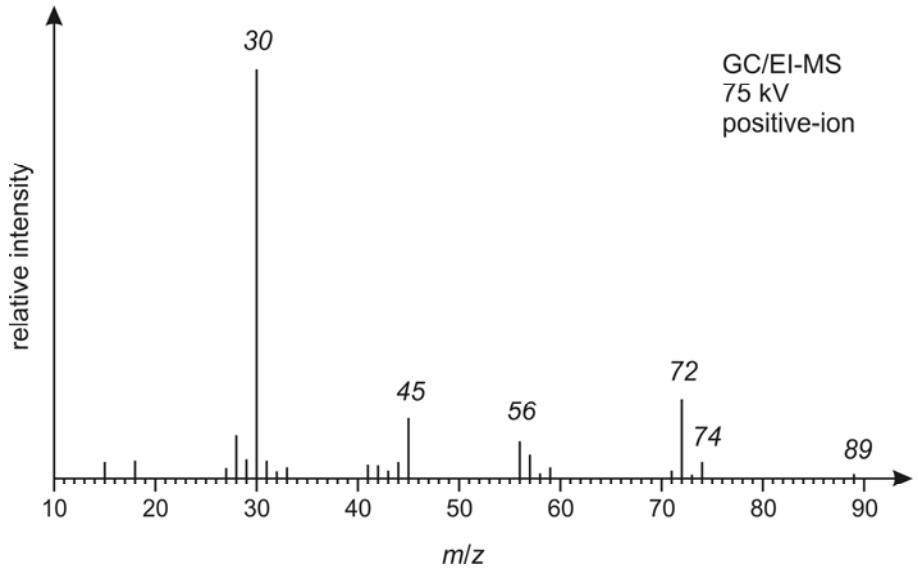
Chemistry 4361/8361 Monday, November 25

Workshop 5
Simple EI Fragmentation Problems

1. You perform a GC-MS experiment on a reaction you've run many times before, and observe two total-ion peaks at retention times you don't expect. The reaction must be contaminated with something—what is it?

   In each case, I'll tell you what the parent ion mass is, and give you the output of an elemental composition calculator so you can make some guesses about the molecular formula. Then, use the mass spectrum to determine the molecular structure of your contaminant. *Hint:* You may want to use two of the summary tables in Pretsch, Table 2.5.7 ("Indicators of the Presence of Heteroatoms") and Table 2.5.9 ("Homologous Mass Series os Indications of Structural Type") to help you use small fragment masses as indicators of which atoms are present in your unknown. For each fragment, try to draw a mechanism that illustrates how the observed fragment is generated by the parent radical cation.

   a.



   For M = 89,

Elemental Composition Calculator v1.0

Calculations for : 89.0000 +/- 0.300 amu
monoisotopic mass

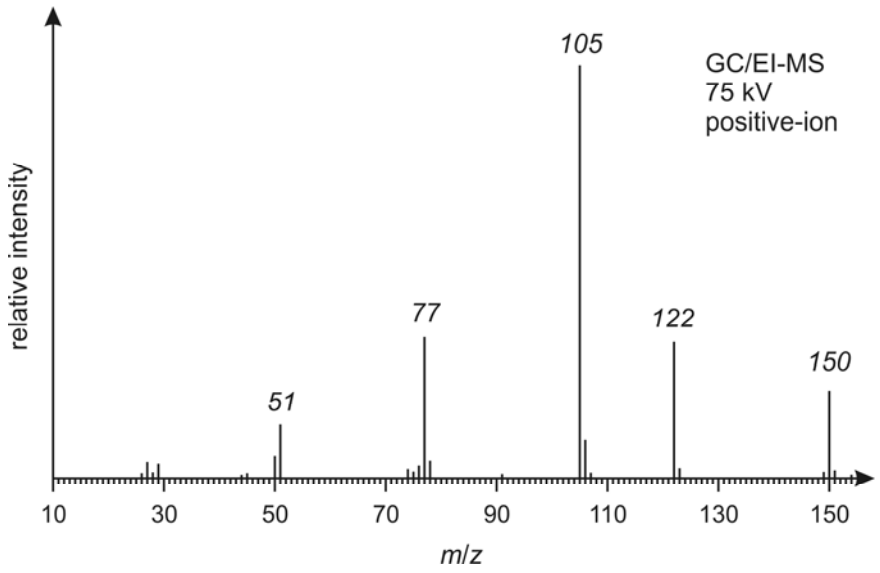
C	12.0000	3	10
H	1.0078	6	12
N	14.0030	0	4

```
O     15.9949     0     4
S     31.9720     0     1

 C  H  N  O  S      mass       diff       ppm

 3 11  3  0  0     89.0952   -0.0952   -1070.7
 4 11  1  1  0     89.0840   -0.0840    -944.5
 3  9  2  1  0     89.0714   -0.0714    -803.2
 4  9  0  2  0     89.0602   -0.0602    -677.0
 3  7  1  2  0     89.0476   -0.0476    -535.6
 4  9  0  0  1     89.0424   -0.0424    -477.4
 3  7  1  0  1     89.0299   -0.0299    -336.1
```

b.



For M = 150,

Elemental Composition Calculator v1.0

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Calculations for :   150.0000 +/-  0.500 amu
monoisotopic mass

  C    12.0000    6   12
  H     1.0078   10   24
  N    14.0030    0    4
  O    15.9949    0    4
  S    31.9720    0    2

  C  H  N  O  S      mass       diff       ppm

 11 18  0  0  0   150.1408   -0.1408    -939.0
 10 16  1  0  0   150.1282   -0.1282    -855.1
  9 14  2  0  0   150.1156   -0.1156    -771.3
  8 12  3  0  0   150.1031   -0.1031    -687.4
  7 24  3  0  0   150.1970   -0.1970   -1313.4
  7 10  4  0  0   150.0905   -0.0905    -603.6
```

C	H	N	O	S	mass	diff	ppm
6	22	4	0	0	150.1844	-0.1844	-1229.6
10	14	0	1	0	150.1044	-0.1044	-696.4
9	12	1	1	0	150.0918	-0.0918	-612.5
8	24	1	1	0	150.1857	-0.1857	-1238.5
8	10	2	1	0	150.0793	-0.0793	-528.7
7	22	2	1	0	150.1732	-0.1732	-1154.7
6	20	3	1	0	150.1606	-0.1606	-1070.9
9	10	0	2	0	150.0680	-0.0680	-453.8
8	22	0	2	0	150.1619	-0.1619	-1079.8
7	20	1	2	0	150.1494	-0.1494	-996.0
6	18	2	2	0	150.1368	-0.1368	-912.1
7	18	0	3	0	150.1255	-0.1255	-837.2
6	16	1	3	0	150.1130	-0.1130	-753.4
6	14	0	4	0	150.0892	-0.0892	-594.7
9	10	0	0	1	150.0503	-0.0503	-335.4
8	22	0	0	1	150.1442	-0.1442	-961.4
7	20	1	0	1	150.1316	-0.1316	-877.6
6	18	2	0	1	150.1190	-0.1190	-793.7
7	18	0	1	1	150.1078	-0.1078	-718.8
6	16	1	1	1	150.0952	-0.0952	-635.0
6	14	0	2	1	150.0714	-0.0714	-476.3
6	14	0	0	2	150.0536	-0.0536	-357.9

3. NMR tells you that an alkane (petroleum) extract has two-fold symmetry, and that the molecule has six methyl groups. Based on the EI mass spectrum of your alkane below, what is a likely structure for the molecule?