

NAME: _____ Section: _____ Student Number: _____

Spring 2018

Chemistry 2600 Midterm

_____/ 60 marks

- INSTRUCTIONS:
- 1) Please read over the test carefully before beginning. You should have 6 pages of questions in addition to this cover page and a periodic table.
 - 2) You have also 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 any papers or other written materials in your model kit.
 - 4) You may use a calculator. It may not have wireless capability. You may not have any other electronic devices (phone, iPod, etc.) with you when you write the exam.
 - 5) If your work is not legible, it will be given a mark of zero.
 - 6) Marks will be deducted for incorrect information added to an otherwise correct answer.
 - 7) You have 2 hours to complete this test.
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Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until after 7:00pm Mountain Time on Friday, February 9th, 2018. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/60 on this exam and removal of the “overwrite midterm mark with final exam mark” option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____

Date: _____

Course: CHEM 2600 (Organic Chemistry II)

Semester: Spring 2018

The University of Lethbridge

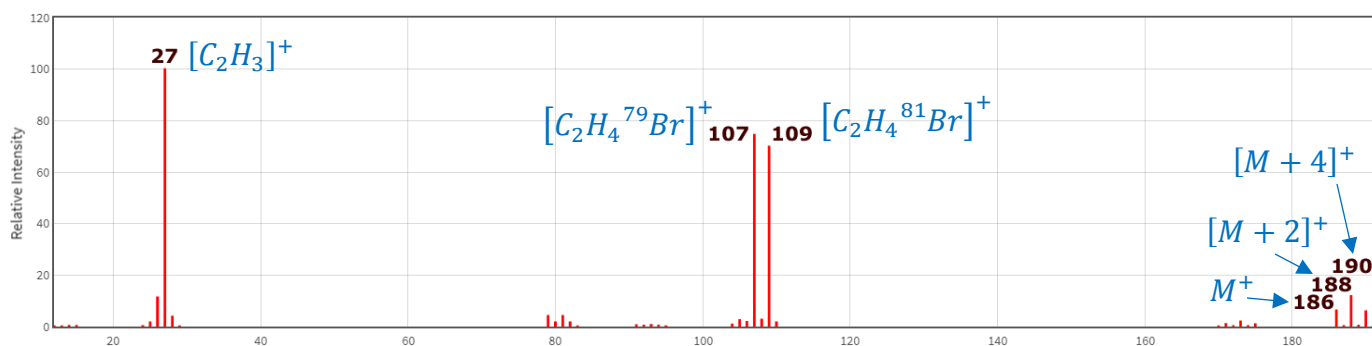
Question Breakdown

Q1	/ 10
Q2	/ 12
Q3	/ 12
Q4	/ 6
Q5	/ 20

Total	/ 60
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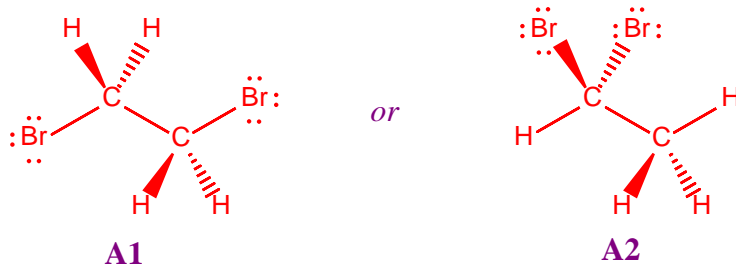
1. The mass spectrum below corresponds to Compound A (which is organic). [10 marks]



- (a) What is the molecular formula for Compound A? [1 mark]
 $C_2H_4Br_2$

- (b) Explain the logic you used to answer part (a). As part of your answer, it should be clear that you know what each of the numbered peaks corresponds to. [5 marks]

- The molecular ion is m/z 186.
- There is a 1 : 2 : 1 ratio for $M^+ : [M + 2]^+ : [M + 4]^+$. This strongly suggests that the molecule contains two bromine atoms – particularly since there are two signals of equal height at m/z 107 and 109. ($106 - 79 = 107$)
- Subtracting the mass of two ^{79}Br from 186 leaves 28 g/mol for the remaining atoms.
- There are two plausible combinations of atoms that would give 28 g/mol (C_2H_4 and CO); however, the peak at m/z 27 would be impossible to explain if the molecular formula were $COBr_2$. If the molecular formula is $C_2H_4Br_2$, the peak at m/z 27 can be $[C_2H_3]^+$ - which would be formed by elimination of HBr from the $[C_2H_4Br]^+$ fragments at m/z 107 and 109.
- Compound A can be either:



- (c) There are two possible structures for Compound A. Briefly explain how you could use 1H NMR to distinguish between them. [2 marks]

The 1H NMR for A1 would show one singlet.

The 1H NMR for A2 would show a doublet integrating to 3H and a quartet integrating to 1H.

- (d) There are two possible structures for Compound A. Briefly explain how you could use ^{13}C NMR to distinguish between them. [2 marks]

The ^{13}C NMR for A1 would show one peak.

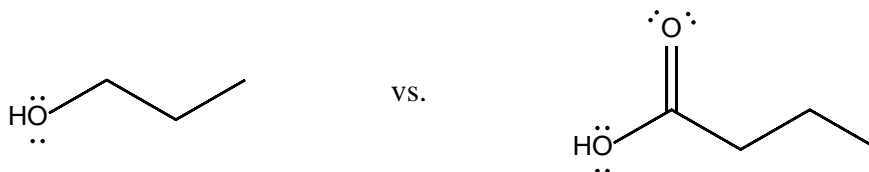
The ^{13}C NMR for A2 would show two peaks.

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2. *I am listing many reasonable answers. You needed two (using different types of spectroscopy).*

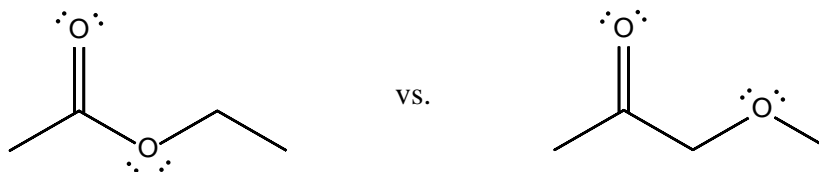
[12 marks]

(a)



IR	no C=O stretch OH stretch between 3200 and 3500 cm ⁻¹	C=O stretch at about 1700-1725 cm ⁻¹ OH stretch extremely broad, very likely to cross below the 3000 cm ⁻¹ line (possibly as far as 2800 cm ⁻¹)
¹³C NMR	3 signals No signals downfield of 100 ppm	4 signals C=O signal at about 160-180 ppm
¹H NMR	Triplet integrating to 2H (CH ₂ next to OH) is at about 3.5 ppm. The other two peaks are upfield of this.	Triplet integrating to 2H (CH ₂ next to C=O) is at about 2.2 ppm. The other two peaks are upfield of this.
MS	Molecular ion is m/z 60	Molecular ion is m/z 88

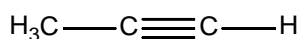
(b)



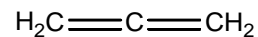
IR	C=O stretch at about 1735-1750 cm ⁻¹	C=O stretch at about 1705-1725 cm ⁻¹
¹³C NMR	C=O signal at about 160-180 ppm Two signals below 40 ppm for the CH ₃ groups.	C=O signal at about 180-220 ppm One signal below 40 ppm for the CH ₃ group next to C=O. (The signal for OCH ₃ will be between 40 and 70 ppm.)
¹H NMR	A quartet integrating to 2H and triplet integrating to 3H are strongly indicative of the ethyl group. (The third peak is a singlet integrating to 3H.)	All three peaks are singlets.
MS	McLafferty rearrangement gives a fragment at m/z 60	McLafferty rearrangement gives a fragment at m/z 58

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(c)



vs.

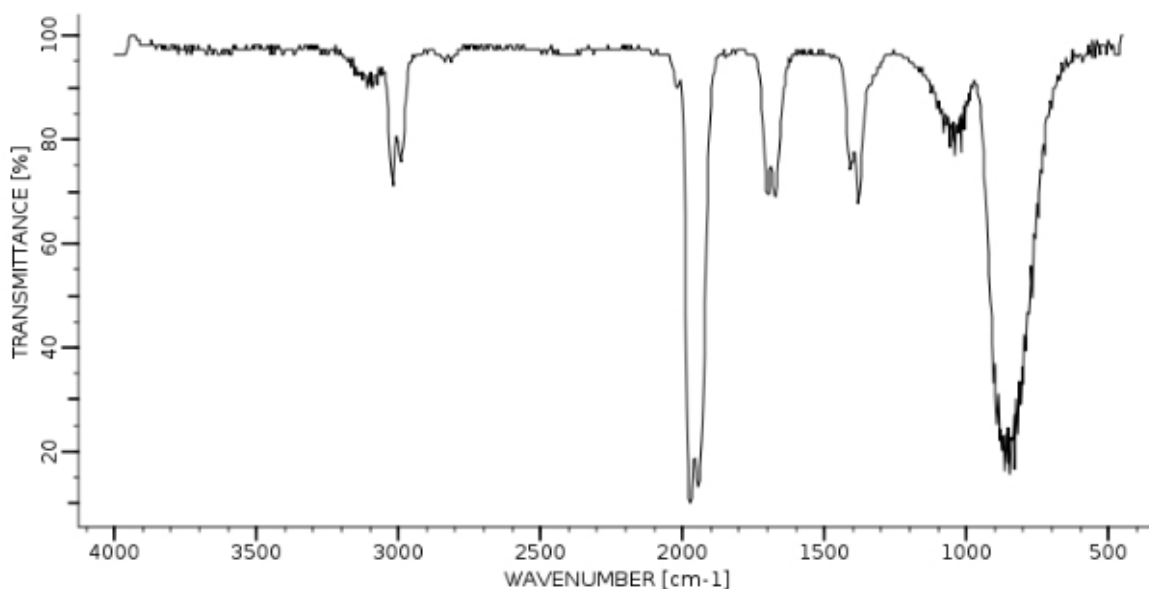


IR	C≡C stretch for terminal alkyne at about 2100-2300 cm ⁻¹ C-H stretch at about 3300 cm ⁻¹ for the carbon atom of the alkyne (and the attached hydrogen atom) and C-H stretch below 3000 cm ⁻¹ for the CH ₃ group	C=C stretch at about 1500-1650 cm ⁻¹ ***** C-H stretch at about 3000-3100 cm ⁻¹
¹³C NMR	3 signals No signals downfield of 110 ppm	2 signals ***
¹H NMR	Two peaks. If long-range coupling is detected, there will be a narrow quartet integrating to 1H and a narrow doublet integrating to 3H. If the coupling constant is too small for long-range coupling to be observed, both peaks will be singlets.	One peak.

*** *Many students assumed that both signals would fall in the alkene region. I did not penalize for that as it was a reasonable supposition given that you have no experience with cumulenes (molecules in which one C is part of two different double bonds). In fact, the two signals for this molecule appear at ~75 ppm and ~215 ppm.*

***** *The IR for cumulene is shown below. As you can see, there are C=C stretches despite the fact that the molecule is symmetrical because an asymmetric stretch will still change the dipole of the molecule. This is analogous to the two peaks for CO₂ commonly seen just over 2300 cm⁻¹*

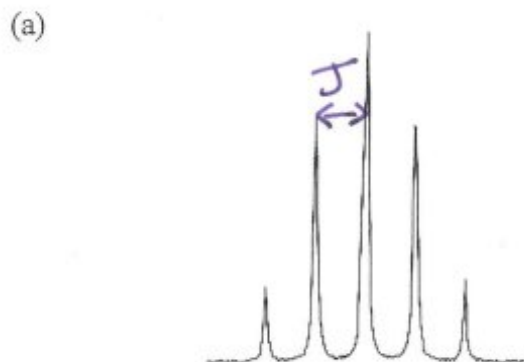
IR Absorption Spectrum



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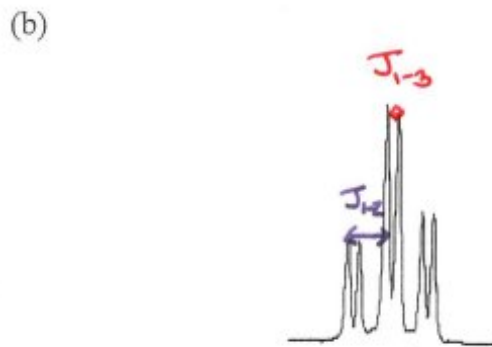
3. For each of the following peaks: [12 marks]

- 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_{1-2} , J_{1-3} , J_{1-4} , etc. *The subscripts refer to which atoms are coupling – not to any peak numbers! So, J_{1-2} is hydrogen 1 coupling to hydrogen 2 while J_{1-3} is hydrogen 1 coupling to hydrogen 3, etc. I am showing one representative coupling constant for each value. You did NOT need to draw them all!!!*



Splitting pattern: pentet

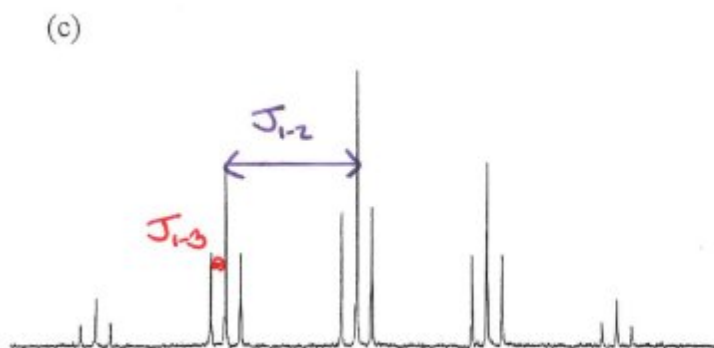
Different J values: 1



Splitting pattern: triplet of doublets

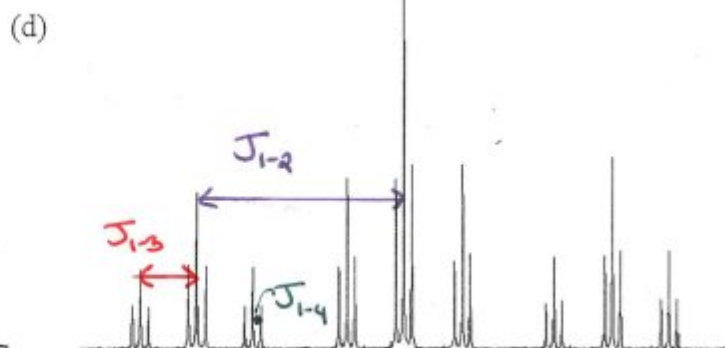
Different J values: 2

Draw coupling constant(s) onto diagrams!



Splitting pattern: pentet of triplets

Different J values: 2



Splitting pattern: triplet of triplets of triplets

Different J values: 3

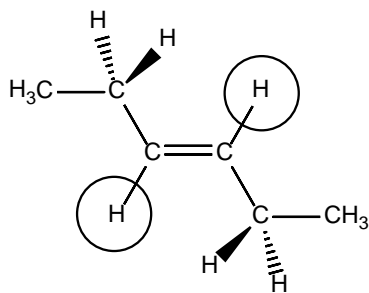
Draw coupling constant(s) onto diagrams!

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4. Below each molecule, write one of the following abbreviations (H, E, D or CD) to indicate the relationship between the circled hydrogen atoms: **[6 marks]**

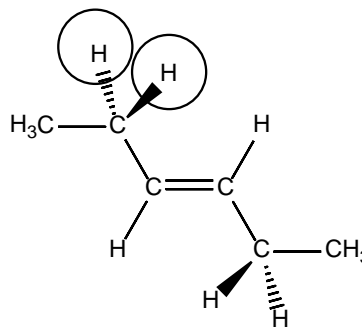
- Homotopic (H)
- Enantiotopic (E)
- Diastereotopic (D)
- Constitutionally different (CD)

(a)



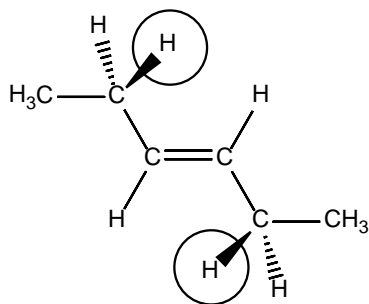
H

(b)



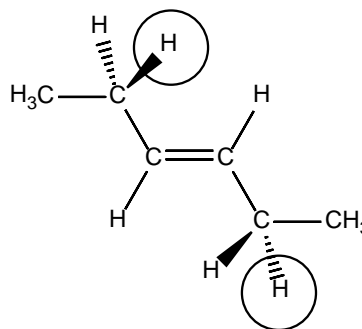
E

(c)



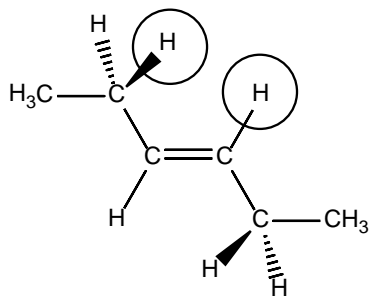
H

(d)



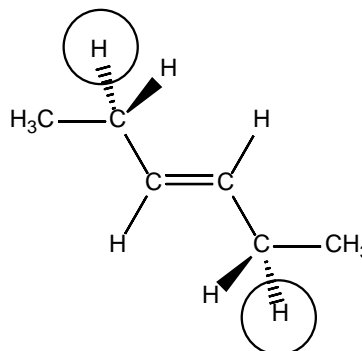
E

(e)



CD

(f)



H

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5. The following page contains spectra for Unknown X ($C_6H_{10}O_6$). [20 marks]
- (a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.
- (b) Use this page to explain your logic. **ALL THREE PEAKS ON THE 1H NMR ARE SINGLETs. YOUR EXPLANATION SHOULD ADDRESS WHY THIS IS THE CASE.**
- (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.

General breakdown of marks:

1 mark for correct answer

2 marks for IR peak assignments

3 marks for 1H NMR assignments (correct for correct answer; "reasonable" for incorrect answers)

3 marks for ^{13}C NMR assignments (correct for correct answer; "reasonable" for incorrect answers)

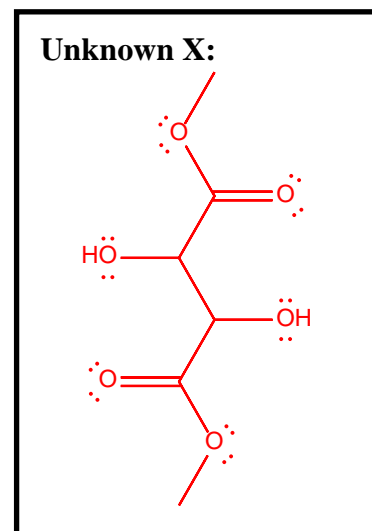
2 marks for explaining why only singlets were observed

(1 mark for noting that shift equivalent H do not couple, even when they're on adjacent carbon atoms;

1 mark for noting that exchangeable H do not couple;)

1 mark for calculating DU

8 marks for logic (this page plus legible rough work on spectra, etc.)



One Way to Arrive at the Answer

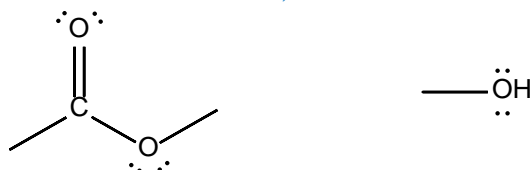
Step 1: Calculate Unsaturation Index (Degrees of Unsaturation)

$$DU = \frac{2C+2+N-X-H}{2} = \frac{2(6)+2-10}{2} = \frac{4}{2} = 2$$

- Therefore, there is either a triple bond, two double bonds, a double bond and a ring, or two rings in this molecule

Step 2: Look at IR for relevant peaks

- The large broad peak from $\sim 3200-3500\text{ cm}^{-1}$ strongly suggests an O-H bond.
 - O-H can mean alcohol or carboxylic acid, but there is no $-\text{CO}_2\text{H}$ peak on the ^1H NMR (no peak over 10 ppm) so it must be an alcohol. Also, a carboxylic acid O-H stretch tends to stretch below 3000 cm^{-1}
- The large peak at $1740-1760\text{ cm}^{-1}$ strongly suggests a C=O bond. This peak must be due to an ester since that is the only type carbonyl that gives a peak in this region except for anhydride (which would give a second peak above 1800 cm^{-1}) or conjugated acid chloride (which would require a Cl in the molecular formula).
 - There is a peak on the ^{13}C NMR at about 170 ppm. That is consistent with an ester.
 - If the molecule contains at least one C=O, it cannot also have a triple bond (since $DU=2$)



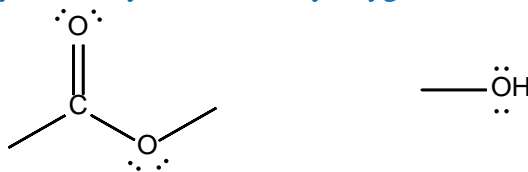
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Step 3: Recognize symmetry

- The integrals on the ^1H NMR add up to 5H, but the molecular formula has 10H, so they have to be doubled.
- The ^{13}C NMR has three peaks, but the molecular formula has 6C. So, there are only three different environments for six carbon atoms.
- Both of these points strongly suggest a symmetrical molecule.

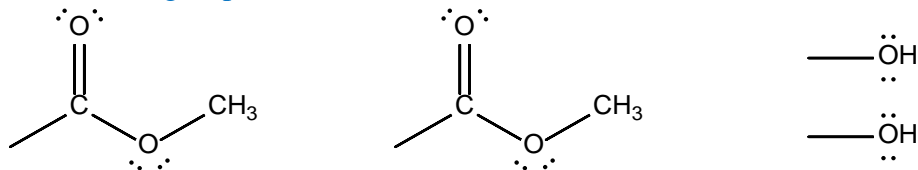
Step 4: Look at ^{13}C NMR for C=C or C=O peaks

- The peak at ~ 170 ppm is most likely the C=O for the ester discussed in the IR section.
- The other peaks are at ~ 70 ppm and ~ 50 ppm. This is too far upfield for C=C carbons, so they must be tetrahedral. They are likely deshielded by oxygen atoms.

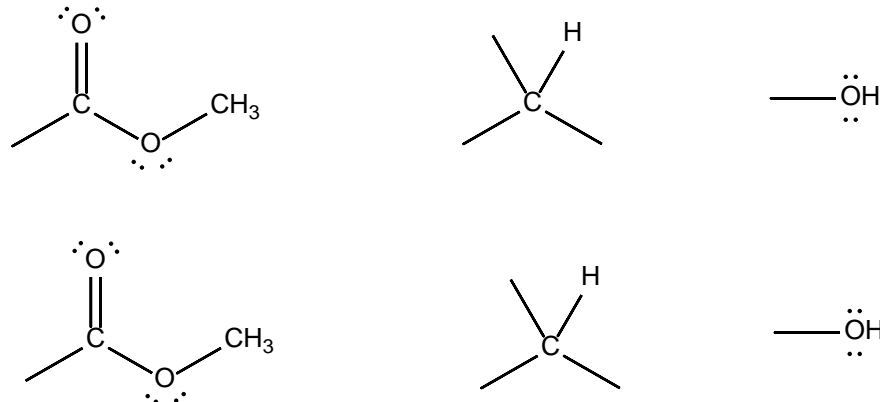


Step 5: Look at ^1H NMR to account for remaining atoms

- Singlet at ~ 3.9 ppm integrates to 6H. This strongly suggests two equivalent CH_3 groups. The chemical shift indicates that they are deshielded. If they were attached to the oxygen atom of an ether, they would have a chemical shift of ~ 3.3 ppm. If they were attached to the oxygen atom of an ester, they would have a chemical shift of ~ 3.7 ppm. Therefore, we probably have two methyl esters.
- Since the other two peaks both integrate to 2H, if there is an alcohol (which IR says there is), there must be two OH groups.



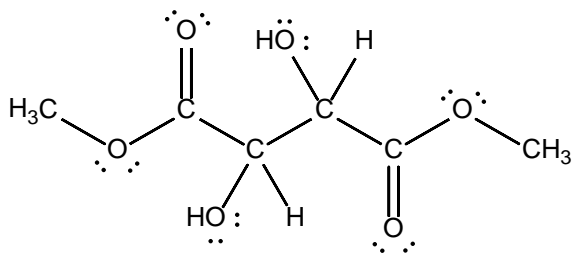
- These pieces consume $\text{C}_4\text{H}_8\text{O}_6$, leaving C_2H_2 and one peak on the ^1H NMR that integrates to 2H. Given the symmetry, that peak should represent two CH groups. This gives us:



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Step 6: Assemble the pieces.

- There is only one way to assemble the pieces that maintains the required symmetry:



Step 6: Rationalize the singlets.

- The CH_3 peaks are singlets because the nearest H are 5 bonds away (and there is no potential for long range coupling in this particular molecule).
- The OH peaks are singlets because they are exchangeable H and therefore do not couple (except at very low temperatures).
- The CH peaks are singlets because the vicinal H are shift equivalent. Shift equivalent H do not couple.

Notes and Rants That Everyone Should Read

- “Ketone” does not mean C=O . Ketones contain a carbonyl group, but not every C=O stretch on the IR corresponds to a ketone.
- Speaking of C=O on the IR, you can (and should) use the exact value for the wavenumber of the peak to help you decide what kind of carbonyl group is in your molecule. The table to the right of the spectrum listed the exact wavenumbers but, even without that, you should have been able to estimate the peak to be about 1750 cm^{-1} (halfway between 1700 and 1800 cm^{-1}) and therefore conclude that it must be from an ester.
- While O-H peaks on a ^1H NMR are often broad, hydrogen bonding can reduce that effect. If the IR says you have an O-H bond and you have a singlet on the ^1H NMR that has the right integration, it’s probably an OH peak even if it isn’t overly broad.
- CH_2 or CH on the ^{13}C NMR table means on a tetrahedral atom. The C from a CH_2 on the end of a double bond shows up in the “alkene” region (110 - 150 ppm) on ^{13}C NMR.
- If you have a C=C double bond, you need TWO peaks in the C=C region (110 - 150 ppm) on your ^{13}C NMR unless your double bond is symmetrical, making the two carbon atoms homotopic. Having a heteroatom (O, Cl, etc.) attached to an alkene carbon might shift it slightly farther downfield (maybe up to 160 ppm – or 170 ppm if there were two heteroatoms on the same carbon) – but nothing will pull it upfield to 70 ppm
- Atoms that are not carbon do not appear on a ^{13}C NMR. I know the data sheet says “alcohol”, but we discussed this in class. That means “C attached to O” – like in an alcohol. Also, it does not guarantee an actual alcohol in your molecule; you could have an ether or ester, for example.
- The CH are on a carbon that is attached to an OH group and a carbonyl group. If they were just CHOH , we would expect the peak to appear at $\sim 3.9\text{ ppm}$. The carbonyl group further deshields those H. It is therefore unreasonable to suggest that the peak at 3.5 ppm is for the CH. The CH have to give the peak at 4.5 ppm . (The peak at 3.5 ppm is therefore for the OH by process of elimination. The fact that it’s shorter than the CH peak but has the same integration suggests that it’s slightly broader, as would be expected – but that’s not conclusive evidence.)

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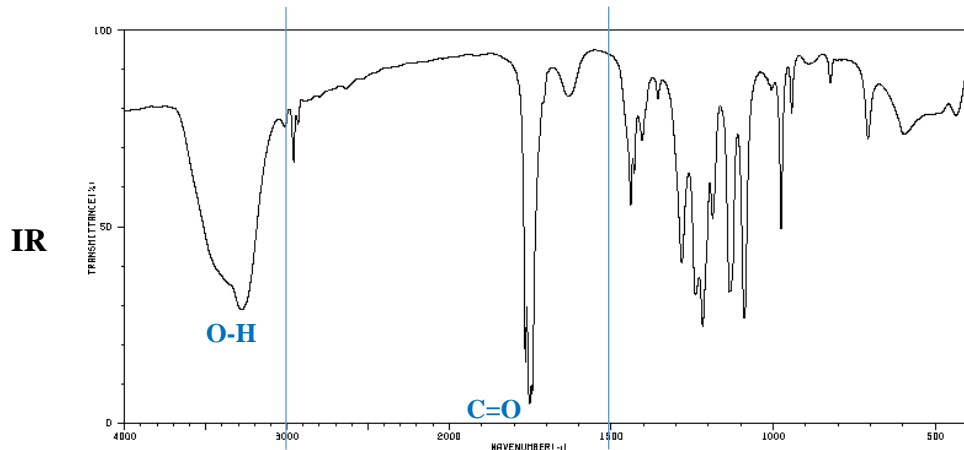
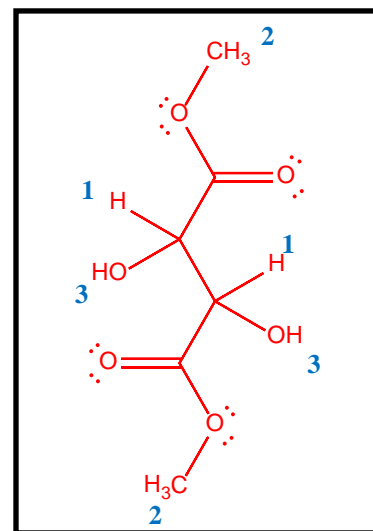
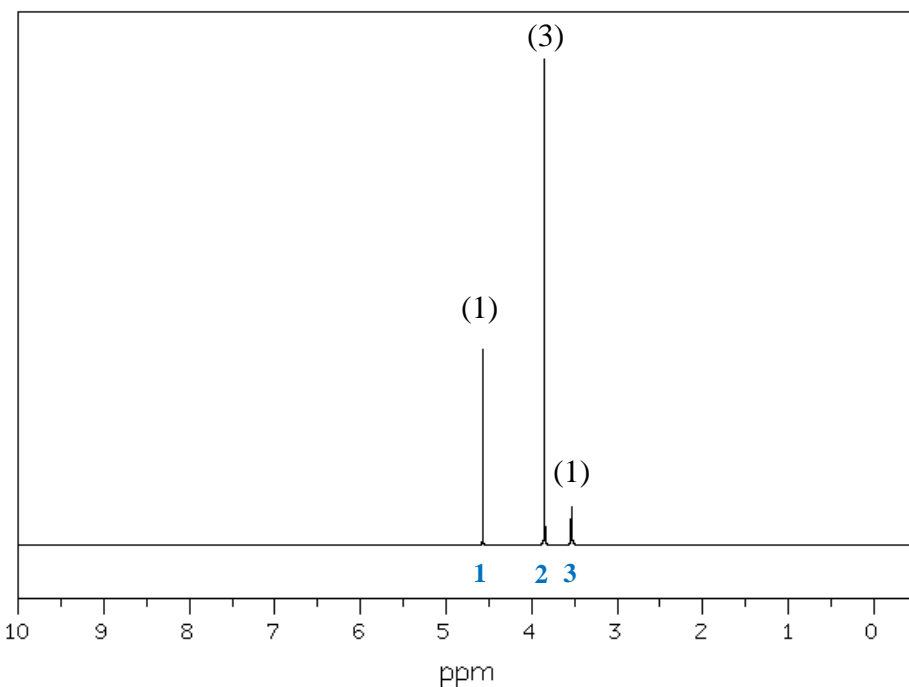


Table of wavenumbers and transmittances

3279	27	1744	7	1241	31	944	77
3013	72	1631	79	1218	23	825	84
2958	84	1440	55	1188	50	708	70
2942	74	1429	60	1136	32	602	70
2931	72	1405	70	1089	26	594	70
1765	15	1357	79	1006	81	437	74
1753	4	1283	38	976	47		

¹H NMR



¹³C NMR

