

Chem 103/113 Lab: Mass Spectrometry, Isotopes, and Molecular Mass¹

1. Bromobenzene has the molecular formula C_6H_5Br . Using average atomic masses, calculate its molecular mass to the nearest 0.1 amu and show your method.

$$6(12.01 \text{ amu/C atom}) + 5(1.008 \text{ amu/H atom}) + 1(79.90 \text{ amu/Br atom})$$

$$= 156.992 \text{ amu} \rightarrow 157.0 \text{ amu}$$

2. In a mass spectrometer, uncharged gaseous molecules are ionized by a beam of electrons, which may put enough energy into a molecule to cause the molecule to lose one of its electrons. What is the formula of the ion (called the **molecular ion**) that would result from such ionization of bromobenzene? (The charge must be indicated in the formula of the ion.) $C_6H_5Br^+$

3. What would be the mass of such an ion to the nearest 0.1 amu? 157.0 amu
(Consider whether the mass of the lost electron may be neglected.) yes!

4. A **mass spectrum** is a graph of the abundance of ions resulting from such ionization processes, plotted on the y axis, versus their mass-to-charge ratios m/z , where m is the mass of the ion in amu and z is its charge (assume $z = +1$), plotted on the x axis. The mass spectrum of bromobenzene is attached. It was obtained by introducing the vapor from liquid bromobenzene into the mass spectrometer. The abundances of the various ions produced are relative to the strongest line, or peak, taken as 100%.

Is there an abundant peak at the mass you found in Question 3? no (If you don't see the reason for this, the following questions should help.)

5. The isotope ^{12}C makes up nearly all of the earth's carbon (there is also a minor isotope ^{13}C). The atomic mass of C is very close to 12.0. The isotope 1H makes up nearly all of natural hydrogen, whose atomic mass is close to 1.0. Bromine has two abundant isotopes ^{79}Br (50.7%) and ^{81}Br (49.3%). Why is the atomic mass of bromine close to 80 (more precisely 79.904) even though the isotope ^{80}Br is negligible?

The atomic mass is a weighted average $\frac{1}{2}$ a ~50:50 mix of $^{79}Br + ^{81}Br$ will weigh ~80.

6. Based on your answer to Question 5, consider why the mass spectrum of bromobenzene shows no abundant peak corresponding to the average molecular mass (found in Question 1) and whether your response to Question 3 should be modified. Discuss briefly.

A sample of C_6H_5Br contains both $C_6H_5^{79}Br$ & $C_6H_5^{81}Br$ in unequal amounts. So we expect a large peak for $C_6H_5^{79}Br^+$ at 156 amu and another for $C_6H_5^{81}Br^+$ at 158 amu. Since there's no $C_6H_5^{80}Br^+$, we don't expect to see a peak at 157 amu. (The small peak that is observed is due to ions like $^{12}C_5^{13}C^1H_5^{79}Br^+$.)

¹ Adapted from S.M. Schildcrout, *J.Chem.Educ.*, 2000, 77, 1433.

7. The relative abundances of each peak are shown on the y-axis of the mass spectrum. Consider the two strong peaks arising from the molecular ion. Estimate their relative abundances as precisely as you can:

peak at $m/z = \underline{156}$ has relative abundance $\underline{\sim 56}$
 peak at $m/z = \underline{158}$ has relative abundance $\underline{\sim 53}$

} really hard to estimate more precisely

Add these two abundances together to find the total abundance of the peaks arising from the molecular ion: $\underline{109}$. Recalculate these two relative abundances so their total is 100%. That is, find the %abundance of each:

peak at $m/z = \underline{156}$ has % abundance $\underline{\frac{56}{109} \Rightarrow 51\%}$
 peak at $m/z = \underline{158}$ has % abundance $\underline{\frac{53}{109} \Rightarrow 49\%}$

Assume these % abundances to be those of the respective Br isotopes. Using the isotopic masses of 78.918 amu and 80.916 amu, calculate the apparent average atomic mass of bromine: $\underline{80}$. Show your work.

$$\begin{aligned} \text{average atomic mass} &= (\text{abund } ^{79}\text{Br})(\text{mass } ^{79}\text{Br}) + (\text{abund } ^{81}\text{Br})(\text{mass } ^{81}\text{Br}) \\ &= (0.51)(78.918 \text{ amu}) + (0.49)(80.916 \text{ amu}) \\ &= 79.897 \rightarrow 80. \text{ (to 2 s.f.)} \end{aligned}$$

Compare this to the accepted value of the average atomic mass (79.904 amu):

Very close!

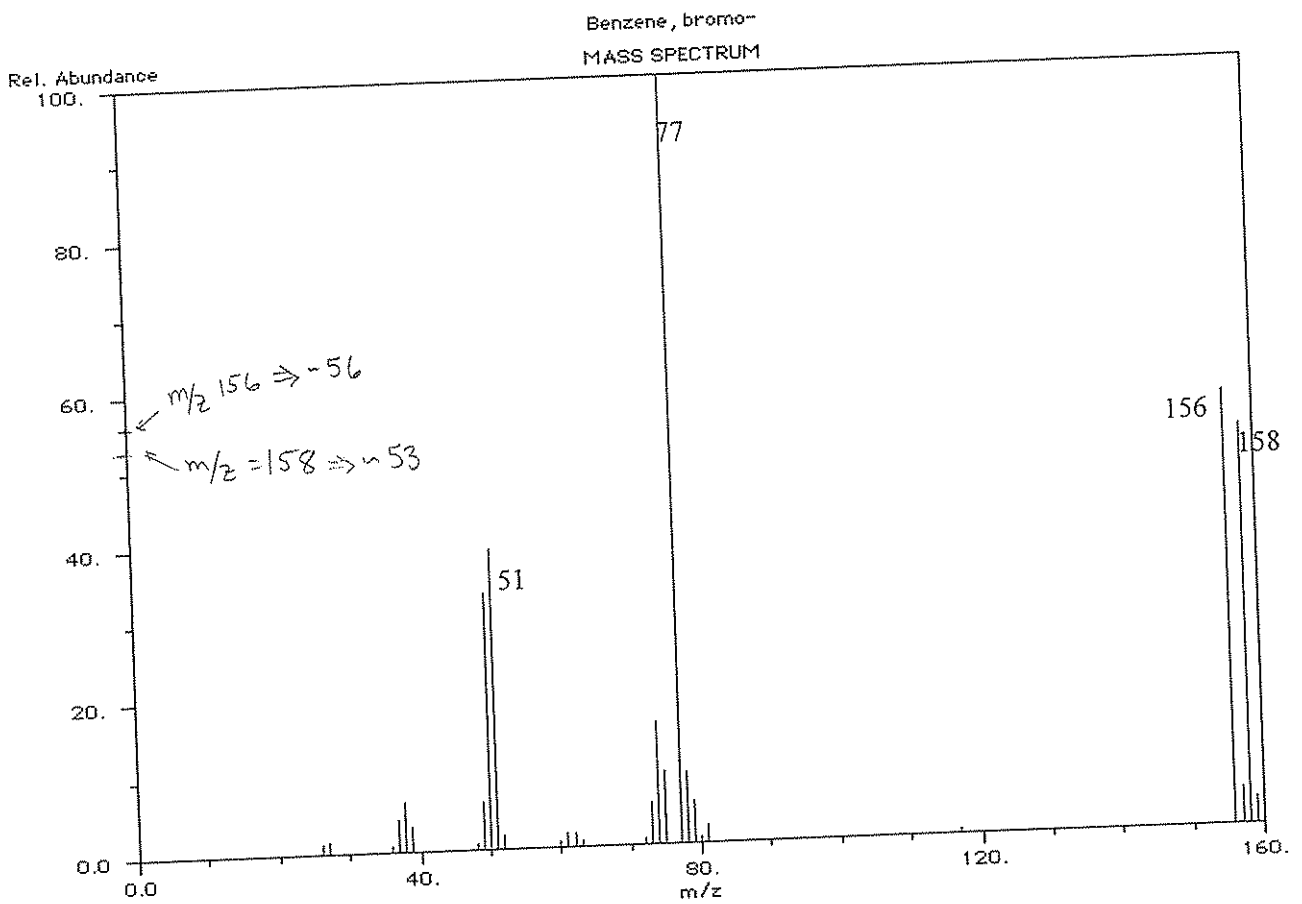
8. Consider the large peak at m/z 77, assuming again that $z = +1$. Does the ion giving this peak contain a Br atom? $\underline{\text{no}}$ Explain briefly how you know.

The lowest mass isotope of Br weighs 78.918 amu.
 This ion weighs less.

9. Suggest a chemical formula for the fragment ion at m/z 77, recalling that it comes from $\text{C}_6\text{H}_5\text{Br}$.

$$\text{C}_6\text{H}_5 \text{ weighs } 6(12.01) + 5(1.008) = 77.10 \text{ amu}$$

so the ion could be C_6H_5^+ .



Note: Besides showing peaks corresponding to the molecular ion, a mass spectrum also shows peaks corresponding to **fragment ions** resulting from the breaking of certain bonds in some of the molecular ions. Fragment ions have lower masses than the molecular ion. They may arise in a series of sequential reactions, or a given reactant ion may decompose to give either of several possible products.

Other peaks, frequently those of low abundance, result from molecules that contain heavy isotopes. For example, the substitution of one deuterium atom (^2H) for one hydrogen (^1H) atom would result in a small peak with m/z one unit higher than if only ^1H atoms were present in the molecule or fragment ion.