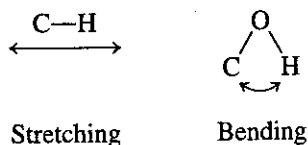


► **FIGURE 2.2** The approximate regions where various common types of bonds absorb (stretching vibrations only; bending, twisting, and other types of bond vibrations have been omitted for clarity).

Outside this range, absorptions are normally due to some other type of bond. For instance, any absorption in the range $3000 \pm 150 \text{ cm}^{-1}$ is almost always due to the presence of a C—H bond in the molecule; an absorption in the range $1715 \pm 100 \text{ cm}^{-1}$ is normally due to the presence of a C=O bond (carbonyl group) in the molecule. The same type of range applies to each type of bond. Figure 2.2 illustrates schematically how these are spread out over the vibrational infrared. Try to fix this general scheme in your mind for future convenience.

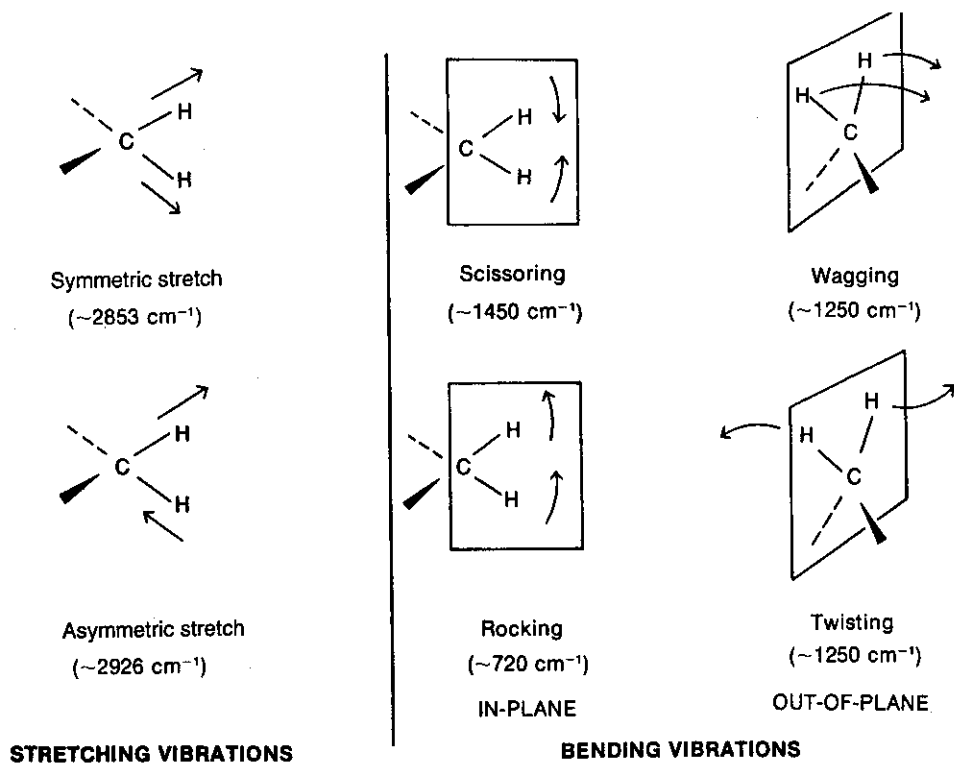
2.3 THE MODES OF STRETCHING AND BENDING

The simplest types, or **modes**, of vibrational motion in a molecule which are **infrared-active**—that is, which give rise to absorptions—are the stretching and bending modes.



However, other, more complex types of stretching and bending are also active. The following illustrations of the normal modes of vibration for a methylene group introduce several terms. In general, asymmetric stretching vibrations occur at higher frequencies than symmetric stretching vibrations; also, stretching vibrations occur at higher frequencies than bending vibrations. The terms **scissoring**, **rocking**, **wagging**, and **twisting** are commonly used in the literature to describe the origins of infrared bands.

In any group of three or more atoms, at least two of which are identical, there are *two* modes of stretching: symmetric and asymmetric. Examples of such groupings are —CH₃, —CH₂— (see page 18), —NO₂, —NH₂, and anhydrides. The methyl group gives rise to a symmetric stretching vibration at about 2872 cm^{-1} and an asymmetric stretch at about 2962 cm^{-1} . The anhydride functional group gives two absorptions in the C=O region because of the asymmetric and symmetric modes of stretch. A similar phenomenon occurs in the amino group, where a primary amine (NH₂) usually has two absorptions in the N—H stretch region while a secondary amine (R₂NH) has only



one absorption peak. Amides exhibit similar bands. There are two strong N=O stretch peaks for a nitro group, with the symmetric stretch appearing at about 1350 cm⁻¹ and the asymmetric stretch appearing at about 1550 cm⁻¹.



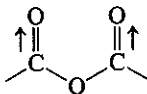
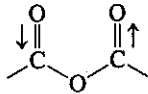




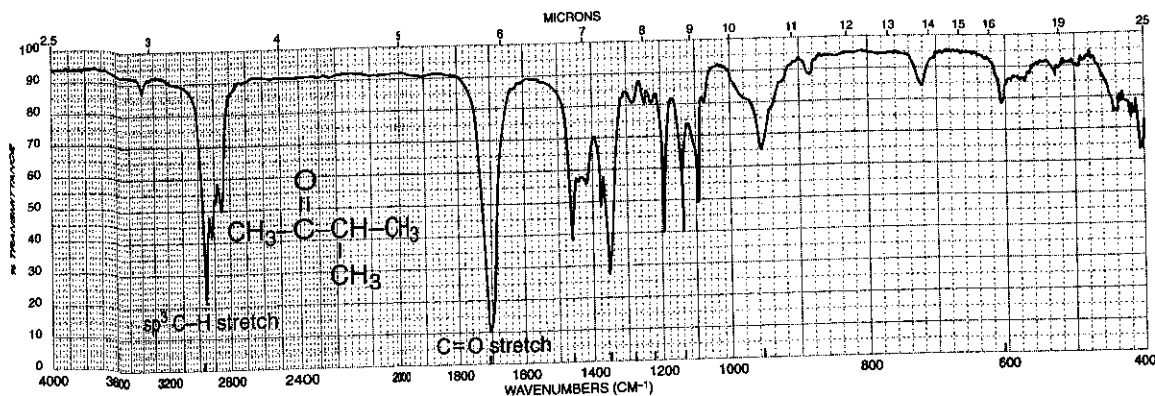
	Symmetric Stretch	Asymmetric Stretch
Methyl	 ~2872 cm ⁻¹	 ~2962 cm ⁻¹
Anhydride	 ~1760 cm ⁻¹	 ~1800 cm ⁻¹
Amino	 ~3300 cm ⁻¹	 ~3400 cm ⁻¹
Nitro	 ~1350 cm ⁻¹	 ~1550 cm ⁻¹

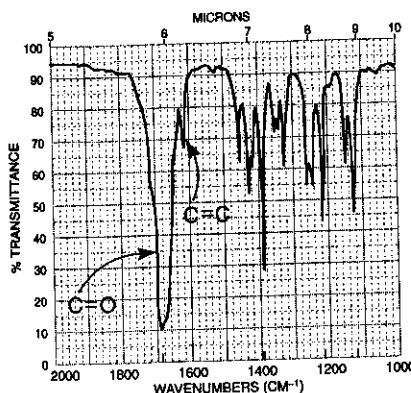
TABLE 2.3

A Simplified Correlation Chart

	Type of Vibration	Frequency (cm ⁻¹)	Intensity	
C—H	Alkanes (stretch)	3000–2850	s	
	—CH ₃ (bend)	1450 and 1375	m	
	—CH ₂ — (bend)	1465	m	
	Alkenes	(stretch)	3100–3000	m
		(out-of-plane bend)	1000–650	s
	Aromatics	(stretch)	3150–3050	s
		(out-of-plane bend)	900–690	s
	Alkyne	(stretch)	ca. 3300	s
	Aldehyde		2900–2800	w
		2800–2700	w	
C—C	Alkane	Not interpretatively useful		
C=C	Alkene	1680–1600	m–w	
	Aromatic	1600 and 1475	m–w	
C≡C	Alkyne	2250–2100	m–w	
C=O	Aldehyde	1740–1720	s	
	Ketone	1725–1705	s	
	Carboxylic acid	1725–1700	s	
	Ester	1750–1730	s	
	Amide	1680–1630	s	
	Anhydride	1810 and 1760	s	
	Acid chloride	1800	s	
	C—O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300–1000	s
	O—H	Alcohols, phenols		
Free		3650–3600	m	
H-bonded		3400–3200	m	
	Carboxylic acids	3400–2400	m	
N—H	Primary and secondary amines and amides (stretch)	3500–3100	m	
	(bend)	1640–1550	m–s	
C—N	Amines	1350–1000	m–s	
C=N	Imines and oximes	1690–1640	w–s	
C≡N	Nitriles	2260–2240	m	
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270–1940	m–s	
N=O	Nitro (R—NO ₂)	1550 and 1350	s	
S—H	Mercaptans	2550	w	
S=O	Sulfoxides	1050	s	
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375–1300 and 1350–1140	s	
C—X	Fluoride	1400–1000	s	
	Chloride	785–540	s	
	Bromide, iodide	< 667	s	



► **FIGURE 2.4** The infrared spectrum of 3-methyl-2-butanone (neat liquid, KBr plates).



► **FIGURE 2.5** A comparison of the intensities of the C=O and C=C absorption bands.

However, the C=O bond is a strong absorber, whereas the C=C bond generally absorbs only weakly (Fig. 2.5). Hence, a trained observer would not interpret a strong peak at 1670 cm^{-1} to be a C=C double bond, nor would he interpret a weak absorption at this frequency to be due to a carbonyl group.

The shape and fine structure of a peak often give clues to its identity, as well. Thus, while the N—H and O—H regions overlap,

$$\text{O—H } 3650\text{--}3200\text{ cm}^{-1}$$

$$\text{N—H } 3500\text{--}3300\text{ cm}^{-1}$$

the N—H absorption usually has one or two *sharp* absorption bands of lower intensity, while O—H, when it is in the N—H region, usually gives a *broad* absorption peak. Also, primary amines give *two* absorptions in this region, whereas alcohols as pure liquids give only one (Fig. 2.6). Figure 2.6 also shows typical patterns for the C—H stretching frequencies at about 3000 cm^{-1} .

TABLE 2.4

Base Values for Absorptions of Bonds

O—H	3400 cm^{-1}	C \equiv C	2150 cm^{-1}
N—H	3400	C=O	1715
C—H	3000	C=C	1650
C \equiv N	2250	C—O	1100

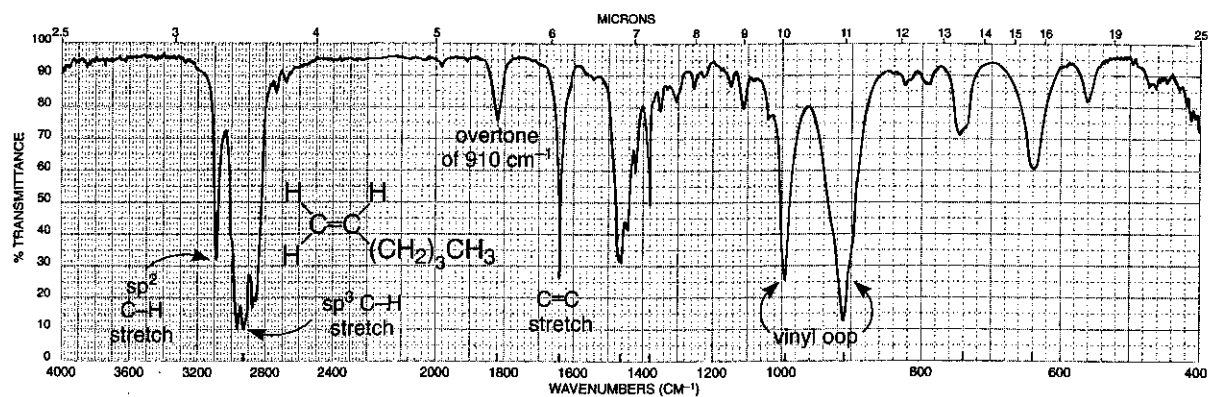
2.9 HOW TO APPROACH THE ANALYSIS OF A SPECTRUM (OR WHAT YOU CAN TELL AT A GLANCE)

When analyzing the spectrum of an unknown, concentrate your first efforts on determining the presence (or absence) of a few major functional groups. The C=O, O—H, N—H, C—O, C=C, C \equiv C, C \equiv N, and NO₂ peaks are the most conspicuous and give immediate structural information if they are present. Do not try to make a detailed analysis of the C—H absorptions near 3000 cm^{-1} ; almost all compounds have these absorptions. Do not worry about subtleties of the exact environment in which the functional group is found. Following is a major checklist of the important gross features.

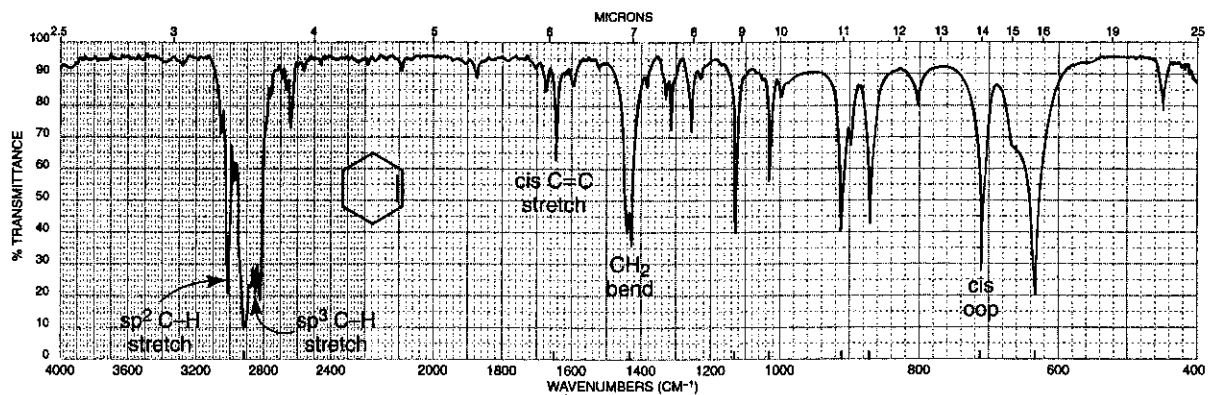
- Is a carbonyl group present? The C=O group gives rise to a strong absorption in the region 1820–1660 cm^{-1} . The peak is often the strongest in the spectrum and of medium width. You can't miss it.
- If C=O is present, check the following types (if it is absent, go to 3).

ACIDS	Is O—H also present?
	• <i>Broad</i> absorption near 3400–2400 cm^{-1} (usually overlaps C—H).
AMIDES	Is N—H also present?
	• Medium absorption near 3400 cm^{-1} ; sometimes a double peak with equivalent halves.
ESTERS	Is C—O also present?
	• Strong-intensity absorptions near 1300–1000 cm^{-1} .
ANHYDRIDES	Two C=O absorptions near 1810 and 1760 cm^{-1} .
ALDEHYDES	Is aldehyde C—H present?
	• Two weak absorptions near 2850 and 2750 cm^{-1} on right side of the aliphatic C—H absorptions.
KETONES	The preceding five choices have been eliminated.
- If C=O is absent:

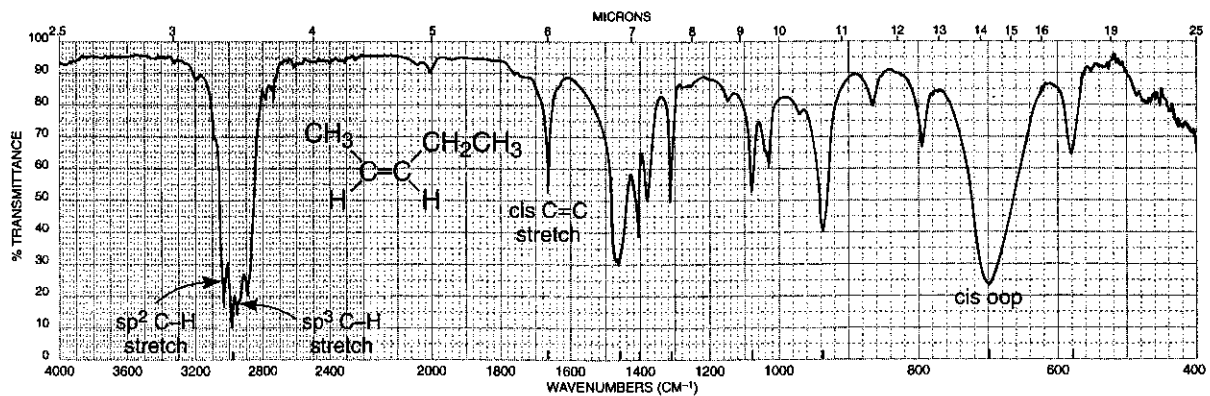
ALCOHOLS, PHENOLS	Check for O—H.
	• <i>Broad</i> absorption near 3400–3300 cm^{-1} .
	• Confirm this by finding C—O near 1300–1000 cm^{-1} .
AMINES	Check for N—H.
	• Medium absorption(s) near 3400 cm^{-1} .



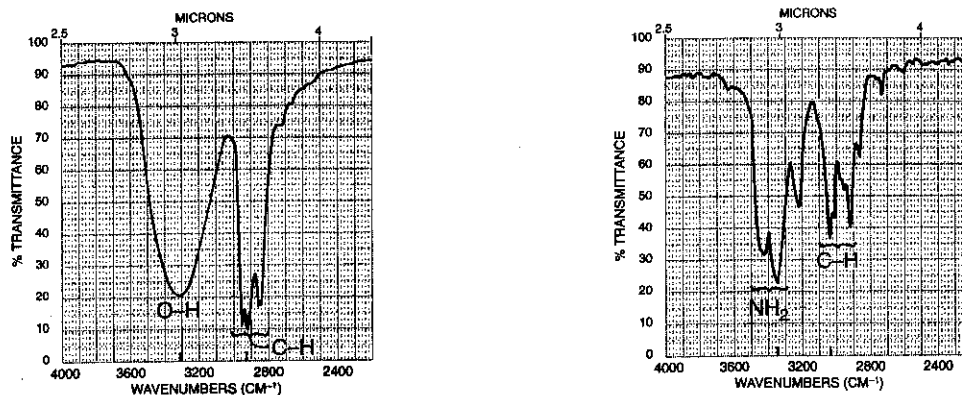
► **FIGURE 2.10** The infrared spectrum of 1-hexene (neat liquid, KBr plates).



► **FIGURE 2.11** The infrared spectrum of cyclohexene (neat liquid, KBr plates).



► **FIGURE 2.12** The infrared spectrum of *cis*-2-pentene (neat liquid, KBr plates).



► **FIGURE 2.6** A comparison of the shapes of the absorption bands for the O—H and N—H groups.

TABLE 2.3

A Simplified Correlation Chart

	Type of Vibration	Frequency (cm ⁻¹)	Intensity	
C—H	Alkanes (stretch)	3000–2850	s	
	—CH ₃ (bend)	1450 and 1375	m	
	—CH ₂ — (bend)	1465	m	
	Alkenes	(stretch)	3100–3000	m
		(out-of-plane bend)	1000–650	s
	Aromatics	(stretch)	3150–3050	s
		(out-of-plane bend)	900–690	s
	Alkyne	(stretch)	ca. 3300	s
	Aldehyde		2900–2800	w
			2800–2700	w
C—C	Alkane	Not interpretatively useful		
C=C	Alkene	1680–1600	m–w	
	Aromatic	1600 and 1475	m–w	
C≡C	Alkyne	2250–2100	m–w	
C=O	Aldehyde	1740–1720	s	
	Ketone	1725–1705	s	
	Carboxylic acid	1725–1700	s	
	Ester	1750–1730	s	
	Amide	1680–1630	s	
	Anhydride	1810 and 1760	s	
	Acid chloride	1800	s	
	C—O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300–1000	s
O—H	Alcohols, phenols			
	Free	3650–3600	m	
	H-bonded	3400–3200	m	
	Carboxylic acids	3400–2400	m	
N—H	Primary and secondary amines and amides (stretch)	3500–3100	m	
	(bend)	1640–1550	m–s	
C—N	Amines	1350–1000	m–s	
C=N	Imines and oximes	1690–1640	w–s	
C≡N	Nitriles	2260–2240	m	
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates	2270–1940	m–s	
N=O	Nitro (R—NO ₂)	1550 and 1350	s	
S—H	Mercaptans	2550	w	
S—S	Sulfides	1050	s	