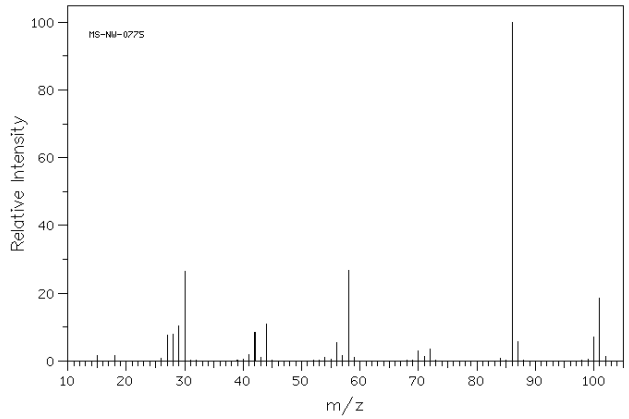
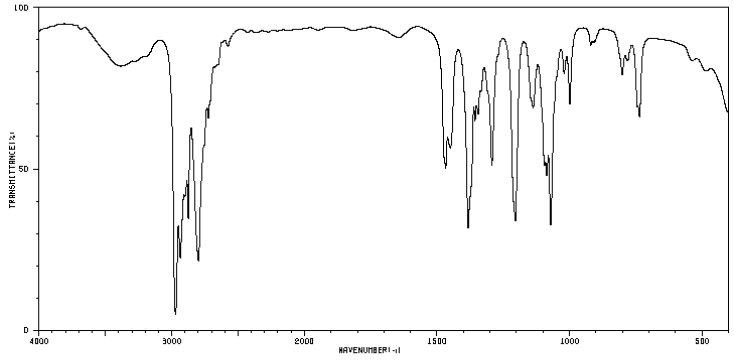
Chem 2061 Fall 2005
Chapter 12 assignment
Due Monday, Oct 24

Answer the following questions on a separate sheet of paper.

A scientist working for a HazMat team arrives at a manufacturing plant where a chemical was spilled. The stench was unbearable, like rotten fish. The scientist took a sample of the chemical and performed GC/MS and IR analysis. The gas chromatogram showed it was a single compound, and the mass spectrum is shown below:



The molecular ion is visible at 101. The infrared spectrum is shown below:



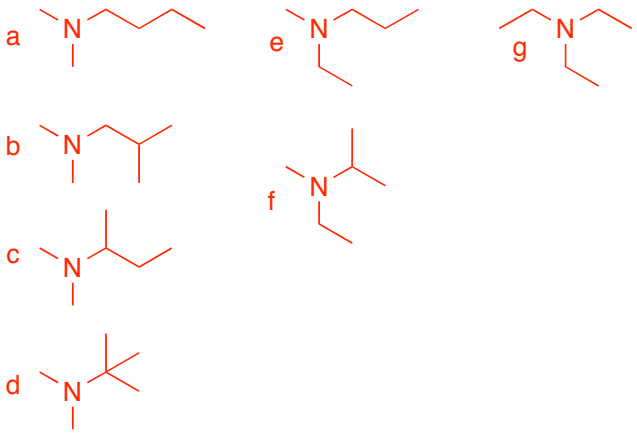
The experimenter assumed that the broad peak above 3000 was too weak to be part of the compound, and was probably just from water.

Assign and rationalize any peaks you can in the above two spectra. Point out any distinctions on the mass spectrum. What common fragments could be lost to give the peaks at 86 and 72?

Draw a few possible structures that could account for the above spectra. How could you confirm your predictions?

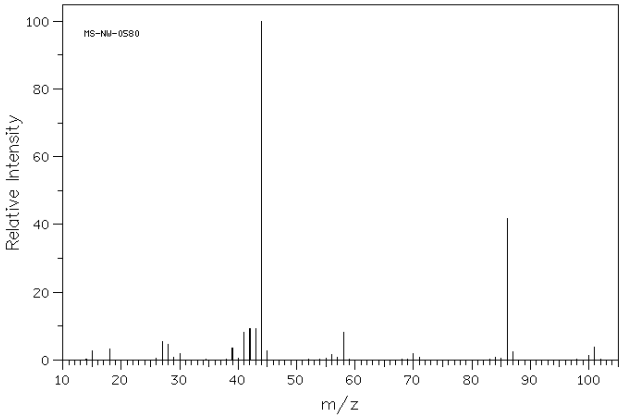
The IR spectrum shows nothing interesting, only sp^3 C–H bonds so this must be a simple hydrocarbon with or without any groups that don't show up on IR (symmetrical alkyne, ether, tertiary amine, etc.)

The odd molecular ion tells us there's an odd number of nitrogens in the compound. The simplest compound would be with 1 nitrogen, and a formula of $C_6H_{15}N$ (from some trial-and error arithmetic). Since there's a nitrogen but no N–H stretch on the IR, this must be a tertiary amine (an N attached to 3 carbons). This limits our possibilities somewhat: (all of the butyl and propyl isomers are helpful to us here)



The peaks at 86 and 72 are the loss of 15 and 29 mass units. This corresponds to the loss of methyl radical and ethyl radical, respectively. So, the compound must have methyl groups to be lost (all of the above possibilities do) but also ethyl groups that can be lost. This eliminates compounds b and d, but we're pretty much left with the rest of them at this point.

The scientist knew of a smelly compound with a molecular weight of 101 in the supplies at her company, so she analyzed it by GC/MS and IR. Its mass spectrum is shown below:



Like the unknown, it has a molecular ion at 101 and a peak at 86, but she instantly noticed it's missing the peak at 72. Instead there's a peak at 58 that wasn't present in the other compound. What are some fragments that could be lost to give a peak at 58?

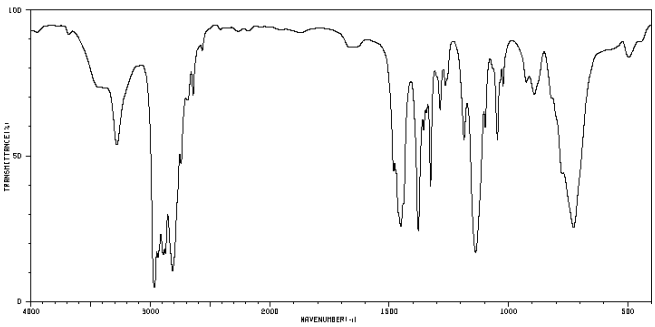
101-58=43. As far as hydrocarbons go, this is a C_3H_7 fragment, which could either be the loss of an n-propyl or an isopropyl radical. So, this new compound must have at least one of those groups present.

Incidentally, there actually is a peak of 58 on the other spectrum but it must come about from rearrangements, since I know the structure on page 1 does not contain any simple fragment that can be lost to give a 58. Using this information, the structures on the first page can be paired down to just c, f, and g.

Remembering that a molecule only fragments in 1 place to give a peak, refine your above predictions to a molecule that could not have fragment with mass of 72.

This molecule *must not* contain an ethyl group, and therefore cannot contain an n-propyl group either. There must be an isopropyl.

The IR is shown below:

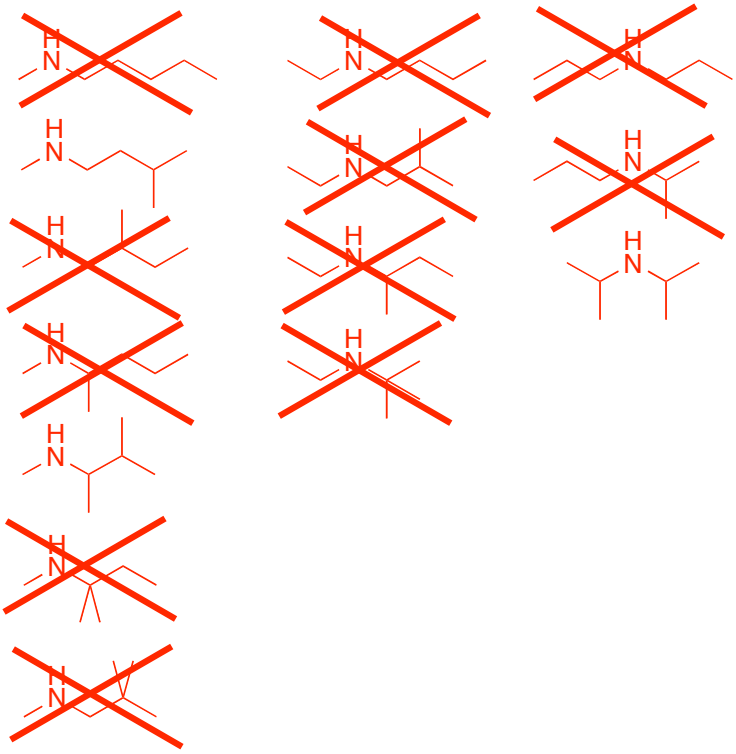


The odd peak around 3300 cm^{-1} instantly grabbed her attention. What kind of stretch is it, and why might the compound on the first page not have this peak? (Hint: both the compounds have the same molecular formula)

That's an N–H stretch, meaning that we're dealing with a 2° amine. The 3° amine on the first page has no N–H stretch of course, because there's no hydrogen attached to the nitrogen!

Using this information, assign a few possible structures to this second compound.

Let's draw all possible 2° amines with 6 carbons and 15 hydrogens, and keep only those with an isopropyl fragment that can be lost, and no ethyl groups.



This leaves us with just 3 structures, but we would need an NMR to decide which of the three this compound is.