Organic Chemistry, *Second Edition*

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Chapter 13
Mass Spectrometry and Infrared Spectroscopy

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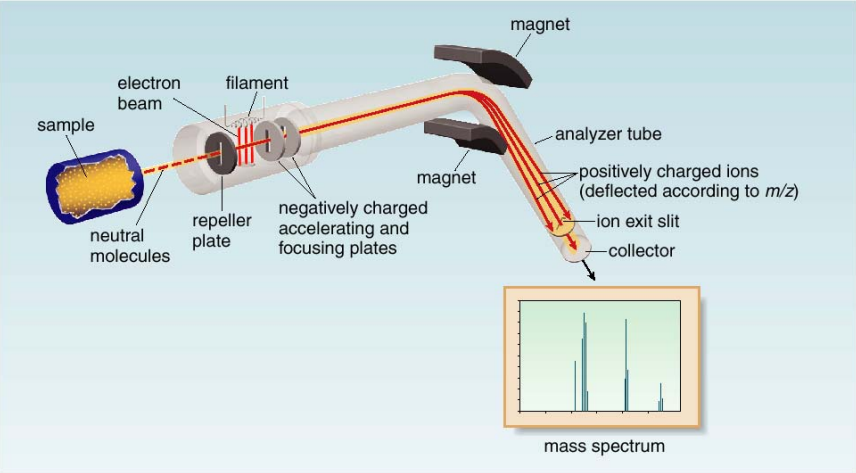
Mass Spectrometry

13.1 Mass Spectrometry

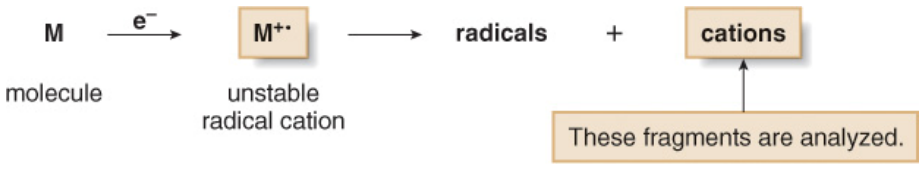
- **Mass spectrometry is a technique used for measuring the molecular weight and determining the molecular formula of an organic compound.**
- **In a mass spectrometer, a molecule is vaporized and ionized by bombardment with a beam of high-energy electrons.**
- **The energy of the electrons is ~ 1600 kcal (or 70 eV).**
- **Since it takes ~100 kcal of energy to cleave a typical σ bond, 1600 kcal is an enormous amount of energy to come into contact with a molecule.**
- **The electron beam ionizes the molecule by causing it to eject an electron.**

Figure 13.1 Schematic of a mass spectrometer



In a mass spectrometer, a sample is vaporized and bombarded by a beam of electrons to form an unstable radical cation, which then decomposes to smaller fragments. The positively charged ions are accelerated toward a negatively charged plate, and then passed through a curved analyzer tube in a magnetic field, where they are deflected by different amounts depending on their ratio of mass to charge (m/z). A mass spectrum plots the intensity of each ion versus its m/z ratio.

- **When the electron beam ionizes the molecule, the species that is formed is called a radical cation, and symbolized as $M^{+\bullet}$.**
- **The radical cation $M^{+\bullet}$ is called the molecular ion or parent ion.**
- **The mass of $M^{+\bullet}$ represents the molecular weight of M.**
- **Because M is unstable, it decomposes to form fragments of radicals and cations that have a lower molecular weight than $M^{+\bullet}$.**
- **The mass spectrometer analyzes the masses of cations.**
- **A mass spectrum is a plot of the amount of each cation (its relative abundance) versus its mass to charge ratio (m/z, where m is mass, and z is charge).**
- **Since z is almost always +1, m/z actually measures the mass (m) of the individual ions.**



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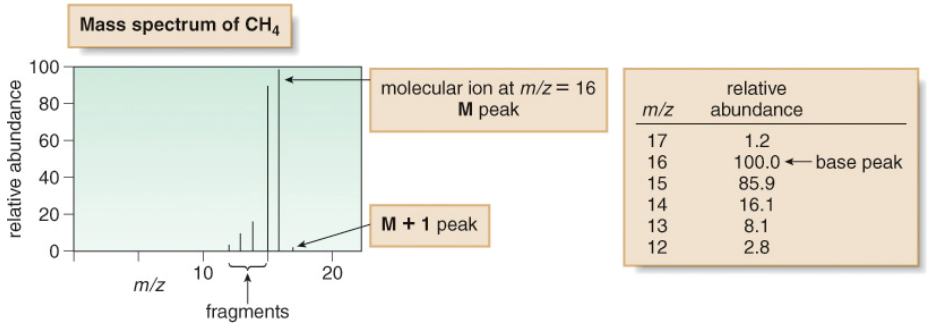
Consider the mass spectrum of CH_4 below:



m/z	relative abundance
17	1.2
16	100.0 ← base peak
15	85.9
14	16.1
13	8.1
12	2.8

- **The tallest peak in the mass spectrum is called the base peak.**
- **The base peak is also the M peak, although this may not always be the case.**
- **Though most C atoms have an atomic mass of 12, 1.1% have a mass of 13. Thus, $^{13}CH_4$ is responsible for the peak at m/z = 17. This is called the M + 1 peak.**

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- **The mass spectrum of CH_4 consists of more peaks than just the M peak.**
- **Since the molecular ion is unstable, it fragments into other cations and radical cations containing one, two, three, or four fewer hydrogen atoms than methane itself.**
- **Thus, the peaks at m/z 15, 14, 13 and 12 are due to these lower molecular weight fragments.**

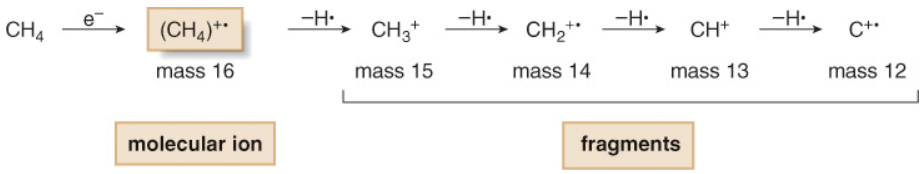

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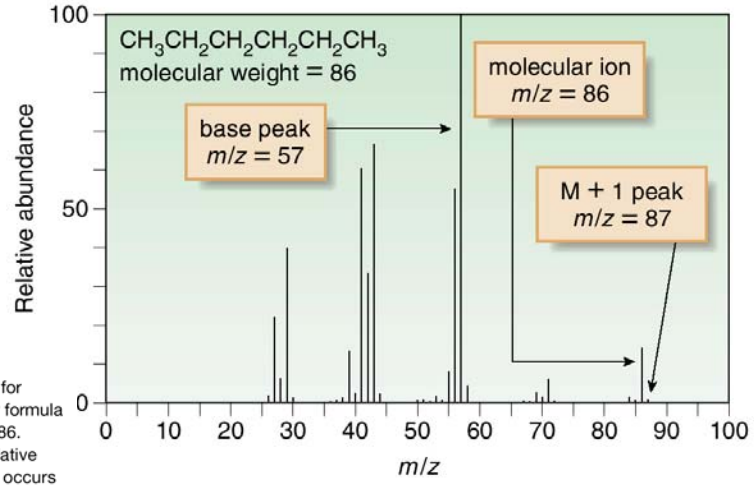
Figure 13.2 Mass spectrum of hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$)



- The molecular ion for hexane (molecular formula C_6H_{14}) is at $m/z = 86$.
- The base peak (relative abundance = 100) occurs at $m/z = 57$.
- A small M + 1 peak occurs at $m/z = 87$.

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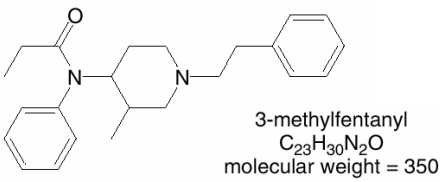
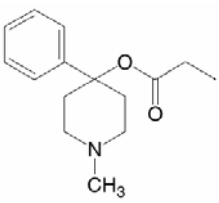
The Nitrogen Rule

- **Hydrocarbons like methane (CH_4) and hexane (C_6H_{14}), as well as compounds that contain only C, H, and O atoms, always have a molecular ion with an even mass.**
- **An odd molecular ion indicates that a compound has an odd number of nitrogen atoms.**
- **The effect of N atoms on the mass of the molecular ion in a mass spectrum is called the nitrogen rule: A compound that contains an odd number of N atoms gives an odd molecular ion. A compound that contains an even number of N atoms (including zero) gives an even molecular ion.**
- **Two "street" drugs that mimic the effect of heroin illustrate this principle.**



3-methylfentanyl
$C_{23}H_{30}N_2O$
molecular weight = 350



MPPP
(1-methyl-4-phenyl-4-propionoxypiperidine)
$C_{15}H_{21}NO_2$
molecular weight = 247

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13.2 Alkyl Halides and the M + 2 Peak

- **Most elements have one major isotope.**
- **Chlorine has two common isotopes, ^{35}Cl and ^{37}Cl, which occur naturally in a 3:1 ratio.**
  - **Thus, there are two peaks in a 3:1 ratio for the molecular ion of an alkyl chloride.**
  - **The larger peak, the M peak, corresponds to the compound containing the ^{35}Cl. The smaller peak, the M + 2 peak, corresponds to the compound containing ^{37}Cl.**
  - **Thus, when the molecular ion consists of two peaks (M and M + 2) in a 3:1 ratio, a Cl atom is present.**
- **Br has two isotopes—^{79}Br and ^{81}Br, in a ratio of ~1:1. Thus, when the molecular ion consists of two peaks (M and M + 2) in a 1:1 ratio, a Br atom is present.**

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Figure 13.3 Mass spectrum of 2-chloropropane [$(CH_3)_2CHCl$]

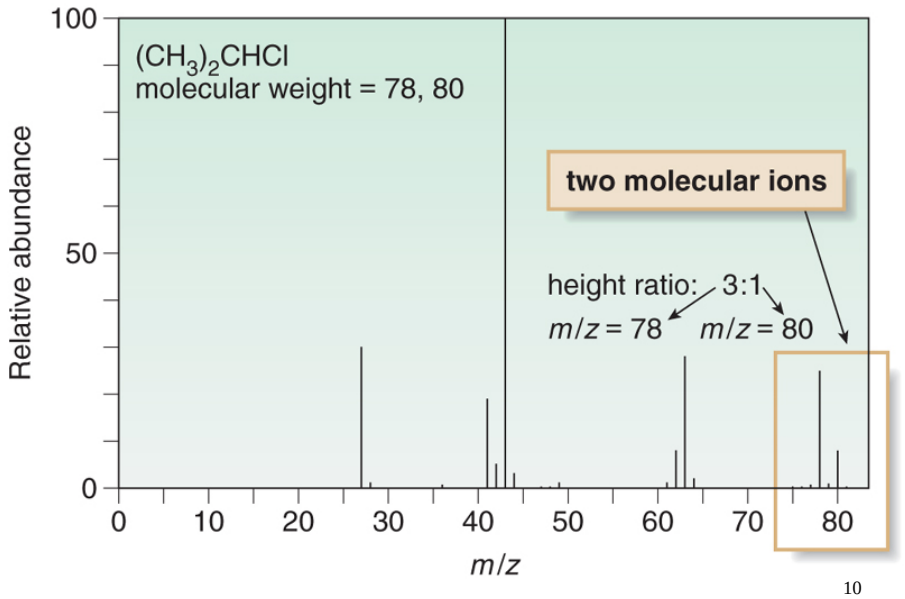

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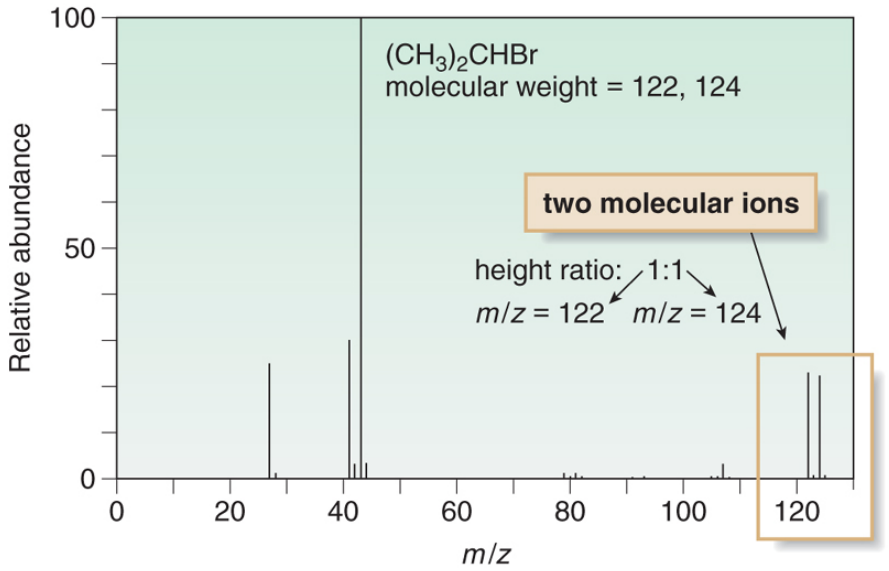
Figure 13.4 Mass spectrum of 2-bromopropane [$(CH_3)_2CHBr$]



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13.3 Other Types of Mass Spectrometry

13.3A High Resolution Mass Spectrometers

- **Low resolution mass spectrometers report *m/z* values to the nearest whole number. Thus, the mass of a given molecular ion can correspond to many different molecular formulas.**
- **High resolution mass spectrometers measure *m/z* ratios to four (or more) decimal places.**
  - **This is valuable because except for ^{12}C whose mass is defined as 12.0000, the masses of all other nuclei are very close—but not exactly—whole numbers.**
  - **Table 13.1 lists the exact mass values for a few common nuclei. Using these values it is possible to determine the single molecular formula that gives rise to a molecular ion.**

Table 13.1

Exact Masses of Some Common Isotopes

Isotope	Mass
^{12}C	12.0000
^{1}H	1.00783
^{16}O	15.9949
^{14}N	14.0031

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High-Resolution Mass Spectrometers

- **Consider a compound having a molecular ion at *m/z* = 60 using a low-resolution mass spectrometer. The molecule could have any one of the following molecular formulas.**

Formula	Exact mass
C_3H_8O	60.0575
$C_2H_4O_2$	60.0211
$C_2H_8N_2$	60.0688

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13.3B Gas Chromatography—Mass Spectrometry (GC-MS)

- **Mass spectrometry can be combined with gas chromatography into a single instrument used to analyze mixtures of compounds.**
- **A gas chromatograph (GC) consists of a thin capillary column containing a viscous high-boiling liquid, all housed in an oven. When the sample is injected into the GC, it is vaporized and swept by an inert gas through the column.**
- **The components travel through the column at different rates, often separated by boiling point, with lower boiling compounds exiting the column before higher boiling compounds.**
- **Each component then enters the mass spectrometer where it is ionized to form a molecular ion and lower molecular weight fragments**
- **The GC-MS records a gas chromatogram of the mixture, and yields a plot of the amount of each component versus its retention time (the time required to travel through the column), and its molecular ion in the mass spectrum.**

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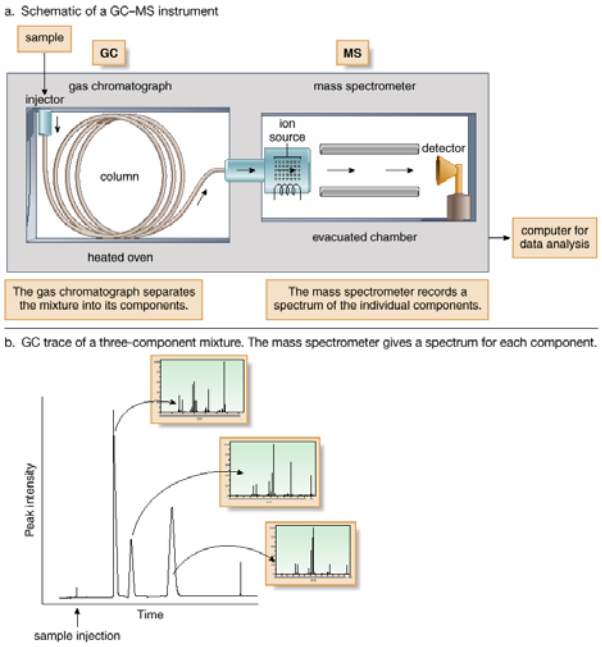
Figure 13.5 Compound analysis using GC–MS



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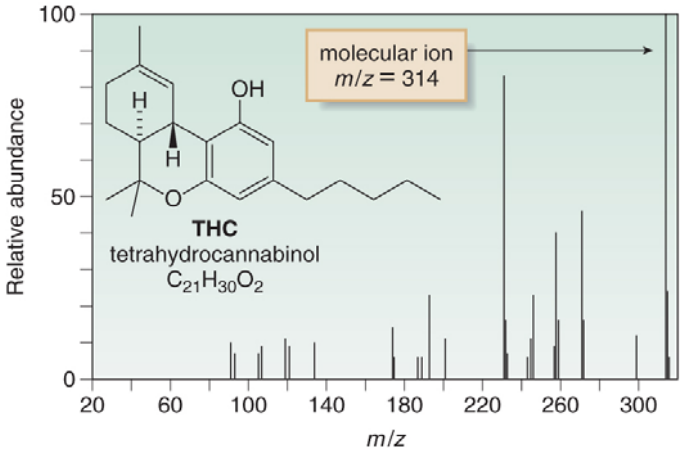
- **To analyze a urine sample for tetrahydrocannabinol, (THC) the principal psychoactive component of marijuana, the organic compounds are extracted from urine, purified, concentrated and injected into the GC-MS.**
- **THC appears as a GC peak, and gives a molecular ion at 314, its molecular weight.**

Figure 13.6 Mass spectrum of tetrahydrocannabinol (THC)



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Infrared Spectroscopy

13.4 Electromagnetic Radiation

- **Electromagnetic radiation is radiant energy having dual properties of both waves and particles.**
- **Particles of electromagnetic radiation are called photons, and each has a discrete amount of energy called a quantum.**
- **Electromagnetic radiation can be characterized by its wavelength and frequency.**

- **Wavelength (λ) is the distance from one point on a wave to the same point on an adjacent wave.**
- **Frequency (ν) is the number of waves passing per unit time. It is reported in cycles per second (s^{-1}), which is also called hertz (Hz).**

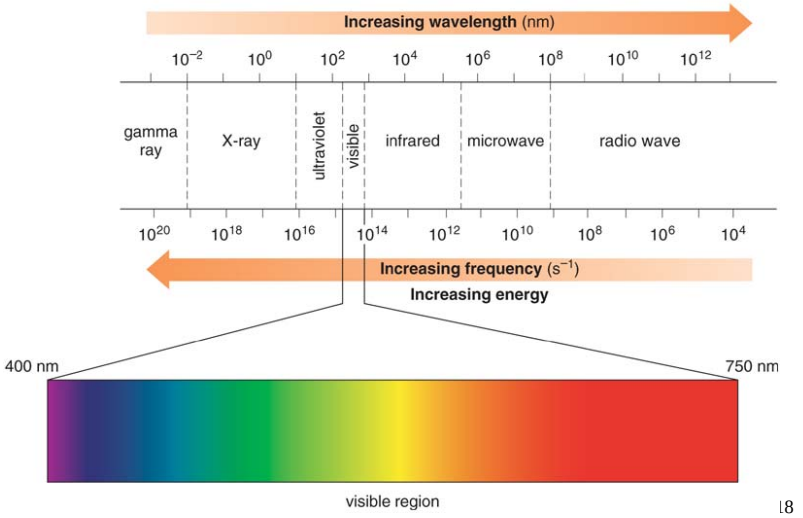
Length units used to report wavelength include:

Unit	Length
meter (m)	1 m
centimeter (cm)	10^{-2} m
micrometer (μm)	10^{-6} m
nanometer (nm)	10^{-9} m
Angstrom (Å)	10^{-10} m

- **The different forms of electromagnetic radiation make up the electromagnetic spectrum.**

Figure 13.7 The electromagnetic spectrum

- Visible light occupies only a small region of the electromagnetic spectrum.



- **The electromagnetic spectrum is arbitrarily divided into different regions.**
- **All electromagnetic radiation travels at the speed of light (*c*), 3.0 x 10^8 m/s.**
- **The speed of electromagnetic radiation (*c*) is directly proportional to its wavelength and frequency:**

$$c = \lambda\nu$$

- **The speed of light (*c*) is a constant, so wavelength and frequency are inversely related:**

$\lambda = c/\nu$ **: Wavelength increases as frequency decreases.**

$\nu = c/\lambda$ **: Frequency increases as wavelength decreases.**

- **The energy (*E*) of a photon is directly proportional to its frequency:**

$E = h\nu$ **;** ***h*** **= Planck's constant (1.58 x 10^{-34} cal•s)**

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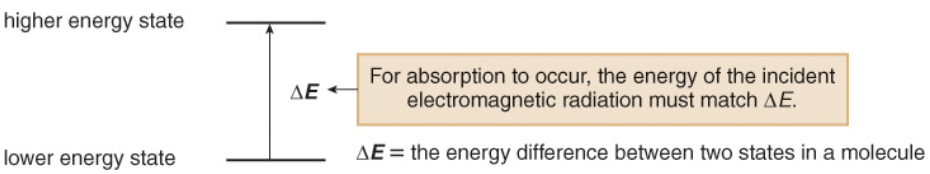
- **Frequency and wavelength are inversely proportional ($\nu = c/\lambda$). Thus, energy and wavelength are inversely proportional.**

$$E = h\nu = hc/\lambda$$

- **E increases as ν increases**
- **E decreases as λ increases**

- **When electromagnetic radiation strikes a molecule, some wavelengths, but not all, are absorbed.**
- **For absorption to occur, the energy of the photon must match the difference between two energy states in the molecule.**



- **The larger the energy difference between two states, the higher the energy of radiation needed for absorption, the higher the frequency, and the shorter the wavelength.**

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13.5 Infrared Spectroscopy

13.5A Background

- **Infrared (IR) spectroscopy is used to identify the functional groups in a compound.**
- **IR radiation is the energy source used in IR spectroscopy.**
- **Frequencies in IR spectroscopy are reported using a unit called wavenumber ($\tilde{\nu}$):**

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

- **Wavenumber is inversely proportional to wavelength and is reported in reciprocal centimeters (cm^{-1}).**
- **Frequency (and therefore, energy) increases as the wavenumber increases.**
- **Using the wavenumber scale, IR absorptions occur from 4000 cm^{-1}– 400 cm^{-1}.**

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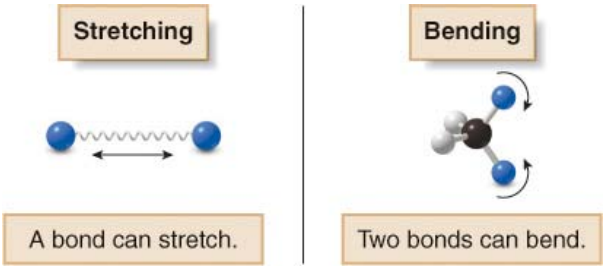
- **Absorption of IR light causes changes in the vibrational motions of a molecule.**
- **The different vibrational modes available to a molecule include stretching and bending modes.**



- **The vibrational modes of a molecule are quantized, so they occur only at specific frequencies which correspond to the frequency of IR light.**

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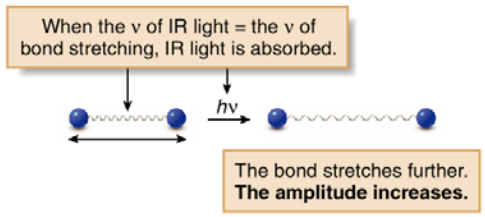
- **When the frequency of IR light matches the frequency of a particular vibrational mode, the IR light is absorbed, causing the amplitude of the particular bond stretch or bond bend to increase.**



- Different kinds of bonds vibrate at different frequencies, so they absorb different frequencies of IR light.
- IR spectroscopy distinguishes between the different kinds of bonds in a molecule, so it is possible to determine the functional groups present.

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13.5B Characteristics of an IR Spectrum

- **In an IR spectrometer, light passes through a sample.**
- **Frequencies that match the vibrational frequencies are absorbed, and the remaining light is transmitted to a detector.**
- **An IR spectrum is a plot of the amount of transmitted light versus its wavenumber.**

Let us now consider the IR spectrum of 1-propanol, $CH_3CH_2CH_2OH$.

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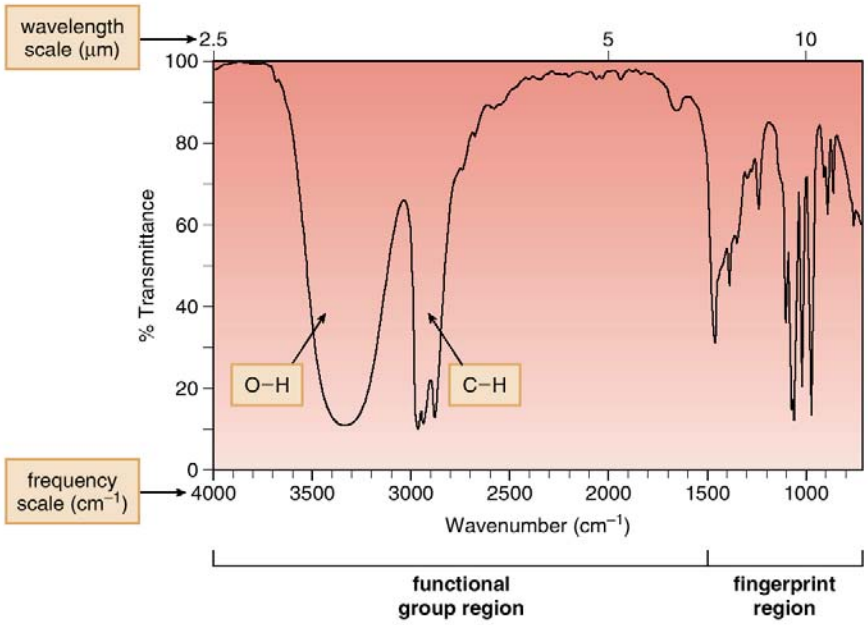
Characteristics of an IR Spectrum—1-Propanol



- **The *y*-axis is % transmittance: 100% transmittance means that all the light shone on a sample is transmitted and none is absorbed. 0% transmittance means that none of the light shone on the sample is transmitted and all is absorbed.**
- **Each peak corresponds to a particular kind of bond, and each bond type (such as O—H and C—H) occurs at a characteristic frequency.**
- **Wavenumber, frequency and energy decrease from left to right.**
- **Where a peak occurs is reported in reciprocal centimeters (cm^{-1}).**

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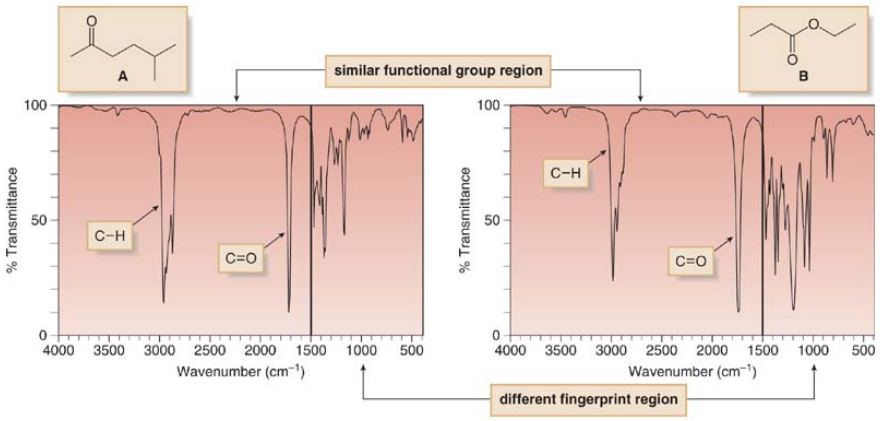
- **The IR spectrum is divided into two regions: the functional group region (at ≥ 1500 cm^{-1}), and the fingerprint region (at < 1500 cm^{-1}).**

Figure 13.8 Comparing the functional group region and fingerprint region of two compounds



- **A** and **B** show peaks in the same regions for their C=O group and sp^3 hybridized C–H bonds.
- **A** and **B** are different compounds, so their fingerprint regions are quite different.

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13.6 IR Absorptions

- **Where a particular bond absorbs in the IR depends on bond strength and atom mass.**
- **Stronger bonds vibrate at a higher frequency, so they absorb at higher wavenumbers.**
- **Bonds with lighter atoms vibrate at higher frequency, so they absorb at higher wavenumbers.**
- **Bonds can be thought of as springs with weights on each end.**
- **The strength of the spring is analogous to the bond strength, and the mass of the weights is analogous to atomic mass.**
- **For two springs with the same weight on each end, the stronger spring vibrates at a higher frequency.**
- **For two springs of the same strength, springs with lighter weights vibrate at a higher frequency than those with heavier weights.**

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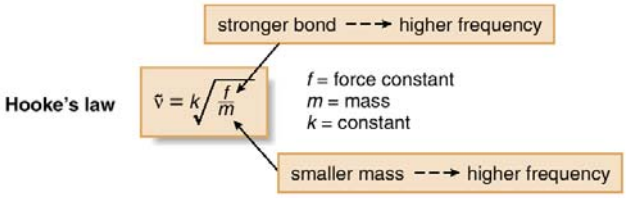
- **Hooke's Law describes the relationship of frequency to mass and bond length.**

Figure 13.9 Hook's law: How the frequency of bond vibration depends on atom mass and bond strength

The frequency of bond vibration can be derived from Hooke's law, which describes the motion of a vibrating spring:



- The force constant (f) is the strength of the bond (or spring). The larger the value of f, the stronger the bond, and the higher the $\tilde{\nu}$ of vibration.
- The mass (m) is the mass of atoms (or weights). The smaller the value of m, the higher the $\tilde{\nu}$ of vibration.

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- **Bonds absorb in four predictable regions of an IR spectrum.**

Figure 13.10 Summary: The four regions of the IR spectrum

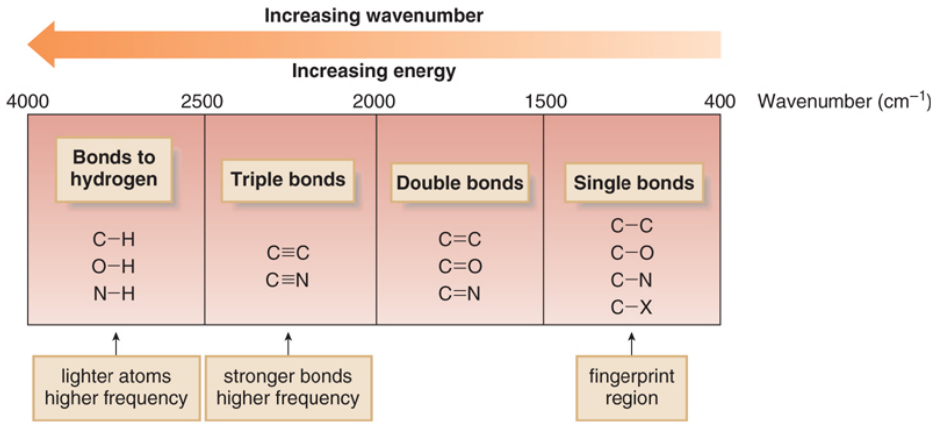

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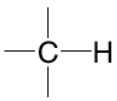
Table 13.2 Important IR Absorptions

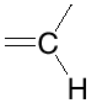
Bond type	Approximate $\tilde{\nu}$ (cm^{-1})	Intensity
O–H	3600–3200	strong, broad
N–H	3500–3200	medium
C–H	~3000	
• C_{sp^3}–H	3000–2850	strong
• C_{sp^2}–H	3150–3000	medium
• C_{sp}–H	3300	medium
C≡C	2250	medium
C≡N	2250	medium
C=O	1800–1650 (often ~1700)	strong
C=C	1650	medium
	1600, 1500	medium

- **Even subtle differences that affect bond strength affect the frequency of an IR absorption.**



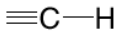
C_{sp^3}–H

25% *s*-character



C_{sp^2}–H

33% *s*-character



C_{sp}–H

50% *s*-character

Increasing percent *s*-character
Increasing $\tilde{\nu}$

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

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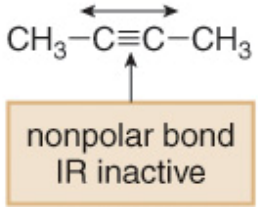
- **For a bond to absorb in the IR, there must be a change in dipole moment during the vibration.**
- **Symmetrical nonpolar bonds do not absorb in the IR. This type of vibration is said to be IR inactive.**

Stretching along the bond axis does not change the dipole moment.



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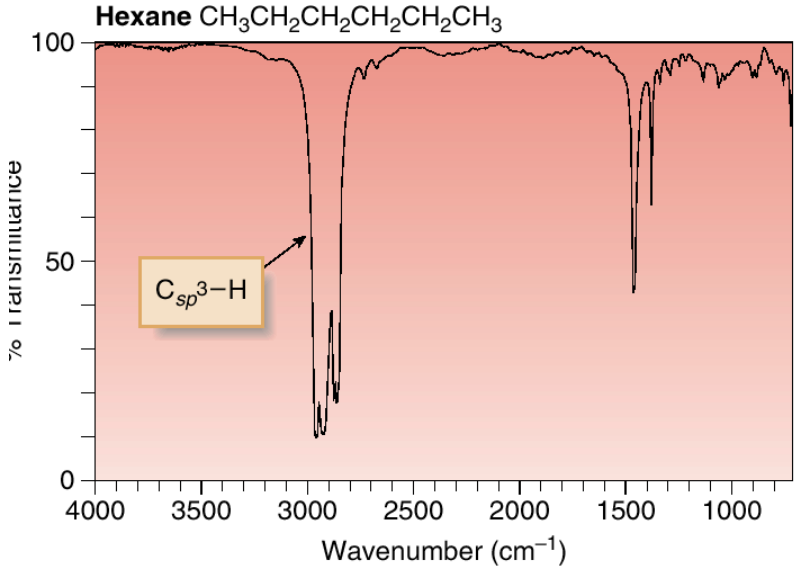
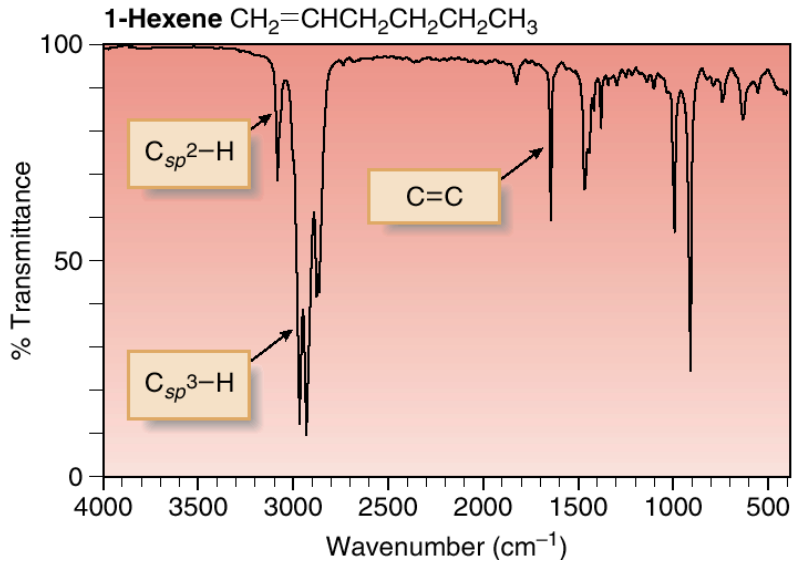
13.6B IR Absorptions in Hydrocarbons

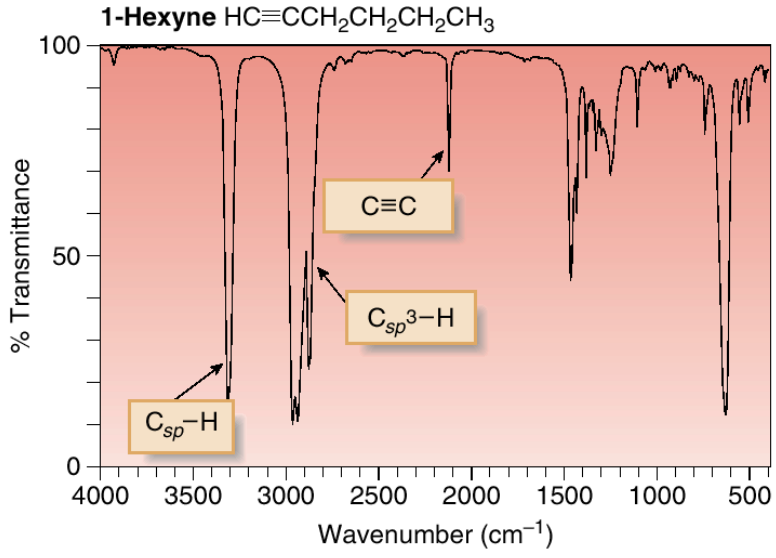
Hexane has only C-C single bonds and *sp*³ hybridized C atoms. Therefore it has only one major absorption at 3000-2850 cm⁻¹.



1-Hexene has a C=C and C_{sp}2-H, in addition to sp^3 hybridized C atoms. Therefore, there are three major absorptions: C_{sp}2-H at 3150-3000 cm^{-1}; C_{sp}3-H at 3000-2850 cm^{-1}; C=C at 1650 cm^{-1}.

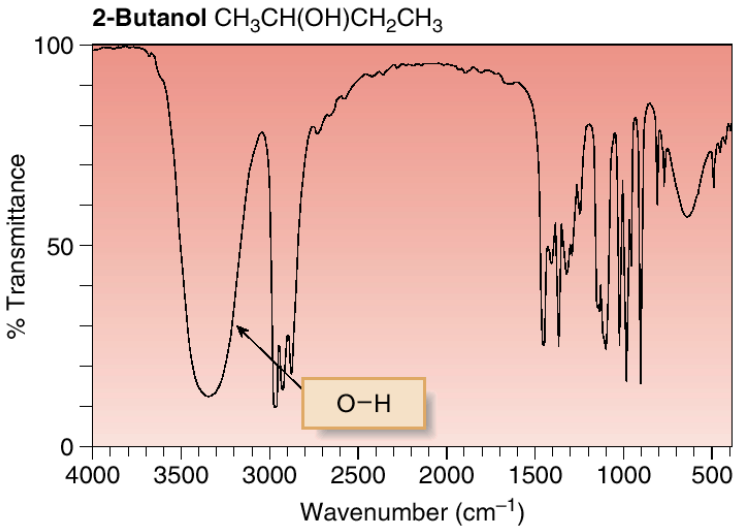


1-Hexyne has a C≡C and C_{sp}-H, in addition to sp^3 hybridized C atoms. Therefore, there are three major absorptions: C_{sp}-H at 3300 cm^{-1}; C_{sp}3-H at 3000-2850 cm^{-1}; C≡C at 2250 cm^{-1}.

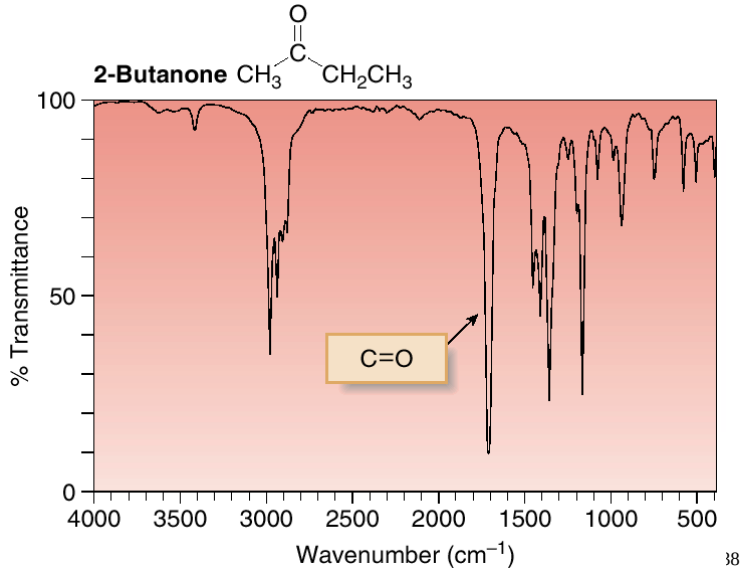


13.6C IR Absorptions in Oxygen Containing Compounds

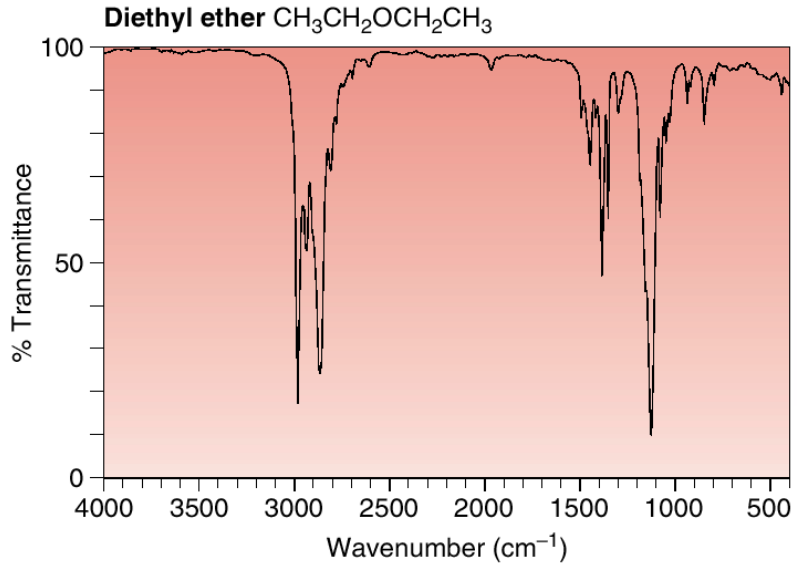
The OH group of the alcohol shows a strong absorption at 3600-3200 cm^{-1}. The peak at ~3000 cm^{-1} is due to sp^3 hybridized C—H bonds.



The C=O group in the ketone shows a strong absorption at ~1700 cm^{-1}. The peak at ~3000 cm^{-1} is due to sp^3 hybridized C—H bonds.

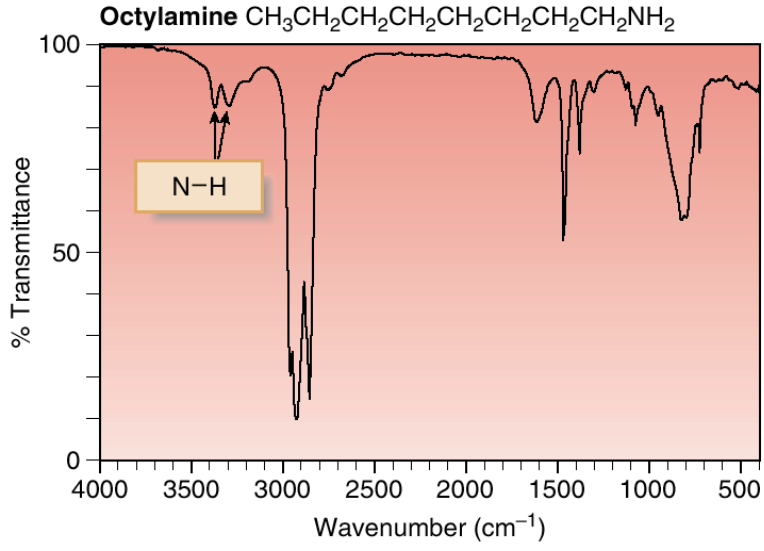


The ether has neither an OH or a C=O, so its only absorption above 1500 cm^{-1} occurs at ~3000 cm^{-1}, due to sp^3 hybridized C—H bonds.

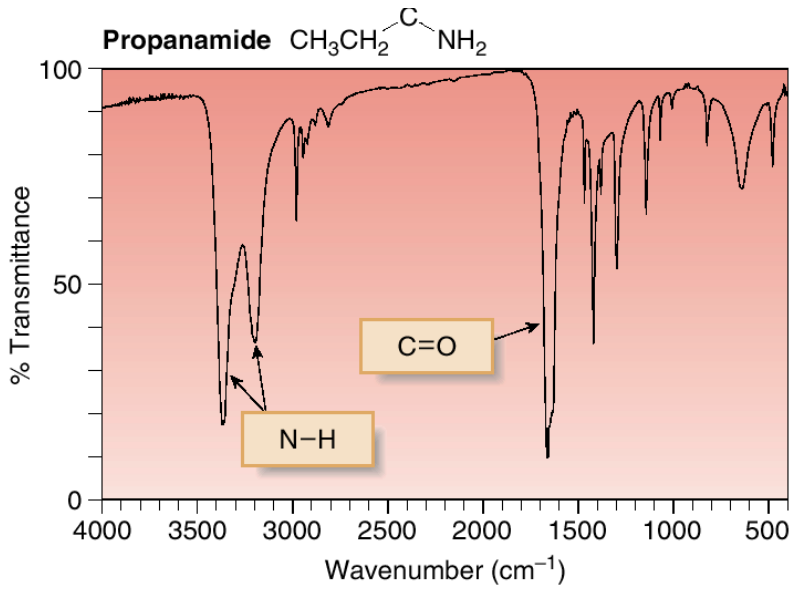


13.6D IR Absorptions in Nitrogen Containing Compounds

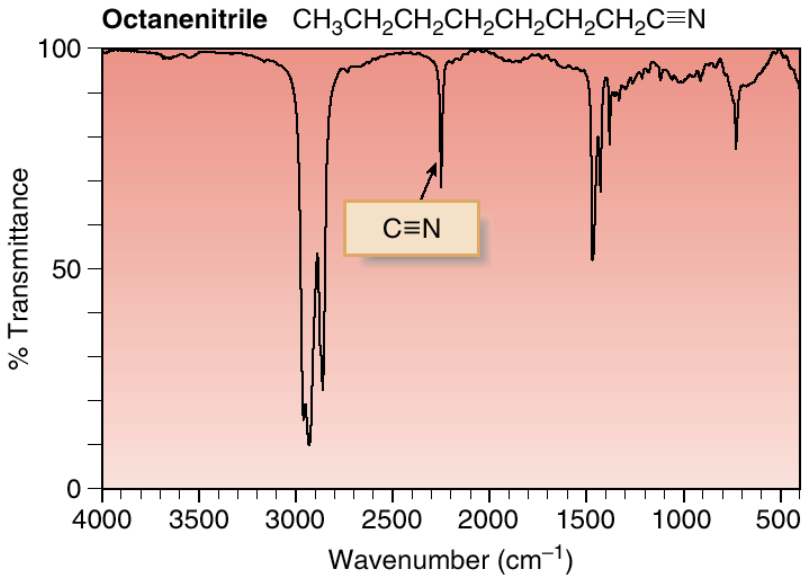
The N—H bonds in the amine give rise to two weak absorptions at 3300 and 3400 cm^{-1}.



The amide exhibits absorptions above 1500 cm^{-1} for both its N—H and C=O groups: N—H (two peaks) at 3200 and 3400 cm^{-1}; C=O at 1660 cm^{-1}.



The C≡N of the nitrile absorbs in the triple bond region at ~2250 cm^{-1}.



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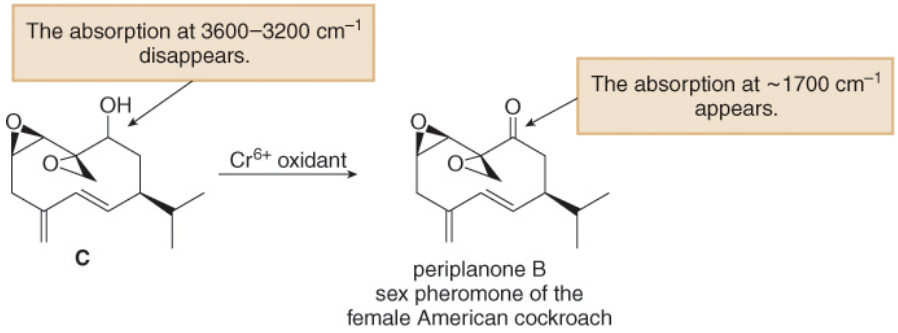
13.7 IR and Structure Determination

IR spectroscopy is often used to determine the outcome of a chemical reaction. For example, oxidation of the hydroxy group in compound C to form the carbonyl group in periplanone B is accompanied by the disappearance of the OH absorption, and the appearance of a carbonyl absorption in the IR spectrum of the product.



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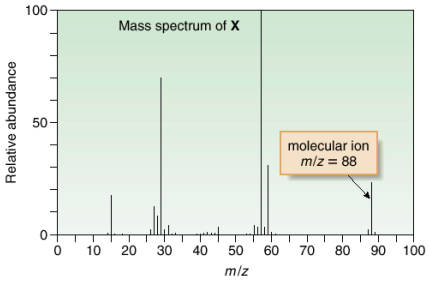
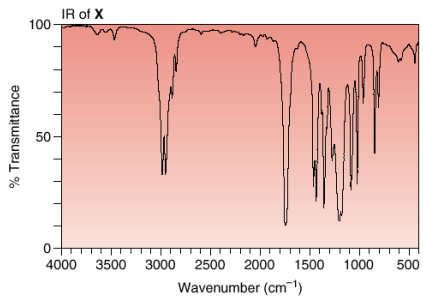
How To **Use MS and IR for Structure Determination**

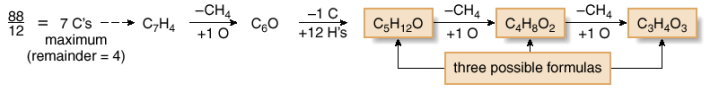
Example What information is obtained from the mass spectrum and IR spectrum of an unknown compound **X**? Assume **X** contains the elements C, H, and O.





Step [1] **Use the molecular ion to determine possible molecular formulas. Use an exact mass (when available) to determine a molecular formula.**

- Use the procedure outlined in Sample Problem 13.2 to calculate possible molecular formulas. For a molecular ion at m/z = 88:



- Discounting C_7H_4 (a hydrocarbon) and C_6O (because it contains no H's) gives three possible formulas for **X.**
- If high-resolution mass spectral data are available, the molecular formula can be determined directly. If the molecular ion had an exact mass of 88.0580, the molecular formula of **X** is **$C_4H_8O_2$** (exact mass = 88.0524) rather than $C_5H_{12}O$ (exact mass = 88.0888) or $C_3H_4O_3$ (exact mass = 88.0160).

Step [2] **Calculate the number of degrees of unsaturation (Section 10.2).**

- For a compound of molecular formula $C_4H_8O_2$, the maximum number of H's = $2n + 2 = 2(4) + 2 = 10$.
- Because the compound contains only 8 H's, it has 10 – 8 = 2 H's fewer than the maximum number.
- Because each degree of unsaturation removes 2 H's, **X** has one degree of unsaturation. **X has one ring or one π bond.**

Step [3] **Determine what functional group is present from the IR spectrum.**

- The two major absorptions in the IR spectrum above 1500 cm^{-1} are due to sp^3 hybridized C–H bonds (~3000–2850 cm^{-1}) and a C=O group (1740 cm^{-1}). Thus, the one degree of unsaturation in **X** is due to the presence of the **C=O.**

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