INTRODUCTION TO ORGANIC SPECTROSCOPY

WHAT IS SPECTROSCOPY??

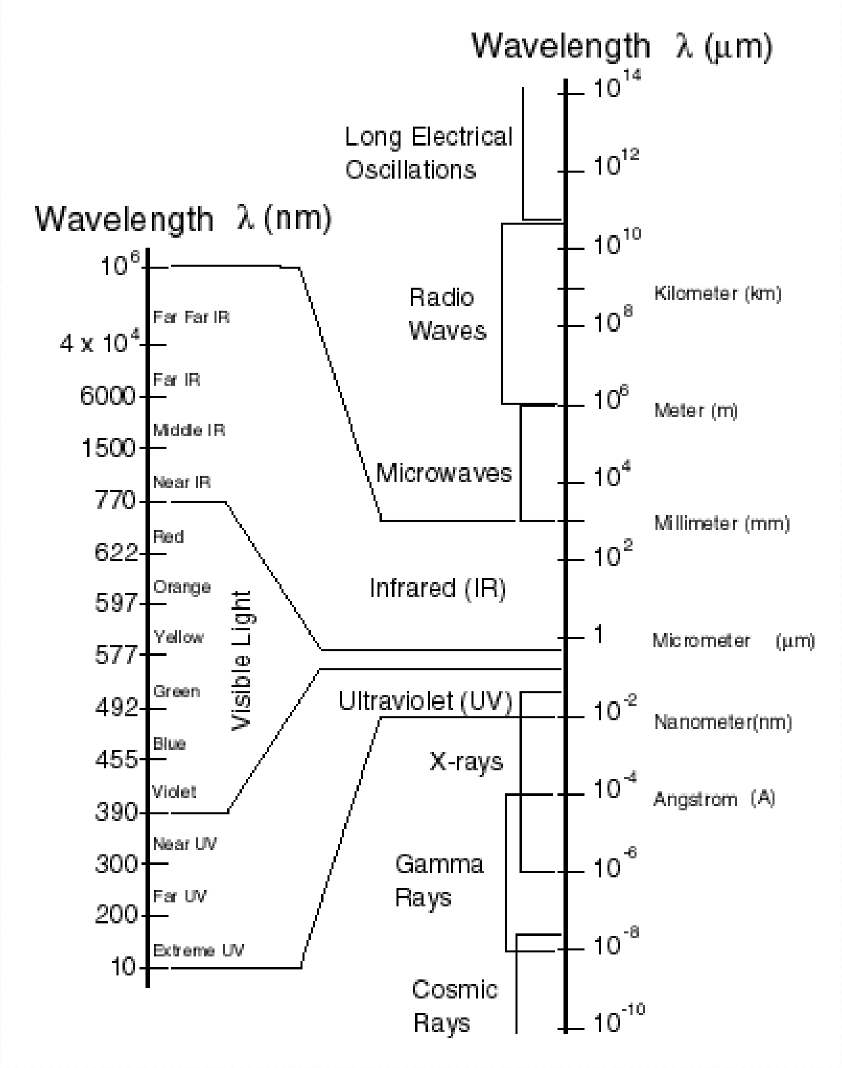
Spectroscopy: The study of the interaction between radiation and matter (i.e. molecules/atoms)

Spectrometry: The measurement of these interactions

Every molecule has it own unique set of spectra. While similar molecules will have some spectra that look similar or near identical, there will be one spectrum that will distinguish them.

The trick is to know what pieces of the puzzle the different methods reveal, as well as what their limitations are.

ELECTROMAGNETIC SPECTRUM



Different effects observed in different areas

- UV – electronic transitions
- IR – bond vibrations
- Microwaves – rotational motion
- Radiowaves – nuclear spin transitions

TECHNIQUES AND WHAT THEY TELL US:

- **Four primary techniques since 1960's**
  - **1. NMR – Nuclear Magnetic Resonance**
  - **2. IR – Infrared**
  - **3. MS – Mass Spectrometry**
  - **4. UV–Vis – Ultraviolet–Visible**
- **Nondestructive (except MS), require very small amounts, <1 mg in many cases.**
- **What information do they give?**

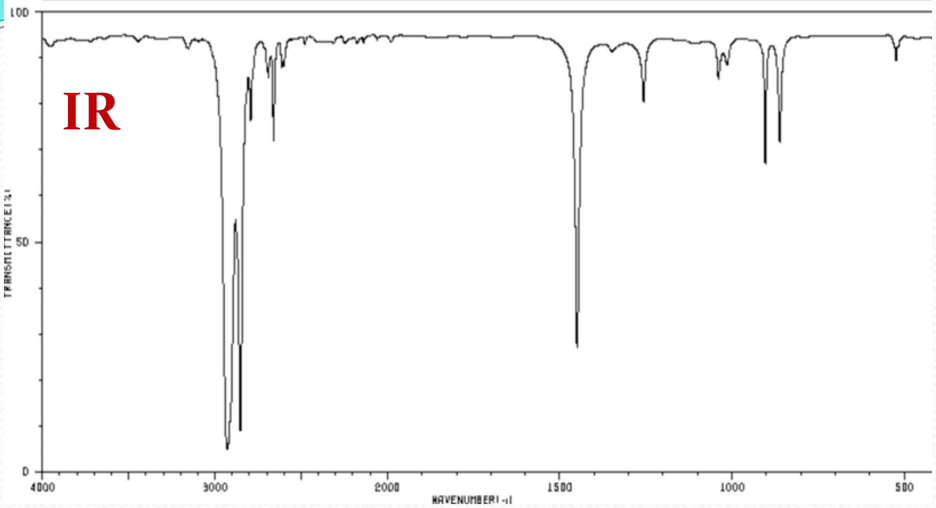
1. IR & UV–Vis: presence (in some cases, absence) of functional groups, limited information about connectivity

2. MS: molecular weight → formula, some information about functional groups, limited information about connectivity

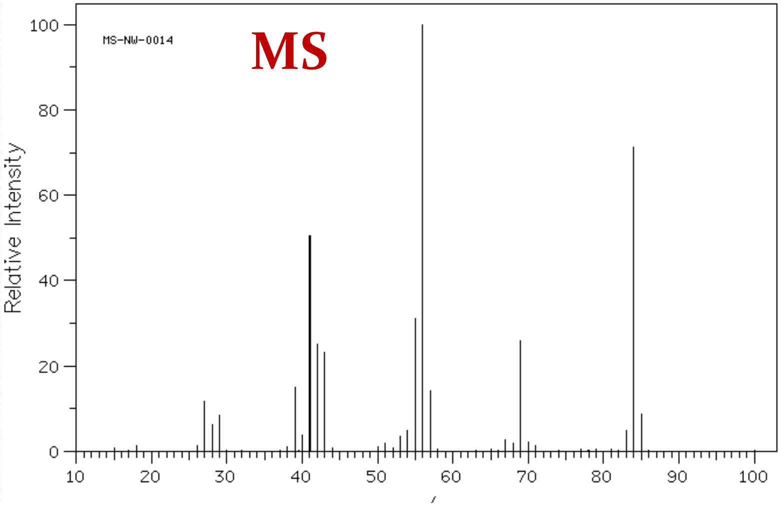
3. NMR (1H, 13C, 2D techniques): further information about function groups, ***connectivity***

- **Most useful for compounds under 1000 amu, but larger weights can be examined as well, but more complicated**

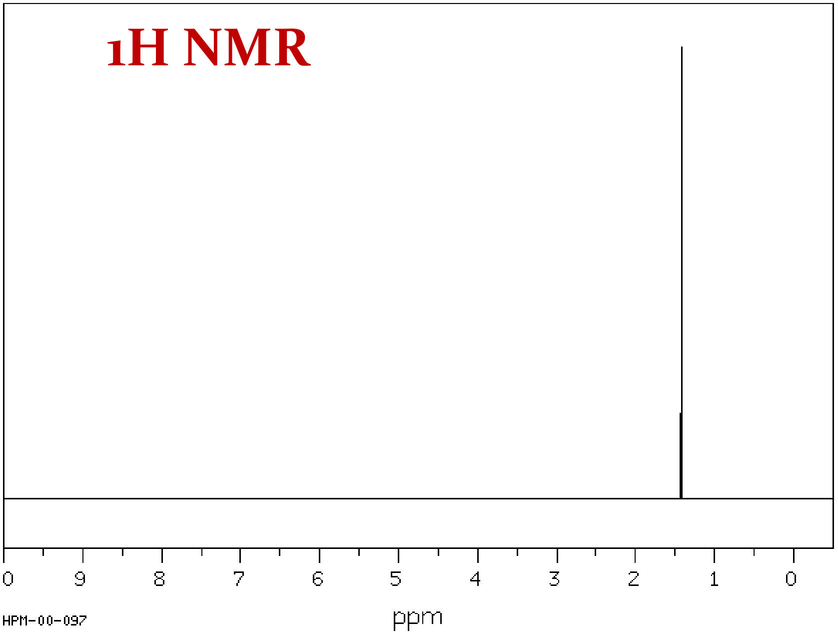
OVERVIEW OF METHODS



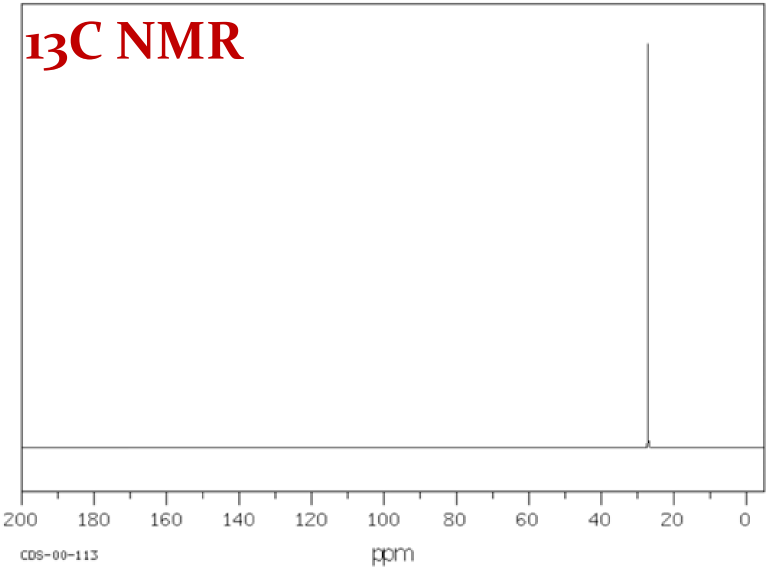
IR



MS



1H NMR

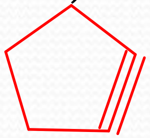


13C NMR

Cyclohexane

WHAT DO YOU NEED FOR SUCCESS??

1. Knowledge about organic structures
   - i. general bonding principles: i.e degree of unsaturation
   - ii. need to know common functional groups
   - iii. need to know what structures are especially stable or unstable (you may be able to form it in situ, but can it actually be isolated?)



   - iv. moieties that easily convert to something else:

2. Apply systematic approach
3. Knowledge of how to interpret spectral trace
4. Being able to use multiple pieces of data (IR, MS, NMR, UV/Vis) to confirm/remove possible structures and be able to return to them repeatedly

GENERAL FLOW FOR SOLVING STRUCTURES

Molecular weight/formula

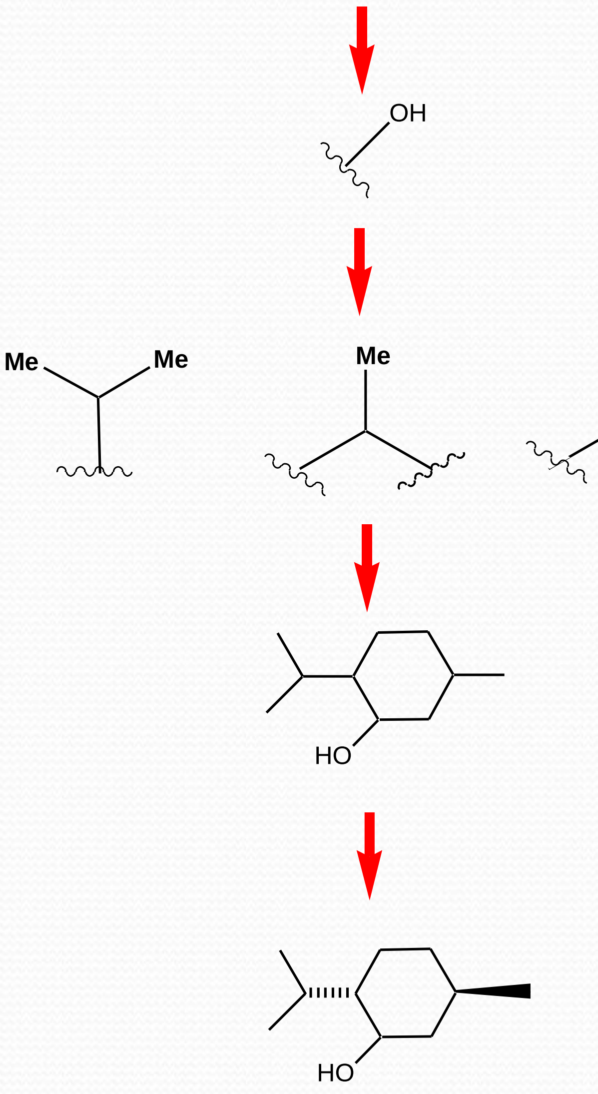
Functional groups

Carbon connectivities (substructures)

Positions of functional groups within framework (gross structure)

Stereochemical issues

$C_{10}H_{20}O$
Exact Mass: 156.1514
Molecular Weight: 156.2652



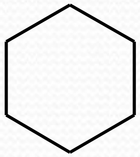
INDEX OF HYDROGEN DEFICIENCY (IHD)

HDI (or UN) = Hydrogen deficiency index (or unsaturation number)

Saturated Alkanes = C_nH_{2n+2}

C_6H_{14}
Hexane

C_6H_{12}
Hexene



C_6H_{12}
Cyclohexane

Rings & Double Bonds require losing 2 H's

What about C_7H_{10}?
(2 x 7) + 2 = 16 H's needed for saturated system
(16–10)÷2 = 3 degrees of unsaturation,
So; 3 rings and/or double bonds

Things to keep in mind:
- smallest ring is 3 atoms
- need at least 4 atoms for bicyclic structure
- aromatics require 4 unsaturations (3 double bonds, 1 ring)

DETERMINATION OF IHD

- **The Index of Hydrogen Deficiency (IHD), is a count of how many molecules of H_2 need to be added to a structure in order to obtain the corresponding saturated, acyclic species. Hence it takes a count of how many rings and multiple bonds are present in the structure, so IHD can also be thought of as (multiple bonds + rings) or (p + r).**
- **When you look at a structure, just count them up (but take care not to count any rings twice !) If you have a molecular formula, $C_cH_hN_nO_oX_x$, then the following equation can be derived:**
- **$IHD = 0.5 * [2c+2-h-x+n]$**

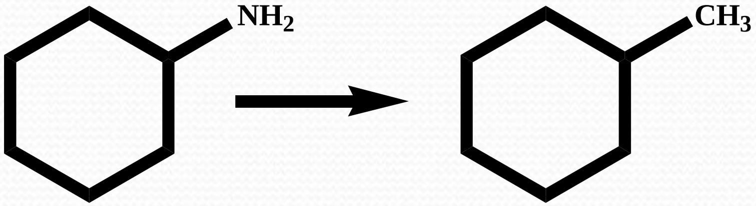
WHERE DOES THIS EQUATION COME FROM?

- Well, the maximum number of hydrogen *atoms* for "c" carbon atoms is 2c+2 (think of the formula of saturated hydrocarbons such as ethane, propane etc.).
- From this number, subtract the "h" hydrogens that you have.
- Since, like hydrogen, a halogen only forms one bond, then they can be treated as if they are hydrogens, so subtract them as well.
- Oxygen forms two bonds, therefore it has no impact (compare H count for methane, CH_4, and methanol, CH_3OH).
- Nitrogen forms three bonds. This means for "n" nitrogens, "n" extra hydrogen atoms are needed (compare the H count for methane, CH_4, and methyl amine, CH_3NH_2), therefore, add "n".
- The factor of 0.5 accounts for us counting H *atoms*, but adding hydrogen, H_2 , *molecules*. OK ?
- Determining the IHD for molecules can be useful for the following reasons:
- Seeing what types of structural units may be possible
- Quickly checking structures to see if they fit the molecular formula rather than simply counting H (when a mistake is possible)

DETERMINATION OF IHD

What about formulas with heteroatoms?

- **Oxygen** – ignore $CH_3CH_2OH \rightarrow CH_3CH_2\text{–}H$ (Also ignore S)
- **Halogen** – Replace by H: $CH_3CH_2Cl \rightarrow CH_3CH_2\text{–}H$
- **Nitrogen** – Replace by CH



$C_6H_{13}N \longrightarrow C_{17}H_{14}$

For C7, 16 H's needed for saturation

14 H's are present

$$\frac{16 - 14}{2} = 1 \text{ Unsaturation}$$

NB: Treat P & B as N

SPECTROSCOPY– RADIATION TERMINOLOGY

- **Wavelength (λ):** length between two equivalent points on successive waves
- **Wavenumber :** the number of waves in a unit of length or distance per cycle - reciprocal of the wavelength
- **Frequency (ν):** is the number of oscillations of the field per second (Hz)
- **Velocity (c):** independent of wavelength – in vacuum is 3.00 x 1010 cm/s (3.00 x 108 m/s)
- **Photon (quanta):** quantum mechanics nature of light to explain photoelectric effect

SPECTROSCOPY - RELATIONS

- **Wavelenght $\lambda = c/\nu$**

  Where: λ (cm); ν (Hz; s-1); c = light velocity
- Units used for wavelength:

  Å = angstrom = 10^{-10} m
  nm = 10^{-9} m
  µm = 10^{-6} m

- **Energy $E = h\nu$**

  Where: h = Planck's constant – 6.62 x 10-34 Js

Proportionality constant : When $\nu = c/\lambda$ is substituted in the last equation we obtain:

$$E = hc/\lambda$$