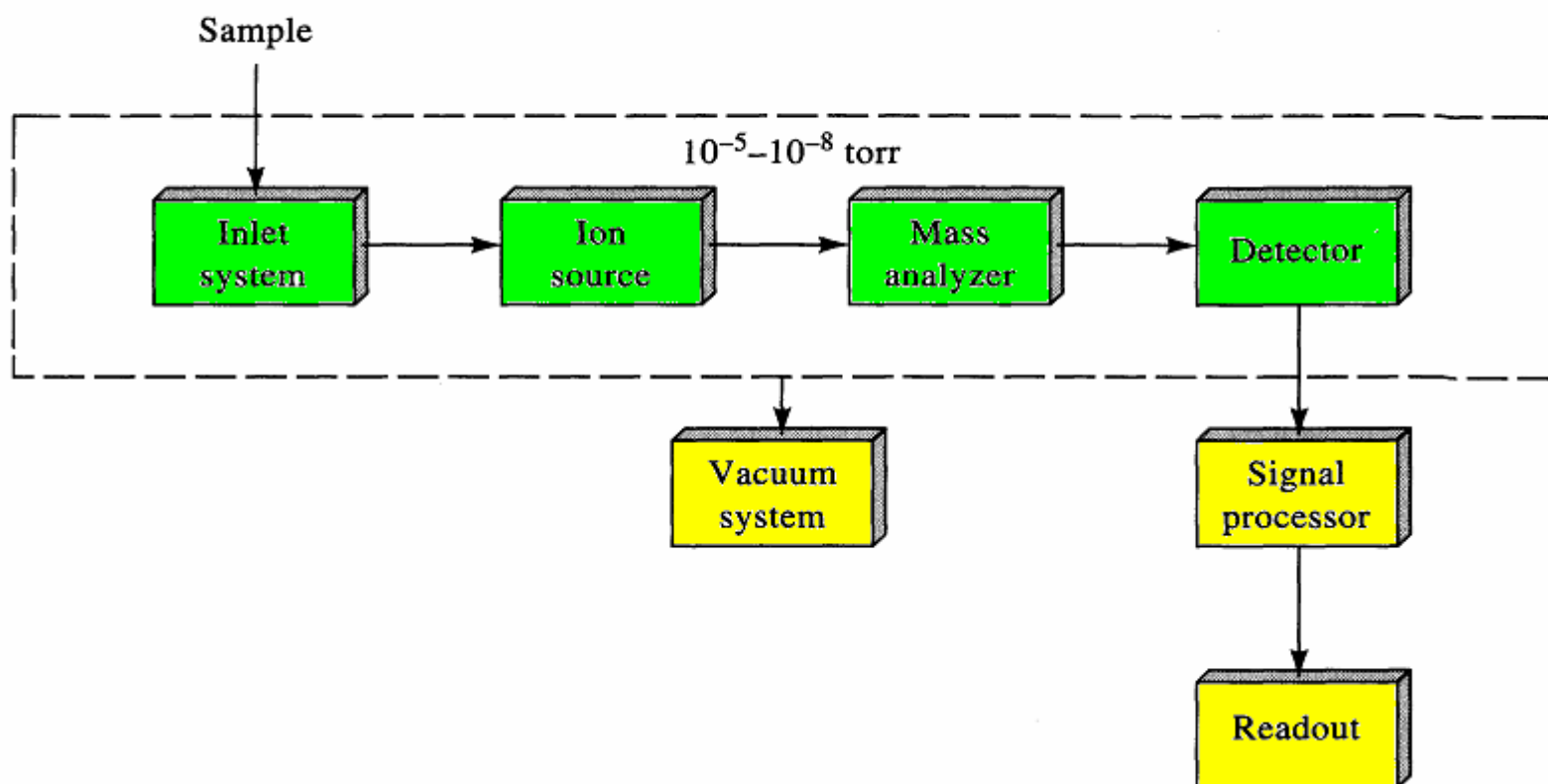


# Simplified Components of MS



# Sample Ionization Mechanisms



# Ionization??

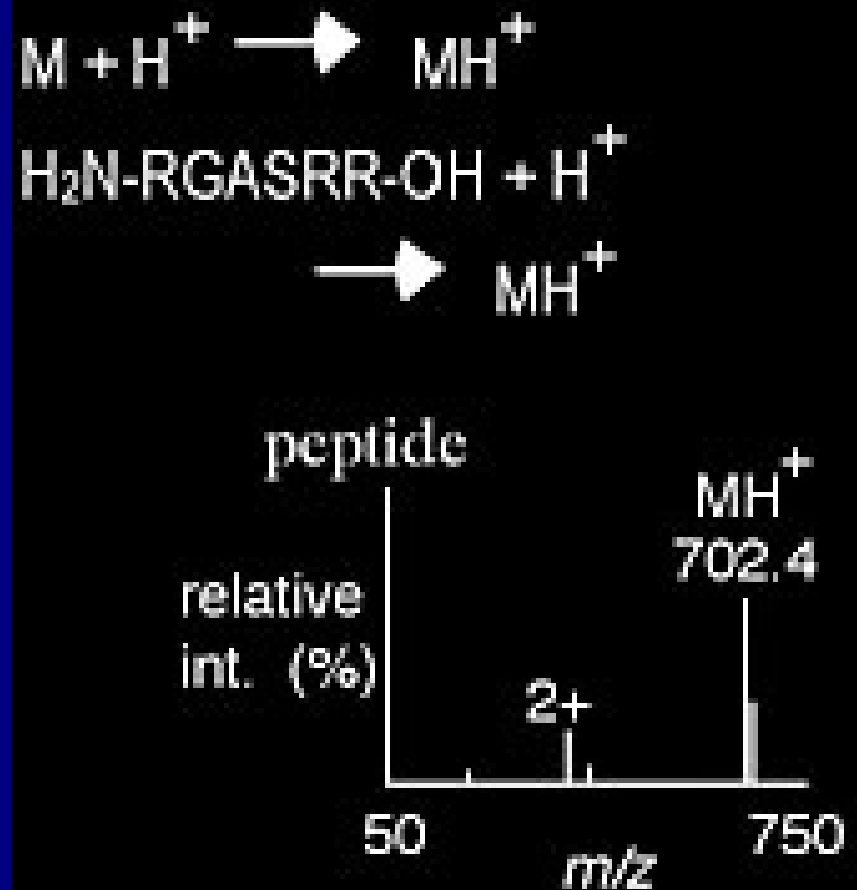
Increasing energy  
content in ion



# Ionization Method I: Protonation

• **Protonation** is a method of ionization by which a proton is added to a molecule, producing a net positive charge of 1+ for every proton added.

• MALDI, ESI, FAB and APCI

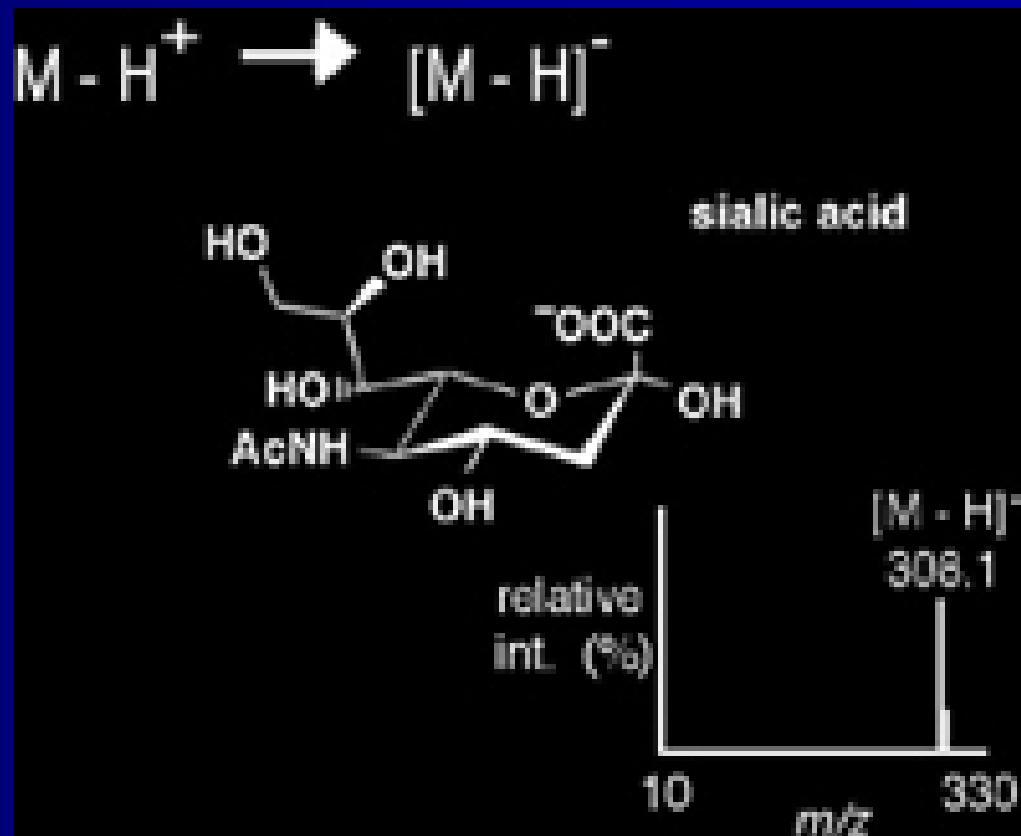


# Ionization Method II: Deprotonation

- **Deprotonation** is an ionization method by which the net negative charge of 1- is achieved through the removal of a proton from a molecule.

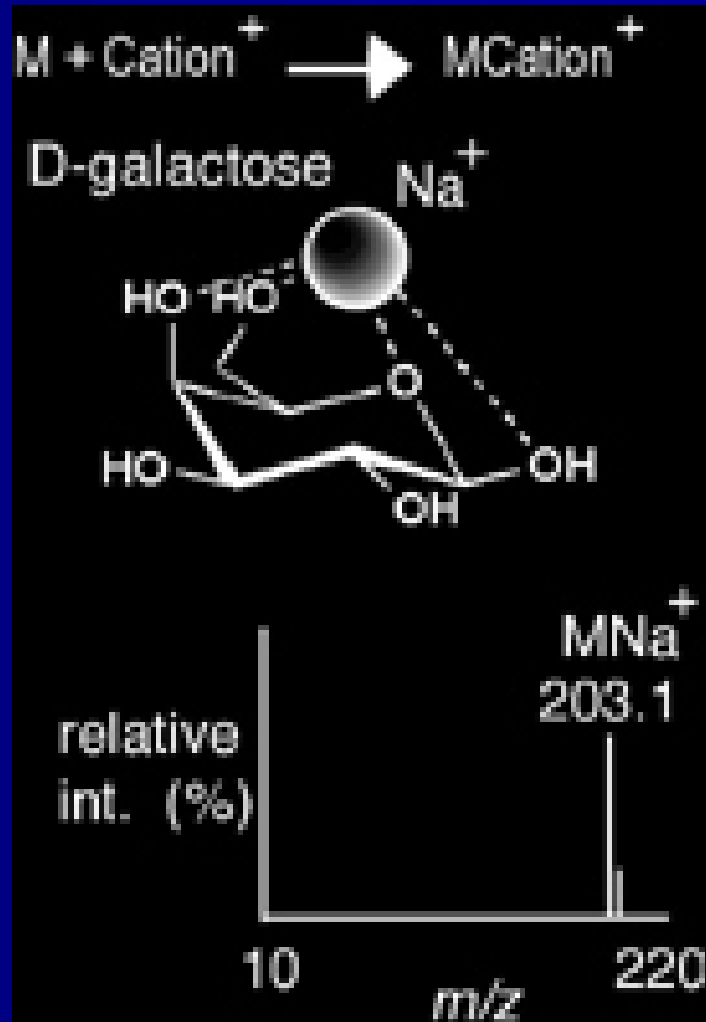
- MALDI, ESI, FAB, and APCI

- Useful for acidic species including phenols, carboxylic acids, and sulfonic acids.



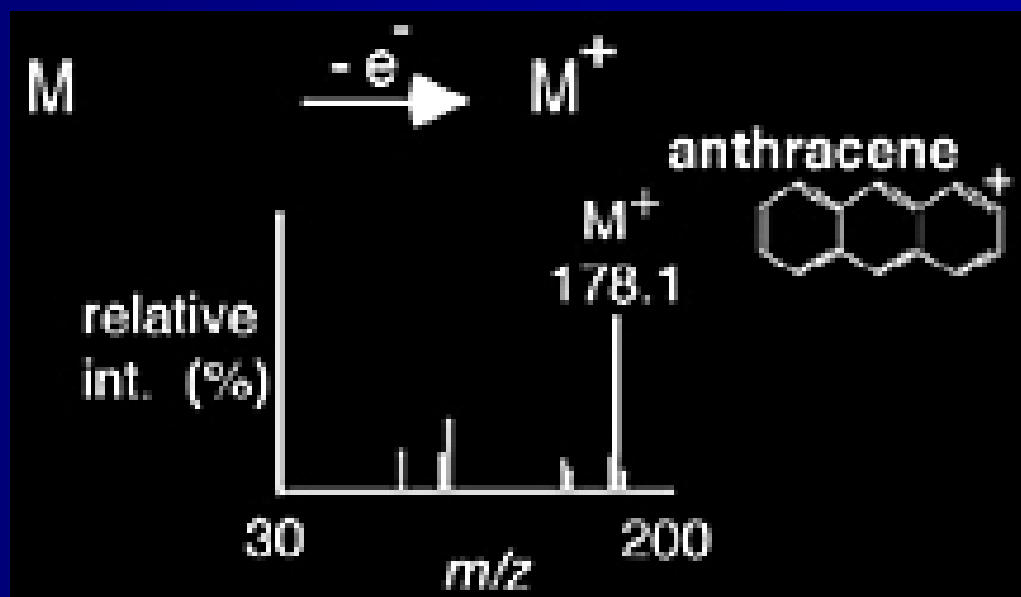
# Ionization Method III: Cationization

- **Cationization** is a method of ionization that produces a charged complex by non-covalently adding a positively charged ion to a neutral molecule: (e.g. alkali, ammonium).
- Useful with molecules unstable to protonation. The binding of cations other than protons to a molecule is naturally less covalent, therefore, the charge remains localized on the cation. This minimizes delocalization of the charge and fragmentation of the molecule.
- MALDI, ESI, FAB and APCI
- Carbohydrates are excellent candidates for this ionization mechanism, with  $\text{Na}^+$  a common cation adduct.



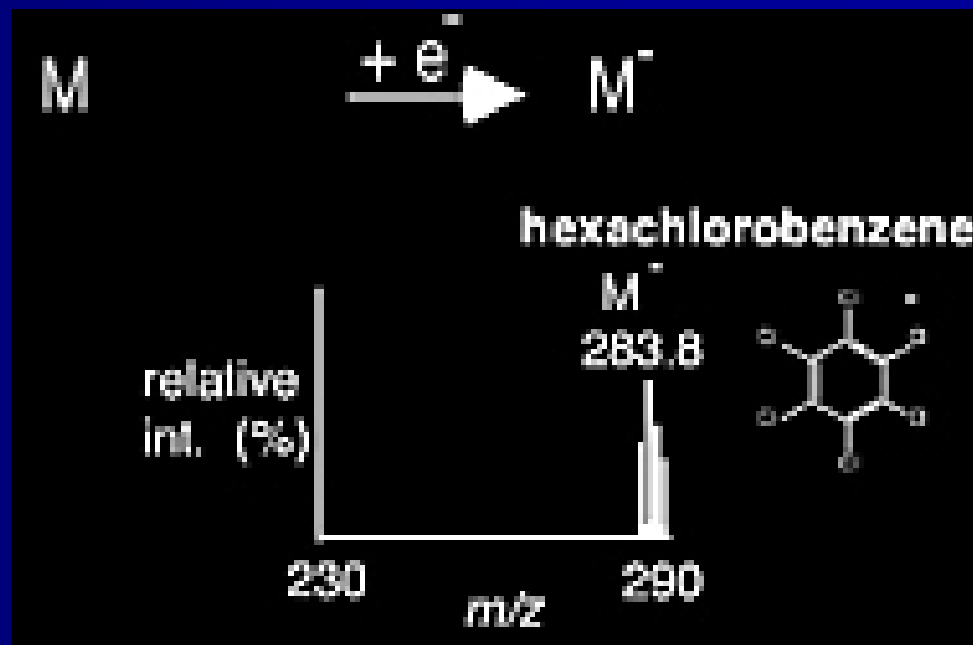
# Ionization Method IV: Electron Ejection

- Electron ejection achieves ionization through the ejection of an electron to produce a 1+ net positive charge, often forming radical cations.
- Electron ionization (EI)
- Usually performed on relatively nonpolar compounds with low molecular weights
- Generate significant fragment ions



# Ionization Method V: Electron Capture

- A net negative charge of 1- is achieved with the absorption or capture of an electron.
- It is a mechanism of ionization primarily observed for molecules with a high electron affinity, such as halogenated compounds.





# **Ionization Techniques**

- **Electrospray Ionization (ESI)**
- **MALDI**
- **Atmospheric Pressure Chemical Ionization (APCI)**
- **Direct Analysis in Real Time (DART)**
- **Electron Ionization (EI)**
- **Chemical Ionization (CI)**
- **Fast Atom Bombardment (FAB)**