Infrared Spectroscopy

Provides information about the vibrations of functional groups in a molecule

Therefore, the functional groups present in a molecule can be deduced from an IR spectrum
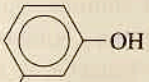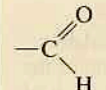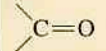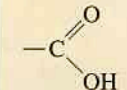
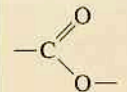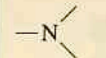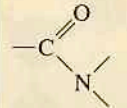Two important parameters in all IR spectra:

The frequency of the signal, ν

The intensity of the signal, I

What structural features of a molecule do ν and I depend on?
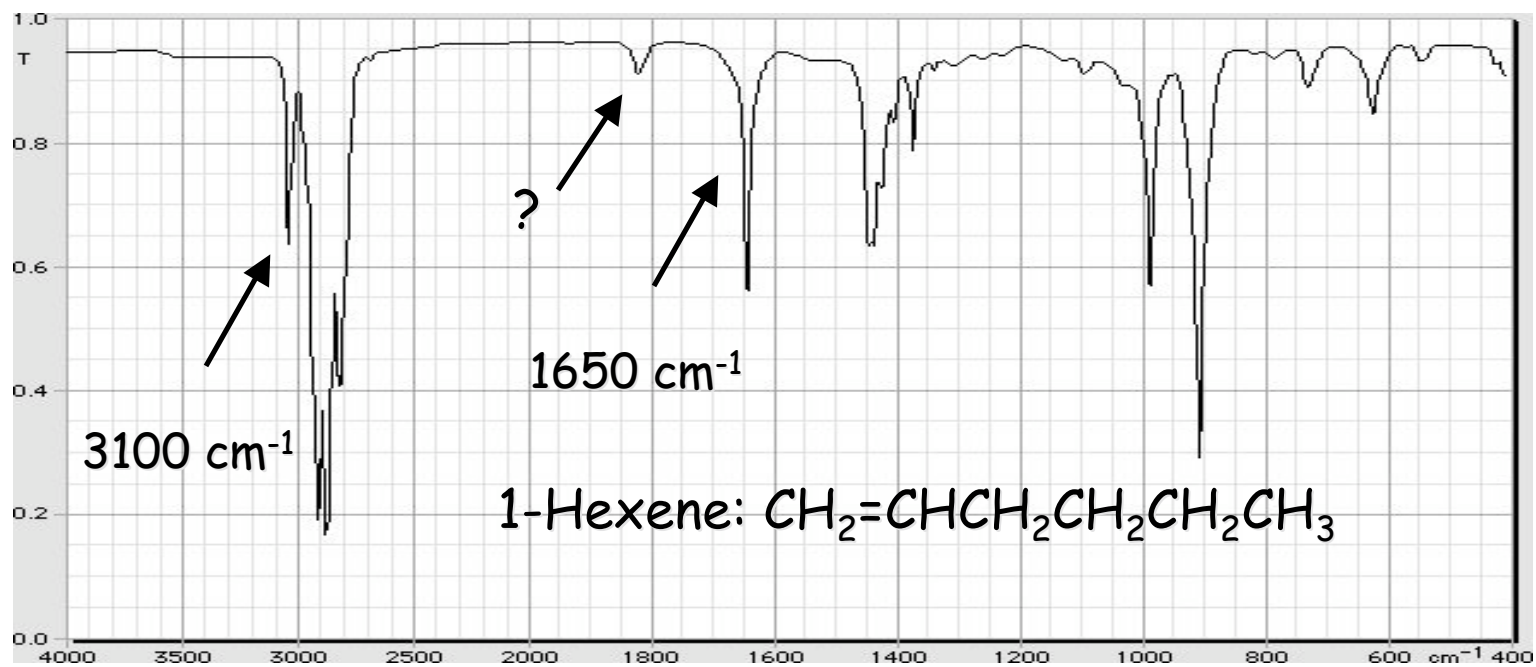
The functional group concept of organic chemistry

IR spectroscopy can identify functional groups!

TABLE 24-2	Some Important Functional Groups in Organic Compounds	
Functional Group	**Type of Compound**	**Examples**
—F, —Cl, —Br, —I	Alkyl or aryl halide	CH_3CH_2Br (bromoethane)
—OH	Alcohol	CH_3CH_2OH (ethanol)
	Phenol	(1,3,-dihydroxybenzene, or resorcinol)
—O—	Ether	CH_3—O—CH_3 (dimethyl ether)
	Aldehyde	$CH_3CH_2CH_2$—C—H (butyraldehyde, or butanal)
C=O	Ketone	CH_3—C—CH_3 (propanone, or acetone)
	Carboxylic acid	CH_3COOH (acetic acid, or ethanoic acid)
	Ester	CH_3—C—O—CH_3 (methyl acetate or methyl ethanoate)
—N	Amine	CH_3NH_2 (methylamine)
	Amide	CH_3—C—NH_2 (acetamide)

Some Important and Characteristic Infrared Absorption Frequencies and Wavelengths for Some Common Stretching Motions

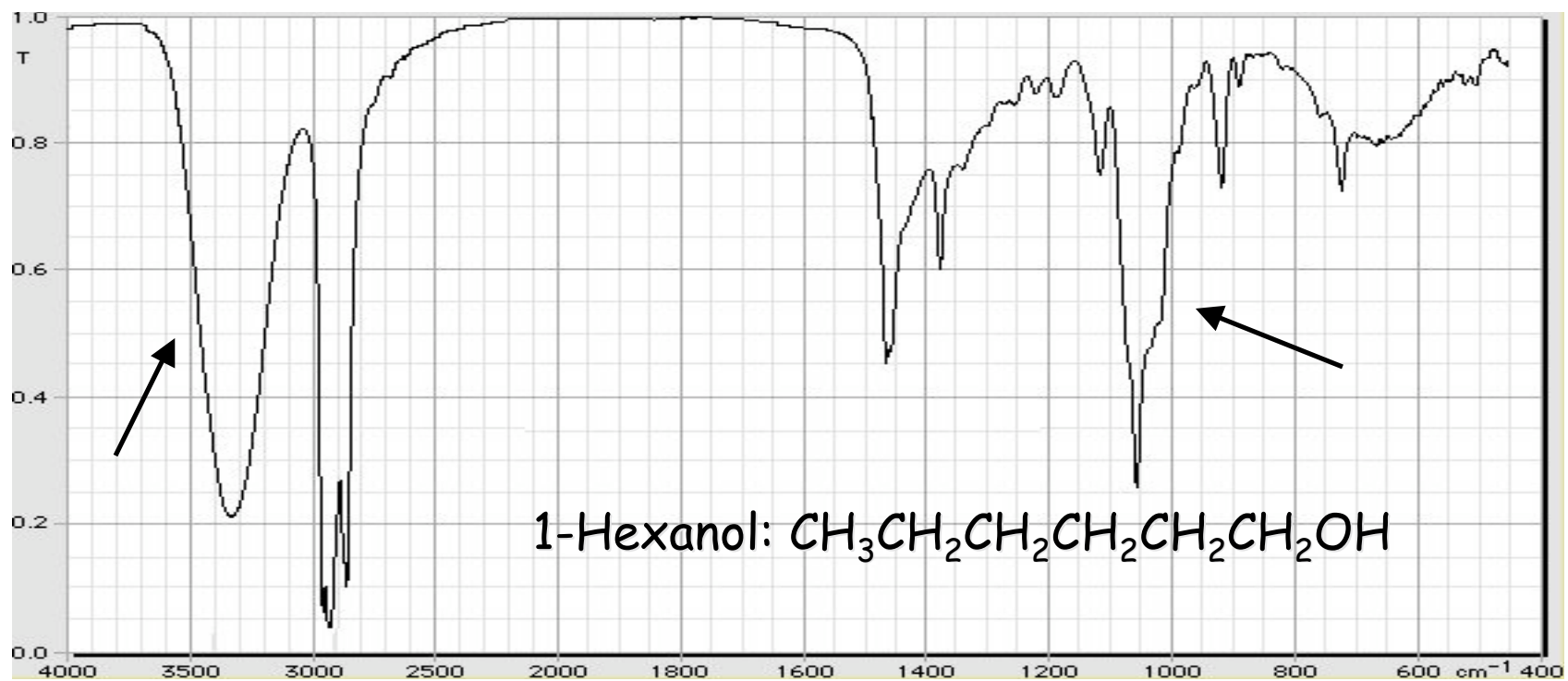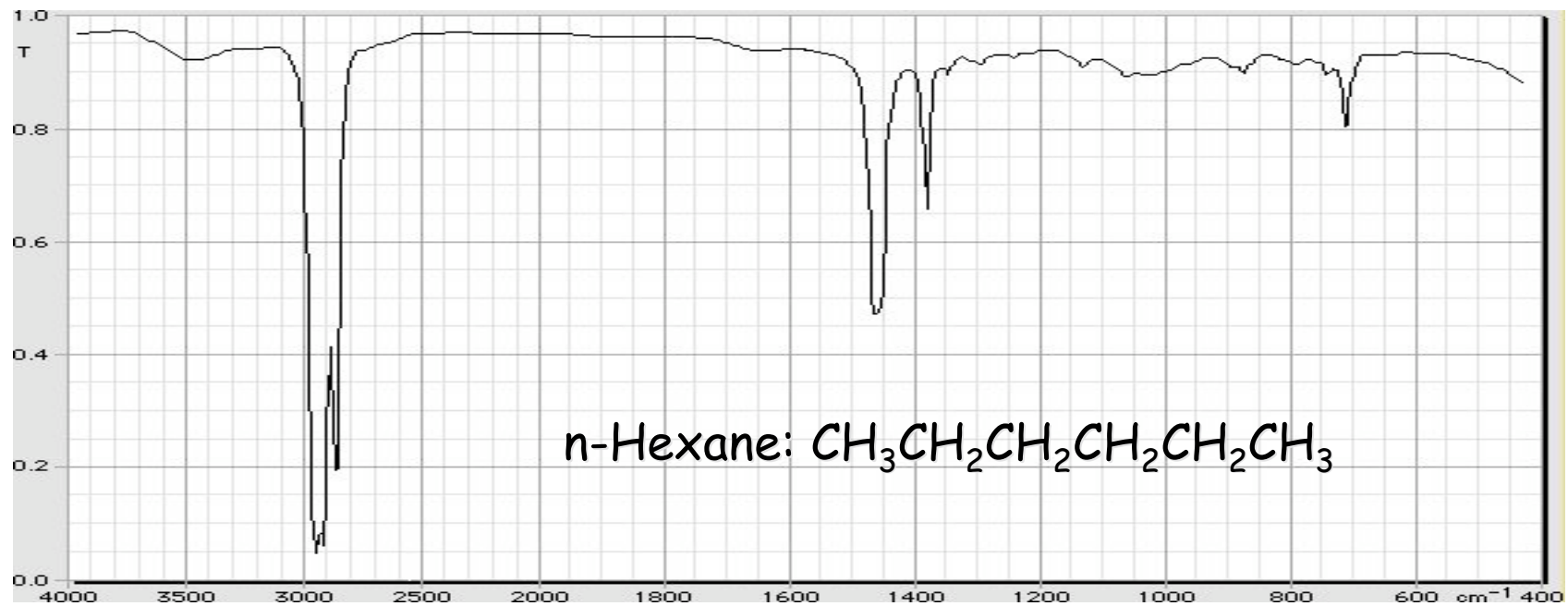| Atom Group	Typical of	Frequency (cm^{-1})	Wavelength (µ)
O-H (free)	Alcohols (dilute)	3550-3650 cm^{-1}	2.8 µ
O-H (H bonded)	Alcohols (concentrated) Carboxylic acids	3200-3400 cm^{-1}	3.0 µ
C≡C—H	Acetylene (CH)	3300 cm^{-1}	3.0 µ
C=C—H	Benzene (CH), Ethylene (CH)	3010-3100 cm^{-1}	3.3 µ
C—C—H	Ethane (CH)	2950-3000 cm^{-1}	3.5 µ
C≡C	Acetylene	2100-2260 cm^{-1}	4.5 µ
C≡N	Nitriles	2000-2300 cm^{-1}	4.5 µ
C=O	Carbonyl	1650-1750 cm^{-1}	5.5- 6.0 µ
C=C	Alkene	1620-1680 cm^{-1}	6.0 µ
C—C	Alkane	600-1500 cm^{-1}	6.7-17 µ
C—O	Alcohols, Ethers	1000-1300 cm^{-1}	10-7.7 µ

In general we will only be using the data in an IR spectrum for stretching vibrations which have energies higher than 1620 cm^{-1}. Although the bands at lower energy are known and assigned, the region below 1620 cm^{-1} is very congested with single bond stretches of two heavy atoms (see C-C and C-O in table) and C-H bends and are beyond the scope of what we want to do.

n-Hexane: $CH_3CH_2CH_2CH_2CH_2CH_3$

1-Hexene: $CH_2=CHCH_2CH_2CH_2CH_3$

3100 cm^{-1}

1650 cm^{-1}

?

n-Hexane: $CH_3CH_2CH_2CH_2CH_2CH_3$

3-heptanone:

n-Hexane: $CH_3CH_2CH_2CH_2CH_2CH_3$

1-Hexanol: $CH_3CH_2CH_2CH_2CH_2CH_2OH$

Where are
the saturated
C-H stretches?

CH$_3$CH$_3$

H$_3$C—C—C—CH$_3$

H H

2,3-dimethyl butane

What's this?

Where are the C-H stretches?

Where are the =C-H stretches?

Where is the C=C stretch?

$CH_2=CHCH_2CH_2CH_2CH_3$

1-hexene

Why are the =C-H stretches of lower intensity than the saturated C-H stretches?

Where is the
the $C{\equiv}N$ stretch?

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2C{\equiv}N$

1-heptyl cyanide

Where is the $C \equiv C$ stretch?

Where is the C-H stretch of $C \equiv C - H$?

$HC \equiv CCH_2CH_2CH_2CH_2CH_3$

1–heptyne

Where is the

$$\overset{O}{\underset{}{\overset{\|}{C}}}$$

stretch?

O
‖
$CH_3CH_2CCH_2CH_2CH_2CH_3$

3-heptanone

T

1.0
0.8
0.6
0.4
0.2
0.0

4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 cm^{-1} 400

What in the world is this peak due to?

Where is the

O
‖
C

stretch?

$CH_3CH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H$

1-heptanal

Where is the OH stretch?

Where is the C=O stretch?

$CH_3CH_2CH_2CH_2CH_2CH_2OH$

1-heptanol

Where is the
OH stretch?

Where is the

$$\overset{O}{\underset{C}{\|}}$$

stretch?

$CH_3CH_2CH_2CH_2CH_2CH_2COH$

1−HeptanolicAcid

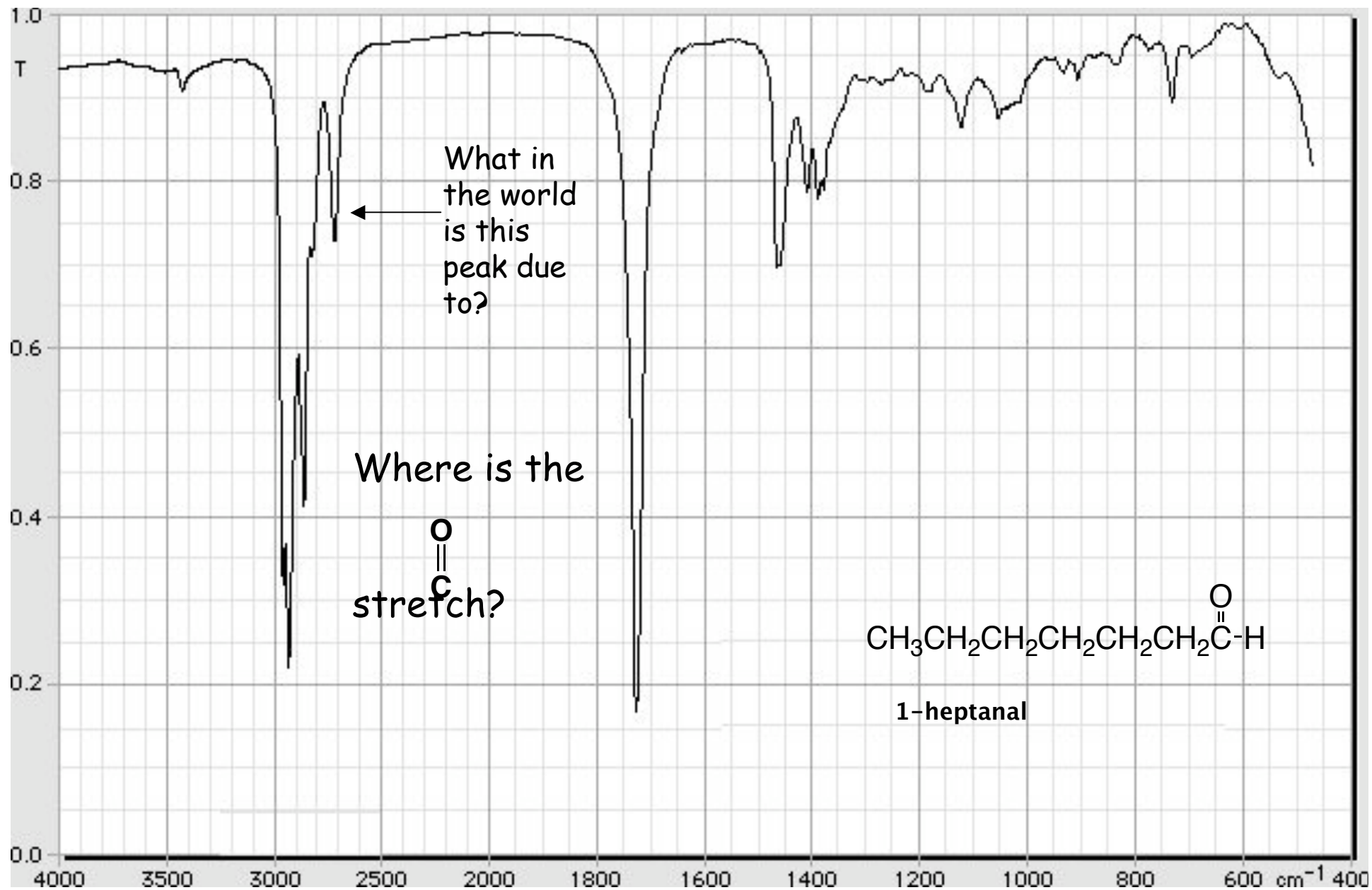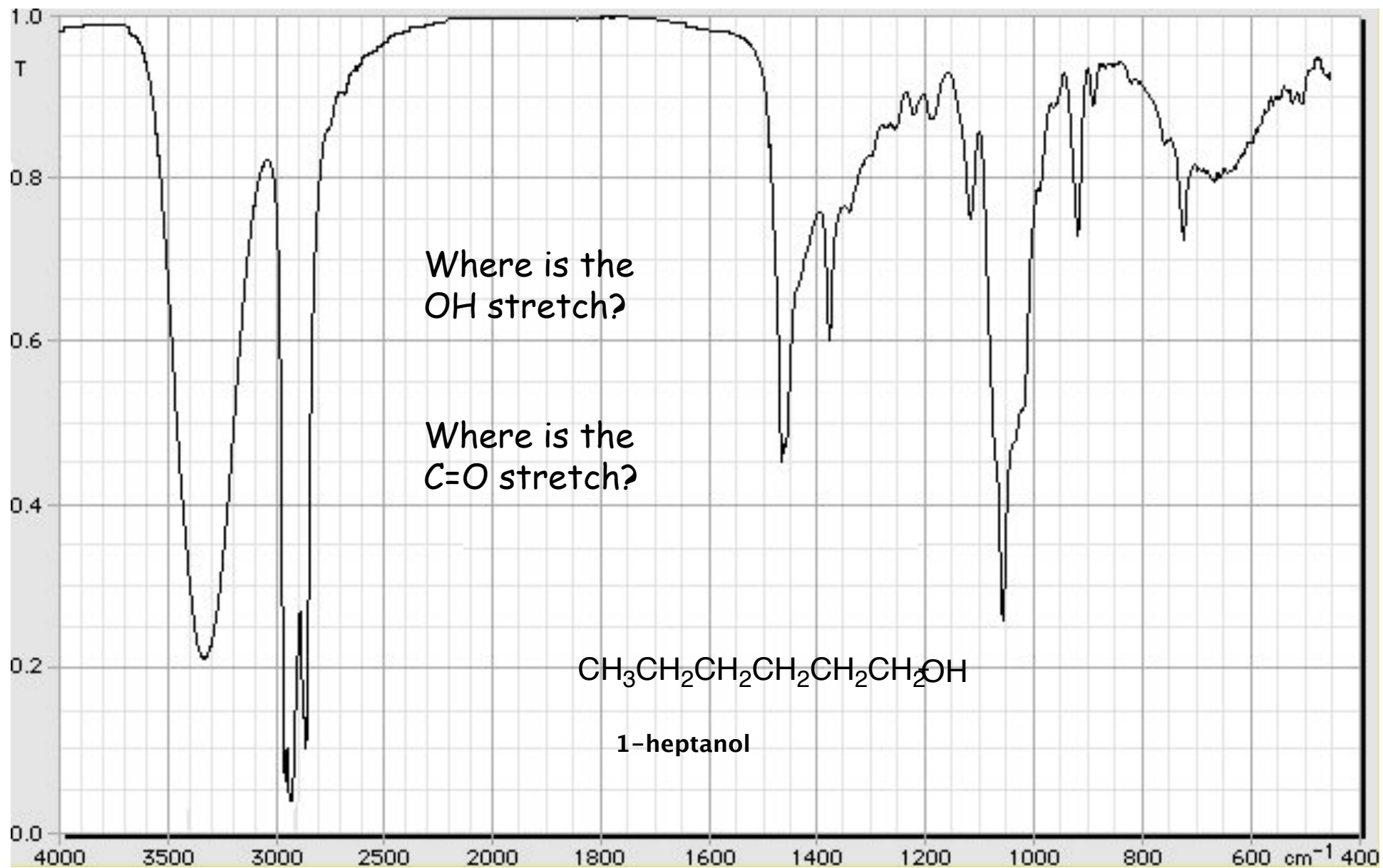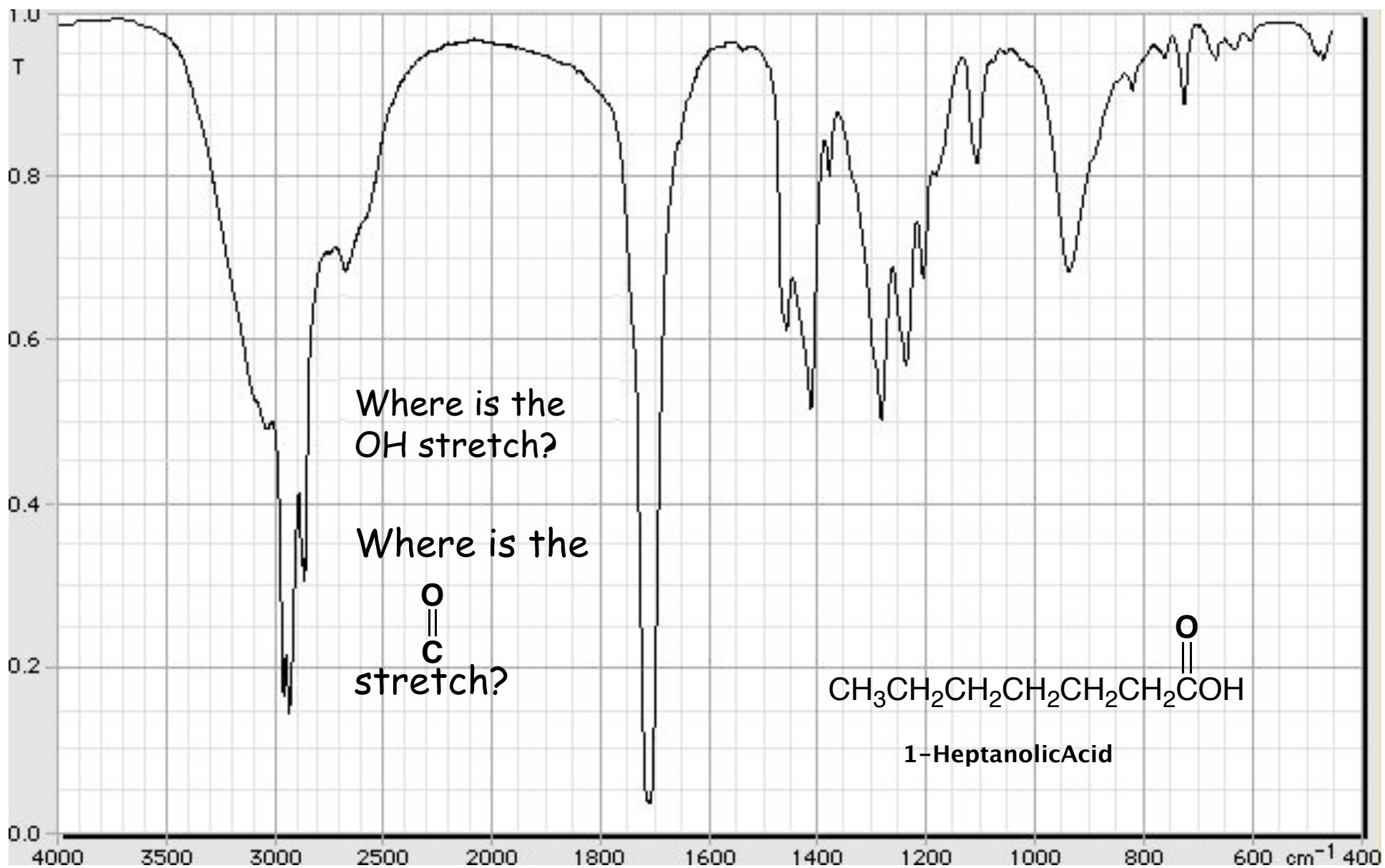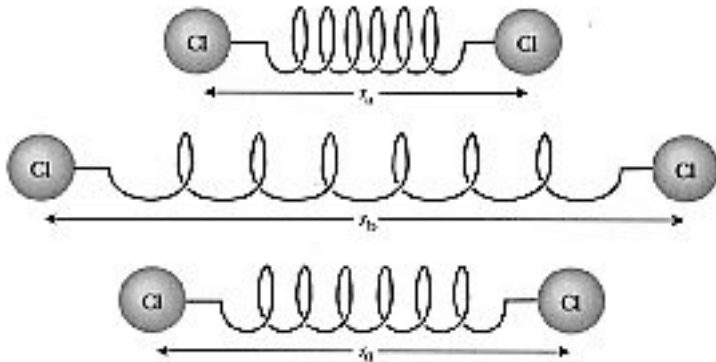# IR: Masses, Atoms and Springs

A Model: Picture the atoms of a diatomic molecule as point masses connected by springs (bonds).

As a first approximation use Hooke's Law

$$F = -kx$$

F = force, restoring back to equilibrium position

k = characteristic **stretching constant**

x = displacement from the equilibrium position

IR Stretching Frequencies of two bonded atoms:

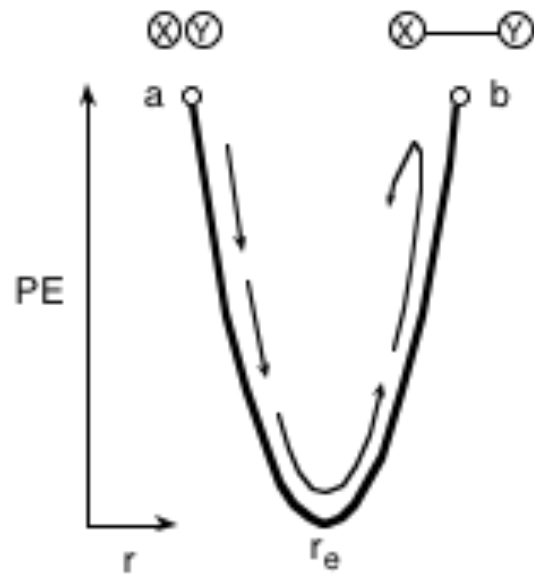## What Does the Frequency, ν, Depend On?

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m_r}} \qquad m_r = \frac{m_1 m_2}{m_1 + m_2}$$

ν = frequency
k = spring strength (bond stiffness)
m_r = reduced mass (~ mass of largest atom)

Vibrations, potential energy and motion

F = dPE/dr

Internuclear separation
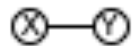
Light atoms and/or strong bonds

Internuclear separation
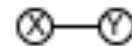
Heavy atoms and/or weak bonds

IR Stretching Frequencies: What Do they Depend On?

Directly on the strength of the bonding between the two atoms ($\nu \sim k$)

Inversely on the reduced mass of the two atoms ($\nu \sim 1/m$)

Expect: ν will increase with increasing bond strength (bond order) and decreasing mass

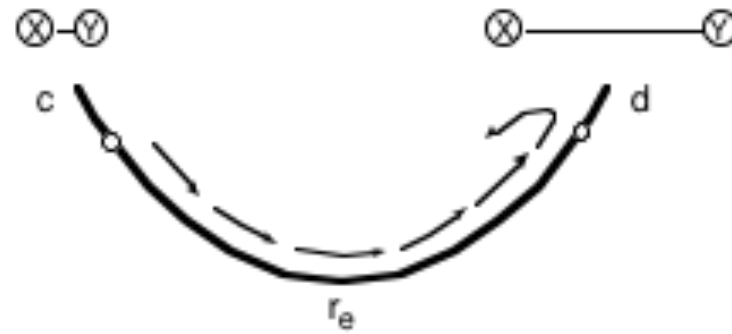# Examples of stretching frequencies and correlations with bond strengths (bond order)

	Bond strength*	Bond order	ν
C-C	350	1	1000 cm^{-1}
C=C	600	2	1600 cm^{-1}
C≡C	840	3	2200 cm^{-1}

*In kJ/mol

For same reduced mass!

Quantum mechanics: The frequency (ν) depends on the energy gap between vibrational levels
$$E = h\nu = hc/\lambda \, (cm^{-1})$$

Only the natural frequency will be absorbed
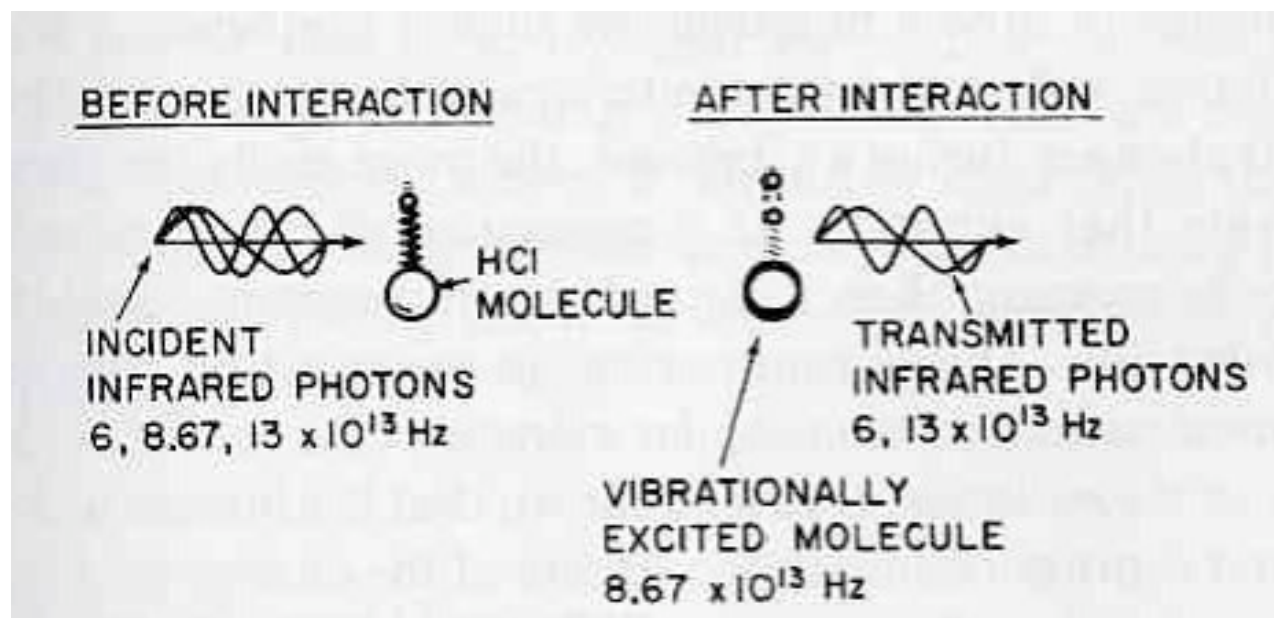
The natural frequency $(8.67 \times 10^{13} \, s^{-1})$ is absorbed selectively

What does the absorption intensity depend on?

The absorption intensity depends on how efficiently the energy of an electromagnetic wave of frequency ν can be transferred to the atoms involved in the vibration

The greater the *change* in dipole moment during a vibration, the higher the intensity of absorption of a photon

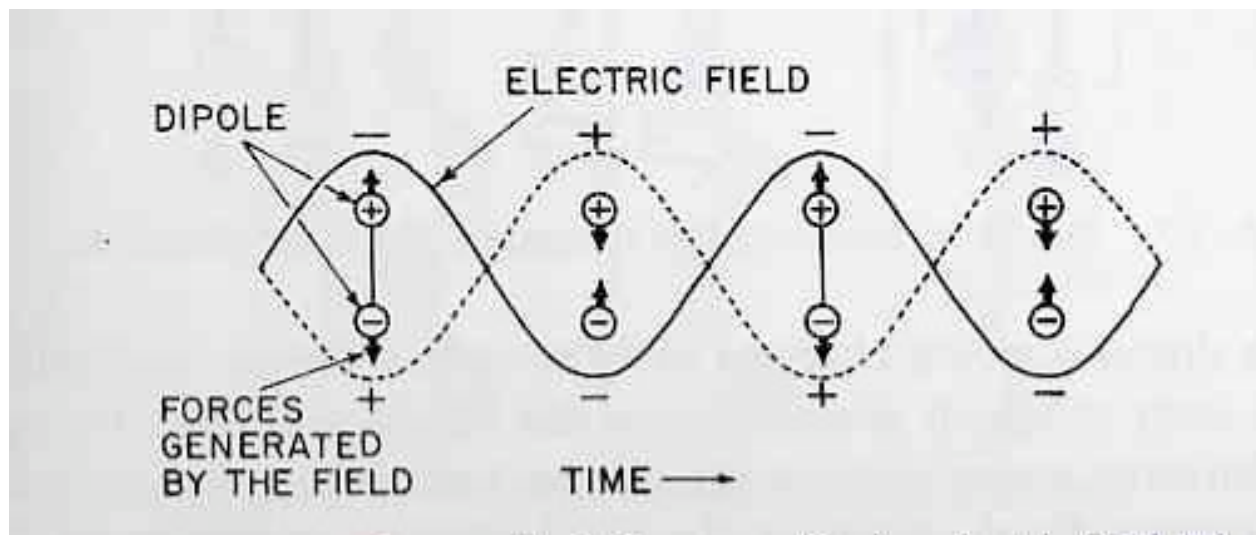# Dipole Moment Must Change during for a vibration to be "IR active"!

- In order to interact strongly with the EM radiation, the motion of the molecule must be such that the dipole moment changes.

FIG. 1.7. Dipole moment changes in certain molecular vibrations.
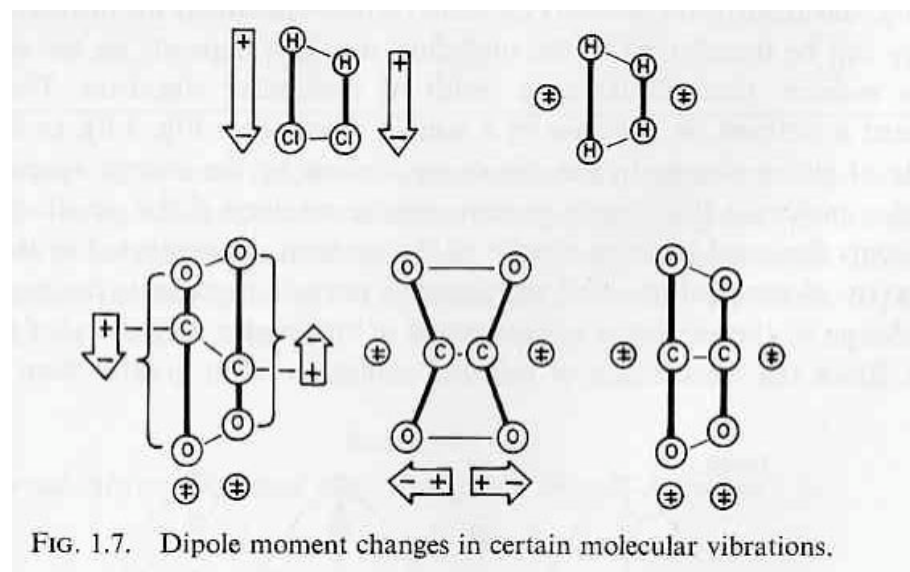
Which of the vibrations are "IR" active"?

What is the intensity of an IR signal of:
O_2 or N_2 or H_2?

Ans: In order to absorb infrared radiation, a molecular vibration must cause a change in the dipole moment of the molecule

O_2, N_2 and H_2 DO NOT ABSORB IR LIGHT!

The are not "Greenhouse" gases

Does O=C=O absorb IR light?

Ans: vibrations of O=C=O which cause a change in the dipole moment of the molecular absorb IR light
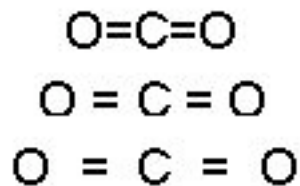
vibrations of O=C=O which do not cause a change in the dipole moment of the molecular DO NOT absorb IR light
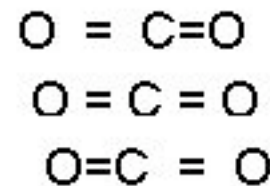
symmetric
stretch
1340 cm^{-1}

© 1996 B. M. Tissue
www.scimedia.com

asymmetric
stretch
2350 cm^{-1}

No dipole
generated

O=C=O
O = C = O
O = C = O

← equilibrium position →

O = C=O
O = C = O
O=C = O

Dipole
generated

Which should have a higher stretching frequency, CO, CO^+, or CO^-? Why?

Ans: The higher the bond order, the stronger the bond and the higher the frequency for the IR stretch.

$CO = (\sigma)^2(\pi)^4$ $CO^+ = (\sigma)^2(\pi)^3$ $CO^- = (\sigma)^2(\pi)^4(\pi*)^1$

Bond order: $CO = 3$, $CO^+ = 5/2$, $CO^- = 5/2$

CO will have the higher stretching frequency

CO^+ and CO^- will have similar, lower frequencies

IR Stretching Frequencies of two bonded atoms:

What Does the Frequency, ν, Depend On?

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m_r}} \qquad m_r = \frac{m_1 m_2}{m_1 + m_2}$$

ν = frequency
k = spring strength (bond stiffness)
m_r = reduced mass (mass of largest atom)

The influence of reduced mass on the stretching frequency ν

For any X-H bond the reduced mass is approximately equal to the mass of the very light hydrogen atom = 1

For a C-C bond the reduced mass is approximately equal to the mass of a carbon atom = 12

From the formula for ν, compute the differences in ν for a X-H and C-C bond of equal strengths.
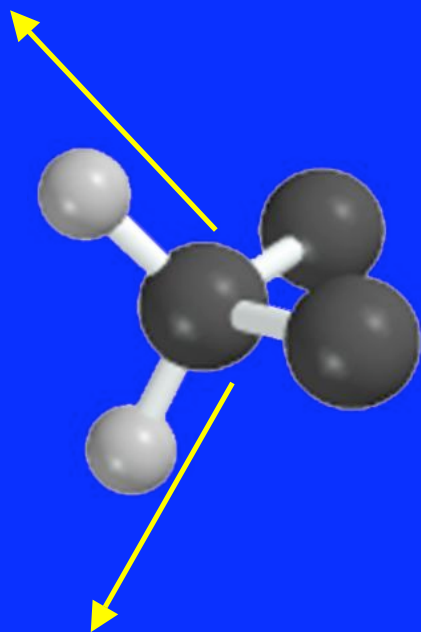
Infrared Spectroscopy: further review

region of infrared that is most useful lies between 2.5-16 μm (4000-625 cm^{-1})

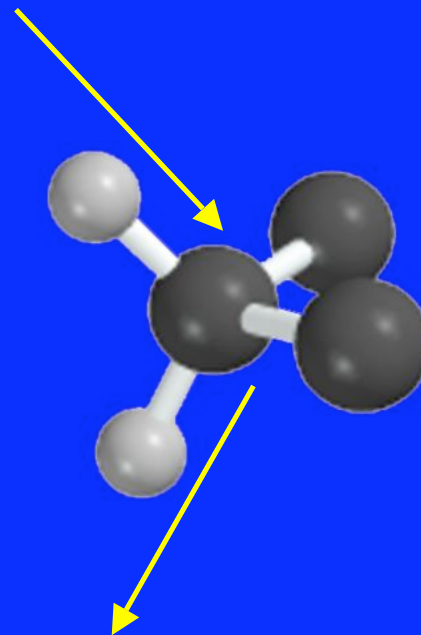depends on transitions between vibrational energy states

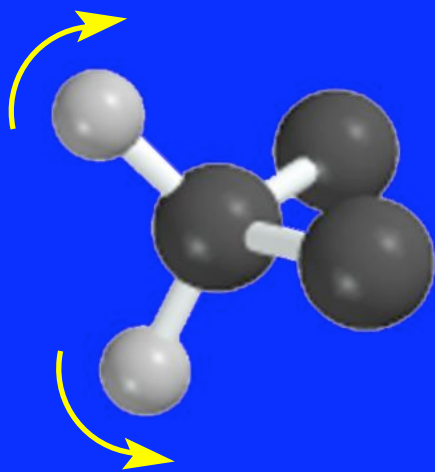stretching

bending
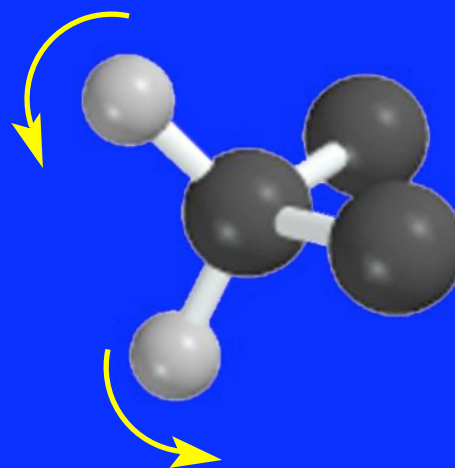
Stretching Vibrations of a CH$_2$ Group

Symmetric

Antisymmetric

Bending Vibrations of a CH$_2$ Group

In plane
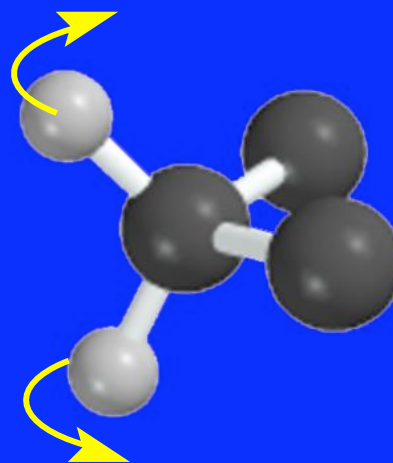
In plane

Bending Vibrations of a CH$_2$ Group
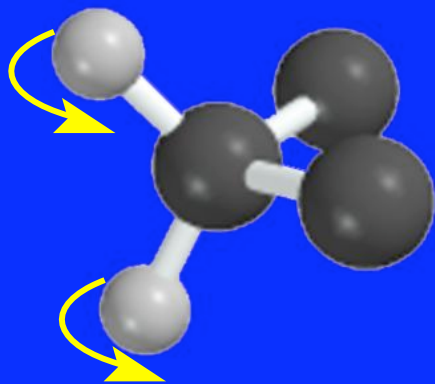
Out of plane

Out of plane

Infrared Spectrum of Hexane

C—H stretching

bending

bending bending

$CH_3CH_2CH_2CH_2CH_2CH_3$

3500 3000 2500 2000 1500 1000 500

Wave number, cm^{-1}
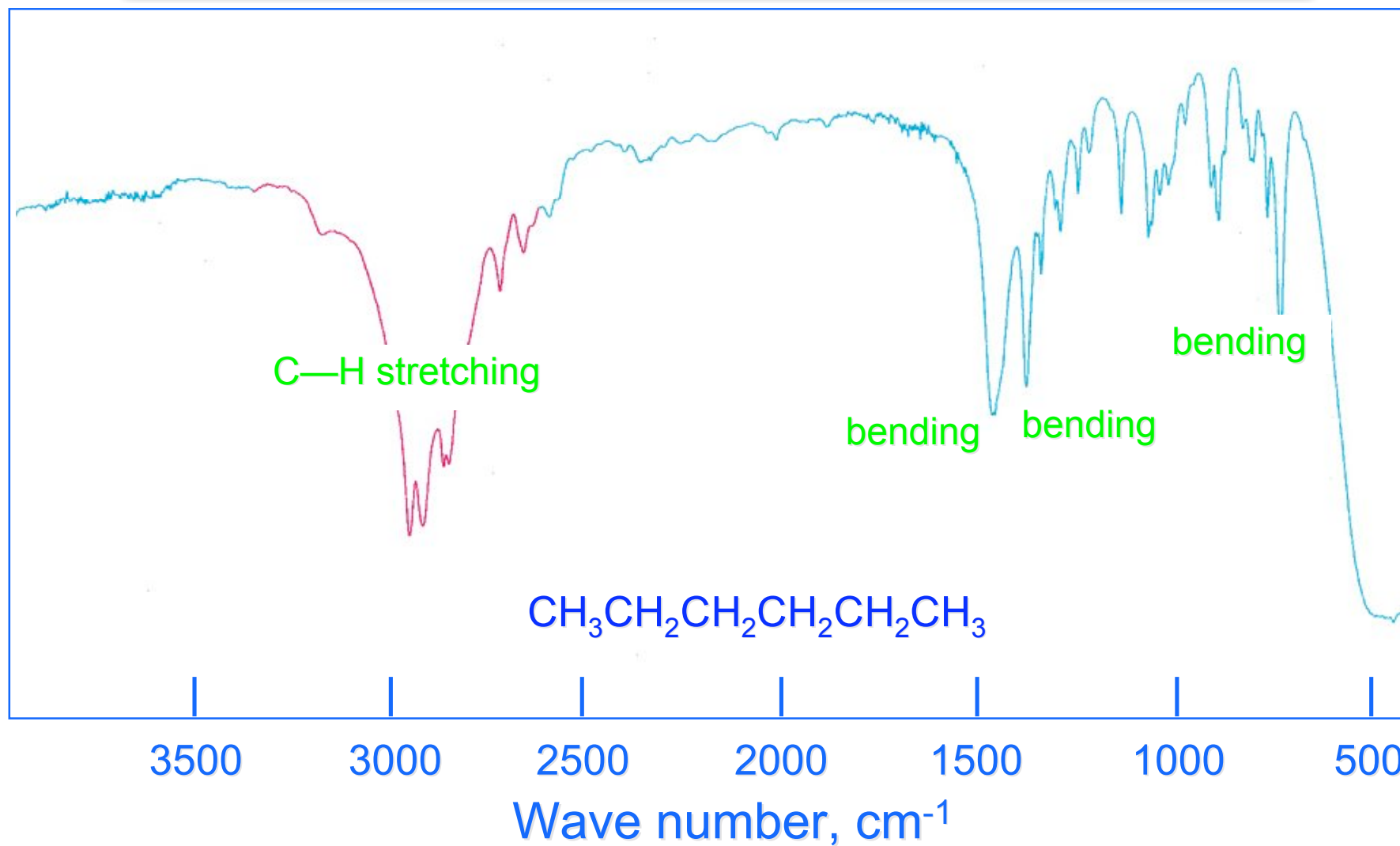
Infrared Spectrum of 1-Hexene
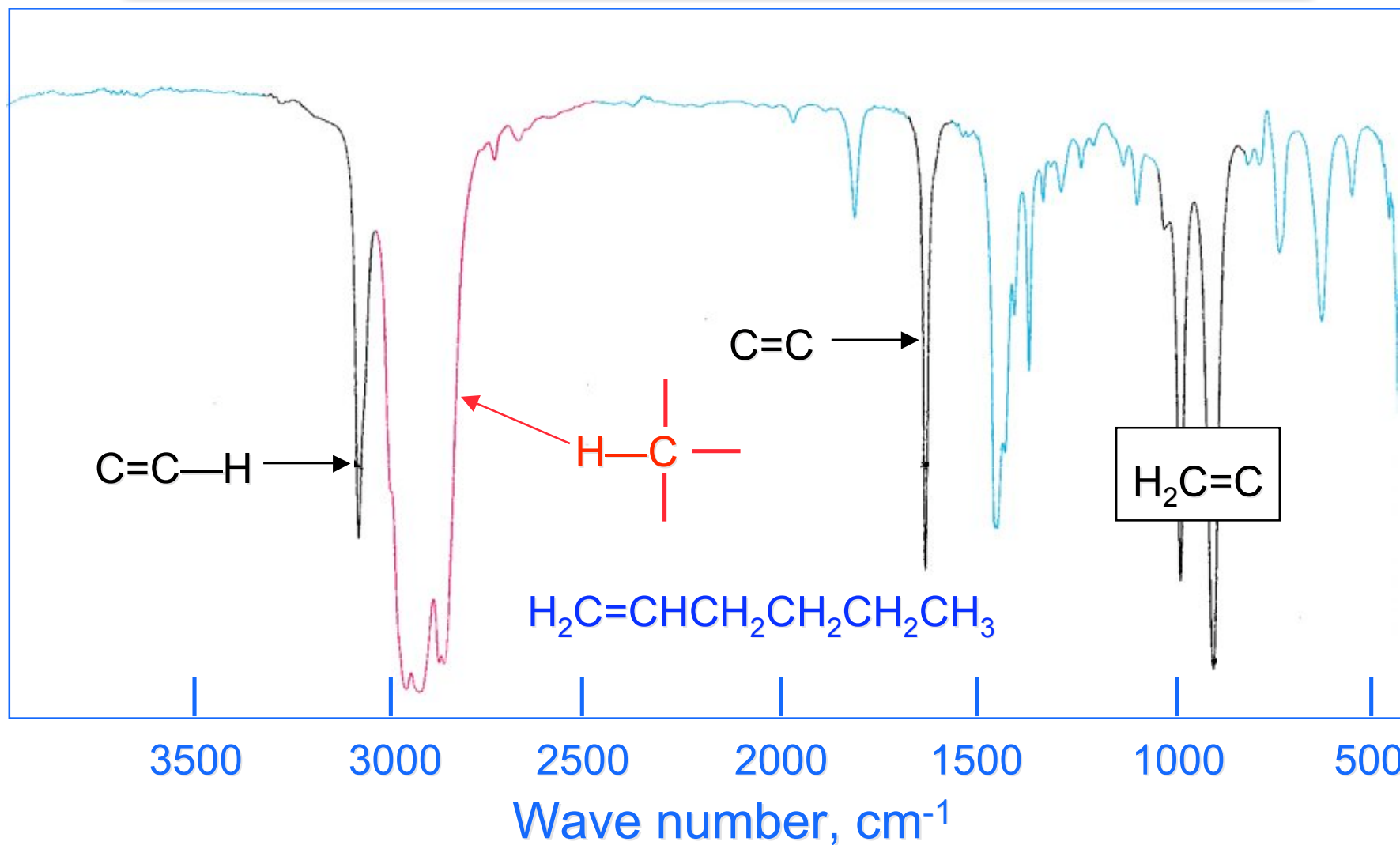
C=C

C=C—H

H—C

$H_2C=C$

$H_2C=CHCH_2CH_2CH_2CH_3$

Wave number, cm^{-1}

3500   3000   2500   2000   1500   1000   500

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 (multiple bonds)
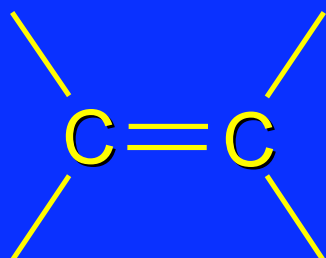
$$C = C$$ 1620-1680
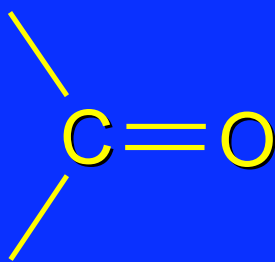
$$—C \equiv C—$$ 2100-2200

$$—C \equiv N$$ 2240-2280

Infrared Absorption Frequencies

$$\diagdown \!\!\!\! C \!\!=\!\! O$$

Structural unit   Frequency, cm^{-1}

Stretching vibrations (carbonyl groups)

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

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

Infrared Absorption Frequencies

Structural unit   Frequency, cm^{-1}

Bending vibrations of derivatives of benzene

Monosubstituted   730-770 and 690-710

Ortho-disubstituted   735-770

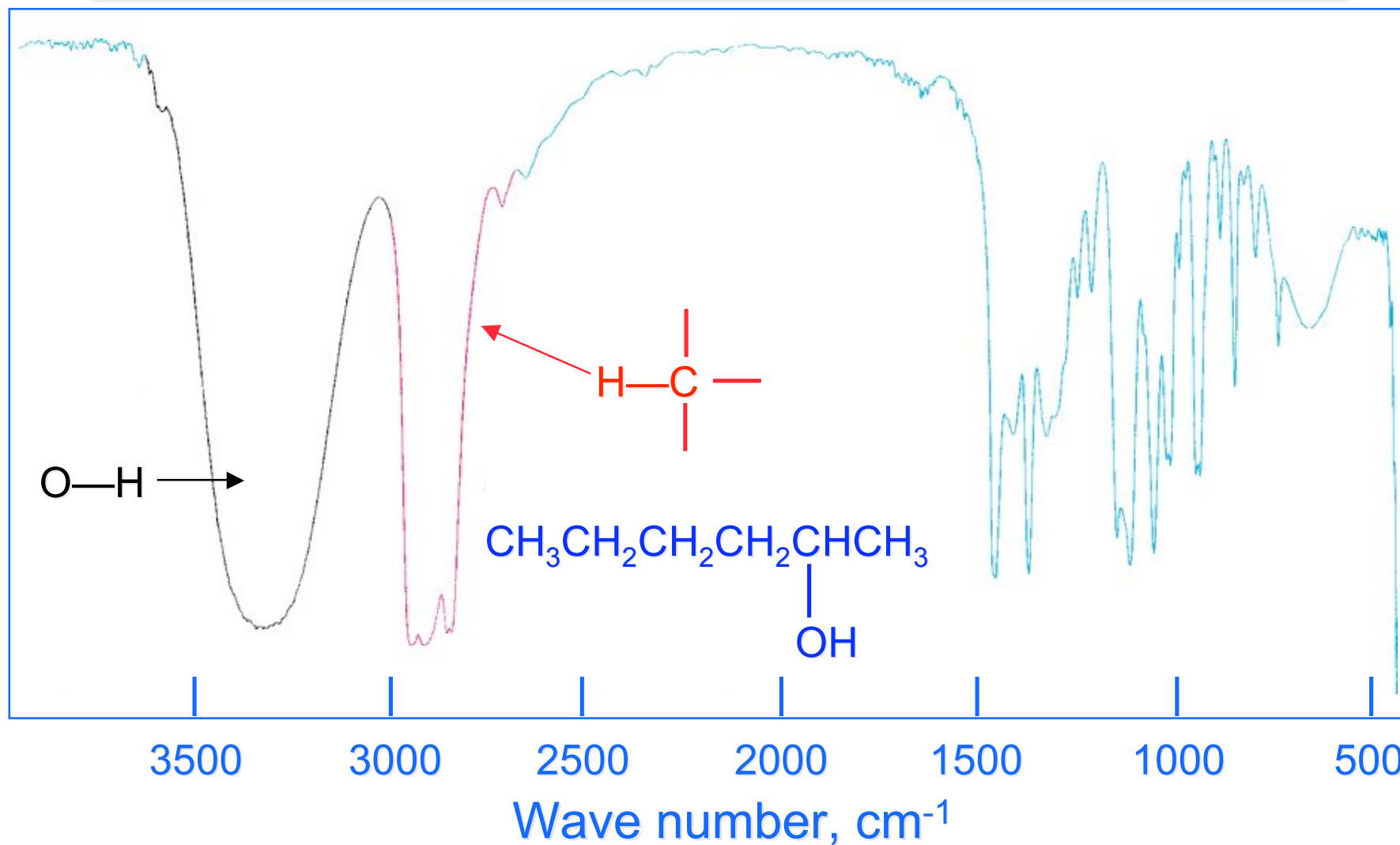Meta-disubstituted   750-810 and 680-730

Para-disubstituted   790-840

Infrared Spectrum of tert-butylbenzene

Ar—H

$C_6H_5C(CH_3)_3$

H—C

Monsubstituted benzene

Wave number, cm^{-1}

3500 3000 2500 2000 1500 1000 500
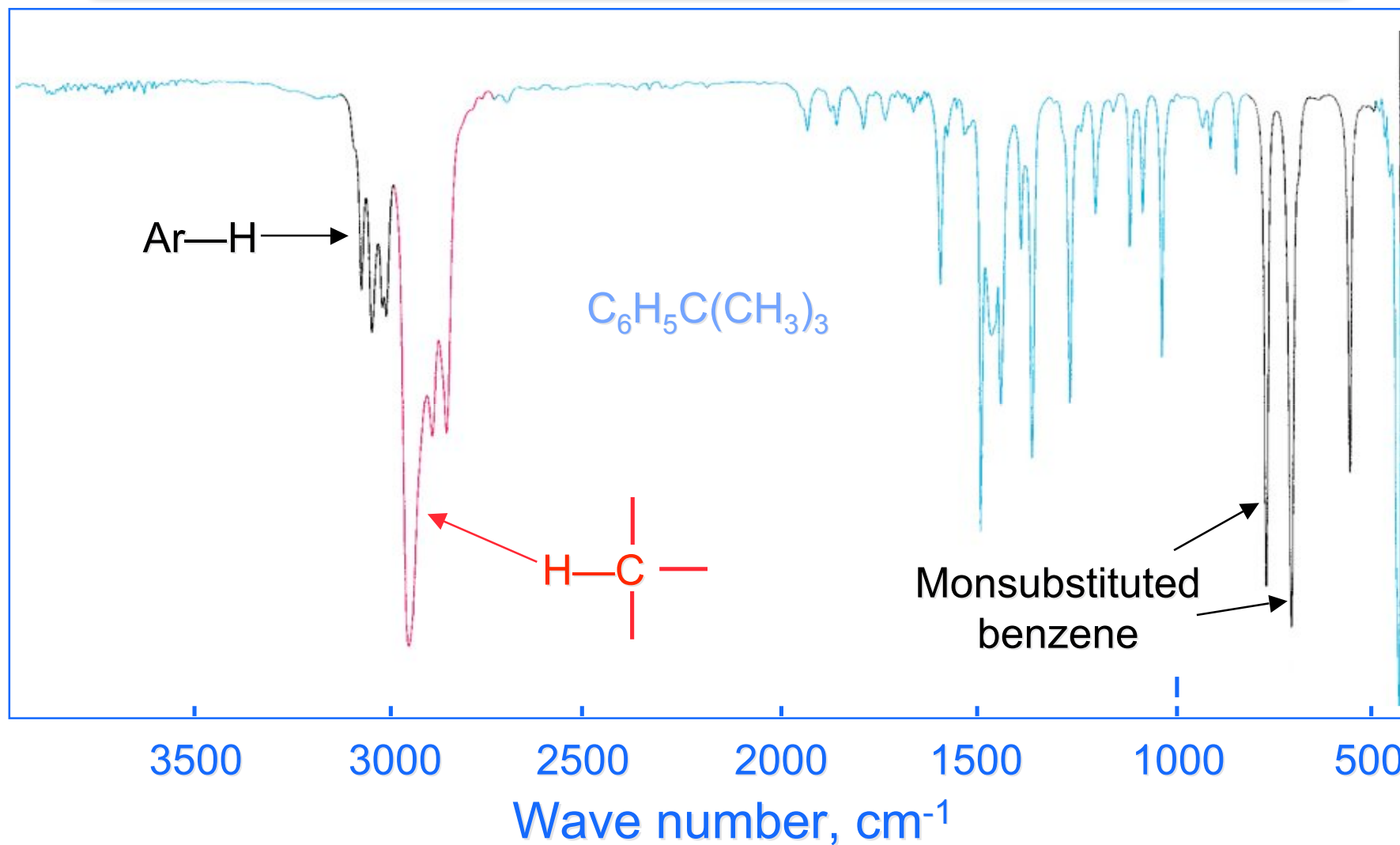
Infrared Absorption Frequencies: functional groups

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

O—H

H—C

$CH_3CH_2CH_2CH_2CHCH_3$

OH

Wave number, cm^{-1}

3500 3000 2500 2000 1500 1000 500

Infrared Spectrum of 2-Hexanone

$CH_3CH_2CH_2CH_2CCH_3$

O

$C=O$

H—C—

Wave number, cm^{-1}

3500   3000   2500   2000   1500   1000   500