Principles and Applications of Electron Paramagnetic Resonance Spectroscopy

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Lecture - 20
Electron Spin Polarisation - 1

Today we are going to see how the EPR spectra recorded when the radicals are just created by a pulse laser light, and how they differ from the steady state EPR spectra, and what can you learn about the mechanism of the radical production.

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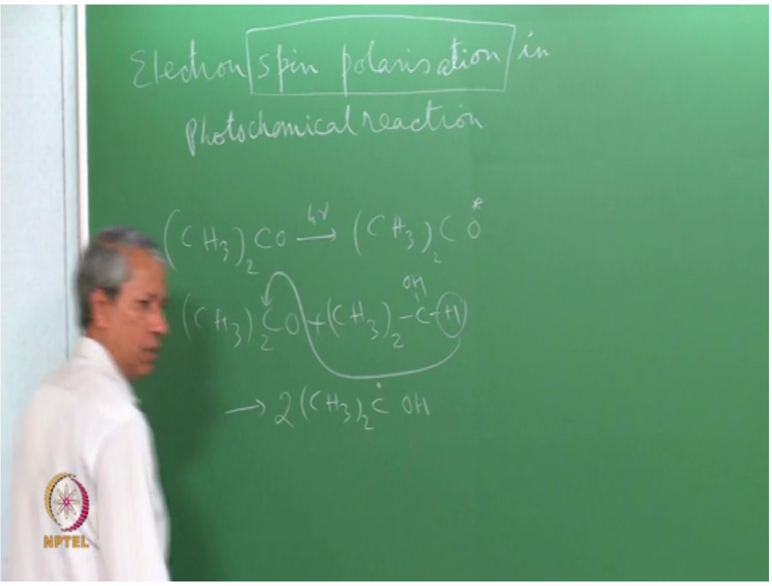

So, here broadly the theme will be electron spin polarisation in photochemical reaction before you understand what is the meaning of this term is let see some example.

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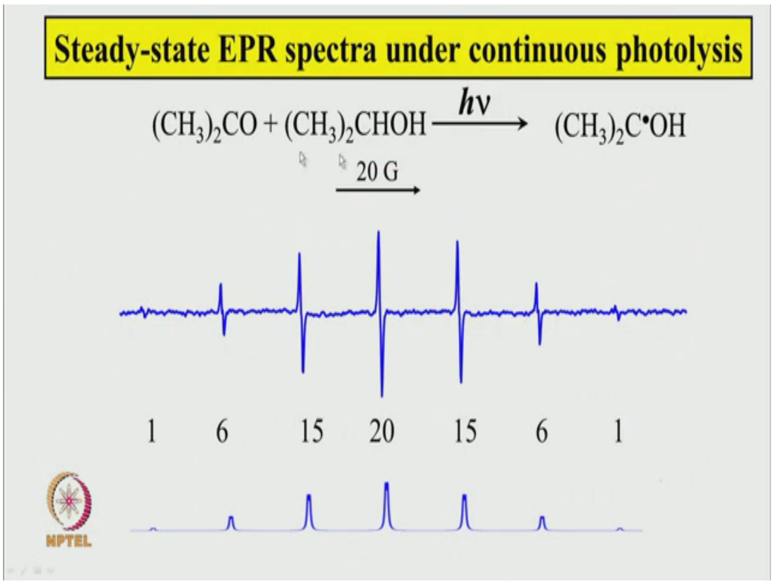

Steady-state EPR spectra under continuous photolysis

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

So, here the Steady-state EPR spectrum of this particular system is shown here there have acetone mixed with isopropanolas solvent and we shine UV light and then light is on all the time we record the EPR spectrum the way normally we do this is the steady state EPR spectra recorded under continuous photolysis this spectra look like this and from the intensities of this various hyperfine lines we can definitely attributed it to this radical.

So, the chemical reaction is this absorbs light. So, this must to be going to the excited state and in that excited state some reaction is taking place this is the isopropanol in the radical that is see here this radical, this protons give a the major 7 lines EPR spectrum and this little splitting comes from this proton here. So, here the reaction is that this hydrogen atom gets Trans extracted by this to produce these 2 radicals of this kind.

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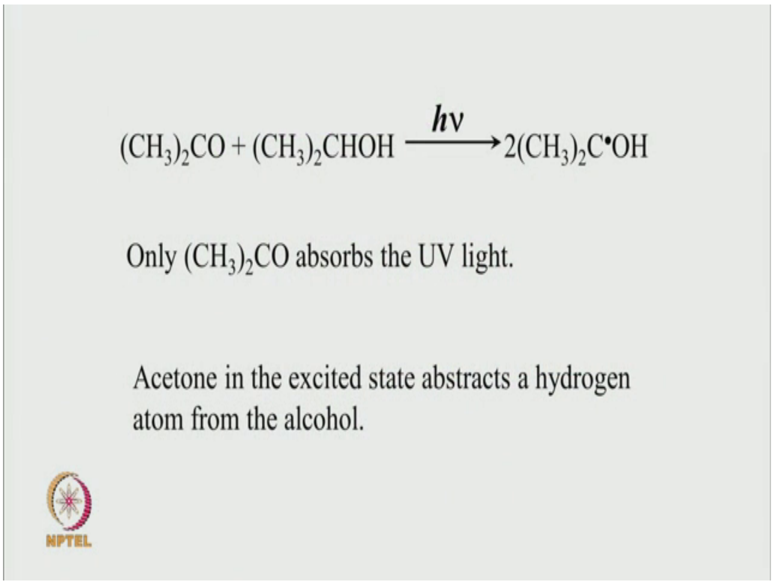

$$(CH_3)_2CO + (CH_3)_2CHOH \xrightarrow{h\nu} 2(CH_3)_2C^{\bullet}OH$$

Only $(CH_3)_2CO$ absorbs the UV light.

Acetone in the excited state abstracts a hydrogen atom from the alcohol.

Now, this is the overall reaction acetone is excited by the light and it abstracts a hydrogen atom from the alcohol.

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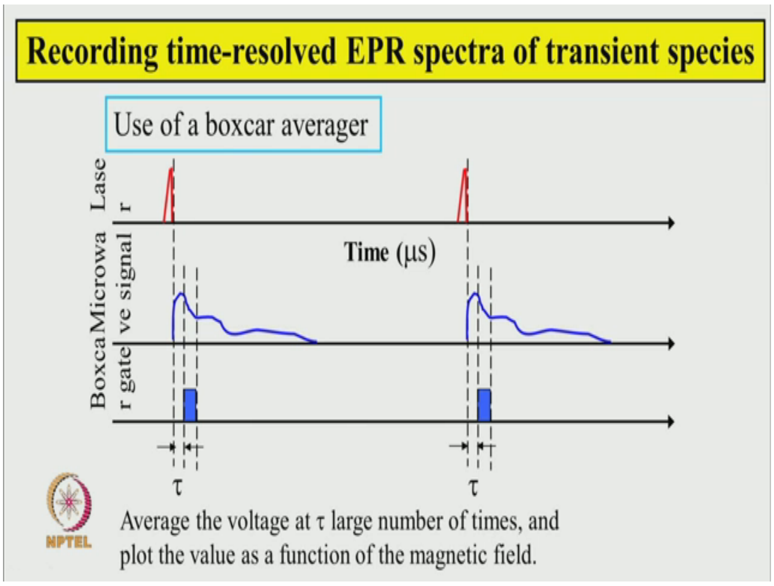

Recording time-resolved EPR spectra of transient species

Use of a boxcar averager

Average the voltage at τ large number of times, and plot the value as a function of the magnetic field.

Now do get the EPR spectrum of this radical just at the time they are created by a laser light we have a pulse laser which repeat it again and again as we look at the microwave signal and try to get the snapshot of the voltage at a given time after the laser pulse. And then average this voltage after every laser pulse to improve the signal to noise ratio is in a boxcar average.

So, you get a spectrum that will be characteristic of whatever it is at a given time after the laser pulse. So, we call this the time result EPR spectrum of the transient species.

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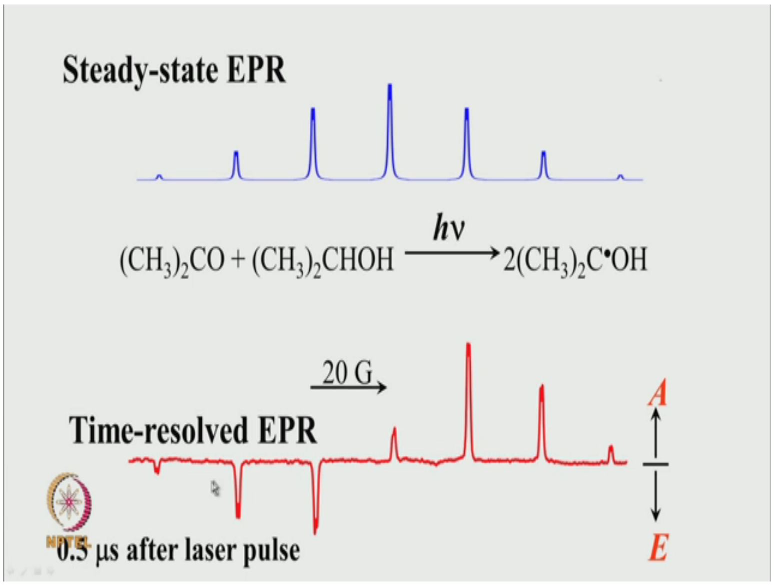

Steady-state EPR

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

Time-resolved EPR

0.5 μs after laser pulse

Now that is way the comparison between steady state EPR spectrum under continuous photolysis and this is the time resolved EPR spectrum under pulse laser light the second one was recorded at a time 0.5 micro, second after the laser pulse an one can see that the line positions are matching perfectly well that is we are getting the same radical here, even in the nothing new is happening. So, far the chemistry is concerned photochemistry is same, but the EPR spectra are quite different.

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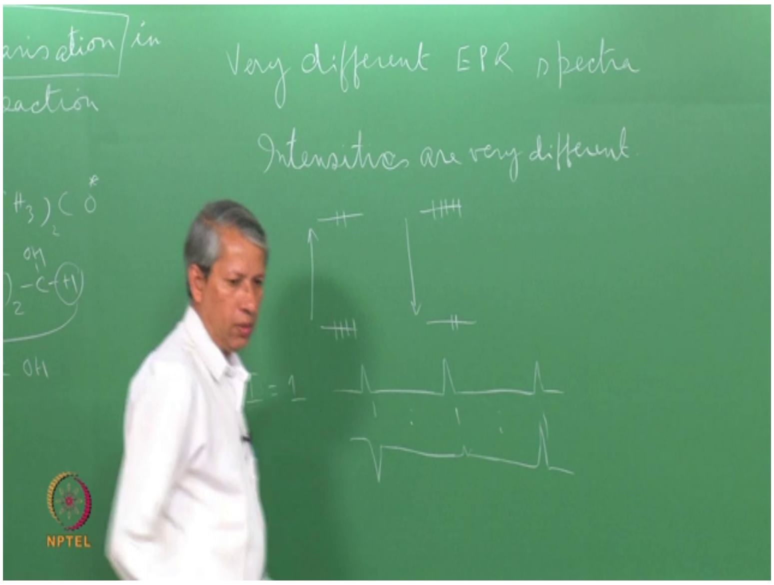

When I do the experiment in the time resolved fashion different in what sense spectrum is actual the coming from the same radical it is the same thing happing there.

So, the line positions are the same only the intensities are very different that is important that it does not produce any different radical; radical is same we only get different intensities and that intensities are very difficult understand from the way we have understood the EPR spectrum that they must follow then usual Pascal triangle type of intensity ratios among the various hyperfine lines or similar type of relative intensity ratios.

So, this spectrum shows that some levels are getting selectively populated some levels of Zeeman spirit line. So, this particular transition involves pair of Zeeman line this involves some other pair of Zeeman line that depends on the nuclear spin state. So, some are populated more than other sometime you needs other round. So, if I set up the spectrum properly to get the absorption spectrum in this fashion the way signal goes off that is then these lines are showing absorptive signal and these lines are showing opposite of absorption and now opposite of absorption means what it has to be only emissive in nature and that is very unusual, because the normal distribution of spins in a pair of Zeeman level will be this is more and less here.

So, we get a negative absorptive signal in this kind. So, when you see emissive signal which mean downwards means this levels are more populated than this one that is the only way one can explain this observation.

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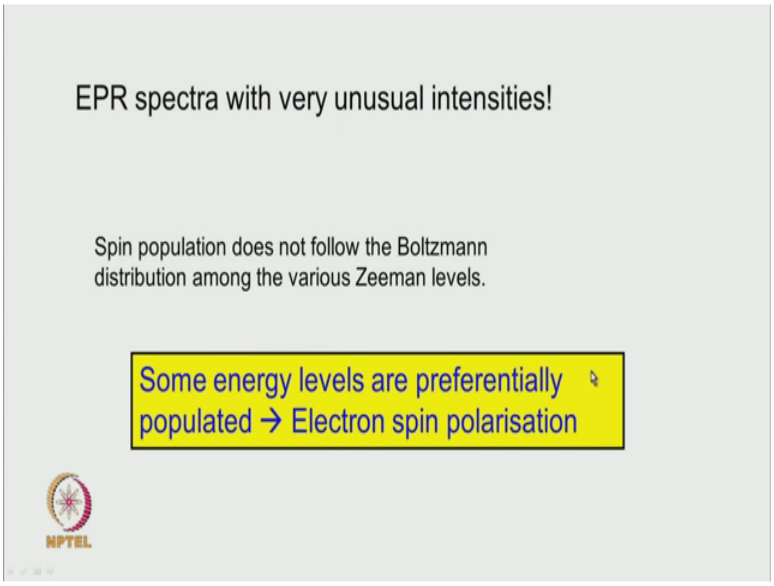

EPR spectra with very unusual intensities!

Spin population does not follow the Boltzmann distribution among the various Zeeman levels.

Some energy levels are preferentially populated → Electron spin polarisation

So, we call this type of radicals which are produced in a selectively populated spin states or we call it electron spin polarise state, there is this some levels are selectively populated electron spin polarisation is the phenomenon we are observing here and therefore, the spin populations at different Zeeman level do not follow the Boltzmann distribution.

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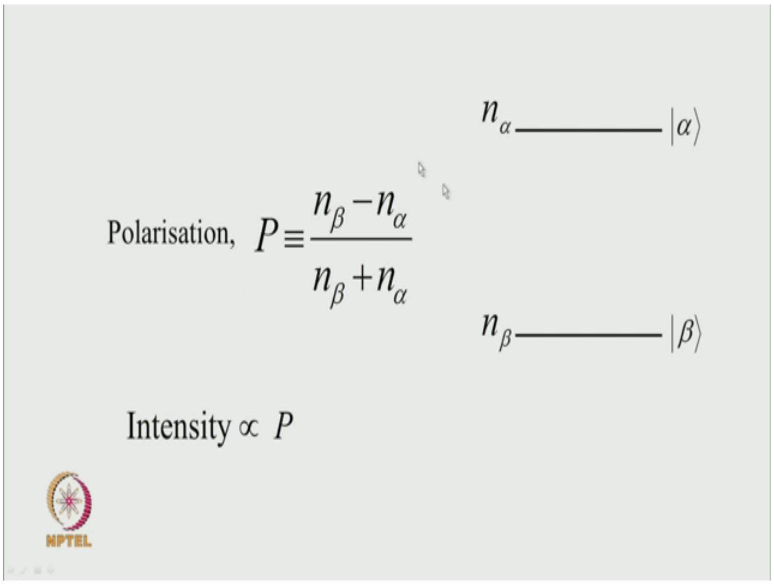

Polarisation, $P \equiv \dfrac{n_\beta - n_\alpha}{n_\beta + n_\alpha}$

Intensity $\propto P$

So, then we can define a quantity called polarization which defined as a number of spins in the beta level and number of spin alpha level n alpha and n beta, then this the way we can define the polarization n beta minus n alpha by the total number of spin the advantage of this is that the EPR signal intensity depends on see among other things the population difference if these 2 are equal we will not get any signal. So, intensity is proportional to the polarization. So, when polarisation is positive I get need to absorptive signal and polarization is negative I can get emissive signal.

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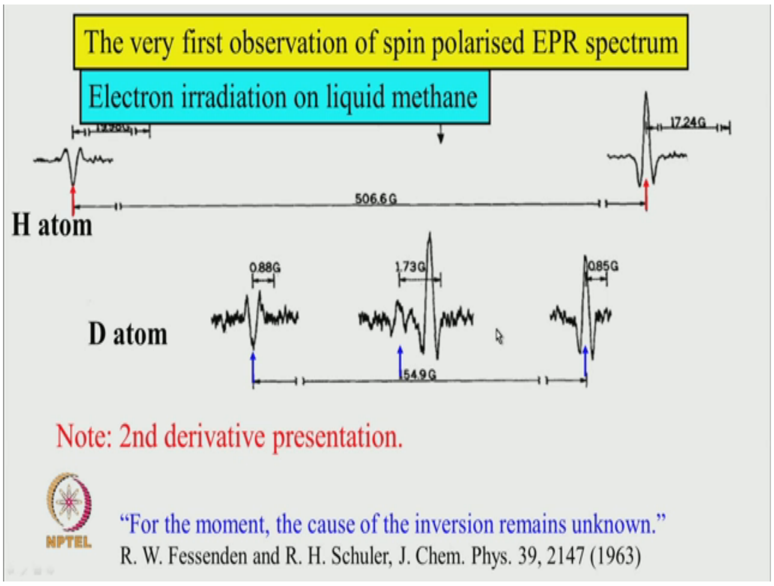
The very first observation of spin polarised EPR spectrum

Electron irradiation on liquid methane

Note: 2nd derivative presentation.

"For the moment, the cause of the inversion remains unknown."
R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 39, 2147 (1963)

Now, the first time such signal was seen was way back in 1963 when this 2 scientist Fessenden and Schuler were actually irradiating liquid methane by an electron pulse, I suppose that this electron beam was breaking this molecule and producing hydrogen atom and what they saw here is a 2 lines hydrogen atom one is here other is there they have exactly opposite phase, please note that these are not the first derivative EPR signal they are second derivative EPR signal.

So, when you going down and here hyperfine line going up as exactly opposite phase is normally hydrogen atom should give 2 lines at a distance of let us say 500 and 9 gauss or so here the intensities this kind. That means, the population is exactly opposite for this pair of transition they even did experiment with deuterium methane. So, that they could produce deuteron atom and deuteron atom has nuclear spin of 1.

So, if I equal to 1 this should give 3 intense line of this equal intensity with a relative intensity of 1 is to 1 is to 1 instead what they found was that this is negative this intensity is not very big and this is the opposite 1 here. So, this is negative intensity this is positive, but small this is the more positive one this is something else.

So, this is the first observations something unusual was happening and they wrote in their paper that “For the moment the cause of the inversion remains unknown”, people probably did not pay much attention, but soon similar observation was seen in a N M R experiment the only dif condition was that when some N M R signal of a reacting system was recorded one could see such unusual signal this are observed emissive signal appear there will see some example soon. Before that I like to point out that one does not necessarily have to go to time resolved EPR experiment even in steady state also one can see similar behaviour.

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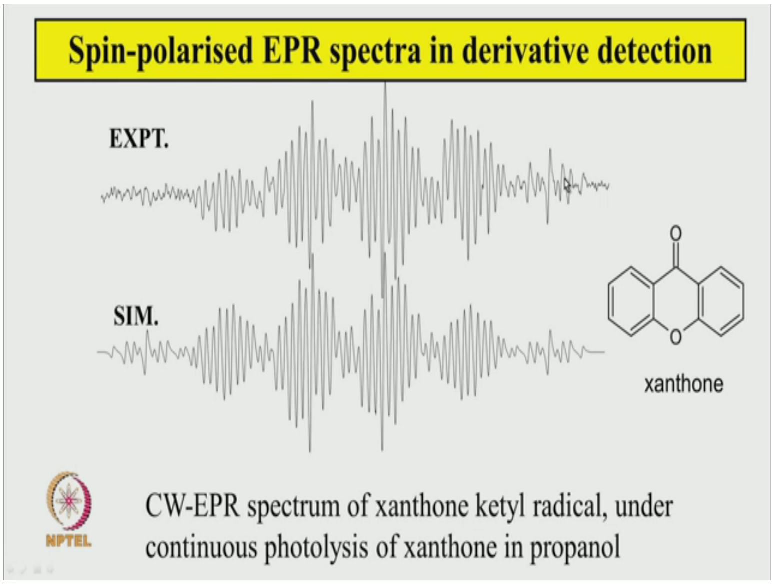

Spin-polarised EPR spectra in derivative detection

CW-EPR spectrum of xanthone ketyl radical, under continuous photolysis of xanthone in propanol

Here this is the xanthone molecule and it is continuous photolysis was done in isopropanol and this is the steady state spectrum you can see the derivative lines here.

Now, but the way the intensities are you can compare with the expected spectrum the similarly spectrum that see this bunch of line is sort of matching with this one, but corresponding bunch of lines absolutely not seen when they varied in the noise level in other words left to right symmetries lost here. So, intensity goes down on this side from right to left which is not consistent with or EPR spectrum that we discussed as a first order spectrum where it will be perfectly symmetric from middle to outside.

So, here the intensities are more on the high field reason than low field reason therefore, it also means that some lines are not following Boltzmann distribution.

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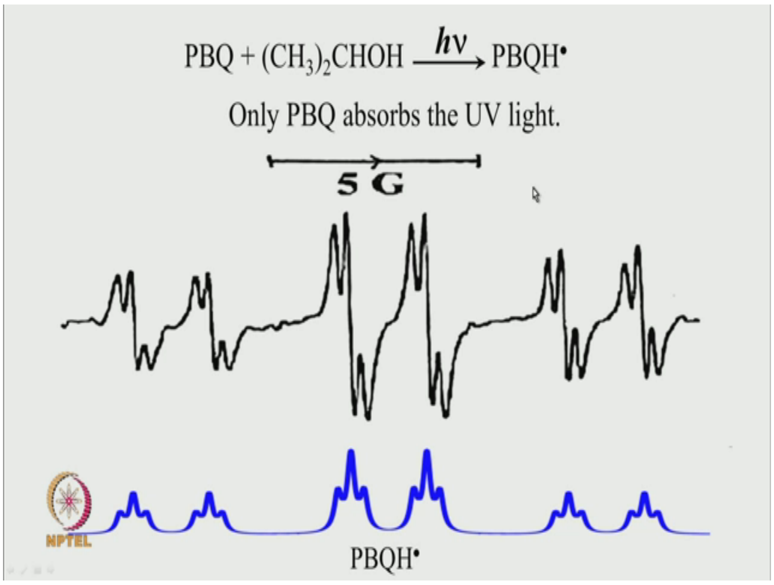

$PBQ + (CH_3)_2CHOH \xrightarrow{h\nu} PBQH^\bullet$

Only PBQ absorbs the UV light.

Here is another comparison when a steady state EPR and time resolved EPR Para benzoquinone photolysis in isopropanolin a steady state UV light. So, one can get the EPR spectrum of this kind and this is the radical that we have attributed to this radical.

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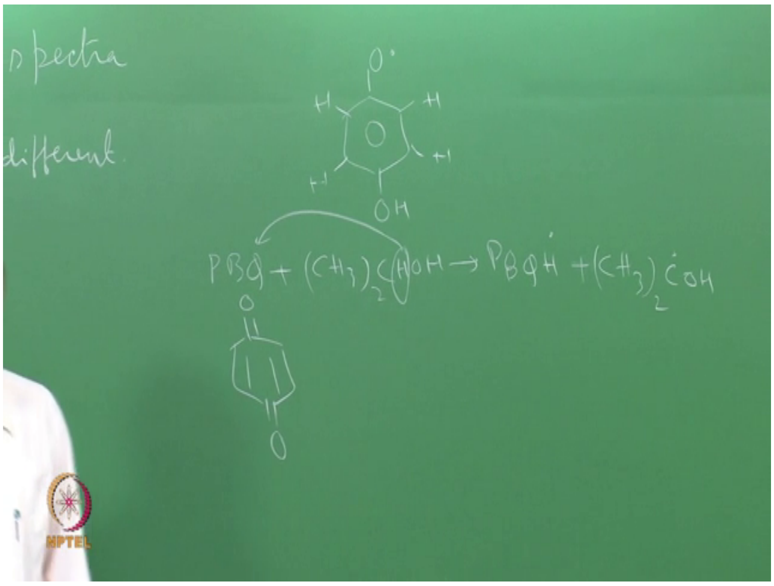

And the reaction on this is Para benzoquinone plus isopropanol gives this Para benzoquinone radical that is what is seen here, let say that is what you say we do not what else is forming there is no evidence of any other signal in the spectrum. So, here again this Para benzoquinone structure is this and if this is a radical is formed there then this is abstracting hydrogen atom from the solvent and producing this radical alright.

Let us see now time resolved spectrum of this one here.

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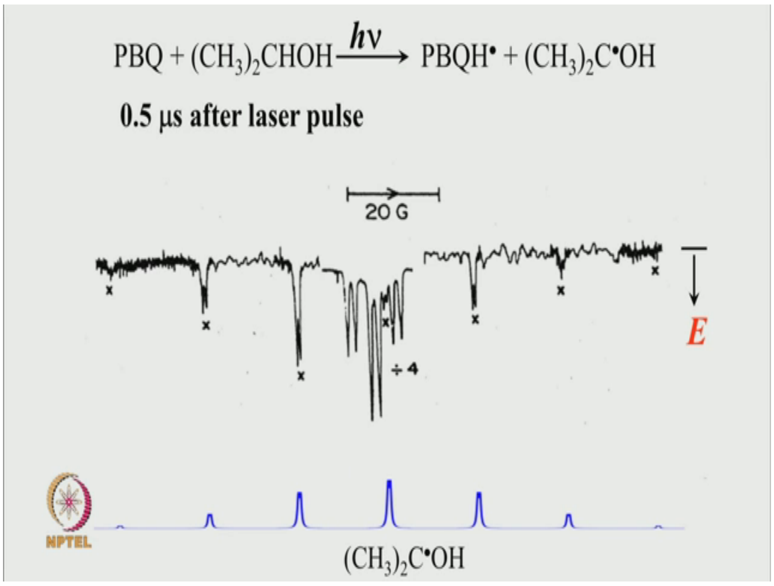

$PBQ + (CH_3)_2CHOH \xrightarrow{h\nu} PBQH^\bullet + (CH_3)_2C^\bullet OH$

0.5 μs after laser pulse

It is the same experiment is done in the time resolved fashion and this spectrum that is seen here is recorded after 0.5 micro second after the laser pulse. So, here this lines which are marked with a little symbol here, they actually match with the spectrum of this radical CH 3 whole 2 C OH they here little here this is not seen, but one could presumably believe that partner of this must be here. That means, this time resolved spectrum shows that the other radical is this one and steady state spectrum did not show this. And this doublet and this doublet they are the 3 doublet corresponding to here this radical here notice the scale here this much is 5 gauss then here this much is 20 gauss naturally it is com compressed here.

So, first thing is that time resolved EPR spectrum gives evidence of presence of both the radicals, but that is not. So, interesting part is that the appearance of the signal all the lines are in the downward phase; that means, all the lines are appearing in the emissive fashion, that is where the main difference between this system and this system. So, something unusually different in the 2 cases even though the chemical reaction is the same this hydrogen atom goes from here to there here also I could write that this hydrogen atom goes from here to this to produce this radical. So, chemically there is no difference there is some difference in the way the spins are populated in the 2 cases just to show that indeed this lines are coming from the semi Quinone radical.

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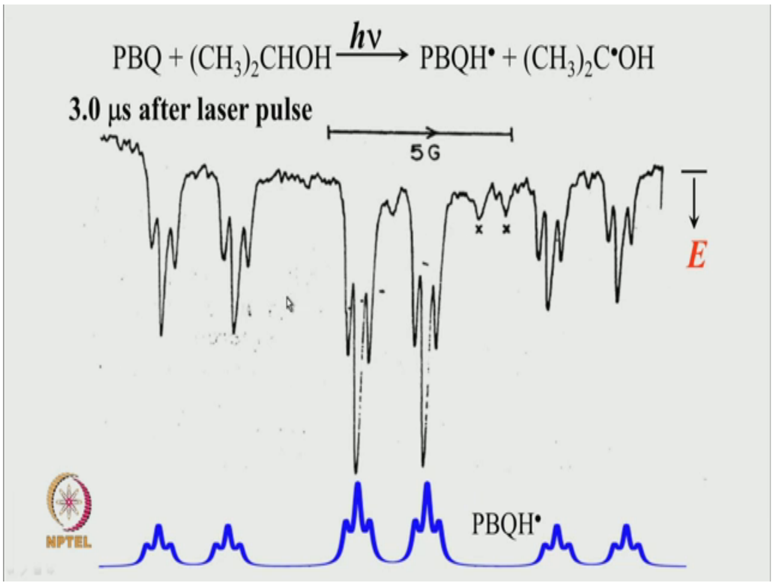

$PBQ + (CH_3)_2CHOH \xrightarrow{h\nu} PBQH^{\bullet} + (CH_3)_2C^{\bullet}OH$

3.0 μs after laser pulse

This is the region expanded and you can see clearly that that matches exactly well with the spectrum due to this.

Now, I said earlier that when this first 1963 observation of Fessenden and Schuler on hydrogen atom given this 2 lines in that this opposite fashion many people may not have paid any attention.

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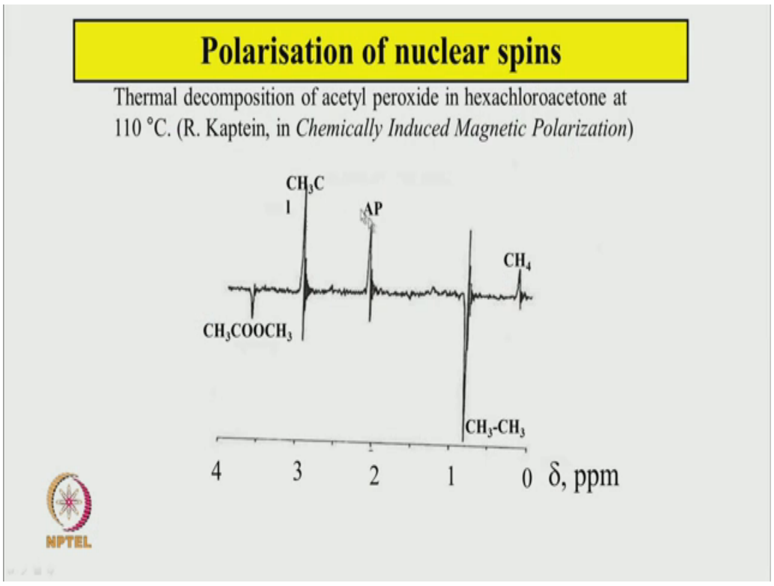

Polarisation of nuclear spins

Thermal decomposition of acetyl peroxide in hexachloroacetone at 110 °C. (R. Kaptein, in *Chemically Induced Magnetic Polarization*)

But now later early sixties N M R experiment showed lots of such signal here let see one of them, this is the N M R spectrum of this chemically reacting system where acetyl peroxide is reacting with this solvent here. Peroxides are known to breakdown whenever they are heated and then they undergo some chemical reactions you now see here this is ethane this is CH 3 C l l has come here.

So, either so spectrum here is all going up these are going down. So, these are absorptive signal these are absorptive signal, but this signal from this molecule and from this signal this molecule they are coming in the opposite sense they are emissive in nature another example.

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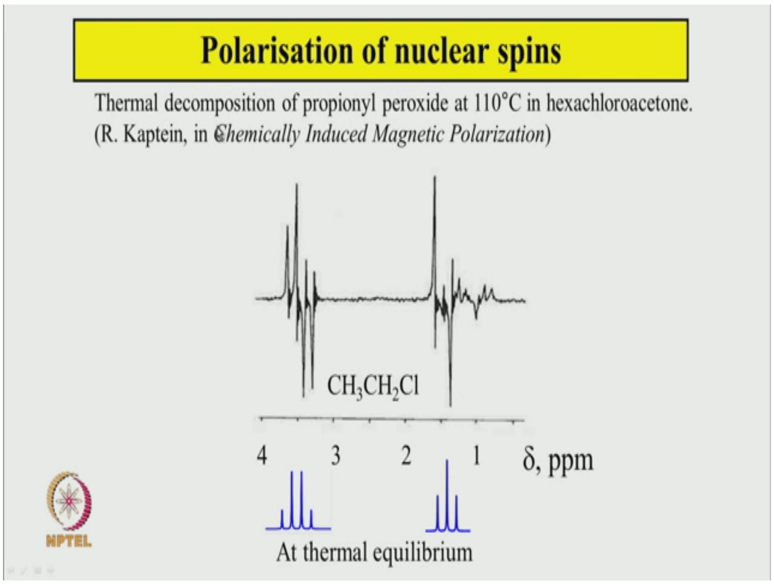

Polarisation of nuclear spins

Thermal decomposition of propionyl peroxide at 110°C in hexachloroacetone.
(R. Kaptein, in *Chemically Induced Magnetic Polarization*)

Here, thermal decomposition of propionyl peroxide in hexachloroacetone when it is heated propionyl peroxide breaks down and it does some chemical reaction to produce ultimately this molecule here; CH 3 CH 2 C l, CH 3 CH 2 C l the N M R spectrum of this is should be very simple to predict.

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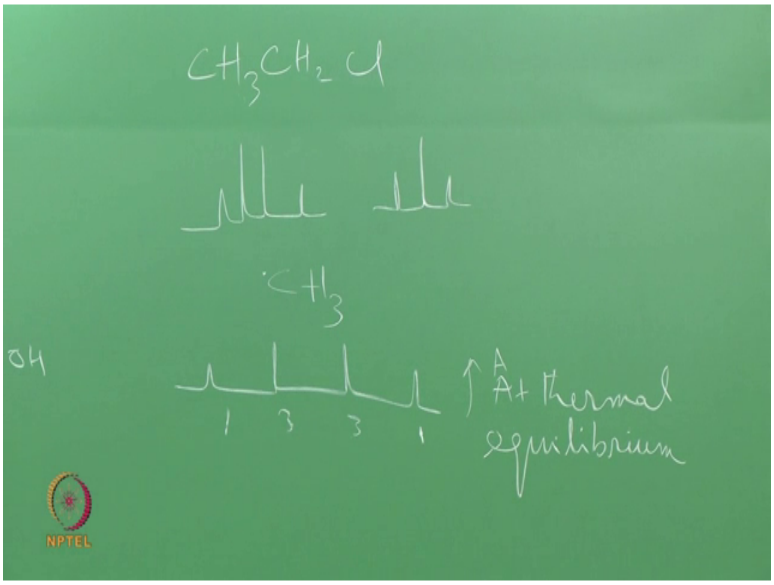

So, this there are 3 protons here 2 protons there. So, this will be split into quarter due to this and this will be split into triplet due to this one. So, this type of thing other will be this type of thing N M R spectrum is expected there.

Now, what is seen here is quite different. So, this is the expected N M R signal from arising from this CH 2 protons for what it is what appears here the first 2 lines are absorptive or other 2 lines are emissive and here for the triplet this line is absorptive this line is emissive and middle line is almost 0 intensity. So, nuclear that is indeed. So, then lots of such an experiment started appearing and then we will remember the years 1963 Fessenden and Schuler indeed saw the hydrogen spectrum appearing in the opposite phase then there lot of activities to understand why such things happening what is so special going on in such cases and one gets unusual N M R signal as well as EPR signal.

So, here selective population of varies nuclear spin levels are taking place here that is why some levels give positive signal and some other levels give emissive signal.

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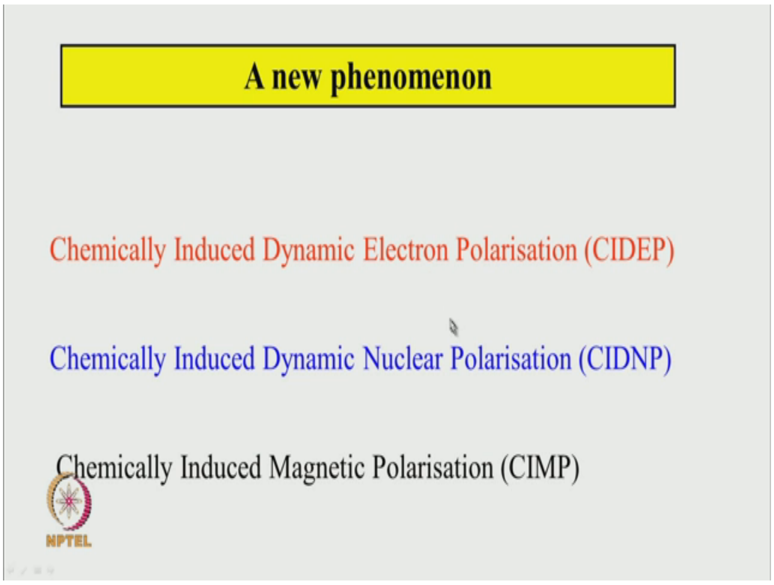

A new phenomenon

Chemically Induced Dynamic Electron Polarisation (CIDEP)

Chemically Induced Dynamic Nuclear Polarisation (CIDNP)

Chemically Induced Magnetic Polarisation (CIMP)

This new phenomenon was termed as chemically induced dynamic electron polarisation, for polarisation of electron spin and for polarisation of nuclear spin this is to be called chemically induced dynamic nuclear polarisation. Even now this terms are used by not they mean that the electron spins are polarised and they are in dynamic state in a sense that they do not stay there forever the electron spin lattice relaxes in process always tries to restore the Boltzmann distribution. Similarly in case of N M R spin also the N M R spin let us relaxation mechanism tries to restore the spin population to thermal distribution.

Now, since the early days almost all examples were seen to arise from chemical processes that are the either N M R signal was recorded for chemical reacting system or EPR signal was recorded at the time of creation of the radical. So, this used to be called chemical induced dynamic electron polarisation or chemical induced dynamic nuclear polarisation and a general term was given as chemically induced magnetic polarisation to which will be inclusive of both of this terms.

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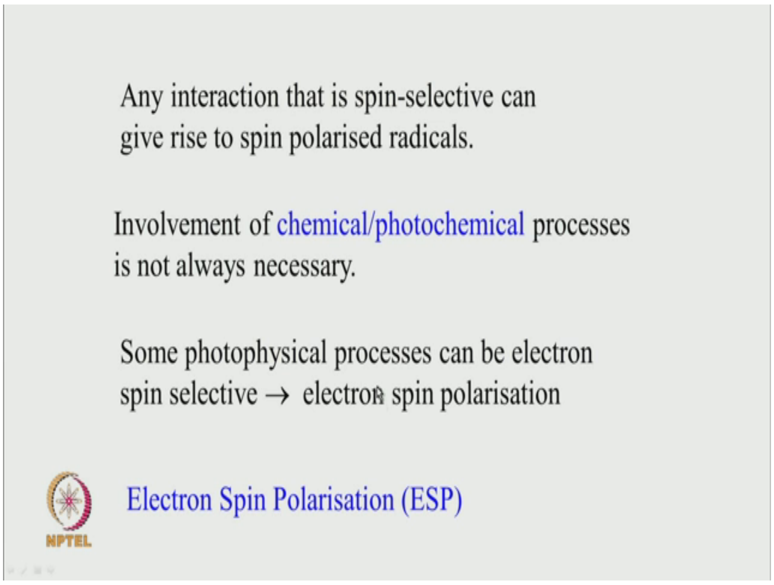

Any interaction that is spin-selective can give rise to spin polarised radicals.

Involvement of chemical/photochemical processes is not always necessary.

Some photophysical processes can be electron spin selective → electron spin polarisation

Electron Spin Polarisation (ESP)

And turned out that any interaction which is spin selective can give rise to spin polarised radicals and it was found out that involvement of chemical or photochemical processes is not always necessary, some photo physical processes can be also electron spin selective and they can give rise to spin polarisation.

So, then the new term was coined and it is called electron spin polarization or ESP. So, today we will going to learn how this set up electron spin polarisation arises.

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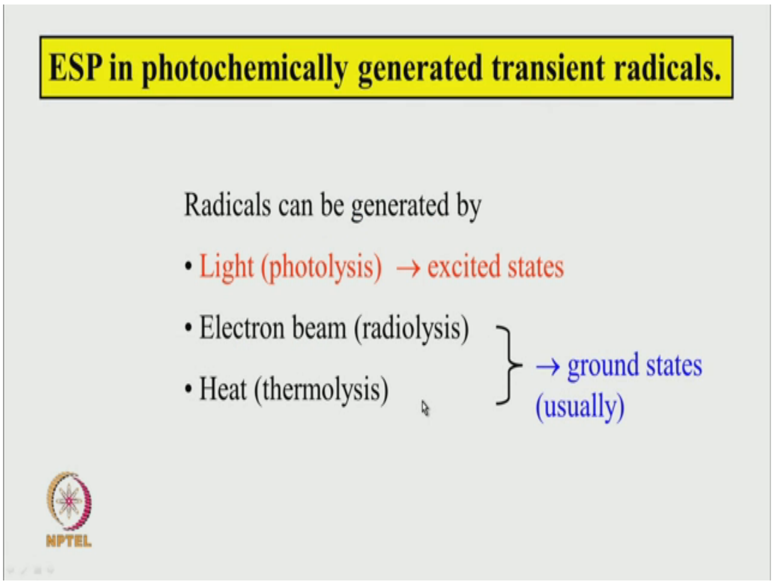

ESP in photochemically generated transient radicals.

Radicals can be generated by

- Light (photolysis) → excited states
- Electron beam (radiolysis)
- Heat (thermolysis)

} → ground states (usually)

ESP in photo chemically generated transient radicals. So, radical can be generated either by light they should bring the molecule excited state or it can be electron beam the way Fessenden and Schuler saw the hydrogen atom this involves radiolysis or one can heat the sample which will be thermolysis. Now in these 2 cases reaction usually takes place in the ground state in a excited state will be of course, a excited state if the light is involved.

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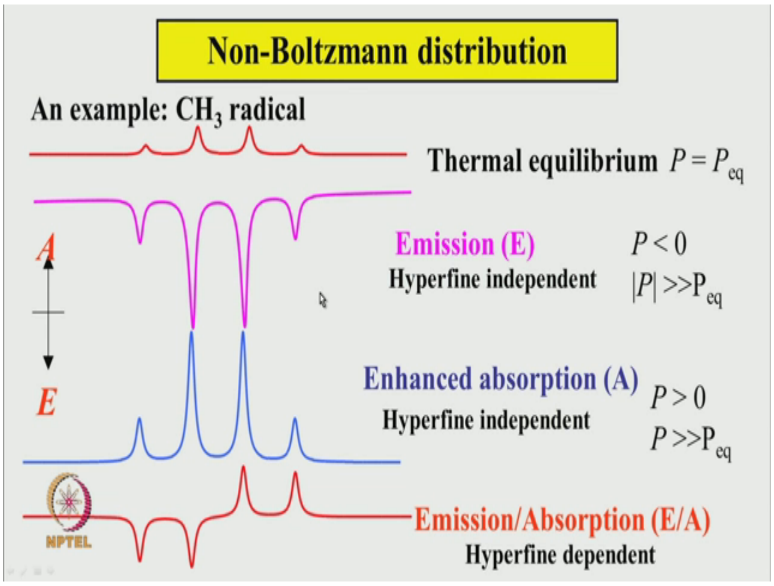

Non-Boltzmann distribution

An example: CH_3 radical

Thermal equilibrium $P = P_{eq}$

Emission (E) $P < 0$

Hyperfine independent $|P| >> P_{eq}$

Enhanced absorption (A) $P > 0$

Hyperfine independent $P >> P_{eq}$

Emission/Absorption (E/A)

Hyperfine dependent

Now, there is some general types of EPR signal that can appear let us take an example of methyl radical methyl radical EPR spectrum will be 3 protons. So, it will be looking like this 1 3 3 1 notice that I will be always drawing the EPR spectrum in this fashion either absorptive or emissive will not use derivative presentation because this experiment involves recording the spectrum using the direct method and that does not use any magnetic field modulation. So, I can get directly the appearance of the spectrum and from there I can decide whether it is absorptive or emissive.

Now, in a steady state condition whatever intensities of this lines are this will follow 1 is to 3 is to 3 is to 1, but actually intensity will depend on the Boltzmann distribution among the various hyperfine levels. So, this is the absorptive signal at thermal equilibrium. So, these are the possibilities that we can encounter one is that all the lines get inverted and intensity is much more than the steady state intensity. So, we say that P the polarisation is negative and value of this one magnetic wise much bigger than the equilibrium value of the polarisation and the otherwise this shape is exactly same as what is seen in the steady state mode. So, relative intensity is still 1 is to 3 is to 3 is to 1. So, we say polarisation is hyperfine independent this is the emissive nature other possibility is that I get absorptive polarisation, but P is greater than 0 at the same time P is much bigger than the equilibrium value. So, I get huge signal, but the relative intensities are such that they are same as the thermal population.

So, again this intensity distribution is hyperfine independent and third possibilities what I showed you for acetone isopropanol system they some lines are emissive other lines are absorptive. So, it could be emissive absorptive and emissive on the low field region and absorptive on the high field region and hyperfine dependent now. So, different hyperfine lines have different intensities it could other one also that low field lines are absorptive and high field lines are emissive. So, these are the various possibilities in general one can expect.

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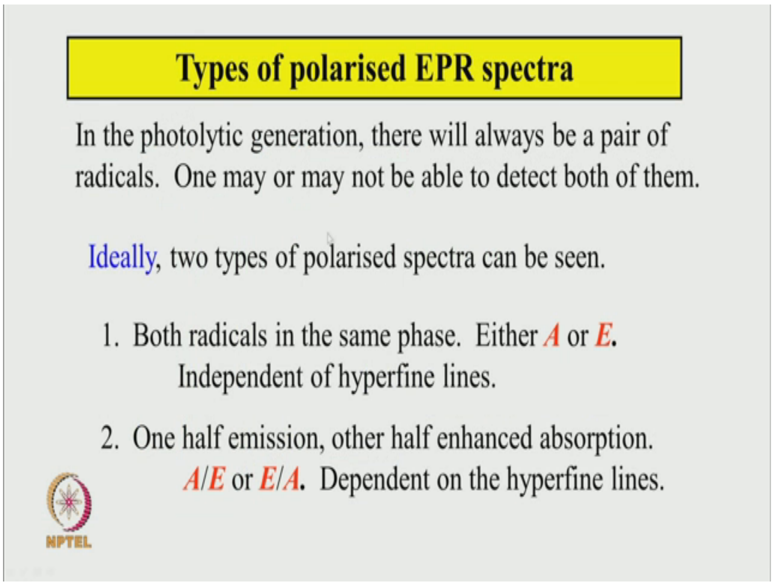

Types of polarised EPR spectra

In the photolytic generation, there will always be a pair of radicals. One may or may not be able to detect both of them.

Ideally, two types of polarised spectra can be seen.

1. Both radicals in the same phase. Either *A* or *E*.
   Independent of hyperfine lines.
2. One half emission, other half enhanced absorption.
   A/*E* or *E*/*A*. Dependent on the hyperfine lines.

What are the general themes we have seen? So, far is that 2 types of spectra can be seen one is that hyperfine independent polarisation here either emissive or absorptive one type of situation and second situation is one of emission other of enhanced absorption A E or E A depending upon the hyperfine line. And also thing which I may not have are turns is earlier is that any of this reaction what we have here or here the starting compounds are always in singular state diamagnetic state there is no unpaired electron.

So, when the reaction takes place there cannot be one radical there has to be 2 radicals produced at the same time. Otherwise you can get this set of radical formation from now here. So, is everything was singular state when a some either bond breaks or electron goes from one to the other there will always pair of radicals, what was seen here see that solvent radical the acetoneketyl radical and the semi Quinone radical both of the same sense of polarisation here both are emissive.

This is the summary is that in photolytic generation there will always be a pair of radicals one may or may not be able to detect both of them, but whatever it is one radical may be more reactive than the another, but there always be 2 radicals produced at the same time and the 2 type of polarisation that we have seen here if both the radical in the same phase either both are absorptive or emissive independent of hyperfine line or one half emission other half enhanced absorption either A E or E A.

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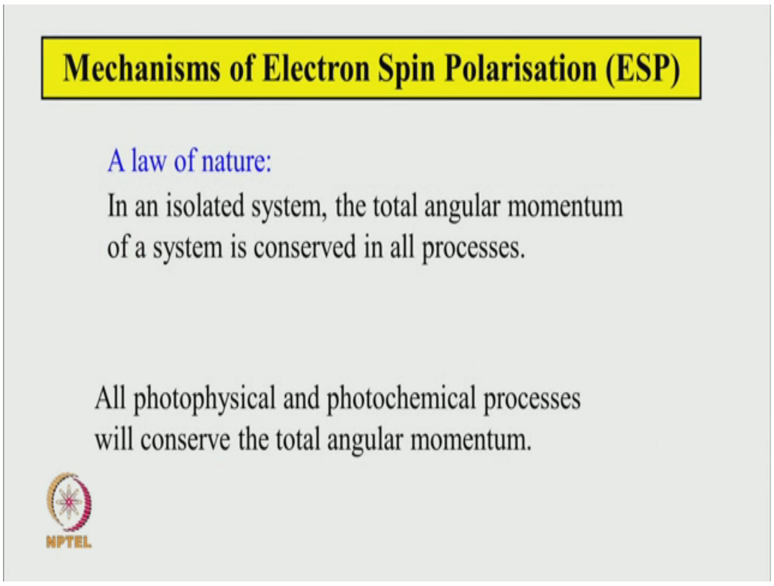

Mechanisms of Electron Spin Polarisation (ESP)

A law of nature:
In an isolated system, the total angular momentum of a system is conserved in all processes.

All photophysical and photochemical processes will conserve the total angular momentum.

This is the Background of observation. Now, let us can you understand why this signals are appearing in this fashion. So, what are the mechanism of electron spin polarisation. So, we make a few key I would not say assumption, but except the laws of nature without questioning because they are. So, fundamental that they are always supposed to be true one of them is this in an isolated system the total angular momentum of a system is conserved in all processes. So, that there cannot be any clear sign of distraction in angular momentum out of nowhere there has to be somebody to do that.

So, all photo physical and photochemical processes will conserve the total angular momentum. So, we take it to be a fundamental law nature and see how much you can progress based on this.

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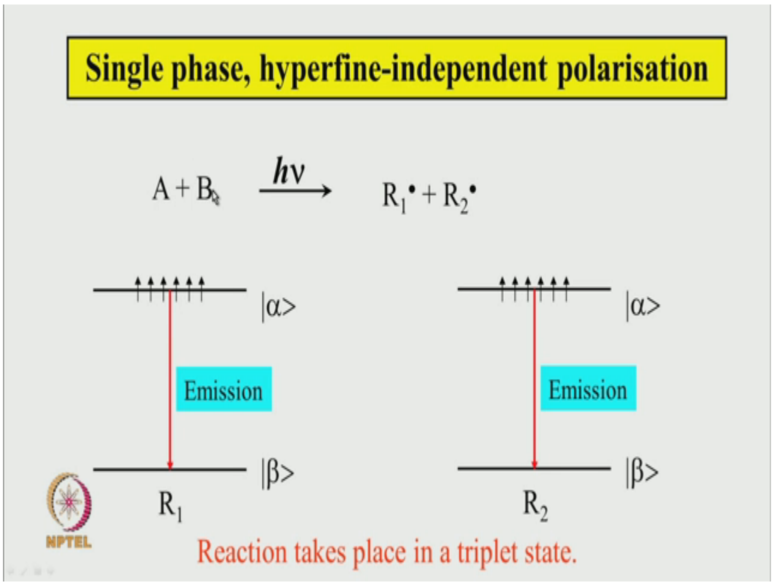

Single phase, hyperfine-independent polarisation

$$A + B \xrightarrow{h\nu} R_1^\bullet + R_2^\bullet$$

Reaction takes place in a triplet state.

Let us first consider this mechanism single phase hyperfine-independent polarisation where the example was the Para benzoquinone reacting in isopropanol giving rise to these 2 radical here, this give emissive spectrum this also give emissive both are in emissive phase this is single phase hyperfine independent polarization. So, we can just symbolically write that instead of this particular reaction let say I have got A and B molecule reacting in the presents of light producing radical number 1 and radical number 2 and both are in emissive polarisation. So, radical 1 therefore, this is got the 2 Zeeman level upper level is mostly populated. So, that it gives emissive signal radical 2 again upper level is mostly populated compared to lower level. So, this also gives emission.

So, then all the electrons are paired when A and B were in a ground state and the and the radicals are formed you see suddenly that radical one has alpha spin state now radical 2 has also alpha spin state. So, here all electrons appear and suddenly these 2 radicals have 2 electron unpaired. So, everything paired in the beginning and then these 2 are unpaired also parallel to each other both are alpha spin how is it possible apparently there is this law of conservation of angular momentum is breaking down; so there something interesting going on there.

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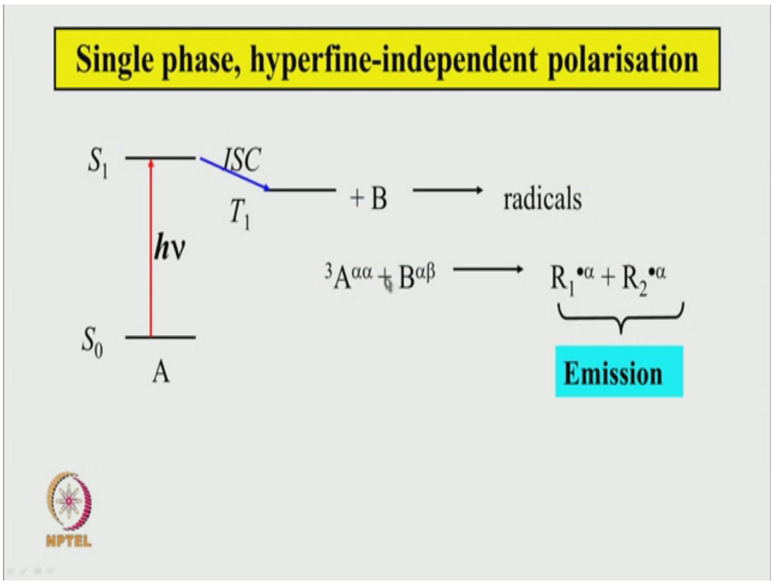

Single phase, hyperfine-independent polarisation

So, if we go back now from this radical one step backward that molecule A that let us say absorbs light goes to A excite state S 1.

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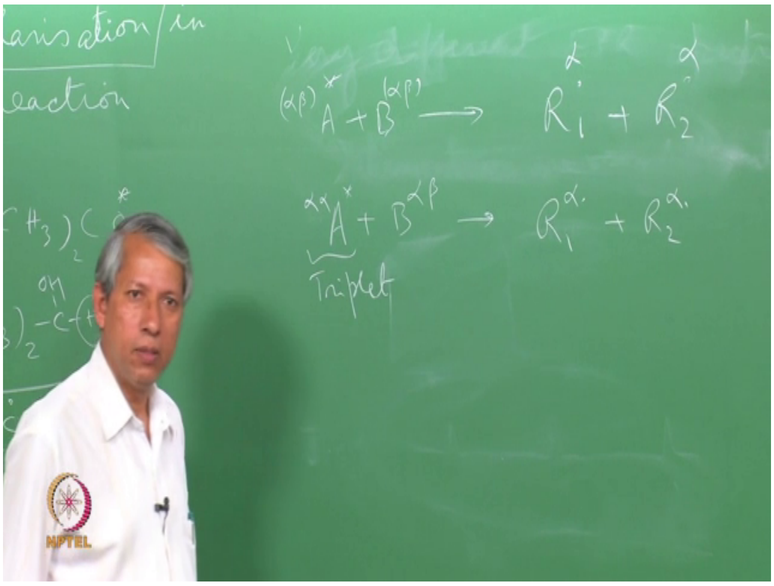

With this scheme we are starting with from the observation our observation is that this has got alpha spin state this also alpha spin state. So, if the reaction A or only A Absorbs light and it will goes to excited state and reaction takes place there. So, if the reaction is the singular state of this one while it is say all spins are paired and here of course, all spins are paired then if just cannot produce a pair of radical with parallel spin. So, this is therefore, singular state cannot react to produce this one the important conclusion one can try immediately how about triplet state now how was A is in the triplet state triplet state what shall I write here I will write in a moment. So, triplet state these being alpha and alpha it is not difficult visualise the this could also be alpha alpha that is this one of the triplet then the angular momentum in terms of the number of spins that are unpaired is perfectly satisfied.

So, we can therefore, develop our reaction scheme in this fashion that it is now the singular state of a that is reacting it is the triplet state that is reacting and triplet particularly not all the 3 triplet level, but only triplet a with alpha alpha spin state. So, then reaction is B and produced 2 radicals A and B everything is conserved here and both of them come in the emissive polarised state.

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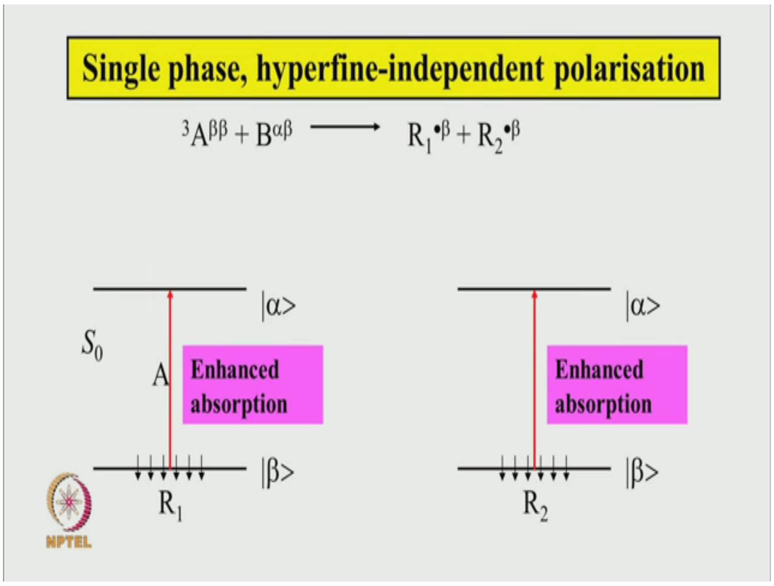

Single phase, hyperfine-independent polarisation

$$^{3}A^{\beta\beta} + B^{\alpha\beta} \longrightarrow R_1{}^{\bullet\beta} + R_2{}^{\bullet\beta}$$

So, similarly if the triplet beta reacts, excited state triplet also, I will get a radical one which is I have beta spin state radical 2 will also beta spin state.

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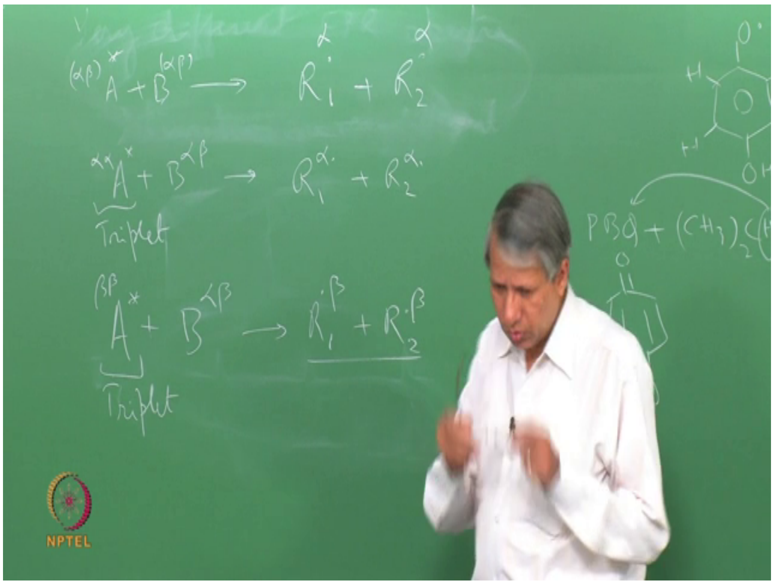

So, this will give a polarisation which will be seen in the form of enhanced absorptive signal for radical A and radical B. So, this is the mechanism which must be taking place to produce polarise signal in this case. So, you see that how the involvement of various now photo physical processes are necessary to have this in a polarised spectrum here turning it other round how much you can learn about the involvement where photo physical processes when you see EPR spectrum of this kind.

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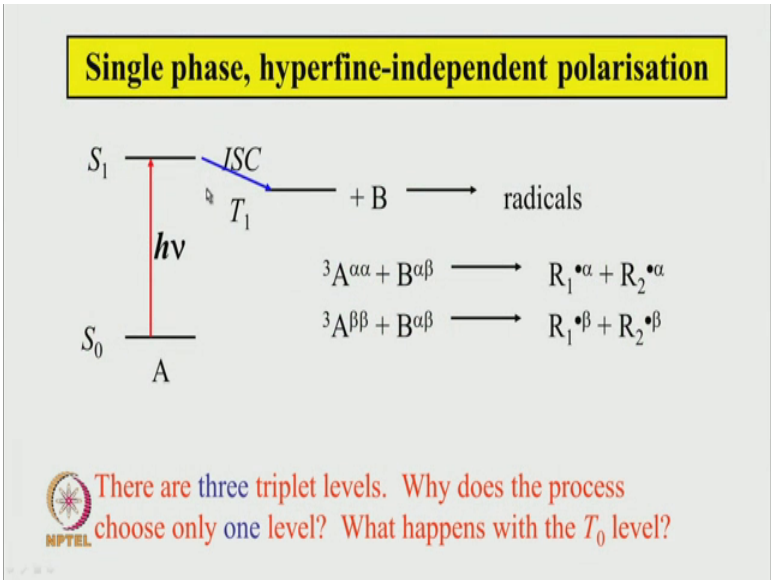

Single phase, hyperfine-independent polarisation

$T_1 + \text{B} \longrightarrow$ radicals

$^3\text{A}^{\alpha\alpha} + \text{B}^{\alpha\beta} \longrightarrow \text{R}_1^{\bullet\alpha} + \text{R}_2^{\bullet\alpha}$

$^3\text{A}^{\beta\beta} + \text{B}^{\alpha\beta} \longrightarrow \text{R}_1^{\bullet\beta} + \text{R}_2^{\bullet\beta}$

There are three triplet levels. Why does the process choose only one level? What happens with the T_0 level?

Now, the triplet level as a the name suggest there are 3 levels present there, now why does only one level react for example, to give a emissive signal only one of them is reacting here not all why not all 3 of them, why does the process choose only one level also, what happens with the T 0 level here the 2 extreme cases I said here is triplet of alpha alpha will produce 2 radicals the emissive phase if the beta beta reacting then this will produce 2 radicals in the absorptive phase enhanced absorptive phase. So, this question still remains to be answered.

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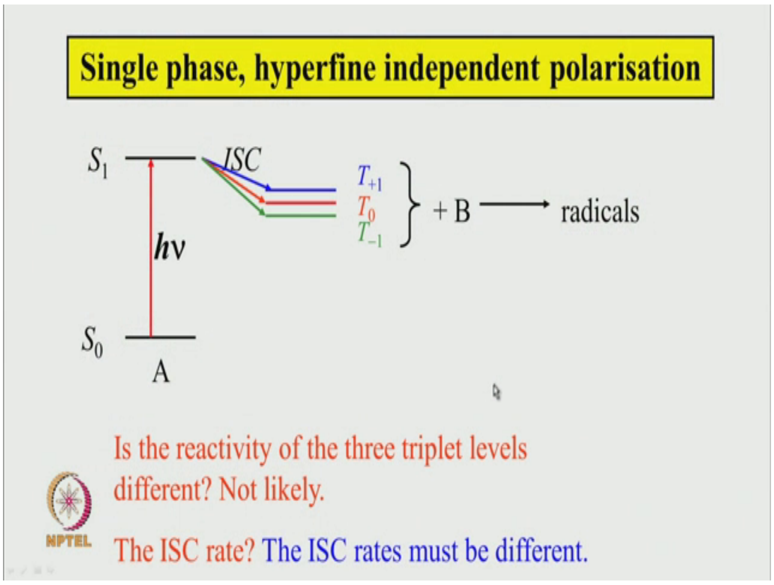

Single phase, hyperfine independent polarisation

Is the reactivity of the three triplet levels different? Not likely.

The ISC rate? The ISC rates must be different.

Here I have shown the 3 typical level since the since the experiments are carried out in the spectrometer in the presence of magnetic field one could write that the triplet state also will experience Zeeman interaction and T 1 T 0 T minus 1 will be 3 Zeeman spirit line of the triplet level. So, what is intersystem crossing process do is to bring this singlet excited state to this 3 triplet sublevels, but I the experiments shows there is only one of them reacting the T plus 1 state is reacting.

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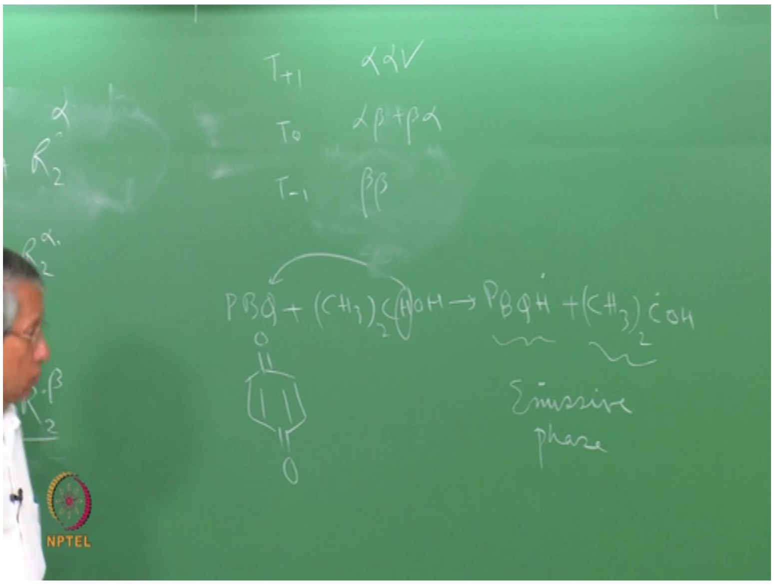

Here that spin states are alpha alpha beta plus beta alpha and beta beta the way the polarisation of these 2 radicals are the; this is the one which reacts.

So, is it likely that reactivity of the 3 triplet levels different that is not very likely why should the reactivity depend on whether it is T 1 T 0 T minus 1. So, that is not very likely reason then how about this intersystem crossing rate with the rates are different that could explain this behaviour that may be all 3 levels are not equally populated. So, we have (Refer Time: 33:58) may be the ISC rates are different for different triplet level.

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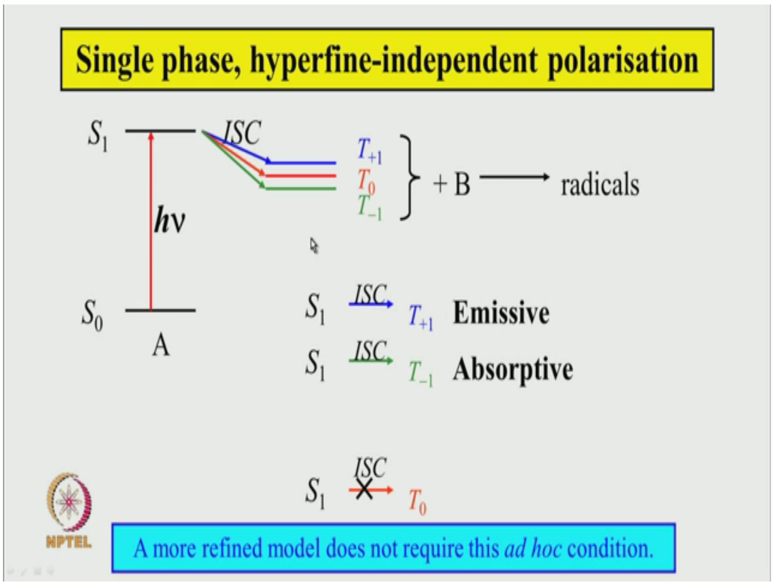

Single phase, hyperfine-independent polarisation

$S_1 \xrightarrow{ISC} T_{+1}$ **Emissive**

$S_1 \xrightarrow{ISC} T_{-1}$ **Absorptive**

$S_1 \overset{ISC}{\not\rightarrow} T_0$

A more refined model does not require this *ad hoc* condition.

See with that assumption one can justify the complete mechanism in this fashion that molecule A absorbs light go to singular state and intersystem crossing brings this molecule to triplet level, but not equally it bring selectively to one of the triplet level, may be dominantly to one of the triplet level and reaction takes place in all the 3 triplet us level, but the one which is got dominant population produces the radical.

So, if S 1 goes to T plus 1 state selectively then it gives emissive signal S 1 goes to T minus 1 state selectively it gives absorptive signal, but it goes to T 0 then what happens. Seems we are going to understand the whole mechanism in quality fashion we just state here that S 1 to T 0 just does not take place which is not rigorously correct and A much better model to which looks in to the detail intersystem crossing and the polarization in the 2 molecules will involve much more refined treatment.

So, then this ad hoc approximation is not necessary we will be satisfied with this one right that we get 2 types of spectrum either totally emissive or totally absorptive and they arrive because of this.

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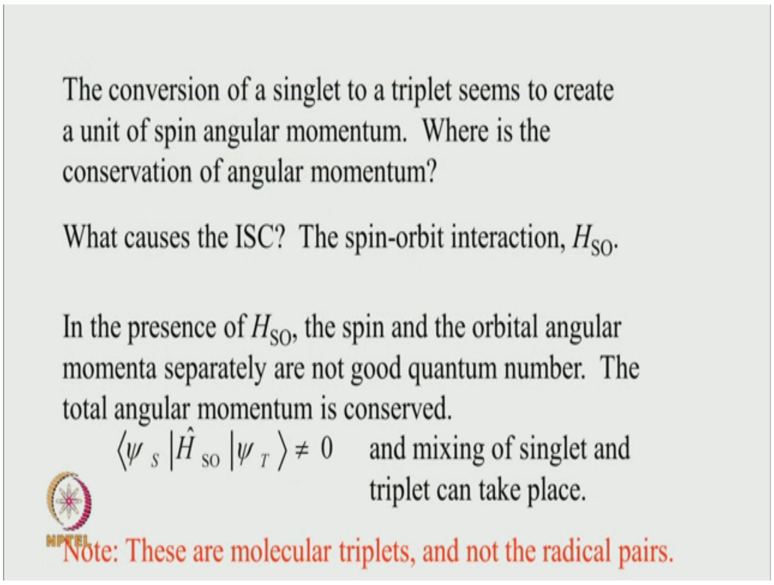

The conversion of a singlet to a triplet seems to create a unit of spin angular momentum. Where is the conservation of angular momentum?

What causes the ISC? The spin-orbit interaction, H_{SO}.

In the presence of H_{SO}, the spin and the orbital angular momenta separately are not good quantum number. The total angular momentum is conserved.

$\langle \psi_S | \hat{H}_{SO} | \psi_T \rangle \neq 0$ and mixing of singlet and triplet can take place.

Note: These are molecular triplets, and not the radical pairs.

So, the conversion of a singlet to a triplet seems to create a unit of spin angular momentum again we are back to some other problem now, we have been talking about the conservation of angular momentum, but when this process takes place S 1 to T 1 S 1 has no angular momentum spin angular momentum that is, but T 1 triplet has A 1 unit of spin angular momentum how is it created now what happened to the conservation of angular momentum rule. So, to understand that let us figure out what is causing the intersystem crossing process the perturbation is the spin orbit interaction equal H S O.

So, in the presence of spin orbit interaction the spin and the orbital angular momentum separately are not good quantum numbers the total angular momentum is conserved.

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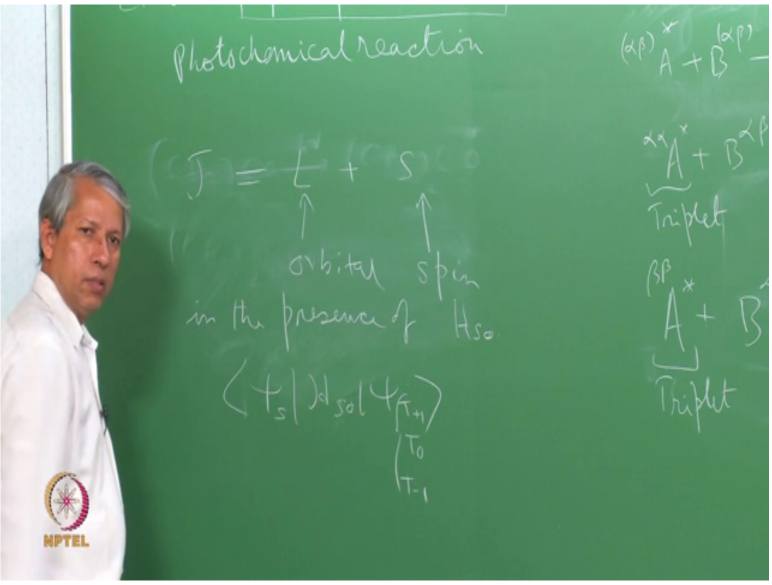

So, we have let say L and S this is the orbital and this is the spin angular momentum and this totally can equals to J in the presence of H S O. So, this is conserved not these and this individually. So, there is A clue to it is now that. So, when the intersystem crossing takes place in the presence of this perturbation then this singlet to psi triplet this may not to be same for all 3 triplet level whether I have got T plus 1 T 0 T minus 1 this might be depended on that that might explain why we get this selective population among the 3 triplet level, while just keep in mind this triplet us are the triplet of the first molecule which get excited for example, here that is the molecule which going excite state not the radical pair.

So, little more understanding will come if we try to see why this thing is possible that different level a triplet level may not be equally efficient in this intersystem crossing to take place. So, for that we have got triplet molecules 2 unpaired electron.

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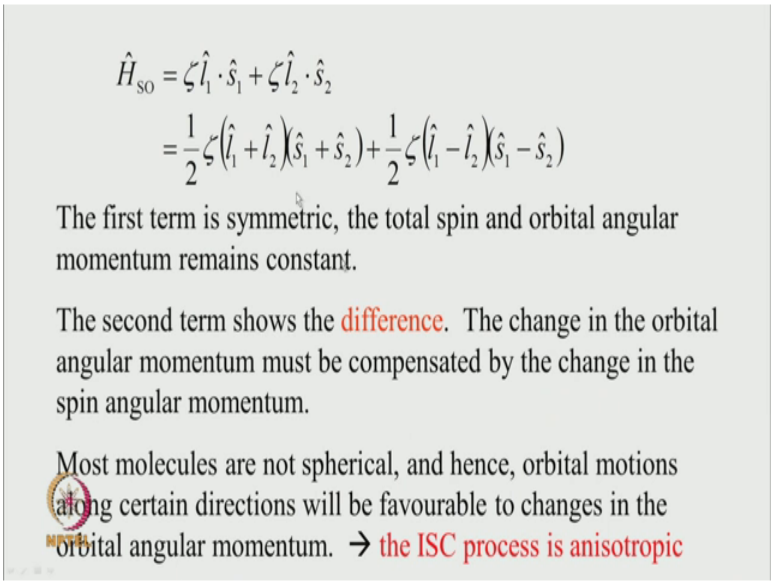

$$\hat{H}_{SO} = \zeta\hat{l}_1\cdot\hat{s}_1 + \zeta\hat{l}_2\cdot\hat{s}_2$$
$$= \frac{1}{2}\zeta\left(\hat{l}_1+\hat{l}_2\right)\left(\hat{s}_1+\hat{s}_2\right) + \frac{1}{2}\zeta\left(\hat{l}_1-\hat{l}_2\right)\left(\hat{s}_1-\hat{s}_2\right)$$

The first term is symmetric, the total spin and orbital angular momentum remains constant.

The second term shows the difference. The change in the orbital angular momentum must be compensated by the change in the spin angular momentum.

Most molecules are not spherical, and hence, orbital motions along certain directions will be favourable to changes in the orbital angular momentum. → the ISC process is anisotropic

So, I could write the inters spin orbit interaction in this fashion l 1 dot S 1 l 2 dot S 2 now this could simply little bit manipulate to write in this fashion now.

Now, here you see the first term is symmetric l 1 plus l 2 S 1 plus S 2. So, the total spin and orbital angular momentum remains constant, but second term is the difference of them l 1 minus l 2 S 1 minus S 2 that is the this is supposed to be conserved J has to be conserved not necessary this and this. So, the difference shows that if one is changing other must change the opposite sense. So, singlet to triplet intersystem crossing means I am creating one unit of spin angular momentum. So, that can be compensated by having one unit of orbital angular momentum changing the opposite sense.

So, that is the key to this conserving the total angular momentum as well as; try to justify why this could be different for different triplet level. So, most molecule are not spherical and hence orbital motions along certain directions will be favourable to changes in the orbital angular momentum. So, the molecule are not spherical let say Quinone itself.

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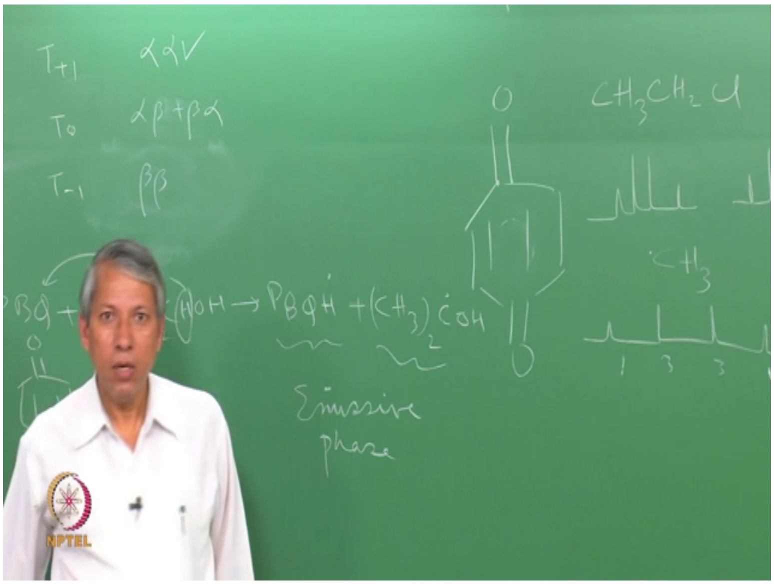

So, it is the carbonyl group which is the reactive centre. So, now, electrons can move about in this direction electron can move much more freely let us say than movement of electron in this direction. So, this movement that I am showing by hand is sort of nothing, but the orbital angular momentum. So, different direction therefore, molecule can have different type of orbital angular momentum and some direction it may be more efficient than the other direction.

So, coming back to this there is some direction this l can change more easily than some other direction. So, these 3 triplet level or molecular triplet level based on the coordinate of the molecule one can think of the along the direction, then these triplet level can be connected to one molecular triplet and then this orbital angular momentum change in the molecular coordinate system can be dependent on the which direction we choose. So, by arguing this fashion we can therefore, see that the intersystem crossing rate may not be same for all 3 triplet level. And therefore, that is the key to the appearance of the selective population of the triplet state, and then finally reaction taking place there to produce the polarised radical.

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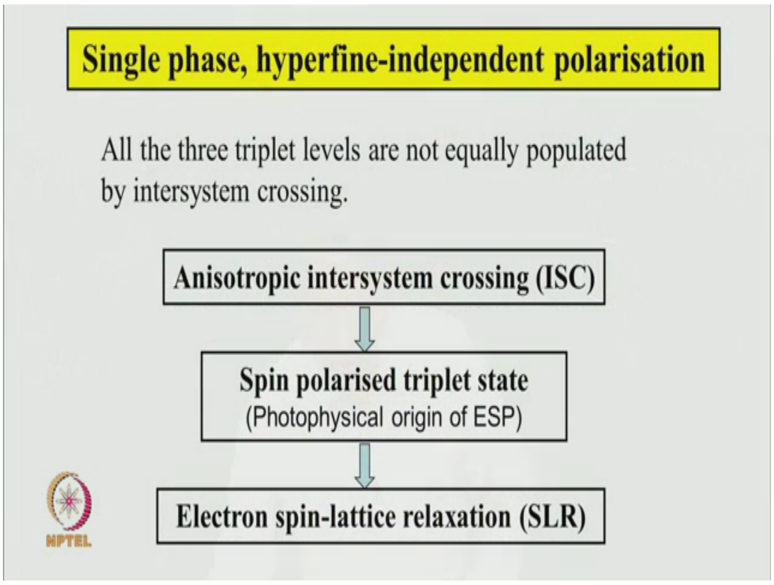

Single phase, hyperfine-independent polarisation

All the three triplet levels are not equally populated by intersystem crossing.

Anisotropic intersystem crossing (ISC)

Spin polarised triplet state
(Photophysical origin of ESP)

Electron spin-lattice relaxation (SLR)

So, let us summarise this single phase hyperfine independent polarisation what is happening there key point is that all 3 triplet levels are not equally populated by intersystem crossing. So, anisotropic intersystem crossing is taking place and so the triplet that itself is produced in the beginning it is polarised triplet because these also does not follow the Boltzmann distribution. So, one might call this as the photo physical origin of electron spin polarised and then electron spin lattice relaxation try to equalize the population here for then if the reaction is competing with this spin lattice relaxation process in the radicals can be produce with the spin selective manner.

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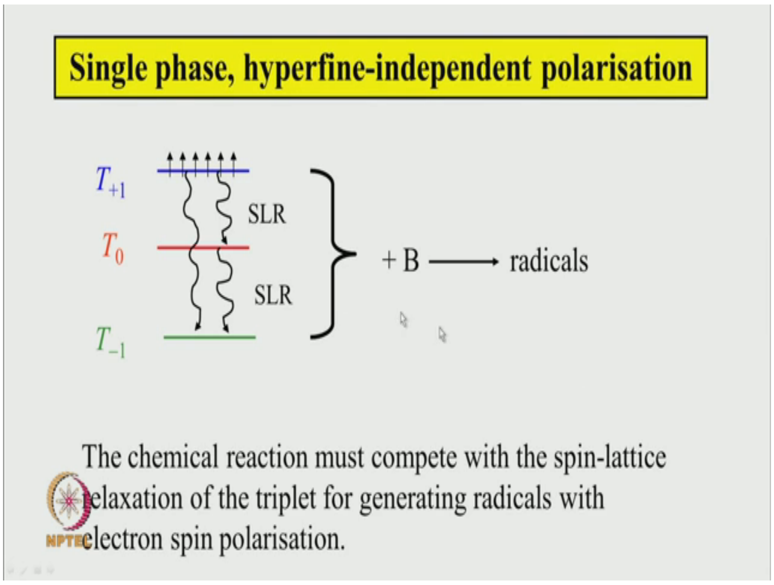

Single phase, hyperfine-independent polarisation

The chemical reaction must compete with the spin-lattice relaxation of the triplet for generating radicals with electron spin polarisation.

So, here figure it will this thing is described here then let us say T 1 state is populated first selectively then this relaxation process are that spin lattice relaxation within the triplet molecules.

So, that this follows the Boltzmann distribution or Boltzmann distribution is restored within the triplet molecule now B molecule comes and reacts with this now the reaction is faster comparable to this rate then these extra populations as spin can be transform the radical. Therefore, the most important is that chemical reaction must compete with the spin lattice relaxation of the triplet for generating radicals with electron spin polarization.

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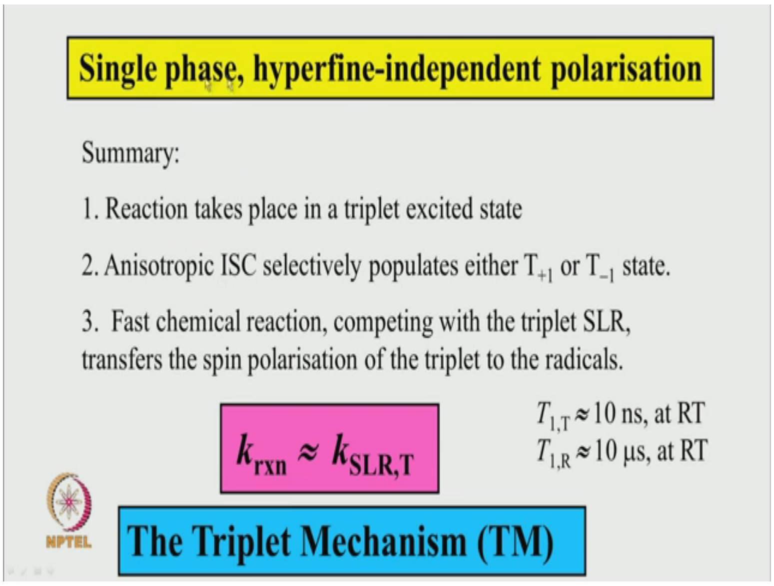

Single phase, hyperfine-independent polarisation

Summary:

1. Reaction takes place in a triplet excited state
2. Anisotropic ISC selectively populates either T_{+1} or T_{-1} state.
3. Fast chemical reaction, competing with the triplet SLR, transfers the spin polarisation of the triplet to the radicals.

$$k_{\mathrm{rxn}} \approx k_{\mathrm{SLR,T}}$$

$T_{1,\mathrm{T}} \approx 10$ ns, at RT
$T_{1,\mathrm{R}} \approx 10$ μs, at RT

The Triplet Mechanism (TM)

The summary of the single phase hyperfine independent polarization is that reaction takes place in A triplet excited state first requirement and anisotropic ISC selectively populates either T plus 1 or T minus 1 state and fast chemical reaction competing with the triplet spin lattice relaxation transfers the spin polarisation of the triplet to the radical therefore, reaction rate must be rate constant must be comparable to the spin lattice relaxation rate constant of the triplet.

Now, this is the condition that needs to be satisfied, but to keep in mind that this is not easy to satisfy because this triplet spin lattice relaxation rate is of the order of 10 nanosecond at room temperature. So, the reaction has to be also comparably must be comparable to this time. So, not most not all reactions are such fast reaction usually electron transfer reaction or hydrogen electron transfer reactions are fast, compared to that the spin lattice relaxation of radical mostly are in the microsecond range. So, that whatever you see the radicals are formed at least they will maintain their spin polarisation for several microsecond for the time EPR spectrometer to record that.

So, these mechanism which primarily centred around triplet state involvement of the photochemical reaction is called the triplet mechanism of electron spin polarisation the characteristic feature of this is that both the radicals will give same type of spin polarisation; either totally absorptive or totally emissive these does not depend on the nuclear spin state the spectrum will be very much like the steady state spectrum, but either it will be going down or going up. Relative intensity will be same as what one sees on steady state EPR spectrum.

So, with this we will stop. And then, in the next class we will take up the other spin polarisation mechanism where one sees the EPR signal which is of this kind this or that the nuclear spin dependent electron spin polarization, what we saw in case of this I rubbed it out acetone isopropanol system.