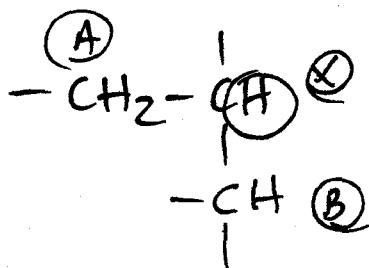
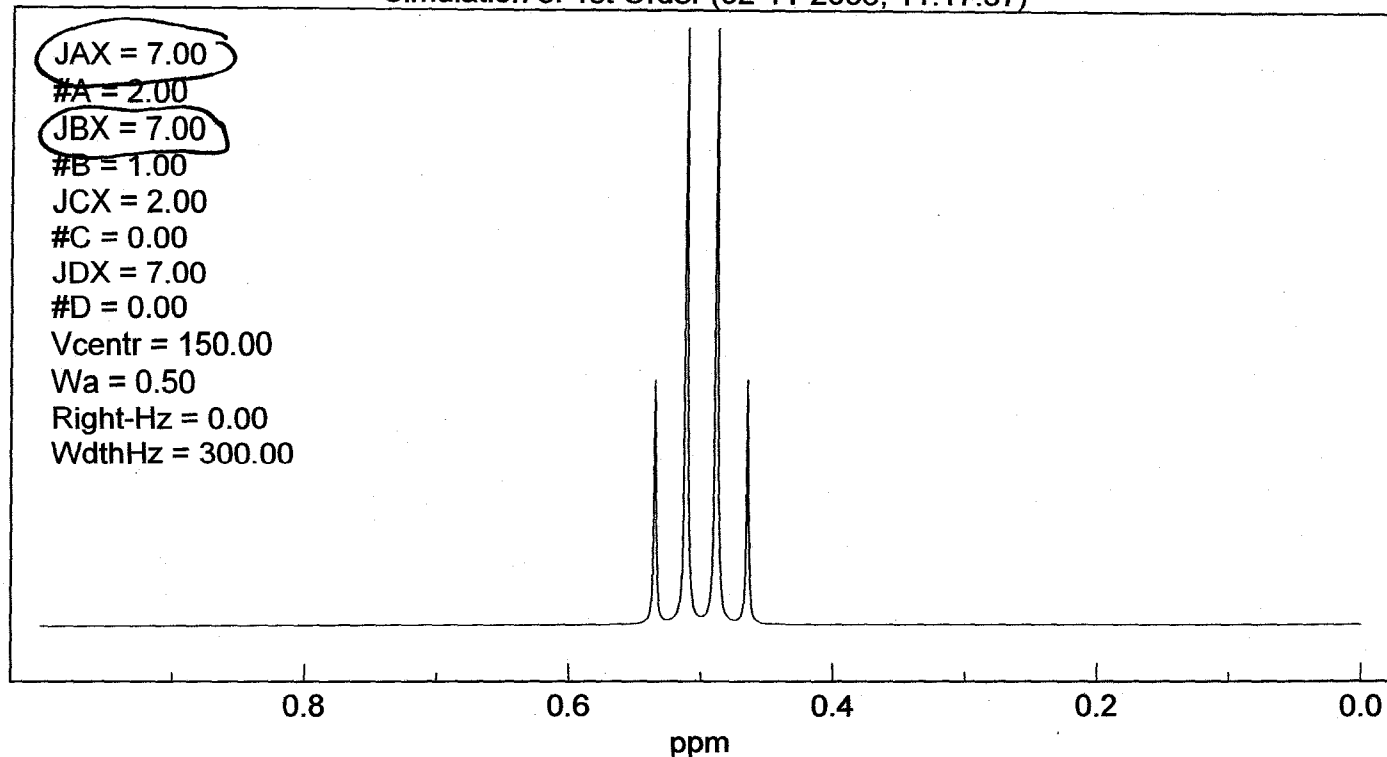


coupling constants

Simulation of 1st Order (02-11-2008, 11:17:37)



X has 3
neighbors
 \Rightarrow quartet

$$J_{AX} = J_{BX}$$

Simulation of 1st Order (02-11-2008, 11:17:12)

JAX = 7.00

#A = 2.00

JBX = 10.00

#B = 1.00

JCX = 2.00

#C = 0.00

JDX = 7.00

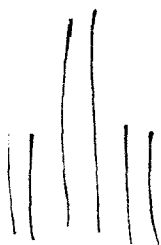
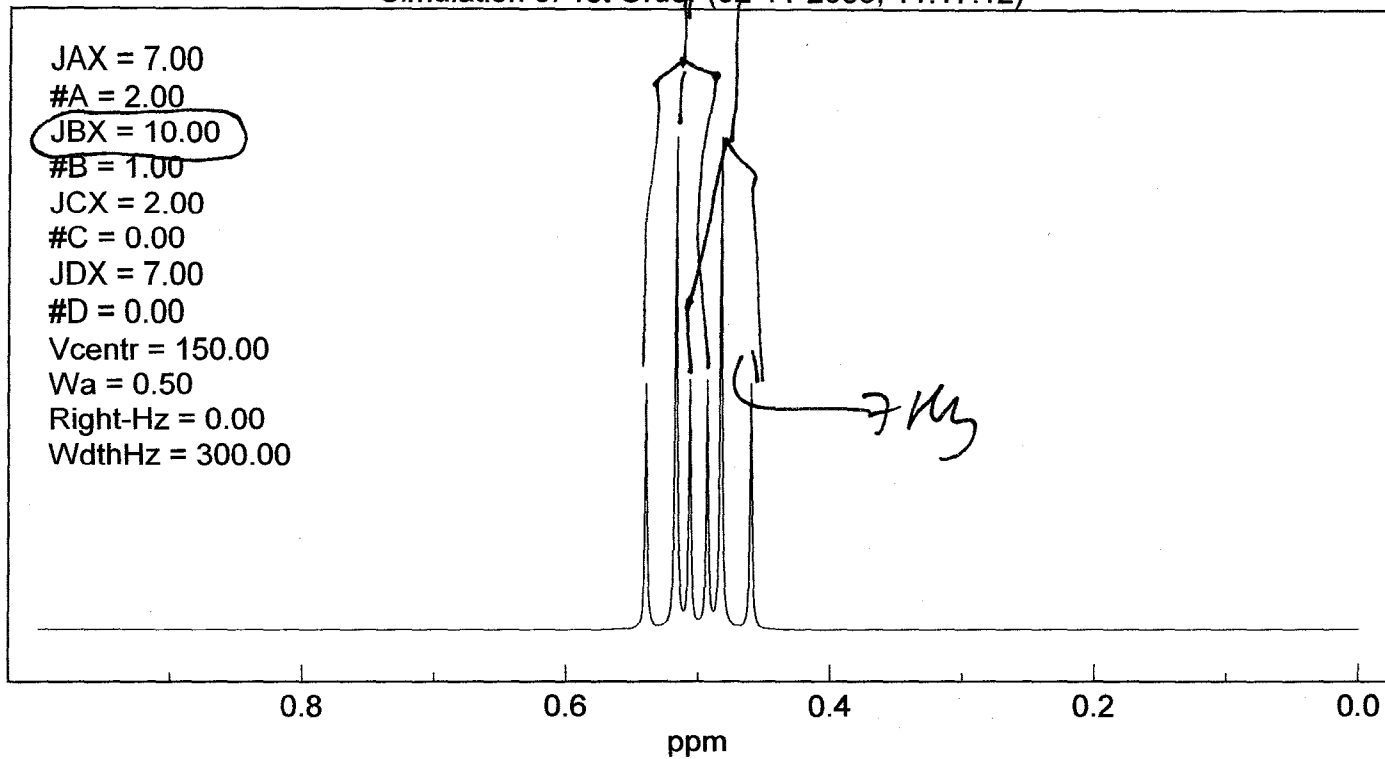
#D = 0.00

Vcentr = 150.00

Wa = 0.50

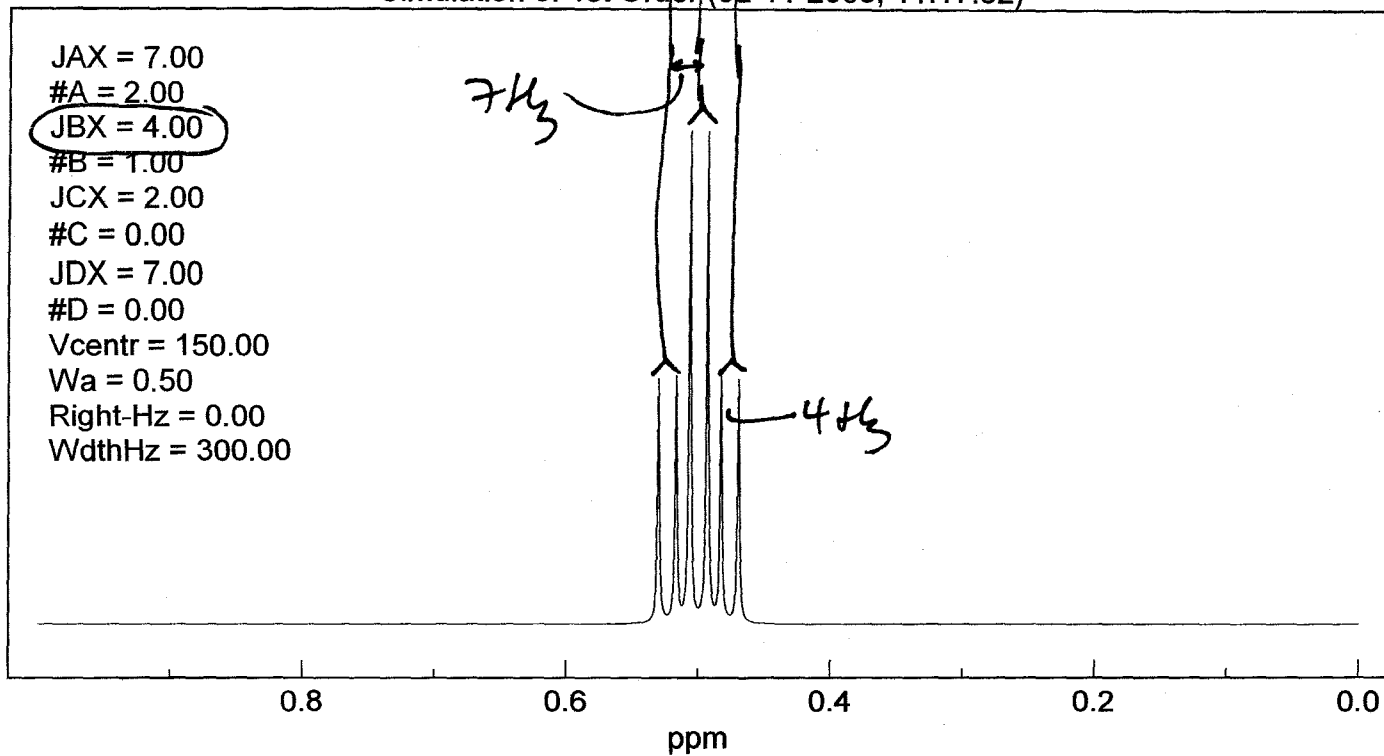
Right-Hz = 0.00

WidthHz = 300.00



$$J_{AX} < J_{BX}$$

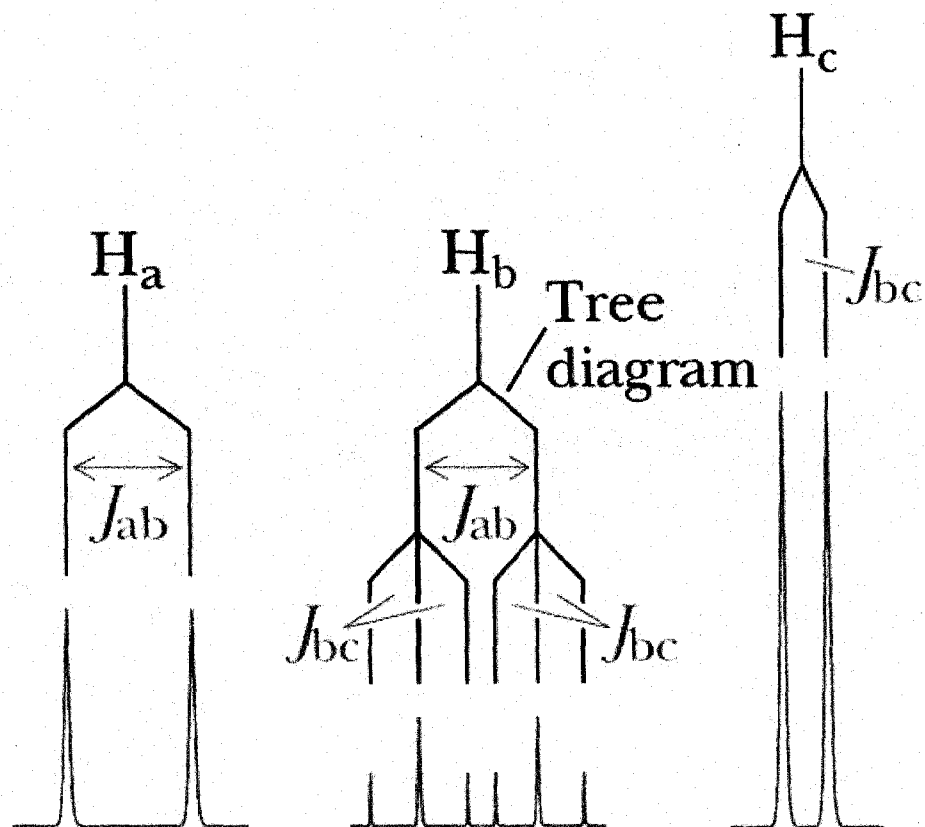
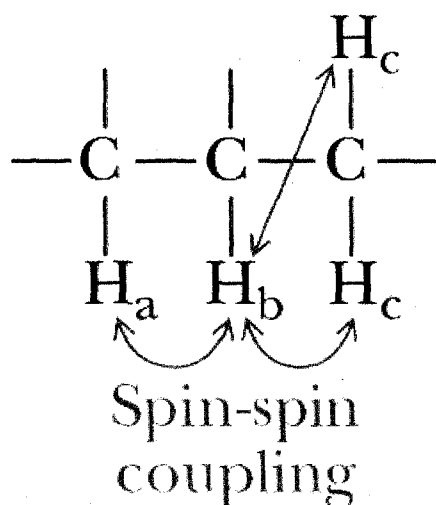
Simulation of 1st Order (02-11-2008, 11:17:52)



$$J_{AX} > J_{BX}$$

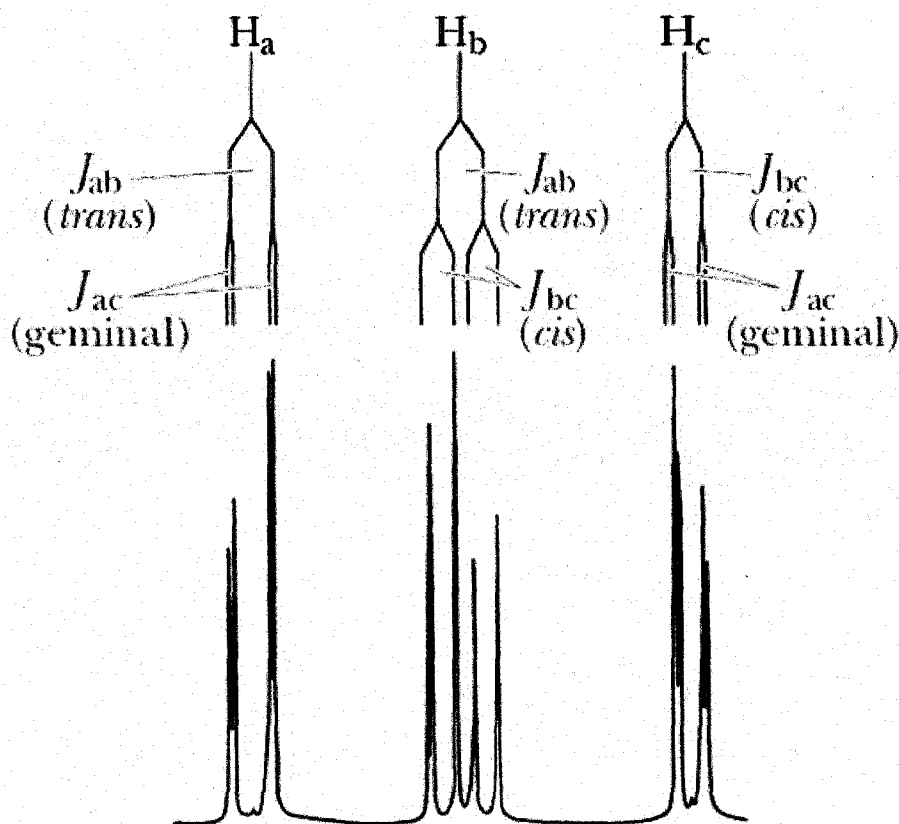
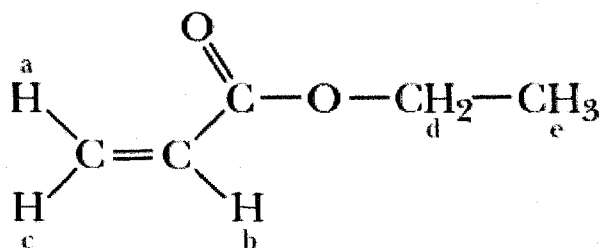
More Complex Splitting Patterns

- if H_c is a set of two equivalent H, then the observed splitting is a doublet of triplets



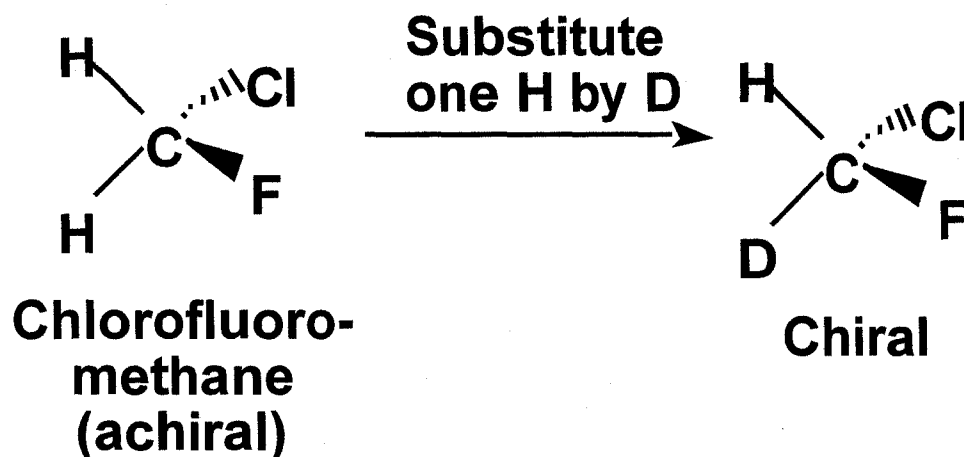
More Complex Splitting Patterns

- a tree diagram for the complex coupling of the three vinylic hydrogens in ethyl propenoate



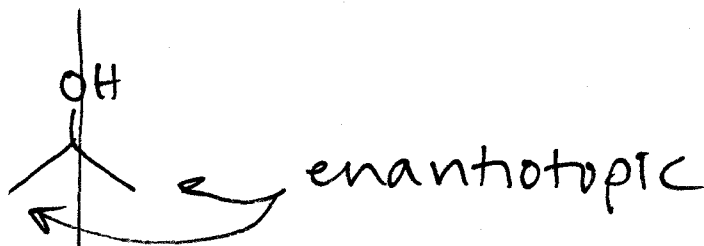
Stereochemistry & Topicity

◆ Enantiotopic groups



Substitution produces a stereocenter; therefore, hydrogens are enantiotopic. Both hydrogens are prochiral; one is pro-R-chiral, the other is pro-S-chiral.

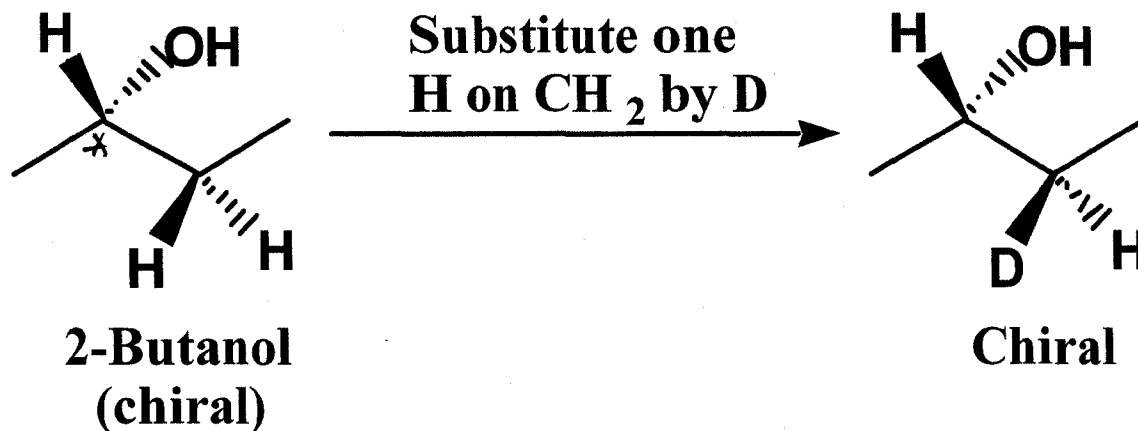
- enantiotopic atoms or groups have identical chemical shifts in achiral environments
- they have different chemical shifts in chiral environments



Stereochemistry & Topicity

◆ Diastereotopic groups

- H atoms on C-3 of 2-butanol are diastereotopic
- substitution by deuterium creates a chiral center
- because there is already a chiral center in the molecule, diastereomers are now possible

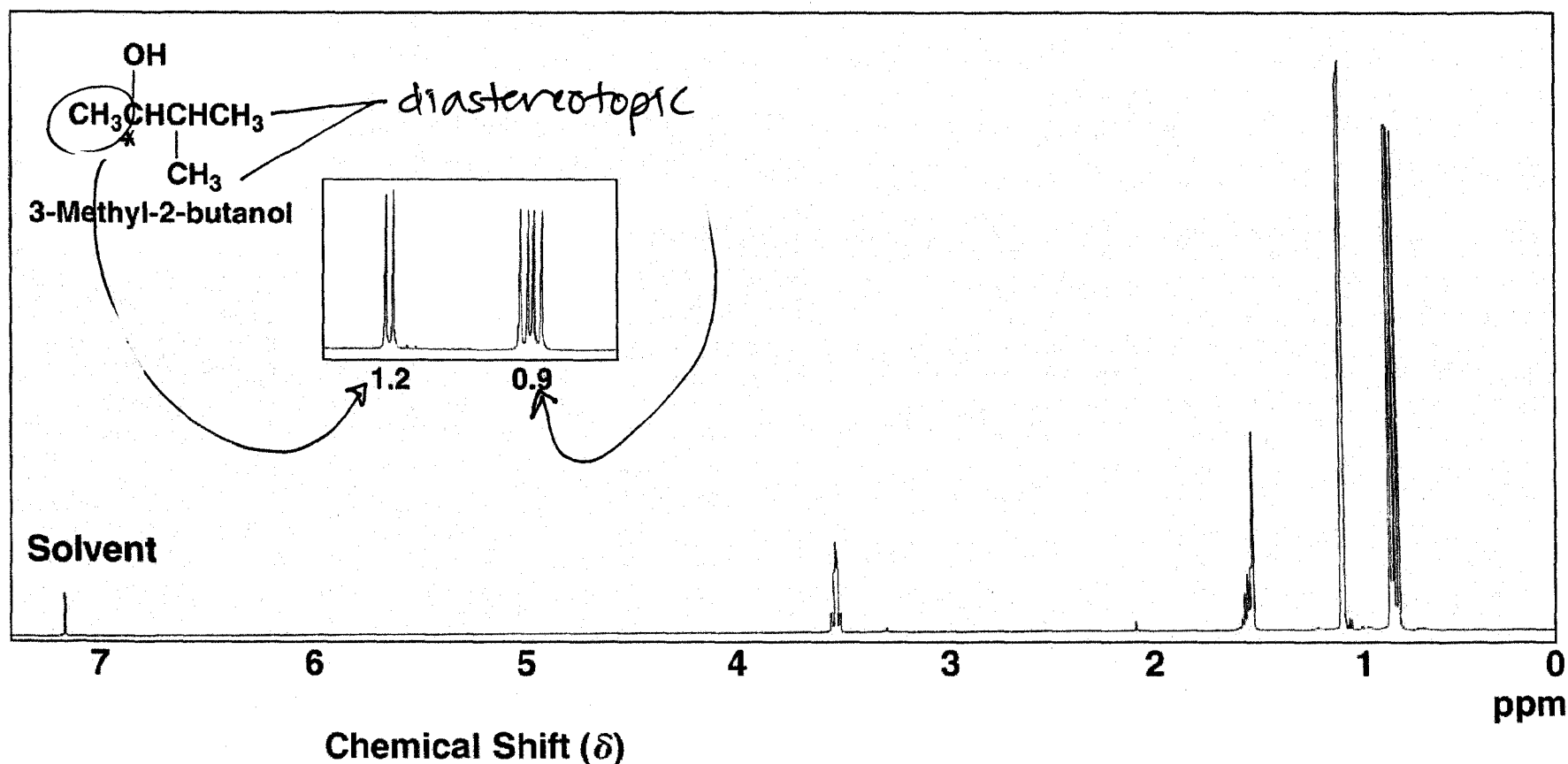


- diastereotopic hydrogens have different chemical shifts under all conditions

Stereochemistry and Topicity

◆ ^1H -NMR spectrum of 3-methyl-2-butanol

- the methyl groups on carbon 3 are diastereotopic and appear as two doublets



¹³C NMR Spectroscopy

The principles of ¹³C NMR are the same as those of ¹H NMR, in that we have a nucleus with spin ½, we place the sample in an external magnetic field to create a separation of the two possible spin states, and we scan through the appropriate radiofrequencies to detect the different types of nuclei.

Differences:

1. ¹³C has about 1.1% natural abundance. Therefore we need a much more sensitive spectrometer to be able to do ¹³C NMR with any degree of accuracy. The development of FT-NMR made this possible.
2. Since ¹³C has only about 1.1% natural abundance, the chances of a molecule containing two ¹³Cs next to each other are slim to none. Therefore, we don't see spin-spin splitting in ¹³C NMR. This simplifies the spectrum considerably.
3. However, the ¹³Cs can be split by the ¹Hs attached to them - this splitting can be removed by using a technique called **broad-band decoupling**. So not a problem.
4. Integrals are meaningless in ¹³C NMR because of a phenomenon called **relaxation**. We won't discuss relaxation, but will take advantage of the absence of integrals to simplify the interpretation of the ¹³C spectra.
5. Where the ¹H NMR spectrum has a scale that runs from 0 to about 12 ppm, ¹³C NMR spectra run from 0 to about 200 ppm. Much larger scale. TMS is still used as a reference.

Basics:

We see one peak for each unique carbon. A monosubstituted benzene, for instance, would show four different peaks.

Chemical shift is the important thing here. (~~See the table on p. 394.~~)

Alkyls (sp ³)	0-50, generally.
Alkyl halide or amine	10-65
C next to an oxygen (alcohol or ether)	50-90
Alkyne (sp)	60-90
Alkene (sp ²)	100-170
Aromatic	100-170
(note: benzene itself comes at 128.5 ppm)	
Nitriles (the C of the CN)	120-130
(note, very different from alkynes unlike IR)	
Amide carbonyl	150-180
Carboxylic acid or ester carbonyl	160-185
Aldehyde or ketone carbonyl	182-215
(note the large difference in different carbonyls)	