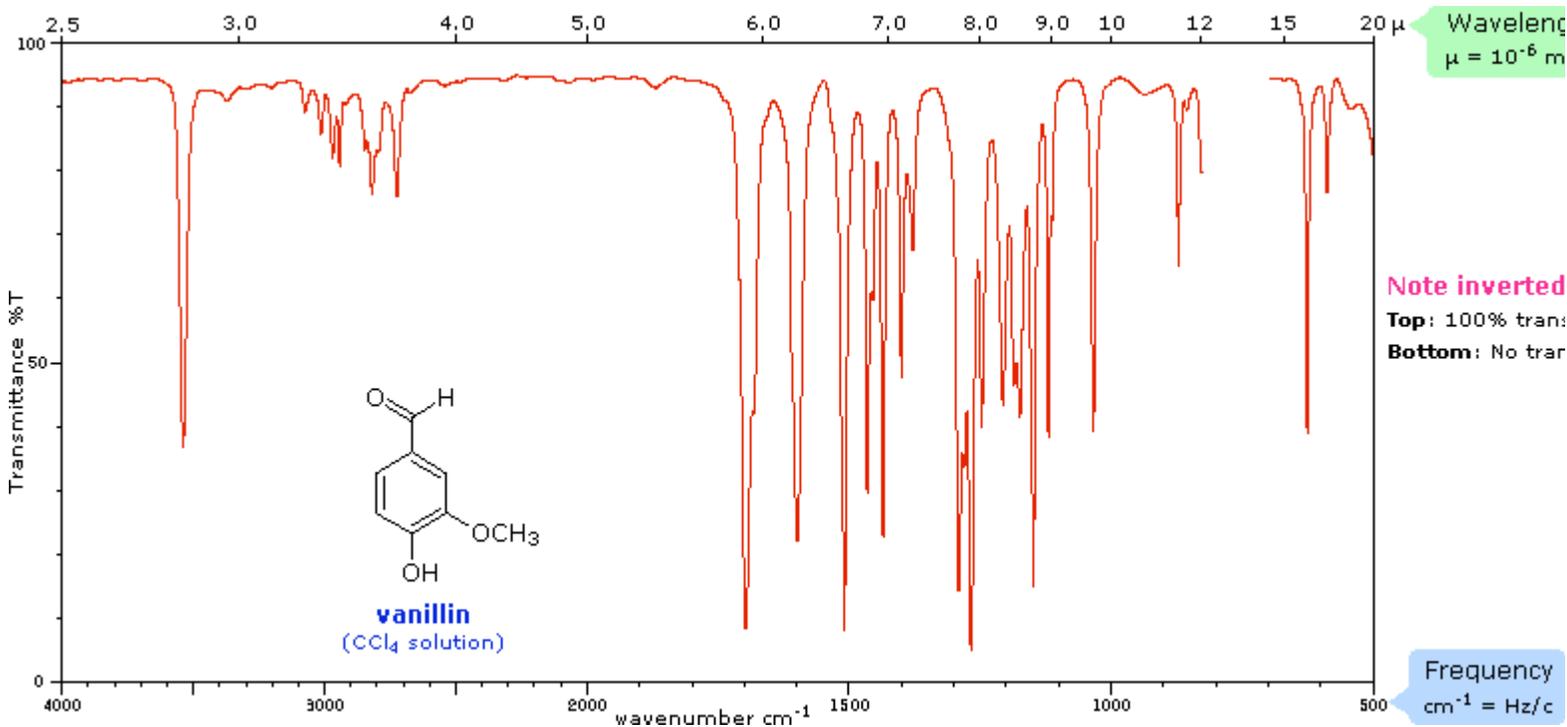# Infrared Spectroscopy

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 $1.9*10^{13}$ to $1.2*10^{14}$ Hz.
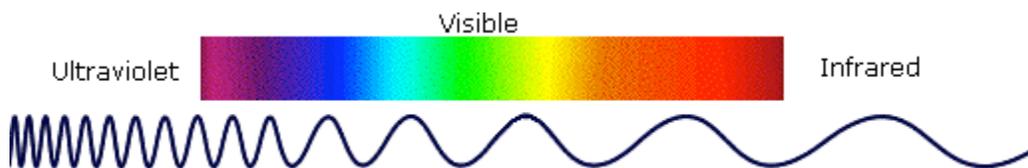
Photon energies associated with this part of the infrared (from 1 to 15 kcal/mole) are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups. The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, 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 cm^{-1} is due to solvent (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 (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*10^{10} cm (the distance covered by light in one second). Wavelength units are in micrometers, **microns (μ)**, 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, H$_2$C=O**
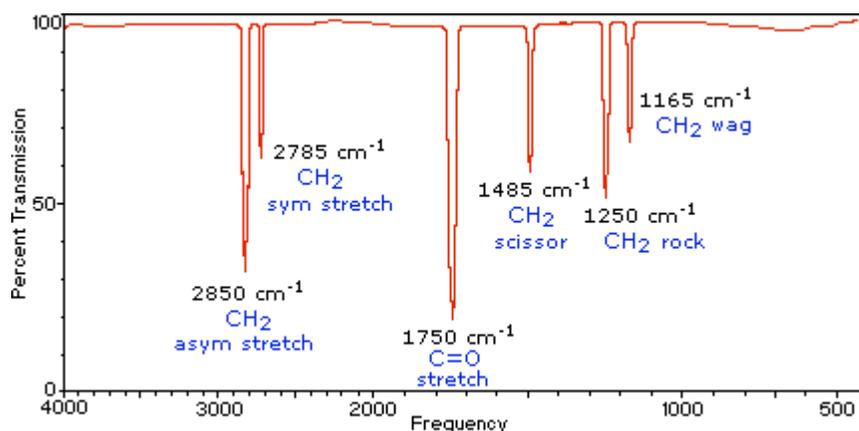
The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. For a more detailed discussion of these factors Click Here. In practice, infrared spectra do not normally display separate absorption signals for each of the 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 C=O bond stretching areusually 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

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 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 cm^{-1} region are usually due to stretching vibrations of diatomic units, and this is sometimes called the **group frequency** region.
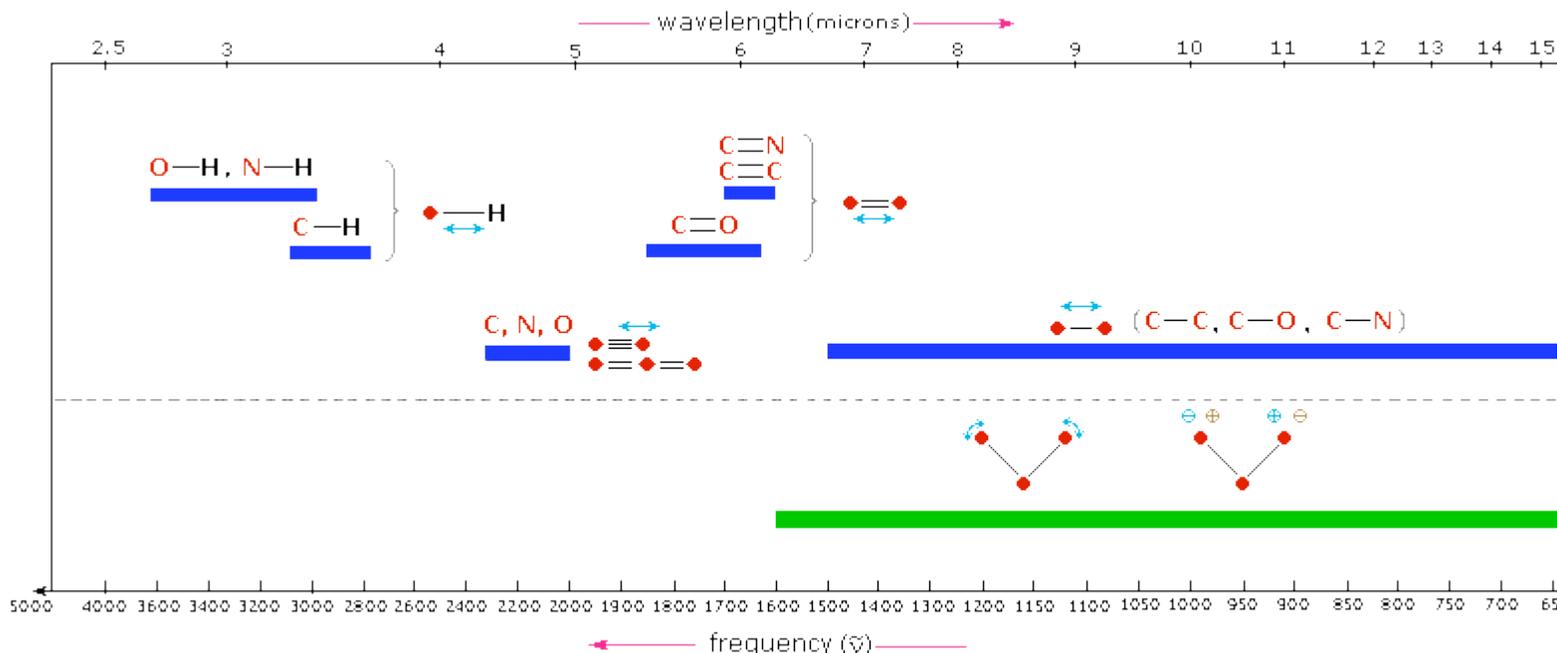
3. Group Frequencies

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 cm^{-1} is due to sp^3 C-H stretching; whereas, absorption above 3000 cm^{-1} is from sp^2 C-H stretching or sp C-H stretching if it is near 3300 cm^{-1}.

Typical Infrared Absorption Frequencies

Functional Class	Stretching Vibrations			Bending Vibrations		
	Range (cm^{-1})	Intensity	Assignment	Range (cm^{-1})	Intensity	Assignment
Alkanes	2850-3000	str	CH$_3$, CH$_2$ & CH 2 or 3 bands	1350-1470 1370-1390 720-725	med med wk	CH$_2$ & CH$_3$ deformation CH$_3$ deformation CH$_2$ rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H & =CH$_2$ (usually sharp) C=C (symmetry reduces intensity)	880-995 780-850	str med med	=C-H & =CH$_2$ (out-of-plane bending) cis-RCH=CHR

			C=C asymmetric stretch	675-730		
Alkynes	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Arenes	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
Alcohols & Phenols	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)
Amines	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$_2$ scissoring (1°-amines) NH$_2$ & N-H wagging (shifts on H-bonding)
Aldehydes & Ketones	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$_3$ bending α-CH$_2$ bending C-C-C bending

Carboxylic Acids & Derivatives	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
		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¡-amide) II band
						N-H (2¡-amide) II band

	1630-1695(amides)					
Nitriles	2240-2260	med	C≡N (sharp)			
Isocyanates,Isothiocyanates, Diimides, Azides & Ketenes	2100-2270	med	-N=C=O, -N=C=S -N=C=N-, -N₃, C=C=O			

To illustrate the usefulness of infrared absorption spectra, examples for five C_4H_8O 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.

cyclobutanol   2-butanone   ethyl vinyl ether   2-methyl-2-propen-1-ol   2-methylpropanal
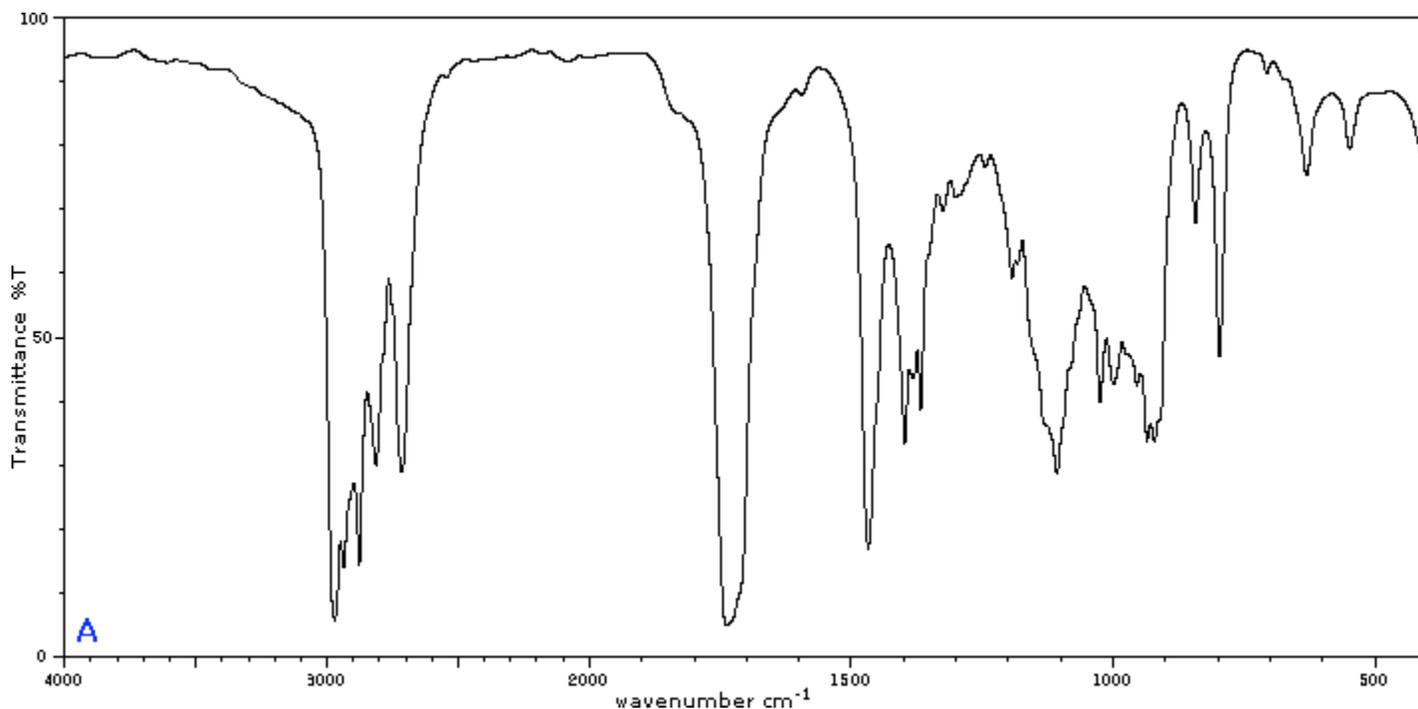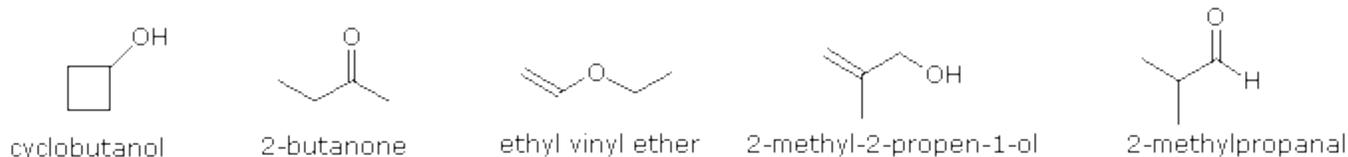
4. Other Functional Groups

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
Sulfur Functions	
S-H thiols	2550-2600 cm⁻¹ (wk & shp)
S-OR esters	700-900 (str)
S-S disulfide	500-540 (wk)

C=S thiocarbonyl	1050-1200 (str)

S=O 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)

Phosphorous Functions	
P-H phosphine	2280-2440 cm^{-1} (med & shp) 950-1250 (wk) P-H bending
(O=)PO-H phosphonic acid	2550-2700 (med)
P-OR esters	900-1050 (str)

P=O phosphine oxide
     phosphonate
     phosphate
     phosphoramide
	1100-1200 (str)
	1230-1260 (str)
	1100-1200 (str)
	1200-1275 (str)

Silicon Functions	
Si-H silane	2100-2360 cm^{-1} (str)
Si-OR	1000-11000 (str & brd)
Si-CH$_3$	1250± 10 (str & shp)
Oxidized Nitrogen Functions	

=NOH oxime
     O-H (stretch)
     C=N
     N-O
	
	3550-3600 cm^{-1} (str)
	1665± 15
	945± 15

N-O amine oxide
     aliphatic
     aromatic
	
	960± 20
	1250± 50

N=O 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

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

= frequency in 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 cm^{-1} for C-N, to 1660 cm^{-1} for C=N, to 2220 cm^{-1} for C≡N.

Approximate Infrared Stretching Frequencies				
B-H	**C-H**	**N-H**	**O-H**	**F-H**
2400 cm^{-1}	3000 cm^{-1}	3400 cm^{-1}	3600 cm^{-1}	4000 cm^{-1}
Al-H	**Si-H**	**P-H**	**S-H**	**Cl-H**
1750	2150	2350	2570	2890
	Ge-H	**As-H**	**Se-H**	**Br-H**
	2070	2150	2300	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 cm^{-1}, but the O-D equivalent is lowered to 2600 cm^{-1}. Since deuterium has a mass = 2, the mass term in the equation changes fron 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.
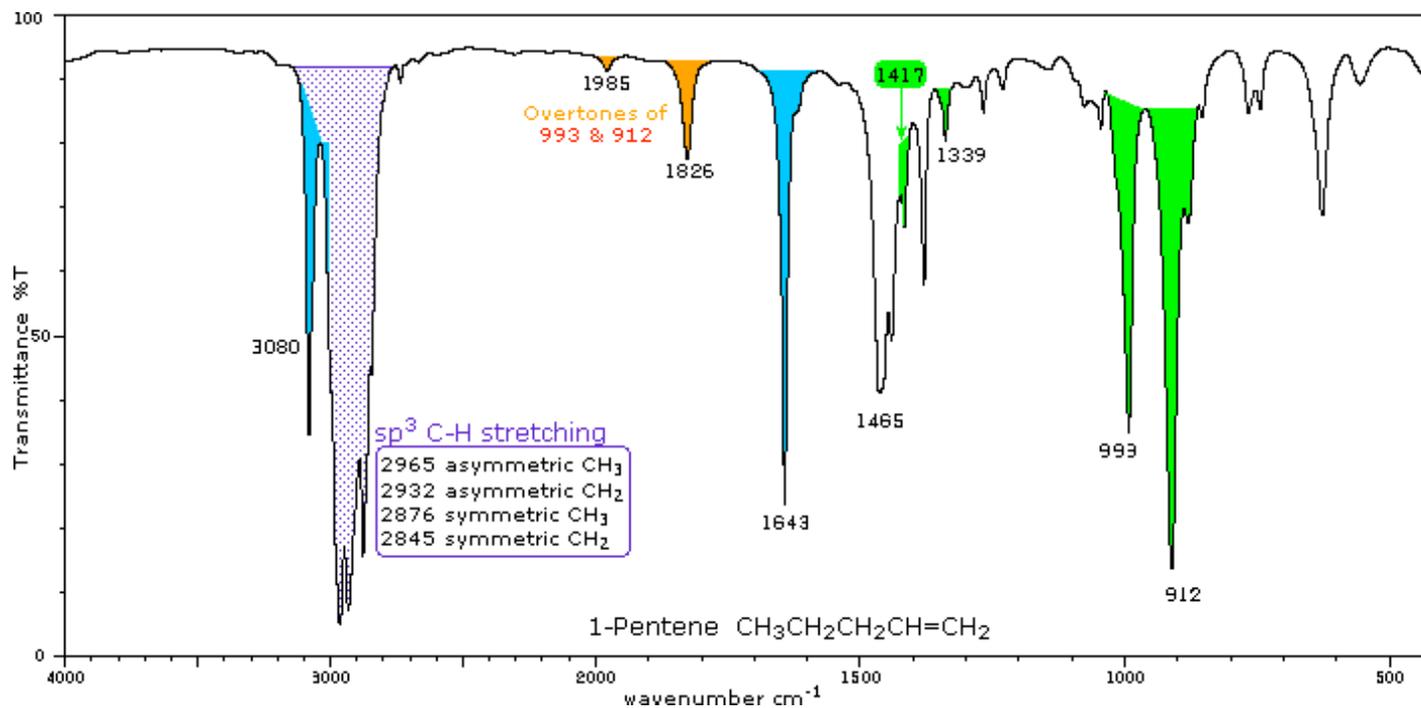
Not all molecular vibrations lead to observable infrared absorptions. In general, a vibration must cause a change in the charge distribution within a molecule to absorb infrared light. The greater the change in charge distribution, the stronger the absorption.

# 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 absprptions in green. Overtones are colored orange. The 3000 cm^{-1} separation between sp^2 and 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 (cm^{-1})	Intensity	Assignment	Range (cm^{-1})	Intensity	Assignment
Mono-Alkyl (vinyl group) 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
Di-Alkyl (cis) RCH=CHR	3010-3040 1658	med med	=C-H C=C (symmetry reduces intensity)	680-730	str	=C-H bending
Di-Alkyl (trans) RCH=CHR	3010-3040 1675	med med	=C-H C=C (symmetry	960-970 & 1295-1310	str & med	=C-H bending

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

(top row fragment: "reduces intensity)")

1-Pentene $CH_3CH_2CH_2CH=CH_2$

Spectrum labels: 3080; 1985; Overtones of 993 & 912; 1826; 1417?; 1339; 1465; 1643; 993; 912; sp³ C-H stretching: 2965 asymmetric CH₃, 2932 asymmetric CH₂, 2876 symmetric CH₃, 2845 symmetric CH₂

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 absprptions 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.

Arene Substitution	Stretching Vibrations			Bending Vibrations		
	Range (cm^{-1})	Intensity	Assignment	Range (cm^{-1})	Intensity	Assignment
Mono-Alkyl (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)
Di-Alkyl ($R_2C_6H_4$) ortho meta para	3000-3070 1500-1600 1500-1600 1500-1600	med 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)

Group							
Tri-Alkyl (R$_3$C$_6$H$_3$) 1,2,3- 1,2,4- 1,3,5-	3000-3070 1500-1600 1500-1600 1500-1600	med	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)	685-720 & 750-810 800-860 & 820-900 685-720 & 820-900	med & str str & med med & str	=C-H bending (out-of-plane) & ring torsion (esp. sym. subst.)
Tetra-Alkyl (R$_4$C$_6$H$_2$) 1,2,3,4- 1,2,3,5- 1,2,4,5-	3000-3070 1500-1600 1500-1600 1500-1600	med	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)	800-840 840-880 840-880	str str str	=C-H bending (out-of-plane)
Penta-Alkyl (R$_5$C$_6$H)	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.
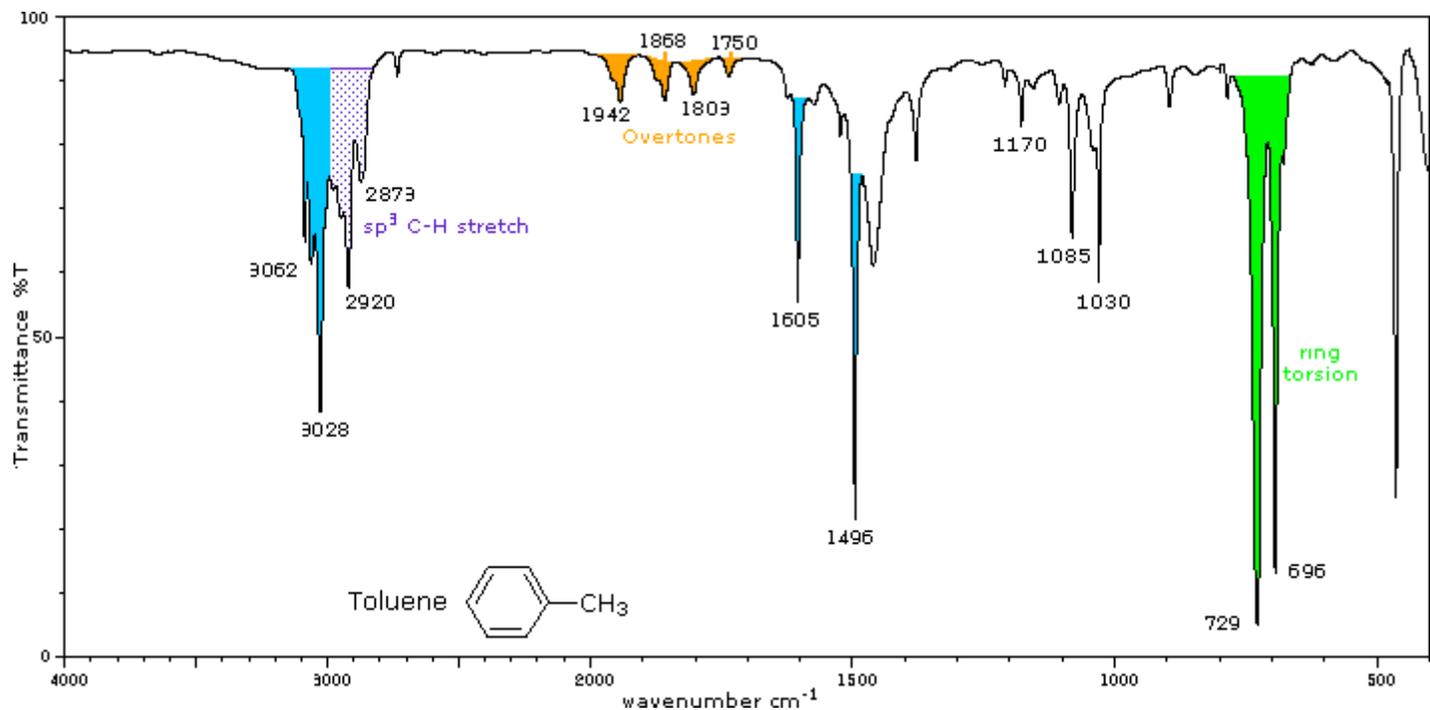

Hydroxyl and Amino Groups

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 CCl_4 solution both monomeric and hydrogenbonded absorptions are evident. Dimeric clusters shift the absorption frequency to 3500 cm⁻¹, but polymeric associations are shifted further, 3200 to 3500 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 cm⁻¹ remain relatively unchanged for the three samples shown below.

1-hexanol $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-OH$

gas phase

CCl₄ solution (0.25 M)

liquid film
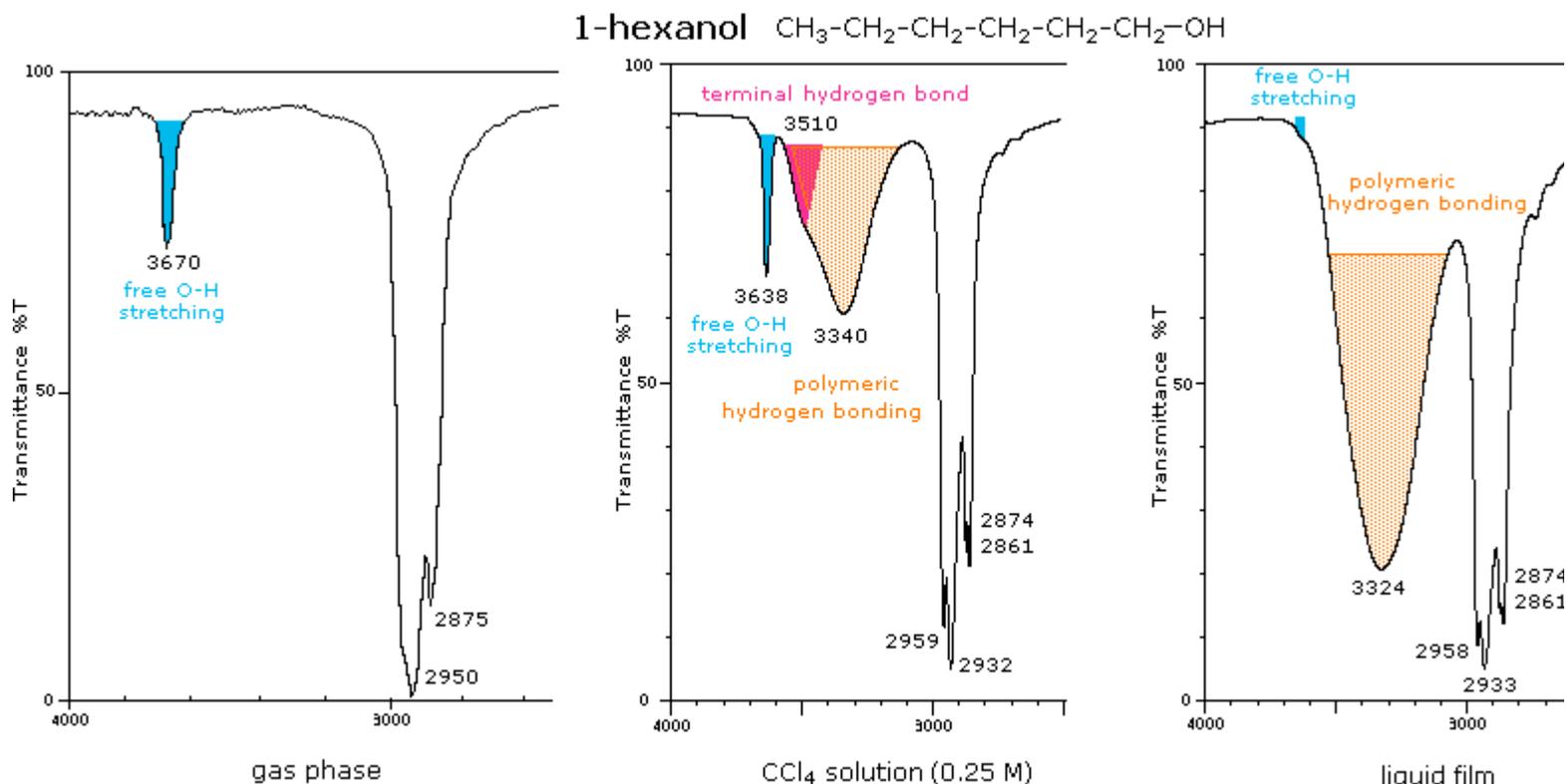
Molecules having both hydrogen bonding donors and acceptors located so that intramolecular hydrogen bonding is favored, display slightly broadened O-H stretching absorption in the 3500 to 3600 cm⁻¹ range. The spectrum of vanillin shows this for the phenolic hydroxyl, which is hydrogen bonded to the adjacent ether oxygen.
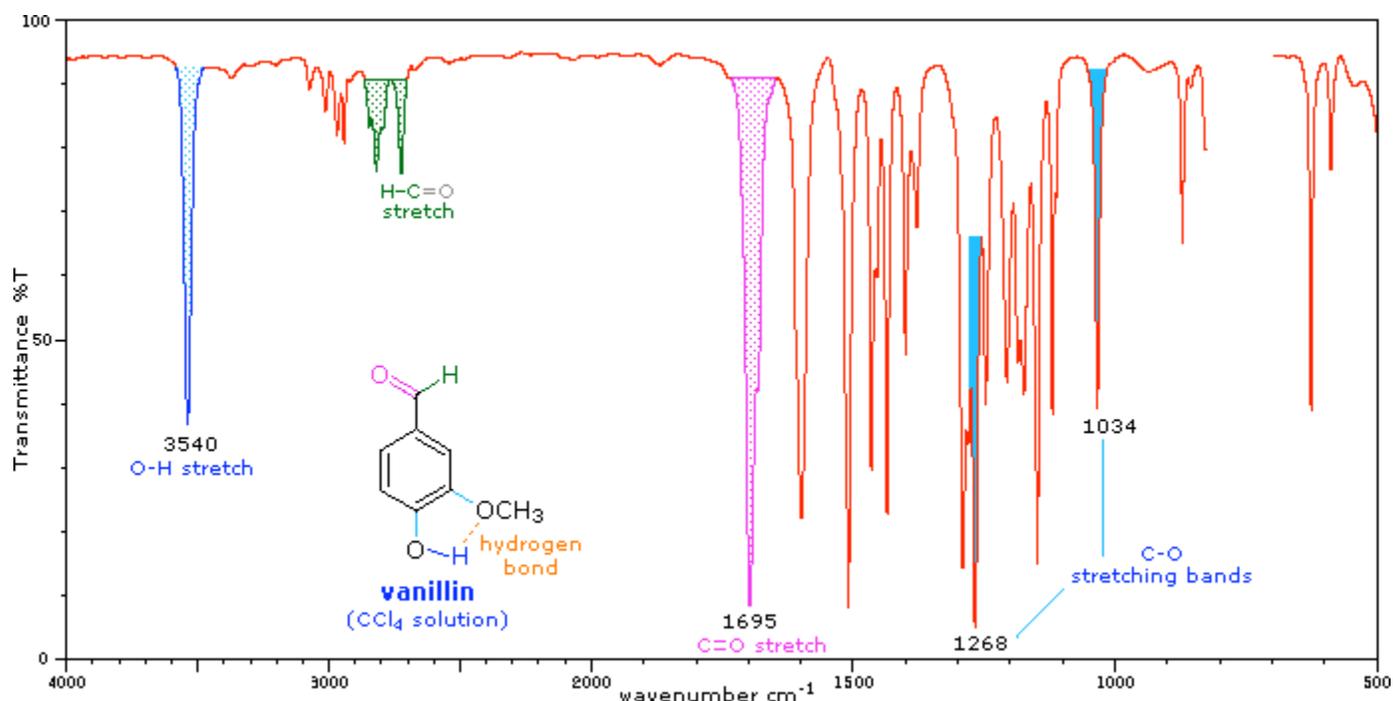
Alcohols also display C-O stretching absorption at 970 to 1250 ⁻¹. This is marked in the preceding spectrum along with the ether C-O absorptions; and the following spectrum of cyclohexanol shows two such absorptions, coming from the equatorial and axial conformers. It is possible to assign each of these absorptions to a specific conformer by examining
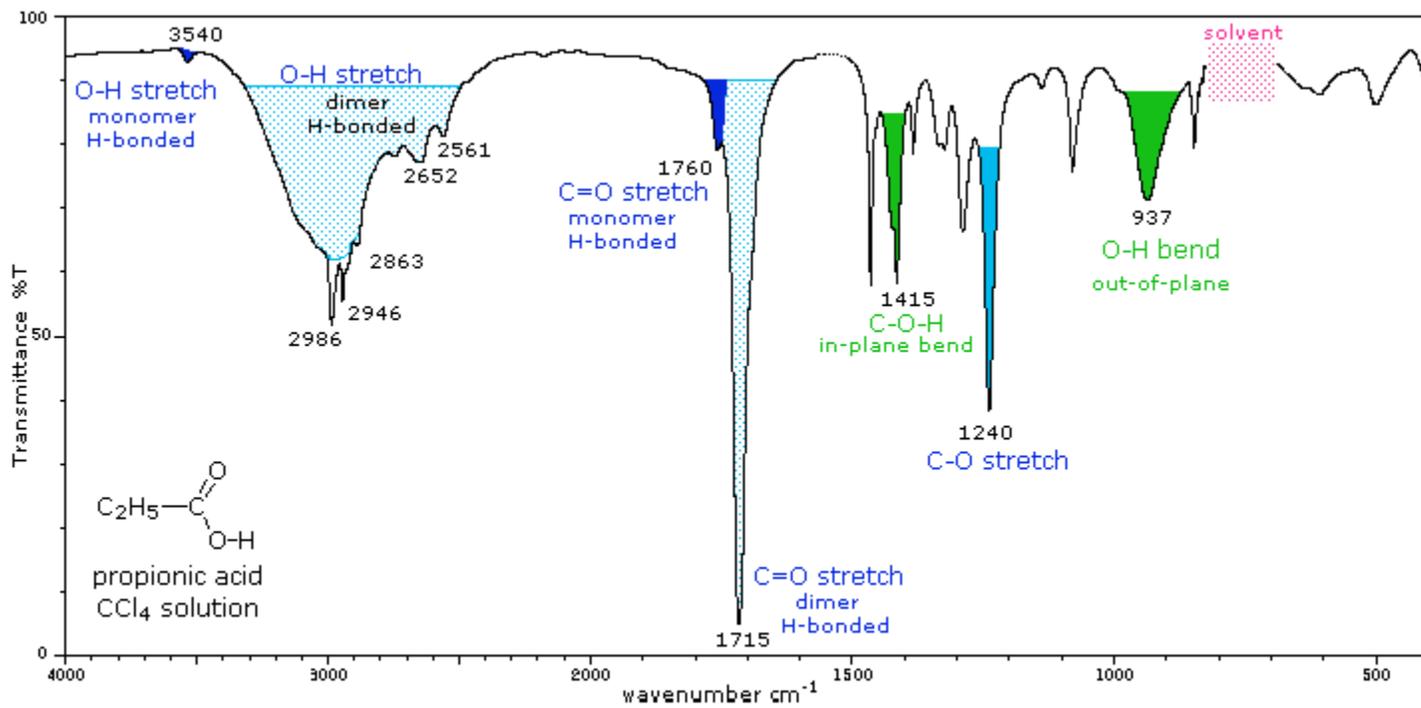
the spectra of the corresponding cis and trans-4-tert-butylcyclohexanol configurational isomers (click on the appropriate structure or name to see its spectrum replace that of cyclohexanol). As expected, the equatorial C-O absorption at 1068 is relatively stronger than the axial C-O absorption at 970, but a reliable analysis of the data requires knowledge of the molar absorptivities of each of the stretching vibrations.
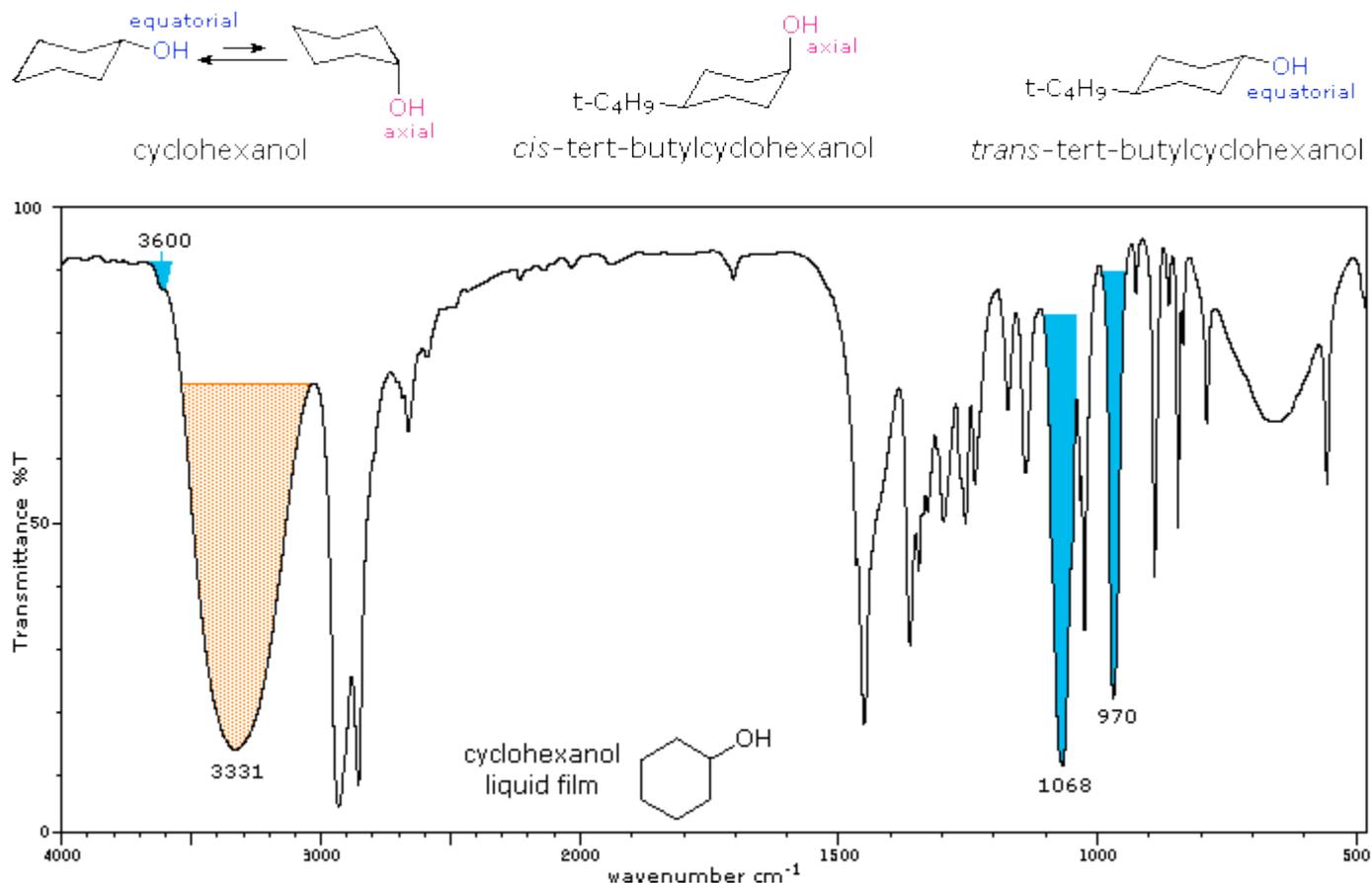
Some interesting features are also present in the O-H stretching absorptions of these compounds. The equatorial -OH group in the trans-isomer appears as a typical polymeric hydrogen bonded envelope near 3300 cm^{-1}(shaded orange). A smaller peak at higher frequency (light blue) is presumed due to less 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$_4$ 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^{-1}. 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^{-1}. 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^{-1} 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^{-1}, but is increased by 25 cm^{-1} or more in the monomeric state. Other characteristic stretching and bending absorptions are marked in the spectrum.

3540

O-H stretch
monomer
H-bonded

O-H stretch
dimer
H-bonded

2561
2652

2863

2946

2986

1760
C=O stretch
monomer
H-bonded

1715
C=O stretch
dimer
H-bonded

1415
C-O-H
in-plane bend

1240
C-O stretch

937
O-H bend
out-of-plane

solvent

C_2H_5-C
O
O-H

propionic acid
CCl$_4$ solution

Transmittance %T

wavenumber cm^{-1}

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

| Secondary (2°)	Secondary amines exhibit only one absorption near 3420 cm^{-1}. Hydrogen bonding in concentrated liquids shifts these absorptions to lower frequencies by about 100 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 to 1350 cm^{-1}(aromatic) and 1000 to 1250 cm^{-1} (aliphatic) as for 1°-amines.	A weak N-H bending absorption is sometimes visible at 1500 to 1600 cm^{-1}. A broad wagging absorption at 650 to 900 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 to 1350 cm^{-1} (aromatic) and 1000 to 1250 cm^{-1} (aliphatic) as for 1°-amines.	Aside from the C-N stretch noted on the left, these compounds have spectra characteristic of their alkyl and aryl substituents.
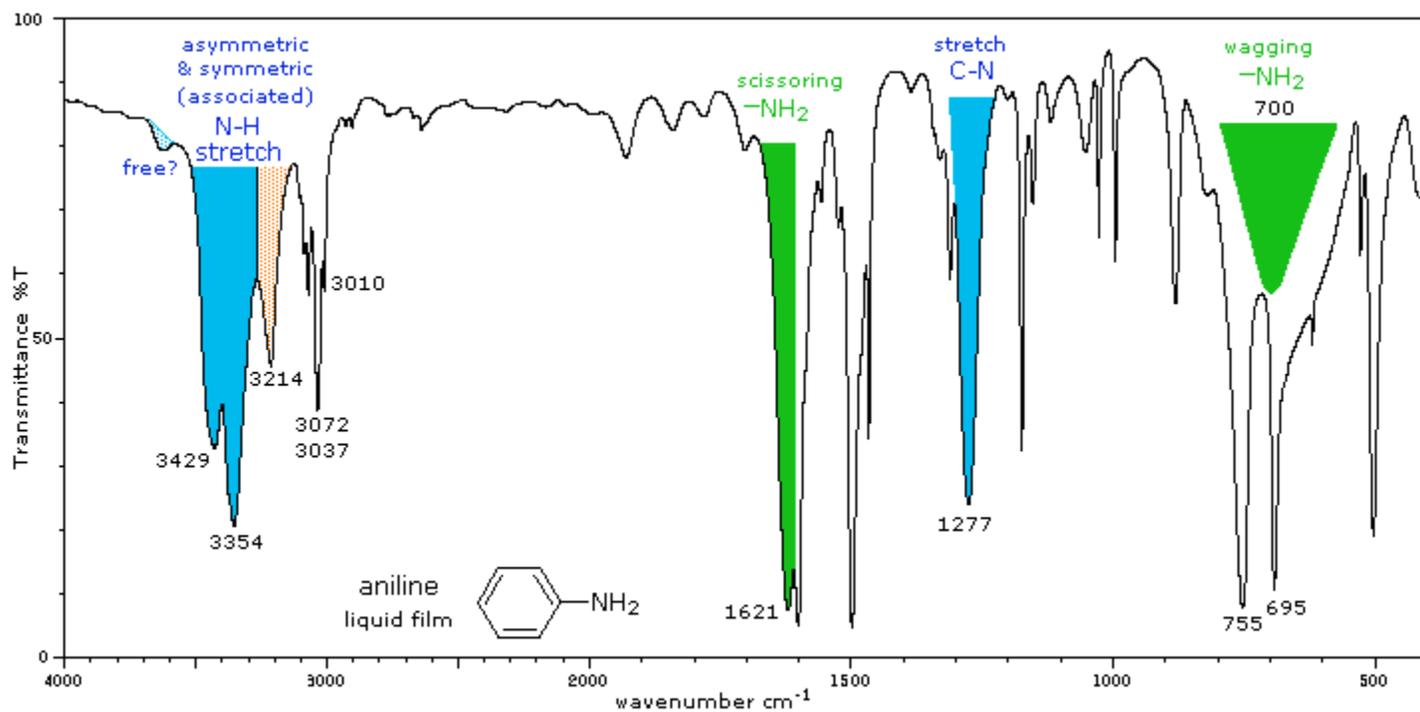
Toggle 1°-Amines   **Toggle 2°-Amines**   **Toggle 3°-Amines**

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 to 3000 cm^{-1} region, with 1°-ammonium salts absorbing at the high frequency end, where overlap with C-H absorption occurs. Salts of 1° and 2°-amines also exhibit strong bending absorptions in the range of 1500 to 1600 cm^{-1}, but the corresponding band from 3°-ammonium salts is relatively weak.

Carbonyl Compounds

1. Aldehydes and Ketones
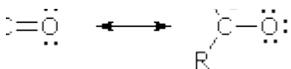
$\overset{..}{\underset{..}{\ddot{O}}}$ ⟷ $\overset{R}{\underset{}{\text{C}}}-\overset{..}{\underset{..}{\ddot{O}}}:$ For simple aldehydes and ketones the stretching vibration of the carbonyl group gives rise to a strong and distinctive infrared absorption at 1710 to 1740 cm^{-1}. As noted in the diagram 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 contributer, ketone carbonyls have slightly lower stretching frequencies, 1715 ± 7 cm^{-1}, compared with aldehydes, 1730 ± 7 cm^{-1}. The values cited here are for pure liquid or CCl$_4$ solution spectra. Hydrogen bonding solvents will lower these frequencies by 15 to 20 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 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.


| 1716 cm^{-1} | 1685 cm^{-1}
1617 (C=C) | 1716 cm^{-1} | 1683 cm^{-1} | 1678 cm^{-1}
1627 (C=C) |
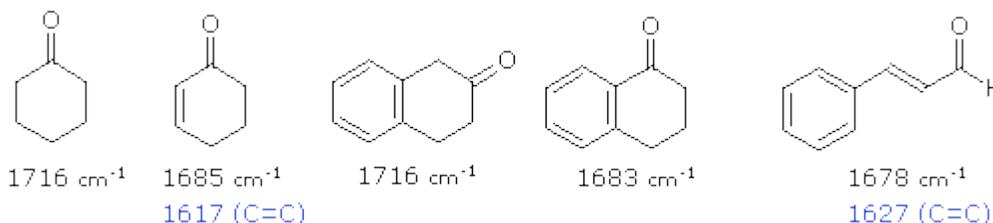
2. Incorporation of the carbonyl group in a small ring (5, 4 or 3-membered), raises the stretching frequency.
The increase in frequency ranges from 30 to 45 cm^{-1} for a 5-membered ring, to 50 to 60 cm^{-1} for a 4-membered ring, and nearly 130 cm^{-1} for a 3-membered ring. This shift also occurs in the presence of the previous conjugative lowering of the stretching absorption. Examples of this effect are shown below.
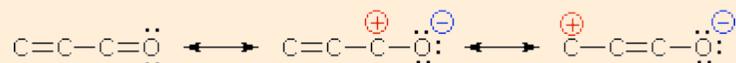

| 1748 cm^{-1} | 1783 cm^{-1} | 1850 cm^{-1} |

| 1710 cm^{-1}
1650 (C=C) | 1712 cm^{-1} | 1750 cm^{-1} |
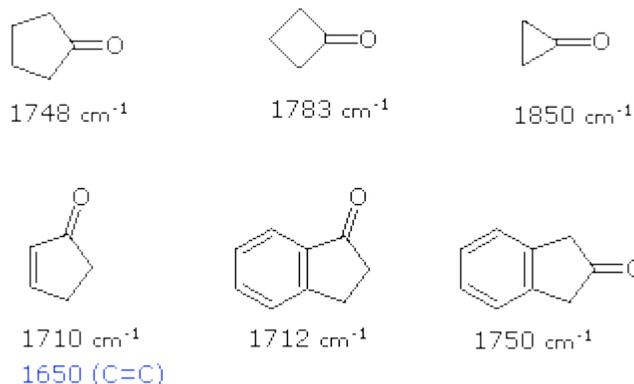
3. Changing an alkyl substituent of a ketone for an electron releasing or withdrawing group.
This effect, which may shift the carbonyl stretching frequency up or down, is particularly important when an alkyl substituent is replaced by a hetero atom such as N, O or X (halogen). Such cases will be discussed as carboxylic acid derivatives. The following examples show the influence of a strongly electron withdrawing group (-CCl$_3$) and a conjugatively electron donating group (-OCH$_3$).

| 1729 cm^{-1} | 1768 cm^{-1} | 1683 cm^{-1} | 1674 cm^{-1} |
| electron withdrawing substituent | | electron donating substituent | |
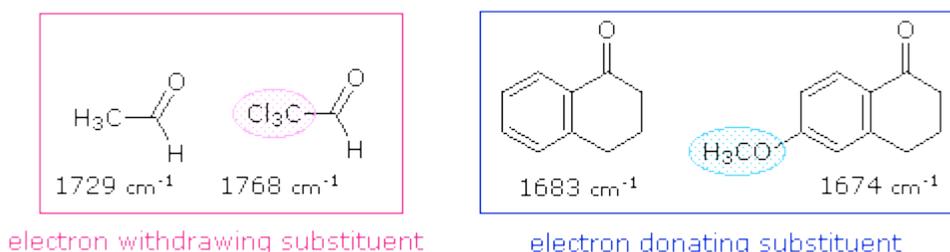
To understand the functioning of these factors consider the following analyses:

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.

$$C=C-C=\ddot{O} \quad \longleftrightarrow \quad C=C-\overset{\oplus}{C}-\overset{\ominus}{\ddot{O}:} \quad \longleftrightarrow \quad \overset{\oplus}{C}-C=C-\overset{\ominus}{\ddot{O}:}$$

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° 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° (5-membered ring), 90° (4-membered ring) or 60° (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.

C=O ṽ stretch
is increased

H₃C-Ö

H₃C-Ö

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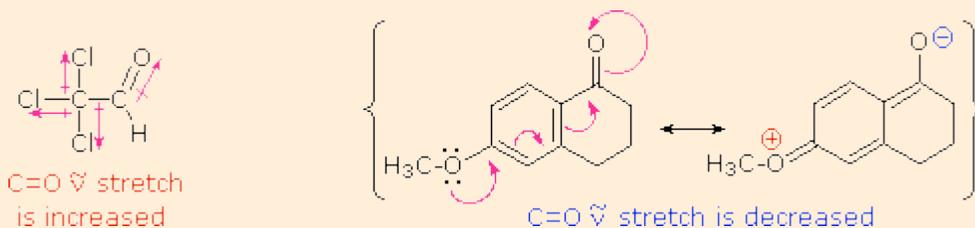
Starting with the spectrum of cyclohexanone, infrared spectra of six illustrative ketones will be displayed below on clicking the "Toggle Spectra" button. The difference between liquid film and solution spectra is shown for cyclohexanone, but all other compounds are examined as liquid films. The carbonyl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

IR spectrum of cyclohexanone, liquid film. Labeled peaks: 3610, 3515, 3407, 2941, 2864, 1716, 1222, 1119.
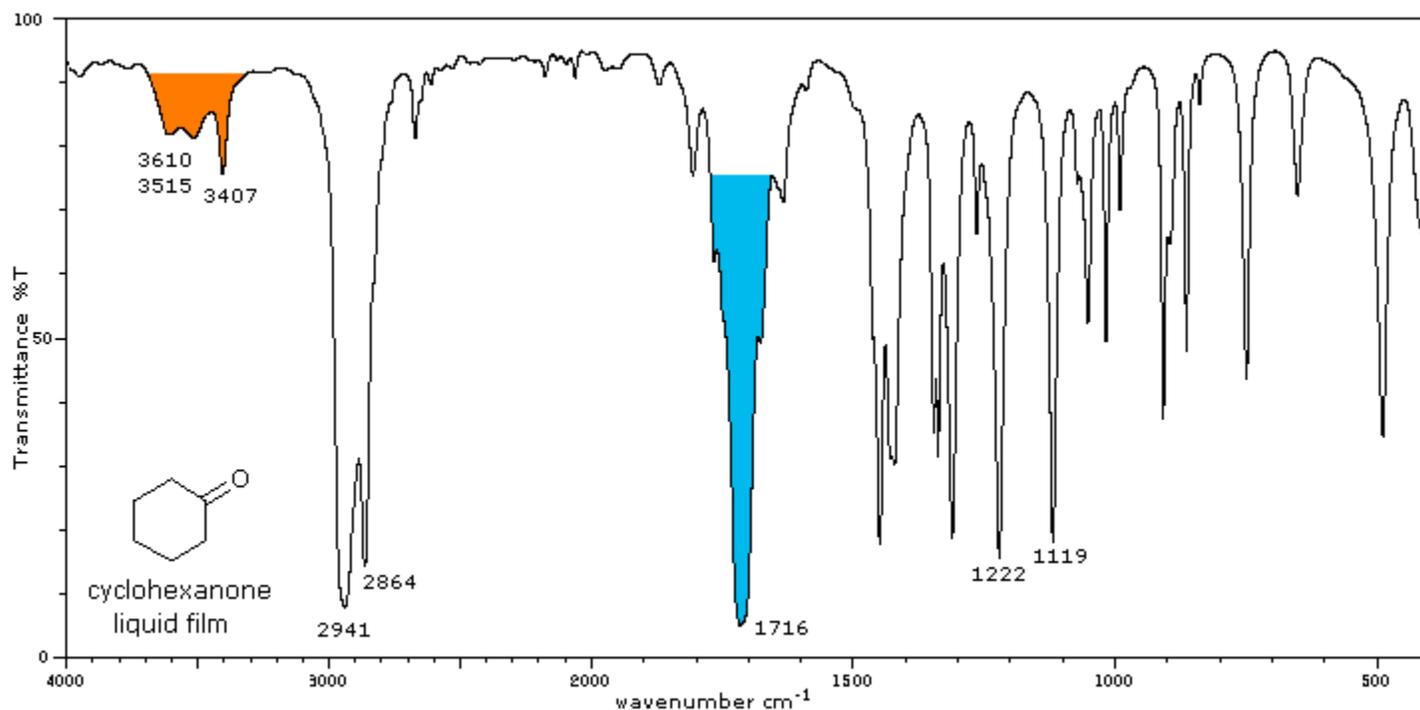
2. Carboxylic Acid Derivatives

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
Acyl Halides (RCOX) X = F X = Cl X = Br	C=O stretch 1860 ± 20 cm^{-1} 1800 ± 15 1800 ± 15	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones. In acyl chlorides a lower intensity shoulder or peak near 1740 cm^{-1} is due to an overtone interaction.
Acid Anhydride, (RCO)₂O acyclic 6-membered ring 5-membered ring	C=O stretch (2 bands) 1750 & 1820 cm^{-1} 1750 &1820 1785 & 1865	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones. The two stretching bands are separated by 60 ± 30 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 to 1300 cm^{-1} region.
Esters & Lactones (RCOOR') esters 6-membered lactone	C=O stretch 1740 cm $\pm$ 10 cm^{-1} 1740 cm $\pm$ 10 1765 cm$\pm$ 5 1840 cm $\pm$ 5	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones Strong CO-O stretching absorptions (one ot two) are found from 1150 to 1250 cm^{-1}

5-membered lactone 4-membered lactone		
Amides & Lactams (RCONR₂) 1° & 2°-amides 3°-amides 6-membered lactams 5-membered lactams 4-membered lactams	**C=O bands** 1510 to 1700 cm⁻¹ (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 **Amide I band**. The lower frequency **Amide II band** (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. **N-H stretch**: 3170 to 3500 cm⁻¹. Two bands for 1°-amides, one for 2°-amides.