CH101 2018

Discussion #3

Chapter 3, Mahaffy, 2e

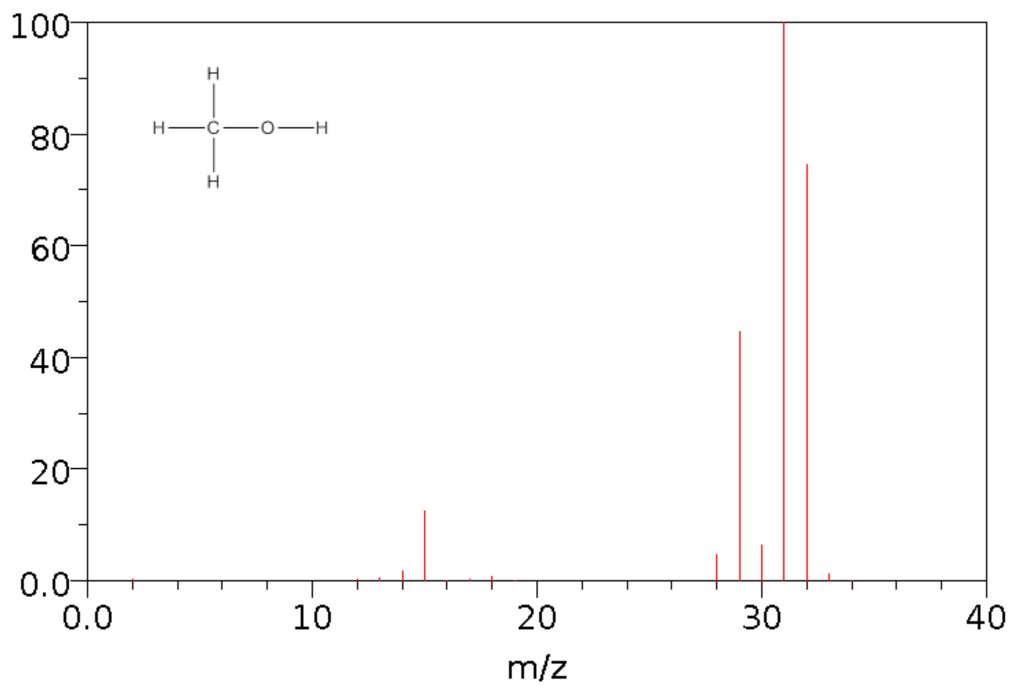
TF's name:________________ Student name________________________Discussion/Time_________

Things you should know when you leave Discussion today:

- Mass spectrometry (MS), Mahaffy, 2e sections 3.8, figure 2.11(p. 33)
    a. Molecular ion peak
    b. Fragment pattern
    c. Isotopologues
- Memorize : Mahaffy, 2e Figs 3.19, 3.20 (p. 75) and 3.24 (p. 80)
- Mahaffy, 2e: Table 3.4 (p. 68) displays the most common isotopes of the elements that we will study using mass spectrometry. You will notice that ^{13}C, ^{18}O, ^{15}N, and ^{2}H are all very rare - so we will ignore their contributions unless you are specifically told to consider them. Table 3.4 is reproduced here:

Element	Isotope	Abundance	Mass	Isotope	Abundance	Mass
Carbon	^{12}C	98.90%	12.00	^{13}C	1.10%	13.00
Oxygen	^{16}O	99.76%	15.99	^{18}O	0.20%	18.00
Nitrogen	^{14}N	99.63%	14.00	^{15}N	0.37%	15.00
Hydrogen	^{1}H	99.99%	1.01	^{2}H	0.01%	2.01
Chlorine	^{35}Cl	75.78%	34.97	^{37}Cl	24.20%	36.97
Bromine	^{79}Br	50.69%	78.92	^{81}Br	49.31%	80.92

1. Below is the structure and mass spectrum of methyl alcohol (methanol).



a. What is the molar mass of methanol?

b. What is the term for the peak that is located at the molar mass?

c. Label the peak that corresponds to the molar mass of the ion.

d. To what do you attribute the four peaks immediately less than m/z=32?

e. What is the most common ion detected by this mass spectrum.

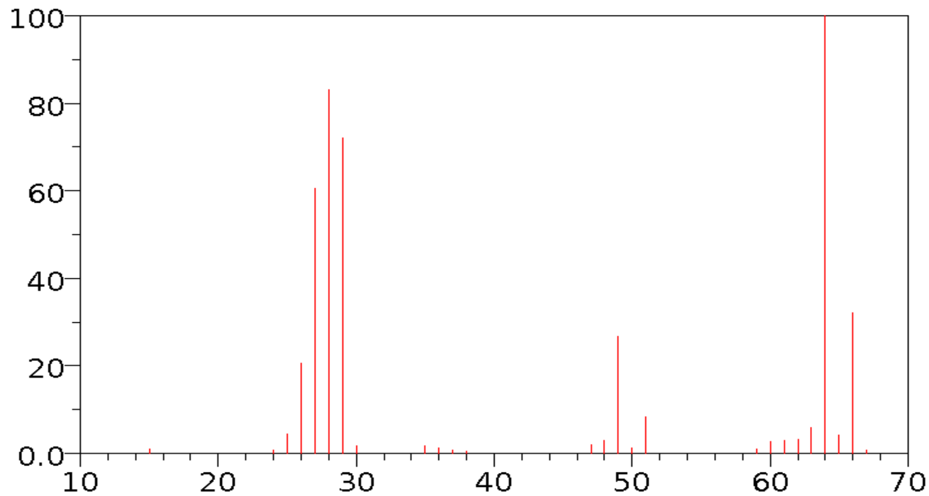
f. Identify fragments and label the peaks that have abundance greater than 10% (remember that they are all ions).

2. Suppose you are working in a chemistry lab, and something has gone completely wrong with your reaction. Your product has an unwanted element in it. You have found out that your product has the formula $C_2H_5X_1$. You take your problem to the professor who suggests you run your sample through mass spectrometry to find out what you have. Below is your spectrum. **What element is X?**

   a. Identify the molecular ion peak(s).

   b. Identify the cluster of peaks (point an arrow at) remaining in an ion that does not have X. (peaks after the loss of X)

   c. What is element X? How do you know? Cite two pieces of evidence.



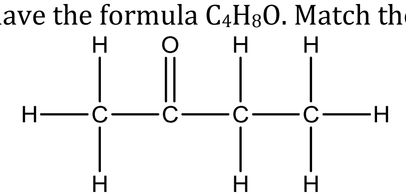
   d. What is the chemical formulas for the molecular ion peaks? How are these two molecules related?

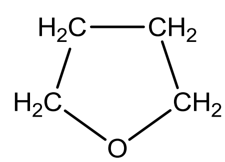
   e. Look at the peak at m/z=51. What fragment broke off the parent molecule to give you this peak?

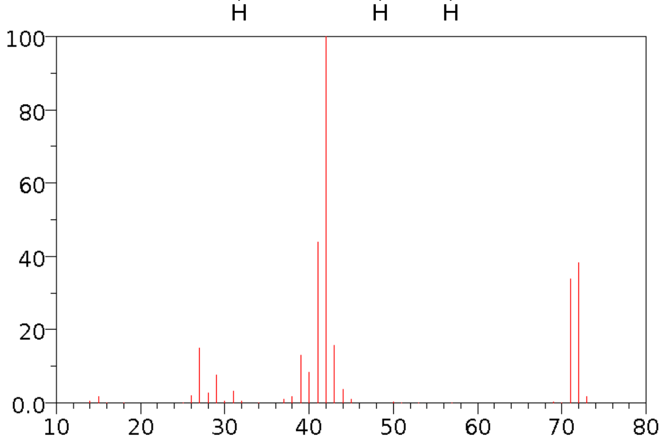
   f. Using the molecular ion peak and the peak at m/z=49, determine the fragment that left. What fragment corresponds to the tiny peak at m/z=15?

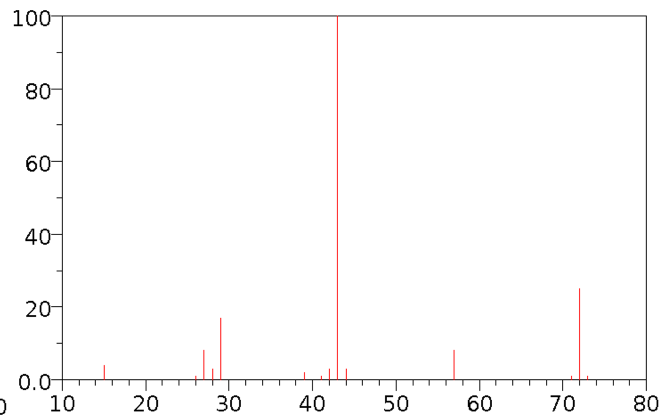
   g. What is the ratio of the intensities of the molecular isotopologue peaks.

3. Below are two mass spectra for 2-butanone (left molecule) and tetrahydrofuran (right molecule). Both have the formula C_4H_8O. Match the structure to the spectrum.

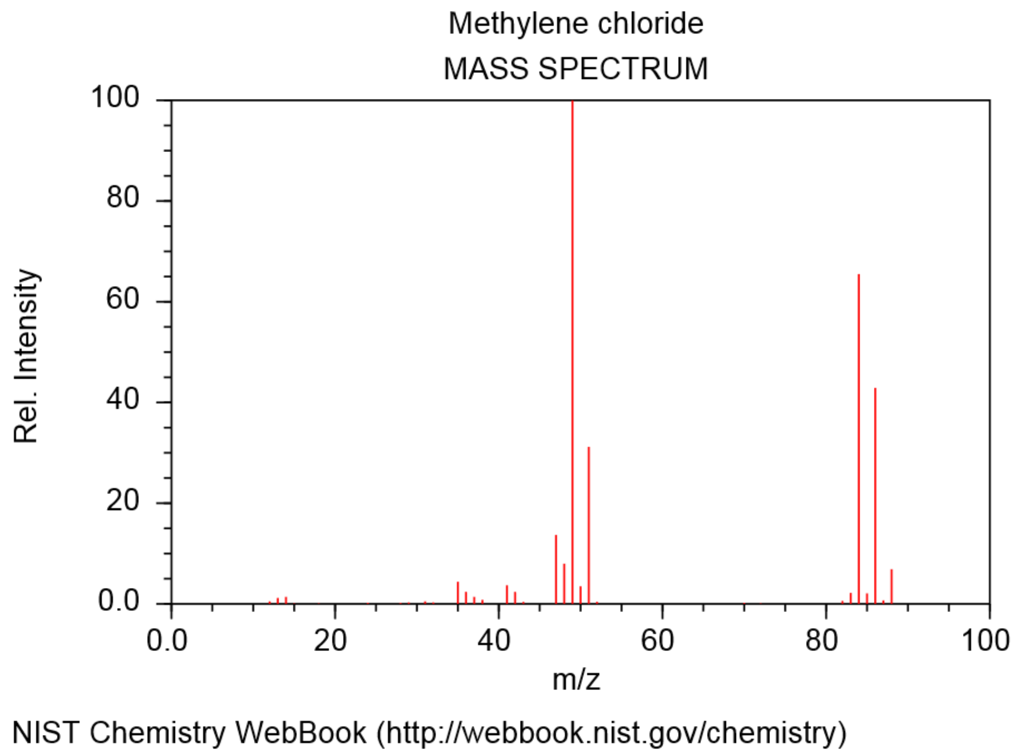








4. Below is a mass spectrum for methylene chloride (CH_2Cl_2).



a. List all the major (above 5%) isotopologues for the parent molecule that can be observed on the mass spectrum. List their m/z values next to their chemical formula. (Order all the isotopologues based on their m/z).

$[CH_2Cl_2]^+$ above 5% isotopologues	m/z	Fraction of abundances

b. What is the ratio of the relative heights of the ***molecular ion isotopologue peaks?*** (Hint: Order all the isotopologues based on their abundance from the table above. It will help if you make a matrix of all the possible isotopologues.)

c. Look at the peaks around m/z=49 and 51. What fragment broke off the parent molecule to give you this peak?

5. Predict m/z and the relative heights of the bromochloromethane molecular ion $[CH_2BrCl]^+$ isotopologue peaks. Check your answer with the spectrum given in the the NIST Chemistry WebBook at http://goo.gl/NkwL1.

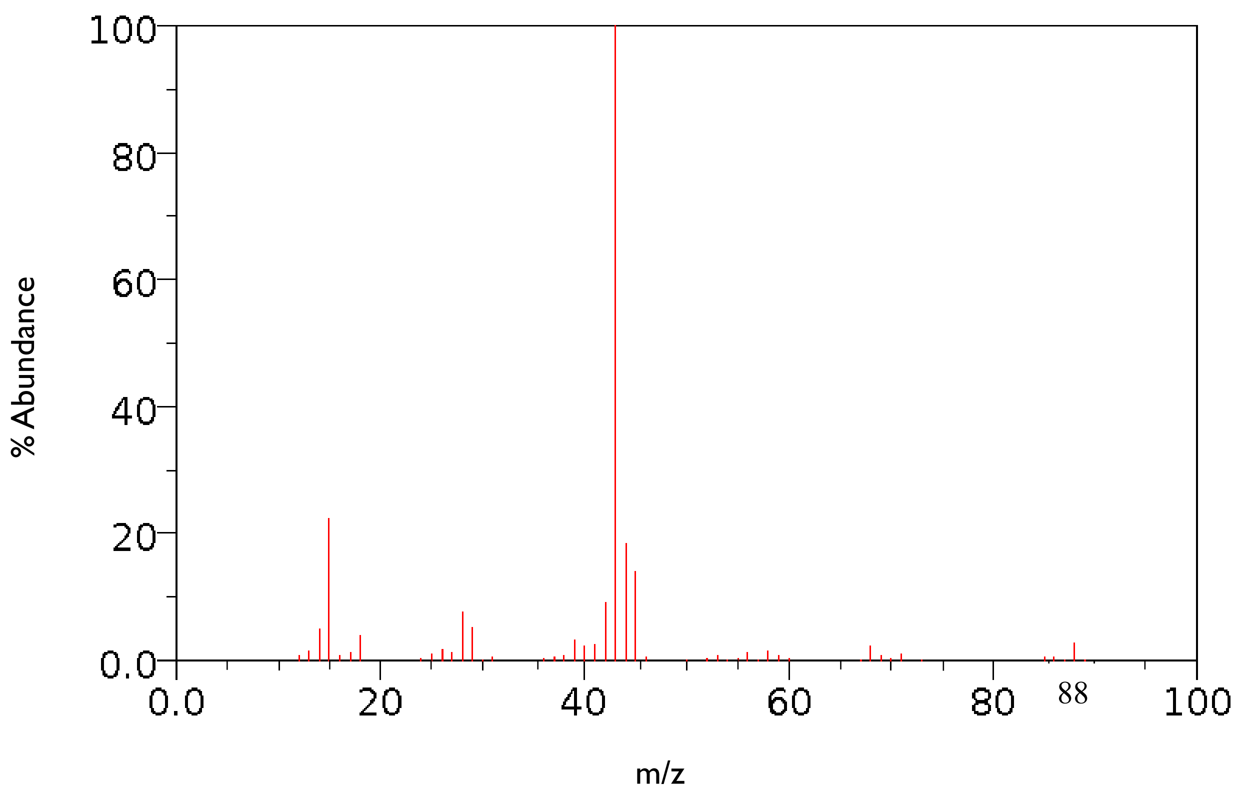
   a. List all the major (above 10%) isotopologues for the parent molecule that can be observed on the mass spectrum. List their m/z values next to their chemical formula.

$[CH_2BrCl]^+$ above 10% isotopologues	m/z	Fraction of abundances

   b. Using the table of abundances, which isotopologue is most abundant?

   c. What is the ratio of the intensities of the molecular isotopologue peaks? (Hint: Order all the isotopologues based on their abundance you can create a punnet square. It will help if you make a matrix of all the possible isotopologues.)

6. The formula for the molecule in this mass spectrum is $C_3H_4O_X$. Using the mass spectrum below, how many oxygens must there be in this molecule?

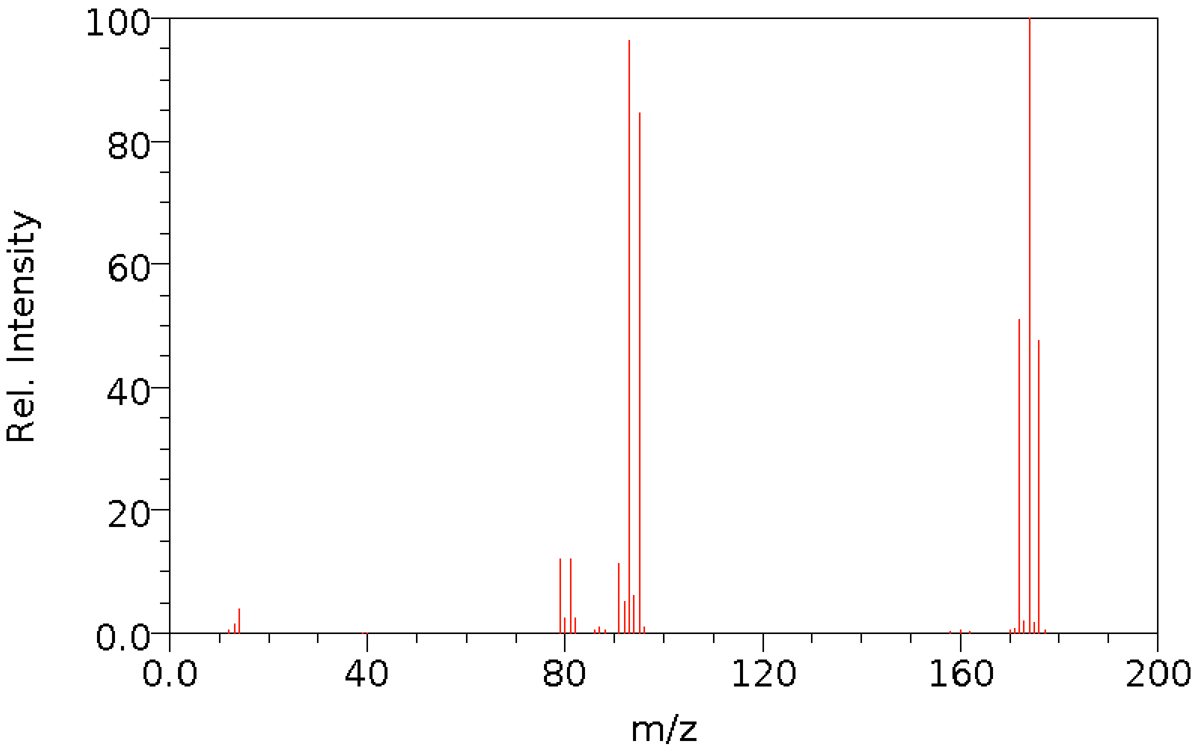


7. Ruthenium (Ru) has 7 stable isotopes. Please answer the questions below using the table provided.
   a. If you only consider the two most abundant isotopes of ruthenium, how many peaks would a mass spectrum of RuCl have if there is no fragmentation (i.e. consider only molecular ion peaks).

   b. Of the peaks in part (a), calculate the ratio the lightest molecular ion to the heaviest molecular ion.

Isotope	Abundance (%)
^{96}Ru	3
^{98}Ru	2
^{99}Ru	13
^{100}Ru	12
^{101}Ru	17
^{102}Ru	33
^{104}Ru	20

8. Below is a mass spectrum for methylene bromide (CH_2Br_2).



   a. List all the major (above 10%) isotopologues for the parent molecule that can be observed on the mass spectrum. List their m/z values next to their chemical formula.

$[CH_2Br_2]^+$ above 10% isotopologues	m/z	Fraction of abundances

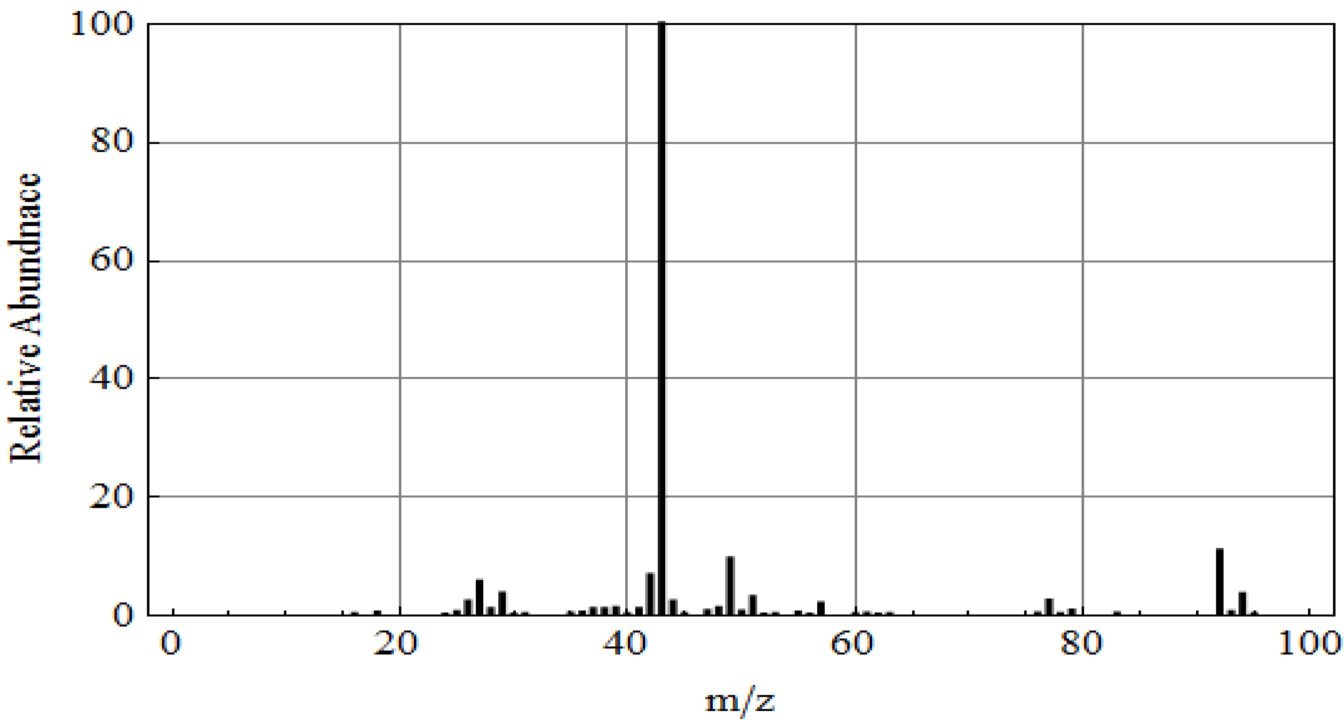
b. Using the table of abundances, which isotopologue is most abundant?

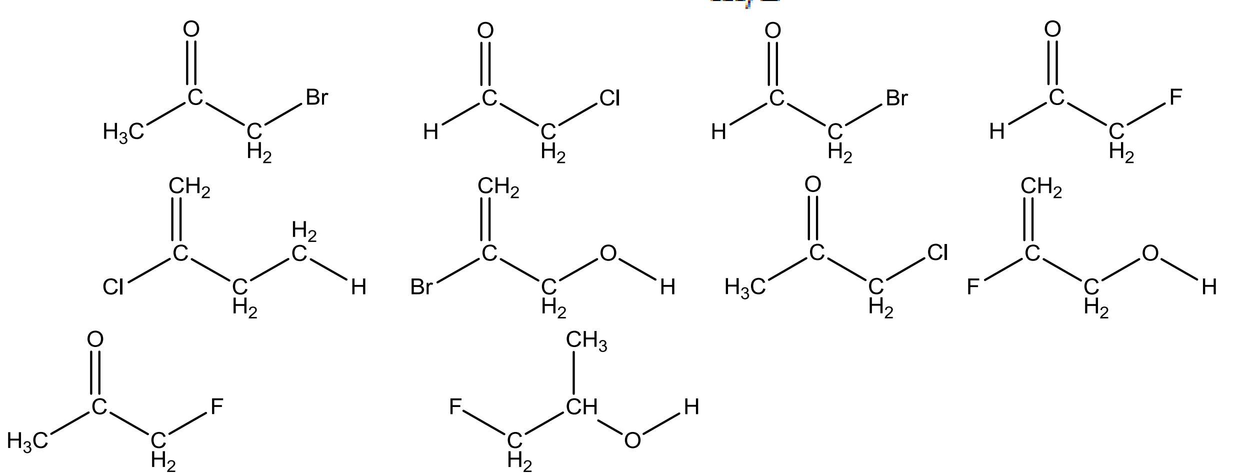
c. What is the ratio of the intensities of the molecular isotopologue peaks. (Hint: Order all the isotopologues based on their abundance you can create a punnet square. It will help if you make a matrix of all the possible isotopologues.)

d. Look at the peaks around m/z=93, 95. What fragment broke off the parent molecule to give you this peak?

Challenge problems to do at home:

9. Below is a mass spectrum for a compound that contains only carbon, hydrogen, oxygen, and a single halogen. Circle the compound below that matches the mass spectrum.





10. How many molecular peaks are in a mass spectrum of $MgCl_2$ assuming no fragmentation. Mg has the following isotopes:

^{24}Mg=80%
^{25}Mg=10%
^{26}Mg=10%

    a. Calculate the ratio of the heights of the molecular ion peaks from to the lightest $[MgCl_2]^+$ isotopologue to that of the heaviest $[MgCl_2]^+$ isotopologue.

11. Predict m/z and the relative heights of the carbon tetrabromide molecular ion $[CBr_4]^+$ isotopologue peaks. Check your answer with the spectrum given in the NIST Chemistry WebBook.

12. One of the fragments in the mass spectrum of carbon tetrachloride (CCl_4) is $[CCl_3]^{+.}$ Predict m/z and the relative heights of the $[CCl_3]^+$ isotopologue peaks. Check your answer with the spectrum given in the NIST Chemistry WebBook at http://goo.gl/VfRNo. (Note: When working on these questions, assuming C, H have only 1 isotope)

Preparation for next week Mahaffy, 2e sections 3.9-3.10:

Show the relationships between wavelength and frequency of light for the different regions of the electromagnetic spectrum. You should know the order of the types of light, and their relative frequencies.

1. If light has a frequency of 3×10^{15} s^{-1}, what are the values of its wavelength (λ) in nm and wave number ($\tilde{\upsilon}$) in cm^{-1}?

2. If light has $\tilde{\upsilon}$ of 2000 cm^{-1}. What are the values of its wavelength (λ) in nm, speed (c) in m/s, and frequency (ν) in Hz? (Useful information: $c = \lambda \cdot \upsilon$ = speed of light where λ is wavelength (m) and υ is frequency (1 s^{-1} = 1 Hz) $\tilde{\upsilon}$ (cm^{-1}) = $\frac{1}{\lambda}$ is wave number and $\upsilon = c \cdot \tilde{\upsilon}$).

3. Consider two waves of light, light wave "A" with wavelength of 800 nm and light wave "B" with wavelength 1600 nm. Circle all the appropriate relationships in the parentheses for the five statements below. (Keep in mind that $\upsilon \sim \sqrt{\frac{k}{m}}$ where *k* represents the strength of the bond and *m* represent mass.)

    i. The speed of light wave "A" is (*greater than / less than / equal to*) the speed of light wave "B".

    ii. The wavenumber of light wave "A" is (*greater than / less than / equal to*) the wavenumber of light wave "B".

    iii. The frequency of light wave "A" is (*greater than / less than / equal to*) the frequency of light wave "B".

    iv. Assuming the same atom masses, light wave "A" will match the frequency of bonds that are (*stronger than / weaker than / the same strength as*) the bonds that match the frequency of light wave "B".

    v. Assuming the same bond strength, light wave "A" will match the frequency of bonds that contain atoms that are (*heavier / lighter*) than the bonds that match the frequency of light wave "B".

Answers:

1.
   a. 32.06 g/mol
   b. Molecular ion peak/parent peak
   c. Furthest peak on right
   d. Loss of proton(s)
   e. Loss of alcohol 'H' (peak 31)
   f. $[CHO]^+$ = 29 m/z; $[CH_3O]^+$ = 31 m/z; $[CH_3OH]^+$ = 32 m/z
2.
   a. 64 m/z and 66 m/z
   b. Peaks between 25-30 m/z
   c. X = chlorine; 75:25 height ratio; peak masses correspond to $[^{35}Cl]^+$ and $[^{37}Cl]^+$
   d. $[CH_3CH_2{}^{35}Cl]^+$ and $[CH_3CH_2{}^{37}Cl]^+$
   e. $[CH_2{}^{37}Cl]^+$
   f. 75:25 or 3:1
3. Left: THF // Right: 2-butanone
4.
   a.

$CH_2{}^{35}Cl_2{}^+$	84	9/16	9
$CH_2{}^{35}Cl\ {}^{37}Cl^+$	86	3/16	6
$CH_2{}^{37}Cl\ {}^{35}Cl^+$	86	3/16	
$CH_2{}^{37}Cl_2{}^+$	88	1/16	1

   b. 1 : 6 : 9
   c. $[CH_2{}^{35}Cl]^+$ = 49 m/z; $[CH_2{}^{37}Cl]^+$ = 51 m/z

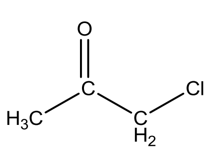
5.
   a.

$CH_2\ {}^{79}Br^{35}Cl^+$	128	3/8	3
$CH_2\ {}^{79}Br^{37}Cl^+$	130	1/8	4
$CH_2\ {}^{81}Br^{35}Cl^+$	130	3/8	
$CH_2\ {}^{81}Br^{37}Cl^+$	132	1/8	1

   b. equally abundant $[CH_2{}^{79}Br^{35}Cl]^+$ and $[CH_2{}^{81}Br^{35}Cl]^+$
   c. 3 : 4 : 1
6. 3 oxygens
7.
   a. 3 peaks
   b. 5:1
8.
   a.

$CH_2{}^{79}Br_2{}^+$	172	¼	1
$CH_2{}^{79}Br^{81}Br^+$	174	¼	2
$CH_2{}^{79}Br^{81}Br^+$	174	¼	
$CH_2{}^{81}Br_2{}^+$	176	¼	1

   b. all equally abundant
   c. 1 : 2 : 1 ($[^{79}Br^{79}Br]^+$: $[^{79}Br^{81}Br]^+$: $[^{81}Br^{81}Br]^+$)
   d. $[CH_2{}^{79}Br]^+$ = 93 m/z; $[CH_2{}^{81}Br]^+$ = 95 m/z
9.



10. 7 peaks
    a. 72 : 1
11. 1 : 4 : 6 : 4 : 1
    $C^{79}Br^{79}Br^{79}Br^{79}Br^+$ = 328
    $C^{79}Br^{79}Br^{79}Br^{81}Br^+$ = 330
    $C^{79}Br^{79}Br^{81}Br^{81}Br^+$ = 332
    $C^{79}Br^{81}Br^{81}Br^{81}Br^+$ = 334
    $C^{81}Br^{81}Br^{81}Br^{81}Br^+$ = 336
12. 117, 119, 121, 123 (m/z)
    27 : 27 : 9 : 1 (ratios)

Preparation for next week

1. $\tilde{\nu} = 1 \times 10^5\ cm^{-1}$; $\lambda = 100$ nm
2. $\lambda = 5000$ nm; $c = 3 \times 10^8\ {}^{m}/_{s}$
   $\nu = 6 \times 10^{13}\ s^{-1}$
3.
   i. Equal to
   ii. Greater than
   iii. Greater than
   iv. Stronger than
   v. Lighter