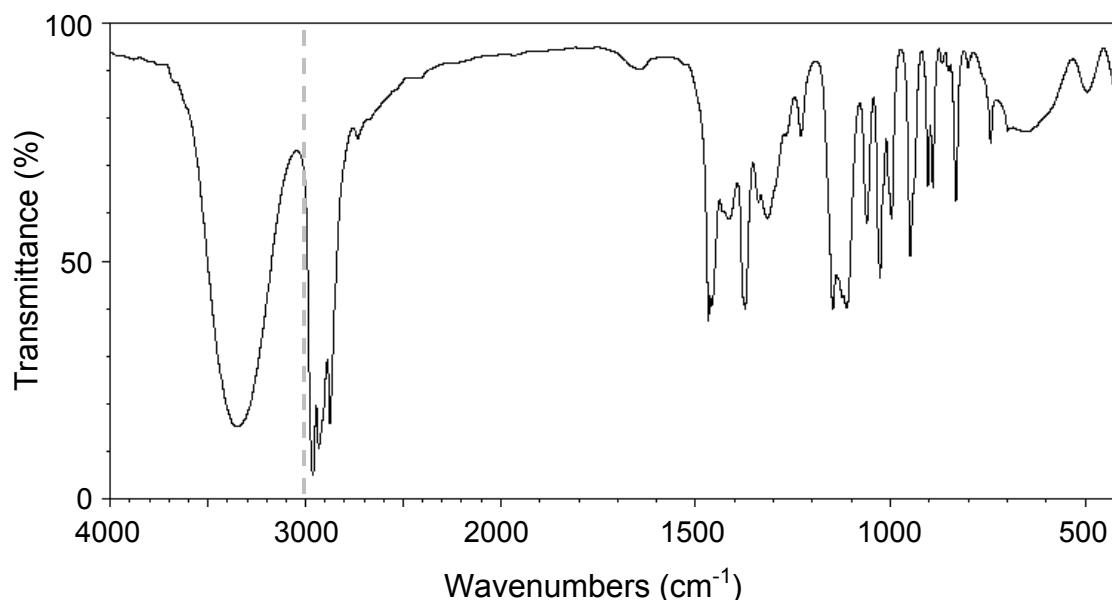
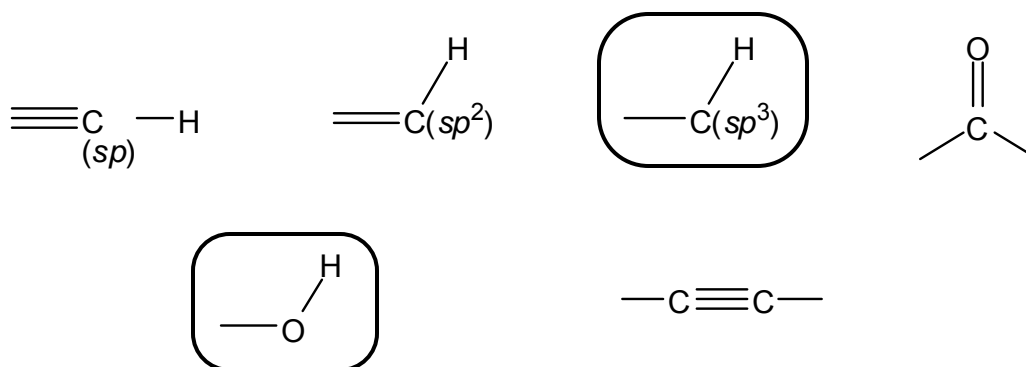


Workshop 25
IR Spectroscopy and MS Fragmentation Patterns

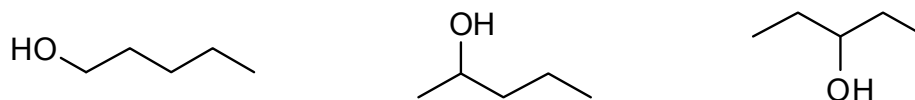
- a. IR spectra are typically interpreted by looking at characteristic resonances in the 1600-3600 cm^{-1} range of the spectrum; the region lower than 1600 cm^{-1} —the “fingerprint region”—is often too complicated to make any sense from. (That is certainly the case here.) Three features of the rest of this spectrum stand out:
- In the C-H region of the spectrum (2800-3200 cm^{-1}), there are peaks with frequencies below 3000 cm^{-1} but not above 3000 cm^{-1} . That means the molecule has only $\text{C}_{sp^3}\text{-H}$ bonds, and not $\text{C}_{sp^2}\text{-H}$ or $\text{C}_{sp}\text{-H}$ bonds.
 - There are no peaks in the 1600-2500 cm^{-1} range. According to the IR frequency table we looked at in class, this rules out some functional groups—our molecule has no carbonyls, and no triple bonds.
 - There is a big blobby peak at $\nu = 3400 \text{ cm}^{-1}$. Assuming our sample isn't wet with adsorbed water (which happens in real life, but won't ever happen on my exams) this means our molecule is an alcohol.



So,

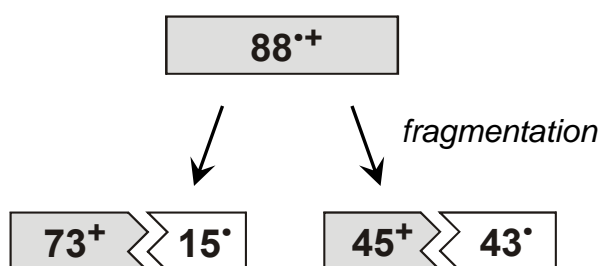


- b. So, if our molecule only has the features from the previous page, and it still has a five-carbon chain backbone, the metabolite must be a pentanol:

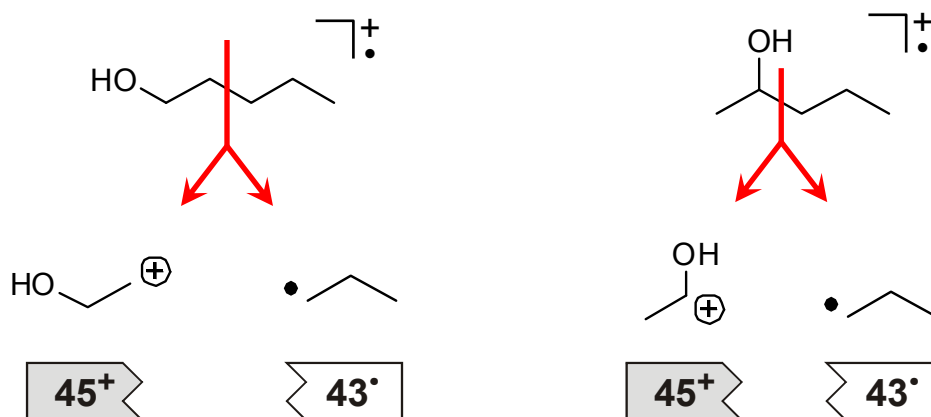


- c. All of the structures above have MW = 88 amu. So they are all candidates.

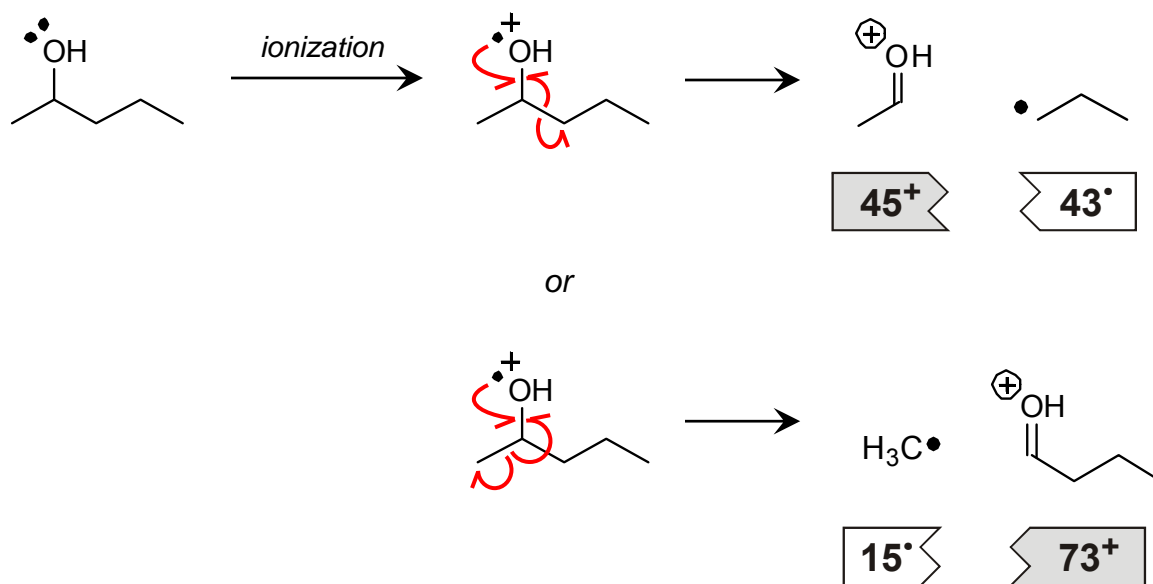
- d. Each of the fragment peaks in the mass spectrum corresponds to a cation; each cation has a fragment partner, a radical, that is not detected by the mass spectrometer. So, by definition, we need to explain two different fragmentations:



In principle, any of the molecules above could lose a mass of 15 to produce a fragment with $m/z = 73$; mass 15 corresponds to a $-\text{CH}_3$ group, and all of the molecules have that. But only the first two could break to make fragments of mass 45 and 43:



That rules out 3-pentanol as a possible structure for the unknown metabolite. I would argue that the first structure, 1-pentanol, also doesn't make a lot of sense; in the mass spectrum, why would only the third and fifth bonds break? Why wouldn't we see other cleavages? On the other hand, for the second molecule the fragmentation pattern is consistent with initial ionization of an oxygen lone-pair electron, followed by α -cleavage of an adjacent bond:



- e. Both of the fragmentation processes above create similarly substituted, resonance-stabilized cations. But, of the radicals, the first (primary) radical should be more stable than the second (methyl) radical. I would expect the first fragmentation pathway should be favored because of this, and so the $m/z = 45$ ions should predominate.