Today

Sections 13.10 - 13.18
Infrared Spectroscopy

Second Class from Today

Section 14.10 - 17
Splitting and Multiplicity

Next Class

Section 14.1 - 14.9
Introduction to Nuclear Magnetic Resonance,
Shielding, Chemical Shift, and Integration

Third Class from Today

Section 14.20
^{13}C {^1H} NMR

Practice Determining Structure Based on
Spectroscopic Data

Strategies for using IR spectroscopy to identify functional groups.

Examine formula and look for possible functional groups in IR spectrum
    use 2n+2 rule to rule π bonds in or out
    Closely examine positions of C–H peaks for additional information
        sp^2 vs sp^3 C atoms
        presence or absence of CH$_3$ groups
    Position of C=O peaks ✐
        ketone vs aldehyde vs ester vs carboxylic acid
    Rule benzene rings in or out using degree of unsaturation (2n+2 rule)

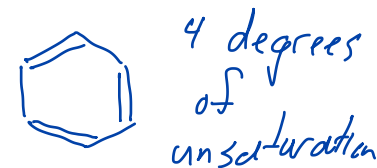If n C atoms then you need 2n+2 H atoms to make an acyclic alkane

C$_4$H$_8$?   2·4+2 = 10 H needed
                    - 8 H actual
                    _____
                    2 H "missing"
                    ___
                    2
                        → one degree
                          of
                          unsaturation

4 degrees of unsaturation

Examine IR spectrum for obvious functional groups
    easily recognizable peaks   O-H, C=O,
    ≡C-H

Double check consistency: for example
    do not claim a C=O peak is an ester if the molecule has only 1 O atom
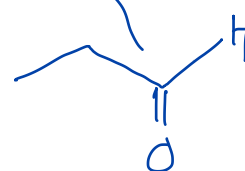   do not claim nitrile if there are no N atoms
    look for confirmation in assignments:
        aldehyde, find both C=O and C(O)-H peaks
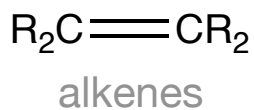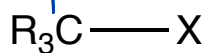   ester C=O and C(O)-O-R peaks

R-C(O)-O-R   R≠H

alkenes
$R_2C{=}CR_2$

alkynes
$R{-}C{\equiv}C{-}R$
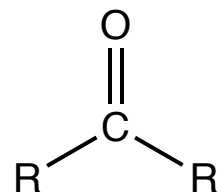
tough to find in fingerprint region
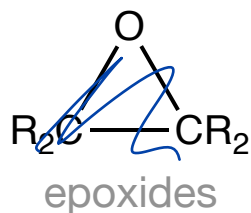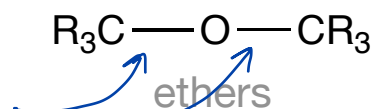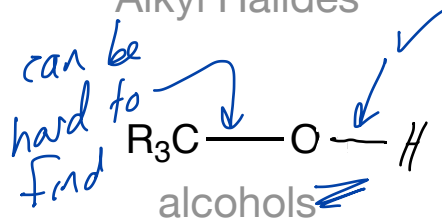
not as useful peak in fingerprint region
$R_3C{-}X$

X = Cl, Br, I
Alkyl Halides

can be hard to find
$R_3C{-}O{-}H$
alcohols

$R_3C{-}O{-}CR_3$
ethers

epoxides

and more…

$R{-}C{\equiv}N$

ketones (R, R' ≠ H) and aldehydes (R or R' = H)

amides
$RC({=}O)NR_2$

esters (R ≠ H)
$RC({=}O)OR$

carboxylic acids
$RC({=}O)OH$

anhydrides

acid chlorides
$RC({=}O)Cl$

nitriles
RCN
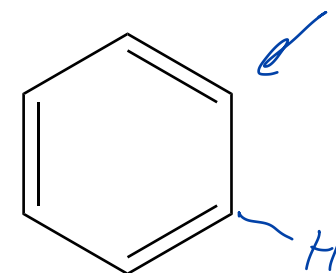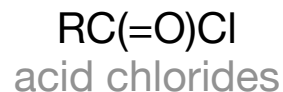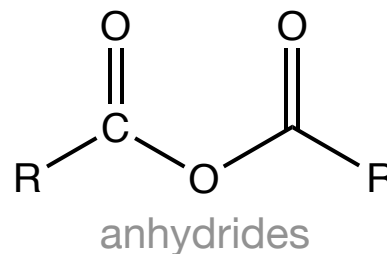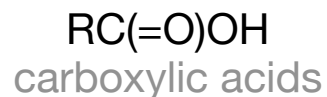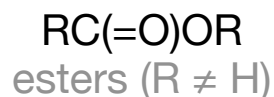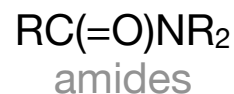
aromatics

and more…

H

IR can distinguish between molecules base on functional group

Wavelength (µm) axis: 2.5 2.6 2.7 2.8 2.9 3 3.5 4 4.5 5 5.5 6 7 8 9 10 11 12 13 14 15 16

Wavenumber (cm^{-1}) axis: 4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1700 1600 1400 1200 1000 800 600

Y-axis: % Transmittance

Annotations on spectrum:
- ≡C-H
- sp^3 C-H
- < 3000 cm^{-1}
- C=O ketone?
- 1720

Structures and notes:
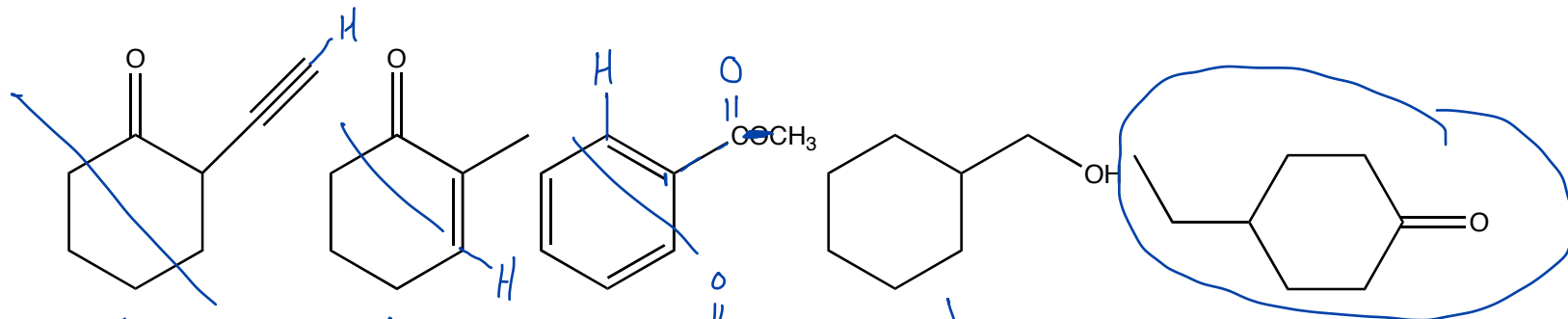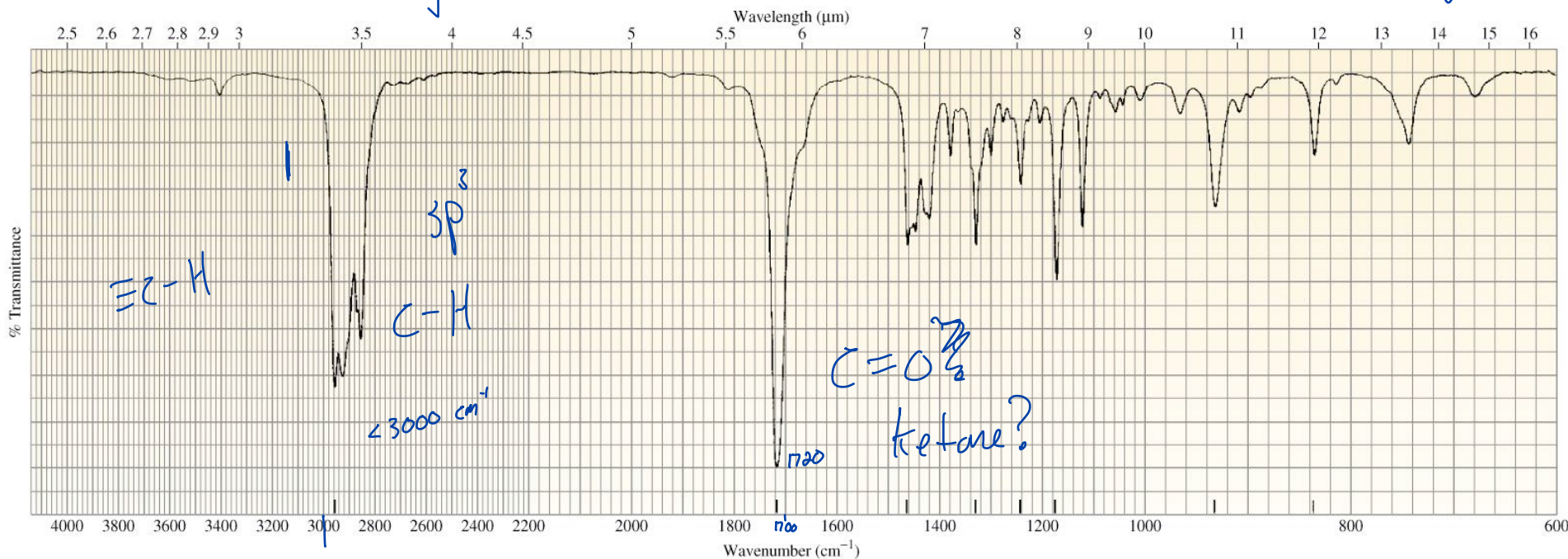
Structure 1 (cyclohexanone with alkyne):
carbonyl ✓
ruled out because
≡C-H should make
a peak at 3300 cm^{-1}

Structure 2 (methyl cyclohexenone):
carbonyl ✓
but too high
in E
no sp^2
C-H ir
spectrum

Structure 3 (benzaldehyde with COCH₃):
$\phi - \overset{O}{\overset{\|}{C}} - CH_3$
carbonyl ✓
but to high
in E
no Ph-H
no Ph C=C

$\bigcirc\!\!\!| = Ph - H \qquad Ph \quad C=C$

Structure 4 (cyclohexylmethanol):
no OH
stretch

Structure 5 (4-ethylcyclohexanone, circled):
C=O ✓
only sp^3 C-H
present ✓

IR data from our textbook: "Organic Chemistry" 8th ed, Bruice. Pearson (2016)

Wavelength (µm)

% Transmittance

Wavenumber (cm^{-1})

Handwritten annotations on spectrum:
- not OH
- ?
- ≡C–H
- sp^3 C–H
- ?
- C≡C
- No C=O present

$CH_3CH_2CH_2C\equiv CCH_3$
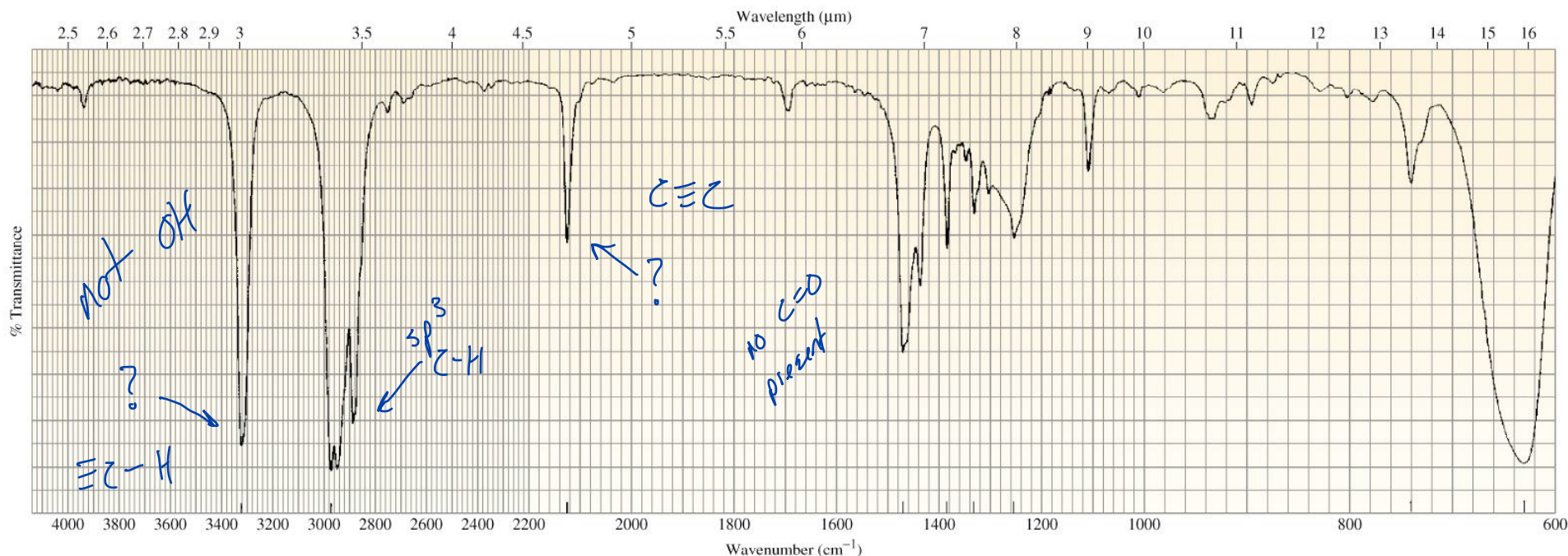
C≡C triple bond

sp^3 C–H's

can't account

for 3300 cm^{-1}

$CH_3CH_2CH_2CH_2C\equiv CH$
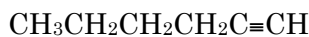
(C≡C triple bond
≡C–H
sp^3 C–H's)

spectrum

has C≡C
+
≡C–H

$CH_3CH_2CH_2CH_2CH_2OH$ *(crossed out)*

sp^3 C–H's

CH_2OH is an
alcohol

No OH

in spectrum

can't account for
peak at 2125 cm^{-1}

$CH_3CH_2CH_2CH_2CO_2H$ *(crossed out)*

sp^3 CH's

? what's a

R–CO$_2$H ?

R–C(–H)(=O)(O) *(structure crossed out with X)*

R–$\overset{O}{\overset{||}{C}}$–O–H

carboxylic acid

IR Spectrum with annotations

$C(O)-H$

c-H bonds bending

Wavelength (µm)

2.5 2.6 2.7 2.8 2.9 3   3.5   4   4.5   5   5.5   6   7   8   9   10   11   12   13   14   15   16

% Transmittance

< 3000 cm⁻¹

position of C=O peak is very sensitive to it's neighbors

1745 cm⁻¹

1700

1195 cm⁻¹

4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600

Wavenumber (cm⁻¹)

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carboxylic acid

ester

aldehyde

ketone

$CH_3CH_2CO_2H$ $CH_3CH_2CO_2CH_2CH_3$ CH_3CH_2CHO $CH_3CH_2COCH_3$

$$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O-H$$

$$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_2CH_3$$

$$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

$$CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

carbonyl ✓   carbonyl ✓   carbonyl ✓   carbonyl ✓

evidence against — can't find OH in IR

carbonyl peak is reasonable for an ester (a bit high)
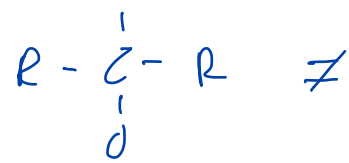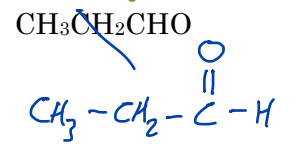
carbonyl is higher than expected — evidence against
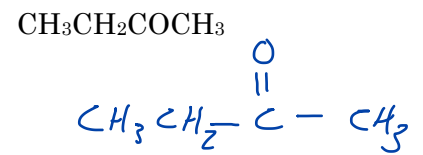
carbonyl peak is higher than expected for — evidence against

evidence against — carbonyl peak is too high for CO_2H

c-o peak at 1195

no C(O)-H peak at 2700 cm⁻¹ — evidence against

a ketone can't account for peak of 1195 cm⁻¹ — evidence against

$$R\,CO_2R \neq R-\overset{\displaystyle}{\underset{\displaystyle O}{\overset{\|}{C}}}-R \neq R\,C-O-O-R$$