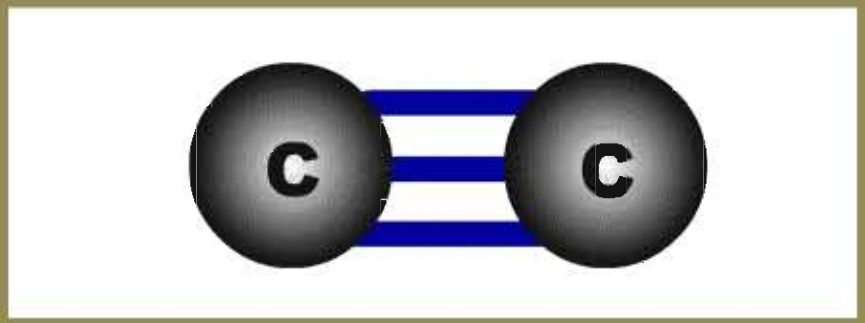
Vibrational Spectroscopy



By: Dr Nikhil Kaushik

Basic Concept :**Gives information about the functional groups in a molecule**

IR Spectroscopy

I. Introduction

A. Spectroscopy is the study of the interaction of matter with the electromagnetic spectrum

1. Electromagnetic radiation displays the properties of both particles and waves

2. The particle component is called a ***photon***

3. The energy (**E**) component of a photon is proportional to the frequency. Where **h** is Planck's constant and ν is the frequency in Hertz (cycles per second)

$$E = h\nu$$

4. The term "photon" is implied to mean a small, massless particle that contains a small wave-packet of EM radiation/light – we will use this terminology in the course

IR Spectroscopy

I. Introduction

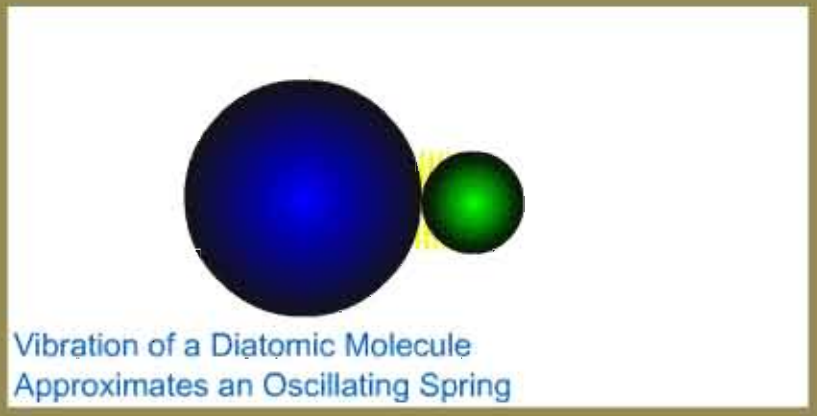
C. The IR Spectroscopic Process

1. The quantum mechanical energy levels observed in IR spectroscopy are those of ***molecular vibration***

2. We perceive this vibration as heat

3. When we say a ***covalent bond*** between two atoms is of a certain length, we are citing an average because the bond behaves as if it were a vibrating spring connecting the two atoms

4. For a simple diatomic molecule, this model is easy to visualize:



Vibration of a Diatomic Molecule
Approximates an Oscillating Spring

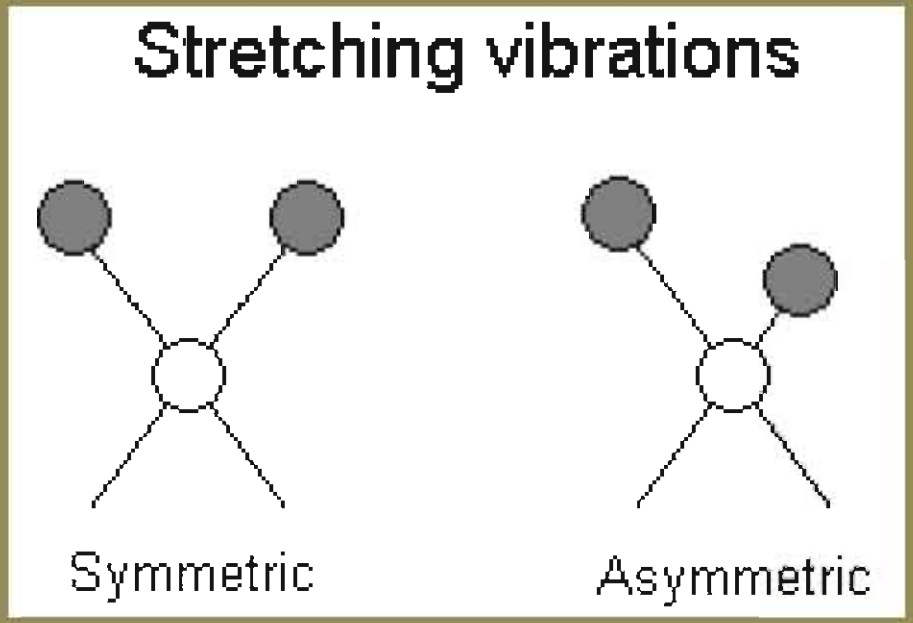
Infrared Spectroscopy

region of infrared that is most useful lies between (4000-625 cm^{-1})

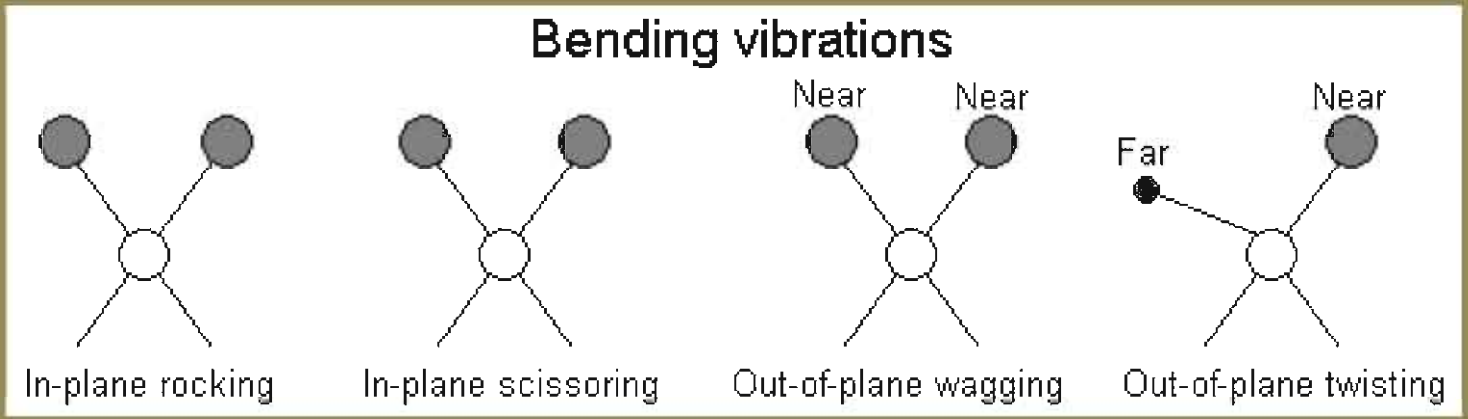
depends on transitions between vibrational energy states

- stretching
- bending

Stretching Vibrations



Bending Vibrations



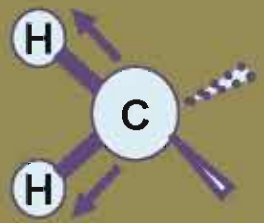
IR Spectroscopy

I. Introduction

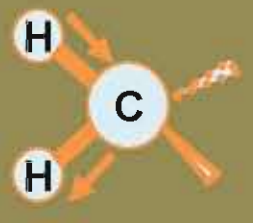
C. The IR Spectroscopic Process

5. There are two types of bond vibration:

- ***Stretch*** – Vibration or oscillation along the line of the bond

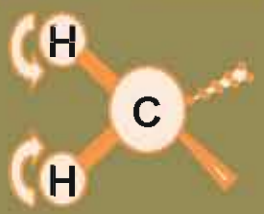


symmetric

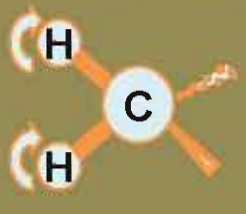


asymmetric

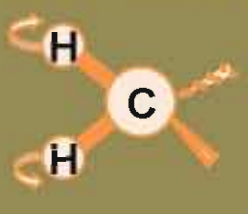
- ***Bend*** – Vibration or oscillation not along the line of the bond



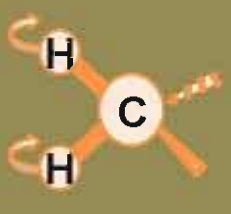
scissor



rock



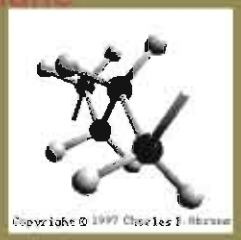
twist



wag

in plane

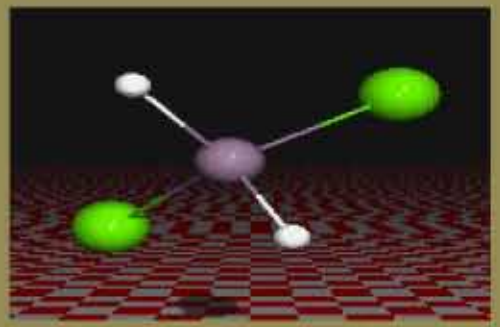
out of plane



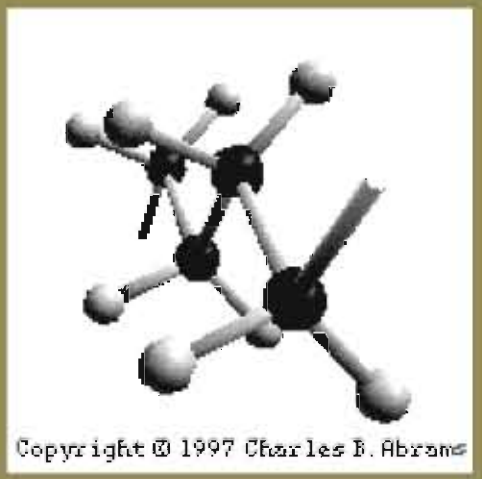
symmetric

asymmetric

In-plane scissoring

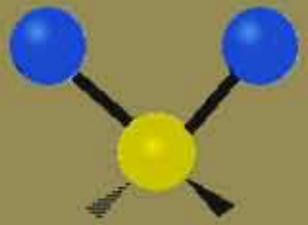


Out-of-plane twisting

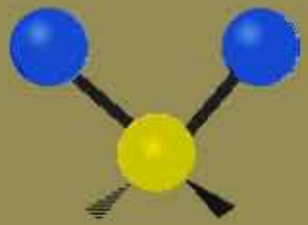


In-plane rocking

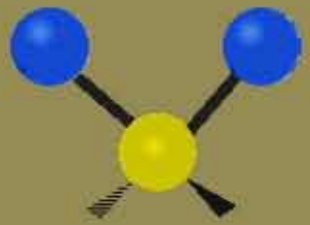
Out-of-plane wagging



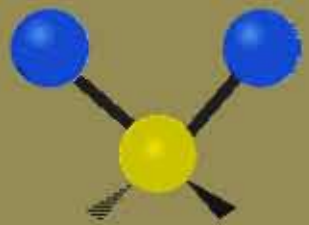
Symmetric stretching



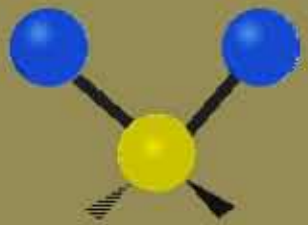
Antisymmetric stretching



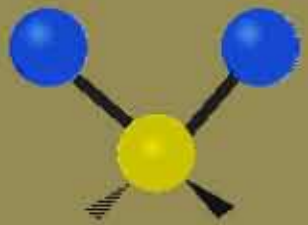
Scissoring



Rocking



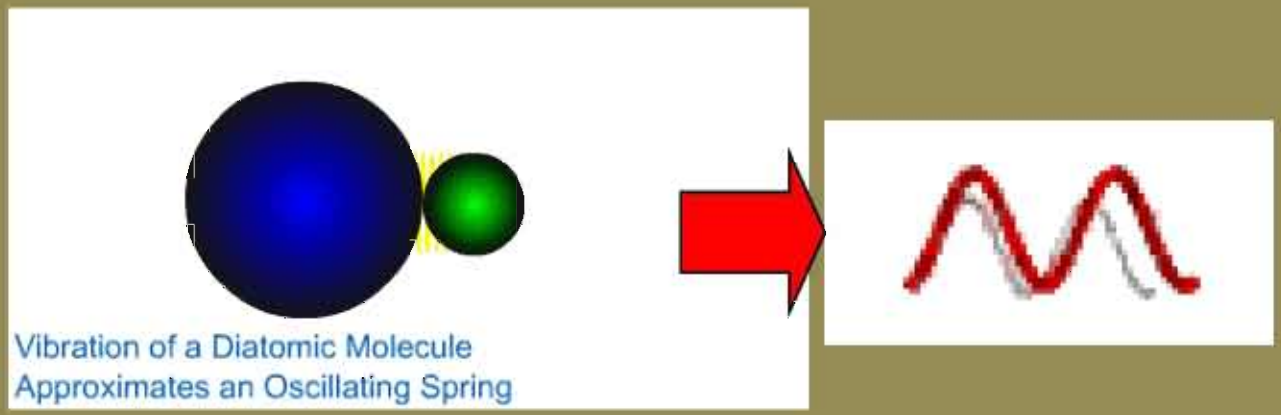
Wagging



Twisting

C. The IR Spectroscopic Process

6. As a covalent bond oscillates – due to the oscillation of the dipole of the molecule – a varying electromagnetic field is produced



Vibration of a Diatomic Molecule
Approximates an Oscillating Spring

7. The greater the dipole moment change through the vibration, the more intense the EM field that is generated

PRINCIPAL MODES OF VIBRATION

3N-6 possible normal modes of vibration

N = number of atoms in a molecule

Degrees of freedom = 3N

H_2O for example

- 3 atoms
- Degrees of freedom = 3 x 3 = 9
- Normal modes of vibration = 9-6 = 3

The Duck

PRINCIPAL MODES OF VIBRATION

Linear Molecules

- Cannot rotate about the bond axis

- Only 2 degrees of freedom describe rotation

3N-5 possible normal modes of vibration

CO_2 for example

- 3 atoms
- Normal modes of vibration = 9-5 = 4

The Duck

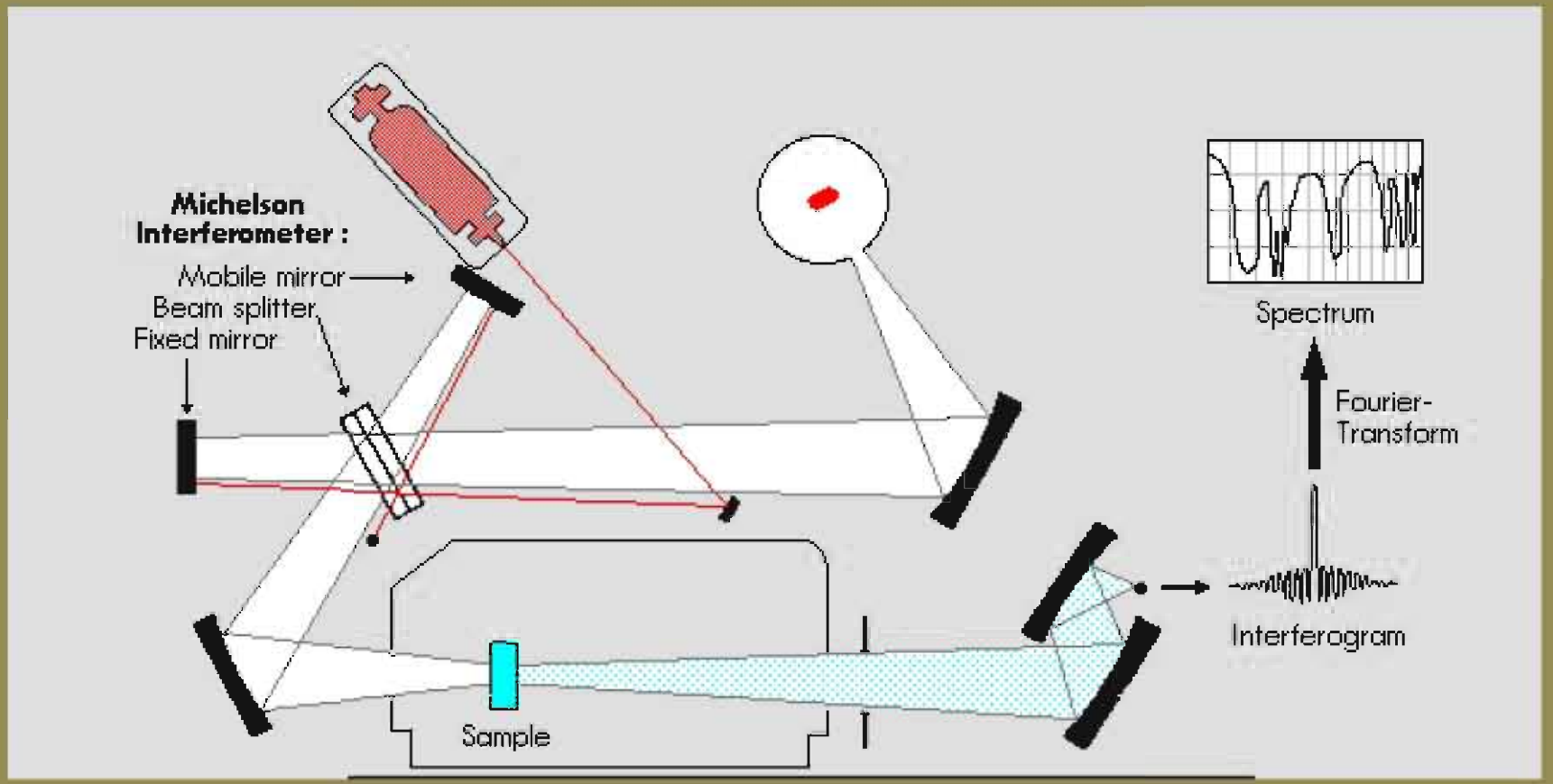
FUNDAMENTAL TRANSITIONS

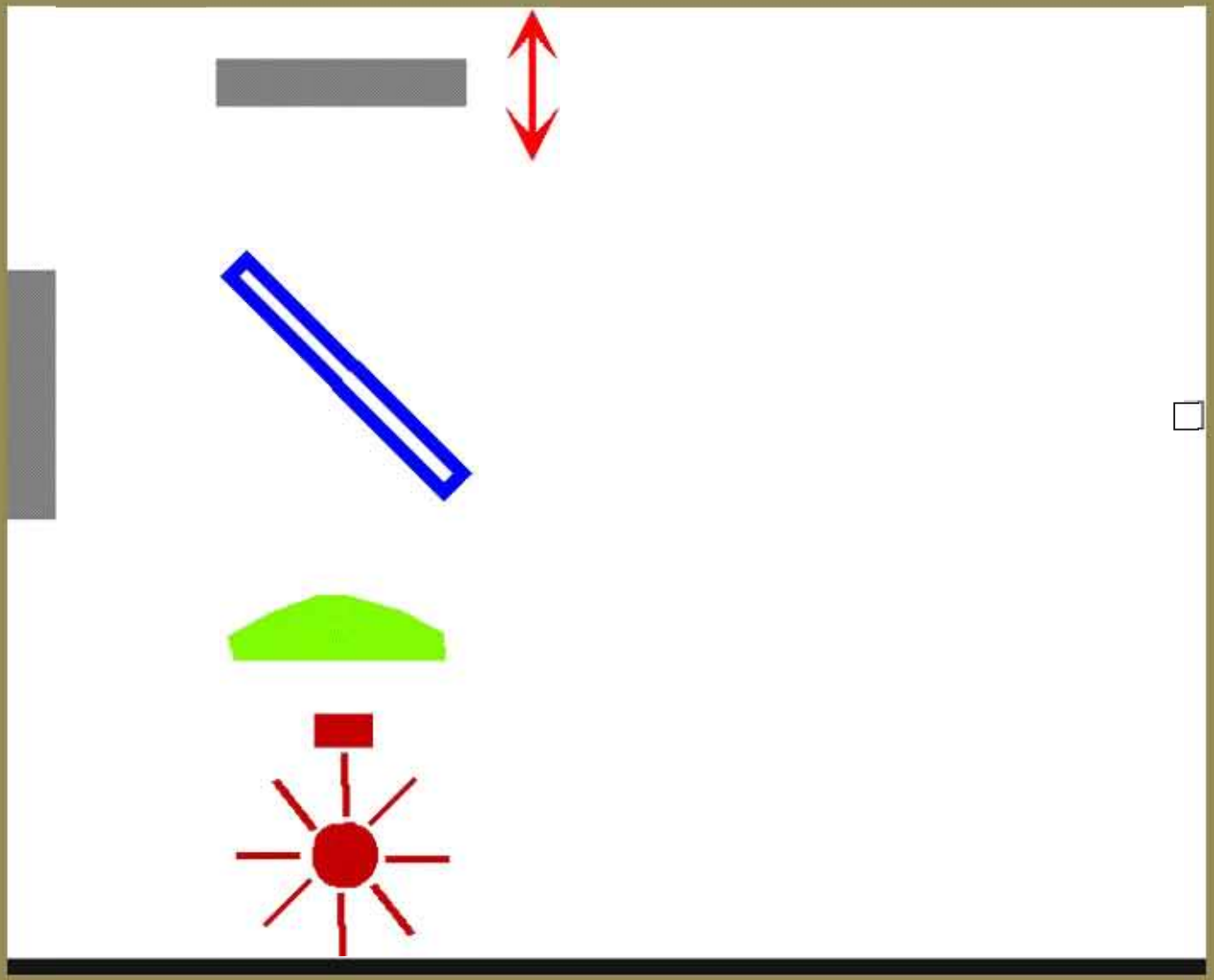
Overtone

- - Excitation from ground state to higher energy states
- - Result in overtone bands that are weaker than fundamental
- - Frequencies are integral multiples of fundamental absorption
- - Fewer peaks are seen than predicted on spectra due to IR-inactive
- vibrations, degenerate vibrations, weak vibrations
- - Additional peaks may be seen due to overtones

The Duck

Infrared Absorbance





Thermo Nicolet

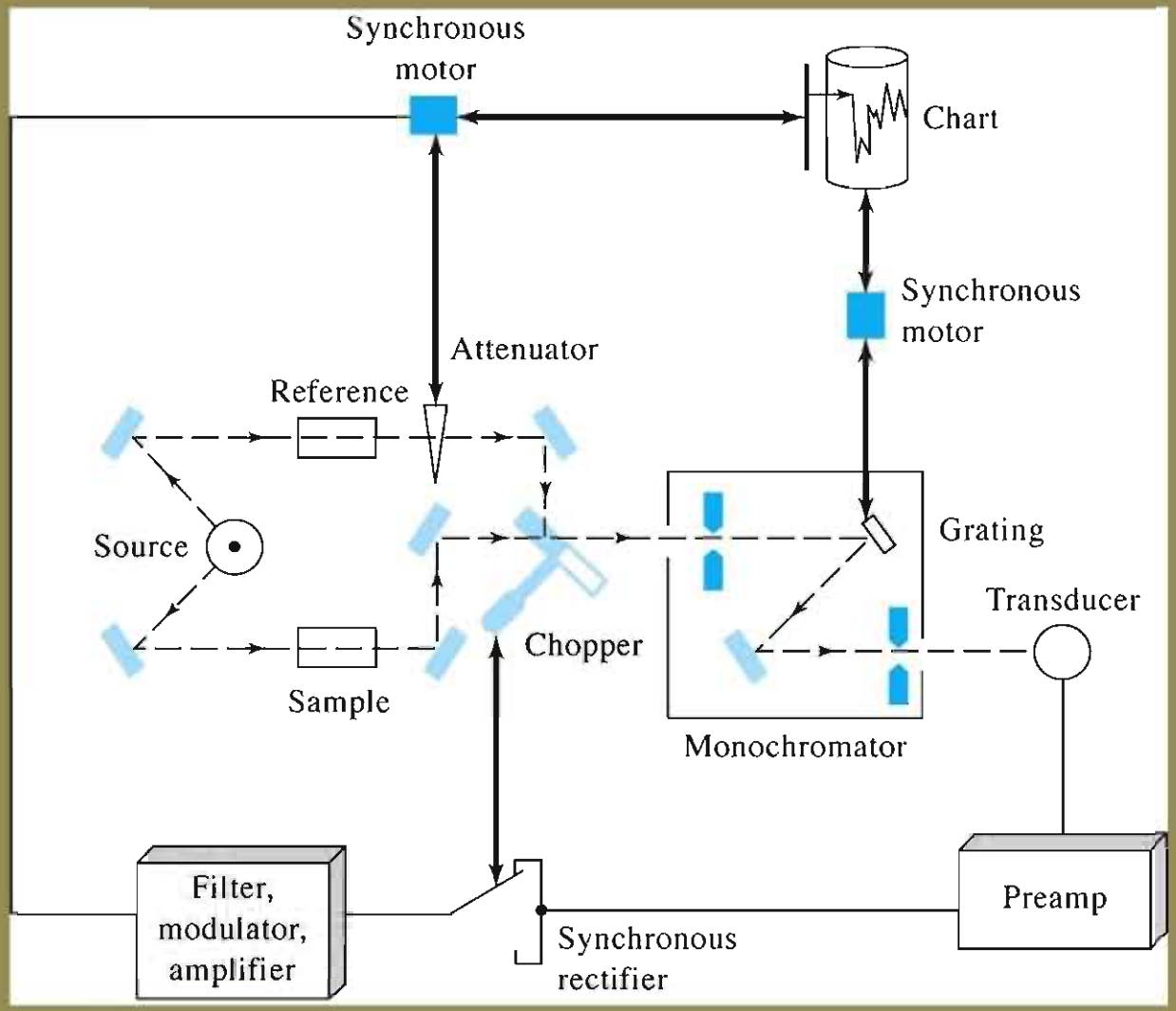
FT-IR System

Optical Bench

C) Instrumentation

1.) Basic Design

- normal IR instrument similar to UV-vis
- main differences are light source & detector

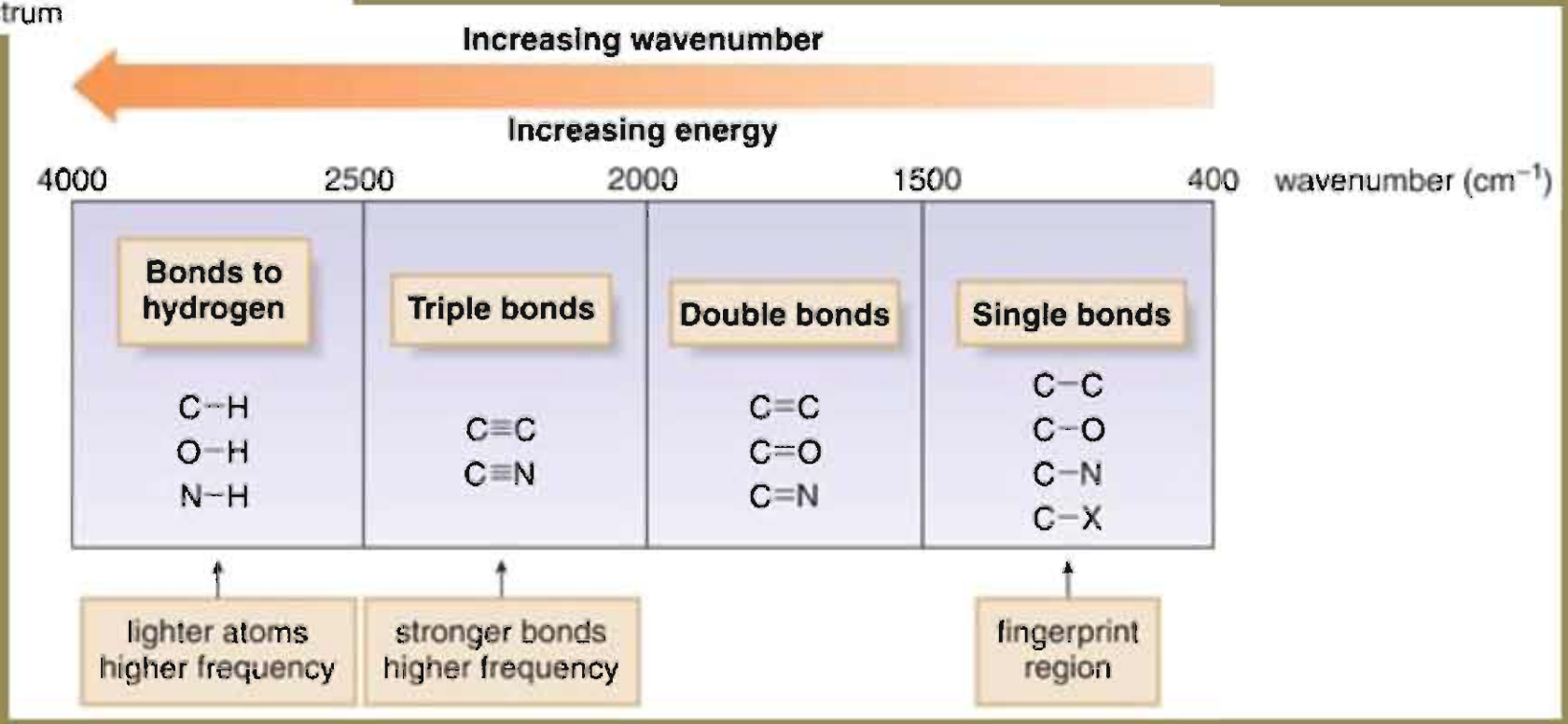


Infrared Spectroscopy

IR Absorptions

- Bonds absorb in four predictable regions of an IR spectrum.

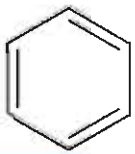
Figure 14.10 Summary: The four regions of the IR spectrum



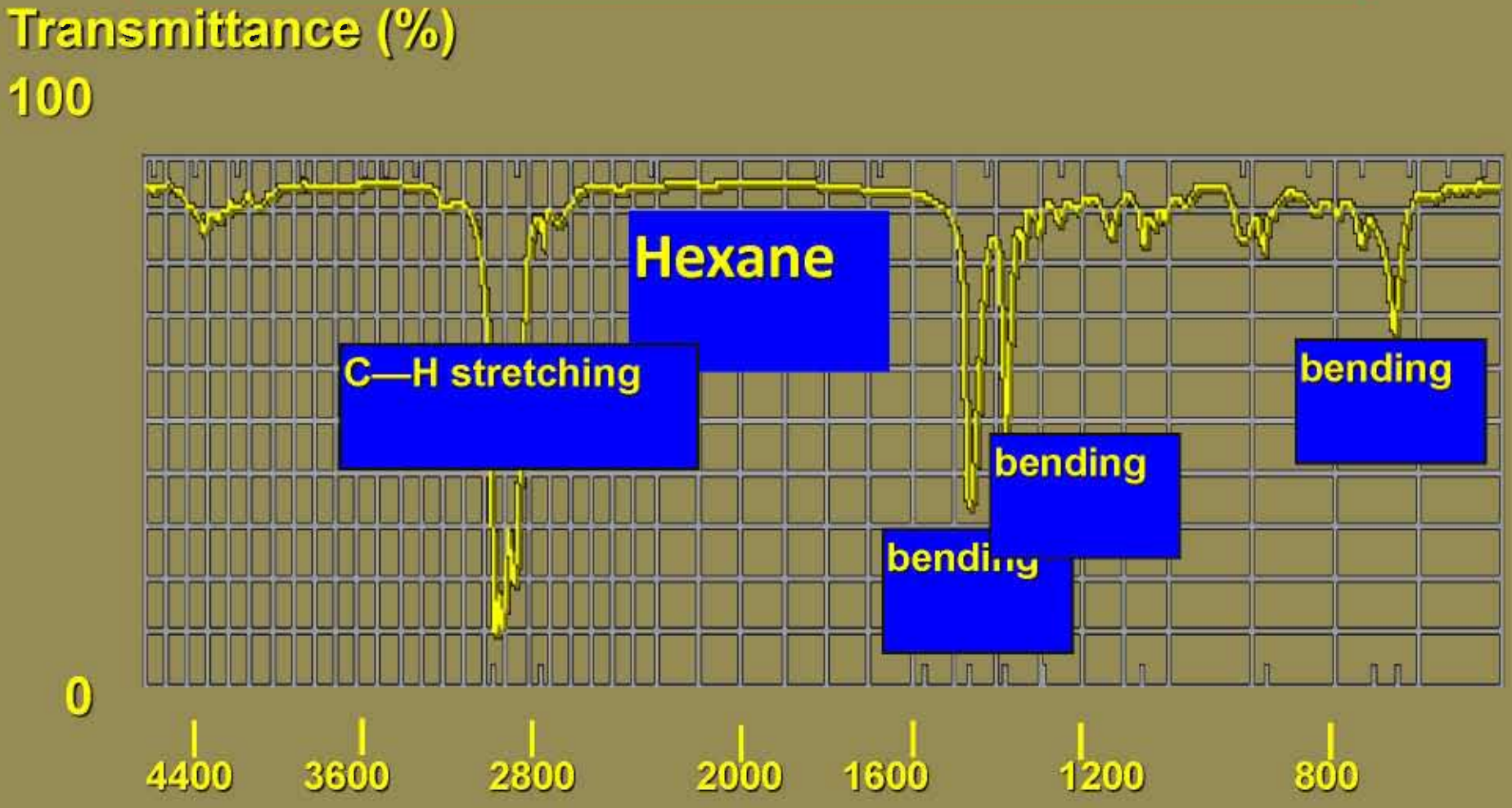
Infrared Spectroscopy

IR Absorptions

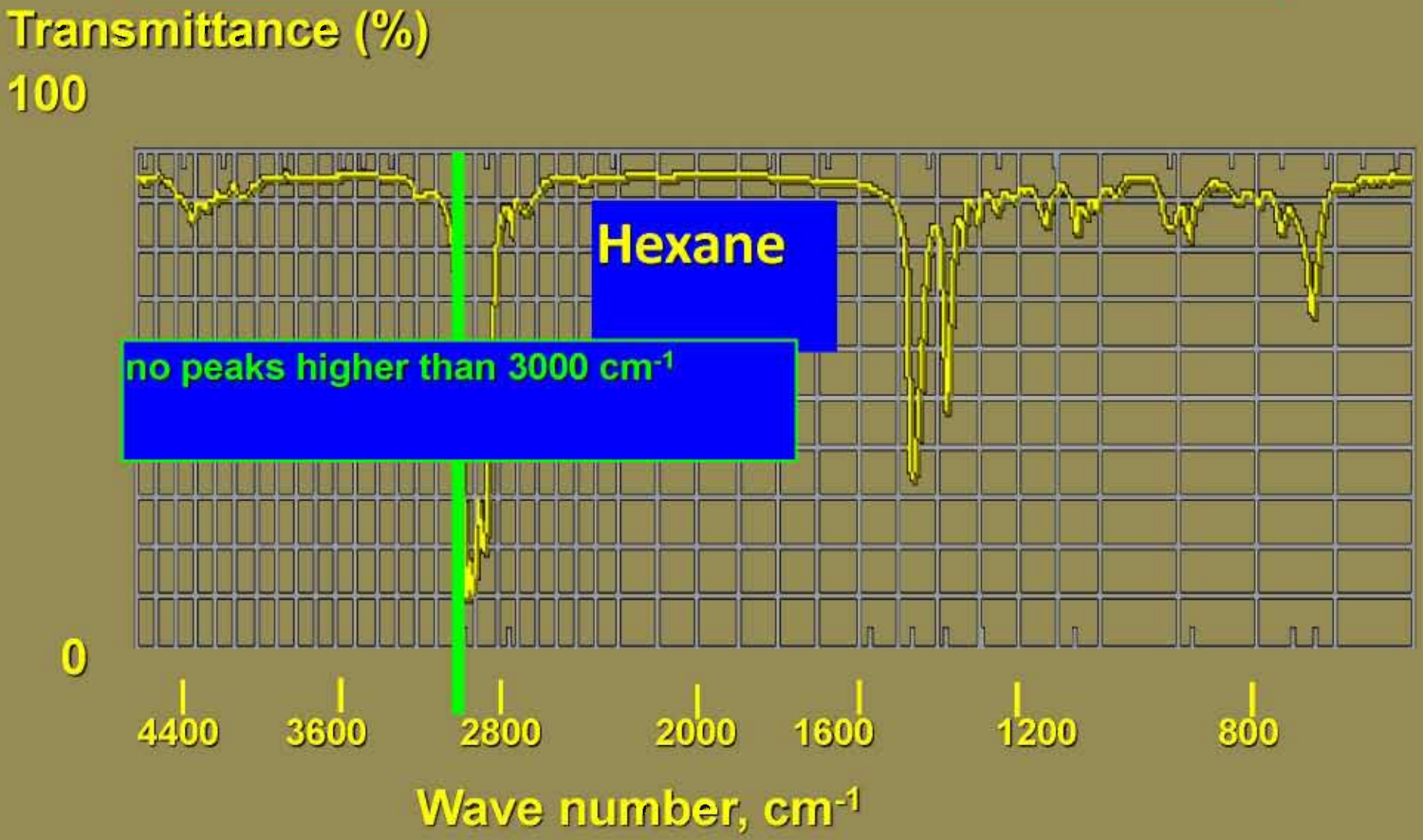
TABLE 14.2 Important IR Absorptions

Bond type	Approximate $\tilde{\nu}$ (cm^{-1})	Intensity
O–H	3600–3200	strong, broad
N–H	3500–3200	medium
C–H	~3000	
• C_{sp^3}–H	3000–2850	strong
• C_{sp^2}–H	3150–3000	medium
• C_{sp}–H	3300	medium
C≡C	2250	medium
C≡N	2250	medium
C=O	1800–1650 (often ~1700)	strong
C=C	1650	medium
	1600, 1500	medium

Example of infrared spectrum



Example of infrared spectrum



Infrared spectrum of 1-hexene

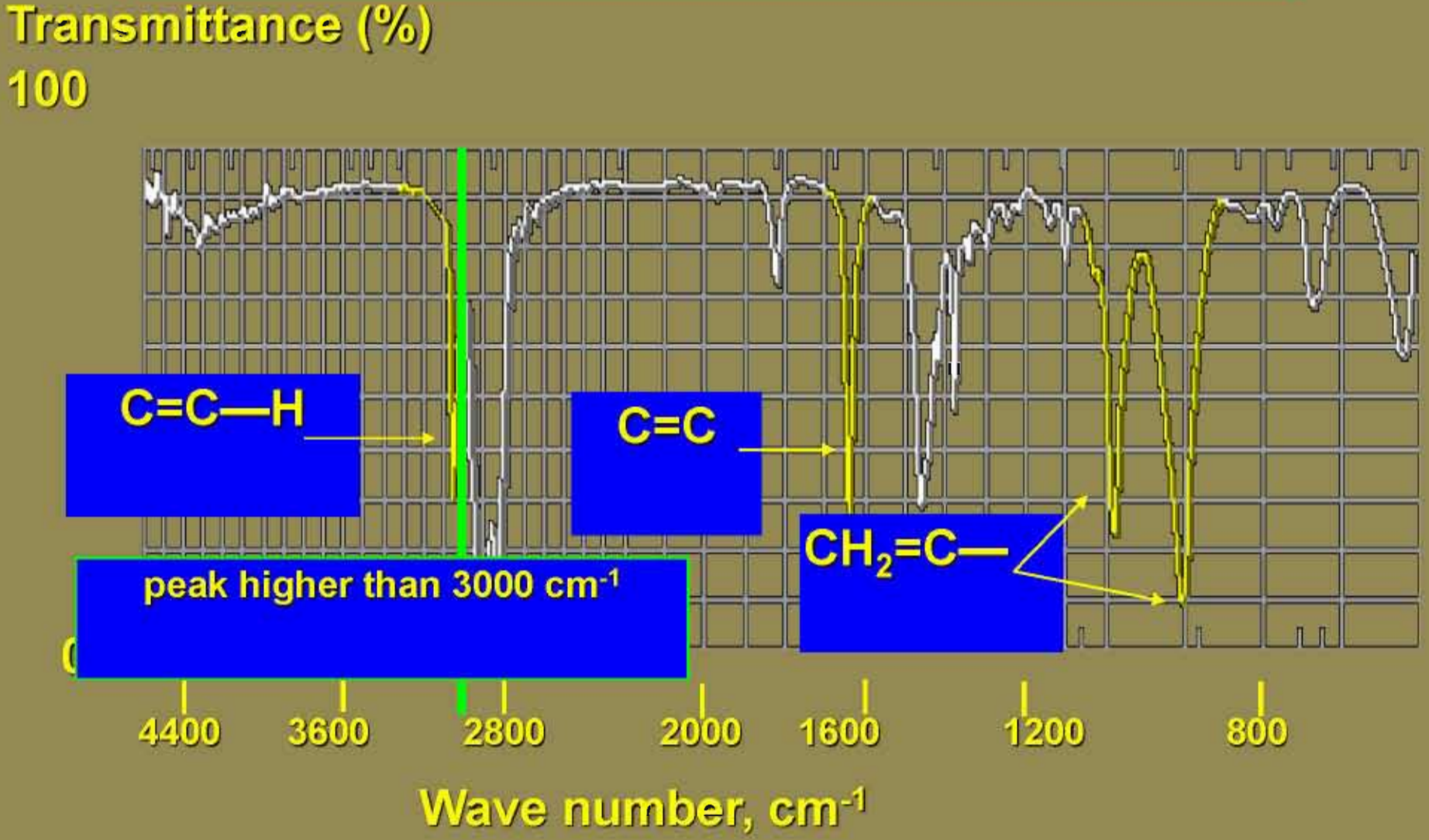


Table 13.4 (p 519)
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
sp C—H	3310-3320
sp^2 C—H	3000-3100
sp^3 C—H	2850-2950
sp^2 C—O	1200
sp^3 C—O	1025-1200

Table 13.4 (p 519)
Infrared Absorption Frequencies

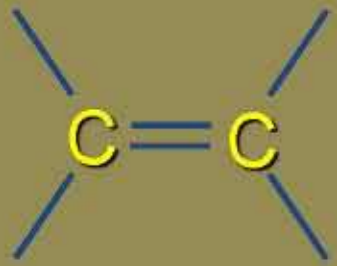
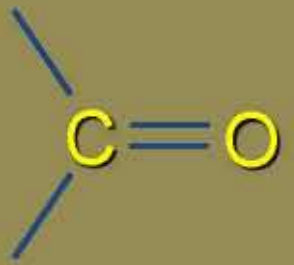
Structural unit	Frequency, cm^{-1}
Stretching vibrations (multiple bonds)	
	1620-1680
—C≡C—	2100-2200
—C≡N	2240-2280

Table 13.4 (p 519)
Infrared Absorption Frequencies



Structural unit	Frequency, cm^{-1}
Stretching vibrations (carbonyl groups)	
Aldehydes and ketones	1710-1750
Carboxylic acids	1700-1725
Acid anhydrides	1800-1850 and 1740-1790
Esters	1730-1750
Amides	1680-1700

Table 13.4 (p 519)
Infrared Absorption Frequencies

Structural unit

Frequency, cm⁻¹

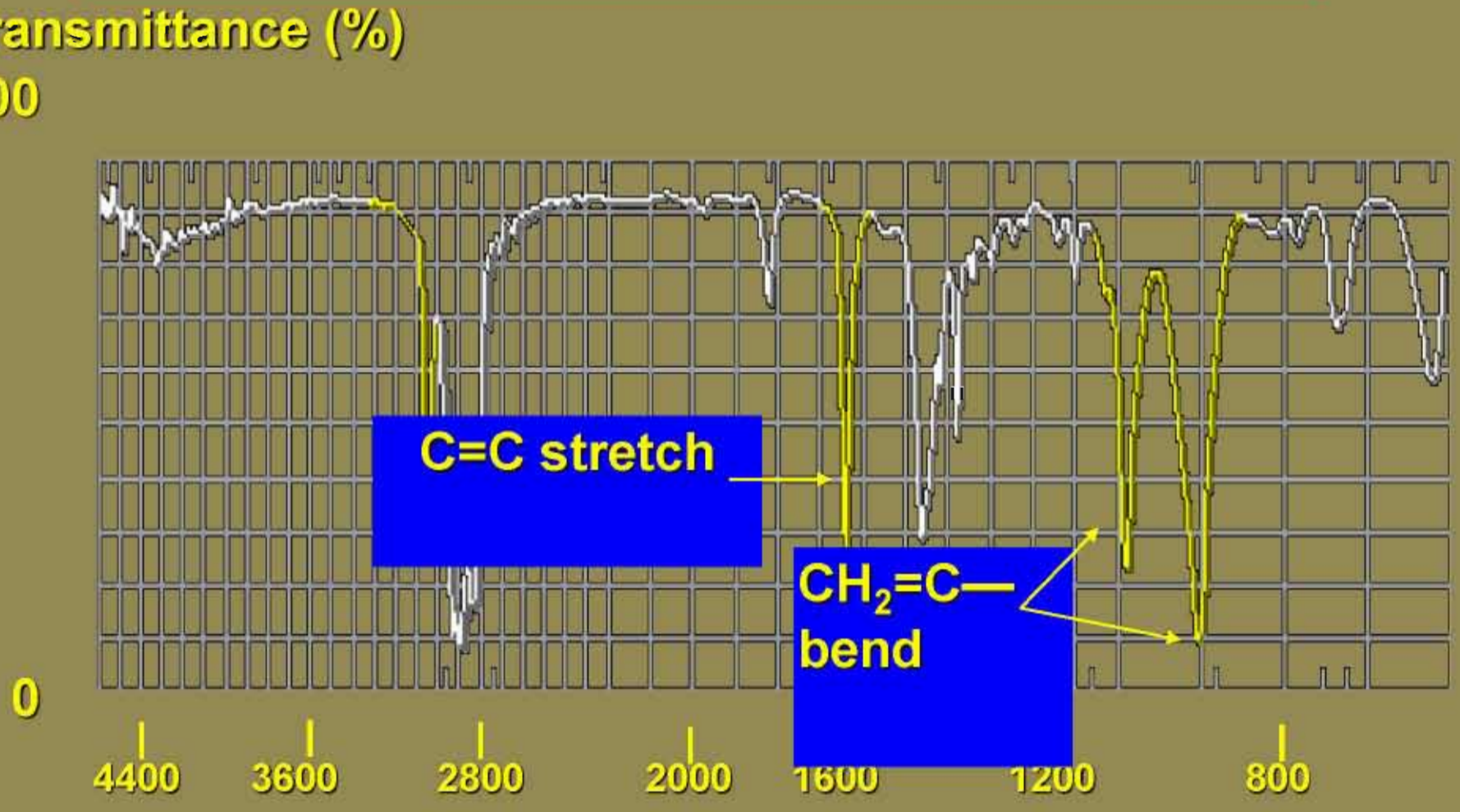
Bending vibrations of alkenes

$RCH{=}CH_2$	910-990
$R_2C{=}CH_2$	890
cis-$RCH{=}CHR'$	665-730
trans-$RCH{=}CHR'$	960-980
$R_2C{=}CHR'$	790-840

Table 13.4 (p 519)
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Bending vibrations of derivatives of benzene	
Monosubstituted	730-770 and 690-710
Ortho-disubstituted	735-770
Meta-disubstituted	750-810 and 680-730
Para-disubstituted	790-840

Infrared spectrum of 1-hexene



Infrared spectrum of *tert*-butylbenzene

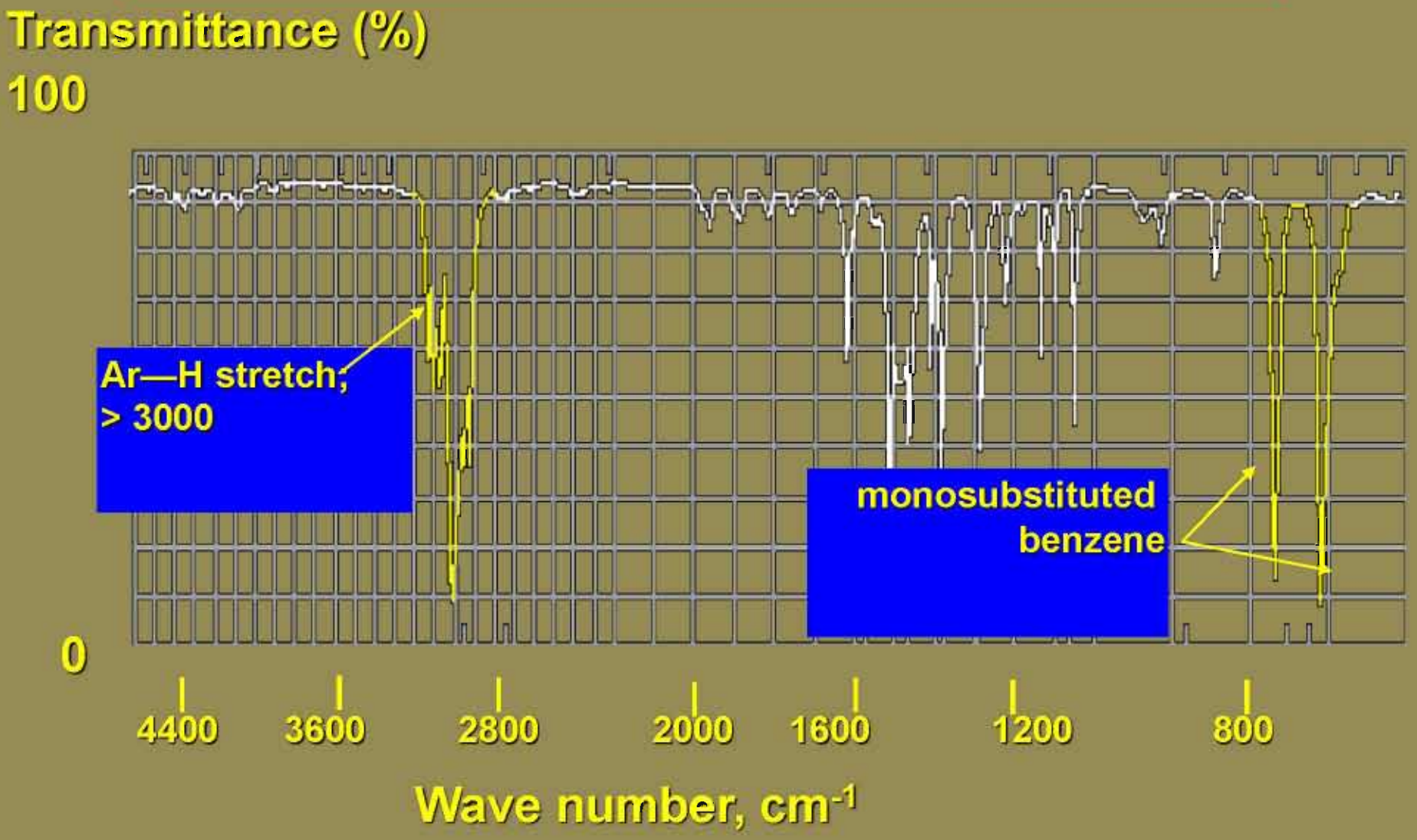
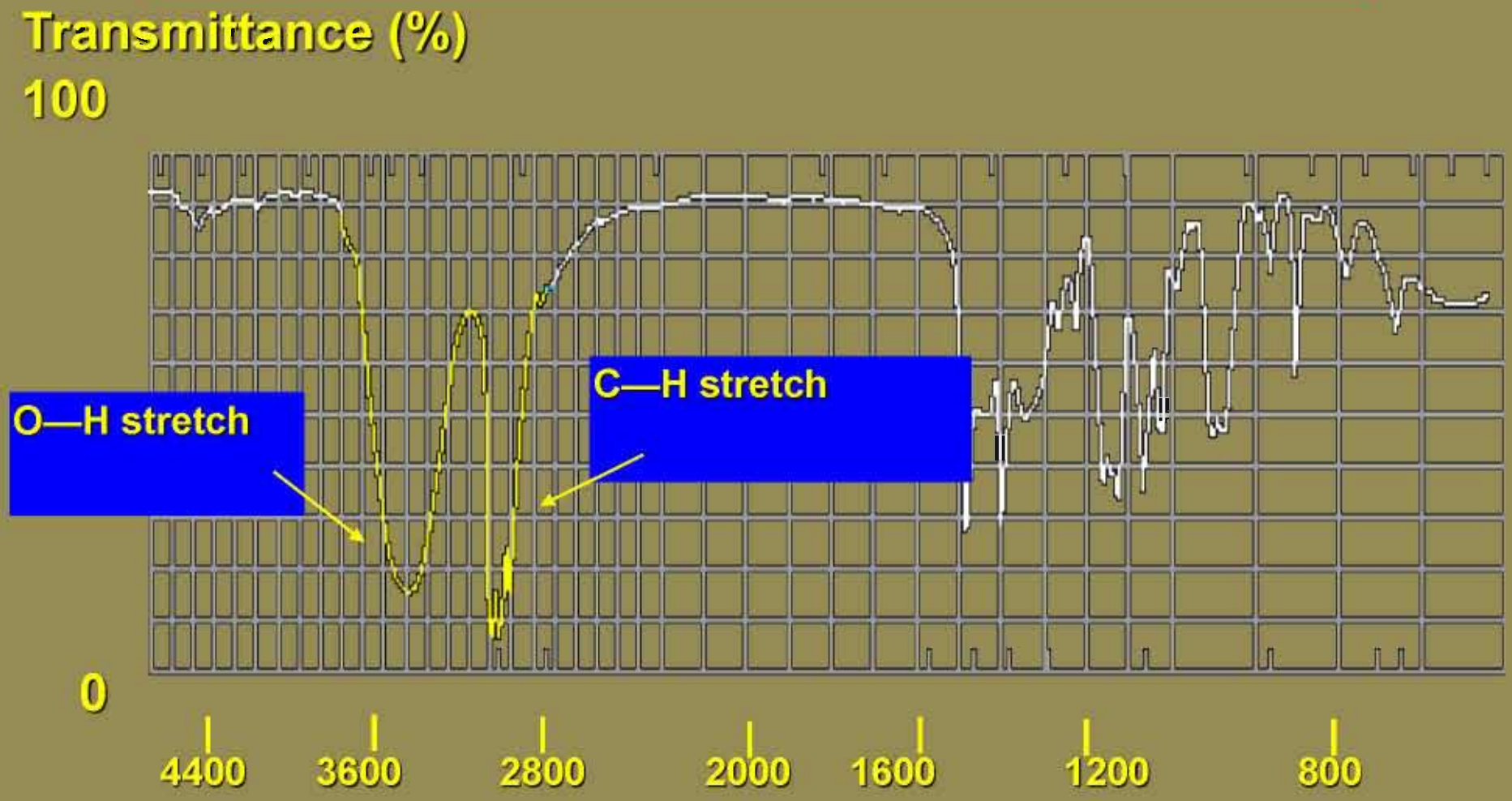


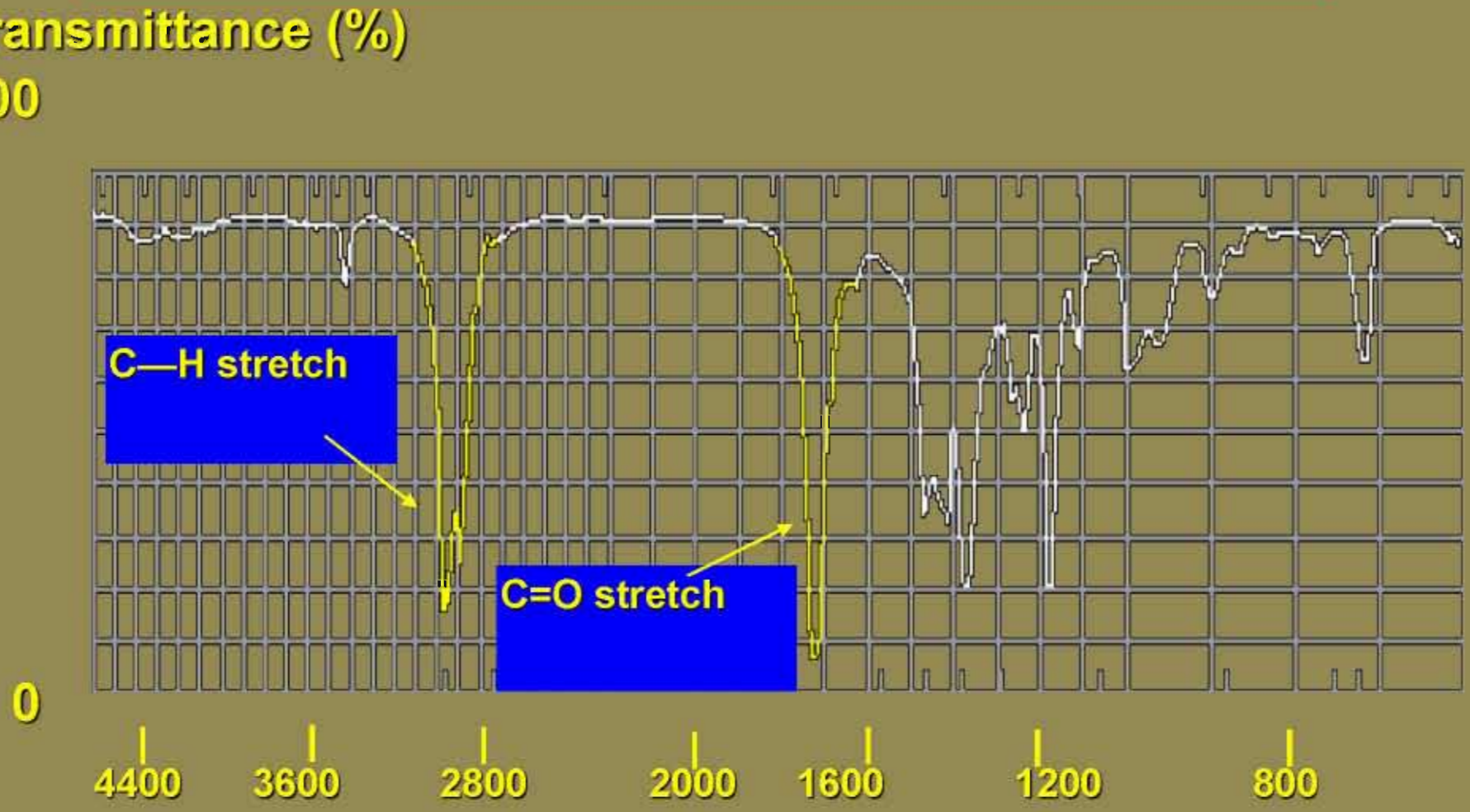
Table 13.4 (p 519)
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
O—H (alcohols)	3200-3600
O—H (carboxylic acids)	3000-3100
N—H	3350-3500

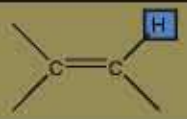
Infrared spectrum of 2-hexanol



Infrared spectrum of 2-hexanone



Abbreviated Table of Group Frequencies for Organic Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C-H	Alkanes	2850-2970	Strong
C-H	Alkenes 	3010-3095 675-995	Medium strong
C-H	Alkynes	3300	Strong
C-H	Aromatic rings	3010-3100 690-900	Medium strong
0-H	Monomeric alcohols, phenols Hydrogen-bonded alchohols, phenols Monomeric carboxylic acids Hydrogen-bonded carboxylic acids	3590-3650 3200-3600 3500-3650 2500-2700	Variable Variable, sometimes broad Medium broad
N-H	Amines, amides	3300-3500	medium
C=C	Alkenes	1610-1680	Variable
C=C	Aromatic rings	1500-1600	Variable
C≡C	Alkynes	2100-2260	Variable
C-N	Amines, amides	1180-1360	Strong
C≡N	Nitriles	2210-2280	Strong
C-O	Alcohols, ethers,carboxylic acids, esters	1050-1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690-1760	Strong
NO_2	Nitro compounds	1500-1570 1300-1370	Strong

Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
O—H (alcohols)	3200-3600
O—H (carboxylic acids)	3000-3100

First examine the absorption bands in the vicinity of 4000-3000 cm^{-1}

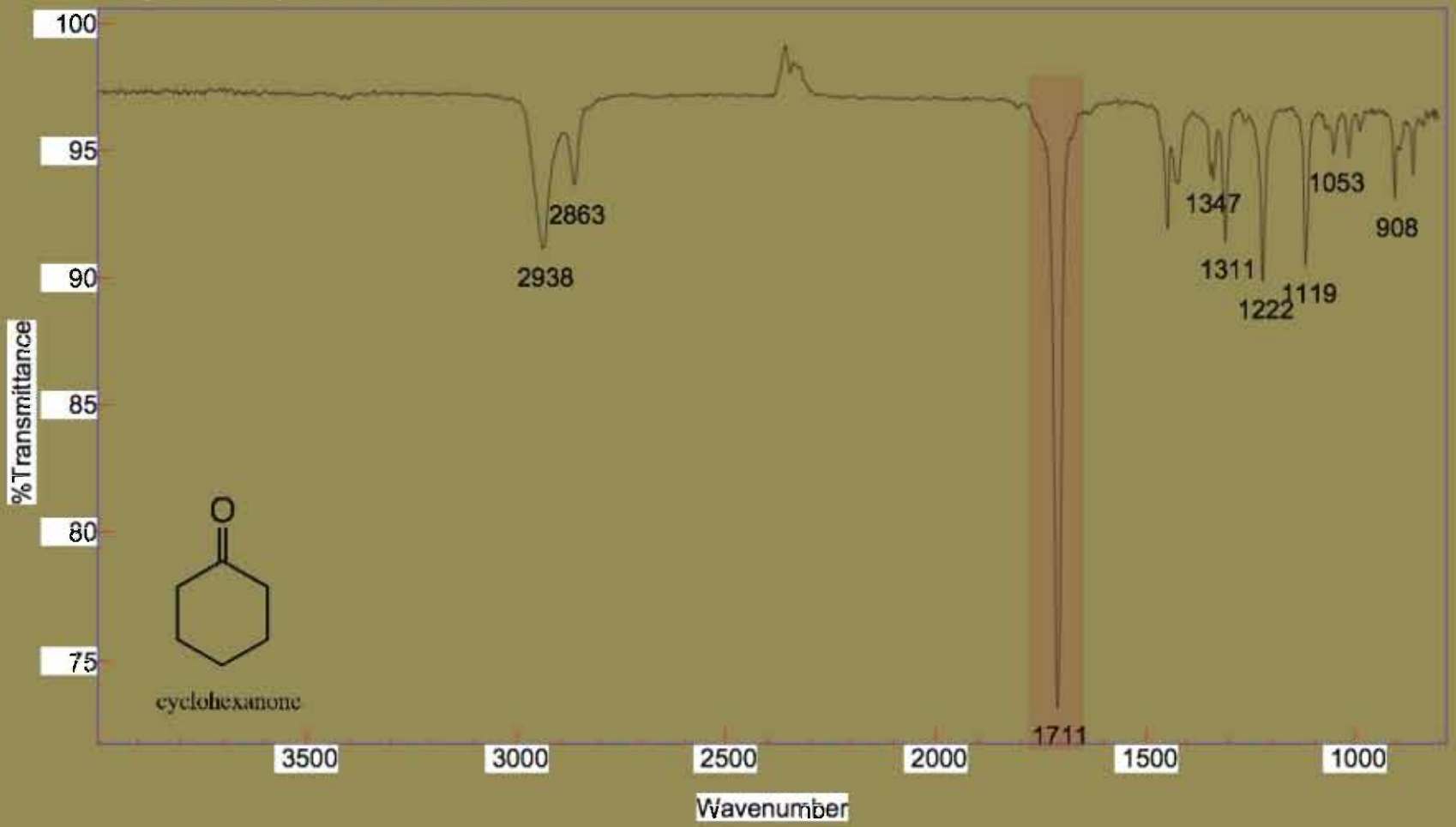
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
sp C—H	3310-3320
sp^2 C—H	3000-3100
sp^3 C—H	2850-2950
sp^2 C—O	1200
sp^3 C—O	1025-1200

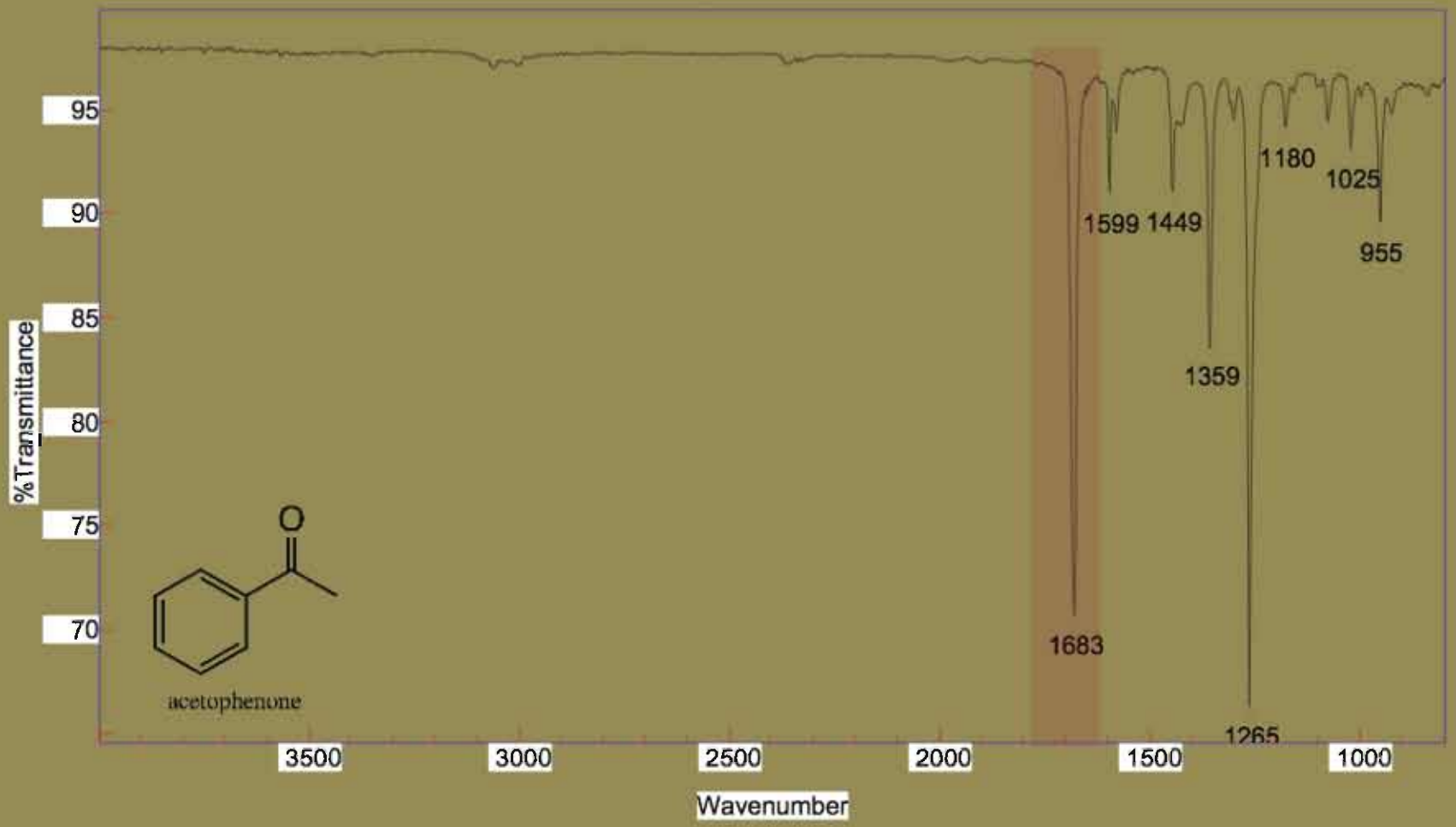
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
sp^2 C—O	1200
sp^3 C—O	1025-1200

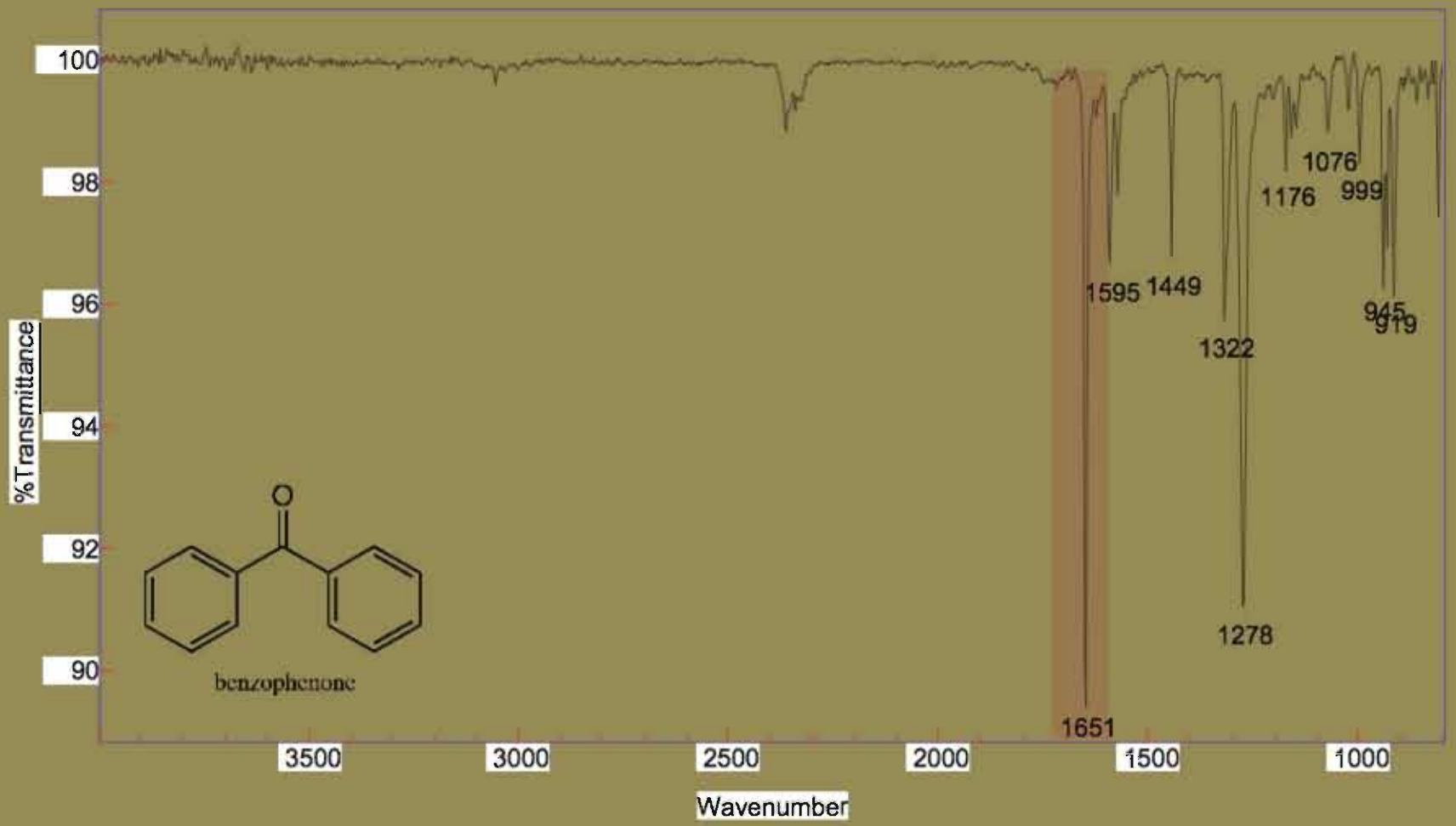
Cyclic aliphatic ketone



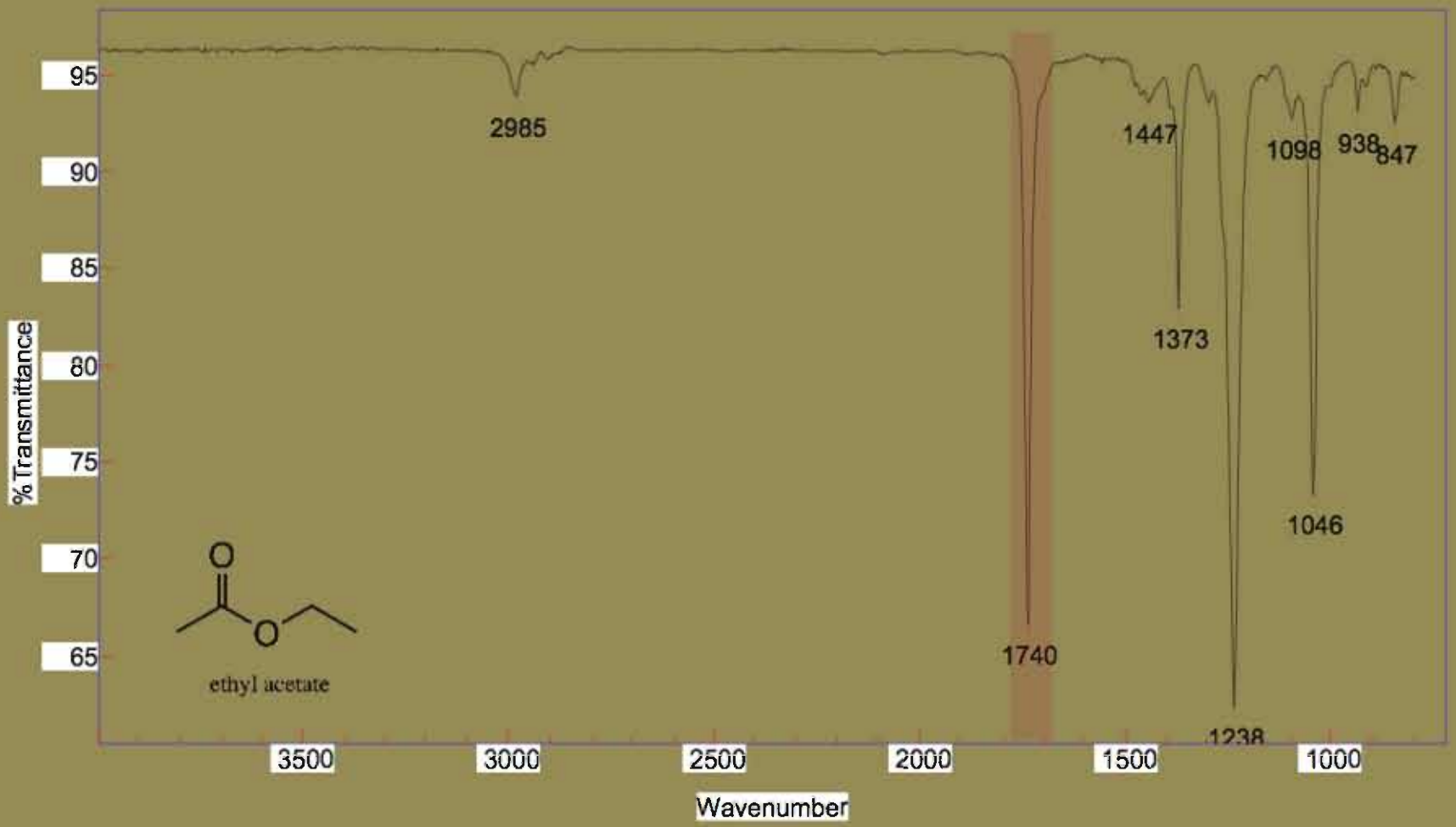
Mono substituted aromatic methyl ketone



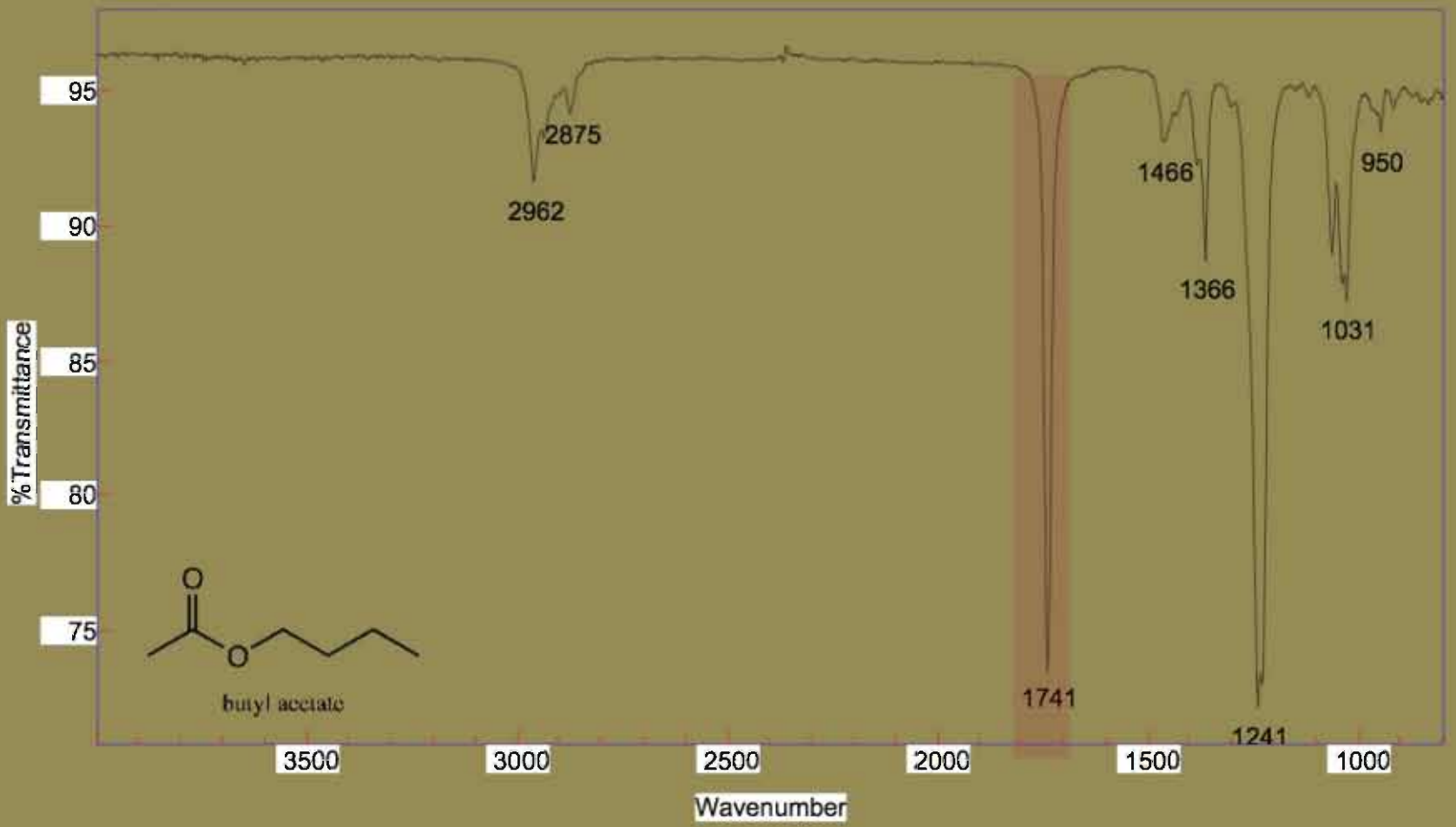
Mono substituted aromatic ketone



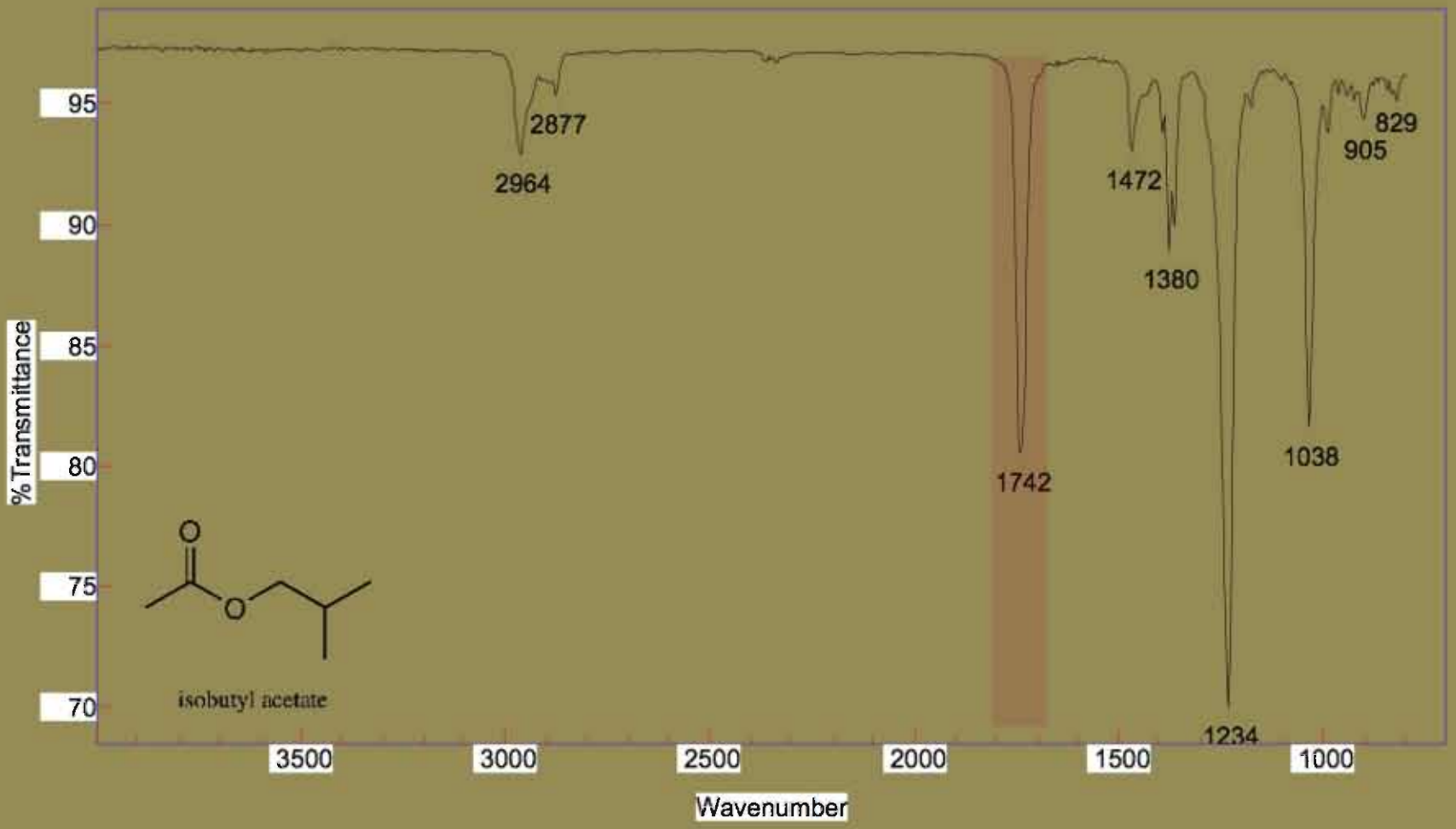
Aliphatic ester I



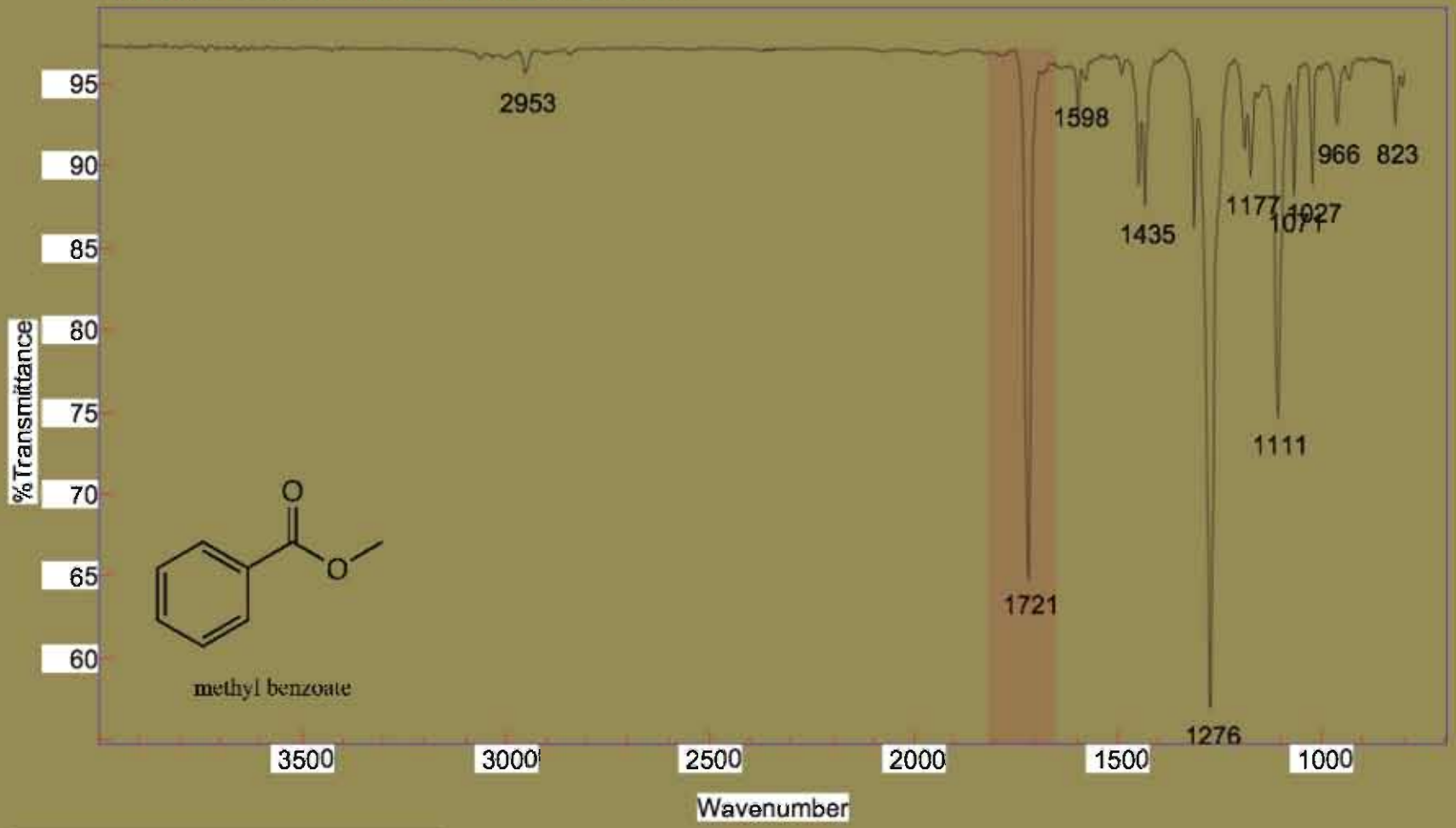
Aliphatic ester II



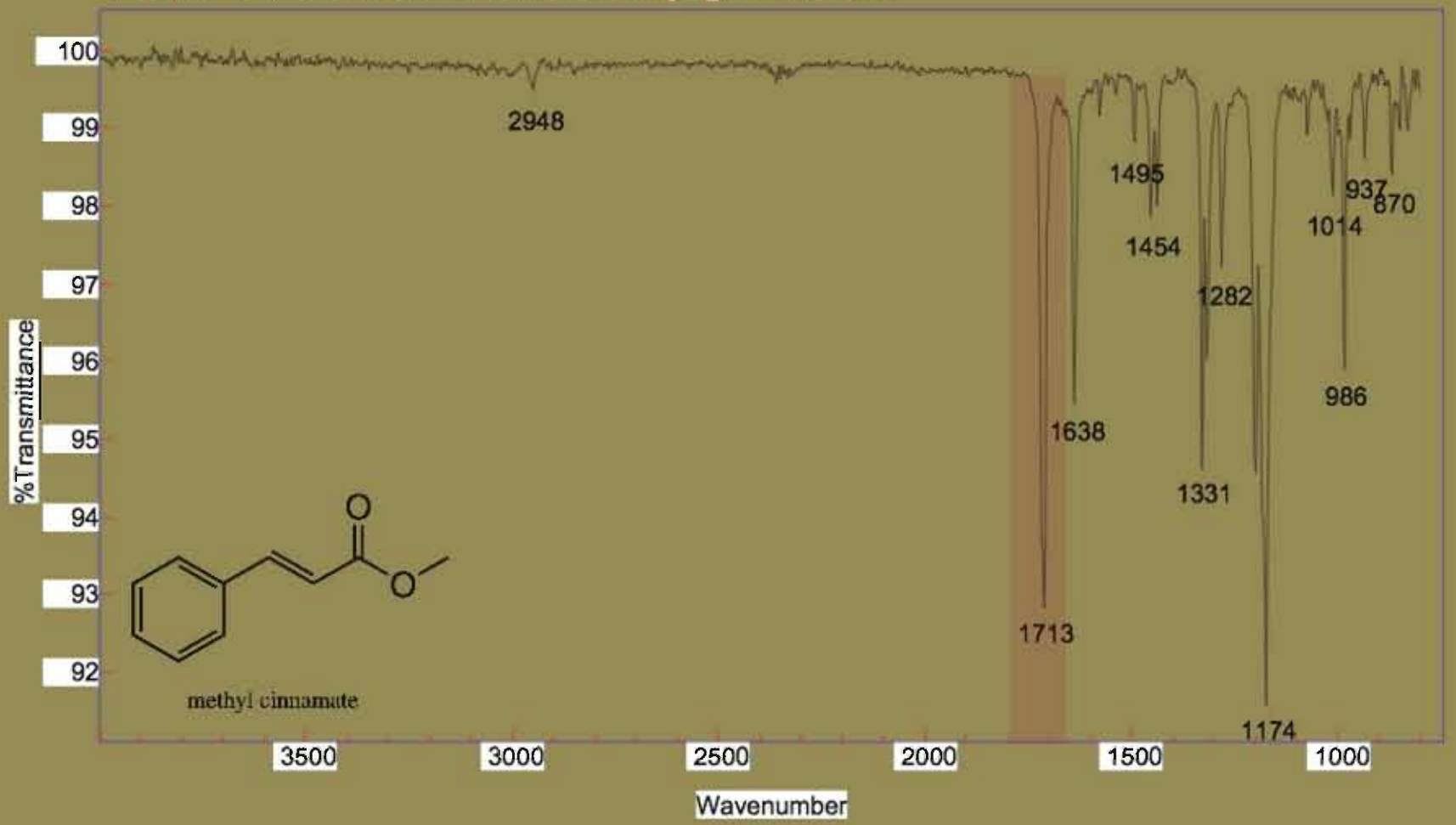
Aliphatic ester III



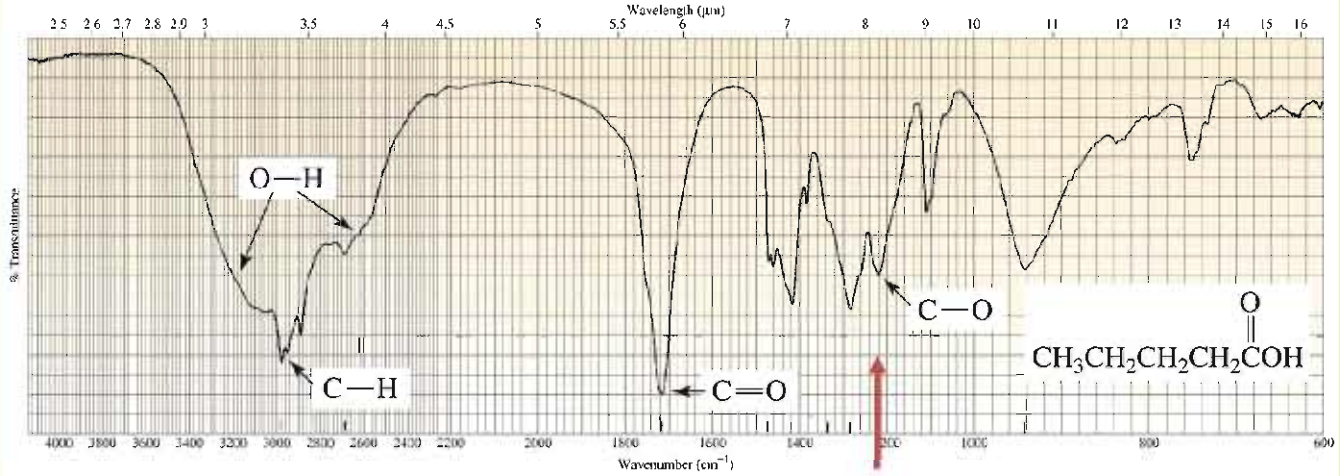
Mono substituted aromatic ester



Mono substituted aromatic conjugated ester



Carboxylic Acid



~1200 cm^{-1}

What is Next