2.6: Interpretation of Mass Spectra

Learning Objectives

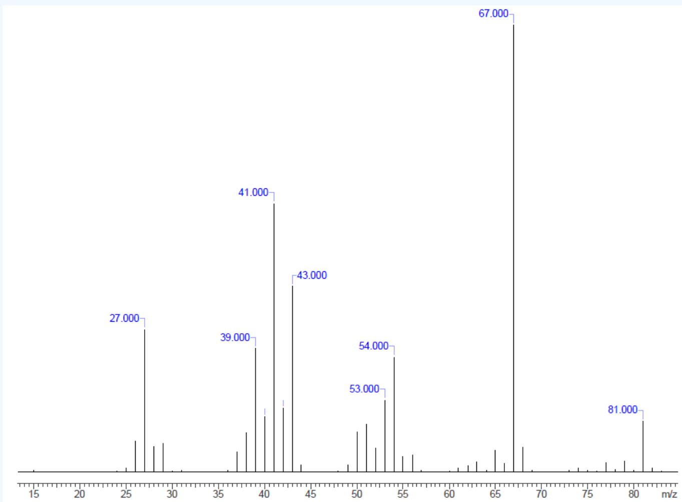
- understand how to determine molecular weight.
- interpret mass spectra.

The first piece of information mass spectra can get is the molecular weight of a molecule. In a mass spectrum of a compound, the x axis is the m/z values and the y axis represents the intensity or relative abundance of a given m/z. In addition, there are a number of other lines at a variety of values of m/z; these correspond to the masses of smaller pieces of those that fall apart during the experiment as well as the unfragmented cation. For these smaller pieces, the more stable an ion is, the more likely it is to form. The more of a particular sort of ion that's formed, the higher its peak height will be. The tallest peak is called the base peak and is assigned 100% intensity. The peak that represents the unfragmented cation radical is called the parent peak or molecular ion (M^+). The parent peak is how you determine the molecular weight of a molecule. Often, the molecular ion peak is not the same as the base peak. Usually, whole numbers are used for the molecular weights in mass spectrometry. The atomic masses in the periodic table are average masses including different isotopes and because mass spectrometry examines individual molecules, whole numbers are used. Complications can arise with determining the molecular ion peak because it is not always abundant, especially when molecules fragment easily. This is where the soft ionization techniques come into play.

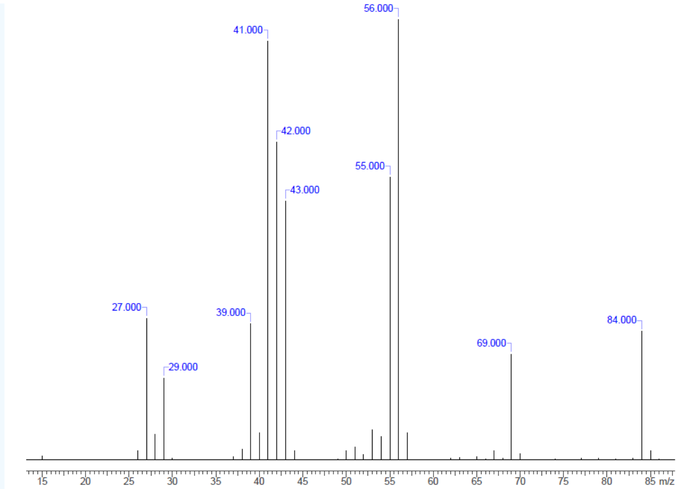
Exercise 2.6.1

Which mass spectrum corresponds to hexane, 1-hexene, and 1-hexyne.

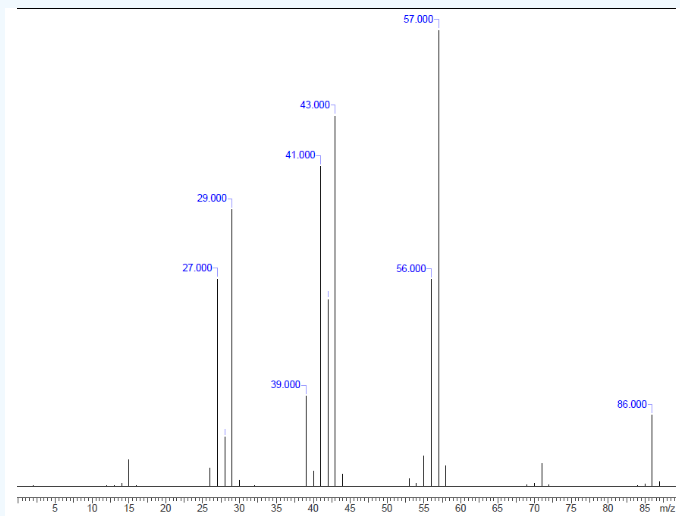
(A)



(B)



(C)



Answer

Each molecule has a different molecular weight. Hexane MW = 86; 1-hexene MW = 84, and 1-hexyne MW = 82

To determine which molecule belongs to which look for the molecular ion peak, which will indicate what the molecular weight is of each molecule.

(A) 1-hexyne

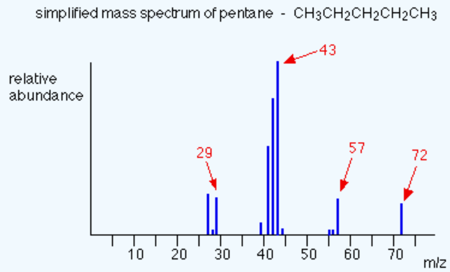
(B) 1-hexene

(C) hexane

Another piece to note is that if you look closely at the mass spectrum of C in exercise 1 above, you will notice a little peak at m/z = 87. This is referred to as the M+1 peak (one greater than the molecular ion), and it arises because of ^{13}C. This compound is referred to as an isotopomer; that means the same compound with a different isotope. The chance that a molecule in a sample contains a ^{13}C atom is related to the number of carbons present. If there is just one carbon atom in the molecule, it has a 1% chance of being a ^{13}C. That means the M+1 peak would be only 1/100th as tall as M+, the peak for the molecular ion.

Example 2.6.1

Let's have another look at the mass spectrum for pentane:



What causes the line at m/z = 57?

Solution

How many carbon atoms are there in this ion? There can't be 5 because 5 x 12 = 60. What about 4? 4 x 12 = 48. That leaves 9 to make up a total of 57. How about $C_4H_9^+$ then?

$C_4H_9^+$ would be $[CH_3CH_2CH_2CH_2]^+$, and this would be produced by the following fragmentation:

$$[CH_3CH_2CH_2CH_2CH_3]^{+\bullet} \longrightarrow [CH_3CH_2CH_2CH_2]^+ + \bullet CH_3$$

The methyl radical produced will simply get lost in the machine.

The line at m/z = 43 can be worked out similarly. If you play around with the numbers, you will find that this corresponds to a break producing a 3-carbon ion:

$$[CH_3CH_2CH_2CH_2CH_3]^{+\bullet} \longrightarrow [CH_3CH_2CH_2]^+ + \bullet CH_2CH_3$$

The line at m/z = 29 is typical of an ethyl ion, $[CH_3CH_2]^+$:

$$[CH_3CH_2CH_2CH_2CH_3]^{+\bullet} \longrightarrow [CH_3CH_2]^+ + \bullet CH_2CH_2CH_3$$

The other lines in the mass spectrum are more difficult to explain. For example, lines with m/z values 1 or 2 less than one of the easy lines are often due to loss of one or more hydrogen atoms during the fragmentation process.

What happens when the molecular weight is the same for the compounds? The fragmentation pattern should be different for the molecules. While knowing the molecular weight is invaluable, mass spectrometry can lend a hand in structure determination. The mass spectrum of a particular compound acts as a "fingerprint," since each compound will fragment in its own unique way (just like a person's fingerprint). In the next section, the fragmentation of functional groups will be discussed.

Exercise 2.6.2

The male sex hormone testosterone contains C, H, and O. It has a mass of 288.2089 amu as determined by mass spectrometry. What is the likely molecular formula for testoterone?

Answer

$C_{19}H_{28}O_2$

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