Chemistry 4361/8361 Monday, November 12

In-Class Exercise Solutions: Halogen Isotope Patterns

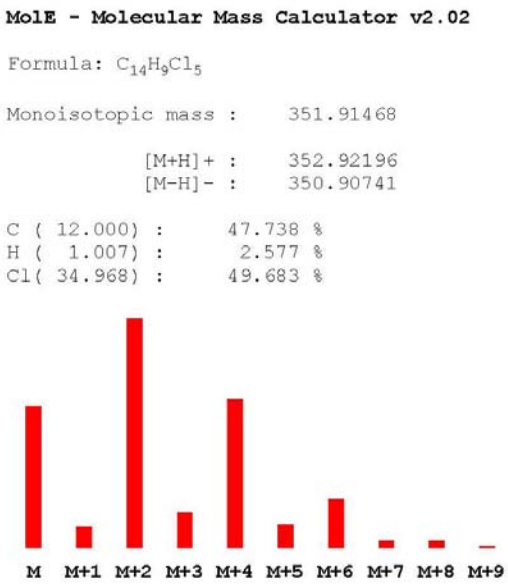
a. The isotopic abundance of Cl is 75% ^{35}Cl and 25% ^{37}Cl. Calculating the probability of an intermediate number of ^{35}Cl and ^{37}Cl atoms is complicated, but calculating the probability that all atoms will be one or the other is pretty simple: it's just P^z, where P is the probability of one atom being a particular type, and z is the number of atoms. So, for

number of Cl atoms (z)	probability of $(^{35}Cl)_z$	probability of $(^{37}Cl)_z$
1	$(0.75)^1 = 0.75$	$(0.25)^1 = 0.25$
2	$(0.75)^2 = 0.56$	$(0.25)^2 = 0.06$
3	$(0.75)^3 = 0.42$	$(0.25)^3 = 0.02$
4	$(0.75)^4 = 0.32$	$(0.25)^4 = 0.00$
5	$(0.75)^5 = 0.24$	$(0.25)^5 = 0.00$
6	$(0.75)^6 = 0.18$	$(0.25)^6 = 0.00$

Note that only the z = 1 row adds to 100%; the other rows have contributions from molecules with some ^{35}Cl and some ^{37}Cl atoms that aren't listed.

Looking at our m/z = 354 multiplet now, we can ask: what fraction of the total intensity is the lowest-mass (m/z = 352) peak? There are four significant peaks in the pattern, with intensities of ~3:4:3:1 maybe. That means that the lowest-mass peak isn't 1/3 of the total intensity, but maybe ~1/4; that would point to the molecule having 5 Cl atoms. The rest of the molecule would then have mass 352 - 5(35) = 177. That could make the molecular formula $C_{13}H_{21}Cl_5$, with an unsaturation number of 1; or $C_{14}H_9Cl_5$, with an unsaturation number of 8. If the molecule is aromatic (minimum UN = 4), the formula must be $C_{14}H_9Cl_5$.

Clearly that is the hard way to do this kind of problem. The easier way would be to use a web-based calculator to show us the isotope pattern we should expect. For example, if I plug $C_{14}H_9Cl_5$ into the calculator at http://library.med.utah.edu/masspec/mole.htm, I get the output shown at right, which is awfully close to the spectrum above.



b. I think each of the lower-mass multiplets match the % ^{35}Cl values we calculated in the chart in part (a). The pattern at 319 has three major peaks with intensities ~3:4:2; that would mean the first peak is abut 33% of the total, and corresponds to a fragment with 4 Cl atoms. The pattern at 282 is a bit messy, but if we consider only the tallest peaks, the first tall peak could be 42% of the total, with 3 Cl atoms. And the “pattern” at 235 has a first peak with over half the total intensity for that group, suggesting a fragment with two Cl atoms.