Beyond Labz: Introduction to Mass Spectrometry

Purpose: In this virtual lab experiment, you will explore the use of infrared spectroscopy and mass spectrometry to analyze the following organic compounds: butyraldehyde, acetophenone, 2-chloro-2-methylpropane, and diethyl ether.

Introduction: You will use the Beyond Labz virtual platform to record the IR spectrum and the mass spectrum for butyraldehyde, acetophenone, 2-chloro-2-methylpropane, and diethyl ether. You will then analyze the spectra by identifying the key absorption peaks in the IR spectrum and identifying the key fragments in the mass spectrum for each of the five compounds.

IR spectroscopy:

We can identify functional groups using infrared (IR) spectroscopy. IR radiation is in the same range of frequencies (4000-600 cm^{-1}) as the stretching and bending vibrations of bonds in organic molecules. When the frequency of the radiation exactly matches the frequency of the bond, the molecule absorbs energy, resulting in an absorption peak in the IR spectrum. Most functional groups show absorption bands in the region of 4000-1400 cm^{-1}.

See the handouts: Characteristic Infrared Absorption Peaks and IR Tutorial UCLA for help identifying the peaks.

Mass Spectrometry:

We can get some information about the structure of a molecule from examining its mass spectrum. In a mass spectrometer, a sample is vaporized, and then ionized. The most common method of ionization is electron ionization (EI). In EI the vaporized compound is bombarded with a beam of high energy electrons (typically around 70 eV). When the electron beam first collides with the vaporized compound the compound loses one electron. This initially formed radical cation, the **molecular ion** or M^+, has the same mass as the starting compound and so can be used to determine the molecular weight. The signals that are displayed in the mass spectrum are reported as their **mass-to-charge ratio (*m/z*)**. In EI mass spectrometry the charge is typically +1 so we can read this number as the mass of the ion. The radical cations formed inside the mass spectrometer are unstable and often fragment before reaching the detector. Only positively charged species are recorded in the mass spectrum. The positively charged fragments that reach the detector in the greatest abundance tend to be the fragments that are the most stable and/or are formed in the greatest quantity. The most abundant fragment is described as the **base peak**.

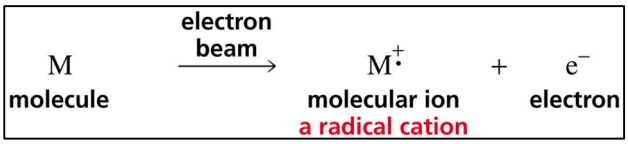


Figure 4.1 Formation of the molecular ion. (From Organic Chemistry by Bruice, 8th Ed.)

Functional groups tend to fragment in somewhat of predictable ways to form stabilized cations. In this virtual lab you will be examining the mass spectra of carbonyl-containing molecules, an alkyl halide, and an ether.

Both butyraldehyde and acetophenone contain a carbonyl (C=O). A common fragmentation pathway for carbonyl-containing molecules is alpha-cleavage. The bond between the carbonyl carbon and the adjacent group cleaves to give a resonance-stabilized acylium ion.

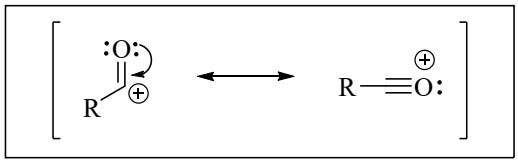


Figure 4.2 Resonance-stabilized acylium ion.

The figure below shows the two possible alpha-cleavage pathways for 2-pentanone. The loss of either the propyl group (M – 43) or the methyl group (M – 15) leads to a resonance-stabilized acylium ion.

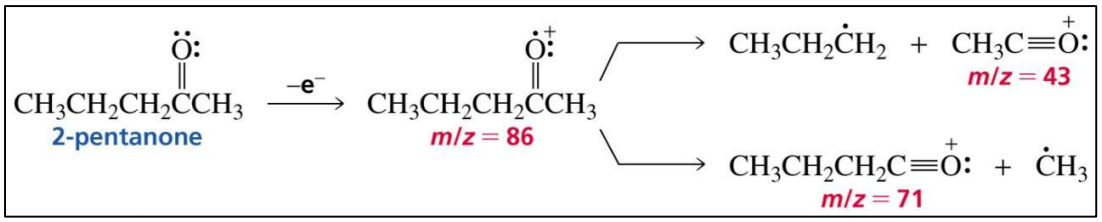


Figure 4.3 Alpha-cleavage of carbonyl containing compounds.
(From Organic Chemistry by Bruice, 8th Ed.)

The 2-chloro-2-methylpropane contains a chlorine atom. Both chlorine and bromine are elements that have a high percentage of a naturally occurring isotope that is two mass units heavier than the most abundant isotope. Naturally occurring chlorine is 75.77% chlorine-35 and 24.23% chlorine-37. In the mass spectrum, any fragment that contains one chlorine atom (^{35}Cl) also has a peak 2 mass units higher that is ⅓ its height (that contains ^{37}Cl). Naturally occurring bromine has two isotopes that are nearly equal in abundance: 50.69% bromine-79 and 49.31% bromine-81. In the mass spectrum, any fragment that contains one bromine atom (^{79}Br) also has a peak 2 mass units higher that is equal in height (that contains ^{81}Br).

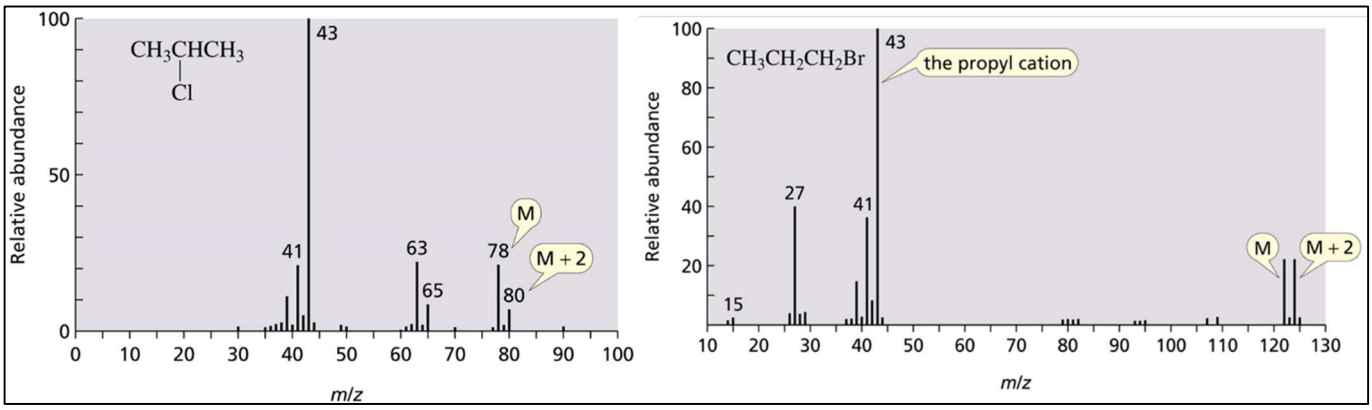


Figure 4.4 M+2 peaks for molecular ions containing chlorine (left) and bromine (right).
(From Organic Chemistry by Bruice, 8th Ed.)

Alkyl halides and ethers tend to undergo two major fragmentation patterns in EI mass spectrometry. They tend to undergo heterolytic cleavage of the carbon-halogen or carbon-oxygen bond, and they tend to undergo alpha-cleavage to form cations that are resonance-stabilized.

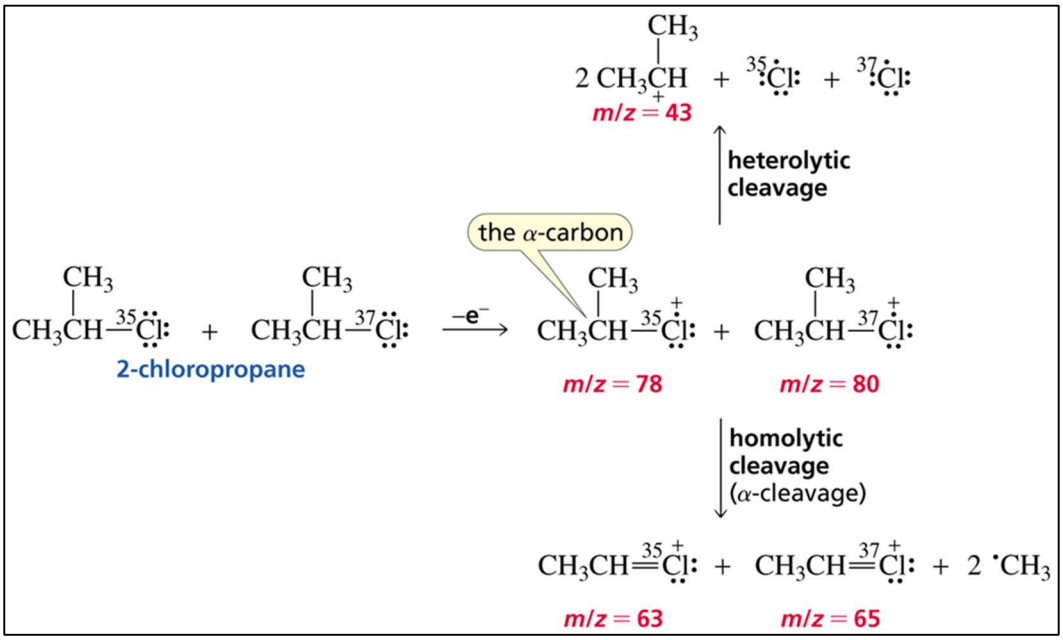


Figure 4.5 Common fragmentation patterns for alkyl halides.
(From Organic Chemistry by Bruice, 8th Ed.)

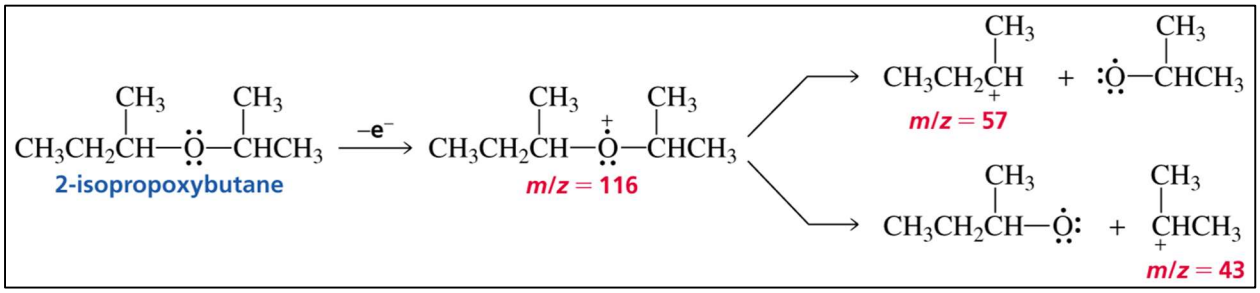


Figure 4.6 Common fragmentation patterns for ethers.
(From Organic Chemistry by Bruice, 8th Ed.)

Figure 4.7 The qualitative analysis virtual lab.

Virtual Lab Instructions (video instructions also available).

1. Open the organic chemistry lab on the Beyond Labz platform. Select "Qualitative Analysis" at the top left of the screen to open the Qualitative Analysis virtual lab.
2. Select "**Aldehydes**" from the chalkboard, then click and drag (or double-click) the reagent bottle for the **butyraldehyde** to add it to the flask.
3. Drag the flask to the cork ring support on the lab bench.
4. Record the IR spectrum by clicking on the IR spectrometer and dragging the salt plate icon to the flask. This will display the IR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. Click ok to close the spectrum.
5. Record the mass spectrum by clicking on the mass spectrometer and dragging the sample vial icon to the flask. This will display the mass spectrum on the screen. **Enter your name and date in the "Common Name" field, and the name of the compound in the "IUPAC Name" field**. To view the m/z values, mouse over each peak - the first number is the m/z value. Record the m/z value of the base peak. Click ok to close the spectrum.
6. Reset the qualitative analysis lab by clicking on the waste container to "clear lab".
7. Select "**Ketones**" from the chalkboard, then click and drag (or double-click) the reagent bottle for the **acetophenone** to add it to the flask.
8. Repeat steps 3-5 to record the IR spectrum and the mass spectrum for the acetophenone.
9. Reset the qualitative analysis lab by clicking on the waste container to "clear lab".
10. Select "**Halides**" from the chalkboard, then click and drag (or double-click) the reagent bottle for the **2-chloro-2-methylpropane** to add it to the flask.
11. Repeat steps 3-5 to record the IR spectrum and the mass spectrum for the 2-methyl-2-chloropropane.
12. Reset the qualitative analysis lab by clicking on the waste container to "clear lab".
13. Select "**Ethers**" from the chalkboard, then click and drag (or double-click) the reagent bottle for the **diethyl ether** to add it to the flask.
14. Repeat steps 3-5 to record the IR spectrum and the mass spectrum for the diethyl ether.
15. Reset the qualitative analysis lab by clicking on the waste container to "clear lab".
16. Your virtual experiment is now complete!

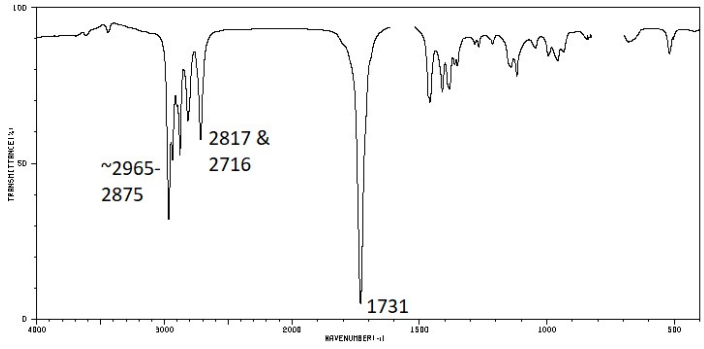
Lab Report Name:_____

Note: an example of a completed table can be found on page 9.

Butyraldehyde Results – Complete the following tables

Infrared Spectrum Analysis

Absorbance peak (cm^{-1})	Bond(s)
2965-2875	
2817 & 2716	
1731	



Mass Spectrum Analysis

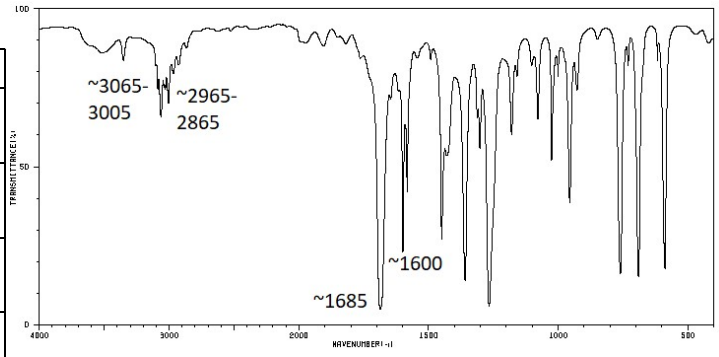
Base peak *m/z* = ☐

m/z value	Charged Fragment	Fragment Lost
72		N/A
71		
57		
44 (McLafferty)		
29		

Acetophenone Results – Complete the following tables.

Infrared Spectrum Analysis

Absorbance peak (cm^{-1})	Bond(s)
3065-3005	
2965-2865	
1685	
1600	



Mass Spectrum Analysis

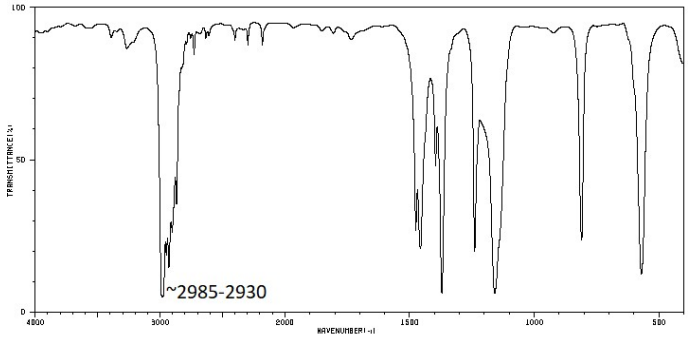
Base peak *m/z* = ____

m/z value	Charged Fragment	Fragment Lost
120		N/A
105		
77		

2-Chloro-2-methylpropane Results – Complete tables and answer questions

Infrared Spectrum Analysis

Absorbance peak (cm^{-1})	Bond(s)
2985-2930	



Mass Spectrum Analysis **Base peak *m/z* =** ____

m/z value	Charged Fragment	Fragment Lost
77*	*indicate Cl isotope in drawing	
57		

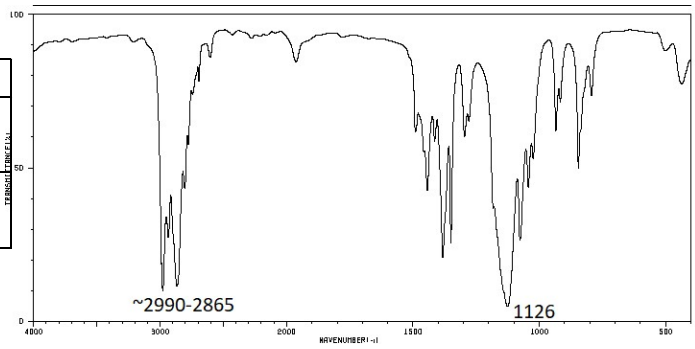
1. The molecular ion is not visible in the mass spectrum of 2-chloro-2-methylpropane. At what *m/z* value would the molecular ion be, if it were present?

2. What evidence is there in the mass spectrum that suggests that the peak at *m/z* = 77 contains a chlorine atom?

Diethyl Ether Results – Complete the following tables.

Infrared Spectrum Analysis

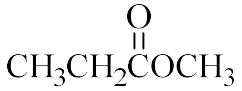
Absorbance peak (cm^{-1})	Bond(s)
2990-2865	
1126	



Mass Spectrum Analysis **Base peak *m/z* =** ____

m/z value	Charged Fragment	Fragment Lost
74		N/A
59		
45		

Solved example: methyl propionate



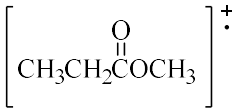
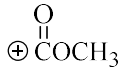
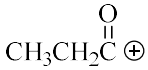
methyl propionate

Infrared Spectrum Analysis

Absorbance peak (cm^{-1})	Bond(s)
2985-2850	sp^3 C-H
1741	C=O, ester (non-conjugated)
1207	C-O, ester

Mass Spectrum Analysis

Base peak *m/z* = 29

m/z value	Charged Fragment	Fragment Lost
88		N/A
59		$\cdot CH_2CH_3$
57		$\cdot OCH_3$