Interpretative Spectroscopy

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Lecture 41

EI Mass Spectra of various molecules-1

Hello everyone, it is a pleasure to welcome you all once again to MSB lecture series on interpretative spectroscopy. In my previous lecture I started showing you mass spectra of organic molecules. So, let us begin looking into more such examples in this lecture. As I had mentioned, let me show you some representative, important and also simple example to understand mass spectra of various molecules having different type of functionalities. Let us first consider saturated hydrocarbons. Mass spectra of linear hydrocarbons display molecular ion peaks which provide the molecular weight.

So, M CH_3 peak, the first methyl group is always weak, and due to the detachment of CH_2, fragments will be 14 mass units apart. That means when the fragmentation is there you can see regular degradation with a loss of 14 mass units due to the detachment of methylene fragments. One such example is n-hexadecane, molecular weight 226, the parent ion peak is here and then we can start here, 16 is not shown. The 14 one means probably a lot $2CH_2$ units and it continues and you can see up to C_2 is there.

Of course, saturated hydrocarbons and linear saturated hydrocarbons, it is quite very simple to analyze and understand, and parent peak can be readily identified. So now let us look into some acyclic saturated hydrocarbons. For example, one such again, this is for C_6H_{14}, hexadecane. Normal hexadecane 86 is there; you can see here and then this one is becoming C_5H_{11} losing one CH_3 fragment, and then again if you see here 58 is there, this is for C_4H_9 plus and this is 57 and 58 is also given here. You can just look into it and then we have 43, 41, 42, 39 and also, we have 27. That means very nicely you can distinguish all these fragments and you can give the right mass for them and then if you make yourself familiar with interpretation in this fashion, it becomes very very easy when you are going for unknown samples. Then here, you can see all of them. I have listed here starting from this is the one after losing one methyl group 71 and then it is 58 and then 57 is there and then we have 56, 55 and then 43, 42, 41. That means up to 27, you can see a large number of fragments, but nevertheless it is very easy to interpret here and now let us look into the mass spectrum of branched saturated hydrocarbons.

So, this cationic radical is always present in branched saturated hydrocarbons and branch fragmentation will also be observed as in 5 methyl pentadecane I have shown here. Here CH_3, C_4H_9 and $C_{10}H_{21}$, hydrogen loss will give intense C_nH_{2n} peaks here. If you look into 5 methyl pentadecane molecular weight is 226 this is the parent peak and then once it loses one methyl group it comes here and when it loses 4 carbon links and it comes here and then here it is 6, it is 5, 4, 3 that means up to 3 we can see here almost loss of everything except for 3 carbon, we can see the fragments here. So, hydrogen loss will give intense C_nH_{2n} peaks in case of saturated branched hydrocarbons. Let us look into now saturated cyclic hydrocarbon. The simplest saturated cyclic hydrocarbon we come across is cyclohexane here, here branches are cleaved if there are any branches, they are cleaved, whereas the increase in the relative stability of molecular ion peaks is also observed more and more molecular species become stabilized here. So, ring when cleaved, consists of even number of fragments. For example, C_2H_4 something like that.

Now we can see here, molecular ion peak, the molecular weight is 84 and then we have 56 here and then 41 here, it is for C_3H_5. Now let us look into cyclic saturated hydrocarbon that is the same thing, cyclohexane is there, little bit more I have elaborated here, giving the peaks, the corresponding peaks and the explanation here. So, M plus is the molecular ion peak with mass to charge ratio 84 due to C_6H_{12} plus here. The small M plus 1 (M+1) peak at 85 is due to ^{13}Carbon atom in it that is $^{13}C^{12}C_5H_{12}$. So now isotope is coming that is abundance of ^{13}C is 1.1 then ^{13}C accounts for 1% more carbon atoms in the molecule, the greater the probability of observing this ^{13}C M plus 1 (M+1) peak. That means, if there are a greater number of carbon atoms, or more abundant ion peaks of cyclohexane, the more possibilities of their observation. Here intensity of M plus 1 (M+1) is 6.6, so the most abundant ion peaks of cyclohexane is m by z (m/z) is 56 and then this goes to C_4H_8 plus and also ethylene comes out. The m by z (m/z) 56 is base peak, the most abundant and stable ion fragment. That is the reason you can see 100% abundance of this one.

It is found by the elimination of ethene from the molecular ion the m by z (m/z) value of 83 69 55 are related to the loss of a mass unit of 14, that is for CH_2 from one fragment ion to the next one you can see here I have listed all of them, mass to charge ratio and the fragment which is essentially cation has to shown from 69 to all the way that means after 1 CH_3 here and then we have C_4H_9 and then we have C_4H_8 C_4H_7 C_3H_7 C_3H_6 C_3H_5 C_3H_3 C_2H_5 and C_2H_3. So, you can clearly see all these fragments and their corresponding mass very nicely in this beautiful mass spectrum of cyclohexane. Now let us look into the mass spectra of olefins, allylic cleavage is a possibility in olefins. So the moment you look into the mass spectrum of olefin, you can see the allylic cleavage and also the fragment having allylic mass. The mass spectrum of M beta-myrcene molecular weight is 136 shows clustering of C_nH_{2n} plus 1 (C_nH_{2n+1}) and C_nH_{2n} and also C_nH_{2n} minus 1 (C_nH_{2n-1}) at intervals of 14 due to the loss of again methylene fragments. For example, CH_3 C_4H_9 $C_{10}H_{21}$ and also hydrogen loss, when hydrogen loss is there, it will give intense peak of molecular mass C_nH_{2n}. So, now you can see here, one such example is given for beta myrcene. Molecular weight is 136, when it loses this allylic radical, you can see here, it comes to 93 here C_7H_9 and then it becomes C_5H_9 we have mass of 69 and 67. Then we get C_4H_7 and then C_3H_5 plus.

The fragmentation as I mentioned here happens and that results in or it can also happen here giving the allylic chain and other possibilities here when this happens here this is allylic you can get here and in this case you can see mass by charge 67 you can identify here C_5H_9 here this is the one and then what we have is here 93 we have C_7H_9 plus so then here you can see again C_5H_9 plus so this is how it fragments it gives some idea about possibility of thinking the way in which the compound can cleave and form different fragments in an unknown sample. This gives lot of information and experience to analyze your own spectrum of unknown samples. Now look into aromatic hydrocarbons, aromatic hydrocarbons show little fragmentation ions but lots of molecular ions due to the loss of H dot H radical and also one can also see the loss of H_2 as well as CH_2 from aromatic compounds and this is the one most common if you just look into the mass spectrum given here of naphthalene. Here molecular weight is 102 and we can see loss of CH_2 and it continues like this. So, this is so this is not 108 this is 128 so then loss of will give you 14, 102 we can also see here some fragments and some fragments here. So now let us look into all kinds substituted benzene which show interesting features in electron impact mass spectra so methylene group gets into ring and ring expansion takes place to form C_7H_7 tropholium cation how that happens for example this is the bond vulnerable for cleavage the alpha beta and then you can get a radical like this and you can get something like this and then this one gives a trophillium by this one getting inserted to the ring here so trophillium cation mass to charge ratio is 91 and then on the other hand through this one hydrogen immigration is there then we get benzylium radical here you can see the naphthalene spectrum I have shown 128 here 128 is the one and 129 is M plus 1 (M+1) due to ^{13}C here. This shows fragment intervals of 14 due to the loss of CH_2 units and aromatic hydrocarbons show little. I already mentioned but lot of molecular ions this is common, so this one is a simulated one, and the values I have shown here, intensity and also this one M plus 1 (M+1). Now let us look into alcohols, ion peaks tend to be very small in case of alcohols and non-existent for tertiary alcohols. This ion peaks may not be observed in case of tertiary alcohols. Beta cleavage to the OH is common, resulting in peaks such as CH_2OH plus 31, MeCHOH or Me_2COH species, respectively, for primary, second, and tertiary alcohols; CH_3OH Me_2CHOH and Me_3COH. Here the mass spectrum is given for ethanol, 46, you can see here. This is the one and then it is giving CH_2OH and also it is giving C_2H_5O and also it is giving C_2H_3 and C_2H_5 plus $C_2H_2C_2H_3O$. As we have mentioned here so and then eventually it gives the last one, CH_3 plus at a 15 value. This is how ethanol mass spectrum look; a few more spectra have shown here. This for 1-butanol and also this for pentanol. Identify the peaks and maybe calculate and then see the difference between the fragments, so that what kind of fragment has come out from here to here and from here to here. You can examine these things leisurely. Now M plus (M^+) is the molecular ion peak in case of ethanol with mass to charge ratio 46 due to C_2H_6O plus, that is, CH_3CH_2OH plus. M plus 1 (M+1) peak at m/z 47 is due to $^{13}C^{12}CH_6O$. Ethanol has 2 carbon atoms, so on average 1 in 50 will have a ^{13}C carbon atom. The most abundant ion of the molecule under mass spectrometry investigation is usually given an arbitrary abundance value of 100 that is called the "base ion peak" and all other abundances are measured against or with respect to the base ion peak. Now a little bit more information I have given about this ethanol fragmentation. This explains the principal fragments of the mass spectrum of ethanol. This may be helpful in analyzing the spectra of organic molecules, especially taken from either electron impact or chemical ionization.

Formation of m by z (m/z) equals 43 and 45 ions:

Peak at m by z (m/z) 45 is due to the loss of a H; actually, a hydrogen radical, from the ionized ethanol, the parent molecular ion is C_2H_6O plus, which gives C_2H_5O plus and H comes out and then the mass change 46 minus 1 equal to 45. So, loss of H_2 from this ion forms the m by z (m/z) 43 and that means if you consider C_2H_6O plus it gives C_2H_3O plus H_2. Then m by z (m/z) ion of 31 is formed by scission of C-C bond in the parent molecular ion. For example, if you consider again C_2H_6O plus, it gives CH_2OH plus and CH_3 and mass changes from 46 to 15 is 31. So, this is the base peak, the most stable fragment and of course you can go back and look into the spectrum and then formation of 28 mass by charge ratio 28 is formed by the elimination of water from the parent molecular ion. For example, if you consider CH_3CH_2OH and if you remove water you get C_2H_4 plus. This has 28 mass, changes 46 minus 18 = 28 (46-18 = 28). This is a systematic analysis of the spectrum that one should do for every spectrum one looks into, Formation of 29 again, 29 means just look into it CH_3CH_2OH plus gives C_2H_5, ethyl radical plus OH. OH is 17, so, mass will be 29, that means 29 is due to ethyl cation and then formation of 27 ion here. If you just take C_2H_5 plus and then C_2H_5OH plus. Then it gives C_2H_3 plus and then OH comes out. So this is for 27 and then the formation of m by z (m/z) equal to 15 and is formed by cation of CH_2OH and CH_3 this is for CH_3. This is how you can completely analyze and give explanation for every fragment you see in the mass spectrum. Now let us look into phenols. The molecular ions are more abundant compared to aliphatic alcohols. Common fragments lost are CO that means minus 28, and CHO, minus 29. Mass spectra of substituted phenols differ because of fragmentation of substituents. The fragmentation happens in different ways. For example, if you look into this one here, there are two possibilities, and in one CH_3 radical can come out and you can generate a species of molecular weight m by z (m/z) 107 or it can get one hydrogen radical coming out to form

CH CH_3 and OH and this species with a m by z (m/z) value of 121. So, these two possibilities are there and a typical example is shown here for this one with a molecular weight of 122. So, this 107 is also shown here and 104, 121 is here and then 77 further goes that is due to eventually the phenol radical.

Let us move on to another example. Mass spectra of aliphatic ethers: the simplest one is diethyl ether. So here we are considering 2-ethoxybutane. This is the one with molecular weight 102 and possible cleavage sites shown, here as well as here and also hydrogen migration also possible here. For example, its molecular weight is 102. When it loses one methyl radical, it is 87 when it loses ethyl radical it is 73, when it loses ethoxy radical, it is 57 and then we get this 45. This is the fragmentation pattern, and cleavage can also happen here to ethoxy group, and these two are important fragments, 87 is shown here and also 73 is shown here, okay. So you can see the loss of ethyl would give 73 and loss of a methyl radical would give 87 value. Now let us look into mass spectra of aromatic ethers. Consider para-dimethoxy benzene. Here the possible cleavage is at O-C bond, so methyl radical would come out and you can get a cationic radical and then this can give you cyclopentane cation 65 and then it can also cleave at both sides to release HCHO to give phenyl cationic C_6H_6 plus radical. If the alkyl portion has a longer chain, then the cleavage leads to the formation of olefin via hydrogen migration. For example, this is the possible site: if you have a longer chain, in that case, what happens, ethylene would come out. Substituted ethylene and we get something like this and eventually this gives this species here. I think this would be enough, just go back into whatever the spectra I had shown. Just look into it once again analyze yourself and see the fragmentation pattern, so that you would be remembering and also it would be very easy to interpret, as I had mentioned, when you look into unknown sample spectra.

See you in my next lecture and have a good time thank you.