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**

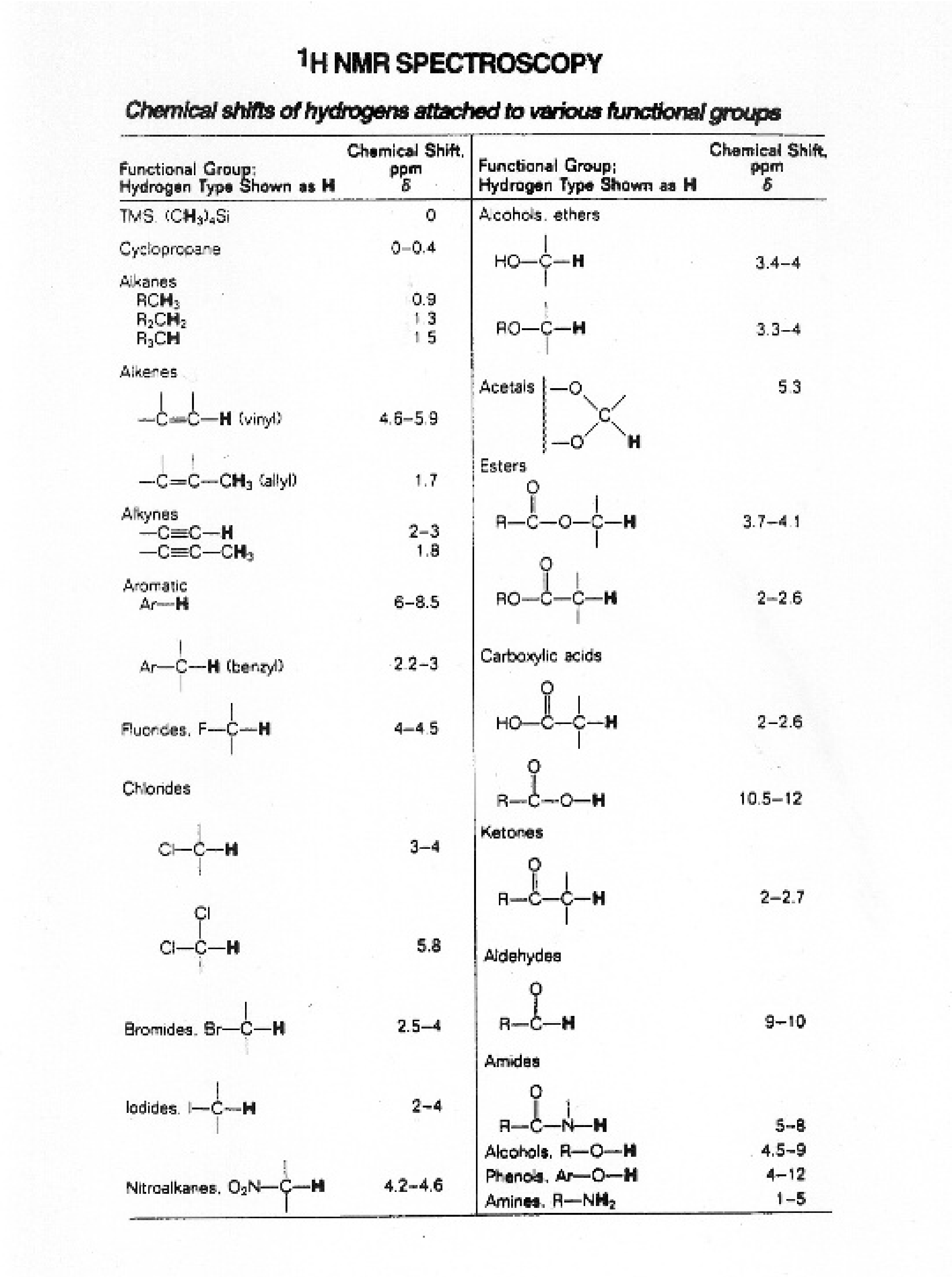
- tabulated in many sources

  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

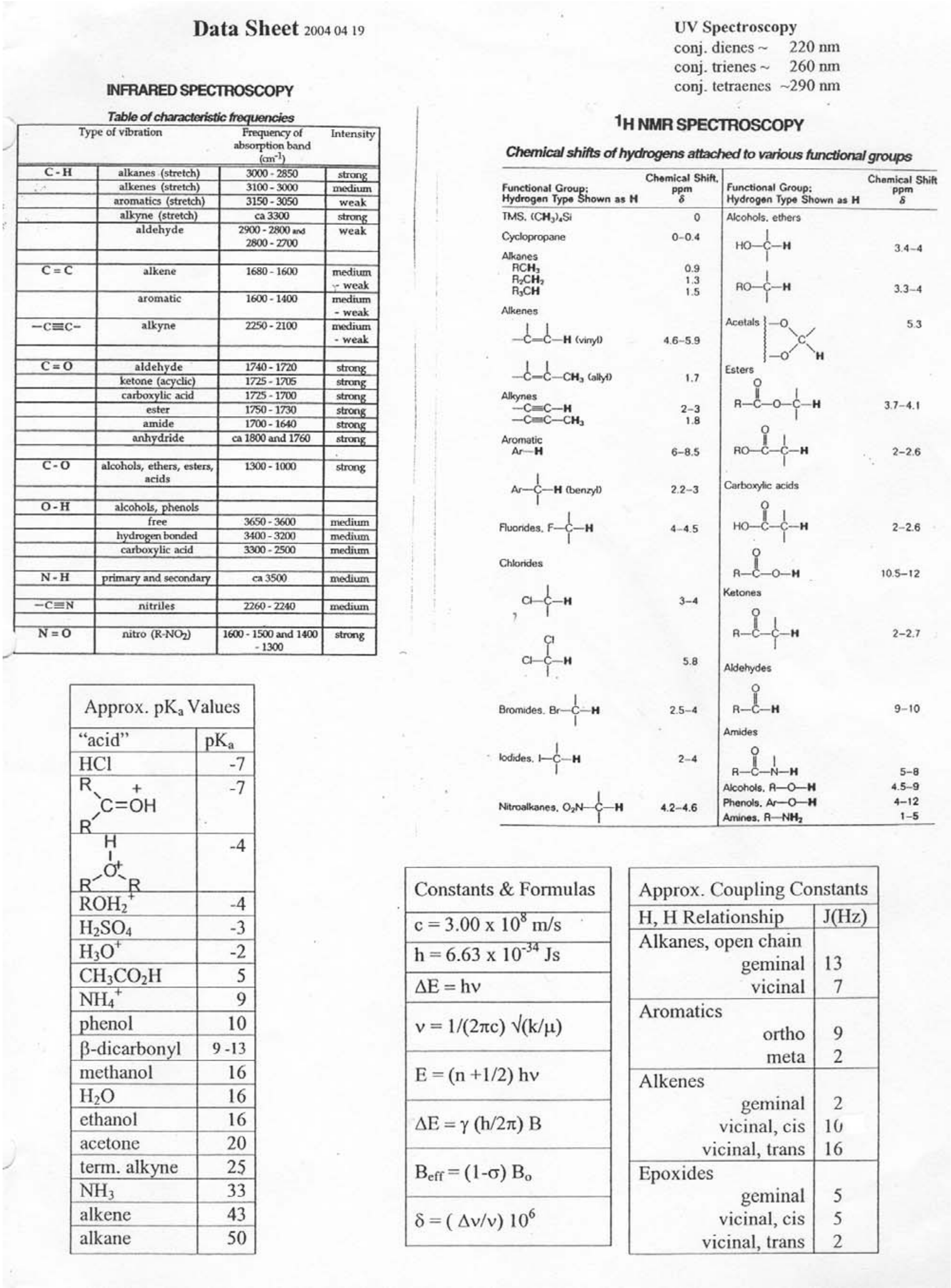


^{1}H NMR SPECTROSCOPY

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	
—C=C—**H** (vinyl)	4.6–5.9
—C=C—CH_3 (allyl)	1.7
Alkynes	
—C≡C—**H**	2–3
—C≡C—CH_3	1.8
Aromatic	
Ar—**H**	6–8.5
Ar—C—**H** (benzyl)	2.2–3
Fluorides, F—C—**H**	4–4.5
Chlorides	
Cl—C—**H**	3–4
Cl—C(Cl)—**H**	5.8
Bromides, Br—C—**H**	2.5–4
Iodides, I—C—**H**	2–4
Nitroalkanes, O_2N—C—**H**	4.2–4.6
Alcohols, ethers	
HO—C—**H**	3.4–4
RO—C—**H**	3.3–4
Acetals (—O)(—O)C—**H**	5.3
Esters	
R—C(=O)—O—C—**H**	3.7–4.1
RO—C(=O)—C—**H**	2–2.6
Carboxylic acids	
HO—C(=O)—C—**H**	2–2.6
R—C(=O)—O—**H**	10.5–12
Ketones	
R—C(=O)—C—**H**	2–2.7
Aldehydes	
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

Data Sheet for HT Org. Exams



Data Sheet 2004 04 19

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 ($R\text{-}NO_2$)	1600 - 1500 and 1400 - 1300	strong

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

UV Spectroscopy

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

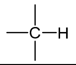
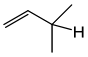
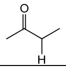
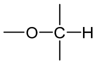
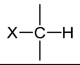
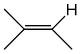
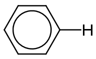
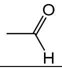
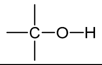
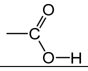
¹H NMR SPECTROSCOPY

Chemical shifts of hydrogens attached to various functional groups

Functional Group; Hydrogen Type Shown as **H**	Chemical Shift, ppm δ	Functional Group; Hydrogen Type Shown as **H**	Chemical Shift ppm δ
TMS, $(CH_3)_4Si$	0	Alcohols, ethers	
Cyclopropane	0–0.4	HO—C—**H**	3.4–4
Alkanes		RO—C—**H**	3.3–4
RCH_3	0.9	Acetals	5.3
R_2CH_2	1.3	Esters	
R_3CH	1.5	$R-\overset{O}{\overset{\parallel}{C}}-O-C-H$	3.7–4.1
Alkenes		$RO-\overset{O}{\overset{\parallel}{C}}-C-H$	2–2.6
—C=C—**H** (vinyl)	4.6–5.9	Carboxylic acids	
—C=C—CH_3 (allyl)	1.7	$HO-\overset{O}{\overset{\parallel}{C}}-C-H$	2–2.6
Alkynes		$R-\overset{O}{\overset{\parallel}{C}}-O-H$	10.5–12
—C≡C—**H**	2–3	Ketones	
—C≡C—CH_3	1.8	$R-\overset{O}{\overset{\parallel}{C}}-C-H$	2–2.7
Aromatic		Aldehydes	
Ar—**H**	6–8.5	$R-\overset{O}{\overset{\parallel}{C}}-H$	9–10
Ar—C—**H** (benzyl)	2.2–3	Amides	
Fluorides, F—C—**H**	4–4.5	$R-\overset{O}{\overset{\parallel}{C}}-N-H$	5–8
Chlorides		Alcohols, R—O—**H**	4.5–9
Cl—C—**H**	3–4	Phenols, Ar—O—**H**	4–12
Cl_2C—**H**	5.8	Amines, R—NH_2	1–5
Bromides, Br—C—**H**	2.5–4		
Iodides, I—C—**H**	2–4		
Nitroalkanes, O_2N—C—**H**	4.2–4.6		

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
		
		
		
		
		
		
		
		
		
		

Illustration

Solomons Fig. 9.3

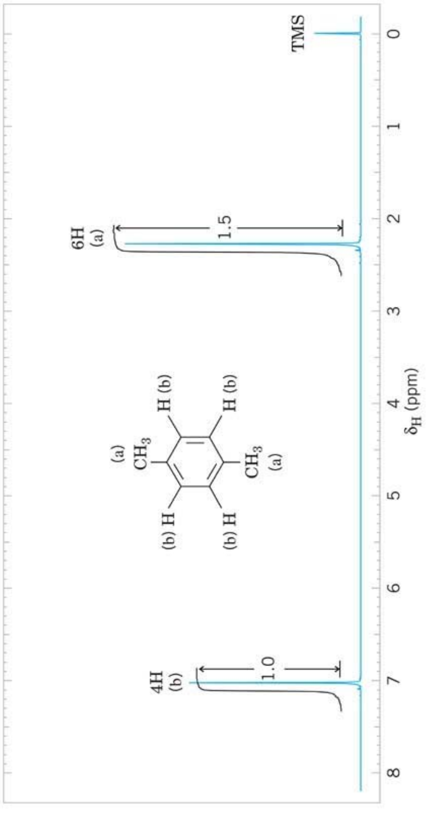


FIGURE 9.3 The 300-MHz ^1H NMR spectrum of 1,4-dimethylbenzene.

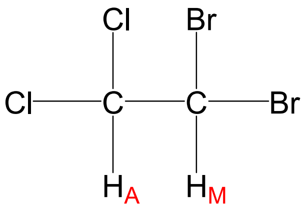
Coupling & Splitting

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

and magnetic effect of neighboring nuclei,

let's call it **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

∴ 1 signal for H_M

consisting of 2 peaks

i.e., doublet due to H_A

C & S

Effect is mutual:

∴ signal for H_A is also split

into doublet byH_M

Illustration

Magnitude of C / S

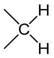
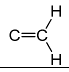
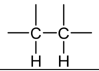
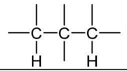
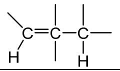
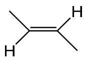
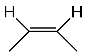
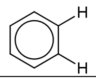
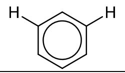
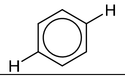
depends on variety of factors:

- 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,

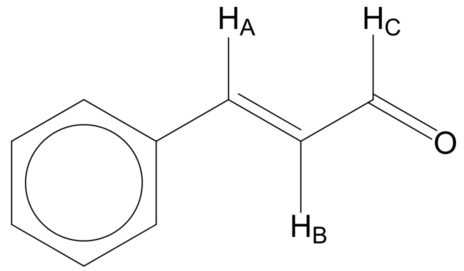
but **independent of B_0**

Important J Values		
"Relationship"		J (Hz)
		
		
		
		
		
		
		
		
		
		

Multiple Coupling

Each add^{l} proton neighbor causes
add^{l} coupling and splitting

Ex.

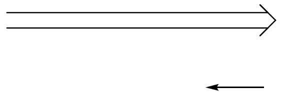


Specific J values:

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

Explanation

B_{eff} at H_B consists of:



B_0

B_{local}

B_N from
$H_{A,}$ H_c

∴ 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*)

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 (Δν / 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 $\Delta\nu$ are very close (e.g. aromatic, sat^{d} hydrocarbons) further complications are observed i.e. “signal heaps” = “unresolved peaks”:

- if $\Delta\nu = 0$, **no splitting**