

IR SPECTROSCOPY

Did you ever wonder how chemists are able to determine whether or not a reaction has produced the desired products? In your textbook, you will learn about many, many reactions. And an obvious question should be: “how do chemists *know* that those are the products of the reactions?”

Until about 50 years ago, it was actually VERY difficult to determine the structures of the products of a reaction. In fact, chemists would often spend many months, or even years to elucidate the structure of a single compound. But things got a lot simpler with the advent of spectroscopy. These days, the structure of a compound can be determined in minutes. Spectroscopy is, without a doubt, one of the most important tools available for determining the structure of a compound. Many Nobel prizes have been awarded over the last few decades to chemists who pioneered applications of spectroscopy.

The basic idea behind all forms of spectroscopy is that electromagnetic radiation (light) can interact with matter in predictable ways. Consider the following simple analogy: imagine that you have 10 friends, and you know what kind of bakery items they each like to eat every morning. John always has a brownie, Peter always has a French roll, Mary always has a blueberry muffin, etc. Now imagine that you walk into the bakery just after it opens, and you are told that some of your friends have already visited the bakery. By looking at what is missing from the bakery, you could figure out which of your friends had just been there. If you see that there is a brownie missing, then you deduce that John was in the bakery before you.

This simple analogy breaks down when you really get into the details of spectroscopy, but the basic idea is a good starting point. When electromagnetic radiation interacts with matter, certain frequencies are absorbed while other frequencies are not. By analyzing which frequencies were absorbed (which frequencies are missing once the light passes through a solution containing the unknown compound), we can glean useful information about the structure of the compound.

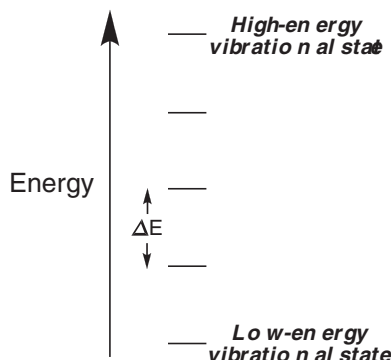
You may recall from your high school science classes that the range of all possible frequencies (of electromagnetic radiation) is known as the electromagnetic spectrum, which is divided into several regions (including X-rays, UV light, visible light, infrared radiation, microwaves, and radio waves). Different regions of the electromagnetic spectrum are used to probe different aspects of molecular structure, as seen in the table below:

Type of Spectroscopy	Region of Electromagnetic Spectrum	Information Obtained
NMR Spectroscopy	Radio Waves	The specific arrangement of all carbon and hydrogen atoms in the compound
IR Spectroscopy	Infrared	The functional groups present in the compound
UV-Vis Spectroscopy	Visible and Ultraviolet	Any conjugated π system present in the compound

We will not cover UV-Vis spectroscopy in this book. Your textbook will have a short section on that form of spectroscopy. In this chapter, we will focus on the information that can be obtained with IR spectroscopy. Chapter 2 will cover NMR spectroscopy.

1.1 VIBRATIONAL EXCITATION

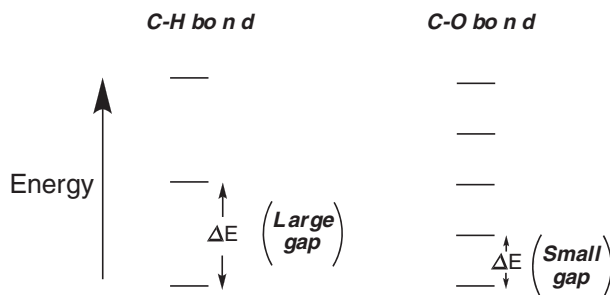
Molecules can store energy in a variety of ways. They rotate in space, their bonds vibrate like springs, their electrons can occupy a number of possible molecular orbitals, etc. According to the principles of quantum mechanics, each of these forms of energy is quantized. For example, a bond in a molecule can only vibrate at specific energy levels:



The horizontal lines in this diagram represent allowed vibrational energy levels for a particular bond. The bond is restricted to these energy levels, and cannot vibrate with an energy that is in between the allowed levels. The difference in energy (ΔE) between allowed energy levels is determined by the nature of the bond. If a photon of light possesses exactly this amount of energy, the bond (which was already vibrating) can absorb the photon to promote a *vibrational excitation*. That is, the bond will now vibrate more energetically (a larger amplitude). The energy of the photon is temporarily stored as vibrational energy, until that energy is released back into the environment, usually in the form of heat.

Bonds can store vibrational energy in a number of ways. They can *stretch*, very much the way a spring stretches, or they can *bend* in a number of ways. Your textbook will likely have images that illustrate these different kinds of vibrational excitation. In this chapter, we will devote most of our attention to stretching vibrations (as opposed to bending vibrations) because stretching vibrations generally provide the most useful information.

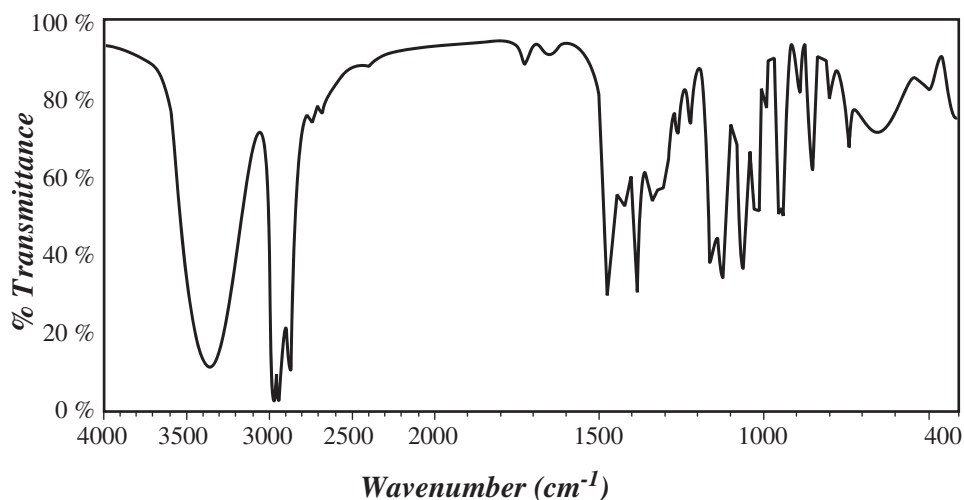
For each and every bond in a molecule, the energy gap between vibrational states is very much dependent on the nature of the bond. For example, the energy gap for a C—H bond is much larger than the energy gap for a C—O bond:



Both bonds will absorb IR radiation, but the C—H bond will absorb a higher energy photon. A similar analysis can be performed for other types of bonds as well, and we find that each type of bond will absorb a characteristic frequency, allowing us to determine which types of bonds are present in a compound. For example, a compound containing an O—H bond will absorb a frequency of IR radiation characteristic of O—H bonds. In this way, ***IR spectroscopy can be used to identify the presence of functional groups in a compound.*** It is important to realize that IR spectroscopy does NOT reveal the entire structure of a compound. It can indicate that an unknown compound is an alcohol, but to determine the entire structure of the compound, we will need NMR spectroscopy (covered in the next chapter). For now, we are simply focusing on identifying which functional groups are present in an unknown compound. To get this information, we simply irradiate the compound with all frequencies of IR radiation, and then detect which frequencies were absorbed. This can be achieved with an IR spectrometer, which measures absorption as a function of frequency. The resulting plot is called an IR absorption spectrum (or IR spectrum, for short).

1.2 IR SPECTRA

An example of an IR spectrum is shown below:

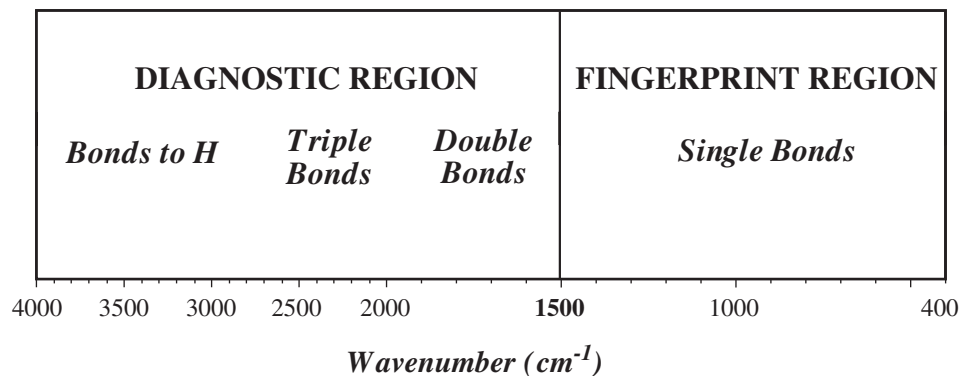


Notice that all signals point down in an IR spectrum. The location of each signal on the spectrum is reported in terms of a frequency-related unit, called wavenumber ($\tilde{\nu}$). The wavenumber is simply the frequency of light (ν) divided by a constant (the speed of light, c):

$$\tilde{\nu} = \frac{\nu}{c}$$

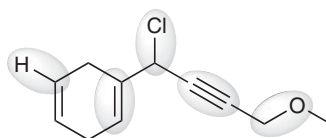
The units of wavenumber are inverse centimeters (cm^{-1}), and the values range from 400 cm^{-1} to 4000 cm^{-1} . Don't confuse the terms wavenumber and wavelength. Wavenumber is proportional to frequency, and therefore, a larger wavenumber represents higher energy. Signals that appear on the left side of the spectrum correspond with higher energy radiation, while signals on the right side of the spectrum correspond with lower energy radiation.

IR spectra can be divided into two main regions, called the diagnostic region and the fingerprint region:

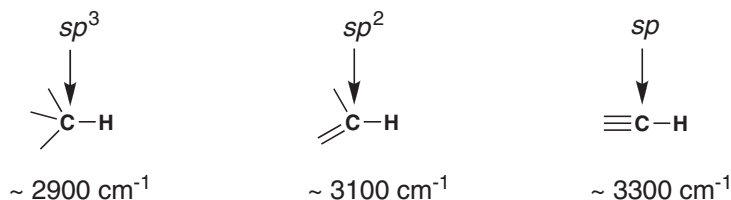


The diagnostic region generally has fewer peaks and provides the most information. This region contains all signals that arise from the stretching of double bonds, triple bonds, and X—H bonds. The fingerprint region contains mostly bending vibrations, as well as stretching vibrations of most single bonds. This region generally contains many signals, and is more difficult to analyze. What appears like a C—C stretch might in fact be another bond that is bending. This region is called the fingerprint region because each compound has a unique pattern of signals in this region, much the way each person has a unique fingerprint. For example, IR spectra of ethanol and propanol will look extremely similar in their diagnostic regions, but their fingerprint regions will look different. For the remainder of this chapter, we will focus exclusively on the signals that appear in the diagnostic region, and we will ignore signals in the fingerprint region. You should check your lecture notes and textbook to see if you are responsible for any characteristic signals that appear in the fingerprint region.

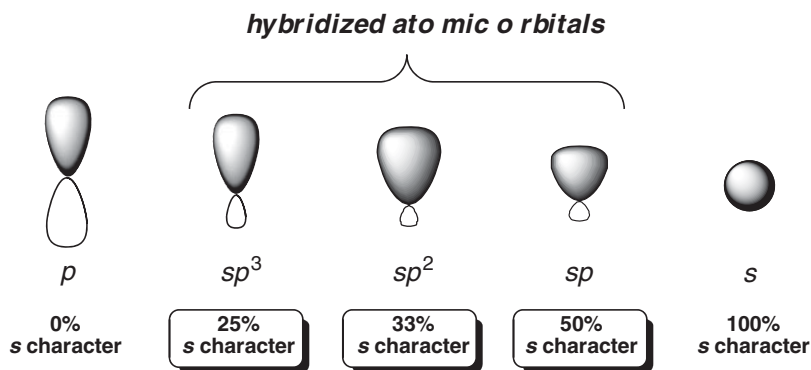
PROBLEM 1.1 For the following compound, rank the highlighted bonds in order of increasing wavenumber.



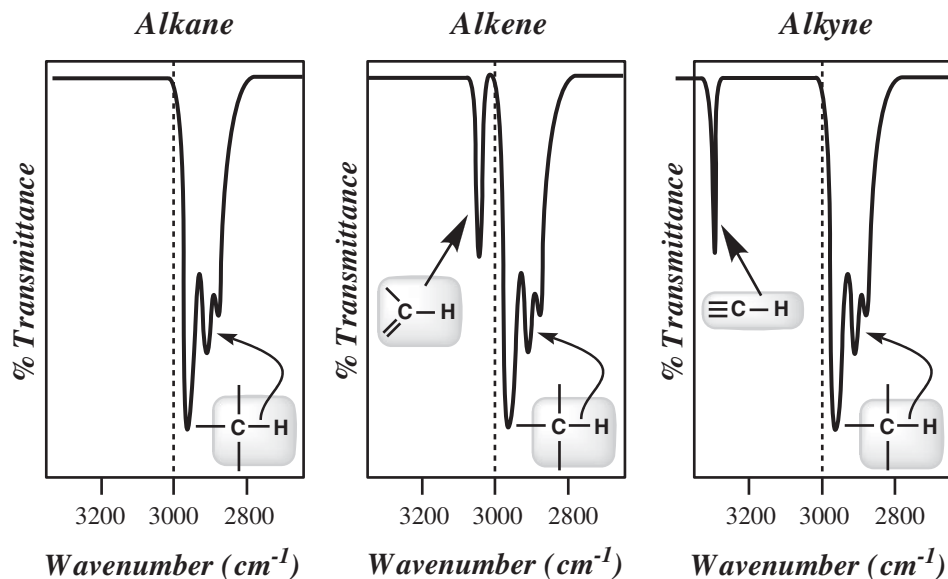
Now let's continue exploring factors that affect the strength of a bond (which therefore affects the wavenumber of absorption). We have seen that bonds to hydrogen (such as C—H bonds) appear on the left side of an IR spectrum (high wavenumber). We will now compare various kinds of C—H bonds. The wavenumber of absorption for a C—H bond is very much dependent on the hybridization state of the carbon atom. Compare the following three C—H bonds:



Of the three bonds shown, the C_{sp} —H bond produces the highest energy signal ($\sim 3300\text{ cm}^{-1}$), while a C_{sp^3} —H bond produces the lowest energy signal ($\sim 2900\text{ cm}^{-1}$). To understand this trend, we must revisit the shapes of the hybridized atomic orbitals:

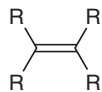


As illustrated, sp orbitals have more s character than the other hybridized atomic orbitals, and therefore, sp orbitals more closely resemble s orbitals. Compare the shapes of the hybridized atomic orbitals, and note that the electron density of an sp orbital is closest to the nucleus (much like an s orbital). As a result, a C_{sp} —H bond will be shorter than other C—H bonds. Since it has the shortest bond length, it will therefore be the strongest bond. In contrast, the C_{sp^3} —H bond has the longest bond length, and is therefore the weakest bond. Compare the spectra of an alkane, an alkene, and an alkyne:

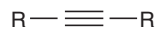


In each case, we draw a line at 3000 cm^{-1} . All three spectra have signals to the right of the line, resulting from C_{sp^3} —H bonds. The key is to look for any signals to the left of the line. An alkane does not have a signal to the left of 3000 cm^{-1} . An alkene has a signal at 3100 cm^{-1} , and an alkyne has a signal at 3300 cm^{-1} . But be careful—the absence of a signal to the left of 3000 cm^{-1} does

not necessarily indicate the absence of a double bond or triple bond in the compound. Tetrasubstituted double bonds do not possess any $C_{sp^2}-H$ bonds, and internal triple bonds also do not possess any $C_{sp}-H$ bonds.

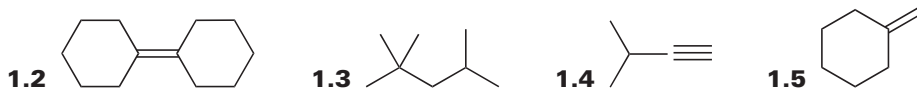


no signal at 300 cm^{-1}
(no $C_{sp^2}-H$)

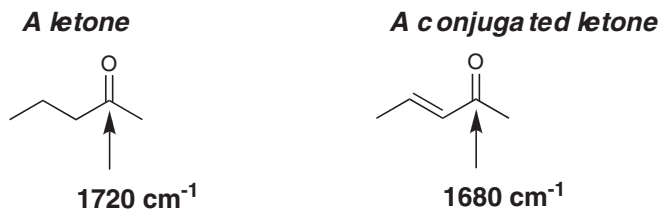


no signal at 300 cm^{-1}
(no $C_{sp}-H$)

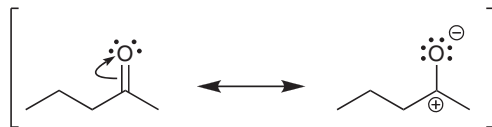
PROBLEMS For each of the following compounds, determine whether or not you would expect its IR spectrum to exhibit a signal to the left of 3000 cm^{-1}



Now let's explore the effects of resonance on bond strength. As an illustration, compare the carbonyl groups ($C=O$ bonds) in the following two compounds:



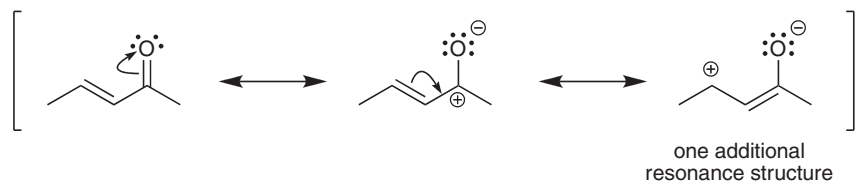
The second compound is called an unsaturated, conjugated ketone. It is *unsaturated* because of the presence of a $C=C$ bond, and it is *conjugated* because the π bonds are separated from each other by exactly one single bond. Your textbook will explore conjugated π systems in more detail. For now, we will just analyze the effect of conjugation on the IR absorption of the carbonyl group. As shown, the carbonyl group of an unsaturated, conjugated ketone produces a signal at lower wavenumber (1680 cm^{-1}) than the carbonyl group of a saturated ketone (1720 cm^{-1}). In order to understand why, we must draw resonance structures for each compound. Let's begin with the ketone.



Ketones have two resonance structures. The carbonyl group is drawn as a double bond in the first resonance structure, and it is drawn as a single bond in the second resonance structure. This means

that the carbonyl group has some double-bond character and some single-bond character. In order to determine the nature of this bond, we must consider the contribution from each resonance structure. In other words, does the carbonyl group have more double-bond character or more single-bond character? The second resonance structure exhibits charge separation, as well as a carbon atom (C^+) that has less than an octet of electrons. Both of these reasons explain why the second resonance structure contributes only slightly to the overall character of the carbonyl group. Therefore, the carbonyl group of a ketone has mostly double-bond character.

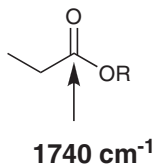
Now consider the resonance structures for a conjugated, unsaturated ketone.



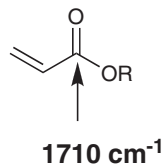
Conjugated, unsaturated ketones have three resonance structures rather than two. In the third resonance structure, the carbonyl group is drawn as a single bond. Once again, this resonance structure exhibits charge separation as well as a carbon atom (C^+) with less than an octet of electrons. As a result, this resonance structure also contributes only slightly to the overall character of the compound. Nevertheless, this third resonance structure does contribute some character, giving this carbonyl group slightly more single-bond character than the carbonyl group of a saturated ketone. With more single-bond character, it is a slightly weaker bond, and therefore produces a signal at a lower wavenumber (1680 cm^{-1} rather than 1720 cm^{-1}).

Esters exhibit a similar trend. An ester typically produces a signal at around 1740 cm^{-1} , but conjugated, unsaturated esters produce lower energy signals, usually around 1710 cm^{-1} . Once again, the carbonyl group of a conjugated, unsaturated ester is a weaker bond, due to resonance.

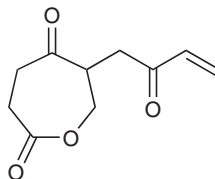
An ester



A conjugated, unsaturated ester

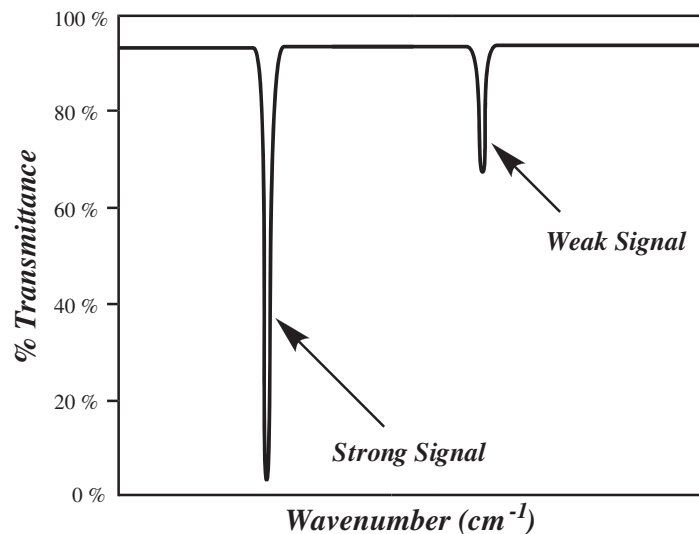


PROBLEM 1.6 The following compound has three carbonyl groups. Rank them in order of increasing wavenumber in an IR spectrum:



1.4 SIGNAL INTENSITY

In an IR spectrum, some signals will be very strong in comparison with other signals on the same spectrum:

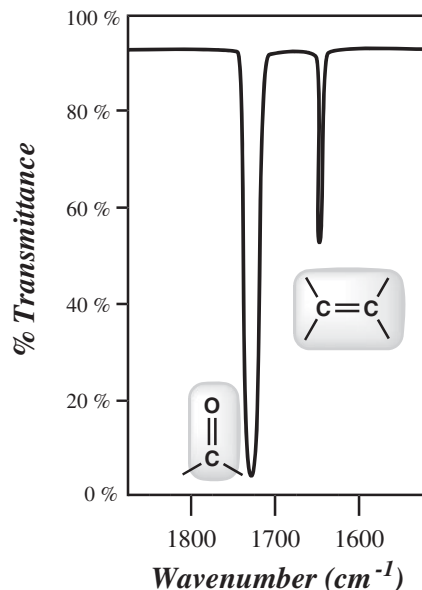


That is, some bonds absorb IR radiation very efficiently, while other bonds are less efficient at absorbing IR radiation. The efficiency of a bond at absorbing IR radiation depends on the strength of the dipole moment for that bond. For example, compare the following two highlighted bonds:

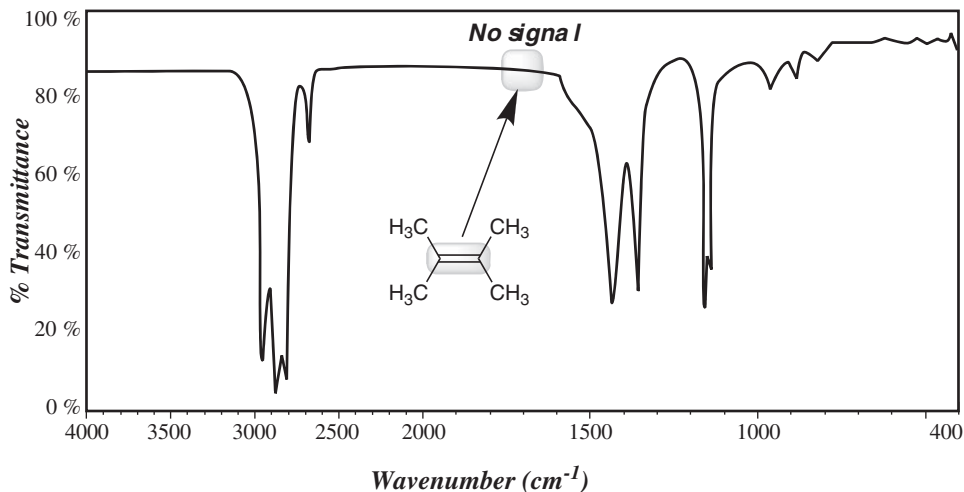


Each of these bonds has a measurable dipole moment, but they differ significantly in strength. Let's first analyze the carbonyl group (C=O bond). Due to resonance and induction, the carbon atom bears a large partial positive charge, and the oxygen atom bears a large partial negative charge. The carbonyl group therefore has a large dipole moment. Now let's analyze the C=C bond. One vinylic position is connected to electron-donating alkyl groups, while the other vinylic position is connected to hydrogen atoms. As a result, the vinylic position bearing two alkyl groups is slightly more electron-rich than the other vinylic position, producing a small dipole moment.

Since the carbonyl group has a larger dipole moment, the carbonyl group is more efficient at absorbing IR radiation, producing a stronger signal:



Carbonyl groups often produce the strongest signals in an IR spectrum, while C=C bonds often produce fairly weak signals. In fact, some alkenes do not even produce any signal at all. For example, consider the IR spectrum of 2,3-dimethyl-2-butene:



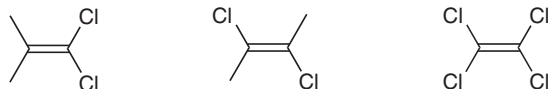
This alkene is symmetrical. That is, both vinylic positions are electronically identical, and the bond has no dipole moment at all. As such, this C=C bond is completely inefficient at absorbing IR radiation, and no signal is observed. The same is true for symmetrical C≡C bonds.

There is one other factor that can contribute significantly to the intensity of signals in an IR spectrum. Consider the group of signals appearing just below 3000 cm⁻¹ in the previous spectrum. These signals are associated with the stretching of the C—H bonds in the compound. The intensity

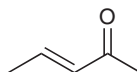
of these signals derives from the number of C—H bonds giving rise to the signals. In fact, the signals just below 3000 cm^{-1} are typically among the strongest signals in an IR spectrum.

PROBLEMS

1.7 Predict which of the following C=C bonds will produce the strongest signal in an IR spectrum:

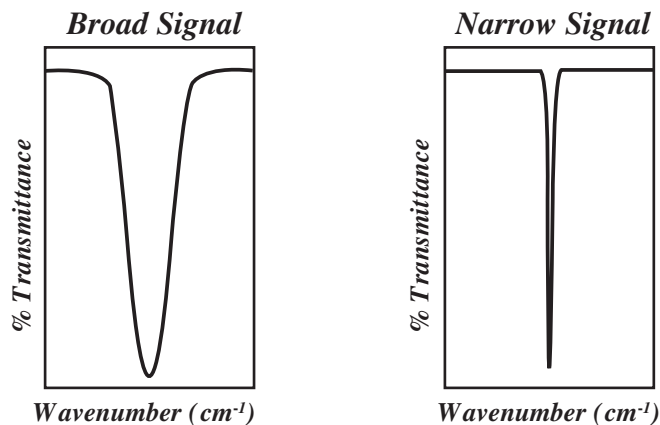


1.8 The C=C bond in the following compound produces an unusually strong signal. Explain using resonance structures:

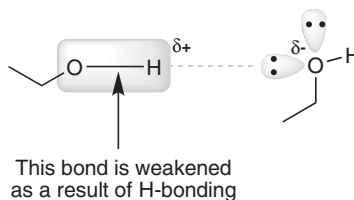


1.5 SIGNAL SHAPE

In this section, we will explore some of the factors that affect the shape of a signal. Some signals in an IR spectrum might be very broad while other signals can be very narrow:



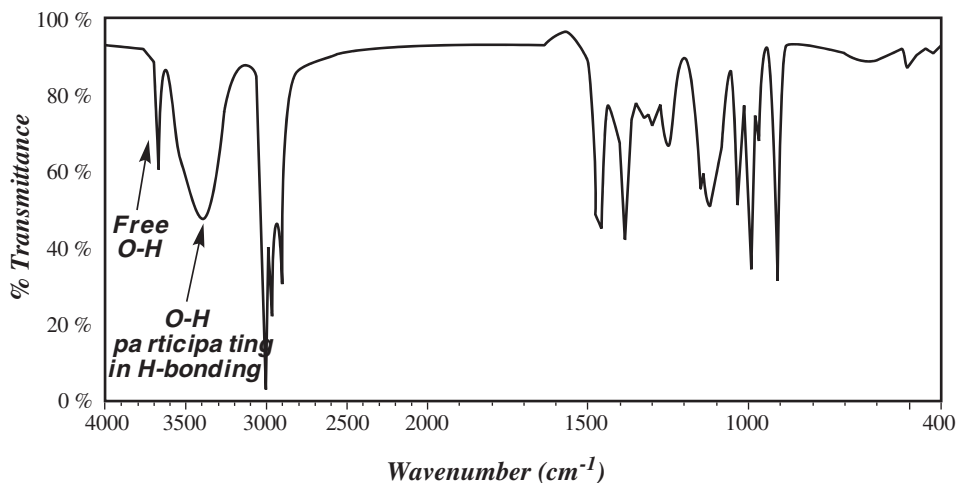
Concentrated alcohols commonly exhibit broad O—H signals, as a result of hydrogen bonding, which weakens the O—H bonds.



At any given moment in time, the O—H bond in each molecule is weakened to a different extent. As a result, all of the O—H bonds do not have a uniform bond strength, but rather, there is

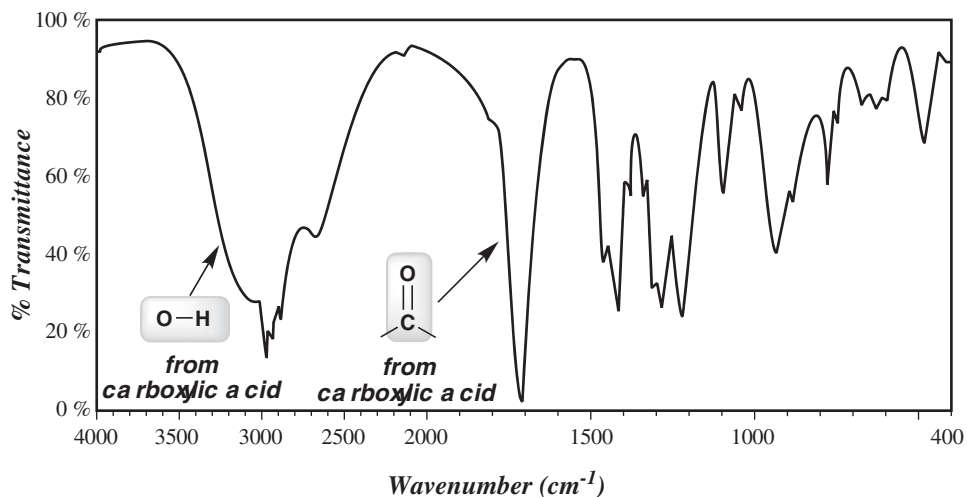
a *distribution* of bond strength. That is, some molecules are barely participating in H-bonding, while others are participating in H-bonding to varying degrees. The result is a broad signal.

The shape of an O—H signal is different when the alcohol is diluted in a solvent that cannot form hydrogen bonds with the alcohol. In such an environment, it is likely that the O—H bonds will not participate in an H-bonding interaction. The result is a narrow signal. When the solution is neither very concentrated nor very dilute, two signals are observed. The molecules that are not participating in H-bonding will give rise to a narrow signal, while the molecules participating in H-bonding will give rise to a broad signal. As an example, consider the following spectrum of 2-butanol, in which both signals can be observed:

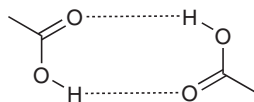


When O—H bonds do not participate in H-bonding, they generally produce a signal at approximately 3600 cm^{-1} . That signal can be seen in the spectrum above. When O—H bonds participate in H bonding, they generally produce a broad signal between 3200 cm^{-1} and 3600 cm^{-1} . That signal can also be seen in the spectrum. Depending on the conditions, an alcohol will either give a broad signal, or a narrow signal, or both.

Carboxylic acids exhibit similar behavior; only more pronounced. For example, consider the following spectrum of a carboxylic acid:

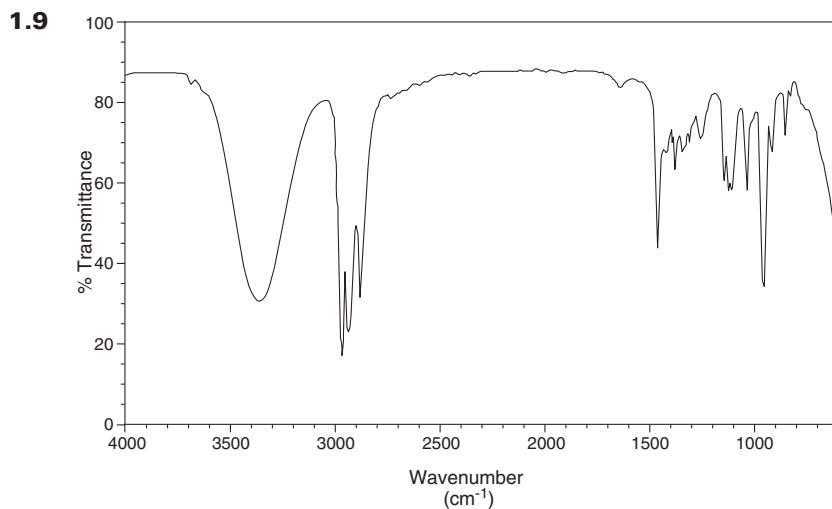


Notice the very broad signal on the left side of the spectrum, extending from 2200 cm^{-1} to 3600 cm^{-1} . This signal is so broad that it extends over the usual C—H signals that appear around 2900 cm^{-1} . This very broad signal, characteristic of carboxylic acids, is a result of H bonding. The effect is more pronounced than alcohols, because molecules of the carboxylic acid can form two hydrogen-bonding interactions, resulting in a dimer.

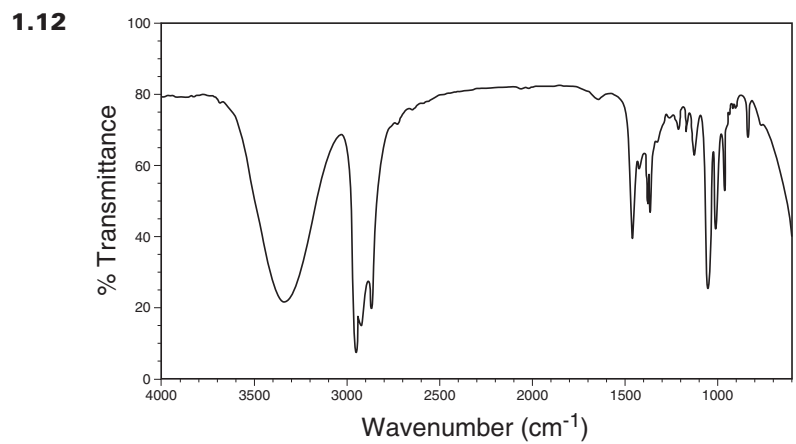
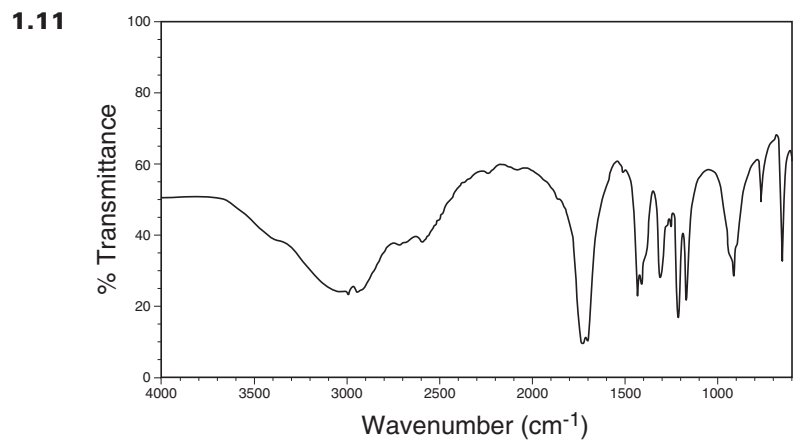
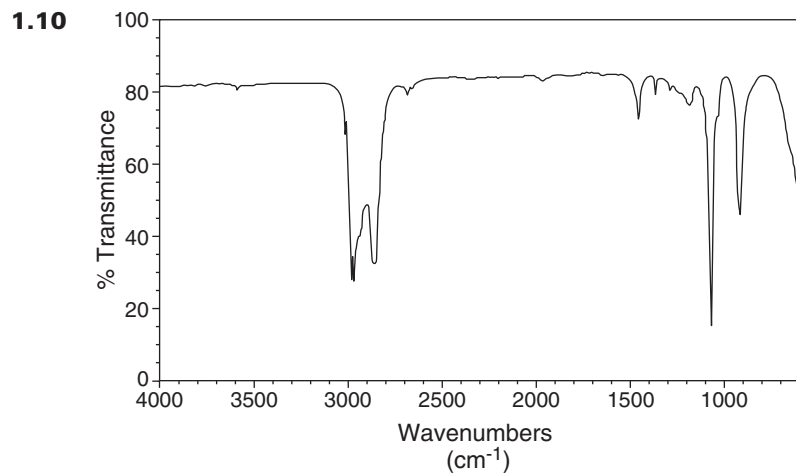


The IR spectrum of a carboxylic acid is easy to recognize, because of the characteristic broad signal that covers nearly one third of the spectrum. This broad signal is also accompanied by a broad C=O signal just above 1700 cm^{-1} .

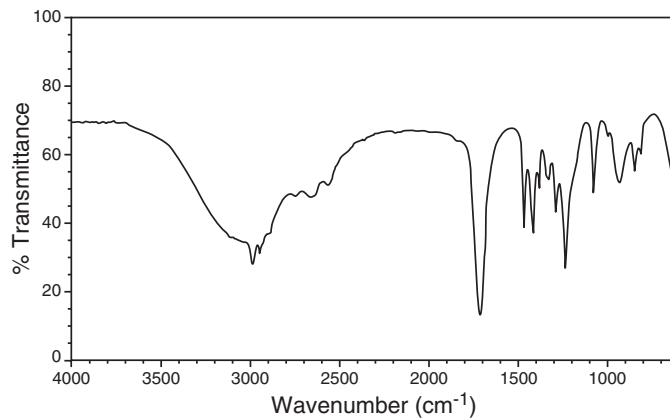
PROBLEMS For each IR spectrum below, identify whether it is consistent with the structure of an alcohol, a carboxylic acid, or neither.



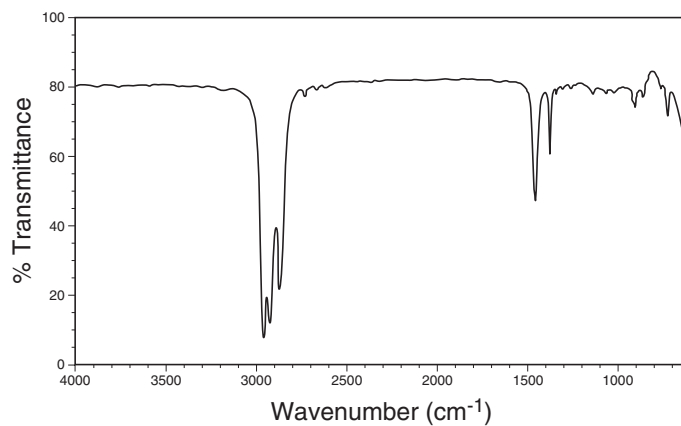
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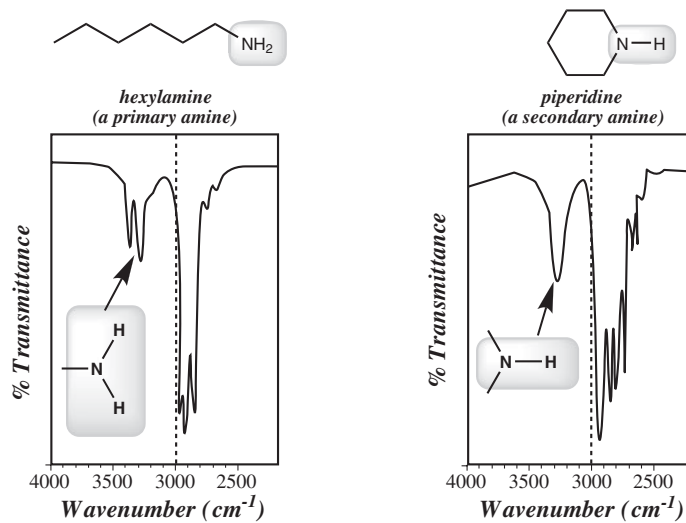
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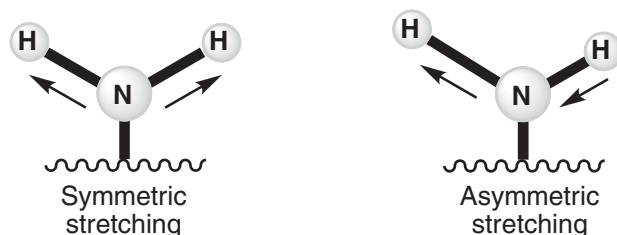
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There is another important factor in addition to H bonding that affects the shape of a signal. Consider the difference in shape of the N—H signals for primary and secondary amines:



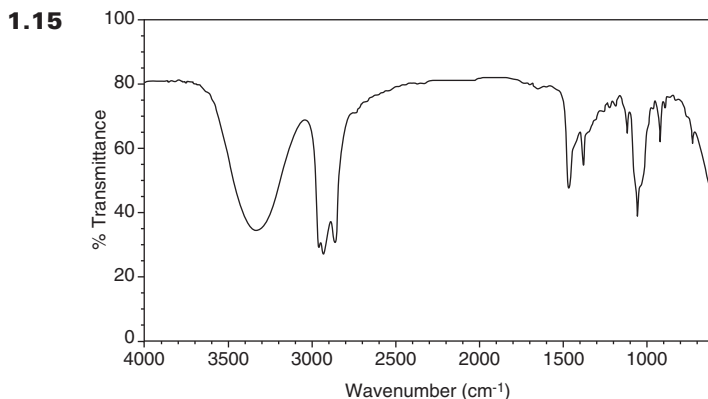
The primary amine exhibits two signals; one at 3350 cm^{-1} and the other at 3450 cm^{-1} . In contrast, the secondary amine exhibits only one signal. It might be tempting to explain this by arguing that each N—H bond gives rise to a signal, and therefore a primary amine gives two signals because it has two N—H bonds. Unfortunately, that simple explanation is not accurate. In fact, both N—H bonds of a single molecule will together produce only one signal. The reason for the appearance of two signals is more accurately explained by considering the two possible ways in which the entire NH_2 group can vibrate. The N—H bonds can be stretching in phase with each other, called *symmetric stretching*, or they can be stretching out of phase with each other, called *asymmetric stretching*:

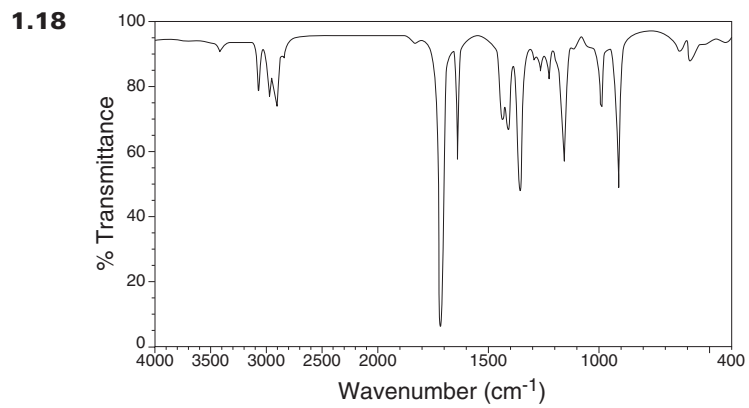
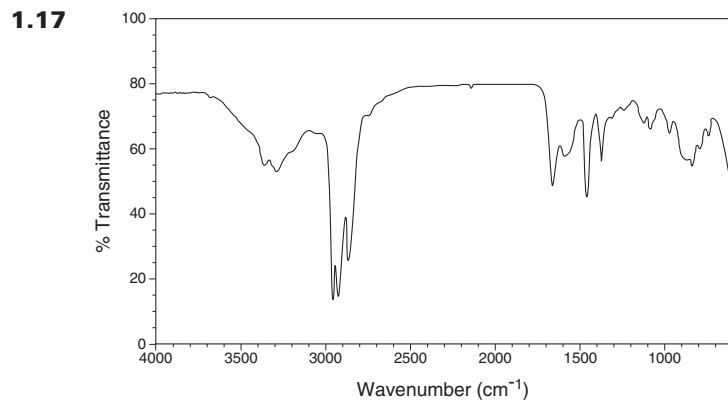
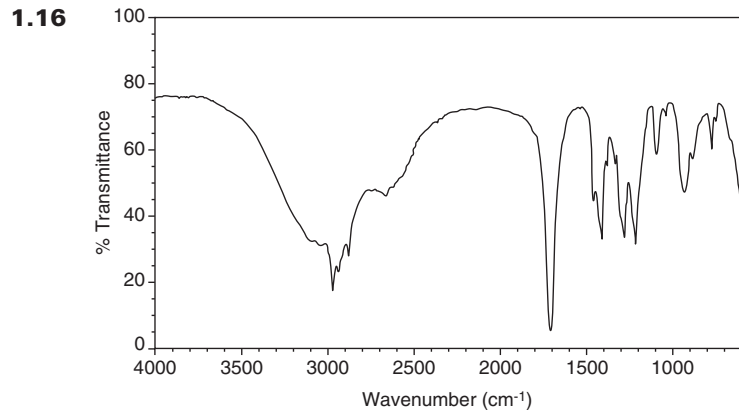


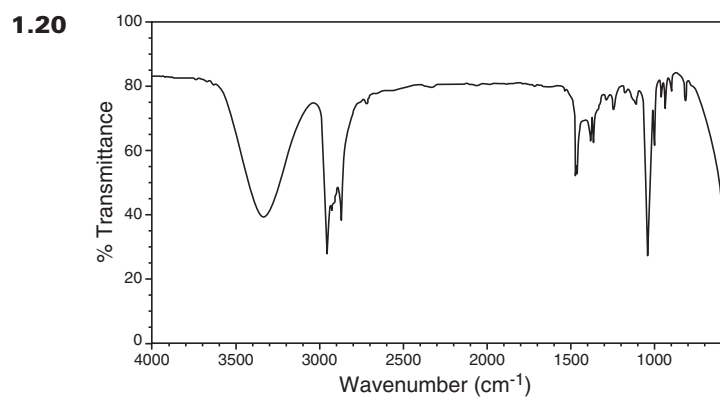
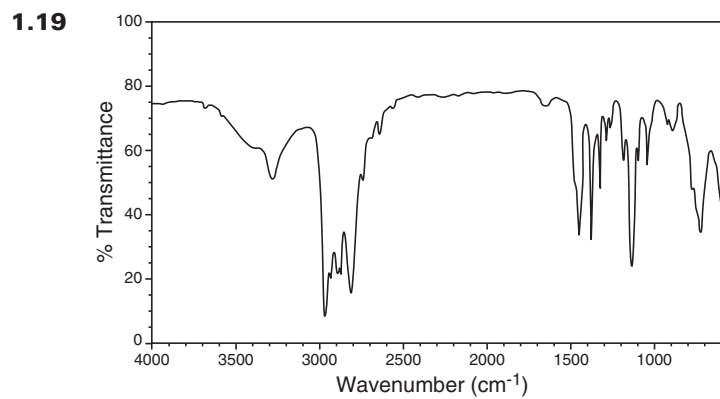
At any given moment in time, approximately half of the molecules will be vibrating symmetrically, while the other half will be vibrating asymmetrically. The molecules vibrating symmetrically will absorb a particular frequency of IR radiation to promote a vibrational excitation, while the molecules vibrating asymmetrically will absorb a different frequency. In other words, one of the signals is produced by half of the molecules, and the other signal is produced by the other half of the molecules.

For a similar reason, the C—H bonds of a CH_3 group (appearing just below 3000 cm^{-1} in an IR spectrum) generally give rise to a series of signals, rather than just one signal. These signals arise from the various ways in which a CH_3 group can be excited.

PROBLEMS For each IR spectrum below, determine whether it is consistent with the structure of a ketone, an alcohol, a carboxylic acid, a primary amine, or a secondary amine.




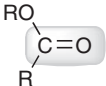

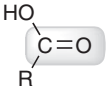



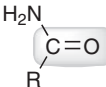
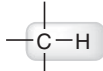


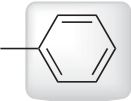

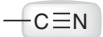






1.6 ANALYZING AN IR SPECTRUM

The following table is a summary of useful signals in the diagnostic region of an IR spectrum:

<i>Useful Signals in the Diagnostic Region</i>			
<u>Structural Unit</u>	<u>Wavenumber (cm⁻¹)</u>	<u>Structural Unit</u>	<u>Wavenumber (cm⁻¹)</u>
<i>Single Bonds (X-H)</i>		<i>Double Bonds</i>	
	3200 - 3600		1750 - 1850
	2200 - 3600		1700 - 1750
	3350 - 3500		1700 - 1750
	~ 3300		1680 - 1750
	3000 - 3100		1650 - 1700
	2850 - 3000		1600 - 1700
	2750 - 2850		1450 - 1600 1650 - 2000
<i>Triple Bonds</i>			
	2100 - 2200		
	2200 - 2300		

When analyzing an IR spectrum, the first step is to draw a line at 1500 cm^{-1} . Focus on any signals to the left of this line (the diagnostic region). In doing so, it will be extremely helpful if you can identify the following regions:

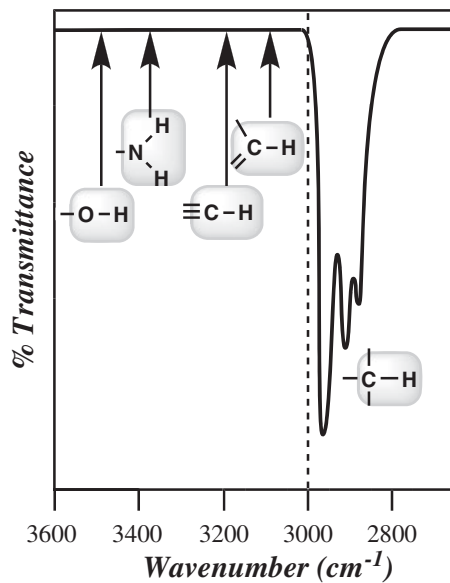
Double bonds: $1600\text{--}1850\text{ cm}^{-1}$

Triple bonds: $2100\text{--}2300\text{ cm}^{-1}$

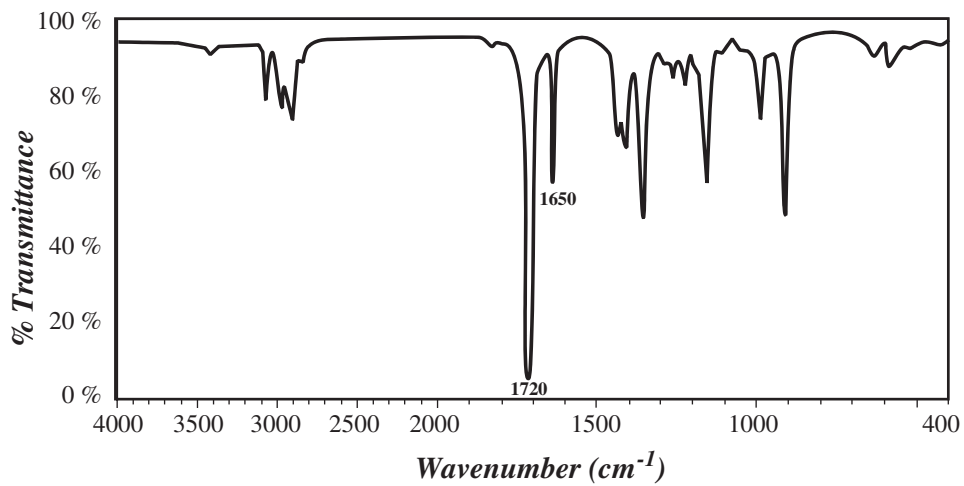
X—H bonds: $2700\text{--}4000\text{ cm}^{-1}$

Remember that each signal appearing in the diagnostic region will have three characteristics (wavenumber, intensity, and shape). Make sure to analyze all three characteristics.

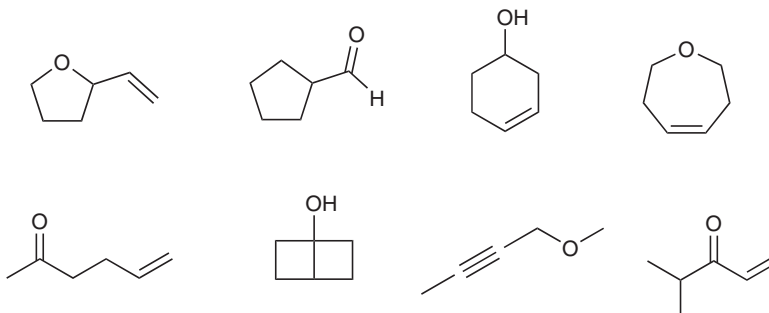
When looking for X—H bonds, draw a line at 3000 cm^{-1} and look for signals that appear to the left of the line:



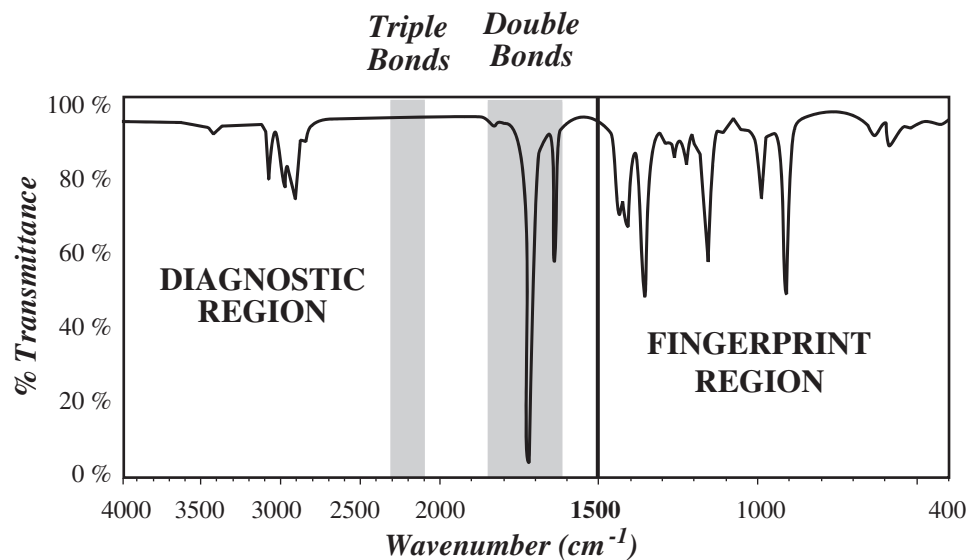
EXERCISE 1.21 A compound with molecular formula $\text{C}_6\text{H}_{10}\text{O}$ gives the following IR spectrum:



Identify the structure below that is most consistent with the spectrum:

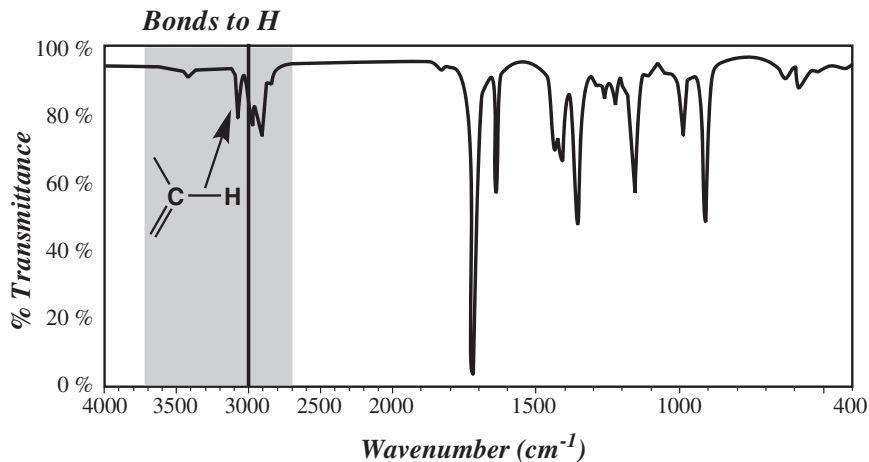


Solution Draw a line at 1500 cm^{-1} , and focus on the diagnostic region (to the left of the line). Start by looking at the double-bond region and the triple-bond region:



There are no signals in the triple-bond region, but there are two signals in the double-bond region. The signal at 1650 cm^{-1} is narrow and weak, consistent with a $\text{C}=\text{C}$ bond. The signal at 1720 cm^{-1} is strong, consistent with a $\text{C}=\text{O}$ bond.

Next, look for $\text{X}-\text{H}$ bonds. Draw a line at 3000 cm^{-1} , and identify if there are any signals to the left of this line.



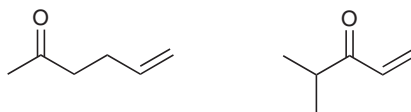
This spectrum exhibits one signal just above 3000 cm^{-1} , indicating a vinylic C—H bond.



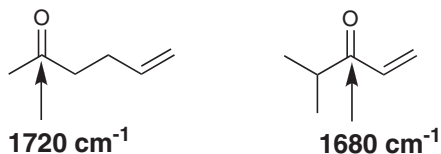
The identification of a vinylic C—H bond is consistent with the observed C=C signal present in the double-bond region (1650 cm^{-1}). There are no other signals above 3000 cm^{-1} , so the compound does not possess any OH or NH bonds.

The little bump between 3400 and 3500 cm^{-1} is not strong enough to be considered a signal. These bumps are often observed in the spectra of compounds containing a C=O bond. The bump occurs at exactly twice the wavenumber of the C=O signal, and is called an overtone of the C=O signal.

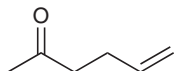
The diagnostic region provides the information necessary to solve this problem. Specifically, the compound must have the following bonds: C=C, C=O, and vinylic C—H. Among the possible choices, there are only two compounds that have these features:



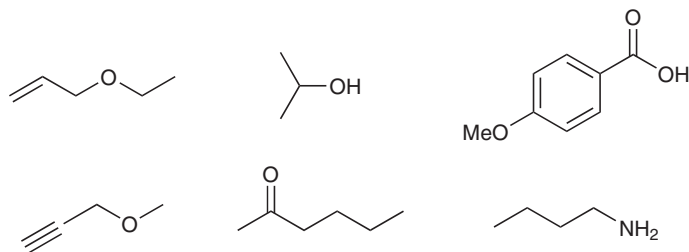
To distinguish between these two possibilities, notice that the second compound is conjugated, while the first compound is *not* conjugated (the π bonds are separated by more than one single bond). Recall that ketones produce signals at approximately 1720 cm^{-1} , while conjugated ketones produce signals at approximately 1680 cm^{-1} .



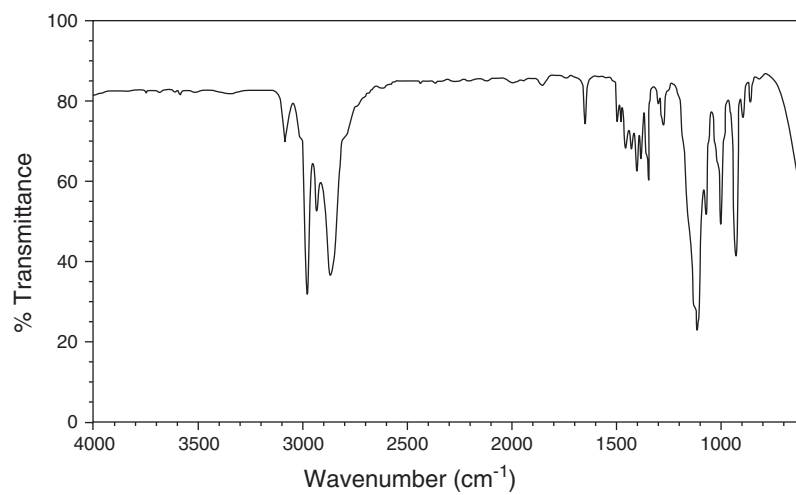
In the spectrum provided, the C=O signal appears at 1720 cm^{-1} , indicating that it is not conjugated. The spectrum is therefore consistent with the following compound:



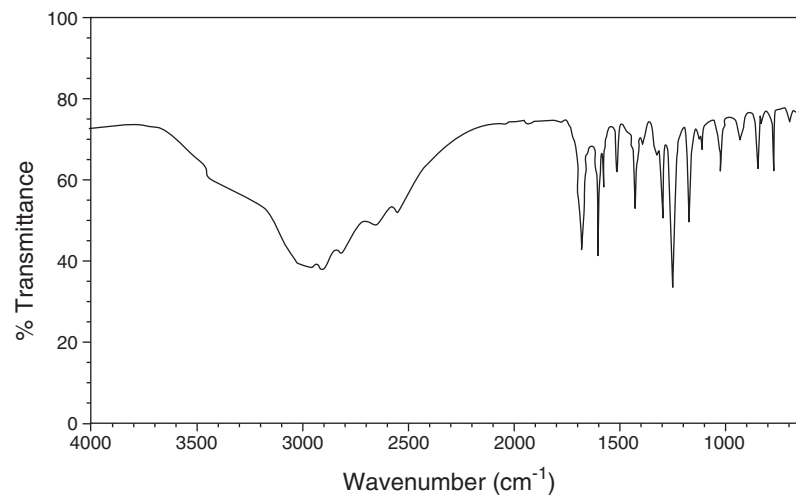
PROBLEM 1.22 Match each compound with the appropriate spectrum



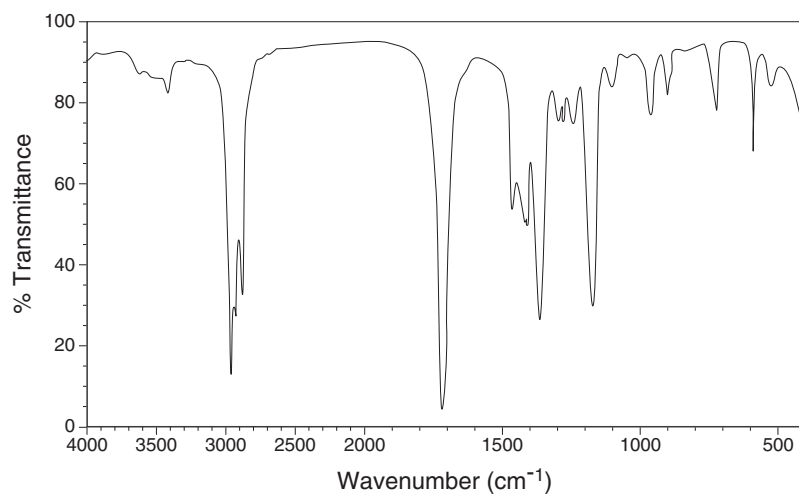
Spectrum A



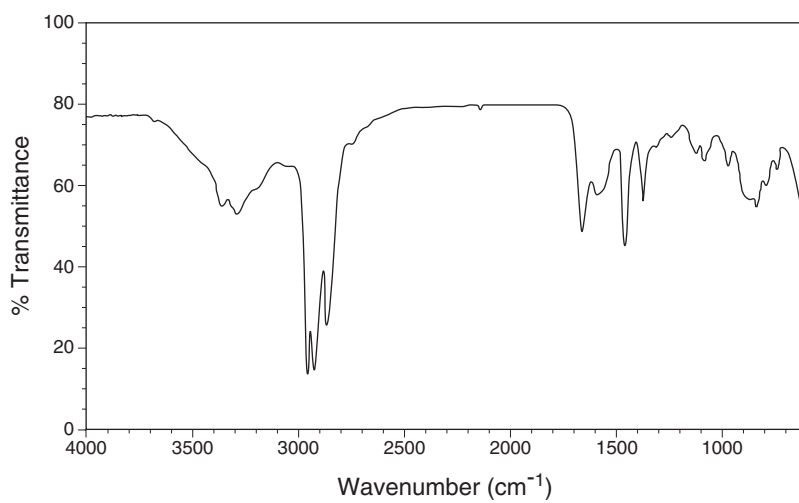
Spectrum B



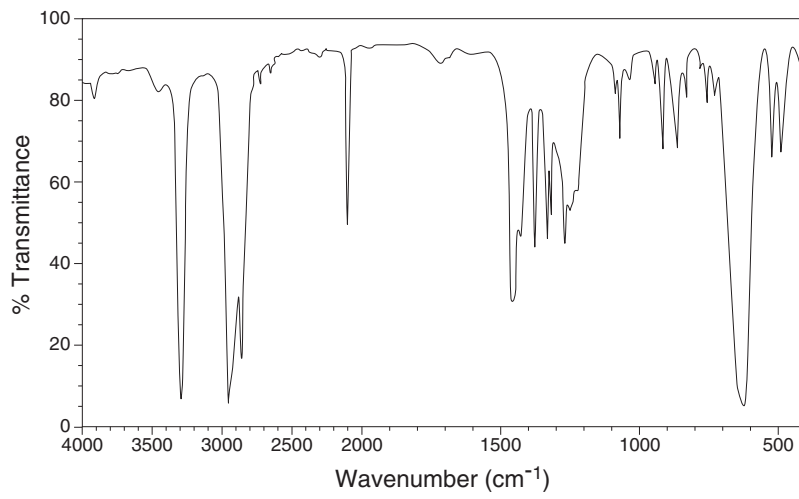
Spectrum C



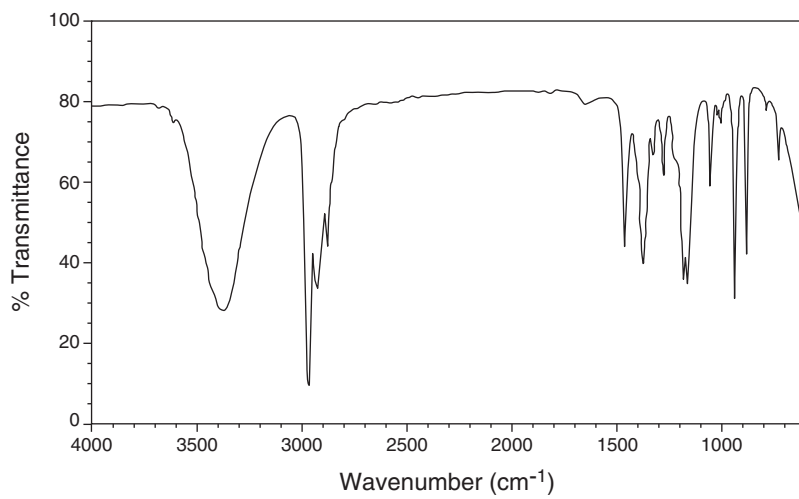
Spectrum D



Spectrum E



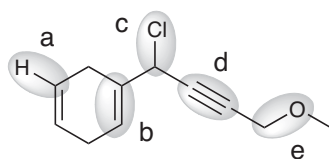
Spectrum F



ANSWERS

CHAPTER 1

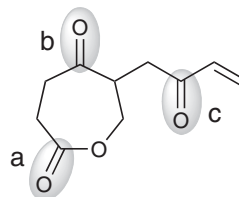
1.1)



1.2) No

1.4) Yes

1.6)



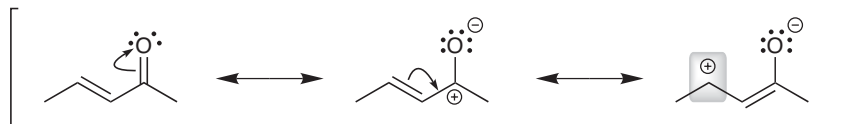
1.3) No

1.5) Yes

1.7)



1.8) Consider the third resonance structure, shown below. This resonance structure has a positive charge, indicating that the highlighted carbon atom is electron-poor. As a result, the C=C bond has an unusually strong dipole moment, leading to an unusually strong signal in IR spectroscopy.



1.9) Alcohol

1.10) Neither

1.11) Carboxylic acid

1.12) Alcohol

1.13) Carboxylic acid

1.14) Neither

1.15) Alcohol

1.16) Carboxylic acid

1.17) Primary amine

1.18) Ketone (the little blip at 3400 can be ignored. See exercise 1.21 for an explanation)

1.19) Secondary amine

1.20) Alcohol

1.21)

