Subject	Chemistry
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1. Learning Outcomes

After studying this module, you shall be able to

- Know what is molecular ion, metastable ion and base peak
- Learn how to calculate molecular formula from molecular mass
- Identify molecular ion peak and base peak in a mass spectrum
- Learn nitrogen rule
- Analyse the presence of chlorine and bromine from the isotope peaks

2. Introduction

A vertical bar graph generally depicts mass spectrum, each bar represents an ion with a specific mass-to-charge ratio (m/z) and the height of the bar depicts the relative abundance of the ion. If the molecule gets devoid of an electron in the process of ionization then a molecular ion is observed that yields its molecular weight and it is indicated as M^+ in the spectrum. As z is more than often +1, m/z actually amounts upto the mass (m) of the individual ions.

For example, the mass spectrum of dopamine has a peak at m/z 153, which is equal to its mass (figure 1).

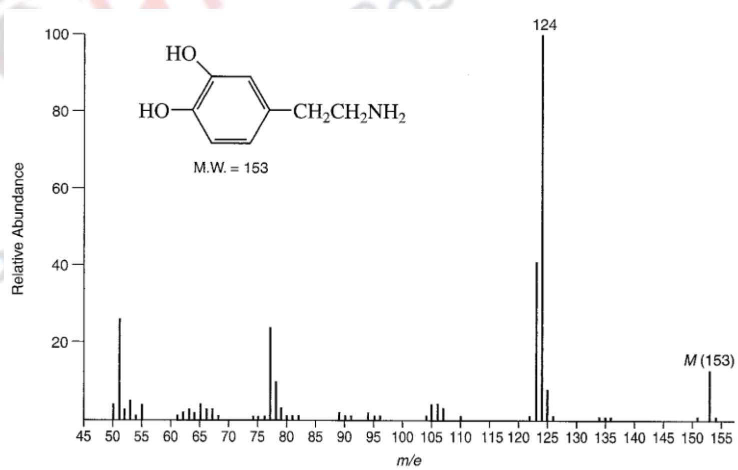

Figure 1: Mass spectrum of dopamine

Radical cation: In the process of ionization of a molecule, the species so formed is known as a radical cation, and is depicted as $M^{+\cdot}$.

Molecular ion or parent ion: The former species mentioned above is also called the molecular ion or the parent ion.
The mass of $M^{+\bullet}$ represents the molecular weight of the molecule. $M^{+\cdot}$ should be the highest m/z in the spectrum, apart from weak satellite peaks that result from other isotopes.

Base peak: The ion formed most abundantly during the process of ionization gives rise to the tallest peak in the mass spectrum which is also known as the base peak. All other peak intensities are obtained are appear as relative to the peak known as the base peak as a percentage.

Fragment ions: When a molecule loses a valence electron, further bonds are broken, and new species are formed called fragment ions.

Index of hydrogen deficiency or Degree of unsaturaion or Double Bond Equivalent (DBE): The Index of hydrogen deficiency is the number of pi bonds and/or rings a molecule contains. One Double Bond Equivalent (DBE) (also known as a degree of unsaturation) is one pi bond or one ring. A triple bond counts as 2 DBE. Having 4 DBE shows the possibility of a benzene ring, since benzene has three pi bonds plus one ring. The formula for DBE is the following:

Metastable ions: The ion appearing at an m/z ratio that depends on its mass as well as the mass of the original ion from which it is formed is called metastable ion. These peaks are usually broad and appear at non integral values of m/z. The presence of metastable ion peak links two peaks together.

$$m_1^+ \longrightarrow m_2^+ + \text{fragment}$$

$$m^* = \frac{(m_2)^2}{m_1}$$

m^* is the apparent mass of the metastable ion
m_1 is the mass of original ion
m_2 is the mass of new fragment ion

e.g. $C_5H_9^+$ (m/z = 69) → $C_3H_5^+$ (41) + C_2H_4 (28)

Calculated m* = $(41)^2/69$ = 24.36, observed m* = 24.4

Metastable ion arise because of fragmentation after the ion has left the ionization chamber. The kinetic energy of such a m_2^+ is smaller than when it would have been formed in the ionization chamber and accelerated there, and it will be detected at a lower m/z than expected.

3. The Nitrogen Rule

Most of the hydrocarbons and other compounds which contain C,H and O atoms, often contains a molecular ion with an even mass. A molecular ion which is odd indicates that that a particular compound has an odd number of nitrogen atoms.

The Nitrogen Rule

The effect of N atoms gen rule a compound that contains an odd number of N atoms has an odd molecular ion. A compon the mass of the molecular ion in a mass spectrum is called the nitrogen rule. According to nitroound that contains an even number of N atoms (including zero) has an even molecular ion.

The 4-methyl-3-pentene-2-one, has no nitrogen so the mass of the molecular ion (m/z = 98) is an even number (figure 2). Most of the fragment ions have odd-numbered masses, and therefore are even-electron cations.

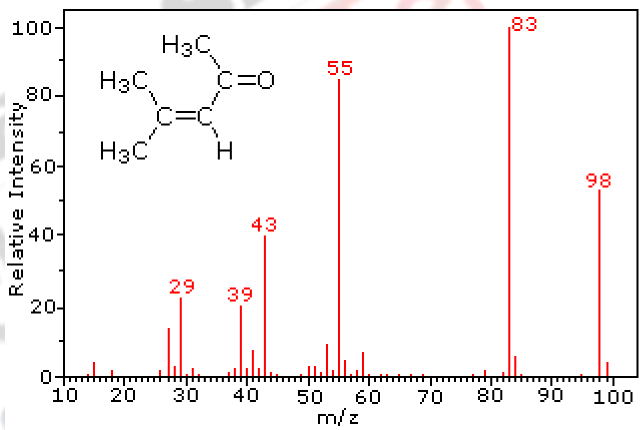

Figure 2: Mass spectrum of 4-methyl-3-pentene-2-one

Diethylmethylamine, has one nitrogen and its molecular mass (m/z = 87) is an odd number. A majority of the fragment ions have even-numbered masses and are even-electron nitrogen cations.

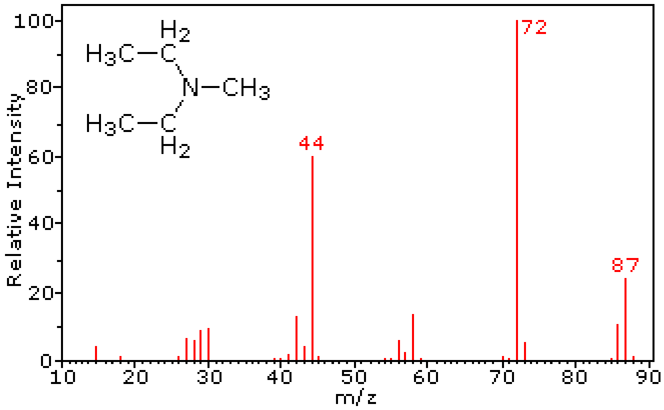

Figure 3: Mass spectrum of N,N-diethylmethylamine

4. The Rule of Thirteen

The Rule of Thirteen: Rule of thirteen is a useful method for determining the possible molecular formula of a compound from its Molecular Mass.
In the Rule of Thirteen first, a base formula is generated which consists of only hydrogen and carbon atoms. This base formula is calculated by dividing the molecular mass by 13 (C + H: 12+ 1 =13).

When a molecular mass, M^+, is known, a base formula can be generated from the following equation:

$$\frac{M}{13} = n + \frac{r}{13}$$

The base formula will be: C_nH_{n+r}

The index of hydrogen deficiency (IHD) or **Double Bond Equivalent** DBE will be:
DBE = (n – r + 2)/2

Q. Calculate molecular formula of a compound with molecular mass 94 amu.

Ans.

$$\frac{94}{13} = 7 + \frac{3}{13}$$

n = 7 and r =3
The base formula is C_7H_{10}
The index of hydrogen deficiency or DBE = (7-3+2)/2 = 3

5. Isotopes in Mass Spectrometry

A mass spectrometer separates and detects ions of slightly different masses and it easily distinguishes different isotopes of a given element.

The molecular ions of 2-methylbutane has *m/ z* values of 72, the spectrum shows a very small peak at m/z = 73 (figure 4). This peak is called M +1 peak because the ion responsible for it is one unit heavier than the molecular ion. The M+1 peak owes its presence to the fact that there are two naturally occurring isotopes of carbon: 98.89% of natural carbon is ^{12}C and 1.11% is ^{13}C. So 1.11% of the molecular ions contain a ^{13}C instead of a ^{12}C and therefore appear at M+1.

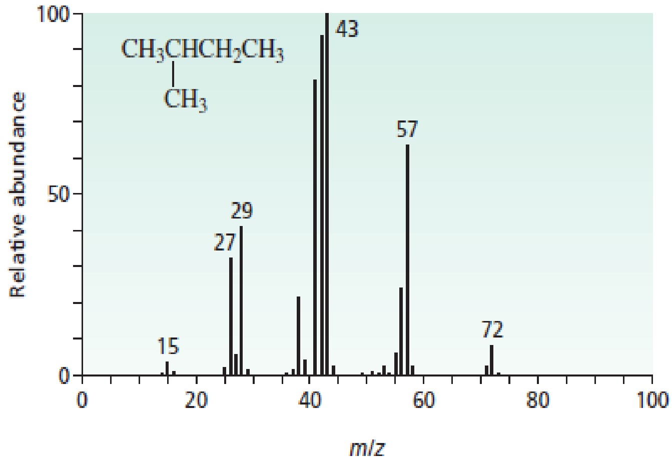

Figure 4: Mass spectrum of 2-methylbutane

Peaks that are attributable to isotopes can help identify the compound responsible for a mass spectrum. For example, if a compound contains five carbon atoms, the relative intensity of the M+1 ion should be 5(1.1%) = 5 (.011), multiplied by the relative intensity of the molecular ion. This means that the number of carbon atoms in a compound can be calculated if the relative intensities of both the M and M+1 peaks are known.

$$\text{number of carbon atoms} = \frac{\text{relative intensity of M + 1 peak}}{.011 \times (\text{relative intensity of M peak})}$$

Table 1: The isotopic distributions of several elements

Element	Natural abundance			
Carbon	^{12}C 98.89%	^{13}C 1.11%		
Hydrogen	^{1}H 99.99%	^{2}H 0.01%		
Nitrogen	^{14}N 99.64%	^{15}N 0.36%		
Oxygen	^{16}O 99.76%	^{17}O 0.04%	^{18}O 0.20%	
Sulfur	^{32}S 95.0%	^{33}S 0.76%	^{34}S 4.22%	^{36}S 0.02%
Fluorine	^{19}F 100%			
Chlorine	^{35}Cl 75.77%		^{37}Cl 24.23%	
Bromine	^{79}Br 50.69%		^{81}Br 49.31%	
Iodine	^{127}I 100%			

From the isotopic distributions, we see why the M+ 1 peak can be used to determine the number of carbon atoms in a compound: It is because the contributions to the M +1 peak by isotopes of H, O, and the halogens are very small or nonexistent. This formula does not work as well in predicting the number of carbon atoms in a nitrogen-containing compound because the natural abundance of ^{15}N is relatively high.

Mass spectra can show M +2 peaks as a result of a contribution from ^{18}O, or from having two heavy isotopes in the same molecule (say, ^{13}C and ^{2}H or two ^{13}Cs). Most of the time, the M+2 peak is very small. The presence of a large M+2 peak is evidence of a compound containing either chlorine or bromine, because each of these elements has a high percentage of a naturally occurring isotope that is two units heavier than the most abundant isotope.

This is majorly observed in compounds containing bromine and chlorine.

Mass spectrum of Br_2

It contains five peaks and has a nearly 50:50 mixture of isotopes having atomic masses of 79 and 81 amu respectively. Thus, the bromine molecule may be composed of two ^{79}Br atoms (mass 2 x 79 = 158 amu), two ^{81}Br atoms (mass 2 x 81 = 162 amu) or the more probable combination of

^{79}Br-^{81}Br (mass 79 + 81 =160 amu). Fragmentation of Br, to a bromine cation then gives rise to equal sized ion peaks at 79 and 81 amu.

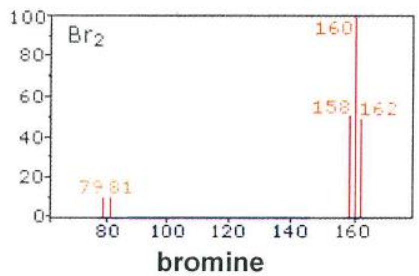

Figure 5: Mass spectrum of bromine (Br_2)

The mass spectrum of bromomethane consists of two peaks of equal intensity (1:1) for $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ (figure 6). If the M and M+2 peaks are about the same height, then the compound contains one bromine atom because the natural abundances of ^{79}Br and ^{81}Br are about the same.

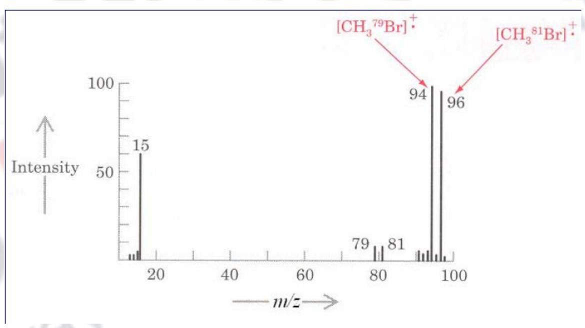

Figure 6: Mass spectrum of bromomethane

The spectra of vinyl chloride and methylene chloride (figure 7) shows that chlorine comprises of two isotopes, the isotope with a greater abundance has a mass of 35 amu and the one with a minor abundance has a mass of 37 amu.

In case of vinyl chloride the molecular ion consists of two peaks at m/z = 62 and 64 in 3:1 ratio for M and M+2 ion. From the natural abundance of the isotopes of chlorine and bromine one can conclude that if the M+2 peak is one-third the height of the molecular ion peak, then the compound contains one chlorine atom because the natural abundance of ^{37}Cl is one-third that of ^{35}Cl.

Consider the molecular ion in the case of methylene chloride which has three peaks at m/z =84, 86 and 88 amu for M, M+2 and M+4 ions.

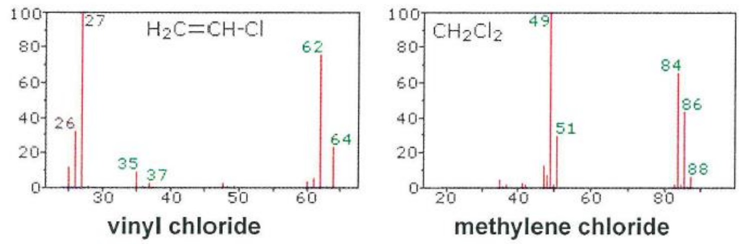

Figure 8: Mass spectrum of vinyl chloride and methylene chloride

Intensity ratios of ions differing by 2 amu indicates the presence of chlorine or bromine in a molecule or ion.

	Relative Intensities			
Halogen	***M***	***M* + 2**	***M* + 4**	***M* + 6**
Br	100	97.7		
Br_2	100	195.0	95.4	
Br_3	100	293.0	286.0	93.4
Cl	100	32.6		
Cl_2	100	65.3	10.6	
Cl_3	100	97.8	31.9	3.47
BrCl	100	130.0	31.9	
Br_2Cl	100	228.0	159.0	31.2
Cl_2Br	100	163.0	74.4	10.4

6. Summary

- A mass spectrum is usually represented by a vertical bar graph, with each bar representing an ion having a specific mass-to-charge ratio (m/z) and the length of the bar indicates the relative abundance of the ion.
- The radical cation $M^{+\bullet}$ is called the molecular ion or parent ion.
- The most abundant ion formed during ionization gives rise to the tallest peak on the mass spectrum which is called the base peak.
- The ion appearing at an m/z ratio that depends on its mass as well as the mass of the original ion from which it is formed is called metastable ion.
- The effect of N atoms on the mass of the molecular ion in a mass spectrum is called the nitrogen rule. A compound that contains an odd number of N atoms gives an odd molecular ion.
- The Rule of Thirteen: Rule of thirteen is a useful method for determining the possible molecular formula of a compound from Molecular Mass.
- If the M and M+2 peaks are about the same height, then the compound contains one bromine atom because the natural abundances of ^{79}Br and ^{81}Br are about the same.
- From the natural abundance of the isotopes of chlorine and bromine one can conclude that if the M+2 peak is one-third the height of the molecular ion peak, then the compound contains one chlorine atom because the natural abundance of ^{37}Cl is one-third that of ^{35}Cl.