Interpretative Spectroscopy

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Lecture 39

Isotope Peaks in Mass Spectrometry

Hello everyone, I am sure you are having great time in understanding interpretative spectroscopy. I once again welcome you all to MSB lectures series on interpretative spectroscopy. In my last lecture, I started discussion on topics such as mass spectrometry. When I concluded my last lecture, I was talking about resolution in mass spectrometry. So, let me continue from where I had stopped.

Resolution of a mass spectrometer: Let us consider molecular weight of M equal to 2000 and R equals 2000, then ΔM equal to 1 the ratio. So, m by z peaks at 1999 or 2001 can be resolved. This is called unit **resolution**. On the other hand, if you have M equal to 200 and say R equal to 2000, then ΔM will be 0.1. Now spectrometry will distinguish masses such as 200.1 and 199.9. So, using HRMS, high resolution can be achieved, that means we call high resolution mass spectra, abbreviated as HRMS.

For example, if we consider two isoelectronic gases such as CO and N_2, we know the mass of 12-carbon is 12.0000 and 14-carbon is 14.0031 and ^{16}O is 15.9949. So, the exact mass, if we consider for N_2, it would be 28.0062 and exact mass of carbon monoxide is 27.9949. The difference ΔM is 0.0113. So, in HRMS, here we have 1, 2, 3, 4 in HRMS up to 3 decimal places is common and can distinguish CO and N_2 and resolution can be even up to 6 decimal places.

So, that is the strength of HRMS, no matter how minute the difference in the mass between two species, that can be understood and analyzed in HRMS. Now let us look into **unit mass molecular ion and isotope peaks**. In order to elucidate the structure, unit resolution for the molecular ion together IR and NMR data is sufficient to know the molecular formula. Sometime although we get vital information about molecular weight and the fragments through ionization, it is always advisable to take some more information from spectroscopic methods such as NMR as well as IR and if needed from UV-visible spectroscopy as well.

Now let us consider an example of C_7H_7NO. Here we have seven 12carbon and 7 hydrogen atoms and one 14-nitrogen and 1 oxygen is there, the unit mass is 121 here. So, unit mass can be higher if molecules contain heavier isotopes such as 13 carbon. The abundance is 1.11 percent and also ^{2}H a very low abundance 0.016 that is deuterium and then ^{15}N is about 0.38 percent and ^{17}O is even less 0.04 percent, the unit mass will be greater if you consider some of these isotopes as well. If you consider let us, say ^{13}C along with ^{12}C and $^{1}H_7$, ^{14}N and ^{16}O we will get M plus 1 isotope because we are adding one ^{13}C in place of one ^{12}C. So, unit mass will become 122 instead of 121. So, other isotopes also contribute to the intensity of M plus 1 peak. For example, you can also have a combination like this: $^{12}C_7$ ^{2}H $^{1}H_6$ ^{14}N and ^{16}O or you can have ^{15}N $^{12}C_7$ ^{1}H or you can also have ^{17}O. So, that means all these will contribute towards the intensity of M plus 1 peak, where the mass unit mass will be 122 rather than 121.

Peak height ratio and reason for observing M plus 1 M plus 2 peaks we should understand now the presence of ^{13}C isotope as I showed you in my previous slide in a molecular species cause an additional peak 1 unit to the rate of the M plus peak and that is called M plus 1 peak. So, instead of 121, we saw 122 due to the addition of one ^{13}C in place of one ^{12}C. So, the presence of chlorine or bromine atom in a compound causes 2 peaks in the molecular ion region that is M plus and M plus 2 peaks depending on that particular ion contains 35 chlorine or 37 chlorine. Same is true in case of bromine as well. That means, when we have halides, we can anticipate M plus and M plus 2 peaks depending upon whether we have 35-chlorine or 37-chlorine or bromine also with a difference of 2 units. Now in a molecule if only C, H, N, O, F, P and I are present, the approximate percentage of M plus 1 intensity can be calculated as follows: For the same molecule, we are considering with the unit mass of 121 in the absence of any of these low abundant isotopes.

Now, for example, if you consider percentage M plus 1 1.11 into number of carbon atoms plus 0.38 into number of nitrogen atoms should be considered. So, that means if you take here the values are given here 1.11 into 7 and then 0.38 into N. So, it gives around 8.15. This comes very close to this value here. So, this is actually. I simulated for this one and I obtained this data and clearly it shows about M plus 2 peak here. So, you can get the value calculated here and we are getting 8.08 here.

Now the relative abundance of common elements I have listed here carbon of course, 99 percent I would say is 12 carbon only 1.11 percent is 13 carbon and relative abundance is 100 and this is 1.11 and then 1H is 100 and here it is 2H deuterium is 0.016 and in case of nitrogen ^{14}N is 100 relative abundance, whereas for ^{15}N is 0.38 and similarly for oxygen ^{16}O it is 100 percent, ^{17}O it is 0.004 and also apart from ^{17}O we also have ^{18}O that is 0.20 relative abundance. In case of fluorine we have only 1 isotope ^{19}O that is 100 percent abundant. In case of silicon again we have 3 isotopes, ^{28}Si relative abundance is 100 percent

^{29}Si 5.10 and then ^{30}Si 3.35. In case of phosphorus now only isotope is ^{31}P which is 100 percent and in case of sulfur again, we have 3 isotopes, ^{32}S 100 percent and ^{33}S 0.78 and then ^{34}S 4.40 and in case of chlorine, we have ^{35}Cl 100 percent and ^{37}Cl 32.5 percent and in case of bromine we have ^{79}Br 100 percent and ^{81}Br we have 98 percent and then in case of ^{127}I, we have only 1 which is 100 percent. So, the contribution from this one is M and contribution from this one is M+1 and contribution from this one would be M+2. So, this clearly shows why we see apart from M, M+1 peaks, and in some cases we also see M+2 peaks, because of the different type of isotopes in different abundance present in the sample. So, the isotope peaks are useful in determining the molecular formula. So, an intense M+2 peak indicate the presence of elements such as sulfur silicon chlorine and bromine. So, that means, in our sample when we are subjecting to mass analysis if you have silicon sulfur chlorine and bromine we will see an intense peak due to M+2 unit. So, while analyzing and interpreting mass spectra one should always check for M+1 and M+4 peaks and other higher isotope peaks as well and one should look into relative intensities to know whether that is present or not.

Now, the relative intensity of the M+2 peak in the mass spectrum of the compound shown here. So, indicate the presence of two sulfur atoms the moment you see this molecular formula isotope components is 148.0380. Moment we see this one it indicates the two sulfur atoms are there and then mass to charge ratio again this I have taken simulated spectrum from that one this data was obtained and you can see here M+2 peaks having the fraction intensity of about 8.27. So, that is seen here 9.7 this is 8.27 and then isotope abundance is m by z 148 for m is 100 percent m by z 150 is M+2 this is about 9.7 percent here. So, now, mass spectrum of pentane is shown here. In this, one should try to identify different peaks. This 72 is for this one. If you calculate the molecular weight, here 60 plus 12 hydrogen atoms, this is 72 and then we have one at 57 we should try to identify what it is due to. So, of course, from here if you remove one CH_3 here.

Then you will get 57 that means one CH_3 is missing here, and here one CH_3 and one CH_2 is missing. Like that, this fragment would give you, how the given sample is fragmenting out and at the end we get a 29 this is CH_3CH_2. So, this 29 is for ethyl group. This is how we can analyze and we can simplify mass spectrum. This is a simplified mass spectrum of pentane here. So, now, let us try to understand little bit more about these isotopes and their influence on unit peak and shifting that one the M+1 or M+2.

So, m plus 1 peak is caused by the presence of the ^{13}C isotope in the molecule ^{13}C is a stable isotope of carbon makes up 1.11 percent of all carbon atoms. That means, basically if you have 100 molecules are there out of 100 molecules one molecule will be having ^{13}C whereas, other will be ^{12}C or if we have 100 atoms are there out of 100 atoms we have 99 atoms 12 carbon and 1 atom is ^{13}C. If you take methane CH_4 one in every 100 will have ^{13}C rather than ^{12}C. One in every 100 molecules will have a mass of 17 rather than 16.

Therefore, mass spectrum will be consisting of two lines due to molecular ions $^{13}CH_4$ plus as well as $^{12}CH_4$ plus. Line at m by z value of 17 will be much smaller in height than the line at m by z value of 16, because the ^{13}C isotope is only 1.11 percent. So, there will be one heavier ion 17 for every 99 lighter one 16. As a result, the M+1 peak is much smaller than the M^+ peak. So, the moment we see, why M+1 peak is much smaller than M^+ peak. M^+ peak represents the isotope which is abundant maximum, whereas the other one for the smaller isotope present in the molecule.

So, now, look into one problem here

A gas was known to contain only elements among ^{1}H, ^{12}C, ^{14}N and ^{16}O. The gas showed a molecular and peak at mass to charge ratio of 28.0312 in high resolution mass spectrum. Identify the gas.

So, here the information what we need is the atomic weight of these four elements.

So, H is 1.0078 ^{12}C is 12.00, ^{14}N is 14.0031 and in case of ^{16}O it is 15.9949. Then if we look into all possible gases, possibly N_2 we can think of CO and C_2H_4 will be 28.0062 and CO will be 27.9949 and C_2H_4 will be 28.0312. So, workout will give a mass of 28.0312 so that means, here 0.0312 28.0312 this is for C_2H_4. So, immediately we can say that this H rms this molecular and peak is due to ethylene gas. So, in the mass spectrum of dodecahedron $C_{20}H_{20}$ the approximate ratio of the peaks at m by z is 260 and 261. So, identify the peak. So, here only carbon atoms are there $C_{20}H_{21}$ and if we consider only one carbon 1.1 into 20 will be 22. So, other will be 100.

So, if you take the ratio of these two it will be 100 by 22 is approximately 5. So, the ratio should be 5 is to 1 is the answer. So, that means, the approximate ratio of the peaks at is question mark this should be 5 is to 1. So, this how some of these simple problems can be understood and solved without any problem.

Now, another example here. In the mass spectrum of 1,2-dichloroethane the ratio of peaks at mass to charge values are 98, 100 and 102. If the ratio of this one is 9 is to 6 is to 1, explain how?

When we look into chlorine, the two isotopes are there 35-chlorine and 37-chlorine. They are in the ratio of 3 is to 1 that is 75 percent and 25 percent ratio. Then we write all possible combination of these two isotopes in dichloroethane. So, one is ^{35}Cl and ^{37}Cl both here it is 75:25. That is the reason, it is 3 into 3 = 9, whereas, here we have two combination: One is ^{35}Cl and ^{37}Cl, otherwise ^{37}Cl and ^{35}Cl. So, now, we have 3 into 1 and plus 1 into 3 that is equal 6 and then we have both of them are 37 here is 102 and this is only 1.

So, that means, this gives the ratio of 9 into 6 is to 1. So, we can tell 98 and 100 and 102 will be in 9 is to 6 is to 1 ratio because of the possible molecules having this type of distribution of isotopes in these, three or four different type of molecules.

Amongst: C_6H_7NS, $C_6H_7NO_2$, C_7H_8FN and $C_8H_{15}N$ (Mol.Wt. of all 125) which one will show EI mass spectral data: 125 (M^+) 55%, 126 $[M+1]^+$ 3.65, 127 $[M+2]^+$ 2.35% C_6H_7NS (125.19), $C_6H_7NO_2$ (125.13), C_7H_8FN (125.14) and $C_8H_{15}N$ (125.21)

Among all the closest 1 to 125 is 125.13. So, it corresponds to this one you can just check molecular rate of 125. If you consider the unit mass in all these things this comes to closer to this one and hence the given peak is due to $C_6H_7NO_2$. So, let me stop here and come up with more information about mass spectrometry and also more interesting problems in my next lecture until then have an excellent time. Thank you.