

Interpretative Spectroscopy
Prof. Maravanji S. Balakrishna
Department of Chemistry
Indian Institute of Technology Bombay
Lecture 59
Problems and Solutions-8

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. So, this is the penultimate lecture in this series of 60 lectures. In the next lecture, the last one I am going to summarize and conclude about whatever we discussed in the last 59 lectures or so. Let me continue solving some more problems in this lecture.

55. Here is a question. **The Fe^{III}-Ru^{II} analogue of Prussian blue, Fe^{III}₄[Ru^{II}(CN)₆]₃·18H₂O, is a dark purple complex, which shows an IVCT band at 495 nm. Compare its properties, such as delocalization of electrons with Prussian blue.** J. N. Behera, D. M. D, Alessandro, N. Soheilnia and J. R. Long, *Chem. Mater.* 2009, **21** 1922

When we talk about delocalization, it is nothing but the charge transfer.

The presence of an IVCT band indicates the delocalization of electrons in the mixed metal ion complex.

The energy of the IVCT band is inversely proportional to the extent of electron delocalization between the metal centres. More delocalization results in lower energy IVCT transitions.

As a result shift in energy from 680 nm (14700 cm⁻¹) for (Fe₄[Fe(CN)₆]₃·xH₂O) to 495 nm (20200 cm⁻¹) for Fe^{III}₄[Ru^{II}(CN)₆]₃·18H₂O indicates a greater extent of electronic delocalization in the mixed iron ruthenium Prussian blue analogue, which is in fact dark purple.

All ruthenium analogue, a dark green complex, shows an IVCT band at 1000 nm (10000 cm⁻¹) indicating greater delocalization.

56. Another question: **The allowed terms for d^7 are $^2H, ^2G, ^4F, ^2F, ^2D, ^2D, ^4P, ^2P$, identify the ground term.**

Just looking at the question, you should be able to tell the one that has a higher spin multiplicity ($2S+1$) value and eventually if $2S$ plus 1 is identical for both, then we come across this one as well as this one in that case, you have to consider the highest L value. Highest L value will be here, if you take S, P, D, F, 0, 1, 2, 3; 3 is there, whereas 1 is for this one, so you can say without any hesitation, this is the one. But on the other hand, you can also solve this one, ground state, ground state you can have electronic arrangement like this, then you can find out $2S$ plus 1 ($2S+1$) value here, $2S$ plus 1 plus equals 2 into 3 by 2 plus 1, so this is equals 4 and then L is 3, so F is there. And then if you want to find out J value here, J will be here L plus S ($J = L+S$) because this is more than half filled, so 3 plus 3 by 2, so equals 9 by 2, so this will be 9 by 2, here this is the one. For example, if you want to know what is the microstate for d^7 , so you should be able to do it.

That is n factorial over r factorial into n minus r factorial ($\frac{n!}{r!(n-r)!}$) and of course n is the total capacity of the sub shell here, d orbital 10 factorial and then r is 7 electrons, 7 factorial and this is 3 factorial. This will be 120,

57. Now let us look into another problem: **In its electronic spectrum, $[V(H_2O)_6]^{3+}$ exhibits two absorption bands, one at 17,800(ν_1) and the second at 25,700 (ν_2) cm^{-1} . The correct assignment of these bands, respectively, is**

Four options are given, you have to choose the correct one. Before that you have to identify what system, it is, it is a d^2 system and should show three transitions.

So, here it is a special case, I would tell you later why it shows only two absorption, it shows two absorption, From simple Orgel diagram, you should be able to find out which is the ground term here, here the ground term is, this one, so here it is, and among them which one is correct, you have to choose, let us say you are choosing this one. So, high energy transition will be this one and this one will be the high energy one and now just go back to this Orgel diagram written for all: d^2, d^3, d^7, d^8 octahedral as well as tetrahedral

complexes of high spin complexes only. Orgel diagrams holds good only for high spin complexes.

If you want to use for both high-spin as well as low-spin, you have to use T-S diagram. So, here you can see here these two transitions are there, one $3T_{1g}$ to $3T_{1g}(P)$ higher in energy and $3T_{1g}(F) \rightarrow 3T_{2g}(F)$ is the second one. This is shown here. These two and then the question is why only two and of course you also know why this is deflected up, we also showed you about Racah of parameters and more details. You can always go back and check. Here the ligand field strength of water results in transitions occurring close to the cross over point between $3T_{1g}(P)$ and $3T_{2g}(F)$. This is more pronounced for this side that means d^7 system or d^8 system here, this is opposite of d^2 . So d^8 system, it comes more here. As a result, what happens, the energy difference is very small and it merges and you get only two transitions, not three transitions, they are not resolved.

Now let us come back to again to mass and NMR related problem,

58. This compound has the molecular formula $C_9H_{11}NO_2$. Included in this problem are the infrared spectrum, 1H NMR with expansions, and ^{13}C NMR spectra data.

So, you have to depict the structure or you have to identify the compound. Molecular formula is there, you have to identify and write the structural formula or structure of the molecule.

We have carbon, hydrogen, nitrogen and oxygen. We shall find out hydrogen deficiency index. It is very simple $9 + 1 - 11/2 + 1/2$. It will be 5.

Here hydrogen deficiency is 5 here, At least there will be a ring and plus four double bonds. Also you should know, there is a CO. You can see here very intense bands are there at 1200. Now look into how many signals are there: 1, 2, 3, 4, 5, 6, 7, 8 and 9 signals are there and all are different and then some splitting is also seen. In the aromatic region further splitting is also shown, whereas here we have a quartet and we have a triplet and also, we have a small one it represents may be OH or NH_2 or something like that. So, we should remember these things in mind and we shall try to work out the structure. Now, the solution means, first calculate a hydrogen deficiency index this we have already calculated

it is 5 and all of this spectra shown in this problem suggest an aromatic ring, aromatic ring is there and plus 4 double bonds are there.

So, it is not an amide it is in a reasonable place for a conjugated ester. So, that means it is a conjugated ester the 1708 cm^{-1} gives that information while NO_2 present in the form suggest a possible nitro group. This cannot be the case because we need two oxygen for the ester functional group. Since we need one for carbonyl and two ester means COOR then you do not have any other oxygen to think of NO_2 . So, NO_2 is absent by simple reason you can rule out the possibilities of a NO_2 . If NO_2 is not there, the other possibilities a primary amine or secondary amine type.

A band around 3400 in the infrared spectrum is perfect for a primary amine this stretching frequency suggest it is NH stretch, suggesting it is a primary amine. That means we found out CO, there is O and NH_2 also there. Then ^{13}C NMR spectrum has 9 peaks which corresponds to 9 carbon atoms. That means all are unique, we have 9 different type of carbon atoms in the molecule. The ester group carbon appears at 167. So, CO appears at 167 the remaining down field carbons are attributed to 6 aromatic ring carbons. From this we know that ring is not symmetrically substituted. It indicates that certainly we do not have a very symmetrical structure at the aromatic carbon atoms that DEPT results confirm the presence of two carbon atoms with no attached protons.

We have two carbons without having any hydrogen atoms, that is 131 and 147 by DEPT measurement experiment and four carbon atoms with one attached proton. That means we have CH unit here. From this information we know that the ring is disubstituted. That means these four hydrogen atoms in the aromatic region. That means if amine group is there and if NH_2 group is there, it has to be on the aromatic ring. The ring must be disubstituted because 4 protons appear in the aromatic ring it should be disubstituted and also it is not symmetrically substituted. That means there are no groups in the relative para position 1,4 position. Now, this information is given.

First calculate the hydrogen deficiency index (5). All of the spectra shown in this problem suggest an aromatic ring (unsaturation index = four). The remaining index of one is assigned to the C=O group found at 1708 cm^{-1} .

This value for the carbonyl group is too high for an amide. It is in a reasonable place for a conjugated ester.

While the NO_2 present in the formula suggests a possible nitro group, this cannot be the case because we need the two oxygens for the ester functional group.

The doublet at about 3400 cm^{-1} in the infrared spectrum is perfect for a primary amine.

The ^{13}C NMR spectrum has nine peaks, which correspond to the nine carbon atoms in the molecular formula.

The ester C=O carbon atom appears at 167 ppm.

The remaining downfield carbons are attributed to the six unique aromatic ring carbons. From this, we know that the ring is not symmetrically substituted.

The DEPT results confirm the presence of two carbon atoms with no attached protons (131 and 147 ppm) and four carbon atoms with one attached proton (116, 199, 120, and 129 ppm). From this information, we now know that the ring is disubstituted

The ring must be disubstituted because four protons appear on the aromatic ring

The pattern suggests a 1,3 disubstituted pattern rather than 1,4- or 1,2-disubstitution

The key observation is that proton f is a narrowly spaced triplet (or dd), suggesting ^4J couplings, but with no ^3J couplings. In other words, that proton must not have any adjacent protons. It is “sandwiched” between two non-proton groups: amino ($-\text{NH}_2$) and carbonyl (C=O).

Protons g and f appear downfield relative to protons e and d because of the deshielding effect of the anisotropy of the C=O group.

The aromatic out-of-plane bending bands in the infrared spectrum suggests *meta*-disubstitution: 680, 760, and 880 cm^{-1} .

The ^1H NMR spectrum shows an ethyl group because of the quartet and triplet found upfield in the spectrum (4.3 and 1.4 ppm, respectively, for the CH_2 and CH_3 groups).

Finally, a broad NH_2 peak, integrating for two protons, appears in the ^1H NMR spectrum at 3.8 ppm.

The compound is ethyl 3-aminobenzoate.

59. Now, let us look into one more example. This compound has the molecular formula $\text{C}_5\text{H}_7\text{NO}_2$ following are the infrared ^1H NMR ^{13}C NMR spectra. Identify it.

So, $\text{C}_5\text{H}_7\text{NO}_2$ is there. Again we can go for hydrogen index deficiency. Here it is 6 minus 7 by 2 is 3.5 and plus 0.5 here ($6 - 7/2 + 0.5$). So, this indicates this is 3. Hydrogen deficiency index is 3 here and also you should remember, 1 2 3 4 5 signals are there and this is for TMS. Five ^{13}C signals are there. And then we have a quartet and a triplet is there again probably a ethyl group is there. That should come automatically to your mind and then we have one in the region where CH_2 and CH_3 aliphatic are expected, but it is not coupled means it is isolated that we should remember then we have here again a CO group. It indicates here probably we have an ester group here. With this information let us try to analyze the spectra and elucidate the structure. Now, we calculated an index of hydrogen deficiency of 3.

The infrared spectrum reveals characteristic $\text{C}\equiv\text{N}$, a nitrile group around 2300. So, now, we have CO and we have an ester group and also we have a $\text{C}\equiv\text{N}$. Now, the infrared spectrum reveals the source of unsaturation implied by an index of 3 a nitrile group at 20 to 60.

Unsaturation is two for this one and then we have a carbonyl group. So, that is taken care of hydrogen index deficiency. So, one triple bond is there and one double bond is there the frequency of the carbonyl absorption indicates an unconjugated ester. So, this is an unconjugated ester. It is coming around little higher 1747. The appearance of several strong CO bands near 1200 confirm the presence of an ester group.

^{13}C NMR spectrum shows 5 peaks and this is consistent with the molecular formula which contains 5 carbon atoms. That means all 5 carbon atoms are unique and then the carbon atom in the C triple bond N group has a characteristic value of 113 ppm. In addition, the carbon atom in the ester appears at 163 ppm one of the remaining carbon atoms, 63 probably lies next to an electronegative oxygen atom. The remaining 2 carbon atoms which absorbed at 25 and 14 are attributed to the remaining methylene and methyl carbon atoms which are coupled in ^1H NMR to show a triplet as well as a quartet. Now the following are the in the same line. In the structure we have $\text{CH}_3\text{CH}_2\text{OCOCH}_2\text{CN}$.

So, you can see here this will be a quartet and this will be a triplet. For this one, a unique a singlet here and then of course see these are the 3 peaks we come across and then C triple bond N is there since we got a peak b singlet that is for methylene which is not coupled to anything. Also, this is little bit in the deshielded region because next to CO group here. So, we can see here now.

Another problem.

Q 60. An organic compound (**X**) is composed of carbon, hydrogen and nitrogen, with carbon constituting over 60% of the mass. Mass spectrum of A shows a molecular ion at $m/z = 112$ amu.

Answer the following questions.

Plausible Molecular Formula for compound X:

Hydrogen deficiency Index is

Some information is there. 60 percent is carbon. 60 percent means, at least 7 carbon atoms should be there. So, you can do like this and then yes 70 to 60 percent. So, it is 70 to 6 carbon atoms will be there and then corresponding H_{12}N_2 you can find out from rule 13 easily. From rule 13, that should tell you, I have shown quite a number of molecules in my earlier slides.

112 divided by 13 will give 8 quotient and 8 remainder. So it should be C_8H_{16} . Remove two CH_2 to add two nitrogen atoms. It becomes $C_6H_{12}N_2$. Now calculate hydrogen index that will give you 2. So, this is the answer. So, plausible molecular form for X is: $C_6H_{12}N_2$. The hydrogen deficiency index is 2 here. Similarly, one can also do the same structure, but what happens here we do not have nitrogen we have carbon hydrogen and oxygen is there and then again if you find out, it comes around $C_6H_8O_2$. Two oxygen atoms are there and hydrogen index is 3 here. Next you can do the same thing here m/z is 180 and carbon is 60.

So, let me stop here continue in my next lecture about summarizing and concluding whatever the lectures we discussed in the last 59 lectures. Thank you.