Interpretative Spectroscopy

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Lecture 48

Examples of Hyperfine Interactions

Hello everyone, welcome you all to MSB lecture series on Interpretative Spectroscopy. In my last lecture after discussing about hyperfine splitting, I showed you lot of very interesting examples with very clean EPR spectra. So, let me continue again, showing more examples to make you familiar with interpretation. This is about naphthalene anion radical, it is very easy to prepare this one. You take naphthalene in 1,2-dimethoxyethane, very dry in freshly distilled 1,2-dimethoxyethane and add sodium or potassium, you can immediately generate potassium or sodium salts of naphthalene. That is essentially in blue color due to the formation of radical.

So, we call it as naphthalene anion radical and it is very interesting to record its EPR spectrum and EPR spectrum would look like here. You can see here, initially there are 1, 2, 3, 4, 5 lines are there and then these 5 lines are further split into 5 lines here, further split into 5 lines. So, how that happens and that we can understand if you look into the naphthalene. In naphthalene we have two different type of hydrogen atoms they are called α and β hydrogen atoms.

We have 1, 2, 3, 4 and we have β -hydrogen atoms are there and then they are coupled non-equally. So, first they are coupled with α to give 5 lines, a quintet and then each line is further split by these 4 αequally to form another quintet, then we get 25 lines. The 25 lines also in a simple manner we can calculate. Take this one set, we have 4 of them, we have another set here, another 4. So, we can use simple formula.

So, α 4 are there, β also 4, α 2 are there, α 3 are there. So, this is how you can calculate very nicely number of hyperfine lines in EPR spectrum here. So, another way is, you can also start writing using splitting tree or we used to call in NMR. So, first it splits into 5 lines and each line will be further split into 5 lines. So, if you take count this one, we have 5 into 5, this also gives 25 lines either this way or simply you can use this equation and you can work out.

If you have 3 or 4 sets of non-equivalent nuclei, this can continue something like this. It can continue like that. The product of this one will show the number of lines in the EPR spectrum. You can see here a beautiful spectrum of the same I have shown here, the splitting also I have shown here. In this one what happens some of the lines are merging as a result what would happen, what we see is a smaller number of lines here.

This one is another interesting copper complex, copper(II) and we know that for copper, I equal to 3 by 2 (3/2). This is a 63 enriched product we have only ^{63}Cu and then we have next to that 2 nitrogen atoms, ^{14}N with I equal to 1, and then we have two different types of hydrogen atoms. The hydrogen atoms on 2 nitrogen atoms are equivalent and next to that, we have these 2 which are identical. That means, we will be seeing coupling of this one 3 by 2 (3/2) first splits into 4 lines and then each line splits further by 2 nitrogen and then 2 hydrogen and then 2 hydrogen. So, it gives a very complex system. For example, if you consider, simply one can write something like this. Initially it gives, if you consider 2nI plus 1 (2nI + 1) here it will be equal to 4 lines. Here 1 2 3 4, and then this will be 2nI plus 1 (2nI + 1). Here nitrogen, it will 5 lines one of them I will take to show. So, next we have 2 hydrogen atoms, it will be split into triplet and then this will be further split into triplet.

So, you can calculate the number of lines, but what happens because of overlapping of some of them very closely spaced what we see is we get 4 multiplets constituting each one 11 lines here in this fashion. So, we get almost 44 lines, instead of more lines we expected, because of overlapping. Something like this happening here. Again, this is also taken from one of the oldest articles published in Journal of Chemical Physics in 1958. Now, let us look into nitrobenzoate dianion radical here. We have one side CO_2, one side NO_2 is there and here if you just consider first, this interacts with nitrogen and, it will give a triplet 2nI plus 1 (2nI + 1) and then it interacts with 2 different type of hydrogen atoms, if you see ortho and meta. That means, first it gives a triplet because of coupling with nitrogen I equal to 1 and then each line of this triplet will be split by these two one identical ortho hydrogen atoms, triplet and then again it will be split by these two identical ones to another triplet.

So, what we get is triplet of triplets of triplets. So, this is the initial triplet of triplets of triplets what we get is we have 27 lines, one can also calculate in this fashion. So, I have designated ortho hydrogen, meta nitrogen here. So, here we get 2nI plus 1 (2nI + 1) will be 3 and here what we get is 2 of them are there 3 and then here we get 3. So, you can get 27 lines.

So, easily this way also you can calculate and you can account how many lines will be there in a given EPR spectrum. So, very nicely this para-nitrobenzoate shows hyperfine splitting in this fashion having 27 lines triplet of triplets of triplets. Now, let us look into benzosemiquinone radical anion here we have. So, this one is coupled equally to 4 hydrogen atoms I equals half. So, you can see a quintet here and also the corresponding transitions also shown in this one.

So, this is for p-benzosemiquinone radical anion. Now, let us look into more examples of hyperfine interactions. Now, if you consider this pyrazine anion, we have 2 nitrogen atoms and four equivalent hydrogen atoms. That means initially what happens this will be first split into a quintet because of two nitrogen's having I equal to 1.

So, we have 1 is to 2 is to 3 is to 2 is to 1 (1:2:3:2:1) ratio, a quintet because of coupling with 2 equivalent nitrogen atoms and then each one will be further split into a quintet because of 4 equivalent hydrogen atoms. We have this ratio: 1 is to 4 is to 6 is to 4 is to 1 (1:4:6:4:1). It continues like this and we get the spectrum, something like this. The spectrum is shown here, you can see here hyper fine due to two equivalent nitrogen and then super hyperfine due to 4H equivalent nuclei. This is called super hyperfine the coupling of the coupling it continues first we call hyper fine and then further continues with more number of nonequivalent, we call super hyperfine after that no matter how many are there, they are all referred to as super hyperfine interactions or super hyperfine splittings we call.

This another beautiful one we will see here again 5 into 5. So, 5 into 5, 25 lines will be there. Either you can calculate this way or one can also go in a step wise manner. The spectrum should intensities of 1 is to 4 is to 6 is to 4 is to 1 (1:4:6:4:1). This again a beautiful EPR spectrum showing hyperfine as well as super hyperfine splitting.

EPR g and anisotropy, let us look into it. We all know that hν equal to gβH ($h\nu = g\beta H$) or sometime the magnetic field is represented by H or most commonly B. Nevertheless one should understand here B equal to H. B or H are essentially same and one can also calculate g by considering this equation. For example, here Planck's constant is given in erg per second, it is minus 6.62517 x 10^{-27} and this value is given here. For a given frequency of 9.114 into 10 rise to 9 (10^9)cycles/sec and then beta is given here and the magnetic field strength is given in Gauss and then g can otherwise be calculated using this radical as a reference.

The relation between J the resultant vector of L and S coupling. J equal to L plus S (L+S) we are considering here where as in case of electronic spectroscopy we consider J equals

L plus or minus S. I mentioned already we are considering J equal to L plus S (L+S), when the sub shell is more than half filled. When the sub shell is less than half-filled, J equal to L minus S (L-S). Two values here, where as in EPR we are considering the resultant vectors L and S coupling that is L plus S (L+S), if L is 0 then J will be equivalent to S. We use this equation, this is the standard known equation:

$$g = 1 + J(J+1) + S(S+1) - L(L+1)/2J(J+1)$$

This is how we can calculate g value. However, actual value of g of free electron is 2.0023, if you recall I mentioned in my earlier lecture, this is due to the relativistic correction. Free radical g value is 2.0023 as unpaired electron is not confined to any localized orbital, moves freely over the orbitals.

In transition metal complexes, unpaired electron remains localized in a particular orbital due to: Loss of orbital degeneracy or spin orbital coupling, and hence g value is different from 2.0023. If it is localized, then the value will change, in that case g value depends on both lambda and Dq (crystal field). One can use this expression to calculate g where the electron is localized. It happens in case of metal complexes.

So, you can use this formula here, k is extent of metal-ligand delocalization under the banner of metal-ligand covalency as per ligand field theory. Lambda equal to spin-orbit coupling constant. 10Dq equal to crystal field splitting and then alpha depends on the ground state term, whether it is 2 = E_g and 4 for A_{2g} state, and if lambda and 10Dq, from UV data, are known, then k can be calculated using experimental g value obtained from EPR.

So, k can be easily calculated and g can be obtained from EPR spectrum. g is very similar to coupling constant in NMR.

Now let us look into another example. For a radical, the magnetic field is 3810 gauss, the frequency of the microwave is 9600 MHz. What is the value of its g-factor?

Just now, I had discussed in one of the earlier slides that hν equal to this. We are using g_e β_B B_o. The field strength B is known, this can be simplified by considering h over B_o (h/B_o).

So, that is considered here. For example, this equation now we can write something like this. G equal to hν over something like this. This term one can simplify after simplifying what we get is we get value 71.4484. So, this is the value of gβ and this is given in megahertz this gives approximately 1.8 g value.

So, this is how you can calculate g value here. So, let me stop here. I am concluding EPR and if there are any interesting problems, I will come back again in my last 8 to 10 lectures, which are devoted to problem solving. I am including problems on all these spectroscopic methods UV, NMR, mass, EPR and also Mossbauer. I might take a couple of lectures on mass bar spectroscopy and later I begin discussion on solving more and more problems to make you familiar with the type of problems and then how to interpret data having data getting from more than one type of spectroscopic methods.

So, it is essentially to make you familiar with interpretation, elucidation and understanding the reactions that are carried out and the product obtained. So, see you in my next lecture. Thank you.