

CHEM / BCMB 4190/6190/8189

Introductory NMR

Lecture 5

Indirect Spin-Spin Coupling:

- 1J : coupling between directly bonded nuclei.
- 2J : geminal coupling; $-\text{CH}_2$ protons.
- 3J : vicinal or three-bond coupling.
- ^{3+n}J : long-range coupling.

Magnitudes of coupling constants:

Table 3-1.

General summary of the orders of magnitude and signs of H,H, C,H and C,C coupling constants.

$J(\text{H,H})$ [Hz]	Sign	$J(\text{C,H})$ [Hz]	Sign	$J(\text{C,C})$ Sign ^{b)} [Hz]
1J 276 ^{a)}	positive	125-250	positive	30-80 positive
2J 0-30	usually neg.	-10 to +20	pos./neg.	<20 pos./neg.
3J 0-18	positive	1-10	positive	0-5 positive
^{3+n}J 0-7	pos./neg.	<1	pos./neg.	<1 pos./neg.

^{a)} For H_2 . ^{b)} Determined in only a few cases.

Factors that Influence Coupling constants:

1. The hybridization of the atoms involved.
2. Bond angles and torsion angles.
3. bond lengths.
4. the presence of neighboring π -bonds.
5. substituent effects.

J-coupling is observed in the spectrum only if the spin orientation of the coupling nuclei in B_0 are maintained for a time longer than $\tau_j = 1/J$

C,H Coupling Constants:

-principal structural significance is that they depend on the *s* character of the bonding carbon orbitals.

$$^1J(\text{C,H}) = 500\ s$$

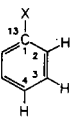
	$\text{H}_3\text{C}-\text{CH}_3$	$\text{H}_2\text{C}=\text{CH}_2$	C_6H_6	$\text{HC}\equiv\text{CH}$
$^1J(\text{C,H})$ [Hz]	124.9	156.4	158.4	249.0
Hybridization	sp^3	sp^2	sp^2	sp
<i>s</i> -fraction	0.25	0.33	0.33	0.5

$^2J(\text{C,H})$ - smaller than $^1J(\text{C,H})$ and show some dependence on the *s* character.

$^3J(\text{C,H})$ - show some dependence on dihedral angles but many other factors are involved and they are not as reliable.

Aromatic Systems:




Some C,H coupling constants for benzene, toluene, chlorobenzene and fluorobenzene.

	X	$^1J(\text{C}^1, \text{H}^1)$	$^2J(\text{C}^1, \text{H}^2)$	$^3J(\text{C}^1, \text{H}^3)$	$^4J(\text{C}^1, \text{H}^4)$	
			[Hz]			
	H	158.4	+ 1.1	+ 7.6	- 1.3	
	CH ₃		+ 0.5	+ 7.6	- 1.4	
	Cl		- 3.4	+ 10.9	- 1.8	
	F		- 4.9	+ 11.0	- 1.7	

C,C Coupling Constants:

- 1:8300 probability of two ^{13}C 's at natural abundance.
- they are highly dependent on hybridization of the bonding orbitals.

Direct $^{13}\text{C}-^{13}\text{C}$ Couplings, $^1J_{\text{C}-\text{C}}$, in Selected Organic Compounds, Illustrating Dependence on s Character of Bonding Orbitals ^a

Entry	Compound	Bonding hybridization	$^1J_{^{13}\text{C}-^{13}\text{C,H}_2}$ (Hz)
1	cyclopropane	$sp^5 - sp^5$	10
2	CH_3-CH_3	$sp^3 - sp^3$	34.6
3	 $\text{C}-\text{CH}_3$	$sp^3 - sp^2$	44.2
4	benzene	$sp^2 - sp^2$	57.0
5	$\text{CH}_2 = \text{CH}_2$	$sp^2 - sp^2$	67.6
6	$\text{CH}_3-\text{C} \equiv \text{CH}$	$sp^3 - sp$	67.4
7	CH_3CN	$sp^3 - sp$	56.5
8	$\text{CH}_2 = \text{C} = \text{C}(\text{CH}_3)_2$	$sp^2 - sp$	99.5
9	 $\text{C}-\text{CN}$	$sp^2 - sp$	80.0
10	$\text{HC} \equiv \text{CH}$	$sp - sp$	171.5
11		$sp^3 - sp^3$	C_2-C_3 35.2 C_3-C_4 33.0

Correlation between C,H and H,H couplings:

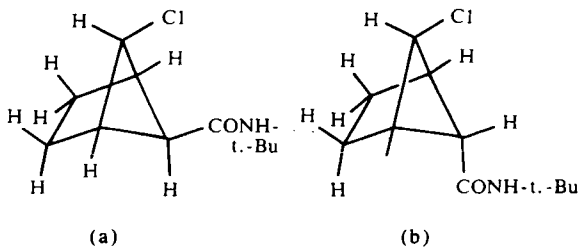
$$^3J(\text{H,H}) \approx ^3J(\text{C,H}) \mathbf{0.6}$$

Long Range Couplings:

- usually you do not see coupling transmitted through four bonds.

Rigid Cyclic Structures:

"W" configuration

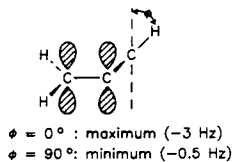


7Hz

0Hz

π Electrons:

-dependent on angle ϕ



$$^3J_{\text{cis}} = 11.7 - 4.7(E_x - E_H)$$

$$^3J_{\text{trans}} = 19.0 - 3.3(E_x - E_H)$$

Proton-proton coupling in aromatic compounds:

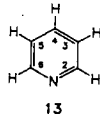
Benzene:

H,H coupling constants in benzene and benzene derivatives.

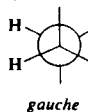
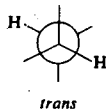
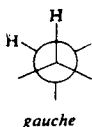
J [Hz]	Benzene	Derivatives
J_o	7.5	7-9
J_m	1.4	1-3
J_p	0.7	< 1

Heteroatoms:

H,H coupling constants in pyridine and pyridine derivatives.

	J (H,H) [Hz]		
	Pyridine	Derivatives	
 13	<i>ortho</i>	2.3 3.4	4.9 7-9
	<i>meta</i>	2.4 3.5 2.6	1.2 1.4 -0.1
	<i>para</i>	2.5	1.0 0-1

There are three rotamers 2 gauche and 1 trans:



$$^3J = 1/3 (2^3J_g + ^3J_t)$$

this is ~ 7Hz if three populations are equal (fast rotation).

If populations vary

$$^3J = x_I J_g + x_{II} J_t + x_{III} J_g$$

Substituent Effects:

- in general electronegative substituents slightly reduce the coupling.

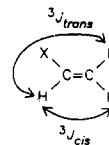
X-CH ₂ -CH ₃		
X	³ J(H,H) [Hz]	E _X ^{a)}
Li	8.4	1.0
H	8.0	2.2
CH ₃	7.3	2.5
Cl	7.2	3.0
OR	7.0	3.5

$$^3J = 8.0 - 0.8(E_x - E_H)$$

- more dramatic effects seen with ethylene derivatives.

Table 3-7.
Vicinal H.H coupling constants in monosubstituted ethylenes.

X	³ J _{cis} [Hz] ^{a)}	³ J _{trans} [Hz] ^{a)}	E _X ^{b)}
Li	19.3	23.9	1.0
H	11.6	19.1	2.2
Cl	7.3	14.6	3.0
OCH ₃	7.1	15.2	3.5
F	4.7	12.8	4.0



Karplus Curves:

- the fact that these couplings are through bonds is best evidence in olefinic double bonds, if through space one would expect *cis* coupling to be stronger than *trans*.

- Karplus gave a valence-bond interpretation of these results and concludes that the vicinal coupling of two protons on adjacent sp^3 orbitals should depend on ϕ , the dihedral angle by the following equations:

$$J = 8.5\cos^2\phi - 0.28(\text{Hz})$$

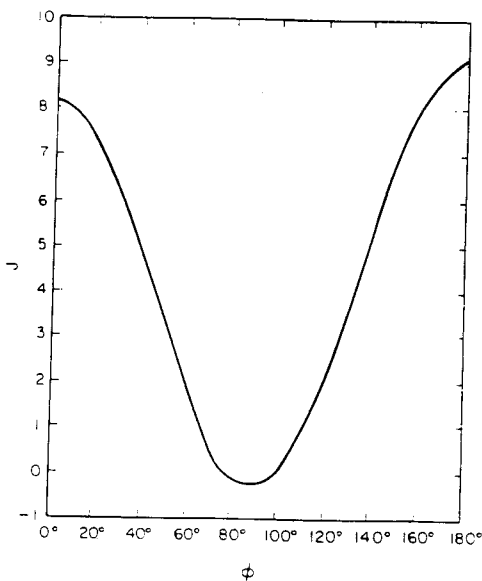
$$0^\circ < \phi < 90^\circ$$

and

$$J = 9.5\cos^2\phi - 0.28(\text{Hz})$$

$$90^\circ < \phi < 180^\circ$$

Values are largest when $\phi = 0^\circ$ and 180° and they are smallest when $\phi = 90^\circ$.



Vicinal proton-proton couplings (3J):

What affects them?

- substituents although less than in geminal case
- variation in geometry (torsion or dihedral angle)
- distance between two carbon atoms concerned.

Table 3-5.
Ranges and typical values of vicinal H,H coupling constants.

Compound		$^3J(\text{H,H})[\text{Hz}]$	
		Range ^{b)}	Typical value ^{b)}
Cyclopropane	<i>cis</i>	6-10	8
	<i>trans</i>	3- 6	5
Cyclobutane	<i>cis</i>	6-10	-
	<i>trans</i>	5- 9	-
Cyclohexane	a, a	6-14	9
	a, e	3- 5	3
	e, e	0- 5	3
Benzene	<i>ortho</i>	6-10	9
Pyridine	2,3	5- 6	5
	3,4	7- 9	8
H-C-C-H		0-12	7
=CH-CH=		9-13	10
-CH=CH ₂	<i>cis</i>	5-14	10
	<i>trans</i>	11-19	16
>CH-CHO		1- 3	3
=CH-CHO		5- 8	6
CH-NH ^{a)}		4- 8	5
CH-OH ^{a)}		4-10	5
CH-SH ^{a)}		6- 8	7

^{a)} Not exchanging. ^{b)} All values are positive.

Geminal proton-proton couplings (2J):

- can vary greatly and can be positive or negative.
- protons on a CH_2 group must be non-equivalent.

sp^3 hybridized groups are usually negative

sp^2 hybridized groups are often positive.

- values highly dependent on angle between the two protons and increases (algebraically) as angle increases.

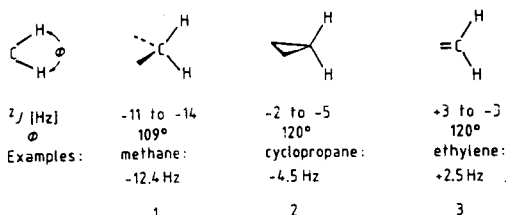


Figure 3-1.
Dependence of geminal coupling constants on the bond angle Φ .

Effects of Substituents:

- can be large and overcome geometrical effects.
- in alkanes EN substituent at α position produce a positive contribution.

Compound	2J [Hz]
CH_4	-12.4
CH_3OH	-10.8
CH_3Cl	-10.8
CH_3F	-9.6
CH_2Cl_2	-7.5
CH_2O	+41.0

X	2J [Hz]	$E_X^{(1)}$
CH_2	-4.5	2.5
S	(\pm) 0.4	2.5
NR	+2.0	3.0
O	+5.5	3.5

- in substituted ethylenes EN substituents at β position cause a negative contribution.

X	$^2J(\text{H}, \text{H})^{(a)}$ [Hz]	$E_X^{(b)}$
Li	+7.1	1.0
H	+2.5	2.2
Cl	-1.4	3.0
OCH_3	-2.0	3.5
F	-3.2	4.0

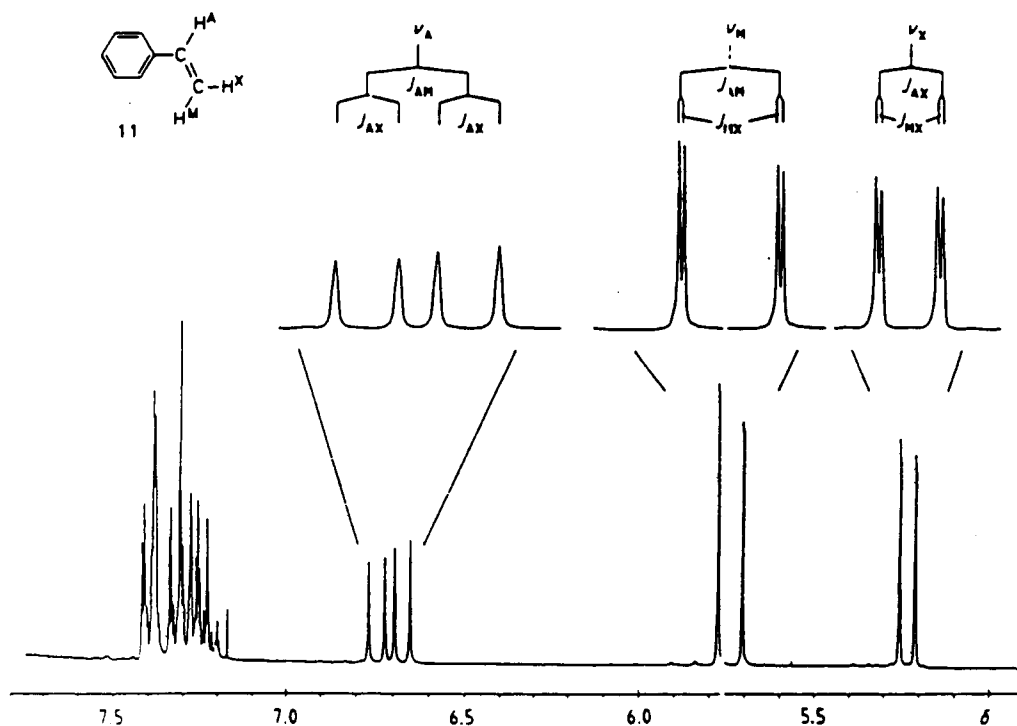
4. AX_n

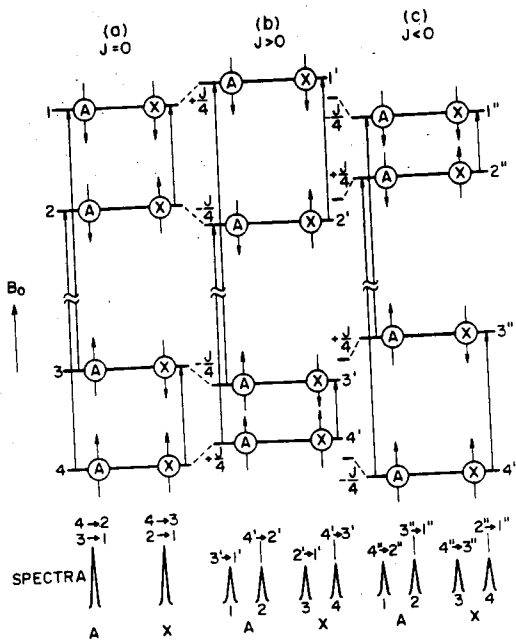
$$M = n + 1$$

M: multiplicity of the NMR signals, number of lines in a multiplet.

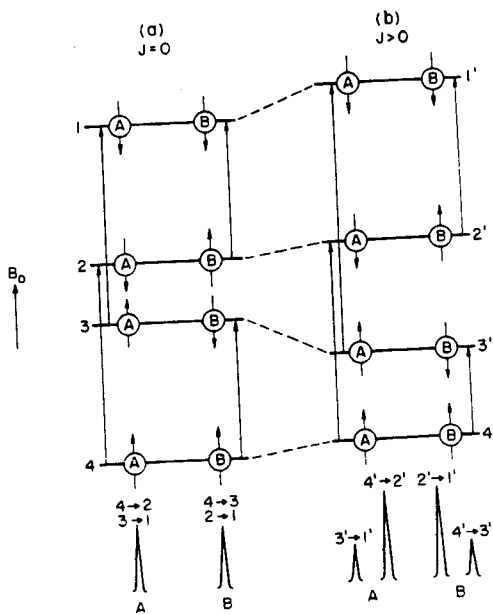
$n = 0$						1
$n = 1$				1	1	
$n = 2$			1	2	1	
$n = 3$		1	3	3	1	
$n = 4$		1	4	6	4	1
\vdots						\vdots

AMX System- three non-equivalent nuclei.





Energy levels and schematic spectra of the AX system.



Energy levels and schematic spectra of the AB system.

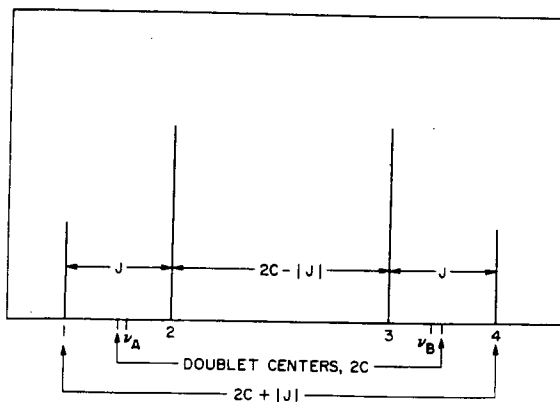
Define a quantity C:

$$C = 1/2 [\Delta\nu^2 + J^2]^{1/2}$$

Transitions of AB and AX Systems

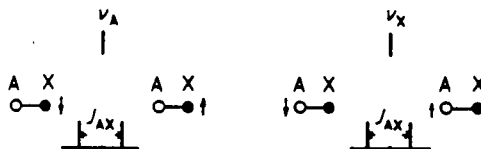
(Line Positions are Referred to the Center of the Spectrum, $\frac{1}{2}(\nu_A + \nu_B)$)

Transition	Line	AX		AB	
		Line position	Relative intensity	Line position	Relative intensity
3→1	1	$\frac{1}{2}(\Delta\nu) + \frac{1}{2}J$	1	$C + \frac{1}{2}J$	$C - \frac{1}{2}J$
4→2	2	$\frac{1}{2}(\Delta\nu) - \frac{1}{2}J$	1	$C - \frac{1}{2}J$	$C + \frac{1}{2}J$
2→1	3	$-\frac{1}{2}(\Delta\nu) + \frac{1}{2}J$	1	$-C + \frac{1}{2}J$	$C + \frac{1}{2}J$
4→3	4	$-\frac{1}{2}(\Delta\nu) - \frac{1}{2}J$	1	$-C - \frac{1}{2}J$	$C - \frac{1}{2}J$



Schematic AB spectrum.

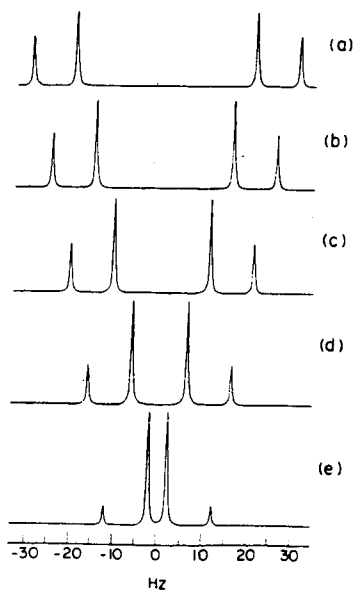
- chemical shift always corresponds to the middle of the doublet which is the position of the signal if there was no coupling.



Coupling values depend on nuclear magnetic moments (μ) thus the values are independent of field strength (B_0) so they are always given in Hz.

AB System:

- $J/\Delta\nu$ becomes larger
- signals are closer together in spectrum.
- analysis of the data becomes more difficult. (it becomes less realistic to assign each nucleus a specific quantum number).



Calculated AB spectra for $J = 10$ Hz and $J/\Delta\nu$ equal to: (a) 0.20, (b) 0.25, (c) 0.33, (d) 0.50, and (e) 1.00.

How does it occur?

- the result of slight polarization of spins and orbital motions of the valence electrons.
- since only s atomic states have finite electron density it can be expected that nuclear couplings will depend to some degree on the fraction of s character in the bond.
- they are not affected by the tumbling of the molecule and is independent of B_0 .
- splitting depends on the probability of paired nuclei finding the others spin to be oriented with or against the applied field.
- usually limited to no more than three intervening bonds.
- couplings between equivalent nuclei or groups of equivalent nuclei are not directly observable.

Order of Spectrum:

Zero - spectrum which contains only singlets.

First - $\Delta\nu \gg J$

Higher - larger values of $J/\Delta\nu$

- zero order usually result of decoupling.
- first order can be analyzed according to rules.
- higher order can be analyzed but much more complicated.

AX spin system:

- large difference in chemical shifts of signals relative to coupling value.
- can be analyzed according to first order rules
- two frequencies ν_a and ν_x if they are coupled we will see two signal for both frequencies.