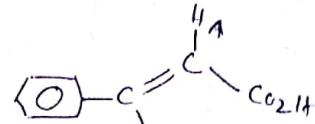


- \* The spectrum contains characteristic pair of doublets, caused by two protons undergoing spin coupling, such a spectrum is called an  $A_X$  spectrum.

e.g. Spectrum of trim cinnamic acid.



Here A and X protons of cinnamic acid give rise to this type of spectrum. (one pair of doublet).

- \* The spectrum consists of doublet and triplet, where two protons coupling with one proton, called  $A_{X_2}$  spectrum.

The Spectrum of 1,1,2-trichloroethane  $\text{CH}_2 \text{---} \overset{\text{H}_A}{\underset{\text{Cl}}{\text{C}}} \text{---} \overset{\text{H}_X}{\text{C}} \text{---} \text{Cl}$  consist of this type of spectra.

- \* The spectrum of 2-chloropropanoic acid  $\text{CH}_3 \text{---} \overset{\text{H}_A}{\underset{\text{Cl}}{\text{C}}} \text{---} \text{CO}_2\text{H}$ , contains a doublet and a quartet, corresponding to the coupling of one proton with neighbour; this is an  $A_{X_3}$  spectrum.

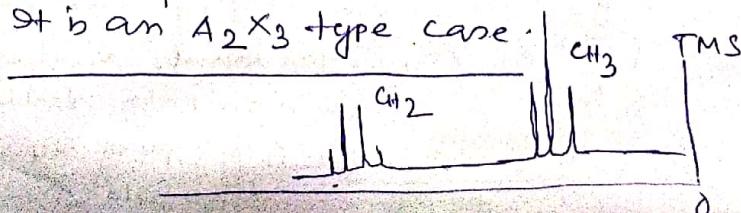
We have already seen the line intensity of doublet, triplet and quartet. One can go further and predict the theoretical line intensities for quintet, sextet, etc., and find that the ratios are the same as the coefficients in the binomial expansion.

Pascal's famous triangle serves to remind:

		Peak area ratio		Signal		
		1		siglet		
				Doublet		
1	1				Triplet	
1	2	1			Quartet	
1	3	3	1			
1	4	6	4	1	Quintet	
1	5	10	10	5	1	Sextet.

The outer lines in the substantial multiplets are of such low intensity that they may be all but unobservable, unless that part of the spectrum is return at increased intensity.

- \* In the spectrum of  $\text{CH}_3 - \text{CH}_2 - \text{Br}$ , triplet and quartet are observed. It is an  $A_2X_3$  type case.

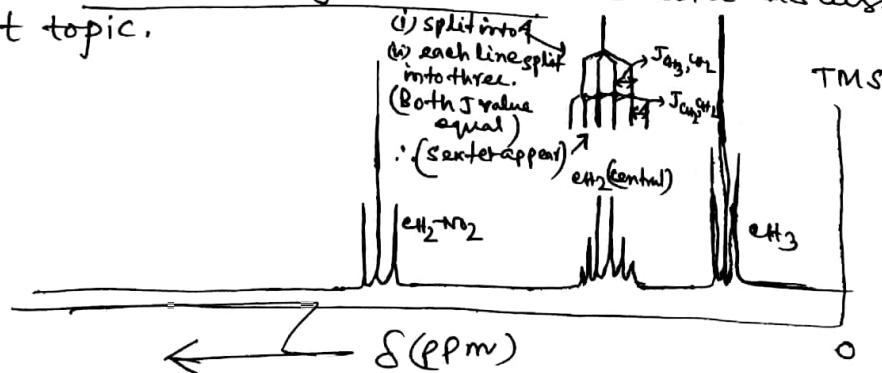


\* NMR spectrum of 1-nitropropane:  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NO}_2$

In the  $^1\text{H}$  NMR spectrum of 1-nitropropane there are three groups of protons, each group coupling with its neighbour. So central methylene group couple with both with methyl protons and terminal methylene protons. The methyl proton appear as triplet, methylene protons. The terminal methylene group also appear as triplet. Since both couple with the central methylene group:  $(n+1) = (2+1) = 3$ . (The methyl protons show no coupling with the terminal methylene protons, since coupling over four  $\sigma$  bond is rarely observed)

The central methylene group can be dealt with by considering the successive coupling, first with the methyl group, and then with the terminal methylene group protons. The methyl protons split the central methylene signal into a quartet; the two terminal methylene protons should now split each line of this quartet into a triplet, giving twelve lines in all. But in the spectrum only six lines are observed, showing that considerable overlapping of the predicted twelve lines has taken place. Actually in this case two coupling constants ( $J_{\text{CH}_3, \text{CH}_2}$  and  $J_{\text{CH}_2, \text{CH}_2}$ ) are equal, and an easier way to consider the central methylene group is to add the total number of neighbours with which it couples ( $\text{CH}_3$  and  $\text{CH}_2$ ) and then apply the  $(n+1)$  rule. As there are total 5 coupling neighbours; therefore, the multiplicity is 6.

\* This simplified approach only succeeds when the two coupling constants are equal. But if two coupling constants are not same, it might have been possible to obtain twelve predicted lines. e.g. Spectrum of ethanol. We will discuss this in the next topic.



\* Spectrum of  $\overset{\text{a}}{\underset{\text{b}}{\text{CH}_2}}-\overset{\text{a}}{\underset{\text{b}}{\text{CH}_2}}-\overset{\text{a}}{\underset{\text{b}}{\text{CH}_2}}-\text{O}$ , two signals are observed.

- ① four protons triplet, downfield
- ② 2 protons quintet, upfield.

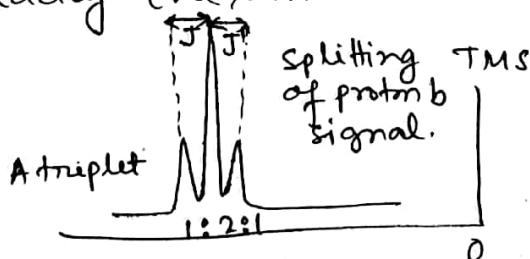
\* Spectrum of  $\overset{\text{a}}{\underset{\text{a}}{\text{CH}_3}}-\overset{\text{b}}{\underset{\text{b}}{\text{CH}-\text{C}\equiv\text{N}}}$ , two signals are observed.

- ① A six proton doublet upfield
- ② A one proton ~~septet~~ Septet [ $(6+1) = 7$ ] downfield

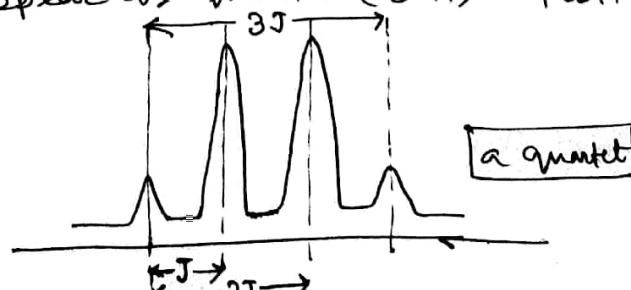
## Coupling Constant (J)

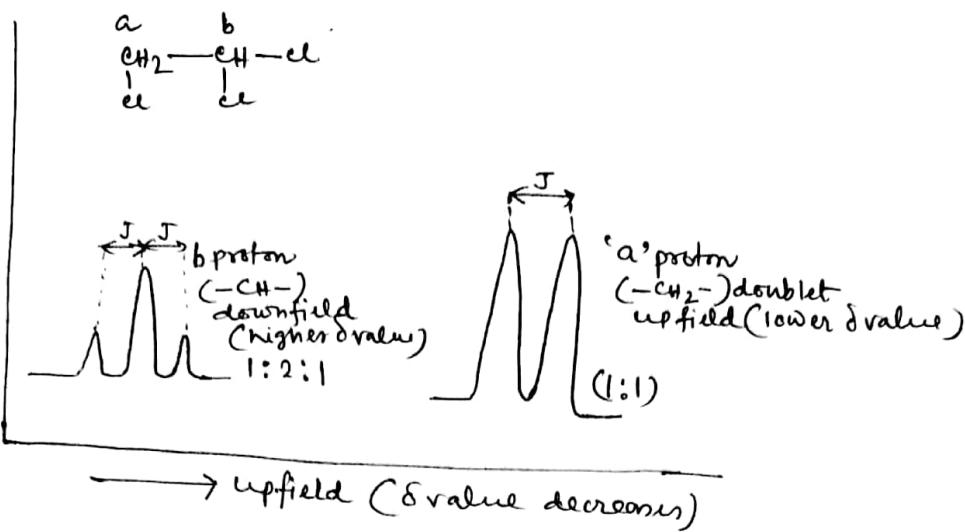
- ④ The distance between the centres of the two adjacent peaks in a multiplet is usually constant and is called Coupling constant (J). The value of the coupling constant is independent of the external field. It is measured in Hertz (Hz) or in cps (cycles per second). It is denoted by the letter J.
- ⑤ If we work the spectrum of a particular compound at different radiofrequencies, the value of J remains same, can't change but the separation of signals due to different chemical shift changes.
- ⑥ From the value of J, one can distinguish between two singlets and one doublet and also a quartet from two doublets.
- ⑦ At two different radiofrequency source, if the separation between ~~the~~ lines does not change, then the signal is a doublet but if the separation between the lines increases with increasing frequency, the signals will be two ~~sig~~ singlet.
- ⑧ The value of J lies between 0 and 20 Hz.

Let us consider a compound  $\text{CH}_2-\text{CH}_2$ , Here two types of proton and so two signals are expected. Under the influence of two equivalent protons 'a', the signal for proton 'b' will appear as a triplet. The distance between two adjacent peaks in a multiplet will be exactly the same.



Similarly, for  $\text{CH}_2-\text{CH}_3$ , here proton 'b' is under influence of three equivalent protons 'a'. So for spin-spin coupling the signals for proton 'b' appear as quartet  $(3+1)=4$  with intensity ratio 1:3:3:1





NMR spectra of 1,1,2 Trichloroethane

- (a) In the spectrum of  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2-\text{O} \\ | \\ \text{CH}_2-\text{Cl}^b \end{array}$ ; a low field triplet ( $4\text{H}$ )<sup>a</sup>, are observed. The value of  $J$  in the triplet as well as in the quintet is found to be same ( $J = 7.1 \text{ cps}$ ).  
 (b) In Isopropyl cyanide  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}-\text{C}\equiv\text{N} \\ | \\ \text{CH}_3 \end{array}$ , two types of protons, (a & b), one 'a' proton  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$  spectrum split into septet ( $(6+1)=7$ ) (higher  $\delta$  value). Six 'b' proton spectrum split into doublet (upfield i.e., low  $\delta$  value). As one neighbouring proton ('a' proton) present. Here  $J$  value for each of these multiplets is  $6.7 \text{ cps}$ .

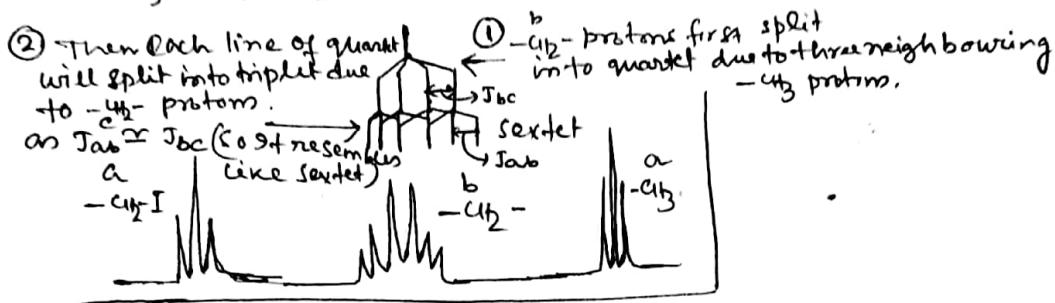
- (c) Butanone,  $\begin{array}{c} (\text{t}) & (\text{a}) & \text{O} \\ \text{CH}_3 & -\text{CH}_2 & \parallel \\ & | & \text{C} \\ & \text{C} & \text{---} \\ & \text{b} & \text{---} \\ \text{---} & \text{CH}_3 & \text{---} \\ \text{---} & | & \text{---} \\ \text{---} & \text{a} & \text{---} \end{array}$  three types of proton.  
 (i) One singlet (for 3 'a' protons)  
 (ii) a low field quartet (for 2 'b' protons).  
 (iii) an upfield triplet (3 'c' protons)

The value of  $J$  in each of these multiplets observed is same and is equal to  $7.3 \text{ cps}$ .

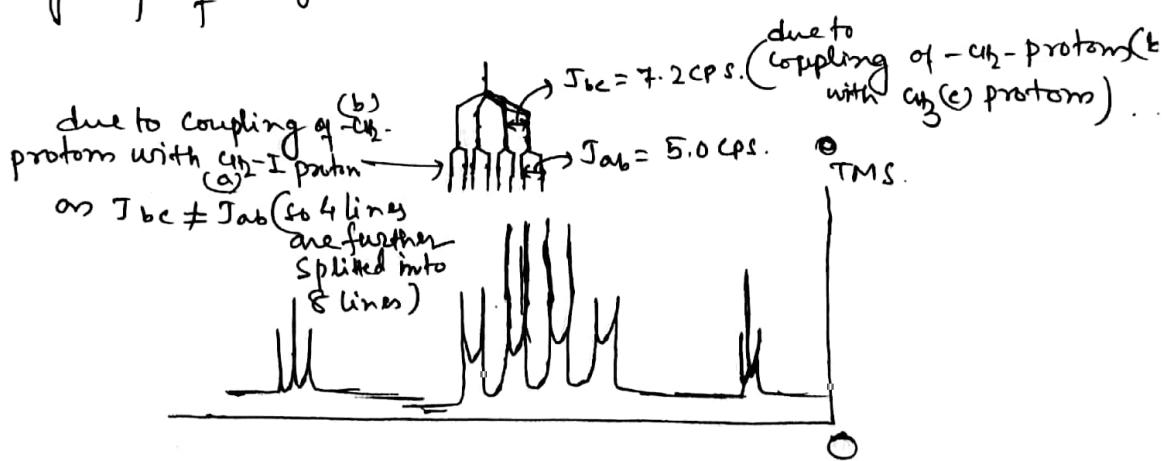
- Note :**
- (1) The value of ' $J$ ' remain same for any two multiplets of a compound in which a signal for one kind of protons is split under the influence of another kind of proton & vice-versa.
  - (2) If a signal is split due to influence of two different sets of protons (protons with different chemical shift), then the peak separations in the multiplets observed will not be equidistant (i.e. different  $J$  value).

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④ Consider an example of propyl iodide,  $\text{CH}_3\text{CH}_2-\overset{\text{b}}{\text{CH}_2}\text{I}$ , there are three types of protons. Here the signal for 'b' kind of protons are under the influence of proton 'a' as well as protons 'c'. As the 'a' kind of protons and 'c' kind of protons are not equivalent, so their coupling constant will not be equal. It has been seen that  $J_{ab} = 6.8 \text{ cps}$  and  $J_{bc} = 7.3 \text{ cps}$  that means the value of  $J$  are close enough, the signals for  $\overset{\text{b}}{\text{CH}_2}$ - protons (multiple) will resemble a sextet. (like  $\text{CH}_3-\overset{\text{b}}{\text{CH}_2}-\overset{\text{c}}{\text{CH}_2}-\text{NO}_2$ , which have been shown before)

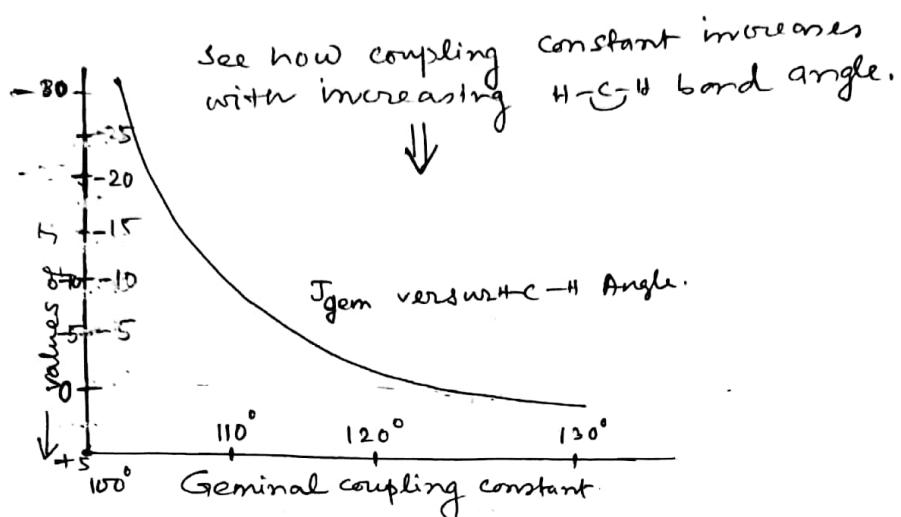


⑤ But in case of  $\overset{\text{c}}{\text{CH}_3}-\overset{\text{b}}{\text{CH}_2}-\overset{\text{a}}{\text{OH}}$ , 'b' protons are under the influence of 'a' protons ( $\text{OH}$ ) as well as 'c' protons. In this case it has been found that  $J_{ab} = 5.0 \text{ cps}$ , &  $J_{bc} = 7.2 \text{ cps}$ . Since the value of coupling constant are much different, so instead of getting quintet, a group of eight lines are observed.



### Various types of coupling.

① Geminal coupling: In the case of geminal protons (protons attached on the same carbon having different chemical environment) of a saturated compound,  $J$  value depends upon the bond angle ( $\text{---} \underset{4}{\text{C}} \overset{4}{\text{H}} \text{---}$ )  $J$  can have any signs.



### A few characteristics of geminal coupling constant ( $J_{\text{gem}}$ )

- ① The value of coupling constant increases with the increase in bond angle (increase in s character).  $J_{\text{gem}}$  is  $-12.4$  cps for methane but  $J_{\text{gem}} = +2.5$  cps for ethylene.
- ② The increase in electronegativity of the atom or group, which withdraw  $\sigma$ -electrons, increase the value of coupling constant. e.g. the coupling constant for methyl ~~chloride~~ chloride is  $-10.8$  cps whereas it is  $-9.4$  cps for methyl fluoride.
- ③ The value of  $J$  decreases if an electronegative substituent withdraws electrons from the  $\pi$  bonds. For example,  $J_{\text{gem}}$  is  $+2.3$  cps for ethene whereas it is  $-3.3$  cps for vinyl fluoride.

<u>Compound</u>	<u>Coupling constants (<math>J_{\text{gem}}</math>)</u>
Methane	$-12.4$ cps
Methyl chloride	$-10.8$ cps
Methyl fluoride	$-9.4$ cps
Ethene	$+2.5$ cps
Formaldehyde	$+41.0$ cps. $\begin{array}{c} \text{H} \\   \\ \text{C}=\text{O} \\   \\ \text{H} \end{array}$