Chapter 13: Mass Spectrometry and Infrared Spectroscopy

♦ Mass spectrometry (MS)

- Mass spectrometry measures the molecular weight of a compound (13.1A).
- The mass of the molecular ion (**M**) = the molecular weight of a compound. Except for isotope peaks at M + 1 and M + 2, the molecular ion has the highest mass in a mass spectrum (13.1A).
- The base peak is the tallest peak in a mass spectrum (13.1A).
- A compound with an odd number of N atoms gives an odd molecular ion. A compound with an even number of N atoms (including zero) gives an even molecular ion (13.1B).
- Organic chlorides show two peaks for the molecular ion (M and M + 2) in a 3:1 ratio (13.2).
- Organic bromides show two peaks for the molecular ion (M and M + 2) in a 1:1 ratio (13.2).
- The fragmentation of radical cations formed in a mass spectrometer gives lower molecular weight fragments, often characteristic of a functional group (13.3).
- High-resolution mass spectrometry gives the molecular formula of a compound (13.4A).

♦ Electromagnetic radiation

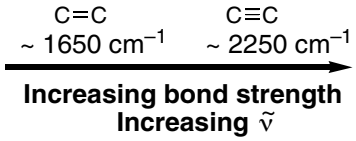
- The wavelength and frequency of electromagnetic radiation are *inversely* related by the following equations: $\lambda = c/\nu$ or $\nu = c/\lambda$ (13.5).
- The energy of a photon is proportional to its frequency; the higher the frequency the higher the energy: $E = h\nu$ (13.5).

♦ Infrared spectroscopy (IR, 13.6 and 13.7)

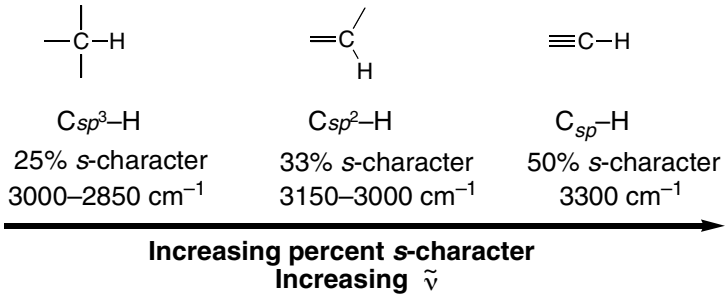
- Infrared spectroscopy identifies functional groups.
- IR absorptions are reported in wavenumbers:

$$\textbf{wavenumber} = \tilde{\nu} = 1/\lambda$$

- The functional group region from **4000–1500 cm^{-1}** is the most useful region of an IR spectrum.
- C–H, O–H, and N–H bonds absorb at high frequency, ≥ 2500 cm^{-1}.
- As bond strength increases, the wavenumber of an absorption increases; thus triple bonds absorb at higher wavenumber than double bonds.



- The higher the percent *s*-character, the stronger the bond, and the higher the wavenumber of an IR absorption.



Chapter 13: Answers to Problems

13.1 The molecular ion formed from each compound is equal to its molecular weight.

a. C_3H_6O	b. $C_{10}H_{20}$	c. $C_8H_8O_2$	d. $C_{10}H_{15}N$
molecular weight = **58**	molecular weight = **140**	molecular weight = **136**	molecular weight = **149**
molecular ion (*m/z*) = **58**	molecular ion (*m/z*) = **140**	molecular ion (*m/z*) = **136**	molecular ion (*m/z*) = **149**

13.2 Some possible formulas for each molecular ion:

a. Molecular ion at 72: C_5H_{12}, C_4H_8O, $C_3H_4O_2$
b. Molecular ion at 100: C_8H_4, C_7H_{16}, $C_6H_{12}O$, $C_5H_8O_2$
c. Molecular ion at 73: $C_4H_{11}N$, $C_2H_7N_3$

13.3 To calculate the molecular ions you would expect for compounds with Cl, calculate the molecular weight using each of the two most common isotopes of Cl (^{35}Cl and ^{37}Cl). Do the same for Br, using ^{79}Br and ^{81}Br.

a. $C_4H_9{}^{35}Cl$ = **92**
$C_4H_9{}^{37}Cl$ = **94**
Two peaks in 3:1 ratio at *m/z* 92 and 94

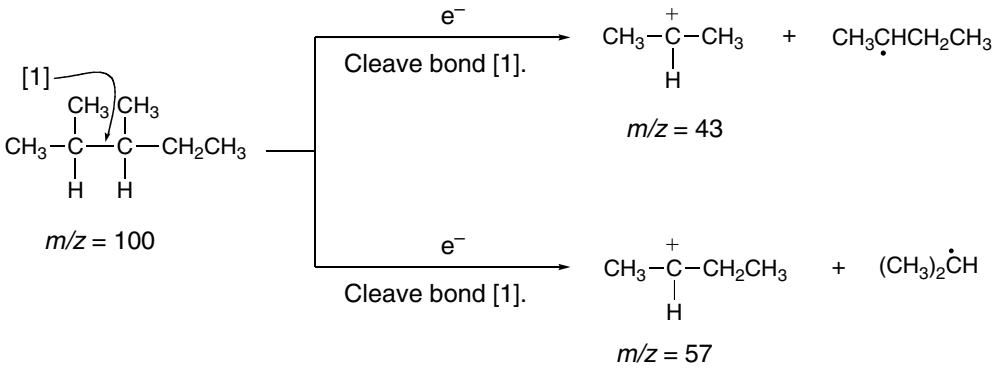
b. C_3H_7F = **62**
One peak at *m/z* 62

c. $C_6H_{11}{}^{79}Br$ = **162**
$C_6H_{11}{}^{81}Br$ = **164**
Two peaks in a 1:1 ratio at *m/z* 162 and 164

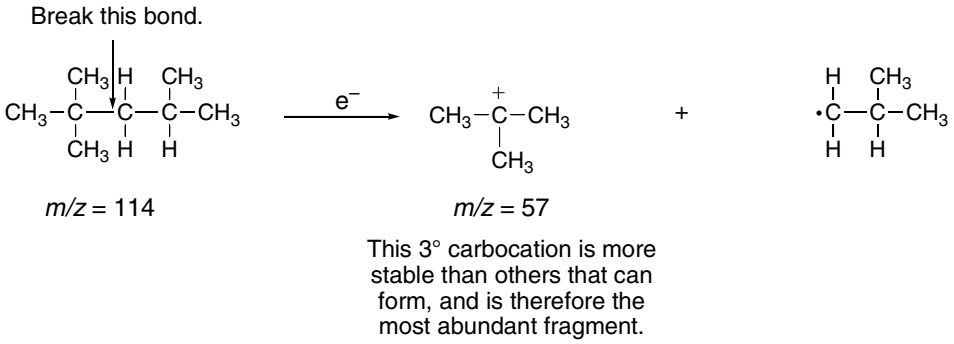
d. $C_4H_{11}N$ = **73**
One peak at *m/z* 73

e. $C_4H_4N_2$ = **80**
One peak at *m/z* 80

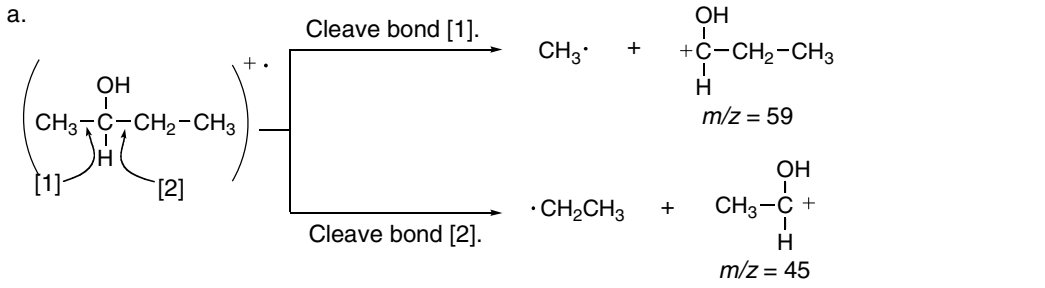
13.4 After calculating the mass of the molecular ion, draw the structure and determine which C–C bond is broken to form fragments of the appropriate mass-to-charge ratio.



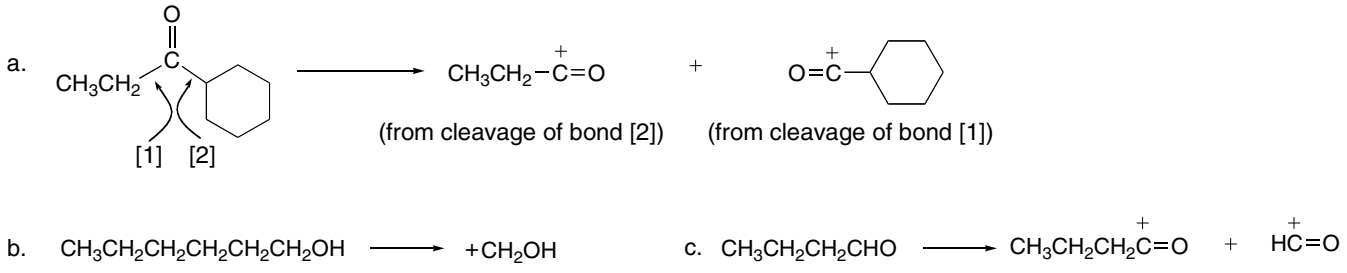
13.5



13.6



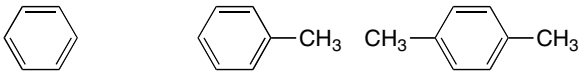
13.7



13.8 Use the exact mass values given in Table 13.1 to calculate the exact mass of each compound.

$C_7H_5NO_3$	$C_8H_9NO_2$	$C_{10}H_{17}N$
mass: 151.0270	mass: 151.0634 compound **X**	mass: 151.1362

13.9



benzene C_6H_6 *m/z* = 78 | toluene C_7H_8 *m/z* = 92 | *p*-xylene C_8H_{10} *m/z* = 106

GC–MS analysis:
Three peaks in the gas chromatogram.
Order of peaks: benzene, toluene, *p*-xylene, in order of increasing bp.
Molecular ions observed in the three mass spectra: 78, 92, 106.

13.10 **Wavelength and frequency are inversely proportional**. The higher frequency light will have a shorter wavelength.

a. Light having a λ of 10^2 nm has a higher ν than light with a λ of 10^4 nm.
b. Light having a λ of 100 nm has a higher ν than light with a λ of 100 μm.
c. Blue light has a higher ν than red light.

13.11 The **energy of a photon** is *proportional* to its **frequency**, and inversely proportional to its wavelength.

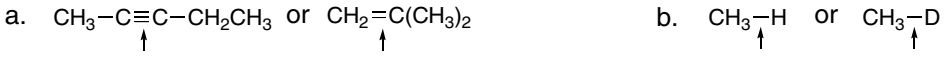
a. Light having a ν of 10^8 Hz is of higher energy than light having a ν of 10^4 Hz.
b. Light having a λ of 10 nm is of higher energy than light having a λ of 1000 nm.
c. Blue light is of higher energy than red light.

13.12 The larger the energy difference between two states, the higher the frequency of radiation needed for absorption. The 400 kJ/mol transition requires a higher ν of radiation than a 20 kJ/mol transition.

13.13 Higher wavenumbers are proportional to higher frequencies and higher energies.

a. IR light with a wavenumber of 3000 cm^{-1} is higher in energy than IR light with a wavenumber of 1500 cm^{-1}.
b. IR light having a λ of 10 μm is higher in energy than IR light having a λ of 20 μm.

13.14 Stronger bonds absorb at a higher wavenumber. Bonds to lighter atoms (H versus D) absorb at higher wavenumber.

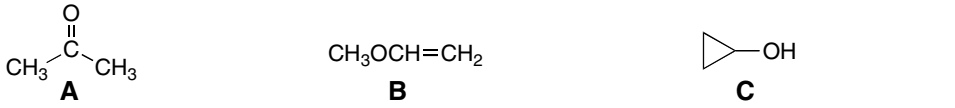


a. $CH_3-C\equiv C-CH_2CH_3$ or $CH_2=C(CH_3)_2$ — stronger bond, higher wavenumber

b. CH_3-H or CH_3-D — lighter atom H, higher wavenumber

13.15 Cyclopentane and 1-pentene are both composed of C–C and C–H bonds, but 1-pentene also has a C=C bond. This difference will give the IR of 1-pentene an additional peak at 1650 cm^{-1} (for the C=C). 1-Pentene will also show C–H absorptions for sp^2 hybridized C–H bonds at 3150–3000 cm^{-1}.

13.16 Look at the functional groups in each compound below to explain how each IR is different.



A | **B** | **C**

A: C=O peak at ~1700 cm^{-1}

B: C=C peak at 1650 cm^{-1}; Csp^2–H at 3150–3000 cm^{-1}

C: O–H peak at 3200–3600 cm^{-1}

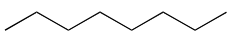
13.17

a. Compound **A** has peaks at ~3150 (sp^2 hybridized C–H), 3000–2850 (sp^3 hybridized C–H), and 1650 (C=C) cm^{-1}.

b. Compound **B** has a peak at 3000–2850 (sp^3 hybridized C–H) cm^{-1}.

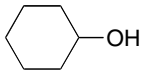
13.18 All compounds show an absorption at 3000–2850 cm^{-1} due to the sp^3 hybridized C–H bonds. Additional peaks in the functional group region for each compound are shown.

a.



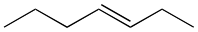
no additional peaks

b.



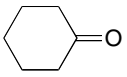
O–H bond at 3600–3200 cm^{-1}

c.



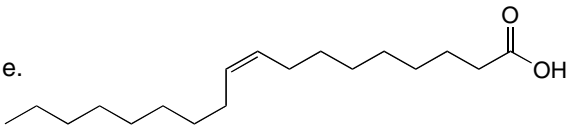
Csp^2–H at 3150–3000 cm^{-1}
C=C bond at 1650 cm^{-1}

d.



C=O bond at ~1700 cm^{-1}

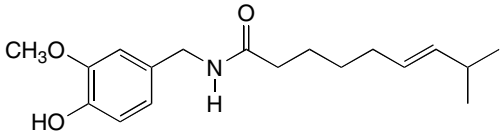
e.



Csp^2–H at 3150–3000 cm^{-1}
C=O at ~1700 cm^{-1}
C=C at 1650 cm^{-1}
O–H above 3000 cm^{-1}

[The OH of a COOH is much broader than the OH of an alcohol and occurs at 3500–2500 cm^{-1} (see Chapter 19).]

f.

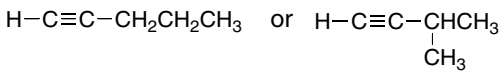


O–H at 3600–3200 cm^{-1}
N–H at 3500–3200 cm^{-1}
Csp^2–H at 3150–3000 cm^{-1}
C=O at ~1700 cm^{-1}
C=C at 1650 cm^{-1}
aromatic ring at 1600, 1500 cm^{-1}

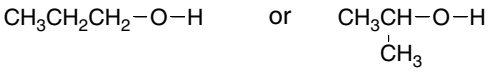
13.19 Possible structures are (a) $CH_3COOCH_2CH_3$ and (c) $CH_3CH_2COOCH_3$. Compounds (b) and (d) also have an OH group that would give a strong absorption at ~3600–3200 cm^{-1}, which is absent in the IR spectrum of **X**, thus excluding them as possibilities.

13.20

a. Hydrocarbon with a molecular ion at $m/z = 68$
IR absorptions at 3310 cm^{-1} = Csp–H bond
3000–2850 cm^{-1} = Csp^3–H bonds
2120 cm^{-1} = C≡C bond
Molecular formula: C_5H_8



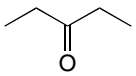
b. Compound with C, H, and O with a molecular ion at $m/z = 60$
IR absorptions at 3600–3200 cm^{-1} = O–H bond
3000–2850 cm^{-1} = Csp^3–H bonds
Molecular formula: C_3H_8O



13.21

a. 

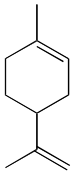
molecular formula: C_6H_6
molecular ion (*m/z*): **78**

c. 

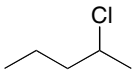
molecular formula: $C_5H_{10}O$
molecular ion (*m/z*): **86**

e. $(CH_3)_3CCH(Br)CH(CH_3)_2$

molecular formula: $C_8H_{17}Br$
molecular ions (*m/z*): **192, 194**

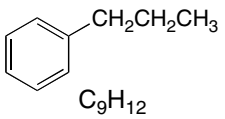
b. 

molecular formula: $C_{10}H_{16}$
molecular ion (*m/z*): **136**

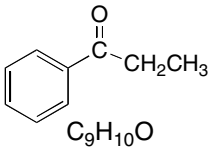
d. 

molecular formula: $C_5H_{11}Cl$
molecular ions (*m/z*): **106, 108**

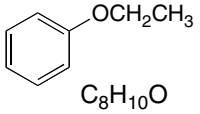
13.22



C_9H_{12}
molecular weight = 120



$C_9H_{10}O$
molecular weight = 134



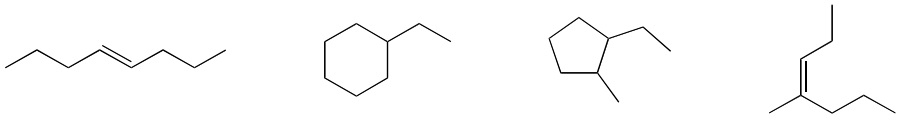
$C_8H_{10}O$
molecular weight = 122

13.23 Examples are given for each molecular ion.

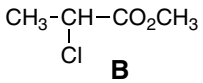
a. molecular ion 102: C_8H_6, $C_6H_{14}O$, $C_5H_{10}O_2$, $C_5H_{14}N_2$
b. molecular ion 98: C_8H_2, C_7H_{14}, $C_6H_{10}O$, $C_5H_6O_2$
c. molecular ion 119: C_8H_9N, $C_6H_5N_3$
d. molecular ion 74: C_6H_2, $C_4H_{10}O$, $C_3H_6O_2$

13.24 Likely molecular formula, C_8H_{16} (one degree of unsaturation—one ring or one π bond).

Four structures with *m/z* = 112

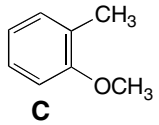


13.25



B
$C_4H_7O_2Cl$
molecular weight: **122, 124**
should show 2 peaks for the molecular ion with a **3:1 ratio**

Mass spectrum [1]



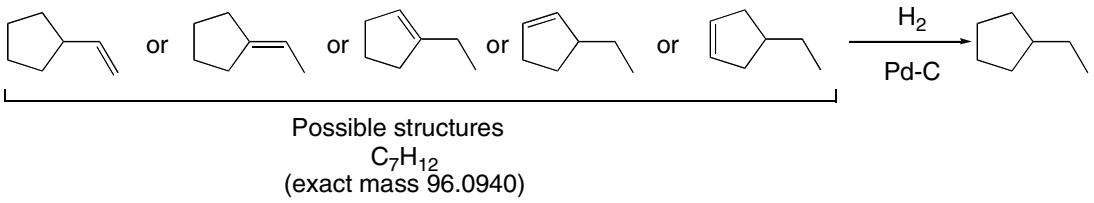
C
$C_8H_{10}O$
molecular weight: **122**

Mass spectrum [2]

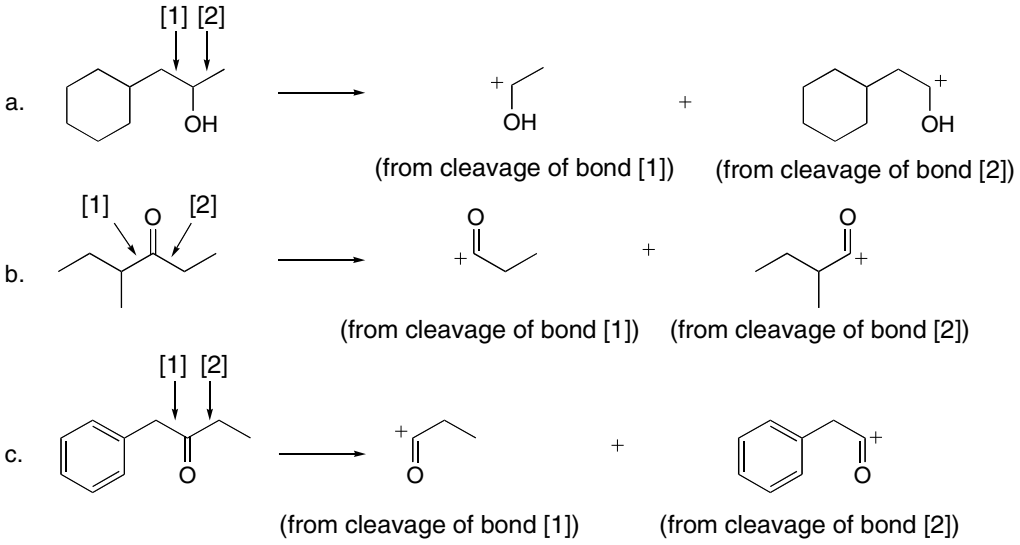
$CH_3CH_2CH_2Br$
A
C_3H_7Br
molecular weight: **122, 124**
should show 2 peaks for the molecular ion with a **1:1 ratio**

Mass spectrum [3]

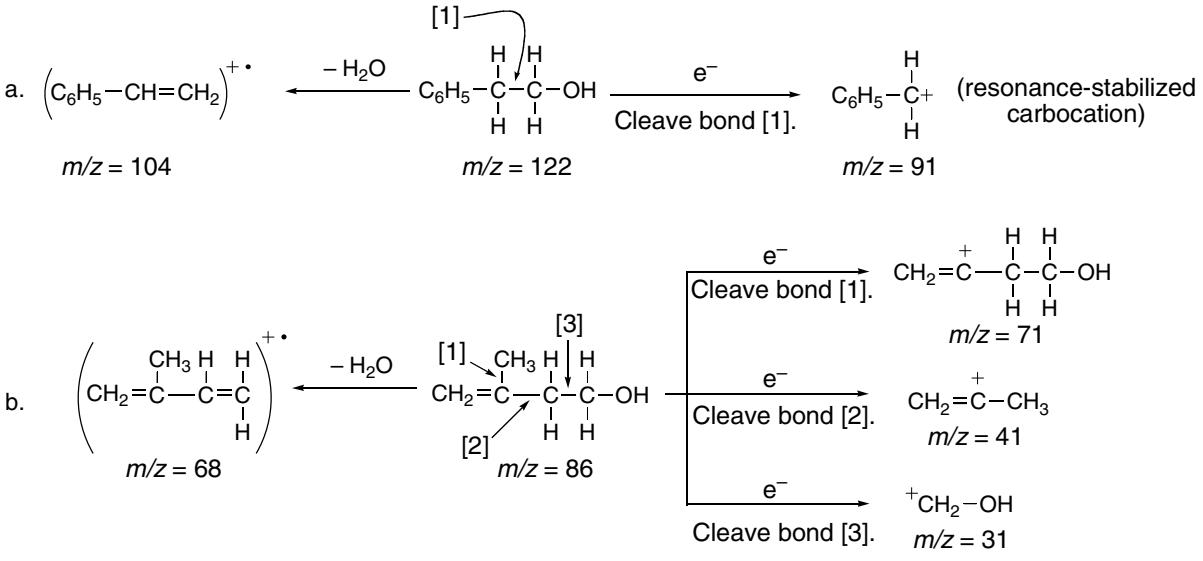
13.26



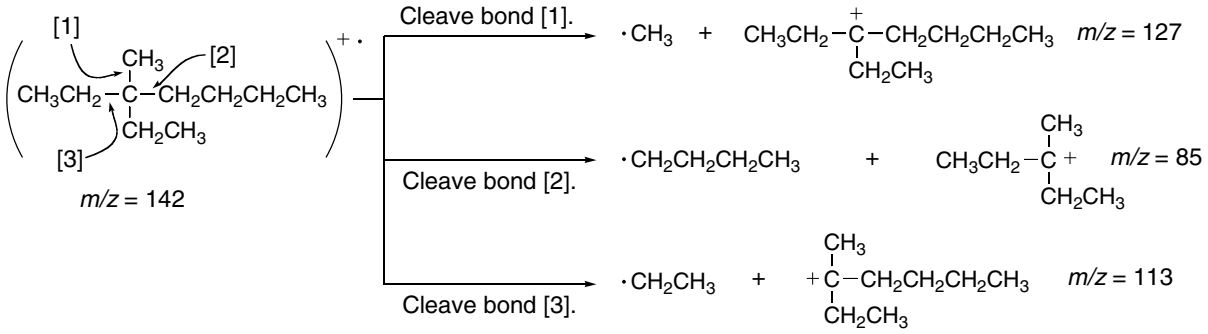
13.27



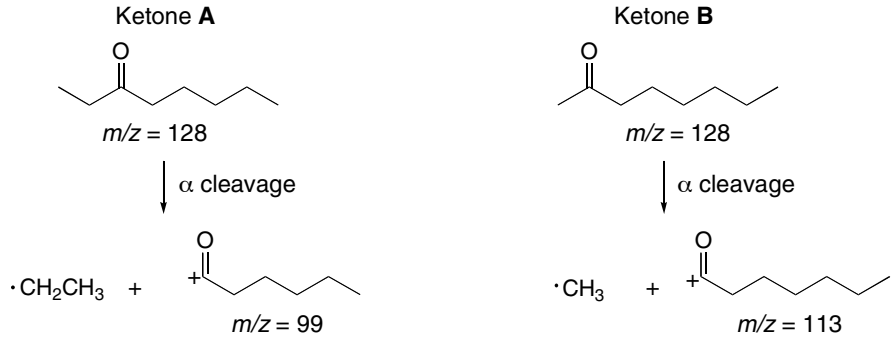
13.28



13.29

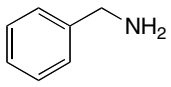


13.30



13.31 One possible structure is drawn for each set of data:

a. A compound that contains a benzene ring and has a molecular ion at *m/z* = 107

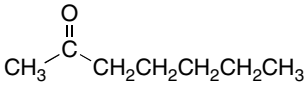


C_7H_9N

b. A hydrocarbon that contains only sp^3 hybridized carbons and a molecular ion at *m/z* = 84

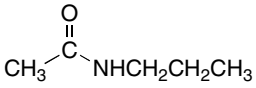
C_6H_{12}

c. A compound that contains a carbonyl group and gives a molecular ion at *m/z* = 114



$C_7H_{14}O$

d. A compound that contains C, H, N, and O and has an exact mass for the molecular ion at 101.0841



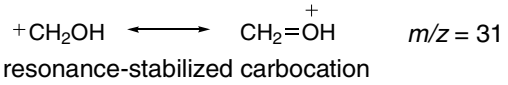
$C_5H_{11}NO$

13.32 Use the values given in Table 13.1 to calculate the exact mass of each compound. $C_8H_{11}NO_2$ (exact mass 153.0790) is the correct molecular formula.

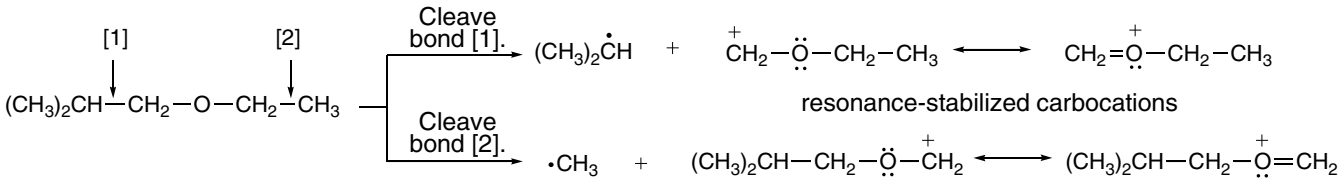
13.33 Molecules with an odd number of N's have an odd number of H's, making the molecular ion odd as well.

13.34 Two isomers such as $CH_2{=}CHCH_2CH_2CH_2CH_3$ and $(CH_3)_2C{=}CHCH_2CH_3$ have the same molecular formulas and therefore give the same exact mass, so they are not distinguishable by their exact mass spectra.

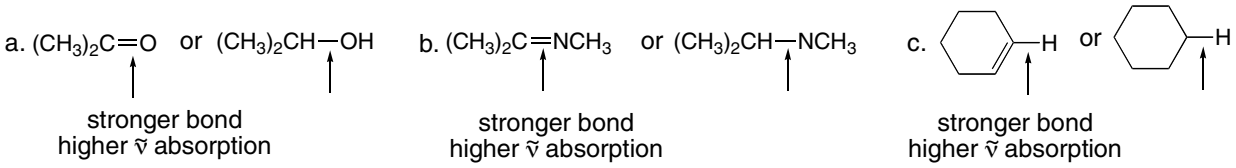
13.35 α Cleavage of a 1° alcohol (RCH_2OH) forms an alkyl radical R• and a resonance-stabilized carbocation with $m/z = 31$.



13.36 An ether fragments by α cleavage because the resulting carbocation is resonance stabilized.



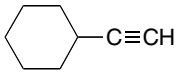
13.37



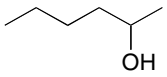
13.38 Locate the functional groups in each compound. Use Table 13.2 to determine what IR absorptions each would have.

a. 

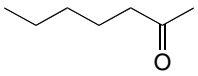
Csp^3–H at 2850–3000 cm^{-1}

b. 

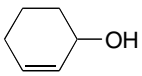
Csp–H at 3300 cm^{-1}
Csp^3–H at 2850–3000 cm^{-1}
C–C triple bond at 2250 cm^{-1}

c. 

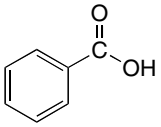
O–H at 3200–3600 cm^{-1}
Csp^3–H at 2850–3000 cm^{-1}

d. 

Csp^3–H at 2850–3000 cm^{-1}
C=O at 1700 cm^{-1}

e. 

O–H at 3200–3600 cm^{-1}
Csp^2–H at 3000–3150 cm^{-1}
Csp^3–H at 2850–3000 cm^{-1}
C=C at 1650 cm^{-1}

f. 

O–H at > 3000 cm^{-1}
Csp^2–H at 3000–3150 cm^{-1}
C=O at ~1700 cm^{-1}
phenyl group at 1600, 1500 cm^{-1}

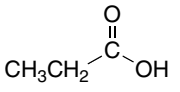
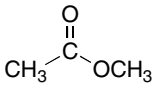
[The OH of the RCOOH is even broader than the OH of an alcohol (3500–2500 cm^{-1}), as we will learn in Chapter 19.]

13.39

a.  and $HC{\equiv}CCH_2CH_2CH_3$

C=C bond
1650 cm^{-1}
C_{sp^2}–H at 3150–3000 cm^{-1}

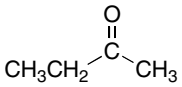
C≡C bond
2250 cm^{-1}
C_{sp}–H at 3300 cm^{-1}

b.  and 

O–H bond
> 3000 cm^{-1}

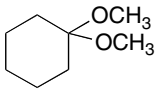
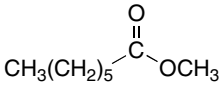
no O–H bond

[See note on OH in Answer 13.38f.]

c.  and $CH_3CH{=}CHCH_2OH$

C=O bond
1700 cm^{-1}

O–H bond
3200–3600 cm^{-1}
C_{sp^2}–H at 3150–3000 cm^{-1}
C=C bond at 1650 cm^{-1}

d.  and 

no C=O bond

C=O bond
~1700 cm^{-1}

e. $CH_3C{\equiv}CCH_3$ and $CH_3CH_2C{\equiv}CH$

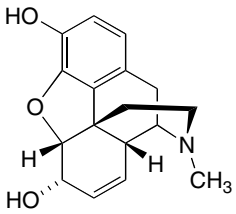
no C≡C absorption due to symmetry

C_{sp}–H bond
3300 cm^{-1}
C≡C bond at ~2250 cm^{-1}

f. $HC{\equiv}CCH_2N(CH_2CH_3)_2$ and $CH_3(CH_2)_5C{\equiv}N$

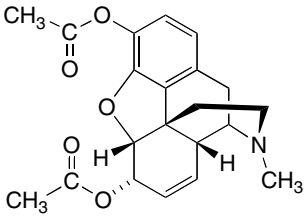
C_{sp}–H bond
3300 cm^{-1}

13.40 The IR absorptions above 1500 cm^{-1} are different for each of the narcotics.



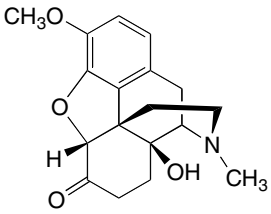
morphine

- O–H bond at ~3200–3600 cm^{-1}
- no C=O bond



heroin

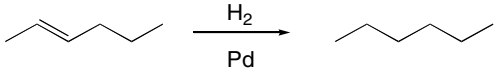
- C=O bond at ~1700 cm^{-1}
- no O–H bond



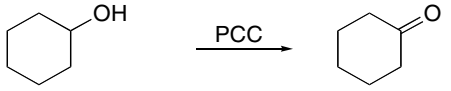
oxycodone

- C=O bond at ~1700 cm^{-1}
- O–H bond at ~3200–3600 cm^{-1}

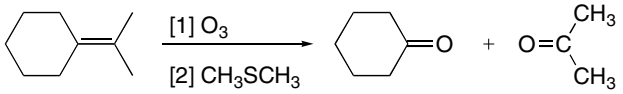
13.41 Look for a **change in functional groups** from starting material to product to see how IR could be used to determine when the reaction is complete.

a. 

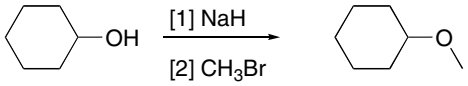
Loss of the C=C will be visible in the IR by disappearance of the peak at 1650 cm^{-1}.

b. 

Loss of the O–H group will be visible in the IR by disappearance of the peak at 3200–3600 cm^{-1} and appearance of the C=O at ~1700 cm^{-1}.

c. 

Loss of the C=C will be visible in the IR by disappearance of the peak at 1650 cm^{-1} and appearance of the C=O at ~1700 cm^{-1}.

d. 

Loss of the O–H will be visible in the IR by disappearance of the peak at 3200–3600 cm^{-1}.

13.42 In addition to Csp^3–H at ~3000–2850 cm^{-1}:

Spectrum [1]:

$CH_2=C(CH_3)CH_2CH_2CH_2CH_3$ (**B**)
C=C peak at 1650 cm^{-1}
Csp^2–H at ~3150 cm^{-1}

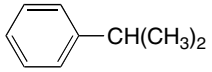
Spectrum [2]:

$(CH_3CH_2)_3COH$ (**F**)
OH at 3600–3200 cm^{-1}

Spectrum [3]:

$(CH_3)_2CHOCH(CH_3)_2$ (**D**)
No other peaks above 1500 cm^{-1}

Spectrum [4]:



(**C**)
Csp^2–H at ~3150 cm^{-1}
Phenyl peaks at 1600 and 1500 cm^{-1}

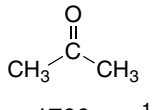
Spectrum [5]:

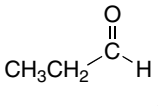
$CH_3CH_2CH_2CH_2COOH$ (**A**)
OH at ~3500–2500 cm^{-1}
C=O at ~1700 cm^{-1}

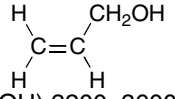
Spectrum [6]:

$CH_3COOC(CH_3)_3$ (**E**)
C=O at ~1700 cm^{-1}

13.43 In addition to Csp^3–H at ~3000–2850 cm^{-1}:

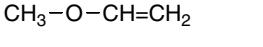

~1700 cm^{-1}

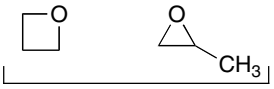

~1700 cm^{-1}


(OH) 3200–3600 cm^{-1}
(C=C)1650 cm^{-1}
(Csp^2–H) 3150–3000 cm^{-1}

No enols (such as $CH_3CH{=}CHOH$) are drawn since these compounds are not stable.

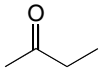

(OH) 3200–3600 cm^{-1}


(C=C)1650 cm^{-1}
(Csp^2–H) 3150–3000 cm^{-1}


No additional peaks above 1500 cm^{-1}

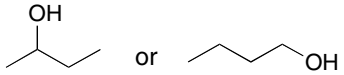
13.44

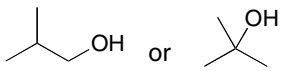
a. Compound with a molecular ion at m/z = 72
IR absorption at 1725 cm^{-1} = C=O bond
Molecular formula: C_4H_8O



b. Compound with a molecular ion at m/z = 55
The odd molecular ion means an odd number of N's present. Molecular formula: C_3H_5N
IR absorption at 2250 cm^{-1} = C≡N bond
$CH_3CH_2C{\equiv}N$

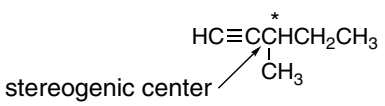
c. Compound with a molecular ion at m/z = 74
IR absorption at 3600–3200 cm^{-1} = O–H bond
Molecular formula: $C_4H_{10}O$



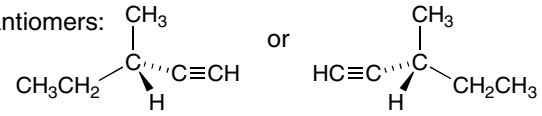


13.45

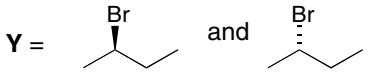
Chiral hydrocarbon with a molecular ion at $m/z = 82$
Molecular formula: C_6H_{10}
IR absorptions at 3300 cm^{-1} = Csp–H bond
3000–2850 cm^{-1} = Csp^3–H bonds
2250 cm^{-1} = C≡C bond



Two possible enantiomers:

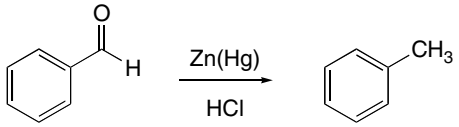


13.46 The chiral compound **Y** has a strong absorption at 2970–2840 cm^{-1} in its IR spectrum due to sp^3 hybridized C–H bonds. The two peaks of equal intensity at 136 and 138 indicate the presence of a Br atom. The molecular formula is C_4H_9Br. Only one constitutional isomer of this molecular formula has a stereogenic center:



two possible enantiomers

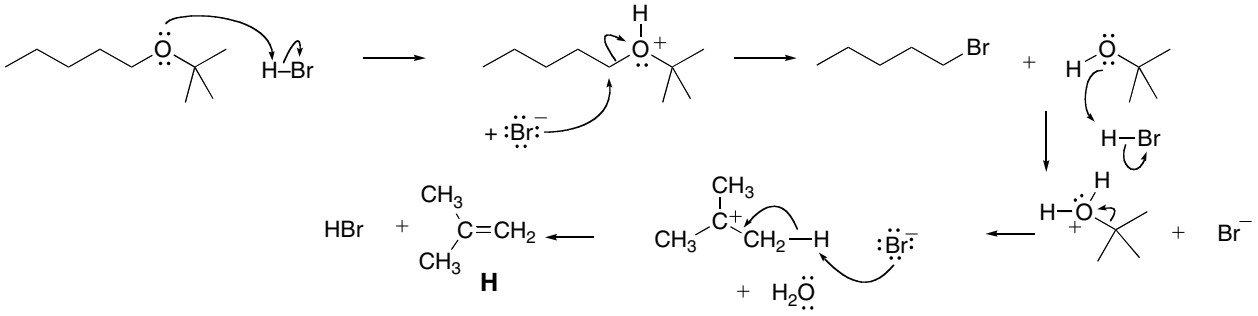
13.47



Z

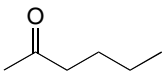
$m/z = 92$; molecular formula C_7H_8
IR absorptions at:
3150–2950 cm^{-1} = Csp^3–H and Csp^2–H bonds
1605 cm^{-1} and 1496 cm^{-1} due to phenyl group

13.48



H

13.49

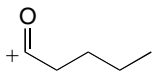


J

$C_6H_{12}O$
$m/z = 100$
IR absorption at 2962 cm^{-1} = Csp^3–H bonds
1718 cm^{-1} = C=O bond

fragments:

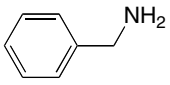
α cleavage product
$m/z = 43$



α cleavage product
$m/z = 85$

The fragment at $m/z = 57$ could be due to $(C_4H_9)^+$ or $(C_3H_5O)^+$.

13.50



K

C_7H_9N

m/z = 107

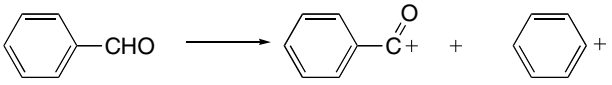
IR absorptions at 3373 and 3290 cm^{-1} = N–H

3062 cm^{-1} = C_{sp^2}–H bonds

2920 cm^{-1} = C_{sp^3}–H bonds

1600 cm^{-1} = benzene ring

The odd molecular ion indicates the presence of a N atom.



L

C_7H_6O

m/z = 106

m/z = 105

m/z = 77

IR absorption at 3068 cm^{-1} = C_{sp^2}–H bonds on ring

2850 cm^{-1} = C_{sp^3}–H bond

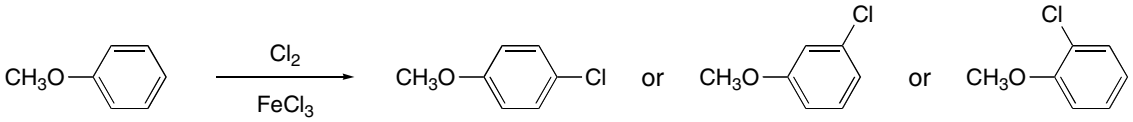
2820 cm^{-1} and 2736 cm^{-1} = C–H of RCHO (Appendix E)

1703 cm^{-1} = C=O bond

1600 cm^{-1} = aromatic ring

13.51

Possible structures of **P**:



C_7H_7ClO

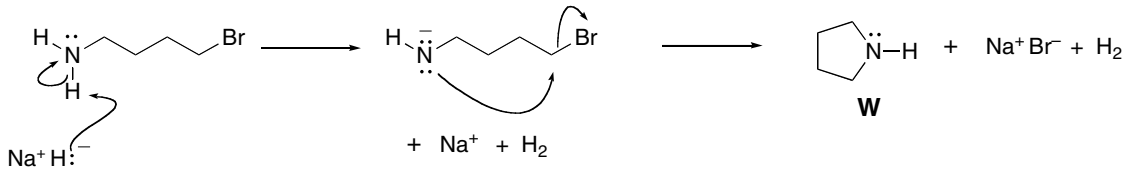
m/z = 142, 144

IR absorption at 3096–2837 cm^{-1} = C_{sp^3}–H bonds and C_{sp^2}–H bonds

1582 cm^{-1} and 1494 cm^{-1} = benzene ring

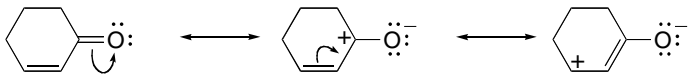
The peak at M + 2 shows the presence of Cl or Br. Since Cl_2 is a reactant, the compound presumably contains Cl.

13.52 The mass spectrum has a molecular ion at 71. The odd mass suggests the presence of an odd number of N atoms; likely formula, C_4H_9N. The IR absorption at ~3300 cm^{-1} is due to N–H and the 3000–2850 cm^{-1} is due to sp^3 hybridized C–H bonds.



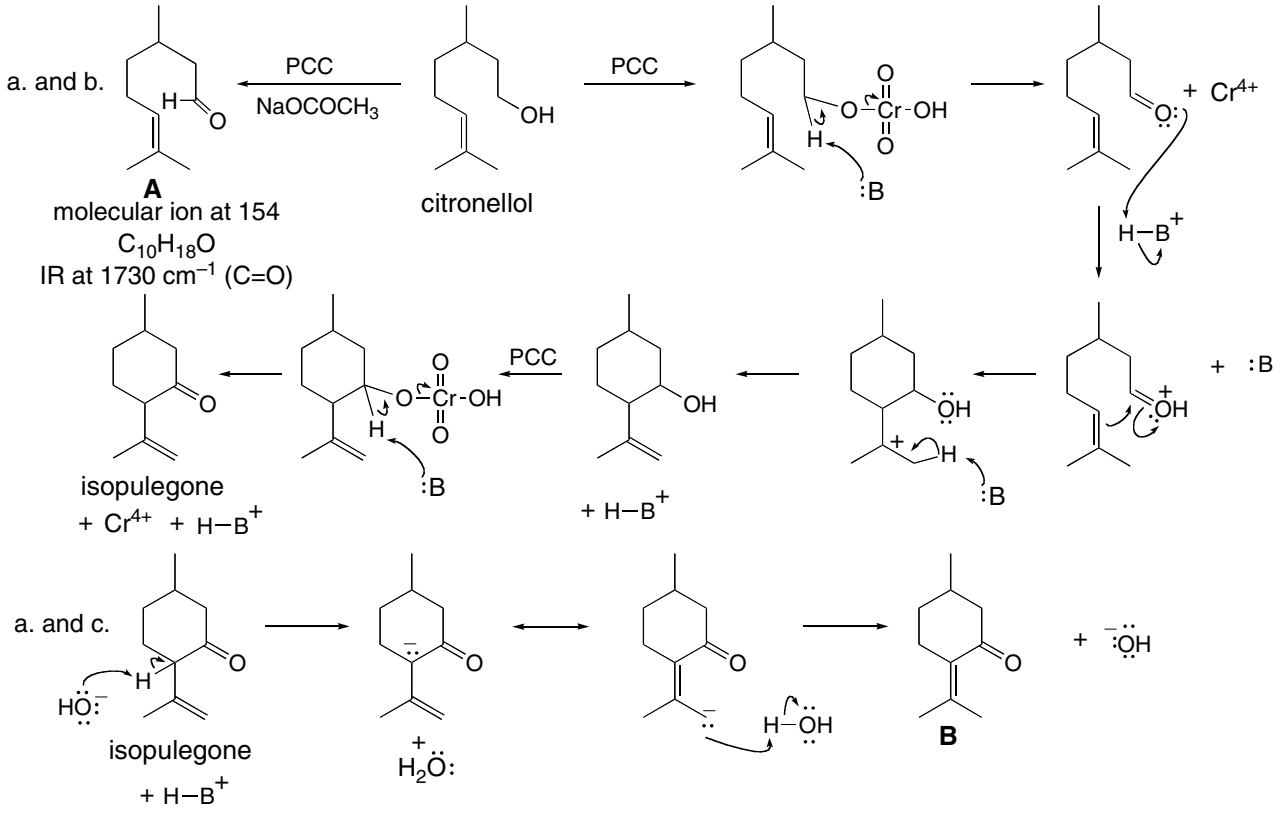
W

13.53 The α,β-unsaturated carbonyl compound has three resonance structures, two of which place a single bond between the C and O atoms. This means that the C–O bond has partial single bond character, making it weaker than a regular C=O bond, and moving the absorption to lower wavenumber.



three resonance structures for 2-cyclohexenone

13.54


a. and b.
PCC
NaOCOCH3
PCC
OH
citronellol
A
molecular ion at 154
C10H18O
IR at 1730 cm−1 (C=O)
+ Cr4+
H−B+
+ :B
PCC
isopulegone
+ Cr4+ + H−B+
+ H−B+
a. and c.
isopulegone
+ H−B+
+ H2O:
H−OH
B
+ ⁻:OH