



Chapter 15

Infrared Spectroscopy: Theory

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 three 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.

15.1 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, as illustrated in Figure 15.1.

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:

$$\nu = \frac{c}{\lambda} \text{ and } \lambda = \frac{c}{\nu} \quad \text{Eq. 1}$$

where c is the speed of light, 3×10^{10} cm/sec

Energy is related to wavelength and frequency by the following formulas:

$$E = h\nu = \frac{hc}{\lambda} \quad \text{Eq. 2}$$

where h = Planck's constant, 6.6×10^{-34} joules-sec

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 (see Figure 15.2). 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. Chemists prefer to work with numbers which are easy to write; therefore IR spectra are sometimes reported in μm , although another unit, $\bar{\nu}$ (nu bar or *wavenumber*), is currently preferred.

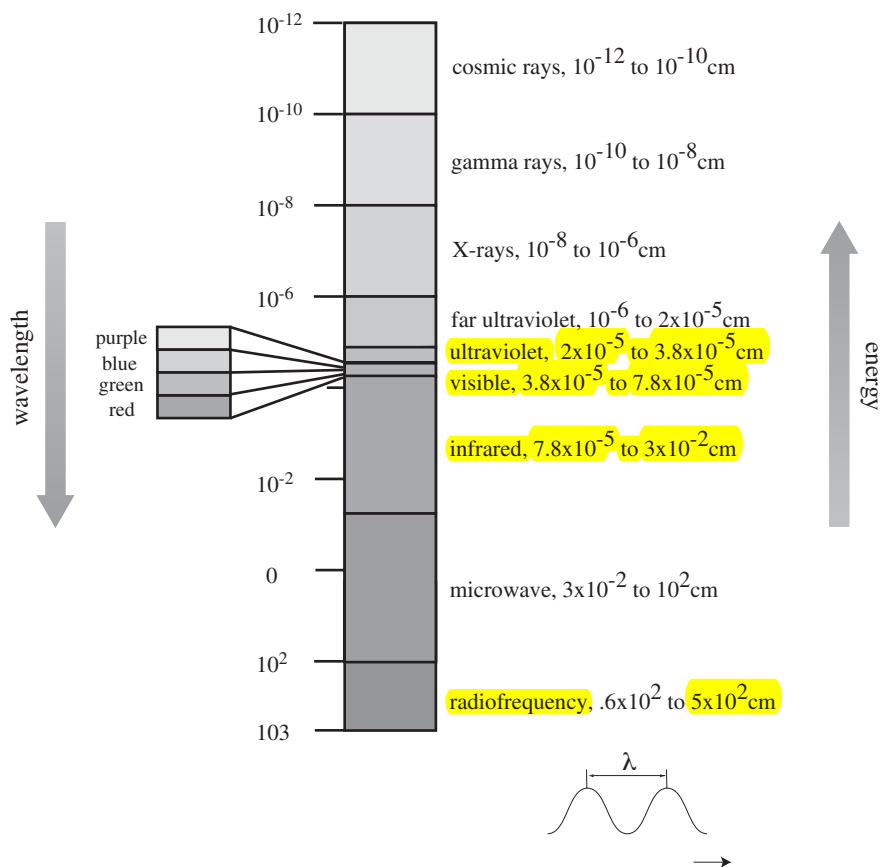


Figure 15.1 The electromagnetic spectrum.

A wavenumber is the inverse of the wavelength in cm:

$$\bar{\nu} = \frac{1}{\lambda} \quad \text{Eq. 3}$$

where ν is in units of cm^{-1} , λ is in units of cm

and now:

$$E = hc\bar{\nu} \quad \text{Eq. 4}$$

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.

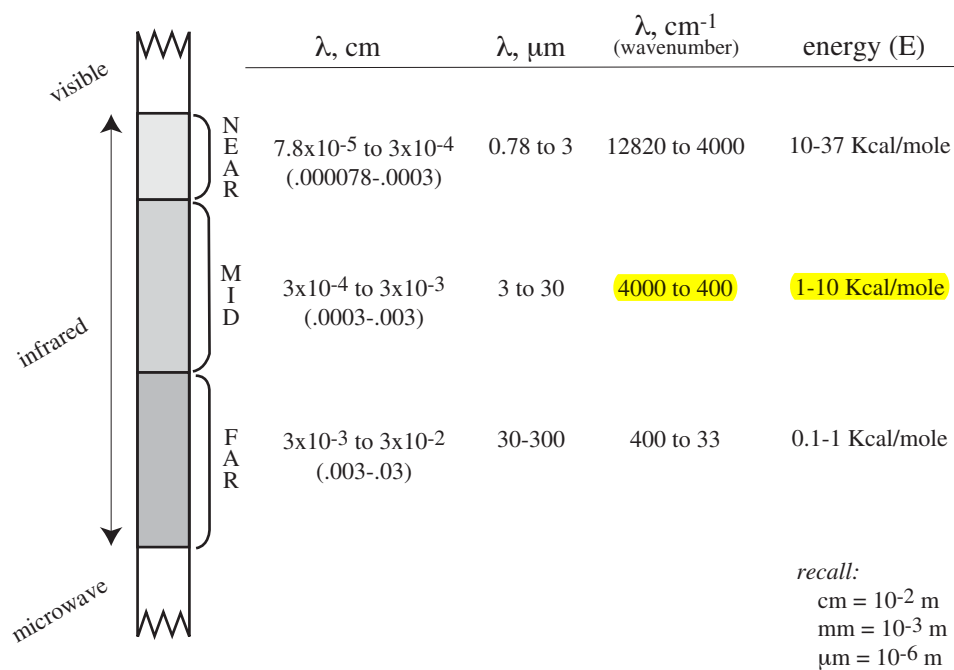


Figure 15.2 The IR regions of the electromagnetic spectrum.

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 15.3).

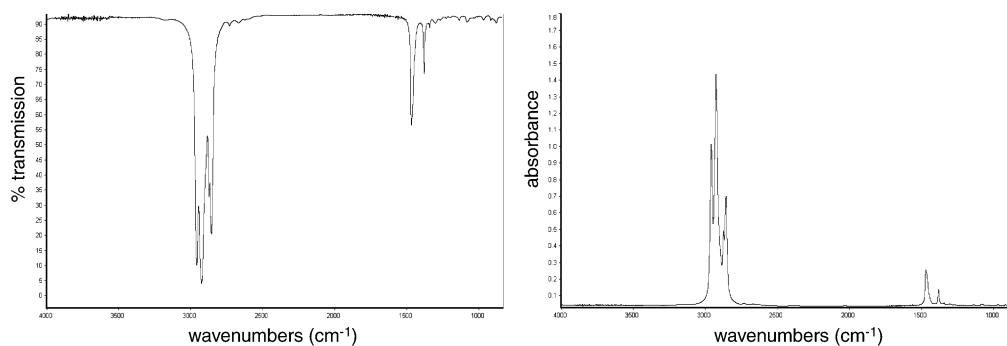


Figure 15.3 The IR spectrum of octane, plotted as transmission (left) and absorbance (right).

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, most well-known of which are those by Sadtler and Aldrich. While in the past these compilations were available only in printed form, they are now available in CD

ROM format for computer analysis. These “libraries” are quite expensive and are not available in our teaching laboratories, although we do have several smaller libraries which you will be able to search to match spectra which you run on our IR instruments.

The wavenumbers (sometimes referred to as *frequencies*) 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 which correlate frequencies with functional groups. The theory behind this relationship is discussed in the next section on molecular vibrations.

15.2 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:

<i>molecule</i>	<i>degrees of freedom</i>
nonlinear	$3n - 6$
linear	$3n - 5$

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.) The fundamental vibrations for water, H_2O , are given in Figure 15.4. Water, which is nonlinear, has three fundamental vibrations.

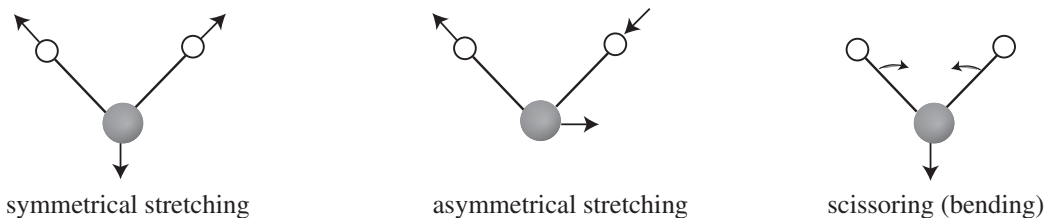


Figure 15.4 : Stretching and bending vibrational modes for H_2O

Carbon dioxide, CO_2 , is linear and hence has four fundamental vibrations (Figure 15.5). The asymmetrical stretch of CO_2 gives a strong band in the IR at 2350 cm^{-1} . You may notice this band in samples which you run on the instruments in the

teaching labs, since CO_2 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} .

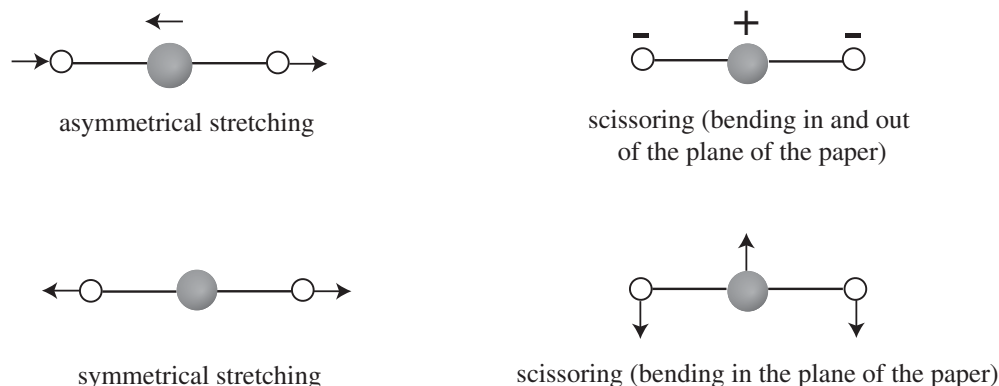


Figure 15.5 : Stretching and bending vibrational modes for CO_2

The symmetrical stretch of CO_2 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.) Of the following linear molecules, carbon monoxide and iodine chloride absorb IR radiation, while hydrogen, nitrogen, and chlorine do not. In general, the larger the dipole change, the stronger the intensity of the band in an IR spectrum.



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 CO_2 , 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 $4000\text{--}400\text{ cm}^{-1}$ 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, $-\text{CH}_2$, are illustrated in Figure 15.6. (The $3n-6$ rule does not apply since the $-\text{CH}_2$ group represents only a portion of a molecule.) Note that bending vibrations occur at lower frequencies than corresponding stretching vibrations.

* 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.

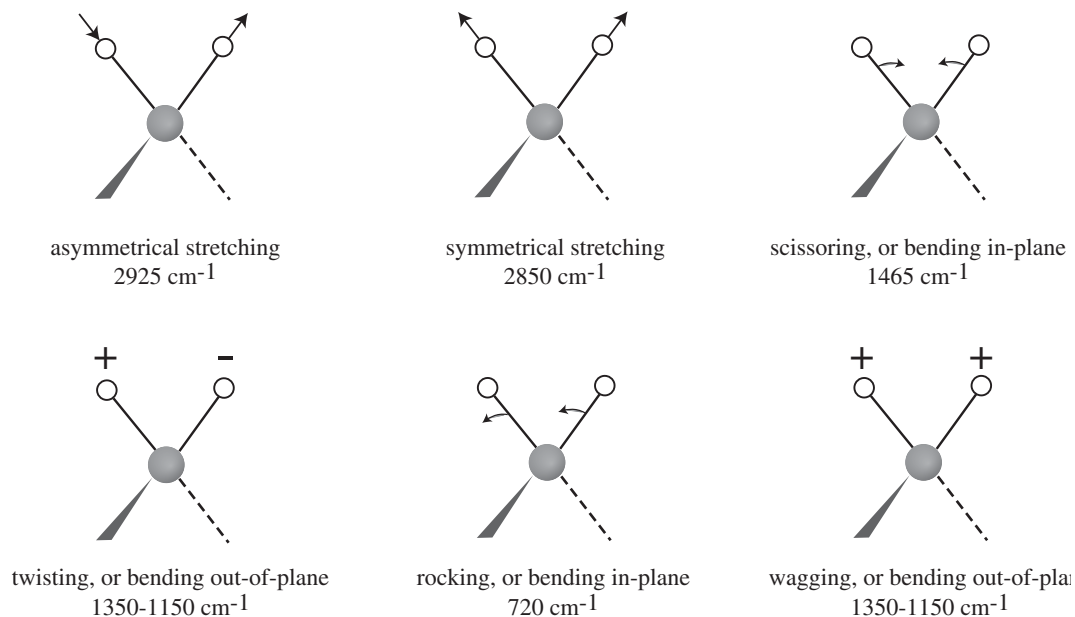


Figure 15.6 : Stretching and bending vibrational modes for a CH_2 group.

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.

15.3 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:



Eq. 5

The energy curve for a simple harmonic oscillator is illustrated in Figure 15.7. According to **Hooke's law**, the frequency of the vibration of the spring is related to the mass and the force constant of the spring, k , by the following formula:

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

where k is the force constant

m is the mass

ν is the frequency of the vibration

In the classical harmonic oscillator, $E = 1/2 kx^2 = h\nu$, 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.

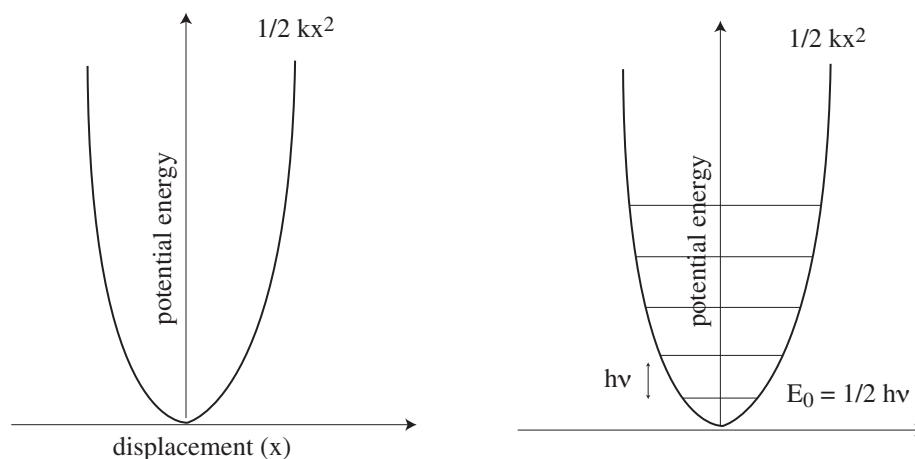


Figure 15.7 : Energy curve for a vibrating spring (left) and energy constrained to quantum mechanical model (right).

However, vibrational motion is *quantized*: it must follow the rules of quantum mechanics, and the only transitions which are allowed fit the following formula:

$$E = (n + 1/2)h\nu \quad \text{Eq. 6}$$

where ν is the frequency of the vibration
 n is the quantum number (0, 1, 2, 3, . . .)

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 $h\nu$. 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 vibration bands.

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 15.8. 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.

The following formula has been derived from Hooke's law. For the case of a diatomic molecule, ($\bar{\nu}$ has been substituted for ν , recall that $\nu = c\bar{\nu}$ from equations 1 and 3):

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}} \quad \text{Eq. 7}$$

where $\bar{\nu}$ is the vibrational frequency (cm^{-1})
 m_1 and m_2 are the mass of atoms 1 and 2, respectively, in g
 c is the velocity of light (cm/s)

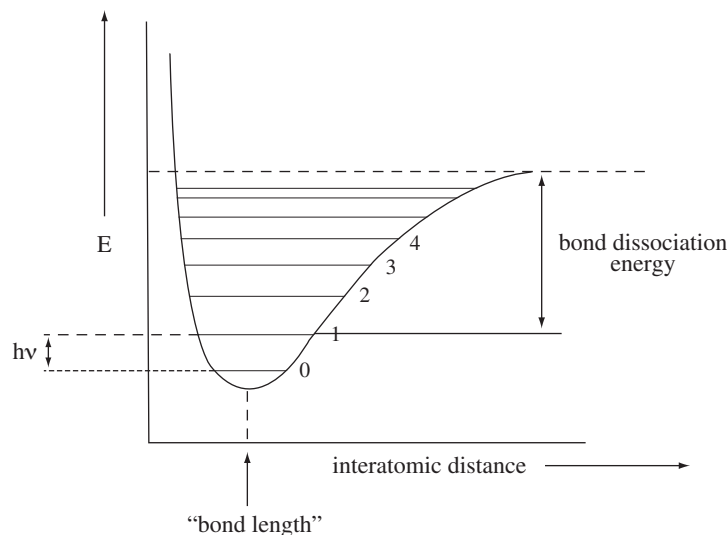


Figure 15.8 : Energy curve for an anharmonic oscillator (showing the vibrational levels for a vibrating bond).

f is the force constant of the bond (dyne/cm)

Equation 7 shows the relationship of bond strength and atomic mass to the wavenumber at which a molecule will absorb IR radiation. As the force constant increases, the vibrational frequency (wavenumber) also increases. The force constants for bonds are:

single bond	5×10^5 dyne/cm
double bond	10×10^5 dyne/cm
triple bond	15×10^5 dyne/cm

As the mass of the atoms increases, the vibration frequency decreases. Using the following mass values:

C, carbon	$12/6.02 \times 10^{23}$
H, hydrogen	$1/6.02 \times 10^{23}$

$\bar{\nu}$ for a C–H bond is calculated to be 3032 cm^{-1} . (Try this calculation!) 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 or bonds to hydrogen. The following table 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.

bond	absorption region, cm^{-1}
C–C, C–O, C–N	800–1300

C=C, C=O, C=N, N=O	1500–1900
C≡C, C≡N	2000–2300
C–H, N–H, O–H	2700–3800

Although 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 superimposed (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 15.6, you note there are two bands in the region for C–H bonds: 2926 cm^{-1} and 2853 cm^{-1} .

