ORGANIC SPECTROSCOPY - IR

BY

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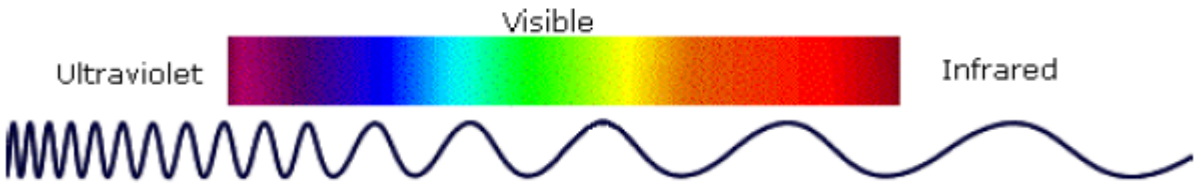
Infrared Spectroscopy

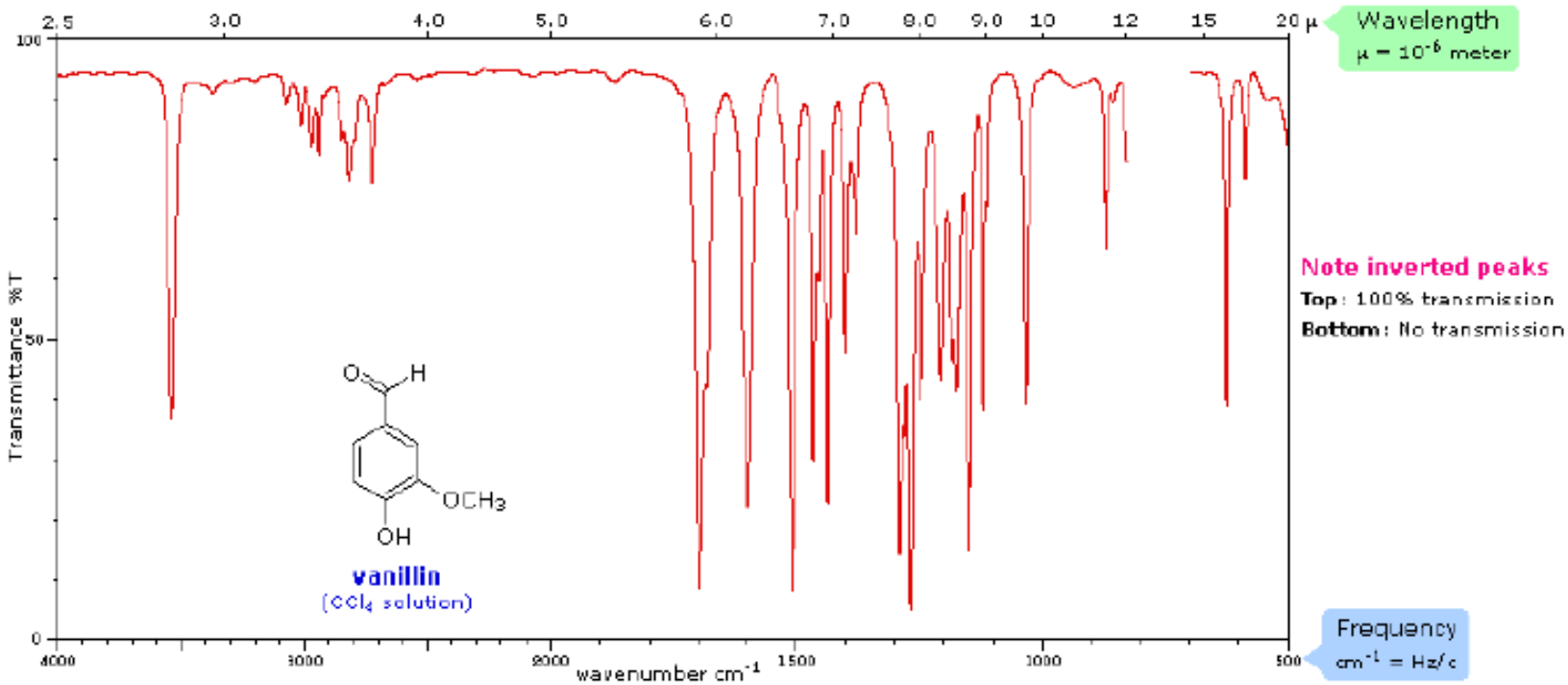
1. Introduction

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*1013 to 1.2*1014 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 (CCl4) 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).

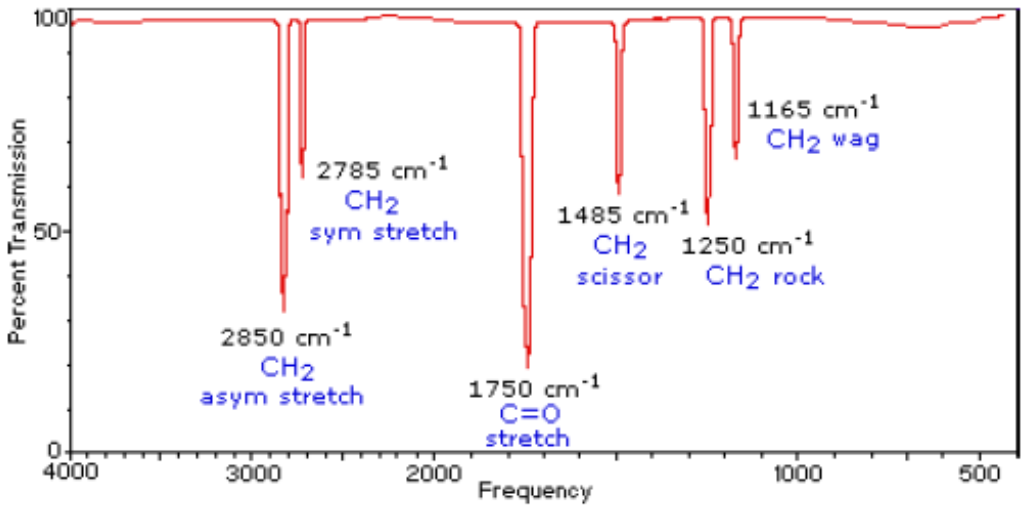
The frequency scale at the bottom of the chart is given in units of reciprocal centimeters (cm-1) rather than Hz, because the numbers are more manageable. The reciprocal centimeter is the number of wave cycles in one centimeter; whereas, frequency in cycles per second or Hz is equal to the number of wave cycles in 3*1010 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.

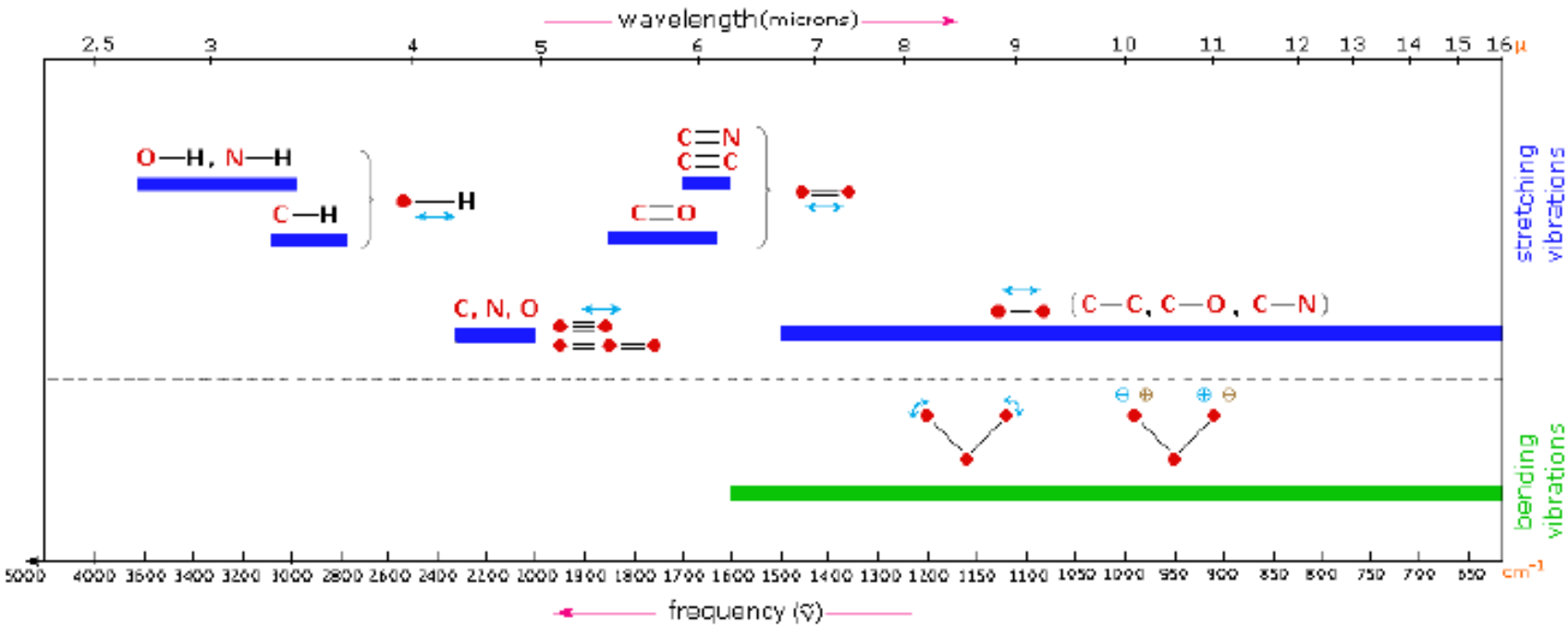
Some General Trends:

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 sp3 C-H stretching; whereas, absorption above 3000 cm-1 is from sp2 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	1030-1060 (str)
sulfone	1325± 25 (as) & 1140± 20 (s) (both str)
sulfonic acid	1345 (str)
sulfonyl chloride	1365± 5 (as) & 1180± 10 (s) (both str)
sulfate	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)

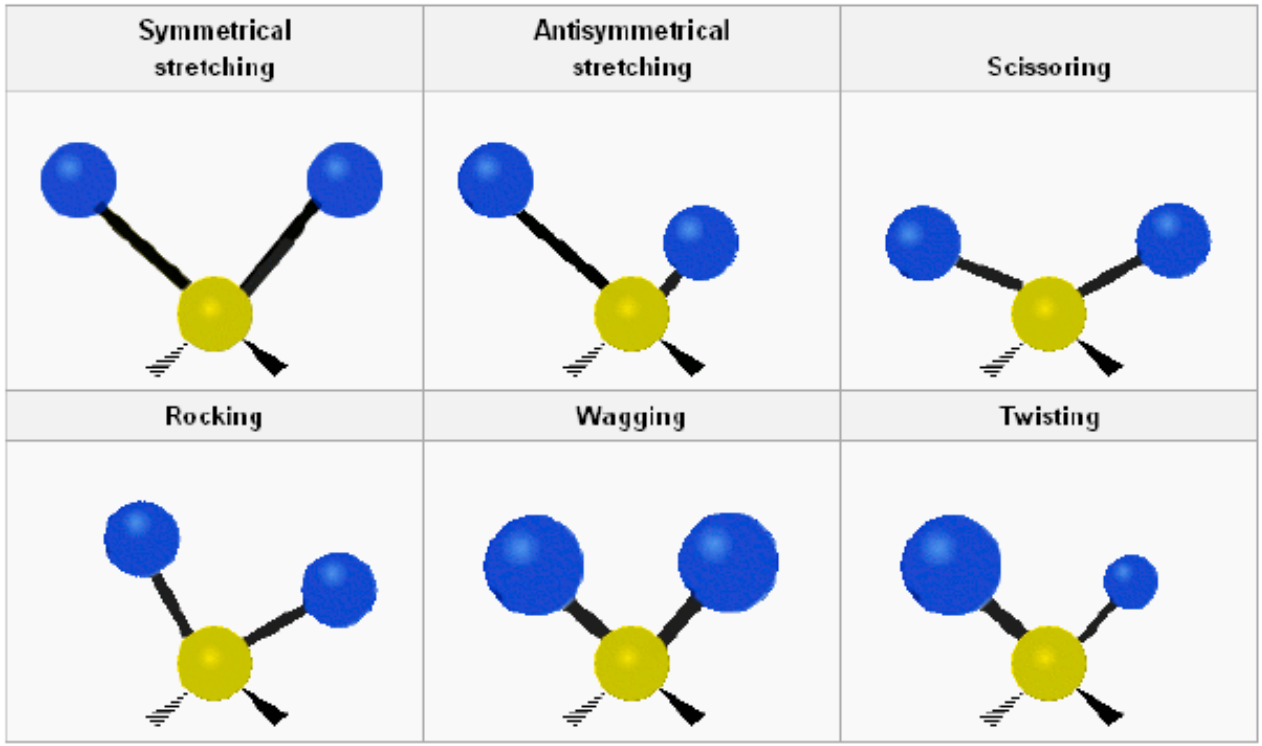
Theory

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.

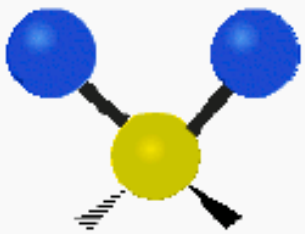
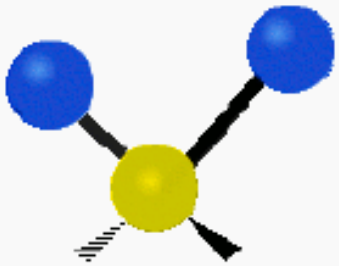
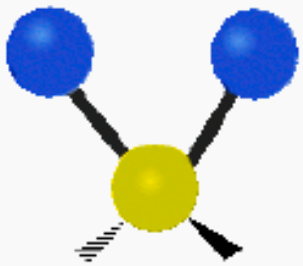
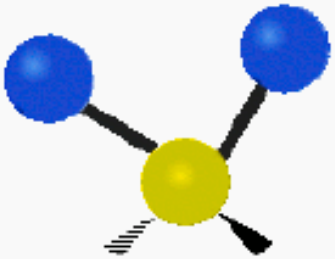
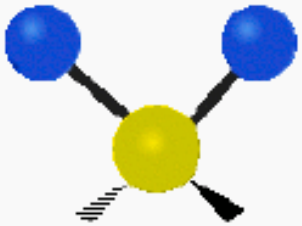
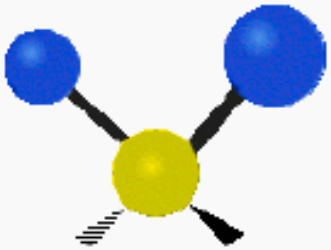
Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels. These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, by the associated vibronic 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.

Mode of Vibration

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 CH2 group, commonly found in organic compounds can vibrate in six different ways: symmetrical and antisymmetrical stretching, scissoring, rocking, wagging and twisting:



Mode of Vibration

Symmetrical stretching	Antisymmetrical stretching	Scissoring
		
Rocking	**Wagging**	**Twisting**
		

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. This can 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).

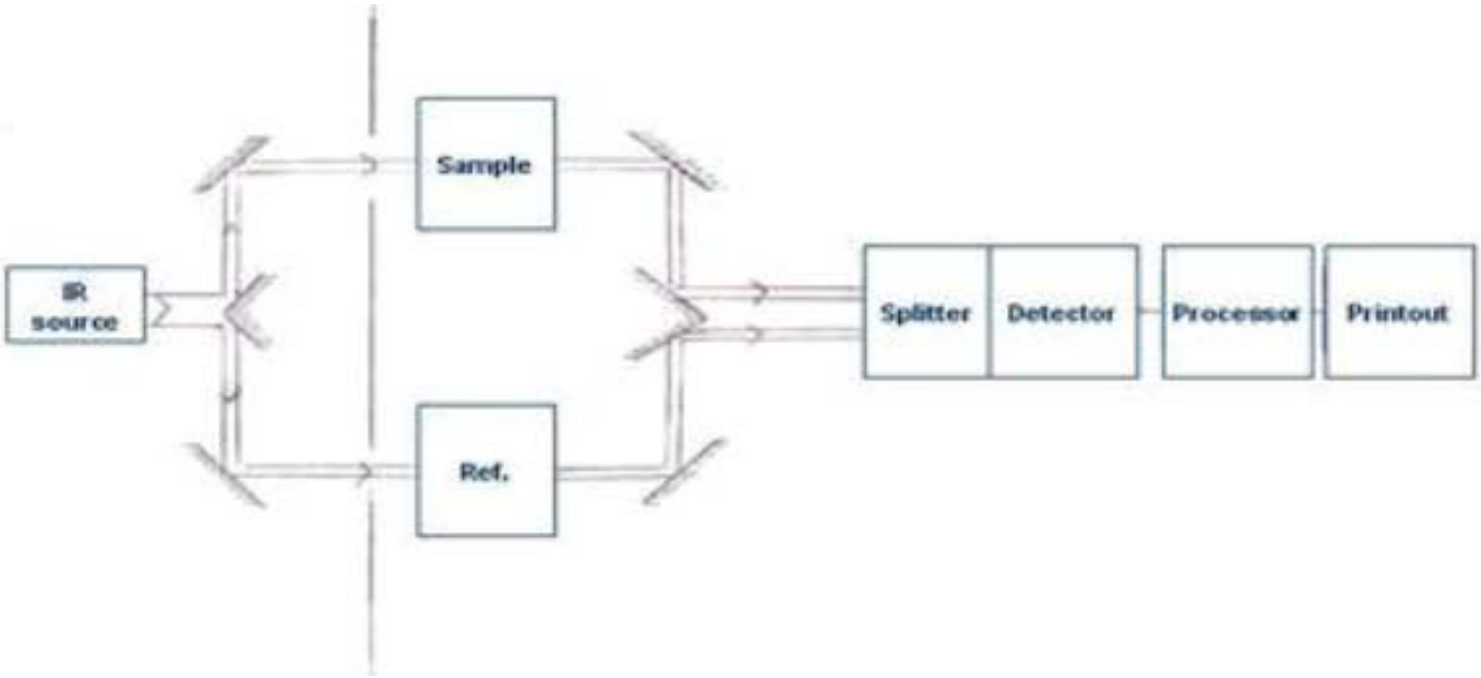
Solid samples can be prepared in two major ways. The first is to crush the sample with a mulling agent (usually nujol) in a marble or agate mortar, with a pestle. A thin film of the mull is applied onto salt plates and measured. The second method is to grind a quantity of the sample with a specially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

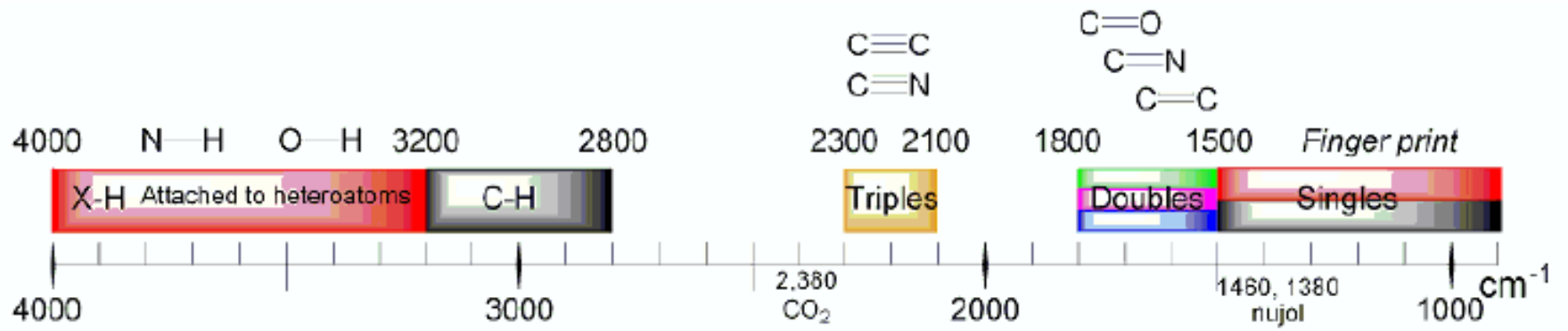
Typical method



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)



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 v(^{16}O-^{16}O) and v(^{18}O-^{18}O) respectively.

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

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

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

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

(mi 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).

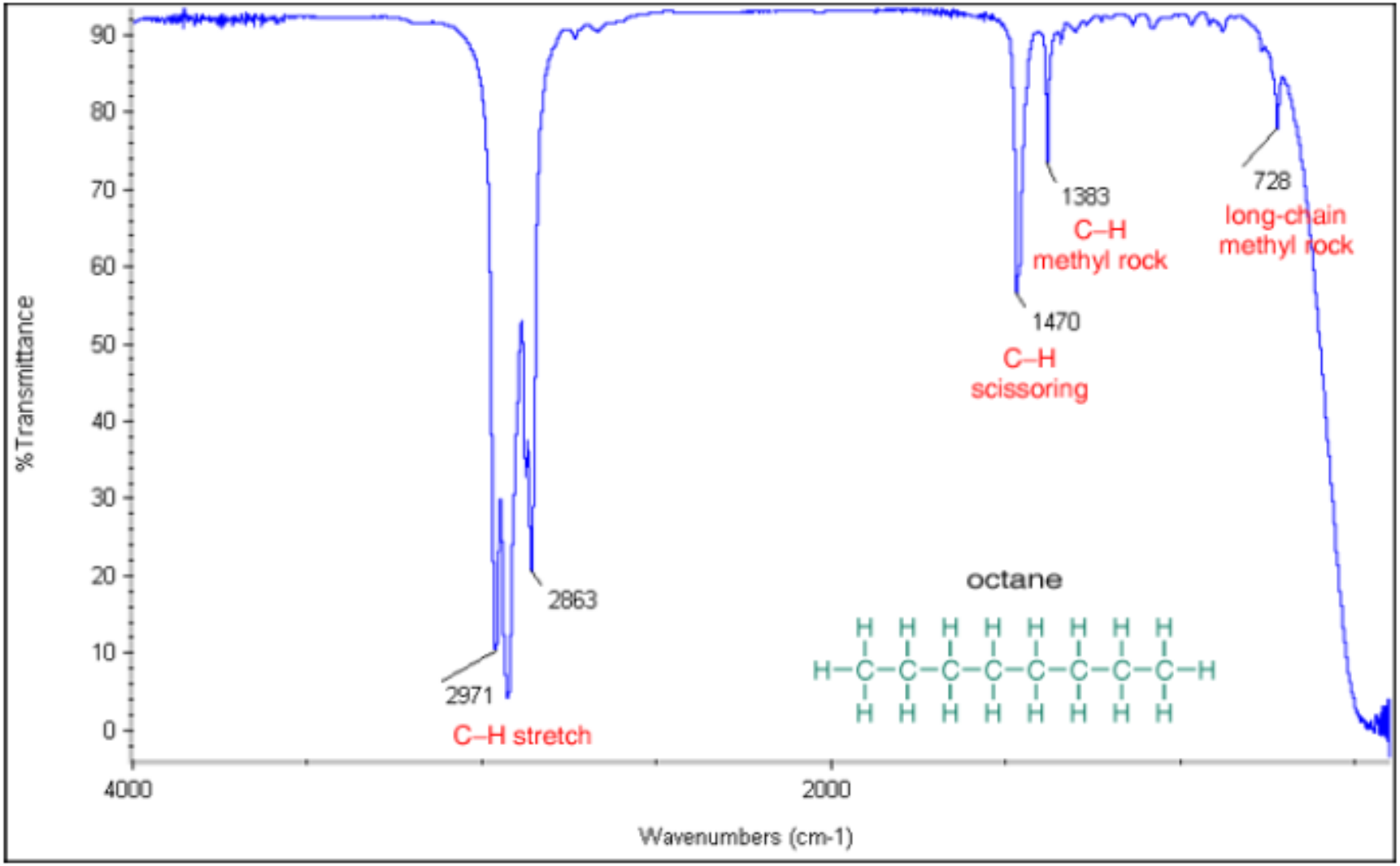
IR Spectroscopy Tutorial: Alkanes

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.


% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
2971
C–H stretch
2863
1470
C–H
scissoring
1383
C–H
methyl rock
728
long-chain
methyl rock
octane

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.

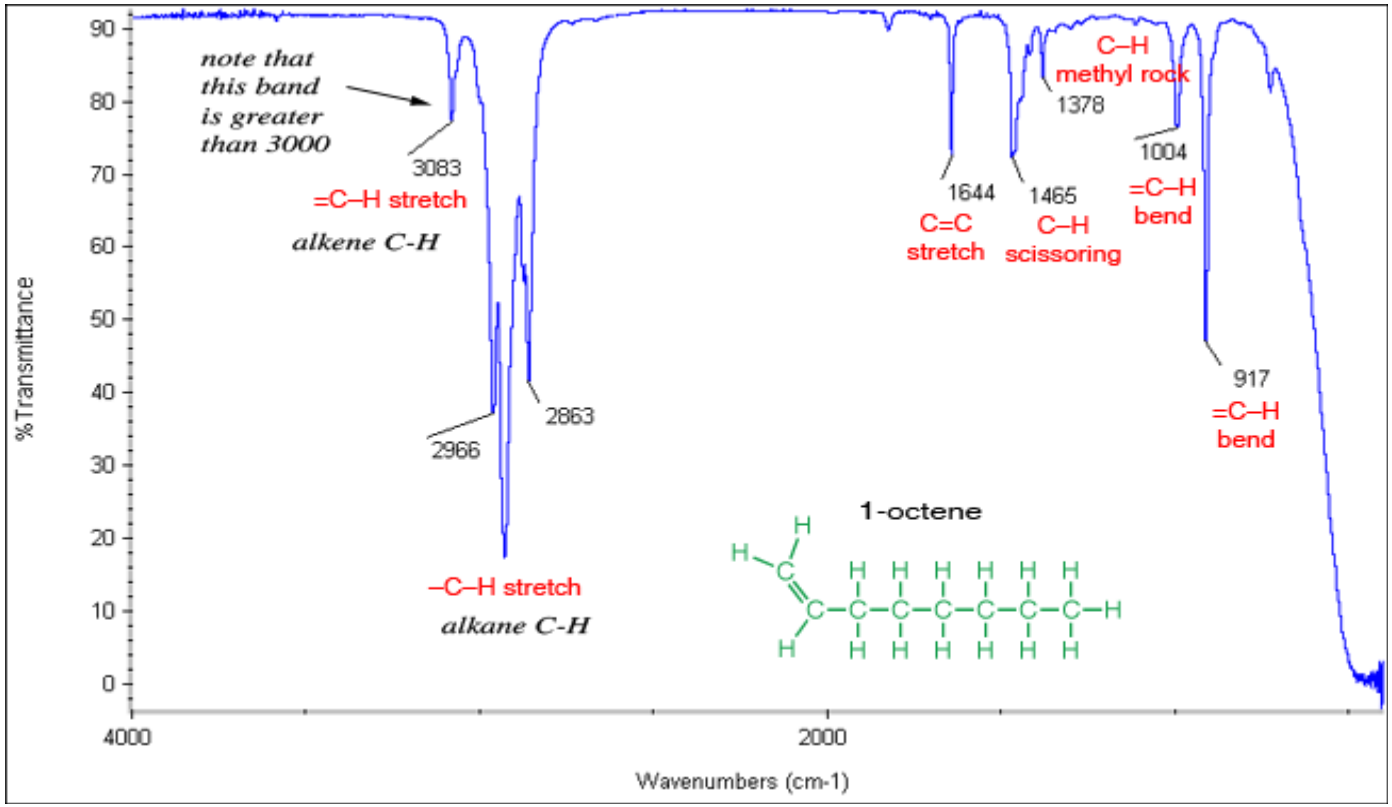
This is a very useful tool for interpreting IR spectra: Only alkenes and aromatics show a C-H stretch slightly higher than 3000 cm-1.

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).

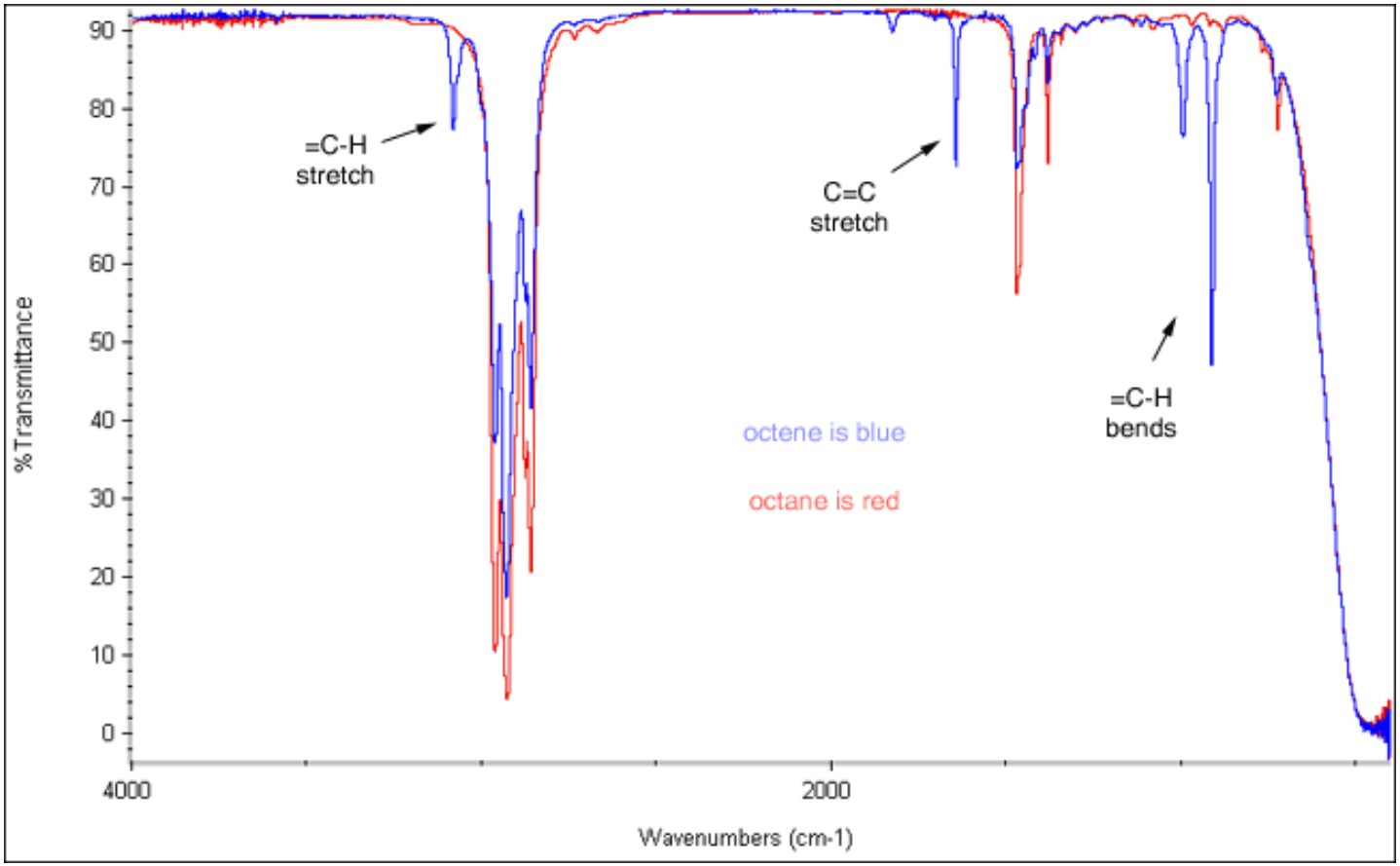
Summary:

- ❑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.

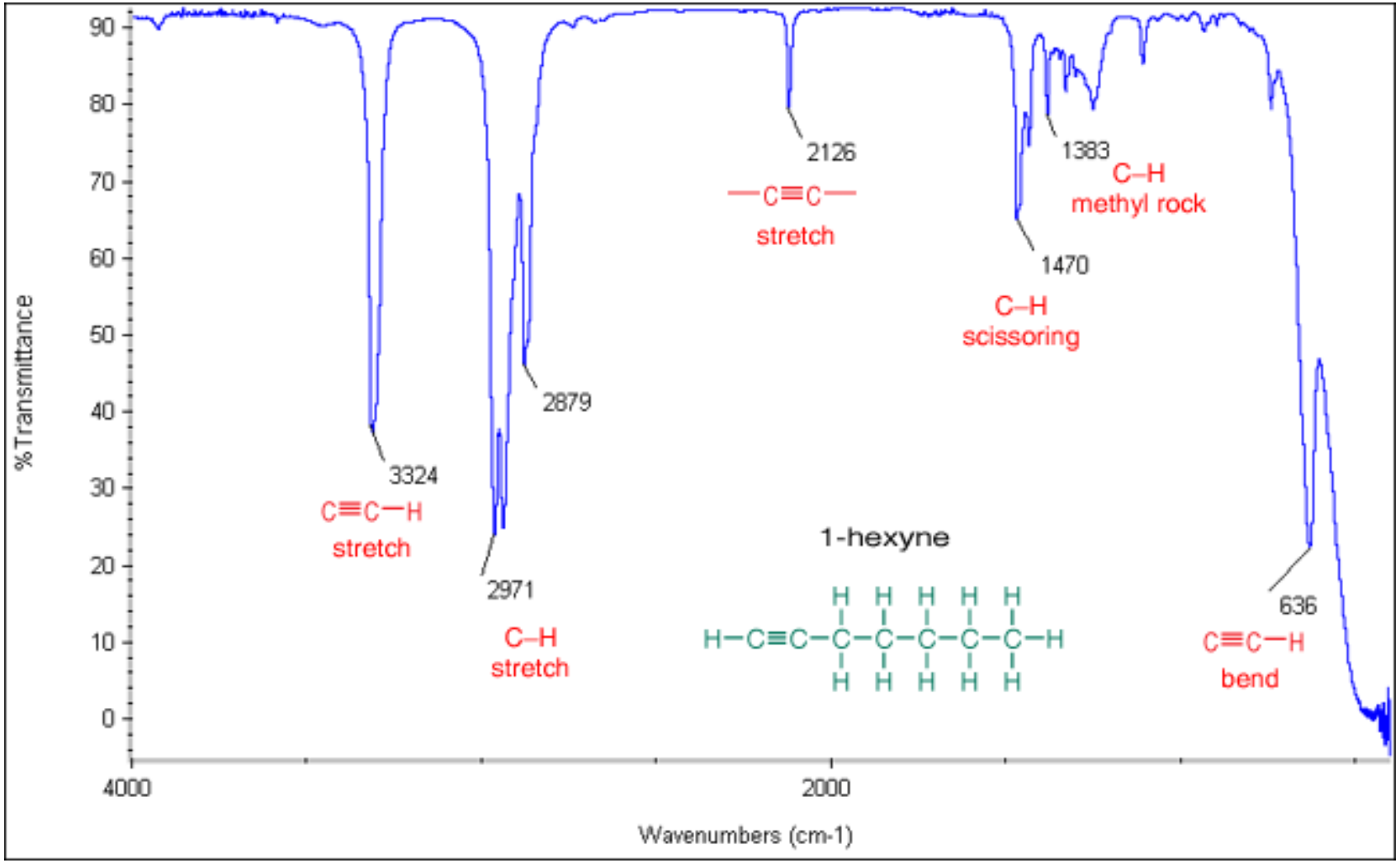
A terminal alkyne (but not an internal alkyne) will show a C-H stretch as a strong, narrow band in the range 3330-3270 cm-1. (Often this band is indistinguishable from bands resulting from other functional groups on the same molecule which absorb in this region, such as the O-H stretch.)

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.


% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
3324
C≡C—H
stretch
2971
C–H
stretch
2879
2126
—C≡C—
stretch
1470
C–H
scissoring
1383
C–H
methyl rock
636
C≡C—H
bend
1-hexyne
H—C≡C—C—C—C—C—C—H

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)

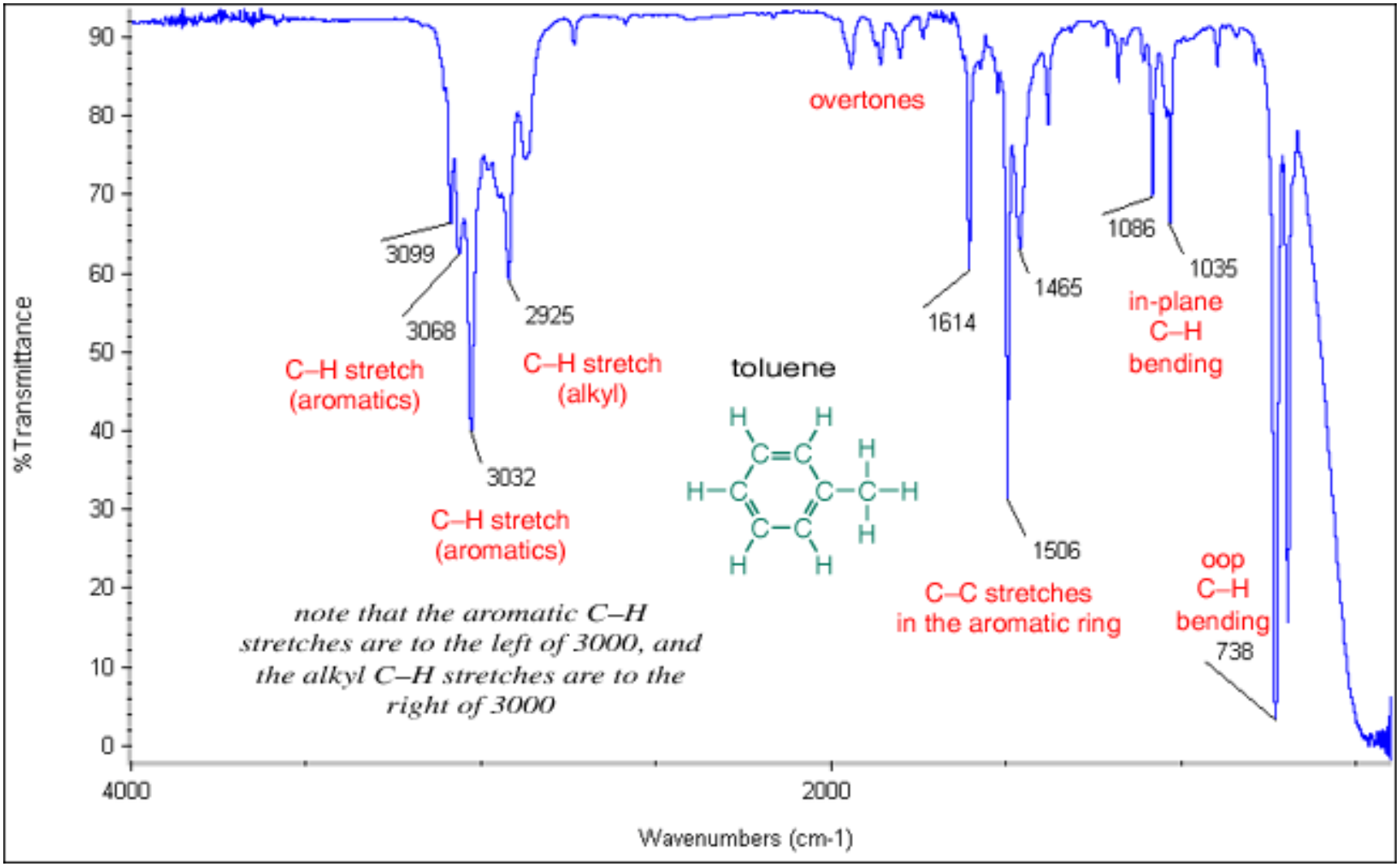
Not only do these bands distinguish aromatics, but they can be useful if you want to determine the number and positions of substituents on the aromatic ring. The pattern of overtone bands in the region 2000-1665 cm-1 reflect the substitution pattern on the ring. The pattern of the oop C–H bending bands 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).

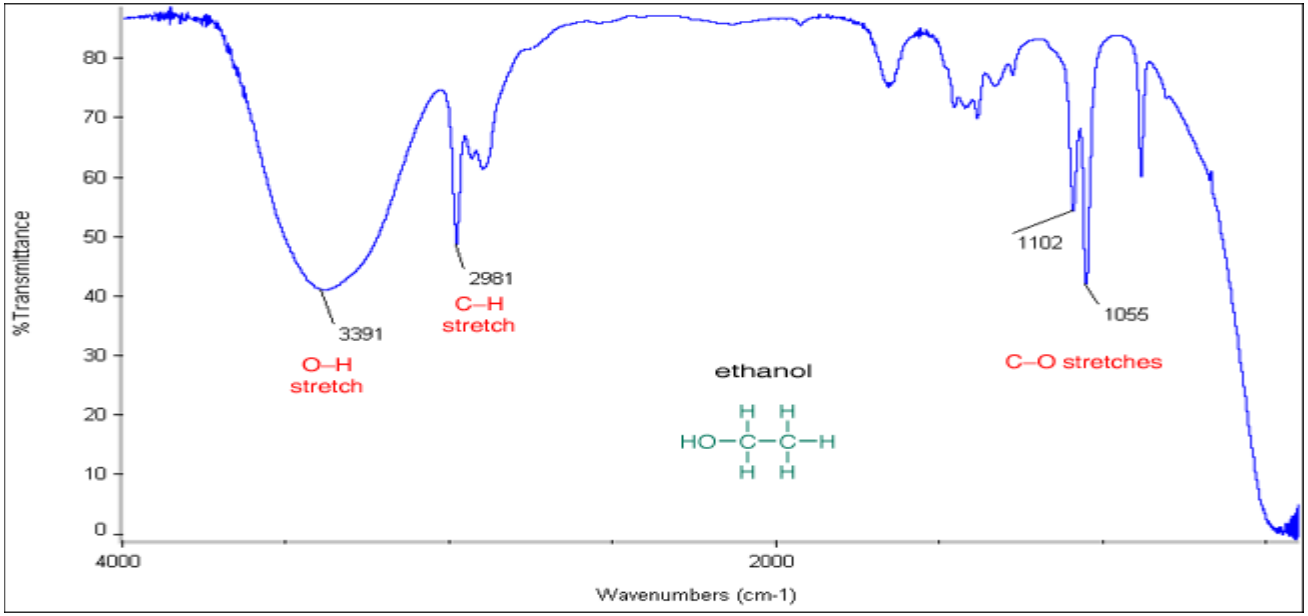

% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
3099
3068
3032
2925
C–H stretch
(aromatics)
C–H stretch
(alkyl)
C–H stretch
(aromatics)
overtones
1614
1506
1465
1086
1035
in-plane
C–H
bending
C–C stretches
in the aromatic ring
oop
C–H
bending
738
toluene
note that the aromatic C–H stretches are to the left of 3000, and the alkyl C–H stretches are to the right of 3000

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).



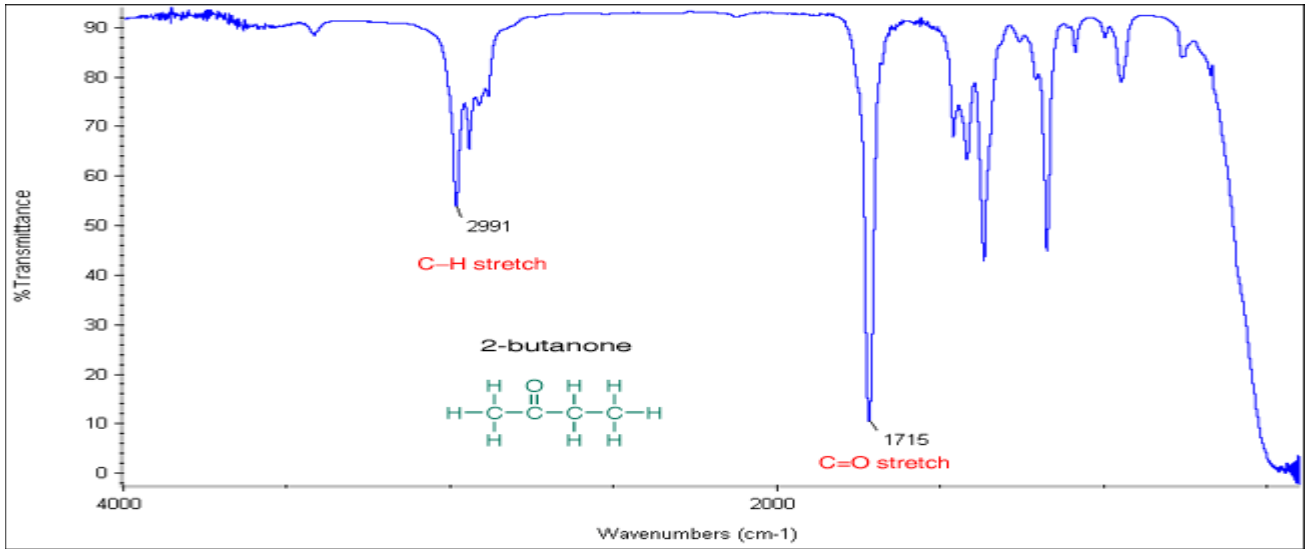
IR Spectroscopy Tutorial: Ketones

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

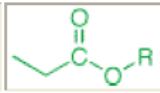
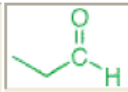
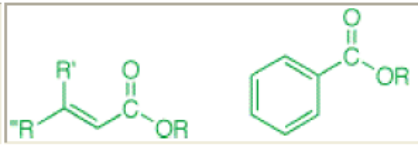
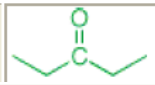
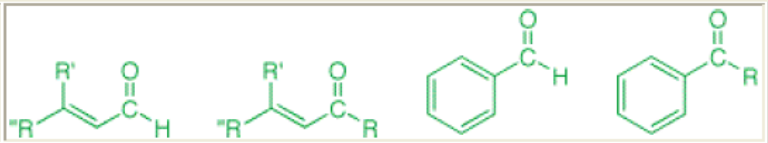
The spectrum of 2-butanone is shown below. This is a saturated ketone, and the C=O band appears at 1715. Note the C–H stretches (around 2991) of alkyl groups. It's usually not necessary to mark any of the bands in the fingerprint region (less than 1500 cm-1).



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.

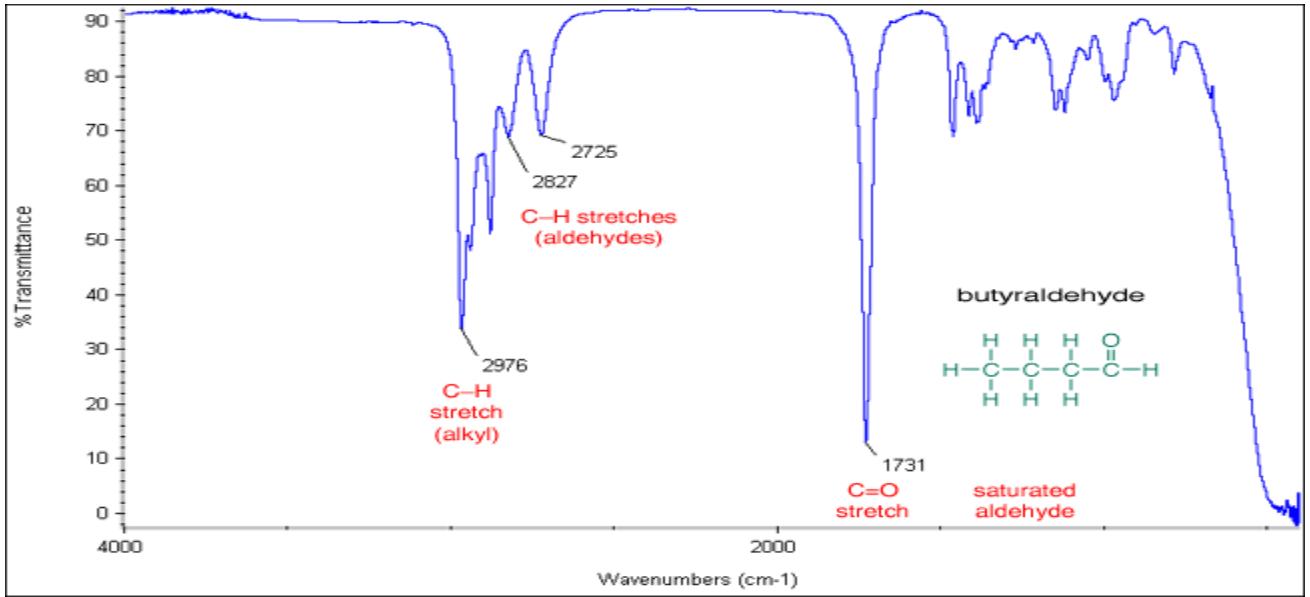
If you suspect a compound to be an aldehyde, always look for a peak around 2720 cm-1; it often appears as a shoulder-type peak just to the right of the alkyl C–H stretches.

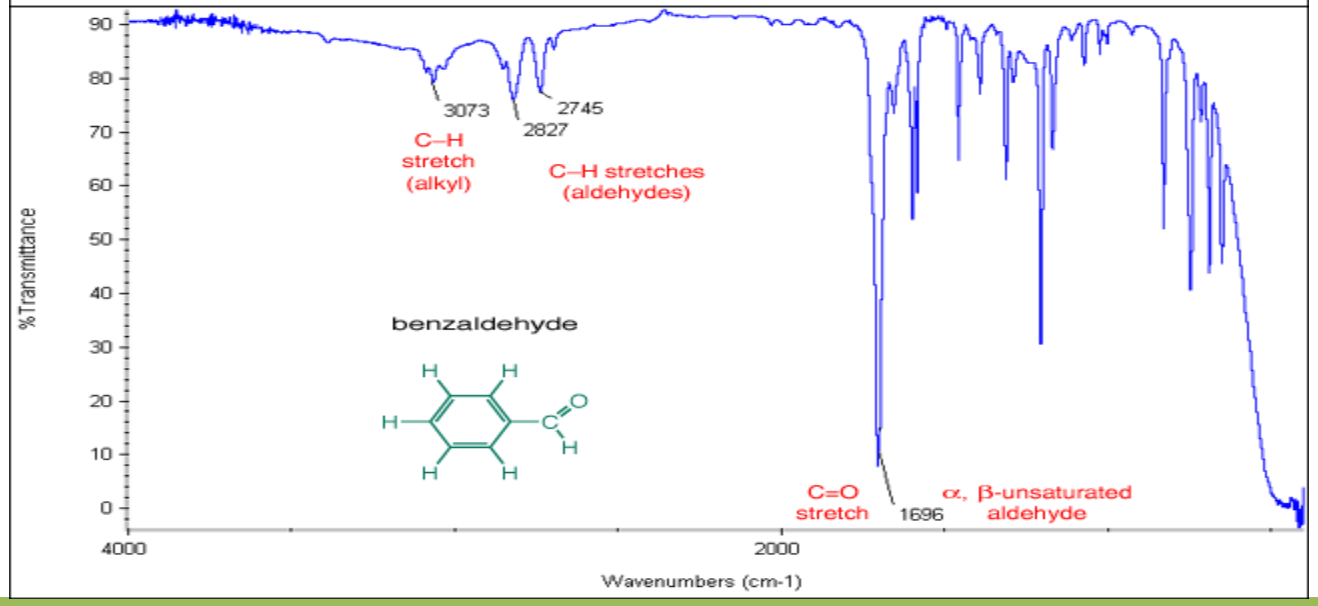
Summary:

- 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.


% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
2725
2827
C–H stretches
(aldehydes)
2976
C–H
stretch
(alkyl)
1731
C=O
stretch
saturated
aldehyde
butyraldehyde


% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
3073
2827
2745
C–H
stretch
(alkyl)
C–H stretches
(aldehydes)
benzaldehyde
C=O
stretch
1696
α, β-unsaturated
aldehyde

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.

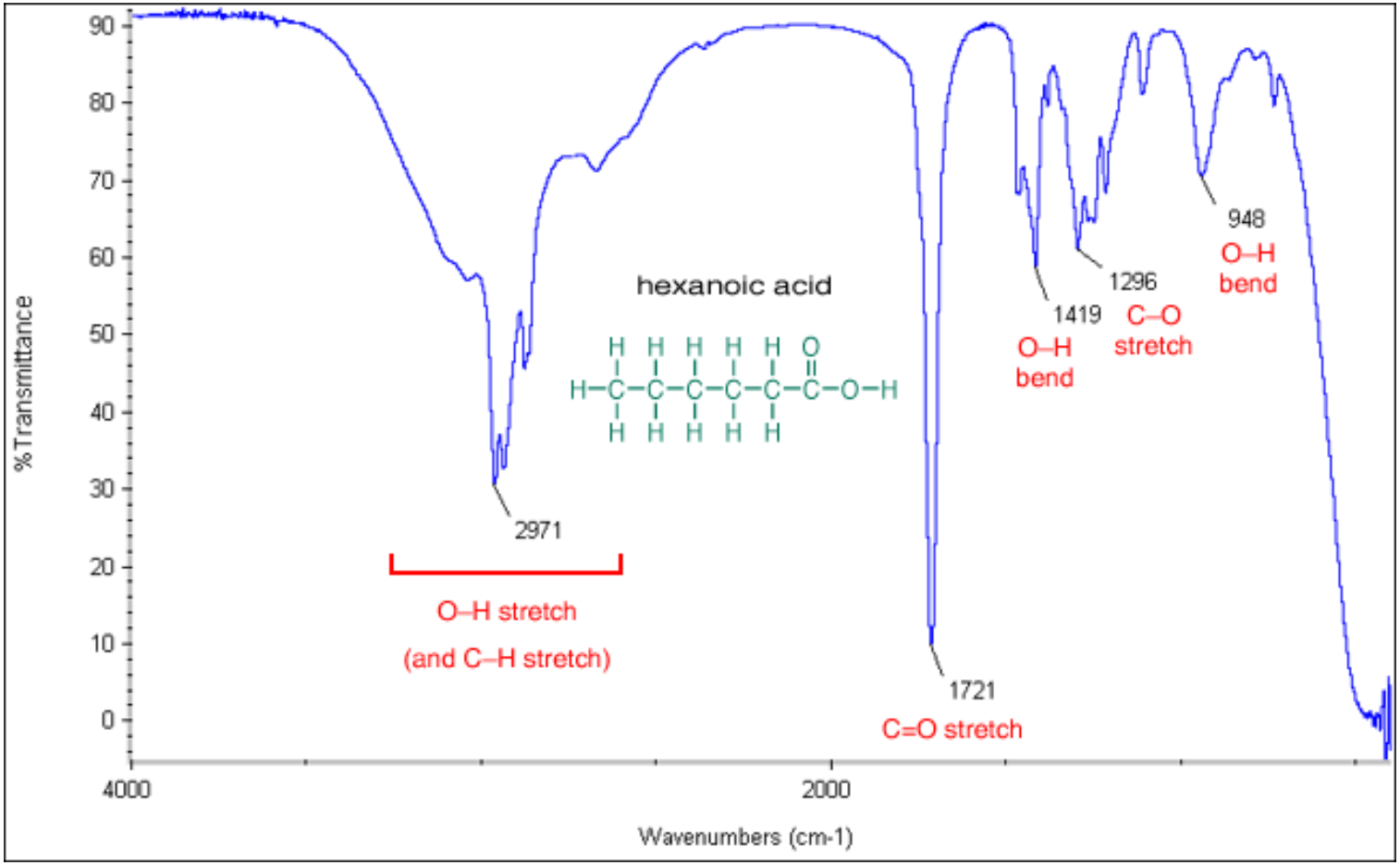
The carbonyl stretch C=O of a carboxylic acid appears as an intense band from 1760-1690 cm-1. The exact position of this broad band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen bonding.

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

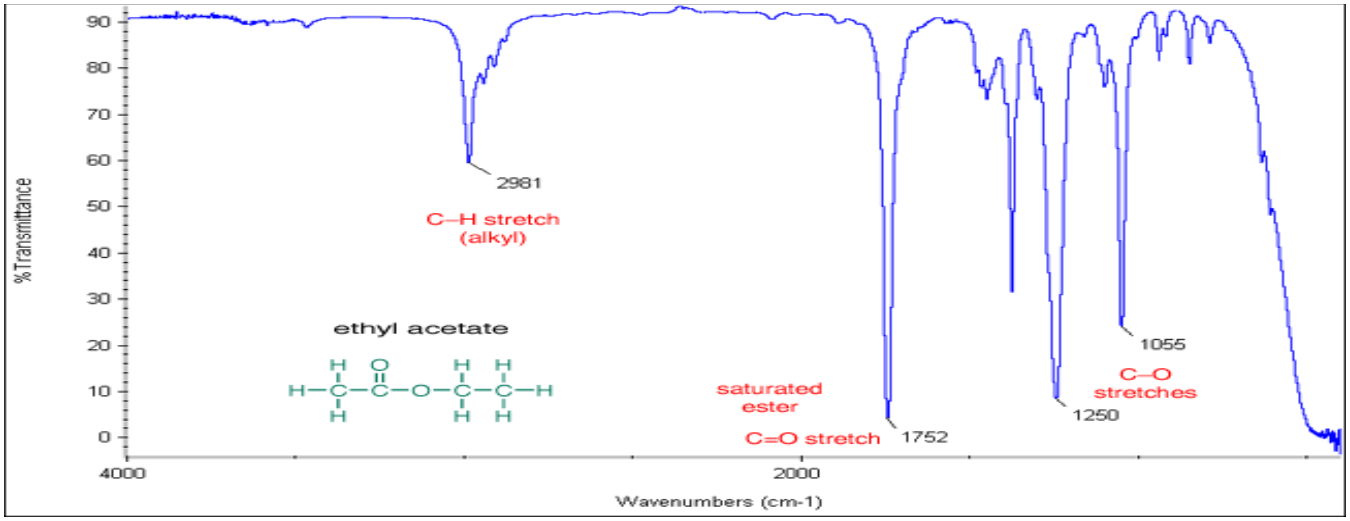
The carbonyl stretch C=O of aliphatic esters appears from 1750-1735 cm-1; that of α, β-unsaturated esters appears from 1730-1715 cm-1.

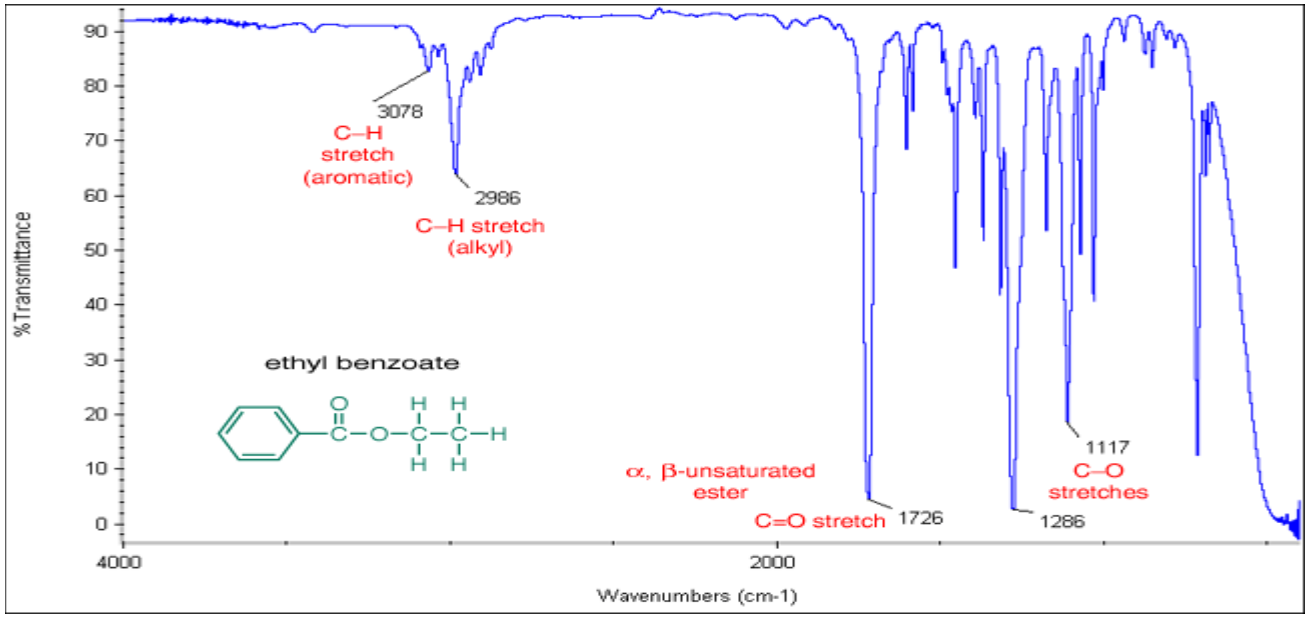
The C–O stretches appear as two or more bands in the region 1300-1000 cm-1.

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.


% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
2981
C–H stretch
(alkyl)
ethyl acetate
saturated
ester
C=O stretch
1752
1250
1055
C–O
stretches


% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
3078
C–H
stretch
(aromatic)
2986
C–H stretch
(alkyl)
ethyl benzoate
α, β-unsaturated
ester
C=O stretch
1726
1286
1117
C–O
stretches

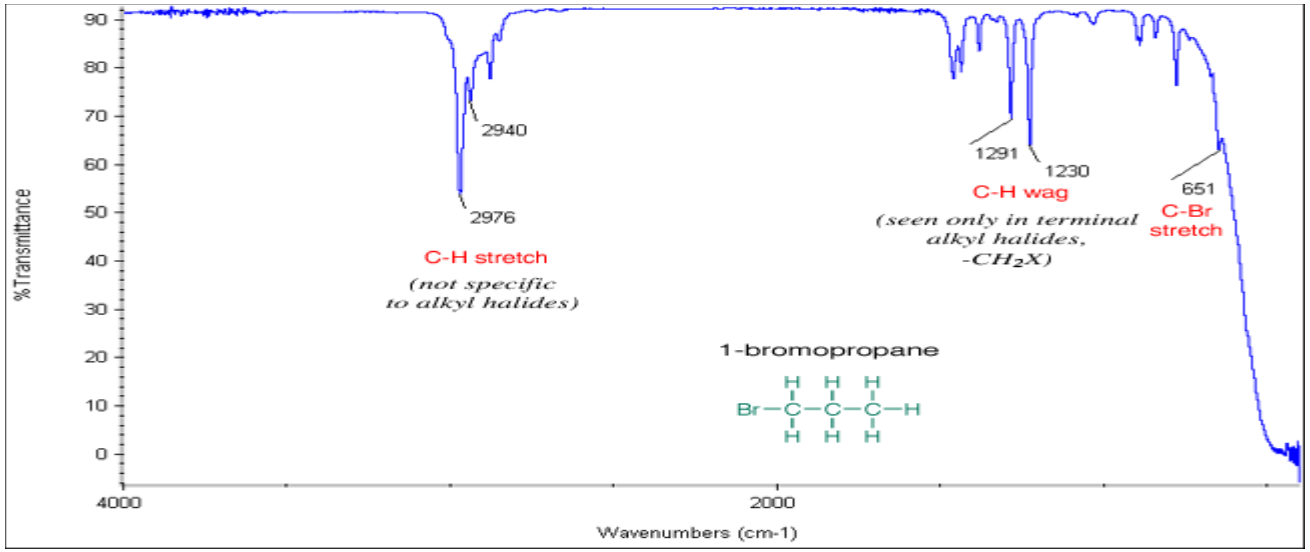
IR Spectroscopy Tutorial: Alkyl Halides

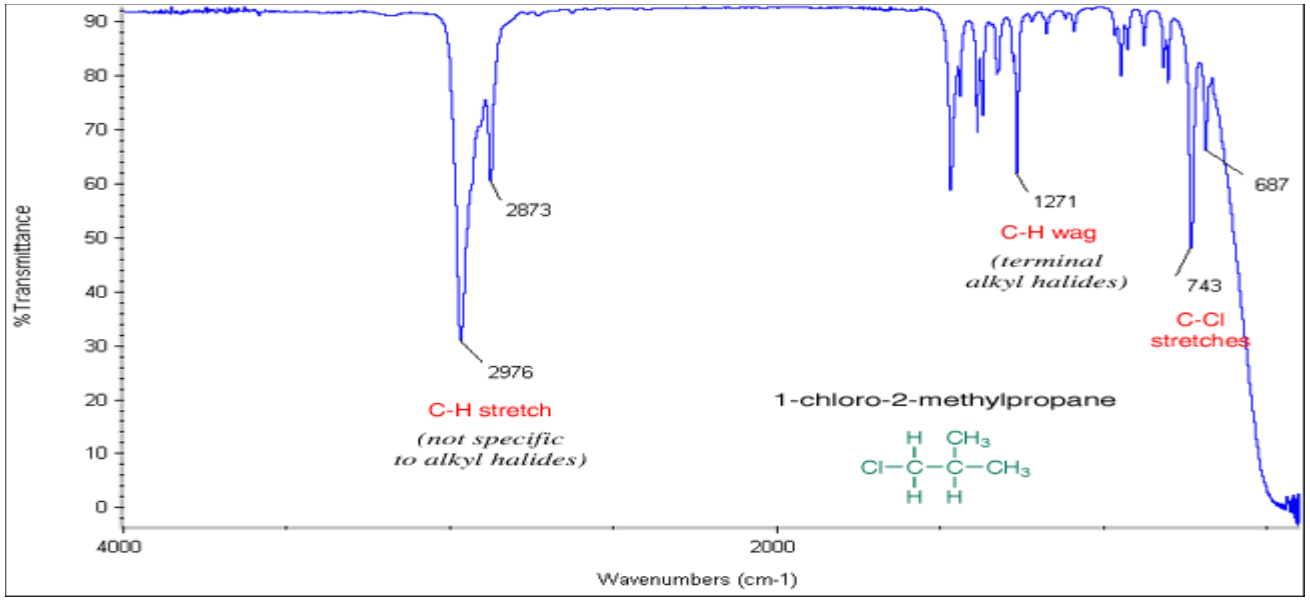
Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorene, or iodine (usually Br or Cl in the organic chemistry teaching labs). In general, C–X vibration frequencies appear in the region 850-515 cm-1, sometimes out of the range of typical IR instrumentation. 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 –CH2X 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:

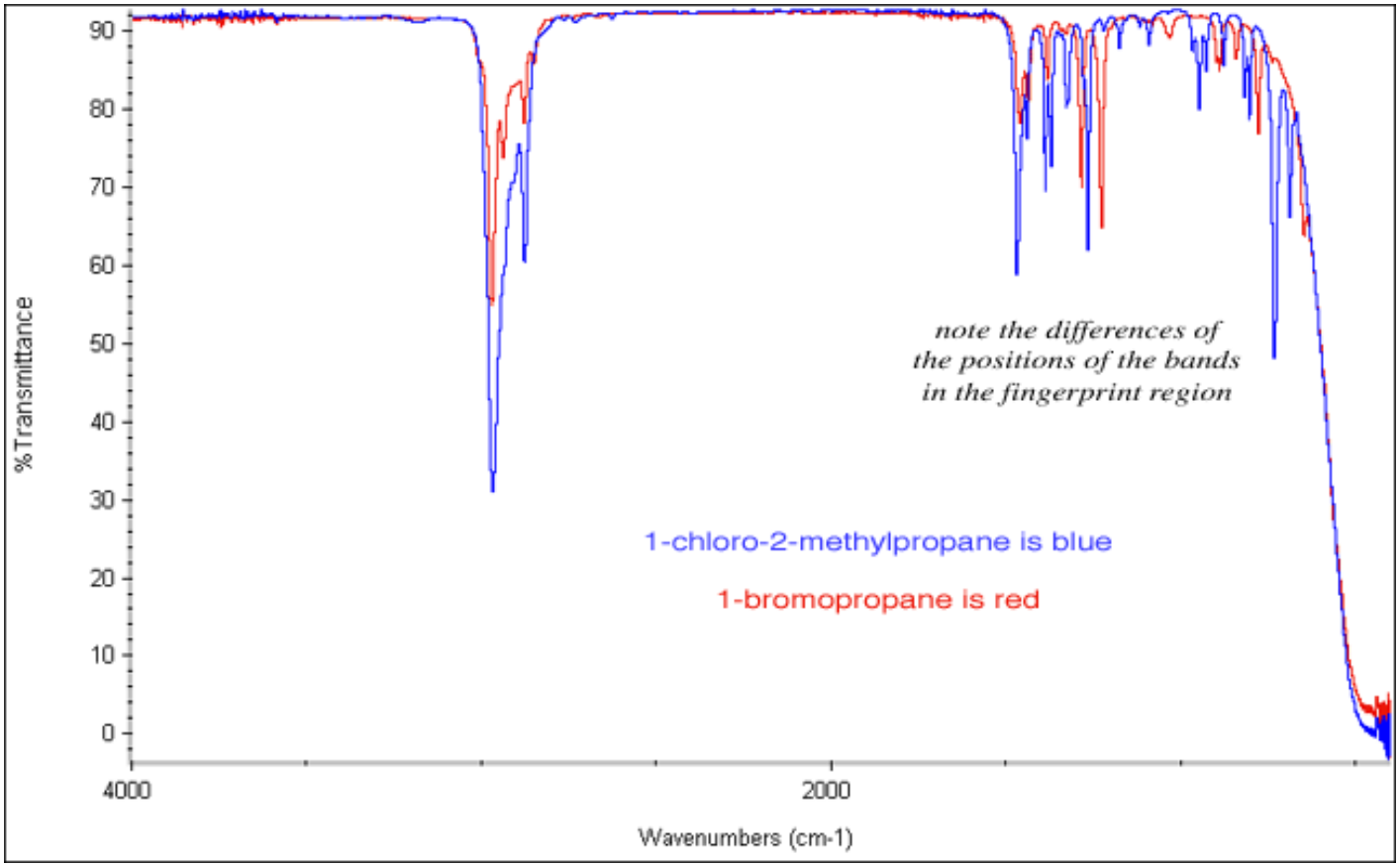
- ❑ C–H wag (-CH2X) from 1300-1150 cm-1
- ❑C–X stretches (general) from 850-515 cm-1
- ❑ o C–Cl stretch 850-550 cm-1
- ❑ o C–Br stretch 690-515 cm-1

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.


%Transmittance
Wavenumbers (cm-1)
2940
2976
C-H stretch
(not specific to alkyl halides)
1291
1230
C-H wag
(seen only in terminal alkyl halides, -CH2X)
651
C-Br stretch
1-bromopropane
Br—C—C—C—H


%Transmittance
Wavenumbers (cm-1)
2873
2976
C-H stretch
(not specific to alkyl halides)
1271
C-H wag
(terminal alkyl halides)
743
687
C-Cl stretches
1-chloro-2-methylpropane
Cl—C—C—CH3

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.)



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 (RNH2), there are two bands in this region, the asymmetrical N–H stretch and the symmetrical N–H stretch.

Secondary amines (R2NH) show only a single weak band in the 3300-3000 cm-1 region, since they have only one N–H bond. Tertiary amines (R3N) 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.)

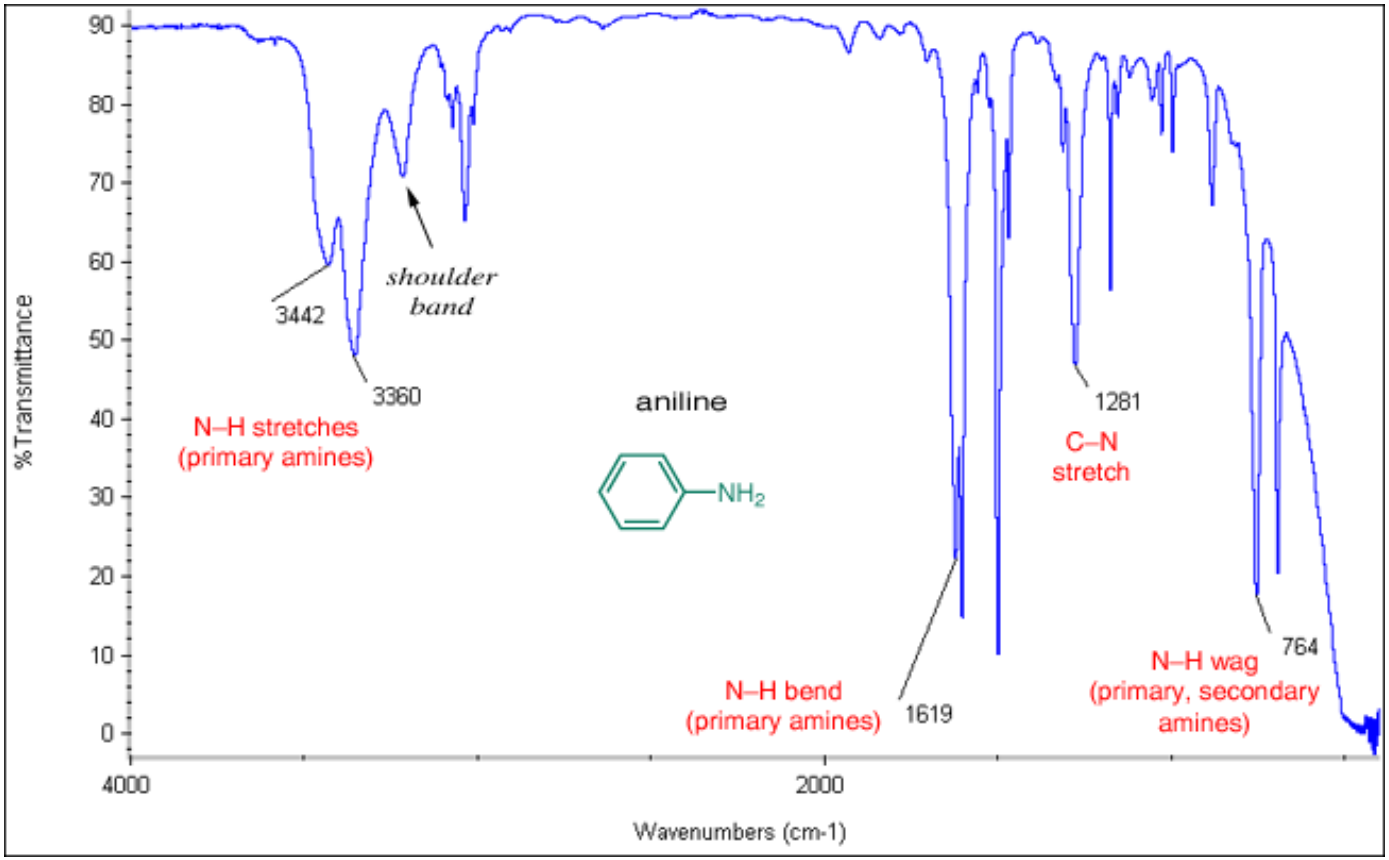
Another band attributed to amines is observed in the region 910-665 cm-1. This strong, broad band is due to N–H wag and observed only for primary and secondary amines.

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.

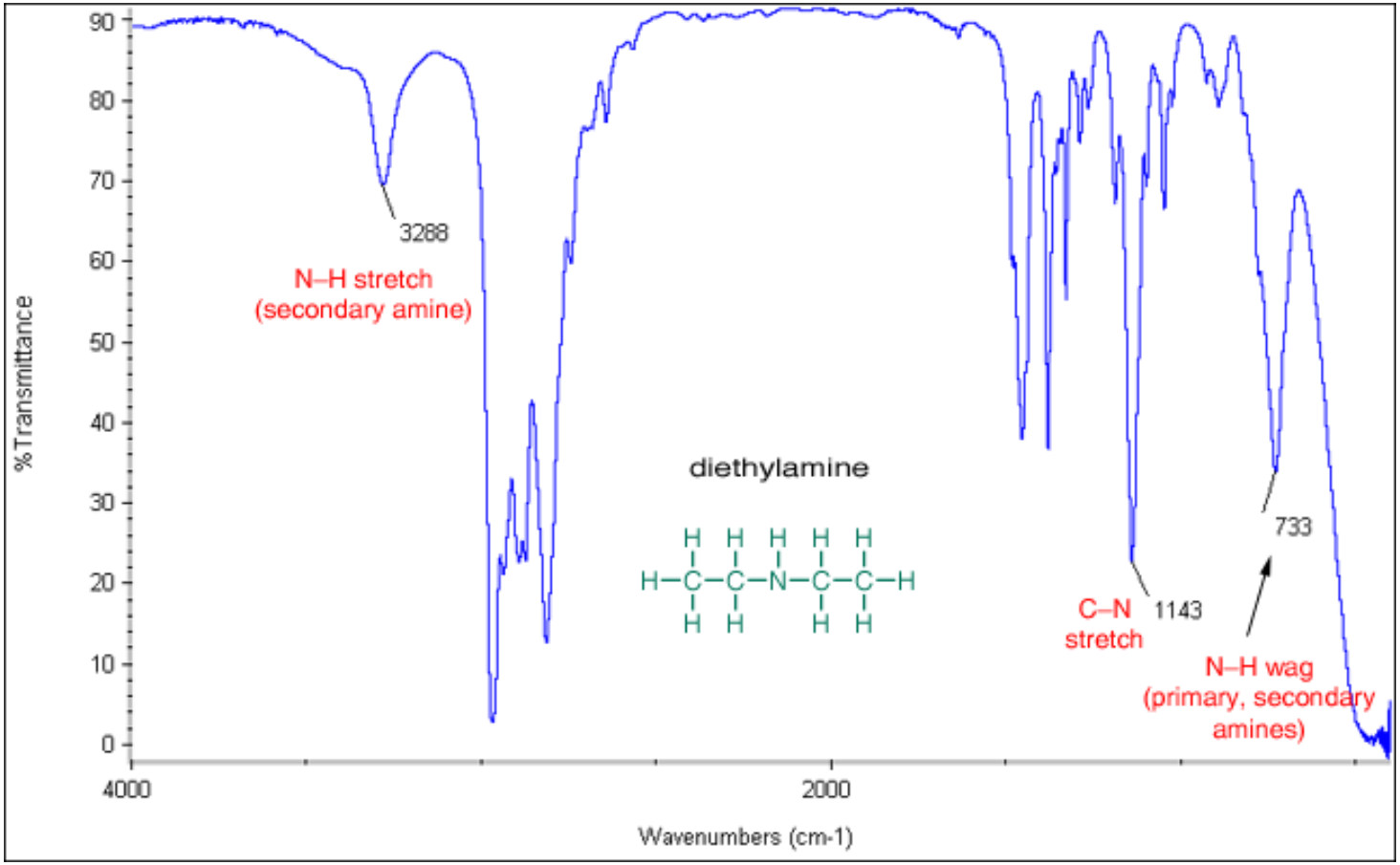
Summary:

- 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

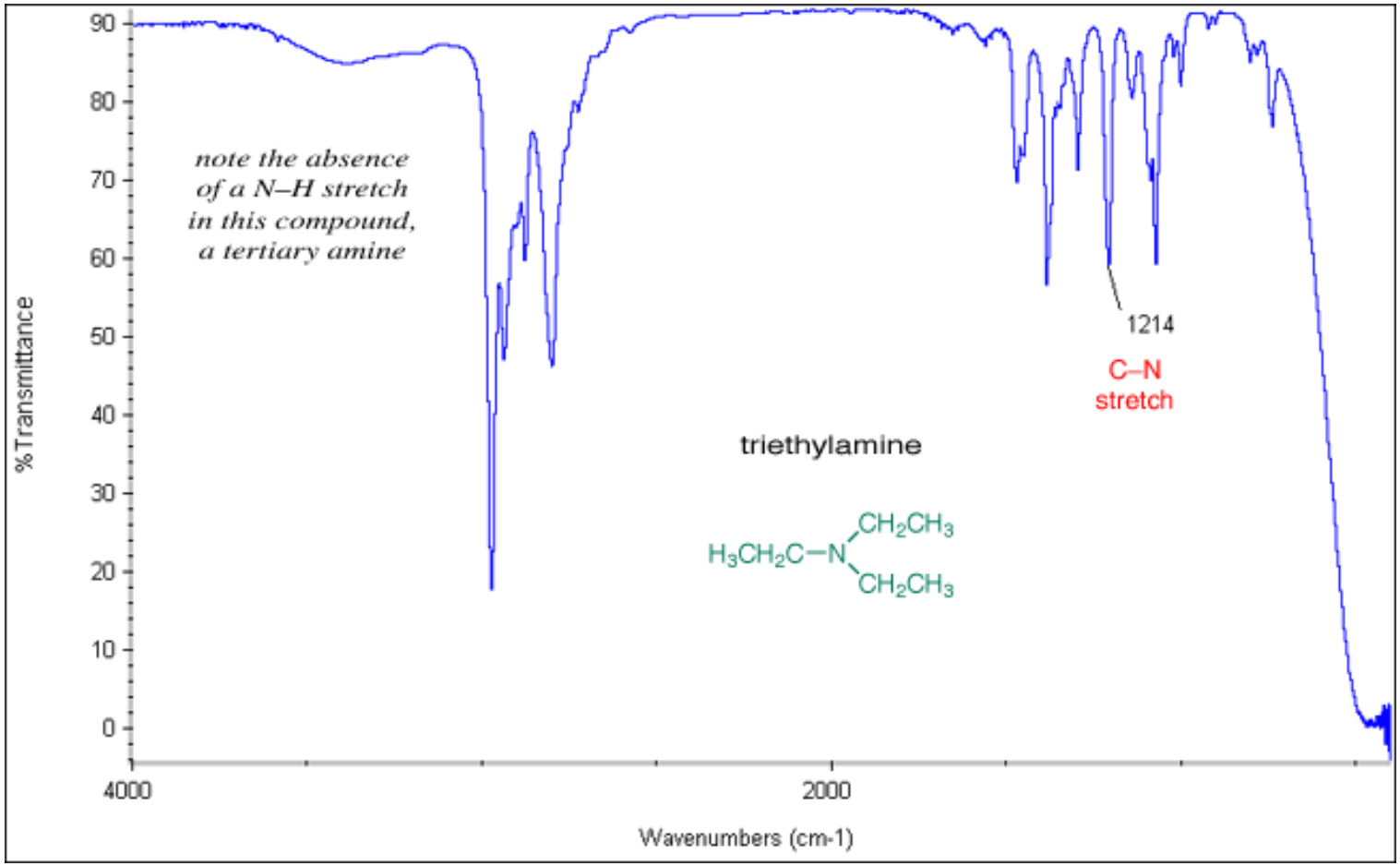
The spectrum of aniline is shown below. This primary amine shows two N–H stretches (3442, 3360); note the shoulder band, which is an overtone of the N–H bending vibration. The C–N stretch appears at 1281 rather than at lower wavenumbers because aniline is an aromatic compound. Also note the N–H bend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



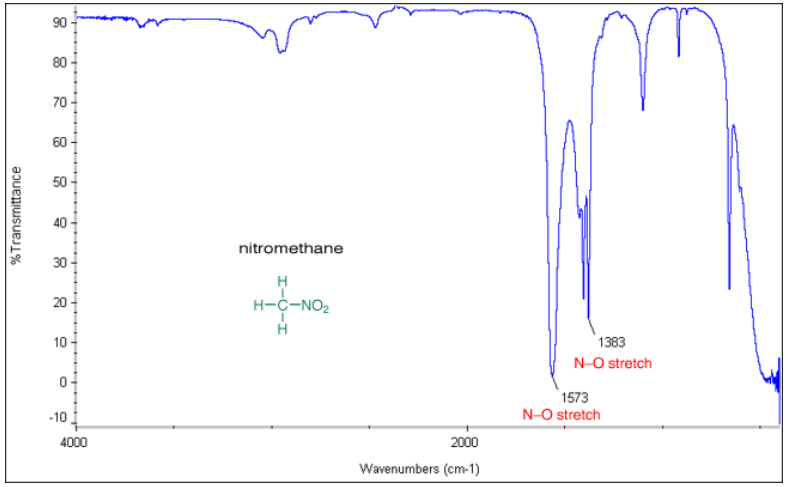
IR Spectroscopy Tutorial: Nitro Groups

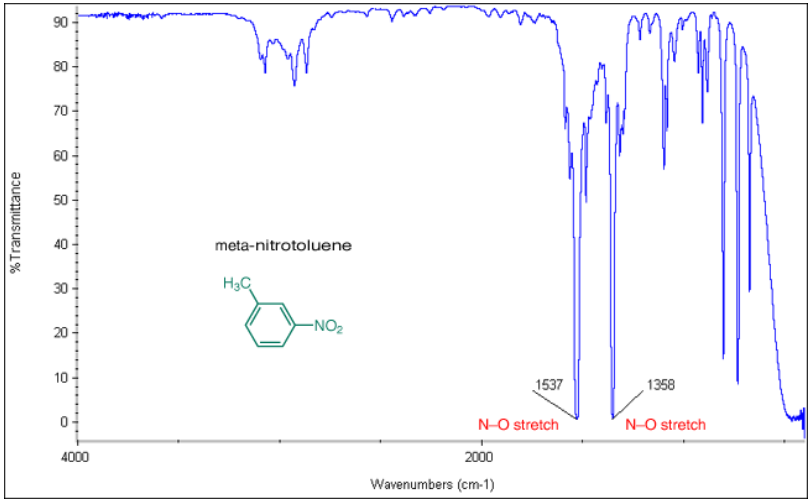
The N–O stretching vibrations in nitroalkanes occur near 1550 cm-1 (asymmetrical) and 1365 cm-1 (symmetrical), the band at 1550 cm-1 being the stronger of the two. If the nitro group is attached to an aromatic ring, the N–O stretching bands shift to down to slightly lower wavenumbers: 1550-1475 cm-1 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

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.

THANK YOU