Mass Spectroscopy Material

(Chem 319, 422, 424)

Beauchamp

Basics of Mass Spectroscopy

The technique of MS only requires very small amounts of sample (µg-ng) for high quality data. MS can be coupled to separation techniques such as gas chromatography (GC, when volatile) and high pressure liquid chromatography (HPLC, when non-volatile). There is also an option for direct inlet of solid samples.
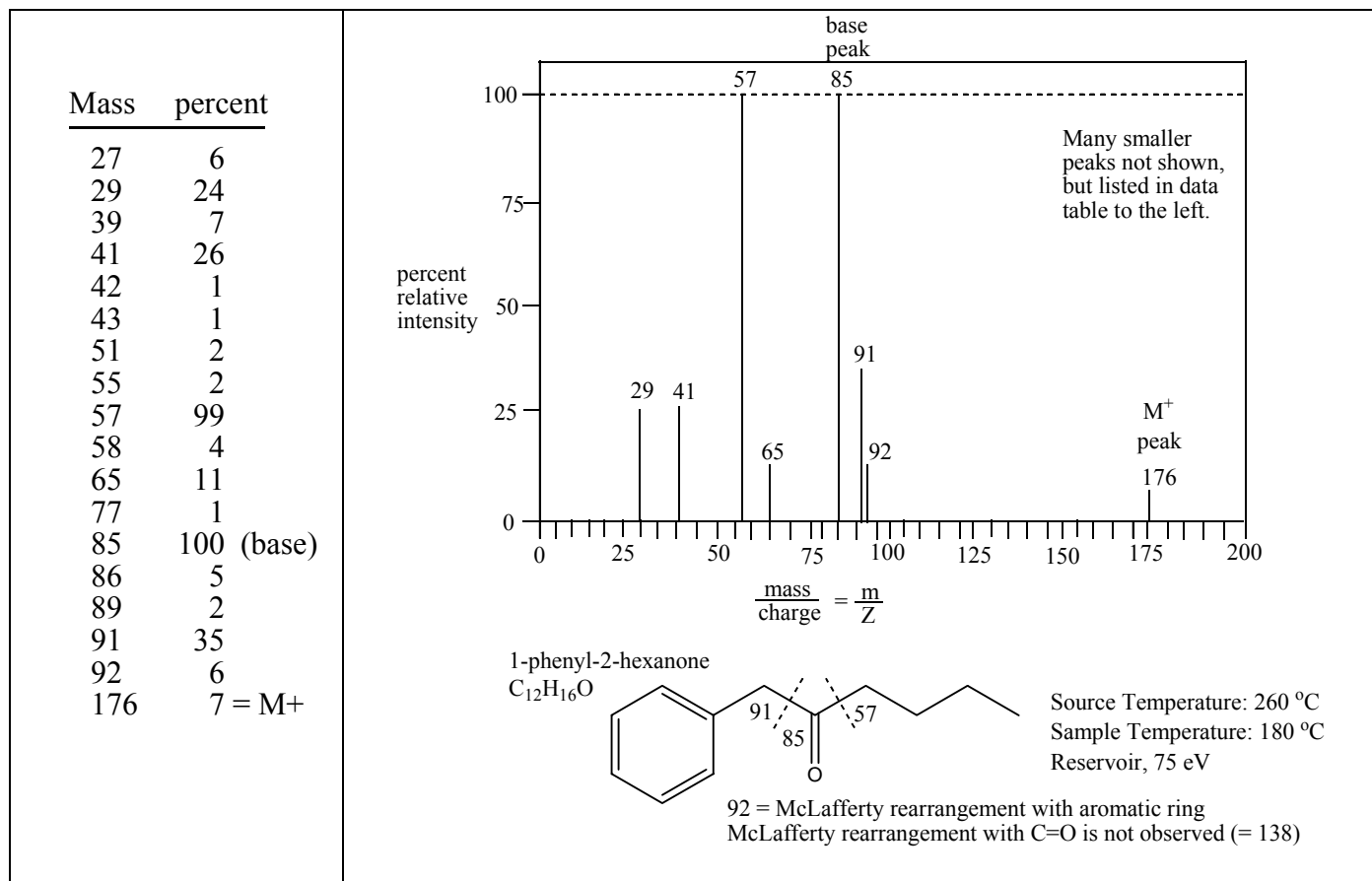
MS is different from the other spectroscopies (UV-Vis, IR, NMR) in that absorption or emission of electromagnetic radiation is not used. Rather, the sample (molecule) is ionized, usually a high energy electron beam = electron impact = EI. The cations formed are accelerated in a high voltage field, focused and separated by mass to charge ratio (m/e) using a magnetic field and/or electric fields. A detector indicates the intensity of each mass signal and the mass data are plotted against this intensity to produce a spectrum This same data is often printed in a tabulated, numerical form (shown with the spectrum below).

The most useful information from the MS is the molecular weight, which can indicate what the formula is (rule of 13 is helpful). The formula will provide the degree of unsaturation, which gives important clues to the possible structures (rings and π bonds). Fragment peaks that are detected provide hints as to the nature of the carbon skeleton, heteroatoms and functional groups present.

Typical MS Instrument Features.
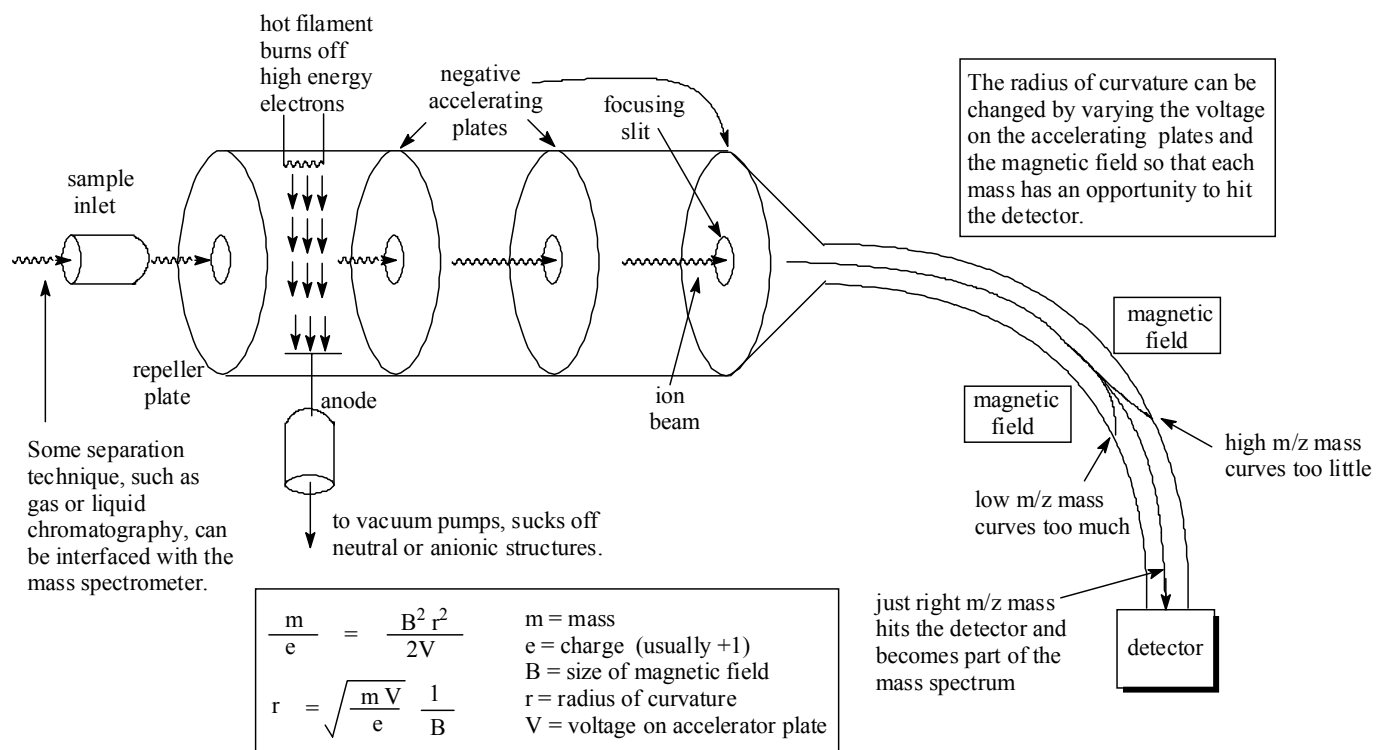
The moving charged cations curve in their direction of flight in a magnetic or electric field. The amount of curvature is determined by the mass of the ions as shown in the following equations. The magnetic field and/or accelerator plate voltage can be altered to cause each possible mass to impact the detector. The charged masses must survive about 10^{-6} to 10^{-5} seconds to make this journey to the detector. Often there is some rational feature to explain each peak's special stability that allows it to last long enough to reach the detector, where it becomes part of the data we examine.

Typical Mass Spectral Data

Mass	percent	
27	6	
29	24	
39	7	
41	26	
42	1	
43	1	
51	2	
55	2	
57	99	
58	4	
65	11	
77	1	
85	100	(base)
86	5	
89	2	
91	35	
92	6	
176	7 = M+	

$$\frac{mass}{charge} = \frac{m}{Z}$$

1-phenyl-2-hexanone
$C_{12}H_{16}O$

Source Temperature: 260 °C
Sample Temperature: 180 °C
Reservoir, 75 eV

92 = McLafferty rearrangement with aromatic ring
McLafferty rearrangement with C=O is not observed (= 138)

Besides just seeing a positively charged mass at the detector, we must resolve it from nearby mass values. MS instruments can be either low resolution (LRMS) or high resolution (HRMS). Low resolution MS instruments can generally resolve single amu values as high as about 2000 amu's (i.e. they can distinguish 300 amu from 301 amu). High resolution MS instruments can resolve masses as close as the fourth decimal place (XXX.XXXX). A molecular formula can be obtained from either LRMS or HRMS, though HRMS is more useful in this regard (and less work!). However, such instruments tend to be more expensive.

The most abundant peak (largest) in the mass spectrum is called the **base peak**. It is assigned a value of 100% and all other detectable masses are indicated as a percent of the base peak. The molecular weight peak is called the **mass peak or molecular ion peak or parent peak** and symbolized with an M. Since this peak is a radical cation, it often also has a + or + · (plus sign and a dot) superscript as well.

> **base peak** = largest peak in spectrum = 100% peak

> **molecular ion** = M = M+ = M+° = parent peak
> = only specific isotopic masses are found in the molecular formula
> (we do not see "average" masses that are listed in the periodic table)

We need to be precise in our calculation of possible masses for each collection of atoms because the atoms in any cation fragment hitting the detector are specific isotopes. The atomic weights listed in the periodic table are average masses based on the abundance and mass of all of the isotopes. For example the atomic weight of bromine in the periodic table is 79.9, though there is no bromine isotope with a mass of 80. The 79.9 atomic weight is a result of an approximate 50/50 mixture of two stable isotopes of mass 78.9 and 80.9. Because of this complication we will require data on the exact masses and the relative abundance of the common isotopes that we expect to encounter. Those most useful to us in organic chemistry and biochemistry are listed below.

Element	Atomic Weight	Nuclide	Mass	Relative Abundance	As Fraction
hydrogen	1.00797	^1H	1.00783	100.0	0.9999
		^2H (D)	2.01410	0.015	0.0001
carbon	12.01115	^{12}C	12.00000	100.0	0.9890
		^{13}C	13.00336	1.11	0.00.11
nitrogen	14.0067	^{14}N	14.0031	100.0	0.9963
		^{15}N	15.0001	0.37	0.0037
oxygen	15.9994	^{16}O	15.9949	100.0	0.9976
		^{17}O	16.9991	0.04	0.0004
		^{18}O	17.9992	0.20	0.0020
fluorine	18.9984	^{19}F	18.9984	100.0	1.0000
silicon	28.086	^{28}Si	27.9769	100.0	0.9223
		^{29}Si	28.9765	5.06	0.0467
		^{30}Si	29.9738	3.36	0.0310
phosphorous	30.974	^{31}P	30.9738	100.0	1.0000
sulfur	32.064	^{32}S	31.9721	100.0	0.9504
		^{33}S	32.9715	0.79	0.0075
		^{34}S	33.9679	4.43	0.0421
chlorine	35,453	^{35}Cl	34.9689	100.0	0.7577
		^{37}Cl	36.9659	31.98	0.2423
bromine	79.909	^{79}Br	78.9183	100.0	0.5068
		^{81}Br	80.9163	97.3	0.4932
iodine	126.904	^{127}I	126.9045	100.0	1.0000

Problem 1 - A low-resolution mass spectrum of 1,10-phenanthroline showed the molecular weight to be 180. This molecular weight is correct for the molecular formulas $C_{14}H_{12}$, $C_{13}H_8O$ and $C_{12}H_8N_2$. A high-resolution mass spectrum provided a molecular weight of 180.0688. Which of the possible molecular formulas is the correct one?

Problem 2 – (+)-Cymarin, a natural product was found by low-resolution mass spectrometry to have a molecular weight of 548. Possible molecular formulas include $C_{29}H_{40}O_{10}$, $C_{30}H_{44}O_9$, and $C_{31}H_{48}O_8$. High-resolution mass spectrometry indicated that the precise molecular weight was 548.2986. What is the correct molecular formula of cymarin?

Obtaining a molecular formula from a HRMS is relatively straight forward. Each possible molecular mass is unique when calculated to four decimal places and computers can do the calculations for us.

To obtain a molecular formula from a LRMS requires more sophistication. Various possible formulas can be generated using the molecular ion peak and the *rule of 13*. The first possible formula assumes that only carbon and hydrogen are present. The molecular mass (M) is divided by 13 generating an integer (n) and a remainder (r). The CH formula becomes C_nH_{n+r}.

each of these weights 13 amu = C + H = n

these are left over hydrogens = r
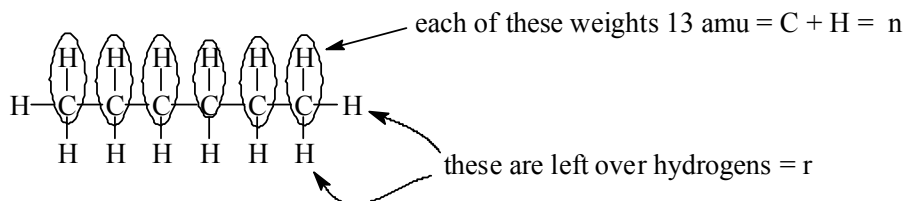
$$\frac{M}{13} = n + \frac{r}{13}$$

M = molecular weight
n = number of CH units
r = left over hydrogens

Possible hydrocarbon molecular formula = C_nH_{n+r}

The degree of unsaturation can be calculated for this formula and possible rings and/or π bonds can be considered. If oxygen and/or nitrogen (and other elements) are present, the C/H numbers in the molecular formula must be changed by an amount equal to the new element's isotope mass. It is assumed, when substituting atoms, that the major isotope is used in all cases, H=1, C=12, N=14, O=16, S=32, Cl=35, Br=79. Since oxygen weighs 16, we can subtract CH_4 (= 16) from the formula and add the oxygen atom. If two oxygen atoms were present, we would subtract $2x(CH_4) = C_2H_8$ and so forth. Nitrogen-14 would substitute for CH_2 and n nitrogen atoms would substitute for $(CH_2)x(n)$.

Information concerning the possible number of nitrogen atoms in the molecular formula is also available in the molecular mass. If the molecular mass is an even number, then the number of nitrogen atoms has to be zero or an even number (= 0, 2, 4......). If the molecular mass is an odd number, then the number of nitrogen atoms has to be odd (= 1, 3, 5.....). Remember, each nitrogen atom in the formula adds an extra bonding position.

$C_nH_{2n+2}O_x$
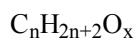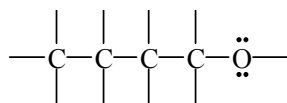
C = even mass
H = even mass
O = even mass
MW = even mass

$C_nH_{2n+3}N_{odd}$
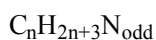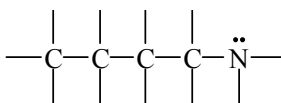
C = even mass
H = odd mass
N = even mass
MW = odd mass

$C_nH_{2n+4}N_{even}$
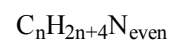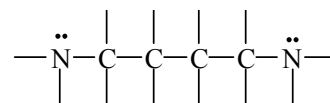
C = even mass
H = even mass
N = even mass
MW = even mass

Problem 3 – What is the degree of unsaturation in 1,10-phenanthroline from problem 1 and (+)-cymarin from problem 2, above?

Problem 4 - An unknown compound has a molecular weight of 142. Use the rule of 13 to figure out different possible formulas. (Show all work.)

a. What are all possible formulas having only carbon and hydrogen? How would the formula change if there were one more carbon atom? What is the degree of unsaturation for each of these possibilities (two calculations)?
b. How would the formula change if there were one oxygen atom, …two oxygen atoms? What is the degree of unsaturation for each of these possibilities (two more calculations)?
c. How would the formula change if nitrogen were present in addition to carbon and hydrogen? What is the minimum number of nitrogen atoms that could be present? What is the degree of unsaturation for each of these possibilities (three more calculations)?
d. Is it possible that the formula has a single nitrogen? If so what would the formula be? If not, why not? What if the molecular weight was 143?

   To choose among the various formulas generated from the rule of 13, we can consider the other possible isotopes present and their relative abundance to calculate the size of the peaks just one mass unit (M+1) and two mass units (M+2) larger than the molecular ion peak (M^+). (Also consider what functional groups appear to be present from the IR and NMR information.) For each possible formula, percents of the M+1 and M+2 peaks versus the M^+ peak are calculated. In this calculation the M^+ peak is assumed to be 100% for comparison, regardless of the base peak. These calculated values are compared to the experimental values to determine the most likely formula. The reason for this is that the relative sizes of the M+1 and M+2 peaks are determined by the number and isotopic abundance of the elements present (C, H, O, N, etc.). We won't go through the calculations for these elements, however, the presence of either chlorine, bromine or sulfur significantly changes the M+2 peak. If there are multiple halogens (Cl and Br), the M+2, M+4, M+6 and beyond can be calculated and compared to the experimental mass spectrum. Let's take a look at how one could calculate the relative size of these peaks (M+1 and M+2).

Chlorine, bromine and sulfur, when present, have very characteristic M+2 peaks (32.6% for Cl, 96.9% for Br and 4.5% for S). If multiple Cl's and/or Br's are present M+2, M+4 and more are indicative of the number and type of halogen(s) present. The various patterns are available in many references. However, you can calculate these values yourself, as was done above for the M+1 and M+2 peaks.

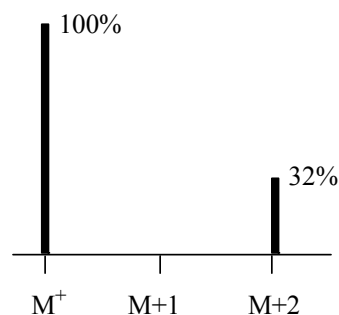<u>one Cl comparison of M$^+$ peak to M+2 peak</u>

M$^+$ peak relative size

probability of ^{35}Cl $= (\dfrac{100}{100 + 32})(1 \text{ way}) = 0.758$

(assigned a normalized value of 100%)

- -

M+2 peak relative size

probability of ^{37}Cl $= (\dfrac{32}{100 + 32})(1 \text{ way}) = 0.242$

percent of M+ peak $= (\dfrac{0.242}{0.758})(100\%) = 32\%$

<u>one Br comparison of M$^+$ peak to M+2 peak</u>

M$^+$ peak relative size

probability of ^{79}Br $= (\dfrac{100}{100 + 97})(1 \text{ way}) = 0.508$

(assigned a normalized value of 100%)

- -

M+2 peak relative size

probability of ^{81}Br $= (\dfrac{97}{100 + 97})(1 \text{ way}) = 0.492$

percent of M+ peak $= (\dfrac{0.492}{0.508})(100\%) = 97\%$
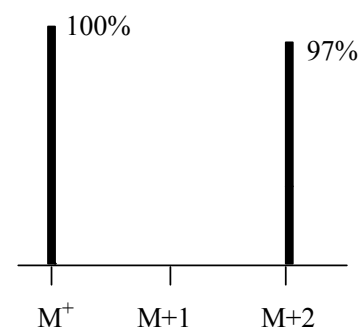
<u>one S comparison of M$^+$ peak to M+2 peak</u>

M+ peak relative size

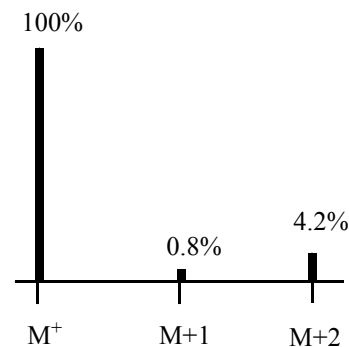probability of ^{32}S $= \left(\dfrac{100}{100 + 0.8 + 4.4}\right)(1 \text{ way}) = 0.95$

(assigned a normalized value of 100%)

probability of ^{33}S $= \left(\dfrac{0.8}{100 + 0.8 + 4.4}\right)(1 \text{ way}) = 0.008$

percent of M$^+$ peak $= 0.8\%$

probability of ^{34}S $= \left(\dfrac{4.4}{100 + 0.8 + 4.4}\right)(1 \text{ way}) = 0.042$

percent of M$^+$ peak $= 4.2\%$

one Br and one Cl comparison of M^+ peak to M+2 and M+4 peaks

M^+ peak relative size

    probablity of ^{79}Br = 0.508 (from above)   probablity of ^{35}Cl = 0.758 (from above)

(probablity of ^{79}Br)(probability of ^{35}Cl)(1 way) = (0.508)(0.758)(1) = 0.385
   (assigned a normalized value of 100%)

- -

M+2 peak relative size

    probablity of ^{81}Br = 0.492 (from above)   probablity of ^{37}Cl = 0.242 (from above)

(probablity of ^{79}Br)(probability of ^{37}Cl)(1 way) = (0.508)(0.242)(1) = 0.123   total = 0.123 + 0.373

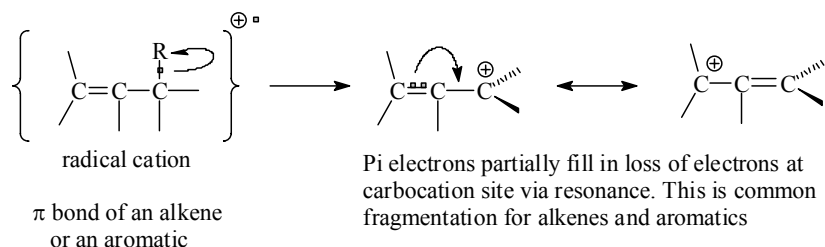(probablity of ^{81}Br)(probability of ^{35}Cl)(1 way) = (0.492)(0.758)(1) = 0.373   = 0.496

                                      percent of M^+ peak = 129%

- -

M+4 peak relative size

(probablity of ^{81}Br)(probability of ^{37}Cl)(1 way) = (0.492)(0.242)(1) = 0.119

                              percent of M^+ peak = 31%

(bar chart: M^+ 100%, M+1 129%, M+2 31%)
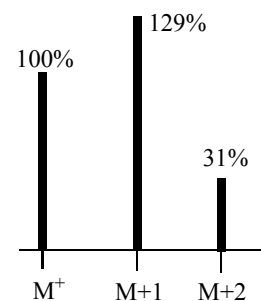
two Cl comparison of M^+ peak to M+2 peak to M+4 peaks

M^+ peak relative size

probability of two ^{35}Cl = $(\frac{100}{100 + 32})^2$(1 way) = 0.602
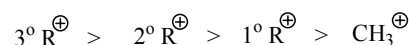
(assigned a normalized value of 100%)

- -

M+2 peak relative size

(probability of ^{37}Cl)(probability ^{35}Cl) = $(\frac{100}{100 + 32})(\frac{32}{100 + 32})$(2 ways) = 0.367

percent of M^+ peak = $(\frac{0.367}{0.602})$(100%) = 61.0%

- -

M+4 peak relative size

probability of two ^{37}Cl = $(\frac{32}{100 + 32})^2$(1 way) = 0.059

percent of M^+ peak = $(\frac{0.059}{0.602})$(100%) = 9.8%

(bar chart: M^+ 100%, M+2 61.0%, M+4 9.8%, with axis labels M^+ M+1 M+2 M+3 M+4)
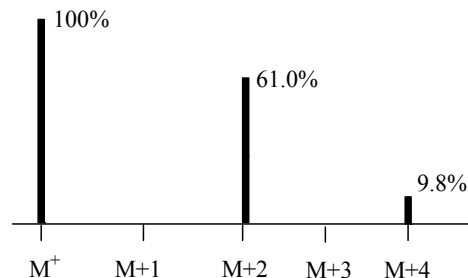
Problem 5 - Calculate the relative intensities (as a percent) of M^+, M+2 and M+4 for Br_2. Use the probabilities from above.

Problem 6 - Calculate the relative intensities (as a percent) of M^+, M+2, M+4 and M+6 for $BrCl_2$ and Br_2Cl. Hint: All of the data you need to perform these calculations are in the examples above. Use the probabilities from above.

Common fragmentation patterns in mass spectroscopy

1. Branch next to a π bond

radical cation

π bond of an alkene
or an aromatic

Pi electrons partially fill in loss of electrons at carbocation site via resonance. This is common fragmentation for alkenes and aromatics

Characteristic carbocation stability also applies.

$$3^o\ R^{\oplus}\ >\ \ 2^o\ R^{\oplus}\ >\ 1^o\ R^{\oplus}\ >\ CH_3^{\oplus}$$
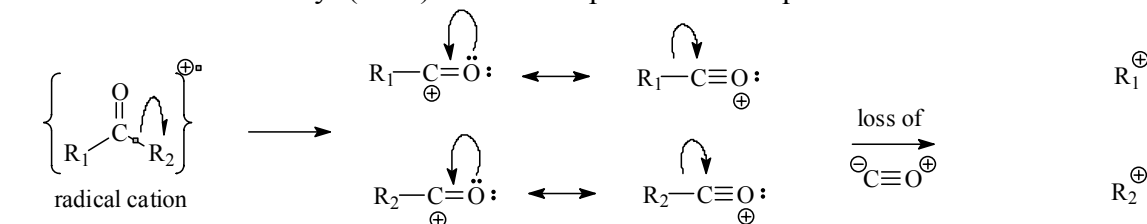
2. Branch next to an atom with a lone pair of electrons

radical cation
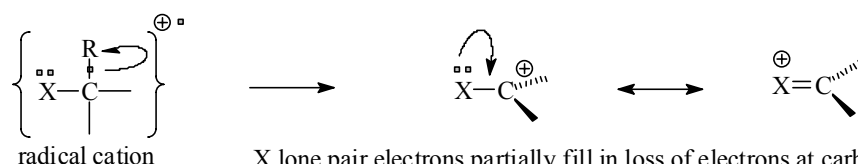
X lone pair electrons partially fill in loss of electrons at carbocation site via resonance. This is a common fragmentation for any atom that has a lone pair of electrons (oxygen = alcohol, ether, ester; nitrogen = amine, amide, sulfur = thiol or sulfide, etc.). Alcohols often lose water (M-18) and primary amines can lose ammonia (M-17).

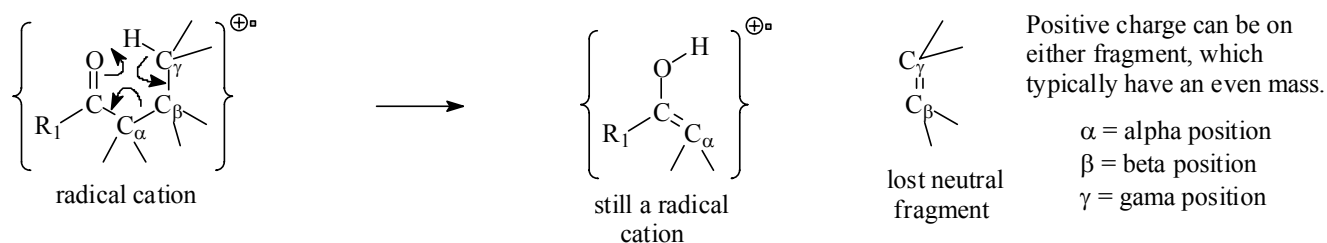3. Branch next to a carbonyl (C=O) bond…and possible subsequent loss of carbon monoxide, CO

radical cation

$R_1 - C \equiv \overset{\cdots}{O} : \quad \longleftrightarrow \quad R_1 - C \equiv O :$

$R_2 - C \equiv \overset{\cdots}{O} : \quad \longleftrightarrow \quad R_2 - C \equiv O :$

loss of
$^{\ominus}C \equiv O^{\oplus}$

$R_1^{\oplus}$

$R_2^{\oplus}$

R_1 or R_2 can be lost from aldehydes, ketones, acids, esters, amides...etc.

An oxygen lone pair partially fill in the loss of electrons at the carbocation site via resonance. This is a common fragmentation pattern for any carbonyl compound and can occur from either side, though some are more common than others.

subsequent loss of CO is possible after α fragmentation so not only can you see loss of an α branch you can see the mass of an α branch.

4. McLafferty Rearrangement

radical cation

still a radical
cation

lost neutral
fragment

Positive charge can be on either fragment, which typically have an even mass.

α = alpha position
β = beta position
γ = gama position
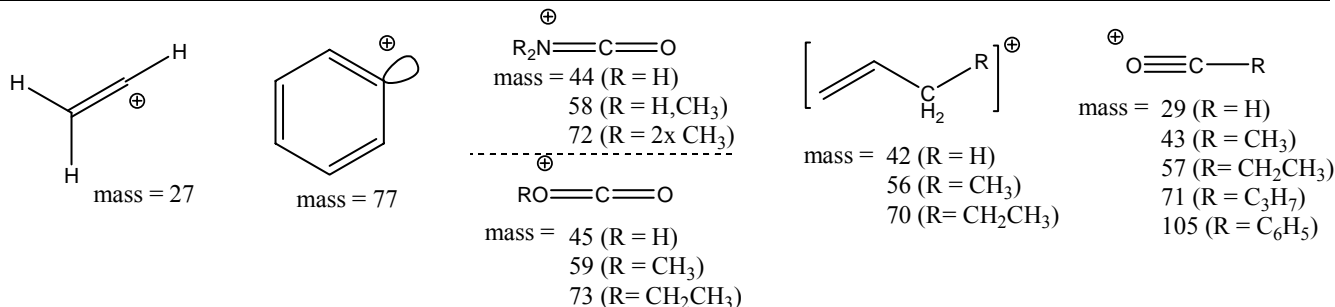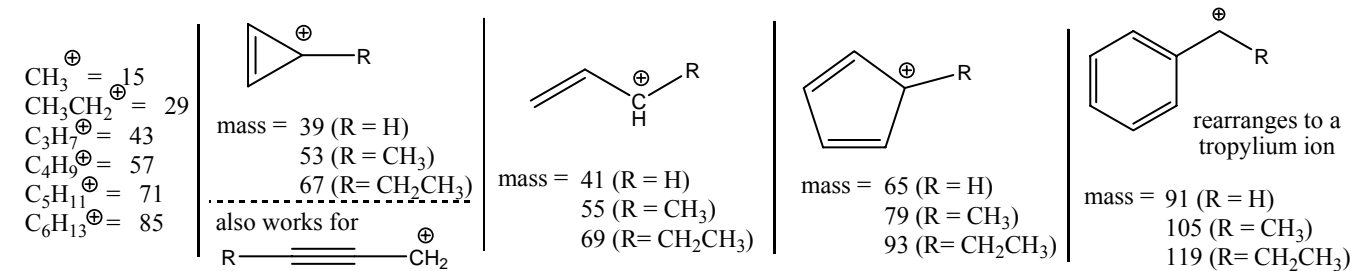
This is another common fragmentation pattern for carbonyl compounds (and other pi systems as well: alkenes, aromatics, alkynes, nitriles, etc.). If the pi bond has at least 3 additional nonhydrogen atoms attached and a hydrogen on the "gama" atom, the branch can curve around to a comfortable 6 atom arrangement and the pi bond can pick up a hydrogen atom and cut off a fragment between the C_α and C_β positions. The positive charge can be seen on either fragment and usually the fragments have an even mass (unless there is an odd number of nitrogen atoms).

Knowing these few fragmentation patterns will allow you to make many useful predictions and interpretations. Loss of small molecules, via elimination is common: $H_2O = 18$, $H_2S = 34$, $CH_3OH = 32$, $C_2H_5OH = 46$, $NH_3 = 17$, $CH_3CO_2H = 62$, $HF = 20$, $HCl = 36/38$, $HBr = 80/82$, etc.

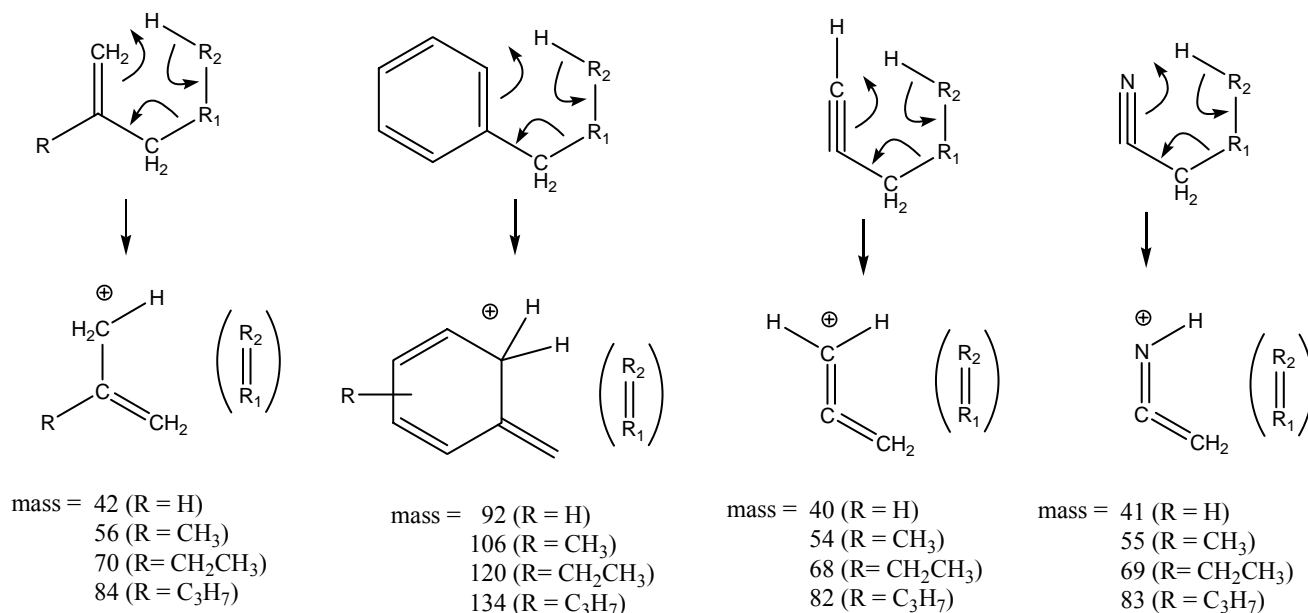**A sampling of unusual and/or miscellaneous peaks that are commonly seen, (even when they don't make sense).**

$CH_3^{\oplus}$ = 15
$CH_3CH_2^{\oplus}$ = 29
$C_3H_7^{\oplus}$ = 43
$C_4H_9^{\oplus}$ = 57
$C_5H_{11}^{\oplus}$ = 71
$C_6H_{13}^{\oplus}$ = 85

mass = 39 (R = H)
      53 (R = CH_3)
      67 (R= CH_2CH_3)

also works for

$R\!-\!\!\equiv\!\!-CH_2$

mass = 41 (R = H)
      55 (R = CH_3)
      69 (R= CH_2CH_3)

mass = 65 (R = H)
      79 (R = CH_3)
      93 (R= CH_2CH_3)

rearranges to a tropylium ion

mass = 91 (R = H)
      105 (R = CH_3)
      119 (R= CH_2CH_3)

mass = 27

mass = 77

$R_2N\!\!=\!\!C\!\!=\!\!O$
mass = 44 (R = H)
      58 (R = H,CH_3)
      72 (R = 2x CH_3)

$RO\!\!=\!\!C\!\!=\!\!O$
mass = 45 (R = H)
      59 (R = CH_3)
      73 (R= CH_2CH_3)

mass = 42 (R = H)
      56 (R = CH_3)
      70 (R= CH_2CH_3)

$O\!\!\equiv\!\!C\!-\!R$
mass = 29 (R = H)
      43 (R = CH_3)
      57 (R= CH_2CH_3)
      71 (R = C_3H_7)
      105 (R = C_6H_5)

Loss of small molecules via elimination reactions. Peak mass = M - (small molecule mass), e.g. ROH often shows peak at M-18.
(loss of water)

	H_2O	H_2S	CH_3OH	C_2H_5OH	NH_3	CH_3CO_2H	HF	HCl	HBr
mass =	18	34	32	46	17	62	20	36 / 38	80 / 82

McLafferty Possibilities

Only positively charged peaks reach the detector. This could be one or the other or both.

Notice! even masses

McLafferty rearrangements

mass = 44 (R = H)
      58 (R = CH_3)
      72 (R= CH_2CH_3)
      86 (R = C_3H_7)

variable mass,

(can sometimes see cation on this side too)

mass = 28 (R = H)
      42 (R = CH_3)
      56 (R= CH_2CH_3)
      70 (R = C_3H_7)

Similar Patterns

mass = 42 (R = H)
      56 (R = CH_3)
      70 (R= CH_2CH_3)
      84 (R = C_3H_7)

mass = 92 (R = H)
      106 (R = CH_3)
      120 (R= CH_2CH_3)
      134 (R = C_3H_7)

mass = 40 (R = H)
      54 (R = CH_3)
      68 (R= CH_2CH_3)
      82 (R = C_3H_7)

mass = 41 (R = H)
      55 (R = CH_3)
      69 (R= CH_2CH_3)
      83 (R = C_3H_7)

Mass Spec Problem Set   Name _____

1. If the molecular ion peak is 142, what molecular formula does the rule of 13 predict if the structure is a hydrocarbon? How would your formula change if there was one more carbon atom than the formula predicted above? What formula is predicted if there is one oxygen atom? Two oxygen atoms? Two nitrogen atoms? What is the degree of unsaturation for each possibility above (5 calculations)? Draw one structure for each possibility.

2. Both CHO^+ and $C_2H_5^+$ have fragment masses of approximately 29, yet CHO^+ has a M+1 peak of 1.13% and M+2 peak of 0.20%, whereas $C_2H_5^+$ has a M+1 peak of 2.24% and M+2 peak of 0.01%. High resolution mass spec shows CHO^+ to have a different fragment mass than $C_2H_5^+$. Explain these observations and show all of your work. Helpful data follow.

Element	Average Atomic Mass	Nuclide (Relative Abundance)	Mass
H	1.00797	^1H (100)	1.00783
		^2H (0.016)	2.01410
C	12.01115	^{12}C (100)	12.00000
		^{13}C (1.08)	13.00336
O	15.9994	^{16}O (100)	15.9949
		^{17}O (0.04)	16.9991
		^{18}O (0.20)	17.9992

3. What relative abundance would the characteristic M (let M be 100%), M+2, M+4, M+6 mass peaks have for: (a) tribromo, Br_3 substituted alkane, (b) trichloro, Cl_3, substituted alkane and (c) bromodichloro, $BrCl_2$ substituted alkane? Show your work. You can use these approximate probabilities (P): $P_{35Cl} = 0.75$, $P_{37Cl} = 0.25$, $P_{79Br} = 0.50$, $P_{81Br} = 0.50$

4. Radical cations of the following molecules (e- + M $\rightarrow$ $M^{+\cdot}$ + 2e-) will fragment to yield the indicated masses as major peaks. The molecular ion peak is given under each structure. The base peak is listed as 100%. Other values listed represent some of the more stable possibilities (hence higher relative abundance), or common fragmentations. For the fragments with arrows pointing at them, show what the fragment is and how it could form from the parent ion. This may be as easy as drawing a line between two atoms of a bond, or it may require drawing curved arrows to show how electrons move (e.g. McLafferty). Explain why each fragment is reasonable. This may involve drawing resonance structures or indicating special substitution patterns ($3° R^+ > 2°R^+ > 1°R^+ > CH_3^+$). If a fragment has an even mass and there is a pi bond, think McLafferty (unless an odd number of nitrogen atoms are present). Even masses can also be formed by elimination of a small molecule such as loss of water from an alcohol of loss of an alcohol from an ether, etc. Make sure you show this.
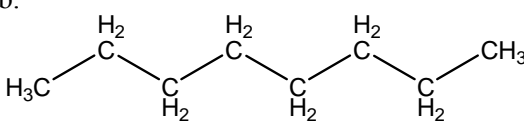
a.

$M^+ = 86$

m/e	% base	
27.0	17.2	
29.0	33.6	←
41.0	49.1	
42.0	5.6	
43.0	100.0	← harder to explain
55.0	11.3	
56.0	28.0	
57.0	98.3	←
71.0	76.7	←
72.0	4.5	
86.0	<1.0	

Explain peaks with arrows.

b.

M⁺ = 114
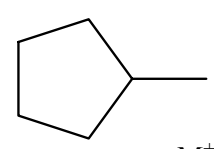
m/e	% base	
27.0	20.1	
29.0	27.4	←
41.0	43.8	← harder to explain
42.0	15.3	
43.0	100.0	←
55.0	11.4	← harder to explain
56.0	18.4	
57.0	33.5	←
70.0	12.1	
71.0	20.4	←
85.0	26.5	←
114.0	6.0	

Explain peaks with arrows.

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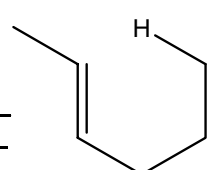
c.

M⁺ = 84
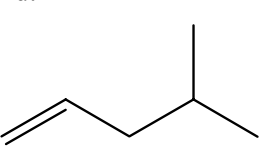
m/e	% base	
27.0	10.0	
41.0	49.5	
42.0	24.7	
43.0	11.2	
56.0	100.0	←
69.0	35.4	←
84.0	17.5	

Explain peaks with arrows.

?

No easy explanation for 56, but if ring opens and forms alkene, McLafferty might work.
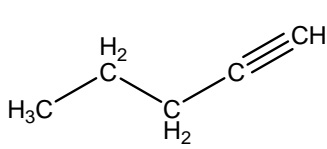
---

d.

M⁺ = 84

m/e	% base	
27.0	20.8	
41.0	68.2	←
42.0	31.4	←
43.0	100.0	←
56.0	49.8	← harder to explain
69.0	16.9	← harder to explain
84.0	11.7	

Explain peaks with arrows.

---

e.
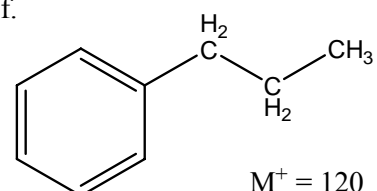
M⁺ = 68

m/e	% base	
27.0	32.9	
29.0	24.4	←
39.0	54.9	←
40.0	61.2	
41.0	22.7	
42.0	22.3	
53.0	44.0	←
67.0	100.0	← Don't remove the sp C-H,
68.0	15.3	there is a better spot (resonance).

Explain peaks with arrows.

---

f.

M⁺ = 120

m/e	% base	
65.0	7.2	←
77.0	2.7	←
91.0	100.0	←
92.0	10.8	←
105.0	3.8	←
120.0	25.9	

Explain peaks with arrows.

---

g.

H_3C — $\overset{H_2}{C}$ — $\overset{H_2}{C}$ — $\overset{}{\underset{H_2}{C}}$ — OH
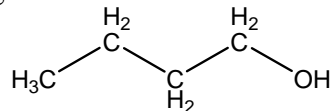
$M^+ = 74$

m/e	% base	
27.0	32.7	
29.0	16.1	←
31.0	83.4	←
41.0	65.6	
42.0	31.6	
43.0	59.3	←
55.0	14.1	
56.0	100.0	←
57.0	5.9	
74.0	<1.0	

Explain peaks with arrows.

56 is an even mass,
but not McLafferty.

h.

OH

H_3C — CH — $\overset{}{\underset{H_2}{C}}$ — CH_3
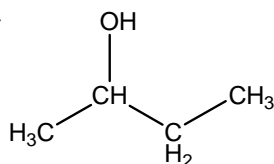
$M^+ = 74$

m/e	% base	
27.0	9.8	
28.0	51.5	← harder to explain
29.0	6.0	←
31.0	16.8	← harder to explain
41.0	11.7	
43.0	9.2	
45.0	100.0	←
56.0	1.5	←
59.0	20.5	←
74.0	<1.0	

Explain peaks with arrows.

i.

H_3C — $\overset{H_2}{C}$ — $\overset{H_2}{C}$ — O — $\overset{H_2}{C}$ — CH_3
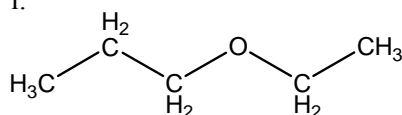
$M^+ = 88$

m/e	% base	
27.0	23.0	
28.0	7.9	←
29.0	34.9	←
31.0	100.0	← harder to explain
42.0	4.1	←
43.0	39.8	←
59.0	98.3	←
73.0	3.3	←
88.0	25.7	

Explain peaks with arrows.

28 and 42 are even, but not
McLafferty. Think like "g",
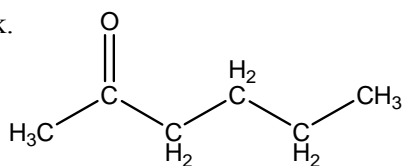but "organic" water. 31 requires
some drastic rearrangements.

j.

H_3C — $\overset{H_2}{C}$ — $\overset{}{\underset{H_2}{C}}$ — $\overset{H_2}{C}$ — NH_2
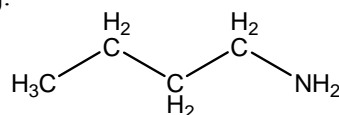
$M^+ = 73$

m/e	% base	
27.0	3.5	
29.0	2.1	←
30.0	100.0	←
43.0	1.2	←
56.0	1.2	←
73.0	7.3	

Explain peaks with arrows.

k.

O

H_3C — $\overset{}{\underset{}{C}}$ — $\overset{H_2}{C}$ — $\overset{H_2}{C}$ — CH_3

$M^+ = 100$

m/e	% base	
27.0	8.2	
29.0	14.8	←
43.0	100.0	← different than $C_3H_7^+$
57.0	15.8	←
58.0	49.8	←
85.0	6.4	←
100.0	8.0	

Explain peaks with arrows.

l.
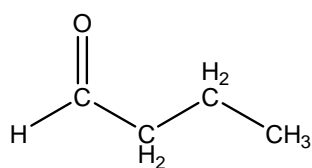
$M^+ = 72$

m/e	% base	
27.0	73.5	
29.0	54.8	← different than $C_2H_5^+$
41.0	69.1	
43.0	75.3	←
44.0	100.0	←
57.0	23.3	
72.0	53.6	

Explain peaks with arrows.

m.

H_3C — O — C(=O) — CH_2 — CH_2 — CH_3
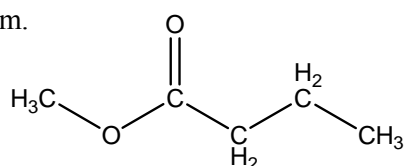
$M^+ = 102$

m/e	% base	
27.0	47.0	
29.0	9.2	←
41.0	45.3	
43.0	100.0	←
59.0	22.2	←
71.0	49.9	←
74.0	64.2	←
87.0	16.4	←
102.0	1.4	

Explain peaks with arrows.

n.

HO — C(=O) — CH_2 — CH_2 — CH_3
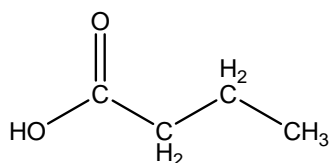
$M^+ = 88$

m/e	% base	
27.0	13.6	
29.0	8.1	←
41.0	16.3	
43.0	14.1	←
45.0	9.9	←
60.0	100.0	←
73.0	32.5	
88.0	2.6	

Explain peaks with arrows.

o.

H_2N — C(=O) — CH_2 — CH_2 — CH_3
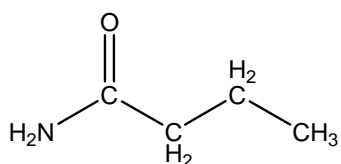
$M^+ = 87$

m/e	% base	
27.0	26.6	
29.0	26.1	←
41.0	53.4	
43.0	32.2	←
44.0	66.3	←
59.0	100.0	←
71.0	8.0	←
72.0	19.2	
87.0	2.9	

Explain peaks with arrows.

Normally 59 would be even, but there is nitrogen present.

p.

N≡C — CH_2 — CH_2 — CH_3
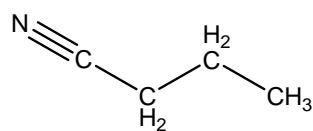
$M^+ = 69$

m/e	% base	
27.0	28.6	
29.0	66.3	←
40.0	3.8	←
41.0	100.0	←
42.0	4.0	←
54.0	1.2	
69.0	0.2	

Explain peaks with arrows.

Normally 41 would be even, but there is nitrogen present.