**Ultrafast Optics and Spectroscopy**
**Dr. Atanu Bhattacharya**
**Department of Inorganic and Physical Chemistry**
**Indian Institute of Science, Bengaluru**

**Lecture – 31**
**Ultrafast Physical Chemistry**

Welcome to module 13 of the course Ultrafast Optics and Spectroscopy. In this module we will go over ultra fast processes is involved in transition metal complexes and biomolecules.

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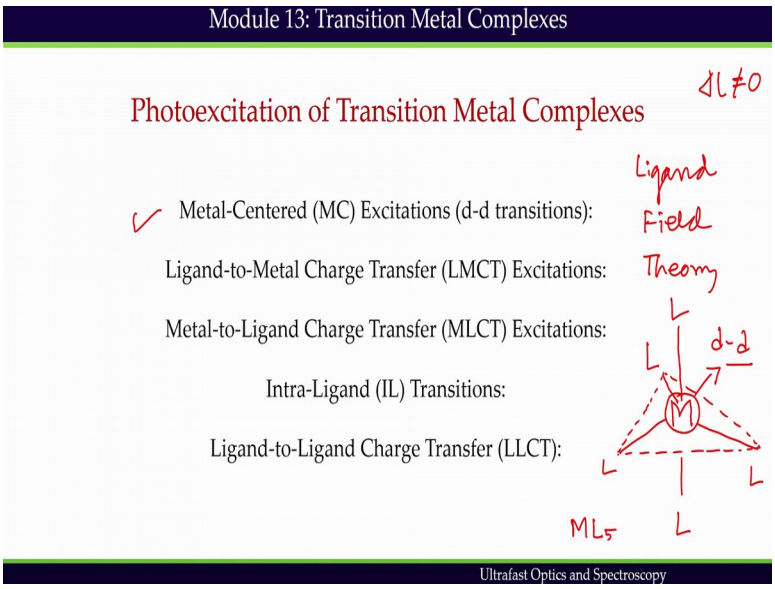


Transition metal complexes exhibit beautiful colors which are related to the their UV visible absorption spectrum. In the first interpretation of the UV visible absorption spectra of transition metal complexes came with the development of the well known ligand field theory this ligand field theory.

This ligand field theory was developed to interpret the UV visible absorption spectrum of transition metal complexes. According to this theory five different electronic transitions can be involved in transition metal complexes. The first one metal to for the first one is metal centered; excitation which is also called d d electronic transition. So, if I assume that I have a transition metal complex something like this we have kind of a structure of let us say this kind of structure we have.

This M representing metal and L representing the ligand what kind of structure we do not need to know immediately, but let us say I have this kind of structure. So, this is your ML 5 complex transition metal complex. In this complex or a complex something like this we can have metal centered excitation where it is the excitation is localized in the metal only where we can have d d transition d orbital to d orbital transition.

The d d electronic transitions are in principle laporte forbidden in centrosymmetric environments laporte forbidden because laporte in order to have laporta allowed transition I need to have delta L equals not equals 0. So, it is laporte forbidden transition; however, they are partially allowed due to vibronic and spin orbit coupling and thus in general they exhibit lower excitation coefficients as compared to charge transfer excitation.

What is charge transfer excitation? The second one is ligand to metal charge transfer. There are two different kind of charge transfer we can have; we can have charge transfer from metal center to ligand center metal to ligand.

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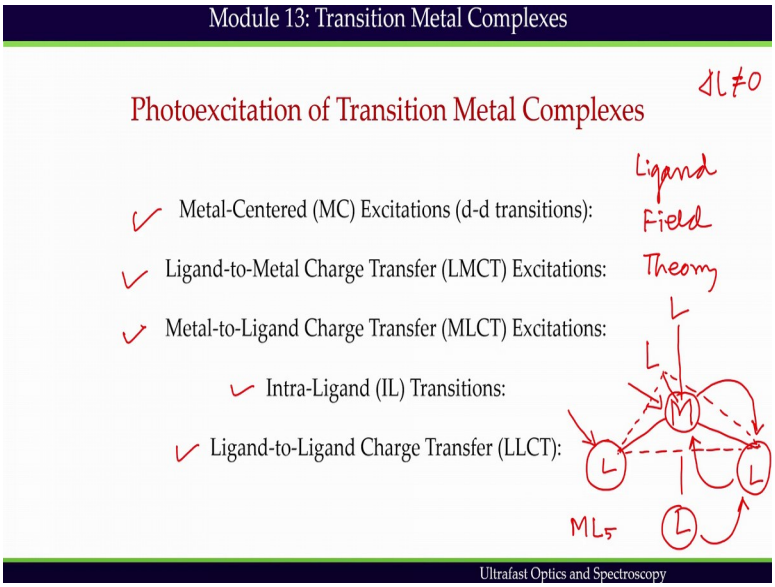


So, I have ligand. So, I can have an electron excitation from metal to ligand or I can have electronic excitation from ligand to metal as well. So, both are charge transfer. So, charge transfer excitation is not a local excitation; it is centered in two different moieties.

In ligand to metal charge transfer we promote electrons from occupied ligand orbital's to the partially empty d orbitals of the metal. Ligand to metal charge transfer excited states are low lying states when at least one of the ligands is easy to oxidize and the metal is easy to reduce. Then we have another charge transfer metal to ligand charge transfer excitation where we promote an we promote an electron from occupied metal d orbital's to the low lying empty orbital located on the ligand. Metal to ligand charge transfer excited states are expected to be low lying once when the metal is easy to oxidize and the ligand is easy to reduce.

Then we can have intra ligand transition inside the ligand I can have just like metal centered excitation we have discussed. Similarly, ligand centered excitation we can have as a local excitation this excitation occurs in the ligand itself intra ligand transition involves a electronic excitation between ligand based orbitals which are located on the same ligand.

These orbitals have to be in the same ligand they are usually present in the UV visible spectra of ligands without complexes session with the metals. So, it is a more like a ligand property and the last one is ligand to ligand charge transfer. So, we can have a electronic excitation from coming from one ligand to another ligand and that is called ligand to ligand charge transfer. This involves orbitals located in different ligands.

Due to presence of different electronic excitations which are possible in transition metal complexes the description of the UV visible spectrum of transition metal complexes are very complicated than for organic molecules. It is not like organic molecules they are more complicated than organic molecules. However, ligand field theory coupled with the different selection rules provides an excellent way a predictive way which enables us to predict the UV visible spectra of transition metal complexes.

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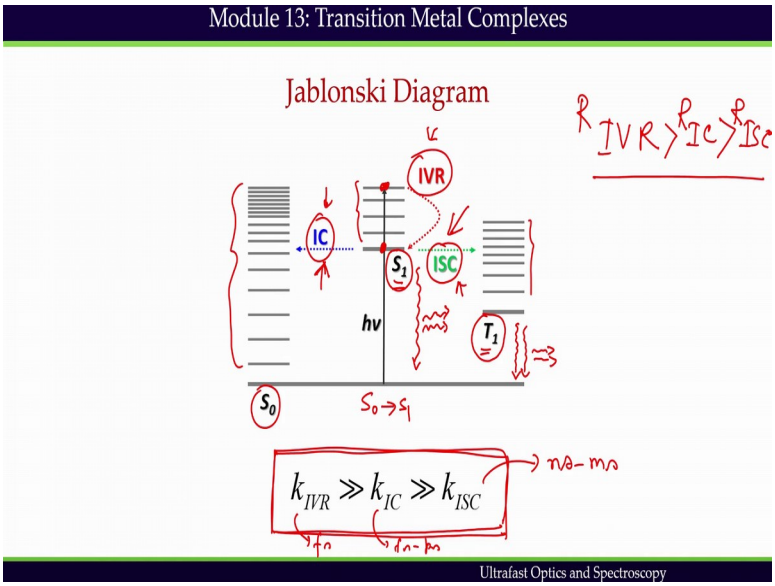


In addition to different vertical excitation processes which we have discussed in the last slide, photochemical and photo physical events in transition metal complexes also involved processes which are opened up after light absorption. And these are processes very common to any system. Possible photochemical pathways are discussed in this Jablonski diagram.

Here several electronic states including the singlet ground state which is shown by S naught electronically excited singlet state S 1 and electronically excited triplet state T 1 are shown here with associated vibrational states. These are vibrational states associated with the corresponding electronic states after Franck Condon vertical excitation to the singlet excited state which is S 0, to S 1 transition. Following this transition this is a vertical transition following this transition nuclear relaxation can lead to several radiative or non radiative pathways.

Radiative process involves fluorescence which means that I can have a return from S 1 to S naught by incoherent emission and that is fluorescence. We can have phosphorescence where I can have population transfer from T 1 to S naught and we can have phosphorescence these are the radiative processes. On the other hand there are three important non radiative processes are shown here IVR, IC and ISC.

These are non radiative process; these are non radiative processes the excited molecule may relax via vibrational excitation vibrational relaxation mediated by solvent

deactivation and molecular collision to a minimum on the excited singlet potential energy surface. This process is called IVR. So, although we are exciting to this upper vibrational state that can relax back to the ground state of the upper excited electronically excited state through this IVR process.

It may also happen that excited molecule with in a vibrational energy may reach regions of the potential energy surface and eventually population is transferred from upper electronic states to the lower electronic states through the non radiative population transfer. There are two different non radiative transfers which can occur. The first one is Inter System Crossing ISC; inter system crossing always will be involving two different spin states. So, we are transferring population from S 1 to T 1.

And another one is internal conversion; internal conversion is also non radiative process where molecule can jump from upper excited state to the lower excited state without radiation and, but we do not change the spin state. So, the primary difference between IC and ISC that we are changing the spin state in the process of ISC and we do not change the spin state in the process of IC. In the context of photochemistry and photo physics of transition metal complexes and all organic molecules as well it is assumed that the fastest process occurring in the course of excited state relaxation is IVR.

So, IVR is the fastest process then I have IC then I have ISC this is this order and this is the rate ok. How fast is going on and this order has been accepted mostly in general photo chemistry and photo physics. And that is why we can write down the rate constant like this. This is anticipated trend, this anticipated trend is largely based on the spin allowed nature of IC versus. The spin forbidden ISC process as well as the expectation that the surface to surface crossing characteristic of both IC and ISC will be slower than single surface processes such as IVR.

So, IVR this is a process involving only one state and that is why it is the fastest process on the other hand IC and ISC they are involving two different states, but there is a major difference IC is involving the same spin state it does not change the spin state that is why it is faster than ISC.

So, this is very well accepted trained in photochemistry and photo physics in general the time scale of ISC falls on the order of nano second to millisecond. So, this time scale is nanosecond to millisecond. On the other hand this could be of there are of femtosecond,

this could be of there are of femtosecond till picosecond time scale. So, this is the kind of a general trend we have accepted in photochemistry and photo physics.

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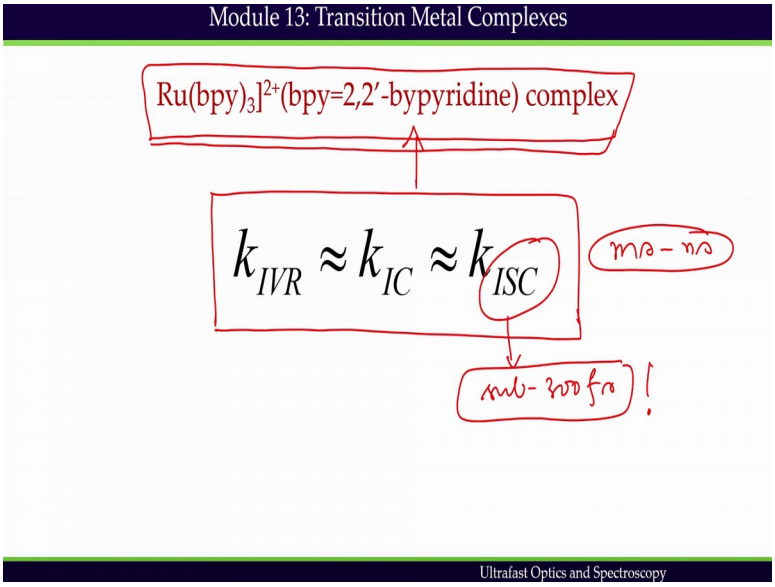


But there is a problem ultra fast relaxation of electronically excited inorganic chromophore rubidium bypyridine complex. What is the structure of this complex I will show you in the next slide, but when the ultra fast spectroscopy was employed to study the relaxation of this complex. With great surprise it has been found that all the rate constants are competing with each other. In particular ISC which is assumed to occur most of the time millisecond to nanosecond time scale this is the assumption this is mostly we have seen.

But in this complex this occurs in sub 300 femtosecond time scale and this is a biggest surprise one can have and that breaks down the traditional picture of our photo chemistry. So, ultra fast relaxation of electronically excited inorganic chromophore revealed a hidden to unknown experimental observation that questioned the validity of the time cascaded model of relaxation stated in the earlier slide.

Revealing a novel pattern of relaxation of the transition state complexes in which IVR, IC and ISC can kinetically compete with each other which means their rate constants are rate constants are comparable. This is not consistent with conventional model for describing photo induced dynamics in transition metal complexes.

Suggesting the need to re evaluate currently accepted views of the excited state behavior of the transition metal complexes and this was revealed only by ultra fast spectroscopy. For the transition metal complexes ISC processes may occur in an ultra fast time scale that is the biggest surprise.

For example, in an experimentally well characterized rubidium bypyridine complex ISC is found to take place in less than 100 femtosecond. This is perhaps the surprisingly fastest ISC ever reported in the literature and almost with the unity of quantum yield. Therefore, it can be anticipated that triplet excited states have a import have an important role in the photochemistry of this transition metal complex and many other perhaps many other transition metal complexes.

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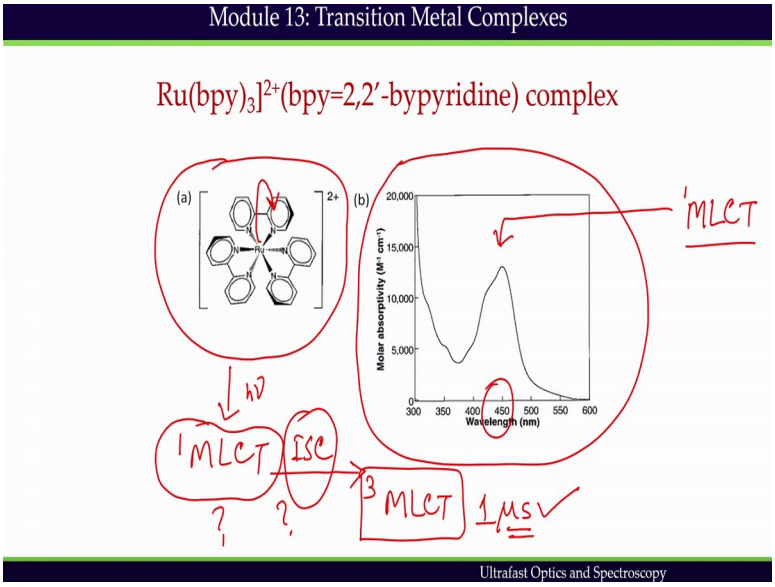


This is the structure of the rubidium complex which has been studied and this is the UV visible absorption spectrum of that complex. The strong visible absorption characteristic of this ruthenium; the strong visible absorptions characteristic of ruthenium complex is described as an electronic excitation from ground to singlet MLCT state. So, this transition is due to the transition metal to ligand charge transfer.

So, from metal centered to the ligand center charge transfer excitation in which an electron located in a metal based d orbital is transferred to a pi star orbital of one of the bypyridine ligand one of the bypyridine ligands. Photo excitation of ruthenium species to

the singlet MLCT state ultimately leads to the formation of a long lived species in triplet MLCT state.

So, what happens? Once we photo excite with this photon energy we excite this system to MLCT singlet MLCT state. After this electronic excitation this system evolves to a triplet MLCT state. So, singlet to triplet transition occurs through inter system crossing and the lifetime of this state is already found to be 1 microsecond that is the lifetime, femtosecond transient absorption spectroscopy.

So, this lifetime of the triplet excited state was known that is 1 microsecond, but the lifetime of this species was not known and lifetime or the timescale of this ISC process was not known and femtosecond spectroscopy was employed to reveal those timescales.

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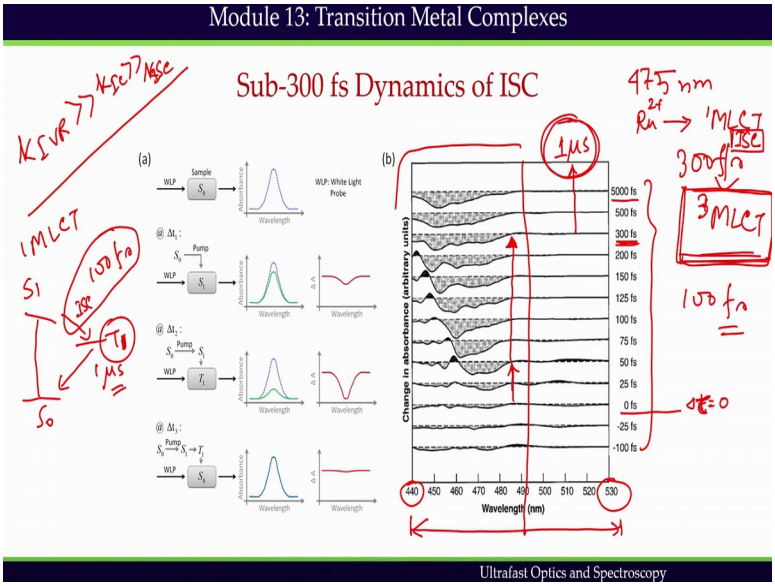


For the experiment a broadband white light pulse it is used to probe the transient absorption that is the way transient absorption spectroscopy is performed. We use white light source and the white light has a band width 440 to 530 nanometers spectral regime and that is why we can monitor the absorption in the entire regime.

So, this white light broadband spectral width is ranging from 440 nanometer to 530 nanometer and a short pulse centered at 475 nanometer is used to photo excite the species to the singlet MLCT transition. So, 475 nanometer was used to excite the species

this ruthenium complex to the singlet metal to ligand charge transfer state and then as a function of time the absorption is monitored.

Different absorption spectra in absence of pump pulse different absorption spectrum are then recorded in the transient absorption measurements excited state different spectra at various time delays, so that the spectral changes in the 440 to 490 nanometer range are quite dramatic.

In this regime the spectral change is quite dramatic, a bleach begins to evolve at 470 nanometer near delta T equals 0. So, this is delta T equals 0 delta tau[$\Delta\tau$] equals 0 and grow substantially in intensity by delta tau 50 femtosecond. So, by 50 femtosecond it is growing this bleach signal is growing. The transient exhibits both are marked blues shaped and changes in a spectral profile in all of the early time data until delta tau 300 femtosecond. So, it is continuously changing up to 300 femtosecond.

And then after 300 femtosecond we do not see any change in the spectrum and this is continued up to 1 microsecond. There is no change up to 1 microsecond although 1 microsecond data has not been shown here are only 5000 femtosecond we have shown. But if it is continued for 1 microsecond there is no change of the spectrum no change in the spectrum. Until 1 microsecond it means that we have already created that triplet state and we know that triplet state exists for 1 microsecond time. This is triplet MLCT. This no change occurs from 300 femtosecond only.

So, by 300 femtosecond the argument from this experiment we can give is that by 300 femtosecond time we have prepared this 3 M LCT state this triplet state already which is long lived species and it staying in the triplet state until 1 microsecond timescale. There is no evidence of any additional significant changes in the absorbed absorption properties of the complex in the spectra collected from 300 femtosecond to 5 picosecond and even for 1 microsecond.

All of the kinetic and spectroscopic data are therefore, consistent with the system being essentially established in the 3 MLCT state in 300 femtosecond implying a half life of the formation of the 3 M LCT state on the order of 100 femtosecond. So, the so in brief what this experimental results suggest that by 300 femtosecond we are preparing a state which is un which remains unchanged until 1 microsecond.

This suggests that we have already prepared 3 MLCT state within 300 femtosecond time scale and half life if we consider then it is going to be almost 100 femtosecond. So, the inter system crossing time scale is of the order of 100 femtosecond which prepares this triplet state. Our traditional notions of photochemistry suggest that IVR, IC, ISC can be distinguished from each other based on characteristic timescales.

Generally we have accepted that k IVR is much greater than k IC is much greater than k ISC this is our traditional concept of photochemistry. However, ultra fast study of this ruthenium complex suggests that all these processes can occur in concert with each other they can be comparable.

This represents a significant change in the convenient conventional model for the excited state relaxation processes, this suggests that increased spin orbit coupling due to the presence of the transition metal atoms makes the formally forbidden singlet triplet transition substantially allowed. Conical intersection between singlet and triplet states can play an important role in the fast ISC processes of transition metal complexes.

An important question is still open here the work presented here shows that S 1 to T 1 transition is surprisingly ultra fast. However, T 1 to S naught transition is traditionally slow. What does it mean for this complex we are seeing that after we excited the S 1 excited state which is nothing, but one metal to ligand charge transfer state, it comes back to the through ISC it comes back to that T 1 state in 100 femtosecond.

But this T 1 with this T 1 state that triplet state does not decay to S naught state because the lifetime of T 1 state is found to be 1 microsecond which is following traditional photochemistry, but this timescale does not follow traditional photochemistry. Question is why T 1 to S naught is slow, but S 1 to T 1 is very very fast? Answer we I mean there is no answer found in literature so far, but this is something which tells us that there is a demand for research on it.

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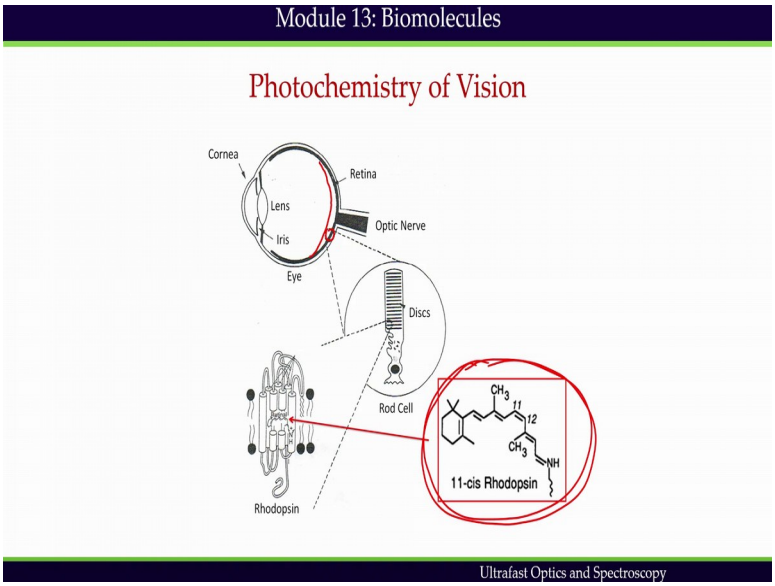


Our next discussion will revolve around ultra fast relaxation of a bio molecule which is involved in photochemistry of vision. Many of the sensory information about our world come to us through our eyes. How do we see? What is the initial step of vision? These are the oldest scientific questions which we have asked for a long time. Vision is the result of conversion of light energy to an electrochemical impulse.

The impulse is transmitted through neurons to the brain where signals from all visual receptors are interpreted. Eye vision is initiated when a photon is absorbed by a pigment called rhodopsin. This is the structure of rhodopsin which is located in the rods of retina. So, this back wall is the retina and in this wall we have a compound called rhodopsin and this compound is excited to the excited state and that is the first step of our vision.

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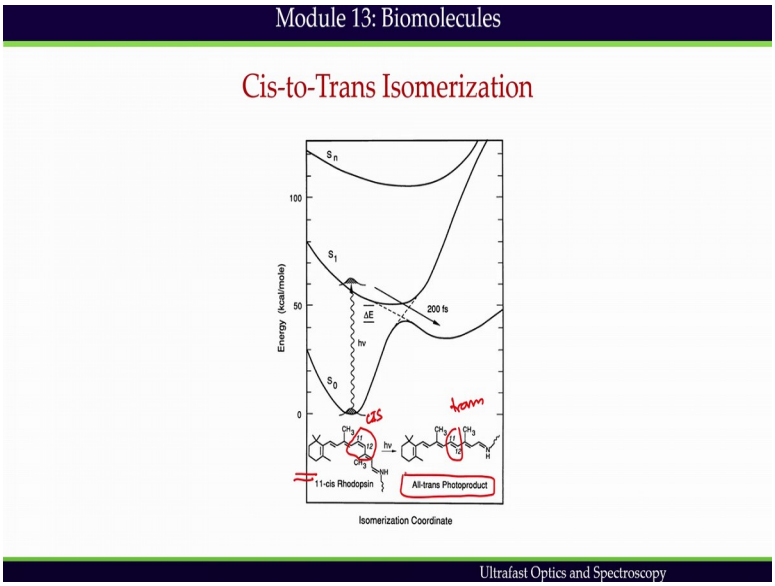


After optical excitation this 11 cis retinal prosthetic group of rhodopsin. If you look at the structure of rhodopsin we see that this moiety is different this is cis moiety. And what is the difference between photoproduct? The photoproduct is the trans moiety. So, what happens after photo excitation this 11 cis retinal prosthetic group of rhodopsin is converted to all trans primary photo product in an efficient and barrier less isomerization process.

This change in shape of retinal apparently gives the signal to obscene to undergo a sequence of dark or thermal reactions involved in triggering neural excitation. So, this cis to trans isomerization is the first step of our vision. Photon the moment we see light. It excites this molecule to the excited state and that excitation leads to a photo product which is all trans product.

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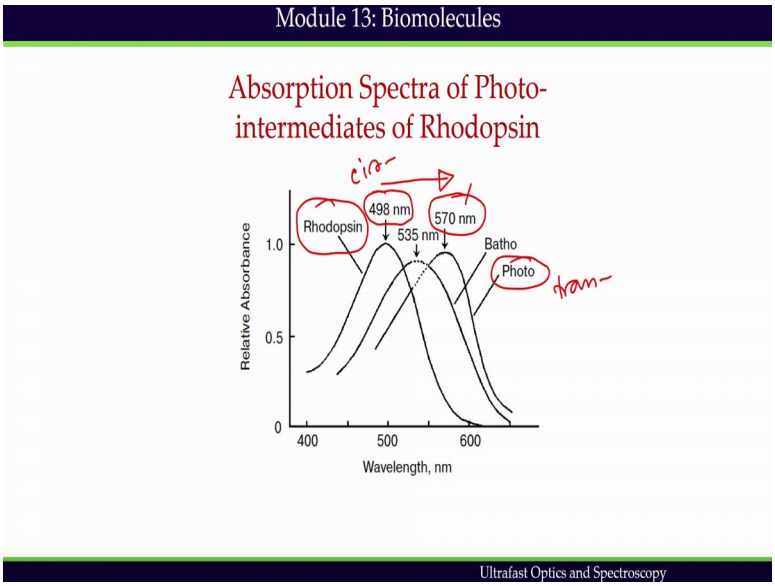


Absorption spectra of photo intermediates of rhodopsin can help one identify the intermediates very easily. This is the rhodopsin absorption spectrum and if you look at the other photo product which is this one let say all trans photo product it is red shifted. So, the peak has moved to the longer wavelength and that is why we can easily identify what is the product we have formed due to photo excitation. If the after photoexcitation if we find that the product is absorbing at 570 nanometer we confirm that this is all trans product and if the product is not absorbing at this.

If we are we are seeing absorption at 498 nanometer it means that we have rhodopsin which is cis. So, this is your cis form and this is the transform. This difference in absorption spectra can be efficiently utilized in transient absorption spectroscopy to monitor formation dynamics of the photo product by recording time evolution of the red shifted absorption of the photo product.

So, if we see that in the ultra fast spectroscopy if we see the absorption is moving towards slowly moving towards the red. Then it is what we are observing is the is the evolution of the of the cis component to the trans component.

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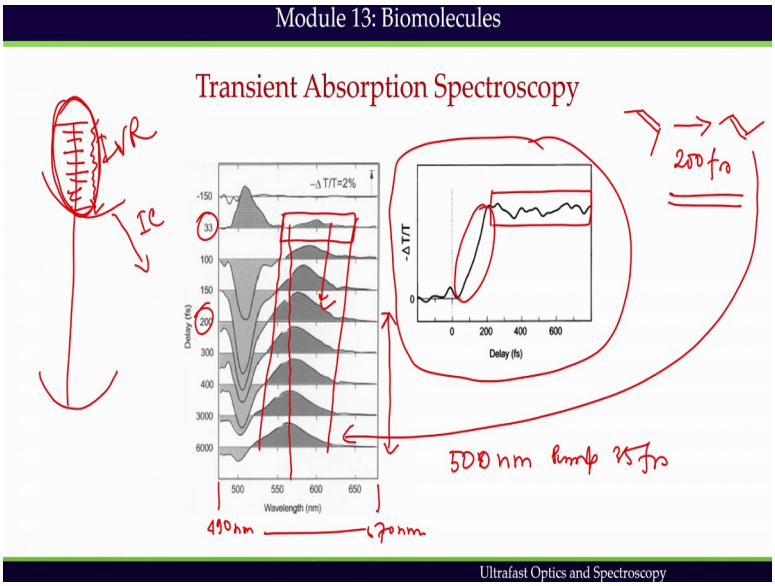


Femtosecond transient absorption measurements of the cis trans isomerization of the rhodopsin molecule is explored was explored and the time scale the formation time for the rhodopsin photo product is found to be 200 femtosecond which occurs via cis trans isomerization. And which is identified as the primary photo chemistry of vision.

Femtosecond transient absorption spectra of rhodopsin following electronic excitation by 35 femtosecond pulse centered at 500 nanometer. So, in this experiment 500 nanometer has been used as pump 35 femtosecond and a broadband 10 femtosecond probe pulse is used to cover the spectral range 490 to 670, this is 490 nanometer to 670 nanometer.

At the 33 femtosecond delay time; at the 33 femtosecond delay time difference absorption spectrum consists of a very weak absorption between 550 and 620. So, in this regime we have very weak absorption. The photo product absorbs in this range, we have seen that photo product will absorb in this range and that is why we are interested in looking at how the change is occurring in this range only.

Because this where photo product will absorb and if you keep monitoring as a function of time will be able to get how the photo products are formed or how quickly the photo product was formed. The absorption of the photo product uniformly grows in strength reaching its largest amplitude by 200 femtosecond. If you look at that by 200 femtosecond, it has reached the maximum amplitude is slowly growing and it has reach the maximum amplitude.

Although the maximum of the photo product absorption shifts from 475 to 5 sorry 575 to 565 nanometer between 200 femtosecond and 6 picosecond there is little change in the integrated area or shape of this absorption feature. So, what we see that after 200 femtosecond and until 6 picosecond timescale we do not have much change in the photo product absorption. That means, photo product has been formed within this time scale 200 femtosecond and then after 200 femtosecond photo product is remaining to be in the same transform. Difference absorbs difference absorbance observed at single probe wavelength. 570 nanometer.

So, when we consider 570 nanometer somewhere here and we checked, how the strength is changing as a function of time that is exactly what is plotted here the difference absorbance as a function of time. Then we see that 200 femtosecond by 200 femtosecond we have created the species already. So, the formation timescale of trans is going to be 200 femtosecond.

So, this all cis product I mean the 11 cis product is converted to trans product in 200 femtosecond and trans is absorbing in this regime. Measurement of the full difference absorption spectrum of the rhodopsin photo product come from that the first step in vision gets over in only 200 femtosecond.

The rapid disappearance of the Franck Condon excited state absorption near 500 nanometer and rapid appearance of the photo product absorption band extending from 530 to 620 nanometer all support the rapidity of the isomerization process. The observation of the cis trans isomerization of rhodopsin which is complete in only 200 femtosecond may have important implications for the photo chemistry of vision and photo chemistry in general.

For the first of all 200 femtosecond time is faster than typical vibrational defacing and vibrational relaxation times. Suggesting that photo chemistry occurs from a non stationary vibrational state this is an important observation because in general when you talk about photochemistry we show like this way.

We have excited the molecule to the excited vibrational states of the upper electronic excited states. They equilibrate and then come back to the lower vibrational state and then they undergo let us say IC intersystem crossing, but the timescale which a

suggesting which is suggested from this experiment 200 femtosecond is even faster than this kind of IVR process.

And if it is faster than IVR which means that the relaxation occurs from a non stationary vibrational state. It is not after equilibrating in the vibrational state in the upper excited state it is relaxing, it is actually relaxing from a non stationary vibrational state the equilibrate.

The equilibrium in the vibrational degrees of freedom in the excited state has not been reached yet before it relaxes back to the ground state. So, this is also an important findings revealed by the ultra fast spectroscopy which also challenges our traditional concept of photochemistry.

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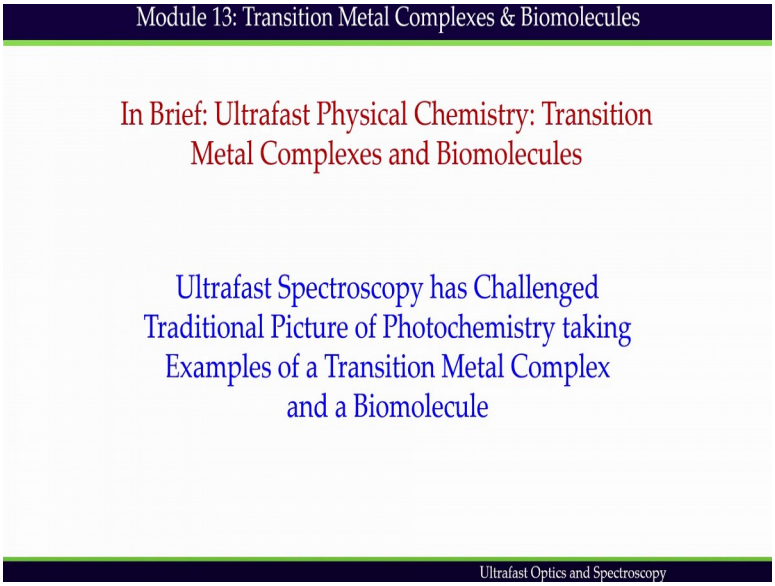


With this we have come to the end of the present module. In this module we have gone over two interesting examples; one example is based on transition metal complex and another example is based on a bio molecule. In both examples we have found that ultra fast spectroscopy has revealed few information which can challenge our traditional concept of photo chemistry and photo physics. We will meet again for the next module.