Welcome!!

Chemistry 328N

Organic Chemistry for Chemical Engineers

Professor: Grant Willson

Teaching Assistants: Michael Maher and Garret Blake

http://willson.cm.utexas.edu

Your Teaching Assistants

Michael Maher

Garret Blake

Please take advantage of the scheduled office hours

Bureaucracy:

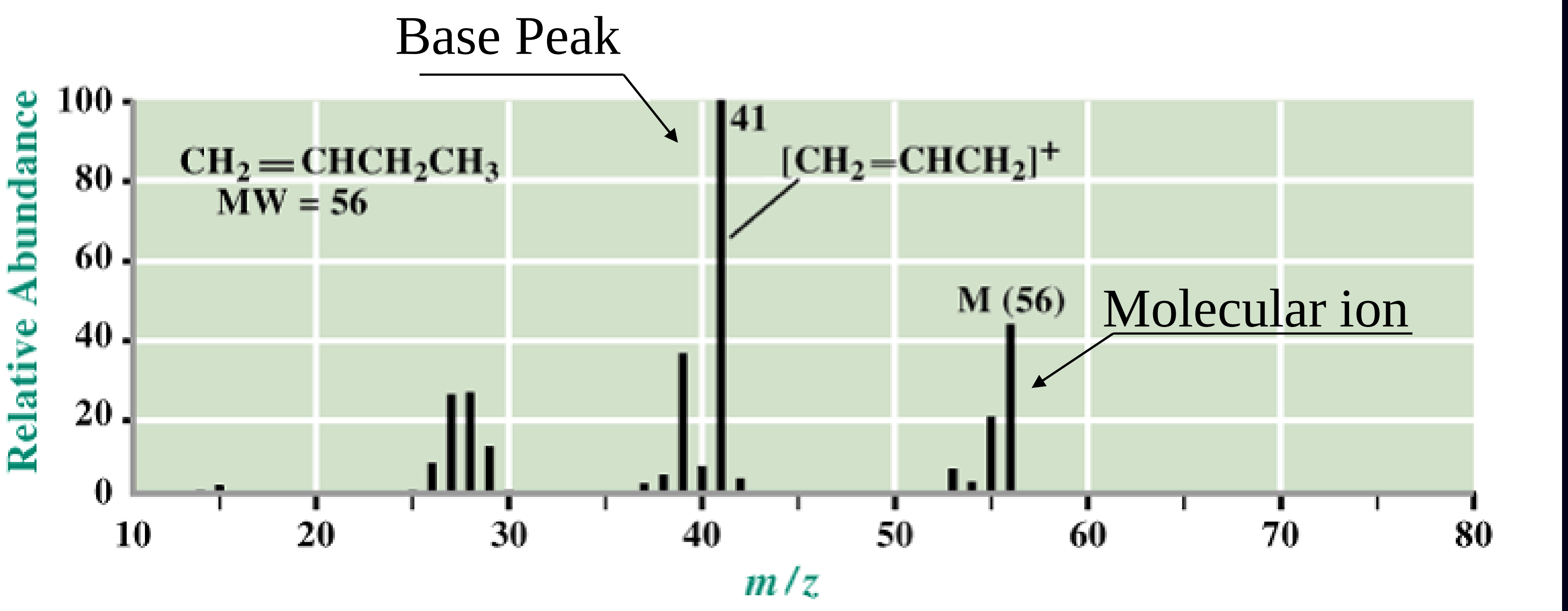
- Please read the syllabus carefully
- Attend all lectures
- Do the homework
- ***Don’t get behind***
- Take advantage of office hours
  - We want to get to know you
- Watch the web page
  - http://willson.cm.utexas.edu (teaching)
- *Keep up with the work!*
- *You can’t “cram” for the exams in this class*
- ***Don’t get behind!!***

Submit Here

WEL 2.246

Collect Here

Mass Spectrometry



A Mass Spectrometer

- A mass spectrometer is designed to do three things:

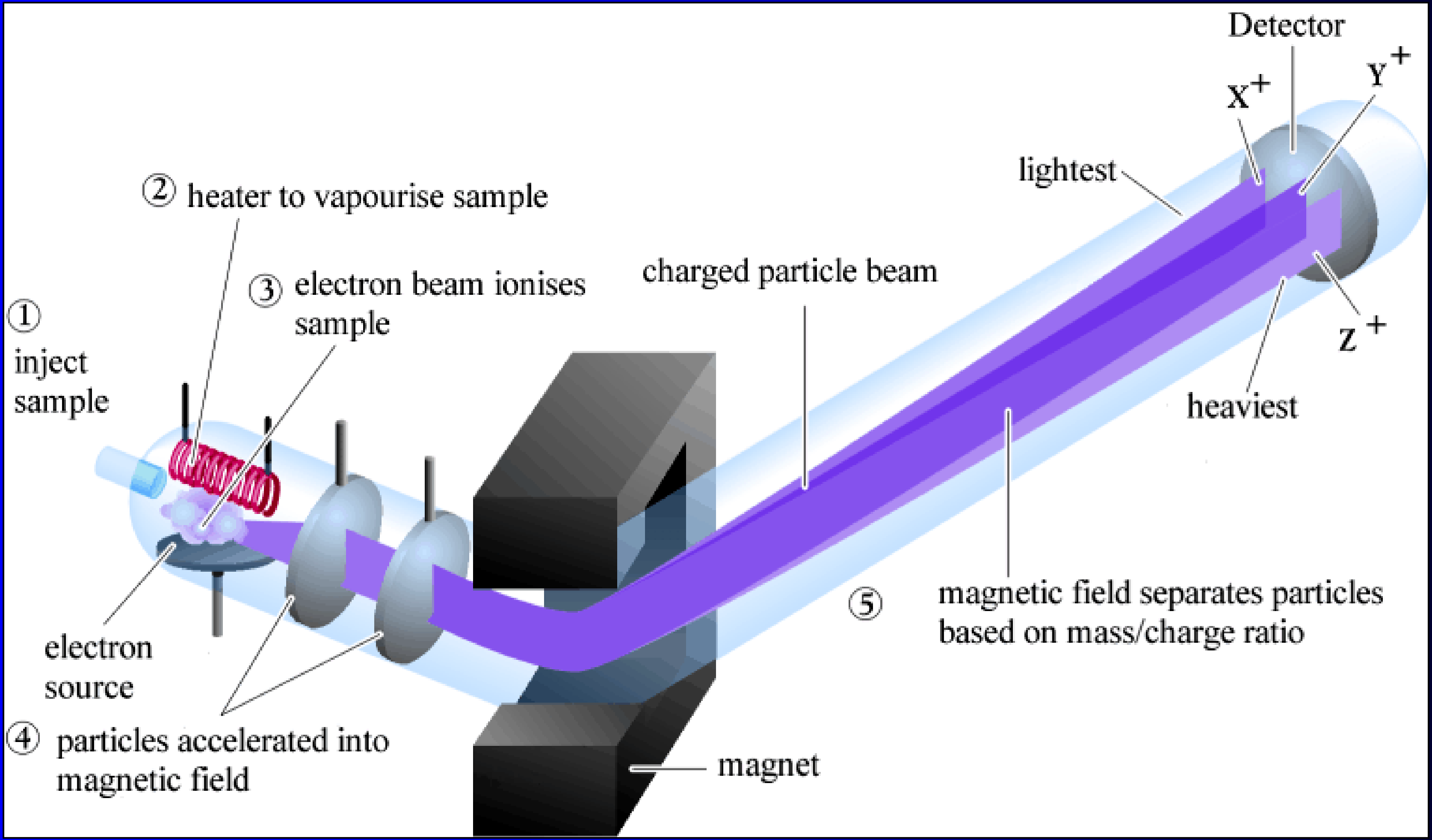
  1. Convert neutral atoms or molecules into a beam of positive (or negative) ions

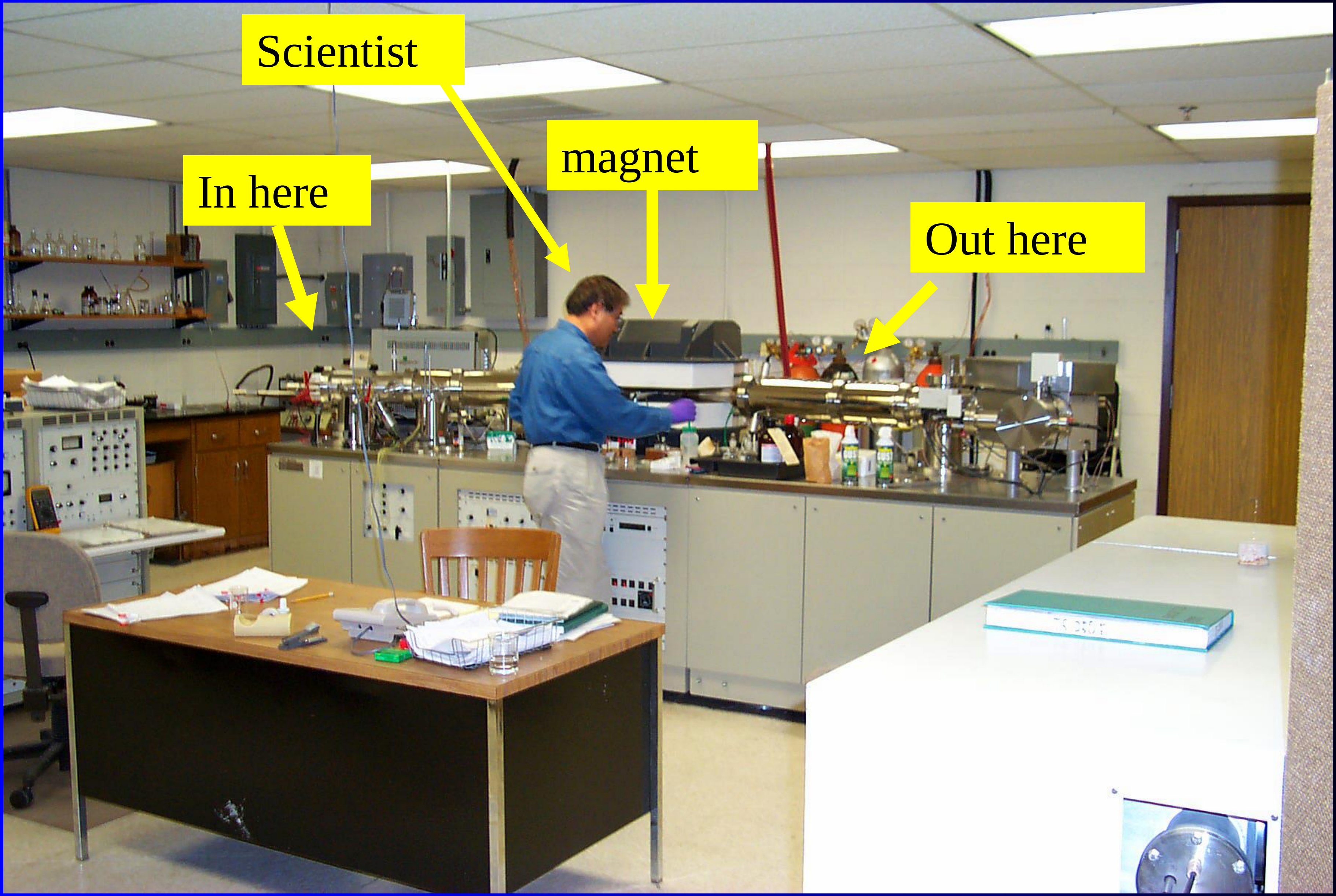
  2. Separate the ions on the basis of their mass-to-charge ratio (m/z)

  3. Measure the relative abundance of each ion

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/MassSpec/masspec1.htm

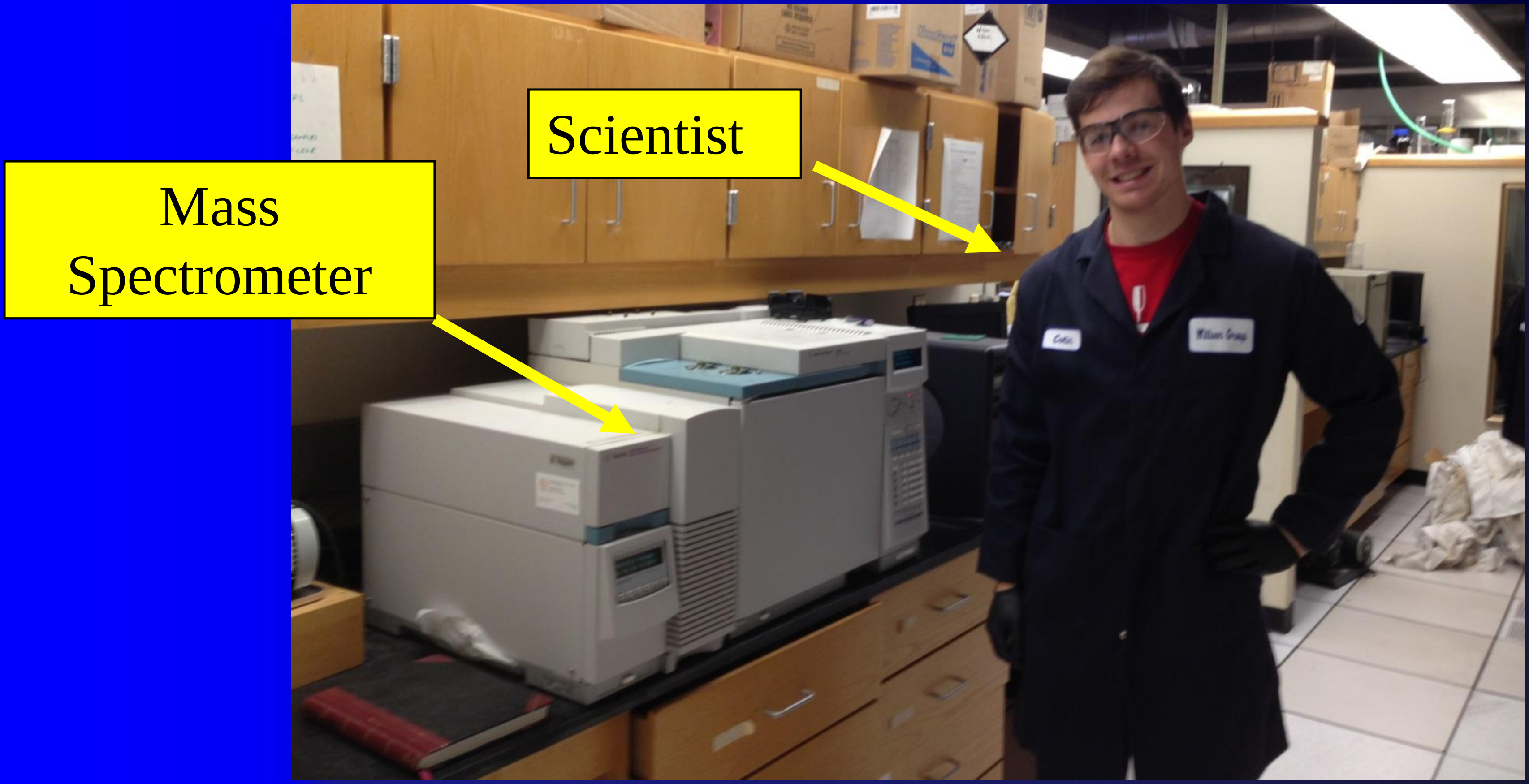
Mass Spectrometer




Scientist
magnet
In here
Out here

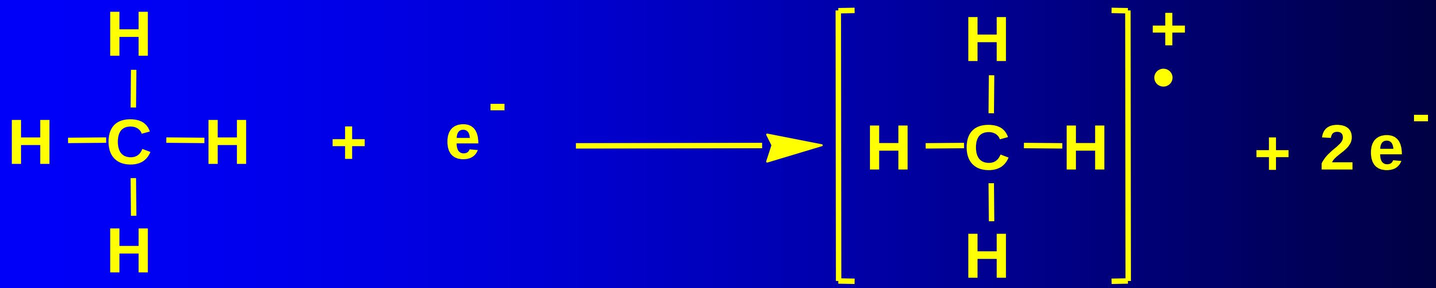
Modern Mass Spectrometer

unit mass resolution



A Mass Spectrometer

- Electron ionization MS
  - In the ionization chamber, the sample is bombarded with a beam of high-energy electrons
  - Collisions between these electrons and the sample result in loss of electrons from sample molecules and formation of positive ions



$$CH_4 + e^- \longrightarrow \left[CH_4\right]^{+\bullet} + 2\,e^-$$

Molecular ion
(A radical cation)

Molecular Ion

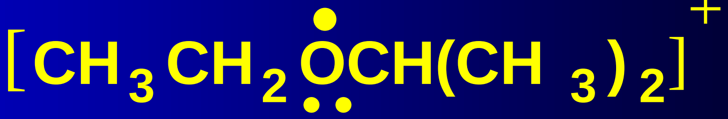
- Molecular ion (M or M^+): the species formed by removal of a single electron from a molecule
- For our purposes, it does not matter which electron is lost; radical cation character is delocalized throughout the molecule. Therefore, we write the molecular formula of the parent molecule in brackets with
  - A plus sign to show that it is a cation
  - A dot to show that it has an odd number of electrons

$$[CH_3CH_2OCH_3]^{+\bullet}$$

Molecular Ion

- At times, however, we find it useful to depict the radical cation at a certain position in order to better understand its reactions

$[CH_3CH_2OCH(CH_3)_2]^{+\bullet}$

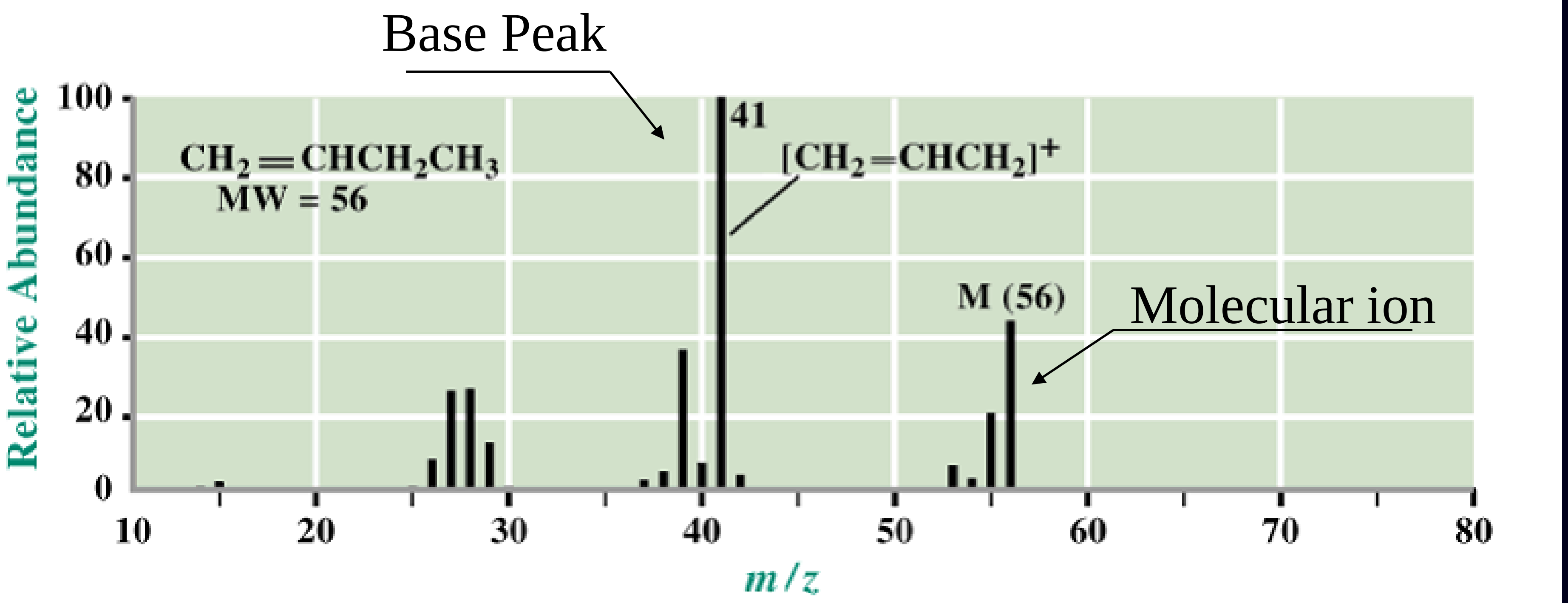


$[CH_3CH_2\overset{\bullet}{\underset{\bullet\,\bullet}{O}}CH(CH_3)_2]^{+}$

Mass Spectrum

- Mass spectrum: a plot of the relative abundance of each ion versus mass-to-charge ratio
- Base peak: the most abundant peak; assigned an arbitrary intensity of 100
- The relative abundance of all other ions is reported as a % of abundance of the base peak

Mass Spectrum of 1-Butene



The Nitrogen Rule

- Nitrogen rule: if a compound has
  - zero or an even number of nitrogen atoms, its molecular ion will have an *even* m/z value
  - an odd number of nitrogen atoms, the molecular ion will have an *odd* m/z value

Other MS Techniques

- What we have described is called electron ionization mass spectrometry (EI MS)

- Other techniques include
  - Fast atom bombardment (FAB)
  - Matrix assisted laser desorption ionization (MALDI)
  - Chemical ionization (CI)
  - And many others….

Resolution

- Resolution: a measure of how well a mass spectrometer separates ions of different mass
  - Low resolution - capable of distinguishing among ions of different nominal mass, that is ions that differ by at least one or more atomic mass units (Daltons)
  - High resolution - capable of distinguishing among ions that differ in mass by as little as 0.0001 mass units

High Resolution Mass Spectrometer

Resolution

- **C_3H_6O and C_3H_8O have nominal masses of 58 and 60 respectively, and can be readily distinguished by low-resolution MS**

- **$C_2H_4O_2$ and C_3H_8O** both have a nominal mass of 60. However, we can still distinguish between them by high-resolution MS

Molecular Formula	Nominal Mass	Precise Mass
C_3H_8O	60	60.05754
$C_2H_4O_2$	60	60.02112

Differences are due to Isotopes

- In nature Carbon is 98.90% ^{12}C and 1.10% ^{13}C. Thus, there are 1.11 atoms of carbon-13 in nature for every 100 atoms of carbon-12…Mass spectroscopists use this measure rather than %!!!!!!

$$\left[\frac{1.10\ ^{13}C}{98.90\ ^{12}C}\right] \times 100\ \ ^{12}C\text{ atoms} \quad = 1.11\ ^{13}C\text{ per }100\ ^{12}C$$

- The **<u>“ relative abundance”</u>** of ^{13}C is defined as 1.11

Precise masses and natural abundances of isotopes

Element	Atomic Weight	Isotope	Precise Mass (amu)	Relative Abundance
hydrogen	1.0079	^{1}H	1.00783	100
		^{2}H	2.01410	0.016
carbon	12.011	^{12}C	12.0000	100
		^{13}C	13.0034	1.11
nitrogen	14.007	^{14}N	14.0031	100
		^{15}N	15.0001	0.38
oxygen	15.999	^{16}O	15.9949	100
		^{17}O	16.9991	0.04
		^{18}O	17.9992	0.20
sulfur	32.066	^{32}S	31.9721	100
		^{33}S	32.9715	0.78
		^{34}S	33.9679	4.40
chlorine	35.453	^{35}Cl	34.9689	100
		^{37}Cl	36.9659	32.5
bromine	79.904	^{79}Br	78.9183	100
		^{81}Br	80.9163	98.0

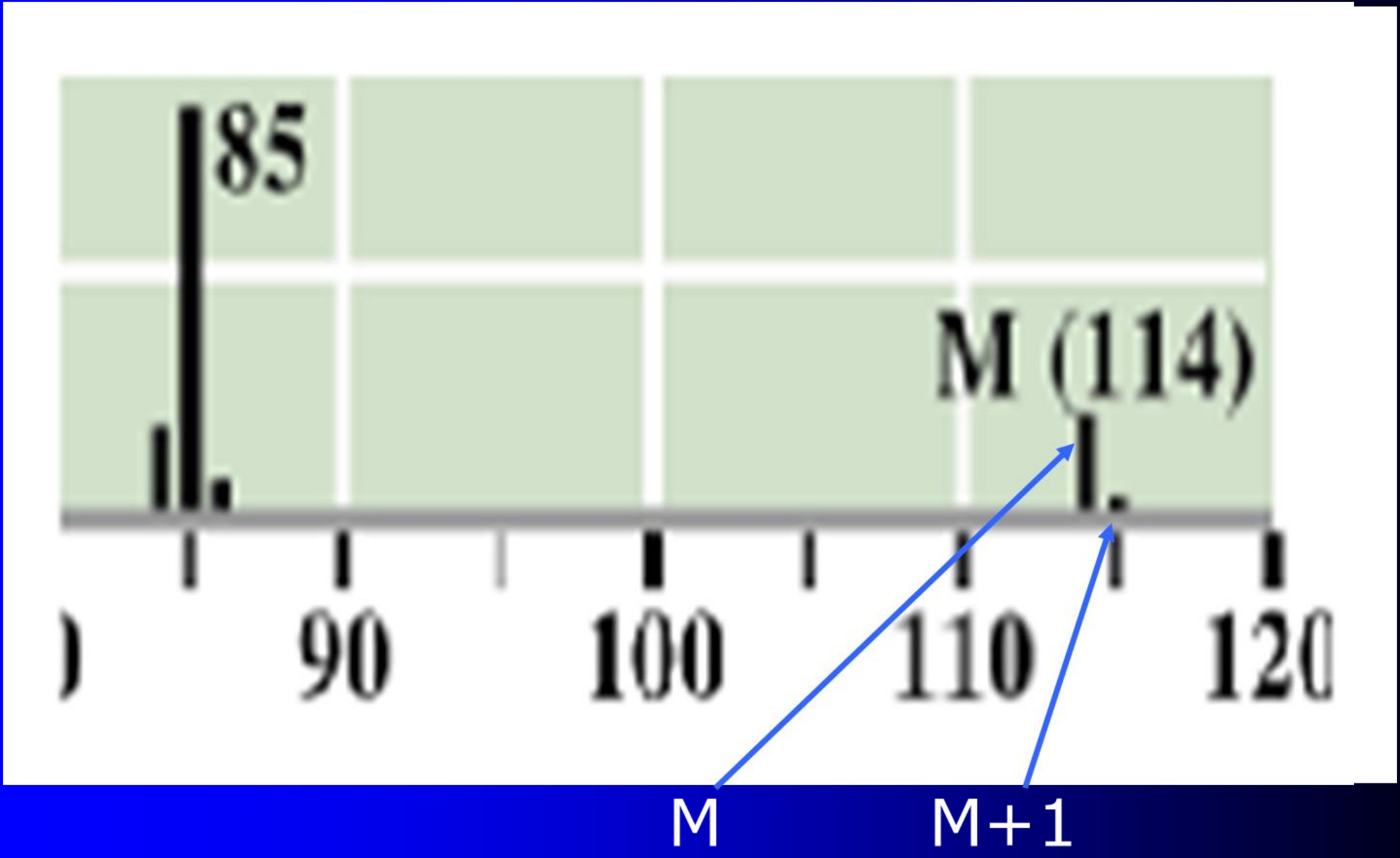
Calculation of Precise Mass

Use mass of most abundant isotope…why??

C_3H_8O and $C_2H_4O_2$

C	12	3	36	2	24
H	1.00783	8	8.06264	4	4.03132
O	15.9949	1	15.9949	2	31.9898
SUM			60.05754		60.02112

http://www.colby.edu/chemistry/NMR/IsoClus.html


85
M (114)
90
100
110
120
M
M+1

Calculating M+1

- M+1 = $\sum$ [(abundance of heavier isotope) x (number of atoms in the empirical formula)]
- Thus, for octane, C_8H_{18}

$$
\begin{aligned}
M+1 &= \sum((1.11\times 8)+(0.016\times 18)) \\
&= 8.88+0.288 \\
&= 9.17\% \text{ of } M
\end{aligned}
$$

Calculated Spectrum

Formula: C_8H_{18}

mass	%
114	100.0
115	8.8
116	0.3
117	0.0

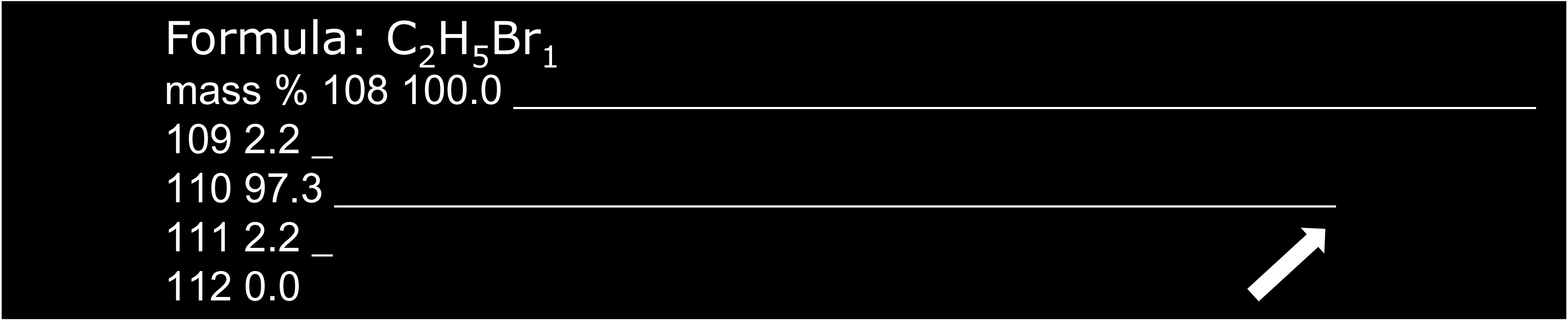
M+1 peak

http://www.sisweb.com/mstools/isotope.htm

http://www.chemcalc.org/

http://fluorine.ch.man.ac.uk/research/mstool2.php

Calculated Spectrum



Formula: $C_2H_5Br_1$

mass % 108 100.0

109 2.2 _

110 97.3

111 2.2 _

112 0.0

An M+2 peak!!

http://www.sisweb.com/mstools/isotope.htm

http://www.chemcalc.org/analyse?mf=C8H18&resolution=0.1&referenceVersion=2012

Isotopes

oxygen	**15.999**	^{16}O	**15.9949**	**100**
		^{17}O	**16.9991**	**0.04**
		^{18}O	**17.9992**	**0.20**
sulfur	**32.066**	^{32}S	**31.9721**	**100**
		^{33}S	**32.9715**	**0.78**
		^{34}S	**33.9679**	**4.40**
chlorine	**35.453**	^{35}Cl	**34.9689**	**100**
		^{37}Cl	**36.9659**	**32.5**
bromine	**79.904**	^{79}Br	**78.9183**	**100**
		^{81}Br	**80.9163**	**98.0**

M+2 Peaks

- Sulfur is the only other element common to organic compounds that gives a significant M + 2 peak and it is small

$^{32}S = 95.02\%$ and $^{34}S = 4.21\%$

Result of isotope pattern calculation

```
Formula: C1H4S1
mass %
48 100.0 _______________~~____________________
49 1.9 _
50 4.5 __
```

M+2 and Statistics-Cl_2

- Possible ways of combining two Chlorines
  - 35-35 (70) , 35-37 (72) and 37-37 (74)
  - Three peaks of what relative intensity?
  - assume that the probability of 35 is 0.75 and of 37 is 0.25 (close to true)

First Cl	**35**				**35**				**35**				**37**			
second Cl	**35**	**35**	**35**	**37**	**35**	**35**	**35**	**37**	**35**	**35**	**35**	**37**	**35**	**35**	**35**	**37**
total	**70**	**70**	**70**	**72**	**70**	**70**	**70**	**72**	**70**	**70**	**70**	**72**	**72**	**72**	**72**	**74**

From the table	**Relative Probability**
Mass 70 = 9	9/16 = 0. 5625 / 0.5625 = 1.00
Mass 72 = 6	6/16 = 0.375 / 0.5625 = .666
Mass 74 = 1	1/16 = 0.0625 / 0.5625 = .111
Total = 16	

Another way…. To look at this

Probability Product

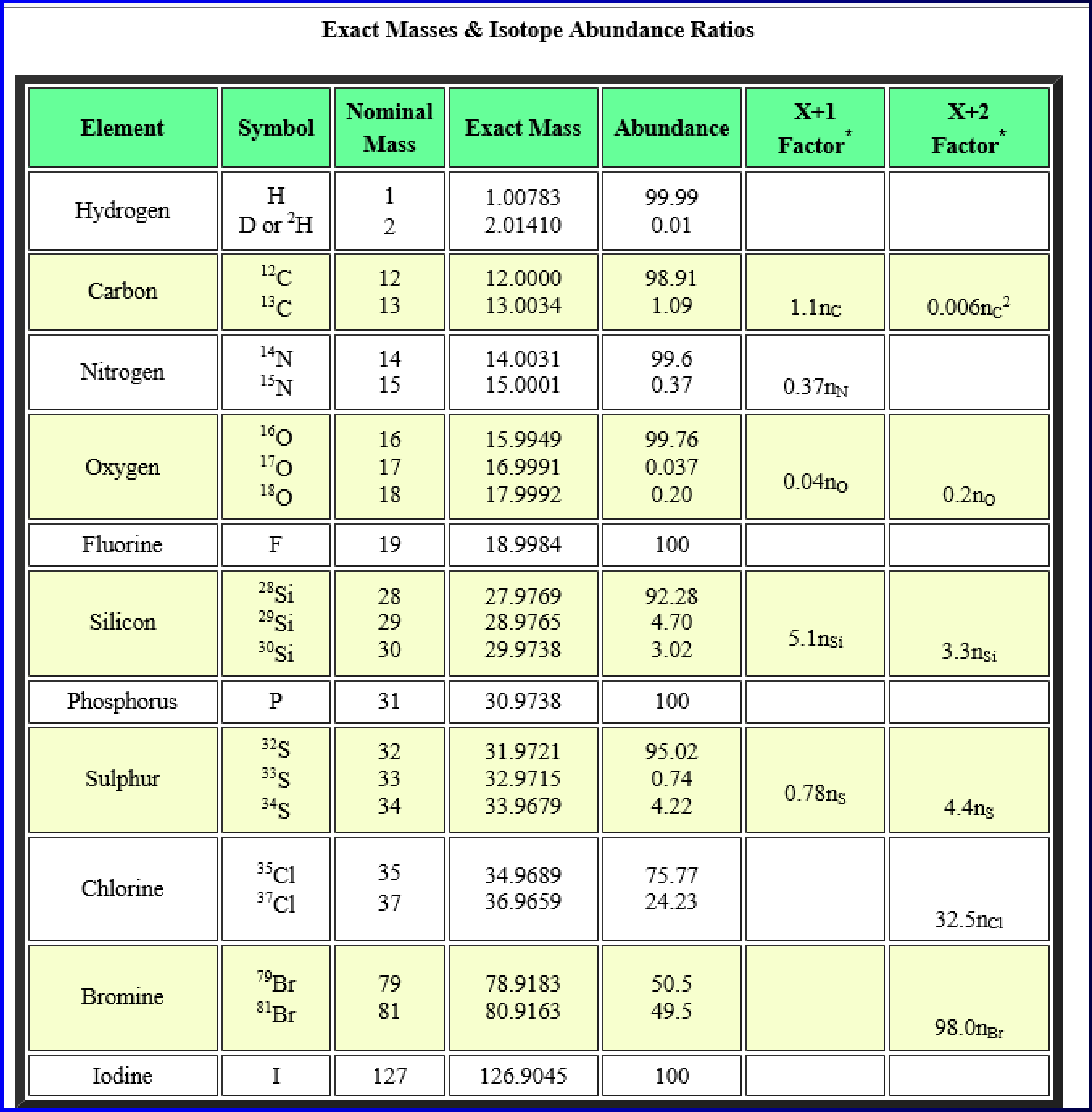
permutations

35,35	.75 x.75	1	0.5625	(0.5625/ 0.5625)x100= **100**
35,37 (or 37,35)	.75 x .25	2	0.3750	(0.3750/ 0.5625)x100= **66.6**
37,37	.25 x .25	1	0.0625	(0.0625/ 0.5625)x100= **11.1**

What is Wrong with these things??

- Using more <u>exact isotope masses</u>

35,35	.7577 x.7577	1	0.5741	100
35,37 (or 37,35)	.7577 x .2423	2	0.3671	(0.3671/0.5741)x100 = 63.9
37,37	.2423 x .2423	1	0.05871	0.05871/0.5741)x100 = **10.2**



Exact Masses & Isotope Abundance Ratios

Element	Symbol	Nominal Mass	Exact Mass	Abundance	X+1 Factor*	X+2 Factor*
Hydrogen	H D or ^{2}H	1 2	1.00783 2.01410	99.99 0.01		
Carbon	^{12}C ^{13}C	12 13	12.0000 13.0034	98.91 1.09	$1.1n_C$	$0.006n_C^2$
Nitrogen	^{14}N ^{15}N	14 15	14.0031 15.0001	99.6 0.37	$0.37n_N$	
Oxygen	^{16}O ^{17}O ^{18}O	16 17 18	15.9949 16.9991 17.9992	99.76 0.037 0.20	$0.04n_O$	$0.2n_O$
Fluorine	F	19	18.9984	100		
Silicon	^{28}Si ^{29}Si ^{30}Si	28 29 30	27.9769 28.9765 29.9738	92.28 4.70 3.02	$5.1n_{Si}$	$3.3n_{Si}$
Phosphorus	P	31	30.9738	100		
Sulphur	^{32}S ^{33}S ^{34}S	32 33 34	31.9721 32.9715 33.9679	95.02 0.74 4.22	$0.78n_S$	$4.4n_S$
Chlorine	^{35}Cl ^{37}Cl	35 37	34.9689 36.9659	75.77 24.23		$32.5n_{Cl}$
Bromine	^{79}Br ^{81}Br	79 81	78.9183 80.9163	50.5 49.5		$98.0n_{Br}$
Iodine	I	127	126.9045	100		

Interpreting MS

1. Check the M+2 region of the spectrum

   The only elements to give significant M + 2 peaks are Cl and Br. If there is no large M + 2 peak then there is no Cl or Br! (remember S ….it is “small)

2. Is the mass of the molecular ion odd or even?

   Apply the Nitrogen Rule:

   a. if a compound has zero or an even number of nitrogen atoms, its molecular ion will appear as a even m/z value

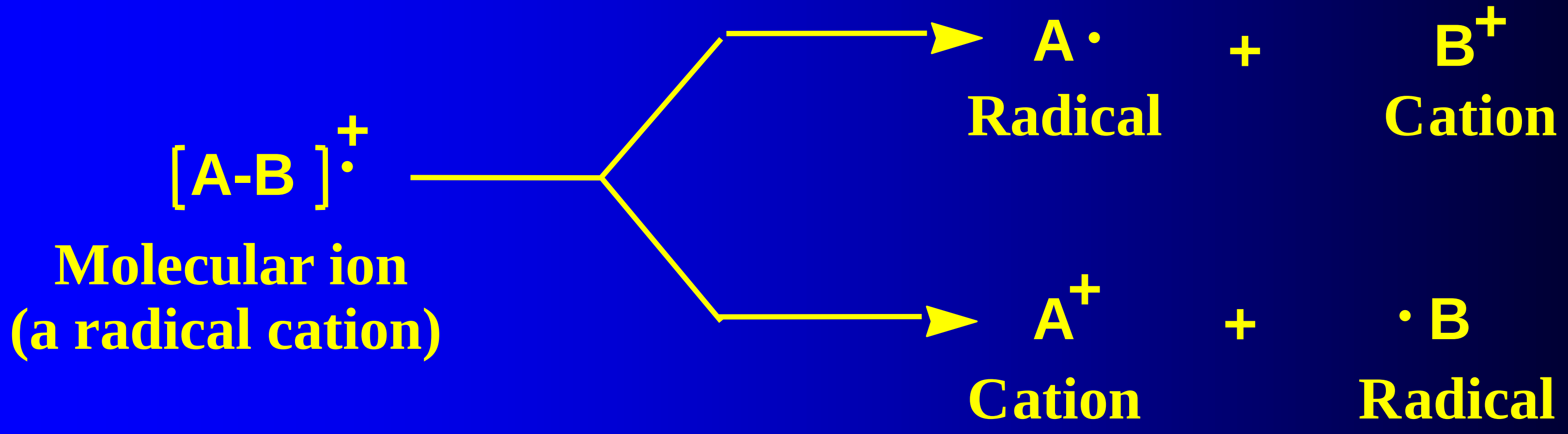
   b. If it has an odd number of nitrogen atoms, its molecular ion will appear as an odd m/z value

Fragmentation of M

- To attain high efficiency of molecular ion formation and give reproducible mass spectra, it is common to use electrons with energies of approximately 70 eV (1600 kcal/mol)
- This energy is sufficient not only to dislodge one or more electrons from a molecule, but also to cause extensive fragmentation
- These fragments may be unstable as well and, in turn, break apart to even smaller fragments

Fragmentation of M

- Fragmentation of a molecular ion, M, produces a radical and a cation. Only the cation is detected by MS



$[\mathrm{A\text{-}B}]^{+\cdot}$

Molecular ion (a radical cation)

$\mathrm{A}\cdot$ + B^{+}

Radical **Cation**

A^{+} + $\cdot\mathrm{B}$

Cation **Radical**

Fragmentation of M

- The chemistry of ion fragmentation can be understood in terms of the formation and relative stabilities of carbocations in solution

- When fragmentation occurs to form new cations, the mode that gives the most stable cation is favored

Fragmentation of M

- The probability of fragmentation to form new carbocations increases in the order

$$CH_3^+ < 1° < 2° < 3°$$

CH_3^+	<	1°	<	2° 1° allylic 1° benzylic	<	3° 2° allylic 2° benzylic	<	3° allylic 3° benzylic

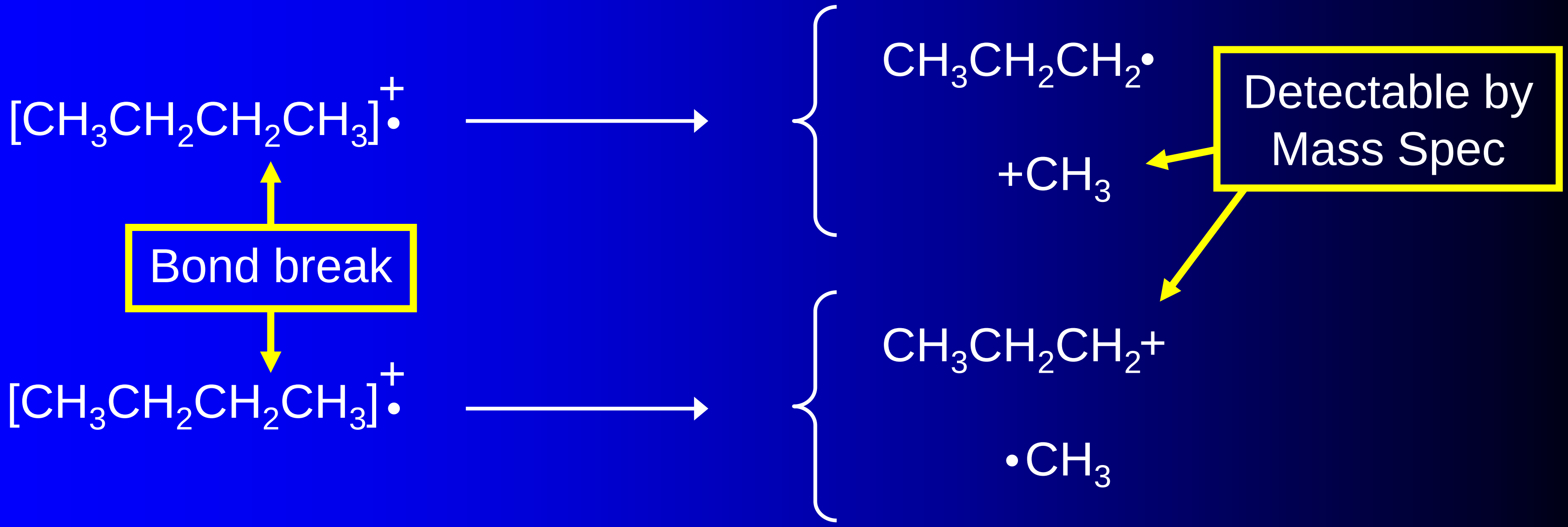
Increasing carbocation stability

Alkanes

- Fragmentation tends to occur in the middle of unbranched chains rather than at the ends
- The difference in energy between allylic, benzylic, 3°, 2°, 1°, and methyl cations is much greater than the difference among comparable radicals
  - where alternative modes of fragmentation are possible, the more stable carbocation tends to form in preference to the more stable radical

Mass Spectrometry

- When the weakened bond breaks, one fragment retains the single electron (becoming neutral) and the other must therefore accept the positive charge



$[CH_3CH_2CH_2CH_3]\overset{+}{\bullet} \longrightarrow \begin{cases} CH_3CH_2CH_2\bullet \\ {}^{+}CH_3 \end{cases}$

Bond break

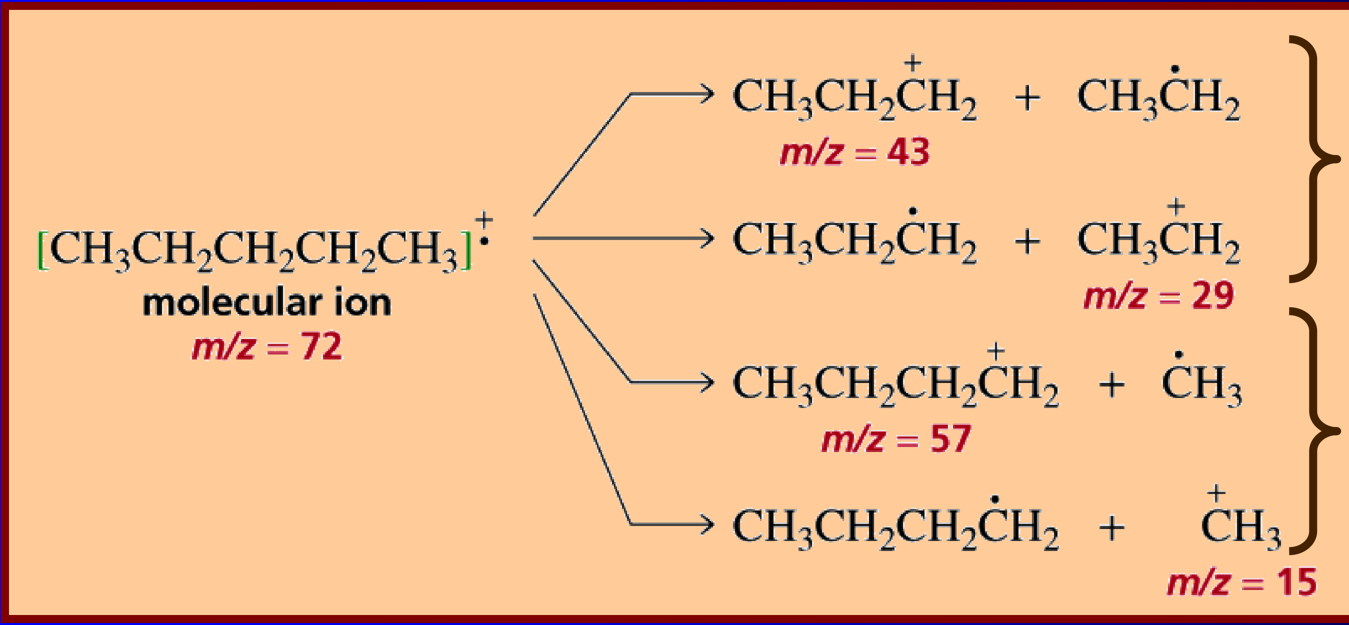
$[CH_3CH_2CH_2CH_3]\overset{+}{\bullet} \longrightarrow \begin{cases} CH_3CH_2CH_2{}^{+} \\ \bullet CH_3 \end{cases}$

Detectable by Mass Spec

- How the molecule actually fragments will depend on the stabilities of the individual pieces formed

Mass Spectrometry

- The pentane molecular ion can split in several ways:



$[CH_3CH_2CH_2CH_2CH_3]^{+\bullet}$

molecular ion

m/z = 72

$\longrightarrow CH_3CH_2\overset{+}{C}H_2 + CH_3\dot{C}H_2$ *m/z* = 43

$\longrightarrow CH_3CH_2\dot{C}H_2 + CH_3\overset{+}{C}H_2$ *m/z* = 29

$\longrightarrow CH_3CH_2CH_2\overset{+}{C}H_2 + \dot{C}H_3$ *m/z* = 57

$\longrightarrow CH_3CH_2CH_2\dot{C}H_2 + \overset{+}{C}H_3$ *m/z* = 15

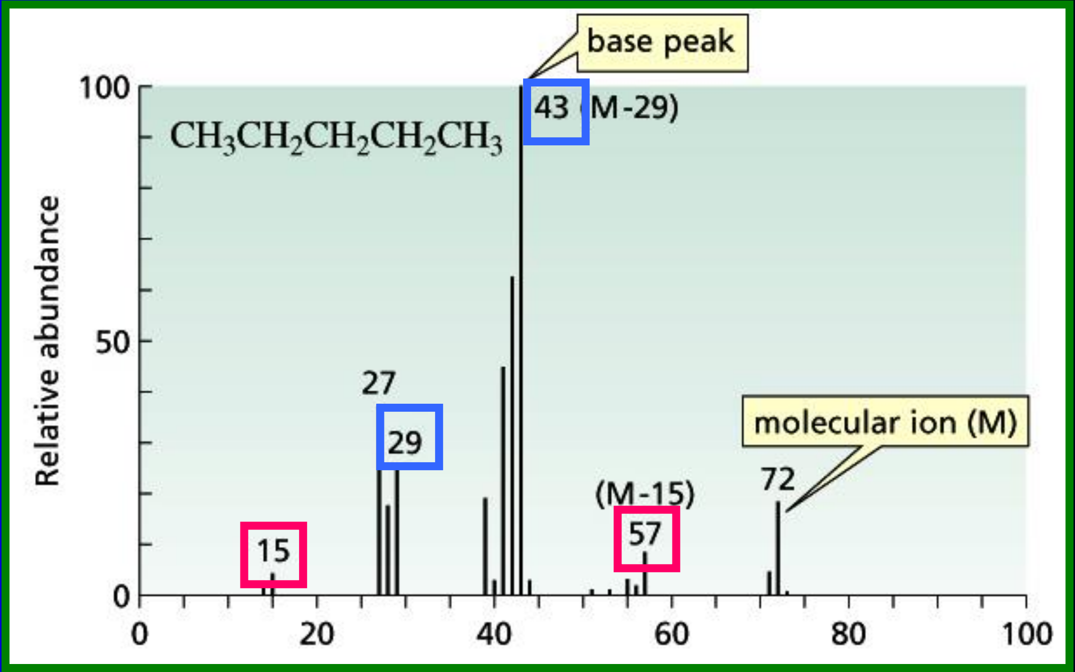
The carbon C2-C3 bond is broken

The carbon C1-C2 bond is broken

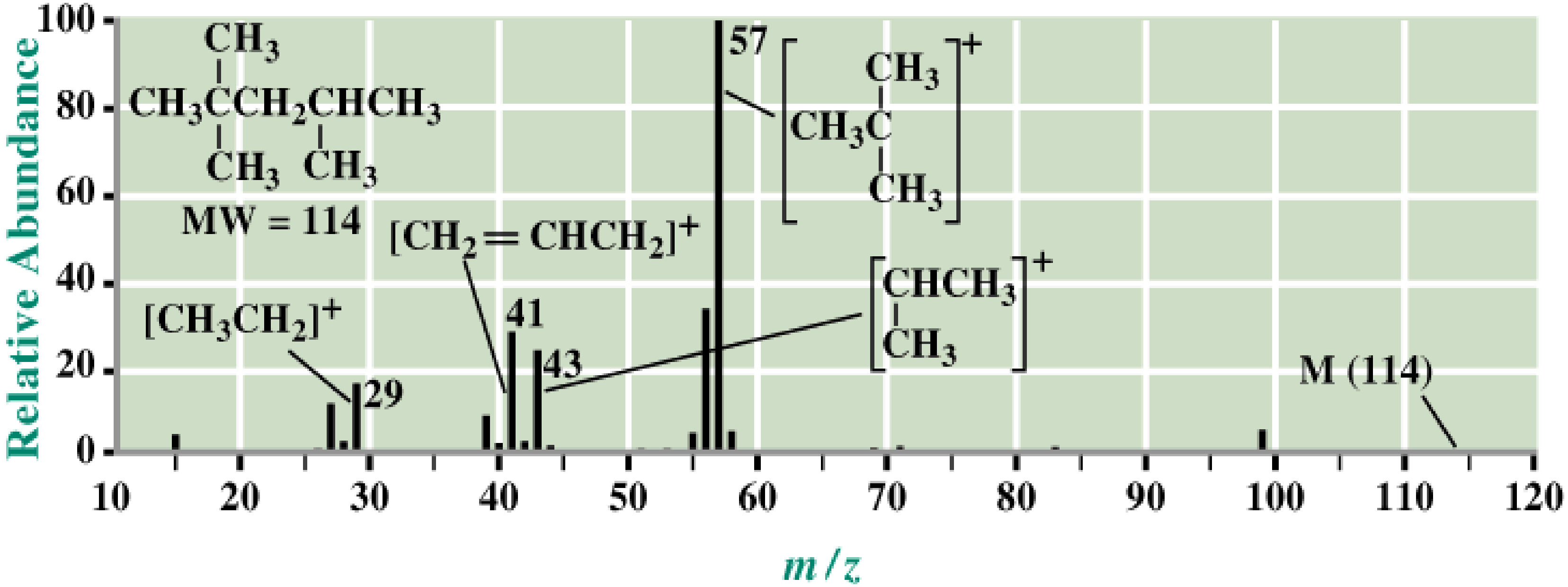
- In each bond breaking case above, the positive charge may reside on either of the fragments
  - The *m*/*z* values for each positive fragment can be determined
  - A line representing that fragment is usually found on the mass spectrum and its abundance can be observed

Mass Spectrometry

- Will one of these bonds break more easily?
- The relative abundances indicate higher amounts of the fragments *m/z* = 29 and 43, and lesser amounts of the fragments *m/z* = 15 and 57
  - This indicates that the C2-C3 bond is more likely to break
- In this case, the increased stability of the resulting C2-C3 radicals/ cations drives the fragmentation at this carbon bond



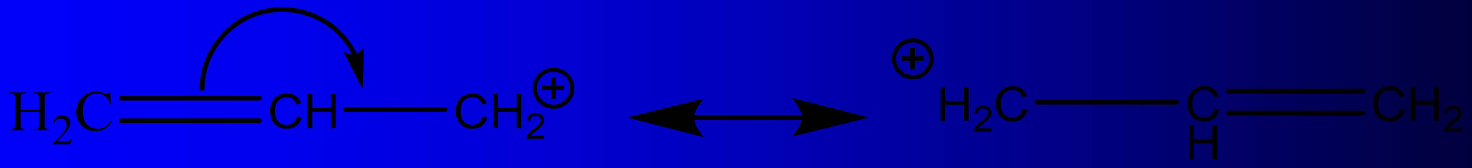
Mass spectrum of 2,2,4-trimethylpentane



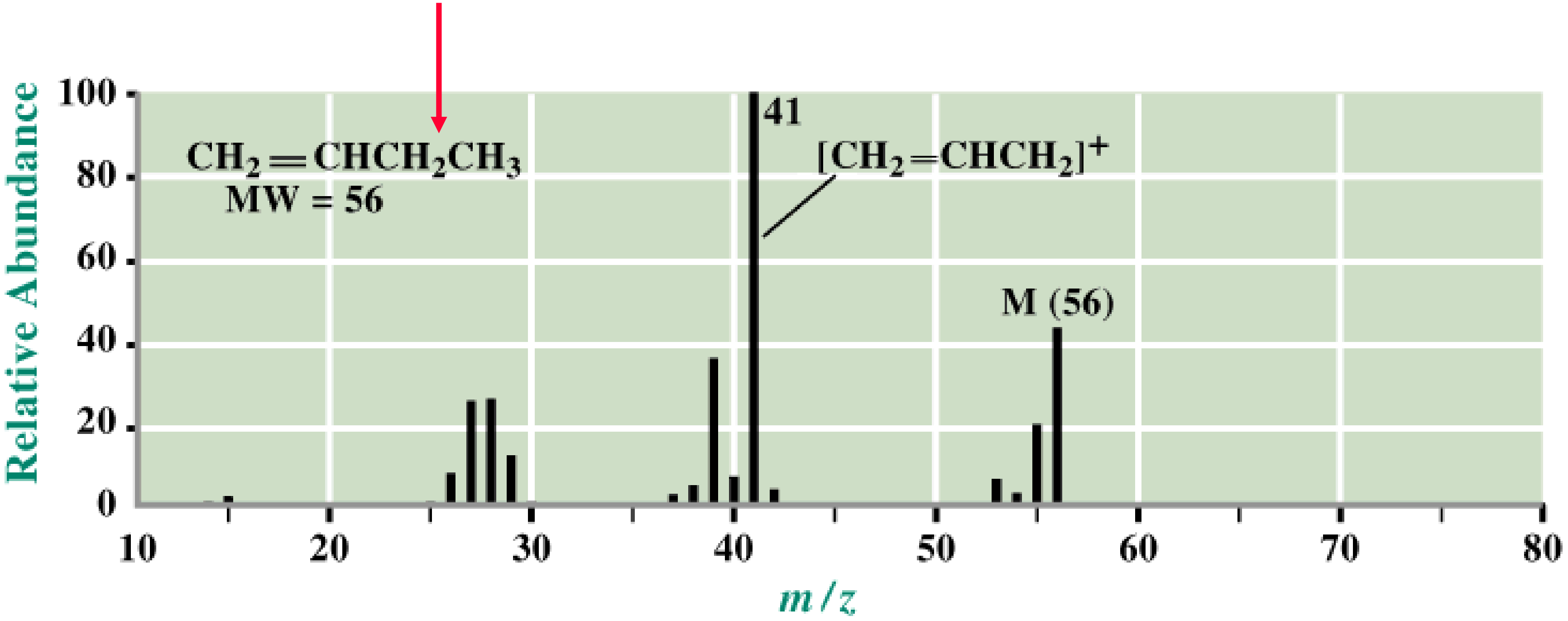
Alkenes

- Alkenes characteristically show a strong molecular ion peak
- They cleave readily to form resonance-stabilized allylic cations

$$[CH_2{=}CHCH_2CH_2CH_3]^{+\bullet} \longrightarrow CH_2{=}CHCH_2^{+} + \cdot CH_2CH_3$$

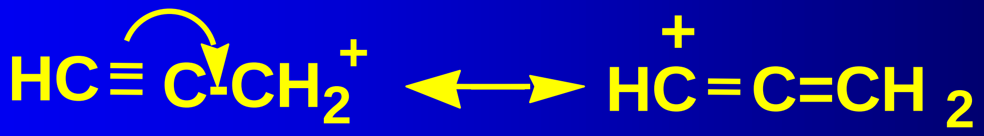


Mass spectrum of 1-butene



Alkynes

- Alkynes typically show a strong molecular ion peak
- They cleave readily to form the resonance-stabilized propargyl cation or a substituted propargyl cation



$$HC\equiv C-CH_2^+ \longleftrightarrow H\overset{+}{C}=C=CH_2$$

resonance-stabilized propargyl cation

Mass spectrum of 1-pentyne