



IR Spectroscopy



Introduction to Spectroscopy

- ❑ The study how the chemical compound interacts with different wavelengths in a given region of electromagnetic radiation is called spectroscopy.
- ❑ Using electromagnetic radiation as a probe to obtain information about atoms and molecules that are too small to see.
- ❑ The collection of measurements signals (absorbance) of the compound as a function of electromagnetic radiation is called a spectrum.
- ❑ The mechanism of absorption energy is different in the Ultraviolet, Infrared, and Nuclear magnetic resonance regions. However, the fundamental process is the absorption of certain amount of energy.
- ❑ The energy required for the transition from a state of lower energy to a state of higher energy is directly related to the frequency of electromagnetic radiation that causes the transition.
- ❑ It destroys little or no sample.

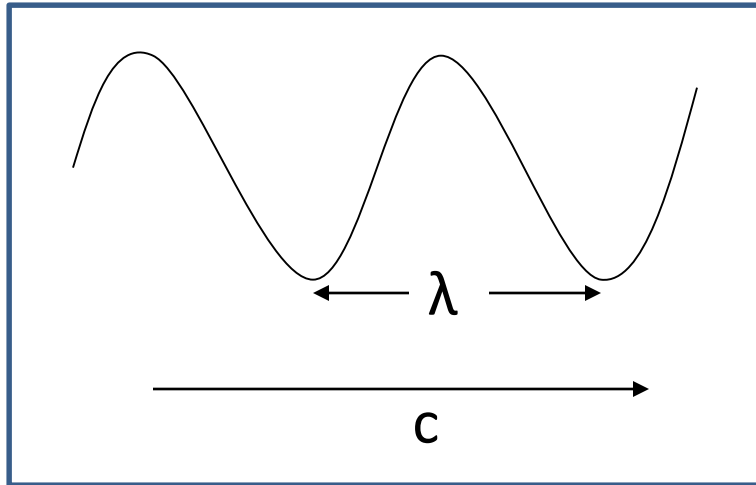


Types of Spectroscopy

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



What is Electromagnetic Radiation



c = speed of light (3×10^{10} cm/sec)

λ = wave length

ν = frequency (cycles/sec or Hz)

V = Wave Number (cm^{-1})

E = kinetic energy

h = Planck's constant (6.62×10^{-34} J sec)

$$\nu = \frac{C}{\lambda}$$

$$E = h\nu = h \frac{C}{\lambda}$$

$$V = \frac{\nu}{C} = \frac{1}{\lambda}$$



EM Spectrum and Molecular Effects

Energy		Wave Number ν	Wavelength λ	Frequency ν			
Kcal/mol	eV	cm^{-1}	cm	Hz			
9.4×10^7	4.9×10^6	3.3×10^{10}	3×10^{-11}	10^{21}	Gamma ray	Gamma ray emission	Nuclear
9.4×10^3	4.9×10^2	3.3×10^6	3×10^{-7}	10^{17}	X-ray	X-ray absorption, emission	Electronic (inner shell)
9.4×10^1	4.9×10^0	3.3×10^4	3×10^{-5}	10^{15}	Ultra violet	UV absorption	Electronic (outer shell)
					Visible		
9.4×10^{-1}	4.9×10^{-2}	3.3×10^2	3×10^{-3}	10^{13}	Infrared	IR absorption	Molecular vibration
9.4×10^{-3}	4.9×10^{-4}	3.3×10^0	3×10^{-1}	10^{11}	Micro-wave	Microwave absorption	Molecular rotation
9.4×10^{-7}	4.9×10^{-8}	3.3×10^{-4}	3×10^3	10^7	Radio	Nuclear magnetic resonance	Magnetically induced spin states



Infrared Spectroscopy

- ❑ Infrared radiation falls between the visible and microwave portions of the electromagnetic spectrum.
- ❑ Infrared waves have wavelengths longer than visible and shorter than microwaves, and have frequencies which are lower than visible and higher than microwaves.
- ❑ The Infrared region is divided into: near, mid and far-infrared.
 - Near-infrared refers to the part of the infrared spectrum that is closest to visible light and far-infrared refers to the part that is closer to the microwave region.
 - Mid-infrared is the region between these two.
- ❑ The primary source of infrared radiation is thermal radiation. (heat)
- ❑ It is the radiation produced by the motion of atoms and molecules in an object. The higher the temperature, the more the atoms and molecules move and the more infrared radiation they produce.
- ❑ Any object radiates in the infrared. Even an ice cube, emits infrared.



Humans, at normal body temperature, radiate most strongly in the infrared, at a wavelength of about 10 microns (A micron is the term commonly used in astronomy for a micrometer or one millionth of a meter). In the image to the left, the red areas are the warmest, followed by yellow, green and blue (coolest).



Infrared radiation

$$\lambda = 2.5 \text{ to } 25 \mu\text{m}$$

Wavenumber (cm^{-1}) or reciprocal of wavelength is more common unit

$$\nu = 4000 \text{ to } 600 \text{ cm}^{-1}$$

These frequencies match the frequencies of covalent bond stretching and bending vibrations. Infrared spectroscopy can be used to find out about **covalent bonds** in molecules.

IR is used to know:

- 1. what type of bonds are present**
- 2. some structural information**



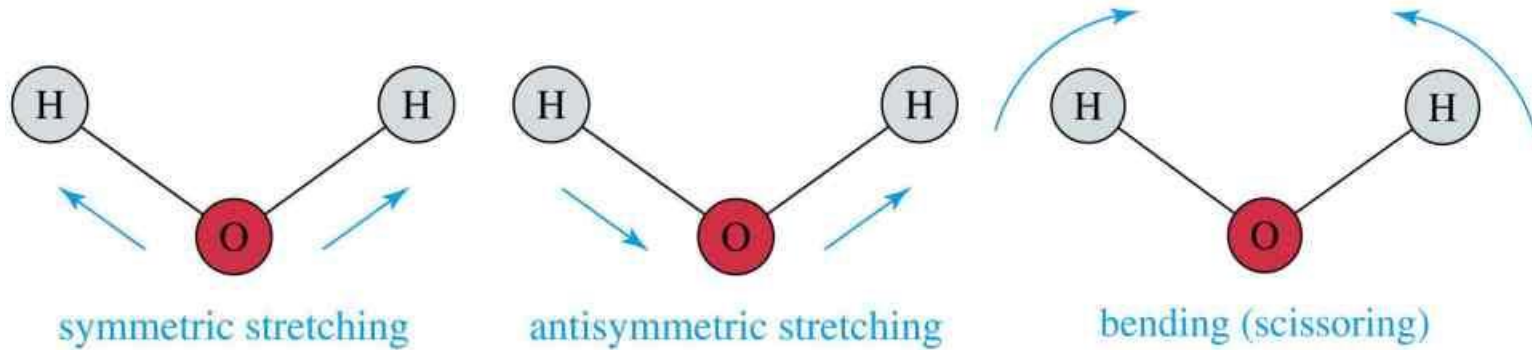
IR – Mechanism of Interaction

- ❑ The interaction between the radiation and the vibrating molecule is through the fluctuating electric field of the radiation and similar field generated by vibration of the molecule
- ❑ An oscillating electric field from a molecule is generated only when there occurs a change in the dipole moment during vibration of the molecule
- ❑ In a diatomic molecule, only one type of vibration i.e. symmetrical stretching occurs in which molecule is alternatively stretched and compressed
- ❑ Homonuclear diatomic molecules are IR inactive as they have zero dipole moment and also there occurs no change in dipole moment during symmetrical stretching
- ❑ Heteronuclear diatomic molecules do have a permanent dipole moment and they also exhibit a change in dipole moment during the vibration and hence they are IR active



Vibrational Modes

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

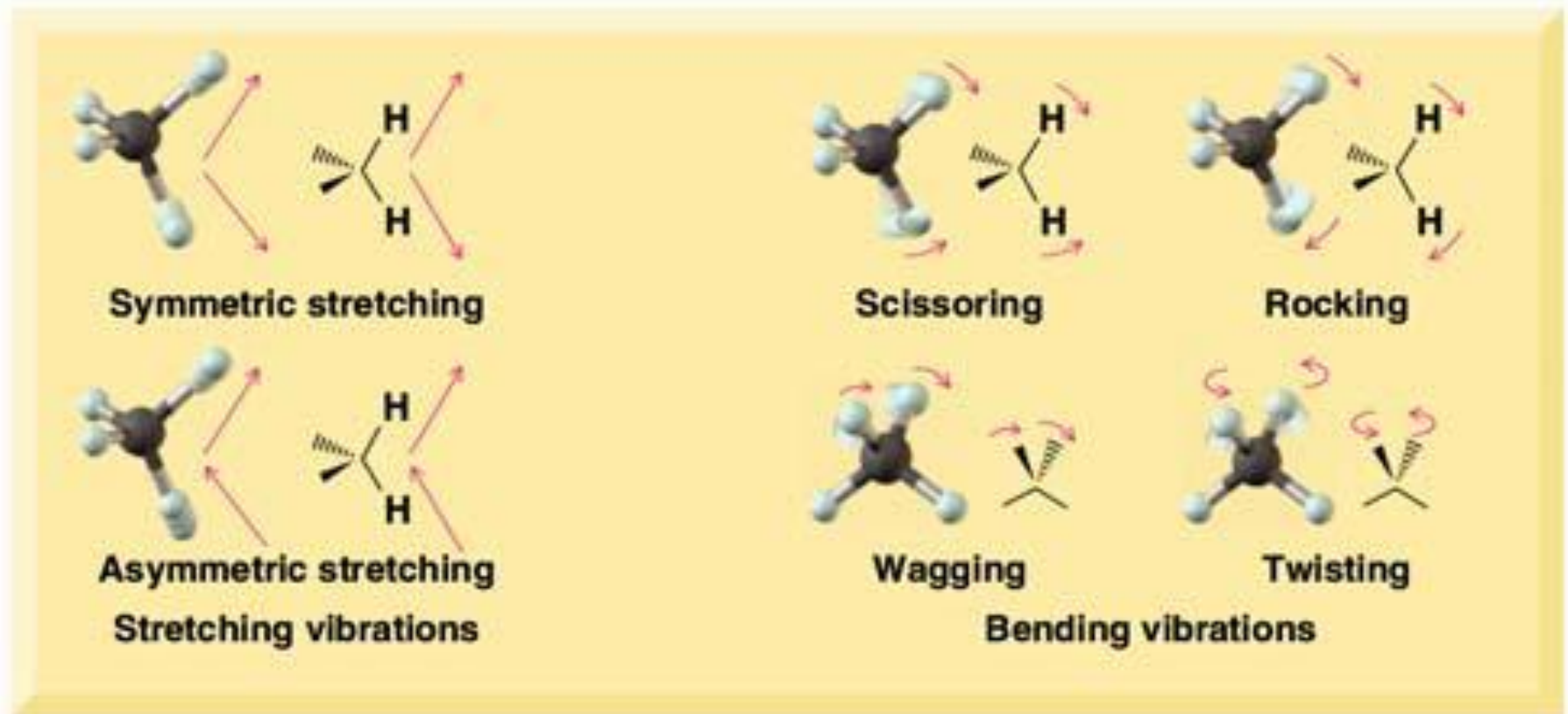


A molecule such as H_2O will absorb infrared light when the vibration (stretch or bend) results in a molecular dipole moment change



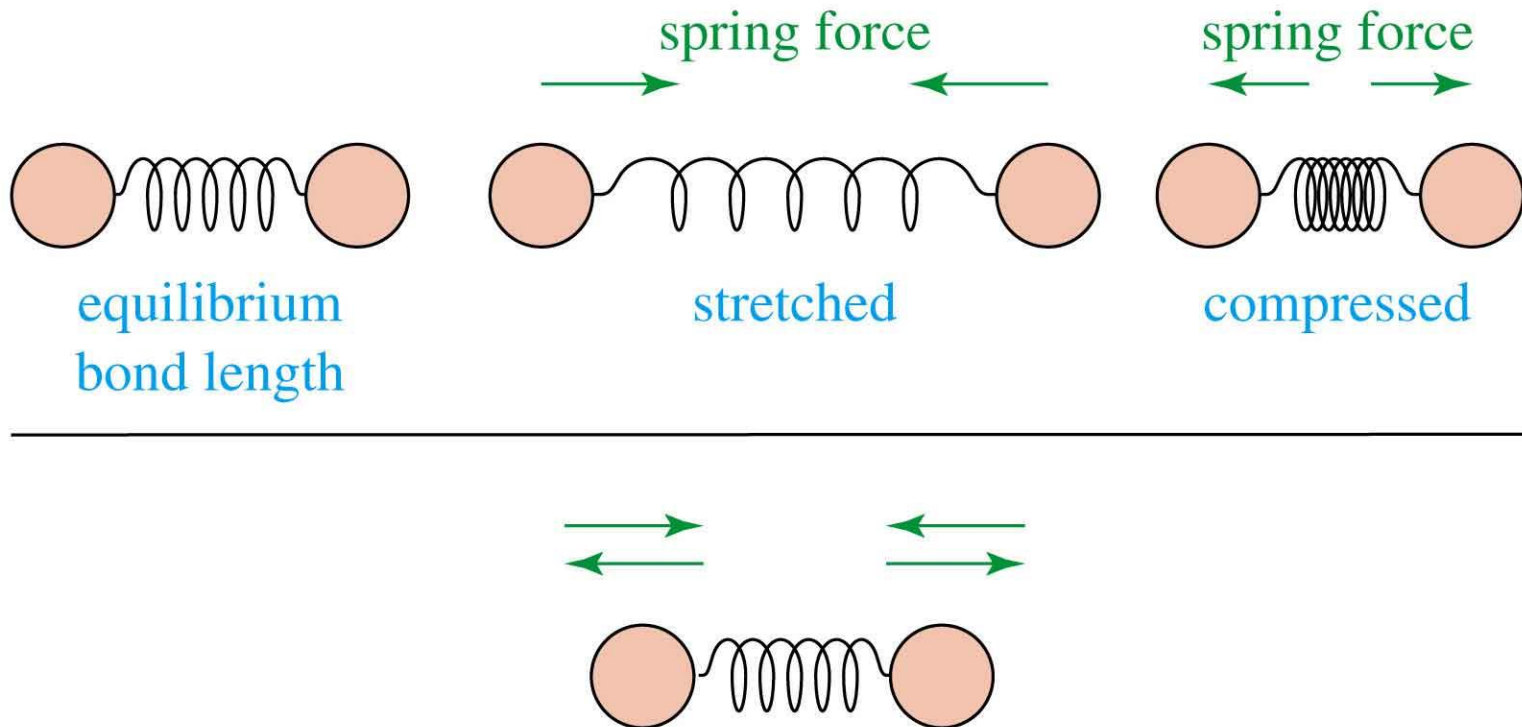
Vibrational Modes

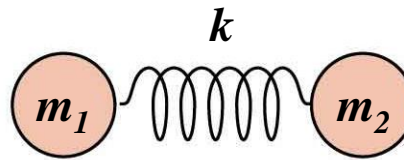
Nonlinear molecule with n atoms usually has $3n - 6$ fundamental vibrational modes.





Covalent bonds vibrate at only certain allowable frequencies
Can be taken as an example of vibrations in a spring





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

$\bar{\nu}$ = frequency

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

μ = reduced mass

To help understand IR, it is useful to compare a vibrating bond to the physical model of a vibrating spring system. The spring system can be described by Hooke's Law, as shown in the equation given on the left.

Consider a bond and the connected atoms to be a spring with two masses attached.

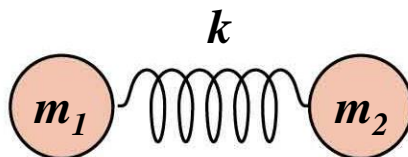
Using the force constant **k** (which reflects the stiffness of the spring) and the two masses **m₁** and **m₂**, then the equation indicates how the frequency, $\bar{\nu}$, of the absorption should change as the properties of the system change.



Hook's Law

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

$\bar{\nu}$ = frequency



$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

μ = reduced mass

Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm ⁻¹)
<i>Frequency dependence on atomic masses</i>		
C—H	100 (420)	3000
C—D	100 (420)	2100
C—C	83 (350)	1200
<div style="display: flex; align-items: center;"> <div style="text-align: right; padding-right: 10px;"> heavier atoms ↓ </div> <div style="text-align: left; padding-left: 10px;"> $\bar{\nu}$ decreases ↓ </div> </div>		
<i>Frequency dependence on bond energies</i>		
C—C	83 (350)	1200
C=C	146 (611)	1660
C≡C	200 (840)	2200
<div style="display: flex; align-items: center;"> <div style="text-align: right; padding-right: 10px;"> stronger bond ↓ </div> <div style="text-align: left; padding-left: 10px;"> $\bar{\nu}$ increases ↓ </div> </div>		

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



IR Spectrum of a Polyatomic Molecule

- ❑ A polyatomic molecule exhibit $3n-5$ (linear) or $3n-6$ (non-linear) normal modes of vibrations
- ❑ Vibrations falls in two categories –
 - Skeletal Vibrations (involves more or less all atoms of the molecule)
 - Group Vibrations (Vibrations of a small group of atoms are more vigorous)
- ❑ Skeletal vibrations exhibit absorption below 1500 cm^{-1} which are characteristics of the molecule as a whole
- ❑ This region is called FINGERPRITING region and is utilized to establish general structure of the molecule such as linear, branched, benzenoid etc.
- ❑ Group vibrations involve vibrations of various functional groups
- ❑ Group vibrations are usually independent of the structure of the molecule as a whole and exhibit absorptions in the region above 1500 cm^{-1} .

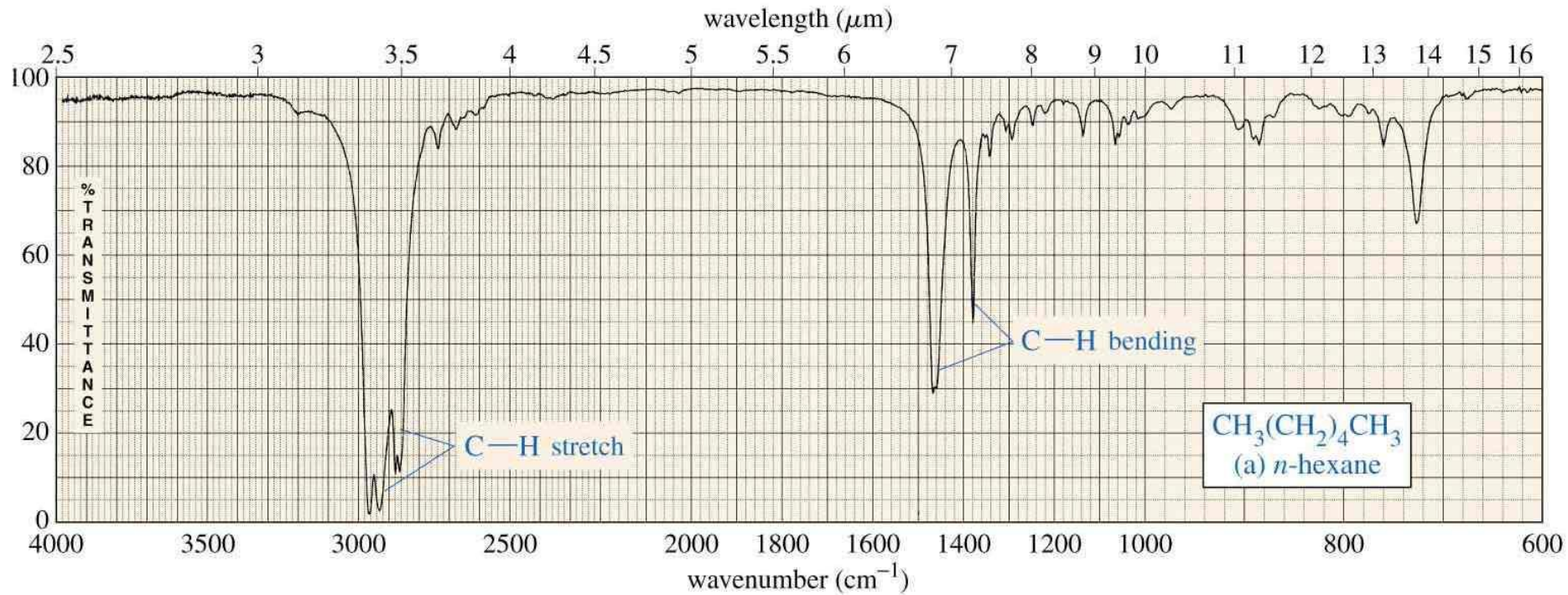


Bonds with more *s* character absorb at a higher frequency.

- 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}

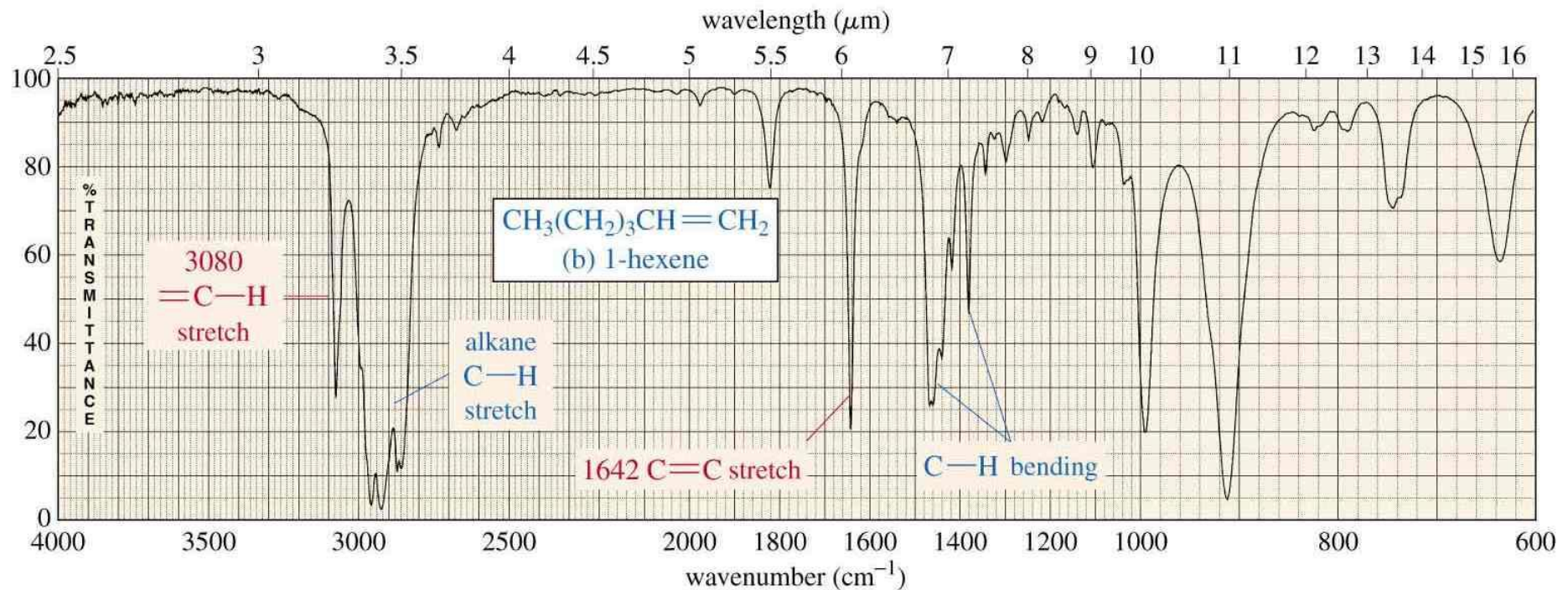


An Alkane Spectrum



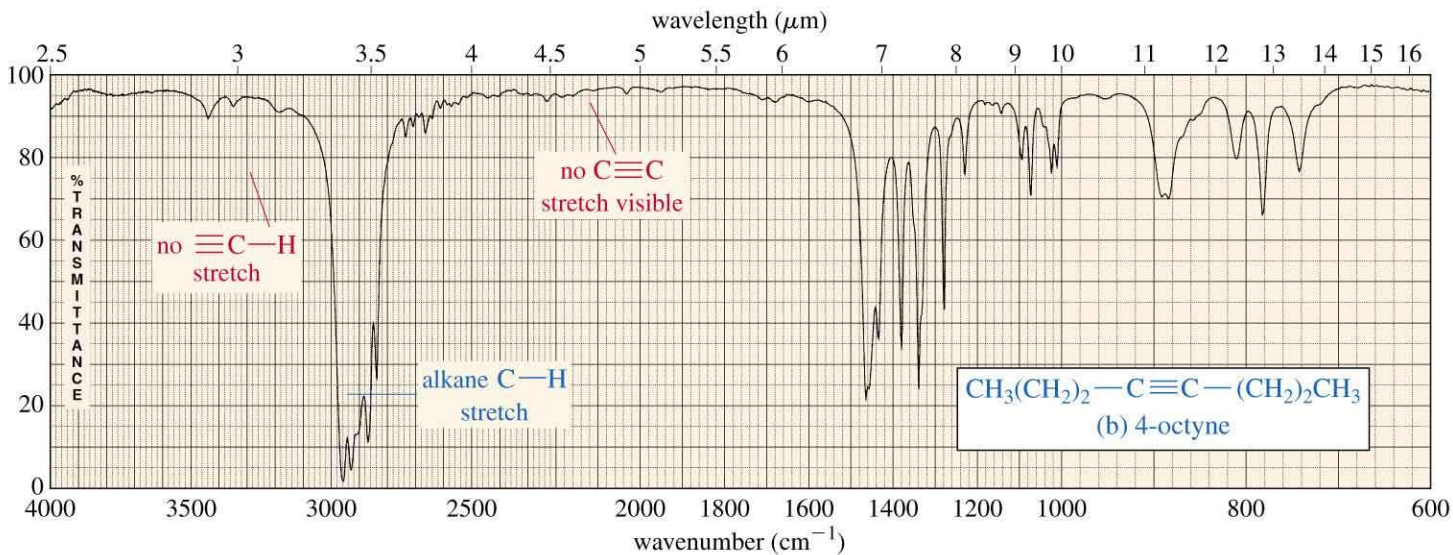
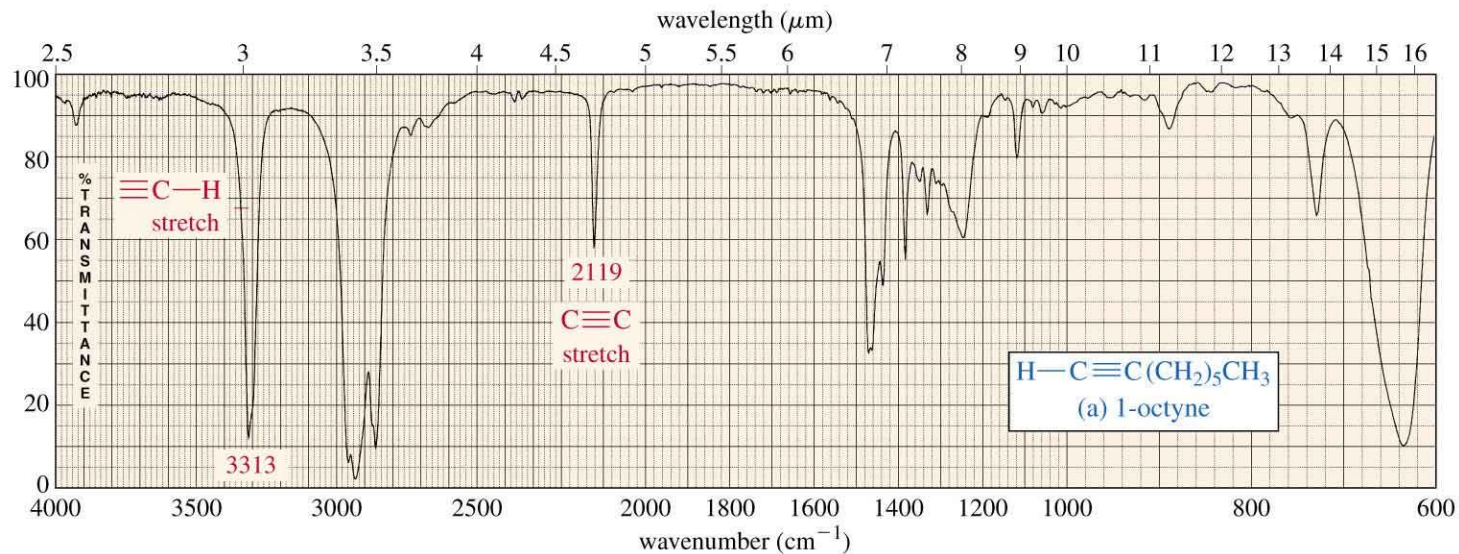


An Alkene Spectrum





Alkyne Spectrum

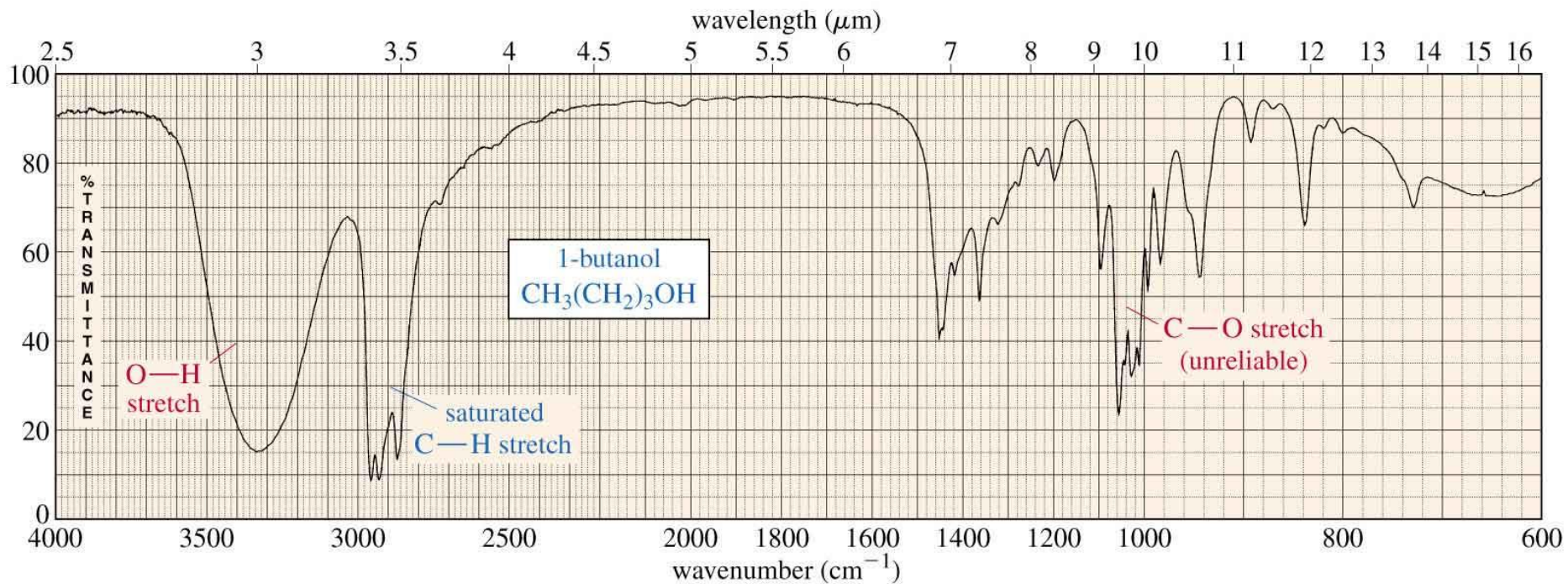




- Both of these occur around 3300 cm^{-1} , but they look different.
 - Alcohol O-H, broad with rounded tip.
 - Secondary amine (R_2NH), broad with one sharp spike.
 - Primary amine (RNH_2), broad with two sharp spikes.
 - No signal for a tertiary amine (R_3N)

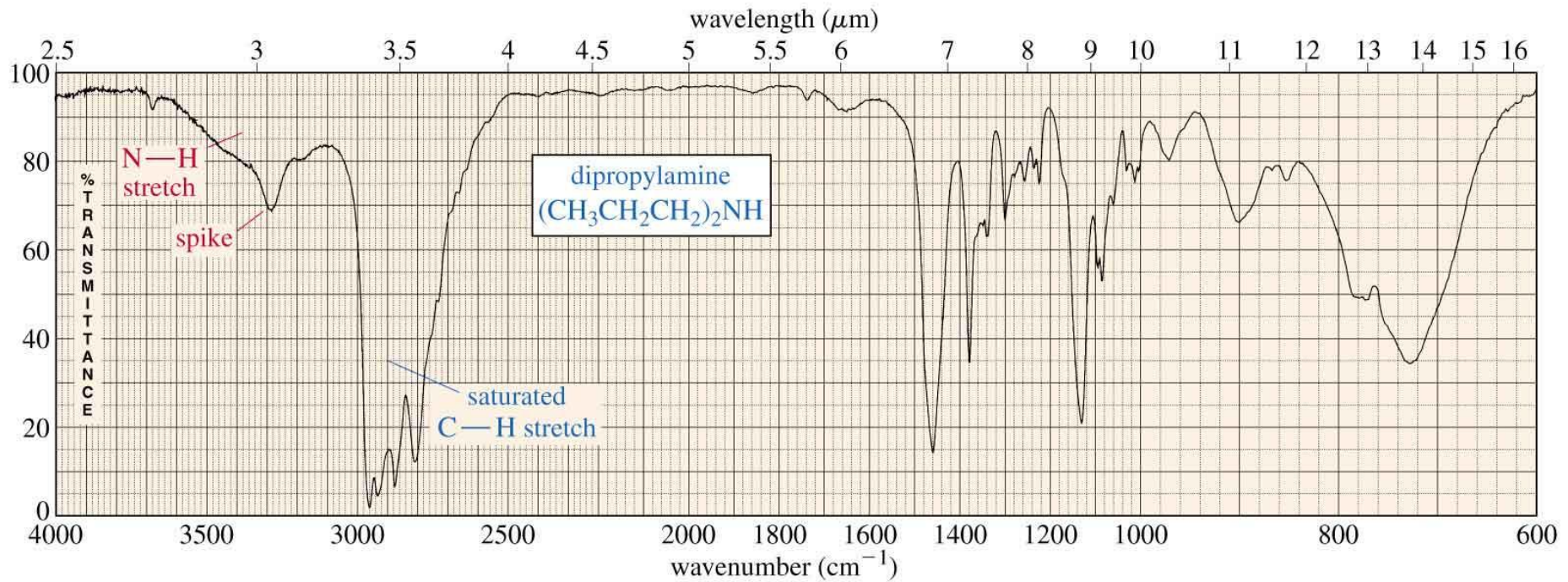


An Alcohol Spectrum





An Amine Spectrum

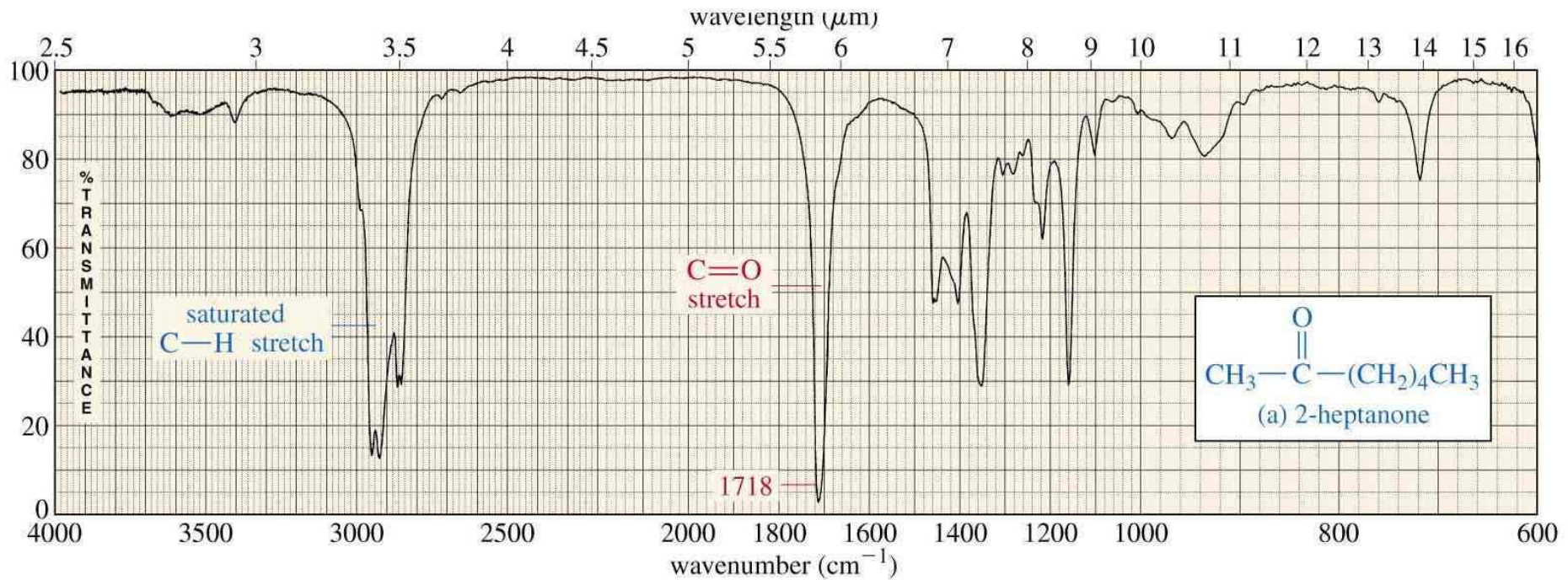




- The C=O bond of simple ketones, aldehydes, and carboxylic acids absorb around 1710 cm^{-1} .
- Usually, it's the strongest IR signal.
- Carboxylic acids will have O-H also.
- Aldehydes have two C-H signals around 2700 and 2800 cm^{-1} .

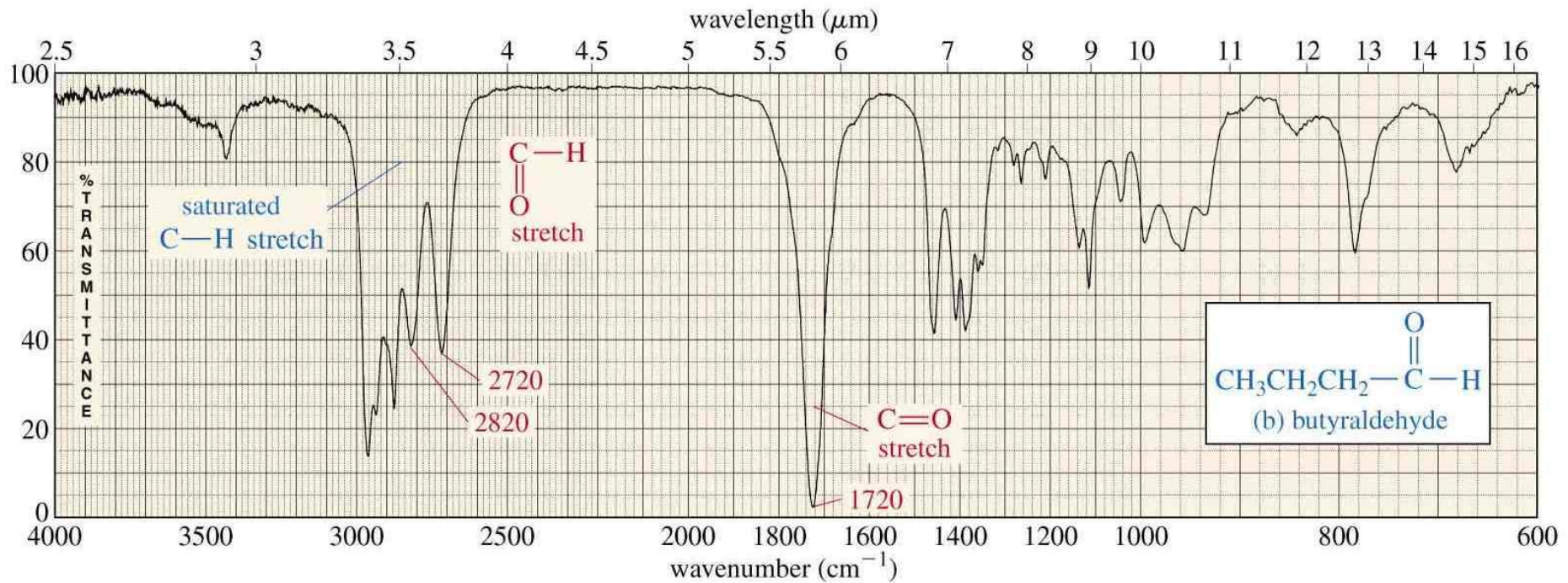


A Ketone Spectrum





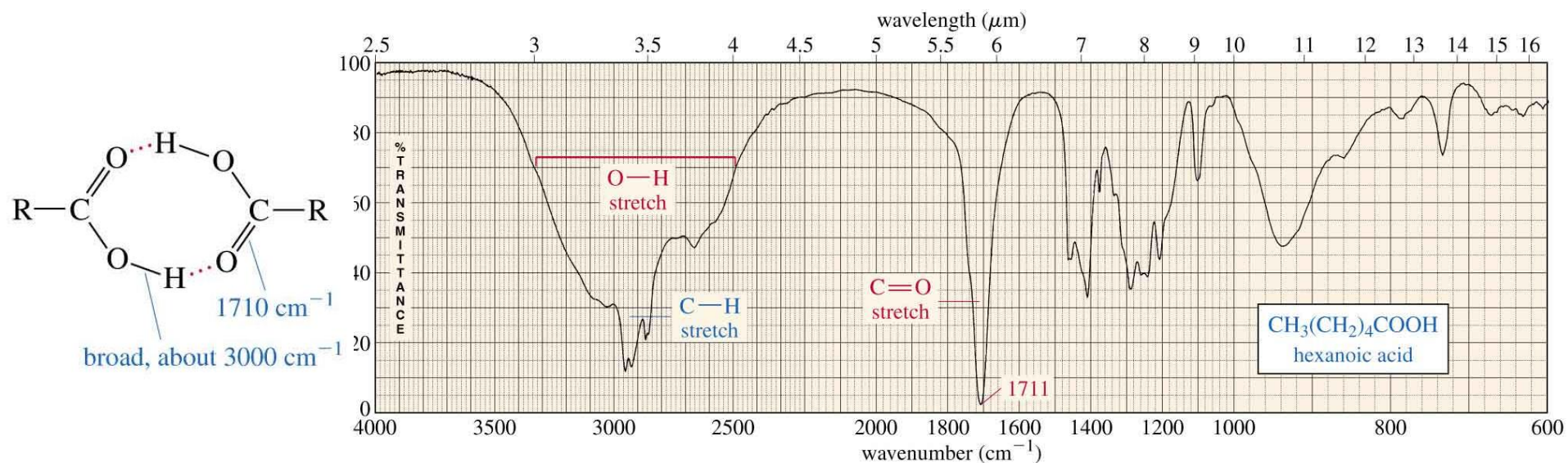
An Aldehyde Spectrum





O – H Stretching of a Carboxylic Acid

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



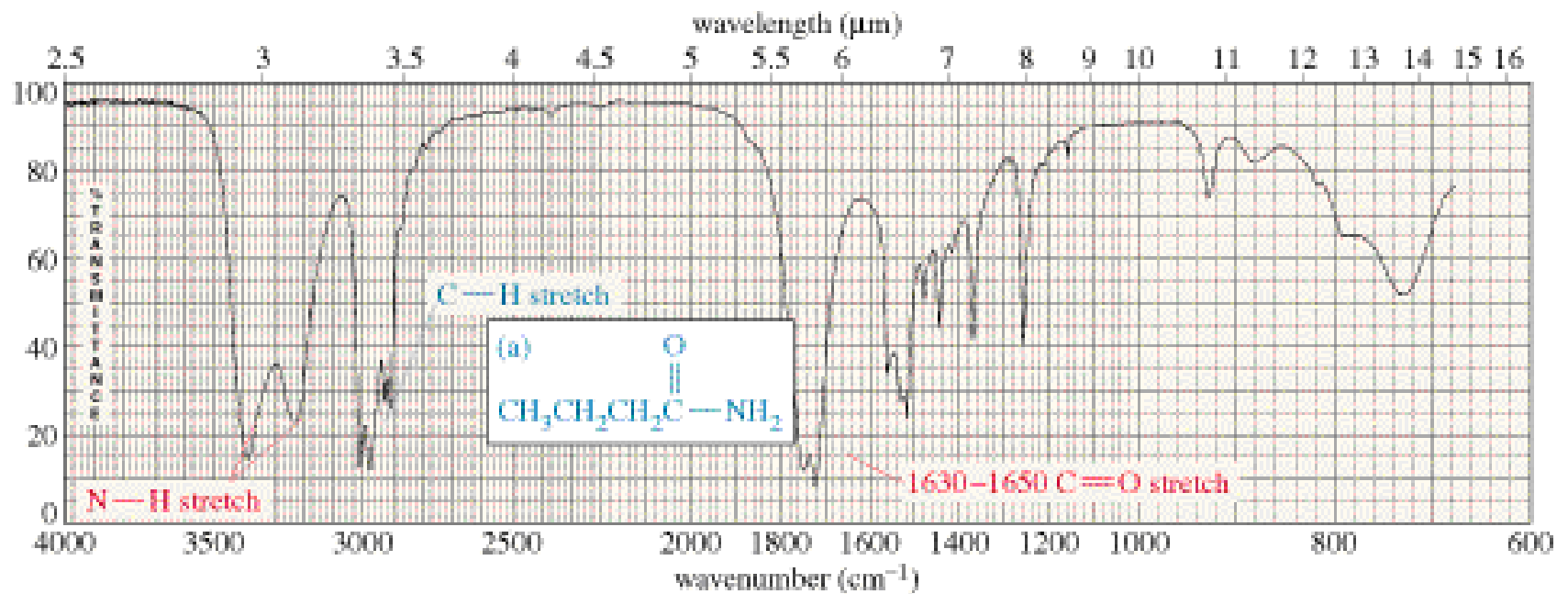


Variations in C=O Absorption

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



An Amide Spectrum

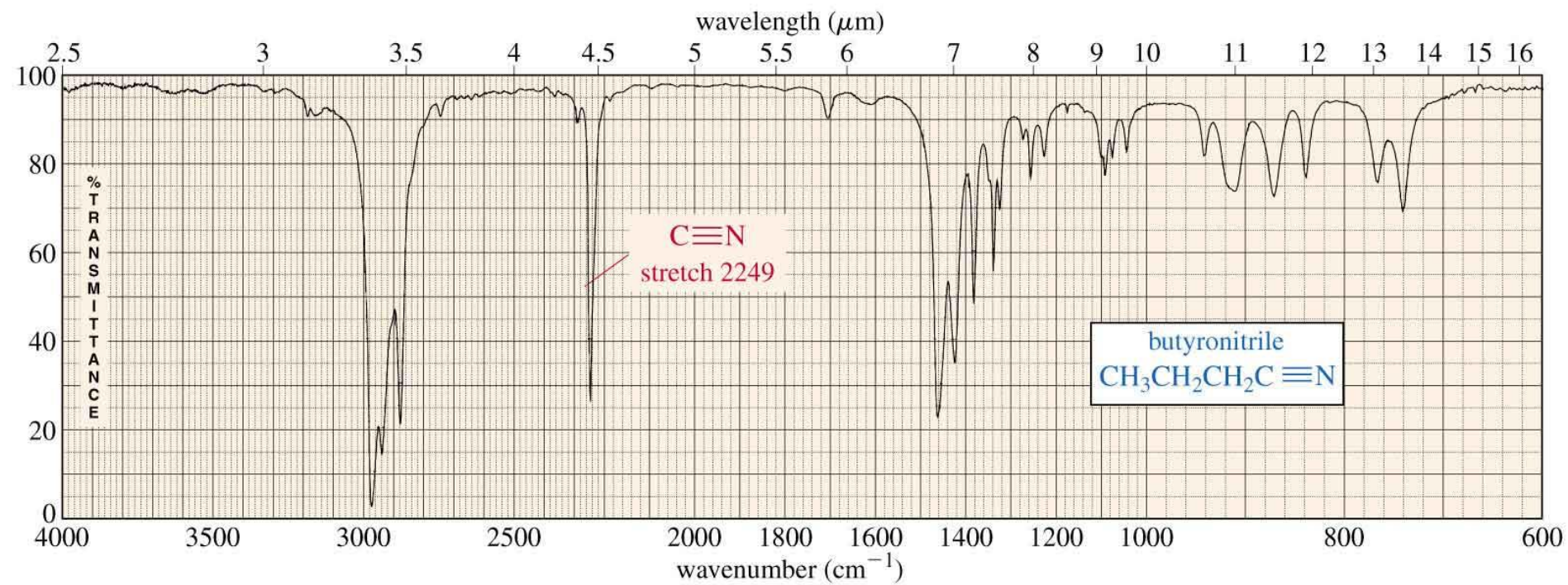




- C - N absorbs around 1200 cm^{-1} .
- C = N absorbs around 1660 cm^{-1} and is much stronger than the C = C absorption in the same region.
- C \equiv N absorbs strongly just *above* 2200 cm^{-1} . The alkyne C \equiv C signal is much weaker and is just *below* 2200 cm^{-1} .

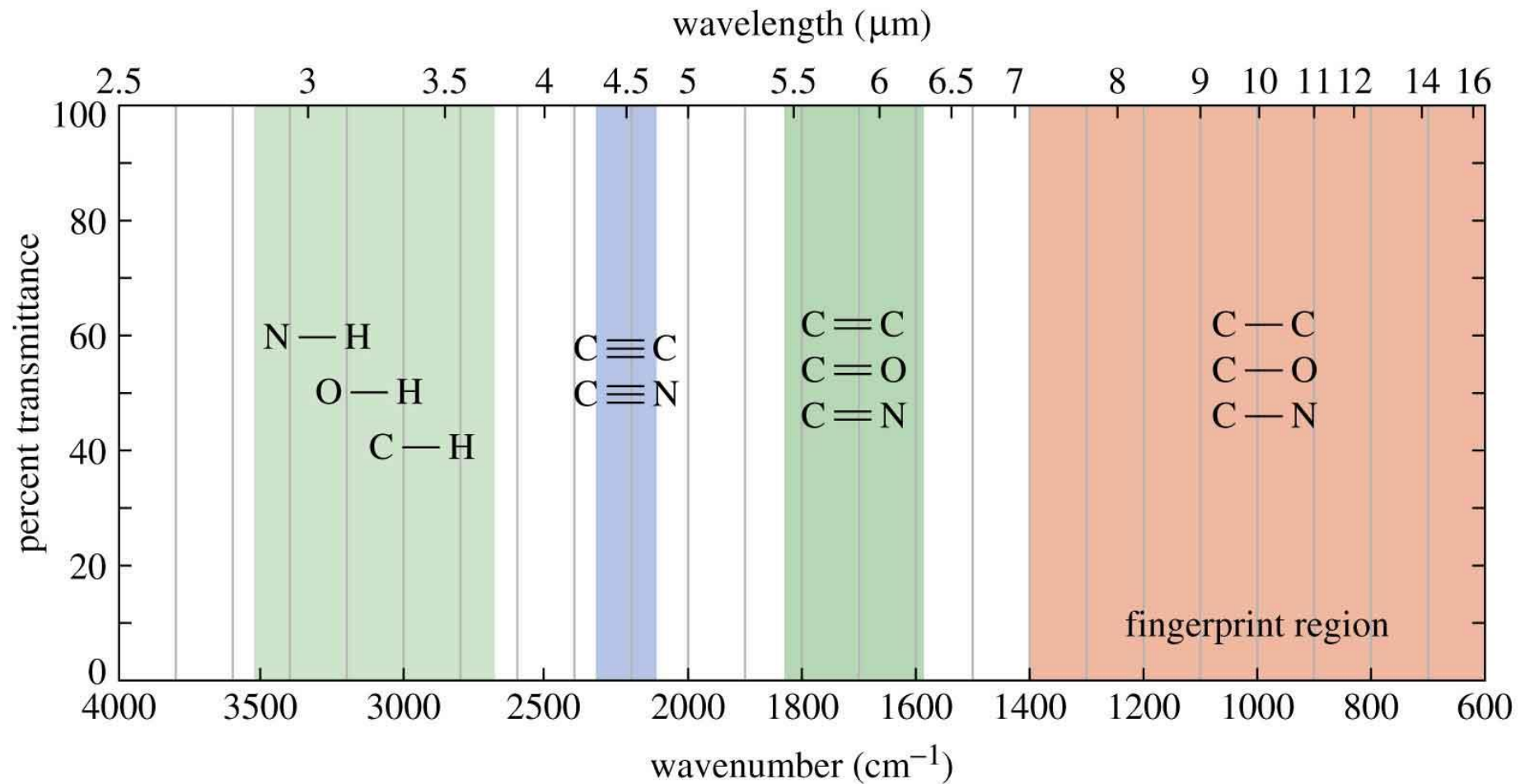


A Nitrile Spectrum





Summary of IR Absorptions





- 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.