

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

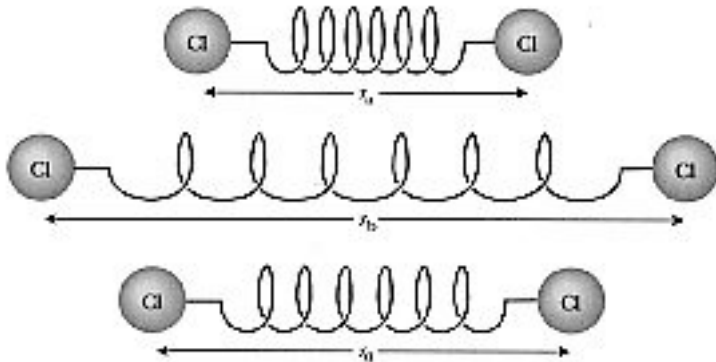
What structural features of a molecule do ν
and I depend on?

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

$$F = -kx$$

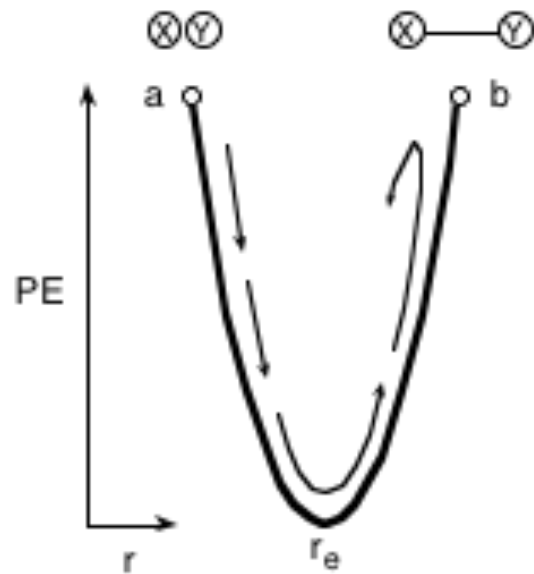


F = force, restoring back to equilibrium position

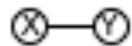
k = characteristic *stretching constant*

x = displacement from the equilibrium position

Vibrations, potential energy and motion



Internuclear separation

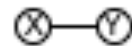


Light atoms
and/or
strong bonds

$$F = dPE/dr$$



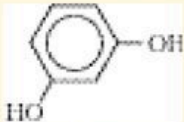

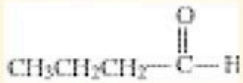

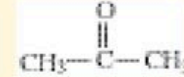
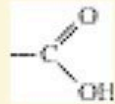
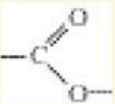
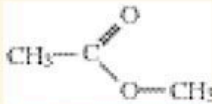

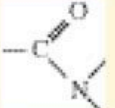
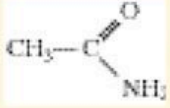
Internuclear separation



Heavy atoms
and/or
weak bonds

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 ₃ CH ₂ Br (bromoethane)
—OH	Alcohol	CH ₃ CH ₂ OH (ethanol)
	Phenol	 (1,3,-dihydroxybenzene, or resorcinol)
—O—	Ether	CH ₃ —O—CH ₃ (dimethyl ether)
	Aldehyde	 (butyraldehyde, or butanal)
	Ketone	 (propanone, or acetone)
	Carboxylic acid	CH ₃ COOH (acetic acid, or ethanoic acid)
	Ester	 (methyl acetate or methyl ethanoate)
	Amine	CH ₃ NH ₂ (methylamine)
	Amide	 (acetamide)

IR Stretching Frequencies of two bonded atoms:

What Does the Frequency, ν , Depend On?

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

ν = frequency

k = spring strength (bond stiffness)

m_r = reduced mass (mass of largest atom)

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)

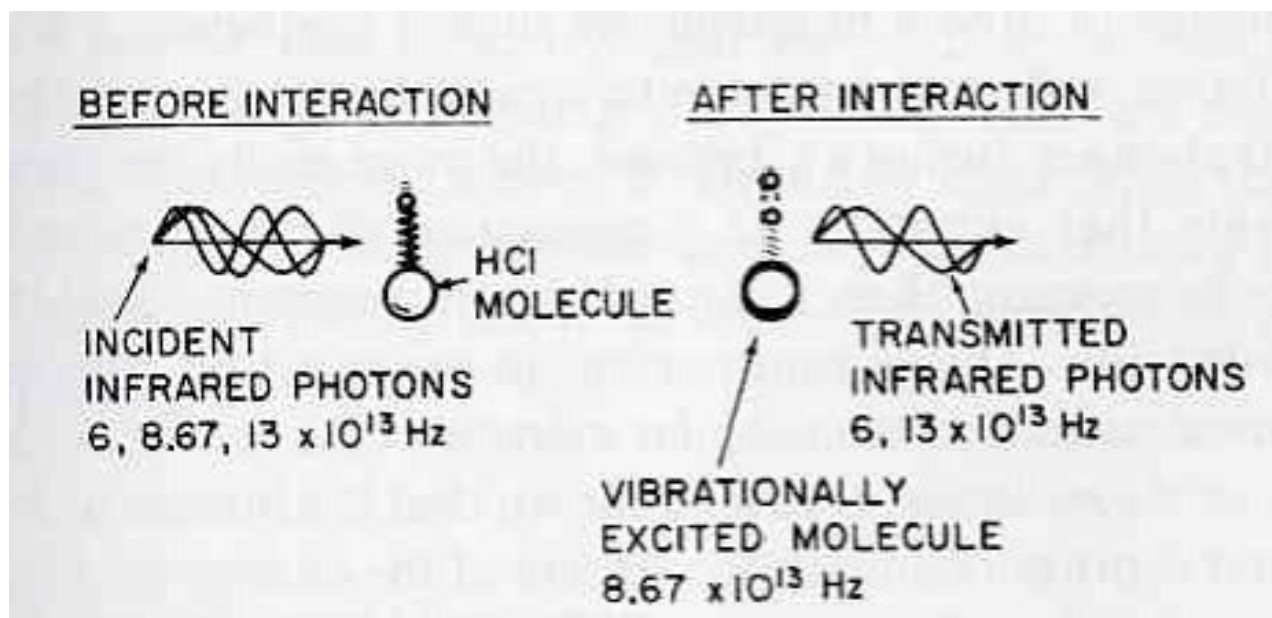
	Bond strength*	Bond order	ν
$C-C$	350	1	1000 cm^{-1}
$C=C$	600	2	1600 cm^{-1}
$C\equiv C$	840	3	2200 cm^{-1}

*In kJ/mol

Quantum mechanics: The frequency (ν) depends on the energy gap between vibrational levels

$$E = h\nu = hc/\lambda \text{ (cm}^{-1}\text{)}$$

Only the natural frequency will be absorbed

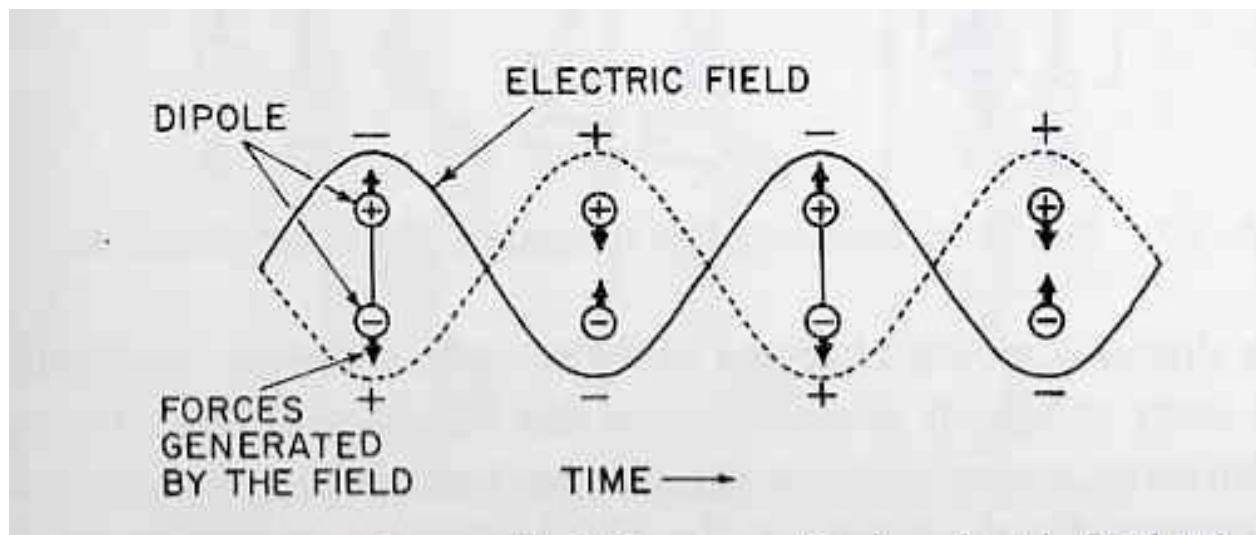


The natural frequency ($8.67 \times 10^{13} \text{ s}^{-1}$) is absorbed selectively

What does the absorption intensity depend on?

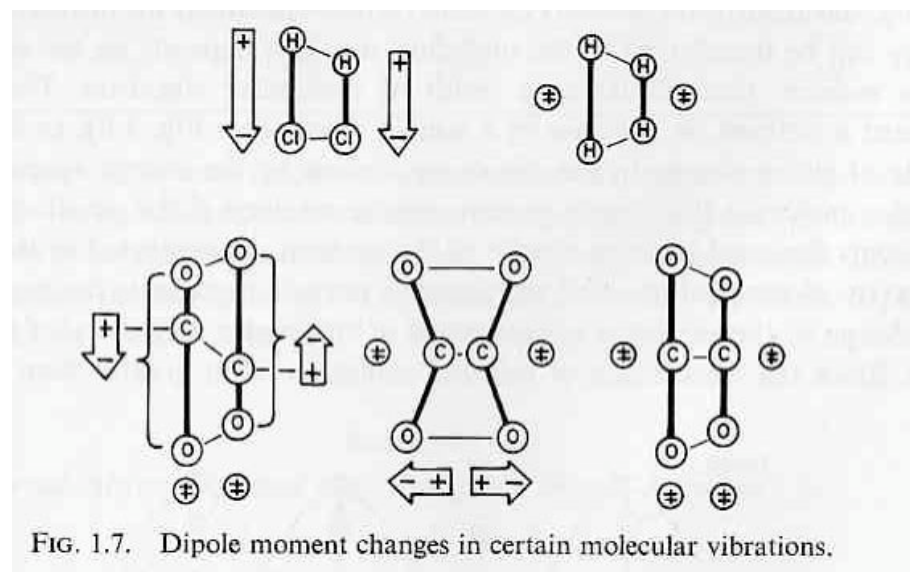
The absorption intensity depends on how efficiently the energy of an electromagnetic wave of frequency ν can be transferred to the atoms involved in the vibration

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.



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

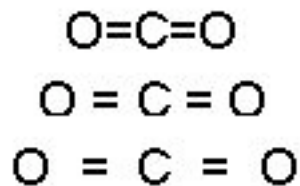
vibrations of $O=C=O$ which do not cause a change in the dipole moment of the molecular DO NOT absorb IR light

symmetric
stretch
 1340 cm^{-1}

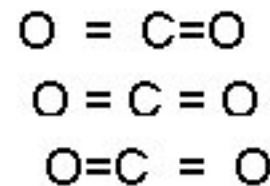
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asymmetric
stretch
 2350 cm^{-1}

No dipole
generated



← equilibrium
position →



Dipole
generated

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

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

Bond order: $\text{CO} = 3$, $\text{CO}^+ = 5/2$, $\text{CO}^- = 5/2$

CO will have the higher stretching frequency

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

Infrared Spectroscopy

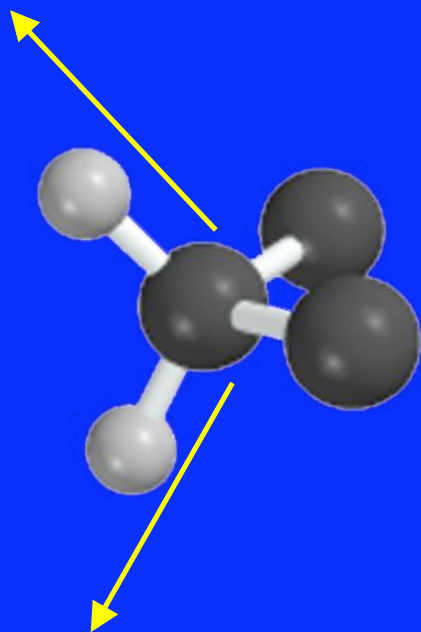
region of infrared that is most useful lies between
2.5-16 μm (4000-625 cm^{-1})

depends on transitions between vibrational
energy states

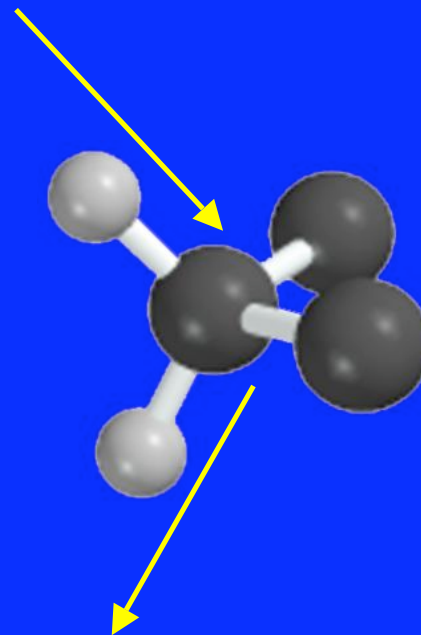
stretching

bending

Stretching Vibrations of a CH₂ Group

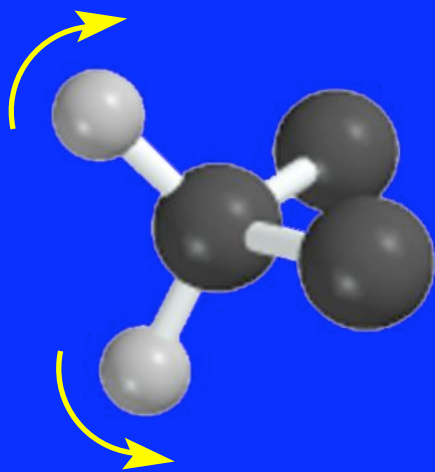


Symmetric

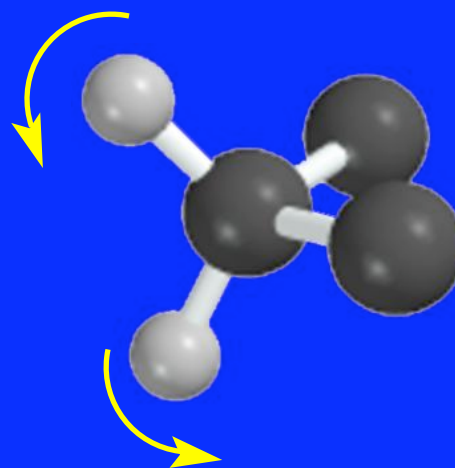


Antisymmetric

Bending Vibrations of a CH₂ Group

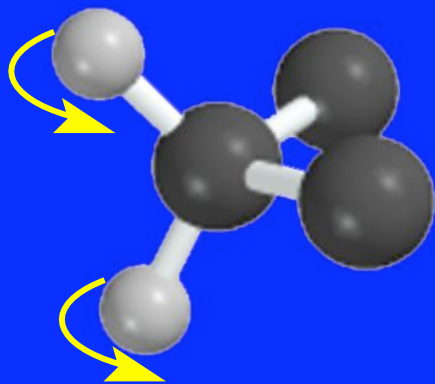


In plane

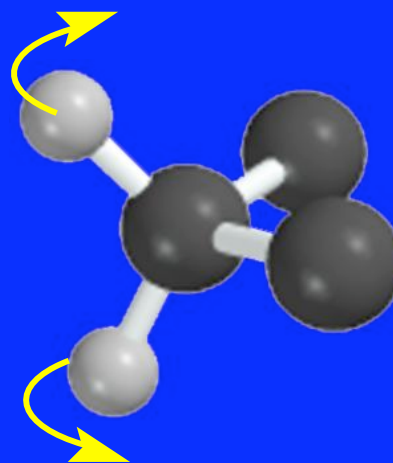


In plane

Bending Vibrations of a CH₂ Group

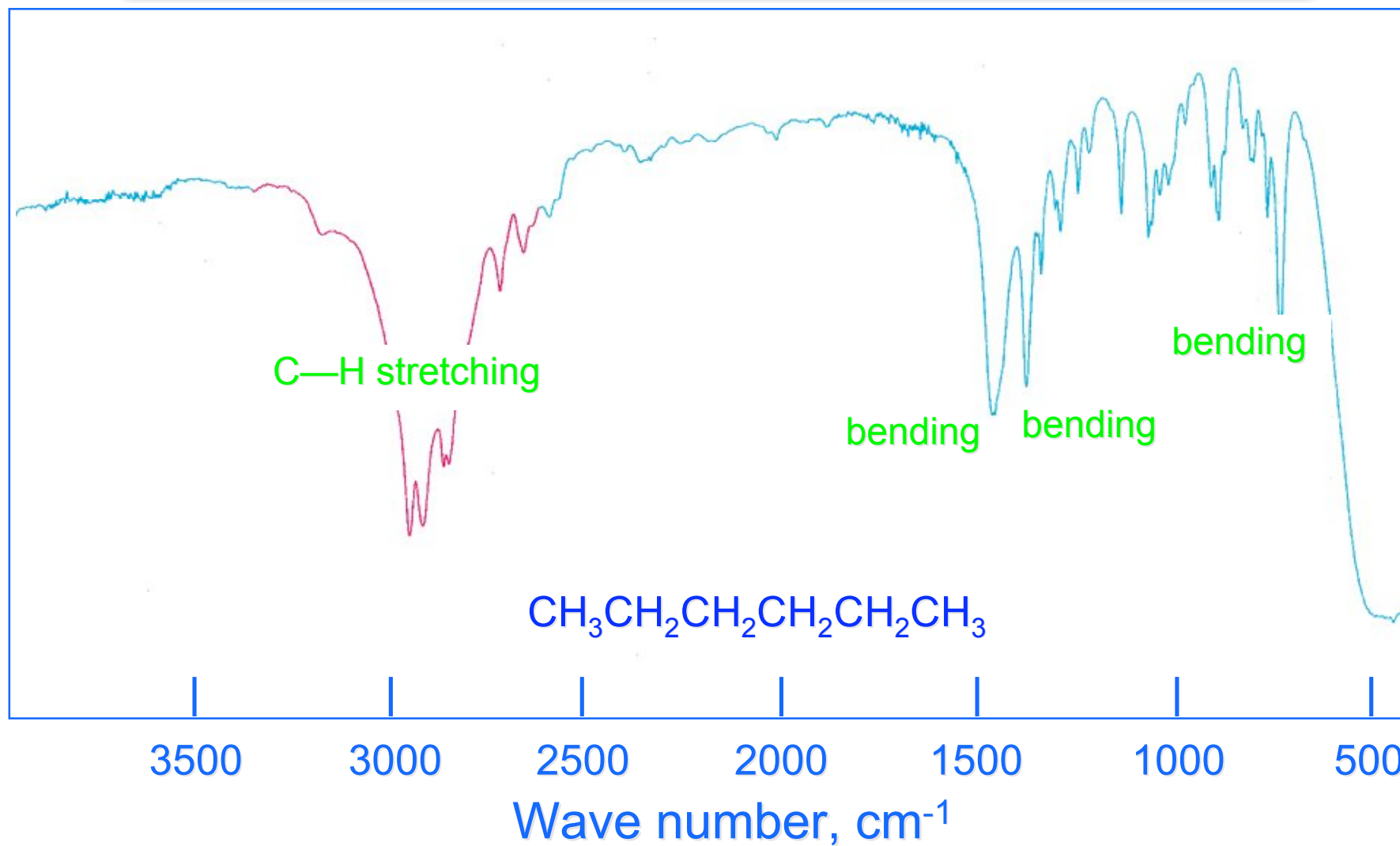


Out of plane

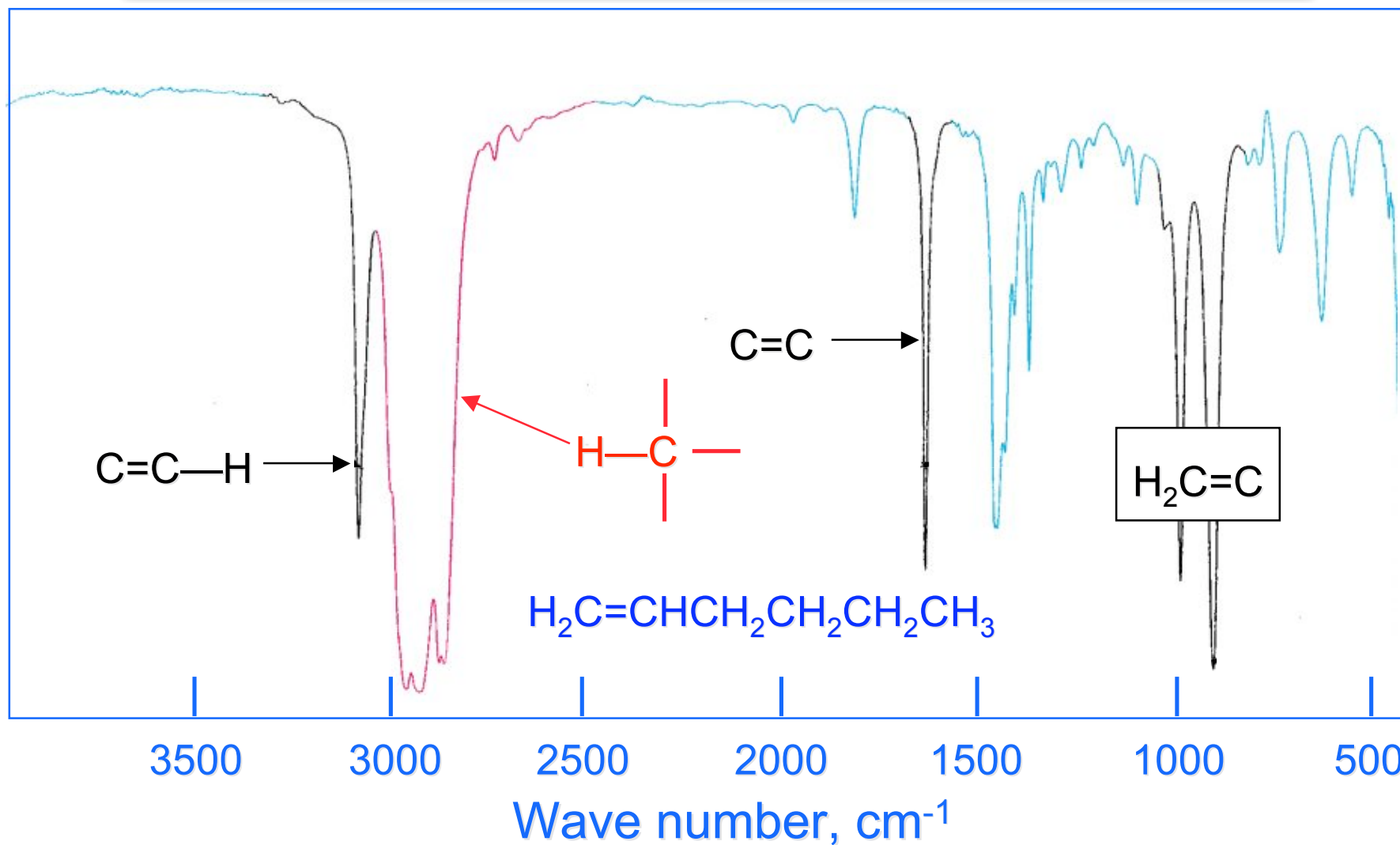


Out of plane

Infrared Spectrum of Hexane



Infrared Spectrum of 1-Hexene



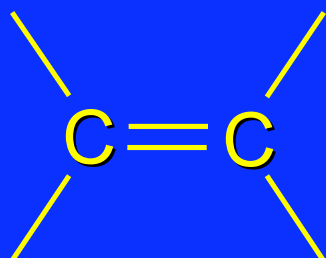
Infrared Absorption Frequencies

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)



1620-1680

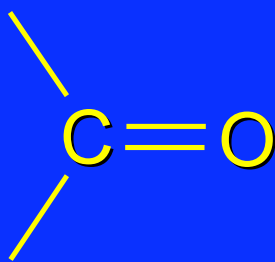


2100-2200



2240-2280

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	

Infrared Absorption Frequencies

Structural unit Frequency, cm^{-1}

Bending vibrations of alkenes

$\text{RCH}=\text{CH}_2$ 910-990

$\text{R}_2\text{C}=\text{CH}_2$ 890

cis- $\text{RCH}=\text{CHR}'$ 665-730

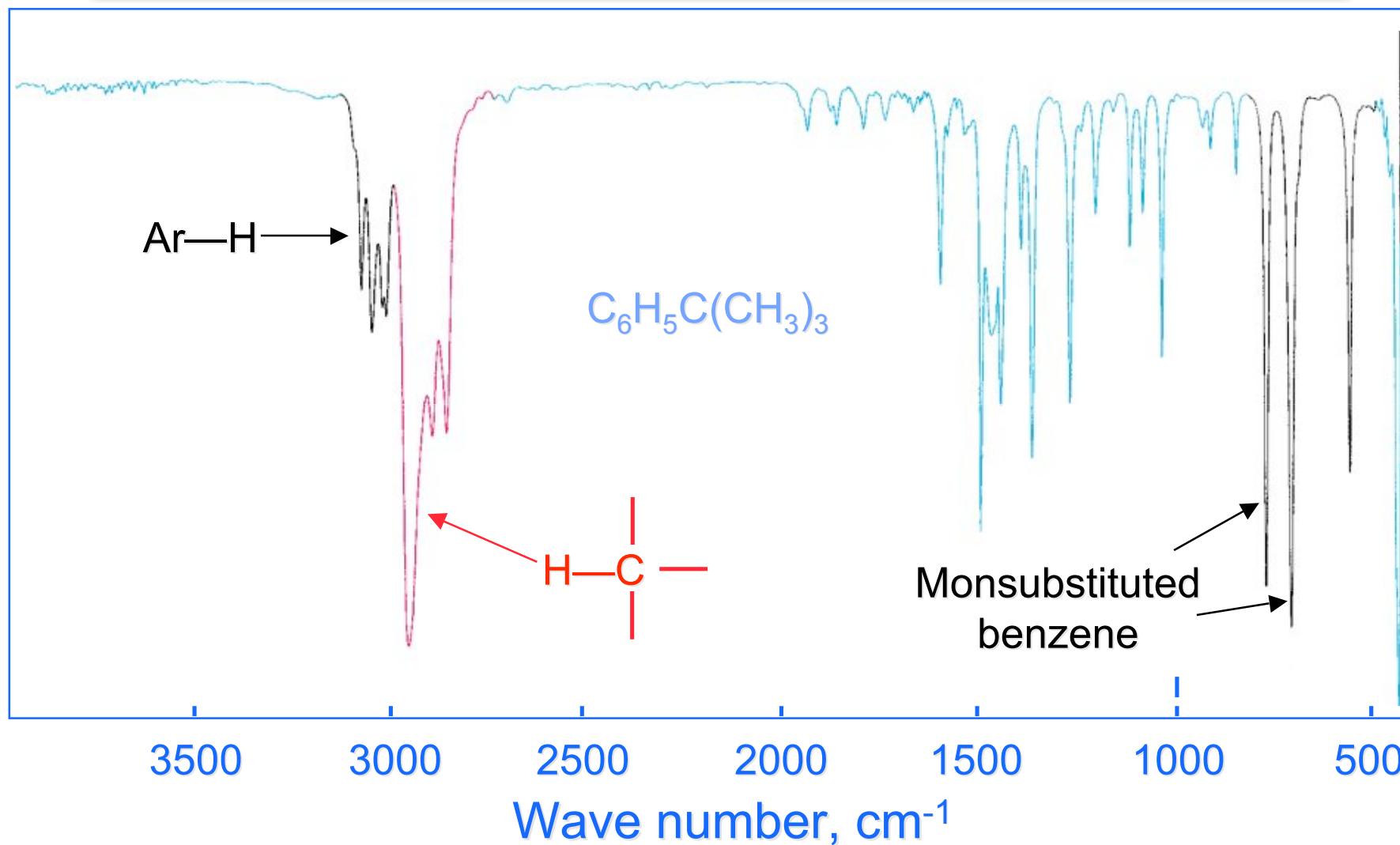
trans- $\text{RCH}=\text{CHR}'$ 960-980

$\text{R}_2\text{C}=\text{CHR}'$ 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

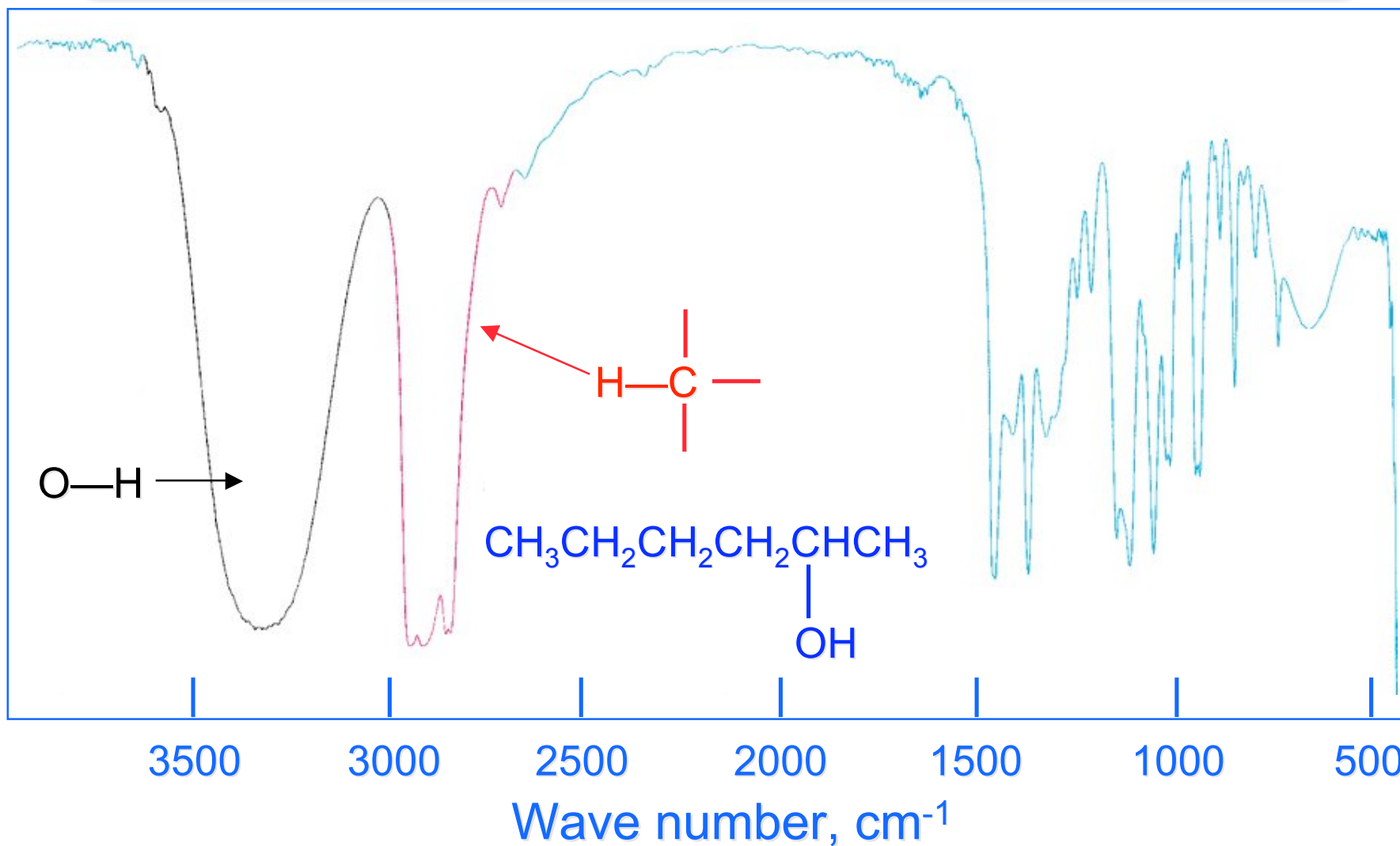
Infrared Spectrum of tert-butylbenzene



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



Infrared Spectrum of 2-Hexanone

