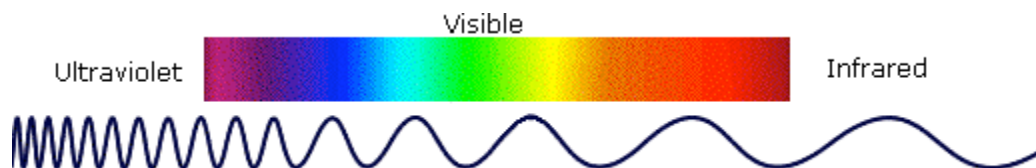


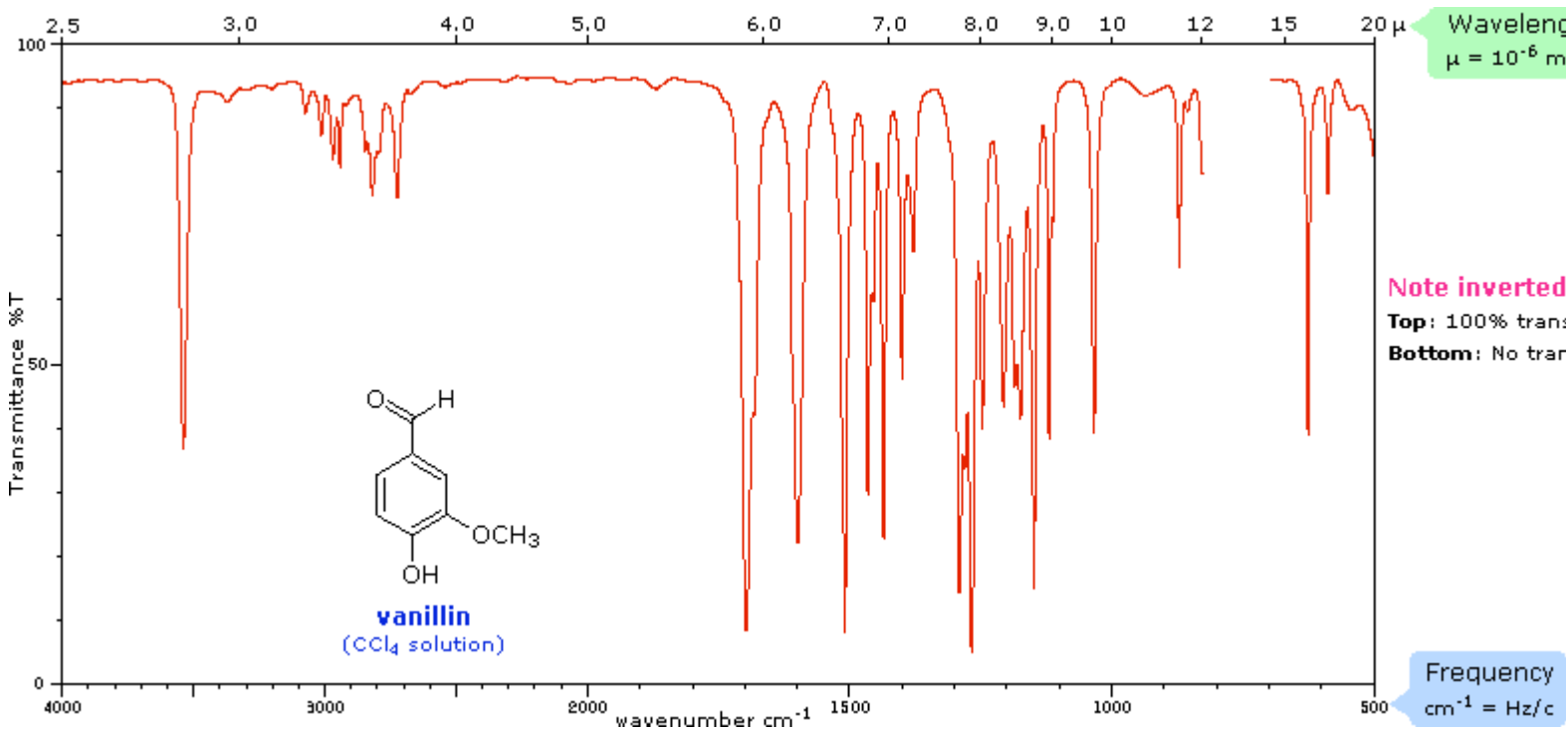
# Infrared Spectroscopy

## 1. Introduction

As noted in a previous chapter, the light our eyes see is but a small part of a broad spectrum of electromagnetic radiation. On the immediate high energy side of the visible spectrum lies the ultraviolet, and on the low energy side is the infrared. The portion of the infrared region most useful for analysis of organic compounds is not immediately adjacent to the visible spectrum, but is that having a wavelength range from 2,500 to 16,000 nm, with a corresponding frequency range from  $1.9 \times 10^{13}$  to  $1.2 \times 10^{14}$  Hz.



Photon energies associated with this part of the infrared (from 1 to 15 kcal/mole) are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups. The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and bent. The mobile nature of organic molecules was noted in the chapter concerning [conformational isomers](#). We must now recognize that, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations. Infrared spectrometers, similar in principle to the UV-Visible spectrometer [described elsewhere](#), permit chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure. An example of such a spectrum is that of the flavoring agent vanillin, shown below.



The complexity of this spectrum is typical of most infrared spectra, and illustrates their use in identifying substances. The gap in the spectrum between 700 & 800  $\text{cm}^{-1}$  is due to solvent ( $\text{CCl}_4$ ) absorption. Further analysis (below) will show that this spectrum also indicates the presence of an aldehyde function, a phenolic hydroxyl and a substituted benzene ring. The inverted display of absorption, compared with [UV-Visible spectra](#), is characteristic. Thus a sample that did not absorb at all would record a horizontal line at 100% transmittance (top of the chart).

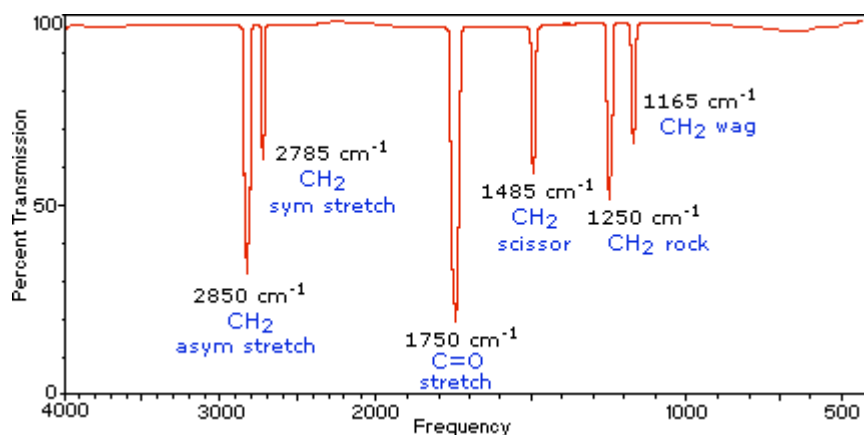
The frequency scale at the bottom of the chart is given in units of **reciprocal centimeters ( $\text{cm}^{-1}$ )** rather than Hz, because the numbers are more manageable. The reciprocal centimeter is the number of wave cycles in one centimeter; whereas, frequency in cycles per second or Hz is equal to the number of wave cycles in  $3 \times 10^{10}$  cm (the distance covered by light in one second). Wavelength units are in micrometers, **microns ( $\mu$ )**, instead of nanometers for the same reason. Most infrared spectra are displayed on a linear frequency scale, as shown here, but in some older texts a linear wavelength scale is used. A calculator for interconverting these frequency and wavelength values is provided on the right. Simply enter the value to be converted in the appropriate box, press "Calculate" and the equivalent number will appear in the empty box.

Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent). If solvents are used to dissolve solids, care must be taken to avoid obscuring important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used. Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates.

## 2. Vibrational Spectroscopy

A molecule composed of  $n$ -atoms has  $3n$  degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves  $3n-6$  degrees of vibrational freedom ( $3n-5$  if the molecule is linear). Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting. The four-atom molecule of formaldehyde, the gas phase spectrum of which is shown below, provides an example of these terms. If a ball & stick model of formaldehyde is not displayed to the right of the spectrum, press the **view ball&stick model** button at the lower right. We expect six fundamental vibrations (12 minus 6), and these have been assigned to the spectrum absorptions. To see the formaldehyde molecule display a vibration, click one of the buttons under the spectrum.

**Gas Phase Infrared Spectrum of Formaldehyde,  $\text{H}_2\text{C}=\text{O}$**



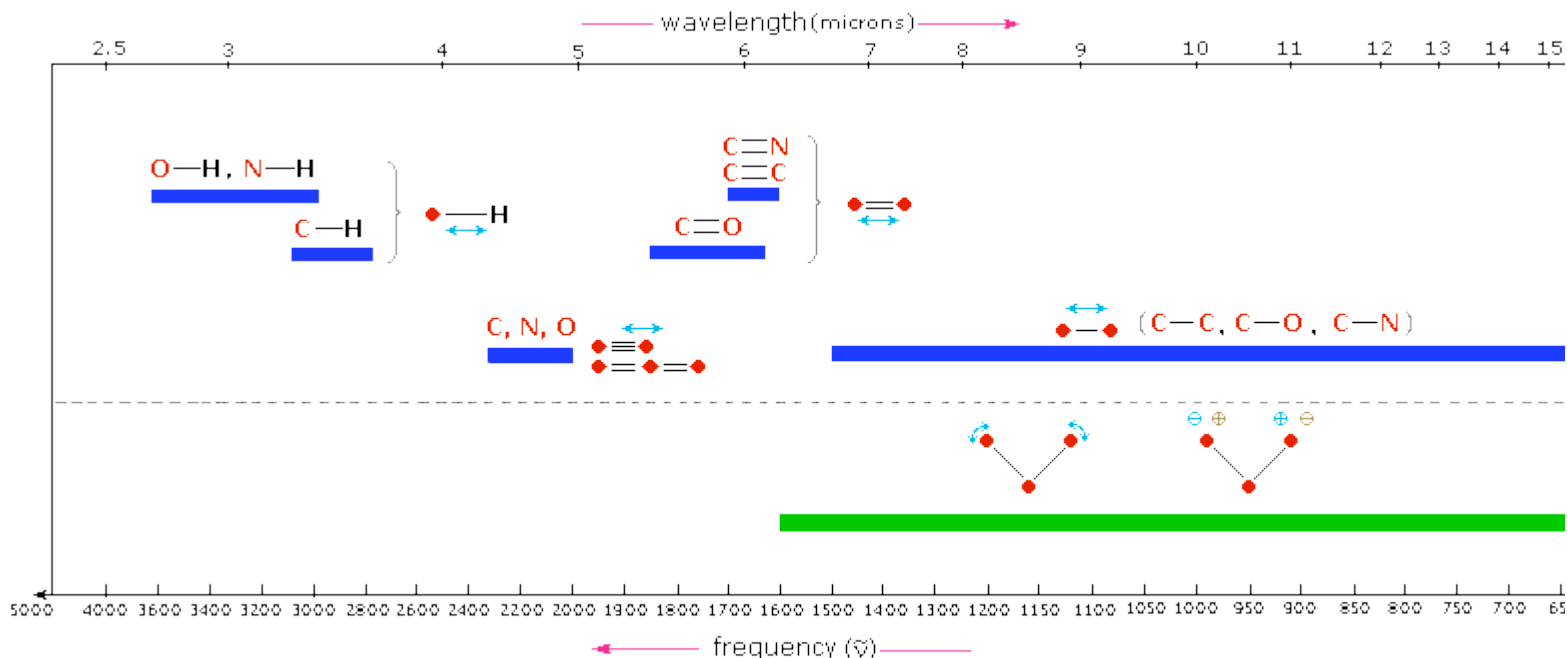
The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. For a more detailed discussion of these factors [Click Here](#). In practice, infrared spectra do not normally display separate absorption signals for each of the  $3n-6$  fundamental vibrational modes of a molecule. The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact. Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules. One selection rule that influences the intensity of infrared absorptions, is that a change in dipole moment should occur for a vibration to absorb infrared energy. Absorption bands associated with  $\text{C}=\text{O}$  bond stretching are usually very strong because a large change in the dipole takes place in that mode.

### Some General Trends:

- i) **Stretching frequencies are higher than corresponding bending frequencies.** (It is easier to bend a bond than to stretch or compress it.)
- ii) **Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.**
- iii) **Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have**

higher frequencies than single bonds.  
(Except for bonds to hydrogen).

The general regions of the infrared spectrum in which various kinds of vibrational bands are observed are outlined in the following chart. Note that the blue colored sections above the dashed line refer to stretching vibrations, and the green colored band below the line encompasses bending vibrations. The complexity of infrared spectra in the 1450 to 600  $\text{cm}^{-1}$  region makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the **fingerprint** region. Absorption bands in the 4000 to 1450  $\text{cm}^{-1}$  region are usually due to stretching vibrations of diatomic units, and this is sometimes called the **group frequency** region.



### 3. Group Frequencies

Detailed information about the infrared absorptions observed for various bonded atoms and groups is usually presented in tabular form. The following table provides a collection of such data for the most common functional groups. Following the color scheme of the chart, stretching absorptions are listed in the blue-shaded section and bending absorptions in the green shaded part. **More detailed descriptions for certain groups (e.g. alkenes, arenes, alcohols, amines & carbonyl compounds) may be viewed by clicking on the functional class name.** Since most organic compounds have C-H bonds, a useful rule is that absorption in the 2850 to 3000  $\text{cm}^{-1}$  is due to  $\text{sp}^3$  C-H stretching; whereas, absorption above 3000  $\text{cm}^{-1}$  is from  $\text{sp}^2$  C-H stretching or  $\text{sp}$  C-H stretching if it is near 3300  $\text{cm}^{-1}$ .

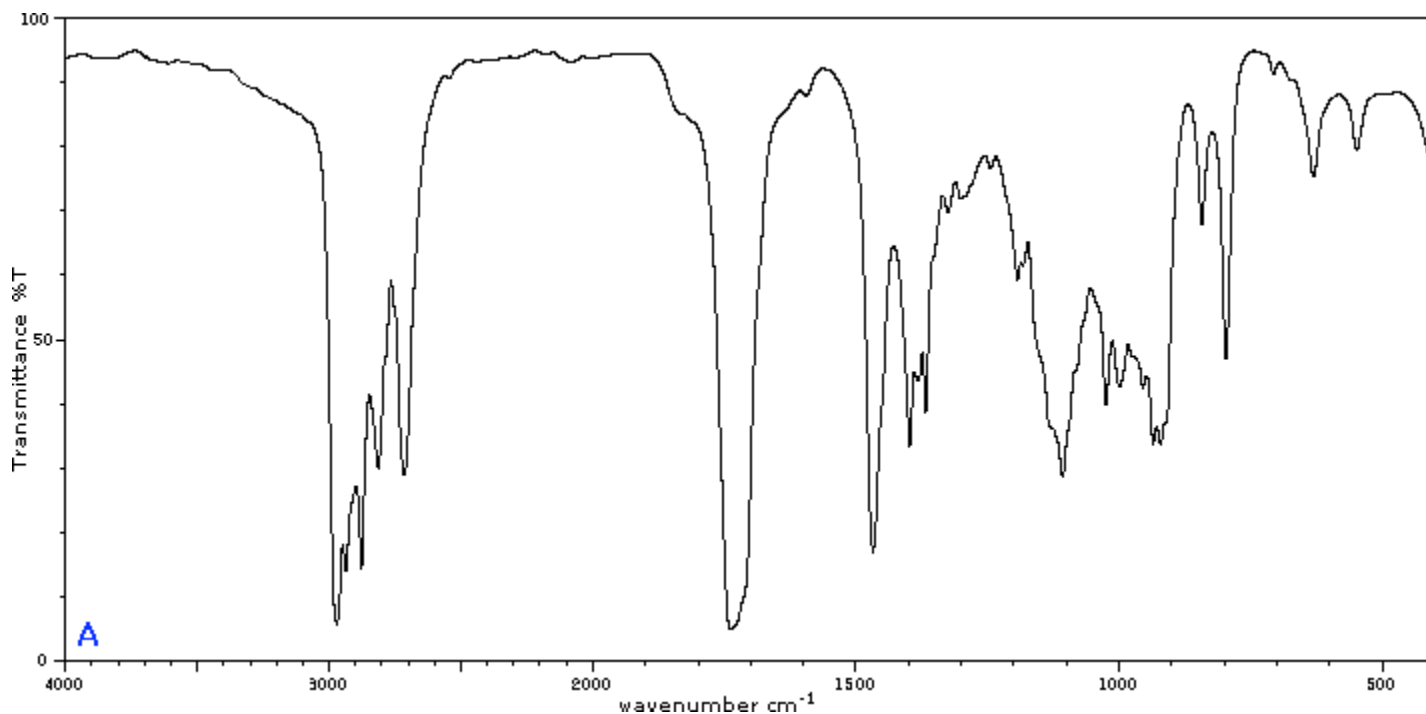
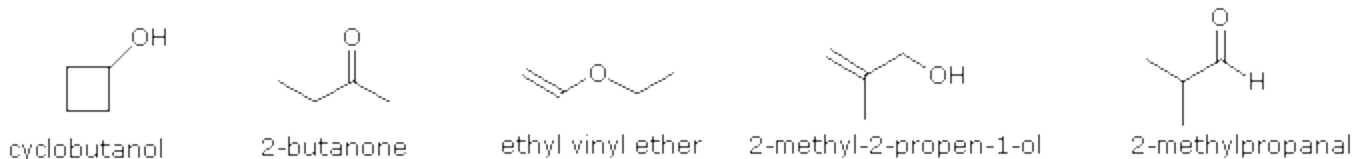
#### Typical Infrared Absorption Frequencies

Functional Class	Stretching Vibrations			Bending Vibrations		
	Range ( $\text{cm}^{-1}$ )	Intensity	Assignment	Range ( $\text{cm}^{-1}$ )	Intensity	Assignment
<b>Alkanes</b>	2850-3000	str	CH <sub>3</sub> , CH <sub>2</sub> & CH 2 or 3 bands	1350-1470	med	CH <sub>2</sub> & CH <sub>3</sub> deformation
				1370-1390	med	CH <sub>3</sub> deformation
				720-725	wk	CH <sub>2</sub> rocking
<b>Alkenes</b>	3020-3100	med	=C-H & =CH <sub>2</sub>	880-	str	=C-H & =CH <sub>2</sub>
	1630-1680	var	(usually sharp)	995	med	(out-of-plane bending)
	1900-2000	str	C=C (symmetry reduces intensity)	780-850	med	cis-RCH=CHR

			C=C asymmetric stretch	675-730		
<b>Alkynes</b>	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
<b><u>Arenes</u></b>	3030 1600 & 1500	var med-wk	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str-med	C-H bending & ring puckering
<b><u>Alcohols &amp; Phenols</u></b>	3580-3650 3200-3550 970-1250	var str str	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)
<b><u>Amines</u></b>	3400-3500 (dil. soln.) 3300-3400 (dil. soln.) 1000-1250	wk wk med	N-H (1°-amines), 2 bands N-H (2°-amines) C-N	1550-1650 660-900	med-str var	NH <sub>2</sub> scissoring (1°-amines) NH <sub>2</sub> & N-H wagging (shifts on H-bonding)
<b><u>Aldehydes &amp; Ketones</u></b>	2690-2840(2 bands) 1720-1740 1710-1720  1690 1675 1745 1780	med str str  str str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone)  aryl ketone α, β-unsaturation cyclopentanone cyclobutanone	1350-1360 1400-1450 1100	str str med	α-CH <sub>3</sub> bending α-CH <sub>2</sub> bending C-C-C bending
<b><u>Carboxylic Acids &amp; Derivatives</u></b>	2500-3300 (acids) overlap C-H 1705-1720 (acids) 1210-1320 (acids)  1785-1815 (acyl halides) 1750 & 1820 (anhydrides) 1040-1100 1735-1750 (esters) 1000-1300	str str med-str  str str str str str	O-H (very broad) C=O (H-bonded) O-C (sometimes 2-peaks)  C=O C=O (2-bands) O-C C=O O-C (2-bands) C=O (amide I band)	1395-1440    1590-1650 1500-1560	med    med med	C-O-H bending    N-H (1 <sub>j</sub> -amide) II band N-H (2 <sub>j</sub> -amide) II band

	1630-1695(amides)				
<b>Nitriles</b>	2240-2260	med	C≡N (sharp)		
<b>Isocyanates, Isothiocyanates, Diimides, Azides &amp; Ketenes</b>	2100-2270	med	-N=C=O, -N=C=S -N=C=N-, -N <sub>3</sub> , C=C=O		

To illustrate the usefulness of infrared absorption spectra, examples for five C<sub>4</sub>H<sub>8</sub>O isomers are presented below their corresponding structural formulas. The five spectra may be examined in turn by clicking the "Toggle Spectra" button. Try to associate each spectrum (A - E) with one of the isomers in the row above it. When you have made assignments check your answers by clicking on the structure or name of each isomer.



## 4. Other Functional Groups

Infrared absorption data for some functional groups not listed in the preceding table are given below. Most of the absorptions cited are associated with stretching vibrations. Standard abbreviations (str = strong, wk = weak, brd = broad & shp = sharp) are used to describe the absorption bands.

Functional Class	Characteristic Absorptions
<b>Sulfur Functions</b>	
<b>S-H</b> thiols	2550-2600 cm <sup>-1</sup> (wk & shp)
<b>S-OR</b> esters	700-900 (str)
<b>S-S</b> disulfide	500-540 (wk)

<b>C=S</b> thiocarbonyl	1050-1200 (str)
<b>S=O</b> sulfoxide sulfone sulfonic acid sulfonyl chloride sulfate	1030-1060 (str) 1325± 25 (as) & 1140± 20 (s) (both str) 1345 (str) 1365± 5 (as) & 1180± 10 (s) (both str) 1350-1450 (str)
<b>Phosphorous Functions</b>	
<b>P-H</b> phosphine	2280-2440 cm <sup>-1</sup> (med & shp) 950-1250 (wk) P-H bending
<b>(O=)PO-H</b> phosphonic acid	2550-2700 (med)
<b>P-OR</b> esters	900-1050 (str)
<b>P=O</b> phosphine oxide phosphonate phosphate phosphoramidate	1100-1200 (str) 1230-1260 (str) 1100-1200 (str) 1200-1275 (str)
<b>Silicon Functions</b>	
<b>Si-H</b> silane	2100-2360 cm <sup>-1</sup> (str)
<b>Si-OR</b>	1000-11000 (str & brd)
<b>Si-CH<sub>3</sub></b>	1250± 10 (str & shp)
<b>Oxidized Nitrogen Functions</b>	
<b>=NOH</b> oxime O-H (stretch) C=N N-O	3550-3600 cm <sup>-1</sup> (str) 1665± 15 945± 15
<b>N-O</b> amine oxide aliphatic aromatic	960± 20 1250± 50
<b>N=O</b> nitroso nitro	1550± 50 (str) 1530± 20 (as) & 1350± 30 (s)

Test your ability to use information from infrared and mass spectrometry to identify an unknown compound. Clicking the button opens a display in which four different problems of this kind may be selected. Answers are provided once an effort to solve the problem has been made.

[Four Spectroscopy Problems](#)

## The Nature of Vibrational Spectroscopy

$$= \frac{1}{2\pi c} \sqrt{\frac{f}{m_1 + m_2}}$$

= frequency in  $\text{cm}^{-1}$   
 = the force constant  
 = the velocity of light

We have noted that the covalent bonds of molecules are not rigid, but are more like stiff springs that can be stretched and bent. At ordinary temperatures these bonds vibrate in a variety of ways, and the vibrational energies of molecules may be assigned to quantum levels in the same manner as are their electronic states. Transitions between vibrational energy states may be induced by absorption of infrared radiation, having photons of the appropriate energy. It requires more energy to stretch (or compress) a bond than to bend it, and as might

be expected, the energy or frequency that characterizes the stretching vibration of a given bond is proportional to the bond dissociation energy.

The equation on the right describes the major factors that influence the stretching frequency of a covalent bond between two atoms of mass  $m_1$  and  $m_2$  respectively. The force constant ( $f$ ) is proportional to the strength of the covalent bond linking  $m_1$  and  $m_2$ . In the analogy of a spring, it corresponds to the spring's stiffness. For example, a C=N double bond is about twice as strong as a C-N single bond, and the C≡N triple bond is similarly stronger than the double bond. The infrared stretching frequencies of these groups vary in the same order, ranging from  $1100 \text{ cm}^{-1}$  for C-N, to  $1660 \text{ cm}^{-1}$  for C=N, to  $2220 \text{ cm}^{-1}$  for C≡N.

Approximate Infrared Stretching Frequencies				
<b>B-H</b> 2400 $\text{cm}^{-1}$	<b>C-H</b> 3000 $\text{cm}^{-1}$	<b>N-H</b> 3400 $\text{cm}^{-1}$	<b>O-H</b> 3600 $\text{cm}^{-1}$	<b>F-H</b> 4000 $\text{cm}^{-1}$
<b>Al-H</b> 1750	<b>Si-H</b> 2150	<b>P-H</b> 2350	<b>S-H</b> 2570	<b>Cl-H</b> 2890
	<b>Ge-H</b> 2070	<b>As-H</b> 2150	<b>Se-H</b> 2300	<b>Br-H</b> 2650

If one of the bonded atoms ( $m_1$  or  $m_2$ ) is a hydrogen (atomic mass = 1), the mass ratio in the equation is roughly unity, but for two heavier atoms it is much smaller. Consequently, C-H, N-H and O-H bonds have much higher stretching frequencies than do corresponding bonds to heavier atoms. Other X-H stretching frequencies are shown in the table to the left, the trends observed being due chiefly to differences in the force constants. The mass effect on stretching frequencies is particularly evident when deuterium isotope equivalents are compared with corresponding hydrogen functions. Thus, the

stretching frequency of a free O-H bond is  $3600 \text{ cm}^{-1}$ , but the O-D equivalent is lowered to  $2600 \text{ cm}^{-1}$ . Since deuterium has a mass = 2, the mass term in the equation changes from 1 to 1/2, and the frequency is reduced by the square root of 2. In this discussion we have focussed on stretching vibrations, and it should be noted that bending vibrations may be treated in a similar fashion.

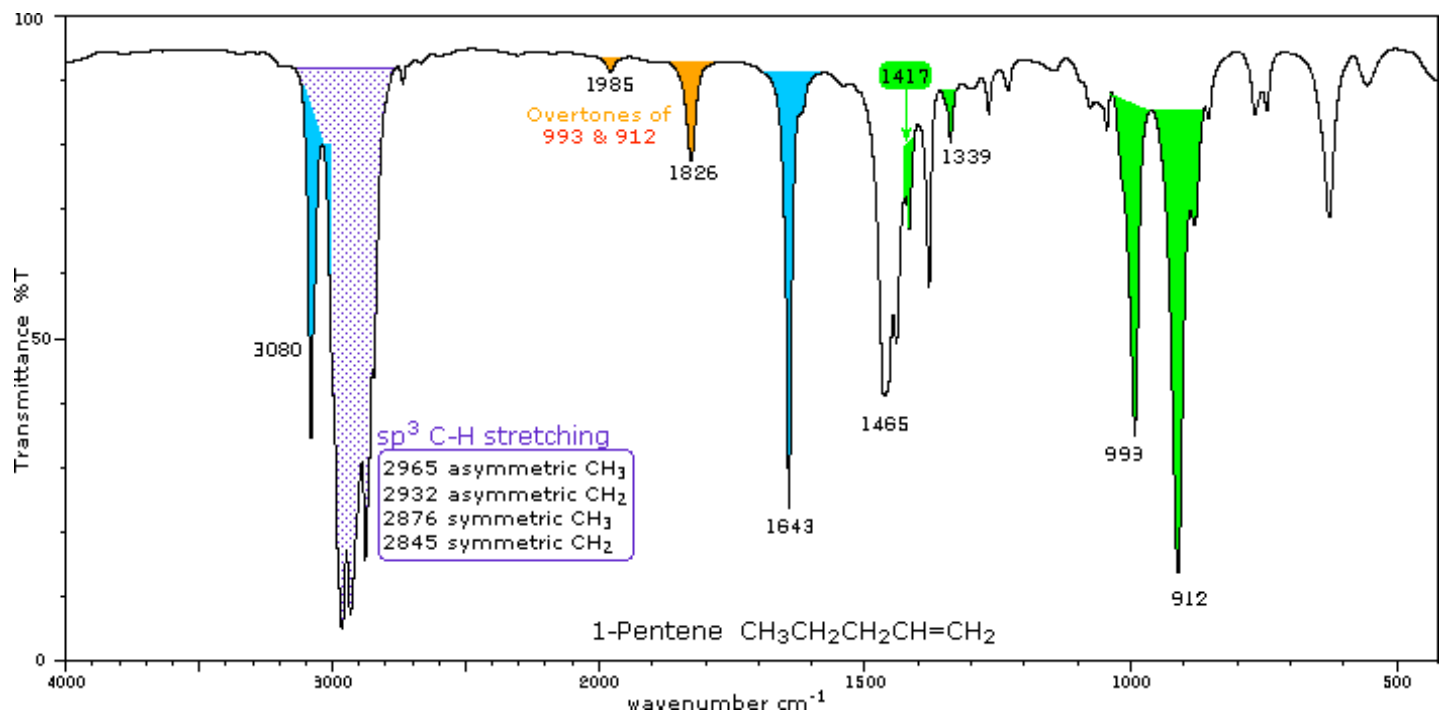
Not all molecular vibrations lead to observable infrared absorptions. In general, a vibration must cause a change in the charge distribution within a molecule to absorb infrared light. The greater the change in charge distribution, the stronger the absorption.

## Alkene Absorption Frequencies

The use of infrared spectroscopy for determining the substitution pattern of alkenes is illustrated by the following data, and the spectra examples underneath. Stretching absorptions are marked in blue, bending absorptions in green. Overtones are colored orange. The  $3000 \text{ cm}^{-1}$  separation between  $\text{sp}^2$  and  $\text{sp}^3$  C-H stretching modes is clearly evident. By clicking on any of the five structural names in the first column, a corresponding spectrum will be displayed beneath the table.

Alkene Substitution	Stretching Vibrations			Bending Vibrations		
	Range ( $\text{cm}^{-1}$ )	Intensity	Assignment	Range ( $\text{cm}^{-1}$ )	Intensity	Assignment
<a href="#">Mono-Alkyl (vinyl group)</a> $\text{R-CH=CH}_2$	3010-3040 & 3075-3095 1645	med med	=C-H (2-bands) C=C	905-920 & 985-1000 1280-1320 & 1410-1420	str & str med & med	=C-H bending
<a href="#">Di-Alkyl (cis)</a> $\text{RCH=CHR}$	3010-3040 1658	med med	=C-H C=C (symmetry reduces intensity)	680-730	str	=C-H bending
<a href="#">Di-Alkyl (trans)</a> $\text{RCH=CHR}$	3010-3040 1675	med med	=C-H C=C (symmetry)	960-970 & 1295-1310	str & med	=C-H bending

				reduces intensity)			
<u>Di-Alkyl (geminal)</u> $R_2C=CH_2$	3075-3095 1653	med med	=C-H C=C		885-895 & 1410-1420	both str	=C-H bending
<u>Tri-Alkyl</u> $R_2C=CHR$	3010-3040 1670	med med	=C-H C=C		790-840	str	=C-H bending



## Arene Absorption Frequencies

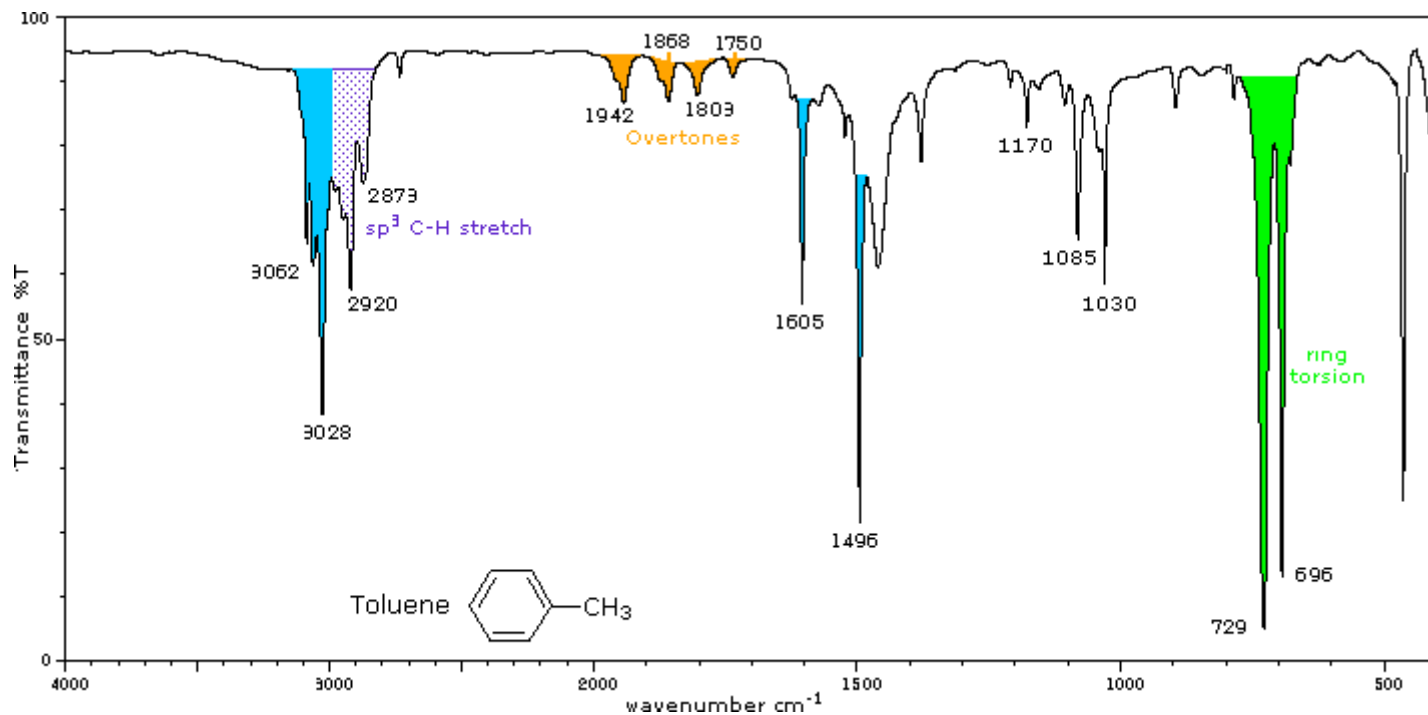
The use of infrared spectroscopy for determining the substituent pattern of substituted benzene rings is illustrated by the following data, and the spectra examples underneath. Stretching absorptions are marked in blue, bending absorptions in green. The 3000  $cm^{-1}$  separation between  $sp^2$  and  $sp^3$  C-H stretching modes is clearly evident. By clicking on any of the ten structural terms in the first column, a corresponding spectrum will be displayed beneath the table.

<u>Arene Substitution</u>	Stretching Vibrations			Bending Vibrations		
	Range ( $cm^{-1}$ )	Intensity	Assignment	Range ( $cm^{-1}$ )	Intensity	Assignment
<u>Mono-Alkyl</u> ( $R-C_6H_5$ )	3000-3070 1500-1600	med med-var	C-H (2 or 3-bands) C=C (ring, 2 or 3-bands)	730-770 & 680-720 950-1225 (2 or 3 bands)	str & str wk & sharp	=C-H bending (out-of-plane) (in-plane & ring torsion)
<u>Di-Alkyl</u> ( $R_2C_6H_4$ )	3000-3070 1500-1600 1500-1600 1500-1600	med med med	C-H (2 or 3-bands) C=C (ring, 2 or 3-bands) C=C (ring, 2 or 3-bands) C=C (ring, usually 2-bands)	735-770 685-720 & 750-810 & 810-900 800-860	str str & str & med str	C-H bending (out-of-plane) & ring torsion (esp. meta)
<u>ortho</u>						
<u>meta</u>						
<u>para</u>						



Tri-Alkyl ( $R_3C_6H_3$ )  <a href="#">1,2,3-</a> <a href="#">1,2,4-</a> <a href="#">1,3,5-</a>	3000-3070	med		C-H (2 or 3-bands)			
	1500-1600		med med med	C=C (ring, 2 or 3-bands)	685-720 & 750-810	med & str str & med med & str	=C-H bending (out-of-plane) & ring torsion (esp. sym. subst.)
	1500-1600		med	C=C (ring, 2 or 3-bands)	800-860 & 820-900		
Tetra-Alkyl ( $R_4C_6H_2$ )  <a href="#">1,2,3,4-</a> <a href="#">1,2,3,5-</a> <a href="#">1,2,4,5-</a>	3000-3070	med		C-H (2 or 3-bands)			
	1500-1600		med med med	C=C (ring, 2 or 3-bands)	800-840 840-880 840-880	str str str	=C-H bending (out-of-plane)
	1500-1600		med	C=C (ring, usually 2-bands)			
Penta-Alkyl ( $R_5C_6H$ )	3010-3040 1670	med med		=C-H C=C	840-880	str	=C-H bending (out-of-plane)

Several sharp, weaker absorptions in the 950 to 1250 range are due to in-plane C-H bending. These are not diagnostically useful, except for indicating a substituted benzene ring. Weak overtone and combination tone absorptions are found in the 1600-2000 region and are colored orange. These are sometimes used for identification, but are only seen in concentrated samples.

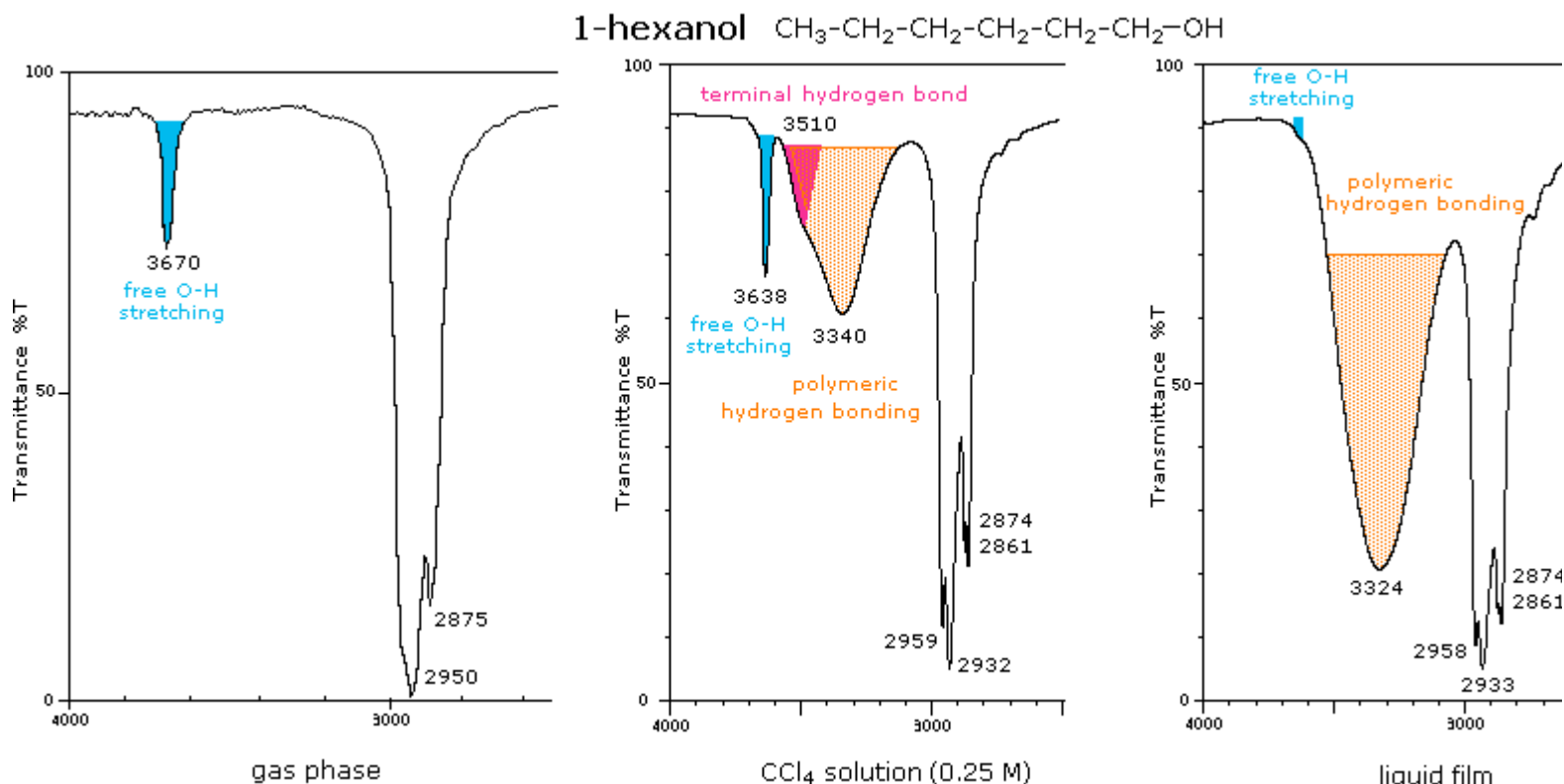


## Hydroxyl and Amino Groups

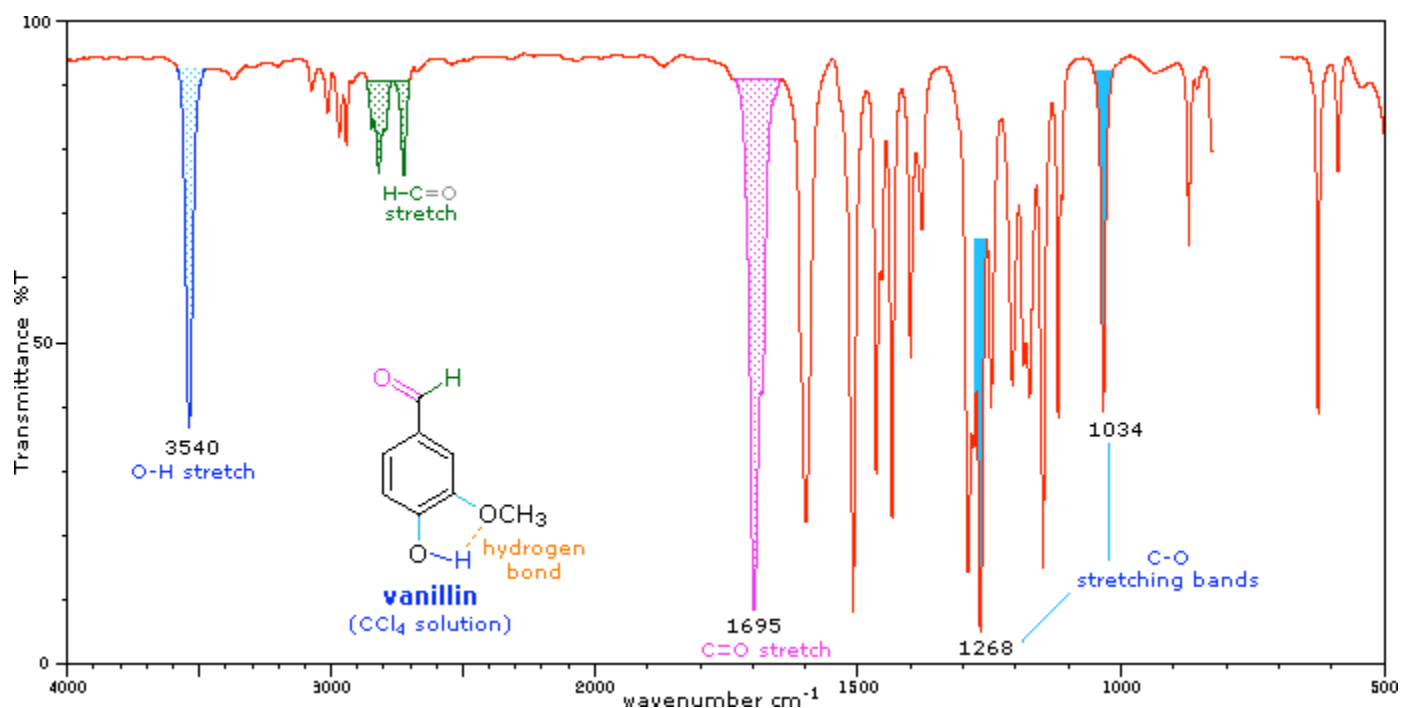
### 1. Alcohols and Phenols

The O-H stretching absorption of the hydroxyl group is sensitive to [hydrogen bonding](#). In the gas phase and in dilute  $CCl_4$  solution (0.01 M) small to moderate sized alcohols exhibit a sharp absorption in the 3620 to 3670  $cm^{-1}$  region. In more concentrated solution, or as a pure liquid, hydrogen bonding of the hydroxyl groups to each other occurs, and this lowers and broadens the stretching frequencies of the participating O-H bonds. This change is illustrated below for 1-

hexanol. The O-H stretching absorption is exclusively monomeric in the gas phase, but in moderately dilute  $\text{CCl}_4$  solution both monomeric and hydrogenbonded absorptions are evident. Dimeric clusters shift the absorption frequency to  $3500\text{ cm}^{-1}$ , but polymeric associations are shifted further,  $3200$  to  $3500\text{ cm}^{-1}$ , and broadened. In the pure liquid the polymeric absorption band dominates this region of the spectrum. Note that the typical C-H stretching absorptions near  $2950$  and  $2870\text{ cm}^{-1}$  remain relatively unchanged for the three samples shown below.

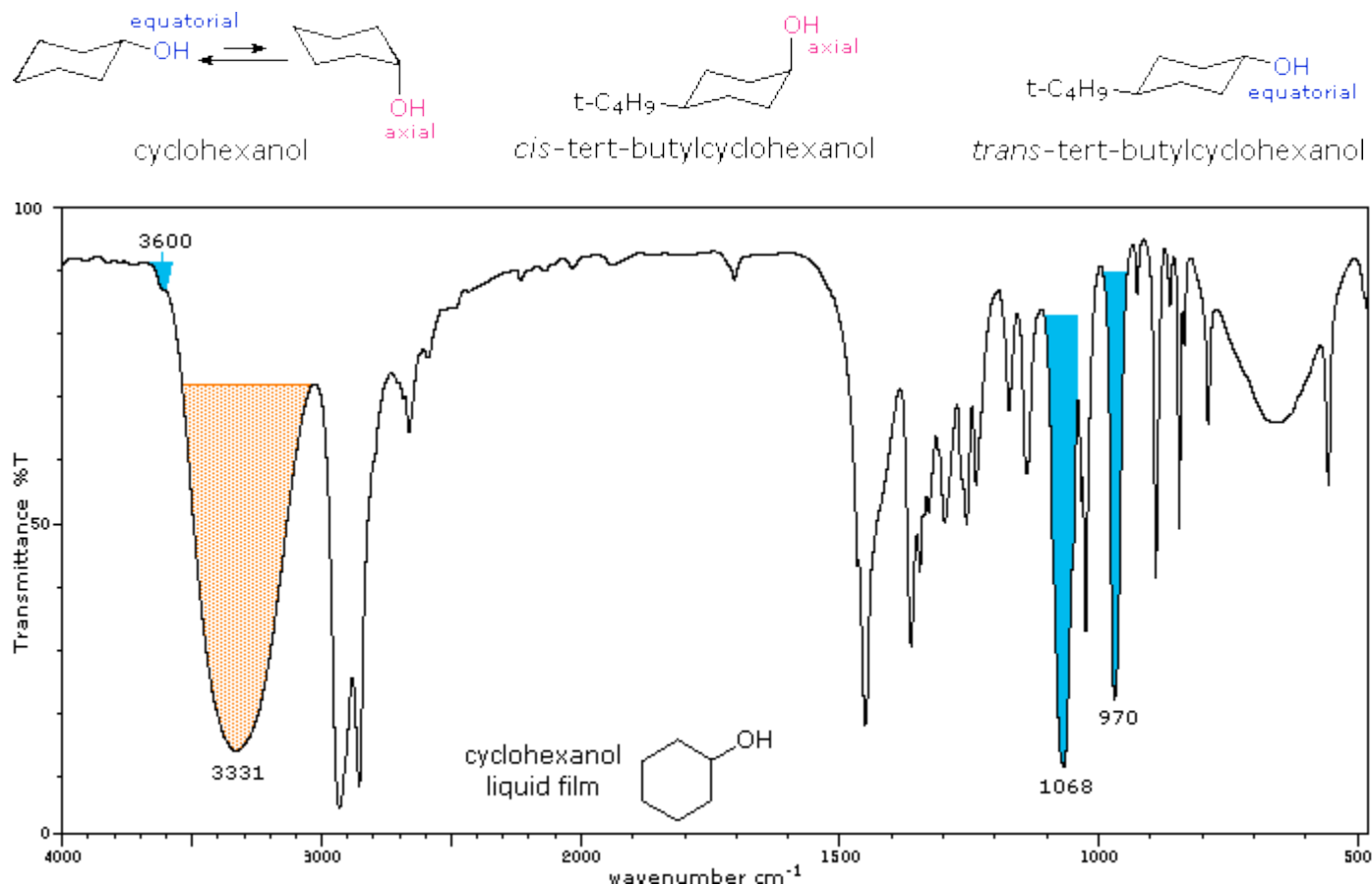


Molecules having both hydrogen bonding donors and acceptors located so that intramolecular hydrogen bonding is favored, display slightly broadened O-H stretching absorption in the  $3500$  to  $3600\text{ cm}^{-1}$  range. The spectrum of vanillin shows this for the phenolic hydroxyl, which is hydrogen bonded to the adjacent ether oxygen.



Alcohols also display C-O stretching absorption at  $970$  to  $1250\text{ cm}^{-1}$ . This is marked in the preceding spectrum along with the ether C-O absorptions; and the following spectrum of cyclohexanol shows two such absorptions, coming from the equatorial and axial conformers. It is possible to assign each of these absorptions to a specific conformer by examining

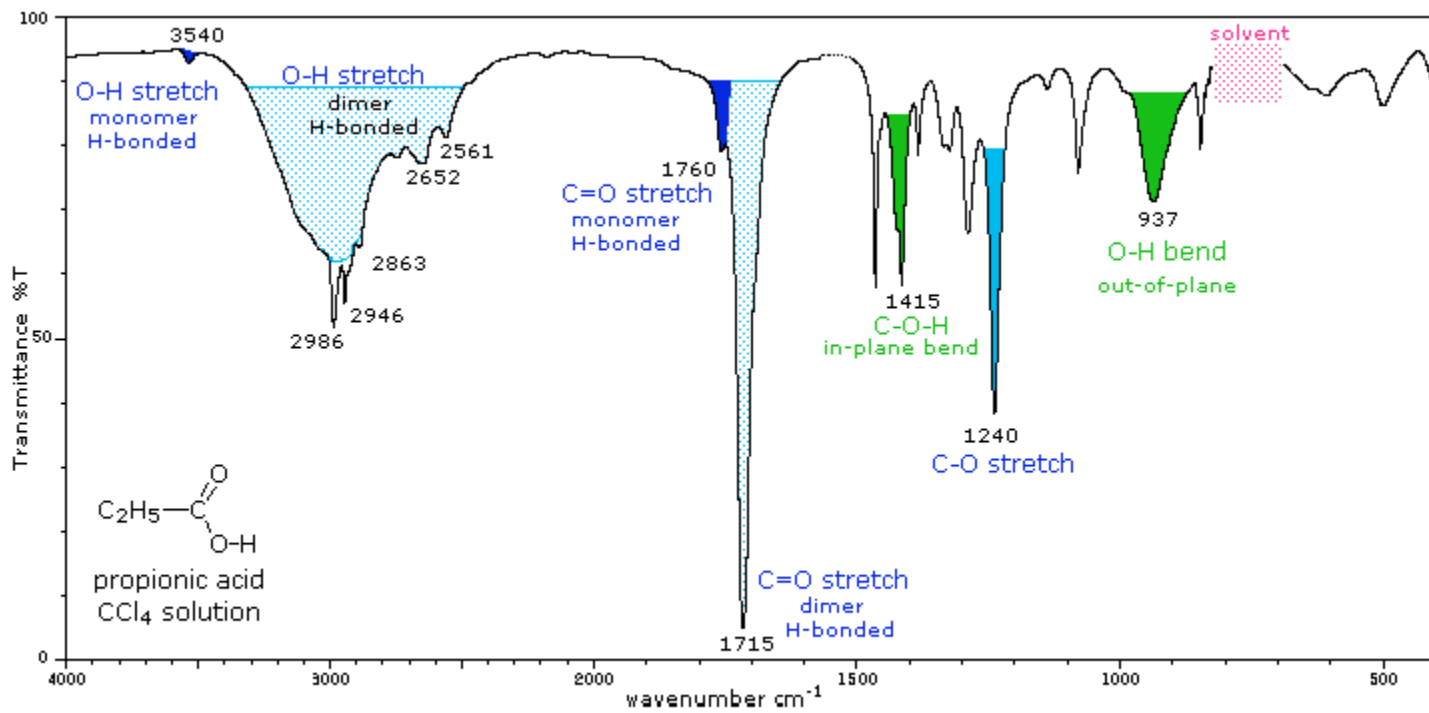
the spectra of the corresponding cis and trans-4-tert-butylcyclohexanol configurational isomers ([click on the appropriate structure or name to see its spectrum replace that of cyclohexanol](#)). As expected, the equatorial C-O absorption at 1068 is relatively stronger than the axial C-O absorption at 970, but a reliable analysis of the data requires knowledge of the molar absorptivities of each of the stretching vibrations.



Some interesting features are also present in the O-H stretching absorptions of these compounds. The equatorial -OH group in the trans-isomer appears as a typical polymeric hydrogen bonded envelope near 3300 cm<sup>-1</sup> (shaded orange). A smaller peak at higher frequency (light blue) is presumed due to less associated clusters. The cis isomer, on the other hand, has a more hindered hydroxyl group which adopts some conformations having smaller hydrogen bonded clusters. The O-H stretching absorption band is therefore split into two (shaded orange and blue).

## 2. Carboxylic Acids

The carboxyl group is associated with two characteristic infrared stretching absorptions which change markedly with hydrogen bonding. The spectrum of a CCl<sub>4</sub> solution of propionic acid (propanoic acid), shown below, is illustrative. Carboxylic acids exist predominantly as [hydrogen bonded dimers](#) in condensed phases. The O-H stretching absorption for such dimers is very strong and broad, extending from 2500 to 3300 cm<sup>-1</sup>. This absorption overlaps the sharper C-H stretching peaks, which may be seen extending beyond the O-H envelope at 2990, 2950 and 2870 cm<sup>-1</sup>. The smaller peaks protruding near 2655 and 2560 are characteristic of the dimer. In ether solvents a sharper hydrogen bonded monomer absorption near 3500 cm<sup>-1</sup> is observed, due to competition of the ether oxygen as a hydrogen bond acceptor. The carbonyl stretching frequency of the dimer is found near 1710 cm<sup>-1</sup>, but is increased by 25 cm<sup>-1</sup> or more in the monomeric state. Other characteristic stretching and bending absorptions are marked in the spectrum.



The buttons beneath the spectrum will display spectra for propionic acid as a pure liquid and in the gas phase. The absorptions in the liquid film spectrum are stronger and broader than those in solution, but are in general the same. The broad O-H bend at 935  $\text{cm}^{-1}$ , for example is typical of the dimeric species. The gas phase spectrum is remarkable for the absence of dimer absorptions, although at higher pressures these are present.

### 3. Amines

The infrared spectrum of aniline is shown beneath the following table. By clicking the "Toggle 1°-Amine" button, solution and gas phase spectra will be displayed sequentially, along with the spectrum of cyclohexylamine, an aliphatic 1°-amine. The "Toggle 2°-Amine" and "Toggle 3°-Amine" buttons display illustrative spectra for these classes of amines. Some of the characteristic absorptions for C-H stretching and aromatic ring substitution are also marked, but not colored.

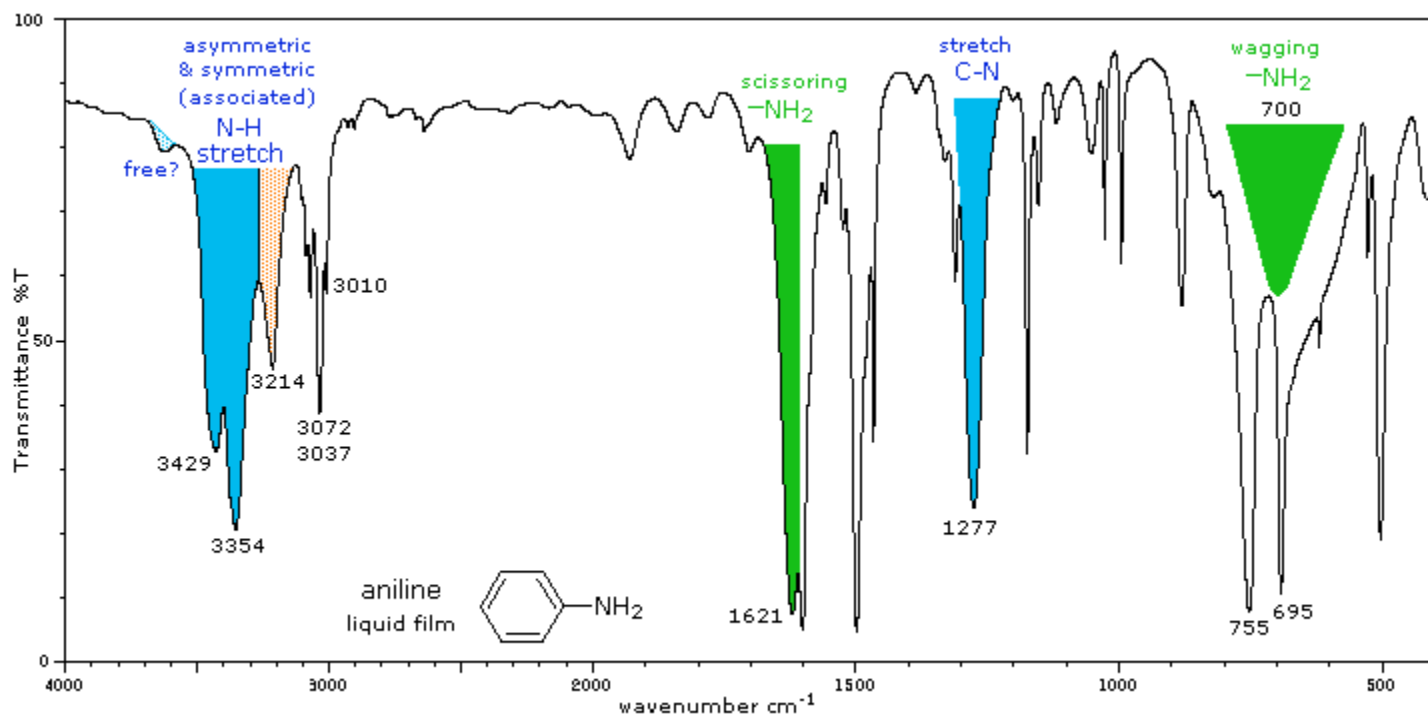
Amine Class	Stretching Vibrations	Bending Vibrations
Primary (1°)	<p>The N-H stretching absorption is less sensitive to hydrogen bonding than are O-H absorptions. In the gas phase and in dilute <math>\text{CCl}_4</math> solution free N-H absorption is observed in the 3400 to 3500 <math>\text{cm}^{-1}</math> region. Primary aliphatic amines display two well-defined peaks due to asymmetric (higher frequency) and symmetric N-H stretching, separated by 80 to 100 <math>\text{cm}^{-1}</math>. In aromatic amines these absorptions are usually 40 to 70 <math>\text{cm}^{-1}</math> higher in frequency. A smaller absorption near 3200 <math>\text{cm}^{-1}</math> (shaded orange in the spectra) is considered to be the result of interaction between an overtone of the 1600 <math>\text{cm}^{-1}</math> band with the symmetric N-H stretching band.</p> <p>C-N stretching absorptions are found at 1200 to 1350 <math>\text{cm}^{-1}</math> for aromatic amines, and at 1000 to 1250 <math>\text{cm}^{-1}</math> for aliphatic amines.</p>	<p>Strong in-plane <math>\text{NH}_2</math> scissoring absorptions at 1550 to 1650 <math>\text{cm}^{-1}</math>, and out-of-plane wagging at 650 to 900 <math>\text{cm}^{-1}</math> (usually broad) are characteristic of 1°-amines.</p>

**Secondary (2°)** Secondary amines exhibit only one absorption near  $3420\text{ cm}^{-1}$ . Hydrogen bonding in concentrated liquids shifts these absorptions to lower frequencies by about  $100\text{ cm}^{-1}$ . Again, this absorption appears at slightly higher frequency when the nitrogen atom is bonded to an aromatic ring. The C-N absorptions are found in the same range,  $1200\text{ to }1350\text{ cm}^{-1}$  (aromatic) and  $1000\text{ to }1250\text{ cm}^{-1}$  (aliphatic) as for  $1^\circ$ -amines.

A weak N-H bending absorption is sometimes visible at  $1500\text{ to }1600\text{ cm}^{-1}$ . A broad wagging absorption at  $650\text{ to }900\text{ cm}^{-1}$  may be discerned in liquid film samples.

**Tertiary (3°)** No N-H absorptions. The C-N absorptions are found in the same range,  $1200\text{ to }1350\text{ cm}^{-1}$  (aromatic) and  $1000\text{ to }1250\text{ cm}^{-1}$  (aliphatic) as for  $1^\circ$ -amines.

Aside from the C-N stretch noted on the left, these compounds have spectra characteristic of their alkyl and aryl substituents.



[Toggle 1°-Amines](#)

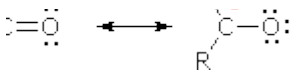
[Toggle 2°-Amines](#)

[Toggle 3°-Amines](#)

Amines are bases, and their corresponding conjugate acid "onium" salts are often the form in which they are commonly encountered. These derivatives display strong, broad N-H stretching absorptions in the  $2250\text{ to }3000\text{ cm}^{-1}$  region, with  $1^\circ$ -ammonium salts absorbing at the high frequency end, where overlap with C-H absorption occurs. Salts of  $1^\circ$  and  $2^\circ$ -amines also exhibit strong bending absorptions in the range of  $1500\text{ to }1600\text{ cm}^{-1}$ , but the corresponding band from  $3^\circ$ -ammonium salts is relatively weak.

## Carbonyl Compounds

### 1. Aldehydes and Ketones

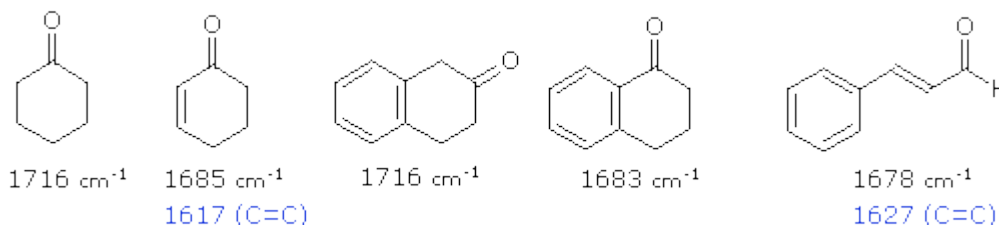


For simple aldehydes and ketones the stretching vibration of the carbonyl group gives rise to a strong and distinctive infrared absorption at  $1710$  to  $1740\text{ cm}^{-1}$ . As noted in the diagram on the right, the dipole moment of this function is increased on stretching (single bond character is greater), and this results in a strong absorption. Since alkyl substituents stabilize the carbocation character of the ionic contributor, ketone carbonyls have slightly lower stretching frequencies,  $1715 \pm 7\text{ cm}^{-1}$ , compared with aldehydes,  $1730 \pm 7\text{ cm}^{-1}$ . The values cited here are for pure liquid or  $\text{CCl}_4$  solution spectra. Hydrogen bonding solvents will lower these frequencies by  $15$  to  $20\text{ cm}^{-1}$ .

### Three factors are known to perturb the carbonyl stretching frequency:

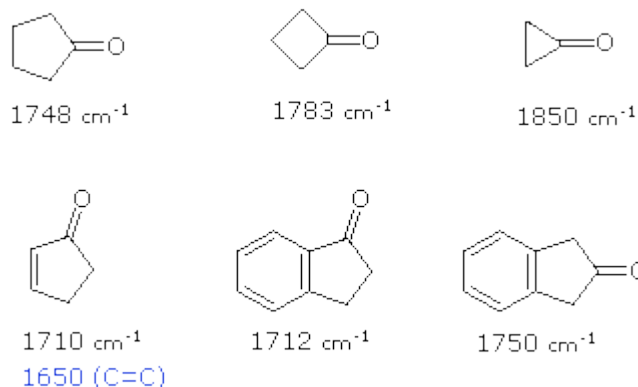
#### 1. Conjugation with a double bond or benzene ring lowers the stretching frequency.

The  $30$  to  $40\text{ cm}^{-1}$  decrease in frequency is illustrated by the following examples. The stretching frequency of the conjugated double bond is also lowered (blue notation) and may be enhanced in intensity. The cinnamaldehyde example (far right) shows that extended conjugation further lowers the absorption frequency, although not to the same degree.



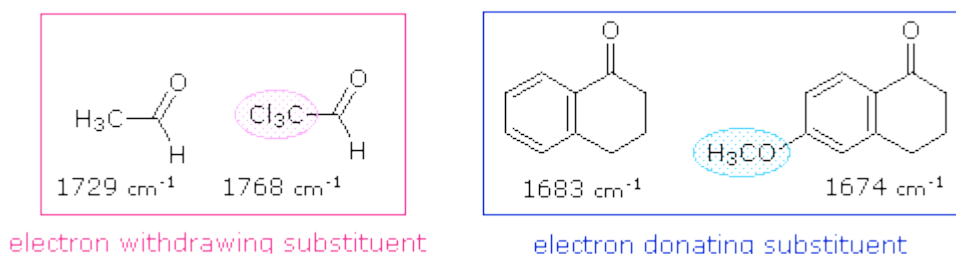
#### 2. Incorporation of the carbonyl group in a small ring (5, 4 or 3-membered), raises the stretching frequency.

The increase in frequency ranges from  $30$  to  $45\text{ cm}^{-1}$  for a 5-membered ring, to  $50$  to  $60\text{ cm}^{-1}$  for a 4-membered ring, and nearly  $130\text{ cm}^{-1}$  for a 3-membered ring. This shift also occurs in the presence of the previous conjugative lowering of the stretching absorption. Examples of this effect are shown below.



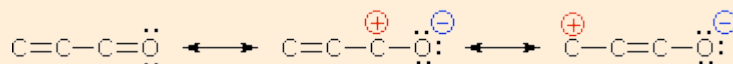
#### 3. Changing an alkyl substituent of a ketone for an electron releasing or withdrawing group.

This effect, which may shift the carbonyl stretching frequency up or down, is particularly important when an alkyl substituent is replaced by a hetero atom such as N, O or X (halogen). Such cases will be discussed as carboxylic acid derivatives. The following examples show the influence of a strongly electron withdrawing group ( $-\text{CCl}_3$ ) and a conjugatively electron donating group ( $-\text{OCH}_3$ ).



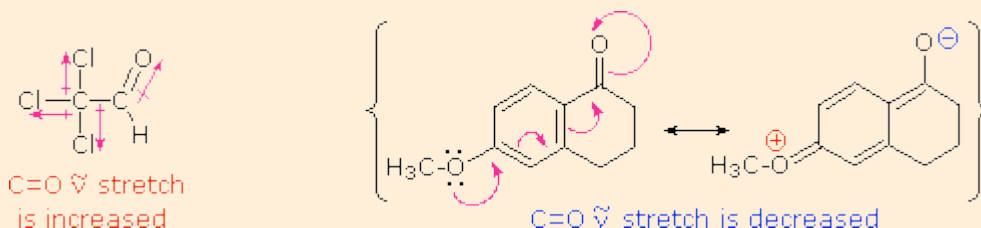
To understand the functioning of these factors consider the following analyses:

1. Conjugation extends the dipolar character of the carbonyl group to the double bond (or aromatic ring) so that the beta-carbon atom shares the positive character of the carbonyl carbon. As illustrated by the following resonance equation, this not only explains [conjugate addition reactions](#) of nucleophiles, but also suggests that the carbonyl double bond has slightly more single bond character than does an unconjugated function. The bond energy (and force constant) of the conjugated C=O group is correspondingly reduced, and this results in a lower stretching frequency.

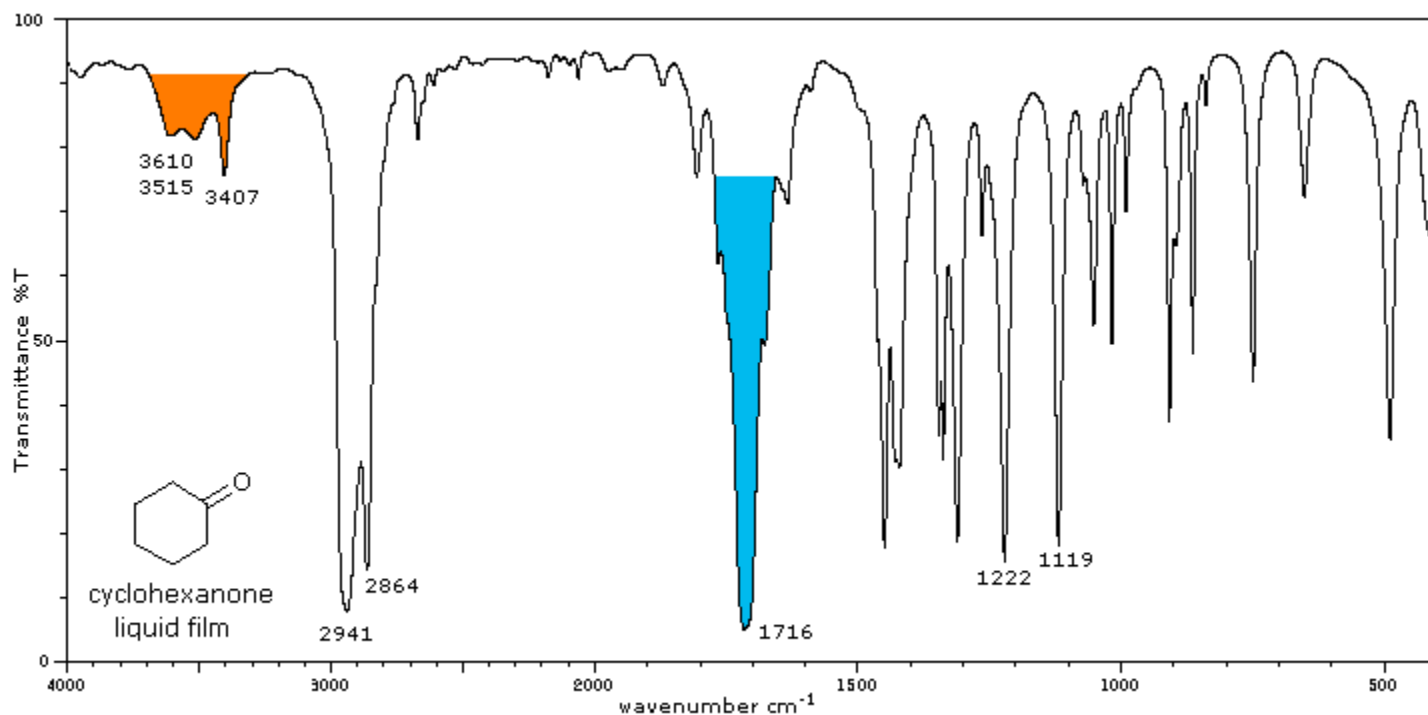


2. Under ideal conditions the carbon atom of a carbonyl group is essentially  $sp^2$  hybridized, which implies that the bond angles will be  $120^\circ$  and the C-O sigma bond has 33% s-character. If this group is incorporated in a small ring, the C-CO-C bond angle is reduced to  $108^\circ$  (5-membered ring),  $90^\circ$  (4-membered ring) or  $60^\circ$  (3-membered ring). When this happens, the C-C bonds of the ring assume greater p-character and the C-O sigma bond has correspondingly greater s-character. The double bond of the carbonyl group is therefore shorter and stronger, and exhibits a larger stretching frequency.

3. Electron donating substituents on the carbonyl group stabilize the ionic resonance contributor, and increase the single bond character of the C=O bond. The stretching frequency is therefore decreased, as noted in the right hand example below. Electron withdrawing groups have an opposite influence, and increase the stretching frequency of the carbonyl group. Trichloroacetaldehyde (left below) provides a good example.



Starting with the spectrum of cyclohexanone, infrared spectra of six illustrative ketones will be displayed below on clicking the "[Toggle Spectra](#)" button. The difference between liquid film and solution spectra is shown for cyclohexanone, but all other compounds are examined as liquid films. The carbonyl stretching absorption is colored blue, and characteristic overtones near  $3400\text{ cm}^{-1}$ , which are only prominent in liquid phase spectra, are colored orange.



## 2. Carboxylic Acid Derivatives

The influence of heteroatom substituents on the reactivity of carbonyl functions toward nucleophiles was discussed earlier with respect to [carboxylic acid derivatives](#). A useful relationship exists between the reactivity of these derivatives and their carbonyl stretching frequencies. Thus, the very reactive acyl halides and anhydrides absorb at frequencies significantly higher than ketones, whereas the relatively unreactive amides absorb at lower frequencies. These characteristics are listed below.

Infrared spectra of many carboxylic acid derivatives will be displayed in the figure below the table by clicking the appropriate buttons presented there.

Carbonyl Derivative	Carbonyl Absorption	Comments
<b>Acyl Halides (RCOX)</b> X = F X = Cl X = Br	<b>C=O stretch</b> $1860 \pm 20 \text{ cm}^{-1}$ $1800 \pm 15$ $1800 \pm 15$	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones. In acyl chlorides a lower intensity shoulder or peak near $1740 \text{ cm}^{-1}$ is due to an overtone interaction.
<b>Acid Anhydride, (RCO)<sub>2</sub>O</b> acyclic 6-membered ring 5-membered ring	<b>C=O stretch (2 bands)</b> $1750 \text{ \& } 1820 \text{ cm}^{-1}$ $1750 \text{ \& } 1820$ $1785 \text{ \& } 1865$	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones. The two stretching bands are separated by $60 \pm 30 \text{ cm}^{-1}$ , and for acyclic anhydrides the higher frequency (asymmetric stretching) band is stronger than the lower frequency (symmetric) absorption. Cyclic anhydrides also display two carbonyl stretching absorptions, but the lower frequency band is the strongest. One or two -CO-O-CO- stretching bands are observed in the $1000 \text{ to } 1300 \text{ cm}^{-1}$ region.
<b>Esters &amp; Lactones (RCOOR')</b> esters 6-membered lactone	<b>C=O stretch</b> $1740 \text{ cm} \pm 10 \text{ cm}^{-1}$ $1740 \text{ cm} \pm 10$ $1765 \text{ cm} \pm 5$ $1840 \text{ cm} \pm 5$	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones Strong CO-O stretching absorptions (one or two) are found from $1150 \text{ to } 1250 \text{ cm}^{-1}$



5-membered lactone 4-membered lactone		
<b>Amides &amp; Lactams (RCONR<sub>2</sub>)</b> 1° & 2°-amides 3°-amides 6-membered lactams 5-membered lactams 4-membered lactams	<b>C=O bands</b> 1510 to 1700 cm <sup>-1</sup> (2 bands) 1650 ± 15 (one band) 1670 ± 10 (one band) 1700 ± 15 1745 ± 15	The effect of conjugation is much less than for aldehydes & ketones. The higher frequency absorption (1665 ± 30) is called the <b>Amide I band</b> . The lower frequency <b>Amide II band</b> (1620 ± 30 in 1° amides & 1530 ± 30 in 2° amides) is largely due to N-H bending trans to the carbonyl oxygen. In concentrated samples this absorption is often obscured by the stronger amide I absorption. Hydrogen bonded association shifts some of these absorptions, as well as the prominent N-H stretching absorptions. <b>N-H stretch:</b> 3170 to 3500 cm <sup>-1</sup> . Two bands for 1°-amides, one for 2°-amides.

