Interpreting Proton NMR Spectra

Information contained in an NMR spectrum includes:

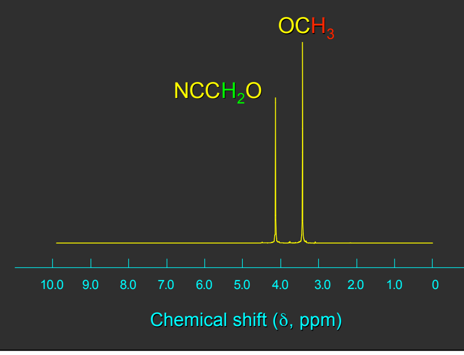
1. number of signals
2. their intensity (as measured by area under peak)
3. splitting pattern (multiplicity)

Number of Signals

protons that have different chemical shifts are chemically nonequivalent

exist in different molecular environment

NMR $N{\equiv}CCH_2OCH_3$



Chemically equivalent protons

are in identical environments

have same chemical shift

replacement test: replacement by some arbitrary "test group" generates same compound

$H_3CCH_2CH_3$

chemically equivalent

Chemically equivalent protons

Replacing protons at C-1 and C-3 gives same compound (1-chloropropane)

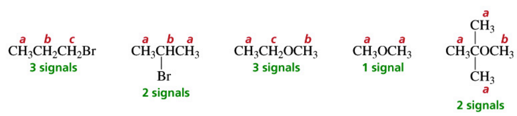
C-1 and C-3 protons are chemically equivalent and have the same chemical shift

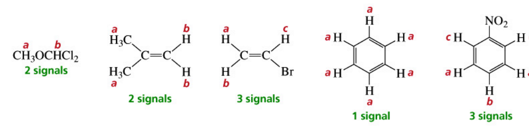
$ClCH_2CH_2CH_3$ ← $H_3CCH_2CH_3$ → $CH_3CH_2CH_2Cl$

chemically equivalent

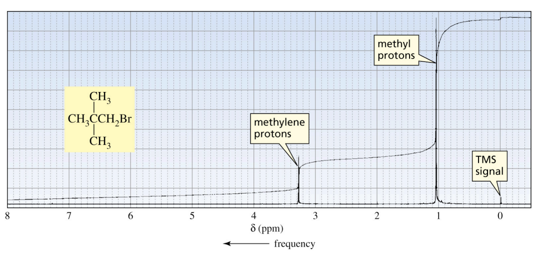
Chemical Shift: Chemically equivalent protons

Each set of chemically equivalent protons in a compound gives rise to a signal in an ^{1}H NMR spectrum of that compound



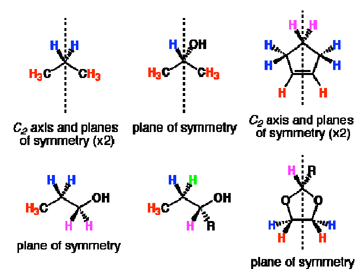


^{1}H NMR spectrum of 1-bromo-2,2-dimethylpropane



Symmetry Elements	Symmetry Operations
axis of symmetry: C_n	rotation
plane of symmetry: σ	reflection
centre of symmetry: i	inversion

chemical shift equivalent protons are shown with the same colour

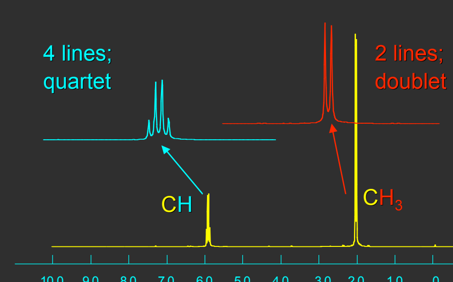


Spin-Spin Splitting
in
NMR Spectroscopy

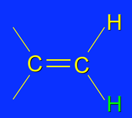
not all peaks are singlets

signals can be split by coupling of nuclear spins

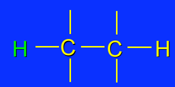
NMR Cl_2CHCH_3



Two-bond and three-bond coupling

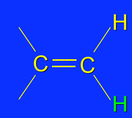


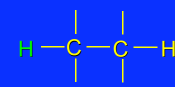
protons separated by two bonds (geminal relationship)



protons separated by three bonds (vicinal relationship)

Two-bond and three-bond coupling

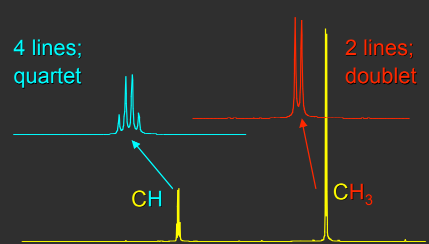




in order to observe splitting, protons cannot have same chemical shift

coupling constant (^2J or ^3J) is independent of field strength

NMR Cl_2CHCH_3

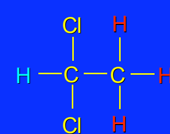


coupled protons are vicinal (three-bond coupling)

CH splits CH_3 into a doublet

CH_3 splits CH into a quartet

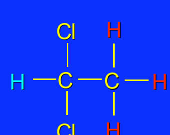
Why do the methyl protons of 1,1-dichloroethane appear as a doublet?



signal for methyl protons is split into a doublet

To explain the splitting of the protons at C-2, we first focus on the two possible spin orientations of the proton at C-1

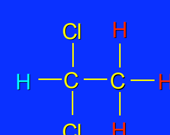
Why do the methyl protons of 1,1-dichloroethane appear as a doublet?



signal for methyl protons is split into a doublet

There are two orientations of the nuclear spin for the proton at C-1. One orientation shields the protons at C-2; the other deshields the C-2 protons.

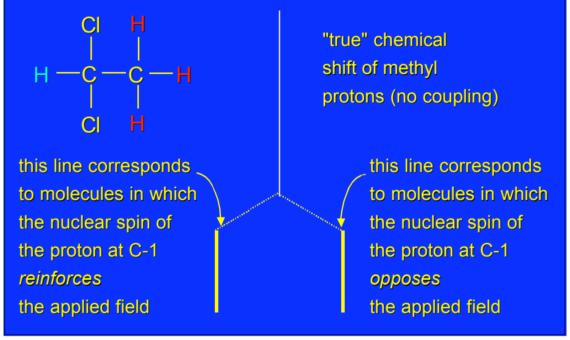
Why do the methyl protons of 1,1-dichloroethane appear as a doublet?

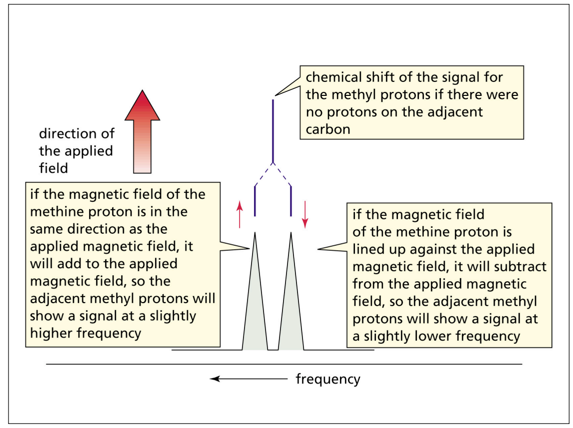


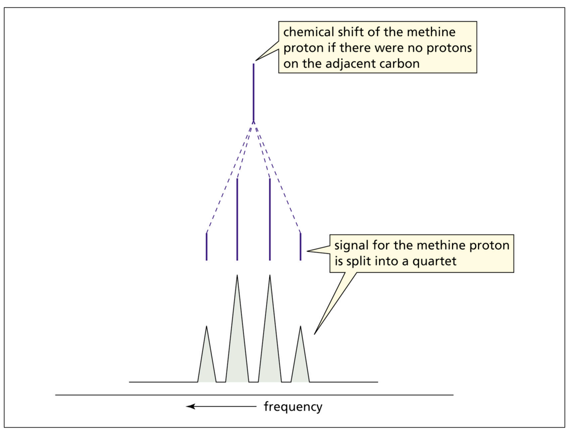
signal for methyl protons is split into a doublet

The protons at C-2 "feel" the effect of both the applied magnetic field and the local field resulting from the spin of the C-1 proton.

Why do the methyl protons of 1,1-dichloroethane appear as a doublet?

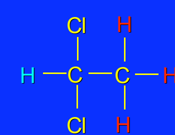






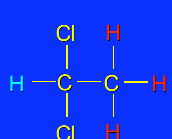
Why does the methine proton of 1,1-dichloroethane appear as a quartet?

signal for methine proton is split into a quartet



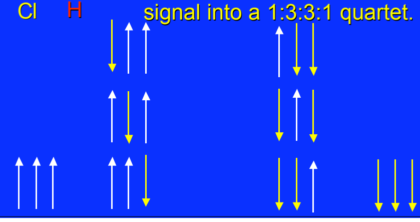
The proton at C-1 "feels" the effect of the applied magnetic field and the local fields resulting from the spin states of the three methyl protons. The possible combinations are shown on the next slide.

Why does the methine proton of 1,1-dichloroethane appear as a quartet?



There are eight combinations of nuclear spins for the three methyl protons.

These 8 combinations split the signal into a 1:3:3:1 quartet.



The splitting rule for ^{1}H NMR

For simple cases, the multiplicity of a signal for a particular proton is equal to the number of equivalent vicinal protons + 1.

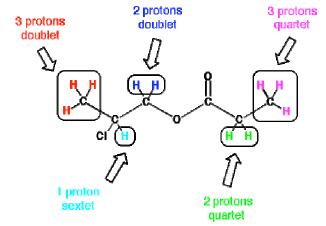
Table

Splitting Patterns of Common Multiplets

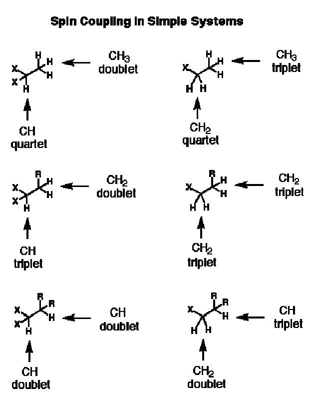
Number of equivalent protons to which H is coupled	Appearance of multiplet	Intensities of lines in multiplet
1	Doublet	1:1
2	Triplet	1:2:1
3	Quartet	1:3:3:1
4	Pentet	1:4:6:4:1
5	Sextet	1:5:10:10:5:1
6	Septet	1:6:15:20:15:6:1

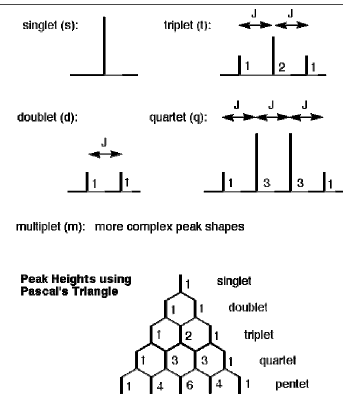
A proton **will** be split (**due** to proton-proton coupling) into **n+1** lines **if** there are **n** protons adjacent to it (i.e. H-C-C-H the protons are separated by 3 bonds in all)

For example, in the following compound the protons indicated (each group are coloured the same are chemical shift equivalent) will be split into various peak shapes in the proton NMR spectrum. The integrations will tell you how many protons there are for each set of signals.



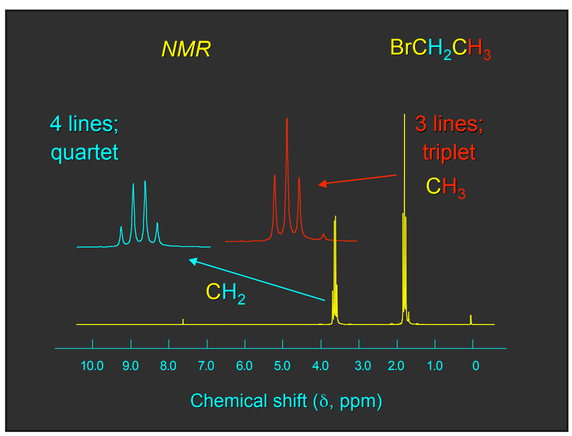
n are "equivalent" protons, i.e., they behave alike chemically.
If protons have certain symmetries they are equivalent.





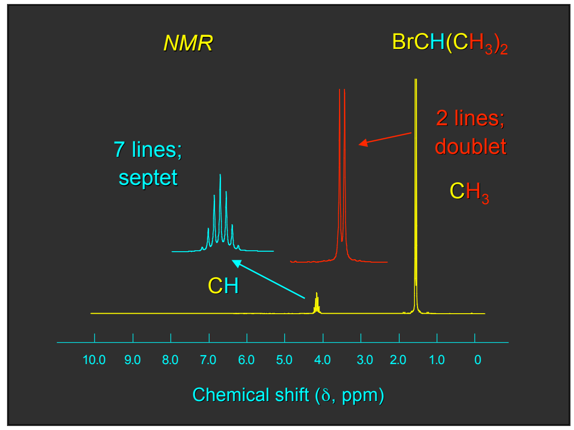
Splitting Patterns:
The Ethyl Group

CH_3CH_2X is characterized by a triplet-quartet pattern (quartet at lower field than the triplet)



Splitting Patterns:
The Isopropyl Group

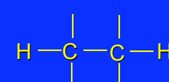
$(CH_3)_2CHX$ is characterized by a doublet-septet pattern (septet at lower field than the doublet)



Splitting Patterns:
Pairs of Doublets

Splitting patterns are not always symmetrical, but lean in one direction or the other when "coupled".

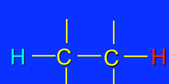
Pairs of Doublets



Consider coupling between two vicinal protons.

If the protons have different chemical shifts, each will split the signal of the other into a doublet.

Pairs of Doublets



Let $\Delta\nu$ be the difference in chemical shift in Hz between the two hydrogens.

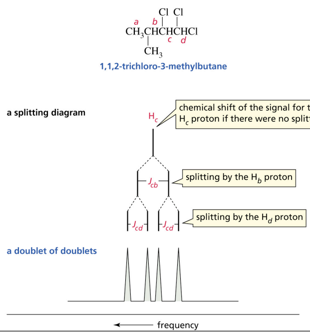
Let J be the coupling constant between them in Hz.

The Difference between a Quartet and a Doublet of Doublets

a quartet
relative intensities: 1 : 3 : 3 : 1

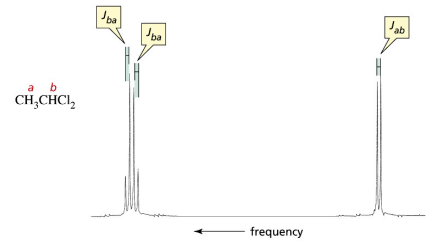
a doublet of doublets
relative intensities: 1 : 1 : 1 : 1

A Splitting Diagram for a Doublet of Doublets



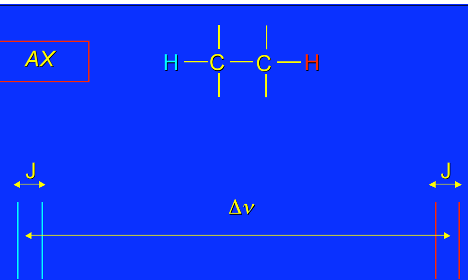
Coupling Constants

The coupling constant (*J*) is the distance between two adjacent peaks of a split NMR signal in hertz



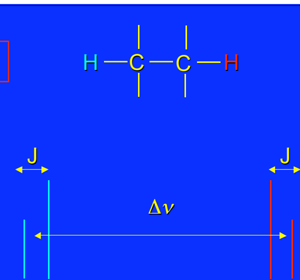
Coupled protons have the same coupling constant

AX



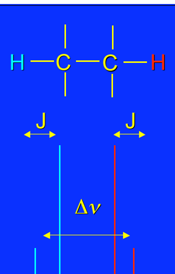
When $\Delta\nu$ is much larger than J the signal for each proton is a doublet, the doublet is symmetrical, and the spin system is called AX.

AM



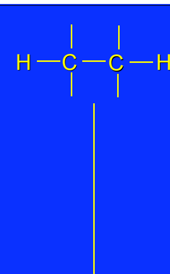
As $\Delta\nu$/J decreases the signal for each proton remains a doublet, but becomes skewed. The outer lines decrease while the inner lines increase, causing the doublets to "lean" toward each other.

AB



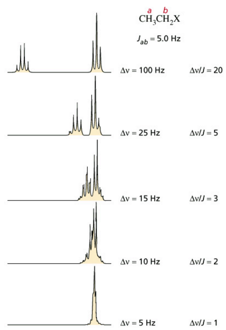
When $\Delta\nu$ and J are similar, the spin system is called AB. Skewing is quite pronounced. It is easy to mistake an AB system of two doublets for a quartet.

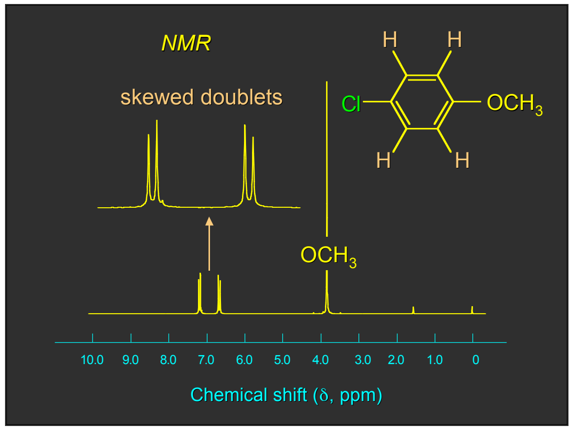
A_2

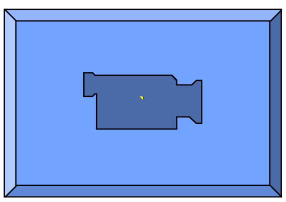


When $\Delta\nu$ = 0, the two protons have the same chemical shift and don't split each other. A single line is observed. The two doublets have collapsed to a singlet.

To observe well-defined splitting patterns, the difference in the chemical shifts (in Hz) must be 10 times the coupling constant values



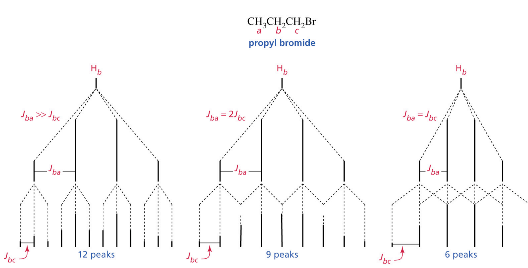


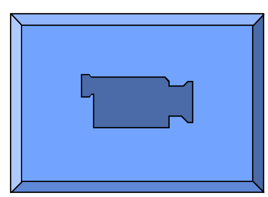


Complex Splitting Patterns

Multiplets of multiplets
MESS-plets

A Splitting Diagram for a Quartet of Triplets

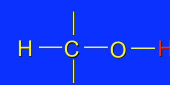




^{1}H NMR Spectra of Alcohols & Amines

What about H bonded to O and N?

O—H



The chemical shift for O—H is variable (δ 0.5-5 ppm) and depends on temperature and concentration.

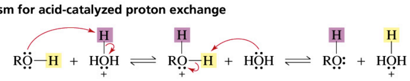
Splitting of the O—H proton is sometimes observed, but often is not. It usually appears as a broad peak.

Adding D_2O converts O—H to O—D. The O—H peak disappears.

Protons Bonded to Oxygen and Nitrogen

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

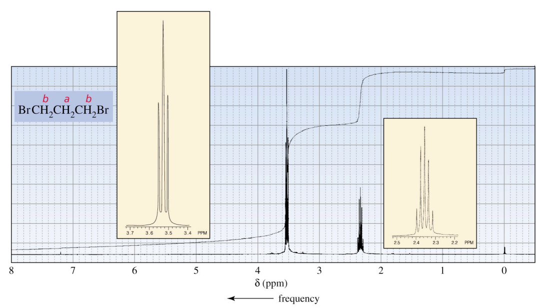
mechanism for acid-catalyzed proton exchange

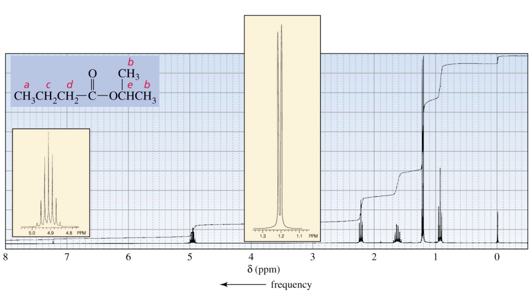


These protons can undergo proton exchange with deuterium.

They appear as broad signals.

More Examples of ^{1}H NMR Spectra





The signals for the H_c, H_d, and H_e protons overlap