INFRARED SPECTROSCOPY (IR)

Theory and Interpretation of
IR spectra

ORGANIC STRUCTURE DETERMINATION

How do we know:

- How atoms are connected together?
- Which bonds are single, double, or triple?
- What functional groups exist in the molecule?
- If we have a specific stereoisomer?

The field of organic structure determination attempts to answer these questions.

?????????????????

Spectroscopy

•“seeing the unseeable”

•Using electromagnetic radiation as a probe to obtain information about atoms and molecules that are too small to see.

•Electromagnetic radiation is propagated at the speed of light through a vacuum as an oscillating wave.

Infrared Spectroscopy

- The structure of new compounds that are isolated from natural sources or prepared in the lab must be determined (and/or verified).
  - – Chemical analysis
  - – Spectroscopy
- Spectroscopic techniques are non-destructive and generally require small amounts of sample

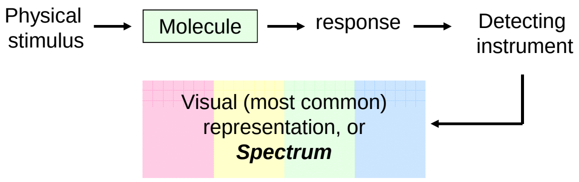
Infrared Spectroscopy

- Four common spectroscopic techniques used to determine structure:
  - – Infrared Spectroscopy (IR)
  - – Mass Spectrometry (MS or Mass Spec)
  - – Nuclear Magnetic Resonance Spectroscopy (NMR)
  - – Ultraviolet Spectroscopy

INSTRUMENTAL METHODS OF STRUCTURE DETERMINATION

1. **Nuclear Magnetic Resonance (NMR)** – Excitation of the nucleus of atoms through radiofrequency irradiation. Provides extensive information about molecular structure and atom connectivity.
2. **Infrared Spectroscopy (IR)** – Triggering molecular vibrations through irradiation with infrared light. Provides mostly information about the presence or absence of certain functional groups.
3. **Mass spectrometry** – Bombardment of the sample with electrons and detection of resulting molecular fragments. Provides information about molecular mass and atom connectivity.
4. **Ultraviolet spectroscopy (UV)** – Promotion of electrons to higher energy levels through irradiation of the molecule with ultraviolet light. Provides mostly information about the presence of conjugated π systems and the presence of double and triple bonds.

SPECTROSCOPY - Study of spectral information



Physical stimulus → Molecule → response → Detecting instrument

Visual (most common) representation, or ***Spectrum***

Upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called a spectrum.

SPECTRUM INTERPRETATION PROCESS

1. Recognize a *pattern.*
2. Associate patterns with *physical parameters.*
3. Identify possible meanings, i.e. *propose explanations.*

Once a spectrum is obtained, the main challenge is to extract the information it contains in abstract, or hidden form. This requires the recognition of certain patterns, the association of these patterns with physical parameters, and the interpretation of these patterns in terms of meaningful and logical explanations.

ELECTROMAGNETIC SPECTRUM

Most organic spectroscopy uses **electromagnetic energy, or radiation,** as the physical stimulus.

Electromagnetic energy (such as visible light) has no detectable mass component. In other words, it can be referred to as “pure energy.”

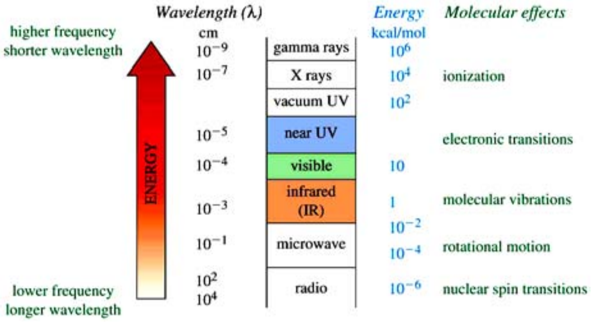
Other types of radiation such as alpha rays, which consist of helium nuclei, have a detectable mass component and therefore cannot be categorized as electromagnetic energy.

The important parameters associated with electromagnetic radiation are:

- **Energy (E)**: Energy is directly proportional to frequency, and inversely proportional to wavelength, as indicated by the equation below.
- **Frequency (μ)**
- **Wavelength (λ)**

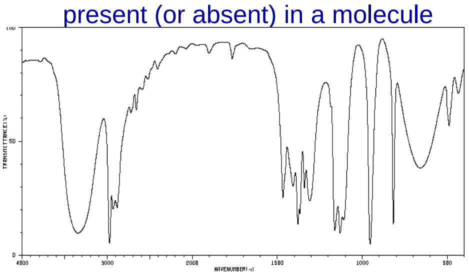
$$\boxed{E = h\mu}$$

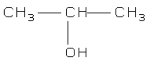
EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES



Infrared Spectroscopy

- Infrared spectroscopy:
  - Used to determine the functional groups present (or absent) in a molecule





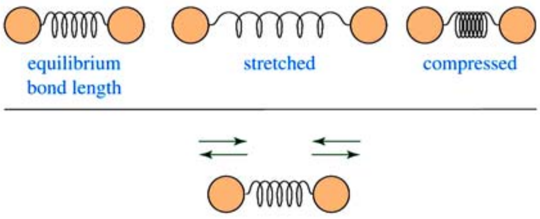
$$\begin{array}{c} CH_3—CH—CH_3 \\ | \\ OH \end{array}$$

INFRARED SPECTROSCOPY

- Infrared radiation stimulates molecular vibrations.
- Infrared spectra are traditionally displayed as %T (percent transmittance) versus wave number (4000-400 cm-1).
- Useful in identifying presence or absence of functional groups.

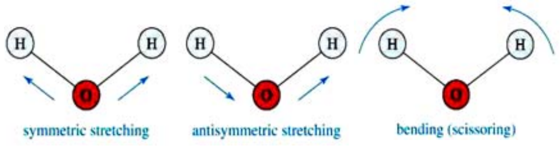
Infrared radiation is largely thermal energy.
It induces stronger **molecular vibrations** in covalent bonds, which can be viewed as springs holding together two masses, or atoms.

Specific bonds respond to (absorb) **specific** frequencies



VIBRATIONAL MODES

- Covalent bonds can vibrate in several modes, including **stretching, rocking, and scissoring**.
- The most useful bands in an infrared spectrum correspond to stretching frequencies, and those will be the ones we'll focus on.

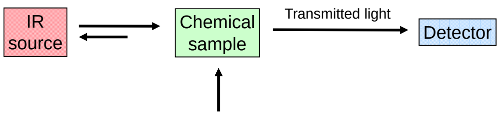


Infrared Spectroscopy

- Since energy is quantized, covalent bonds can vibrate/stretch only at certain allowed frequencies.
  - The position of an absorption band correlates with the type of chemical bond.

TRANSMISSION vs. ABSORPTION

When a chemical sample is exposed to the action of **IR LIGHT**, it can **absorb** some frequencies and **transmit** the rest. Some of the light can also be reflected back to the source.

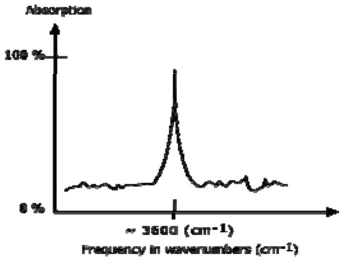


From all the frequencies it receives, the chemical sample can **absorb** (retain) **specific frequencies** and allow the rest to pass through it (transmitted light).

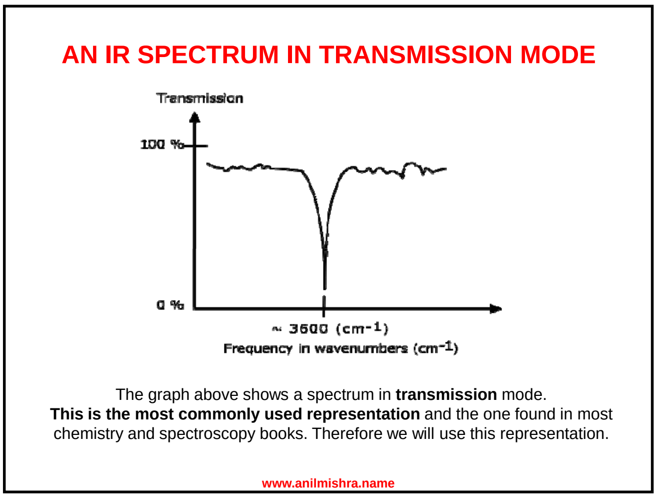
The detector detects the transmitted frequencies, and by doing so also reveals the values of the absorbed frequencies.

AN IR SPECTRUM IN ABSORPTION MODE

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the *x*-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the *y*-axis in percentage units.

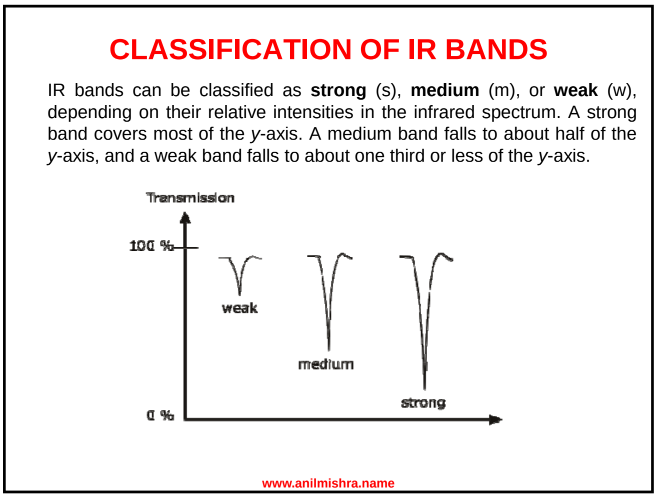


The graph above shows a spectrum in **absorption** mode.



AN IR SPECTRUM IN TRANSMISSION MODE

The graph above shows a spectrum in **transmission** mode. **This is the most commonly used representation** and the one found in most chemistry and spectroscopy books. Therefore we will use this representation.

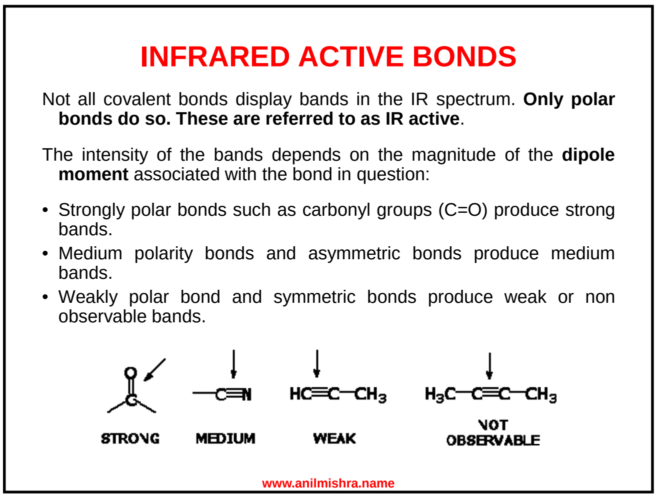


CLASSIFICATION OF IR BANDS

IR bands can be classified as **strong** (s), **medium** (m), or **weak** (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the *y*-axis. A medium band falls to about half of the *y*-axis, and a weak band falls to about one third or less of the *y*-axis.

Infrared Spectroscopy

- The polarity of a bond has a significant impact on the intensity of an IR absorption band.
  - Vibrations that cause a significant change in the dipole moment of a chemical bond lead to strong absorption bands.
  - Vibrations that result in no change/very little change in dipole moment lead to very weak or no absorption band.
    - Symmetrical bonds often exhibit very weak or no absorption band.

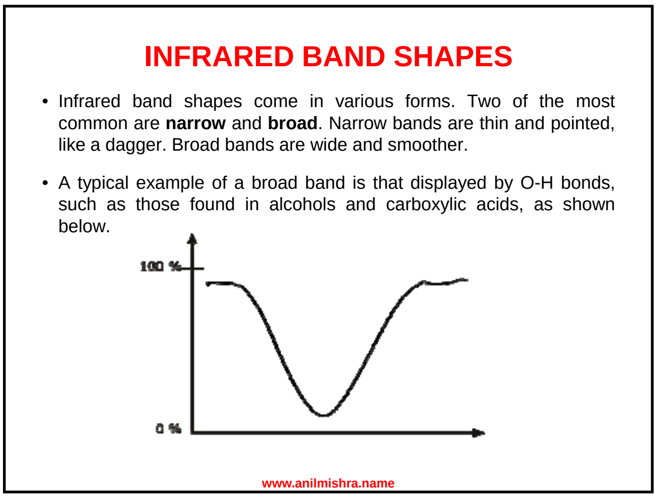


INFRARED ACTIVE BONDS

Not all covalent bonds display bands in the IR spectrum. **Only polar bonds do so. These are referred to as IR active**.

The intensity of the bands depends on the magnitude of the **dipole moment** associated with the bond in question:

- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.



INFRARED BAND SHAPES

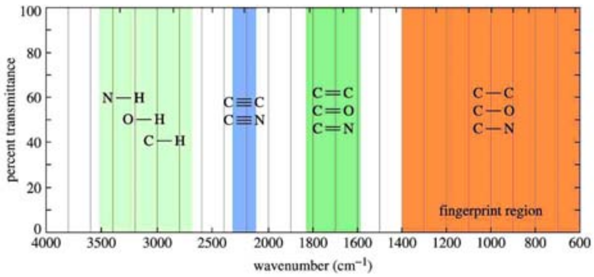
- Infrared band shapes come in various forms. Two of the most common are **narrow** and **broad**. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.
- A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.

INFORMATION OBTAINED FROM IR SPECTRA

- IR is most useful in providing information about the presence or absence of specific **functional groups**.
- IR can provide a **molecular fingerprint** that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.
- IR **does not** provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.
- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.

IR ABSORPTION RANGE

The typical IR absorption range for covalent bonds is **600 - 4000 cm^{-1}**. The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example a sharp band around 2200-2400 cm^{-1} would indicate the possible presence of a C-N or a C-C triple bond.

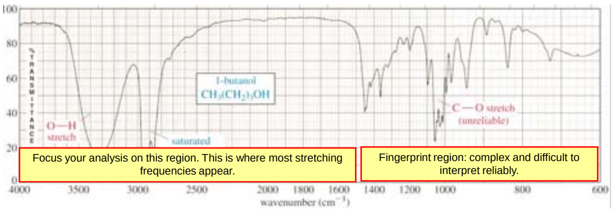


Infrared Spectroscopy

- Each molecule has a unique IR spectrum.
  - The IR spectrum is a “fingerprint” for the molecule.
- IR spectrum results from a combination of all possible stretching and/or bending vibrations of the individual bonds and the whole molecule.
  - Simple stretching: ~1600-4000 cm^{-1}.
  - Complex vibrations: 600-1400 cm^{-1}, called the “fingerprint region.”

THE FINGERPRINT REGION

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm^{-1}** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm^{-1}.



Focus your analysis on this region. This is where most stretching frequencies appear.

Fingerprint region: complex and difficult to interpret reliably.

Carbon-Carbon Bonds

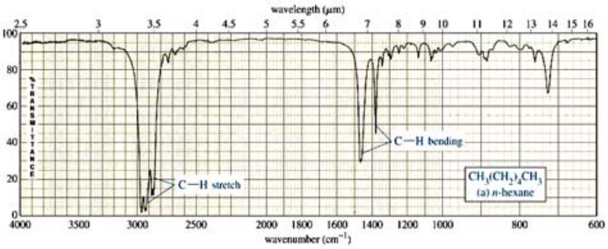
- Increasing bond order leads to higher frequencies:
  - C-C 1200 cm^{-1} (fingerprint region)
  - C=C 1600 - 1680 cm^{-1}
  - C≡C 2200 cm^{-1} (weak or absent if internal)
- Conjugation lowers the frequency:
  - isolated C=C 1640-1680 cm^{-1}
  - conjugated C=C 1620-1640 cm^{-1}
  - aromatic C=C approx. 1600 cm^{-1}
- C=C peaks are generally weak to moderate in intensity.

Carbon-Hydrogen Bonds

- Bonds with more *s* character absorb at a higher frequency.
  - *sp*^{3} (alkane) C-H
    - just below 3000 cm^{-1} (to the right)
  - *sp*^{2} (alkene or aromatic hydrocarbon) C-H
    - just above 3000 cm^{-1} (to the left)
  - *sp* (alkyne) C-H
    - at 3300 cm^{-1}

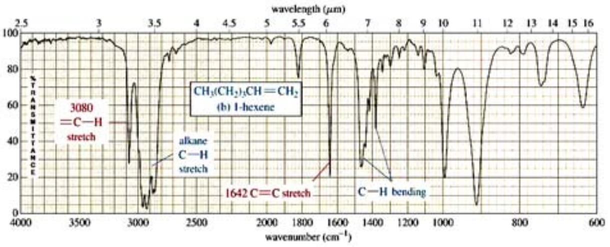
IR SPECTRUM OF ALKANES

Alkanes have no functional groups. Their IR spectrum displays only C-C and C-H bond vibrations. Of these the most useful are the **C-H bands**, which appear around **3000 cm^{-1}**. Since most organic molecules have such bonds, most organic molecules will display those bands in their spectrum.



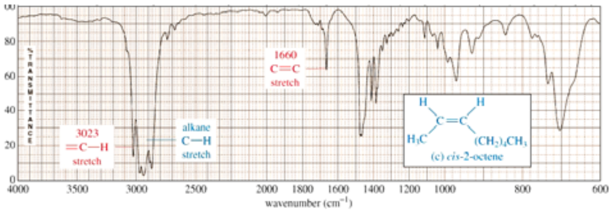
IR SPECTRUM OF ALKENES

Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the **C=C bond stretching vibration** at about **1600-1700 cm^{-1}**. Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm^{-1}** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm^{-1} (see next slide)



IR SPECTRUM OF ALKENES

This spectrum shows that the band appearing around **3080 cm^{-1}** can be obscured by the broader bands appearing around 3000 cm^{-1}.

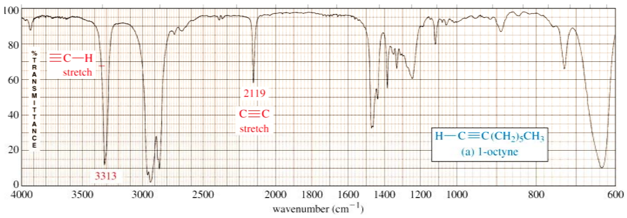


IR SPECTRUM OF ALKYNES

The most prominent band in alkynes corresponds to the **carbon-carbon triple bond**. It shows as a sharp, weak band at about **2100 cm^{-1}**. The reason it's weak is because the triple bond is not very polar. In some cases, such as in highly symmetrical alkynes, it may not show at all due to the low polarity of the triple bond associated with those alkynes.

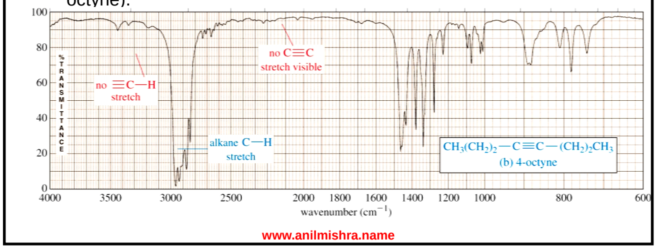
Terminal alkynes, that is to say those where the triple bond is at the end of a carbon chain, have C-H bonds involving the *sp* carbon (the carbon that forms part of the triple bond). Therefore they may also show a sharp, weak band at about **3300 cm^{-1}** corresponding to the C-H stretch.

IR SPECTRUM OF ALKYNES



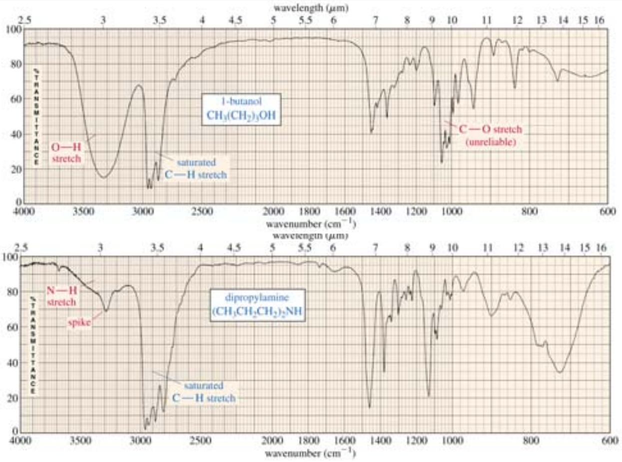
IR SPECTRUM OF ALKYNES

- Internal alkynes, that is those where the triple bond is in the middle of a carbon chain, do not have C-H bonds to the *sp* carbon and therefore lack the aforementioned band.
- The following slide shows a comparison between an unsymmetrical terminal alkyne (1-octyne) and a symmetrical internal alkyne (4-octyne).



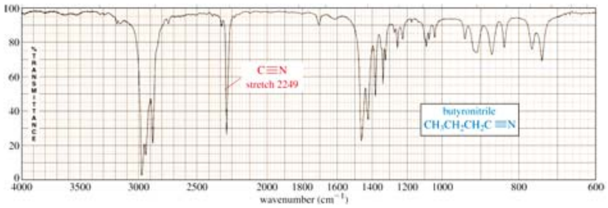
O-H and N-H Bonds

- Both O-H and N-H stretches appear around 3300 cm^{-1}, but they look different.
  - Alcohol O-H
    - broad with rounded tip when hydrogen bonding is present (sharp in the absence of hydrogen bonding)
  - Secondary amine (R_2NH)
    - Broad (usually) with one sharp spike
  - Primary amine (RNH_2)
    - Broad (usually) with two sharp spikes.
  - No signal for a tertiary amine (R_3N)



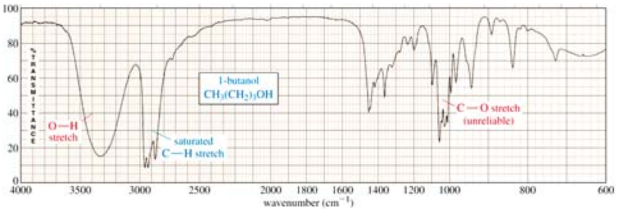
IR SPECTRUM OF A NITRILE

In a manner very similar to alkynes, nitriles show a prominent band around **2250 cm^{-1}** caused by the **CN triple bond**. This band has a sharp, pointed shape just like the alkyne C-C triple bond, but because the CN triple bond is more polar, this band is stronger than in alkynes.



IR SPECTRUM OF AN ALCOHOL

The most prominent band in alcohols is due to the **O-H bond**, and it appears as a strong, broad band covering the range of about **3000 - 3700 cm^{-1}**. The sheer size and broad shape of the band dominate the IR spectrum and make it hard to miss.

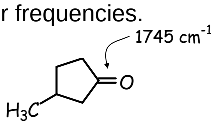


Carbonyls

- Carbonyl stretches are generally strong:

– Aldehyde	~1710 cm^{-1}
– Ketone	~1710 cm^{-1}
– Carboxylic acid	~1710 cm^{-1}
– Ester	~1730 - 1740 cm^{-1}
– Amide	~1640-1680 cm^{-1}

- Conjugation shifts all carbonyls to lower frequencies.
- Ring strain shifts carbonyls to higher frequencies.



IR SPECTRUM OF ALDEHYDES AND KETONES

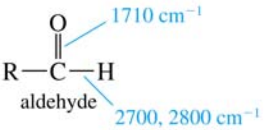
Carbonyl compounds are those that **contain the C=O functional group**. In aldehydes, this group is at the end of a carbon chain, whereas in ketones it's in the middle of the chain. As a result, the carbon in the C=O bond of aldehydes is also bonded to another carbon and a hydrogen, whereas the same carbon in a ketone is bonded to two other carbons.

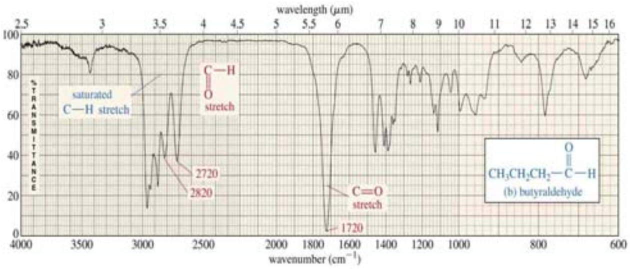
Aldehydes and ketones show a strong, prominent, stake-shaped band around **1710 - 1720 cm^{-1}** (right in the middle of the spectrum). This band is due to the **highly polar C=O bond**. Because of its position, shape, and size, it is hard to miss.

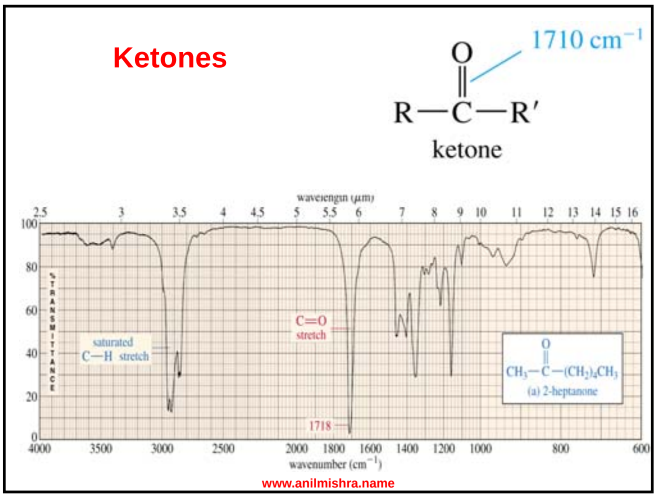
Because aldehydes also contain a C-H bond to the *sp*^{2} carbon of the C=O bond, they also show a pair of medium strength bands positioned about **2700** and **2800 cm^{-1}**. These bands are missing in the spectrum of a ketone because the *sp*^{2} carbon of the ketone lacks the C-H bond.

The following slide shows a spectrum of an aldehyde and a ketone. Study the similarities and the differences so that you can distinguish between the two.

Aldehydes







Ketones

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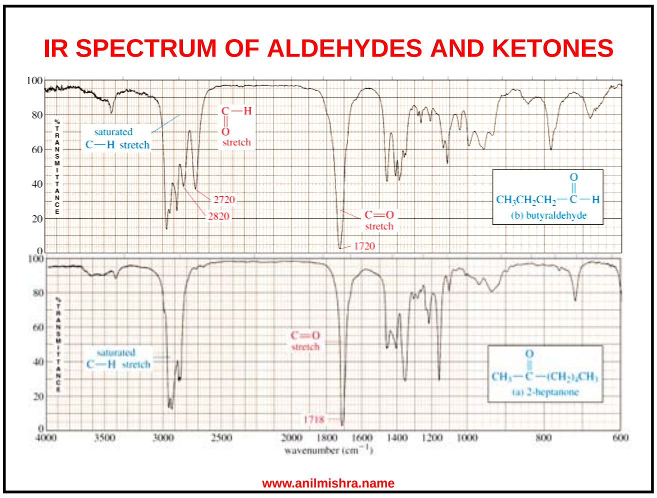

IR SPECTRUM OF ALDEHYDES AND KETONES

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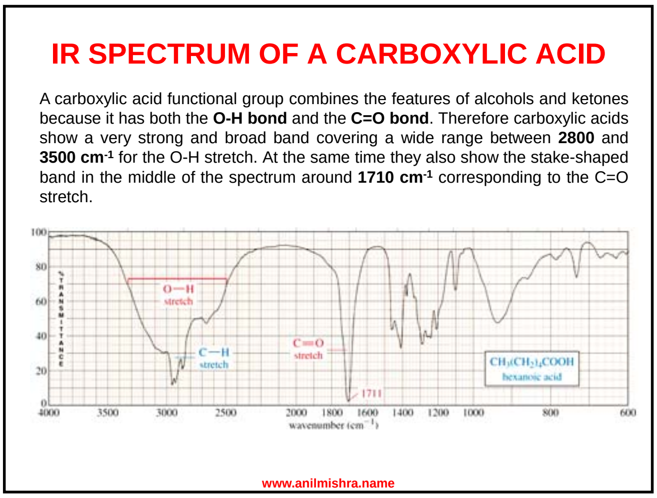

IR SPECTRUM OF A CARBOXYLIC ACID

A carboxylic acid functional group combines the features of alcohols and ketones because it has both the **O-H bond** and the **C=O bond**. Therefore carboxylic acids show a very strong and broad band covering a wide range between **2800** and **3500 cm^{-1}** for the O-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** corresponding to the C=O stretch.

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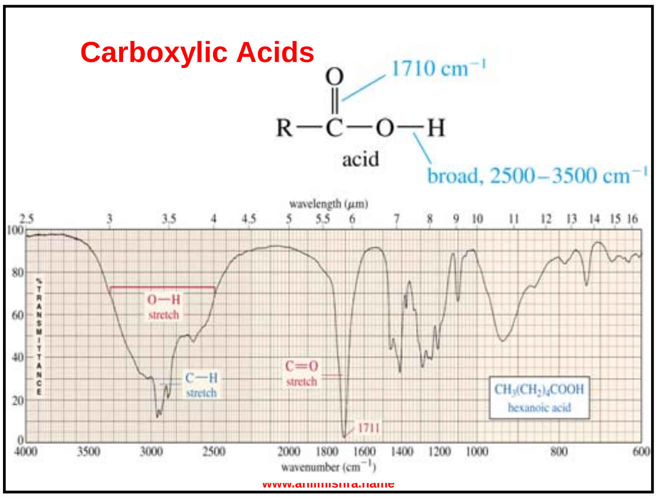

Carboxylic Acids

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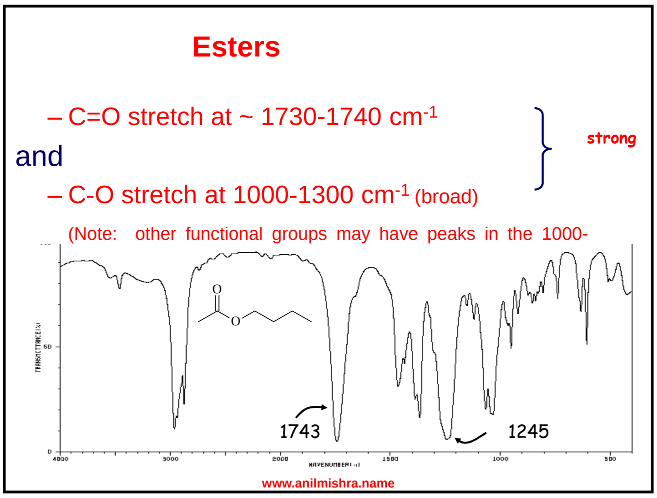

Esters

– C=O stretch at ~ 1730-1740 cm^{-1}

and

– C-O stretch at 1000-1300 cm^{-1} (broad)

strong

(Note: other functional groups may have peaks in the 1000-

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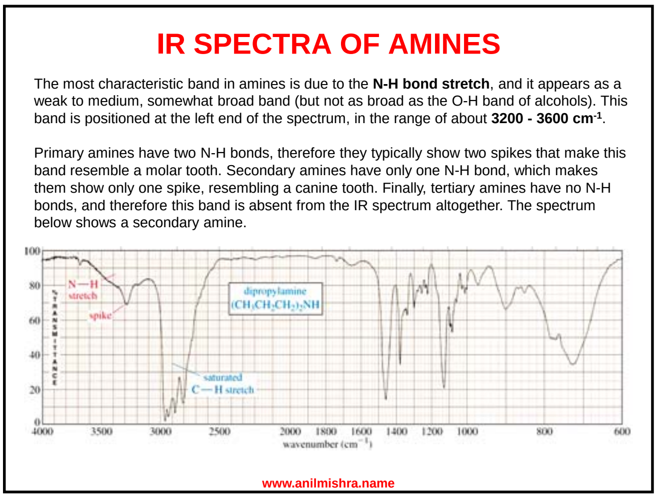

IR SPECTRA OF AMINES

The most characteristic band in amines is due to the **N-H bond stretch**, and it appears as a weak to medium, somewhat broad band (but not as broad as the O-H band of alcohols). This band is positioned at the left end of the spectrum, in the range of about **3200 - 3600 cm^{-1}**.

Primary amines have two N-H bonds, therefore they typically show two spikes that make this band resemble a molar tooth. Secondary amines have only one N-H bond, which makes them show only one spike, resembling a canine tooth. Finally, tertiary amines have no N-H bonds, and therefore this band is absent from the IR spectrum altogether. The spectrum below shows a secondary amine.

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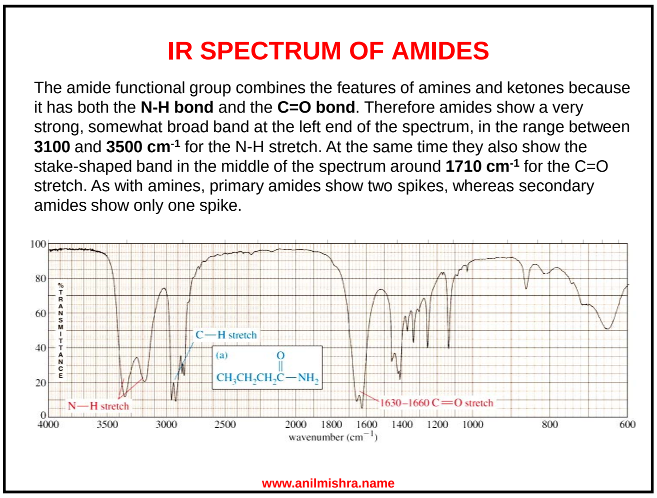

IR SPECTRUM OF AMIDES

The amide functional group combines the features of amines and ketones because it has both the **N-H bond** and the **C=O bond**. Therefore amides show a very strong, somewhat broad band at the left end of the spectrum, in the range between **3100** and **3500 cm^{-1}** for the N-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** for the C=O stretch. As with amines, primary amides show two spikes, whereas secondary amides show only one spike.

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