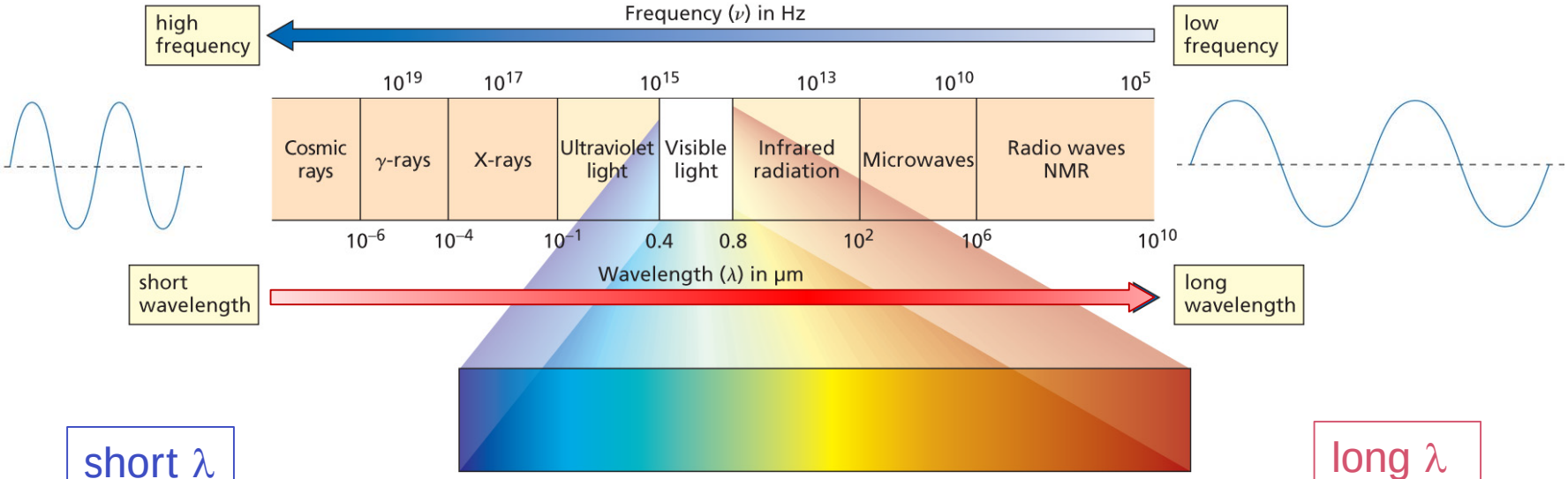
Spectroscopy

- interaction of matter with electromagnetic radiation
- EM spectrum



short λ
high ν
high E
large ṽ

blue

$$E = h\nu = \frac{hc}{\lambda}$$

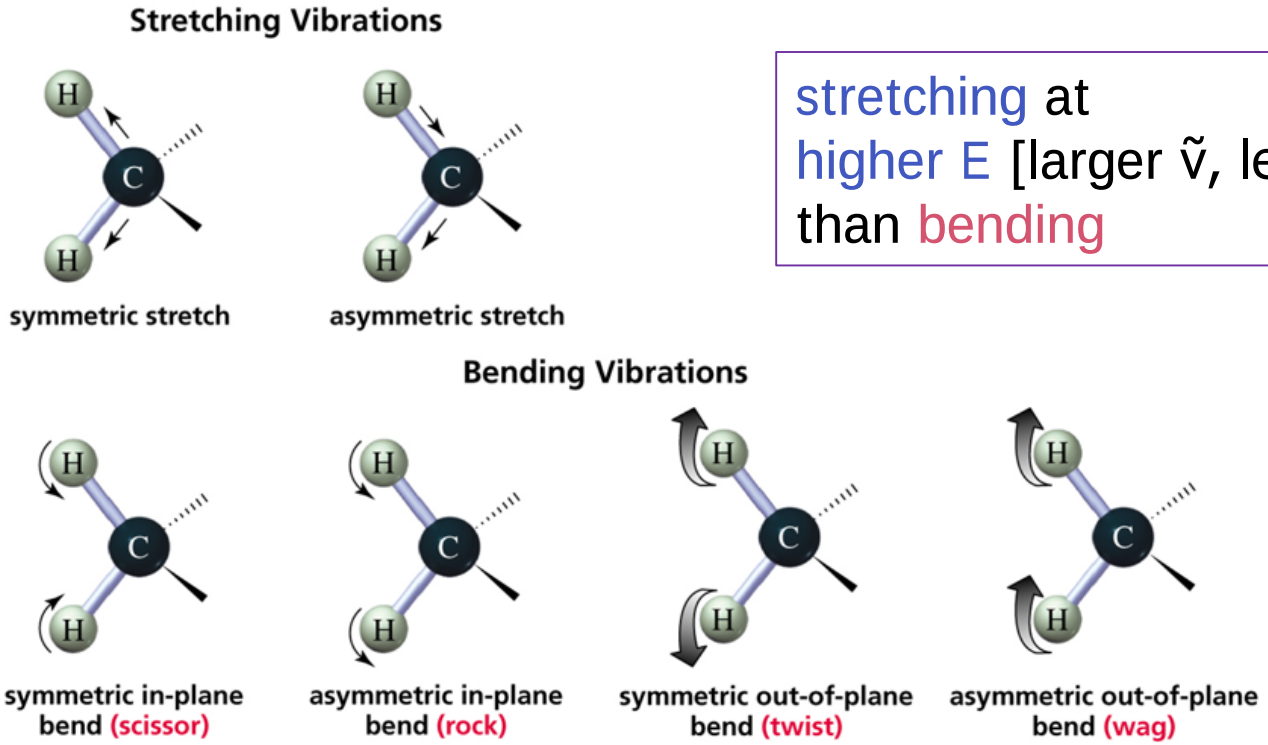
red

long λ
low ν
low E
small ṽ

- ṽ = # of waves/cm → $\tilde{\nu}\ (\mathrm{cm}^{-1}) = \dfrac{10^4}{\lambda\ (\mu\mathrm{m})}$

Infrared [IR] spectroscopy

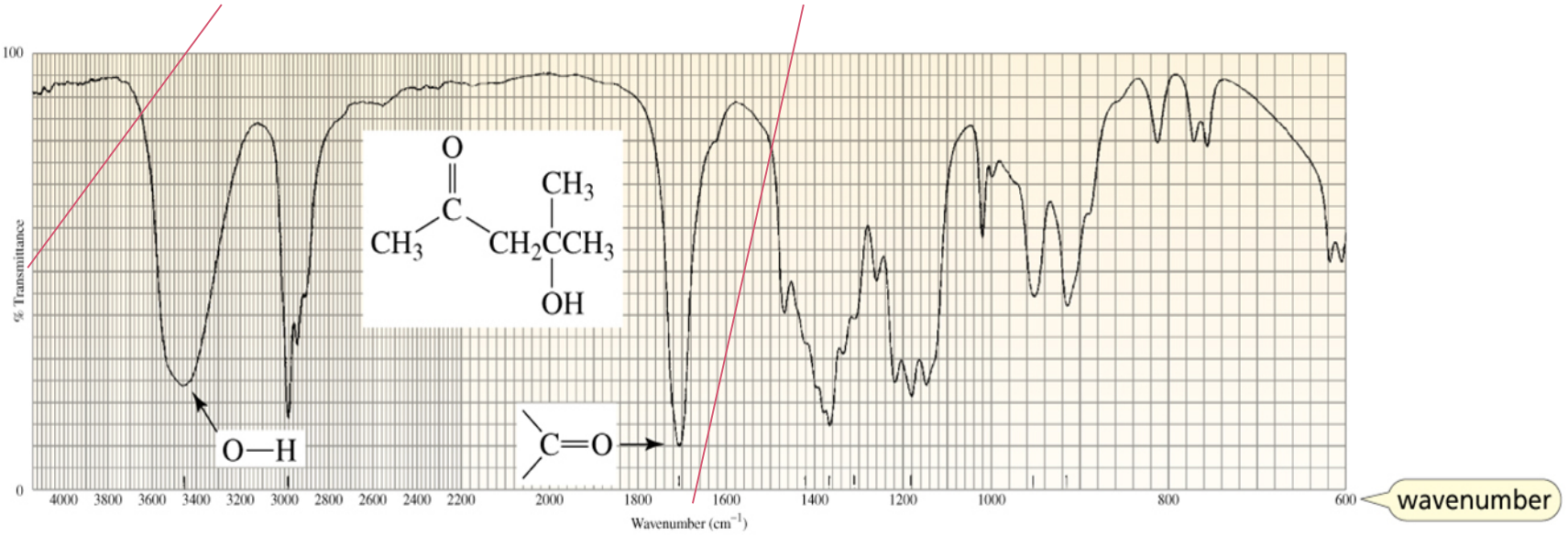
- a vibrational spectroscopy
  - freq of bond vibrations are in the range of IR freq
  - $\tilde{\nu}$ from 4000 to 600 cm^{-1} [λ = 2.5 – 15 μm]
- stretching vs bending vibrations



stretching at higher E [larger $\tilde{\nu}$, left-side] than bending

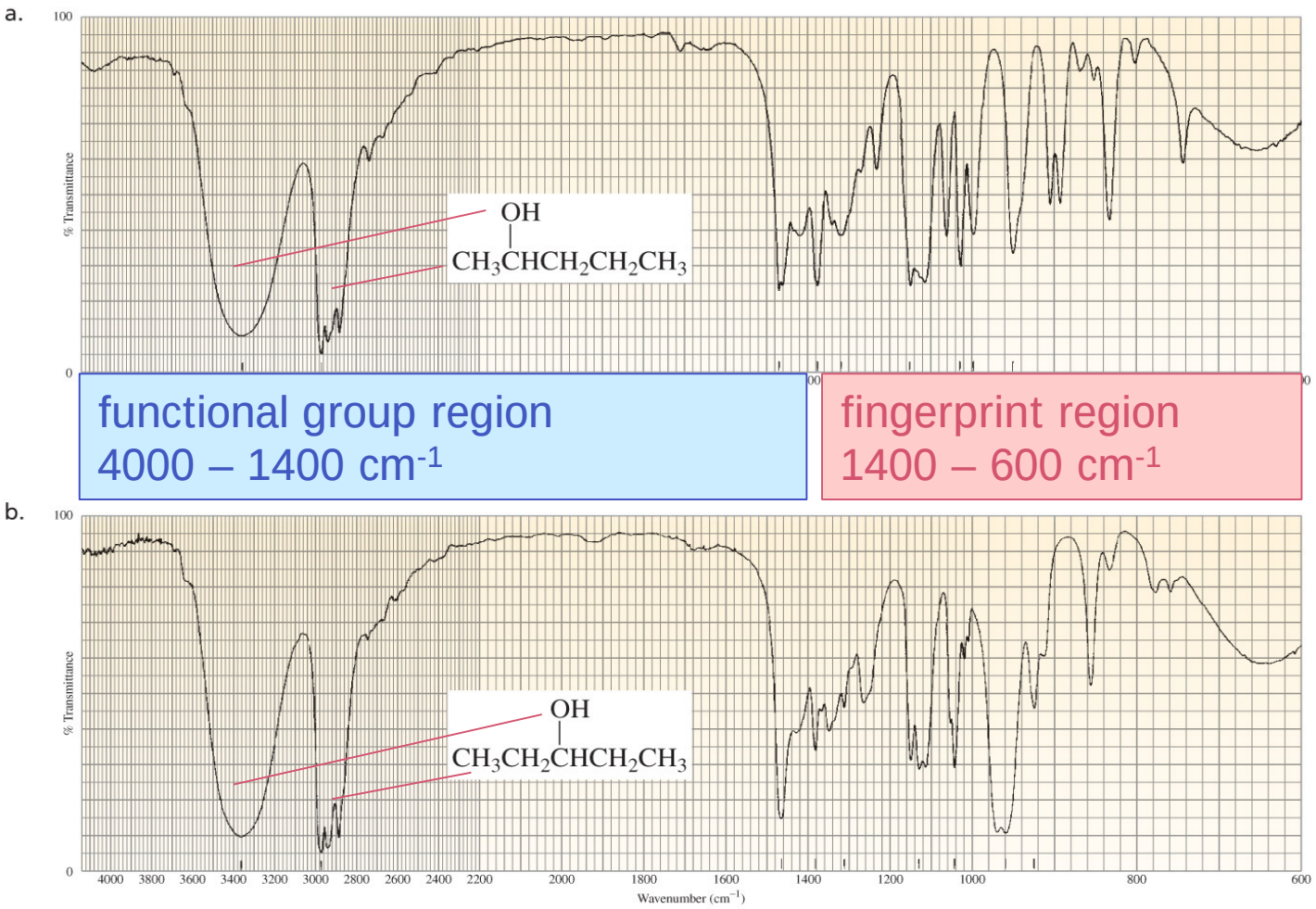
IR spectrum

- % transmittance vs wavenumber [$\tilde{\nu}$, cm^{-1}]



- IR freq scan → energy absorbed at vibration freq of bond → give absorption band at characteristic $\tilde{\nu}$
- Fourier transform IR [FTIR]
  - all freq simultaneously → multiple measure → averaging

Two regions of IR spectrum



functional group region
4000 – 1400 cm^{-1}

fingerprint region
1400 – 600 cm^{-1}

- characteristic of ft'nal group
- identify by gathering groups
- mostly stretching bands

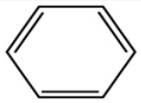
- unique to the comp'd
- identify by comparing
- mostly bending bands

Identifying compounds

- with characteristic absorption band
  - commonly using stretching bands

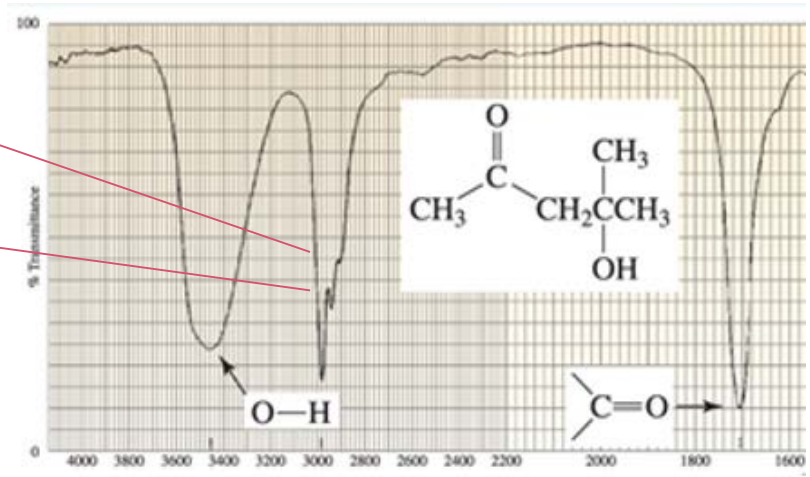
Table 13.4 will be given in the exam.

Table 13.4 Frequencies of Important IR Stretching Vibrations

Type of bond	Wavenumber (cm^{-1})	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium

Intensity of band

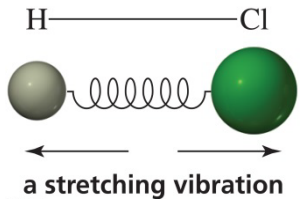
- depends on
  - polarity of bond
    - The more polar the bond, the more intense the absorption.
    - stretching → change in dipole moment → intensity
    - O–H > N–H > C–H
    - C=O > C=C
  - # of bonds
  - concentration of sample
- expressed
  - (s), (m), (w)
  - sharp, broad



Position of bands: mass and strength

- bond as spring ~ Hooke's law

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



$\sigma = E\,\varepsilon$ [(stress) = (modulus)(strain)]
(force) = (spring constant)(distance)

- lighter atom [lower m] at higher freq [larger $\tilde{\nu}$]
- stronger bond [higher f] at higher freq [larger $\tilde{\nu}$]
  - higher bond order vibrate at higher freq

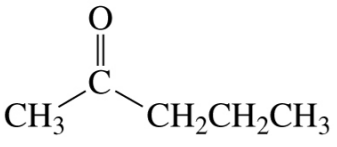
C—H
~3000 cm^{-1}
C—D
~2200 cm^{-1}
C—O
~1100 cm^{-1}
C—Cl
~700 cm^{-1}

C≡N
~2200 cm^{-1}
C=N
~1600 cm^{-1}
C—N
~1100 cm^{-1}

C=O
~1700 cm^{-1}

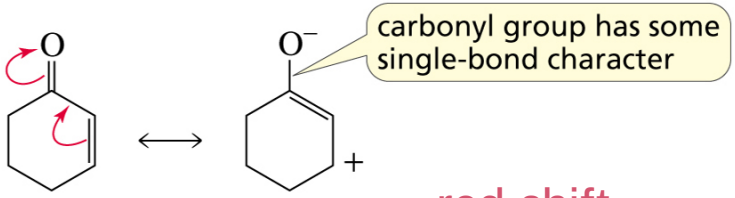
Position: resonance and inductive

- C=O stretching



2-pentanone

C=O at 1720 cm^{-1}



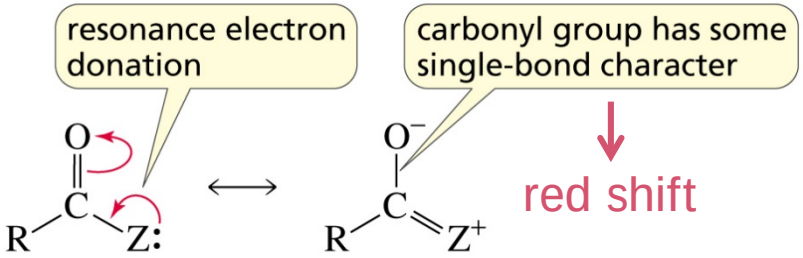
2-cyclohexenone

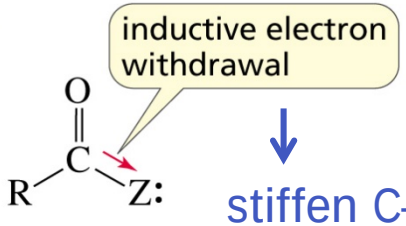
C=O at 1680 cm^{-1}

red shift
due to resonance

- when N, O, X present ~ resonance ED [+M]; inductive EW [–I]

§8.10 p378



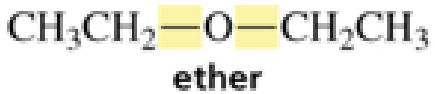


stiffen C–O → blue shift

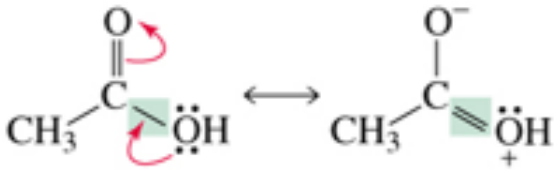
Y	ν (cm-1)
Cl	1810
OR	1735
NH_2	1660

- Z = O, X ~ –I > +M ~ higher EN (+ size for X)
- Z = N ~ +M > –I ~ lower EN

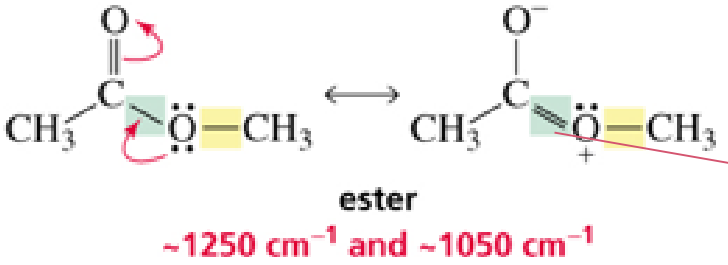
- C–O stretching

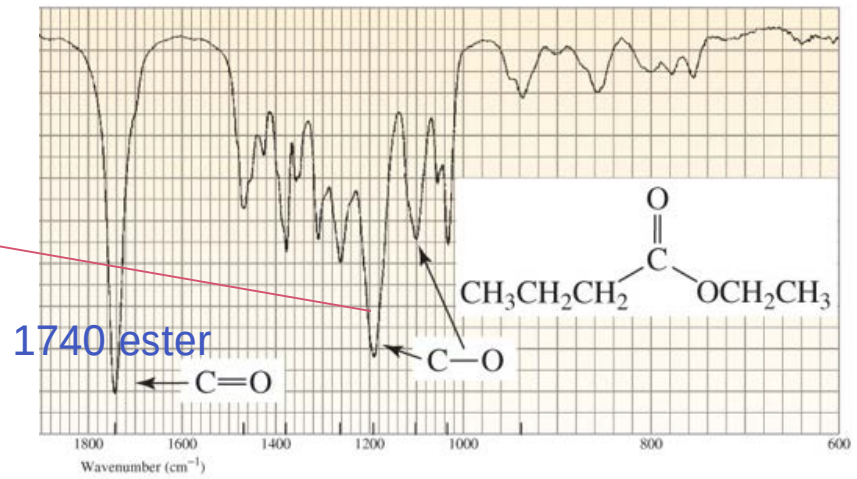


pure single bond



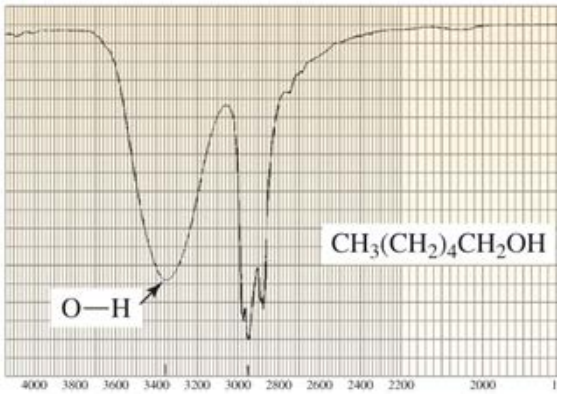
partial double bond → blue shift



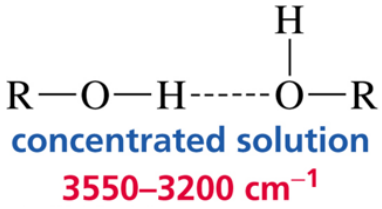


Position: hydrogen bonding

- hydrogen bonding
  - easier stretching → smaller $\tilde{\nu}$ [red shift]
  - H-bonds vary in strength → broad peak

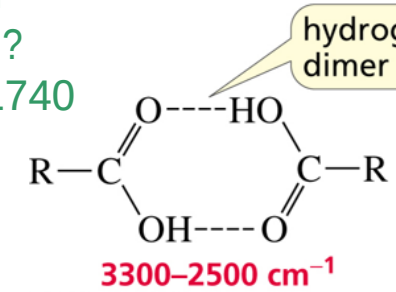


R—O—H
dilute solution
3650–3590 cm^{-1}



concentrated solution
3550–3200 cm^{-1}

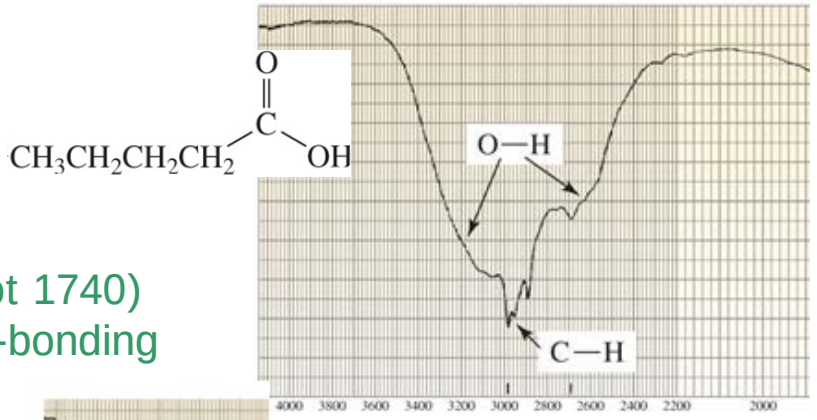
RCOOH
dil sol'n?
3600, 1740



3300–2500 cm^{-1}

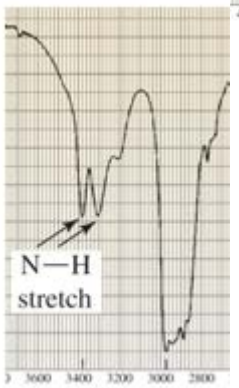
intensive H-bonding

this C=O at 1700 (not 1740)
~ loosened due to H-bonding



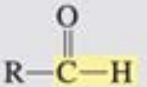
'messy'
[overlap w/ C-H]

- N–H
  - less polar and weaker H-bond
    → weaker and narrower peak

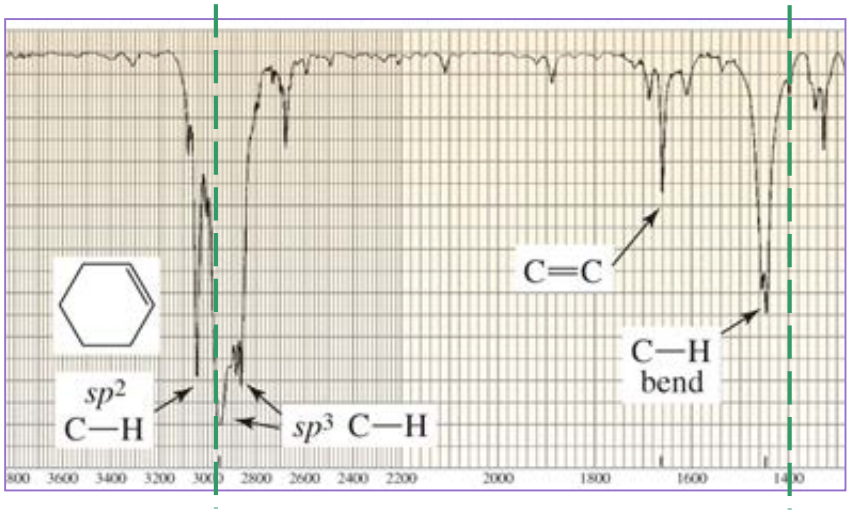


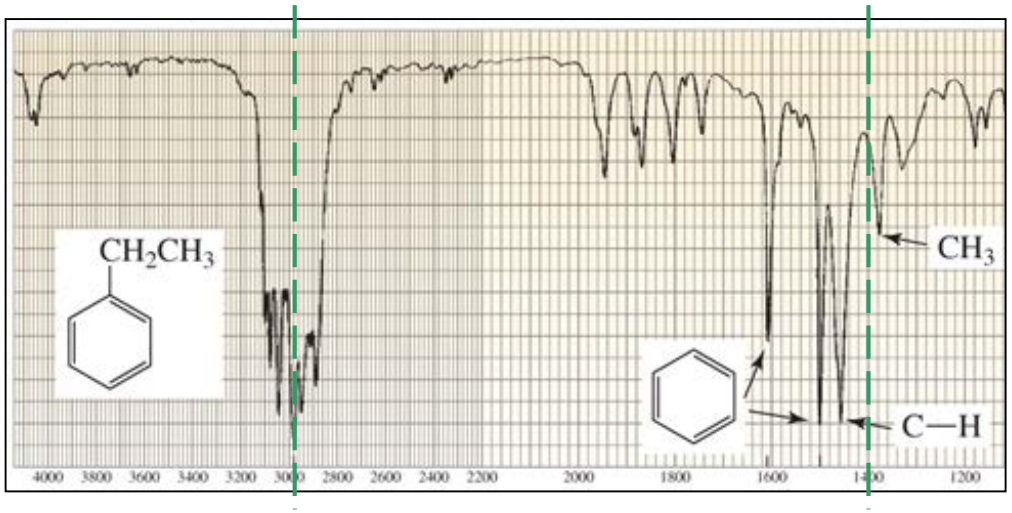
C–H bands

- C–H stretching
  - C(sp)–H > C(sp^2)–H > C(sp^3)–H
    - ≡C–H, =C–H ~ left of 3000 cm^{-1}
    - –C–H ~ right of 3000 cm^{-1}
  - aliphatic C=C vs aromatic C=C
    - one vs two peak(s)

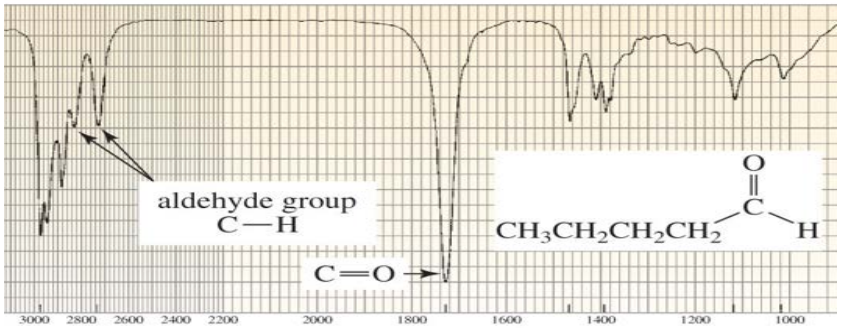
C≡C—H	~3300
C=C—H	3100–3020
C—C—H	2960–2850
	~2820 and ~2720

C=C	1680–1600
C=N	1650–1550
	~1600 and ~1500–1430

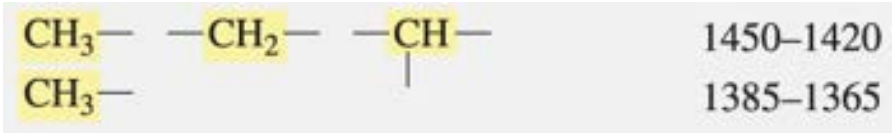


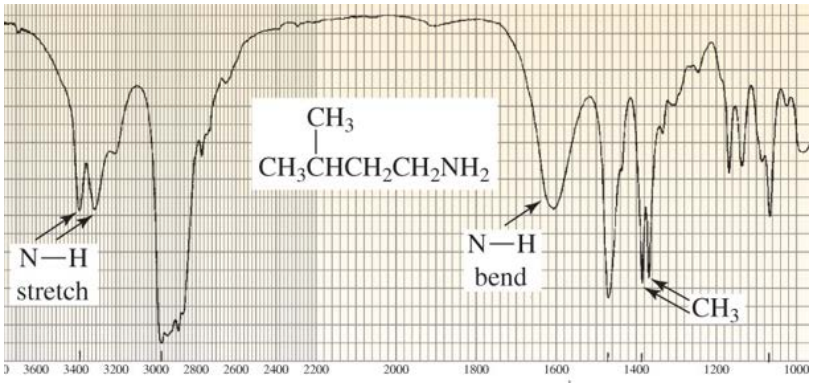


- C–H stretching (cont'd)
  - aldehyde C–H stretching
    - 2 peaks (sym + asym)
    - around 2800 cm^{-1}

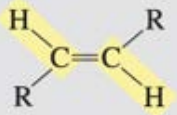
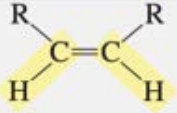
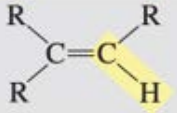
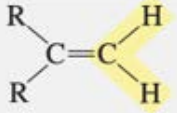
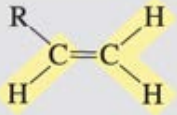


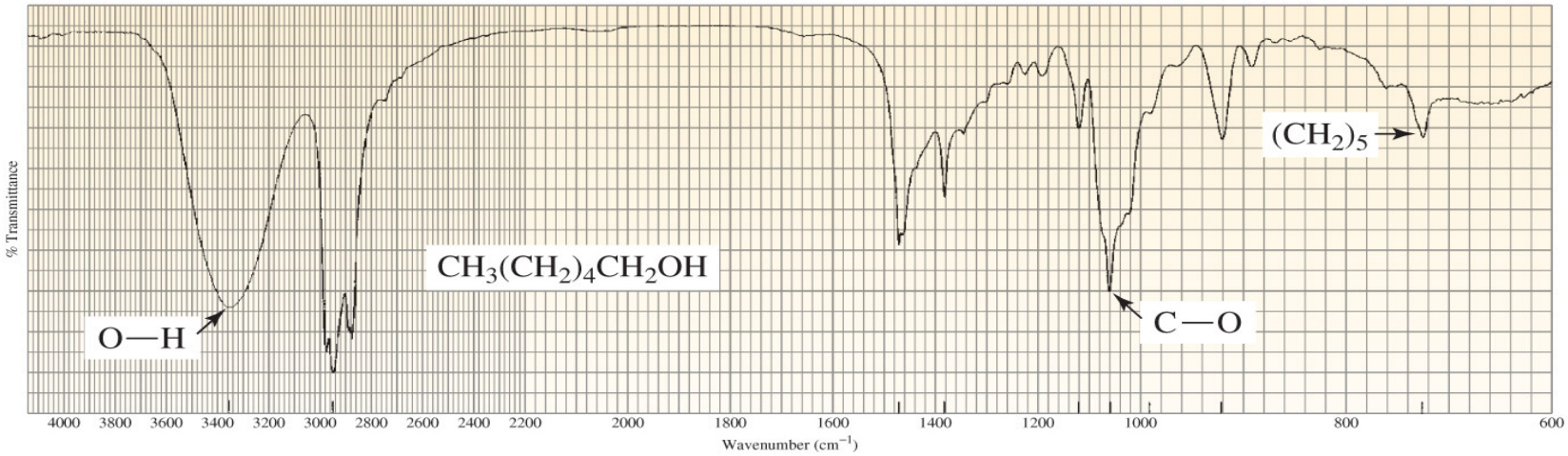
- C–H bending
  - C(sp^3)–H
    - CH, CH_2 ~ only left of 1400 cm^{-1}
    - CH_3 ~ left and right of 1400 cm^{-1}
  - N–H bending at 1600 cm^{-1}
    - broader and stronger
    - with stretching at 3400 cm^{-1}





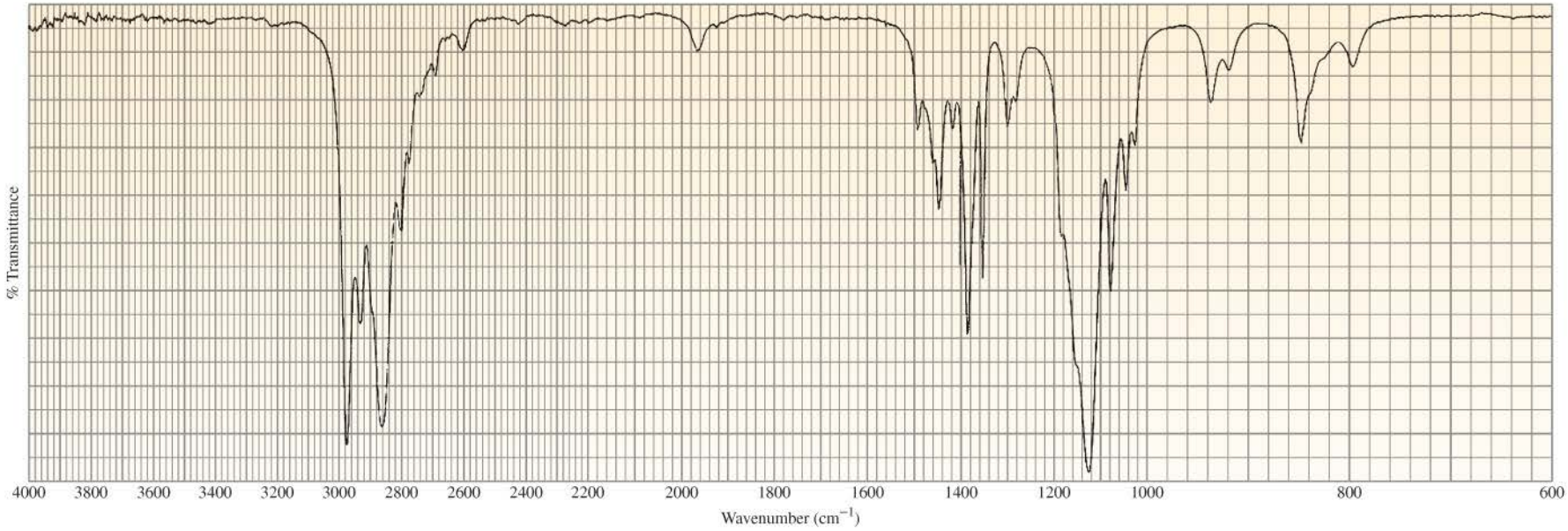
- C–H bending (cont'd)
  - C(sp^2)-H
    - 1000 - 600 cm^{-1}
    - depending on # of substitution and configuration
    - shift by substituents
  - $(CH_2)_n$ with n > 4 at 720 cm^{-1}

CH_3- $-CH_2-$ $-CH-$ CH_3-		1450–1420 1385–1365
	trans	980–960
	cis	730–675
	trisubstituted	840–800
	terminal alkene (disubstituted)	890
	terminal alkene (monosubstituted)	990 and 910



Absence of bands

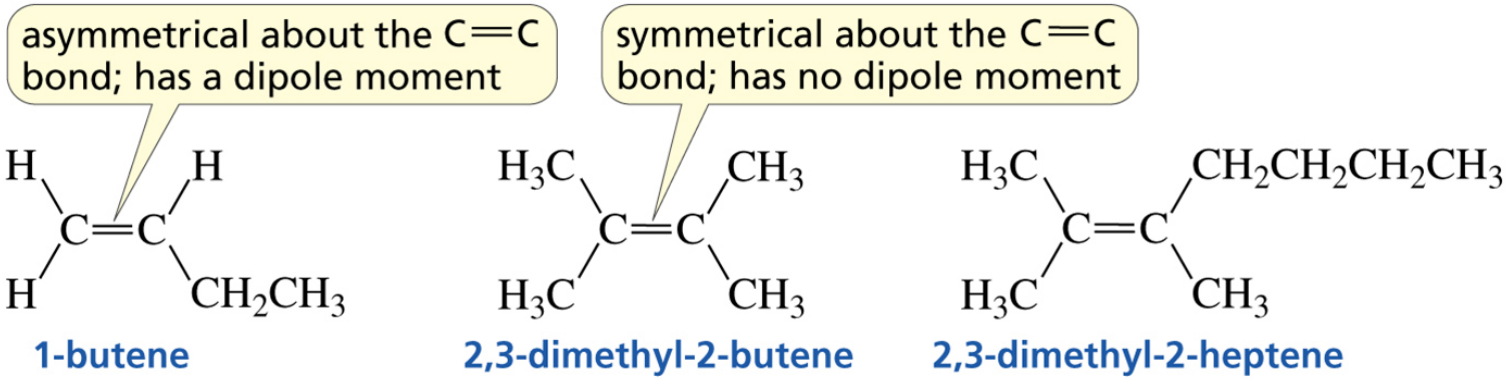
- can be useful
- eg



  - 1100 → C-O stretching
  - no band at 3300 (OH), > 3000 (C=C), 1700 (C=O)
  - (aliphatic) ether

IR-inactive vibration

- IR-active vibration only with change in dipole moment.



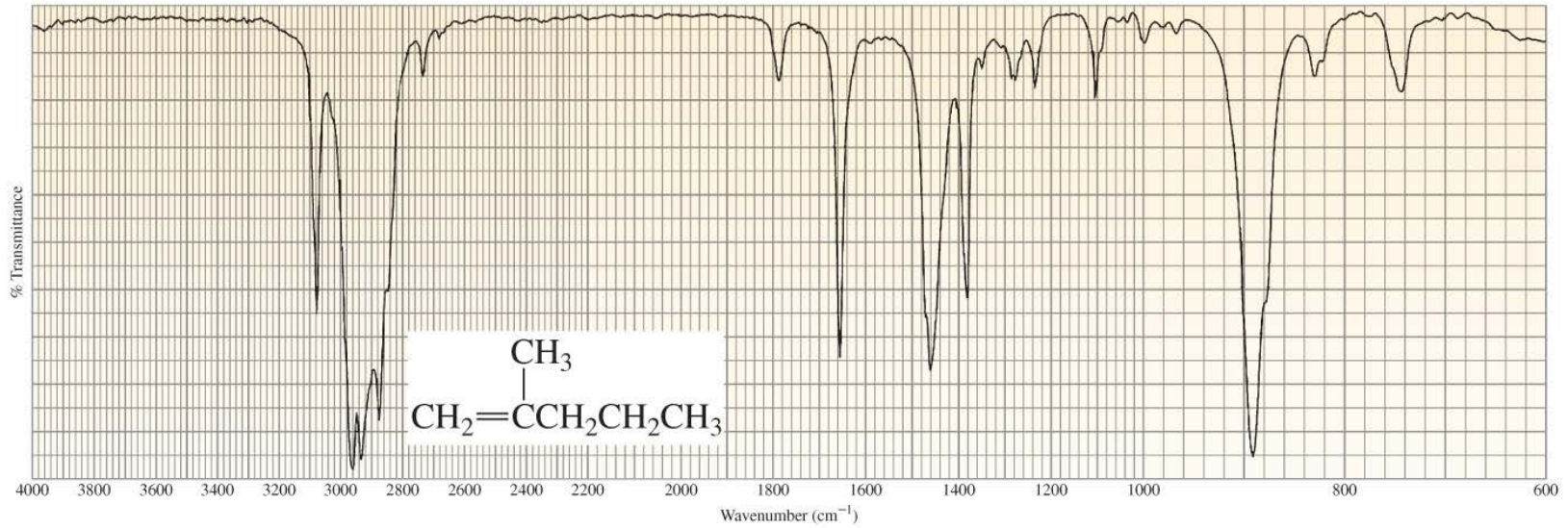
IR-active

IR-inactive
no band

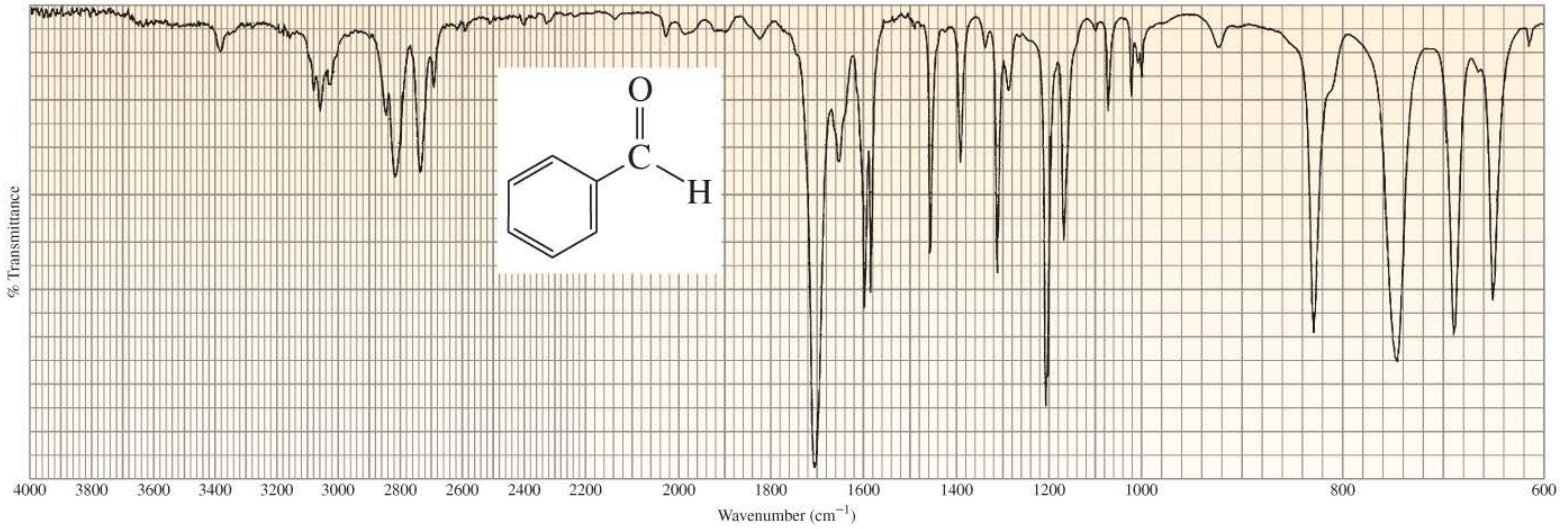
very small dipole moment
very weak band

Interpretation examples

- ‘IR not to inform what it is, but to fit the structure told.’
- Comp’d 1
  - no O-H, N-H, or C=O
  - left and right of 3000 → =C-H and –C-H
  - 1600 without 1500 → aliphatic C=C
  - left and right of 1400 → CH_3
  - 890 → disubstituted terminal alkene



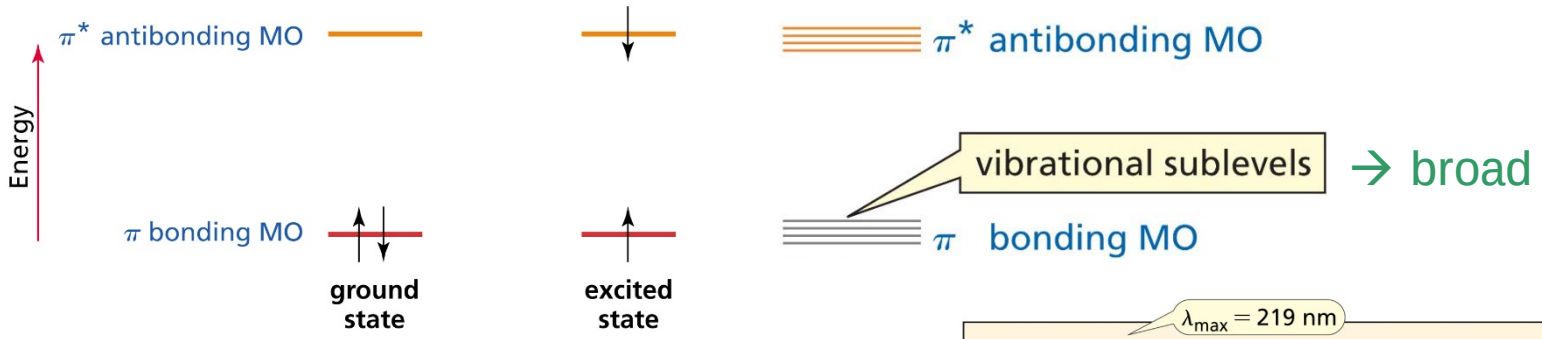
- Comp'd 2
  - no O-H or N-H, but has C=O (1700)
  - only at left of 3000 → ?
  - 1600 and 1450 → ?
  - two peaks at around 2800 → aldehyde
- 'not surprising to find that it is benzaldehyde'



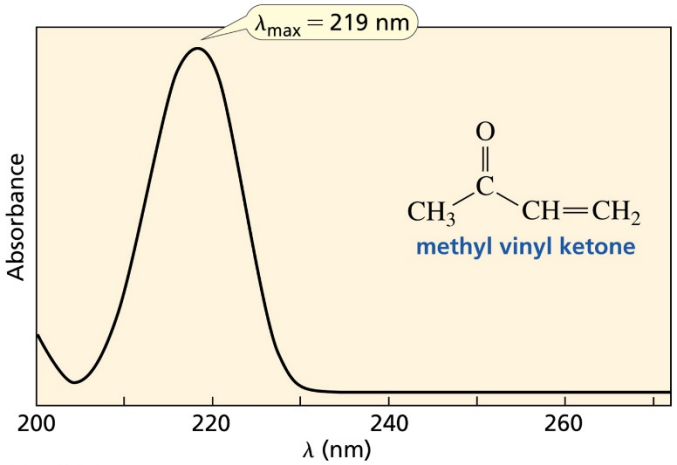
- Do comp'd 3, 4, 5.

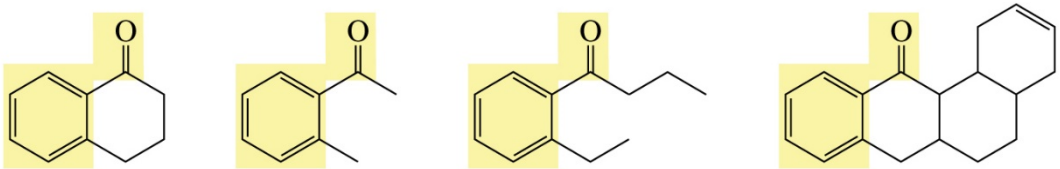
Ultraviolet/Visible spectroscopy

- Energy of UV (180–400) and visible light (400–780 nm) → electronic transition from π to π*
  - Only comp'ds with = are UV/Vis-active.



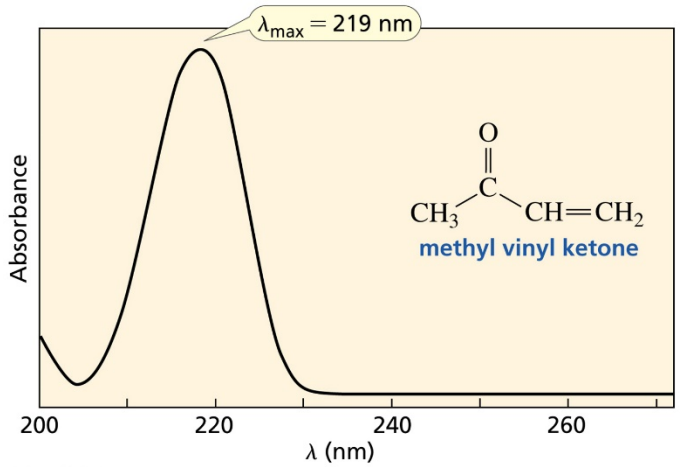
  - broad absorption band with a λ_{max}
  - due to the chromophore **[發色團]**
    - C=O? C=C?



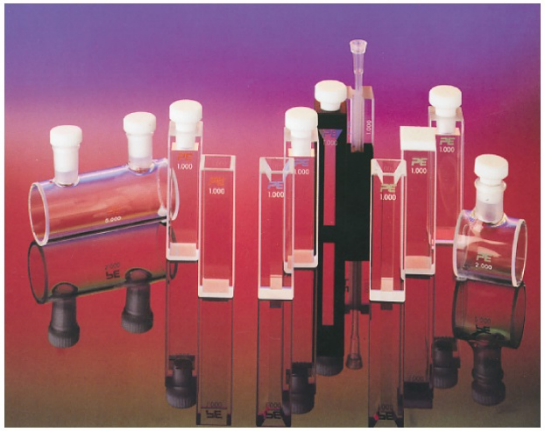


Absorbance: Beer-Lambert law

- $A = c\, l\, \varepsilon$
  - A = absorbance
  - c = concentration [M]
  - l = length of sample cell [cm]
  - ε = molar absorptivity [$M^{-1}cm^{-1}$]
    = extinction coefficient

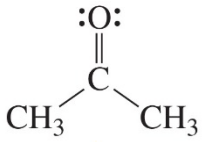


- for MVK,
  λ_{max} = 219 nm (ε_{max} = 14000, hexane)



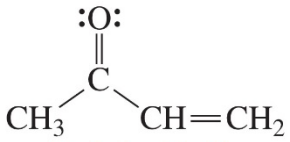
λ_{max}

- conjugation



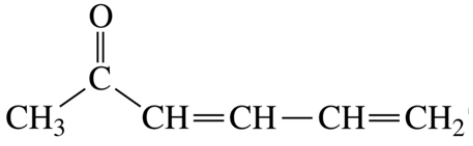
acetone

λ_{max} = 195 nm



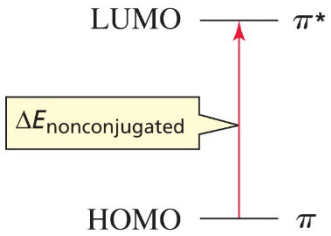
methyl vinyl ketone

λ_{max} = 219 nm

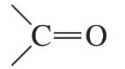


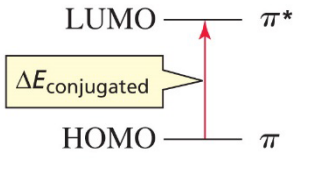
3,5-hexadien-2-one

λ_{max} = 249 nm



nonconjugated π electrons





conjugated π electrons

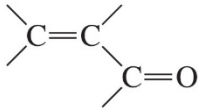


Table 14.6 Values of λ_{max} and ε for Ethylene and Conjugated Polyenes

Compound	λ_{max} (nm)	ε (M^{-1} cm^{-1})
$H_2C=CH_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

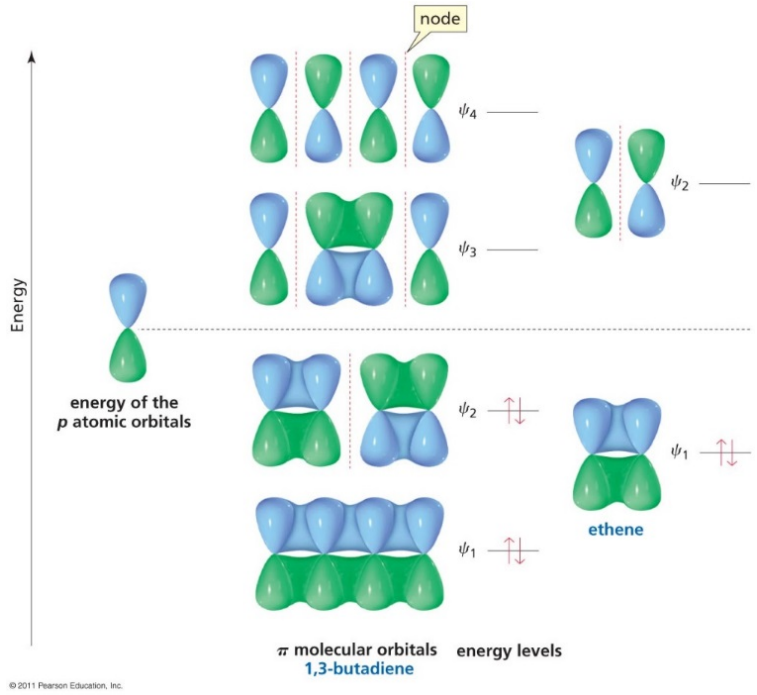
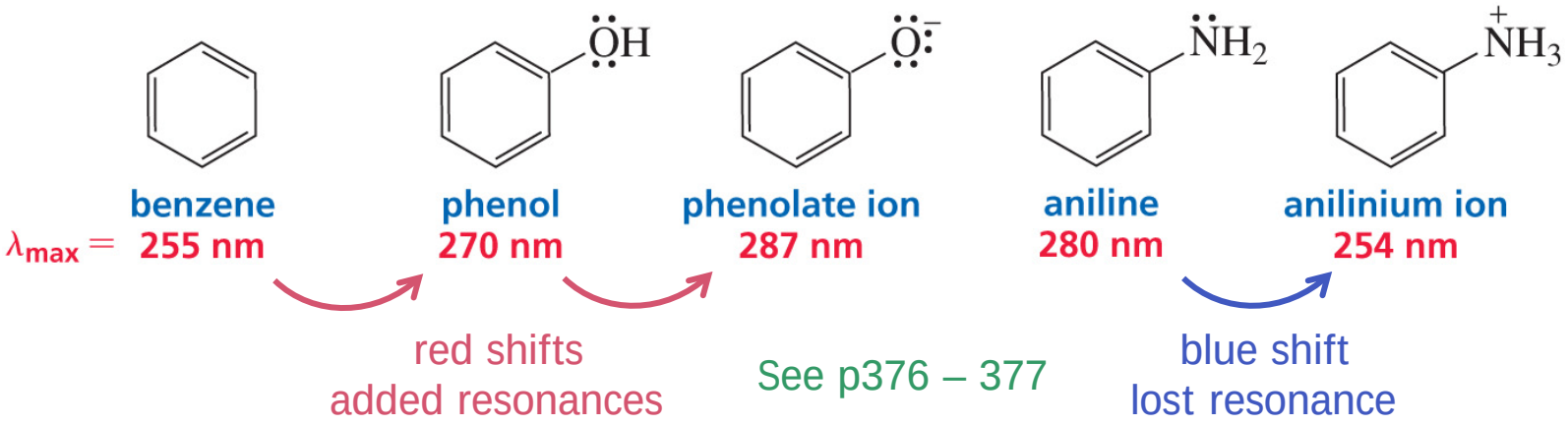
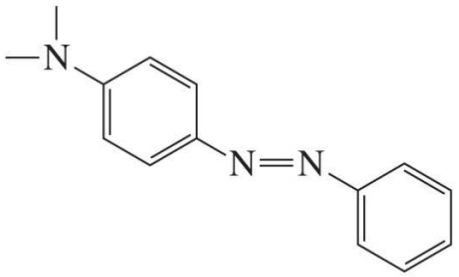


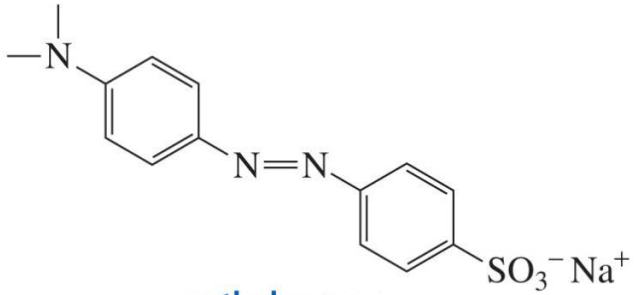
Fig 8.11 p373

- auxochrome [助色團]
  - alters λ_{max} and A





butter yellow
an azobenzene



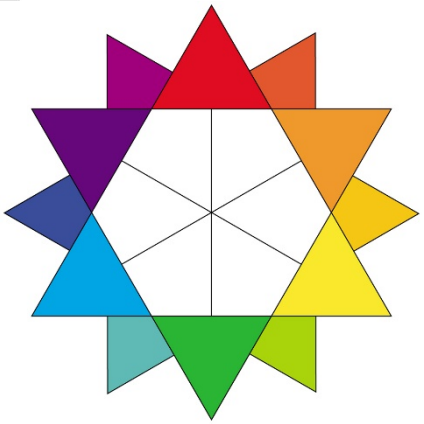
methyl orange
an azobenzene

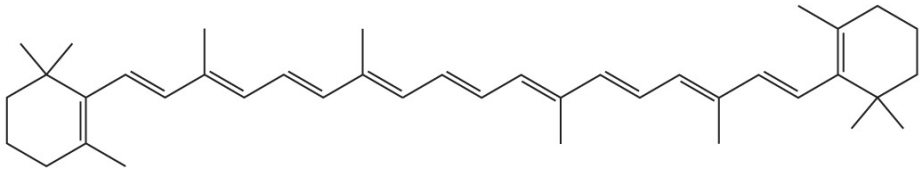
Color

- many conj = → absorb Vis → color
- 'The λ not absorbed produces the color.'

Table 14.7 Dependence of the Color Observed on the Wavelength of Light Absorbed

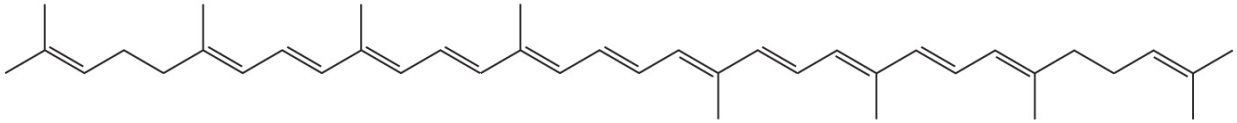
Wavelengths absorbed (nm)	Color absorbed	Color observed
380–460	blue-violet	yellow
380–500	blue	orange
440–560	blue-green	red
480–610	green	purple
540–650	orange	blue
380–420 and 610–700	purple	green





β-carotene
λ_{max} = 455 nm

absorbs blue → color orange

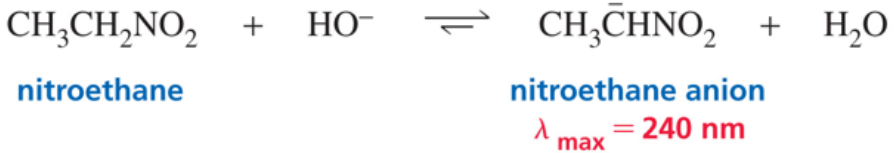


lycopene
λ_{max} = 474 nm

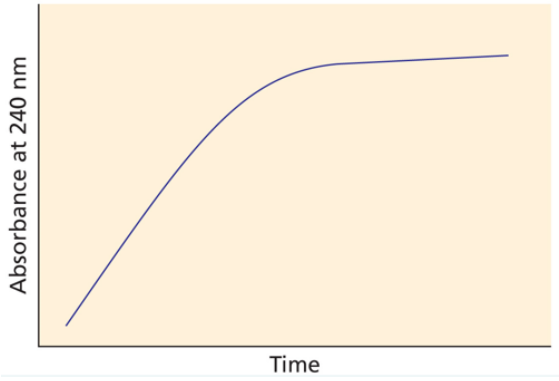
absorbs blue-green → color red

Uses of UV/Vis

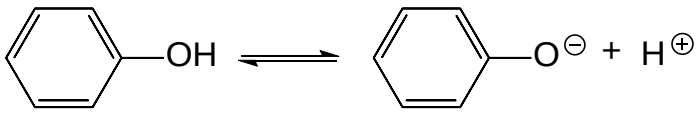
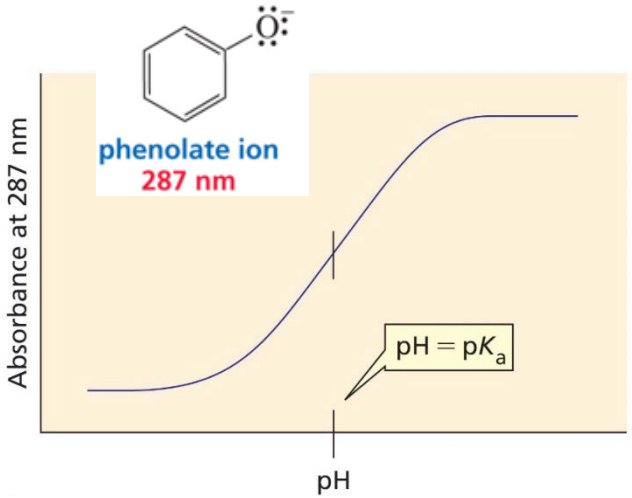
- not very useful for structure determination
  - 'No absorption at 200–800 nm means no chromophore.'
- useful for (quantitative analysis of)
  - reaction rate ~ monitoring reaction



the only UV-active



- pK_a the Henderson–Hasselbalch equation

$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$

p106