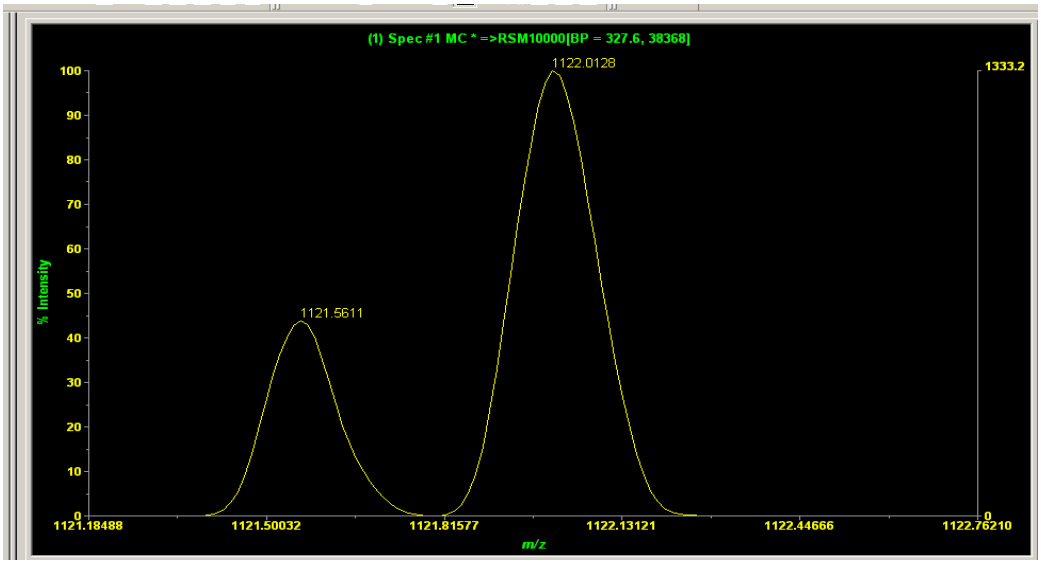
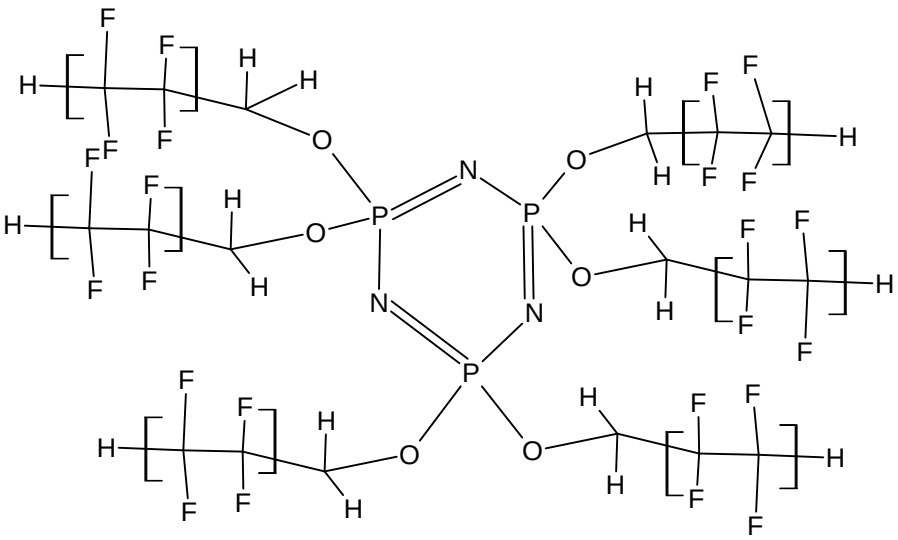
CHEMISTRY 133
Spring, 2015 Homework Set 3
Set 3.2 - Additional Problems:

1. The mass spectrum below shows the separation between an ultramark compound (general structure I) and a contaminant. This was obtained using positive ESI ionization (thus usually requires addition of H to produce the charge as M + H) with a time of flight mass spectrometer.



Structure I – Ultramark – parts in brackets can consist of 1, 2 or 3 units.



Answer the following questions:

a) Determine which peak in the mass spectrum is from Ultramark and which is from the contaminant. To figure this out, you may need to calculate a monoisotopic mass. Also determine the size of the attachments to the N, and P containing core (-CF_2CF_2- in brackets consists of repeating units of 1, 2, or 3). Determine the total number of repeating units for the whole structure. Note that the calibration for the Ultramark peak is not perfect (error somewhat larger than 5 ppm due to the contaminant causing a slight shift in the centroid mass).

b) Using the $m_{1/2}$ definition (you may need a ruler for this), estimate the resolution.

c) Determine where you would expect the ultramark peak would be if it was charged through a sodium ion adduct formation instead of through protonation (give mass to 7 places).

Bonus Additional Problem 1:

Calculate the expected isotopic ratios for M+2/M, M+4/M, and M+6/M peaks for $C_2H_3BrCl_2$. Give as ratios to 100 (e.g. 22/100). You can ignore the contributions from ^{13}C and ^{2}H.

Bonus Additional Problem 2:

A peptide (only one compound) in a liquid sample is analyzed using electrospray ionization mass spectrometry in the positive mode. Protonation is expected. The largest peaks are observed at 640.8, 427.2, and 320.8 Daltons.

a) What is the molecular mass of the most common isotope of the peptide?

b) What charge is associated with each of the above peaks?