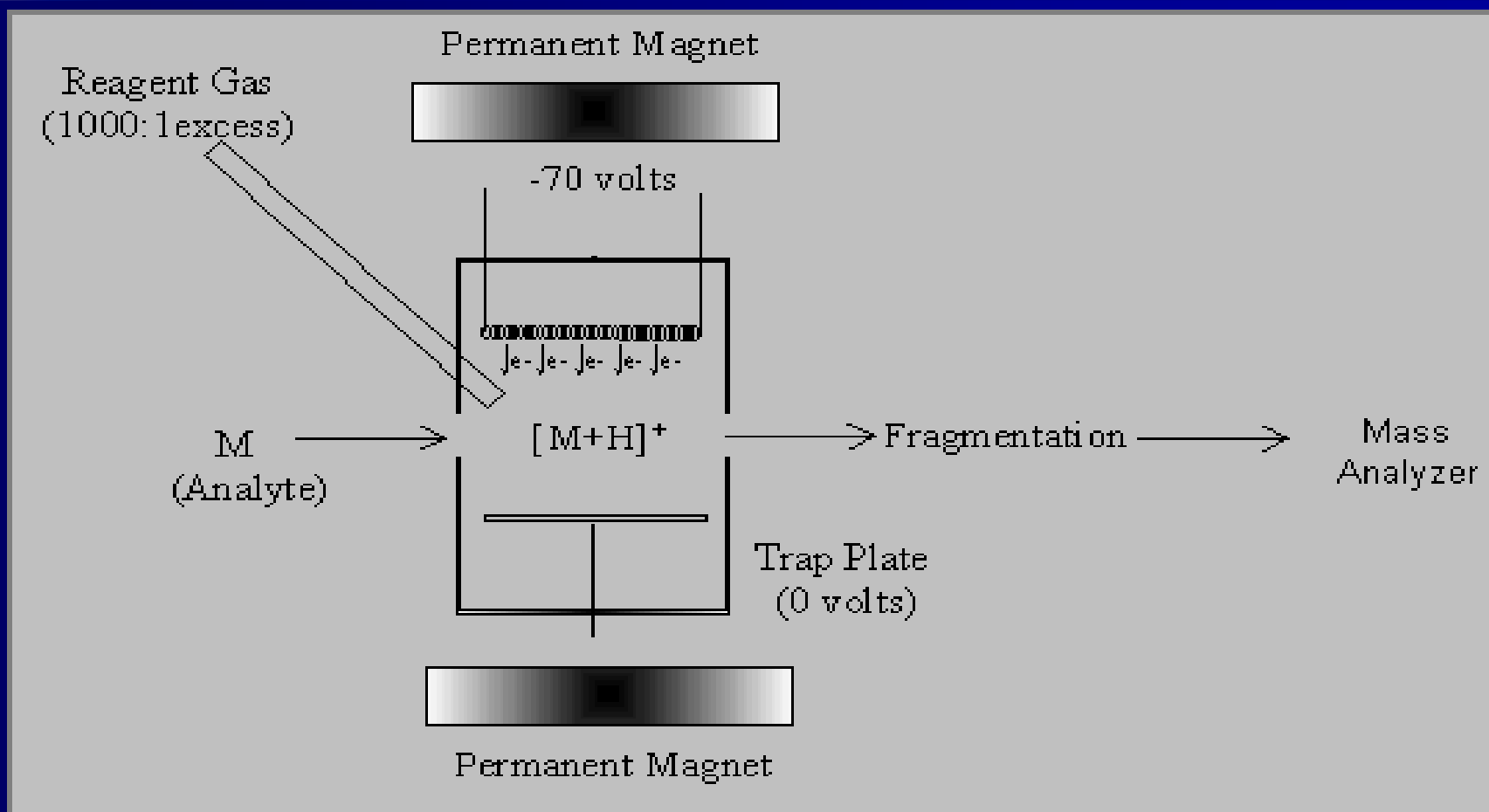


# Chemical Ionization (CI)

# Chemical Ionization (CI)



# Chemical Ionization (CI)

- Involves ionization of a gas molecule ( $\text{CH}_4$ ) to protonate the analyte (at pressures of 1 Torr)
- Ionizing gas usually present at concentrations  $10^3$ - $10^4$  times the analyte molecules
- Ionized by an electron beam
- $\text{CH}_4$  produces ions from analyte molecule by  $\text{H}^+$  or  $\text{H}^-$  transfer
- Other gases used are  $\text{NH}_3$ , iso- $\text{C}_4\text{H}_{10}$
- Soft Ionization Technique
- Is an especially useful technique when no molecular ion is observed in EI mass spectrum
- Produces molecular ions  $[\text{M}+\text{H}]^+$  called quasimolecular ions (diff from  $\text{M}^+$ )

## +ve Ion CI

### Ionizing gas : Methane

- $\text{CH}_4 + e \text{ -----} \rightarrow \text{CH}_4^{+\cdot} + 2e \text{ -----} \rightarrow \text{CH}_3^+ + \text{H}\cdot$
- $\text{CH}_4^{+\cdot} + \text{CH}_4 \text{ -----} \rightarrow \text{CH}_5^+ + \text{CH}_3\cdot$
- $\text{CH}_4^{+\cdot} + \text{CH}_4 \text{ -----} \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 + \text{H}\cdot$

In methane positive ion mode CI, the relevant peak observed are  $\text{MH}^+$ ,  $[\text{M}+\text{CH}_5]^+$ , and  $[\text{M}+\text{C}_2\text{H}_5]^+$ ; but mainly  $\text{MH}^+$

## +ve Ion CI

**Ionizing gas: Isobutane**



**In isobutane positive ion mode CI, the main peak observed is  $\text{MH}^+$**

## +ve Ion CI

### Ionizing gas: Ammonia

- $\text{NH}_3 + e \rightarrow \text{NH}_3^{\cdot+} + 2e$
- $\text{NH}_3^{\cdot+} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^{\cdot}$
- $\text{NH}_4^+ + \text{NH}_3 \rightarrow \text{N}_2\text{H}_7^+$

In ammonia positive ion mode CI, the main peaks observed are  $\text{MH}^+$  and  $[\text{M}+\text{NH}_4]^+$

## CI (contd...)

- Ions have less tendency to fragment
- High sensitivity can be achieved
- Can be used in direct probe as well as interfaced

# Plus and Minus of CI

## Advantages:

- Parent ion is obtd
- Interface to GC
- Insoluble samples

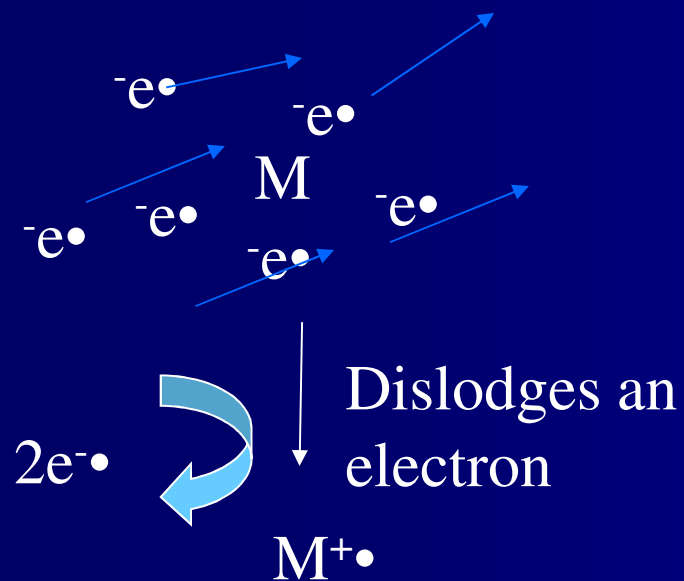
## Disadvantages:

- No fragment library
- Need volatile samples
- Need thermal stability
- Low mass compounds (<1000DA)
- Picomolar samples

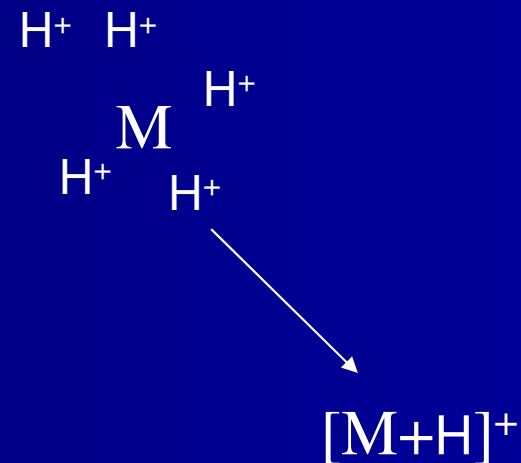


# Molecular Ions Tell Us The Molecular Mass

Electron Impact

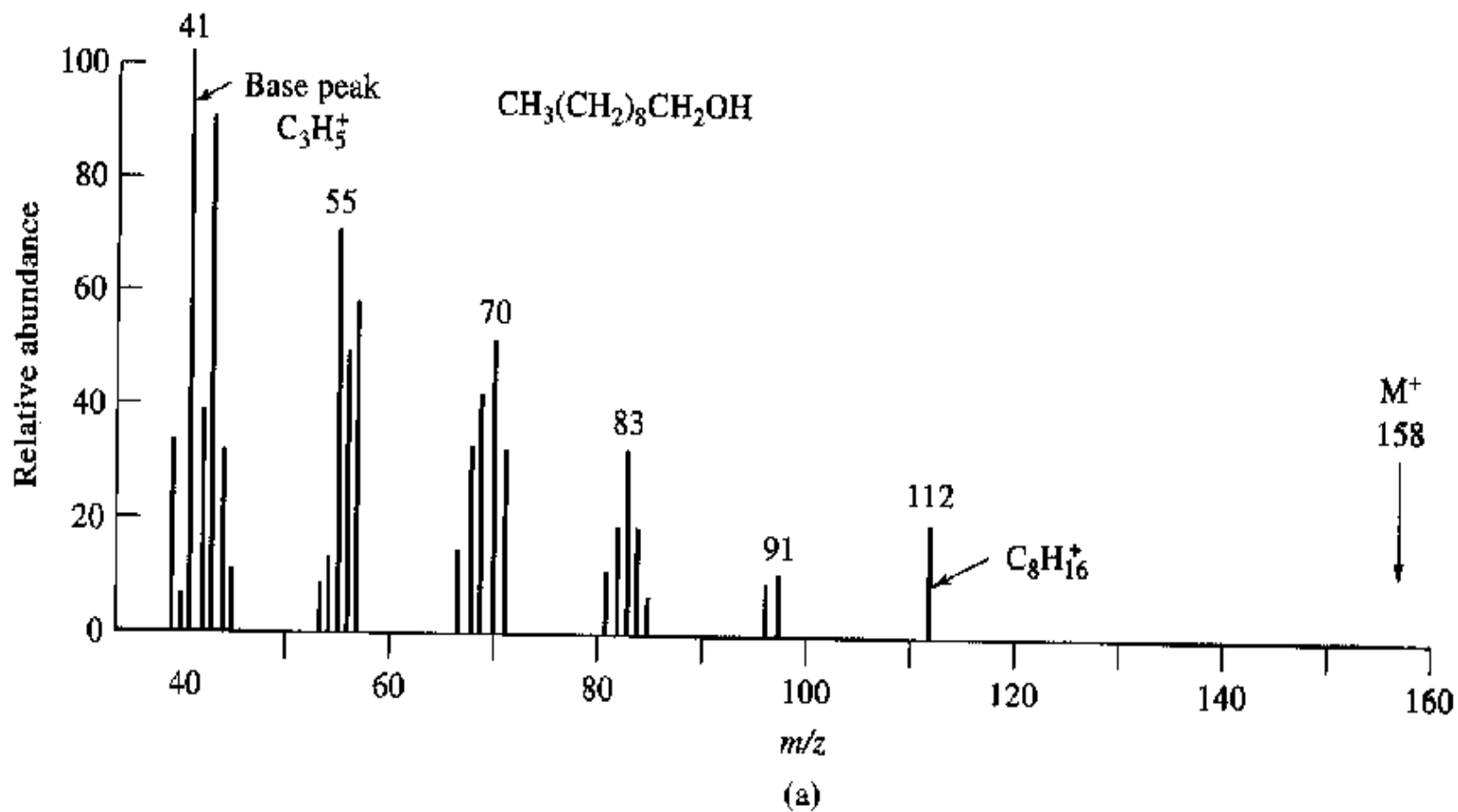


Chemical Ionization



Weighs *one more* than MW

# EI Spectra of 1-Decanol: More Fragmentation — Hard Ionization



# CI Spectra of 1-Decanol: Simpler Spectra — Soft Ionization

