Mass Spec and Molecular Formula
S343 Lecture Problem Set

Basic questions:

1. Give three molecular formulas that are consistent with $M^+ = 122$.

Rule of 13 gives 9 remainder 5. C_9H_{14}, $C_8H_{12}O$, $C_7H_{10}O_2$, $C_7H_{10}N_2$

2. Why is there a small peak at $M^+ = 32$ for CH_3NH_2?

This is the M^++1 peak arising from ^{13}C isotope.

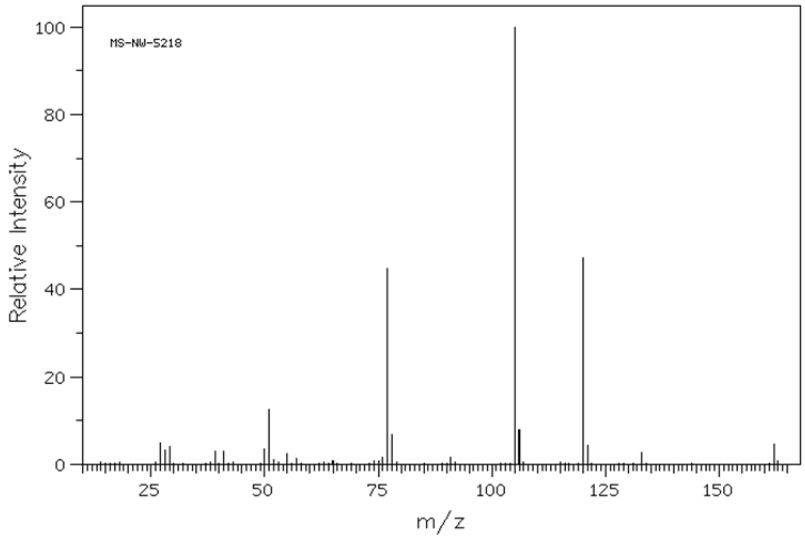
3. What is a MS library, and how is it used?

It is a database of Mass Spectra of known compounds. A computer algorithmically checks an unknown sample MS against a library, giving a very useful technique for identifying unknowns with high probability.

4. What is high resolution MS, and what advantage does is have over low resolution MS?

HRMS is able to determine a mass to charge ratio to four places past the decimal. Therefore, it can be used to dtistinguish between MF with the same nominal m/z. For example, both C_9H_{14} and $C_8H_{12}O$ have the same nominal mass of 122, but they are distinct at high resolution. (C_9H_{14} = 122.2075 and $C_8H_{10}O$ = 122.1644.

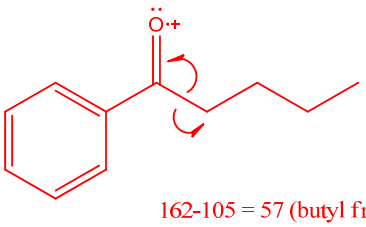
5. The questions below refer to this Mass Spectrum of 1-phenylpentan-1-one:



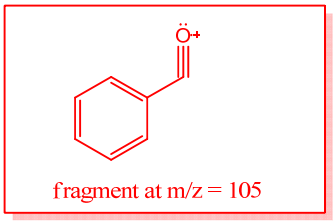
A. What causes the small peak at m/z 162?

This is the molecular ion peak. It is small, suggesting a large degree of fragmentation

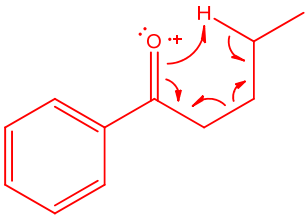
B. Provide a mechanism and fragment structure that lead to formation of the base peak at m/z = 105.



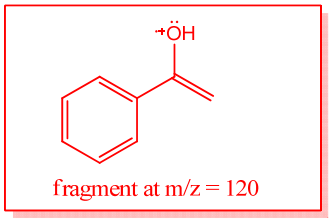
162-105 = 57 (butyl fragment)



C. Provide a mechanism and fragment structure that lead to formation of the significant peak at m/z = 120.



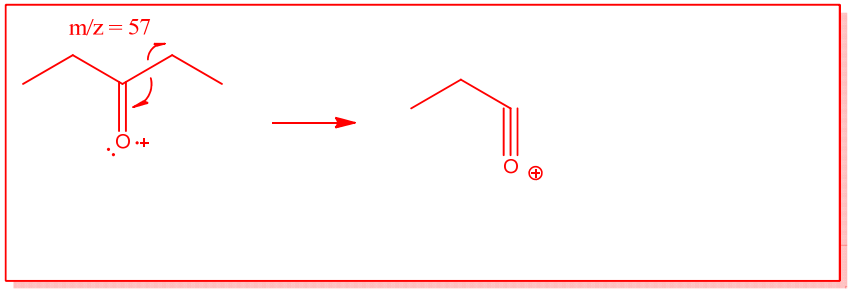
120 is even--McLafferty

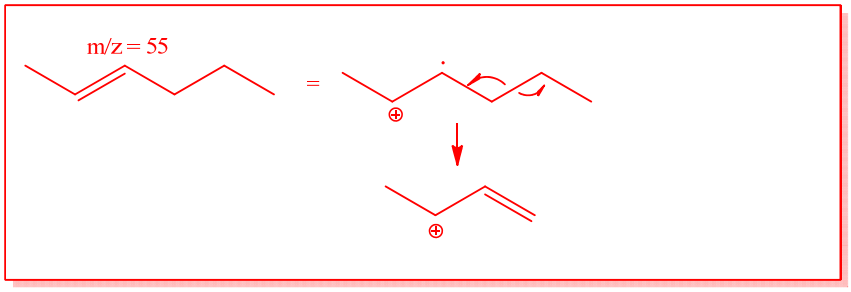


6. Use the rule of 13 to come up with 3 likely formulas that fit M^+ = 102.

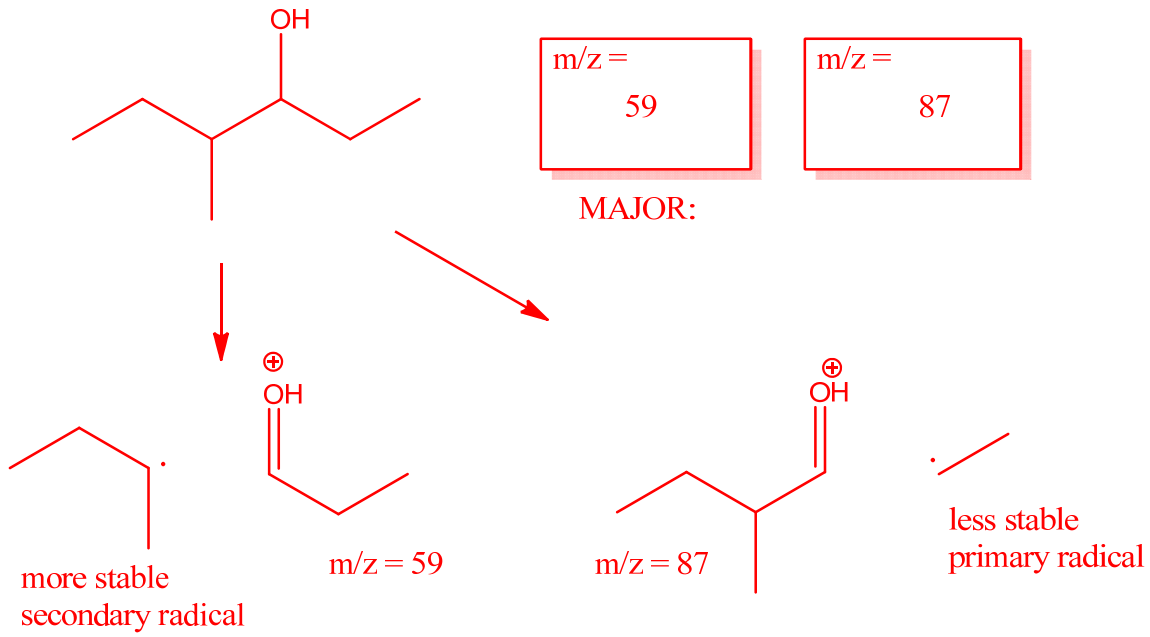
Rule of thirteen gives 7 remainder 11, but this gives an impossible formula of C_7H_{18}. Acceptable formula would include $C_6H_{14}O$, $C_5H_{10}O_2$, and $C_4H_6O_3$.

7. Provide mechanisms to account for the fragments seen in the mass spectrum of these compounds.





8. Give the m/z values of two major fragments you would expect to see in the mass spectrum of the following compound. Mark the one that is most likely to show up as the base peak, and explain.



9. What two circumstances lead to fragments with even m/z values?

A. Molecular ion is ODD (contains nitrogen, etc.)
B. McLafferty rearrangement

10. Give three important pieces of information about the molecular formula of the compound (other than the molecular weight) that you can obtain from this mass spec data.

m/z	Relative abundance
34	21
52	35
91	100
102	22
111 (M^+)	10
113	3.3

m/z of 91 indicates likely trypolium ion

Odd M^+ = likely nitrogen atom

M^++ 2 with 1/3 relative abundance suggests chlorine

11. What are these abbreviations: CI, EI, FAB, ESI, MALDI-TOF

Chemical Ionization—a more mild ionization technique that can lead to less fragmentation
Electron ionization—a standard ionization technique. Molecules get an electron knocked off and become radical cations, which can be sorted by MS
Fast Atom Bombardment—a mild ionization technique
Electrospray ionization—a mild ionization technique useful for large molecules such as proteins
Matrix-assisted Laser desorption ionization-Time of Flight: this mild ionization is often connected to a time of flight mass sorter

Problems

1. The mass spectrum of an unknown compound shows the following peaks. Determine the molecular formula and propose a structure.

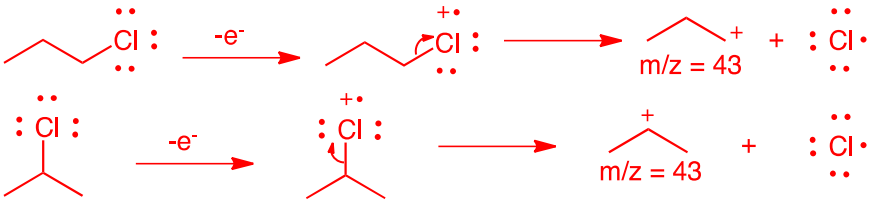
m/z	Relative Abundance
43	100 (base)
78	23.6 (M)
79	1.00
80	7.55
81	0.25

The peak that jumps out first is the M + 2 peak (m/z = 80). The ratio of M to M+2 is around 3, which indicates the presence of a Cl.

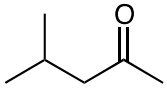
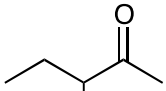
Rule of 13: 78/13 = 6; → C_6H_6 or C_5H_{18}
We guessed that there is a Cl (M = 35 = C_2H_{11}), so the molecular formula would be **C_3H_7Cl**
(You could also subtract 35 from M (78-35=43), and apply the rule of 13 to this mass. You would get the same answer.)

UN = (2 x 3 + 2 – 7 – 1)/2 = 0 → No rings or double bonds. Possible structures:

M – Cl (from above) is 43 – this is also the base peak. This fragment arises from inductive cleavage, and we can't rule out either structure.

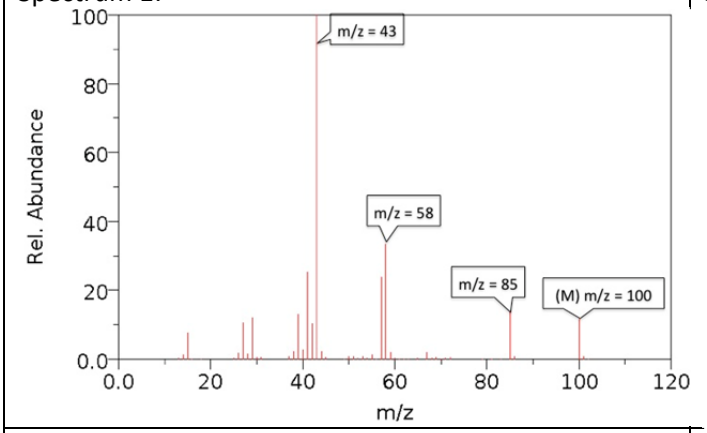


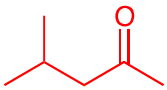
2. The EI mass spectra of the following ketones are shown below.

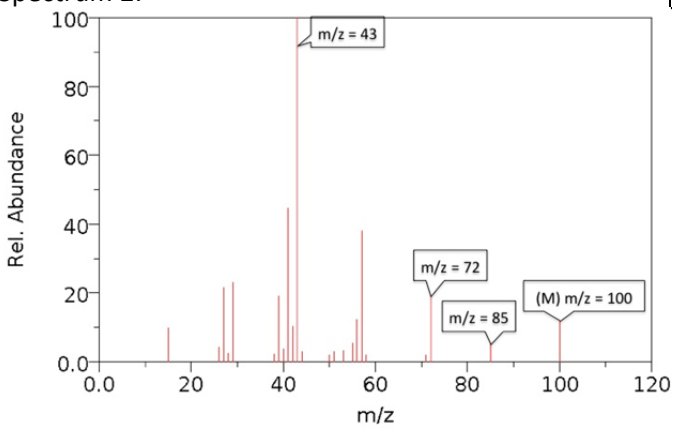
a) Determine which mass spectrum corresponds to each compound, and label the spectra underneath in the space provided.

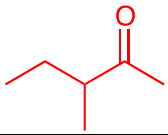
Spectrum 1:



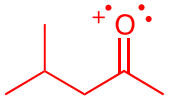
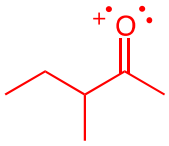
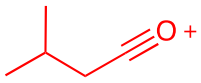
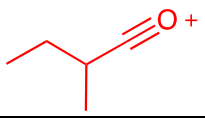
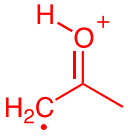
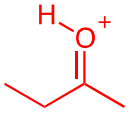
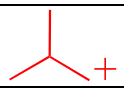
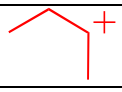


Spectrum 2:





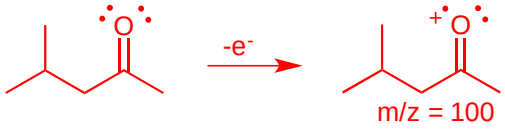
b) Provide structures for each labeled ion in the space provided on the next page. All charges, number of hydrogens, and number of electrons must be clearly indicated in order to receive full credit.

Spectrum 1	**Structure of ion**	**Spectrum 2**	**Structure of ion**
m/z = 100		m/z = 100	
m/z = 85		m/z = 85	
m/z = 58		m/z = 72	
m/z = 57		m/z = 57	
m/z = 43		m/z = 43	

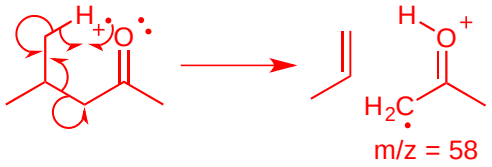
mechanisms:

4-methyl-2-pentanone

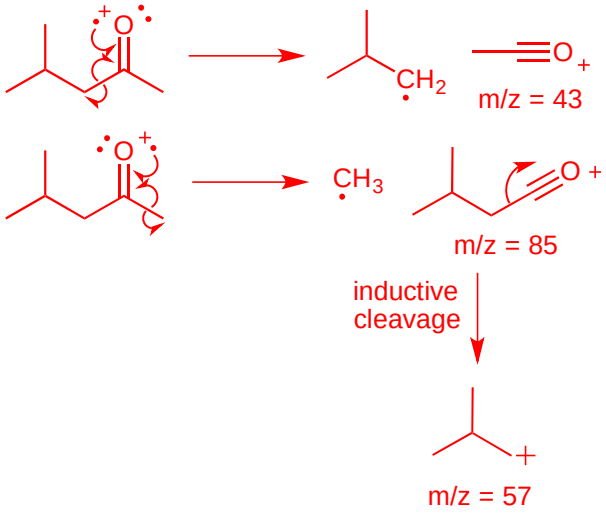
Ionization



McLafferty Rearrangement

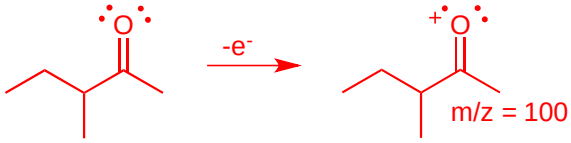


α-fragmentations

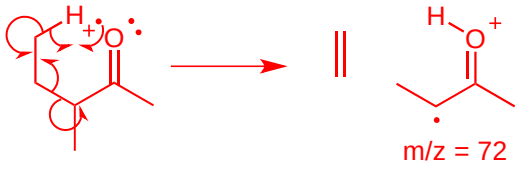


3-methyl-2-pentanone

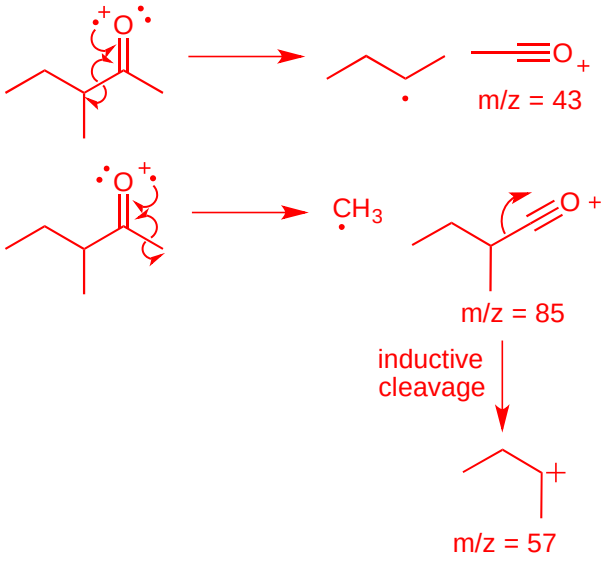
Ionization



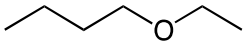
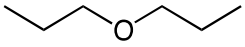
McLafferty Rearrangement



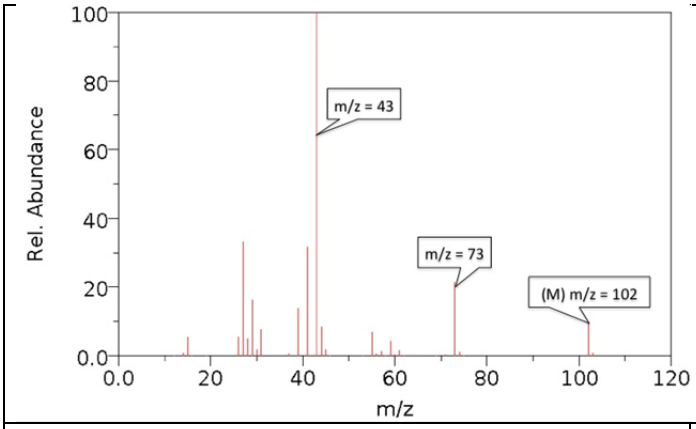
α-fragmentations

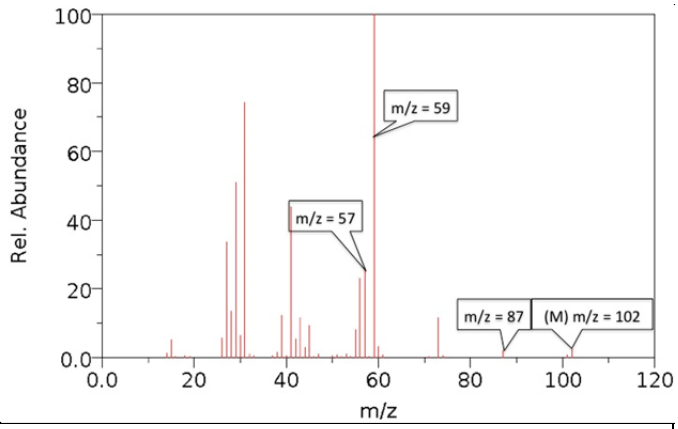


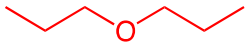
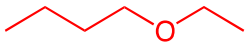
3. The EI mass spectra of the following two ethers are shown below.

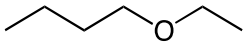
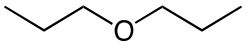
a) Determine which mass spectrum corresponds to each compound, and label the spectra underneath in the space provided.

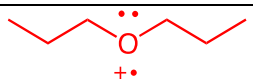
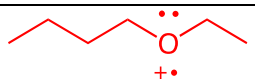
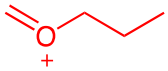
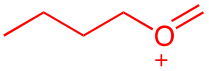
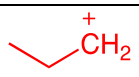
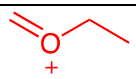




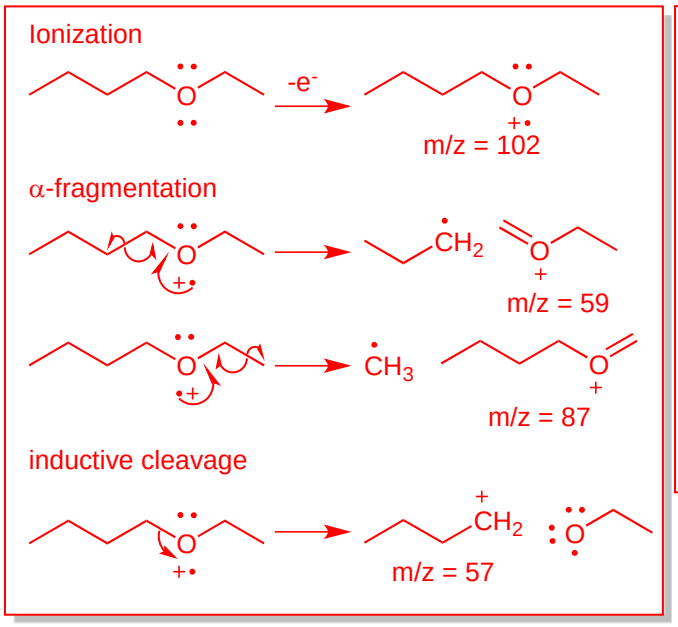



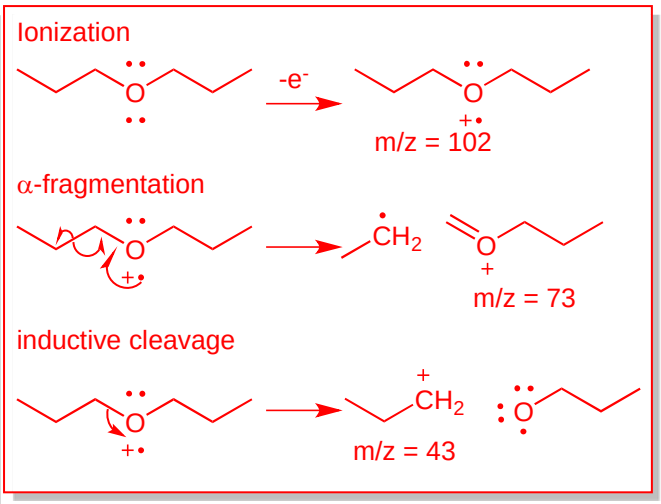
b) Provide structures for each labeled ion in the space provided on the next page. All charges, number of hydrogens, and number of electrons must be clearly indicated in order to receive full credit.

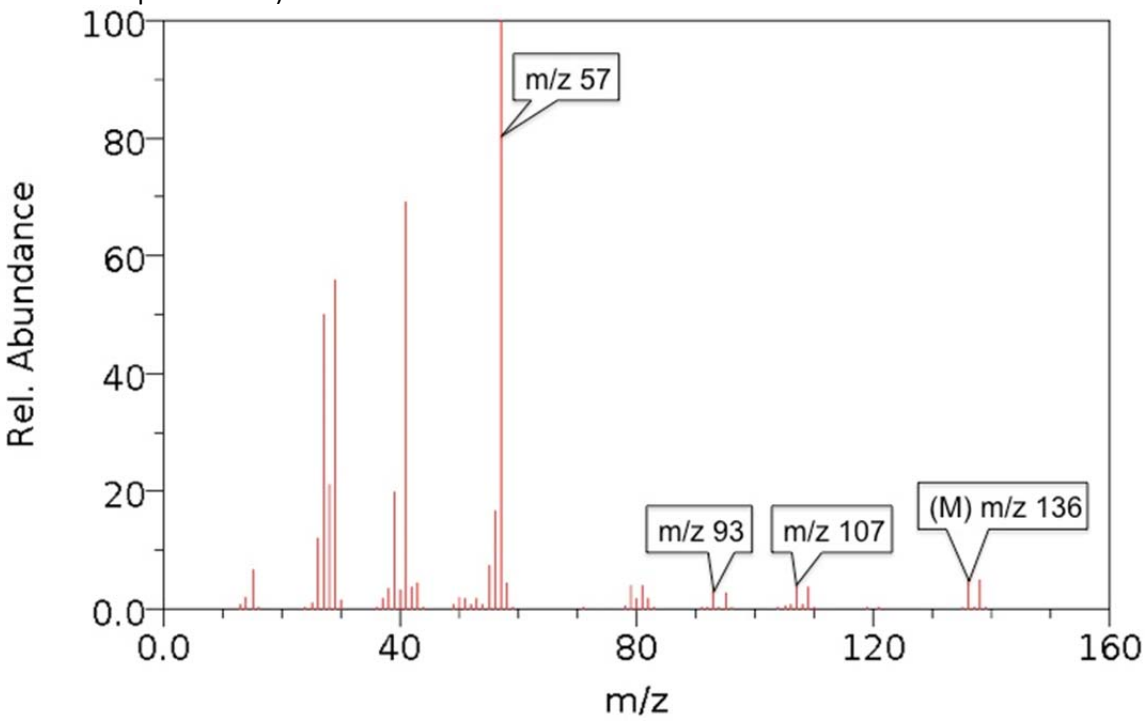
Spectrum 1	Structure of ion	Spectrum 2	Structure of ion
m/z = 102		m/z = 102	
m/z = 73		m/z = 87	
m/z = 43		m/z = 59	
		m/z = 57	

mechanisms:


Ionization
-e-
m/z = 102
α-fragmentation
CH2
m/z = 59
CH3
m/z = 87
inductive cleavage
CH2
m/z = 57


Ionization
-e-
m/z = 102
α-fragmentation
CH2
m/z = 73
inductive cleavage
CH2
m/z = 43

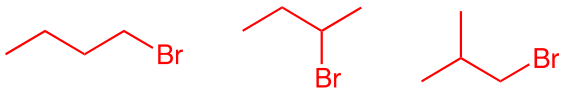
4. Determine the structure of the unknown and account for fragments at 136, 107, 93, and 57. (Why is there no M+2 peak at 59?)



The peak that jumps out first is the M + 2 peak (m/z = 138). The ratio of M to M+2 is around 1, which indicates the presence of a Br.

Subtract Br (79) from M: 136-79 = 57
Rule of 13: 57/13 = 4 5/13; → **C_4H_9Br**

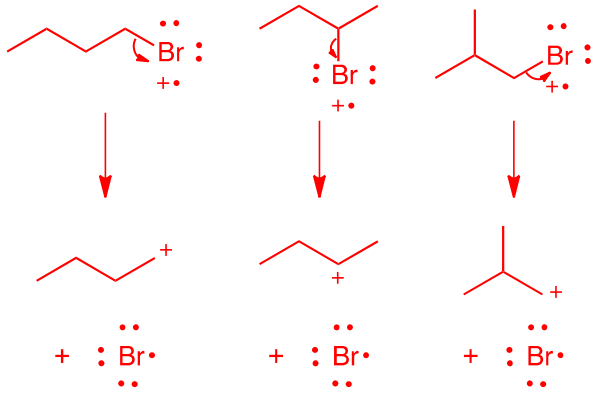
UN = (2 x 4 + 2 – 9 – 1)/2 = 0 → No rings or double bonds. Possible structures:



Draw out all fragmentations using mechanisms you've seen in class, and one new one (formation of bromonium ion). **Molecule is most likely 2-bromobutane**.

Inductive cleavage:

M – **Br** (from above) is 57 – this is also the base peak. There is no Br in this charged fragment, so no M+2 fragment peak at m/z=59. This fragment arises from inductive cleavage and all isomers have it:



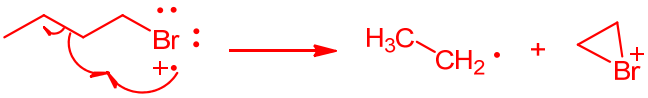
m/z: 57.07 (100.0%), 58.07 (4.3%)

n-bromobutane (m/z = 93, 107)

-fragmentation:

m/z: 92.93 (100.0%), 94.93 (97.3%), 93.94 (1.1%), 95.94 (1.1%)

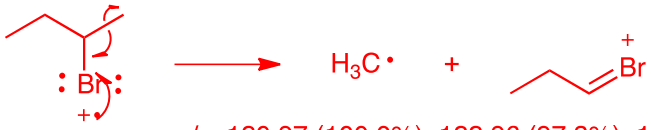
formation of bromonium ion:



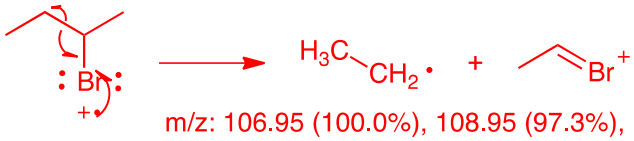
m/z: 107 (100.0%), 109 (97.3%), 108 (2.2%), 110 (2.1%)

2-bromobutane (m/z = 121, 107, 121)

-fragmentations:

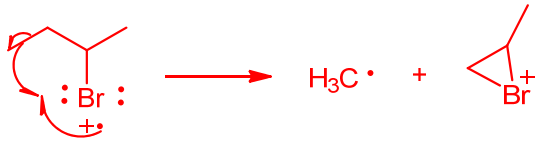


m/z: 120.97 (100.0%), 122.96 (97.3%), 121.97 (3.3%), 123.97 (3.2%)



m/z: 106.95 (100.0%), 108.95 (97.3%), 107.95 (2.2%), 109.95 (2.1%)

formation of bromonium ion:



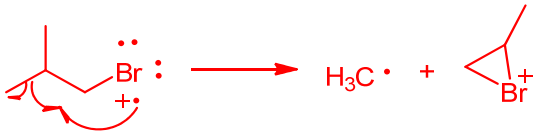
m/z: 121 (100.0%), 123 (97.3%), 122 (3.3%), 124 (3.2%)

iso-butylbromide (m/z = 93, 121)

-fragmentation:

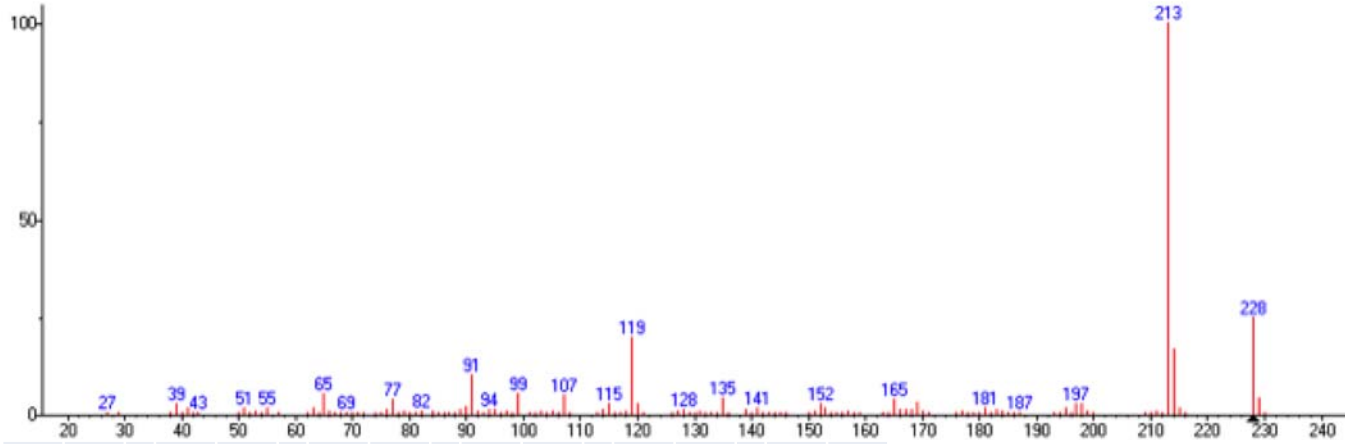
m/z: 92.93 (100.0%), 94.93 (97.3%), 93.94 (1.1%), 95.94 (1.1%)

formation of bromonium ion:



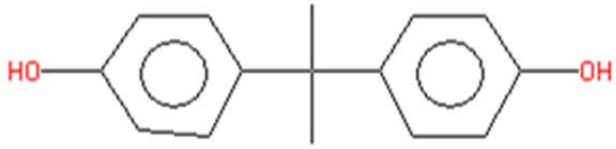
m/z: 121 (100.0%), 123 (97.3%), 122 (3.3%), 124 (3.2%)

5. How many C atoms does the following molecule most likely contain? (M = 228)

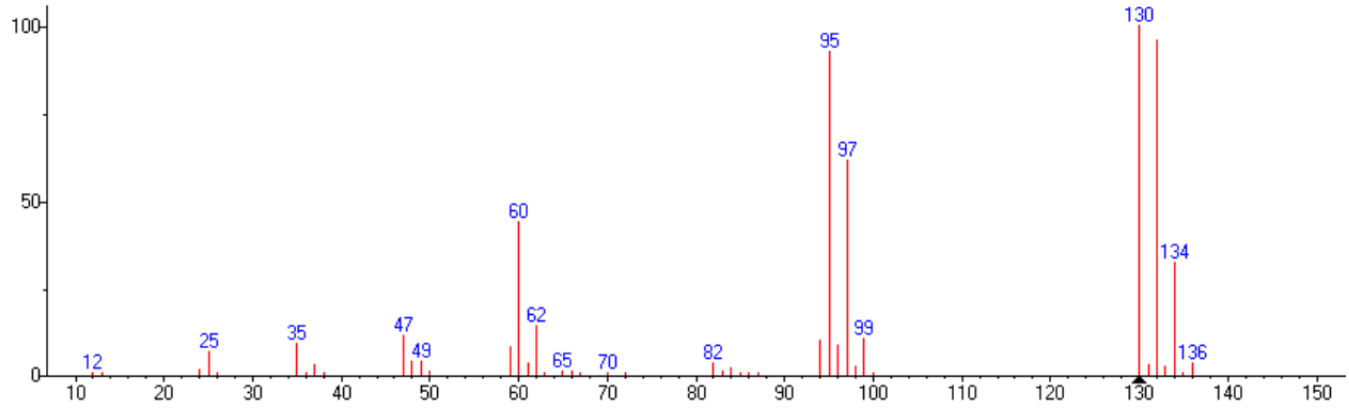


m/z	int	m/z	int	m/z	int	m/z	int	m/z	int	m/z	int
27	5	78	7	104	5	135	43	168	13	211	9
39	29	79	11	105	11	136	4	169	30	213	999
41	16	82	10	107	51	139	12	170	9	214	169
50	5	84	8	114	12	141	15	171	5	215	17
51	15	89	14	115	29	142	5	176	6	228	248
53	10	90	21	116	5	144	6	177	11	229	41
55	15	91	100	118	8	145	7	181	16	230	4
62	5	92	10	119	198	151	9	182	5		
63	18	94	12	120	28	152	26	183	14		
64	7	95	13	121	5	153	15	184	9		
65	53	97	9	127	11	155	6	194	6		
66	10	99	52	128	14	157	11	195	17		
75	7	101	7	131	10	165	38	197	29		
76	14	102	5	133	5	166	14	198	26		
77	38	103	8	134	6	167	12	199	10		

41/248=0.1653
0.1653/0.011=15.03



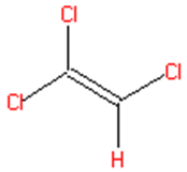
6. How many C and Cl atoms does the following molecule most likely contain? (M = 130)



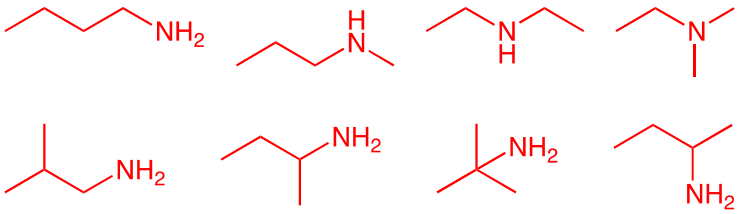
m/z	int	m/z	int	m/z	int	m/z	int
24	17	60	438	94	100	134	322
25	65	61	36	95	924	135	7
35	90	62	141	96	85	136	35
36	8	65	13	97	613		
37	30	66	12	98	24		
47	112	70	5	99	102		
48	39	82	34	130	999		
49	39	83	11	131	25		
50	13	84	22	132	954		
59	83	85	7	133	24		

#C = (I131/I130)/0.011
= (25/999)/.011
= 2.28 → 2

#Cl = (I132/I130)/0.32
= (954/999)/.32
= 2.98 → 3



7. The mass spectrum of an unknown molecule shows a molecular ion peak at m/z = 73. Provide a reasonable structure.
   Odd # indicates presence of nitrogen. UN = 0 (no double bonds or rings), so any of the following structures is reasonable:



8. A researcher analyzed an unknown solid (MW = 420) to determine its percent composition. An 11.32 mg sample was burned in a combustion apparatus. The carbon dioxide (24.87 mg) and water (5.82 mg) were collected and weighed. **Determine the empirical and molecular formulas of the unknown, and the Unsaturation Number (UN).**

Atom	**Atomic weight**
C	12.011 g/mol
H	1.008 g/mol
O	16.000 g/mol

Empirical formula: _____ $C_7H_8O_3$_____

Molecular formula: _____ $C_{21}H_{24}O_9$_____

Unsaturation Number (UN): ____10_____

mg C = 24.87 mg CO2 x (12.011 g/mol C)/(44.010 g/mol CO2) = 6.787 mg C
%C = (6.787 mg C/11.32 mg unknown) x 100 = 59.956 %C

mg H = 5.82 mg H2O x (2 x 1.008 g/mol H)/(18.015 g/mol H2O) = 0.65 mg H
%H = (0.65 mg H/11.32 mg unknown) x 100 = 5.75 %H

%O = 100% - 60 %C – 5.75 %H = 34.25% O

mmol C (assuming 100 mg sample) = 59.956 mg C /12.011 g/mol = 5.0 mmol C

mmol H (assuming 100 mg sample) = 5.75 mg H / 1.008 g/mol = 5.70 mmol H

mmol O (assuming 100 mg sample) = 34.25 mg O / 16.000 g/mol = 2.14 mmol O

Divide by lowest # (2.14): 2.33 mmol C; 2.66 mmol H; 1 mmol O
Multiply by 3 to get whole #: 7 mmol C; 8 mmol H; 3 mmol O → **$C_7H_8O_3$**
empirical weight = 7x12 + 8x1 + 3x16 = 140
MW = 420: 420/140 = 3 → molecular formula = **$C_{21}H_{24}O_9$**

UN = (2xC +2 – H)/2 = (42 + 2 – 24)/2 = 20/2 = **10**