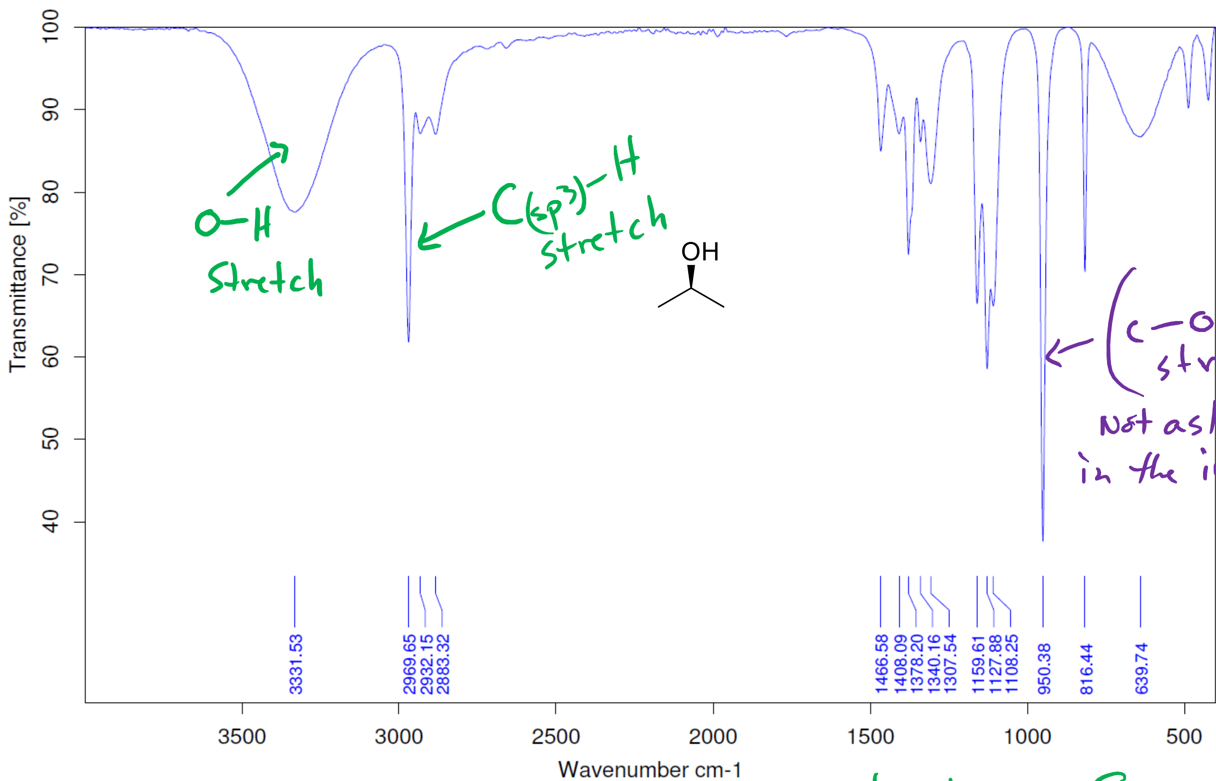
Chemistry 344: Spectroscopy and Spectrometry Problem Set 1

Name (print): ______________________________________

TA Name (print): ___________________________________

most important region for Chem344

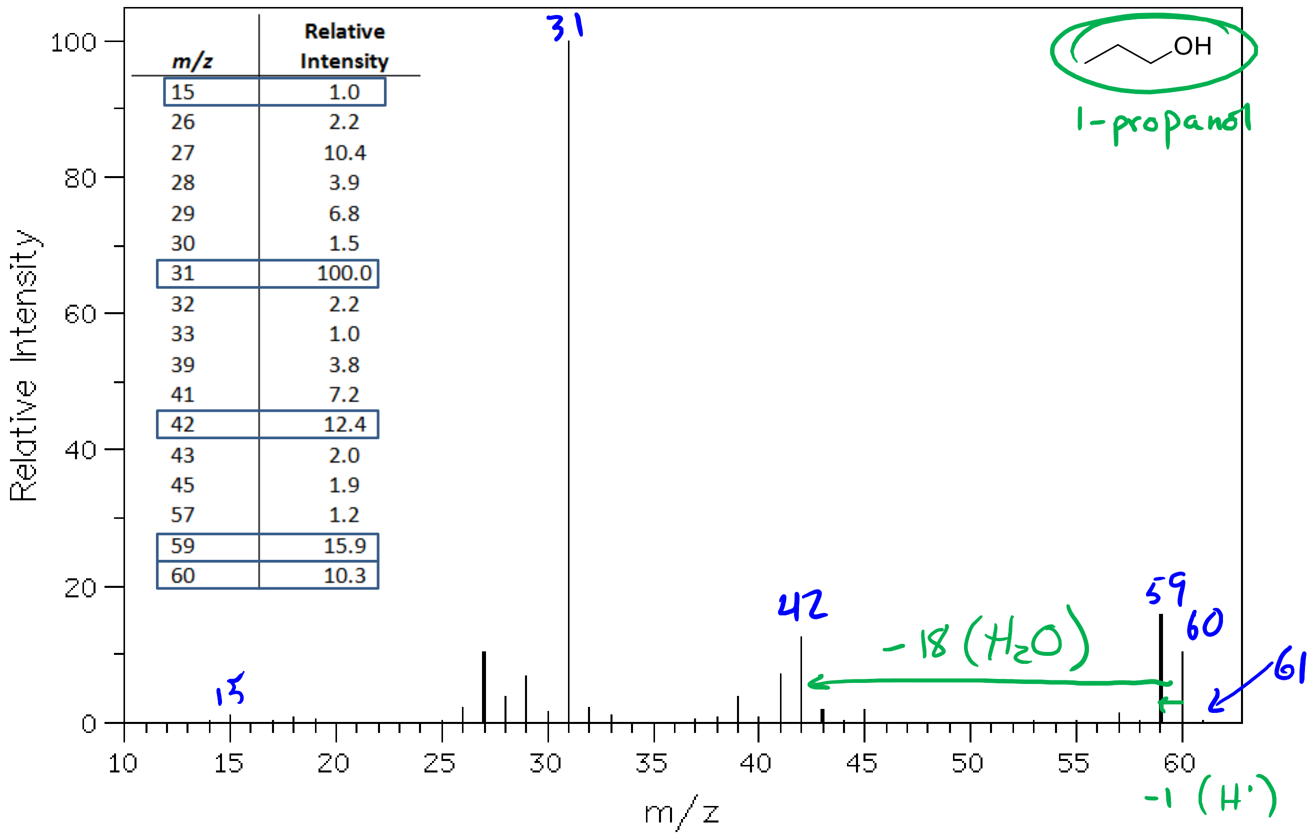
I. The IR spectrum below is for isopropanol; identify any useful IR absorptions >1500 cm^{-1}. Based upon the spectrum, comment on whether you expect that it was a pure sample or diluted in a different solvent.



Since the O–H stretch is broad and at lower freq. (cm^{-1}), the sample has sufficient concentration to be H-bonded. No evidence of a free O–H stretch is present as would be expected in the gas-phase or dilute solution.

See Section 12.4D in Loudon.

II. Using the mass spectrum of 1-propanol shown below, answer the questions that follow about its fragmentation. Remember that you are not expected to interpret all signals in a mass spectrum.

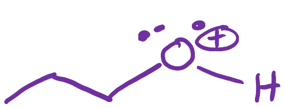


m/z	Relative Intensity
15	1.0
26	2.2
27	10.4
28	3.9
29	6.8
30	1.5
31	100.0
32	2.2
33	1.0
39	3.8
41	7.2
42	12.4
43	2.0
45	1.9
57	1.2
59	15.9
60	10.3

A. Why does the peak at *m/z* = 15 have such a low relative intensity?

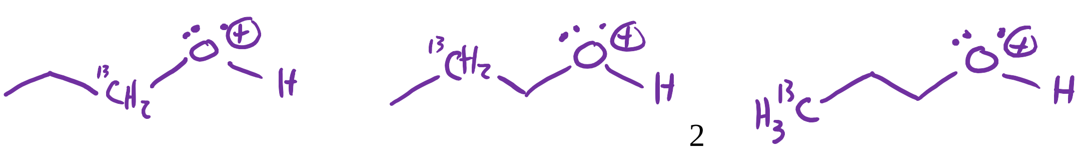
Methyl cation ($^{\oplus}CH_3$) is not a stable fragment relative to its parent ion(s). The central C-atom is very electron deficient.

B. Draw a valid resonance structure of the molecular ion (*m/z* = 60). Draw a molecular ion responsible for the small peak at *m/z* = 61.

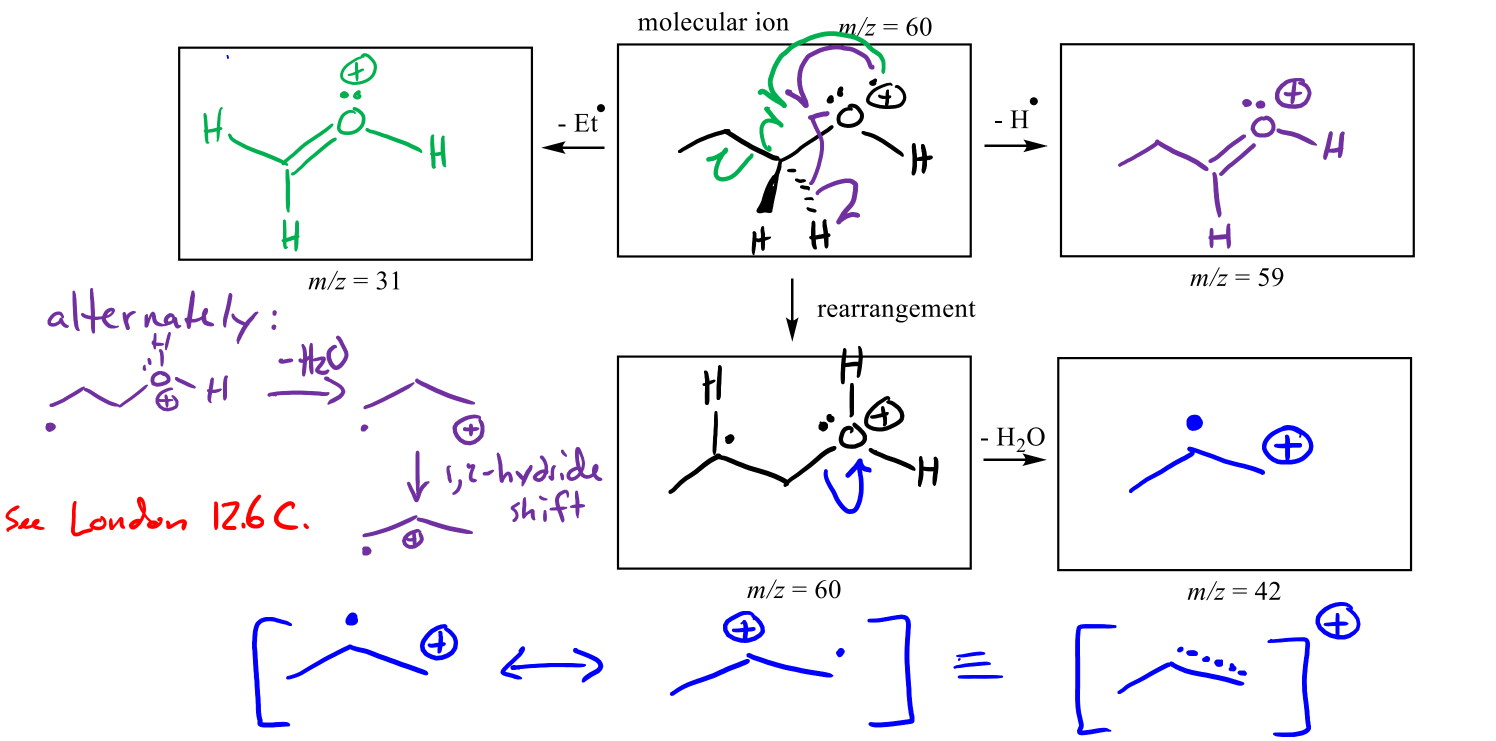


m/z = 60

The small peak at m/z = 61 is due to heavy isotope substitution, mostly ^{13}C sustitution at natural abundance (~1.1%).



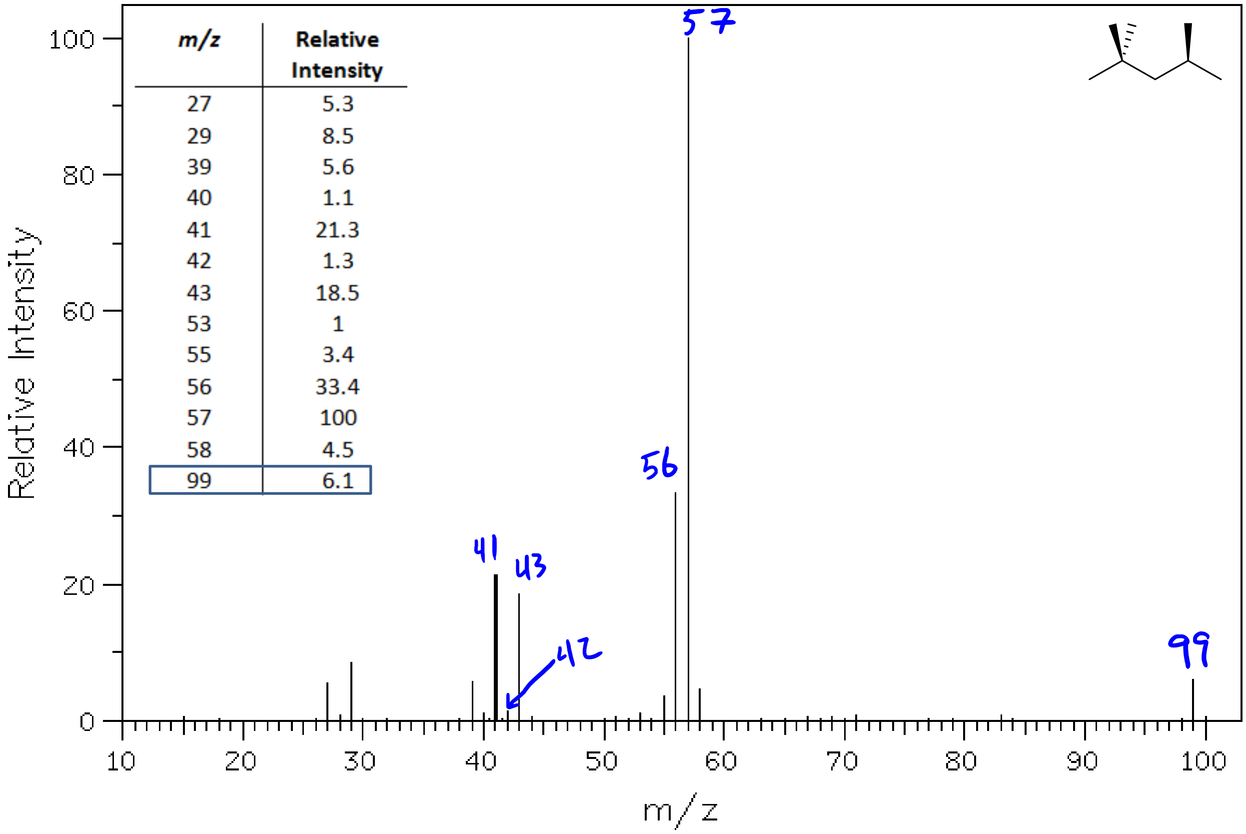
C. In fragmentations of cations and radical cations, a single molecular (parent) ion can give rise to several fragments. Provide fragmentation mechanisms from the molecular ion (m/z = 60) that will rationalize the formation of ions with values of m/z = 59, 42, and 31. For clarity, it may help to show each fragmentation in a different color



D. What can you conclude about the formation and decomposition of the ion responsible for the signal at m/z = 31?

The signal at m/z = 31 is the base peak and its intensity is automatically set to 100%. The ion(s) responsible for the base peak must form easily/rapidly and decompose relatively slowly for a large population of m/z = 31 particles to arrive at the detector.

III. Using the mass spectrum of 2,2,4-trimethylpentane (isooctane, C_8H_{18}) shown below, answer the questions that follow about its fragmentation.



m/z	Relative Intensity
27	5.3
29	8.5
39	5.6
40	1.1
41	21.3
42	1.3
43	18.5
53	1
55	3.4
56	33.4
57	100
58	4.5
99	6.1

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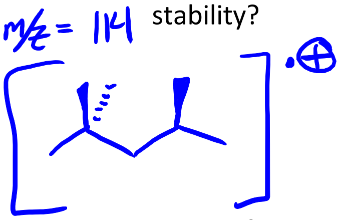
See Loudon Study Problem 12.4.

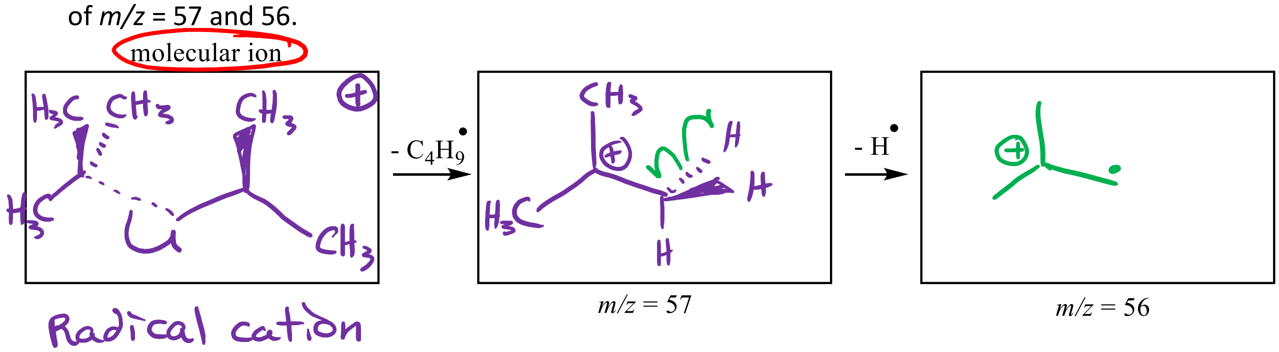
A. In this case, the molecular ion is of such a low intensity it is not detected. Draw the molecular ion of 2,2,4-trimethylpentane and determine its *m/z* value. What does the low intensity indicate about its stability?

m/z = 114



The molecular ion decomposes so rapidly that very, very little of it arrives at the detector. All σ bonds are weakened!!!

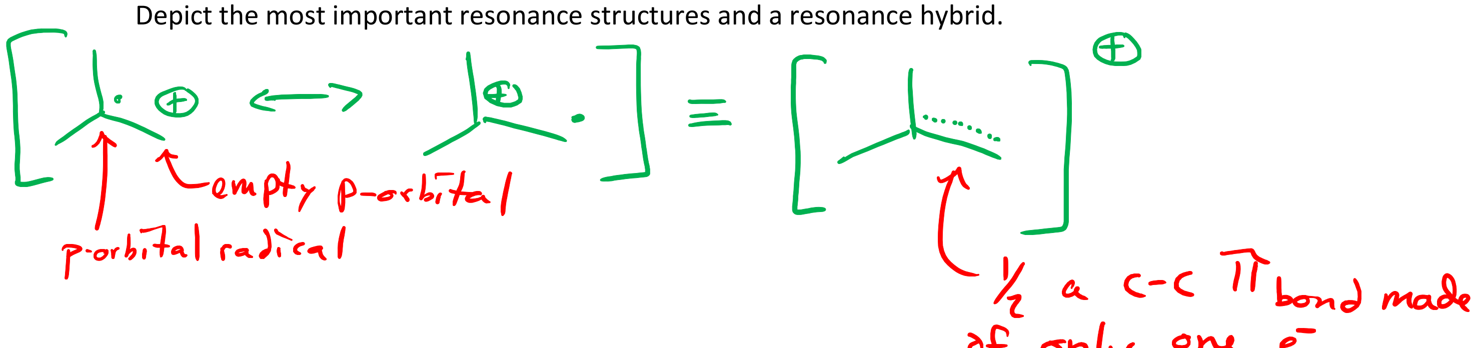
B. Draw a fragmentation mechanism that explains how the molecular ion can produce ions with values of *m/z* = 57 and 56.



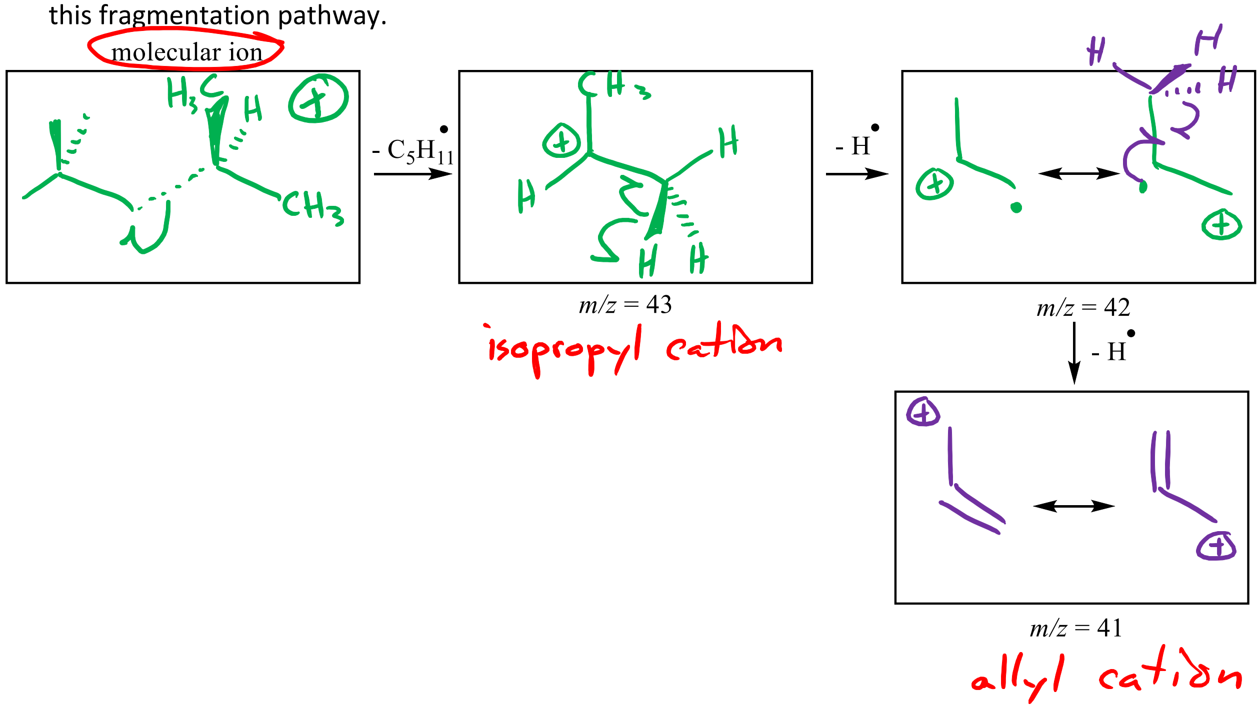
Radical cation

...... ½ σ bond is made of one e⁻ only.

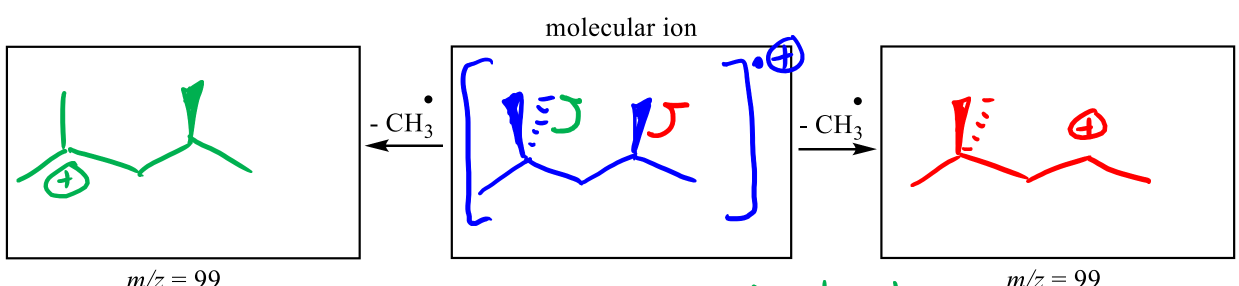
C. The ion responsible for the signal at m/z = 56 can be represented by a set of resonance structures. Depict the most important resonance structures and a resonance hybrid.



D. An alternate fragmentation mechanism from the molecular ion can be used to rationalize the production of ions with values of m/z = 43, 42, and 41. Provide an electron pushing mechanism for this fragmentation pathway.

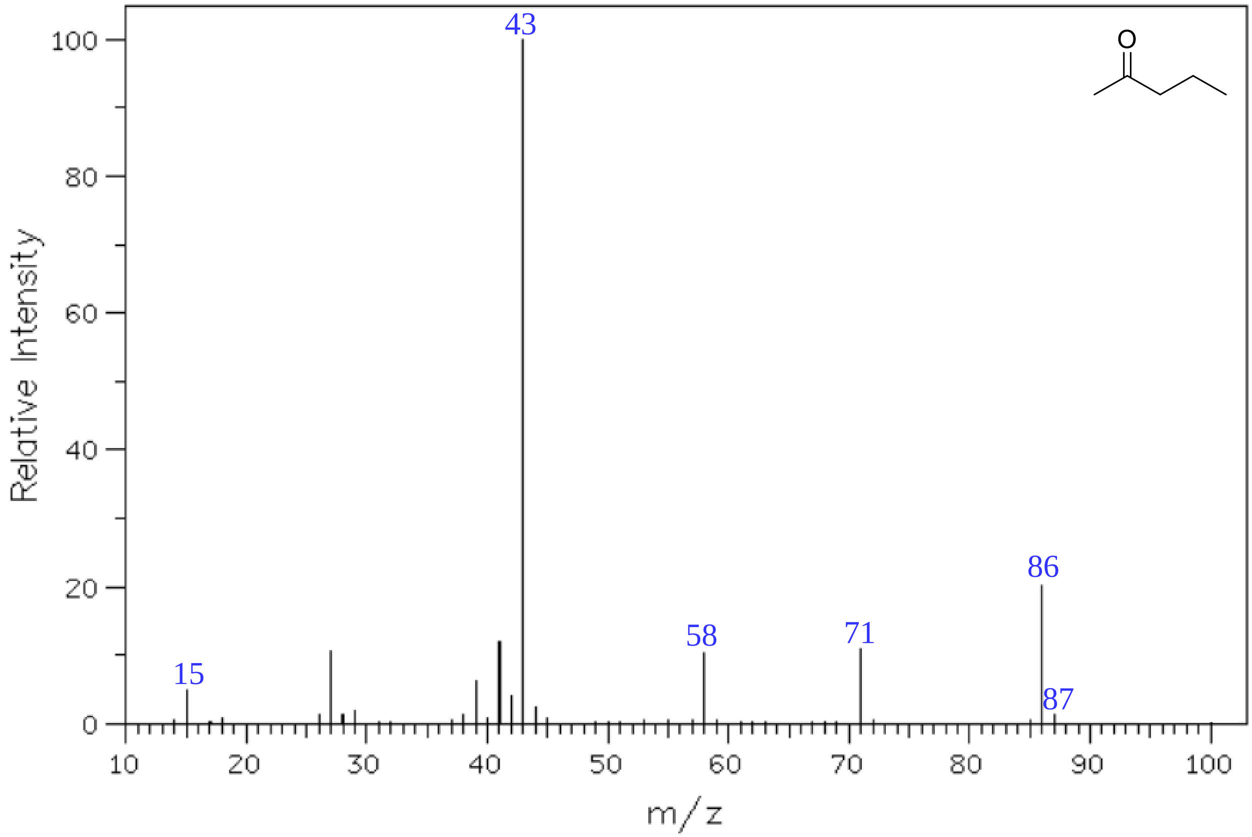


E. Two separate fragmentations of the molecular ion can lead to ions with m/z values of 99; provide them below.



The tertiary cation is much more stable than the secondary cation, which makes the tertiary cation MUCH more abundant. Also, there is a 3/2 statistical preference for the 3° cation due to the greater number of available methyl groups.

IV. Using the mass spectrum of 2-pentanone ($C_5H_{10}O$) shown below, answer the questions that follow about its fragmentation.



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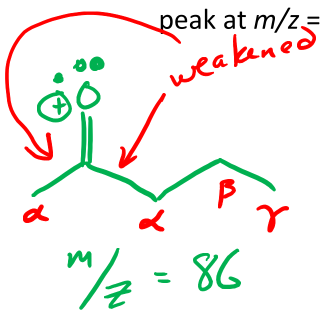
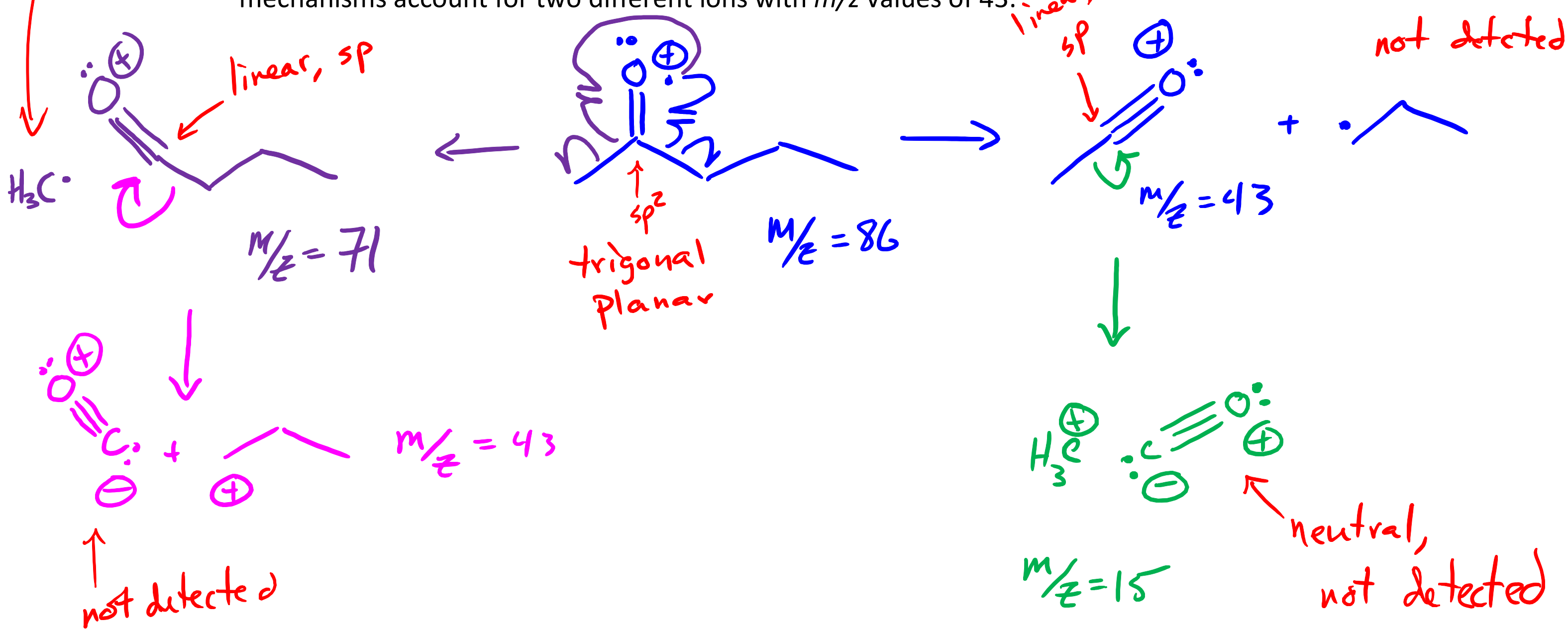
A. Draw a valid resonance structure of the molecular ion (*m/z* = 86). Explain the source of the small peak at *m/z* = 87.



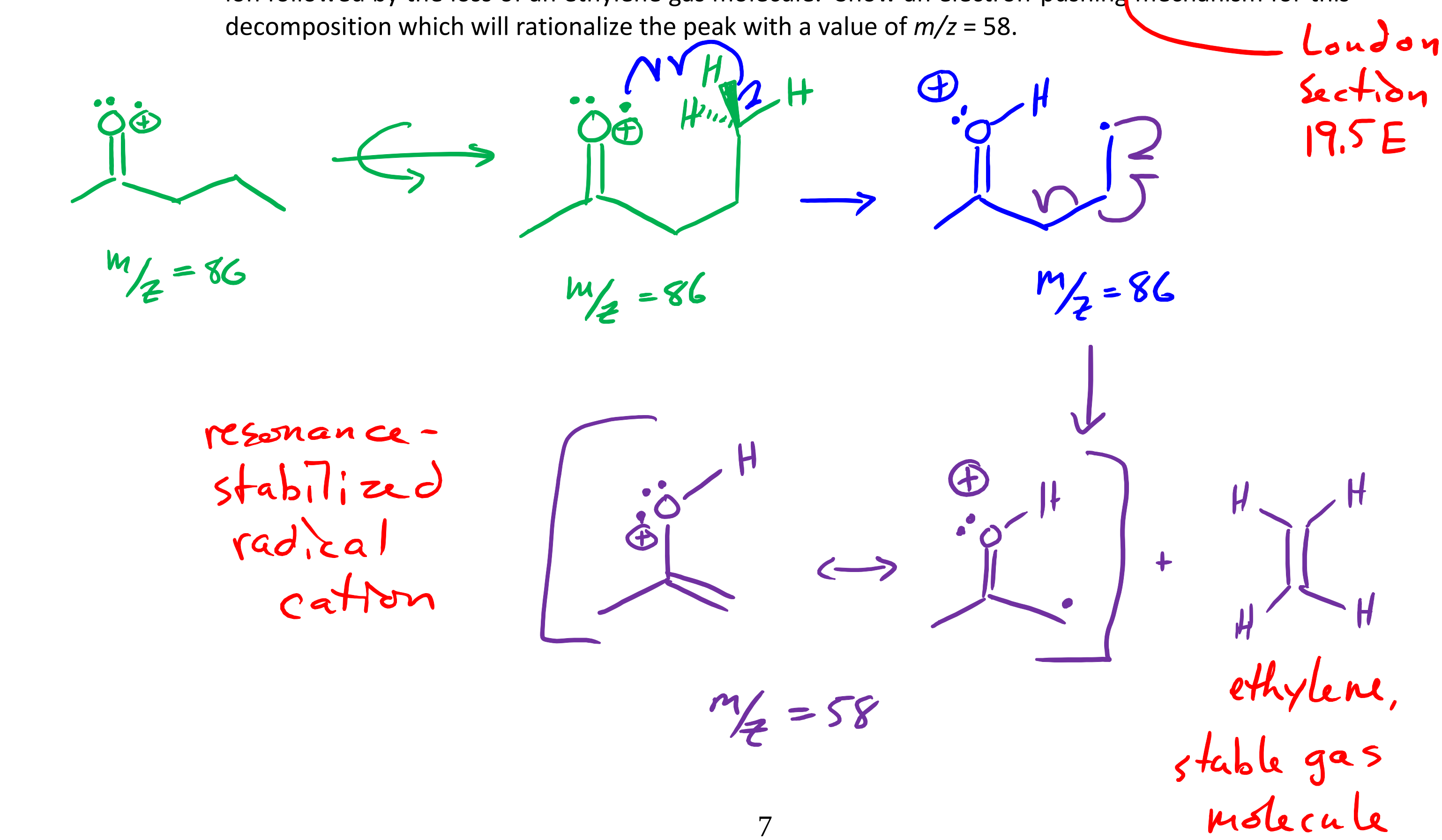
The peak at m/z = 87 is mostly due to the naturally-occurring ^{13}C-atom substitution.

Carbonyl-containing radical cations have weakened σ-bonds between the carbonyl C-atom and their α-substituents (see London Section 19.5E)

B. Important decomposition pathways for the molecular ion of carbonyl-containing compounds such as 2-pentanone involve α-cleavage. Beginning with both viable α-cleavage decomposition pathways, draw fragmentation mechanisms that lead to ions with *m/z* values of 71, 43, 15. Make sure your mechanisms account for two different ions with *m/z* values of 43.

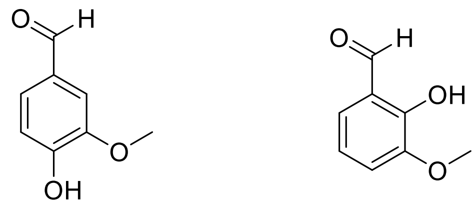


C. The other major decomposition pathway arises from a McLafferty rearrangement of the molecular ion followed by the loss of an ethylene gas molecule. Show an electron-pushing mechanism for this decomposition which will rationalize the peak with a value of *m/z* = 58.

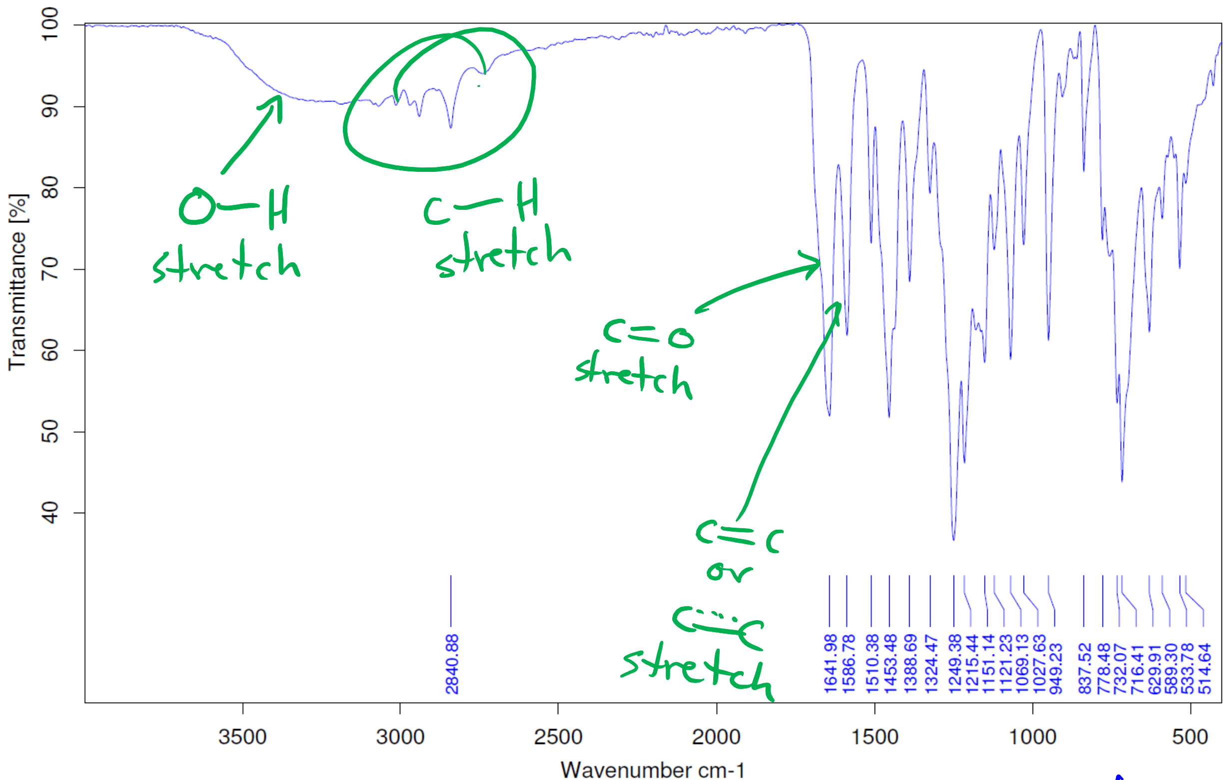


V. A mixture of regioisomers *o*-vanillin and vanillin ($C_8H_8O_3$) were analyzed by IR and GC-MS. Analyze the spectra below and answer the accompanying questions.

vanillin *o*-vanillin

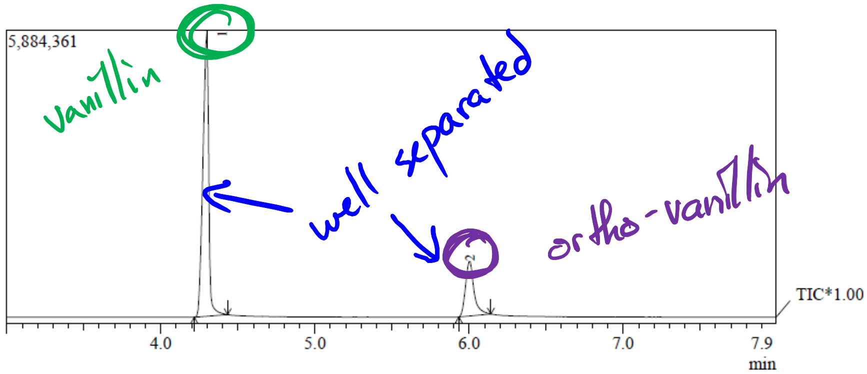


A. Identify any useful IR absorptions that can help identify this sample as a mixture of *o*-vanillin and vanillin. Is it possible to use the IR of the mixture to identify each component?



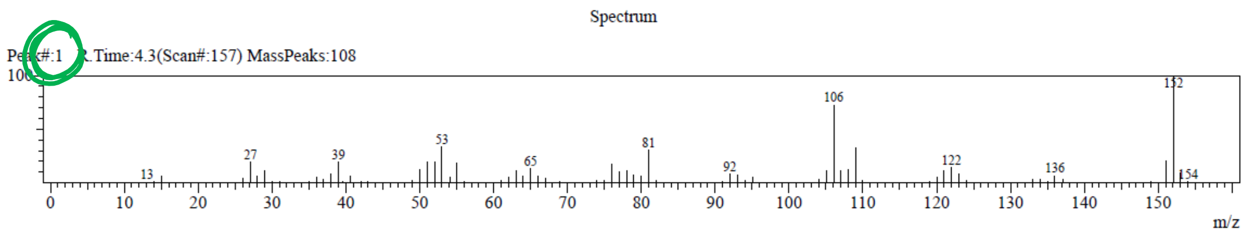
The molecules are too similar to be easily distinguished by IR spectroscopy without a detailed study of the fingerprint region.

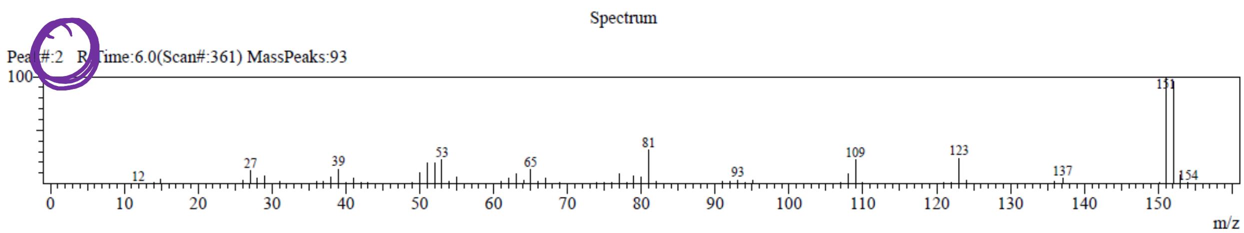
B. Use the GC-Mass spectrum of the mixture provided below to determine the ratio of vanillin to *o*-vanillin. The most intense signals of vanillin are *m/z* values of 152 and 106, while the most intense signals of *o*-vanillin are *m/z* values of 152 and 151.



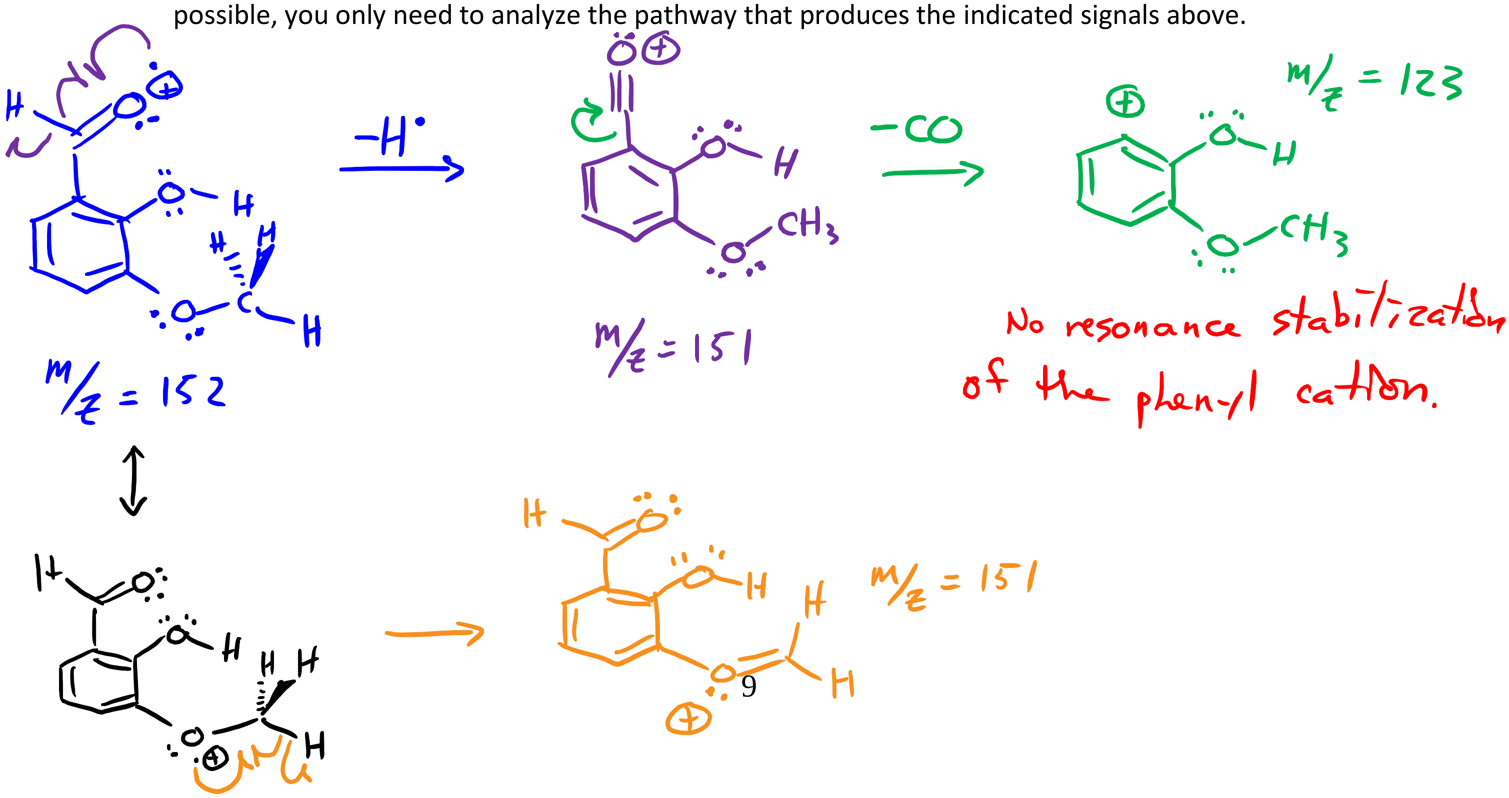
Peak Report TIC

Peak#	R.Time	Area	Area%
1	4.297	14914128	77.91
2	6.003	4228392	22.09
		19142520	100.00

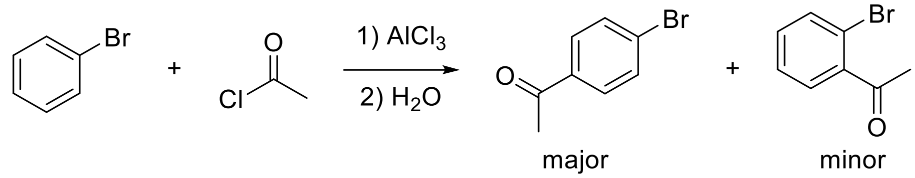




C. Provide an electron-pushing mechanism for the fragmentation of *o*-vanillin that can rationalize the presence of ions with *m/z* values of 152, 151, and 123. There are many other fragmentations possible, you only need to analyze the pathway that produces the indicated signals above.



VI. Use the GC-Mass spectrum of the student product obtained from the Friedel-Crafts acylation of bromobenzene (shown on page 12) to answer the following questions. ***Only signals with intensity greater than 15% relative intensity to the base peak are shown for clarity***.

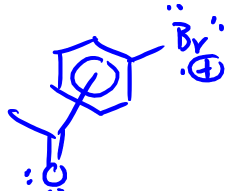


A. Which of the peaks (1 – 3) detected in the GC are the reactant(s)? Which of the peak(s) in the GC are the product(s)?

Peak 1 = Reactant

$m/z = 156, 158$

Peaks 2 + 3 = products



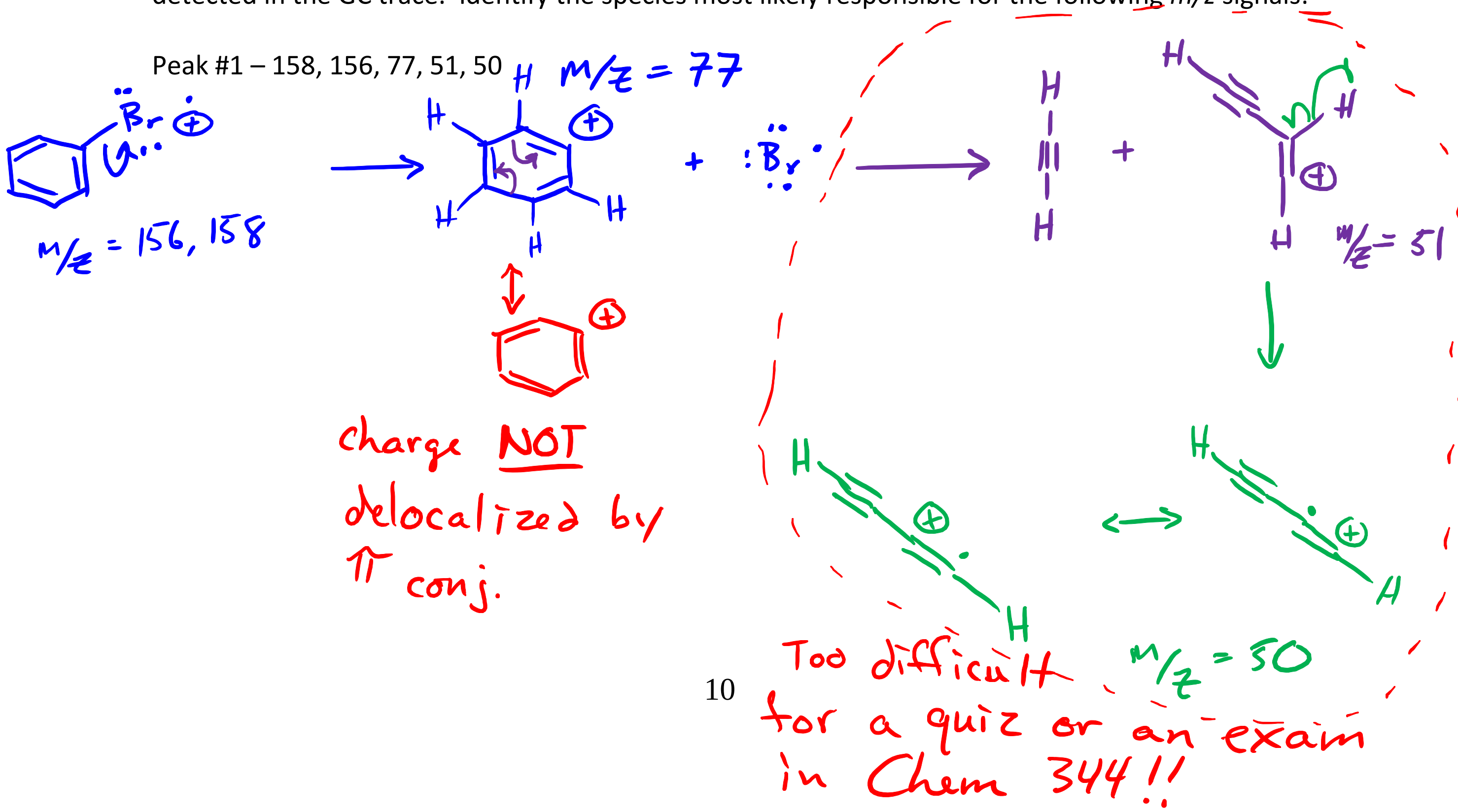
$m/z = 198, 200$

B. In any of the mass spectra provided for GC peaks 1 – 3, how can you tell which ions contain bromine?

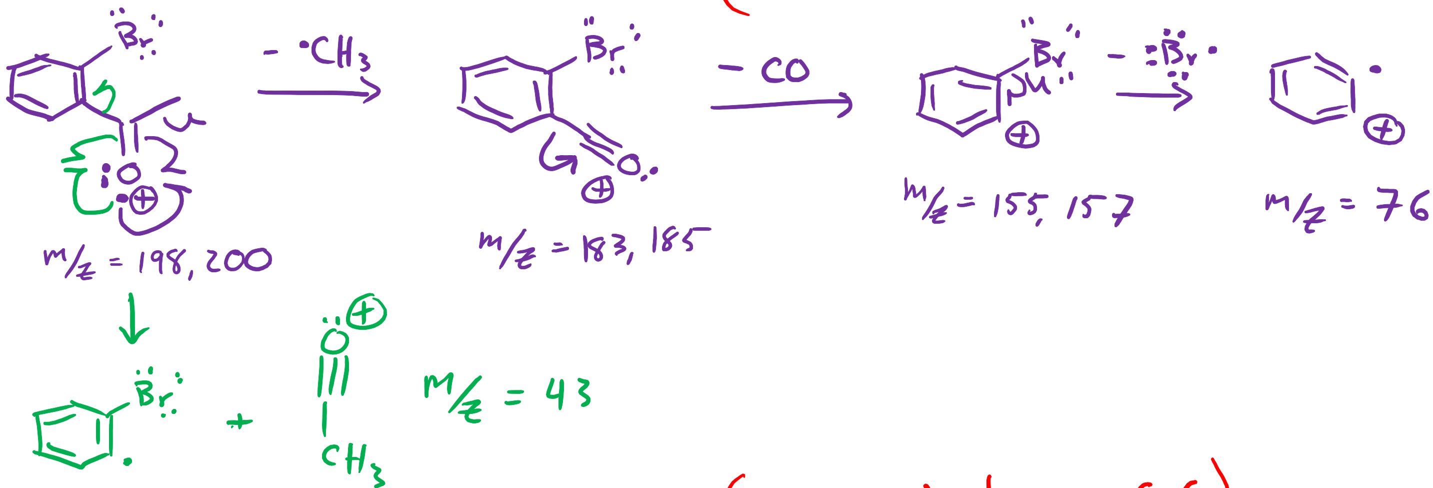
$m/z \geq 79, 81$ with approximately 1:1 intensity separated by 2 m/z units. This pattern occurs due to the natural abundances of ^{79}Br + ^{81}Br.

C. Provide a fragmentation mechanism that will account for the signals listed below for each molecule detected in the GC trace. Identify the species most likely responsible for the following *m/z* signals:

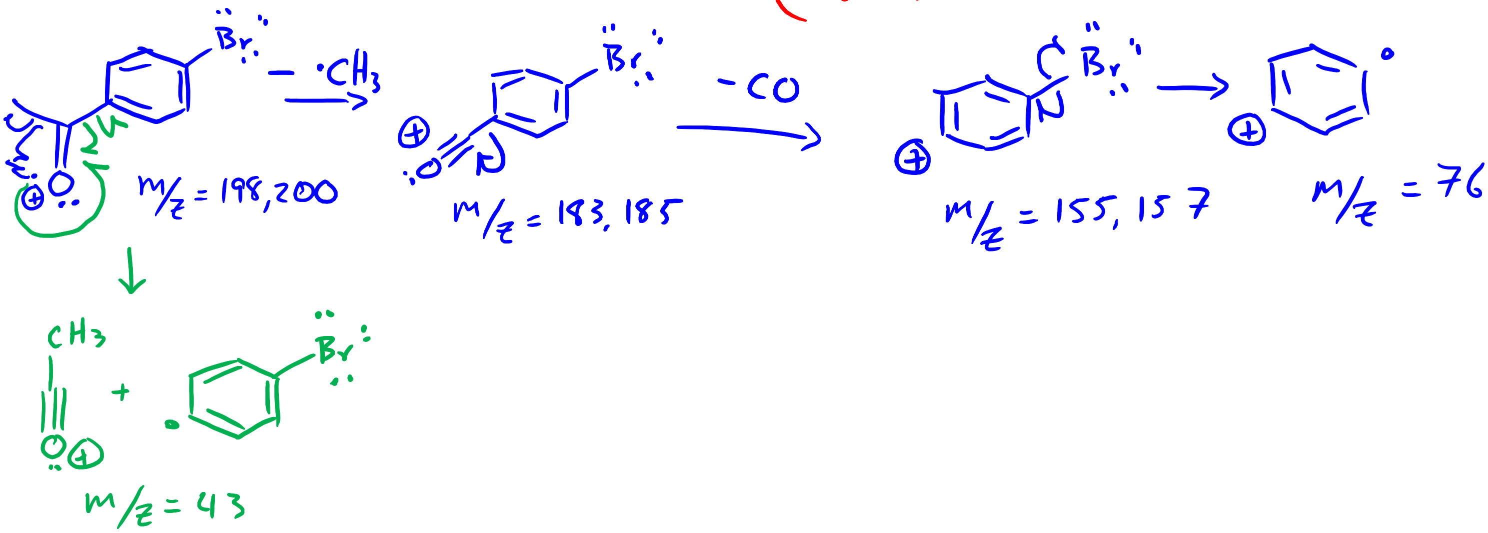
Peak #1 – 158, 156, 77, 51, 50



Peak #2 – 200, 198, 185, 183, 157, 155, 76, 43 (minor product, see GC)



Peak #3 – 200, 198, 185, 183, 157, 155, 76, 43 (major product, see GC)



D. What is the conversion percentage from reactant to the total products by GC?

A total of ≈85.27% of the sample is due to the major and minor product. Approximately, 14.73% is the starting material.

E. What is the ratio of the major to minor product by GC?

$$\frac{82.77\%\ \text{Major}}{2.50\%\ \text{Minor}} = \frac{33.1\ \text{major}}{1\ \text{minor}}$$ or 33.1 : 1 major : minor

Peak Report TIC

Peak#	R.Time	Area	Area%
1	2.488	842786	14.73
2	6.345	143248	2.50
3	8.081	4736553	82.77
		5722587	100.00