Interpretative Spectroscopy

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Lecture 43

EI Mass Spectra of various molecules-3

Hello everyone, I once again welcome you all to MSB lecture series on Interpretative Spectroscopy. In my last couple of lectures, I have been discussing on mass spectrometry and discussing about different type of organic molecules having different functionalities, how they fragment, how the molecular ion looks like and what are the incremental degradation of molecules and all those things. Let us continue from where I had stopped. Let us look into mass spectra of amides. In case of amides we do get intense molecular ion peaks. So, primary amides show a strong peak at m/z 44 due to H_2NCO cation and this is how the fragmentation happens initially.

This bond cleaves here and we get a species of mass m by z (m/z) equal to 44 and also β-cleavage is quite possible and it dominates when we are considering secondary amides having more than three carbon-carbon bonds in this R group and then that leads to eventually the carbon monoxide cleavage to form something like this, this species. This is the base peak, it becomes and m by z (m/z) equal to 30 here. You can see here bond breaks here, this is called beta cleavage and then this radical comes out and after that one in the subsequent step in from this radical cation, this bond breaks, CN bond breaks and then this species comes out and this is formed here. So, this is a typical fragmentation of amides.

Let us look into mass spectra of aromatic amides. In case of aromatic amides, loss of NH_2 radical results in resonance stabilized benzoyl cation, that also eventually cleaves to form phenyl cation. For example, you can see this is the base peak for benzamide and then one NH_2 comes out and then eventually CO also comes out and we get 77. This is for phenyl cation. This is how steps involved in the degradation or decomposition or fragmentation of benzamide here and base peak can be clearly seen here.

Now, let us look into mass spectra of nitro compounds. In nitro compounds initially, elimination of NO_2 is possible or NO is possible. In those cases what we get is characteristic peak with m by z (m/z) value of 92 or 108 and if NO_2 is lost, we get 92 and in case NO is lost, we get 108 which eventually gives a phenyl cation similar to what we saw in case of amides after CO elimination. For example, initially it can break here or it can break here when it breaks here we get NO, NO_2 will come out, if it breaks here and then we get

anilinium cation and from that one HCN comes out and we get C_5H_5 and then if NO is eliminated, then we get this radical cation and this one eliminates one CO to form this one here phenyl cation. So, this is also very similar to what we saw in case of aromatic amides. Now, let us look into mass spectra of sulphur compounds.

So, sulphur containing compounds can be readily identified by characteristic M plus 2 (M+2) peaks due to the presence of 4.4 percent of ^{34}S isotope here. The size of M plus 2 (M+2) peaks provides information about the number of sulphur atoms. This is one advantage with Sulphur, invariably we see M plus 2 (M+2) characteristic peaks. Thiols such as $R_{alkyl}SH$ form fragments similar to corresponding alcohols.

The fragmentation is very similar to considering alkyl alcohols and β-cleavage results in the elimination of this cation with m by z (m/z) value of 47 and again primary thiols eliminate H_2S to give a strong M minus 34 (M-34) peak which in turn eliminates ethylene. Primary and secondary thiols lose readily branches if there are any and cleavage of sulphides are very similar to β-cleavage, we come across in case of ethers. Let us look into one example. Let us look into this compound, here initially a cleavage happens next to beta and then we get the elimination of C_4H_9 radical that results in the formation of this mass fragment with m by z (m/z) of 117 and then further decomposition happens. These are the possible cleavage products either H migration can happen or C-S bond can break and we can get a species here and also eventually what we are getting is this species cation with m by z (m/z) value of 47. You can see here, this is the base peak here. From this one, what we lose is this 47 goes off and then we get 117, where we have this portion, this breaks to give this one but initially this one would break another CH_2 moiety to give 103 peak and then from 103 peak, this goes off to give this 71 that means basically one goes here and then this migration takes place and then this portion will be there C_5H_{10} that is what it shows here and also you can see the relative intensities of peaks here M is 174 100 percent M plus 1 (M+1) is 11.33 percent and M plus 2 (M+2) is 4.6. You can see here.

Let us look into a mass spectra of halogen compounds. Characteristic isotopic patterns can be readily recognized in case of halogenated compounds, similar to what we saw in case of sulfur compounds. Compounds containing one chlorine atom will have M plus 2 (M+2) peak with one third of the intensity of M. For example M [^{37}Cl by ^{35}Cl] ([$^{37}Cl/^{35}Cl$]) is 32.5 by 100, roughly it is one third of the intensity. So, M plus 2 (M+2) peak in a compound with one bromine atom will have the same intensity as that of M and compounds containing two halogen atoms, Cl_2 ClBr or Br_2, display a distinct M plus 4 (M+4) peak from which we should be able to distinguish and we can immediately tell or we can get information about the presence of halogens in the molecules.

If we have instead of chlorine or bromine, fluorine or iodine, they have only one isotope. This is ^{19}F 100 percent abundant, it is 127 100 percent abundant. This chart what I have shown here will tell you about the molecular ion peaks for bromide and chloride compounds. The application of isotope contribution is limited by weak molecular ion peaks, but the fragments containing halides can be readily recognized.

You can see here in case of chlorine and Cl_2 when you have Cl_3 and also when you have Br is there in BrCl is there $BrCl_2$ $BrCl_3$ Br_2 Cl Br_2 Cl_2 Br_2 Cl_3 Br_3 Cl. All these combination is shown here, typical ion peaks containing bromide and chlorides. So, this is a very useful chart that I have shown here a guide to interpreting mass spectra. For example, if a methyl cation is coming out you know what is the m by z value, it is 15 or ethyl is coming 29 or if you are getting a nitrogen carbon fragment. So, all this information is there and also some vital information is also given at the left hand side of the chart here. Also how the mass is detected, how typical mass spectrometry instrument works also shown here.

This is a useful chart got it from, this site here. So, please go through it, this is very useful site for reference. Let us look into some more spectra here. This is the mass spectrum of ferrocene and of course, this one I simulated and collected the data here and 100 percent abundant one can be seen here 269 and 270 and this is for diacetyl ferrocene here, the base peak should be around 270 to 271 and then it fragments out. I have another one to show here and the different masses I have shown here. Just look into it, what fragment is coming out, whether first acetyl group is coming out and then eventually Cp group comes out and it is getting stabilized with eventually CpFe plus. But here we should go further to see that one that is the typical peak we observe at the end in case of ferrocene. If the number of atoms with more than one isotope increases in a molecule, the distribution becomes more complex. For example, if you have too many atoms having many isotopes in the system, then the distribution becomes more complex and also understanding becomes more difficult. So, I have shown here one such CCl_4, of course, you should remember when we are considering CCl_4 we are considering ^{35}Cl ^{37}Cl and also ^{12}C and ^{13}C and CCl_3. It shows the pattern something like this and if you have CCl_2 it shows and CCl it shows 2 and Cl it shows 2. I think I have more examples.

Let us look into fullerene, C_{60}. Despite fullerene not having halogens or sulphur shows 4 ions with significant abundances. So, 1 2 3 4 here and then if you look into the parent peak because it is 60 and molecular weight will be 720 and this is how it is split with M peak 720 m plus 1 (M+1), m plus 2 (M+2), and m plus 3 (M+3) of course, the combination also I have shown here. This is 100 percent and this you can see combination of ^{13}C and 12 and here we have $^{13}C_2$ and then 12 and here we have $^{13}C_3$ here and base peak comes here plus

m plus 1 (M+1) is shown here. What would happen if the number of carbon atoms in the molecule increases then what kind of molecule ion peaks we get to see is shown here.

For example, if molecule M is 100 and, if let us say we have 10 carbon atoms, then we will see m plus 1 (M+1) and 11, in case of 25 it is 27, 50, it is 55 and for 99, it is 100 and if you have m plus 2 (M+2), in case of C_{25} we will see 3 and 15 for 50 and 49 for 90 and similarly m plus 3 we will see 2 in case of C 50 and above and C 90 it is 16 and m plus 4 only in case of C_{90} that means, when you have 90 carbon atoms we will see here 3. This gives some information about higher analogs of similar molecules. This shows typical isotopic pattern for compounds containing different elements. The first one is about main group elements of course, when hydrogen is there, it is very simple, carbon is there we will see 2 this is because of ^{13}C and ^{12}C and nitrogen we will see because of ^{14}N and ^{15}N and oxygen we will see 16 and 17 and then fluorine only 1 because ^{19}F is 100 percent abundant. The same thing is true in case of phosphorus ^{31}P 100 percent abundant sulfur we have 32 34 and 33 and we see 3. In case of Cl again we have 35 and 37. So, this is the typical isotopic pattern one should remember, whenever we look into the mass spectra having these elements in the molecule.

Now similar chart I have given here for transition metals. For example, ruthenium, this is the typical pattern and rhodium again 103 we have 100 percent, we do not see anything else and palladium we have this and silver we have and then in case of cadmium it is little bit more complex and indium we have 2 and tin again it is bit more complex and in case of antimony we will see 2 isotopic patterns 2 peaks here. So, isotope patterns of polyatomic ions are calculated using binomial expansion as I mentioned, if you have more atoms having a greater number of isotopes then how to calculate the isotope patterns, we see in the molecular ion peak that can be simply understood by using the binomial expansion. This is the binomial expansion we use here and what is a_A b_A or c_A etcetera are the fractional abundance of the isotopes of ^{x}A ^{y}B and ^{z}A of element a and the n number of atoms of present in the ion. So, the n represents similarly for m atoms of b it continues like. This if you have more than 2 or 3 different atoms having different isotopes simply we can calculate using this formula.

Now let us look into one example here: This is dicarbonyldichloroiridium anion. Iridium has 2 isotopes: 191 that is about 37 percent, and 193 that is 63 percent and similarly we have 2 isotopes of chlorine ^{35}Cl is 76 percent or 77 percent and ^{37}Cl is 24 percent. The contributions of minor isotopes of carbon is ^{13}C 1 percent and oxygen-17 very minute 0.00038 percent and also ^{18}O is about 0.008 percent or one can neglect this oxygen isotopes such as ^{17}O and ^{18}O. Following table what I have shown, shows how to calculate the relative abundances of each of the peaks in the isotope pattern with mass spectrum of this one, mass spectrum, I will be showing you in the next slide. For example, one can start writing ion composition, one should not do any mistake. First you can consider ^{191}Ir and $^{35}Cl_2$ both

are 35 and CO_2 is there and this is 317 and fractional abundance we have to take 0.37 for this one and 0.76 for 35 chlorine and here the total value will be 0.214 and this will constitute 43 percent and then if you consider ^{191}Ir and 191 now we are considering second case ^{191}Ir and same ^{35}Cl, we are considering both of them and here this is 319, because it increases and then by 2 and now 0.63 is considered for ^{191}Ir and then 0.76 continues. When you sum up you will get 0.364, this constitutes 100 percent and then we can take the combination. Now take ^{191}Ir and take the combination of both ^{35}Cl and ^{37}Cl. Here, the fractional abundance can be calculated like this. Into 2 we have to use because the ion intensity is made up of contribution from 35 and ^{37}Cl so here it is 0.135. It is a small quantity and then of course in the same combination we can also have 193 35 and 37. This also comes here. Similarly, we have taken the fractions here and some of these two will be coming around 50 percent and then another one is now change the iridium to 193 to 191 and consider both Cl and that is 323 and then we get this calculation done and it shows you 0.021 and now we can consider ^{193}Ir and both 37, so that amounts to this value and at the end we get the value of 7 percent so that means basically we can see three peaks with almost 1 is to 2 is to 1 ratio in the spectrum of this iridium dichlorodicarbonyl anion. So, you can see here, this shows 3: one is coming around about 43 percent, one is coming around 50 percent close to and the other one is 100 percent. You can see the peaks here. Whatever the calculation we have made here is reflected in the spectrum, we have observed here. This how one can calculate and get to know how to interpret the molecular ion peak or fragment peaks in this fashion, if you have more isotopes.

This is a very beautiful mass spectrum of hexaphenyl tin compound this is a cationic compound and I have identified the major peaks here and of course this comes something like this. Very beautiful one, this is again simulated using simple software. I simulated this one and also collected all the data for all the peaks observed here.

This is a very useful periodic table. This gives about the entire periodic table and then all possible isotopes and their abundance. Everything is listed in this periodic table so whenever you get time you just go through it. For example, cadmium is there and almost all elements are there. For reference, cadmium is taken here and now let us look into one example here. Inorganic complex Ru(cymene)(PTA)(Cl_2). PTA is phosphatriaza adamantane, a monophosphine. This is bound to ruthenium and this is the cymene. we call this as methyl-4 -isopropyl benzene this is taken in methanol in the presence of lithium salt Li plus (Li^+) and left one what I have shown here is the normal scan and resolution is 1000. You see the broader peaks for the weakly bound solvent like here. You can see the broad one for weakly bound solvent and the right one is expanded one, the resolution of M plus Li (M+Li) peak has improved to 3000 and the weakly bound solvent adducts have disappeared to be replaced by unresolved peak here so this again a very interesting mass spectrum of ruthenium 2 compound. Ruthenium is in plus 2 state.

Before I conclude this lecture, I will show you one more. This is crown ether and I am sure you know how to name the crown ether you start numbering like this. This one, the number of atoms in the ring are 18 crown and 6 oxygen atoms are there. This is called 18 crown 6 ether and this can conveniently encapsulate a positive ion such as alkali metals or alkaline earth metal ion to impose an octahedral geometry. This one will go up and this will come out and they will remain in the plane. This is the typical mass spectrum of 18 crown 6 ether, the molecular ion peak is 264 from 264 it becomes 221 that means basically it is losing one C_2H_3O cation and you get 221. 221 Onwards what happens, the incremental decrease in the loss of C_2H_4O moiety is coming here and then you can see here incrementally it is losing and at the end eventually we get 45. So if you see here, this one we are losing and from here we are losing another one and one more we are losing and then one more we are losing and this becomes the base peak for C_2H_4OH plus. This is again typical for crown ether and in case of crown ethers, the fragmentation happens with regular decrease in the molecular ion peak with a mass of 44 that corresponds to CH_2CH_2O.

Let me continue in my next lecture with more examples. Before I conclude mass spectrometry and of course I have lot of problems on mass spectrometry as well. In the end I would try to combine some of these issues related with mass spectrometry with NMR or IR to solve the problems. Until then have an excellent time thank you.