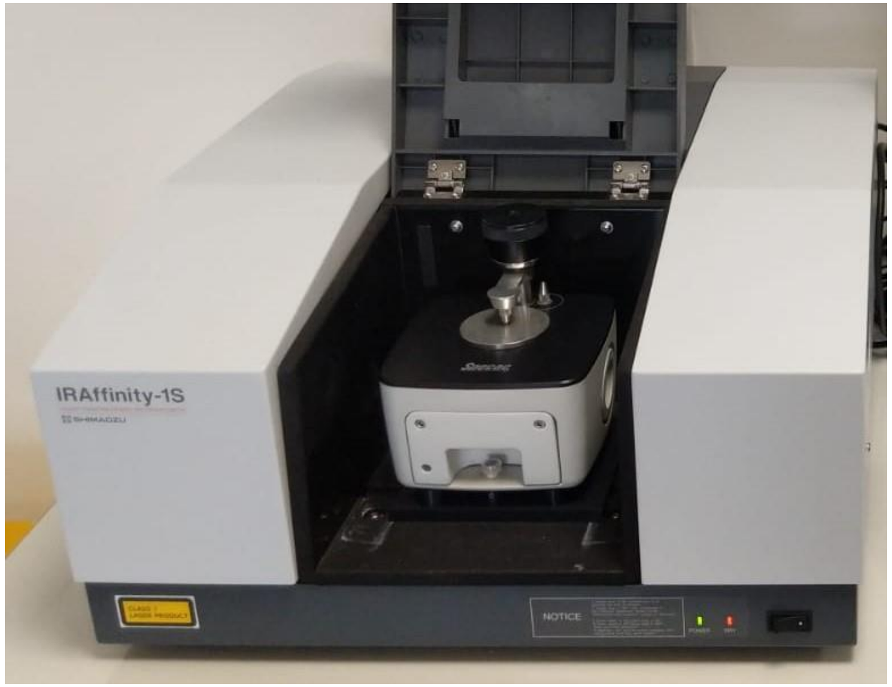
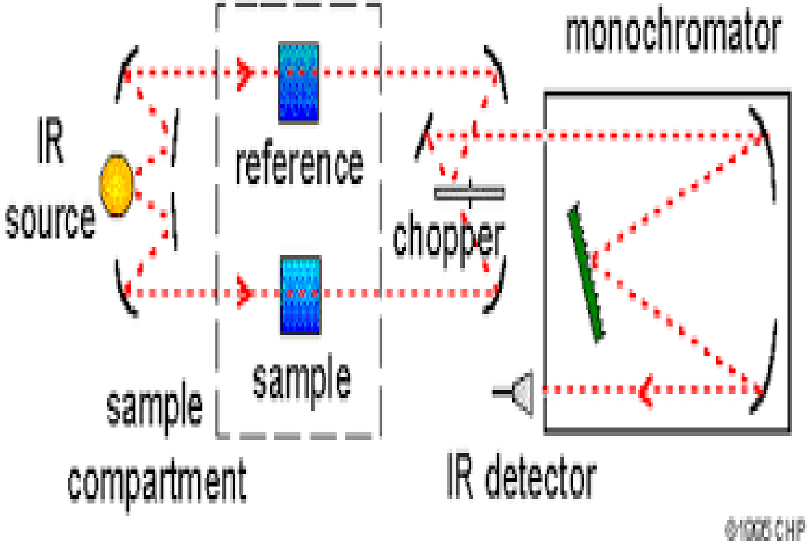




SPECTROMETRY INFRA RED

Introduction

- Spectroscopy is an analytical technique which helps determine structure.
- It destroys little or no sample.
- The amount of light absorbed by the sample is measured as wavelength is varied.

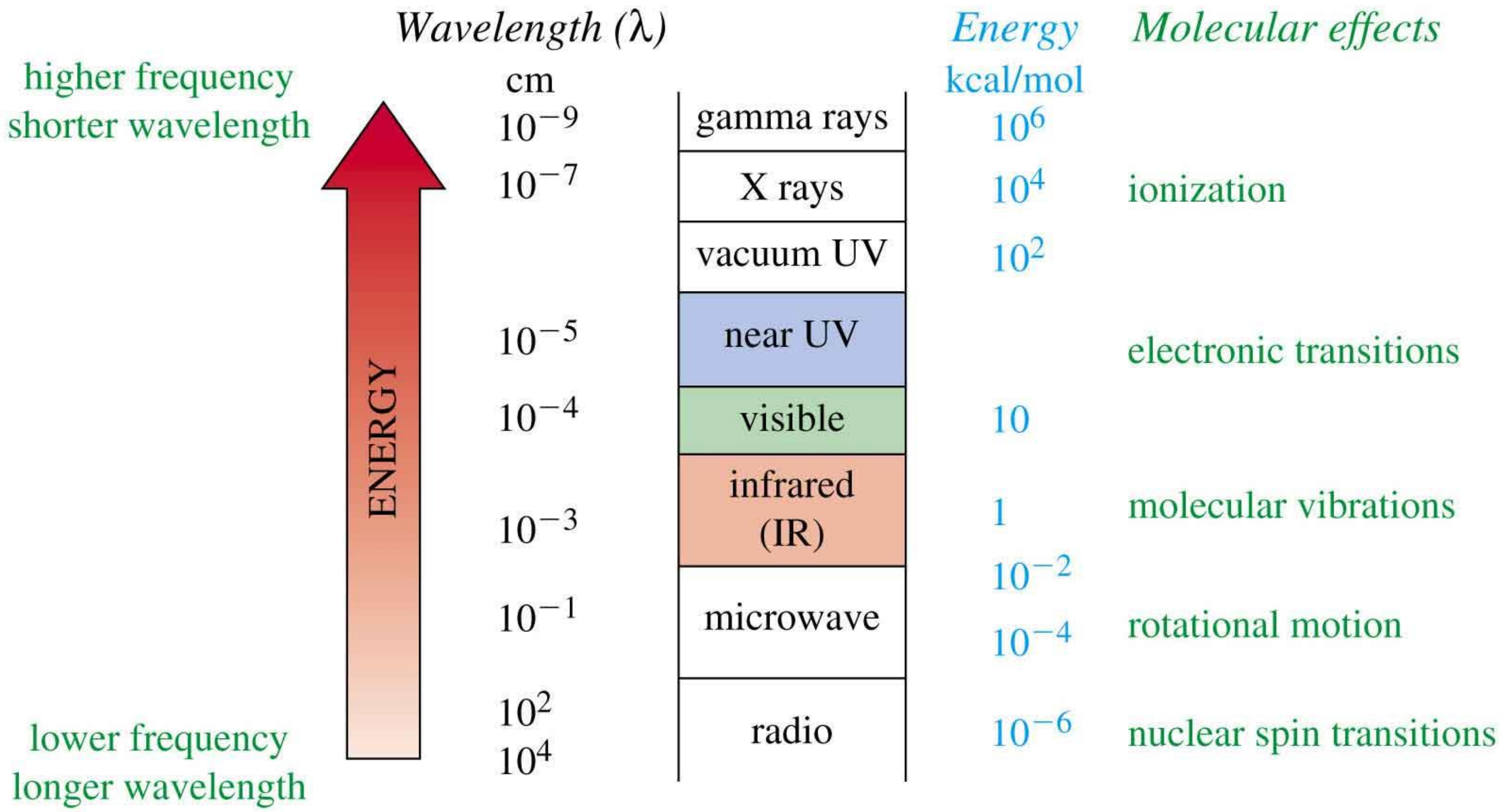
Types of Spectroscopy

- Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group.
- Mass spectrometry (MS) fragments the molecule and measures the masses.
- Nuclear magnetic resonance (NMR) spectroscopy detects signals from hydrogen atoms and can be used to distinguish isomers.
- Ultraviolet (UV) spectroscopy uses electron transitions to determine bonding patterns.

Electromagnetic Spectrum

- Examples: X rays, microwaves, radio waves, visible light, IR, and UV.
- Frequency and wavelength are inversely proportional.

The Spectrum and Molecular Effects

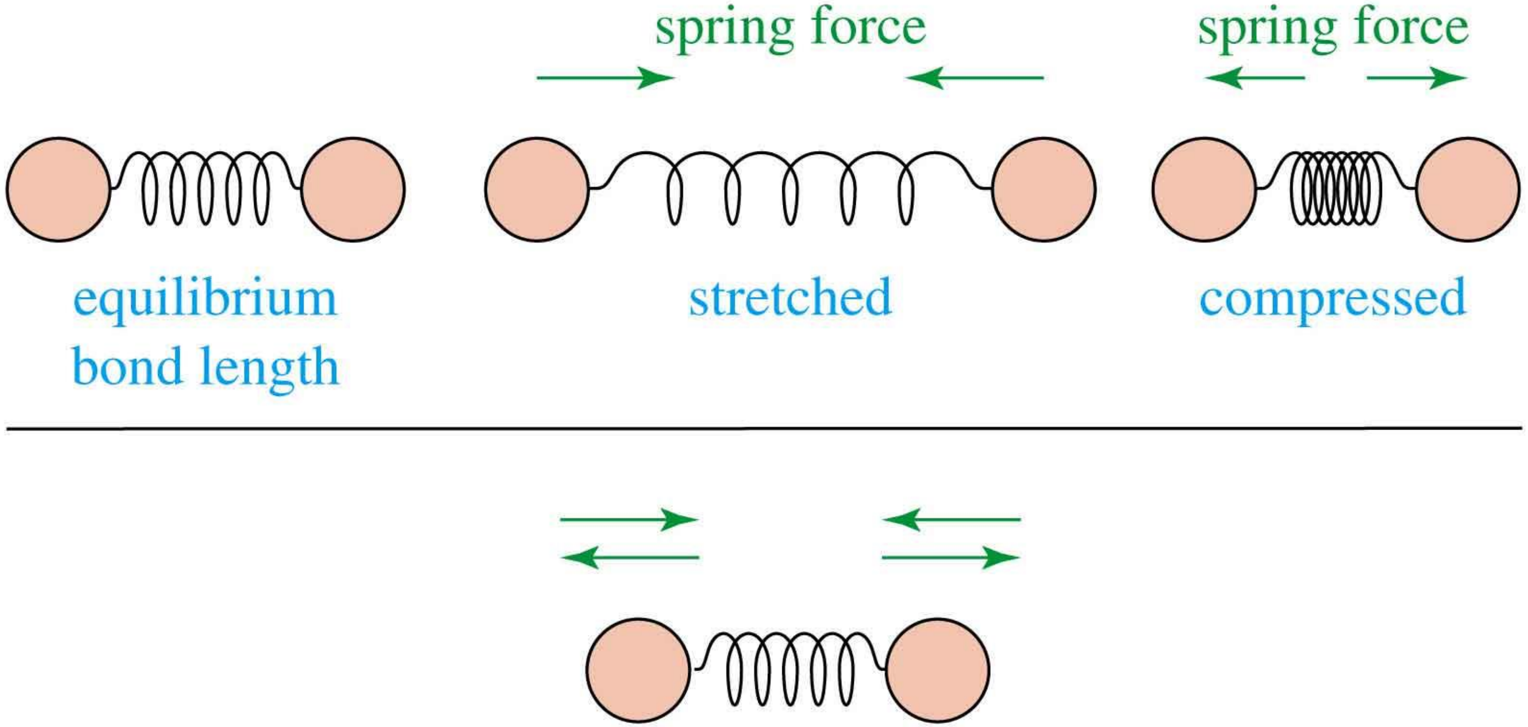


The IR Region

- Just below red in the visible region.
- Wavelengths usually 2.5-25 μm.
- More common units are wavenumbers, or cm^{-1}, the reciprocal of the wavelength in centimeters.
- Wavenumbers are proportional to frequency and energy.

Molecular Vibrations

Covalent bonds vibrate at only certain allowable frequencies.



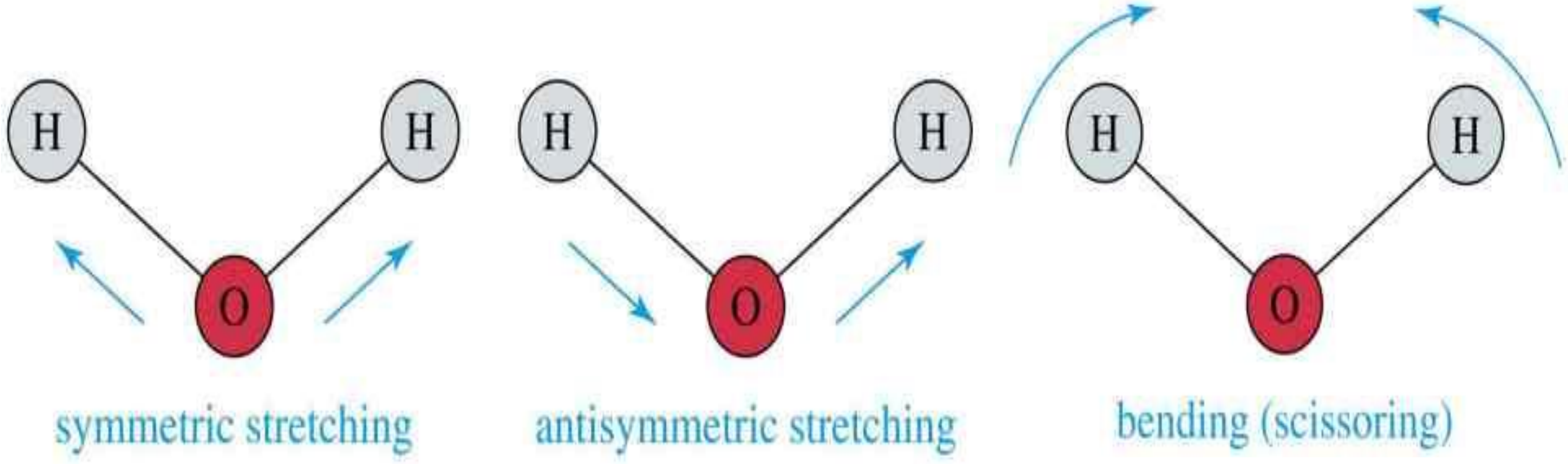
Stretching Frequencies

Bond		Bond Energy [kcal (kJ)]		Stretching Frequency (cm^{-1})	
		Frequency dependence on atomic masses			
C—H	heavier atoms ↓	100 (420)		3000	$\bar{\nu}$ decreases ↓
C—D		100 (420)		2100	
C—C		83 (350)		1200	
		Frequency dependence on bond energies			
C—C		83 (350)	stronger bond ↓	1200	$\bar{\nu}$ increases ↓
C=C		146 (611)		1660	
C≡C		200 (840)		2200	

- Frequency decreases with increasing atomic weight.
- Frequency increases with increasing bond energy.

Vibrational Modes

Nonlinear molecule with *n* atoms usually has 3*n* - 6 fundamental vibrational modes.

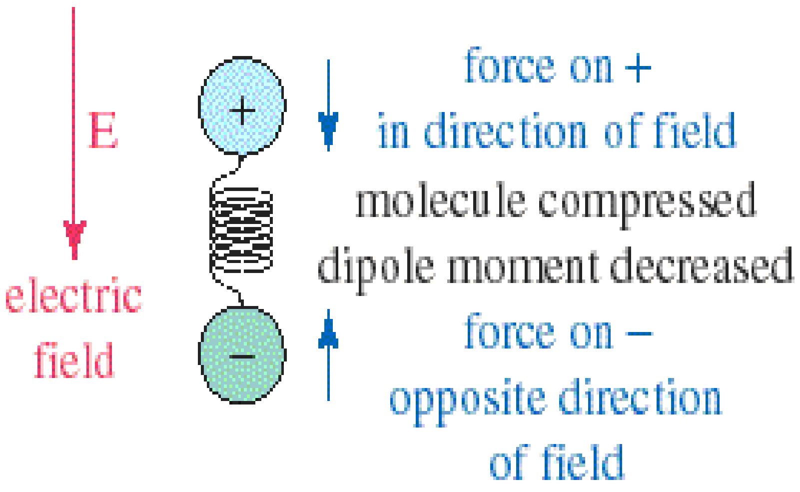


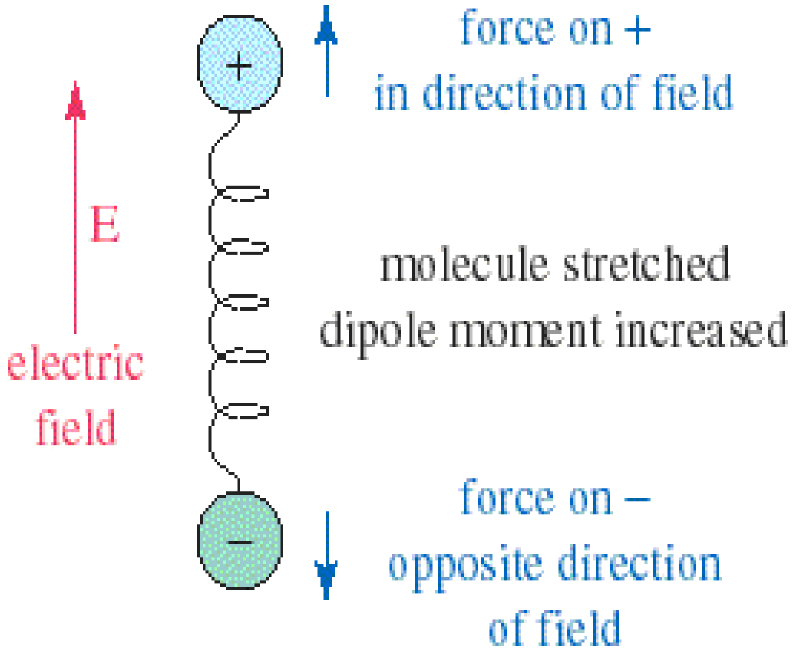
Fingerprint of Molecule

- Whole-molecule vibrations and bending vibrations are also quantitized.
- No two molecules will give exactly the same IR spectrum (except enantiomers).
- Simple stretching: 1600-3500 cm^{-1}.
- Complex vibrations: 600-1400 cm^{-1}, called the "fingerprint region."

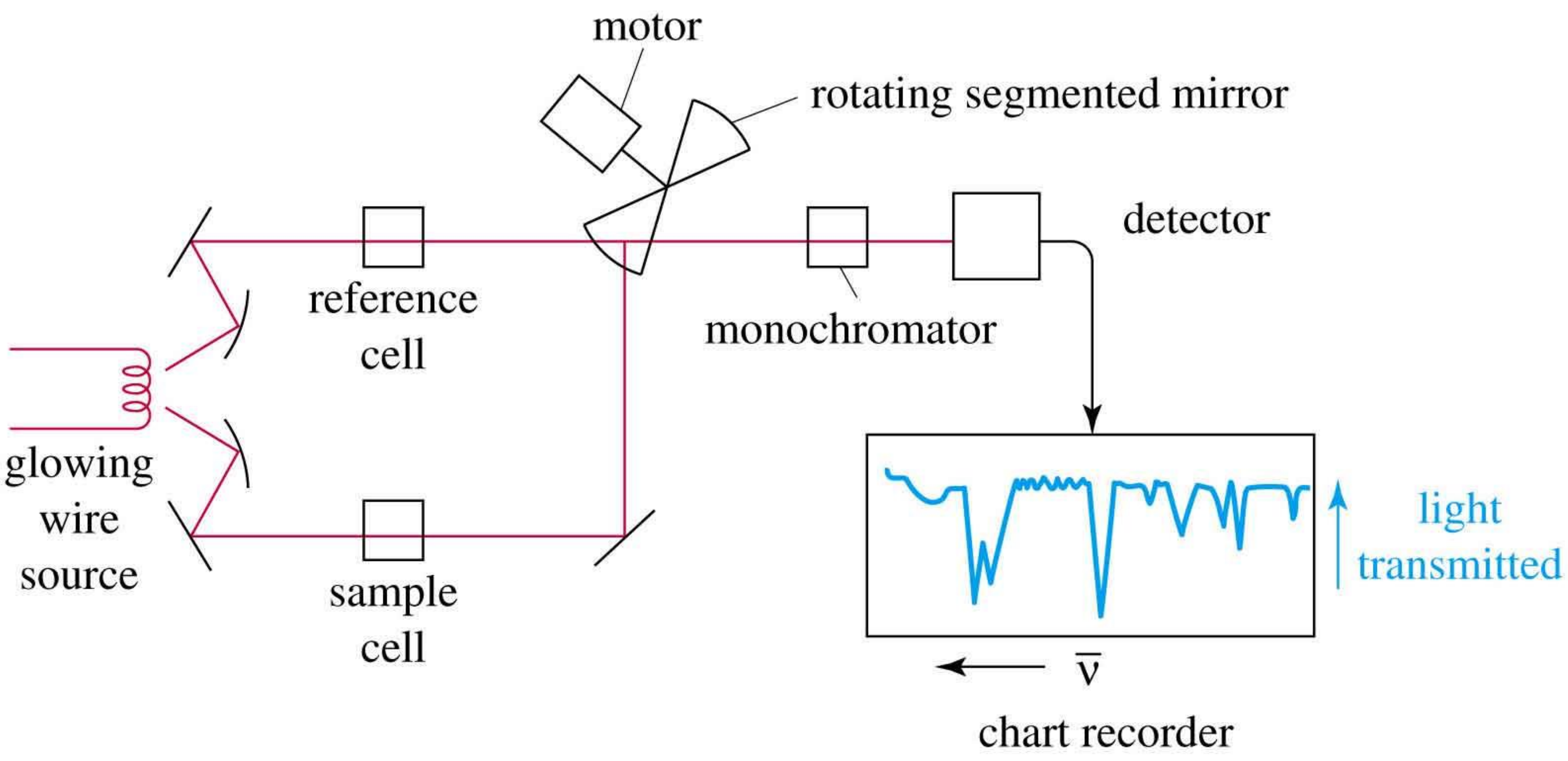
IR-Active and Inactive

- A polar bond is usually IR-active.
- A nonpolar bond in a symmetrical molecule will absorb weakly or not at all.



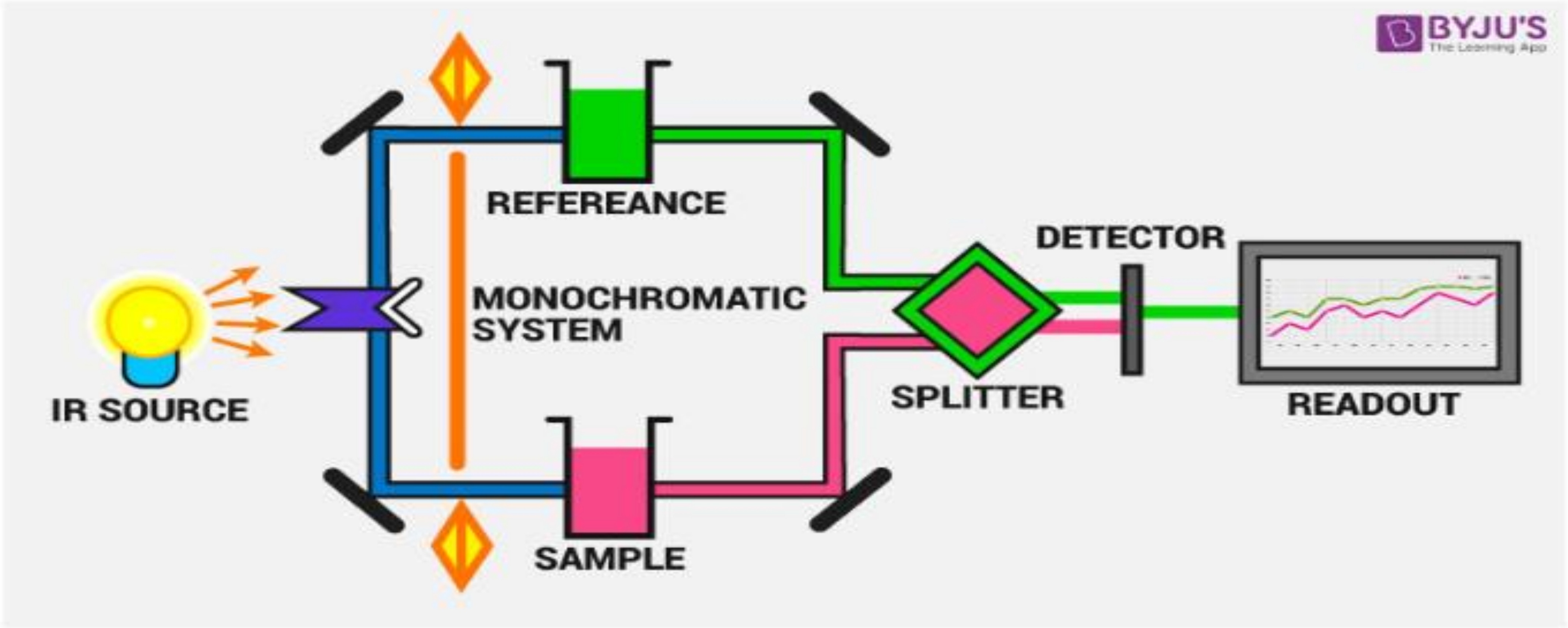


An Infrared Spectrometer



IR Spectroscopy Instrumentation

The instrumentation of infrared spectroscopy is illustrated below. First, a beam of IR light from the source is split into two and passed through the reference and the sample respectively.



Now, both of these beams are reflected to pass through a splitter and then through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector.

Which lamp is used in IR spectroscopy?
For infrared spectroscopy, a Globar is employed as a thermal light source. It's a silicon carbide rod with a diameter of 5 to 10 mm and a length of 20 to 50 mm that's been electrically heated to 1,000 to 1,650°C (1,830 to 3,000 degrees Fahrenheit).
Which solvent are used in IR spectroscopy?
Carbon Tetrachloride (CCl_4) and Carbon Disulfide (CD) are the most prevalent solvents (CS_2). Solvents for polar materials include chloroform, methylene chloride, acetonitrile, and acetone. Solids reduced to fine particles can be analysed as a thin paste or mull.
Carbon tetra chloride is used as a solvent in IR spectroscopy because it absorbs at a shallow frequency below 1600 cm^{-1}. Moreover, carbon tetrachloride is a non-polar solvent, i.e. it does interfere with the absorption spectra.
Can we use water in IR spectroscopy?
Because water has two high infrared absorption peaks, it cannot be employed as a solvent for IR spectroscopy. Also, water is a polar solvent that dissolves alkali halide disks, which are extensively employed in IR.

Sample Preparation

Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous).

Liquid samples can be sandwiched between two plates of a 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 do not introduce any lines onto the spectra.

Sampling of solids

Various techniques used for preparing solid samples are as follows

a) **Mull technique:** In this technique, the finely crushed sample is mixed with Nujol (mulling agent) in n a marble or agate mortar, with a pestle to make a thick paste. A thin film is applied onto the salt plates. This is then mounted in a path of IR beam and the spectrum is recorded.

b) **Solid run in Solution –** In this technique, solid sample may be dissolved in a non-aqueous solvent provided that there is no chemical interaction with the solvent and the solvent is not absorbed in the range to be studied. A drop of solution is placed on the surface of alkali metal disc and solvent is evaporated to dryness leaving a thin film of the

c) **Case film technique –** If the solid is amorphous in nature then the sample is deposited on the surface of a KBr or NaCl cell by evaporation of a solution of the solid and ensured that the film is not too thick to pass the radiation.

d) **Pressed pellet technique –** In this technique, a small amount of finely ground solid sample is mixed with 100 times its weight of potassium bromide and compressed into a thin transparent pellet using a hydraulic press. These pellets are transparent to IR radiation and it is used for analysis.

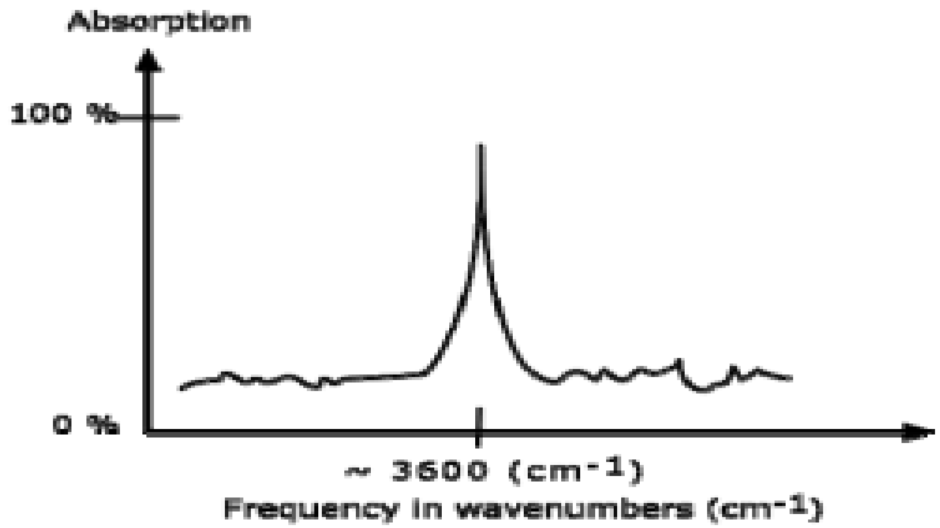
A large benchtop hydraulic press

FT-IR Spectrometer

- Uses an interferometer.
- Has better sensitivity.
- Less energy is needed from source.
- Completes a scan in 1-2 seconds.
- Takes several scans and averages them.
- Has a laser beam that keeps the instrument accurately calibrated.

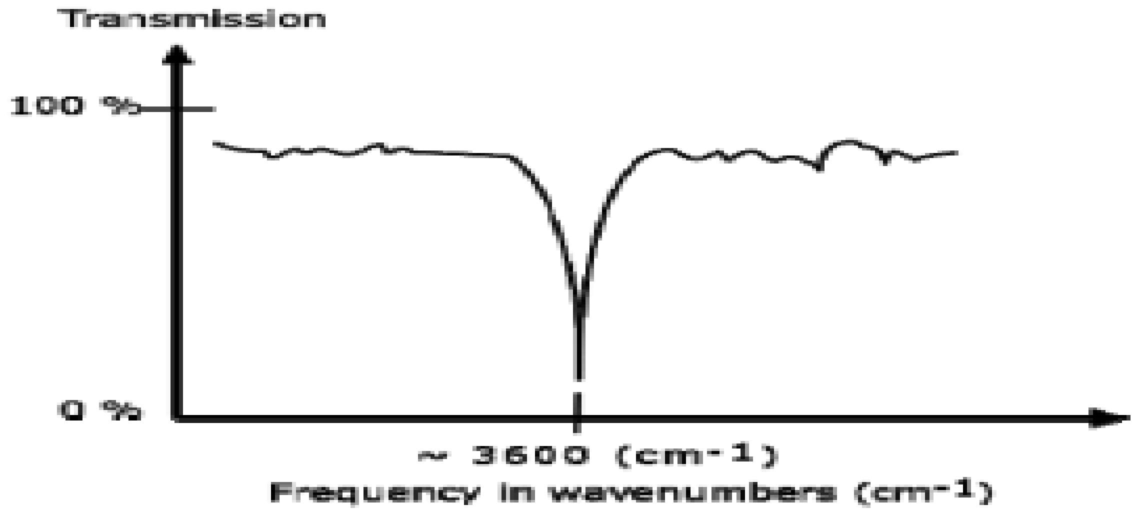
AN IR SPECTRUM IN ABSORPTION MODE

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.

The absorption band intensity depends on:

1) The size of the change in dipole moment associated with the vibration.

Change in dipole moment Absorption intensity

OH > NH > CH

2) The number of bonds responsible for the absorption.

Ex. C-H stretch is more intense for Octyl iodide (17 C-H) than for Methyl iodide (3 C-H)

3) The sample concentration. Concentrated samples have greater numbers of absorbing molecules.

Vibrational frequency or wave number depend upon the following:

1. BOND STRENGTH

The frequency of vibration will be directly proportional to strength of bond (K).

E.g.- Stretching vibration of triple bond will appear at high frequency than that of either a double or single bond

	C≡C	C=C	C-C
Frequency=	2150 cm^{-1}	650 cm^{-1}	200 cm^{-1}

2. MASS :

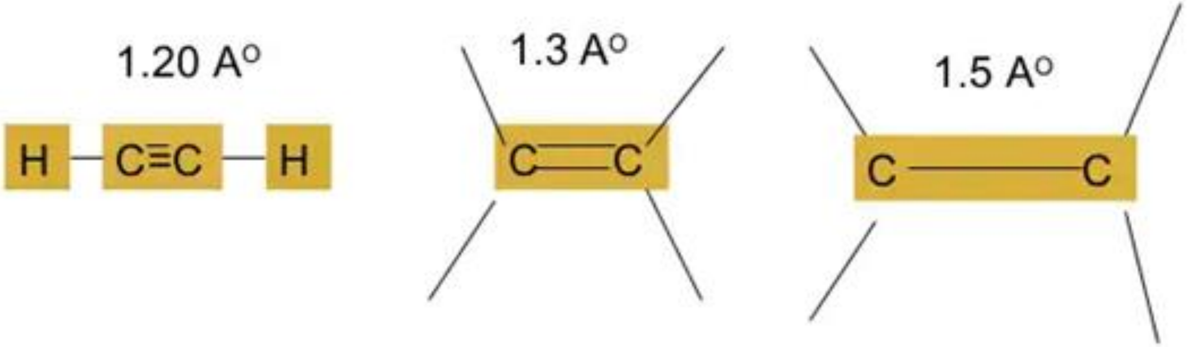
Vibrational frequency is inversely proportional to the masses at the ends of the bond.

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

3. Hybridization:

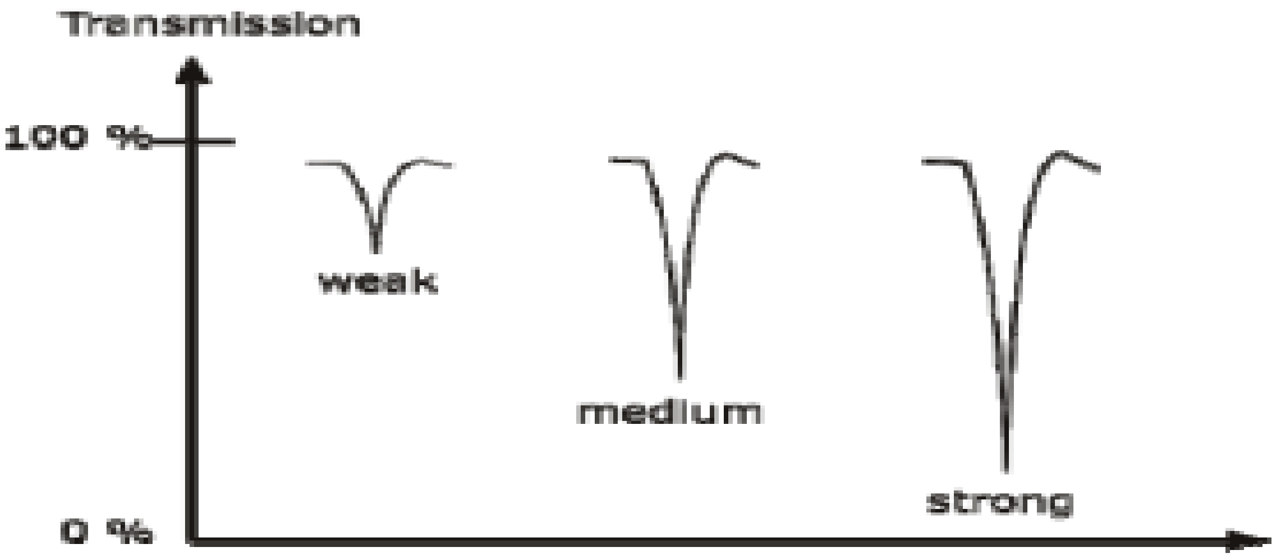
- Hybridization affects the bond strength or force constant(K).
- Bonds are stronger in order :

SP	>	SP^2	>	sp^3
3300 cm^{-1}		3100 cm^{-1}		2900 cm^{-1}



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.

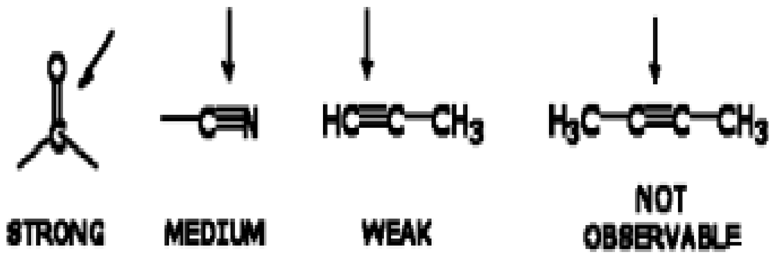


INFRARED ACTIVE BONDS

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:

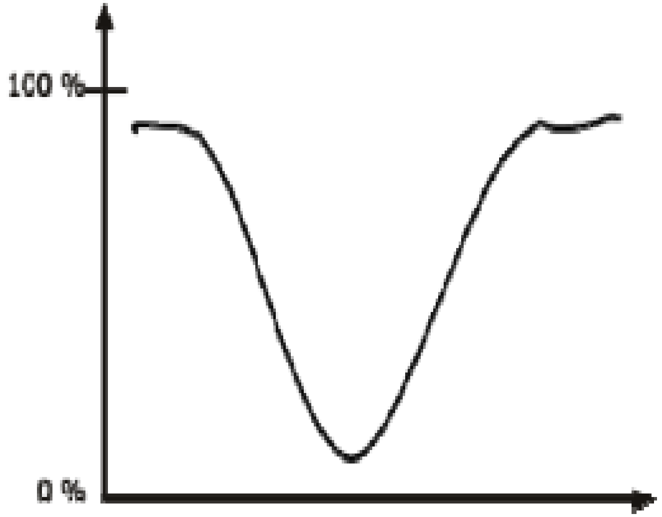
- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.



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.

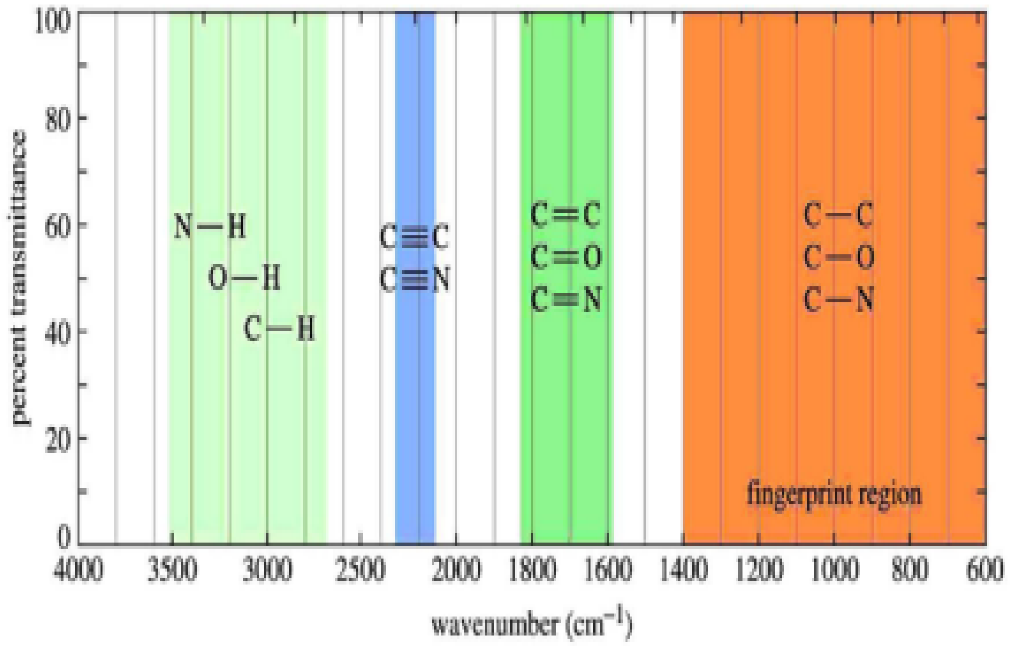


INFORMATION OBTAINED FROM IR SPECTRA

- 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

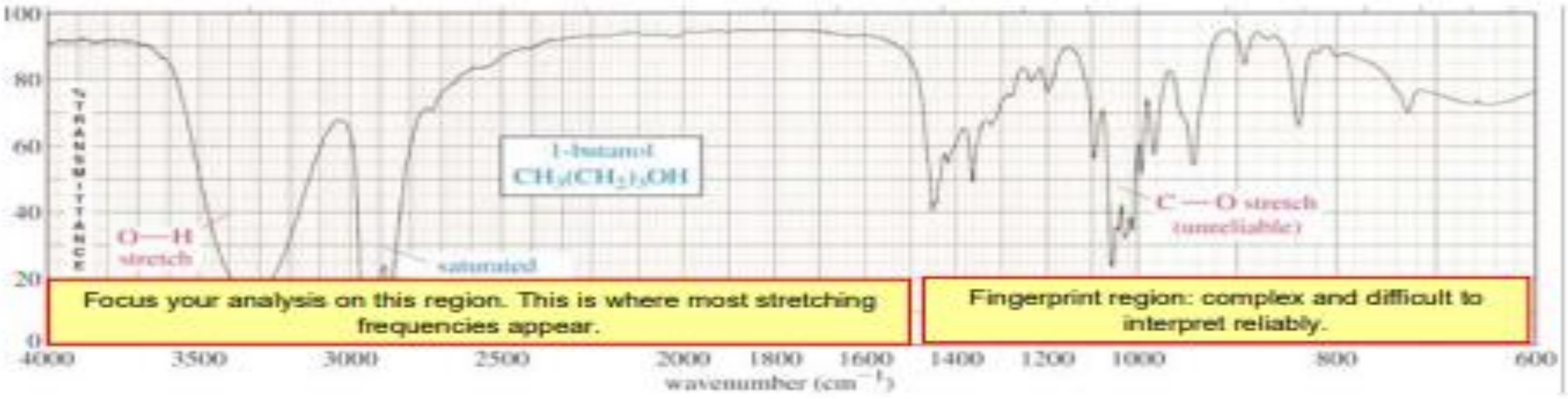
The typical IR absorption range for covalent bonds is **600 - 4000 cm^{-1}**. The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example a sharp band around 2200-2400 cm^{-1} would indicate the possible presence of a C-N or a C-C triple bond.



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

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}.



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

Carbon-Carbon Bond Stretching

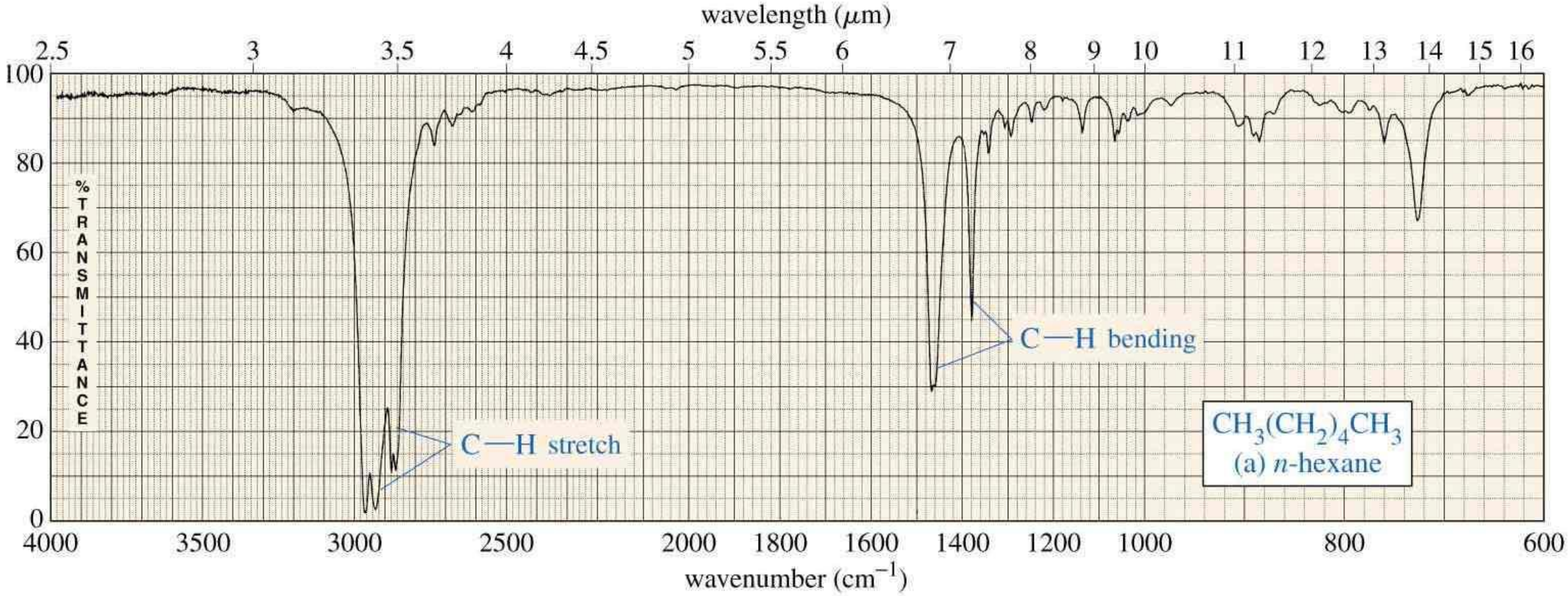
- Stronger bonds absorb at higher frequencies:
  - C-C 1200 cm^{-1}
  - C=C 1660 cm^{-1}
  - C≡C 2200 cm^{-1} (weak or absent if internal)
- Conjugation lowers the frequency:
  - isolated C=C 1640-1680 cm^{-1}
  - conjugated C=C 1620-1640 cm^{-1}
  - aromatic C=C approx. 1600 cm^{-1}

Carbon-Hydrogen Stretching

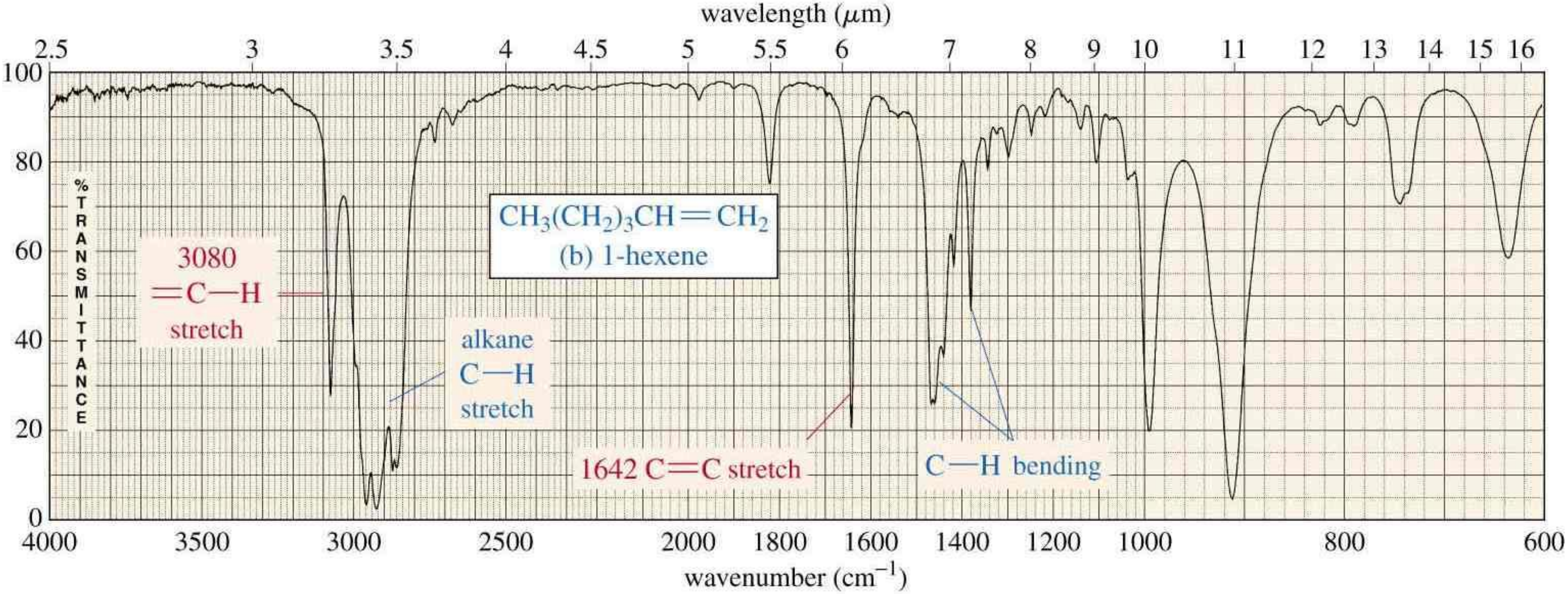
Bonds with more *s* character absorb at a higher frequency.

- *sp*^{3} C-H, just below 3000 cm^{-1} (to the right)
- *sp*^{2} C-H, just above 3000 cm^{-1} (to the left)
- *sp* C-H, at 3300 cm^{-1}

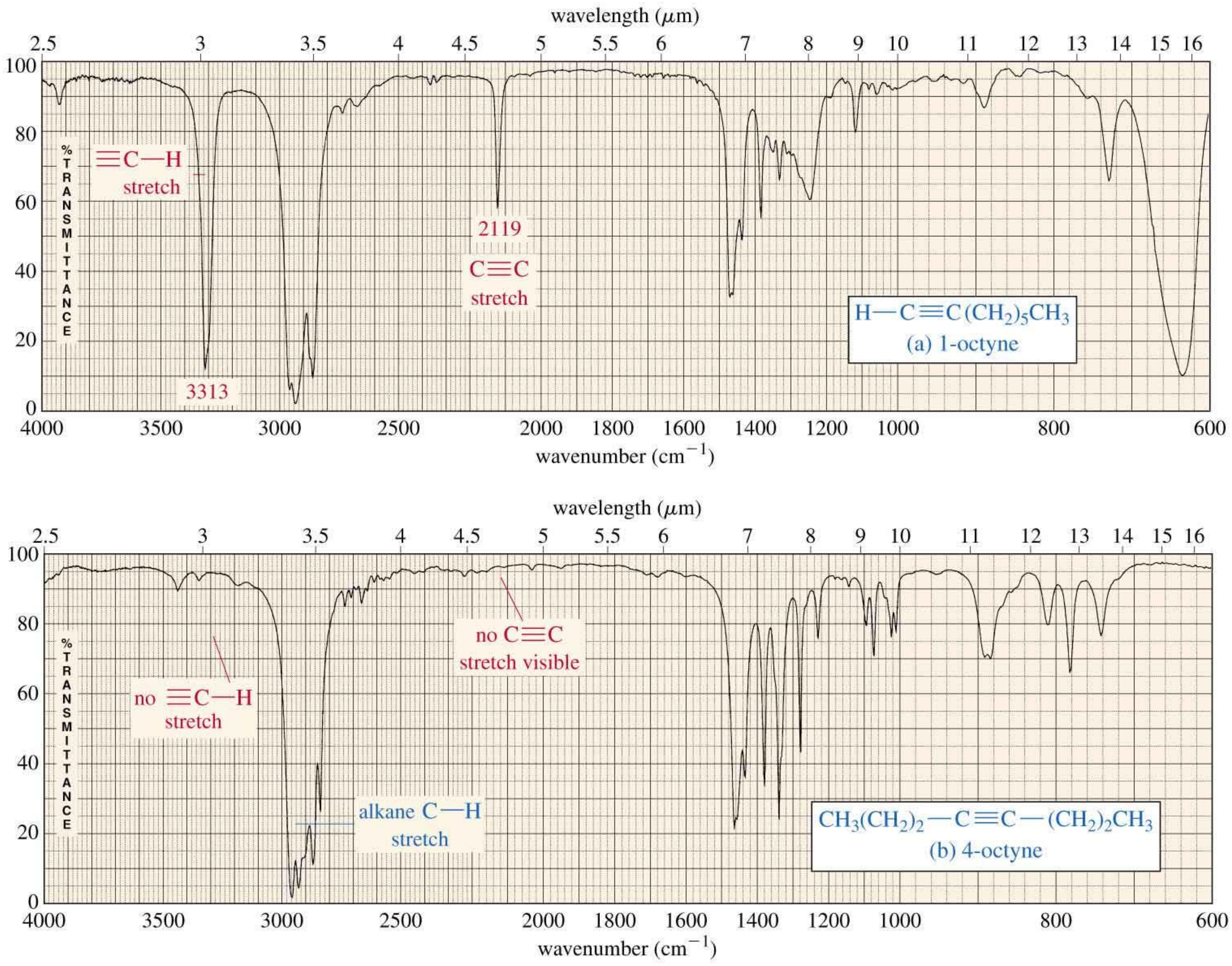
An Alkane IR Spectrum



An Alkene IR Spectrum



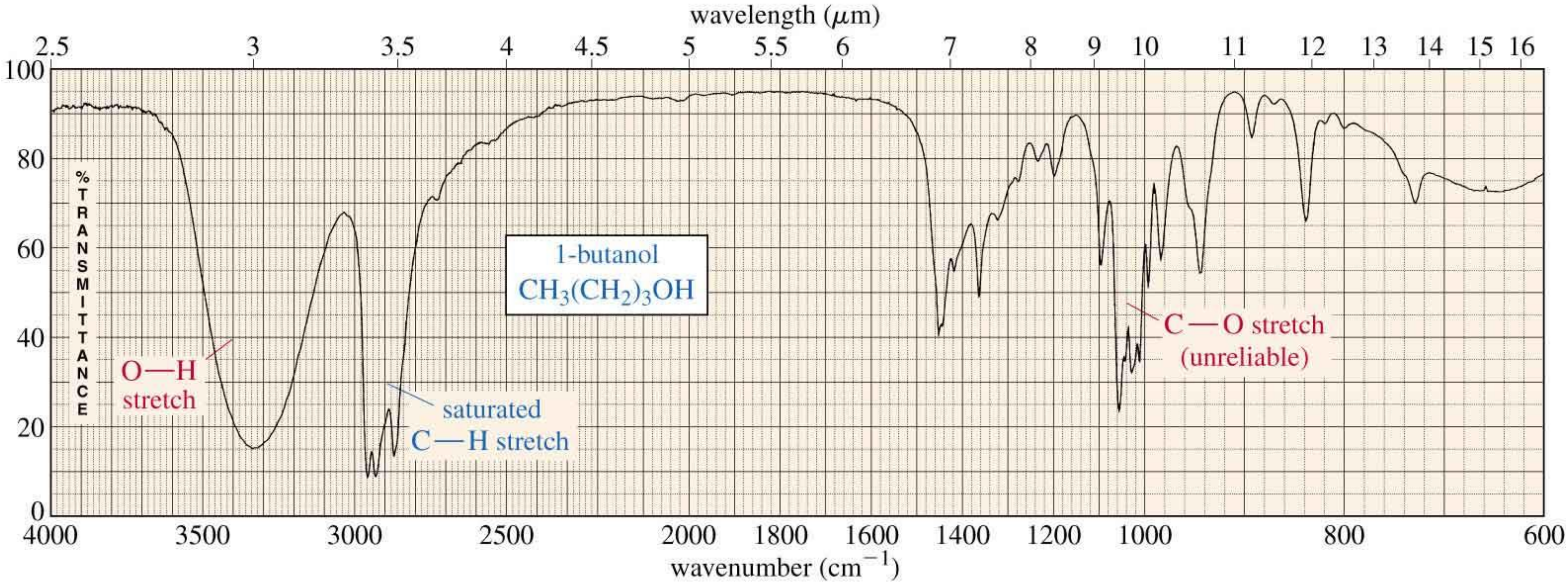
An Alkyne IR Spectrum



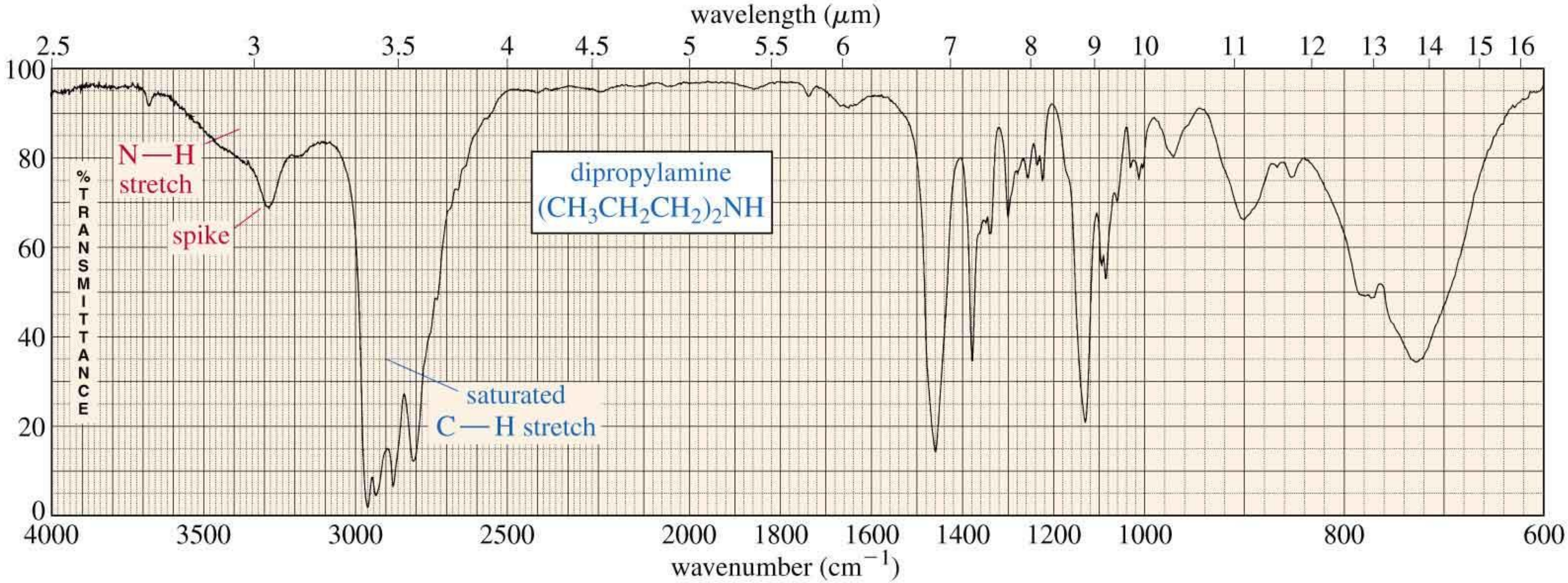
O-H and N-H Stretching

- Both of these occur around 3300 cm^{-1}, but they look different.
  - Alcohol O-H, broad with rounded tip.
  - Secondary amine (R_2NH), broad with one sharp spike.
  - Primary amine (RNH_2), broad with two sharp spikes.
  - No signal for a tertiary amine (R_3N)

An Alcohol IR Spectrum



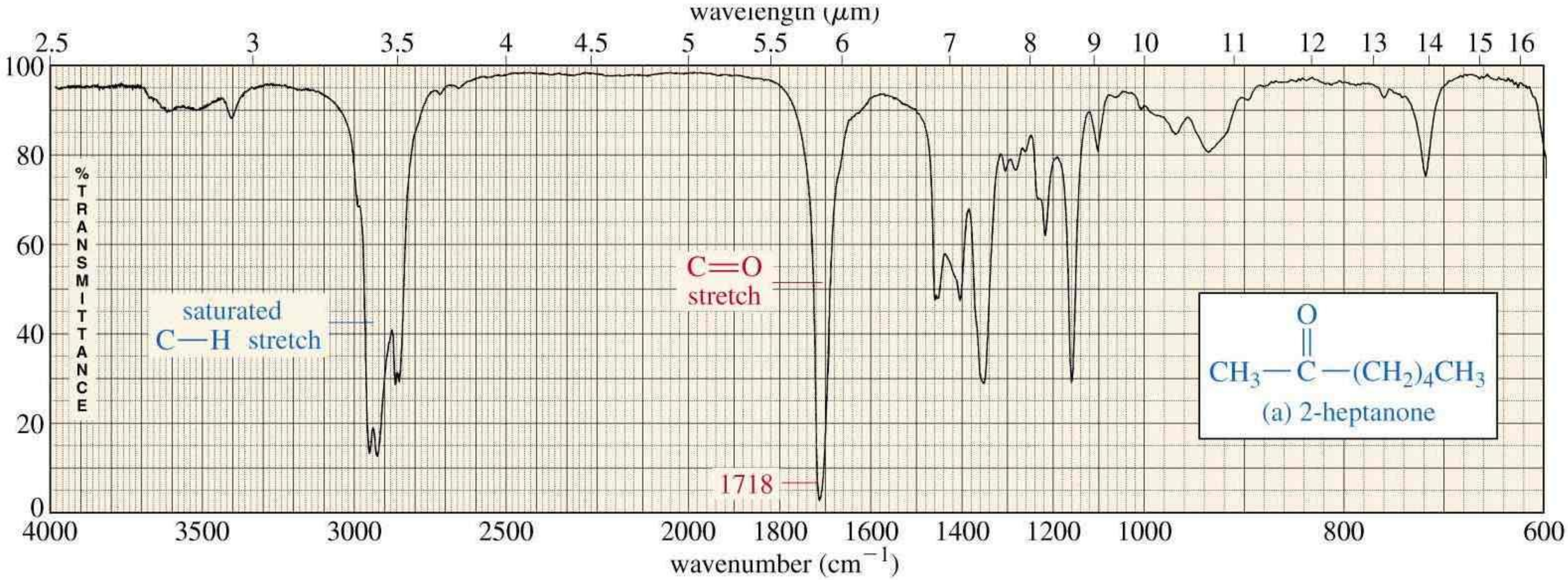
An Amine IR Spectrum



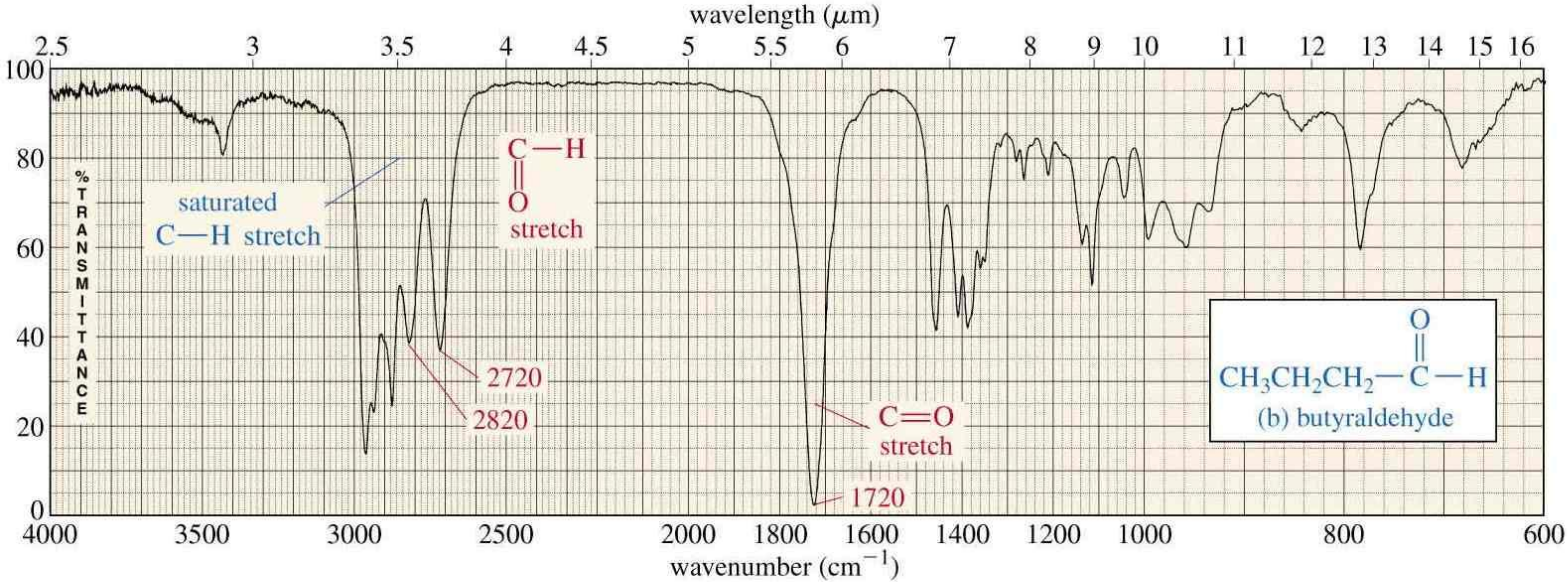
Carbonyl Stretching

- The C=O bond of simple ketones, aldehydes, and carboxylic acids absorb around 1710 cm^{-1}.
- Usually, it’s the strongest IR signal.
- Carboxylic acids will have O-H also.
- Aldehydes have two C-H signals around 2700 and 2800 cm^{-1}.

A Ketone IR Spectrum

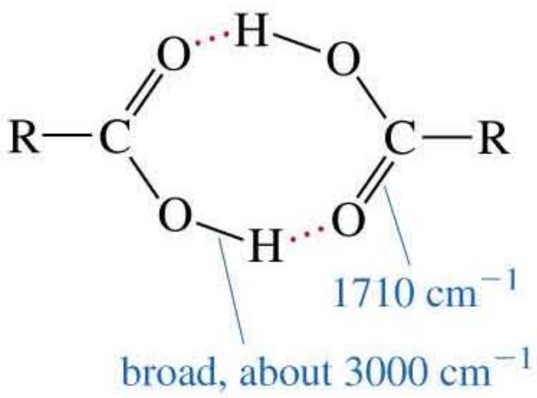


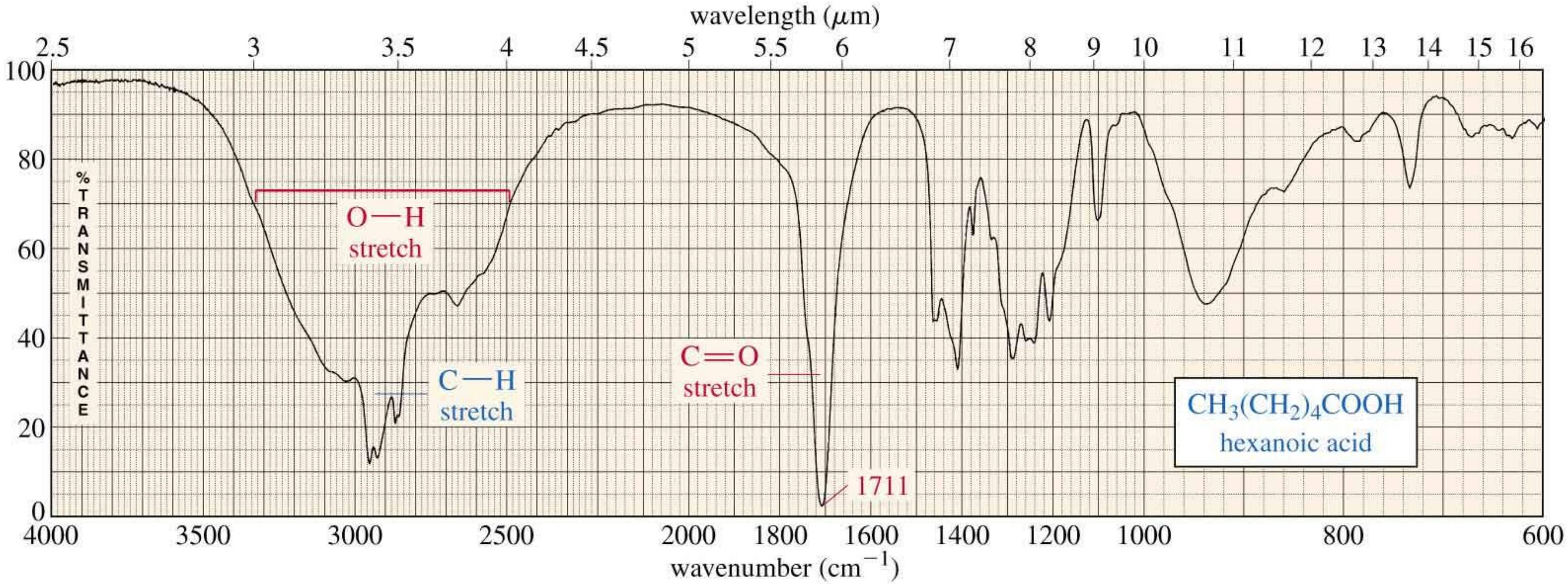
An Aldehyde IR Spectrum



O-H Stretch of a Carboxylic Acid

This O-H absorbs broadly, 2500-3500 cm^{-1}, due to strong hydrogen bonding.

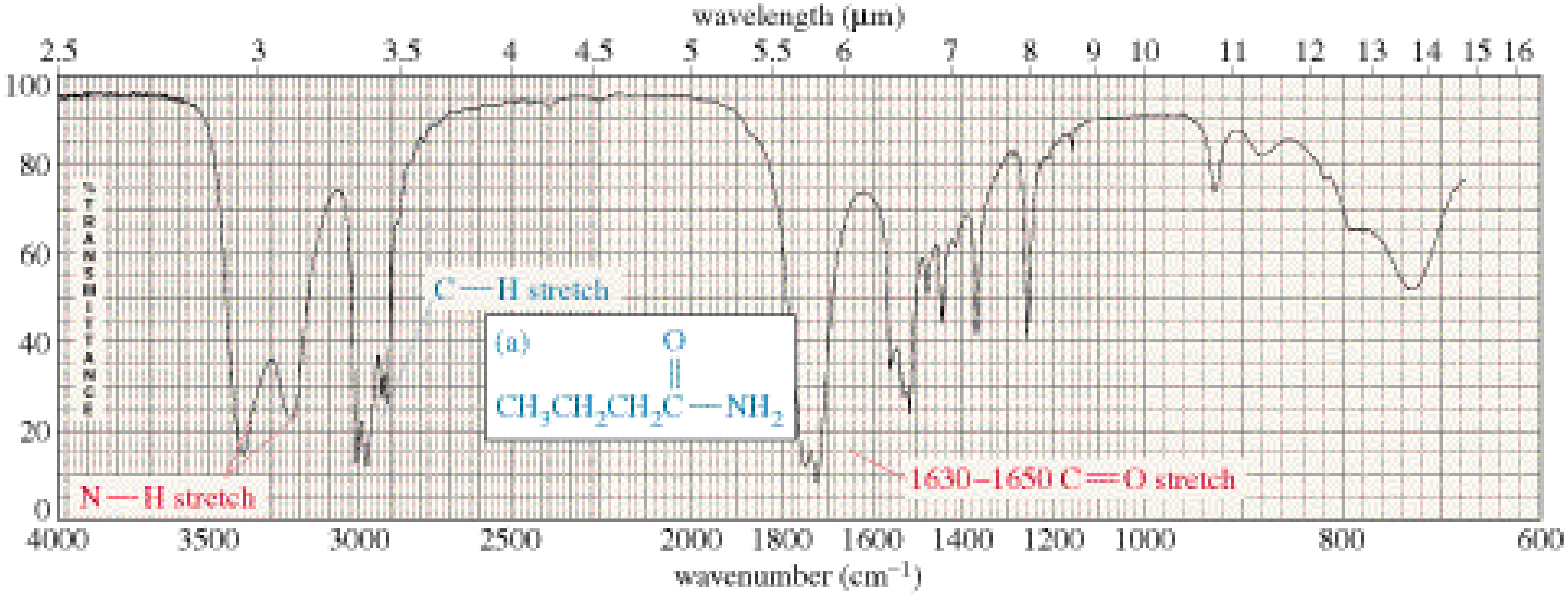




Variations in C=O Absorption

- Conjugation of C=O with C=C lowers the stretching frequency to ~1680 cm^{-1}.
- The C=O group of an amide absorbs at an even lower frequency, 1640-1680 cm^{-1}.
- The C=O of an ester absorbs at a higher frequency, ~1730-1740 cm^{-1}.
- Carbonyl groups in small rings (5 C's or less) absorb at an even higher frequency.

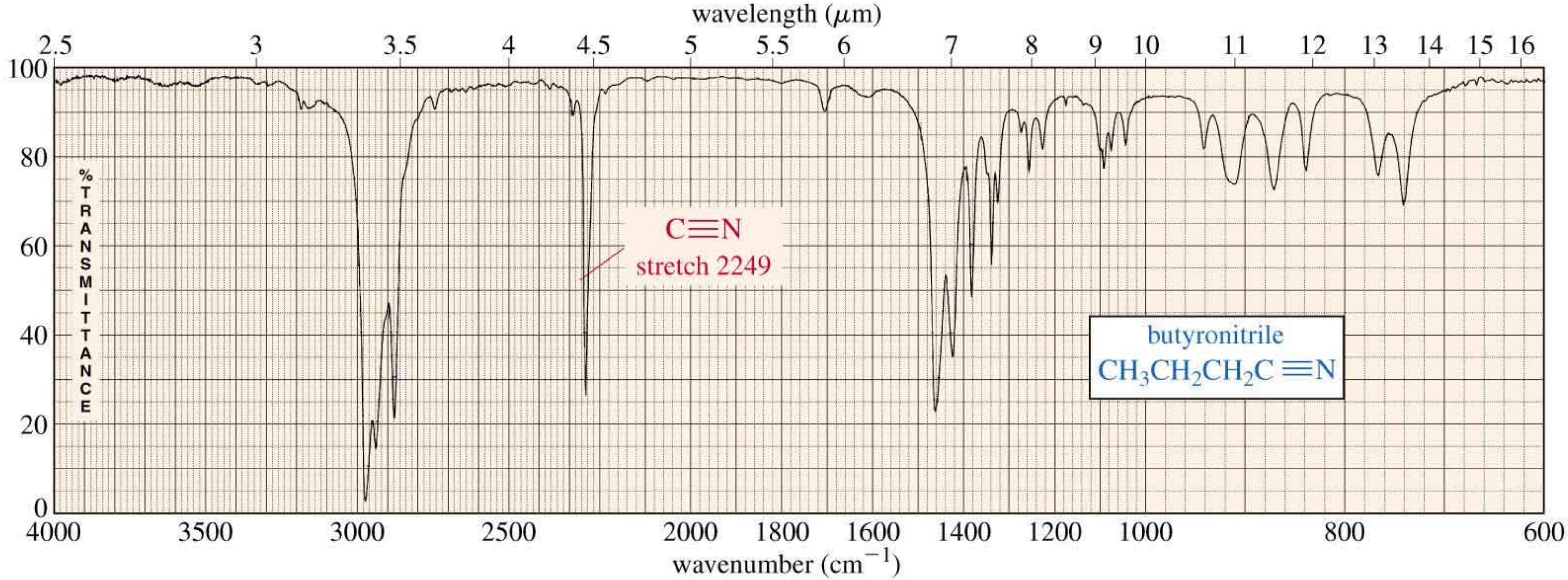
An Amide IR Spectrum



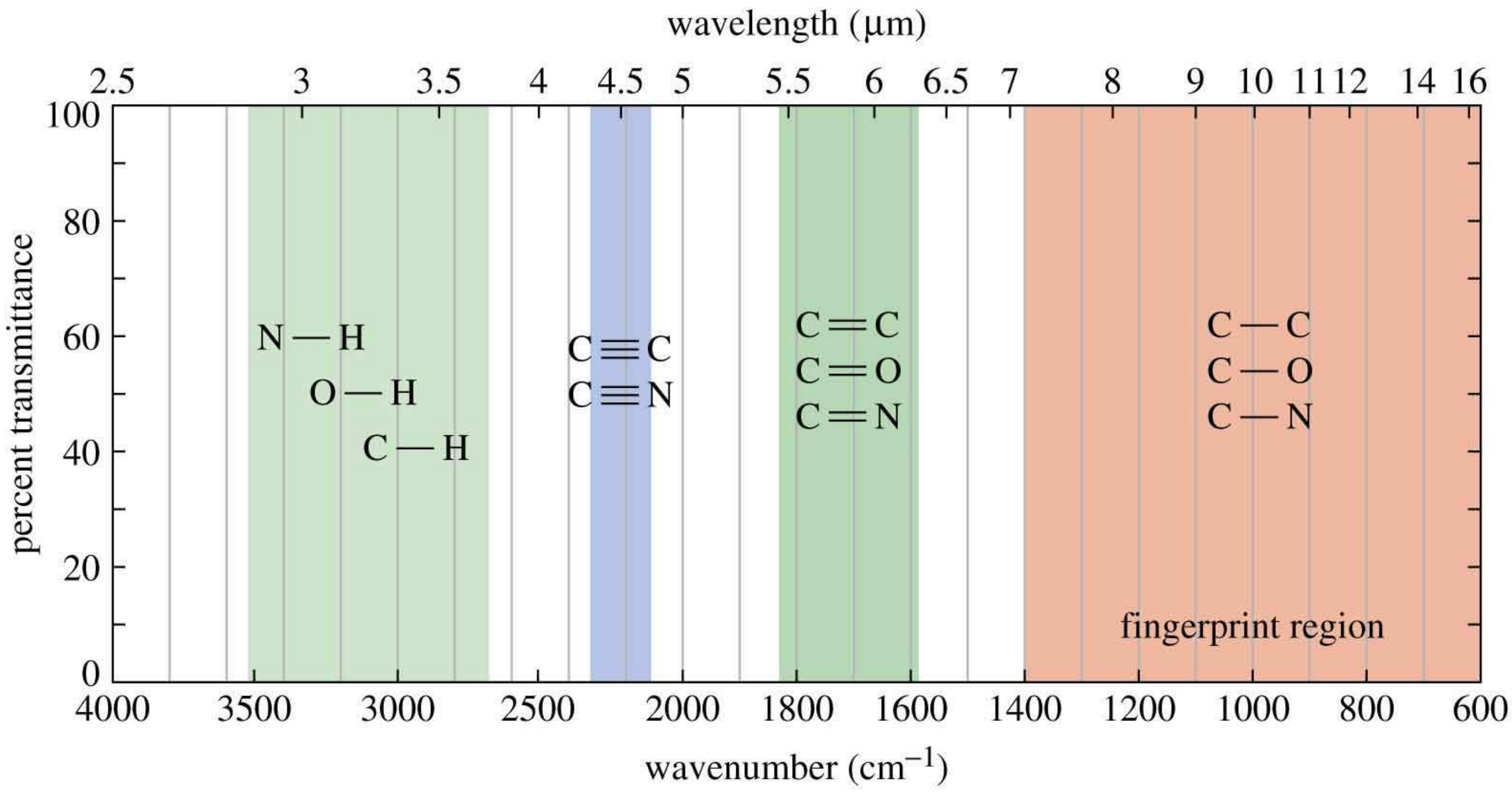
Carbon – Nitrogen Stretching

- C - N absorbs around 1200 cm^{-1}.
- C = N absorbs around 1660 cm^{-1} and is much stronger than the C = C absorption in the same region.
- C $\equiv$ N absorbs strongly just *above* 2200 cm^{-1}. The alkyne C $\equiv$ C signal is much weaker and is just *below* 2200 cm^{-1} .

A Nitrile IR Spectrum



Summary of IR Absorptions

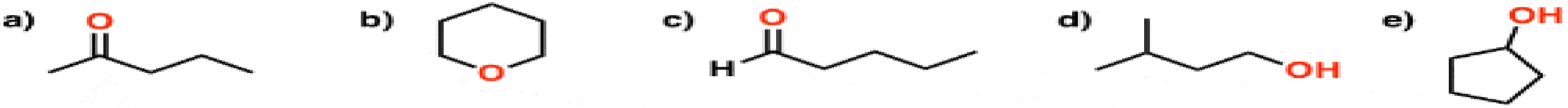


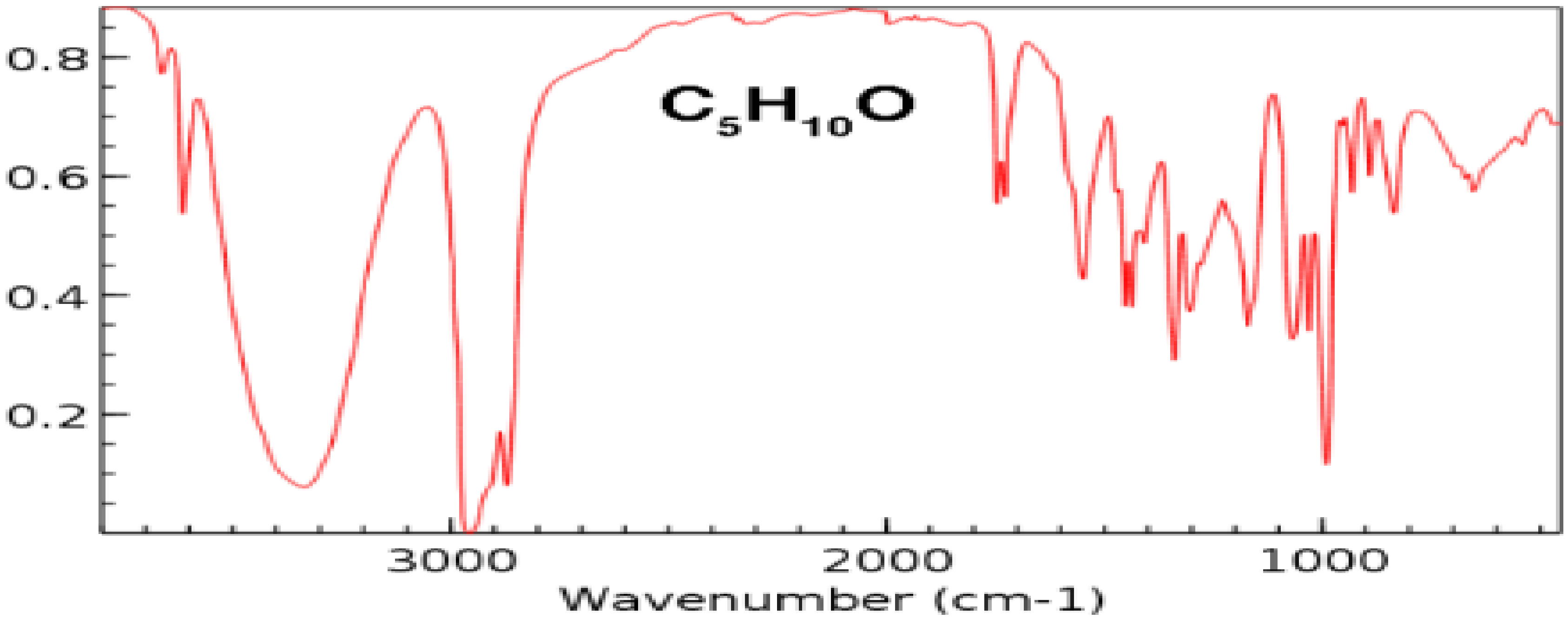
Strengths and Limitations

- IR alone cannot determine a structure.
- Some signals may be ambiguous.
- The functional group is usually indicated.
- The *absence* of a signal is definite proof that the functional group is absent.
- Correspondence with a known sample's IR spectrum confirms the identity of the compound.

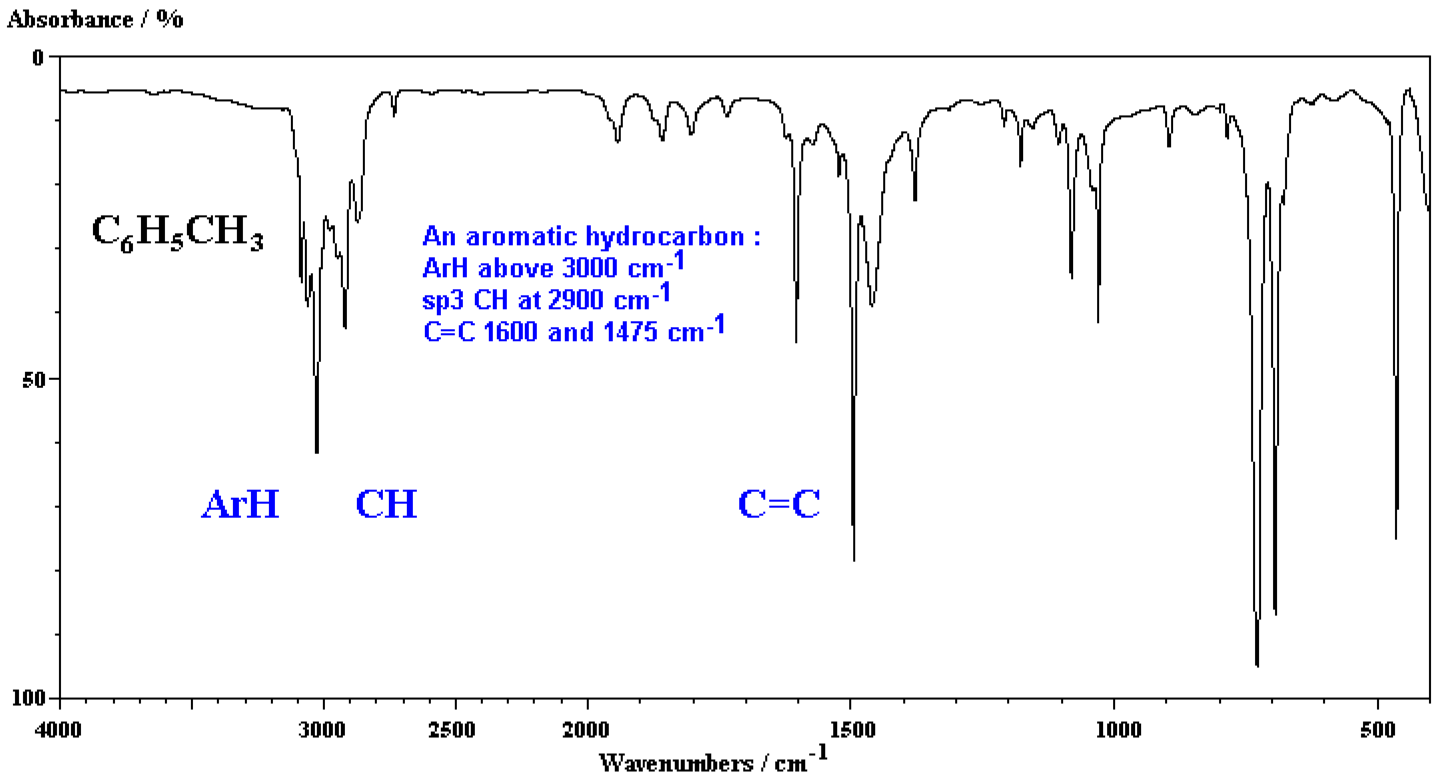
e

Which of these molecules best corresponds to the IR spectrum below?



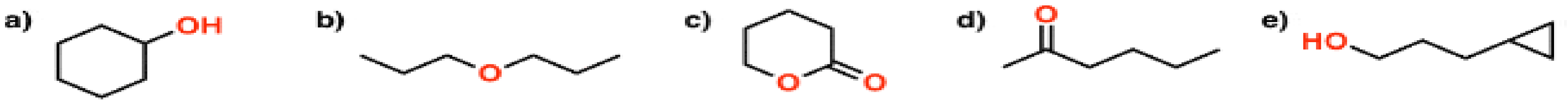


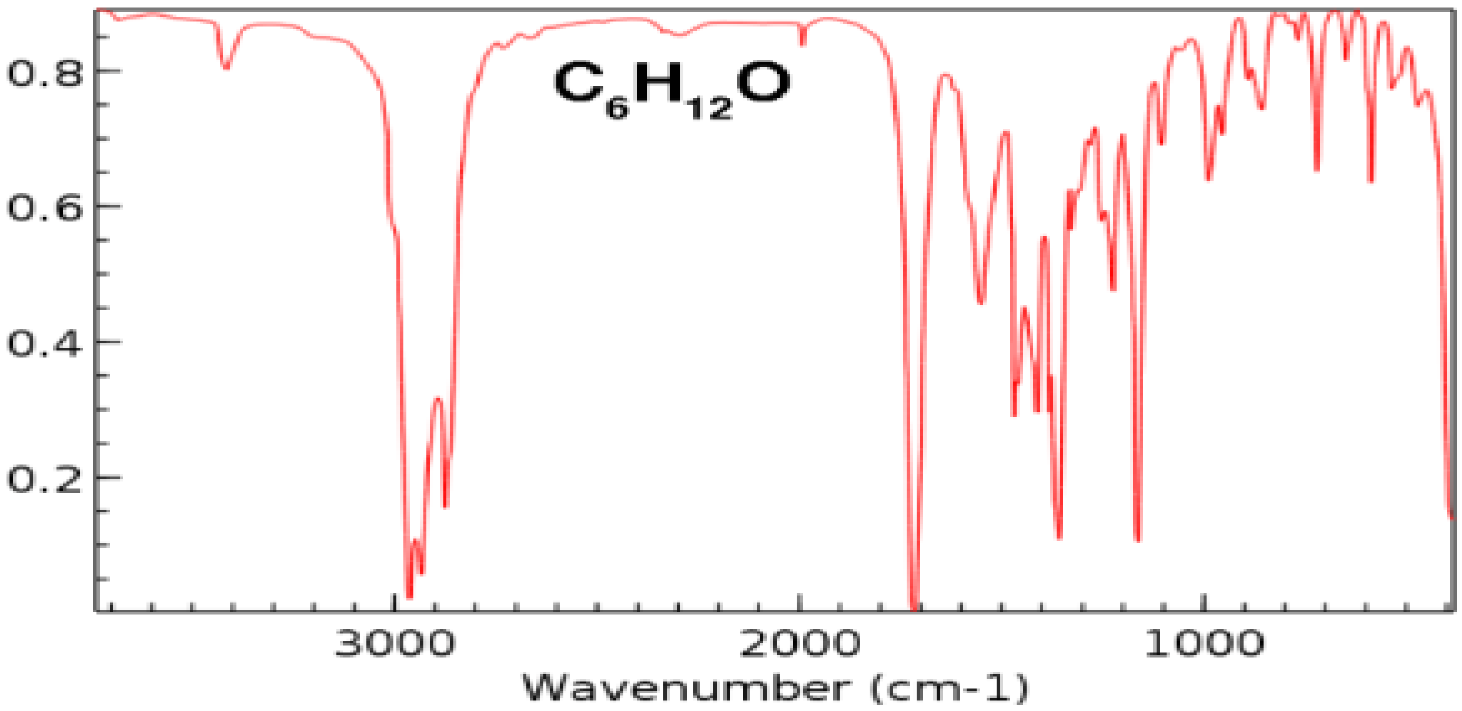
toluene, we can see both the aromatic and aliphatic CH stretches, and two absorptions for the aromatic C=C stretches.



d

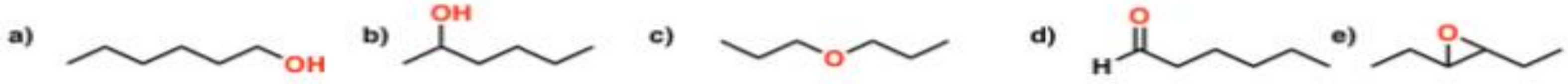
Which of these molecules best corresponds to the IR spectrum below?

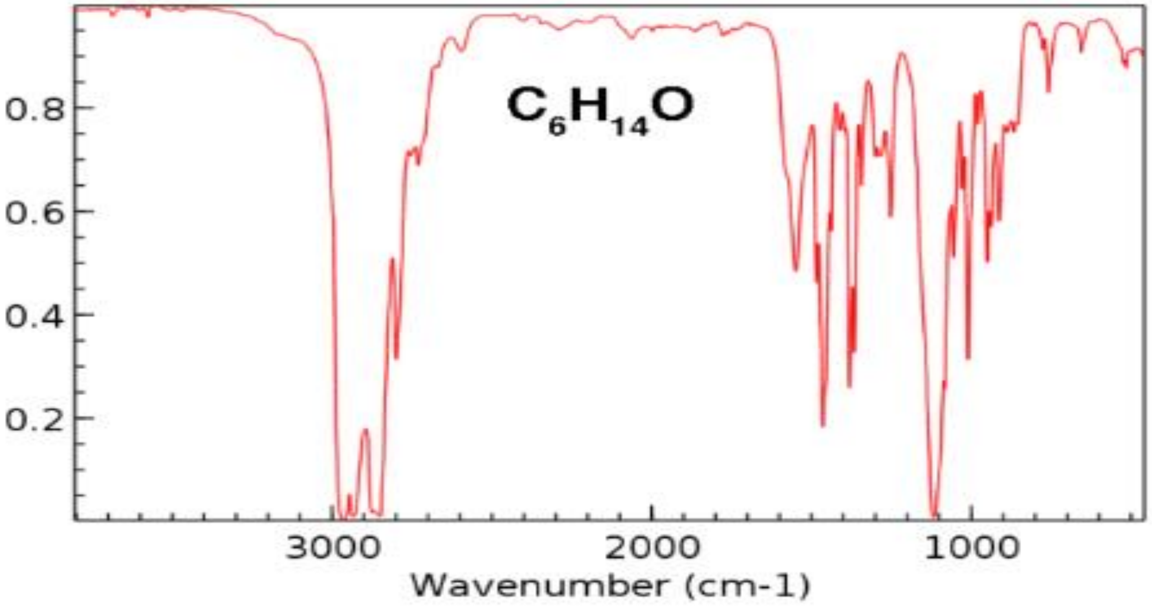




C

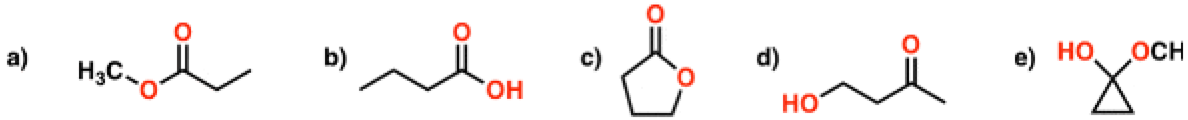
Which of these molecules best corresponds to the IR spectrum below with molecular formula $C_6H_{14}O$?

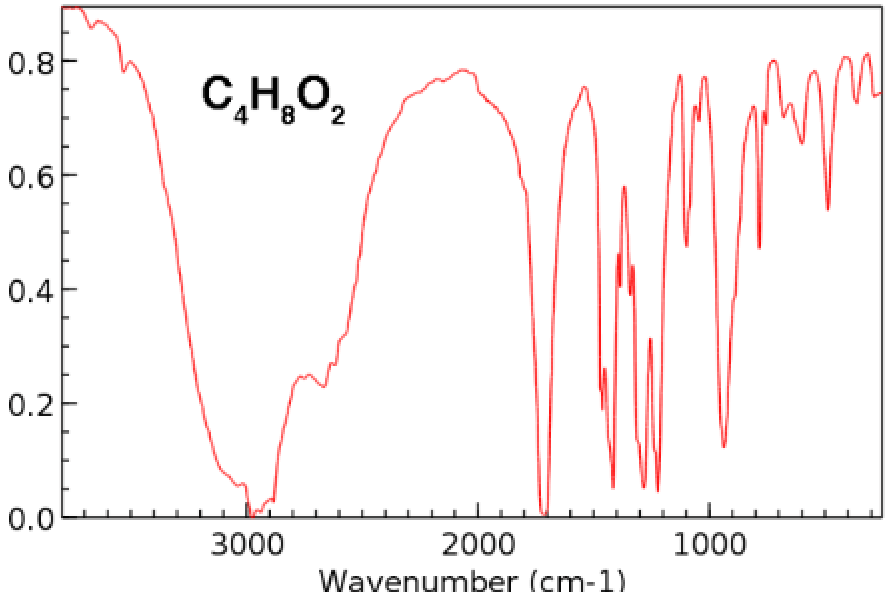




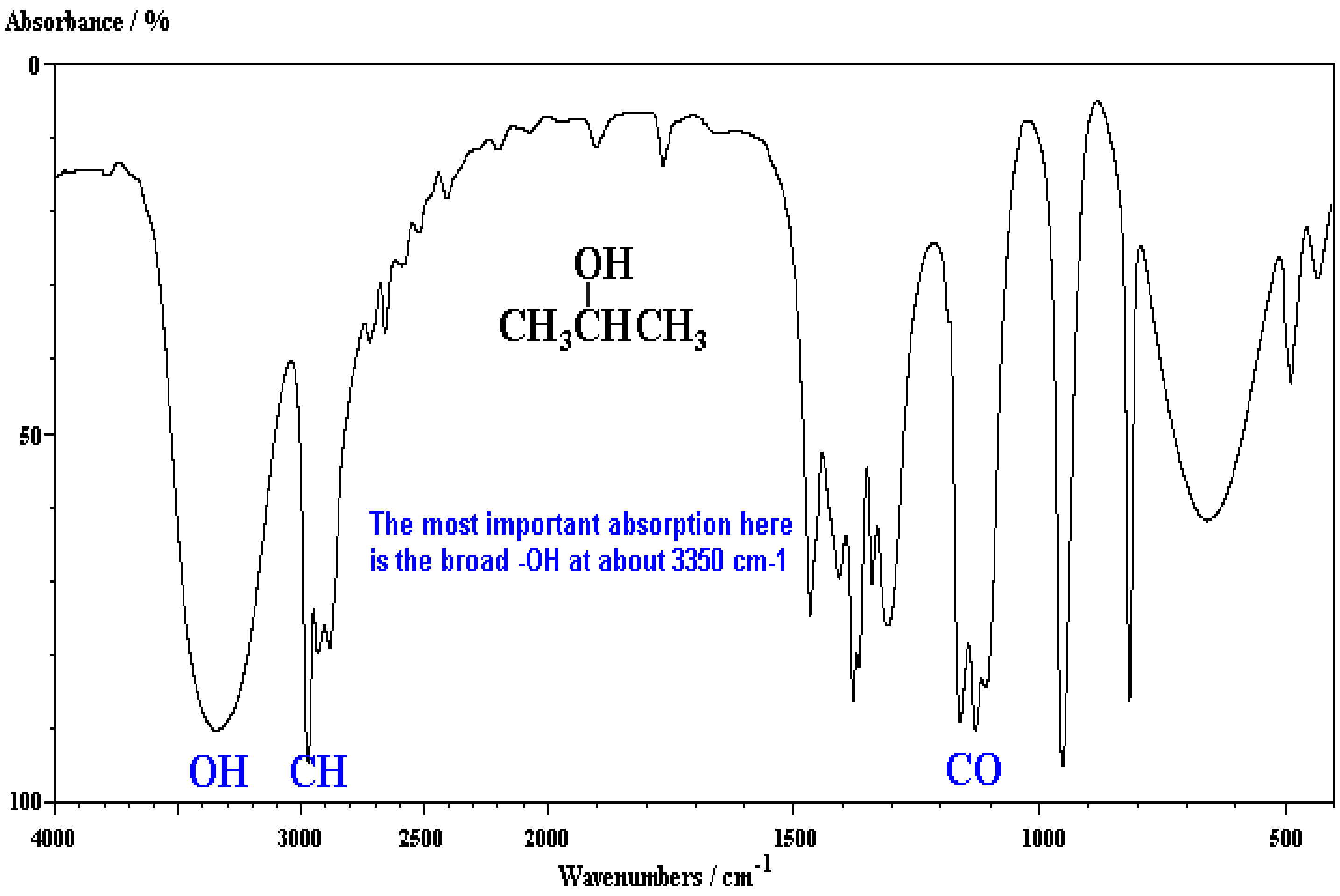
b

Which of these molecules best corresponds to the IR spectrum below?

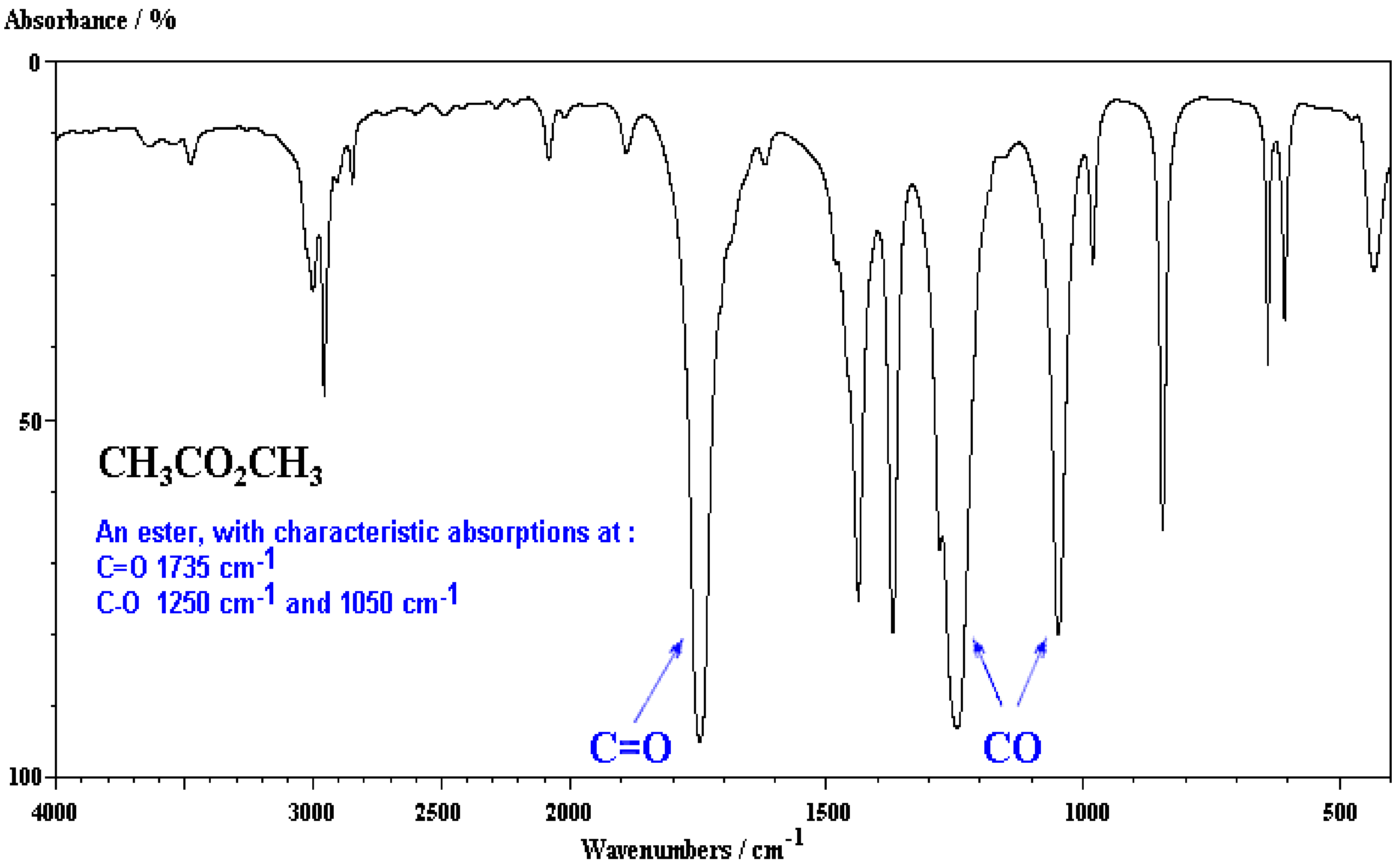




\n **alcohol**. The characteristic absorption of an alcohol, such as 2-propanol, is the broad band due to the hydrogen bonded -OH group around 3200-3400 cm



An **ester** has the following key absorptions, the C=O (here 1746 cm^{-1}) and typically two bands for the C-O (not always easy to identify, here at a sp^3 C-O and sp^2 C-O bonds.



This example is propionitrile, $CH_3CH_2C{\equiv}N$. This is is characterised by the strong and sharp C≡N at 2250 cm^{-1} (Note that this is in the same region as the alkyne C≡C).