

NMR Spectroscopy

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Introduction; nuclear spin; NMR active molecules; basic principles of Proton Magnetic Resonance; choice of solvent and internal standard; equivalent and non-equivalent protons; chemical shift and factors influencing it; ring current effect; significance of the terms: up-/downfield, shielded and deshielded protons; spin coupling and coupling constant (1st order spectra); relative intensities of *first-order* multiplets: Pascal's triangle; chemical and magnetic equivalence in NMR ; anisotropic effects in alkene, alkyne, aldehydes and aromatics; NMR peak area, integration; relative peak positions with coupling patterns of common organic compounds (both aliphatic and benzenoid-aromatic); rapid proton exchange; interpretation of NMR spectra of simple compounds.

Spin coupling and Coupling constant (J)

Chemical shift and “integral value” provide information about **the number and types of hydrogen in the molecule**. Another important phenomena is spin-spin coupling or j-coupling

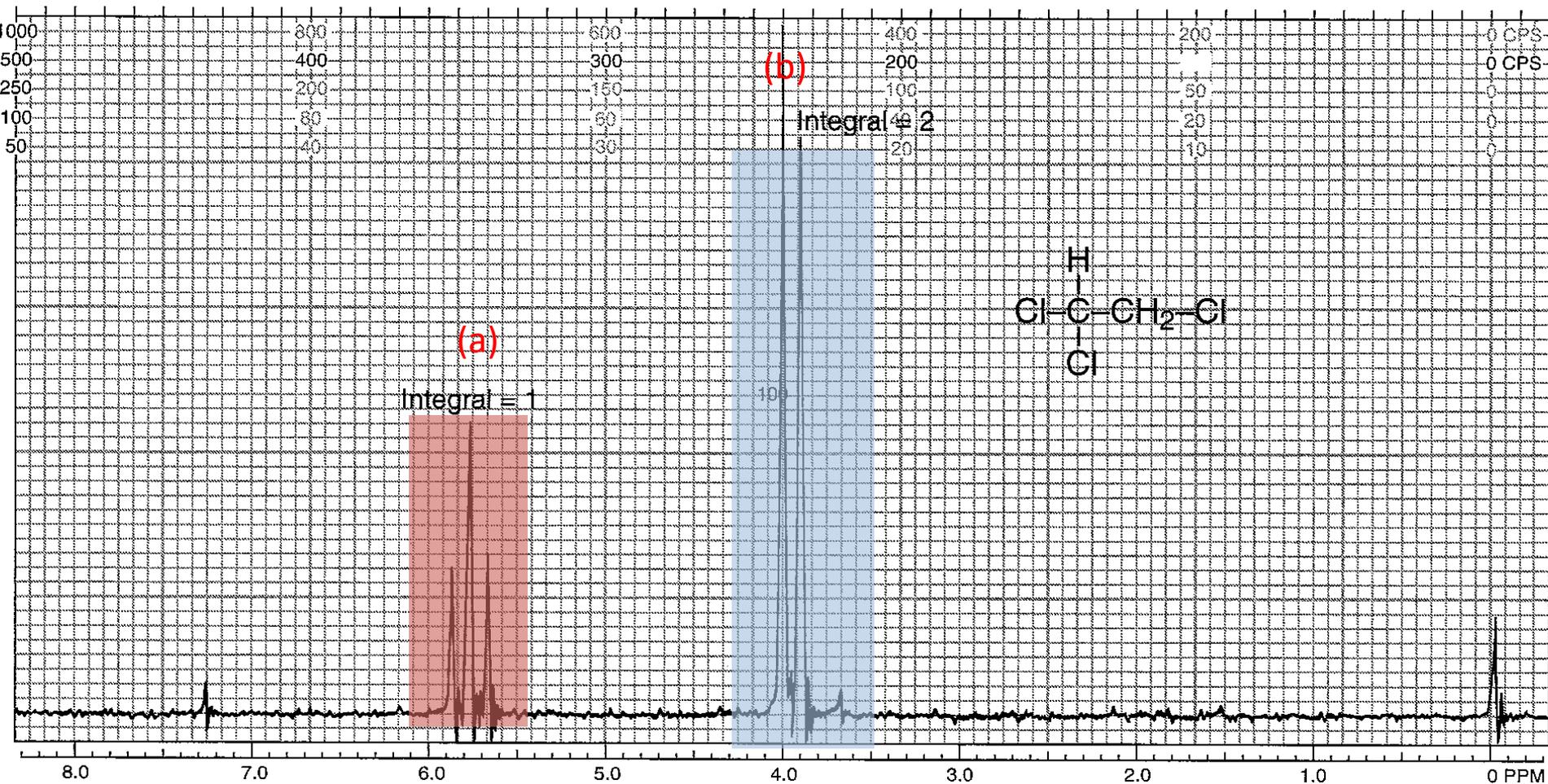
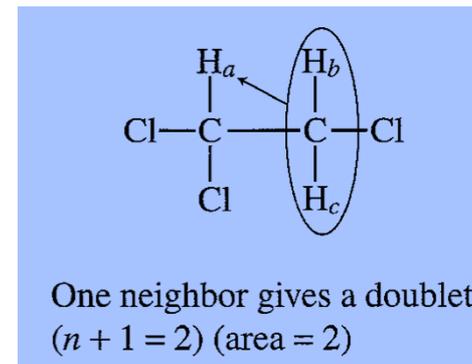
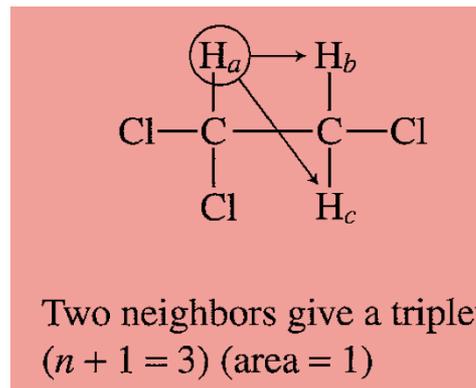
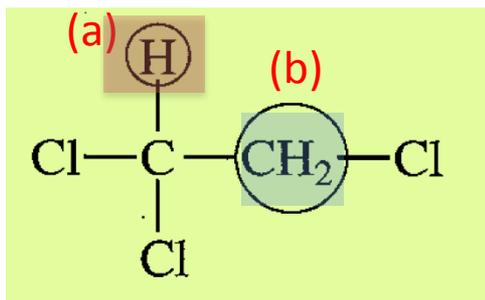
In the ^1H -NMR spectra of most organic molecules contain proton signals that are 'split' into two or more sub-peaks.

The source of signal splitting is a phenomenon called **spin-spin coupling**, a term that describes the magnetic interactions between neighboring, non-equivalent NMR-active nuclei.

($n+1$) Rule

Each type of proton recognizes the number of equivalent protons (n) on the carbon atom(s) next to the one which it is bonded, and its resonance peak is split into ($n+1$) components

Example

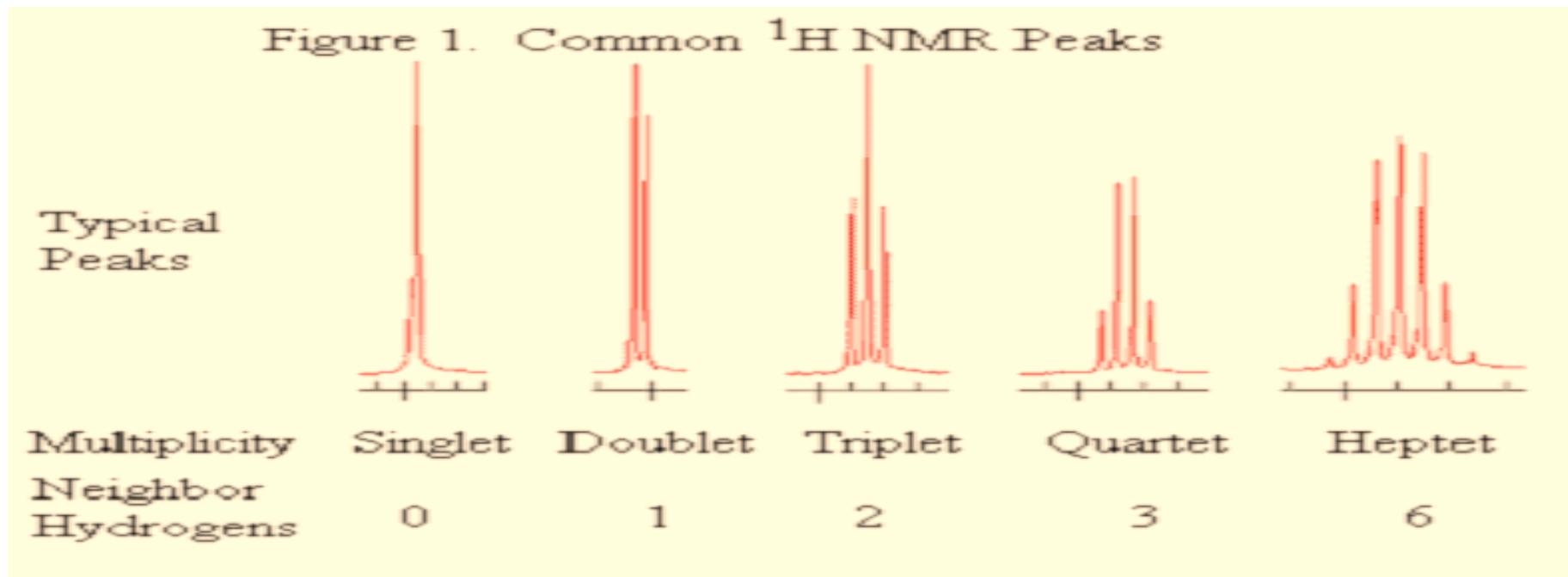


(n=1) rule

Therefore,

n= Number of protons in nearby nuclei

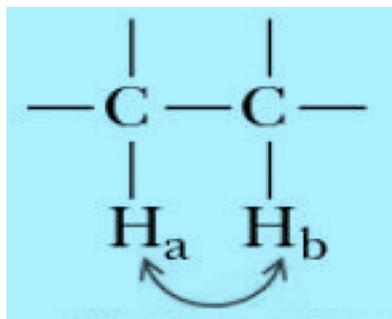
- ✓ Zero H atom as neighbor $n+1= 0+1= 1$ (singlet) or s
- ✓ One H atom as neighbor $n+1= 1+1 = 2$ (doublet) or d
- ✓ Two H atom as neighbor $n+1= 2+1 = 3$ (triplet) or t
- ✓ Three H atom as neighbor $n+1= 3+1 = 4$ (quartet)
- ✓ Four H atom as neighbor $n+1= 4+1 = 5$ (quintet)
- ✓ More hydrogen then multiplet or m. If broad signal then bs



Summary of (n+1) rule

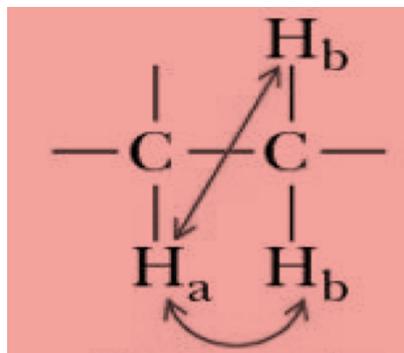
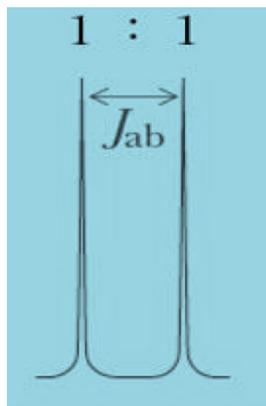
- Equivalent protons do not couple with each other.
- A hydrogen does not cause splitting with itself, but only with neighboring hydrogens
- If you have N number of magnetically equivalent hydrogens causing the splitting then you have N+1 peaks in the spectrum
- Must be within a short distance to allow the small magnetic field of one hydrogen to affect the magnetic field around another
- Splitting is observed if the protons are separated by more than three single bonds
- Splitting of signal depend on neighboring proton
- Signal split according to $2nI+1$ where $I = 1/2$ for proton i.e by n+1 Where n = number of neighboring proton

Intensity of splitting



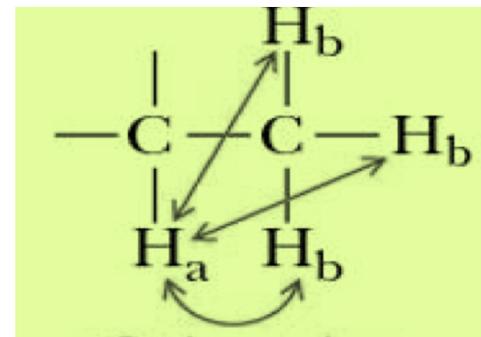
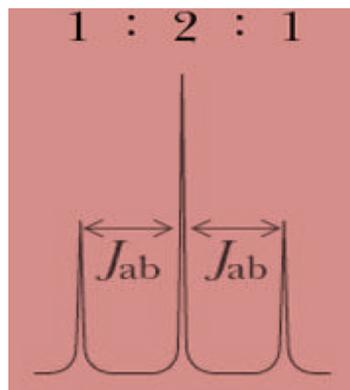
Doublet

H_a proton



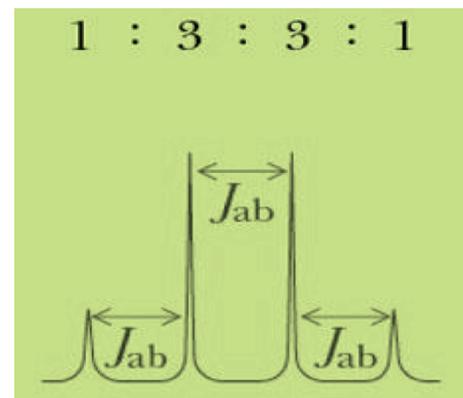
Triplet

H_a proton



quartet

H_a proton



Pascal's Triangle

Relative intensities of first order multipletes

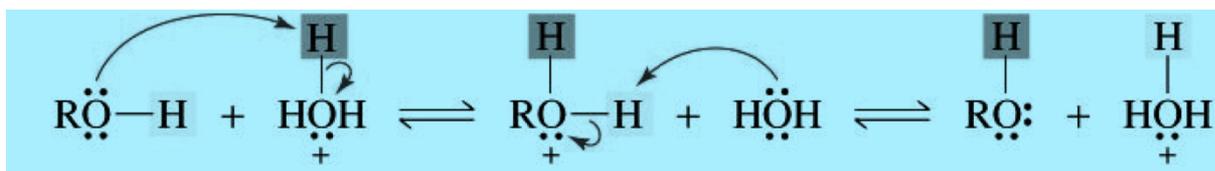
n = number of equivalent nuclei	Relative Intensity							
0					1			
1				1		1		
2			1		2		1	
3			1		3		3	
4			1		4		6	
5			1		5		10	

Broad peak in NMR (bs-broad singlet)

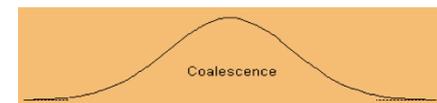
- In NMR spectra, we get a sharp peak line for splitting as s, d, t etc
- But some peaks are not sharp
- They show as broad peak
- Protons which are exchangeable shows such peaks or protons which attached to $-\text{OH}$, $-\text{NH}_2$

The greater the extent of the hydrogen bond, the greater the chemical shift

Mechanism for acid catalysed proton exchange



These protons can undergo proton exchange

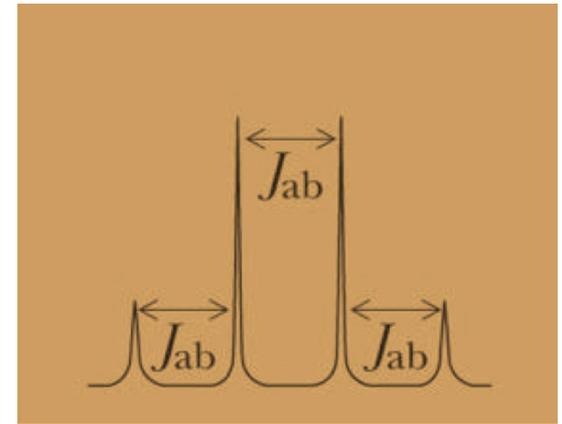
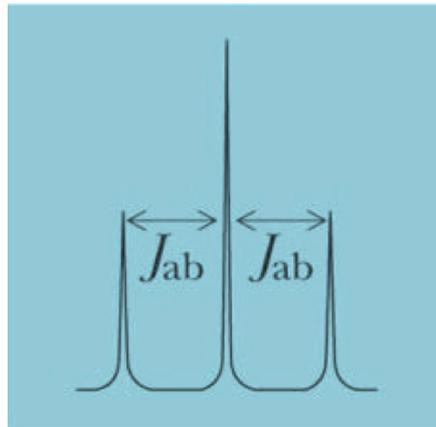
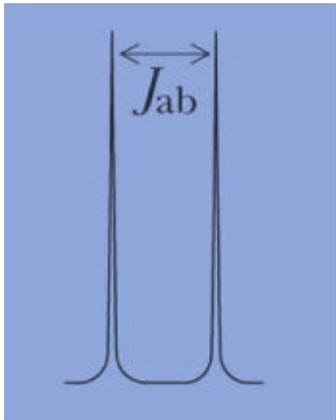


Broad peak

Protons Bonded to Oxygen and Nitrogen will not split even they have neighboring proton

Coupling constant (J)

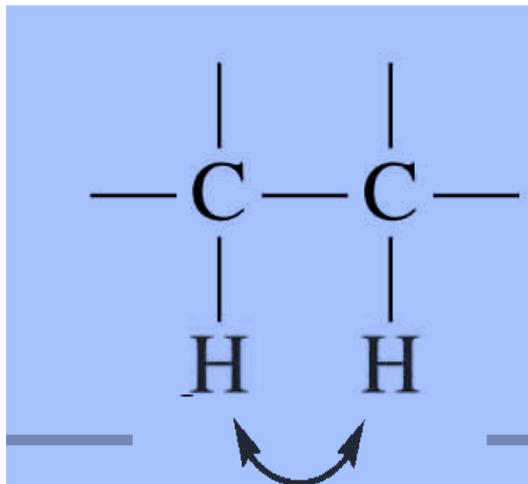
- ❖ The coupling constant (J) is the distance between two adjacent peaks of a split NMR signal in hertz
- ❖ Generally fall into range 0 to 18 Hz



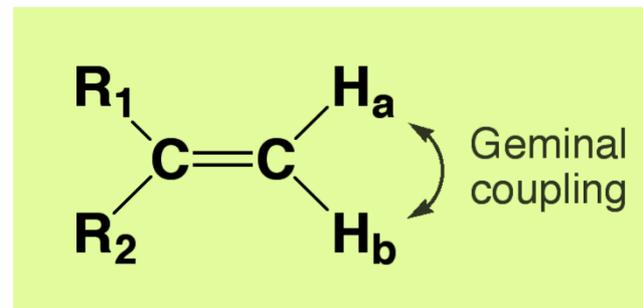
J is a measure of the amount of interaction between the two sets of hydrogens creating the multiplet.

Types of coupling

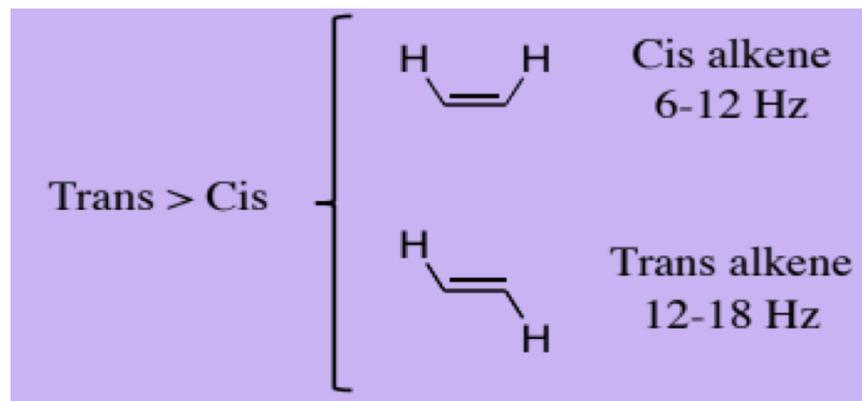
Vicinal Coupling



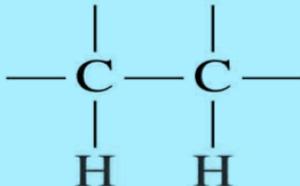
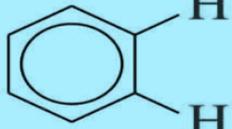
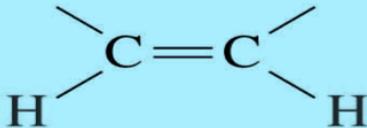
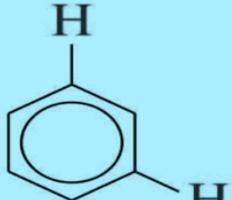
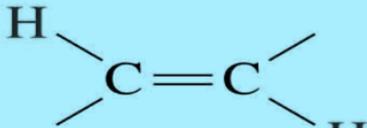
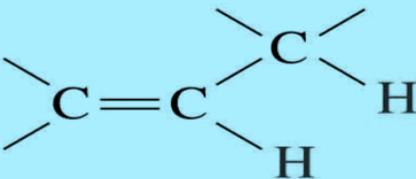
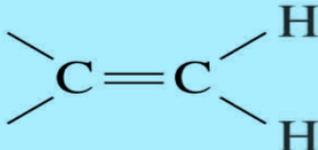
Geminal Coupling



Cis and Trans coupling

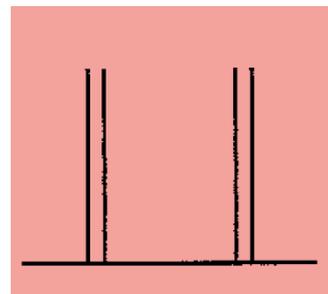
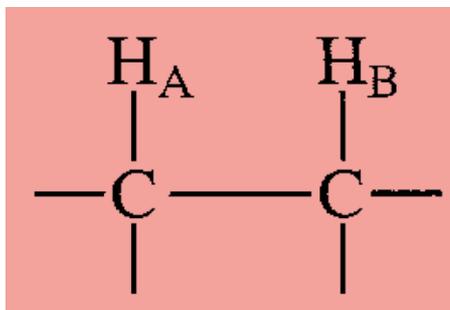


Some Typical Coupling Constant value

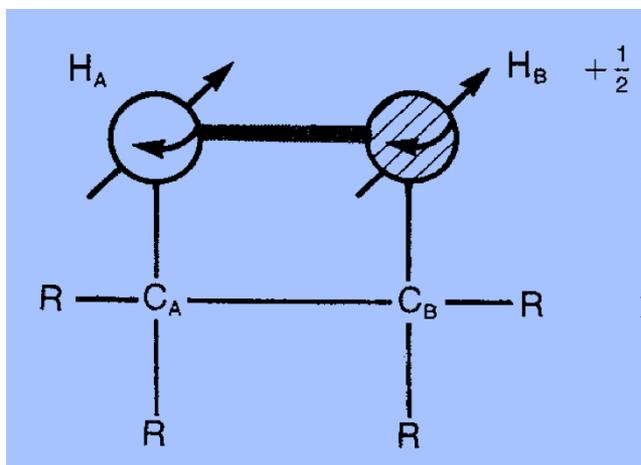
		<u>Approx. J</u>			<u>Approx. J</u>
	(free rotation)	7 Hz ^a		(ortho)	8 Hz
	(cis)	10 Hz		(meta)	2 Hz
	(trans)	15 Hz		(allylic)	6 Hz
	(geminal)	2 Hz			

^aThe value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon-carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.

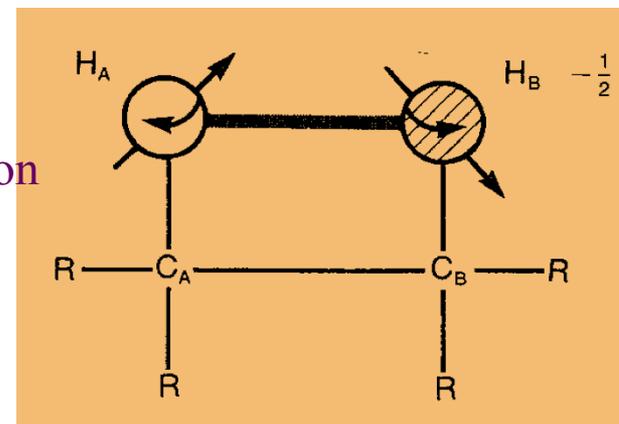
The Origin of Spin-Spin Coupling



Both H_A and H_B appear as doublet

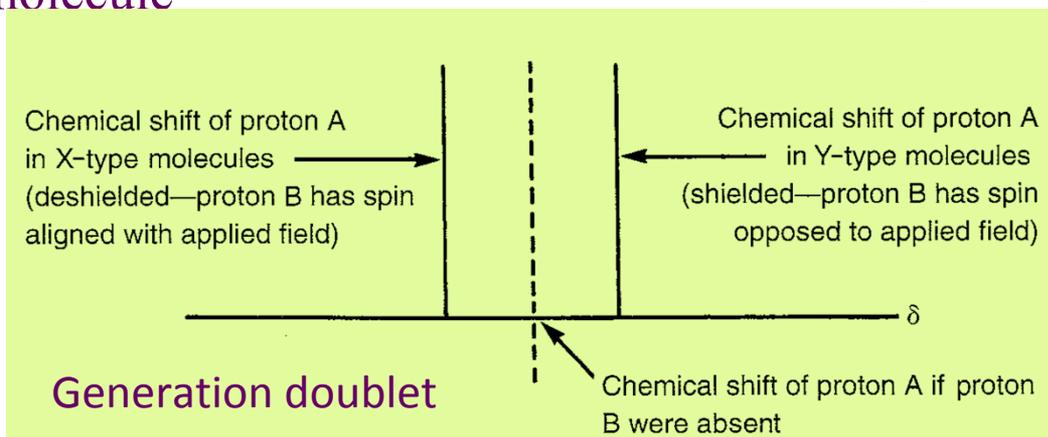


Two spin orientation is possible in (1:1) ratio



Y-type molecule

X-type molecule



Origin of Intensities of split peak

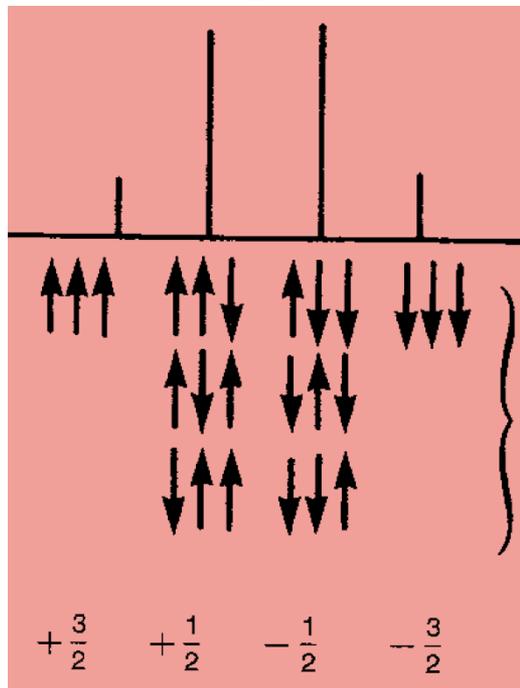


Ethyl Iodide



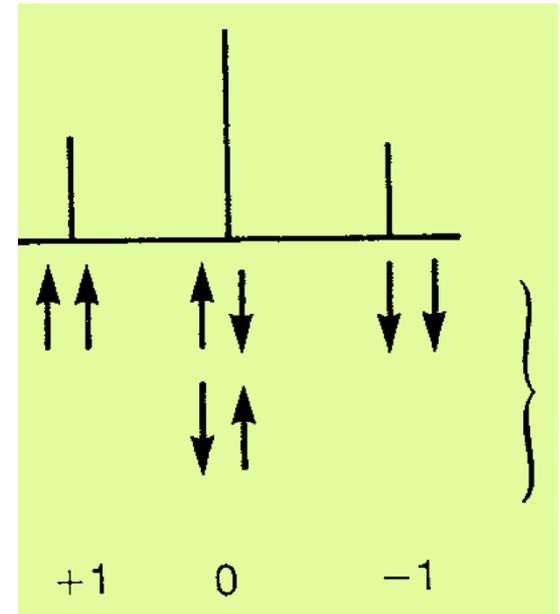
Splitting pattern

-CH₂- Group



1 : 3 : 3 : 1

-CH₃- Group



1 : 2 : 1

Suppose
Up-deshielded
Down-shielded

↑ = spin $+\frac{1}{2}$
↓ = spin $-\frac{1}{2}$

Source: Introduction to Spectroscopy by Pavia