Chapter 12

12.1 Write as many molecular formulas as you can for compounds that have the following molecular ions in their mass spectra. Assume that all the compounds contain C and H and that O may or may not be present.

(a) $M^+ = 86$
Solution: $C_4H_{14}$, $C_3H_{10}O$, $C_4H_{10}O_2$, $C_3H_4O_3$

(b) $M^+ = 128$
Solution: $C_{10}H_8$, $C_9H_{20}$, $C_8H_4O$, $C_7H_2O_2$, $C_6H_6O_3$, $C_5H_4O_4$

(c) $M^+ = 156$
Solution: $C_{12}H_{12}$, $C_{11}H_{24}$, $C_{11}H_8O$, $C_{10}H_{26}O$, $C_{10}H_2O_2$, $C_9H_{18}O_2$, $C_9H_{12}O_3$, $C_8H_6O_4$, $C_7H_4O_5$

12.2 The male sex hormone testosterone contains C, H, and O and has a mass of 288.2089 amu as determined by high-resolution mass spectrometry. What is the molecular formula of testosterone?
Solution: $C_{19}H_{28}O_2$

12.3 Two mass spectra are shown. One corresponds to 2-methyl-2-pentene; the other, to 2-hexene. Which is which? Explain.
Solution:

Sample B shows a base peak at $m/z=55$, corresponds to the loss of a $-CH_2CH_3$ (29 mass units) from the molecular ion. But sample A has only a small peak at $m/z=55$.

While it's hard for 2-methyl-2-pentene to loss a $-CH_2CH_3$ unit.

Conversely, sample A shows a big peak at $m/z=69$, corresponds to the loss of a $-CH_3$ (15 mass units) from the molecular ion. But sample B has only a small peak at $m/z=69$.

Base peak ($m/z=41$) will be the allylic cation. Molecular ion losses 43 mass units step by step, not in a single way (no propyl group could be lost in a single step).

12.4 What are the masses of the charged fragments produced in the following cleavage pathways?
(a) Alpha cleavage of 2-pentanone.
Solution:
Loss of –CH₃ (15 mass units): 71

Loss of –CH₂CH₂CH₃ (43 mass units)

(b) Dehydration of cyclohexanol

Solution:

Loss of H₂O: 100-18=82

(c) McLafferty rearrangement of 4-methyl-2-pentanone.

Solution:

Loss of

\[
\text{H}_3\text{C} \quad \text{100-42=58}
\]

(d) Alpha cleavage of triethylamine.

Loss of –CH₃ (15 mass units): 101-15=86

12.5 List the masses of the parent ion and of several fragments you might expect to find in the mass spectrum of the following molecule (red=O):
Which has higher energy, infrared radiation with $\lambda = 1.0 \times 10^{-6} m$ or an X ray with $\lambda = 3.0 \times 10^{-9} m$?

Solution: It will be obvious that the X ray has higher energy.

Which has the higher energy, radiation with $\nu = 4.0 \times 10^{9} Hz$ or radiation with $\lambda = 9.0 \times 10^{-6} m$?

Solution:

$$E_1 = h\nu = 6.626 \times 10^{-34} \times 4.0 \times 10^{9} \text{ J} = 2.65 \times 10^{-24} \text{ J}$$

$$E_2 = hc/\lambda = 6.626 \times 10^{-34} \times 3.0 \times 10^{8}/9.0 \times 10^{9} \text{ J} = 2.21 \times 10^{-28} \text{ J}$$

Definitely the radiation with $\lambda = 9.0 \times 10^{-6} m$ has a more higher energy.

It is useful to develop a feeling for the amounts of energy that is corresponding to different parts of the electromagnetic spectrum. Calculate the energies of each of the following kinds of radiation.
using the relationships  
\[ E = 1.20 \times 10^{-4} \text{kJ/mol} / \lambda (\text{m}) \]  
and \( \nu = c / \lambda \.

(a) A gamma ray with \( \lambda = 5.0 \times 10^{-11} \text{ m} \)
(b) An X-ray with \( \lambda = 3.0 \times 10^{-9} \text{ m} \)
(c) Ultraviolet light with \( \nu = 6.0 \times 10^{15} \text{ Hz} \)
(d) Visible light with \( \nu = 7.0 \times 10^{14} \text{ Hz} \)
(e) Infrared radiation with \( \lambda = 2.0 \times 10^{-5} \text{ m} \)
(f) Microwave radiation with \( \nu = 1.0 \times 10^{11} \text{ Hz} \)

Solution

(a) \[ E_2 = \frac{N_A}{\lambda} \frac{hc}{\lambda} = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 3.0 \times 10^8 \times 5.0 \times 10^{-11} \text{kJ/mol} = 2.4 \times 10^6 \text{kJ/mol} \]
(b) \[ E_2 = \frac{N_A}{\lambda} \frac{hc}{\lambda} = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 3.0 \times 10^8 \times 3.0 \times 10^{-9} \text{kJ/mol} = 4.0 \times 10^4 \text{kJ/mol} \]
(c) \[ E_1 = \frac{N_A}{\lambda} \nu = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 6.0 \times 10^{15} \text{kJ/mol} = 2.4 \times 10^5 \text{kJ/mol} \]
(d) \[ E_1 = \frac{N_A}{\lambda} \nu = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 7.0 \times 10^{14} \text{kJ/mol} = 2.8 \times 10^5 \text{kJ/mol} \]
(e) \[ E_2 = \frac{N_A}{\lambda} \frac{hc}{\lambda} = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 3.0 \times 10^8 \times 2.0 \times 10^{-5} \text{kJ/mol} = 6.0 \text{kJ/mol} \]
(f) \[ E_1 = \frac{N_A}{\lambda} \nu = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 1.0 \times 10^{11} \text{kJ/mol} = 4.0 \times 10^3 \text{kJ/mol} \]

12.9 Because IR absorptions can be expressed either in micrometers or in wavenumbers, it’s useful to be able to interconvert between units. Do the following conversions.

(a) 3.10 \( \mu \text{m} \) to \( \text{cm}^{-1} \)  
Solution: 3.10 \( \mu \text{m} = 3225 \text{ cm}^{-1} \)
(b) 5.85 \( \mu \text{m} \) to \( \text{cm}^{-1} \)  
Solution: 5.85 \( \mu \text{m} = 1710 \text{ cm}^{-1} \)
(c) 2250 \( \text{cm}^{-1} \) to \( \mu \text{m} \)  
Solution: 2250 \( \text{cm}^{-1} = 4.44 \mu \text{m} \)

12.10 Refer to Table 12.1, and make educated guesses about what functional groups the following molecules might contain:
(a) A compound with a strong absorption at 1710 \( \text{cm}^{-1} \)
(b) A compound with a strong absorption at 1540 \( \text{cm}^{-1} \)
(c) A compound with strong absorption at 1720 \( \text{cm}^{-1} \) and at 2500–3100 \( \text{cm}^{-1} \)

Solution: (a)  
\[
\begin{array}{c}
\text{O} \\
\text{C}
\end{array}
\]
(b) NO_2
(c)  
\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{OH}
\end{array}
\]

12.11 How might you use IR spectroscopy to distinguish between the following pairs of isomers?
(a) CH_3CH_2OH and CH_3OCH_3  (b) Cyclohexane and 1-hexene
(b) CH_3CH_2COOH and HOCH_2CH_2CHO

Solution: (a) CH_3CH_2OH has a strong and broad H-O absorption at 3400 to 3650 \( \text{cm}^{-1} \) while the CH_3OCH_3 without this absorption.
(b) 1-hexene has a C=C at 1640-1680 \( \text{cm}^{-1} \), while the cyclohexane without this absorption.
(c) CH_3CH_2COOH has a strong and broad O-H absorption at 2500-3100 \( \text{cm}^{-1} \), while HOCH_2CH_2CHO has a strong O-H absorption at 3400-3650 \( \text{cm}^{-1} \).

12.12 The IR spectrum of phenylacetylene is shown in Figure 12.15. What absorption bands can you
identify?  
Solution: \(3300 \text{ cm}^{-1}\) \(-\text{C} \equiv \text{C} - \text{H}\) absorption  
\(3030 \text{ cm}^{-1}\) aromatics \(-\text{C} \equiv \text{C}\) absorption (weak)  
\(1450-1600 \text{ cm}^{-1}\) \(-\text{C} \equiv \text{C}\) absorption  
\(2100-2260 \text{ cm}^{-1}\) \(-\text{C} \equiv \text{C}\) absorption

12.13 Where might the following compounds have IR absorption?  
(a) \[
\text{COCH}_3
\]
Solution: \(\text{C} \equiv \text{C}\) 1640–1680 cm\(^{-1}\)  
\(\text{C}=\text{O}\) 1715 cm\(^{-1}\)

(b) \[
\text{HC} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}
\]
Solution: \(\text{C} \equiv \text{C}\) 2100–2260 cm\(^{-1}\)  
\(\equiv\text{C}-\text{H}\) 3300 cm\(^{-1}\)  
\(\text{C} = \text{O}\) 1730 cm\(^{-1}\)

(c) \[
\text{CO}_2\text{H}
\]
Solution: \(-\text{OH}\) (alcohol) 3400–3650 cm\(^{-1}\)  
\(-\text{OH}\) (carboxylic acid) 2500–3100 cm\(^{-1}\)  
\(\text{C} = \text{O}\) 1715 cm\(^{-1}\)  
\(1660–2000\text{ cm}^{-1}\)  
\(1450–1600\text{ cm}^{-1}\)

12.14 Where might the following compound have IR absorptions? (Red=O, blue=N)
Solution: $\equiv C$ 2210–2260 cm$^{-1}$

\[ C=O 1690 \text{ cm}^{-1} \]

\[ C=C 1640–1680 \text{ cm}^{-1} \]

12.15 Where in the IR spectrum would you expect each of the following molecules to absorb?

(a): 1730 cm$^{-1}$ (C=O), 1540 cm$^{-1}$ (NO$_2$) and 1450-1600 cm$^{-1}$ (benzene)

(b): 1640-1680 cm$^{-1}$ (RCH=CH$_2$) and 1735 cm$^{-1}$ (C=O)

(c): 1715 cm$^{-1}$ (C=O) and 3400-3650 cm$^{-1}$ (O-H)
12.16 Show structure of the likely fragments you would expect in the mass spectra of the following molecules.

(a)

(b)

Solution:

12.17 Write the molecular formulas of all hydrocarbons corresponding to the following molecular ions. How many degrees of unsaturation (double bonds and/or rings) are indicated by each formula?

(a) M⁺=86

Solution:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Degrees of Unsaturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅H₂</td>
<td>7</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>0</td>
</tr>
</tbody>
</table>

(b) M⁺=110
Solution:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Degrees of Unsaturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄H₂</td>
<td>9</td>
</tr>
<tr>
<td>C₄H₁₄</td>
<td>2</td>
</tr>
</tbody>
</table>

(c) $M^+ = 146$

Solution:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Degrees of Unsaturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂H₂</td>
<td>12</td>
</tr>
<tr>
<td>C₁₁H₁₄</td>
<td>5</td>
</tr>
</tbody>
</table>

(d) $M^+ = 190$

Solution:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Degrees of Unsaturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₅H₁₀</td>
<td>11</td>
</tr>
<tr>
<td>C₁₄H₂₂</td>
<td>4</td>
</tr>
</tbody>
</table>

12.18 Draw the structure of a molecule that is consistent with the mass-spectral data in each of the following molecules:

(a) A hydrocarbon with $M^+ = 132$

Solution: The formula is $C_{10}H_{12}$, one of the isomers is

![Structure of C_{10}H_{12}](image)

(b) A hydrocarbon with $M^+ = 166$

Solution: The formula is $C_{13}H_{10}$ or $C_{12}H_{22}$, one of the isomers of $C_{13}H_{10}$ is

![Structure of C_{13}H_{10} or C_{12}H_{22}](image)

and one of the isomers of $C_{12}H_{22}$ is

(c) A hydrocarbon with $M^+ = 84$

Solution: The formula is $C_6H_{12}$, one of the isomers is

![Structure of C_6H_{12}](image)
12.19: Write molecular formulas for compounds that show the following molecular ions in their high-resolution mass spectra. Assume that C, H, N and O might be present, and use the exact atomic masses described in Section 12.2.  
(a) $M^+ = 98.0844$;  
(b) $M^+ = 123.0320$.

Solution: (a): As $M^+/M_C = 8.0844 / 12.0107 = 0.67$, so the probable molecular formulas are $C_7H_{14}$ or $C_6H_{10}O$, but the exact mass spectra of $C_6H_{10}O$ is 98.0732 which is not the same as $M^+$, so the exact molecular formulas is $C_7H_{14}$.

(b): $M^+/M_C = 10.25$, as the residual is an odd number so there should be a N, the probable molecular formulas are $C_8H_{13}N$ or $C_6H_5NO_2$, but the exact mass spectra of $C_8H_{13}N$ is not the same as $M^+$, so the exact molecular formula is $C_6H_5NO_2$.

12.20: Camphor, a saturated monoketone from the Asian camphor tree, is used among other things as a moth repellent and as a constituent of embalming fluid. If camphor has $M^+ = 152.1201$ by high-resolution mass spectrometry, what is its molecular formula? How many rings does camphor have?

Solution: As the camphor is a monoketone, and $M^+/M_C = 12.1201 / 12.0107 = 1.005$, so the molecular formula should be $C_10H_{16}O$, so the number of rings is $(10*2 - 16)/2 = 2$.

12.21: The nitrogen rule of mass spectrometry says that a compound containing an odd number of nitrogens has an odd-numbered molecular ion. Conversely, a compound containing an even number of nitrogens has an even-numbered $M^+$ peak. Explain.

Solution: Nitrogen is trivalent, thus requiring an odd number of hydrogen atoms in a molecular. So a compound containing an odd number of nitrogens has an odd-numbered molecular ion. Conversely, a compound containing an even number of nitrogens has an even-numbered $M^+$ peak.

12.22: In light of the nitrogen rule mentioned in Problem 12.21, what is the molecular formula of pyridine, $M^+ = 79$?

Solution: The molecular formula of pyridine: $C_5H_5N$

12.23: Nicotine is a diamino compound isolated from dried tobacco leaves. Nicotine has two rings and $M^+ = 162.1157$ by high-resolution mass spectrometry. Give a molecular formula for nicotine, and calculate the number of double bonds.

Solution: The molecular formula of nicotine is $C_{10}H_{14}N_2$ and it has 3 double bonds.

12.24: The hormone cortisone contains C, H, and O, and shows a molecule ion at $M^+ = 360.1937$ by high-resolution mass spectrometry. What is the molecular formula of cortisone? (The degree of unsaturation of cortisone is 8)

Solution: The molecular formula is $C_{21}H_{28}O_5$

12.25: Halogenated compounds are particularly easy to identify by their mass spectra because both chlorine and bromine occur naturally as mixtures of two abundant isotopes. Chlorine occurs as $^{35}\text{Cl}(75.8\%)$ and $^{37}\text{Cl}(24.2\%)$; bromine occurs as $^{79}\text{Br}(50.7\%)$ and $^{81}\text{Br}(49.3\%)$. At what masses do the molecular ions occur for the following formulas? What are the relative percentages of the each molecular ion?
(a) Bromomethane, CH$_3$Br

Solution:

<table>
<thead>
<tr>
<th>Molecular ion</th>
<th>CH$_3^{79}$Br$^+$</th>
<th>CH$_3^{81}$Br$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>94</td>
<td>96</td>
</tr>
<tr>
<td>Relative percentage</td>
<td>50.7%</td>
<td>49.3%</td>
</tr>
</tbody>
</table>

(b) 1-Chlorohexane, C$_6$H$_{13}$Cl

Solution:

<table>
<thead>
<tr>
<th>Molecular ion</th>
<th>C$<em>6$H$</em>{13}^{35}$Cl$^+$</th>
<th>C$<em>6$H$</em>{13}^{37}$Cl$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>120</td>
<td>122</td>
</tr>
<tr>
<td>Relative percentage</td>
<td>75.8%</td>
<td>24.2%</td>
</tr>
</tbody>
</table>

12.26 Molecular ions can be particularly complex for polyhalogenated compounds. Taking the natural abundance of Cl into account (See Problem 12.25), calculate the masses of the molecular ions of the following formulas. What are the relative percentages of each ion?

(a) Chloroform, CHCl$_3$

Solution:

<table>
<thead>
<tr>
<th>Molecular ion</th>
<th>CH$^{13}$Cl$_3^+$</th>
<th>CH$^{35}$Cl$^{13}$Cl$_2^+$</th>
<th>CH$^{35}$Cl$^{37}$Cl$_2^+$</th>
<th>CH$^{37}$Cl$_3^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>118</td>
<td>120</td>
<td>122</td>
<td>124</td>
</tr>
<tr>
<td>Relative percentage</td>
<td>43.55%</td>
<td>47.71%</td>
<td>13.32%</td>
<td>1.42%</td>
</tr>
</tbody>
</table>

(b) Freon 12, CF$_2$Cl$_2$ (Fluorine occurs only as $^{19}$F.)

Solution:

<table>
<thead>
<tr>
<th>Molecular ion</th>
<th>CF$_2^{35}$Cl$_2^+$</th>
<th>CF$_2^{35}$Cl$^{37}$Cl$^+$</th>
<th>CF$_2^{37}$Cl$_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>120</td>
<td>122</td>
<td>124</td>
</tr>
<tr>
<td>Relative percentage</td>
<td>57.46%</td>
<td>36.69%</td>
<td>5.90%</td>
</tr>
</tbody>
</table>

12.27 By knowing the natural abundances of minor isotopes, it’s possible to calculate the relative heights of M$^+$ and M+1 peaks. If $^{13}$C has a natural abundance of 1.10%, what are the relative heights of the M$^+$ and M+1 peaks in the mass spectrum of benzene, C$_6$H$_6$?

Solution: The M+1 peak is 6.6% ($1.1\% \times 6$) as high as the M$^+$ peak.

12.28 Propose structures for compounds that fit the following data:

(a) A ketone with M$^+$=86 and fragments at m/z=71 and m/z=43

(b) An alcohol with M$^+$=88 and fragments at m/z=73, m/z=70, and m/z=59

Solution:

(a) $\text{H}_3\text{CH}_2\text{CH}_2\text{C}O\text{CCH}_3$

(-CH$_3$: 86-71=15; -CH$_2$CH$_2$CH$_3$: 86-43=43)

(b)
12.29 2-Methylpentane (C₆H₁₄) has the mass spectrum shown. Which peak represents M⁺? Which is the basic peak? Propose structures for fragment ions of m/z = 71, 57, 43 and 29. Why does the base peak have mass it does?

Solution:
The molecule weight of 2-Methylpentane (C₆H₁₄) is about 86, so the final peak represents M⁺ according to its molecular weight. The base peak is the peak with m/z = 43. The structure of fragment ions shows in the following structure:

- **Exact Mass**: 71.09
- **Mol. Wt.**: 71.14
- **m/e**: 71.09 (100.0%), 72.09 (5.7%)
  - C, 84.42; H, 15.59

- **Exact Mass**: 57.07
- **Mol. Wt.**: 57.11
- **m/e**: 57.07 (100.0%), 58.07 (4.4%)
  - C, 84.12; H, 15.88

- **Exact Mass**: 43.05
- **Mol. Wt.**: 43.09
- **m/e**: 43.05 (100.0%), 44.06 (3.4%)
  - C, 83.63; H, 16.38

- **Exact Mass**: 29.04
- **Mol. Wt.**: 29.06
- **m/e**: 29.04 (100.0%), 30.04 (2.2%)
  - C, 82.66; H, 17.34
Exact Mass: 29.04
Mol. Wt.: 29.06
m/e:
C, 82.66; H, 17.34
The base peak is the peak that the carbocation with the molecular weight of 43, as it’s the most stable carbocation in the process.

12.30 Assume that you are in a laboratory carrying out the catalytic hydrogenation of cyclohexene to cyclohexane. How would you use a mass spectrometer to determine when the reaction is finished?

Solution:
GC-MS should be used.

12.31 What fragments might you expect in the mass spectra of the following compounds?
(a)
12.32 Convert the following IR absorption values from micrometers to wavenumbers:

(a) An alcohol, 2.98 μm
   \( \nu = 1/\lambda = 3355.7 \text{cm}^{-1} \)

(b) An ester, 5.81 μm
   \( \nu = 1/\lambda = 1721.2 \text{cm}^{-1} \)

(c) A nitrile, 4.93 μm
   \( \nu = 1/\lambda = 2028.4 \text{cm}^{-1} \)

12.33 Convert the following IR absorption values from wavenumbers to micrometers:

(a) A cyclopentanone, 1755 cm\(^{-1}\)
   \( \lambda = 1/\nu = 0.5698 \text{mm} \)

(b) An amine, 3250 cm\(^{-1}\)
   \( \lambda = 1/\nu = 0.3077 \text{mm} \)

(c) An aldehyde, 1725 cm\(^{-1}\)
   \( \lambda = 1/\nu = 0.5797 \text{mm} \)

(d) An acid chloride, 1780 cm\(^{-1}\)
   \( \lambda = 1/\nu = 0.5618 \text{mm} \)

12.34 How might you use IR spectroscopy to distinguish among the three isomers 1-butyne, 1,3-butenediene, and 2-butyne?

Solution: To 1,3-butenediene, there will be two strong absorption at 3020-3100 and 1640-1680.
To 1-butyne, there will be two strong absorption at 3300 and 2100-2260.
To 2-butyne, there will be a strong absorption at 2100-2260 but not 3300.

12.35 Would you expect two enantiomers such as (R)-2-bromobutane and (S)-2-bromobutane to have identical or different IR spectra? Explain.
12.36 Would you expect two diastereomers such as meso-2,3-dibromobutane and (2R,3S)-dibromobutane to have identical or different IR spectra? Explain.

Solution: Different. The reason: Diastereomers are not mirror-image compounds, so every bond of one compound can't find another bond of the other compound that has the identical circumstance, and the absorptions of the two compounds obviously are different.

12.37: Propose structures for compounds that meet the following description:
(a) C₂H₆, with IR absorptions at 3300 and 2150 cm⁻¹
(b) C₃H₇O, with a strong IR absorption at 3400 cm⁻¹
(c) C₃H₇O, with a strong IR absorption at 1715 cm⁻¹
(d) C₄H₁₀, with IR absorption at 1600 and 1500 cm⁻¹

Solution: (a) is \( \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 \)
(b) is \( \text{H}_3\text{CHC}==\text{CHCH}_2\text{OH} \)
(c) is \( \text{H}_3\text{C}==\text{C}==\text{CH}_2\text{CH}_3 \)
(d) is \( \text{C}==\text{C}==\text{CH}_3\)

12.38: How could you use infrared spectroscopy to distinguish between the following pairs of isomers?
(a) \( \text{HC}==\text{CCH}_2\text{NH}_2 \) and \( \text{H}_3\text{CH}_2\text{CC}==\text{N} \)
(b) \( \text{CH}_3\text{COCH}_3 \) and \( \text{CH}_3\text{CH}_2\text{CHO} \)

Solution: (a): \( \text{HC}==\text{CCH}_2\text{NH}_2 \) with IR absorption at 3300 and 2100—2260 cm⁻¹
(\( \text{H}_3\text{CH}_2\text{CC}==\text{N} \), with a strong IR absorption at 2210—2260 cm⁻¹
(b) \( \text{CH}_3\text{COCH}_3 \) with a strong IR absorption at 1715 cm⁻¹
\( \text{CH}_3\text{CH}_2\text{CHO} \) with a strong IR absorption at 1730 cm⁻¹
12.39 Two infrared spectra are shown. One is the spectrum of cyclohexane, and the other is the spectrum of cyclohexene. Identify them, and explain your answer.

Solution: (b) is the spectrum of cyclohexene because it shows a characteristic C=C absorption at 1640 cm⁻¹ and a vinylic =C-H absorption at 3020 cm⁻¹.

12.40 At what approximate positions might the following compounds show IR absorptions?

Solution:

(a)
\[
\begin{align*}
\text{CO}_2\text{H} \\
\text{C-H} & \quad 3030 \quad \text{weak} \\
\text{1660~2000} & \quad \text{weak} \\
\text{1450~1600} & \quad \text{medium} \\
\text{C-O} & \quad 1670~1780 \quad \text{strong} \\
\text{O-H} & \quad 2500~3100 \quad \text{strong, very broad}
\end{align*}
\]

(b)
\[
\begin{align*}
\text{CO}_2\text{CH}_3 \\
\text{C-H} & \quad 3030 \quad \text{weak} \\
\text{1660~2000} & \quad \text{weak} \\
\text{1450~1600} & \quad \text{medium} \\
\text{C-O} & \quad 1670~1780 \quad \text{strong} \\
\text{CH}_3 & \quad 2850~2960 \quad \text{medium to strong}
\end{align*}
\]
12.41 How would you use infrared spectroscopy to distinguish between the following pairs of constitutional isomers?

(a) \( -\equiv\equiv- \) and \( -\equiv\equiv- \)

(b) \( -\equiv\equiv\equiv\equiv- \) and \( -\equiv\equiv\equiv- \)

(c) \( -\equiv\equiv\equiv\equiv\equiv- \) and \( -\equiv\equiv\equiv\equiv\equiv\equiv\equiv- \)

Solution:

(a) \( -\equiv\equiv- \) has a strong absorption at the position of \( 3300\text{cm}^{-1} \) of \( -\equiv\equiv\equiv\equiv\equiv- \).

(b) \( -\equiv\equiv\equiv\equiv- \) has a special strong absorption at \( 1690\text{cm}^{-1} \) of \( -\equiv\equiv\equiv\equiv- \) because of the
conjugation π bond, and should have separated typical absorption of c=O and c≡c.

(c). has a distinguishing absorption at 1730 cm\(^{-1}\) of aldehydes which is different from those of c≡c and o.

12.42 At what approximate positions might the following compounds show IR absorptions?

(a) o (b) (c) (d) o

Solution:
(a). Absorption: 1670-1780 cm\(^{-1}\) of c=O.
(b). Absorption: 3300 cm\(^{-1}\) of ===C–H; 2100-2260 cm\(^{-1}\) of ===C–C–.
(c). Absorption: 3020-3100 cm\(^{-1}\) of ===C–H; 1640-1680 cm\(^{-1}\) of c≡c.

(d). Absorption: 1735 cm\(^{-1}\) of typical o.
(e). Absorption: 1690 cm\(^{-1}\) of c=O next to the aromatic ring; 1450-1600 cm\(^{-1}\) and 1660-2000 cm\(^{-1}\) (should be overlapped) of benzene ring; 3030 cm\(^{-1}\) of H.

12.43 Assume you are carrying out the dehydration of 1-methylcyclohexanol to yield 1-methylcyclohexene. How could you use infrared spectroscopy to determine when the reaction is complete?

Solution: When there is no absorption in the area of 3400-3650 where O-H has absorption peak, it shows that the reaction is complete.

12.44. Assume that you are carrying out the base-induced dehydrobromination of 3-bromo-3-methylpentane to yield an alkene. How could you use IR spectroscopy to tell which of two possible elimination products is formed?

Solution: Because \(R_2C\equiv CH_2\) has a big absorption in the 890 cm\(^{-1}\), we only need to find whether there is an absorption in the 890 cm\(^{-1}\), if there is an absorption, the product will be

\[
\begin{array}{c}
H_3C-C-C-C-C-CH_3 \\
H_2 \\
\end{array}
\]
if not, it is

\[ \text{H}_3\text{C} = \text{C} = \text{CH}_2 \]

12.45 Which is stronger, the C=O bond in an ester (1735 cm\(^{-1}\)) or the C=O bond in a saturated ketone (1715 cm\(^{-1}\))? Explain.

**Solution:** 1735 > 1715, so the C=O bond in an ester (1735 cm\(^{-1}\)) is stronger than the C=O bond in a saturated ketone (1715 cm\(^{-1}\)). Strong bonds vibrate at a higher energy and a higher frequency.

12.46 Carvone is an unsaturated ketone responsible for the odor of spearmint. If carvone has M\(^+\) = 150 in its mass spectrum and contains three double bonds and one ring, what is its molecular formula?

**Solution:** \( \text{C}_{10}\text{H}_{14}\text{O} \)

12.47 Carvone (Problem 12.46) has an intense infrared absorption at 1690 cm\(^{-1}\). What kind of ketone does carvone contain?

**Solution:** Carvone contains ketone next to a double bond. As follow:

12.48 The mass spectrum (a) and the infrared spectrum (b) of an unknown hydrocarbon are shown. Propose as many structures as you can.

**Solution:**

**IR:**
- The region from 3500 to 3000 cm\(^{-1}\) corresponding to absorptions caused by \( \equiv \text{C-H} \)
- The region from 2200 to 2000 cm\(^{-1}\) is where \( \equiv \text{C} \) stretching occurs.

So there is a terminal \( \equiv \text{C-H} \) in the molecule.

**MS:**

The base peak is m/z = 67. It is not the M\(^+\) because the mass of hydrocarbon can not be odd. So the M\(^+\) might be 68 or 82.

If M\(^+\)’s mass is 68, the formula might be \( \text{C}_5\text{H}_8 \), and the structure may be

\[ \equiv \equiv \equiv \equiv \equiv \equiv \equiv \equiv \equiv \equiv \]

or

If the loss of a methyl radical from the molecule gives rise to the base peak, the mass of the molecule is 67 + 15 = 82, which is hexyne. The structure might be
The answer is 1-pentyne.

12.49 The mass spectrum and the infrared spectrum of another unknown hydrocarbon are shown. Propose as many structures as you can.

Solution:: 

or
12.50 Propose structures for compounds that meet the following descriptions:

(a) An optically active compound C₅H₁₀O with an IR absorption at 1730 cm⁻¹
(b) An non-optically active compound C₅H₉N with an IR absorption at 2215 cm⁻¹

Solution:

(a) Saturated aldehyde absorb at 1730 cm⁻¹, and the compound is optically active, so the possible structure is:

\[
\begin{align*}
\text{C}_5\text{H}_2\text{CHO} & \quad \text{or} \quad \text{C}_5\text{H}_2\text{O}\text{H} \\
\end{align*}
\]

(b) Nitriles (−C≡N) absorb at 2215 cm⁻¹ and the compound is non-optically active.

The possible structure is:

\[
\begin{align*}
\text{C}_5\text{H}_2\text{C} & \quad \text{or} \quad \text{C}_5\text{H}_2\text{C} \\
\end{align*}
\]

12.51 4-Methyl-2-pentanone and 3-methylpentanal are isomers. Explain how you could tell them apart, both by mass spectrometry and by infrared spectroscopy.

4-Methyl-2-pentanone 3-methylpentanal

solution:

by mass spectrometry: we can get different base peak to tell them apart
by infrared spectroscopy: the aldehyde absorb at 1730 cm⁻¹, while the ketone absorb at 1715 cm⁻¹

12.52 Grignard reagents undergo a general and very useful reaction with ketones. Methylmagnesium bromide, for example, reacts with cyclohexanone to yield a product with the formula C₇H₁₄O. What is the structure of this product if it has an IR absorption at 3400 cm⁻¹?( See Section 17.6)

Solution:

The hydroxyen group results in the IR absorption at 3400 cm⁻¹.

12.53 Ketones undergo a reduction when treated with sodium borohydride, NaBH₄. What’s the structure of the compound produced by reaction of 2-Butanone with NaBH₄ if it has an IR
absorption at 3400 cm\(^{-1}\) and \(M^+ = 74\) in the mass spectrum? (See Section 17.5)

\[
\begin{array}{c}
\text{CH}_3 \\
\text{C} \quad \text{C} \quad \text{H}_2 \\
\text{H}_3\text{C} \\
\end{array}
\]

1. \(\text{NaBH}_4\)
2. \(\text{H}_3\text{O}^+\)

Solution:
Cause the Function Group O-H’s Band position is 3400–3650, so there should be a \(-\text{OH}\) group in the product. And \(M^+ = 74\), which indicates that the product should be \(\text{C}_4\text{H}_10\text{O}\). So the structure of the product should be

\[
\begin{array}{c}
\text{OH} \\
\text{H}_3\text{C} \quad \text{CH} \quad \text{CH}_3 \\
\text{H}_2 \\
\end{array}
\]

12.54 Nitriles, \(\text{R-CN}\), undergo a hydrolysis reaction when heated with aqueous acid. What is the structure of the compound produced by hydrolysis of propanenitrile, \(\text{CH}_3\text{CH}_2\text{CN}\), if it has IR absorption at 2500 cm\(^{-1}\) and 1710 cm\(^{-1}\) and has \(M^+ = 74\)?

Solution:
\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{C} \quad \text{C} \quad \text{N} \\
\text{H}_2 \\
\end{array}
\]

\[
\begin{array}{c}
\text{H}_3\text{O}^+ \\
\text{H}_3\text{C} \quad \text{C} \quad \text{H}_2 \quad \text{C} \quad \text{O} \quad \text{OH} \\
\text{H}_3\text{C} \quad \text{C} \quad \text{H}_2 \quad \text{C} \quad \text{O} \quad \text{OH} \\
\text{H}_2 \\
\end{array}
\]

The IR absorption between 2500 cm\(^{-1}\) and 1710 cm\(^{-1}\) shows the \(\text{C}=\text{O}\) functional group. By calculating the molecular mass, the product is an acid.