Fundamentals of Spectroscopy

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Lecture 53
ESR Spectroscopy – 1

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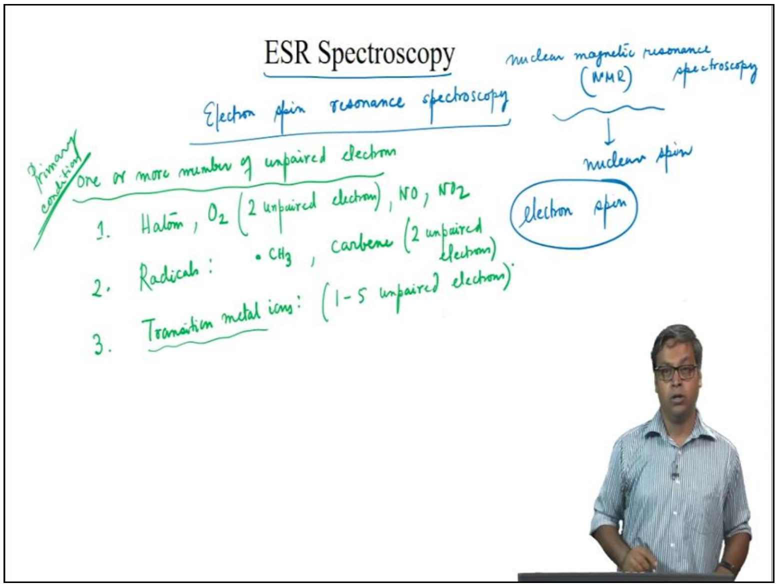

ESR Spectroscopy

nuclear magnetic resonance (NMR) spectroscopy → nuclear spin

Electron spin resonance spectroscopy

electron spin

Primary condition

One or more member of unpaired electron

1. Halon, O_2 (2 unpaired electron), NO, NO_2
2. Radicals : $\cdot CH_3$, carbene (2 unpaired electron)
3. Transition metal ions: (1-5 unpaired electron)

Hello all welcome to the lecture in the last few lectures we were discussing about nuclear magnetic resonance spectroscopy or NMR spectroscopy in other words we discussed about nuclear spin. So, from today's lecture we would focus on a different spin which is the electron spin. So, we would focus on electron spin that means we would start discussing electron spin resonance spectroscopy or as I have already mentioned before it is also known as ESR spectroscopy.

So this ESR is shown by the species which has one or more number of unpaired electrons. So, this is the primary condition for ESR spectroscopy. So, this is the primary condition. So, the primary condition for ESR spectroscopy is the presence of this unpaired electrons and this unpaired electrons can be found for example in let us say hydrogen atom. In oxygen in oxygen we have actually two unpaired electrons.

In other molecules like NO NO2 etc it can also be found in radicals. So, in free radicals so for example I have a let us say methyl radical which is represented by CH3 dot or radicals like carbines in carbines we have again two unpaired electrons and third it is found in the transition metal ions. So, if you are dealing with transition metal ions ESR spectroscopy can come handy and this transition metal ions has 1 to 5 unpaired electrons.

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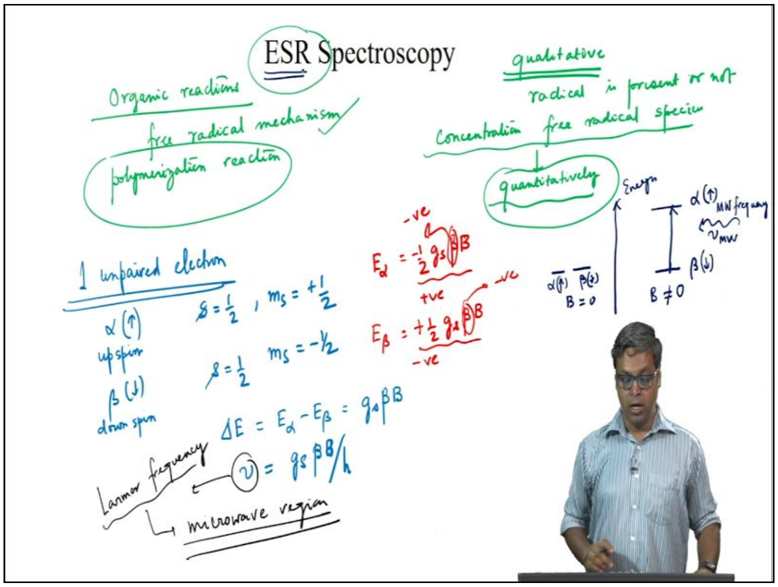

So we know that many reactions in organic chemistry so these organic reactions. So, many reactions in organic chemistry takes place this free radical mechanism. So, what are these kind of reactions one common example is that of the polymerization reaction. So, it is well known that the polymerization reaction happens to the free radical mechanism but let us say we do not know whether really the polymerization reaction goes to the free radical mechanism.

So whether the reaction proceeds by our free radical mechanism can be found out or can be ascertained by doing this ESR studies. So, one can get qualitative information that means qualitatively we can say whether this radical is present or not from studying the ESR signal and not only we can get qualitative information but if we monitor the concentration of the free radical species and we can monitor this you actually in a quantitative way.

So, if we can quantitatively monitor the concentration of the free radical species we can also get some quantitative information about the free radical mechanism. So, let us look into the case of unpaired electrons. So, we are talking about one unpaired electron. So, this one unpaired electron can have two spin states. So, one is the Alpha that means the up spin and this is the case where the spin quantum number s equals 1/2 and m s equals +1/2 and the other state is better which is the down spin is so here s equals 1/2 and m s equals -1/2 so these are the two spin states.

So now let us look into the energy of the spin states in the presence of an external magnetic field that is P. So, this E alpha or the energy of this alpha state is given by -1/2 g s beta B and this is positive as this beta is negative. So, here the gs as we had already discussed is the g factor and the beta is the Bohr Magneton and B is the external magnetic field. So, similar to E alpha we can write E beta equals +1/2 g s beta B and this is negative as this beta is negative.

So now because we have the energies of these two states we can actually look into the difference in energy that is Delta E. So, Delta E is given by E alpha minus E beta and which is g s beta B so this energy difference is large when we compare this with the energy difference we got an NMR and the resonance frequency as we know is given by nu that is new is gs beta B by h. So, this is the frequency of the larmor precision of the spin vector, so this nu is the larmor frequency.

So this frequency if we actually put the values will come in the microwave region. So, now let us try to draw like the transition here in other words when there is no magnetic field that is B equals 0 this alpha the top spin state and the better or the down spin state are degenerate because I have this vertical axis as the energy axis. However in the presence of an externally applied magnetic field that is B 0 equals 0 this two splits and the lower energy is that of the beta state and the upper energy is that of the Alpha state.

So this is down spin and this is up speed so in the presence of an externally applied magnetic field the degeneracy is lifted and we have two states alpha and beta. And now if a light in the microwave frequency falls on the system. So, we can write this as new microwave it will lead to a transition from the beta state to the alpha state. So, in this case we can see there is only one transition and because there is only one transition we have one spectral line in ESR spectrum.

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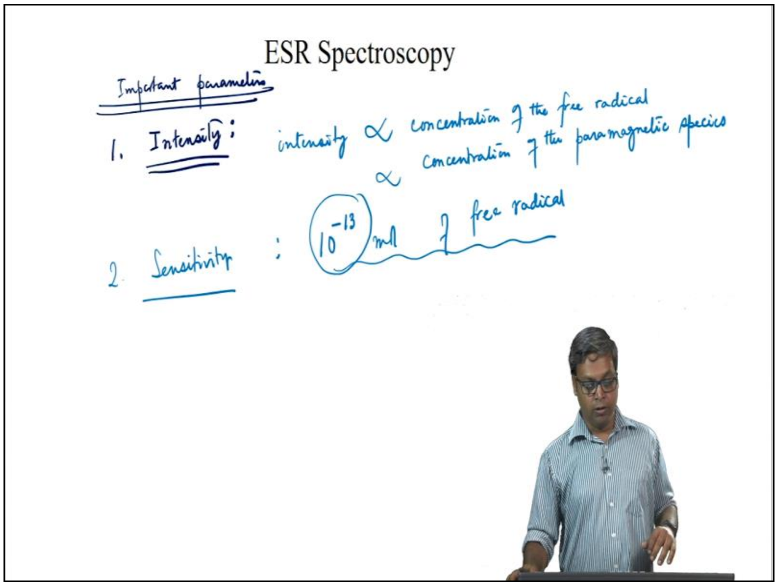

ESR Spectroscopy

Important parameters

1. Intensity: intensity $\propto$ concentration of the free radical

$\propto$ concentration of the paramagnetic species

2. Sensitivity : 10^{-13} mol of free radical

So, now let us look into some of the important parameters. So, these important parameters are related to the ESR spectrum so let us look into this parameters one by one. So, the first parameter that we will discuss is intensity. So, in an ESR spectrum this intensity is proportional to the concentration of the free radical. So, we can write is proportional to the concentration of the free radical or we can write is proportional to the concentration of the paramagnetic species because we are talking about species with unpaired electrons.

And when we are talking about concentration immediately the question that comes to our mind is what is the sensitivity of this ESR spectroscopy in other words what kind of concentration can it actually measure. So, the sensitivity is our second point sensitivity so this can detect up to 10 to the power -13 moles of free radical. So, this ESR spectroscopy is sensitive enough to detect up to 10 to the power -13.

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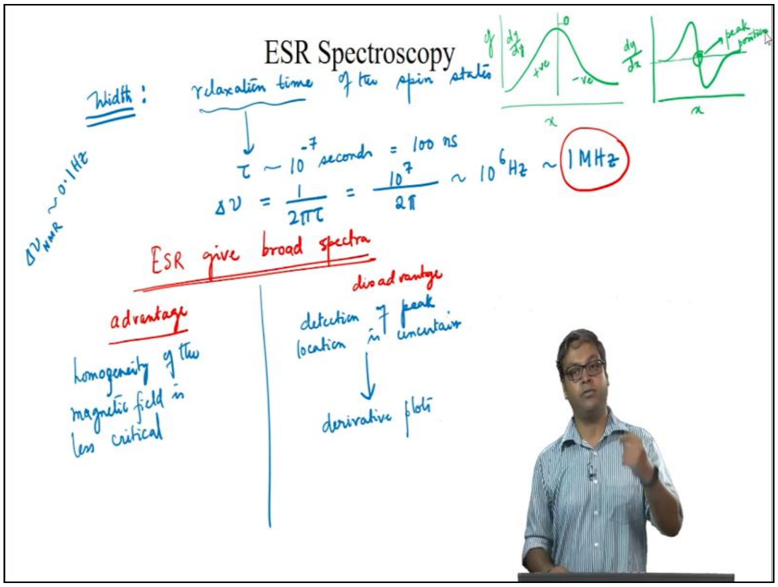

ESR Spectroscopy

Width : relaxation time of the spin states

$\tau \sim 10^{-7}$ seconds = 100 ns

$\Delta\nu = \frac{1}{2\pi\tau} = \frac{10^7}{2\pi} \sim 10^6$ Hz $\sim \boxed{1 \text{MHz}}$

$\Delta\nu_{NMR} \sim 0.1$ Hz

ESR give broad spectra

advantage

homogeneity of the magnetic field is less critical

disadvantage

detection of peak location is uncertain

derivative plots

So, now let us look into the third parameter because we know for every spectrum there is an associated width which we normally talk about in terms of full width at half maximum. So, the width of the peak in ESR spectrum depends on the relaxation time of the spin states. This is exactly what we saw in case of NMR also but for most of the sample a typical relaxation time so which is denoted let us say by tau in ESR is of the order of 10 to the power -7 seconds in other words we can write this as 100 nanoseconds.

And because we have a time and because of this uncertainty there is a spectral width and the width is given by 1 by 2 pi tau and that if we put now so this is 10 to the power 7 divided by 2 pi so it comes around 10 to the power 6 Hertz or we can write around 1 megahertz. Now if you remember when we were talking about NMR spectra the Delta nu in NMR was in the order of 0.1 Hertz however in case of ESR this is 1 megahertz or 10 to the power 6 Hertz so thus one thing that is extremely clear from this calculation is that the ESR gives very broad spectrum.

So, now we can ask the question what are the consequences of this broad spectrum first of all there is an advantage and also there is a disadvantage. So, let us first look into the advantage. So, the advantage of this broad spectrum is the homogeneity of the magnetic field is less critical on the other hand the disadvantage is because the speaks are broad it is extremely difficult to detect the peak position or we can say in other words the detection of the location of the peak becomes uncertain.

And because the detection of peak location is uncertain what is generally done or practiced is the ESR plots are derivative plots. So, what do you mean by derivative plots let us say we have a spectrum which is very broad so it is very difficult because this is brought to find the exact peak position but all we can see here that this is my y-axis this is my x-axis so if we think about the slope or dy dx this part has a positive slope this part as a negative slope and this part has 0 slope.

So, now instead of y against x if I plot dy dx against x what I get are yet like this so this is where the value of dy dx is 0 and this point gives me the peak position in other words if the spectrum is broad and it is very difficult to find the actual peak position we can resort to the derivative plots it can be the first derivative it can be the second derivative which will give us the exact location of the peak. In ESR normally the first derivative plots are being used.

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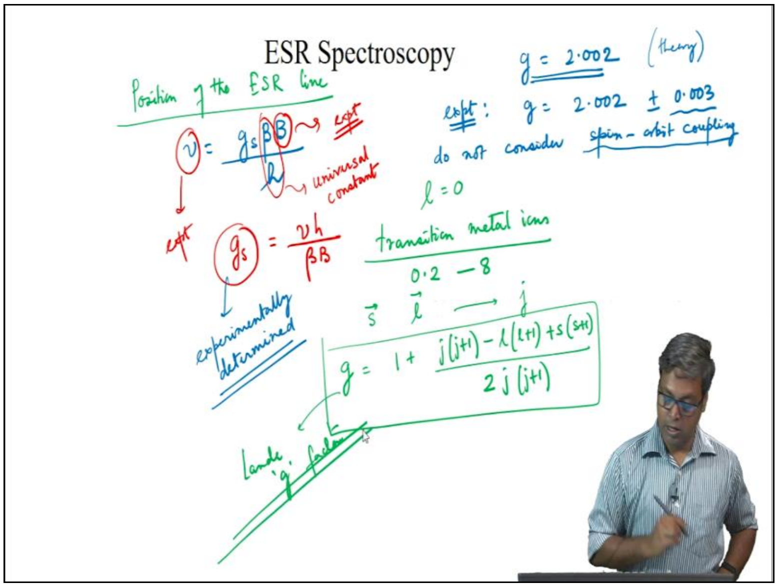

ESR Spectroscopy

Position of the ESR line

$\nu = \frac{g_s \beta B}{h}$ ~ expt

universal constant

expt

$g_s = \frac{\nu h}{\beta B}$

experimentally determined

$g = 2.002$ (theory)

expt: $g = 2.002 \pm 0.003$

do not consider spin-orbit coupling

$l = 0$

transition metal ions

0.2 – 8

$\vec{s} \quad \vec{l} \longrightarrow j$

$$g = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$$

Lande 'g' factor

And now we look into another parameter that is the position of the ESR line. So, we know that the frequency is given by g s beta B divided by h so if we look carefully we can see this beta by h this is a universal constant this frequency this can be found from experiment and this magnetic field can also be found from experiment or we know what kind of magnetic field is being applied. So, in other words we can write g s is nu h by beta B and we can see that g s can be experimentally determined or we can say it can be experimental it estimated.

So for a free electron the value of g is 2.002 and we have stated this in the initial lecture on resonance spectroscopy. So, let us say this is the value we get from theoretical calculations so from experiments so from experiments the value of g that we obtain is 2.002 +- 0.003 so this is the error bar but the error var is pretty small. So, we can see the same value is obtained both from theory and experiment and in when we were doing the theoretical calculation we only considered the electron spin that is the spin angular momentum.

In other words we do not consider spin orbit coupling which means we do not consider any coupling between the spin angular momentum and the orbital angular momentum and even if we do not consider this coupling we get to the value of g that is the experimental value and the error var is very, very small. So, in theory no spin orbit coupling is needed to be considered to arrive at the experimental value of g what does this mean for a free electron it means that the electron is either in a state where the orbital angular momentum which is given by l so either l is 0 or the electron moves in the entire molecule freely that is the electron is not localized on a particular atom.

However now if you look into the transition metal ions the value of g that is obtained is of the range of 0.228 but in this case if we just consider the spin angular momentum our theoretical calculations do not deliver the experimentally obtained value. So, in this case we need to consider the spin orbit coupling to arrive at the experimental value. So, what does this mean this means the electron here is localized to a particular atom.

And because it is localized to a particular atom the spin angular momentum vector which is given by s couples with the orbital angular momentum vector that is l to give a total angular momentum vector which is given by j. In other words now the g is not simply coming from the spin angular momentum but because of the spin orbit coupling we can write g equals 1 plus then we will write j times j+ 1 - l times l + 1 + s times s +1/2 times j times j + 1.

So this is the expression if we put then we will get to the experimental value of g and this g is known as the lambda g factor. So, we will end this lecture here we have given a brief introduction to ESR spectroscopy we have seen that the ESR spectroscopy happens when we have unpaired electrons we have seen which are the cases where we have these unpaired electrons then we looked into the two spin States the frequency there is a larmor frequency that is a frequency needed for the transition.

And finally we saw that g or the g factor can be experimental determined and from the theoretical and experimental values we can find whether the spin orbit coupling is necessary or not. So, in the next lecture we will continue with ESR spectroscopy and we will talk about the hyperfine structure in the ESR spectrum these are like the fine structures we saw in a high resolution NMR spectrum.