

Introduction to Organic Spectroscopy

Chem 4010/5326:
Organic Spectroscopic Analysis

What is spectroscopy??

From Wikipedia

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

Spectrometry: The measurement of these interactions

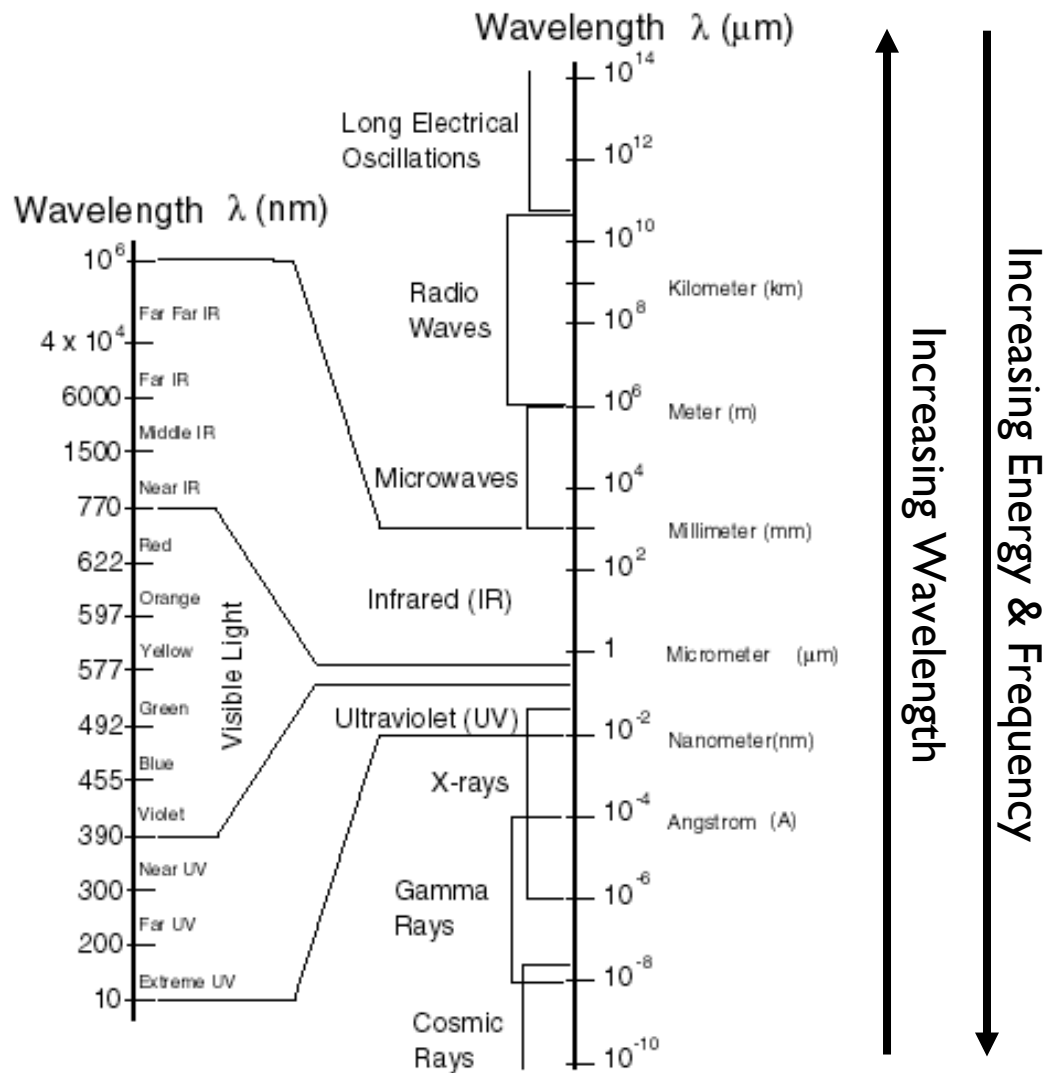
Every molecule has its own unique set of spectra. While similar molecules will have some spectra that look similar or near identical, there will be one spectrum that will distinguish them.

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

THIS CLASS!!



Electromagnetic spectrum



Different effects observed in different areas

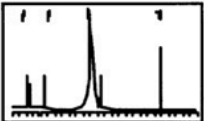
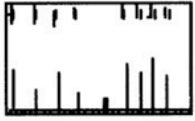
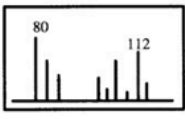

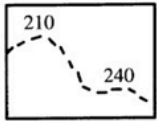


- UV – electronic transitions
- IR – bond vibrations
- Microwaves – rotational motion
- Radiowaves – nuclear spin transitions

Taken from: <http://www4.nau.edu/microanalysis/Microprobe/Xray-Spectrum.html>

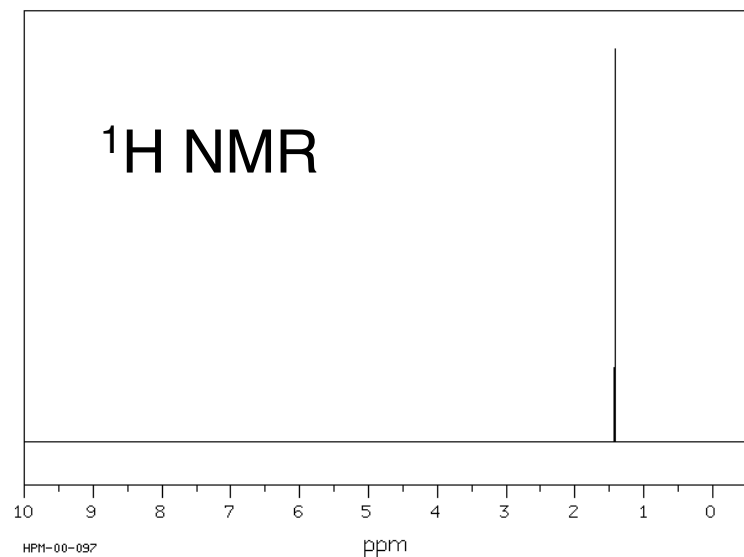
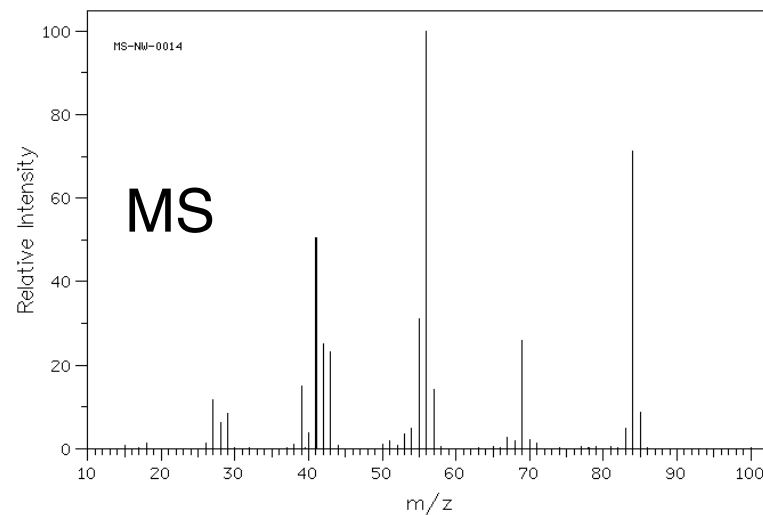
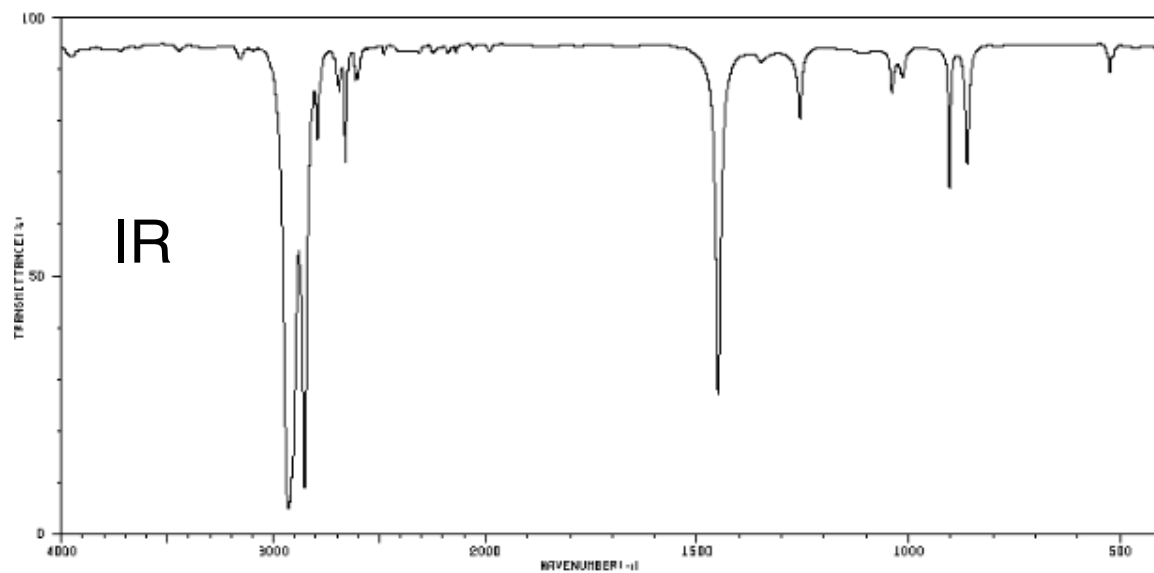
Techniques and what they tell us

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

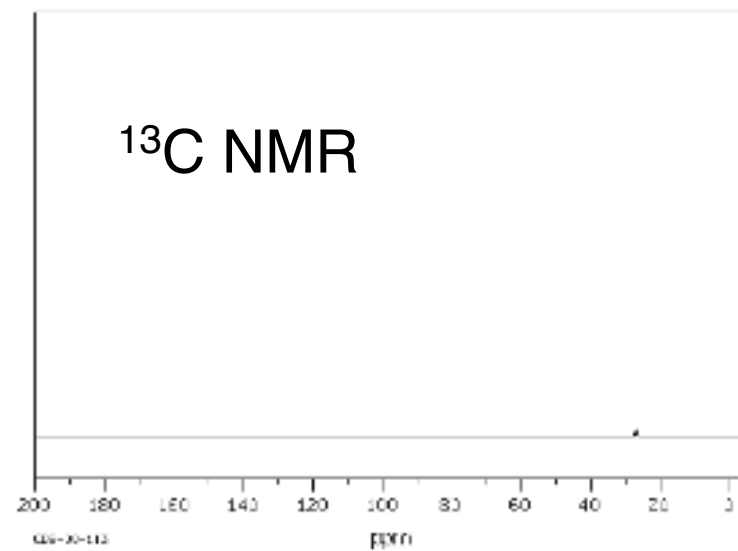
Overview of methods

	<i>H-1</i>	<i>C-13</i>	<i>MS</i>	<i>IR/RAMAN</i>	<i>UV-VIS</i>	<i>ORD/CD</i>	<i>X-RAY</i>
•Radiation type	RF	RF	Not relevant	IR	UV to visible	UV to visible	X-ray
•Spectral scale	0-15 ppm	0-220 ppm	50-4000 amu	400-4000 cm ⁻¹	200-800 nm	185-600 nm	Not relevant
•Average sample	≅ 1 mg	≅ 5 mg	< 1 mg	< 1 mg	< 1 mg	< 1 mg	Single crystal
•Molecular formula	Partial	Partial	Yes	No	No	No	Yes
•Functional groups	Yes	Yes	Limited	Yes	Very limited	Very limited	Yes
•Substructures	Yes	Limited	Yes	Limited	Limited	No	Yes
•Carbon connectivity	Yes	Yes	No	No	No	No	Yes
•Substituent regiochemistry	Yes	Yes	No	Limited	No	No	Yes
•Substituent stereochemistry	Yes	Yes	No	Limited	No	No	Yes
•Analysis of isomer mixtures	Yes	Yes	Yes (by GC/MS LC/MS)	Yes (by GC/IR)	No	No	Yes (if separate)
•Purity information	Yes	Yes	Yes	Yes	Limited	Limited	Limited
•What is measured	Peak areas Chemical shifts Coupling relaxation	Chemical shifts Coupling relaxation	Singly or multiple charged ions	Vibrational transitions	Electronic transitions	[α]	Relative atom positions <i>R/S</i> absolute stereochemistry
•Typical units	δ (ppm)	δ (ppm)	<i>m/z</i>	cm ⁻¹	nm	nm	-
•Typical representations							

Amount of information not the same



Cyclohexane



What do you need for success??

1. Knowledge about organic structures

i. general bonding principles including stereochemistry

i.e. NO C's with five+ bonds

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?)

e.g.



iv. moieties that easily convert to something else

e.g.



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

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

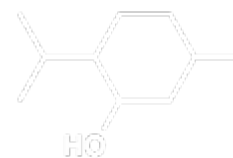
Functional groups



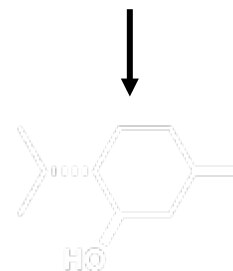
Carbon connectivities (substructures)



Positions of functional groups within framework (gross structure)



Stereochemical issues



Determination of HDI

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

****Saturated alkane = C_nH_{2n+2} ****



C_6H_{14}



C_6H_{12}



C_6H_{12}

Rings & Double Bonds require losing 2 H's

What about C_7H_{10} ?

$(2 \times 7) + 2 = 16$ H's needed for saturated system

$(16 - 10) \div 2 = 3$ degrees of unsaturation

\therefore 3 rings and/or double bonds

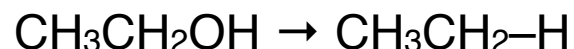
Things to keep in mind:

- smallest ring is 3 atoms
- need at least 4 atoms for bicyclic structure
- aromatics require 4 unsaturations (3 double bonds, 1 ring)

Determination of HDI

What about formulas with heteroatoms?

Oxygen – ignore



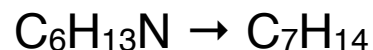
Halogen – Replace by H



Also ignore S

Treat P & B as N

Nitrogen – Replace by CH

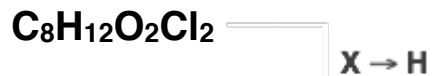


For C₇, 16 H's needed for saturation

14 H's are present

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

Some examples



X → H



ignore O_2



$$HDI = \frac{18 - 14}{2} = 2$$

2 rings, or 2 double bonds,
or
1 ring & 1 double bond



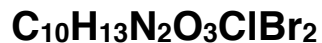
X → H



N → CH



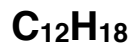
$$HDI = \frac{18 - 6}{2} = 6$$



X → H



$N_2 \rightarrow C_2H_2$
ignore O_3



$$HDI = \frac{26 - 18}{2} = 4$$

A Crash Course in Interpretation

- Refresher on basic interpretation of IR and NMR spectra
- Should be a review from undergraduate courses
- Much will be covered later in greater detail
- Important aspects you may (will) need for the first exam and/ or problem set

A Crash Course in Interpretation

Infrared

- If a peak is present then the corresponding functional group is present
- Many times, if the peak is not there than the functionality is also absent, BUT not always true

KEY STRETCHES



3600-3200 cm^{-1} (broad)



1850-1640 cm^{-1}
(exact position depends
on type of carbonyl)



3300-2700 cm^{-1}



1680-1580 cm^{-1}
(exact position depends
on structure)



2300-2100 cm^{-1}
(internal alkynes
difficult to see)

Fingerprint
Region

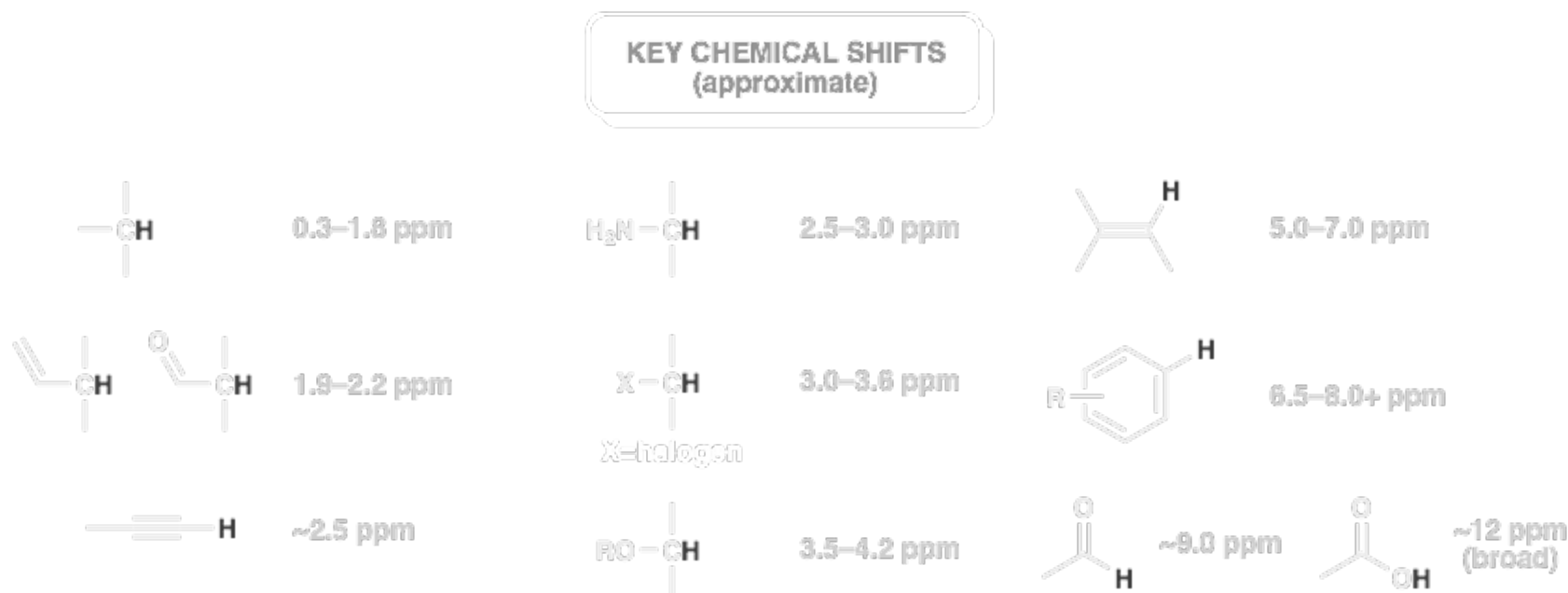
1600-600 cm^{-1}
(unique for each compound,
some useful peaks)

Know these ranges!!

A Crash Course in Interpretation

^1H NMR

- Integrals tell how many protons of that type there are
- Splitting tells us how many protons are next door (n+1 rule)
doublet (2 peaks, 1 proton), triplet (3 peaks, 2 protons), quartet (4 peaks, 3 protons), etc.

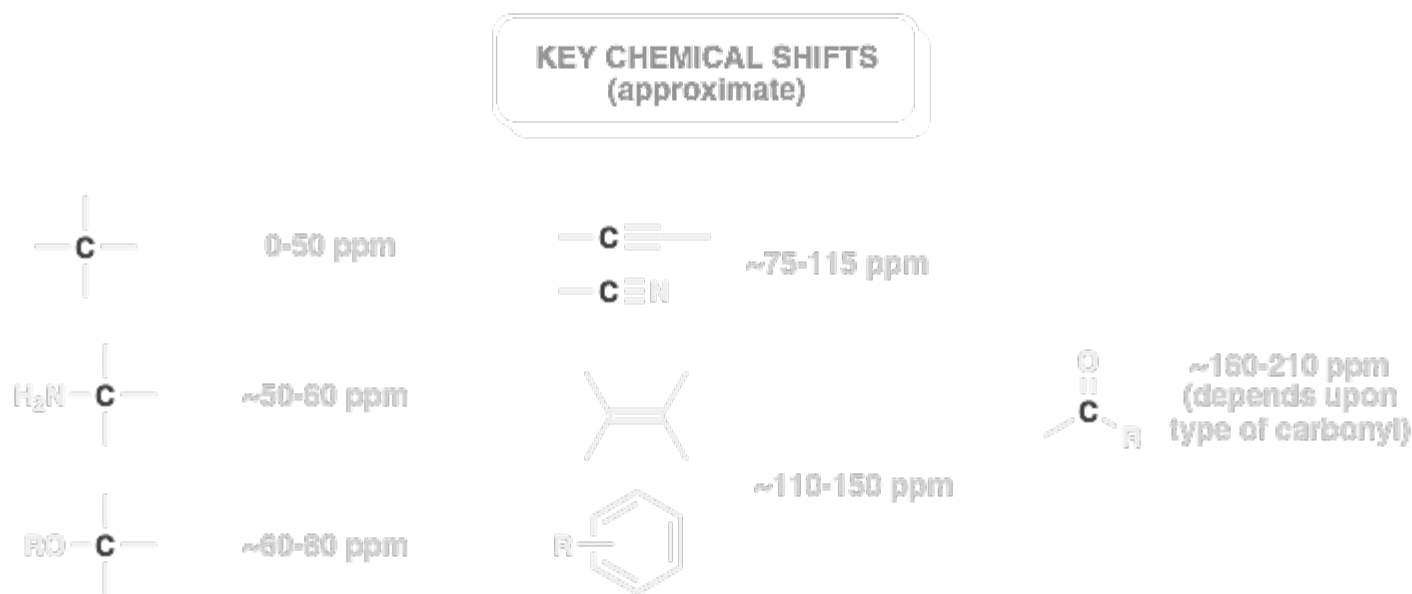


Know these ranges!!

A Crash Course in Interpretation

^{13}C NMR

- Usually can't integrate
- Pay attention to the number of carbon/proton signals and formula
⇒ symmetry in molecule



Know these ranges!!