

### Workshop 30 Solutions Using IR, MS and NMR Data for Structure Elucidation

a.

**Elemental Composition Calculator v1.0**

Calculations for : 88.0524 +/- 0.003 amu  
monoisotopic mass

atom	mass	min	max
C	12.0000	0	10
H	1.0078	0	20
N	14.0030	0	10
O	15.9949	0	10
S	31.9720	0	2
P	30.9737	0	2

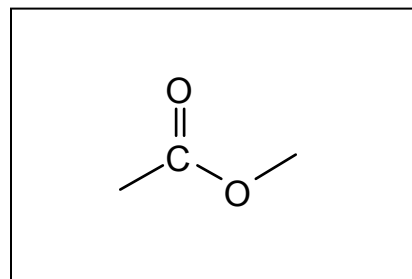
possible molecular formulae:

C	H	N	O	S	P	mass	diff
0	4	6	0	0	0	88.0497	0.0026
2	6	3	1	0	0	88.0510	0.0013
4	8	0	2	0	0	88.0524	0.0000

Number of hits : 3

From the calculator, it looks like the closest guess to the measured exact mass for our molecules is  $C_4H_8O_2$ . (The other two guesses are goofier—it would be hard to imagine what the first guess,  $N_6H_4$ , would look like as a molecule.)

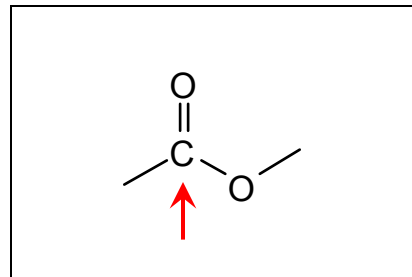
- b. An IR peak at  $\nu \approx 1742 \text{ cm}^{-1}$  indicates an ester. To know this, you'd have to look beyond the table within the chapter in Wade, which says that a peak near  $1710 \text{ cm}^{-1}$  is a  $C=O$  bond stretch; as I mentioned in class, the exact frequency of the peak says a lot about what else is attached to the  $C=O$  bond. Looking at a chart I showed in class,



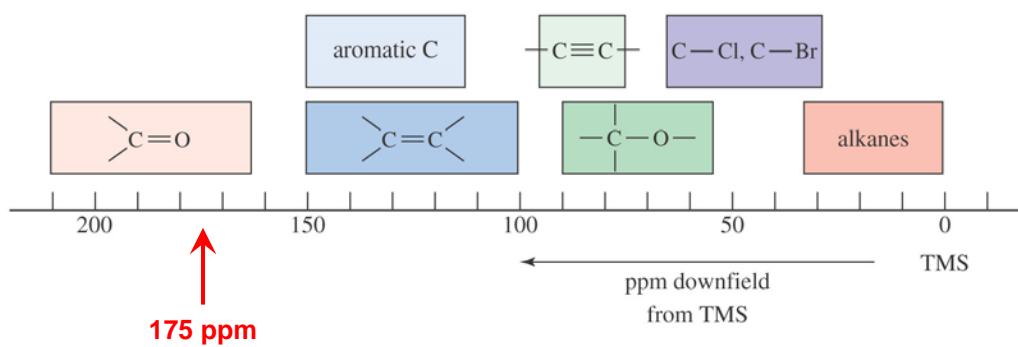
← $\text{cm}^{-1}$ →							
1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

it looks as though the expected frequency of an ester,  $1735\text{ cm}^{-1}$ , is closest to our observed peak frequency. This is great, because it explains the two oxygen atoms in the molecular formula.

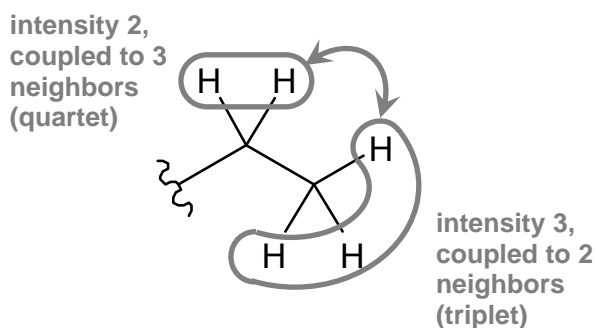
- c. Both  $^{13}\text{C}$  NMR spectra show a peak at  $\delta \approx 175$  ppm, again consistent with a  $\text{C}=\text{O}$  being in each molecule. The plot below from Chapter 13 shows this, but the more detailed table in Appendix 1C confirms that 175 ppm is typical of esters (and not, say, of ketones or aldehydes).



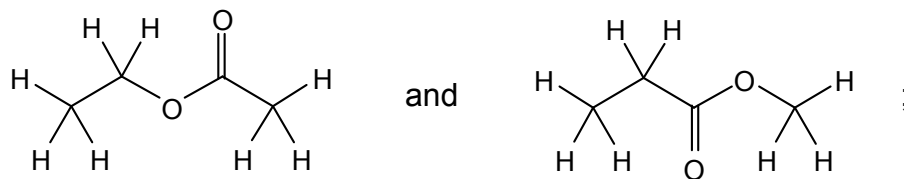
Typical  $^{13}\text{C}$  NMR chemical shifts:



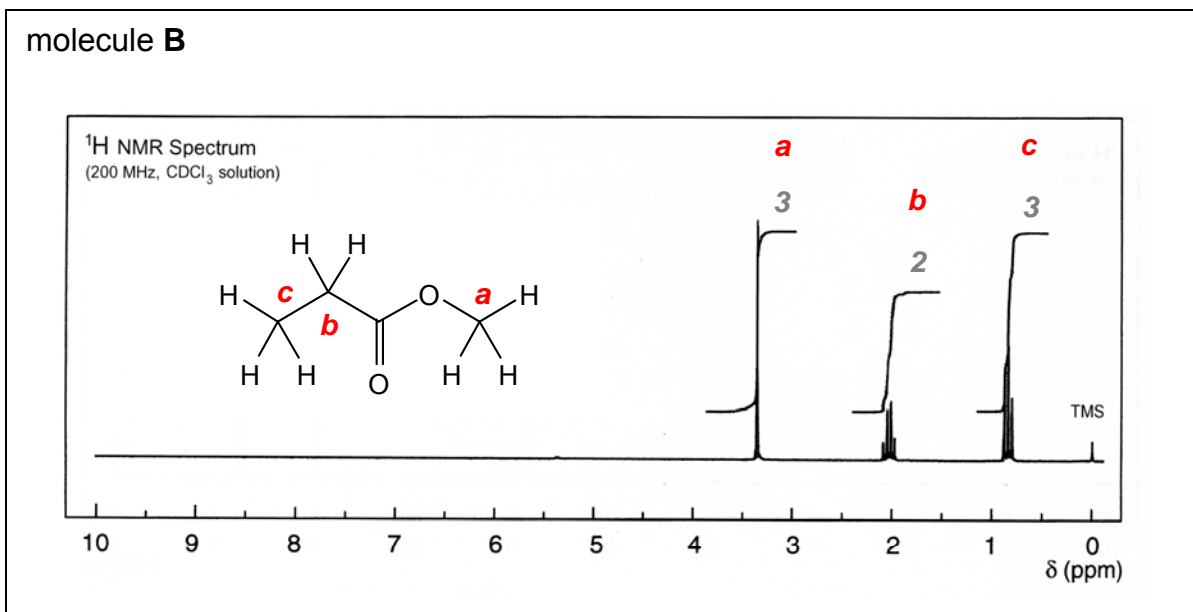
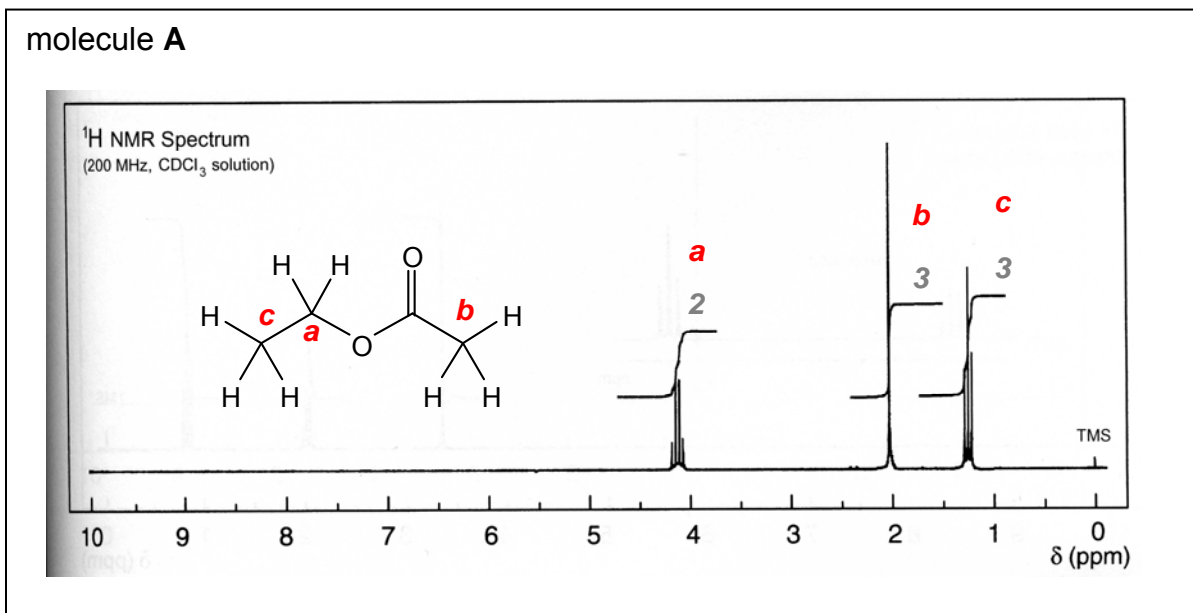
- d. The  $^1\text{H}$  NMR spectra of the two molecules are very similar; each has a singlet of intensity 3, a triplet of intensity 3, and a quartet of intensity 2. The triplet and the quartet in each spectrum are coupled, and most likely represent an ethyl group:



That leaves just an uncoupled methyl group ( $-\text{CH}_3$ ) to account for the other three protons in each spectrum. Taking all of this information together—the ester, the ethyl and methyl groups—means that molecules **A** and **B** must be



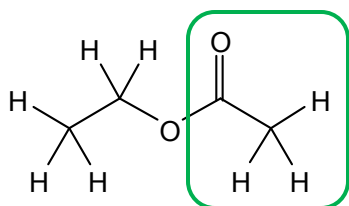
but which is **A** and which is **B**? Chemical shift tables are a good resource for distinguishing these two. Just to give one example of what I mean, the  $^1\text{H}$  shift tables say that  $^1\text{H}$ 's near an electronegative atom (say, as  $\text{H-C-O}$ ) will be downfield of alkanes, at 3-4 ppm, because of the deshielding effect of the oxygen atom. So in the molecule on the left above, the H's that are farthest downfield (at highest  $\delta$ ) must be the  $-\text{CH}_2-\text{O}$ , whereas the H's that are farthest downfield on the right structure must be the  $\text{O}-\text{CH}_3$ .



e. See previous page.

f. The mass spectra of the two molecules are very different, in that each shows a unique fragment mass not present in the other molecule's spectrum. In each of the boxes below, draw your best guess for what the molecule's structure might be, and then circle the portion of the molecule that would give the indicated fragment mass.

molecule **A**: mass 43



molecule **B**: mass 57

