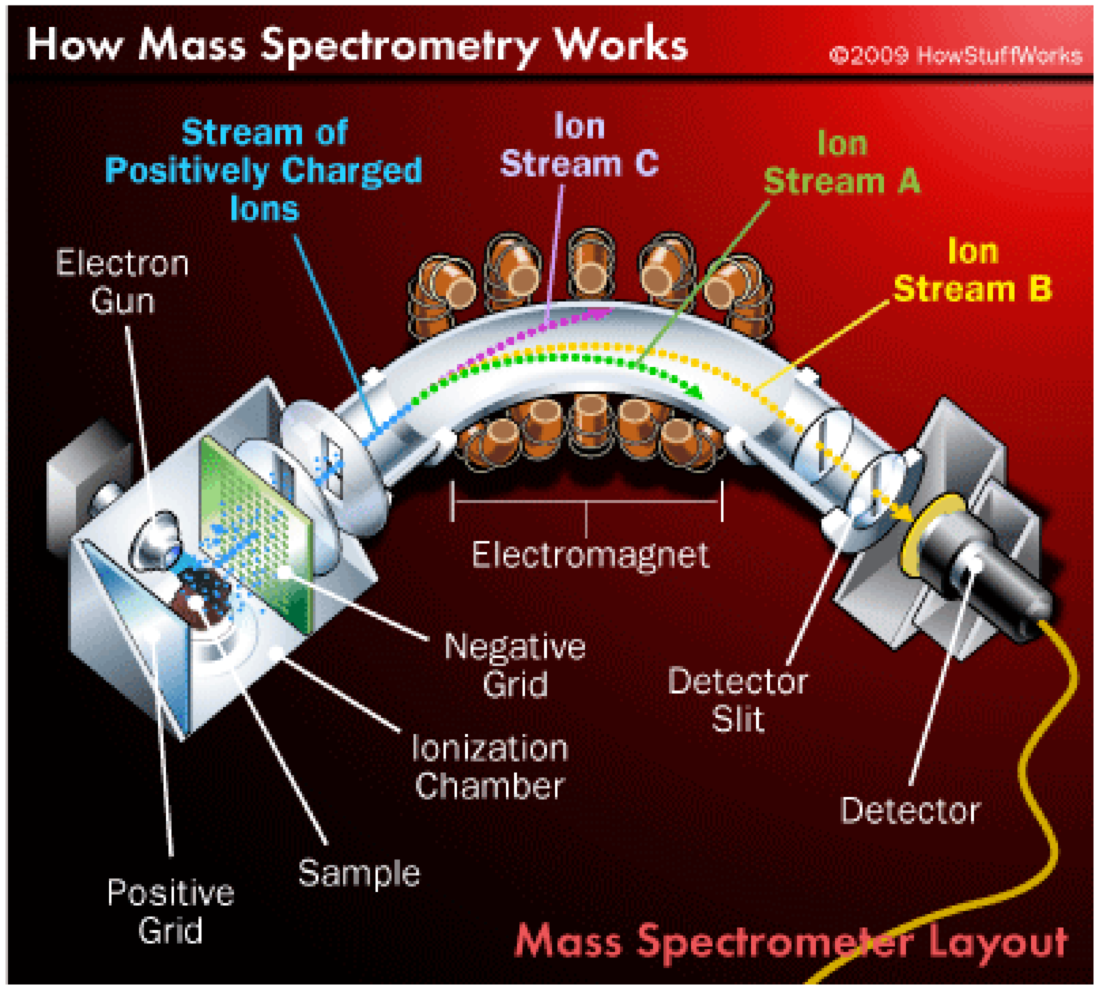
Lecture 2

Mass Spectroscopy



January 23, 2019

Chemistry 328N

Syllabus for Chemistry 328N (v1.22)

Organic Chemistry for Chemical Engineers

Spring 2019 - 50120
T/Th 12:30 - 2:00 p.m. WEL 2.122

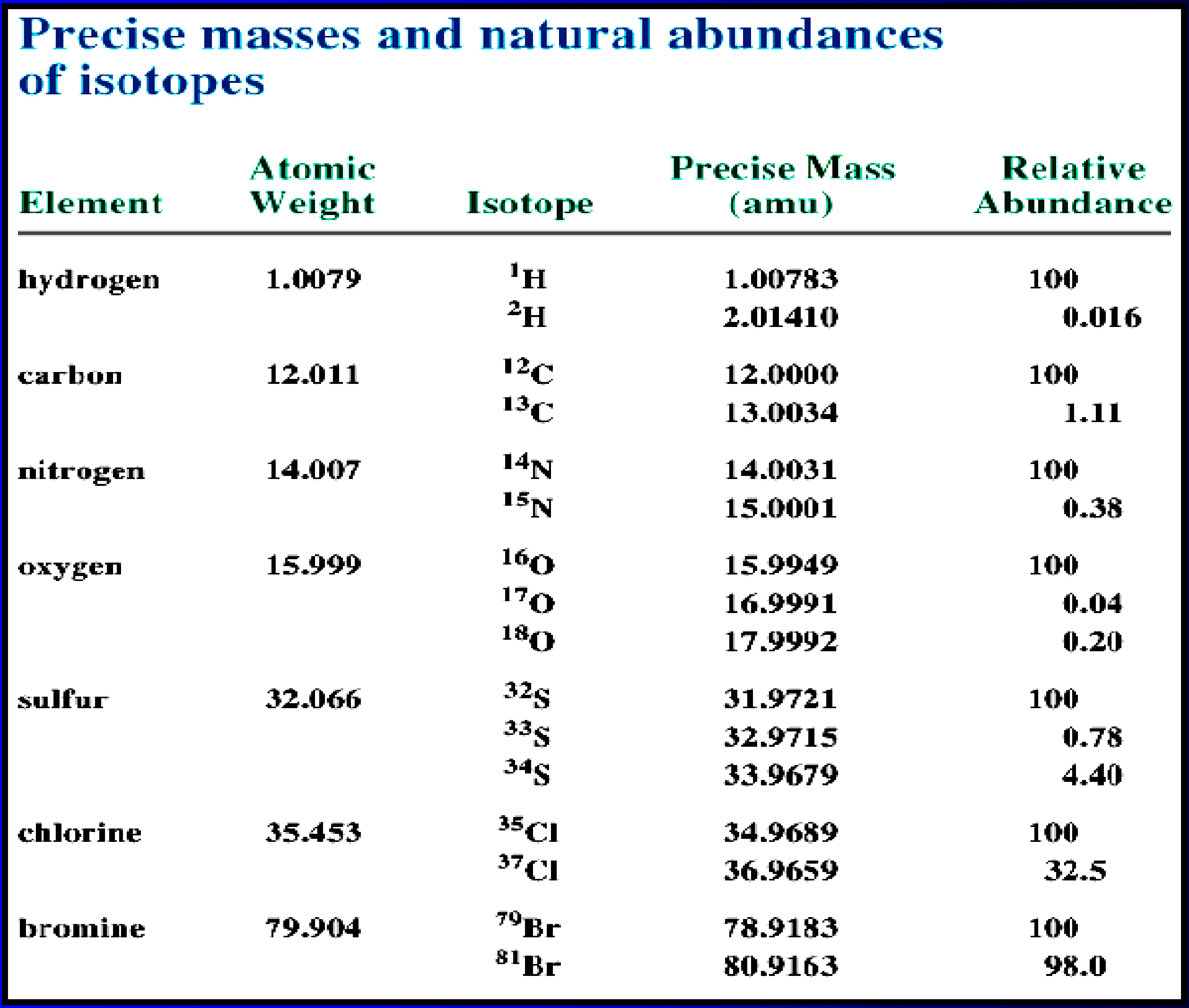
Professor: *C. Grant Willson*
Phone 471-3975 or 471-4342
Office: NHB 5.136
Email: willson@che.utexas.edu
Office Hours: Mon 10:30 – 11:30 a.m. and Thurs 3:00 – 4:00 p.m. in NHB 5.136
Class Web page: http://willson.cm.utexas.edu (Select "teaching")

Teaching Assistants:

Mr. Paul Meyer	Mr. Qingjun Zhu	Mr. Josh Saunders
paul.meyer@utexas.edu	qingjunzhu@utexas.edu	saundersjosh@utexas.edu
512-471-6364	512-471-6364	940-230-5418

Office Hours with TAs

Wednesdays 9 - 10 AM	Tuesdays 9-10 AM	Fridays 2 - 3 PM
CPE 3.448	*CPE 3.448*	*CPE 3.448*



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

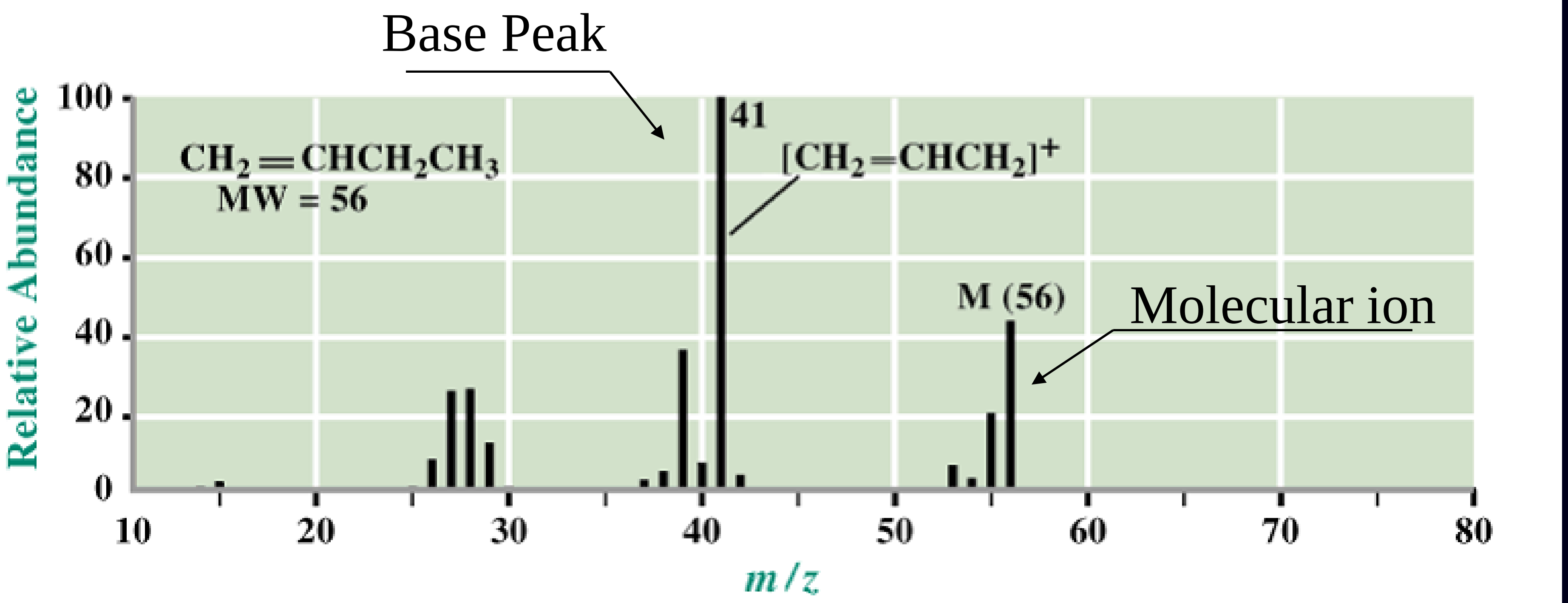
Use mass of most abundant isotope…why??

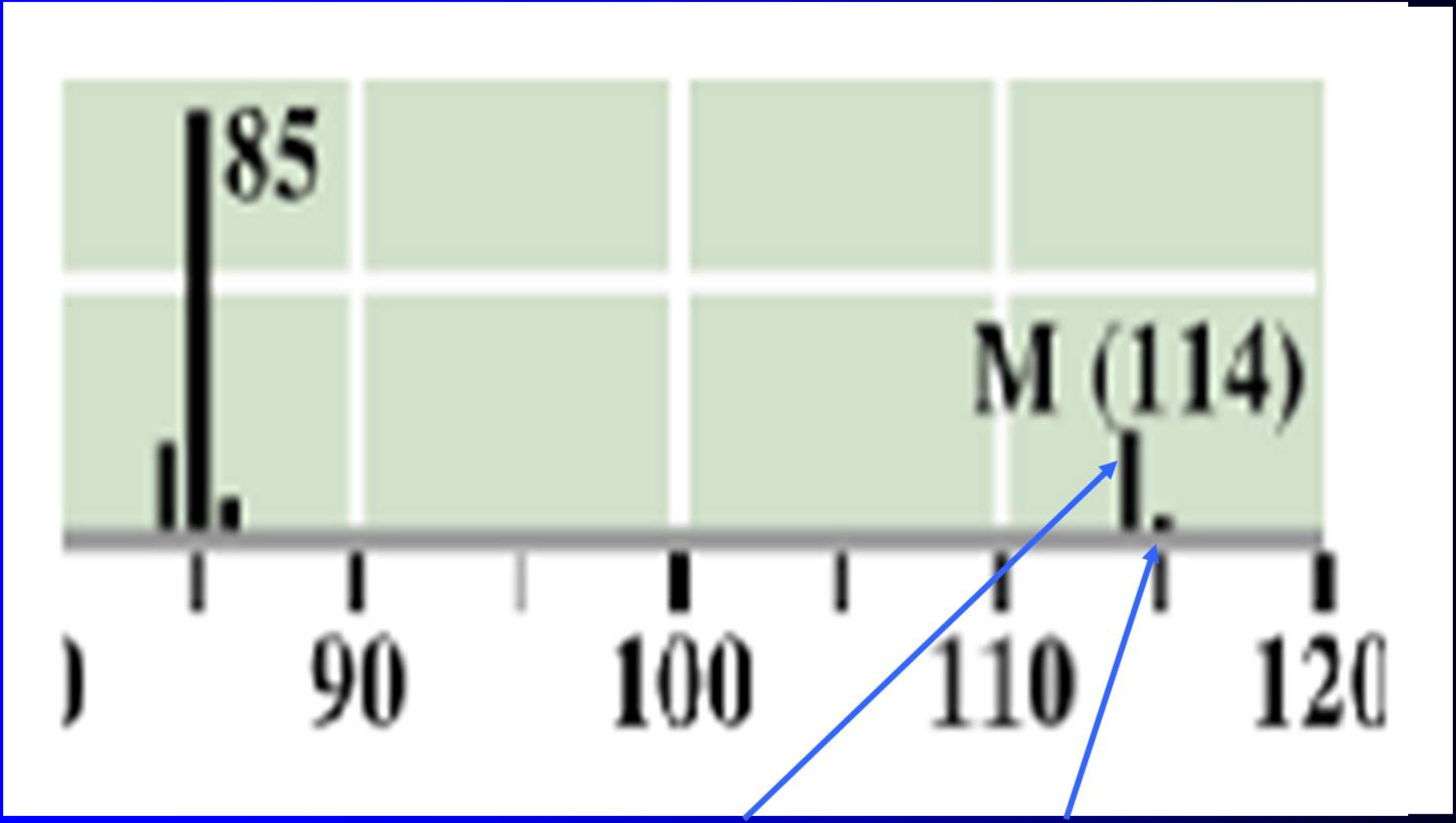
C_3H_8O and $C_2H_4O_2$

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

Mass Spectrum of 1-Butene





M

M+1

Precise masses and natural abundances of isotopes

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

Calculating M+1

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

$$M+1 = \sum((1.11 \times 8) + (0.016 \times 18))$$

$$= 8.88 + 0.288$$

$$= 9.17\% \text{ of } M$$

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://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

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 exact isotope masses

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**

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

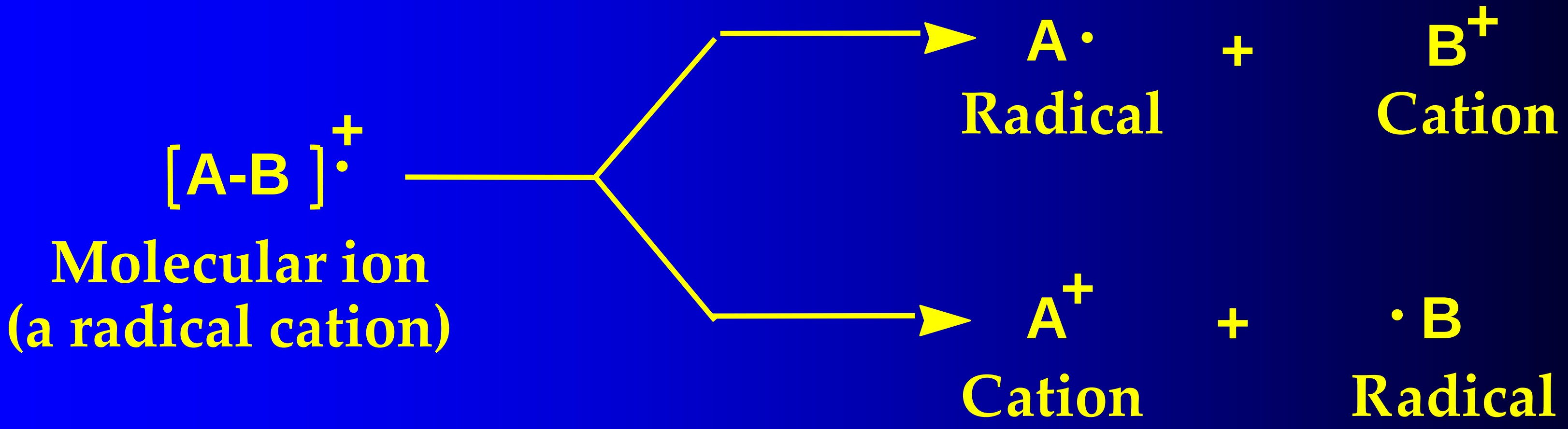
- To attain high efficiency of molecular ion formation and give reproducible mass spectra, it is common to use electrons with energies of approximately 70 eV (1600 kcal/mol)

- 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



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

Molecular ion
(a radical cation)

$\text{A}\bullet$ + B^{+}

Radical **Cation**

A^{+} + $\bullet\text{B}$

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

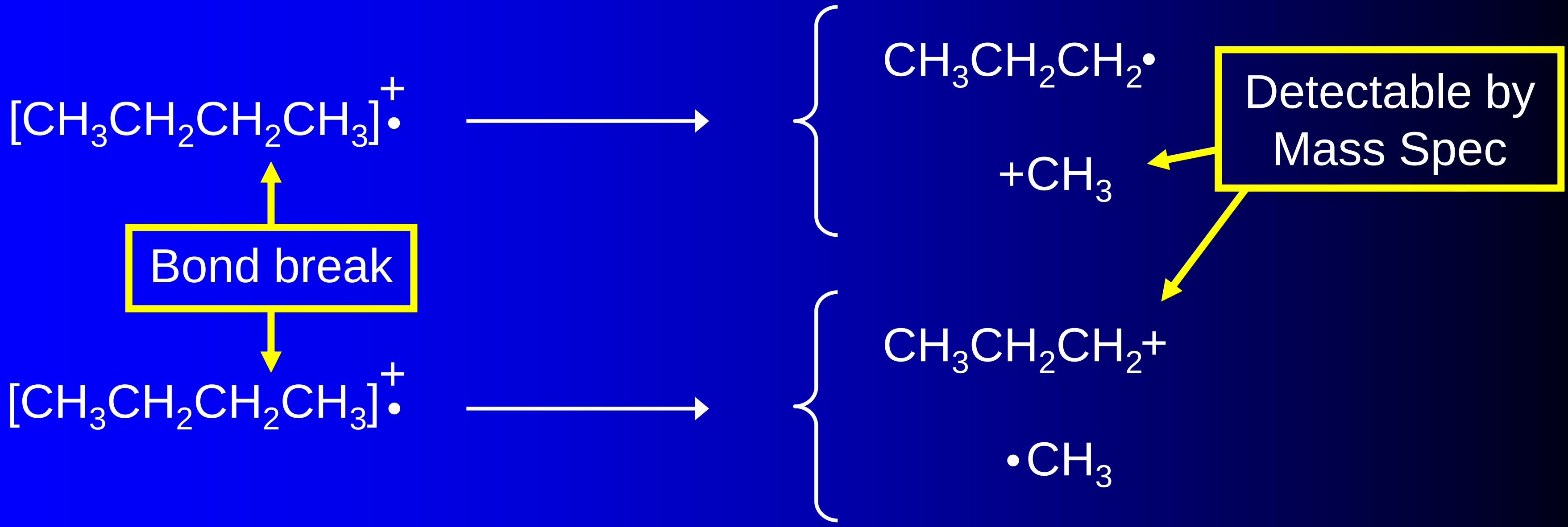
Increasing carbocation stability

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



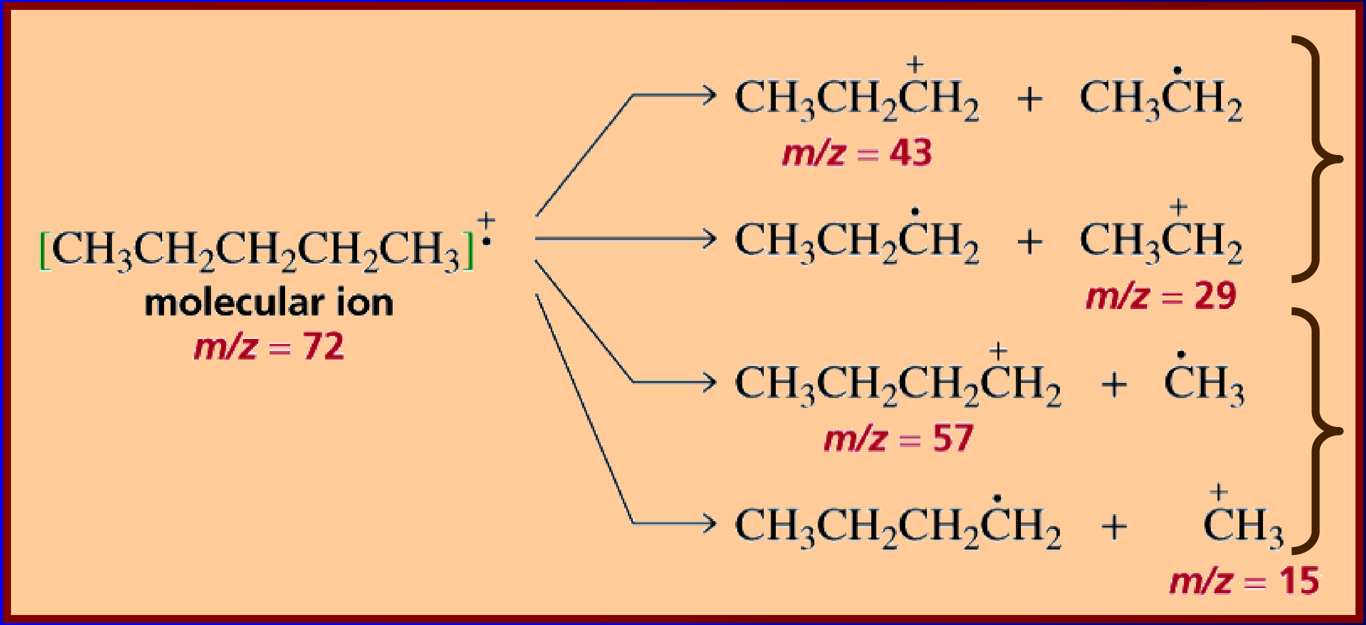
$[CH_3CH_2CH_2CH_3]^{+\bullet} \longrightarrow \left\{ \begin{array}{l} CH_3CH_2CH_2\bullet \\ {}^{+}CH_3 \end{array} \right.$

$[CH_3CH_2CH_2CH_3]^{+\bullet} \longrightarrow \left\{ \begin{array}{l} CH_3CH_2CH_2^{+} \\ \bullet CH_3 \end{array} \right.$

- 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

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

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

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

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

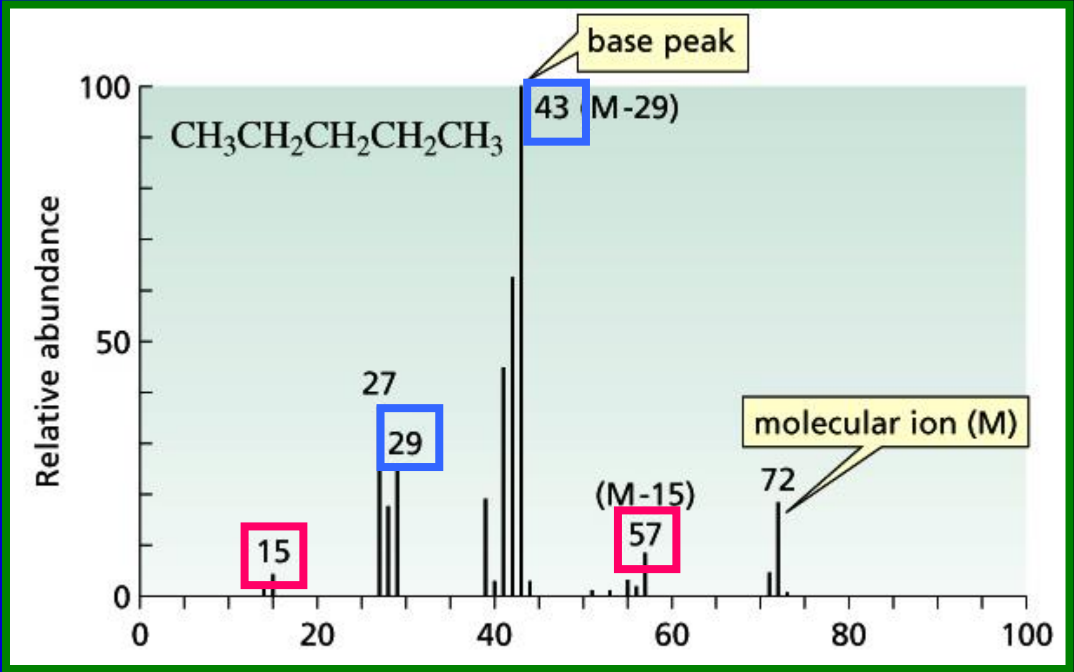
The carbon C2-C3 bond is broken

The carbon C1-C2 bond is broken

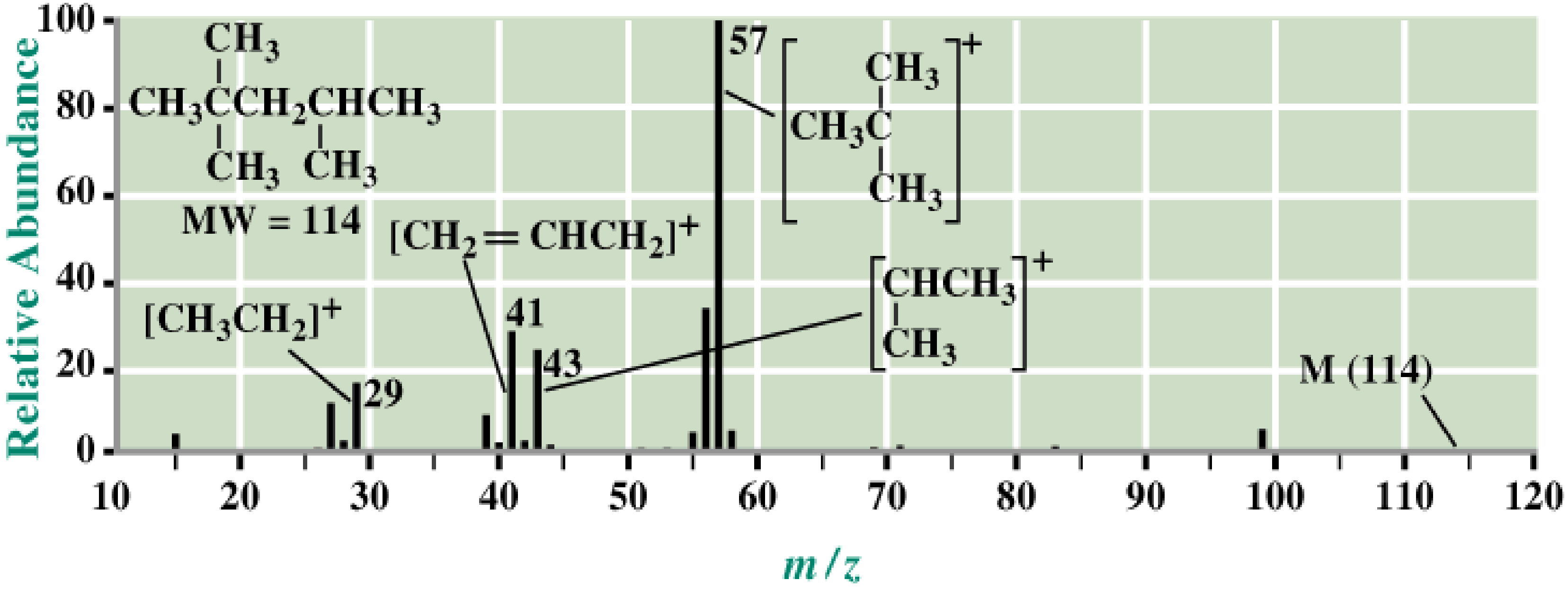
- In each bond breaking case above, the positive charge may reside on either of the fragments
  - The *m*/*z* values for each positive fragment can be determined
  - A line representing that fragment is usually found on the mass spectrum and its abundance can be observed

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



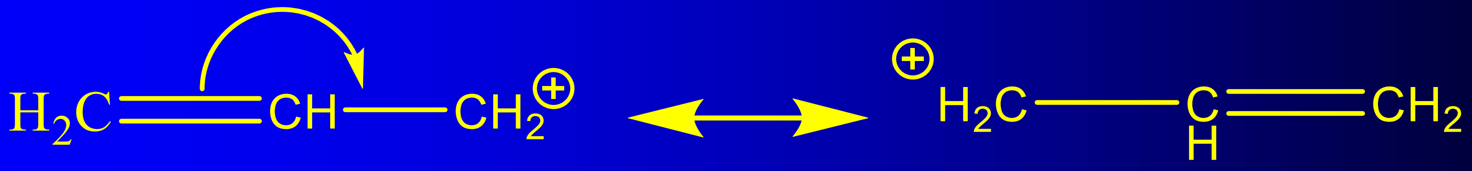
Mass spectrum of 2,2,4-trimethylpentane



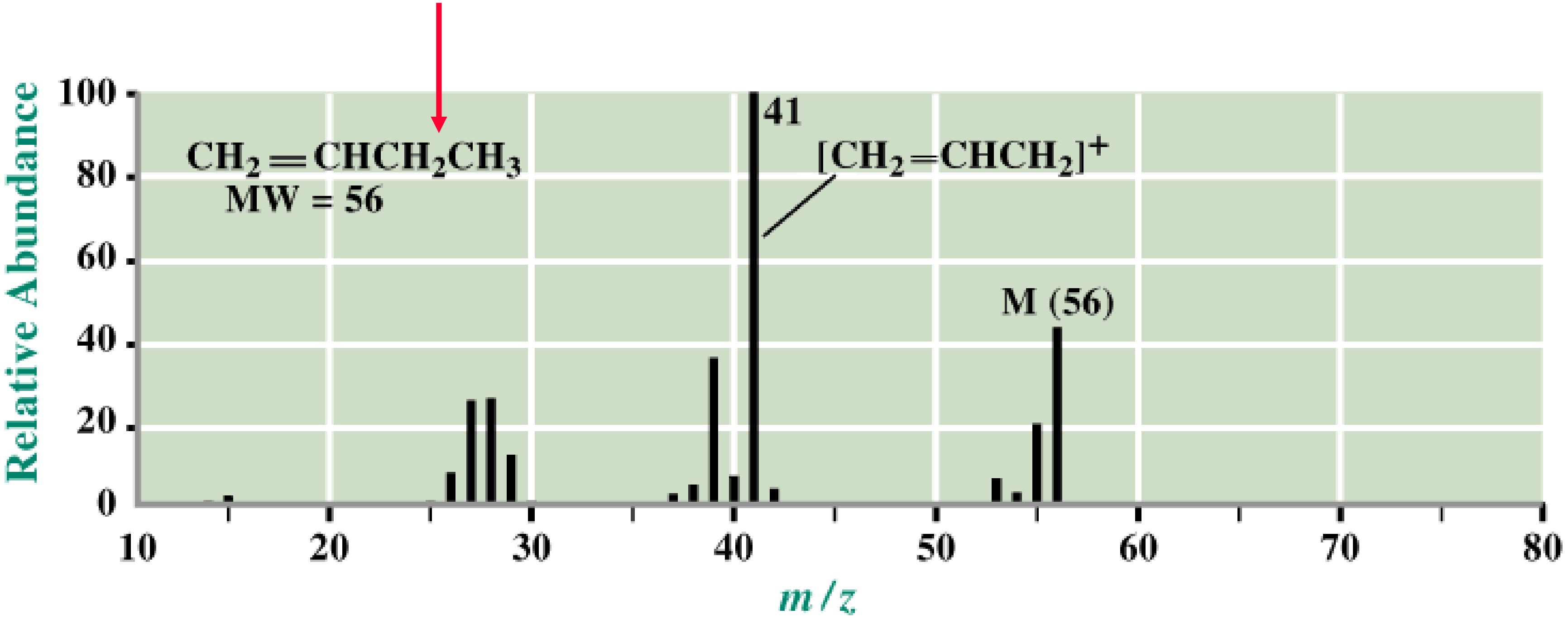
Alkenes

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

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

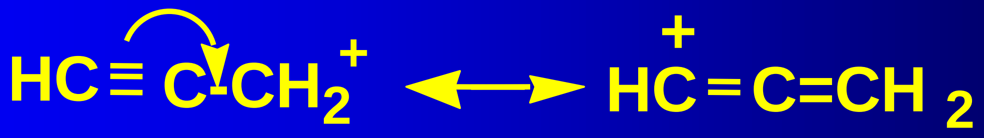


Mass spectrum of 1-butene



Alkynes

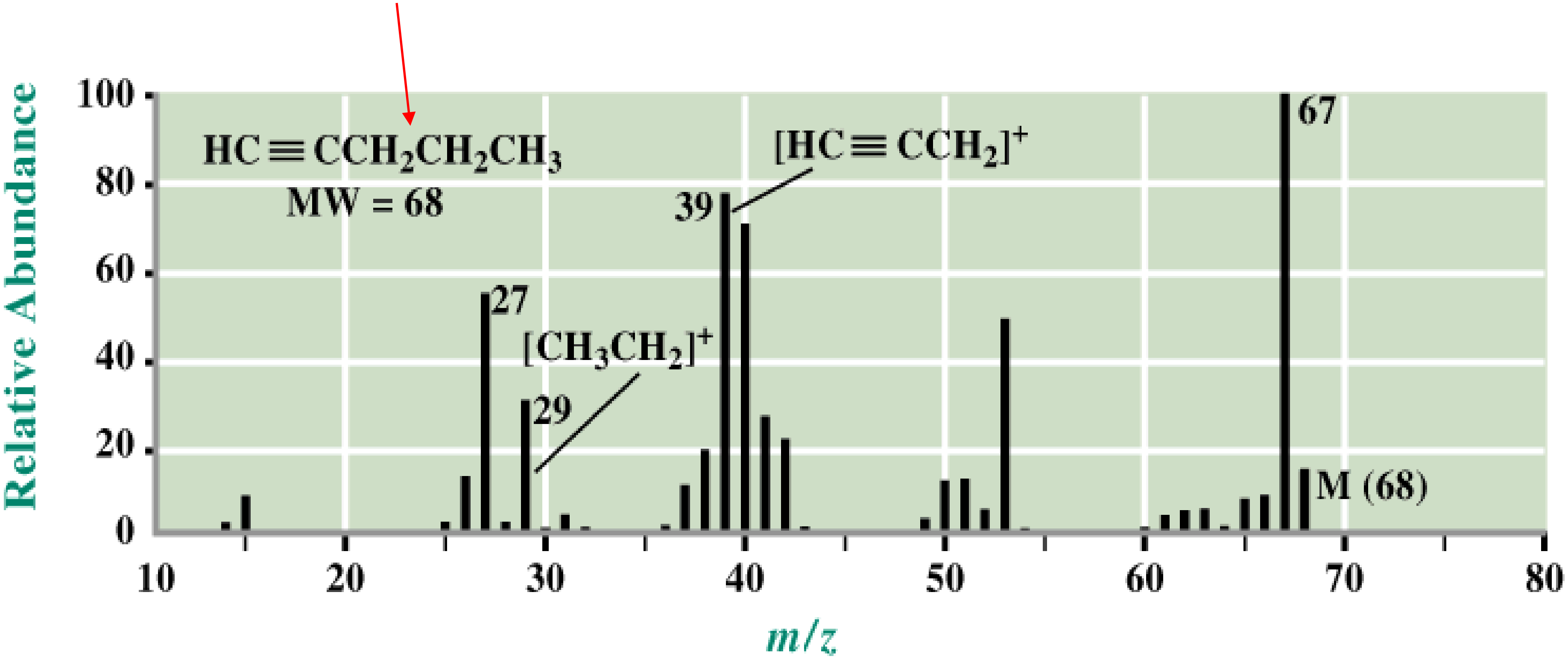
- Alkynes typically show a strong molecular ion peak
- They cleave readily to form the resonance-stabilized propargyl cation or a substituted propargyl cation



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

resonance-stabilized propargyl cation

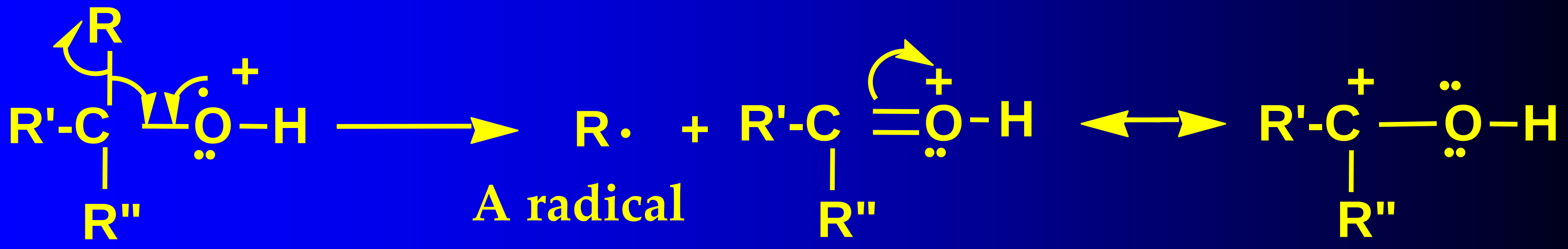
Mass spectrum of 1-pentyne



Alcohols

- A common fragmentation gives M-18 (loss of water)
- The other fragmentation produces the alkyl radical ion from the carbon bearing the OH group

Alcohols



Molecular ion
(a radical cation)

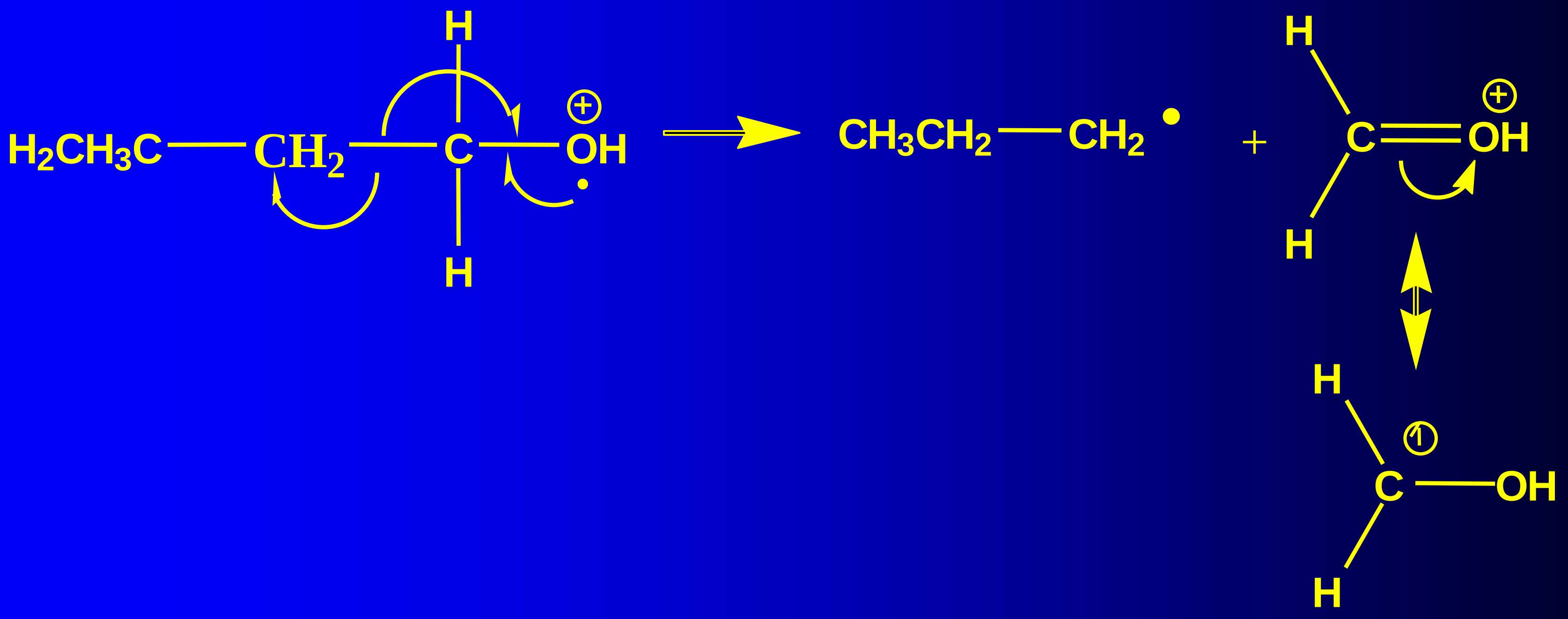
A radical

A resonance-stabilized
oxonium ion

Most stable *radical* is lost!

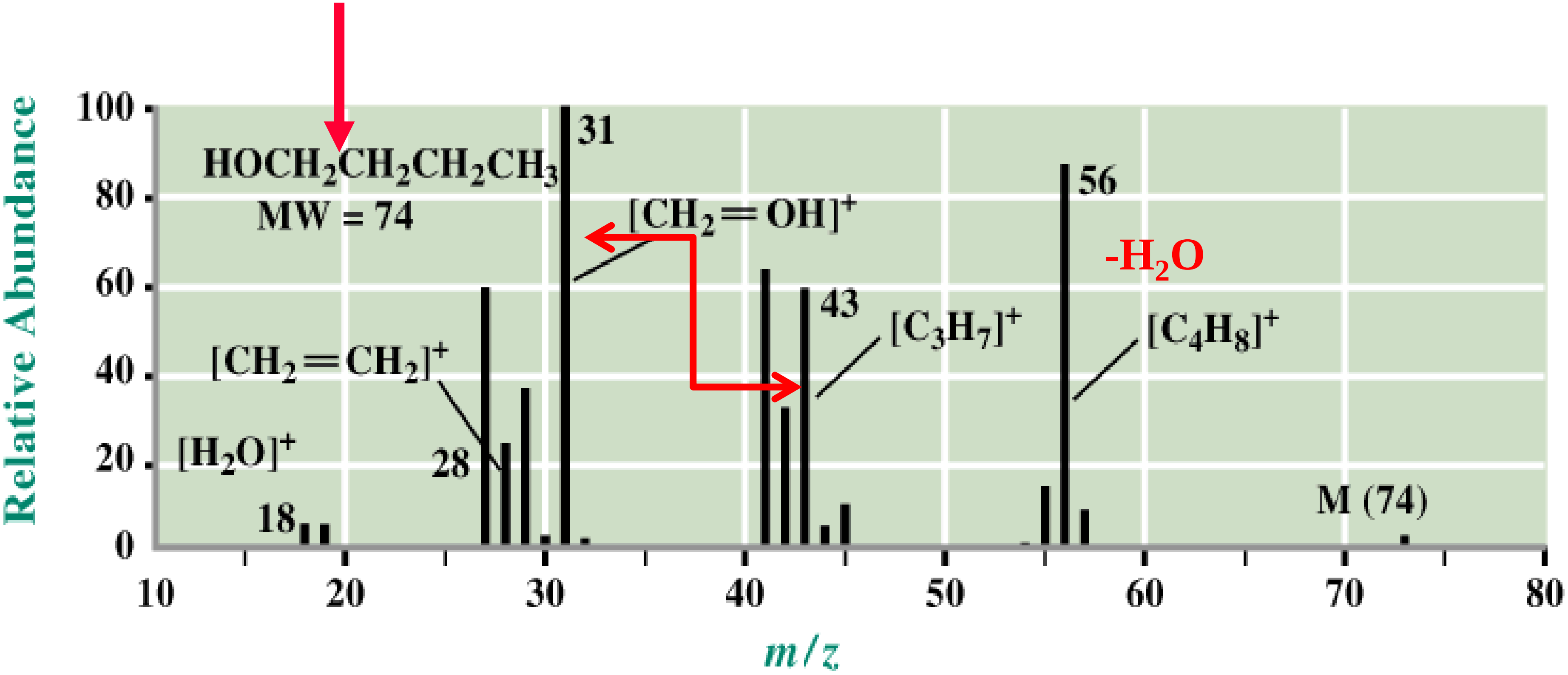
Please analyze for primary, secondary and tertiary alcohols.

1-butanol



M/Z=31

Mass spectrum of 1-butanol



Summary… you need to know

- How mass Spectrometry measures m/z
- Basic Function of the Spectrometer
  - Base Peaks, molecular ions
- Application of unit mass resolution
  - Calculating M+1 and M+2 (S, Cl, Br)
- Application of High resolution
  - How to use isotope tables (relative abundance)
  - Allows differentiation between molecules with identical Mw at unit mass

Summary. . . stuff you need to know

- The nitrogen rule
- Structures can be differentiated by fragmentation pattern analysis
- Fragmentation follows carbocation stability trends
  - Alcohols fragment to lose most stable <u>radical</u>
- We need to know a bit about fragmengtation of :
  - Alkanes, alkenes, alkynes and alcohols