

## Infrared Radiation

Infrared radiation (IR) is the term we use to describe the portion of the electromagnetic spectrum that encompasses frequencies lower (longer wavelengths) than the color red and higher (shorter wavelengths) than microwaves. Basically, it is radiant heat.

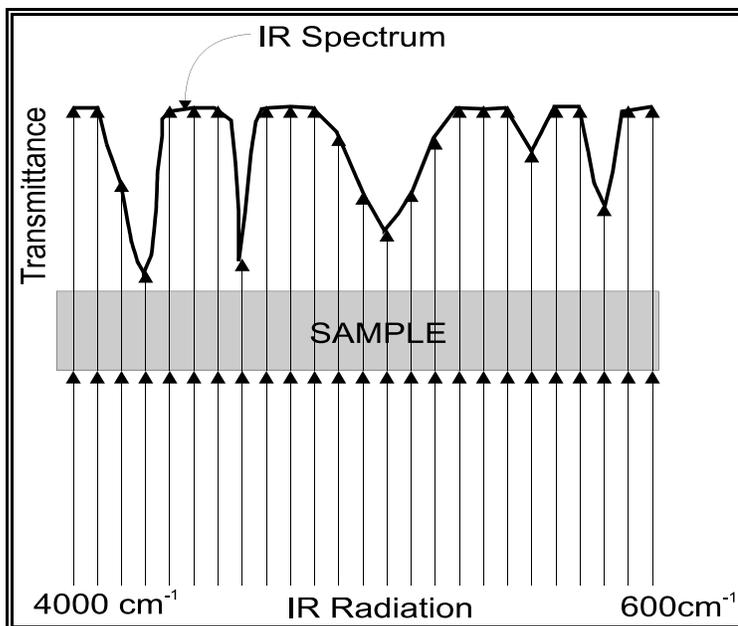
The fundamental properties of infrared radiation are its frequency,  $\nu$ , its wavelength,  $l$ , and its velocity,  $c$ , through the medium it is traversing. These are related by the relationship  $\nu l = c$ , where  $c$  is the velocity of light in the medium through which the radiation is passing. Since  $c$  is a constant for a given material, once the frequency is known, so is the wavelength and *vice versa*. Since wavelength and velocity change (proportionally) from material to material, but frequency remains the same, we usually discuss IR in terms of frequency. Consequently,  $\nu$  (in cycles per second or Hertz) =  $c$  (in centimeters/second) /  $l$  (in centimeters). Perversely, it is not fashionable to speak of cps or Hertz when discussing IR. The term that is in fashion is *wavenumber*. Wavenumber,  $\bar{\nu}$ , is proportional to frequency:  $\bar{\nu} = 1/l$ ; it has the units,  $\text{cm}^{-1}$ . It is common, but not really correct, for people to say, "The frequency is [so many] wavenumbers."

Infrared radiation has a wavelength (in air or a vacuum) of 2-50 microns [1 micron =  $1 \times 10^{-6}$  m =  $1 \times 10^{-4}$  cm].

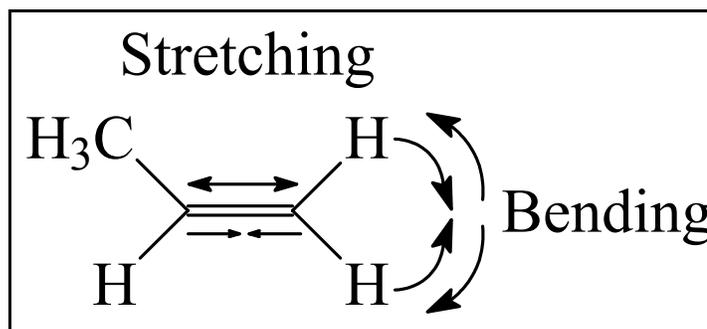
## The Infrared (IR) Spectrum

The most useful region of infrared radiation for spectroscopy is that between 2 and 15 microns, or, in wave numbers (a measure of frequency), 5,000-650  $\text{cm}^{-1}$  [wave numbers =  $1/\text{wavelength in cm}$ ].

Molecules of a particular compound may absorb certain frequencies of infrared radiation, but not other frequencies. To obtain the *infrared spectrum* of a compound a graph of the amount of radiation transmitted through a sample of the compound vs. its frequency is produced.



The IR radiation which is absorbed causes molecular vibration: bonds stretch and compress and bond angles oscillate (bending).



Certain groups of atoms absorb IR in a certain region of frequencies, more or less independently of where the group is found. Consequently, tables of *group frequencies* are available and if a compound shows absorptions characteristic of a particular group it's a good **guess** that that group is present. One such table can be found at <http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/InfraRed/infrared.htm>

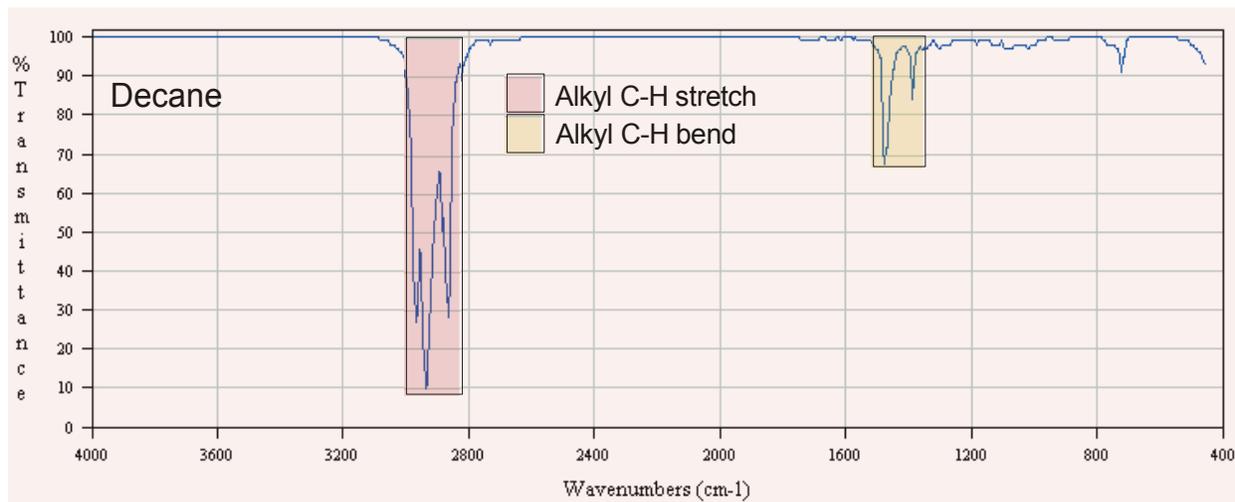
Group frequencies can be altered (shifted) to some extent by certain structural features in the molecule (eg, conjugation, electron withdrawing groups, steric strain, hydrogen bonding) especially those which are near the group giving rise to the absorption. Comprehensive tables take some of these effects into account.

The most useful group frequencies occur between 4,000  $\text{cm}^{-1}$  and  $\sim 1,300 \text{ cm}^{-1}$ . The region between  $\sim 1,300 \text{ cm}^{-1}$  and  $650 \text{ cm}^{-1}$  is known as the *fingerprint region*. It is not very useful for detecting functional groups, but is useful for discriminating between two compounds with similar functional groups.

Perhaps the best approach to take is to look for IR absorptions corresponding to the common functional groups. If the absorptions are present this is *prima facie* evidence of the group. Conversely, if absorptions characteristic of a group are not present that is *prima facie* evidence of the absence of that group.

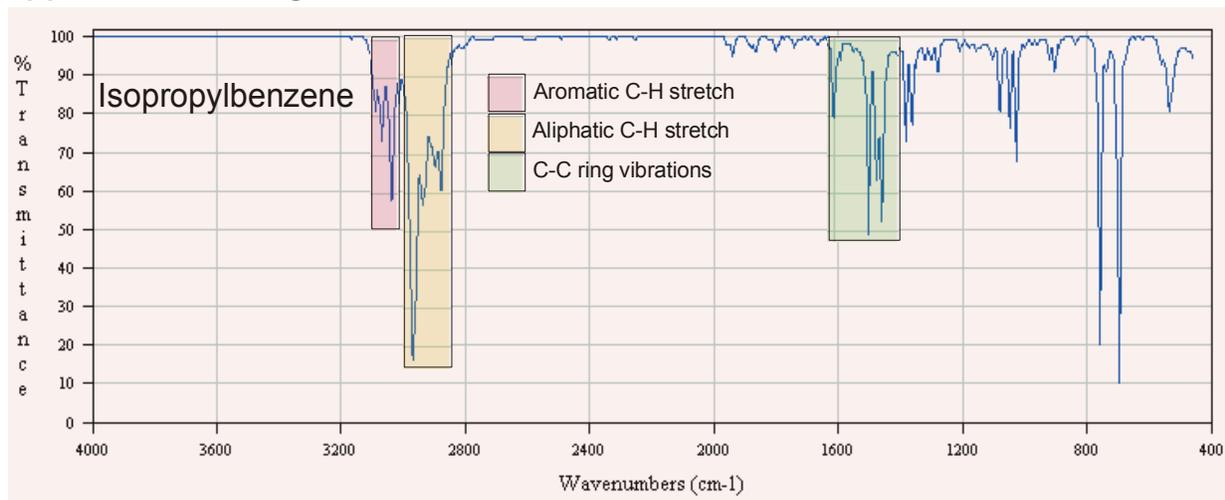
## Alkyl Groups

The presence of alkyl groups is usually revealed by weak to medium absorptions (strong in the example below) in the 2850-2990  $\text{cm}^{-1}$  region, owing to  $\text{sp}^3\text{C-H}$  stretching vibrations. C-H bending vibrations may also be observed at about 1375 and 1450  $\text{cm}^{-1}$ .



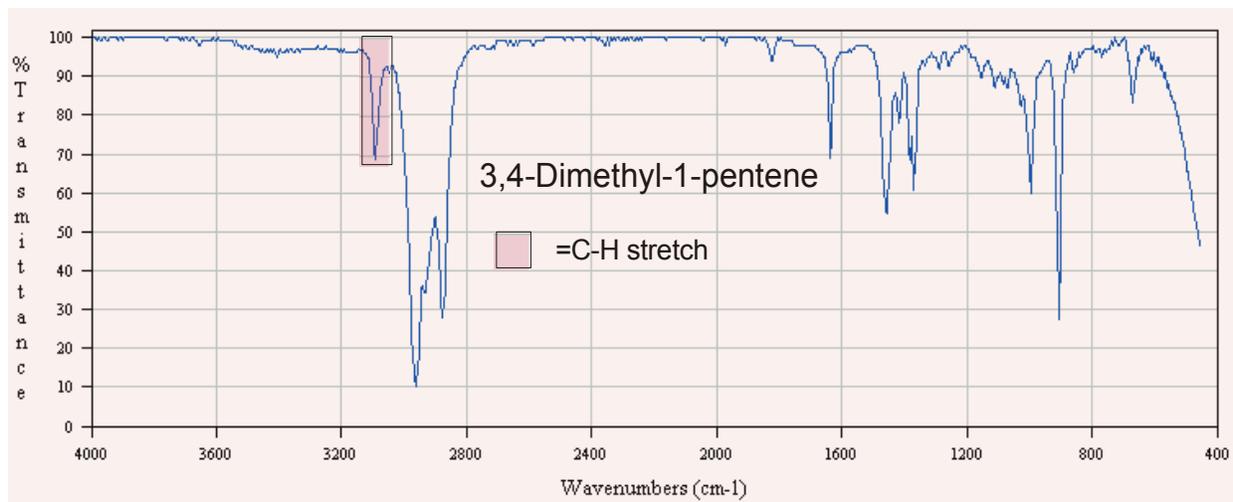
## Aromatic Groups

Aromatic groups generally have weak  $\text{sp}^2\text{C-H}$  stretching vibrations between 3000 and 3100  $\text{cm}^{-1}$ . Usually there is one located very close to 3030  $\text{cm}^{-1}$ . C-C ring stretching occurs at about the following frequencies: 1450, 1500, 1580, and 1600  $\text{cm}^{-1}$ . These may range from weak to strong and one or two may be missing. Out of plane bending vibrations of aromatic rings appear in the range 675-900  $\text{cm}^{-1}$ .



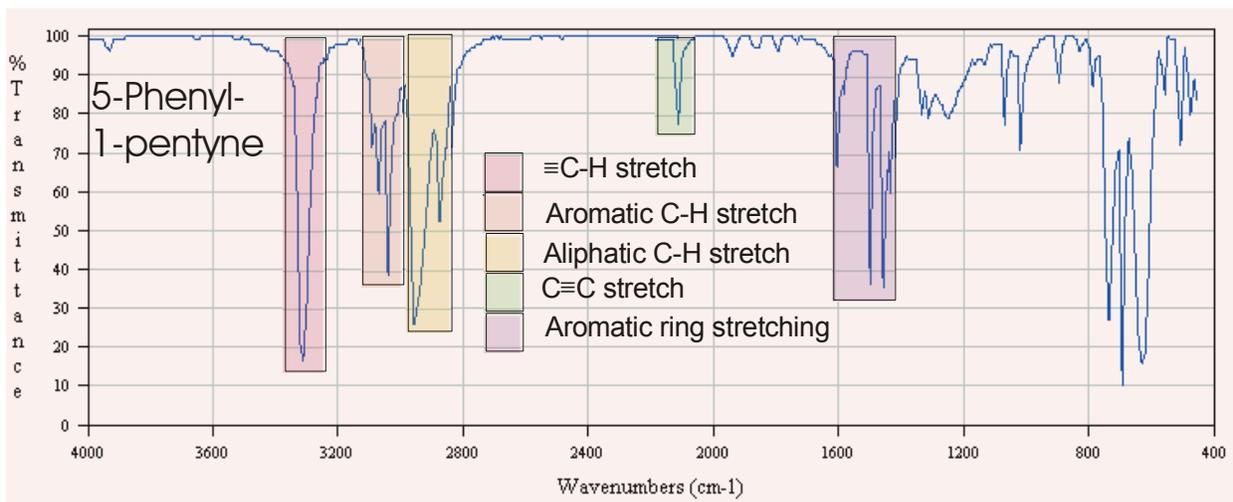
## Alkenes

The vinylic hydrogen ( $=\text{C-H}$ ) stretches appear just above  $3000\text{ cm}^{-1}$ ; they overlap the aromatic  $\text{C-H}$  stretches. The  $\text{C}=\text{C}$  stretch is medium to non-existent between  $1640$  and  $1670\text{ cm}^{-1}$ . The most characteristic vibrational modes of alkenes are the out-of-plane  $\text{C-H}$  bending vibrations between  $650$  and  $1000\text{ cm}^{-1}$ . Unfortunately, these absorptions are in the fingerprint region.



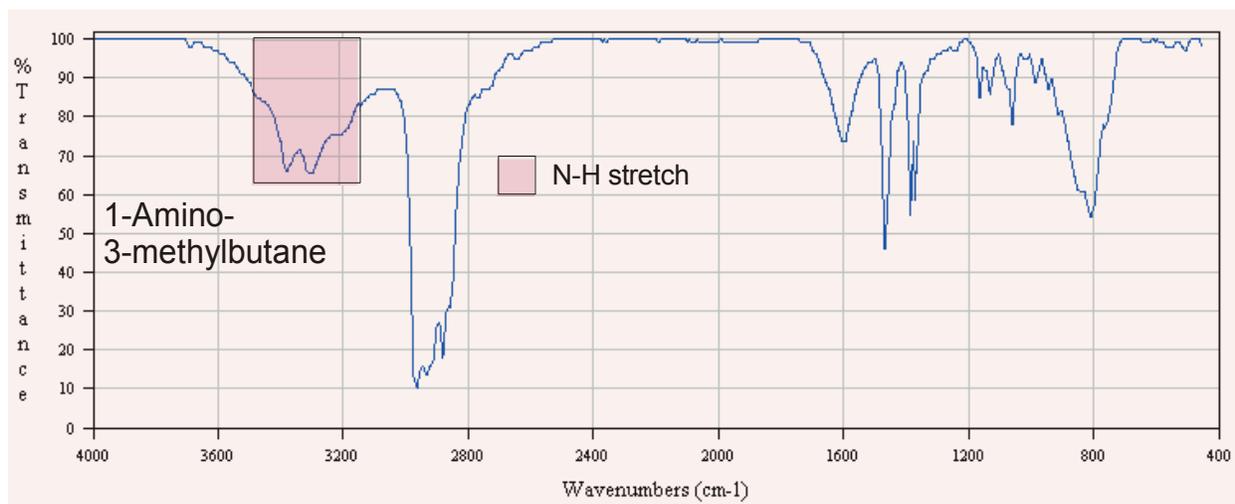
## Alkynes

The  $\text{C}\equiv\text{C}$  stretch is weak but sharp between  $2100$  and  $2260\text{ cm}^{-1}$ . Alkynes symmetrical around the triple bond do not have this peak. The  $\equiv\text{C-H}$  stretch of terminal alkynes shows up between  $3260$  and  $3330\text{ cm}^{-1}$ . This is a medium to strong absorption and is sharper than the typically broader hydrogen bonded  $\text{N-H}$  and  $\text{O-H}$  stretches.



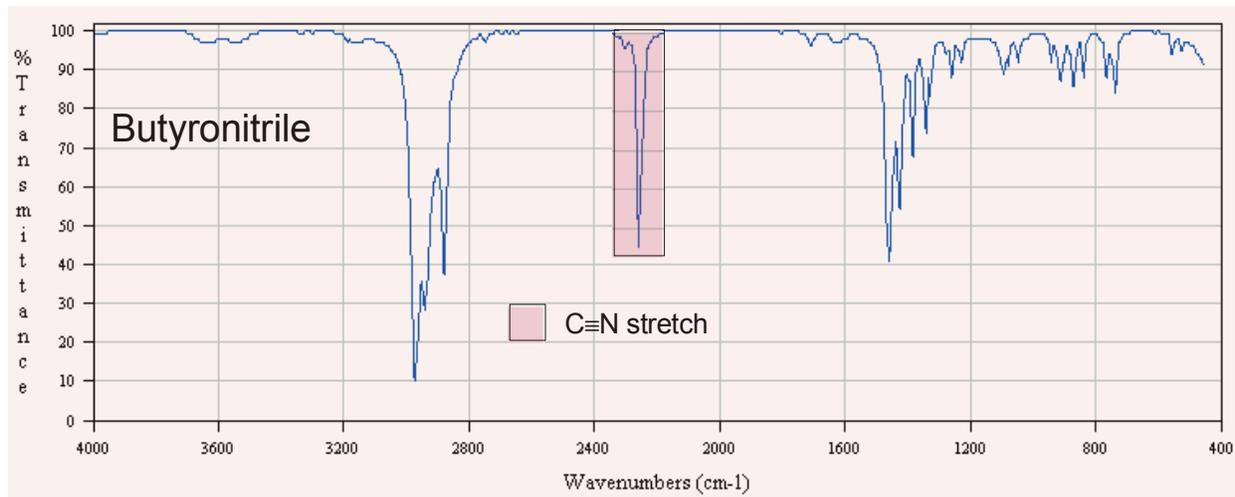
## Amines

N-H stretch gives rise to medium absorption in the range from 3300 and 3500  $\text{cm}^{-1}$ . Primary amines ( $\text{RNH}_2$ ) have two or three bands. Secondary amines ( $\text{R}_2\text{NH}$ ) have one or two bands. Tertiary amines ( $\text{R}_3\text{N}$ ) do not have an N-H stretch.



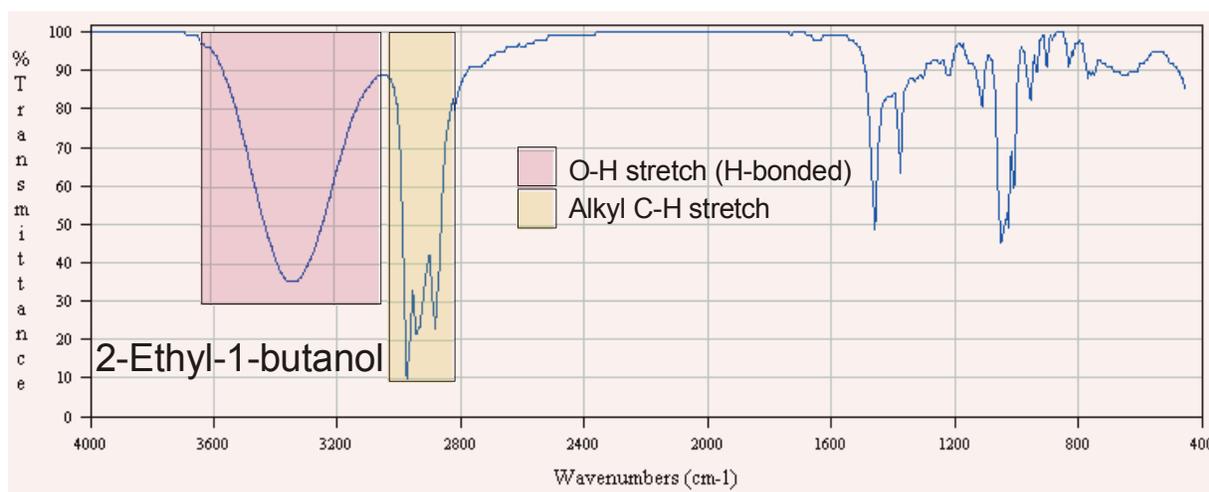
## Nitriles

The  $\text{C}\equiv\text{N}$  stretch is a sharp absorption near 2250  $\text{cm}^{-1}$ . Conjugation moves the absorption to the right.



## Alcohols and Phenols

The hydroxyl group of alcohols and phenols presents a medium to strong O-H stretch in the region between 3200 and 3650  $\text{cm}^{-1}$ . In cases where hydrogen bonding is present (as it would be in neat liquids, unless it is prevented by steric hindrance) this absorption is fairly broad and usually between 3200 and 3600  $\text{cm}^{-1}$ . In dilute solution a non-hydrogen-bonded O-H stretch may show up as a sharp peak at 3600-3650  $\text{cm}^{-1}$ ; in some cases, especially when the solution is not so dilute, two peaks appear, a broad one from hydrogen bonded O-H stretching, and a sharp one from non-hydrogen-bonded stretching. The N-H stretch of amines and amides may also appear in the 3200 and 3650  $\text{cm}^{-1}$  region. Typically, these absorptions are not as broad as an H-bonded O-H and may consist of two or three bands.

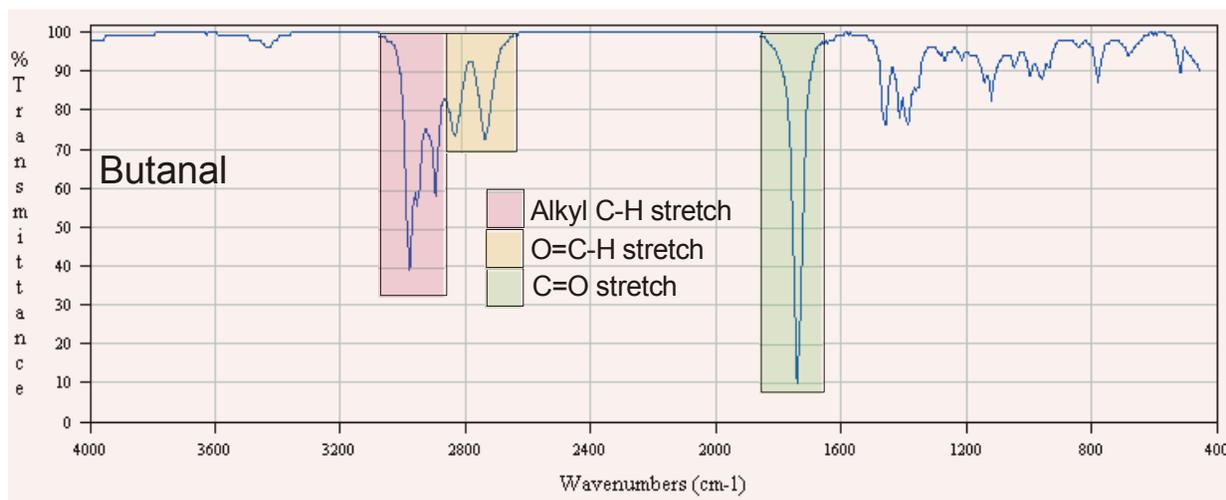


## The Carbonyl Group

A strong absorption in the range 1650-1800  $\text{cm}^{-1}$  is good evidence for the C=O group. The carbonyl group occurs in several functional groups: aldehydes, ketones, carboxylic acids, acid chlorides, acid anhydrides, amides, and esters.

## Aldehydes

The C=O stretch is strong and located near  $1725\text{ cm}^{-1}$ . Conjugation ( $\text{Y}=\text{Z}-\text{C}=\text{O}$ ) moves this absorption to lower frequency. The O=C-H stretch produces two weak to medium peaks at about  $2750$  and  $2850\text{ cm}^{-1}$ . These are slightly to the right of alkyl C-H stretching frequencies.

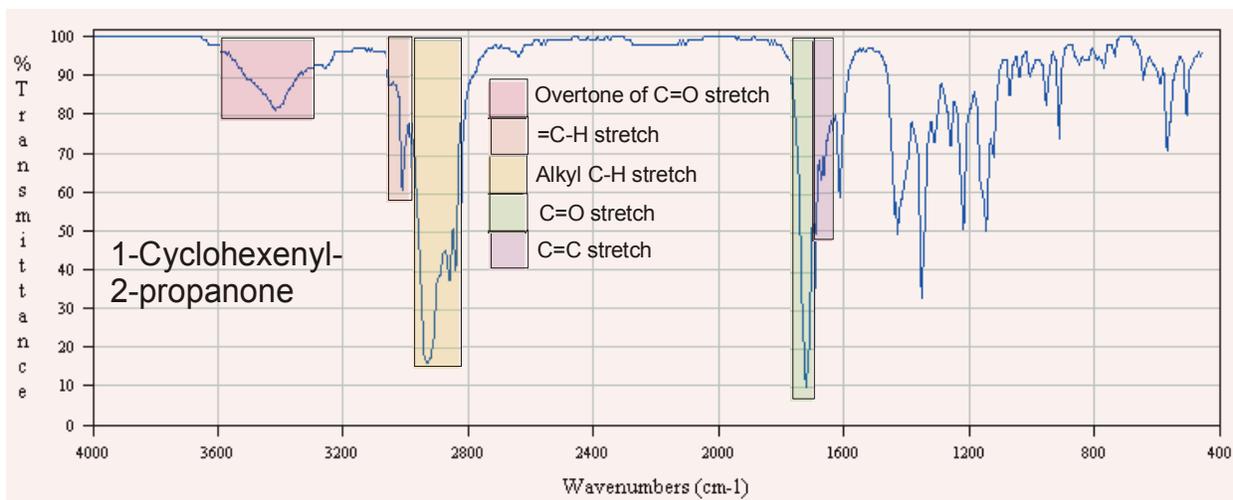


## Ketones

The C=O stretch is strong and located near  $1715\text{ cm}^{-1}$ . Conjugation moves this absorption to the right. Ring strain in cyclic ketones moves it to the left.

The ketone below is also an alkene and has characteristic alkene absorptions. Note that the C=C stretching causes very small peaks that are easily overlooked. On the other hand, the C=O cannot be overlooked; it is often the strongest absorption in the spectrum, as it is here.

This spectrum also shows an overtone band that is centered at  $3416\text{ cm}^{-1}$ . This is exactly twice the frequency of the C=O band that shows up at  $1708\text{ cm}^{-1}$ . Overtone bands sometimes appear at exactly twice the frequency of another absorption in the spectrum. Usually the absorption causing the overtone will be fairly strong.



## Carboxylic Acids

In the case of carboxylic acids the O-H stretch is very broad (strong H-bonding) and typically extends from around 2500 to 3300 cm<sup>-1</sup>, traversing the C-H stretch region. The C=O stretch is strong and typically shows up between 1700 to 1730 cm<sup>-1</sup>. Conjugation moves the absorption to the right.

