Interpretative Spectroscopy

Prof. Maravanji S. Balakrishna
Department of Chemistry
Indian Institute of Technology Bombay

Lecture 08

Second Order Coupling

Hello everyone, I am sure you are having good time. Welcome you once again to MSB lecture series on interpretative spectroscopy. In my previous lecture I discussed first order spin system taking several examples and one such example I considered was styrene. In styrene although it appeared like a first order spectrum, it is actually not first order spectrum. So that means geminal coupling we come across, although magnitude was about 1.4 or so.

So how that happens and how to interpret that, let us look into now second order spin system. We looked into the examples of ^1H NMR spectra, where we discussed first order coupling. That means the chemical shift difference we call it as delta-delta ($\Delta\delta$) between the nuclei is considerably greater than the coupling constant ($\Delta\delta >> J$), usually 5 times greater, that means, if delta-delta is greater than J, then it is called first order coupling. When delta J (ΔJ) is larger than nuclei involved in the spectrum are designated with letters from the extreme ends of alphabet, that means, for example, A and X, AMX, AX_2, A_2X_2 depending upon how many such nuclei are there in a given molecule.

So when delta ($\Delta\delta$) is less than 5 J ($\Delta\delta < 5$ J), that means chemical shift difference is much smaller than the coupling constant, then for such system we use letters close together in the alphabet. For example, AB, ABC, A_2BC something like that. So, in those cases what happens, the Larmor frequencies of nuclei of different elements are always very large. In those cases, in a first order spectrum, the Larmor frequencies of nuclei of different elements are always very large. Second order coupling can occur only between the nuclei of the same isotope. One should remember that, nuclei of the same isotope only can exhibit second order coupling. For example, as I said protons on same carbon atom, when they are chemically equivalent and magnetically non-equivalent, we come across second order, but vicinal fluorine and hydrogen can never be second order coupling, there is always first order spectrum.

Second order coupling can occur only between the nuclei of the same isotope, example between two ^{1}H nuclei, three ^{19}F or three phosphorus (^{31}P), since the chemical shift differences are very small for ^{1}H, the majority of second order couplings are observed in ^{1}H NMR spectrum. Here surrounding hydrogen, we have only 1S electrons and it is spherically symmetrical and hence chemical shifts have a very small range of 1 to 10 (1-10 ppm), only in exceptional cases where we have coordination compounds and Metal to hydrogen bond, we come across up to 60 ppm. Otherwise in most of the organic molecules, it does not go beyond 10 ppm. That means, as a result what happens since the chemical shift differences are very small in ^{1}H, the majority of second order couplings are observed only in ^{1}H NMR spectrum, and we also come across in case of phosphorus (^{31}P) NMR also.

So, let us consider a simple second order spectrum such as AB. Since the chemical shifts of the nuclei in a second order system are similar, the energy levels are much closer compared to the same in the first order. This is very very important. When we differentiate between first order coupling and second order coupling, the chemical shifts of the nuclei in a second order system are very similar that means they have chemical shifts much closer in energy compared to the same in first order spectrum. I have shown a series of spectra here. They represent typically AB case. In AB, the middle energy levels are similar to A_2 here. If you see when these middle levels become closer, it becomes difficult to tell which nucleus has which m_I value. That is the problem we come across in second order splitting as this middle level becomes closer, it becomes difficult to tell which nucleus has which m_I value, whether it has plus half or minus half (+1/2 or -1/2). Similar to A_2 case, consider the linear combination of two wave functions here. Since these new functions are mixtures, it is no longer possible to designate the transitions whether they are due to change in m_I of A or B. As a result, by simply looking into spectrum, it is no longer possible to determine the chemical shifts of A and B. So general patterns of the AB spectrum depend on delta ($\Delta\delta$) of A and B and the corresponding *J* value, so to what extent delta *J* is comparable, delta delta ($\Delta\delta$) is comparable with delta *J* that would tell you the separation. The spectra shown here are for *J* equal to 10 (J=10 Hz) and a variety of delta delta ($\Delta\delta$) values, so here in all of them, if you just look into it, coupling constant is kept 10 and then a different variety of delta delta values are given. When delta delta ($\Delta\delta$) is very large relative to *J*, spectrum appears as a distorted doublet (d), the intensity of inner lines increases as *J* by delta ($J/\Delta\delta$) increases, when delta delta equals 0 ($\Delta\delta$=0), the spectrum is reduced to a single line as in case of A_2 system. So, this is how you can correlate and also all these cases are of different AB, depending upon the difference in delta delta ($\Delta\delta$) with respect to *J* value.

Few points to remember in case of second order coupling is: in a first order spin system delta delta ($\Delta\delta$) must be greater than *J* ($\Delta\delta >>> J$), all chemically equivalent nuclei must also be magnetically equivalent. This is very important in first order spectrum: All chemically equivalent nuclei also magnetically equivalent that means if you are considering two geminal hydrogen atoms so they are chemically equivalent as well as magnetically equivalent. What is the meaning of chemical equivalent, magnetically equivalent. Two are more nuclei are chemically equivalent, if they can be interchanged by the operation of some symmetry elements of the molecule. For example, let us take phenol (C_6H_5OH) and we have ortho hydrogen atoms and simply by doing a C_2 rotation with respect to OH and para-hydrogen atom, what happens, if we cannot distinguish them then we can say both are chemically equivalent. In case of AB system, we are giving this delta AB equals delta 1 minus delta 4 into delta 2 minus delta 3 ($\Delta\delta_{AB} = (\delta_1 - \delta_4)(\delta_2 - \delta_3)$), and thus middle point will be given as delta (δ) usually and then *J* can be calculated: delta 1 minus delta 2 or that is nothing but equal to delta 3 minus delta 4 ($J = \delta_1 - \delta_2 = \delta_3 - \delta_4$). This is how the *J* is determined here and chemical shift also determined here. For delta-AB (δ_{AB}), we have to take the middle of this one. Now let us consider some examples: Let us consider here chlorobenzene (C_6H_5Cl): Consider this as a rotational axis and if you do C_2 rotation and 1 and 5 cannot be distinguishable or they are indistinguishable. Similarly, H_4 and H_2 are indistinguishable; these two are called chemically equivalent and these two are called chemically equivalent, and again if you take this one, all these are chemically equivalent here, and then again if you consider here again, they are chemically equivalent here because you cannot distinguish them. Similarly, if you consider this picture, I have shown here, H on C_2 and C_4. This one and the hydrogens we have on C_2 and C_4 are cis to CH_3CH_3 and are equivalent, so as H on C_2 and C_4 trans to CH_3 plane.

Plane extending through C_1 and C_3 makes C_2 and C_4 equivalent. Similarly, if you look into Fe to C_1 and, here the axis through Fe-Fe bond make terminal and bridging COs are equivalent. These three are equivalent and these three are equivalent also these are equivalent. So, this is how we can identify whether some symmetry operations can make them indistinguishable after that symmetry operation so that means now we can have a better understanding of chemical and magnetically equivalence or non-equivalence. So, if you say chemically and magnetically equivalent nuclei, that means magnetically equivalent means each member of a chemically equivalent set of nuclei must be equally coupled to each member of any other chemically equivalent set in the spin system. So that means here in chlorobenzene, if you consider H_1 and H_5 are equivalent so as H_2 and H4. These two are identical, these two are identical and the third set is H_3 is H_1 coupled to H_2. Is H1 coupled to H_2 is same as H_5 coupled to H_2, the answer is no, because of the distance. That means if each member of one equivalent set is not equally coupled to each member of second set it cannot be first order. So, this how you can determine whether a given molecule would give a first order coupling or a second order coupling when you have situation like this. If H_1 we are considering: the H_1 interaction of H_1 and H_2 is different from H_5 and H_2. Similarly, H_2 interaction with H_1 is different from H_2 interaction with H_5 or we can consider H_4 interaction with H_5 is different from H_4 interaction with H_1. So, in this case what happens, it cannot be first order, so chlorobenzene is an example of three spin systems. If you designate this as A this is A prime and B, B prime and C (AA'BB'C). We call this one A and then A prime (AA'), what we say is one nucleus with prime says that they are not magnetically equivalent A and A prime (A') are chemically equivalent but they are not magnetically equivalent, and similarly, B and B prime (B') are chemically equivalent, but they are not magnetically.

So, the prime A here represents chemically equivalent but not magnetically. So, letters in the same region or nearby alphabet indicate the similarity in their chemical shift, that is the reason, when we take AABB and C, that means they have almost very similar chemical shift values. If the chemical shifts of H1 and H5 are significantly different from that of H_2 and H_5, then the spin system would be ABB'XX', that can happen if the magnetic field strength is much larger as delta delta ($\Delta\delta$) would be larger, so this is where the significance of going from a low field NMR instrument to high field NMR happens. So, when you go for higher and higher magnetic field instruments, what happens if you take chemical shifts in hertz, the separation will be much larger, all complicated second spectra can be converted into very simple first order spectra. This is where people always look for 400, 500, 600 megahertz (MHz) instruments instead of using 200 or 300 or even hundred megahertz instruments. The moment we designate with AA'BB'C, that means A and A prime are chemically equivalent but they are not magnetically, that one should remember and that one can understand by simple analogy. Whatever I have shown here, the ideal example is chlorobenzene. Now let us look into three spin order system for calculating the spin multiplicity or the number of lines in a peak. 2nI plus 1 rule (2nI+1) is not useful for second order spectrum, and it is only for the first order spectrum. Again. using 2nI plus 1 rule (2nI+1), where n is number of identical or equivalent nuclei and I is the nuclear spin, this one holds good along with the corresponding Pascal triangle, only in case of first order spectrum, but in the second order spectrum we cannot use this rule at all. Let us consider a ^{19}F NMR spectrum of and this molecule. Here trifluoroethylene ($F_2C=CHF$) and this is an example of a AMX spin system, consists of three sets of doublet of doublets (dd). ^{19}F is also hundred percent abundant and I equal to half ($I=1/2$), and very similar to ^{1}H NMR or ^{31}P NMR. So now if you just look into F_A and we have doublet of doublet, F_M we have doublet of doublets (dd) and F_X we have doublet of doublets (dd). The corresponding coupling is given. AM and AX coupling is there, and AM coupling is there and MX coupling is larger again trans coupling and then next AM coupling is there and that is 56 hertz (J_{AM}= 56 Hz) and AX coupling is there that is 76 hertz (J_{AX}= 76 Hz) so you can see here. This appears like a first order spectrum so when two of the three nuclei have similar chemical shifts, I am repeating again when two of the three nuclei have similar chemical shift, the spin system is designated as ABX in which the relative sign of the coupling constants of affect the spectrum. So, AB portion consists of eight lines that resembles two sets of quartets often they are overlapped, giving different type of intensities for lines and the X portion consists of six lines with two lines being very weak and almost there in the baseline transition from AB, AMX to ABX is shown in the next spectrum. I am going to show here so you can see here how AMX spectrum, where it appears like a first order spectrum is converted into a second order spectrum, because of the very little difference in the chemical shifts of A and M. So here, let's look into few points, I have listed here these series of spectra, what I have shown from 1 to 4 represent transition of first order spectrum AMX to ABX, and eventually to A to X. So now these are all simulated spectra AMX with respective chemical shifts of 4, 2 and 1.1 ppm, where J_{AM} coupling is 12 ($J_{AM} = 12$ Hz) and then J_{AX} coupling is 3 ($J_{AX} = 3$ Hz) and J_{MX} coupling is 10 Hertz ($J_{MX} = 10$ Hz). In the second one, again this ABX system with respective chemical shifts of same 4, 3.6 and 0.1 ppm and J_{AB} value is brought down to 9 ($J_{AB} = 9$ Hz) and then BX is 3 ($J_{BX} = 3$ Hz) and AX is 7 ($J_{AX} = 7$ Hz) here so now spectrum 3 represents ABX system with AB chemical shifts of 4, X of 0.1 here only 1 and 0.1 ppm and the coupling constants are same as that we saw in case of 2, 9, 3 and 7 Hertz (J_{AB} (9 Hz), J_{BX} (3 Hz), J_{AX} (7 Hz)). Now in the A to X system, here what happens with A chemical shift of 4 here and then this is 0.1 and then J_{AX} is only shown that is about 9 Hertz ($J_{AB} = 9$ Hz). So sometime you can see some of these variations and as I said, these values depend on the chemical shift difference between A and M and as the chemical shifts of X nuclei moves closer to those of A and B. It becomes ABC system eventually now we saw M moving very close towards CA to become AB in the same fashion, if the signal due to X also starts moving towards B. It becomes say ABC system spectrum can have up to 15 lines here we can see here this is a typical ABC spectrum here ABC spin system I have given two here one at 100 megahertz (100 MHz) the chemical shift values for ABC are 4, 3.7 and 3.4 for AB and C and the corresponding coupling constants of AB is 9 Hertz, BC 3 Hertz and AC 7 Hertz (J_{AB} (9 Hz), J_{BC} (3 Hz), J_{AC} (7 Hz)), and the same coupling constants are kept and the spectrum recorded at 300 megahertz (300 MHz) would be something like this here. You can see clearly as the field strength increases, they are moving away from each other when they are moving away from each other and it is, for example, if you go for 400- or

500-megahertz NMR (400 or 500 MHz), they will move even further apart and then it becomes simple AMX system, so this is the advantage of recording spectra at higher magnetic field strength. Let us consider another simulated spectrum with ABX spin system. Here, ABX spin system is there and delta A minus delta B equal to 10 Hertz (δ_A - δ_B = 10 Hz), and then delta AB equal to 10 Hertz ($|J_{AB}|$ = 10 Hz), and since we do not know the sign, always we represent the magnitude but we are not mentioning the sign and we are ignoring the sign. It is always ideal to represent in modulus. So, this one is minus 4 and this is 1 Hertz ($|J_{BX}|$ = -4 Hz, $|J_{AX}|$ = 1 Hz). That means basically if you consider the ABX spin system, X resonance resembles a doublet expected for a first order spectrum here with X only coupled to B. Close examination of expanded version actually shows six lines for X. This one show six lines and it is not first order, in such cases where resonance appears to be not affected by another nucleus H_A or X, are said to be virtually coupled.

That means this a typical system, where we have this kind of coupling values and chemical shifts, and come across virtual coupling. Let me stop here and continue more discussion on second order system.