

SPECTROSCOPY

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Factors affecting Chemical Shifts

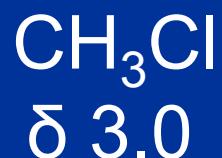
Important factors which influence the proton chemical shifts are:

1. Inductive effects
2. Anisotropic effects
3. Hydrogen bonding

Inductive effects

The proton chemical shifts (in δ -value) increases as the electronegativity of the atom attached to the carbon atom bearing hydrogen s increases because as the electron density around that proton decreases which causes deshielding. Thus higher the electronegativity higher the deshielding and hence higher the δ -value of the chemical shift i.e. towards the downfield.

Further greater the number of electronegative atom, greater the deshielding hence higher the δ -value i.e. downfield.

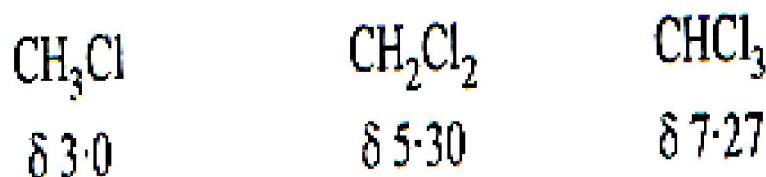


Further the distance of the proton from the halogen increases, deshielding also decreases hence lower the δ -value i.e. upfield.

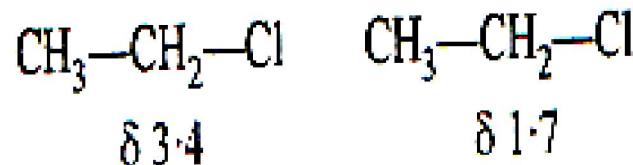


Compound CH_3-X	CH_3F	CH_3OH	CH_3Cl	CH_3Br	$\text{CH}_3\text{-I}$	CH_4	$(\text{CH}_3)_4\text{Si}$
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.0	2.8	2.5	2.1	1.8
Chemical shift δ	4.26	3.40	3.0	2.68	2.16	0.9	0
τ	5.74	6.60	7.0	7.32	7.84	9.1	10

Further, greater the number of halogen atoms, greater is the deshielding. For example,



As the distance of the proton from the halogen increases, the deshielding also decreases. For example,



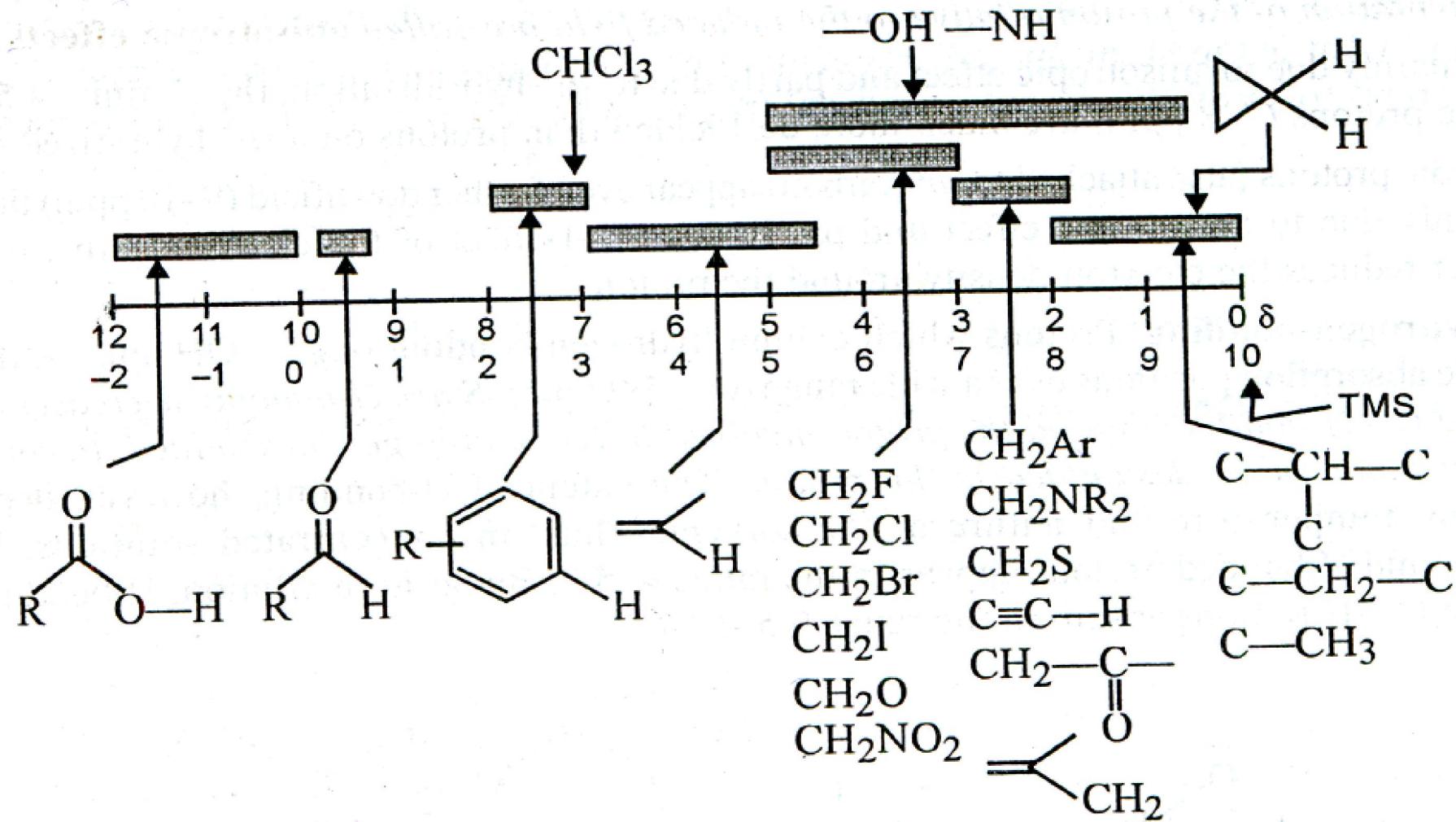
Anisotropic effects.

The effect which depend the orientation of the proton relative to the induced field produced by the circulation of π -electrons are called anisotropic effects.

The olefin protons	δ 4.5 – 5.9
The aromatic protons	δ 7.0 – 8.0
The Aldehydic proton	δ 9.0 – 10.0
The carboxylic proton	δ 11.0 – 12.0

Hydrogen bonding.

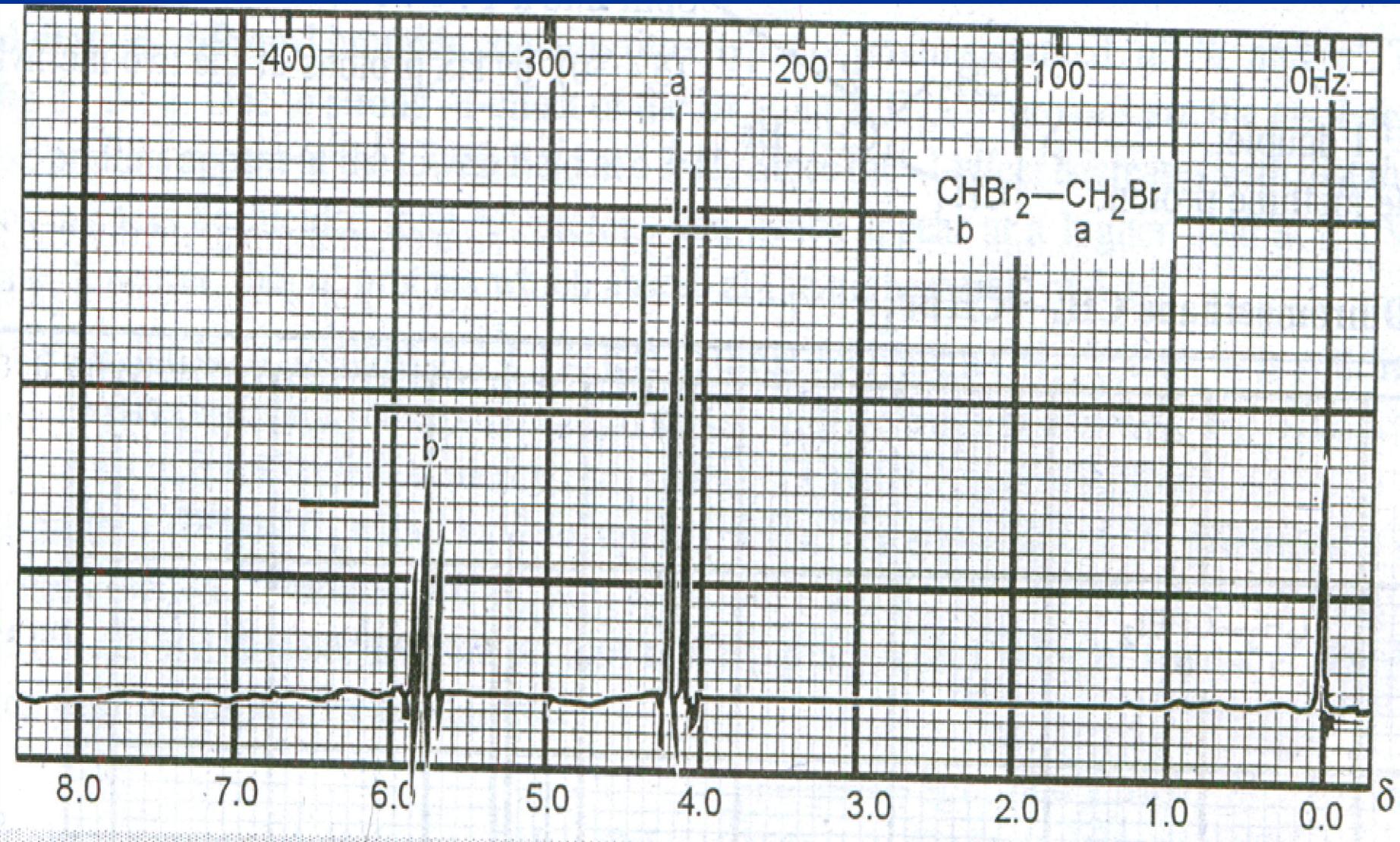
Due to hydrogen bonding the electron density in the O-H bond decreases, thus the proton involving H-bonding gets deshielded thus higher the δ -value i.e. downfield.



Splitting of signals. Spin – Spin coupling.

Number of signals in a NMR spectrum is equal to the number of types of protons in the molecule. There is one signal each for every set of equivalent protons. But the NMR spectra of most of the molecules are much more complicated than we can expect in view of the above statement.

Let us consider the PMR spectra of 1,1,2-Tribromoethane.



This compound contains two set of equivalent protons thus there should be only two signals. But its actual PMR spectrum shows as many as five peaks.

Thus a signal from each set of equivalent protons dose not appear as a single peak but appears as a group of peaks. This is known as **splitting of PMR signals**.

Cause of splitting.

The splitting of signals can be determined by the environment of the absorbing protons with respect to the neighboring protons. Because of the different spin states and the resultant magnetic moment of the neighboring protons, the actual magnetic field experienced by the given protons may be modified in the number of ways.

As such the absorbing proton may experienced each of the modified fields and its absorption signal may split up into different peaks.

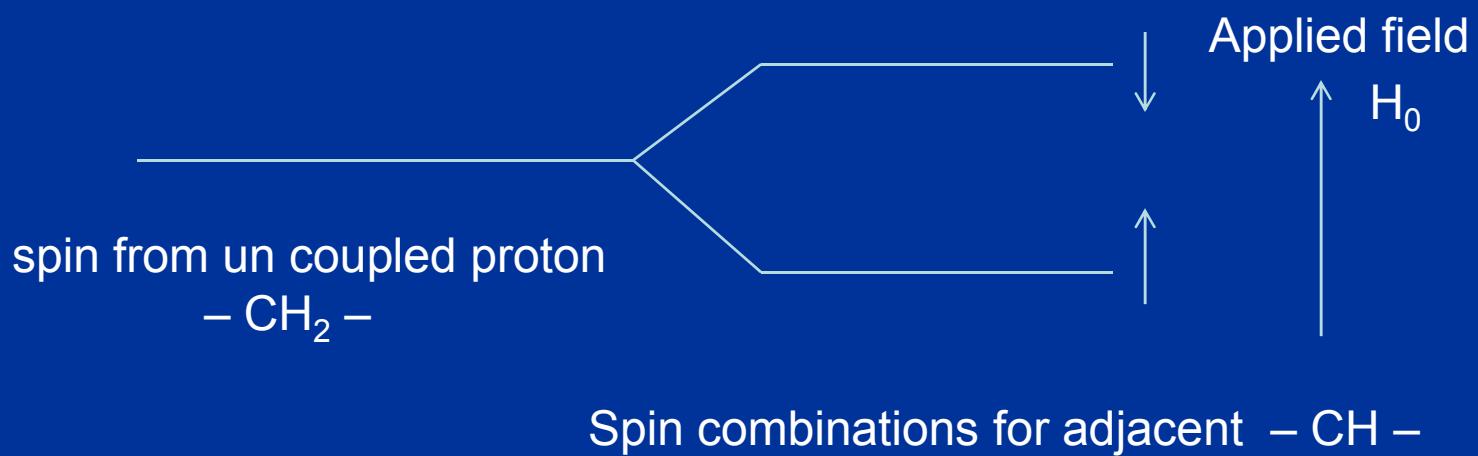
Thus it is the spin – spin coupling of the absorbing and neighboring protons which is responsible for the splitting of peaks.

Let us consider two adjacent carbon atoms-
One carrying two secondary H atoms and other
carrying one tertiary H atom.



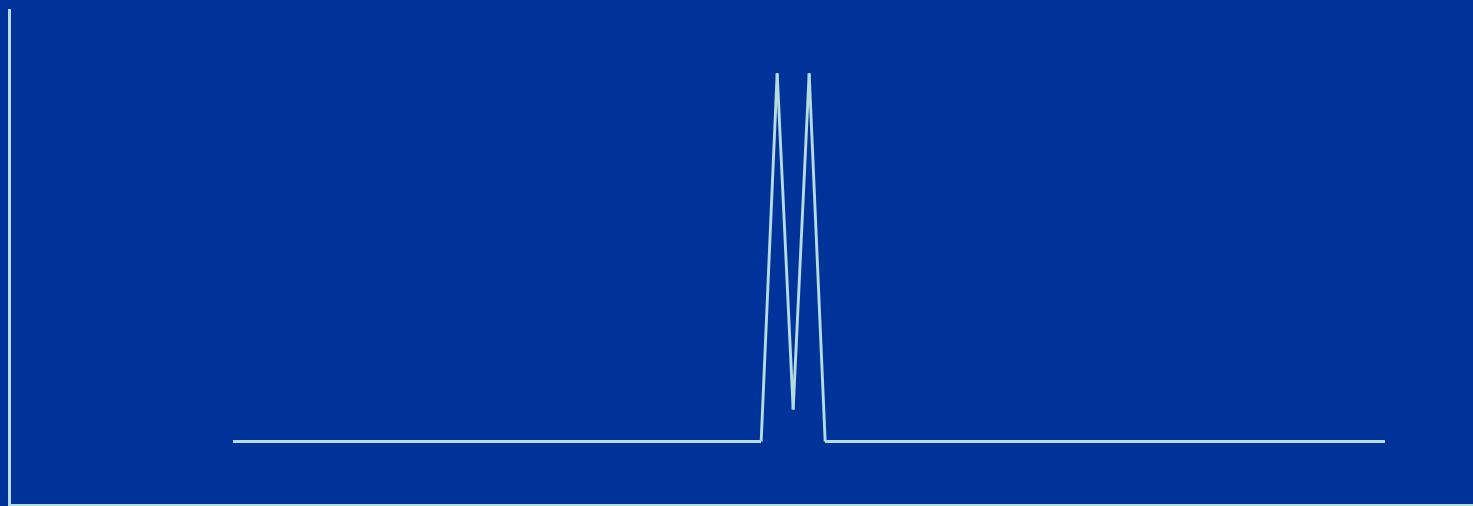
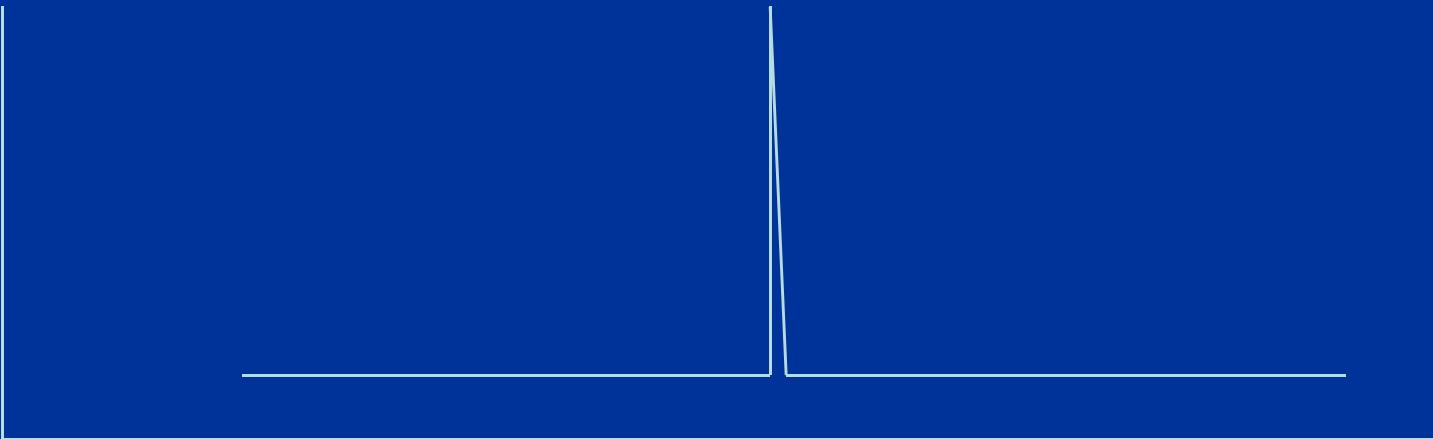
The effective field experienced by a secondary H at a particular moment may get increased or decreased slightly by spin orientation of the nearby tertiary H.

The field would be increased if the spin of the tertiary H is found to be aligned with the field at that moment and decreased if the spin of the tertiary H is found to be against the field.

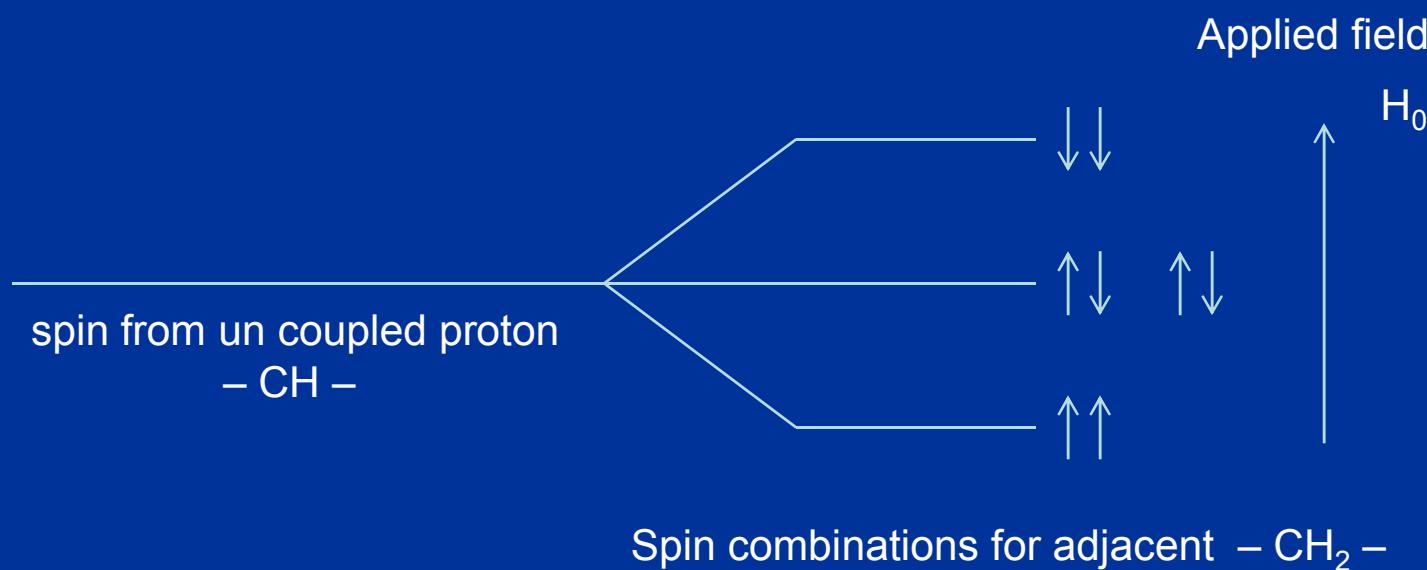


We may say that for half of the molecules the secondary H will feel an increased effective field and absorption will take place slightly downfield.

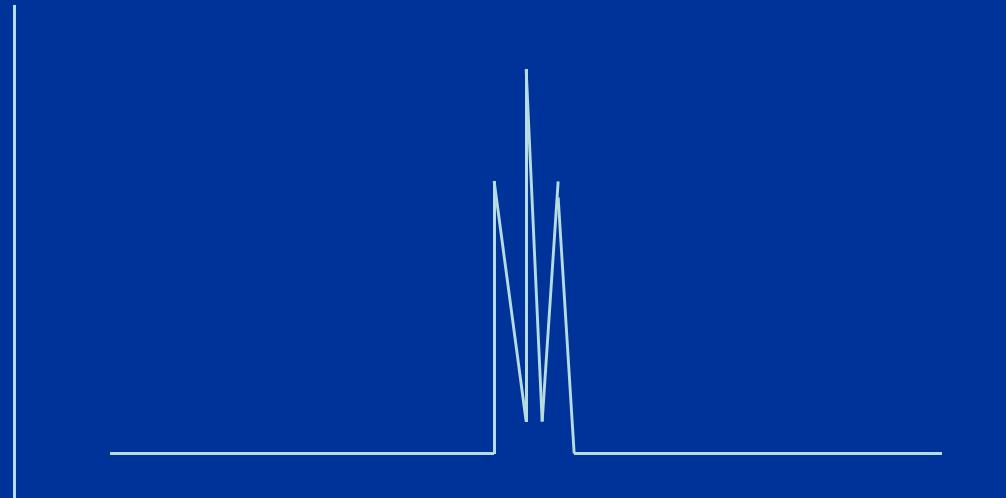
On the other hand, for the other half of the molecules the secondary H will feel a decreased effective field and absorption will be shifted slightly upfield. Thus the absorption signal is split into two peaks, called **doublet**, with equal intensities(1:1) as shown in the fig.



The absorption of the tertiary proton is, in turn, influenced by the spins of both the neighboring secondary H atoms thus there can be four possible combinations of spin alignment out of which two are equivalent as shown in fig. Hence there are only three effective combinations.



Thus the tertiary H will experience any one of the three fields at any moment. As such its signal splits up into three equally spaced peaks called triplet. The relative intensities of the peaks in this triplets are 1:2:1, the central peak being almost doubled in intensity due to the combined probability of two equivalent combinations of spin states.



Rules of splitting of Proton Signals.

Following are the rules used to predict or interpreting the splitting of protons signals.

1. Splitting of one proton signal is only caused by non-equivalent neighboring or vicinal proton .
2. Splitting of one proton by another proton on the same carbon is seen only when the two geminal protons are non-equivalent.
3. The number of peaks into which a given proton signal is split is equal to one more than the number of vicinal protons.

In other words, the multiplicity of a proton signal is given by $(n + 1)$ rule. Where ‘n’ is the number of vicinal protons. The relative intensities of the component of the peaks can easily remembered by using the Pascal triangle.

	1	singlet
	1 : 1	doublet
	1 : 2 : 1	triplet
	1 : 3 : 3 : 1	quartet
	1 : 4 : 6 : 4 : 1	quintet
	1 : 5 : 10 : 10 : 5 : 1	sextet

4. All the peaks of a given multiplet do not have exactly the same intensity as predicted above.

Coupling Constant

The distance between the adjacent peaks in a multiplet is called the coupling constant. It is denoted by the symbol “J”, the numerical value of J is expressed in Hz or cps.

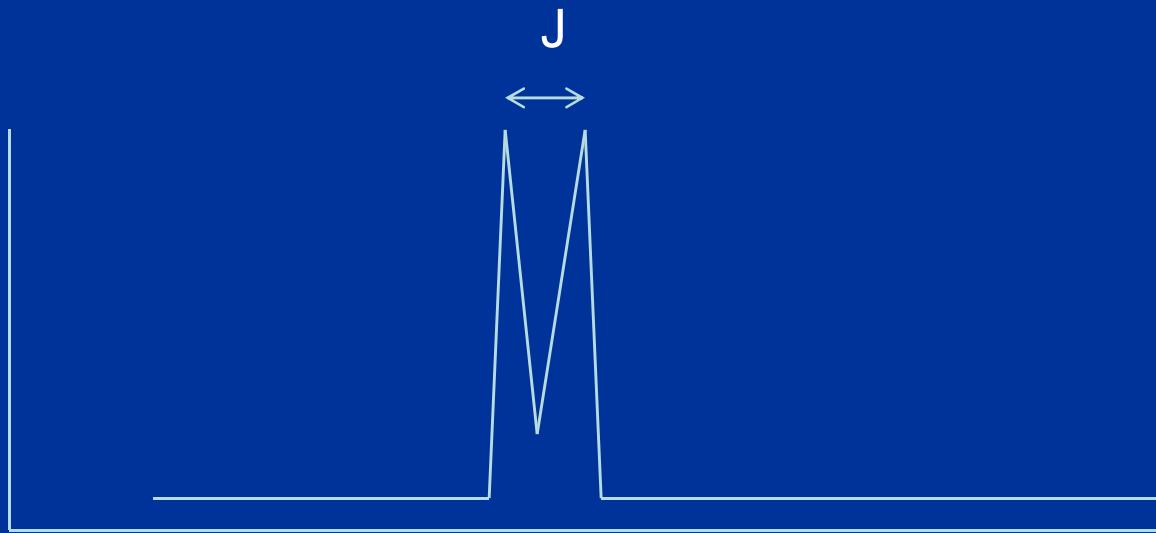
Unlike the chemical shifts, the values of J are independent of the applied field strength and depend only upon the molecular structure.

How can PMR spectroscopy be used to distinguish between ethane, ethene and ethyne?

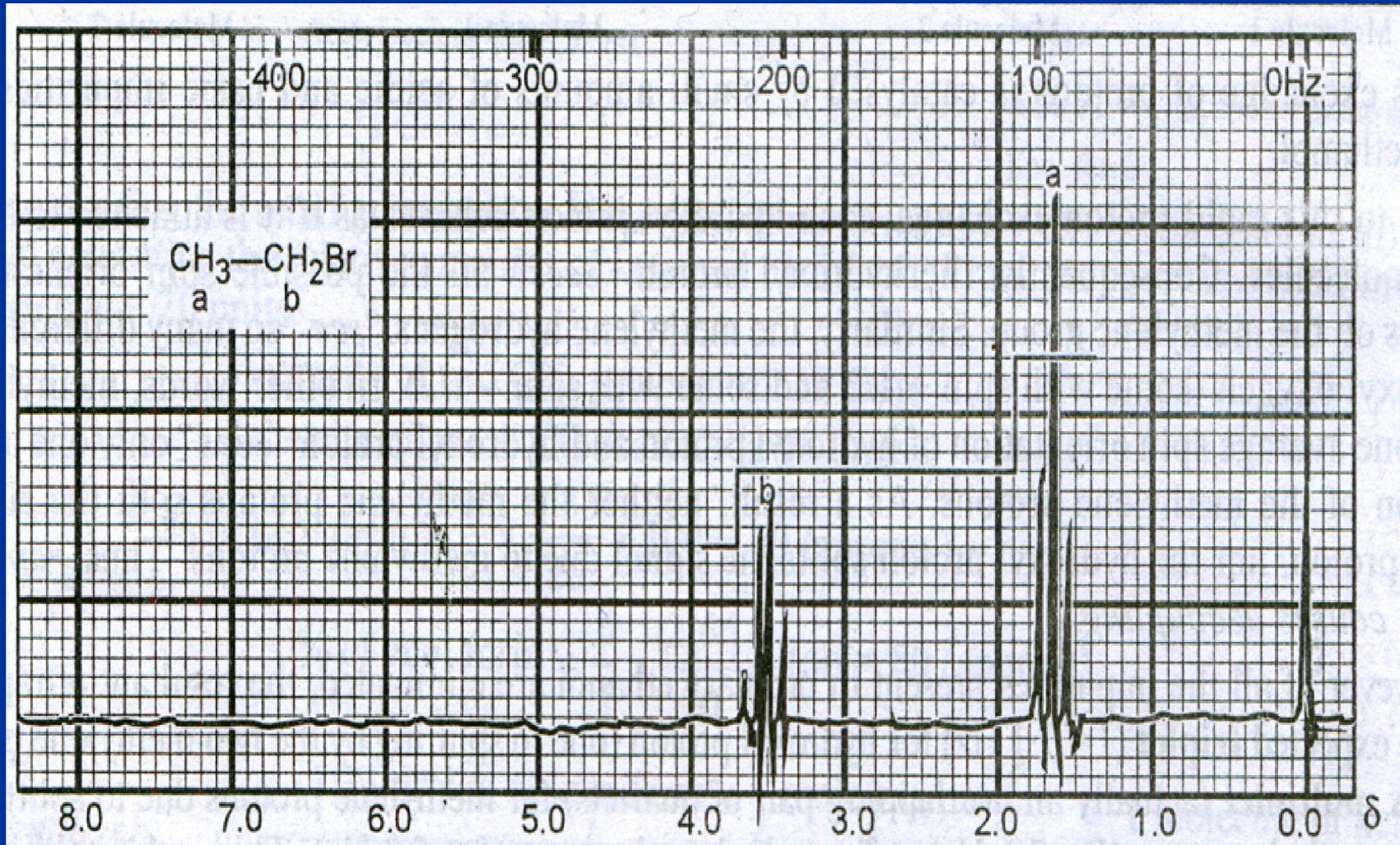
0.9, 5.3 2.0

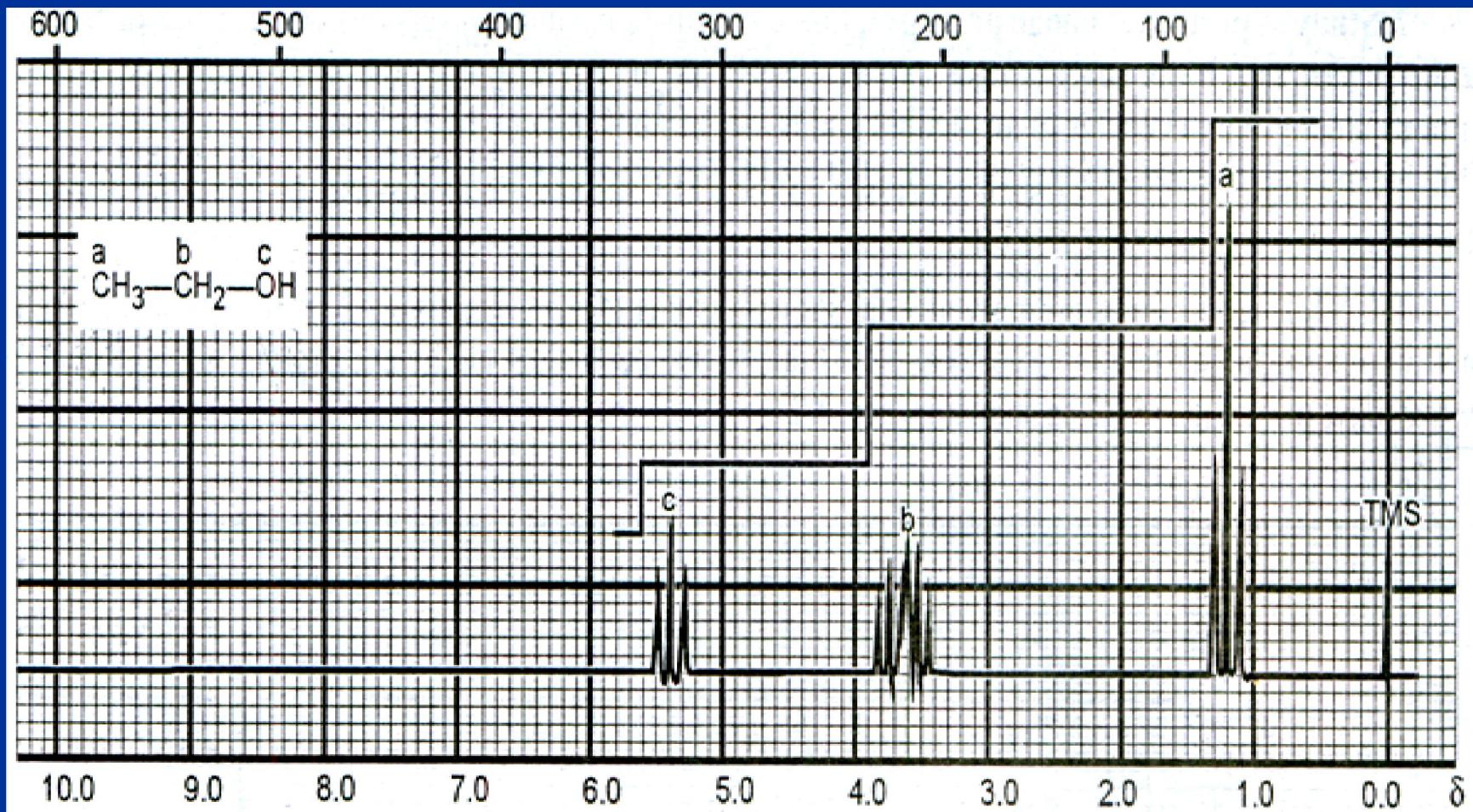


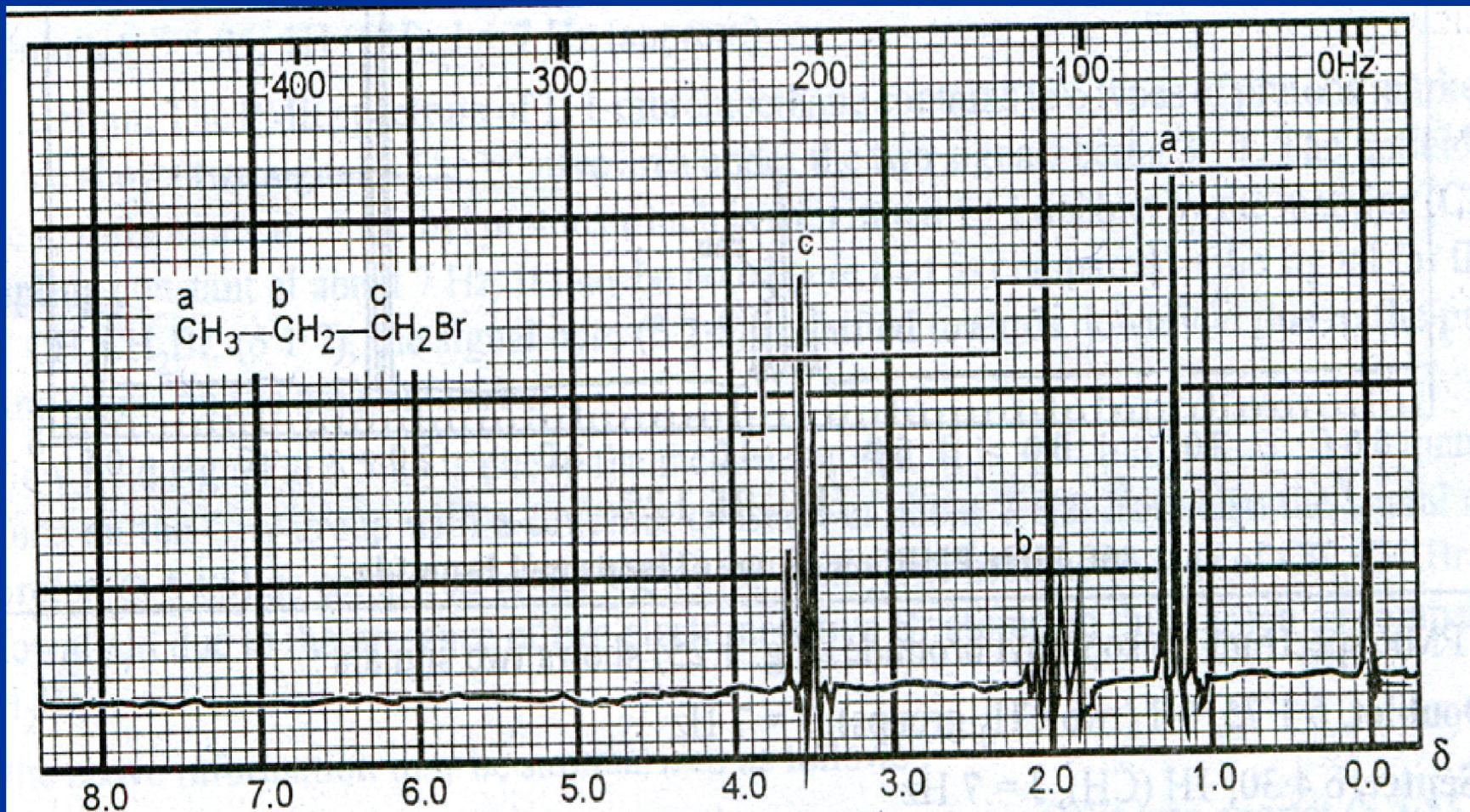
- **Magnitude of coupling constants.**
- The magnitude of the coupling constants depends on the number and kinds of intervening bonds, spatial positions of the two coupled protons and the structure of the molecule.

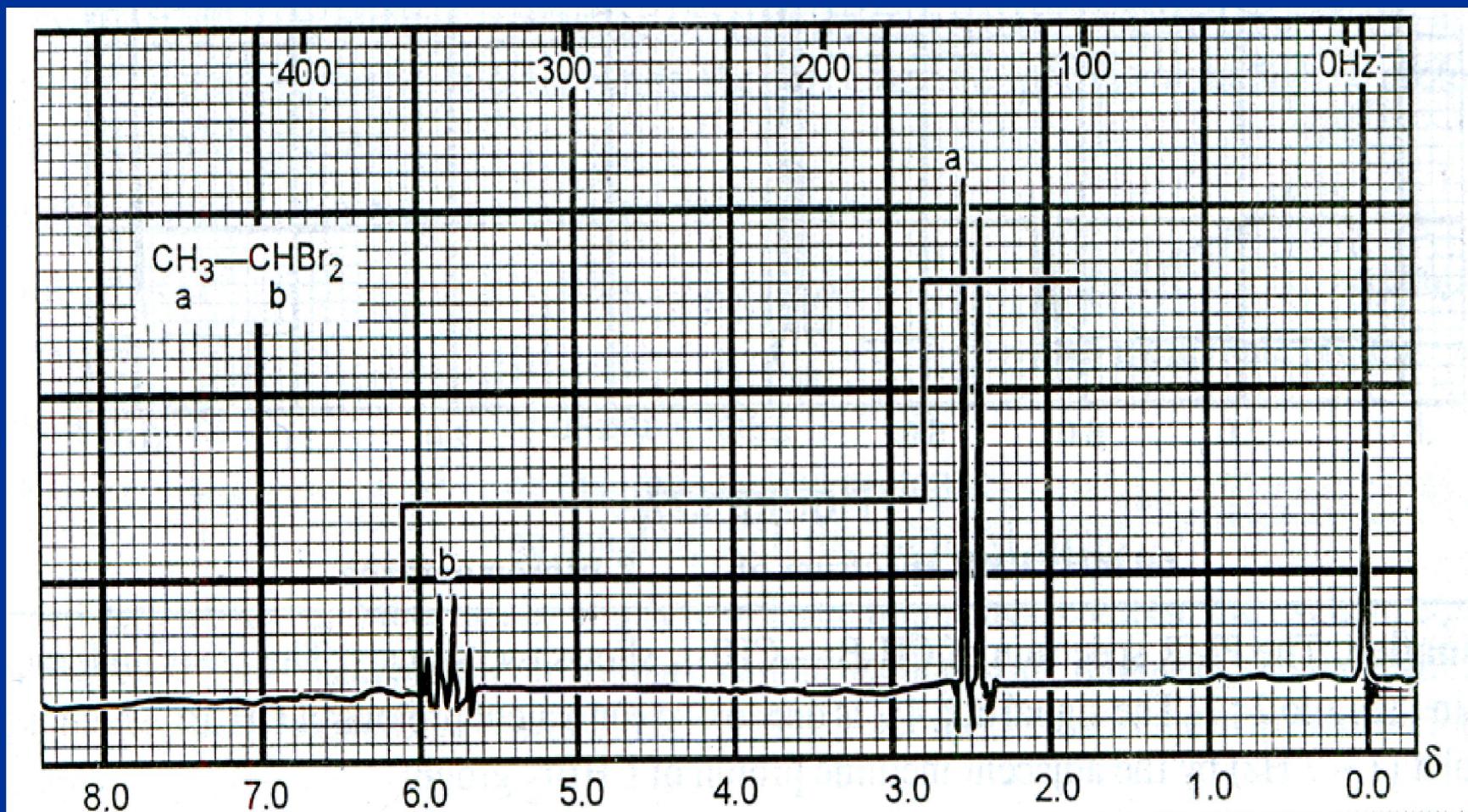


1. For vicinal protons $J = 2 - 14\text{Hz}$
2. For geminal protons $J = 0 - 20\text{Hz}$
3. For allylic protons $J = 2 - 13\text{Hz}$
4. For aromatic protons J decreases as
the distances between the two protons
increases. For ortho $J = 8-10\text{Hz}$, for meta
 $J = 1-3\text{Hz}$ and for para $J = 0-1\text{Hz}$.









CH₃ CH₂ O CH₃

Thank you

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