Winter 2025 **Chemistry 2600 Midterm #1** ____/57 marks

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam with (or in the presence of) any CHEM 2600 student who has yet to write it. I understand that breaking this agreement would constitute academic misconduct. The minimum penalty would be a mark of 0/57 on this exam.

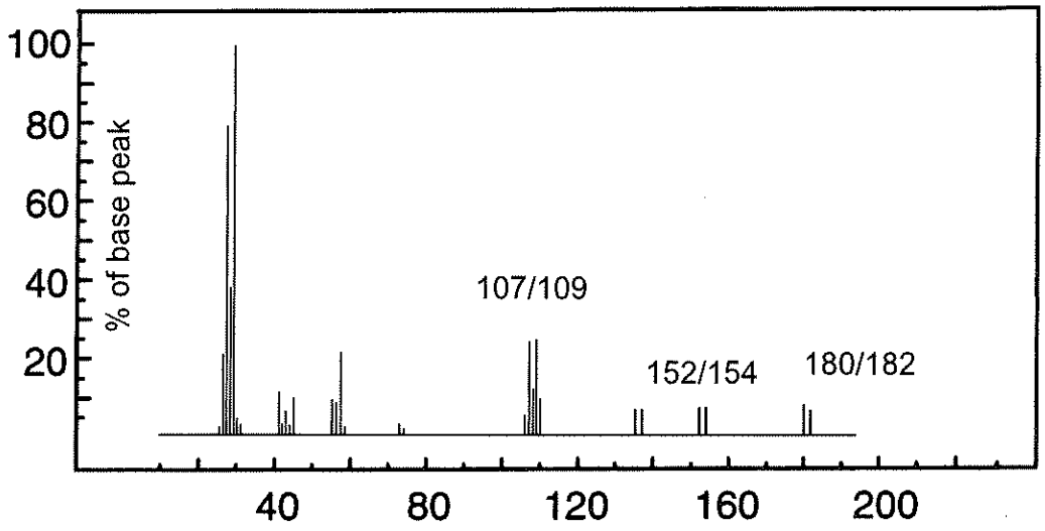
Signature: _____ Date: _____

1) Please read the test carefully before starting. It has 6 pages of questions and a periodic table.
2) You have been given a 6-page Spectroscopy Data Package. **PLEASE DO NOT WRITE ON THE SPECTROSCOPY DATA PACKAGE**! If you need scrap paper, use the back of any page of the test. On questions with spectra, you may also do rough work directly on the spectra.
3) You may use a molecular model kit and ruler. You may not have written materials in your model kit.
4) You may use a calculator but only for calculation. No other electronic devices are allowed.
5) **DO NOT WRITE ON ANY QR CODE!!!** Work on pages without a QR code will not be graded.
6) If your work is not legible, it will be given a mark of zero. For full credit, explanations must be complete. In many cases, complete explanations include drawing relevant structures. If delocalization of electrons is invoked, the relevant resonance structures must be drawn.
7) Marks will be deducted for incorrect information added to an otherwise correct answer.
8) You have 2 hours to complete this test.

Question Breakdown

Q1	**Q2**	**Q3**	**Q4**	**Q5**	**Q6**									**Total**
/ 3	/ 2	/ 12	/ 6	/ 12	/ 22									/ 57

1. The following mass spectrum corresponds to a compound containing one halogen atom. **[3 marks]**



(a) Clearly label the molecular ion on the mass spectrum. *[1 mark]*

M^+ is m/z 180

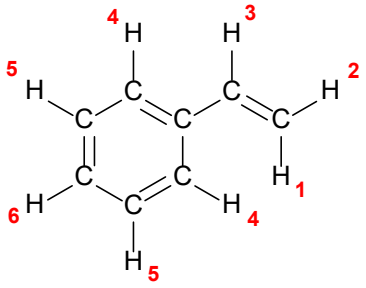
(b) Of which element is the halogen atom, and how can you tell? *[2 marks]*

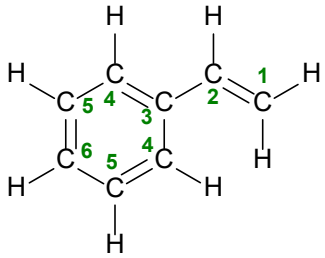
Bromine.

The molecular ion region has two peaks of approximately equal height (1 : 1 ratio) with a gap of m/z 2 between them – one for each isotope of bromine. (^{79}Br and ^{81}Br exist in approximately 1 : 1 ratio.)

This same pattern (two peaks in a 1 : 1 ratio with m/z 2 between them) can be seen at m/z 107 and 109 and at m/z 152 and 154.

2. For both parts of this question, assume that you are using an instrument capable of resolving all distinct peaks. In other words, do **not** attempt to account for peaks that might coincidentally overlap. **[2 marks]**





(a) How many peaks would you expect to see on the ^{1}H NMR of styrene (drawn above)?

6

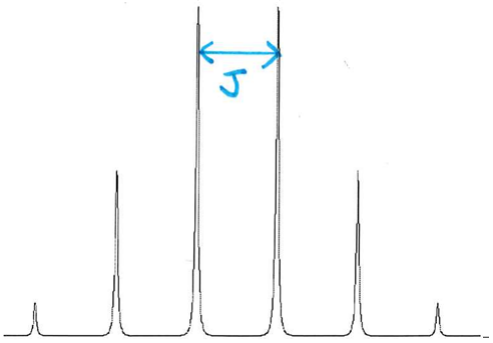
(b) How many peaks would you expect to see on the ^{13}C NMR of styrene (drawn above)?

6

3. For each of the following peaks: **[12 marks]**

- Identify the splitting pattern. *In other words, name the multiplicity, or shape, of the peak.*
- Indicate the number of different coupling constants required to generate this splitting pattern. *(**Not** the number of neighbouring atoms. The number of different J values!)*
- On the diagram, clearly show the distance corresponding to each coupling constant. (Just do this once for each coupling constant!) You do not need to give numerical values for the coupling constants; label them as $J_{1\text{-}2}$, $J_{1\text{-}3}$, $J_{1\text{-}4}$, etc.

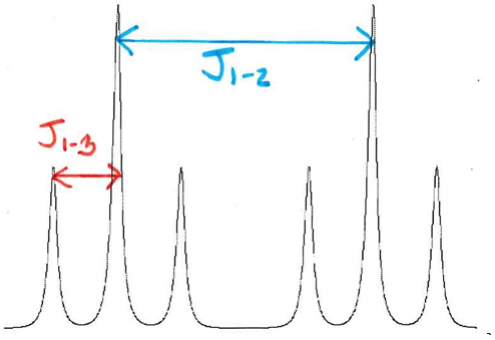
(a)



Splitting pattern: sextet

Different J values: 1

(b)

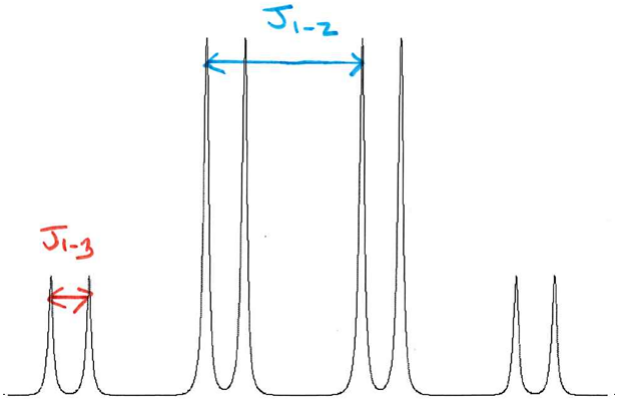


Splitting pattern: doublet of triplets

Different J values: 2

Draw coupling constant(s) onto diagrams!

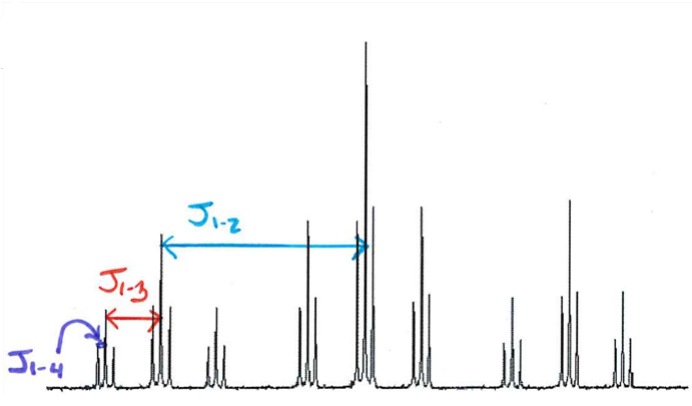
(c)



Splitting pattern: quartet of doublets

Different J values: 2

(d)

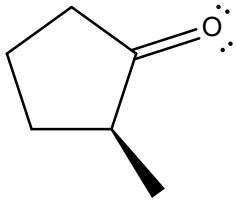


Splitting pattern: triplet of triplets of triplets

Different J values: 3

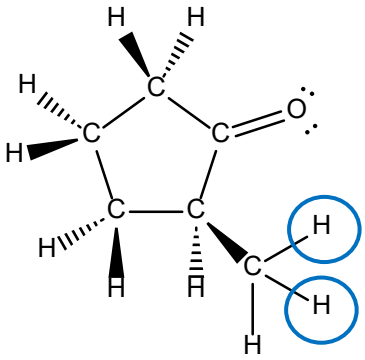
Draw coupling constant(s) onto diagrams!

4. Consider the following molecule: **[6 marks]**



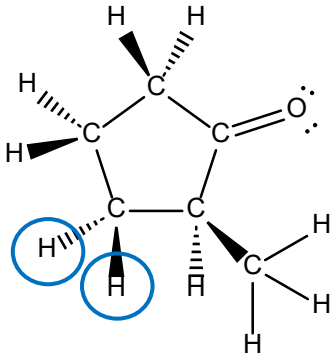
A sample answer has been provided for each question. These were not the only valid answers.

(a) On the picture below, circle two hydrogen atoms which are homotopic. *[2 marks]*



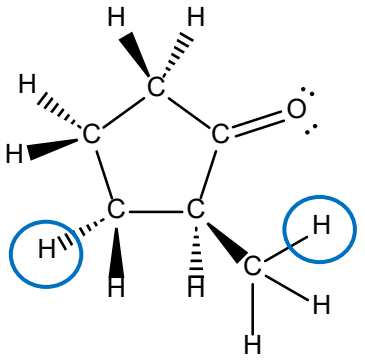
Any two of the three methyl group hydrogen atoms

(b) On the picture below, circle two hydrogen atoms which are diastereotopic. *[2 marks]*



Any pair of hydrogen atoms bonded to the same carbon atom (not including the methyl group) because one hydrogen is cis to the methyl group while the other is trans to the methyl group

(c) On the picture below, circle two hydrogen atoms which are constitutionally different. *[2 marks]*

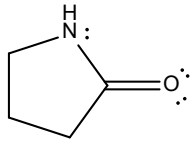


5. For each of the following pairs of molecules, explain how you would use **two** different spectroscopic methods to distinguish between them. Be specific. What peak(s) are you looking for? Where are they? Give numbers or ranges where possible. Unless the distinguishing feature of a spectrum is its lack of interesting peaks, mention at least one peak per molecule. **[12 marks]**

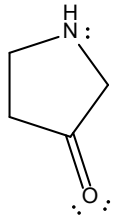
You may choose from ^{1}H NMR, ^{13}C NMR, IR and MS. You may choose different spectroscopic methods for each pair of molecules. It must be clear which methods you have chosen.

The answers below are intended to be representative not exhaustive. Other valid answers may exist.

(a)

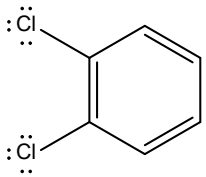


vs.

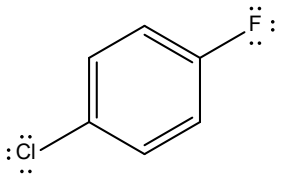


^{1}H NMR	Splitting patterns and integrations: • Triplet integrating to 2H • Pentet integrating to 2H • Triplet integrating to 2H • Singlet integrating to 1H	Splitting patterns and integrations: • Triplet integrating to 2H • Triplet integrating to 2H • Singlet integrating to 1H • Singlet integrating to 2H
	The exchangeable NH proton (the one that disappears after shaking with D_2O) has a chemical shift between 5 and 9 ppm.	The exchangeable NH proton (the one that disappears after shaking with D_2O) has a chemical shift between 1 and 2 ppm.
	After shaking with D_2O, only one peak is upfield of 2ppm: • Pentet (2H) at ~1 to 1.5 ppm	After shaking with D_2O, all peaks are downfield of 2ppm: • Singlet (2H) is between carbonyl and N so maybe at ~4 ppm • Triplets are either next to carbonyl or next to N so at ~2-2.5 ppm
^{13}C NMR	Carbonyl C for amide is expected to appear between 160 and 180 ppm.	Carbonyl C for ketone is expected to appear between 175 and 220 ppm.
IR	An unconjugated secondary amide gives a C=O stretch between 1670 and 1700 cm^{-1}.	An unconjugated ketone gives a C=O stretch between 1705 and 1725 cm^{-1}.

(b)

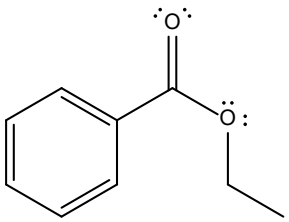


vs.

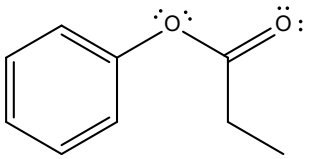


^{1}H NMR	Two peaks in the aromatic region (6-9 ppm) which are likely to exhibit fine splitting due to long-range coupling. They may be discernable as doublets or doublets or may just be messy multiplets.	Two doublets in the aromatic region (6-9 ppm); long range coupling is not possible so no fine splitting.
^{13}C NMR	3 peaks	4 peaks
MS	Molecular ion region features a $9{:}\,6{:}\,1$ ratio of $M^{+}{:}\,[M+2]^{+}{:}\,[M+4]^{+}$ M^{+} is $^{m}/_{z}\,146$	Molecular ion region features a $3{:}\,1$ ratio of $M^{+}{:}\,[M+2]^{+}$ M^{+} is $^{m}/_{z}\,130$

(c)



vs.



^{1}H NMR	The quartet integrating to 2H is expected to appear at ~4-4.5 ppm because the CH_2 group is next to O.	The quartet integrating to 2H is expected to appear at ~2-2.5 ppm because the CH_2 group is next to a carbonyl carbon.
	Aromatic protons *ortho* and *para* to the carbonyl group will be deshielded because that group is electron withdrawing via resonance. As such, expect the doublet (2H) and triplet (1H) to appear downfield of the triplet (2H).	Aromatic protons *ortho* and *para* to the oxygen atom will be shielded because the lone pair of the oxygen atom makes it electron-donating via resonance. As such, expect the triplet (2H) to appear downfield of the doublet (2H) and triplet (1H).
^{13}C NMR	Expect four aromatic peaks fairly close together at ~110-140 ppm in addition to the carbonyl peak (160-180 ppm), the CH_2O peak (40-70 ppm) and the CH_3 peak (15-30 ppm)	Expect three aromatic peaks fairly close together at ~110-140 ppm and one aromatic peak (the C attached to O) significantly downfield of the others (~150-165 ppm) in addition to the carbonyl peak (160-180 ppm), the CH_2O peak (40-70 ppm) and the CH_3 peak (15-30 ppm)
IR	A conjugated ester gives a C=O stretch between 1715 and 1730 cm^{-1}	An unconjugated ester gives a C=O stretch between 1735 and 1750 cm^{-1}

6. The following page contains spectra for Unknown X ($C_5H_9BrO_2$). **[22 marks]**

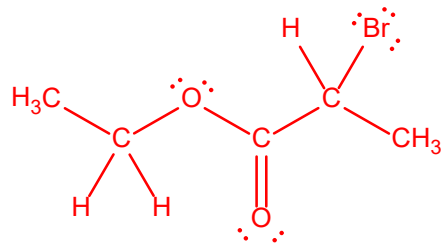
(a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.

(b) Use this page to explain your reasoning. **Calculation of integrals is required for full marks.**

(c) On both NMR spectra, assign as many peaks as you can by numbering the peaks from left to right, drawing Unknown X in the box provided, and labeling each carbon or hydrogen atom with the appropriate peak number. For atoms that cannot be assigned with certainty, list the signals to which they might reasonably correspond.

(d) Label any important peaks on the IR, clearly identifying which bond(s) correspond(s) to each peak.

Unknown X:



General breakdown of marks:
1 mark for correct answer
1 mark for calculating DU
2 marks for calculating integrals for ^{1}H NMR
1 mark for IR peak assignment
4 marks for ^{1}H NMR assignment (correct for correct answer; "reasonable" for incorrect answers)
4 marks for ^{13}C NMR assignments (correct for correct answer; "reasonable" for incorrect answers)
9 marks for logic (this page plus legible rough work on spectra, etc.); verbal explanation is required for full credit

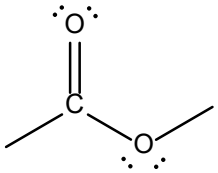
One Way to Arrive at the Answer

Step 1: Calculate Unsaturation Index (Degrees of Unsaturation)

- $DU = \frac{2C+2+N-X-H}{2} = \frac{2(5)+2-1-9}{2} = \frac{2}{2} = 1$
- The unknown therefore contains either a double bond or a ring.

Step 2: Look at IR for relevant peaks

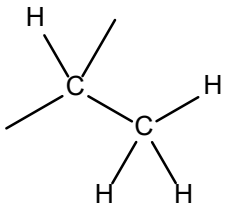
- The large peak at 1740 cm^{-1} strongly suggests a $C = O$ bond that most likely corresponds to an ester.
  - There is a peak on the ^{13}C NMR at about 170 ppm. This chemical shift is consistent with the carbonyl of an ester or carboxylic acid.



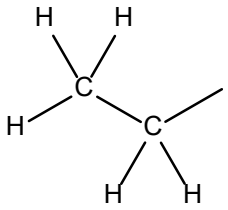
Step 3: Consider the peaks on ^{1}H NMR

- There are four peaks on the ^{1}H NMR spectrum. The integral trail heights are approximately 3mm : 6mm : 9mm : 9mm, so the integral ratio is 1 : 2 : 3 : 3. This is consistent with the nine hydrogen atoms in the molecular formula.
- The four peaks are:
  - a quartet at ~4.4 ppm (1H) – CH next to CH_3
  - a quartet at ~4.2 ppm (2H) – CH_2 next to CH_3
  - a doublet at ~1.8 ppm (3H) – CH_3 next to CH
  - a triplet at ~1.2 ppm (3H) – CH_3 next to CH_2

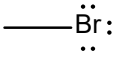
- The peaks for "CH next to CH_3" and "CH_3 next to CH" almost certainly correspond to adjacent groups, giving



- The peaks for "CH_2 next to CH_3" and "CH_3 next to CH_2" almost certainly correspond to adjacent groups, giving

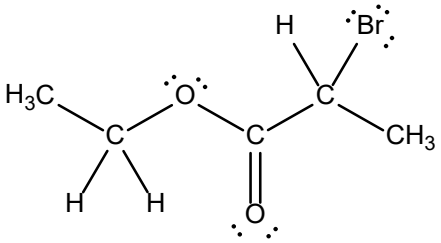


- The three pieces proposed so far use up all carbon, hydrogen and oxygen atoms in the molecular formula. The remaining piece must be a bromine atom

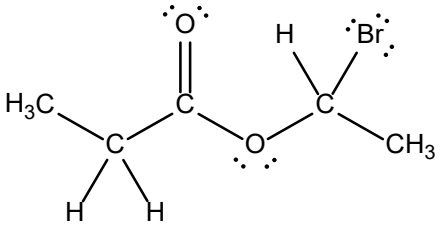


Step 4: Assemble the pieces and decide between the two options.

- There are two different ways in which these pieces can be assembled:

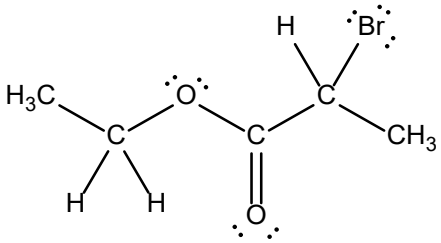


or



- The easiest way to distinguish between these two options is to look at the chemical shifts of the quartets:
  - The compound on the left would be expected to give a quartet (2H) at about 4 ppm for CH_2-O of an ester and another quartet (1H) at about 4.5-5 ppm for CH that is both attached to Br (deshields to ~4 ppm in isolation) and a carbonyl group (further deshields the CH group).
  - The compound on the right would be expected to give a quartet (2H) at about 2 ppm for CH_2 next to the carbonyl of an ester and another quartet (1H) at about 6-7ppm for CH that is both attached to O of an ester (deshields to ~5 ppm in isolation) and a Br (further deshields the CH group)
- Given that the two quartets both have chemical shifts between 4 and 4.5 ppm. It is clear that the structure on the right cannot be correct therefore the structure on the left must be correct.

Explanations which do not address both possibilities will not get full credit (unless previous logic includes a good reason why the incorrect one would not have been considered).



Step 5: Check your answer against the spectra and assign the peaks.

- IR
  - A $C = O$ stretch is visible at 1740 cm^{-1}. This is within the usual range for esters.
- ^{1}H NMR
  - The quartet at ~4.4 ppm on the ^{1}H NMR is consistent with a CH group attached to both Br and CO. It's a quartet because it's next to a CH_3 group. It integrates to 1H.
  - The quartet at ~4.2 ppm on the ^{1}H NMR is consistent with a CH_2 group attached to O of an ester. It's a quartet because it's next to a CH_3 group. It integrates to 2H.
  - The doublet at ~1.8 ppm on the ^{1}H NMR is consistent with a CH_3 group close to (but not directly attached to) deshielding groups. It's a doublet because it's next to a CH group. It integrates to 3H.
  - The triplet at ~1.2 ppm on the ^{1}H NMR is consistent with a CH_3 group close to (but not directly attached to) deshielding groups. It's a triplet because it's next to a CH_2 group. It integrates to 3H.
- ^{13}C NMR
  - The peak at ~170 ppm is consistent with $C = O$ of an ester.
  - The peak at ~60 ppm is consistent with $C - O$ (C on the other side of the ester).
  - The peak at ~40 ppm is consistent with CH attached to Br.
  - The peaks at ~12 ppm and ~22 ppm are consistent with the two CH_3 groups. It's likely that the peak at ~22 ppm is for the CH_3 group next to CHBr as that would be expected to be more deshielded than the one next to CH_2.

6. *…continued*

$C_5H_9BrO_2$

