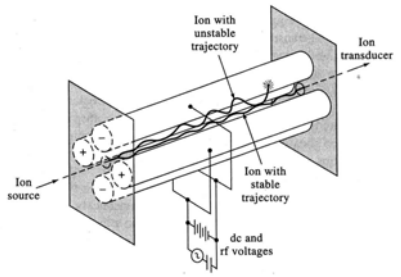
April 15, 2005

- **Website updates!**
  - ✓Prob Set Solutions
  - ✓Exam #3 Info Page
- **Review Session:** Monday, 5 pm, B203
- **Exam #3:** Wednesday, 7 pm, B104
- **Office Hours: Cancelled for today ☹**

Quadrupole Mass Analyzers

- Based on *path stability* of ions in an oscillating electric field:



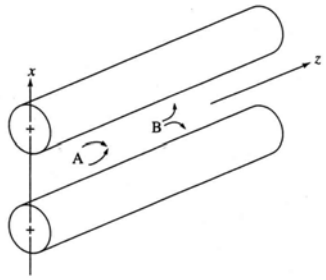
How do they work?

DC Potential:

-affects ALL ions (indep of mass)

AC Potential:

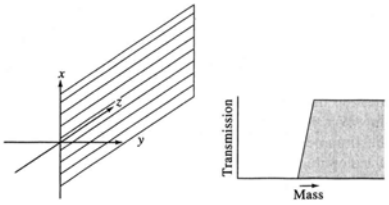
-affects LIGHT ions



First BiPole Pair: Pos. DC

•+ DC potential
repels ALL ions

•AC (rf) potential
attracts light ions

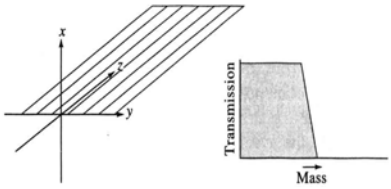


High Mass Pass Filter

Second BiPole Pair: Neg. DC

•- DC potential
attracts ALL ions

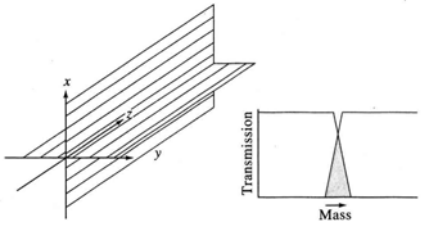
•AC (rf) potential
repels light ions



Low Mass Pass Filter

Putting it all together

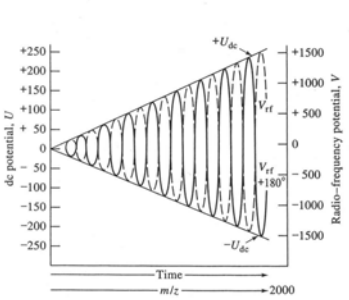
Combo of the two filters results in transmission of only a narrow range of masses:



- *Variable mass filter*
- Mass and mass range vary with ac and dc potentials

Scanning a Quad

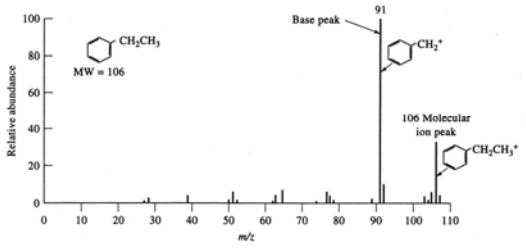
- **Resolution:**
  - -controlled by ac/dc (max res. at ~6)



Properties of Quad Analyzers

- **Resolution:** up to ~1500
- ***Fast!*** can obtain spectrum in *ms*
- Small, rugged, *cheap*
- Higher ion throughput than magsectors
  - Circular versus slit aperture

A Mass Spectrum



Applications: MW Determination

- Need *pure compound*
- Determine m/z for molecular ion
  - Vary electron gun potential to confirm molecular ion assignment
  - use a milder ionization method (e.g., *Chemical Ionization)*

Chemical Ionization (CI)

- Add a *reagent gas* to the EI source
- *Reagent ion* is formed by interaction with e^- beam
- Analyte is ionized by reaction with the *reagent ion*

- Example:

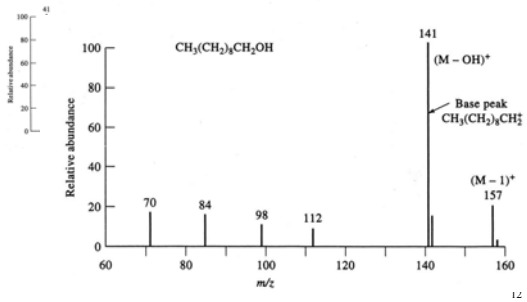
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$

$CH_5^+ + M \rightarrow MH^+ + CH_4$ ***(M+1)⁺ mol ion peak***

$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$

$C_2H_5^+ + M(H) \rightarrow M(-H)^+ + C_2H_6$ ***(M-1)⁺ mol ion peak***

EI versus CI: Decanol



Molecular Formula Determination

- ***Brute Force* Method**
  -get molecular weight from mass spectrum
  -compare MW with MWs of suspected compounds

  BUT, this requires a *high-resolution* mass spectrum . . . not always an available option

- **Isotope Ratio Method**
  -use isotope natural abundances to decipher multiple peaks due to *isotopomers*

Isotope Ratio Method

- Consider CH_4:

  $^{12}CH_4 \rightarrow$ m/z = 16 M (100)

  $^{13}CH_4 \rightarrow$ m/z = 17 M+1 (1.1)

  Relative abundance of ^{13}C = 1.1% of ^{12}C

- Consider Cl_2:

  -Relative abundance of ^{37}Cl = 33% of ^{35}Cl

  -3 possible combos *(isotopomers):*

  $^{35}Cl^{35}Cl$ or $^{35}Cl^{37}Cl$ or $^{37}Cl^{37}Cl$

  (56.5%) (37.3%) (6.2%)

  M (70) M+2 (72) M+4 (74)