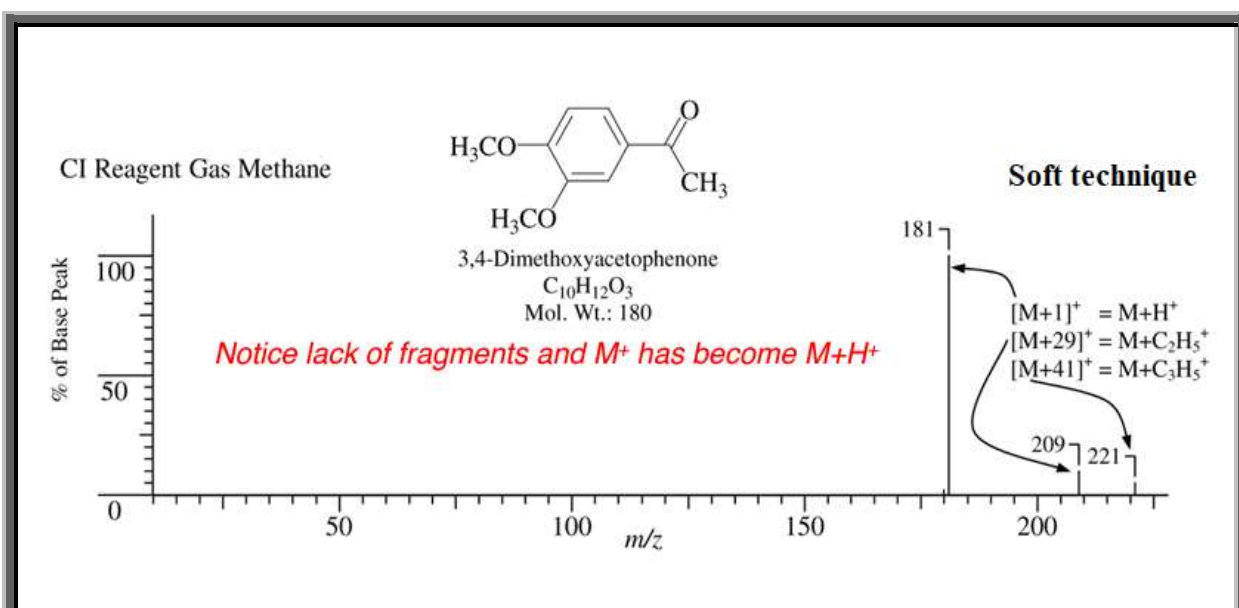
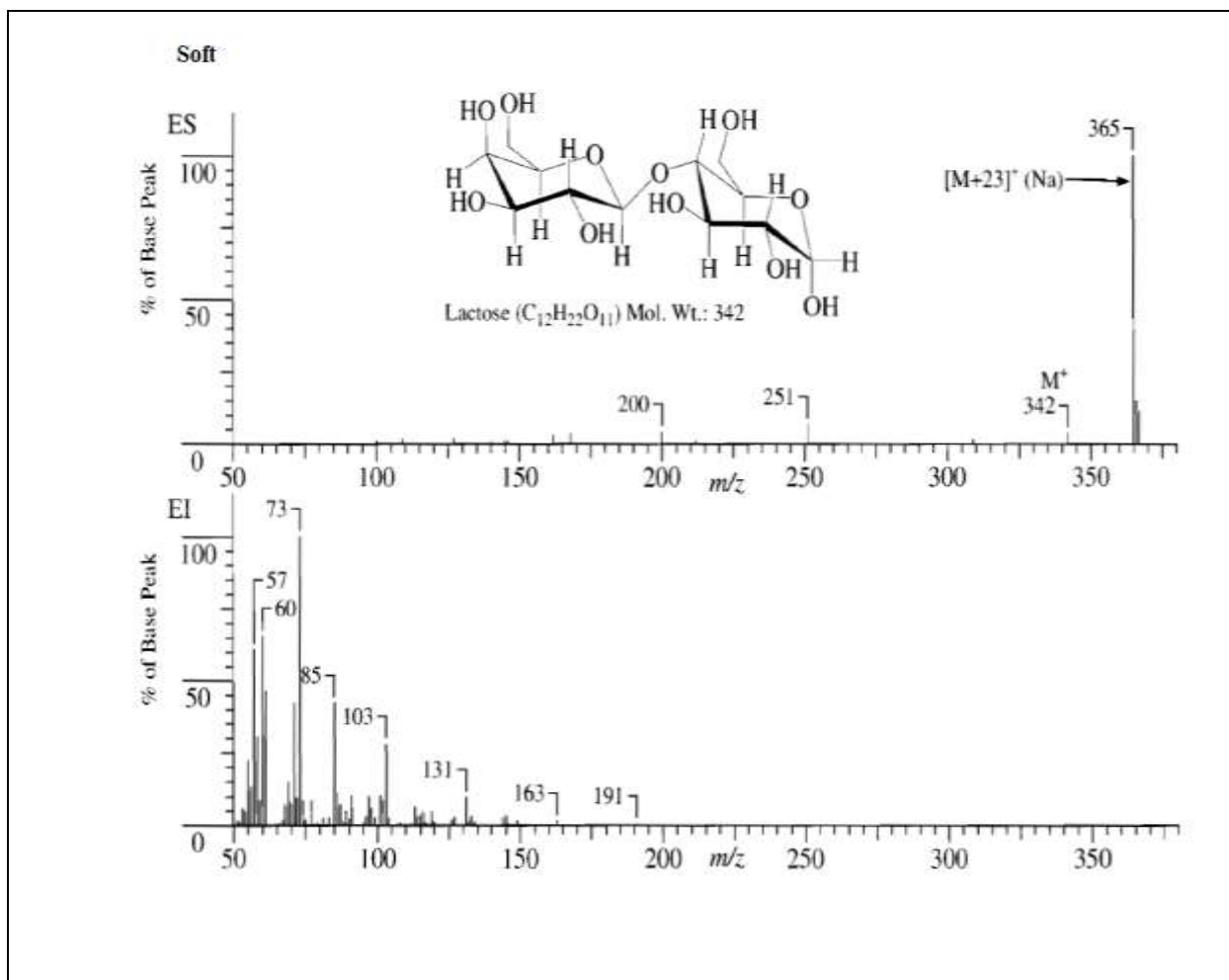


Hard ionization techniques typically yield in a larger number of lower mass fragments as oppose to higher mass.



Soft ionization technique yields a larger amount of high mass fragments.

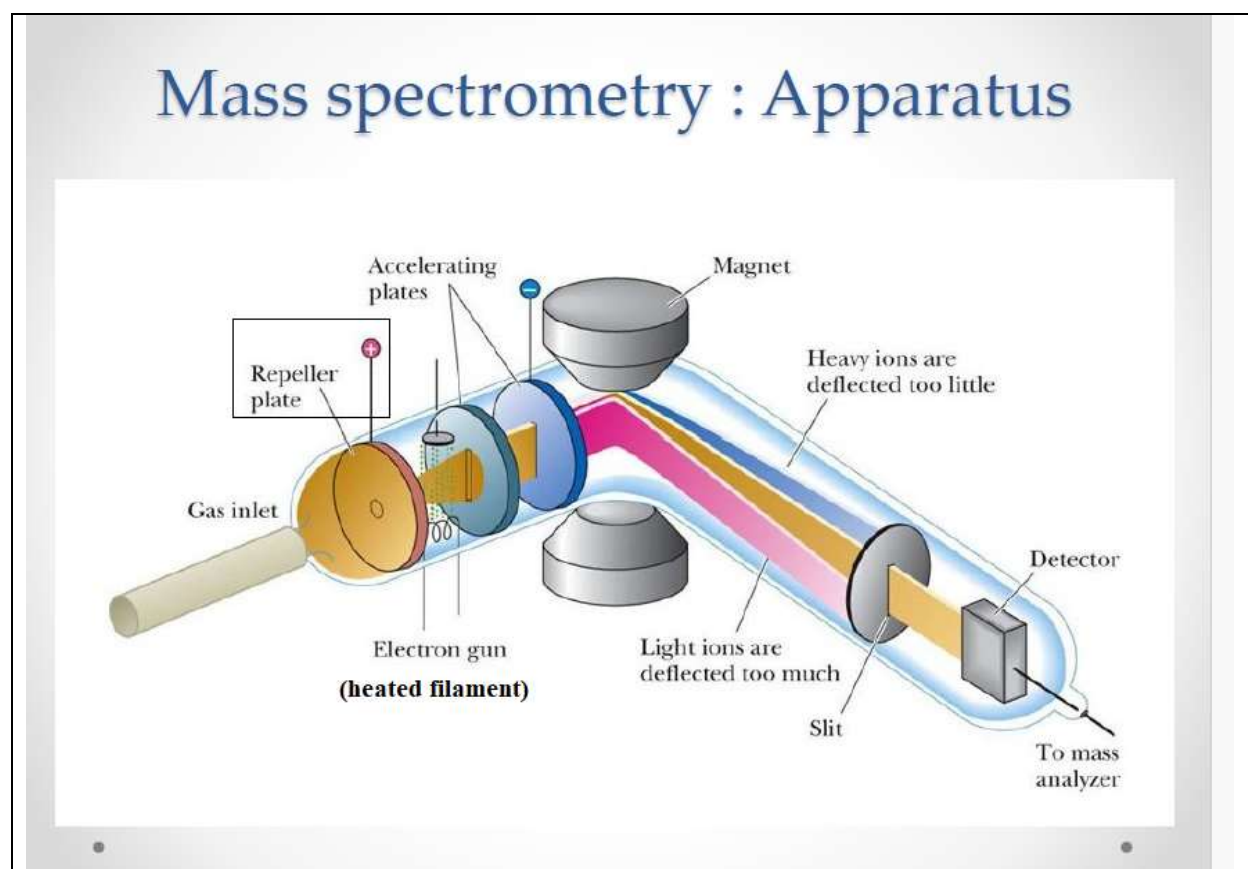


## Electron Ionization or Electron Impact(EI)

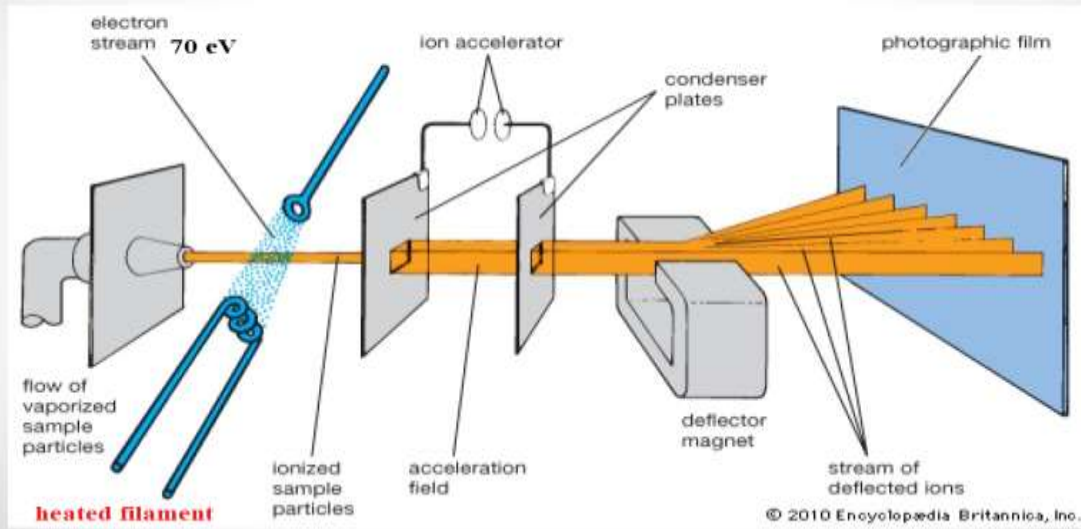
EI is the classical ionization method in MS. The sample for analysis is introduced into the ion source (Figure 1) (held under high vacuum,  $10^{-7}$ – $10^{-5}$  mbar) from a reservoir (in the case of gases and volatile liquids), from a heated probe (for involatile liquids and solids), or as the eluent from a

GC. It is essential that the sample enters the ion source in the gaseous state and the ability to heat the source and solids probe are important to successful sample analysis. Sample molecules collide with high-energy electrons (typically 70 eV), produced by a glowing filament of either tungsten or rhenium, and if the energy transferred, exceeds the molecules' ionization energy, ions are formed.

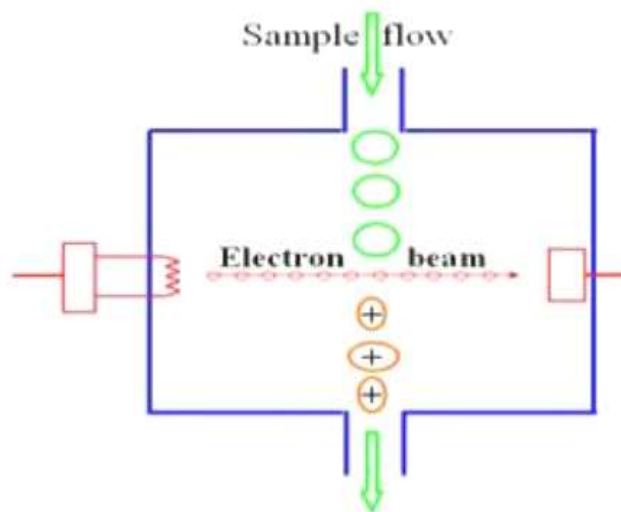
● A potential of 70 V is applied between the cathode and the source block in order to accelerate the electrons to 70 eV. At approximately 70 eV, the de Broglie wavelength of the electrons equals the length of a typical organic molecular bond.



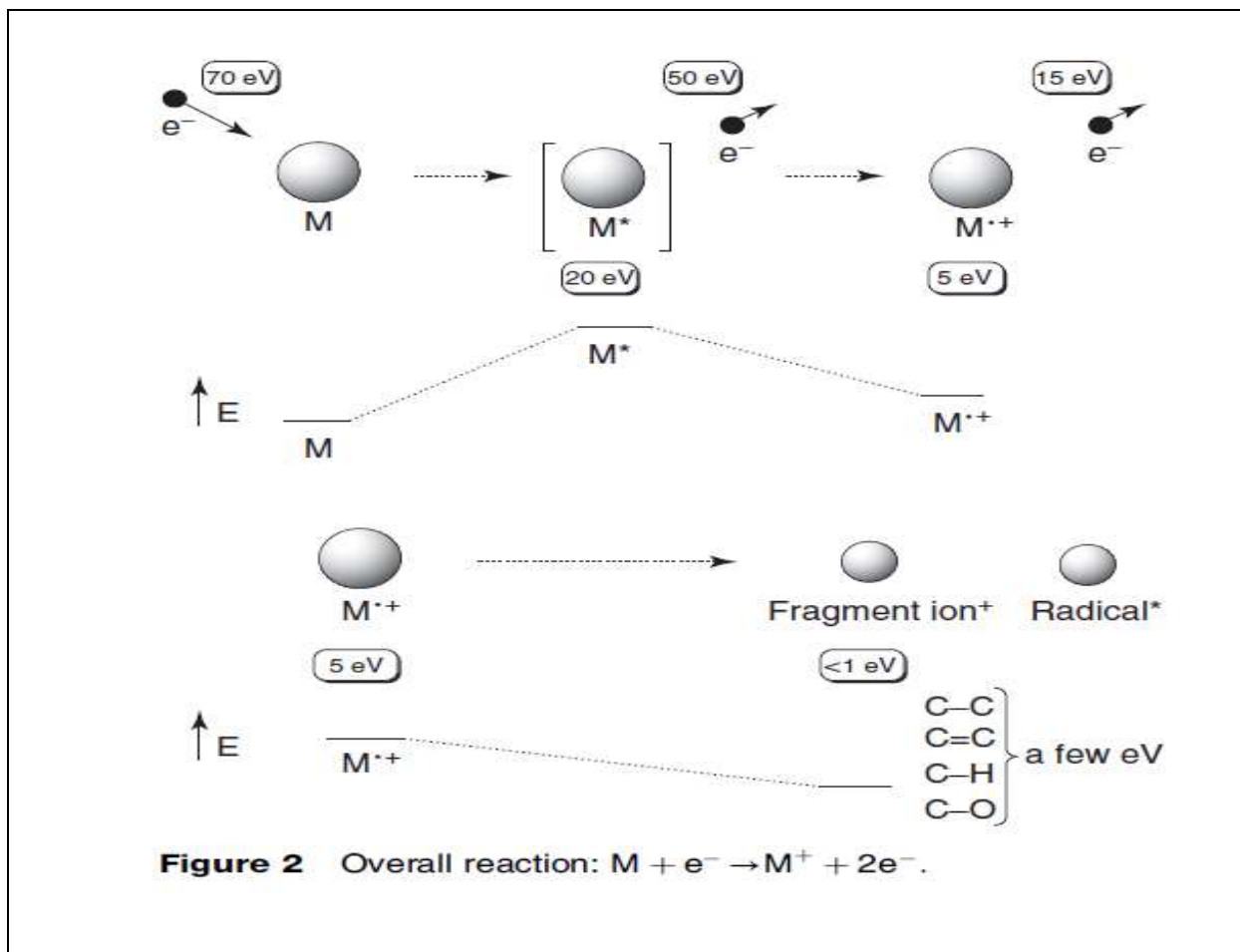
# Mass spectrometry :Aparatus



# Electron Ionization (EI) – Ionization Chamber



EI ion formation is outlined in Figure 2. In this example, 20 eV is transferred to the sample molecule following its collision with a 70 eV (1eV = 96.4152206 kJ/mole). Since the ionization energy of most organic molecules is of the order of 15 eV, an electron is expelled to produce a radical cation  $M^{+\bullet}$  with 5 eV excess energy. Once formed, the radical cation can be accelerated out of the source, mass analyzed, and detected as the molecular ion. **Given that the mass of an electron is MINOR** in comparison to that of an organic molecule, the mass of the molecular ion is effectively the molecular mass  $M_r$  of the sample. When we take into account that the covalent bond strength within an organic molecule is typically only a few electron volts, any individual molecular ions with internal energies higher than this will be more probable to fragment. In the example given in Figure 2, the molecular ion is 5 eV above the ground state and there is easily sufficient energy to cause fragmentation. Fragments may be lost as radicals or as neutral molecules. MS is only capable of detecting ions, hence neutral molecules and radicals do not appear in the spectrum.



● Ion-molecule reactions do not occur since the pressure stays low ( $10^{-7}$  -  $10^{-5}$  mbar), hence the proton transfer-related  $[M + H]$  signal is not observed.

● Cations formed by the electron bombardment are pushed away by a charged repeller plate (anions are attracted to it), and accelerated toward other electrodes, having slits through which

the ions pass as a beam (The positive ions move toward the cathode and the negative ions toward the anode).

## **Advantages and disadvantages.**

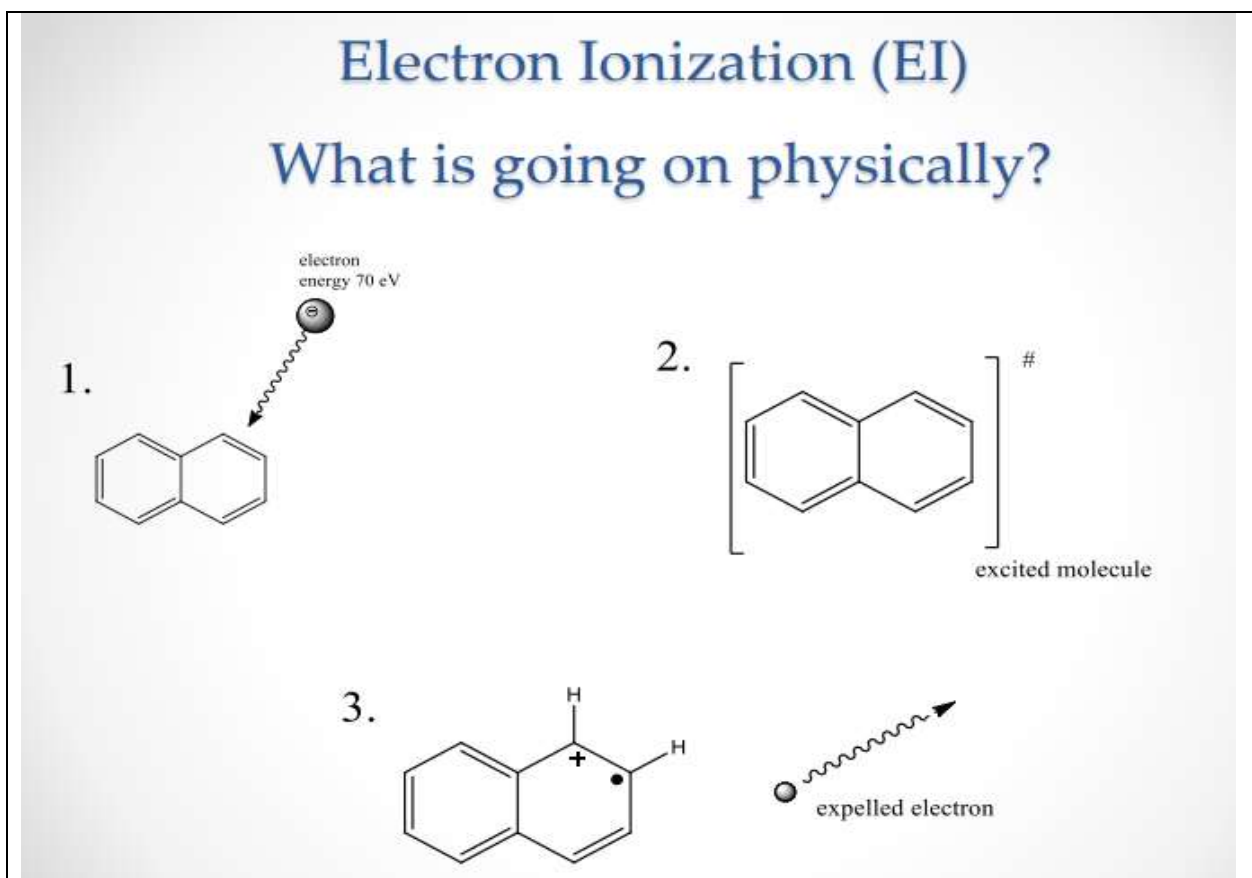
### **a) Advantages**

- 1- High fragmentation can aid in molecular characterization.
- 2- Sample can be solid, liquid, or gas
- 3- High fragmentation allows for a well defined fingerprint spectra
- 4- Can be equipped to many different mass analyzers including time-of-flight, GC-MS, LC-MS etc.
- 5- Fast and easy (typically first method of choice when screening samples)

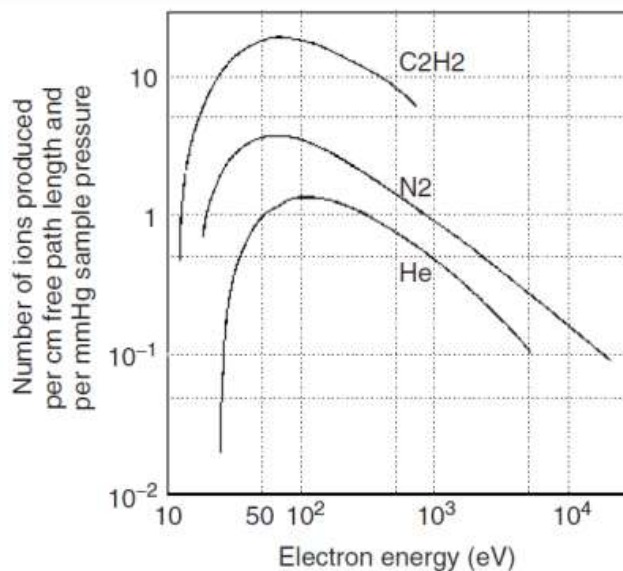
### **b) Disadvantages**

- 1- Characterization of large molecules is nearly impossible(it is very difficult to obtain information of large proteins and their interaction pathways)
- 2- Sample must be volatile
- 3- Multiple charges can result in very confusing mass spectra.

- 4- Low mass ranges typically less than 600 Da. (Proteins can be in the kDa range)
- 5- Extensive fragmentation can make it difficult to interpret data.
- 6- Only positive ions are formed.



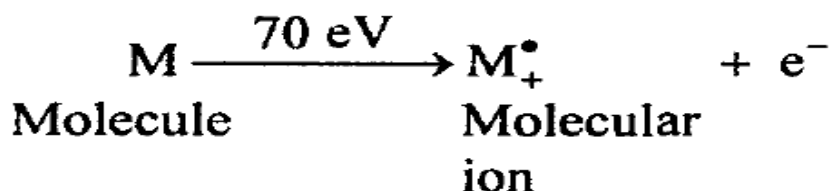




Number of ions produced as a function of the electron energy.

### **Molecular ion peak :**

A molecular ion peak is the peak produced by an ion formed by the removal of one electron from a molecule. It is important to recognize the molecular ion peak because this gives the molecular weight of the compound.



Sometimes there is a small peak 1 unit to the right

of the molecular ion peak – this is called the M+1 peak. It has low abundance. An M+1 peak is a peak produced by a molecular ion with an increased mass due to the presence of one carbon-13 atom.

- **Absence of molecular ions** (or an extremely weak  $[M]^+$  peak) is characteristic of highly branched molecules whatever the functional class. Alcohols and molecules with long alkyl chains also fragment easily and lead to very weak  $[M]^+$  peaks.

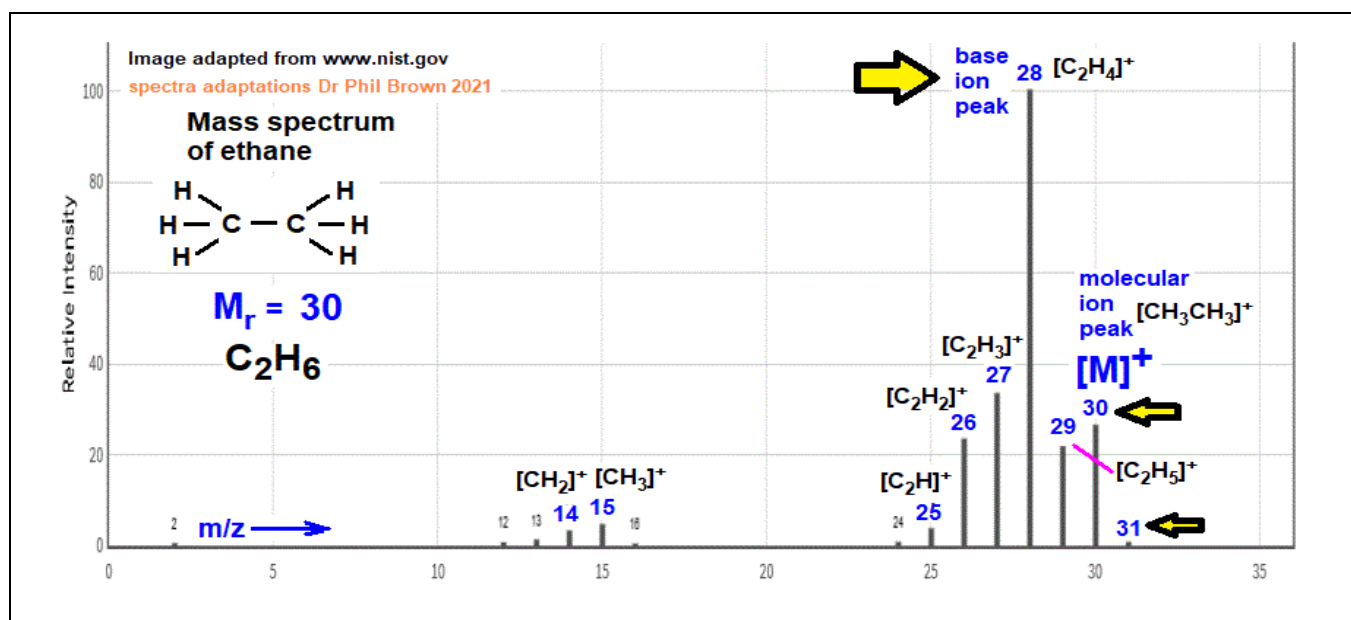
- **The base peak** is the peak of greatest abundance in a mass spectrum( Assigned 100% intensity). The molecular ion peak may sometimes be the base peak.

- **Fragmentation** is the term used to describe the split of a molecule ion into smaller or daughter ions.

- **A fragmentation ion** is a positively charged ion produced when the molecular ion breaks apart.

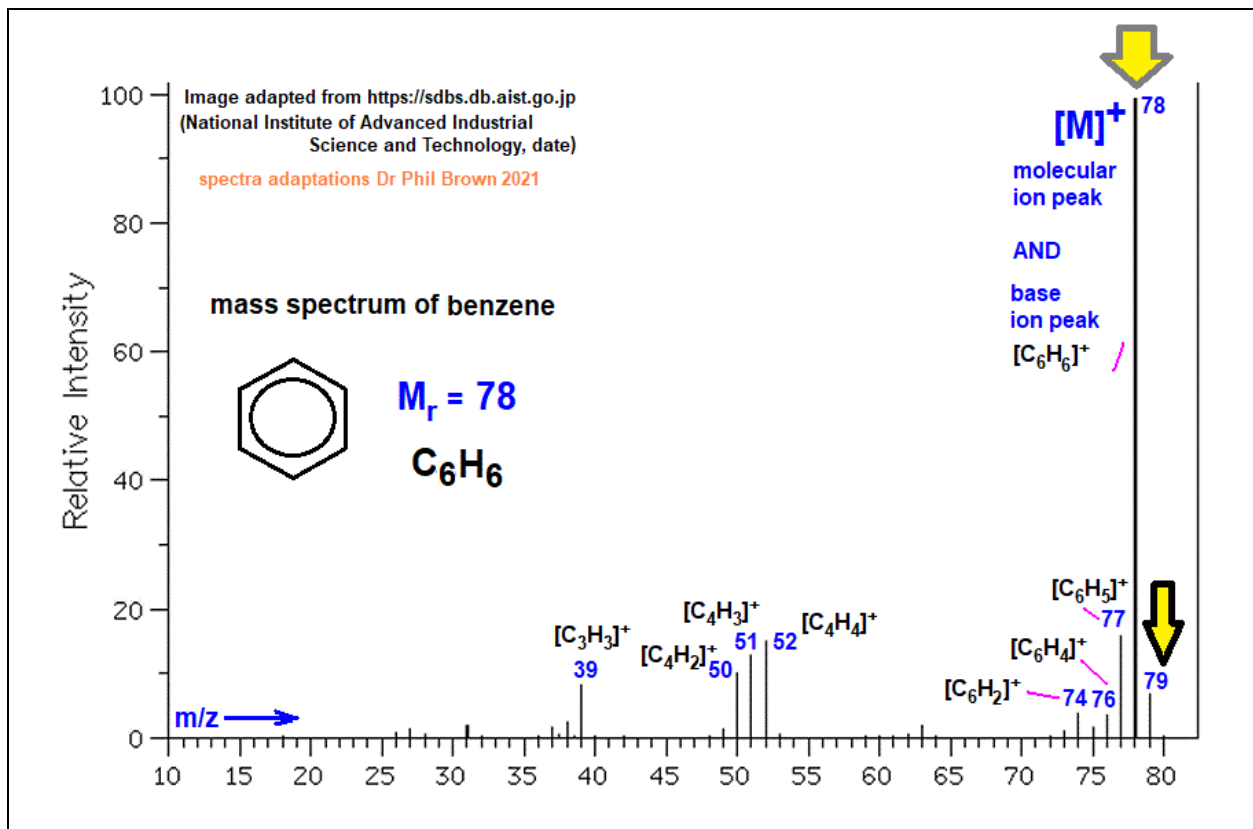
- **Unusual fragment ions** should make one suspicious: for example, molecular ions can give rise to a series of weaker ions at  $M - 1$ ,  $M - 2$  and  $M - 3$  due to successive loss of hydrogen, but a *specific* fragmentation leading directly to  $M - 3$  (or  $M - 4$  or  $M - 5$ ) is never observed.

- **Isotopic peaks**: due to presence of isotopes of C, H, O, N,... in the sample molecule and appear around the main peaks.



$[M]^+$  is the molecular ion peak (M) with an  $m/z$  of 30 corresponding to  $[C_2H_6]^+$ , the original ethane molecule minus an electron,  $[CH_3CH_3]^+$

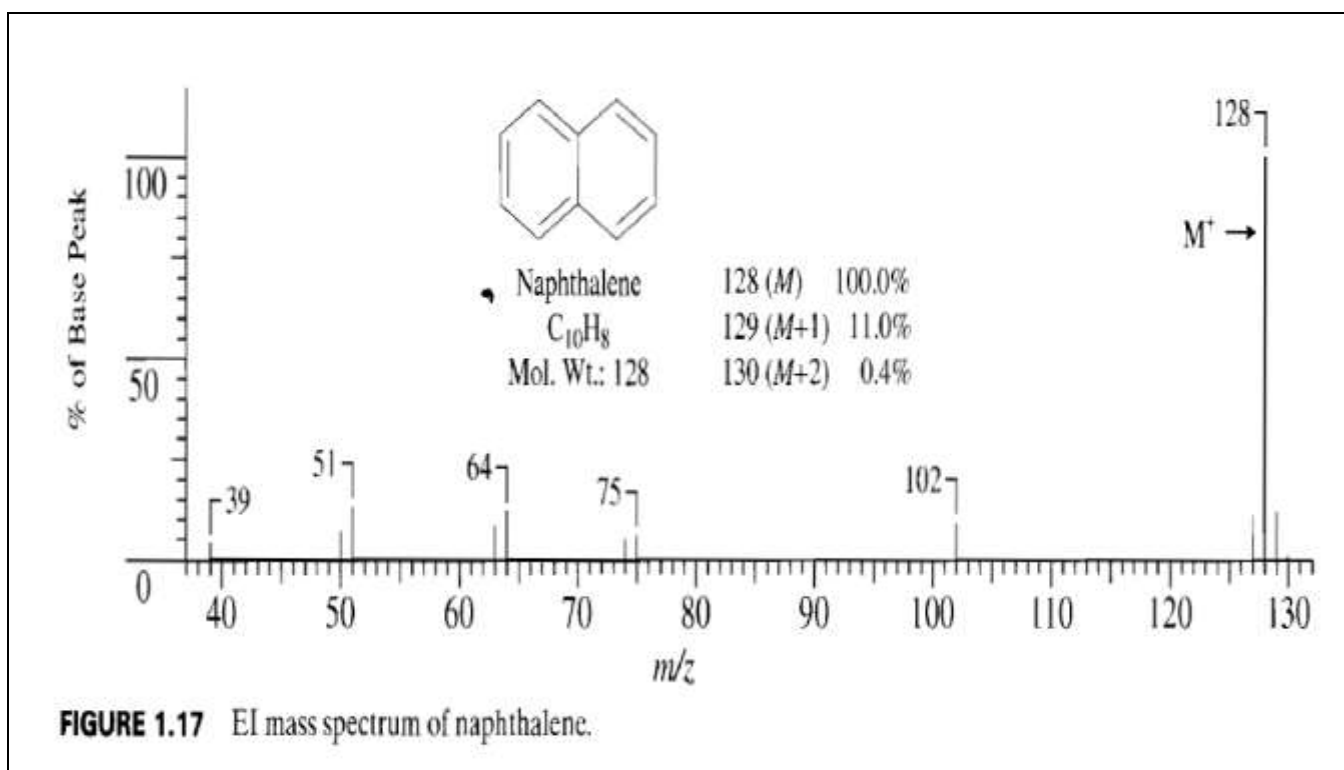
The tiny  $M+1$  ion peak at  $m/z$  31, corresponds to an ionized ethane molecule with one  $^{13}C$  atom in it i.e. an ionized ethane molecule of formula  $[^{13}C^{12}CH_6]^+$



$[M]^+$  is the molecular ion peak (M) with an  $m/z$  of 78 corresponding to  $[C_6H_6]^+$ , the original molecule minus an electron.

The small M+1 peak at m/z 79, corresponds to an ionised benzene molecule with one  $^{13}\text{C}$  atom in it i.e. an ionised molecule of formula  $[\text{}^{13}\text{C}^{12}\text{C}_5\text{H}_6]^+$

**In this case the base peak ion is also the molecular ion of benzene itself  $[\text{C}_6\text{H}_6]^+$**



$[\text{M}]^+$  is the molecular ion peak (M) with an m/z of 128. In this case the base peak ion is also the molecular ion of Naphthalene.

## **Stability of the molecular ion**

The intensity of the molecular ion peak depends on the stability of the molecular ion. The most stable molecular ions are those of purely aromatic systems. If substituents that have favorable modes of cleavage are present, the molecular ion peak will be less intense, and the fragment peaks relatively more intense. In general, the following group of compounds will, in order of decreasing ability, give prominent molecular ion peaks:

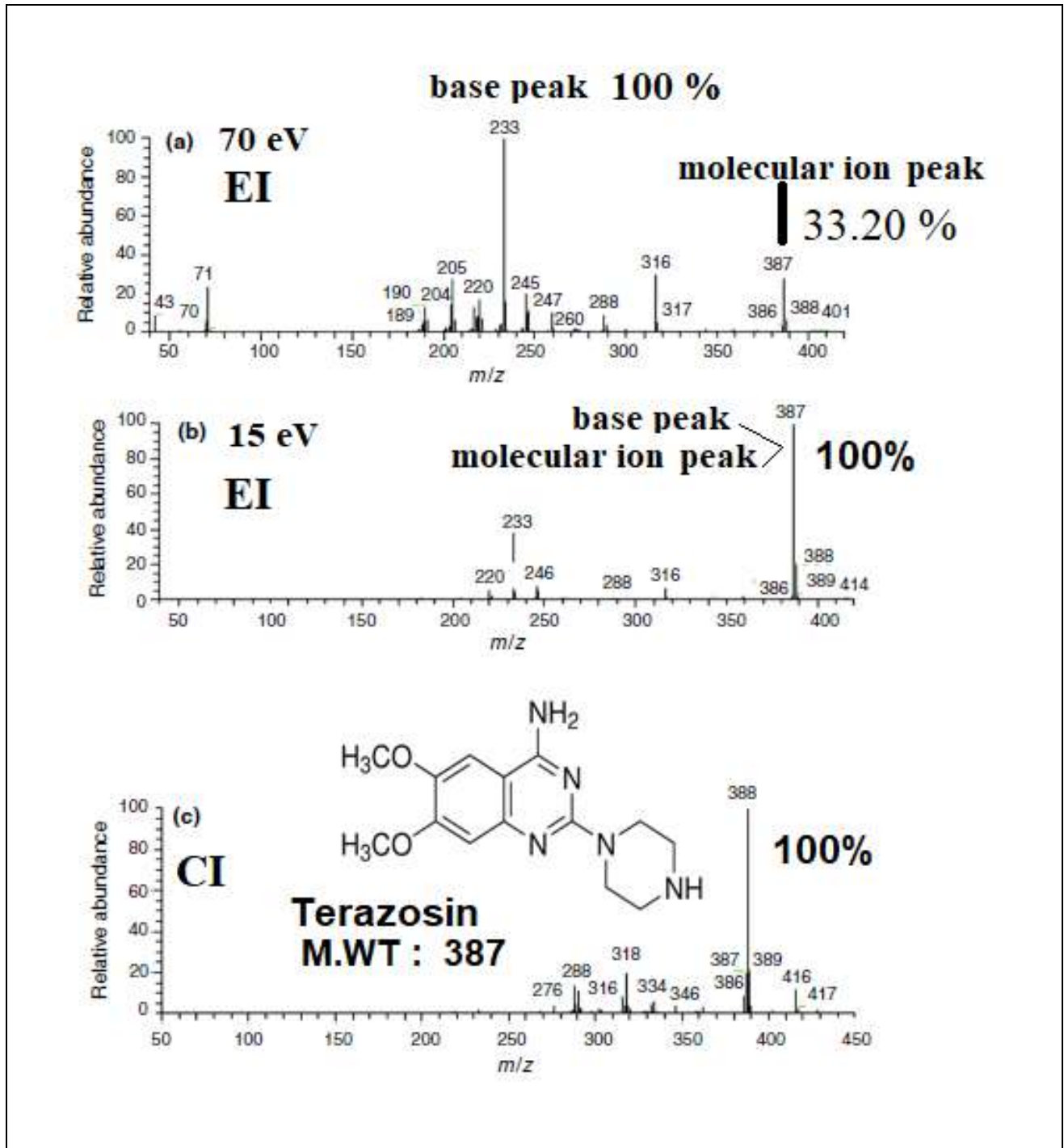
aromatic compounds > conjugated alkenes > cyclic compounds  
organic sulfides > short, normal alkanes > mercaptans.

Identify able molecular ions are usually produced for these compounds in order of decreasing ability:

ketones > amines > esters > ethers > carboxylic acids  
acids  $\approx$  aldehydes  $\approx$  amides  $\approx$  halides.

The molecular ion is frequently not detectable in aliphatic alcohols, nitrites, nitrates, nitro compounds, nitriles, and in highly branched compounds.

# Low energy, low temperature mass-spectra



Terazosin ( $C_{19}H_{25}N_5O_4$ , MW = 387) drug is used for lowering the blood pressure. Also, it used for treatment of symptoms of an enlarged prostate and is therefore a drug of choice for men with hypertension and prostate enlargement. On measurement of mass spectra of terazosin by EI at lower power of 15 eV (Fig. 4b) and using CI technique (Fig. 4c) refers to change in nature of the main and fragment ions using EI at 70 eV. At 15 eV, the base peak becomes  $m/z = 387$  (RI = 100 %), and on using CI (soft technique), it appears at  $m/z = 388$  (RI = 100 %) of  $[M]^+$  of the drug main molecule and the fragment ion of  $m/z = 233$  (RI = 40 %) which completely disappear on using CI technique. This means that, lowering of energy of the power source increases RI of the drug main molecular ion and makes lot of fragment ions obtained at 70 eV of low RI and/or completely disappeared.

	Elemental formula, name, & Mol. weight	No. of atom	M + Abund. %	
			70 eV EI	14 eV EI
1	Nitrobenzene $C_6H_5NO_2$ MW = 123.031	14	50.7	98.6
2	Toluene $C_7H_8$ MW = 92.062	15	60.0	100



**Camphene C<sub>10</sub>H<sub>16</sub>**  
**MW = 136.125**

