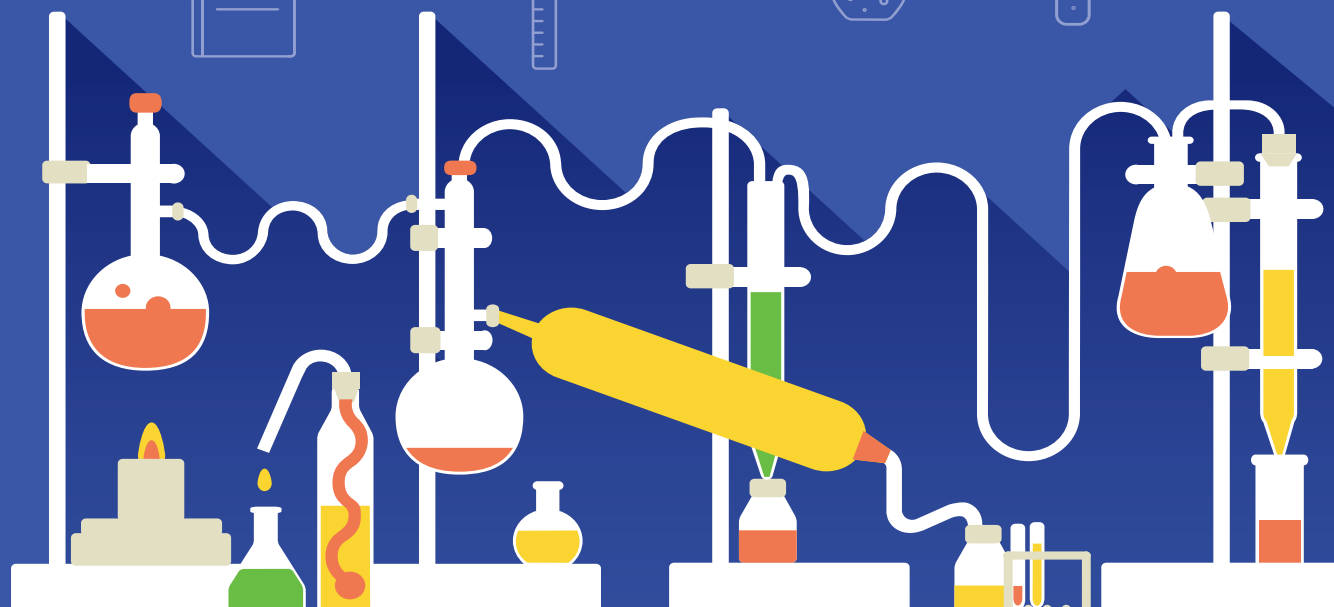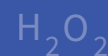# CHM247H:

Introductory Organic Chemistry II

Winter 2021

Week 1

STRUCTURE ELUCIDATION

SOME METHODS OF DETERMINING STRUCTURE

1. High resolution mass spectroscopy → determining empirical formula
2. Gas chromatography
3. High-pressure liquid chromatography
4. IR
5. NMR
6. Melting point/boiling point

DEGREE OF UNSATURATION

- number of pi bonds and/or rings in a molecule
  1. Formula

$$DOU = \frac{2C + 2 - H - X + N}{2}$$

C: Number of carbon atoms.
H: Number of hydrogen atoms.
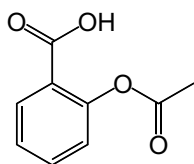X: Number of halogen atoms (F, Cl, Br, I, …)
N: Number of nitrogen atoms.

  2. Count DOU from structure

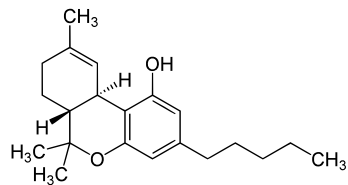| Structure	DOU
Double Bond	1
Triple Bond	2
Ring	1

Calculate and count the DOU for the following compounds:
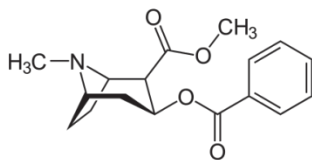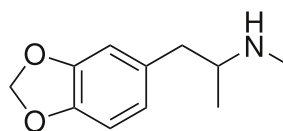
Aspirin: $C_9H_8O_4$

THC: $C_{21}H_{31}O_2$
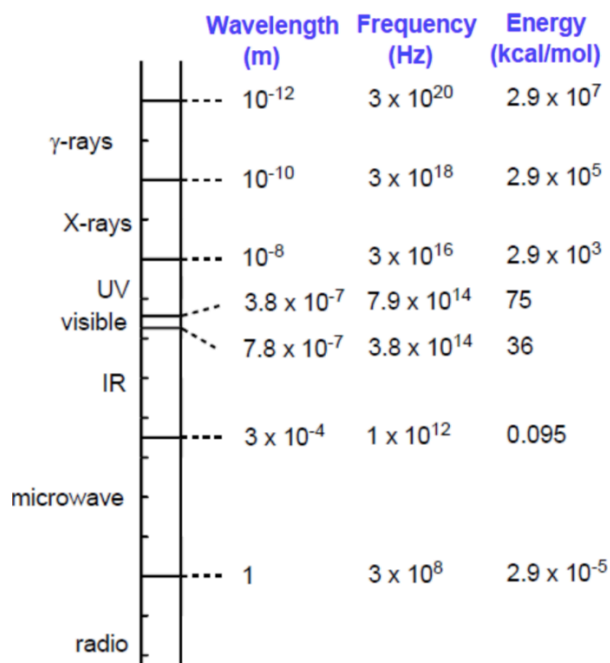
Cocaine: $C_{17}H_{21}NO_4$

MDMA: $C_{11}H_{15}NO_2$

SPECTROSCOPY

- Organic compounds can absorb certain wavelength of electromagnetic radiation.
- The wavelength of electromagnetic radiation being absorbed depends on the energy difference between states
- Some important formula:

$$\nu = \frac{c}{\lambda} \qquad \Delta E = h\nu$$

	Wavelength (m)	Frequency (Hz)	Energy (kcal/mol)
	10^{-12}	3×10^{20}	2.9×10^{7}
γ-rays			
	10^{-10}	3×10^{18}	2.9×10^{5}
X-rays			
	10^{-8}	3×10^{16}	2.9×10^{3}
UV	3.8×10^{-7}	7.9×10^{14}	75
visible	7.8×10^{-7}	3.8×10^{14}	36
IR			
	3×10^{-4}	1×10^{12}	0.095
microwave			
	1	3×10^{8}	2.9×10^{-5}
radio			

Spectroscopic Methods and Quantized Transitions

Spectroscopic Method	Energy	Molecular Effects
—	> 10^4 kcal mol^{-1}	ionization
ultraviolet / visible (UV-vis)	40 - 300 kcal mol^{-1}	electronic transitions
infra-red (IR)	1 - 10 kcal mol^{-1}	molecular vibrations
microwave	~ 1 kcal mol^{-1}	molecular rotation
nuclear magnetic resonance (NMR)	~ 10^{-5} kcal mol^{-1}	nuclear spin transitions

INFRARED SPECTROSCOPY

- In IR radiation, the absorbed energy causes bonds to **vibrate** (stretching and bending).

| Symmetrical Stretching | Unsymmetrical Stretching | In-Plane Bending | Out-of-Plane Bending |
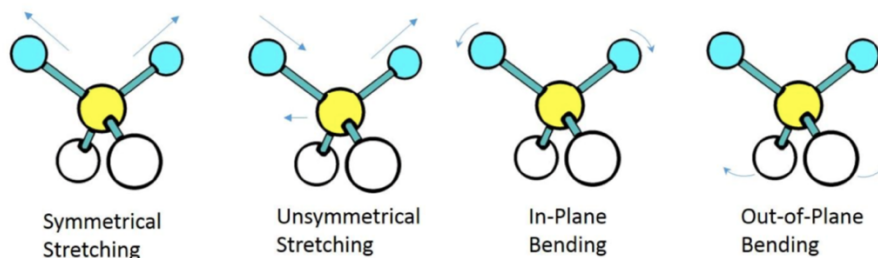
- Only vibrational modes that cause dipole moment changes are IR active
  Ex. Symmetric stretching of O=C=O is IR inactive
- Important equation to remember:

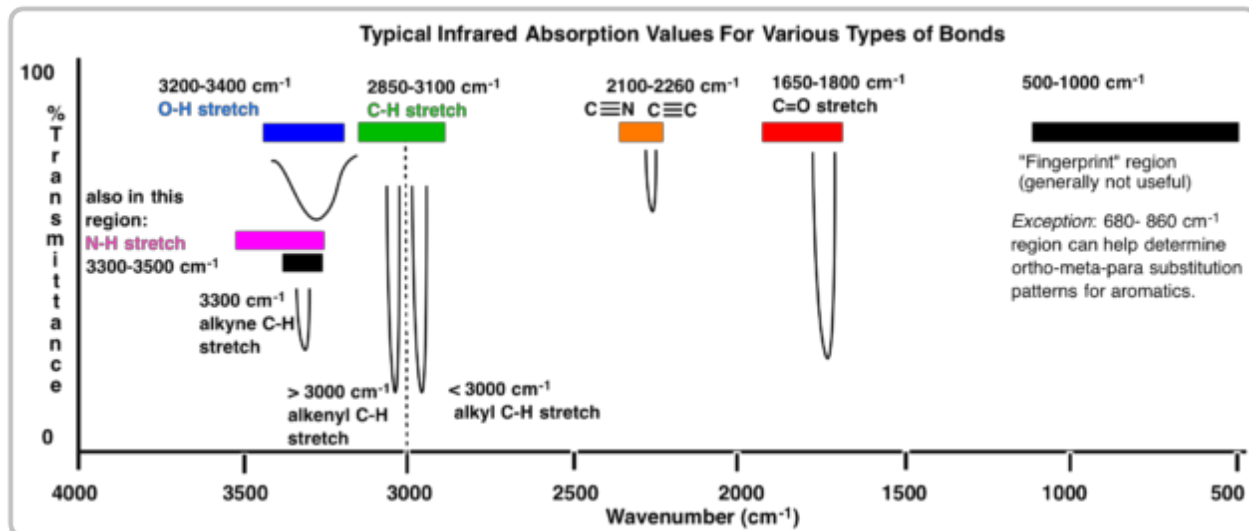$$v = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

- Stronger bonds and lighter atoms vibrate at higher frequencies
- Intensity of the peak depends on the dipole moment of the bond: higher dipole moment → high intensity
- IR spectrum is often used to determine the **<u>functional groups</u>** in the compounds.

1. IR spectrum
    - Example: 2-heptanone
    - The x-axis of an IR spectrum is wavenumber = 1/wavelength, unit: cm^{-1}
    - Higher wavenumber → higher frequency and energy

INFRARED SPECTRUM

2. Characteristic peaks
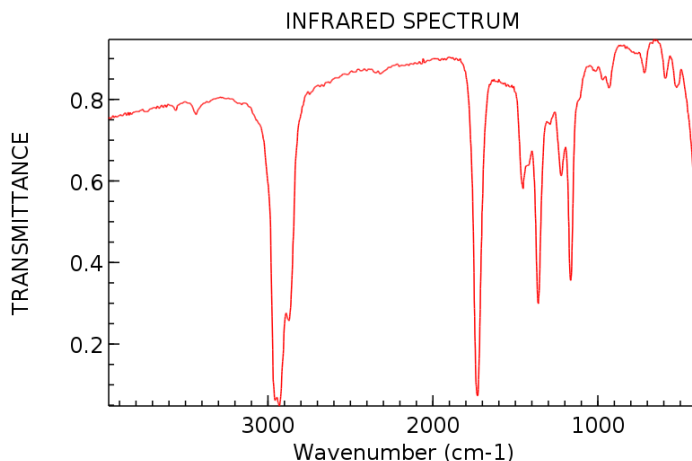
Typical Infrared Absorption Values For Various Types of Bonds

3. IR correlation table
- Some important functional groups: O-H, N-H, double bond, triple bond, carbonyl, benzene

| Functional Group		Wavenumber (cm⁻¹)	Functional Group		Wavenumber (cm⁻¹)
O-H (alcohols)		3200 – 3600 (*s, b*)	C=C		1640 – 1680 (*m*)
O-H (acids)		2500 – 3200 (*s, b*)	C≡C		2100 – 2260 (*w*)
N-H		3300 – 3500 (*w, b*)	C=C (aromatic)		1500 – 1600 (*m*)
C-H	(sp³)	2800 – 3000 (*s*)	C-N		1180 – 1360 (*w*)
	(sp²)	3000 – 3100 (*s*)	C≡N		2110 – 2260 (*m*)
	(sp)	3300 – 3325 (*s*)	C-O		1080 – 1300 (*s*)
C-H (benzenes)			C=O (acids)		1710 – 1800 (*s*)
	(Mono-sub)	730 – 770, 690 – 710		(aldehydes)	1720 – 1740 (*s*)
	(o-sub)	735 – 776, (1 peak)		(ketones)	1708 – 1720 (*s*)
	(m-sub)	750 – 780, 680 – 730		(esters)	1735 – 1750 (*s*)
	(p-sub)	790 – 840, (1 peak)		(acid chlorides)	1785 – 1815 (*s*)
C-H (aldehyde)		2695 – 2850		(acid anhydrides)	1740 – 1870 (*s*)
				(amide)	1626 – 1786 (*s*)
s = strong, m = medium, w = weak, b = broad					

4. Conjugation effect
   - Conjugation weakens pi system
   - Conjugation lowers the wavenumber of C=O stretching by about 30 cm^{-1}
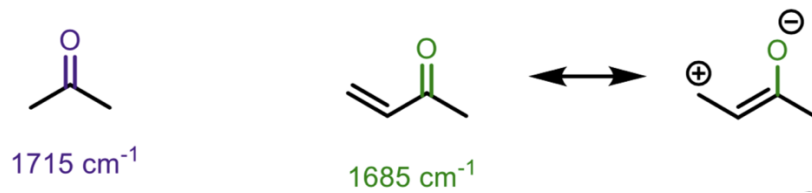
1. The following sets of structure have the same chemical formula $C_5H_{10}O$. What characteristic IR peaks would you expect to see for each compound, based on the functional groups in each molecule? Assign approximate wavelength and peak intensity based on the IR correlation table.
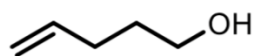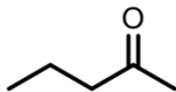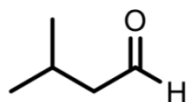
2. Assign the IR spectra to the compound, based on the expected peaks from the functional groups in each compound
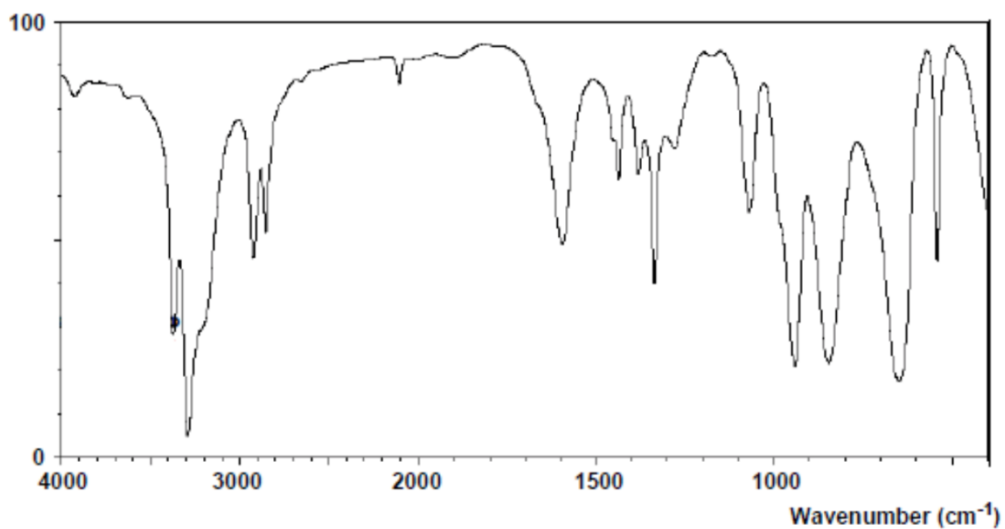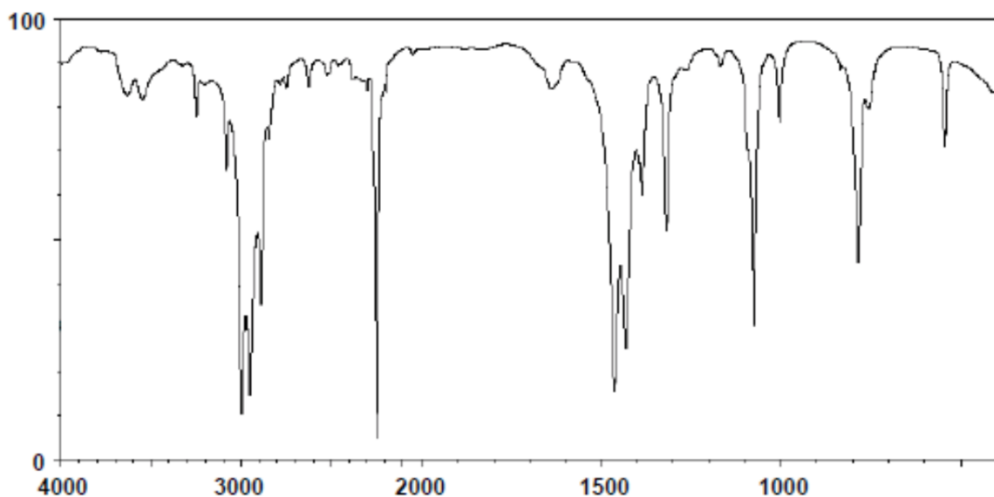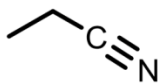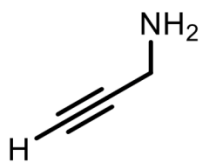
3. Determine the degree of unsaturation and structure for the following unknown compound giving the following information. Identify all major bands in the IR spectrum.

$$C_5H_8$$
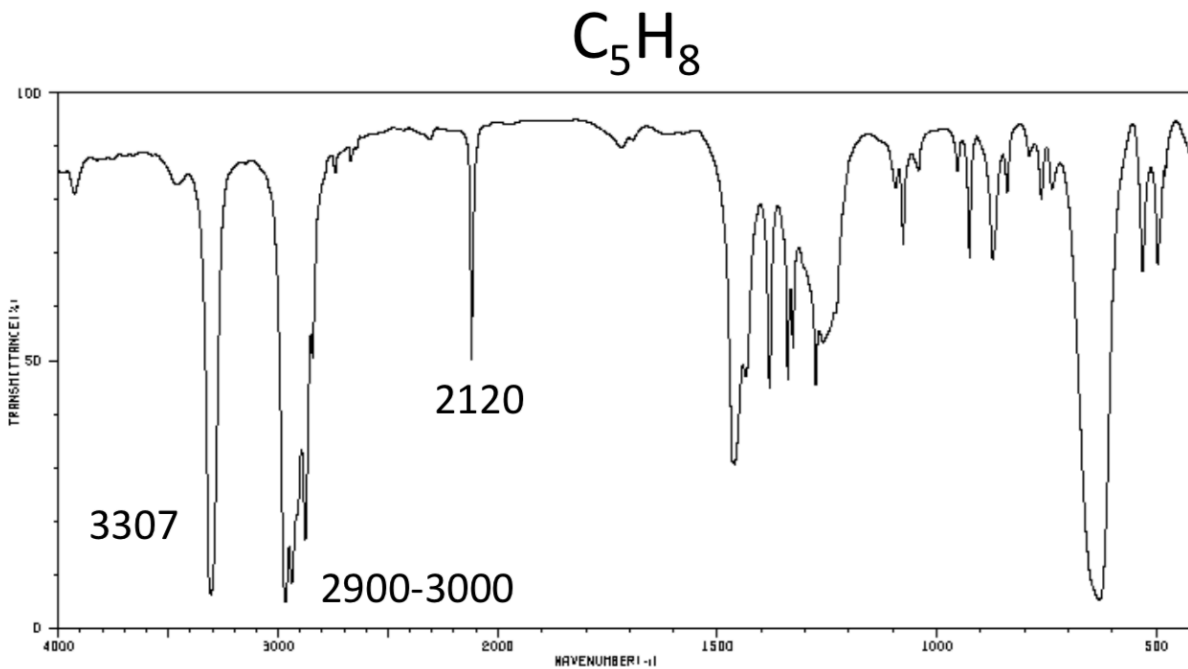
NMR SPECTROSCOPY

- NMR spectroscopy is used to determine the molecular framework of carbon (C) and hydrogen (H).
- It can detect ^{1}H and ^{13}C with different chemical environments

THOERY OF NMR

- charged rotating sphere creates magnetic angular momentum **p**. Normally: **p** is randomly distributed

- In the presence of an external field B$_0$, **p** aligned with B$_0$
- Only nucleus with l ≠ 0 are NMR active
- Nuclei that are commonly detected in NMR: ^{1}H, ^{13}C, ^{19}F, ^{31}P (l=1/2), ^{15}N (l=3/2)
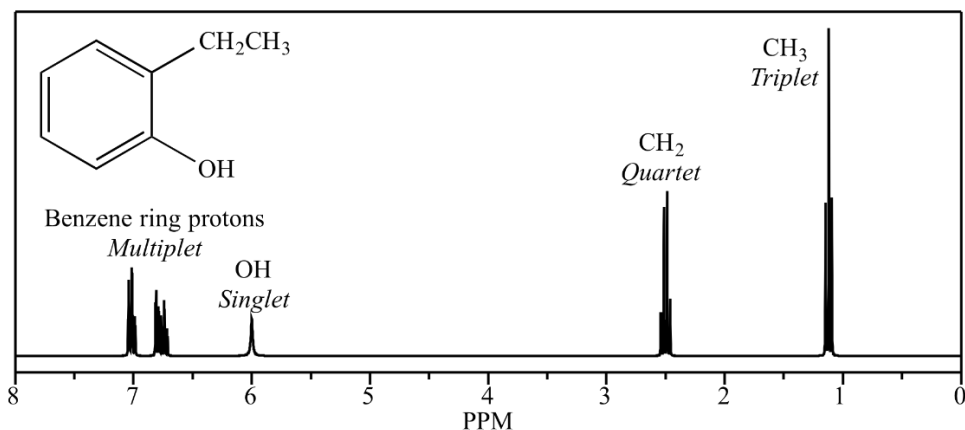
^{1}H NMR

- l = ½, there are 2 energy levels of spin
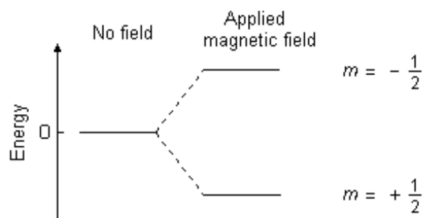
- m = -1/2: spin opposite to B$_0$, m = 1/2: spin in the same direction as B$_0$
- The energy difference:

$$\Delta E_l = E_{-\frac{1}{2}} - E_{+\frac{1}{2}} = \gamma B_0 \frac{h}{2\pi}$$

- When spin at m = ½ absorb radio-frequency energy, it will be excited to m = -1/2, this absorption/emission can be detected by the computer.
- Sensitivity of NMR: depends on the population difference between m=1/2 and m=-1/2: very small for most nuclei.
  Solution: use very high B$_0$ (usually 300-500 MHz)

- Three important aspects of ^1H NMR spectrum:
  - chemical shift → chemical environment
  - integration → relative number of protons
  - coupling → number of neighboring protons

CHEMICAL SHIFT

- Electrons around nucleus create a small magnetic field which oppose the external B_0 → nucleus feels less of the external B_0 → smaller energy difference → absorb at lower radio frequency.
- Nucleus with more electrons around: lower v (Hz/ppm) → shielded (upfield)
- Nucleus with less electrons around: higher v (Hz/ppm) → deshielded (downfield)
- Reference point: TMS (trimethylsilane) in ^1H NMR.
- Chemical shifts are reported as ppm values. The values are independent of the field strength
- Chemical shift = [v_{sample} (Hz) − $v_{reference}$ (Hz)] / $v_{spectrometer}$ (MHz) = ppm
- The chemical shift of a proton depends upon its <u>chemical environment</u>