

Objective 4. Determine (characterize) the structure of a compound using IR, NMR, MS.

Skills: Draw structure

IR: match bond type to IR peak

NMR: ID number of non-equivalent H's, relate peak splitting to number of H's on adjacent C

MS: ID molecular ion peak = molecular weight

Key ideas:

Given structure, determine # of non-equivalent H's.

Given structure, determine multiplicity.

Given simple organic compound, draw H NMR spectrum (# of peaks and splitting).

Given NMR, IR, MS spectra, determine structure.

There Are Many Ways To Identify A Substance

It Is Fairly Easy to Identify A Substance If You Are Given A Few Choices

Objective: Choose an Identification method

You are given a sample of a colorless liquid and told it is either ethanol (C_2H_5OH) or rubbing alcohol ($CH_3CHOHCH_3$). What method would you use to identify this liquid? Give reasons.

- a) IR
- b) Boiling point
- c) Density

Objective: Choose an Identification method

You are given a sample of a colorless liquid and told it is C_4H_{10} . C_4H_{10} has two isomers. What method would you use to determine which isomer of C_4H_{10} you were given? Give reasons.

- a) IR
- b) Boiling point
- c) Density

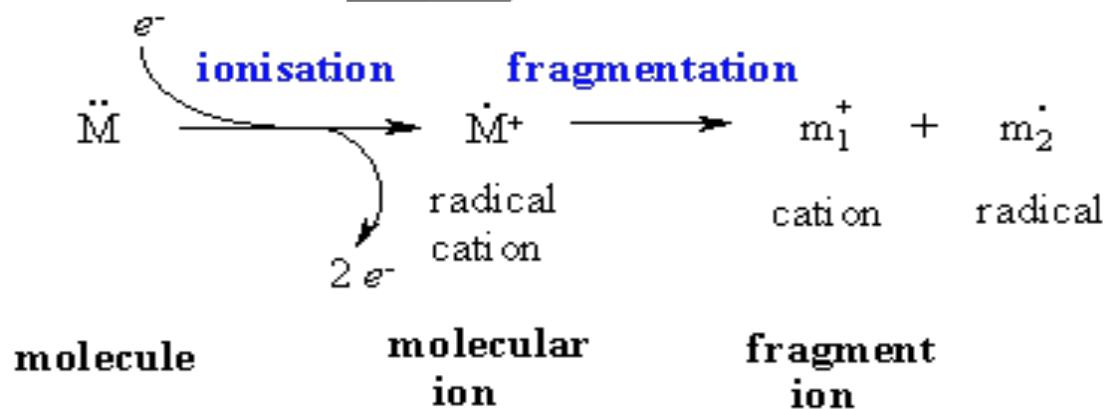
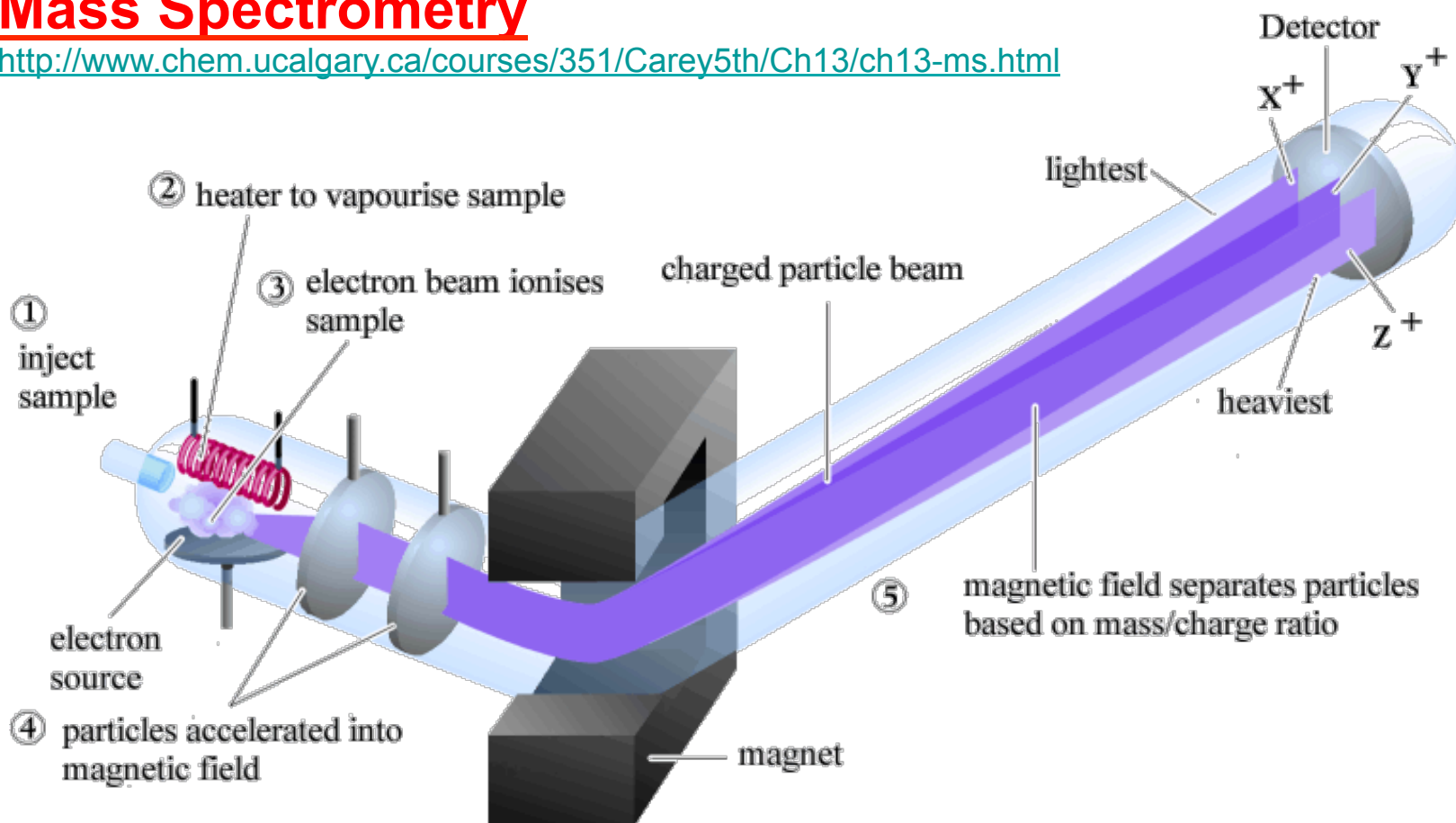


To Determine the Structure of a Compound, IR, NMR, MS, and UV/VIS Are Used

- **IR** (*Infrared Spectroscopy*) Is Used to Identify Bond Types and Functional Groups
- **NMR** (*Nuclear Magnetic Resonance Spectroscopy*) Is Used to Identify The Carbon Skeleton and the Number of H' s Bonded to C
- **MS** (*Mass Spectrometry*) Is Used to Determine the Molecular Weight of a Compound ==> determine chemical formula
- **UV/VIS** (*Ultraviolet/Visible Spectroscopy*) Is Used to Study Conjugated Systems

Mass Spectrometry

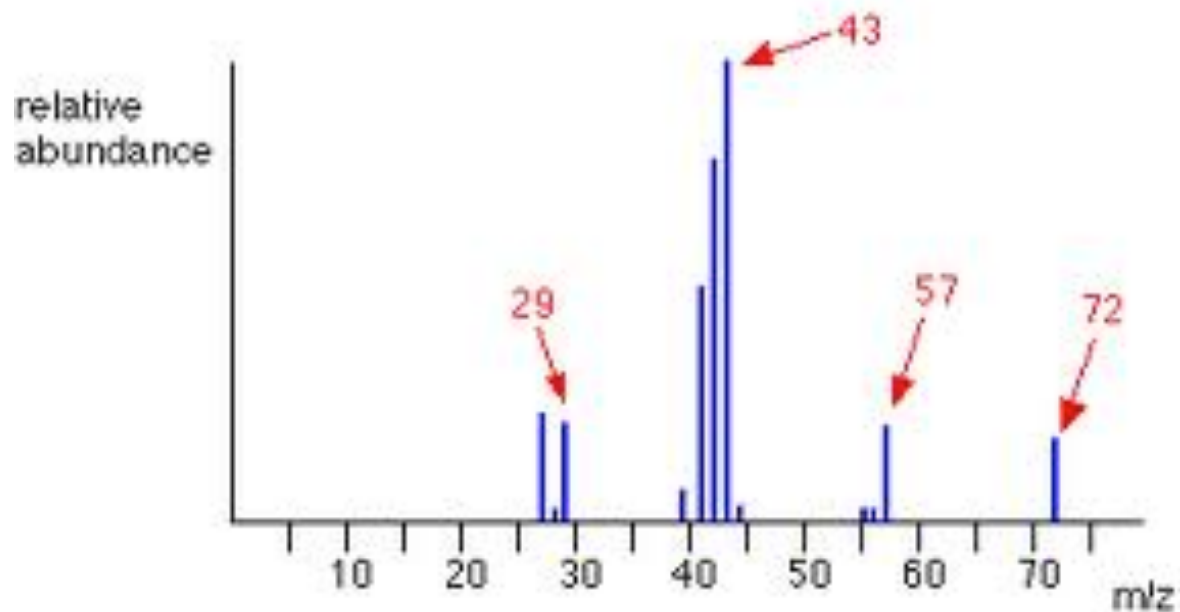
<http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-ms.html>



Mass Spectrometry (MS) - the ***Molecular Ion ($M^{+\bullet}$)*** peak tells ***you the molecular weight***

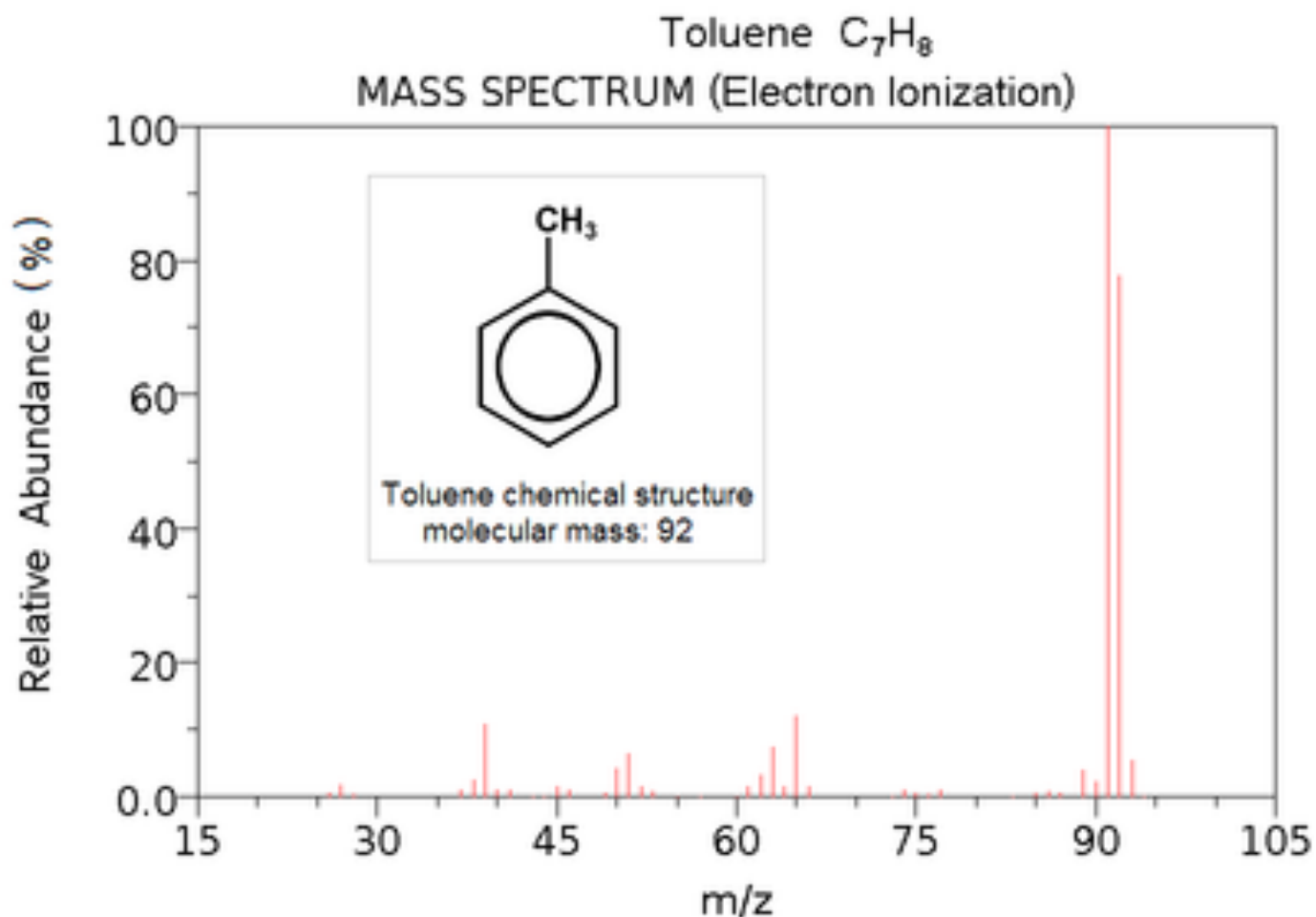
Molecular Ion ($M^{+\bullet}$) peak = peak (often the largest) with highest m/z ratio.

simplified mass spectrum of pentane - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



<http://www.chemguide.co.uk/analysis/masspec/fragment.html>

Which peak is the **Molecular Ion peak**?



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Molecular Weight \implies Chemical Formula

From Chemical Formula \implies determine **Hydrogen Deficiency Index** (HDI) for number of pi bonds or rings

From molecular weight, you can determine the chemical formula of a compound.

E.g., alkane (C_nH_{2n+2}) MW = 16 + 14 (n-1)

Formula Treat X the same as H. Ignore O.	# of π bonds or rings or combo = HDI
C_nH_{2n+2}	0 bonds or rings: alkane
C_nH_{2n}	1 bond (alkene) or 1 ring (cycloalkane)
C_nH_{2n-2}	2 π bonds or rings or combo equaling 2
C_nH_{2n-4}	3 π bonds or rings or combo equaling 3
C_nH_{2n-6}	4 π bonds or rings or combo equaling 4

HDI for compounds with O, N, X

Reduce chemical formula to C_xH_y formula:

- Ignore O
- Treat X (F, Cl, Br, I) like H
- For each N, subtract one H

Examples: C_2H_6O reduces to C_2H_6 so $HDI = 0.5 (6-6) = 0$

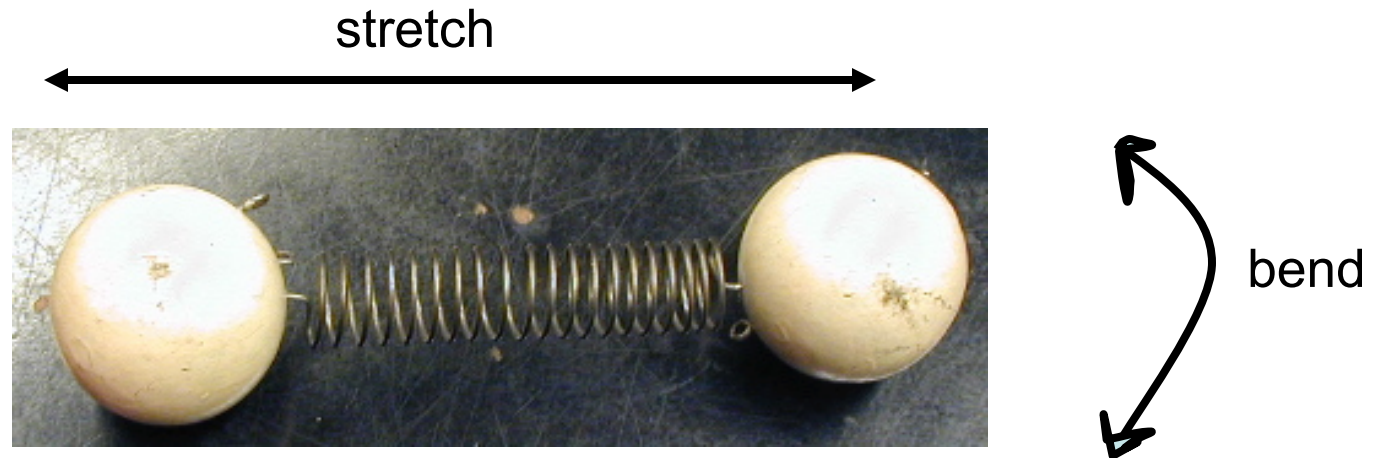
C_3H_7Cl reduces to C_3H_8 so $HDI = 0$

C_2H_7N reduces to C_2H_6 so $HDI = 0$

$HDI = 0.5 (\text{\# of H's in alkane chain} - \text{\# of H's in formula})$

Use $C_n H_{2n+2}$ to determine # of H's in alkane chain

Infrared (IR) radiation causes a bond to *vibrate* (stretch/bend)



http://teacher.pas.rochester.edu/PhysicsDemos/Mechanics/MA_ElasticSolids/MA-01/MA-01.html

Bond Types are determined by IR Spectroscopy

Use an IR Correlation Table to Interpret IR Spectra

	Bond	Base Value, cm⁻¹	Strength / Shape	Comments
1	C=O	1715	s, "finger"	Exact position depends on type of carbonyl
2	O-H	3200-600	s, broad	Broad due to H bonding
3	N-H	3500	m	Can tell primary from secondary
4	C-O	1100-1300	s	Also check for OH and C=O
5	C=C	1650	w alkene m-s aromatic	Alkene w due to low polarity Aromatic usually in pairs
6	C≡C	2150	w, sharp	Most obvious in terminal alkynes
7	C-H	3000 (stretch) 1375 and 1450 (bend)	s m	As hybridisation of C changes sp ³ -sp ² -sp, the frequency increases
8	C≡N	2250	m, sharp	Characteristic since little else around it

Objective: interpret an IR spectrum

When I interpret an IR spectrum, I look at:

3200-3500 cm^{-1} region \implies O-H bond \implies alcohol or _____

1600-1700 cm^{-1} region \implies C=O bond \implies aldehyde or _____
 \implies C=C bond \implies alkene

1100-1300 cm^{-1} region \implies C-O bond \implies _____

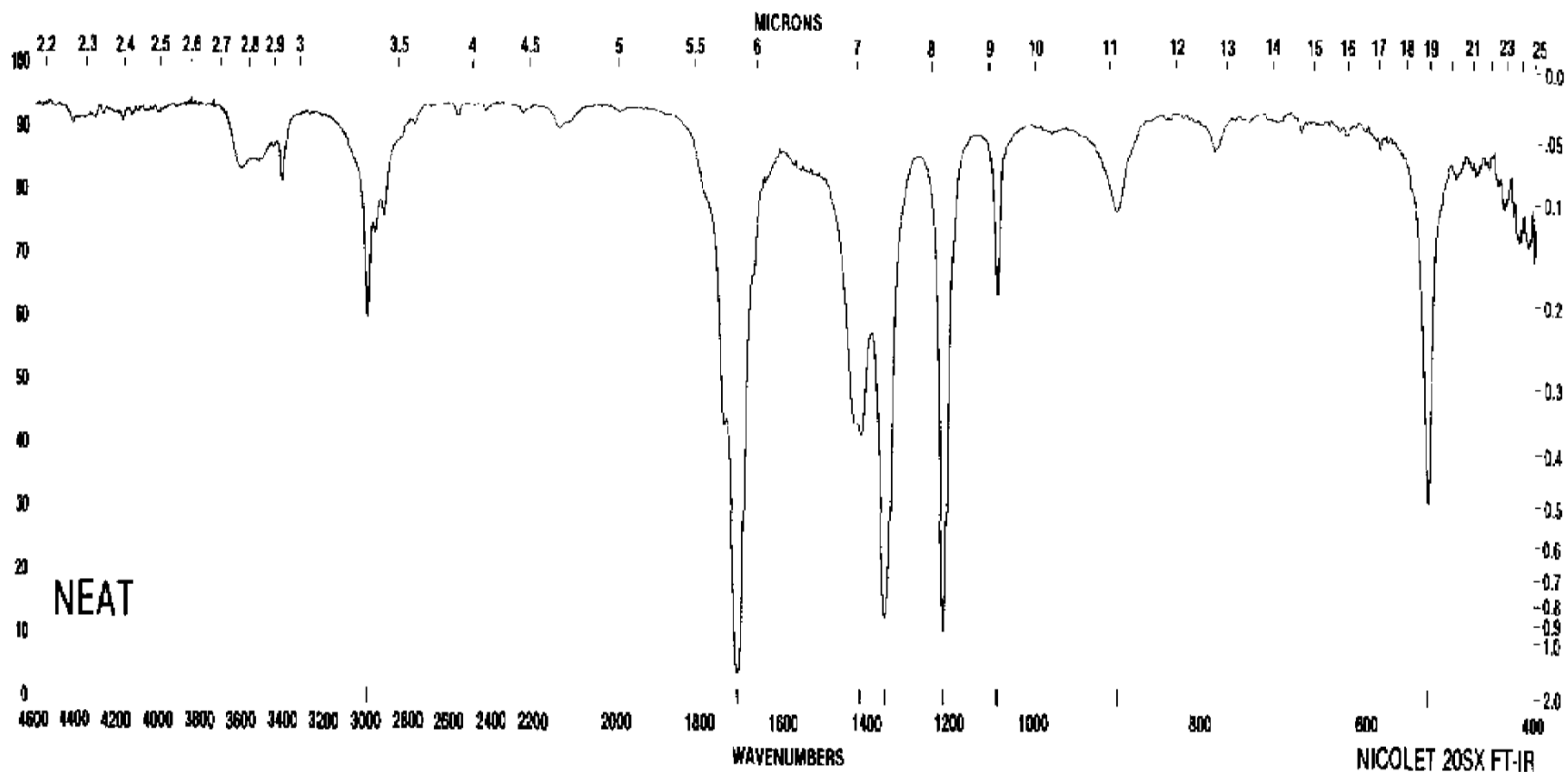
I know most organic compounds have C-H bond at around 3000 cm^{-1} .

> 3000 cm^{-1} \implies alkene, alkyne, or aromatic C-H

< 3000 cm^{-1} \implies alkyl C-H

The IR spectrum of _____ is shown below. The compound is:

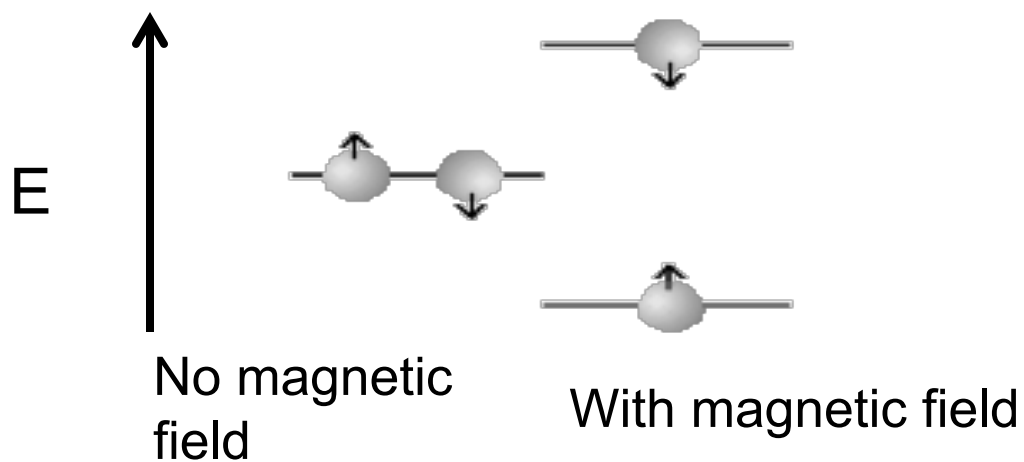
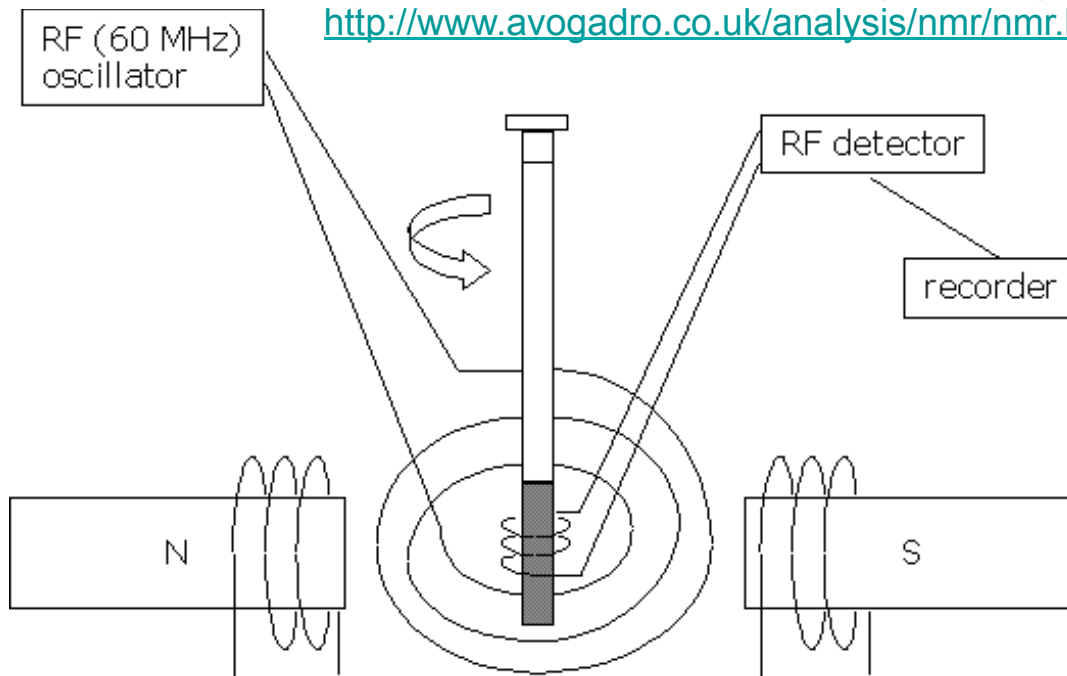
- a) Ethanol
- b) Butane
- c) acetone



<http://www.bluffton.edu/~bergerd/classes/cem222/infrared/oxygen.html>

Nuclear Magnetic Resonance (NMR) spectroscopy

<http://www.avogadro.co.uk/analysis/nmr/nmr.htm>



^1H and ^{13}C Are The Most Common Nuclei Studied Using NMR

Electrons have spin. So do some nuclei. See Nuclear spin:

<http://www.pascal-man.com/periodic-table/periodictable.html>

NMR basics:

<http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-0.html>

<http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm>

Doing an NMR experiment:

http://arrhenius.rider.edu:16080/nmr/NMR_tutor/pages/nmr_tutor_home.html

In **^1H NMR**, look at

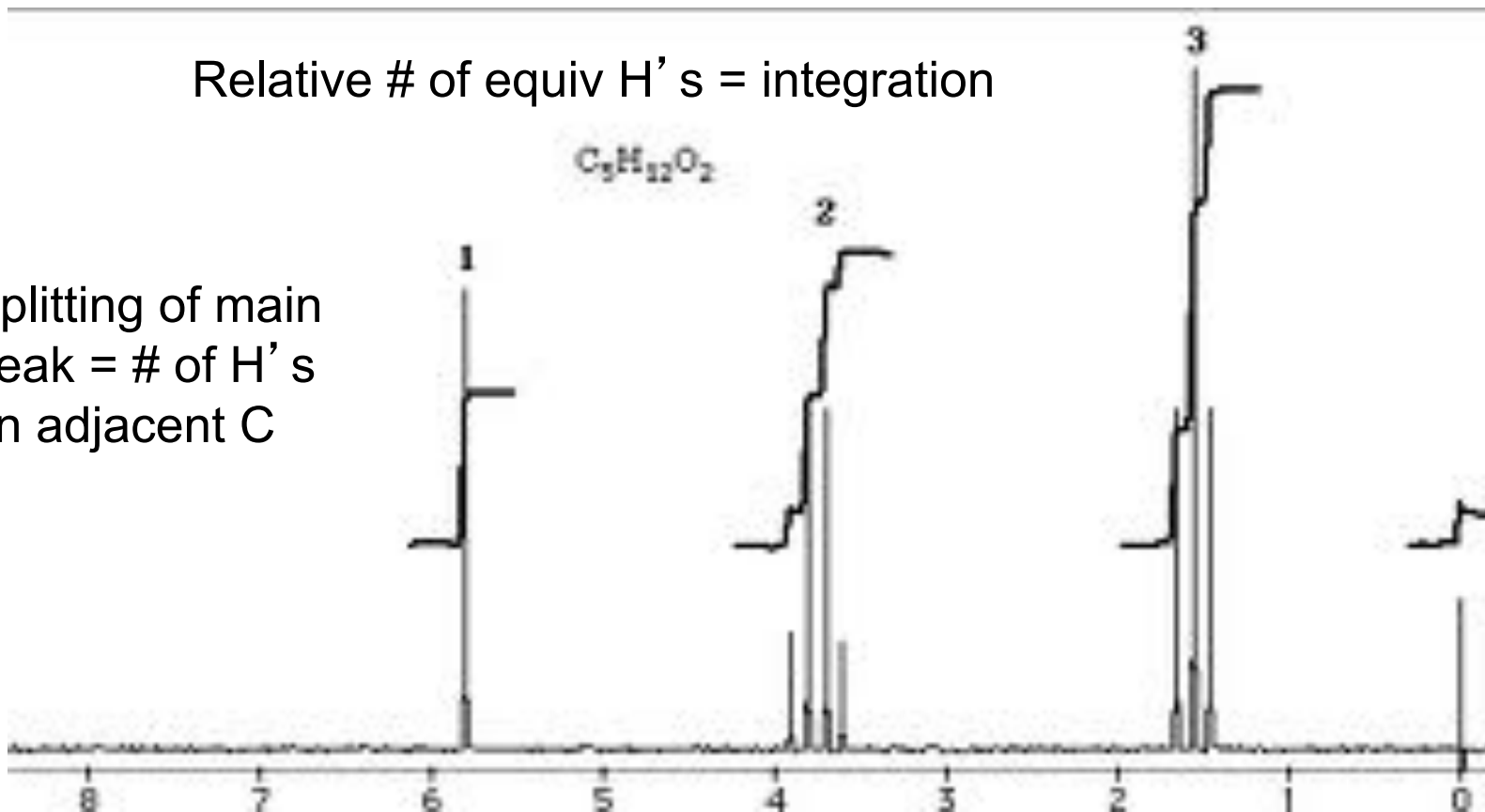
1. ***Number and Location of signal*** (peak) – **equivalent** H' s.
2. ***Intensity of peak*** relative to other peaks - # of H' s bonded to each C (or other atom)
3. ***Multiplicity*** (splitting of main peak into multiple peaks) - # of H' s bonded to adjacent C are “coupled”

^1H nmr spectrum shows:

Relative # of equiv H' s = integration



Splitting of main peak = # of H' s on adjacent C



Downfield -
“deshielded” H' s δ = chemical shift, ppm
Inductive effect

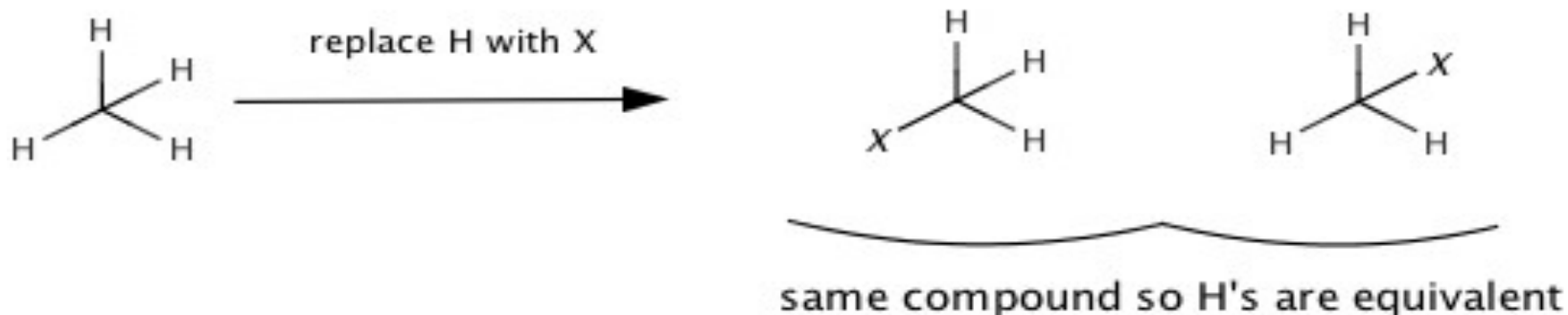
Upfield -
“shielded”
H' s

<http://lsc.ucdavis.edu/~holliste/jim118A/ProtonNMR.Probs.html>

Objective: Determine which H's are **Equivalent** by Replacing H with X

If the 2 structures are the same, then H's are equivalent

E.g., Are the H's in CH_4 equivalent? **YES**

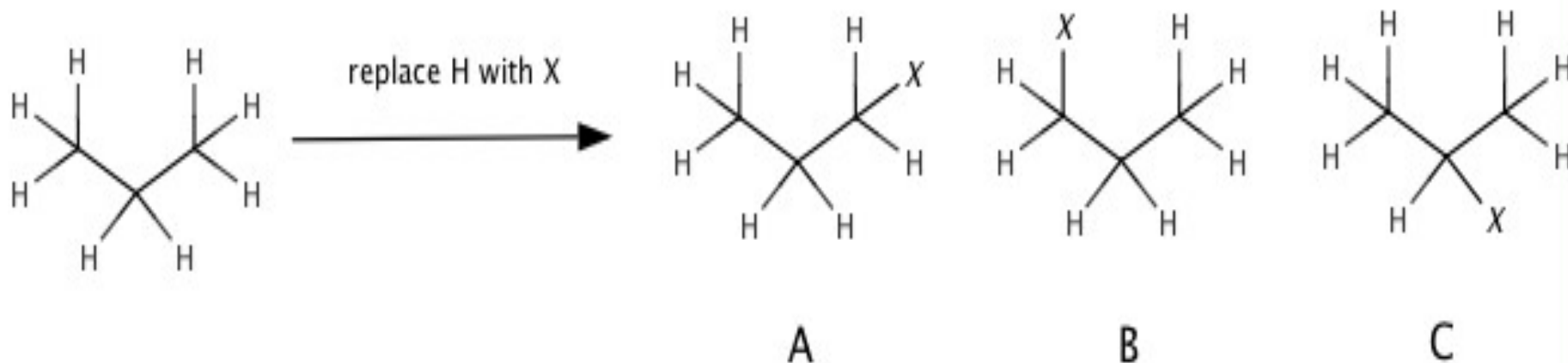


Which H's in C_3H_8 are equivalent?

(i) A and B

(ii) A and C

(iii) B and C



Objective: Given structure, what does the H NMR spectrum look like?

Problem solving method:

- (i) Determine the number of equivalent and non-equivalent H' s (to determine number of peaks and ratio of non-equiv H' s).
- (ii) Determine peak splitting by H' s on adjacent C (3 bonds away) using (n+1) rule, where n = # of equivalent H' s on adjacent C.

1. For CH₄,

a. How many equivalent H' s?

(i) 1

(ii) 2

(iii) 3

(iv) 4

b. How many peaks? (i) 1 (ii) 2 (iii) 3 (iv) 4

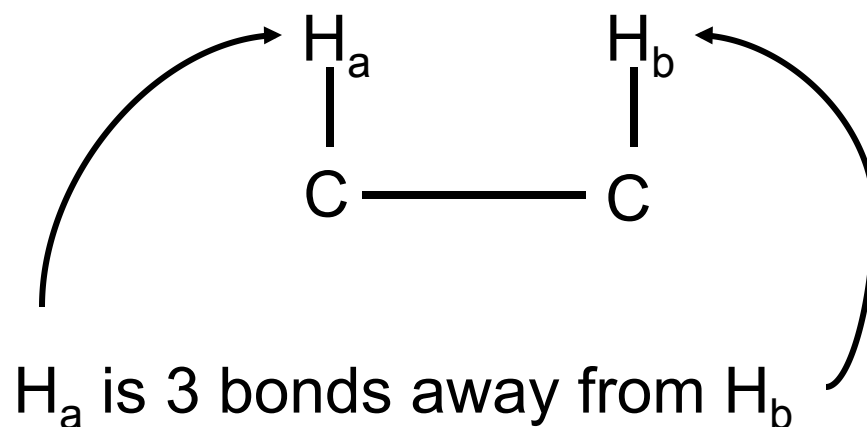
c. If 2 or more peaks, what is ratio of non-equivalent H' s?

d. If 2 or more peaks, what is splitting?

USE ChemDoodle to look at predicted NMR spectrum

A H is affected by a Non-Equivalent H on an Adjacent Carbon

Multiplicity - splitting of main peak into two or more peaks



H_b affects the shielding (environment) around H_a

H_a Signal (peak) is split into two or more peaks:

$n + 1$ rule

where n is the number of equivalent H' 's coupled to H_a signal

For C_3H_8

<http://www.muhlenberg.edu/depts/chemistry/chem201nmrexamples.html>

a. How many non-equivalent H' s?

(i) 1

(ii) 2

(iii) 3

(iv) 4

b. How many peaks? (i) 1 (ii) 2 (iii) 3 (iv) 4

c. If 2 or more peaks, what is ratio of non-equivalent H' s?

d. If 2 or more peaks, what is splitting?

For $\text{C}_2\text{H}_5\text{OH}$

<http://www.muhsenberg.edu/depts/chemistry/chem201nmreexamples.html>

a. How many non-equivalent H' s?

(i) 1

(ii) 2

(iii) 3

(iv) 4

b. How many peaks? (i) 1 (ii) 2 (iii) 3 (iv) 4

c. If 2 or more peaks, what is ratio of non-equivalent H' s?

d. If 2 or more peaks, what is splitting?

For $(\text{CH}_3)_2\text{CO}$

<http://www.muhlenberg.edu/depts/chemistry/chem201nmrexamples.html>

a. How many non-equivalent H' s?

(i) 1

(ii) 2

(iii) 3

(iv) 4

b. How many peaks? (i) 1 (ii) 2 (iii) 3 (iv) 4

c. If 2 or more peaks, what is ratio of non-equivalent H' s?

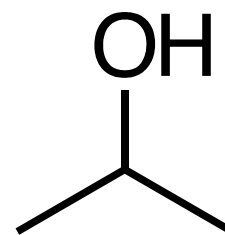
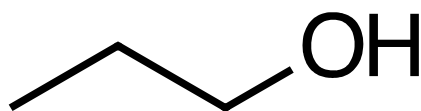
d. If 2 or more peaks, what is splitting?

Can ^1H NMR be used to distinguish between Butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$) and isobutane ($(\text{CH}_3)_3\text{CH}$)?

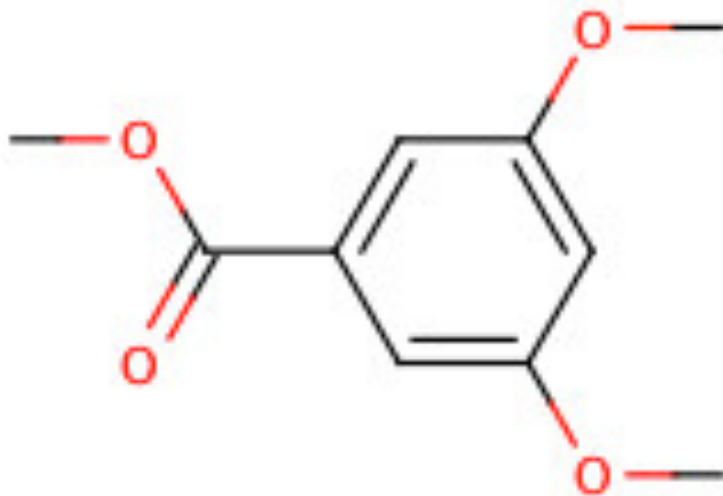


Can you use H nmr to distinguish between the following compounds?

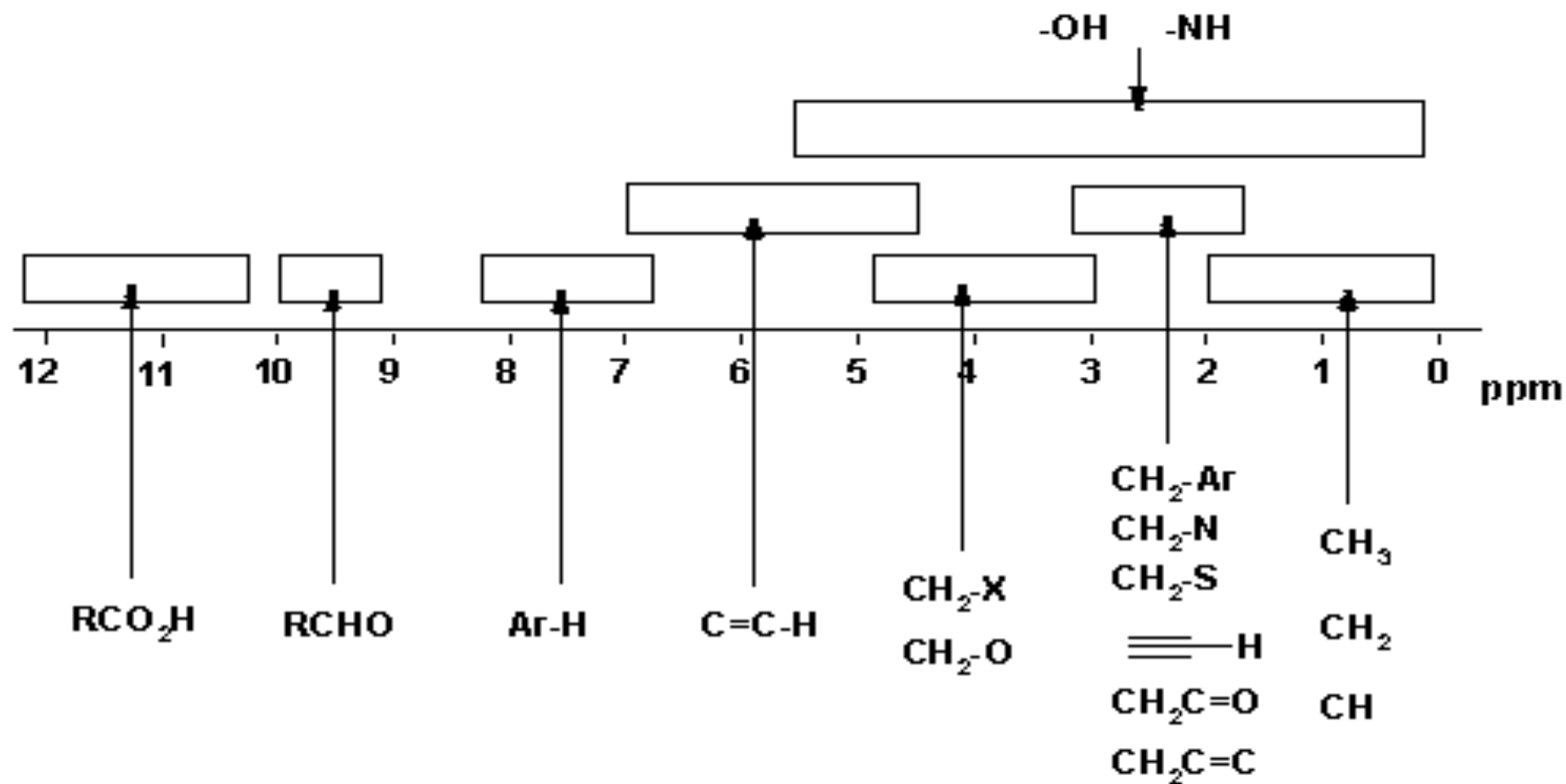
Hint: Determine the number of non-equivalent hydrogens.



How many signals (peaks) will you see in a ¹H nmr spectrum?



Given ^1H NMR Spectrum (and chemical formula), Determine Structure
 ^1H NMR Correlation Table Helps Us Interpret Spectra



Deshielded H
Downfield

Shielded H
Upfield

When I interpret a ^1H NMR spectrum, I look at:

Number of peaks \implies tells me how many non-equivalent H' s
E.g., 2 peaks \implies 2 different types of H' s

Peak integration \implies tells me ratio of non-equivalent H' s
E.g., 2:1 ratio \implies 2:1 or 4:2 or 6:3 ratio of the different H' s

Splitting (multiplicity) of peaks \implies tells me how many H' s on adjacent C

E.g., Peak is split into a quartet \implies 3 H on adjacent C using (n+1) rule so $-\text{CH}_3$ group

Peak is split into a triplet \implies 2 H on adjacent C so $-\text{CH}_2-$ group

Put the puzzle together so the NMR data fit the structure \implies structure solved!

Given ^1H NMR Spectrum (and chemical formula), Determine Structure

C_8H_{18} ; 1 peak at $\delta = 0.9$

How many non-equivalent H' s?

(i) 1

(ii) 2

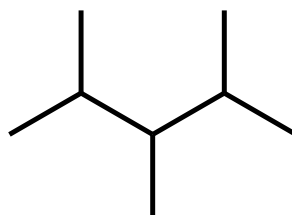
(iii) 3

(iv) 4

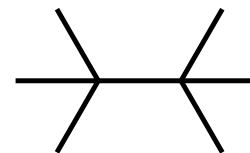
Which structure fits the data?



A



B



C

Given ^1H NMR Spectrum (and chemical formula), Determine Structure

C_8H_{10} ; 3 peaks at $\delta = 1.2$ (triplet, 3 H), $\delta = 2.6$ (quartet, 2 H), $\delta = 7.1$ (broad singlet, 5 H)

How many rings or pi bonds?

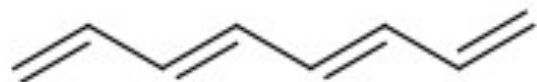
(i) 2

(ii) 3

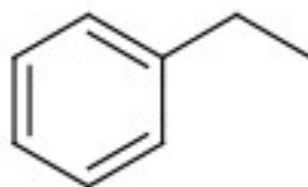
(iii) 4

(iv) 5

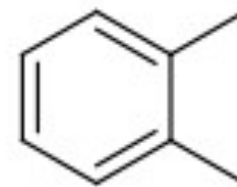
Which structure fits data?



A



B



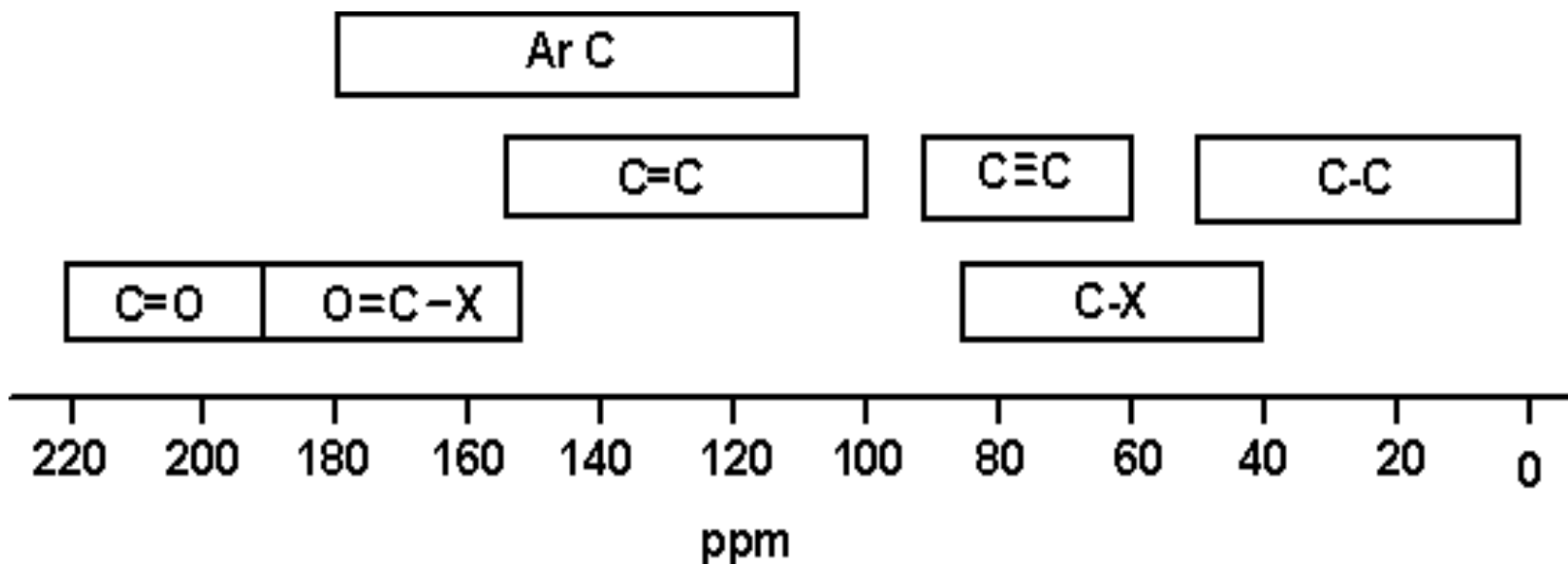
C

^{13}C NMR is a Little Different Than ^1H NMR

In ^{13}C NMR, look at

1. Number and Location of signal (peak) – equivalent C's.
2. ~~Intensity of peak relative to other peaks~~
3. ~~Multiplicity – splitting of main peak into multiple peaks~~

^{13}C NMR Correlation Table



Interpret ^{13}C NMR spectrum: Klein, Ch. 16

Review: Each Characterization Method Gives Different Information

1. a. What information does MS tell you?
 - b. What information does IR tell you?
 - c. What information does ^1H NMR tell you?
 - d. What information does ^{13}C NMR tell you?
2. a. What information does the chemical formula tell you?
 - b. What method tells you about the chemical formula?
3. a. What method tells you whether a pi bond is present?
 - b. Can your method in part 3a tell you whether a ring is present?
 - c. Can your method in part 3a tell you whether a methylene (CH_2) group is next to a methyl group? If not, which method gives you this information?

Structure Characterization Often Requires A Combination of IR, NMR, and MS

1. Determine the structure:

<http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-0.html>

(i) Use H and C nmr, IR, MS spectra:

(ii) Chemical formula: index of H deficiency

a. Spectra Problem #1

b. Interactive Spectroscopy Problem 1

2. Webspectra

<http://www.chem.ucla.edu/~webspectra/>

a. Problem 1

A compound ($C_8H_{10}O$) has the IR and 1H NMR spectra data below.

IR:

Peak	Wavenumber, cm^{-1}	
1	3400	Strong, broad
2	3000	Strong
3	1100	Strong

1H NMR:

Chemical Shift, ppm	Intensity	Splitting
1.6	3	doublet
4.2	1	singlet
4.9	1	quartet
7.5	5	singlet

Draw the structure of this compound.