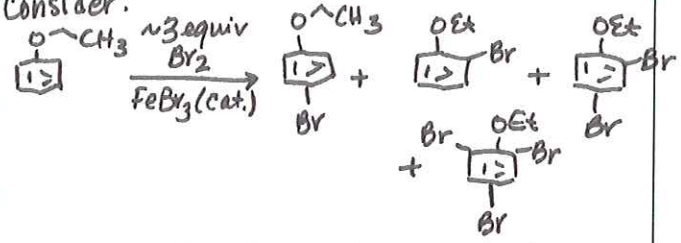
①

WEEK 5: ANALYTICAL CHEMISTRY OF ORGANIC COMPOUNDS (CHAPTER 15)

Midterm 1: H's over, but not graded yet. Will be returned in labs.

②

Consider:



What do we do w/ our 4 products?

1) Separate
2) Identify each component/product.

③

SEPARATION/PURIFICATION

Methods:

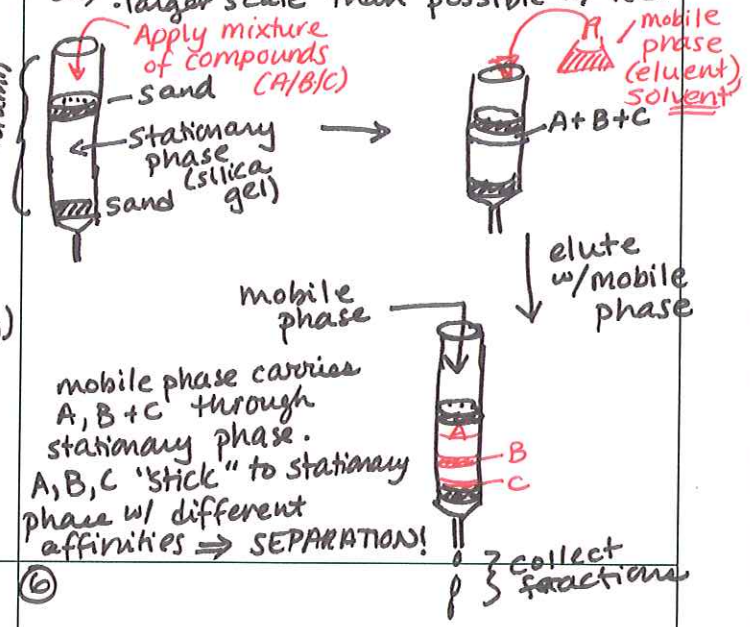
① Crystallization (if solid)

② Distillation (if liquid & each component has substantially different bp)

③ Chromatography
- TLC (thin layer chromatography) - you've done this in lab.
- Column
- HPLC
- Gas (GC)

④

3a) Column Chromatography - larger scale than possible w/ TLC. ≈50g of material



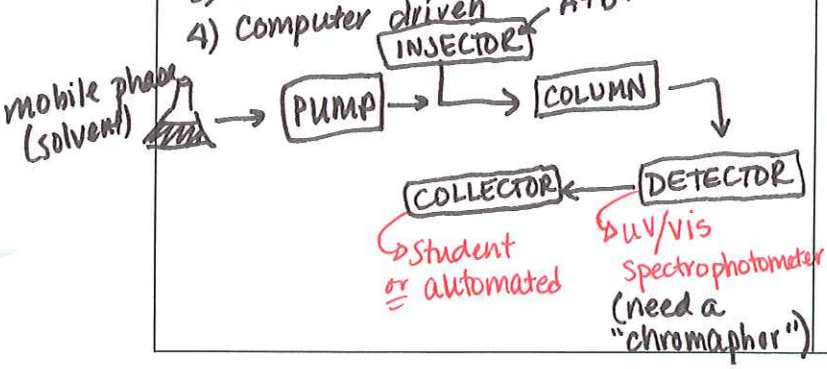
mobile phase carries A, B + C through stationary phase.

A, B, C "stick" to stationary phase w/ different affinities ⇒ SEPARATION!

⑤

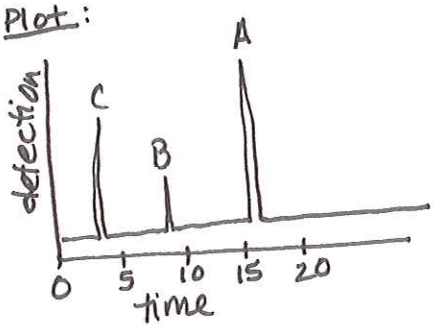
3b) HPLC (High Performance Liquid Chromatography)

Same thing, but
1) Pumps deliver mobile phase
2) Columns are smaller
3) Attach a detector
4) Computer driven



⑥

Plot:

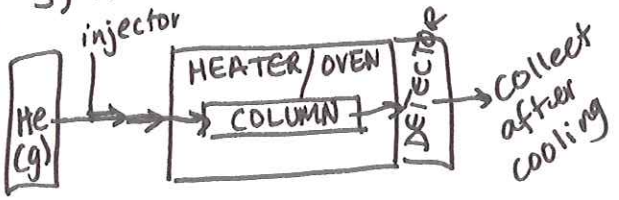


Good for larger, more polar molecules.

(7) Gas Chromatography (GC)

Same thing, but...

1) mobile phase = gas (He or H_2)
2) stationary phase = silicone polymers
3) Heat the column



~good for hydrophobic (greasy) small molecules.

(8) once pure, How do you figure out what it is? Lots of options, usually need >1.

ELEMENTAL - COMBUSTION ANALYSIS

Derive Empirical Formula by "burning" the compound.

ex: Unknown + $O_2 \longrightarrow H_2O + CO_2$

STEP 1:

1) Derive C content of unknown from weight of CO_2 produced.
2) Derive H content from weight of H_2O.
3) Oxygen content by a "difference calculation" (substraction).

(9)

10 mg unknown $\xrightarrow{\text{burn}}$ 29.31 mg CO_2 + 5.99 mg H_2O

Carbon Content:

$$wt(C) = \frac{MW(C)}{MW(CO_2)} * wt(CO_2)$$

$$= \frac{12.011\ g/mol}{44.0099\ g/mol} \times 29.31\ mg$$

$$= 8\ mg\ C$$

(10)

Hydrogen Content:

$$wt(H) = \frac{2\,MW(H)}{MW(H_2O)} \times wt(H_2O)$$

$$= \frac{2(1.0089\ g/mol)}{18.015\ g/mol} \times 5.99\ mg$$

$$= 0.67\ mg\ H$$

$$\%\,C = \frac{8.0\ mg\ C \times 100}{10.0\ mg} = 80\%\ C$$

$$\%\,H = \frac{0.67\ mg\ H \times 100}{10\ mg} = 6.7\%\ H$$

$$\%\,O = 100 - 80 - 6.7 = 13.3\%\ O$$

(11)

STEP 2: Derive Empirical Formula from % values:

Calculate # moles of each element (assuming we have 100g):

$$C = 80\,g \times \frac{1\ mol}{12.01\,g} = 6.66\ mol$$

$$H = 6.7\,g \times \frac{1\ mol}{1.01\,g} = 6.63\ mol$$

$$O = 13.3\,g \times \frac{1\ mol}{16.0\,g} = 0.831\ mol$$

Empirical Formula is

$C_{6.66}H_{6.63}O_{0.831}$ What?!?

(12)

Divide by smallest # to make all integers:

$$\frac{C_{6.66}}{0.831}\ \frac{H_{6.63}}{0.831}\ \frac{O_{0.831}}{0.831}$$

$\Rightarrow C_8H_8O$

(13) STEP 3: Determine degrees of unsaturation (for common organic species)

- Convert Actual Molecular formula to Hydrocarbon Formula (HCF).

RULES:

Each atom of:	is removed and:
F, Cl, Br, I	replaced by H
O, S	ignored
N, P, B, Al, Si	one H removed also replaced by C.

ex: $C_8H_8O \longrightarrow C_8H_8$
(Actual) (HCF)

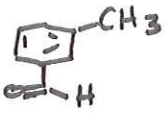
(14)

- Calculate # of H's for an alkane of same # of carbons

$C_8 \Rightarrow C_nH_{(2n+2)} \rightarrow C_8H_{18}$

- Find difference in H's

Alkane 18
− HCF 8
10/2 = 5 degrees of unsaturation
⇓
π bonds, rings

~~Ex~~: C_8H_8O could be 

end of Mon.

(15) Mass Spectrometry

- Determination of Molecular Weight (p. 699 for good picture)

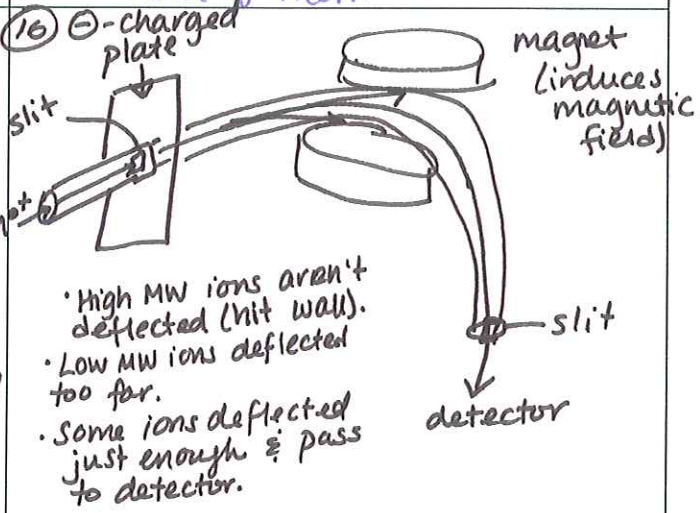
How? M = molecule

1) Bombard M w/ an e⁻ (70eV)

$M + e^- \longrightarrow 2e^- + M^{\cdot +}$

(e⁻ is ejected from M)

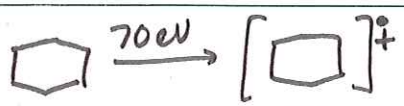
2) Radical cation ($M^{\cdot +}$) is accelerated towards plate of opposite charge.

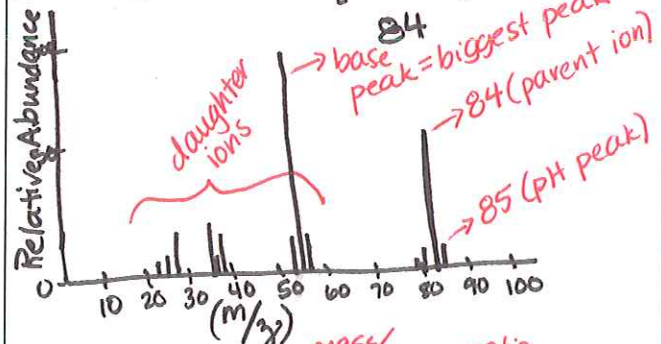
(16) 

- High MW ions aren't deflected (hit wall).
- Low MW ions deflected too far.
- Some ions deflected just enough & pass to detector.

↑ ions of appropriate weight.

Magnetic field tuned to detect different MW ions.

(17) ex: 



↳ mass/charge ratio
mostly, charge (z) = +1
∴ m/z = mass

end of Tues.

(18)

Parent Ion: mass of the molecule

(pH) peak: results from relative abundance of isotopes of elements

Here: Carbon

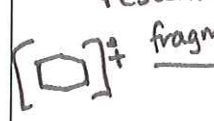
	Relative Abundance	Atomic Wt.
^{12}C	98.9	12.00
^{13}C	1.1	13.00

for ⬡, 6 C's, all w/ 1.1% probability of being ^{13}C, so...

6 × 1.1 ≈ 7% chance that mass of ⬡ will be one unit higher.

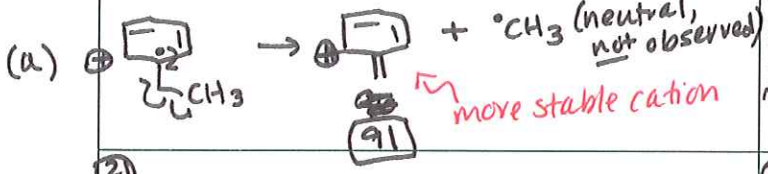
Here: pH peak 7% parent ion peak.

(19) **Daughter Ions**: Charged species resulting from fragmentation



*fragmentation results in most stable (+) ions.

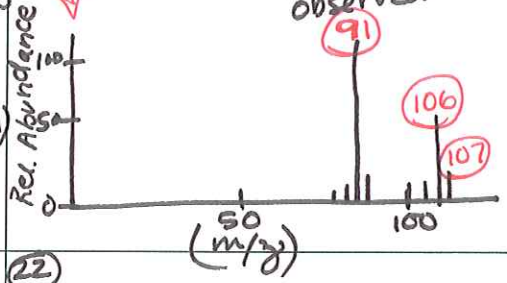
ex: 

(a) 

(20) (a) 

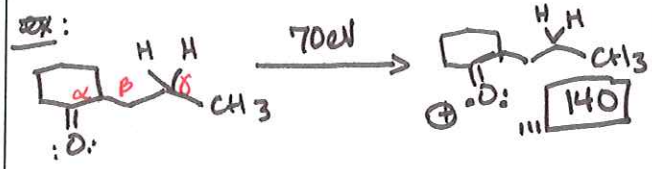
vs.

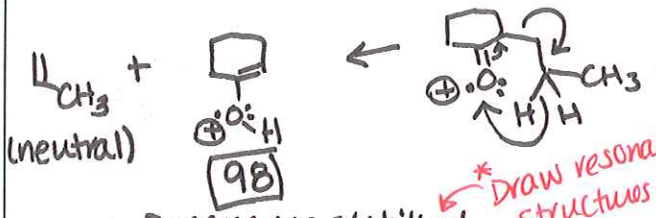
(b) 



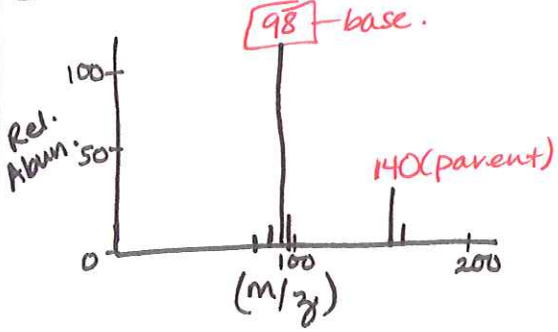
(21) Fragmentation can involve rearrangements:

ex: **McLafferty Rearr.**
-occur w/ carbonyl compounds containing a γ-hydrogen

ex: 

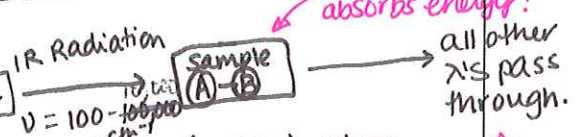


Resonance stabilized * Draw resonance structures

(22) 

(23) **INFRARED SPECTROSCOPY (IR)**

Process:



IR radiation: radiation (energy) whose λ is $1 \times 10^{-4} - 1 \times 10^{-2}$ cm.

or $\tilde{\nu} = \frac{1}{\lambda} = 10{,}000 - 100\ cm^{-1}$ * wavenumbers

Absorbed Energy (absorption energy is quantized) goes into

(a) Molecular Rotations & (b) Molecular Vibrations (stretching & bending)

(24) Wavelength of Absorption depends on

(a) relative masses of atoms in molecule

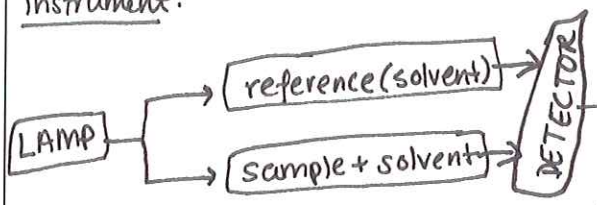
(b) force constant (strength) of bonds connecting the atoms.

measure absorbed energy.

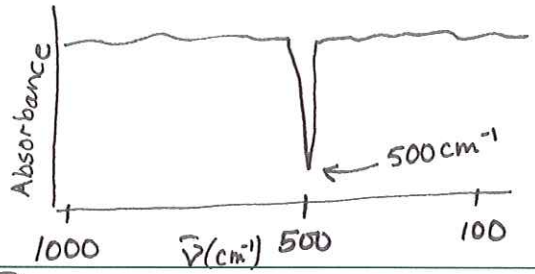
end of Wed.

(25)

Instrument:



If a molecule only absorbs $500\ cm^{-1}$



(26)

IR spectra of organic molecules are complex!

Every bond that vibrates affects the vibrations of all other bonds in the molecule.

Use IR to

① Fingerprint molecules (ex: drug testing)

② Identify characteristic absorptions of common fxnal groups.

Table 15.3 in book (will be given on exam)

Sample Spectra (overhead)

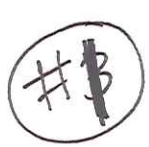
(27)

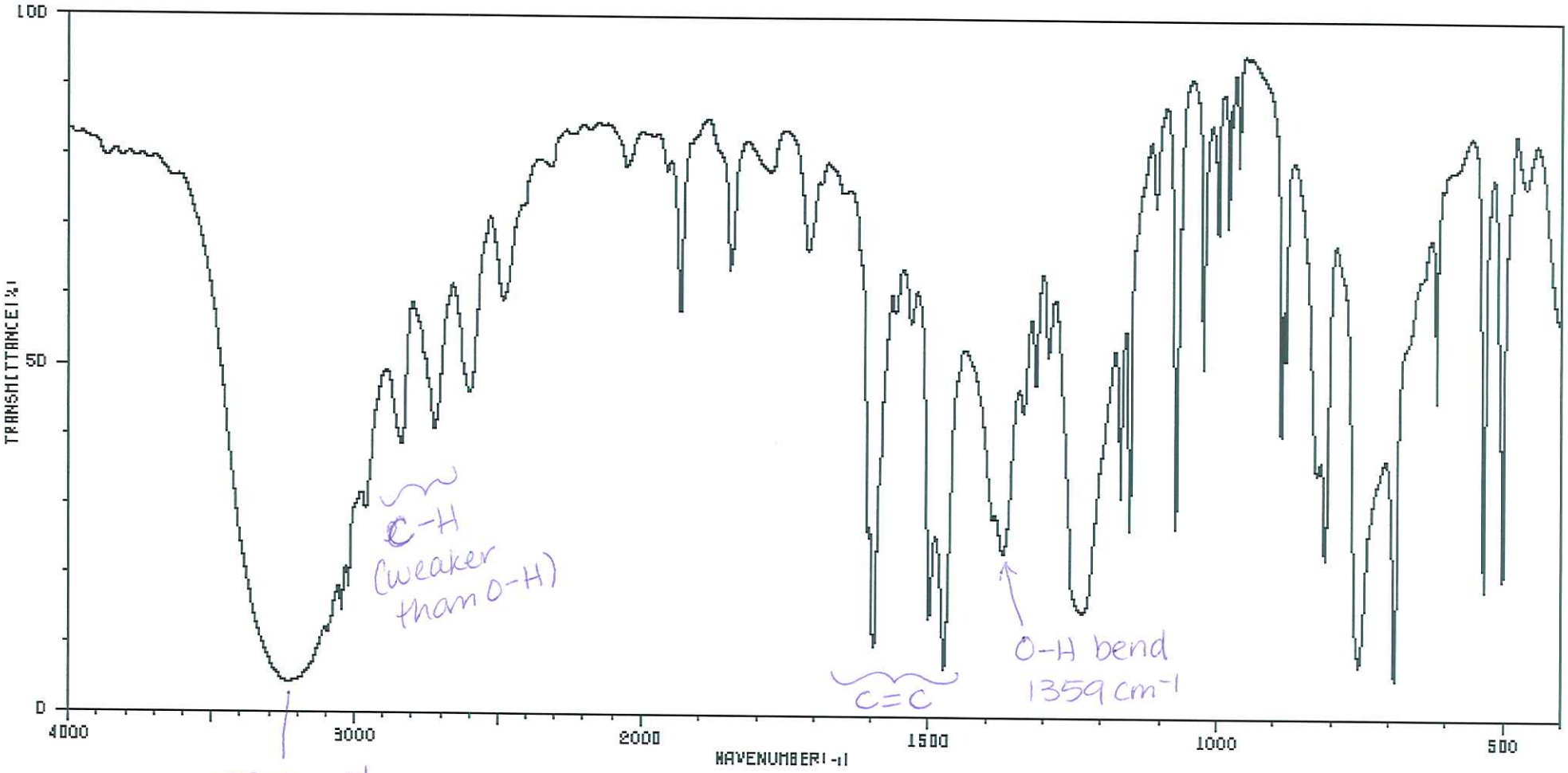
(28)

(29)

(30)

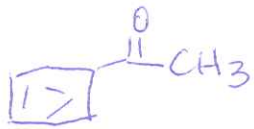
#3

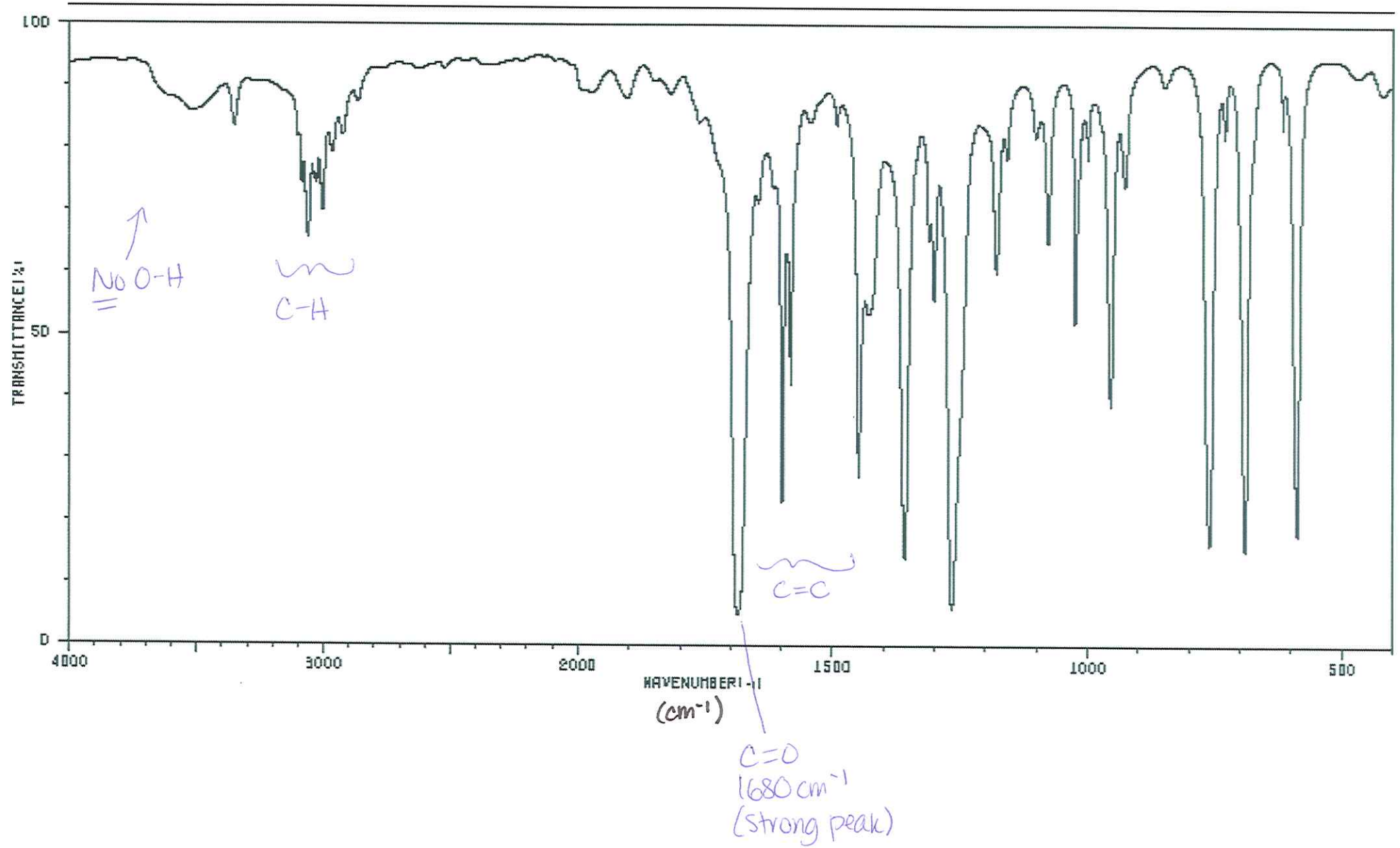

OH


100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]
C-H
(weaker
than O-H)
C=C
O-H bend
1359 cm-1
3300cm-1
broad, strong peak
O-H

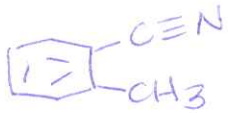
Unknown 2
IR Spectrum

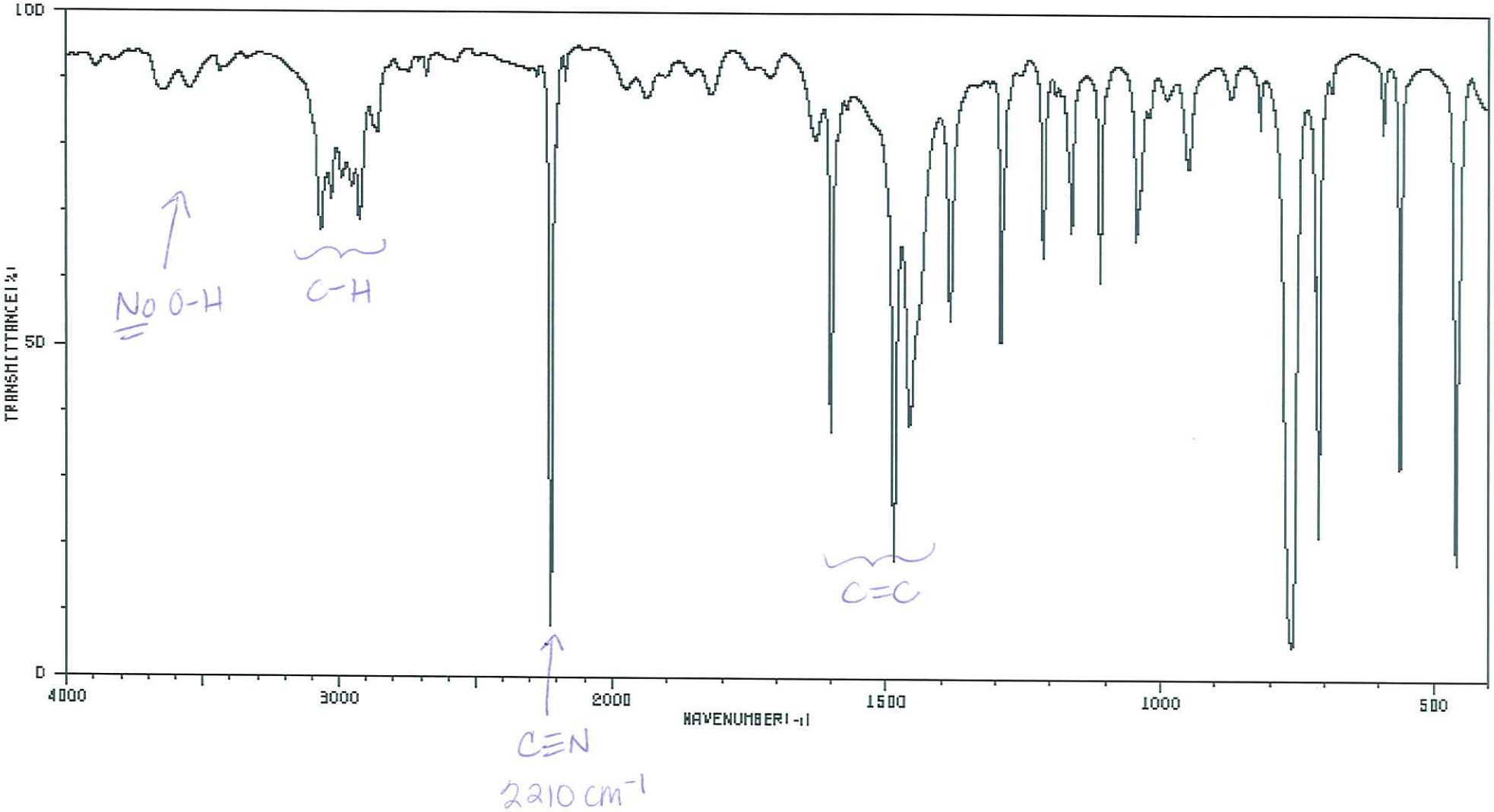
#2





#3


C≡N
CH3


100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]
No O-H
C-H
C=C
C≡N
2210 cm⁻¹