

Interpretative Spectroscopy
Prof. Maravanji S. Balakrishna
Department of Chemistry
Indian Institute of Technology Bombay
Lecture 47
Hyperfine Interactions

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. Let me continue discussion on EPR spectroscopy. In my last lecture I started discussion on hyperfine splitting. So, let me continue. If you can see here, to find number of lines, very similar to NMR, we use the rule $2nI$ plus 1 rule ($2nI + 1$). n is the number of equivalent species, nucleus or other species and then I is the spin value. In all these things, we are considering n equal to 1 and in the absence of any radical or anion will show because of presence of only one electron, it shows no interaction. You will see only one line.

When it interacts with one nucleus with spin I equal to half. We see two lines, simple rule, just in case of one, I will show you here. We see two lines here and similarly when the nuclear spin I equal to 1. We observe three lines and then in case of spin 3 by 2 ($3/2$), we observe four lines. When we have two equivalent nuclei with spin I equal to half, then it will be 2 into 2. We expect three lines here, and similarly, when we have three equivalent nuclei with I equal to half, we will see four lines, and when we have four equivalent nuclei with I equal to 1, we will see nine lines. This is how, we can understand hyperfine splitting, simply applying this to $2nI$ plus 1 rule ($2nI + 1$).

So, how this hyperfine splitting happens? Because of hyperfine interaction, if an electron couples to several sets of nuclei, then the overall pattern is determined by first applying the coupling to the nearest nuclei and then splitting each of the lines by coupling to next nearest nuclei and so on. This is how it goes very similar to what we do while writing splitting tree or coupling interactions in case of NMR. The number of hyperfine lines is called NHFS. Hyperfine lines from a group of n equivalent nuclei of spin I . We use $2nI$ plus 1 ($2nI + 1$), that is what I showed you in my previous slide. Now let us look into the relative intensities

for I equal to half. Again I equal to half, I equal to 1, I equal to 3 by 2 ($3/2$), we were using Pascal's triangles in case of NMR. Similarly, we can also look into the relative intensity of the lines when you observe hyperfine splitting. For example, for 0 we will see only one line when n equal to 1. We will see 2 lines when n equal to 2. We see 3 lines, the intensities are 1 is to 2 is to 1 ($1:2:1$). In case of 3, we have 4 lines: 1 is to 3 is to 3 is to 1 ($1:3:3:1$), when we have 4, we have 5 lines: 1 is to 4 is to 6 is to 4 is to 1 ($1:4:6:4:1$), and it continues like this. Now, you can see, in case of n equal to 1, we will see 2 lines, doublet. 3, we will see triplet and when 4, we will see a quartet. When 5, we will see a quintet, and when 6 are there, we call it sextet and when we have 7 we will see a septet line.

So, this relative intensity diagram, whatever I have shown, holds good for nuclear spin I equals half. Similarly, one can also write relative intensities for I equal to 1, and again 0 one line will be there. For example, if you consider $2nI + 1$ equal to 1 and then when you have 2 will be having 5 lines: 1 is to 2 is to 3 is to 2 is to 1 ($1:2:3:2:1$) ratio, when we have 3, we will be having 7 lines: 1 is to 3 is to 6 is to 7 is to 6 is to 3 is to 1 ($1:3:6:7:6:3:1$). For 6, we will be having 13 lines. This how we can calculate and find out the relative intensities, when they are interacting with nuclei with I equal to 1.

Now, let us look into some examples to begin with we shall consider a simple radical such as methyl radical. In methyl radical, we are talking about this electron here. This will interact with 3 protons of I equal to half, then if you see here if you apply $2nI + 1$ rule ($2nI + 1$), we expect 4 lines and how these 4 lines will come. Again, it is very similar to NMR. If you assume these 4 lines, for example, these 3 lines would be interacting in this fashion. For example, all of them will be aligned with respect to the applied magnetic field or 1 can be down and they have 3 combination and 2 can be down and 1 up we have this combination and they are all degenerate and, when we have all 3 opposing the applied magnetic field, will be having this one. So, we can arrive at 1 is to 3 is to 3 is to 1 ($1:3:3:1$). This is exactly similar to NMR, where we look into the coupling. This how we will observe the EPR spectrum in case of methyl radical and if you want to assign the m_i values, this is plus 3 by 2 ($3/2$), half ($1/2$), minus half ($-1/2$) and minus 3 by 2 ($-3/2$).

Now, let us look into this radical anion and here this electron would first couple with these 4 ^{14}N that means, if we use $2nI + 1$ rule ($2nI + 1$) again, we are expecting 9 lines I am not worried right now these things, and also hydrogens we have here. If you just leave and look into this one primarily, we get 9 lines having this intensity ratio here. So, this is for radical anion.

So, now let us look into examples of metal complexes coupled with nonequivalent nuclei. So, one is ^{15}N , one is H, hydrogen. Both of them are nonequivalent and they couple one after the other and now we can use either this way. So, if you recall how we were writing.

So, first if you see here one doublet will be there this is either coupled with this one or this one both are having spin i equals half and then each one will be again. So, 4 lines will be there. So, that is what we see here we see doublet of doublets that can be seen when a is coupled or interacting with nuclei which are nonequivalent. Then you can also use this ($2nI + 1$) into $(2m_i + 1) ((2nI + 1) \times (2mI + 1))$. You can use for two different ones and multiply, which also gives the same number here. If you want to look into the transitions, to begin with, we have something like this and then it is split like this. First it will be split into say nitrogen and then if it is hydrogen. We have and then if you see here this 1, 2, 3, 4 possible transitions can be seen and that is observed in the EPR spectrum of this metal complex. Only highlighted is one hydrogen and one ^{15}N here.

This is about ^{14}N here. Earlier we considered ^{15}N . So, I equal to half now, if you consider here; first it is with hydrogen it is a doublet and then it will be split into triplet of intensity 1 is to 1 is to 1 (1:1:1). This what is shown here and then of course, here these are all m_i values for ^{14}N and this is for ^1H and then you can see 6 lines will be there. 6 transitions are shown here 1 2 3 4 5 6 and we see here. This is a very beautiful EPR spectrum with non-equivalent, one with I equal 1 and one I equal to half.

Now, let us look into benzene radical anion benzene radical anion. This will couple with 6 equivalent hydrogen atoms. 7 lines will be there.

So, if you look into a benzene radical anion. So, this how we see EPR spectrum in the form of a septet with a_H value of 3.75 gauss or this one is 375 mT. Similarly, one can also look into 1-hydroxy ethyl radical. In this one we get a quartet of doublets here. That means, this one first couples with CH_3 protons then it gives a quartet and then each line in the quartet will be split further because of hydrogen to doublet and we call it as quartet of doublets. We can see here this for 1-hydroxy ethyl radical.

Let us look into acetamide radical. Here in acetamide radical, we have to consider this one and also, we have to consider this one and also we have to consider this one. So, first let us say it couples with nitrogen it gives 3 lines and then each line will be split by 2 hydrogens. Again it will be a triplet and then these two will split further into triplet and we get something like, if you try to write here. So, each one this one will be 3 2 plus 1 (2+1), 3 and then this will be giving 3 1 and this will be 3. So, we get 27 lines.

So, benzyl radical if you see, first it splits into a triplet 3 and then we have 1 2 3 4 5 6 means, we will see 18 lines here. So, we can also tell how an EPR spectrum of benzyl radical would look like and then acetamide radical would look like.

Now, let us look into hexaaquamanganese 2 plus $[Mn(H_2O)]^{2+}$ and here electron spin is S equal to half and nuclear spin is I equal to 5 by 2 ($5/2$). Since it is I equal to 5 by 2 ($5/2$), it will split into 6 lines here. So, we can see 6 lines here. That means if you record EPR spectrum for hexaaqua manganese 2 plus $[Mn(H_2O)]^{2+}$, this is how EPR spectrum would look like and also if you expand here you can write all possible states between which transition occurs or zeeman splitting happens can be seen here 1 2 3 4 5 6 lines.

This is how you can show, it is very similar to splitting or coupling tree we show in case of NMR spectroscopy. Now let us look into one more metal complex, vanadate acac. Here I equals 7 by 2 ($7/2$). This interaction with vanadium nucleus would be something like this you can expect. Since it is 7 by 2 ($7/2$) one can expect 8 lines and 8 lines can be seen here very beautiful spectrum. The corresponding transitions are shown here. So, this is how one

can analyze EPR spectra and then interpret. First you find out equivalent nuclei that are going to interact and how they are going to split or how the hyperfine splitting looks like, what are the relative intensities, and then you can also show how the coupling or interaction happens. In this fashion, and your job is done. Here 8 lines are and here the g value is 2.0023.

Now, let us look into, of course I showed you benzene radical. In case of benzene radical, as I mentioned, 6 hydrogen atoms are there and 6 hydrogen atoms will interact with lone electron to give 7 lines. Again this is a beautiful EPR spectrum of benzene radical anion. Sometime one can also write here, this also shown like this here.

Now, this is again interesting. very nicely hyperfine splitting is shown in case of 1,3-butadiene anion radical here. You can see here, so here we have this, if I say designate H_a they are equivalent first it would couple with these 4 equivalent nuclei. So, that means basically 5 lines will be there. You can see a quintet initially and then these 2 will couple equally and each one will be a triplet here.

So, there will be total of 15 lines. This is from one of the old journals; Journal of Chemical Physics. Initially it splits with 4 equivalent hydrogen atoms to give this quintet and then each one would be coupled with H_b . These 2 identical equivalent ones and a triplet and then we have triplets of quintet. You can say quintet of triplets. Now, let us look into cyclopentadiene as radical. This is anion radical here, and now this is coupled with 5 equivalent hydrogen atoms. So, again use same $2nI + 1$ ($2nI + 1$) rule, it should show 6 lines here.

Now, let us look into naphthalene anion radical, how it is made? You take naphthalene in say 1,2-dimethoxyethane, add potassium and immediately you can see the blue coloration due to the formation of naphthalene anion radical. When you look into this radical in its EPR, which shows very nice hyperfine splitting. You can see here, initially it splits into 1 2 3 4 5 lines why that 5 lines are observed. Yes, you should be able to see. Naphthalene has 8 hydrogen atoms; 8 hydrogen atoms can be designated something like this. We have

this is one type of proton, you can call it as beta-proton and then we have this alpha-protons are another 4. So, that means in 1 is to 1 ratio we have 2 nonequivalent hydrogen atoms. They would interact with this electron radical and split that in this fashion. First it splits into a quintet and then each line is further split into a quintet to show this kind of multiple peaks, that one can also see by just looking into it as I mentioned, $2nI$ plus 1 into $2nI$ plus 1 $((2nI + 1) \times (2nI + 1))$. So, 25 lines you can expect here. Very nicely you can see 25 lines.

So, one unpaired electron interacting with 2 sets α and β of 4 equivalent protons. So, the ESR spectrum would thus show $2nI$ plus 1 into $2nI$ plus one $((2nI + 1) \times (2nI + 1))$. Two designations are given: this is α and this is β and then 4 plus 1 $(4 + 1)$ here 4 plus 1 $(4 + 1)$, $5 \times 5 = 25$ lines by considering the pattern and coupling constant of a_1 is 4.90 g and a_2 equal to 1.83 g of hyperfine splitting. The species formed is consistent with naphthalene radical anion.

So, this is a very beautiful one and this naphthalene anion is extensively used in organic chemistry and especially when sodium and potassium we want in stoichiometric amount. In very small quantities, it is very difficult to use by fresh sodium cutting and weighing because of its reaction with water to form sodium hydroxide or sodium oxide. In that case, what happens no matter how careful we are, it is very difficult to weigh exact amount of sodium or potassium, but on the other hand if we make something like this and if we standardize the solution we know the molarity and then we can use that solution as a source of sodium. From that point of view sodium naphthalene or potassium naphthalene is quite useful in organic synthesis and also in organometallic synthesis.

So, let me stop and continue discussion on more EPR problems in my next lecture until then have an excellent time. Thank you.