Bioinorganic Chemistry
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Lecture - 14
Electron Transfer in Photosynthesis – I

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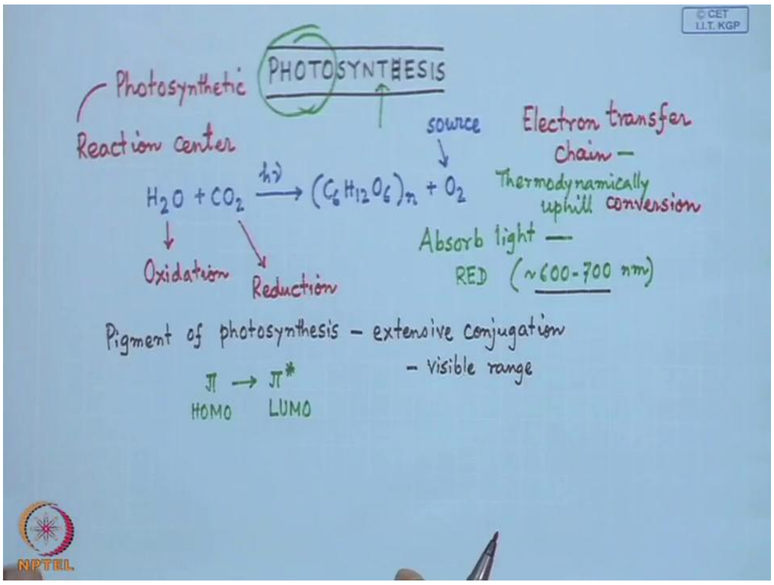

Welcome to this class. In this particular class we will be talking about photosynthesis and we will be taking the help of photons for this particular reaction and what we know from our childhood days that there is a typical reaction center which we call it as a photosynthetic reaction center, and the very basic reaction what we use there is nothing but the reaction of water with carbon dioxide. Now, we will introduce something else, what we have not encountered in some of the previously studied electron transfer reactions that using these we basically get C 6 H 12 O 6 and in its different forms and oxygen is liberated.

So, starting from these two species; that means water and carbon dioxide, what we find that O 2 is liberated and this O 2 has also been established the source of this O 2. So, this particular electron transfer reaction if we consider that there is something where we get this; that means we should be looking for oxidation of water molecule and at the same time reduction of carbon dioxide. So, this definitely gives us some idea that what we are talking here is definitely something which is one type of electron transfer reaction. So, electron transfer change is also there.

So, like what we have studied in case of cytochrome C and cytochrome C oxydase where we were able to consume the dioxygen molecule. Now we are doing something which is reverse of that; that means how this particular electron transfer chain is involved to convert this water molecule and carbon dioxide molecule to glucose molecule. So, in that particular case we also know that it absorbs light. So, the presence of light is essential; without this light we cannot go for this sort of reaction. So, that is why we require there the photons; the photons are required and we are looking for something what is your synthesis. So, that gives birth of a very huge subject that photoelectron transfers. So, these photoelectron transfers how they are going to take place and in this particular case we know that all the green vegetables.

So, what type absorption is taking place? Basically it absorbs the red light as well as some amount of blue light in the range of 600 to 700 nanometer. So, something is there; that means, some pigment definitely is present and that pigment of photosynthesis which is responsible for this absorption of light and there is some extensive conjugation there. And that extensive conjugation tells us that if we are talking about something which is responsible for our well known transition; these we every time we encounter when we have the pie electron cloud or pie electron density. So, pie of highest occupied molecular orbital is transferring electron to lowest unoccupied molecular orbital.

So, this particular thing; that means when we have that extensive conjugation, we get absorption in the visible range. So, this particular range is in the visible range. So, visible range of electromagnetic radiation is responsible for this conversion. But if we just consider that how facile is your oxidation of water molecule and your carbon dioxide molecule, we can consider this transformation as thermodynamically uphill conversion. So, this is not thermodynamically visible process. So, how we go for that conversion? This class we will just see that that how you can change the corresponding electron from one particular side to other side.

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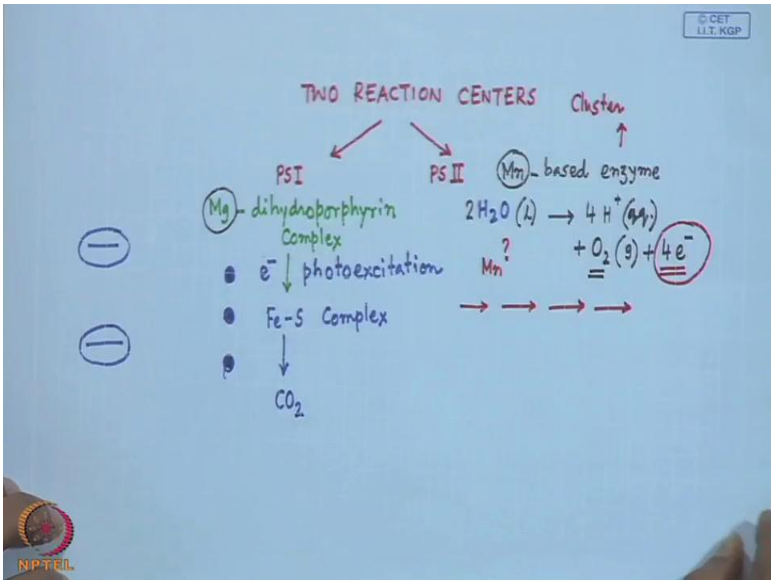

And for that particular reason when we have the reaction center and we can have basically two reaction centers, not a single reaction center but two reaction centers. One is known as photosystem I, another is known as photosystem II. Because we have two species; one is water, another is carbon dioxide. So, the photosystem I will take care about that carbon dioxide; that means the reduction of carbon dioxide is taking place over there and we have some complex which is a magnesium-based complex. So, magnesium we are now bringing into the picture that magnesium in the biology is helping us a lot. So, magnesium dihydroporphyrin again the porphyrin dihydroporphyrin complex is present and this particular complex. So, we already accepted that the photons are required. So, photon will be there and we just want to transfer electron to it.

So, at this particular step we can consider it has a photoexcitation step. So, photons are required for the excitation. So, the property of that particular species is always changing because when we go for this photoexcitation we are talking something about in the excited state. And whatever chemical property or electronic property we talk all the times starting from your P K, P K V, etc, the ground state property is completely different from the excited state behavior. So, if we are unable to use certain species for reduction reaction in the ground state, we can go for in the excited state and in that excited state both electron transfer as well as electron acceptance is readily available from there.

So, this magnesium dihydroporphyrin complex if it is not easy to reduce that particular one, but during photoexcitation it can be reduced and in an excited from it goes and it can transfer some other species; that means the ferredoxin type of molecules are there. So, it can transfer that electron to ferredoxin type of molecule iron sulfur protein. So, this particular iron sulfur protein remains initially in the oxidized form; when it gets from the electron from this particular complex it is in the reduced from.

So, basically a different E 0 values we are transferring these electrons and ultimately we are able to transfer those to carbon dioxide. So you have note, this is a only two I am showing here where several other species are involved that we will see in detail when we just go for the entire steps related to the different E 0 values. But here we will see that between this magnesium dihydroporphyrin complex and carbon dioxide, you can have sudden electron transfer mediators.

So, these redox mediators the way we have seen in case of cytochromes and cytochrome C oxidases that stepwise you can transfer and you can go for the different reduction equivalence to ultimately to carbon dioxide molecules. So this is photosystem I, one particular reaction center and the photosystem II which we just handled there that oxidation of water molecule and here we will just introduce one other metal center. So, remember these that when we will be talking about the photosynthesis, we are talking about magnesium, we will be talking in one point about the manganese. So, this is a manganese based enzyme and that manganese based enzyme is responsible for oxidizing your water molecule to give you certain numbers of protons aqueous plus O 2 gas plus 4 electron.

So, you can have. So, this is compared to this is also a complex system because in case of cytochrome C oxidases and other system what we have seen that when we are going for respiration, we are taking out dioxygen and that dioxygen is utilized for food burning and we are producing water molecules. So, the reverse process we have discussed earlier and in all these cases in this particular one and there also we have seen that you can transfer 4 electrons. So, you have to have some mechanism; that way you can store 4 electrons. So, state wise one after another. So, sequentially you can go for 4 electron transfer step. So, that is also a typical manganese based enzyme which can show that one after another electron transfer can take place and also the importance in the manganese oxidation state, how we can go for those change in those manganese oxidation state and how these manganese oxidation states can change and what are these things; that means when we think of that at least 4 electron transfer can take place.

We can think of about these manganese based enzyme; it cannot be a mononuclear enzyme, it is a multinuclear cluster type of arrangement. So, it is a manganese based cluster system which will be responsible for the oxidization of water molecule and at this particular point which is a very crucial step for photosynthetic that dioxygen is liberated from that particular step. So, slowly we will see that how this magnesium dihydroporphyrin complex is responsible for this photoexcitation and the corresponding electron transfer to the carbon dioxide molecule.

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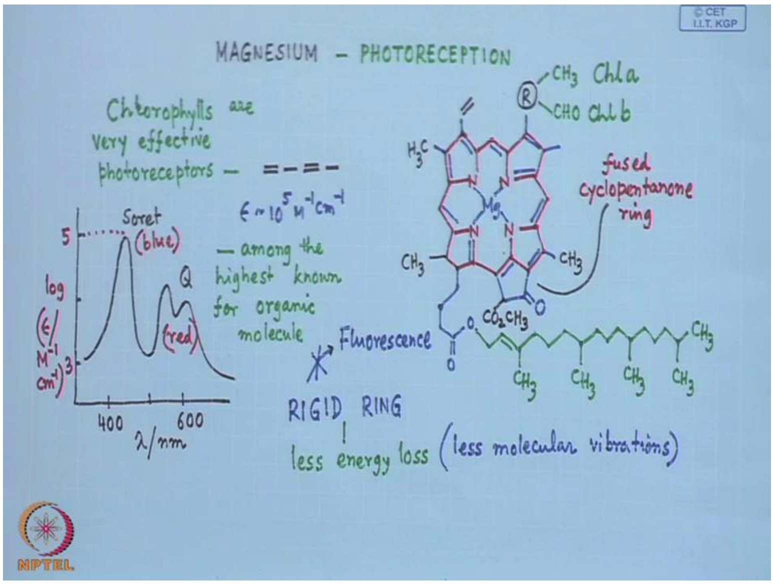

So, we are just going for something that you have magnesium and this magnesium is responsible for absorption of photons; that means magnesium can be involved in photoreception and one very well known molecule from your school days you were knowing that. So, we have the chlorophyll. So, these chlorophylls, you can have more than one type of chlorophyll. So, chlorophylls they are basically very effective photoreceptors. So, we know the definition for receptors and all. So, it can take up that photons and we have a network of alternating double bound and single bound such that your absorption comes down to the visible range. And one particular band what we call for characterizing the porphyrin units, we all know now which is your Soret band, the Soret band which is also present in cytochrome P-450.

So, if we just look at the corresponding absorptions for this chlorophyll, it has a very characteristic and the shape is also very much chararteristic in the visible region between 400 to 600 nanometer and this molar absorptivity is also very high; it is 3, it is 4 and it is 5 and the unit of a logarithmic scale epsilon unit is mole inverse, centimeter inverse. So, when we get something which is close to 5, we get a corresponding epsilon value about 10 to the power 5 mole inverse, centimeter inverse and this sort of species which is responsible for the photoabsorption for this highest possible molar absorptivity because we are looking for only pie-pie star transition and that pie-pie star transition is something which we encounter everywhere starting from our ethylene molecule and it is among the highest known for all organic molecules this molar absorptivity. So, it is the highest possible molar absorptivity; it can show the highest known value for any organic molecule.

So, the extended from of the conjugation will tell us something that what we have that the prophyrin of different structure which we encounter in cytochromes or hemoglobin or myogolbin. So, this is again the same tetrapyrrole unit, just you club them; that means 4 tetrapyrrole units you can have. Basic skeleton, very easy to draw; all the time whatever you draw for the myoglobin molecule hemoglobin molecule or different cytochromes and we all know that the number is keen what are the different groups because sometime we see that one of the ring is reduced or partly reduced. So, we number from top left is the first ring, this is the second ring and then we have the third ring and apart from that something else is there where we have a ring few cyclopentanone ring.

So, at this point we have a cyclopentanone ring and the reason behind having this cyclopentanone ring we will discuss soon. So, you have 4 such rings and we just get magnesium at the center which is tetra-coordinated and like other pyrrole unit we have the substitutions. This part we know that propionic acid functions. The propionic acid functions are very common for all sorts of these biological molecules and here we have one methyl, this is also methyl, this is by vinyl and this is a typical one because you can have the different chlorophyll, this is methyl. So, when R is equal to methyl or R can be your aldehyde function, this is chlorophyll a and this is chlorophyll b.

So, not only within the backbone of this porphyrin ring is helping for absorption of light in this particular region and this range basically this is our Soret band; we consider that this 400 band is Soret band and these two we consider it is as the Q band and this is blue and this is red. So, this typical feature for this absorption and the huge amount of this epsilon value immediately identify people that not only this extended conjugation is this but we have a tail also. This particular tail we can have which is the five tail group. So, one the long chain is attached in the symmetrical also and this cyclopentanone ring has also a carboxyl ester end methyl carboxyl ester end. So, this is different from the other type of porphyrin ring; you have a fused cyclopentanone ring.

So, this particular fusion of this tetrapyrrole unit; so what we have, 4 tetrapyrrole units are there plus we have few cyclopentanone ring basically providing us something which we consider as a very rigid ring. So, we get a rigid ring as a ligand and which is strongly attached to magnesium because magnesium is a main group element. It has no other preference for its corresponding geometry. So, when it is in the free state it can have a tetrahedral geometry or it can have octahedral geometry but never it goes for a square planar geometry. So, this rigid ring has also some other important role to play that whenever it is excited, the photoexcitation is taking place.

So, it can go for less amount of energy loss because the system is rigid and we expect less molecular vibrations. So, vibrational energy loss should be less. So, whatever energy it is stored during excitation will be converted for some useful purposes only and here also we do not expect any fluorescence behavior because whenever we talk something; that means the photoexcitation or some property related to the excitation of the species, we will see that whether this particular system can show any kind of fluorescence and it is not showing any fluorescence; it is sitting inside a rigid structure. So, two things immediately we can tag on this particular magnesium center and little bit if we can identify related to its properties.

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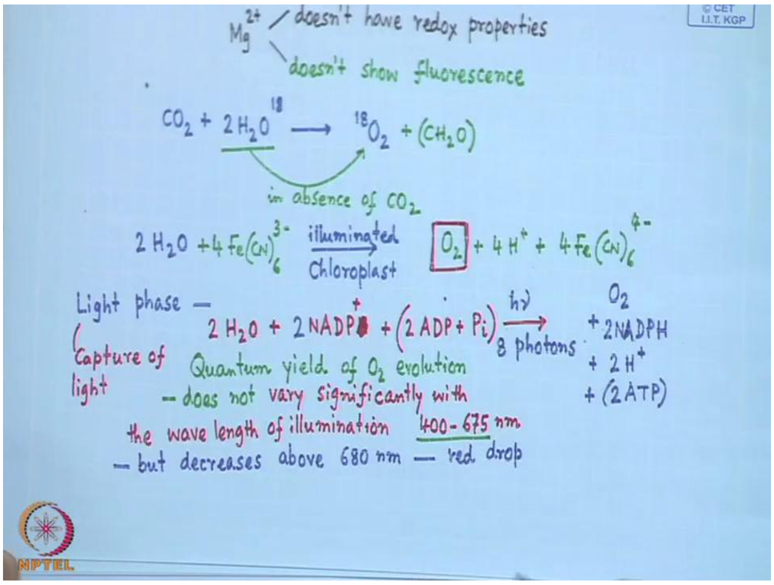

So, if we find any magnesium center in any other phosphate transfer reagent and all other thing, what are the basic coordination behavior and how it is functioning there? So, definitely it does not show any redox behavior which is very important and what we are talking ironically in this particular arrangement that we are talking some electron transfer behavior, but magnesium center is not responsible for that and it also does not show any kind of fluorescence behavior any kind of fluorescence behavior. So, it is absorbing from the Soret band and Q band; what we have seen that in the blue and red region it is absorbing the radiation and the species what is coming out as dioxygen can be studied very easily by knowing that this particular carbon dioxide can react with water molecule which can be leveled.

So, the leveling of this particular dioxygen system what is coming out from there, we can tell that what is the source for that dioxygen. So, water is giving us the dioxygen. So, entirely all the dioxygen molecule what is coming out from the system should be leveled and we can go for the reduced from of carbon dioxide. So, if we get this particular one; that means we are entirely getting this dioxygen molecule from the water. So, we can study some of these steps; that means we have in photosynthesis one phase we call it as a light phase and another we call it as a dark phase. So, in absence of carbon dioxide also this O 2 evolution can also take place because your O 2 evolution is coming only from this water molecule.

So, O 2 evolution in absence of C O 2 can take place; in absence of C O 2 we only need some species which can take out that electron. So, sometime if the chloroplast can give directly this O 2 from water molecule only we can have the illuminated; that means we have the proper radiation which is falling on the chloroplast where we have the chlorophyll. And it is illuminated chlorophyll and this illuminated chloroplast when it is reacting with something else not that carbon dioxide but other electron accepted, say, ferricyanide. So, if we use ferricyanide over there also Fe CN whole 6 3 minus, it can also produce O 2. So, this particular case you can also produce O 2 plus 4 H plus plus 4 because it is a 4 electron transfer step the ferricyanide to ferrocyanide. So, in this particular case we have a phase which is a light phase, another is a dark phase.

So, what happens there therefore? In light phase, so your water is involved and we capture light. So, we take the help of something which is NADP plus; it is the oxidized form plus during this process we produce ADP. So, ADP should be there and inorganic phosphate should also be available. So, two of water is reacting means two of this N ADP plus illuminated with h mu and we require because we can find out the number of photon absorption also. So, 8 photons are absorbed at this particular step giving first O 2 then like that reduced form of ferricyanide is giving ferrocyanide. So, it is the reduced form of this 7 NADPH. So twice of NADPH, then 2 H plus and 2 of this combined form; that means two ATP.

So, there are a few important observations over here. Because in the light phase there is capture of light and this particular light is responsible for excitation and when we get that; that means one particular centre; that means this particular centre is responsible; that means water is getting oxidized to O 2 and which is a different centre compared to the centre where you have the reduction of C O 2 molecule. So, O 2 is liberated and since we know that way we calculate in case of when we study the person’s behavior, the excited state behavior, you can find out in this particular case also the quantum yield of O 2 production. So, the quantum yield of O 2 evolution can be determined how efficient the system is for producing O 2 evolution.

And whether there is any dependence of that O 2 evolution; that means the quantum yield for this particular evolution is depended on the wave length, means, now we can vary the wave length. What we find during the person’s measurement all, we should know the absorbance first and at particular point when you excite the system. So, when we find that the absorption corresponding absorption band we know, the Soret band we know, the Q band we know when you excite the system at that particular wave length and your system is going from the ground state to the excited state and if at that particular point it is giving you the fluorescence behavior it basically goes down. So, whether you have some dependence on the wave length; that means at which particular wave length you can excite.

You have the Soret band and you have the A band and one of is in the longer wave length and one of in the shorter wave length. So, use the shorter wave length. So, most of the cases we excite the system by UV light in our system. So, whether there is any dependence on the wave length, but it has been observed that it does not vary significantly with the wave length. So, the quantum yield does not vary significantly with the wave length of illumination in the range of what you basically looking for in the range of 400 to 675 nanometer. So, this particular range; that means this is our useful range for O 2 evolution and your quantum yield is also not changing when you are restricting your excitation within this particular range; that means 400 to 675 nanometer, but what happens if we go above? But when we increase the wave length; that means, when you go above 680 nanometer it decreases.

So, this quantum yield then decreases but decreases above 680 nanometer and this particular thing is well known and is known as red drop. So, there is a drop in quantum yield if you go above 680 nanometer. So, that immediately gives us some clue basically that we started our discussion with the knowledge that you have one system; that means the photosystem I and the photosystem II. So, one we can activate below 680 nanometer and another above 680 nanometer; that means this is the borderline where you can find that one is for the photosystem I and another is the photosystem II. So, after this light phase we get the dark phase.

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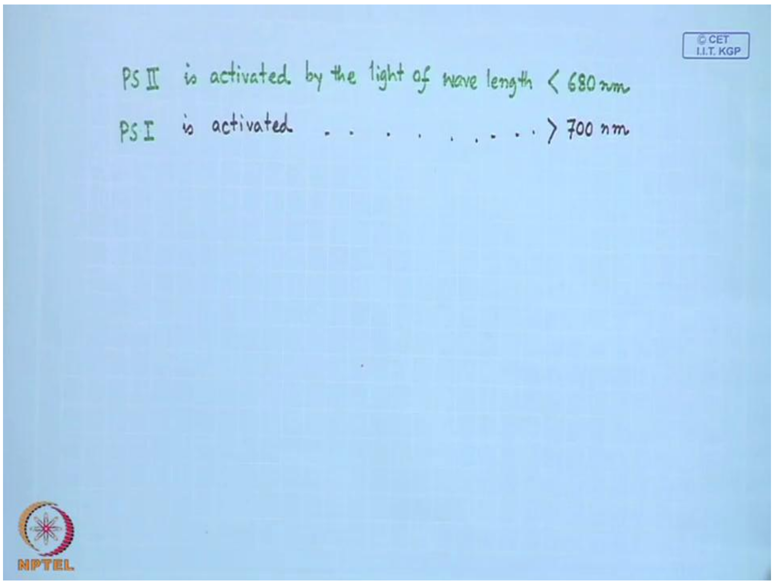

So, immediately from these wave length criteria we can write that photosystem II and photosystem I, this PS II is activated by the light of wave length below 680 nanometer. So, we are making it as the border case and PS I is activated by the light of wave length above 680, but we can write safely above 700 nanometer. So, these two centers immediately tell us that one particular case you have PS I, in another particular case we have PS II and this PS I and PS II are responsible for one phase which we known as the light phase and another as the dark phase.

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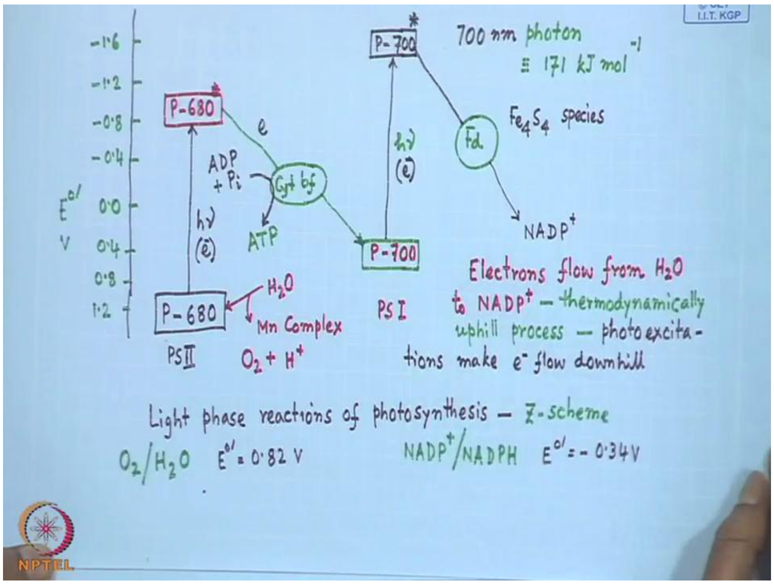

So, if we go for this corresponding case of PS I in the potential scale; that means you have that E 0 prime in volt starting from minus 1.2 to plus 1.2, minus 0.4 unit, 0.12 and this is minus 1.6, minus 1.2, minus 0.8, minus 0.4. So, in this potential range everything is operating there. So we have that PS 2 first, we will just go for P S2 and which is in this particular point which we consider now has P-680; P stands for the pigment the colored pigment which is responsible for this particular light absorption and here we have the centre as photosystem II. So, at 680 basically where we have we find that we are looking for this water oxidation, at PS 2 we are looking for water oxidation. So, water is there and that is oxidized by our manganese complex and this manganese complex is responsible for the evolution of O 2 as well as proton.

So, this particular one when it is 1.2 volt, it is not showing any kind of this activity in PS II. So, you can photoexcite it to a point which is somewhere here and this P-680, the same species only it is excited; that means stared only, we just level it as stared and this particular one. So, it is absorbing the radiation here and this particular one is known as very famous Z-scheme. So, what we are doing here is nothing but the light phase reactions of photosynthesis which is also popularly known as Z-scheme; this will go down and again go. So, from this side it will look like a z. So, here for photosystem I and close to 0.4 volt we have the reaction centre and we already know that PS I will be operating above 700 nanometer. So, it will be leveled as P-700 which is your PS I the photosystem I.

And this particular species can again be excited close to minus this 1.6 volt to the same version, but in stared form; that means the excited form. So, we get due to this oxidation some electron. So, this should be connected through several mediators but here we will just write down only one which is cytochrome based mediator cytochrome, say, b f; f is related to the leaf and is providing the redox equivalent; that means reduction equivalent to photosystem I centre and at that point when it is going from there and at that particular site, you can have the formation of what we used the ADP plus P i the inorganic phosphates. ADP plus P I the inorganic phosphate will provide you two ATP molecules. So, here everywhere you have this excitation.

So, in PS I also you have this photoexcitation and depending upon the corresponding amount of energy we can also calculate the corresponding threshold for these reactions; that means in this particular case when we are handling a wave length of 700 nanometer of photon. So, this photon we can calculate out the corresponding photon energy which is equivalent to 171 kilo Joule per mole. So, basically what particular wave length you required to move this particular species from here to here; that means some species which is highly oxidizing can be moved to the other step where you can have the corresponding system can function as a reducing agent because it can transfer the electron in the excited state only. So, these vary here.

So, all this potential difference can be found out by if we you just correlate it in corresponding energy change. So, this when excited to P-700 star it is connected to ferredoxin molecule because this is now the mediator for the photosystem I. So, this is again your mediator and that mediator basically transfer in your ferredoxin molecule from the oxidized state to the reduced form because this is basically a Fe 4 S 4 species and this then goes to NADP plus. So, whatever reaction we get from there is basically this NADP plus is produced and this NADP can be converted to NADP H and these particular two steps; that means this is when we see that it is are thermodynamically unfavorable. So due to excitation, due to this photoexcitation we move from here to here and another case; that means in case of photosystem I you move from this step to the other step.

So, when we go for these. So, you will have the electrons. So, those electrons will flow from here; it is moving from here. So, this is H nu. So, H nu can be responsible for electron transfer this. This H nu can also be responsible for electron transfer. So, from here it is moving to NADP. So, electron flow is taking place from H2 O to NADP plus because we know that why we need this excitations because these excitations tells us that if we know the corresponding redox couples of O 2 and water and NADP plus and NADPH. If they are thermodynamically favorable we can use directly for them. In this particular case, this E 0 prime is equal to 0.82 volt and here it is minus 0.34 volt. So, we need photoexcitation and that photoexcitation when it transfers those electrons from water to NADP plus, we get a thermodynamically uphill process. So, here we get basically uphill process.

So, this thermodynamic uphill conversion is due to this photoexcitation. So, photoexcitation is responsible for making the electron flow from here where we get the water oxidation, we get large amount of electrons. So, those electrons are ultimately transferred to NADP plus and those NADP plus are ultimately reacting with your carbon dioxide molecule and that carbon dioxide molecules are converted to glucose molecule. So, here one important thing is our photoexcitation. So, photoexcitation makes electron flow which was not possible otherwise downhill. So, we move from here to there and during this process it is the chlorophyll which is basically taking the important role.

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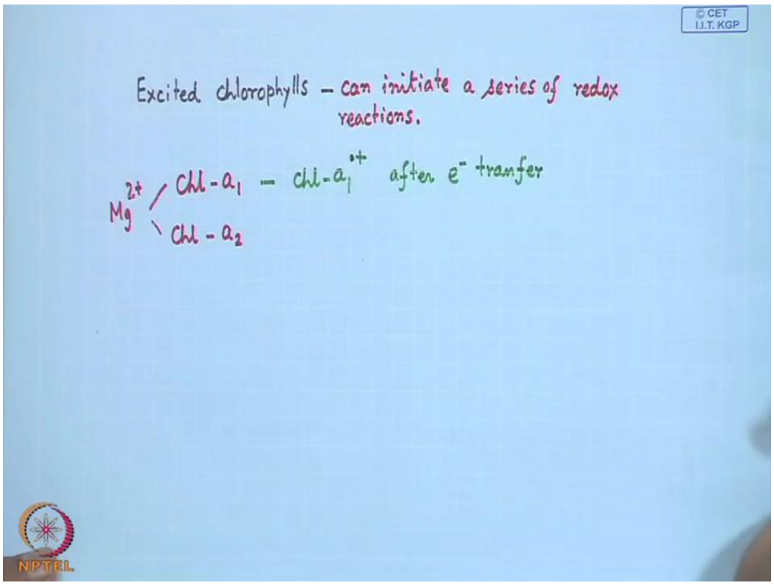

So, we have in all these cases where electron is coming out, we have the excited chlorophylls and those excited chlorophylls basically are responsible for those electron transfer transitions and therefore these excited chlorophylls can initiate a series of redox reactions. So at one point you have chlorophyll a 1, in another point you have the chlorophyll a 2 and those chlorophylls are oxidized. So, when these chlorophyll species are oxidized. So, these are chlorophyll a 1.

So, we have a 1 and another case you have chlorophyll a 2 and those are all attached to our magnesium 2 plus, but we are unable to change the oxidation state of magnesium. So, like that of our other system where we know that organic part can be oxidized. So, we have chlorophyll a 1 cation radical. So, these are produced basically after electron transfer. So, that is the thing; that means you can oxidize the chlorophyll centre and that chlorophyll when they form the cation radical, they basically react with all these other species. So that we will see, what we are getting for the other centre in our next class.