QUALITATIVE ANALYSIS

Determination of Molecular Mass by Molecular Ion Peak in Mass Spectrometry

1. Molecular Ion Peak ($M^{+\cdot}$) and Molecular Mass

The molecular ion peak ($M^{+\cdot}$) is the peak in a mass spectrum that represents the molecular ion. The molecular ion is formed when a molecule loses one electron, resulting in a radical cation ($M^{+\cdot}$). This peak appears at the highest m/z value in the mass spectrum, except for small isotope peaks. The m/z value of the molecular ion peak is numerically equal to the molecular mass of the compound because most ions carry a single positive charge (z = +1). Therefore,

$$m/z = \frac{\textbf{Molecular Mass}}{+1}$$

2. Base Peak

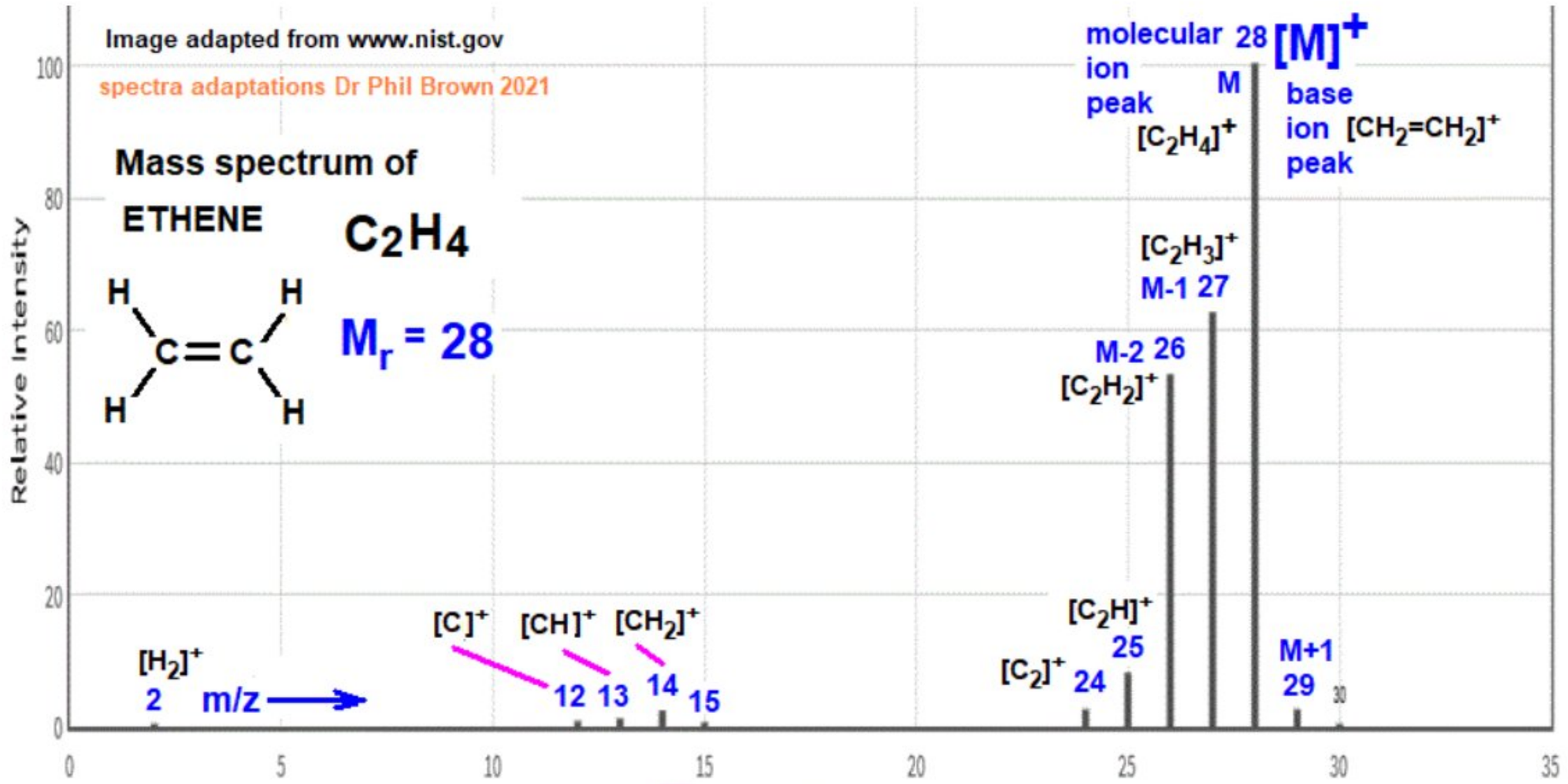
The base peak is the tallest peak in the mass spectrum and represents the most abundant ion formed during fragmentation. It is assigned a relative abundance of 100%, and all other peaks are compared to it. The base peak is not necessarily the molecular ion peak, because the molecular ion may be unstable and break into fragments.

3. Isotope Peaks (M+1, M+2, etc.)

Isotope peaks appear at m/z values greater than the molecular ion peak due to the presence of heavier isotopes. The M+1 peak occurs one unit above the molecular ion peak and is mainly caused by the presence of the carbon-13 isotope (^{13}C), which has a natural abundance of about 1.1%, therefore the M+1 peak is usually small. The M+2 peak appears two units above the molecular ion peak and may be due to the presence of two ^{13}C atoms, or heavier isotopes such as ^{18}O or ^{34}S. Compounds containing chlorine or bromine show strong and easily recognizable M+2 or M+4 patterns because these halogens have highly abundant heavy isotopes.

4. Fragment Ion Peaks

All peaks appearing at m/z values lower than the molecular ion peak are called fragment ion peaks. These peaks are produced when the molecular ion breaks into smaller ions during fragmentation. Fragment ion peaks provide important information for determining the structure of the compound.



Identification of a Molecule by Fragmentation Pattern

Fragmentation Process

When high-energy electrons from the electron gun strike the sample molecules, they cause the molecules to undergo fragmentation. The bonds break depending on the functional groups present, and usually the weakest bonds break first. The most stable ions are formed among the fragments, and only positively charged ions (cations) are detected by the mass spectrometer.

Fragmentation Pattern of n-Pentane

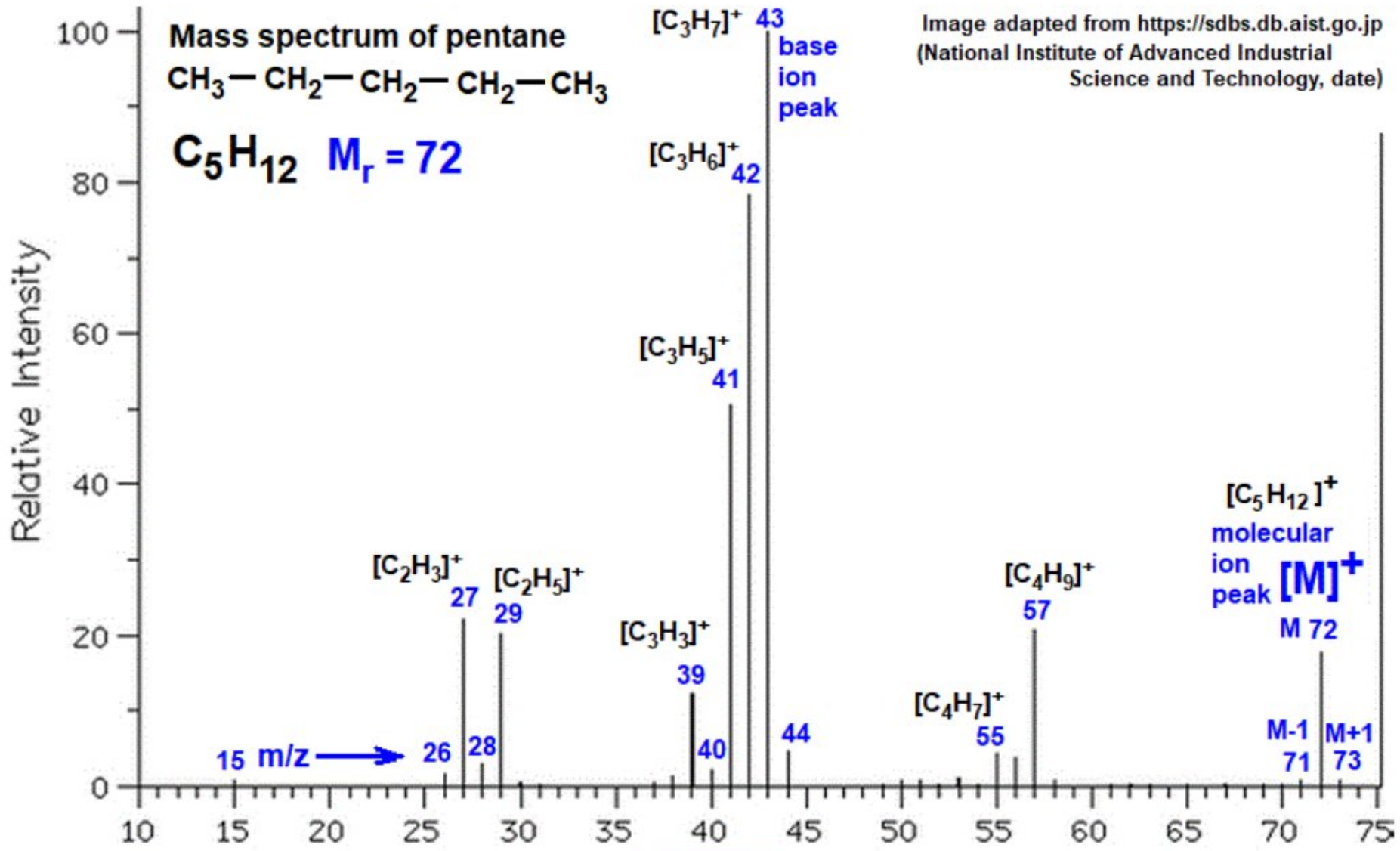
In the mass spectrum of n-pentane, characteristic fragments appear at different m/z values. Peaks at m/z = 15 and m/z = 14 are produced due to the formation of the methyl cation (CH_3^+). A peak at m/z = 29 corresponds to the ethyl cation ($CH_3CH_2^+$), and a peak at m/z = 43 represents the propyl cation ($CH_3CH_2CH_2^+$). Additionally, the peak at m/z = 41 is formed when two hydrogen atoms are removed from the propyl cation, giving propylene cation ($CH_2CH{=}CH_2^+$). Some stable ions are also formed by rearrangement of unstable ions.

Molecular Ion Peak of n-Pentane

The molecular ion peak for n-pentane is observed at m/z = 72. This molecular ion undergoes fragmentation to form ethyl radicals and propyl cations, and both pathways have equal probability of occurrence. During fragmentation, CH_2 fragments are also produced, giving rise to peaks that help in structure determination. Therefore, the fragmentation pattern and the molecular ion peak provide important clues about the molecular structure.

Fragmentation in Alcohols

In alcohols, a peak at M – 1 is observed due to the loss of a hydrogen atom from the OH group. By losing the whole OH group, a peak at M – 17 is formed. This OH group may also appear as a cation (OH^+), resulting in a peak at m/z = 17. These characteristic fragmentation peaks help in identifying alcohol functional groups.



Deduction of Carbon Number in a Molecule (C-Number)

In mass spectrometry, the **number of carbon atoms** in an organic molecule can be determined by comparing the intensities of the **molecular ion peak (M)** and the **M+1 peak**.

Formula

$$\text{Number of carbon atoms} = \frac{100 \times \text{abundance of M+1 peak}}{1.1 \times \text{abundance of M peak}}$$

Reason

The M+1 peak mainly results from the presence of the isotope **C-13**, which naturally exists at **1.1% abundance** relative to C-12.

Example

Given:

- Molecular ion peak (M) intensity = **27.32%**
- M+1 peak intensity = **2.10%**

Solution

$$\textbf{Number of C atoms} = \frac{100 \times 2.10}{1.1 \times 27.32} = 6.947 \approx 7$$

Conclusion

The molecule contains **7 carbon atoms**.

Deduction of the Presence of Chlorine and Bromine

Isotopes of **Cl** and **Br** produce characteristic peak patterns in mass spectra that help in identifying their presence in a molecule.

Detection of Chlorine (Cl)

Chlorine has two naturally occurring isotopes:

Isotope	Relative Abundance
Cl-35	75.77%
Cl-37	24.23%

Mass Spectral Pattern

- Main molecular ion peak M (due to Cl-35)
- A second peak M+2 (due to Cl-37)
- Intensity ratio approx. 3 : 1

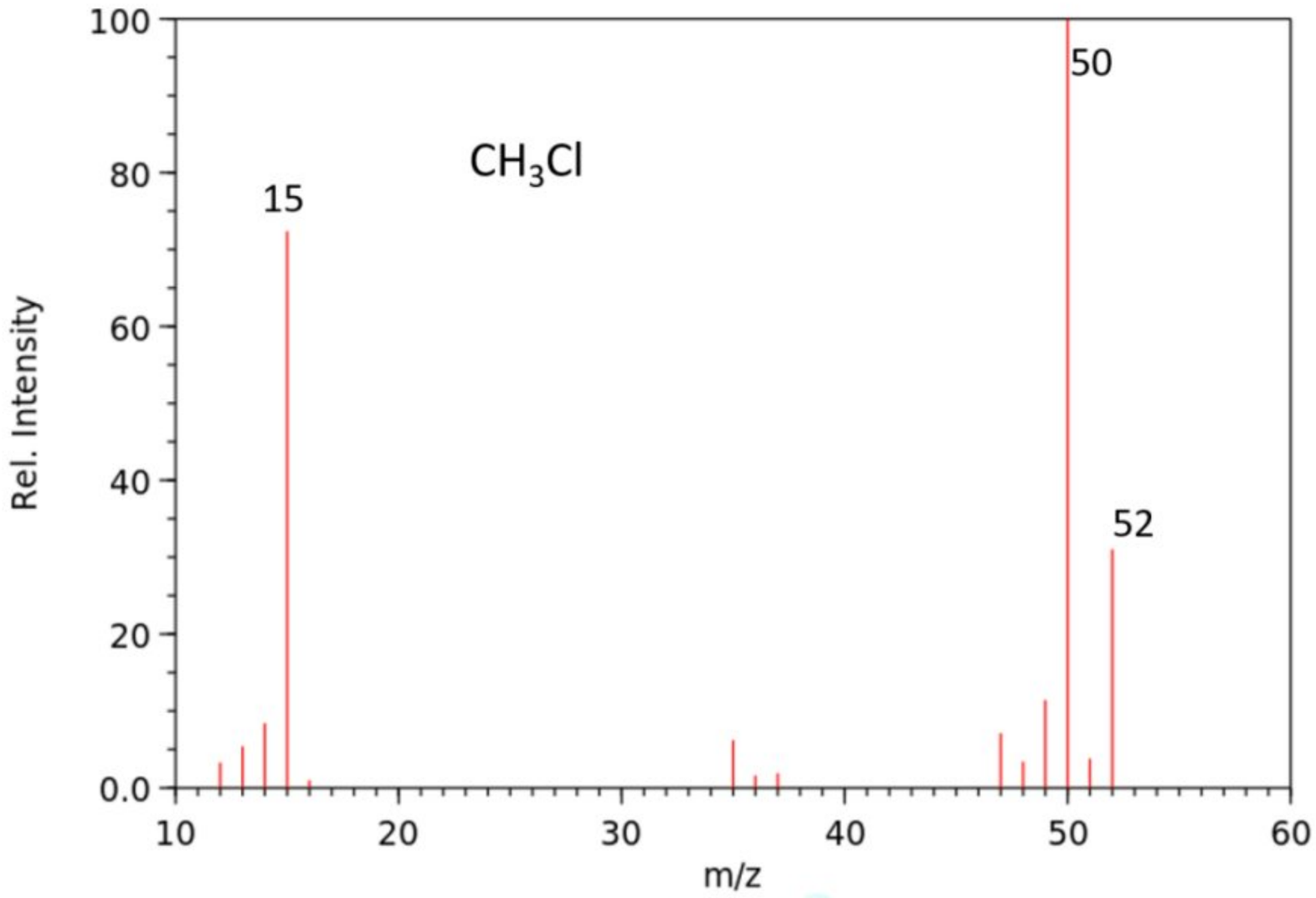
Example

In chloromethane (CH_3Cl)**:**

- M peak at m/z = 50
- M+2 peak at m/z = 52**,** approximately one-third height of M

Conclusion

Presence of M and M+2 peaks in 3:1 ratio confirms chlorine**.**



Detection of Bromine (Br)

Bromine has two isotopes:

Isotope	Relative Abundance
Br-79	50.50%
Br-81	49.50%

Mass Spectral Pattern

- Two peaks M and M+2
- Nearly equal intensities (1 : 1 ratio)

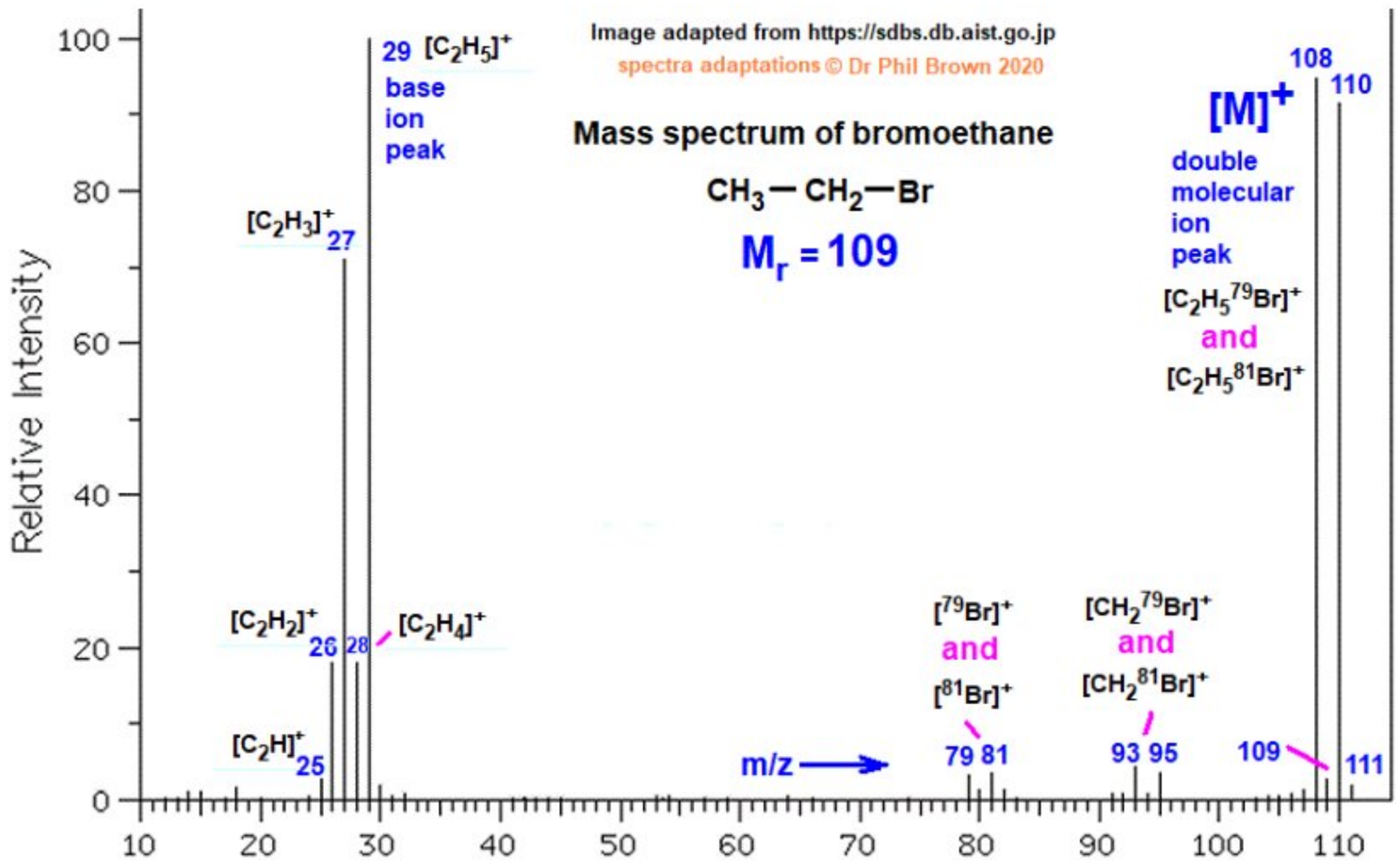
Example

In bromoethane (C_2H_5Br)**:**

- M peak at m/z = 108
- M+2 peak at m/z = 110**, of** almost equal height

Conclusion

Presence of two equal peaks (M and M+2) proves the presence of bromine.



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