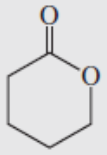
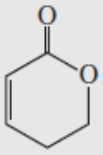
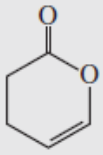
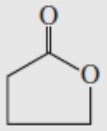
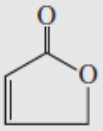
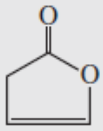
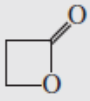
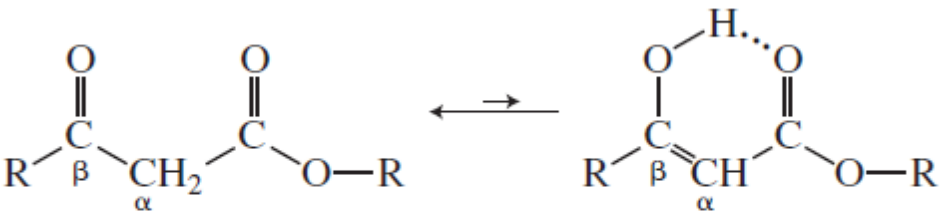
Lecture # 4-2

TABLE 2.8
EFFECTS OF RING SIZE, α,β UNSATURATION, AND CONJUGATION WITH OXYGEN ON THE C=O VIBRATIONS IN LACTONES

Ring-Size Effects (cm^{-1})	α,β Conjugation (cm^{-1})	Conjugation with Oxygen (cm^{-1})
 1735	 1725	 1760
 1770	 1750	 1800
 1820		

β-Keto Esters. Although this class of compounds exhibits tautomerization like that observed in β-diketones, less evidence exists for the enol form because β-keto esters do not enolize to as great an extent. β-Keto esters exhibit a *strong-intensity* doublet for the two carbonyl groups at about 1720 and 1740 cm^{-1} in the "keto" tautomer, presumably for the ketone and ester C=O groups. Evidence for the *weak-intensity* C=O band in the "enol" tautomer (often a doublet) appears at about 1650 cm^{-1}. Because of the low concentration of the enol tautomer, one generally cannot observe the broad O—H stretch that was observed in β-diketones.



Keto tautomer Enol tautomer

C—O Stretching Vibrations in Esters. Two (or more) bands appear for the C—O stretching vibrations in esters in the range from 1300 to 1000 cm^{-1}. Generally, the C—O stretch next to the carbonyl group (the "acid" side) of the ester is one of the strongest and broadest bands in the spectrum. This absorption appears between 1300 and 1150 cm^{-1} for most common esters; esters of aromatic acids absorb nearer the higher-frequency end of this range, and esters of saturated acids absorb nearer the lower-frequency end. The C—O stretch for the "alcohol" part of the ester may appear as a weaker band in the range from 1150 to 1000 cm^{-1}. In analyzing the 1300- to 1000-cm^{-1} region to confirm an ester functional group, do not worry about fine details. It is usually sufficient to find at least one very strong and broad absorption to help identify the compound as an ester.

Amides

Amides show a very strong band for the C=O group that appears in the range of 1700–1640 cm^{-1}. The N—H stretch is observed in the range of 3475–3150 cm^{-1}. Unsubstituted (primary) amides, R—CO—NH_2, show two bands in the N—H region, while monosubstituted (secondary) amides, R—CO—NH—R, show only one band. The presence of N—H bands plus an unusually low value for the C=O would suggest the presence of an amide functional group. Disubstituted (tertiary) amides, R—CO—NR_2, will show the C=O in the range of 1680–1630 cm^{-1}, but will not show an N—H stretch.

SPECTRAL ANALYSIS BOX

AMIDES

C=O	Stretch occurs at approximately 1700—1640 cm^{-1}.
N—H	Stretch in primary amides (—NH_2) gives two bands near 3350 and 3180 cm^{-1}. Secondary amides have one band (—NH) at about 3300 cm^{-1}.
N—H	Bending occurs around 1640–1550 cm^{-1} for primary and secondary amides.

Examples: propionamide (Fig. 2.53) and *N*-methylacetamide (Fig. 2.54).

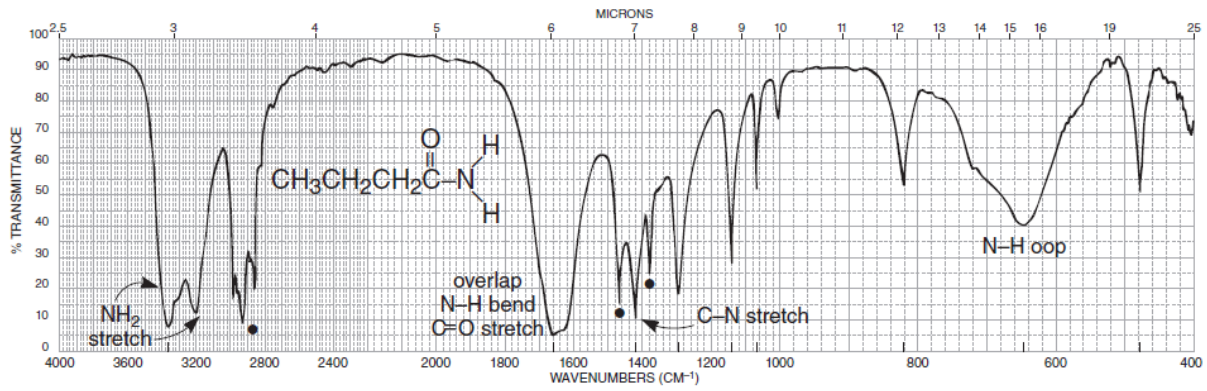
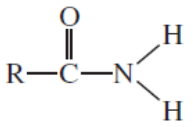
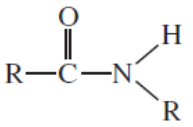


FIGURE 2.53 The infrared spectrum of propionamide (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

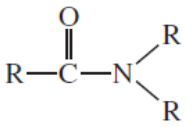
Carbonyl Absorption in Amides. Primary and secondary amides in the solid phase (potassium bromide pellet or Nujol) have broad C=O absorptions in the range from 1700–1640 cm^{-1}. The C=O band partially overlaps the N−H bending band which appears in the range 1680–1630 cm^{-1}, making the C=O band appear as a doublet. In very dilute solution, the band appears at about 1690 cm^{-1}. This effect is similar to that observed for carboxylic acids, in which hydrogen bonding reduces the frequency in the solid state or in concentrated solution. Tertiary amides, which cannot form hydrogen bonds, have C=O frequencies that are not influenced by the physical state and absorb in about the same range as do primary and secondary amides (1700–1640 cm^{-1}).



Primary amide

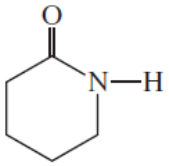


Secondary amide

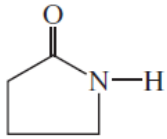


Tertiary amide

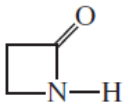
Cyclic amides (lactams) give the expected increase in C=O frequency for decreasing ring size, as shown for lactones in Table 2.8.



~1660 cm^{-1}



~1705 cm^{-1}



~1745 cm^{-1}

N−H and C−N Stretching Bands. A pair of fairly strong N−H stretching bands appears at about 3350 cm^{-1} and 3180 cm^{-1} for a primary amide in the solid state (KBr or Nujol). The 3350- and 3180-cm^{-1} bands result from the asymmetric and symmetric vibrations, respectively (Section 2.3). Figure 2.53 shows an example, the spectrum of propionamide. In the solid state, secondary amides and lactams give one band at about 3300 cm^{-1}. A weaker band may appear at about 3100 cm^{-1} in secondary amides; it is attributed to a Fermi resonance overtone of the 1550-cm^{-1} band. A C−N stretching band appears at about 1400 cm^{-1} for primary amides.

N−H Bending Bands. In the solid state, primary amides give strong bending vibrational bands in the range from 1640 to 1620 cm^{-1}. They often nearly overlap the C=O stretching bands. Primary amides give other bending bands at about 1125 cm^{-1} and a very broad band in the range from 750 to 600 cm^{-1}. Secondary amides give relatively strong bending bands at about 1550 cm^{-1}; these are attributed to a combination of a C−N stretching band and an N−H bending band.

Acid Chlorides

Acid chlorides show a very strong band for the C=O group that appears in the range of 1810–1775 cm^{-1} for aliphatic acid chlorides. Acid chloride and anhydrides are the most common functional groups that have a C=O appearing at such a high frequency. Conjugation lowers the frequency.

SPECTRAL ANALYSIS BOX

ACID CHLORIDES

C=O Stretch occurs in the range 1810–1775 cm^{-1} in unconjugated chlorides. Conjugation lowers the frequency to 1780–1760 cm^{-1}.

C—Cl Stretch occurs in the range 730–550 cm^{-1}.

Examples: acetyl chloride (Fig. 2.55) and benzoyl chloride (Fig. 2.56).

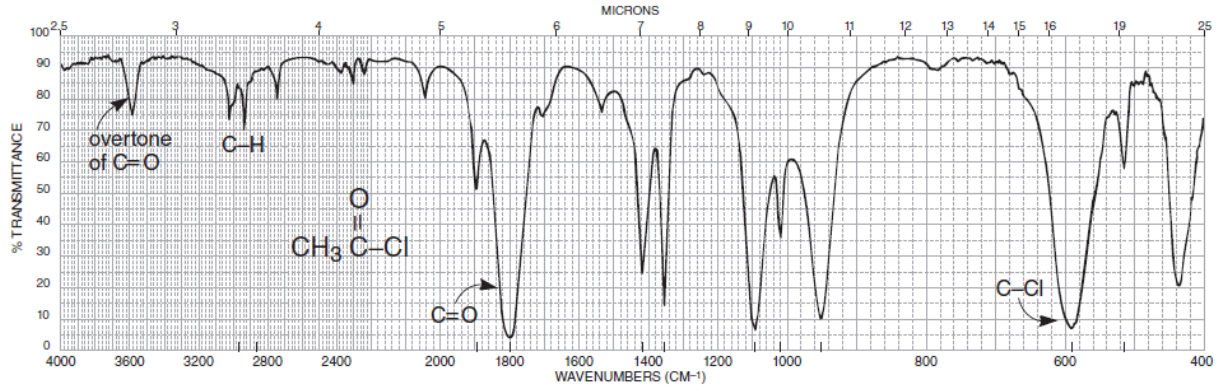


FIGURE 2.55 The infrared spectrum of acetyl chloride (neat liquid, KBr plates).

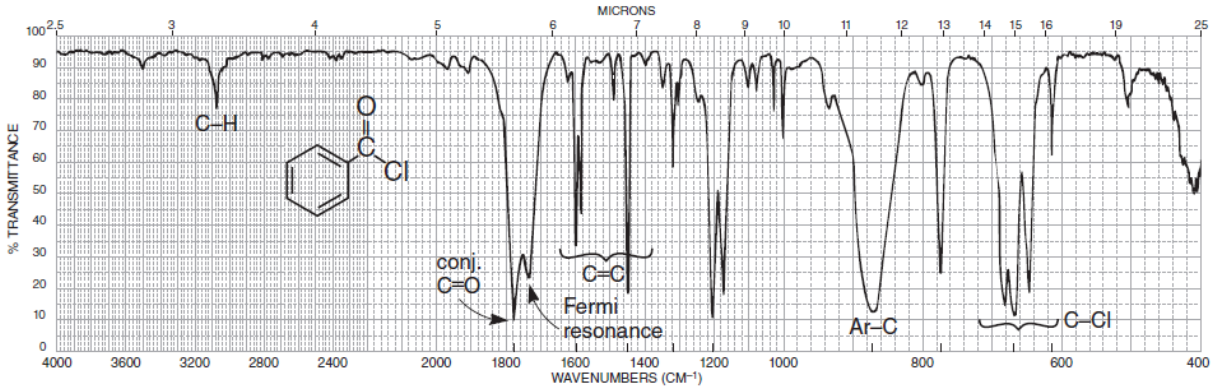


FIGURE 2.56 The infrared spectrum of benzoyl chloride (neat liquid, KBr plates).

C=O Stretching Vibrations. By far the most common acid halides, and the only ones discussed in this book, are acid chlorides. The strong carbonyl absorption appears at a characteristically high frequency of about 1800 cm^{-1} for saturated acid chlorides. Figure 2.55 shows the spectrum of acetyl chloride. Conjugated acid chlorides absorb at a lower frequency (1780 to 1760 cm^{-1}), as predicted in Section 2.14A. Figure 2.56 shows an example of an aryl-substituted acid chloride, benzoyl chloride. In this spectrum, the main absorption occurs at 1774 cm^{-1}, but a weak shoulder appears on the higher-frequency side of the C=O band (about 1810 cm^{-1}). The shoulder is probably the result of an overtone of a strong band in the 1000- to 900-cm^{-1} range. A weak band is also seen at about 1900 cm^{-1} in the spectrum of acetyl chloride (Fig. 2.55). Sometimes, this overtone band is relatively strong.

In some aromatic acid chlorides, one may observe another rather strong band, often on the lower-frequency side of the C=O band, which makes the C=O appear as a doublet. This band, which appears in the spectrum of benzoyl chloride (Fig. 2.56) at about 1730 cm^{-1}, is probably a Fermi resonance band originating from an interaction of the C=O vibration, with an overtone of a strong band for aryl-C stretch often appearing in the range from 900 to 800 cm^{-1}. When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called **Fermi resonance.** The Fermi resonance band may also appear on the higher-frequency side of the C=O in many aromatic acid chlorides. This type of interaction can lead to splitting in other carbonyl compounds as well.

C−Cl Stretching Vibrations. These bands, which appear in the range from 730 to 550 cm^{-1}, are best observed if KBr plates or cells are used. One strong C−Cl band appears in the spectrum of acetyl chloride. In other aliphatic acid chlorides, one may observe as many as four bands due to the many conformations that are possible.

Anhydrides

Anhydrides show two strong bands for the C=O groups. Simple alkyl-substituted anhydrides generally give bands near 1820 and 1750 cm^{-1}. Anhydrides and acid chlorides are the most common functional groups that have a C=O peak appearing at such a high frequency. Conjugation shifts each of the bands to lower frequencies (about 30 cm^{-1} each). Simple five-membered ring anhydrides have bands at near 1860 and 1780 cm^{-1}.

SPECTRAL ANALYSIS BOX

ANHYDRIDES

C=O Stretch always has two bands, 1830–1800 cm^{-1} and 1775–1740 cm^{-1}, with variable relative intensity. Conjugation moves the absorption to a lower frequency. Ring strain (cyclic anhydrides) moves the absorptions to a higher frequency.

C−O Stretch (multiple bands) occurs in the range 1300–900 cm^{-1}.

Example: propionic anhydride (Fig. 2.57).

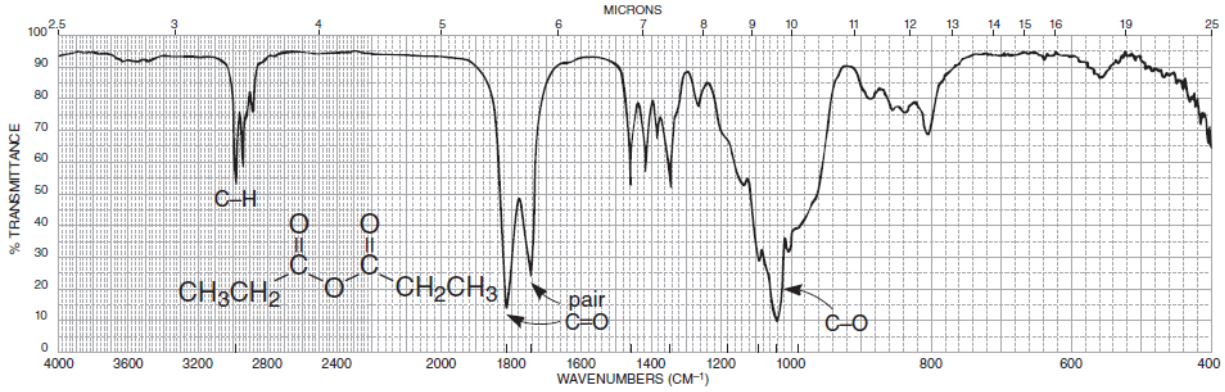


FIGURE 2.57 The infrared spectrum of propionic anhydride (neat liquid, KBr plates).

The characteristic pattern for noncyclic and saturated anhydrides is the appearance of *two strong bands,* not necessarily of equal intensities, in the regions from 1830 to 1800 cm^{-1} and from 1775 to 1740 cm^{-1}. The two bands result from asymmetric and symmetric stretch (Section 2.3). Conjugation shifts the absorption to a lower frequency, while cyclization (ring strain) shifts the absorption to a higher frequency. The *strong* and *broad* C−O stretching vibrations occur in the region from 1300 to 900 cm^{-1}. Figure 2.57 shows the spectrum of propionic anhydride.

2.15 AMINES

Primary amines, $R-NH_2$, show two N−H stretching bands in the range 3500–3300 cm^{-1}, whereas secondary amines, R_2N-H, show only one band in that region. Tertiary amines will not show an N−H stretch. Because of these features, it is easy to differentiate among primary, secondary, and tertiary amines by inspection of the N−H stretch region.

SPECTRAL ANALYSIS BOX

AMINES

N—H	Stretch occurs in the range 3500–3300 cm^{-1}. Primary amines have two bands. Secondary amines have one band: a vanishingly weak one for aliphatic compounds and a stronger one for aromatic secondary amines. Tertiary amines have no N—H stretch.
N—H	Bend in primary amines results in a broad band in the range 1640–1560 cm^{-1}. Secondary amines absorb near 1500 cm^{-1}.
N—H	Out-of-plane bending absorption can sometimes be observed near 800 cm^{-1}.
C—N	Stretch occurs in the range 1350–1000 cm^{-1}.

Examples: butylamine (Fig. 2.58), dibutylamine (Fig. 2.59), tributylamine (Fig. 2.60), and *N*-methylaniline (Fig. 2.61).

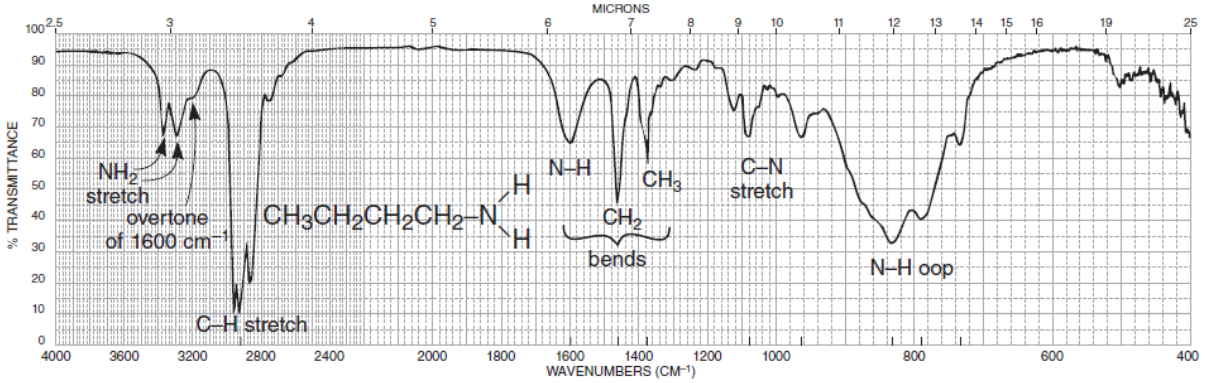


FIGURE 2.58 The infrared spectrum of butylamine (neat liquid, KBr plates).

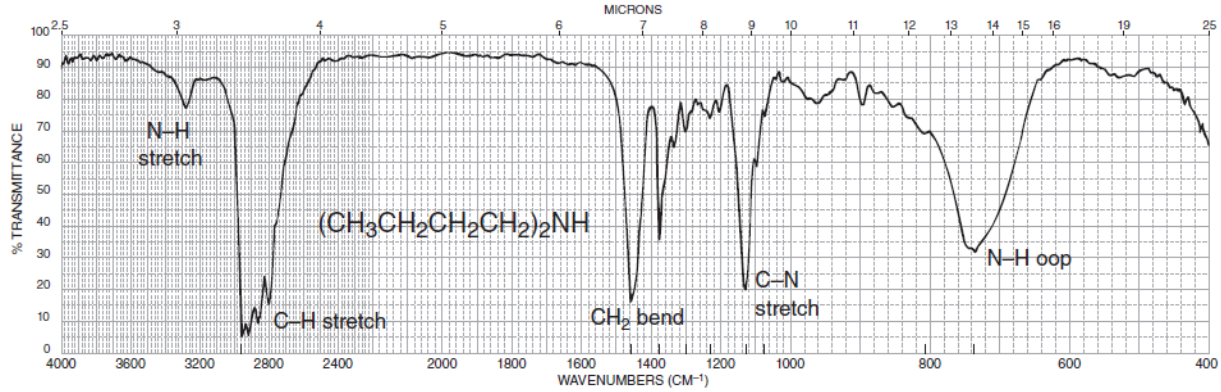


FIGURE 2.59 The infrared spectrum of dibutylamine (neat liquid, KBr plates).

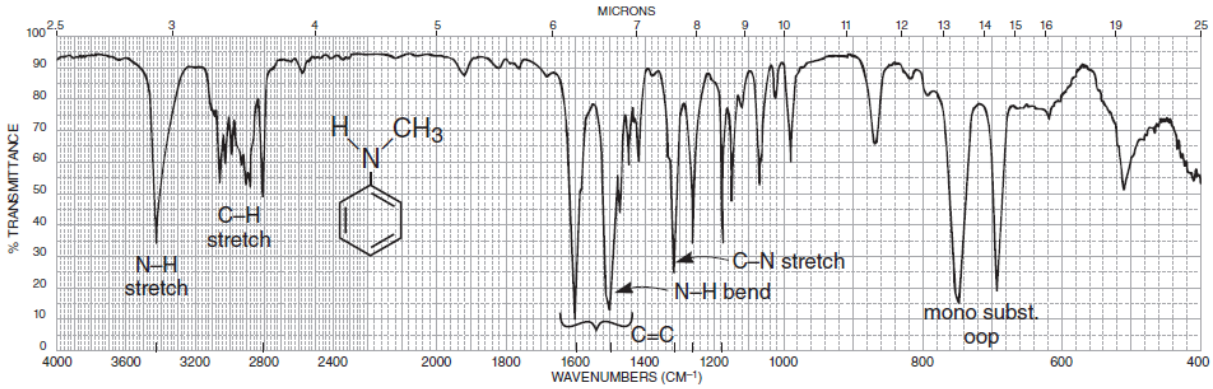


FIGURE 2.61 The infrared spectrum of *N*-methylaniline (neat liquid, KBr plates).

The N—H stretching vibrations occur in the range from 3500 to 3300 cm^{-1}. In neat liquid samples, the N—H bands are often weaker and sharper than an O—H band (see Fig. 2.6). Amines may sometimes be differentiated from alcohols on that basis. Primary amines, determined as neat liquids (hydrogen bonded), give *two bands* at about 3400 and 3300 cm^{-1}. The higher-frequency band in the pair is due to the asymmetric vibration, whereas the lower-frequency band results from a symmetric vibration (Section 2.3). In dilute solution, the two free N—H stretching vibrations are shifted to higher frequencies. Figure 2.58 shows the spectrum of an aliphatic primary amine. A low-intensity shoulder appears at about 3200 cm^{-1} on the low-frequency side of the symmetric N—H stretching band. This low-intensity band has been attributed to an overtone of the N—H *bending* vibration that appears near 1600 cm^{-1}. The 3200-cm^{-1} shoulder has been enhanced by a Fermi resonance interaction with the symmetric N—H stretching band near 3300 cm^{-1}. The overtone band is often even more pronounced in aromatic primary amines.

Aliphatic secondary amines determined as neat liquids give *one band* in the N—H stretching region at about 3300 cm^{-1}, but the band is often vanishingly weak. On the other hand, an aromatic secondary amine gives a stronger N—H band near 3400 cm^{-1}. Figures 2.59 and 2.61 are the spectra of an aliphatic secondary amine and an aromatic secondary amine, respectively. Tertiary amines do not absorb in this region, as shown in Figure 2.60.

In primary amines, the N—H bending mode (scissoring) appears as a medium- to strong-intensity (broad) band in the range from 1640 to 1560 cm^{-1}. In aromatic secondary amines, the band shifts to a lower frequency and appears near 1500 cm^{-1}. However, in aliphatic secondary amines the N—H bending vibration is very weak and usually is not observed. The N—H vibrations in aromatic compounds often overlap the aromatic C=C ring absorptions, which also appear in this region. An out-of-plane N—H bending vibration appears as a broad band near 800 cm^{-1} for primary and secondary amines. These bands appear in the spectra of compounds determined as neat liquids and are seen most easily in aliphatic amines (Figs. 2.58 and 2.59).

The C—N stretching absorption occurs in the region from 1350 to 1000 cm^{-1} as a medium to strong band for all amines. Aliphatic amines absorb from 1250 to 1000 cm^{-1}, whereas aromatic amines absorb from 1350 to 1250 cm^{-1}. The C—N absorption occurs at a higher frequency in aromatic amines because resonance increases the double-bond character between the ring and the attached nitrogen atom.

2.16 NITRILES, ISOCYANATES, ISOTHIOCYANATES, AND IMINES

Nitriles, isocyanates, and isothiocyanates all have *sp*-hydridized carbon atoms similar to the C≡C bond. They absorb in the region 2100–2270 cm^{-1}. The C=N bond of an imine has an sp^2 carbon atom, however. Imines and similar compounds absorb near where double bonds appear, 1690–1640 cm^{-1}.

SPECTRAL ANALYSIS BOX

NITRILES R–C≡N

−C≡N Stretch is a medium-intensity, sharp absorption near 2250 cm^{-1}. Conjugation with double bonds or aromatic rings moves the absorption to a lower frequency.

Examples: butyronitrile (Fig. 2.62) and benzonitrile (Fig. 2.63).

ISOCYANATES R–N=C=O

−N=C=O Stretch in an isocyanate gives a broad, intense absorption near 2270 cm^{-1}.

Example: benzyl isocyanate (Fig. 2.64).

ISOTHIOCYANATES R–N=C=S

−N=C=S Stretch in an isothiocyanate gives one or two broad, intense absorptions centering near 2125 cm^{-1}.

IMINES R_2C=N–R

−C=N− Stretch in an imine, oxime, and so on gives a variable-intensity absorption in the range 1690–1640 cm^{-1}.

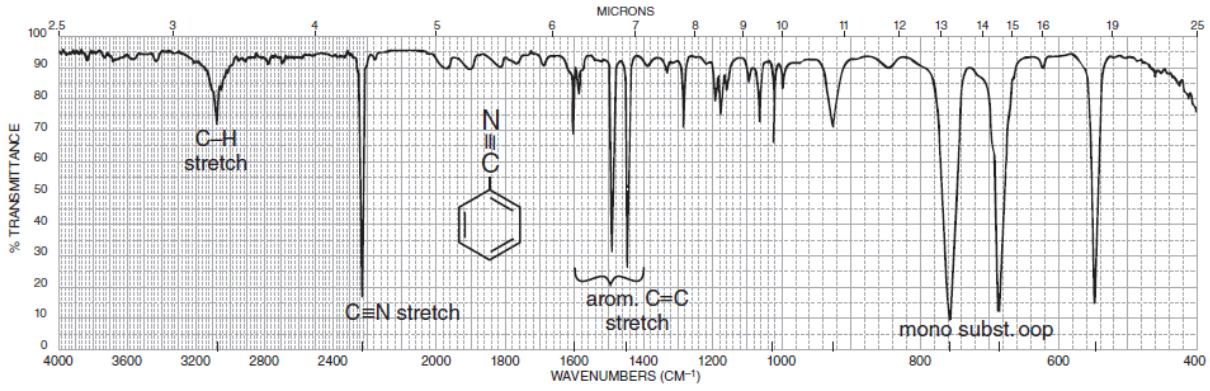


FIGURE 2.63 The infrared spectrum of benzonitrile (neat liquid, KBr plates).

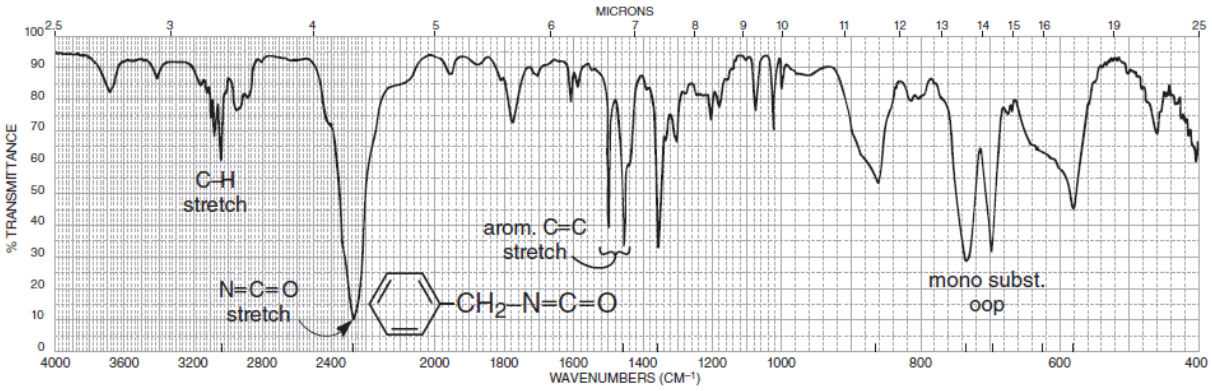


FIGURE 2.64 The infrared spectrum of benzyl isocyanate (neat liquid, KBr plates).

sp-*Hybridized Carbon.* The C≡N group in a nitrile gives a medium-intensity, sharp band in the triple-bond region of the spectrum (2270 to 2210 cm^{-1}). The C≡C bond, which absorbs near this region (2150 cm^{-1}), usually gives a weaker and broader band unless it is at the end of the chain. Aliphatic nitriles absorb at about 2250 cm^{-1}, whereas their aromatic counterparts absorb at lower frequencies, near 2230 cm^{-1}. Figures 2.62 and 2.63 are the spectra of an aliphatic nitrile and an aromatic nitrile, respectively. Aromatic nitriles absorb at lower frequencies with increased intensity because of conjugation of the triple bond with the ring. Isocynanates also contain an *sp*-hybridized carbon atom (R−N=C=O). This class of compounds gives a broad, intense band at about 2270 cm^{-1} (Fig. 2.64).

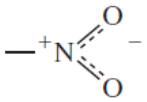
sp^2-*Hybridized Carbon.* The C=N bond absorbs in about the same range as a C=C bond. Although the C=N band varies in intensity from compound to compound, it usually is more intense than that obtained from the C=C bond. An oxime (R−CH=N−O−H) gives a C=N absorption in the range from 1690 to 1640 cm^{-1} and a broad O−H absorption between 3650 and 2600 cm^{-1}. An imine (R−CH=N−R) gives a C=N absorption in the range from 1690 to 1650 cm^{-1}.

2.17 NITRO COMPOUNDS

Nitro compounds show two strong bands in the infrared spectrum. One appears near 1550 cm^{-1} and the other near 1350 cm^{-1}. Although these two bands may partially overlap the aromatic ring region, 1600–1450 cm^{-1}, it is usually easy to see the NO_2 peaks.

SPECTRAL ANALYSIS BOX

NITRO COMPOUNDS



Aliphatic nitro compounds: asymmetric stretch (strong), 1600–1530 cm^{-1}; symmetric stretch (medium), 1390–1300 cm^{-1}.

Aromatic nitro compounds (conjugated): asymmetric stretch (strong), 1550–1490 cm^{-1}; symmetric stretch (strong), 1355–1315 cm^{-1}.

Examples: 1-nitrohexane (Fig. 2.65) and nitrobenzene (Fig. 2.66).

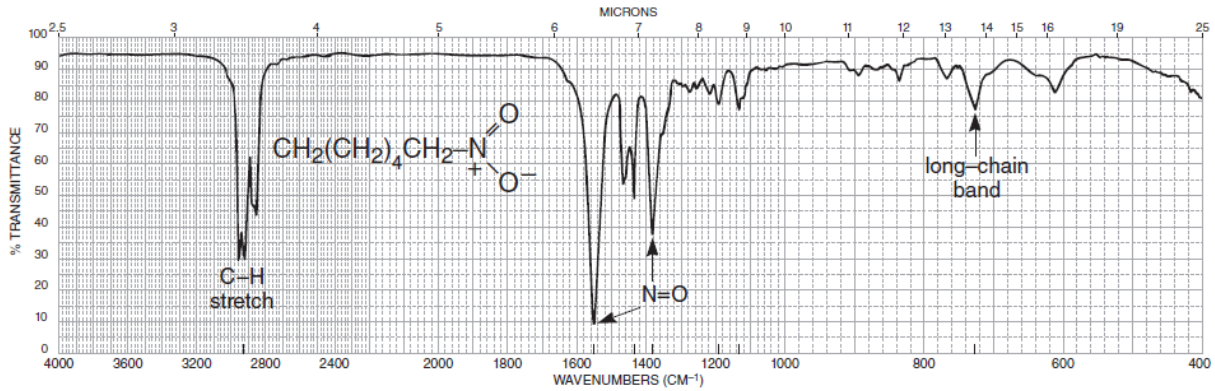


FIGURE 2.65 The infrared spectrum of 1-nitrohexane (neat liquid, KBr plates).

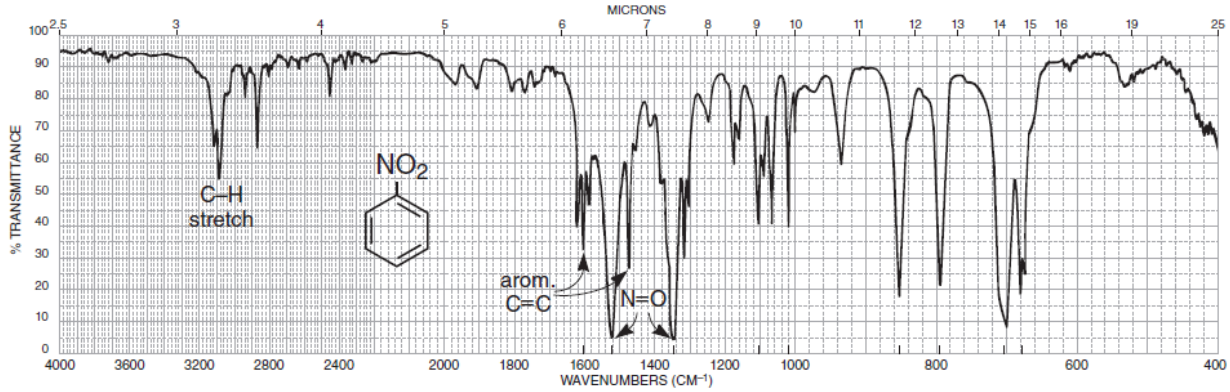


FIGURE 2.66 The infrared spectrum of nitrobenzene (neat liquid, KBr plates).

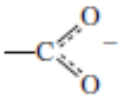
The nitro group (NO_2) gives two strong bands in the infrared spectrum. In aliphatic nitro compounds, the asymmetric stretching vibration occurs in the range from 1600 to 1530 cm^{-1}, and the symmetric stretching band appears between 1390 and 1300 cm^{-1}. An aliphatic nitro compound—for example, 1-nitrohexane (Fig. 2.65)—absorbs at about 1550 and 1380 cm^{-1}. Normally, its lower-frequency band is less intense than its higher-frequency band. In contrast with aliphatic nitro compounds, aromatic compounds give two bands of nearly equal intensity. Conjugation of a nitro group with an aromatic ring shifts the bands to lower frequencies: 1550–1490 cm^{-1} and 1355–1315 cm^{-1}. For example, nitrobenzene (Fig. 2.66) absorbs strongly at 1525 and 1350 cm^{-1}. The nitroso group (R—N=O) gives only one strong band, which appears in the range from 1600 to 1500 cm^{-1}.

2.18 CARBOXYLATE SALTS, AMINE SALTS, AND AMINO ACIDS

This section covers compounds with ionic bonds. Included here are carboxylate salts, amine salts, and amino acids. Amino acids are included in this section because of their zwitterionic nature.

SPECTRAL ANALYSIS BOX

CARBOXYLATE SALTS $R-\overset{\overset{O}{\|}}{C}-O^- \; Na^+$



Asymmetric stretch (strong) occurs near 1600 cm^{-1}; symmetric stretch (strong) occurs near 1400 cm^{-1}.

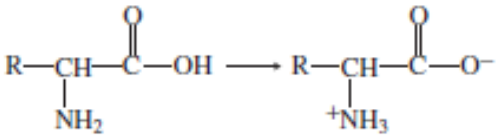
Frequency of C=O absorption is lowered from the value found for the parent carboxylic acid because of resonance (more single-bond character).

AMINE SALTS NH_4^+ RNH_3^+ $R_2NH_2^+$ R_3NH^+

N—H — Stretch (broad) occurs at 3300–2600 cm^{-1}. The ammonium ion absorbs to the left in this range, while the tertiary amine salt absorbs to the right. Primary and secondary amine salts absorb in the middle of the range, 3100–2700 cm^{-1}. A broad band often appears near 2100 cm^{-1}.

N—H — Bend (strong) occurs at 1610–1500 cm^{-1}. Primary (two bands) is asymmetric at 1610 cm^{-1}, symmetric at 1500 cm^{-1}. Secondary absorbs in the range 1610–1550 cm^{-1}. Tertiary absorbs only weakly.

AMINO ACIDS



These compounds exist as zwitterions (internal salts) and exhibit spectra that are combinations of carboxylate and primary amine salts. Amino acids show NH_3^+ stretch (very broad), N—H bend (asymmetric/symmetric), and COO^- stretch (asymmetric/symmetric).

Example: leucine (Fig. 2.67).

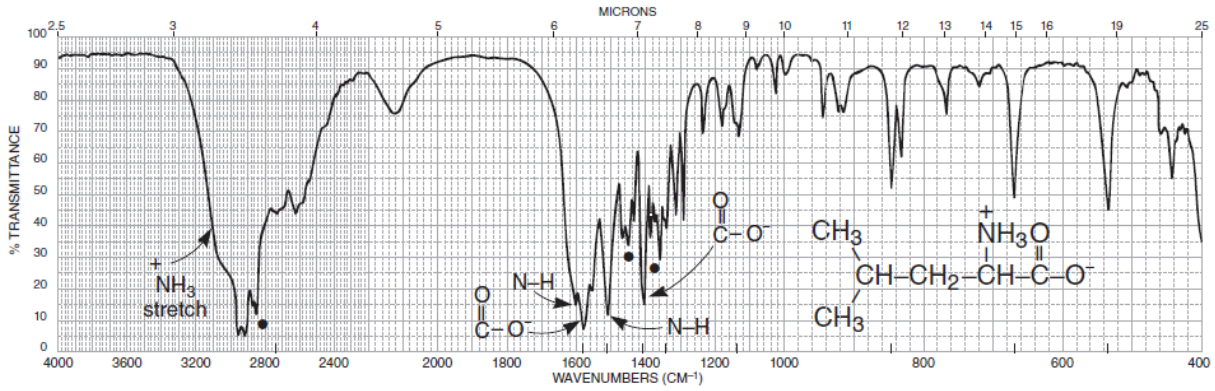


FIGURE 2.67 The infrared spectrum of leucine (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

2.19 SULFUR COMPOUNDS

Infrared spectral data for sulfur-containing compounds are covered in this section. Included here are single-bonded compounds (mercaptans or thiols and sulfides). Double-bonded S=O compounds are also included in this section.

SPECTRAL ANALYSIS BOX

MERCAPTANS (THIOLS) R–S–H

S–H Stretch, one weak band, occurs near 2550 cm^{-1} and virtually confirms the presence of this group because few other absorptions appear here.

Example: benzenethiol (Fig. 2.68).

SULFIDES R–S–R

Little useful information is obtained from the infrared spectrum.

SULFOXIDES R—S(=O)—R

S=O Stretch, one strong band, occurs near 1050 cm^{-1}.

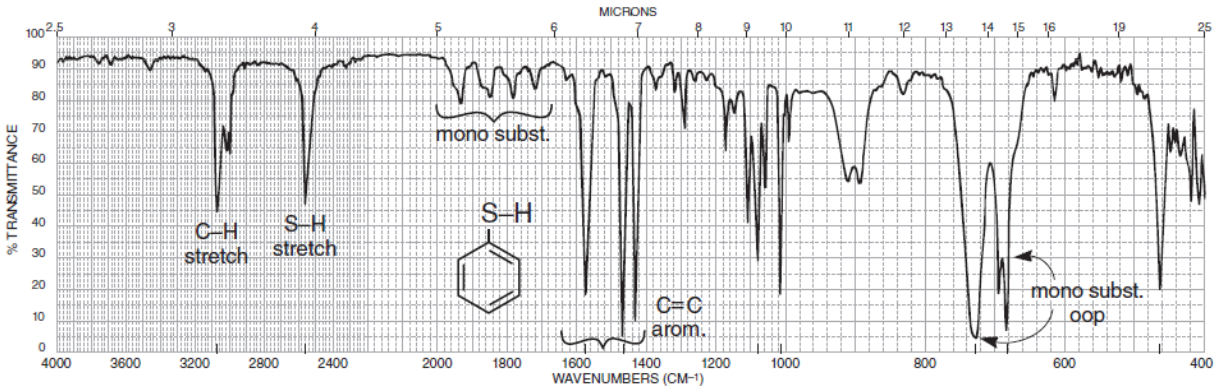
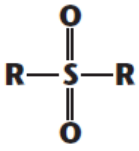


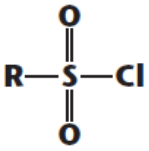
FIGURE 2.68 The infrared spectrum of benzenethiol (neat liquid, KBr plates).

SULFONES



S=O Asymmetric stretch (strong) occurs at 1300 cm^{-1}, symmetric stretch (strong) at 1150 cm^{-1}.

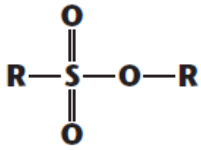
SULFONYL CHLORIDES



S=O Asymmetric stretch (strong) occurs at 1375 cm^{-1}, symmetric stretch (strong) at 1185 cm^{-1}.

Example: benzenesulfonyl chloride (Fig. 2.69).

SULFONATES



S=O Asymmetric stretch (strong) occurs at 1350 cm^{-1}, symmetric stretch (strong) at 1175 cm^{-1}.

S−O Stretch, several strong bands, occurs in the range 1000–750 cm^{-1}.

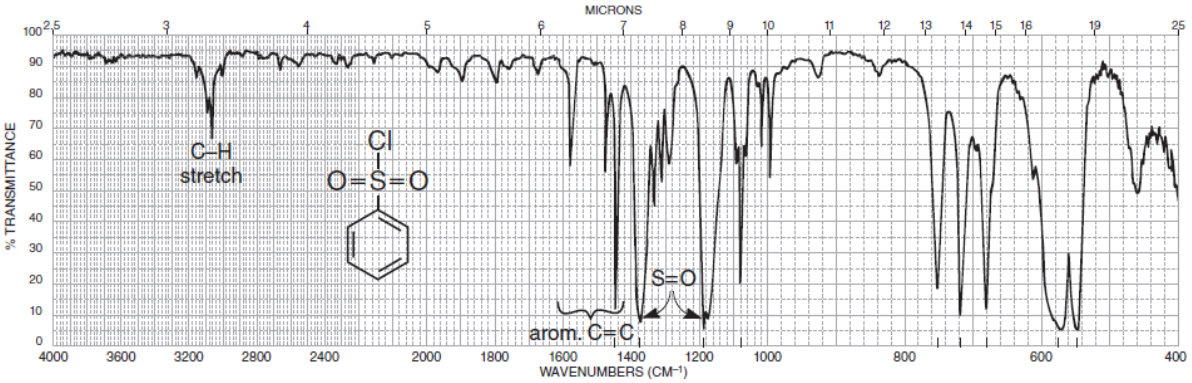
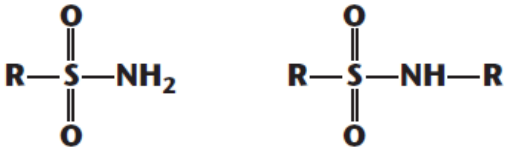


FIGURE 2.69 The infrared spectrum of benzenesulfonyl chloride (neat liquid, KBr plates).

Example: methyl *p*-toluenesulfonate (Fig. 2.70).

SULFONAMIDES (Solid State)



S=O Asymmetric stretch (strong) occurs at 1325 cm^{-1}, symmetric stretch (strong) at 1140 cm^{-1}.

N–H Primary stretch occurs at 3350 and 3250 cm^{-1}; secondary stretch occurs at 3250 cm^{-1}; bend occurs at 1550 cm^{-1}.

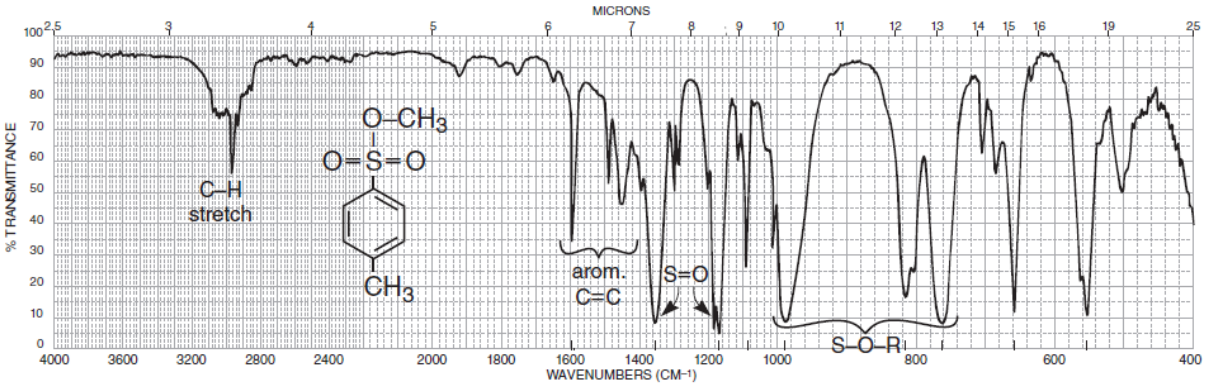
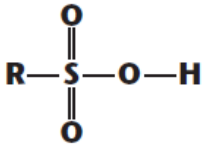


FIGURE 2.70 The infrared spectrum of methyl *p*-toluenesulfonate (neat liquid, KBr plates).

Example: benzenesulfonamide (Fig. 2.71).

SULFONIC ACIDS (Anhydrous)



S=O Asymmetric stretch (strong) occurs at 1350 cm^{-1}, symmetric stretch (strong) at 1150 cm^{-1}.

S−O Stretch (strong) occurs at 650 cm^{-1}.

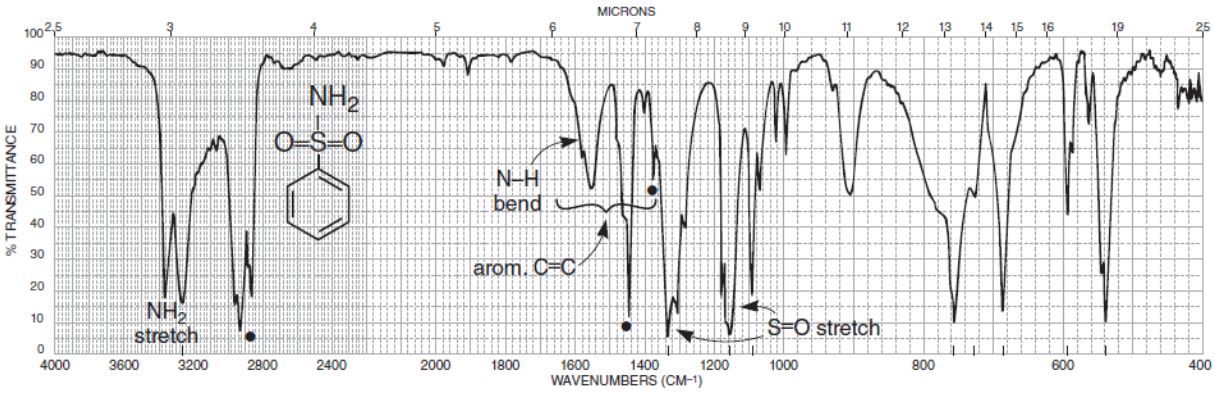


FIGURE 2.71 The infrared spectrum of benzenesulfonamide (Nujol mull, KBr plates). Dots indicate the Nujol (mineral oil) absorption bands (see Fig. 2.8).

2.20 PHOSPHORUS COMPOUNDS

Infrared spectral data for phosphorus-containing compounds are covered in this section. Included here are single-bonded compounds (P−H, P−R, and P−O−R). Double-bonded P=O compounds are also included in this section.

SPECTRAL ANALYSIS BOX

PHOSPHINES RPH_2 R_2PH

P—H	Stretch, one strong, sharp band, at 2320–2270 cm^{-1}.
PH_2	Bend, medium bands, at 1090–1075 cm^{-1} and 840–810 cm^{-1}.
P—H	Bend, medium band, at 990–885 cm^{-1}.
$P—CH_3$	Bend, medium bands, at 1450–1395 cm^{-1} and 1346–1255 cm^{-1}.
$P—CH_2—$	Bend, medium band, at 1440–1400 cm^{-1}.

PHOSPHINE OXIDES $R_3P{=}O$ $Ar_3P{=}O$

P=O	Stretch, one very strong band, at 1210–1140 cm^{-1}.

PHOSPHATE ESTERS $(RO)_3P{=}O$

P=O	Stretch, one very strong band, at 1300–1240 cm^{-1}.
R—O	Stretch, one or two strong bands, at 1088–920 cm^{-1}.
P—O	Stretch, medium band, at 845–725 cm^{-1}.

2.21 ALKYL AND ARYL HALIDES

Infrared spectral data for halogen-containing compounds are covered in this section. Except for fluorine-containing samples, it is difficult to determine the presence or the absence of a halide in a compound via infrared spectroscopy. There are several reasons for this problem. First, the C–X absorption occurs at very low frequencies, to the extreme right of the spectrum, where a number of other bands appear (fingerprint). Second, the sodium chloride plates or cells that are often used obscure the region where halogens absorb (these plates are transparent only above 650 cm^{-1}).

The spectra of carbon tetrachloride and chloroform are shown in this section. These solvents are often used to dissolve solids for determining spectra in solution. Notice that these compounds have multiple chlorine atoms giving rise to strong C–Cl stretches at about 785 cm^{-1} and 759 cm^{-1}, respectively. It is seldom useful to analyze compounds with a single chlorine atom because they are likely to be obscured by fingerprint peaks. Bromides and iodides absorb out of the range of normal NaCl plates. Mass spectral methods (Sections 3.7 and 4.9) provide more reliable information for halogen-containing compounds.

SPECTRAL ANALYSIS BOX

FLUORIDES R–F

C–F — Stretch (strong) at 1400–1000 cm^{-1}. Monofluoroalkanes absorb at the lower-frequency end of this range, while polyfluoroalkanes give multiple strong bands in the range 1350–1100 cm^{-1}. Aryl fluorides absorb between 1250 and 1100 cm^{-1}.

CHLORIDES R–Cl

C–Cl — Stretch (strong) in aliphatic chlorides occurs in the range 785–540 cm^{-1}. Primary chlorides absorb at the upper end of this range, while tertiary chlorides absorb near the lower end. Two or more bands may be observed due to the different conformations possible.

Multiple substitution on a single-carbon atom results in an intense absorption at the upper-frequency end of this range: CH_2Cl_2 (739 cm^{-1}), $HCCl_3$ (759 cm^{-1}), and CCl_4 (785 cm^{-1}). Aryl chlorides absorb between 1100 and 1035 cm^{-1}.

CH_2–Cl — Bend (wagging) at 1300–1230 cm^{-1}.

Examples: carbon tetrachloride (Fig. 2.72) and chloroform (Fig. 2.73).