Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Paper Code: CHC-107

Paper Title: Organic Chemistry

Unit: (Section A)

Module Name: Mass Spectrometry: Principle, Theory, Instrumentation, Base Peak, Molecular Ion Peak and Metastable Ion

Module No: 30

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Notes:

Mass spectrometry is used by organic chemists to characterize organic molecules in two principal ways:

(1) To measure exact molecular weights, and from this, exact molecular formulae can be determined.

(2) To indicate within a molecule the points a which it prefers to fragment; from this, the presence of certain structural units in the organic compound can be recognized.

Refer to the following slides hereafter.

PART – 1:

Mass Spectrometry

Mass spectrometry

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(1) To measure exact molecular weights, and from this, exact molecular formulae can be determined.

(2) To indicate within a molecule the points a which it prefers to fragment; from this, the presence of certain structural units in the organic compound can be recognized.

One should remember…

Mass spectrometry is **not** a **true spectroscopic technique**…

… because **absorption of electromagnetic energy** is **not involved** in any way.

PART – 2:

Mass spectrometer: How does it work?

The sample of interest (organic molecule) is introduced in the mass spectrometer where it is heated and converted into vapor form.

↓

Sample is then bombarded with high energy electrons (electrons of energy greater than ionization energy for most compounds).

↓

Sample therefore loses an electron: this species is referred to as radical cation and is represented by $\mathbf{M^{+\cdot}}$ (often written as M^+ for simplification).

M + e^- → $M^{+\cdot}$ + $2e^-$

M (Neutral molecule) + **e^-** (high energy electron) → **$M^{+\cdot}$** Radical cation (Molecular ion) + **$2e^-$** the in-coming electron and ejected electron

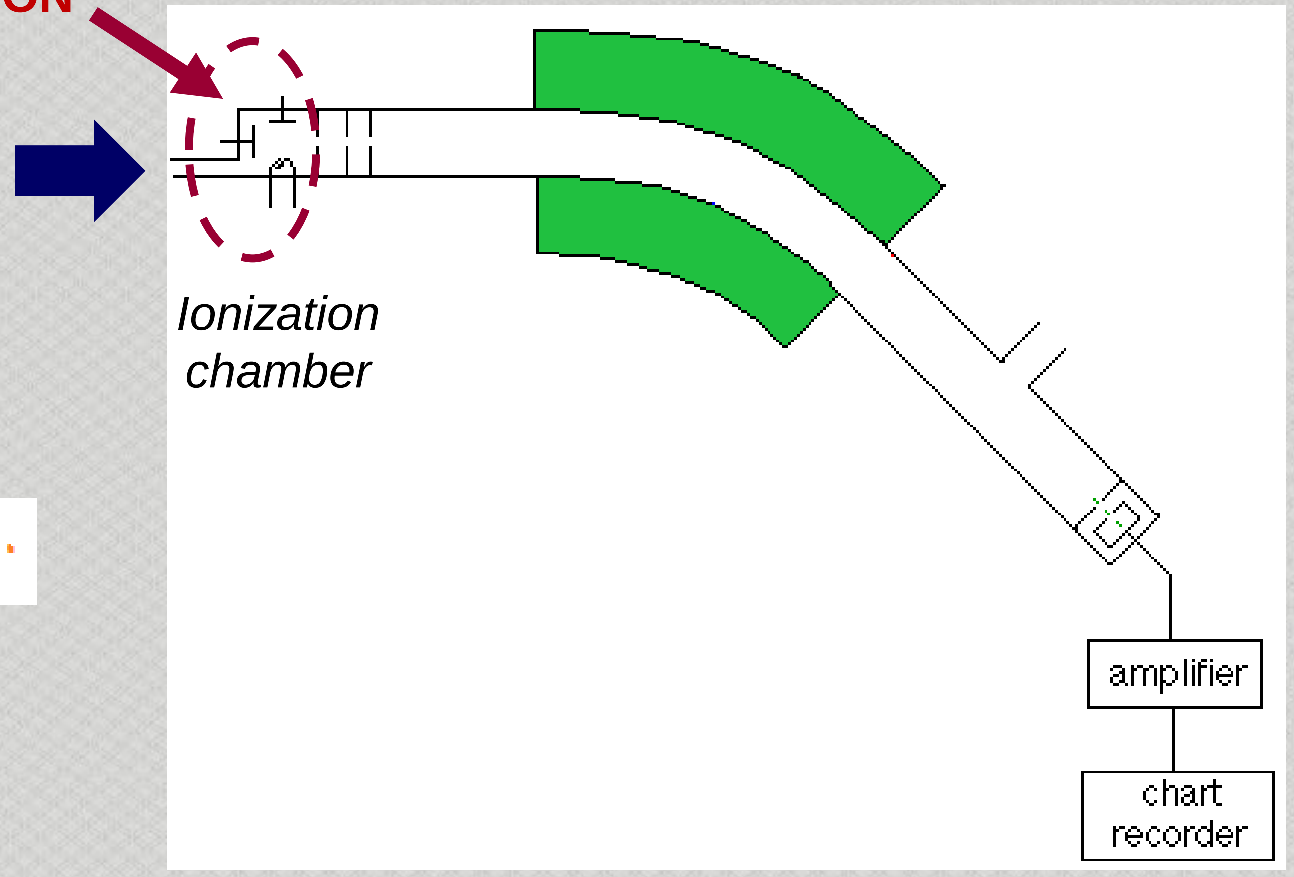
Which electron can easily be removed? (Methanol taken as an example)

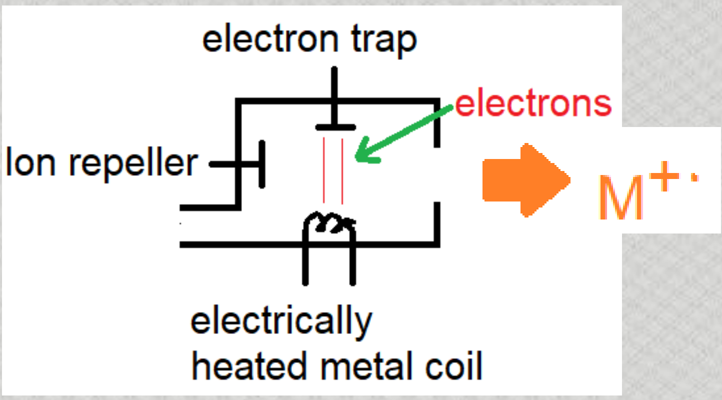
❑ Non-bonding electrons of nitrogen, oxygen and π electrons of alkenes are more loosely held as compared to electrons involved in sigma bonds.

(Neutral molecule) **Radical cation (Molecular ion)**

- The molecular ion represents the intact molecule which has the same weight as the starting molecule (weight of the electron lost is negligible).

Instrumentation (overview)





- The vaporized sample passes into the ionization chamber (the electrically heated metal coil gives off electrons which are attracted to the electron trap which is a positively charged plate).

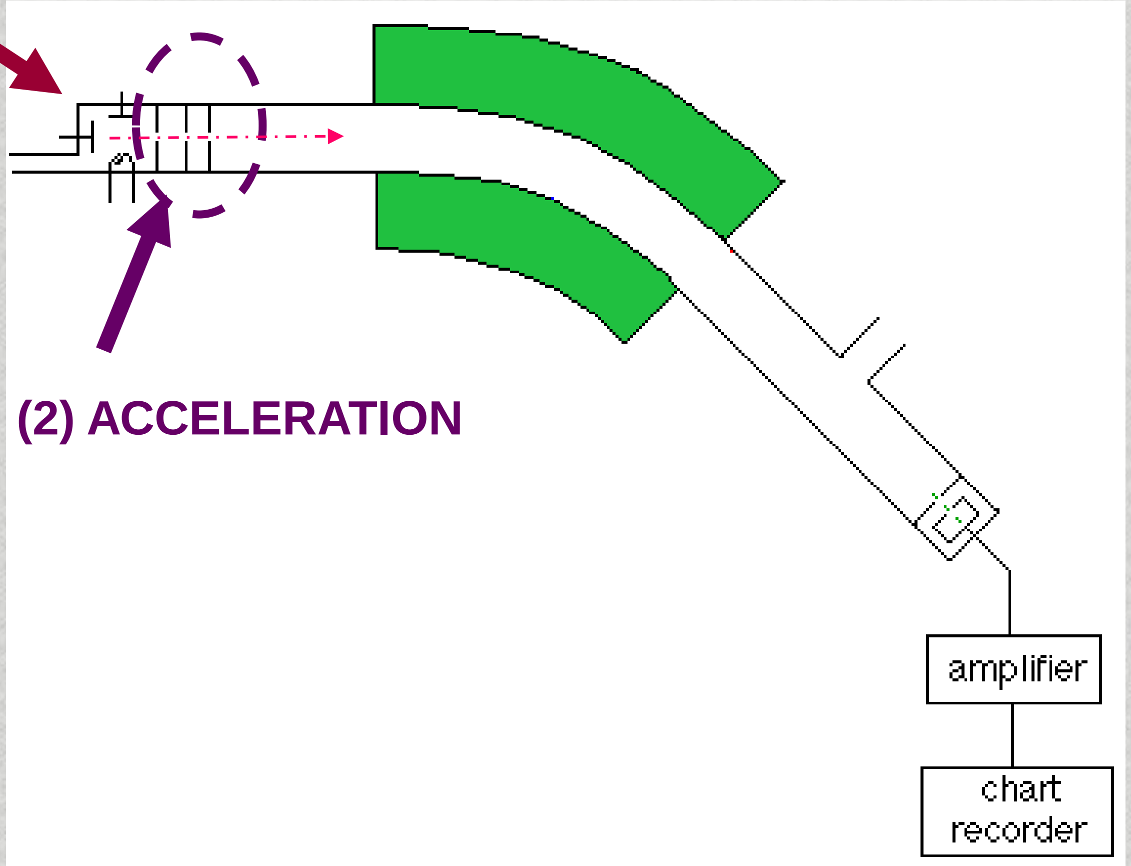
- The particles in the sample (atoms or molecules) are therefore bombarded with a stream of electrons, and some of the collisions are energetic enough to knock one or more electrons out of the sample particles to make positive ions.

- Most of the positive ions formed will carry a charge of +1 because it is much more difficult to remove further electrons from an already positive ion.

- These positive ions are persuaded out into the rest of the machine by the ion repeller which is another metal plate carrying a slight positive charge.

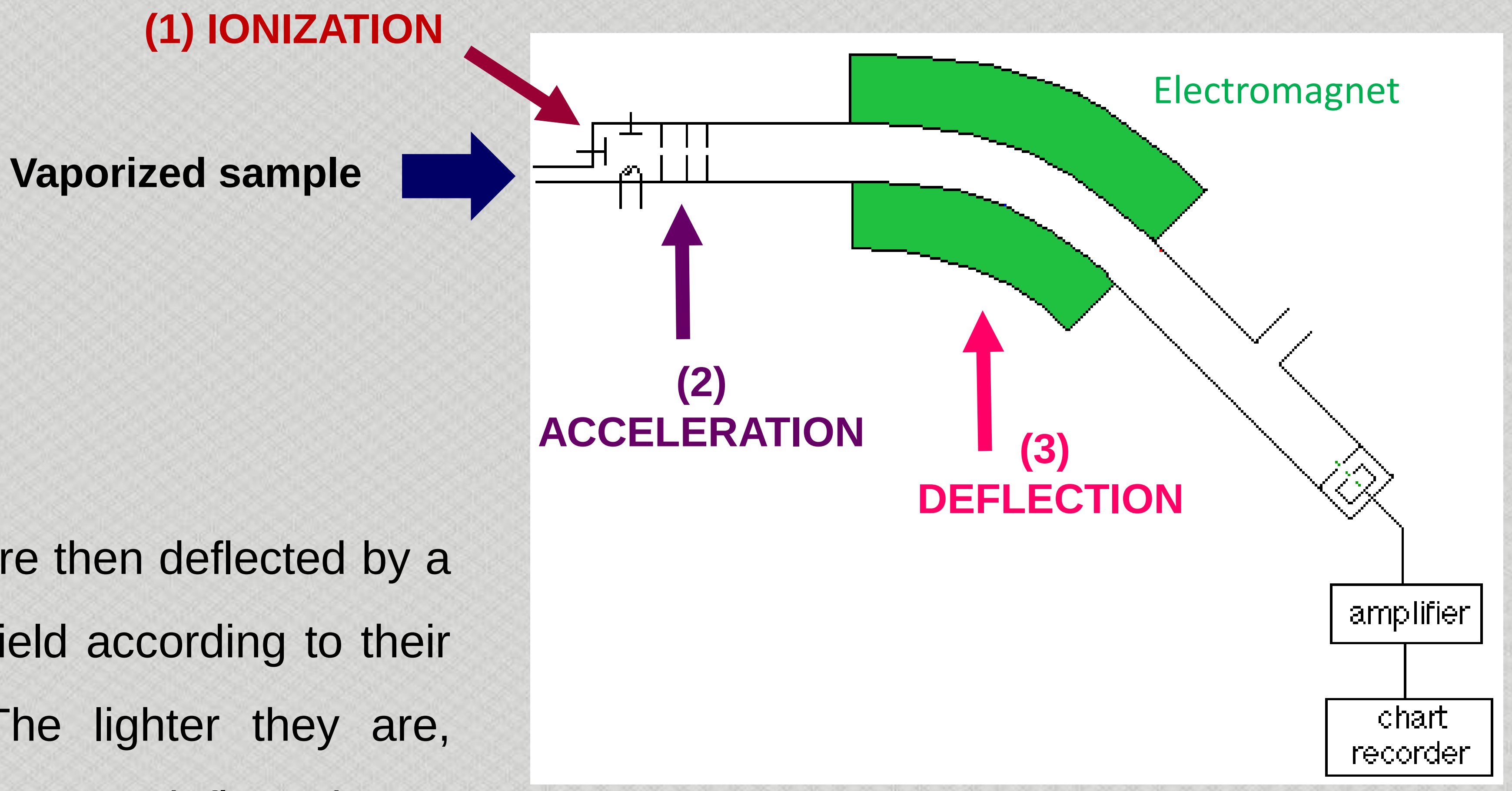
(1) IONIZATION

Vaporized sample



(2) ACCELERATION

- The positive ions are repelled away from the very positive ionization chamber and pass through three slits, the final one of which is at 0 volts. The middle slit carries some intermediate voltage.



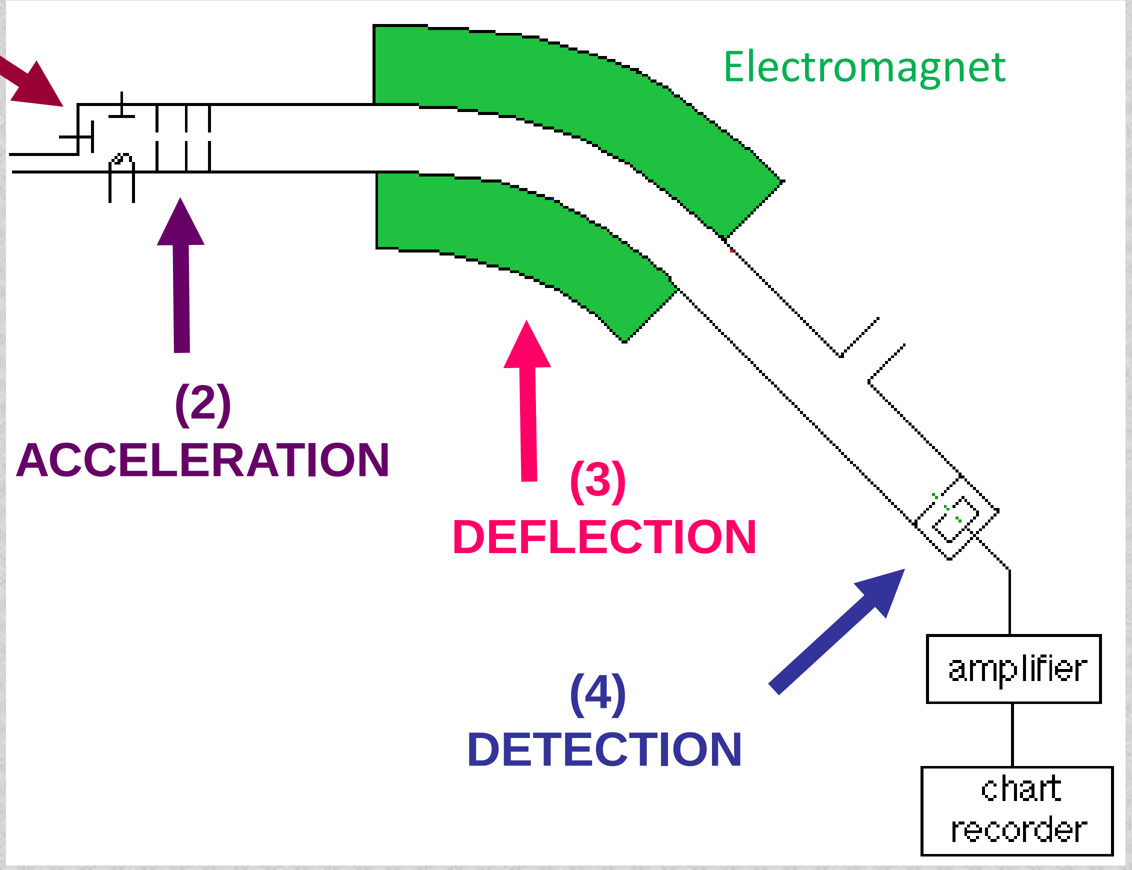
- The ions are then deflected by a magnetic field according to their masses. The lighter they are, the more they are deflected.

- The amount of deflection also depends on the number of positive charges on the ion – in other words, on how many electrons were knocked off in the first stage. The more the ion is charged, the more it gets deflected.

Different ions are deflected by the magnetic field by different amounts. The amount of deflection depends on:

- The mass of the ion. Lighter ions are deflected more than heavier ones.
- The charge on the ion. Ions with 2 (or more) positive charges are deflected more than ones with only 1 positive charge.

These two factors are combined into the ***mass/charge ratio.*** Mass/charge ratio is given the symbol m/z (or sometimes m/e)



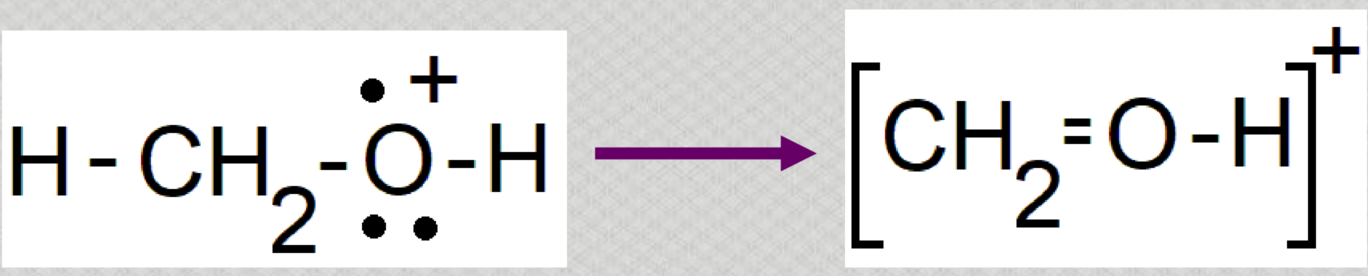
- The beam of ions passing through the machine is detected electrically.

PART 3:

- What is the fate of molecular ion?
- Output of mass spectrometry

- The molecular ion undergoes fragmentation, a process in which free radicals or neutral molecules are lost from the molecular ion.

- The general tendency is to form the most stable fragments possible.



m/z = 32 **m/z = 31**

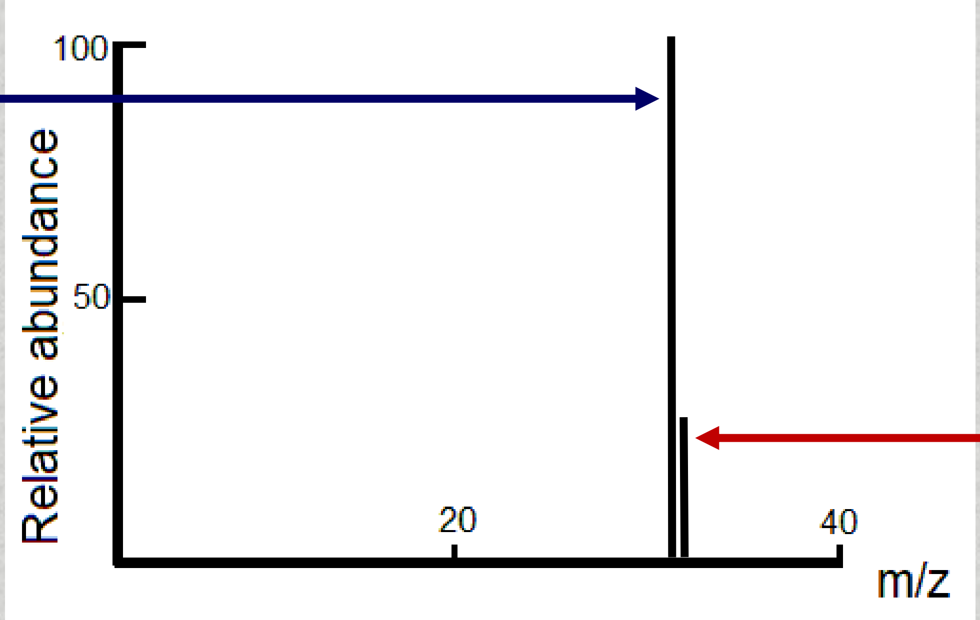
Note: Several other fragments also generated.

Output from mass spectrometer

- ❑ Mass spectrum: graphic representation of the mass spectrum of a compound is constructed by plotting mass/charge ratio (m/z) versus relative abundance.

m/z = 31
The base peak

- ❑ Most intense
- ❑ Assigned arbitrary value of 100.



m/z = 32
molecular ion

- **Molecular ion peak**: The peak in the mass spectrum with highest m/z value is the molecular ion peak (unless the molecular ion breaks into fragments before reaching the collector plate).

- **Base peak:** peak in the mass spectrum with highest intensity.

The base peak is assigned a relative intensity of 100 % and the relative intensity of other peaks is reported as a percentage of the base peak.

Metastable ion

- Metastable ions are those that dissociate en route from an ion source, through a mass analyser to an ion detection device.

- That ions can dissociate in flight was recognized by ***J. A. Hipple*** and ***E. U. Condon*** when they provided the explanation for the presence of the diffuse peaks that they had observed in normal, electron ionization (EI) mass spectra obtained with a single-focusing magnetic sector mass spectrometer.

- It should be emphasized that the term metastable refers only to ions that are able to fragment in flight by virtue of internal energy that they acquired within the ion source, not after acceleration therefrom, nor by collisions with a target gas, nor by radiative excitation as they traverse the apparatus. They are thus unimolecular dissociations.

- The lifetime of an ion may be so small that it undergoes decomposition during its passage between the source and collector units in the spectrometer.
- The ions resulting from the decomposition between the source region and the magnetic analyser are called metastable ions which appear in the spectrum as broad peaks at non-integral mase numbers.
- Such peaks are weaker in intensity but are useful in studying the mechanism of fragmentation. However, these are not used for the study of structure.

Relationship between m/z of metastable ion and its parent molecule:

$$m_1^+ \rightarrow m_2^+ + m_0$$

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

m_1: mass of parent ion,

m_2: mass of daughter (metastable) ion;

m_0: mass of neutral fragment;

m*: apparent mass of metastable ion.