MS process

Ionization

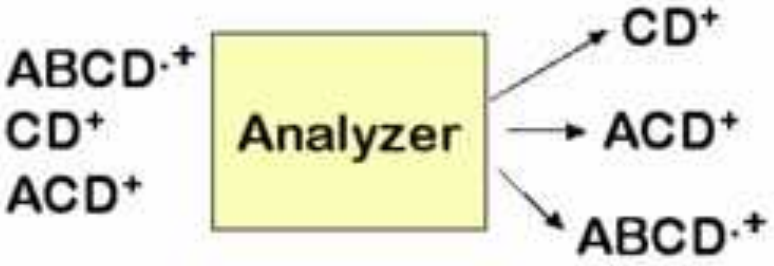
$$ABCD + e^- \longrightarrow ABCD^{\cdot +} + 2e^-$$

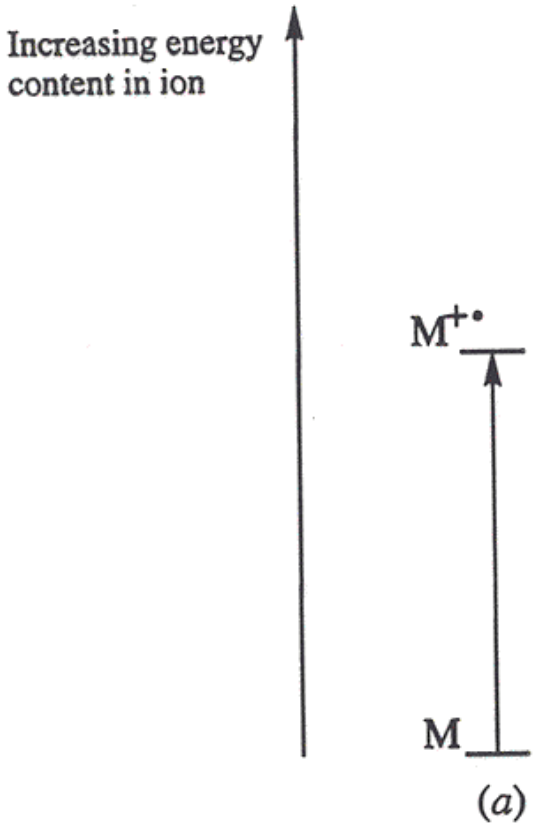
Fragmentation

$$ABCD^{\cdot +} \longrightarrow AB^{\cdot} + CD^+$$
$$ABCD^{\cdot +} \longrightarrow AB^+ + CD^{\cdot}$$
$$ABCD^{\cdot +} \longrightarrow ACD^+ + B^{\cdot}$$

and so on.

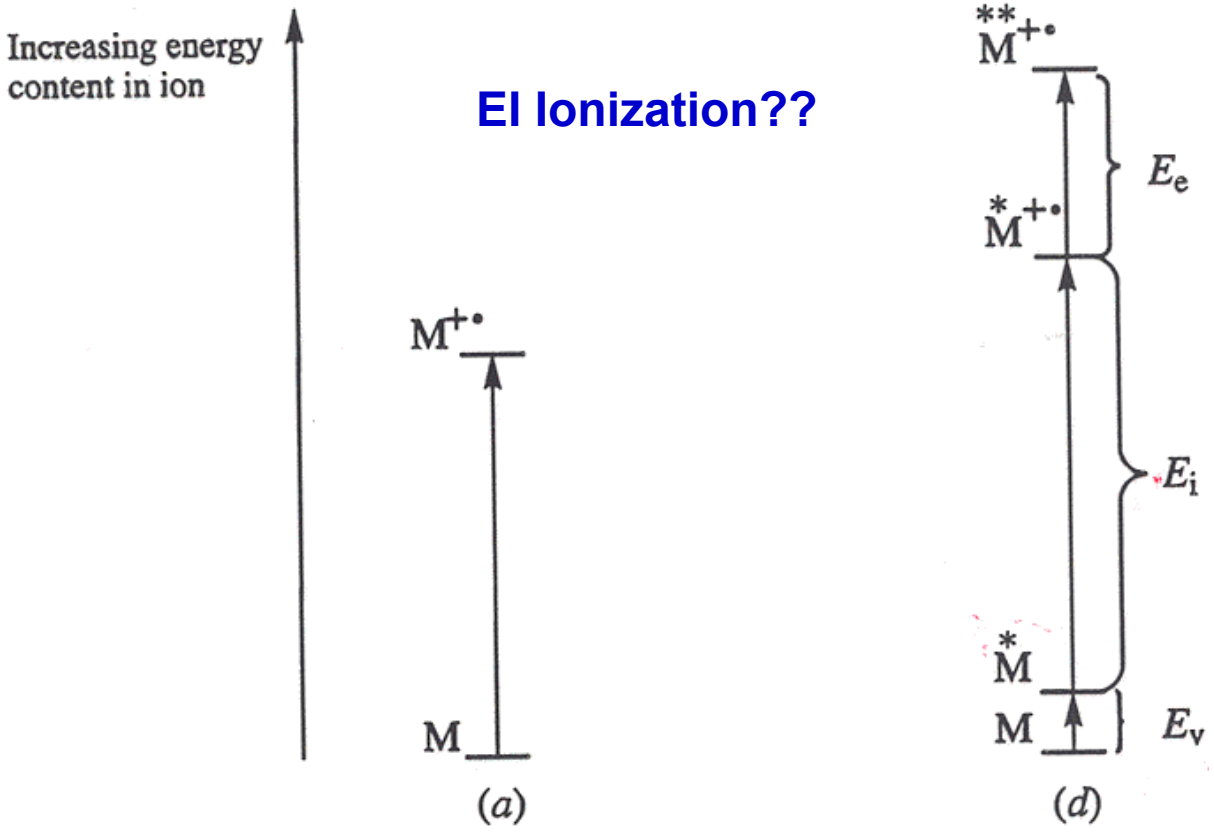
Mass analysis and detection



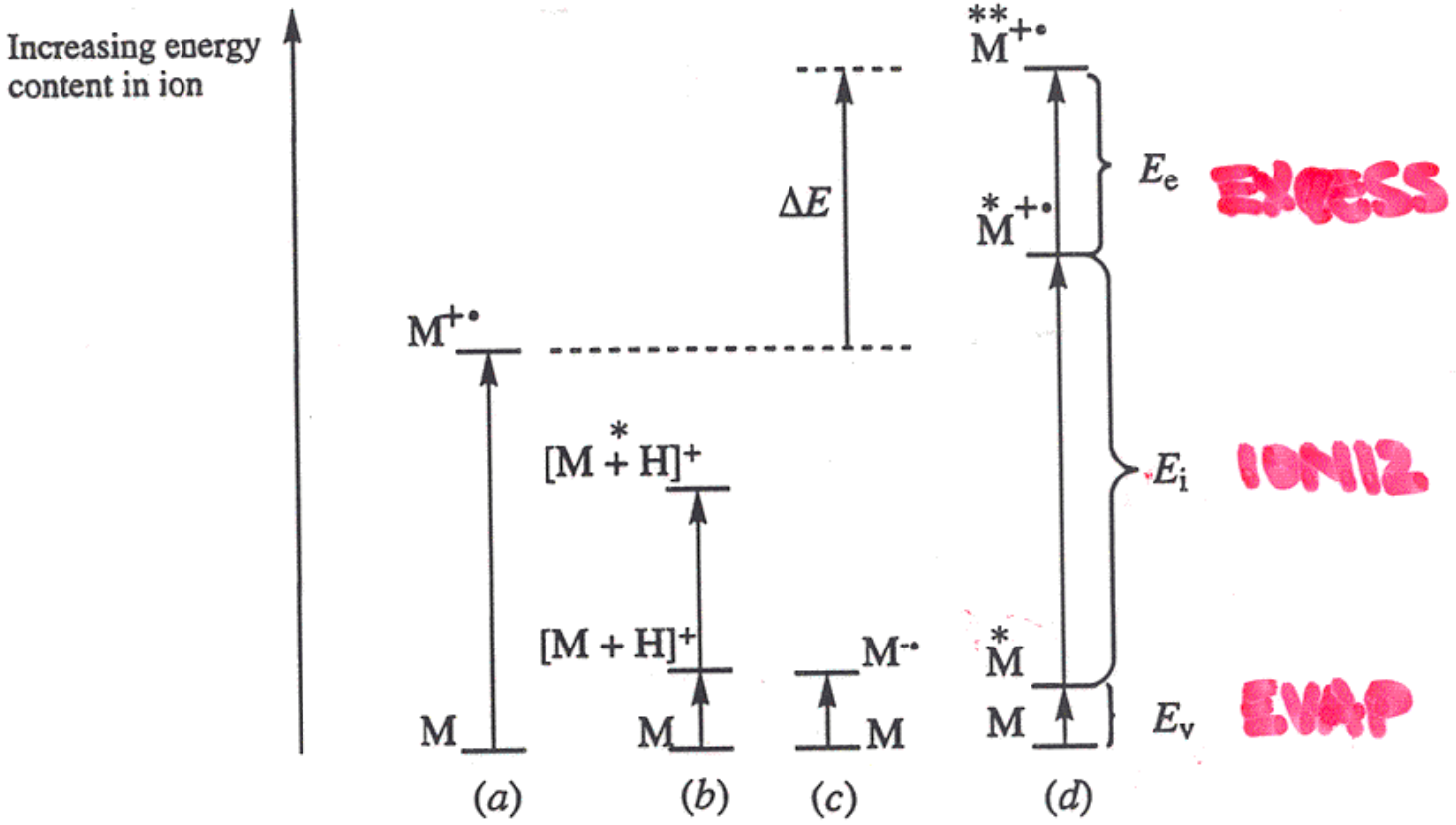


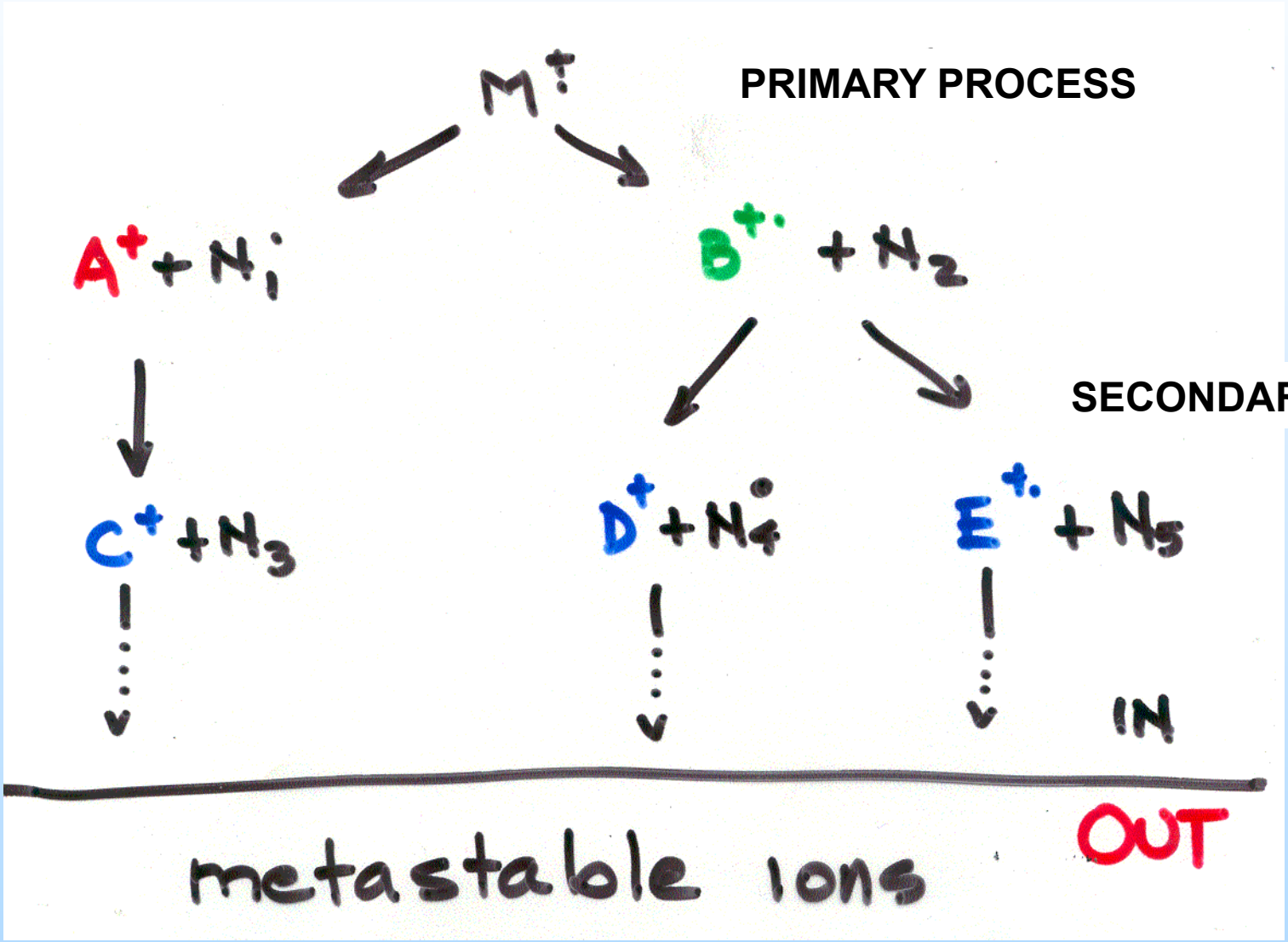
Ionization energy?

EI Ionization??



SOFT vs. HARD IONIZATION METHODS???



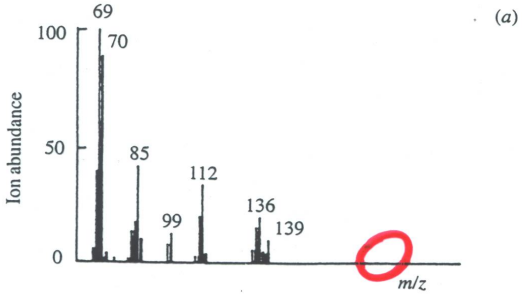

PRIMARY PROCESS
SECONDARY PROCESS
IN
OUT
metastable ions

ionization method	typical mass range	polarity of the analyte	positive ions	negative ions	HR-MS	GC-MS	metastable ions	collisionally induced dissociation
EI	1-1000	low	yes	no	yes	yes	yes	yes
CI	60-1200	low-medium	yes	yes	(yes)	yes	yes	yes
FD	1-5000	low-high	yes	no	(yes)	no	no	yes
ESI	100-50000	medium-very high	yes	yes	yes	no	no	yes
FAB	300-5000	low-high	yes	yes	yes	no	yes	yes
LDI	1-1500	low-medium	yes	yes	no	no	no	no
MALDI	500->100000	low-high	yes	yes	no	no	no	no

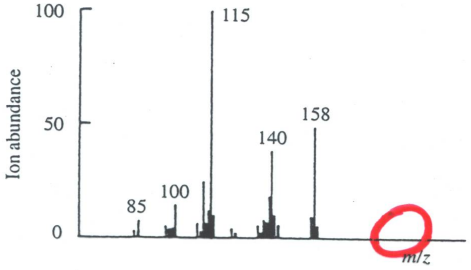
Sample introduction/ionization method:

Ionization method	Typical Analytes	Sample Introduction	Mass Range	Method Highlights
Electron Impact (EI)	Relatively small volatile	GC or liquid/solid probe	to 1,000 Daltons	Hard method versatile provides structure info
Chemical Ionization (CI)	Relatively small volatile	GC or liquid/solid probe	to 1,000 Daltons	Soft method molecular ion peak $[M+H]^+$
Electrospray (ESI)	Peptides Proteins nonvolatile	Liquid Chromatography or syringe	to 200,000 Daltons	Soft method ions often multiply charged
Fast Atom Bombardment (FAB)	Carbohydrates Organometallics Peptides nonvolatile	Sample mixed in viscous matrix	to 6,000 Daltons	Soft method but harder than ESI or MALDI
Matrix Assisted Laser Desorption (MALDI)	Peptides Proteins Nucleotides	Sample mixed in solid matrix	to 500,000 Daltons	Soft method very high mass

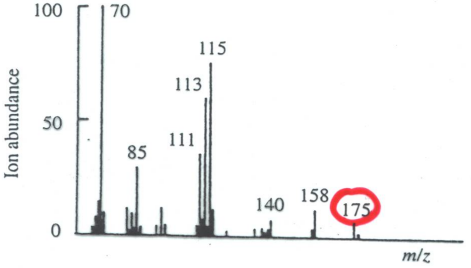
EI



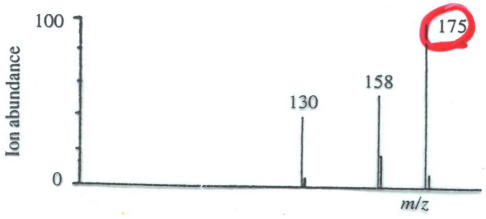
CI
Isobutane



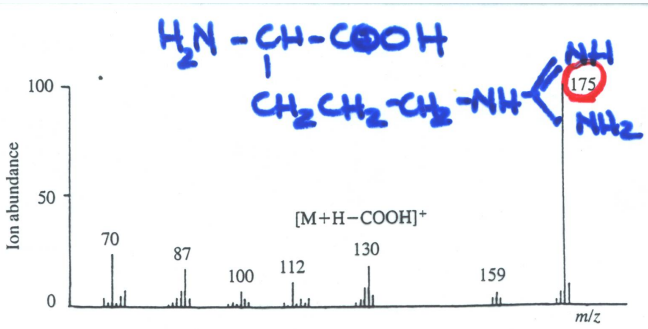
In-beam
CI
Isobutane



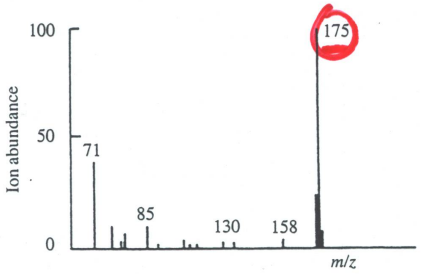
FD



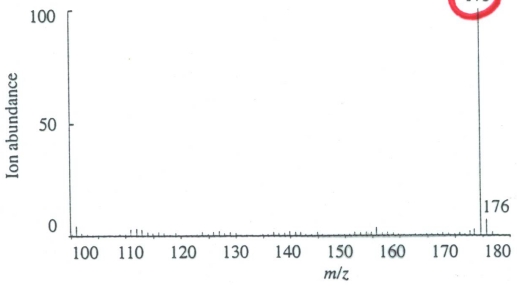
FAB



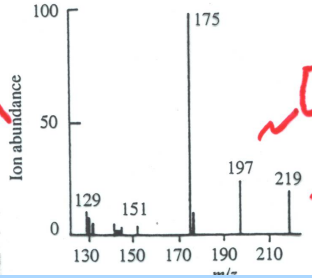
Thermo
spray



ESI



plasma
desorption



Ionization

A number of ionization techniques exist.

Electron impact (EI)

Chemical ionization (CI)

Fast atom bombardment (FAB)

Field ionization

Plasma desorption

How does a molecule become charged?

- The sample is introduced into the mass spectrometer, which is generally kept under high vacuum (<10^{-5} torr). ???
- Compounds are converted into gas phase molecules either before or during the charging or ionization process, which takes place in the ion source.
- Many types of ionization mode are available: the type of compound to be analyzed and the specific information required determines which ionization mode is the most suitable. (SIZE, STRUCTURE, CHEMISTRY)
- Once ionized, the molecule ion may fragment, producing ions of lower mass than the original precursor molecule. These fragment ions are dependent on the structure of the original molecule.

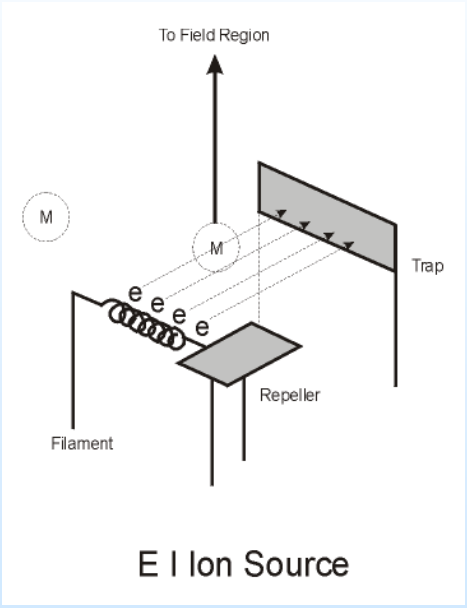
Ionization methods

Electron impact and chemical ionization are the two methods most widely used in GC/MS work

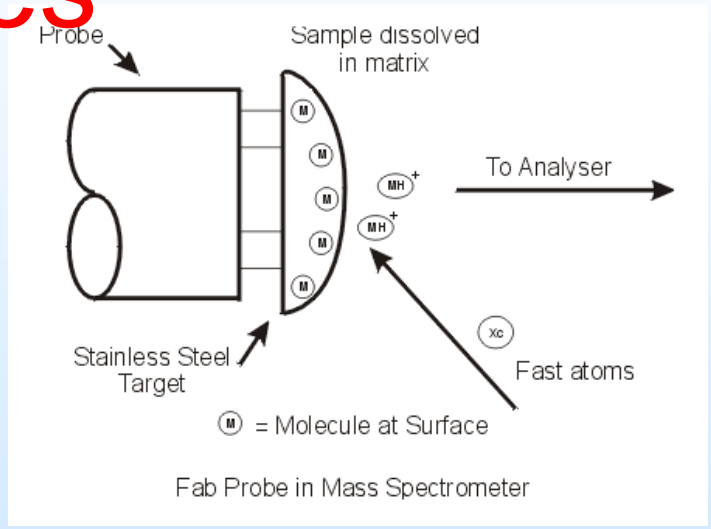
Electron impact (EI) - most common.

Chemical ionization (CI) - a modification of EI which results in 'softer' ionization
- less fragmentation.

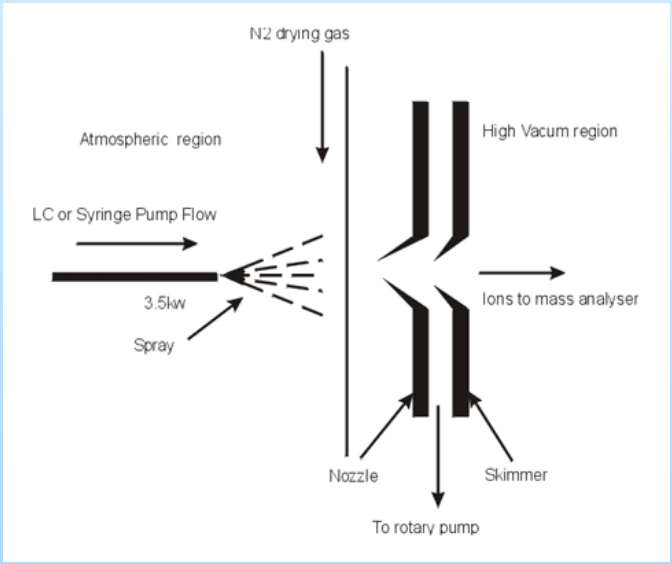
Ion Sources

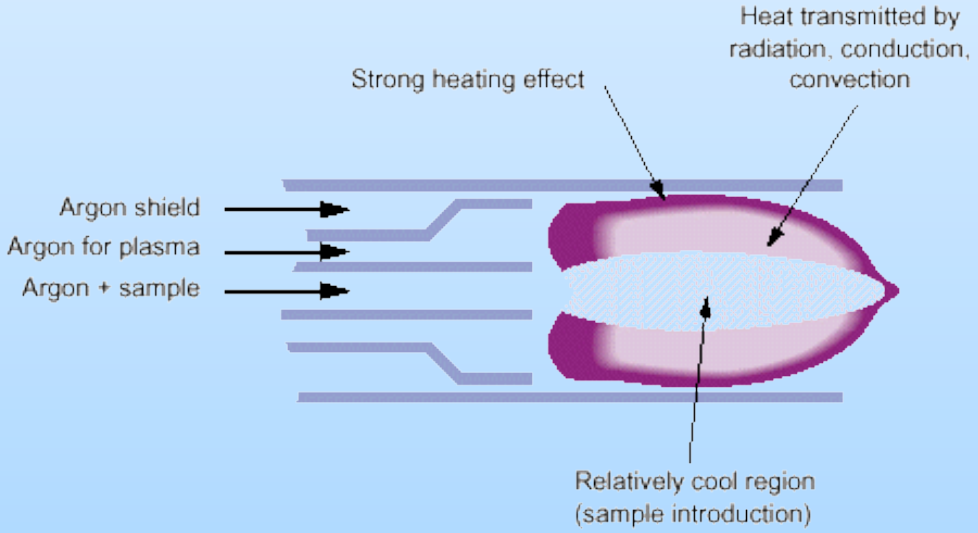


E I Ion Source



Fab Probe in Mass Spectrometer





Electron impact process

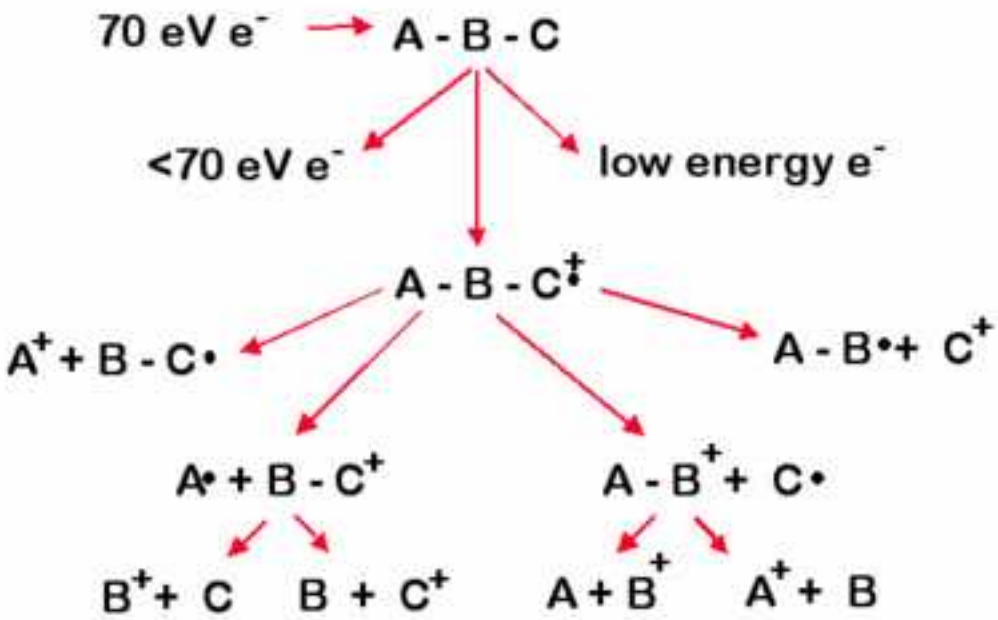
An electron (70 eV) strikes a neutral molecule.

This knocks out a second electron, producing a molecular ion - with some additional energy.

This additional energy is internalized via a series of vibrations, rotations and molecular rearrangements

This results in fragmentation of the molecule.

Electron impact process

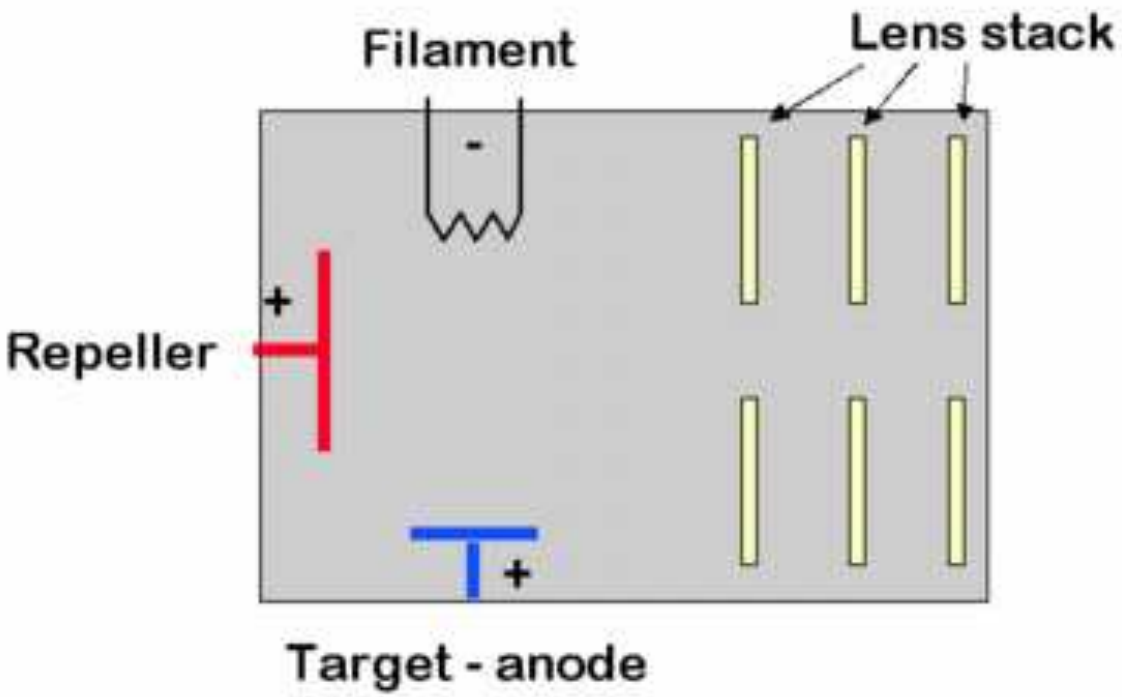


$$e^- + M \longrightarrow M^{\bullet +} + 2e^- \qquad (1)$$

$$e^- + M \longrightarrow M^{\bullet +} + 2e^- \longrightarrow A^+, B^+, \text{etc.} \qquad (2)$$

$$e^- + M \longrightarrow M^{\bullet -} \qquad (3)$$

Electron impact source



Electron impact source

Filament - Typically made of Re. Our source of 70 eV electrons.

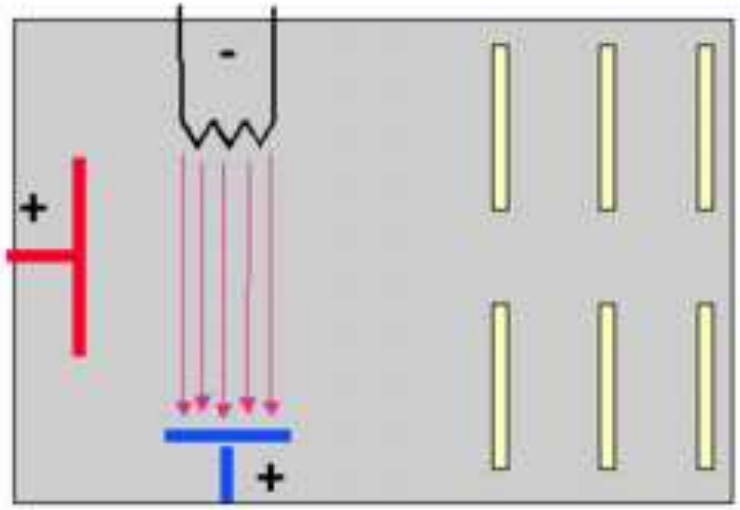
Target - anode used in association with the filament to produce electrons.

Repeller - positively charged electrode used to 'push' positive ions out of the ionization source.

Lens stack - series of increasingly more negative electrodes used to accelerate our ions to constant kinetic energy.

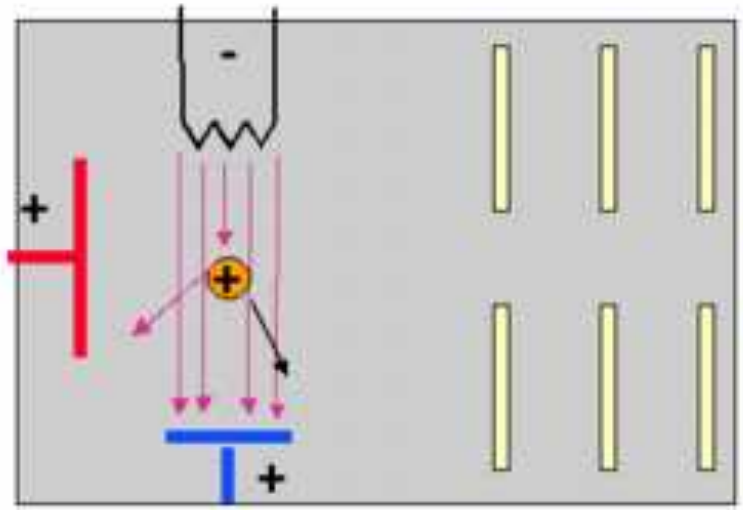
Electron impact source

A known current of 70 eV electrons is produced in our source.



Electron impact source

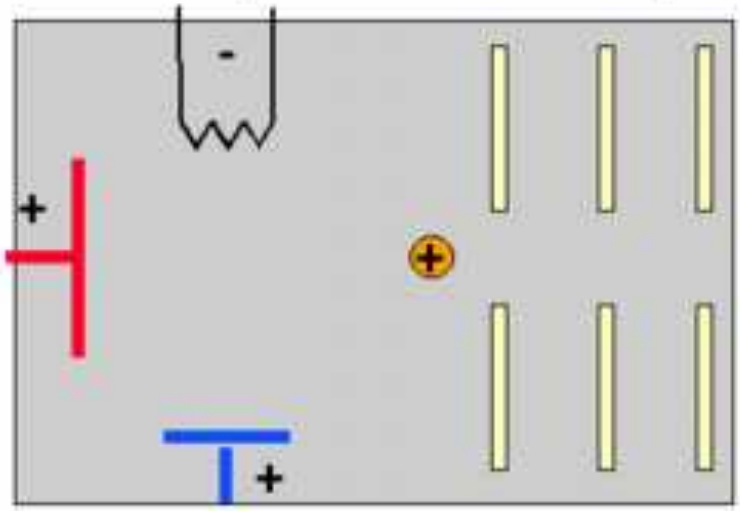
When a sample molecule enters the source, it passer through the electron beam and is ionized.



Electron impact source

The repeller insures that the ion is rapidly pushed out of the source, towards the lens stack.

Any negative ions are pulled into the repeller.

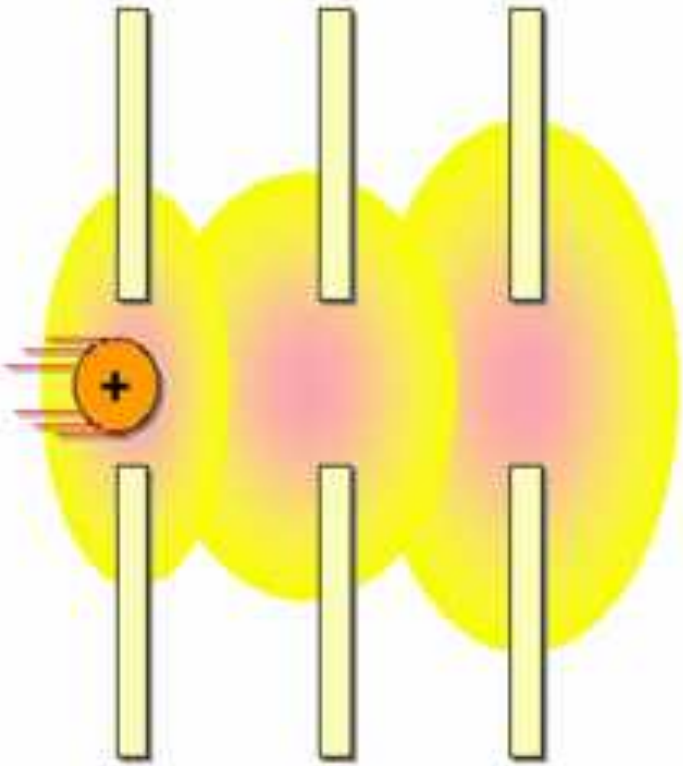


Electron impact source

As an ion accelerates towards the first lens, it comes under the influence of the next, more negative lens. It passes the first lens and accelerates towards the next.

By the final lens, it is traveling so fast that it simply passes directly into the analyzer.

- constant KE



Electron impact

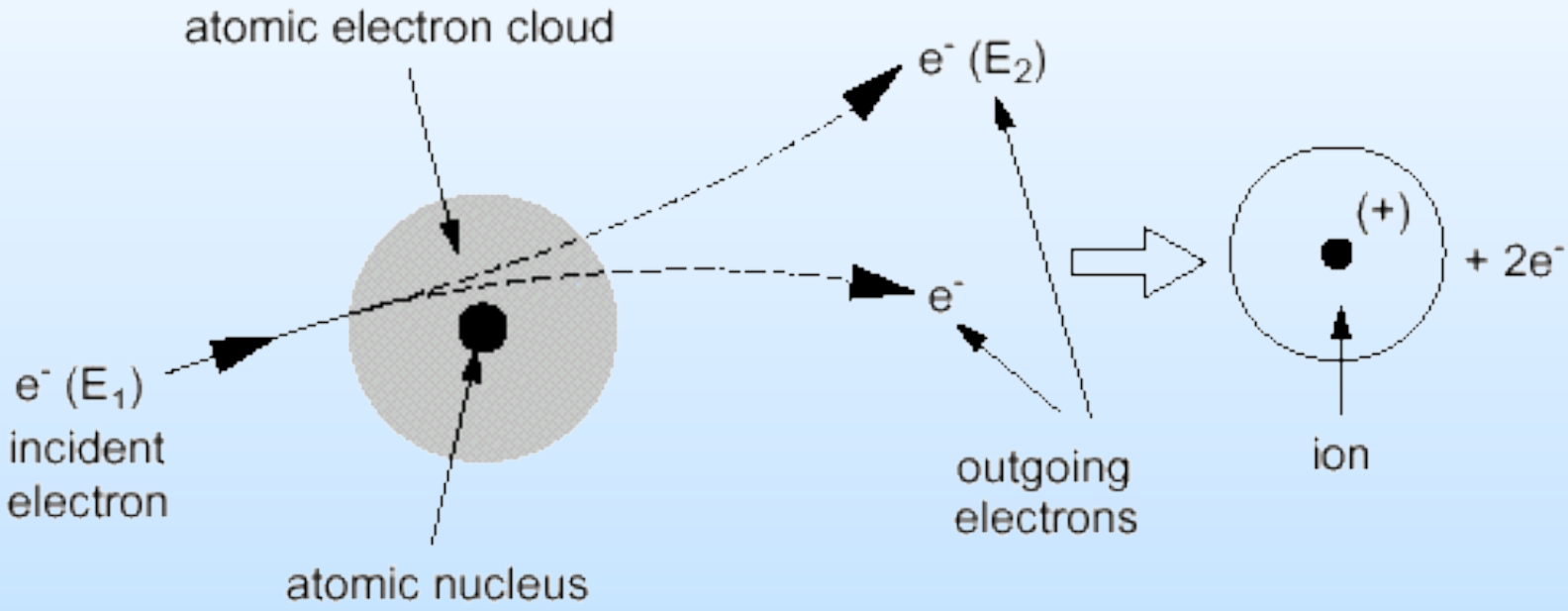
EI is a 'hard' ionization method.

While it yields structural information via fragmentation, at times the fragmentation can be too extensive.

This is especially true as our molecules become larger.

The molecular ion can be difficult or impossible to find.

Electron Impact vs. Electron ionization (EI??)



Ion Nomenclature

Positive ion

An atom, radical, or molecule, may lose one or more electrons to leave a residual positive charge. Alternatively, a positive ion results from the attachment of an existing positive ion to a neutral species.

$$A \rightarrow A^+ + e^-$$
$$A + X^+ \rightarrow AX^+$$

Negative ion

An atom, radical, or molecule, may gain one or more electrons, so as to give a negatively charged species. Alternatively, a negative ion can result from interaction with other negative ions.

$$A + e^- \rightarrow A^-$$
$$A + X^- \rightarrow AX^-$$

Dimeric ion

An ion formed either when a chemical species exists in the vapor phase as a dimer and can be detected as such, or when a molecular ion can attach to a neutral molecule within the ion source to form an ion such as $[2M]^{+\cdot}$,where M represents the molecule.

Rearrangement ion

An electrically charged dissociation product, of a molecular or fragment ion, in which atoms or groups of atoms have transferred from one part of the molecule to another before or during the fragmentation process.

$$XYZ^+ \rightarrow [XZY^+] \rightarrow XZ^+ + Y$$

Ion Nomenclature

Protonated molecule

An ion formed by interaction of a molecule with a proton, which may be abstracted from an ion. Such a process occurs in chemical ionization, according to the reaction:

$$M + XH^+ \rightarrow MH^+ + X \quad \text{or } [M+H]^+$$

Adduct ion

An ion formed by interaction of two species, an ion and one or more molecules, and often within the ion source, to form an ion containing all the constituent atoms of one species as well as an additional atom or atoms:

$$3M + XY^+ \rightarrow [3M + Y]^+ + X \quad Y= H, Na, Li, NH4 \text{ etc.}$$

Cluster ion

An ion formed by the combination of two or more molecules of a chemical species, often in association, with a second species. For example, $[nH_2O+H]^+$ is a cluster ion. Cluster ions are extensions of adduct ions.