University of Illinois
at Chicago
UIC

Lecture 13
Organic Chemistry 1

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February 23, 2010

Spectroscopy & Spectrometry

Chapter 13

University of Illinois
at Chicago
UIC

Introduction to Analytical Methods

Sections: 13.1-13.2

Spectroscopy vs. Spectrometry

Spectroscopy

study of the interaction of electromagnetic radiation with matter; typically involves the absorption of electromagnetic radiation

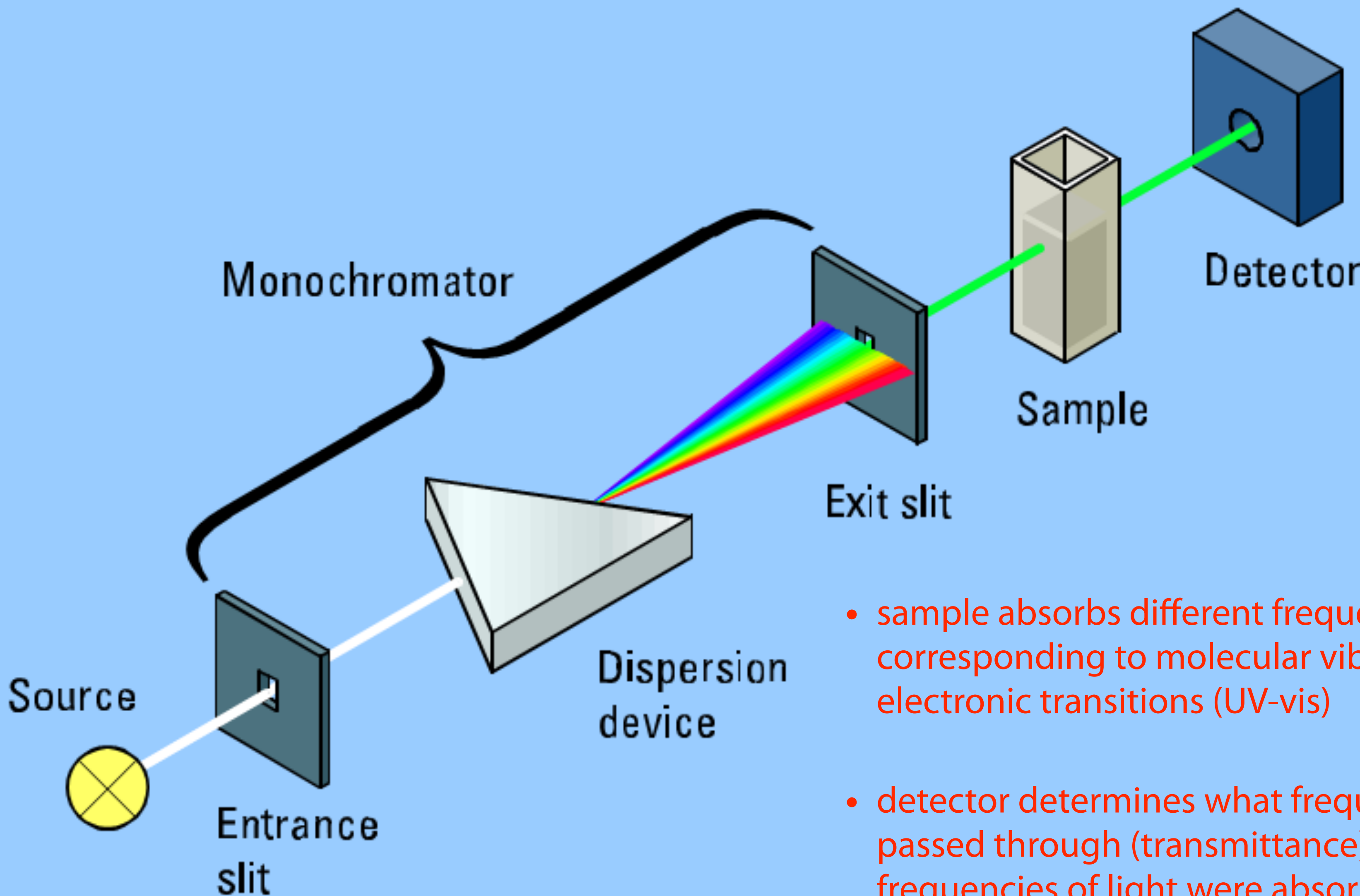
Spectrometry

evaluation of molecular identity and/or properties that does not involve interaction with electromagnetic radiation

Spectroscopic Methods

Method	Measurement/Application
Infrared Spectroscopy	• vibrational states: stretching and bending frequencies of covalent bonds that contain a dipole moment • functional group determination
Ultraviolet-Visible (UV-vis) Spectroscopy	• electronic states: energy associated with promotion of an electron in a ground state to an exited state • chromophore determination
Mass Spectrometry	• molecular weight: of parent molecule and fragments produced by bombardment with "free" electrons • fragment and isotope determination
Nuclear Magnetic Resonance Spectroscopy	• nuclear spin states: energy associated with spin states of nuclei in the presence of a magnetic field • determine structural groups and connectivity

Absorption/Transmission Spectroscopy: Simplified Principles

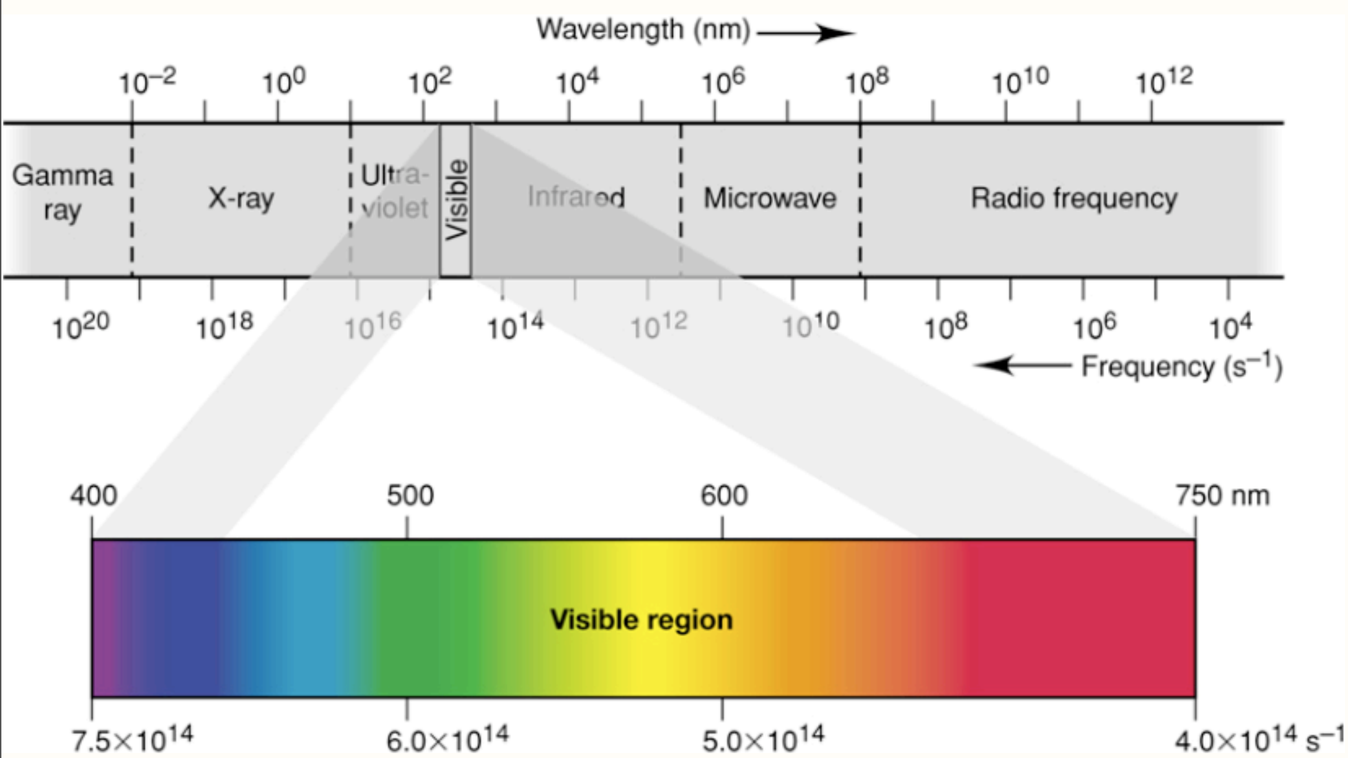


- sample absorbs different frequencies of light corresponding to molecular vibrations (IR) or electronic transitions (UV-vis)
- detector determines what frequencies of light passed through (transmittance) and what frequencies of light were absorbed (absorbance)

Electromagnetic Spectrum

shorter wavelength (λ)
higher frequency (ν)
higher energy (E)

longer wavelength (λ)
lower frequency (ν)
lower energy (E)

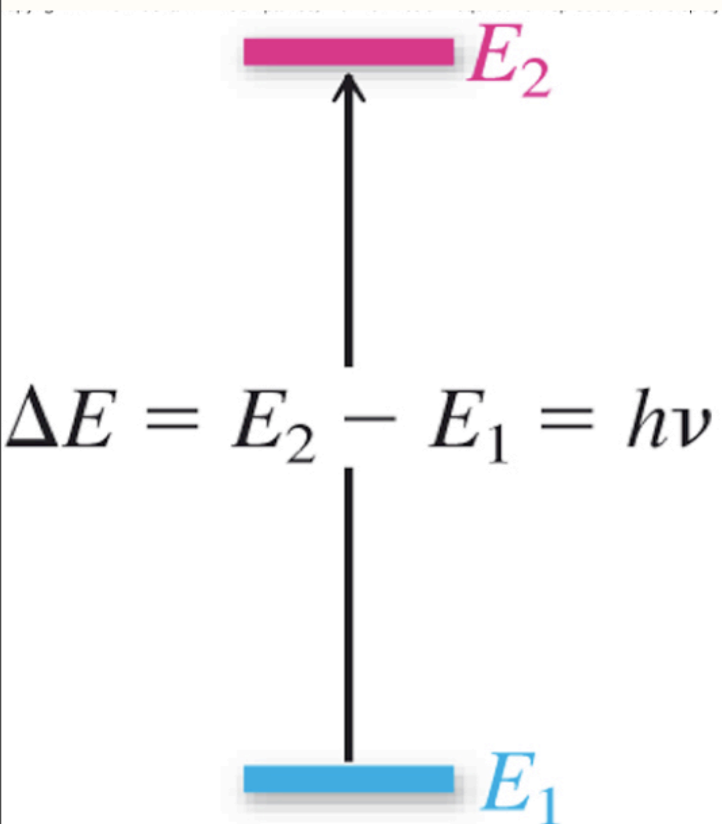


Electromagnetic Radiation

- propagated at the speed of light (3 x10^8 m/s)
- has properties of particles and waves
- energy is directly proportional to frequency
- energy is indirectly proportional to wavelength

$E = h\nu$ $c = \nu\lambda$

Quantized Energy States



Types of States	Energy Range (λ)	Spectroscopic Method
nuclear spin	radiofrequency 1-10 m	NMR
rotational	microwave 10-100 cm	Microwave
vibrational	infrared 0.78-1000 µm	IR
electronic	ultraviolet 800-200 nm	UV-vis

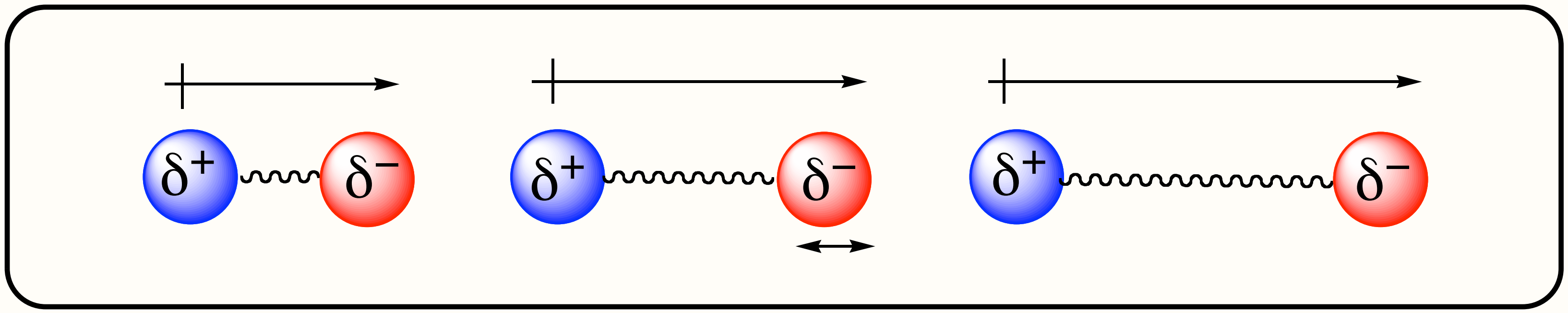
Infrared Spectroscopy

Sections: 13.20-13.22

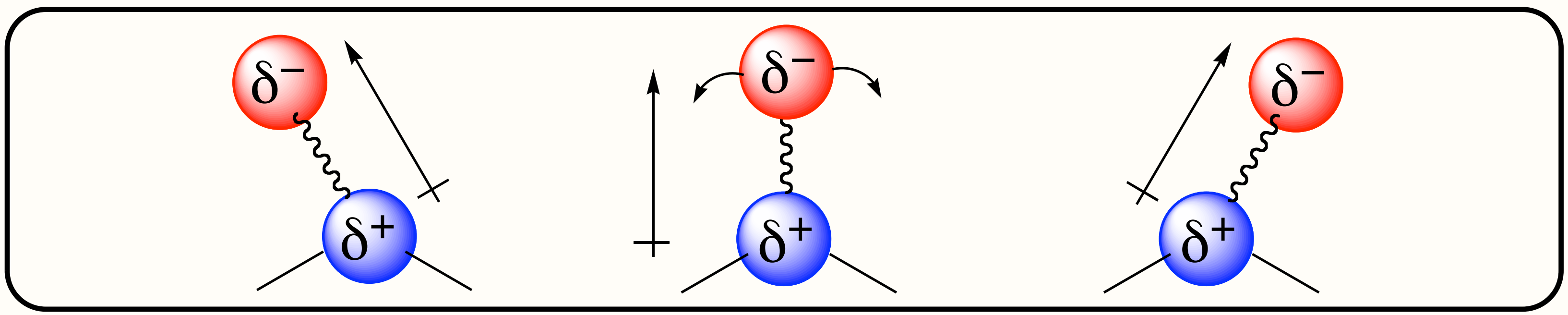
Principles of Infrared Spectroscopy

<u>IR:</u> Measures the vibrational energy associated with stretching or bending bonds that contain a dipole moment (μ).

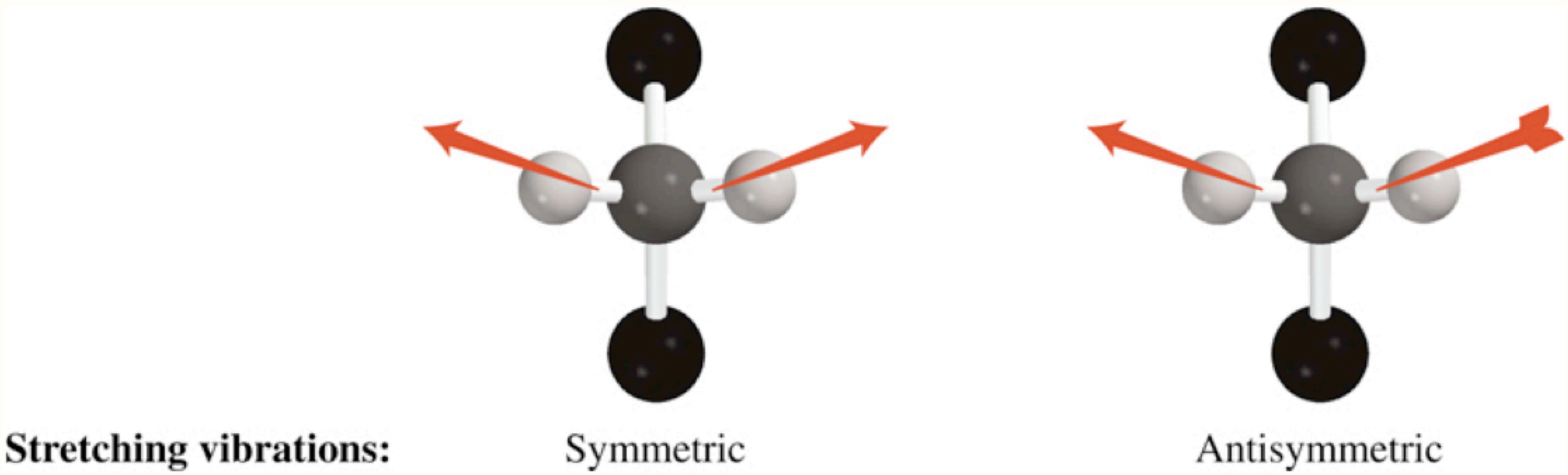
Stretching

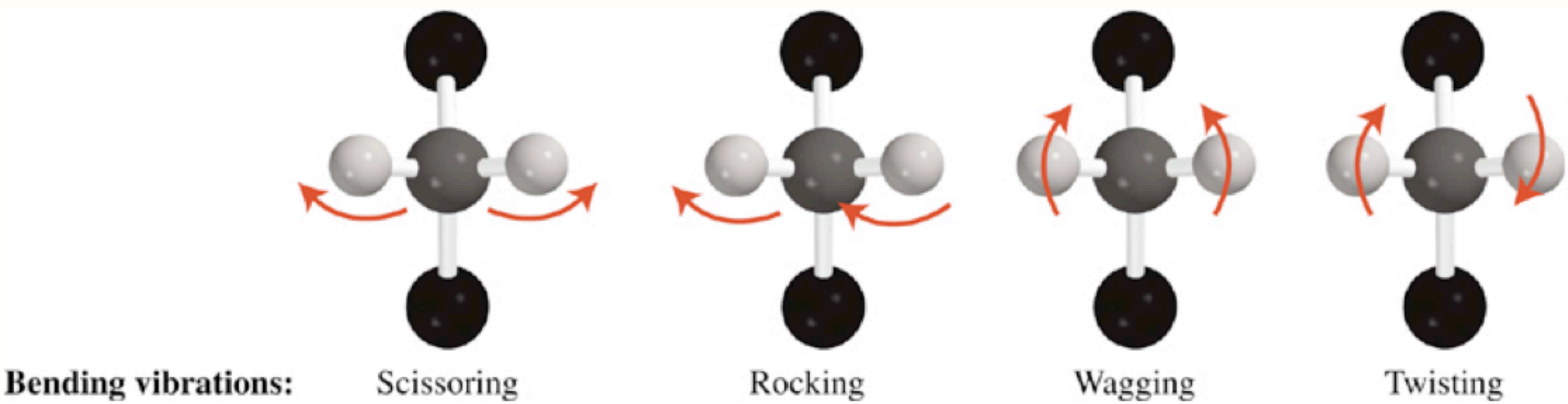


Bending

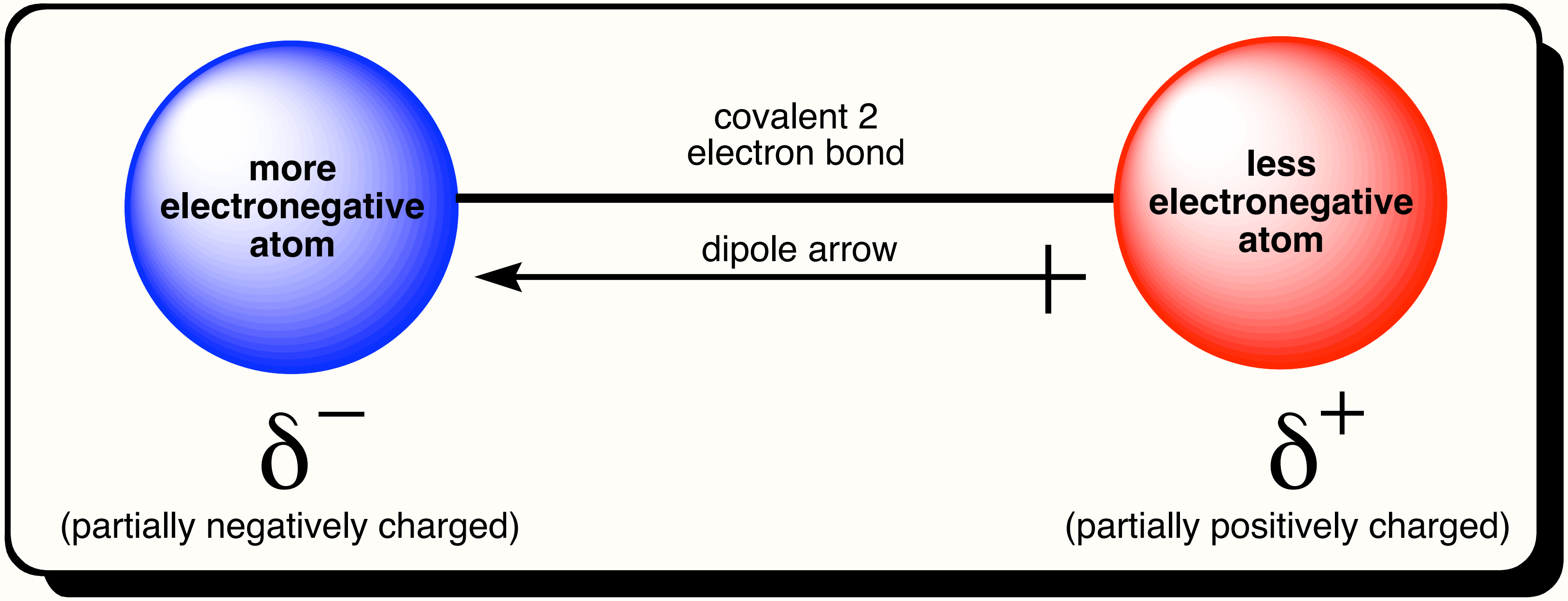


Stretching & Bending Vibrations





Dipole Moment



In order to measure the stretching or bending frequency of a covalent bond, it must have a dipole moment (μ).

Hooke's Law: Bonds are Like Springs

Vibrational Energy Depends *both* on bond strength (spring force constant) and the mass of atoms (objects) attached

$$\tilde{\nu} = k\sqrt{f * \frac{(m_1 + m_2)}{(m_1 * m_2)}}$$

$\tilde{\nu}$ = vibrational "frequency" in wavenumbers (cm^{-1})

k = constant ($1/2\pi c$)

f = force constant; strength of bond (spring)

m_1, m_2 = masses (not molecular weights) of attached atoms

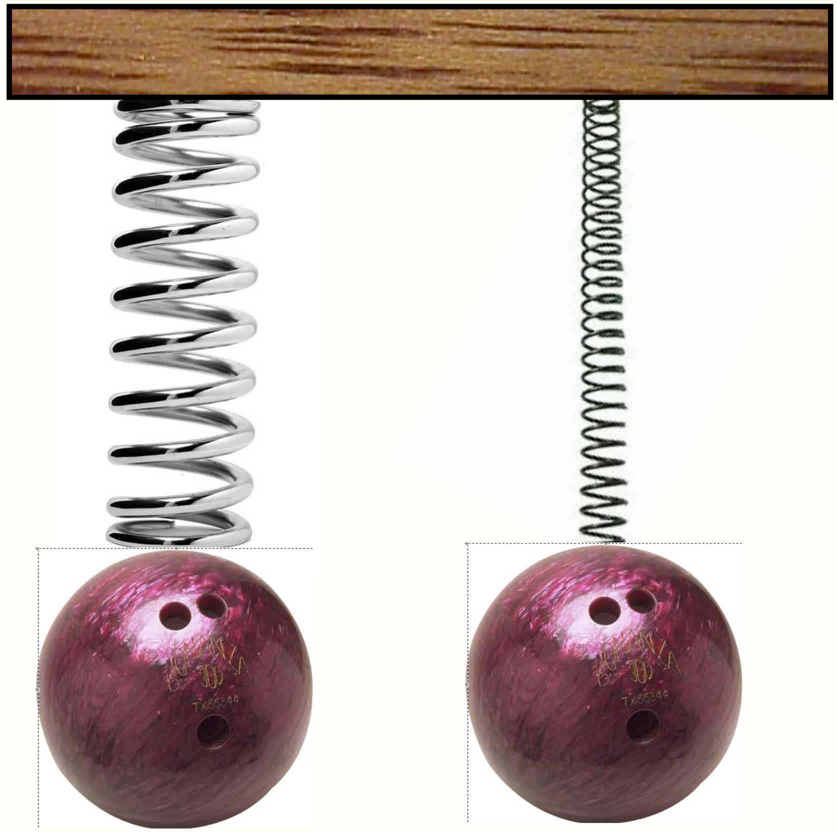
Trends:

↑ bond strength =
↑ frequency

↑ mass =
↓ frequency

Spring Analogy

smaller mass =
higher frequency =
higher energy



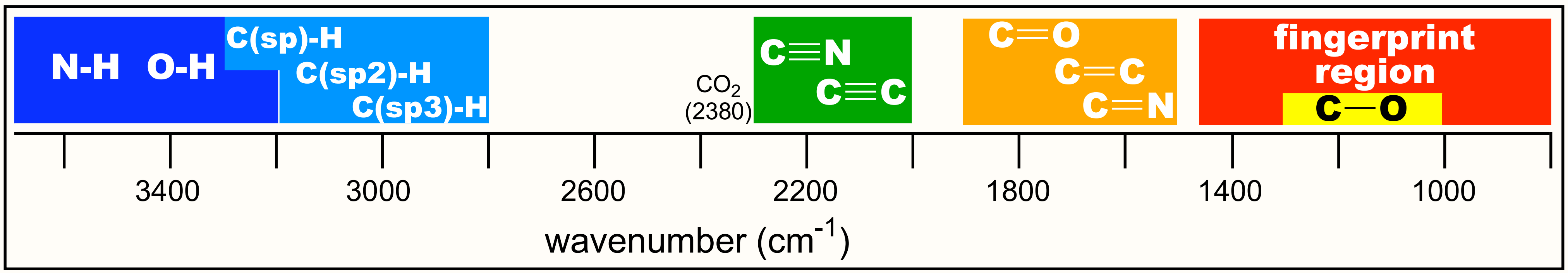
stronger spring (bond) =
higher frequency =
higher energy

Wavenumber ($\bar{\upsilon}$) and Infrared Scale

$$\bar{\upsilon}\ (\mathrm{cm}^{-1}) = \frac{1}{\lambda\ (\mathrm{cm})}$$

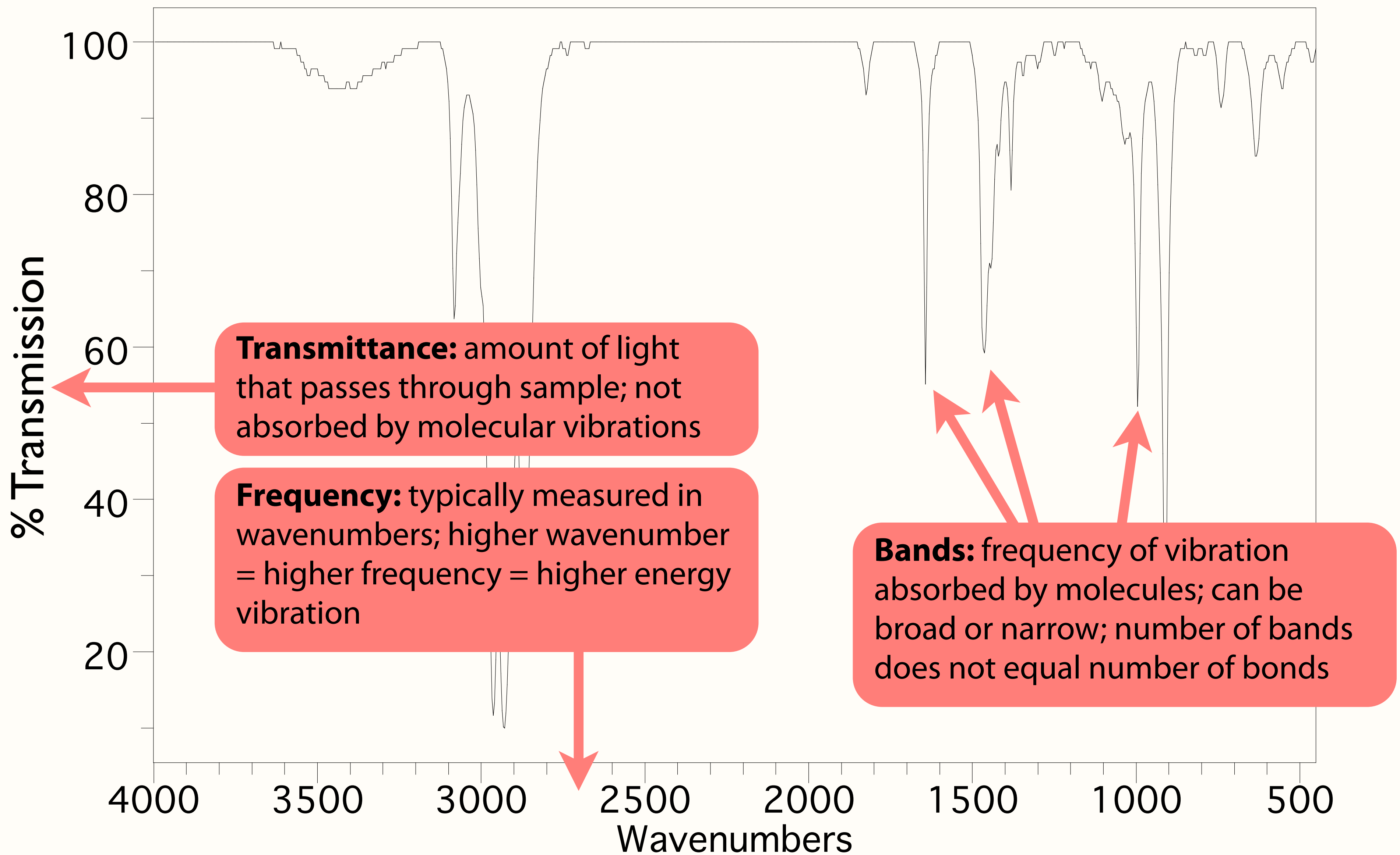
higher wavenumber ($\bar{\upsilon}$) =
higher frequency (υ) =
lower wavelength (λ) =
higher energy (E)

lower wavenumber ($\bar{\upsilon}$) =
lower frequency (υ) =
longer wavelength (λ) =
lower energy (E)

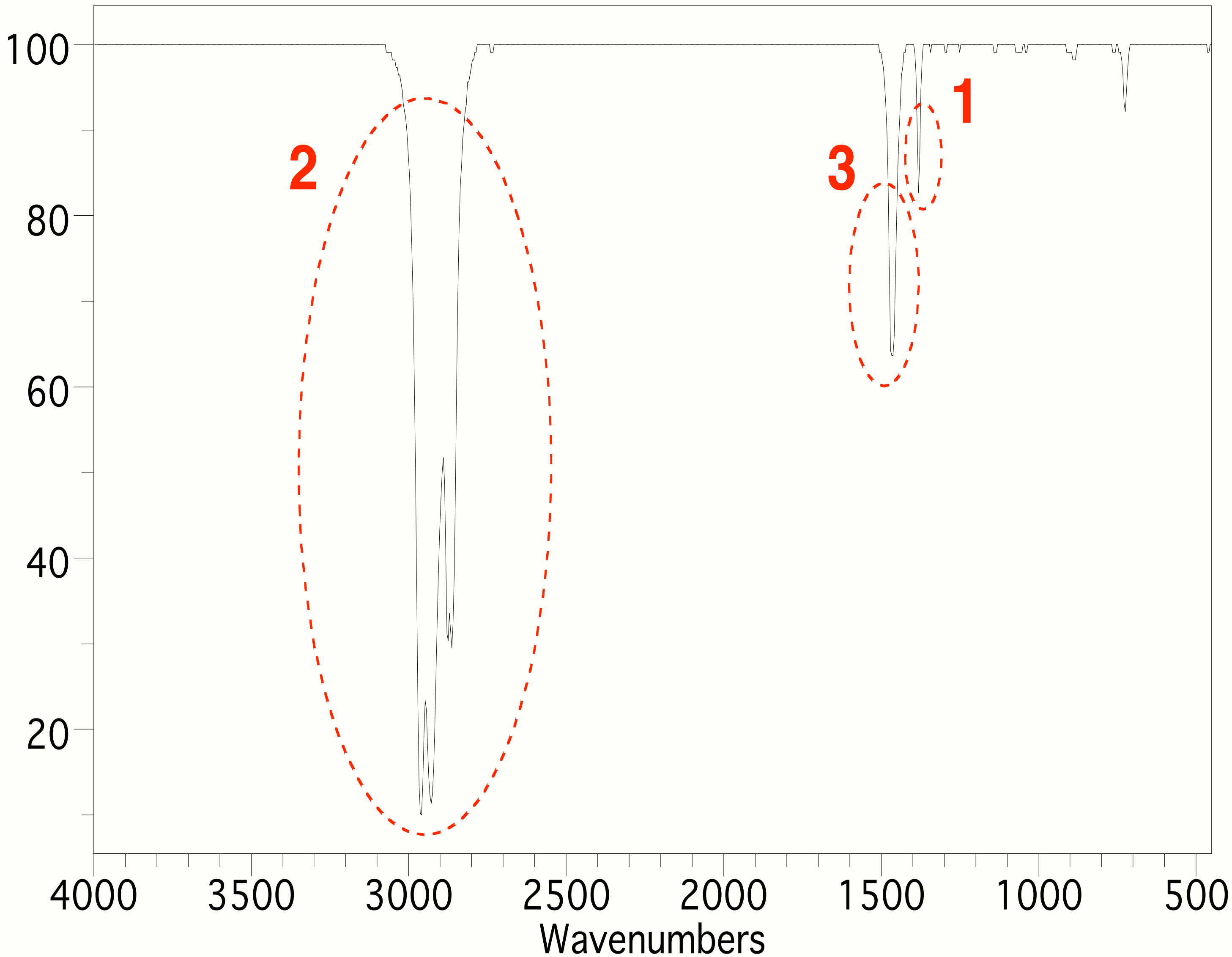


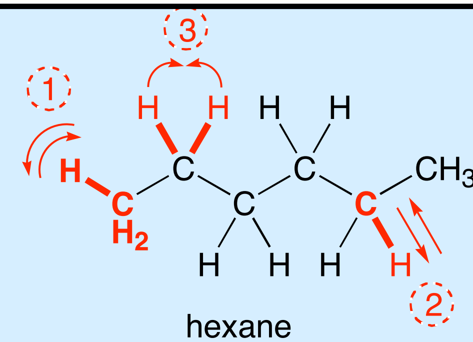
wavenumber = reciprocal of the wavelength measured in centimeters (cm); directly proportional to frequency

Infrared Spectrum



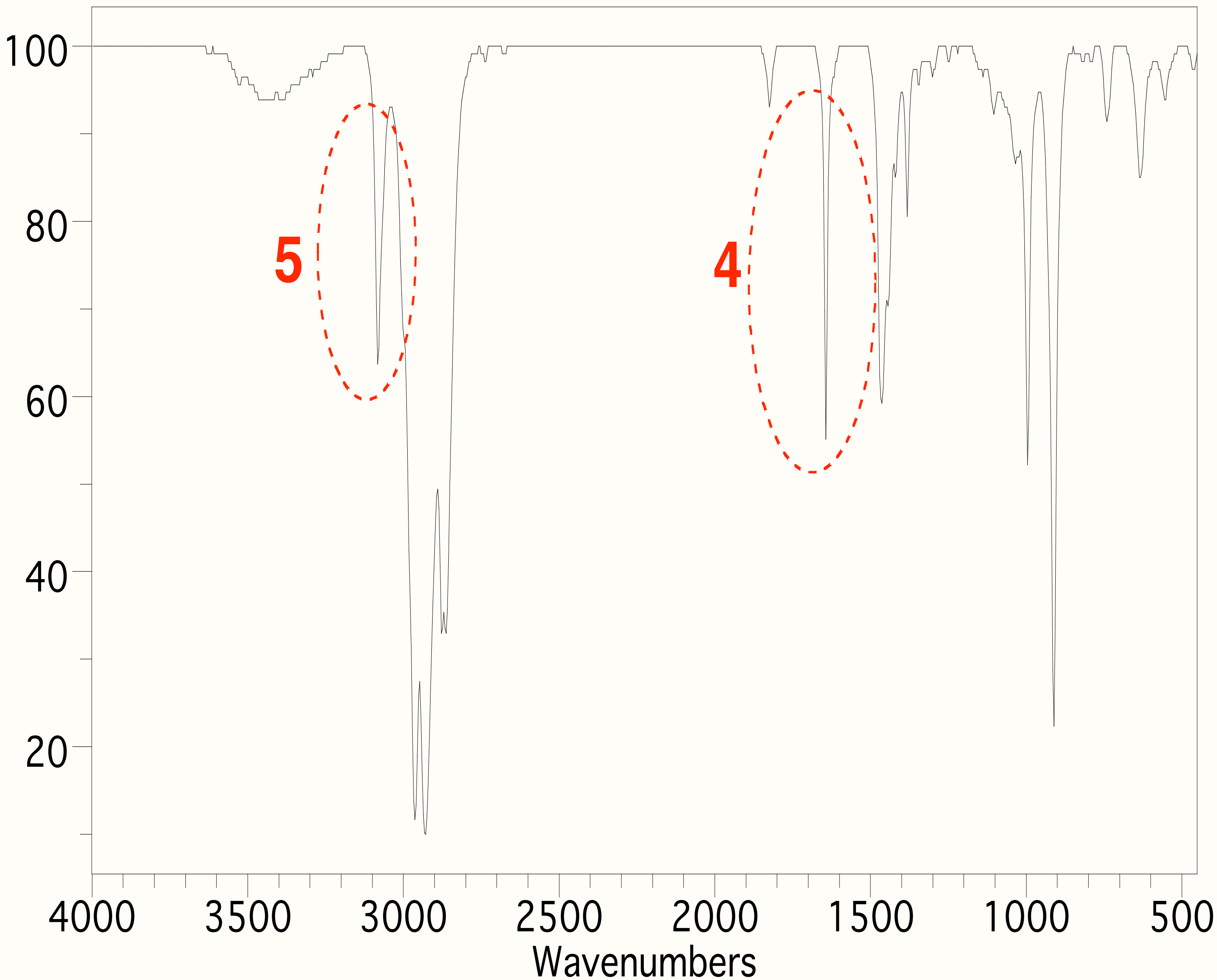
Characteristic Stretches - Alkanes

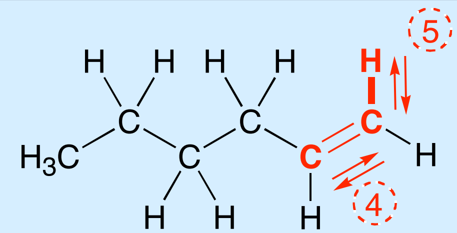




- **2** = sp^3 C-H bond stretching motion; general absorb around 2850-2950 cm^{-1}
- **1** = C-H rocking motion when C atom is part of a methyl group ($-CH_3$); 1370-1350 cm^{-1}
- **3** = scissor motion of $-CH_3$ hydrogen atoms; 1470-1450 cm^{-1}
- 1300-900 cm^{-1} = fingerprint region for organic molecules; typically complex and unhelpful

Characteristic Stretches - Alkenes

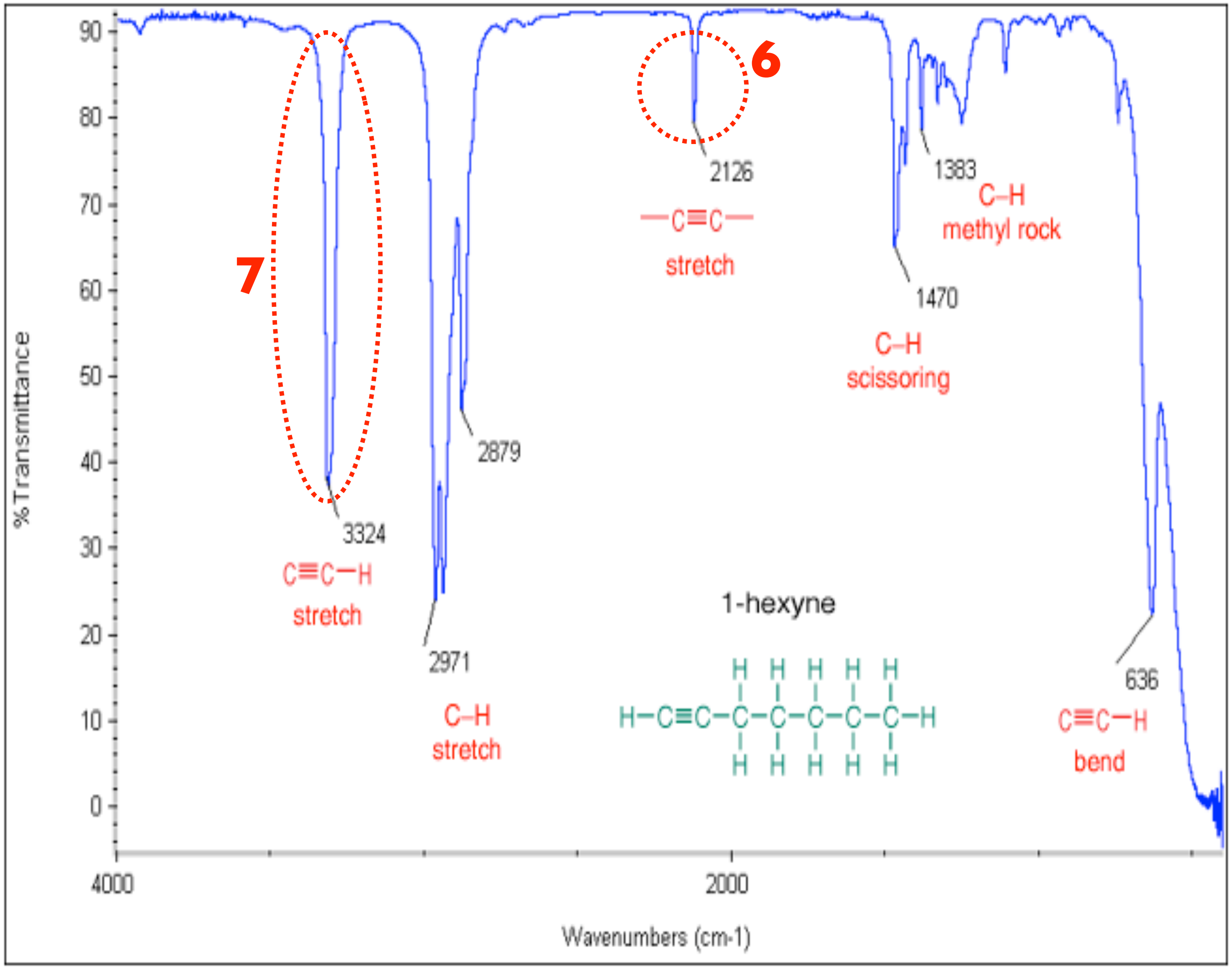


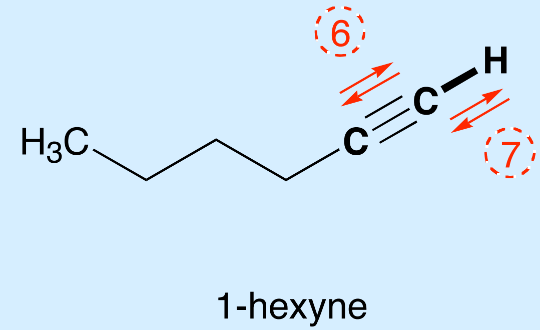


1-hexene

- **5:** notice sp^2 C-H (~3100 cm^{-1}) at higher frequency than sp3 C-H (~2950 cm^{-1})
- more *s*-character = stronger bond = higher frequency
- **4:** also, C=C bond at higher frequency than C-C bond; ~1600 cm^{-1}

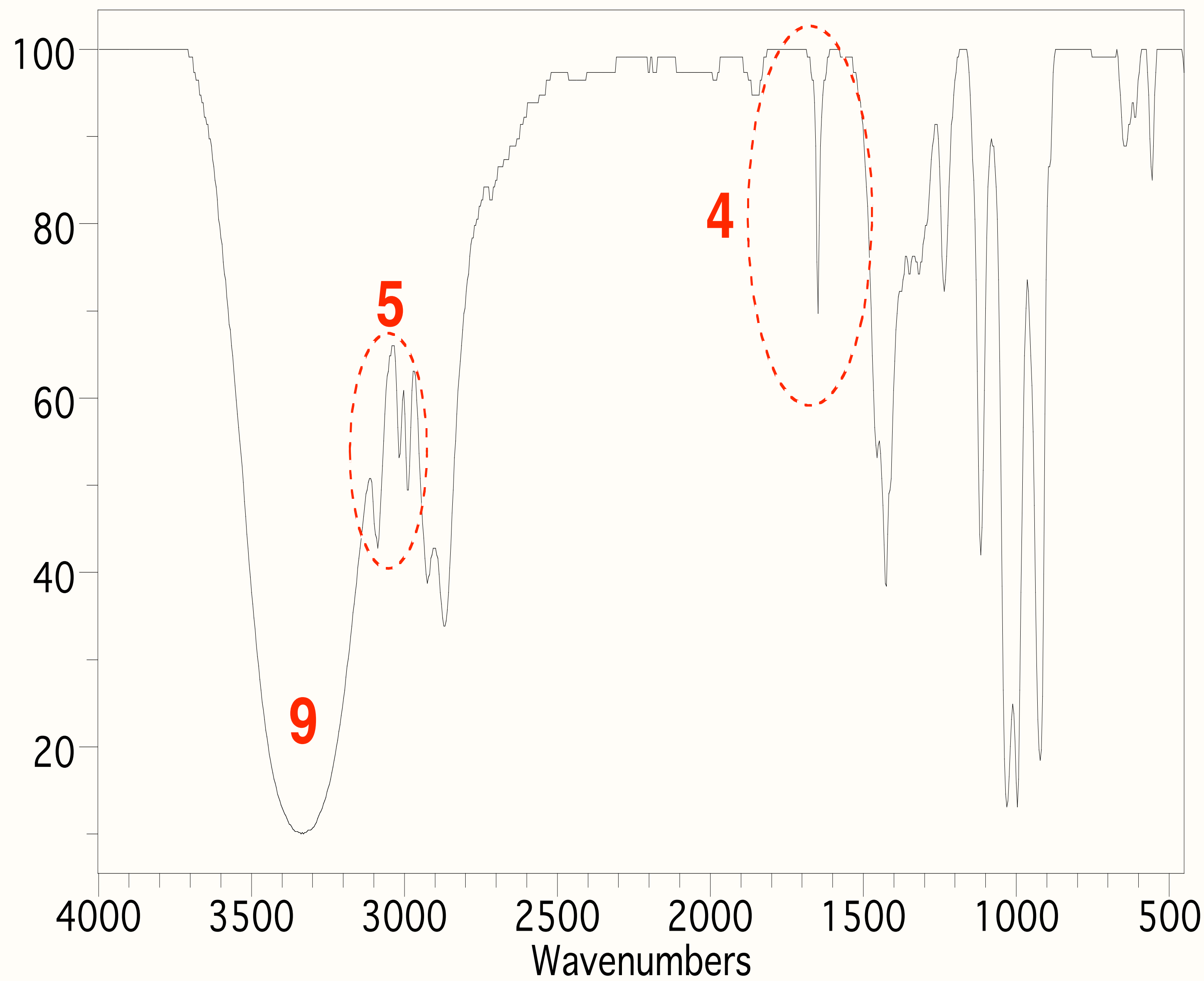
Characteristic Stretches - Alkynes

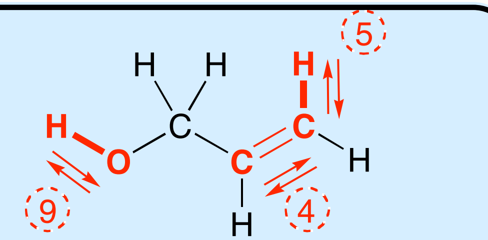




- **7:** notice sp C-H (~3300 cm^{-1}) at higher frequency than sp^2 C-H (~3100 cm^{-1}), which was higher than sp^3 C-H (~2950 cm^{-1})
- **6:** C≡C stretch is very weak because carbons have almost identical electronegativities = small dipole moment

Characteristic Stretches - Alcohols

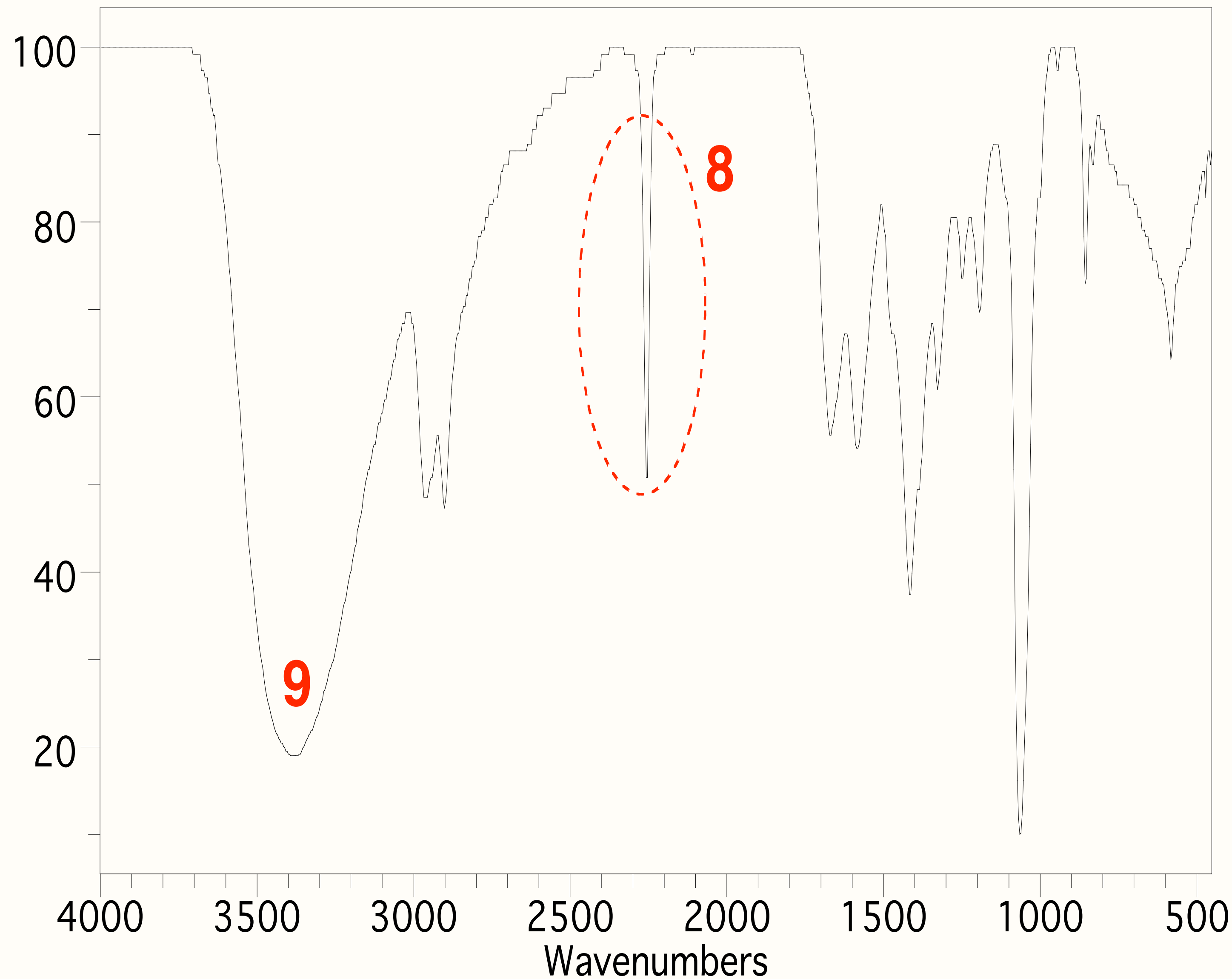


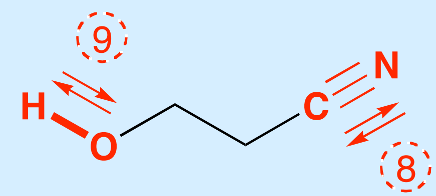


prop-2-en-1-ol
(allyl alcohol)

- **9:** hydroxyl groups (-OH) exhibit strong broad bands; ~3300 cm^{-1}
- broad peak is a result of hydrogen bonding; width depends on solution concentration
- lower concentration = less hydrogen bonding = more narrow -OH band

Characteristic Stretches - NItriles

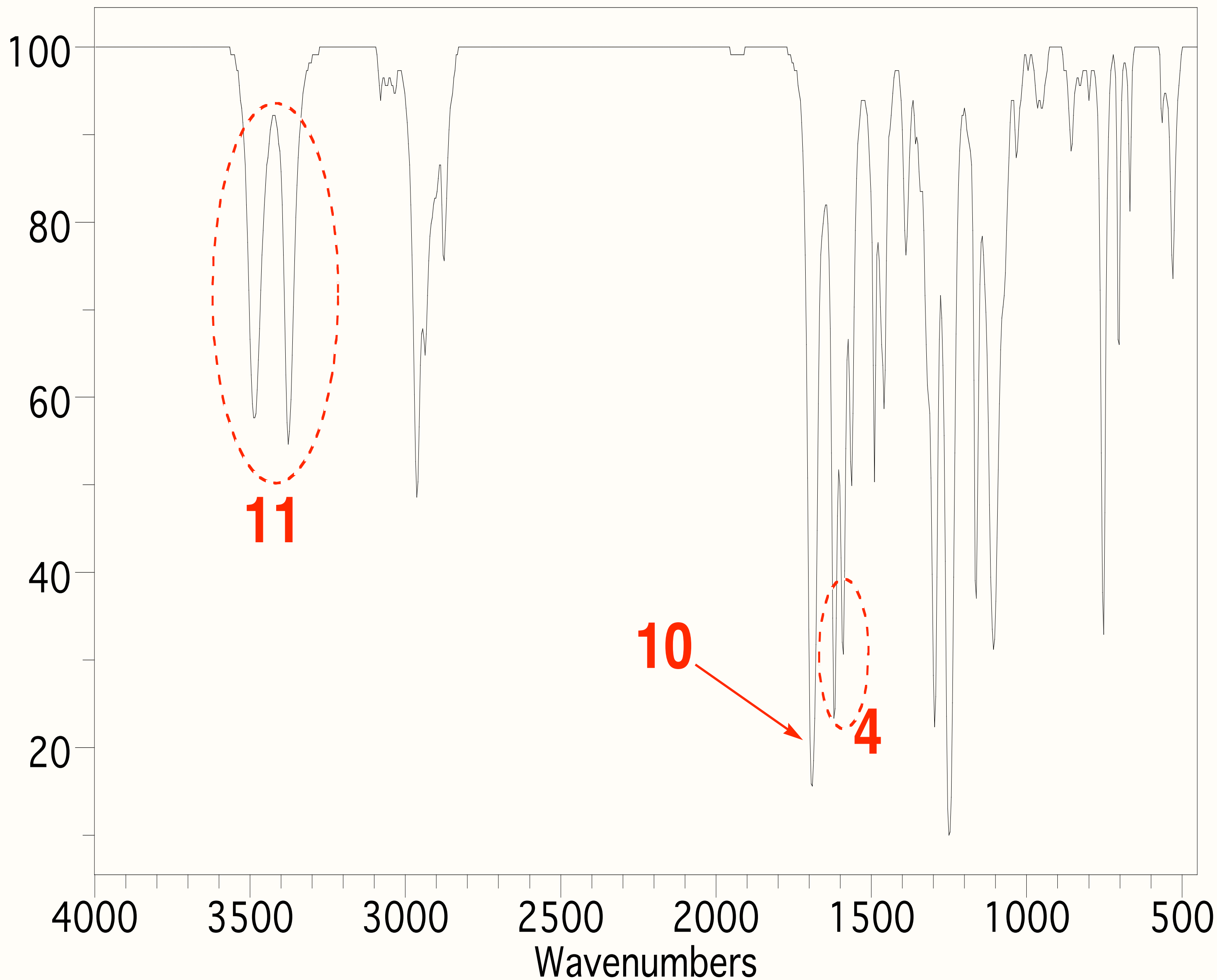


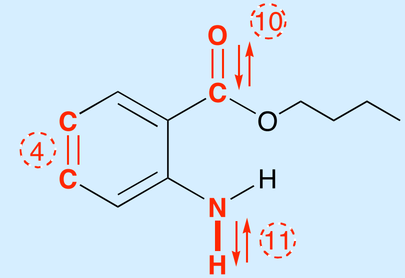


3-hydroxy-propionitrile

- **8:** nitriles ~2200 cm^{-1}
- nitriles (C≡N) absorb a greater magnitude of energy than alkynes (C≡C) because they have a larger dipole moment
- larger dipole moment = more intense peak
- size of the dipole does NOT affect frequency of vibration

Example: Ester, Amine, Benzene

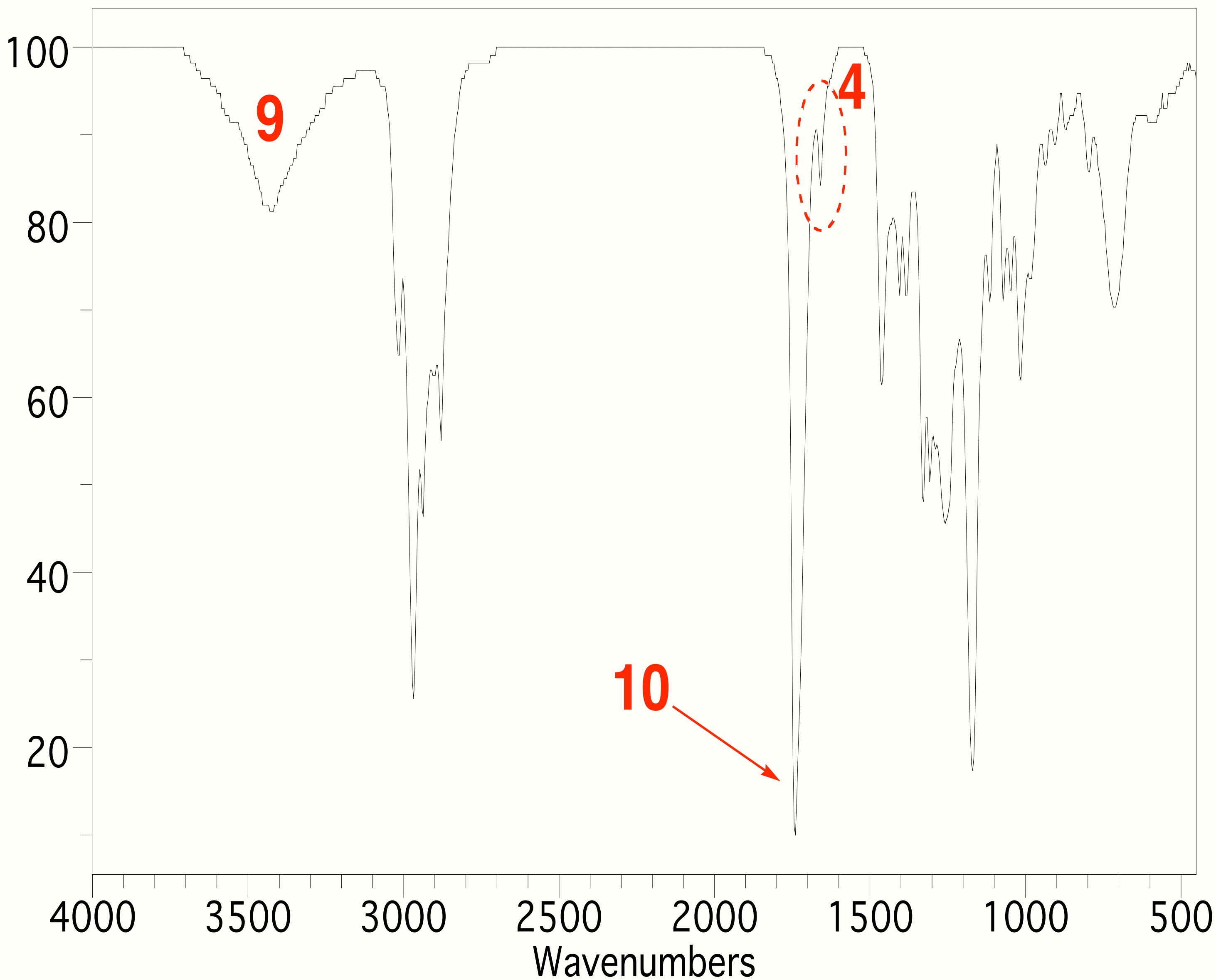


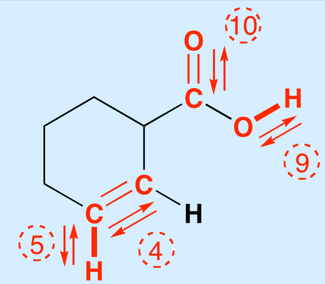


2-amino-benzoic acid butyl ester

- **10:** strong carbonyl (C=O) band ~1700 cm^{-1}
- **11:** amines; secondary amines (-NH) give one band; primary amines (-NH_2) gives two bands
- **4:** several alkene bands ~1600 cm^{-1} for benzene ring C=C double bonds

Characteristic Stretches - Carboxylic Acids

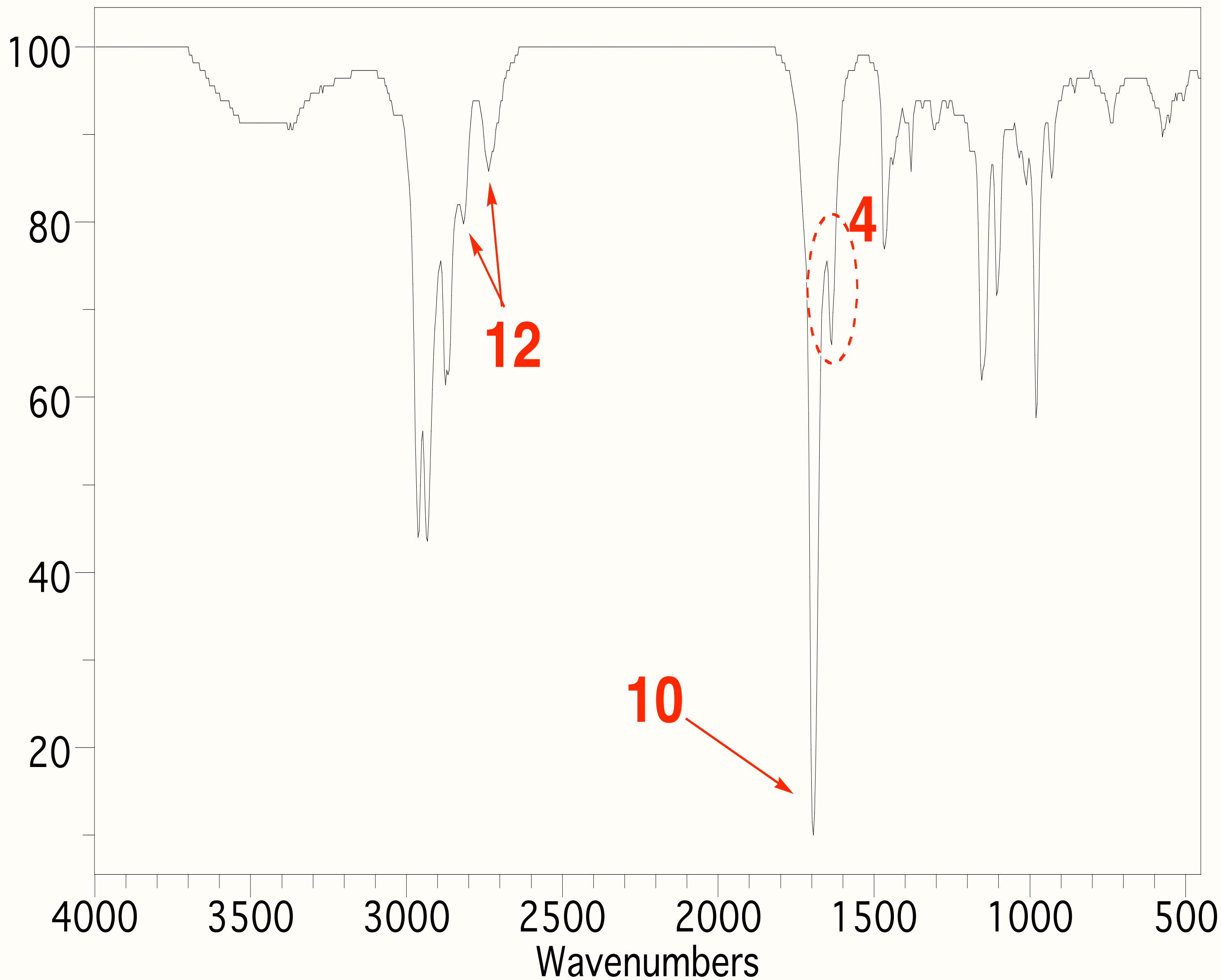


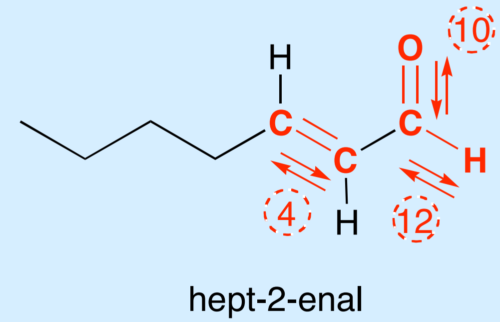


cyclohex-2-enecarboxylic acid

- **10:** strong carbonyl (C=O) band ~1700 cm^{-1}
- **9:** hydroxyl band (-OH) can be less intense and sharper in carboxylic acids
- **4:** weak alkene band (C=C) since small dipole moment

Characteristic Stretches - Aldehydes

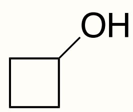




- **12:** usually two bands for C-H of aldehydes; may overlap with sp^3 C-H bands

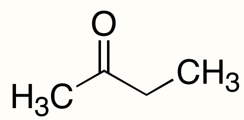
Self Test Questions

Which molecule is represented by the IR below?



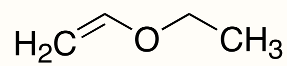
cyclobutanol

a.



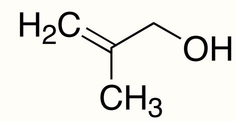
2-butanone

b.



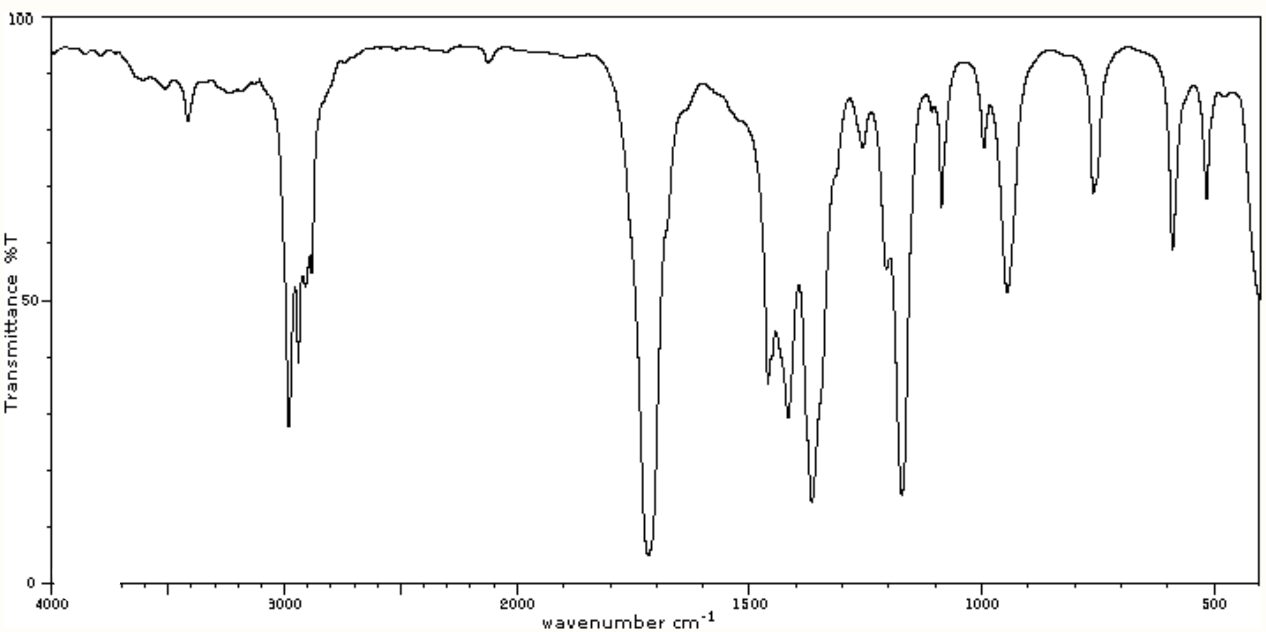
ethyl vinyl ether

c.



2-methyl-2-propen-1-ol

d.



A. a
B. b
C. c
D. d

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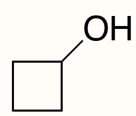

cyclobutanol
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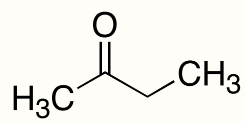
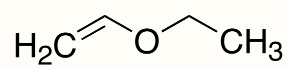
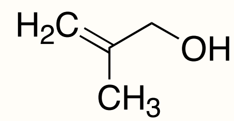


2-butanone
b.



ethyl vinyl ether
c.



2-methyl-2-propen-1-ol
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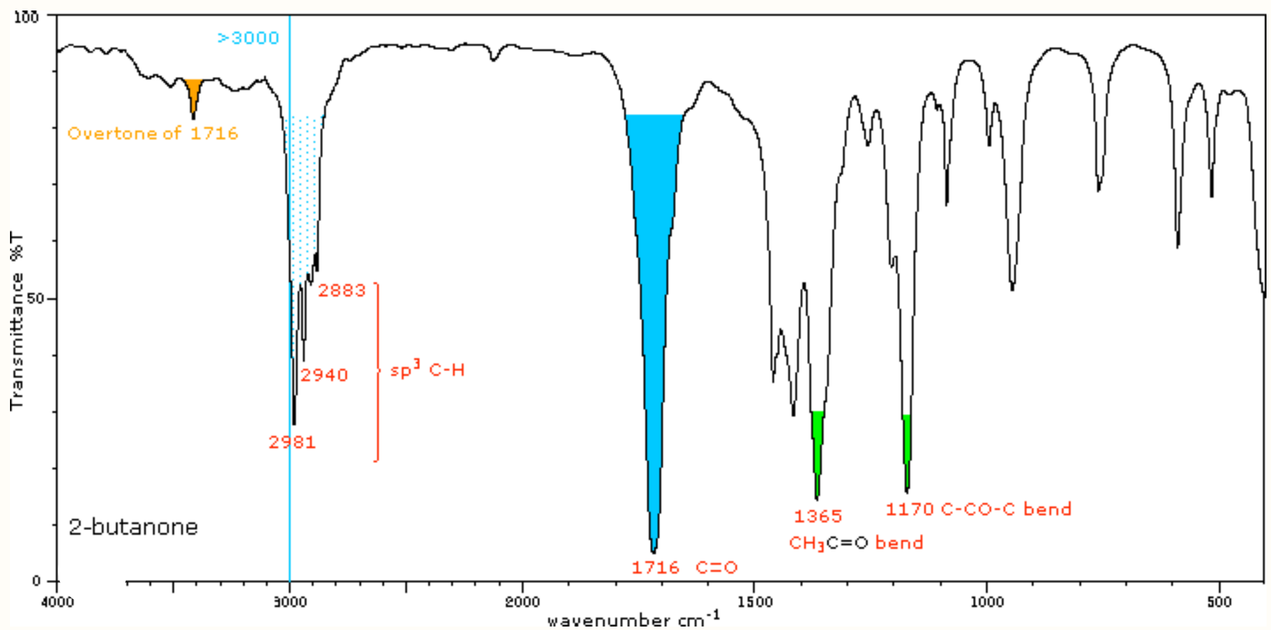

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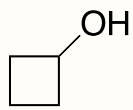

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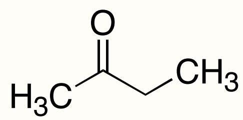
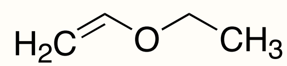


2-butanone

b.



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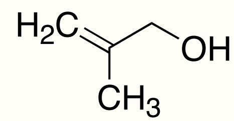

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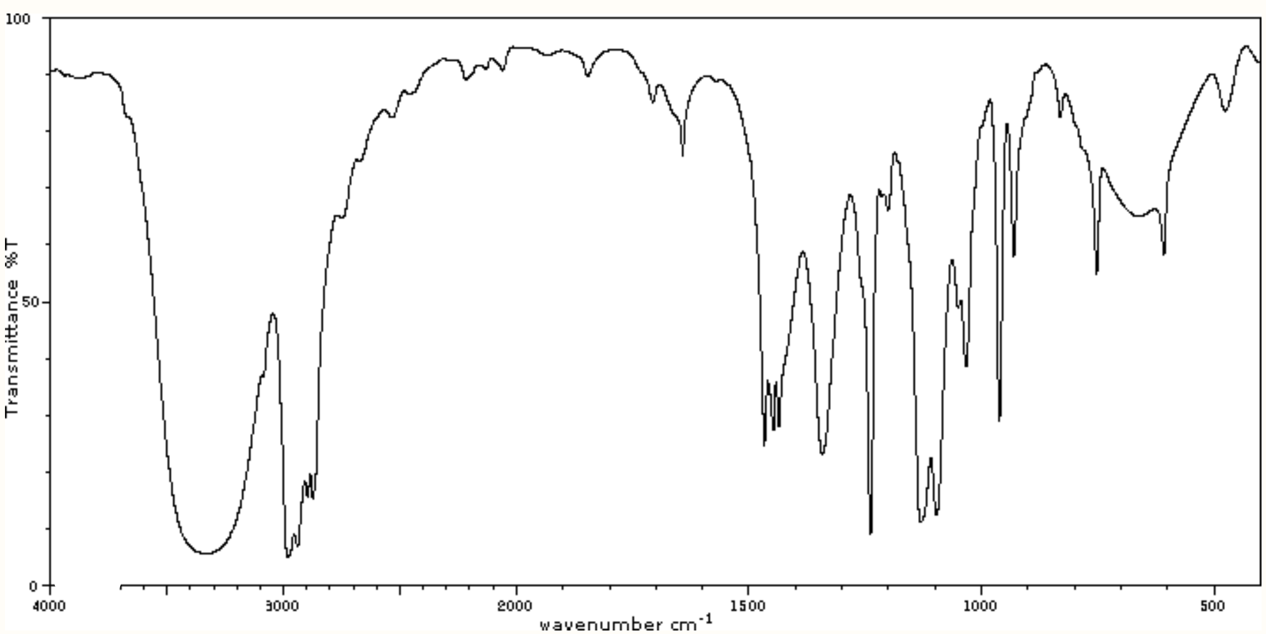

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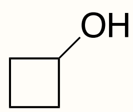

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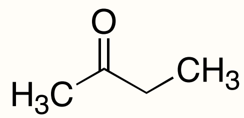
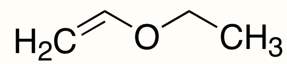


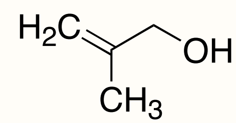
2-butanone

b.



ethyl vinyl ether

c.



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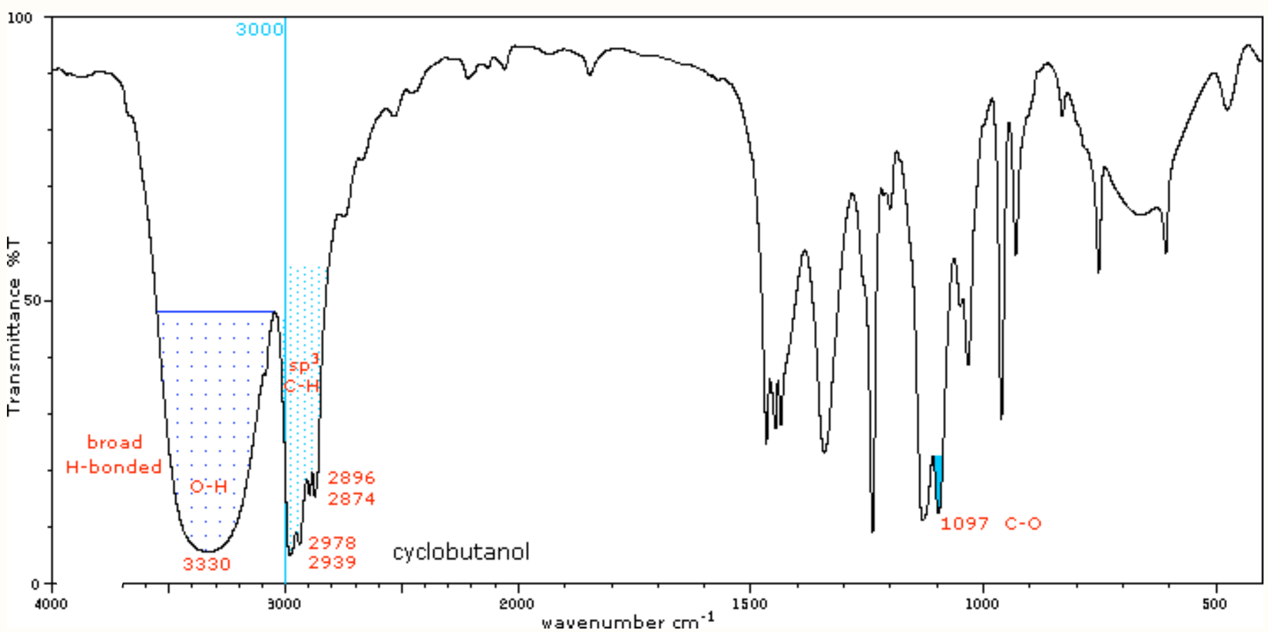

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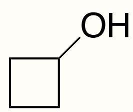

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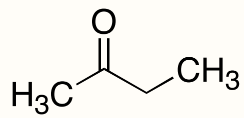

2-butanone

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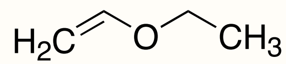

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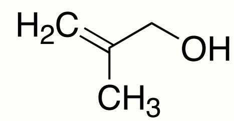

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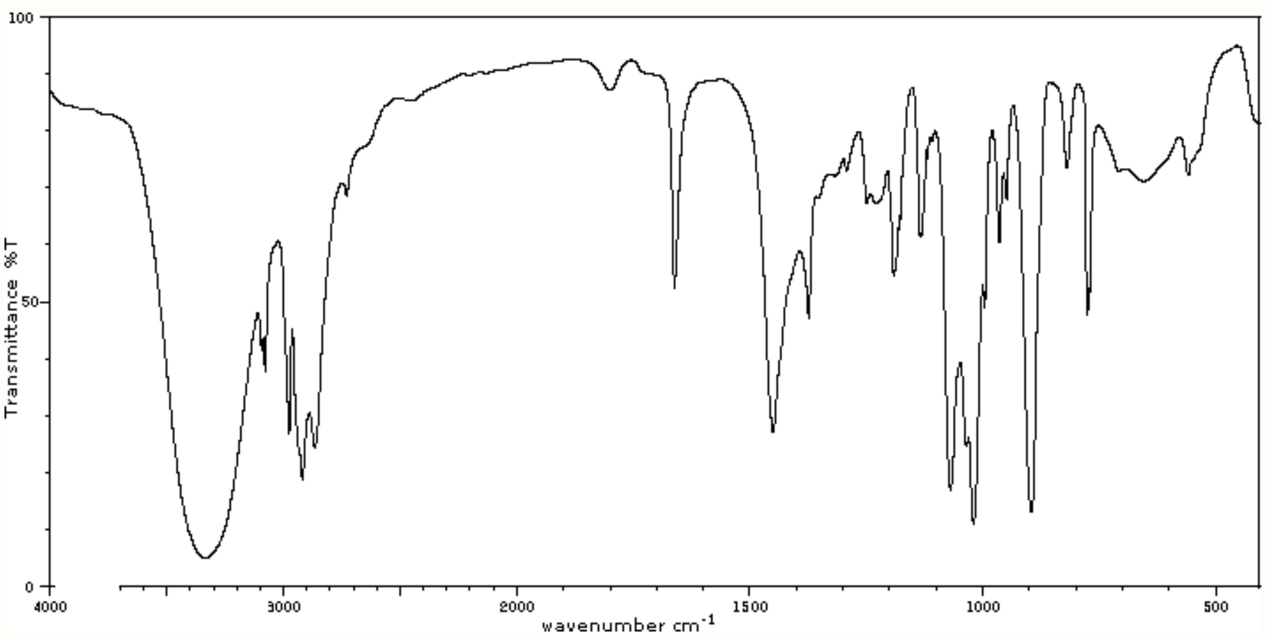

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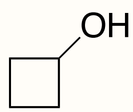

cyclobutanol

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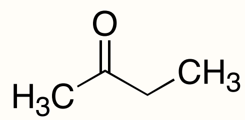
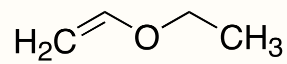


2-butanone

b.



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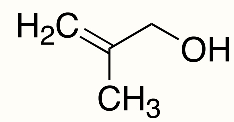

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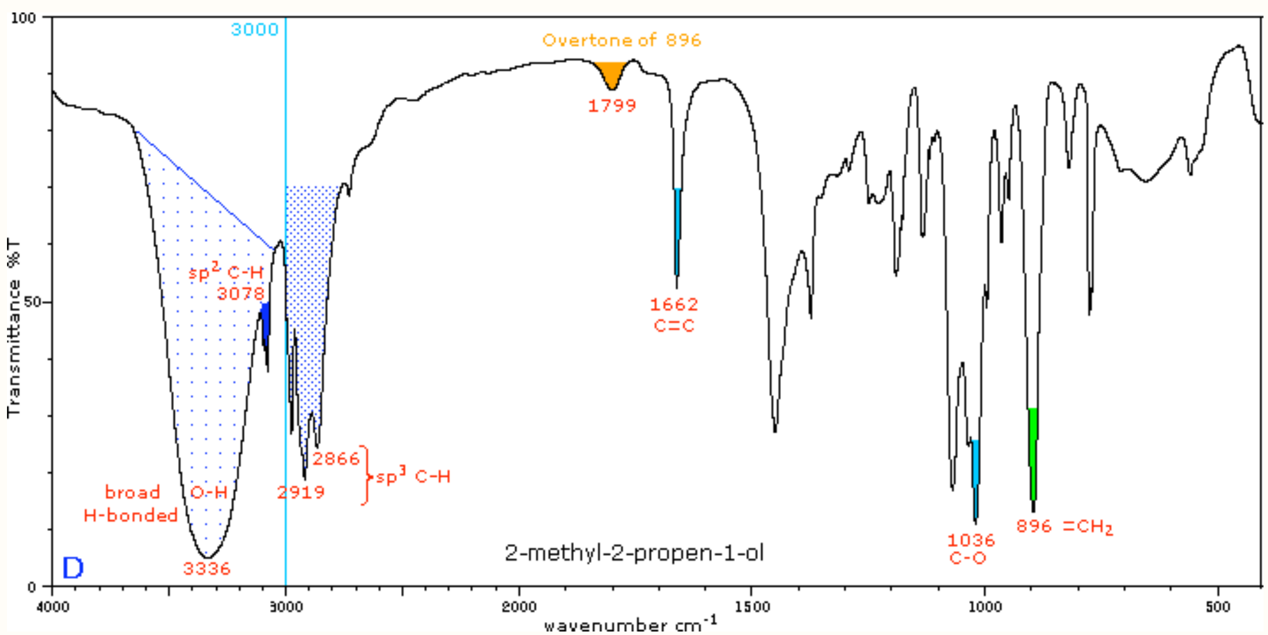


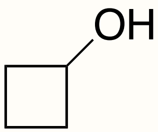
A. a

B. b

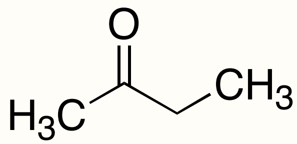
C. c

D. d

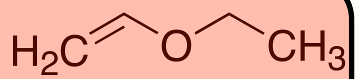
Example



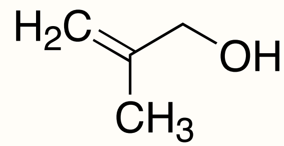
cyclobutanol



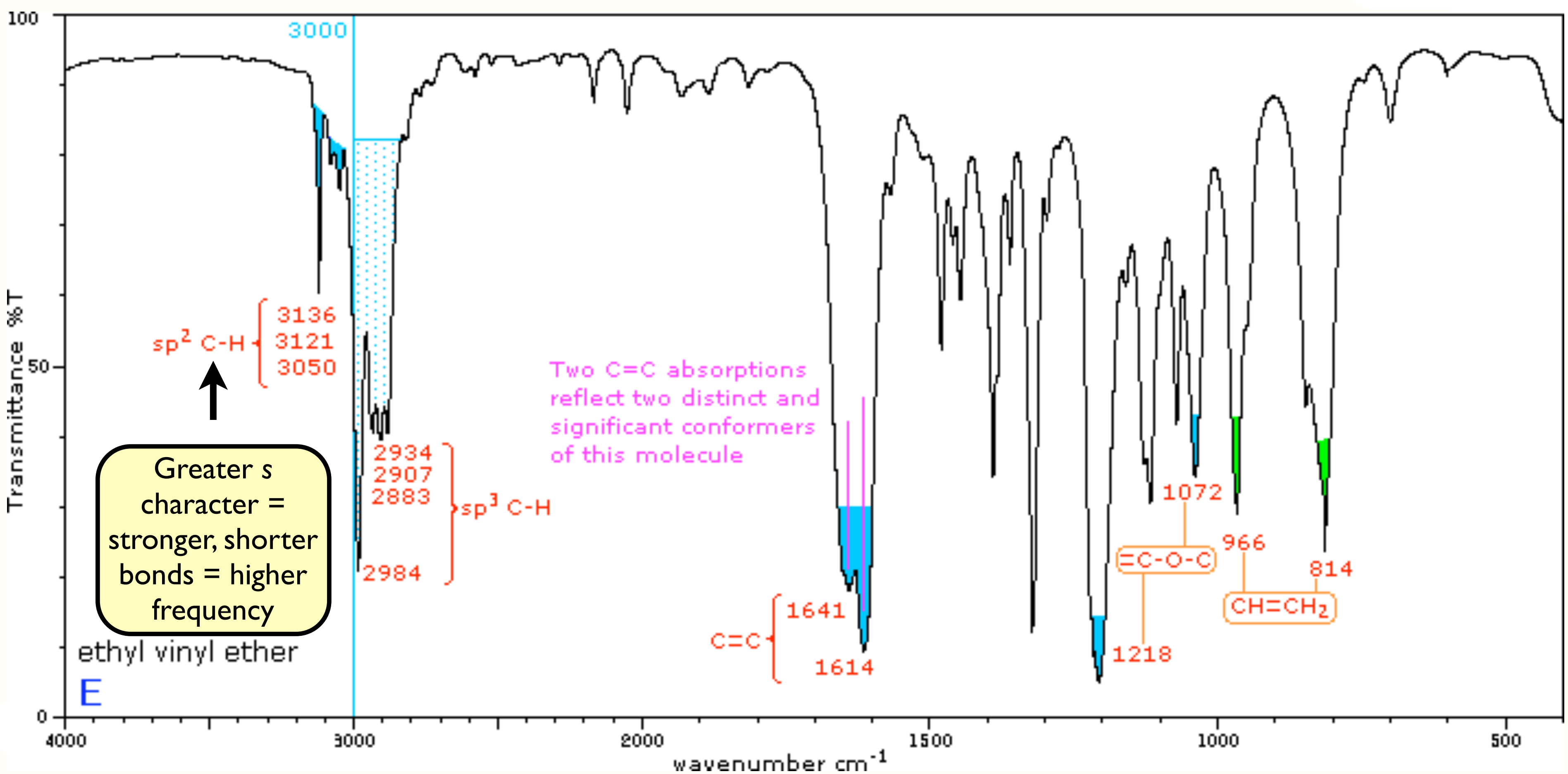
2-butanone



ethyl vinyl ether



2-methyl-2-propen-1-ol



Ultraviolet-Visible Spectroscopy

Section: 13.23

This topic will be covered in Chapter 10.

Next Lecture. . .

Chapter 13: Sections 13.23,13.24, 13.25

Problem Set 1 has been posted

Quiz This Week. . .

Chapter 5 & 6