Mass Spectrometry

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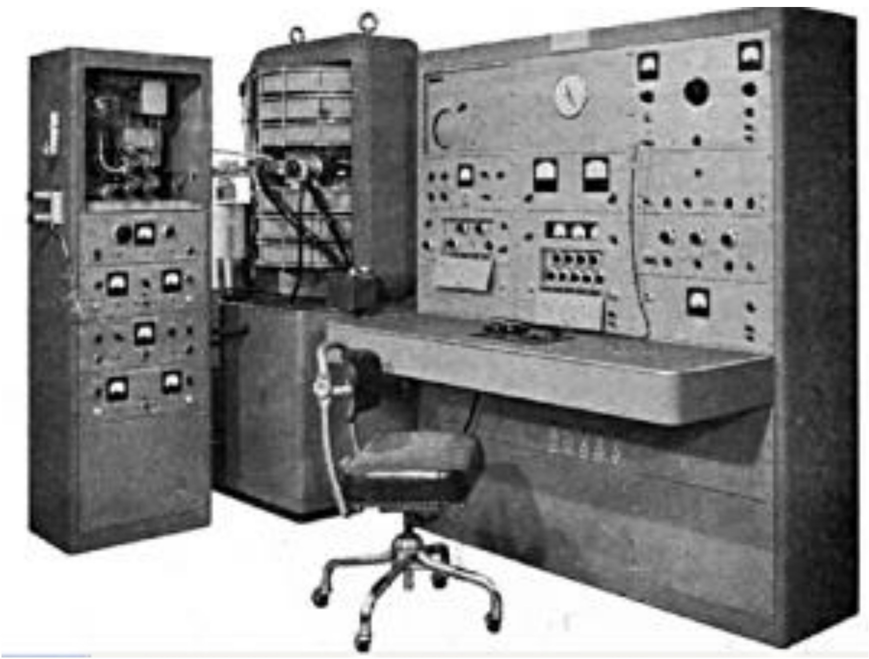
Mass Spectrometry

The mass spectrometers are verified during long years of development from big to compact machines

Old big machine



Compact machine

What are the main features of a Mass Spectrometry

- A key Tool for the chemist’s toolbox.
- The logic is, we always want the ***molecular weight.***
- Second, we can smash out ***fragments*** that are intact structurally
- These are easier to solve and ***relate*** back to the ***starting structure***

Implication is, we don’t get the sample back; a ***destructive*** method

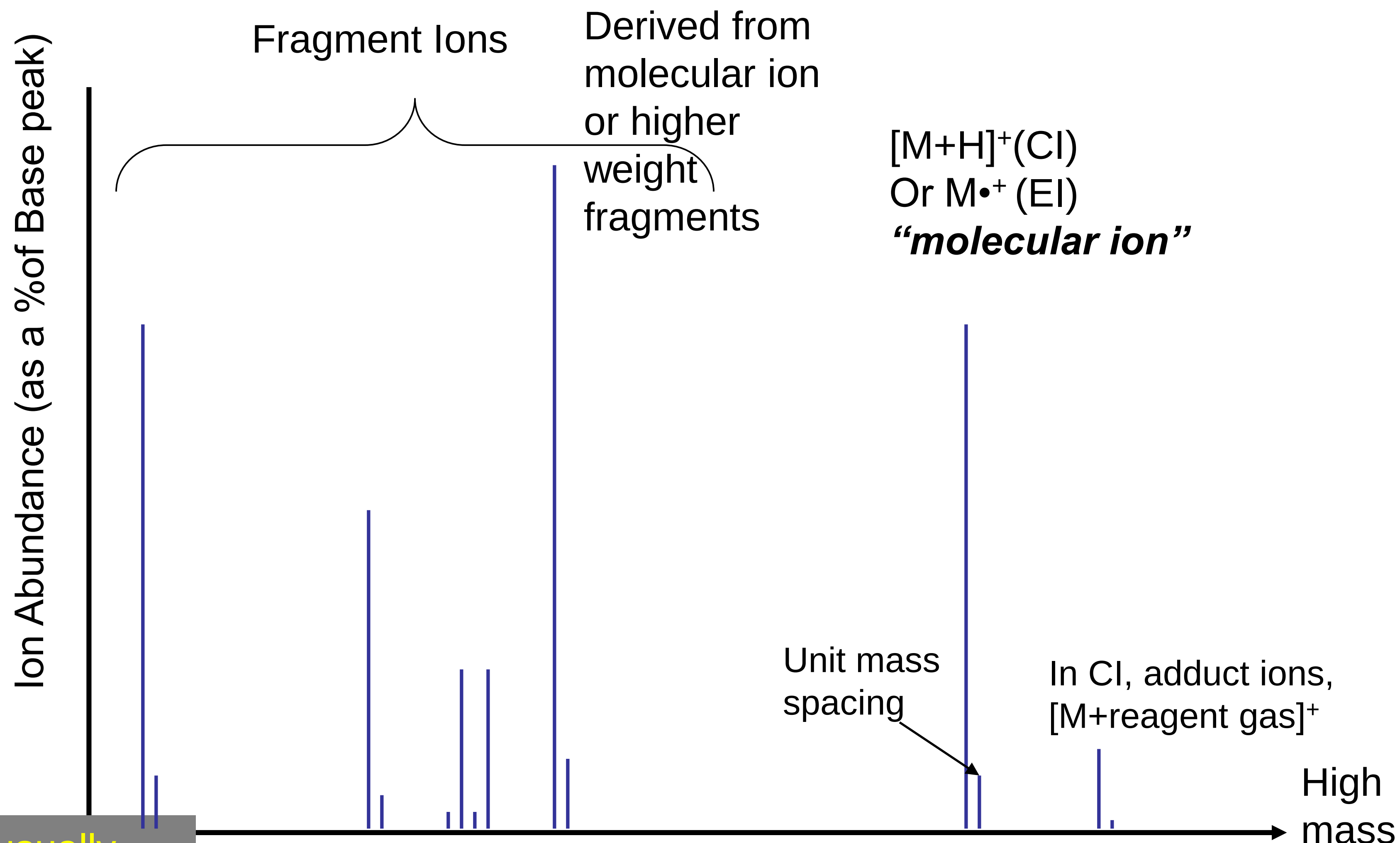
Mass Spectrometry

- A primary tool for chemists from almost every discipline
- Molecular Weights are fundamental to almost every structural question. Molecular weight is not ambiguous. A compound has a unique MW.
- Our ability to analyze compounds on this basis, depends completely on being able to generate ions from the compound. Specifically molecular ions*, whose weight is equal to the MW of the compound, are critical.
- Once produced, our analysis according to MW depends on differential mobility or acceleration of ions proportionate to the MW.

What can a Mass Spectrometer do?

1) A mass spectrometer (MS) is a device which aims to weigh atoms, molecules, cluster, nano-particle, virus, cell and etc. In general, it can only determine mass.
2) Indeed, present mass spectrometers can not even measure mass directly, it can only measure mass-to-charge ratio (M/Z) for a particle in gas phase. For most mass spectrometers, Z is equal to 1 so that mass can be determined.

What's in a Mass Spectrum?

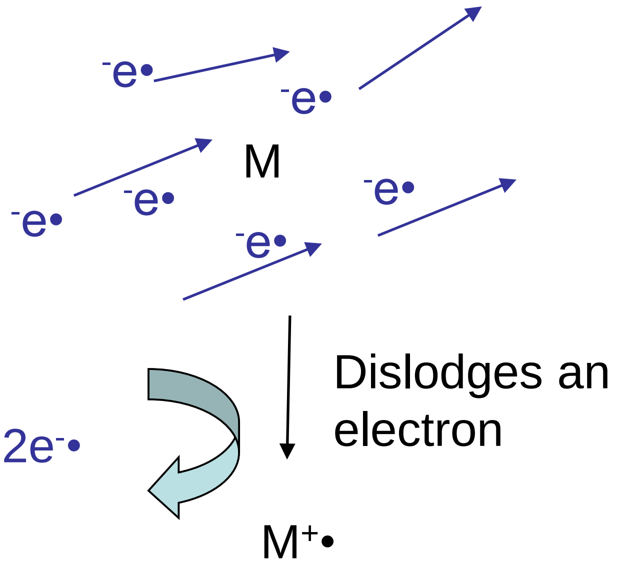


Not usually scanned below m/z=32

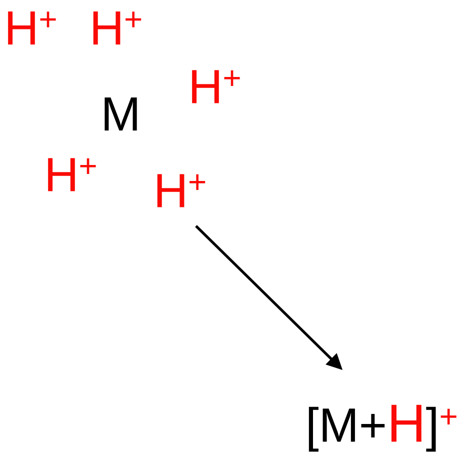
Mass, as ***m/z***. Z is the charge, and for doubly charged ions (often seen in macromolecules), masses show up at half their proper value

Molecular Ions give us the molecular mass

Electron Impact



Chemical Ionization

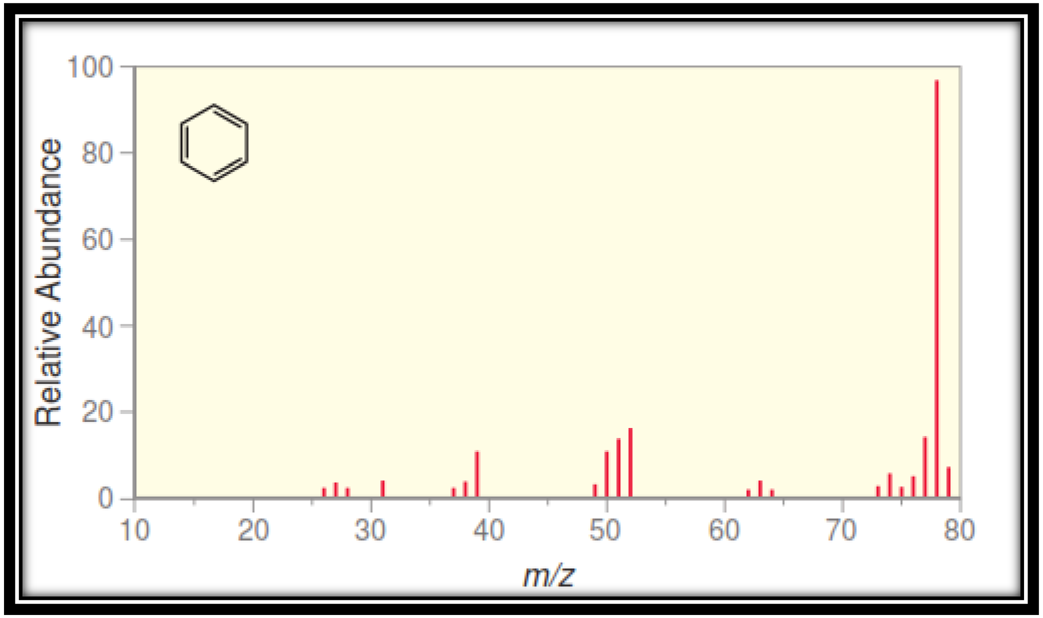


Weighs ***one more*** than MW

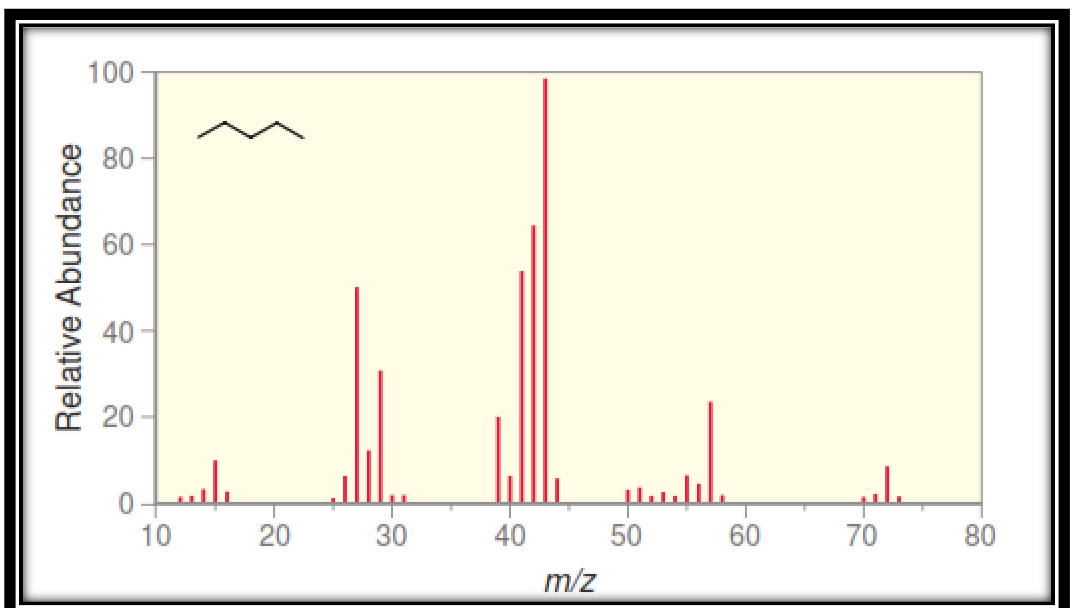
Identifying Molecular Ions

- Potential question; Is the largest m/z the molecular ion or is it a prominent fragment from an even heavier molecule?
- Increase sample loading
- In EI, can lower the beam voltage (make the $M^{\bullet +}$ less energetic, perhaps more long-lived.)
- Logical interval between significant peaks and suspected $M^{\bullet +}$. i.e. the loss of 3-14 mass units is unusual, as is loss of 19-25 (except F). Loss of 33, 35, 38 also unusual. However a loss of 15, 18, 31 is good evidence for a molecular ion.
- Switch to CI, vary reagent gas. Positive, negative probes. Check for CI adduct ions. e.g. $C_2H_5^+$, CH_5^+, $C_3H_5^+$
- Find MW by other method
- Prepare derivative

Other compounds present may give ions that deceive us. May be more detectable. MS intensities are problematic



100
80
60
40
20
0
Relative Abundance
10
20
30
40
50
60
70
80
m/z



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Electron Impact and Chemical Ionization

EI

Sometimes too energetic for molecular ion to survive

Rich harvest of fragment ions

“fingerprint” nature of fragment patterns lends itself to database library searches

CI

Stronger, more reliable molecular ions

Fewer fragments

Can choose different reagent gasses and exploit chemistry, giving different fragmentation. e.g. NH_3/ND_3

Adduct ions give support to identities

Nitrogen rule works but inverted

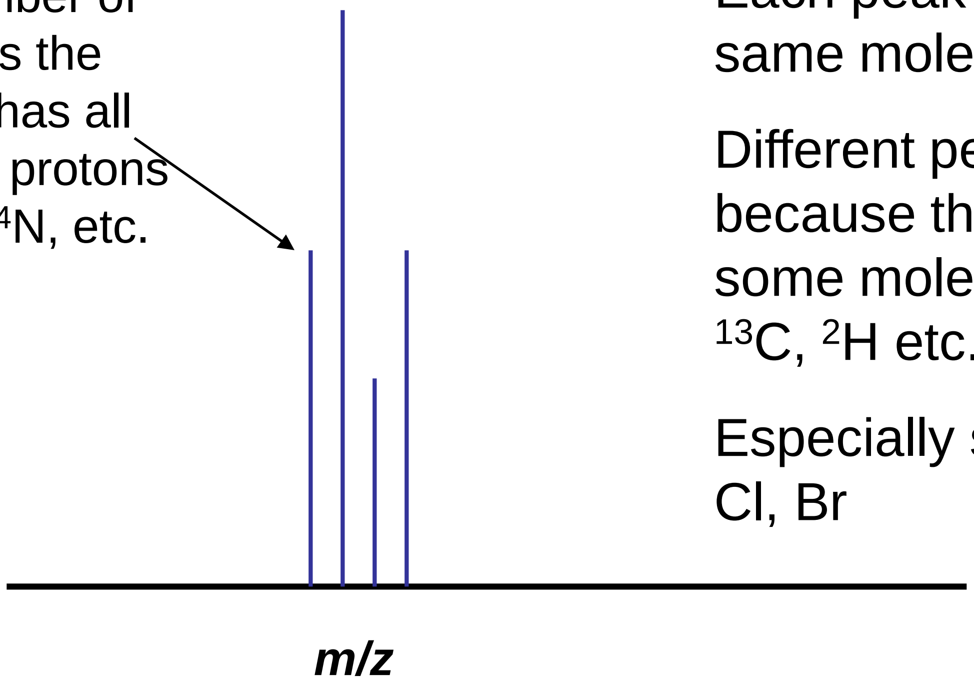
Can do negative ion Mass Spec

EI

CI

Clusters of Ions

The ***Nominal*** mass is m/z of the lowest member of the cluster. This is the ***isotopomer*** that has all the C's as ^{12}C, all protons as ^{1}H, all N's as ^{14}N, etc.



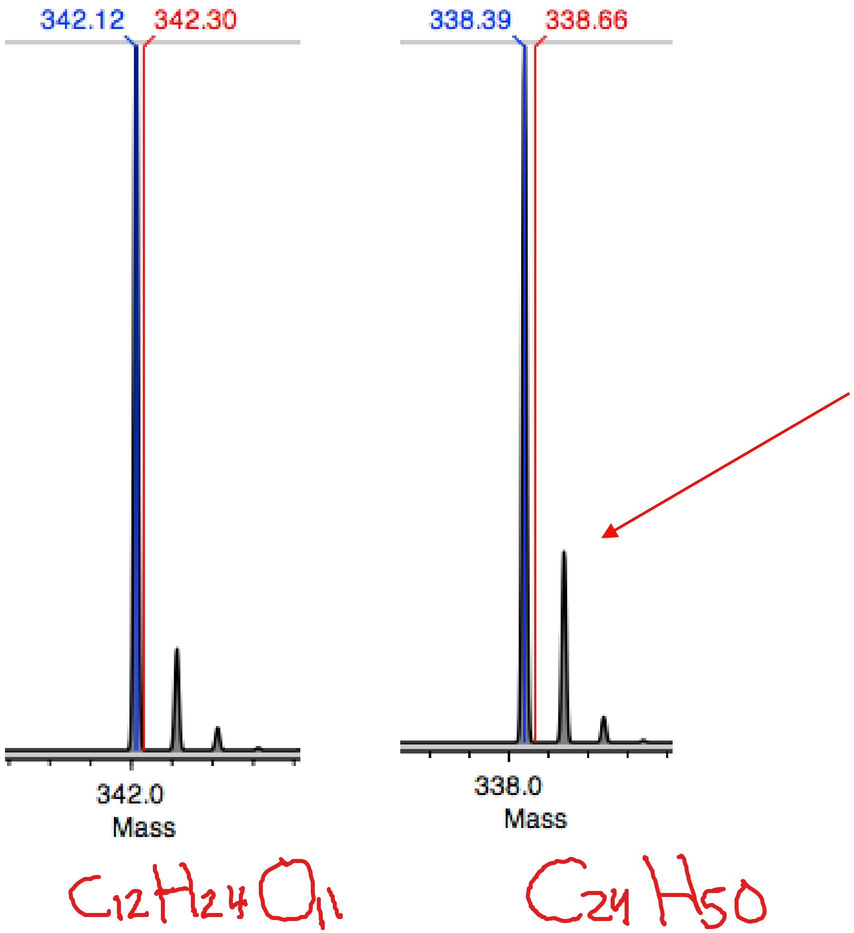
Spaced by unit mass

Each peak is for the same molecular formula

Different peaks because there are some molecules with ^{13}C, ^{2}H etc.

Especially significant for Cl, Br

Isotope Patterns in Ion Clusters



Here are two molecular ions of nearly the same m/z. One of them is “carbon-rich”, and has a larger number of ^{13}C’s

The other, presumably has proportionately, more heteroatoms