Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
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Lecture – 21
Electron Spin Polarisation – II

We have been discussing electron spin polarization in photochemical systems.

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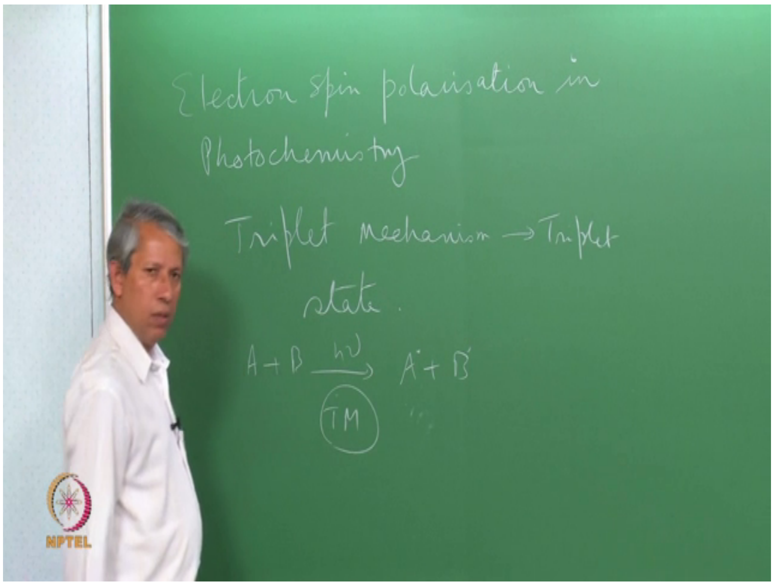

We have learnt how the single phase hyperfine independent polarization appears, and the spectra appear in this fashion either it totally down or totally up. Nevertheless, both of them are very much away from the thermal distribution. Now we are going to discuss and learn the mixed phase hyperfine dependent polarization.

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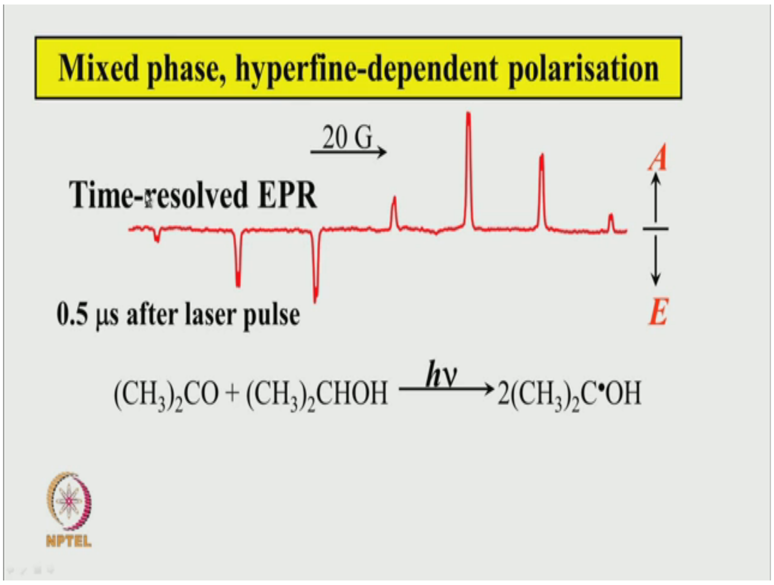

Mixed phase, hyperfine-dependent polarisation

Time-resolved EPR

0.5 μs after laser pulse

$$(CH_3)_2CO + (CH_3)_2CHOH \xrightarrow{h\nu} 2(CH_3)_2C^{\bullet}OH$$

The example of that is shown here in the slide. This is the a familiar acetone isopropanol experiment, in the presence of u v light it produces identical pair of radical and if the experiment is done in the direct detection mode. The time resolved EPR spectrum after point 5 microsecond shows this pattern. The low field lines are emissive high field lines are absorptive, and there is no relation what isoever with respect to the thermal EPR signal, where the middle line is expected to be most intentional other lines will be smaller and smaller intensity.

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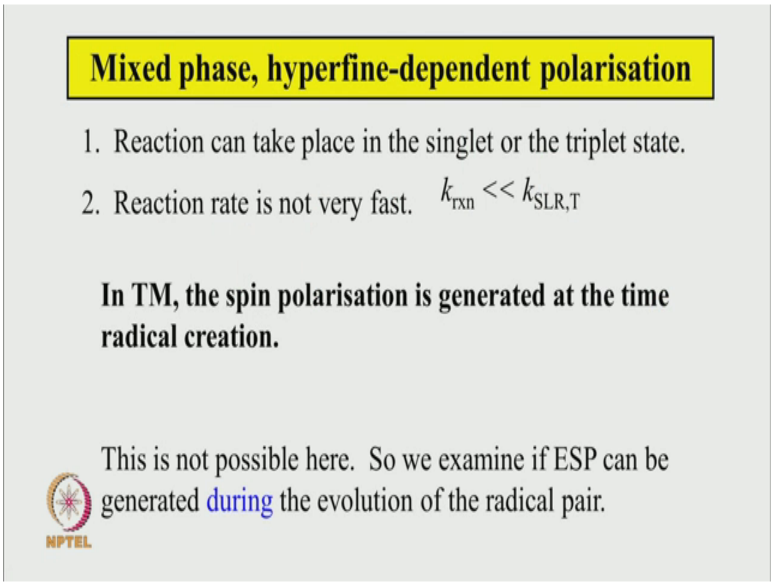

Mixed phase, hyperfine-dependent polarisation

1. Reaction can take place in the singlet or the triplet state.
2. Reaction rate is not very fast. $k_{rxn} << k_{SLR,T}$

In TM, the spin polarisation is generated at the time radical creation.

This is not possible here. So we examine if ESP can be generated during the evolution of the radical pair.

Here this sort of signal comes when this conditions has satisfied. One is that the reaction can takes place either singlet or triplet state. This is the triplet mechanism that we discussed earlier, the triplet mechanism triplet state triplet state. So, if the reaction takes place in the triplet state or singlet state, this polarization mechanism that we are going to discuss can work. And the reaction need not be very fast compared to the spiller S reaction of the triplet state. But here that combination was necessary that reaction has to be very fast, and be comparable to the triplet spiller S reaction state. In TM the polarization was created when the radical was created at the same time. When we get this sort of signal this conditions are not satisfied.

So, we examine if the electron spin polarization can be generated during the evolution of the radical pair; that is, the (Refer Time: 03:07) A and B reacts something like this happens. So, during the generation process I get triplet mechanism. So, if this condition for TM is not satisfied, then can the polarization develop as the radicals are evolving. May be, that is the way the other mechanism works. So, we will have to understand how the radicals evolve after they are produced.

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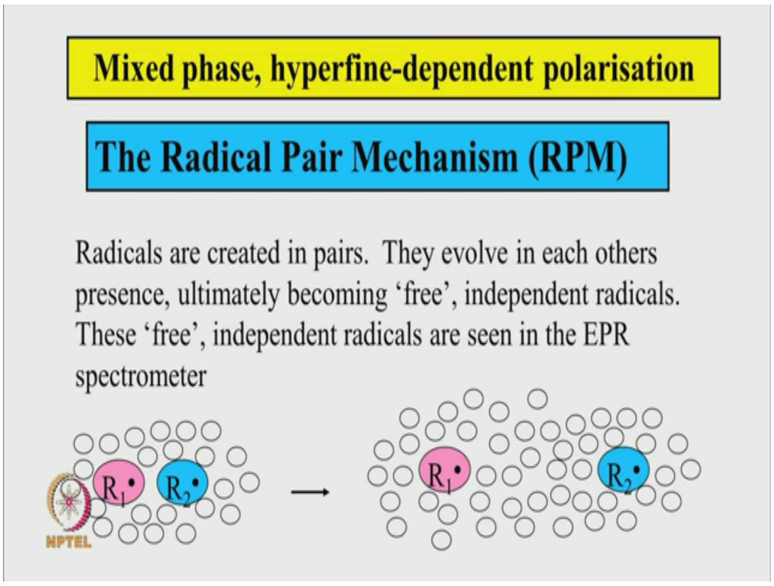

Mixed phase, hyperfine-dependent polarisation

The Radical Pair Mechanism (RPM)

Radicals are created in pairs. They evolve in each others presence, ultimately becoming 'free', independent radicals. These 'free', independent radicals are seen in the EPR spectrometer

So, this mechanism is called radical pair mechanism.

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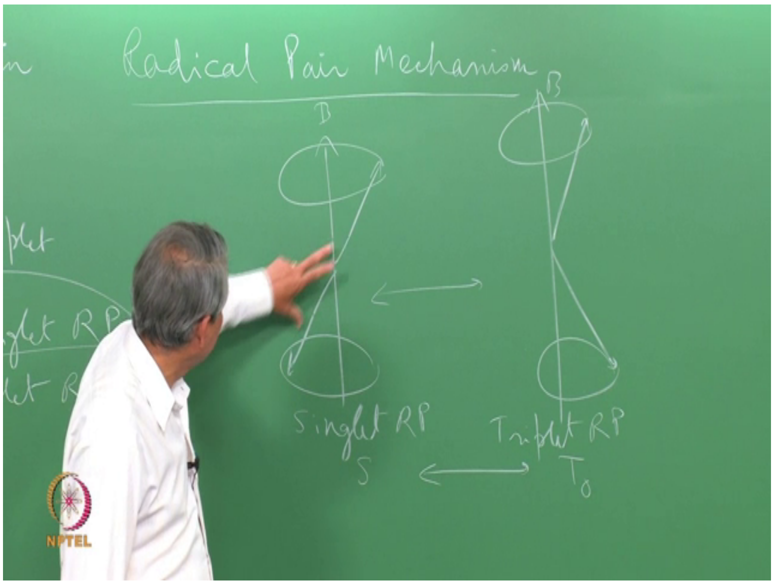

And we will see that the formation of the radical pair is the key to this mechanism that radicals are created in pair and they are evolving in each others presence.

So, when they are created they evolve in each others presence they ultimately becoming free. What do you mean by that? The moment they are created that is in a solution these radicals are surrounded by this solvent molecules. And they are influencing each other when they are very close to each other. But after sometime once they go away from each other and each of them gets solvated I call them the set of free radical; that is, free from each others presence and if EPR spectrometer actually sees this radicals. So, going from here to there what sort of interaction can produce spin polarization.

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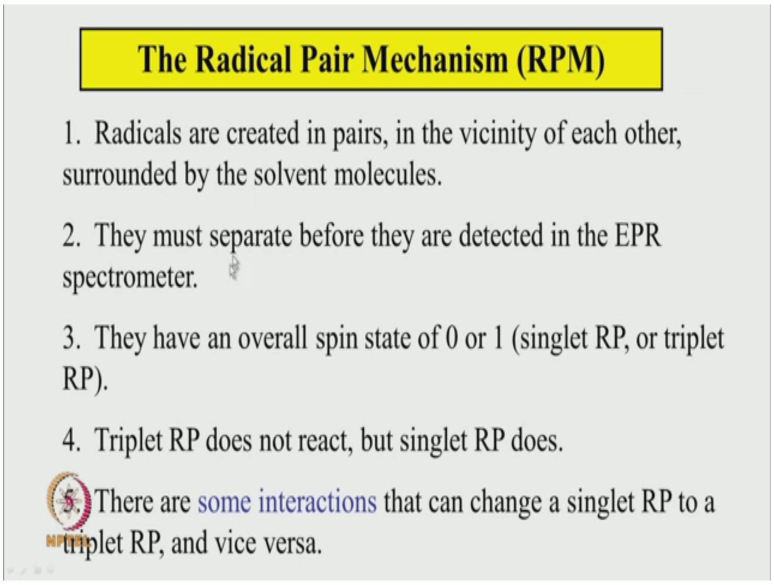

The Radical Pair Mechanism (RPM)

1. Radicals are created in pairs, in the vicinity of each other, surrounded by the solvent molecules.
2. They must separate before they are detected in the EPR spectrometer.
3. They have an overall spin state of 0 or 1 (singlet RP, or triplet RP).
4. Triplet RP does not react, but singlet RP does.
5. There are some interactions that can change a singlet RP to a triplet RP, and vice versa.

So now make some basic statements which are so obvious that we will accept them with true. For example, radicals are created in pairs and in the vicinity of each other, surrounded by the solvent molecules. They must separate before they are detected in the EPR spectrometer. And number 3 is very important. They have an overall spin state of 0 or 1. That is, they could be either singlet radical pair or triplet radical pair. What do you mean by that? This A and B when they are together surrounded by solvent it has got a spin of let us say some unpaired electron this some unpaired electron. So, 1 overall spin state can be constituted which will be some combination of this and this.

So, alpha and beta. So, alpha and beta can be either here alpha or beta this can be here alpha or beta.

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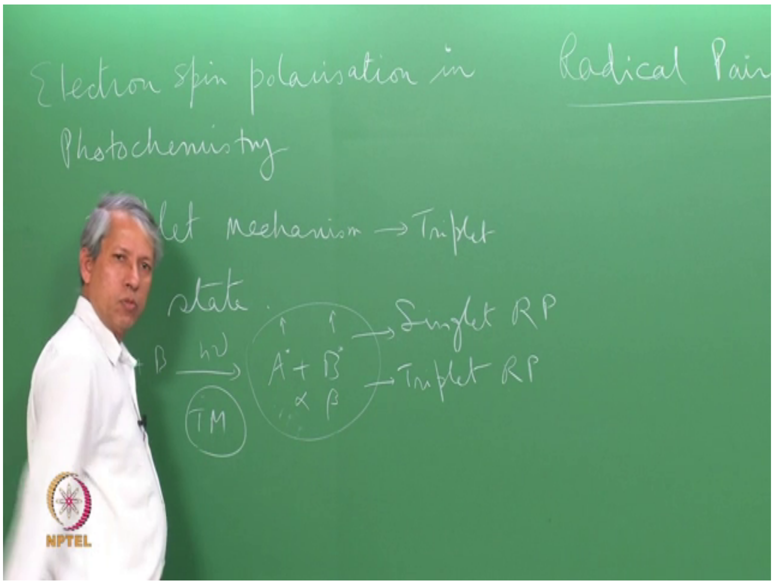

So, overall spin state will depend on the relative orientation of this spin over this spin. So, this could be a singlet radical pair or triplet radical pair depending upon the relative orientation of this 2 space. So, that is number 3. Number 4 is that if they are in a vicinity of each other these 2 radical can as well react this 2 radical of the this sort of spin that they come together. And then their opposite then they can form bond that is the basic requirement for forming a covalent bond the 2 spins must be opposite.

So, here that same simple principle is applied here that if A and B have opposite spin; that is, if they are singlet radical pair then they can react and disappear as a diamagnetic product. On the other hand, if they are parallel spin like this then they even they come closer they may not react and go away from each other and go back to the bulk of the solution. So, that is very important physical expectation that we have about the evolution of the system. That radical pair will undergo this row evolution such that the triplet radical pair does not react, but singlet radical pair does.

So, each of these conditions are very, very simple and understandable, but nevertheless they will have profound effect on the ultimate outcome of the spin distribution in the radicals. And last point is that there are some interactions that can change a singlet radical pair to a triplet radical pair and vice versa. This is not very obvious, but we will therefore, investigate this in detail a little later. The point I am trying to make here is that, this radical pair no matter what they are spin state is the number 5 says that a triplet radical pair starts with this one they can change over to this to become a singlet radical pair, or a singlet radical pair comes in this fashion some interaction can flip the spin to produce a triplet radical pair. Why it is happening? Or why it can happen is something we will see very soon.

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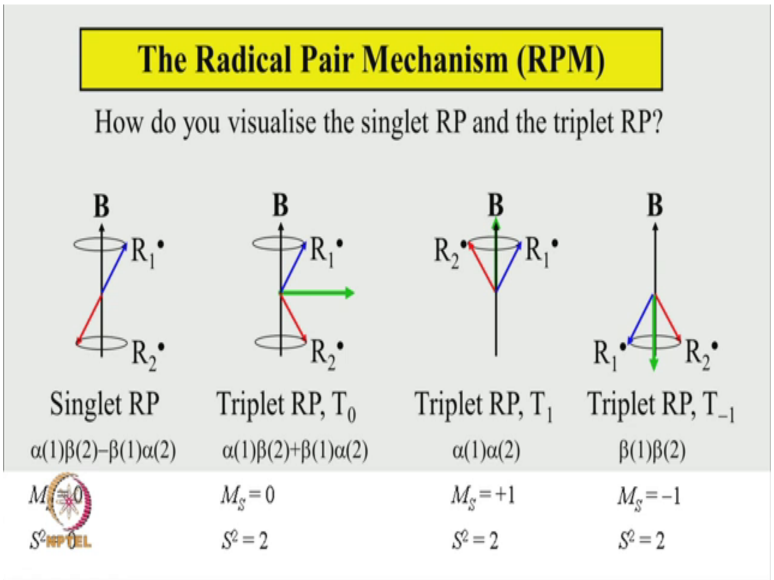

The Radical Pair Mechanism (RPM)

How do you visualise the singlet RP and the triplet RP?

Singlet RP	Triplet RP, T_0	Triplet RP, T_1	Triplet RP, T_{-1}
$\alpha(1)\beta(2)-\beta(1)\alpha(2)$	$\alpha(1)\beta(2)+\beta(1)\alpha(2)$	$\alpha(1)\alpha(2)$	$\beta(1)\beta(2)$
$M_S=0$	$M_S=0$	$M_S=+1$	$M_S=-1$
$S^2=0$	$S^2=2$	$S^2=2$	$S^2=2$

How do you visualize the singlet radical pair and the triplet radical pair? This is the spin multiplicity of the overall pair of radicals. So, I must visualize them as a combination of 2 spins of the 2 radical. So, here in a magnetic field of the EPR spectrometer, this spins are processing in this fashion, radical 1 radical 2 they are colour coded. So, when I say the radical pair is singlet spin state, then they have this set of wave function alpha 1 beta 2 beta 1 alpha 2 net M S 0, and net S square is also 0. If you see here the way these are exactly pointing in the opposite direction. So, there is no net z component here in the direction of magnetic field. This this is therefore, singlet radical pair in contrast till that we will say look at this one here.

So, R 1 and R 2 both point in the same direction around the magnetic field. So, here if you say the total component of the electron spin along this direction, I get one unit of angular momentum. So, this is a triplet radical pair with M z equal to plus 1 and M square will be 2. So, wave function for this is alpha 1 alpha 1. Similarly, the triplet radical pair with a M z minus 1 will have this row speed orientation, but the triplet state with the 0 component of magnetization along this direction has this set of spin orientation. Because net is given by this green arrow this is a M square is 2 green is present here green is there.

Here there is no green because M square is 0. So, the way these are oriented R 1 and R 2 net component along this direction is 0, but it has still a net component in this direction. So, this is the triplet radical pair. In fact, this is the main difference between singlet radical pair and triplet radical pair, both of them have got M z equal to 0, but this has no m at all no magnetic movement. Here there is one there is one this unit of this magnetic movement is present here.

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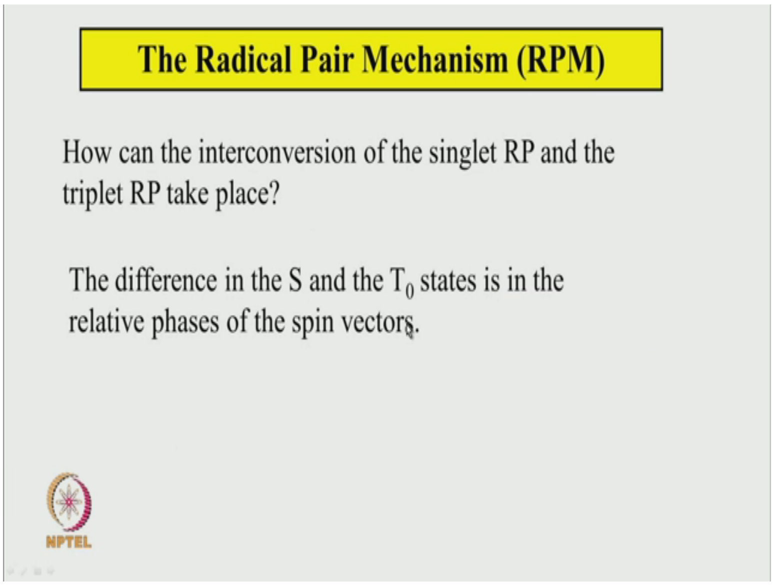

The Radical Pair Mechanism (RPM)

How can the interconversion of the singlet RP and the triplet RP take place?

The difference in the S and the T_0 states is in the relative phases of the spin vectors.

So, how can the inter conversion of the singlet r p, and the triplet R P take place. So, the way this relative orientations are it is not easy to visualize that this can flip over to this or this. On the other hand, these 2-same reasonably similar, what do you when reasonably similar is a of course, that one spin is in this fashion other is this way.

So, this is singlet R P and second one is just this and this triplet R P. Only difference is the relative phase of these 2. So, presumably inter conversion between these 2, and these 2 does not look very, very unlikely. In fact, will see that is what is happening here. On the other hand, between singlet to this triplet us are very unlikely because spin has to really flip from this direction to that direction that is not so likely compared to there here, the phase has to change from this to this.

The difference in the S and T 0 states is in the relative phases of the spin vector. So, we see if such a inter conversion between S and T 0 is possible or not what is necessary for that conversion to take place all that is necessary is that, this phase would change to this now minor difference is in this direction and they are processing in this way. So, how can they relative phase change from this to this, very simple, if they precess at a just little bit different frequency. So, if the precision frequency different for these 2 radical, then this relative phase can change to this or this phase it can change to this. So, that is what is claimed here now.

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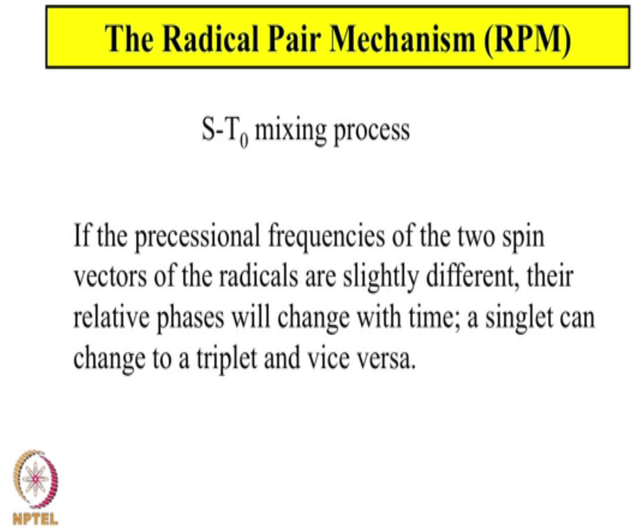

The Radical Pair Mechanism (RPM)

S-T_0 mixing process

If the precessional frequencies of the two spin vectors of the radicals are slightly different, their relative phases will change with time; a singlet can change to a triplet and vice versa.

If the precessional frequencies of the 2 spin vectors of the radicals are slightly different, just slightly different.

Their relative phases will change with time, then a singlet can change to a triplet and vice versa.

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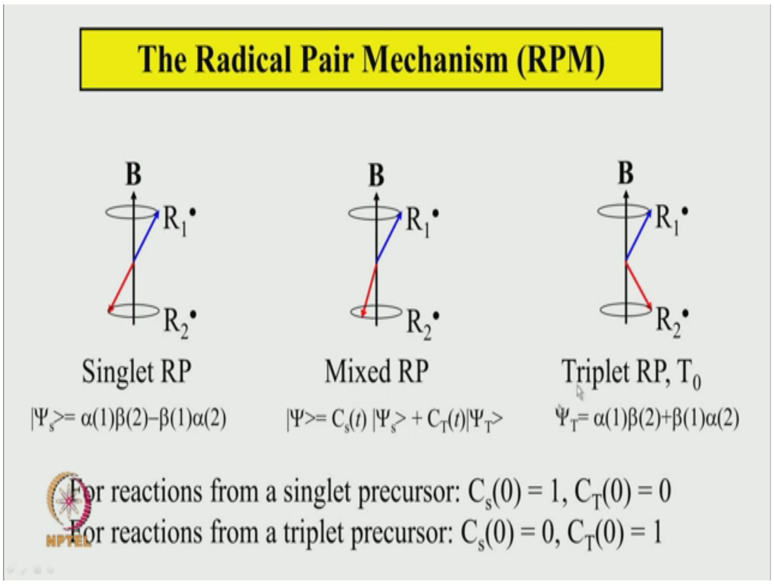

The Radical Pair Mechanism (RPM)

Singlet RP | Mixed RP | Triplet RP, T_0

$|\Psi_s\rangle = \alpha(1)\beta(2) - \beta(1)\alpha(2)$ | $|\Psi\rangle = C_s(t)\,|\Psi_s\rangle + C_T(t)|\Psi_T\rangle$ | $\Psi_T = \alpha(1)\beta(2) + \beta(1)\alpha(2)$

For reactions from a singlet precursor: $C_s(0) = 1$, $C_T(0) = 0$

For reactions from a triplet precursor: $C_s(0) = 0$, $C_T(0) = 1$

So now more pictorially one can understand a this S T 0 mixing process.

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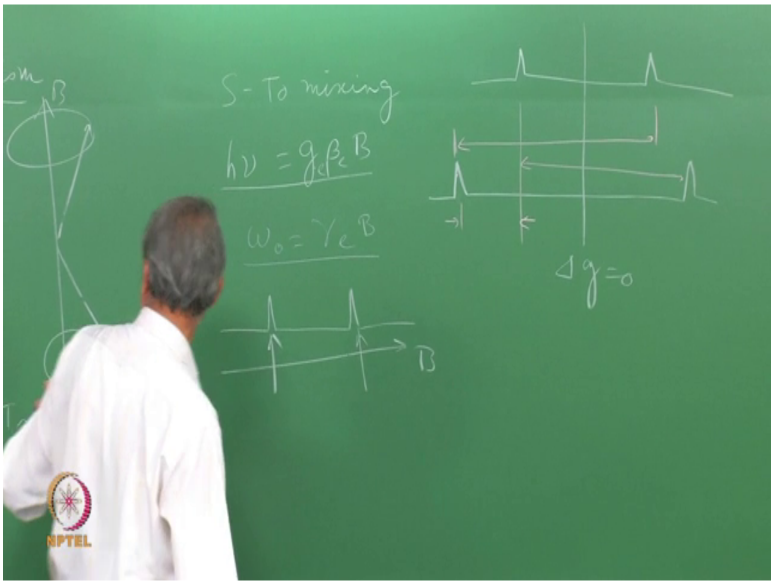

This is singlet and triplet 0 state in the mixing process. Once more, when the relative orientation of this 2 radicals exactly opposite, I get singlet radical pair with a singlet wave function alpha 1 beta 2 minus beta 1 alpha 2 and when these 2 are in the same direction. I get triplet radical pair with wave function of the triplet state is alpha 1 beta 2 plus beta 1 alpha 2.

So, here you see the difference in sign is nothing but depicting the difference in their relative phases of this. When the phases are somewhat in between, then one can call it a mixed state. So, this is a wave function with a mixture of singlet radical pair state and triplet radical pair state, and this is a coefficient. And since this is now the static situation, because they keep on precessing in this fashion, and with the frequencies are different they can keep on changing their relative phases. So, intermediate phase will be a mixture of singlet and triplet radical pair and the coefficients are going to be dependent on time that S very important.

Now, comes the way the radicals are generated, right. At the time let us say pulse of laser comes, and the radicals are created, that at that instant the spin state of this will be decided by what the precursor states were there. So, if the precursor state were singular state, reacting then the nascent radical will also have all the electrons paired in a sense that the this is alpha there will be beta this is alpha this is beta that is overall spin state of the radical pair will be also singlet state. On the other hand, if the reaction was in the triplet state, suppose a was a triplet state, then overall spin state of this (Refer Time: 14:36) pair will also be triplet.

So, mathematically that could be set as the initial condition. For reactions from a singlet precursor, C S at time T equal to 0 is 1. That is at the triplet component here is 0. Similarly, if the reaction from a triplet precursor is C S component is 0 and C T component is 1, but these coefficients are the initial condition, and in course of time of course, these values are going to change.

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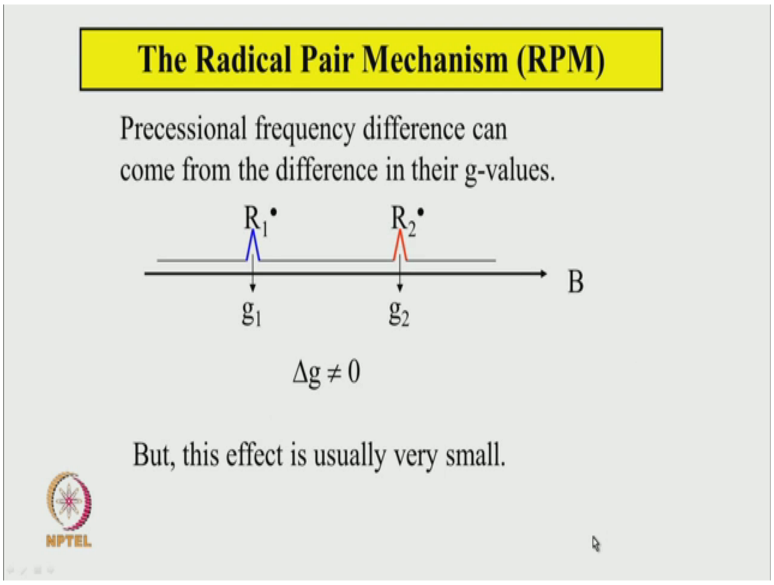

The Radical Pair Mechanism (RPM)

Precessional frequency difference can come from the difference in their g-values.

$\Delta g \neq 0$

But, this effect is usually very small.

So, all that is necessary is the difference in the precession frequency. So, which one decides the precessional frequency difference individual precession frequency given by the normal frequency type of thing resonance combination of EPR transition or in terms of precessional frequency it is gamma B. And these and this are related. So, if the g factors are different for the 2 radicals. Then the preserved frequency will also be different. So, all that is required here is that the 2 radicals that I have here has slightly different if the g values. So, in the other word the spectrum may look like appearing at 2 different places in the magnetic field this is B this is radical number one radical number 2 this is decided by the g value. So, this should not appear exact at the same place. Just a little bit away from each other. So, that is pictorial is found here.

So, radical 1 appears here let us say it is value g value is g 1 radical 2 has g value of g 2, then they are appearing at different place. So, delta g is not equal to 0. So, this is enough for this 2 radicals to have different precessional frequency, but in practice most of the organic radicals which you have seen their g values are very nearly equal to free electron g value, 2.00 something. So, this effect is not very large. In fact, the effect is very small, it is not a very significant factor to produce the type of signal that we see here.

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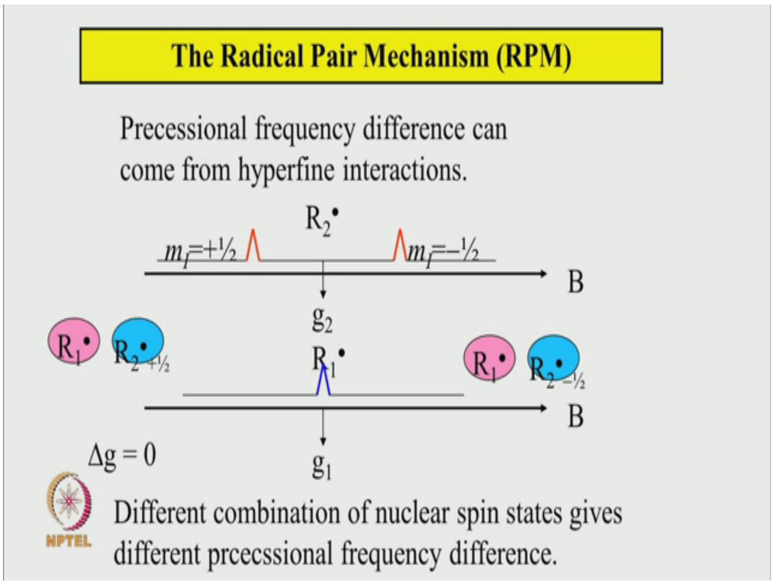

The Radical Pair Mechanism (RPM)

Precessional frequency difference can come from hyperfine interactions.

Different combination of nuclear spin states gives different prcecssional frequency difference.

So, what other way the precessional frequency can be different? We bring in now the role of hyperfine interaction. Let us say radical 1 has no hyperfine line. So, it appears at g equal to this g 1, a radical 2 also appears at the same place; that is, delta g is 0 for both of them, but it has a one spin half nuclear. So, they give doublet line, one line here, other line there. So, this axis is the magnetic field axis, but one can think of this as also as a frequency axis. So, of this line is appearing in this place, then between this and this if the difference in their precessional frequency. Similarly, between this and this is the difference in their precessional frequency.

Therefore, the difference of the precessional frequency of radical 1 and 2 will depend on what the nuclear spin state of this radical is, if it is plus half it will have one type of difference if it is a minus half it is equal to other type of difference. It is so happened that the magnitude is same, but sign is different. So, different combination of nuclear spin states give different precessional frequency difference.

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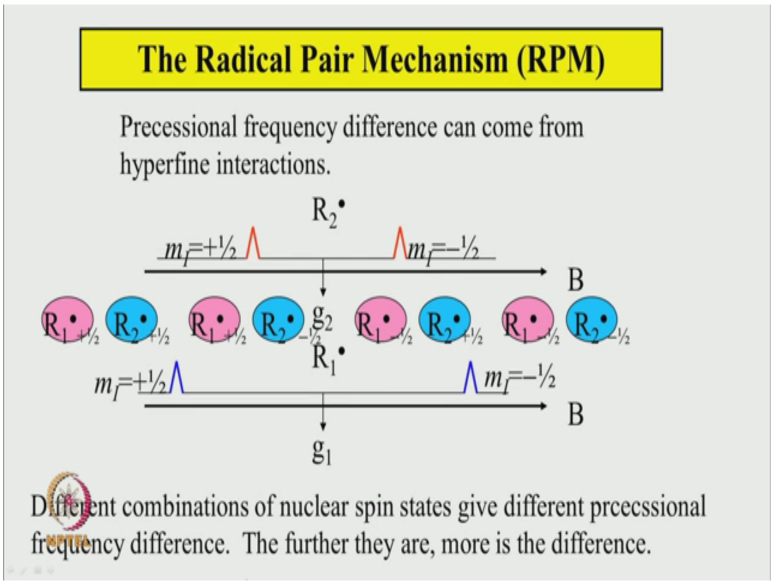

The Radical Pair Mechanism (RPM)

Precessional frequency difference can come from hyperfine interactions.

Different combinations of nuclear spin states give different prcecssional frequency difference. The further they are, more is the difference.

We can extend the argument further. And say the let us say R 1 and R 2 both have hyperfine line. This is also doublet, and R 1 also a doublet of the different value. So, this is smaller coupling constant this is a bigger coupling constant.

Now, there are 4 possible arrangement for the radical when they encounter each other. So, radical 1 can have alpha or plus half nuclear spin, radical 2 can have plus half spin state; that means, this transition is here for R 2 this is here. So, difference in precessional frequency is this much, between this and that. Similarly, here both could be minus then the difference in precessional frequency is between this. And this let me do it here.

So, this is the same plane delta g is equal to 0. So, one possibility between this and that; this is one differential pressure on frequency, when this has got alpha spin for the nucleus which you have taken alpha spin for the nucleus. This much is the difference in precessional frequency, but then the radical scan have all possible nucleus free state, plus half and minus half for both of them. So, another combination could be that between this and this. That is, this radical comes with alpha spin, and this radical comes with a beta spin. Then this much is the difference in precessional frequency. Same is true for the other one from between this and that. So, you see that it depends on what set of nuclear spin states are involved in this radical pair here or there, the precessional frequency is going to depend on that.

So, higher the difference in precessional frequency, more effective will be this set of singlet to triplet radical pair mixing, more quickly it will go from this to this. So, more efficient mixing, will take place for those pair where the difference in a precessional frequency larger. So, outside line pair of line will experience more such mixing more efficient mixing of this kind. So, further there more is the difference and more effective will be the singlet triplet interconversion. One of the condition was that on the radical pair has singlet nature there is finite probability that they can react and disappear as a diamagnetic product. But when they got parallel spin then they will survive. Second here the difference in their survival.

Now, if the radical pair started with a let us say singular radical pair, that reaction took place as a singular state. Initially they were in the opposite phase. So, those radicals which get converted to the triplet nature, they will survive. And those which are not they will die away. So, survival probability for a singlet radical pair depends on how quickly they evolve to a triplet radical pair. And they will be seen as the free radical free from each other and detected in the spectrometer. On the other hand, if the reaction took place in the triplet state, then at the time with a creation both the radicals cause the parallel spin. So, radical pair is a triplet nature. Then this set interconversion will convert them to a singlet state and they will disappear. So, whatever surviving probability that these 2 radical have they will be seen in the EPR spectrometer, and I can get a spectrum.

So, the difference is again the way the precursor are the precursor decides how the final fate is going to be. In one case the one which is evolving to the singlet state will die if the reaction started from the triplet state. In other case those who are starting from the singlet radical pair whatever is evolving with the triplet state will survive, but in the case of other way around is that whatever is not evolving, they will survive.

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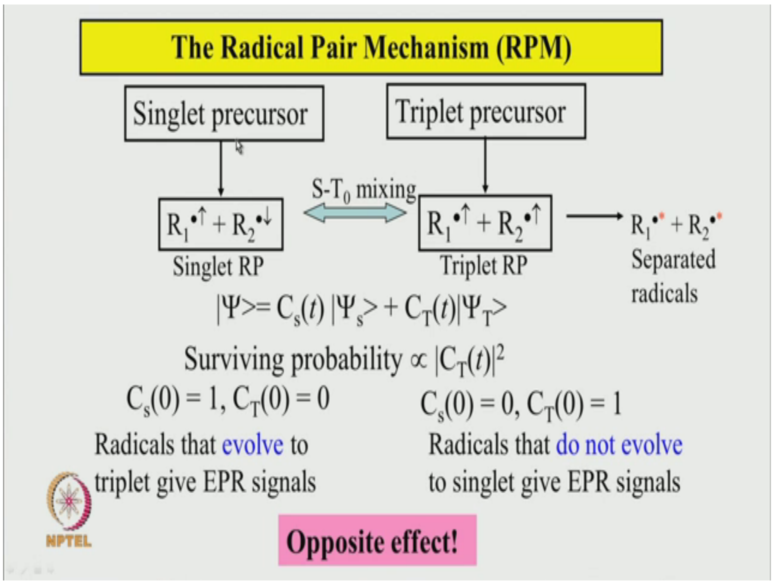

The Radical Pair Mechanism (RPM)

Singlet precursor

Triplet precursor

$R_1^{\bullet\uparrow} + R_2^{\bullet\downarrow}$

Singlet RP

$S\text{-}T_0$ mixing

$R_1^{\bullet\uparrow} + R_2^{\bullet\uparrow}$

Triplet RP

$R_1^{\bullet} + R_2^{\bullet}$

Separated radicals

$$|\Psi\rangle = C_s(t)\,|\Psi_s\rangle + C_T(t)\,|\Psi_T\rangle$$

Surviving probability $\propto |C_T(t)|^2$

$C_s(0) = 1,\ C_T(0) = 0$

Radicals that evolve to triplet give EPR signals

$C_s(0) = 0,\ C_T(0) = 1$

Radicals that do not evolve to singlet give EPR signals

Opposite effect!

Again, summarize the dynamics of this one. So, the precursor resides the evolution in this fashion that for a singlet precursor at the time of creation these 2 radicals have opposite spin, we call singlet R P. And for triplet precursor the initial the spins of the 2 radicals are parallel. So, we call them triplet radical pair. And then this h S T 0 mixing takes place by this set of difference in the precessional frequency.

So, the wave function here has this mixture of singlet radical pair and triplet radical pair. And these coefficients depend on time, the survival probability depends on to the extent that the triplet us have been produced. That is square of this one and initial conditions is that C S 0 is 1, C T 0 is 0 for this singlet precursor, and for triplet precursor exactly the opposite. C T 0 is 1, C S 0 is 0. So, here radicals that evolve to triplet give EPR signal. Here radicals that do not evolve to singlet give EPR signal. Then you see that exactly opposite effect is everywhere. And that is what we see in the experiment also that when the singular state react we get one type of the set of behavior, and the triplet reacts we get other type of behavior. And from this radical pair when they separate away from each other, these radicals are with a stared signs where the polarized radical those are seen in the experiment.

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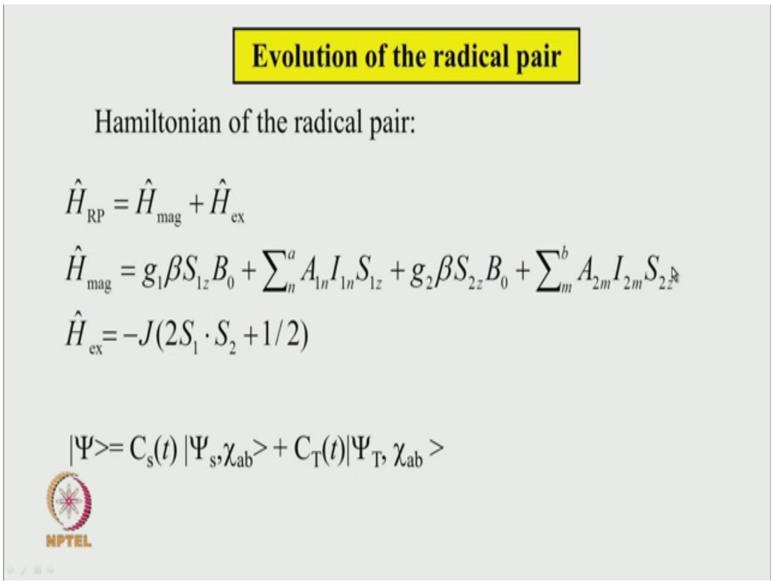

Evolution of the radical pair

Hamiltonian of the radical pair:

$$\hat{H}_{\mathrm{RP}} = \hat{H}_{\mathrm{mag}} + \hat{H}_{\mathrm{ex}}$$

$$\hat{H}_{\mathrm{mag}} = g_1 \beta S_{1z} B_0 + \sum_n^a A_{1n} I_{1n} S_{1z} + g_2 \beta S_{2z} B_0 + \sum_m^b A_{2m} I_{2m} S_{2z}$$

$$\hat{H}_{\mathrm{ex}} = -J(2S_1 \cdot S_2 + 1/2)$$

$$|\Psi> = \mathrm{C_s}(t)\, |\Psi_{\mathrm{s}}, \chi_{\mathrm{ab}}> + \mathrm{C_T}(t) |\Psi_{\mathrm{T}}, \chi_{\mathrm{ab}}>$$

NPTEL

Now, more mathematically this qualitatively we understand why it is undergoing this singlet to triplet inter conversion, now we can quantitatively calculate that by knowing their precessional frequency. So, hamiltonian of the radical pair will be hamiltonian of the radical individually plus, this exchange introduction when they are nearby. What is that when they are formed in the in the vicinity of each other they can influence each other and form a triplet pair or singlet pair depending upon the exchange introduction between them. So, that is given here. You see the other magnetic interaction here is a this is the Zeeman interaction of the first radical, and it is own hyper finite reaction electron nuclear hyperfine interaction. This is for the second radical it is Zeeman interaction and electronical hyperfine interaction. This is the exchange interaction.

So, total wave function is a combination of the singlet state, radical pair and it is own nuclear spin function, which could be dependent on the nuclear spin state.

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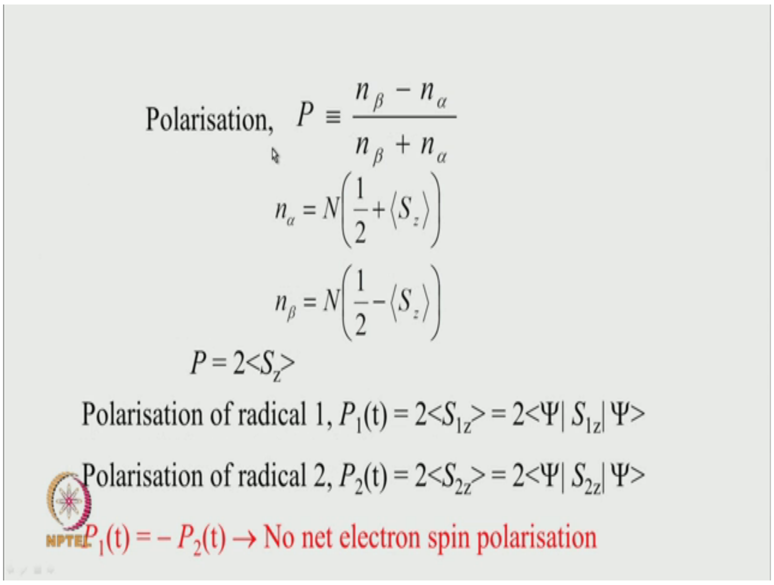

Polarisation, $P \equiv \dfrac{n_\beta - n_\alpha}{n_\beta + n_\alpha}$

$$n_\alpha = N\left(\frac{1}{2}+\langle S_z\rangle\right)$$

$$n_\beta = N\left(\frac{1}{2}-\langle S_z\rangle\right)$$

$P = 2<S_z>$

Polarisation of radical 1, $P_1(t) = 2<S_{1z}> = 2<\Psi| S_{1z}|\Psi>$

Polarisation of radical 2, $P_2(t) = 2<S_{2z}> = 2<\Psi| S_{2z}|\Psi>$

$P_1(t) = -P_2(t)$ → No net electron spin polarisation

Similarly, for triplet radical pair function and the nuclear coordinates of the corresponding radical pair. Remember that we defined the polarization to be in beta minus n alpha by total number of spin. So, we can you know this can be easily calculated from this sort of average value of the S z angular momentum. That gives alpha spin and minus S z gives the beta spin. So, that P will be equal to 2 times the average S z the way. Now this equations are written that polarization of radical 1 at time T is 2 times S 1 z that average value of the z component of the spin angular momentum of radical 1, and this is given by this one. Wave function and this is the S z operator. Similarly, for the radical 2 again this is the similar expression.

Now, the way these are you see they are exactly opposite. P 1 T is equal to minus P 2 T. And no net electron spin polarization takes place there. It only shows that the spin simply get distributed such a way that one becomes this way. Other becomes that way there is no net polarization.

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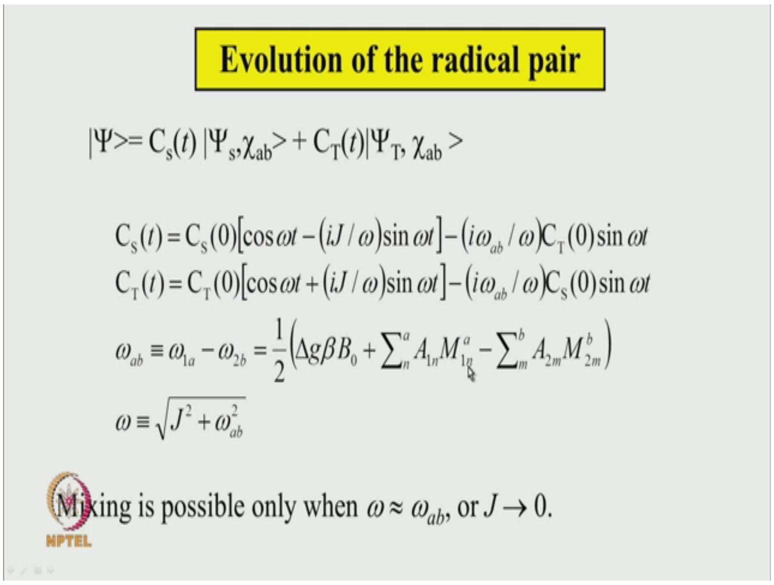

Evolution of the radical pair

$$|\Psi\rangle = C_S(t)\,|\Psi_S,\chi_{ab}\rangle + C_T(t)|\Psi_T,\chi_{ab}\rangle$$

$$C_S(t) = C_S(0)\left[\cos\omega t - (iJ/\omega)\sin\omega t\right] - (i\omega_{ab}/\omega)C_T(0)\sin\omega t$$
$$C_T(t) = C_T(0)\left[\cos\omega t + (iJ/\omega)\sin\omega t\right] - (i\omega_{ab}/\omega)C_S(0)\sin\omega t$$
$$\omega_{ab} \equiv \omega_{1a} - \omega_{2b} = \frac{1}{2}\left(\Delta g\beta B_0 + \sum_n^a A_{1n}M_{1n}^a - \sum_m^b A_{2m}M_{2m}^b\right)$$
$$\omega \equiv \sqrt{J^2 + \omega_{ab}^2}$$

Mixing is possible only when $\omega \approx \omega_{ab}$, or $J \to 0$.

Now, we can use the time dependent (Refer Time: 26:52) equation to see how the wave function is going to evolve, and in all the coefficients are going to evolve. That is the way the equation is. So, here the term which are looking very unfamiliar is actually this one, but who is carefully this is quite meaningful. Because this is the precessional frequency difference, to the omega of first radical second radical this one difference in precessional frequency.

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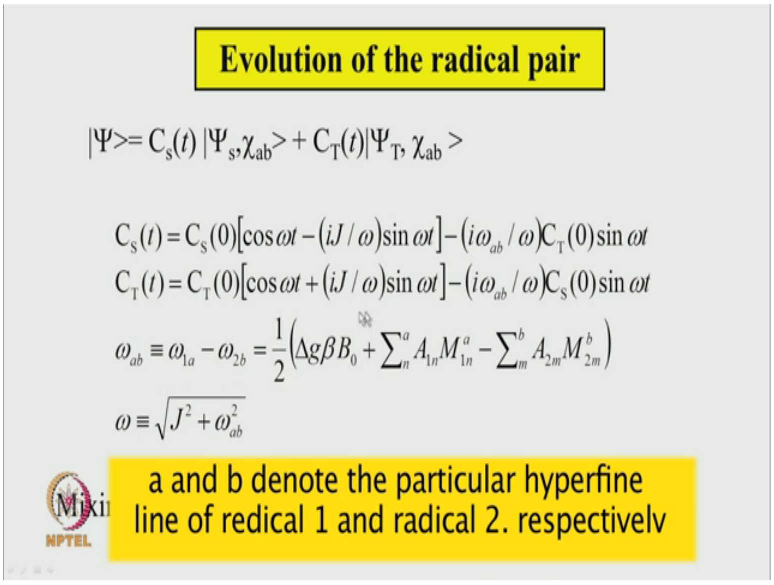

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$$\omega_{ab} \equiv \omega_{1a} - \omega_{2b} = \frac{1}{2}\left(\Delta g\beta B_0 + \sum_n^a A_{1n}M_{1n}^a - \sum_m^b A_{2m}M_{2m}^b\right)$$
$$\omega \equiv \sqrt{J^2 + \omega_{ab}^2}$$

a and b denote the particular hyperfine line of redical 1 and radical 2. respectivelv

So, that is decided by the delta g value. We have already encountered that delta g decides the precessional frequency difference. And also, it is decided by the hyperfine coupling constant of various nuclear and the corresponding Mi value. It is here. These are the different Mi values, which pair is present in a particular radical pair.

So, that is for first radical and second radical. So, this is perfectly understandable. Now mixing is possible only when this singlet triplet energy is or almost degenerate. That is j is very nearly going to 0. Otherwise this mixing will not take place, because singlet energy level is here triplet is there, unless they come closer, they will not be able to mix.

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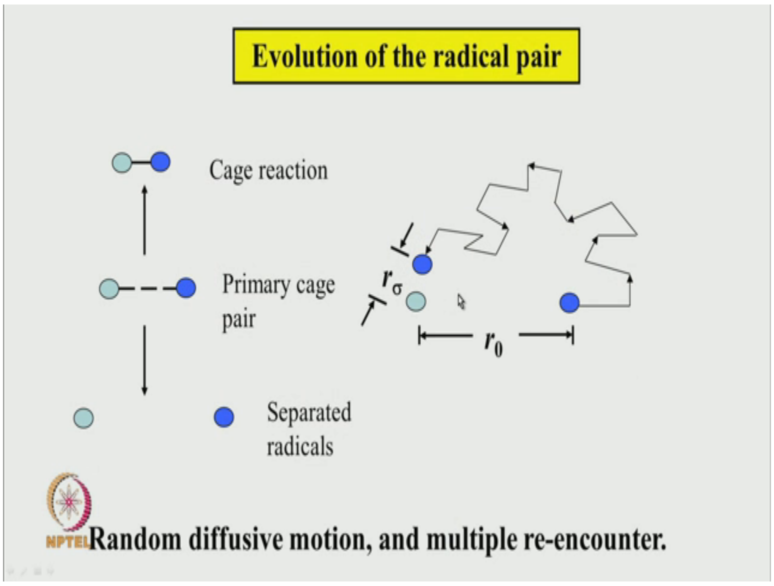

Evolution of the radical pair

Random diffusive motion, and multiple re-encounter.

So, the way the radicals are evolving, that aim is that when they are in the vicinity of each other, they have to go away from each other being a radical Separated from the other one radical B we can separate it from each other.

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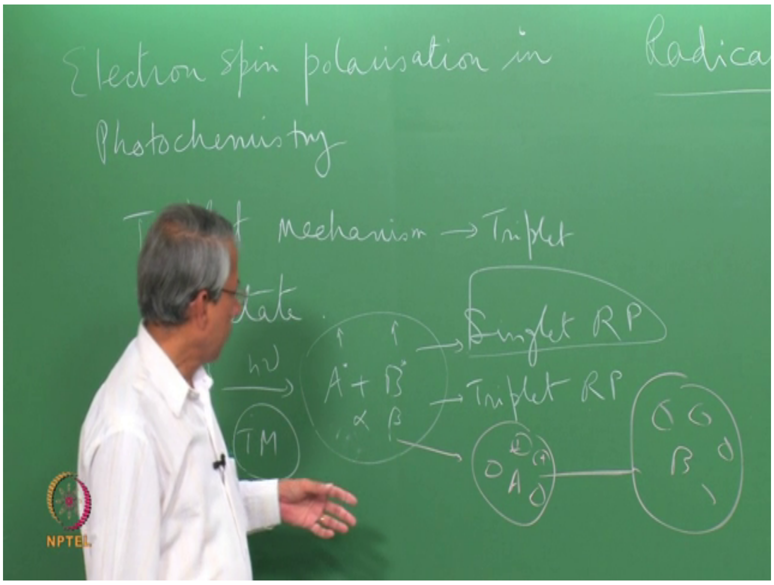

So, these they have to physically go away from each other.

Now, for that to happen lot of solvents must collide with each other this random Brownian motion will try to push them away from each other. So, there will be lot of interactions that diffusive motion that A and B will literally go away then again come back this set of multiple reencounter will take place. And every time they are nearby too close then their splitting increases, they do not mix when they become comparable they again mix.

So, this mixing takes place continuously for quite sometime, before they go away from each other. So, during that process, then whatever survival probability that is there for the triplet radical pair, they will be seen to produce the EPR signal. And you see that interaction is very much dependent on predominantly by the nuclear hyperfine coupling constant and the which pair of lines are involved there. So, outer lines will have maximum difference in precessional frequency, they will show maximum effect in a polarization.

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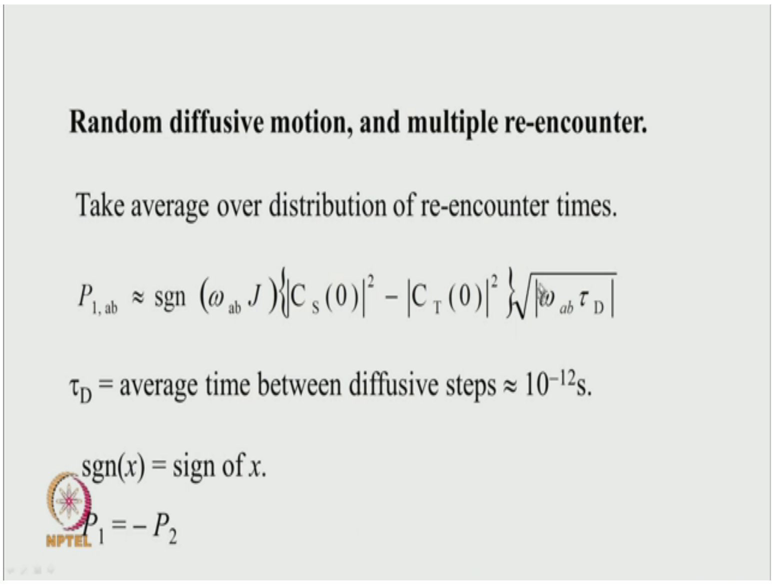

Random diffusive motion, and multiple re-encounter.

Take average over distribution of re-encounter times.

$$P_{1,\text{ab}} \approx \text{sgn}\,(\omega_{\text{ab}} J)\left\{|C_S(0)|^2 - |C_T(0)|^2\right\}\sqrt{|\omega_{ab}\tau_D|}$$

τ_D = average time between diffusive steps ≈ 10^{-12}s.

sgn(x) = sign of x.

$P_1 = -P_2$

So, these are further mathematics which I have only written the final result. Random diffusive motion and multiple reencounter is involved there before the radical separate away from each other. So, the polarization of radical 1 for this A and B, a b is that what sort of pair you have in mind let us say, this is nuclear spin A and nuclear spin B whatever that is this type of pair A and B that depends on the magnitude of this, and also sign of this 1 plus, depends on the initial condition. Sign is (Refer Time: 30:35) because one pair if it is looking at the polarization of this one, for this 2 this is positive, for other one here for these 2 this is negative.

So, polarization is going to be opposite. Also depends on the magnitude of that in a square root of fashion, and the initial condition. In singular state is the reacting state or the triplet state is initially reacting state that we have already understood earlier, that how it is going to be different for the initial state. Initial state decides the overall outcome sgn means the sign of this one. This is positive we will have one type of polarization is negative it is a other type of polarization. And it is already true that polarization of one radical is exactly opposite of the other one.

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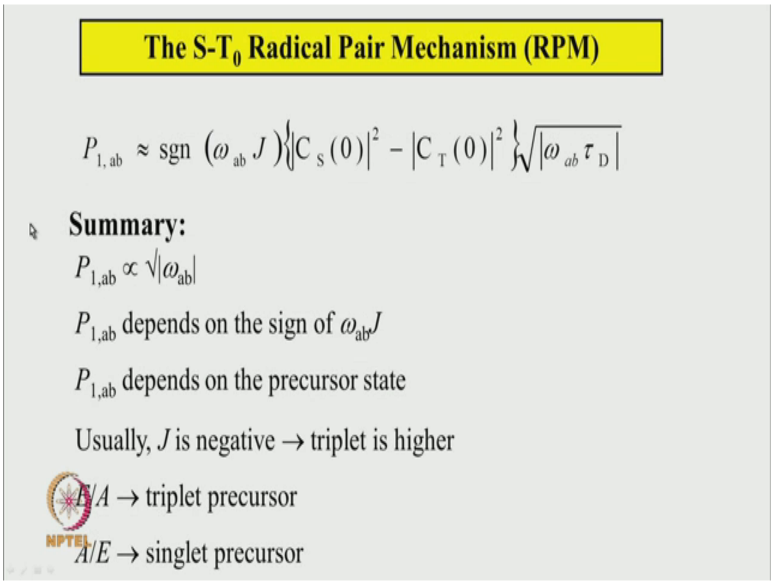

The S-T$_0$ Radical Pair Mechanism (RPM)

$$P_{1,ab} \approx \mathrm{sgn}\,(\omega_{ab} J)\{|C_S(0)|^2 - |C_T(0)|^2\}\sqrt{|\omega_{ab}\tau_D|}$$

Summary:

$P_{1,ab} \propto \sqrt{|\omega_{ab}|}$

$P_{1,ab}$ depends on the sign of $\omega_{ab}J$

$P_{1,ab}$ depends on the precursor state

Usually, J is negative → triplet is higher

E/A → triplet precursor

A/E → singlet precursor

So, this is the final expression of the polarization of radical 1, for a given pair of spin state, sign of this and the J value is sign of this and this together. J decides the triplet is higher or the singlet is higher for the radical pair an initial condition and square root of this magnitude of that one. So, summary is that polarization depends on the square root of the precessional frequency, difference this all depends on the sign of product of this. And this this depends on the precursor. It is singlet state or triplet state. Usually triplet state is higher than the singlet state because this is usual bond formation.

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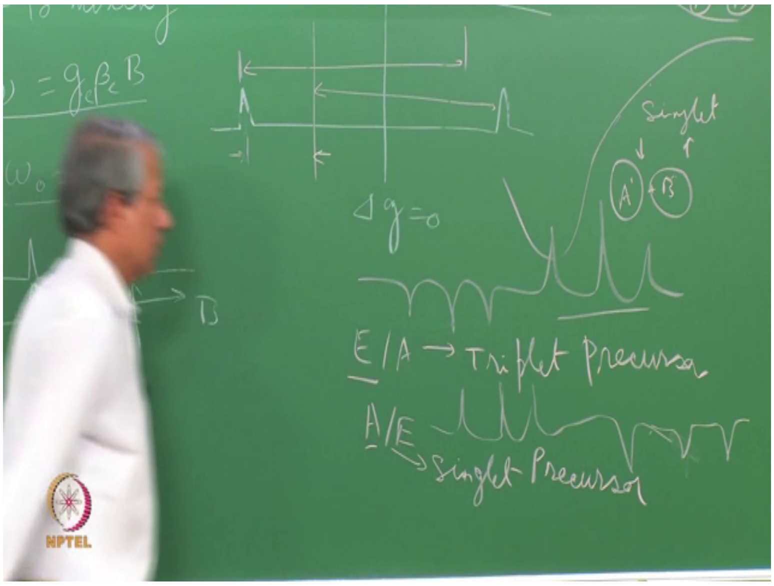

The 2 radical A and B is are coming together, then when they have got this singlet nature that is opposite spin, they form a bond of this kind; here, on the other hand if they are triplet that is spin parallel A and B, then they will not form a bond energetically not possible. And in all this ultimately the net result is that you see the how the precursor state decides the sign of this exactly opposite person, that if the triplet is reacting, the spectrum will look like E A type; that is, this type of thing low field line are emissive, and high field lines are absorptive. This is for triplet precursor.

Similarly, if it is A E which will look like this type of line usually this low field lines are absorptive, and high field lines are emissive. This is for singlet precursor. That is the summary of this radical pair mechanism.

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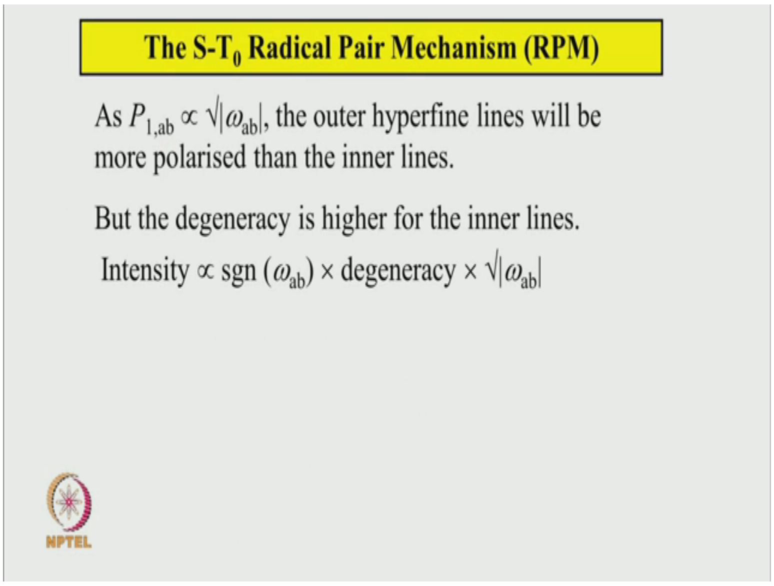

The S-T_0 Radical Pair Mechanism (RPM)

As $P_{1,ab} \propto \sqrt{|\omega_{ab}|}$, the outer hyperfine lines will be more polarised than the inner lines.

But the degeneracy is higher for the inner lines.

Intensity $\propto$ sgn $(\omega_{ab}) \times$ degeneracy $\times \sqrt{|\omega_{ab}|}$

Now, a little more quantitative discussion that as this polarization depends on the square root of this difference in precessional frequency, the outer lines will be more polarized than the inner lines. But the degeneracies are there the outer lines have lower intensity than the inner lines. So, they go in the opposite fashion. Net reserved will be the observe intensity will be a product of the degeneracy factor, and the square root of the precessional frequency difference, and the sign.

So, this complex way the ultimately the spectrum will look like what we see here. The outer lines are more polarized, than the inner lines, but the inner lines have more contribution from degeneracy. So, together this will be the overall appearance of that, but then you have considered 2 mechanisms. The radical pair mechanism is we have just discussed, and earlier we have discussed triplet mechanism.

So, in reality it is not exclusively this or that. It is the combination of both the mechanisms that usually will always operate.

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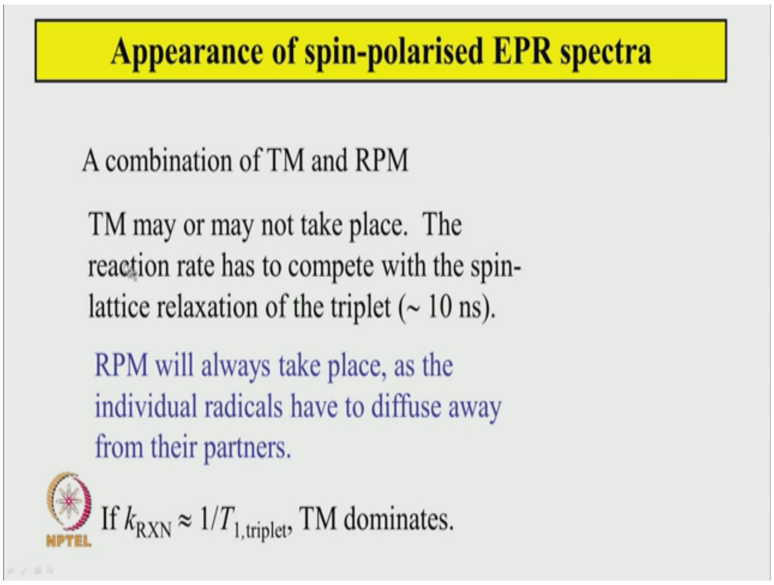

Appearance of spin-polarised EPR spectra

A combination of TM and RPM

TM may or may not take place. The reaction rate has to compete with the spin-lattice relaxation of the triplet (~ 10 ns).

RPM will always take place, as the individual radicals have to diffuse away from their partners.

If $k_{\mathrm{RXN}} \approx 1/T_{1,\mathrm{triplet}}$, TM dominates.

But then TM may or may not take place, reason being that the reaction has to compete with the spin lattice relaxation of the triplet, and which is very fast. But RPM will always take place as the individual radicals have to diffuse away from their partners. That is this is the sort of (Refer Time: 35:32) radical pairs are created, and they have to diffuse away from each other. That will always be the case whether the triplet reacts or the singlet state react. So, this RPM will always take place, TM may or may not take place. Only thing is that for TM to take place triplet state must react and also. The rate of reaction has to be very fast and be comparable to the spinlars relaxation rate of the triplet state. Then only TM will dominate.

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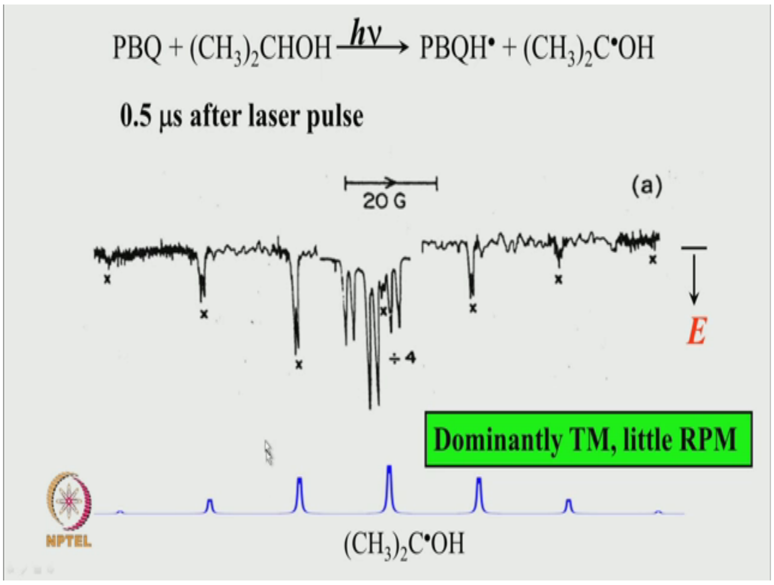

$PBQ + (CH_3)_2CHOH \xrightarrow{h\nu} PBQH^{\bullet} + (CH_3)_2C^{\bullet}OH$

0.5 μs after laser pulse

Dominantly TM, little RPM

$(CH_3)_2C^{\bullet}OH$

So, here is the example where the TM dominates now. But then RPM is also there if you see very carefully that this height of this line is more than the height here this correspondent line. But for a true TM this will be same as this, the way the absorptive spectrum is. This line should have same intensity as this one. This intensity should be say intensity of this one, but this is not true. So, there S a little bit of net absorptive singlet as present here, this dominantly TM and little RPM, that is why this (Refer Time: 36:37) is somewhat smaller. And so, this is also consistent with this prediction that for E A, it will be I mean this set of polarization. This lines will be emissive, this line will be absorptive. So, that little absorptive component is causing these 2 become smaller even the quinone radical here. These lines have slightly bigger intensity than these lines here. I mean this is also slightly bigger than that one. So, there is a residual amount of net absorptive singular is present here. So, it is also so, dominantly TM and little RPM.

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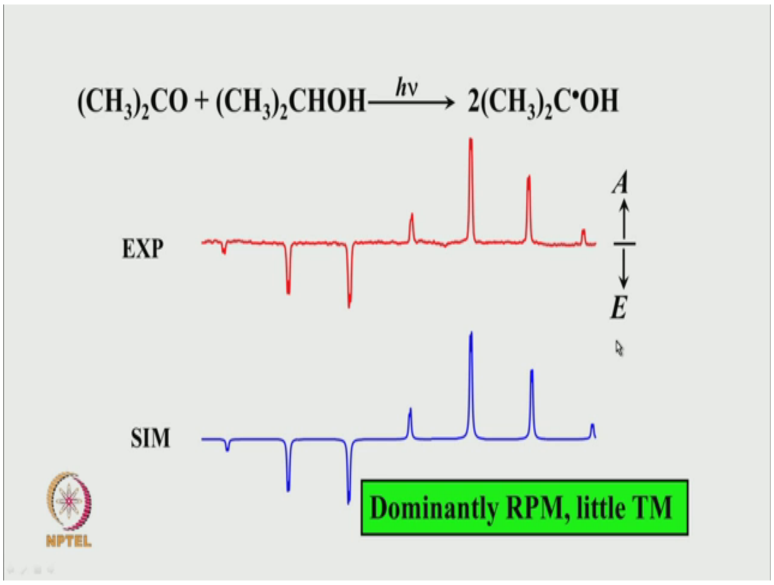
$(CH_3)_2CO + (CH_3)_2CHOH \xrightarrow{h\nu} 2(CH_3)_2C^{\bullet}OH$

Dominantly RPM, little TM

Then here if it is pure RPM then the 2 radicals are identical. So, delta g is 0 precisely for both of them.

So, intensity for these if we calculate now.

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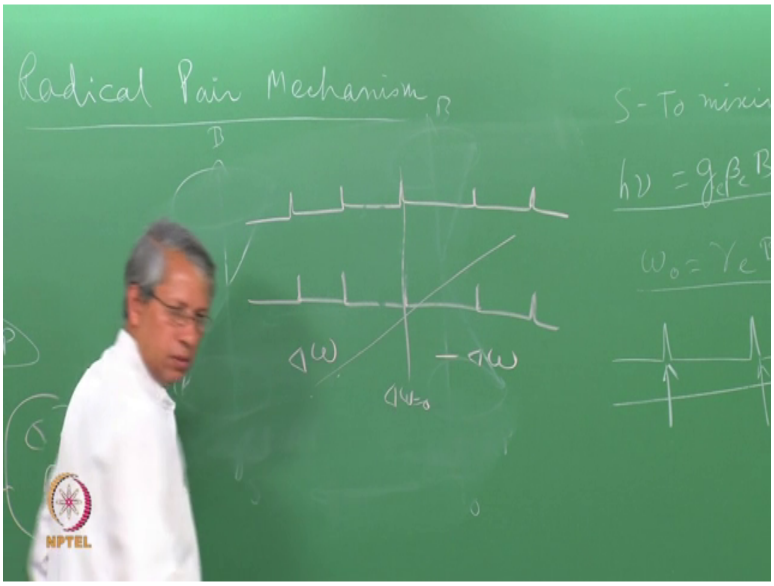

So, radical 1 if I calculate in this fashion. Something like this radical 2 is exactly same. So, the for the this middle hyperfine line precessional frequency is precisely 0. So, here it is the if the values are delta omega, this side be minus delta omega. But here it is actually delta omega is equal to 0. So, intensity should be precisely 0 here, but that is not true.

Again, for RPM this will be exactly anti symmetric, in this type of thing. That whatever intensity I see here, I should get exactly opposite value in the other side. So, the signal will be exactly anti symmetric; because the values are in this fashion, but that is not happening here. So, these lines are somewhat more absorptive than these lines; that mean, it also has a residual absorptive signal present here, which might be due to a little bit of triplet present here. Though there are controversies whether this indeed triplet or not, but we will not get into that debate right now, at least it shows that it is not a pure RPM which is operating here.

So now we have really come to an end of this discussion on electron spin polarization in photochemical system. And we have seen that many interesting things can happen, and just a pure observation of such polarized EPR spectrum gives us a wealth of information about the detail reaction dynamics of the system, not just the chemical reaction chemical reaction often very simple.

One does not need this set of technique to establish that. But the power of this is that it gives insight into the detail evolution of the spin system, and the chemical dynamics if you want to call it. That is, starting from here how it goes to the singlet state or a triplet state and then whether the interstitial crossing is fast enough or not reaction is taking place at the comparable rate or not. I may not be able to measure most of the properties. But I can make a firm conclusion by looking at the spectrum which looks like this, or which looks like this. So, all these are the power of this experimental observation and the mechanism which most definitely play say something about the photo physical process and photochemical processes, and their relative rates of evolution that are all built into this appearance of the spectrum. And that is not a very trivial conclusion.

Most of the time interstitial crossing rate are so fast that it is very difficult to measure them. And EPR spectroscopy here is very slow in that sense. It looks at signal in the time scale of 100s of nanosecond. By then everything is over. It just so happened the relaxation time of the radicals which are that is of a few microsecond, maintains the history of the evolution of the spin system.

So, all these detailed interactions which eventually produce the radicals which are free from each other, they have been sort of maintained as a memory and the EPR spectrum reveal this history of the evolution of the photo physical and photo chemical nature of this particular chemical reaction. So, that is what the power and beauty of this technique is that is all.