Introduction to 1D and 2D NMR Spectroscopy

(2) 1D Spectrum Interpretation

Lecturer: Weiguo Hu

7-1428

weiguoh@polysci.umass.edu

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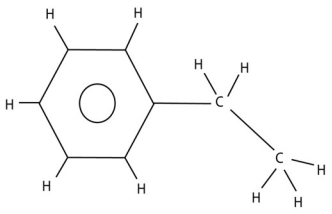
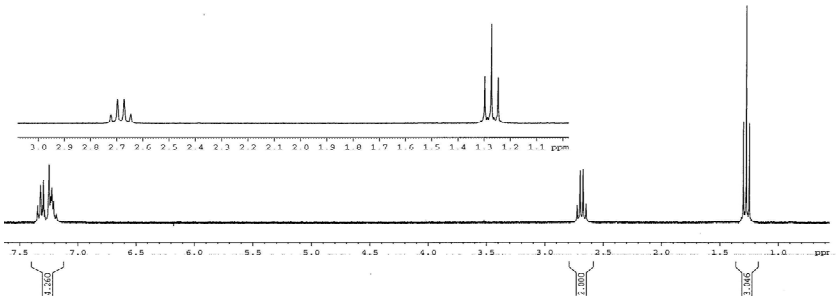
1

Important Concepts

- Chemical shift
  - Shielding effect due to electrons
- J-coupling
  - Due to nucleus-nucleus interactions
    - ^{1}H-^{1}H coupling
    - ^{1}H-^{13}C coupling

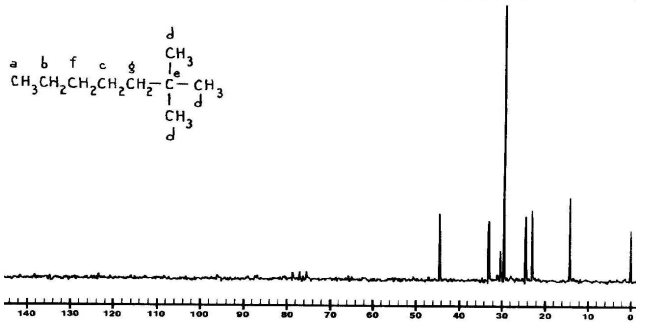




2

Chemical Shift

- ^{1}H typical spectrum range: 0-10ppm
- ^{13}C typical spectrum range: 0-200ppm
  - ^{13}C chemical shift is more useful than ^{1}H
- Heavier nuclei have larger CS range
  - e.g. ^{205}Tl has a chemical shift range of 7000ppm
- Chemical shift reference (0 ppm):
  - ^{13}C, ^{1}H, ^{29}Si: tetramethylsilane (TMS)



Can you assign the tallest peak? How about the shortest one?

3

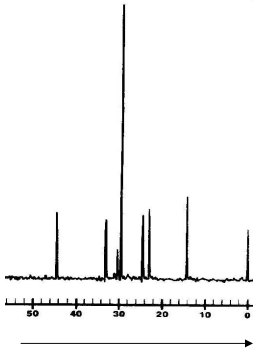
Shielding effect

- Electrons provide "shielding" to nuclei
- More shielded = lower ppm value = upfield
  - When neighbors have low electronegativity
  - Where would H-M appear in a proton spectrum?
- Less shielded = higher ppm value = downfield
  - When neighbors have high electronegativity
  - Example: O, F
  - *How about alcoholic proton vs. acidic proton?*

R_1 - **C**H_2 - R_2 ~ 20 ppm

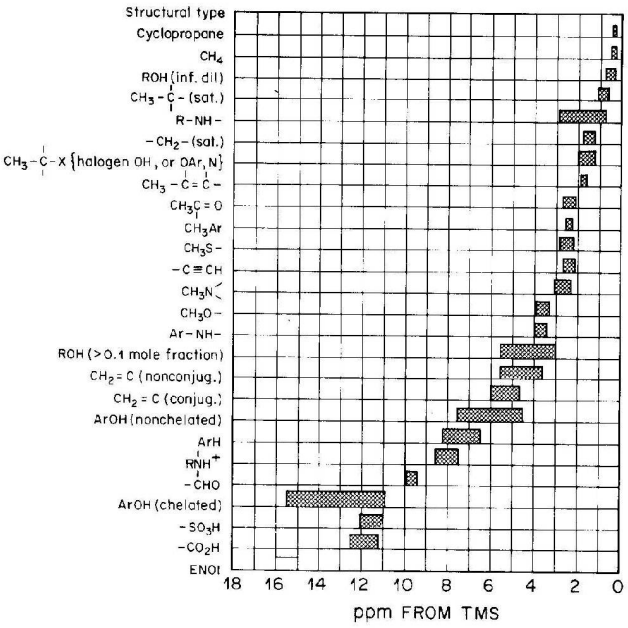
R_1 - **C**H_2 - O - R_2 ~ 70 ppm

R_1 - **C** - R_2 (C=O) ~ 200 ppm



4

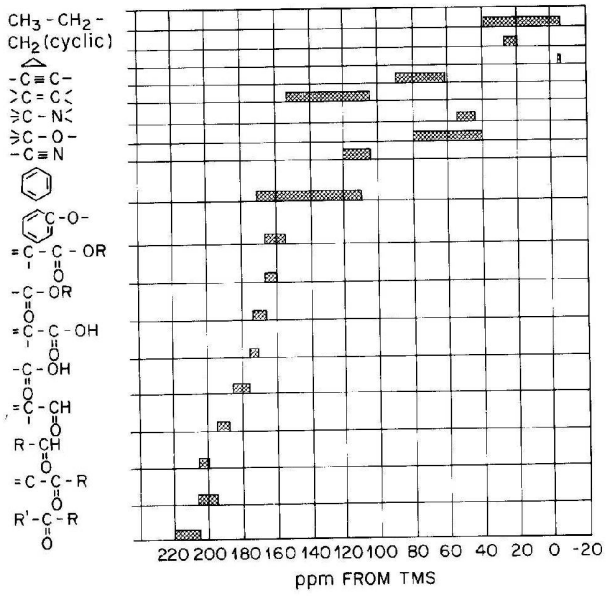
- ^{1}H chemical shift range:
  - Aliphatic
  - Heteroatoms
  - Unsaturated
  - Aromatic
  - Labile



Ref.: Bovey, *Nuclear Magnetic Resonance Spectroscopy*

5

- ^{13}C chemical shift range:
  - Aliphatic
  - Heteroatoms
  - Unsaturated
  - Aromatic
  - Ketone

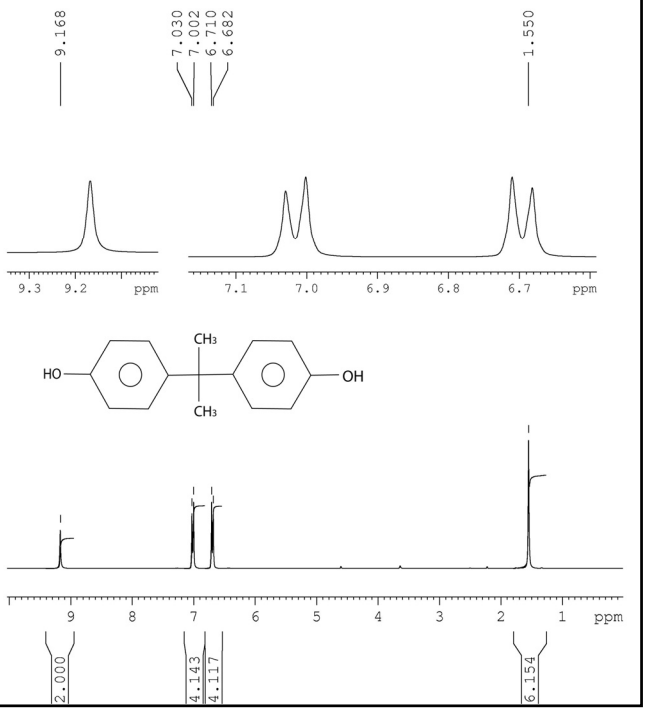


Ref.: Bovey, *Nuclear Magnetic Resonance Spectroscopy*

6

Example: ^{1}H spectrum of Bisphenol-A

- Please use the table on page 5 to assign the peaks
- Do the integrations agree with your assignment?



^{13}C NMR Chemical Shifts – Effect of More Distant Neighbors

A1 vs. A5 B2 vs. B7	Symmetric carbons have the same chemical shift
A5 vs. B5	Electron-drawing neighbors move peak toward down field – deshielding effect
A1 vs. B1 A2 vs. B2	Farther neighbors have smaller influence (ε ~ 0.1ppm; δ ~ 0.3ppm)

1 2 3 4 5 6 7 8

A $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

14.2 22.8 34.8 22.8 14.2

B $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

14.1 23.1 32.3 29.8 29.8 32.3 23.1 14.1

8

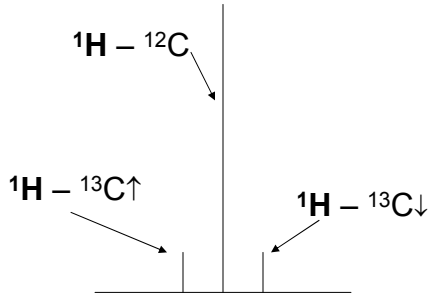
Chemical Shift is a Sensitive Measure. However…

- Chemical shift is dependent on many factors
  - Solvent
    - Example: $CHCl_3$ is 7.25 ppm in itself and 8 ppm in acetone
      - *Can you guess why?*
  - Temperature
    - CS of labile protons is more temperature dependent than stable protons
      - *At higher temperature, does ^1H peak in water become more or less shielded?*
  - Labile protons have an extremely broad chemical shift range
    - Can range from 1 ppm (trace H_2O in non polar solvent) all the way to 14+ ppm (Strongly hydrogen-bonded protons)
  - Chemical shifts of polymer is a strong function of conformation
    - $(CH_2)_n$ in *trans* and *gauche* states are apart by ~6ppm
- Precise prediction of chemical shift based on molecular structure is not easy

9

Couplings Between Nuclei

- J coupling: neighboring nuclei act as small local "magnets"
  - Nomenclature e.g. $^1J_{13C\text{-}H}$
- Couplings give splitting of peaks (multiplets)
  - There are a lot of small "magnets" in your molecule!
  - A spin ½ nucleus splits to two populations in magnetic field: up and down



10

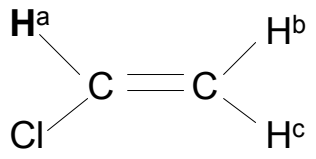
J-Coupling

- Heteronuclear J-coupling
  - Example: ^{13}C-^{1}H
- Homonuclear J-coupling
  - Example: ^{1}H-^{1}H
- Hz vs. ppm
  - J-coupling is independent of global field B_0 – expressed in Hz
    - Nuclei are “permanent magnets”
  - Chemical shift is proportional to B_0 – expressed in ppm
    - The paired electrons in the molecule are “induced magnets”
  - Your 300MHz and 400MHz spectra look different!

11

Coupling with Non-Equivalent Nuclei

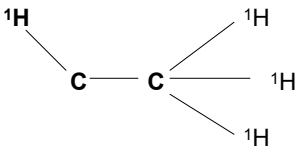
- Coupling with *n* non-equivalent nuclei gives 2^n peaks.
- Example: chloroethylene
  - All 3 protons give 4-peak splitting each
  - A total of 12 peaks!



12

Coupling with Equivalent Nuclei: Pascal Triangle

- Coupling with *n* equivalent nuclei gives *n*+1 peaks.
  - *Ideally*, multiplet splitting and intensities follow Pascal Triangle
  - *Actually*, intensity ratio would deviate from Pascal triangle when the chemical shift of the two groups get very close

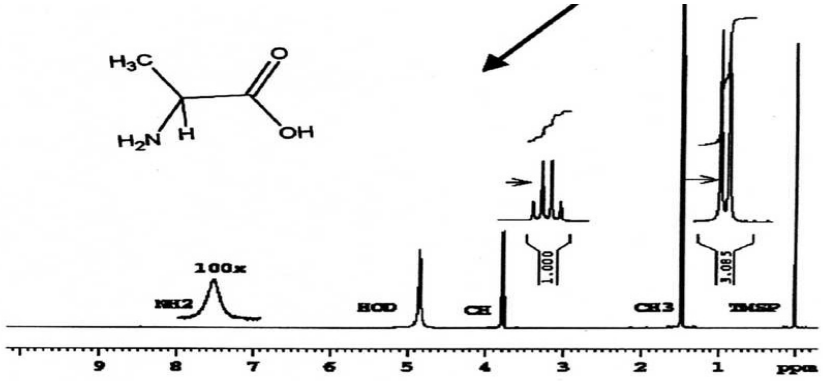


No. of neighbors	No. of peaks	pattern	Example
1	2	**1:1** ↑ : ↓	^{1}**H**-C-CH
2	3	**1:2:1** ↑↑ : (↑↓ + ↓↑) : ↓↓	^{1}**H**-C-CH_2
3	4	**1:3:3:1** ↑↑↑ : (↑↑↓ + ↑↓↑ + ↓↑↑) : (↑↓↓ + ↓↓↑ + ↓↑↓) :↓↓↓	^{1}**H**-C-CH_3

1
1 1
1 2 1
1 3 3 1

13

Example - Alanine



Solvent: D_2O

–Distance between adjacent multiplet peaks gives J-coupling strength (in Hz)

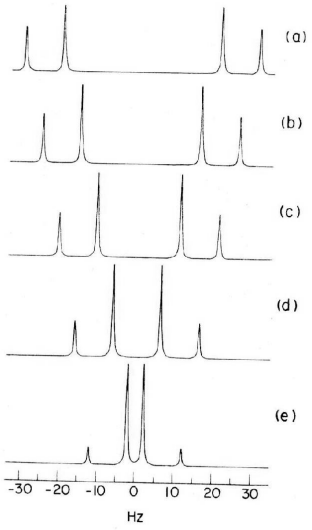
–*The multiplet splitting amplitudes of CH and CH_3 groups are the same. Is this coincidental?*

–*How many peaks would the CH_2 group in propane have?*

14

Interplay of Chemical Shift and J-Coupling

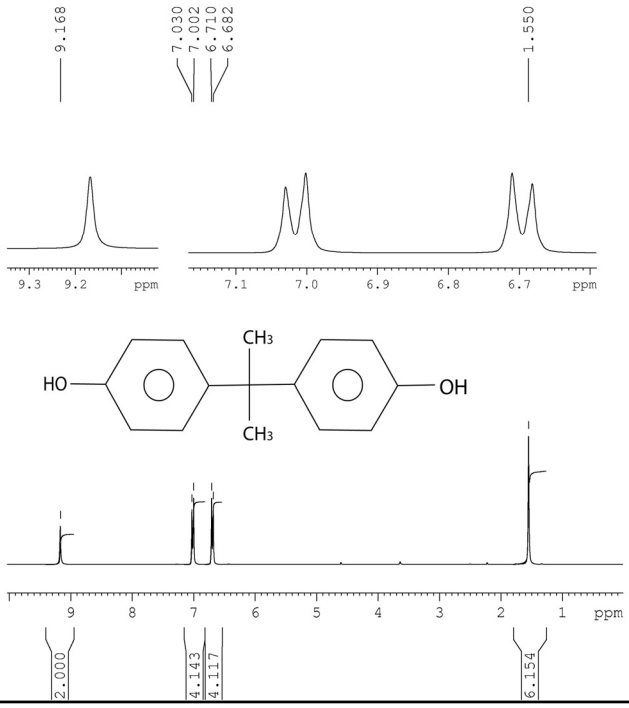
- "Spin system" is defined by *chemical shift difference* vs. *J-coupling*
- Deviation from Pascal Triangle
  - "Inside peaks" are always taller than "outside peaks"
  - AX system: CS difference >> coupling
    - Alanine: AX_3 system
    - Intensities follows Pascal Triangle
  - AB system: CS difference ~ coupling
    - Intensities deviate from Pascal Triangle
  - A_2 system: NO splitting
    - "Equivalent nuclei"



15

Example: Bisphenol-A

- Why are the area ratios in the doublets not 1:1?
- Why is the methyl peak a singlet?
- Why is the OH peak a singlet?

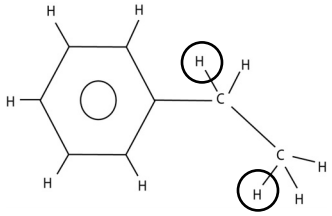


Equivalent Nuclei

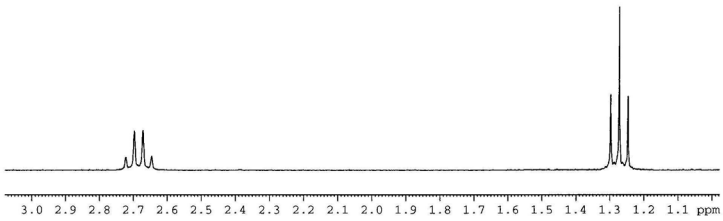
- Coupling between equivalent protons does not exhibit splitting
  - Example: benzene only has one peak (singlet) on ^1H spectrum
    - *Compare benzene and aromatic region of ethylbenzene*
    - *Compare chloroethylene and 1,2-dichloroethylene*
  - There is no multiplet splitting due to J-couplings between the protons within a CH_3
  - The two protons on CH_2 are equivalent if the next carbon is chiral
    - Example: The CH_2 in isotactic polypropylene
    - *How about syndiotactic polypropylene?*

17

Example: Ethylbenzene



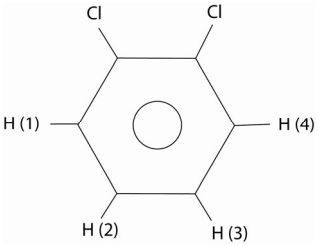
Consider only the ethyl branch (ignore the benzene ring):
•*what spin system?*



CH_2 CH_3

18

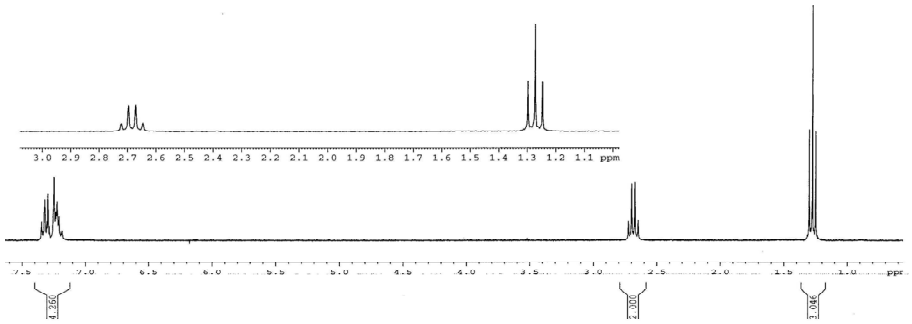
J Coupling Dependence on Number of Bonds Separated



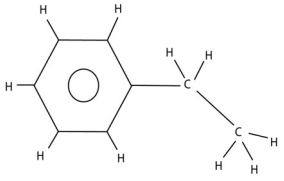
- Example: orthodichlorobenzene
  - $^{3}J_{12}$ = 8.1 Hz
  - $^{3}J_{23}$ = 7.5 Hz
  - $^{4}J_{13}$ = 1.5 Hz
  - $^{5}J_{14}$ = 0.3 Hz
- $^{1}J_{CH}$ ~ 120 Hz; $^{2}J_{CH}$ and $^{3}J_{CH}$~ 5 Hz;
- J-coupling strengths are also dependent on molecule geometry (eg. cis vs. trans)

19

Ethylbenzene Once More…



- Why are the aromatic signal region so “messy”?
- Why are ethylene peaks broader than methyl?
- Are the splitting distance for methyl and methylene the same? Should they be?
- Area ratio: C_6H_5 :CH_2 : CH_3 = 4.3 : 2 : 3

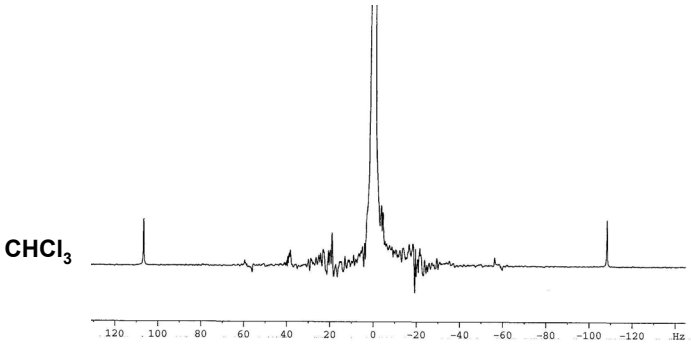


20

Spectrum Artifacts on ^{1}H Spectra

- Spinning sidebands
  - Distance to center peak is multiples of spinning speed
- Vibration artifacts
  - Usually < 20 Hz

- ^{13}C satellites (*not directly from ^{13}C but from ^{1}H with a neighboring ^{13}C*)
  - Due to ^{1}H-^{13}C J-coupling
  - Equal intensity – 0.55% of big peak
  - Equal distance to big peak
  - Distance between the satellites is $^{1}J_{13C-H}$ coupling constant
  - Should always be reminded if you try to assign a small peak on the side of a big peak



21

Summary: ^{1}H-^{1}H J-Coupling

- Protons that are connected by covalent bonds have J-coupling
- The J coupling between a pair of protons is dependent on the number of bonds in between
  - ^{3}J ~ 10 Hz; ^{4}J ~ 1 Hz; ^{5}J ~ 0.3 Hz
- J-coupling causes ^{1}H signal splitting into multiplets
  - Think neighboring nuclei as small magnets
  - n non-equivalent neighbors give 2^{n} splittings
  - n equivalent neighbors give n+1 splittings
- Spin systems: AX, AB, A_2X_3 , AX_3 etc.
- Multiplet intensity ratio deviates from Pascal triangle when chemical shift difference between the members of the spin group is not much greater than the J-splitting
- J-coupling between equivalent nuclei does not generate splitting

22

Strategy for ^{1}H and ^{13}C Spectrum Assignment

- Integration – estimate number of protons/carbons in each group of signal
  - Note: integration of "lone protons" may be < 1.
  - Note: integration of unprotonated carbons are often < 1
- Multiplet - get information about neighboring protons by examining splitting pattern
  - Splitting pattern of A_nB_m system
  - Equivalent nuclei
- Chemical shift
  - Make good use of modern spectra library (e.g. SDBS)

23