

Modern Techniques in Chemistry: Infrared Spectroscopy

Spectroscopy is a method analysis based on the interaction of electromagnetic radiation and matter. Modern experimental chemistry uses many spectroscopic techniques, among them ultraviolet and visible spectroscopy, infrared spectroscopy, and nuclear magnetic resonance spectroscopy, and electron spin resonance spectroscopy. All depend in some manner on the absorption of energy by a collection of molecules, the energy involved being in different regions of the electromagnetic spectrum. In this experiment we shall use infrared spectroscopy in various ways.

Infrared spectroscopy is widely used by chemists and forensic scientists as it is a well developed technique to identify chemical compounds or monitor changes occurring in the course of a chemical reaction. For example, the spectra of two related molecules, 1-propanol (an alcohol), and propanoic acid (a carboxylic acid) are given on page 2. Their spectra are considerably different in the 3000-3500 and 1600-1800 wavenumber regions, and there are less prominent differences in the region less than 1500 wavenumbers. In this experiment you will learn how to tell what important features a molecule has by looking at its infrared spectrum.

INTRODUCTION TO INFRARED SPECTROSCOPY

Basic Principles

Except at very, very low temperatures, all molecules are in motion in some manner. Molecules *translate* (move from place to place), they *rotate* in space, and, importantly for this experiment, they *vibrate*. In the case of the triatomic, bent molecule SO_2 , the seemingly random vibrations of the molecule can actually be broken down into three so-called “normal modes” of vibration (*Figure 1*). These normal modes are a bending of the molecule and two stretching motions. In the bending motion, the O atoms wag in and out. In one stretch-

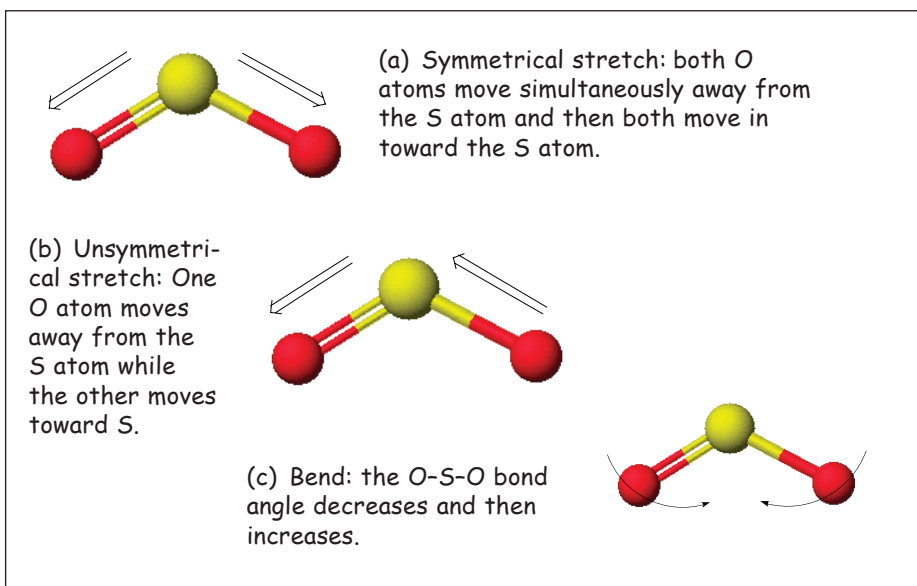
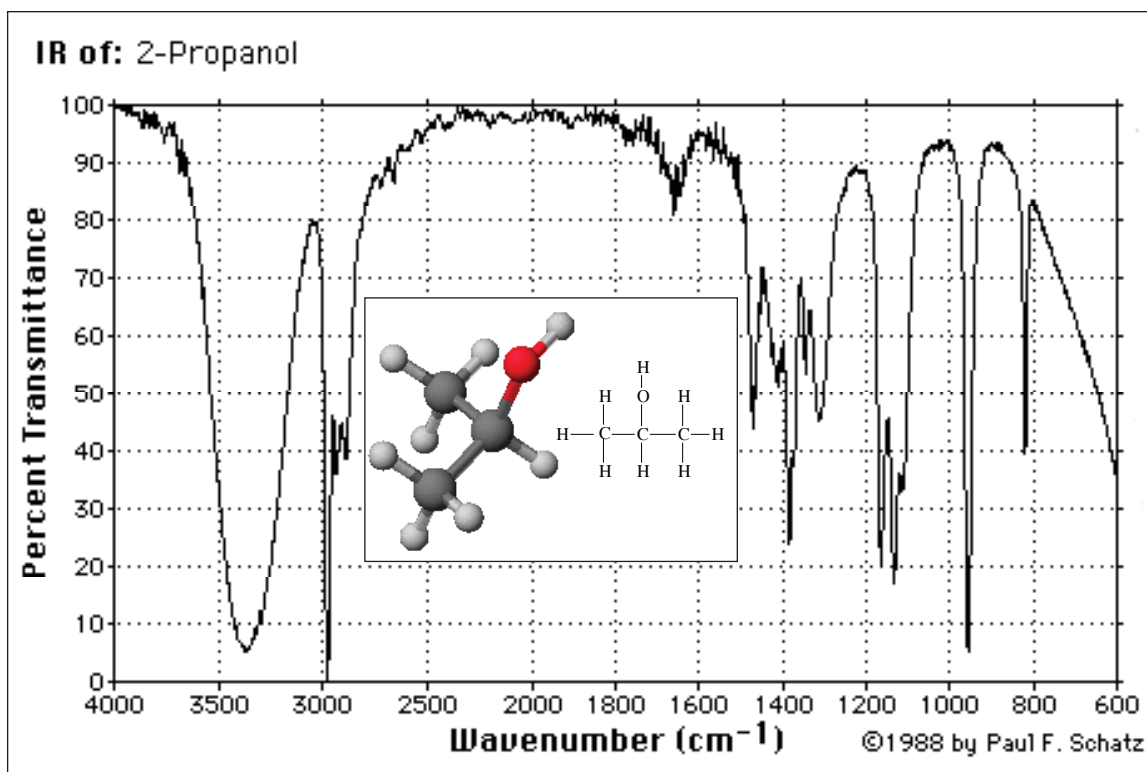
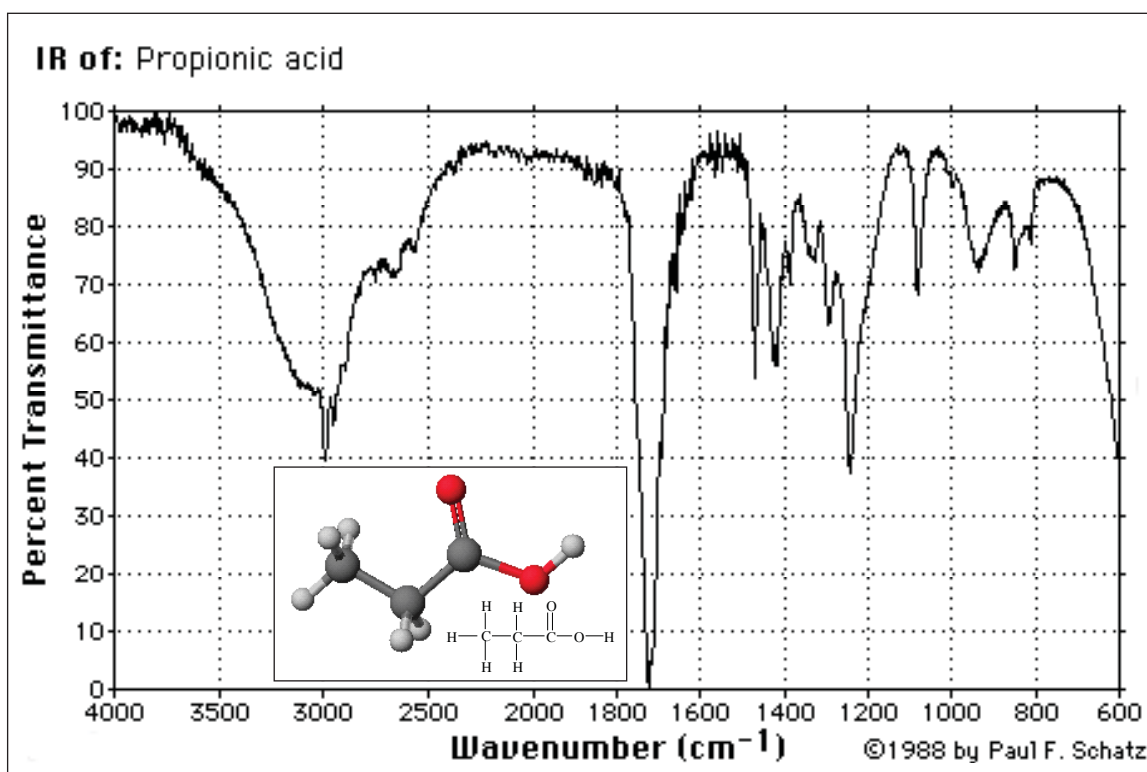


Figure 1 The three normal modes of SO_2 . See the calculated spectrum of SO_2 in *Figure 2* on page 95.

Cooking food in a microwave “oven” is closely related to the various forms of spectroscopy. In a microwave, molecules of water absorb energy in the microwave region of the spectrum. The molecules are “excited” to a higher energy. They ultimately pass that energy on to the medium in which they are found, the food product.



The infrared spectra of two common organic molecules, 2-propanol and propanoic acid.



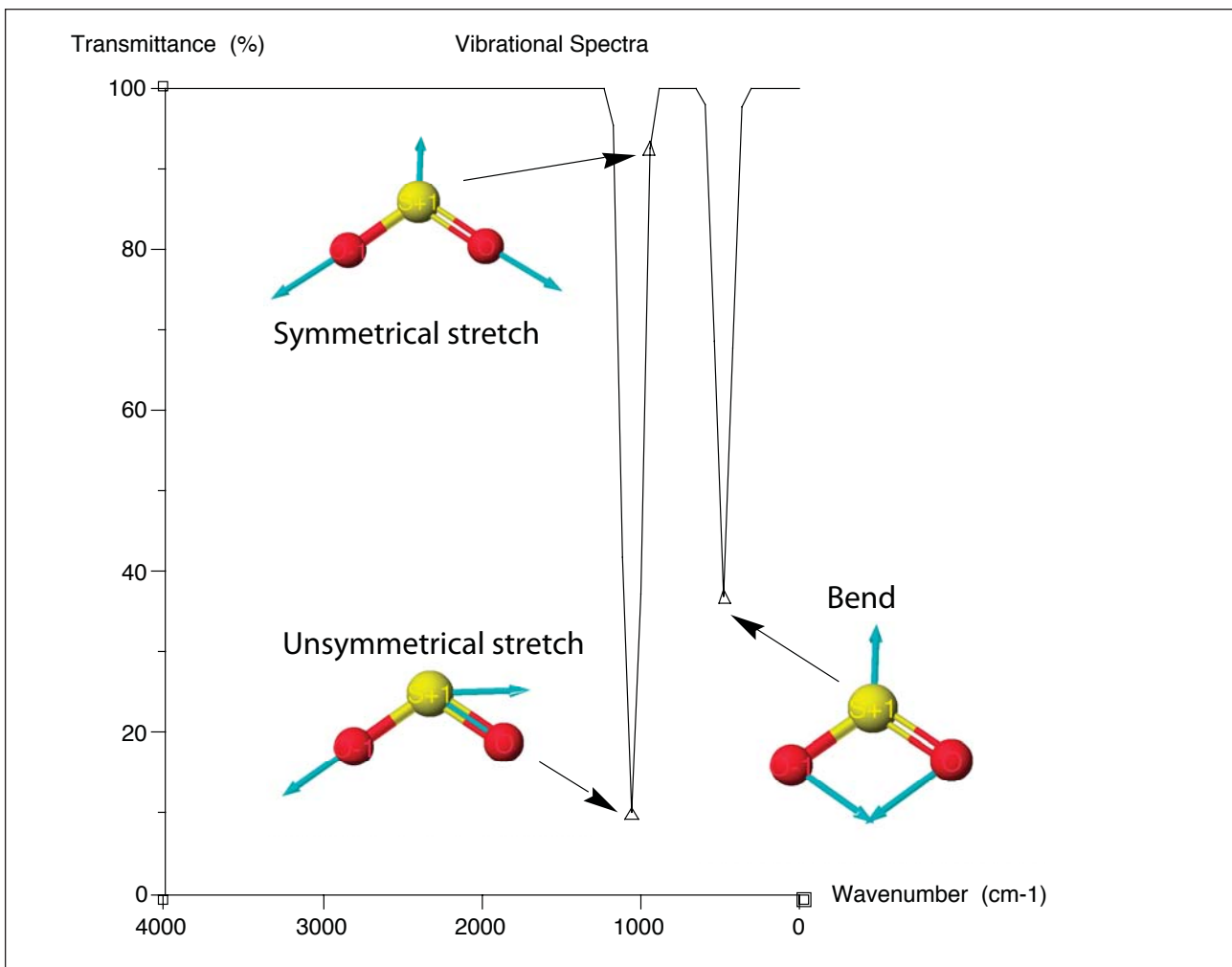


Figure 2. Calculated infrared spectrum of SO_2 gas. Notice that the stretching vibrations are at a higher energy than the bending vibration.

This spectrum is not the actual spectrum of SO_2 but it was calculated using the CAChe Worksystem software. If a model, for which the spectrum has been calculated, is opened, one can observe the calculated spectrum on a Macintosh computer by going to the menu item ANALYZE and choosing VIBRATIONAL SPECTRA. Click on a band in the spectrum (denoted by a \blacktriangle) and arrows appear on the model showing the movement of atoms in the course of the vibration. (In this figure the models have been added to the spectrum as it appears on the computer.)

ing motion, the two O atoms move symmetrically in and out relative to the S atom, whereas in the other motion the two O atoms move unsymmetrically in and out. That is, as one moves out the other moves in, and vice versa. Bending and stretching motions occur in all molecules. The only difference is that more complex molecules have many more bending and stretching motions.

The energy of infrared radiation is sufficient to change the vibrational energy states of a molecule. If the dipole moment of a molecule changes as it vibrates, infrared radiation can interact with the molecule. When the frequency of the radiation matches the frequency of a particular vibration, energy is transferred to the molecule, increasing the amplitude of the vibration. One

The requirement that there must be a change in the dipole moment of the molecule for it to interact with infrared radiation is met by a change either in the size of the dipole moment or in its location.

observes the transfer of energy because light equal in energy to the molecular vibration is absorbed from the beam of incident infrared light. In *Figure 2* you see a *calculated* spectrum of SO₂. Here we have plotted energy on the horizontal axis and the percent of light transmitted along the vertical axis. As the energy of the radiation becomes less and less, light is absorbed by the unsymmetrical stretch. You observe this as an absorption band. At still lower energies we see first light absorbed by the symmetrical stretch and then by the bending motion.

With these ideas in mind, we have at least two things to explore:

- The energies involved in infrared spectra and their units
- Characteristic patterns in infrared spectra

The Energies and Frequencies of Molecular Vibrations

The frequency of vibrations is obtained from Hooke's law,

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

where ν is the vibrational frequency (in wavenumbers, cm⁻¹), μ is the reduced mass of atoms in the bond (in grams), c is the velocity of light (2.998 × 10¹⁰ cm•s⁻¹), and k is the force constant of the bond (in dyne•cm⁻¹). Let us look at each part of the equation:

a) Frequency:

Recall that the energy of electromagnetic radiation is proportional to frequency ($E = h\nu$) and that frequency is given by

$$\text{Frequency} = \frac{\text{velocity of light (cm/sec)}}{\text{wavelength (cm)}}$$

Because the velocity of light is a constant, we recognize that the frequency is simply proportional to the reciprocal of the wavelength.

$$\text{Frequency} \propto \frac{1}{\text{wavelength (cm)}} \text{ or } (1/\text{wavelength})\text{cm}^{-1}$$

In infrared spectroscopy a typical wavelength for a vibration is 4.0 × 10⁻⁴ cm. Taking the reciprocal, we have 2500 cm⁻¹. Chemists say that this vibration has a frequency of 2500 "wavenumbers." The infrared spectra you will see will have energies in the range of 4000 cm⁻¹ to 500 cm⁻¹.

b) Reduced mass, μ :

The reduced mass is the quotient of the product of the masses of the two bonded atoms divided by their sum.

$$\text{Reduced mass} = \mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

The important point is that the energy involved in a vibration is inversely related to the masses of the atoms involved. That is, the heavier the atoms involved, the lower the energy. (You will see the effects of this in this

INTERNET RESOURCES

Courses and tutorials on infrared spectroscopy on the Internet: http://kerouac.pharm.uky.edu/asrg/cnirs/ir_spec.htm#tuts

Newton's Apple activity on IR: <http://www.ktca.org/newtons/11/infrared.html>

The Relation of Atomic Masses and Vibrational Frequency

Bond	Energy (cm ⁻¹)
H—F	4100
H—Cl	3000
H—Br	2650
H—I	2300

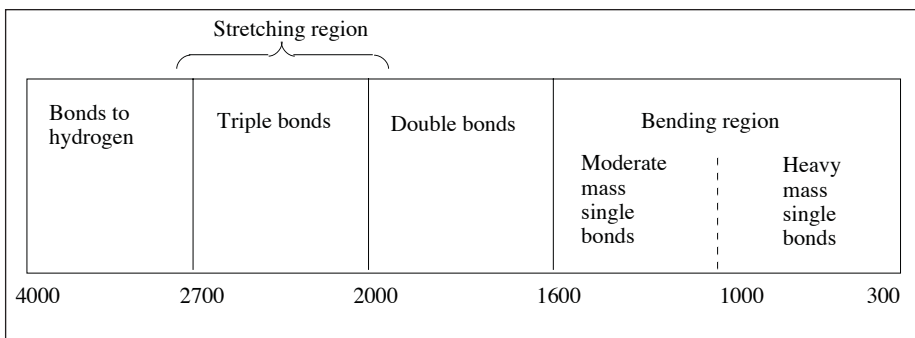


Figure 3. Characteristic wavelength regions (in wavenumbers, cm^{-1}) for different vibrations.

experiment.) In the margin is a table showing that as the masses of atoms involved in a bond increase, the energy (given in wavenumbers) declines.

c) *Force constant, k:*

The force constant, which can be thought of as a measure of bond “stiffness,” can be correlated with such bond properties as bond order and bond strength. Because the frequency is related directly to the square root of the force constant, we know that the frequency of bond vibrations should decrease as bonds decrease in strength. This trend is illustrated by the series of carbon-nitrogen bond frequencies given in the table in the margin.

The force constant, and thus the vibrational frequency, is also related to the electronegativity difference between the atoms of the bond. As the electronegativity difference increases, the bond strength increases. This means the force constant should increase, and so the vibrational frequency should also increase. This is seen in the series of bonds having an H atom attached to C, N, O, and F.

Characteristic Patterns in Infrared Spectra

Just as each person has a unique set of fingerprints, each chemical compound has a unique infrared spectrum. If you have available an enormous library of reference spectra, and a powerful computer, in principle you could match the spectrum of an unknown compound with the library and uniquely identify the compound. This is in fact done—the Chemistry Department has an infrared system with this capability.

But what if you have a spectrum of a completely new compound, or one that is not in your database? It turns out that different parts of a molecule—its *functional groups*—give rise to infrared vibrations in reasonably well defined regions of the infrared region. For example, as *Figure 3* shows, stretching vibrations of bonds to H usually occur at higher energies, triple bonds have higher energy stretching vibrations than those of double bonds, whereas bending vibrations occur at lower energies. Extensive experience has led to the compilation of correlation tables. For example, chemists know that the stretching motions of bonds commonly found in organic compounds occur in the ranges given in the table below.

The Relation of Bond Order and Vibrational Frequency

Bond	Energy (cm^{-1})
$\text{C}\equiv\text{N}$	2150
$\text{C}=\text{N}$	1650
$\text{C}-\text{N}$	1100

The Relation Between the Electronegativity of the Bonded Atoms and Vibrational Frequency

Bond	Energy (cm^{-1})
$\text{H}-\text{C}$	2861.6
$\text{H}-\text{N}$	3300
$\text{H}-\text{O}$	3735.2
$\text{H}-\text{F}$	4183.5

<u>Bond</u>	<u>Frequency (cm⁻¹)</u>	<u>Shape and Intensity</u>
O—H	3650-2500	Often broad, strong
N—H	3400-3200	Sharp, variable
—C—H	2960-2850	Sharp, medium
=C—H	3100-3000	Sharp, medium
≡C—H	3300	Sharp, medium
C=C	1680-1620	Sharp, variable
C≡C	2230-2100	Sharp, variable
C=O	1800-1630	Sharp, strong,
C—O	1300-1000 (variable)	Sharp, strong
C—N	1360-1020	

Much more extensive correlation tables of infrared bands can be found in books on infrared spectroscopy and instrumental analysis.

To see how these arise in real spectra, look at the spectra of a few organic compounds on pages 94 and 100-102.

Identifying Compounds

The compounds for which spectra are given on pages 94 and 100-102 are from various classes of organic compounds. Each is characterized by a *functional group*, an atom or group of atoms within the molecule that give the compound its characteristic chemistry. Chapter 11 of *Chemistry & Chemical Reactivity* is a very brief discussion of the various functional groups and their characteristic chemical and physical properties.

Some classes of organic compounds, their functional groups, and their characteristic vibrations are given in *Figure 4* (page 99). A glance at this figure shows that the different classes of compounds have characteristic vibrations that are unique. Therefore, a chemist skilled in “reading” an infrared spectrum can often decide what type of compound has given rise to the spectrum. Furthermore, if reference spectra are available in a catalog, or in a database searchable by computer, the exact identity of the compound can be determined. This is widely used by research chemists, chemists responsible for quality control in pharmaceutical production, for example, and by forensic chemists.

Chemists in “crime” laboratories use infrared spectroscopy to identify chemical compounds implicated in crimes.

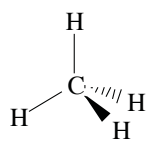
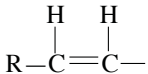
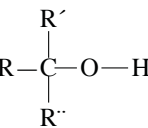
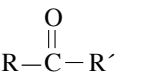
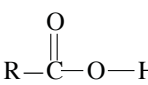
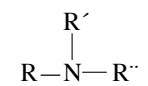
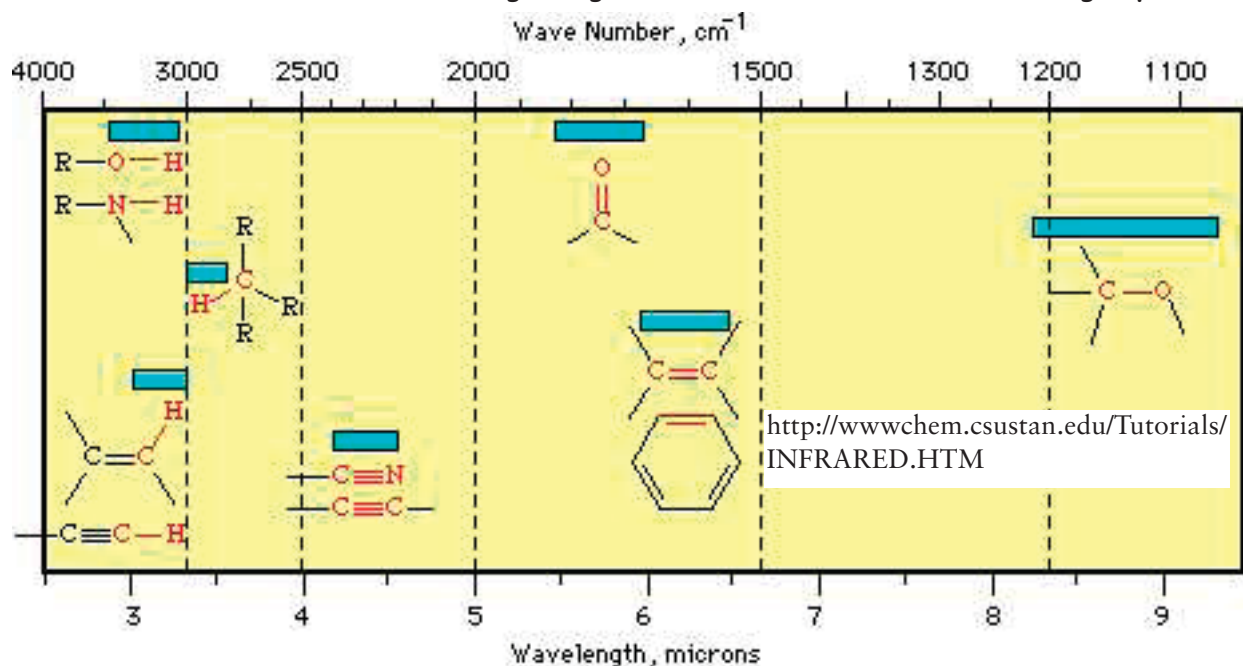
Schematic Structure	Class of Compound	Characteristic Vibrations	
	Alkane, C_nH_{2n+2}	Only C–H vibrations	
	Alkene	C=C double bond stretch	3-Bromo-1-propene on page 100 is an alkene.
	Alcohol	O–H stretch	2-Propanol on pages 94 and 100 is an alcohol.
	Aldehyde (when $R' = H$) Ketone (when $R' = \text{organic group}$)	C=O stretch	Acetophenone on page 101 is a ketone.
	Carboxylic acid	C=O and O–H vibrations	Propionic (propanoic) acid on pages 94 and 101 is a carboxylic acid.
	Amine	N–H stretch	N-Methylbenzylamine on page 102 is an amine.

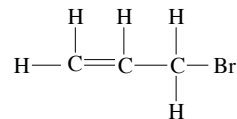
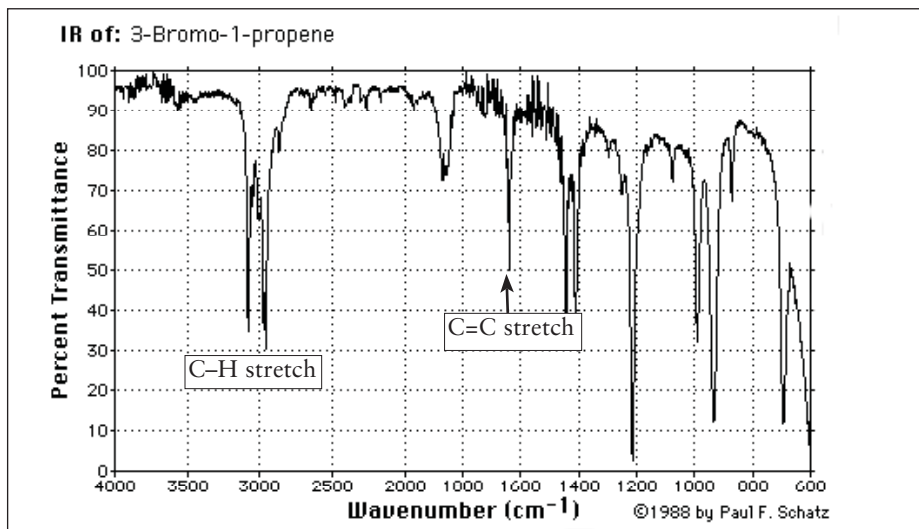
Figure 4 Some classes of organic compounds, their functional groups, and characteristic vibrations of those groups.

CORRELATION CHART: wavelength regions for vibrations of some common groups.

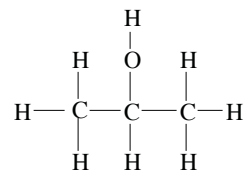
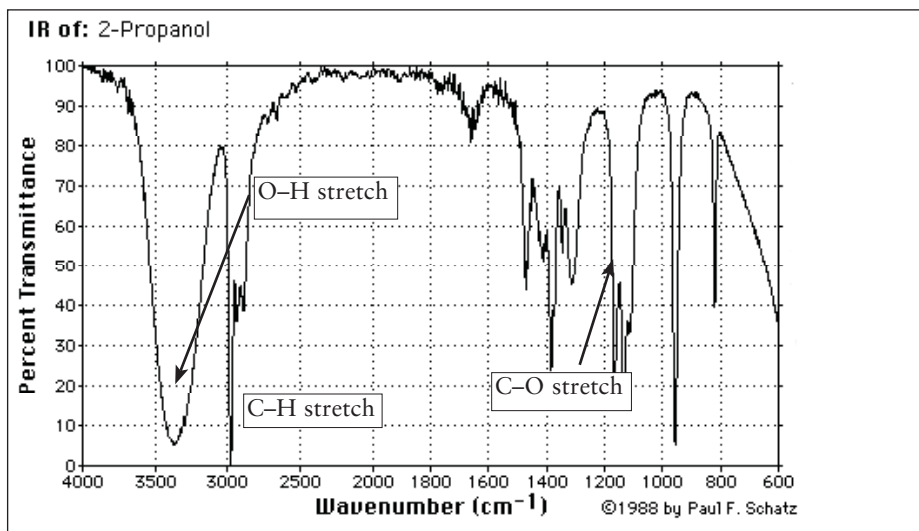


Representative Infrared Spectra

3-Bromo-1-propene

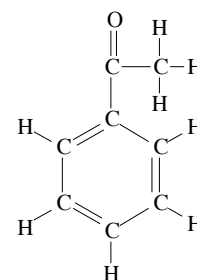
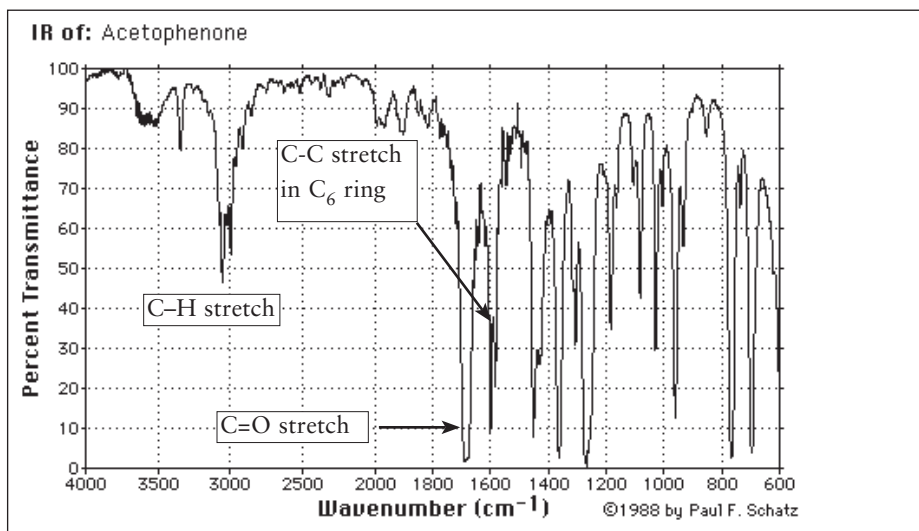


This molecule has a carbon-carbon double bond that has a sharp band at about 1650 cm^{-1} . The sharp bands at about $2950\text{-}3100$ are C–H stretches. The band at about 3100 cm^{-1} is due to the C–H bonds around the C=C double bond, whereas the band at 2950 cm^{-1} is C–H bonds of the $-\text{CH}_2\text{Br}$ group.

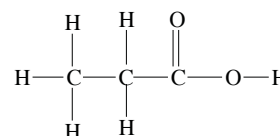
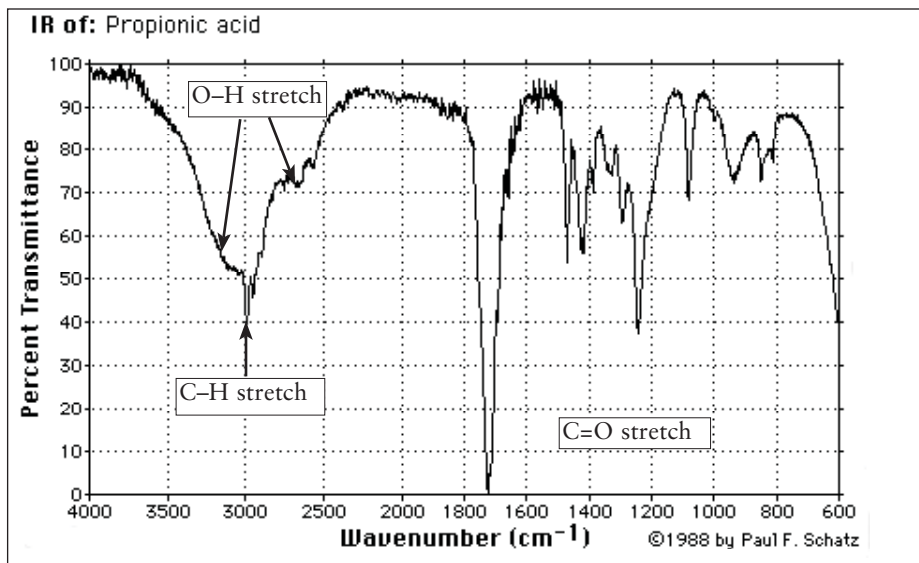


2-Propanol

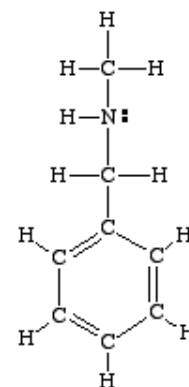
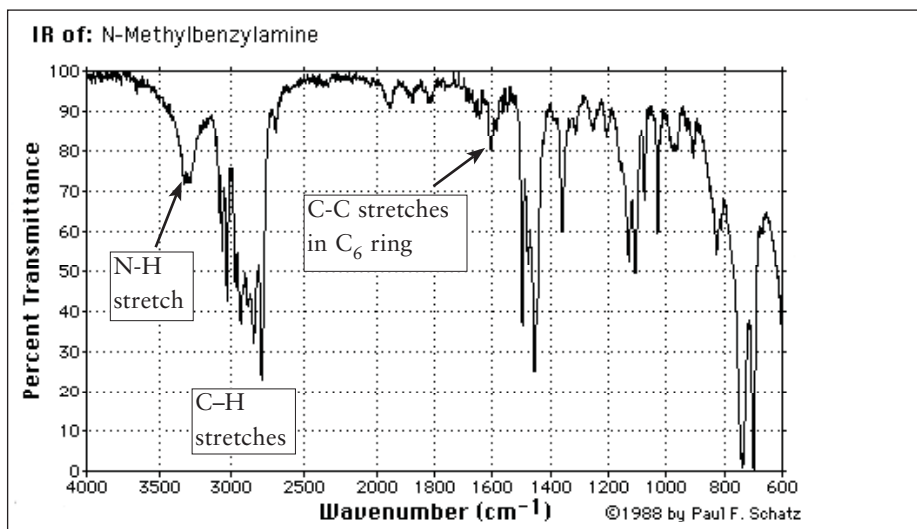
This alcohol has an obvious, broad and strong band at about 3400 cm^{-1} . This is characteristic of an O–H stretching vibration. The C–H stretch is again at about 3000 cm^{-1} . Finally, you now see a C–O stretch in the $1100\text{-}1200 \text{ cm}^{-1}$ region.

Acetophenone

Acetophenone is classified by organic chemists as a ketone (because of the C=O group), and this group is attached to an benzene ring. The spectrum shows characteristic bands of these pieces of the molecule. Most importantly, the sharp, strong band at about 1700 cm^{-1} is characteristic of the C=O group (called a “carbonyl group”). In addition, the bands at about 1600 cm^{-1} are characteristic of the C–C stretches of the C_6 ring.

Propanoic Acid

An organic acid is characterized by the $-\text{CO}_2\text{H}$ group (the carboxylic acid group). This group has a very clear infrared fingerprint. Here you see the strong, broad O–H stretching band (overlapping the C–H stretch) and the sharp, strong C=O band.

N-Methylbenzylamine

This molecule is classified by organic chemists as an “amine.” In this case, there is an H atom attached to the N, and this has a characteristic medium intensity band at about 3400 cm^{-1} (see page 5). In addition, there is a group of bands around 3000 cm^{-1} that arise from C–H stretching vibrations. Finally, we again see a weakish set of bands at about 1600 cm^{-1} that arise from the stretching of the C–C bonds in the C_6 benzene ring. (See the spectrum of acetophenone on the preceding page.)