

1. The molar mass of 2-butanone ( $\text{CH}_3\text{CH}_2\text{COCH}_3$ ) is 72.11 g/mol. Why does the mass spectrum of the molecule have peaks at  $m/z$  equal to 72.06 and 73.06?

1. \_\_\_\_\_

Molar mass is based on the average mass

2. \_\_\_\_\_

72.06 is the exact mass of 2-butanone molecules that contain only  $^{12}\text{C}$

3. \_\_\_\_\_

73.06 is the exact mass of the 2-butanone molecules that have 1  $^{13}\text{C}$  atom present.

4. \_\_\_\_\_

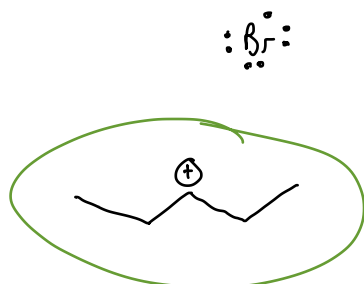
2.. In a mass spectrometer, radical, cationic alkyl halides fragment using homolytic and heterolytic mechanisms. (a. 12 pts.) Draw the fragments that would form from the most likely heterolytic and homolytic cleavage reactions, and (b. 6 pts.) circle the fragments that would be observed in the mass spectrum.

5. \_\_\_\_\_

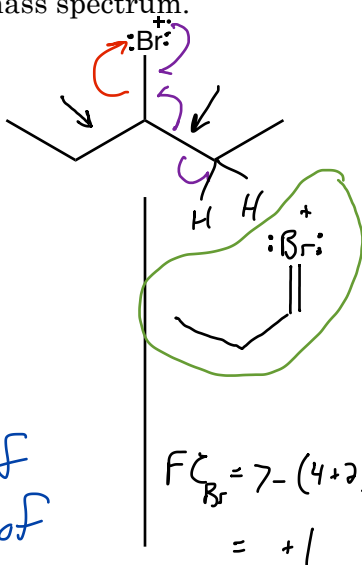
heterolytic cleavage products

$\alpha$ -cleavage  
homolytic cleavage products

6. \_\_\_\_\_



charge moves because of uneven distribution of  $e^-$ 's



$$FC_{Br} = 7 - (4 + 2) = +1$$

$$FC_c = 4 - (1 + 3) = 0$$

charge doesn't move because  $e^-$ 's evenly shared

7. \_\_\_\_\_

8. \_\_\_\_\_

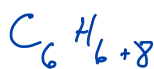
9. \_\_\_\_\_

10. \_\_\_\_\_

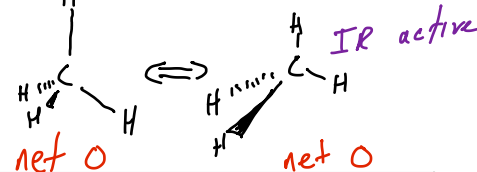
11. \_\_\_\_\_

3. (10 pts.) What is the formula of the hydrocarbon (a molecule containing only carbon and hydrogen atoms) that has a peak at a charge to mass ratio of 86.

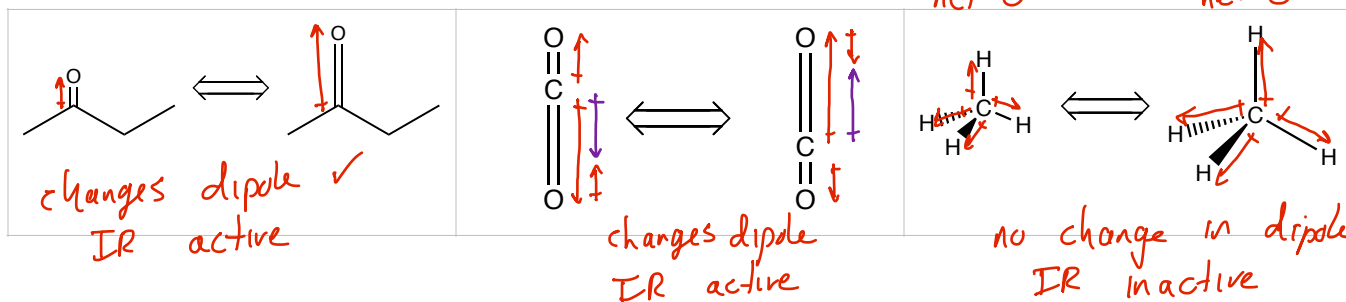
$$\begin{array}{r} 6 \text{ C} = 8 \\ 13 \overline{)86} \\ \underline{78} \\ 8 \end{array}$$



if other atoms are present you need to pull out C's + H's to make room



4. (12 pts.) Circle the drawings that represent IR active vibrations.



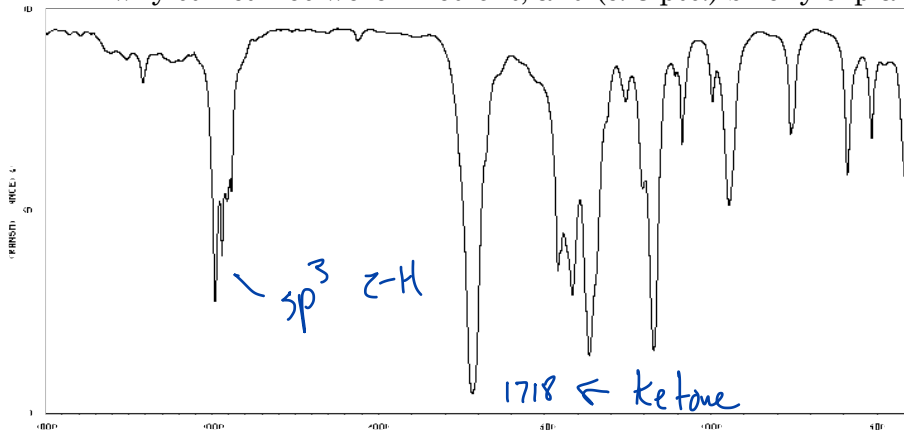
5. a. (8 pts.) C-H, O-H, and N-H stretching vibrations all appear at  $2700\text{ cm}^{-1}$  or higher. On the other hand, C-C, C-N, and C-O stretching vibrations absorb IR light at  $1250\text{ cm}^{-1}$  or lower. Briefly explain this difference.

big atom small atom  $\swarrow$  less inertia higher freq vibration  
 big atom big atom  $\swarrow$  the bonds between 1 big atoms vibrate more slowly because big atoms have more inertia

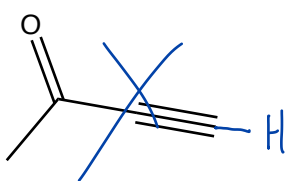
b. (4 pts.) Would you expect a C-Br bond to stretch at a higher or lower frequency than a C-O bond?

C-O since O is less massive than Br

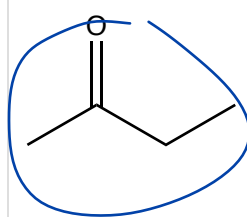
6. (a. 2 pts.) Circle the molecule that produced the following spectrum, (b. 9 pts.) briefly explain why structures were ruled out, and (c. 3 pts.) briefly explain why your choice is the correct one.



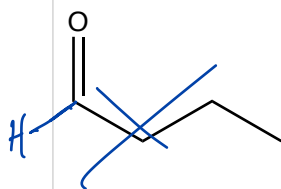
3611	84	1718	4	1173	14
3416	79	1461	34	1087	64
2981	26	1454	38	996	74
2964	44	1417	27	946	49
2940	37	1366	13	761	66
2909	50	1257	74	590	57
2883	62	1206	69	617	66



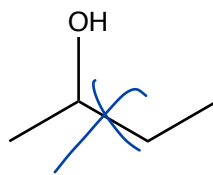
$\equiv\text{C}-\text{H}$  not in IR  
 $\text{C}\equiv\text{C}$  not in IR



C=O in IR in reasonable position  
 all C-H's are  $\text{sp}^3\text{ C}'\text{s}$

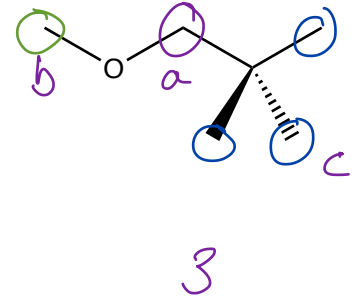
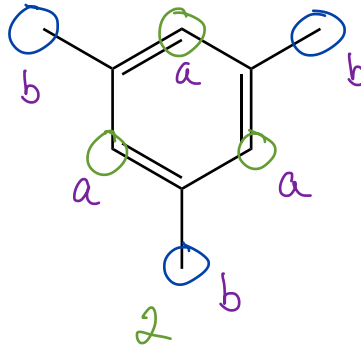
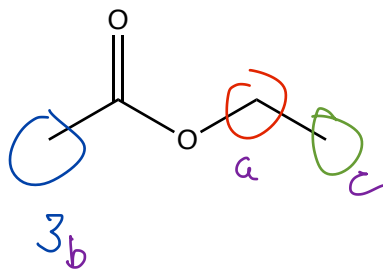


C=O in IR looks like ketone this is an aldehyde  
 aldehyde C-H not in IR



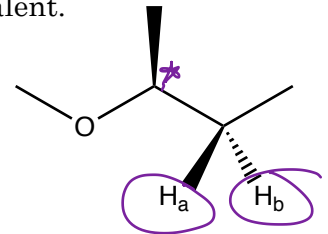
no alcohol peak

7. a. (9 pts.) Determine the number of peaks that are expected in the  $^1\text{H}$  NMR spectra of the following molecules, and

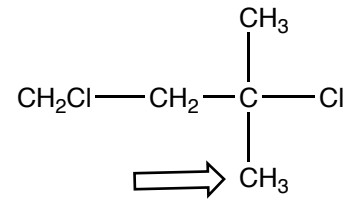
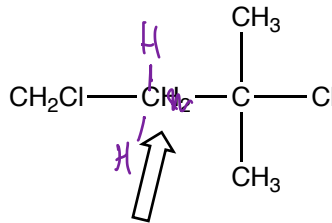
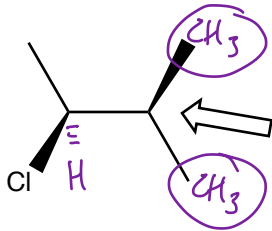


8. (6 pts.) Explain why  $\text{H}_a$  and  $\text{H}_b$  are chemically and magnetically inequivalent.

$\text{H}_a + \text{H}_b$  are diastereotopic



9. (12 pts.) Determine the multiplicity of the peak attributed to the indicated protons.

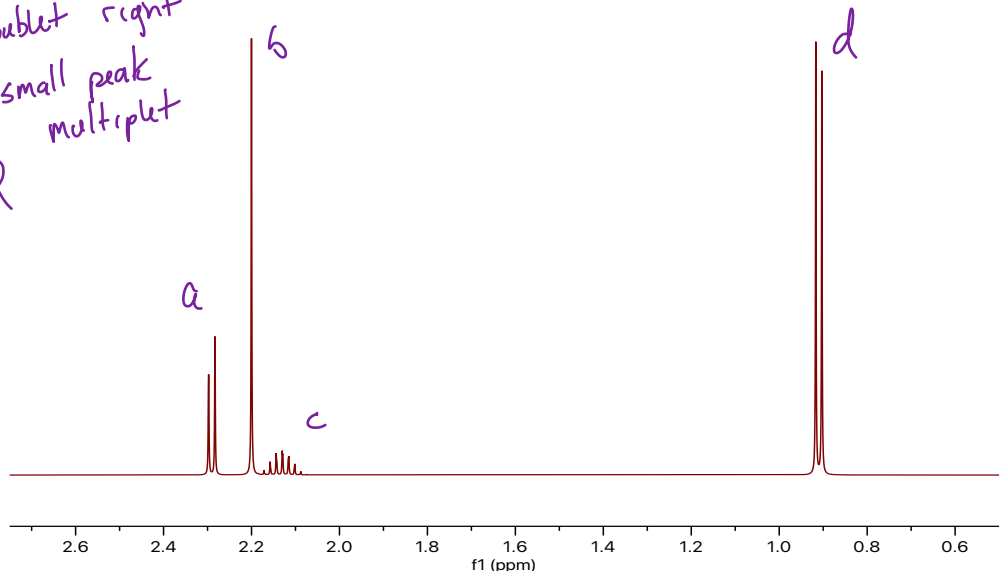
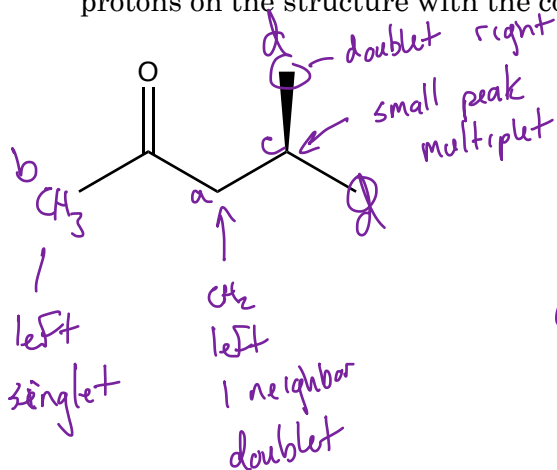


doublet quartets quartets  
or line spectrum

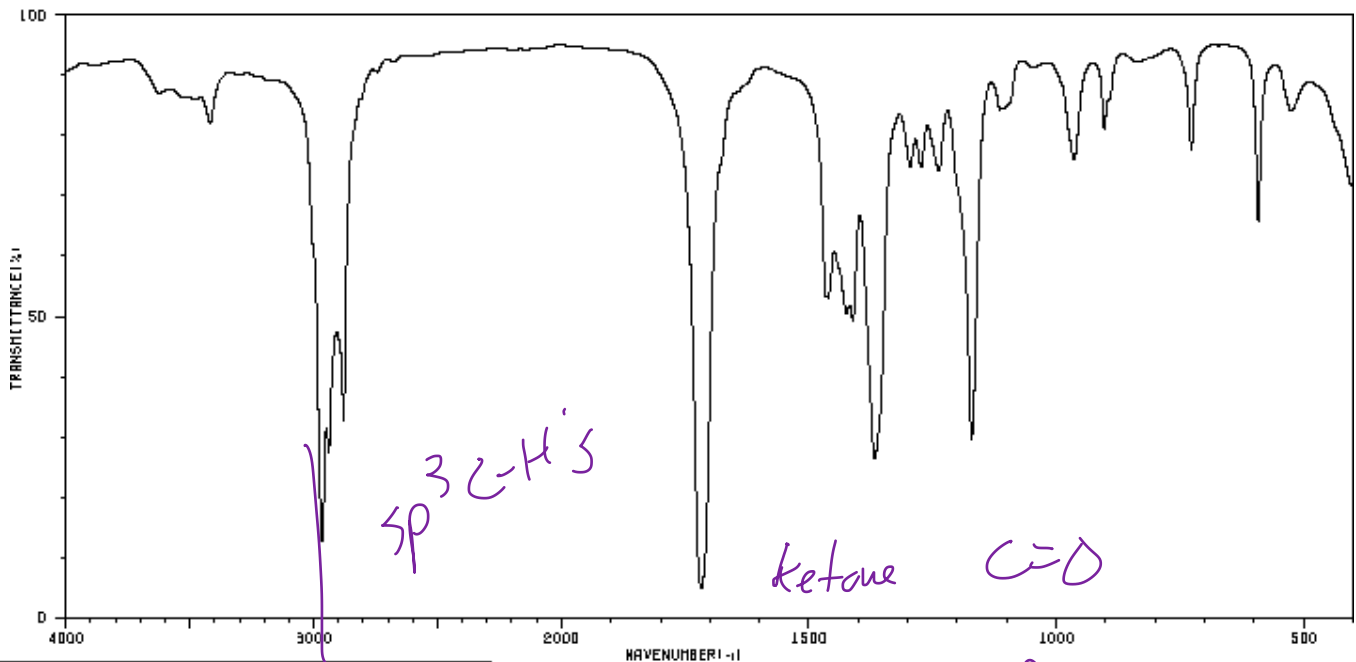
triplet

singlet

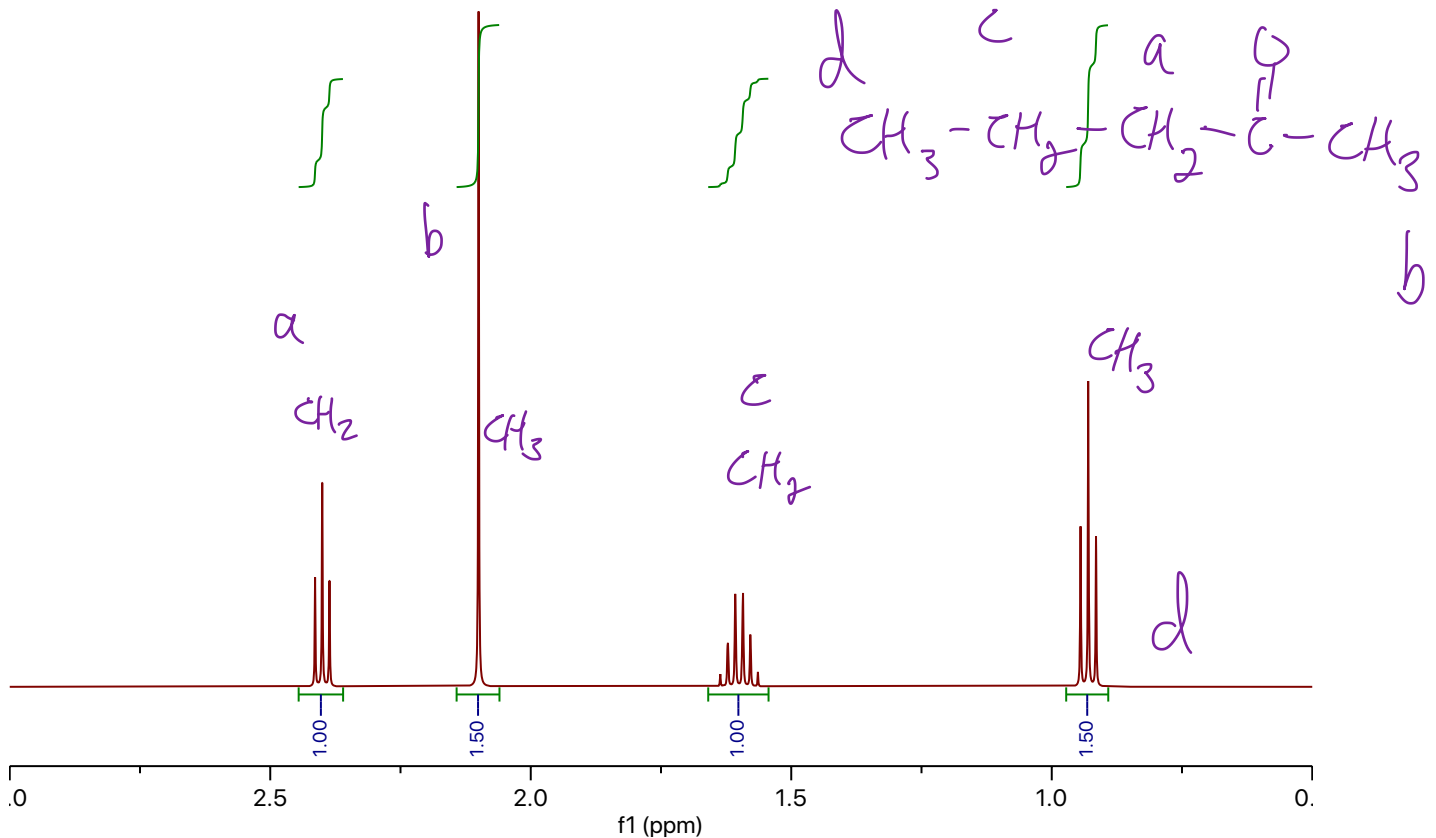
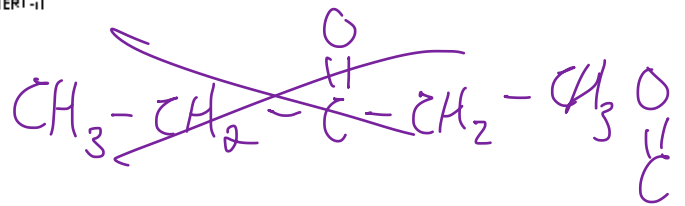
10. (12 pts) Assign the peaks in the following  $^1\text{H}$  NMR spectrum; that is, label each peak in the  $^1\text{H}$  NMR spectrum alphabetically starting with an "a" at the left end of the spectrum and label the protons on the structure with the corresponding letter.



11. A molecule with the formula  $C_5H_{10}O$  produced the following IR and NMR spectra. Based on the spectral data provided below (a. 10 pts.) determine the structure of the unknown  $C_5H_{10}O$ , (b. 4 pts.) identify the peaks for two functional groups in the IR spectrum, and (c. 4 pts.) unambiguously assign the peaks in the  $^1H$  NMR spectrum. That is, label each peak in the  $^1H$  NMR spectrum alphabetically starting with an "a" at the left end of the spectrum and label the protons on your structure with the corresponding letter.



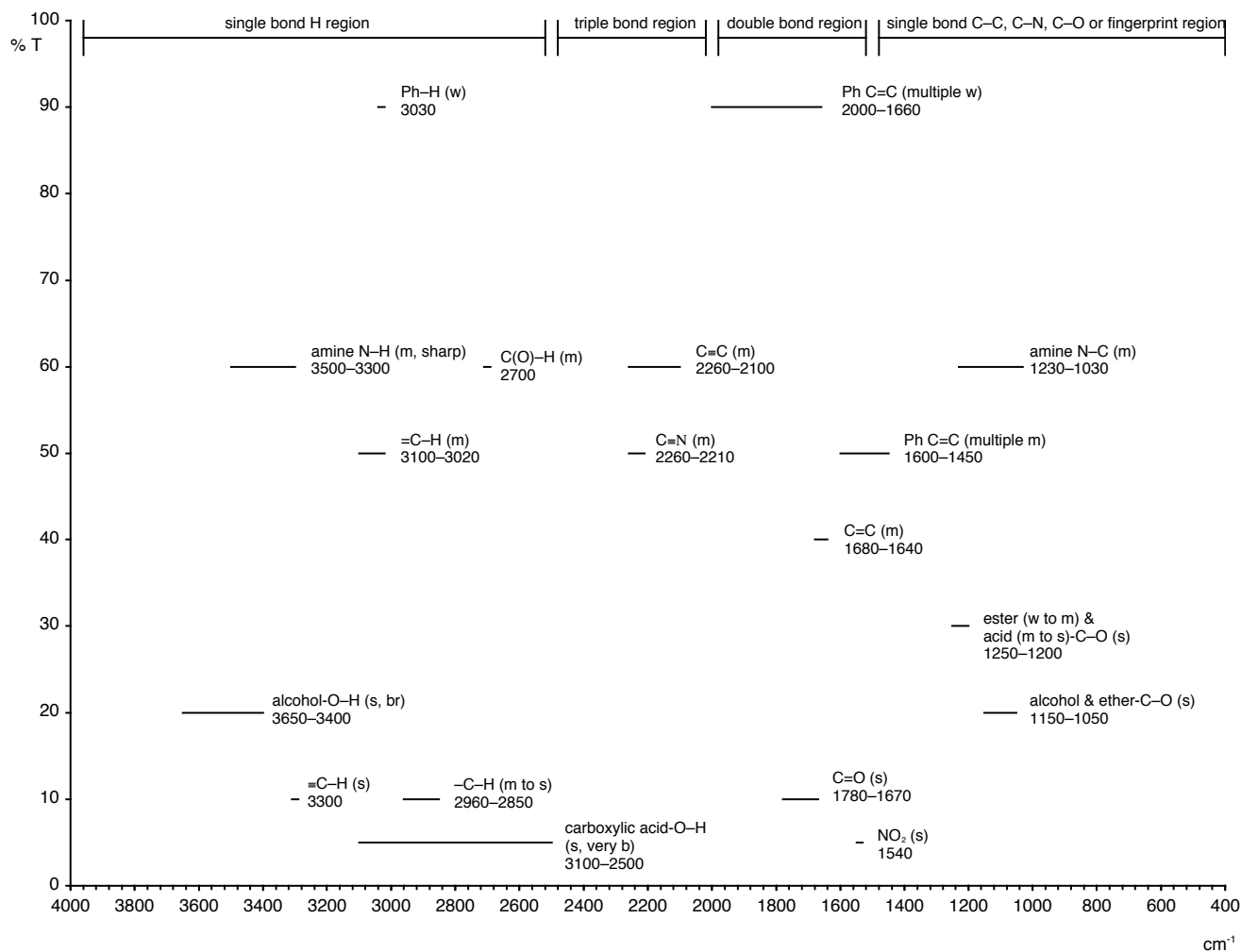
3419	79	1426	49	1114	81	592	64
2966	12	1412	47	1105	81	526	81
2939	26	1367	25	1100	81		
2879	31	1296	72	964	72		
1717	4	1274	72	903	79		
1467	50	1237	72	894	81		
1461	60	1172	28	727	74		



1	<b>H</b> 1.0079																	2	<b>He</b> 4.0026																
3	<b>Li</b> 6.941	4	<b>Be</b> 9.012																	10	<b>Ne</b> 20.1797														
11	<b>Na</b> 22.989	12	<b>Mg</b> 24.305																	18	<b>Ar</b> 39.948														
19	<b>K</b>	20	<b>Ca</b>	21	<b>Sc</b>	22	<b>Ti</b>	23	<b>V</b>	24	<b>Cr</b>	25	<b>Mn</b>	26	<b>Fe</b>	27	<b>Co</b>	28	<b>Ni</b>	29	<b>Cu</b>	30	<b>Zn</b>	31	<b>Ga</b>	32	<b>Ge</b>	33	<b>As</b>	34	<b>Se</b>	35	<b>Br</b> 79.904	36	<b>Kr</b>
37	<b>Cs</b>	38	<b>Sr</b>	39	<b>Y</b>	40	<b>Zr</b>	41	<b>Nb</b>	42	<b>Mo</b>	43	<b>Tc</b>	44	<b>Ru</b>	45	<b>Rh</b>	46	<b>Pd</b>	47	<b>Ag</b>	48	<b>Cd</b>	49	<b>In</b>	50	<b>Sn</b>	51	<b>Sb</b>	52	<b>Te</b>	53	<b>I</b>	54	<b>Xe</b>
55	<b>Rb</b>	56	<b>Ba</b>	57	<b>La</b>	72	<b>Hf</b>	73	<b>Ta</b>	74	<b>W</b>	75	<b>Re</b>	76	<b>Os</b>	77	<b>Ir</b>	78	<b>Pt</b>	79	<b>Au</b>	80	<b>Hg</b>	81	<b>Tl</b>	82	<b>Pb</b>	83	<b>Bi</b>	84	<b>Po</b>	85	<b>At</b>	86	<b>Rn</b>
87	<b>Fr</b>	88	<b>Ra</b>	89	<b>Ac</b>	104	<b>Rf</b>	105	<b>Db</b>	106	<b>Sg</b>	107	<b>Bh</b>	108	<b>Hs</b>	109	<b>Mt</b>	110		111		112		114										118	

58	<b>Ce</b>	59	<b>Pr</b>	60	<b>Nd</b>	61	<b>Pm</b>	62	<b>Sm</b>	63	<b>Eu</b>	64	<b>Gd</b>	65	<b>Tb</b>	66	<b>Dy</b>	67	<b>Ho</b>	68	<b>Er</b>	69	<b>Tm</b>	70	<b>Yb</b>	71	<b>Lu</b>
90	<b>Th</b>	91	<b>Pa</b>	92	<b>U</b>	93	<b>Np</b>	94	<b>Pu</b>	95	<b>Am</b>	96	<b>Cm</b>	97	<b>Bk</b>	98	<b>Cf</b>	99	<b>Es</b>	100	<b>Fm</b>	101	<b>Md</b>	102	<b>No</b>	103	<b>Lr</b>



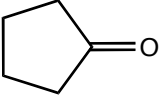


Additional information for analyzing C=O stretches:

amide:  $R(C=O)NH_2 < 1700$

acid: 1710 usually broad for a C=O

unstrained ketone:  $RC(=O)R$  1715, resonance stabilized ketone  $R=CHC(=O)R$  1690

strained ketone:  1750

aldehyde:  $RC(=O)H$  1730, resonance stabilized aldehyde  $R=CHC(=O)H$  1705

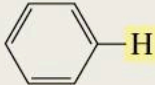
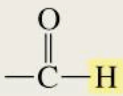
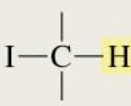
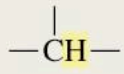
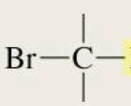
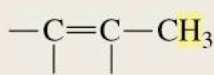
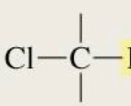
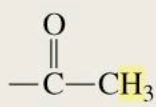
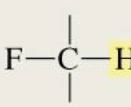
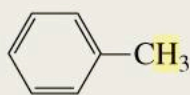
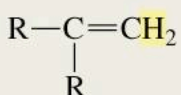
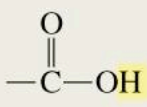
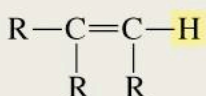
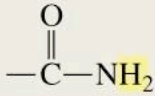
ester:  $RC(=O)OR$  1735, resonance stabilized ester  $R=CHC(=O)OR$  1715.

Additional information for analyzing C-H stretches:

If  $sp^3$  C-H stretch at  $< 3000$  cm<sup>-1</sup> then look around 1400,  $sp^3$  C-H bend is at 1430 and if peak at 1380 also present then  $sp^3$  C-H is  $CH_3$ .

If  $sp^2$  C-H stretch at  $> 3000$  cm<sup>-1</sup>, and not benzene gives rise to bending vibrations from 1000-600.

**Table 14.1 Approximate Values of Chemical Shifts for  $^1\text{H}$  NMR<sup>a</sup>**

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(\text{CH}_3)_4\text{Si}$	0		6.5–8
$-\text{CH}_3$	0.9		9.0–10
$-\text{CH}_2-$	1.3		2.5–4
	1.4		2.5–4
	1.7		3–4
	2.1		4–4.5
	2.3	$\text{RNH}_2$	Variable, 1.5–4
$-\text{C}\equiv\text{C}-\text{H}$	2.4	$\text{ROH}$	Variable, 2–5
$\text{R}-\text{O}-\text{CH}_3$	3.3	$\text{ArOH}$	Variable, 4–7
	4.7		Variable, 10–12
	5.3		Variable, 5–8

<sup>a</sup>The values are approximate because they are affected by neighboring substituents.