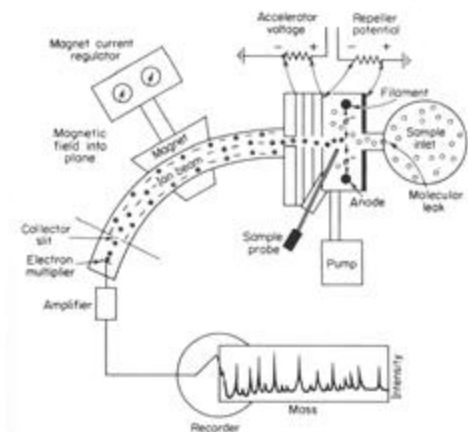
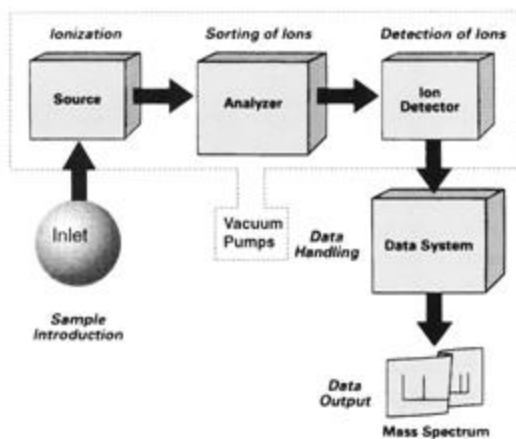


I. Mass spectrometry: capable of providing both quantitative and qualitative information about samples as small as 100 pg (!) and with molar masses in the 10^4 - 10^5 kDalton range

A. The mass spectrometer has three functions

1. Produce ions
2. Separate the ions based on their mass to charge (m/e) ratio
3. Measure the relative abundance of the ions that are produced

B. Instrumentation



1. Sample may be solid, liquid, or vapor
 - a. Solids and liquids may be converted to the vapor phase via sublimation or evaporation through the combination of elevated temperature and low pressure
 - b. Ion beams may also be used to vaporize samples
2. The sample is vaporized, introduced into a vacuum chamber, and ionized
 - a. Electron impact

- b. Chemical ionization
 - c. Fast atom bombardment
 - d. Secondary ion MS (SIMS)
 - e. Laser desorption
 - f. Field desorption
 - g. Electrospray
 - h. Californium-252
3. Ions are accelerated into a mass analyzer and sorted by m/e ratio
 - a. Magnetic sector and/or electrostatic field
 - b. Quadrupole
 - c. Time of flight (TOF)
 - d. Ion trapping and Fourier transform - ion cyclotron resonance (FT-ICR MS)
 4. Ions with the appropriate m/e ratio pass through the mass analyzer to the detector
 5. In the detector ions generate a signal proportional to the number of ions that reach the detector

C. Theory

1. Sample vapor is bombarded with an electron beam which ionizes a small percentage of the vapor phase molecules
2. Both positive and negative ions are formed
3. Positive ions are accelerated into the magnetic field: $\frac{1}{2}mv^2 = eV$
 - a. m: ion mass
 - b. v: ion velocity
 - c. V: accelerating plate potential
 - d. e: electron charge
4. Ions are deflected in the magnetic field along a curved path as described by: $r = mv/eB$

- a. r: path radius
 - b. m: ion mass
 - c. v: ion velocity
 - d. B: field strength
 - e. e: electron charge
5. The equations can be recombined: $m/e = B^2 r^2 / 2V$
 6. At given values of B and V, only particles with a specific m/e ratio will pass through the B field and reach the detector
 7. Ions are usually only singly charged (why?)
 8. Spectra can be generated either by scanning through V or B
- D. Resolution: the ability to present as separate two peaks with nearly equal m/e values, peak overlap 10% or less of peak height
1. $R = M/dM$
 - a. R: resolution
 - b. M: mass of the higher mass peak
 - c. dM: difference in mass between the peaks
 2. Values of resolution and implications
 - a. Low resolution: around 2 - 3,000 (2000/2000-1999)
 - b. High resolution: 10,000 - 15,000 and higher; resolution of 25,000 - 50,000 can be achieved and resolutions in excess of 700,000 have been reported
 - c. An instrument with a resolution of 10,000 can separate an ion of mass 500.00 from an ion of mass 499.95
 - d. An instrument with a resolution of only 3,000 can provide information that is correct within 0.00001 amu for compounds with molar masses in the 25-50 amu range
- E. The mass spectrum: a mass spectrum is a graph of ion abundance vs. mass to charge ratio
1. The two most important features on a mass spectrum are the molecular ion and the base peak
 2. The molecular ion corresponds to the molecular weight of the compound

- One of the fundamental goals in MS: to identify the molecular ion peak
- The base peak is the most intense peak and given a relative abundance value of 100%; the intensities of all other peaks are expressed relative to the intensity of the base peak
- The molecular ion peak is not always the base peak
- Fragmentation of molecules very often occurs; the masses of fragments can also be used to help identify compounds
- The masses of peaks are the sums of the masses of specific isotopes, not the average masses found on the Periodic Table
 - Exact masses and abundances of isotopes** (pdf, 6 kb)

- A comparison of four compounds with nominal masses of 28

CO	N ₂	CH ₂ N	C ₂ H ₄
¹² C 12.0000	¹⁴ N ₂ : 14.0031 x 2	¹² C 12.0000	¹² C 12.0000
¹⁶ O: 15.9949		¹ H: 1.00783 x 2	¹ H: 1.00783 x 4
		¹⁴ N ₂ : 14.0031	
total: 27.9949	total: 28.0062	total: 28.0187	total: 28.0312

- A mass spectrometer with a resolution greater than 3,000 at this mass will be able distinguish between all four molecules

F. Recognition of the molecular ion peak

- Sometimes the molecular ion is weak or does not appear at all, based on ion stability
- Prominent molecular ion peaks: aromatic compounds > conjugated alkenes > cyclic compounds > organic sulfides > short unbranched alkanes > mercaptans
- Recognizable molecular ion peaks: ketones > amines > esters > ethers > carboxylic acids > aldehydes > amides > halides
- Frequently not detectable: aliphatic alcohols, nitrites, nitrates, nitro compounds, nitriles, and highly branched compounds
- The presence of an (M - 15) peak due to loss of a CH₃- group, an (M-18) peak due to the loss of H₂O, or an (M-31) peak due to the loss of CH₃O- in esters or ethers is taken as confirmation of a molecular ion peak

6. (M-1) and (M-2) peaks are also common due to the loss of H or H₂
7. (M-16) due to loss of O, (M-17) due to loss of OH or (M-18) due to loss of water occur in oxygenated compounds
8. (M-3) through (M-14) and (M-19) through (M-25) are rare

G. Determination of molecular formula

1. If the isotope peaks are sufficiently intense to be measured accurately (usually this is always the case with a high resolution instrument), the relative intensities of the isotope peaks (M + 1, M + 2) can usually help determine the molecular formula
 - a. The M+1 peak is the peak containing one isotope with a mass number one greater than that of the molecular ion peak.
 - b. Most commonly only ¹³C, ¹⁵N, and ³³S contribute significantly
 - c. Calculate the ratio of the M+1 peak height for dinitrobenzene (C₆H₄N₂O₄)

¹³ C	6 x 1.08% = 6.48%
² H	2 x 0.016% = 0.060%
¹⁵ N	2 x 0.38% = 0.76%
¹⁷ O	4 x 0.04% = 0.16%
M+1 total	7.46%

- d. The M+2 peak contains one atom with an isotope mass of two greater than the molecular ion peak
 - e. Most commonly only ³⁴S, ³⁷Cl, and ⁸¹Br contribute significantly
2. The "nitrogen rule:" a molecule with an even-number molecular weight must contain no nitrogen atoms or an even-number of nitrogen atoms; a molecule with an odd-number molecular weight must contain an odd-number of nitrogen atoms
 - a. This rule works because even though N has an even molecular weight (14.0067 amu), it is generally trivalent in organic compounds (?)
 - b. For a molecule containing nitrogen, fragmentation of an even-numbered ion at a single bond gives a fragment with an odd mass, assuming the new fragment contains all of the N atoms

- c. For a molecule containing nitrogen, fragmentation of an odd-numbered ion at a single bond gives a fragment with an even mass, assuming the new fragment contains all of the N atoms
- d. Compounds containing odd numbers of N atoms in the Beynon tables with even molecular weights must not be naturally occurring but fragments formed during various events after ionization occurs
3. Tables (e.g. commonly Beynon Tables) of formula masses, M+1, and M+2 values make it possible to identify the molecular formula for a given mass
- a. A compound gives the following mass spectrum

m/e	percent
100 (M)	100
101 (M+1)	5.64
102 (M+2)	0.60

The molecular formula is ascertained by comparing the empirical data to **Beynon tables** (pdf file, 8.6 Mb)

100			
CN ₄ O ₂	2.68	0.43	100.0022
C ₂ N ₂ O ₃	3.04	0.63	99.9909
C ₂ H ₂ N ₃ O ₂	3.42	0.45	100.0147
C ₂ H ₄ N ₄ O	3.79	0.26	100.0386
C ₃ O ₄	3.40	0.84	99.9796
C ₃ H ₂ NO ₃	3.77	0.65	100.0034
C ₃ H ₄ N ₂ O ₂	4.15	0.47	100.0273
C ₃ H ₆ N ₃ O	4.52	0.28	100.0511
C ₃ H ₈ N ₄	4.90	0.10	100.0750
C ₄ H ₄ O ₃	4.50	0.68	100.0160
C ₄ H ₆ NO ₂	4.88	0.50	100.0399
C ₄ H ₈ N ₂ O	5.25	0.31	100.0637
C ₄ H ₁₀ N ₃	5.63	0.13	100.0876
C ₅ H ₈ O ₂	5.61	0.53	100.0524
C ₅ H ₁₀ NO	5.98	0.35	100.0763
C ₅ H ₁₂ N ₂	6.36	0.17	100.1001
C ₆ H ₁₂ O	6.71	0.39	100.0888
C ₆ H ₁₄ N	7.09	0.22	100.1127
C ₆ N ₂	7.25	0.23	100.0062
C ₇ H ₁₆	7.82	0.26	100.1253
C ₇ O	7.60	0.45	99.9949
C ₇ H ₂ N	7.98	0.28	100.0187
C ₈ H ₄	8.71	0.33	100.0313

C₅H₈O₂ gives the best fit

b. A compound gives the following mass spectrum

m/e	percent
150 (M)	100
151 (M+1)	10.2
152 (M+2)	0.88

The molecular formula is ascertained by comparing the empirical data to **Beynon tables** (pdf file, 8.6 Mb)

150			
$C_4H_{10}N_2O_4$	5.40	0.92	150.0641
$C_4H_{12}N_3O_3$	5.78	0.74	150.0879
$C_4H_{14}N_4O_2$	6.15	0.56	150.1118
$C_5H_{12}NO_4$	6.13	0.96	150.0766
$C_5H_{14}N_2O_3$	6.51	0.78	150.1005
$C_5N_3O_3$	6.66	0.79	149.9940
$C_5H_2N_4O_2$	7.04	0.62	150.0178
$C_6H_{14}O_4$	6.86	1.00	150.0892
C_6NO_4	7.02	1.01	149.9827
$C_6H_2N_2O_3$	7.40	0.84	150.0065
$C_6H_4N_3O_2$	7.77	0.67	150.0304
$C_6H_6N_4O$	8.14	0.49	150.0542
$C_7H_2O_4$	7.75	1.06	149.9953
$C_7H_4NO_3$	8.13	0.89	150.0191
$C_7H_6N_2O_2$	8.50	0.72	150.0429
$C_7H_8N_3O$	8.88	0.55	150.0668
$C_7H_{10}N_4$	9.25	0.38	150.0907
$C_8H_6O_3$	8.86	0.95	150.0317
$C_8H_8NO_2$	9.23	0.78	150.0555
$C_8H_{10}N_2O$	9.61	0.61	150.0794
$C_8H_{12}N_3$	9.98	0.45	150.1032
$C_9H_{10}O_2$	9.96	0.84	150.0681
$C_9H_{12}NO$	10.34	0.68	150.0919
$C_9H_{14}N_2$	10.71	0.52	150.1158
C_9N_3	10.87	0.54	150.0093
$C_{10}H_{14}O$	11.07	0.75	150.1045
$C_{10}H_{16}N$	11.44	0.60	150.1284
$C_{10}NO$	11.23	0.77	149.9980
$C_{10}H_2N_2$	11.60	0.61	150.0218
$C_{11}H_{18}$	12.17	0.68	150.1409
$C_{11}H_2O$	11.96	0.85	150.0106
$C_{11}H_4N$	12.33	0.70	150.0344
$C_{12}H_6$	13.06	0.78	150.0470

$C_9H_{10}O_2$ gives the best fit, although $C_8H_{10}N_2O$ is also a possibility

c. When elements other than C, H, N, and O are present, the number of type of each atom must be determined and the sum subtracted from the observed molecular weight

H. The molecular formula and the index of hydrogen deficiency

1. The molecular formula provides information about the numbers and types of atoms in a compound
2. It also provides information about the index of hydrogen deficiency, i.e., the number of pairs of hydrogen atoms the compound is missing due either to the presence of double bonds, triple bonds, and rings
 - a. The index is also known as double bond equivalence
3. Index = # carbons (tetravalent atoms) - (monovalent atoms/2) + (trivalent atoms/2) + 1
 - a. Tetravalent atoms: C, Si
 - b. Monovalent atoms: H, halogens
 - c. Divalent atoms: O, S
 - d. Trivalent atoms: N, P
4. The Octet Rule must be obeyed when drawing the Lewis structures that correspond to predicted structures, i.e., every atom in the structure must have an octet regardless of any resulting formal charges
5. Examples
 - a. Methane CH_4 $I = 1 - 4/2 + 1 = 0$
 - b. Ethene C_2H_4 $I = 2 - 4/2 + 1 = 1$
 - c. Ethyne C_2H_2 $I = 2 - 2/2 + 1 = 2$
 - d. 1,3 butadiene C_4H_6 $I = 4 - 6/2 + 1 = 2$
 - e. Cyclohexane C_6H_{12} $I = 6 - 12/2 + 1 = 1$
 - f. Cyclohexene C_6H_{10} $I = 6 - 10/2 + 1 = 2$
 - g. Benzene C_6H_6 $I = 6 - 6/2 + 1 = 4$

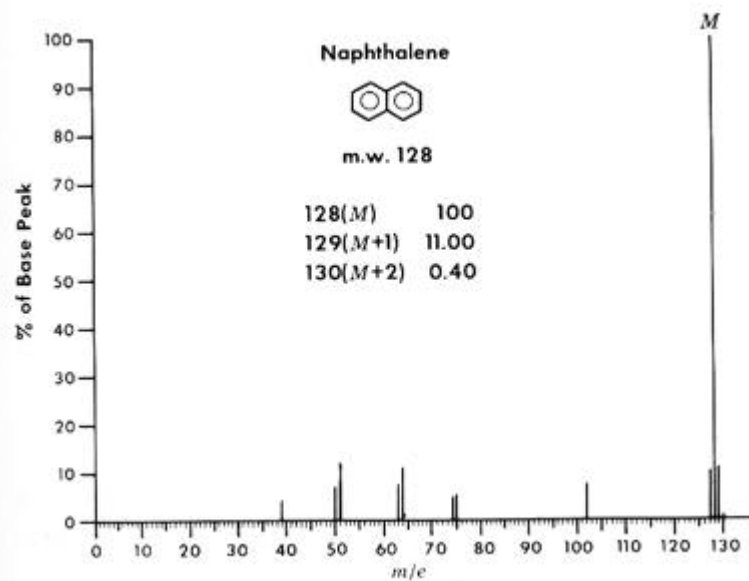
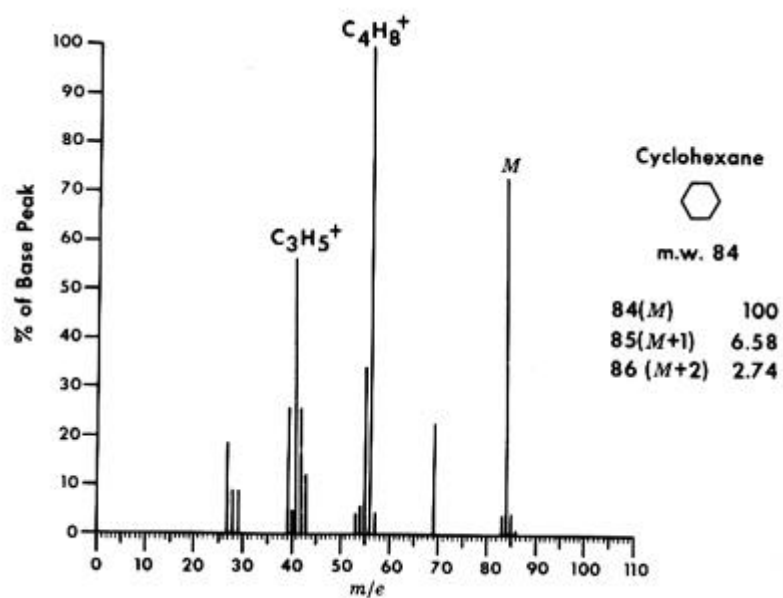
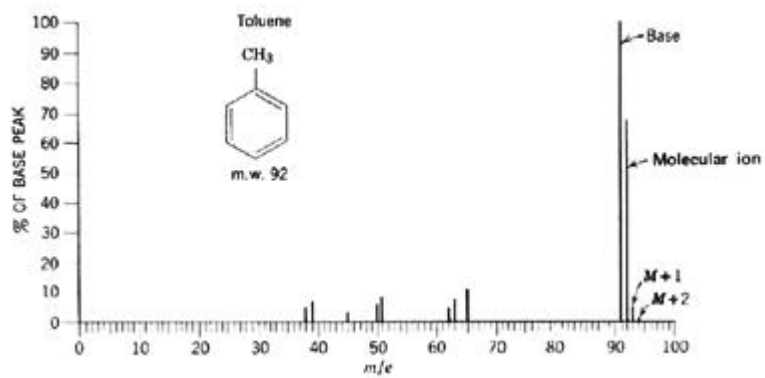
I. General rules for EI fragmentation: usually interpretation of fragmentation patterns can be based on the known behavior of carbocations in solution

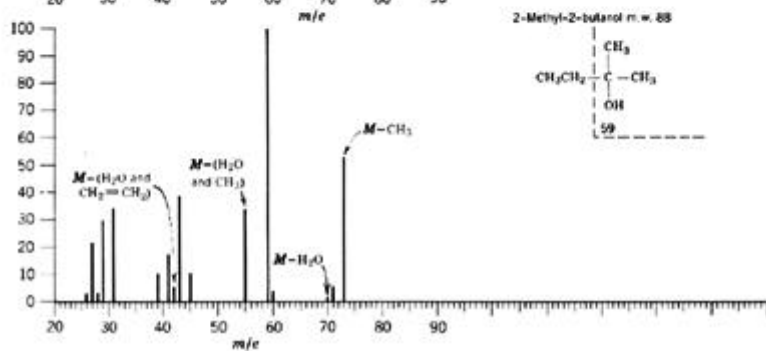
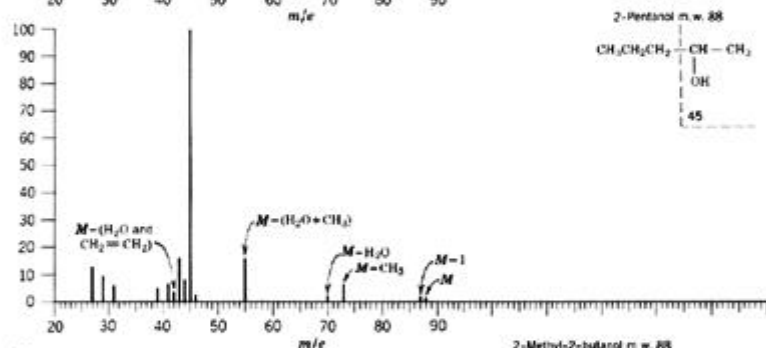
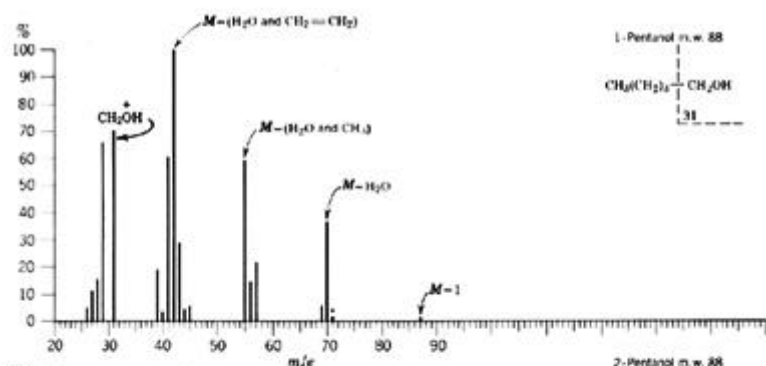
1. The relative height of the molecular ion peak is greatest for straight-chain compounds and decreases as the degree of branching increases
2. The relative height of the molecular ion peak usually decreases with increasing molecular weight in a homologous series
3. Cleavage is favored at substituted carbons in accord with the known

stabilities of the various carbocations and free radicals. The generally the largest substituent at a branch is eliminated and often as a radical in which the structure is stabilized by electron delocalization throughout the structure

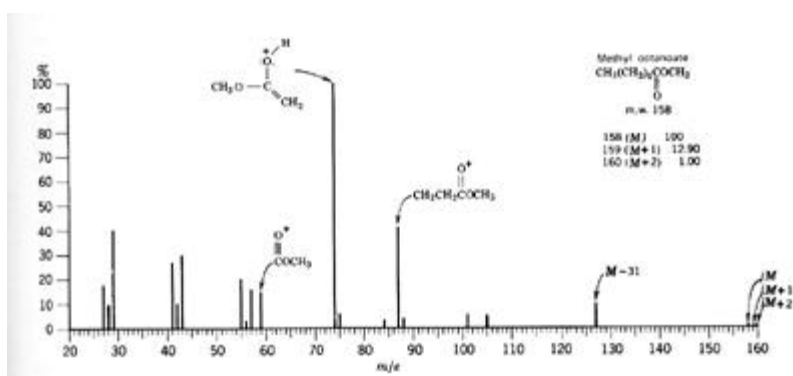
4. Double bonds, cyclic structures, and especially aromatic/heteroaromatic rings stabilize the molecular ion and increase the likelihood of its appearance
 5. Double bonds favor allylic cleavage and result in allylic stabilized carbocations
 6. Saturated rings tend to lose side chains at the alpha bond, i.e., the bond between the the ring and the substituent. Unsaturated rings can undergo retro Diels-Alder reactions, yielding a diene and a dienophile.
 7. In alkyl-substituted aromatic rings cleavage is often at the bond beta to the ring (i.e., between the first two carbons in the substituent backbone) resulting in a resonance stabilized benzyl carbocation
 8. C-C bonds next to a heteroatom are often cleaved, leaving the charge on the heteroatom which can provide resonance stabilization of the charge with nonbonding pairs of electrons
 9. Cleavage resulting in the formation and elimination of small neutral molecules such as water, carbon monoxide, olefins, ammonia, hydrogen sulfide, hydrogen cyanide, mercaptans, ketene, and alcohols is common
- J. Rearrangements: often indicated by the presence of fragments that cannot be accounted for by simple bond breaking
1. Rearrangements are common and often result in prominent spectral peaks
 2. Rearrangements can be as simple as a hydride shift and are often the result of the elimination of stable neutral molecules and/or the formation of a more stable product
 3. Since the excited state achieved by EI is much higher than the excited state normally achieved in chemical reactions, many products of rearrangement are more complex than might be expected and defy prediction e.g., neopentane and CH_3CH_2^+ ion

K. Additional interpretation:





4.



5.

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