

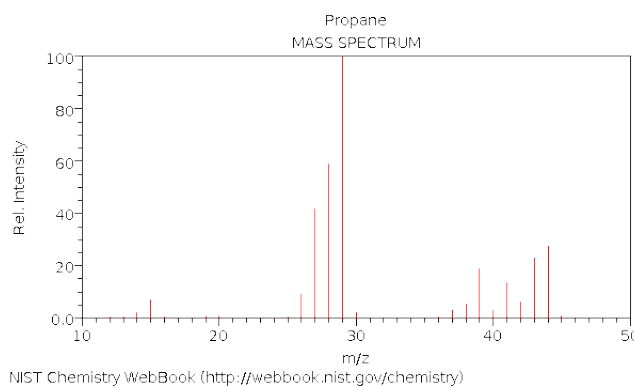
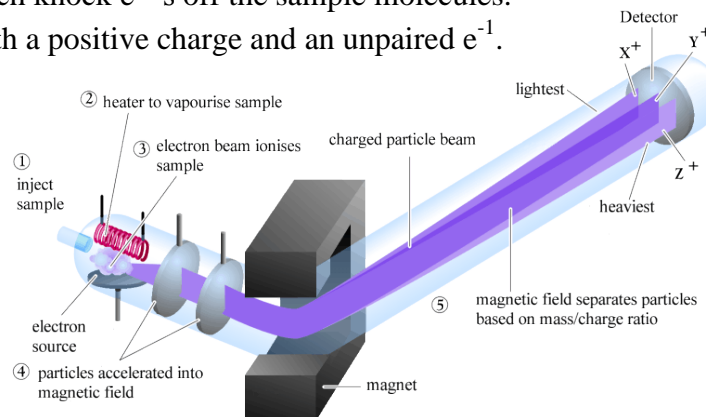
## Ch 12 Structure Determination (Mass Spectroscopy and Infrared)

### Part 1: Mass Spectroscopy

- The sample is bombarded with  $e^{-1}$ 's, which knock  $e^{-1}$ 's off the sample molecules.
- This forms **cation radicals** ( $+•$ ), with both a positive charge and an unpaired  $e^{-1}$ .
- Some of the cations then fragment into smaller cations.
- The cations are sorted by a magnetic field according to their mass to charge ( $m/z$ ) ratios.
- The total number of each cation is counted by a detector.
- The numbers are divided by the number for the most abundant cation detected.
- This converts the counted numbers to **Relative Abundance (%)**.
- A **mass spectrum** plots Relative Abundance on the y-axis versus ( $m/z$ ) on the x-axis.
- The unfragmented cation radical has  $m/z$  equal to the molecular mass for the compound.
- This unfragmented cation is called the **molecular ion** ( $M^+$ ), and its corresponding peak on the mass spectrum is called the **parent peak**.
- The tallest peak (100%) results from the most abundant cation and is called the **base peak**.
- The base peak and parent peak are not necessarily the same.

The parent peak for propane ( $C_3H_8$ ) is at  $m/z = 44$  (same as the MW).

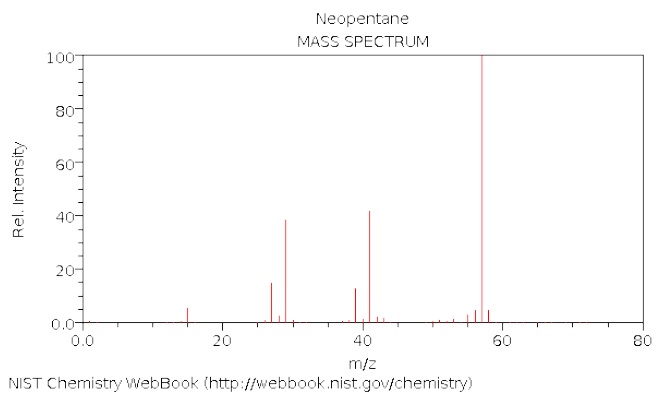
The base peak is at  $m/z = 29$ , because the ethyl cation is the most abundant.



### Molecular Weight (MW) Determination

- A double-focusing mass spec has an  $m/z$  resolution of  $\sim 0.0005$  amu, so that it can distinguish between molecules with similar MW's.
- For instance, the instrument can distinguish between n-pentane ( $C_5H_{12}$ ) and THF ( $C_4H_8O$ ), which both have MW's near 72 **amu** (atomic mass units). But, their MW's are not exactly the same:  
MW = 72.0939 amu for n-pentane and MW = 72.0575 amu for THF.

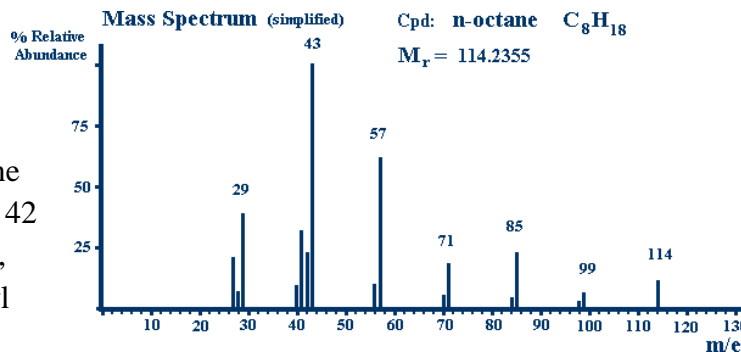
- The mass of a particular molecule cannot be obtained from the atomic masses on the periodic table because the mass depends on which atomic isotopes are present. The mass of the molecular ion will be the sum the exact masses of the most abundant isotopes of its atoms:  
 $^{12}\text{C} = 12.00000 \text{ amu}$ ,  $^{16}\text{O} = 15.99491 \text{ amu}$ , and  $^1\text{H} = 1.00783 \text{ amu}$ .
- Periodic Table masses are **weighted averages** of all isotopes according to their natural abundances. For instance C's atomic weight is 12.011 because natural carbon is 98.9%  $^{12}\text{C}$  and 1.1%  $^{13}\text{C}$ . So,  $(0.989 \times 12.000) + (0.011 \times 13.000) = 12.011$ , as on the periodic table.
- Sometimes, the molecular ion is not present on the spectrum, because it fragments too easily under  $e^{-1}$  bombardment, as is the case with 2,2-dimethylpropane (neopentane). In this case, other (soft) ionization methods can be used, such as chemical ionization (CI), electrospray ionization (ESI), or fast-atom bombardment (FAB).



### Fragmentation Pattern

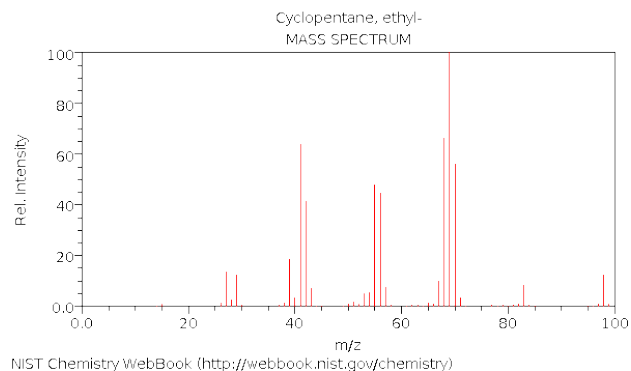
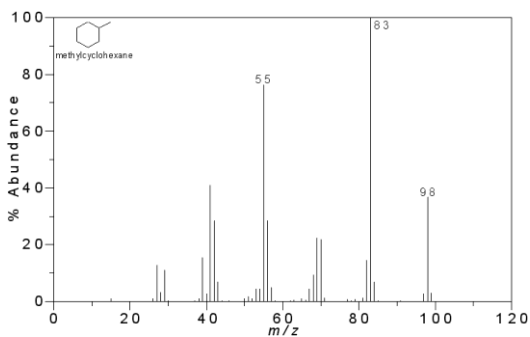
- Unique for each molecule. A spectrum can be compared with a database, such as the *Registry of Mass Spectral Data*, to find the best matches.
- The more abundant cations can be analyzed to find a fragmentation pattern, that is, how the molecule splits into smaller pieces.
- For instance, the mass spectrum of propane ( $\text{C}_3\text{H}_8$ ) on the previous page shows peaks at  $m/z = 44$  and  $m/z = 29$ . The  $m/z = 29$  is ( **$M - 15$** ). This occurs where the molecular ion has lost a methyl group ( $\text{CH}_3$ ), which has a mass of 15 amu.
- When a cation splits into two fragments, one will carry the positive charge and will be detected. The other fragment will not have a charged and will not be detected.
- The positive charge will remain where it is most stabilized, such as on a  $3^\circ$  carbocation.
- For example, the mass spectrum (above) for 2,2-dimethylpropane shows no molecular ion ( $m/z = 72$ ), while the base peak is  $m/z = 57$  (or  $M - 15$ ). The molecule loses one of the four methyl groups very easily because it results in the  $(\text{CH}_3)_3\text{C}^+$  cation, which is a **stable  $3^\circ$  carbocation**.

- As with loss of a methyl creates an  $M-15$  cation, loss of ethyl results in  $M-29$ , loss of propyl results in  $M-43$ , and loss of butyl results in  $M-57$ .
- Note that these cations are 14  $m/z$  units apart, which is the  $m/z$  of each additional  $\text{CH}_2$  unit.
- It is also common to observe alkyl cations, such as methyl ( $m/z = 15$ ), ethyl ( $m/z = 29$ ), propyl ( $m/z = 43$ ), and butyl ( $m/z = 57$ ).
- The mass spectrum (right) for n-octane shows not only  $M-15$ ,  $M-29$ ,  $M-42$  and  $M-57$  from loss of alkyl groups, but also  $m/z = 29$ , 43, and 57 for alkyl cations.



### Distinguishing between similar mass spectra (methylcyclohexane and ethylcyclopentane)

- Each molecule has  $\text{MW} = 98$ , and both spectra show this parent peak.
- Methylcyclohexane loses the methyl group easily, and has its base peak at  $m/z = M-15 = 83$ . This corresponds with spectrum B.
- Ethylcyclopentane loses the ethyl group easily, and has its base peak at  $m/z = M-29 = 69$ . This corresponds with spectrum A.



## Mass Spectrometry of Common Functional Groups

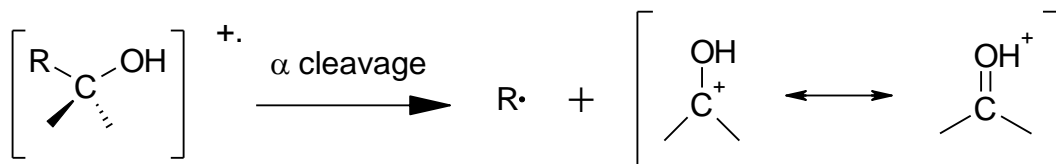
### Alcohols (ROH)

- Alcohols can lose an alkyl group connected to the hydroxyl C.

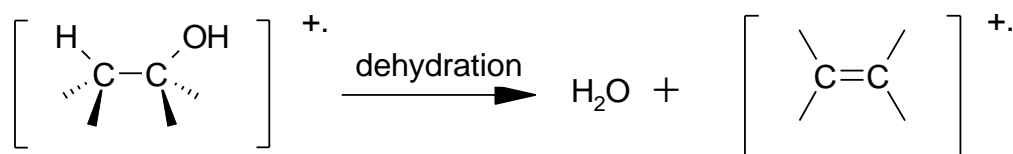
This is called **alpha cleavage**.

The result is  $M - 15$ ,  $M - 29$ ,  $M - 43$ , etc., depending on the size of the alkyl group.

Note that the new cation is stabilized by **resonance** ( $\leftrightarrow$ ).

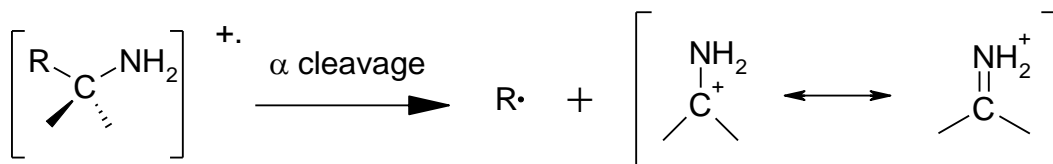


- Alcohols can also undergo **dehydration**, where they lose a water molecule, which results in  $M - 18$ .



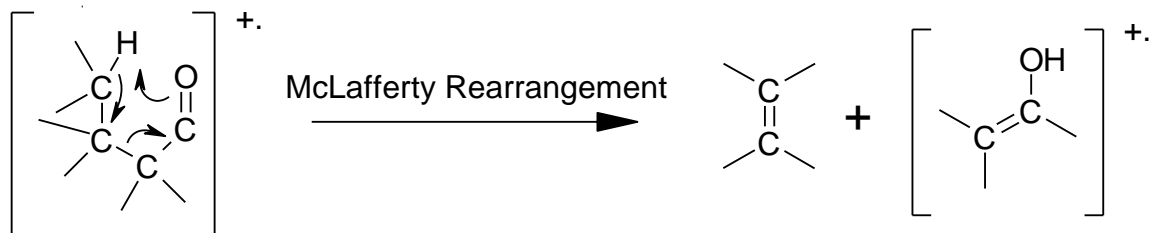
### Amines (RNH<sub>2</sub>)

- Amines can also undergo **alpha cleavage** to obtain  $M - 15$ ,  $M - 29$ ,  $M - 43$ , etc., depending on the size of the alkyl group.



Carbonyl Compounds (contain C=O)

- A carbonyl compound with an H on a C that three C atoms away from the carbonyl C can undergo a **McLafferty rearrangement**, where an alkene molecule, such as C<sub>2</sub>H<sub>4</sub> (ethene), is lost. The result is **M - 28**, **M - 42**, or **M - 56**, depending on the size of the alkene lost.



- Carbonyl Compounds can also undergo **alpha cleavage** to obtain M-15, M-29, M-43, etc., depending on the size of the alkyl group. The result will be a resonance-stabilized **acyl cation**.

