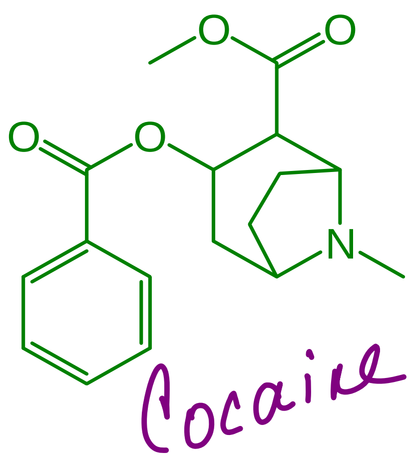
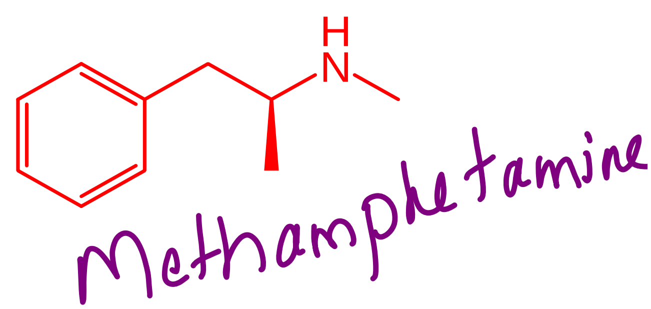
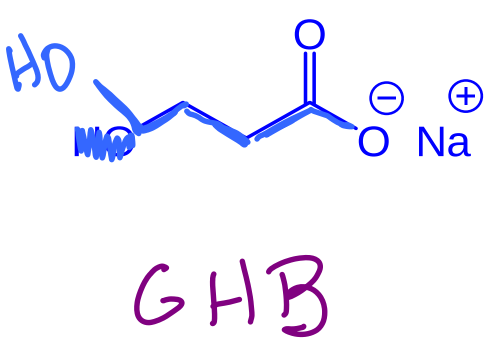
Chem 020

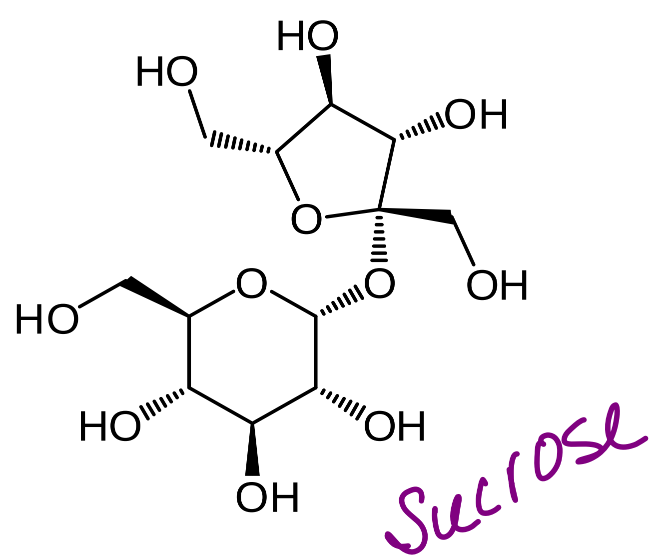
Infrared Spectroscopy: Identification of Unknown Substances

- Suppose a white powder is one of the four following molecules. How can they be differentiated?







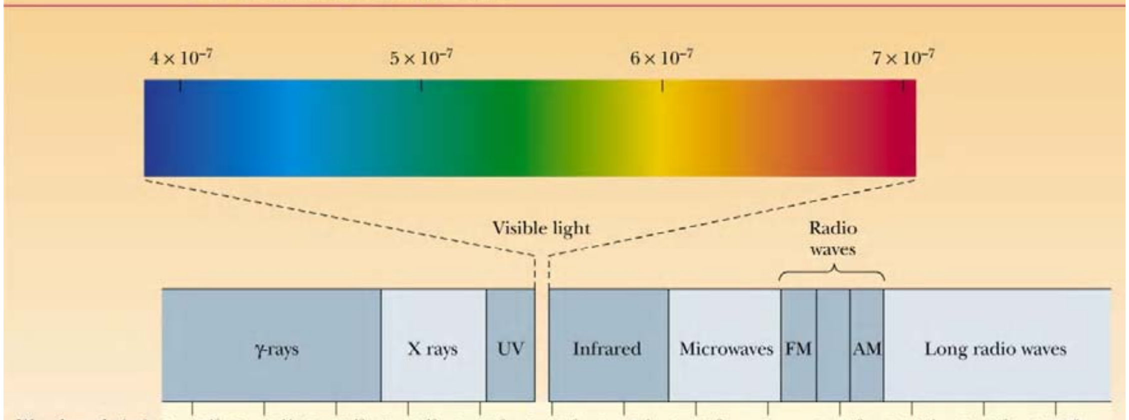


- A technique that is very frequently used to assist in the identification of unknown compounds uses infrared (IR) light, a form of electromagnetic radiation.

Electromagnetic Radiation

- Energy is transmitted through space in the form of electromagnetic radiation, which are oscillating waves. This term is used to describe all the component waves found in the continuous electromagnetic spectrum.

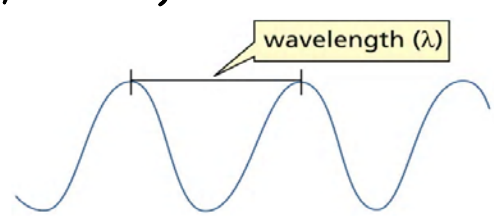
TABLE 11.1 Wavelength, Frequency, and Energy Relationships of Some Regions of the Electromagnetic Spectrum



Wavelength (m)	3×10^{-16}	3×10^{-14}	3×10^{-12}	3×10^{-10}	3×10^{-8}	3×10^{-6}	3×10^{-4}	3×10^{-2}	3	3×10^{2}	3×10^{4}	3×10^{6}	3×10^{8}
Frequency (Hz)	10^{24}	10^{22}	10^{20}	10^{18}	10^{16}	10^{14}	10^{12}	10^{10}	10^{8}	10^{6}	10^{4}	10^{2}	10
Energy (kcal)	10^{13}	10^{11}	10^{9}	10^{7}	10^{5}	10^{3}	10^{1}	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}

1 nm = 10^{-9} m

- Electromagnetic radiation propagates at the speed of light (*c*). Radiation is characterized by its wavelength (λ) or frequency (waves per second, ν in s^{-1}).
- The shorter the λ, the higher the ν (more waves go by per second if the wavelength is shorter).

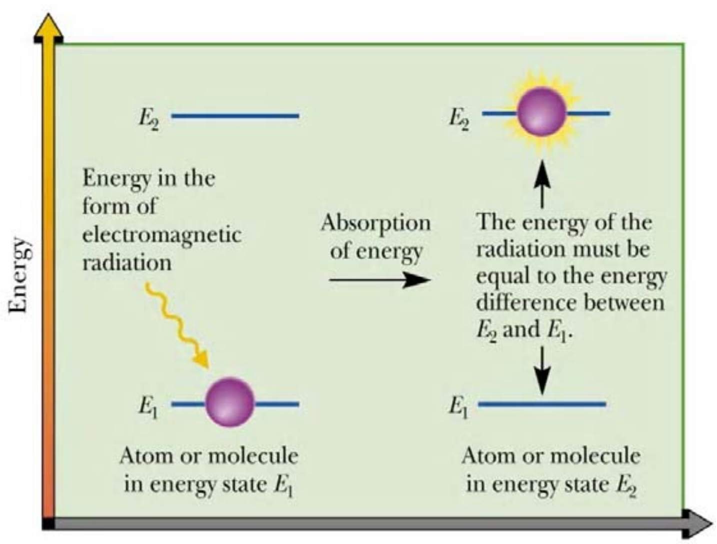


- Humans can see the *visible region*, approx. 400 – 700 nm.

- There is an inverse relationship between λ and energy.
    - Shorter wavelength = higher energy
    - Longer wavelength = lower energy

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

- IR light corresponds to an energy of about 5 – 50 kJ mol^{-1}. This compares very well to the energy differences of various conformations, suggesting that the absorption of IR results in conformational changes.
- However, the energy of IR that is absorbed must correspond to exactly that of the conformational change. This is because energy is quantized; there are discrete energy levels between ground and excited states.



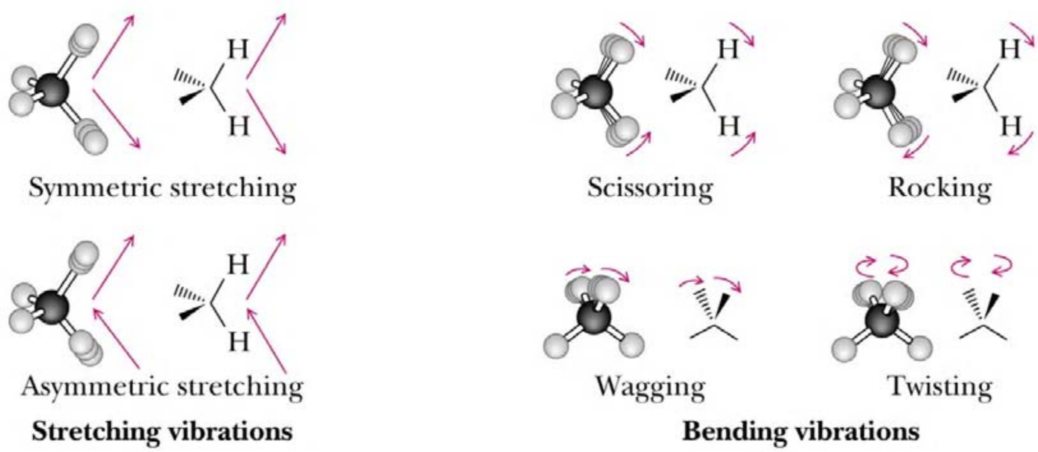
state 2

state 1

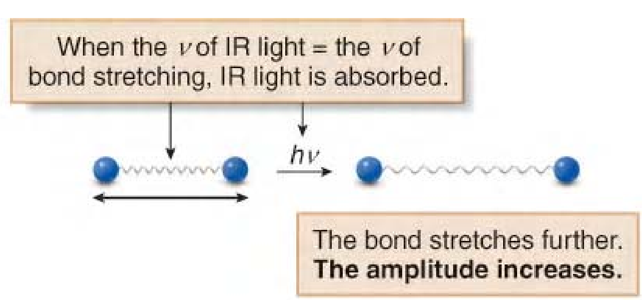
- A molecule will absorb light of wavelength λ_1 only if λ_1 has an energy that is equal to ΔE.

IR Spectroscopy

- Why do molecules absorb IR? At room temp, atoms within molecules are constantly vibrating about their equilibrium positions at specific frequencies.



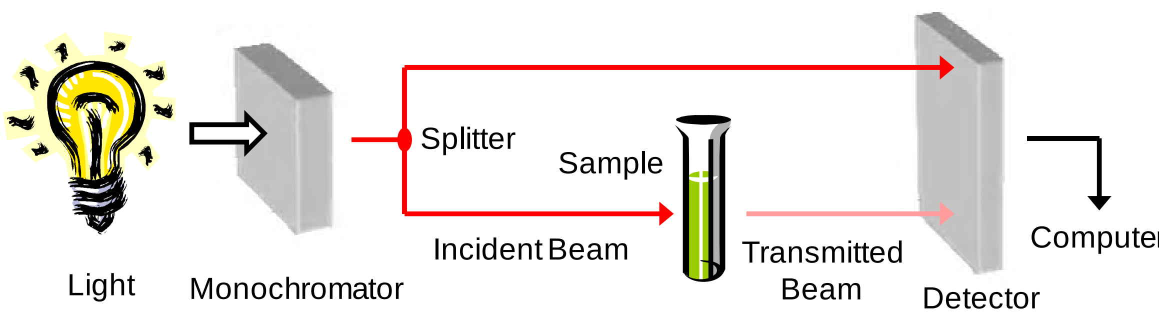
- If the frequency of the IR light matches the frequency of the vibration (stretching or bending), the bond will absorb the energy and vibrate to a greater extent.



Vibrational excitation due to IR

- An important concept about IR spectroscopy is that different types of bonds, hence different functional groups, have different IR absorption frequencies.

- Thus, by measuring the different wavelengths that are absorbed by a molecule, we can learn about its structure. An infrared spectrometer measures IR absorption.



Source of IR

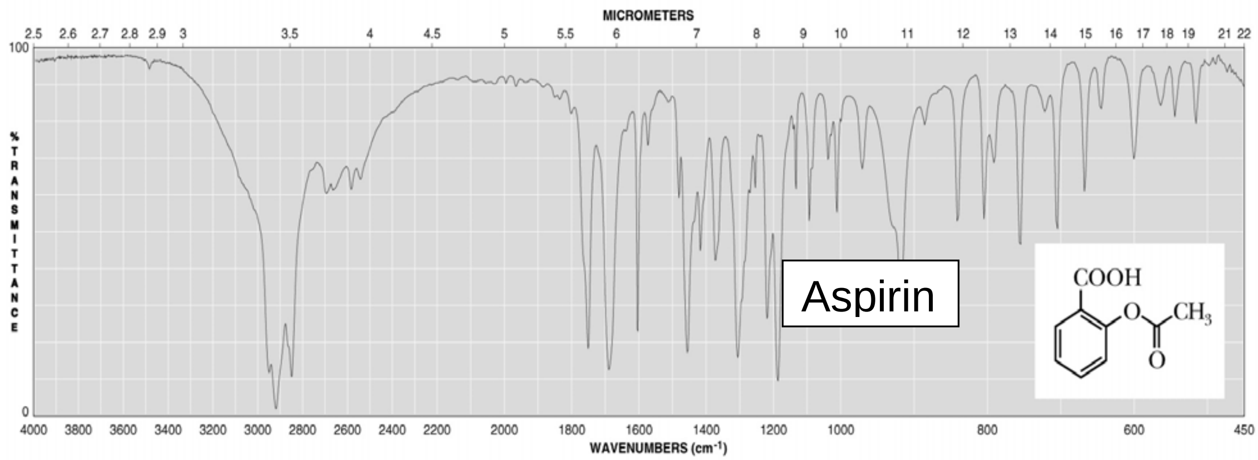
↳ picks λ

- The detector compares the sample beam with the reference beam, and the difference is the amount absorbed.

- The instrument plots a chart % transmittance plotted against wavenumber (reciprocal of λ when in cm). Absorption appears as peaks of lowered transmittance.

$$\text{Wavenumber} = \frac{1}{\lambda\ (cm)}$$

- IR spectra are normally "scanned" 4000 – 600 cm^{-1}



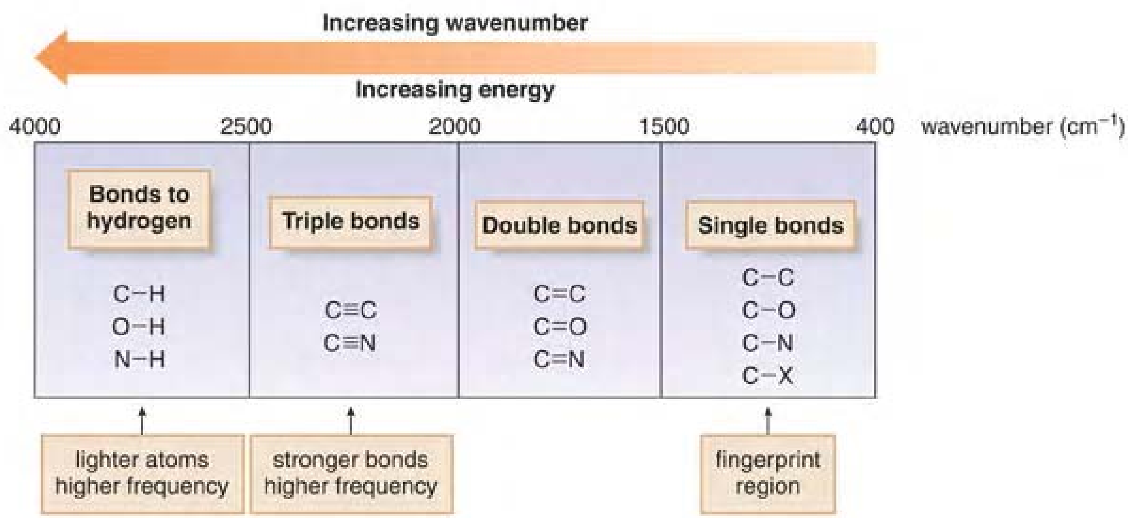
Functional Groups Fingerprint

- The full interpretation of an IR spectrum is difficult because most organic molecules are so large that they have dozens of different bond stretching and bending motions, and accordingly, an IR spectrum is usually complex.

- The region from about 1400 – 600 cm^{-1} is called the fingerprint region and is hard to interpret. It is a very complex absorption pattern, and if two molecules give the same fingerprint, they are most likely the same molecule.

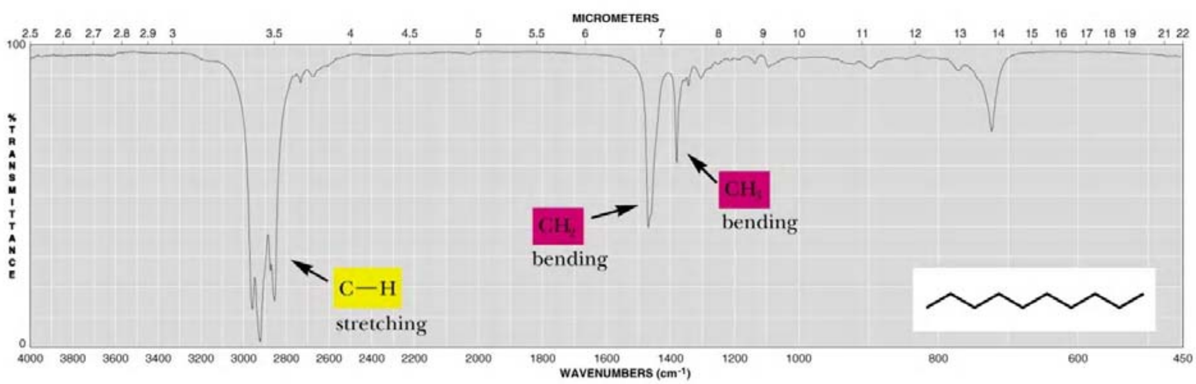
- However, one region of the IR spectrum, from about 4000 – 1400 cm^{-1}, is relatively useful and easy to interpret because it identifies the functional groups.

- Functional groups have characteristic absorption peaks. These peaks (dips in the spectrum) are identified by their frequency (energy) in wavenumbers and intensity of the absorption (weak, medium, strong).



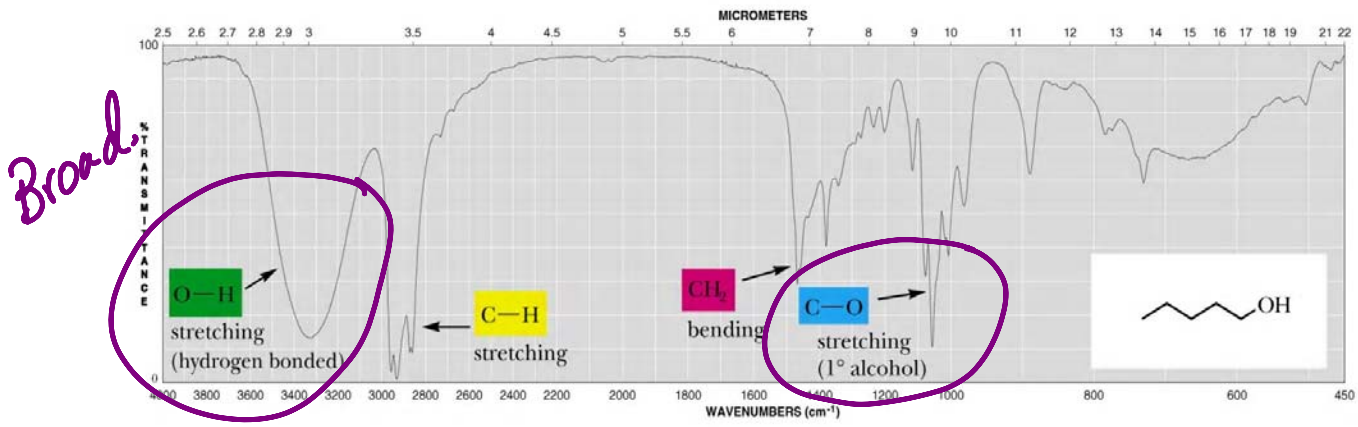
DO NOT MEMORIZE

- Alkanes show CH signals from saturated carbons, but they're not very useful diagnostically, because most organic compounds contain alkyl groups.

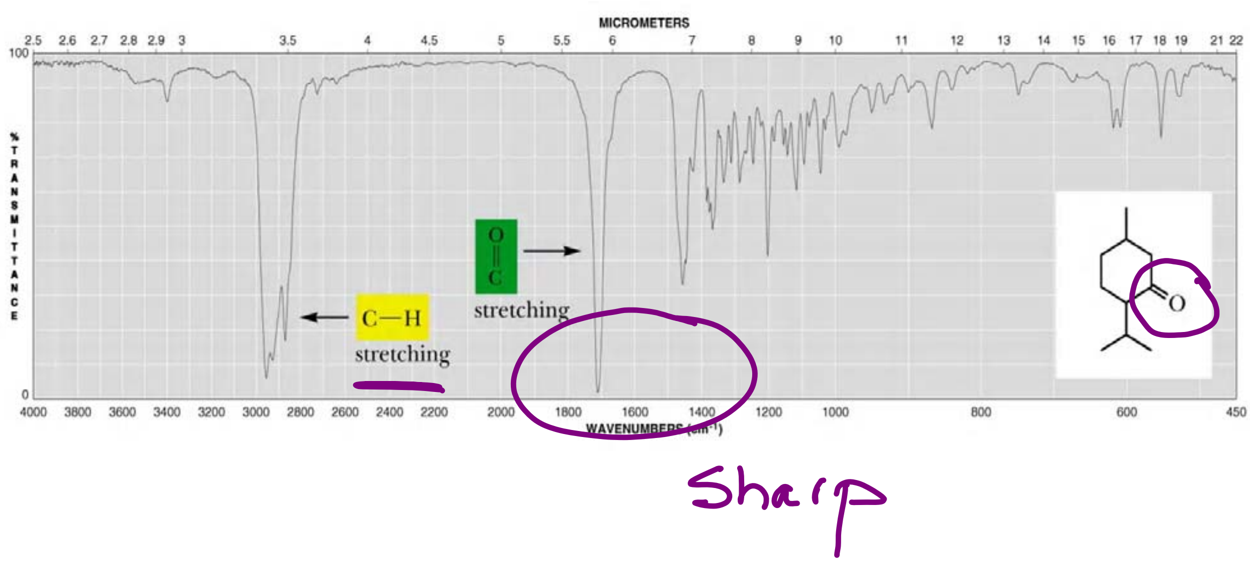


absorption wavenumbers will be given, if necessary

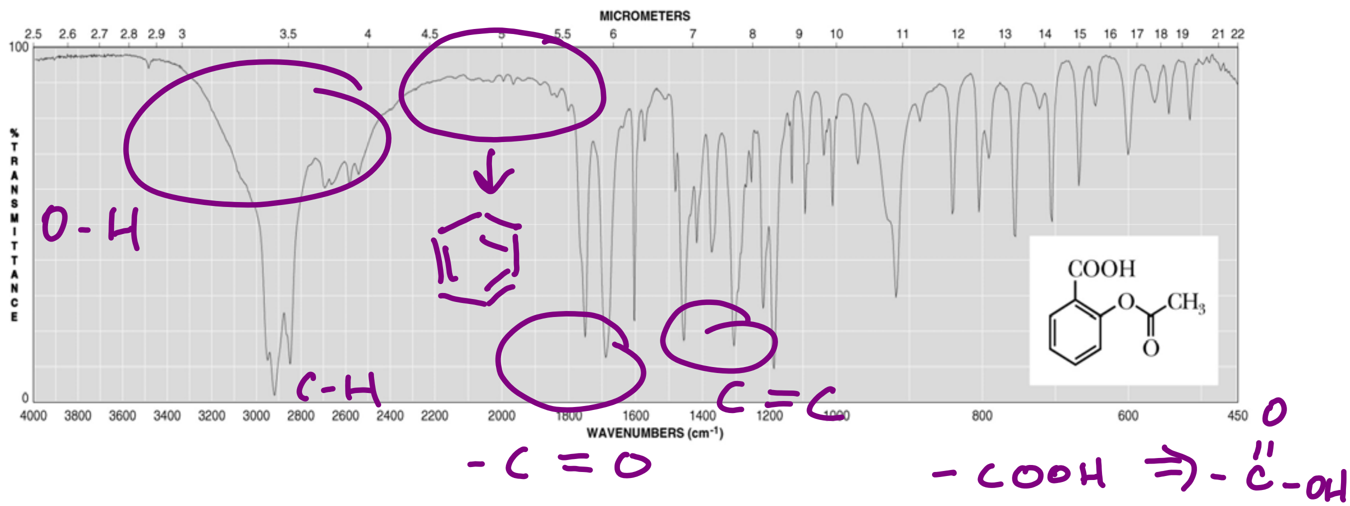
- Alcohols have a strong, broad OH stretch at 3200 – 3500 cm^{-1}, and a strong CO stretch at 1050 – 1250 cm^{-1}. The CH signals from the alkyl carbons are still present.



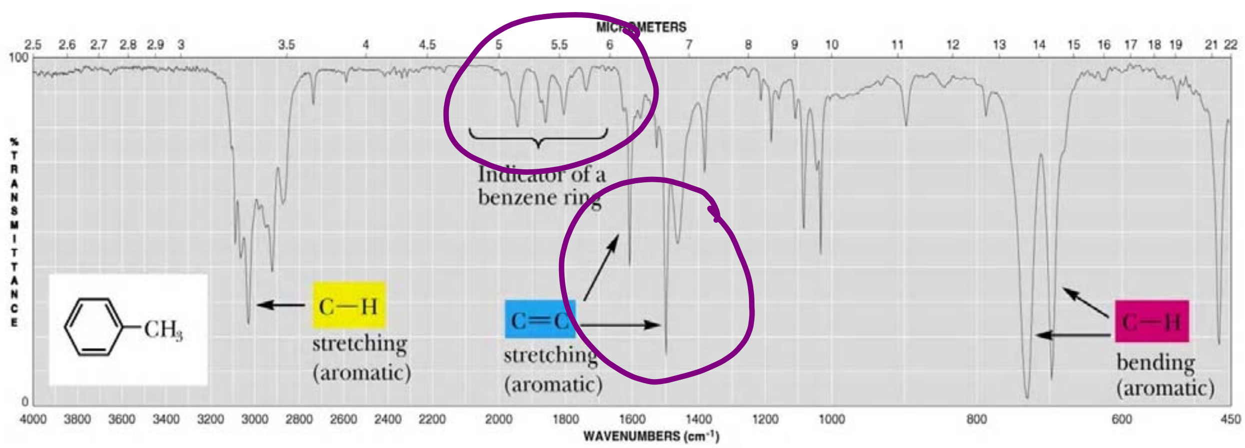
- Carbonyl groups (C=O) tend to absorb at 1600 – 1800 cm^{-1}, depending on the group (aldehyde, acid, ester, etc).



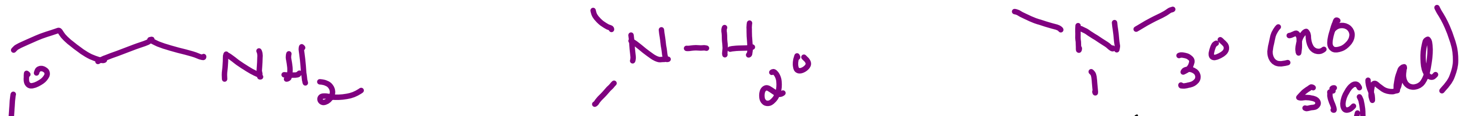
- Refer again to the spectrum of aspirin. There are two C=O signals, since there is an acid and an ester.
    - The OH of a carboxylic acid is slightly lower, at 2400 – 3400, than that of an alcohol OH. This allows chemists to differentiate between alcohols and acids.



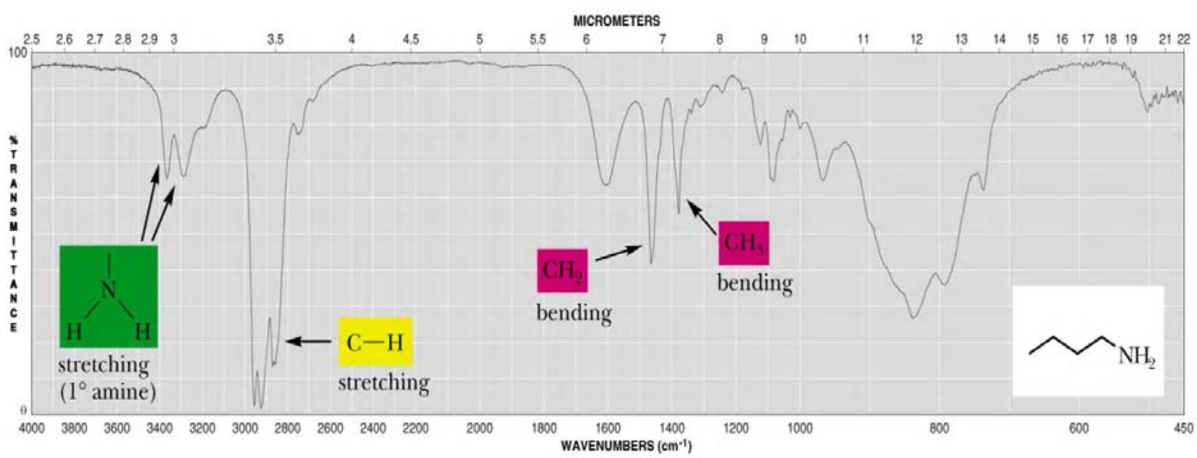
- Aromatic rings have a few characteristic IR absorptions. These absorptions are a little more complex.



See both for an aromatic ring.



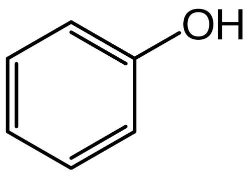
- Amines have N–H signals in the 3100 – 3500 cm^{-1} region. The number of signals depends on the number of H atoms connected to the N. Primary amines have two peaks, while secondary amines have one.
  - Primary amine = one carbon connected to N (2 H)
  - Secondary amine = two carbons connected to N (1 H)



- It is also possible to obtain structural information from an IR spectrum by noticing which absorptions are *absent.*
  - For example, if an IR spectrum does not have a strong, sharp absorption near 1600 – 1800 cm^{-1}, then the compound does not have a C=O.

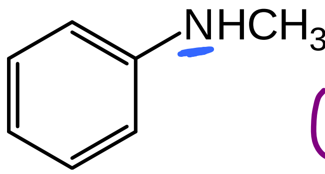
- Exercise: match these spectra to the proper compounds...

(1)



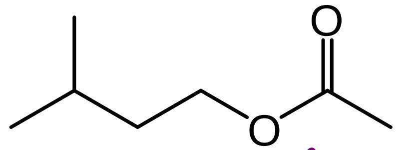
- benzene ring, OH

(2)



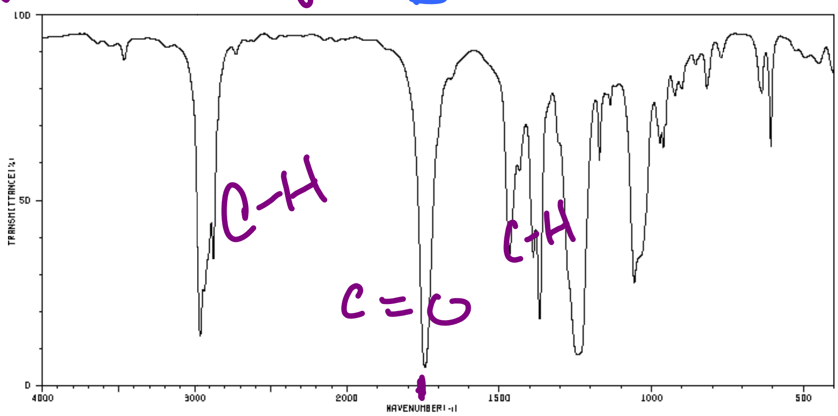
- benzene ring 2° amine

(3)

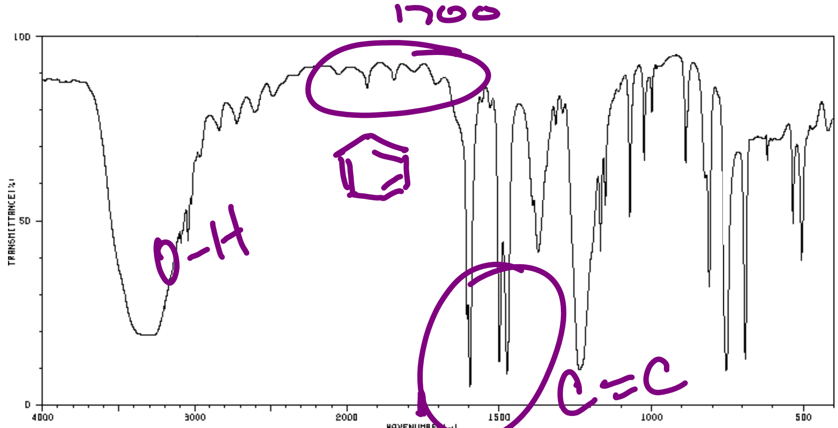


C = O
C - O

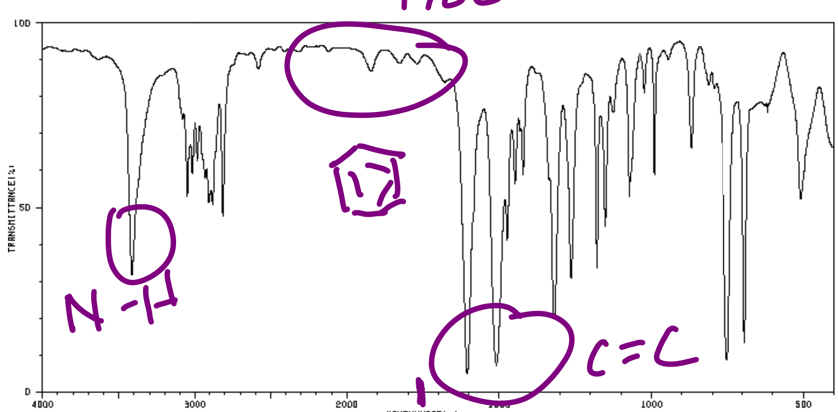
(3)



(1)

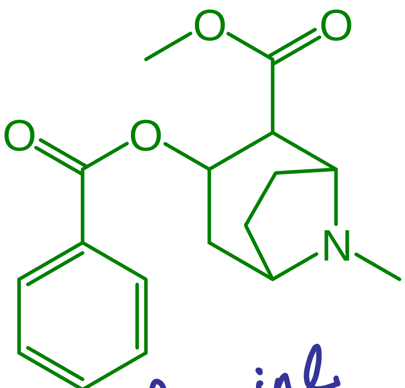


(2)



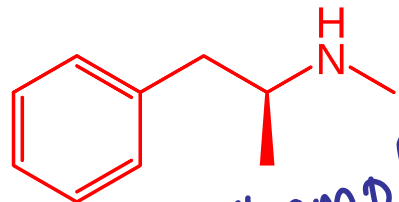
- Now, our unknowns. What diagnostic IR signals would be expected to be present for each compound?

2 C=O,



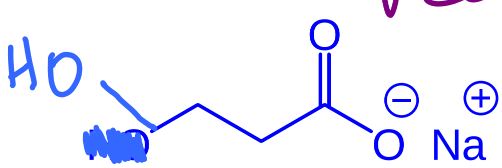
Cocaine

2° amine



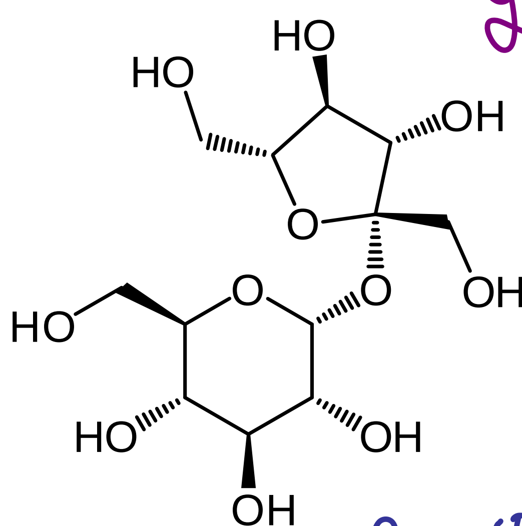
Methamphetamine

OH, C=O (from COOH)



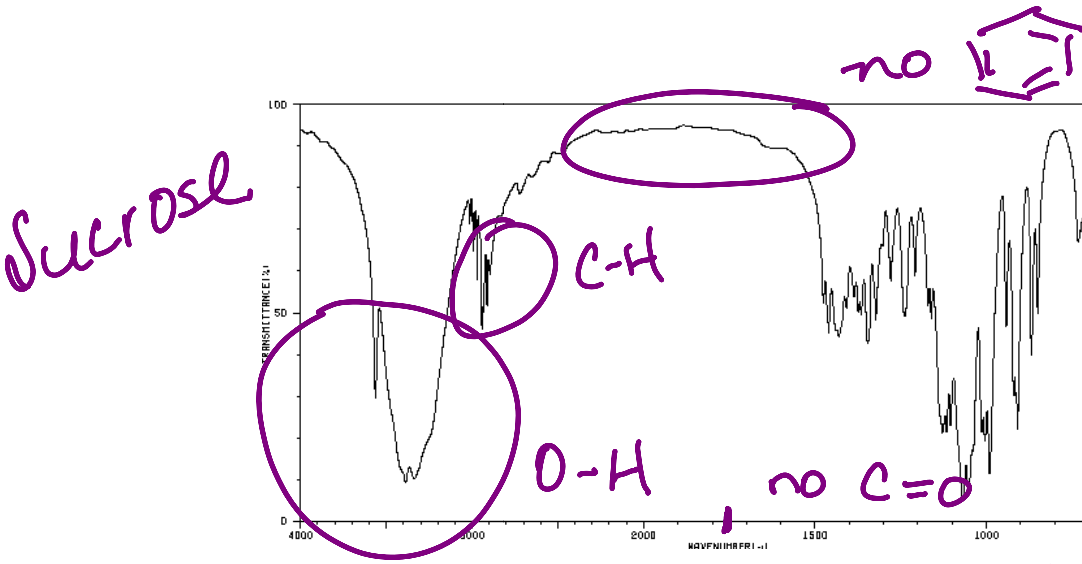
GHB

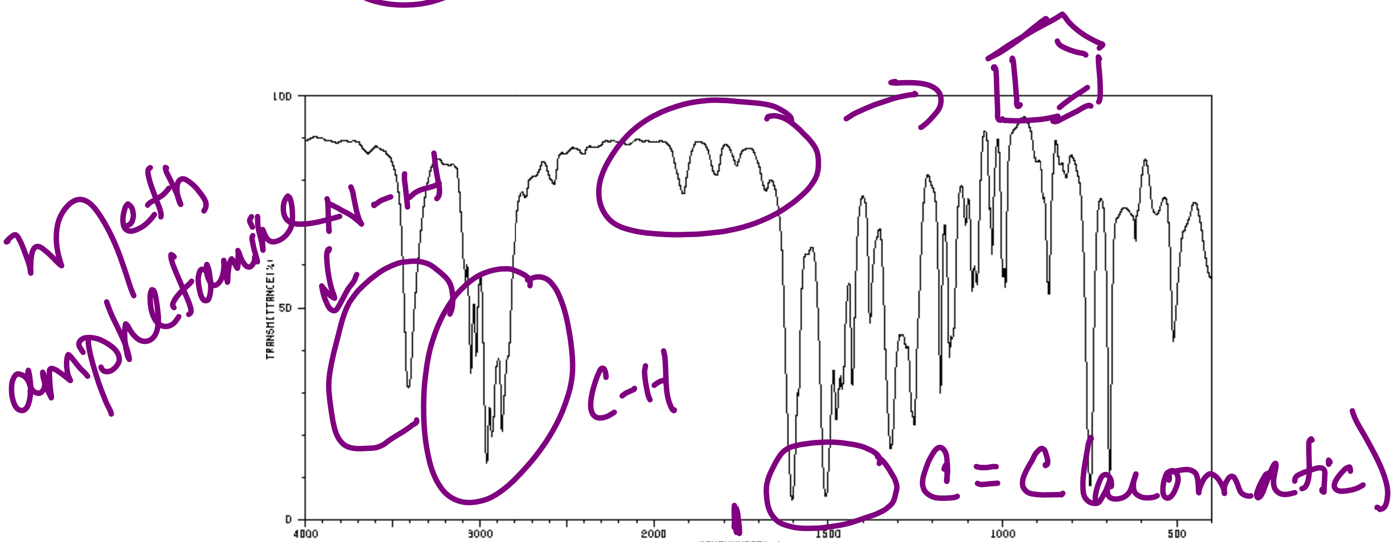
Lots of OH's

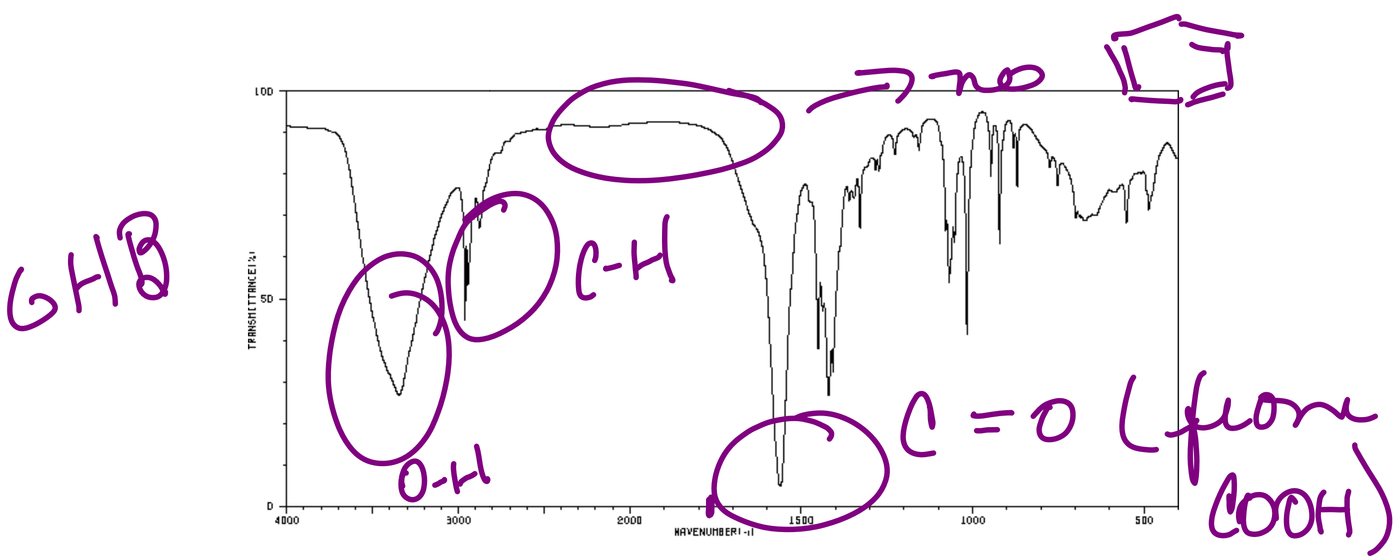


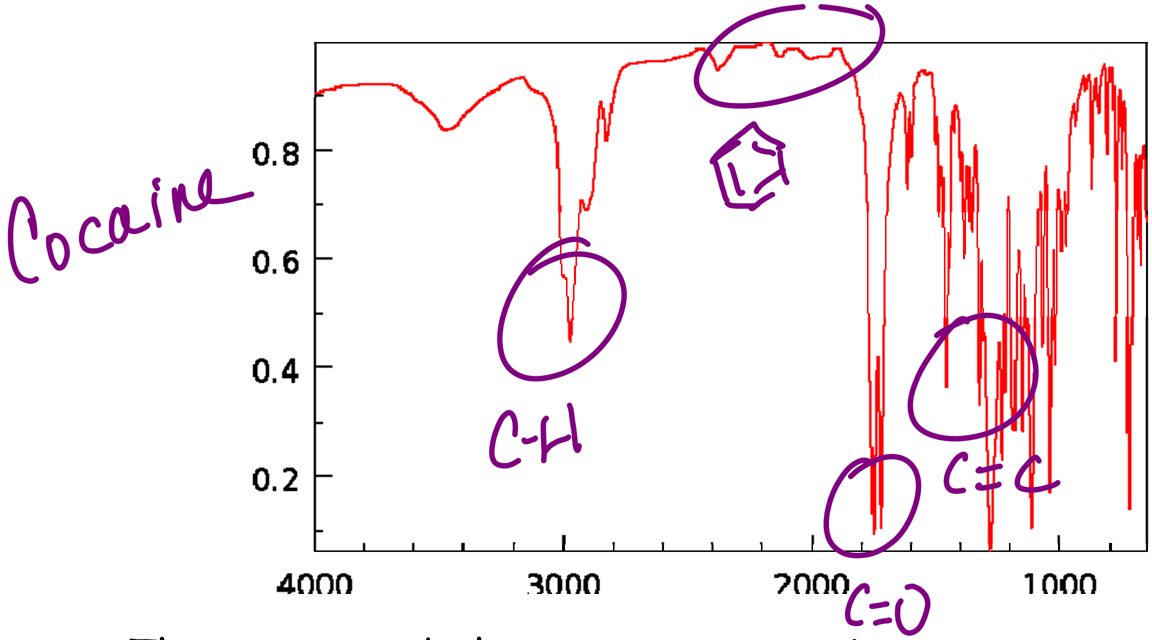
Sucrose

- Match the four following spectra to the unknowns...

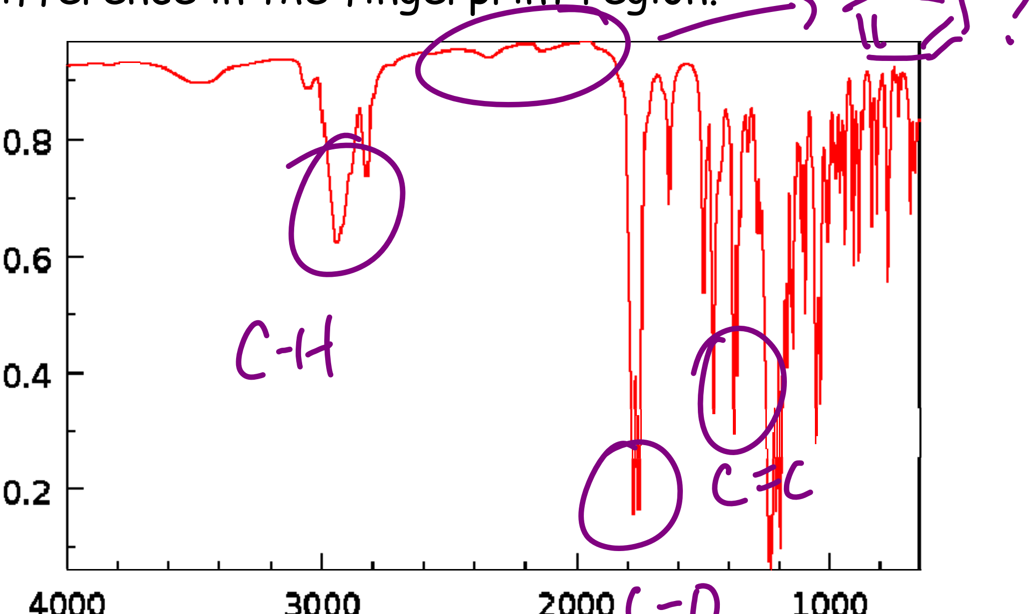

Sucrose
no
C-H
O-H
no C=O
TRANSMITTANCE(%)
WAVENUMBER(-1)
100
50
0
4000
3000
2000
1500
1000
500


Meth amphetamine
N-H
C-H
C=C (aromatic)
TRANSMITTANCE(%)
WAVENUMBER(-1)
100
50
0
4000
3000
2000
1500
1000
500


GHB
no
C-H
O-H
C=O (from COOH)
TRANSMITTANCE(%)
WAVENUMBER(-1)
100
50
0
4000
3000
2000
1500
1000
500



- The spectrum below represents an important compound with similar functional groups as the one above, but notice the difference in the fingerprint region.



IR spectroscopy is just one of the many analytical techniques available. Usually, it is used in conjunction with nuclear magnetic resonance spectroscopy, mass spectrometry, and chromatography, which you'll encounter in second-year.