

Chapter 17: IR Spectroscopy

An important tool of the organic chemist is Infrared Spectroscopy, or IR. IR spectra are acquired on a special instrument, called an IR spectrometer. IR is used both to gather information about the structure of a compound and as an analytical tool to assess the purity of a compound. IR spectra are quick and easy to run, and since the teaching labs are fortunate enough to have four of these instruments, students are encouraged to acquire spectra of compounds made in the laboratory throughout the first and second semesters of the lab course.

17.1 The Electromagnetic Spectrum

Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions. Electromagnetic spectrum refers to the seemingly diverse collection of radiant energy, from cosmic rays to X-rays to visible light to microwaves, each of which can be considered as a wave or particle traveling at the speed of light. These waves differ from each other in the length and frequency (Figure 17-1).

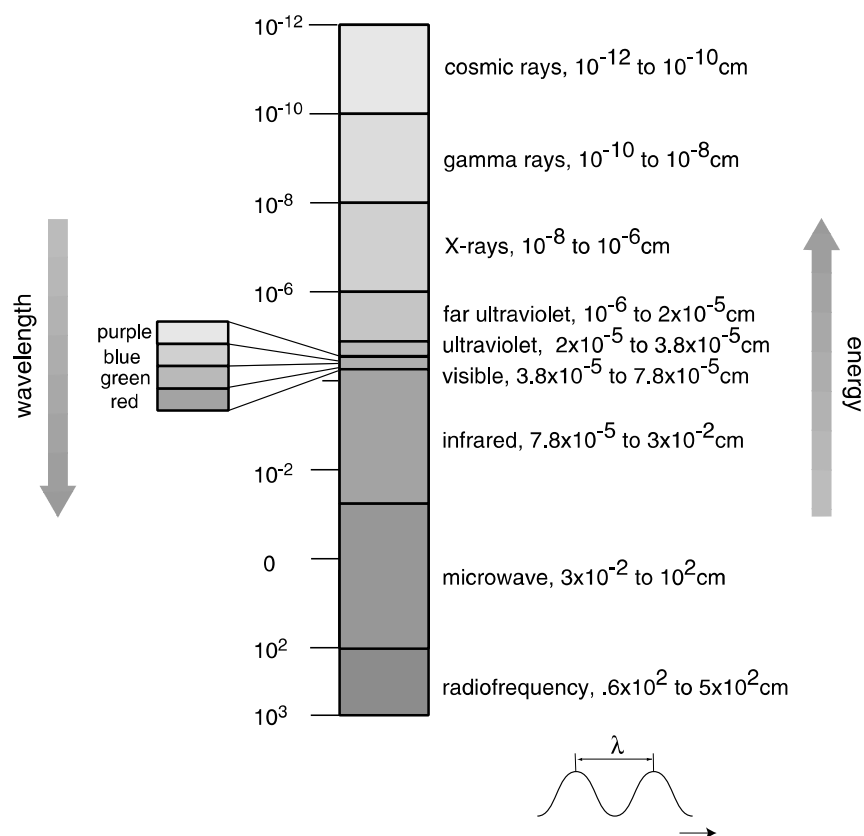


Figure 17-1: The electromagnetic spectrum.

Frequency, ν (nu), is the number of wave cycles that pass through a point in one second. It is measured in Hz, where 1 Hz = 1 cycle/sec. Wavelength, λ (lambda), is the length of one complete wave cycle. It is often measured in cm (centimeters). Wavelength and frequency are inversely related:

$$\nu = \frac{c}{\lambda} \quad \text{and} \quad \lambda = \frac{c}{\nu}$$

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where c is the speed of light, 3×10^{10} cm/s. Energy is related to wavelength and frequency by the following formulas:

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

where h is Planck's constant, 6.6×10^{-34} J/Hz or Js. Note that energy is directly proportional to frequency and inversely proportional to wavelength.

The IR region is divided into three regions: the near, mid, and far IR (Figure 17-2). The mid IR region is of greatest practical use to the organic chemist. This is the region of wavelengths between 3×10^{-4} and 3×10^{-3} cm. To avoid having to use scientific notation, these numbers are usually reported in wavenumber ($\bar{\nu}$ or nu bar), which has units of cm^{-1} .

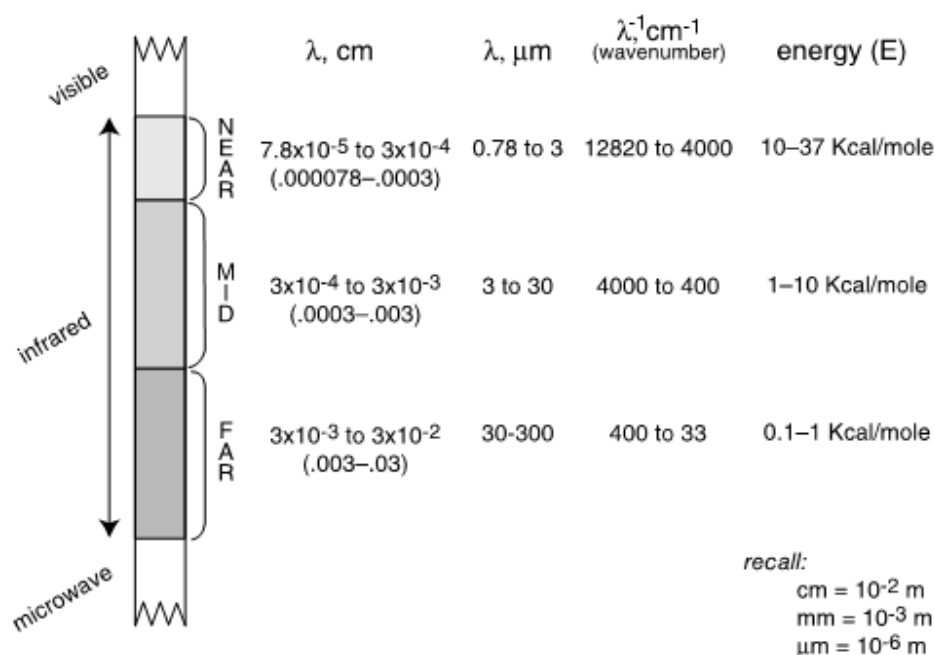


Figure 17-2: The IR regions of the electromagnetic spectrum.

A wavenumber is the inverse of the wavelength in cm:

$$\bar{\nu} = \frac{1}{\lambda}$$

Where ν is in units of cm^{-1} and λ is in units of cm. Based on this,

$$E = hc\bar{\nu}$$

In wavenumbers, the mid IR range is $4000\text{--}400 \text{ cm}^{-1}$. An increase in wavenumber corresponds to an increase in energy. As you will learn later, this is a convenient relationship for the organic chemist.

Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration. In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy matches the energy of a specific molecular vibration, absorption occurs. A typical IR spectrum is shown below. The wavenumber, plotted on the X-axis, is proportional to energy; therefore, the highest energy vibrations are on the left. The percent transmittance (%T) is plotted on the Y-axis. An absorption of radiant energy

is therefore represented by a “trough” in the curve: zero transmittance corresponds to 100% absorption of light at that wavelength.

Band intensities can also be expressed as absorbance (A). Absorbance is the logarithm, to the base 10, of the reciprocal of the transmittance:

$$A = \log_{10} (1/T)$$

Note how the same spectrum appears when plotted as T and when plotted as A (Figure 17-3).

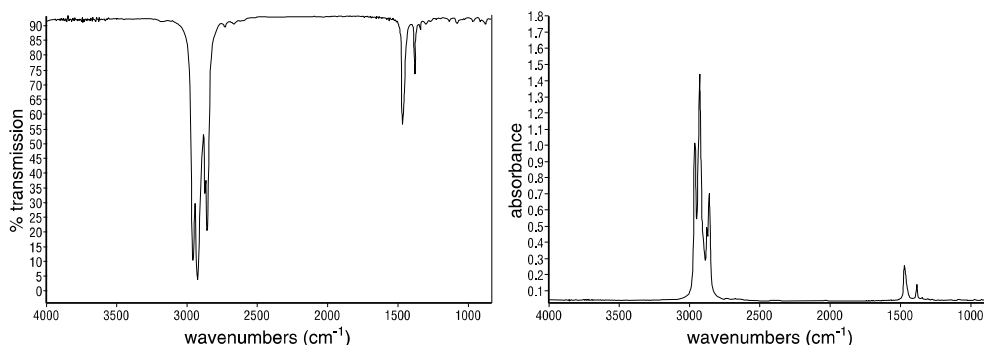


Figure 17-3: The IR spectrum of octane, plotted as transmission (left) and absorbance (right).

As illustrated in the spectrum of octane, even simple organic molecules give rise to complex IR spectra. Both the complexity and the wavenumbers of the peaks in the spectra give the chemist information about the molecule. The complexity is useful to match an experimental spectrum with that of a known compound with a peak-by-peak correlation. To facilitate this analysis, compilations of IR spectra are available in many places in the chemical literature.

The wavenumbers at which an organic molecule absorbs radiation give information on functional groups present in the molecule. Certain groups of atoms absorb energy and, therefore, give rise to bands at approximately the same frequencies. The chemist analyzes a spectrum with the help of tables that correlate frequencies with functional groups. The theory behind this relationship is discussed in the next section on molecular vibrations.

17.2 Molecular Vibrations

There are two types of molecular vibrations, stretching and bending. As a student of chemistry, you may have come to think of a molecule as having rigid bond lengths and bond angles, as when you work with your molecular model sets. This is not the actual case, since bond lengths and angles represent the *average* positions about which atoms vibrate.

A molecule consisting of n atoms has a total of $3n$ degrees of freedom, corresponding to the Cartesian coordinates of each atom in the molecule. In a nonlinear molecule, 3 of these degrees are rotational and 3 are translational and the remaining correspond to fundamental vibrations; in a linear molecule, 2 degrees are rotational and 3 are translational. The net number of fundamental vibrations for nonlinear and linear molecules is therefore $(3n-6)$ for nonlinear molecules, and $(3n-5)$ for linear molecules.

Calculation reveals that a simple molecule such as propane, C_3H_8 , has 27 fundamental vibrations, and therefore, you might predict 27 bands in an IR spectrum! (The actual number is sometimes different as discussed in part later.) Water, which is nonlinear, has three fundamental vibrations (Figure 17-4).

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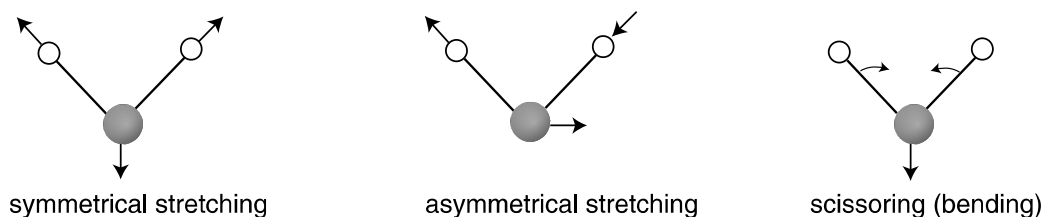


Figure 17-4: Stretching and bending vibrational modes for H₂O.

Carbon dioxide, CO₂, is linear and hence has four fundamental vibrations (Figure 17-5). The asymmetrical stretch of CO₂ gives a strong band in the IR at 2350 cm⁻¹. You may notice this band in samples that you run on the instruments in the teaching labs, since CO₂ is present in the atmosphere. The two scissoring or bending vibrations are equivalent and therefore, have the same frequency and are said to be *degenerate*, appearing in an IR spectrum at 666 cm⁻¹.

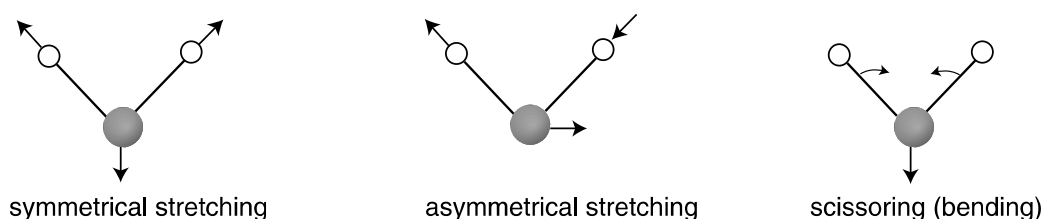


Figure 17-5: Stretching and bending vibrational modes for CO₂.

The symmetrical stretch of CO₂ is inactive in the IR because this vibration produces no change in the dipole moment of the molecule. In order to be IR active, a vibration must cause a change in the dipole moment of the molecule. (The reason for this involves the mechanism by which the photon transfers its energy to the molecule, which is beyond the scope of this discussion.) Recall that the dipole moment is defined as the product of the charge and the distance of separation. The distance has direction, therefore, dipole moments are vectors. Symmetrical diatomic molecules will therefore not absorb IR at all (Figure 17-6). In general, the larger the dipole change, the stronger the intensity of the band in an IR spectrum.

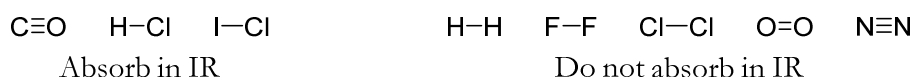


Figure 17-6: Linear molecules only absorb in IR if vibration changes their dipoles.

Only two IR bands (2350 and 666 cm⁻¹) are seen for carbon dioxide, instead of four corresponding to the four fundamental vibrations. Carbon dioxide is an example of why one does not always see as many bands as implied by our simple calculation. In the case of CO₂, two bands are degenerate, and one vibration does not cause a change in dipole moment. Other reasons why fewer than the theoretical number of IR bands are seen include: an absorption is not in the 4000–400 cm⁻¹ range; an absorption is too weak to be observed; absorptions are too close to each other to be resolved on the instrument. Additional weak bands which are overtones or combinations of fundamental vibrations are observed.

The stretching and bending vibrations for the important organic group, methylene (–CH₂–), are illustrated in Figure 17-7. (The 3*n*–6 rule does not apply since the –CH₂– group represents only a portion of a molecule.) Note that bending vibrations occur at lower frequencies than corresponding stretching vibrations.

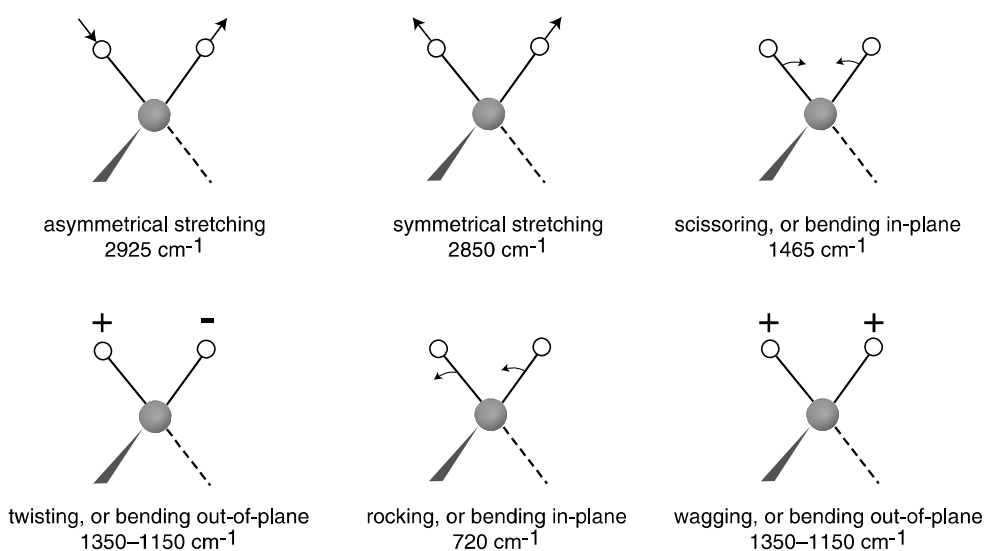


Figure 17-7: Stretching and bending vibrational modes for a CH_2 group.

Both the stretching and bending vibrations of a molecule as illustrated in the above figures can be predicted mathematically, at least to a useful approximation, especially using computers. The mathematics of stretching vibrations will be sketched in the following section. An understanding of these vibrations can help even the beginning student correlate high and low frequencies in an IR spectrum.

17.3 Stretching Vibrations

The stretching frequency of a bond can be approximated by Hooke's Law. In this approximation, two atoms and the connecting bond are treated as a simple harmonic oscillator composed of 2 masses (atoms) joined by a spring (Figure 17-8).



Figure 17-8: A harmonic oscillator consists of two masses connected by a spring.

According to Hooke's law, the frequency of the vibration of the spring (ν) is related to the mass of each atom (m , assuming they have the same mass) and the force constant of the spring (k) by the following formula:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

In the classical harmonic oscillator, the energy of any given vibration (E) is given by

$$E = \frac{1}{2} kx^2 = h\nu$$

where x is the displacement of the spring. Thus, the energy or frequency is dependent on how far one stretches or compresses the spring, which can be any value. If this simple model were true, a molecule could absorb energy of any wavelength.

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However, vibrational motion is *quantized*: it can only exist at certain discrete levels, and the only transitions which are allowed fit the following formula.

$$E = \left(n + \frac{1}{2} \right) h\nu$$

The lowest energy level is $E_0 = 1/2 h\nu$, the next highest is $E_1 = 3/2 h\nu$. According to the selection rule, only transitions to the next energy level are allowed; therefore molecules will absorb an amount of energy equal to $(3/2 - 1/2) h\nu$, or $1 h\nu$. This rule is not inflexible, and occasionally transitions of $2 h\nu$, $3 h\nu$, or higher are observed. These correspond to bands called overtones in an IR spectrum. They are of lower intensity than the fundamental vibrational bands. Energy diagrams for both a simple harmonic oscillator and a quantized harmonic oscillator are shown in Figure 17-9.

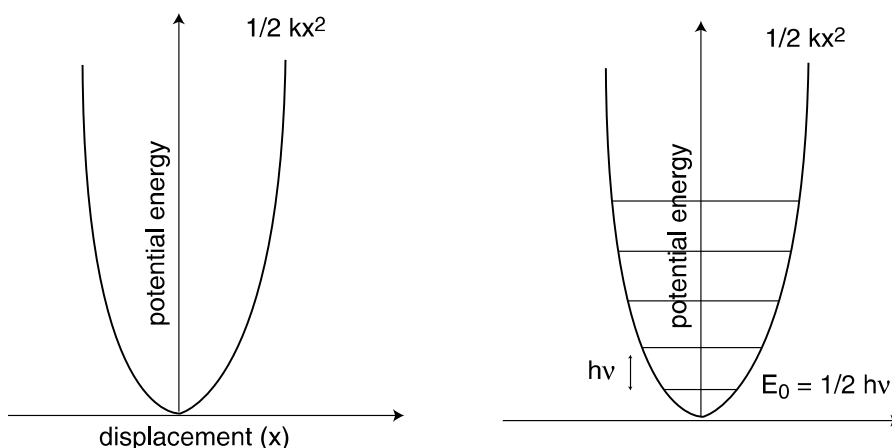


Figure 17-9: Energy curves for a simple harmonic oscillator (left) and a quantized harmonic oscillator (right).

A molecule is not just two atoms joined on a spring, of course. A bond can come apart, and it cannot be compressed beyond a certain point. A molecule is actually an *anharmonic* oscillator. As the interatomic distance increases, the energy reaches a maximum, as seen in Figure 17-10. Note how the energy levels become more closely spaced with increasing interatomic distance in the anharmonic oscillator. The allowed transitions, $h\nu$, become smaller in energy. Therefore, overtones can be lower in energy than predicted by the harmonic oscillator theory.

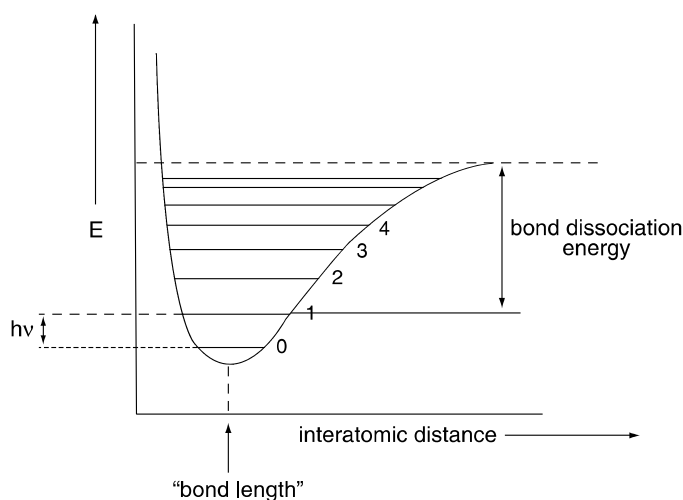


Figure 17-10: Energy curve for a quantized anharmonic oscillator.

The following formula has been derived from Hooke's law.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}}$$

where m_1 and m_2 are the masses of the two atoms in g, and f is the force constant of the bond in dynes/cm. Typical force constants for some types of bonds are given in Table 17-1.

Table 17-1: Typical force constants for different bond types.

Bond	Force Constant (dyne/cm)
Single	5×10^5
Double	10×10^5
Triple	15×10^5

As the mass of the atoms increases, the vibration frequency decreases. The mass of a carbon atom is 1.99×10^{-23} g, and the mass of a hydrogen atom is 1.66×10^{-24} g. By using these values, you can calculate that the wavenumber of vibration for a C-H bond should be 3032 cm^{-1} . The actual range for C-H absorptions is $2850\text{--}3000 \text{ cm}^{-1}$. The region of an IR spectrum where bond stretching vibrations are seen depends primarily on whether the bonds are single, double, or triple bonds, or single bonds to hydrogen. Table 17-2 shows where absorption by single, double, and triple bonds are observed in an IR spectrum. You should try calculating a few of these values to convince yourself that the Hooke's law approximation is a useful one.

Table 17-2: Calculated absorptions for different types of bonds.

Bond	Absorption region (cm^{-1})
C-C, C-O, C-N	800-1300
C=C, C=O, C=N, N=O	1500-1900
$\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$	2000-2300
C-H, N-H, O-H	2700-3800

Although this is a useful approximation, the motion of two atoms in a large molecule cannot be isolated from the motion of the rest of the atoms in the molecule. In a molecule, two oscillating bonds can share a common atom. When this happens, the vibrations of the two bonds are coupled. As one bond contracts, the other bond can either contract or expand, as in asymmetrical and symmetrical stretching. In general, when coupling occurs, bands at different frequencies are observed, instead of super-imposed (or degenerate) bands as you might expect from two identical atoms in a bond vibrating with an identical

force constant. In the case of the $-\text{CH}_2$ group in Figure 17-7, you should note there are two bands in the region for C–H bonds: 2926 cm^{-1} and 2853 cm^{-1} .

17.4 Characteristic Functional Group Vibrations

Typically, certain functional groups have characteristic absorptions. This section goes through different functional groups and gives some example spectra for each. The region from $4000\text{--}1300\text{ cm}^{-1}$ is particularly useful for identifying the presence of specific functional groups, although functional group bands in the region below 1300 cm^{-1} can also be useful on occasion. The *fingerprint region* is the region 1300 cm^{-1} to 900 cm^{-1} , and while band patterns in this region may be too complex to help you determine the functional groups present, it is useful when you compare (or *overlay*) two spectra: a known compound and a compound whose identity is in question. Typically, vibrations in the fingerprint region are characteristic of the molecule as a whole vibrating, and not individual functional groups in the molecule. However, the region from $900\text{--}650\text{ cm}^{-1}$ is useful in identifying aromatic compounds, which show strong absorption bands (bending vibrations) in this region. Broad, moderate absorptions in this region indicate carboxylic acids, amines, or amides.

A. Alkanes

The IR spectra of simple alkanes have been studied in detail and are characterized by absorptions due to C–H stretching and bending (the C–C stretching and bending bands are either too weak or of too low a frequency to be detected in IR spectroscopy). The theoretical stretching and bending modes for a methylene ($-\text{CH}_2-$) group are diagrammed in Figure 17-7. In practice, asymmetrical and symmetrical stretching of C–H in both methylene and methyl ($-\text{CH}_3$) groups give rise to bands in the region $3000\text{--}2850\text{ cm}^{-1}$. Bands in the region $1470\text{--}1450\text{ cm}^{-1}$ are assigned to bending in-plane (scissoring) of the C–H of methyl and methylene groups. The methyl group “rock” shows as a separate band in the region $1380\text{--}1350\text{ cm}^{-1}$. Long chain, unbranched alkanes will show a methylene rocking vibration at $725\text{--}720\text{ cm}^{-1}$. Bending out-of-plane (twisting or wagging) leads to bands in the region $1350\text{--}1150\text{ cm}^{-1}$, although these bands are weaker than the other absorptions and are not of diagnostic value. Branching and cyclizing of the carbon chain adds a number of absorptions due to skeletal vibrations in the region $1250\text{--}910\text{ cm}^{-1}$. These bands are useful when comparing the fingerprint regions of a known and an unknown compound.

Table 17-3: Alkane diagnostic bands.

C–H stretching, methyl and methylene	$3000\text{--}2850\text{ cm}^{-1}$ (m)
C–H bend or scissoring, methyl and methylene	$1470\text{--}1450\text{ cm}^{-1}$ (m)
C–H rock, methyl	$1370\text{--}1350\text{ cm}^{-1}$ (m)
C–H rock, methylene (long chain)	$725\text{--}720\text{ cm}^{-1}$ (m)

Compare the IR spectra of octane, 2,3-dimethylbutane, and cyclohexane (Figure 17-11). Each of these alkanes has bands in the $3000\text{--}2850\text{ cm}^{-1}$ region (A) corresponding to C–H stretch. They also each show

a band for C–H scissoring in the $1470\text{--}1450\text{ cm}^{-1}$ region (B). Note that cyclohexane does not have a band in the B region at $1370\text{--}1350\text{ cm}^{-1}$. This is because cyclohexane does not have a methyl group. Of the alkanes illustrated, only the relatively long-chain octane shows a band in the $725\text{--}720\text{ cm}^{-1}$ region (C) due to C–H rock. Note the many weak bands in both the branched compound (2,3-dimethylbutane) and the cyclic compound (cyclohexane) in the region $1250\text{--}910\text{ cm}^{-1}$.

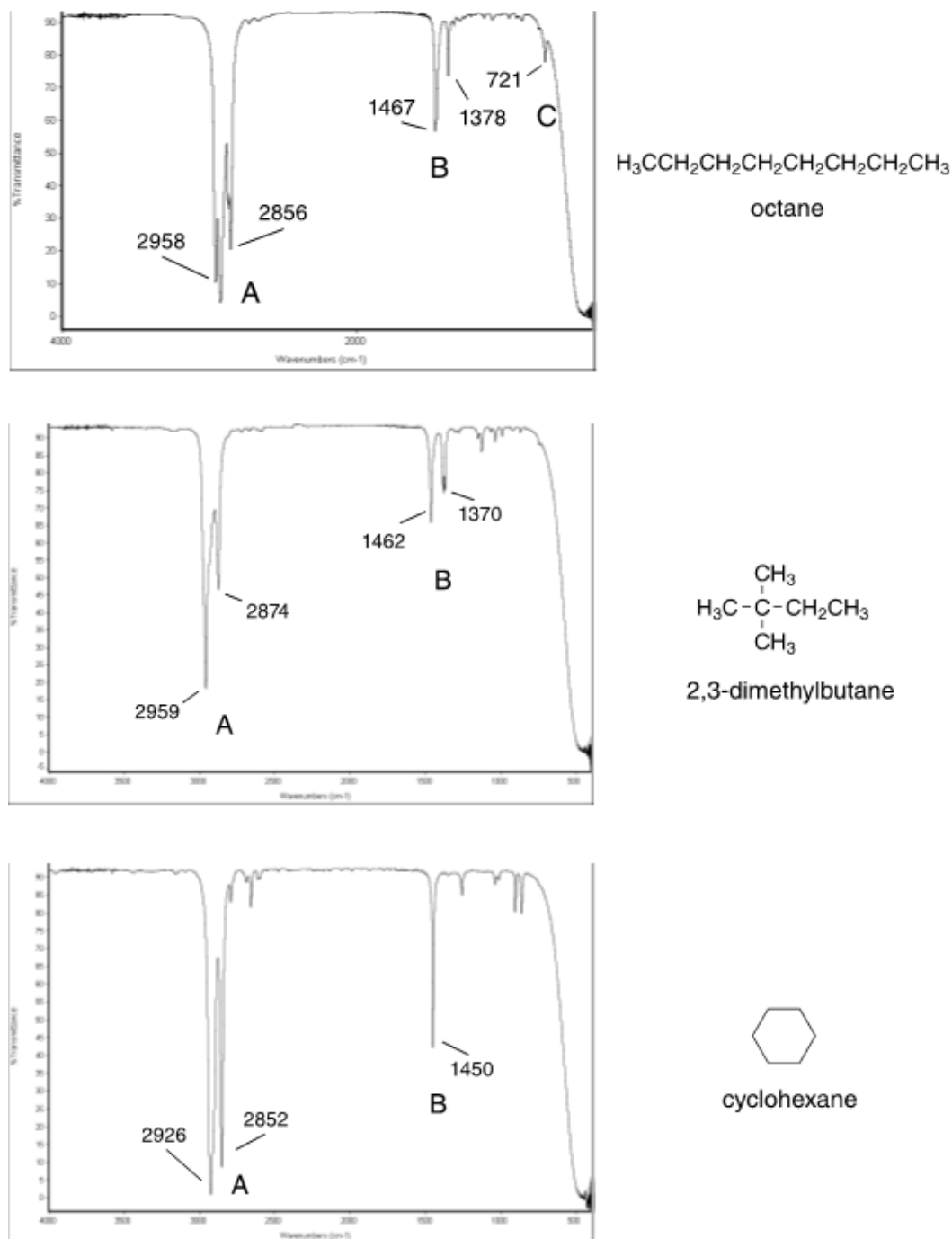
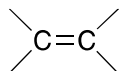


Figure 17-11: Representative alkane spectra.

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The IR bands due to C–H stretching and bending discussed above are not useful when trying to deduce the functional group on an organic molecule, because almost all organic compounds will show these bands. The presence of these bands and the absence of bands due to specific functional groups will lead one to conclude that the compound being analyzed is a simple hydrocarbon. Also, the simplicity of alkane spectra are of interest to the beginning student because most of the bands can be assigned according to the simple models discussed in the theory section on spectroscopy.

B. Alkenes



Stretching vibrations of C–H when the hydrogen is attached to the carbon in a carbon-carbon double bond are of higher frequency than in alkanes, shifting the IR bands to the region 3100–3000 cm^{-1} (region A in the spectrum of 1-octene, Figure 17-12). The stretching vibration of carbon-carbon double bonds (region B in the spectrum of 1-octene), is of a higher frequency than carbon-carbon single bonds because they have a larger bond energy and thus a larger force constant. Unlike carbon-carbon single bonds, the carbon-carbon double bond usually gives rise to a moderate rather than a weak band. This moderate band is observed in the region 1680–1640 cm^{-1} . The strongest bands in the spectra of alkenes are those attributed to the carbon-hydrogen bending vibrations of the =C–H group. These characteristic bands are in the region 1000–650 cm^{-1} (region C in the spectrum of 1-octene). Examination of this region of the IR of an alkene can reveal further structural information about the compound. For instance, bands are at 1000 and 910 cm^{-1} indicate the presence of a –CH=CH₂ group in the alkene. Bands at 970 cm^{-1} and 770–665 cm^{-1} indicate, respectively, a *trans* or a *cis* form of the grouping R–CH=CH–R'.

Table 17-4: Alkene diagnostic bands.

=C–H stretch	3100–3000 cm^{-1} (m)
–C=C– stretch	1680–1640 cm^{-1} (m)
=C–H bend	1000–650 cm^{-1} (s)

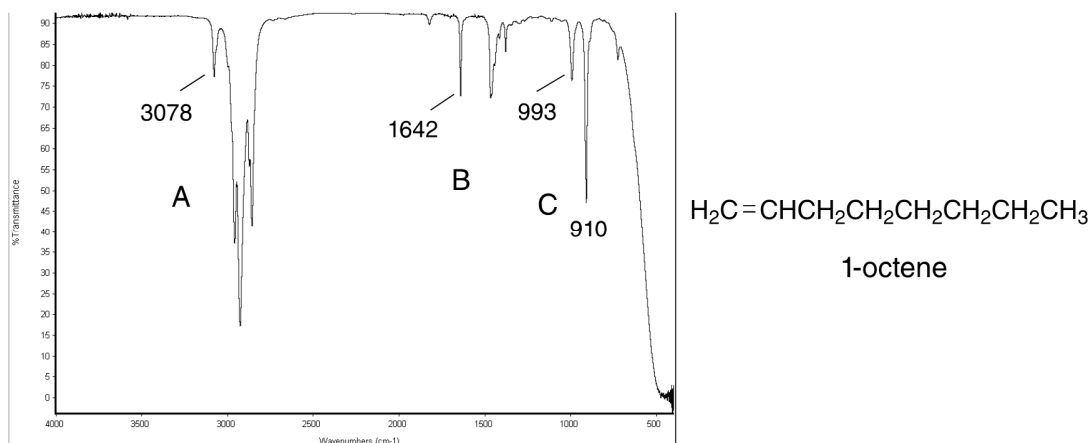
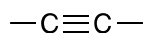


Figure 17-12: Representative alkene spectrum.

C. Alkynes



The $-\text{C}\equiv\text{C}-$ stretch appears as a weak band from $2260\text{--}2100\text{ cm}^{-1}$ (B in the region of 1-hexyne, Figure 17-13). In a terminal alkyne, as in $-\text{C}\equiv\text{C}-\text{H}$, the C–H stretch is seen as a strong, narrow band in the range $3330\text{--}3270\text{ cm}^{-1}$ (A in the spectrum of 1-hexyne), although this band may be indistinguishable from bands resulting from other functional groups on the same molecule that absorb in this region, such as the O–H stretch. The C–H bending vibration of a terminal alkyne shows as a strong, broad band in the region $700\text{--}610\text{ cm}^{-1}$ (C in the spectrum of 1-hexyne).

Table 17-5: Alkyne diagnostic bands.

$-\text{C}\equiv\text{C}-\text{H}$: C–H stretch	$3330\text{--}3270\text{ cm}^{-1}$ (n, s)
$-\text{C}\equiv\text{C}-$ stretch	$2260\text{--}2100\text{ cm}^{-1}$ (w)
$-\text{C}\equiv\text{C}-\text{H}$: C–H bend	$700\text{--}610\text{ cm}^{-1}$ (b, s)

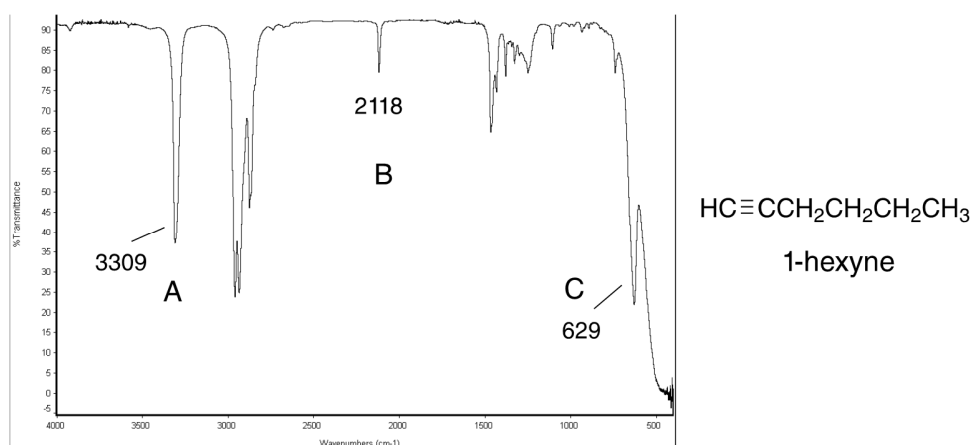
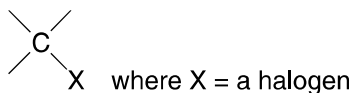


Figure 17-13: Representative alkyne spectrum.

D. Alkyl Halides



IR spectra of alkyl halides have absorptions due to the stretching vibrations of the carbon-halogen bond and bands due to C–H stretching and bending vibrations characteristic of alkanes (discussed in section 17.4A). In general, carbon-halogen vibration frequencies appear from $850\text{--}515\text{ cm}^{-1}$, sometimes out of the range of typical IR instrumentation. Specifically, C–Cl absorptions appear in the broad region $850\text{--}550\text{ cm}^{-1}$ and C–Br absorptions appear in the region $690\text{--}515\text{ cm}^{-1}$. In terminal alkyl halides, the C–H wag of the $-\text{CH}_2\text{X}$ group (where X is Br, Cl, or I) is seen at $1300\text{--}1150\text{ cm}^{-1}$. Complicating the spectra is a profusion of absorptions throughout the region $1250\text{--}770\text{ cm}^{-1}$, especially in the smaller alkyl halides. While not useful for diagnostic purposes, these bands can be useful for purposes of fingerprinting.

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The spectra of 1-chloro-2-methylpropane, 1-bromopropane, and 1-bromohexane are shown in Figure 17-14. Each of the spectra shows bands in the A region, 1300–1150 cm^{-1} , due to C–H wag of the $-\text{CH}_2\text{Br}$ or $-\text{CH}_2\text{Cl}$ group.

Table 17-6: Alkyl halide diagnostic bands.

C–H wag ($-\text{CH}_2\text{X}$)	1300–1150 cm^{-1} (m)
C–X stretch (general)	850–515 cm^{-1}
C–Cl stretch	850–550 cm^{-1}
C–Br stretch	690–515 cm^{-1}

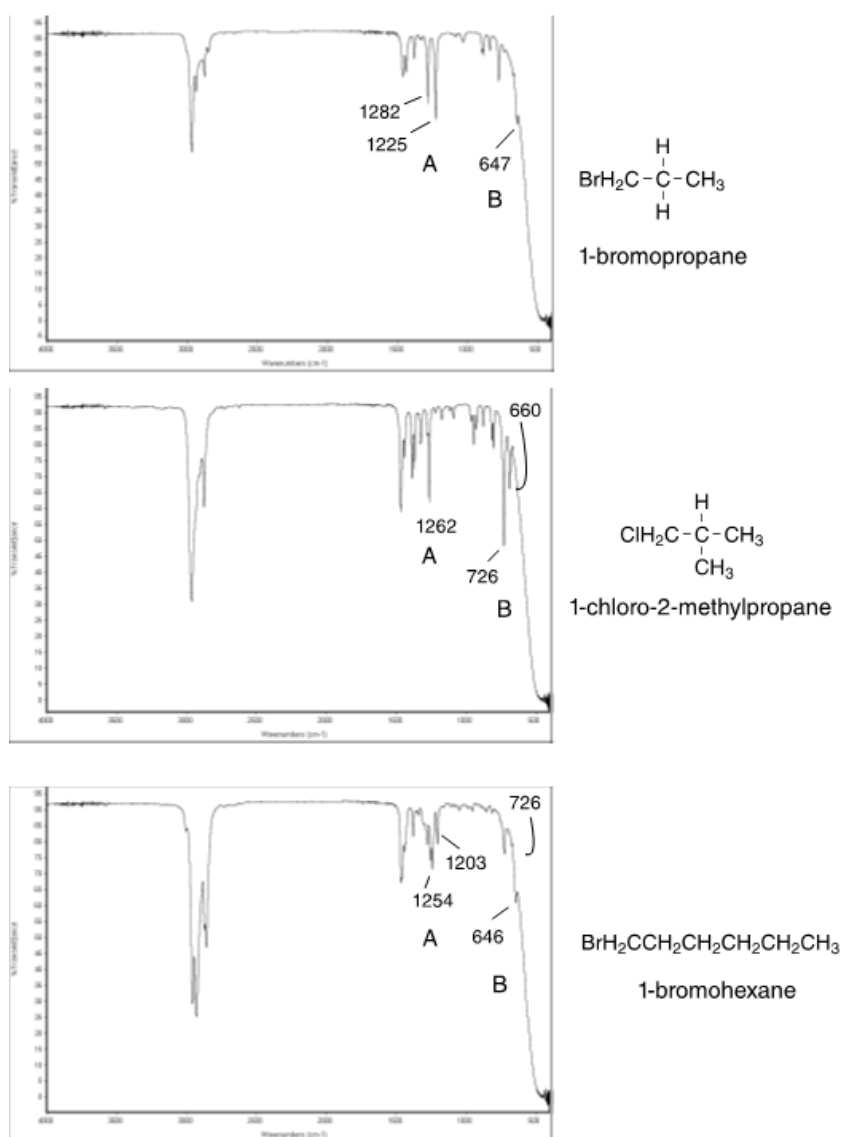


Figure 17-14: Representative alkyl halide spectra.

E. Aromatics

The C–H stretch in aromatics is observed at 3100–3000 cm^{-1} (A in the spectrum of toluene, Figure 17-15). Note that this is at slightly higher frequency than is the C–H stretch in alkanes. Aromatic hydrocarbons show absorptions in the regions 1600–1585 cm^{-1} and 1500–1400 cm^{-1} due to C–C stretching vibrations in the aromatic ring (B in the spectrum of toluene). Bands in the region 1250–1000 cm^{-1} are due to C–H in-plane bending (C in the spectrum of toluene), although these bands are too weak to be observed in most aromatic compounds.

Two regions of the infrared spectra of aromatics are important in diagnosing the number and positions of substituents on the aromatic ring. The pattern of overtone and combination bands in the region 2000–1665 cm^{-1} (weak bands) reflect the substitution pattern on the ring. The pattern of the out-of-plane (“oop”) C–H bending bands in the region 900–675 cm^{-1} (D in the spectrum of toluene) are also characteristic of the aromatic substitution pattern. The correlation between aromatic substitution and IR bands in these regions works best for alkyl group substituents. If one of the substituents is a carbonyl, as in benzoates and benzoic acids, the IR patterns are disturbed.

Table 17-7: Aromatic diagnostic bands.

C–H stretch	3100–3000 cm^{-1} (s)
overtone bands	1600–1585 cm^{-1} (w)
C–C stretch (in-ring)	1600–1585 cm^{-1} (m)
C–C stretch (in-ring)	1500–1400 cm^{-1} (m)
C–H “oop”	900–675 cm^{-1} (s)

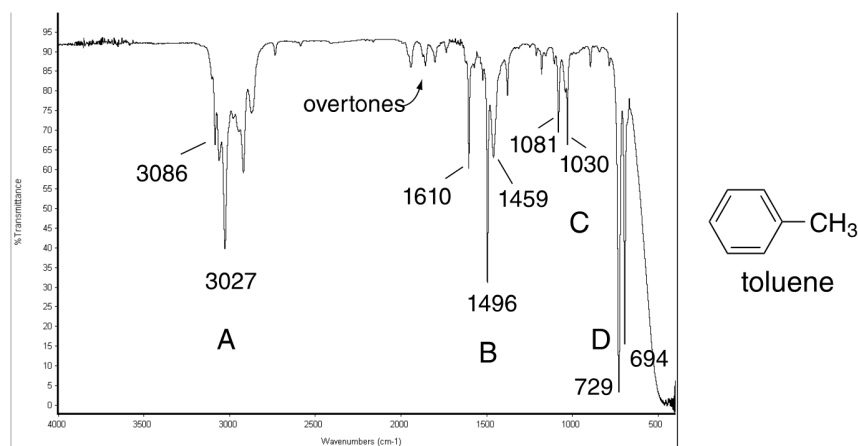
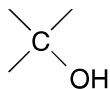


Figure 17-15: Representative aromatic spectrum.

F. Alcohols



Alcohols have characteristic IR absorptions due to the O–H stretching vibrations. When run as a thin liquid film, or “neat,” the O–H stretch of alcohols appears in the region 3500–3200 cm^{-1} and is a very intense, broad band (region A in the spectrum of ethyl alcohol, Figure 17-16). When a liquid alcohol is diluted with a solvent such as carbon tetrachloride, the O–H stretch shifts to 3640–3610 cm^{-1} and is a sharp peak of moderate intensity. The reason is due to intermolecular hydrogen bonding in the concentrated or neat samples. The diluted, non-hydrogen bonded peak is called a “free” hydroxyl peak. Most of the samples of alcohols that you will run in the organic chemistry teaching laboratories will be run as thin liquid films, and thus will show the hydrogen bonded hydroxyl peak at 3500–3200 cm^{-1} .

Another band to look for in spectra of alcohols is the C–O stretch in the region 1260–1050 cm^{-1} (region B in the spectrum of ethanol).

Table 17-8: Alcohol diagnostic bands.

O–H stretch, free hydroxyl	3640–3610 cm^{-1} (s, sh)
O–H stretch, hydrogen bonded	3500–3200 cm^{-1} (s, b)
C–O stretch	1260–1050 cm^{-1} (s)

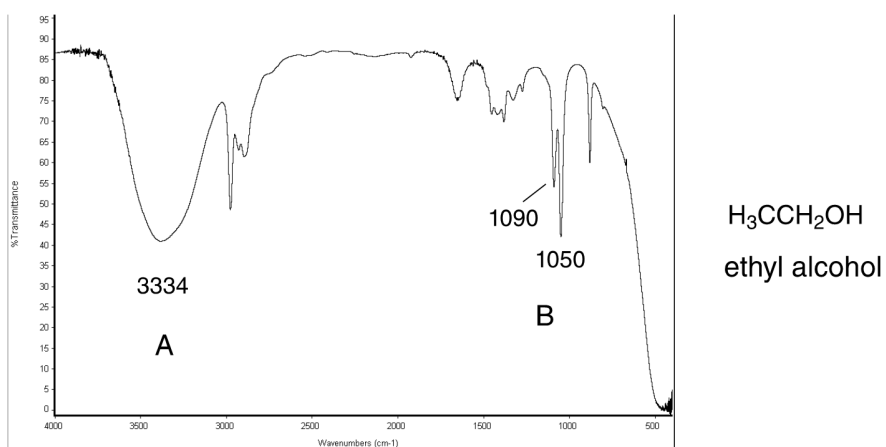
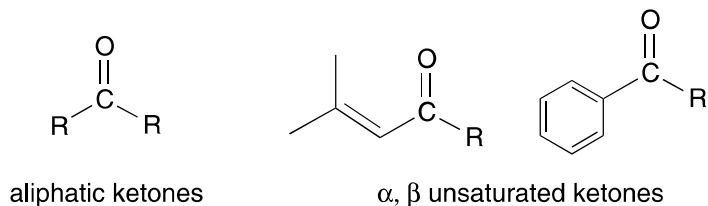


Figure 17-16: Representative alcohol spectrum.

G. Ketones



All carbonyl compounds absorb in the region $1760\text{--}1665\text{ cm}^{-1}$ due to the stretching vibration of the C=O bond. The carbonyl band is particularly useful for diagnostic purposes because it has a characteristic high intensity and few other functional groups absorb in this region. Different carbonyl compounds absorb in narrow ranges within the general carbonyl region.

The carbonyl stretching vibration band of saturated aliphatic ketones appears at 1715 cm^{-1} (B in the spectrum of 2-butanone, Figure 17-17). Conjugation of the carbonyl group with carbon-carbon double bonds or phenyl groups, as in α, β -unsaturated aldehydes and benzaldehyde, shifts this band to lower wavenumbers ($1685\text{--}1666\text{ cm}^{-1}$). Substitution of an alpha carbon with other atoms or groups shifts the carbonyl band to either higher or lower wavenumbers.

Table 17-9: Ketone diagnostic bands.

C=O stretch:	
aliphatic ketones	1715 cm^{-1}
α, β unsaturated ketones	$1685\text{--}1666\text{ cm}^{-1}$

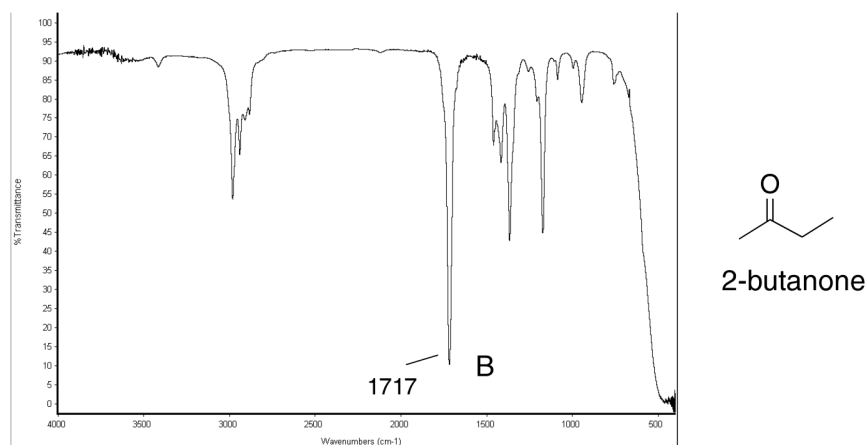
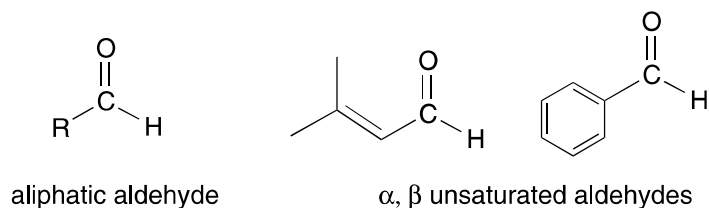


Figure 17-17: Representative ketone spectrum.

H. Aldehydes

The carbonyl stretch of aliphatic aldehydes is observed in the region $1740\text{--}1720\text{ cm}^{-1}$. As in ketones, if the carbons adjacent to the aldehyde group are unsaturated, this vibration is shifted to lower wavenumbers ($1710\text{--}1685\text{ cm}^{-1}$). Compare the carbonyl bands of benzaldehyde and butyraldehyde (region B in both spectra, Figure 17-18). If the alpha carbon is substituted with an electronegative atom, as in Cl_3CHO , this stretching vibration is shifted to higher wavenumbers (1765 cm^{-1}).

The C–H stretch of the aldehyde functionality generally appears as one or two bands of moderate intensity in the region $2830\text{--}2695\text{ cm}^{-1}$ (A in the spectra of butyraldehyde and benzaldehyde). Since the band near 2830 cm^{-1} is usually indistinguishable from other C–H stretching vibration bands, the presence of a moderate band near 2720 cm^{-1} is more likely to be helpful in determining whether or not a compound is an aldehyde.

Table 17-10: Aldehyde diagnostic bands.

H–C=O: C–H stretch	$2830\text{--}2695\text{ cm}^{-1}$ (m)
C=O stretch:	
aliphatic aldehydes	$1740\text{--}1720\text{ cm}^{-1}$
α , β unsaturated aldehydes	$1710\text{--}1685\text{ cm}^{-1}$

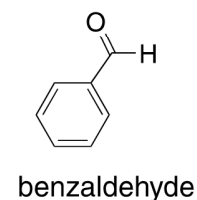
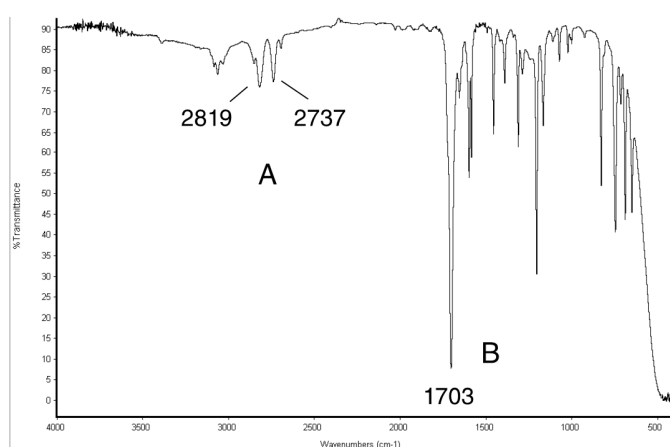
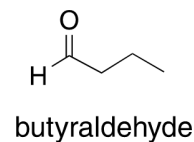
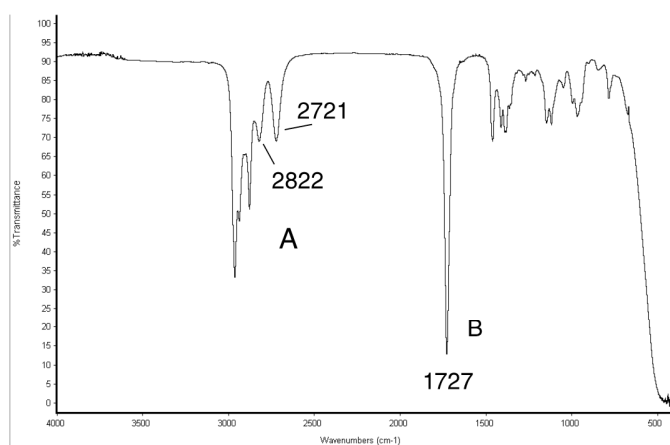
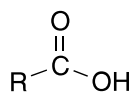
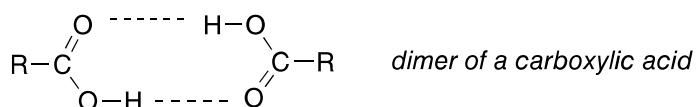


Figure 17-18: Representative aldehyde spectra.

I. Carboxylic Acids



Carboxylic acids usually exist as dimers, where two molecules bond to each other. Because of hydrogen bonding of these dimers, the O–H stretching vibration appears as a broad band in the region 3300–2500 cm^{-1} , centered at about 3000 cm^{-1} . This band is often seen superimposed on the sharp C–H stretching bands in this same region.



The characteristic O–H band of carboxylic acids is readily observed in the spectrum of hexanoic acid (Figure 17-19). Note the broad peak due to O–H stretch superimposed on the sharp band due to C–H stretch (region A). The carbonyl stretch, C=O, of the carboxylic acid group appears as an intense band in the region 1760–1690 cm^{-1} (region B in the spectrum of hexanoic acid). The exact position of this band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen

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bonding. The C–O stretch is in the region $1320\text{--}1210\text{ cm}^{-1}$ (region C). A band attributed to O–H bend is in the region $1440\text{--}1395\text{ cm}^{-1}$. Since this is also the region where the C–H bend is observed, this band due to O–H bend may not be distinguishable from other bands in the same region. Another band due to O–H bending vibrations is observed in the region $950\text{--}910\text{ cm}^{-1}$ (region D).

Table 17-11: Carboxylic acid diagnostic bands.

O–H stretch	$3300\text{--}2500\text{ cm}^{-1}$ (m)
C=O stretch	$1760\text{--}1690\text{ cm}^{-1}$ (s)
O–H bend	$1440\text{--}1395\text{ cm}^{-1}$ (s)
C–O stretch	$1320\text{--}1210\text{ cm}^{-1}$ (s)
O–H bend	$950\text{--}910\text{ cm}^{-1}$ (m)

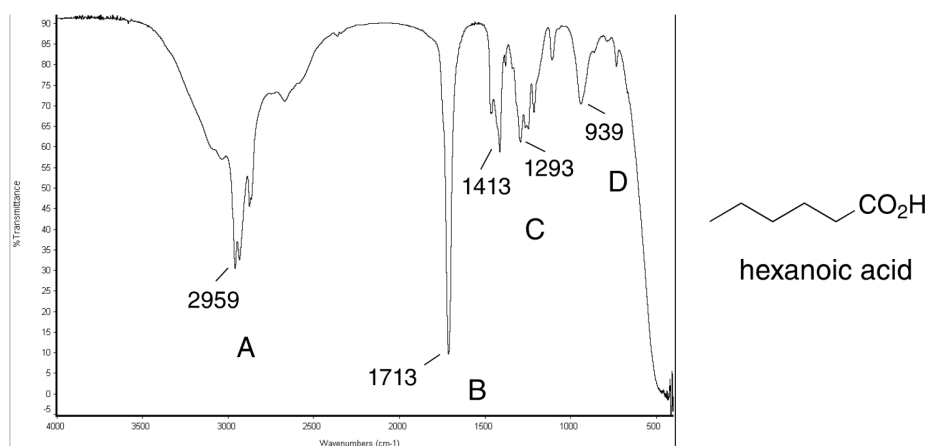
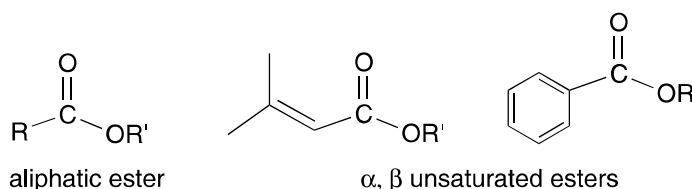


Figure 17-19: Representative carboxylic acid spectrum.

J. Esters



The carbonyl stretch of esters appears at higher wavenumbers than the carbonyl stretch of normal ketones. In aliphatic esters, this stretch is in the range $1750\text{--}1735\text{ cm}^{-1}$ (region A in the spectrum of ethyl acetate, Figure 17-20). In α, β unsaturated esters and in benzoates, the stretch is from $1730\text{--}1715\text{ cm}^{-1}$ (region A in the spectrum of ethyl benzoate.) The C–O stretches appear as two or more bands in the region $1300\text{--}1000\text{ cm}^{-1}$ (region B in the spectra of ethyl acetate and ethyl benzoate).

Table 17-12: Ester diagnostic bands.

C=O stretch:	
aliphatic	1750–1735 cm^{-1} (s)
α , β -unsaturated esters and benzoates	1730–1715 cm^{-1} (s)
C–O stretch	1300–1000 cm^{-1} (s)

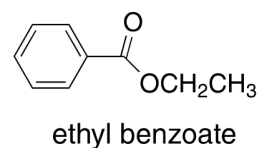
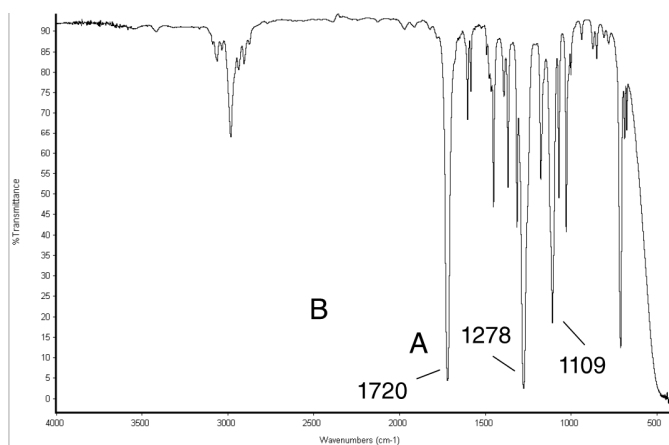
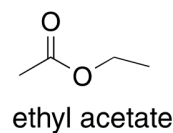
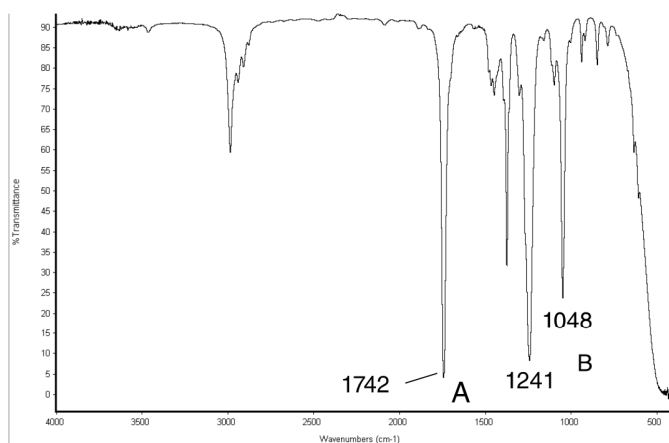


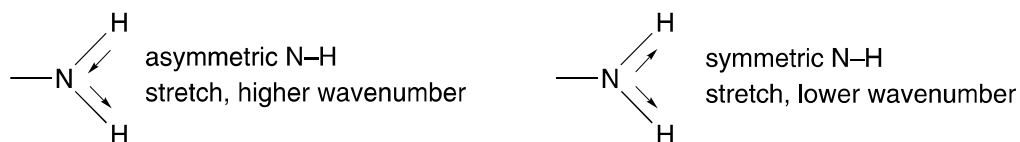
Figure 17-20: Representative ester spectra.

K. Amines

The N–H stretch of amines occurs in the range 3300–3000 cm^{-1} as weak bands. (The N–H stretch is observed at 3550–3320 cm^{-1} if the amine is run in dilute solution. This is called “free” N–H stretch, as opposed to hydrogen-bonded N–H stretch. Most of the spectra that you run in this course are run “neat”; amines run in this manner are subject to hydrogen bonding and thus will show the N–H stretch at 3300–3000 cm^{-1} .) Generally, amine bands are weaker and sharper than the O–H bands that appear in the same

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region. In aromatic amines, this band is shifted to slightly higher wavenumbers. In primary amines, there are two bands in this region, the asymmetrical N–H stretch and the symmetrical N–H stretch. (A shoulder usually appears on the lower wavenumber side in primary and secondary liquid amines arising from the overtone of the NH bending band: this can confuse interpretation. See the spectrum of aniline in Figure 17-21.) Secondary amines show only a single weak band in this region, since they have only one N–H bond. Tertiary amines, R_3N , do not have an N–H bond, and therefore do not show any bands in this region. Compare regions A of the spectra of aniline, diethylamine, and triethylamine (Figure 17-21).



The N–H bending vibration of primary amines is observed in the region $1650\text{--}1580\text{ cm}^{-1}$. Usually, secondary amines do not show a band in this region and tertiary amines never show a band in this region. (Region B in the spectrum of aniline.)

Another band attributed to the N–H group is observed in the region $910\text{--}665\text{ cm}^{-1}$. This strong, broad band is due to N–H wag and observed only for primary and secondary amines. (Region D in the spectra of aniline and diethylamine.)

The C–N stretching vibration of aliphatic amines is observed as medium or weak bands in the region $1250\text{--}1020\text{ cm}^{-1}$. (Region C in the spectrum of all three amines.) In aromatic amines, the band is usually strong and in the region $1335\text{--}1250\text{ cm}^{-1}$.

Table 17-13: Amine diagnostic bands.

N–H stretch:	$3400\text{--}3250\text{ cm}^{-1}$ (m)
1° amine: two bands	$3400\text{--}3300$ and $3330\text{--}3250\text{ cm}^{-1}$ (m)
2° amine: one band	$3350\text{--}3310\text{ cm}^{-1}$ (m)
3° amine: no bands	none
N–H bend (1° amines only)	$1650\text{--}1580\text{ cm}^{-1}$ (m)
C–N stretch (aromatic amines)	$1335\text{--}1250\text{ cm}^{-1}$ (s)
C–N stretch (aliphatic amines)	$1250\text{--}1020\text{ cm}^{-1}$ (m)
N–H wag (1° and 2° amines only)	$910\text{--}665\text{ cm}^{-1}$ (s, b)

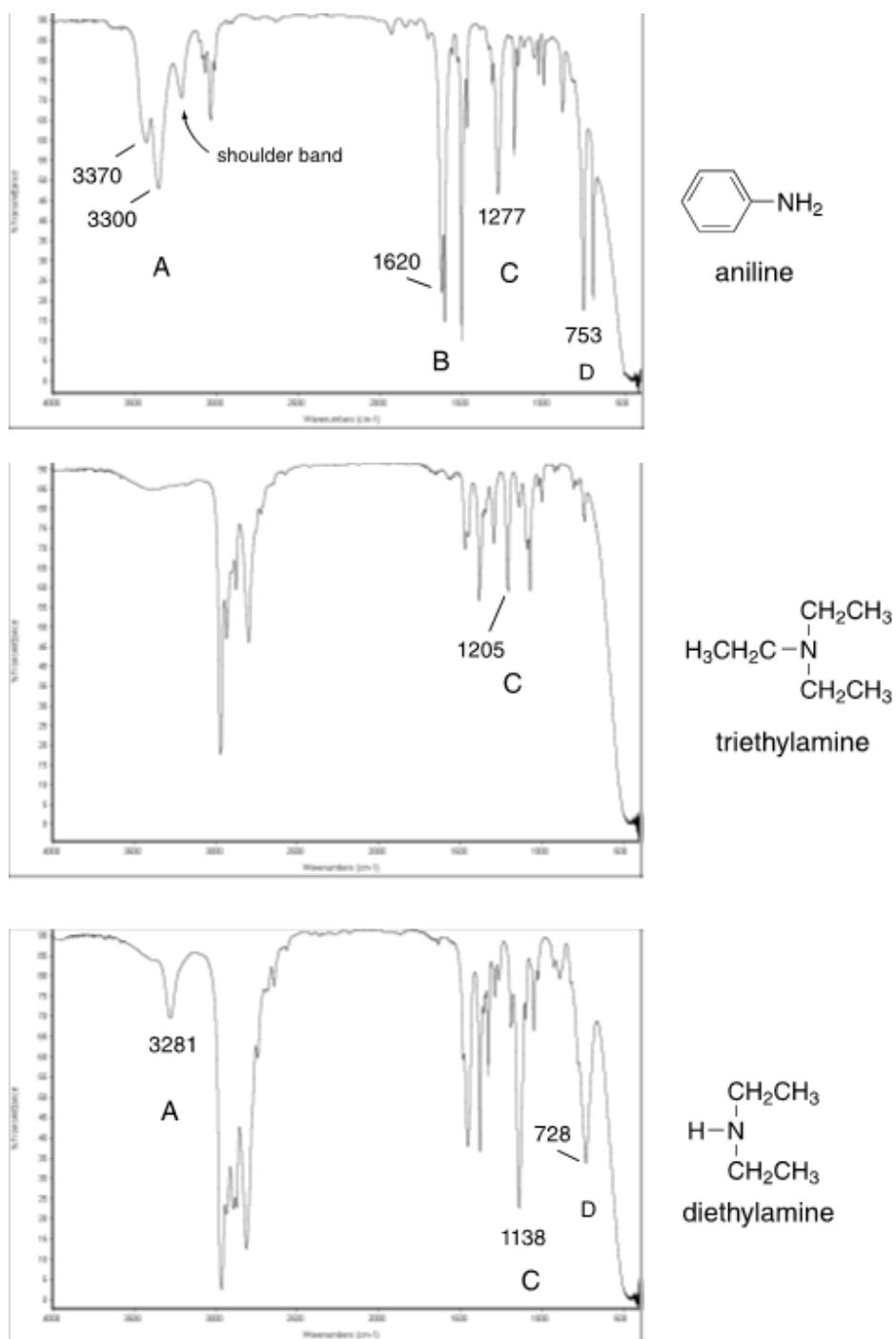


Figure 17-21: Representative amine spectra.

L. Nitro Compounds

The N–O stretching vibrations in nitroalkanes (alkanes containing $-\text{NO}_2$) occur near 1550 cm^{-1} (asymmetrical) and 1365 cm^{-1} (symmetrical); the band at 1550 cm^{-1} being the stronger of the two. If the nitro group is attached to an aromatic ring, these bands shift to $1550\text{--}1475\text{ cm}^{-1}$ and $1360\text{--}1290\text{ cm}^{-1}$. Compare the spectra of nitromethane and nitrotoluene, Figure 17-22.

Table 17-14: Nitro diagnostic bands.

N–O asymmetric stretch	1550–1475 cm^{-1} (s)
N–O symmetric stretch	1365–1290 cm^{-1} (m)

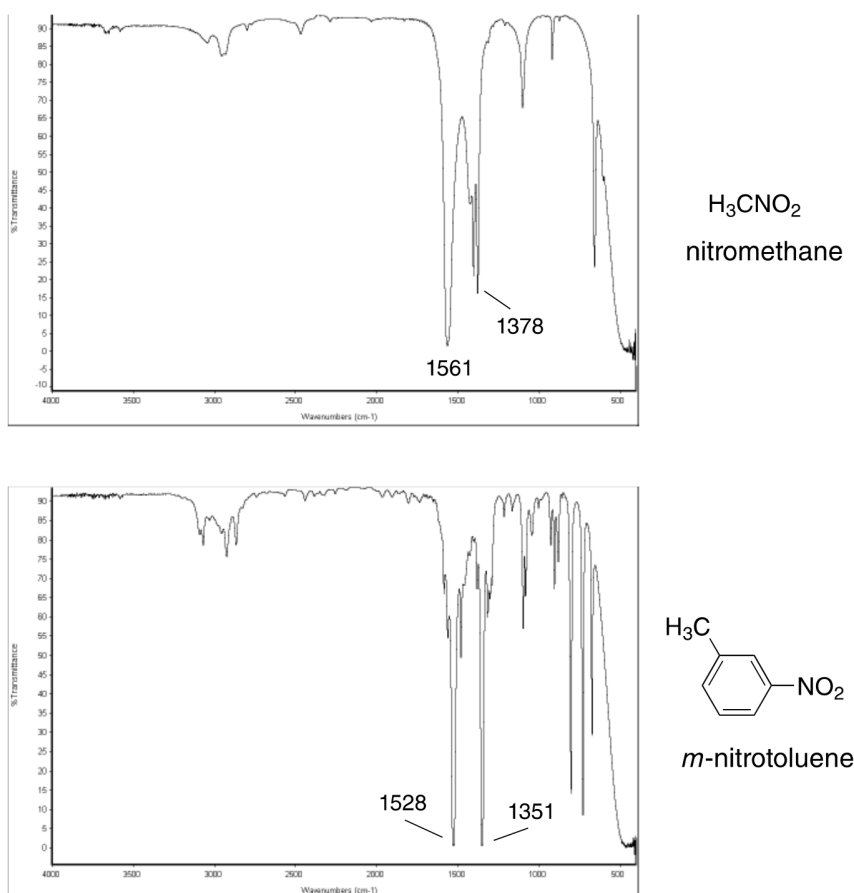


Figure 17-22: Representative nitro compound spectra.

17.5 How to Analyze an IR Spectrum

So how can IR spectra be used to analyze details of a molecular structure? When analyzing an IR spectrum of an unknown, look first for conspicuous bands, such as O–H, C=O, C–O, C=C, C≡C, C≡N, and NO₂. See Table 17-15 for a list of IR bands and the functional groups that they represent.

The following is an outline of how to approach the analysis of an IR spectrum by looking for important infrared stretching frequencies.

Look at the C—H stretches around 3000 cm⁻¹:

- Are any to the right of 3000 cm⁻¹? → alkyl groups in the molecule
- Are any to the left of 3000 cm⁻¹? → alkene or aromatic

Is a carbonyl present?**If a carbonyl is present, check for the following types:**

- Is an O—H band also present? → carboxylic acid
- Is an N—H band also present? → amide
- Is a C—O band also present? → ester
- Is an aldehydic C—H band also present? → aldehyde
- Are none of the above present? → ketone

If carbonyl is absent:

- Is O—H present? → alcohol or phenol
- Is N—H present? → amine
- Is C—O present? → ether

Other structural features to check for:

- Double bonds and/or aromatic rings
- Triple bonds
- Nitro groups
- Hydrocarbons: The absence of major functional group bands. The IR of a hydrocarbon is a very simple spectrum with major absorptions in the C—H region near 3000–2800 cm⁻¹.

As a beginning student, you should not try to assign or interpret every peak in the spectrum. Concentrate on learning the major bands and recognizing their presence and absence in any given spectrum.

Table 17-15: Table of characteristic IR absorptions.

Wavenumber, cm ⁻¹	Bond	Functional group
3640–3610 (s, sh)	O—H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O—H stretch, H-bonded	alcohols, phenols
3400–3250 (m)	N—H stretch	1°, 2° amines, amides
3300–2500 (m)	O—H stretch	carboxylic acids
3330–3270 (n, s)	—C≡C—H: C—H stretch	alkynes (terminal)
3100–3000 (s)	C—H stretch	aromatics
3100–3000 (m)	=C—H stretch	alkenes
3000–2850 (m)	C—H stretch	alkanes
2830–2695 (m)	H—C=O: C—H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	—C≡C— stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids

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1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α , β -unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1685 (s)	C=O stretch	α , β -unsaturated aldehydes
1685–1666 (s)	C=O stretch	α , β -unsaturated ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH ₂ X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H “oop”	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides
m = medium, w = weak, s = strong, n = narrow, b = broad, s = sharp		