Spectroscopy and the Electromagnetic Spectrum
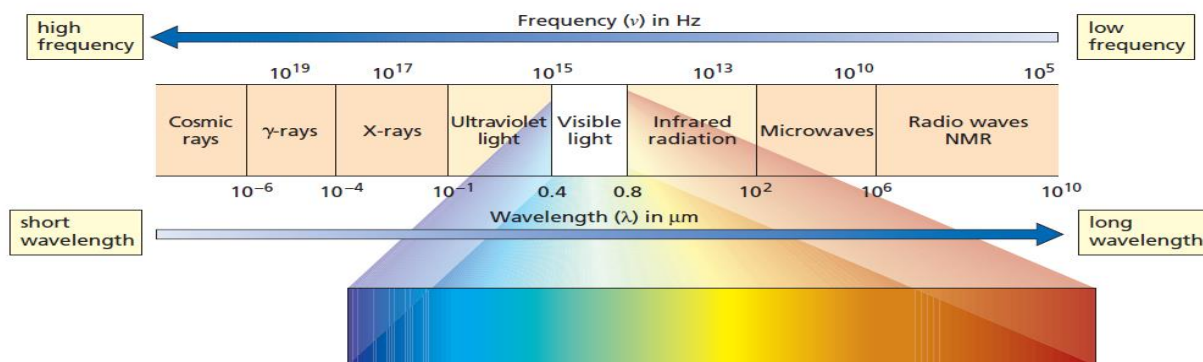
Spectroscopy used as a necessary tool for structure determination.

Spectroscopy is the study of the interaction of matter and electromagnetic radiation.

Electromagnetic radiation is a form of energy. The light that we see is a very small part of the entire electromagnetic spectrum. Electromagnetic radiation is different from sound in that it can travel in space and does not need a medium like air or water to travel through. Electromagnetic radiation is made when an atom absorbs energy. The absorbed energy causes one or more electrons to change their place within the atom. When the electron returns to its original position, an electromagnetic wave is produced. Depending on the kind of atom and the amount of energy, this electromagnetic radiation can take the form of heat, light, ultraviolet, or other electromagnetic waves.

There are different types of electromagnetic radiation—each type associated with a particular energy range—constitutes the electromagnetic spectrum.

Short wavelenths have high frequencies, and long wavelengths have low frequencies.

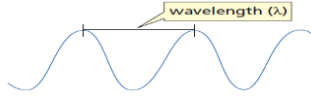| high frequency				Frequency (v) in Hz					low frequency
	10^{19}	10^{17}		10^{15}		10^{13}	10^{10}	10^5	
	Cosmic rays	γ-rays	X-rays	Ultraviolet light	Visible light	Infrared radiation	Microwaves	Radio waves NMR	
	10^{-6}	10^{-4}		10^{-1}	0.4 0.8	10^2	10^6	10^{10}	
short wavelength				Wavelength (λ) in μm					long wavelength

Each of the spectroscopic techniques used to identify organic compounds employs a different type of electromagnetic radiation. A particle of electromagnetic radiation is called a *photon*. We may think of electromagnetic radiation as photons traveling at the speed of light. Each type of electromagnetic radiation is characterized by either its frequency (v) or its wavelength (λ) or wavenumbers ($\acute{v}$).

Frequency (v) is defined as the number of waves which can pass through a point in one second, measured in cycles per second (cps) or hertz (Hz) (1Hz= 1 cps).

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Wavelength is the distance from any point on one wave to the corresponding point on the next wave. Wavelength is generally measured in micrometers or nanometers. One micrometer (μ) is 10^{-6} m ; one nanometer (nm) is 10^{-9} m.

The frequency of electromagnetic radiation, therefore, is equal to the speed of light (c) divided by the radiation's wavelength:

$$\nu = \frac{c}{\lambda} \qquad c = 3 \times 10^{10}\,\text{cm/s} \qquad E = h\nu = \frac{hc}{\lambda}$$

wavelength (λ)

The relationship between the energy (E) of a photon and the frequency (or the wavelength) of the electromagnetic radiation is described by the equation, where h is the Proportionality constant called *Planck's constant*, named after the German physicist who discovered the relationship.

Wavenumber ($\tilde{\nu}$) is another way to describe the *frequency* of electromagnetic radiation, and the one most often used in infrared spectroscopy. It is the number of waves in one centimeter, so it has units of reciprocal centimeters (cm^{-1}). Scientists use wavenumbers in preference to wavelengths because, unlike wavelengths, wavenumbers are directly proportional to energy. The relationship between wavenumber (in cm^{-1}) and wavelength (in μm) is given by the equation below. So high frequencies, large wavenumbers, and short wavelengths are associated with high energy.

$$\tilde{\nu}(\text{cm}^{-1}) = \frac{10^4}{\lambda(\mu\text{m})} \qquad (\text{because } 1\,\mu\text{m} = 10^{-4}\,\text{cm})$$

TYPES OF ENERGY TRANSITIONS IN EACH REGION OF THE ELECTROMAGNETIC SPECTRUM

Region of Spectrum	Energy Transitions
X-rays	Bond breaking
Ultraviolet/visible	Electronic
Infrared	Vibrational
Microwave	Rotational
Radiofrequencies	Nuclear spin (nuclear magnetic resonance) Electronic spin (electron spin resonance)

Infrared Spectroscopy

Infrared(IR) spectroscopy deals with the infrared region of the electromagnetic spectrum, with a longer wavelength and lower frequency than visible light.
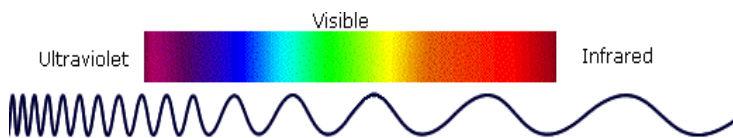
It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it is useful for analysis of organic compounds. The infrared portion of the electromagnetic spectrum is usually divided into **three regions**; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher energy near-IR, approximately $14000–4000$ cm^{-1} ($0.8–2.5$ μm wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately $4000–400$ cm^{-1} ($2.5–25$ μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately $400–10$ cm^{-1} ($25–1000$ μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.
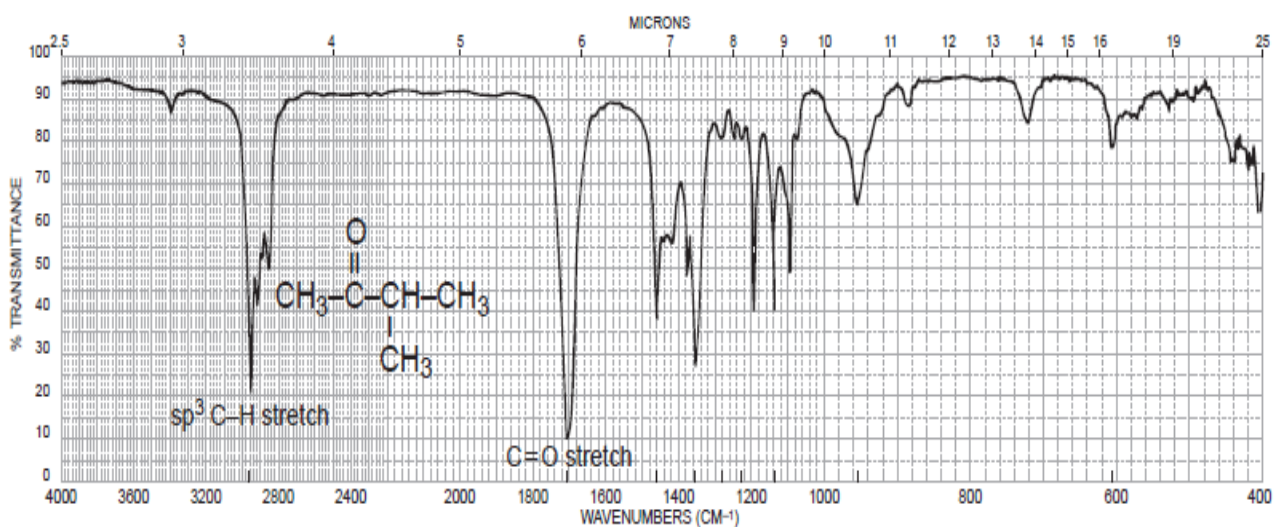
Principles of infrared spectroscopy

The energies associated with this part of the infrared (from 1 to15 kcal/mole) are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups.

It causes an excitation of molecule to higher vibrational level, the absorbing energy converts to molecular vibration and appears as bands rather than lines because a single vibrational change accompanied by a number of rotational energy changes.

The infrared spectra are considered as vibrational-rotational spectra. All bonds in a molecule are not capable of absorbing infrared energy but only those bonds which are accompanied by a change in dipole moment will absorb in the infrared region, called (infrared active).
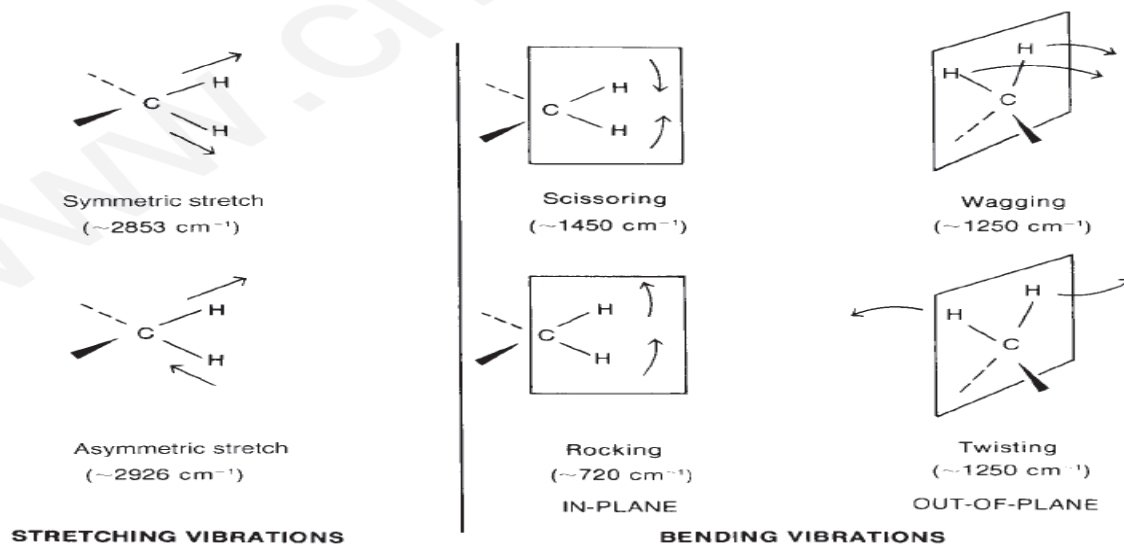
The simplest types, or **modes,** of vibrational motion in a molecule that are **infrared active** are the **stretching** and **bending** modes.
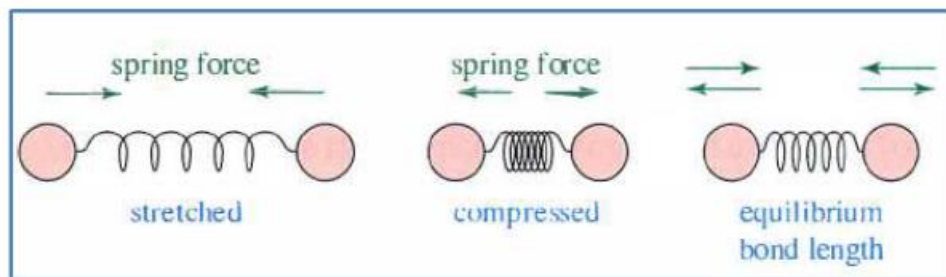
Two types of stretching symmetric and asymmetric, in general, asymmetric stretching vibrations occur at higher frequencies than symmetric stretching vibrations; also, stretching vibrations occur at higher frequencies than **bending vibrations**. The terms **scissoring, rocking, wagging,** and **twisting** are commonly used to describe the origins of infrared bands.

In stretching vibrations the bond length changes, or the distance between atoms increase and decreases but the bond angle remains unchanged. While in bending vibration the bond angle will changes.

In any group of three or more atoms, at least two of which are identical, there are *two* modes of stretching: symmetric and asymmetric. Examples of such groupings are $-CH_3$, $-CH_2-$, $-NO_2$, $-NH_2$, and anhydrides. While a secondary amine (R_2NH) has only one absorption peak. Amides exhibit similar bands. There are two strong N=O stretch peaks for a nitro group, with the symmetric stretch appearing at about 1350 cm^{-1} and the asymmetric stretch appearing at about 1550 cm^{-1}.


Symmetric stretch (~2853 cm^{-1})	Scissoring (~1450 cm^{-1})	Wagging (~1250 cm^{-1})
Asymmetric stretch (~2926 cm^{-1})	Rocking (~720 cm^{-1})	Twisting (~1250 cm^{-1})
	IN-PLANE	OUT-OF-PLANE
STRETCHING VIBRATIONS	**BENDING VIBRATIONS**	

	Symmetric Stretch	**Asymmetric Stretch**
Methyl	~2872 cm^{-1}	~2962 cm^{-1}
Anhydride	~1760 cm^{-1}	~1800 cm^{-1}
Amino	~3300 cm^{-1}	~3400 cm^{-1}
Nitro	~1350 cm^{-1}	~1550 cm^{-1}

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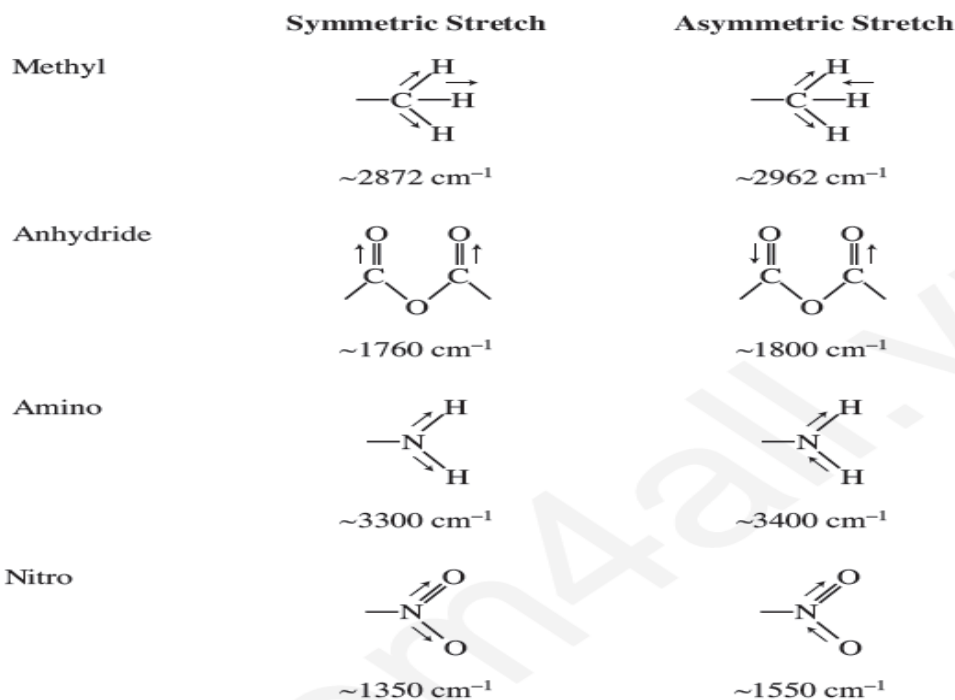
Vibrational above are called **fundamental absorptions** they arise from excitation from the ground state to the lowest-energy excited state. Usually, the spectrum is complicated because of the presence of weak **overtone, combination, and difference bands** which called **non-fundamental absorptions. Overtones** result from excitation from the ground state to higher energy states, which correspond to integral multiples of the frequency of the fundamental (n). For example, you might observe weak overtone bands at 2n, 3n. An absorption in the infrared at 500 cm^{-1} may well have an accompanying peak of lower intensity at 1000 cm^{-1} an overtone. **Combination band:** This band is the sum of the two interacting bands (v comb = v1+v2).

Difference bands: The observed frequency in this case results from the difference between the two interacting bands (v diff = v1 − v2).

Fermi resonance: When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called **Fermi resonance.**

Types of molecular vibrations
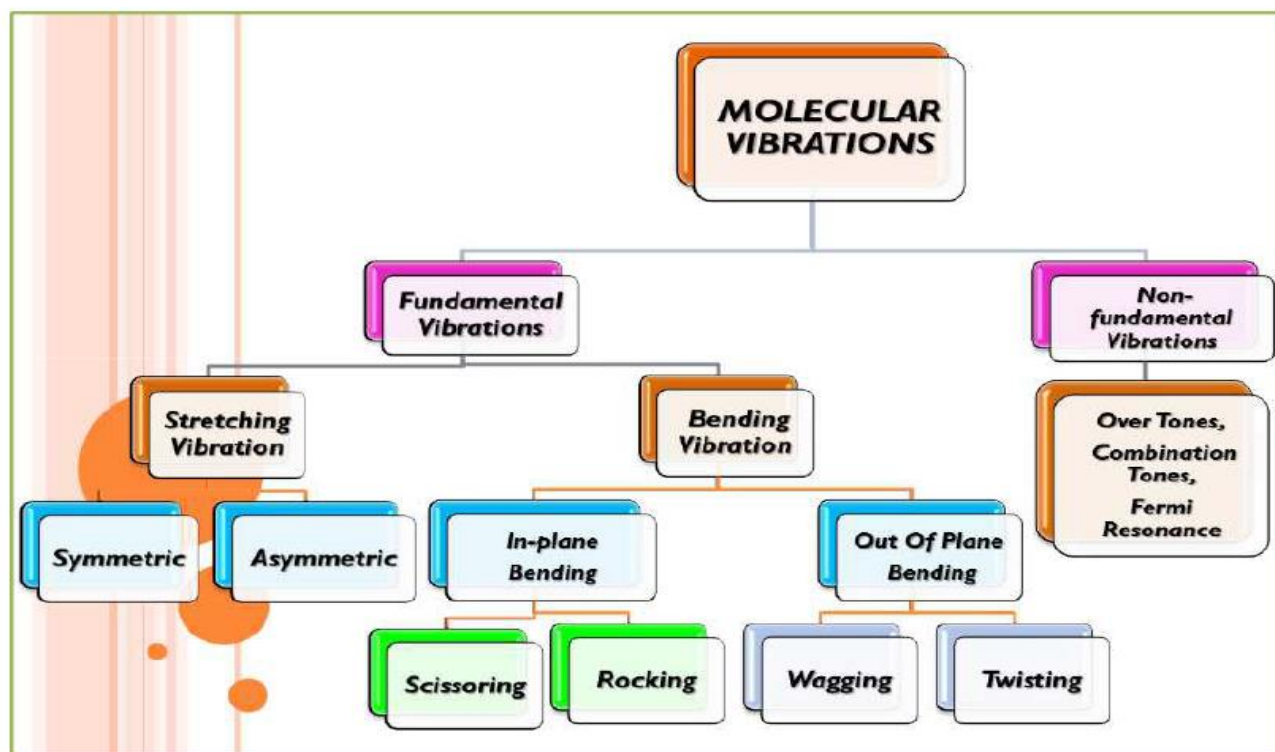
The Position of Absorption Bands

The amount of energy required to stretch a bond depends on the **strength** of the bond and the **masses** of the bonded atoms. The stronger the bond, the greater the energy required to stretch it, because a stronger bond corresponds to a tighter spring. The frequency of the vibration is inversely related to the mass of the atoms attached to the spring, so heavier atoms vibrate at lower frequencies.

The approximate wavenumber of absorption can be calculated from the following equation derived from **Hooke's law**, which describes the motion of a vibrating spring:

$$\overline{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$\overline{v}$ = frequency in cm^{-1}

c = velocity of light = 3×10^{10} cm/sec

K = force constant in dynes/cm

$\mu = \dfrac{m_1 m_2}{m_1 + m_2}$, masses of atoms in grams,

or $\dfrac{M_1 M_2}{(M_1 + M_2)(6.02 \times 10^{23})}$, masses of atoms in amu

Removing Avogadro's number (6.02×10^{23}) from the denominator of the reduced mass expression (μ) by taking its square root, we obtain the expression

$$\overline{v} = \frac{7.76 \times 10^{11}}{2\pi c} \sqrt{\frac{K}{\mu}}$$

A new expression is obtained by inserting the actual values of π and c:

$$\overline{v}(cm^{-1}) = 4.12 \sqrt{\frac{K}{\mu}}$$

$\mu = \dfrac{M_1 M_2}{M_1 + M_2}$, where M_1 and M_2 are atomic weights

K = force constant in dynes/cm (1 dyne = 1.020×10^{-3} g)

K is a constant that varies from one bond to another. K for Single bond: **5×10^5 dynes/ cm, double bond: 10×10^5 dynes/ cm, and triple bond: 15×10^5 dynes/cm,** and the bonds between atoms of higher masses (larger reduced mass, μ) vibrate at lower frequencies than bonds between lighter atoms. The C-H stretch occurs at about 3000 cm^{-1}. As the atom bonded to carbon increases in mass, the reduced mass (μ) increases, and the frequency of vibration decreases (wavenumbers get smaller):

C≡C	C=C	C—C
$2150 \ cm^{-1}$	$1650 \ cm^{-1}$	$1200 \ cm^{-1}$

← Increasing *K*

C—H	C—C	C—O	C—Cl	C—Br	C—I
$3000 \ cm^{-1}$	$1200 \ cm^{-1}$	$1100 \ cm^{-1}$	$750 \ cm^{-1}$	$600 \ cm^{-1}$	$500 \ cm^{-1}$

Increasing μ →
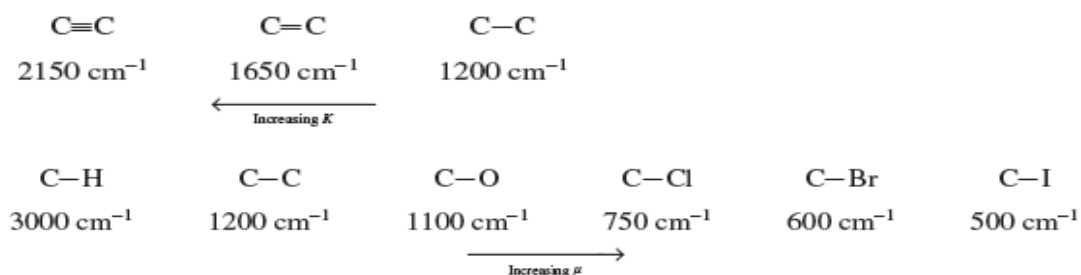
Bending motions occur at lower energy (lower frequency) than the typical stretching motions because of the lower value for the bending force constant K.

C—H stretching	C—H bending
~$3000 \ cm^{-1}$	~$1340 \ cm^{-1}$
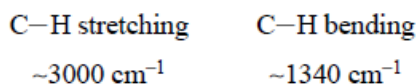
Hybridization affects the force constant K, also. Bonds are stronger in the order sp > sp2 > sp3, and the observed frequencies of C-H vibration illustrate this nicely.

sp	*sp^2*	*sp^3*
≡C—H	=C—H	—C—H
$3300 \ cm^{-1}$	$3100 \ cm^{-1}$	$2900 \ cm^{-1}$
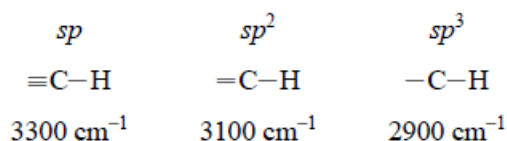
Resonance also affects the strength and length of a bond and hence its force constant *K*. Thus, whereas a normal ketone has its C=O stretching vibration at 1715 cm^{-1}, a ketone that is conjugated with a C=C double bond absorbs at a lower frequency, near 1675 to 1680 cm^{-1}. That is because resonance lengthens the C=O bond distance and gives it more single-bond character: Resonance has the effect of reducing the force constant *K*.

CALCULATION OF STRETCHING FREQUENCIES FOR DIFFERENT TYPES OF BONDS

C=C bond:

$$\bar{v} = 4.12\sqrt{\frac{K}{\mu}}$$

$K = 10 \times 10^5$ dynes/cm

$$\mu = \frac{M_C M_C}{M_C + M_C} = \frac{(12)(12)}{12 + 12} = 6$$

$$\bar{v} = 4.12\sqrt{\frac{10 \times 10^5}{6}} = 1682 \text{ cm}^{-1} \text{ (calculated)}$$

$\bar{v} = 1650$ cm^{-1} (experimental)

C—H bond:

$$\bar{v} = 4.12\sqrt{\frac{K}{\mu}}$$

$K = 5 \times 10^5$ dynes/cm

$$\mu = \frac{M_C M_H}{M_C + M_H} = \frac{(12)(1)}{12 + 1} = 0.923$$

$$\bar{v} = 4.12\sqrt{\frac{5 \times 10^5}{0.923}} = 3032 \text{ cm}^{-1} \text{ (calculated)}$$

$\bar{v} = 3000$ cm^{-1} (experimental)

C—D bond:

$$\bar{v} = 4.12\sqrt{\frac{K}{\mu}}$$

$K = 5 \times 10^5$ dynes/cm

$$\mu = \frac{M_C M_D}{M_C + M_D} = \frac{(12)(2)}{12 + 2} = 1.71$$

$$\bar{v} = 4.12\sqrt{\frac{5 \times 10^5}{1.71}} = 2228 \text{ cm}^{-1} \text{ (calculated)}$$

$\bar{v} = 2206$ cm^{-1} (experimental)

a. Which will occur at a larger wavenumber?
1. a C≡C stretch or a C=C stretch
2. a C—H stretch or a C—H bend
3. a C—N stretch or a C=N stretch

b. Assuming that the force constants are the same, which will occur at a larger wavenumber?
1. a C—O stretch or a C—Cl stretch
2. a C—O stretch or a C—C stretch

The Intensity of Absorption Bands

The intensity of an absorption band depends on the size of the change in dipole moment associated with the vibration: The greater the change in dipole moment, the more intense the absorption. Recall that the dipole moment of a bond is equal to the magnitude of the charge on one of the bonded atoms, multiplied by the distance between the two charges. When the bond stretches, the increasing distance between the atoms increases the dipole

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moment. The stretching vibration of an O-H bond will be associated with a greater change in dipole moment than that of an N-H bond because the O-H bond is more polar than N-H. Consequently, the stretching vibration of the O-H bond will be more intense. Likewise, the stretching vibration of an N-H bond is more intense than that of a C-H bond because the N-H bond is more polar than C-H.

relative bond polarities
relative intensities of IR absorption

O—H   >   N—H   >   C—H

increasing polarity

increasing intensity
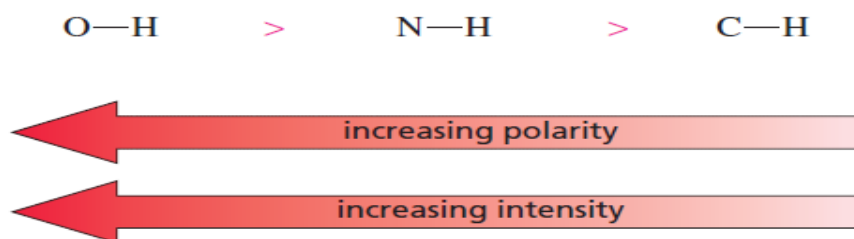
The intensity of an absorption band also depends on the number of bonds responsible for the absorption. For example, the absorption band for the C-H stretch will be more intense for a compound such as octyl iodide, which has 17C-H bonds, than for methyl iodide, which has only three C-H bonds. The concentration of the sample used to obtain an IR spectrum also affects the intensity of the absorption bands. Concentrated samples have greater numbers of absorbing molecules and, therefore, more intense absorption bands. In the chemical literature, you will find intensities referred to as strong (s), medium (m), weak (w), broad, and sharp.

Transmission

100 %

weak

medium

strong

0 %
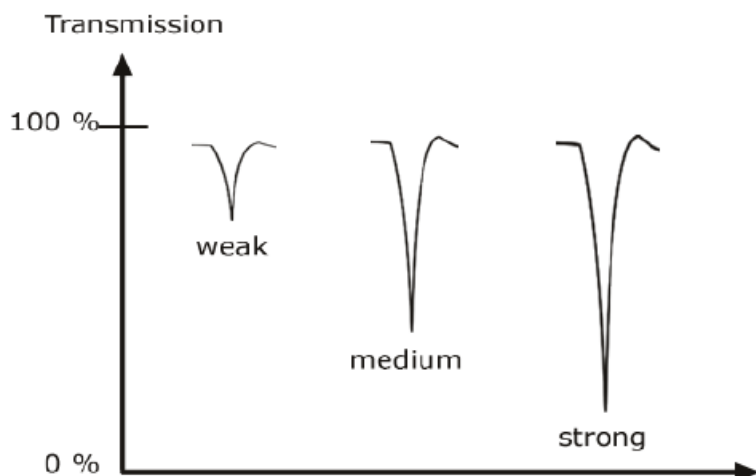
The Shape of Absorption Bands

The shape of an absorption band can be helpful in identifying the compound responsible for an IR spectrum. For example, both (O-H and N-H) bonds stretch at wavenumbers above (3100 cm^{-1}) but the shapes of their stretches are distinctive. Notice the difference in the shape of these absorption bands in the IR spectra of 1-hexanol, pentanoic acid, and isopentylamine. An N-H absorption band (~3300 cm^{-1}) is narrower and less intense than an O-H absorption band (~3300 cm^{-1}) and the O-H absorption band of a carboxylic acid (~3300-2500cm^{-1}) is broader than the O-H absorption band of an alcohol. The position, intensity, and shape of an absorption band are helpful in identifying functional groups.

a. Why is an O-H stretch more intense than an N-H stretch?

b. Why is the O-H stretch of a carboxylic acid broader than the O-H stretch of an alcohol?

IR Active Vibrations:

- In order for molecule to absorb IR radiation:

1. Vibration at same frequency as in light

2. A change in its **net dipole moment** as a result of the vibration, not zero.

3. The molecule must have no center of symmetry. **For example**:

1-butene   2,3-dimethyl-2-butene   2,3-dimethyl-2-heptene

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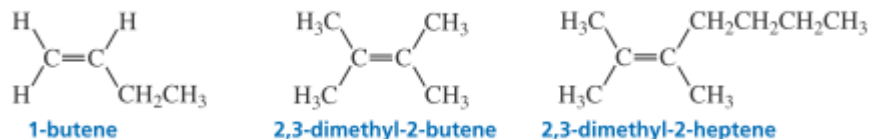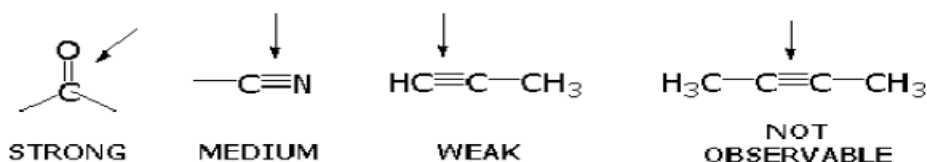
Infrared Spectrum

An infrared spectrum is obtained by passing infrared radiation through a sample of the compound. A detector generates a plot of percent transmission of radiation versus the wavenumber (or wavelength) of the radiation transmitted. The detector detects the transmitted frequencies, and by doing so also reveals the values of the absorbed frequencies
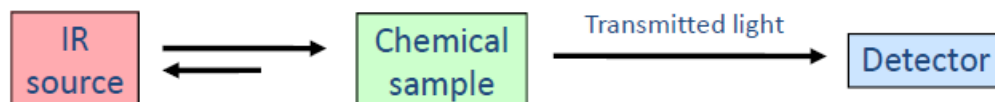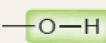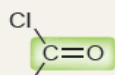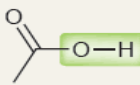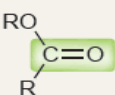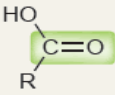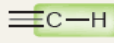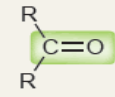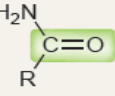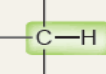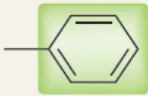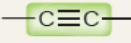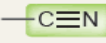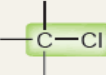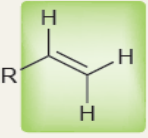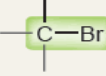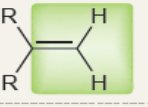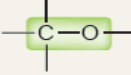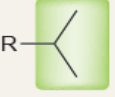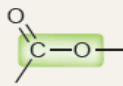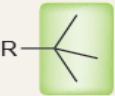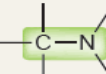

An IR spectrum can be divided into two areas. The left-hand two-thirds of an IR spectrum (4000- 1500 cm^{-1}) are where most of the functional groups show absorption bands. This region is called the **functional group region**. The right-hand third (1500- 400 cm^{-1}) of the IR spectrum is called the **fingerprint region,** which contains many signals resulting from the vibrational excitation of most single bonds (stretching and bending) and is more difficult to analyze. This region is called the fingerprint region because each compound has a unique pattern of signals in this region, much the way each person has a unique fingerprint.
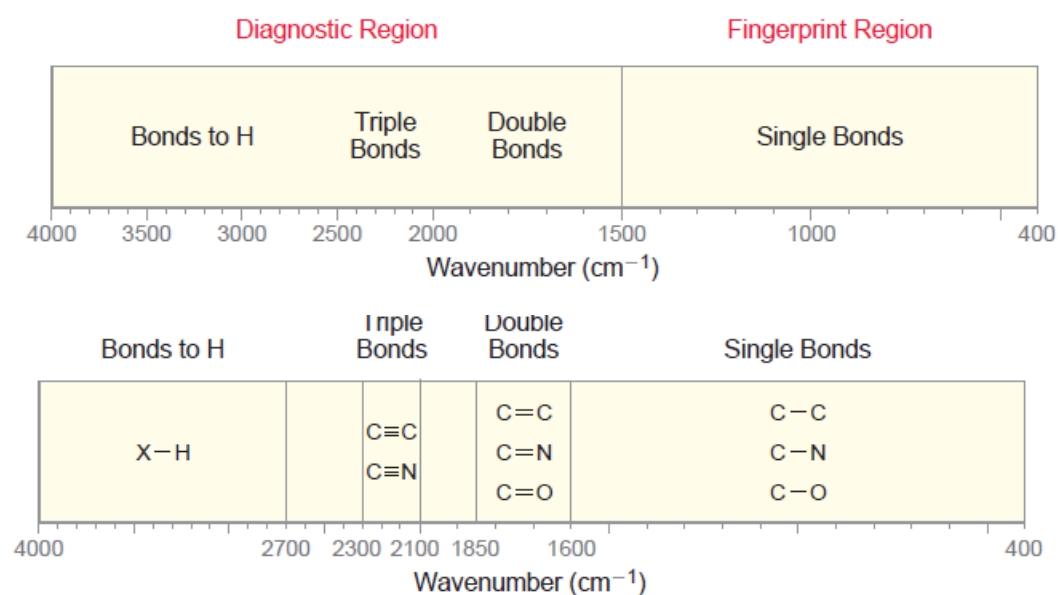
Analyzing an IR Spectrum

Below tables is a summary of useful signals in the diagnostic region of an IR spectrum as well as some useful signals in the fingerprint region.

STRUCTURAL UNIT	FREQUENCY (cm^{-1})	STRUCTURAL UNIT	FREQUENCY (cm^{-1})
	USEFUL SIGNALS IN THE DIAGNOSTIC REGION		
Single Bonds (X—H)		**Double Bonds**	
O—H	3200–3600	Cl–C=O	1750–1850
O—H (carboxylic acid)	2200–3600	RO–C=O	1700–1750
N—H	3350–3500	HO–C=O	1700–1750
≡C—H	~3300	R–C=O (R)	1680–1750
C—H (vinyl)	3000–3100	H$_2$N–C=O	1650–1700
C—H (alkyl)	2850–3000	C=C	1600–1700
C—H (aldehyde, O=C—H)	2750–2850	aromatic ring	1450–1600, 1650–2000
Triple Bonds			
C≡C	2100–2200		
C≡N	2200–2300		
	USEFUL SIGNALS IN THE FINGERPRINT REGION		
C—Cl	600–800	R–CH=CH$_2$	900–920, 980–1000 (bending)
C—Br	500–600	R$_2$C=CH$_2$	880–900 (bending)
C—O	1000–1100	isopropyl	1370, 1380 (bending)
O=C—O	1250–1350	tert-butyl	1370, 1390 (bending)
C—N	1000–1200		

A SIMPLIFIED CORRELATION CHART

Type of Vibration			Frequency (cm⁻¹)	Intensity
C—H	Alkanes	(stretch)	3000–2850	s
	—CH₃	(bend)	1450 and 1375	m
	—CH₂—	(bend)	1465	m
	Alkenes	(stretch)	3100–3000	m
		(out-of-plane bend)	1000–650	s
	Aromatics	(stretch)	3150–3050	s
		(out-of-plane bend)	900–690	s
	Alkyne	(stretch)	ca. 3300	s
	Aldehyde		2900–2800	w
			2800–2700	w
C—C	Alkane		Not interpretatively useful	
C=C	Alkene		1680–1600	m–w
	Aromatic		1600 and 1475	m–w
C≡C	Alkyne		2250–2100	m–w
C=O	Aldehyde		1740–1720	s
	Ketone		1725–1705	s
	Carboxylic acid		1725–1700	s
	Ester		1750–1730	s
	Amide		1680–1630	s
	Anhydride		1810 and 1760	s
	Acid chloride		1800	s
C—O	Alcohols, ethers, esters, carboxylic acids, anhydrides		1300–1000	s
O—H	Alcohols, phenols			
	Free		3650–3600	m
	H-bonded		3400–3200	m
	Carboxylic acids		3400–2400	m
N—H	Primary and secondary amines and amides			
	(stretch)		3500–3100	m
	(bend)		1640–1550	m–s
C—N	Amines		1350–1000	m–s
C=N	Imines and oximes		1690–1640	w–s
C≡N	Nitriles		2260–2240	m
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates		2270–1940	m–s
N=O	Nitro (R—NO₂)		1550 and 1350	s
S—H	Mercaptans		2550	w
S=O	Sulfoxides		1050	s
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides		1375–1300 and 1350–1140	s
C—X	Fluoride		1400–1000	s
	Chloride		785–540	s
	Bromide, iodide		< 667	s

How to approach the analysis of a spectrum (or what you can tell at a glance)

When analyzing the spectrum of an unknown, concentrate your first efforts on determining the presence or absence of a few major functional groups. The C=O, O-H, N-H, C-O, C=C, C≡C, C≡N, and NO_2 peaks are the most conspicuous and give immediate structural information if they are present. Do not try to make a detailed analysis of the C-H absorptions near 3000 cm^{-1}; almost all compounds have these absorptions. Do not worry about subtleties of the exact environment in which the functional group is found. Following is a major checklist of the important gross features.

1. Is a carbonyl group present? The **C= O** group gives rise to a strong absorption in the region **1820–1650 cm^{-1}**. The peak is often the strongest in the spectrum and of medium width. You can't miss it.

2. If **C=O** is present, check the following types (if it is absent, go to step 3):

ACIDS   Is O-H also present?

• Broad absorption near **3400–2400 cm^{-1}** (usually overlaps C-H).

AMIDES   Is N-H also present?

• Medium absorption near 3400 cm^{-1}; sometimes a double peak with equivalent halves.

ESTERS   Is C-O also present?

• Strong-intensity absorptions near 1300–1000 cm^{-1}.

ANHYDRIDES   Two C=O absorptions near 1810 and 1760 cm^{-1}.

ALDEHYDES   Is aldehyde C-H present?

• Two weak absorptions near 2850 and 2750 cm^{-1} on right side of the aliphatic C-H absorptions.

KETONES   The preceding five choices have been eliminated.

3. If C= O is absent:

ALCOHOLS, PHENOLS   Check for O-H.

• Broad absorption near 3400–3300 cm^{-1}.

• Confirm this by finding C-O near 1300–1000 cm^{-1}.

AMINES   Check for N-H.

• Medium absorption(s) near 3400 cm^{-1}.

ETHERS   Check for **C-O** near 1300–1000 cm^{-1}(and absence of O-H near 3400).

4. Double bonds and/or aromatic rings

• **C=C** is a weak absorption near 1650 cm^{-1}.

• Medium-to-strong absorptions in the region 1600–1450 cm^{-1}; these often imply an aromatic ring.

• Confirm the double bond or aromatic ring by consulting the C-H region; aromatic and vinyl C- H occur to the left of 3000 cm^{-1}(aliphatic C- H occurs to the right of this value).

5. Triple bonds

• C≡N is a medium, sharp absorption near 2250 cm^{-1}.

• C≡C is a weak, sharp absorption near 2150 cm^{-1}.

• Check also for acetylenic C-H near 3300 cm^{-1}.

6. Nitro groups

• Two strong absorptions at 1600–1530 cm^{-1} and 1390 – 1300 cm^{-1}.

7. Hydrocarbon

• None of the preceding is found.

• Major absorptions are in C-H region near 3000 cm^{-1}.

• Very simple spectrum; the only absorption appear near 1460-1375 cm^{-1}.

• Absence of Absorption Bands

The absence of an absorption band can be as useful as the presence of a band in identifying a compound by IR spectroscopy. For example, the spectrum of an unknown shows a strong absorption at (~1100 cm^{-1}) indicating the presence of a C-O bond.

Clearly, the compound is not an alcohol , because there is no absorption above (3100cm^{-1}). Nor is it an ester or any other kind of carbonyl compound because there is no absorption at (~1700 cm^{-1}). The compound has no C≡N, C=N, C≡C, C= C or C-N bonds. We may deduce, then, that the compound is ether. Its C-H absorption bands

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show that it has only sp3 hybridized carbons and that it has a methyl group. We also know that the compound has fewer than four adjacent methylene groups, because there is no absorption at ($\sim$720 cm^{-1}) The compound is actually diethyl ether.
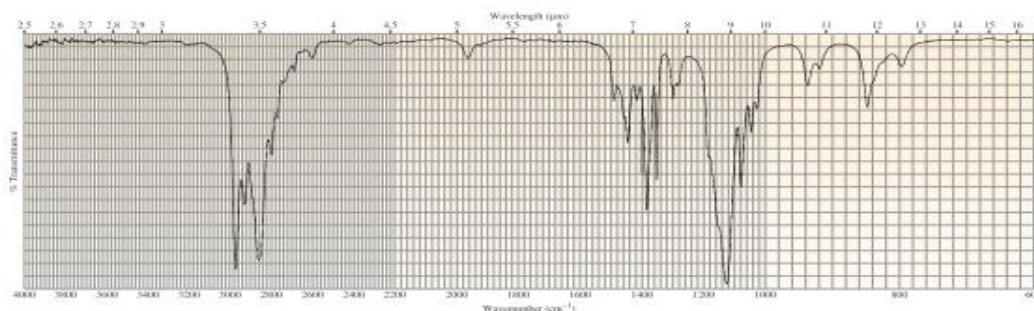
Questions: Q1/

a. An oxygen-containing compound shows an absorption band at $\sim$1700 cm^{-1} and no absorption bands at $\sim$3300 cm^{-1}, $\sim$2700 cm^{-1}, or $\sim$1100 cm^{-1}. What class of compound is it?

b. A nitrogen-containing compound shows no absorption band at $\sim$3400 cm^{-1} and no absorption bands between 1700 cm^{-1} and 1600 cm^{-1}. What class of compound is it?

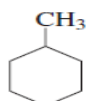Q2/Identify how IR spectroscopy might be used to monitor the progress of the following reactions?
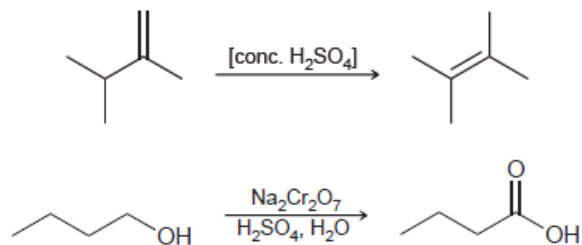
Q3/

For each of the following pairs of compounds, give one absorption band that could be used to distinguish between them:

a. $CH_3CH_2CH_2CH_3$ and $CH_3CH_2OCH_3$

b. $CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_3$ and $CH_3CH_2\overset{O}{\overset{\|}{C}}OH$

c. $CH_3CH_2\overset{O}{\overset{\|}{C}}OH$ and $CH_3CH_2CH_2OH$

d. CH_3CH_2C≡CCH_3 and CH_3CH_2C≡CH

e. and

f. and

Q4/ When 1-chlorobutane is treated with sodium hydroxide, two products are formed. Identify the two products, and explain how these products could be distinguished using IR spectroscopy.

Q5/ Match the expected compound with the appropriate IR spectrum: