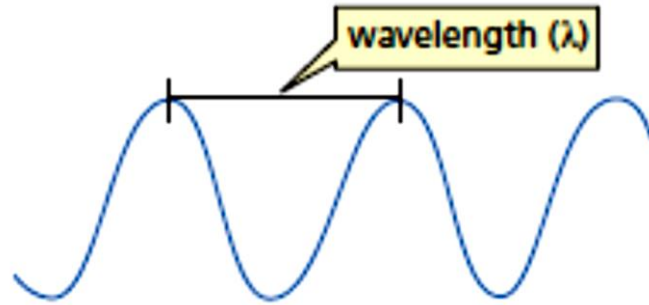


COURSE CODE: SC202(CHEMISTRY)
COURSE INSTRUCTOR: DR. SANGITA TALUKDAR &
DR. DEBARATI MITRA
LECTURE- UV-VIS & IR SPECTROSCOPY
DEPT. OF SCIENCE AND MATHEMATICS
IITG, GUWAHATI
DATE: 7.3.2023

Spectroscopy

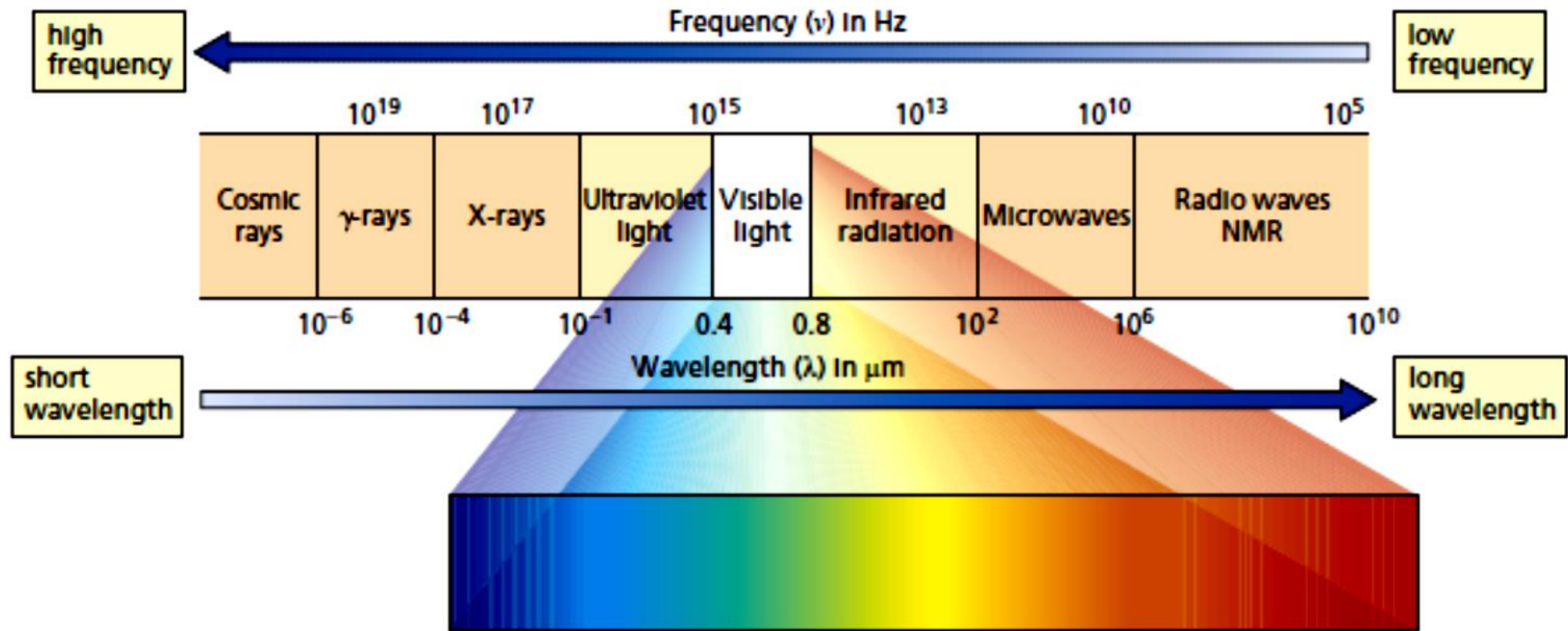
Spectroscopy is the study of the interaction between matter and electromagnetic radiation—radiant energy that displays the properties of both particles and waves.



Wave-like propagation of light

From **wavelength** λ , we can calculate the inverse of this $1/\lambda$, which is the number of waves per unit of length. This is called the **wavenumber** $\bar{\nu}$ (m^{-1} , cm^{-1}).

From the *velocity of light* with which it travels through space ($c = 2.998 \times 10^8 \text{ ms}^{-1}$), we can calculate the number of waves per second as the **frequency** of the light, $\nu = c/\lambda \text{ (s}^{-1}\text{)}$.



The complete electromagnetic spectrum, with wavelengths λ and frequency ν .

The electromagnetic spectrum is made up of the following components:

- ***Cosmic rays*** consist of radiation discharged by the sun, have the highest energy, the highest frequencies and the shortest wavelengths.
- **γ rays (gamma rays)** are emitted from the nuclei of certain radioactive elements and because of their high energy, can severely damage biological organisms.
- ***X-rays*** are somewhat lower in energy than γ rays and less harmful, except in high doses. Low-dose X-rays are used to examine the internal structure of organisms. The denser the tissue, the more it blocks X-rays.
- ***Ultraviolet (UV)*** light is responsible for sunburns and repeated exposure can cause skin cancer by damaging DNA molecules in skin cells.
- ***Visible light*** is the electromagnetic radiation we see.
- We feel ***infrared radiation*** as heat.
- We cook with ***microwaves*** and use them in radar.
- ***Radio waves*** have the lowest energy (lowest frequency). We use them for radio and television communication, digital imaging, remote controls and wireless linkages for laptop computers. Radio waves are also used in NMR spectroscopy and in magnetic resonance imaging (MRI).

<i>Radiation absorbed</i>	<i>Effect on the molecule (and information deduced)</i>
<i>Ultraviolet-visible</i>	Changes in electronic energy levels within the molecule (extent of π -electron systems, presence of conjugated unsaturation, and conjugation with nonbonding electrons)
<i>Infrared (mid infrared)</i>	Changes in the vibrational and rotational movements of the molecule (detection of functional groups, which have specific vibration frequencies, e.g., C=O, NH ₂ , OH, etc.)
<i>Radiofrequency</i>	Nuclear magnetic resonance; induces changes in the magnetic properties of certain atomic nuclei, notably that of Hydrogen and the ¹³ C isotope of carbon (Hydrogen and Carbon atoms in different environments can be detected and counted, etc.)

The energy associated with regions of the electromagnetic spectrum is related to wavelengths and frequency by the equation.

$$E = h\nu = hc/\lambda$$

h = **Planck's constant**

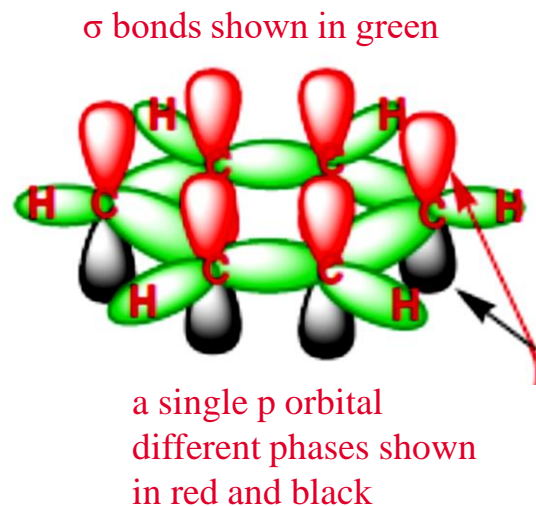
c = **velocity of light**

λ = **wavelength**

Problem 1: For ultraviolet light of wavelength 200 nm, calculate (a) the frequency of this light, (b) the amount of energy absorbed by one molecule when it interacts with this light and (c) the corresponding amount of energy absorbed by one mole of substance.

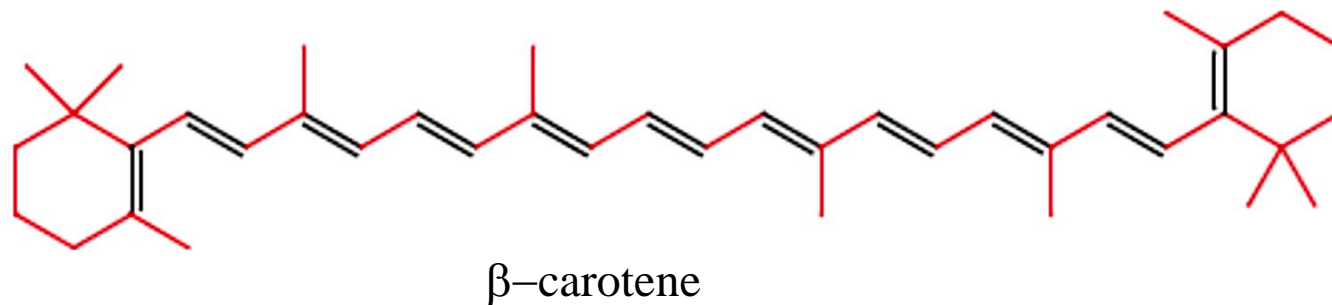
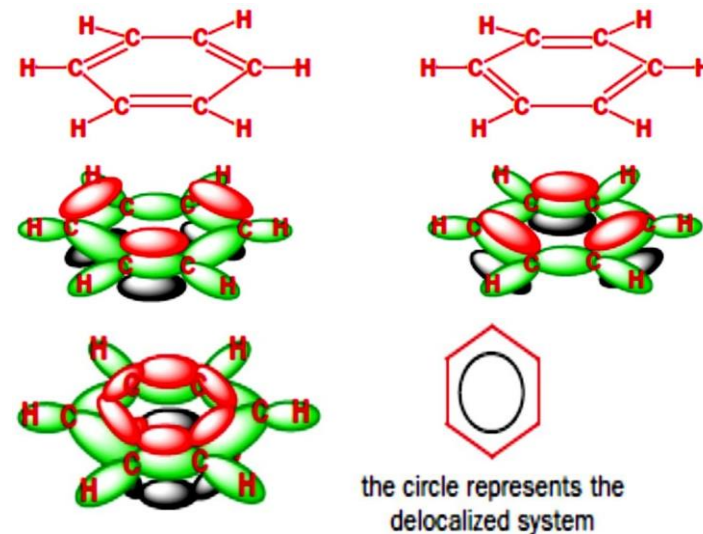
Ans : (a) $\nu = 1.5 \times 10^{15} \text{ s}^{-1}$ (b) $E = h\nu = (6.6 \times 10^{-34} \text{ Js}) \times (1.5 \times 10^{15} \text{ s}^{-1}) = 9.9 \times 10^{-19} \text{ J}$, (c) To the amount of energy absorbed by one mole of substance, we must multiply E by the Avogadro constant $N_A (= 6.023 \times 10^{23} \text{ mol}^{-1})$, giving approximately $6 \times 10^5 \text{ J mol}^{-1}$.

Delocalization and Conjugation



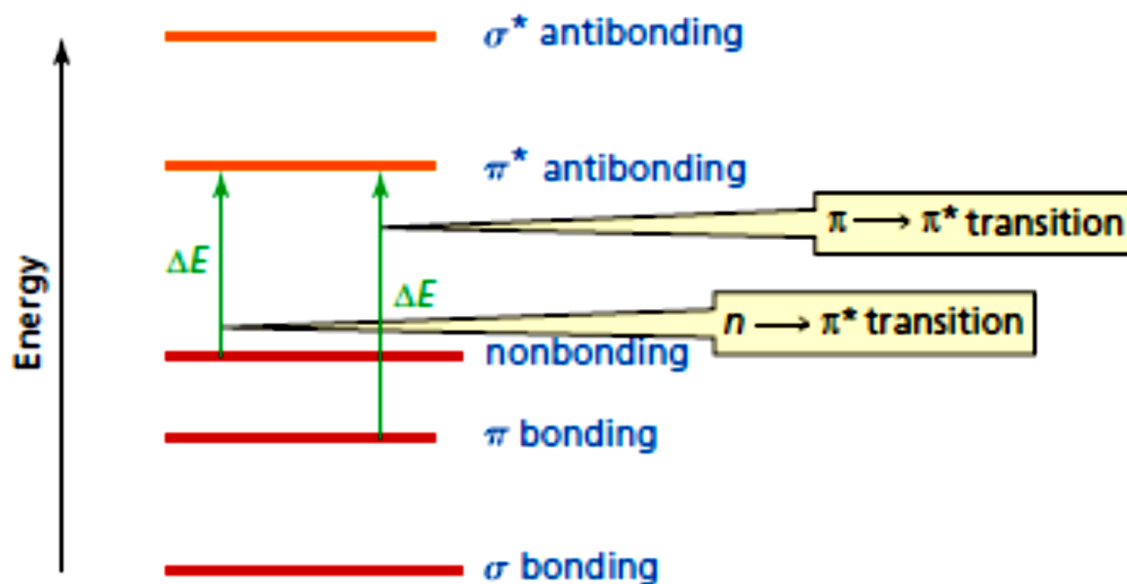
π electrons in benzene are **delocalized**, i.e., no longer localized in specific double bonds between two particular carbon atoms but spreaded out, or delocalized, over all six atoms in the ring.

Combining different pairs of p orbitals puts the double bonds in different positions



Ultraviolet and Visible Spectroscopy

The normal electronic configuration of a molecule is known as its **ground state**—all the electrons are in the lowest-energy molecular orbitals. When a molecule absorbs light of an appropriate wavelength and an electron is promoted to a higher energy molecular orbital, the molecule is then in an **excited state**. Thus, an **electronic transition** is the promotion of an electron to a higher energy MO. The relative energies of the bonding, nonbonding, and antibonding molecular orbitals are shown in Figure.



Only organic compounds with π electrons can produce UV-Vis spectra.

The Beer–Lambert Law

It was proposed by Wilhelm Beer and Johann Lambert, that at a given wavelength, the absorbance of a sample depends on the amount of absorbing species that the light encounters as it passes through a solution of the sample. In other words, *absorbance depends on both the concentration of the sample and the length of the light path through the sample.*

The relationship among absorbance, concentration, and length of the light path is known as the **Beer–Lambert law** and is given by:

$$A = \epsilon cl$$

A = absorbance of the sample = $\log I_o/I$

I_o = intensity of the radiation entering the sample

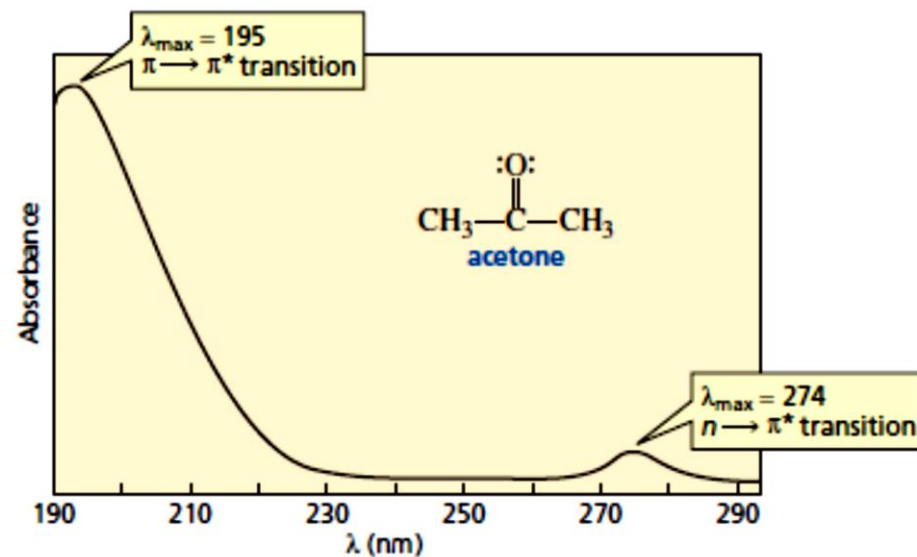
I = intensity of the radiation emerging from the sample

c = concentration of the sample, in moles/liter

l = length of the light path through the sample, in centimeters

ϵ = molar absorptivity (litre mol⁻¹ cm⁻¹)

The **molar absorptivity** (formerly called the extinction coefficient) of a compound is a constant and is the absorbance that would be observed for a 1.00 M solution in a cell with a 1.00 cm path length.

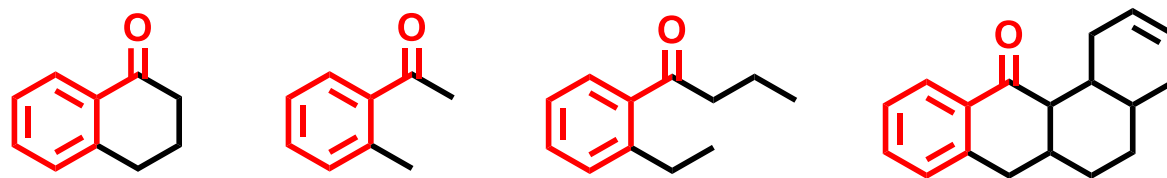


The UV spectrum of acetone

Acetone has both π electrons and lone-pair (nonbonding) electrons. Thus, there are two **absorption bands**: one for the $\pi \rightarrow \pi^*$ transition and one for the $n \rightarrow \pi^*$ transition.

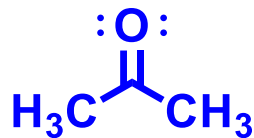
The $\pi \rightarrow \pi^*$ transition corresponds to the λ_{max} at the shorter wavelength because that transition requires more energy than the $n \rightarrow \pi^*$ transition.

A **chromophore** is that part of a molecule that absorbs UV or visible light. The carbonyl group is the chromophore of acetone. The following four compounds all have the same chromophore, so they all have approximately the same λ_{max} .



Effect of Conjugation on λ_{\max}

Non conjugated π - electrons



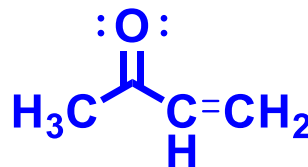
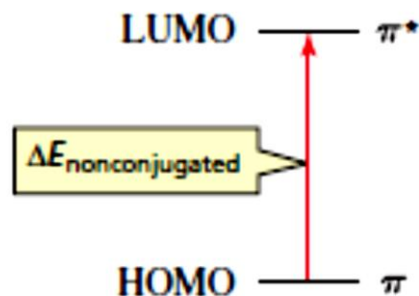
Acetone

$n \rightarrow \pi^*$

$$\lambda_{\max} = 274 \text{ nm}$$

$\pi \rightarrow \pi^*$

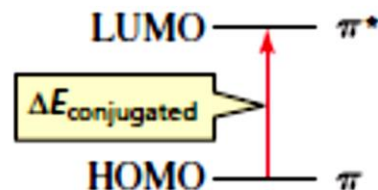
$$\lambda_{\max} = 195 \text{ nm}$$



Methyl vinyl ketone

$$\lambda_{\max} = 331 \text{ nm}$$

$$\lambda_{\max} = 203 \text{ nm}$$



Conjugated π - electrons

Conjugation raises the energy of the HOMO and lowers the energy of the LUMO.

If a compound has enough conjugated double bonds, it will absorb visible light ($\lambda_{\max} > 400 \text{ nm}$) and the compound will be colored.



β -carotene

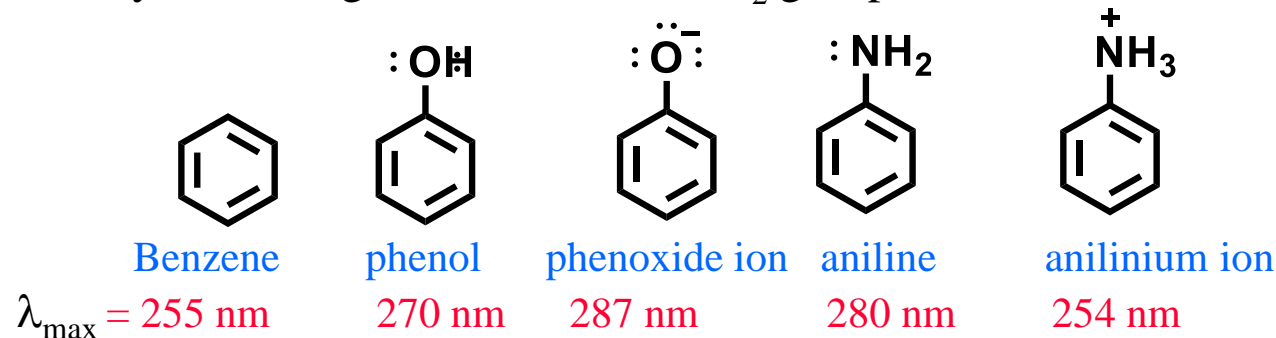
$$\lambda_{\max} = 455 \text{ nm}$$



lycopene

$$\lambda_{\max} = 474 \text{ nm}$$

An **auxochrome** is a substituent that when attached to a chromophore, alters the λ_{max} and the intensity of the absorption, usually increasing both; -OH and -NH₂ groups are auxochromes.



Wavelengths of red light are longer than those of blue light, so, a shift to a longer wavelength is called a **red shift** (*bathochromic shift*); and a shift to a shorter wavelength is called a **blue shift** (*hypsochromic shift*).

Deprotonation of phenol results in a red shift, whereas protonation of aniline produces a blue shift.



A **hyperchromic effect** is one that leads to increased intensity of absorption.

A **hypochromic effect** is the one that leads to decreased intensity of absorption.

1. A local radio station transmits (a) at approximately 95 MHz on its VHF transmitter and (b) at 810 kHz on medium wave. Calculate the wavelengths of these transmissions.

Ans: $c = 3 \times 10^8 \text{ ms}^{-1}$, and $\lambda = c/\nu$. Thus, wavelength corresponding to (a) 95 MHz, or $95 \times 10^6 \text{ s}^{-1}$ is 3.158 m and (b) 810 kHz, is 370 m.

2. An α,β -unsaturated ketone of relative molecular mass 110 has an absorption band with λ_{max} at 215 nm and ϵ 10,000. A solution of this ketone showed absorbance $A = 2.0$ with a 1 cm cell. Calculate the concentration of the ketone in this solution, expressed in grams per liter, g l^{-1} .

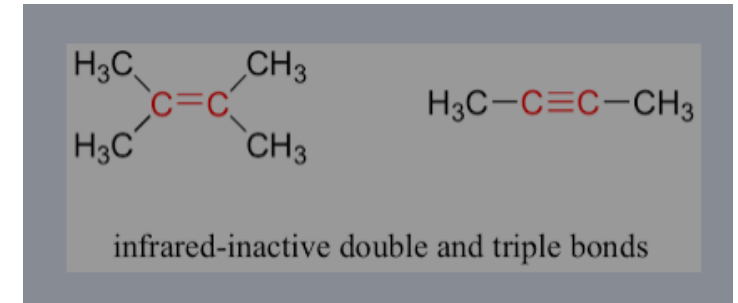
Ans: Using the formula: $A = \epsilon cl$, $c = 2 \times 10^{-4} \text{ mol/l}$. We know that the relative molecular mass is 110, so the concentration can be expressed as $2 \times 110 \times 10^{-4}$ or $2.2 \times 10^{-2} \text{ g l}^{-1}$.

Infrared Spectroscopy

- The vibrational IR extends from $2.5 \times 10^{-6} \text{ m}$ ($2.5 \text{ }\mu\text{m}$) to $2.5 \times 10^{-5} \text{ m}$ ($25 \text{ }\mu\text{m}$).
- Expressed in wavenumbers, the vibrational IR extends from 4000 cm^{-1} to 400 cm^{-1} .

$$\bar{\nu} = \frac{10^{-2} \text{ m} \cdot \text{cm}^{-1}}{2.5 \times 10^6 \text{ m}} = 4000 \text{ cm}^{-1} \quad \bar{\nu} = \frac{10^{-2} \text{ m} \cdot \text{cm}^{-1}}{2.5 \times 10^5 \text{ m}} = 400 \text{ cm}^{-1}$$

- For a molecule to absorb IR radiation
 - the bond undergoing vibration must be polar
 - its vibration must cause a periodic change in the bond **dipole moment**.
- Covalent bonds which do not meet these criteria are said to be **IR inactive**
 - the C-C double and triple bonds of symmetrically substituted alkenes and alkynes, e.g., 2,3-dimethyl but-2-ene and acetylene are IR inactive because they are not polar bonds.

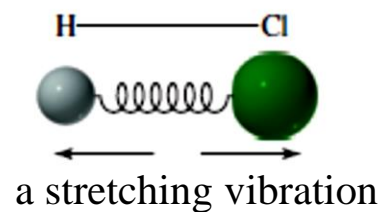


- For a nonlinear molecule containing n atoms, there are $3n - 6$ allowed fundamental vibrations and for a linear molecule it is $3n - 5$.
- For even a relatively small molecule, a large number of vibrational energy levels exist and patterns of IR absorption can be very complex.
- The simplest vibrational motions are bending and stretching vibrations.

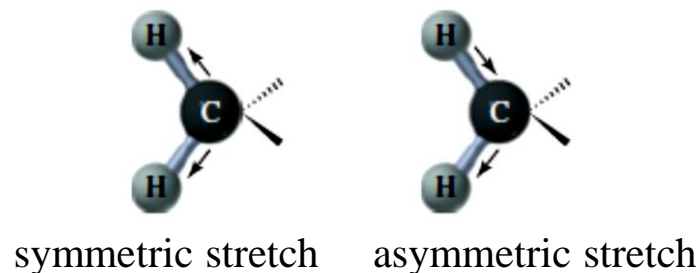
Infrared Spectroscopy

Stretching and Bending Vibrations

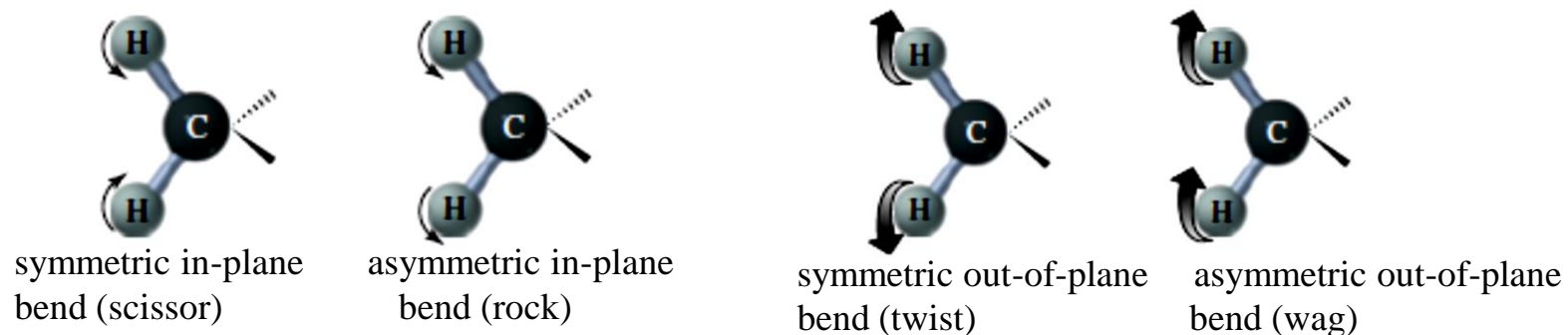
- A *stretch* is a vibration occurring along the line of the bond that changes the bond length.
- A *bend* is a vibration that does *not* occur along the line of the bond, but changes the bond angle.



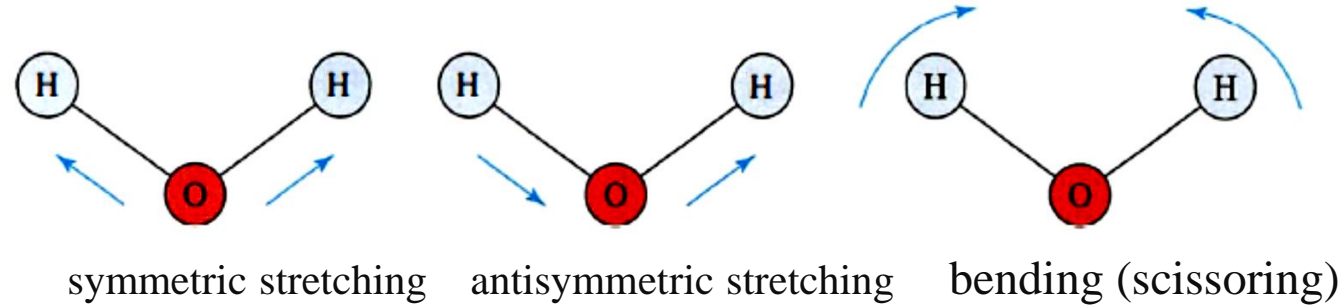
- A molecule containing three or more atoms can experience symmetric and asymmetric stretches and bends.



- **Bending vibrations** are often referred to by the descriptive terms *rock*, *scissor*, *wag*, and *twist*.



- For a nonlinear molecule containing n atoms, there are $3n - 6$ allowed fundamental vibrations
- Water (3 atoms) has $3 \times (3) - 6 = 3$ fundamental modes:

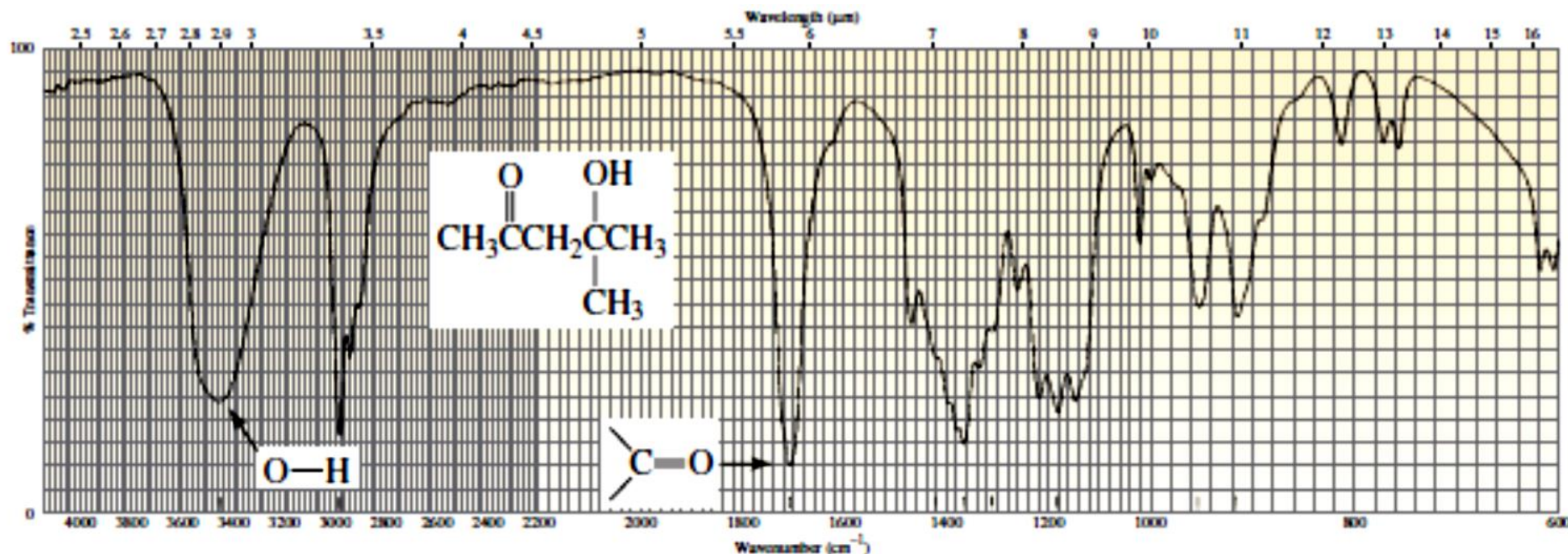


IR-Active and IR- Inactive Vibrations

- A bond with a dipole moment can be visualized as a positive charge and a negative charge separated by a spring. If this bond is placed in an electric field, it is either stretched or compressed, depending on the direction of the field.
- If a bond is symmetrical and has zero dipole moment, the electric field does not interact with the bond. For example, the triple bond of acetylene has zero dipole moment, and the dipole moment remains zero if the bond is stretched or compressed. Because the vibration produces no change in the dipole moment, there is no absorption of energy. This vibration is said to be IR inactive.
- ***The key to an IR-active vibration is that the vibration must change the dipole moment of the molecule.***
e.g., HF

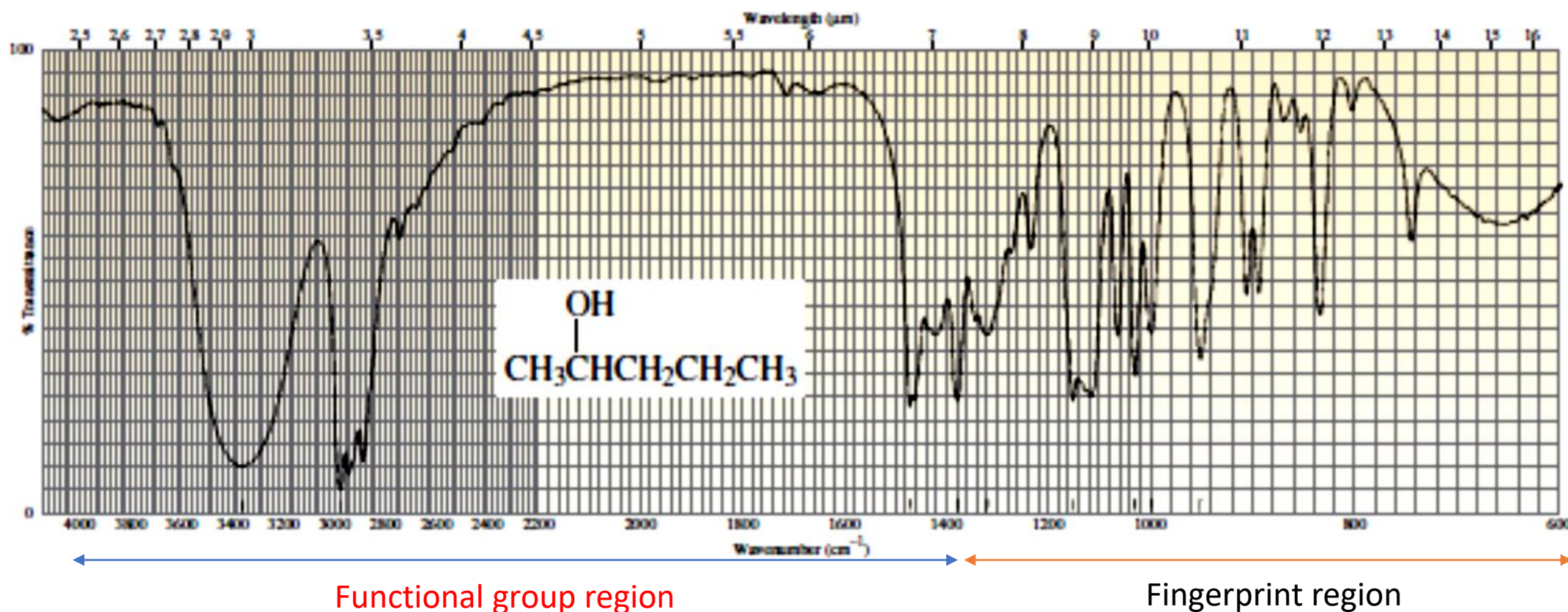
Obtaining an Infrared Spectrum

- The instrument used to obtain an *infrared spectrum* is called an *IR spectrometer*.
- 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.
- Lower values of percent transmission mean that some of the energy is being absorbed by the compound. Each downward spike in the IR spectrum represents absorption of energy.
- The spikes are called **absorption bands**.



The Functional Group and Fingerprint Regions

- An IR spectrum can be divided into two areas. The left-hand two-thirds of an IR spectrum is where most of the functional groups show absorption bands. This region is called the **functional group region**.
- The right-hand one-third of the IR spectrum ($1450\text{--}600\text{ cm}^{-1}$) is called the **fingerprint region** because it is characteristic of the compound as a whole, just as a fingerprint is characteristic of an individual.



The Position of Absorption Bands

Hooke's Law

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

$$\tilde{\nu} = \frac{1}{2\pi c} \left[\frac{f(m_1 + m_2)}{m_1 m_2} \right]^{1/2}$$

where c = velocity of light, $\tilde{\nu}$ = wavenumber of the stretching vibration, f = force constant of the bond,

m_1 and m_2 are the masses of the atoms (in grams) joined by the bond. The force constant is a measure of the strength of the bond. The equation shows that *stronger bonds* and *lighter atoms* give rise to higher frequencies.

Lighter atoms show absorption bands at larger wavenumbers (cm⁻¹).

C-H ~ 3000

C-Cl ~ 700

C-O ~ 1100

C-D ~ 2200

Stronger bonds show absorption bands at larger wavenumbers (cm⁻¹).

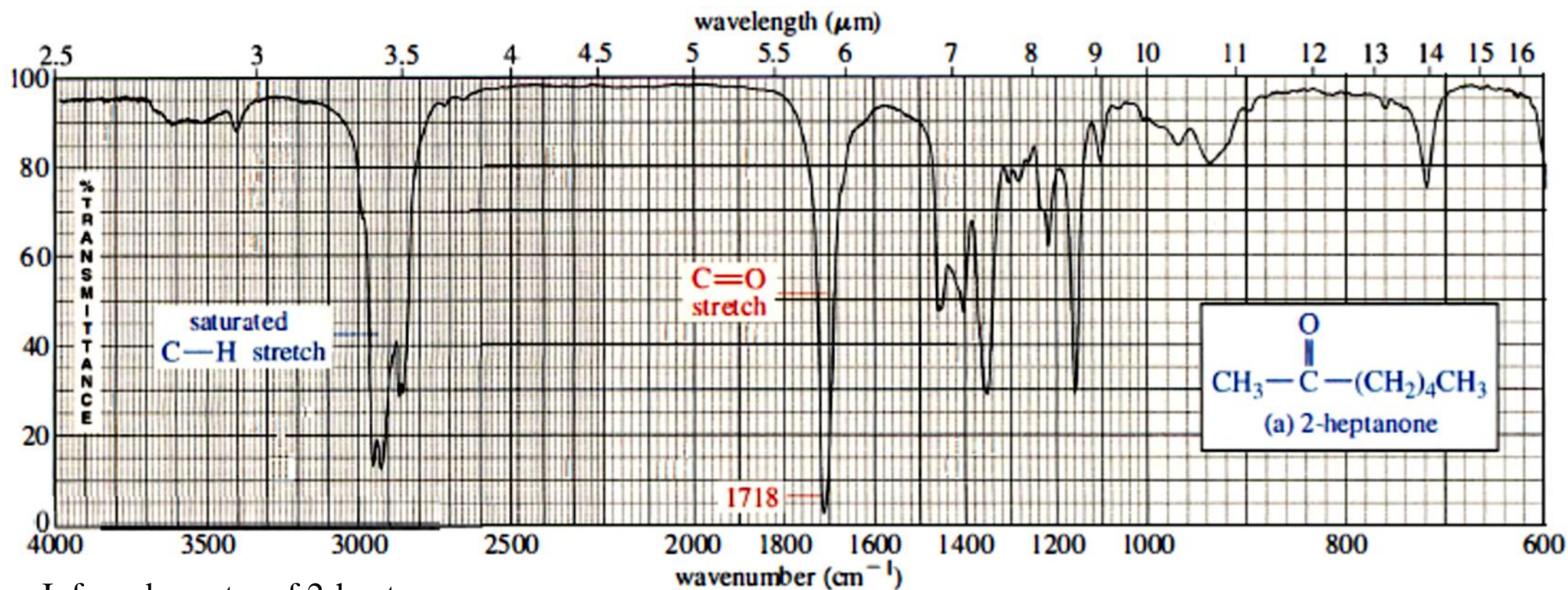
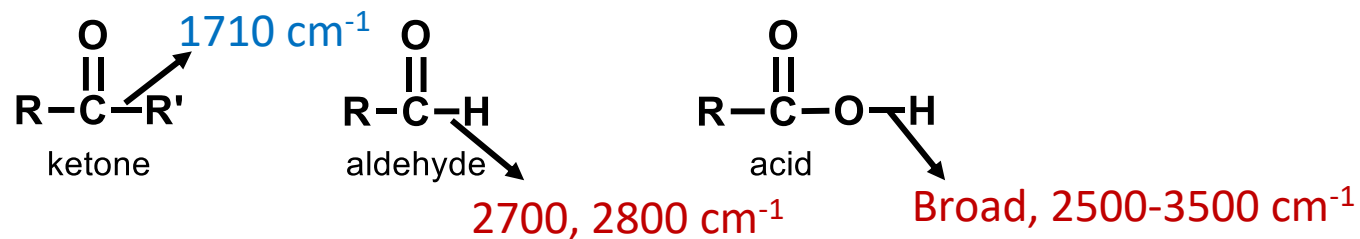
$\text{--C}\equiv\text{N}$ ~2200

$\diagup\text{C}=\text{N}$ ~1600

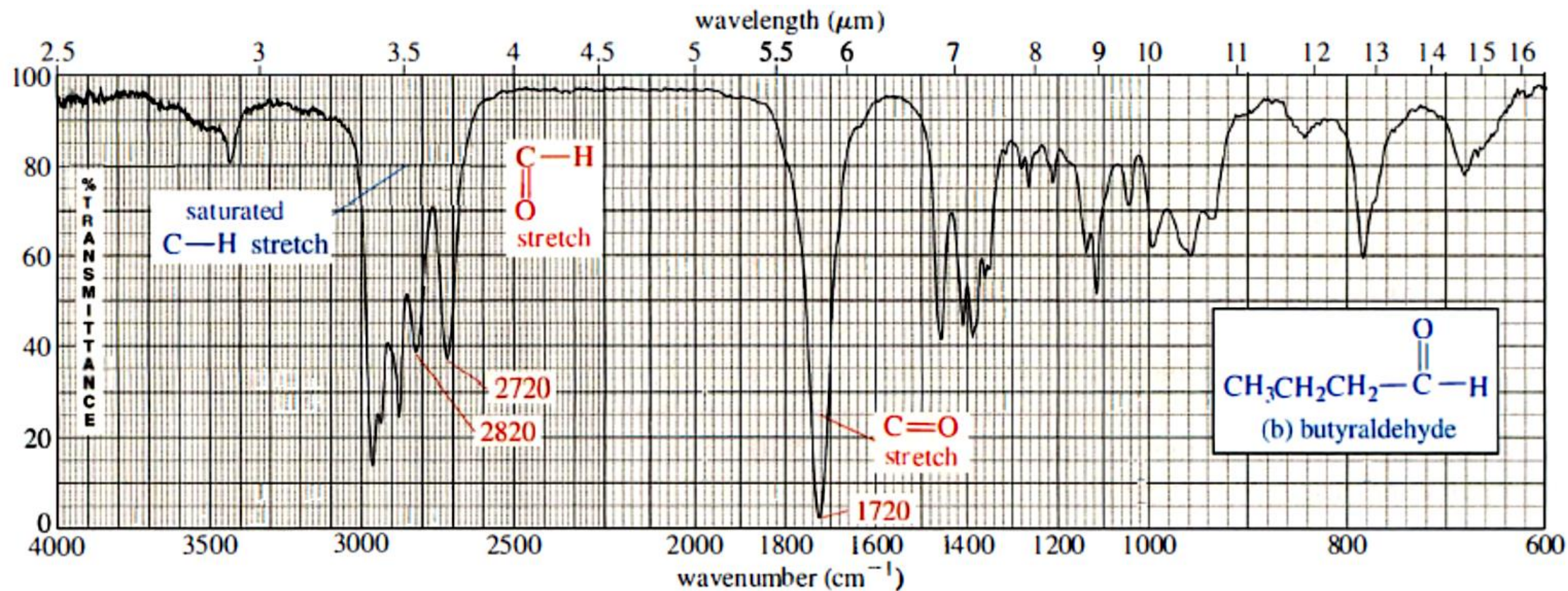
C-N ~1100

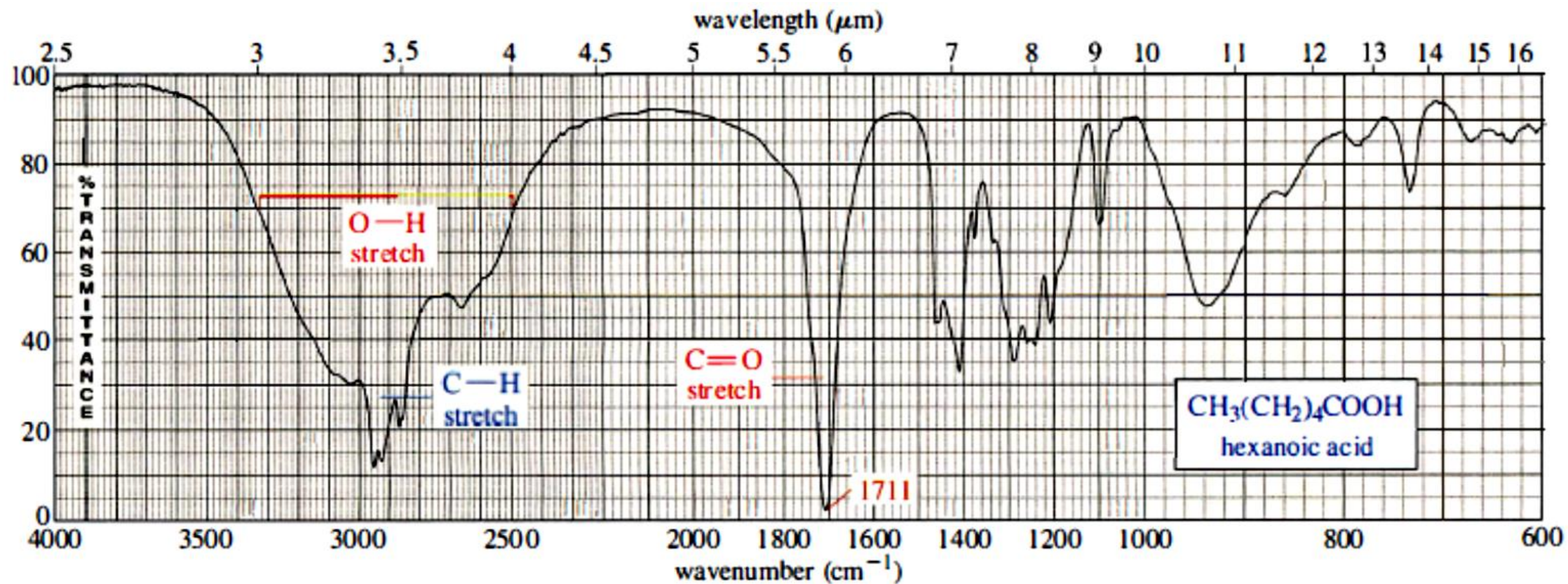
Characteristic Absorptions of Carbonyl Compounds

Simple Ketones, Aldehydes, and Acids

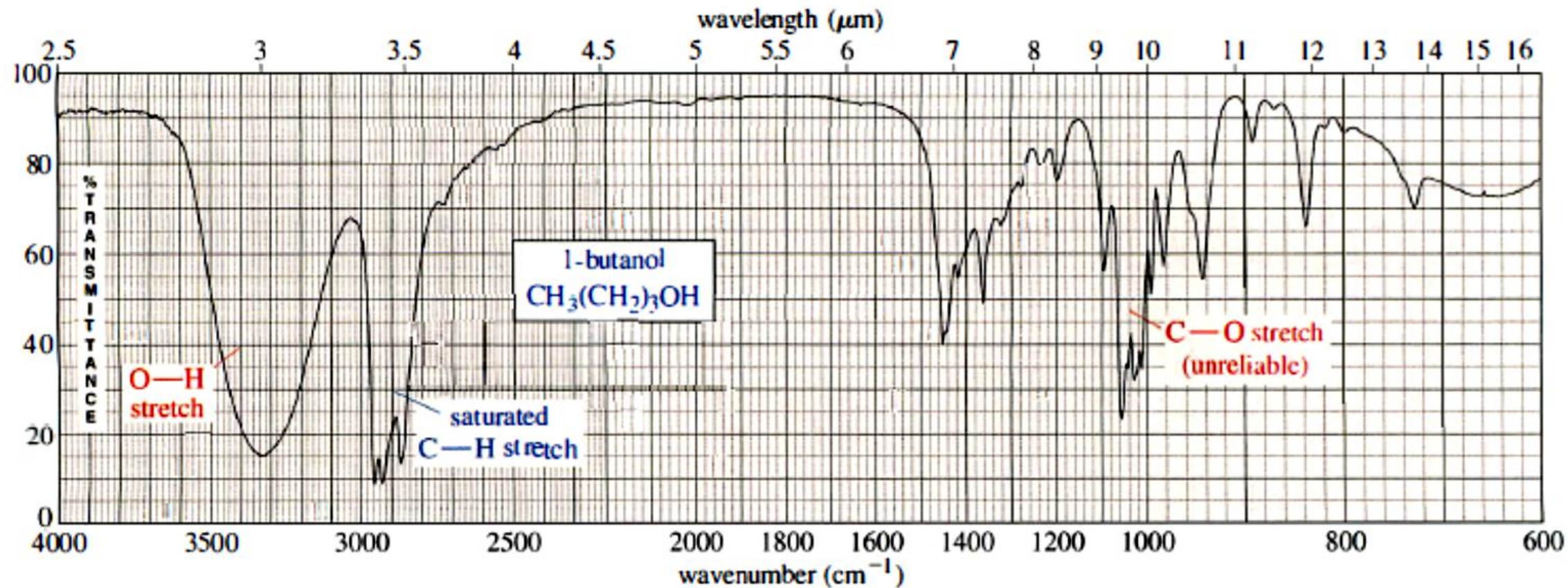


Infrared spectra of 2-heptanone







Infrared spectrum of hexanoic acid. Carboxylic acids show a broad O-H absorption from about 2500 to 3500 cm^{-1} .



The IR spectrum of 1-butanol shows a broad, intense O-H stretching absorption centered around 3300 cm^{-1} .

Summary of IR Stretching Frequencies

Frequency (cm ⁻¹)	Functional Group	Comments
3300	alcohol O-H amine, amide N-H alkyne $\equiv\text{C-H}$	always broad may be broad, sharp, or broad with spikes always sharp, usually strong
3000	alkane -C-H Alkene =C-H acid O-H	just below 3000 cm ⁻¹ just above 3000 cm ⁻¹ very broad
2200	alkyne $\text{-C}\equiv\text{C}$ Nitrile $\text{—}\equiv\text{N}$	just below 2200 cm ⁻¹ just above 2200 cm ⁻¹
1700 (very strong)	Carbonyl 	ketones, aldehydes, acids esters higher, about 1735 cm ⁻¹ conjugation lowers frequency amides lower, about 1650 cm ⁻¹
1660	Alkene 	conjugation lowers frequency aromatic C=C about 1600 cm ⁻¹

References:

1. Organic Chemistry, Clayden
2. Organic Spectroscopy, William Kemp
3. Introduction to Spectroscopy, D. Pavia
4. Organic Chemistry, L.G.Wade, Jr.
5. Organic Chemistry, Paula Bruice