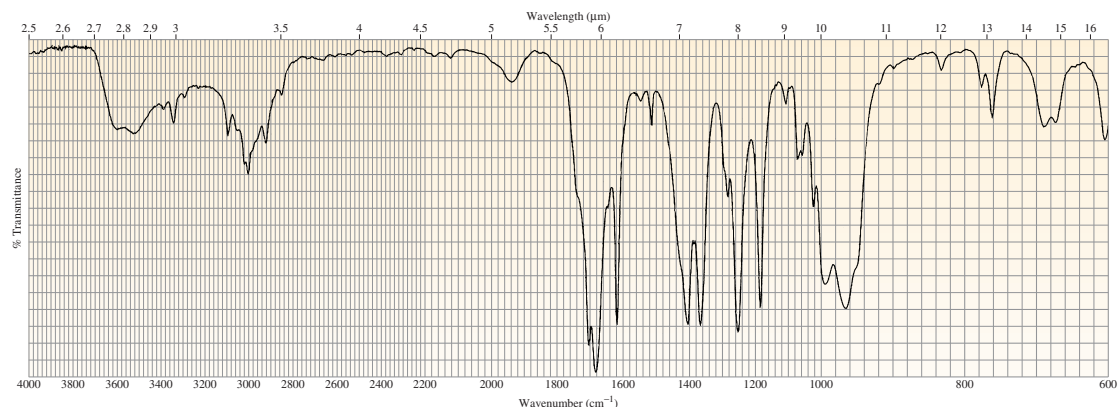


▲ **Figure 13.33**
The IR spectrum of Compound 5.

PROBLEM 29◆

A compound with molecular formula C_4H_6O gives the infrared spectrum shown in Figure 13.34. Identify the compound.



▲ **Figure 13.34**
The IR spectrum for Problem 29.

Summary

Mass spectrometry allows us to determine the *molecular mass* and the *molecular formula* of a compound, as well as certain structural features. In mass spectrometry, a small sample of the compound is vaporized and then ionized as a result of an electron's being removed from each molecule, producing a **molecular ion**—a radical cation. Many of the molecular ions break apart into cations, radicals, neutral molecules, and other radical cations. The bonds most likely to break are the weakest ones and those that result in the formation of the most stable products. The mass spectrometer records a **mass spectrum**—a graph of the relative abundance of each positively charged fragment, plotted against its m/z value.

The molecular ion (M) peak is due to the fragment that results when an electron is knocked out of a molecule; the m/z

value of a molecular ion gives the molecular mass of the compound. The “nitrogen rule” states that if a compound has an odd-mass molecular ion, the compound contains an odd number of nitrogen atoms. Peaks with smaller m/z values—**fragment ion peaks**—represent positively charged fragments of the molecule. The **base peak** is the peak with the greatest intensity. High-resolution mass spectrometers determine the exact molecular mass, which allows a compound's molecular formula to be determined.

The $M + 1$ peak occurs because there are two naturally occurring isotopes of carbon. The number of carbon atoms in a compound can be calculated from the relative intensities of the M and $M + 1$ peaks. A large $M + 2$ peak is evidence of a compound containing either chlorine or bromine; if it is one-third the height of the M peak, the compound contains

one chlorine atom; if the M and $M + 2$ peaks are about the same height, the compound contains one bromine atom.

Characteristic fragmentation patterns are associated with specific functional groups. Electron bombardment is most likely to dislodge a lone-pair electron. A bond between carbon and a more electronegative atom breaks *heterolytically*, with the electrons going to the more electronegative atom. A bond between carbon and an atom of similar electronegativity breaks homolytically; α cleavage occurs because the species that is formed is a resonance-stabilized cation.

Spectroscopy is the study of the interaction of matter and **electromagnetic radiation**. A continuum of different types of electromagnetic radiation constitutes the electromagnetic spectrum. High-energy radiation is associated with *high frequencies, large wavenumbers, and short wavelengths*.

Infrared spectroscopy identifies the kinds of functional groups in a compound. Bonds vibrate with stretching and bending motions. Each stretching and bending vibration occurs with a characteristic frequency. It takes more energy to stretch a bond than to bend it. When a compound is bom-

barded with radiation of a frequency that exactly matches the frequency of one of its vibrations, the molecule absorbs energy and exhibits an **absorption band**. The **functional group region** of an IR spectrum ($4000\text{--}1400\text{ cm}^{-1}$) is where most of the functional groups show absorption bands; the **fingerprint region** ($1400\text{--}600\text{ cm}^{-1}$) is characteristic of the compound as a whole.

The position, intensity, and shape of an absorption band help identify functional groups. The amount of energy required to stretch a bond depends on the *strength* of the bond: Stronger bonds show absorption bands at larger wavenumbers. Therefore, the frequency of the absorption depends on bond order, hybridization, electronic, and resonance effects. The frequency is inversely related to the *mass* of the atoms, so heavier atoms vibrate at lower frequencies. The intensity of an absorption band depends on the size of the change in dipole moment associated with the vibration and on the number of bonds responsible for the absorption. In order for a vibration to absorb IR radiation, the dipole moment of the molecule must change when the vibration occurs.

Key Terms

absorption band (p. 500)

base peak (p. 486)

bending vibration (p. 499)

α cleavage (p. 490)

electromagnetic radiation (p. 497)

fingerprint region (p. 501)

fragment ion peak (p. 485)

frequency (p. 497)

functional group region (p. 501)

Hooke's law (p. 503)

infrared radiation (p. 500)

infrared spectroscopy (p. 483)

infrared spectrum (p. 500)

mass spectrometry (p. 483)

mass spectrum (p. 485)

McLafferty rearrangement (p. 494)

molecular ion (p. 484)

nominal molecular mass (p. 485)

radical cation (p. 484)

spectroscopy (p. 497)

stretching frequency (p. 502)

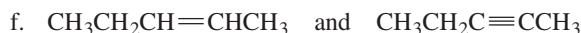
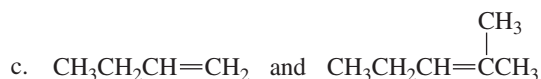
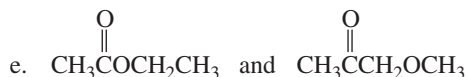
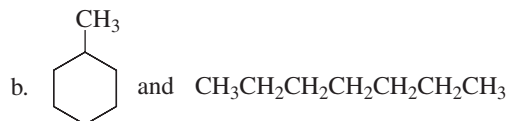
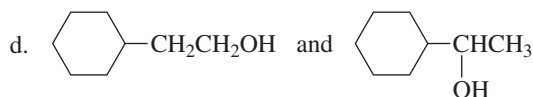
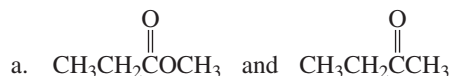
stretching vibration (p. 499)

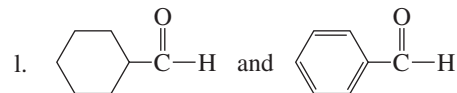
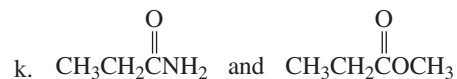
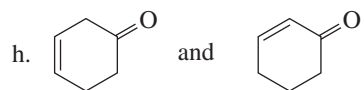
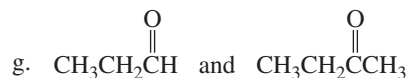
wavelength (p. 497)

wavenumber (p. 498)

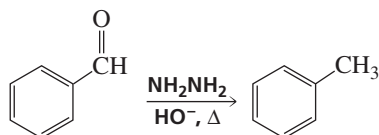
Problems

30. Which peak would be more intense in the mass spectrum of the following compounds—the peak at $m/z = 57$ or the peak at $m/z = 71$?
- a. 3-methylpentane
- b. 2-methylpentane
31. List three factors that influence the intensity of an IR absorption band.
32. For each of the following pairs of compounds, identify one IR absorption band that could be used to distinguish between them:

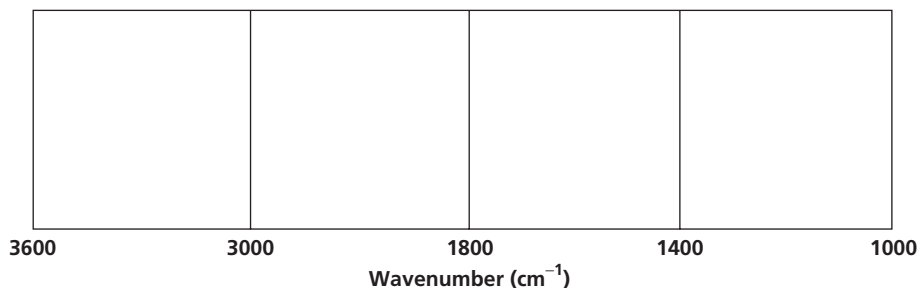




33. a. How could you determine by IR spectroscopy that the following reaction had occurred?

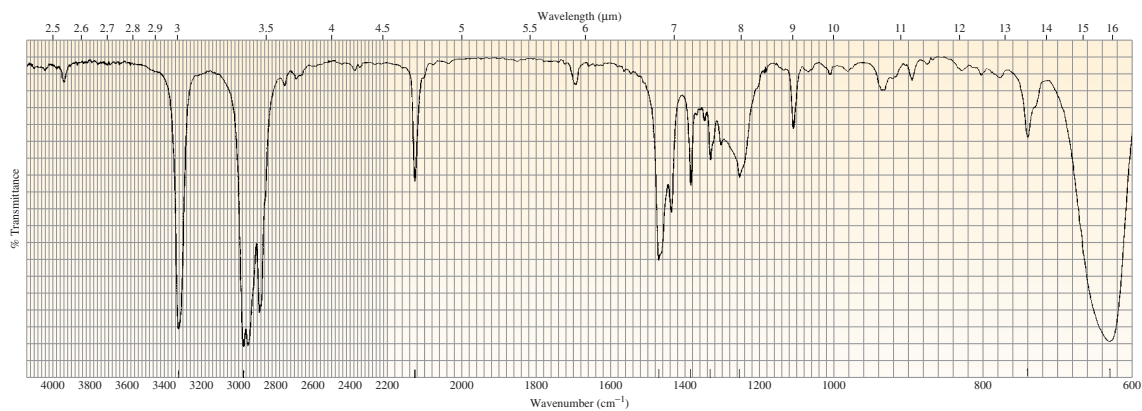


- b. After purifying the product, how could you determine that all the NH_2NH_2 had been removed?
34. What identifying characteristics would be present in the mass spectrum of a compound containing two bromine atoms?
35. Assuming that the force constant is approximately the same for C—C, C—N, and C—O bonds, predict the relative positions of their stretching vibrations.
36. A mass spectrum shows significant peaks at $m/z = 87, 115, 140,$ and 143 . Which of the following compounds is responsible for that mass spectrum: 4,7-dimethyl-1-octanol, 2,6-dimethyl-4-octanol, or 2,2,4-trimethyl-4-heptanol?
37. How could IR spectroscopy distinguish between 1,5-hexadiene and 2,4-hexadiene?
38. A compound gives a mass spectrum with peaks at $m/z = 77$ (40%), 112 (100%), 114 (33%), and essentially no other peaks. Identify the compound.
39. What hydrocarbons will have a molecular ion peak at $m/z = 112$?
40. In the following boxes, list the types of bonds and the approximate wavenumber at which each type of bond is expected to show an IR absorption:

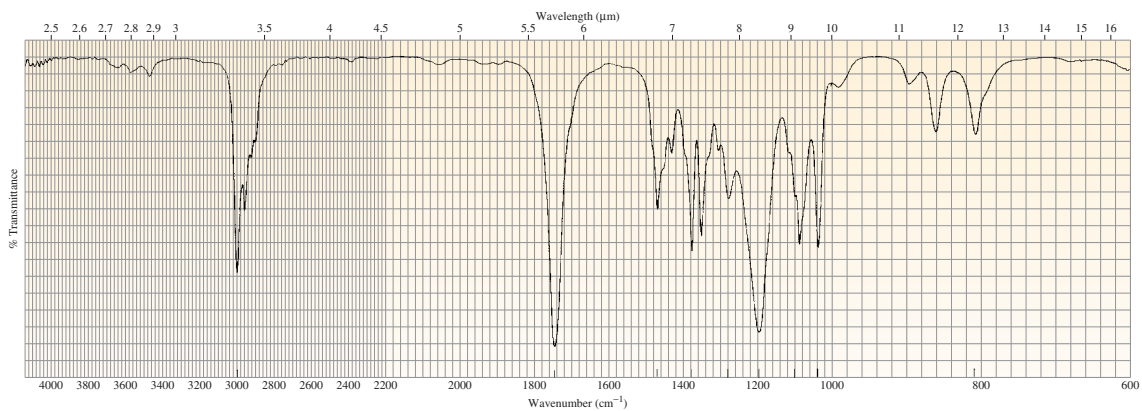
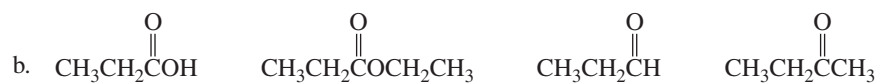


41. For each of the IR spectra in Figures 13.35, 13.36, and 13.37, four compounds are shown. In each case, indicate which of the four compounds is responsible for the spectrum.

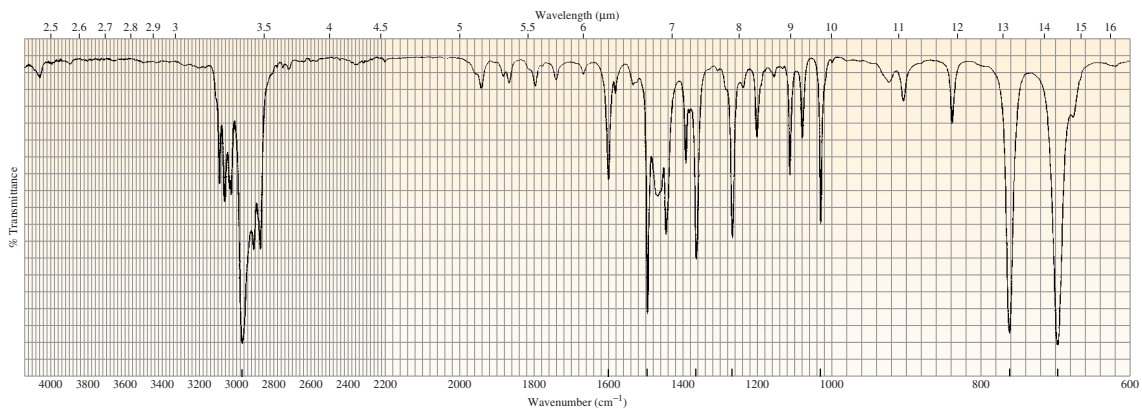
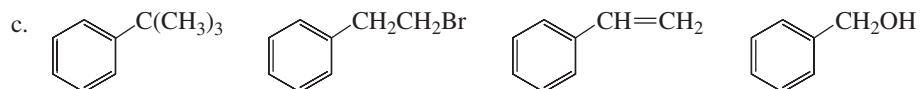




▲ **Figure 13.35**
The IR spectrum for Problem 41a.

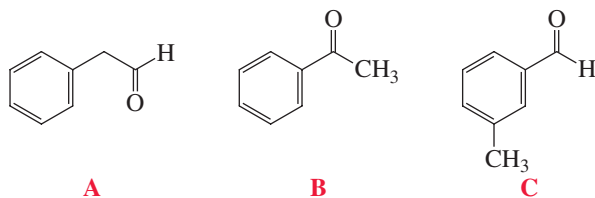


▲ **Figure 13.36**
The IR spectrum for Problem 41b.



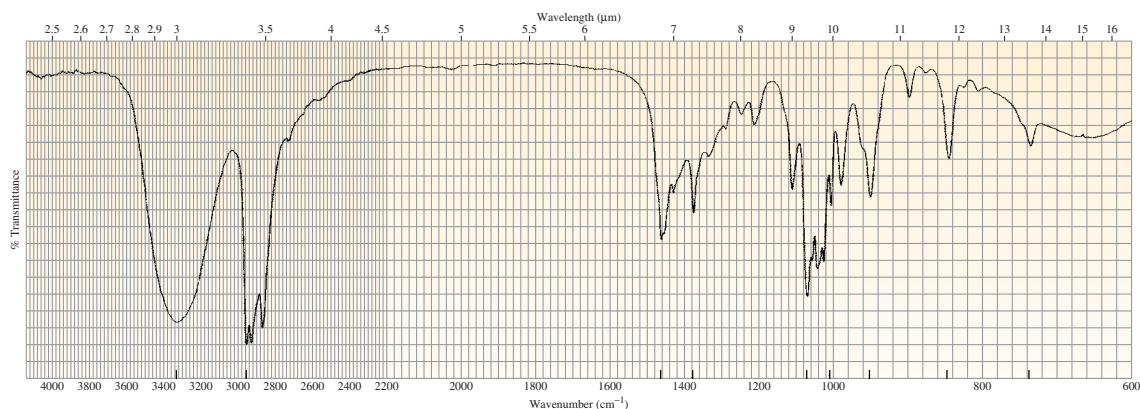
▲ **Figure 13.37**
The IR spectrum for Problem 41c.

42. What peaks in their mass spectra would be used to distinguish between 4-methyl-2-pentanone and 2-methyl-3-pentanone?
43. A compound is known to be one of those shown here. What absorption bands in the compound's IR spectrum would allow you to identify the compound.

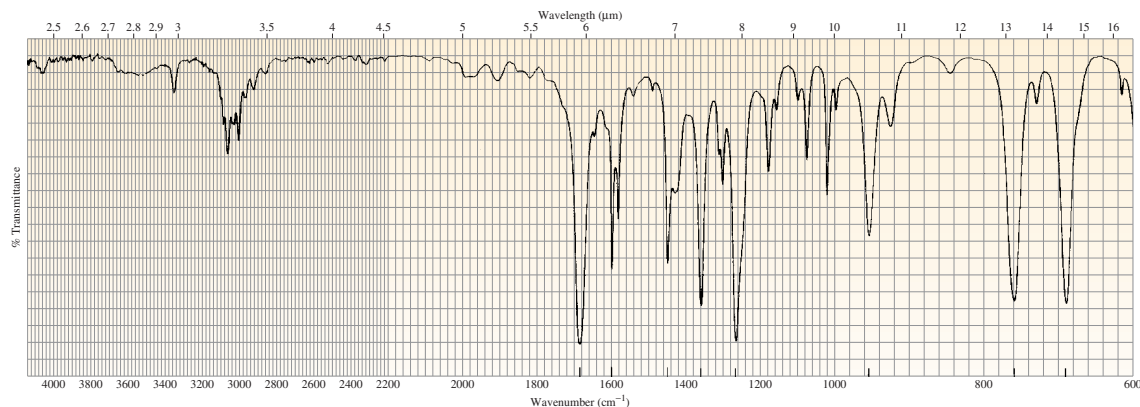
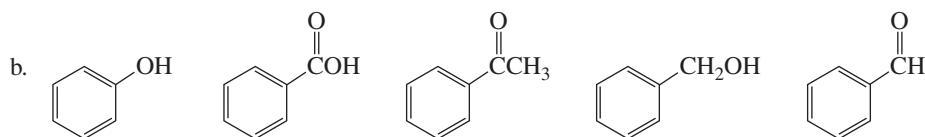


44. How could IR spectroscopy distinguish among 1-hexyne, 2-hexyne, and 3-hexyne?
45. For each of the IR spectra in Figures 13.38, 13.39, and 13.40, indicate which of the five given compounds is responsible for the spectrum.

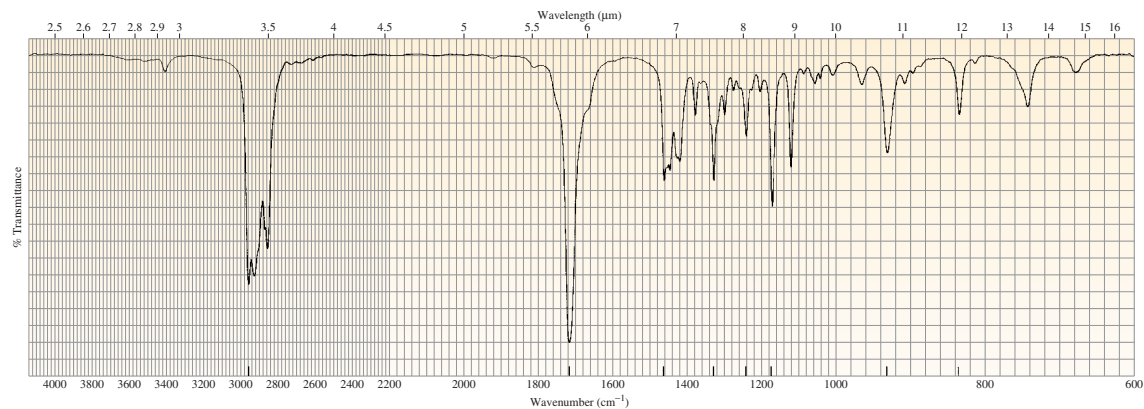
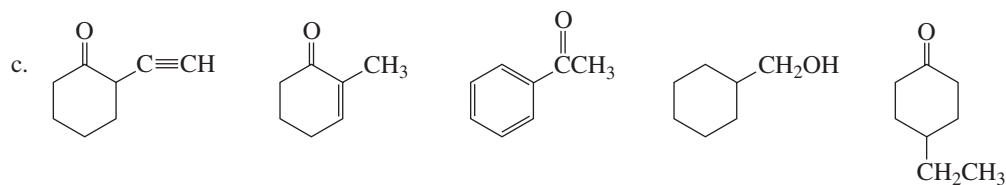
- a. $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$



▲ **Figure 13.38**
The IR spectrum for Problem 45a.



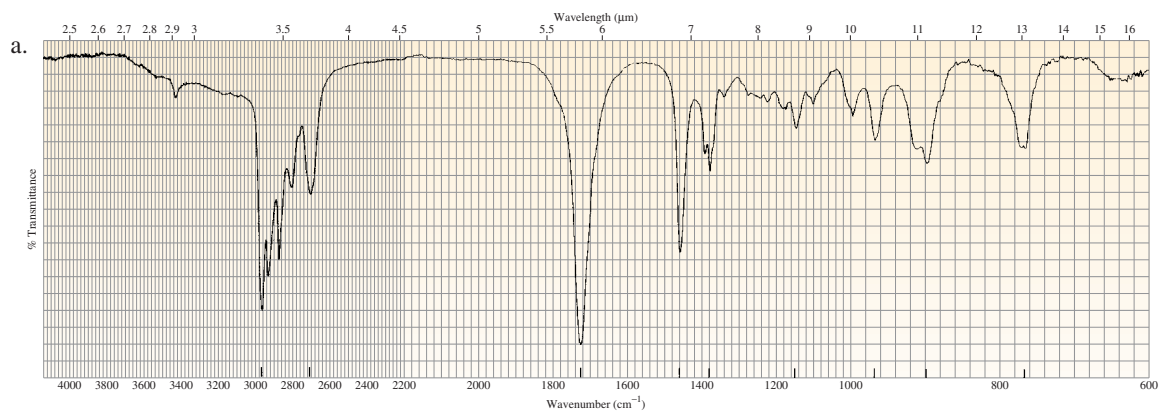
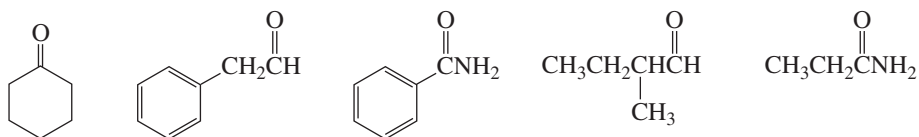
▲ **Figure 13.39**
The IR spectrum for Problem 45b.



▲ Figure 13.40

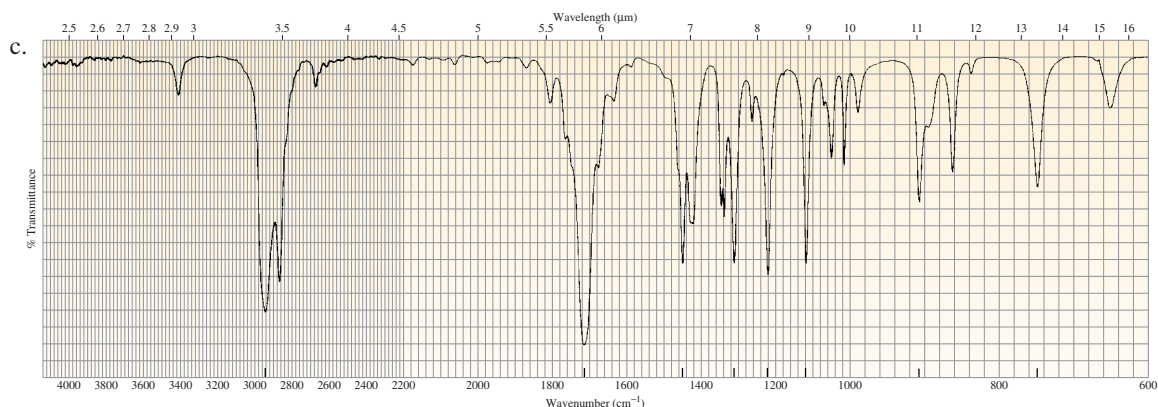
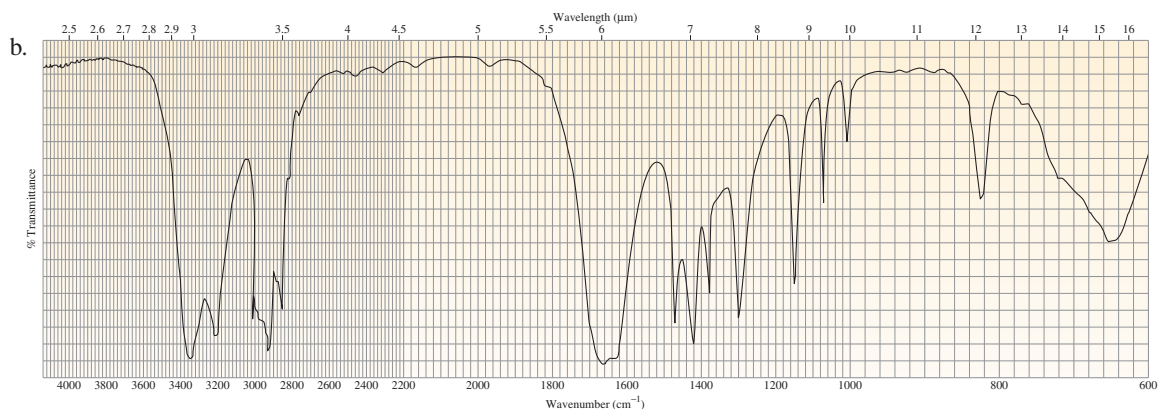
The IR spectrum for Problem 45c.

46. Each of the IR spectra shown in Figure 13.41 is the spectrum of one of the following compounds. Identify the compound that is responsible for each spectrum.



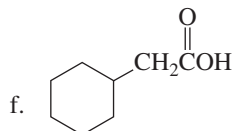
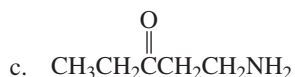
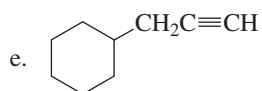
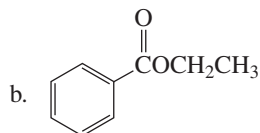
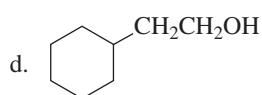
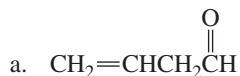
▲ Figure 13.41

The IR spectra for Problem 46.



▲ Figure 13.41 (continued)

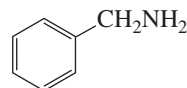
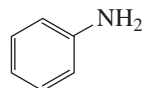
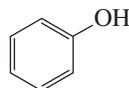
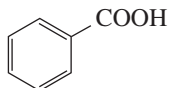
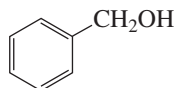
47. Predict the major characteristic IR absorption bands that would be given by each of the following compounds:

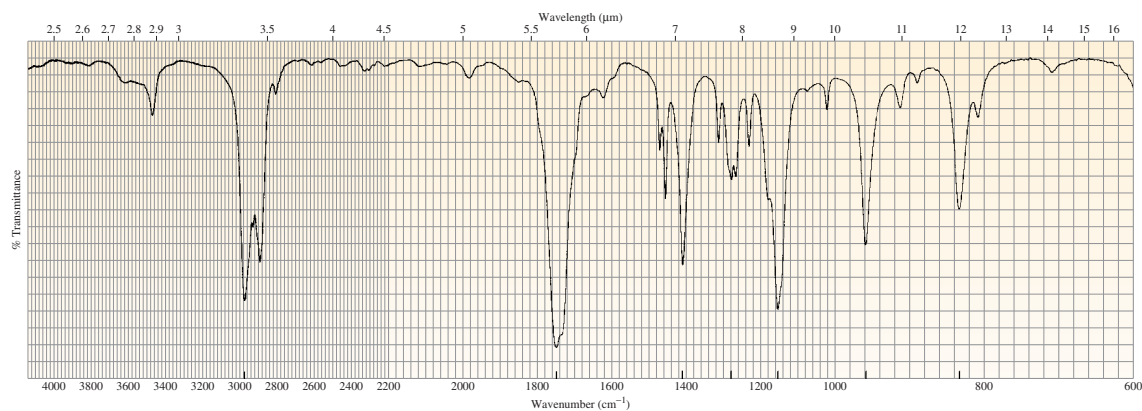


48. Given that the force constants are similar for C—H and C—C bonds, explain why the stretching vibration of a C—H bond occurs at a greater wavenumber.

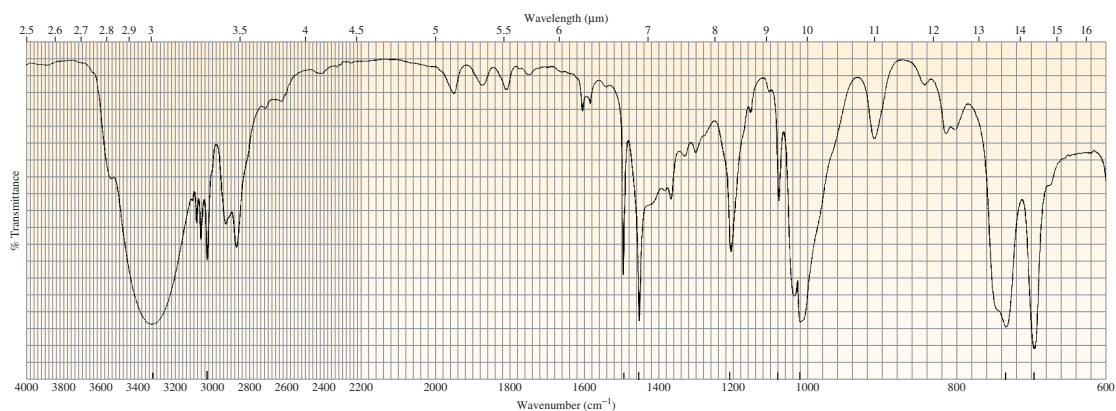
49. The IR spectrum of a compound with molecular formula $\text{C}_5\text{H}_8\text{O}$ was obtained in CCl_4 and is shown in Figure 13.42. Identify the compound.

50. The IR spectrum shown in Figure 13.43 is the spectrum of one of the following compounds. Identify the compound.



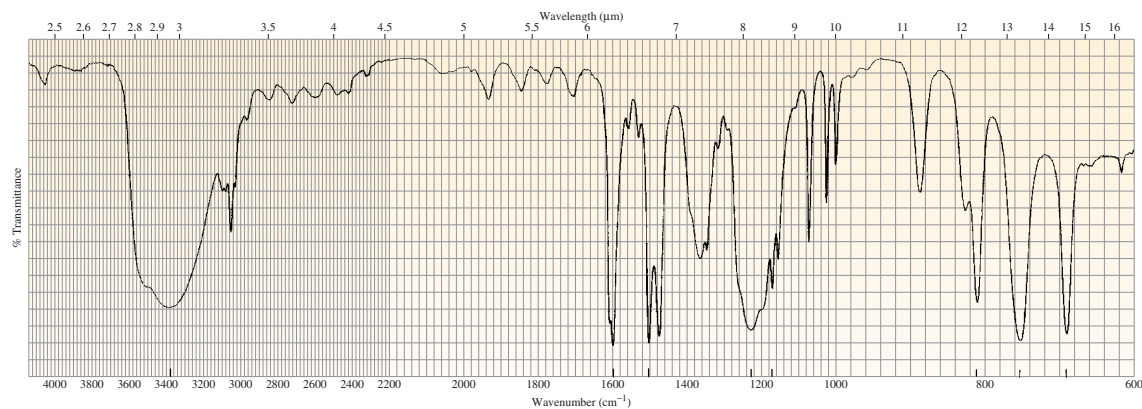
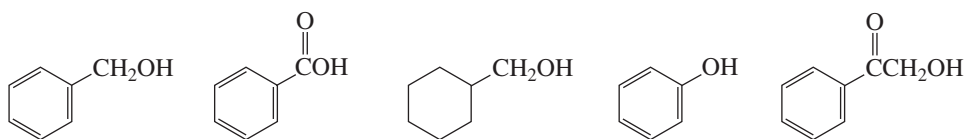


▲ **Figure 13.42**
The IR spectrum for Problem 49.



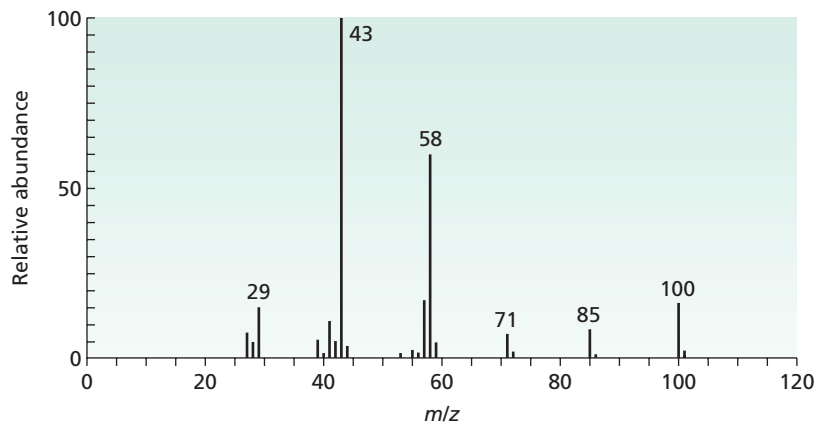
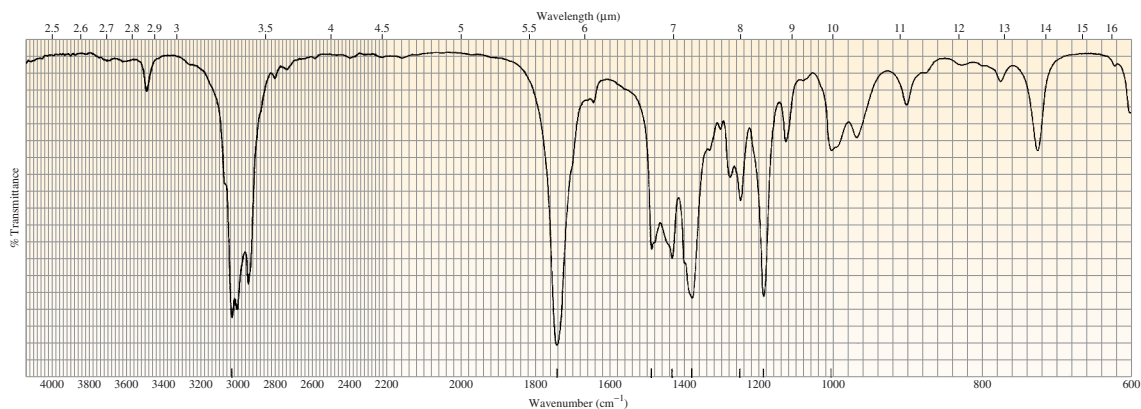
▲ **Figure 13.43**
The IR spectrum for Problem 50.

51. The IR spectrum shown in Figure 13.44 is the spectrum of one of the following compounds. Identify the compound.



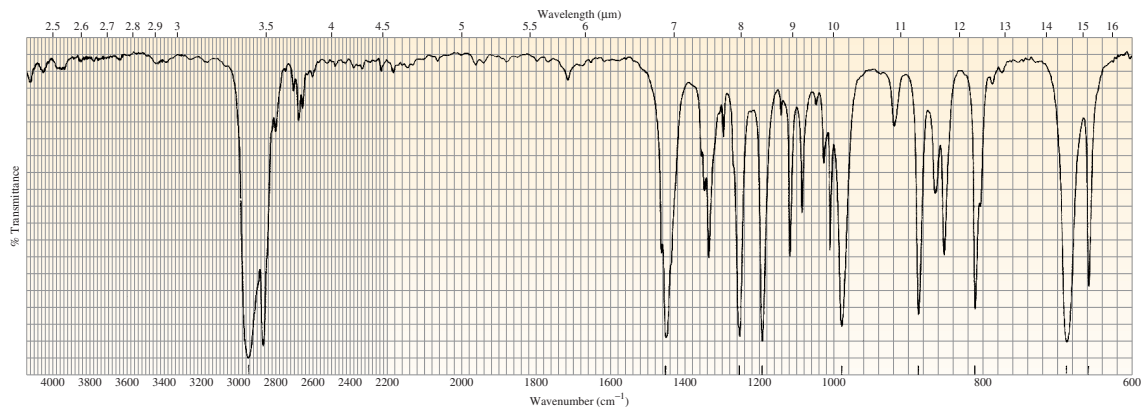
▲ **Figure 13.44**
The IR spectrum for Problem 51.

52. Determine the molecular formula of a saturated acyclic hydrocarbon with an M peak at $m/z = 100$ with a relative intensity of 27.32%, and an M + 1 peak with a relative intensity of 2.10%.
53. Calculate the approximate wavenumber at which a C=C stretch will occur, given that the force constant for the C=C bond is $10 \times 10^5 \text{ gs}^{-2}$.
54. The IR and mass spectra for three different compounds are shown in Figures 13.45–13.47. Identify each compound.



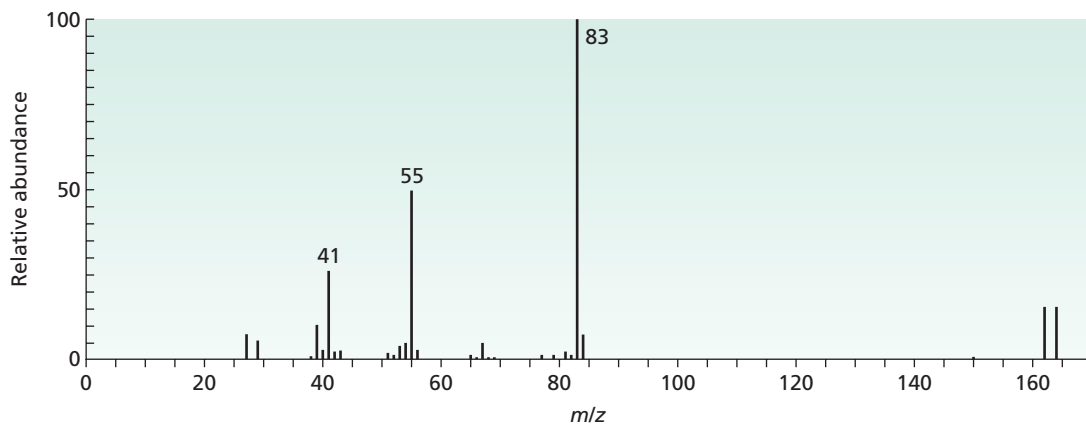
▲ **Figure 13.45**

The IR and mass spectra for Problem 54a.

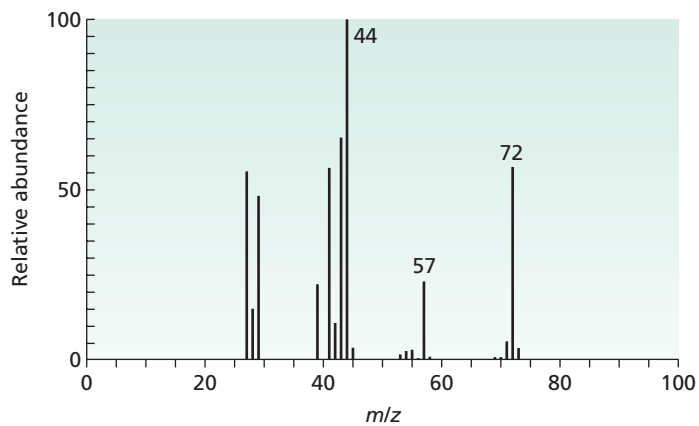
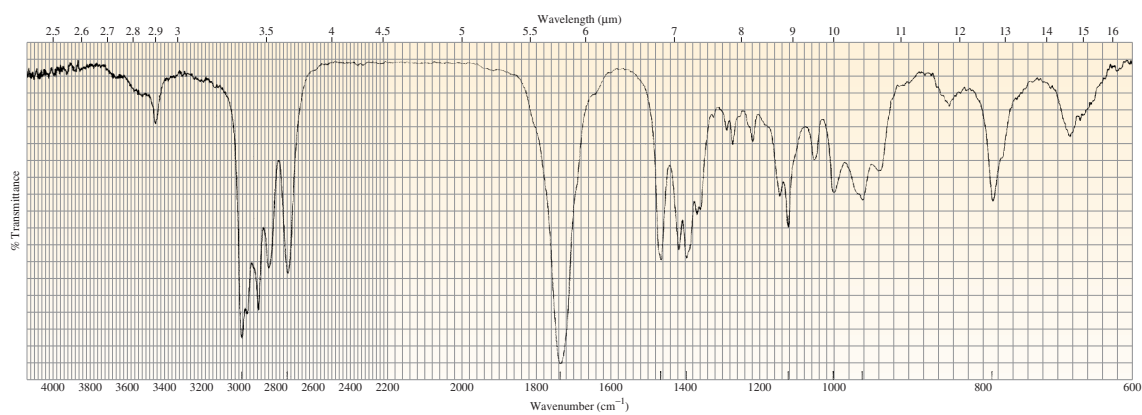


▲ **Figure 13.46**

The IR and mass spectra for Problem 54b.



▲ Figure 13.46 (continued)



▲ Figure 13.47

The IR and mass spectra for Problem 54c.