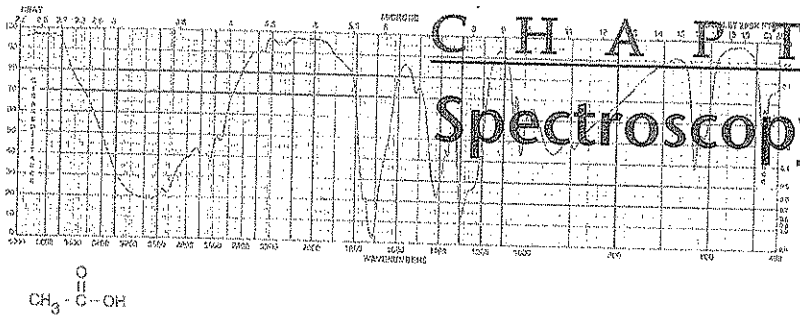


CHAPTER 18
Spectroscopy

Determining the structures of compounds is central to the science of organic chemistry. In the early part of the twentieth century and before, this could be a tedious and time-consuming task. An array of test-tube assays could give information about functional groups. The unknown compound might be chemically degraded into smaller compounds of known structure or converted into a recognizable derivative for structural information. Independent synthesis of the unknown from known compounds was and often still is used to confirm structures. But in the 1940s instrumental techniques became available for chemical analysis; they have become increasingly sophisticated and important in the past few decades. These electronic instruments greatly shortened the time and increased the capacity for obtaining structural information, and required very small amounts of sample. We will look at some of these techniques in this chapter.

spectroscopy
instrumental method in which the interaction of chemical compounds with electromagnetic radiation is measured

18.1 Spectroscopy

All chemical substances interact with **electromagnetic radiation** in some way. Measuring this interaction can provide valuable information about the substance. When a molecule absorbs energy, a transformation or perturbation occurs that may be either temporary or permanent. Low-energy radiation may merely cause a molecular rotation or a bond vibration. Higher-energy radiation may affect the promotion of electrons to higher energy levels; and radiation of even greater energy can result in bond cleavage and permanent disruption of the molecule.

electromagnetic radiation
various wavelengths of energy

Energy can be visualized as traveling in waves (Figure 18.1). The distance between waves is the **wavelength,** and the number of waves that pass by a point in a given time or the number of waves per unit of distance is the **frequency,** expressed in cycles per second, or hertz (Hz). The relationship between energy ϵ and wavelength or frequency is given by the following equation, where h is a proportionality constant called Planck's constant.

wavelength
the distance between two maxima in an energy wave

frequency
number of waves per unit distance or per unit time [cycles per second, or Hertz (Hz)]

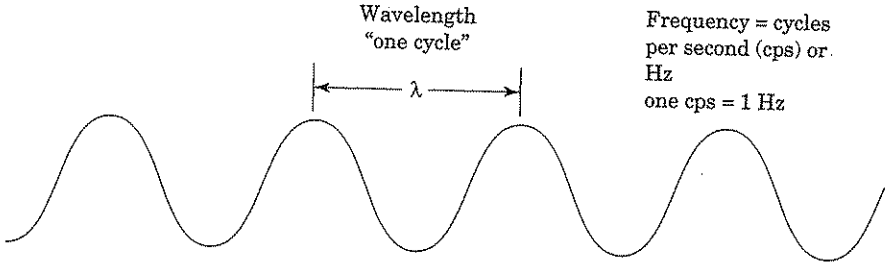


Figure 18.1
Electromagnetic radiation travels in waves characterized by a wavelength λ and frequency υ.

$$\epsilon = h\nu = \frac{hc}{\lambda}$$

h = Planck's constant
c = speed of light
ν = frequency
λ = wavelength

Radiation of a particular wavelength or frequency has a definite, constant amount of energy associated with it. High-energy radiation is characterized by short wavelengths and high frequency, and low-energy radiation by long wavelengths and low frequency. Figure 18.2 shows the spectrum of electromagnetic energy varying in wavelengths from a fraction of an angstrom to thousands of kilometers.

As we have indicated, the interaction of a molecule with electromagnetic radiation causes molecular transformations. Whether the transformation involves molecular rotation, bond vibration, or electronic transition, the molecule absorbs only the wavelength of radiation with exactly the energy necessary for the transition. The processes are quantized and will occur only with specific frequencies or wavelengths. It is not possible either to accumulate radiation of lower energies to attain the total needed for molecular transition or to extract it from higher-energy radiation. The situation is analogous to a vending machine that takes only a single dollar bill. You can obtain your item only if you have a dollar. Trying to insert four quarters is useless. Likewise, a five dollar bill will not be accepted.

Since the absorption of radiation is selective for the particular transition and this transition depends on molecular structure, spectroscopy is invaluable both qualitatively and quantitatively. By measuring the absorption spectra of known compounds, we can correlate the wavelengths of energy absorbed with characteristic structural features. This information is then used to identify structural units in unknowns. The instrument used to measure the absorption of energy by a compound is called a **spectrometer.**

spectrometer
an instrument that measures the absorption of energy by a chemical compound

GETTING INVOLVED

- ✓ What is the difference between wavelength and frequency in describing electromagnetic radiation?
- ✓ Is the energy of a wave directly or inversely related to wavelength? To frequency? Does high frequency correspond to short or long wavelengths and high or low energy? Rationalize your concepts with familiar waves presented in Figure 18.2.
- ✓ What does it mean that a molecular transformation or absorption of energy by a molecule is quantized? What is a spectrometer?

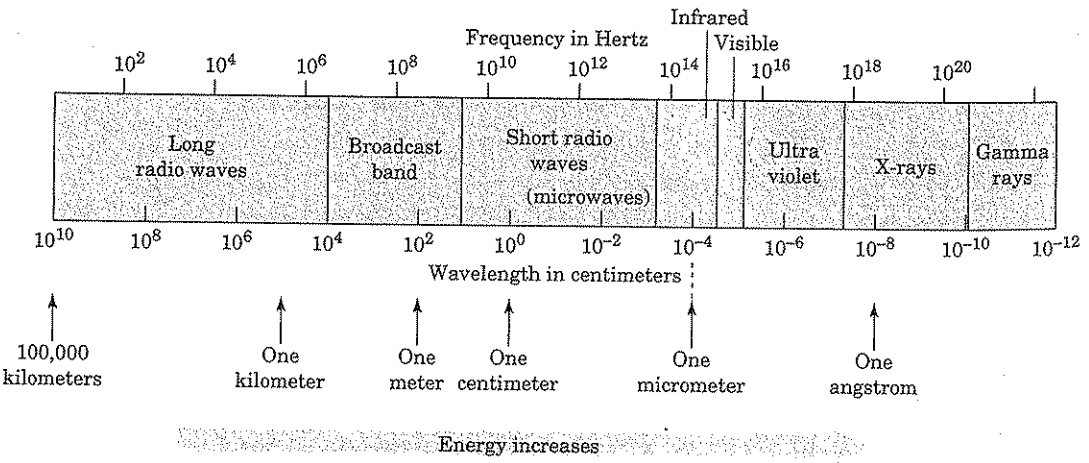


Figure 18.2 The spectrum of electromagnetic radiation.

18.2 Infrared Spectroscopy

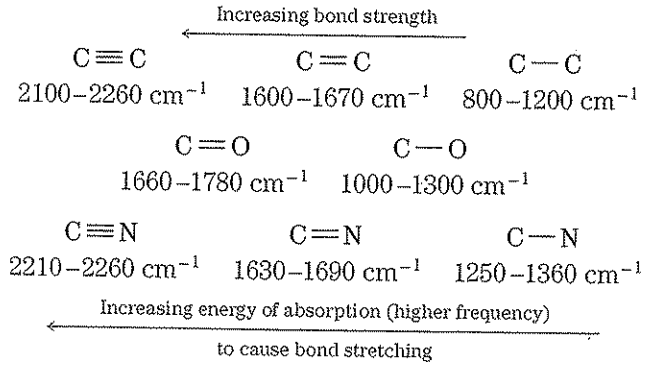
infrared spectroscopy spectroscopy using infrared radiation; used to determine bond types and functional groups in organic compounds

infrared radiation for infrared spectroscopy it is radiation with wavelengths of 2–15 micrometers or frequencies of 5000 cm^{-1} to 670 cm^{-1}

wavenumber the number of cycles or waves in a distance of one centimeter

An **infrared spectrometer** subjects a sample compound to **infrared radiation** in the 2–15 micrometer (μm) wavelength range. This region is more frequently described in terms of **wavenumber** (frequency), 5000 cm^{-1} to 670 cm^{-1}, which is essentially the number of cycles or waves in a distance of 1 centimeter calculated as $1/\lambda$, with λ in centimeters. Although this radiation is unable to inflict permanent alteration on a molecule, it does supply sufficient energy for bonds in the molecule to vibrate by stretching, scissoring, bending, rocking, twisting, or wagging (Figure 18.3). The atoms of a molecule can be conceived of as linked by springs that are set in motion by the application of energy. As the molecule is subjected to radiation with frequencies in the 5000 cm^{-1} to 670 cm^{-1} range, it absorbs only those possessing exactly the energy required to cause a particular vibration. Energy absorptions are recorded as bands on chart paper.

Since different bonds and functional groups absorb at different frequencies, an infrared spectrum is usually applicable in qualitative analysis, that is, in determining what types of groups are in a molecule. For example, a carbon-carbon triple bond is stronger than a double bond and requires a higher frequency (greater energy) radiation to stretch. The same considerations apply to carbon-oxygen and carbon-nitrogen bonds.



Usually one can identify an absorbing bond (group) by the position of the absorption peak. Figure 18.4 illustrates the general area in which various bonds absorb in the infrared.

An infrared spectrum is usually studied in two sections. The area from about 1400 cm^{-1} to 3500 cm^{-1} is the functional group area. The bands in this region are particularly useful in determining the types of groups—alkene, alkyne, aldehyde, ketone, alcohol, acid—present in the molecule. The remainder of the spec-

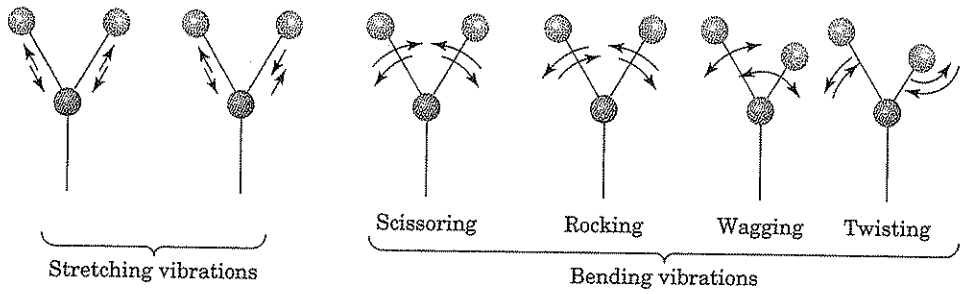


Figure 18.3 Molecular vibrations caused by infrared radiation.

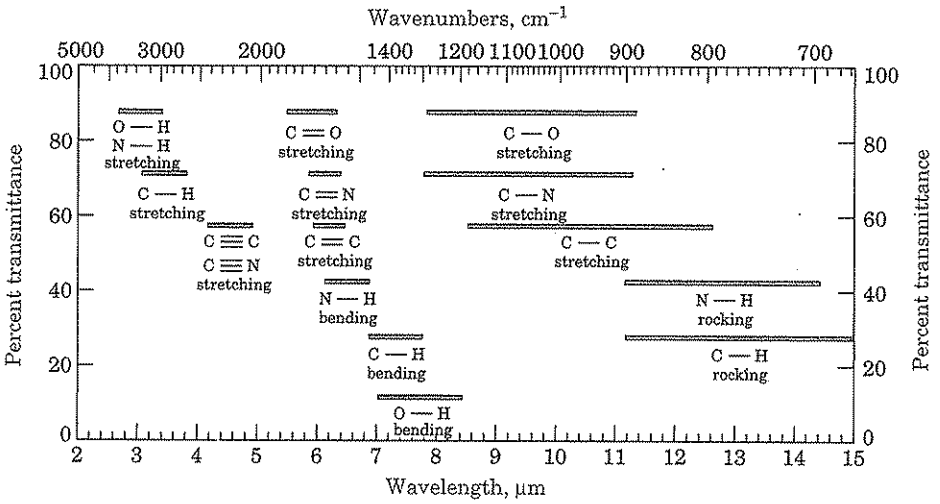


Figure 18.4 Areas of absorption of infrared radiation by various bonds. The lower scale is the wavelength in micrometers (μm). The upper scale is frequency expressed in wavenumbers (the number of waves in 1 cm). The vertical scale describes percentage of transmittance of the sample beam.

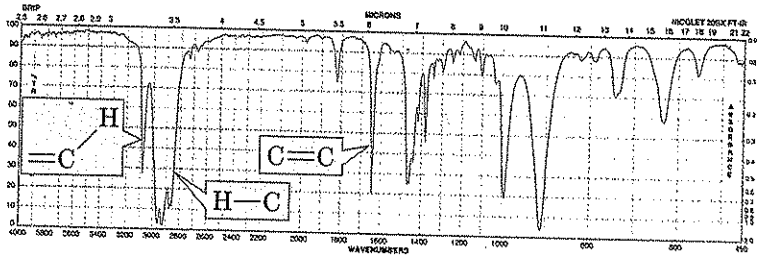
trum is called the *fingerprint region*. A peak-by-peak match of an unknown spectrum with the spectrum of the suspected compound in this region can be used, much like a fingerprint, to confirm the unknown's identity. Figure 18.5 contains some sample spectra, and Table 18.1 summarizes some infrared assignments useful in functional group analysis.

You may wish to consider ways to arrange some of the assignments in Table 18.1 in your mind. For example:

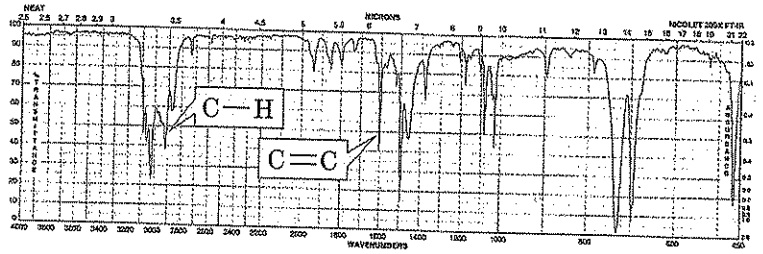
1. Alkanes, alkenes, and aromatics show C—H stretches around 2800–3100 cm^{-1}, but for alkynes, the ≡C—H stretch is around 3300 cm^{-1}. O—H and N—H stretches are in the 3000–3500 cm^{-1} range.
2. Double bonds stretch between 1600 cm^{-1} and 1800 cm^{-1} with carbon-carbon double bonds in the lower frequencies and carbon-oxygen in the higher frequencies.
3. Triple bonds, C≡C or C≡N, absorb around 2100–2300 cm^{-1}.

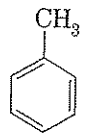
GETTING INVOLVED

- ✓ What frequency range is used in infrared spectroscopy? What does wavenumber mean? How does wavenumber relate to energy of infrared radiation? Does a high wavenumber describe high or low energy radiation?
- ✓ What kinds of perturbations does infrared radiation cause on organic molecules? Why does a triple bond require radiation with a higher wavenumber for stretching than a double bond and a double bond higher than a single bond?
- ✓ In an infrared spectrum, what is meant by the functional group region and the fingerprint region?
- ✓ Using Figure 18.4 and Table 18.1 become familiar with the characteristic infrared absorptions of the functional groups such as alkenes, alkynes, aldehydes, ketones, carboxylic acids, and alcohols. Specifically develop a feel for stretching frequencies of carbon-carbon and carbon-oxygen double bonds, carbon-carbon and carbon-nitrogen triple bonds, and oxygen-hydrogen and nitrogen-hydrogen bonds.

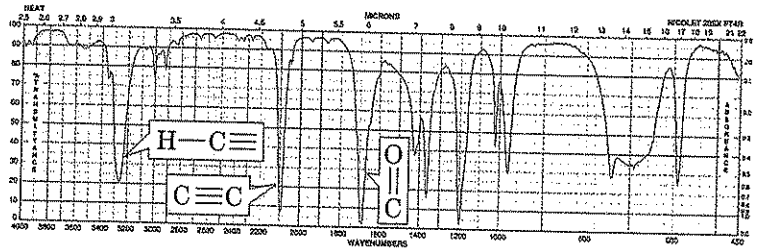


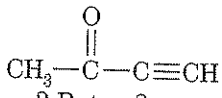
$CH_3CH_2CH_2CH_2CH{=}CH_2$
1-Hexene



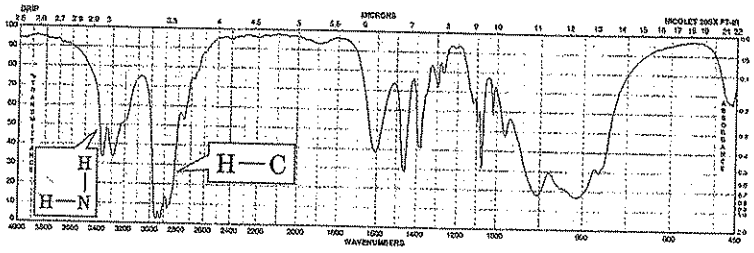


Toluene



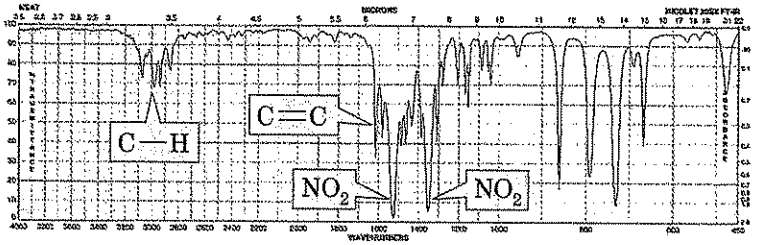


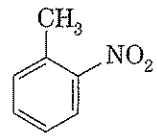
3-Butyn-2-one



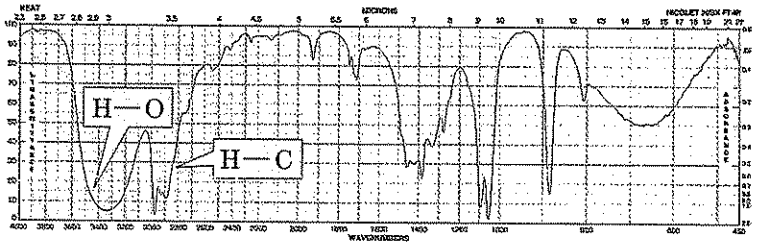
$CH_3CH_2CH_2NH_2$
Propylamine

Figure 18.5 Infrared absorption spectra. Compare bands in the 4000–1380 cm^{-1} region with assignments for each functional group in Table 18.1.

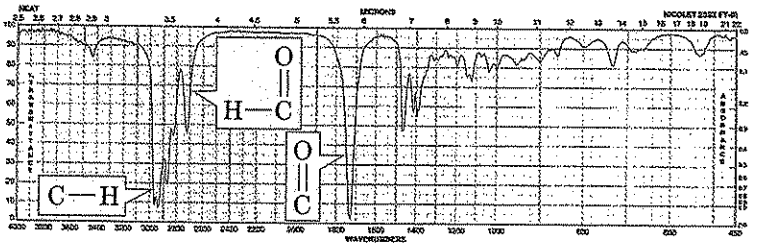




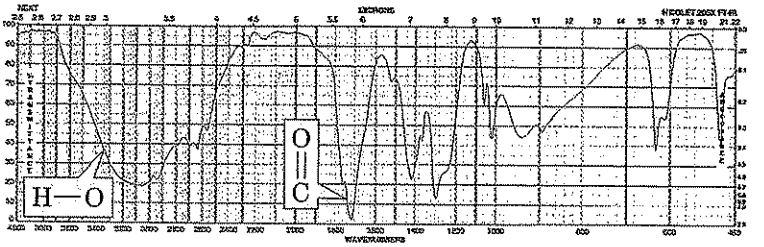
Ortho nitrotoluene



CH_3CH_2OH
Ethanol



$CH_3(CH_2)_3CH_2—C(=O)—H$
Hexanal



$CH_3—C(=O)—OH$
Acetic acid

Figure 18.5 (*cont.*)

Example 18.1

How would infrared spectroscopy be useful in distinguishing between the following compounds?

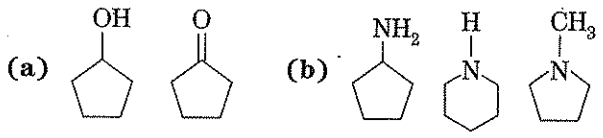
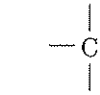
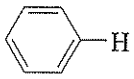


TABLE 18.1 ◆ Infrared Absorption Assignments

		Hydrocarbons		
	Alkanes	Alkenes	Alkynes	Aromatics
C—H stretch				
	2850–2960 cm^{-1}	3000–3100 cm^{-1}	3300 cm^{-1}	3000–3100 cm^{-1}
C—C stretch				
	800–1200 cm^{-1}	1600–1670 cm^{-1}	2100–2260 cm^{-1}	1450–1600 cm^{-1}
		Nitriles		
C≡N stretch		2210–2260 cm^{-1}		
		Nitro Compounds		
		Two bands: 1500–1570 cm^{-1} and 1300–1370 cm^{-1}		
		Amines		
N—H stretch				
	two bands	one band	no bands	
	3300–3500 cm^{-1}	3300–3500 cm^{-1}		
		Alcohols and Ethers		
		Alcohol	Ether	
O—H stretch		3400–3650 cm^{-1}	None	
		Aldehydes, Ketones, Acids, Esters		
C=O stretch	1660–1780 cm^{-1}			
			C—H stretch	
	Aldehydes	C—H stretch	Sharp spike, shoulder, or two bands 2700–2820 cm^{-1}	
				
	Acids	—COH	O—H stretch	Broad band 2500–3300 cm^{-1}

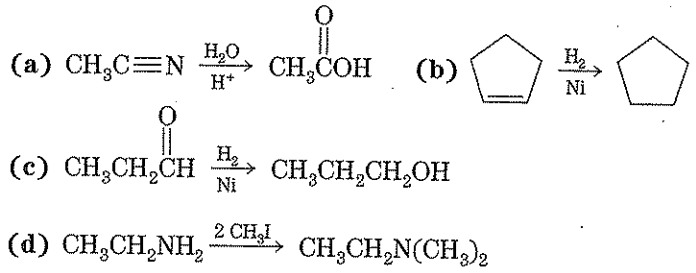
Solution

(a) The difference between the compounds is that the first is an alcohol and the second a ketone. The alcohol will show an O—H stretch around 3400–3650 cm^{-1} but will show no C=O stretch. The ketone will have no O—H stretch, but will show a C=O stretch around 1660–1780 cm^{-1}.

(b) The first compound is a primary amine and will show two N—H stretching bands in the 3200–3500 cm^{-1} region. The second compound is a secondary amine and will show only one N—H stretching vibration in this area. The third compound is a tertiary amine; it has no N—H bonds and will show no such stretching bands.

Problem 18.1

Each of the following reactions have been covered in this textbook. Using infrared wavenumber assignments, describe how the reactant and product in each case could be distinguished to confirm the reaction actually occurred.



See related problem 18.14.

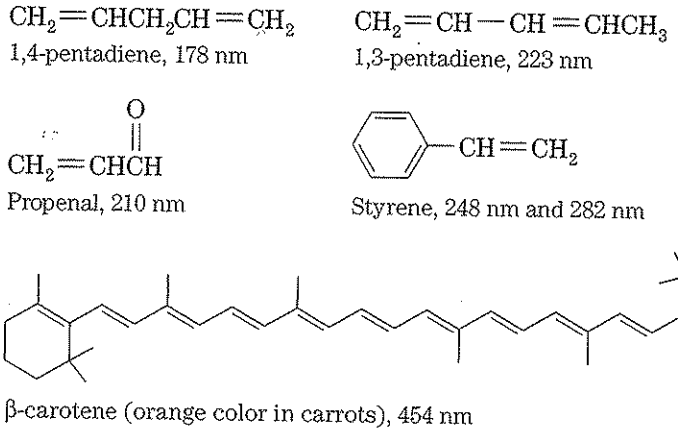
18.3 Ultraviolet-Visible Spectroscopy

ultraviolet spectroscopy spectroscopy using ultraviolet radiation with wavelengths in the 200–400 nm range

visible spectroscopy spectroscopy using visible light with wavelengths in the 400–750 nm range

In **ultraviolet-visible spectroscopy,** the 200–750-nanometer* region of the electromagnetic spectrum is used. This includes both the visible, 400–750 nm, and near ultraviolet, 200–400 nm. Radiation of these wavelengths is sufficiently energetic to cause the promotion of loosely held electrons, such as nonbonding electrons or electrons involved in a π bond, to higher energy levels. For absorption in this particular region of the ultraviolet, however, there must be conjugation of double bonds. An alternating system of double and single bonds lowers the energy of transition of an electron moving to a higher energy level. If the conjugation is extensive, the molecule may absorb in the visible region and show color (Connections 10.4).

In general, ultraviolet-visible spectroscopy is not used for functional-group analysis as extensively as infrared analysis. Rather, it shows the presence of conjugated unsaturated systems such as the ones illustrated.



1,4-pentadiene, 178 nm

1,3-pentadiene, 223 nm

Propenal, 210 nm

Styrene, 248 nm and 282 nm

β-carotene (orange color in carrots), 454 nm

Compounds that absorb in this area have characteristic wavelengths of absorption. Thus their presence and concentration in a solution can be detected and measured. This is useful in identifying product ratios and reaction rates and also

*A nanometer is 10^{-9} meter.

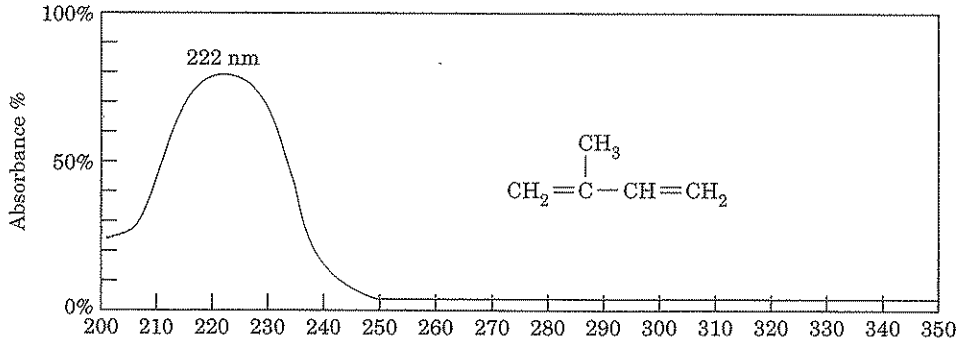


Figure 18.6 Ultraviolet spectrum of isoprene.

in determining other quantitative data. Figure 18.6 shows the ultraviolet spectrum of isoprene.

GETTING INVOLVED

✓ What is the difference in ultraviolet and visible spectroscopy in terms of wavelength of radiation used? What type of structural features are characterized by ultraviolet-visible spectroscopy?

Problem 18.2

Why can the following compounds be distinguished by ultraviolet-visible spectroscopy? (For **c** and **d** refer to Connections 5.3 on terpenes for structures.) **(a)** 1,3-cyclohexadiene and 1,4-cyclohexadiene; **(b)** propanone and propenal; **(c)** menthol (peppermint) and carvone (spearmint); **(d)** squalene (shark liver oil) and vitamin A.

18.4 Nuclear Magnetic Resonance: ^{1}H NMR

The nuclei of some atoms spin. In doing so, they generate a magnetic moment along their axis of spin, acting as tiny bar magnets. The nucleus of the hydrogen atom, mass number of 1 (one proton, no neutrons), exhibits this property and is the one most often analyzed by **nuclear magnetic resonance (NMR) spectroscopy.** If a hydrogen atom is placed in an external magnetic field, its nucleus can align with the field (the more stable arrangement) or against the field (a more energetic, less stable state) (Figure 18.7). Although the energy difference between the states is not great, there is a slightly greater proportion of nuclei in the more stable state in which they are aligned with the external field.

nuclear magnetic resonance spectroscopy spectroscopy in which compound is placed in a magnetic field and exposed to radio-frequency radiation. It provides information about the carbon and hydrogen structure of an organic compound

To make a nucleus flip from alignment to nonalignment, energy in the radio-frequency range must be applied. For example, a hydrogen nucleus in an external field of 14,092 gauss requires a frequency of 60 million hertz (cycles per second) for the transition. When this frequency is applied, it is absorbed, and the absorption is recorded on chart paper. In practice, either the magnetic field can be held constant and the radio frequency varied, or the radio frequency can be held constant and the magnetic field varied. Student model NMR's are often 60 MHz but modern research instruments are 100–300 MHz or higher.

GETTING INVOLVED

✓ In NMR, hydrogen nuclei are subjected to a magnetic field and then radio frequency energy. What happens before and after the presentation of the field and the radio frequency radiation?

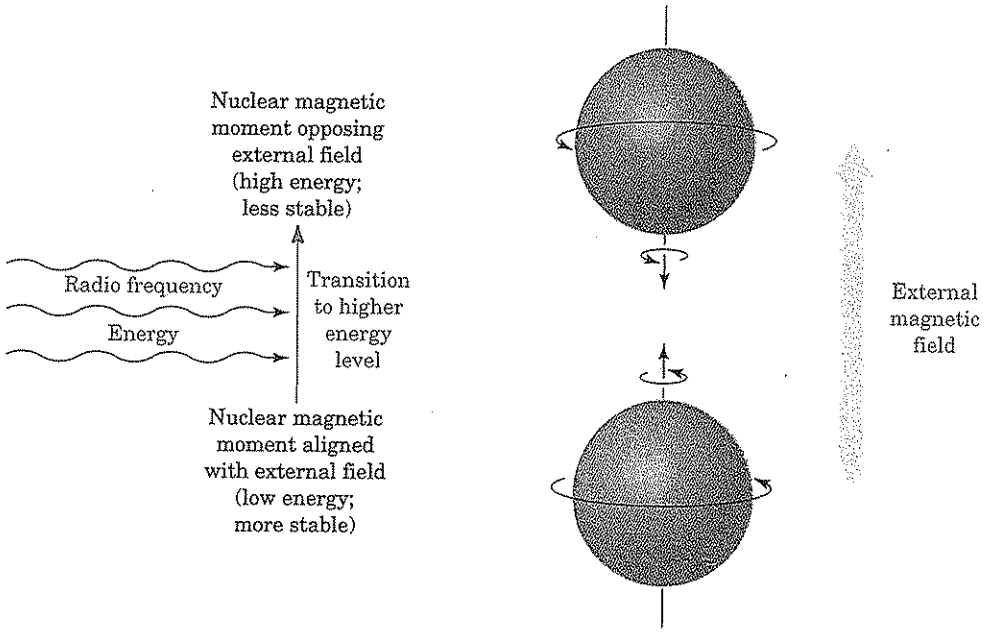


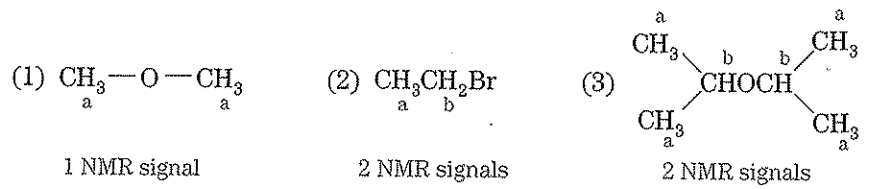
Figure 18.7 The spinning nucleus of the hydrogen atom acts like a tiny magnet that can go into alignment or nonalignment with an externally applied magnetic field. Applying radio-frequency energy can flip protons in the more stable aligned state to nonalignment.

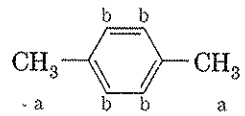
chemical shift
the position on NMR chart paper where a carbon or hydrogen nucleus absorbs relative to an internal standard, TMS; measured in δ units

A. Chemical Shift

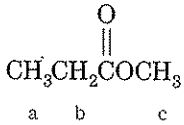
If NMR's main feat were to detect the presence of hydrogen in a molecule, it would not be worth discussing here. Nuclear magnetic resonance spectroscopy can, however, distinguish between hydrogens in different chemical environments within a molecule. Hydrogens on a benzene ring, on a carbon bearing a chlorine, or on a carbon adjacent to a carbonyl group absorb radio-frequency energies at different applied magnetic fields, which appear at different locations on the recording paper. Furthermore, the position of absorption is relatively constant for hydrogens in a particular chemical or structural environment. Hence, the number of signals recorded on the NMR chart paper indicates the number of different types of hydrogens in a molecule. The position of the peak can give information about the molecular structure in the vicinity of the hydrogens.

To understand fully the value of NMR, then, we must gain a concept of equivalent and nonequivalent hydrogens. Equivalent hydrogens are positioned in structurally and chemically equivalent areas in the molecule. For example, consider the following molecules and convince yourself of the different types of hydrogens shown. The first compound has two methyl groups connected to the same oxygen. The hydrogens on these carbons are chemically equivalent. However, in the second example, bromoethane, the $-CH_2-$ group is bonded to a carbon and a bromine and the CH_3- is bonded to just a carbon. The hydrogens on these two carbons are in significantly different chemical environments and are nonequivalent. In the third and fourth examples, note that the methyl groups are equivalent, but in the fifth example the two methyl groups are in two different chemical environments and are nonequivalent.

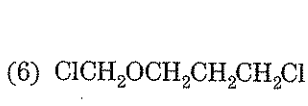


(4) 

2 NMR signals

(5) 

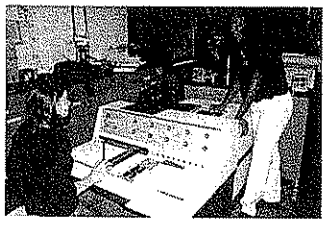
3 NMR signals

(6) 

4 NMR signals

The chart paper for proton nmr is rectangular with a linear scale of so-called δ units across the bottom. Most signals in ^{1}H NMR appear from zero to eight or ten δ units, although peaks at higher values can be recorded easily. To every sample to be analyzed by NMR, a small amount of tetramethylsilane (TMS) $(CH_3)_4Si$, is added as a reference; the TMS signal, caused by the 12 equivalent hydrogens, is defined as δ = 0. The signals of the hydrogens in the molecule being analyzed are compared to TMS; their chemical shift is defined as the number of δ units that the signal is shifted from that of TMS.

The chemical shift of a hydrogen depends on how strongly it experiences the external magnetic field. Electron density in the vicinity of a hydrogen nucleus can shield it from the field. Electron-withdrawing groups can decrease this electron density and shielding. Thus different hydrogens experience the external field to varying degrees and require different amounts of energy to flip from alignment to nonalignment. We see these differences in the NMR as differences in chemical shift. For example, chlorine is strongly electronegative, and the hydrogens on chloromethane are shifted significantly from those on methane. As we add a second and third chlorine, the shift to higher δ values continues by a fairly uniform amount as the hydrogens are progressively deshielded from the external field.



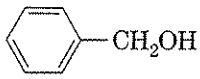
NMR instrumentation

	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$
δ-value	0.5	3.1	5.3	7.2

(approximate)

Knowing the effect of chlorine or any other group on chemical shift is very useful in the interpretation of NMR spectra. Table 18.2 summarizes the characteristic chemical shifts of hydrogens in different types of environments.

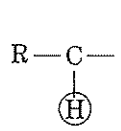
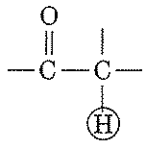
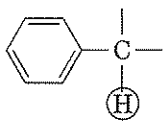
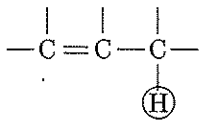
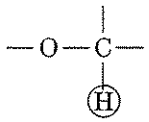
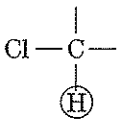
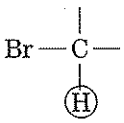
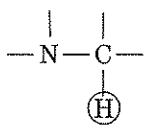
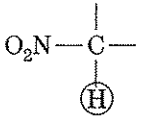
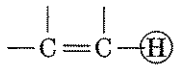
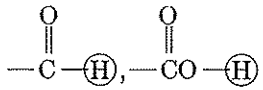
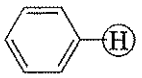
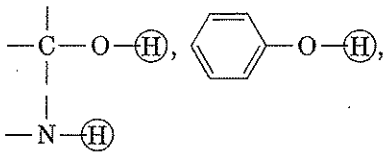
Now let us consider a specific example, benzyl alcohol [NMR in Figure 18.8(a)].



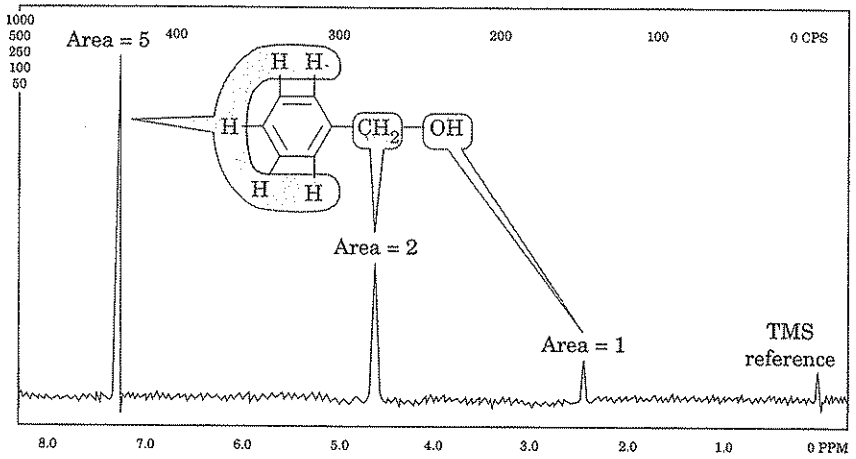
Benzyl alcohol

The NMR spectrum has three distinct peaks at δ = 2.4, δ = 4.6, and δ = 7.3 (δ = 0 is the TMS reference). Examination of the molecule confirms three types of hydrogen present: one hydrogen bonded to an oxygen, two hydrogens bonded equivalently to a carbon, and five essentially equivalent hydrogens attached to the benzene ring. Using Table 18.2, we can now assign each hydrogen type to a signal. Aromatic hydrogens occur between δ = 7 and 8, while hydroxy hydrogens have variable δ values. So the δ = 7.3 must belong to the five benzene hydrogens. The third column in Table 18.2 indicates that the methylene hydrogens, if attached to an alkyl group, R — CH_2 —, would generate a signal at 0.9–1.6. However, the fourth column specifies the chemical shift due to adjacent groups. Since a benzene ring (Z = aromatic) and an oxygen (Z = 0) are in those positions, their influences will shift the methylene hydrogen's signal 1.4 and 2.8 units, respectively. Added to the normal signal (δ = 1.0), the sum is δ = 5.2, very close to the 4.6 δ value. By elimination, the δ = 2.4 signal must be due to the hydroxy hydrogen.

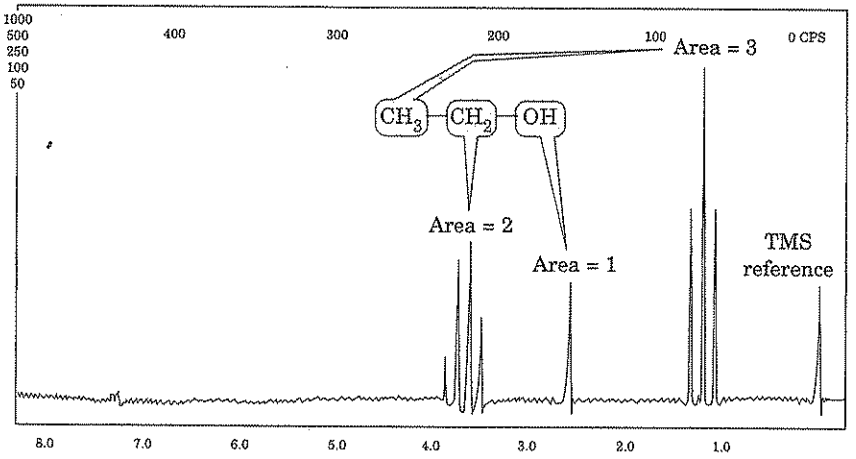
Table 18.2 Chemical Shifts

Z—C—H		Actual δ Value	Chemical Shift Relative to Alkyl H
	Z Groups[a]		
Z = alkyl		0.9–1.6	0
Z = 		2–2.5	1
Z = aromatic		2.3–2.9	1.3–1.5
Z = alkene		1.8–2.8	0.9–1.2
Z = O		3.3–5	2.4–3.4
Z = Cl		3.2–4	2.3–2.6
Z = Br		2.7–3.8	1.8–2.2
Z = amines		2.2–3	1.3–1.4
Z = NO_2		4.4–4.6	3–3.5
	Other Groups		
Vinyl hydrogens		4.5–6	—
Aldehydes, acids		9–12	—
Aromatic hydrogens		7–8	—
Alcohol, phenols, amines		variable	—
Tetramethylsilane, TMS reference	$(CH_3)_4Si$:	0	—

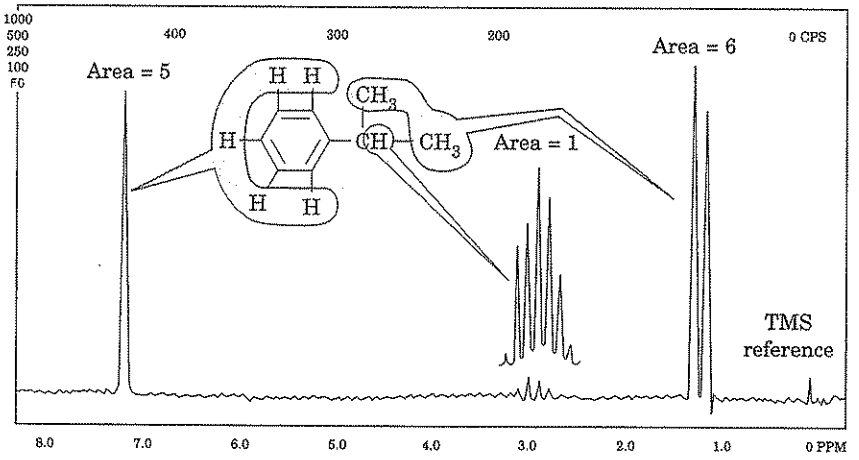
[a]The table indicates the shift of the circled hydrogen under the influence of the Z group.



(a)



(b)



(c)

Figure 18.8 Some NMR spectra. (a) Benzyl alcohol. (b) Ethyl alcohol. (c) Isopropylbenzene NMR spectra, courtesy of Varian Associates.

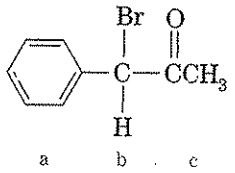
The tone indicates the shift of the circled hydrogen when the influence of the *a* group.

GETTING INVOLVED

- ✓ What is a chemical shift? What does it tell you about hydrogens in a molecule?
- ✓ What are δ-units? What is the purpose of TMS and what is its chemical shift assignment in δ-units?
- ✓ If a hydrogen is shielded from the magnetic field, does it require more or less energy to flip? What if it is deshielded? Do high δ-values result from shielded or deshielded hydrogens?
- ✓ Can you use Table 18.2 to predict the value of chemical shifts?

Example 18.2

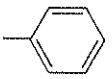
Predict the chemical shifts of the three types of hydrogens in the following molecule:



Solution

(a) aromatic δ = 7–8

(b) 1.0 normal δ value
1.0 adjacent C=O
2.0 adjacent Br
1.4 adjacent
δ = 5.4 total



(c) Z = C=O δ = 2–2.5

Problem 18.3

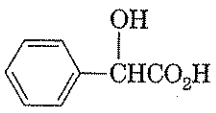
How many NMR signals would be produced by each of the following molecules? **(a)** ethanal; **(b)** propanal **(c)** propanone; **(d)** butanone; **(e)** 2-pentanone; **(f)** 3-pentanone.

Problem 18.4

Using Table 18.2 calculate the chemical shifts of the different types of hydrogens in each of the following molecules.

(a) $CH_3CCH_2CCH_3$ (O, O)

(b) $BrCH_2CH_2CCHCl_2$ (O)

(c) 

B. Integration

integration
in ^{1}H NMR a technique that provides the relative numbers of hydrogens in a compound; it is the area under a peak

The relative areas under the various peaks of an NMR spectrum are in proportion to the number of hydrogens contributing to each signal. These areas can be electronically integrated by an NMR spectrometer. Comparison of the areas provides the ratio among the various kinds of hydrogens in the molecule. Consider the NMR spectrum of benzyl alcohol [Figure 18.8(a)], for example. The hydrogens in the molecule are in a 1:2:5 ratio, like the corresponding peak areas in the spectrum.

GETTING INVOLVED

What information does integration in NMR provide?

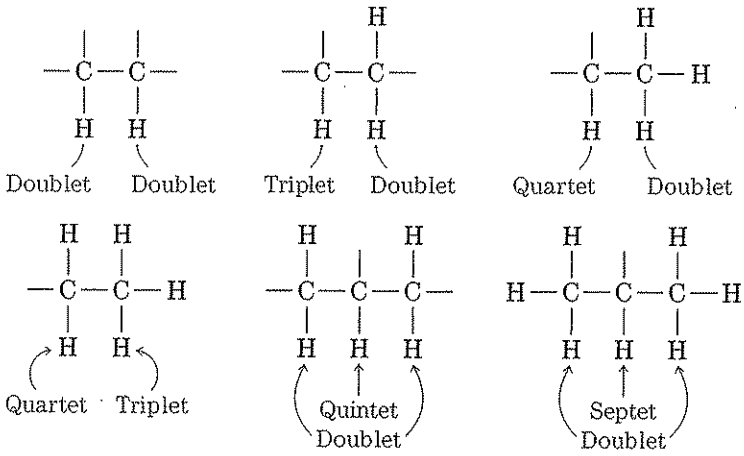
Problem 18.5

A compound with the formula C_8H_{10} gives three NMR signals with the following chemical shifts and integration values: δ=7 (149); δ=2.3 (58); and δ=1.1 (91). How many hydrogens are represented by each signal?

C. Peak Splitting

peak splitting
in ^{1}H NMR a phenomenon in which hydrogens on an adjacent carbon split the signal of hydrogens on the other carbon

Hydrogens on adjacent carbons, each with a different chemical shift, can influence the signal of one another. This influence appears as peak splitting. We can generalize the phenomenon by saying that the number of peaks into which a particular hydrogen's signal is split equals one more than the total number of hydrogens on directly adjacent carbons. Assuming that each of the following types of hydrogens is nonequivalent, we should obtain the indicated splitting patterns.



In Figure 18.8(b) (ethyl alcohol), note that the ethyl group is indicated by a quartet and a triplet and that the isopropyl group in Figure 18.8(c) (isopropyl benzene) shows as a septet and a doublet.

Let's use the ethyl alcohol example [Figure 18.8(b)] to explain how splitting occurs. In the presence of an external magnetic field, some hydrogens align with the field and some against. Since the energy difference between the two alignments is not great, the proportion in each state is similar; there is a slightly higher proportion in the aligned state, however. When the hydrogens on a carbon align

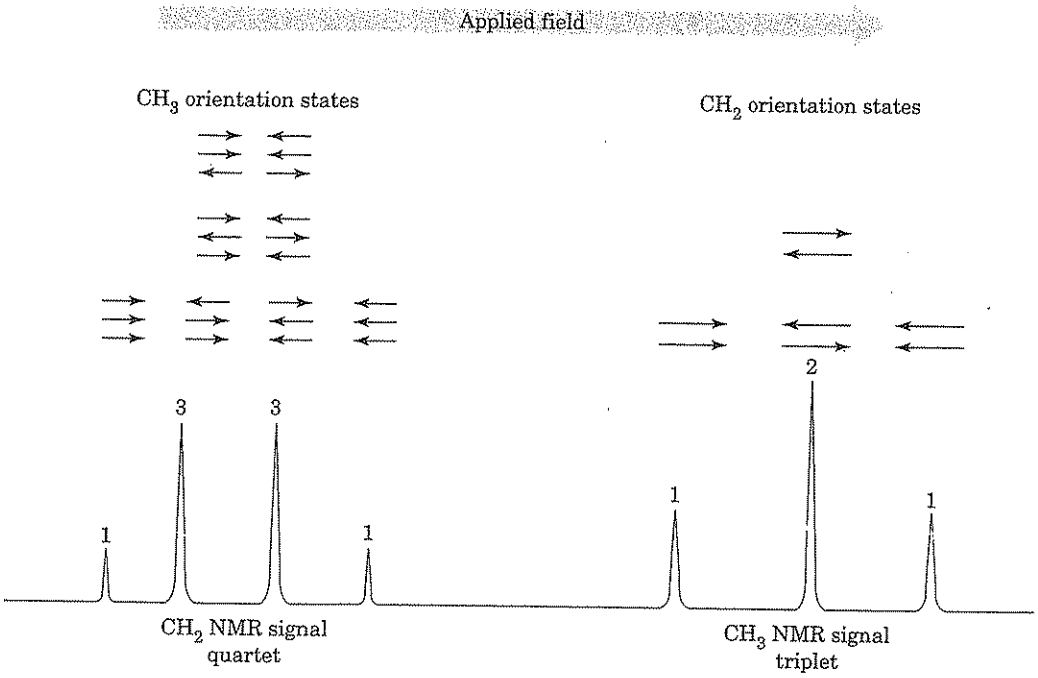


Figure 18.9
Explanation of spin–spin splitting patterns in ethyl alcohol, CH_3CH_2OH.

with the external field, they increase the effective magnetic field felt by the hydrogens on an adjacent carbon. Alternatively, in nonalignment they oppose the external field and decrease the effective field experienced by the hydrogens on an adjacent carbon. These differences cause small but observable differences in chemical shift, which we call splitting.

In the ethyl alcohol example, the three methyl hydrogens have four possible ways to align with the external field: all can be aligned; two can be aligned, one nonaligned; one aligned, two nonaligned; or all three nonaligned. The hydrogens on the adjacent carbon will have different chemical shifts depending on which state the methyl group is in. In the middle two cases, there are three ways to create the alignment/nonalignment possibilities and thus these states are three times as likely as either of the extremes. As a result of the four possibilities, the adjacent hydrogens are split into four peaks, which appear in relative heights of 1:3:3:1. Similar reasoning applies to the effect of the CH_2 group on the CH_3. The two CH_2 hydrogens can be aligned, nonaligned, or one aligned and one nonaligned in two different ways. As a result, the hydrogens on the adjacent carbon are split into three peaks in a 1:2:1 ratio. This is illustrated in Figure 18.9.

GETTING INVOLVED

- ✓ How are splitting patterns of hydrogens practically recognized? What effect do adjacent hydrogens have on one another?
- ✓ Can you give a simple explanation of why splitting occurs?

Problem 18.6

Predict the splitting patterns of the hydrogens in the following molecules (ignore aromatic hydrogens and those on oxygens): **(a)** ethanol; **(b)** 1-phenylethanol; **(c)** 2-phenylethanol; **(d)** 1-phenylpropanol; **(e)** 2-propanol.

D. Summary of NMR

The following aspects of NMR provide information.

Chemical Shift. The number of signals corresponds to the number of different types of hydrogens in the molecule. The position of each signal gives information about the structural environment of the hydrogens.

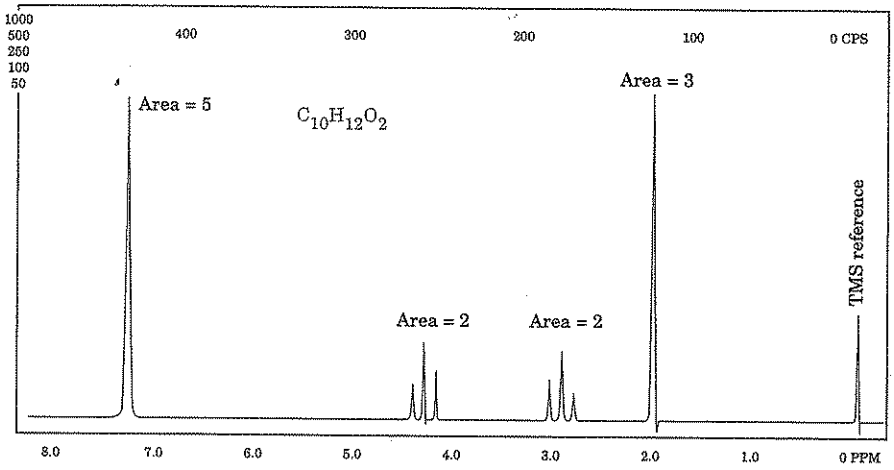
Integration. The relative areas under the signals give the ratio of the numbers of each hydrogen type in the molecule. If the molecular formula is known, the actual number of each type of hydrogen can be determined.

Splitting. The number of peaks into which a signal is split is one more than the total number of hydrogens on directly adjacent carbons.

GETTING INVOLVED

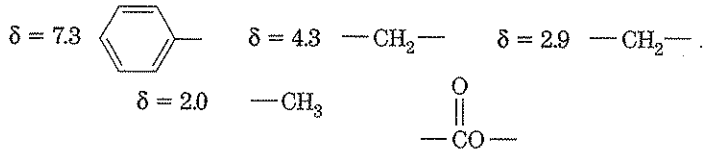
Example 18.3

To conclude our discussion of NMR, let us go through a procedure for identifying the compound with the formula $C_{10}H_{12}O_2$ using the following NMR spectrum.



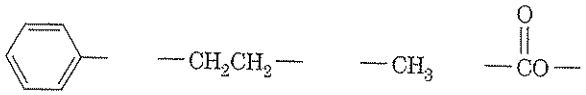
Solution

The four signals indicate four different types of hydrogens. At $\delta = 7.3$, five hydrogens are in the aromatic region—probably a monosubstituted benzene ring. The simplest way of expressing two equivalent hydrogens, indicated by the signal at $\delta = 2.9$ and also at $\delta = 4.3$, is with methylene (CH_2) groups. Finally, the signal at $\delta = 2$ suggests three hydrogens, most simple expressed as a methyl group. Remaining in the formula are a a carbon and two oxygens; these are most simply expressed as $-\overset{\overset{O}{\|}}{CO}-$. Although obviously there are other arrangements of all the groups mentioned, these are the simplest expressions and should be considered first. The pieces of the puzzle are

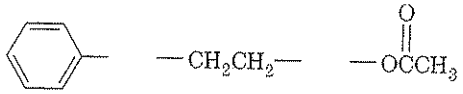


The spectrum shows that the two methylene groups split each other and thus must be adjacent to each other ($-CH_2CH_2-$). In this arrangement, each methylene splits

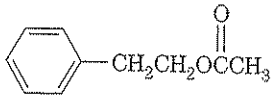
the other into a triplet (one more peak than the number of hydrogens). Now the puzzle has fewer pieces.



The methyl group is not split; it must be bonded to the oxygen or the carbonyl carbon. If it were bonded to one of the CH_2's it would be a triplet instead of a singlet. Since its chemical shift is 2.0, it must be bonded to the carbonyl; if it were bonded to the oxygen, the shift would be 3.5 to 5.0. The puzzle now has three pieces.



There is only one way these pieces fit together and the chemical shifts of the two CH_2 groups correspond to this structure.

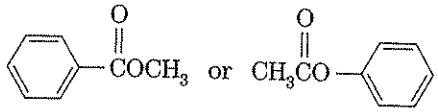


Problem 18.7

^{1}H Nuclear Magnetic Resonance: In each of the following problems, an nmr spectrum is described (chemical shift, splitting, ratio of hydrogens), and two or three isomeric compounds are given. Pick the compound whose spectrum is described and explain your choice.

(a) $\delta = 2.2$ singlet: $CH_3CH_2\overset{\overset{O}{\|}}{C}H$ or $CH_3\overset{\overset{O}{\|}}{C}CH_3$

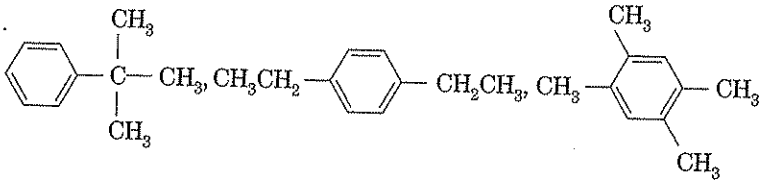
(b) $\delta = 3.9$ singlet (3), $\delta = 7.8$ (5):



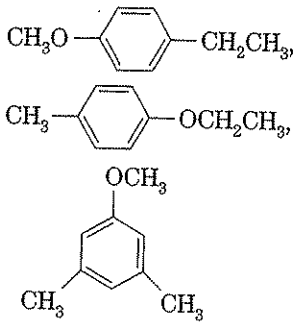
(c) $\delta = 1.1$ doublet (6), $\delta = 3.1$ singlet (3), $\delta = 3.5$ heptet (1):

$CH_3CH_2OCH_2CH_3$, or $CH_3O\overset{\overset{CH_3}{|}}{C}HCH_3$

(d) $\delta = 1.3$ triplet (3), $\delta = 2.7$ quartet (2), $\delta = 7.2$ singlet (2):



(e) $\delta = 1.2$ triplet (3), $\delta = 2.6$ quartet (2), $\delta = 3.7$ singlet (3), $\delta = 7.0$ singlet (4):



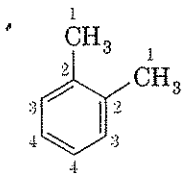
See related problems 18.15–18.16.

18.5 Carbon-13 NMR

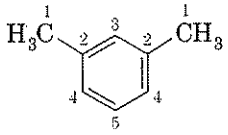
Like hydrogen (^1H), carbon-13 (^{13}C), an isotope of carbon, gives NMR spectra. Since organic chemistry is based on carbon, one can imagine that ^{13}C NMR could be an exciting analytical tool. However, ^{13}C has an isotopic abundance of only 1.1% in nature; only about one in 100 carbon atoms is this NMR active isotope. ^{12}C, normal carbon, is not active in NMR. In a sample of a simple organic compound, most molecules would not even have a carbon-13 as one of the carbons. However, even very small samples have uncountable numbers of molecules and among these are many molecules with a carbon-13, thus providing an analyzable quantity for each position of carbon. Very sophisticated instrumentation is required to record the ^{13}C NMR because of the low concentrations of ^{13}C isotope. This instrumentation became available around 1970 and is in common use today.

^{13}C NMR is useful in the following ways:

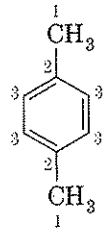
1. *The number of peaks in the spectrum is the number of nonequivalent carbons in the molecule.* Each different carbon gives a signal. Consider, for example, the xylenes (dimethylbenzenes), which can clearly be distinguished by ^{13}C NMR because of their different substitution patterns on the benzene ring resulting in several nonequivalent carbons (within each structure below, equivalent carbons have equivalent identifying numbers).



ortho
four peaks



meta
five peaks



para
three peaks

The ortho isomer has four different carbons and the ^{13}C NMR shows four peaks. Using the same reasoning, the meta isomer shows five peaks and the para isomer, only three in the ^{13}C NMR's.

2. *The chemical shift provides information about the structural environment of each carbon.* ^{13}C NMR uses tetramethylsilane as a reference and a scale of δ units, as does ^1H NMR. The chemical shifts in ^{13}C NMR, however, range over more than 200 δ units rather than the 10–15 units common in ^1H NMR. Some representative chemical shifts for carbons in various chemical environments follow.

C—C	C=C		C≡C	C—N	C—O	C=O	C—Cl	C—Br
10–60	100–150		70–90	30–60	40–80	160–210	30–80	

3. *The number of peaks into which a signal is split is one more than the number of hydrogens bonded to that carbon.* Because it is unlikely that a simple molecule will have even one carbon-13, much less two side by side, carbon-carbon splitting does not occur. However, splitting of a ^{13}C by attached hydrogens does occur for the reasons described in 18.4.C. A ^{13}C NMR spectrum can be run in a manner that will either show splitting of the carbons by attached hydrogens or not show the splitting. This is illustrated in Figure 18.10(a)–(b), which shows ^{13}C NMR of 2-bromobutane. Figure 18.10(a) shows the spectrum without splitting. A single peak appears for each of the four nonequivalent carbons. Splitting

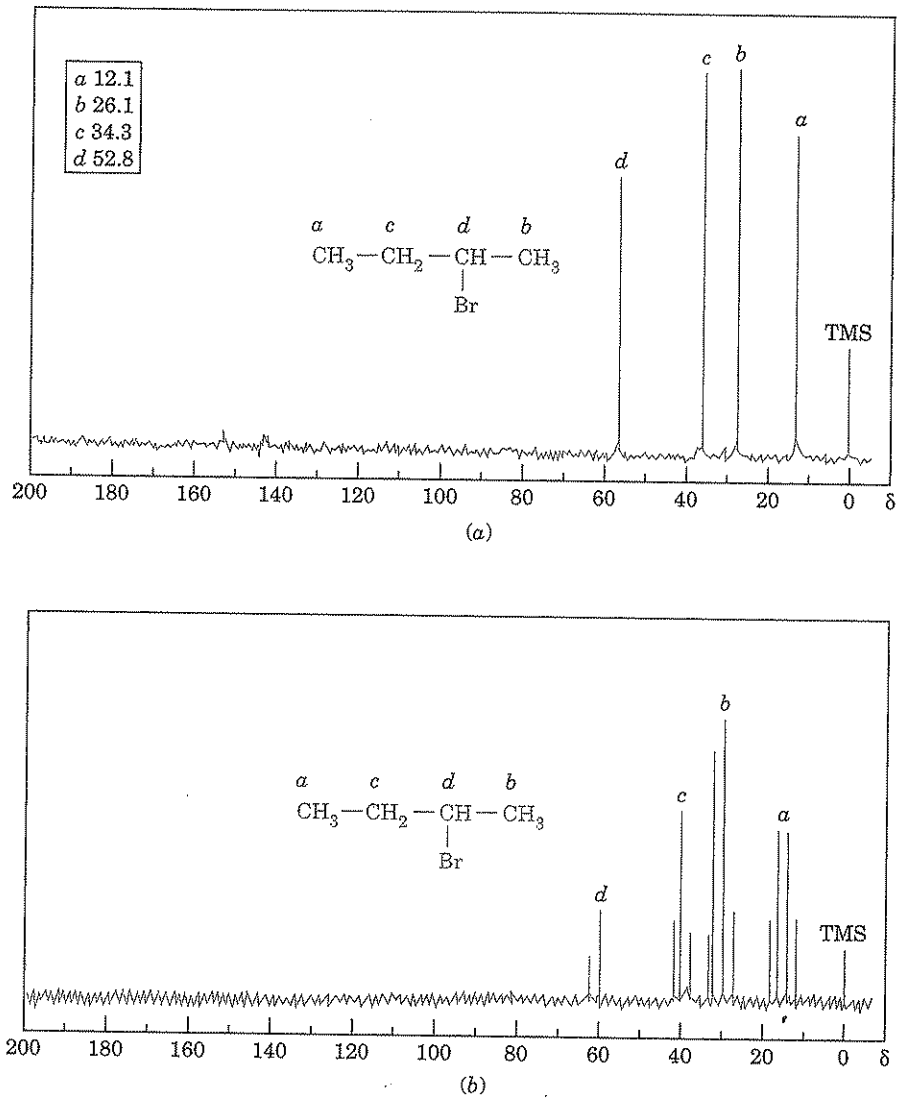


Figure 18.10 ^{13}C nmr spectra of 2-bromobutane. (a) Spectrum without splitting; (b) spectrum showing splitting of ^{13}C signals as a result of coupling with attached hydrogens. The signal at $\delta = 0$ in (a) is the TMS reference.

is shown in Figure 18.10(b). Note that the signal for each carbon is split into one more peak than the number of attached hydrogens.

GETTING INVOLVED

- ✓ Describe the three types of information that can be derived from carbon-13 NMR.
- ✓ What do the number of peaks mean? What is the difference in the chemical shift of a carbon involved in a single bond, triple bond, double bond, or benzene ring? What determines the number of peaks into which a carbon is split?

Problem 18.8

Which of the three trimethylbenzenes gives only three carbon-13 NMR signals at 138, 127, and 21? Which signal(s) correspond to carbons in the benzene ring? How many signals do each of the other two trimethylbenzene isomers show?

Problem 18.9

There are three tetramethylbenzenes. One gives carbon-13 NMR signals at 135, 134, 127, 21, and 16; another at 134, 131, and 19; and the third gives signals at 136, 134, 132, 128,

21, 20, and 15. Identify each of the isomers by the given spectrum. In each spectrum indicate which signals correspond to the methyl groups.

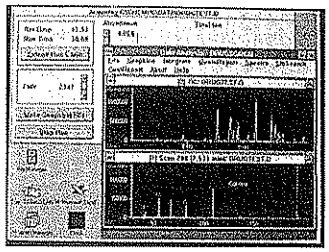
Problem 18.10

How many carbon-13 NMR signals would be predicted for the spectrum of hexamethylbenzene?

Problem 18.11

There are three isomers of C_3H_8O. One gives a carbon-13 spectrum that consists of a quartet and two triplets. Another shows two quartets and a triplet, and the third shows one quartet and a doublet. Draw the structure consistent with each spectrum.

See related problems 18.17–18.20.



Mass spectrum of an illicit drug

18.6 Mass Spectrometry

By **mass spectral analysis,** it is possible to determine the molecular weight and molecular formula of a compound. The structure of the compound is determined by breaking the molecule into smaller, identifiable fragments and then mentally piecing them back together, like a puzzle.

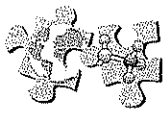
mass spectrometry
an instrumental analysis in which a molecule is fragmented with radiation and the individual fragment ions are identified for use in determining the structure of the compound analyzed

Mass spectral analysis is initiated by bombarding a vaporized sample with an electron beam. This can cause an electron to be dislodged from the molecule, producing a positive molecular ion. If the electron beam is sufficiently energetic, it may cause the molecule to rupture into a variety of positive fragments.

$$\underset{\text{Molecule}}{\text{ABC}} \xrightarrow[\text{beam}]{\text{Electron}} \begin{matrix} \text{ABC}^+ & & \\ \text{AB}^+ & \text{C}^+ & \\ \text{A}^+ & \text{BC}^+ & \end{matrix}$$

ABC$^+$: Molecular ion

AB$^+$, C$^+$, A$^+$, BC$^+$: Fragmentation ions

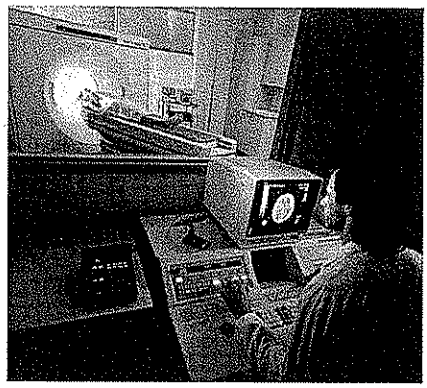


Connections 18.1 www.prenhall.com/bailey

MRI: Magnetic Resonance Imaging

Magnetic resonance imaging (MRI) is an established diagnostic tool in medicine; it provides information about anatomy and the functioning of cells and organs. MRI is actually a form of nuclear magnetic resonance, ^{1}H NMR (proton NMR) specifically. The human body is largely water (around 70%), which is found in all tissues. Since water has hydrogens, it is NMR active, and, as a result, there is the potential to probe the entire body.

In laboratory NMR used for chemical analysis, a sample is placed in a small, narrow tube and lowered into a powerful magnet. The spinning nuclei of hydrogen atoms act as tiny magnets that align either with or opposite the external magnetic field. The sample is exposed to radio waves, and some hydrogens in alignment are transformed to the less stable nonalignment state. The radio frequency at which this transformation occurs depends on the chemical and structural environment of the hydrogens in the molecules being analyzed. The same principle applies to MRI. The patient is placed in a tunnel surrounded by a large and powerful magnet. The body is magnetically scanned in selected cross-sectional planes. When exposed to radio waves, the body's hydrogen atoms flip from alignment to nonalignment with the external magnetic field, and this transformation is recorded. Hydrogens in different environments, for example,



MRI machine

Connections 18.1 *(cont.)*

healthy or diseased tissue or areas of high versus low water content, behave differently in MRI. These differences are recorded and computer analyzed; the result is a high-quality cross-sectional image of body structures and organs.

MRI became available in the early 1980s in some medical facilities. Its use has expanded and diagnostic applications are still being developed. It allows images to be constructed in any plane and is particularly valuable in studying the brain and spinal cord, revealing and diagnosing tumors, examining the heart and important blood vessels, determining blood flow, examining joints, and detecting abnormalities in internal anatomy. MRI is a noninvasive procedure and unlike X-ray radiography, CAT scanning, and radionuclide imaging, MRI does not employ potentially harmful radiation. There are no known risks or side effects and thus it can be used repeatedly.

The ions are then subjected to magnetic and electric fields. Since most of them have a single positive charge, they are separated according to mass (actually, mass to charge ratio, m/e), and the separation is recorded on chart paper. Each ion shows as a peak, the intensity of which describes the relative abundance of that particular ion. Usually the spectrum is then recorded in tabular form, correlating the mass and relative abundance of each ion. For example, the mass spectrum of carbon dioxide is as shown in Table 18.3.

base peak
the most intense peak in a mass spectrum

molecular ion
the peak corresponding to the molecule minus one electron in a mass spectrum

fragment ions
peaks caused by rupture of the molecule into fragments with m/e less than the molecular ion

The most intense peak in the mass spectrum is called the **base peak** and is assigned a value of 100%. The peak formed by the loss of one electron from the molecule is called the **molecular ion** M. In CO_2, the base peak and molecular ion peak are the same. Any peaks of less mass than the molecular ion are called **fragment ions.**

GETTING INVOLVED

What happens to a molecule when it is subjected to mass spectral analysis? What are a base peak, molecular ion peak, and fragment ions? What does it mean that the structure can be determined by piecing together the fragment ions like a puzzle?

A. Molecular Formula Determination

The atomic weights of common elements are averages of the weights of naturally occurring isotopes. For example, the atomic weight of chlorine is 35.5, since there are two abundant isotopes of chlorine in nature: Cl^{35}, 75%; and Cl^{37}, 25%. The mass spectrometer detects each isotope separately, and for chlorine there would be a peak at $m/e = 35$ and a peak at $m/e = 37$, one-third (25/75) as high. By considering such isotopic abundances, one can often determine the elemental composition of a compound.

1. ***Carbon.*** Most natural carbon is ^{12}C but about 1.1% is ^{13}C. For every carbon in the molecular ion M, the next higher ion M + 1 is 1.1% of the M ion. Note in Table 18.3 that the M + 1 ion of CO_2 is 1.11% of the M ion.

Table 18.3 Mass Spectrum of Carbon Dioxide

Mass (m/e)	Relative Abundance, %
28	20
29	0.2
44	100
45	1.11

$$\text{Number of carbons in M ion} = \frac{\text{rel. abund. M} + 1}{0.011 \times \text{rel. abund. M}}$$

	C_5H_{12}				$C_{10}H_{24}$		
$C_5^{12}H_{12}$	M	72	100%	$C_{10}^{12}H_{24}$	M	144	100%
$C_4^{12}C^{13}H_{12}$	M + 1	73	5.5%	$C_9^{12}C^{13}H_{24}$	M +1	145	11%

2. ***Chlorine.*** In compounds containing chlorine, the M + 2 ion (two mass units heavier than molecular ion) is about 33% of the molecular ion for each chlorine.

	CH_3Cl				CH_2Cl_2		
CH_3Cl^{35}	M	50	100%	$CH_2Cl_2^{35}$	M	84	100%
CH_3Cl^{37}	M + 2	52	33%	$CH_2Cl^{35}Cl^{37}$	M + 2	86	66%

3. ***Bromine.*** Naturally occurring bromine is almost equally abundant in Br^{79} and Br^{81}. So for every bromine in a molecule, the M + 2 ion is approximately 100% of the M ion.

	CH_3Br				CH_2Br_2		
CH_3Br^{79}	M	94	100%	$CH_2Br_2^{79}$	M	172	100%
CH_3Br^{81}	M + 2	96	99%	$CH_2Br^{79}Br^{81}$	M + 2	174	198%

4. ***Sulfur.*** For compounds containing sulfur, the M + 2 ion is 4.5% of the M ion for each sulfur, owing to the small isotopic abundance of S^{34} compared with S^{32}.

5. ***Nitrogen.*** If the molecular ion has an odd mass number, there is an odd number of nitrogens in the compound.

6. ***Hydrogen, Oxygen.*** Hydrogen, oxygen, and other common elements must be deduced by elimination after the other elemental components have been determined.

GETTING INVOLVED

- ✓ Describe how one determines the number of carbons in a molecule from mass spectrometry.
- ✓ How are chlorine, bromine, and sulfur detected and the number determined? How is nitrogen possibly identified? How are oxygen and hydrogen deduced?

Problem 18.12

For each of the following compounds, the M, M + 1, and M + 2 ions are given. Calculate the molecular formula.

(a) 96=100%, 97=7.7%, 98=0.1%;
(b) 92=100%, 93=3.3%, 94=33%;
(c) 156=100%, 157=6.6%, 158=98%;
(d) 234=49%, 235=3.3%, 236=98%;
(e) 91=100%, 92=2.2%, 93=4.5%.

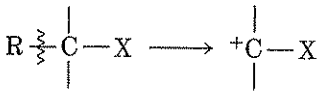
See related problem 18.21.

B. Fragmentation Patterns

Using the M, M + 1, and M + 2 ion, we can obtain the molecular mass and either a partial or a complete molecular formula. How do we obtain a structural formula? This is accomplished by analyzing the fragment ions. In mass spec-

Table 18.4 Main Cleavage Patterns in Mass Spectrometry

A. Resonance-Stabilized Ions



Prominent cleavage

X = O Alcohols and ethers 31, 45, 59, 73, 87, . . .

Alcohols $^{+}CH_2OH$ (31); $^{+}CH(CH_3)OH$ (45); $^{+}CH(CH_2CH_3)OH$ (59); $CH_3\overset{+}{C}(CH_3)OH$ (59)

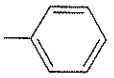
Ethers $^{+}CH_2OCH_3$ (45); $^{+}CH_2OCH_2CH_3$ (59); $^{+}CH_2OCH_2CH_2CH_3$ (73)

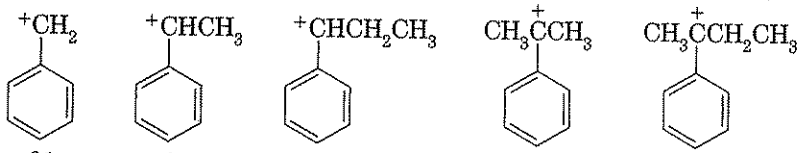
X = N Amines 30, 44, 58, 72, 86, . . .

$^{+}CH_2NH_2$ (30); $^{+}CH_2NHCH_3$ (44); $^{+}CH(CH_3)NH_2$ (44); $^{+}CH_2NHCH_2CH_3$ (58)

X = C=C Alkenes 41, 55, 69, 83, 97, 111, . . .

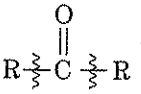
$^{+}CH_2CH{=}CH_2$ (41); $^{+}CH_2CH{=}CHCH_3$ (55); $^{+}CH_2CH{=}CHCH_2CH_3$ (69)

X =  Aromatic compounds 91, 105, 119, 133, . . .

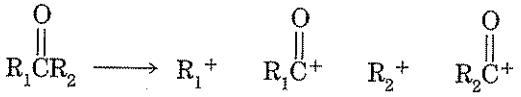


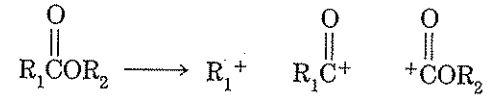
91 105 119 119 133

B. Carbonyl Compounds



Prominent cleavages

Aldehydes and ketones 

Carboxylic acids and esters 

R^+ 15, 29, 43, 57, 71, 85, 99, . . .

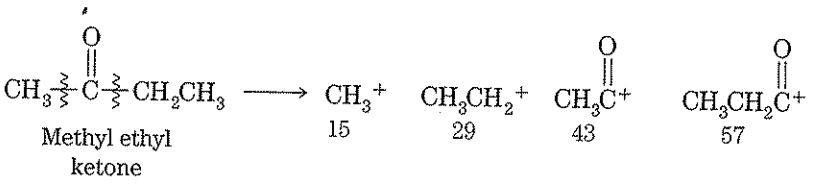
 43, 57, 71, 85, 99, 113, . . .  45, 59, 73, 87, 101, 115, . . .

Note: This table does not by any means summarize all important fragmentation patterns; it is a good start, however.

trometry, we take a large molecule whose structure is unknown and break it down with a beam of electrons into smaller, more easily identifiable fragments. The fragments are then pieced back together to obtain the structure of the unknown molecule.

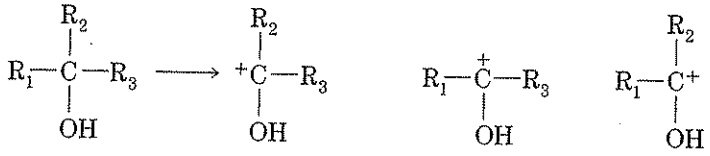
In a mass spectrometer, a molecule can undergo almost any possible cleavage to form all imaginable fragment ions. Fortunately, not all fragment ions form with equal ease. In general, we can say that the probability of fragmentation depends on: (1) bond strengths—almost all important fragmentations in organic molecules are at single bonds rather than at stronger double and triple bonds; and (2) carbocation stability—the fragments are positive, and the more stable the fragment, the greater the ease of formation. Table 18.4 summarizes some of the main cleavage patterns for the types of compounds we have studied in this text. The table also summarizes the numerical sequences of mass numbers associated with the particular fragment types. For example, consider the masses of alkyl groups. The simplest, methyl, CH_3^+, has a mass of 15. Ethyl, $CH_3CH_2^+$, is 29, 14 more, and each of the subsequent alkyl fragments has a mass 14 units more than the one before.

Let us take a specific example, methyl ethyl ketone. From Table 18.4, we see that ketones fragment predominantly on either side of the carbonyl group, giving four principal ions; in this case at m/e = 15, 29, 43, and 57. See Example 18.4.



It is evident that both alkyl (R—) and acyl (RC(=O)—) groups have the same numerical sequence. However, if we were to piece this together, we should assign the lowest mass number to the smaller alkyl group and the largest to the larger acyl group.

Another approach to structure determination is to identify the group that must have fallen off the molecule to produce an abundant fragment. To do this, we determine the mass difference between the molecular ion and the important fragment ions. For example, from Table 18.4 we see that alcohols preferentially cleave at the carbon bearing the hydroxy group. See Example 18.5.



GETTING INVOLVED

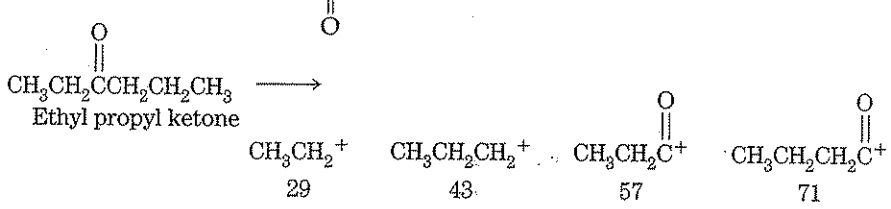
- ✓ What are fragment ions and how do they arise? What two principles largely determine where a fragmentation will occur?
- ✓ Make sure you understand the fragmentation patterns in Table 18.4 and begin learning the mass sequences that result.

Example 18.4

Now let us identify an unbranched ketone with the formula $C_7H_{14}O$ and principal ions at 29, 43, 57, and 71.

Solution

The smallest fragment, 29, corresponds to an ethyl group $CH_3CH_2^+$ and the largest, 71, to the acyl group $CH_3CH_2CH_2C^+=O$. The compound is ethyl propyl ketone.

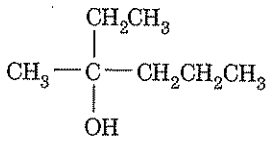


Example 18.5

Suppose we have an unknown alcohol that gives a mass spectrum with a molecular ion of 116 and principal ions at 101, 87, and 73.

Solution

First, determine the difference between the molecular ion and fragment ion, M-101, M-87, and M-73. The peak M-101 is 15. One of the R groups then must have a mass of 15 and be a methyl. M-87 is 29, and must represent an ethyl group. Finally, M-73 is 43, either a propyl or an isopropyl group. A possible structure then for the unknown is one in which $R_1 = -CH_3$, $R_2 = -CH_2CH_3$, and $R_3 = -CH_2CH_2CH_3$.



Problem 18.13

In each of the following problems, a partial description of an unknown compound and the important ions in its mass spectrum are presented. Write a structure consistent with the information.

(a) a straight-chained ketone with the formula $C_7H_{14}O$ (M=114) with major fragments at 29, 57, and 85; **(b)** a monosubstituted benzene with the formula $C_{10}H_{16}$ (M=134) with major fragments at 77, 105, and 119; **(c)** a straight-chained secondary alcohol with the formula $C_5H_{12}O$ (M=88) and major fragments at 45 and 73; **(d)** a straight-chained ester with the formula $C_4H_8O_2$ (M=88) and major fragments at 15, 43, and 73; **(e)** a straight-chained alkene with the formula C_6H_{12} (M=84) and a major fragment at 69.

See related problems 18.21–18.23.

Problems

18.14 **Infrared Spectroscopy:** How could one distinguish between the members of the following sets of compounds by infrared spectroscopy? Give the wavenumber of an easily identifiable absorption band that would appear in one molecule but not the other. Identify the bond responsible for the absorption.