1. The molar mass of 2-butanone ($CH_3CH_2COCH_3$) 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. _____

2. _____
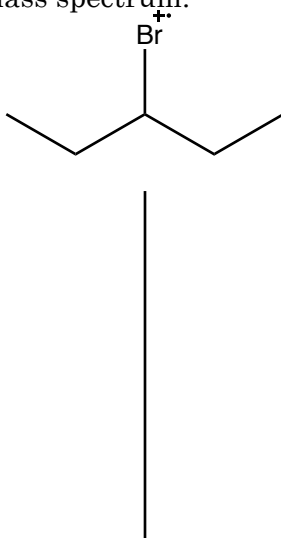
3. _____

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. _____

6. _____

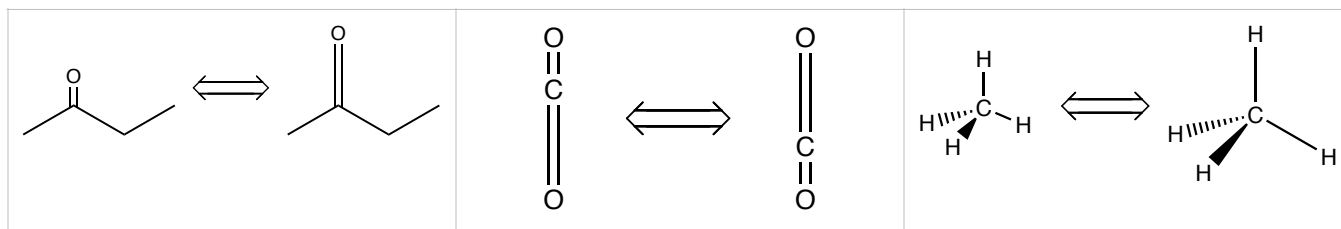heterolytic cleavage products

homolytic cleavage products

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.

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 cm⁻¹ or higher. On the other hand, C–C, C–N, and C–O stretching vibrations absorb IR light at 1250cm⁻¹ or lower. Briefly explain this difference.

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

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.
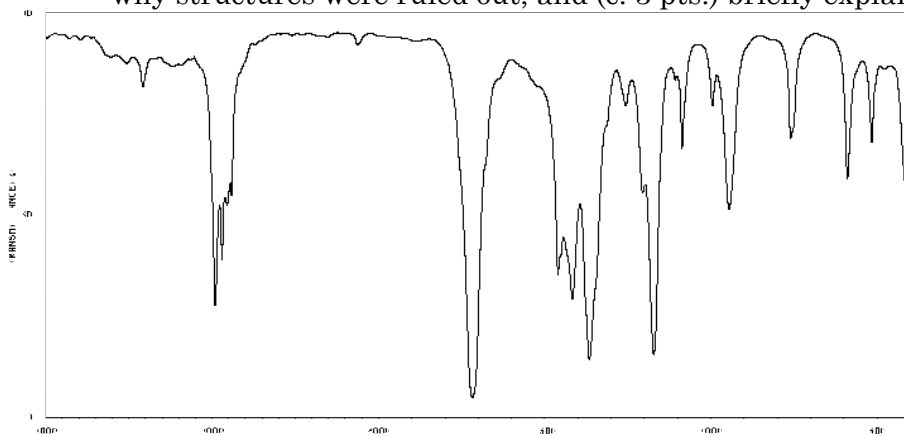

| 3611	84	1718	4	1173	14
3416	79	1461	34	1087	64
2981	26	1454	36	996	74
2964	44	1417	27	946	49
2940	37	1366	13	761	66
2909	50	1257	74	590	57
2883	62	1206	69	617	66
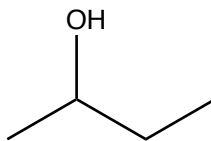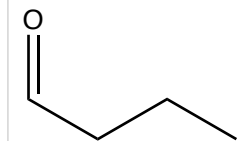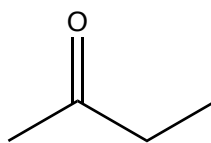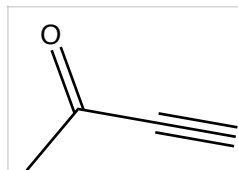
7. a. (9 pts.) Determine the number of peaks that are expected in the ^{1}H NMR spectra of the following molecules, and

   b. (9 pts.) determine the relative positions of the peaks in the ^{1}H NMR spectrum and label the protons alphabetically starting with the proton(s) that resonate at the highest frequency.
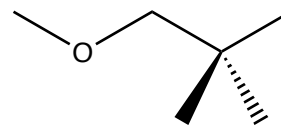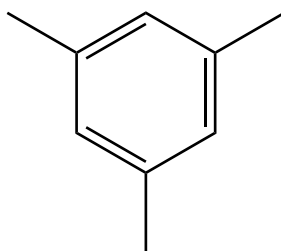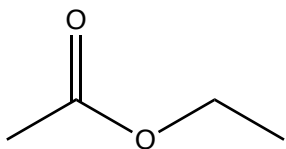
8. (6 pts.) Explain why H$_a$ and H$_b$ are chemically and magnetically inequivalent.
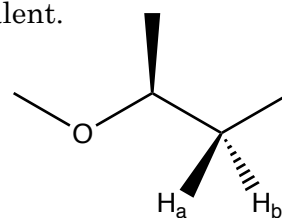
9. (12 pts.) Determine the multiplicity of the peak attributed to the indicated protons.
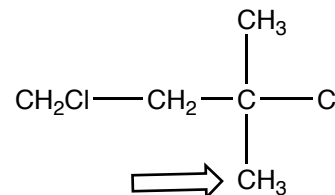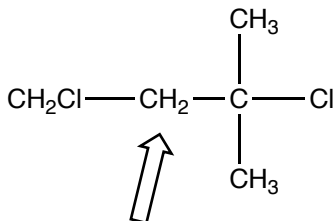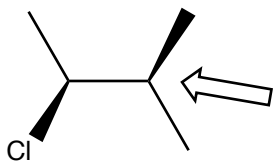
10. (12 pts) Assign the peaks in the following ^{1}H NMR spectrum; that is, label each peak in the ^{1}H NMR spectrum alphabetically starting with an "a" at the left end of the spectrum and label the protons on the structure with the corresponding letter.
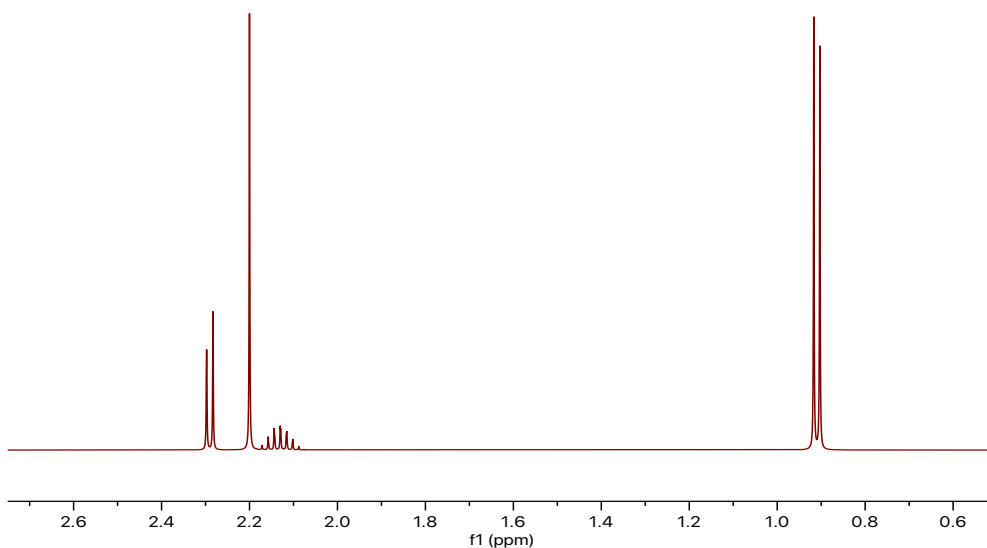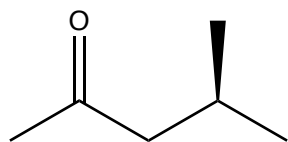
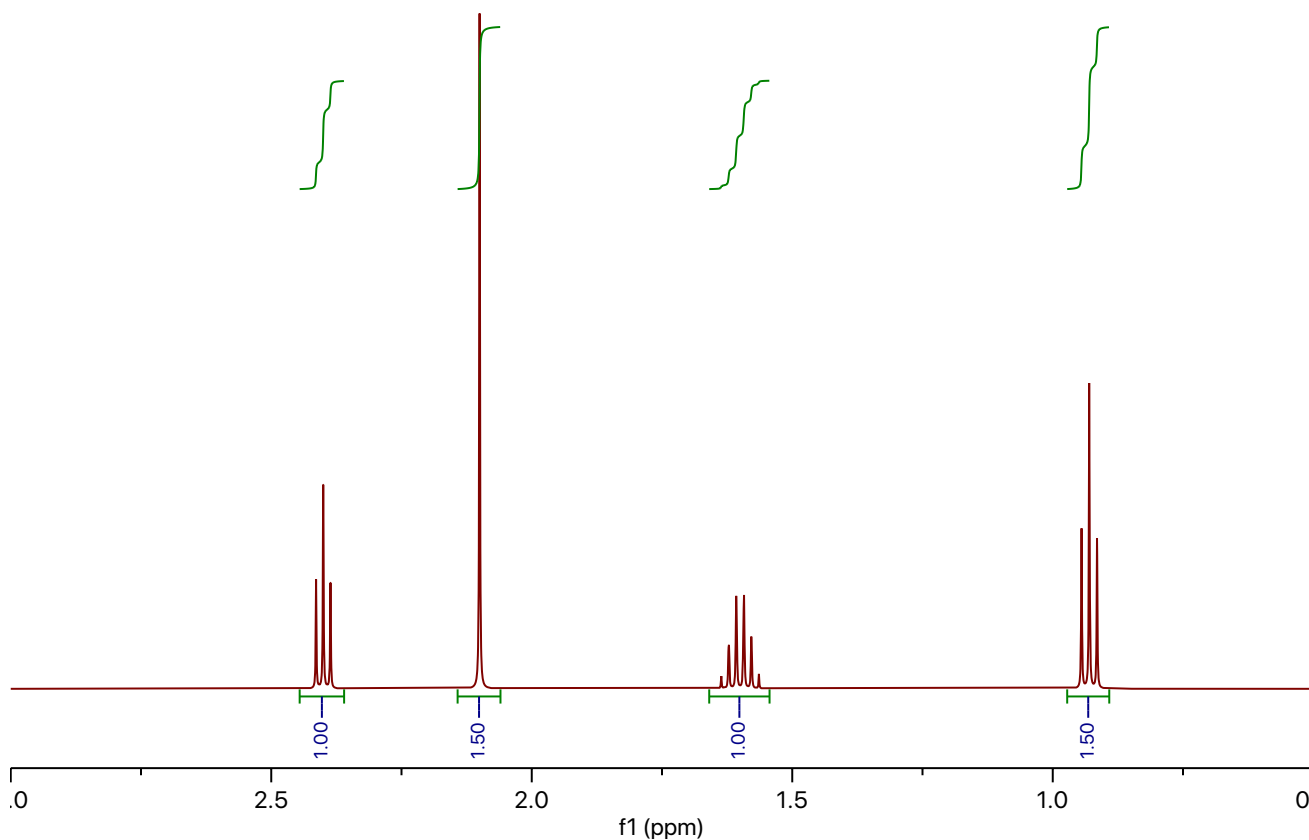11. A molecule with the formula $C_5H_{10}O$ produced the following IR and NMR spectra. Based on the spectral data provided below (a. 10 pts.) determine the structure of the unknown $C_5H_{10}O$, (b. 4 pts.) identify the peaks for two functional groups in the IR spectrum, and (c. 4 pts.) unambiguously 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.
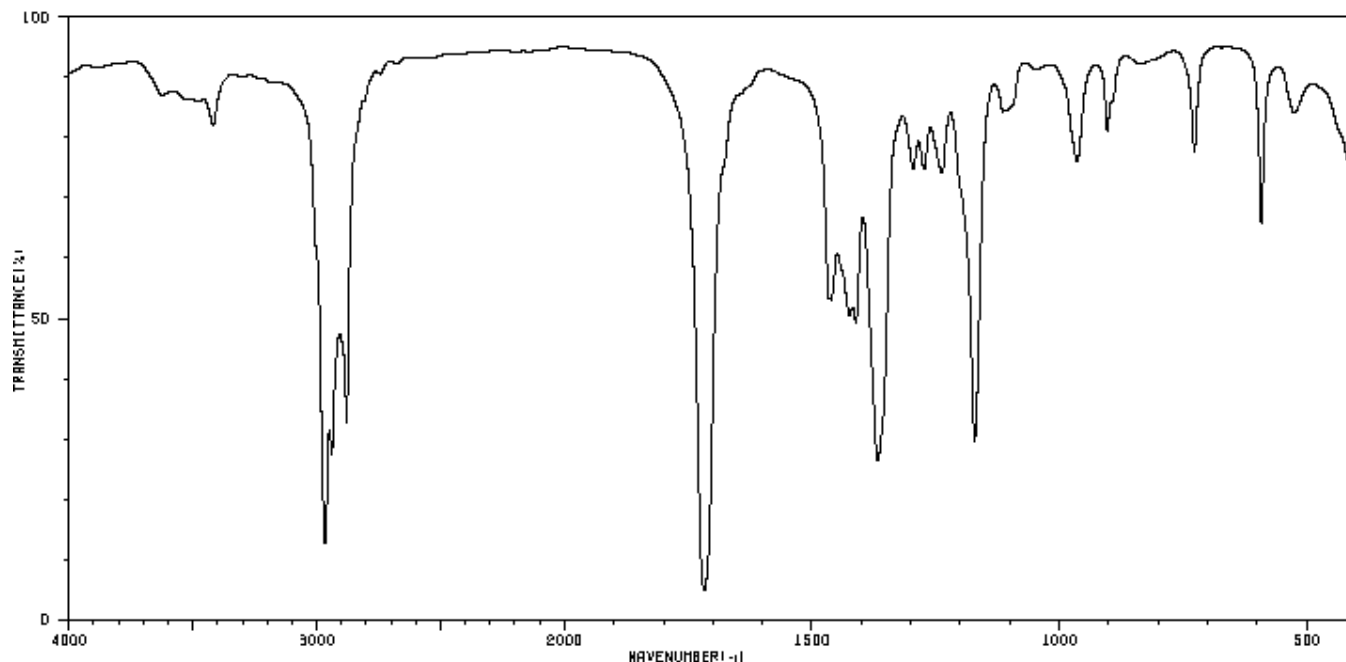
3419	79	1426	49	1114	81	692	64
2966	12	1412	47	1105	81	526	81
2939	26	1367	25	1100	81		
2879	31	1296	72	964	72		
1717	4	1274	72	903	79		
1467	50	1237	72	894	81		
1461	60	1172	28	727	74		

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.1797
11 Na 22.989	12 Mg 24.305											13 Al 26.981	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br 79.904	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		118

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

IR Correlation Chart

100 % T

| single bond H region | triple bond region | double bond region | single bond C–C, C–N, C–O or fingerprint region |

- Ph–H (w) 3030
- Ph C=C (multiple w) 2000–1660

- amine N–H (m, sharp) 3500–3300
- C(O)–H (m) 2700
- C≡C (m) 2260–2100
- amine N–C (m) 1230–1030

- =C–H (m) 3100–3020
- C≡N (m) 2260–2210
- Ph C=C (multiple m) 1600–1450

- C=C (m) 1680–1640

- ester (w to m) & acid (m to s)-C–O (s) 1250–1200

- alcohol-O–H (s, br) 3650–3400
- alcohol & ether-C–O (s) 1150–1050

- ≡C–H (s) 3300
- –C–H (m to s) 2960–2850
- C=O (s) 1780–1670

- carboxylic acid-O–H (s, very b) 3100–2500
- NO₂ (s) 1540

x-axis: 4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400

cm⁻¹

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: [cyclopentanone structure] =O 1750

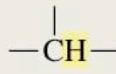   aldehyde: RC(=O)H 1730, resonance stabilized aldehyde R=CHC(=O)H 1705
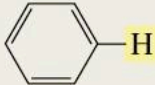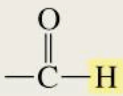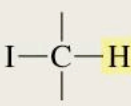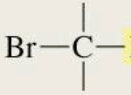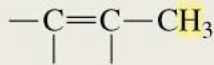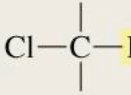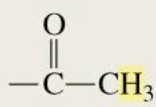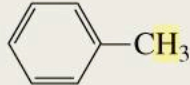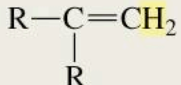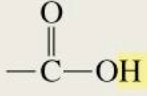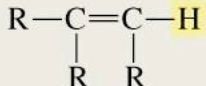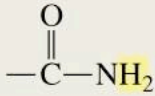
   ester: RC(=O)OR 1735, resonance stabilized ester R=CHC(=O)OR 1715.

Additional information for analyzing C–H stretches:
   If sp^3 C–H stretch at < 3000 cm⁻¹ 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⁻¹, and not benzene gives rise to bending vibrations from 1000–600.

Table 14.1 Approximate Values of Chemical Shifts for ^{1}H NMR[a]

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	⬡—H (benzene)	6.5–8
—CH_3	0.9	—C(=O)—H	9.0–10
—CH_2—	1.3	I—C—H	2.5–4
—CH—	1.4	Br—C—H	2.5–4
—C=C—CH_3	1.7	Cl—C—H	3–4
—C(=O)—CH_3	2.1	F—C—H	4–4.5
⬡—CH_3	2.3	RNH_2	Variable, 1.5–4
—C≡C—H	2.4	ROH	Variable, 2–5
R—O—CH_3	3.3	ArOH	Variable, 4–7
R—C(R)=CH_2	4.7	—C(=O)—OH	Variable, 10–12
R—C(R)=C(R)—H	5.3	—C(=O)—NH_2	Variable, 5–8

[a]The values are approximate because they are affected by neighboring substituents.