CHEM 222 section 01

LECTURE #13 **Tues.**, Oct.16, 2007

Lecture topics & readings

Today's class
- finish NMR spectroscopy (Ch.13)

Before next class
- practice interpreting NMR spectra
- practice determining structures from spectral data

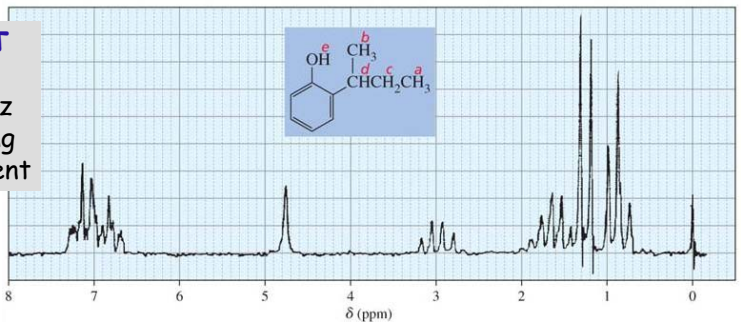
Next class
- start reactions of dienes: Ch.7.4-7.12

Problem set quiz: due on Tues. Oct. 23
Midterm exam: on Tues. Oct. 30

13.18 Resolution: stronger magnet ⇨ better peak separation

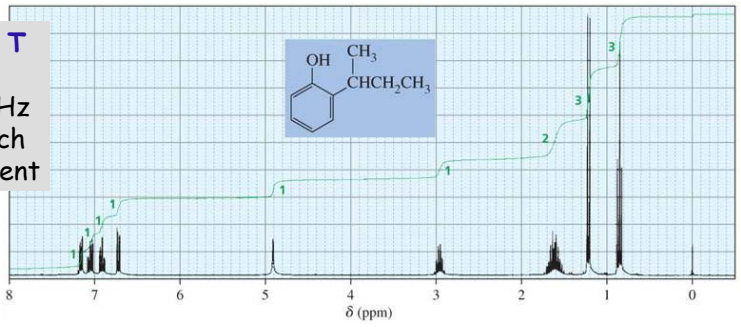
1.47 T

60 MHz Teaching instrument



7.046 T

300 MHz Research instrument



13.13 Splitting diagrams ("trees") explain multiplicity

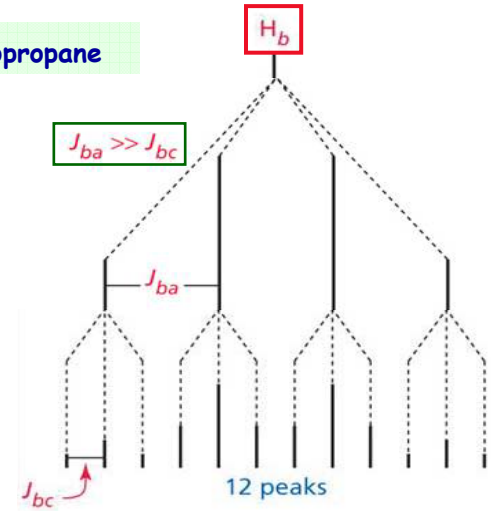
Complex spin-spin coupling:

- non-equivalent Hs couple to each other (if close enough…)
- if >1 type of coupled H ⇨ resulting peak shape can be complicated

Complex splitting in 1-bromopropane

a b c

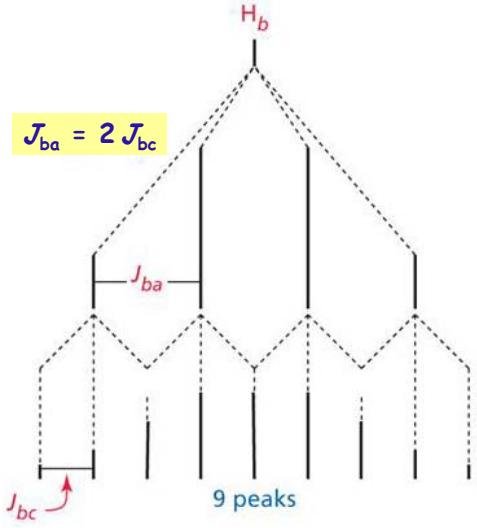
$CH_3CH_2CH_2Br$

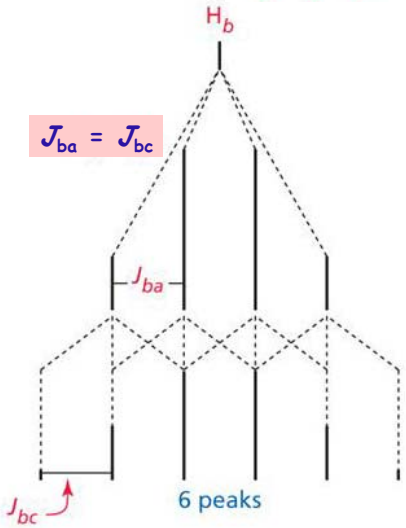


But what if we're wrong about the relative sizes of the coupling constants?

(3)

Complex splitting in 1-bromopropane might look simpler… $CH_3CH_2CH_2Br$ (a b c)





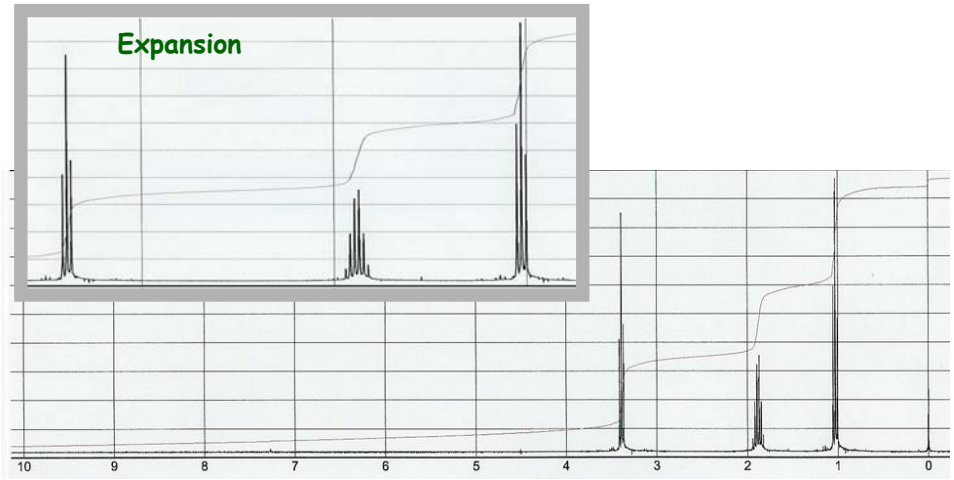
Makes H_a & H_c seem equivalent. Remember, they are not.

THUS: Assign complex multiplets last… & have flexible expectations

300 MHz ^{1}H NMR spectrum of 1-bromopropane

$\overset{a}{CH_3}\overset{b}{CH_2}\overset{c}{CH_2}Br$

Makes H_a & H_c seem equivalent. Remember, they are not.



(5) From Sigma-Aldrich Co. website: www.sial.com

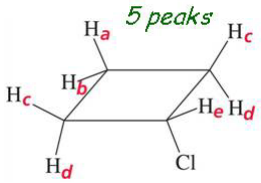
13.14 Diastereotopic hydrogens are not equivalent…

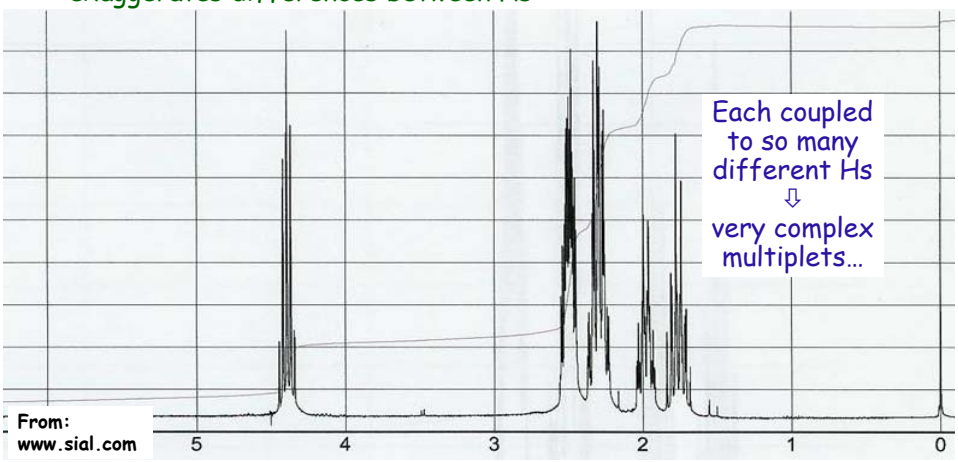
= Hs adjacent to a stereocentre

- nearly identical chemical environment
  - ⇨ similar chemical shift: **overlap?**

HERE:

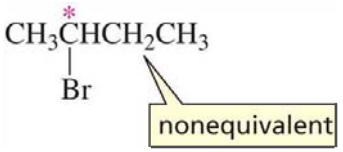
- ring limits movement
- exaggerates differences between Hs

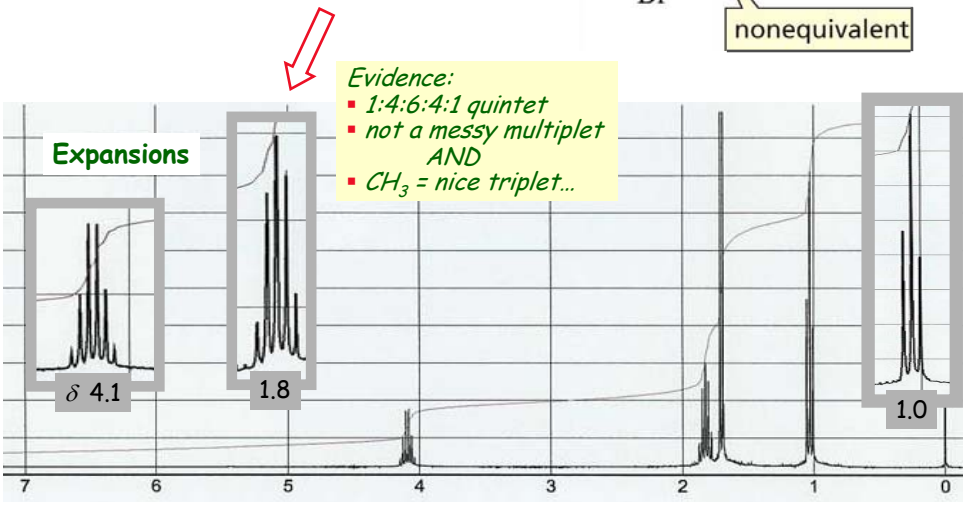




Diastereotopic H's peaks are sometimes coincident

- nearly identical chemical environment
  ⇨ **peaks usually overlap** each other
  BUT **may exactly coincide**





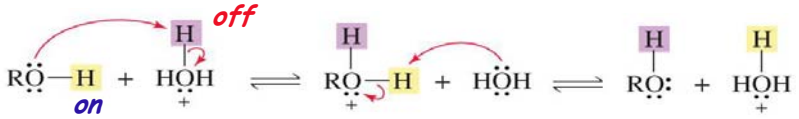
(7) From: www.sial.com

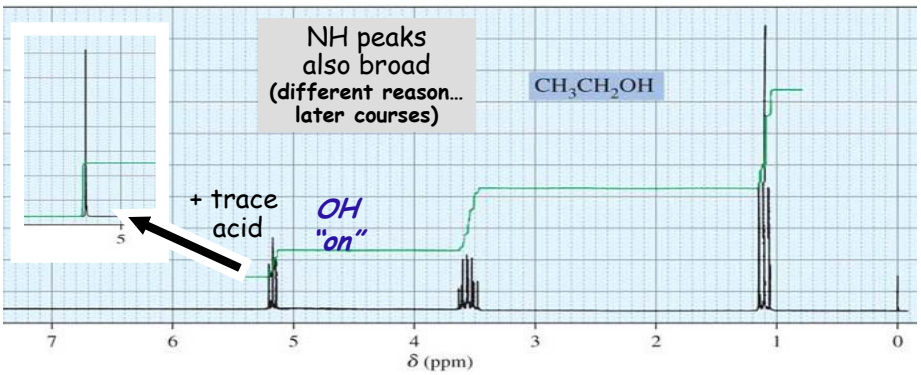
13.16 Hs bonded to O = "exchangeable"

Proton-exchange causes…

(i) loss of coupling: see average δ for *on* vs. *off* molecule

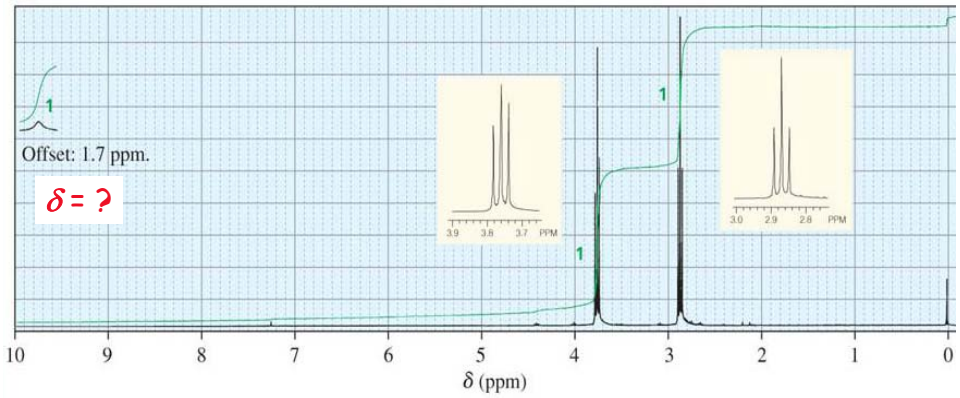
(ii) broadening of peak: too fast to see sharp multiplet = *on*
too slow for singlet = *off*





Carboxylic acids: very easily exchanged COO-H

Identify this carboxylic acid: $C_3H_5CO_2Cl$ (Bruice Prob.#20)



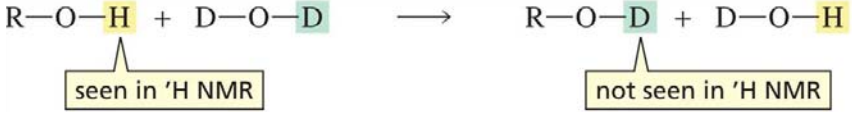
13.17 The use of deuterium in ^1H NMR spectroscopy

Deuterium signals do not appear in the 0-12 ppm range

1. **Use deuterated solvents**
   - no extra peaks from solvent in sample's spectrum…
   - only see tiny "residual H" peak from 99.9% deuterated $CDCl_3$, *etc*

   see previous spectrum:
   tiny peak at δ 7.2 ppm

2. **Use to identify exchangeable hydrogens**
   - can exchange OH or NH hydrogens by shaking with H^+/D_2O
   - removes the peaks from spectrum

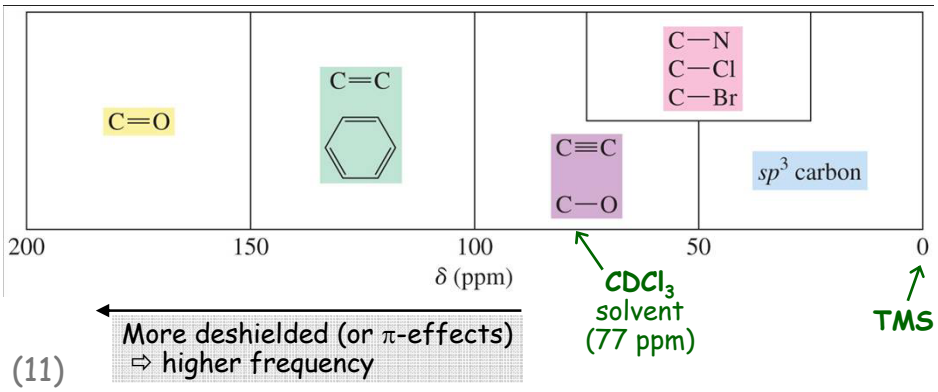


13.19 ^{13}C NMR Spectroscopy ⇨ less info., but useful

Information available: **# peaks = # types of Cs**

- no integration
- no splitting observed ⇨ all singlets (in routine ^{13}C spectra)
  - not from other ^{13}Cs: low abundance nuclei ⇨ 2 per molecule is rare
  - not from ^{1}Hs: with *decoupled* setting ⇨ no ^{1}H coupling seen

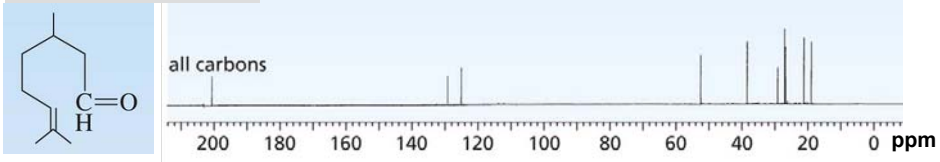
Typical ^{13}C chemical shifts (see Table 13.4 for details):



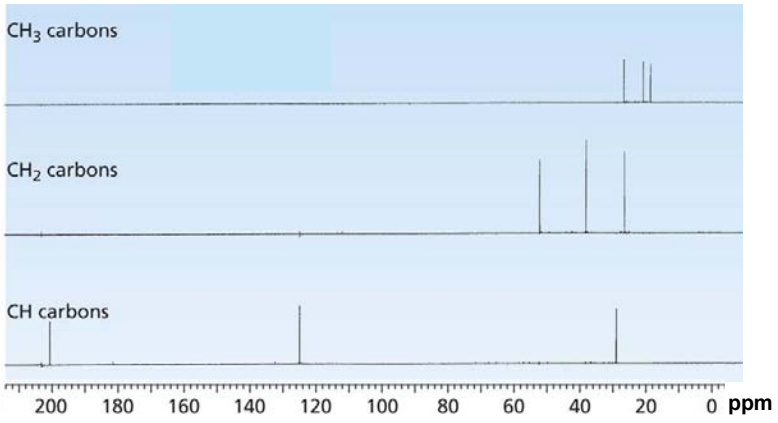
(11)

13.20 DEPT ^{13}C NMR Spectra ⇨ reveal 1°, 2°, 3°, 4° Cs

Regular ^{13}C spectrum

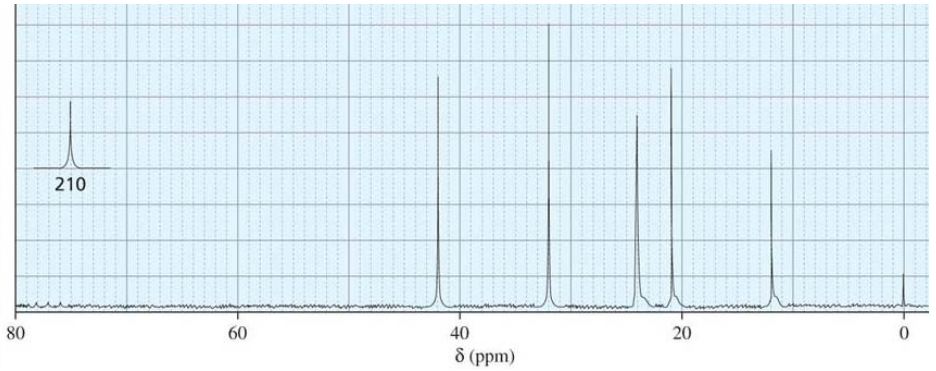


DEPT spectra

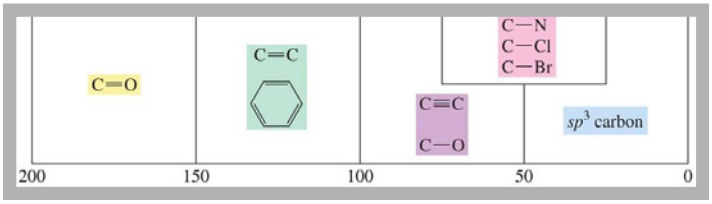


(12)

PROBLEM 41◆ Use the ^{13}C NMR spectrum to identify: $C_{11}H_{22}O$



(13)



Covered in more advanced courses:

13.15 Time dependence of NMR spectroscopy

13.21 Two-dimensional NMR

Read for your own interest:

13.22 Magnetic resonance imaging