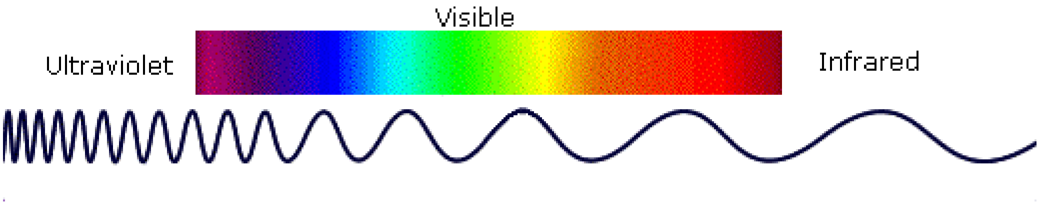
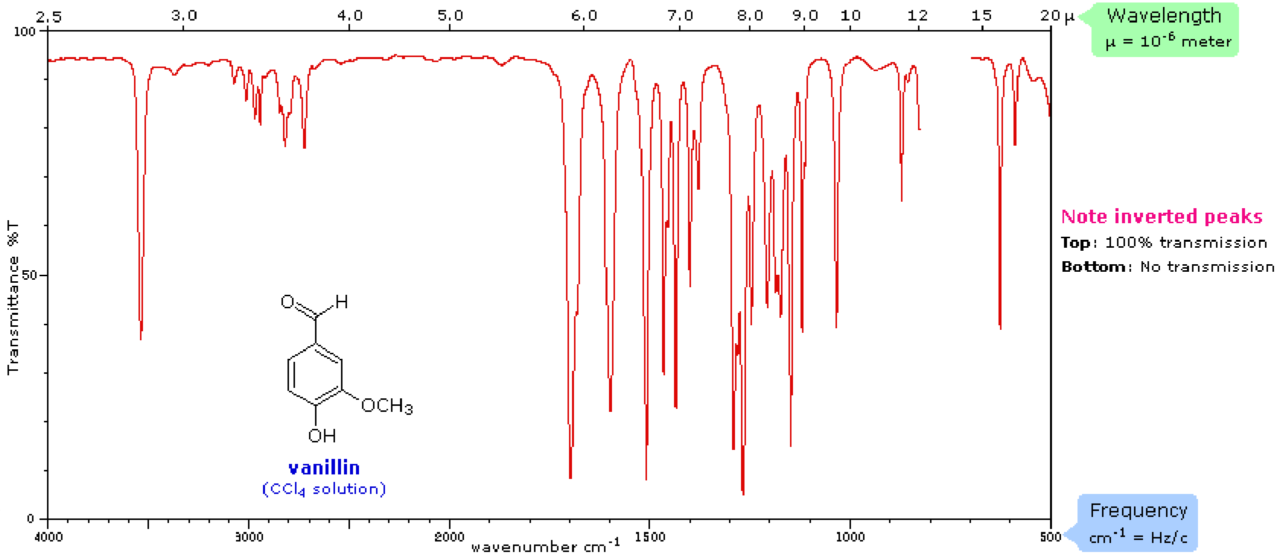
Infrared Spectroscopy

1. Introduction

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.. 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, 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.

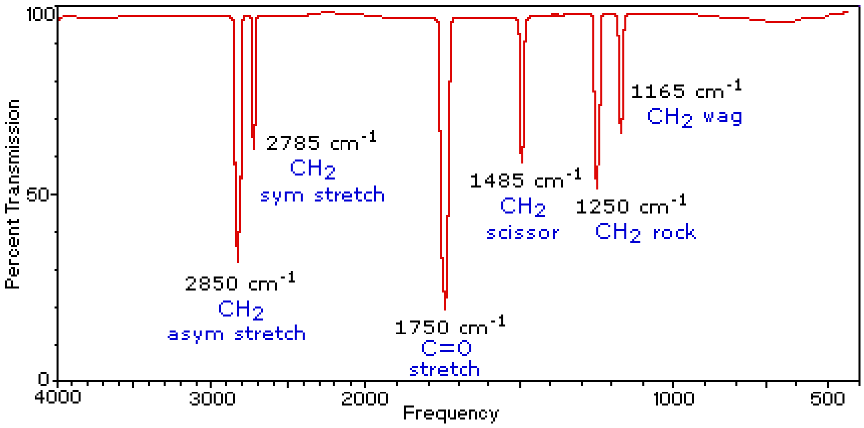
2. Vibrational Spectroscopy

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.

Gas Phase Infrared Spectrum of Formaldehyde, $H_2C=O$



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 .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.)

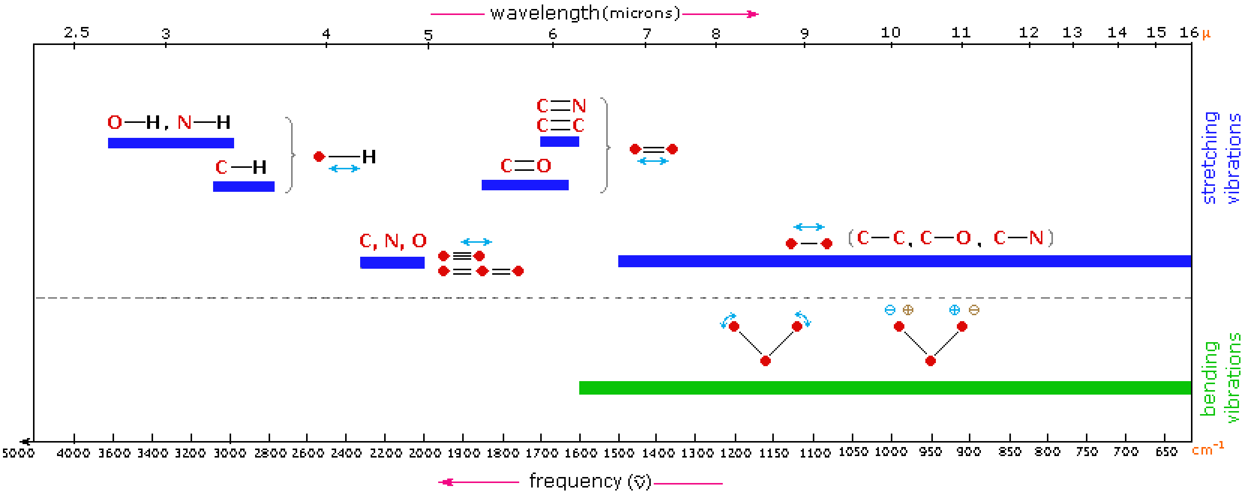
ii) Bonds to hydrogen have higher stretching frequencies than those to heavier

atoms.

iii) Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have 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 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. More detailed descriptions for certain groups (e.g. alkenes, arenes, alcohols, amines & carbonyl compounds) may be viewed later. 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}.

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)	**3550-3600 cm^{-1} (str)**
C=N	**1665± 15**
N-O	**945± 15**
N-O amine oxide	
aliphatic	**960± 20**
aromatic	**1250± 50**
N=O nitroso	**1550± 50 (str)**
nitro	**1530± 20 (as) & 1350± 30 (s)**

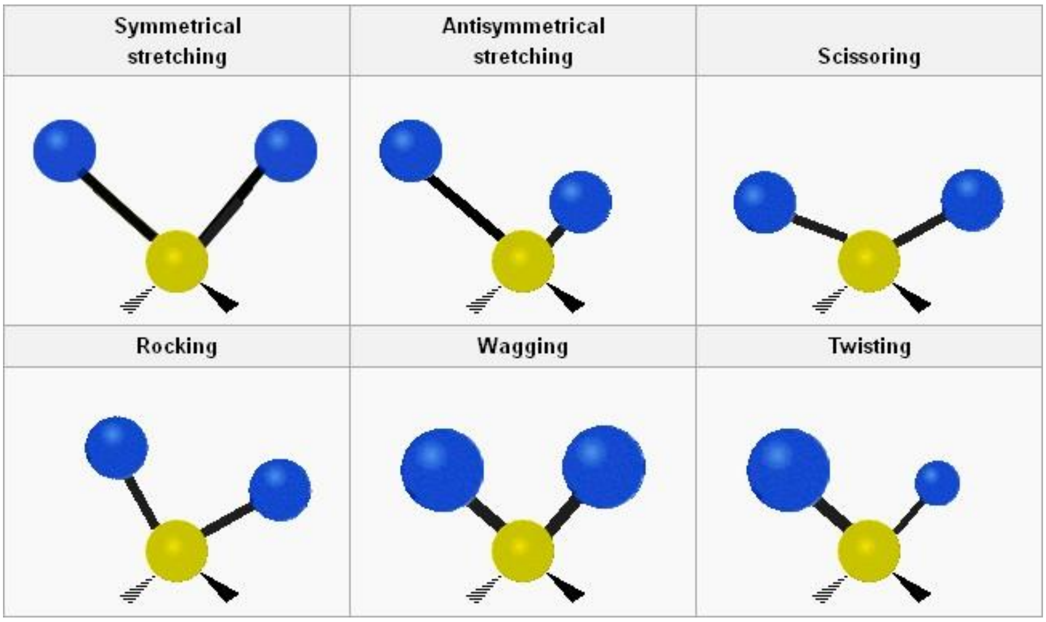
Theory

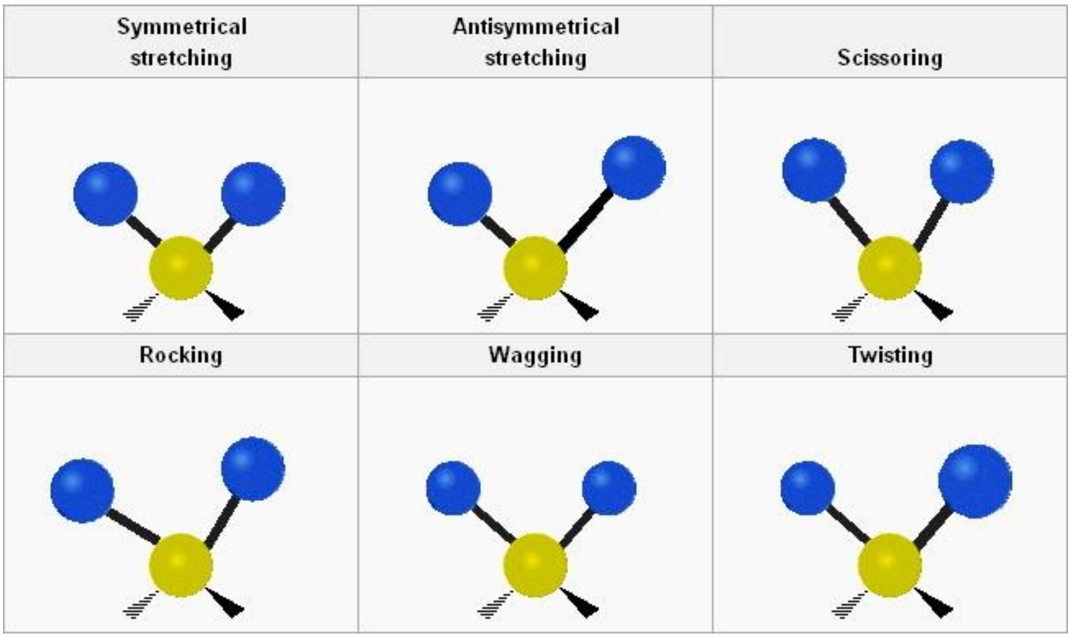
The infrared portion of the electromagnetic spectrum is divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The far-infrared, approximately 400-10 cm^{-1} (1000–30 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid-infrared, approximately 4000-400 cm^{-1} (30–1.4 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The higher energy near-IR, approximately 14000-4000 cm^{-1} (1.4–0.8 μm) can excite overtone or harmonic vibrations. The names and classifications of these subregions are merely conventions. They are neither strict divisions nor based on exact molecular or electromagnetic properties.

Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels. These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, by the associated vibronic coupling. In order for a vibrational mode in a molecule to be IR active, it must be associated with changes in the permanent dipole. In particular, in the Born-Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are determined by the normal modes corresponding to the

molecular electronic ground state potential energy surface. Nevertheless, the resonant frequencies can be in a first approach related to the strength of the bond, and the mass of the atoms at either end of it. Thus, the frequency of the vibrations can be associated with a particular bond type.

Simple diatomic molecules have only one bond, which may stretch. More complex molecules have many bonds, and vibrations can be conjugated, leading to infrared absorptions at characteristic frequencies that may be related to chemical groups. For example, the atoms in a CH_2 group, commonly found in organic compounds can vibrate in six different ways: symmetrical and antisymmetrical stretching, scissoring, rocking, wagging and twisting:





Modos de vibração

The infrared spectra of a sample is collected by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. Thiscan be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample.

This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures.

Sample preparation

Gaseous samples require little preparation beyond purification, but a sample cell with a long pathlength (typically 5-10 cm) is normally needed, as gases show relatively weak absorbances.

Liquid samples can be sandwiched between two plates of a high purity salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide or calcium fluoride are also used). The plates are transparent to the infrared light and will not introduce any lines onto the spectra. Some salt plates are highly soluble in water, so the sample and washing reagents must be anhydrous (without water).

Solid samples can be prepared in two major ways. The first is to crush the sample with a mulling agent (usually nujol) in a marble or agate mortar, with a pestle. A thin film of the mull is applied onto salt plates and measured.

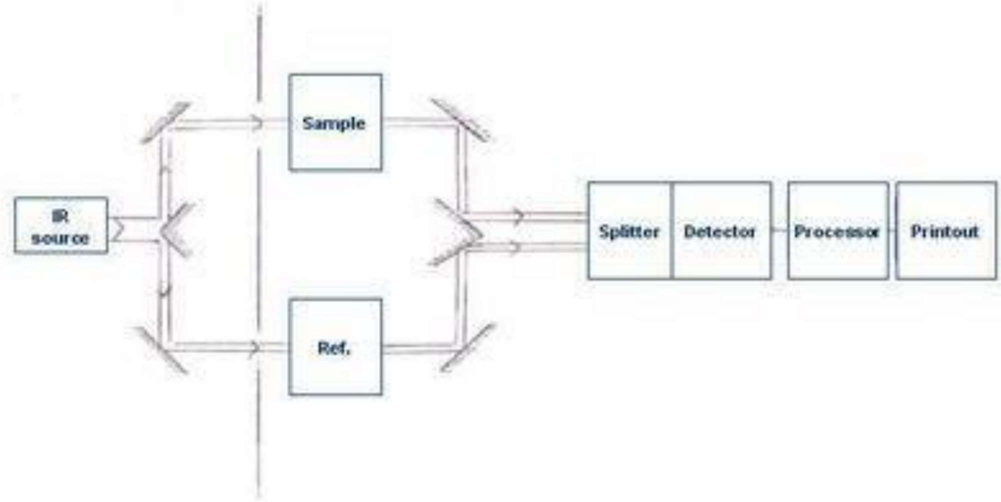
The second method is to grind a quantity of the sample with a specially purified salt (usually potassium bromide) finely (to remove scattering effects from large crystals). This powder mixture is then crushed in a mechanical die press to form a translucent pellet through which the beam of the spectrometer can pass.

It is important to note that spectra obtained from different sample preparation methods will look slightly different from each other due to differences in the samples' physical states.

The last technique is the Cast Film technique.

Cast film technique is used mainly for polymeric compound. Sample is first dissolved in suitable, non hygroscopic solvent. A drop of this solution is deposited on surface of KBr or NaCl cell. The solution is then evaporated to dryness and the film formed on the cell is analysed directly. Care is important to ensure that the film is not too thick otherwise light cannot pass through. This technique is suitable for qualitative analysis.

Typical method



Typical apparatus

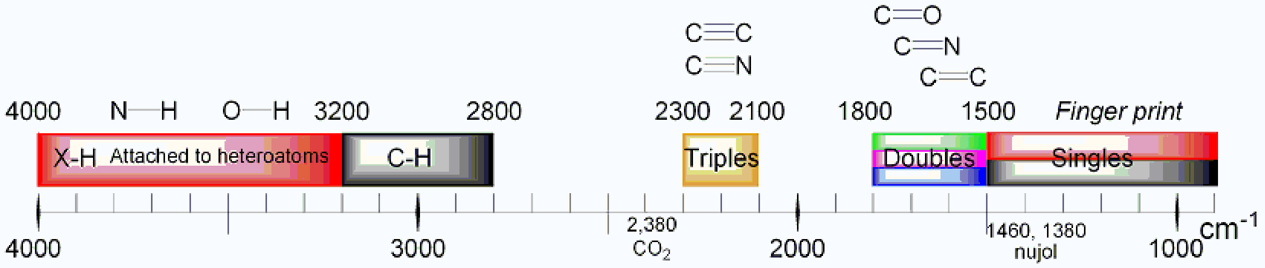
A beam of infrared light is produced and split into two separate beams. One is passed through the sample, the other passed through a reference which is often the substance the sample is dissolved in. The beams are both reflected back towards a detector, however first they pass through a splitter which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained.

A reference is used for two reasons:

- **This prevents fluctuations in the output of the source affecting the data**
- **This allows the effects of the solvent to be cancelled out (the reference is usually a pure form of the solvent the sample is in)**

Summary of absorptions of bonds in organic molecules

Main article: Infrared Spectroscopy Correlation Table



Wavenumbers listed in cm^{-1}.

Uses and applications

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and dynamic measurement. The instruments are now small, and can be transported, even for use in field trials. With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment). Some machines will also automatically tell you what substance is being measured from a store of thousands of reference spectra held in storage.

By measuring at a specific frequency over time, changes in the character or quantity of a particular bond can be measured. This is especially useful in measuring the degree of polymerization in polymer manufacture. Modern research machines can take infrared measurements across the whole range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.

Techniques have been developed to assess the quality of tea-leaves using infrared spectroscopy. This will mean that highly trained experts (also called 'noses') can be used more sparingly, at a significant cost saving.

Infrared spectroscopy has been highly successful for applications in both organic and inorganic chemistry. Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics: for example, infrared spectroscopy can be applied to semiconductors like silicon, gallium arsenide, gallium nitride, zinc selenide, amorphous silicon, silicon nitride, etc.

Isotope effects

The different isotopes in a particular species may give fine detail in infrared spectroscopy. For

example, the O-O stretching frequency of oxyhemocyanin is experimentally determined to be 832 and 788 cm^{-1} for ν(^{16}O-^{16}O) and ν(^{18}O-^{18}O) respectively.

By considering the O-O as a spring, the wavelength of absorbance, ν can be calculated:

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

where k is the spring constant for the bond, and μ is the reduced mass of the A-B system:

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

(m_i is the mass of atom i).

The reduced masses for ^{16}O-^{16}O and ^{18}O-^{18}O can be approximated as 8 and 9 respectively. Thus

$$\frac{\nu_{^{16}O}}{\nu_{^{18}O}} = \sqrt{\frac{9}{8}} \approx \frac{832}{788}$$

IR Spectroscopy Tutorial

An important tool of the organic chemist is Infrared Spectroscopy, or "IR". IR spectra are acquired on a special instrument, called an IR spectrometer. IR is used to gather information about compound's structure, assess its purity, and sometimes to identify it.

Infrared radiation is that part of the electromagnetic spectrum between the visible and microwave regions. Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration, either stretching or bending. Different types of bonds, and thus different functional groups, absorb infrared radiation of different wavelengths. A IR spectrum is a plot of wavenumber (X-axis) vs percent transmittance (Y-axis).

IR Spectroscopy Tutorial: Alkanes

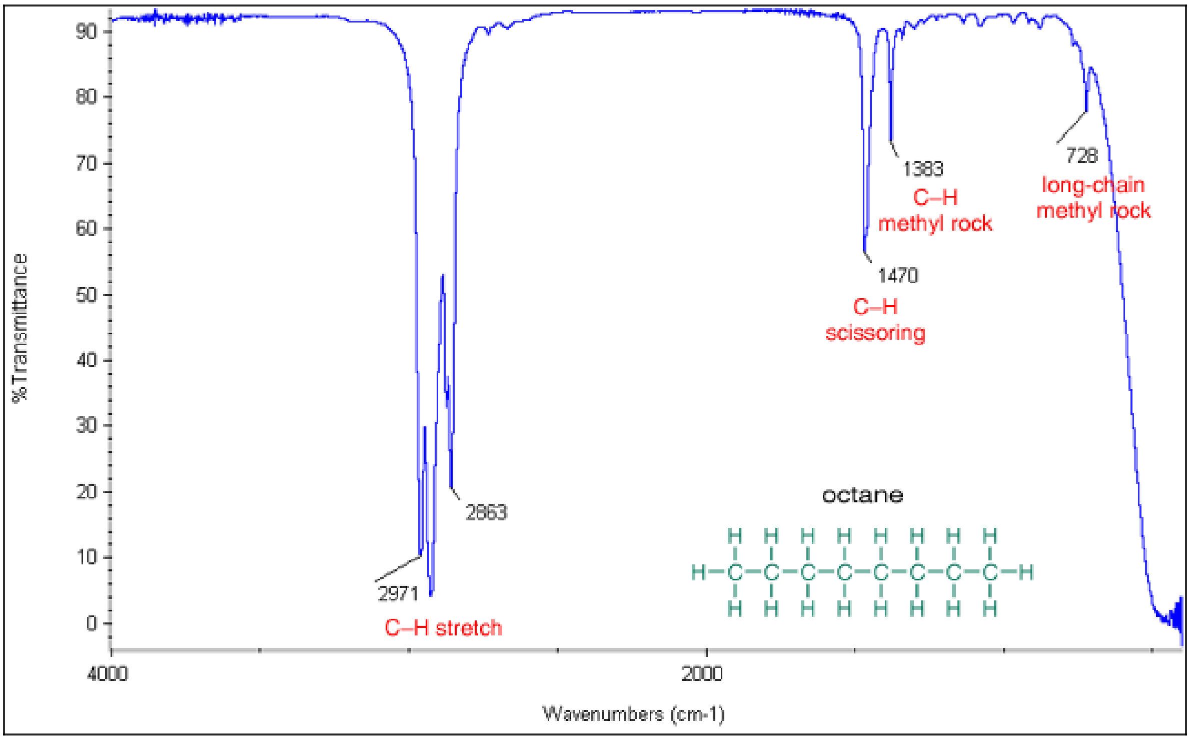
The spectra of simple alkanes are characterized by absorptions due to C–H stretching and bending (the C–C stretching and bending bands are either too weak or of too low a frequency to be detected in IR spectroscopy). In simple alkanes, which have very few bands, each band in the spectrum can be assigned.

- **C–H stretch from 3000–2850 cm^{-1}**
- **C–H bend or scissoring from 1470-1450 cm^{-1}**

- **C–H rock, methyl from 1370-1350 cm^{-1}**
- **C–H rock, methyl, seen only in long chain alkanes, from 725-720 cm^{-1}**

The IR spectrum of octane is shown below. Note the strong bands in the 3000-2850 cm^{-1} region due to C-H stretch. The C-H scissoring (1470), methyl rock (1383), and long-chain methyl rock (728) are noted on this spectrum. Since most organic compounds have these features, these C-H vibrations are usually not noted when interpreting a routine IR spectrum.

The region from about 1300-900 cm^{-1} is called the fingerprint region. The bands in this region originate in interacting vibrational modes resulting in a complex absorption pattern. Usually, this region is quite complex and often difficult to interpret; however, each organic compound has its own unique absorption pattern (or fingerprint) in this region and thus an IR spectrum be used to identify a compound by matching it with a sample of a known compound.



IR Spectroscopy Tutorial: Alkenes

Alkenes are compounds that have a carbon-carbon double bond, –C=C–. The stretching vibration of the C=C bond usually gives rise to a moderate band in the region 1680-1640 cm^{-1}.

Stretching vibrations of the –C=C–H bond are of higher frequency (higher wavenumber) than those of the –C–C–H bond in alkanes.

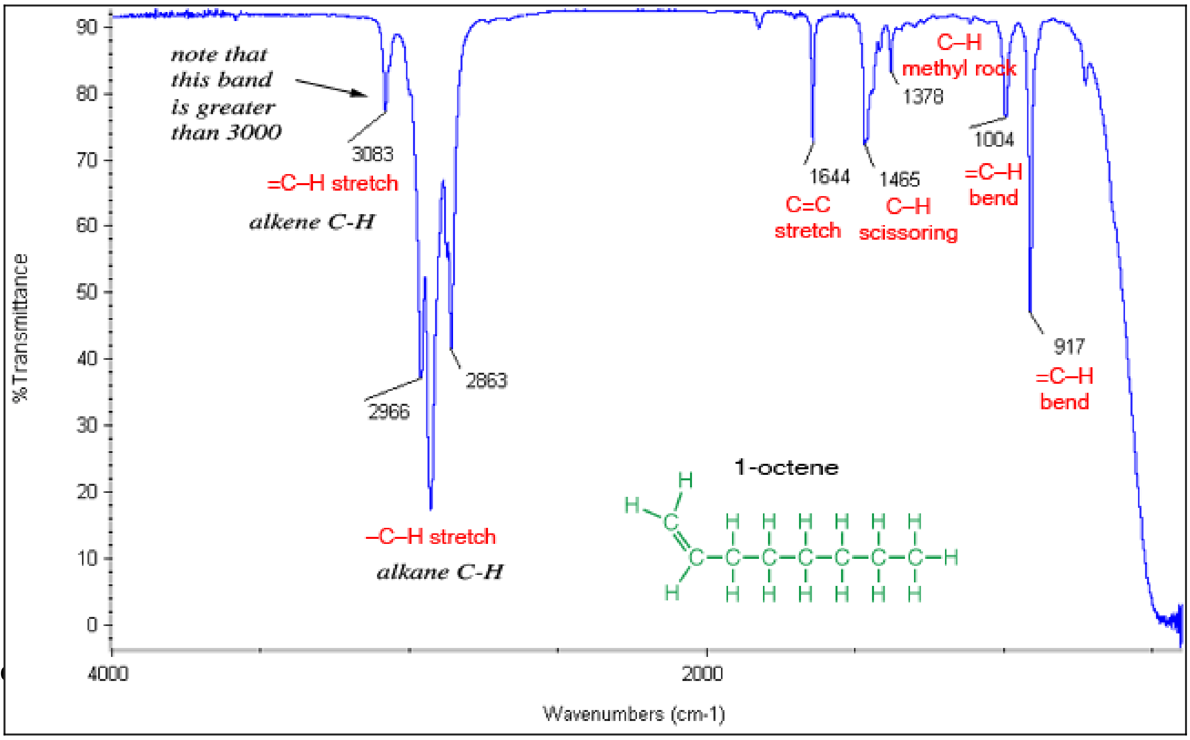
This is a very useful tool for interpreting IR spectra: Only alkenes and aromatics show a C-H stretch slightly higher than 3000 cm^{-1}. Compounds that do not have a C=C bond show C-H stretches only below 3000 cm^{-1}.

The strongest bands in the spectra of alkenes are those attributed to the carbon-hydrogen bending vibrations of the =C–H group. These bands are in the region 1000-650 cm^{-1} (Note: this overlaps the fingerprint region).

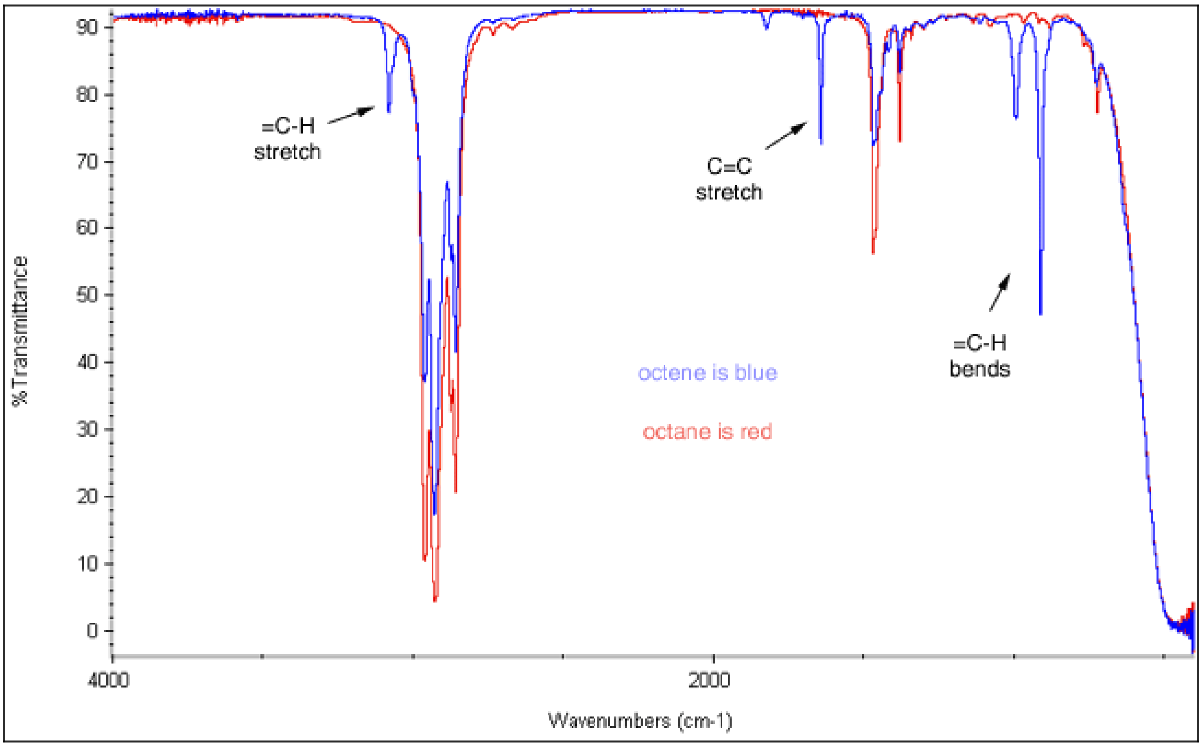
Summary:

- **C=C stretch from 1680-1640 cm^{-1}**
- **=C–H stretch from 3100-3000 cm^{-1}**
- **=C–H bend from 1000-650 cm^{-1}**

The IR spectrum of 1-octene is shown below. Note the band greater than 3000 cm^{-1} for the =C–H stretch and the several bands lower than 3000 cm^{-1} for –C–H stretch (alkanes). The C=C stretch band is at 1644 cm^{-1}. Bands for C–H scissoring (1465) and methyl rock (1378) are marked on this spectrum; in routine IR analysis, these bands are not specific to an alkene and are generally not noted because they are present in almost all organic molecules (and they are in the fingerprint region). The bands at 917 cm^{-1} and 1044cm^{-1} ^{are} attributed to =C&Mac173;H bends.



It **is interesting to overlay a spectrum of 1-octene with octane (shown below). Note how similar they are, except for the bands due to C=C or C=C–H stretches/bends.**



IR Spectroscopy Tutorial: Alkynes

Alkynes are compounds that have a carbon-carbon triple bond (–C≡C–). The –C≡C– stretch appears as a weak band from 2260-2100 cm^{-1}. This can be an important diagnostic tool because very few organic compounds show an absorption in this region.

A terminal alkyne (but not an internal alkyne) will show a C–H stretch as a strong, narrow band in the range 3330-3270 cm^{-1}. (Often this band is indistinguishable from bands resulting from other functional groups on the same molecule which absorb in this region, such as the O-H stretch.)

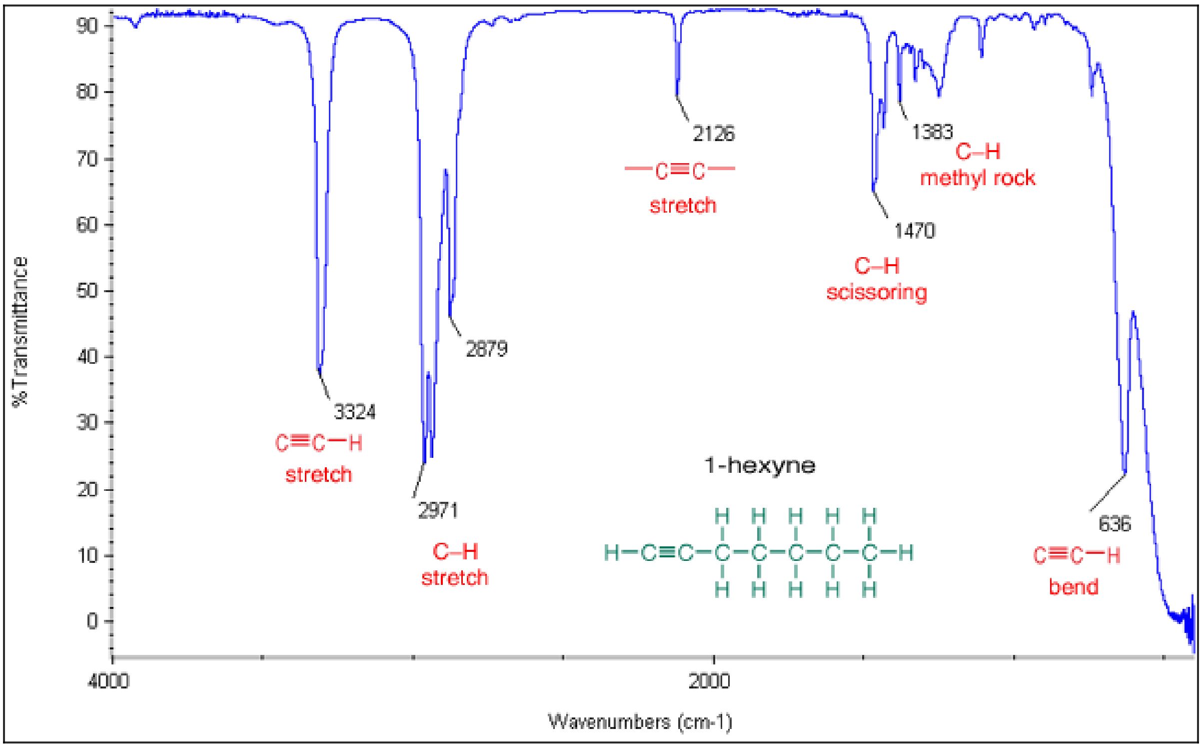
A terminal alkyne will show a C–H bending vibration in the region 700-610 cm^{-1}.

Summary:

- **–C≡C– stretch from 2260-2100 cm^{-1}**
- **–C≡C–H: C–H stretch from 3330-3270 cm^{-1}**

- **–C≡C–H: C–H bend from 700-610 cm^{-1}**

The spectrum of 1-hexyne, a terminal alkyne, is shown below. Note the C–H stretch of the C–H bond adjacent to the carbon-carbon triple bond (3324), the carbon-carbon triple bond stretch (2126), and the C–H bend of the C-H bond adjacent to the carbon-carbon triple bond (636). The other bands noted are C–H stretch, scissoring, and methyl rock bands from the alkane portions of the molecule.



IR Spectroscopy Tutorial: Aromatics

The =C–H stretch in aromatics is observed at 3100-3000 cm^{-1}. Note that this is at slightly higher frequency than is the –C–H stretch in alkanes.

This is a very useful tool for interpreting IR spectra: Only alkenes and aromatics show a C–H stretch slightly higher than 3000 cm^{-1}. Compounds that do not have a C=C bond show C–H stretches only below 3000 cm^{-1}.

Aromatic hydrocarbons show absorptions in the regions 1600-1585 cm^{-1} and 1500-1400 cm^{-1} due to carbon-carbon stretching vibrations in the aromatic ring.

Bands in the region 1250-1000 cm^{-1} are due to C–H in-plane bending, although these bands are too weak to be observed in most aromatic compounds.

Besides the C–H stretch above 3000 cm^{-1}, two other regions of the infrared spectra of aromatics distinguish aromatics from organic compounds that do not have an aromatic ring:

- **2000-1665 cm^{-1} (weak bands known as "overtones")**
- **900-675 cm^{-1} (out-of-plane or "oop" bands)**

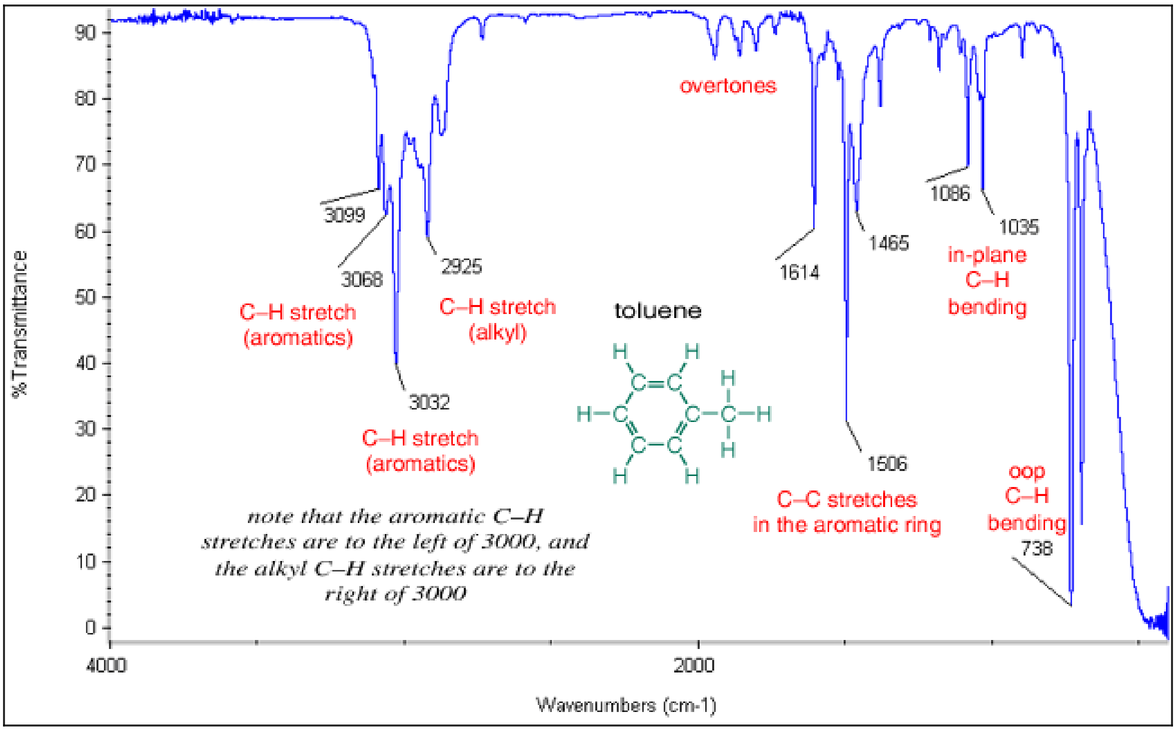
Not only do these bands distinguish aromatics, but they can be useful if you want to determine the number and positions of substituents on the aromatic ring. The pattern of overtone bands in the region 2000-1665 cm^{-1} reflect the substitution pattern on the ring. The pattern of the oop C–H bending bands in the region 900-675 cm^{-1} are also characteristic of the aromatic substitution pattern. Details of the correlation between IR patterns in these two regions and ring substitution are available in the literature references linked in the left frame (especially the books by Shriner and Fuson, Silverstein et. al., and the Aldrich Library of IR Spectra).

In some instances, it is useful to remember that aromatics in general show a lot more bands than compounds that do not contain an aromatic ring. If you are presented with two spectra and told that one is aromatic and one is not, a quick glance at the sheer multitude of bands in one of the spectra can tell you that it is the aromatic compound.

Summary:

- **C–H stretch from 3100-3000 cm^{-1}**
- **overtones, weak, from 2000-1665 cm^{-1}**
- **C–C stretch (in-ring) from 1600-1585 cm^{-1}**
- **C–C stretch (in-ring) from 1500-1400 cm^{-1}**
- **C–H "oop" from 900-675 cm^{-1}**

The spectrum of toluene is shown below. Note the =C–H stretches of aromatics (3099, 3068, 3032) and the –C–H stretches of the alkyl (methyl) group (2925 is the only one marked). The characteristic overtones are seen from about 2000-1665. Also note the carbon-carbon stretches in the aromatic ring (1614, 1506, 1465), the in-plane C–H bending (1086, 1035), and the C–H oop (738).

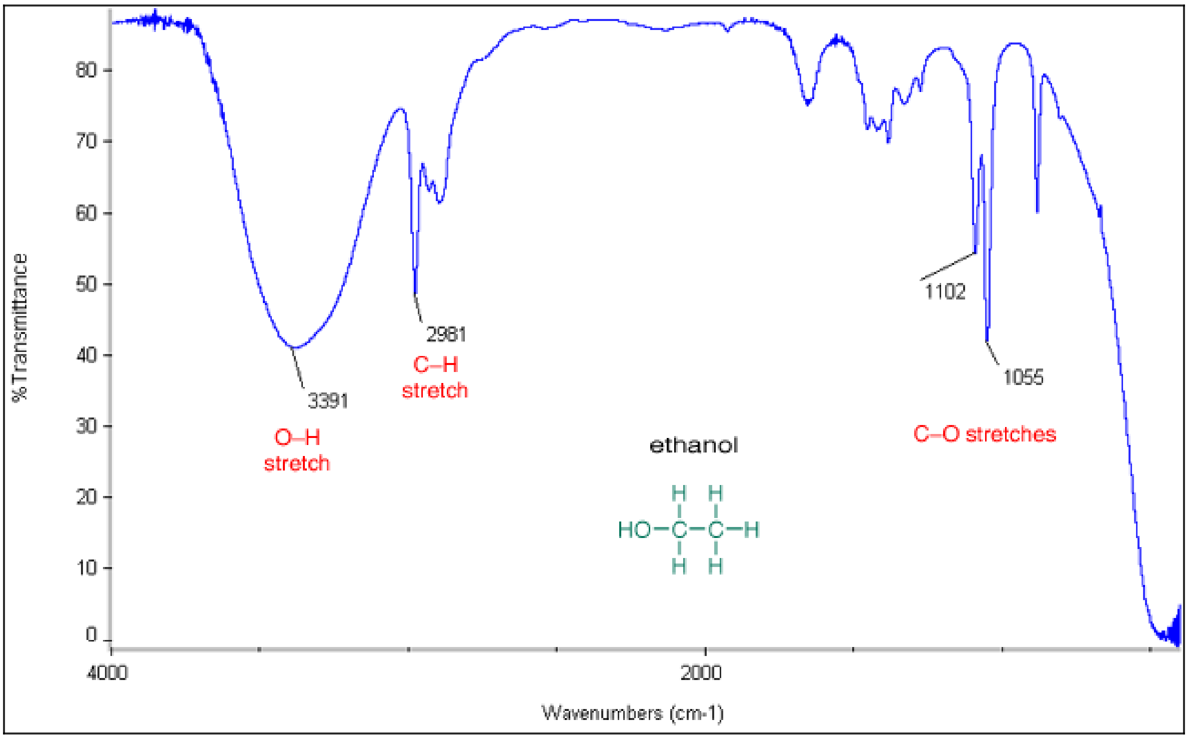


IR Spectroscopy Tutorial: Alcohols

Alcohols have characteristic IR absorptions associated with both the O-H and the C-O stretching vibrations. When run as a thin liquid film, or "neat", the O–H stretch of alcohols appears in the region 3500-3200 cm^{-1} and is a very intense, broad band. The C–O stretch shows up in the region 1260-1050 cm^{-1}.

- **O–H stretch, hydrogen bonded 3500-3200 cm^{-1}**
- **C–O stretch 1260-1050 cm^{-1} (s)**

The spectrum of ethanol is shown below. Note the very broad, strong band of the O–H stretch (3391) and the C–O stretches (1102, 1055).



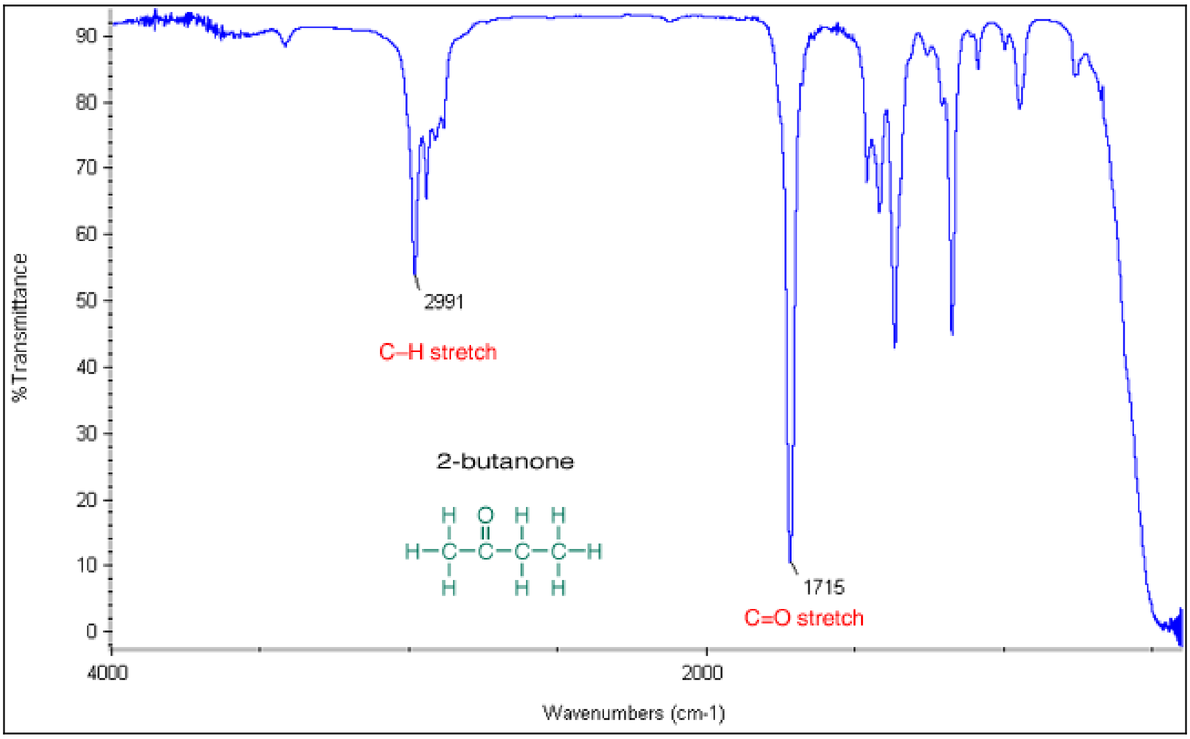
IR Spectroscopy Tutorial: Ketones

The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears at 1715 cm^{-1}. Conjugation of the carbonyl group with carbon-carbon double bonds or phenyl groups, as in alpha, beta-unsaturated aldehydes and benzaldehyde, shifts this band to lower wavenumbers, 1685-1666 cm^{-1}.

Summary:

- **C=O stretch:**
    - **aliphatic ketones 1715 cm^{-1}**
    - **α, β-unsaturated ketones 1685-1666 cm^{-1}**

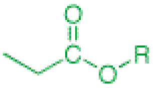
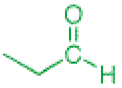
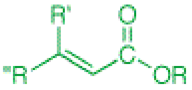
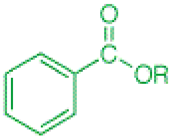
The spectrum of 2-butanone is shown below. This is a saturated ketone, and the C=O band appears at 1715. Note the C–H stretches (around 2991) of alkyl groups. It's usually not necessary to mark any of the bands in the fingerprint region (less than 1500 cm^{-1}).

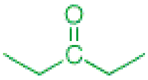


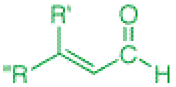
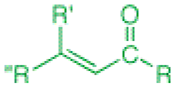
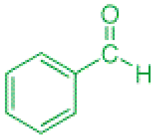
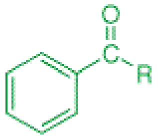
IR Spectroscopy Tutorial: Carbonyl Compounds

All carbonyl compounds absorb in the region 1760-1665 cm^{-1} due to the stretching vibration of the C=O bond. This distinctive carbonyl band is particularly useful for diagnostic purposes because it has a characteristic high intensity and few other functional groups absorb in this region. Different carbonyl compounds absorb in narrow ranges within the general carbonyl region.

The exact wavenumber of the C=O stretch can give you clues as to whether the compound is a ketone, aldehyde, ester, or carboxylic acid; furthermore it can tell you whether it is an alpha, beta- carbonyl.

range	*type of compound*	*such as:*
1750-1735 cm^{-1}	saturated aliphatic esters	
1740-1720 cm^{-1}	saturated aliphatic aldehydes	
1730-1715 cm^{-1}	α, β-unsaturated esters	 

1715 cm^{-1}	**saturated aliphatic ketones**	

1710-1665 cm^{-1}	**α, β-unsaturated aldehydes and ketones**	   

IR Spectroscopy Tutorial: Aldehydes

The carbonyl stretch C=O of saturated aliphatic aldehydes appears from 1740-1720 cm^{-1}. As in ketones, if the carbons adjacent to the aldehyde group are unsaturated, this vibration is shifted to lower wavenumbers, 1710-1685 cm^{-1}.

Another useful diagnostic band for aldehydes is the O=C–H stretch. This band generally appears as one or two bands of moderate intensity in the region 2830-2695 cm^{-1}. Since the band near 2830 cm^{-1} is usually indistinguishable from other C–H stretching vibration bands (recall that the C–H stretches of alkanes appear from 3000-2850 cm^{-1}), the presence of a moderate band near 2720 cm^{-1} is more likely to be helpful in determining whether or not a compound is an aldehyde.

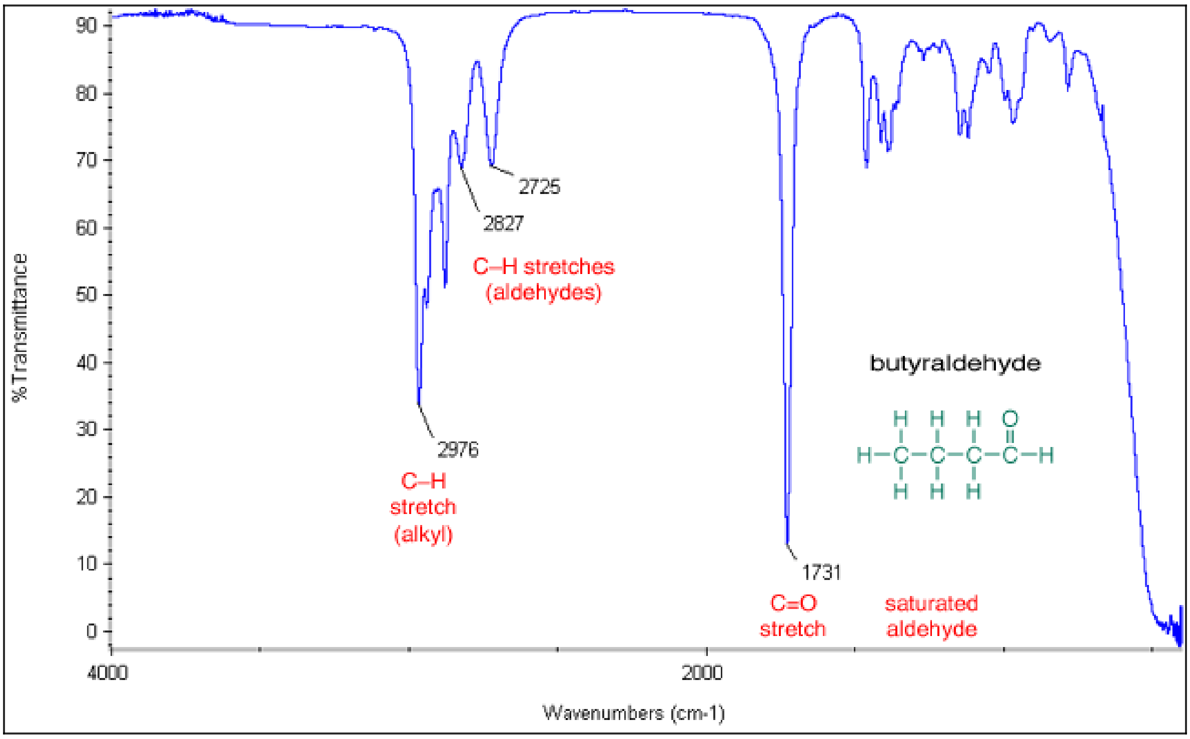
If you suspect a compound to be an aldehyde, always look for a peak around 2720 cm^{-1}; it often appears as a shoulder-type peak just to the right of the alkyl C–H stretches.

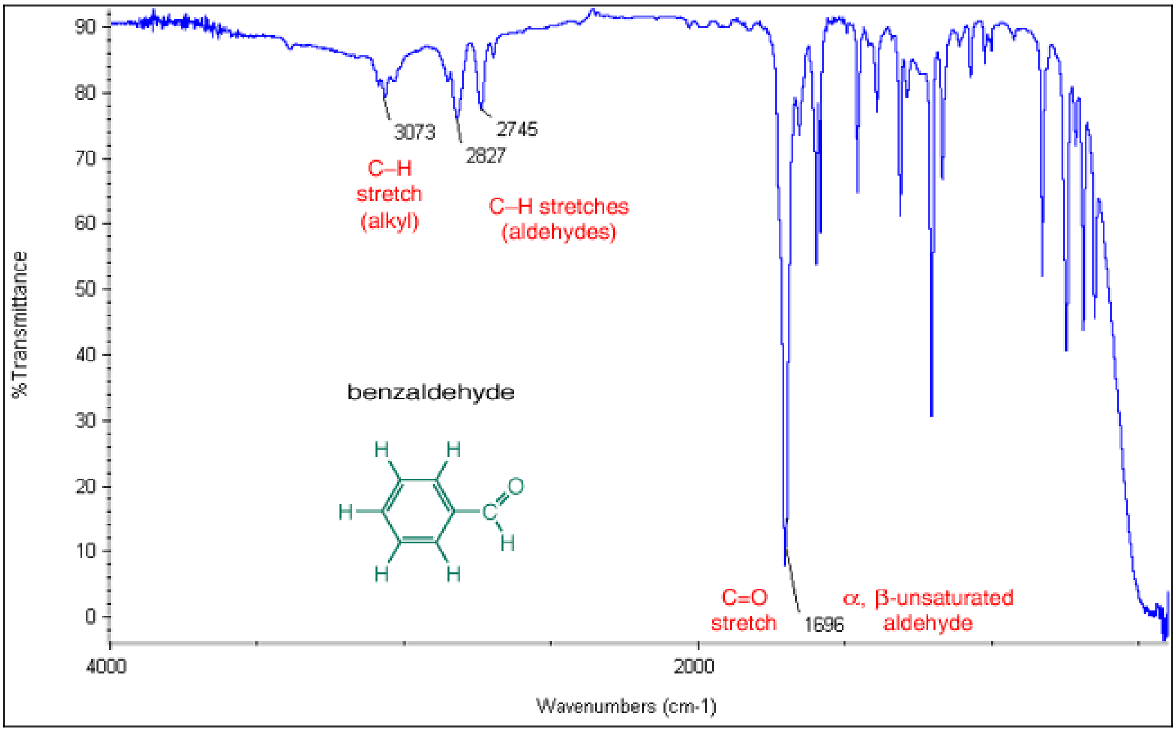
Summary:

- **H–C=O stretch 2830-2695 cm^{-1}**
- **C=O stretch:**
    - **aliphatic aldehydes 1740-1720 cm^{-1}**
    - **alpha, beta-unsaturated aldehydes 1710-1685 cm^{-1}**

The spectra of benzaldehyde and butyraldehyde are shown below. Note that the O=C stretch of the alpha, beta-unsaturated compound -- benzaldehyde -- is at a lower wavenumber than that of the saturated butyraldehyde.

Note the O=C–H stretches in both aldehydes in the region 2830-2695 cm^{-1}, especially the shoulder peak at 2725 cm^{-1} in butyraldehyde and 2745 cm^{-1} in benzaldehyde.





IR Spectroscopy Tutorial: Carboxylic Acids

Carboxylic acids show a strong, wide band for the O–H stretch. Unlike the O–H stretch band observed in alcohols, the carboxylic acid O–H stretch appears as a very broad band in the region 3300-2500 cm^{-1}, centered at about 3000 cm^{-1}. This is in the same region as the C–H stretching bands of

both alkyl and aromatic groups. Thus a carboxylic acid shows a somewhat "messy" absorption pattern in the region 3300-2500 cm^{-1}, with the broad O–H band superimposed on the sharp C–H stretching bands. The reason that the O–H stretch band of carboxylic acids is so broad is becase carboxylic acids usually exist as hydrogen-bonded dimers.

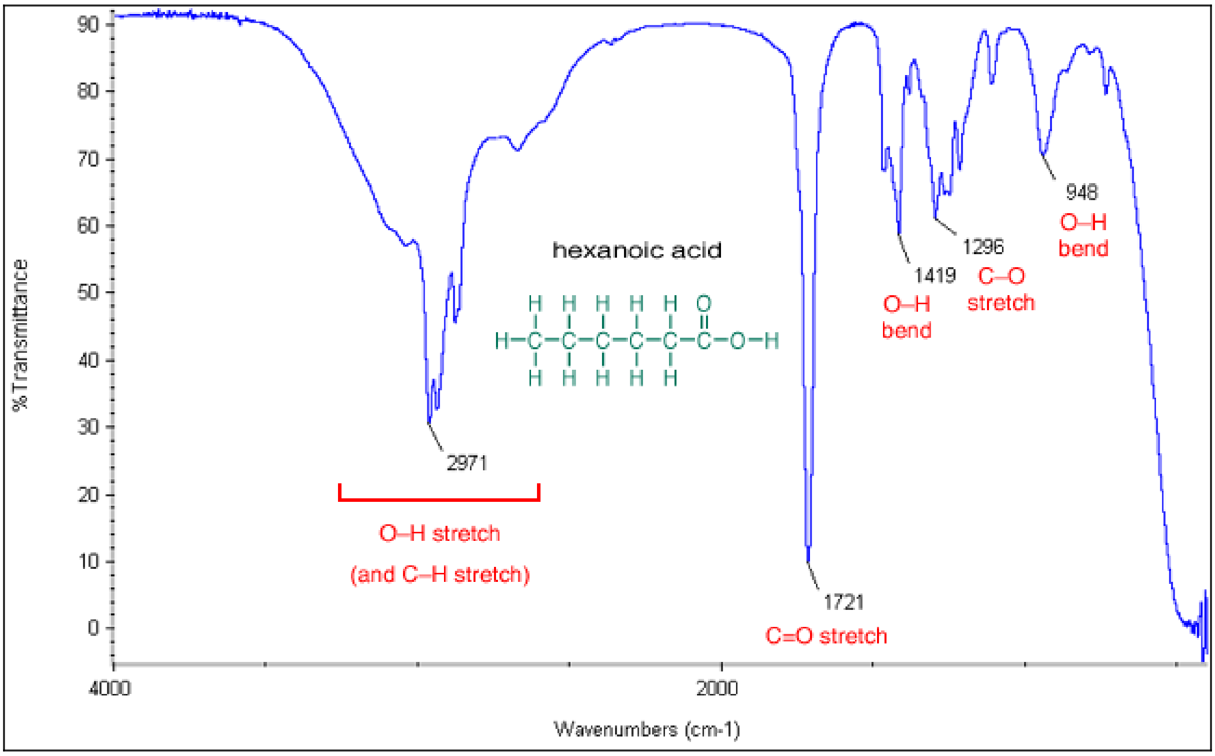
- The carbonyl stretch C=O of a carboxylic acid appears as an intense band from 1760-1690 cm^{-1}. The exact position of this broad band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen bonding**.**

The C–O stretch appears in the region 1320-1210 cm^{-1}, and the O–H bend is in the region 1440-1395 cm^{-1} and 950-910 cm^{-1}, although the 1440-1395 band may not be distinguishable from C–H bending bands in the same region.

Summary:

- **O–H stretch from 3300-2500 cm^{-1}**
- **C=O stretch from 1760-1690 cm^{-1}**
- **C–O stretch from 1320-1210 cm^{-1}**
- **O–H bend from 1440-1395 and 950-910 cm^{-1}**

The spectrum of hexanoic acid is shown below. Note the broad peak due to O–H stretch superimposed on the sharp band due to C–H stretch. Note the C=O stretch (1721), C–O stretch (1296), O–H bends (1419, 948), and C–O stretch (1296).



IR Spectroscopy Tutorial: Esters

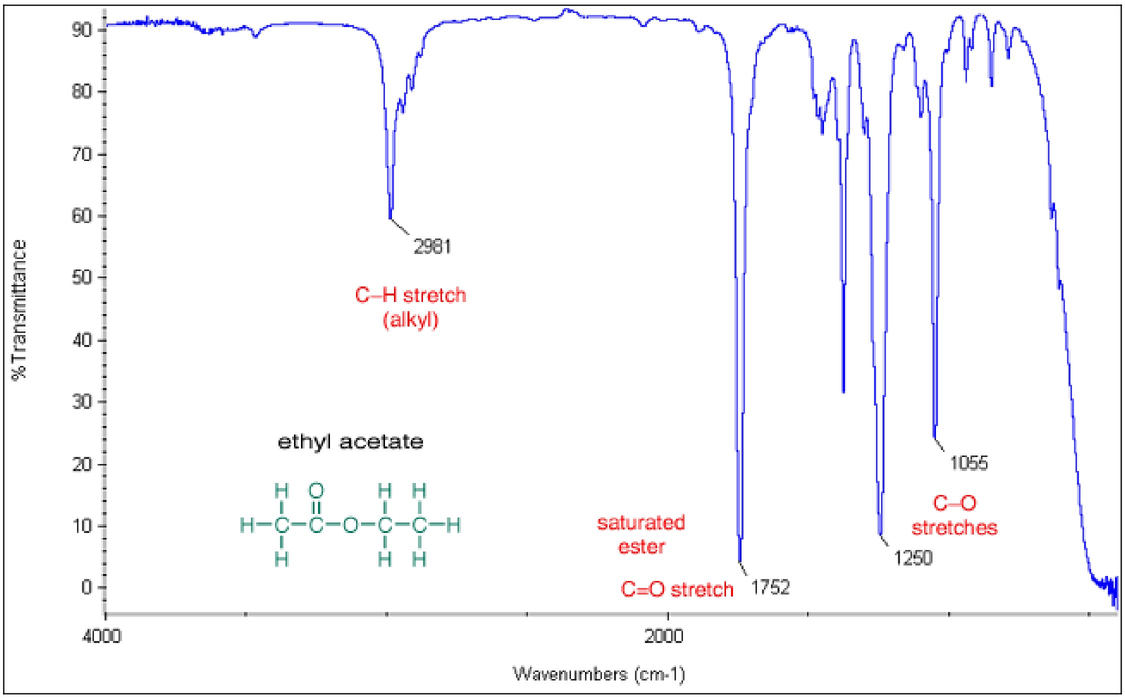
- **The carbonyl stretch C=O of aliphatic esters appears from 1750-1735 cm^{-1}; that of α, β-unsaturated esters appears from 1730-1715 cm^{-1}.**

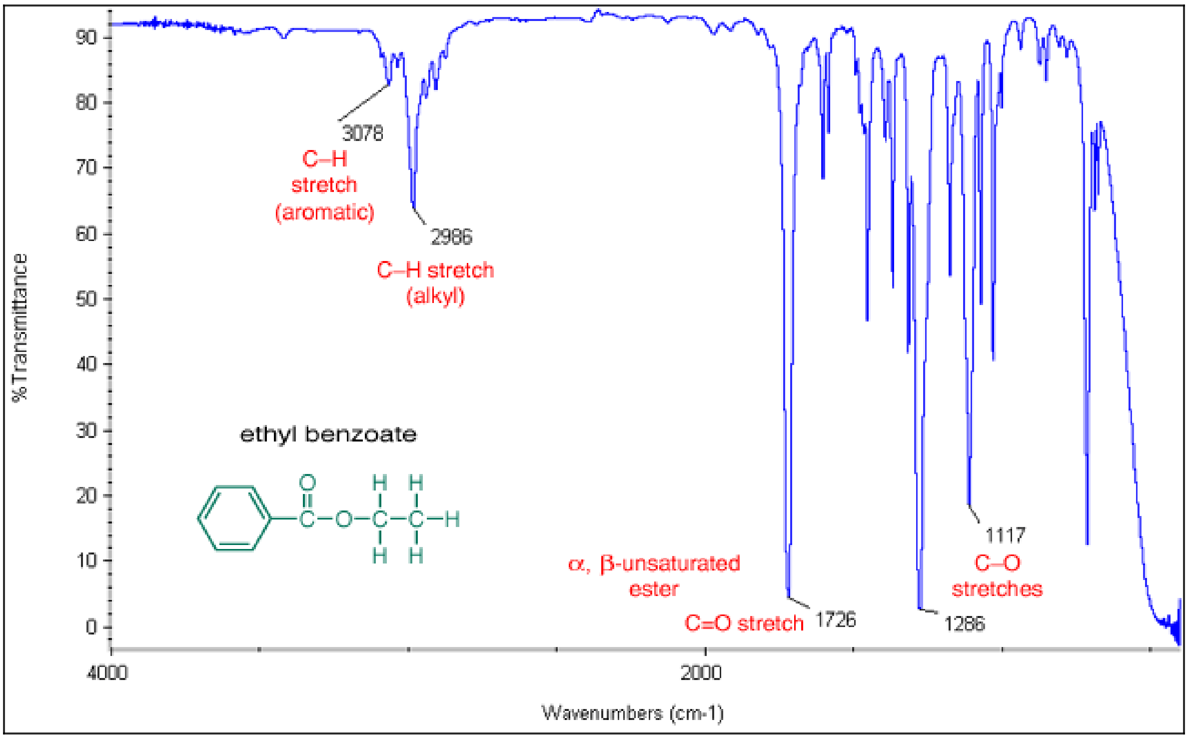
The C–O stretches appear as two or more bands in the region 1300-1000 cm^{-1}.

Summary:

- **C=O stretch**
  - **aliphatic from 1750-1735 cm^{-1}**
  - **α, β-unsaturated from 1730-1715 cm^{-1}**
- **C–O stretch from 1300-1000 cm^{-1}**

The spectra of ethyl acetate and ethyl benzoate are shown below. Note that the C=O stretch of ethyl acetate (1752) is at a higher wavelength than that of the α, β-unsaturated ester ethyl benzoate (1726). Also note the C–O stretches in the region 1300-1000 cm^{-1}.





IR Spectroscopy Tutorial: Alkyl Halides

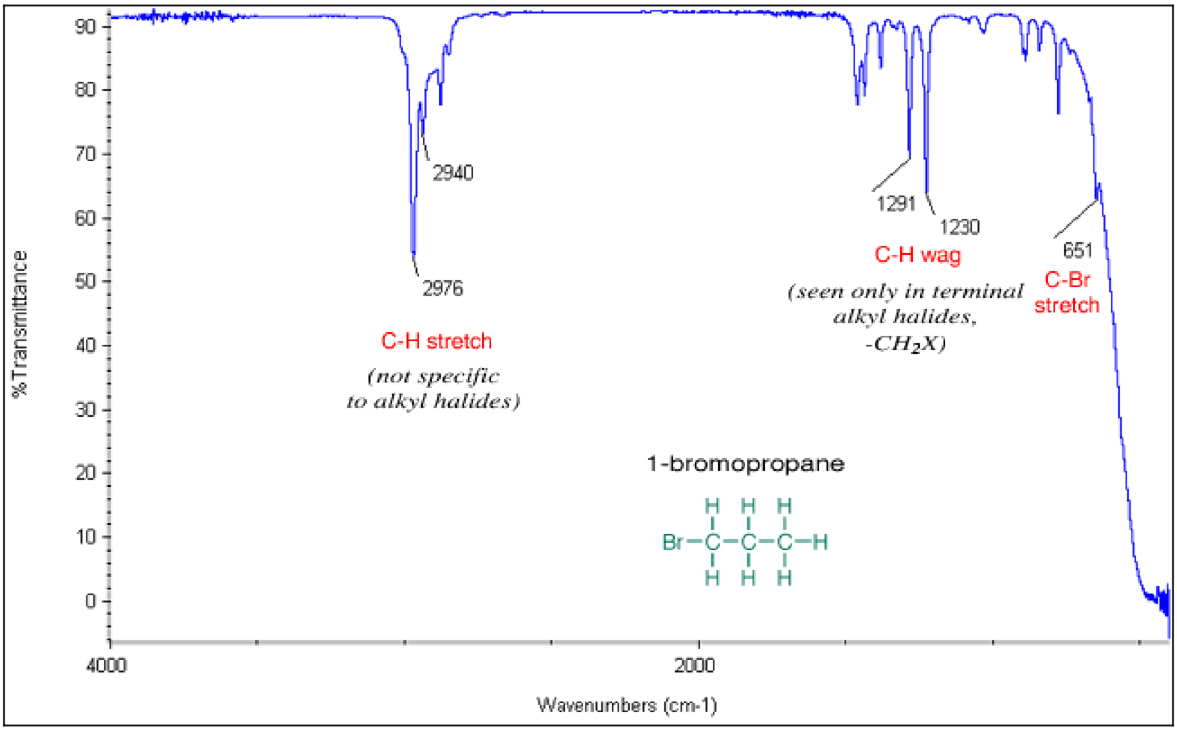
Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorene, or iodine (usually Br or Cl in the organic chemistry teaching labs). In general, C–X vibration frequencies appear in the region 850-515 cm^{-1}, sometimes out of the range of typical IR instrumentation. C–Cl stretches appear from 850–550 cm^{-1}, while C–Br stretches appear at slightly lower wavenumbers from 690-515 cm^{-1}. In terminal alkyl halides, the C–H wag of the $–CH_2X$ group is seen from 1300-1150 cm^{-1}. Complicating the spectra is a profusion of absorptions throughout the region 1250-770 cm^{-1}, especially in the smaller alkyl halides. Note that all of these bands are in the fingerprint region.

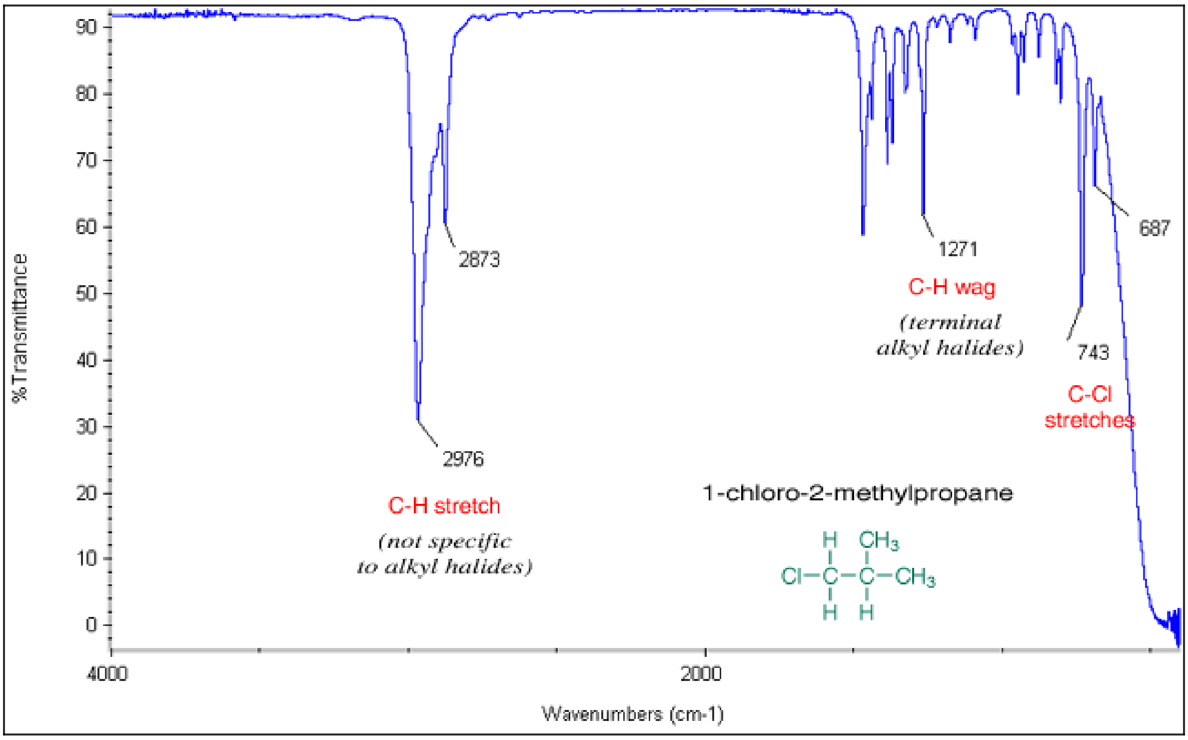
In summary, the following bands are specific to alkyl halides:

- **C–H wag ($-CH_2X$) from 1300-1150 cm^{-1}**
- **C–X stretches (general) from 850-515 cm^{-1}**
    - **C–Cl stretch 850-550 cm^{-1}**
    - **C–Br stretch 690-515 cm^{-1}**

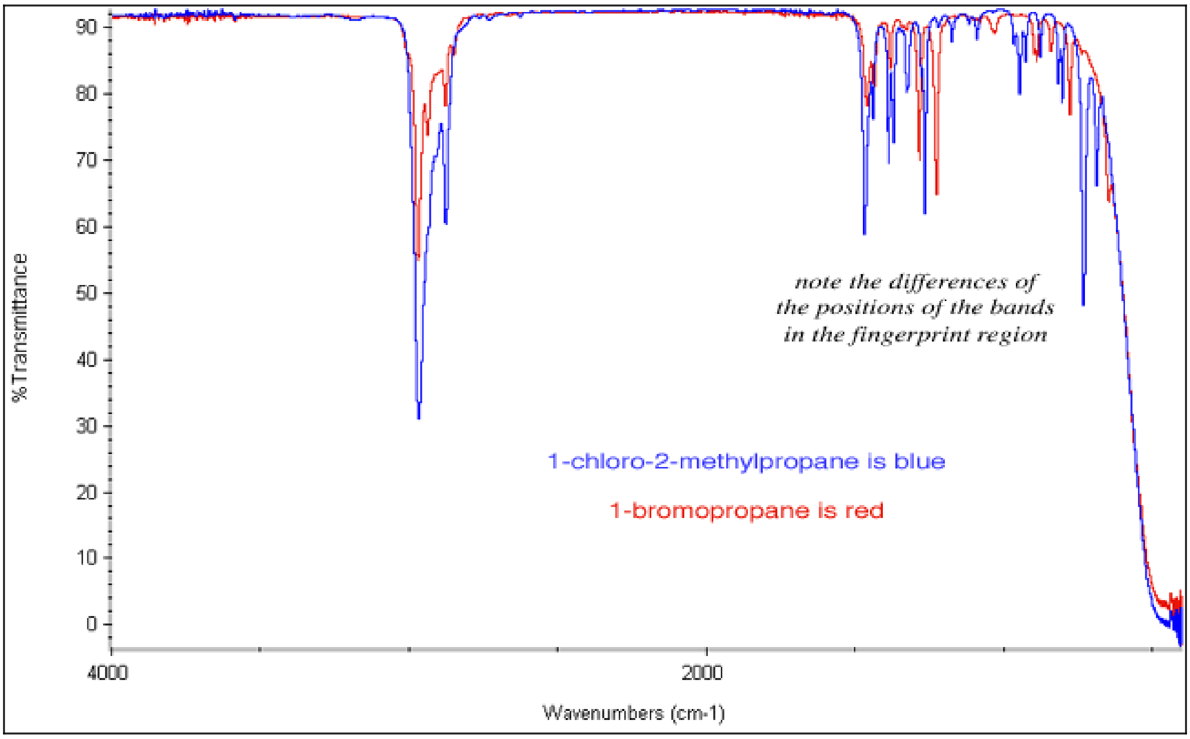
The spectra of 1-bromopropane and 1-chloro-2-methylpropane are shown below. Note the C–Br or C–Cl stretches in the region 850-515 cm^{-1}. They also show C–Br or C–Cl wag in the region 1300-1150 cm^{-}

1.





Even though both 1-bromopropane and 1-chloro-1-methylpropane have similar spectra and the bands that distinguish one from the other are in the fingerprint region, if the two spectra are overlayed, examination of the fingerprint region readily shows that they are different compounds. (Shown below.)



note the differences of the positions of the bands in the fingerprint region

IR Spectroscopy Tutorial: Amines

The N–H stretches of amines are in the region 3300-3000 cm^{-1}. These bands are weaker and sharper than those of the alcohol O–H stretches which appear in the same region. In primary amines (RNH$_2$), there are two bands in this region, the asymmetrical N–H stretch and the symmetrical N–H stretch.

Secondary amines (R$_2$NH) show only a single weak band in the 3300-3000 cm^{-1} region, since they have only one N–H bond. Tertiary amines (R$_3$N) do not show any band in this region since they do not have an N–H bond.

(A shoulder band usually appears on the lower wavenumber side in primary and secondary liquid amines arising from the overtone of the N–H bending band: this can confuse interpretation. Note the spectrum of aniline, below.)

The N–H bending vibration of primary amines is observed in the region 1650-1580 cm^{-1}. Usually, secondary amines do not show a band in this region and tertiary amines never show a band in this region. (This band can be very sharp and close enough to the carbonyl region to cause students to interpret it as a carbonyl band.)

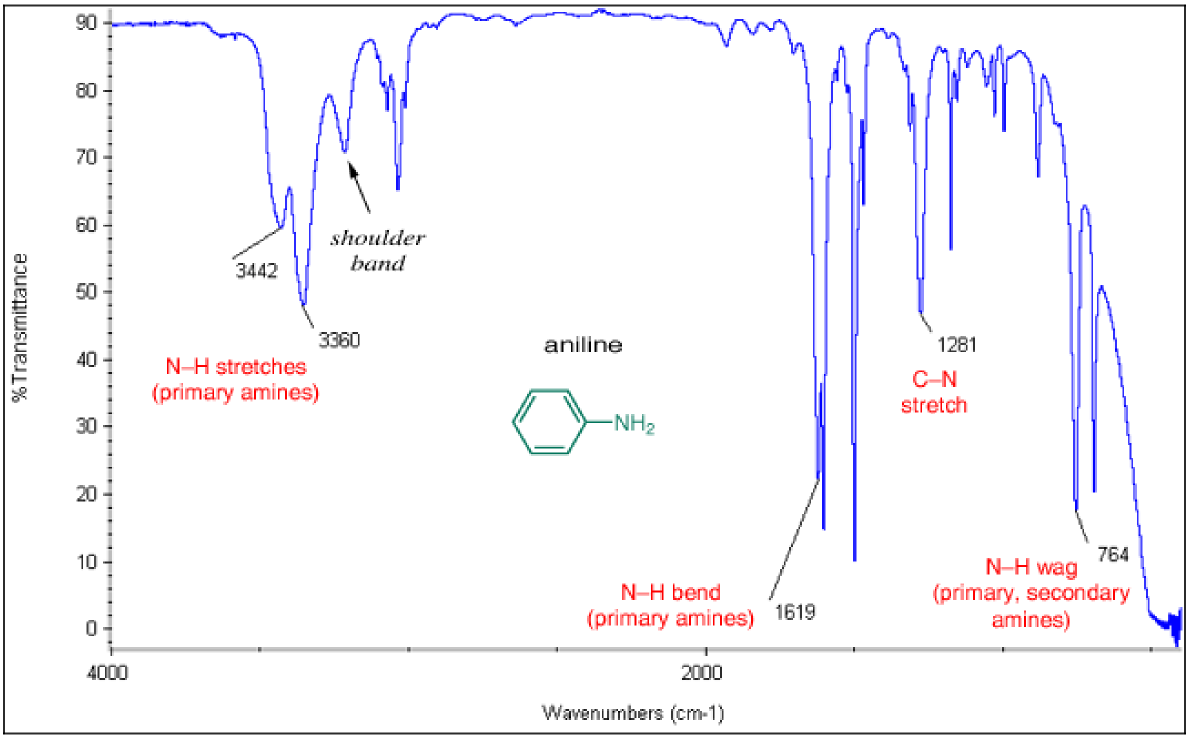
Another band attributed to amines is observed in the region 910-665 cm^{-1}. This strong, broad band is due to N–H wag and observed only for primary and secondary amines.

The C–N stretching vibration of aliphatic amines is observed as medium or weak bands in the region 1250-1020 cm^{-1}. In aromatic amines, the band is usually strong and in the region 1335-1250 cm^{-1}.

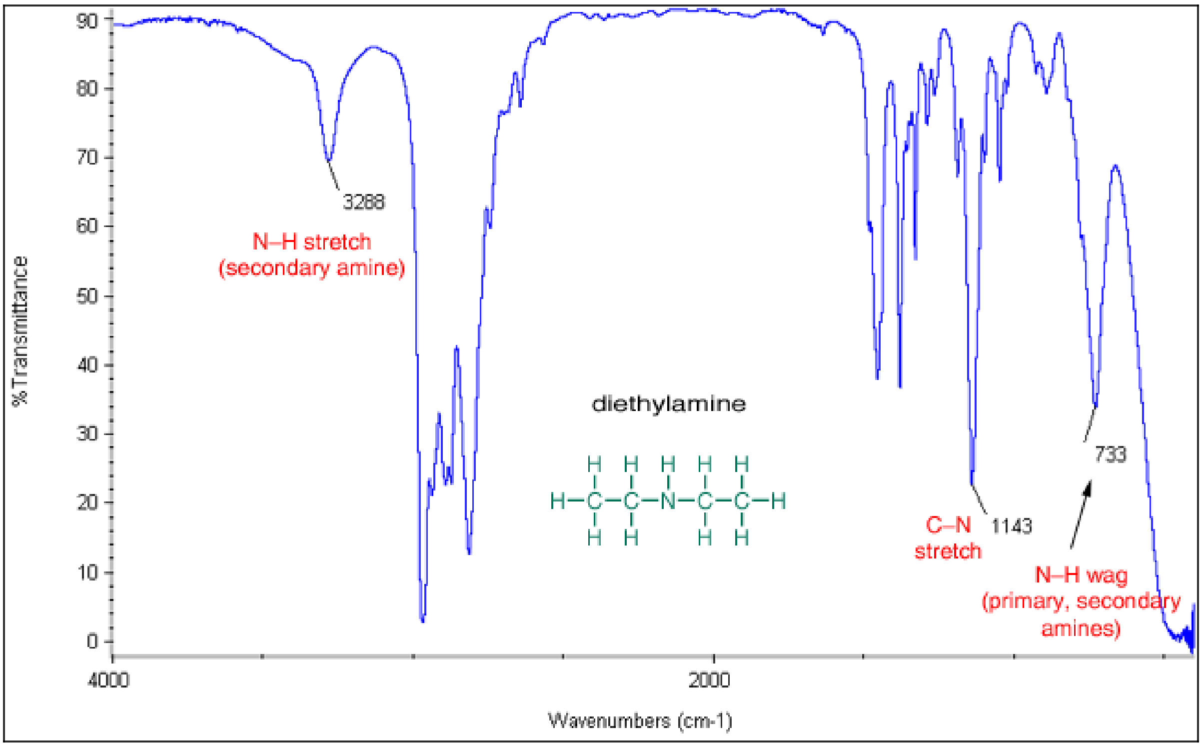
Summary:

- **N–H stretch 3400-3250 cm^{-1}**
  - **1° amine: two bands from 3400-3300 and 3330-3250 cm^{-1}**
  - **2° amine: one band from 3350-3310 cm^{-1}**
  - **3° amine: no bands in this region**
- **N–H bend (primary amines only) from 1650-1580 cm^{-1}**
- **C–N stretch (aromatic amines) from 1335-1250 cm^{-1}**
- **C–N stretch (aliphatic amines) from 1250–1020 cm^{-1}**
- **N–H wag (primary and secondary amines only) from 910-665 cm^{-1}**

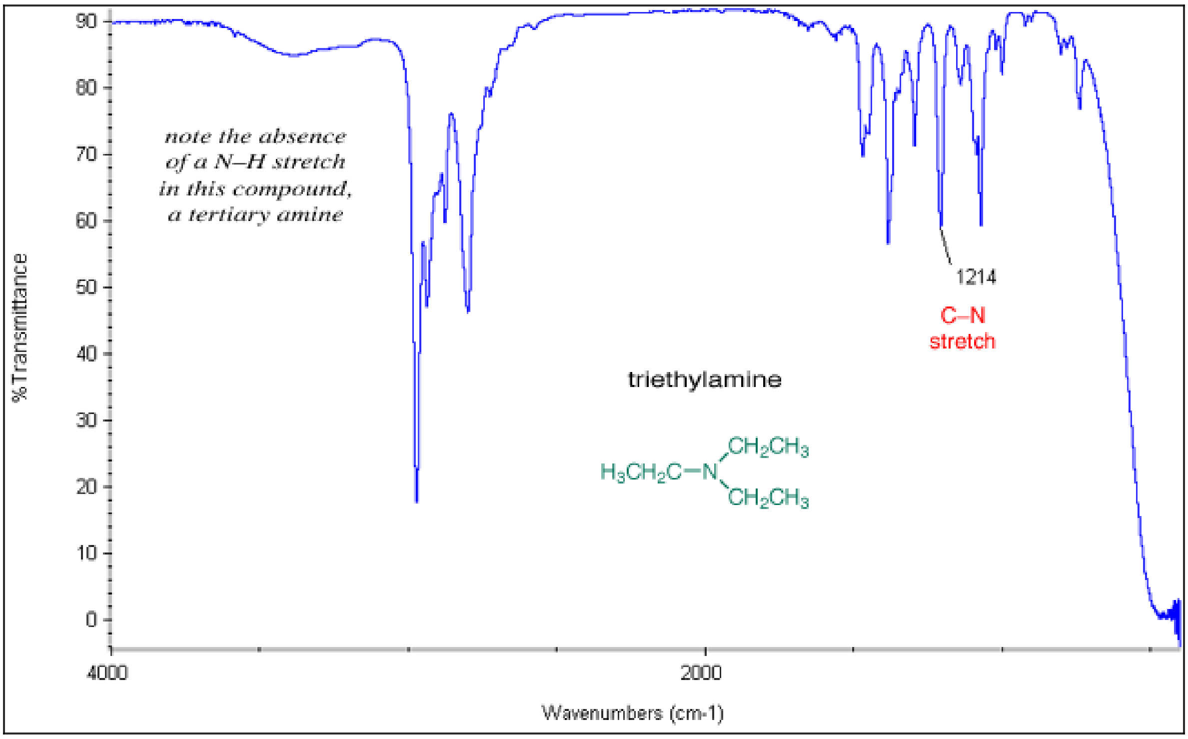
The spectrum of aniline is shown below. This primary amine shows two N–H stretches (3442, 3360); note the shoulder band, which is an overtone of the N–H bending vibration. The C–N stretch appears at 1281 rather than at lower wavenumbers because aniline is an aromatic compound. Also note the N–H bend at 1619.



The spectrum of diethylamine is below. Note that this secondary amine shows only one N–H stretch (3288). The C–N stretch is at 1143, in the range for non-aromatic amines (1250-1020). Diethylamine also shows an N–H wag (733).



Triethylamine is a tertiary amine and does not have an N–H stretch, nor an N–H wag. The C–N stretch is at 1214 cm^{-1} (non-aromatic).



IR Spectroscopy Tutorial: Nitro Groups

The N–O stretching vibrations in nitroalkanes occur near 1550 cm^{-1} (asymmetrical) and 1365 cm^{-1}

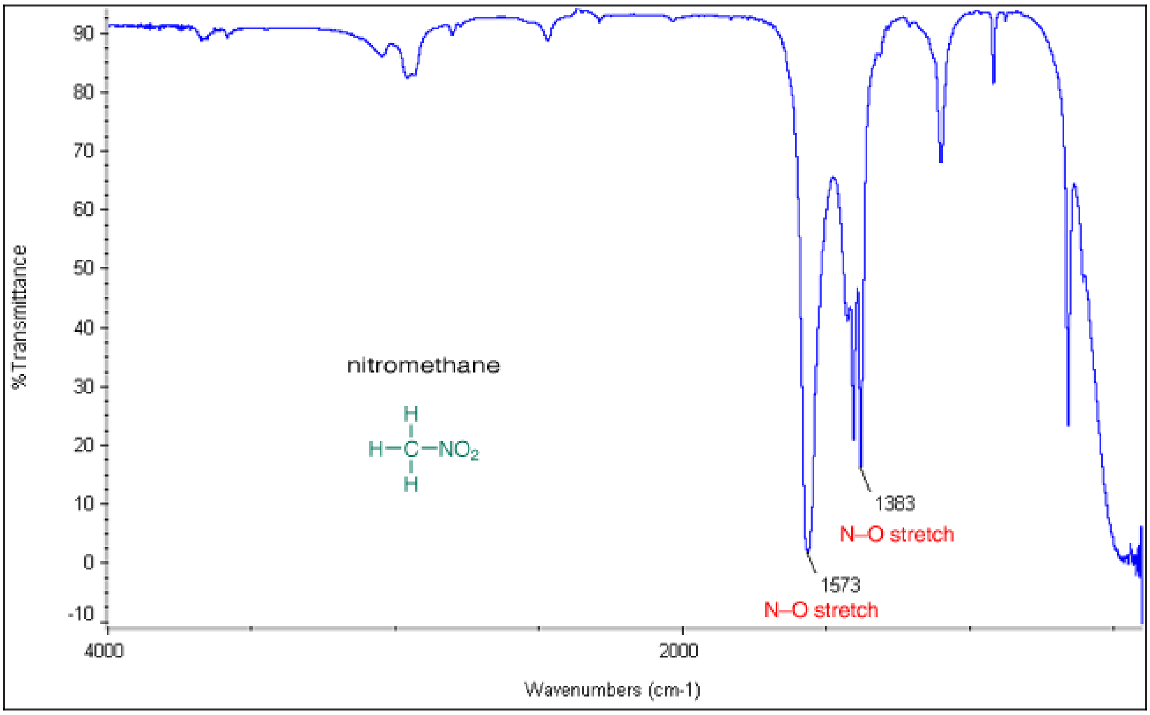
(symmetrical), the band at 1550 cm^{-1} being the stronger of the two.

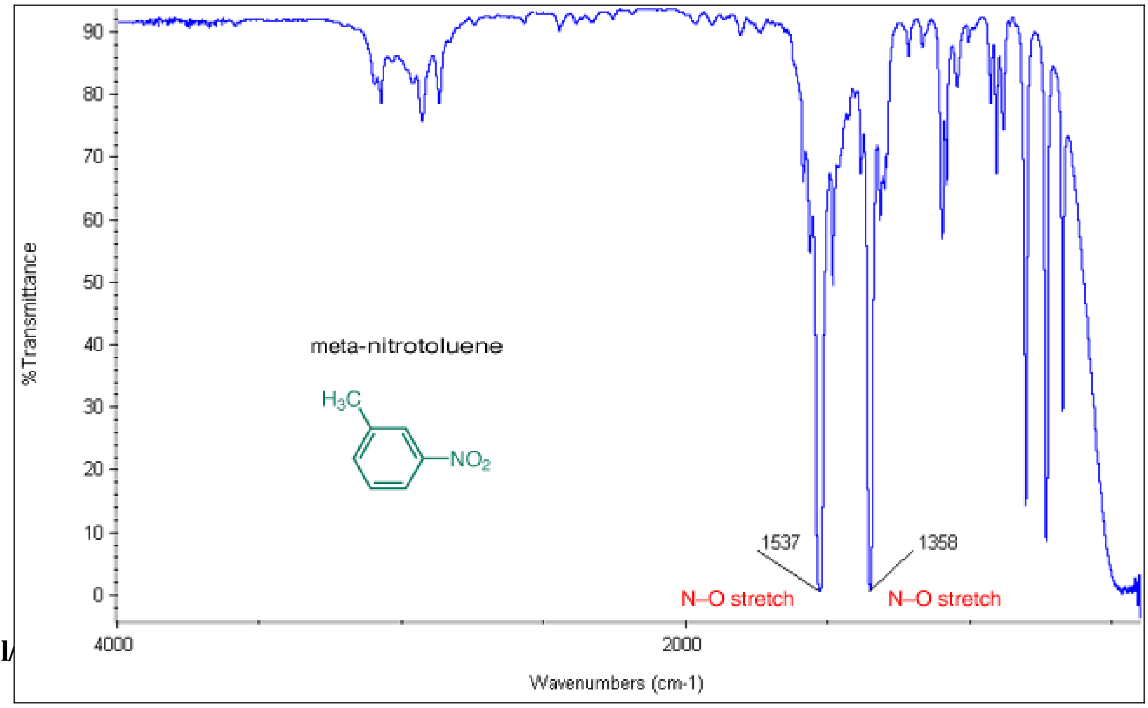
If the nitro group is attached to an aromatic ring, the N–O stretching bands shift to down to slightly lower wavenumbers: 1550-1475 cm^{-1} and 1360-1290 cm^{-1}.

Summary:

- **N–O asymmetric stretch from 1550-1475 cm^{-1}**
- **N–O symmetric stretch from 1360-1290 cm^{-1}**

Compare the spectra of nitromethane and m-nitrotoluene, below. In nitromethane, the N–O stretches are at 1573 and 1383, while in nitrotoluene, they are a little more to the right, at 1537 and 1358.





IR Spectroscopy Tutorial: How to analyze IR spectra

If you have followed this tutorial group-by-group, you will realize that in even rather simple, mono-functional molecules there are so many IR bands that it is not feasible to assign every band in an IR spectrum. Instead, look for tell-tale bands -- the region from 4000-1300 cm^{-1} is particularly useful for determining the presence of specific functional groups. You can rely on the IR correlation charts (linked in the left frame), but we recommend (in fact, in organic chem 1 lab, we require) that you memorize the distinctive bands of the common functional bands:

3500-3300 cm^{-1}	N–H stretch	1&Mac251;, 2&Mac251; amines
3500-3200 cm^{-1}	O–H stretch	alcohols, a broad, strong band
3100-3000 cm^{-1}	C–H stretch	alkenes
3000-2850 cm^{-1}	C–H stretch	alkanes
1760-1665 cm^{-1}	C=O stretch	ketones, aldehydes, esters
1680-1640 cm^{-1}	C=C stretch	alkenes

Begin by looking in the region from 4000-1300. Look at the C–H stretching bands around 3000:

	Indicates:
Are any or all to the right of 3000?	alkyl groups (present in most organic molecules)
Are any or all to the left of 3000?	a C=C bond or aromatic group in the molecule

Look for a carbonyl in the region 1760-1690. If there is such a band:

	Indicates:
Is an O–H band also present?	a carboxylic acid group
Is a C–O band also present?	an ester
Is an aldehydic C–H band also present?	an aldehyde

Is an N–H band also present?	**an amide**
Are none of the above present?	**a ketone**

(also check the exact position of the carbonyl band for clues as to the type of carbonyl compound it is)

Look for a broad O–H band in the region 3500-3200 cm^{-1}. If there is such a band:

	Indicates:
Is an O–H band present?	**an alcohol or phenol**

Look for a single or double sharp N–H band in the region 3400-3250 cm^{-1}. If there is such a band:

	Indicates:
Are there two bands?	**a primary amine**
Is there only one band?	**a secondary amine**

Other structural features to check for:

	Indicates:
Are there C–O stretches?	**an ether (or an ester if there is a carbonyl band too)**
Is there a C=C stretching band?	**an alkene**
Are there aromatic stretching bands?	**an aromatic**
Is there a C≡C band?	**an alkyne**
Are there -NO2 bands?	**a nitro compound**

If there is an absence of major functional group bands in the region 4000-1300 cm^{-1} (other than C–H stretches), the compound is probably a strict hydrocarbon.

Also check the region from 900-650 cm^{-1}. Aromatics, alkyl halides, carboxylic acids, amines, and amides show moderate or strong absorption bands (bending vibrations) in this region.

As a beginning student, you should not try to assign or interpret every peak in the spectrum. Concentrate on learning the major bands and recognizing their presence and absence in any given spectrum.

In the organic chem teaching labs, you usually know what compound you started with and what compound you are trying to make. For instance, if you are oxidizing an alcohol to a ketone, your product should show a carbonyl band but no hydroxyl band. If no carbonyl band is present, the experiment was not successful. If both carbonyl and hydroxyl bands are present, the product is not pure.

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http://www.umsl.edu/~orglab/documents/IR/IR.html

Infrared Spectroscopy

Most of us are quite familiar with infrared radiation. We have seen infrared lamps keep food hot and often associate infrared radiation with heat. While the generation of heat is a probable event following the absorption of infrared radiation, it is important to distinguish between the two. Infrared is a form of radiation that can travel through a vacuum while heat is associated with the motion and kinetic energy of molecules. The concept of heat in a vacuum has no meaning because of the lack of molecules and molecular motion. Infrared spectroscopy is the study of how molecules absorb infrared radiation and ultimately convert it to heat. By examining how this occurs, we will not only learn about how infrared radiation is absorbed, but we will also learn about molecular structure and how the study of infrared spectroscopy can provide information about the structure of organic molecules. An infrared spectrum of a chemical substance, is very much like a photograph of a molecule. However, unlike a normal photograph which would reveal the position of nuclei, the infrared spectrum will only reveal a partial structure. It is the purpose of this narrative to provide you with the tools necessary to interpret infrared spectra, successfully. In some respects, this process is similar to reading an X-ray of the chest. While most of us could easily identify the gross structural features of the chest such as the ribs, most of us would need some guidance in identifying those features of the X-ray associated with disease.

In order to interpret infrared spectra, having some idea or model of the physical process involved when a molecule interacts with infrared radiation would be useful. You may recall in introductory chemistry, the discussion of how atoms interact with electromagnetic radiation led to the development of quantum theory and the introduction of quantum numbers. The interaction of infrared radiation with molecules requires a similar treatment. While the use of quantum theory is necessary to explain this interaction, most of us live in a world that appears continuous to us and we do not have much experience discussing phenomena that occur is discrete steps. The discussion that follows will attempt to develop a model of how molecules interact with infrared radiation that is based as much as possible on classical physics. When necessary, we will insert the modifications required by quantum mechanics. This model, while perhaps oversimplified, will contain the physical picture that is useful to understand the phenomena and will be correct from a quantum mechanical standpoint.

Let's begin first by considering two isolated atoms, a hydrogen and a bromine atom moving toward each other from a great distance. What do you suppose will happen once the atoms approach each other and can feel each others presence? The potential energy curve for the H-Br molecule is shown in Figure 1. As the two atoms approach each other notice that the potential energy drops. If we recall that energy must be conserved, what must happen to the kinetic energy? The two atoms must attract each other and accelerate toward each other, thereby increasing their kinetic energy. The change in kinetic energy is illustrated by the dotted line in the figure. At some point they will "collide" as indicated by the part of the potential energy curve that rises steeply at small interatomic distances and then the atoms will begin to move away from each other. At this point, we might ask, "Will the molecule of HBr survive the collision"? Unless some energy from this system is lost, say by emission of a photon of light or collision by a third body to remove some energy, these are two ships passing in the night. The kinetic energy resulting from the coulombic attraction of the two atoms will exactly equal the drop in potential energy and the two atoms will fly apart. The spontaneous emission of a photon of light is improbable, so this mechanism is unlikely to drop the HBr molecule into the well. Most Probable from a physical perspective, is the

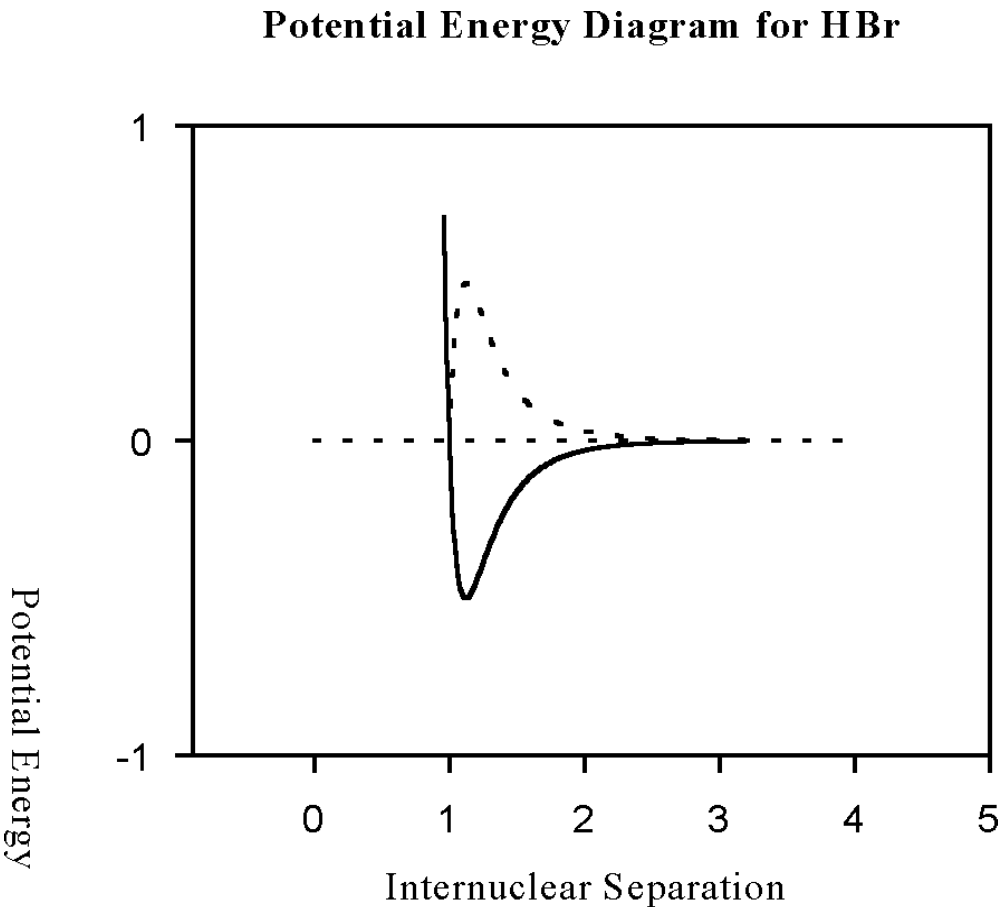


Figure 1. The potential (solid line) and kinetic energy (dotted line) of HBr as a function of the separation of the two nuclei. The kinetic energy at every point illustrated by the dotted line is equal to the potential energy plus the small amount of kinetic energy associated with initial motion of the two nuclei when separated at large distances.

collision of our HBr with a third body which will remove some energy and result in the trapping of the HBr molecule in the well. Though very excited, this molecule will now survive until other collisions with less energetic molecules leads to an HBr molecule at the bottom of the well and the generation of heat (kinetic energy) that would be experienced in the exothermic reaction of hydrogen and bromine atoms to form hydrogen bromide. Let us now consider a hydrogen bromide molecule that has lost a little kinetic energy by collision and has been trapped in the potential energy well of Figure 1. We might ask, "How would a molecule that does not have enough kinetic energy to escape the well behave in this well? A molecule with some kinetic energy below this threshold value (total energy slightly less than 0 in Fig. 1) will be able to move within this well. The internuclear separation will vary within the limits governed by the available kinetic energy. Since this motion involves a stretching or compression of the internuclear distance it is usually described as a vibration. Additional collisions with other molecules will eventually lead to the dissipation of the energy associated with formation of the hydrogen bromide bond. At this point we might ask the following question. If we remove all the excess kinetic energy from HBr, what will be its kinetic and potential energy? Alternatively we might ask, "Will the hydrogen bromide molecule reside at the very bottom of the well when it is cooled down to absolute zero Kelvin?" Before we answer this question, let's digress for a little and discuss the relative motions of the hydrogen and bromine atoms in terms of the physics of everyday objects. Once we learn how to describe the classical behavior of two objects trapped in a potential energy well, we will return to the question we have just posed.

One model we can use to describe our hydrogen bromide molecule is to consider our HBr molecule to be made up of balls of uneven mass connected to each other by means of a spring. Physicists found many years ago some interesting properties of such a system which they referred to as a harmonic oscillator. Such a system repeatedly interconverts potential and kinetic energy, depending on whether the spring is exerting a force on the balls or the momentum of the balls is causing the spring to be stretched or compressed. The potential energy of this system (PE) is given by the parabola,

$$PE = k(x-xo)2 \quad 1$$

where x-xo is the displacement of the balls from their equilibrium condition when the system is at rest and k is a measure of the stiffness of the spring. While this simple equation does not apply to molecules, please notice how similar the potential energy surface of the parabola (Figure 3) is to the bottom of the surface of Figure 1. The constant k is used to describe chemical bonds and is referred to as the **force constant**. As you might imagine, it is a measure of the stiffness of the chemical bond.

Several other relationships were observed that do carry over in describing molecular systems. For example, they found that when a ball was suspended on a spring from a horizontal wall, the frequency of vibration or oscillation, ν, depended only on the mass of the ball and the stiffness of the spring. The term A is a constant of the proportionality. By varying the mass of the ball and the stiffness of the spring, they were able to uncover the following simple relationship between frequency, mass and force constant:

$$\nu = A\sqrt{\frac{k}{m}}\ 2$$

Suspending a ball and spring from a horizontal surface is a special case of the more general situation when you have two more comparable masses attached to each other. Under these circumstances, when two similar masses are attached to a spring, the relationship between frequency of vibration, mass and force constant is given by:

$$\nu = A\sqrt{\frac{k}{\mu}} \quad 3$$

where μ, represents the product of the masses divided by their sum (m1m2/(m1+m2). This latter term is found in other physical relationships and has been given the name, the **reduced mass**. It can easily be seen that equation 2 is a special case of the more general relationship given by equation 3. If we consider m1to be much larger than m2, the sum of m1+ m2 ≈ m1 and substituting this approximation into (m1m2/(m1+m2) ≈ m2. Substituting m2 into equation 3 where m2 is the smaller of the two masses gives us exactly the same relationship as we had above when the ball was suspended from a horizontal wall. The horizontal wall is much more massive than the ball so that the vibration of a smaller ball has very little effect on the wall. Despite their simplicity, equations 2 and 3 play an important role in explaining the behavior of molecular systems. However, before we discuss the important role these equations play in our understanding of infrared spectroscopy, we need to review some of the properties of electromagnetic radiation, particularly radiation in the infrared range.

The electromagnetic spectrum is summarized in Figure 2. On the extreme right we find radiowaves and scan from right to left we encounter of terms which have become familiar to us; microwave, infrared, visible ultraviolet and X-rays. All of these forms of electromagnetic radiation

Wavenumbers, cm-1

1010 108 106 2x105 1x105 4000 650 12 5 x10-2 10-3 10-6

10-2 4x10-2 4x10-2 2.5 15.4 830 4x105 107 1010

Figure 2. The electromagnetic spectrum.

Wavelength (microns)

Gamma Rays	X-Rays	Ultraviolet	Visible Light	Near IR	Infra red	Far Infrared	Micro wave	TV Waves	Radio

10-6
10-4

are related to each other in a simple and obvious way. First let us discuss why we refer to these different forms of light as electromagnetic radiation. Simply stated, all these forms of radiation have an electric and magnetic field associated with them that varies as shown for the standing wave in Figure 3. Only the electric field is shown in this figure. If we were to include the magnetic field it would look exactly as the electric field but would be rotated 90 ° out of the plane of the paper and would oscillate above and below the plane of the paper like a sin or cos wave. In

infrared spectroscopy, only the electric field associated with the electromagnetic radiation is important and we will limit our present discussion to how this field varies with time. We called the light wave associated with Figure 4 a standing wave because this is how the electric field would

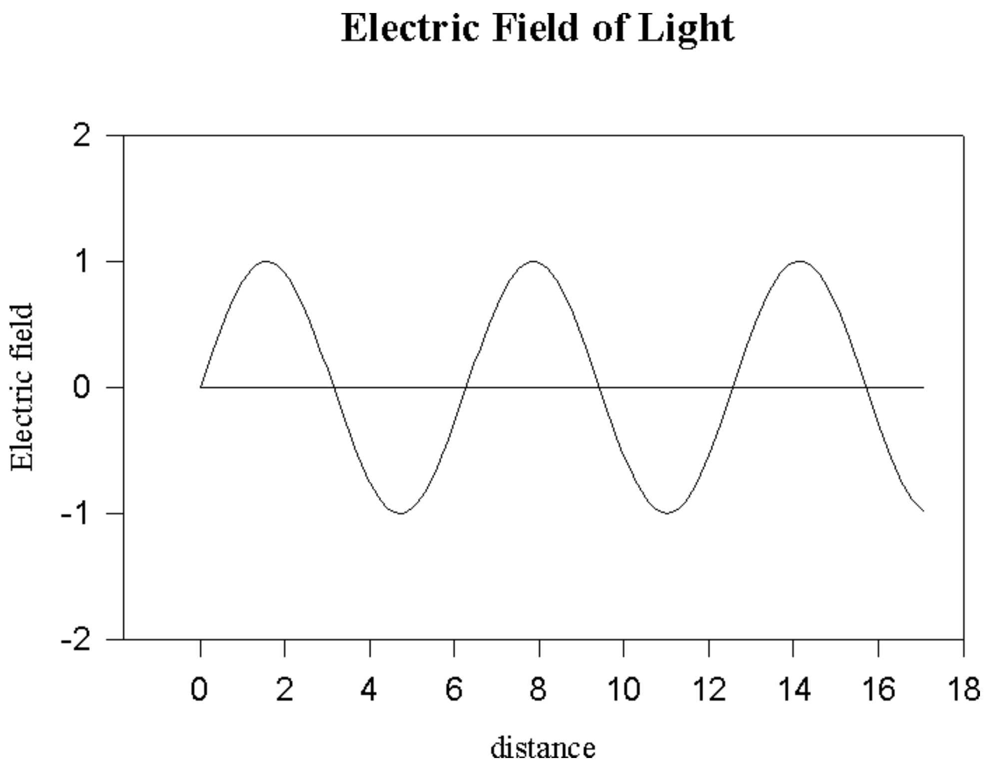


Figure 3. The electric field of light associated with a standing wave with a fixed wavelength.

vary if we took a picture of the wave. One of the properties of all electromagnetic radiation is that it travels in a vacuum at the speed of 3 x 1010 cm/sec. Therefore, if we were to turn this standing wave "on" we would observe this oscillating field rapidly passing us by. If we examine the electric field (or the magnetic field which is not shown), we observe that the field is repetitive, varying as a cos or sin wave. The length of the repeat unit along the x axis is called the wavelength, λ, and it is this property which varies continuous from 106 cm (1010 microns) for radio waves down to 10-13 cm (10-6 microns) for cosmic radiation. A unit of length that is frequently used in infrared spectroscopy is the micron. A micron is equivalent to 10-4 cm. If we were to "stand on the corner and watch all the wavelengths go by", since all electromagnetic radiation would be traveling at 3 x 1010 cm/sec, the frequency, , at which the shorter wavelengths would have to pass by would have to increase in order to keep up with the longer wavelengths. This relationship can be described in the following mathematical equation:

$\lambda\nu = c$; ($c = 3 \times 1010$ cm/sec). 4

The frequency of the light times the wavelength of the light must equal the speed at which the light is traveling.

In addition to having wave properties such as the ones we have been discussing, electromagnetic radiation also has properties we would normally attribute to particles. These "particle like" properties are often referred to as characteristics of **photons**. We can discuss the wave properties of photons by referring to the wavelength (eqn. 4) and frequency associated with a photon. The energy of a single photon is a measure of a property we would normally associate with a particle. The relationship which determines the energy associated with a single photon of light, E, and the total energy incident at on a surface by monochromatic light, ET, is given by:

$E = h\nu$ (or equivalently, $E = hc/\lambda$, from equation 4), 5

$ET = nh\nu$ 6

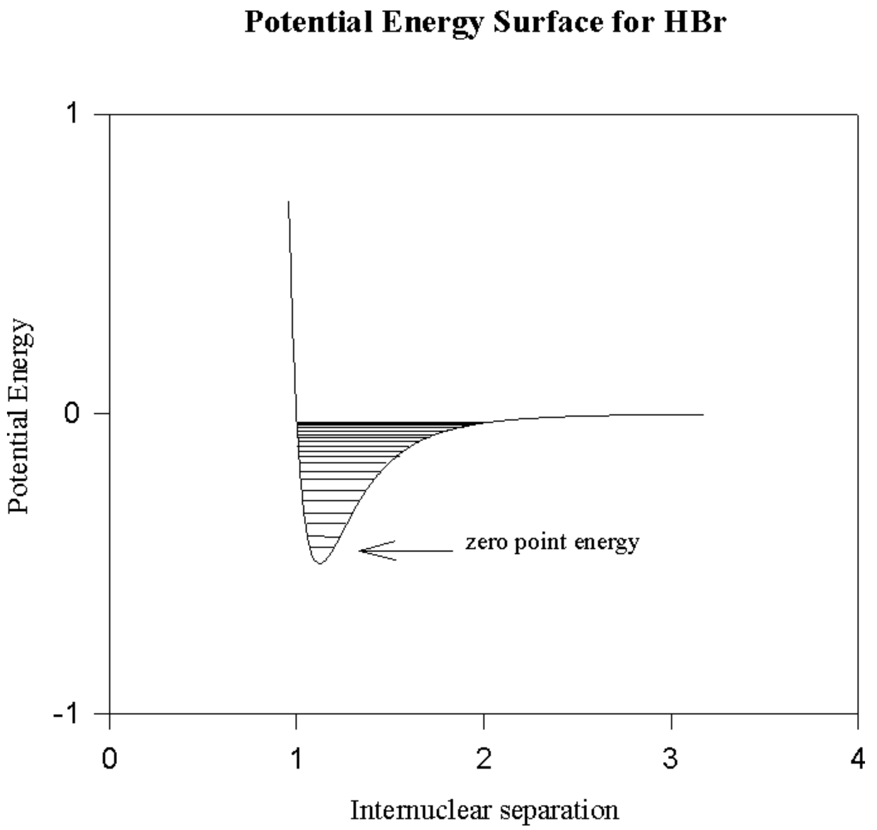
where h is Planck's constant and is numerically equal to 6.6 x 10-27 erg s and n is the number of photons. Equations 4 and 5 tell us that photons with short wavelengths, in addition to having higher frequencies associated with them, also carry more punch! The energy associated with a photon of light is directly proportional to its frequency.

At this point we are ready to return to a discussion of how infrared radiation interacts with molecules. Following our discussion of balls and springs, you have probably figured that infrared spectroscopy deals with the vibration of molecules. Actually, both rotation and vibration of molecules is involved in the absorption of infrared radiation, but since molecular rotation is not usually resolved in most infrared spectra of large organic molecules, we will ignore this additional consideration. In order to derive the relationship between vibrational energy and molecular structure, it is necessary to solve the Schoedinger equation for vibrational-rotational interactions. Since solution of this equation is beyond the scope of this treatment, we will simply use the relationship that is derived for a harmonic oscillator from this equation. As you see, the quantum mechanical solution of a harmonic oscillator, equation 7, is remarkably simple and very similar to the relationship we obtained from considering the classical model of balls and springs.

$$E = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(n + \frac{1}{2}\right)$$

Before discussing the implications of equation 7, let's take a moment to see how similar it is to equations 3 and 5. From equation 5, we see that substituting equation 3 for ν results in equation 7 except for the (*n* + 1/2) term. However we should point out that we have substituted the vibrational frequency of two masses on a spring for a frequency associated with the number of wave maxima (or minima, null points. *etc.*) passing a given point (or street corner) per unit time. We are able to do this because of the presence of the (n +1/2) term. Let's discuss the significance of the (n + 1/2) term before we returning to answer this question. The previous time you encountered the Schroedinger equation was probably when studying atomic spectra in Introductory Chemistry. An important consequence of this encounter was the introduction of quantum numbers, at that time the principle quantum number, *N*, the azimuthal quantum number, *l*, the magnetic, m*l*, and spin quantum number, *s*. This time is no exception. Meet *n*, the vibrational quantum number. These numbers arise in a very similar manner. The Schroedinger equation is a differential equation which vanishes unless certain terms in it have very discrete values. For *n*, the allowed values are 0,1,2,... Let us now consider the energy of vibration associated with a molecule in its lowest energy of vibration, n = 0.

According to equation 6, the energy of vibration is given by $E = \frac{h}{4\pi}\sqrt{\frac{k}{\mu}}$, when n = 0, the zero point energy. This equation allows us to answer the question posed earlier about what would happen to the vibrational energy of a molecule at absolute zero. According to quantum theory the molecule would continue to vibrate. From the relationship E = h ν, we can evaluate the vibrational frequency as $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, the same as found by classical physics for balls and springs. This equation states that the vibrational frequency of a given bond in a molecule depends only on the stiffness of the chemical bond and the masses that are attached to that bond. Similarly, according to equation 7, once the structure of a



molecule

Figure 4. The potential energy surface for a HBr molecule illustrating how the vibrational energy levels vary in energy with increasing vibrational quantum number.

is defined, the force constants and reduced mass are also defined by the structure. This also defines the vibrational frequencies and energy of absorption. Stated in a slightly different manner, a molecule will not absorb vibrational energy in a continuous fashion but will do so only in discrete steps as determined by the parameters in equation 7 and illustrated for the HBr molecule in Figure 4. We have pointed out that the vibrational quantum number can have positive integer values including a value of zero. Upon absorption of vibration energy, this vibrational quantum number can change by +1 unit. At room temperature, most molecules are in the n = 0 state.

Figure 4 illustrates the real vibrational levels for HBr. Notice that equation 7 predicts that the energy level spacings should all be equal. Notice according to Figure 4, the spacings actually converge to a continuum for large values of n. For small values of n, n = 0, 1, 2, equation 7 gives a good approximation of the vibrational energy levels for HBr. Equation 7 was derived from the approximation that the potential energy surface is like a parabola. Near the minimum of this surface, around the zero point energy, this is a good approximation. As you go up from the minimum, the resemblance decreases and the assumptions made in solving the Schroedinger equation no longer are valid.

Let us now return and question the wisdom of substituting the vibrational frequency of a molecule for the frequency of electromagnetic radiation in equation 5. I hope at this point of the discussion this does not seem so absurd. If the vibrational frequency of the molecule, as determined by the force constant and reduced mass, equals the frequency of the electromagnetic radiation, then this substitution makes good sense. In fact, this gives us a mechanism by which we can envision why a molecule will absorb only distinct frequencies of electromagnetic radiation. It is known that symmetrical diatomic molecules like nitrogen, oxygen and hydrogen, do not absorb infrared radiation, even though their vibrational frequencies are in the infrared region. These homonuclear diatomic molecules have no permanent dipole moment and lack a mechanism of interacting with the electric field of the light. Molecules like HBr and HCl which have a permanent dipole, resulting from an unequal sharing of the bonding electrons, have a dipole which oscillates as the bond distance between the atoms oscillate. As the frequency of the electric field of the infrared radiation approaches the frequency of the oscillating bond dipole and the two oscillate at the same frequency and phase, the chemical bond can absorb the infrared photon and increase its vibrational quantum number by +1. This is illustrated in Figure 5. Of course, some HBr molecules

may not be correctly oriented toward the light to interact and these molecules will not absorb light. Other factors will also influence the intensity and shape of the absorption. However, when the frequency of the electromagnetic radiation equals the vibrational frequency of a molecule, absorption of light does occur and this leads to an infrared spectrum that is characteristic of the structure of a molecule.

Up to now we have discussed molecules changing their vibrational quantum number by +1. A change of -1 is also equally possible under the influence of infrared radiation. This would lead to emission of infrared radiation. The reason why we have not discussed this possibility is that most molecules at room temperature are in the ground vibrational level (n=0) and cannot go any lower. If we could get a lot of molecules, let say with n = 1, use of infrared could be used to stimulate emission. This is how an infrared laser works.

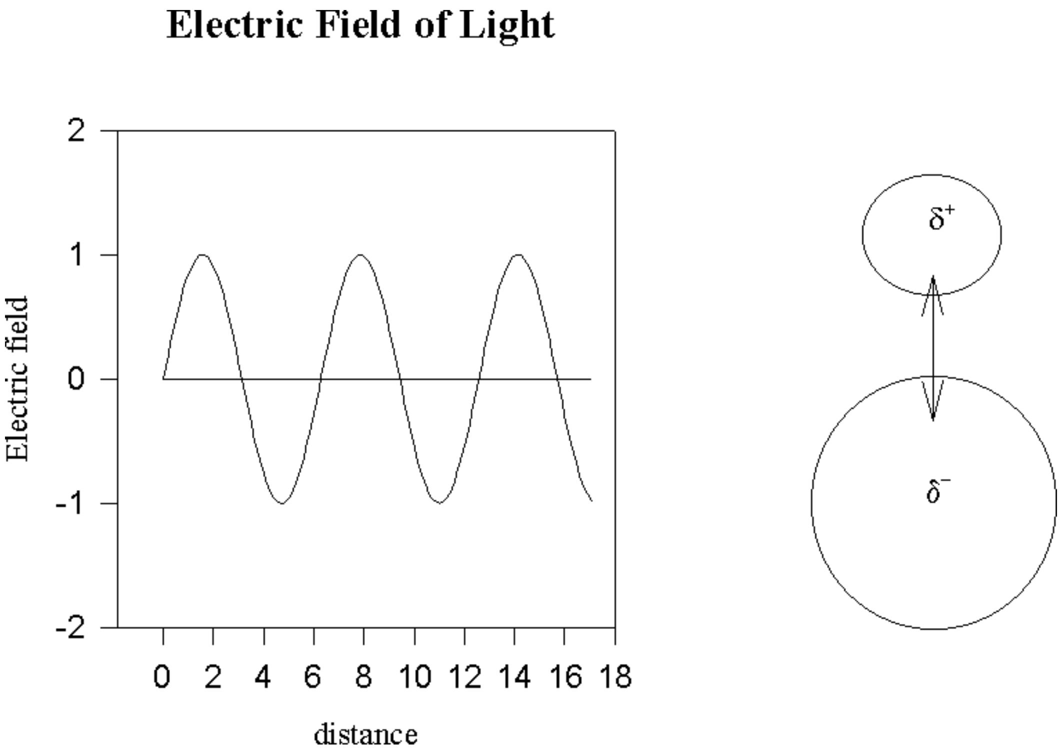


Figure 5. An HBr molecule interacting with electromagnetic radiation. In order for this interaction to occur successfully, the frequency of the light must equal the natural vibrational frequency of the HBr and the electric field must be properly orientated.

We have previously discussed the infrared region of the electromagnetic spectrum in terms of the wavelength of the light that is involved, 1-40 μ ((1-40)x10-4 cm) (Figure 3). According to equation 4, we can also express this region of the electromagnetic spectrum in terms of the frequency of the light. There is an advantage to discussing the absorption of infrared radiation in frequency units. According to equation 5, energy is directly proportional to frequency. The energy associated with an absorption occurring at twice the frequency of another can be said to require twice the energy. Occasionally, weak bands occur at twice the frequency of more intense bands. These are called overtones and result when the vibrational quantum number changes by +2. While these transitions are weak and are theoretically forbidden (i.e. they occur with an intensity of less than 5 % of the same transition that involves a change of +1 in the vibrational quantum number) they are easy to identify when units of frequency are used. Sometimes absorption bands involving a combination of frequencies occur. There is no physical significance to adding together wavelengths - there is a physical significance to the addition of frequencies since they are directly proportional to energy. To convert wavelength to frequency according to equation 4, we need to multiply the speed of light by the reciprocal of wavelength. Since the speed of light is a universal constant, a curious convention of simply using the reciprocal of wavelength has evolved. Thus a peak at 5 μ would be expressed as 1/(5x10-4 cm) or 2000 cm-1. You will note that 2000 cm-1 is not a true frequency. A true frequency would have units of cycles/sec. To convert 2000 cm-1 to a true frequency one would need to multiply by the speed of light (cm/sec). However, 2000 cm-1 is proportional to frequency and this is how frequency units in infrared spectroscopy are expressed.

Functional Group	Type		Frequencies cm-1	Peak Intensity	Examples Figure No.
C-H	sp3 hybridized	R3C-H	2850-3000	M(sh)	6, 18, 22
	sp2 hybridized	=CR-H	3000-3250	M(sh)	7, 13, 42
	sp hybridized	≡C-H	3300	M-S(sh)	13
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)	14, 15
N-H	primary amine, amide	RN-H2, RCON-H2	3300, 3340	S,S(br)	18, 19
	secondary amine, amide	RNR-H, RCON-HR	3300-3500	S(br)	20, 21
	tertiary amine, amide	RN(R3), RCONR2	none		22, 23
O-H	alcohols, phenols	free O-H	3620-3580	W(sh)	17, 24, 25
		hydrogen bonded	3600-3650	S(br)	24, 25, 28
	carboxylic acids	R(C=O)O-H	3500-2400	S(br)	26, 27, 29, 30
C≡N	nitriles	RC≡N	2280-2200	S(sh)	31
C≡C	acetylenes	R-C≡C-R	2260-2180	W(sh)	32
		R-C≡C-H	2160-2100	M(sh)	13
C=O	aldehydes	R(C=O)H	1740-1720	S(sh)	14
	ketones	R(C=O)R	1730-1710	S(sh)	35
	esters	R(CO2)R	1750-1735	S(sh)	33, 34
	anhydrides	R(CO2CO)R	1820, 1750	S, S(sh)	36
	carboxylates	R(CO2)H	1600, 1400	S,S(sh)	37
C=C	olefins	R2C=CR2	1680-1640	W(sh)	10, 39, 40
		R2C=CH2	1600-1675	M(sh)	9, 35

		R2C=C(OR)R	1600-1630	S(sh)	41
-NO2	nitro groups	RNO2	1550, 1370	S,S(sh)	28

At this point we are ready to leave diatomic molecules and start talking about complex organic molecules. Before doing so, it should be pointed out that the discussion that follows is an over simplification of the true vibrational behavior of molecules. Many vibrational motions of molecules are motions that involve the entire molecule. Analyze of such motions can be very difficult if you are dealing with substances of unknown structure. Fortunately, the infrared spectrum can be divided into two regions, one called the functional group region and the other the fingerprint region. The functional group region is generally considered to range from 4000 to approximately 1500 cm-1 and all frequencies below 1500 cm-1 are considered characteristic of the fingerprint region. The fingerprint region involves molecular vibrations, usually bending motions, that are characteristic of the entire molecule or large fragments of the molecule. Hence the origin of the term. Used together, both regions are very useful for confirming the identity of a chemical substance. This is generally accomplished by comparison to an authentic spectrum. As you become more proficient in analyzing infrared spectra, you may begin to assign bands in this region. However, if you are just beginning to interpret spectra of organic molecules, it is best to focus on identifying the characteristic features in the functional group region. The functional group region tends to include motions, generally stretching vibrations, that are more localized and characteristic of the typical functional groups found in organic molecules. While these bands are not very useful in confirming identity, they do provide some very useful information about the nature of the components that make up the molecule. Perhaps most importantly, the frequency of these bands are reliable and their presence or absence can be used confidently by both the novice and expert interpreter of infrared spectra. The discussion which follows focuses primarily on the functional group region of the spectrum. Some functional groups are discussed in more detail than others. You will find that all this information is summarized in Table 1 which should prove useful to you when you try to interpret an unknown spectrum. Finally, you should bear in mind that although we have developed a model that can help us understand the fundamental processes taking place in infrared spectroscopy, interpretation of spectra is to a large extent an empirical science. Information about the nature of a compound can be extracted not only from the frequencies that are present but also by peak shape and intensity. It is very difficult to convey this information in Table form. It is only by examining real spectra will you develop the expertise to accurately interpret the information contained within. Be sure to examine the spectra contained in this handout carefully. Whenever you interpret a spectrum and extract structural information, check your assignments by examining the spectrum of a known substance that has similar structural features.

Carbon-Hydrogen Stretching Frequencies

Let's take one more look at equation 6 and consider the carbon-hydrogen stretching frequencies. Since k and mH are the only two variables in this equation, if we assume that all C-H stretching force constants are similar in magnitude, we would expect the stretching frequencies of all C-H bonds to be similar. This expectation is based on the fact that the mass of a carbon atom

Table 1. A summary of the principle infrared bands and their assignments.

R is an aliphatic group.

and whatever else is attached to the carbon is much larger the mass of a hydrogen. The reduced mass for vibration of a hydrogen atom would be approximately the mass of the hydrogen atom which is independent of structure. All C-H stretching frequencies are observed at approximately 3000 cm-1, exactly as expected.

Fortunately, force constants do vary some with structure in a fairly predictable manner and therefor it is possible to differentiate between different types of C-H bonds. You may recall in your study of organic chemistry, that the C-H bond strength increased as the s character of the C-H bond increased. Some typical values are given below in Table 2 for various hydridization states of carbon. Bond strength and bond stiffness measure different properties. Bond strength measures the depth of the potential energy well associated with a C-H. Bonds stiffness is a measure of how much energy it takes to compress or stretch a bond. While these are different properties, the stiffer bond is usually associated with a deeper potential energy surface. You will note in Table 2 that increasing the bond strength also increases the C-H bond stretching frequency.

Table 2. Carbon Hydrogen Bond Strengths as a Function of Hybridization

Type of C-H bond Bond Strength IR Frequency

kcal/mol cm-1

sp3 hybridized C-H	$CH_3CH_2CH_2$-H	99	<3000
sp2 hybridized C-H	CH_2=CH-H	108	>3000
sp hybridized C-H	HC≡C-H	128	3300

C-H sp3 hybridization

Methyl groups, methylene groups and methine hydrogens on sp3 carbon atoms all absorb between 2850 and 3000 cm-1. While it is sometimes possible to differentiate between these types of hydrogen, the beginning student should probably avoid this type of interpretation. It should be pointed out however, that molecules that have local symmetry, will usually show symmetric and asymmetric stretching frequencies. Take, for example, a CH_2 group. It is not possible to isolate an individual frequency for each hydrogen. These two hydrogens will couple and will show two stretching frequencies, a symmetric stretching frequency in which stretching and compression of both hydrogens occurs simultaneously, and an asymmetric stretching frequency in which stretching of one hydrogen is accompanied by compression of the other. While these two motions will occur at different frequencies, both will be found between the 2850-3000 cm-1 envelope. This behavior is found whenever this type of local symmetry is present. We will find other similar examples in the functional groups we will be discussing. Some examples of spectra containing only sp3 hybridization can be found in Figures 5-6, and located at the end of this discussion. These peaks are usually sharp and of medium intensity. Considerable overlap of several of these bands usually results in absorption that is fairly intense and broad in this region.

C-H sp2 hybridization

Hydrogens attached to sp2 carbons absorb at 3000-3250 cm^{-1}. Both aromatic and vinylic carbon hydrogen bonds are found in this region. Examples of spectra that contain only sp^2 hybridization can be found in Figure 7. Examples of molecules that contain only sp^2 C-H bonds along with other functional groups include Figures 23, 24 and 25. Examples of hydrocarbons that contain both sp2 and sp3 hybridization can be found in Figures 8-12. These peaks are usually sharp and of low to medium intensity.

check fig 23-25

C-H sp hybridization

Hydrogens attached to sp carbons absorb at 3300 cm-1. An examples of a spectrum that contains sp hybridization can be found in Figure 13. These peaks are usually sharp and of medium to strong intensity.

C-H aldehydes

Before concluding the discussion of the carbon hydrogen bond, one additional type of C-H stretch can be distinguished, the C-H bond of an aldehyde. The C-H stretching frequency appears as a doublet, at 2750 and 2850 cm-1. Examples of spectra that contain a C-H stretch of an aldehyde can be found in Figures 14 and 15.

C-H exceptions

In summary, it is possible to identify the type of hydrogen based on hybridization by examining the infrared spectra in the 3300 to 2750 cm-1 region. Before concluding, we should also mention some exceptions to the rules we just outlined. Cyclopropyl hydrogens which are formally classified as sp3 hybridized actually have more s character than 25 %. Carbon-hydrogen frequencies greater than 3000 cm-1 are observed for these stretching vibrations. Halogen substitution can also affect the C-H stretching frequency. The C-H stretching frequencies of hydrogens attached to a carbon also bearing halogen substitution can also be shifted beyond 3000 cm-1. This is illustrated in Figure 16. The last exception we will mention is an interesting case in which the force constant is increased because of steric interactions. The infrared spectrum of tri-t-butylcarbinol is given in Figure 17. In this case, the hydrogens are sp3 hybridized but stretching the C-H bonds leads to increased crowding and bumping, and this is manifested by a steeper potential energy surface and an increase in k, the force constant in equation 6.

Nitrogen Hydrogen Stretching Frequencies

Much of what we have discussed regarding C-H stretching frequencies is also applicable here. There are three major differences between the C-H and N-H stretching frequencies. First, the force constant for N-H stretching is stronger, there is a larger dipole moment associated with the N-H bond, and finally, the N-H bond is usually involved in hydrogen bonding. The stronger force constant leads to a higher frequency for absorption. The N-H stretching frequency is usually observed from 3500-3200 cm-1. The larger dipole moment leads to a stronger absorption and the presence of hydrogen bonding has a definite influence on the band shape and frequency position. The presence of hydrogen bonding has two major influences on spectra. First, its presence causes the a shift toward lower frequency of all functional groups that are involved in hydrogen bonding and second, the peaks are generally broadened. Keep these two factors in mind as you examine the following spectra, regardless of what atoms and functional groups are involved in the hydrogen bonding.

The N-H stretching frequency is most frequently encountered in amines and amides. The following examples will illustrate the behavior of this functional group in a variety of circumstances.

Primary amines and amides derived from ammonia

The N-H stretching frequency in primary amines and in amides derived from ammonia have the same local symmetry as observed in CH2. Two bands, a symmetric and an asymmetric stretch are observed. It is not possible to assign the symmetric and asymmetric stretches by inspection but their presence at approximately 3300 and 3340 cm-1 are suggestive of a primary amine or amide. These bands are generally broad and a third peak at frequencies lower than 3300 cm-1, presumably due to hydrogen bonding, is also observed. This is illustrated by the spectra in Figures 18 and 18 for n-butyl amine and benzamide.

Secondary amines and amides

Secondary amines and amides show only one peak in the infrared. This peak is generally in the vicinity of 3300 cm-1. This is illustrated in Figures 20 and 21. Again notice the effect of hydrogen bonding on the broadness of the N-H peak.

Tertiary amines and amides

Tertiary amines and amides from secondary amines have no observable N-H stretching band as is illustrated in Figures 22 and 23.

N-H bending motions

You may recall that we will be ignoring most bending motions because these occur in the fingerprint region of the spectrum. One exception is the N-H bend which occurs at about 1600 cm-1. This band is generally very broad and relatively weak. Since many other important bands occur in this region it is important to note the occurrence of this absorption lest it be mistakenly interpreted as another functional group. Figure 18 illustrates the shape and general intensity of the bending motion. Most other functional groups absorbing in this region are either sharper or more intense.

Hydroxyl Stretch

The hydroxyl stretch is similar to the N-H stretch in that it hydrogen bonds but does so more strongly. As a result it is often broader than the N-H group. In those rare instances when it is not possible to hydrogen bond, the stretch is found as a relative weak to moderate absorption at 3600-3650 cm-1. In tri-t-butylmethanol where steric hindrance prevents hydrogen bonding, a peak at 3600 cm-1 is observed as shown in Figure 17. Similarly for hexanol, phenol, and hexanoic acid, Figures 24, 25, and 26, gas phase and liquid phase spectra illustrate the effect of hydrogen bonding on both the O-H stretch and on the rest of the spectrum. In should be pointed out that, in general, while gas phase spectra are usually very similar, frequencies are generally shifted to slightly higher values in comparison to condensed phase spectra. Gas phase spectra that differ significantly from condensed phase spectra are usually taken as evidence for the presence of some sort of molecular association in the condensed phase.

The hydroxyl group in phenols and alcohols usually is found as a broad peak centered at about 3300 cm-1 in the condensed phase as noted above and in the additional examples of Figures 24, 28, and 29. The O-H of a carboxylic acid, so strongly associated that the O-H absorption in these materials, is often extended to approximately 2500 cm-1. This extended absorption is clearly observed in Figures 26, 27, and 29 and serves to differentiate the O-H stretch of a carboxylic acid from that of an alcohol or phenol. In fact, carboxylic acids associate to form intermolecular hydrogen bonded dimers both in the solid and liquid phases.

The nitrile group

The nitrile group is another reliable functional group that generally is easy to identify. There is a significant dipole moment associated with the C≡N bond which leads to a significant change when it interacts with infrared radiation usually leading to an intense sharp peak at 2200-2280 cm-1. Very few other groups absorb at this region with this intensity. The only exception to this is if another electronegative atom such as a halogen is attached to the same carbon as the nitrile group. The spectrum in Figure 31 illustrates the typical behavior of this functional group.

The carbon-carbon triple bond

The C≡ C bond is not considered to be a very reliable functional group. This stems in part by considering that the reduced mass in equation 6 is likely to vary. However it is characterized by a strong force constant and because this stretching frequency falls in a region where very little else absorbs, 2100-2260 cm-1, it can provide useful information. The terminal carbon triple bond (C≡ C-H) is the most reliable and easiest to identify. We have previously discussed the C-H stretching frequency; coupled with a band at 3300 cm-1, the presence of a band at approximately 2100 cm-1 is a strong indication of the -C≡C-H group. The spectrum in Figure 13 illustrates the presence of this group.

An internal -C≡C- is more difficult to identify and is often missed. Unless an electronegative atom such as nitrogen or oxygen is directly attached to the sp hybridized carbon, the dipole moment associated with this bond is small; stretching this bonds also leads to a very small change. In cases where symmetry is involved, such as in diethyl acetylenedicarboxylate, Figure 32, there is no change in dipole moment and this absorption peak is completely absent. In cases where this peak is observed, it is often weak and difficult to identify with a high degree of certainty.

The carbonyl group

The carbonyl group is probably the most ubiquitous group in organic chemistry. It comes in various disguises. The carbonyl is a polar functional group that frequently is the most intense peak in the spectrum. We will begin by discussing some of the typical acyclic aliphatic molecules that contain a carbonyl group. We will then consider the effect of including a carbonyl as part of a ring and finally we will make some comments of the effect of conjugation on the carbonyl frequency.

Acyclic aliphatic carbonyl groups

Esters, aldehydes, and ketones

Esters, aldehydes, and ketones are frequently encountered examples of molecules exhibiting a C=O stretching frequency. The frequencies, 1735, 1725, 1715 cm-1 respectively, are too close to allow a clear distinction between them. However, aldehydes can be distinguished by examining both the presence of the C-H of an aldehyde (2750, 2850 cm-1) and the presence of a carbonyl group. Examples of some aliphatic esters, aldehydes and ketones are given in Figures 14, 33, 34, 36, and 36, respectively.

Carboxylic acids, amides and carboxylic acid anhydrides

Carboxylic acids, amides and carboxylic acid anhydrides round out the remaining carbonyl groups frequently found in aliphatic molecules. The carbonyl frequencies of these molecules, 1700-1730 (carboxylic acid), 1640-1670 (amide) and 1800-1830, 1740-1775 cm-1 (anhydride), allow for an easy differentiation when the following factors are also taken into consideration.

A carboxylic acid can easily be distinguished from all the carbonyl containing functional groups by noting that the carbonyl at 1700-1730 cm-1 is strongly hydrogen bonded and broadened as a result. In addition it contains an O-H stretch which shows similar hydrogen bonding as noted above. Spectra which illustrate the effect of hydrogen bonding include Figures 27, and 29.

Amides are distinguished by their characteristic frequency which is the lowest carbonyl frequency observed for an uncharged molecule, 1640-1670 cm-1(Amide I). In addition, amides from ammonia and primary amines exhibit a weaker second band (Amide II) at 1620-1650 cm^{-1} and 1550 cm^{-1} respectively, when the spectra are run on the solids. Amides from secondary amines do not have a hydrogen attached at nitrogen and do not show an Amide II band. The Amide I band is mainly attributed to the carbonyl stretch. The Amide II involves several atoms including the N-H bond. We will return to the frequency of the amide carbonyl when we discuss the importance of conjugation and the effect of resonance on carbonyl frequencies. The spectra of benzamide, a conjugated amide (Figure 19), and N-methyl acetamide (Figure 21) clearly identify the Amide I and II bands. The spectrum of N,N dimethyl acetamide (Figure 23) illustrates an example of an amide from a secondary amine.

Anhydrides can be distinguished from other simple carbonyl containing compounds in that they contain and exhibit two carbonyl frequencies. However, these frequencies are not characteristic of each carbonyl. Rather they are another example of the effects of local symmetry similar to what we have seen for the CH2 and NH2 groups. The motions involved here encompass the entire anhydride (-O=C-O-C=O-) in a symmetric and asymmetric stretching motion of the two carbonyls. The two carbonyl frequencies often differ in intensity. It is not possible to assign the peaks to the symmetric or asymmetric stretching motion by inspection nor to predict the more intense peak. However, the presence of two carbonyl frequencies and the magnitude of the higher frequency (1800 cm-1) are a good indication of an anhydride. Figure 36 contains a spectrum of an aliphatic anhydride.

Cyclic aliphatic carbonyl containing compounds

The effect on the carbonyl frequency as a result of including a carbonyl group as part of a ring is usually attributed to ring strain. Generally ring strain is believed to be relieved in large rings because of the variety of conformations available. However as the size of the ring gets smaller, this option is not available and a noticeable effect is observed. The effect of increasing ring stain is to increase the carbonyl frequency, independent of whether the carbonyl is a ketone, part of a lactone, anhydride or lactam. The carbonyl frequencies for a series cyclic compounds is summarized in Table 3.

Table 3. The Effect of Ring Strain on the Carbonyl Frequencies of Some Cyclic Molecules

Ring Size	ketone: cm-1	lactones: cm-1	lactams: cm-1
3	cyclopropanone: 1800		
4	cyclobutanone: 1775	β-propiolactone: 1840	
5	cyclopentanone: 1751	γ-butyrolactone: 1750	γ-butyrolactam: 1690
6	cyclohexanone: 1715	δ-valerolactone: 1740	δ-valerolactam: 1668
7	cycloheptanone: 1702	ε–caprolactone: 1730	ε–caprolactam: 1658

Carbon carbon double bond

Like the C≡C bond, the C=C bond stretch is not a very reliable functional group. However, it is also characterized by a strong force constant and because of this and because the effects of conjugation which we will see can enhance the intensity of this stretching frequency, this absorption can provide useful and reliable information.

Terminal C=CH2

In simple systems, the terminal carbon carbon double bond (C=C-H2) is the most reliable and easiest to identify since the absorption is of moderate intensity at 1600-1675 cm-1. We have previously discussed the C-H stretching frequency of an sp2 hybridized C-H. The spectrum in Figure 9 illustrates the presence of this group. In addition the terminal C=CH2 is also characterized by a strong band at approximately 900 cm-1. Since this band falls in the fingerprint region, some caution should be exercised in its identification.

Internal C=C

An internal non-conjugated C=C is difficult to identify and can be missed. The dipole moment associated with this bond is small; stretching this bonds also leads to a very small change. In cases where symmetry is involved, such as in 4-octene, Figure 10, there is no change in dipole moment and this absorption peak is completely absent. In cases where this peak is observed, it is often weak. In 2,5-dihydrofuran, Figure 39, it is difficult to assign the C=C stretch because of the presence of other weak peaks in the vicinity. The band at approximately 1670 cm-1 may be the C=C stretch. In 2,5-dimethoxy-2,5-dihydrofuran, Figure 40, the assignment at 1630 cm-1 is easier but the band is weak.

There is one circumstance that can have a significant effect on the intensity of both internal and terminal olefins and acetylenes. Substitution of a heteroatom directly on the unsaturated carbon to produce, for example, a vinyl or acetylenic ether, or amine leads to a significant change in the polarity of the C=C or C≡

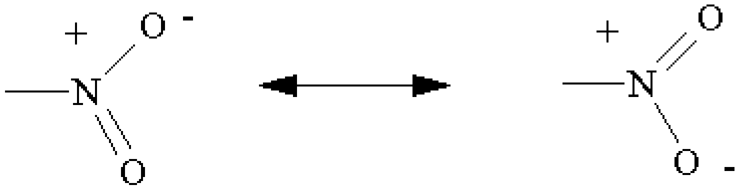
C bond and a substantial increase in intensity is observed. The C=C in 2,3-dihydrofuran is observed at 1617.5 cm-1 and is one of the most intense bands in the spectrum (Figure 41). Moving the C=C bond over one carbon gives 2,5-dihydrofuran attenuates the effect and results in a weak absorption (Figure 39).

Aromatic ring breathing motions

Benzene rings are encountered frequently in organic chemistry. Although we may write benzene as a six membered ring with three double bonds, most are aware that this is not a good representation of the structure of the molecule. The vibrational motions of a benzene ring are not isolated but involve the entire molecule. To describe one of the fundamental motions of benzene, consider imaginary lines passing through the center of the molecule and extending out through each carbon atom and beyond. A symmetric stretching and compression of all the carbon atoms of benzene along each line is one example of what we might describe as a ring breathing motion. Simultaneous expansions and compressions of these six carbon atoms lead to other ring breathing motions. These vibrations are usually observed between 1450 and 1600 cm-1 and often lead to four observable absorptions of variable intensity. As a result of symmetry, benzene, Figure 7, does not exhibit these bands. However most benzene derivatives do and usually 2 or 3 of these bands are sufficiently separate from other absorptions that they can be identified with a reasonable degree of confidence. The least reliable of these bands are those observed at approximately 1450 cm-1 where C-H bending motions are observed. Since all organic molecules that contain hydrogen are likely to have a C-H bond, absorptions observed at 1450 cm-1 are not very meaningful and should usually be ignored. Two of the four bands around 1600 cm-1 are observed in *ortho* and *meta* xylene, identified by the greek letter ϕ and a third band at about 1500 cm-1 is assigned (Figure 11 and 12). We will return to a discussion of these bands when we discuss the effects of conjugation on the intensities of these motions.

Nitro group

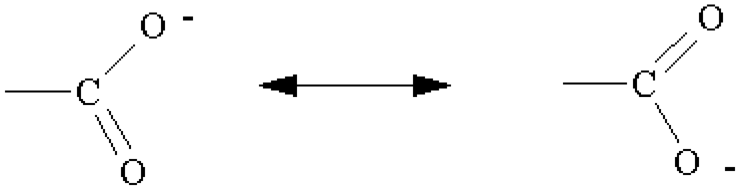
The final functional group we will include in this discussion is the nitro group. In addition to being an important functional group in organic chemistry, it will also begin our discussion of the importance of using resonance to predict effects in infrared spectroscopy. Let's begin by drawing a Kekule or Lewis structure for the nitro group. You will find that no matter what you do, it will be necessary to involve all 5 valence electrons of nitrogen and use them to form the requisite number of bonds to oxygen. This will lead to a positive charge on nitrogen and a negative charge on one oxygen. As a result of resonance, we will delocalize the negative charge on both oxygens and as shown, this leads to an identical structure. Since the structures are identical, we would expect the correct structure to be a resonance hybrid of the two. In terms of geometry, we would expect the structure to be a static average of the two geometric structures both in terms of bond distances and bond angles. Based on what we observed for the CH2 and NH2 stretch, we would expect a symmetric and an asymmetric stretch for the N-O bond in the nitro group halfway between



the N=O and N-O stretches. Since both of those functional groups are not covered in this discussion, we will need to assume for the present that this is correct. Two strong bands are observed, one at 1500-1600 cm-1 and a second between 1300-1390 cm-1, Figure 28.

Effect of resonance and conjugation on infrared frequencies

Let's continue our discussion of the importance of resonance but shift from the nitro group to the carboxylate anion. The carboxylate anion is represented as a resonance hybrid by the following figure:

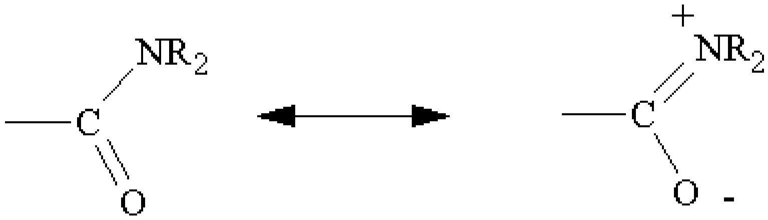


Unlike the nitro group which contained functional groups we will not be discussing, the carboxyl group is made up of a resonance hybrid between a carbon oxygen single bond and a carbon oxygen double bond. According to resonance, we would expect the C-O bond to be an average between a single and double bond or approximately equal to a bond and a half. We can use the carbonyl frequency of an ester of 1735 cm-1 to describe the force constant of the double bond. We have not discussed the stretching frequency of a C-O single bond for the simple reason that it is quite variable and because it falls in the fingerprint region. However the band is known to vary from 1000 to 1400 cm-1. For purposes of this discussion, we will use an average value of 1200 cm-1. The carbonyl frequency for a bond and a half would be expected to fall halfway between 1735 and 1200 or at approximately 1465 cm-1. The carboxyl group has the same symmetry as the nitro and CH2 groups. Both a symmetric and asymmetric stretch should be observed. The infrared spectrum of sodium benzoate is given in Figure 42. An asymmetric and symmetric stretch at 1410 and 1560 cm-1 is observed that averages to 1480 cm-1, in good agreement with the average frequency predicted for a carbon oxygen bond with a bond order of 1.5. While this is a qualitative argument, it is important to realize that the carboxylate anion does not show the normal carbonyl and normal C-O single bond stretches (at approximately 1700 and 1200 cm-1) suggested by each of the static structures above.

In the cases of the nitro group and the carboxylate anion, both resonance forms contribute equally to describing the ground state of the molecule. We will now look at instances where two or more resonance forms contribute unequally to describing the ground state and how these resonance forms can effect the various stretching frequencies.

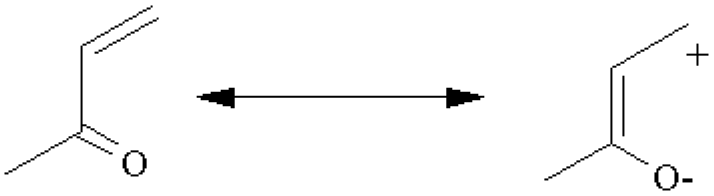
Carbonyl frequencies

Most carbonyl stretching frequencies are found at approximately 1700 cm-1. A notable exception is the amide carbonyl which is observed at approximately 1600 cm-1. This suggests that the following resonance form makes a significant contributions to describing the ground state of amides:

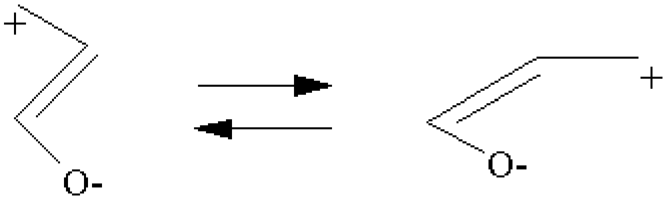


You may recall that resonance forms that lead to charge separation are not considered to be very important. However the following information support the importance of resonance in amides. X-ray crystal structures of amides show that in the solid state the amide functional group is planar. This suggests sp2 hybridization at nitrogen rather than sp3. In addition the barrier to rotation about the carbon nitrogen bond has been measured. Unlike the barrier of rotation of most aliphatic C-N bonds which are of the order of a few kcal/mol, the barrier to rotation about the carbon nitrogen bond in dimethyl formamide is approximately 18 kcal/mol. This suggests an important contribution of the dipolar structure to the ground state of molecule and the frequency of 1600 cm-1, according to the arguments given above for the carboxylate anion, is consistent with more C-O single bond character than would be expected otherwise.

Conjugation of a carbonyl with and C=C bond is thought to lead to an increase in resonance interaction. Again the resonance forms lead to charge separation which clearly de-emphasizes their importance.



However this conjugative interaction is useful in interpreting several features of the spectrum. First it predicts the small but consistent shift of approximately 10 cm-1 to lower frequency, observed when carbonyls are conjugated to double bonds or aromatic rings. This feature is summarized in Table 4 for a variety of carbonyl groups. Next the dipolar resonance form suggests a more polar C=C than that predicted for an unconjugated C=C. In terms of the change in dipole moment, contributions from this structure suggests that the intensity of infrared absorption of a C=C double bond would increase relative to an unconjugated system. Comparison of Figures 9, 10 and 35 with Figures 43, and 44-47 shows this to be the case. Conjugation is associated with an increase in intensity of the C=C stretching frequency. Finally, examination of Figures 43-46 reveals an intricacy not previously observed with simple non-conjugated carbonyls. The carbonyls of Figures 43-46 which are all conjugated appear as multiplets while those unconjugated carbonyls such as those in Figures 14 and 35 appear as single frequencies. Note however that not all conjugated carbonyls appear as multiplets (Figures 15 and 47. Resolution of this additional complicating feature can be achieved if we consider that conjugation requires a fixed conformation. For most conjugated carbonyls, two or more conformations are possible. The *s-cis* form is shown above and the *s-trans* form is shown below.



If the resonance interaction in these two forms differ, the effect of resonance on the carbonyl will differ leading to similar but different frequencies. The presence of multiple carbonyl frequencies is a good indication of a conjugated carbonyl. In some conjugated systems such as benzaldehyde and benzyl 4-hydroxyphenylketone (Figures 15 and 47), only one conformation by symmetry is possible and conjugation does not lead to any additional carbonyl frequencies.

Table 4. The effect of conjugation on carbonyl frequencies.

Non-conjugated Compound	Frequency cm-1	Conjugated Compound	Frequency cm-1		Frequenc cm-1
butanal	1725	2-butenal	1691	benzaldehyde	1702
2-butanone	1717	methyl vinyl ketone	1700, 1681	acetophenone	1685
propanoic acid	1715	propenoic acid	1702	benzoic acid	1688
ethyl propionate	1740	ethyl acrylate	1727	ethyl benzoate	1718
butanoic anhydride	1819 1750	2-butenoic anhydride	1782 1722	benzoic anhydride	1786 1726
cis-cyclohexane-1,2-dicarboxylic anhydride	1857 1786	1-cyclohexene-1,2-dicarboxylic anhydride	1844 1767	phthalic anhydride	1852 1762

Experimental infrared spectra

Up to now we have been focusing in on theory and interpretation of infrared spectra. At this point we should spend some time discussing the practical aspects of how infrared spectra are obtained and the factors to take into consideration when trying to interpret the results. Let's first start by considering gas phase spectra.

Cells and gas phase spectra

These type of spectra were more a curiosity and of theoretical interest until the introduction of the combined techniques of gas chromatography-Fourier transfer infrared spectroscopy (GC-FTIR). The major advantages of this method is that spectra can be obtained on micrograms of material and the spectra do not show the effects of interations between molecules characteristic of condensed phase spectra. These spectra are usually obtained at elevated temperatures. Condensed phase spectra however will continue to be important because of the fact that many compounds do not survive injection into a gas chromatograph. Currently, most frequency correlations for various functional groups are reported for the condensed phase. Frequencies observed in the gas phase are usually slightly higher than those observed for the same functional group in the condensed phase.

Gas phase spectra can also be taken at room temperature. All that is needed is a sample with a vapor pressure of several millimeters and a pathlength of about a decimeter (10 cm). Cells with NaCl or KBr windows are commercially available or can be built easily. Crystals of KBr are transparent from 4000-250 cm-1 and are perfectly acceptable for most uses. They have the disadvantage of being hydroscopic and must be stored in a desiccator. Cells of sodium chloride are transparent from 4000-600 cm-1, less expensive and less hydroscopic. These cells are also acceptable for routine spectra.

Cells and condensed phase spectra

Condensed phase spectra can be taken as a solid or as a liquid. Comparison of the same sample in the liquid and solid phase will differ. However the major differences observed will be in the fingerprint region. In cases where infrared spectroscopy is used as a criteria of identity, the spectra under comparison should be obtained under identical experimental conditions. Liquid phase spectra are the easiest to obtain. All that is needed are two polished disks of NaCl or KBr, both commercially available. A thin film is prepared by depositing a drop of the liquid between the two plates and mounting them in the beam of the spectrometer. This is referred to as a neat liquid. Glass is not a useful material in infrared spectroscopy because of the strong absorptions due to the Si-O group. The infrared spectrum of quartz is shown in Figure 49.

Spectra of solids can be obtained in a variety of ways. The method of choice varies depending on the physical properties of the material under consideration. We will list several methods that can be used satisfactorily along with the limitations and advantages of each.

Neat Spectra (thin film)

In order to obtain an infrared spectrum of a solid, it is necessary to get light, mainly infrared through the sample. This can be achieved in various ways and we will outline some that have proven successful in the past. A thin layer of a solid deposited as a solution on an infrared cell and allowed to evaporate has proven successful with many solids. Solvents such as $CHCl_3$, CH_2Cl_2 and CCl_4 have been frequently been used. The solid sample should have an appreciable solubility in one of these solvents. A drop of a solution left to evaporate will deposit a thin film of crystal that will often transmit sufficient light to provide an acceptable infrared spectrum. This method suffers from the disadvantage that a spectrum of the solvent must also be run to determine whether all the solvent has evaporated.

Nujol mull

A mull is a suspension of a solid in a liquid. Under these conditions, light can be transmitted through the sample to afford an acceptable infrared spectrum. The commercial sample of Nujol, or mineral oil, which is a long chain hydrocarbon is often used for this purpose. Most solids do not dissolve in this medium but can be ground up in its presence. A small mortar and pestle is used for this purpose. If the grinding process gives rise to small particles of solid with diameters roughly the same as the wavelength of the infrared radiation being used, 2-5 microns, these particles will scatter rather than transmit the light. The effect of poor grinding is illustrated in Figures 29 and 30 for a sample of benzoic acid. If you find this type of band distortions with either a Nujol mull or a KBr pellet (discussed below), simply continue grinding the sample up until the particles become finer.

The major disadvantage of using a Nujol mull is that the information in the C-H stretching region is lost because of the absorptions of the mulling agent. A spectrum of Nujol is shown in Figure 5. To eliminate this problem, it may be necessary to run a second spectrum in a different mulling agent that does not contain any C-H bonds. Typical mulling agents that are used for this purpose are perfluoro- or perchlorohydrocarbons. Examples include perchlorobutadiene, perfluorokerosene or a perfluorohydrocarbon oil (Figure 48).

KBr pellets

A KBr pellet is a dilute suspension of a solid in a solid. It is usually obtained by first grinding the sample in anhydrous KBr at a ratio of approximately 1 part sample to 100 parts KBr. Although it is best to weigh the sample (1 mg) in the KBr (100mg), with some experience it is possible to use your judgment in assigning proportions of sample to KBr. The mixture is the ground up in an apparatus called a Wiggle-Bug, frequently used by dentists to prepare amalgams. The ground up sample mixture is then placed on a steel plate containing a paper card with a hole punched in it. The sample is placed in the hole, making sure that some sample also overlaps the paper card. Paper the thickness and consistency of a postcard is usually used and the hole is positioned on the card so that it will lie in the infrared beam when placed on the spectrometer. A second steel plate is placed over the sample and card and the steel sandwich is placed in a hydraulic press and subjected to pressures of 15000 psi for about 20 seconds. Removal of the paper card following decompression usually results in a KBr pellet that is reasonably transparent both to visible light and infrared radiation. Some trial and error may be necessary before quality pellets can be obtained routinely. Samples that are not highly crystalline sometimes prove difficult and do not produce quality pellets. However good quality spectra can be obtained on most samples. The only limitation of KBr is that it is hydroscopic. Because of this, it is usually a good idea to obtain a spectrum run as a Nujol mull on your sample as well. The two spectra should be very similar and since Nujol is a hydrocarbon and has no affinity for water, any absorption in Nujol between 3400-3600 cm-1 can be attributed to the sample and not to the absorption of water by KBr.

PE 1600 FT Infrared Spectrometer

The operation of the Perkin Elmer 1600 FTIR, the instrument that you will be using in this laboratory, will be demonstrated. However before learning how to use it you should familiarize yourself with some of the general operating features of the instrument and its capabilities and limitation. In addition this brief tutorial will serve as a useful reminder once you have learned how to use the instrument. A discussion of the performance of a Fourier Transfer infrared spectrometer is beyond the scope of this publication. However the following will summarize some of the essential features of the PE 1400. To begin with the PE 1400 is a single beam instrument. Unlike a double beam instrument that simultaneously corrects for absorptions due to atmospheric water vapor and carbon dioxide, most FTIR spectrometers correct for the background absorption by storing an interferogram and background spectrum before recording your spectrum. An interferogram contains the same information as a regular spectrum, frequency vs. intensity, but this information is contained in the form of intensity vs. time. The Fourier Tranform is the mathematical process which coverts the information from intensity and time to intensity and frequency. One of the major advantages of a FTIR instrument, is that is takes on the order of a second to record an entire spectrum. This makes it very convenient to record the same spectrum a number of times and display an average spectrum.

Since the signal to noise ratio varies as the square root of the number of scans averaged, it is easy to obtain good signal to noise on this type of instrument, even if you have very little sample. On a typical spectrum you should average at least four spectra. Be sure you average a similar number of background spectra.

Looking at the keyboard of the instrument you will find keys with a permanent function. Two functions are defined on some keys and these functions can be accessed by pressing the key directly or by a combination of the shift + function key. A number of other keys, those directly under the monitor, are defined by the screen and their function may vary depending on the screen. The instrument has four active memory sites where spectra can be stored and retrieved. These are called the background, x, y and z. Once the instrument has been turned on and has passed the self tests, it is usually a good idea to allow the infrared source to warm up for 5 min. With the sample pathway empty , pressing "scan + background + the key under the monitor prompt consistent with the number of scans you which to average" will produce a background interferogram. Placing your sample in the beam and pressing "scan x, y, or z + the number of scans you desire" will produce an interferogram with the requisite number of scans that will be corrected for the background and displayed on the screen. You may wish to record a spectrum, make some adjustments to see if they improve the quality of the spectrum. Storing the second spectrum in a different memory region allows you to evaluate the adjustments. If the first spectrum was stored in x and the second in y, pressing x or y allows you to retrieve either.

To plot your spectrum on the HP plotter, simply turn the plotter on, load paper on the plotter, and make sure the plotter is equipped with at least one pen. Press "plot" and the monitor will tell you the number of peaks the instrument has detected that satisfy the current settings. The frequency of each peak identified as meeting these criteria will be printed out. If the number of peaks is too large or too few peaks are identified, it may be necessary to change the current setting on the instrument. Simply press "cancel + plot (the key is located on the monitor)".

To change the peak threshold, press the following keys located on the monitor: press "setup", "view", "peaks". You can change the threshold value using the number pad on the left of the console. Increasing the threshold will decrease the number of peaks while decreasing the existing value will include more peaks. Next press "execute"; and exit. Additional details and instructions are generally available at the instrument.

When you are first learning to make KBr pellets, you will be using a paper punch to produce a hole on a paper card. You will need to adjust the size and position of the hole properly so that it will allow sufficient infrared light to pass through the card. To monitor how much radiation is reaching the detector, press "shift + monitor and then the energy key under the monitor". This will let you know how much energy is reaching the detector. With nothing else in the beam except the paper card with the hole punched in, at least 60-70% of the energy should reach the detector. If you observe a reading much less than this, you may either have to adjust the position of the aperture or enlarge it or both. The cancel key under the monitor will return you to normal mode.

The Degree of Unsaturation

Once the molecular formula of an unknown is known, it is a simple matter to determine the degree of unsaturation. The degree of unsaturation is simply the sum of the number of carbon-carbon multiple bonds and rings. Each reduces the number of hydrogens (or any other element with a valance of one) by two. There is a general formula that can be memorized and used:

unsaturation number, U = #C + 1 - 1/2 (X-N) where X=monovalent atoms, N=trivalent atoms, and C=tetravalent atoms. Note that divalent atoms are not counted.

Consider C6Cl6 as an example: U = 6 + 1 - 1/2 (6-0) = 7 - 3 = 4; the degree of unsaturation is four. An unsaturation factor of four is required for a single benzene ring.

Consider C_5H_9NO as another example. U = 5 + 1 - 1/2 (9-1) = 2. Clearly this compound cannot have a benzene ring but the oxygen atom could be part of a carbonyl group.

Application of the degree of unsaturation to the interpretation of an infrared spectrum is quite straightforward. Clearly some functional groups can be eliminated by composition. Amines, amides, nitriles and nitro groups can be eliminated if the molecule does not contain any nitrogen. Alternatively everything but amines can be eliminated if the molecular formula contains nitrogen and no degrees of unsaturation.

Interpretation of Infrared Spectra--A Beginner’s Guide

We have just concluded a discussion of a large number of frequencies and the functional groups that are generally associated with these frequencies. At this point you may be asking yourself how to begin to interpret these frequencies with regards to obtaining information of molecular structure. There are a number of different approaches that can be used and often the best approach to use depends on the nature of the information you would like to obtain from your infrared spectrum. For example, if you are repeating a synthesis in the laboratory and you wish to determine whether you have successfully isolated the material you intended to prepare, you may be able to compare your spectrum to an infrared spectrum of an authentic sample. In this case, you are using infrared analysis for establishing the identity of your sample. Assuming that your spectrum has been run under the same conditions, as your reference, i.e. neat sample, KBr pellet, etc., you should be able to reproduce the spectrum of the reference material, peak for peak. The presence of some additional peaks in your spectrum may indicate a contamination with solvent, starting material or an impurity that has not been removed. The presence of fewer peaks than your reference is of more concern. This generally indicates a failure to obtain the desired material.

If the structure of the material of interest is unknown, then a more systematic analysis of your spectrum will be necessary. You should be aware that it is not usually possible to determine molecular structure from the infrared spectrum alone. Usually, some supplemental spectroscopic and/or structural information (such as molecular formula) is also necessary. For the unknowns in this course, you will generally be using infrared spectroscopy to differentiate between a few possible compounds. Frequently, this can be achieved by an analysis of the functional groups in your spectrum. The discussion which follows, uses a more generalized approach to analyze spectra. This approach should be applicable in a variety of different circumstances. If a portion of the discussion is not relevant to you, simply skip it and continue until it does become relevant.

The following steps should serve as a general protocol to follow and should prove useful regardless of the structure of your unknown or whether the degree of unsaturation is known.

1. Look in the carbonyl region, typically 1800-1620 cm-1 , for a strong absorption band. So many classes of compounds contain a carbonyl group (carboxylic acids, esters, amides, ketones, aldehydes, etc) and the absorption is so obvious that it is the perfect starting point. If there is no carbonyl absorption, you have eliminated a large number of possibilities.

2. Examine the C-H stretching frequencies at 3000 cm-1. Absorption bands at frequencies slightly larger than 3000 cm-1 are indicative of vinyl or/and aromatic hydrogens. The presence of these peaks should be consistent with the degree of unsaturation of your molecule. The absence of absorption above 3000 cm-1 but the presence of some unsaturation in the molecular formula are consistent with a cyclic compound.

If your degree of unsaturation is 4 or greater, look for 2 to 4 absorption peaks between 1600-1450 cm-1 and weak peaks at 2000-1667 cm-1. These are characteristic of aromatic compounds.

3. Next look for a doublet at 2750 and 2850 cm-1 characteristic of an aldehyde. The presence of these two bands should also be accompanied by a strong absorption at approximately 1700 cm-1. Most spectra display strong absorption in the 1800-1700 cm-1 region. If your spectrum does, check to see if the carbonyl is a closely spaced doublet or multiplet. Closely spaced multiplicity in the carbonyl region accompanied by C-H absorption at 3000-3100 cm-1 is frequently characteristic of an α, β- unsaturated carbonyl compounds. Check to make sure that the carbonyl frequency is consistent with conjugation.

4. If your unknown contains broad absorption from 3600-3000 cm-1, your molecule could have an O-H or N-H stretch. Check the multiplicity of this peak. A doublet is characteristic of a primary amine or and amide derived from ammonia. Check the carbonyl region at around 1650-1600 cm-1. Two bands in this region are consistent of an amide from ammonia or a primary amine. Remember a broad and relatively weak band at about 1600 cm-1 is characteristic of N-H bending. Usually you will only see this band in amines, since that carbonyl group of the amide will interfere. Be sure to look for the effect of hydrogen bonding which usually results in a general broadening of the groups involved.

5. If the broad band starting at 3600 cm-1 expands to nearly 2400 cm-1, look for the presence of a broad carbonyl at approximately 1700 cm-1. This extremely broad OH band is only observed in carboxylic acids and enols from β-diketones. The presence of a relatively intense but broad band at approximately 1700 cm-1 is good evidence for a carboxylic acid.

6. Don’t try to over-interpret your spectrum. Usually, it is not possible to arrive at a unique structure based on infrared analysis alone. Your goal is to determine the class of compound and other possible functional groups (eg, double bonds, benzene rings). These can be confirmed with classification tests. Sometimes, the information is confusing and you will have to determine which tests and which data are most reliable. You can learn a great deal about your unknown from your spectrum but be sure to use other important physical

data such as melting point, boiling point and solubility characteristics of your unknown to assist you in narrowing down the different structural possibilities.

Question:

For a C_3H_6O compound, what is the degree of unsaturation? Write several possible structures for a compound with this molecular formula.

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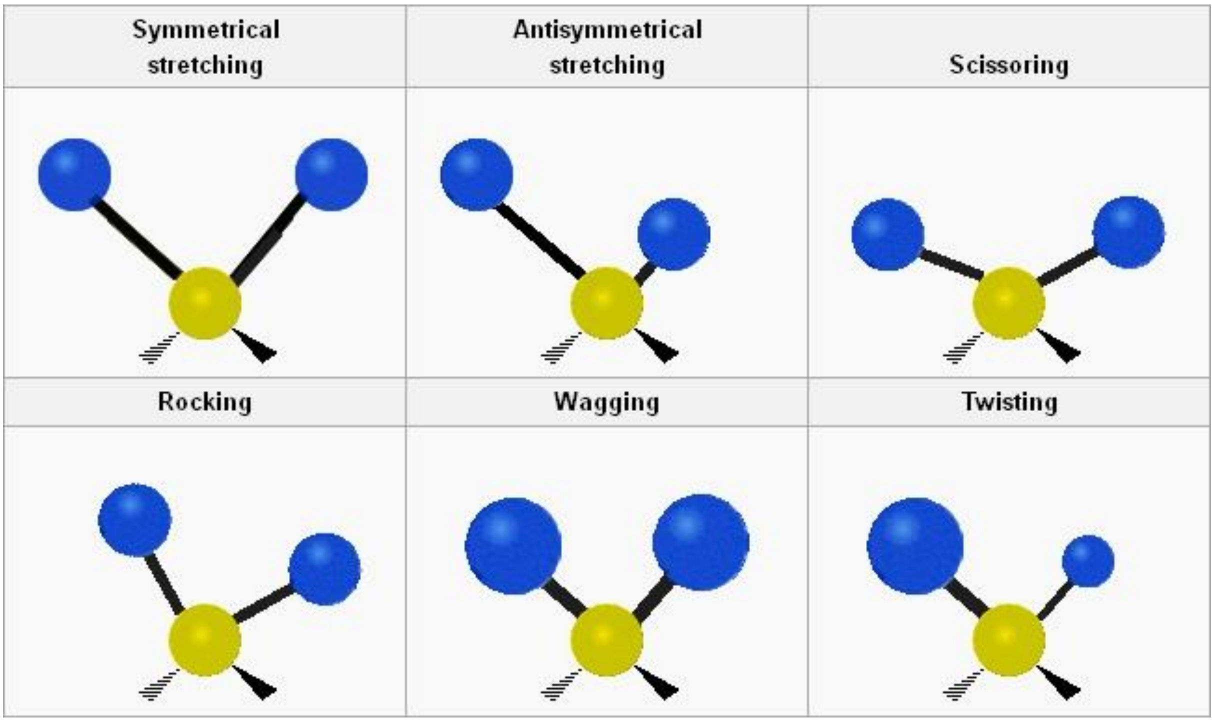
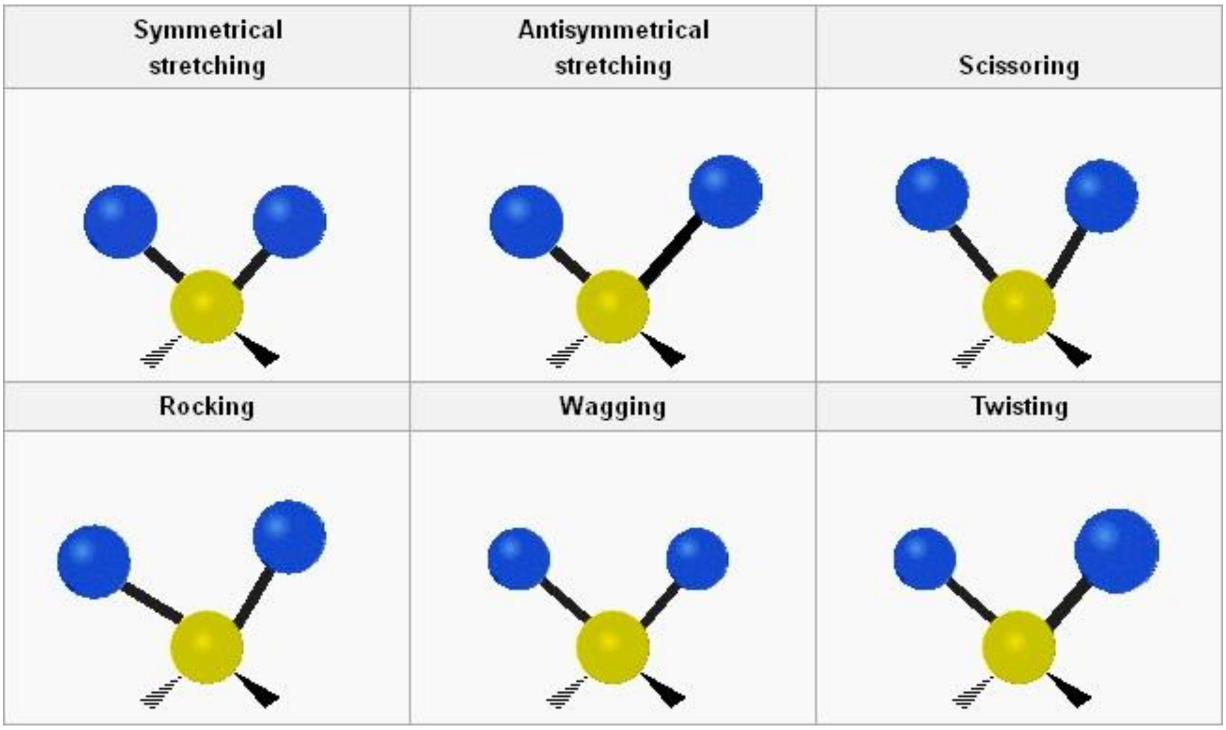
http://en.wikipedia.org/wiki/Infrared_spectroscopy





Modos de vibração

http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Vibrational_Spectroscopy/Infrared_Spectroscopy/Infrared%3A_Interpretation#Inorganic_Compounds

Infrared: Interpretation

Infrared spectroscopy is the study of the interaction of infrared light with matter. The fundamental measurement obtained in infrared spectroscopy is an infrared spectrum, which is a plot of measured infrared intensity versus wavelength (or frequency) of light.

Introduction

In infrared spectroscopy, units called wavenumbers are normally used to denote different types of light. The frequency, wavelength, and wavenumber are related to each other via the following equation(1):

$$c = \nu\lambda$$

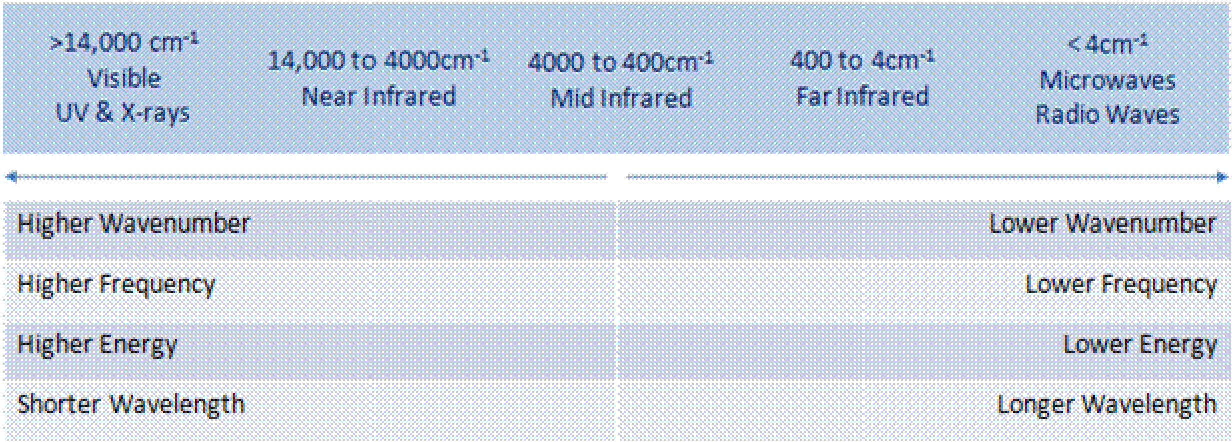
c = the speed of light (cm/sec)
ν = frequency in Hertz (sec^{-1})
λ = wavelength in cm

$$W = 1/\lambda$$

W = wavenumber in cm^{-1}
λ = wavelength in cm

(1)

These equations show that light waves may be described by their frequency, wavelength or wavenumber. Here, we typically refer to light waves by their wavenumber, however it will be more convenient to refer to a light wave's frequency or wavelength. The wavenumber of several different types of light are shown in table 1.



>14,000 cm^{-1} Visible UV & X-rays	14,000 to 4000cm^{-1} Near Infrared	4000 to 400cm^{-1} Mid Infrared	400 to 4cm^{-1} Far Infrared	< 4cm^{-1} Microwaves Radio Waves

Higher Wavenumber	Lower Wavenumber
Higher Frequency	Lower Frequency
Higher Energy	Lower Energy
Shorter Wavelength	Longer Wavelength

Table 1. The Electromagnetic spectrum showing the wavenumber of several different types of light.

When a molecule absorbs infrared radiation, its chemical bonds vibrate. The bonds can stretch, contract, and bend. This is why infrared spectroscopy is a type of vibrational spectroscopy. Fortunately, the complex vibrational motion of a molecule can be broken down into a number of constituent vibrations called normal modes. For example, when a guitar string is plucked, the string vibrates at its normal mode frequency. Molecules, like guitar strings, vibrate at specfic frequencies so different molecules vibrate at different frequencies because their structures are different. This is why molecules can be distinguished using infrared spectroscopy. The first necessary condition for a molecule to absorb infrared light is that the molecule must have a vibration during which the change in dipole moment with respect to distance is non-zero. This condition can be summarized in equation(2) form as follows:

$$\frac{\partial \mu}{\partial x} \neq 0 \qquad \begin{aligned} \partial \mu &= \text{change in dipole moment} \\ \partial x &= \text{change in bond distance} \end{aligned} \tag{2}$$

Vibrations that satisfy this equation are said to be infrared active. The H-Cl stretch of hydrogen chloride and the asymmetric stretch of CO_2 are examples of infrared active vibrations. Infrared active vibrations cause the bands seen in an infrared spectrum.

The second necessary condition for infrared absorbance is that the energy of the light impinging on a molecule must equal a vibrational energy level difference within the molecule. This condition can be summarized in equation(3) form as follows:

$$\Delta E_{vib} = hcW$$

$$\begin{aligned} \Delta E_{vib} &= \text{vibrational energy level difference in a molecule} \\ h &= \text{Planck's Constant (Joule-sec)} \\ c &= \text{the speed of light (cm/sec)} \\ W &= \text{wavenumber in } cm^{-1} \end{aligned}$$

(3)

If the energy of a photon does not meet the criterion in this equation, it will be transmitted by the sample and if the photon energy satisfies this equation, that photon will be absorbed by the molecule.(See Infrared: Theory for more detail)

As any other analytical techniques, infrared spectroscopy works well on some samples, and poorly on others. It is important to know the strengths and weaknesses of infrared spectroscopy so it can be used in the proper way. Some advantages and disadvantages of infrared spectroscopy are listed in table 2.

Advantages	**Disadvantages**
Solids, Liquids, gases, semi-solids, powders and polymers are all analyzed The peak positions, intensities, widths, and shapes all provide useful information Fast and easy technique Sensitive technique (Micrograms of materials can be detected routinely) Inexpensive	Atoms or monatomic ions do not have infrared spectra Homonuclear diatomic molecules do not posses infrared spectra Complex mixture and aqueous solutions are difficult to analyze using infrared spectroscopy

Table 2. The Advantage and Disadvantage of Infrared Spectroscopy

The Orgin of Infrared Peak Positions, Intensities, and Widths

Peak Positions

The equation(4) gives the frequency of light that a molecule will absorb, and gives the frequency of vibration of the normal mode excited by that light.

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

ν = frequency in cm^{-1}

k = force constant in N/cm

μ = reduced mass in Kg

(4)

Only two variables in equation(4) are a chemical bond's force constant and reduced mass. Here, the reduced mass refers to $(M_1M_2)/(M_1+M_2)$ where M_1 and M_2 are the masses of the two atoms, respectively. These two molecular properties determine the wavenumber at which a molecule will absorb infrared light. No two chemical substances in the universe have the same force constants and atomic masses, which is why the infrared spectrum of each chemical substance is unique. To understand the effect of atomic masses and force constant on the positions of infrared bands, table 3 and 4 are shown as an example, respectively.

Table 3. An Example of an Mass Effect

Bond	**C-H Stretch in cm^{-1}**
C-^{1}H	**~3000**
C-^{2}D	**~2120**

The reduced masses of C-^{1}H and C-^{2}D are different, but their force constants are the same. By simply doubling the mass of the hydrogen atom, the carbon-hydrogen stretching vibration is reduced by over 800cm^{-1}.

Table 4. An Example of an electronic Effect

Bond	**C-H Stretch in cm^{-1}**
C-H	**~3000**
H-C=O	**~2750**

When a hydrogen is attached to a carbon with a C=O bond, the C-H stretch band position decrease to ~2750cm^{-1}. These two C-H bonds have the same reduced mass but different force constants. The oxygen in the second molecule pulls electron density away from the C-H bond so it makes weaken and reduce the C-H force constant. This cause the C-H stretching vibration to be reduced by ~250cm^{-1}.

The Origin of Peak Intensities

The different vibrations of the different functional groups in the molecule give rise to bands of differing intensity. This is because $\partial\mu\partial x$ is different for each of these vibrations. For example, the most intense band in the spectrum of octane shown in Figure 3 is at 2971, 2863 cm^{-1} and is due to stretching of the C-H bond. One of the weaker bands in the spectrum of octane is at 726cm^{-1}, and it is due to long-chain methyl rock of the carbon-carbon bonds in octane. The change in dipole moment with respect to distance for the C-H stretching is greater than that for the C-C rock vibration, which is why the C-H stretching band is the more intense than C-C rock vibration.

Another factor that determines the peak intensity in infrared spectra is the concentration of molecules in the sample. The equation(5) that relates concentration to absorbance is Beer's law,

$A = \varepsilon l c$ $A = \text{absorbance}$

$\varepsilon = \text{absorptivity}$

$l = \text{pathlength}$

$c = \text{concentration}$

(5)

The absorptivity is the proportionality constant between concentration and absorbance, and is dependent on $(\partial\mu/\partial x)^2$. The absorptivity is an absolute measure of infrared absorbance intensity for a specific molecule at a specific wavenumber. For pure sample, concentation is at its maximum, and the peak intensities are true representations of the values of $\partial\mu/\partial x$ for different vibrations. However, in a mixture, two peaks may have different intensities because there are molecules present in different concentration.

The Orgins of Peak Widths

In general, the width of infrared bands for solid and liquid samples is determined by the number of chemical environments which is related to the strength of intermolecular interactions such as hydrogen bonding. Figure 1. shows hydrogen bond in water molecules and these water molecules are in different chemical environments. Because the number and strength of hydrogen bonds differs with chemical environment, the force constant varies and the wavenumber differs at which these molecules absorb infrared light.

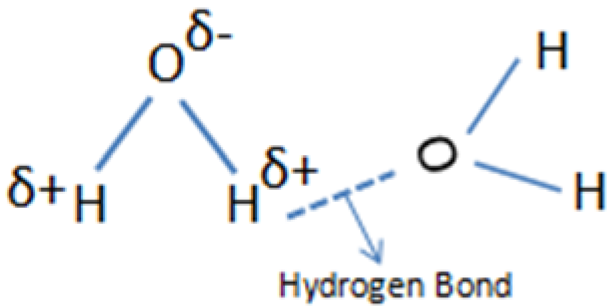


Figure 1. Hydrogen Bonding in water molecules

In any sample where hydrogen bonding occurs, the number and strength of intermolecular interactions varies greatly within the sample, causing the bands in these samples to be particularly broad. This is illustrated in the spectra of ethanol(Fig7) and hexanoic acid(Fig11). When intermolecular interactions are weak, the number of chemical environments is small, and narrow infrared bands are observed.

The Origin of Group Frequencies

An important observation made by early researchers is that many functional group absorb infrared radiation at about the same wavenumber, regardless of the structure of the rest of the molecule. For example, C-H stretching vibrations usually appear between 3200 and 2800cm^{-1} and carbonyl(C=O) stretching vibrations usually appear between 1800 and 1600cm^{-1}. This makes these bands diagnostic markers for the presence of a functional group in a sample. These types of infrared bands are called group frequencies because they tell us about the presence or absence of specific functional groups in a sample.

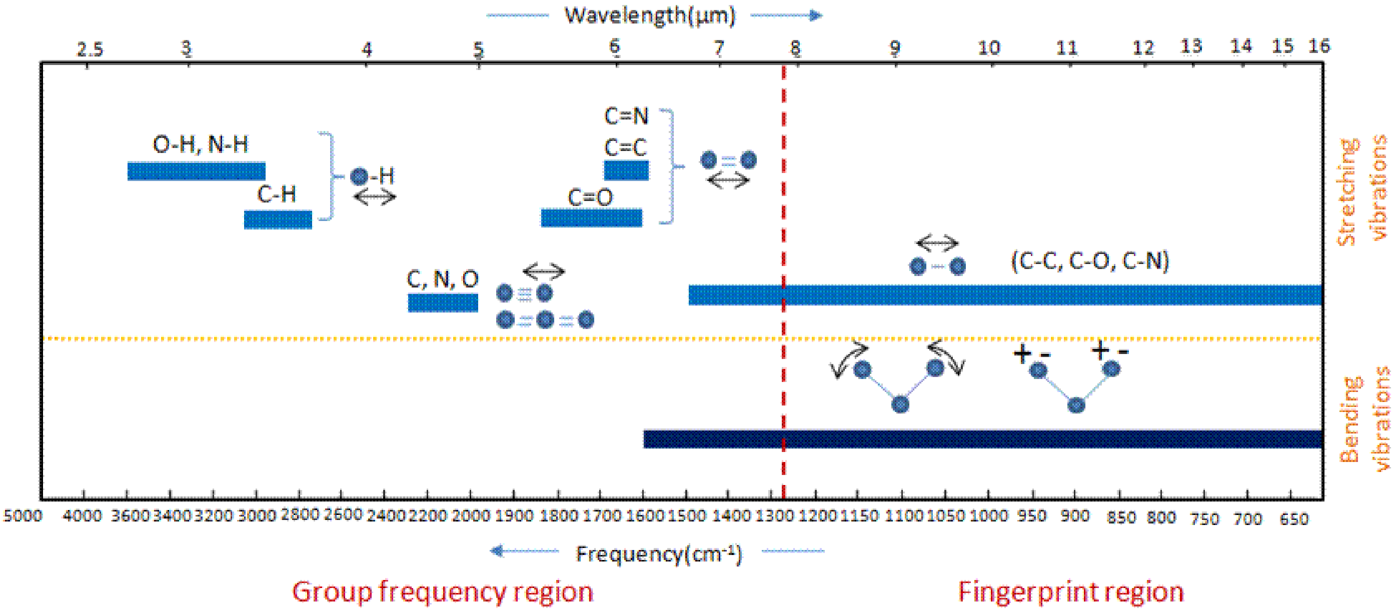


Figure 2. Group frequency and fingerprint regions of the mid-infrared spectrum

The region of the infrared spectrum from 1200 to 700 cm^{-1} is called the fingerprint region. This region is notable for the large number of infrared bands that are found there. Many different vibrations, including C-O, C-C and C-N single bond stretches, C-H bending vibrations, and some bands due to benzene rings are found in this region. The fingerprint region is often the most complex and confusing region to interpret, and is usually the last section of a spectrum to be interpreted. However, the utility of the fingerprint region is that the many bands there provide a fingerprint for a molecule.

Spectral Interpretation by Application of Group Frequencies

Organic Compounds

One of the most common application of infrared spectroscopy is to the identification of organic compounds. The major classes of organic molecules are shown in this category and also linked on the bottom page for the number of collections of spectral information regarding organic molecules.

Hydrocarbons

Hydrocarbons compounds contain only C-H and C-C bonds, but there is plenty of information to be obtained from the infrared spectra arising from C-H stretching and C-H bending.

In alkanes, which have very few bands, each band in the spectrum can be assigned:

- **C–H stretch from 3000–2850 cm^{-1}**
- **C–H bend or scissoring from 1470-1450 cm^{-1}**
- **C–H rock, methyl from 1370-1350 cm^{-1}**
- **C–H rock, methyl, seen only in long chain alkanes, from 725-720 cm^{-1}**

Figure 3. shows the IR spectrum of octane. Since most organic compounds have these features, these C-H vibrations are usually not noted when interpreting a routine IR spectrum. Note that the change in dipole moment with respect to distance for the C-H stretching is greater than that for others shown, which is why

the C-H stretch band is the more intense.

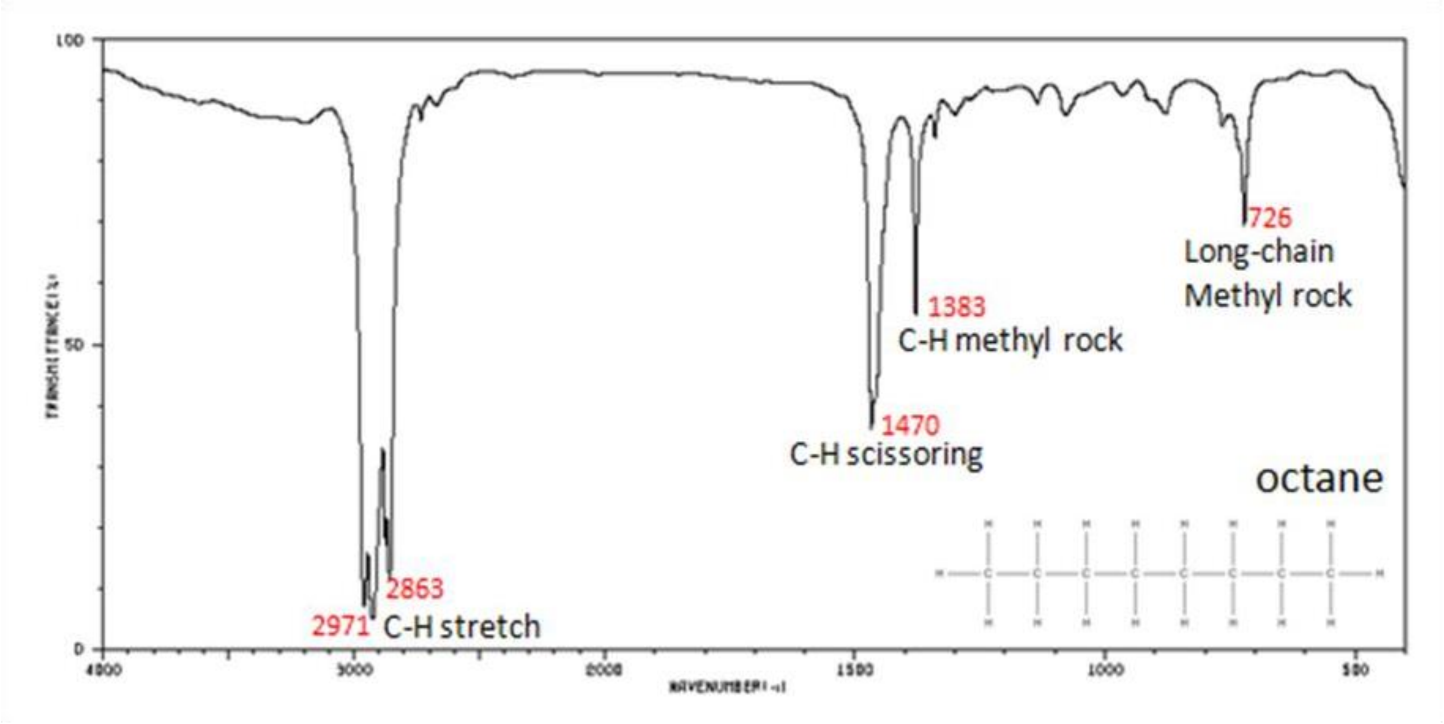


Figure 3. Infrared Spectrum of Octane

In alkenes compounds, each band in the spectrum can be assigned:

- **C=C stretch from 1680-1640 cm^{-1}**
- **=C–H stretch from 3100-3000 cm^{-1}**
- **=C–H bend from 1000-650 cm^{-1}**

Figure 4. shows the IR spectrum of 1-octene. As alkanes compounds, these bands are not specific and are generally not noted because they are present in almost all organic molecules.

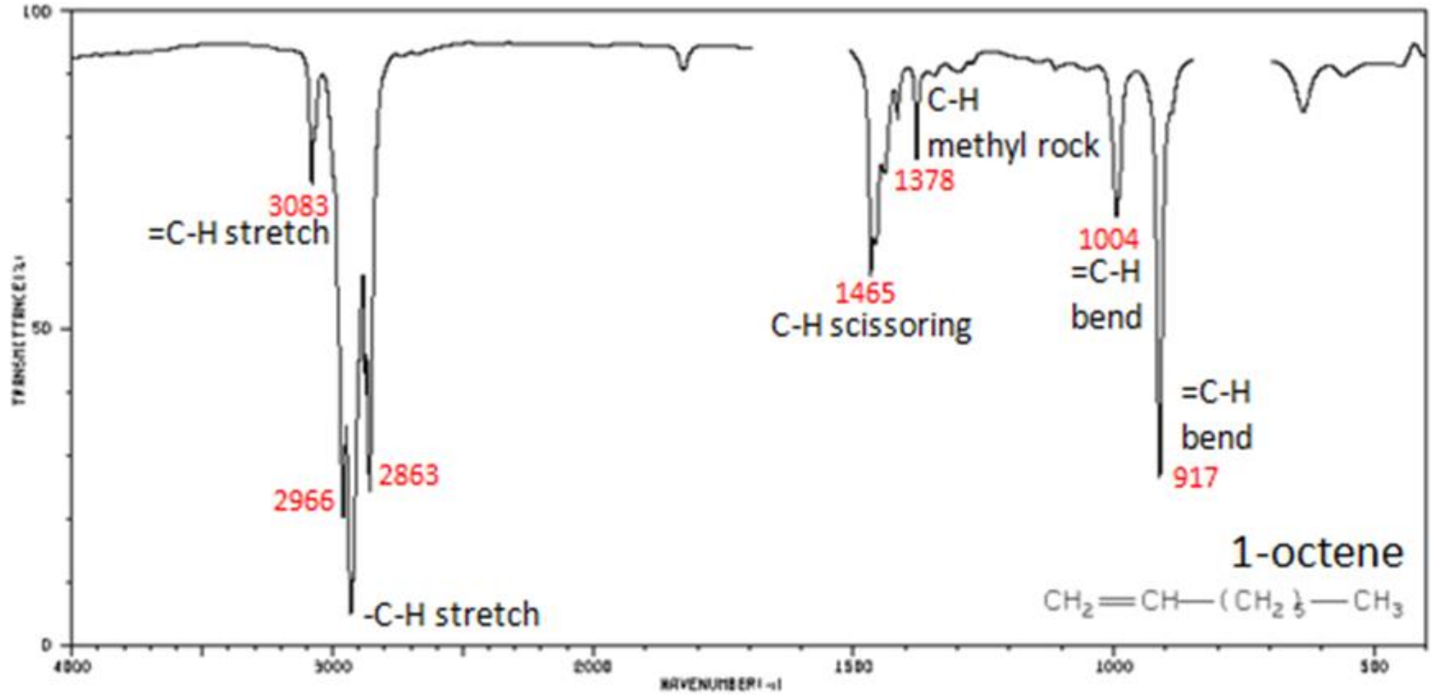


Figure 4. Infrared Spectrum of 1-Octene

In alkynes, each band in the spectrum can be assigned:

- **–C?C– stretch from 2260-2100 cm^{-1}**
- **–C?C–H: C–H stretch from 3330-3270 cm^{-1}**
- **–C?C–H: C–H bend from 700-610 cm^{-1}**

The spectrum of 1-hexyne, a terminal alkyne, is shown below.

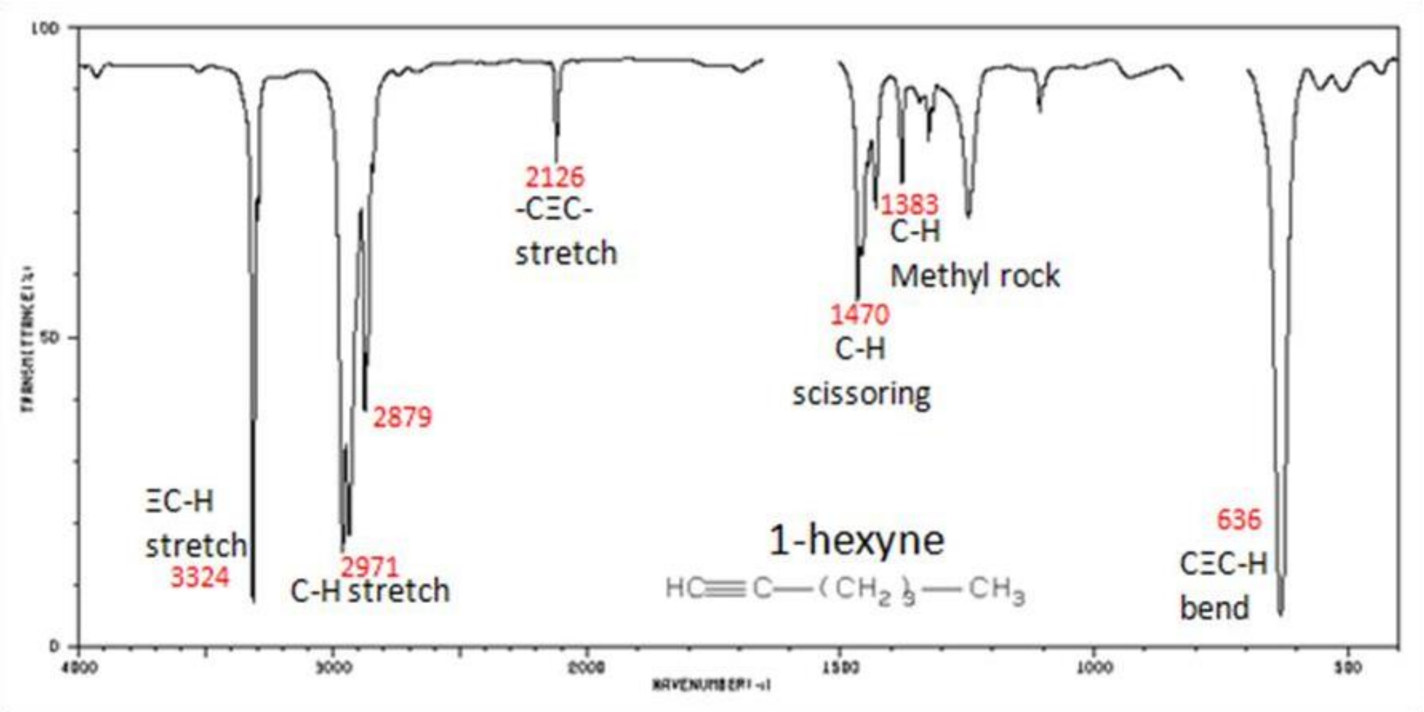


Figure 5. Infrared Spectrum of 1-Hexyne

In aromatic compounds, each band in the spectrum can be assigned:

- **C–H stretch from 3100-3000 cm^{-1}**
- **overtones, weak, from 2000-1665 cm^{-1} C–**
- **C stretch (in-ring) from 1600-1585 cm^{-1}C–**
- **C stretch (in-ring) from 1500-1400 cm^{-1}C–**
- **H "oop" from 900-675 cm^{-1}**

Note that this is at slightly higher frequency than is the –C–H stretch in alkanes. This is a very useful tool for interpreting IR spectra. Only alkenes and aromatics show a C–H stretch slightly higher than 3000 cm^{-1}.

Figure 6. shows the spectrum of toluene.

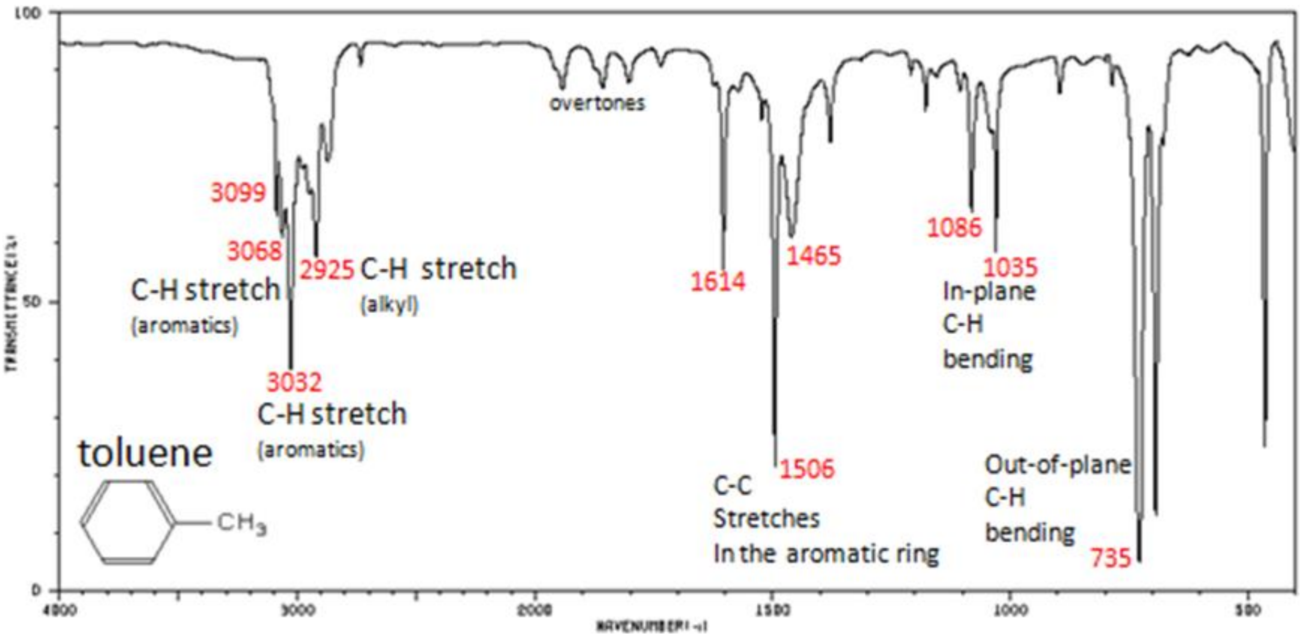


Figure 6. Infrared Spectrum of Toluene

Functional Groups Containing the C-O Bond

Alcohols have IR absorptions associated with both the O-H and the C-O stretching vibrations.

- **O–H stretch, hydrogen bonded 3500-3200 cm^{-1}**
- **C–O stretch 1260-1050 cm^{-1} (s)**

Figure 7. shows the spectrum of ethanol. Note the very broad, strong band of the O–H stretch.

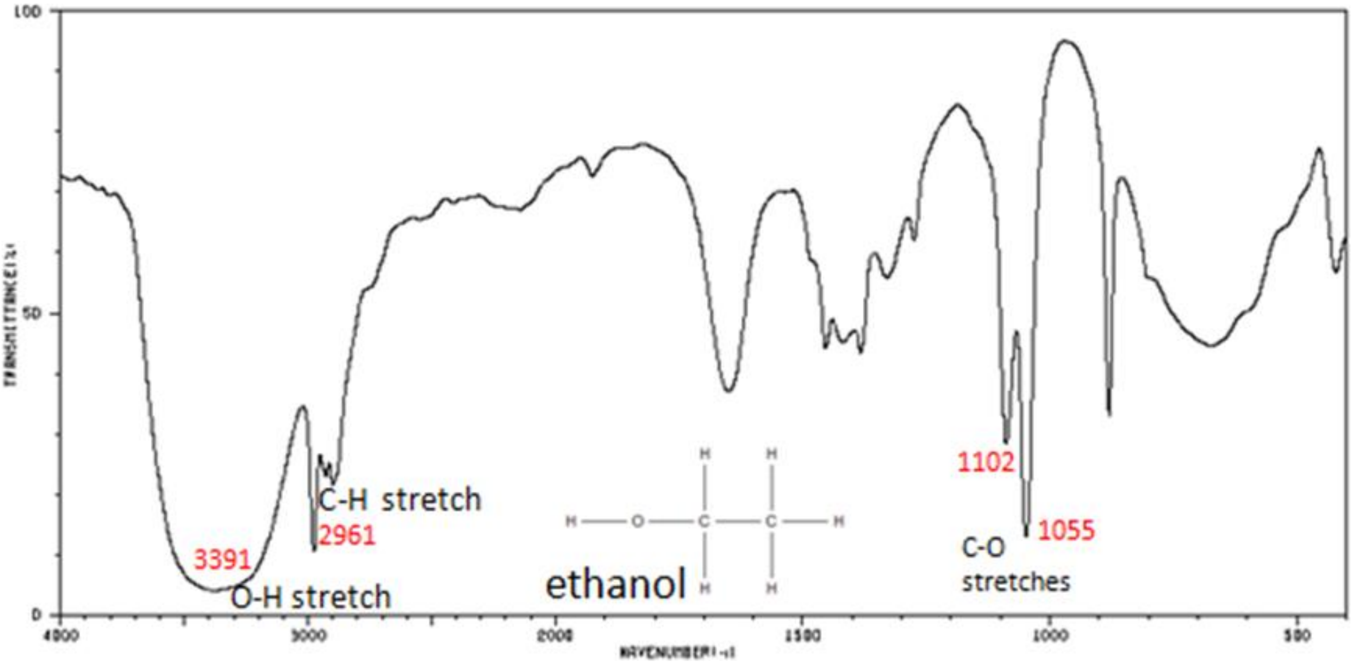


Figure 7. Infrared Spectrum of Ethanol

The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears:

- **C=O stretch - aliphatic ketones 1715 cm^{-1}**

  - ?, ?-unsaturated ketones 1685-1666 cm^{-1}

Figure 8. shows the spectrum of 2-butanone. This is a saturated ketone, and the C=O band appears at 1715.

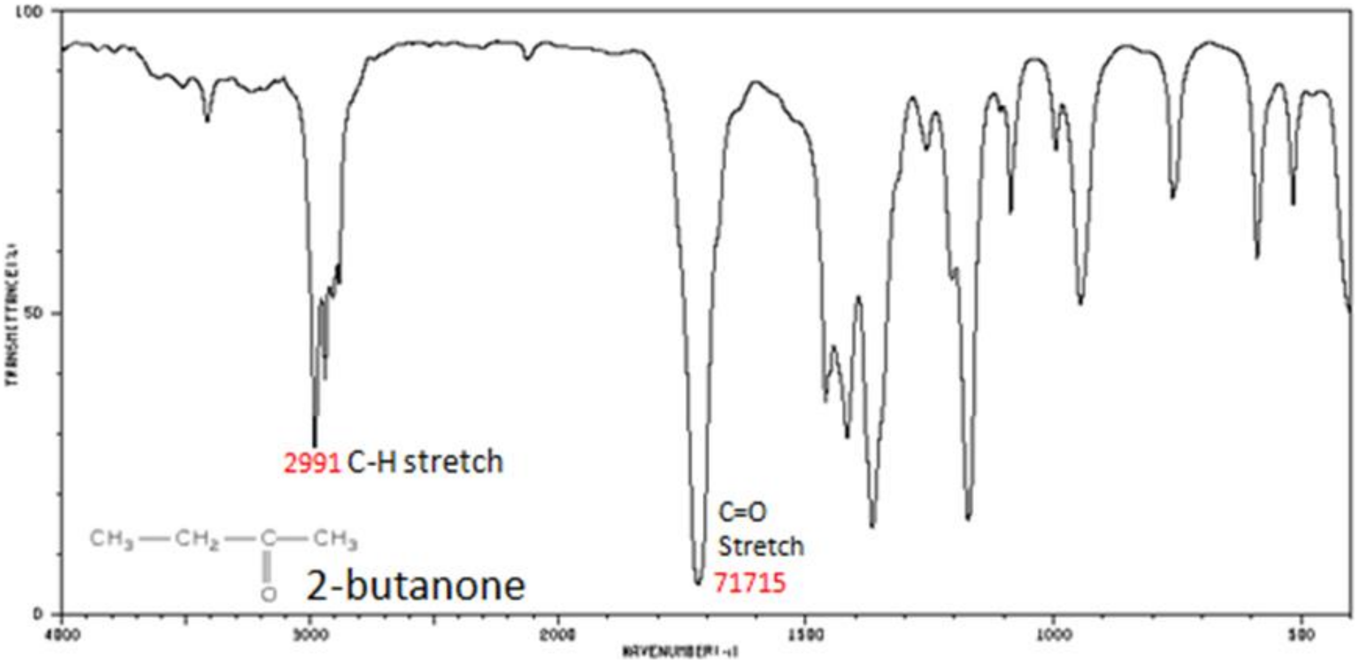


Figure 8. Infrared Spectrum of 2-Butanone

If a compound is suspected to be an aldehyde, a peak always appears around 2720 cm^{-1} which often appears as a shoulder-type peak just to the right of the alkyl C–H stretches.

- **H–C=O stretch 2830-2695 cm^{-1}**
- **C=O stretch:**
  - **aliphatic aldehydes 1740-1720 cm^{-1}**
  - **alpha, beta-unsaturated aldehydes 1710-1685 cm^{-1}**

Figure 9. shows the spectrum of butyraldehyde.

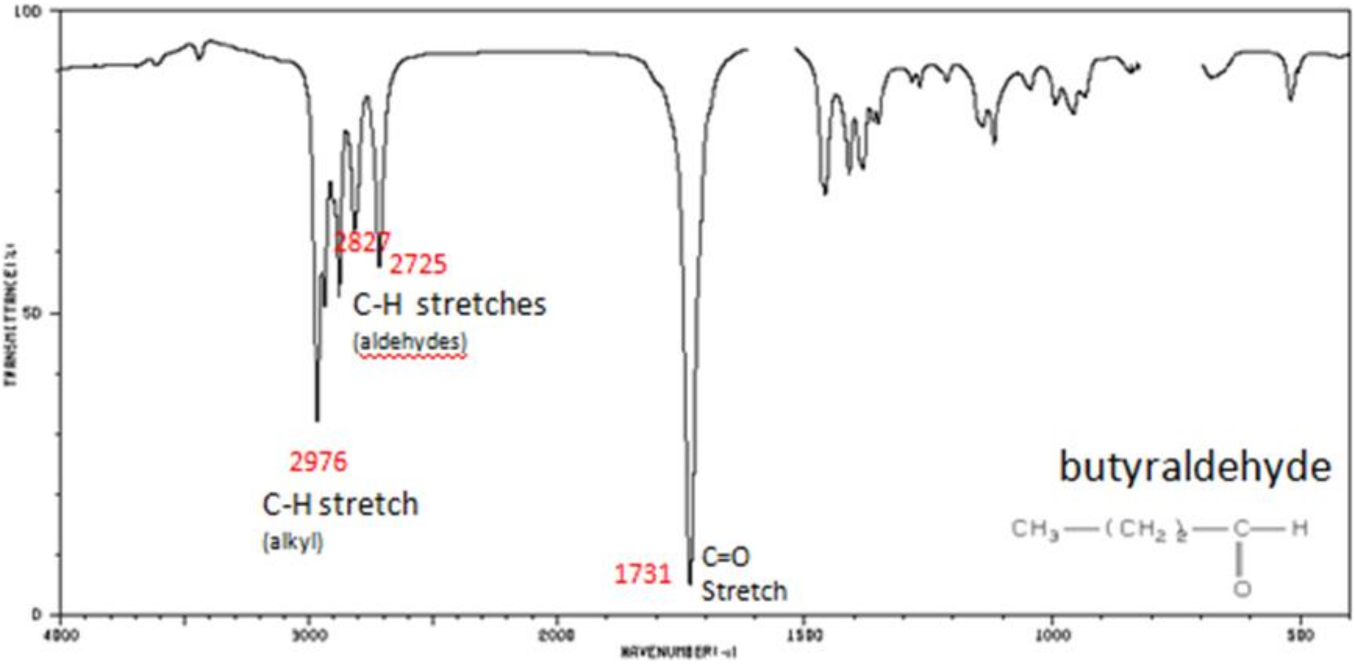


Figure 9. Infrared Spectrum of Butyraldehyde

The carbonyl stretch C=O of esters appears:

- **C=O stretch**
  - **aliphatic from 1750-1735 cm^{-1}**
  - **?, ?-unsaturated from 1730-1715 cm^{-1}**
- **C–O stretch from 1300-1000 cm^{-1}**

Figure 10. shows the spectrum of ethyl benzoate.

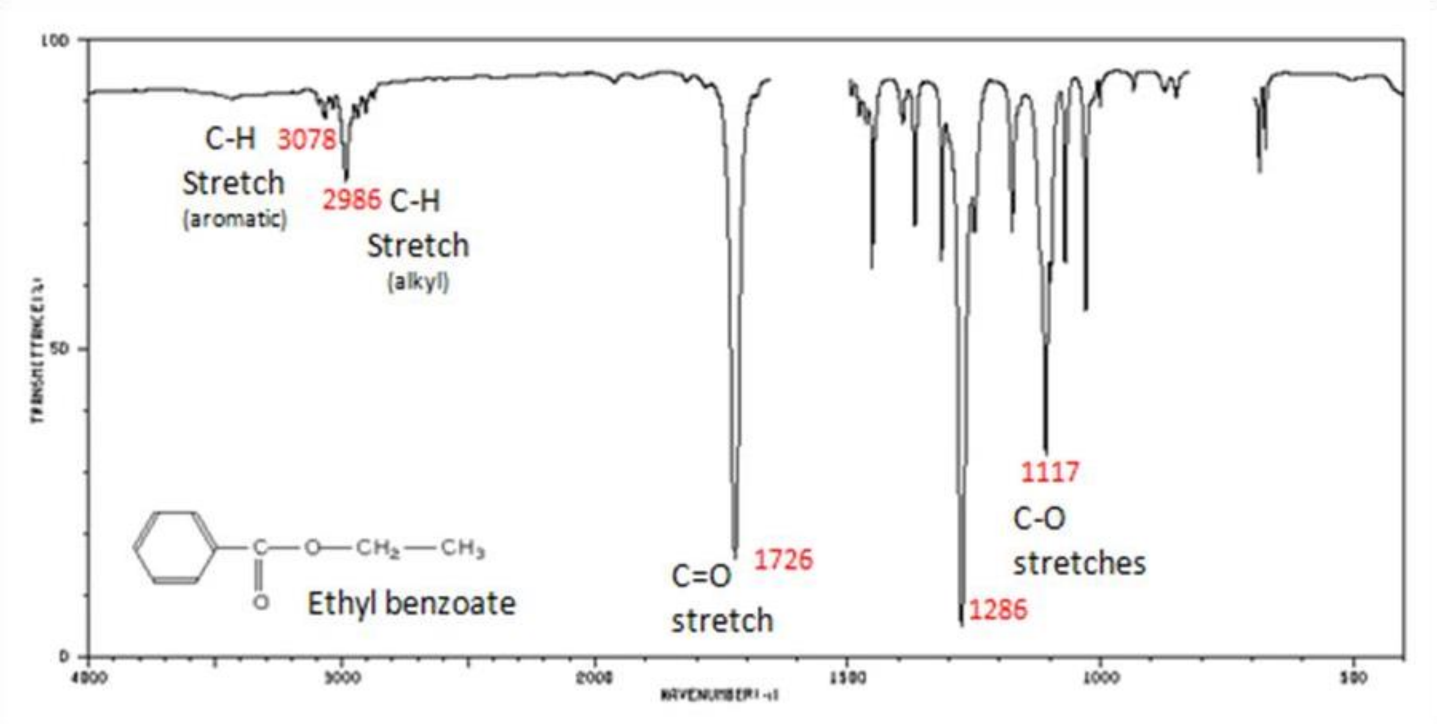


Figure 10. Infrared Spectrum of Ethyl benzoate

The carbonyl stretch C=O of a carboxylic acid appears as an intense band from 1760-1690 cm^{-1}. The exact position of this broad band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen bonding.

- **O–H stretch from 3300-2500 cm^{-1}**
- **C=O stretch from 1760-1690 cm^{-1}**
- **C–O stretch from 1320-1210 cm^{-1}**
- **O–H bend from 1440-1395 and 950-910 cm^{-1}**

Figure 11. shows the spectrum of hexanoic acid.

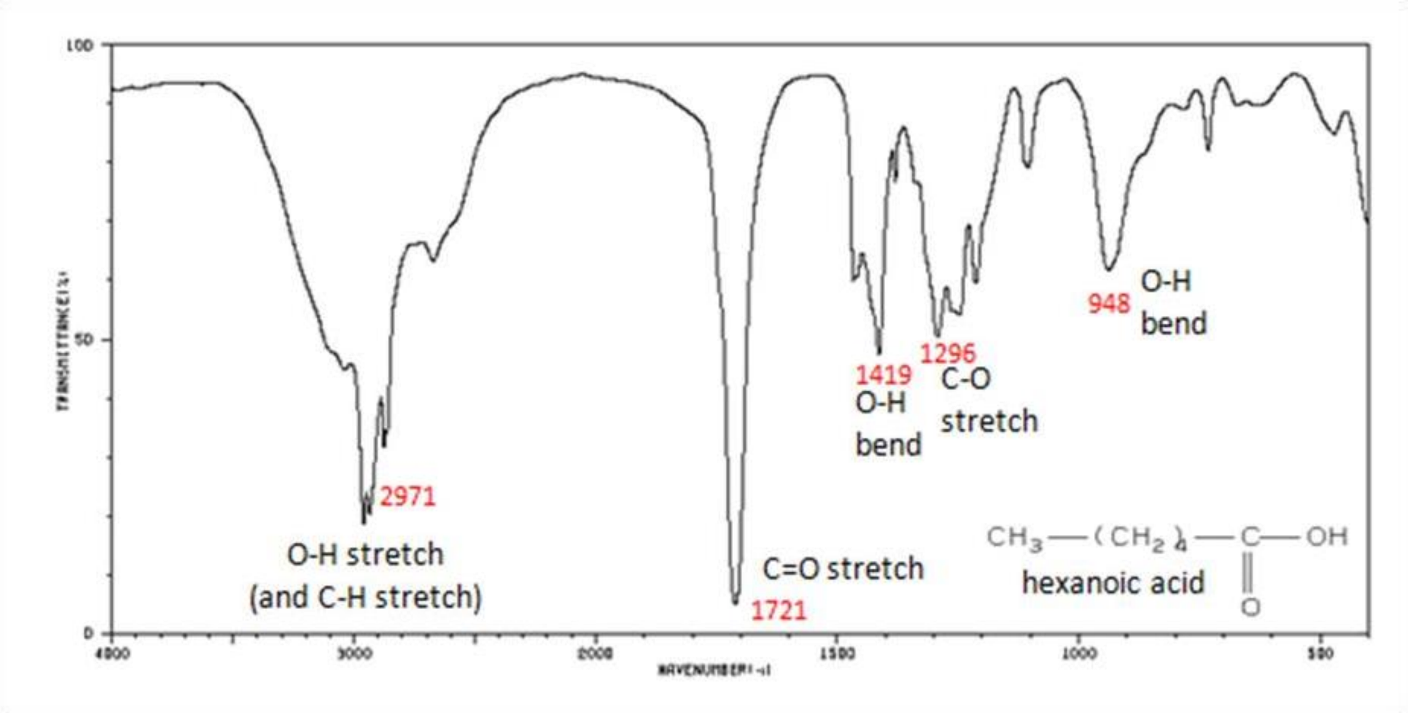


Figure 11. Infrared Spectrum of Hexanoic acid

Organic Nitrogen Compounds

- **N–O asymmetric stretch from 1550-1475 cm^{-1}**
- **N–O symmetric stretch from 1360-1290 cm^{-1}**

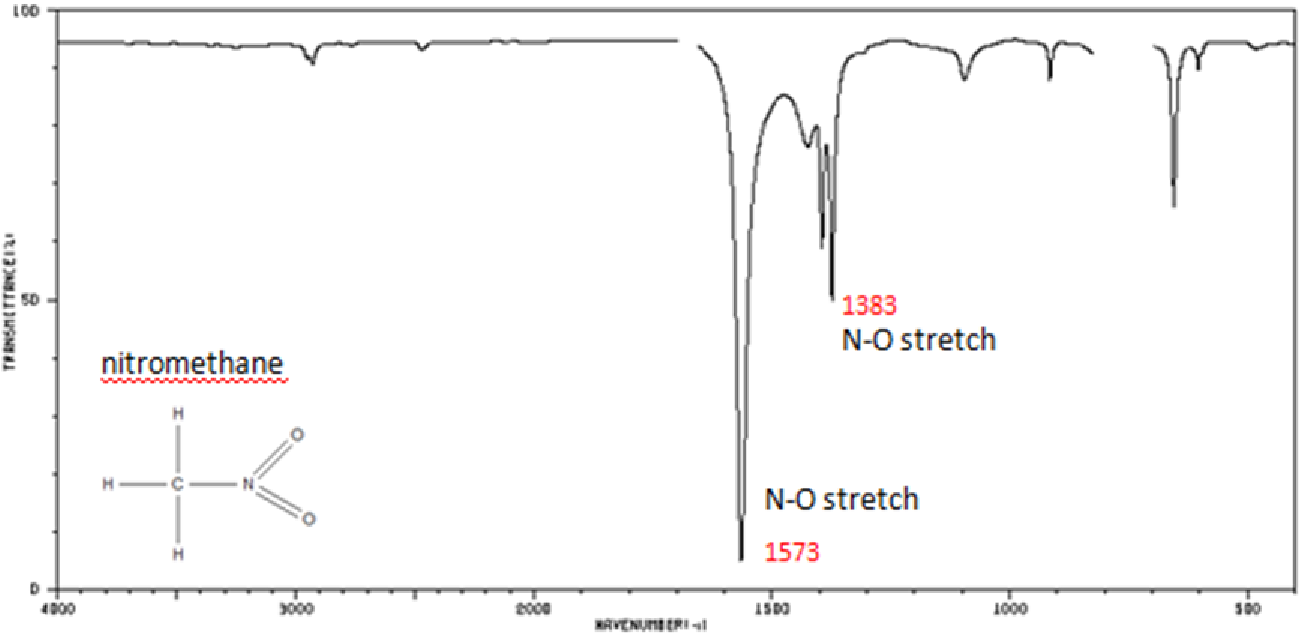


Figure 12. Infrared Spectrum of Nitomethane

Organic Compounds Containing Halogens

Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorene, or iodine.

- **C–H wag (-CH_2X) from 1300-1150 cm^{-1} C–**
- **X stretches (general) from 850-515 cm^{-1}**
  - **C–Cl stretch 850-550 cm^{-1}**
  - **C–Br stretch 690-515 cm^{-1}**

The spectrum of 1-chloro-2-methylpropane are shown below.

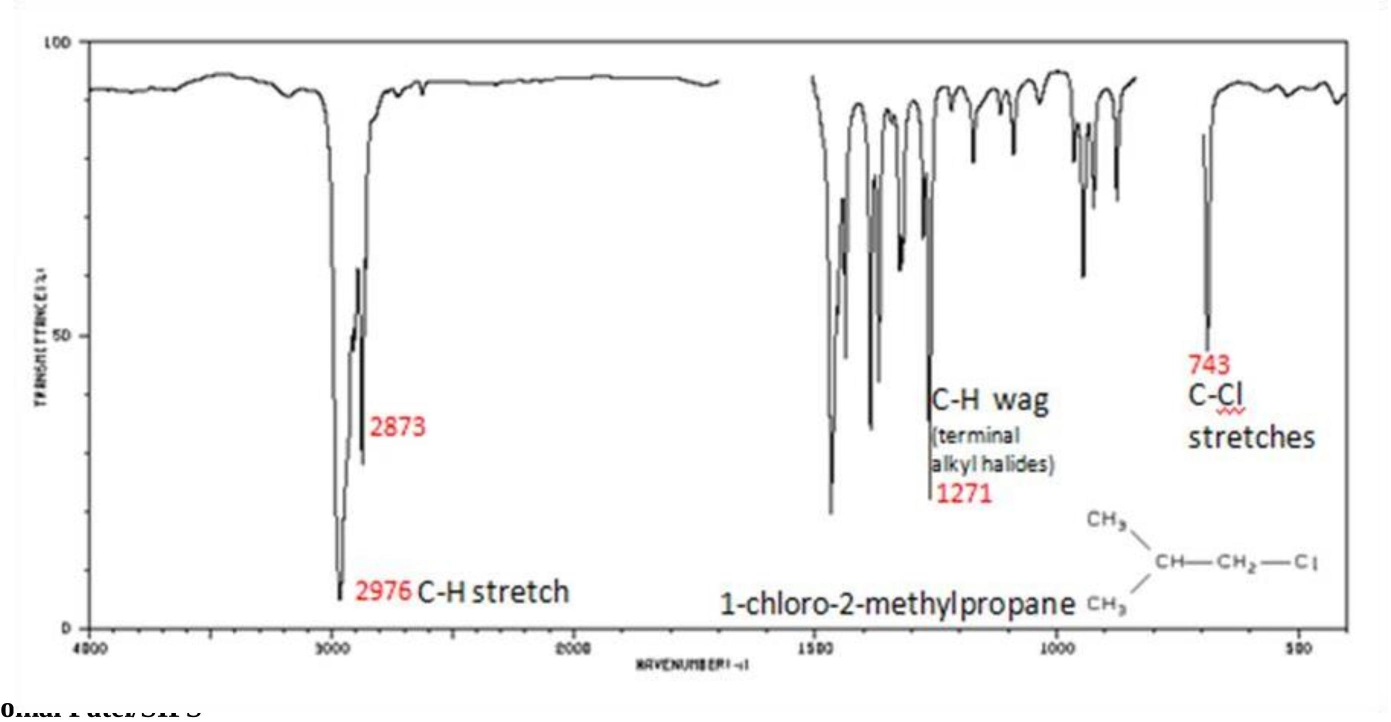


Figure 13. Infrared Spectrum of 1-chloro-2-methylpropane

For more Infrared spectra Spectral database of organic molecules is introduced to use free database. Also, the infrared spectroscopy correlation tableis linked on bottom of page to find other assigned IR peaks.

Inorganic Compounds

Generally, the infrared bands for inorganic materials are broader, fewer in number and appear at lower wavenumbers than those observed for organic materials. If an inorganic compound forms covalent bonds within an ion, it can produce a characteristic infrared spectrum.

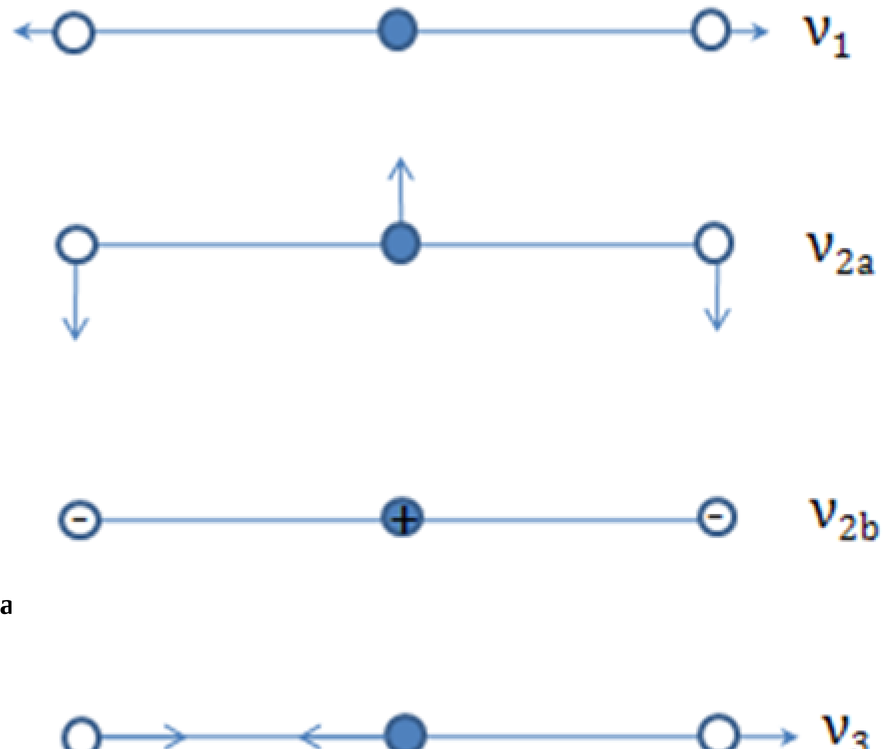
Main infrared bands of some common inorganic ions:

- **CO_3^{2-} 1450-1410, 880-800cm^{-1}**
- **SO_4^{2-} 1130-1080, 680-610cm^{-1}**
- **NO_3^- 1410-1340, 860-800cm^{-1}**
- **PO_4^{3-} 1100-950cm^{-1}**
- **SiO_{42}^- 1100-900cm^{-1}**
- **NH_4^+ 3335-3030, 1485-1390cm^{-1}**
- **MnO_4^- 920-890, 850-840cm^{-1}**

Diatomic molecules produce one vibration along the chemical bond. Monatomic ligand, where metal s coordinate with atoms such as halogens, H, N or O, produce characteristic bands. These bands are summarized in below.

Chracteristic infrared bands of diatomic inorganic molecules: M(metal), X(halogen)

M-H stretching	**2250-1700cm^{-1}**
M-H bending	**800-600cm^{-1}**
M-X stretching	**750-100cm^{-1}**
M=O stretching	**1010-850cm^{-1}**
M=N stretching	**1020-875cm^{-1}**



The normal modes of vibration of linear and bent triatomic molecules are illustrated and some common linear and bent triatomic molecules are shown below. Note that some molecules show two bands for ?$_1$because of Fermi resonance.

Characteristic infrared bands(cm^{-1}) of triatomic inorganic molecules:

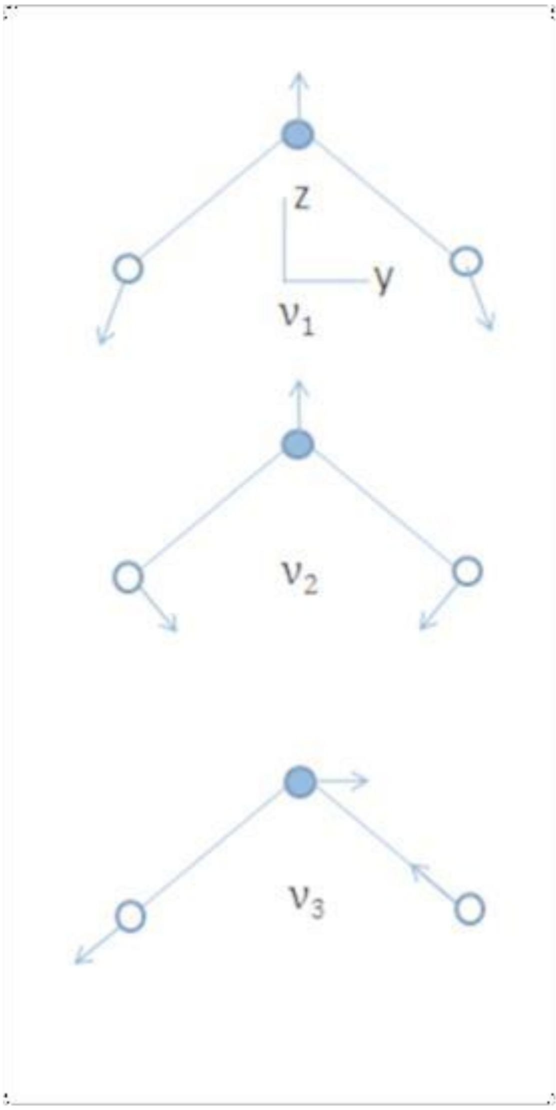
Linear Molecules

OCO HCN NCS^-
ClCN $MgCl_2$

1388,
1286 3311 2053 71
4, 784 327

667	712	486, 471	380	249
2349	2049	748	2219	842

Bent Molecules	H_2O	O_3	$SnCl_2$
	3675	1135	354
	1595	716	120
	3756	1089	334



Identification

There are a few general rules that can be used when using a mid-infrared spectrum for the determination of a molecular structure. The following is a suggested strategy for spectrum interpretation:[2]

1. **Look first at the high-wavenumber end of the spectrum(>1500cm^{-1}) and concentrate initially on the major bands**
2. **For each band, 'short-list' the possibilities by using a correlation table**
3. **Use the lower-wavenumber end of the spectrum for the confirmation or elaboration of possible structural elements**
4. **Do not expect to be able to assign every band in the spectrum**
5. **Keep 'cross-checking' wherever possible.**
6. **Exploit negative evidence as well as positive evidence**
7. **Band intensities should be treated with some caution. Under certain circumstances, they may vary considerably for the same group**
8. **Take care when using small wavenumber changes. If in solution, some bands are very 'solvent-sensitive'**
9. **Do not forget to subtract slovent bands if possible**

Infrared spectroscopy is used to analyze a wide variety of samples, but it cannot solve every chemical analysis problem. When used in conjunction with other methods such as mass spectroscopy, nuclear magnetic resonance, and elemental analysis, infrared spectroscopy usually makes possible the positive identification of a sample.

References

1. **Infrared Spectral Interpretation by Brian Smith, CRC Press, 1999**
2. **Infrared Spectroscopy: Fundamentals and Applications by Barbara Atuart, John Wiley&Sons, Ltd., 2004**
3. **Interpretation of Infrared Spectra, A Practical Approach by John Coates in Encyclopedia of Analytical Chemistry pp. 10815-10837, John Wiley&Sons Ltd, Chichester, 2000**

Outside Links

- **Spectral Database for Organic Compounds SDBS: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, date of access)**
- **Infrared Spectroscopy Correlation Table: http://en.wikipedia.org/wiki/Infrared_spectroscopy_correlation_table**
- **FDM Reference Spectra Databases: http://www.fdmspectra.com/index.html**
- **Other Usuful Web Pages:**
    - **http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/InfraRed/infrared.htm**
    - **Fermi resonance : http://en.wikipedia.org/wiki/Fermi_resonance**

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http://www.lsbu.ac.uk/water/vibrat.html

Water Absorption Spectrum

Water and global warming
Absorption spectra of gaseous, liquid and solid water
The vibrational spectra of liquid water
The visible and UV spectra of liquid water

Water and global warming

Water is the main absorber of the sunlight in the atmosphere. The 13 million million tons of water in the atmosphere (~0.33% by weight) is responsible for about 70% of all atmospheric absorption of radiation, mainly in the infrared region where water shows strong absorption. It contributes significantly to the greenhouse effect ensuring a warm habitable planet, but operates a negative feedback effect, due to cloud formation reflecting the sunlight away, to attenuate global warming. The water content of the atmosphere varies about 100-fold between the hot and humid tropics and the cold and dry polar ice deserts.

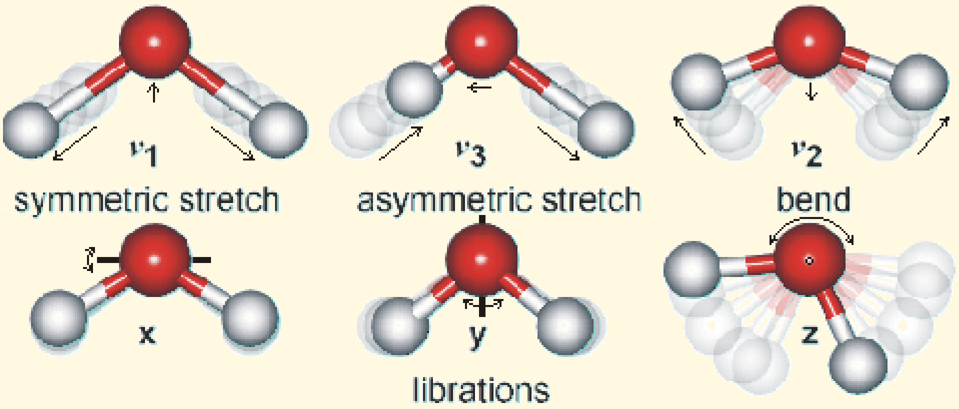
Absorption spectra of gaseous, liquid and solid water

The water absorption spectrum is very complex. Water's vapor spectroscopy has been recently reviewed [348]. The water molecule may vibrate in a number of ways. In the gas state, the vibrations [607] involve combinations of symmetric stretch (ν_1), asymmetric stretch (ν_3) and bending (ν_2) of the covalent bonds with absorption intensity ($H_2{}^{16}O$) $\nu_1;\nu_2;\nu_3 = 0.07;1.47;1.00$ [8]. The stretch vibrations of $HD^{16}O$ refer to the single bond vibrations, not the combined movements of both bonds. Gas phase rotations [1701] are complex and are combined with these vibrations. Rotations in the liquid phase are totally dominated by hydrogen bonding.

Main vibrations of water isotopologues

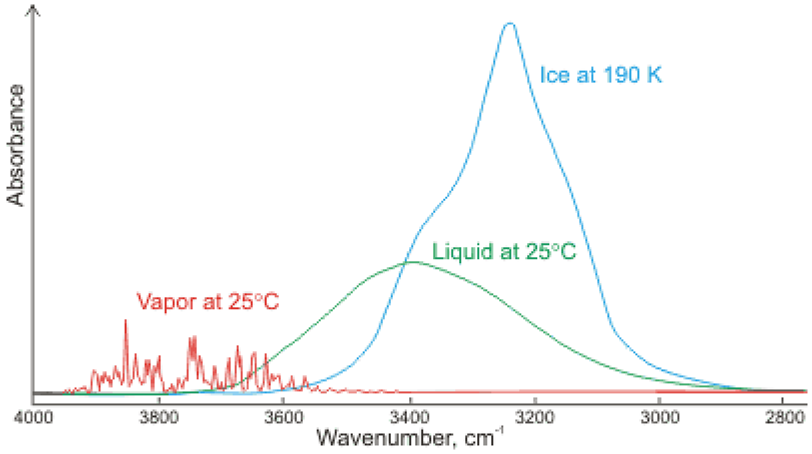
Gas	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}
$H_2{}^{16}O$	**3657.1**	**1594.7**	**3755.9**
$H_2{}^{17}O$	**3653.2**	**1591.3**	**3748.3**
$H_2{}^{18}O$	**3649.7**	**1588.3**	**3741.6**
$HD^{16}O$	**2723.7**	**1403.5**	**3707.5**
$D_2{}^{16}O$	**2671.7**	**1178.4**	**2787.7**
$HT^{16}O$	**2299.8**	**1332.5**	**3716.6**
$T_2{}^{16}O$	**2237.2**	**995.4**	**2366.6**

ab initio calculated values [607, 1728]



Shown opposite are the main vibrations occurring in water. The movements are animated using the cursor. The dipole moments change in the direction of the movement of the oxygen atoms as shown by the arrows. As the H-atoms are light, the vibrations have large amplitudes.

The water molecule has a very small moment of inertia on rotation which gives rise to rich combined vibrational-rotational spectra in the vapor containing tens of thousands to millions of absorption lines. In the liquid, rotations tend to be restricted by hydrogen bonds, giving the librations. Also, spectral lines are broader causing overlap of many of the absorption peaks.

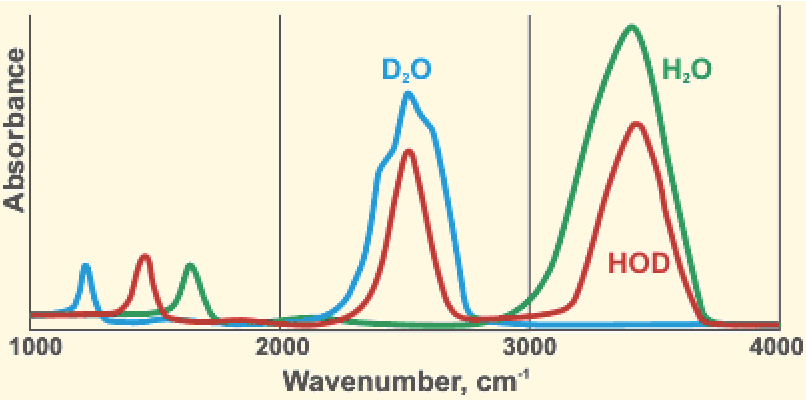


Opposite is shown a comparison of the gas, liquid and solid spectra of the same amount of H_2O [1392]. On mousing over the Figure, the high (HDL) and low (LDL) density liquid water forms are shown [1738].

The main stretching band in liquid water is shifted to a lower frequency (ν_3, 3490 cm^{-1} and ν_1, 3280 cm^{-1} [8]) and the bending frequency increased (ν_2, 1644 cm^{-1} [942]) by hydrogen bonding. As seen, increased strength of hydrogen bonding typically shifts the stretch vibration to lower frequencies (red-shift) with greatly increased intensity in the infrared (but not Raman) due to the increased dipoles. Blue-shifting hydrogen bonds are described elsewhere. [Back to Top]

The vibrational spectra of liquid water

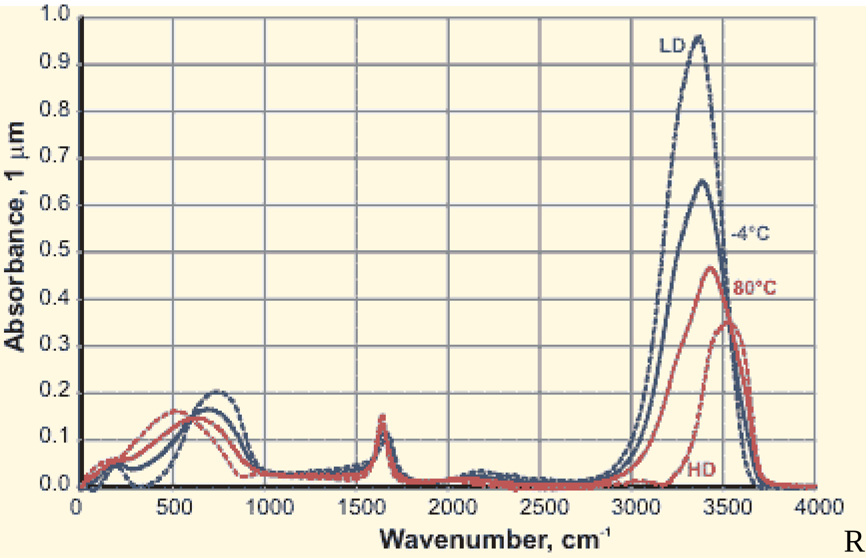
Main vibrations of liquid ordinary and heavy water					
Vibration(s) [942]	liquid H_2O (25 °C)		liquid D_2O (25 °C)		liquid T_2O [1848]
	ν, cm^{-1}	E_0, M^{-1} cm^{-1}	ν, cm^{-1}	E_0, M^{-1} cm^{-1}	ν, cm^{-1}
ν_2	**1643.5**	**21.65**	**1209.4**	**17.10**	**1024**
combination of ν_2+ libration	**2127.5**	**3.46**	**1555.0**	**1.88**	
ν_1, ν_3 , and overtone of ν_2	**3404.0**[e]	**100.61**	**2504.0**	**69.68**	**2200**



HDO (50 mole % H_2O plus 50 mole % D_2O; ~50% HDO, ~25% H_2O, ~25% D_2O) has maxima at 3415 cm^{-1}, 2495 cm^{-1} 1850 cm^{-1} and 1450 cm^{-1} assigned to OH stretch, OD stretch,[h] combination of v_2+ libration and HDO bending respectively [786] (see right for comparative spectra). HTO and DTO (50 mole % mixtures as HDO above) have v_2 bend maxima at 1388 cm^{-1} and 1130 cm^{-1} respectively [1848].

Variations in the environment around each liquid water molecule gives rise to considerable line broadening with vibration shifts in a hydrogen-bond-donating water molecule being greater than in a hydrogen-bond accepting molecule but both acting in the same direction [679], and accumulating with the number of hydrogen bonds. The strength of the hydrogen bonding depends on the cooperative/anticooperative nature of the surrounding hydrogen bonds with strongest hydrogen bonds giving the lowest vibrational frequencies [852]. Stretching frequency increases about 360 (at 3.1 Å) -1000 (at 2.6 Å) cm^{-1}Å^{-1} with increasing O···O distance and about 9 cm^{-1} degree^{-1} with increasing O-H·· O bend [446]. The absorption intensity of these bands is $v_1;v_2;v_3 = 0.87;0.33;1.00$ [8]. In supercooled water, the spectra is shifted to lower frequency with a 70 cm^{-1} shift of the stretch frequency and 30% increase in its intensity between 298 K and 238 K [1065]. Ultimately a stretch peak at 3120 cm^{-1} dominates, as it also does in amorphous ice (LDA) [1252]. In hexagonal ice, these bands are shifted further (v_1, 3085 cm^{-1}, v_2, 1650 cm^{-1},v_3, 3220 cm^{-1}).

In liquid water the molecular stretch vibrations shift to higher frequency, on raising the temperature (as hydrogen bonding weakens, the covalent O-H bonds strengthen causing them to vibrate at higher frequencies) whereas the intermolecular vibrations shift to lower frequencies and the molecular bend vibration peak shifts to lower frequencies and becomes both narrower [696] and stronger. These differences between stretch and bend vibrations are due to the increased importance of intermolecular hydrogen bonding at lower temperatures that tends to reduce intermolecular bending whilst encouraging stretching. Thus in the extreme non-hydrogen bonded state, the 'dangling' O-H bond stretch frequency at surfaces where the water molecule has three hydrogen bonds (two accepting and one donating) is at 3697 cm^{-1} [1246]. Raising the temperature also lowers the intensity of the stretching bands. This divergent behavior of bending and stretching vibrations allows their contributions to combination bands to be discerned. Thus, combinations of stretching vibrations shift to higher frequency with temperature with this trend reduced when bending vibrations are also combined. As examples, the first overtone combination of symmetric and asymmetric stretching shows a shift from strongly hydrogen-bonded structures (6707 cm^{-1}) to weakly hydrogen bonded structures (7082 cm^{-1}) with increasing temperature [237], and the combination band at about 5200 cm^{-1} shifts to slightly higher wavenumbers with reduced hydrogen bond strength [282]. The second overtone of the stretching band gives rise to a significant peak in the near-infrared spectrum (λ 970 nm).



Recent work, using attenuated total reflectance (ATR) infrared spectroscopy, shows isobestic points for both ordinary and heavy liquid water, with respect to temperature. For H_2O these are at around 600, 1600, 1680, & 3550 cm^{-1} [1738], in agreement with earlier work [530 ,699].[g] Shown opposite are the ATR spectra of liquid water at -4 °C (blue solid line; 61% LD, 39% HD) and 80 °C (red solid line; 31% LD, 69% HD) and those of the low density (LD, blue dashed line) and high density (HD; red dashed line) forms that make up the liquid water [1738] in a linear combination. Similar conclusions have been gained from Raman spectroscopy where the LD peak is analysed as tetrahedral fully-hydrogen bonded H_2O molecules and the HD peak analysed as molecules with single acceptor and donor hydrogen bonds [1980]. Also, similar conclusions (at different wavenumbers) are drawn for D_2O [1738]. Unsurprisingly, such changes in absorption with temperature extend into the near infrared and visible spectrum [1974]. These conclusions are in qualitative agreement with recent wide-angle X-ray diffraction measurements [1755] and supportive of progressively changing two-phase models such as described here.

Increasing the pressure on water decreases the O·· O distances (graphed elsewhere) so increasing the covalent O-H distances and lowering their stretch frequency [804]. Raised pressure also causes a reduction in long, weak or broken bonds and an increase in bent and short, strong hydrogen bonds [804].

The overtone bands of water (~1100 nm - 2500 nm, in a scientific discipline known as AquaPhotomics) have been shown to be good discriminatory, and non-destructive, indicators of changes in aqueous structuring in disease diagnosis and protein conformation and have aided the understanding of the role of water in biological systems [1615a]. A database of such interactions is being built up [1615b], with comparison being made using polar graphs (Aquagrams) [1615c].

The spectra for isotopic variants of water (for example, HDO, D_2O and $H_2{}^{18}O$) are all different; in particular the H-O (~3400 cm^{-1}) and D-O (~2500 cm^{-1}) stretching vibrations are not connected in HDO but the related vibrations in H_2O and D_2O involve both hydrogen atoms.

Assignment of the IR vibrational absorption spectrum of liquid water[*]

Wavelength	cm^{-1}	Assignment		Wavelength**	cm^{-1}	Assignment
0.2 mm	**50**	**intermolecular**		**1200 nm**	**8330**	**$av_1 + v_2 + bv_3$; a+b=2**

		bend				
55 µm	**183.4**	**intermolecular stretch**		**970 nm**	**10310**	$a\nu_1 + b\nu_3$; **a+b=3**
25 µm	**395.5**	**L_1, librations**		**836 nm**	**11960**	$a\nu_1 + \nu_2 + b\nu_3$; **a+b=3**
15 µm	**686.3**	**L_2, librations**		**739 nm**	**13530**	$a\nu_1 + b\nu_3$; **a+b=4**
6.08 µm	**1645**	**ν_2, bend**		**660 nm**	**15150**	$a\nu_1 + \nu_2 + b\nu_3$; **a+b=4**
4.65 µm	**2150**	$\nu_2 + L_2$ [b]		**606 nm**	**16500**	$a\nu_1 + b\nu_3$; **a+b=5 [526]**
3.05 µm	**3277**	**ν_1, symmetric stretch**		**514 nm**	**19460**	$a\nu_1 + b\nu_3$; **a+b=6 [526]**
2.87 µm	**3490**	**ν_3, asymmetric stretch**		**449 nm**	**22270**	$a\nu_1 + b\nu_3$; **a+b=7 [1937]**
1900 nm	**5260**	$a\nu_1 + \nu_2 + b\nu_3$; **a+b=1**		**401 nm**	**24940**	$a\nu_1 + b\nu_3$; **a+b=8 [1937]**
1470 nm	**6800**	$a\nu_1 + b\nu_3$; **a+b=2**		**Note that a and b are integers, ≥ 0 ms.**		

* Raman peaks are given in [805].
**Wavelength (nm) = 10^7/wavenumber (cm^{-1}) (nm ~3.3 attosecond)

The near-infrared (NIR) bands (at about λ 970-1940 nm) are suited to rapid non-destructive water determination [479], all shifting a few nm to longer wavelength (lower frequency) with strengthening hydrogen bonding due to shifts from high density water (that is, increasing CS) to low density water (that is, increasing ES) [489]. A shoulder at about 3250 cm^{-1} on the side of the only strongly active Raman peak, and recently described in the IR spectrum at 3220 cm^{-1} [699], (symmetric O-H stretch, ν_1) of liquid water has been assigned to the collective in-phase symmetric O-H vibrations of strongly tetrahedrally-bonded water patches. The ratio of this to the remaining peak at about 3400 cm^{-1} has been used to determine the fraction of such water but such comparisons, although commonly used, should be treated with caution, as their absorbencies are unlikely to be identical and other possible vibrations, such as the first bend (ν_2) overtone, will interfere. This remaining peak has been analyzed in many ways (for example, as zero, single, double and triple coordinated hydrogen-bonded water) but most convincingly in terms of three-coordinate (double acceptor single donor, 3400 cm^{-1}; single acceptor double donor, 3535 cm^{-1}) and two-coordinate (single acceptor single donor, 3630 cm^{-1}) hydrogen-bonded water molecules [699]. There is clearly much structural information hidden in the vibrational spectra of water, if only it can be unambiguously interpreted (see methods page). Some success has recently been made using femtosecond mid-infrared nonlinear spectroscopy [189, 190] and the theoretical Raman spectra of water clusters [483]. ▲

In liquid water and ice the infrared and Raman spectra are far more complex than the vapor due to vibrational overtones and combinations with librations (restricted rotations; that is, rocking motions). These librations are due to the restrictions imposed by hydrogen bonding (minor L_1 band 395.5 cm^{-1}; major L_2 band 686.3 cm^{-1}; both for liquid water at 0 °C, the absorbance of L_1 increasing with increasing temperature whereas L_2 absorbance decreases but broadens with reduced wavenumber with increasing temperature [177]). Ice has a sharper major band at 819 cm^{-1} (-10 °C) with a very minor band at about 510 cm^{-1} [1219].

The librations depend on the moments of inertia such that the almost doubling of the moments of inertia of D_2O, relative to H_2O, reduces the frequencies by about a factor of √2. Cluster vibrations such as translational vibrations involve combinations of hydrogen bond O-H ··O stretching and bending at around 200 cm^{-1} (6

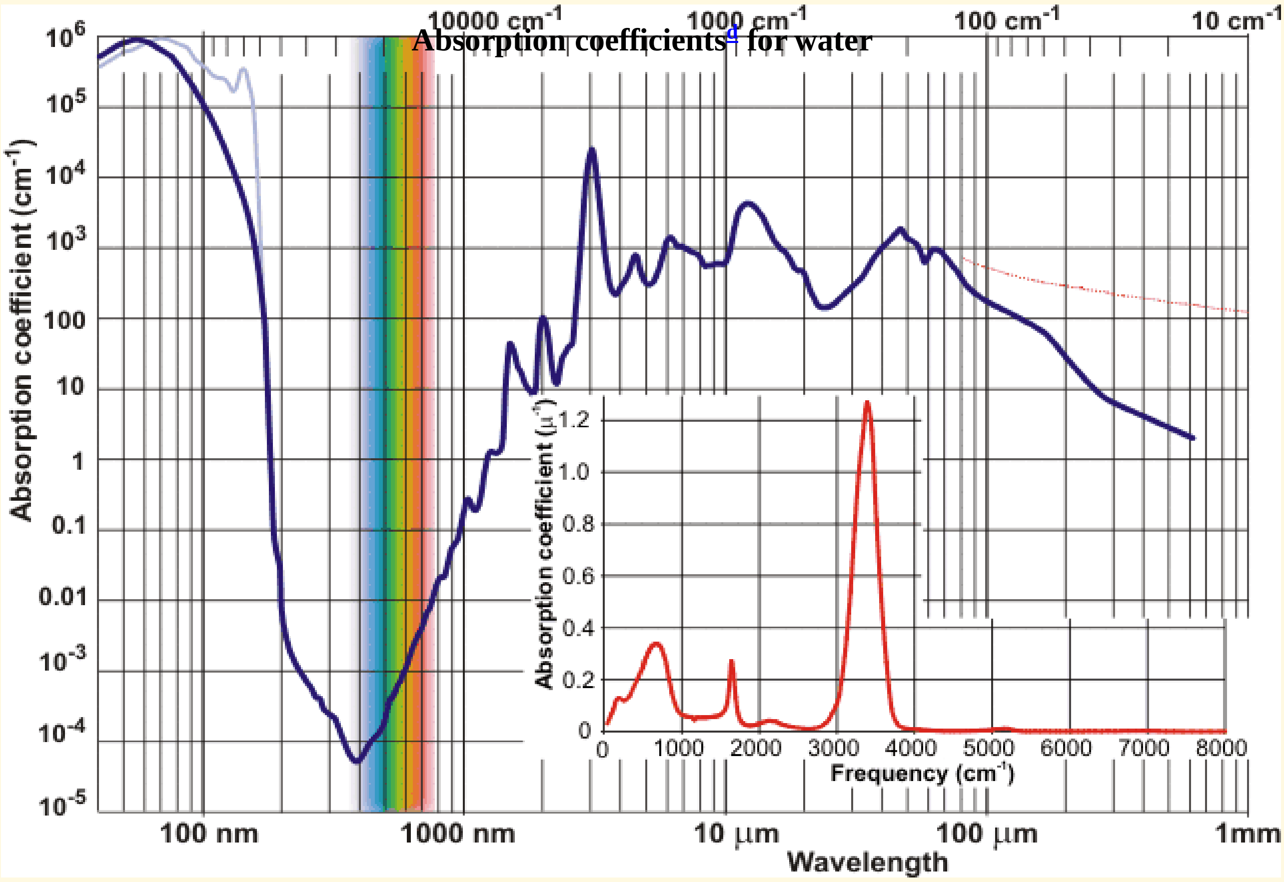
THz) [240] (S or connectivity band, 183.4 cm^{-1} (5.5 THz); at 0 °C, the hydrogen bond stretch absorbance increasing with decreasing temperature [819][a]; with a major sharp band at 215 cm^{-1} (6.4 THz) and a minor sharp band at 155 cm^{-1} (4.6 THz) in ice Ih at -10 °C [1219]. These involve hydrogen-bonded network movements along linear or near-linear hydrogen bonds[i] and show relatively small differences between H_2O and D_2O, due to their slightly different masses [1004]. These vibrations around 5 THz (165 cm^{-1}) overlap with the longitudinal acoustic (LA) phonon modes (i.e. hydrogen bond network vibrations in the direction of propagation). The Raman spectrum also involves an overlapping band involving the reorienting of the molecular dipoles around the hydrogen bonds [1384]. Some report bending vibrations of the hydrogen bonds also occur, due to out of alignment translations relative to the hydrogen bonds (B band ~40 - 60 cm^{-1} (1.2-1.8 THz); at 0 °C, the absorbance increasing with temperature [608]) [1004]. It seems likely that this 60 cm^{-1} peak is strongly localized within a local cluster and not connected with the more extensive hydrogen-bonded network [1549].[f] These vibrations around 1 THz (33 cm^{-1}) overlap with the transverse acoustic (TA) phonon modes (i.e. hydrogen bond network vibrations perpendicular to the direction of propagation). Also in liquid water there is a small but significant combination band (IR and Raman) of the bending (ν_2) and libration modes at 2125 cm^{-1} (2270 cm^{-1} in ice Ih; the 'association band').[b]

A contribution to the Raman scattering of water at 50 cm^{-1} (1.5 THz) has been attributed to the low-frequency vibrations of oxygen-oxygen bonds at the vertices of pentagonal dodecahedral structures [165] or simply O····O ·· O bending motions [901]. Such low-frequency features (centered around 60 cm^{-1}, 1.8 THz) are also observed in the spectra of dense non-associated liquids, such as the noble gases, and may be attributed to non-bonded 'cage effects' where translations are frustrated [448]. This same effect, however, may also operate within hydrogen bonded 'cage effects' consistent with the 60 cm^{-1} absorption band [900]. Further confirmation of the hydrogen-bonding source for this absorption comes from the use of an intense source of far infrared radiation showing temperature dependent peaks at a number of wavelengths in the 40-90 cm^{-1} (1.2-2.7 THz) range [656]. The infrared spectrum runs into the β-relaxation band (~0.2 THz; due to rattling of molecules in a cage of surrounding molecules) and absorption due to microwave radiation at longer wavelengths. This interacts with the water dipole, moving the molecules backwards and forwards and so stretching and bending the hydrogen bonds, which generates heat. If the radiation is at too high a frequency (> 1000 GHz, $\lambda < 0.3$ mm), the molecules do not have time to react to the electromagnetic field changes and no heat is generated. If the radiation is at lower frequencies (< 1 GHz, $\lambda > 30$ cm), the molecules react to the electromagnetic field changes but so slowly that effectively no heat is generated. Pure water is almost totally transparent to such low frequency radiation. The maximum absorption varies to higher frequencies at higher temperatures when the weaker hydrogen bonding allows a quicker response to changes in the field [136]. Microwave ovens typically use radiation at 2.450 GHz (λ 12.24 cm). More details on the response of water to microwave radiation are available on another page.

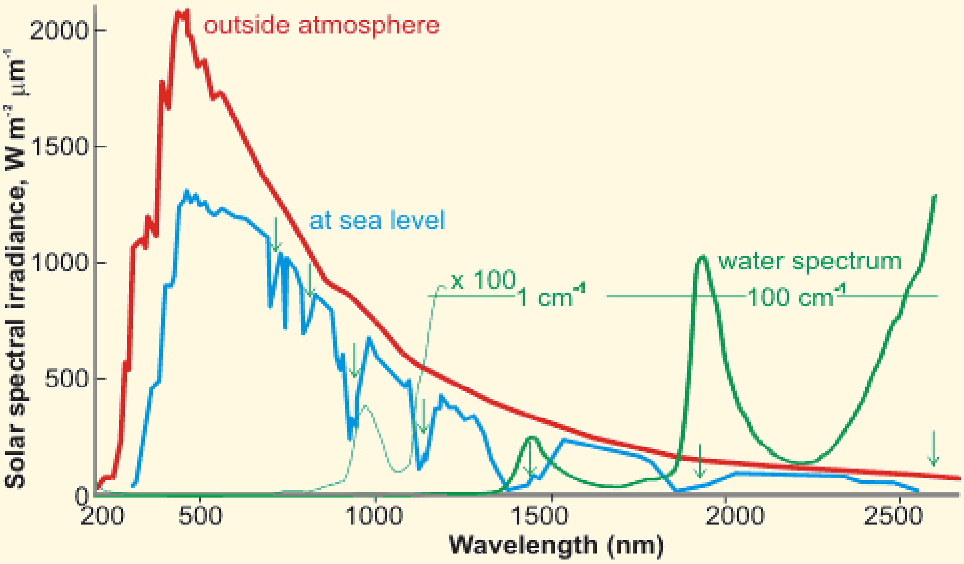
Anions may be classified as kosmotropes or chaotropes according to how the effect the water's stretch vibrations; ionic kosmotropes (for example, F^-) causing broadening and movement to lower wavenumbers whereas chaotropes (for example, I^-) causing narrowing and movement to higher wavenumbers [758]. Primarily this seems due to water's ability to hydrogen bond to the anions. The vibrational spectra of $H_3O_2^-$ and $H_5O_2^+$ are described on another page.

The reported structuring absorption of sound by water is not generally accepted. [Back to Top ▲]

The visible and UV spectra of liquid water



Absorption coefficients[d] for water



Water is almost perfectly transparent to 'visible' light, a property which is made good use of by photosynthesis and allowing production of both biomass and oxygen. However, some absorption is achieved by atmospheric water (see right, which shows seven absorption bands). Water is very slightly blue in color [131][c] as overtone and combination vibrational absorption bands (albeit far less intense, see above [130]) extend through the red part of the visible spectrum with a small peak at 739 nm and shoulder at 836 nm, plus a smaller fourth overtone of the v_1:v_3 stretch at 606 nm, and very small fifth overtone (at 514 nm) and combined overtone (at 660 nm) bands. These overtone and combination vibrational bands increase and sharpen somewhat with increasing temperature [268] in line with the expectation from the two state water model. This absorption spectrum of water (red light absorbs 100 times more than blue light), together with the five-times greater scattering of blue light over red light, contributes to the blue color of lake, river and ocean waters. Colloidal silica may contribute to the outstanding blue color of certain, often hydrothermal, pools and lakes [372]. Ice is also blue [159] for similar reasons but liquid D_2O does not absorb in the red region (as the absorption band is shifted into the infrared) and is blue solely because of the light scattering effect [159].

Although the absorptions of water's overtone bands within the visible spectrum are quite small (~0.3-0.01 m^{-1}), they are sufficient to create spectral niches amongst photosynthetic organisms; thus directing water ecology and evolution [1281].

The first peak in the far UV of gaseous water (166.5 nm [902], shown light blue in the spectrum above) is due to excitation from the occupied p_z^2-type molecular $1b_1$orbital (interactive orbitals are available, COW only [Plug-in, ActiveX]). Absorption of UV close-by (~125 nm), excites the $3a_1$ orbital leading to dissociation into OH + H (photodissociation; higher energy absorption produces charged fragments [1299]). Such dissociation can also be achieved by consecutive absorption of two 266 nm photons [589]. Absorption of two higher energy photons, at 200 nm, gives rise to a hydrated electron by $H_2O + h\nu \rightarrow H_2O^+ + e^-_{aq}$ [1057]. Inelastic x-ray scattering studies find this far UV peak to be absent in liquid water [355], where the major peak is at about 56 nm. [Back to Top]

Footnotes

[a] Dielectric studies showed an opposite effect with the absorbance at around 200 cm^{-1} increasing with increasing temperature to about 30 °C before reducing with increasing temperature due to hydrogen bond breakage [608]. The discrepancy may be due to additional relaxation processes detected by these dielectric studies in addition to the hydrogen bond stretching detected by infrared spectroscopy [819]. The Raman absorption at 180 cm^{-1} has been proposed to be used to monitor tetrahedrally hydrogen bonded water molecules ('bound' water) [1963]. [Back]

[b] This band may be due to third overtone of the libration band, with the second overtone introducing asymmetry into the bend (ν_2) vibration [699b]. The dependence of this band on hydrogen bonding makes it sensitive to changes in liquid and solution structuring, although this importance is seemingly often overlooked. [Back]

[c] The sky is blue due to molecular light scattering, with neither tiny air-borne particles nor its small and variable content of gaseous water having significant effect [710]. [Back]

[d] This curve(s) has been generated using data for liquid and frozen water to give a continuous curve showing the main features. For exact data please consult the original references [130]. The absorption coefficient, $\mu_{a(\lambda)}$, with units of cm^{-1}, at a particular wavelength (λ) is given by theequation $\frac{I}{I_0} = e^{-\mu_{a(\lambda)} d}$ where I is

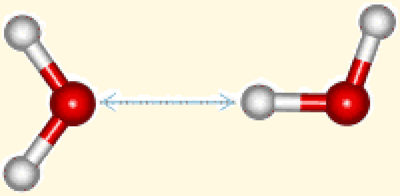
the transmitted intensity of the light, I_0 is the incident intensity of the lightand l is the path length (cm). The absorbance (A, in optical density units) is defined by the equation $A = -Log_{10}\left(\frac{I}{I_0}\right)$. The transmittance (*T*) of a sample is defined by $T = \left(\frac{I}{I_0}\right)$. The molar extinction coefficient $\varepsilon_{(\lambda)}$, with units liters mole^{-1} cm^{-1}, is defined by the equation $A = \varepsilon_{(\lambda)}cl$ where *c* is the molar concentration (= 55.345 M for liquid water at 25 °C) and *l* is the path length (cm). Comparison of these definitions shows that $A = \frac{\mu_a l}{2.303}$ and $\varepsilon_{(\lambda)} = \frac{\mu_{a(\lambda)}}{2.303c}$ (note that $\log_e(10) = 2.302585$). [Back]

[e] This band in the Raman spectrum has been clearly separated into three peaks at ~3210, 3450 and 3650 cm^{-1} [1310]. The two dominant components at 3210 and 3450 cm^{-1} were assigned to ice-like (for example ES) and disordered (for example CS) [1310]. [Back]

[f] This assignment, for 40 cm^{-1} in the far infrared, is disputed as being caused by collective vibrations, with no temperature dependence found between 10 °C-70 °C [1676]. [Back]

[g] The presence of isobestic points have been disputed [526], but has also been found by Raman spectroscopy of optically levitated supercooled micron-sized water droplets between -34.6 °C and 46.0 °C at about 3340 cm^{-1} [1909] and between -25 °C and 25.0 °C at 3330 cm^{-1} using a confocal micro-Raman system in a backscattering geometry [1980] . [Back]

[h] The peak at 2495 cm^{-1} can be used to quantify moderate HDO contents. [Back]



[i] The peak at about 200 cm^{-1} (~6 THz) involves molecular translational vibrations involving the hydrogen bond (but not the O-H covalent bond), such as shown right [1992]. [Back]