ency of the radiation: the higher the
e greater the gain in energy.

$h\nu$

n ergs
t, 6.5×10^{-27} erg sec

in this way may bring about increased
raise electrons to higher energy levels.
t a given molecule can absorb depends
s or electronic states that are permitted
um of a compound is a plot that shows
orbed (or transmitted) at each frequency.
ound's structure.

npound, the one that, by itself, gives the
tructure is its infrared spectrum.
s bonds *stretch* (and contract), and *bend*
ibrations of a molecule are caused by
eyond (lower frequency, longer wave-
pectrum.
um is referred to either by its wavelength
its frequency. Wavelength is expressed
). Frequency is expressed, not in hertz,
ciprocal centimeters; the wavenumber is
er, and is equal to the reciprocal of the

ed spectrum is a highly characteristic
r example, the spectra in Fig. 17.2—and
y of two compounds and to reveal the

frared spectra are, in effect, identical in
—the absorption of light at thousands of
ertainly be the same compound. (One
ppropriately, the *fingerprint* region.)
al the structure of a new compound by
bsent from—the molecule. A particular
bsorption bands; that is to say, a particu-
cies that are much the same from com-
-OH group of alcohols absorbs strongly
tones at 1710 cm^{-1}; the —C≡N group
nd 1375 cm^{-1}.
n is not a simple matter. Bands may be
ds. Overtones (harmonics) may appear
nental band. The absorption band of a
s structural features—conjugation, elec-
ent, angle strain or van der Waals strain,

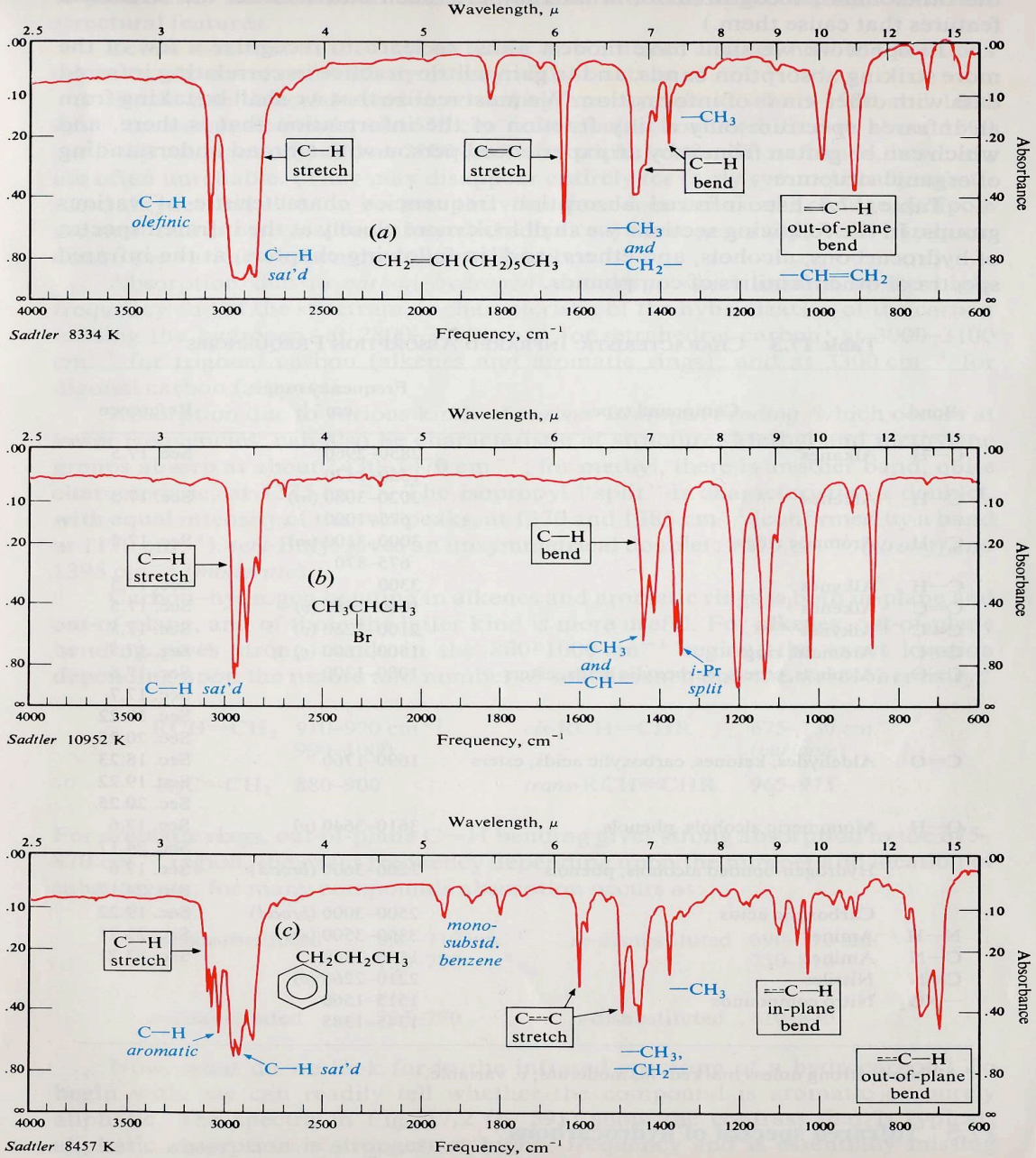

Figure 17.2 Infrared spectra. (*a*) 1-Octene; (*b*) isopropyl bromide; (*c*) *n*-butylbenzene.

hydrogen bonding—and be mistaken for a band of an entirely different group. (On the other hand, recognized for what they are, such shifts *reveal* the structural features that cause them.)

In our work we shall have modest aims: to learn to recognize a few of the more striking absorption bands, and to gain a little practice in correlating infrared data with other kinds of information. We must realize that we shall be taking from an infrared spectrum only a tiny fraction of the information that is there, and which can be gotten from it by an experienced person with a broad understanding of organic structure.

Table 17.3 lists infrared absorption frequencies characteristic of various groups. In the following sections we shall look more closely at the infrared spectra of hydrocarbons, alcohols, and ethers; and, in following chapters, at the infrared spectra of other families of compounds.

Table 17.3 CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES[a]

Bond	Compound type	Frequency range, cm^{-1}	Reference
C—H	Alkanes	2850–2960 1350–1470	Sec. 17.5
C—H	Alkenes	3020–3080 (*m*) 675–1000	Sec. 17.5
C—H	Aromatic rings	3000–3100 (*m*) 675–870	Sec. 17.5
C—H	Alkynes	3300	Sec. 17.5
C=C	Alkenes	1640–1680 (*v*)	Sec. 17.5
C≡C	Alkynes	2100–2260 (*v*)	Sec. 17.5
C···C	Aromatic rings	1500, 1600 (*v*)	Sec. 17.5
C—O	Alcohols, ethers, carboxylic acids, esters	1080–1300	Sec. 17.6 Sec. 17.7 Sec. 19.22 Sec. 20.25
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Sec. 18.23 Sec. 19.22 Sec. 20.25
O—H	Monomeric alcohols, phenols	3610–3640 (*v*)	Sec. 17.6 Sec. 24.17
	Hydrogen-bonded alcohols, phenols	3200–3600 (*broad*)	Sec. 17.6 Sec. 24.17
	Carboxylic acids	2500–3000 (*broad*)	Sec. 19.22
N—H	Amines	3300–3500 (*m*)	Sec. 23.21
C—N	Amines	1180–1360	Sec. 23.21
C≡N	Nitriles	2210–2260 (*v*)	
$-NO_2$	Nitro compounds	1515–1560 1345–1385	

[a] All bands strong unless marked: *m*, moderate; *v*, variable.

17.5 Infrared spectra of hydrocarbons

In this first encounter with infrared spectra, we shall see absorption bands due to vibrations of carbon–hydrogen and carbon–carbon bonds: bands that will constantly reappear in all the spectra we meet, since along with their various functional groups, compounds of all kinds contain carbon and hydrogen. We must expect to find these spectra complicated and, at first, confusing. Our aim is to learn to pick out of the confusion those bands that are most characteristic of certain structural features.

Let us look first at the various kinds of vibration, and see how the positions of the bands associated with them vary with structure.

Bands due to *carbon–carbon stretching* may appear at about 1500 and 1600 cm^{-1} for aromatic bonds, at 1650 cm^{-1} for double bonds (shifted to about 1600 cm^{-1} by conjugation), and at 2100 cm^{-1} for triple bonds. These bands, however, are often unreliable. (They may disappear entirely for fairly symmetrically substituted alkynes and alkenes, because the vibrations do not cause the change in dipole moment that is essential for infrared absorption.) More generally useful bands are due to the various carbon–hydrogen vibrations.

Absorption due to *carbon–hydrogen stretching*, which occurs at the high-frequency end of the spectrum, is characteristic of the hybridization of the carbon holding the hydrogen: at 2800–3000 cm^{-1} for tetrahedral carbon; at 3000–3100 cm^{-1} for trigonal carbon (alkenes and aromatic rings); and at 3300 cm^{-1} for digonal carbon (alkynes).

Absorption due to various kinds of *carbon–hydrogen bending*, which occurs at lower frequencies, can also be characteristic of structure. Methyl and methylene groups absorb at about 1430–1470 cm^{-1}; for methyl, there is another band, quite characteristic, at 1375 cm^{-1}. The isopropyl "split" is characteristic: a doublet, with equal intensity of the two peaks, at 1370 and 1385 cm^{-1} (confirmed by a band at 1170 cm^{-1}). *tert*-Butyl gives an unsymmetrical doublet: 1370 cm^{-1} (*strong*) and 1395 cm^{-1} (*moderate*).

Carbon–hydrogen bending in alkenes and aromatic rings is both in-plane and out-of-plane, and of these the latter kind is more useful. For **alkenes**, out-of-plane bending gives strong bands in the 800–1000 cm^{-1} region, the exact location depending upon the nature and number of substituents, and the stereochemistry:

$RCH=CH_2$	910–920 cm^{-1} 990–1000	*cis*-RCH=CHR	675–730 cm^{-1} (*variable*)
$R_2C=CH_2$	880–900	*trans*-RCH=CHR	965–975

For **aromatic rings**, out-of-plane C—H bending gives strong absorption in the 675–870 cm^{-1} region, the exact frequency depending upon the number and location of substituents; for many compounds absorption occurs at:

monosubstituted	690–710 cm^{-1} 730–770	*m*-disubstituted	690–710 cm^{-1} 750–810
o-disubstituted	735–770	*p*-disubstituted	810–840

Now, what do we look for in the infrared spectrum of a hydrocarbon? To begin with, we can readily tell whether the compound is aromatic or purely aliphatic. The spectra in Fig. 17.2 (p. 591) show the contrast that is typical: aliphatic absorption is strongest at higher frequency and is essentially missing below 900 cm^{-1}; aromatic absorption is strong at lower frequencies (C—H out-of-plane bending) between 650 and 900 cm^{-1}. In addition, an aromatic ring will show C—H stretching at 3000–3100 cm^{-1}; often, there is carbon–carbon stretching at 1500 and 1600 cm^{-1} and C—H in-plane bending in the 1000–1100 cm^{-1} region.

An alkene shows C—H stretching at 3000–3100 cm^{-1} and, most characteristically, strong out-of-plane C—H bending between 800 and 1000 cm^{-1}, as discussed above.

A terminal alkyne, RC≡CH, is characterized by its C—H stretching band, a strong and sharp band at 3300 cm^{-1}, and by carbon–carbon stretching at 2100 cm^{-1}. A disubstituted alkyne, on the other hand, does not show the 3300 cm^{-1} band and, if the two groups are fairly similar, the 2100 cm^{-1} band may be missing, too.

Some of these characteristic bands are labeled in the spectra of Fig. 17.2 (p. 591).

Problem 17.2 What is a likely structure for a hydrocarbon of formula C_6H_{12} that shows strong absorption at 2920 and 2840 cm^{-1}, and at 1450 cm^{-1}; none above 2920 cm^{-1}; and below 1450 cm^{-1} none until about 1250 cm^{-1}?

Problem 17.3 Give a structure or structures consistent with each of the infrared spectra in Fig. 17.4 (pp. 595–596).

17.6 Infrared spectra of alcohols

In the infrared spectrum of a hydrogen-bonded alcohol—and this is the kind that we commonly see—the most conspicuous feature is a strong, broad band in the 3200–3600 cm^{-1} region due to O—H stretching (see Fig. 17.3).

O—H stretching, *strong, broad*

Alcohols, ROH (or phenols, ArOH) 3200–3600 cm^{-1}

(A monomeric alcohol gives a sharp, variable band at 3610–3640 cm^{-1}.)

Another strong, broad band, due to C—O stretching, appears in the 1000–1200 cm^{-1} region, the exact frequency depending on the nature of the alcohol:

C—O stretching, *strong, broad*

1° ROH	about 1050 cm^{-1}	3° ROH	about 1150 cm^{-1}
2° ROH	about 1100 cm^{-1}	ArOH	about 1230 cm^{-1}

(Compare the locations of this band in the spectra of Fig. 17.3.)

Phenols (ArOH) also show both these bands, but the C—O stretching appears at somewhat higher frequencies. Ethers show C—O stretching, but the O—H band is absent. Carboxylic acids and esters show C—O stretching, but give absorption characteristic of the carbonyl group, C=O, as well. (For a comparison of certain oxygen compounds, see Table 20.3, p. 786.)

Problem 17.4 Upon hydrogenation, compound A (C_4H_8O) is converted into B ($C_4H_{10}O$). On the basis of their infrared spectra (Fig. 17.6, p. 598), give the structural formulas of A and B.

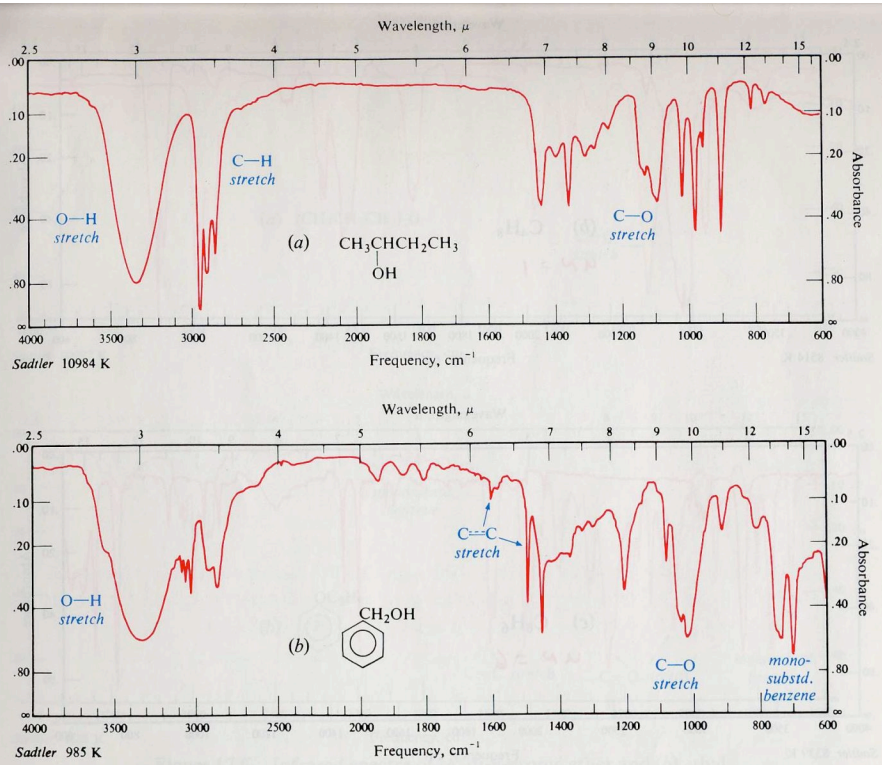

Figure 17.3 Infrared spectra of (*a*) *sec*-butyl alcohol and (*b*) benzyl alcohol.

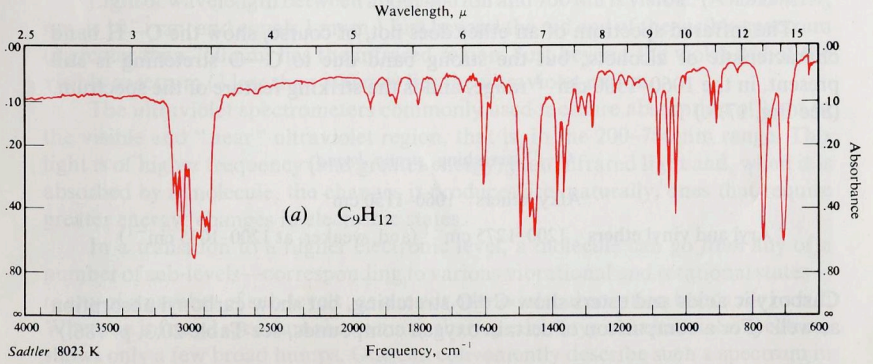

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Figure 17.4(a) Infrared spectra for Problem 17.3, p. 594.

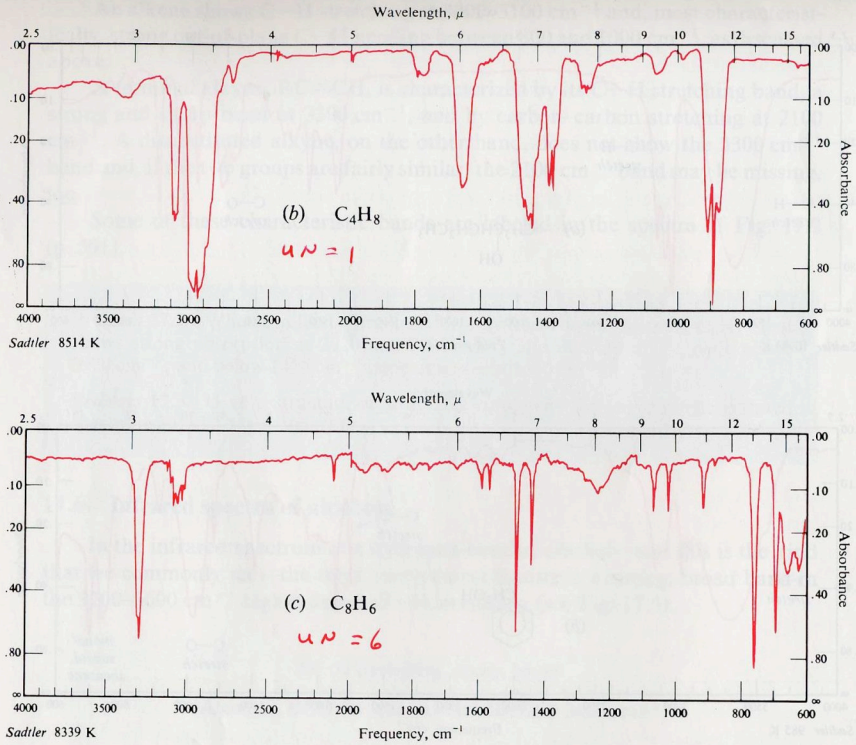

Figure 17.4(b), (c) Infrared spectra for Problem 17.3, p. 594.

17.7 Infrared spectra of ethers

The infrared spectrum of an ether does not, of course, show the O—H band characteristic of alcohols; but the strong band due to C—O stretching is still present, in the 1060–1300 cm^{-1} range, and is the striking feature of the spectrum. (See Fig. 17.5.)

C—O stretching, *strong, broad*

Alkyl ethers 1060–1150 cm^{-1}

Aryl and vinyl ethers 1200–1275 cm^{-1} (and, weaker, at 1200–1075 cm^{-1})

Carboxylic acids and esters show C—O stretching, but show carbonyl absorption as well. (For a comparison of certain oxygen compounds, see Table 20.3, p. 786.)

Problem 17.5 Give a structure or structures for the compound whose infrared spectrum is shown in Fig. 17.7 (p. 598).

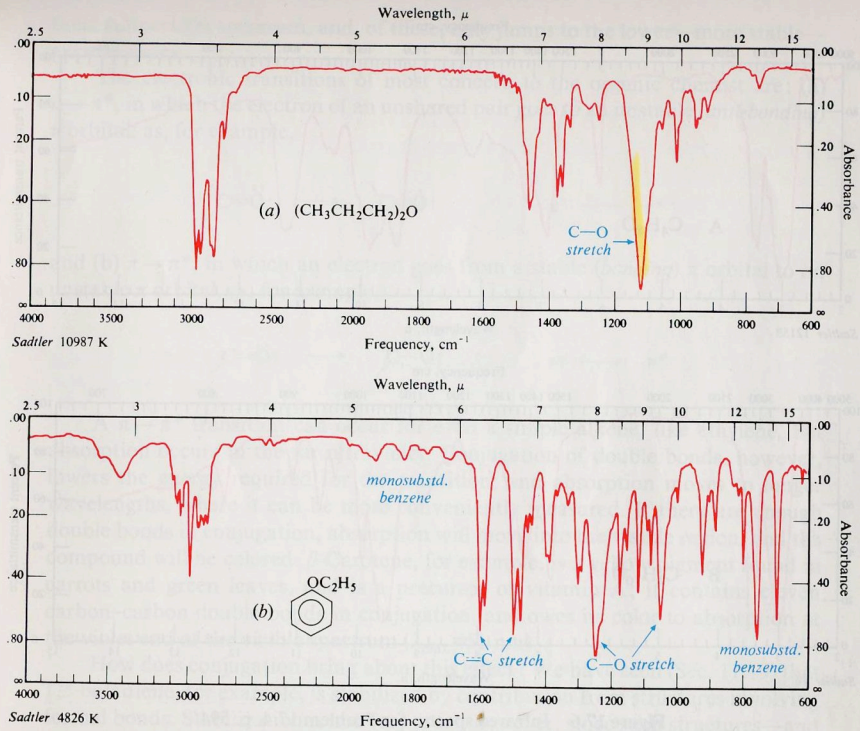

Figure 17.5 Infrared spectra of (*a*) di-*n*-propyl ether and (*b*) ethyl phenyl ether.

17.8 The ultraviolet spectrum

Light of wavelength between about 400 nm and 750 nm is visible. (A *nanometer*, nm, is 10^{-7} cm, and equals 1 mμm.) Just beyond the red end of the visible spectrum (λ greater than 750 nm) lies the infrared region. Just beyond the violet end of the visible spectrum (λ less than 400 nm) lies the ultraviolet region.

The ultraviolet spectrometers commonly used measure absorption of light in the visible and "near" ultraviolet region, that is, in the 200–750 nm range. This light is of higher frequency (and greater energy) than infrared light and, when it is absorbed by a molecule, the changes it produces are, naturally, ones that require greater energy: changes in electronic states.

In a transition to a higher electronic level, a molecule can go *from* any of a number of sub-levels—corresponding to various vibrational and rotational states—*to* any of a number of sub-levels; as a result, ultraviolet absorption bands are broad. Where an infrared spectrum shows many sharp peaks, a typical ultraviolet spectrum shows only a few broad humps. One can conveniently describe such a spectrum in terms of the *position* of the top of the hump (λ_{max}) and the *intensity* of that absorption (ϵ_{max}, the extinction coefficient).

When we speak of a molecule as being raised to a higher electronic level, we mean that an electron has been changed from one orbital to another orbital of