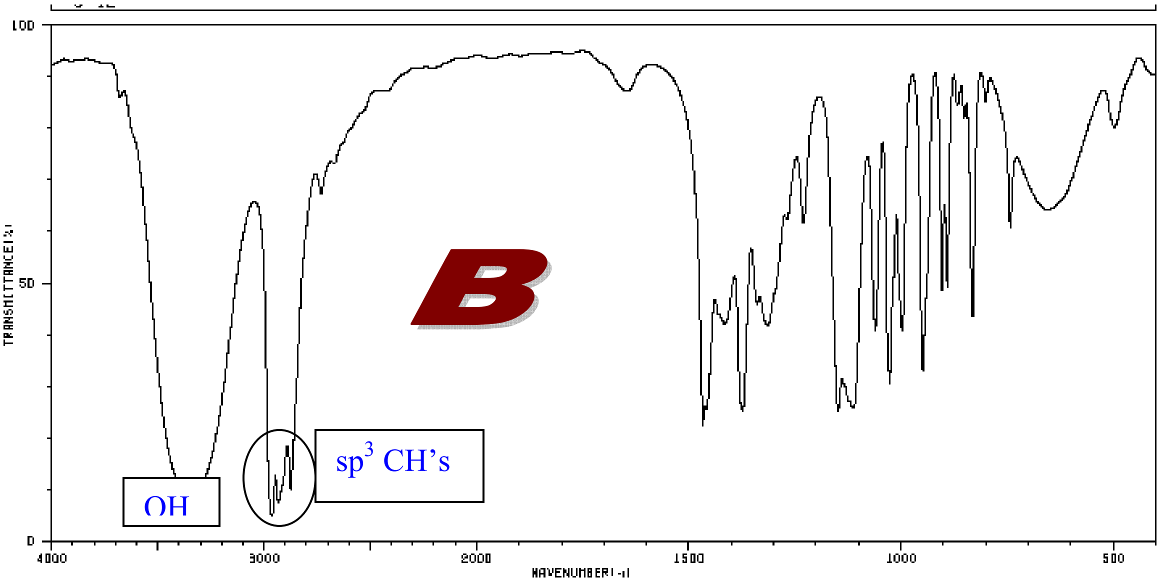
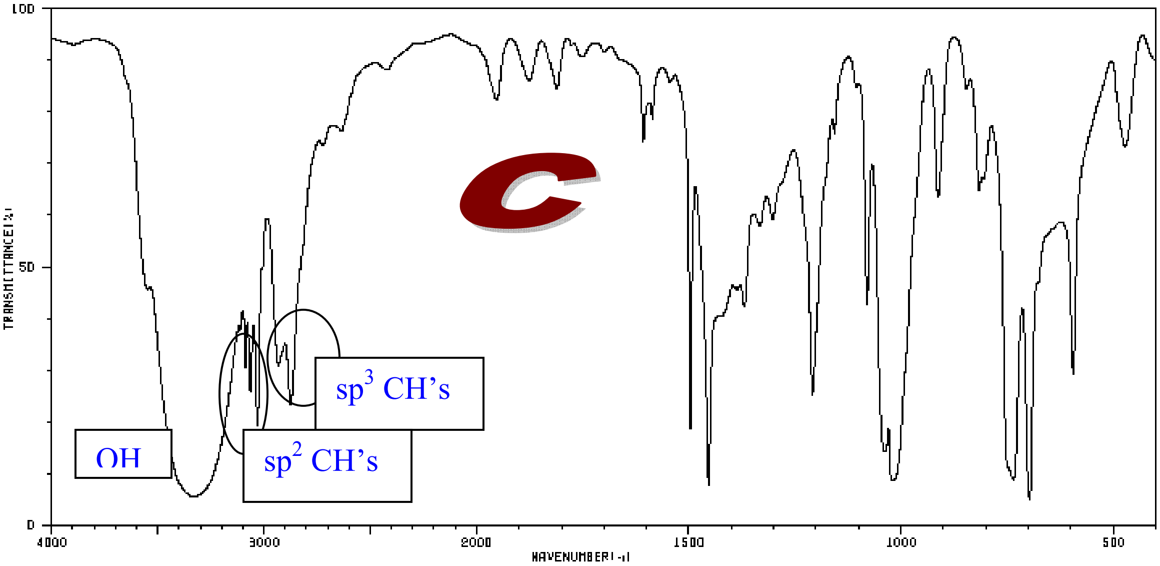
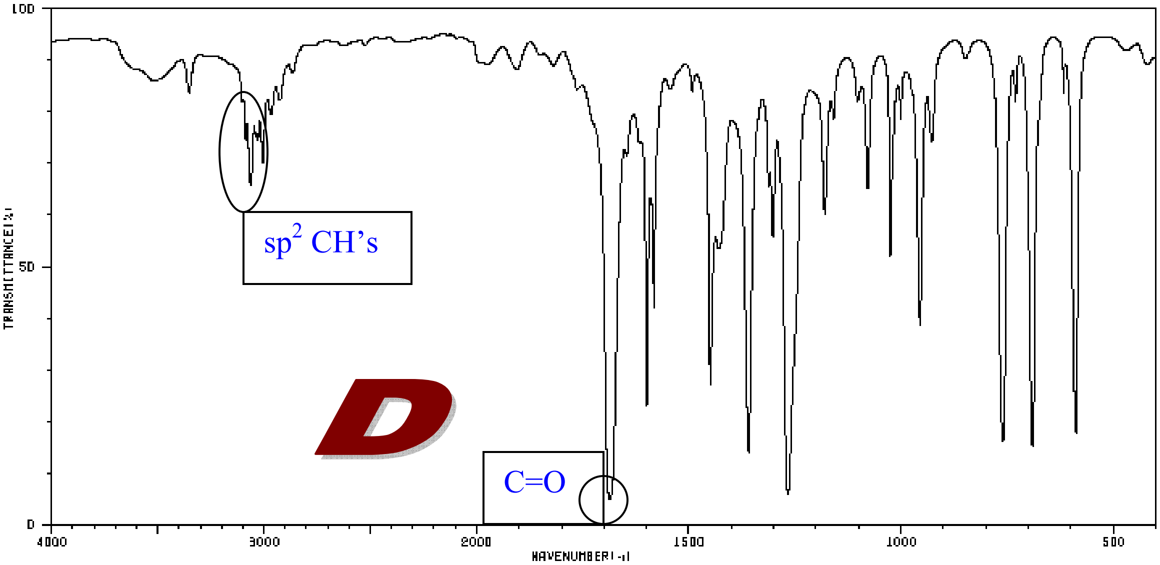
CHM 2120 – Assignment 5 – ANSWERS

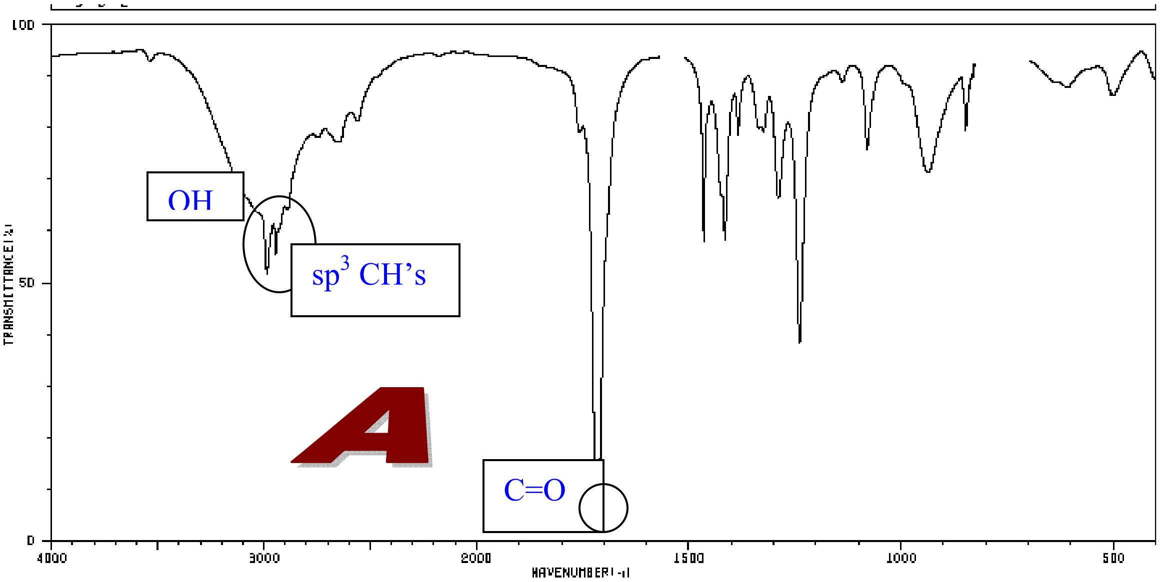
1. Associate each of the following IR spectra with one of the following compounds and justify your answer.
    a. Propanoic acid: look for a carbonyl stretch and a broad OH stretch
    b. 2-Pentanol: look for an OH peak (broad). No carbonyl peak, no sp^2 CH's.
    c. Benzyl alcohol; Look for an OH peak and sp^2 CH's. No carbonyl peak.
    d. Acetophenone: Look for a carbonyl peak and sp^2 CH's. No OH peak.

Note: the key functional groups must be identified. Identifying the peaks on the spectrum directly is an straightforward way to do this.



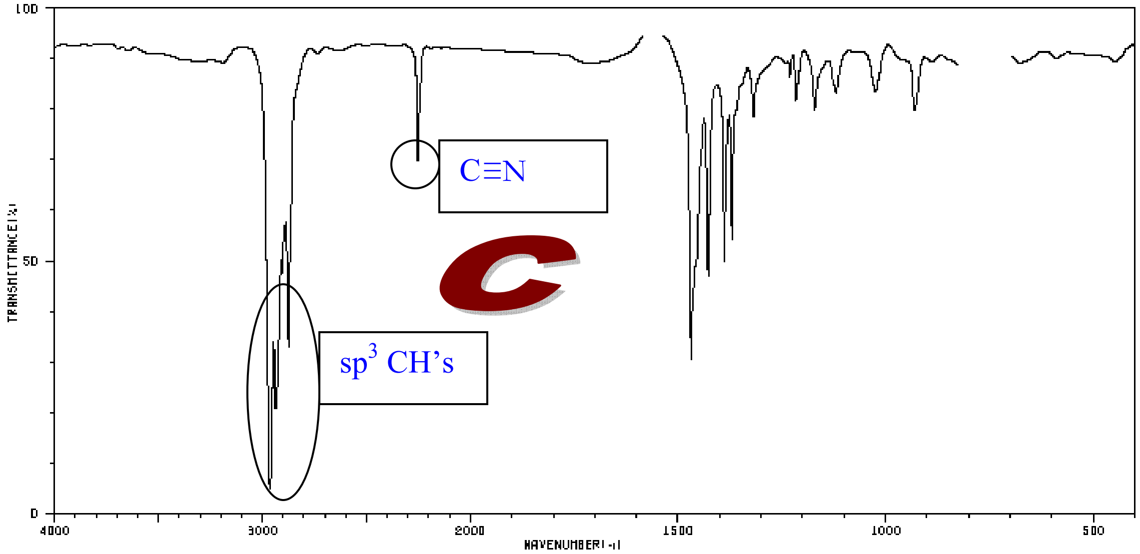


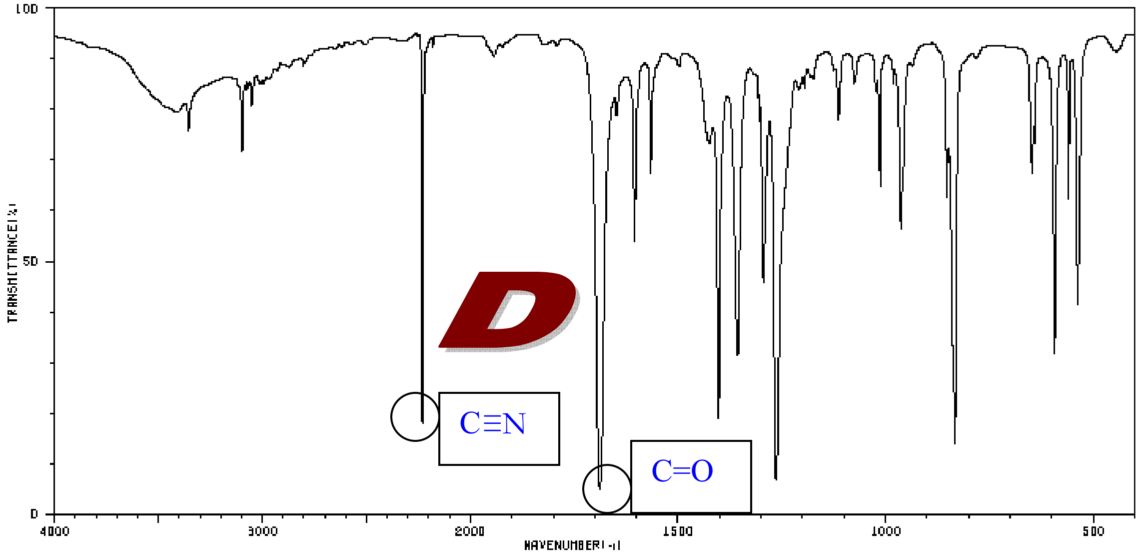

100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
sp^2 CH's
C=O
D

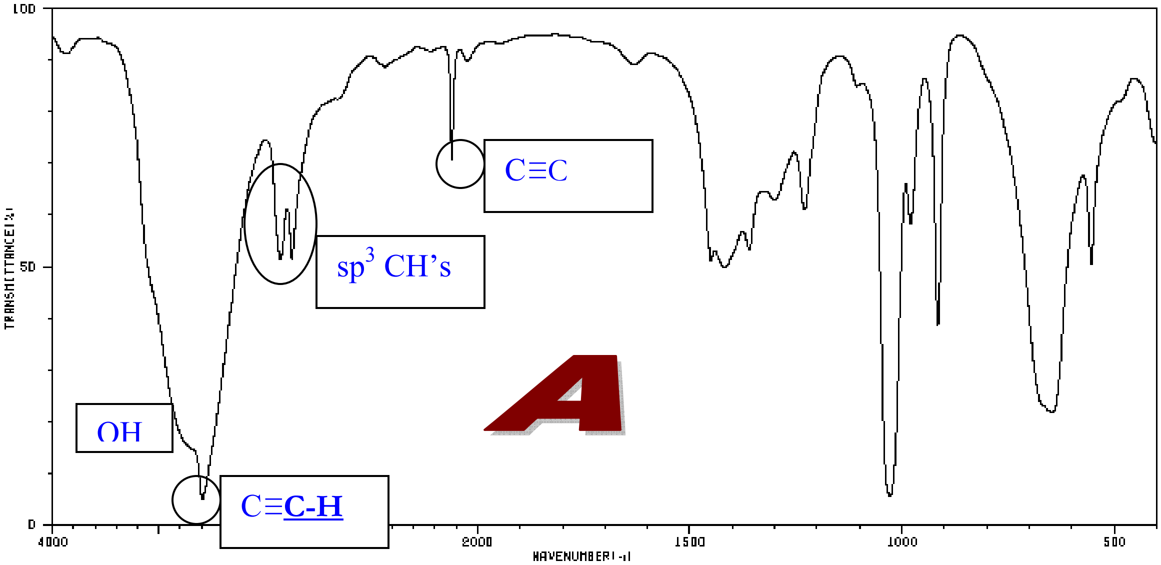

100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
OH
sp^3 CH's
C=O
A

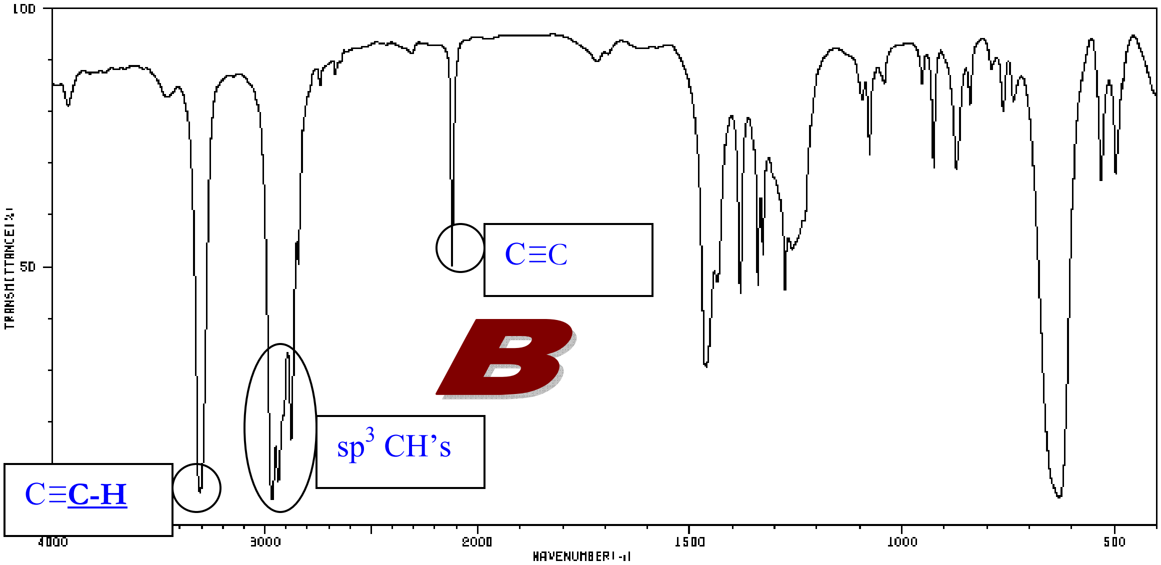
2. Associate each of the following IR spectra with one of the following compounds and justify your answer.
   a. 2-Propyn-1-ol: Look for an alkyne peak C≡C plus an OH peak (broad) and a ≡CH.
   b. 1-Pentyne: Look for an alkyne peak C≡C plus ≡CH. No other key groups.
   c. 4-Methylpentanenitrile: Look for a C≡N. No OH, C=O or ≡CH.
   d. p-Acetylbenzonitrile: Look for C=O, sp^2 CH's and C≡N. No ≡CH.

   Note: the key functional groups must be identified. Identifying the peaks on the spectrum directly is an straightforward way to do this.





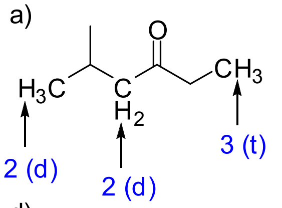

100
50
0
TRANSMITTANCE(%)
4000
2000
1500
1000
500
WAVENUMBER(-1)
C≡C
sp^3 CH's
A
OH
C≡**C-H**


100
50
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
C≡C
B
sp^3 CH's
C≡**C-H**

3. Give the number of peaks expected for the indicated protons in each of the following structures:

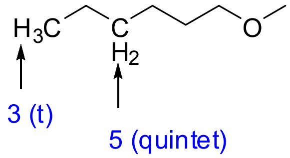
Note: s = singlet, d = doublet, t = triplet, q = quartet

a)



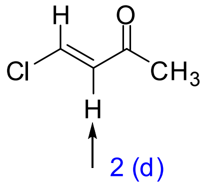
2 (d)
2 (d)
3 (t)

b)



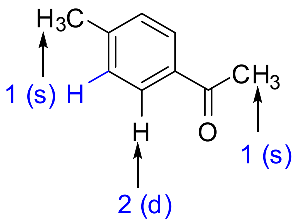
3 (t)
5 (quintet)

c)



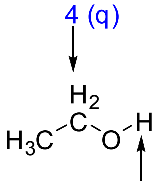
2 (d)

d)



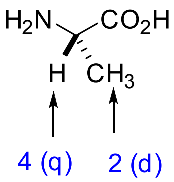
1 (s)
2 (d)
1 (s)

e)



4 (q)
1 (s)
Note: usually a broad singlet

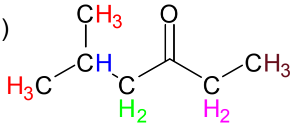
f)



4 (q)
2 (d)

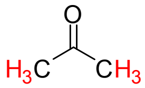
4. How many signals would be expected in the following molecules?

a)



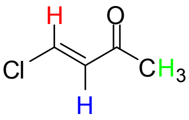
5 signals

b)



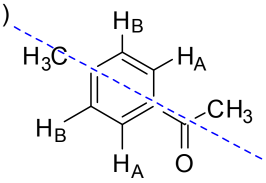
1 signal

c)



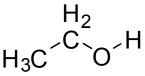
3 signals

d)



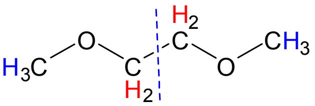
4 signals

e)



3 signals

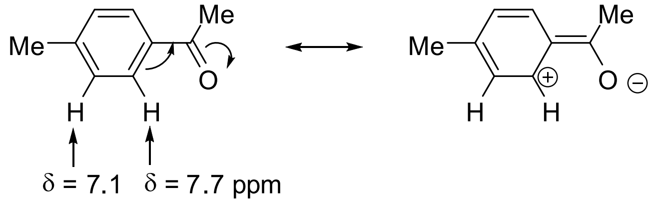
f)



2 signals

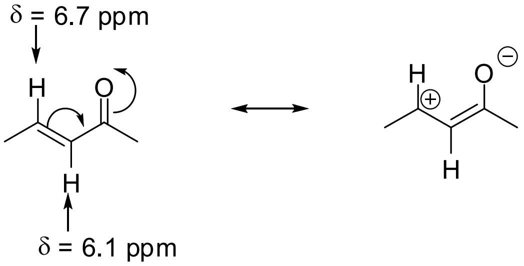
5. Explain the following differences in chemical shift.

a)



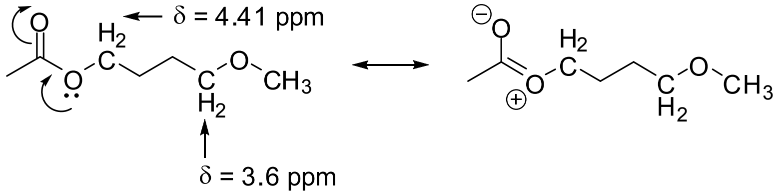
The "H" at 7.7 ppm is deshielded by resonance. Another way to put this is that resonance with the carbonyl group removes electron density from the proton.

b)



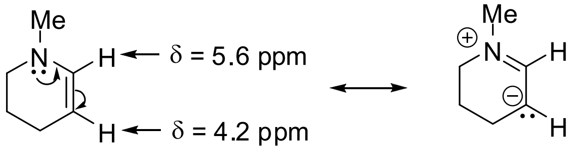
The "H" at 6.7 ppm is strongly deshielded by resonance. The proton at 6.1 ppm is deshielded only by proximity to the electron-withdrawing carbonyl group. This inductive effect is less powerful than the resonance effect.

c)



The oxygen of the ester is even more electronegative than the oxygen of the ether because resonance in the ester is strongly drawing electron density to the carbonyl oxygen. Electron density is consequently pulled more strongly away from the H's at 4.41 ppm.

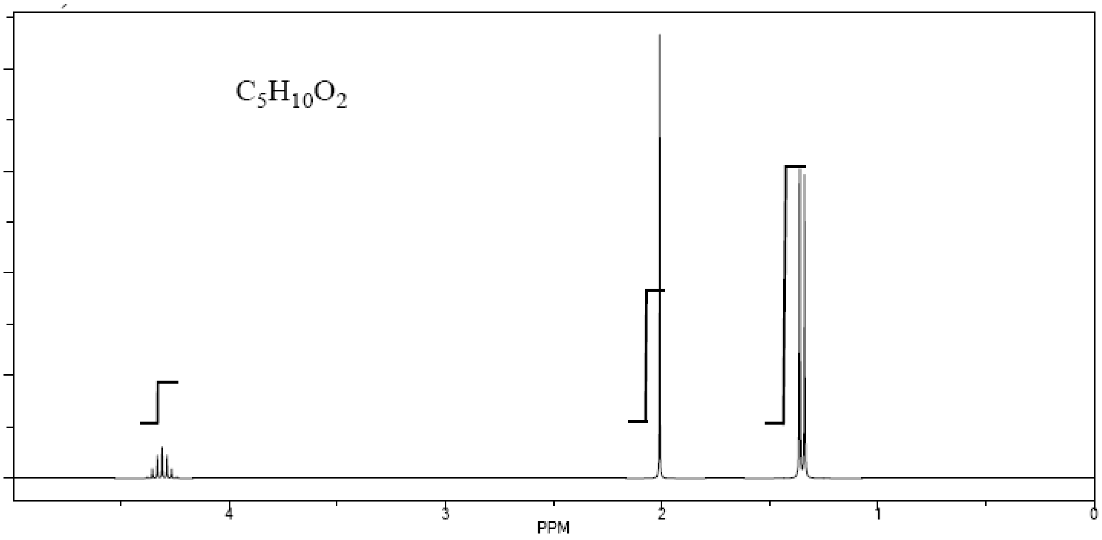
d)



Resonance with the nitrogen pushes electron density onto the H at 4.2 ppm, effectively "shielding" it with electrons.

6. Determine the structure of the following unknowns using the table to fill in your answers.

   a.

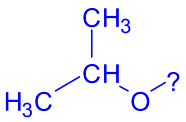


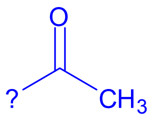
Signal	δ	Integration	Multiplicity	Comments
A	~4.3	1H	m (multiplet) or septet	CH next to O (based on δ)
B	~2.0	3H	s	CH_3 next to C=O
C	~1.3	6H	d	2 x CH3 (identical) next to CH (i.e. an isopropyl group)

DU = [5(2) + 2 – 10]/2 = 1

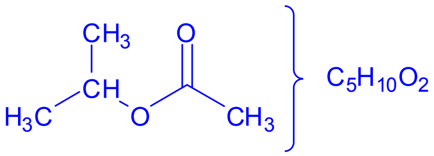
Integration: (6 mm + 18 + 34)/10H = 5.8 mm/H

The pieces:

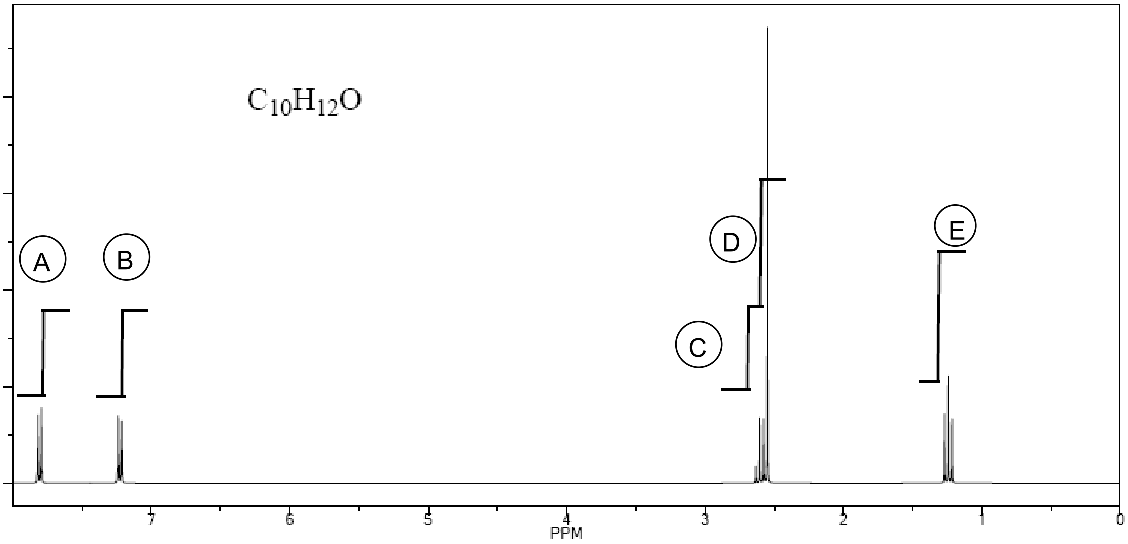


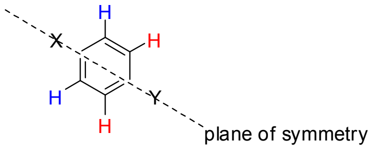


The molecule:



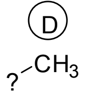
b.



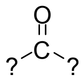
Signal	δ	**Integration**	**Multiplicity**	**Comments**
A	~7.8	2H (CH_2 or 2 x CH)	d	Not all the 2H's can be CH_2 or there wouldn't be enough carbons accounted for in the molecule (there are 10 carbons in the molecule); These H's are in the aromatic region—they can't be CH2's – only CH group exist on aromatic rings. Each CH is next to another CH  The red H has one neighbor (n = 1) and is therefore a doublet.
B	~7.2	2H (CH_2 or 2 x CH)	d	See explanation above
C	~2.7	2H (CH_2 or 2 x CH)	q	CH_2 next to CH_3 (b/c the peak is a quartet); not directly next to O, could be next to C=O (based on δ)
D	~2.6	3H	s	CH_3 next to C=O (based on δ) or on phenyl ring (which acts like an electron-withdrawing group)
E	~1.2	3H	t	CH_3 next to CH_2

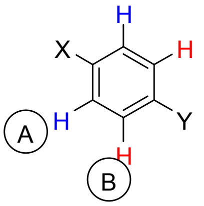
DU = [10(2) + 2 -12]/2 = 5
HINT: DU of 4 = phenyl ring…
In this molecule, there is probably a phenyl ring (DU = 4) + one ring or one double bond
Integration: (11 mm + 11 + 11 + 17 + 17)/12H's = 5.6 mm/H

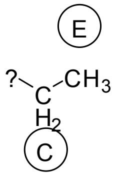
The pieces:



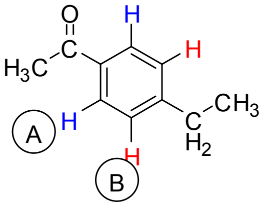
? = carbonyl or phenyl



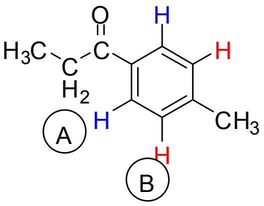




The molecule:

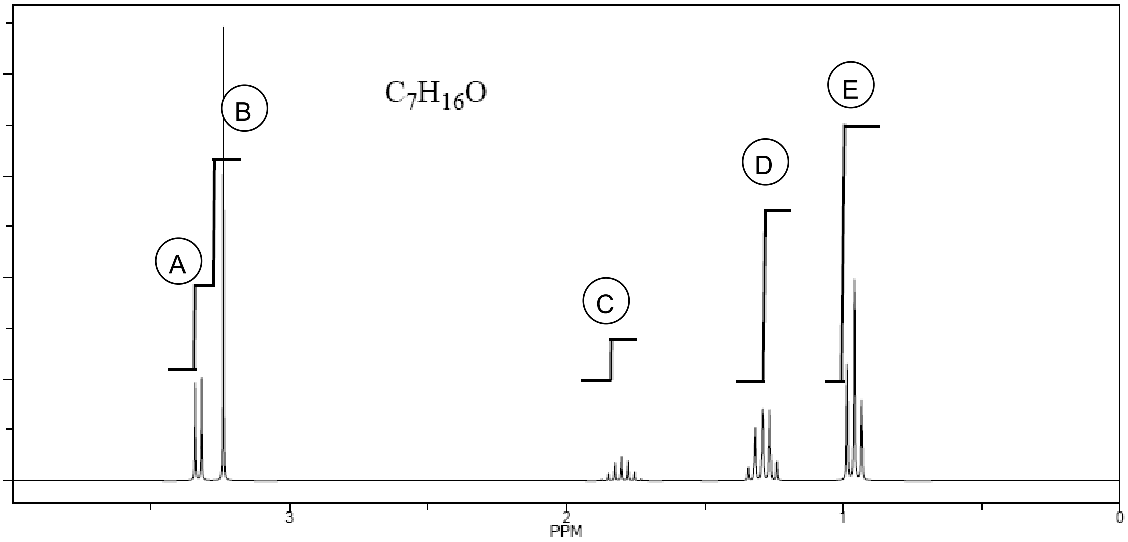


OR



Note: Carbonyl group should be placed at "X". We can tell this because H_A is the most deshielded of the aromatic protons (by resonance with the carbonyl group).

c.

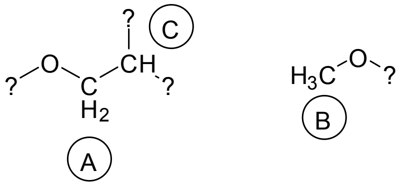


Signal	δ	Integration	Multiplicity	Comments
A	~3.4	2H	d	CH_2 (probably not 2 x CH, but keep this in mind, just in case), next to the CH, next to O (based on δ)
B	~3.3	3H	s	CH_3 isolated, next to O (based on δ)
C	~1.8	1H	m	CH multiplet (hard to say what the neighbors are)
D	~1.3	4H	m	2 x CH_2 (identical—symmetry exists in the molecule); hard to say what the neighbors are
E	~0.9	6H	t	2 x CH_3, identical in chemical environment, each next to CH_2 (also identical)

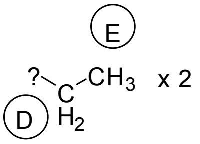
DU = [7(2) + 2 – 16]/2 = 0 → no rings or double bonds

Integration: (12 mm + 17 + 6 + 23 + 34) / 16 H's = 5.8 mm/H

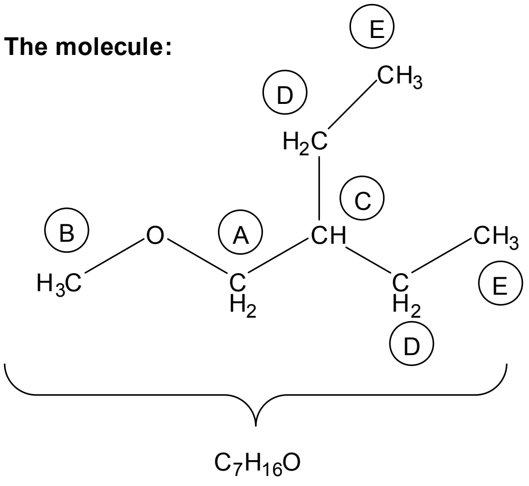
The pieces:



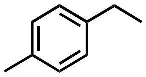
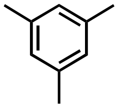
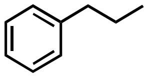
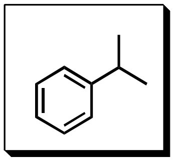
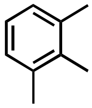
Note: the formula contains only one oxygen



The molecule:

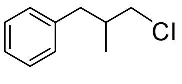


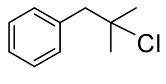
7. Determine the most likely structure of a compound, with the molecular formula C_9H_{12}, which gave a ^{1}H NMR spectrum consisting of:
   a doublet at δ 1.25
   a septet at δ 2.90 and
   a multiplet at δ 7.25

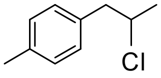






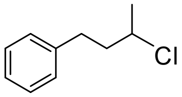
8. A compound with the molecular formula $C_{10}H_{13}Cl$ gave the following ^{1}H NMR spectrum:
   singlet, δ 1.6
   singlet, δ 3.1
   multiplet, δ 7.2 (5H)

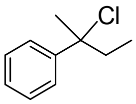
The most likely structure for the compound is:


I


II

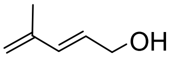

III

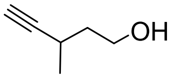

IV


V

9. Determine the likely structure for a compound A ($C_6H_{10}O$), which is found to decolorize bromine in carbon tetrachloride. Its spectral data is as follows:

^{1}H NMR		IR
triplet, δ 1.0	singlet, δ 2.4	2200 cm^{-1} (sharp)
singlet, δ 1.4	singlet, δ 3.4	3300 cm^{-1} (sharp)
quartet, δ 1.6		3500 cm^{-1} (broad)


I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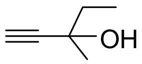
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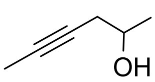
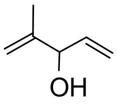
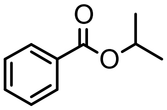
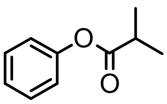

IV


V

10. Briefly explain how you might distinguish between the following substances by comparing their ^{1}H-NMR spectra:

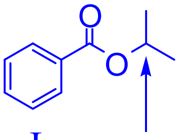


I



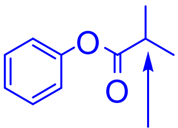
II

The main difference would likely be in the chemical shift of the methine proton of the isopropyl group. The methine proton in I is likely to be more deshielded, and produce a signal (septet) at about 3.5 ppm, while the analogous proton in II is likely to be found, also as a septet, at about 2.3 ppm.



I

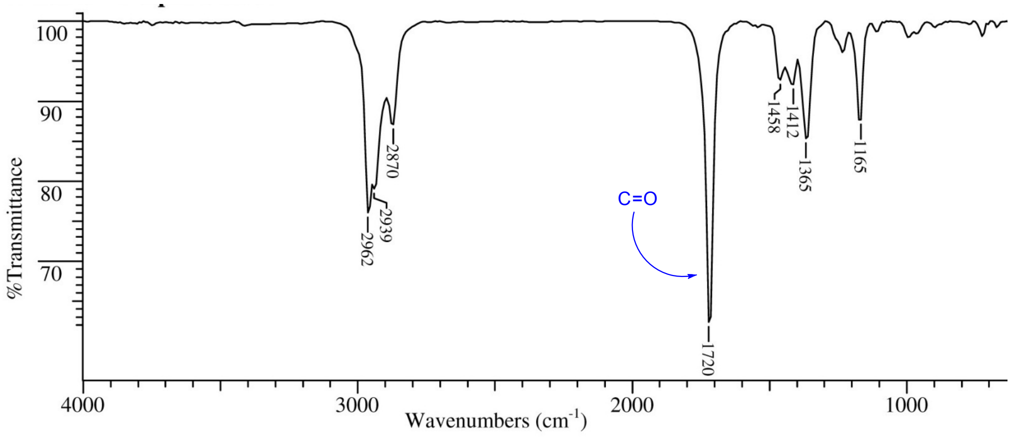
~3.5 ppm

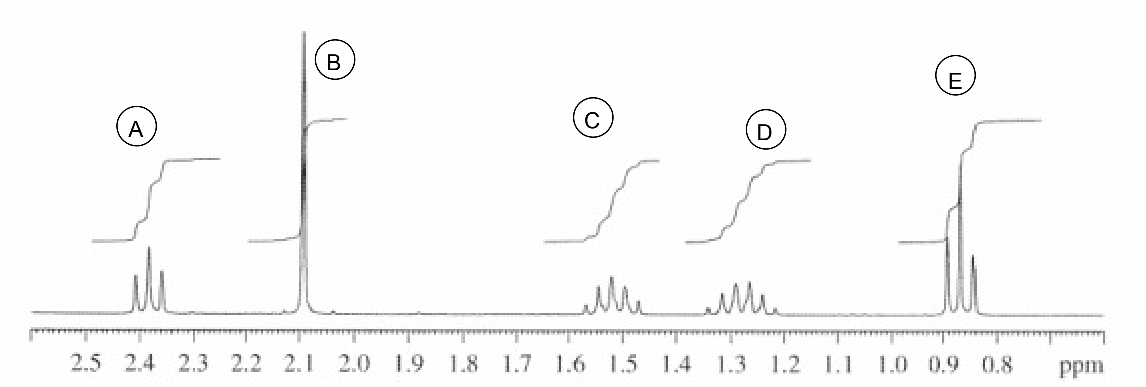


II

~2.3 ppm

11. An unknown compound has the formula $C_6H_{12}O$. Elucidate the structure of the molecule by scrutinizing its IR, ^1H NMR and ^{13}C NMR spectra, shown below.

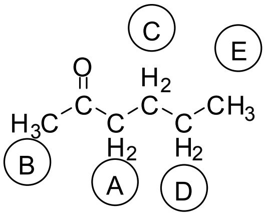




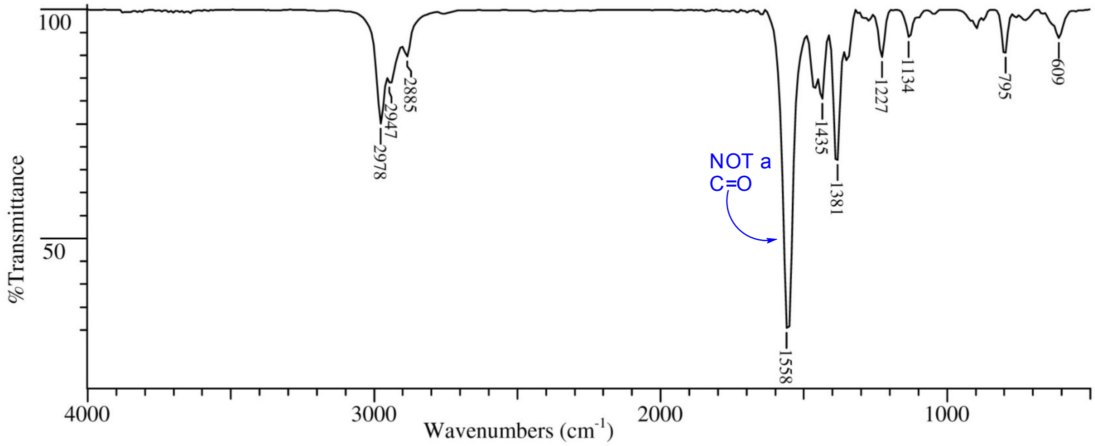
Signal	δ	Integration	Multiplicity	Comments
A	~2.4	2H	Triplet (t)	CH_2 next to CH_2 (based on multiplicity) and next to C=O (based on δ)
B	~2.1	3H	Singlet (s)	CH_3 next to C=O (based on δ)
C	~1.6	2H	Multiplet (m)	CH_2
D	~1.3	2H	Multiplet (m)	CH_2
E	~0.9	3H	Triplet (t)	CH_3 next to CH_2 (based on multiplicity)

DU = $[\,6(2) + 2 - 12]/2 = 1 \rightarrow$ C=O (based on IR)
Integration: (9 mm + 13 + 10 + 10 + 14) / 12 H's = 4.7 mm/H

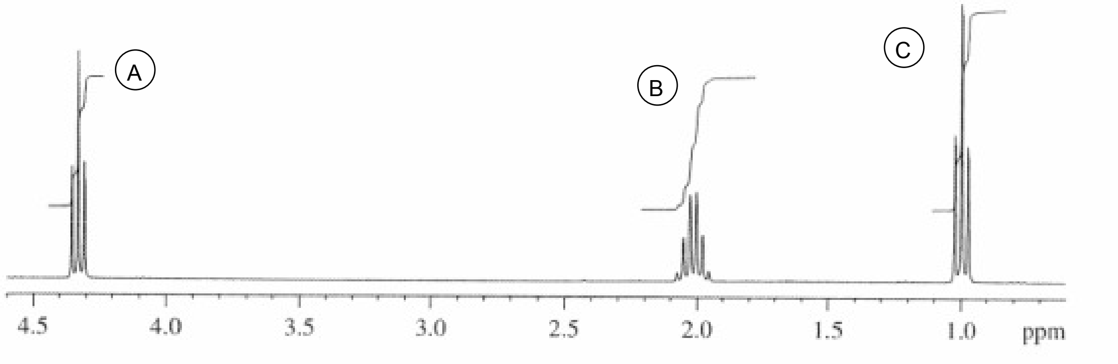
The molecule:



An unknown compound, **I**, has the formula $C_3H_7NO_2$. Elucidate the structure of **I** by scrutinizing its IR, ^{1}H NMR and ^{13}C NMR spectra, shown below.



NOT a C=O



Signal	**δ**	**Integration**	**Multiplicity**	**Comments**
A	~4.4	2H	Triplet (t)	CH_2, next to CH_2 (based on multiplicity), next to O or NO_2 (based on δ)
B	~2.0	2H	M	CH_2
C	~1.0	3H	t	CH_3, next to CH_2

DU = [3(2) + 2 +1 – 7] /2 = 1 → NOT a C=O based on IR… maybe NO_2?

Integration: (17 mm + 17 + 26) / 7H's = 8.6 mm/H

The molecule: