in large excess, part of the energy may be given to the molecular ions $[A-B-C-D]^+$, which undergo fragmentation after acquiring energy that is necessary for bond breaking. The smaller fragment ions are further broken down similarly. The fragmentation of the molecular ion may be represented by the following equations.

$$[A-B-C-D]^+ = A^+ + [B-C-D]^\cdot \rightarrow (II)$$

$$[A-B-C-D]^+ = [A-B]^+ + [C-D]^\cdot \rightarrow (III)$$

$$[A-B]^+ \rightarrow A^+ + B^\cdot \rightarrow (IV)$$

$$[A-B]^+ \rightarrow A^\cdot + B^+ \rightarrow (V)$$

$$[A-B-C-D]^+ \rightarrow [A-B]^\cdot + [C-D]^+ \rightarrow (VI)$$

$$[C-D]^+ \rightarrow C^+ + D^\cdot \rightarrow (VII)$$

$$[C-D]^+ \rightarrow C^\cdot + D^+ \rightarrow (VIII).$$

$$[A-B-C-D]^+ \rightarrow [A-D]^+ + [B-C]^\cdot \text{ etc} \rightarrow (IX)$$

$$[A-B-C-D]^+ \rightarrow [B-C]^+ + [A-D]^\cdot \text{ etc.} \rightarrow (X).$$

If A, B, C and D have different masses, the peaks corresponding to mass to charge ratio (m/e) of $[A-B-C-D]^+$, $[A-B]^+$, A^+, B^+, $[C-D]^+$, C^+, D^+, $[A-D]^+$ and $[B-C]^+$ will occur in the mass spectrum.

What are molecular ions or parent ion and base peak ?

Molecular ion :- Some minimum electron beam energy (higher than the ionisation energy) is needed to initiate the ionization process for generation of mass spectrum

$$M + e^- \rightarrow M^+ + 2e^-$$

In this case M stands for the molecule and M^+ represents the molecular ions or parent ion. The mass of the molecular ion M^+ is identical to the molecular weight of the compound. Thus it is possible to calculate the molecular mass of the sample from the molecular ion peak. Under any given set of conditions, the intensity molecular ion peak depends upon the stability of ionised particle.

The stability of the molecular ion increases a molecule contain a π-electron system.

This is so because a π - electron system can adjust more easily to the loss of electron in comparison to a σ - bond.

The order of decrease of height of parent peak (or intensity of the parent peak) is as follows :—

Aromatic compd's > conjugated olefins > alicyclic compds > straight chain ~~compd~~ hydrocarbon > ketones > amines > esters > ethers > carboxylic acid > branched chain hydrocarbons > alcohols.

Base Peak :— The most intense (tallest) peak in the mass spectra due to the ions with the greatest relative abundance is called base peak. Base peak is not always due to molecular ion and molecular ion does not always gives the base peak.

Mc Lafferty rearrangement :— The Mc Lafferty rearrangement is a reaction observed in mass spectrometry during the fragmentation of organic molecules. A molecule containing a keto group undergo β- cleavage, with the gain of the γ - hydrogen ato