Interpretative Spectroscopy

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Lecture 58

Problems and Solutions-7

Hello everyone, I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. In the last few lectures I have been solving problems and then finding out solutions by considering problems having data from more than one type of spectra. Let me continue doing that in this lecture as well.

44. There is a problem I will read out.

While running a new reaction, a chemist notices the evolution of a gas. A sample of this gas gave a mass spectrum in which the molecular ion (m/z = 44) was the largest ion peak. The only other significant peaks were observed at m/z = 28 & m/z = 16.

Just for curiosity, it is very easy to predict the gas, the moment gas means probably we will be thinking of CO, CO_2, N_2 or ethylene something like that. To begin with, to examine this, let us use rule number 13 and also hydrogen deficiency. This molecule is having very low mass to charge ratio, 44. So divide by 13 C3, H will be 3+5 now, C_3H_5 is there and then evolution of a gas is there.

So that means basically there should be carbon monoxide, if ethylene is a different thing. Ethylene may not be there, because this formula gives C_3H_5 so it is little more than that. Let us add one oxygen and see what would happen. For oxygen we have to remove CH_4, so C_2H_4. This is not actually, it should be more. Add one more oxygen C_2H_4 to by removing one CH_4, it becomes CO_2.

So straight away we get this one, this corresponds to 44. So obviously we can tell this is CO_2 and then observed peak at m/z at 16 is O, and CO is 28. So this information is sufficient to say that the gas evolved is CO_2.

Okay easy, it works well with even small molecules.

45. Now another example is there here.

A liquid compound gave a mass spectrum showing a strong molecular ion at m/z = 156. The only fragment ions are seen at m/z = 127 and 129. Suggest a structure for this. The moment we talk about 127, so one element comes to our mind having atomic weight of 127 is iodine.

So probably iodine is there in this molecule. Let us check. First. we take 156 divided by 13 and it divides completely. This is $C_{12}H_{12}$.

If I want to add iodine, how much I should take out for iodine. Iodine 127, that means $C_{10}H_7$, so 120 plus 7. So I have to take out $C_{10}H_7$ here, that means C_2H_5 iodine. Well if it is C_2H_5 iodine, one can write this way CH_3CH_2I. So it ends here.

Yes, possibly this is ethyl iodide. It is also very simple but using this rule. And then adding iodine here and taking out equivalent to 127, $C_{10}H_7$ moiety, we can arrive at the structure of ethyl iodide here. When we look into ^1H NMR, it can show very nicely something like this. Also, ^{13}C will give you two signals.

47. The lowest wavelength light visible to the human eye is 390 nm. What is the corresponding frequency?

It is given in nm. We have number, then we have to convert into frequency here. We know that lambda equal to C by nu ($\lambda = \frac{c}{\nu}$) and nu equal to C by lambda ($\nu = \frac{c}{\lambda}$)

So for this one we have to consider light. Velocity of light is 3 into 10 raise to 8 meters (3×10^8) and over 390 into 10 raised to -9 meters (390×10^{-9}). If we divide this one, we get 0.00769 into 10 raise to 17 (0.00769×10^{17}) here. So then if we remove decimals here and make it 0.769, then it should be 10 to the power of 14 here.

This is per second or we can call it as hertz. So this is the corresponding frequency in this case. The lowest wavelength light visible to human eye is 390 nm. The corresponding frequency is 7.69 into 10 raised to 14 hertz.

So now let us look into one more.

48. In which region of the electromagnetic spectrum is an emission from a neodymium laser corresponding to a transition between electronic energy levels at 11502 and then 2111 cm^{-1}?

So, we have to find out the energy of this emission between them, the transition between the energy levels that corresponds to. That means two levels are there. What we should do is, we have to subtract first or take the difference that should give you 9391 cm^{-1}.

The corresponding wavelength we have to calculate. This is wave number. We know that it is 1 by lambda($1/\lambda$). So here 1 by 9391 = 1.065 x 10^{-9} nm.

So, the corresponding transition energy is 1065 nm.

49. Now what is the color of the solution giving rise to the spectrum shown below? This spectrum is for pentaaquavanadate compound. Vanadium is d^3s^2. Here it is in +2 state.

From this one now let us see whether we should be able to answer this question by looking to this one. So here if we focus our attention to the absorption between 500 to 1000, which comes in the red region as well as partly in green region. You can see it comes around 500 here and then it is coming up to here. That means basically what it does is, it is absorbing from this portion to this portion. As a result it appears blue here. The color of the solution will be blue.

Next Question

50. **Predict which one of the following complexes will have the more intense d-d transitions: *cis*-$[Co(en)_2F_2]^+$ or *trans*-$[Co(en)_2F_2]^+$ (en = $H_2NCH_2CH_2NH_2$),**

Both of them have 2 fluorine and 2 ethylenediamines. If we look into the structures here. This is cis one. This is the trans compound. One thing we can quickly notice about is inversion center or center of symmetry.

So, in this one, we have center of symmetry, whereas in this case there is no center of symmetry. So now the d-d transition itself is Laporte forbidden. But because of mixing of s and p orbitals in a complex, d-orbitals are no longer pure d-orbitals. As a result, Laporte allowed transitions are seen. Nevertheless, their molar absorptive coefficient is very low. But here which one will be more intense. If you look into trans compound inversion center is there.

Cis compound is more intense in color compared to trans compound. Because cis compound lacks inversion center of symmetry. Whereas trans has inversion center.

Another question.

51. What sort of coordination and environment should be best for a commercial pigment based on d-d transitions in a transition metal complex?

I have given some text here. The molar absorptivity (ε_{max}) is greatest for compounds without an inversion centre. Therefore, among all preferred and most common geometries adopted by transition metal complexes, tetrahedral geometry would be the best (it does not have an inverse centre) as this would give the maximum colour per metal centre based on the type of d-d transitions.

However, for their utility as pigments, the highest colour density per metal centre is required and hence charge transfer complexes are preferable.

52. There is one more question here. **The spectrum of $[TiCl_6]^{3-}$ has an absorption at 769 nm, that of $[TiF_6]^{3-}$ at 518 nm and $[TiBr_6]^{3-}$ at 877 nm. Calculate Δ_{oc} (in cm^{-1}) for each of these, and comment on the values.**

We should take the reciprocal and we have calculated that one. This comes around 11400 cm^{-1} for bromo compound.13000 for chloro and 19300 for fluoro compound here.

When we look into this data, we can recollect the position of these ligands in the spectrochemical series. The relative strength of these ligands can also be obtained directly from these values. I have also given an extended spectrochemical series here.

This also I have given in the beginning while discussing about UV spectra of d^1 to d^{10} systems.

53. Now here one more example is there. Electronic absorption spectra of $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ are shown below. Determine Δ_{oct} for these two complexes.

The electronic spectra are given here. Both are octahedral nickel(II) complexes and both are d^8 system. They show three spin allow transitions. I already told many times while discussing UV visible spectroscopy that d1, d4, d6 and d9 show one single d-d transition. Because all of them were put into one group because d1has one electron and d4 has one less than half field, whereas d2, d3, d7, d8 show three transitions.

In the spectrum, if you just see here this is the first one here. This shows at approximately 8500 cm^{-1}, whereas in case of this one it is around 11250 cm^{-1}.

54. One more problem is given here. The spectrum of $[Rh(NH_3)_6]^{3+}$ has two d-d transitions at 32800 and 39200 cm^{-1}, and in the spectrum of $[Ir(NH_3)_6]^{3+}$ they are at 39800 and 46800 cm^{-1}. Estimate Δ_{oct} for these complexes, and compare the values to that of $[Co(NH_3)_6]^{3+}$ (Δ_{oct} for $[Co(NH_3)_6]Cl_3$ is 23000 cm^{-1}).

As you know cobalt rhodium iridium are all d^7s^2 system. We are going from 3d to 4d to 5d; cobalt rhodium and iridium. Then how to calculate that Δ_{oct}. To calculate Δ_{oct} what we should do is, we should take the difference of these two and then one quarter of that one should be added to the lowest one.

That should give you approximately Δ_{oct}. For example, 32800 subtract from 39200 and we get 6400, divide it by 4, it will be 1600. Add 32800. This will give you 34400. So this is nothing but Δ_{oct} for rhodium(III).

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Here rhodium is in +3 state and is d^6 system. d^6 system shows only one transition and it is showing two transitions here. Same calculation we can do here also. 46800 minus 39800 gives 7000. Divided by 4 times will be 1750. 1750 + 39800 = 41550 cm^{-1}. This is Δ_{oct} for

iridium(III). Now if you just compare: Cobalt value is given is 23000. So then if you look into rhodium it is 34400 and for iridium it is 41550 cm^{-1}.

When we go from 3d to 4d to 5d what basically happens is your crystal field energy increases. As we go down higher orbitals, orbits become larger in size. When they are larger in size the greater the difference between the extent of interaction of the t_{2g} and e_g orbital. Then increase in the energy between T2g and Eg is possible as a result of this one and hence what happens? Δ_{oct} increases down the group.

So, I think let me stop today and continue in my next lecture. Thank you.