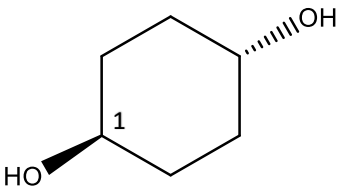
Last Name _____ SID _____

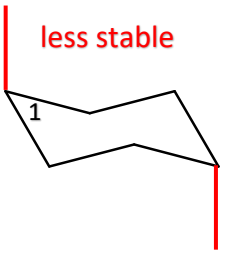
1. **Cyclic Structures** (12 pts)

   a. Draw both chair conformations for the following molecules, and indicate which conformation is more stable (or indicate equivalence).

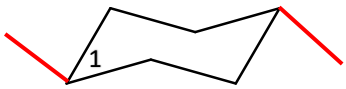
      i. (3 pts)



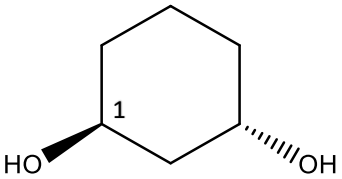
less stable

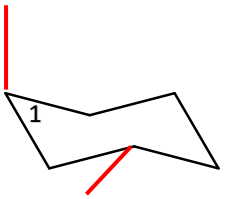


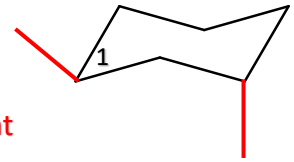
more stable



      ii. (3 pts)







equivalent

   b. (3 pts) The below diagram shows the combustion reaction of cyclopentane. Would cyclobutane have a lower (*more negative*) or higher (*less negative*) heat of combustion per CH_2 group? **Briefly** state your reasoning.

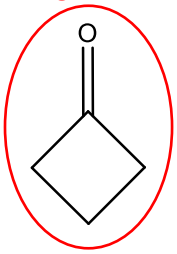
$+ \ 7.5\ O_2 \rightarrow 5\ CO_2 + 5\ H_2O$

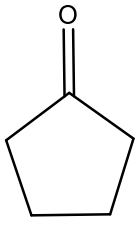
$\Delta H_{(\text{combustion per } CH_2)}$ = **-664 kJ/mol**

more negative due to higher ring strain (instability)

   c. (3 pts) Circle the molecule with a C=O stretch occurring at a **higher IR frequency**. **Briefly** state your reasoning.

ring strain → more s character → stronger bond → higher IR frequency





Last Name _____ SID _____

2. **Mass Spectrometry** (14 pts)

   a. (6 pts) Tabulated mass spectrum data for the unknown Molecule A is shown below.

m/z	Relative Abundance
162 (M)	34.2% ← even num N
163 (M+1)	2.8% ← 7 carbons (after removing influence of S)
164 (M+2)	1.5% ← presence of S

Which of the following formulae are possible for Molecule A? Circle **Yes** or **No**. If a formula is not possible, provide a **brief** (less than 10 words) explanation why.

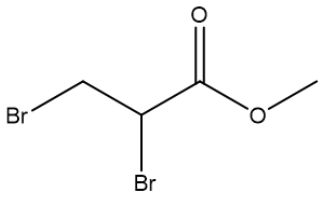
Formula	Possible?	Brief Explanation (if "No")
$C_7H_{30}OS$	Yes / **No**	Too many hydrogens (more than 2n + 2 + N)
$C_7H_{14}O_2S$	**Yes** / No	
$C_7H_{11}O_2Cl$	Yes / **No**	Presence of Cl
$C_7H_{18}N_2S$	**Yes** / No	
$C_7H_{13}NOCl$	Yes / **No**	Odd number of N, presence of Cl
$C_8H_{18}O_3$	Yes / **No**	No Sulphur, too many carbons

   b. (2 pts) You're told that Molecule A has a **cyclic ring**. Given this new information, and assuming that Molecule A is listed in the chart above, what is the **only possible** molecular formula? **Briefly** state your reasoning.

Molecular formula of A | **$C_7H_{14}O_2S$**

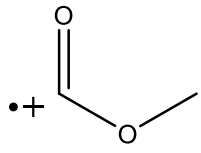
Only possible formula with DBE > 0

   c. A mass spectrum is also collected for Molecule B (structure on the left). Significant peaks are found at **m/z = 59** and **m/z = 248**.



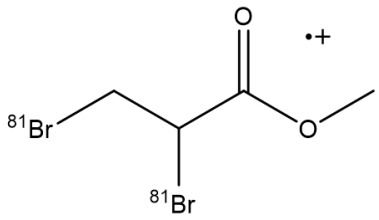
Molecule B

i. (3 pts) Draw the ion responsible for the peak found at **m/z = 59**.



ii. (3 pts) Draw (and/or describe) the ion responsible for the peak at **m/z = 248**.

248 is an M+4 peak. The molecule producing that peak has two ^{81}Br isotopes.

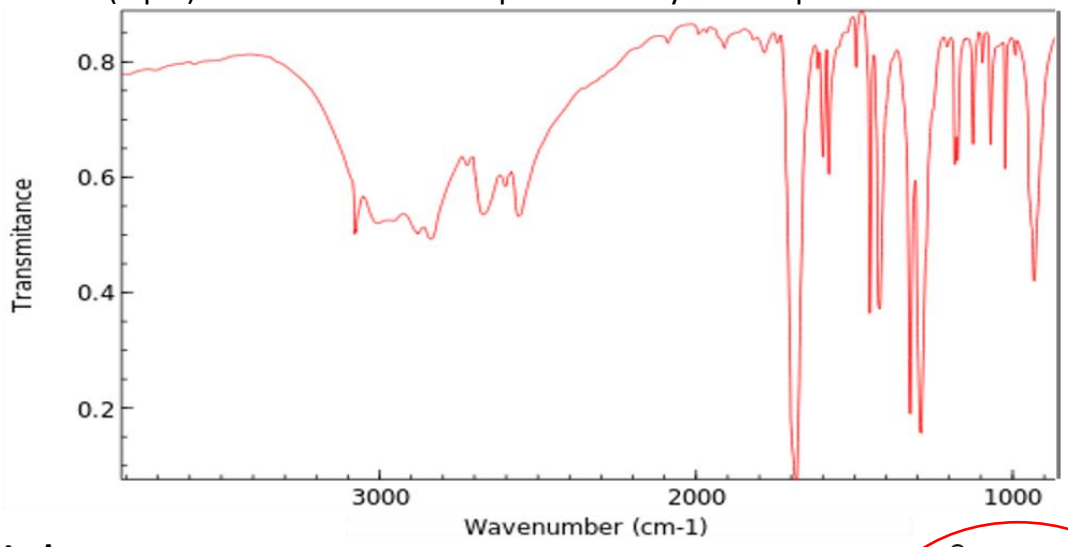


possible diagram

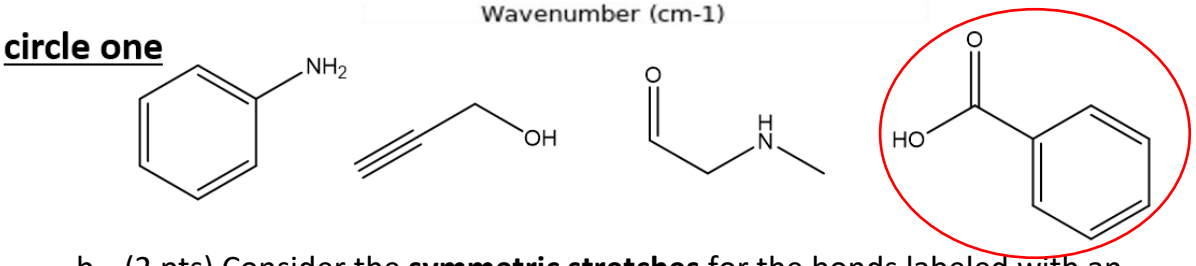
Last Name _____ SID _____

3. **Infrared Spectroscopy** (12 pts)

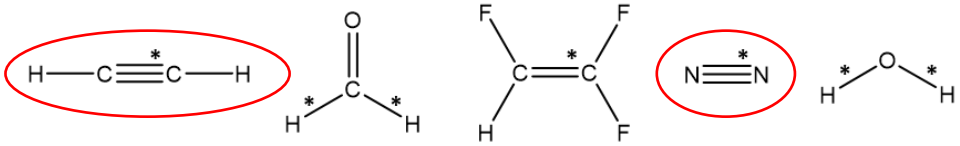
   a. (4 pts) Which molecule is represented by the IR spectrum below?



circle one



   b. (2 pts) Consider the **symmetric stretches** for the bonds labeled with an asterisk (*) below. Circle all the molecules with **IR inactive** labeled bonds.

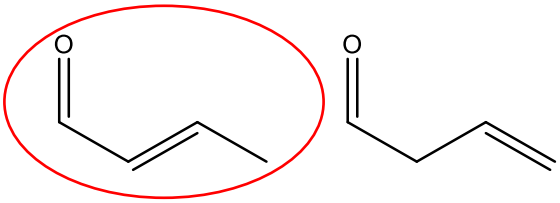


   c. (3 pts) As per the description in your IR peak table, the peak corresponding to an O-H stretch is “usually strong”, while an N-H peak is considered “medium”. **Briefly** explain why an N-H peak tends to be **weaker** than an O-H peak.

An O-H peak is stronger because O-H is a more polar bond (higher EN difference) than N-H.

   d. (3 pts) Circle the molecule with a C=O stretch occurring at a **lower IR frequency**. Explain your reasoning.

The first molecule is conjugated, this delocalizes the pi bonds, lowering the effective strength of the bond (leading to lower IR freq).



Last Name _____ SID _____

4. **NMR Spectroscopy** (9 pts + 1 bonus pt)

   a. (2 pts) Which of the following isotopes could be studied using NMR techniques? Circle all that apply.

   ^{20}Ne ^{31}P ^{2}H ^{14}C ^{28}Si ^{14}N

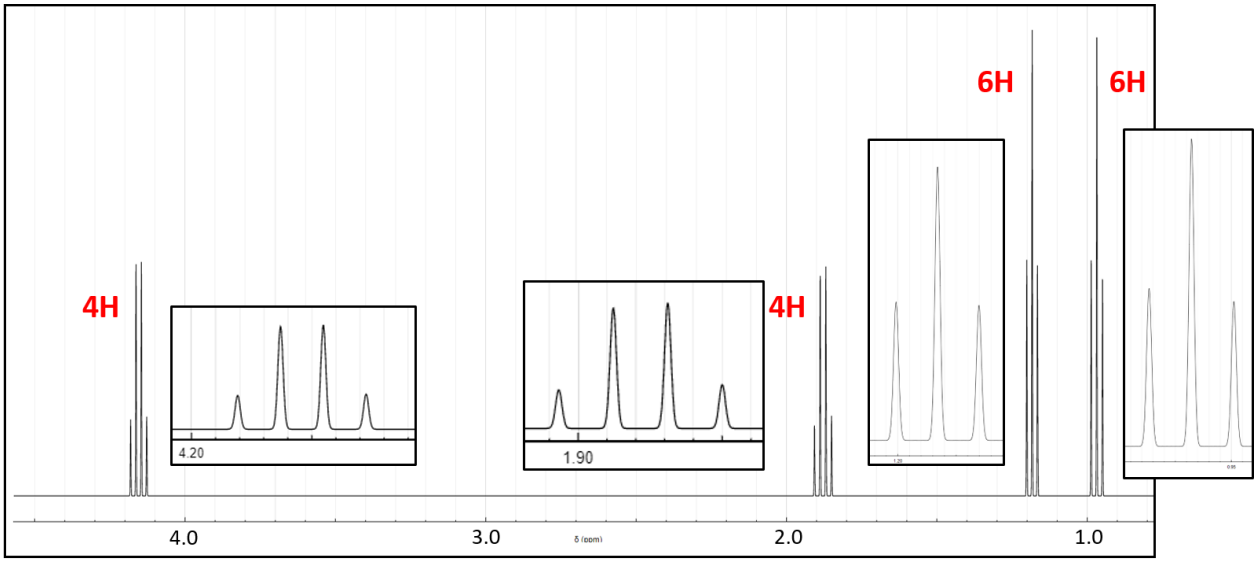
   b. (3 pts) Consider a splitting pattern created by four nonequivalent, neighboring protons. List all the protons spin sets contributing to the **highest peak** of this pattern. Use 'u' for up spins, and 'd' for down spins.

   uudd, udud, dudu, dduu, duud, uddu

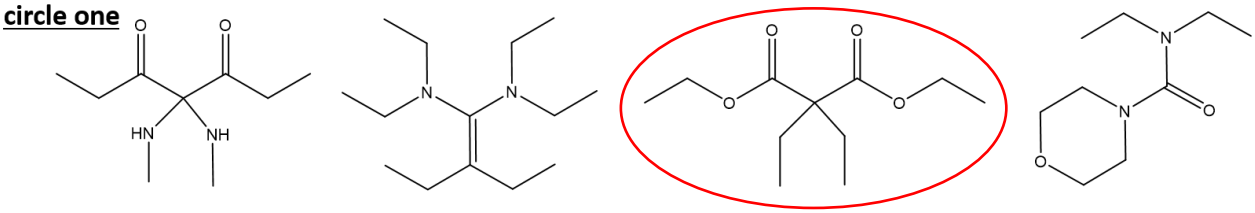
      i. Extra Credit - For 1 bonus point, describe how this test is going using one of the above spin sets.

      any attempt here is worth +1

   c. (4 pts) Which molecule is represented by the NMR spectrum below?



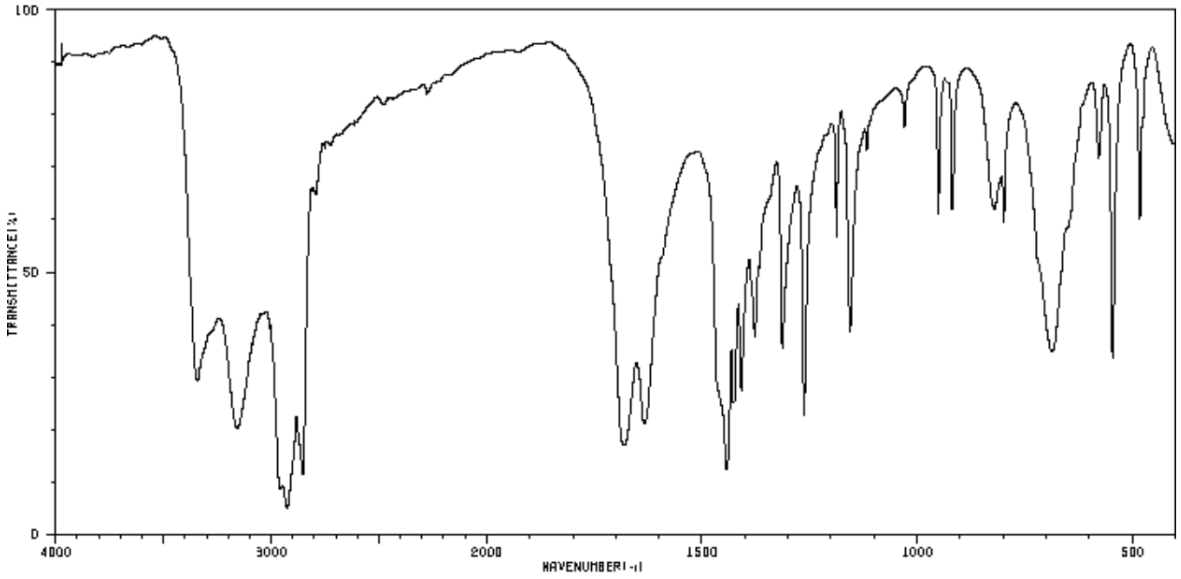
circle one

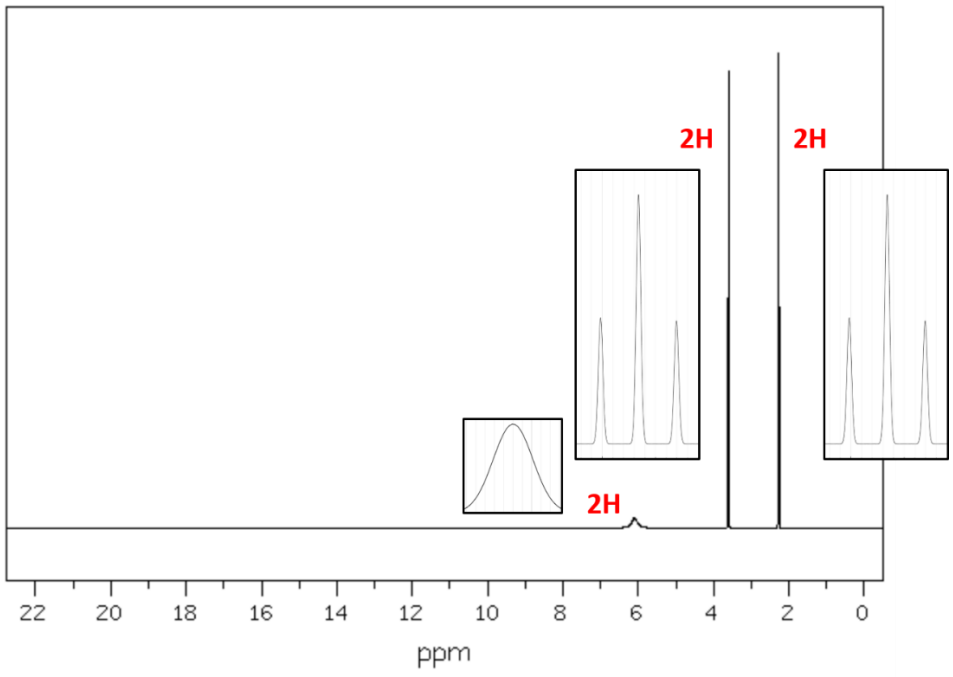


Last Name _____ SID _____

5. **Mixed Spectra** (13 pts) Using the following data and spectra, deduce the molecular structure of the unknown compound X. For the possibility of partial credit (in case your structure is incorrect), provide legible and relevant information you deduced in the box provided on the following page.

m/z	Relative Abundance
107	32% ← Br-CH_2-CH_2 fragment
151 (M)	100% ← odd num N
152 (M+1)	3.5% ← 3 carbons
153 (M+2)	97.2% ← presence of Br





Last Name _____ SID _____

a. (4 pts) Provide the molecular formula for the unknown compound X.

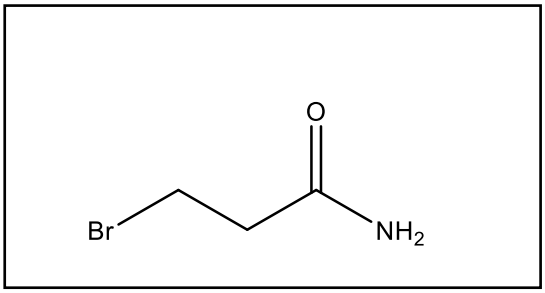
Molecular formula of X C_3H_6NOBr

b. (1 pt) Provide the DBE for the unknown compound X here: 1

c. (8 pts) Clearly draw the structure of compound X in the box below.

Molecular structure of X

(see announcements for other possible answers)



Relevant Work/Analysis for Mixed Spectra Problem