Lecture 2
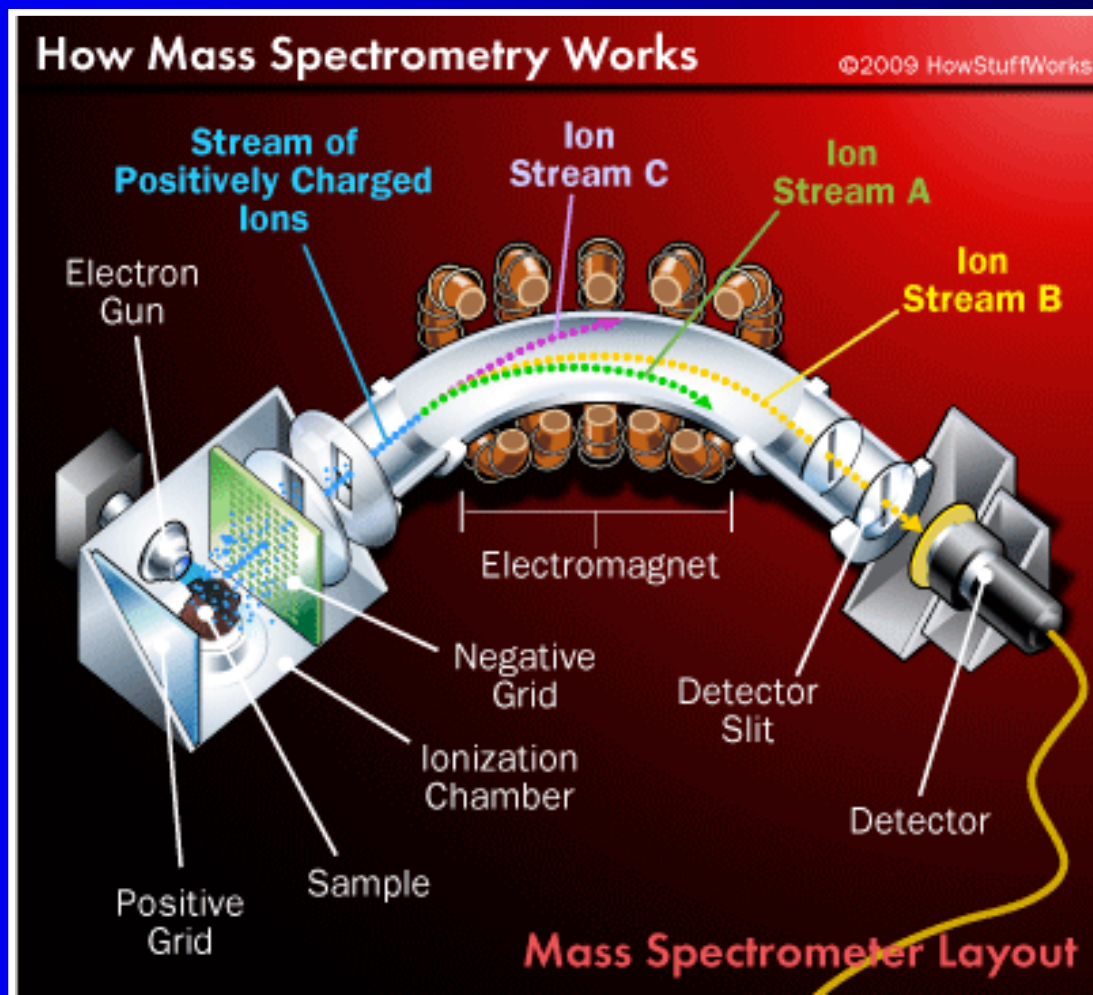# Mass Spectroscopy

Please see me after class
Enrollment issue

- Hugo Nicolas Eichner

- Nurbol Kaliyev

M+1 Peaks

Formula: C_8H_{18}

mass	%
114	100.0
115	8.8
116	0.3
117	0.0

M+1 peak

Calculating M+1

- M+1 = $\sum$ [(abundance of heavier isotope) x (number of atoms in the empirical formula)]

- Abundance is in Table 14.2 on page 561

- 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	____ ← M+1 peak
116	0.3	
117	0.0	

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

http://www.chemcalc.org/

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

http://www.ciaaw.org/index.htm

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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

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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

permutations

<u>Cl$_2$</u>

	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**

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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**

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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?
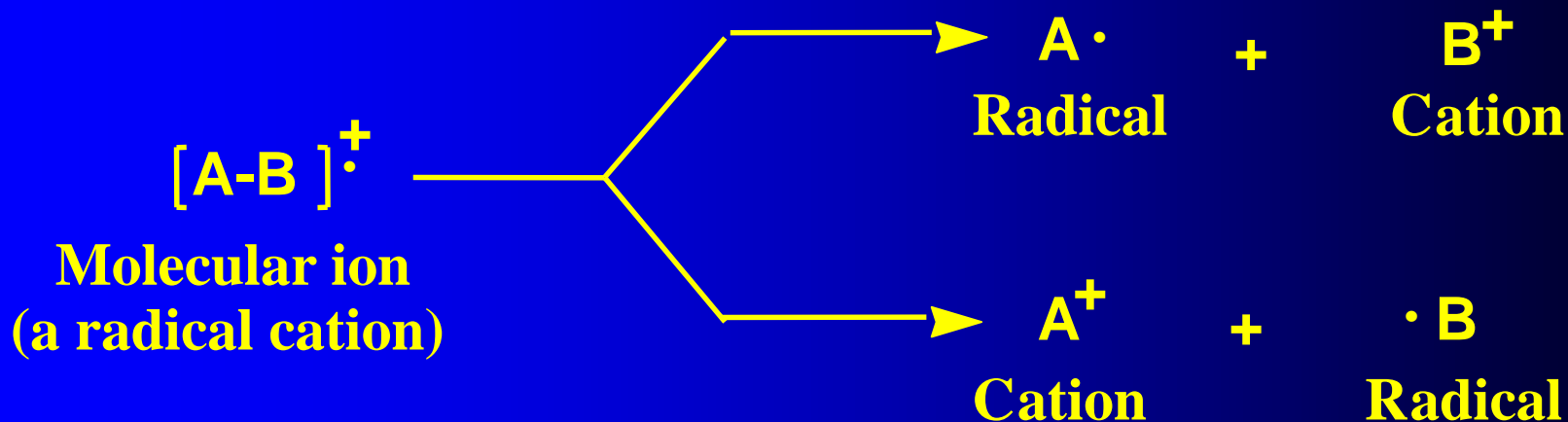
    Apply the Nitrogen Rule:

    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

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Fragmentation of M

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

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

**Molecular ion
(a radical cation)**

$A\bullet$ + B^+
Radical   **Cation**
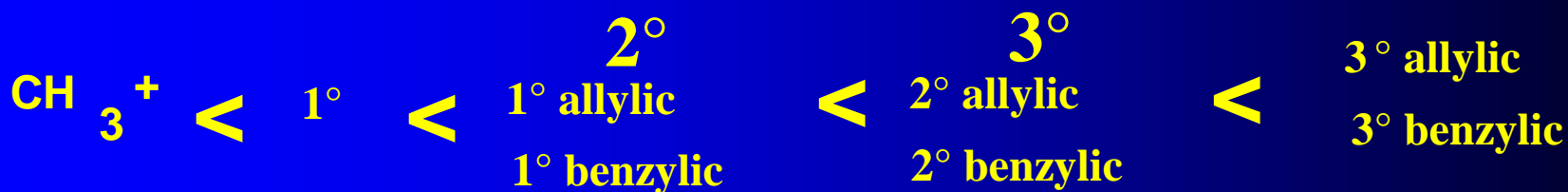
A^+ + $\bullet B$
Cation   **Radical**

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 <u>carbocations</u> increases in the order

$$CH_3{}^+ < 1° < 2° < 3°$$
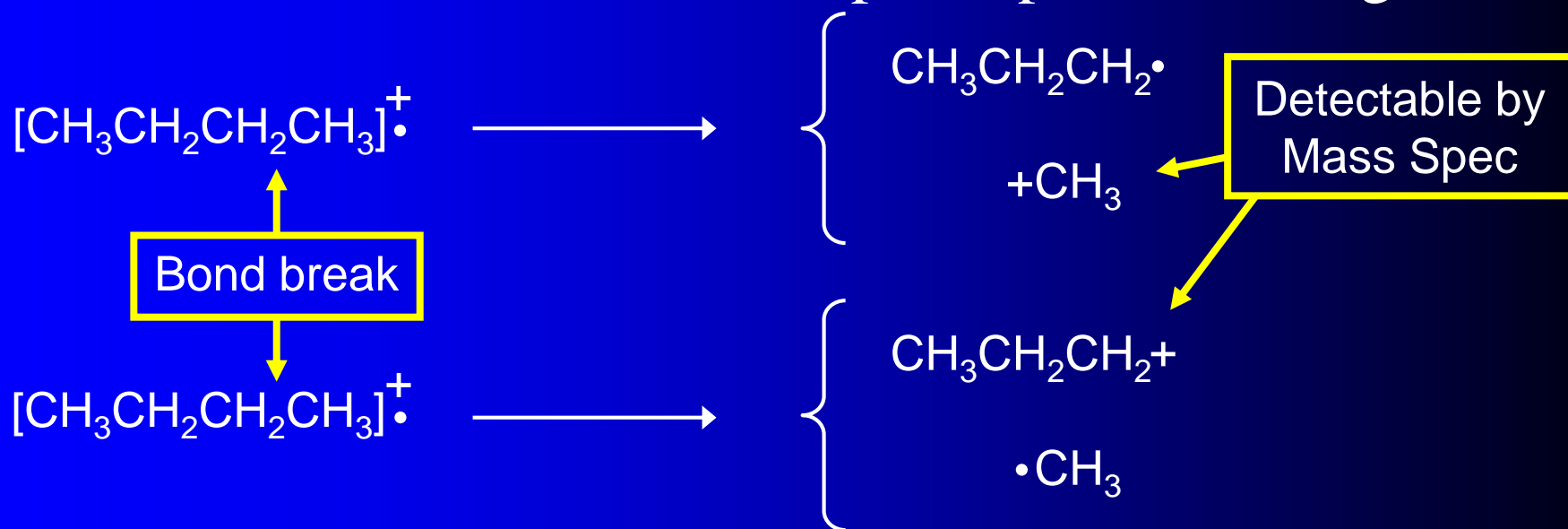
$CH_3{}^+$ < 1° < **2°** < **3°**

1° allylic — 2° allylic — 3° allylic

1° benzylic — 2° benzylic — 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
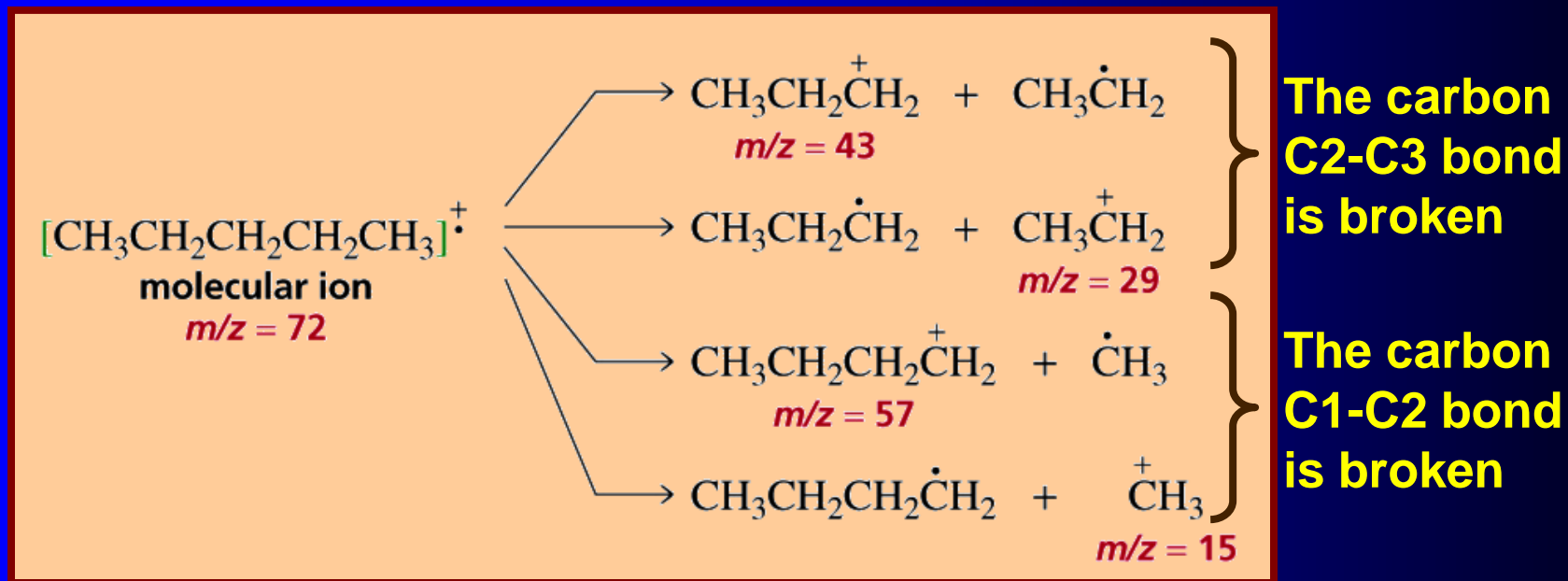
Mass Spectrometry

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

$[CH_3CH_2CH_2CH_3]^{+\bullet}$ $\longrightarrow$ $CH_3CH_2CH_2\bullet$

$+CH_3$

Bond break

Detectable by Mass Spec

$[CH_3CH_2CH_2CH_3]^{+\bullet}$ $\longrightarrow$ $CH_3CH_2CH_2+$

$\bullet CH_3$

- 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:

$[CH_3CH_2CH_2CH_2CH_3]^{+\cdot}$
molecular ion
$m/z = 72$

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

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

The carbon C2-C3 bond is broken

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

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

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
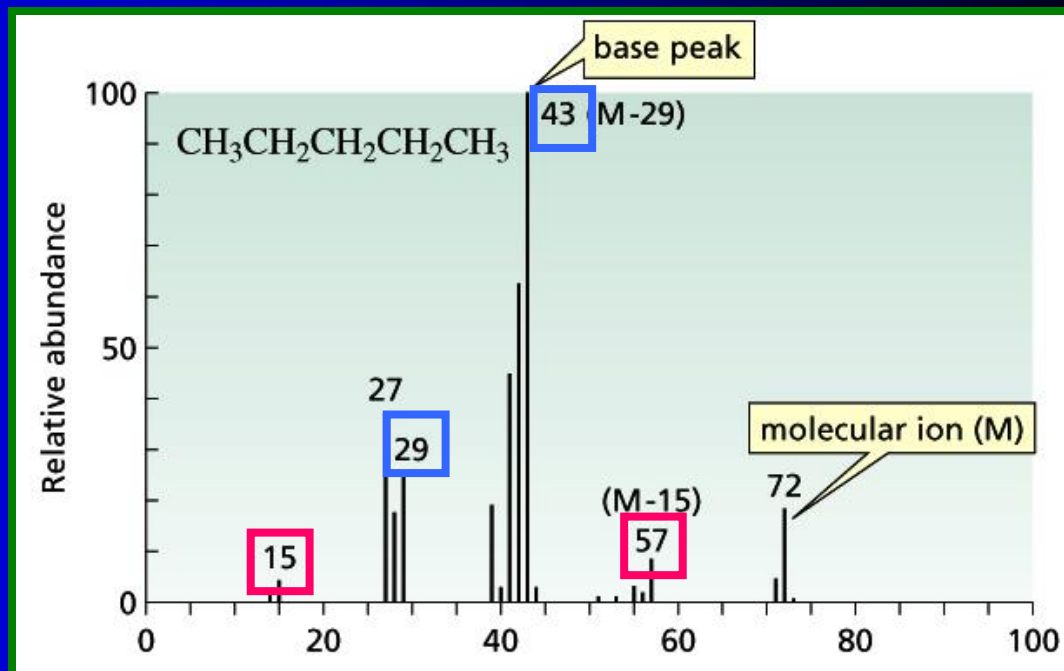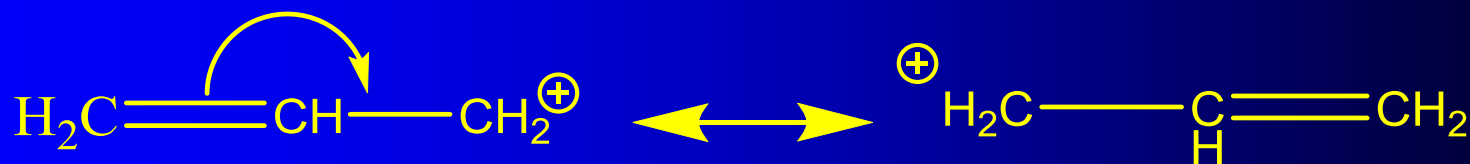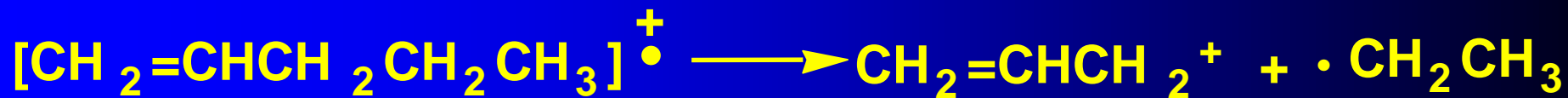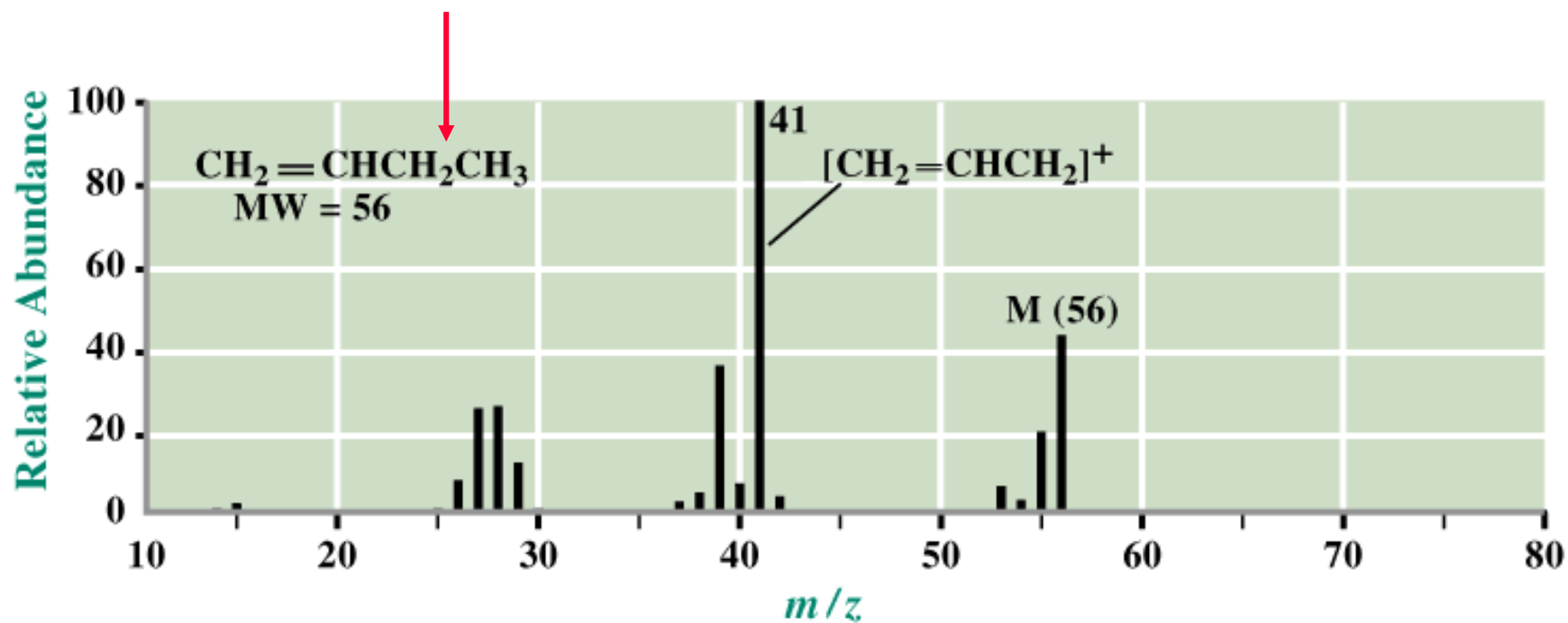
Mass spectrum of 2,2,4-trimethylpentane
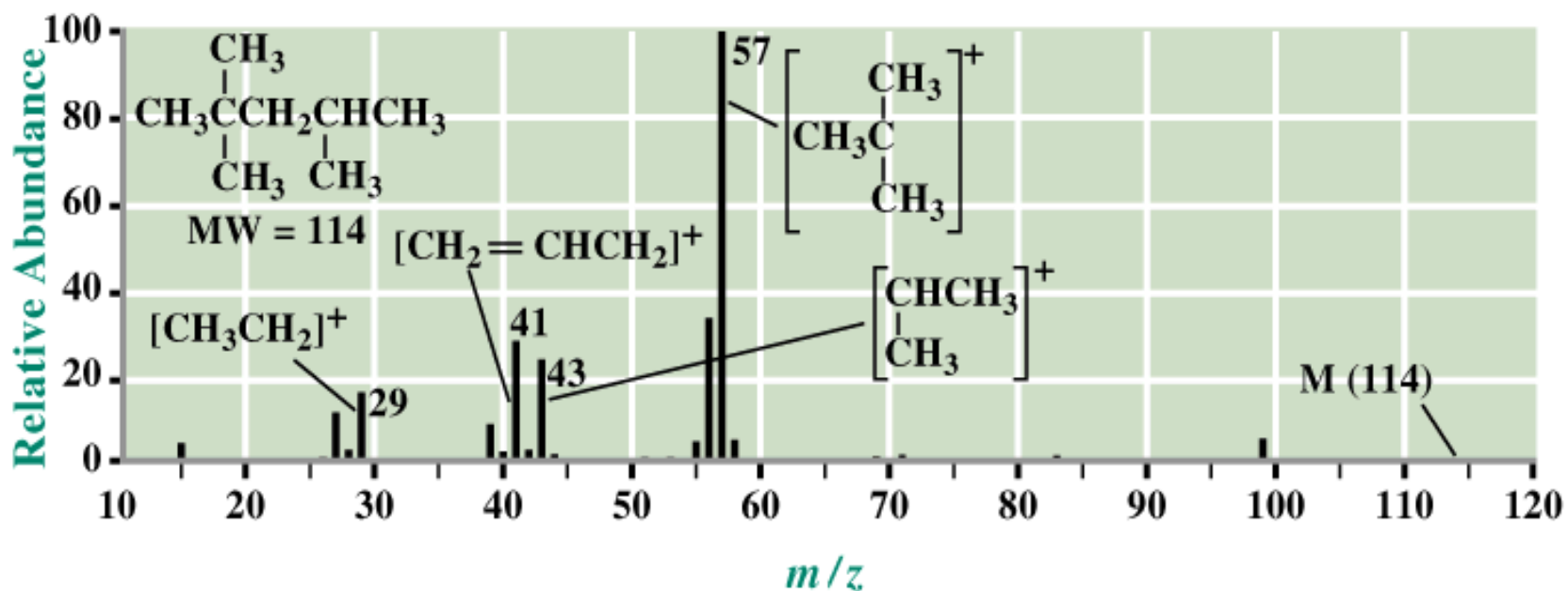
Alkenes

- Alkenes characteristically show a strong molecular ion peak

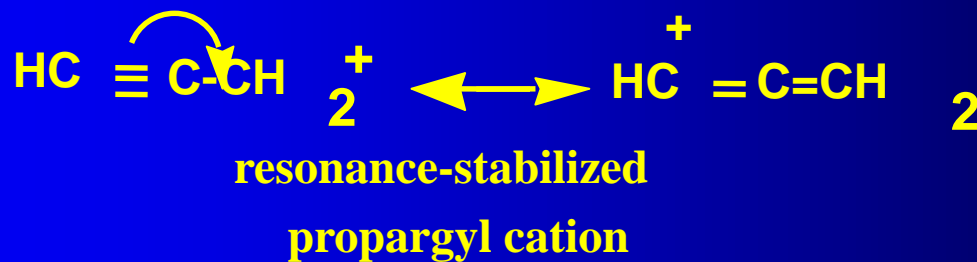- They cleave readily to form resonance-stabilized allylic cations

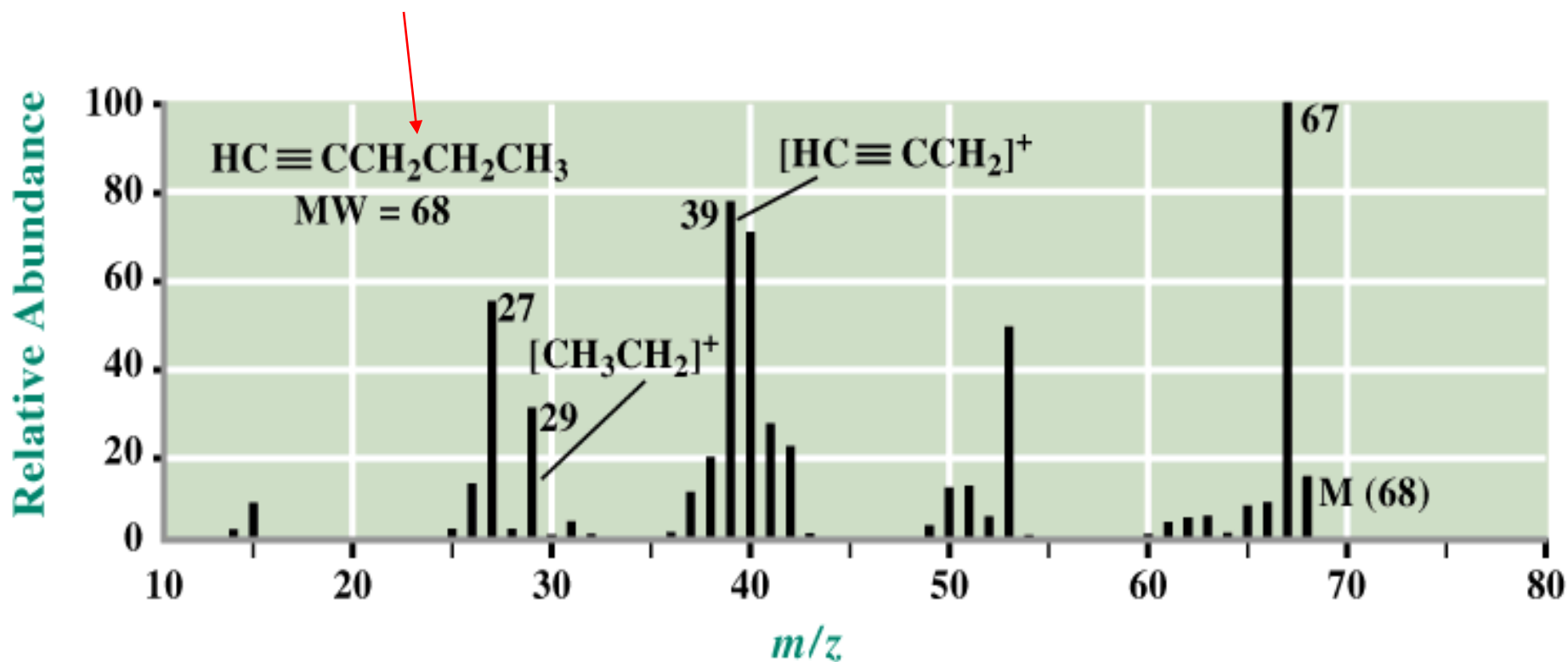$$[CH_2=CHCH_2CH_2CH_3]^{+\bullet} \longrightarrow CH_2=CHCH_2^+ \;+\; \bullet CH_2CH_3$$

Mass spectrum of 1-butene

CH_2=$CHCH_2CH_3$
MW = 56

41

$[CH_2$=$CHCH_2]^+$

M (56)

Relative Abundance

m / z

Alkynes

- Alkynes typically show a strong molecular ion peak

- They cleave readily to form the resonance-stabilized propargyl cation or a substituted propargyl cation

$$HC \equiv C-CH_2^+ \longleftrightarrow HC^+ = C=CH_2$$

resonance-stabilized

propargyl cation

Mass spectrum of 1-pentyne

$HC \equiv CCH_2CH_2CH_3$

MW = 68

$[HC \equiv CCH_2]^+$

39

27

$[CH_3CH_2]^+$

29

67

M (68)

Relative Abundance

100

80

60

40

20

0

m/z

10   20   30   40   50   60   70   80

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

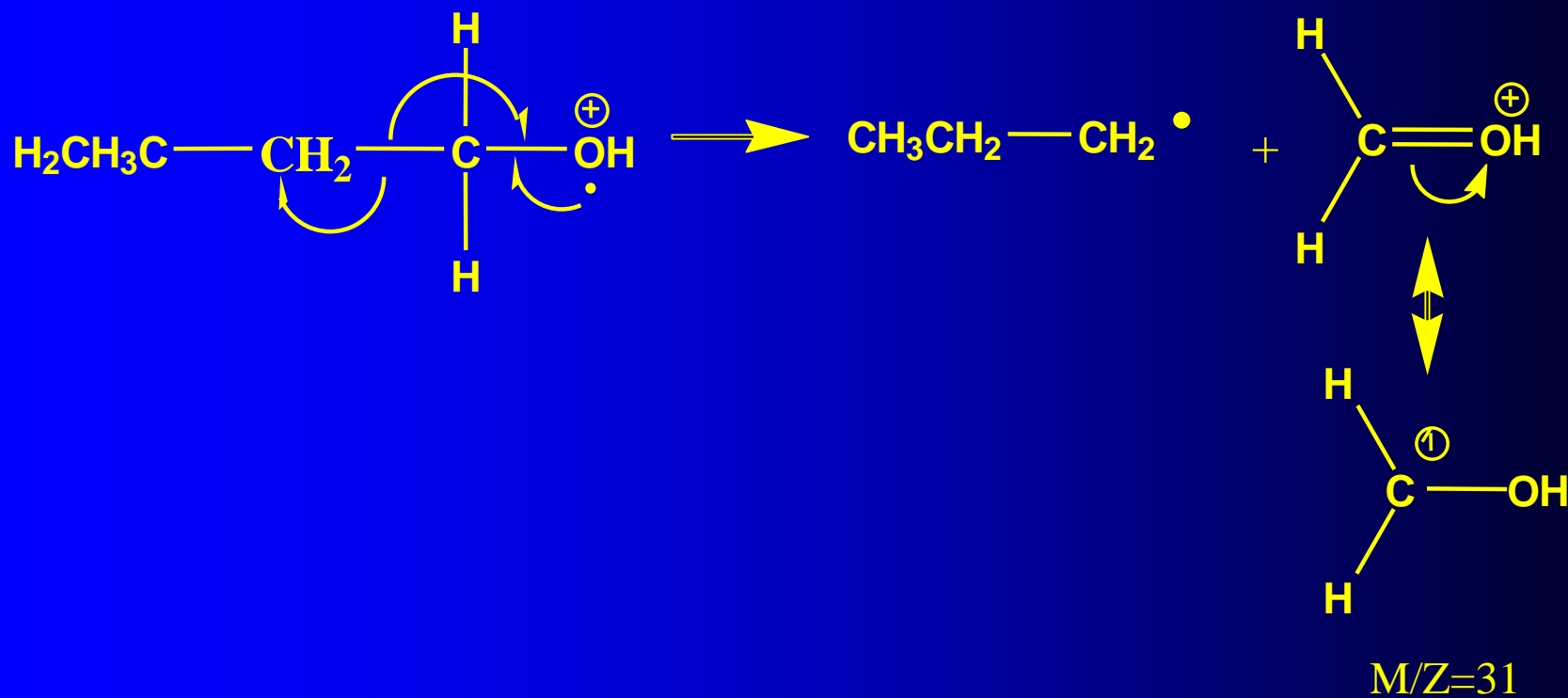# Alcohols
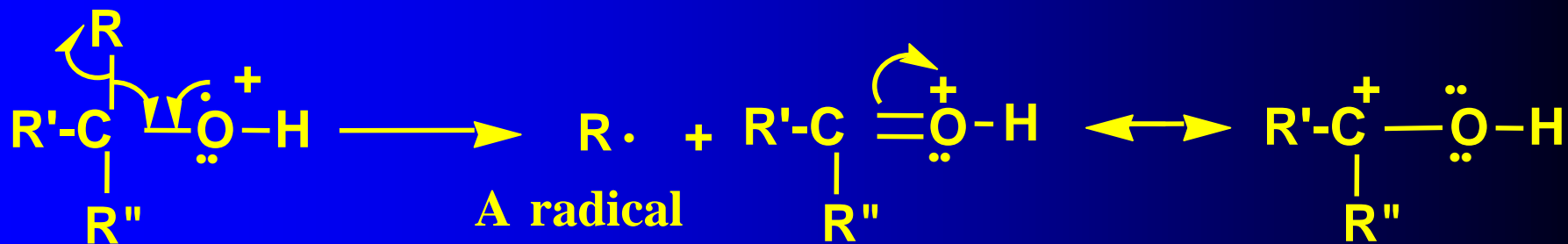
**Molecular ion
(a radical cation)**
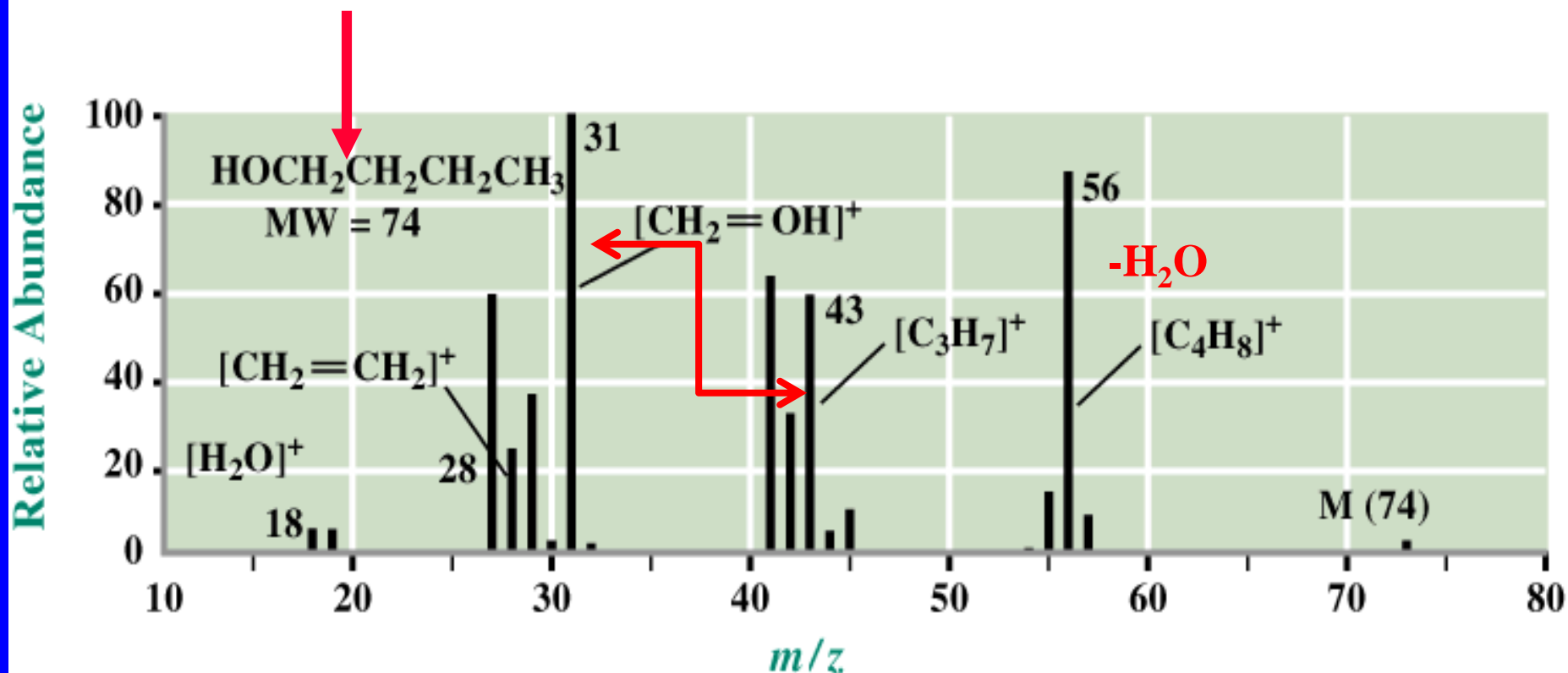
A radical

**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

$HOCH_2CH_2CH_2CH_3$
MW = 74

$[CH_2{=}OH]^+$ — 31

$[CH_2{=}CH_2]^+$
$[H_2O]^+$
18
28
43
$[C_3H_7]^+$
56
-H_2O
$[C_4H_8]^+$
M (74)

Relative Abundance
m/z

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

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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 radical

- We need to know a bit about fragmengtation of :
  - Alkanes, alkenes, alkynes and alcohols

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Molecular Spectroscopy

- Molecular spectroscopy: the study of the frequencies of electromagnetic radiation that are absorbed or emitted by substances and the correlation between these frequencies and aspects of molecular structure

The electromagnetic spectrum

E = hν
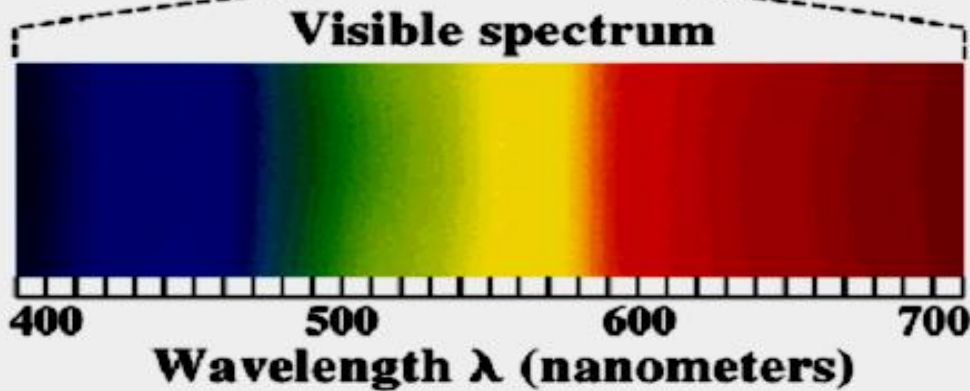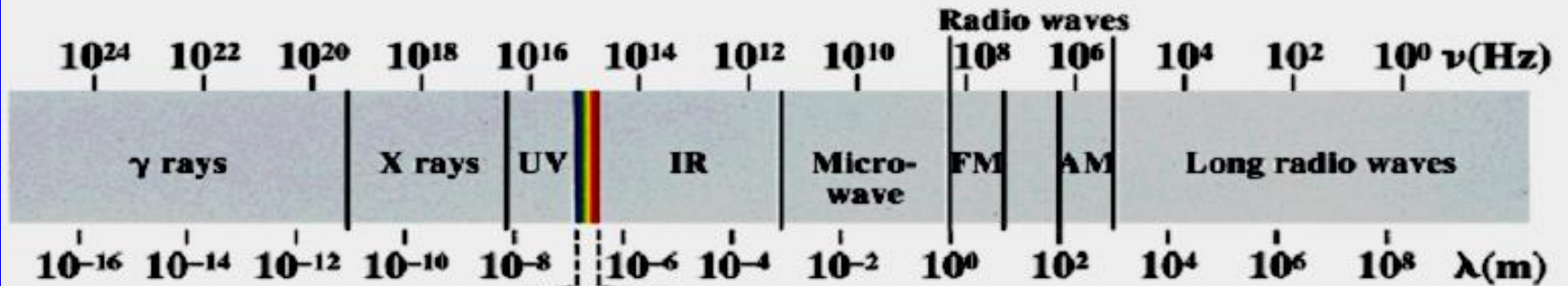
Energy per photon

Frequency

Wave Length

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Electromagnetic Radiation

- Electromagnetic radiation: light and other forms of radiant energy

- Wavelength (λ): the distance between consecutive identical points on a wave

- Frequency (ν): the number of full cycles of a wave that pass a point in one second

- Hertz (Hz): the frequency unit; s^{-1} (read "per second")

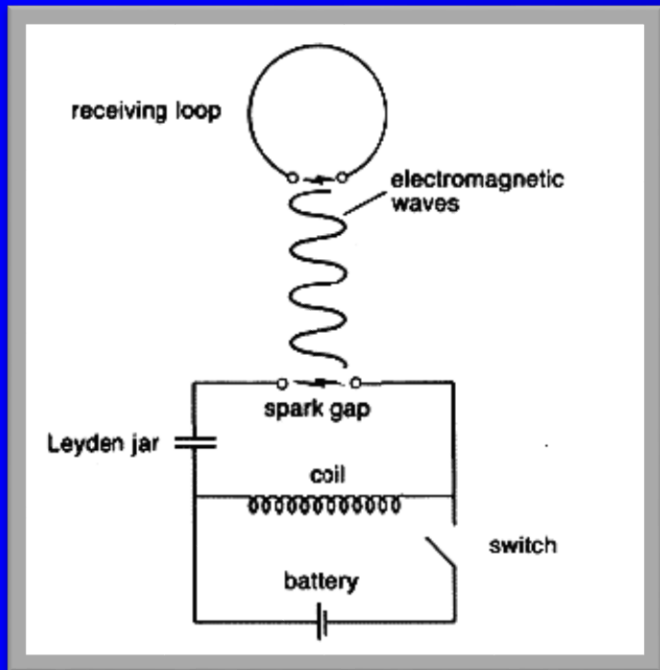# Heinrich Rudolph Hertz

Born: 22 February 1857 in Hamburg
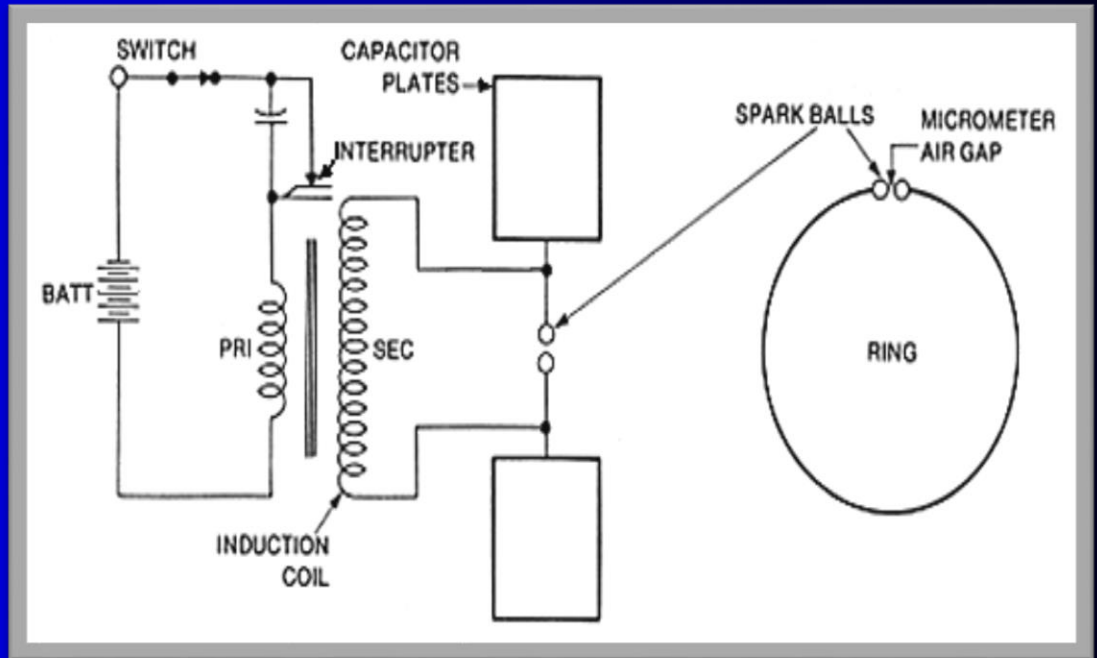**Died: 1 January 1894 in Bonn**

- **Hertz (Hz)**
  - the SI unit of frequency, equal to one cycle per second. The hertz is used to measure the rates of events that happen periodically in a fixed and definite cycle. The frequencies of radio and television waves are measured in kilohertz (kHz), megahertz (MHz), or even gigahertz (GHz), and the frequencies of light waves in terahertz (THz). The unit is named for the German physicist Heinrich Rudolf Hertz (1857-1894), who proved in 1887 that energy is transmitted through a vacuum by electromagnetic waves.

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The Hertz Experiment 1887

CONCEPTUAL DESIGN

MORE DETAIL

The Hertz Experiment

2. Spark produces electromagnetic waves

3. Electromagnetic waves create electric current in resonator, produces small spark in spark gap

1. Induction coil produces high voltage