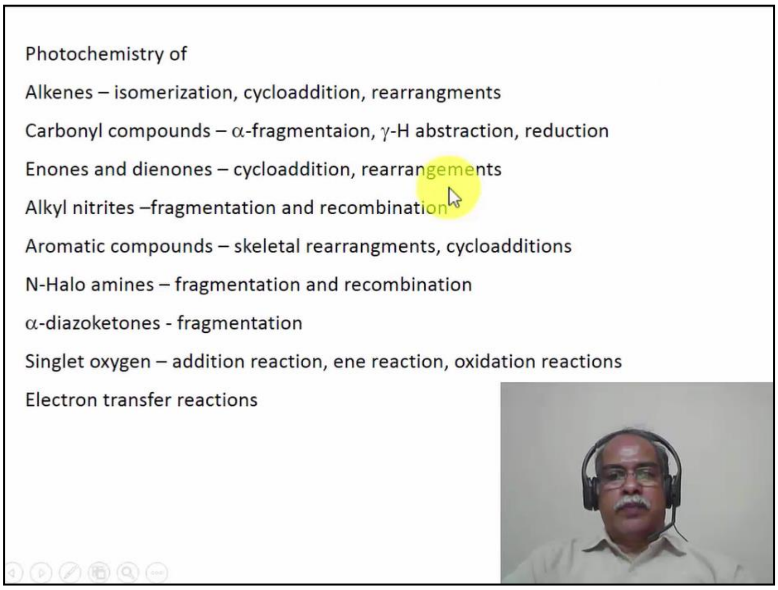

Photochemistry of

Alkenes – isomerization, cycloaddition, rearrangments

Carbonyl compounds – α-fragmentaion, γ-H abstraction, reduction

Enones and dienones – cycloaddition, rearrangements

Alkyl nitrites –fragmentation and recombination

Aromatic compounds – skeletal rearrangments, cycloadditions

N-Halo amines – fragmentation and recombination

α-diazoketones - fragmentation

Singlet oxygen – addition reaction, ene reaction, oxidation reactions

Electron transfer reactions

The kind of reactions, that are going to see in the future modules are, for example, the Photochemistry of Alkenes, which would involve isomerization, which is Cis-Trans isomerization. Cycloaddition processes, we are going to concern, only about non-Concerted cycloaddition processes. Because, we have already seen the Concerted cycloaddition processes, in the earlier example. Certain rearrangements also, we will see, just like the Di-PI-Methane rearrangements, is one example of an Alkene isomerization.

Photochemistry of Carbonyl compounds, essentially deal with Alpha fragmentation, Gama Hydrogen abstraction, and Photochemical reduction of Ketones, and so on. The Enone, and Dienone, cycloaddition process, and rearrangement process, in the Photochemistry of Enone, and Dienone. The Photochemistry of Alkyl Nitrates, we will talk about fragmentation and recombination, which is known as the Barton’s reaction. Photochemistry of Aromatic compounds, in terms of Skeletal rearrangement, and cycloaddition reaction.

Photochemistry of N-Halo-Amines, in terms of fragmentation processes, and recombination processes. Photochemistry of Alpha Diazo Ketones, we essentially talk about, production of Carbene and Nitrogen, from decomposition of Diazo Ketones. Finally, Photochemistry of Singlet Oxygen. We will talk about, Addition reaction, Ene reaction, and Oxidation reaction.

We also talk about Photoelectron transfer reaction, which is a separate category of reaction, which we will deal with in detail, at a later stage.

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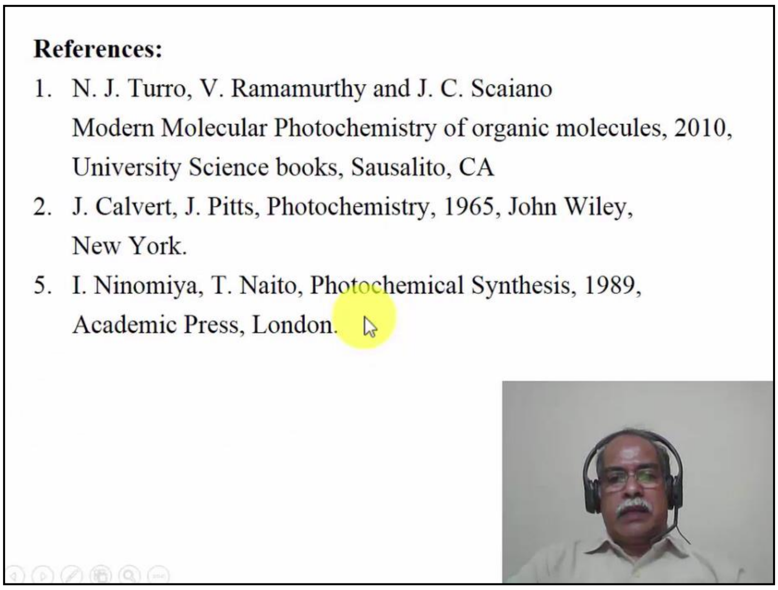

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   Modern Molecular Photochemistry of organic molecules, 2010, University Science books, Sausalito, CA
2. J. Calvert, J. Pitts, Photochemistry, 1965, John Wiley, New York.
5. I. Ninomiya, T. Naito, Photochemical Synthesis, 1989, Academic Press, London.

Now, the Resources for these particular Photochemistry modules are, the Book by NJ Turro, Ramamoorthy, and Sciano. This is, Modern Molecular Photochemistry of Organic Molecules. A very recent Book. Exhaustive information is available, in this Book. It is a fairly bulky Book to read. Nevertheless, highly informative Book. Many examples are taken, from this particular Book.

Calvert and Pitts Book. Pitts is a very classical Photochemistry Book. It is a very old Book. It is out of print, probably not easy to get, this particular one. Ninomiya and Naito, this is purely for Synthetic purposes. They describe Photochemical synthesis, published in 1989.

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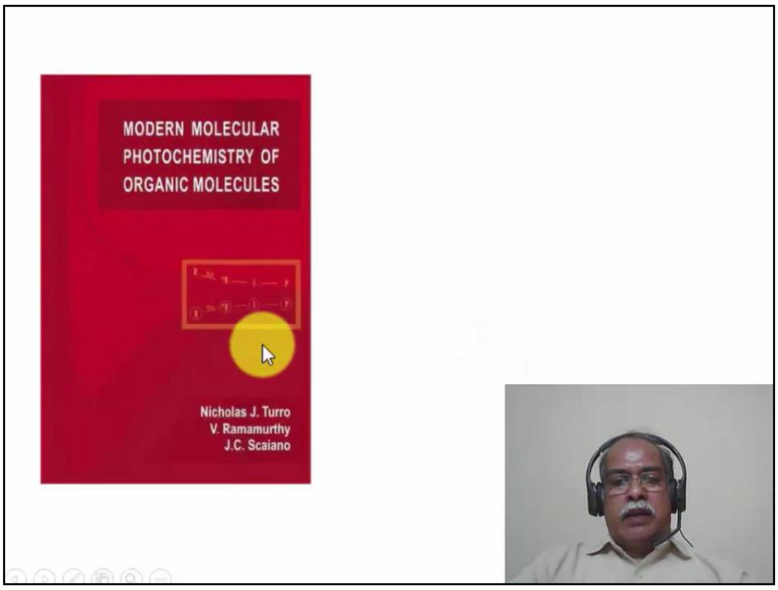

And, this is the Book, we will be, i am talking about. This particular Book, Ramamurthy, Turro, and Sciano. This is a very useful Book, for this particular course. I hope, you enjoyed this, introductory Photochemistry lecture. Thank you very much, for your kind attention.