NMR IV

Correlation Charts

Coupling & Splitting (C & S)

Ref 9: 8 (8th ed.); 9: 9 (9th ed.)

Prob 9: 5 – 9; (31); 34 (8th ed.)
9: 7 – 9; 11; (30); 33 (9th ed.)

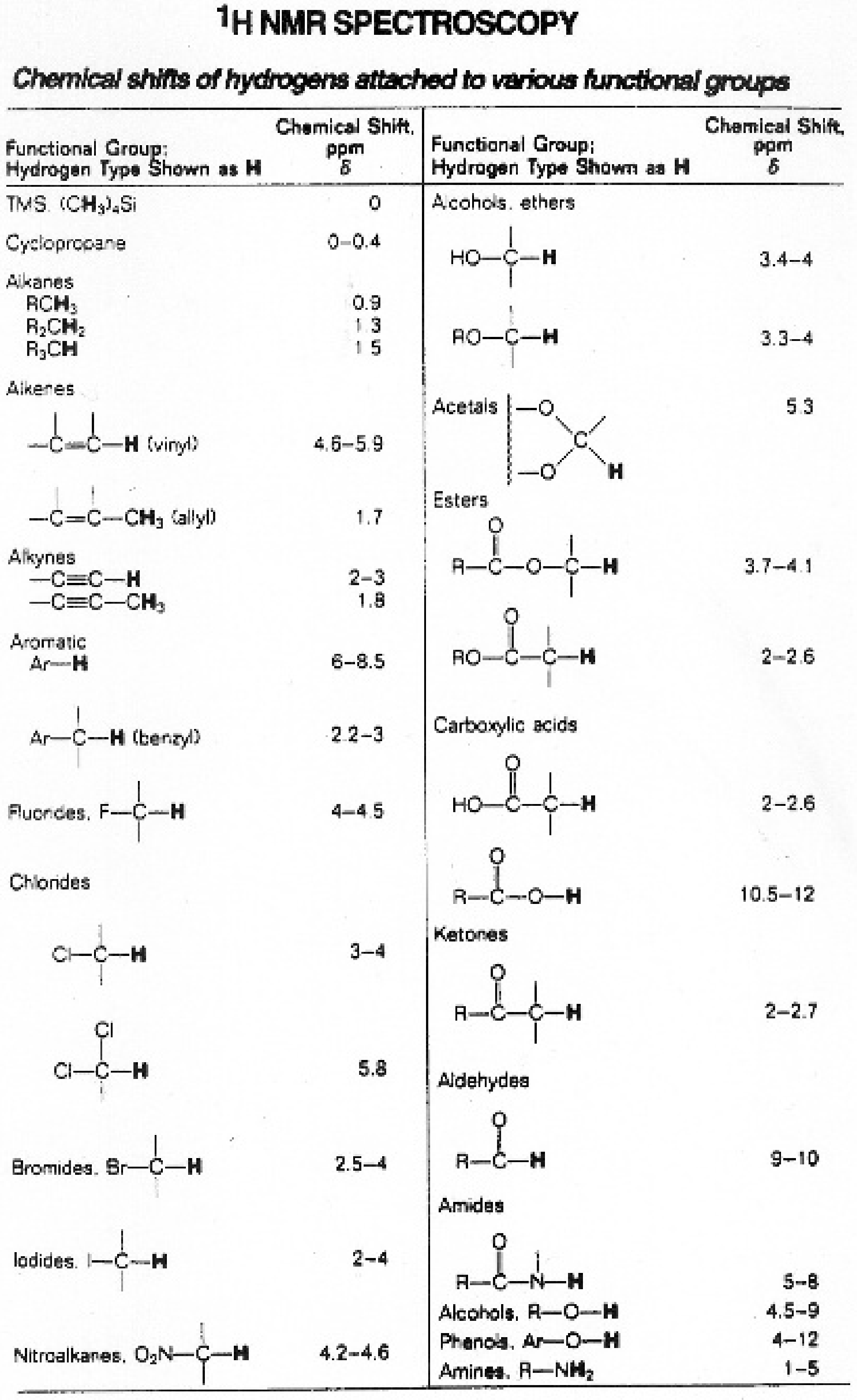
HMWK #3

Adv Rdg 9: 3D (8th ed.); 9: 2B (9th ed.)

Correlation Charts

- similar to IR (UV, ...)
- δ values can be used to
  identify **functional groups** and
  especially, **structural arrangements**
- tabulated in many sources
  e.g., Solomons, p.395(8th ed.), p.366 (9th ed.)
  Lab Manual, inside back cover
  (*this will be used for exams*)

Copy of Chart in Lab Manual

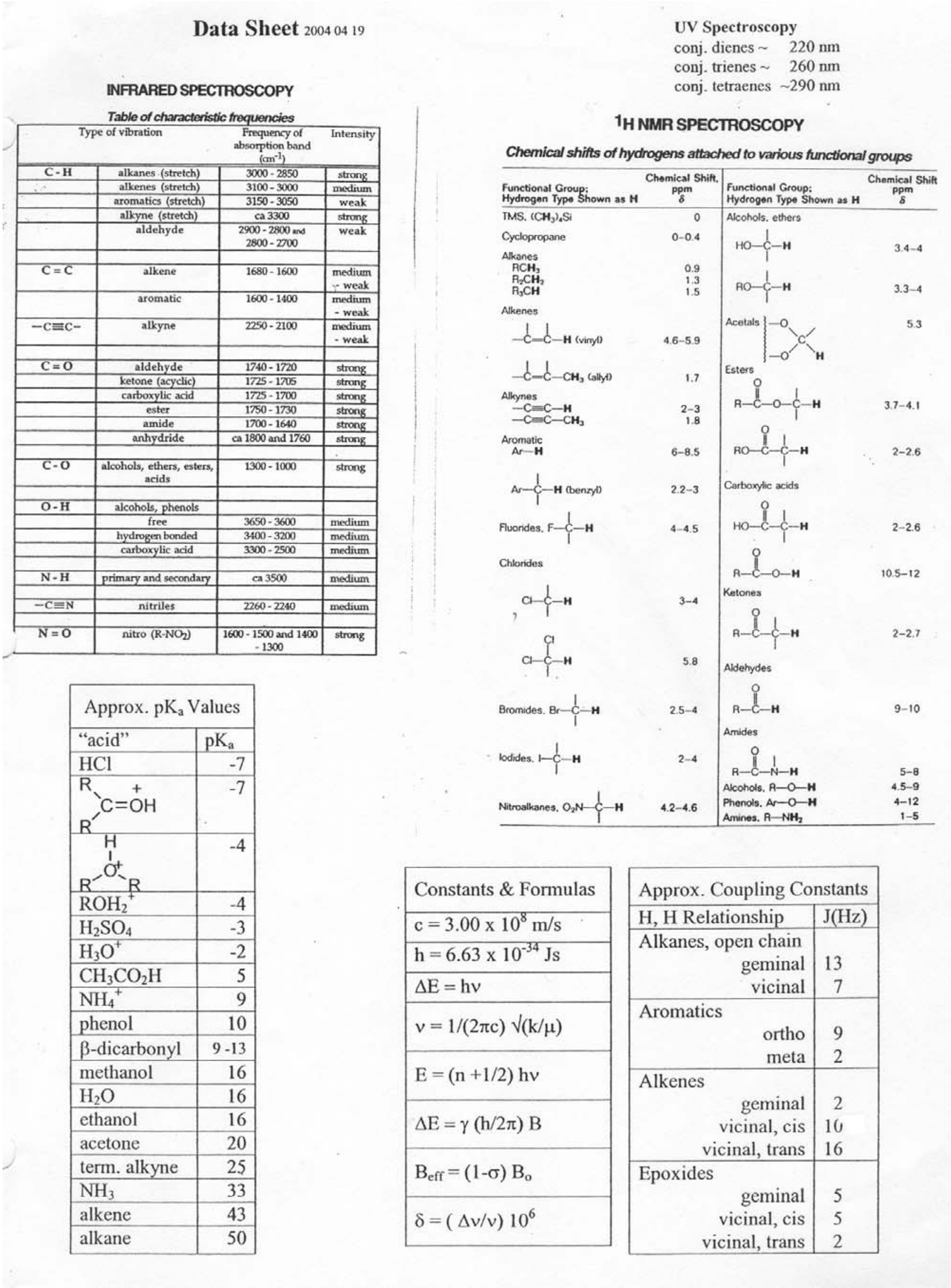


^{1}H NMR SPECTROSCOPY

Chemical shifts of hydrogens attached to various functional groups

Functional Group; Hydrogen Type Shown as **H**	Chemical Shift, ppm δ
TMS, $(CH_3)_4Si$	0
Cyclopropane	0–0.4
Alkanes	
RCH_3	0.9
R_2CH_2	1.3
R_3CH	1.5
Alkenes	
$-\overset{\mid}{C}=\overset{\mid}{C}-H$ (vinyl)	4.6–5.9
$-\overset{\mid}{C}=\overset{\mid}{C}-CH_3$ (allyl)	1.7
Alkynes	
$-C\equiv C-H$	2–3
$-C\equiv C-CH_3$	1.8
Aromatic	
$Ar-H$	6–8.5
$Ar-\overset{\mid}{\underset{\mid}{C}}-H$ (benzyl)	2.2–3
Fluorides, $F-\overset{\mid}{\underset{\mid}{C}}-H$	4–4.5
Chlorides	
$Cl-\overset{\mid}{\underset{\mid}{C}}-H$	3–4
$Cl-\overset{Cl}{\underset{\mid}{C}}-H$	5.8
Bromides, $Br-\overset{\mid}{\underset{\mid}{C}}-H$	2.5–4
Iodides, $I-\overset{\mid}{\underset{\mid}{C}}-H$	2–4
Nitroalkanes, $O_2N-\overset{\mid}{\underset{\mid}{C}}-H$	4.2–4.6
Alcohols, ethers	
$HO-\overset{\mid}{\underset{\mid}{C}}-H$	3.4–4
$RO-\overset{\mid}{\underset{\mid}{C}}-H$	3.3–4
Acetals $\begin{matrix}-O\\-O\end{matrix}\!>\!C-H$	5.3
Esters	
$R-\overset{O}{\overset{\Vert}{C}}-O-\overset{\mid}{\underset{\mid}{C}}-H$	3.7–4.1
$RO-\overset{O}{\overset{\Vert}{C}}-\overset{\mid}{\underset{\mid}{C}}-H$	2–2.6
Carboxylic acids	
$HO-\overset{O}{\overset{\Vert}{C}}-\overset{\mid}{\underset{\mid}{C}}-H$	2–2.6
$R-\overset{O}{\overset{\Vert}{C}}-O-H$	10.5–12
Ketones	
$R-\overset{O}{\overset{\Vert}{C}}-\overset{\mid}{\underset{\mid}{C}}-H$	2–2.7
Aldehydes	
$R-\overset{O}{\overset{\Vert}{C}}-H$	9–10
Amides	
$R-\overset{O}{\overset{\Vert}{C}}-\overset{\mid}{N}-H$	5–8
Alcohols, $R-O-H$	4.5–9
Phenols, $Ar-O-H$	4–12
Amines, $R-NH_2$	1–5

Data Sheet for HT Org. Exams



Data Sheet 2004 04 19

UV Spectroscopy

conj. dienes ~	220 nm
conj. trienes ~	260 nm
conj. tetraenes	~290 nm

INFRARED SPECTROSCOPY

Table of characteristic frequencies

Type of vibration		Frequency of absorption band (cm^{-1})	Intensity
C - H	alkanes (stretch)	3000 - 2850	strong
	alkenes (stretch)	3100 - 3000	medium
	aromatics (stretch)	3150 - 3050	weak
	alkyne (stretch)	ca 3300	strong
	aldehyde	2900 - 2800 and 2800 - 2700	weak
C = C	alkene	1680 - 1600	medium - weak
	aromatic	1600 - 1400	medium - weak
—C≡C—	alkyne	2250 - 2100	medium - weak
C = O	aldehyde	1740 - 1720	strong
	ketone (acyclic)	1725 - 1705	strong
	carboxylic acid	1725 - 1700	strong
	ester	1750 - 1730	strong
	amide	1700 - 1640	strong
	anhydride	ca 1800 and 1760	strong
C - O	alcohols, ethers, esters, acids	1300 - 1000	strong
O - H	alcohols, phenols		
	free	3650 - 3600	medium
	hydrogen bonded	3400 - 3200	medium
	carboxylic acid	3300 - 2500	medium
N - H	primary and secondary	ca 3500	medium
—C≡N	nitriles	2260 - 2240	medium
N = O	nitro ($R-NO_2$)	1600 - 1500 and 1400 - 1300	strong

^{1}H NMR SPECTROSCOPY

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Iodides, $I-C-H$	2–4
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$R-C(=O)-C-H$	2–2.7
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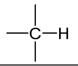
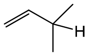
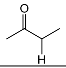
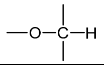
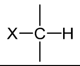
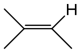
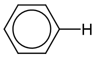
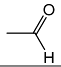
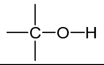
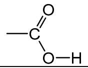
$R-C(=O)-H$	9–10
Amides	
$R-C(=O)-N-H$	5–8
Alcohols, $R-O-H$	4.5–9
Phenols, $Ar-O-H$	4–12
Amines, $R-NH_2$	1–5

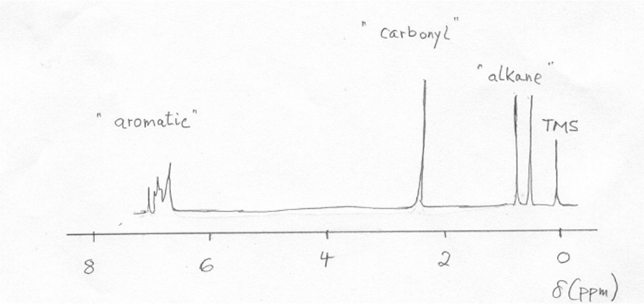
Approx. pK_a Values	
"acid"	pK_a
HCl	-7
$R_2C=OH^+$	-7
R_2OH^+	-4
ROH_2^+	-4
H_2SO_4	-3
H_3O^+	-2
CH_3CO_2H	5
NH_4^+	9
phenol	10
β-dicarbonyl	9 -13
methanol	16
H_2O	16
ethanol	16
acetone	20
term. alkyne	25
NH_3	33
alkene	43
alkane	50

Constants & Formulas
$c = 3.00 \times 10^8$ m/s
$h = 6.63 \times 10^{-34}$ Js
$\Delta E = h\nu$
$\nu = 1/(2\pi c)\sqrt{(k/\mu)}$
$E = (n + 1/2) h\nu$
$\Delta E = \gamma (h/2\pi) B$
$B_{eff} = (1-\sigma) B_o$
$\delta = (\Delta\nu/\nu) 10^6$

Approx. Coupling Constants	
H, H Relationship	J(Hz)
Alkanes, open chain	
geminal	13
vicinal	7
Aromatics	
ortho	9
meta	2
Alkenes	
geminal	2
vicinal, cis	10
vicinal, trans	16
Epoxides	
geminal	5
vicinal, cis	5
vicinal, trans	2

Important δ Values		
δ (ppm)	“Bonding”	Functional Group/ Molecular Feature
~ 1		alkane
1.7		allylic, benzilic
2.5		α to carbony
3.5		alcohol, ether
~ 4		halide
5		vinylic
7		aromatic
~ 10		aldehyde
4 - 6		alcohol –OH
~ 11		acid –OH

Illustration



Solomons Fig. 9.3

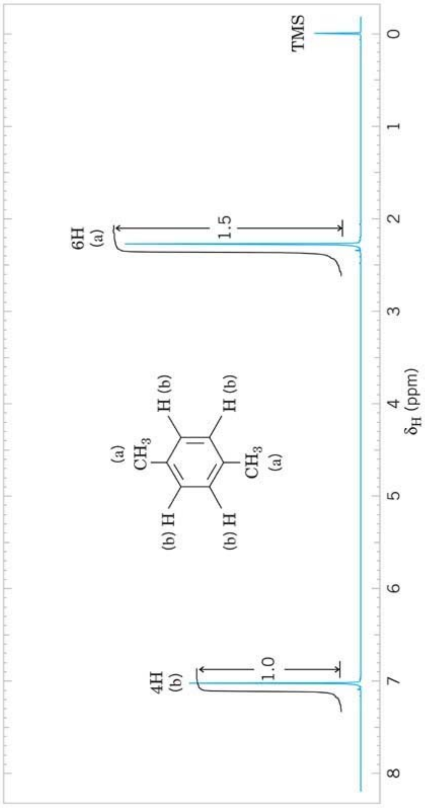


FIGURE 9.3 The 300-MHz ^{1}H NMR spectrum of 1,4-dimethylbenzene.

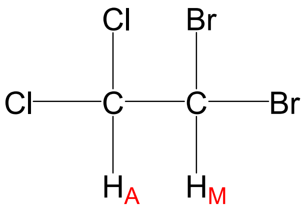
Coupling & Splitting

B_{eff} depends on B_0 , B_{local}

and magnetic effect of neighboring nuclei,

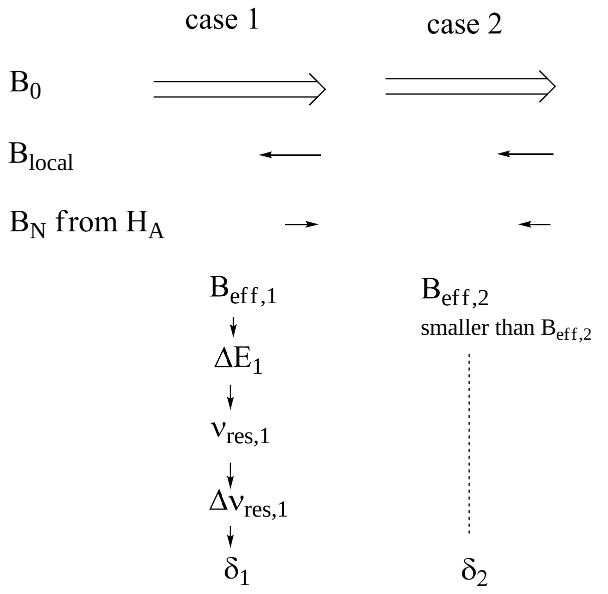
let’s call it $\mathbf{B_N}$

Ex.



Let’s observe B_{eff} at H_M

Observations at H_M



case 1 case 2

B_0

B_{local}

B_N from H_A

$B_{eff,1}$ → ΔE_1 → $\nu_{res,1}$ → $\Delta\nu_{res,1}$ → δ_1

$B_{eff,2}$
smaller than $B_{eff,2}$

δ_2

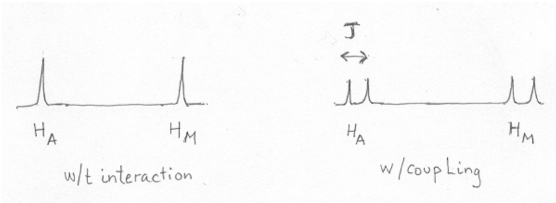
$\therefore$ 1 signal for H_M
consisting of 2 peaks
i.e., doublet due to H_A

C & S

Effect is mutual:

$\therefore$ signal for H_A is also split
into doublet byH_M

Illustration



Magnitude of C / S

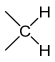
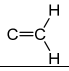
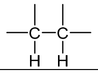
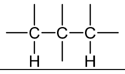
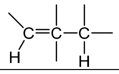
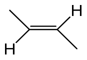
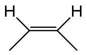
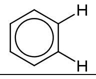
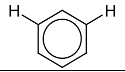
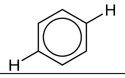
depends on variety of factors:

- distance between H_A & H_M
- electronic surroundings
- geometry of molecule
- “works through σ bonds”

expressed as coupling constant **J,** measured in Hz

changes with relationship of coupling atoms,
but **independent of B_0**

Important J Values

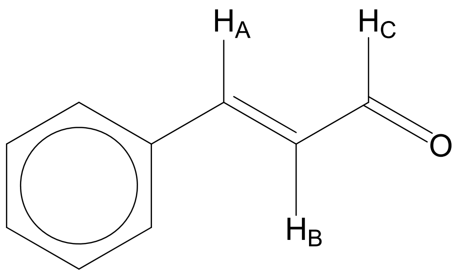
“Relationship”		J (Hz)
	geminal	13
		2
	vicinal, mobile structures	7
	(*distant*)	0
	allylic	1.5
	trans	16
	cis	10
	ortho	9
	meta	2
	para	0.5

Multiple Coupling

Each add^{l} proton neighbor causes

add^{l} coupling and splitting

Ex.

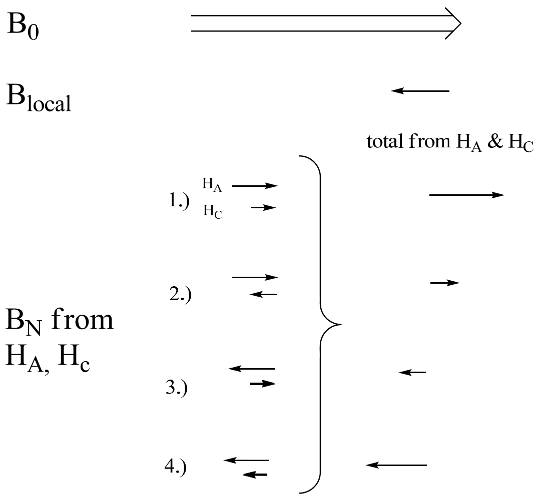


Specific J values:

J_{AB} = 12 Hz, J_{BC} = 6 Hz, J_{AC} = 0 Hz

Explanation

B_{eff} at H_B consists of:



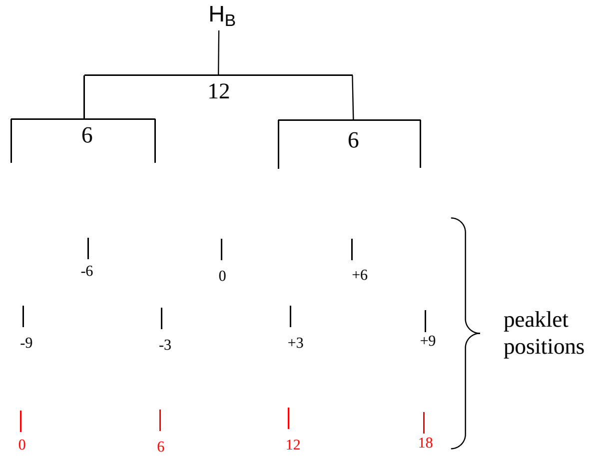
∴ 4 different $B_{eff.}$'s at H_B

∴ 4 different peaks for H_B

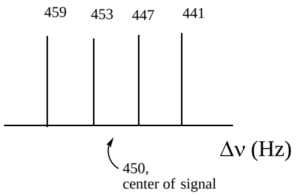
= "doublet of doublets" = "d of d"

Splitting Tree

helps to derive signal pattern
(*number and separation of peaks*)



Assume center of signal is at Δν = 450 Hz
then we get the following peak pattern (nmr trace)



Further Splitting

In general, any add^{l} neighbor causes

add splitting of the signal.

# of neighbors	splitting tree lvls	signal pattern
1	1	d (2 peaks)
2	2	d of d (4 peaks)
3	3	d of d of d (8)
4	4	d of d of d of d (16)

Construction of Splitting Trees

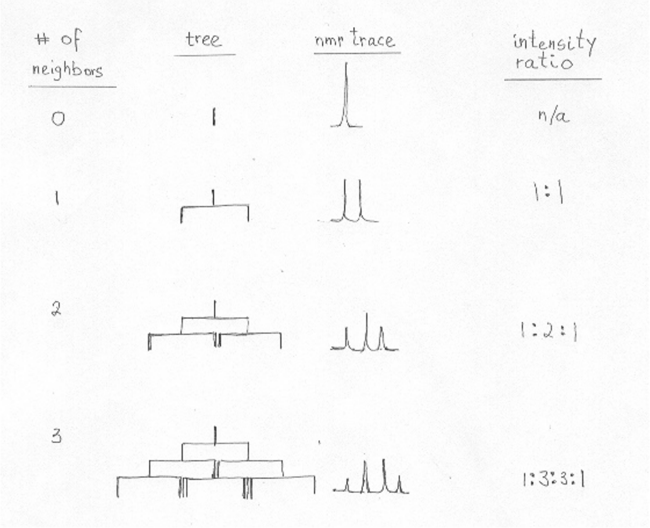
- similar to "2 neighbors" case
- start with largest J
- then go down to smaller ones (*most convenient*)
- "branching" might criss-cross

Do HMWK #3 for Practice

Special Case: J’s identical

(*covered in lab manual*)

esp., vicinal coupling in open chain, sp^3 systems



Generalization: “n + 1” Rule

(*valid only for identical J’s*)

$$N = n + 1$$

where N = # of peaks in signal

n = # of coupling neighbors w/ identical J;

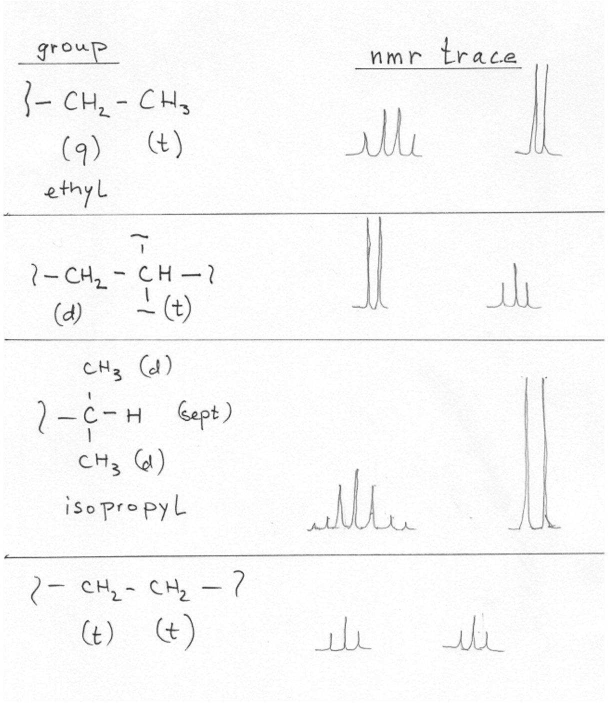
in particular, # of vicinal H’s

Pascal’s Triangle

indicates intensity ratios of peaks

1	singlet (s)
1 1	doublet (d)
1 2 1	triplet (t)
1 3 3 1	quartet (q)
1 4 6 4 1	quintet
1 5 10 10 5 1	sextet
1 6 15 20 15 6 1	septet

Common Splitting Patterns



C & S Notes

- no splitting between identical (“equiv.”) H’s
- if J & Δν are close in value ($\Delta\nu / J < 10$) Pascal’s Triangle breaks down, “leaning/tilting” of peaks towards the “coupling partner” is observed; i.e., facing peaks are larger

Illustration

Comments ...

- if J and Δν are very close
  (e.g. aromatic, sat^{d} hydrocarbons)
  further complications are observed
  i.e. “signal heaps” = “unresolved peaks”:

- if Δν = 0, **no splitting**