CHEM 344 Fall 2016 Spectroscopy and WebMO Exam (75 pts)

Name:

TA Name:

Exam Length = 90 min
DO NOT REMOVE ANY PAGES FROM THIS EXAM PACKET.

Directions for drawing molecules, reactions, and electron-pushing mechanisms:

Draw all lone pairs, bonds, arrows, formal charges, and stereochemistry explicitly in all molecular structures.

Directions for all calculations:

Explicitly show all work on all calculations and include all important labels.

Directions for analyzing graded spectra:

- Label each set of equivalent protons using the H_a, H_b, H_c etc. labeling system. Assign each **^{1}H-NMR** signal and write your assignments directly onto the spectrum. Use the empirical chemical shift parameters (Curphy-Morrison parameters) or chemical shift tables found at the end of the exam to ***assist*** your ^{1}H-NMR analysis and signal assignments.

- Assign the hybridization of the ^{13}C-atoms responsible for each **^{13}C-NMR** signal. Identify specific functional group signals; you do not need to assign individual carbon atoms to each signal.

- Assign each key **IR** absorption band >1500 cm^{-1} to a specific functional group. Draw a part structure responsible for the vibration next to each band.

- Draw fragments for all labeled peaks in the **EI-MS** directly onto the spectrum (you do not need to show the fragmentation mechanism unless directed to do so).

1) The spectra below were obtained from an organic molecule ($C_8H_6O_3$). Determine the structure of the molecule using the spectra provided and by answering the questions below. **(23 pts total)**

a) Calculate the number of double bond equivalencies, unsaturation number, or the index of hydrogen deficiency for this molecule using the equation provided. **(2 pts)**

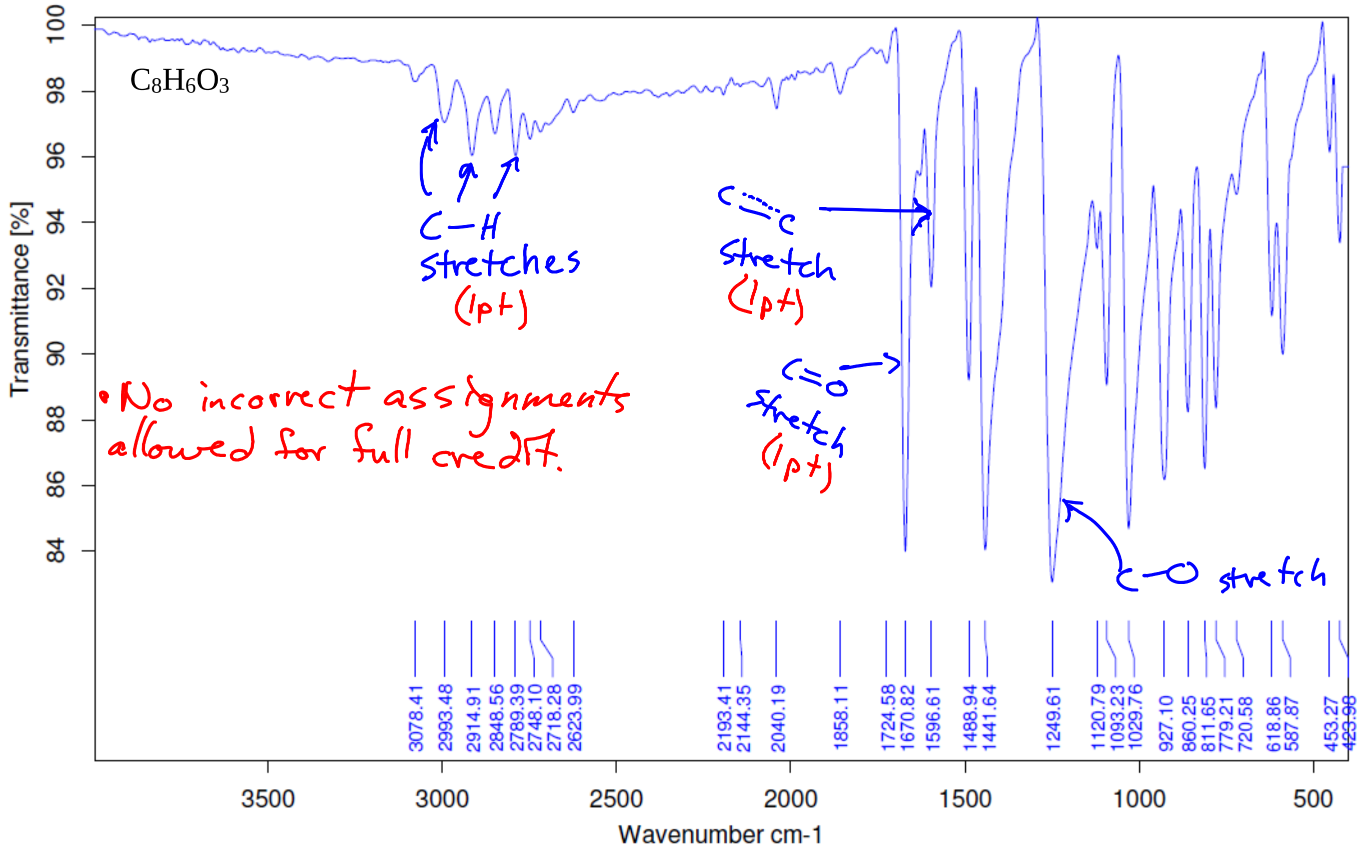
$$IHD = \frac{2C + N - H - X + 2}{2}$$

$$IHD = \frac{16 + 0 - 6 - 0 + 2}{2} = \frac{12}{2} = \boxed{6}$$

(2pts) - all or nothing

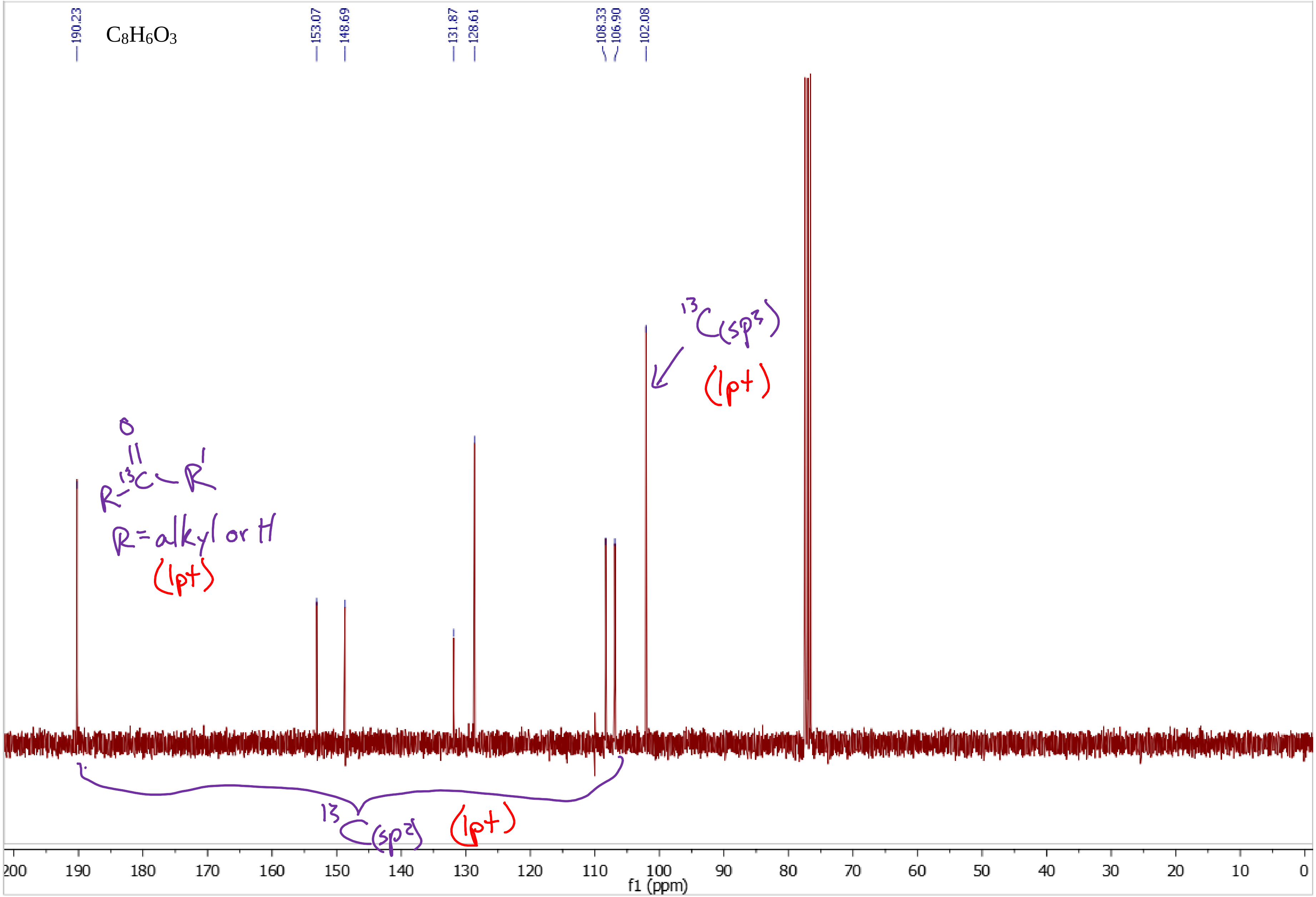
$$C_8H_6O_3 \longrightarrow C_8H_6 \xrightarrow{\boxed{6\ H_2}} C_8H_{18}$$

b) Based upon the chemical formula, index of hydrogen deficiency, and the IR spectrum below, suggest which organic functional groups are possible/likely in this molecule. Label the signal from each suggested functional group. **(3 pts)**



• No incorrect assignments allowed for full credit.

c) Use the ^{13}C-NMR spectrum below, collected in $CDCl_3$, to identify the hybridization of each ^{13}C-atom and identify any key functional group signals. Only the peak-picked signals are from the desired molecule, $C_8H_6O_3$. **(3 pts)**



$R-{}^{13}C(=O)-R'$

R = alkyl or H

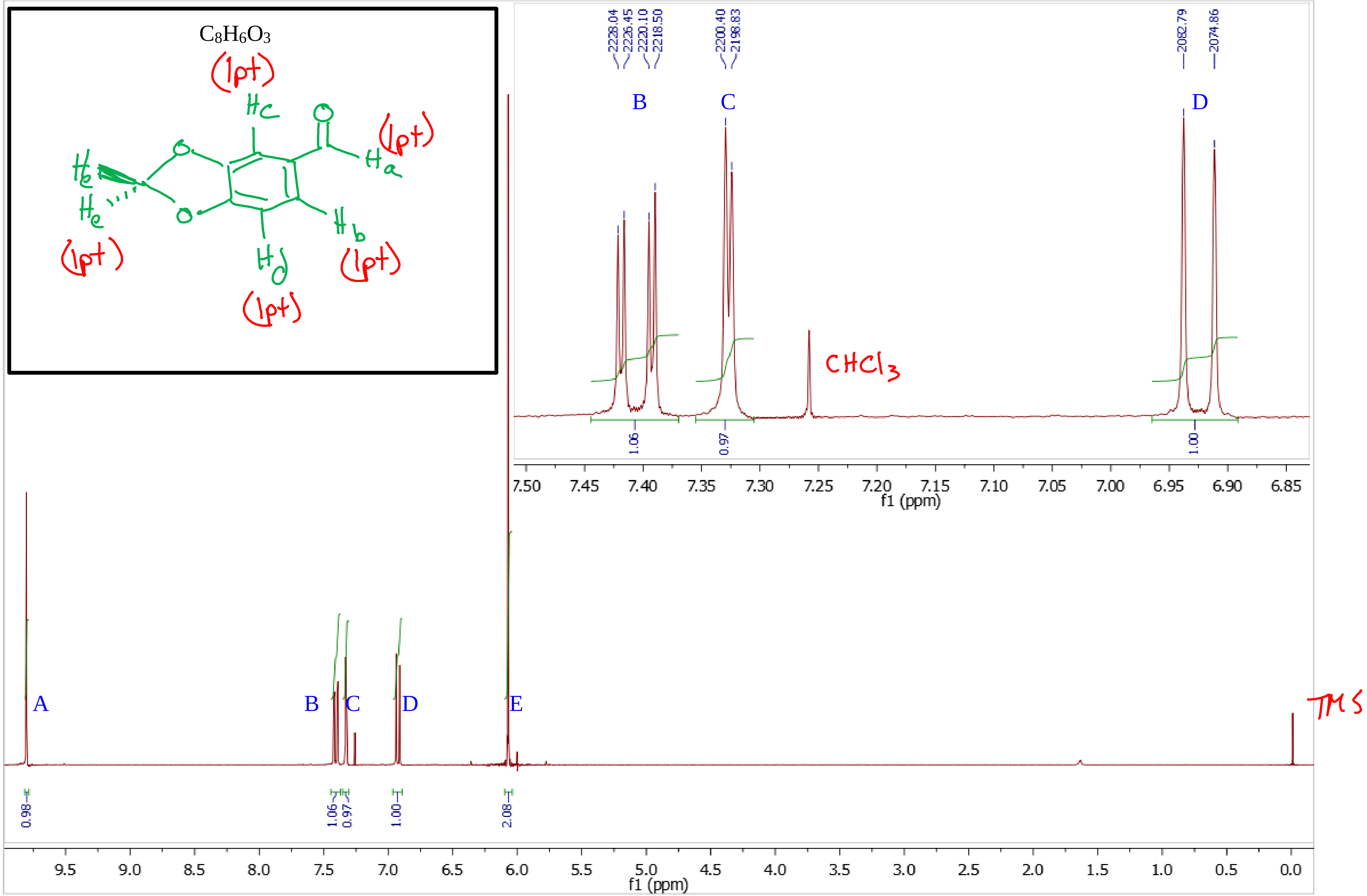
(1pt)

${}^{13}C(sp^3)$

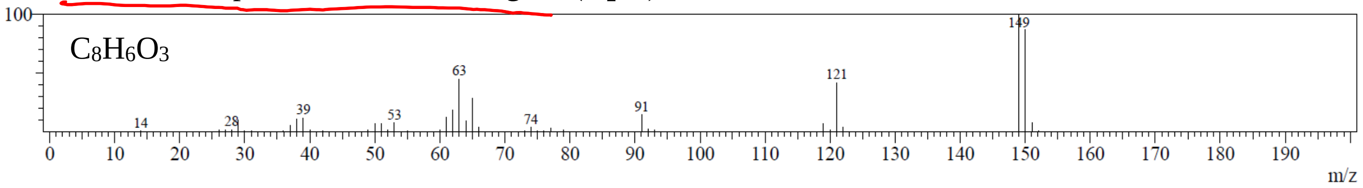
(1pt)

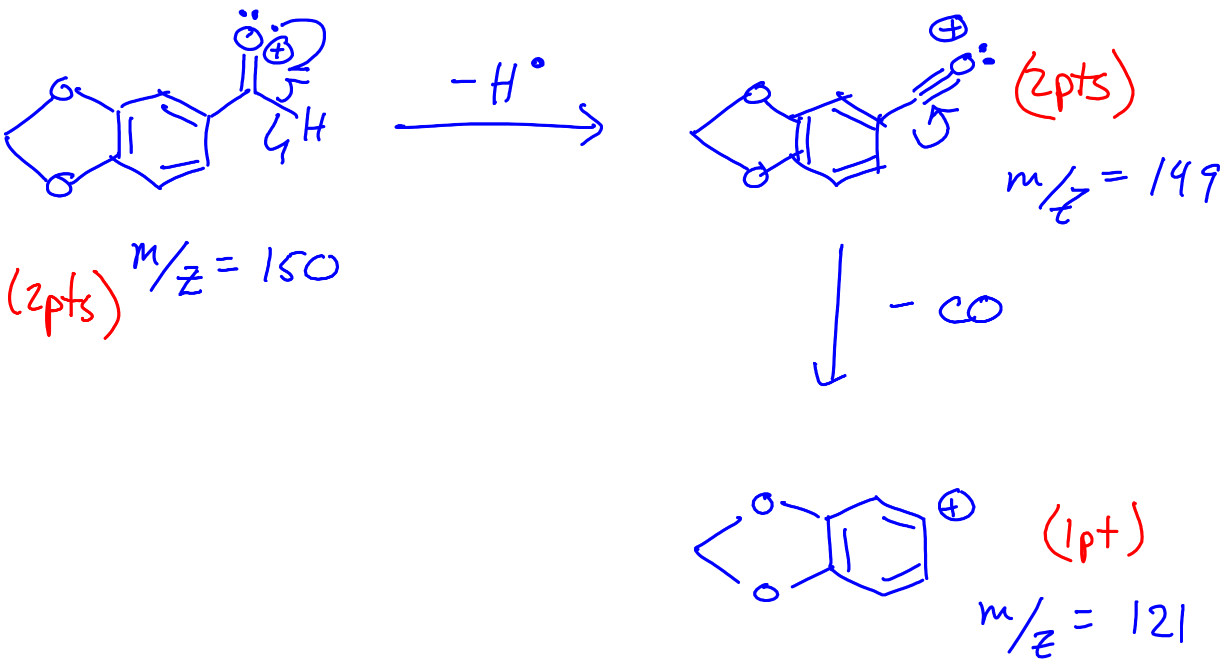
${}^{13}C(sp^2)$ (1pt)

d) Use the information from parts a – c and the ^{1}H-NMR spectrum (collected in $CDCl_3$) below to determine the structure of the molecule and assign each ^{1}H-atom. Label each set of equivalent protons using the *H*H_a, H_b, H_c, *etc.* labeling system. Draw your answer in the box on this page. **(10 pts)**

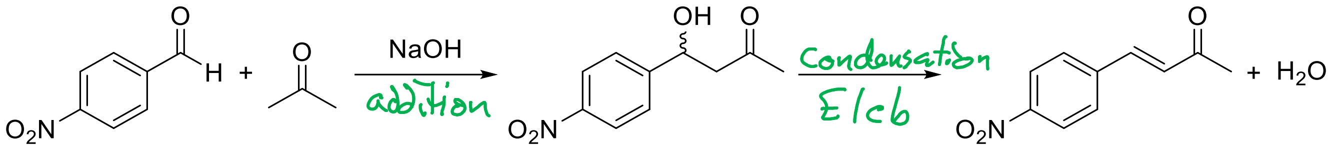


e) Confirm your structure determination by use of the EI-Mass spectrum provided below. Provide an electron pushing mechanism that accounts for the appearance of signals with *m/z* = 150, 149, and 121. Show all lone pairs and formal charges. **(5 pts)**

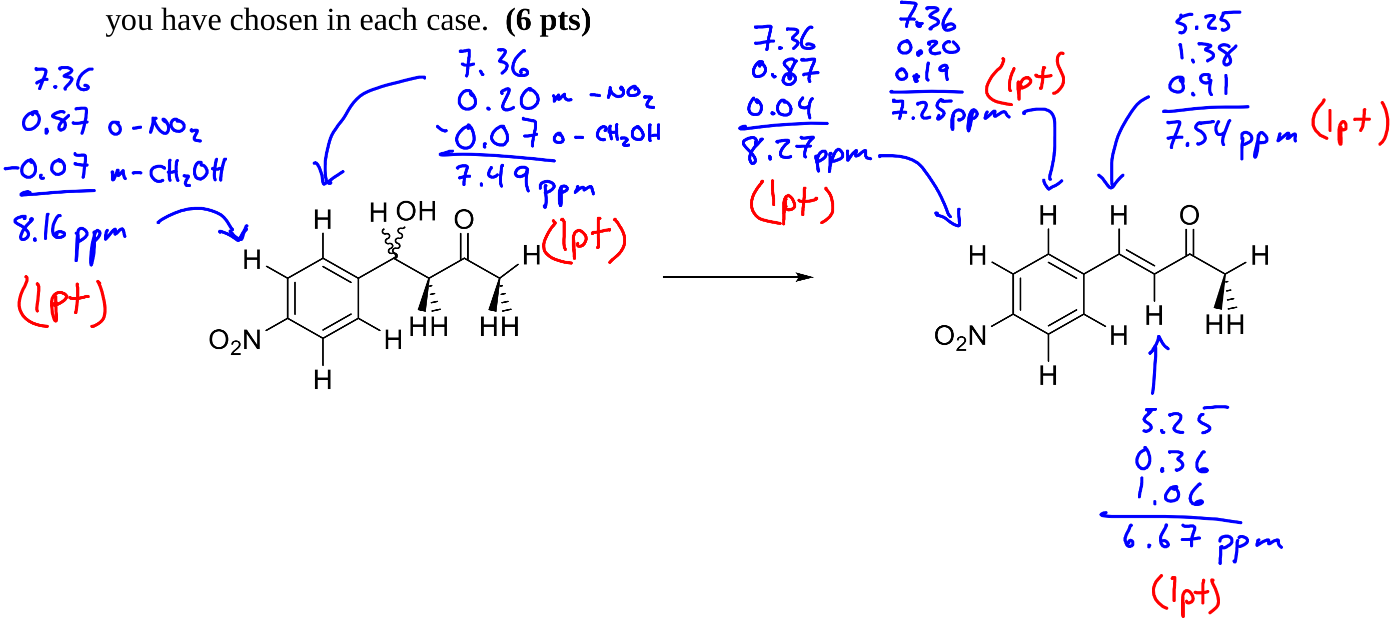




2) Aldol condensation reactions are effective methods for forming C–C bonds between electrophilic and nucleophilic C-atoms. The specific reaction below is the Claisen-Schmidt reaction which is a variant of the aldol addition/condensation involving an aldehyde and a ketone. Depending on conditions the final product can be a β-hydroxy ketone or an α,β-unsaturated ketone (*via* E1cb) as shown below. **(27 pts total)**



a) Estimate the ^{1}H-NMR chemical shifts of each ^{1}H-atom attached to an aryl or vinyl group in the two most likely products below using empirical (Curphy-Morrison) parameters. Clearly label which values you have chosen in each case. **(6 pts)**



7.36
0.87 o-NO2
-0.07 m-CH2OH
8.16 ppm
(1pt)

7.36
0.20 m -NO2
-0.07 o-CH2OH
7.49 ppm
(1pt)

7.36
0.87
0.04
8.27ppm
(1pt)

7.36
0.20
0.19
7.25ppm
(1pt)

5.25
1.38
0.91
7.54 ppm
(1pt)

5.25
0.36
1.06
6.67 ppm
(1pt)

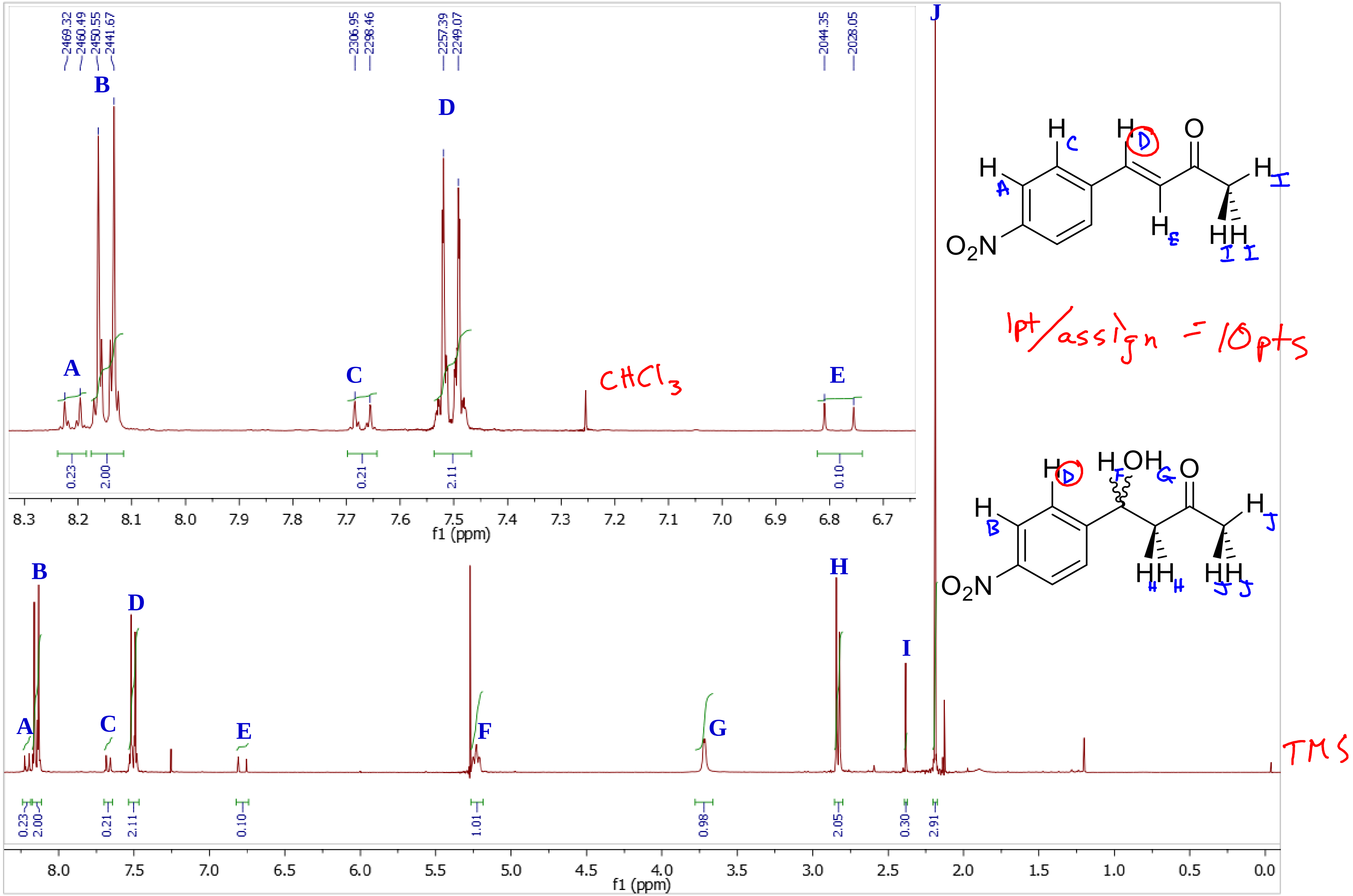
b) What spectroscopic evidence is there for the *trans* stereochemical assignment of the α,β-unsaturated carbonyl compound? Make specific reference to the spectrum of the product mixture on the subsequent pages. **(3 pts)**

The ^3J value for the observable H-atom signal is 16.3 Hz. (2pts) This is consistent with a $^3J_{trans}$ coupling value. (1pt)

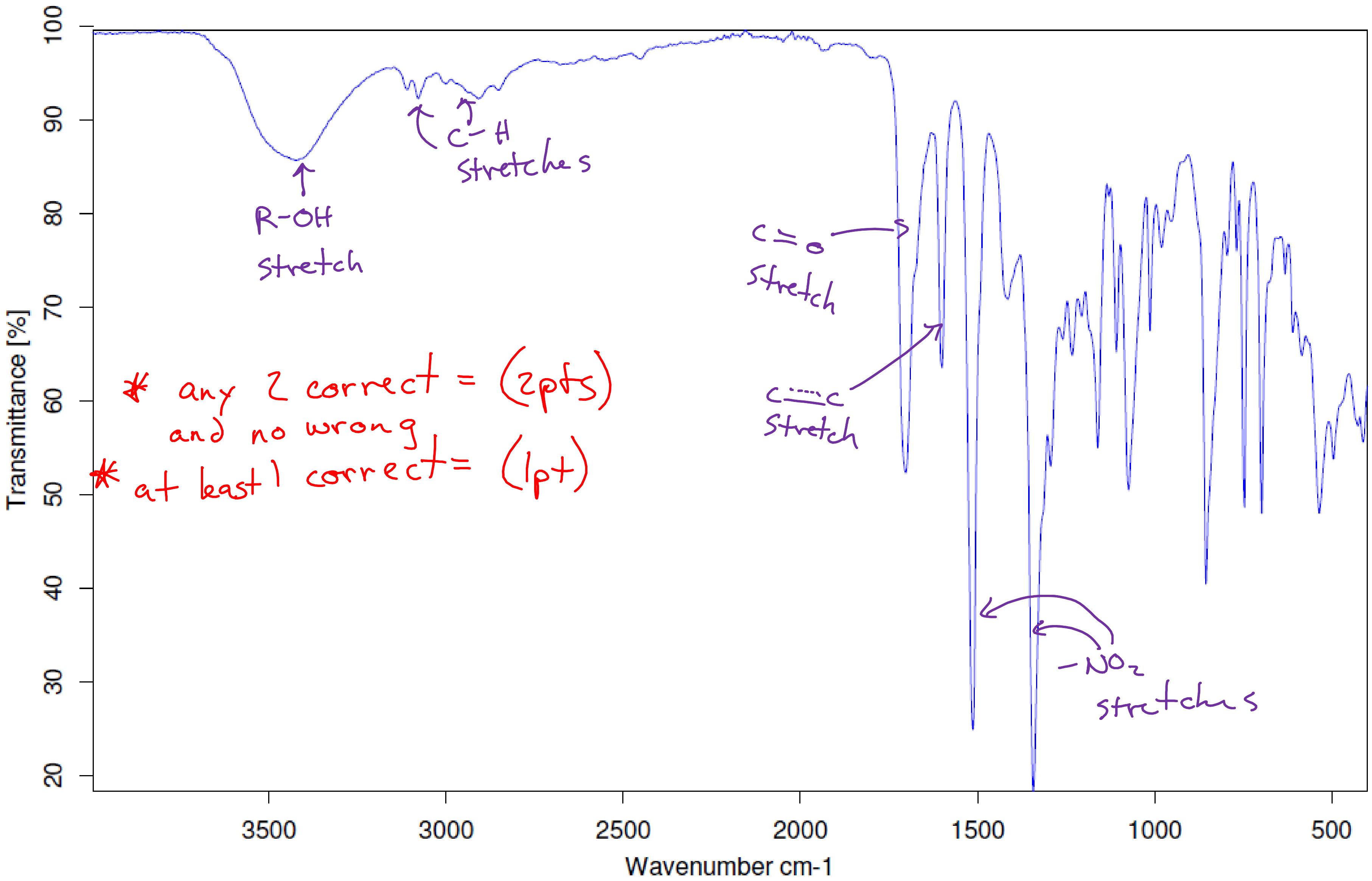
c) While two stereoisomeric β-hydroxy ketones can be formed in this reaction, only a single unique ^{1}H-NMR spectrum is generated by this mixture. Explain why these two isomers produce the same spectrum. **(3 pts)**

(2pts) The two stereoisomers are enantiomers. Absent a chiral solvent or auxilary, enantiomers have identical spectra. (1pt)

d) On the spectrum below collected in $CDCl_3$, assign all ^1H-NMR signals to their corresponding ^1H-atoms in the product(s) using the H_A through H_J labeling system given. Write all assignments on the product structure provided on the ^1H-NMR spectrum. In cases of overlapping signals, non-equivalent ^1H-atoms can be given the same label. **(10 pts)**



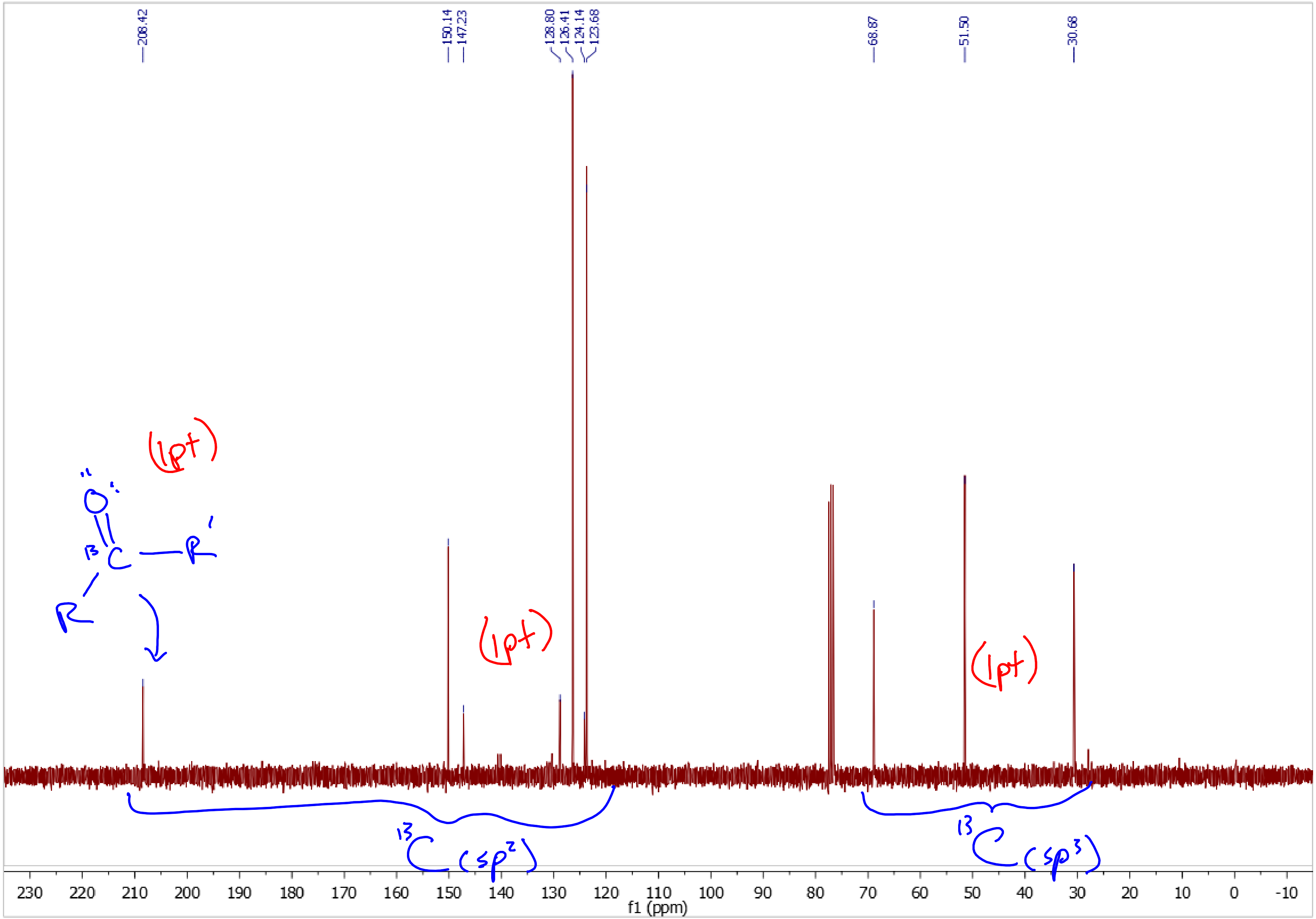
e) On the spectrum below, assign the IR signals produced by the key functional groups in the product mixture. **(2 pts)**



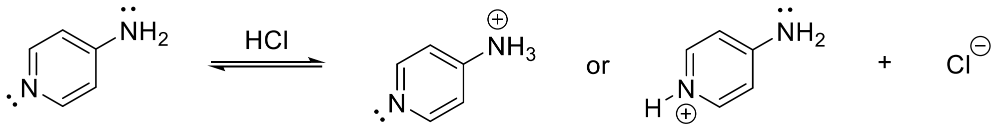
* any 2 correct = (2pts) and no wrong

* at least 1 correct = (1pt)

f) In the ^{13}C-NMR spectrum below collected in $CDCl_3$, identify the hybridization of each ^{13}C-atom and identify any key functional group signals for each peak-picked signal. **(3 pts)**



3) The aromatic heterocycle 4-aminopyridine readily reacts with HCl to produce one of two potential protonated species. With two nitrogen atoms 4-aminopyridine could potentially be protonated at two sites; however, only one protonated species is obtained from this reaction. Investigate this reaction using computational chemistry. **(25 pts)**

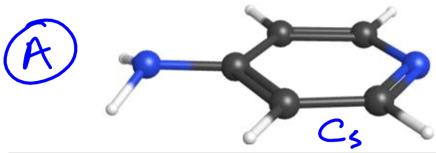


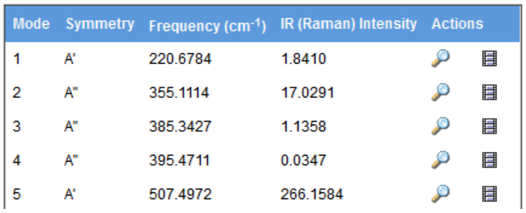
4-aminopyridine

amino-protonated 4-aminopyridine

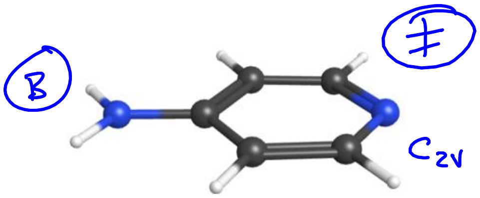
pyridyl-protonated 4-aminopyridine

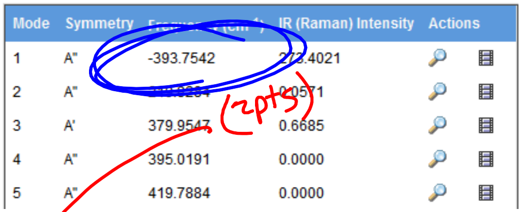
a) The conformational potential energy surface of 4-aminopyridine has two structures that can be optimized, one with C_s symmetry and one with C_{2v} symmetry. Given their structures and the information provided regarding their vibrational frequencies, depict the location of each isomer on a potential energy surface. **(4 pts)**





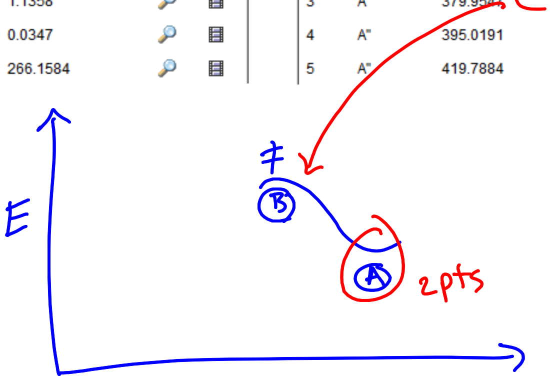
Mode	Symmetry	Frequency (cm⁻¹)	IR (Raman) Intensity	Actions	
1	A'	220.6784	1.8410	🔍	▤
2	A"	355.1114	17.0291	🔍	▤
3	A"	385.3427	1.1358	🔍	▤
4	A"	395.4711	0.0347	🔍	▤
5	A'	507.4972	266.1584	🔍	▤



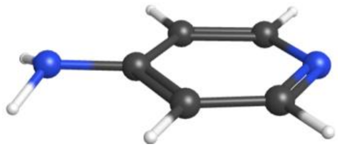


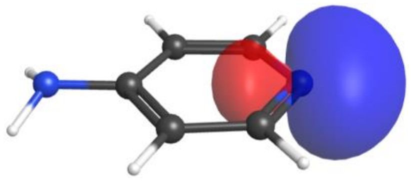
Mode	Symmetry	Frequency (cm⁻¹)	IR (Raman) Intensity	Actions	
1	A"	-393.7542	273.4021	🔍	▤
2	A"	[illegible]	0.0571	🔍	▤
3	A'	379.9547	0.6685	🔍	▤
4	A"	395.0191	0.0000	🔍	▤
5	A"	419.7884	0.0000	🔍	▤

(2pts)

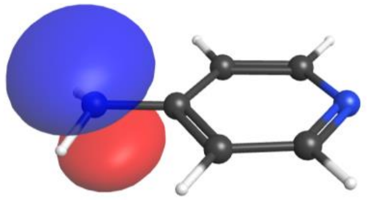


b) The two *N*-atom lone pairs are substantially different in their hybridization, orientation, and impact on the stability of 4-aminopyridine. Using the B3LYP/6-31G(d) optimized structures and the NBO output excerpt below, provide the VSEPR-predicted and the NBO-predicted hybridization of each N-atom lone pair in the sp^x notation. **(4 pts)**





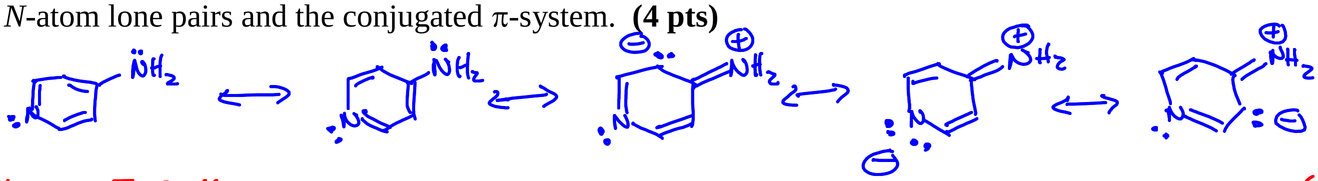
LP(1)N2
s(30.88%)p2.23(68.99%)d0.00(0.13%)



LP(1)N8
s(10.17%)p8.83(89.77%)d0.01(0.06%)

NBO-predicted hybridization	$sp^{2.2}$ (1pt)	$sp^{8.8}$ (1pt)
VSEPR-predicted hybridization	sp^2 (1pt)	sp^3 (1pt)

c) Draw a series of resonance structures for 4-aminopyridine that depict any interaction between the two *N*-atom lone pairs and the conjugated π-system. **(4 pts)**



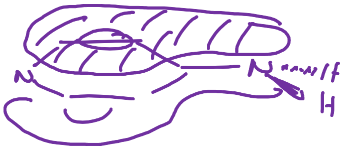
4pts = 5 fully correct structures including all lone pairs + formal charges.

3pts ≥ 3 correct

2pts ≥ 2 correct

1pt ≥ 1 correct

d) Draw a rough sketch of the π_1 molecular orbital of 4-aminopyridine. **(2 pts)**



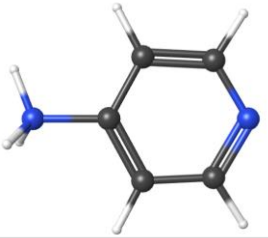
(2pts)

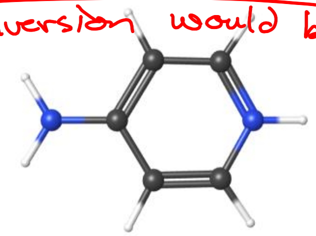
e) Basicity is a thermodynamic property, because simple H^+ transfers are fully reversible processes. Therefore the relative basicity of two atoms in the same molecule can be estimated by considering the stabilities of their protonated forms. Using the optimized structures below of each *N*-protonated-4-aminopyridine, determine the relative energy of each species in kcal/mol setting the lowest energy isomer to 0.0 kcal/mol. **(4 pts)**

627.509 kcal/mol = 1 Hartree

conversion would be provided

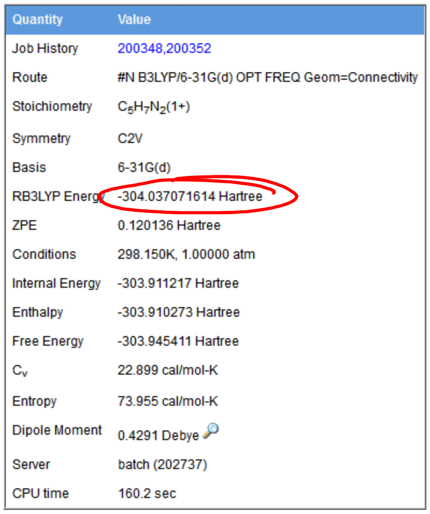
36.3 kcal/mol





0.0 kcal/mol

Quantity	Value
Job History	200348,200351,200353
Route	#N B3LYP/6-31G(d) OPT FREQ Geom=Connectivity
Stoichiometry	$C_5H_7N_2(1+)$
Symmetry	CS
Basis	6-31G(d)
RB3LYP Energy	-303.97925617 Hartree
ZPE	0.119753 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-303.853367 Hartree
Enthalpy	-303.852423 Hartree
Free Energy	-303.890280 Hartree
C_v	22.295 cal/mol-K
Entropy	79.677 cal/mol-K
Dipole Moment	9.6197 Debye
Server	batch (202738)
CPU time	351.4 sec



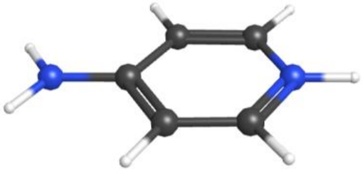
Quantity	Value
Job History	200348,200352
Route	#N B3LYP/6-31G(d) OPT FREQ Geom=Connectivity
Stoichiometry	$C_5H_7N_2(1+)$
Symmetry	C2V
Basis	6-31G(d)
RB3LYP Energy	-304.037071614 Hartree
ZPE	0.120136 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-303.911217 Hartree
Enthalpy	-303.910273 Hartree
Free Energy	-303.945411 Hartree
C_v	22.899 cal/mol-K
Entropy	73.955 cal/mol-K
Dipole Moment	0.4291 Debye
Server	batch (202737)
CPU time	160.2 sec

f) Identify which *N*-atom is most basic. Rationalize its relative basicity based upon the computational data. **(4 pts)**

(2pts)

The most basic N-atom is the N-atom in the pyridine ring. The protonation of that N-atom does not break the π conjugation and allows the π system to donate (2pts) electron density to help stabilize the electron deficient N-atom.

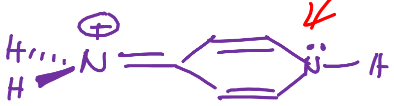
g) When the pyridyl *N*-atom is protonated in 4-aminopyridine, the amino group at the other end of the molecule flattens. Rationalize this structure change with appropriate chemical concepts and depictions. **(3 pts)**



(2pts)

The amino N-atom becomes more electron-donating, which requires greater N-atom p-orbital character in its lone pair.

(1pt)



← more important

CHEM 344 Fall 2016 Spectroscopy and WebMO Exam (75 pts)

Name:

TA Name:

Problem 1	**Problem 2**	**Problem 3**
a) ______ /2	**a) ______ /6**	**a) ______ /4**
b) ______ /3	**b) ______ /3**	**b) ______ /4**
c) ______ /3	**c) ______ /3**	**c) ______ /4**
d) ______ /10	**d) ______ /10**	**d) ______ /2**
e) ______ /5	**e) ______ /2**	**e) ______ /4**
	f) ______ /3	**f) ______ /4**
		g) ______ /3
Total______ /23	**Total______ /27**	**Total______ /25**

Total = ______ /75

Double check = ______ /75