Learning Guide for Chapter 3 - Infrared Spectroscopy

I. Introduction to spectroscopy

Characterizing compounds

What does it mean to characterize a compound?

figure out the identity and structure of a compound

What are some examples of when you would need to do this?

confirming the identity of a compound you've made

isolating a useful compound from nature

identifying a pollutant

What are some physical properties of organic compounds, and how can they be used in characterization?

mp, bp, solubility, color, odor, density -only useful to confirm a hypothesis

How are chemical tests used to characterize organic compounds?

test for whether a functional group is present

bromine test - add Br_2 to a compound, if it has a C=C the brown color disappears

Tollen's test - add Ag^+ ions to a compound, if it has an aldehyde, Ag is formed

What does spectroscopy use to characterize a compound?

light

What are the most common kinds of spectroscopy used in organic chemistry, and what kinds of information do they give?

* IR (infrared) - gives information about bonds, used to determine functional groups
* NMR (nuclear magnetic resonance) - gives information about atoms, used to determine structure

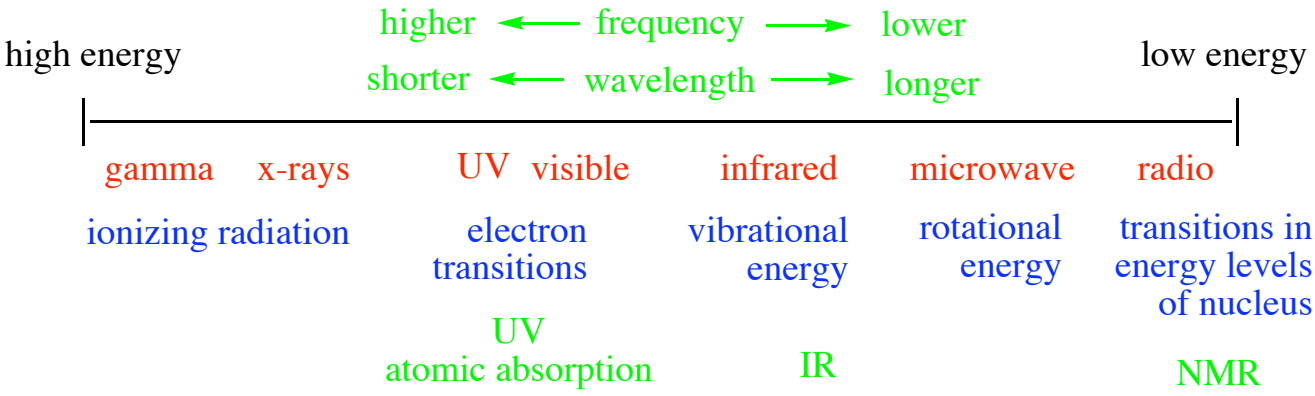
UV (ultraviolet) - gives information about pi bonds

MS (mass spectroscopy) - gives MW, information about structure

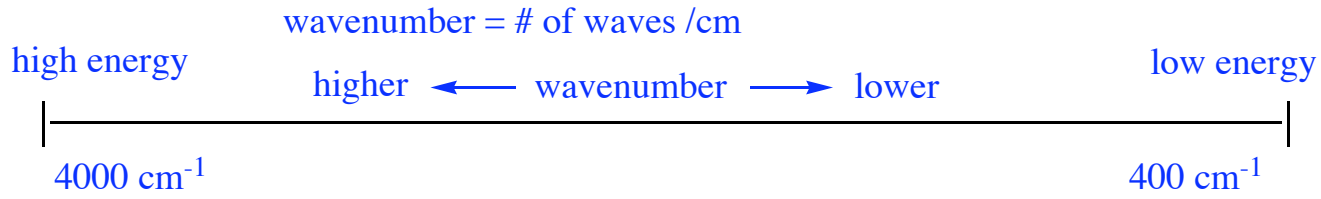
* we will focus on these

The Electromagnetic Spectrum

What kinds of light are present in the electromagnetic spectrum? How do they affect atoms and molecules?

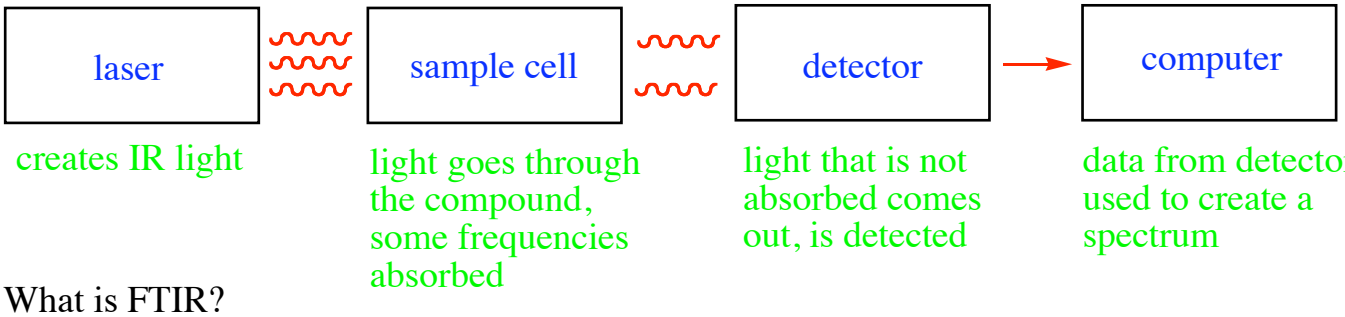


What unit of frequency is used in IR spectroscopy? What is the range of frequencies used in IR spectroscopy?



The IR Spectrometer and and IR Spectrum

What are the essential components of an IR spectrometer?



What is FTIR?

Fourier transform IR - uses all frequencies at once, sorts it out mathematically

only kind currently used

How can you take the IR of a liquid compound?

thin film, neat - a few drops on a salt plate or crystal

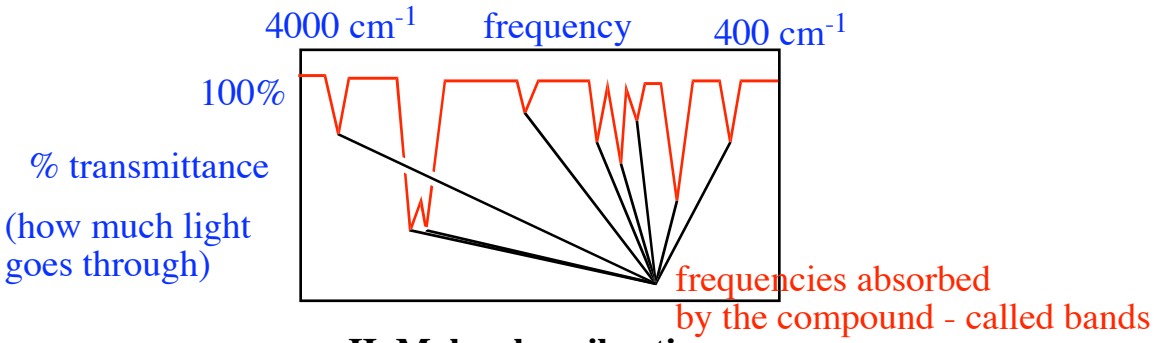
How can you take an IR of a solid compound?

melt - heat the compound on a salt plate

nujol mull - make a paste with a hydrocarbon oil

KBr pellet - grind compound with KBr, press it into a transparent pellet

What does an IR spectrum look like?



II. Molecular vibrations

Types of vibrations

Why do molecules absorb infrared light?

frequency of the light matches the frequency of a bond vibration in the molecule

What are the two types of vibrations that molecules can undergo?

stretching - bond length changes

bending - bond angles changes

What does a stretching vibration look like in an HCl molecule?

What does a symmtrical and unsymmetrical vibration look like in a water molecule?

symmetrical unsymmetrical

Which of these is the molecule actually doing? both - at different frequencies

Which of the following represent the scissor, rocking, wagging, and twisting vibrations of a CH_2 group?

scissor rocking

wagging twisting

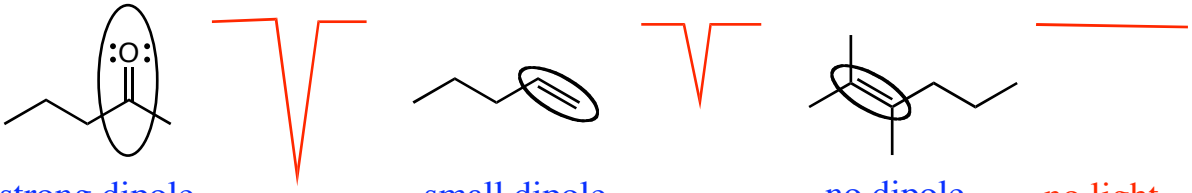
Which vibrations in a molecule will we be concerned with?

the ones that give us useful information (there will be many that won't!)

Factors which affect a band

Predict which of the following vibrations will absorb more light, and explain why.

1) strength of dipole

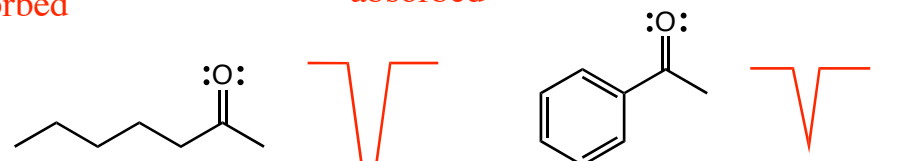


strong dipole — lots of light absorbed

small dipole — some light absorbed

no dipole — no light absorbed

2) number of bonds



14 C-H bonds — lots of light absorbed

8 C-H bonds — some light absorbed

Predict which of the following bands will have the higher frequency, and explain why.

1) size of atoms

C–H 3000 cm^{-1} — lighter atom, higher frequency — faster

C–C 1200 cm^{-1} — heavier atom, lower frequency — slower

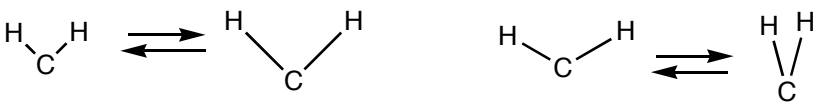
2) bond order

C≡C 2200 cm^{-1} — triple bond, higher frequency — faster (tight spring)

C=C 1660 cm^{-1}

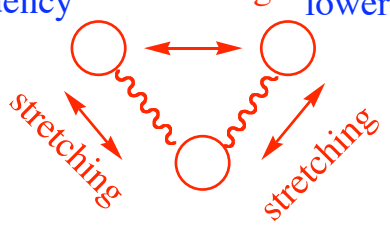
C–C 1200 cm^{-1} — single bond, lower frequency — slower (loose spring)

3) type of vibration



2920 cm^{-1} — stretching vibration, higher frequency

1380 cm^{-1} — bending vibration, lower frequency



Regions of the IR Spectrum

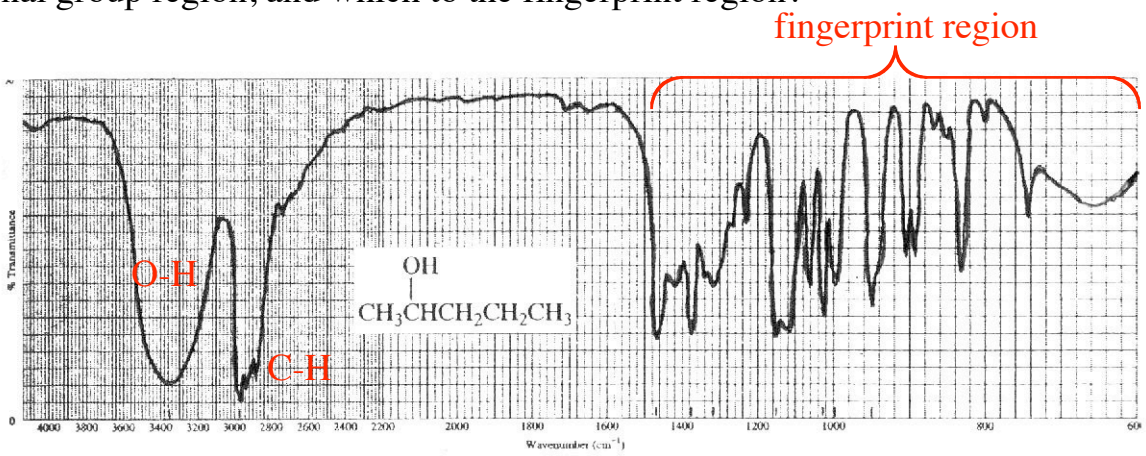
What are the two main regions of the frequency axis?

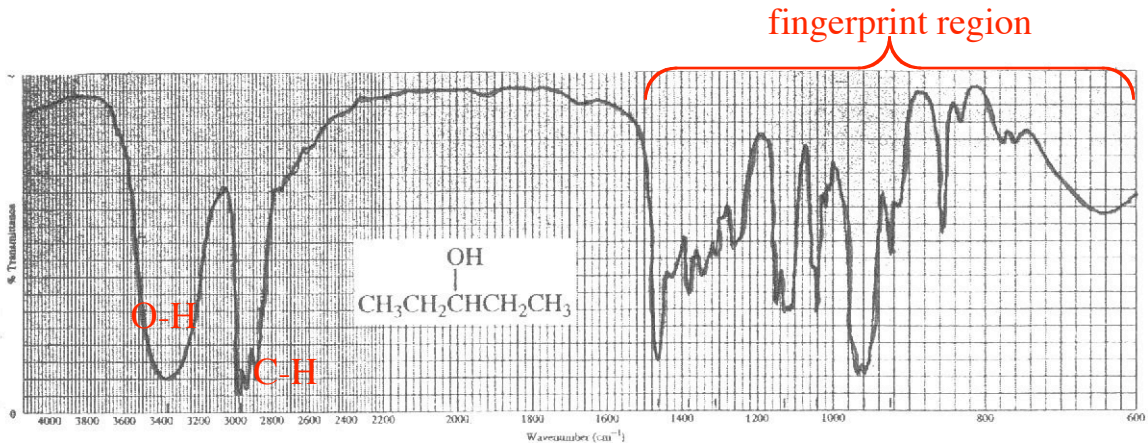
functional group region - bands that are tell you the functional group

fingerprint region - bands that are unique to the compound

4000 - 1300 cm^{-1}	1300 - 400 cm^{-1}
functional group region	fingerprint region

The spectra of two different alcohols are shown below. Which bands belong tot he functional group region, and which to the fingerprint region?





functional group bands
bands are the same

fingerprint bands
bands are different

If you take a spectum of an unknown compound, what can you deduce about it from the spectum?

functional group

What would you need to be able to identify the compound?

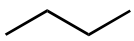
a spectrum of the real compound to match it up to

III. Identifying functional groups

The following bonds absorb IR light at known frequencies. They are useful for deducing the functional groups of compounds.

C–H	C=O	NH_2 bending
C–H on C=C	C≡N	CH_2 bending
C–H on C=O	C–O	C=C bending
C–H on C≡C	O–H	COOH dimer
C=C	O–H on C=O	aromatic overtones
C=C aromatic	N–H	
C≡C	C–X	

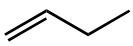
For each of the functional groups below, write down which of these bands it should have. The number of bands you should look for is given in ( ).

<u>alkane</u> (2) 

C–H

CH_2 bending

(most compounds have these)

<u>alkene</u> (5) 

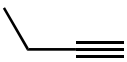
C–H

CH_2 bending

C=C

C–H on C=C

C=C bending

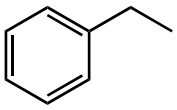
<u>alkyne</u> (4) 

C–H

CH_2 bending

C≡C

C–H on C≡C

<u>aromatic ring</u> (5) 

C–H

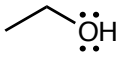
CH_2 bending

C=C aromatic

C–H on C=C

aromatic overtones

(no C=C bending)

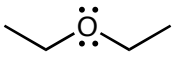
<u>alcohol</u> (4) 

C–H

CH_2 bending

O–H

C–O

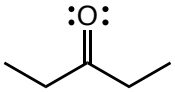
<u>ether</u> (3) 

C–H

CH_2 bending

C–O

ketone (3)



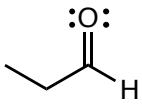
C–H

CH_2 bending

C=O

(no C-H on C=O!)

aldehyde (4)



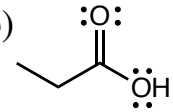
C–H

CH_2 bending

C=O

C–H on C=O

carboxylic acid (6)



C–H

CH_2 bending

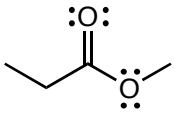
O–H on C=O

C=O

COOH dimer

C–O

ester (4)



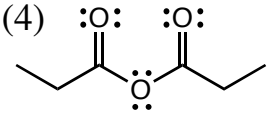
C–H

CH_2 bending

C=O

C–O

anhydride (4)



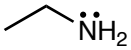
C–H

CH_2 bending

C=O (x 2)

C–O

amine (4)



C–H

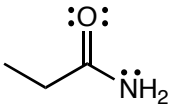
CH_2 bending

N–H

NH_2 bending (if 1°)

(no C-N!)

amide (5)



C–H

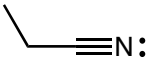
CH_2 bending

N–H

C=O (no C-N!)

NH_2 bending (if 1°)

nitrile (3)

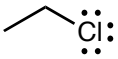


C–H

CH_2 bending

C≡N

alkyl halide (3)



C–H

CH_2 bending

C–X

Which bands would you expect to find in the following ranges?

3400-3200 cm^{-1}	3100-2700 cm^{-1}	2250-2100 cm^{-1}	2000-1600 cm^{-1}	1300-400 cm^{-1}
O–H	C–H	C≡C	C=C	(fingerprint)
N–H	C–H on C=C		C=O	C–O
C–H on C≡C	C–H on C=O	C≡N	NH_2 bending	C–X
	O–H on C=O		aromatic overtones	C=C bending
	COOH dimer			

Using the charts on the previous pages, identify the important bands for each functional group.

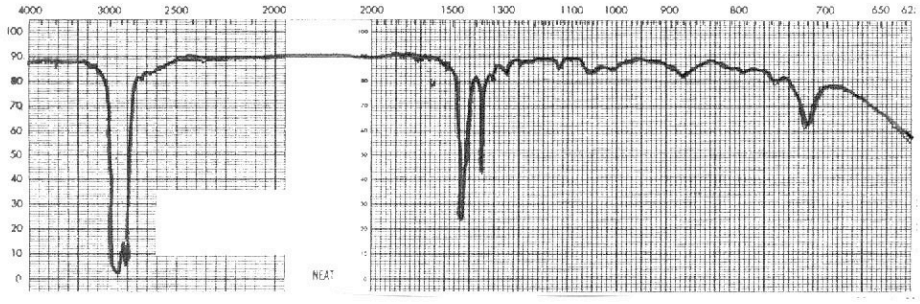
Alkane

hexane

expected bands:

C-H

CH_2 bending



C–H

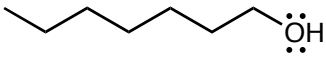
3000-2850 cm^{-1}

CH_2 bending

1460, 1380 cm^{-1}

useful reference points
most compounds contain them

Alcohol

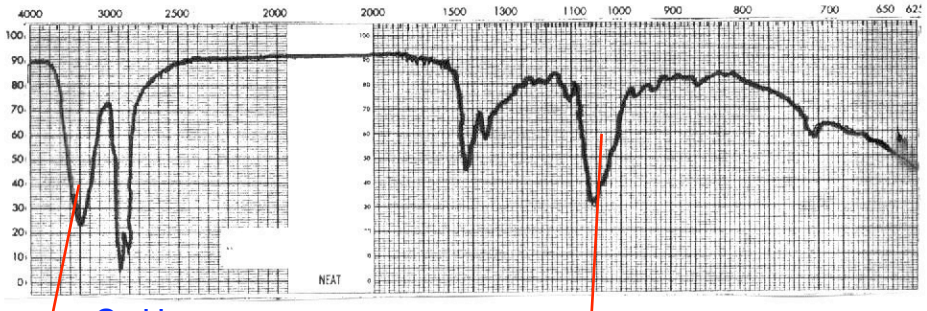


1-heptanol

expected bands:

O-H

C-O



C–H

CH_2 bending

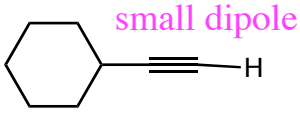
O–H

3400-3200 cm^{-1}
(broad, round)
main band to look for

C–O

1300-1000 cm^{-1}
(must be large!)
confirmation band

Alkyne



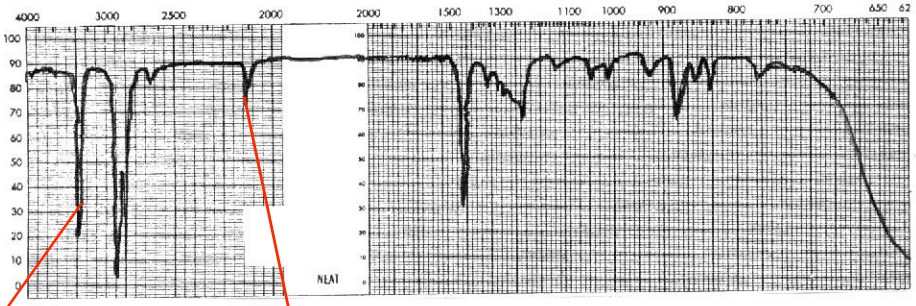
small dipole

cyclohexylacetylene

expected bands:

C-H on C---C

C---C



C–H

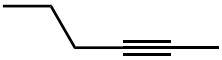
CH_2 bending

C≡C

2200-2100 cm^{-1}
*internal alkynes only

C–H on C≡C

~ 3300 cm^{-1}



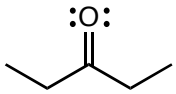
no dipole!

no C–H on C≡C

no C≡C (no dipole)

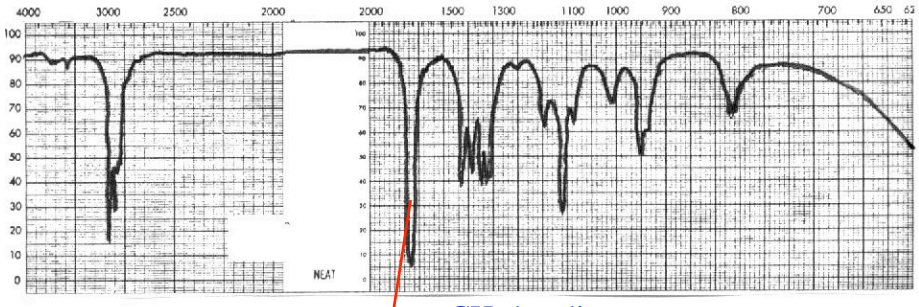
What would it look like? alkane

Ketone



3-pentanone

expected bands:
C=O



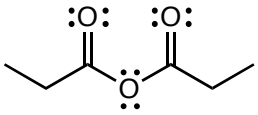
C–H

CH_2 bending

C=O

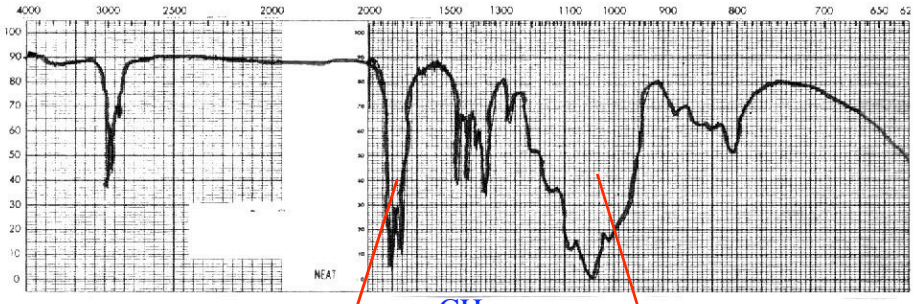
1800-1650 cm^{-1}

Anhydride



propanoic anhydride

expected bands:
C=O (two)
C-O



C–H

C=O

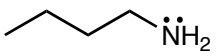
1800-1650 cm^{-1}
(two prominent bands)

CH_2 bending

C–O

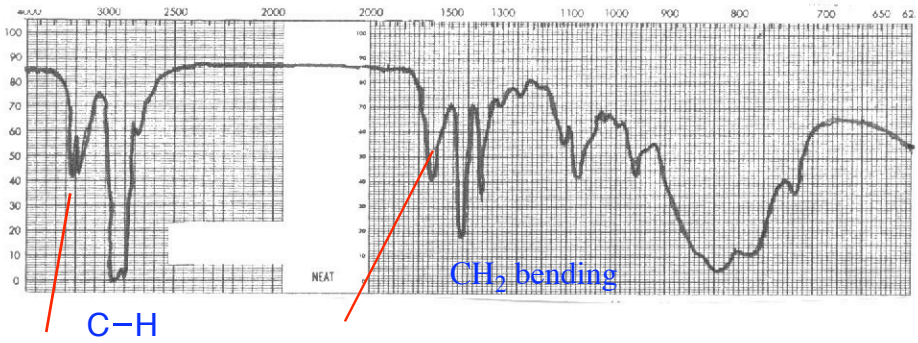
1300-1000 cm^{-1}
only one, very large

Amine



butyl amine
1° amine

expected bands:
N-H
NH_2 bending



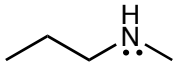
C–H

CH_2 bending

N–H

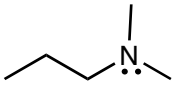
3400-3200 cm^{-1}
(broad)

NH_2 bending
~1600 cm^{-1}
(often a triangular)
*only if 1°



2° amine

only one N-H band
no NH_2 bending



3° amine

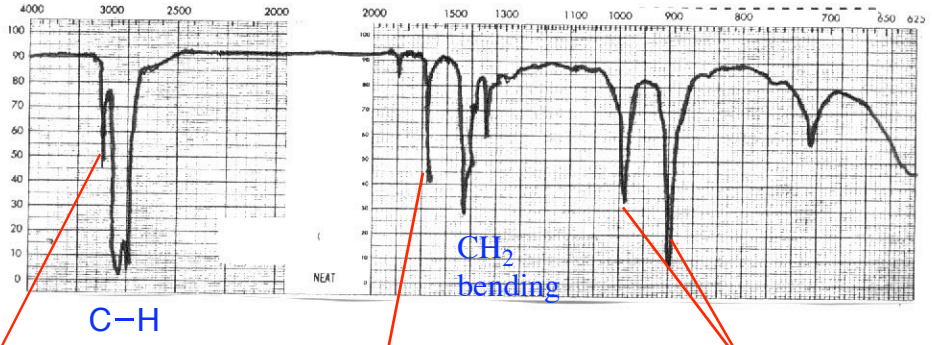
no N-H bands
no NH_2 bending
(like an alkane!)

Alkene

1-octene

expected bands:

C-H on C=C
C=C
C=C bending

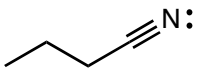


C–H on C=C
3100-3000 cm^{-1}

C=C
1680-1620 cm^{-1}

C=C
bending
960-730 cm^{-1}
(confirmation only)

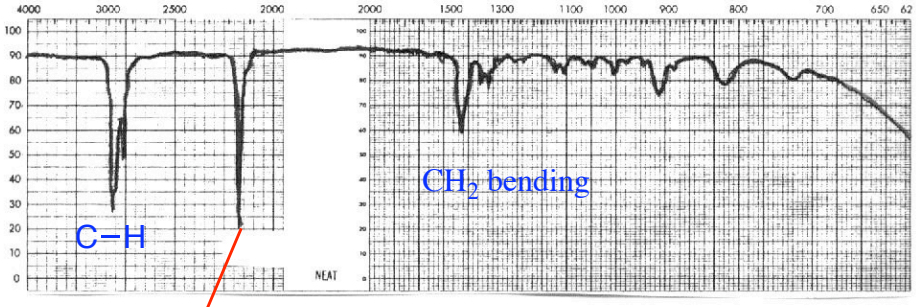
Nitrile



butanenitrile

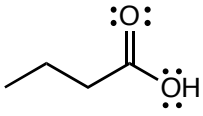
expected bands:

C---N



C≡N
2260-2200 cm^{-1}

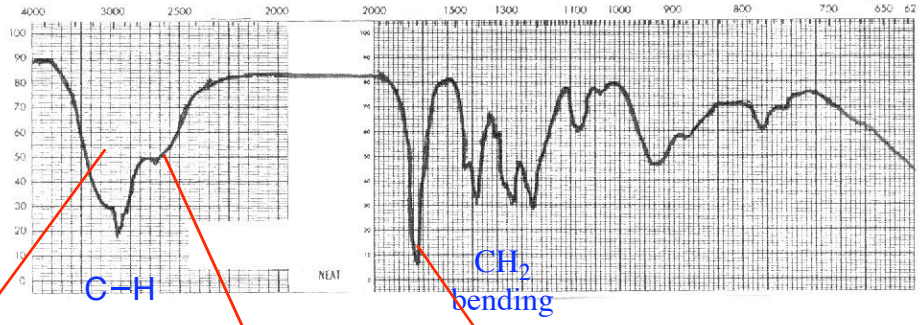
Carboxylic acid



butanoic acid

expected bands:

O-H on C=O
C=O
COOH dimer
C-O



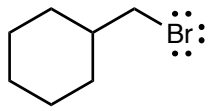
O–H on C=O
3400-2400 cm^{-1}
very broad
overlaps C-H stretching

COOH dimer
2700 cm^{-1}
(sometimes two)

C=O
1800-1650 cm^{-1}

C-O
1300-1000 cm^{-1}
(not always visible)

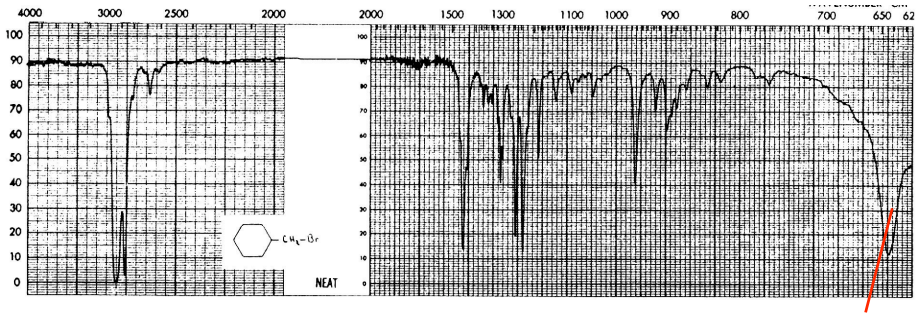
Alkyl halide



bromomethyl cyclohexane

expected bands:

C-X



C–H

CH_2 bending

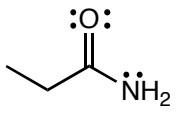
C–X

C-Br 690-515 cm-1

C-Cl 850-550 cm-1

often hard to distinguish (must be large!)

Amide



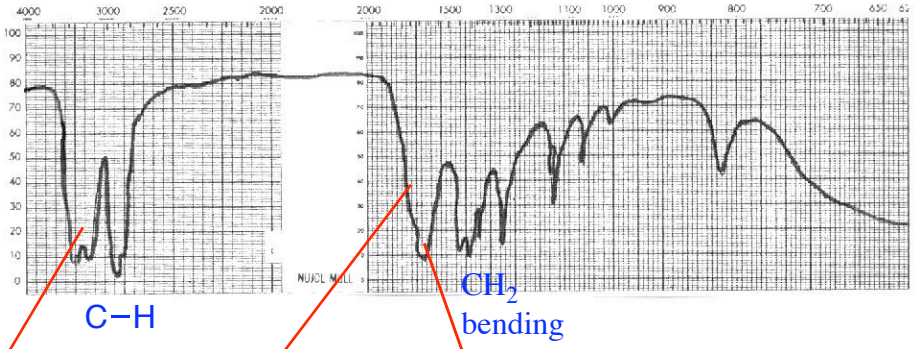
N-methylpropanamide

expected bands:

N-H

C=O

NH_2 bending



C–H

CH_2 bending

N–H

3400-3200 cm^{-1} (broad)

NH_2 bending ~1600 cm-1 (broad) *only if 1o

C=O

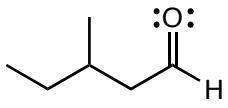
1800-1650 cm^{-1}

1º - NH_2 - 2 N-H bands

2º - NH - 1 N-H band

3º - N - no N-H bands

Aldehyde

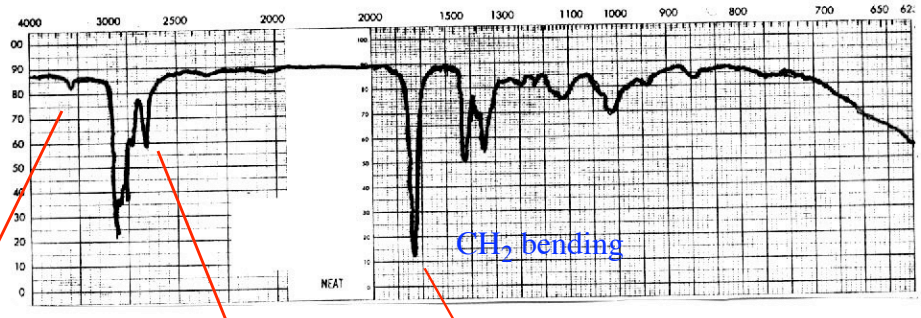


3-methylpentanal

expected bands:

C=O

C-H on C=O



C–H

CH_2 bending

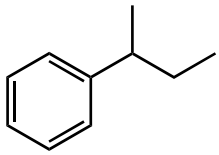
O-H may show up equilibrium with hydrate

C-H on C=O ~2720 cm^{-1} (2 bands)

C=O

1800-1650 cm^{-1}

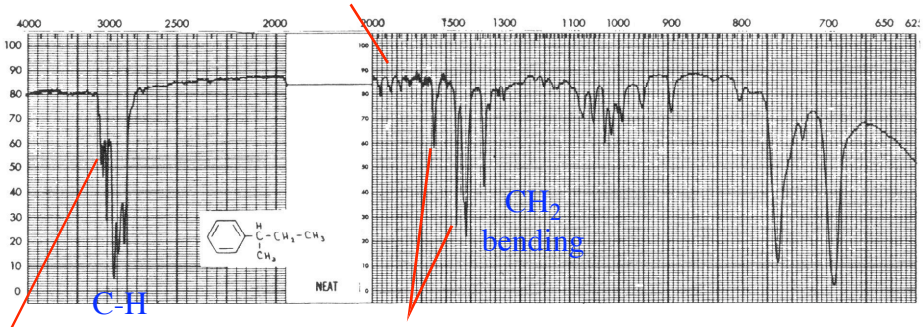
Aromatic



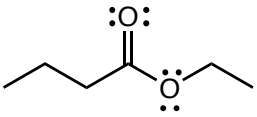
sec-butyl benzene

expected bands:

C-H on C=C
C=C aromatic
overtones



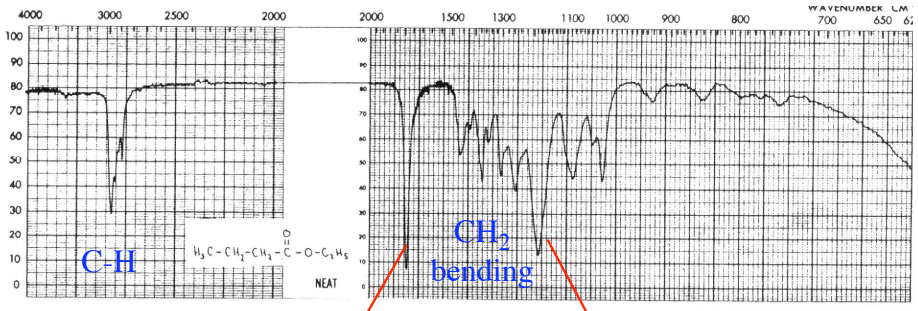
Ester



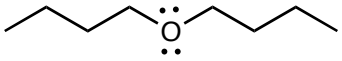
ethyl butyrate

expected bands:

C=O
C-O



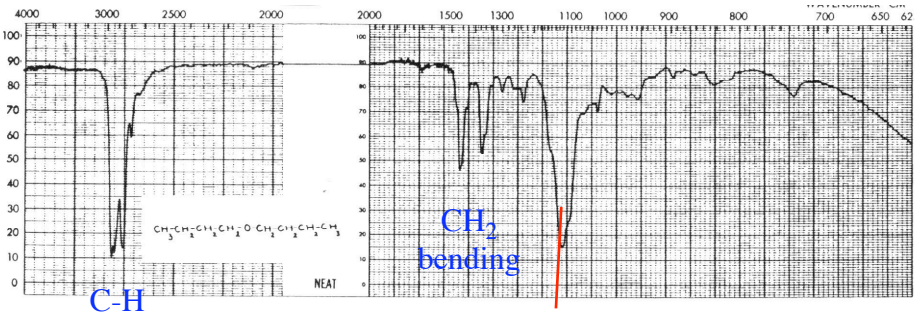
Ether



dibutyl ether

expected bands:

C-O



IV. Interpreting an IR spectrum

If you think you know the identity of a compound that you have a spectrum of, what should you do?

figure out all of the bands it should have, see if they are there

alcohol O-H, C-O

ester C=O, C-O

you need to know which bands each functional group has from memory! flash cards

alkene C=C, C-H on C=C, C=C bending

If you don't know the identity of the compound you have a spectrum of, what should you do?

1) find C-H and CH_2 bending to use as reference points

2) look in each area for bands that stick out

O-H, N-H, O-H on C=O, C---C, C---N, C=O

3) then look for bands that confirm, or narrow it down

if you see an O-H, look for: C-O (alcohol)

if you see an N-H, look for: NH_2 bending (amine/amide)

C=O (amide)

if you see a C≡C or C≡N, look for: C-H on C---C (alkyne will have it, nitrile won't)

if you see a C=O, look for: C-O (ester)

O-H on C=O, dimer (carboxylic acid)

C-H on C=O (aldehyde)

N-H, NH_2 bending (amide)

two of them, C-O (anhydride)

none of these (ketone)

if there are no obvious bands, look for: C=C, C-H on C=C (alkene)

C-O (ether)

C-X (alkyl halides)

How would you tell spectra of the following compounds apart?

aldehyde vs. ketone? aldehyde has C-H next to C=O, ketone doesn't

alkane vs. ether? ether has C-O, alkane doesn't

ketone vs. ester? ester has C-O, ketone doesn't

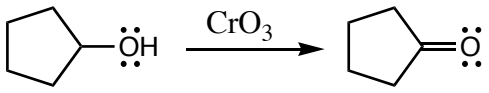
amide vs. amine? amide has C=O, amine doesn't

nitrile vs. alkyne? alkyne has C-H next to C---C, nitrile doesn't, C---N larger

alcohol vs. amine? O-H and N-H are in the same region, but O-H is broader
if NH_2, two bands + NH_2 bending, alcohol has C-O

alcohol vs. carboxylic acid? alcohol OH smaller, doesn't cover CH
COOH has C=O, dimer band

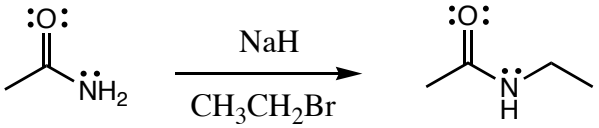
What would you look for in the IR spectum of the following reactions?



alcohol O-H
C-O

ketone C=O

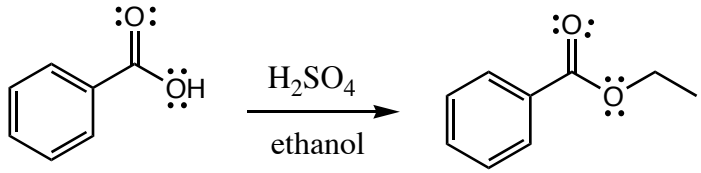
O-H should disappear
C-O should disappear
C=O should appear



1° amide C=O
N-H (2)
NH_2 bending

2° amide C=O
N-H (1)

C=O should still be there, unchanged
N-H should go from 2 bands to 1 band
NH_2 bending should disappear



aromatic carboxylic acid C=O
O-H
dimer
C=C aromatic
overtones
C-H on C=C

aromatic ester C=O
C-O
C=C aromatic
overtones
C-H on C=C

large O-H should disappear
C=O should still be there, may shift
C-O should appear
C=C aromatic, C-H on C=C,
overtones still there