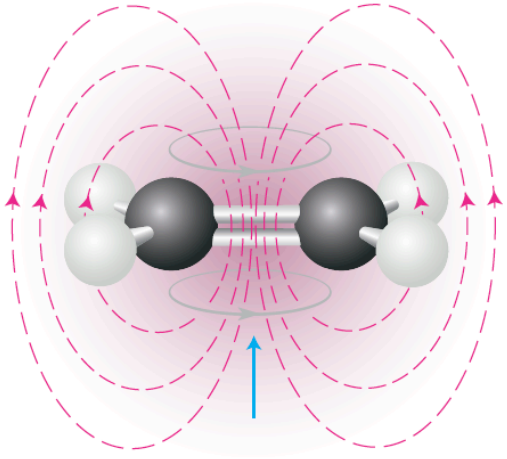
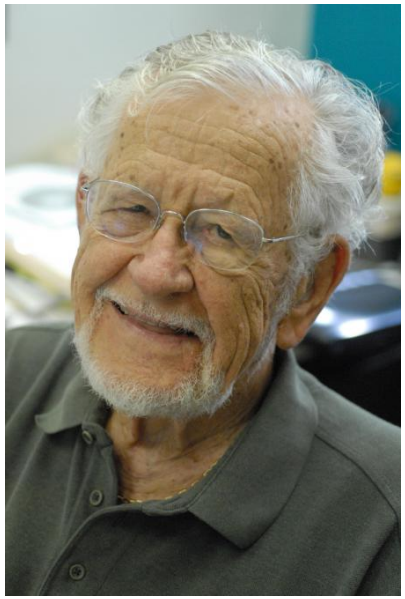
Ch41b 2018:
Lecture 5 Figures (Part 1)



Nuclear Magnetic Resonance Spectroscopy
(Chapter 13, Loudon)

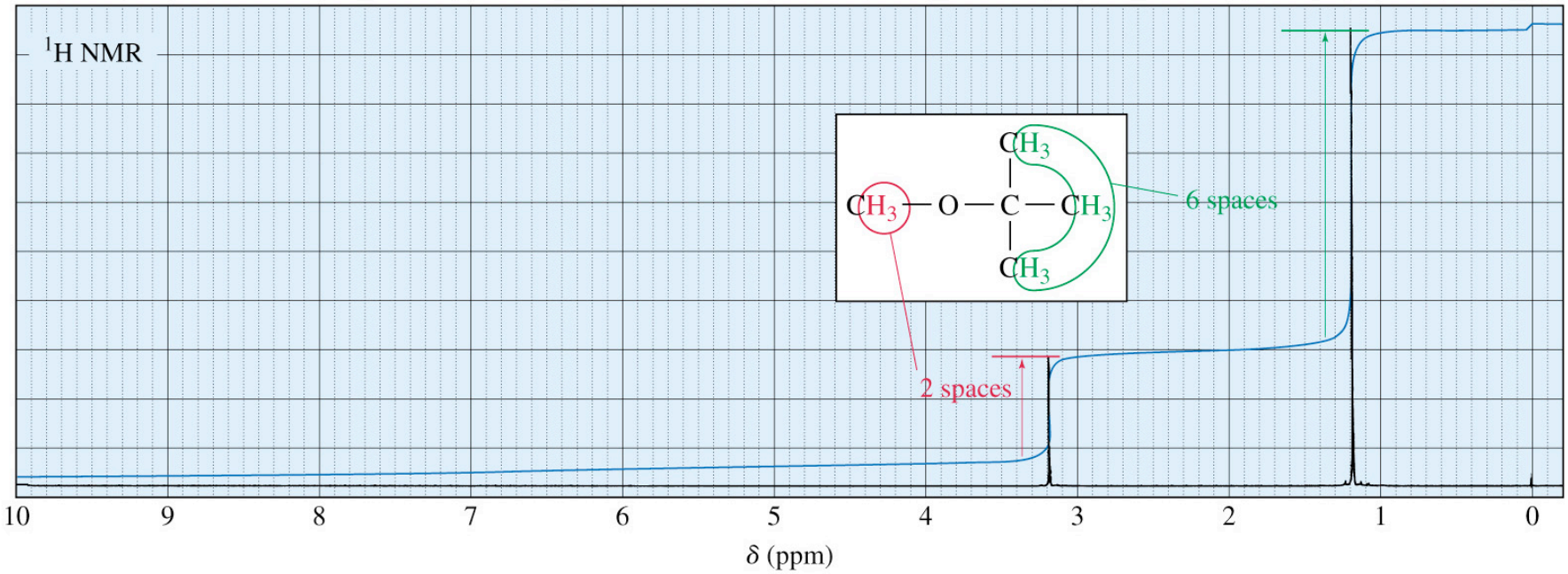
CCE Division Liquid NMR Facility

500 MHz NMR

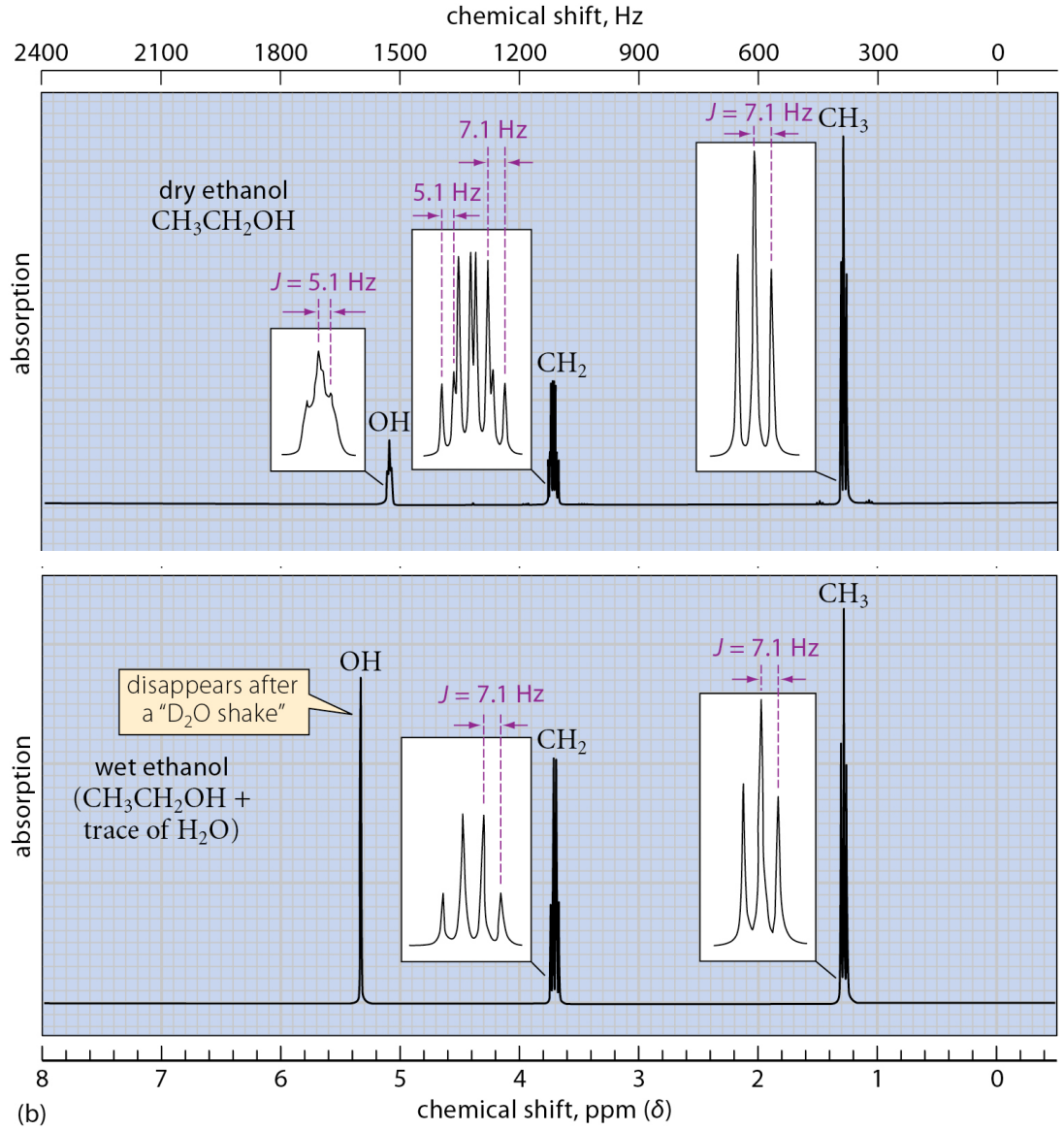


Prof. John D. Roberts
(1918-2016)

^{1}H NMR Spectrum of Methyl *t*-Butyl Ether



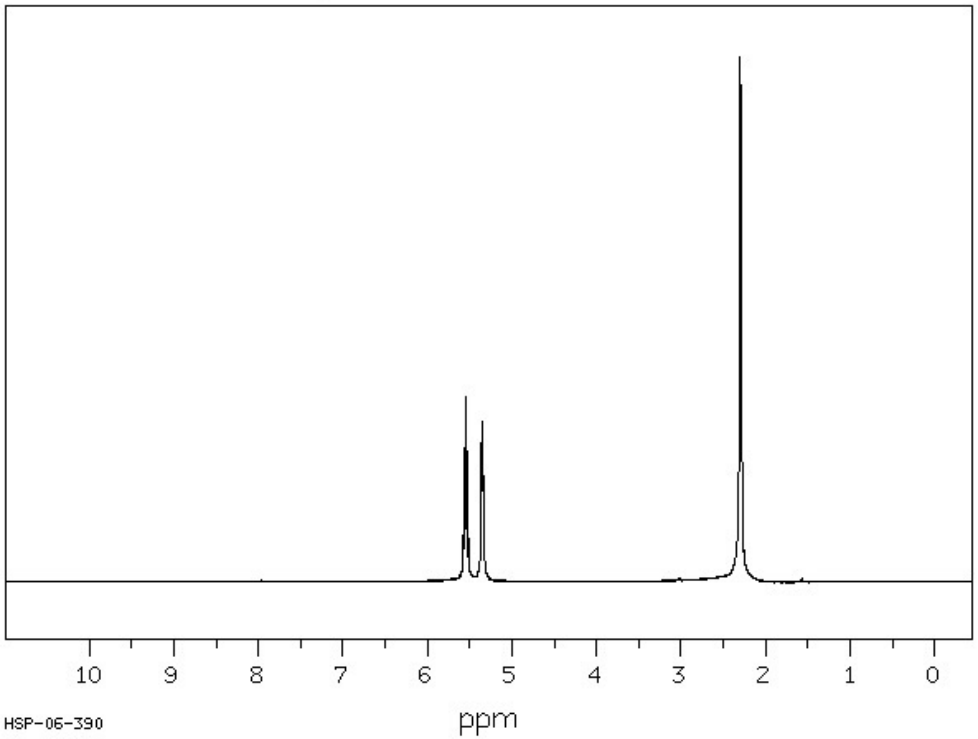
NMR Spectra of Ethanol

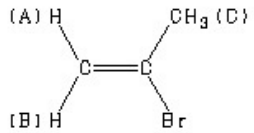


^{1}H NMR Spectrum of 2-Bromopropene

89.56 MHz

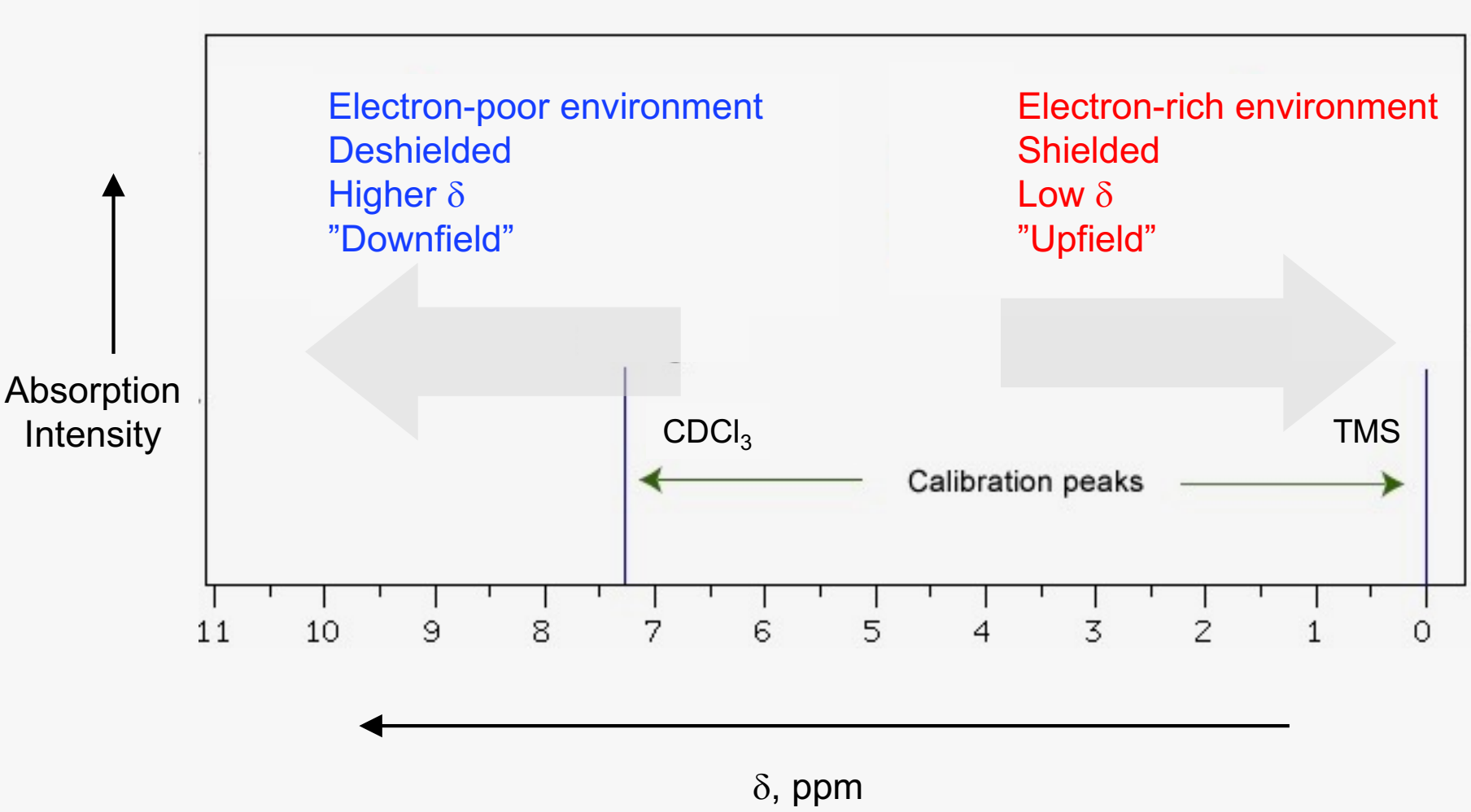
0.05 ml : 0.5 ml $CDCl_3$



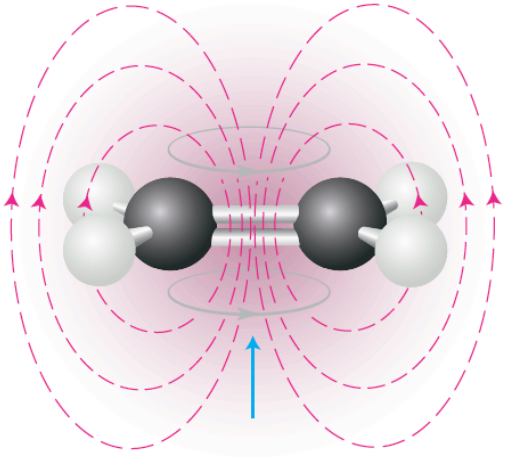


标记氢	化学位移(ppm)
A	5.540
B	5.346
C	2.294

Summary


Electron-poor environment
Deshielded
Higher δ
”Downfield”
Electron-rich environment
Shielded
Low δ
”Upfield”
Absorption Intensity
CDCl3
TMS
Calibration peaks
11
10
9
8
7
6
5
4
3
2
1
0
δ, ppm

Ch41b 2018:
Lecture 6 Figures (Part 2)



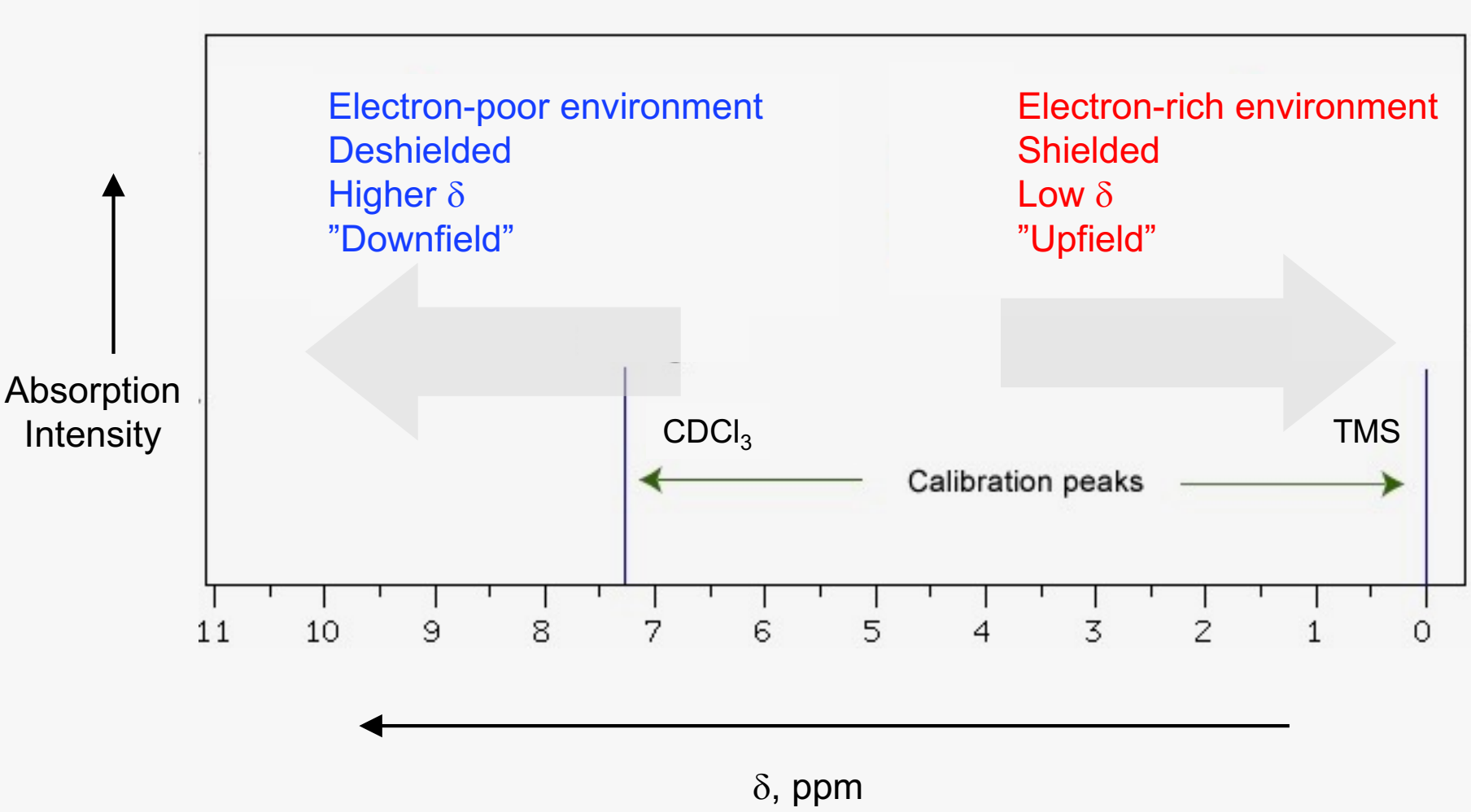
Nuclear Magnetic Resonance Spectroscopy
(Chapter 13, Loudon)

The ^{1}H NMR Spectrum

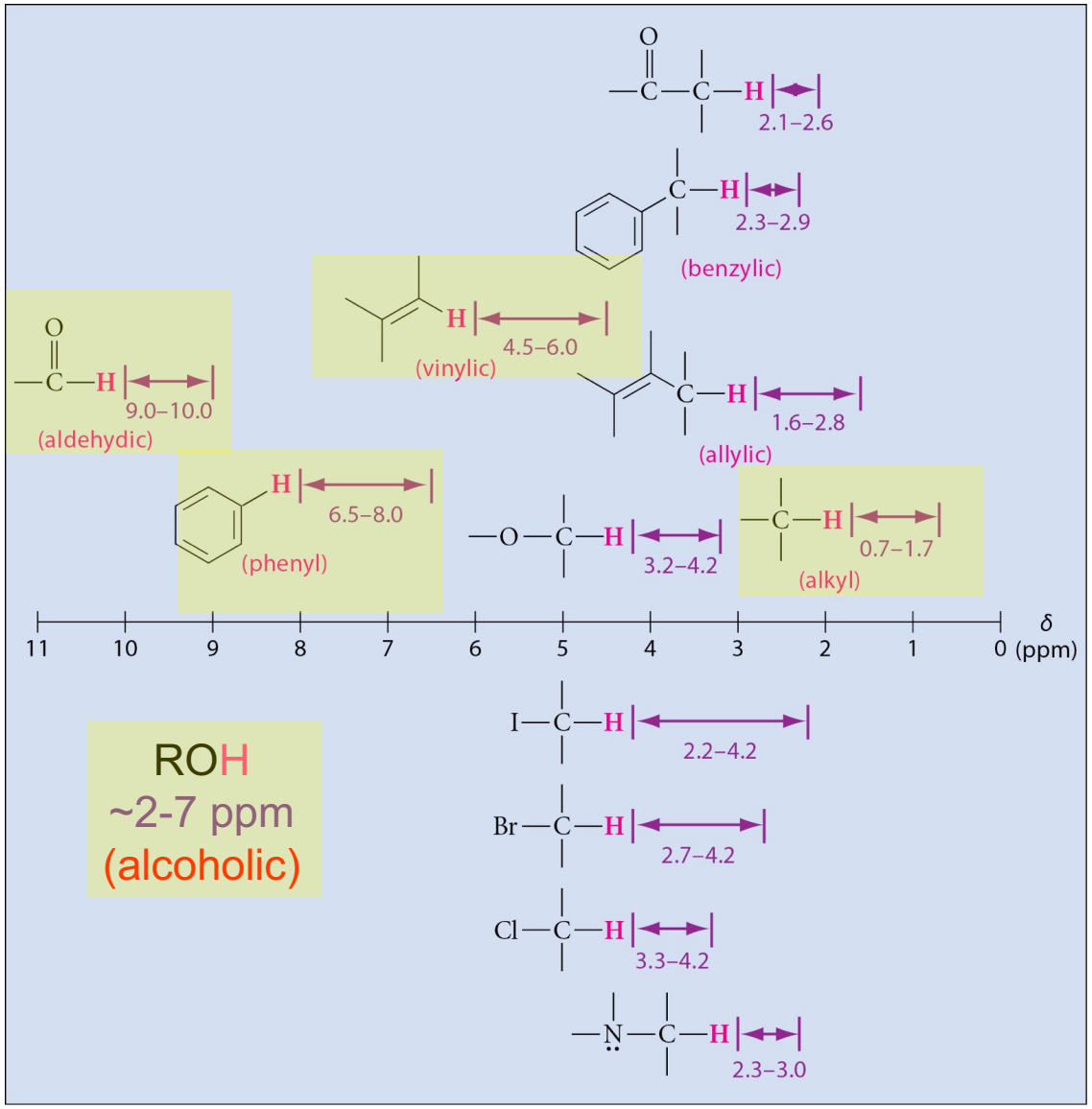
Proton NMR provides these types of information:

1. the number of sets of *chemically equivalent and non-equivalent protons*
2. the *number of protons* within each set (or their relative ratios)
3. the *chemical environments* of each set of protons (chemical shift)

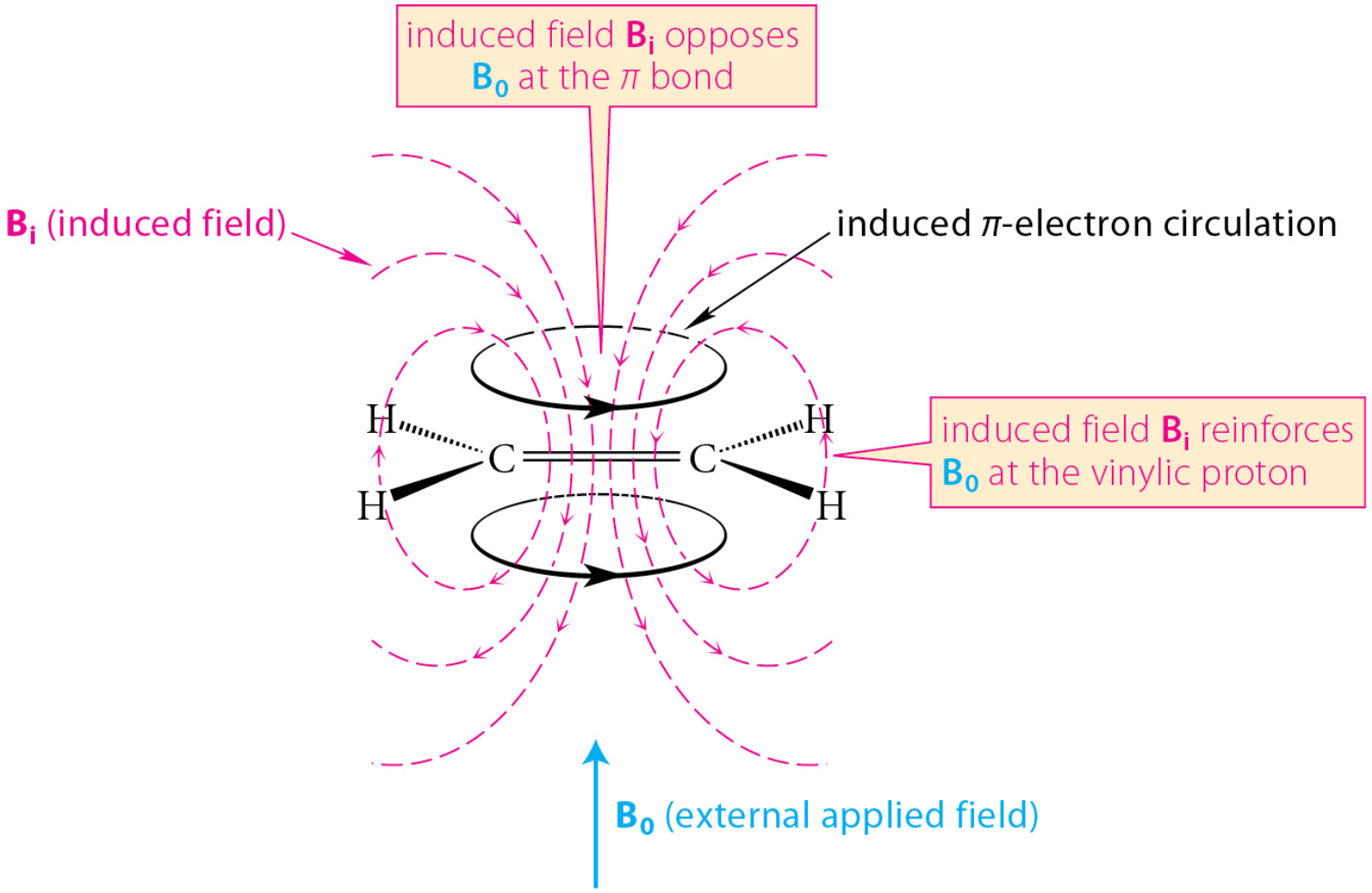
Summary


Electron-poor environment
Deshielded
Higher δ
”Downfield”
Electron-rich environment
Shielded
Low δ
”Upfield”
Absorption Intensity
CDCl3
TMS
Calibration peaks
11
10
9
8
7
6
5
4
3
2
1
0
δ, ppm

Chemical Shift



NMR Spectra of Alkenes

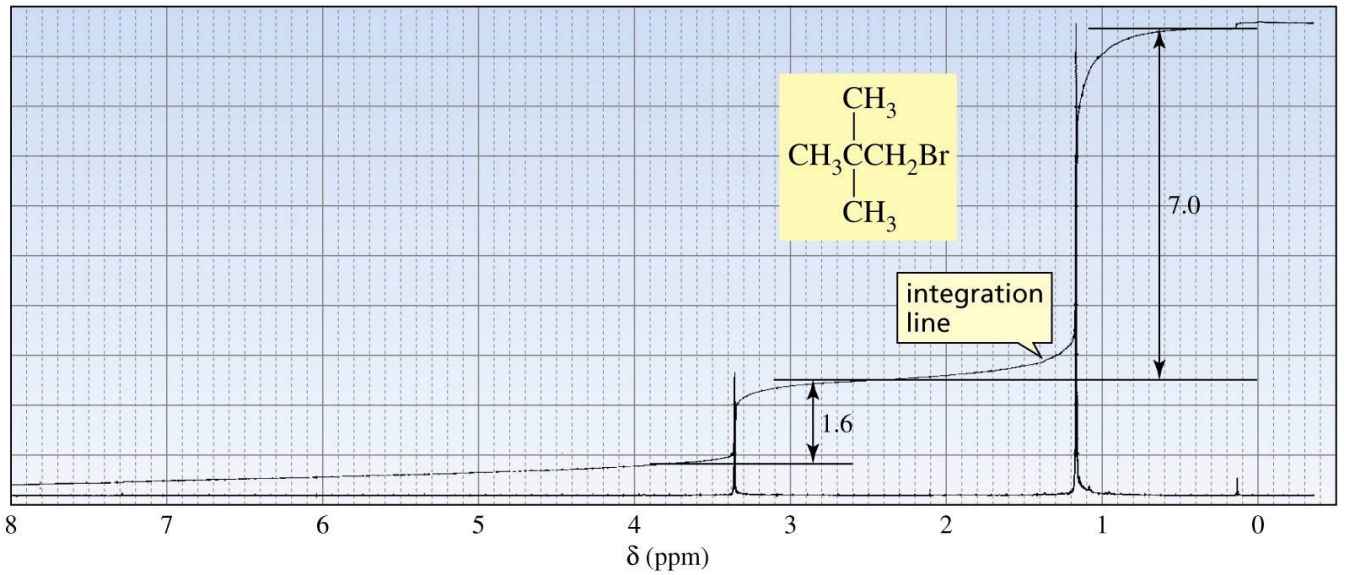


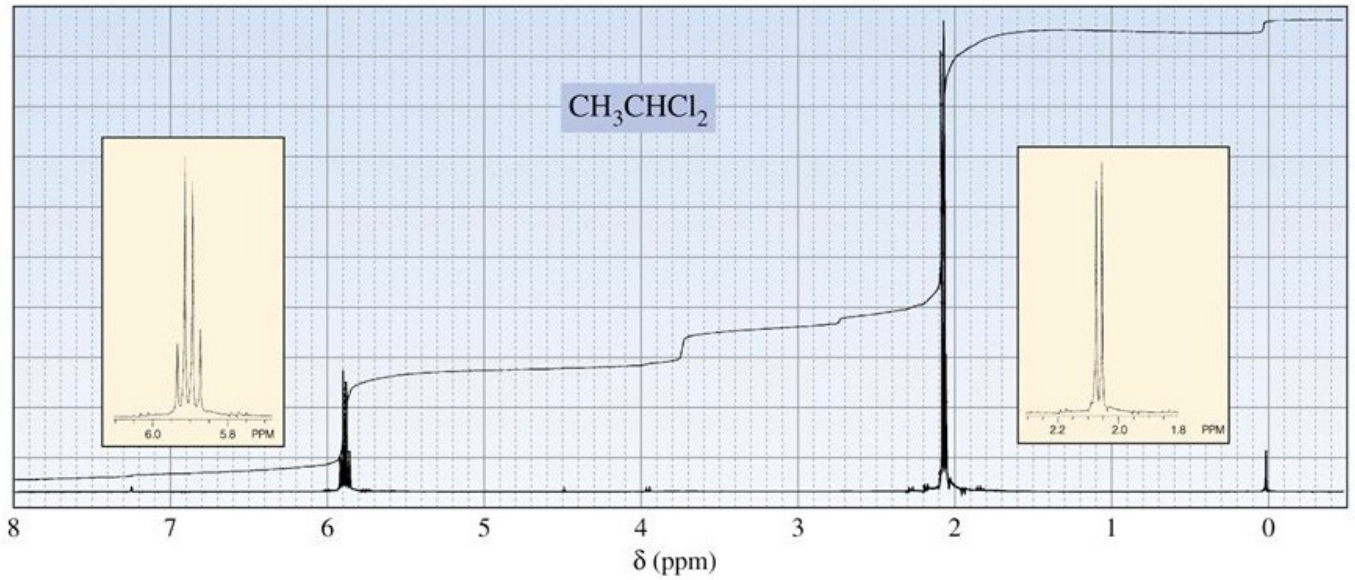
The ^{1}H NMR Spectrum

Proton NMR provides these types of information:

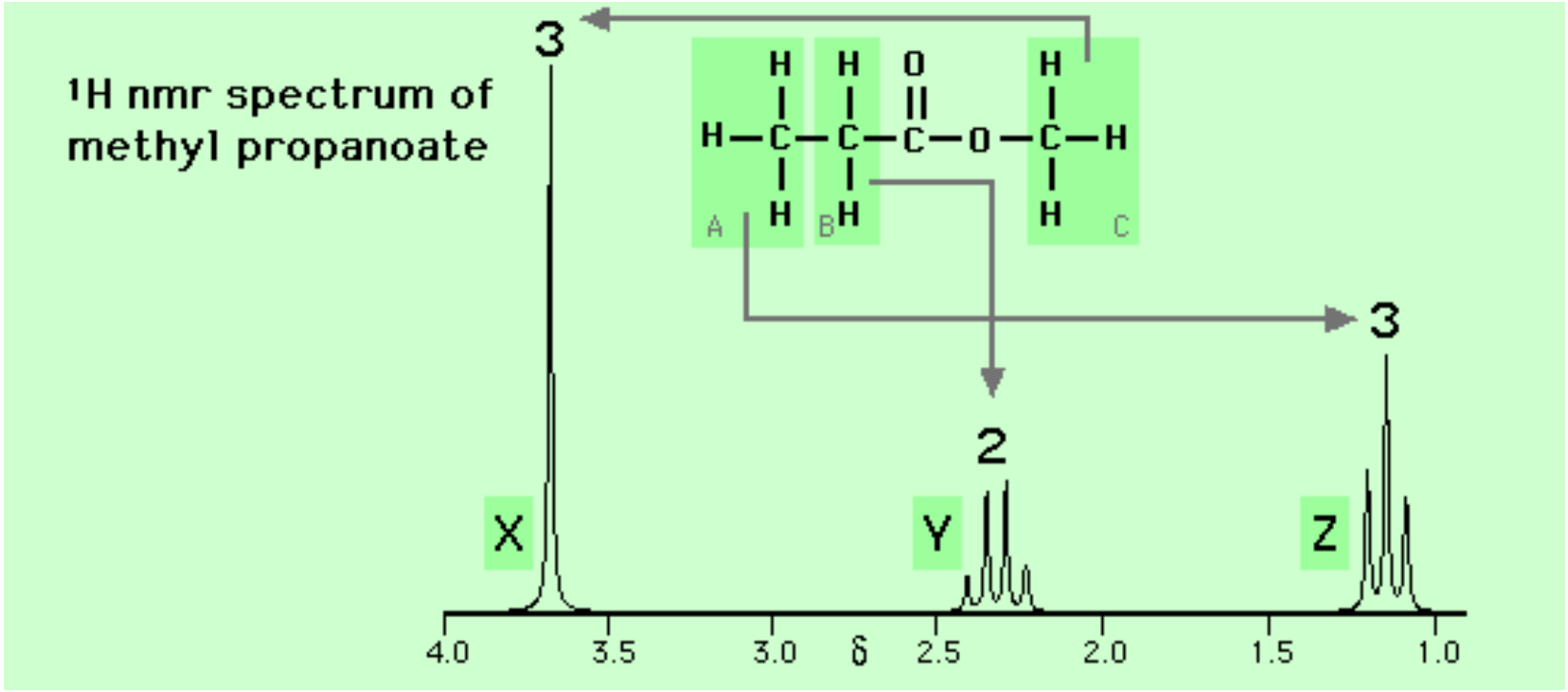
1. the number of sets of *chemically equivalent and non-equivalent protons*
2. the *number of protons* within each set (or their relative ratios)
3. the *chemical environments* of each set of protons (chemical shift)
4. the number of adjacent sets of protons or *connectivity*

^{1}H NMR spectra of 1-bromo-2,2-dimethylpropane and 1,1-dichloroethane

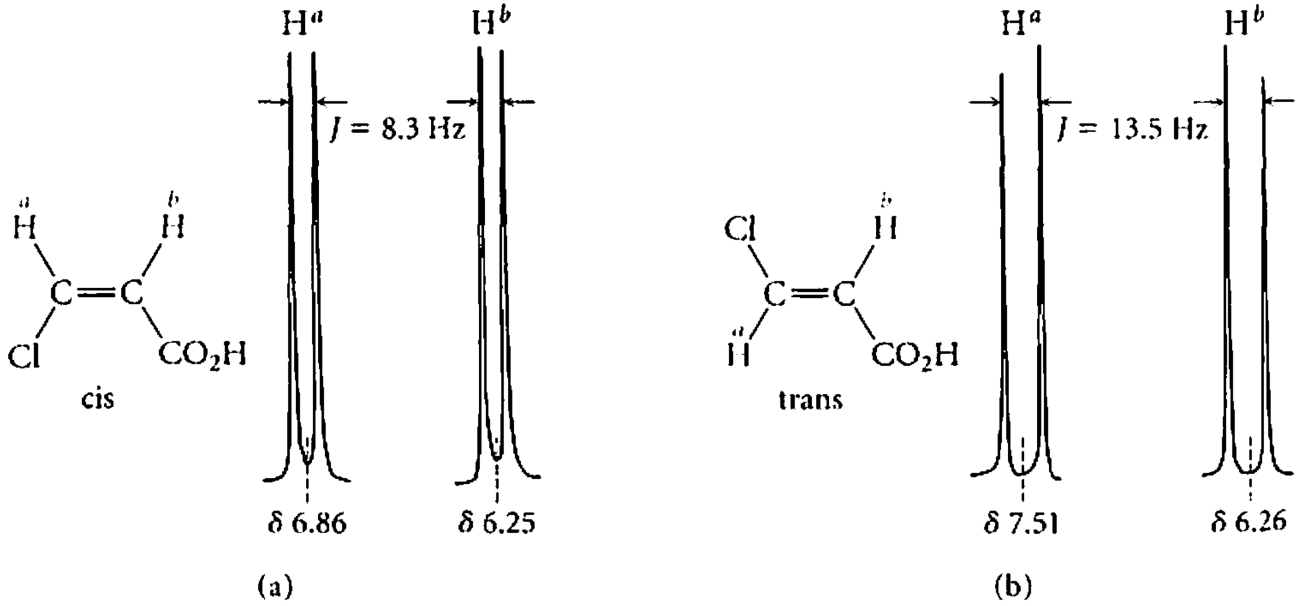




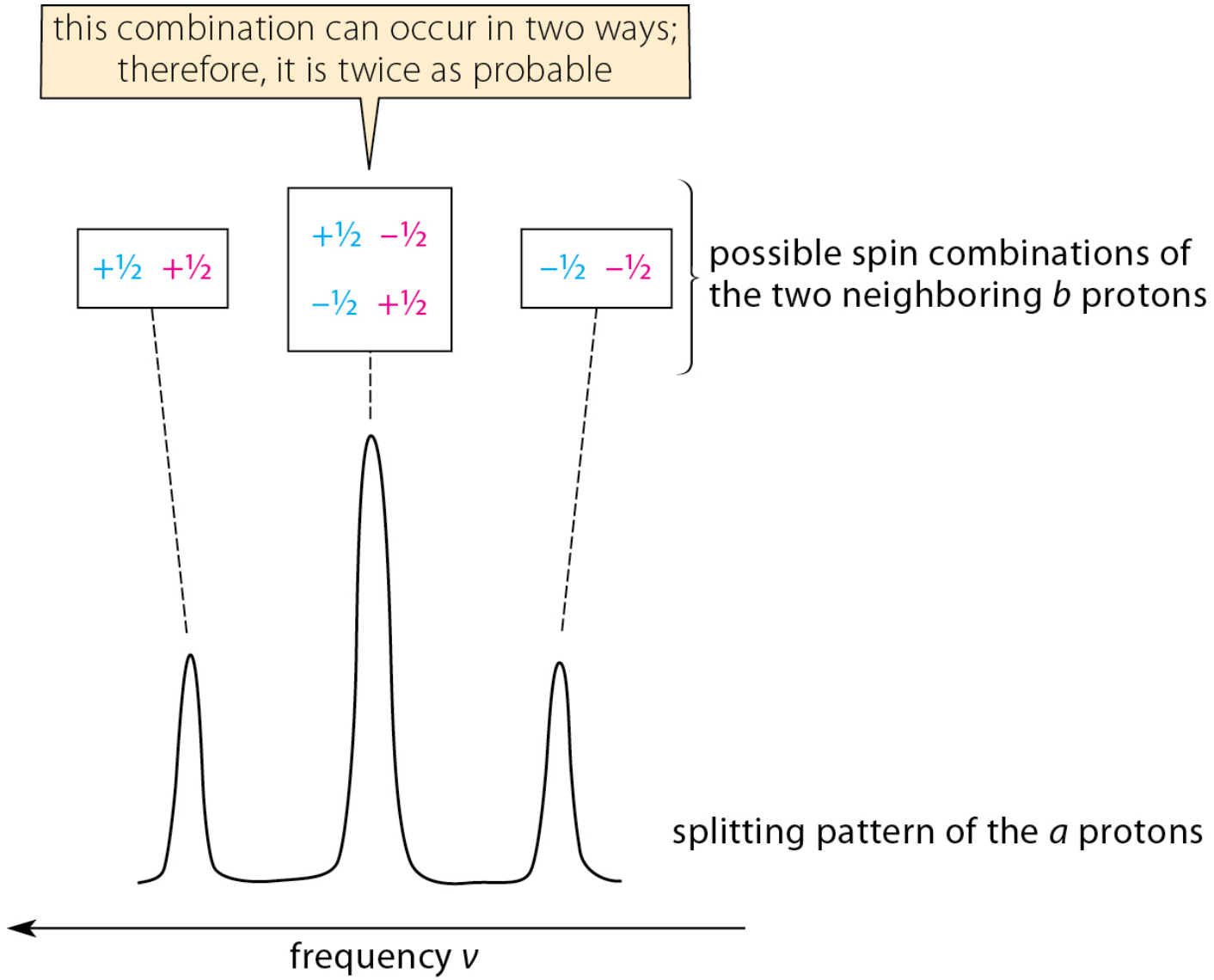
^{1}H NMR spectrum of methyl propanoate



Coupling Constants Can Report on Stereochemical Relationships: *Cis* vs. *Trans*



Why Splitting Occurs

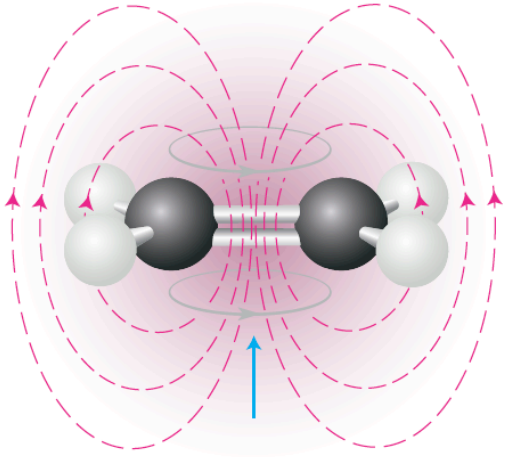


Splitting Patterns

- The intensities of split signals have well defined ratios.

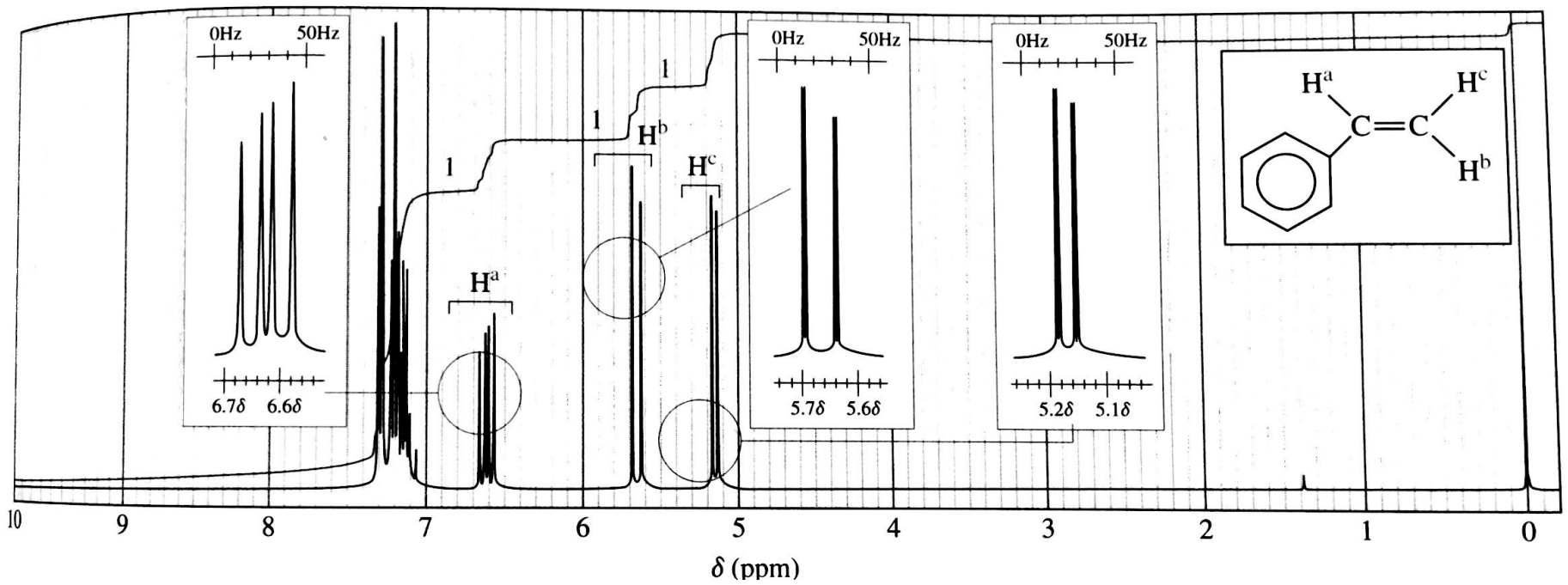
Number of equivalent adjacent protons	Number of lines in splitting pattern (name)	Relative line intensity within splitting pattern
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

Ch41b 2018:
Lecture 7 Figures (Part 3)

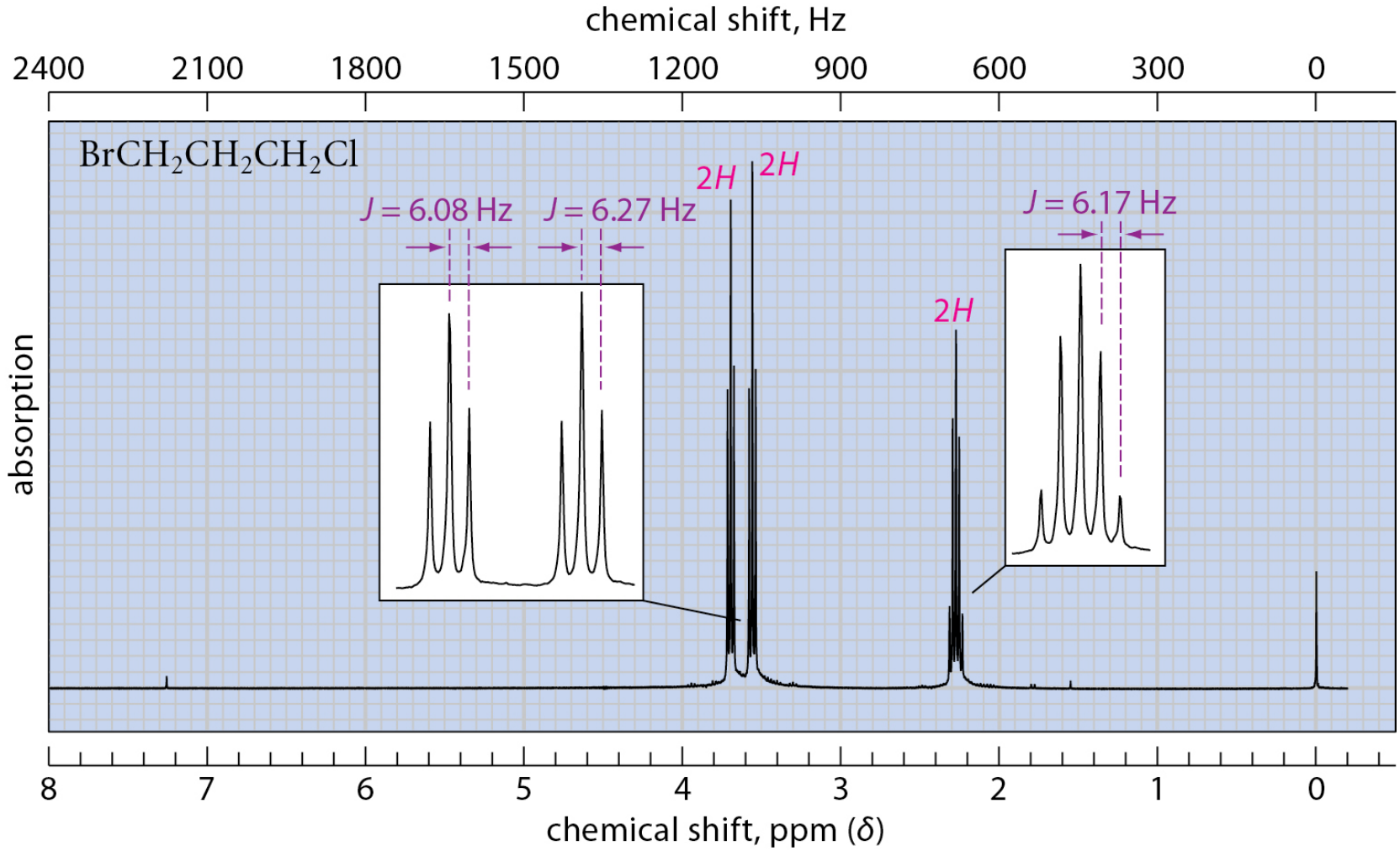


Nuclear Magnetic Resonance Spectroscopy
(Chapter 13, Loudon)

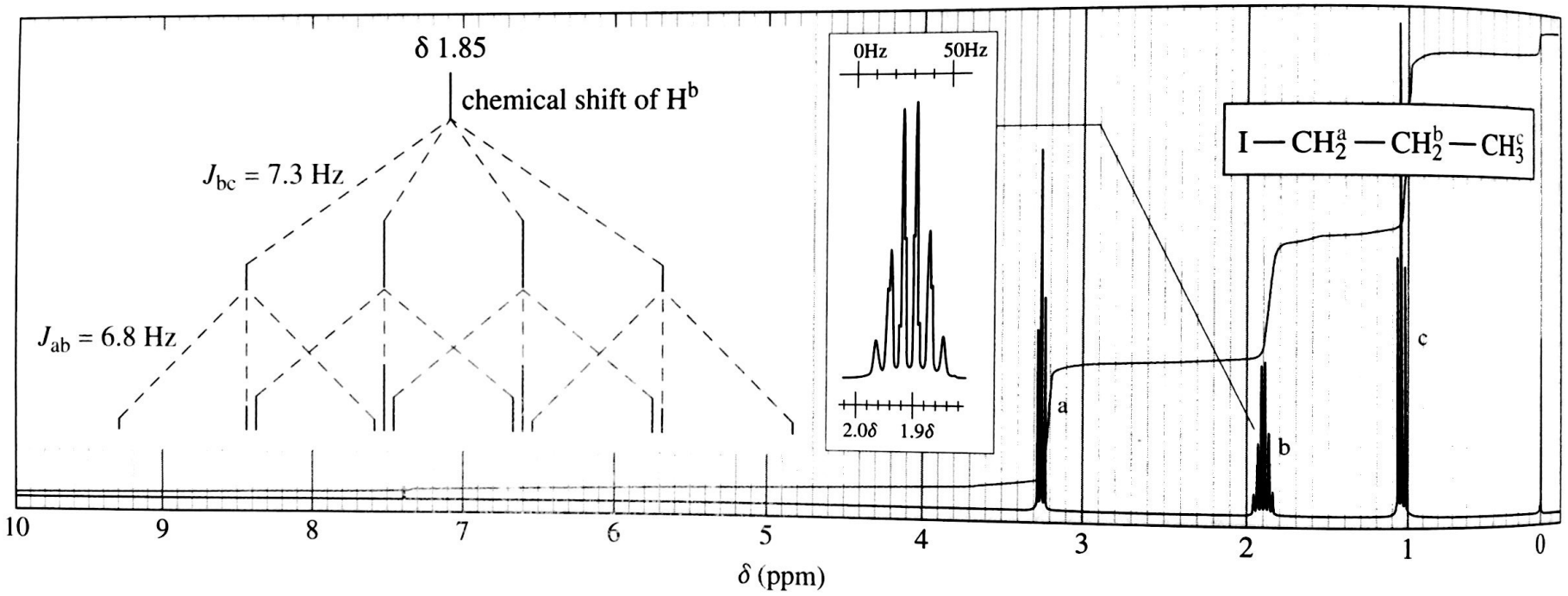
Multiplicative Splitting: Spectrum of Styrene



Spectrum of 1-bromo-3-chloropropane

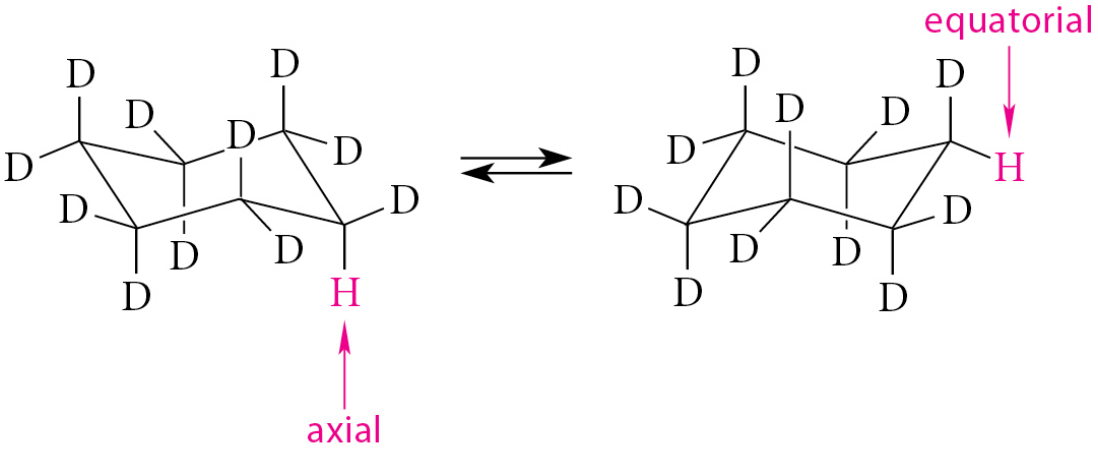


Spectrum of 1-iodopropane

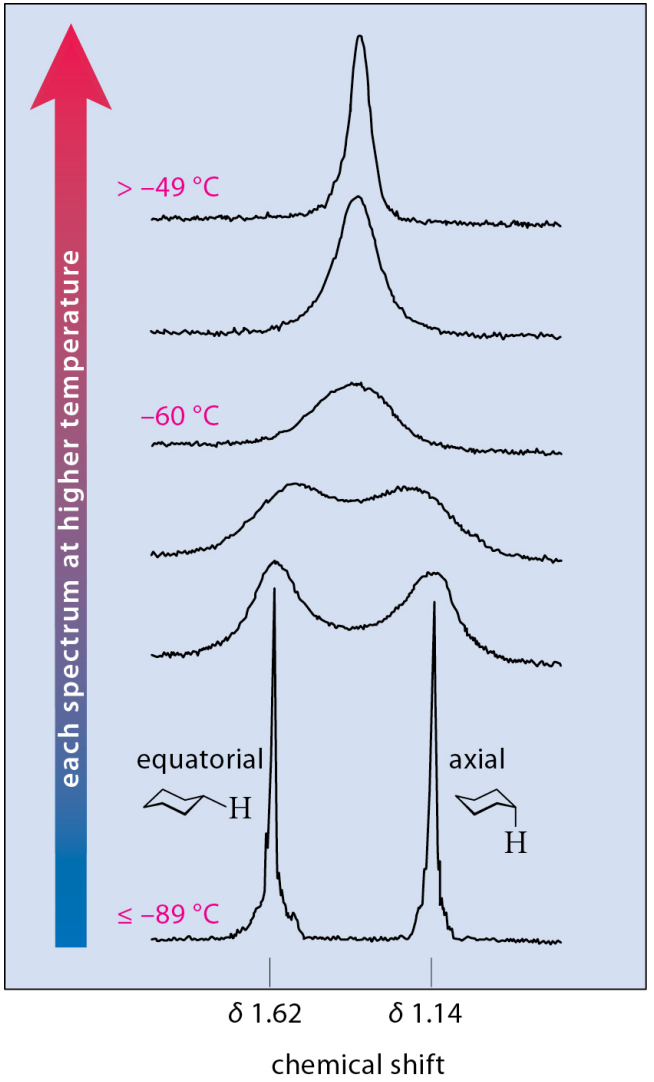


Dynamic Systems: The Time Dependence of NMR

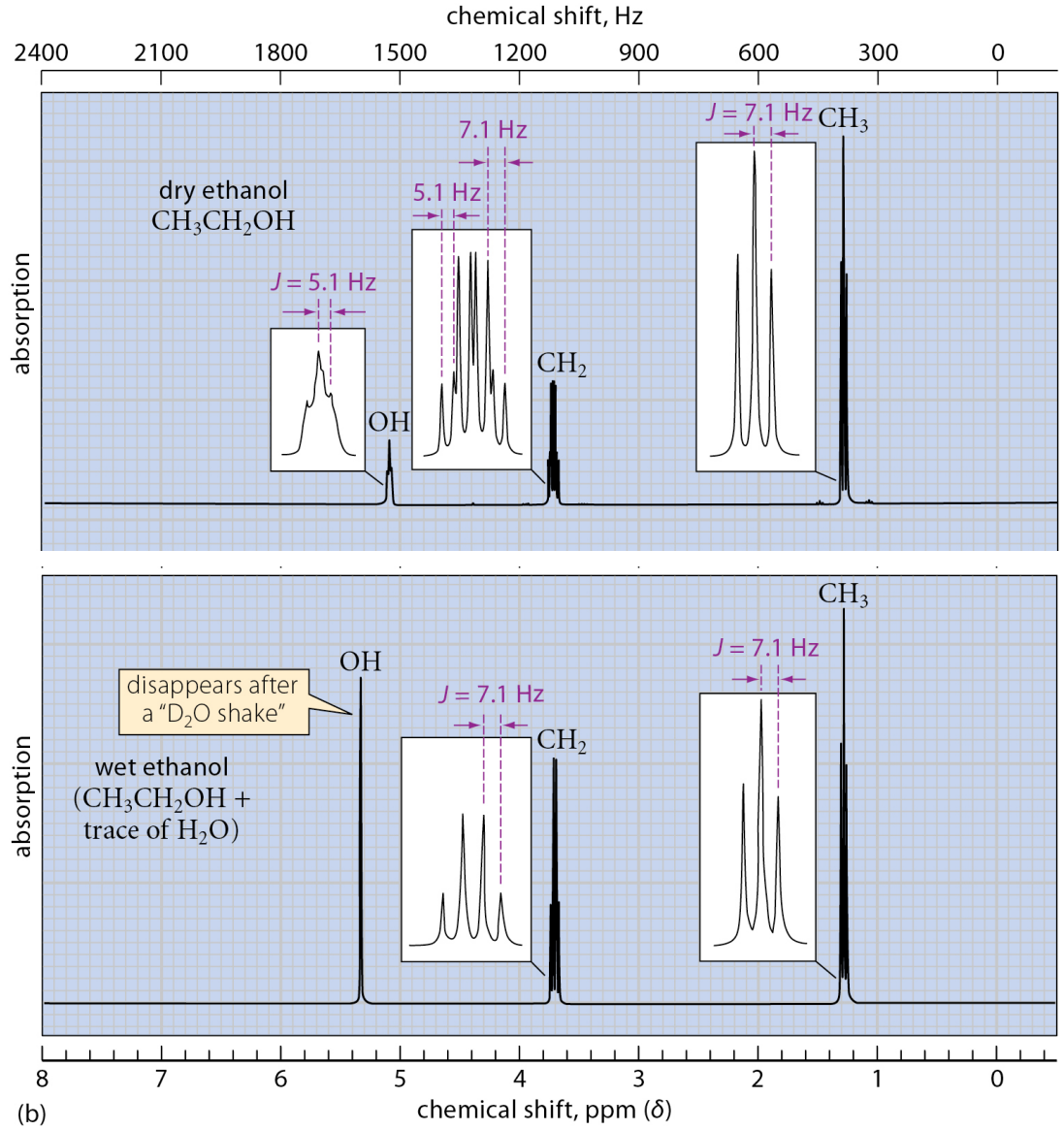
- Both diastereotopic protons can be observed if the rate of chair interconversion is reduced by lowering the temperature.



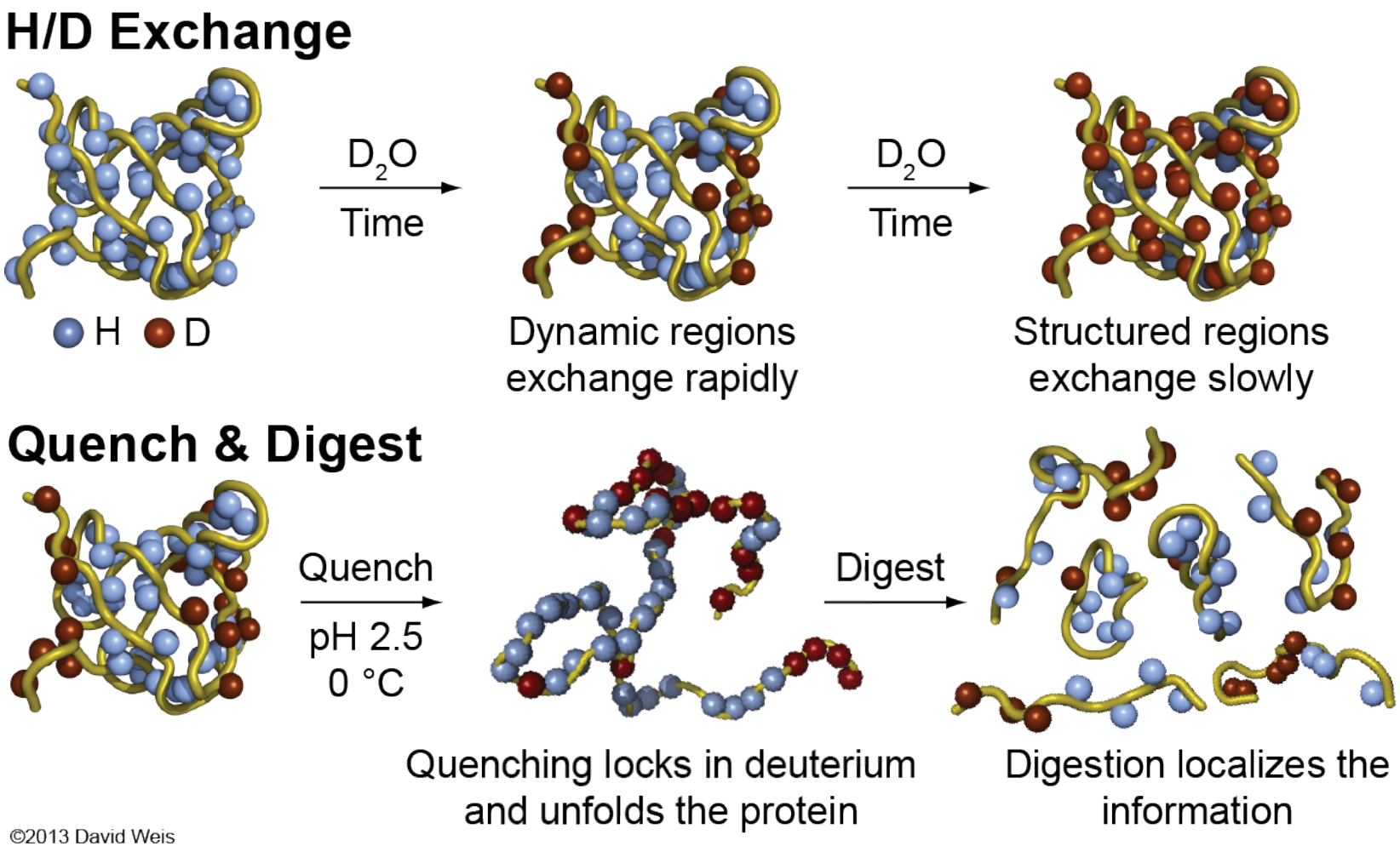
cyclohexane-d_{11}



Fast Proton Transfers: NMR Spectra of Ethanol



H/D Exchange to Study Protein Structure



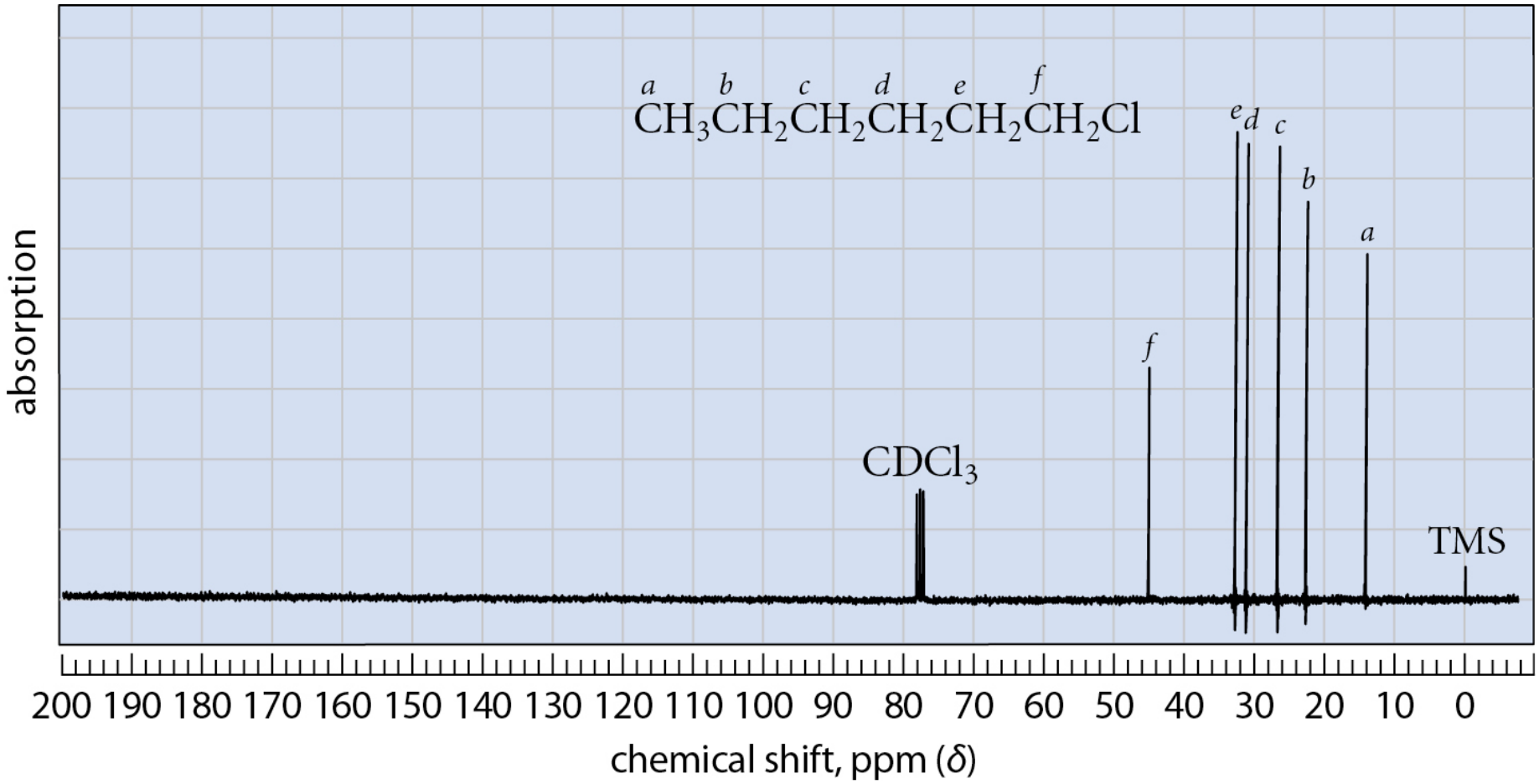
NMR of Other Nuclei

- Many other spin active nuclei may also be observed by NMR.

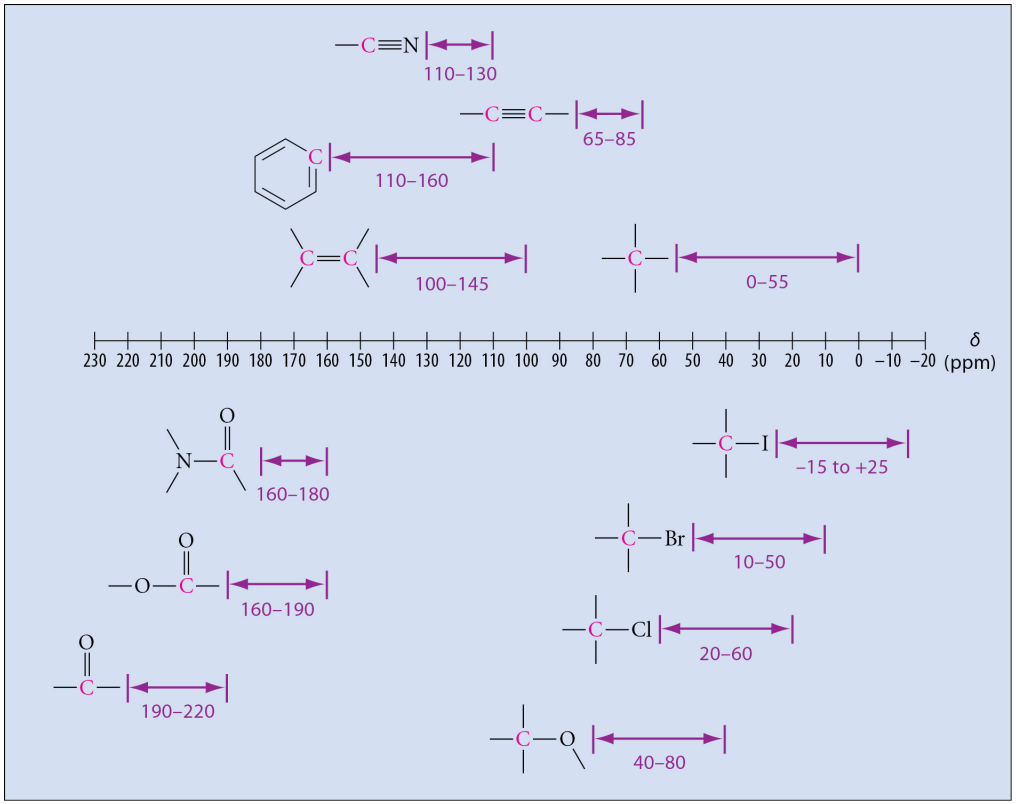
Isotope	Relative sensitivity	Natural abundance, %	Observation frequency ν_n, MHz*	Gyromagnetic ratio‡
^{1}H	(1.00)	99.98	300	26,753
^{13}C	0.0159	1.10	75	6728
^{19}F	0.834	100	282	25,179
^{31}P	0.0665	100	122	10,840

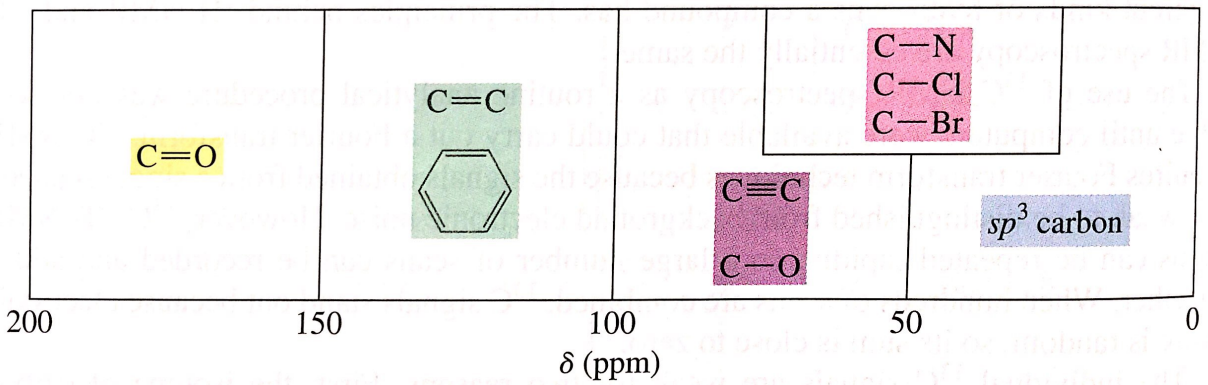
* At magnetic field B_0 = 70,500 gauss. ‡ In radians gauss^{-1} s^{-1} defined in Eq. 13.17.

Proton-Decoupled ^{13}C NMR

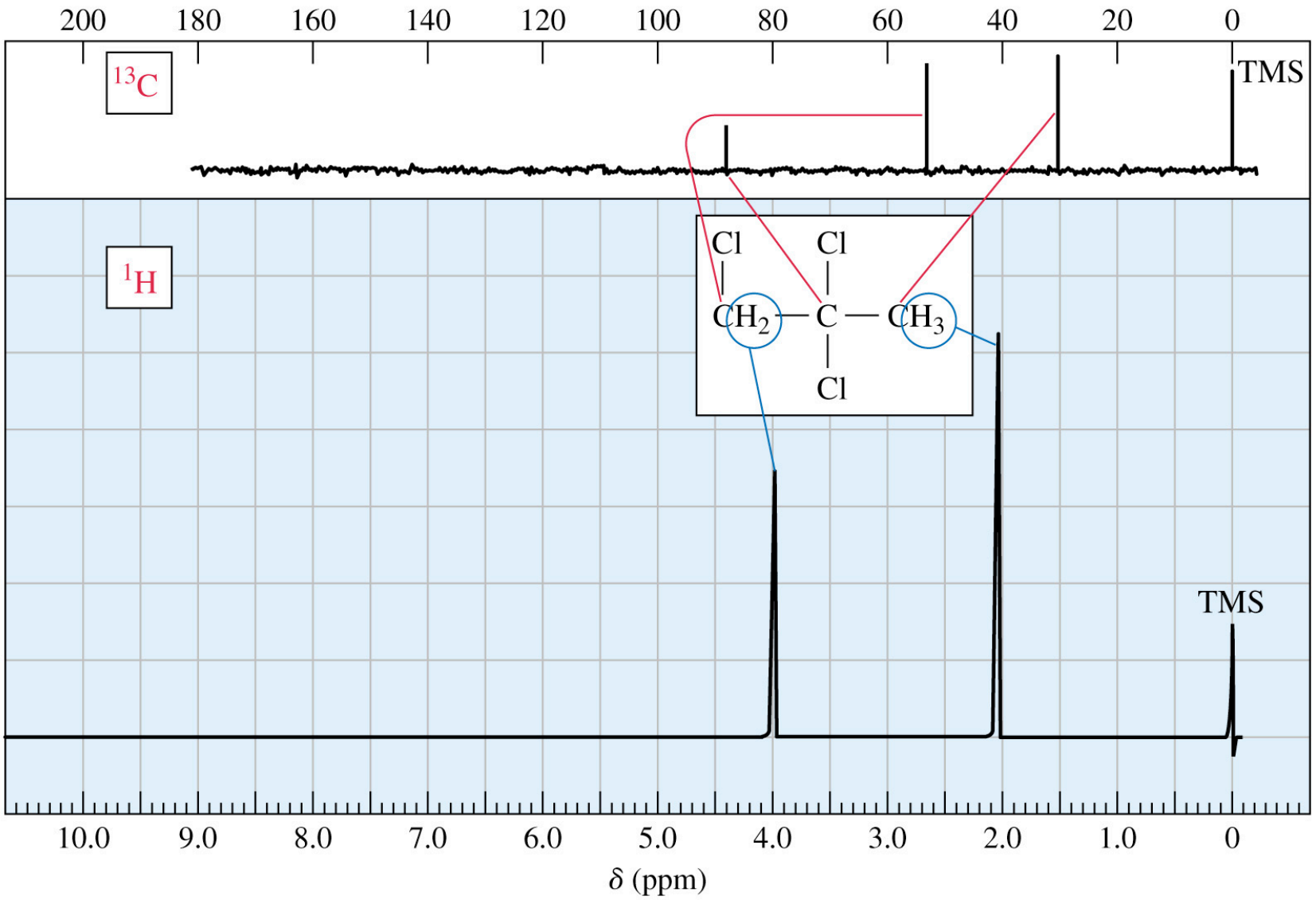


Chemical Shift in ^{13}C NMR

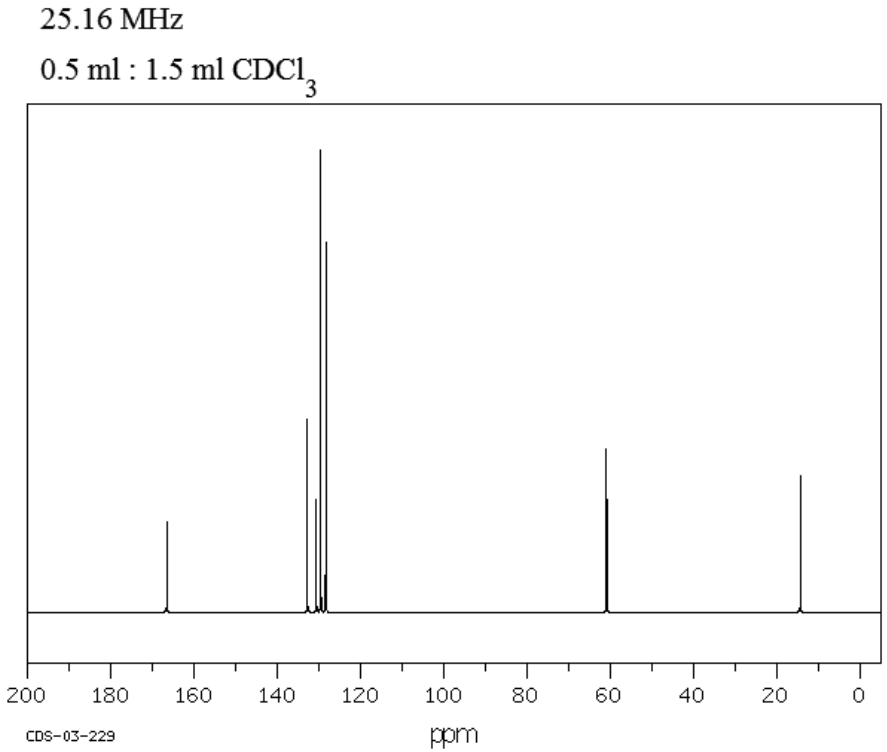


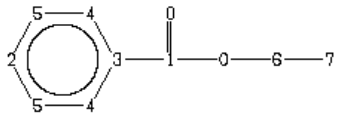


^{1}H and ^{13}C NMR Spectra of 1,2,2-trichloropropane



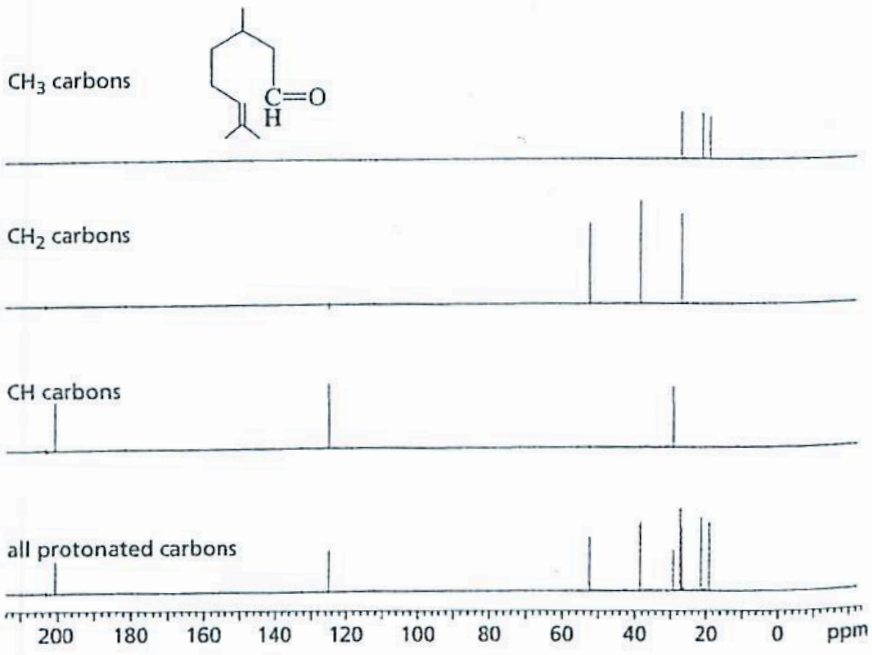
^{13}C NMR Spectrum of Ethyl Benzoate



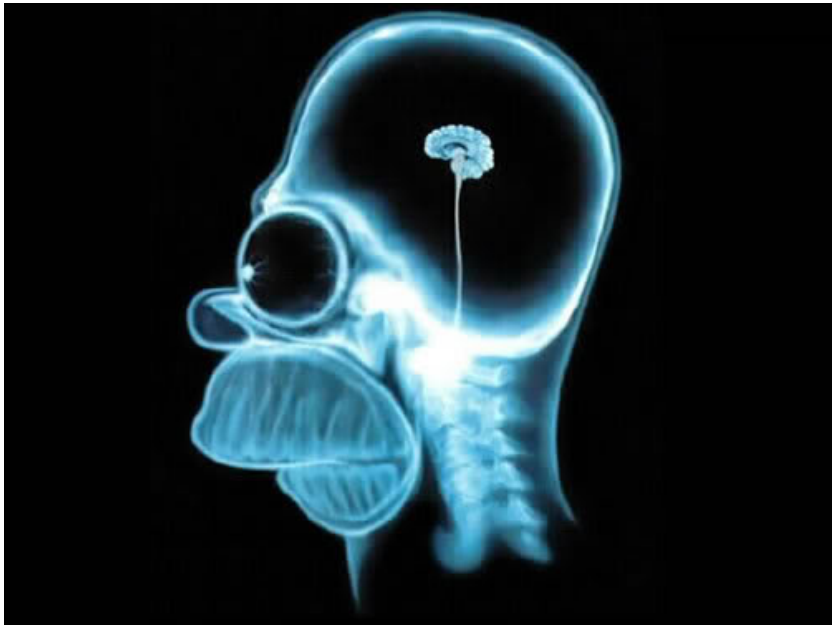


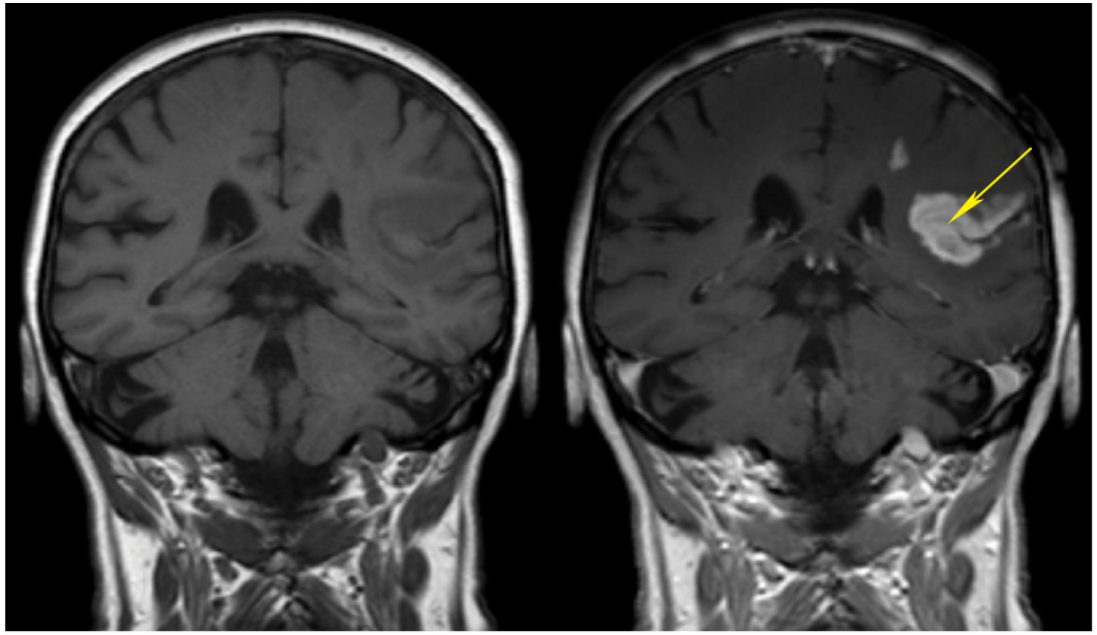
ppm	Int.	标记碳
166.54	194	1
132.80	418	2
130.62	244	3
129.57	1000	4
128.34	801	5
60.90	353	6
14.33	294	7

DEPT ^{13}C NMR Spectrum of Citronellal



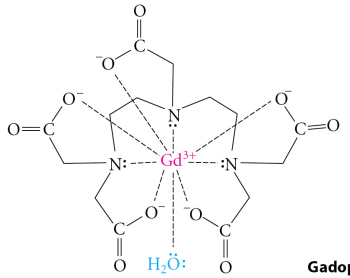
Magnetic Resonance Imaging





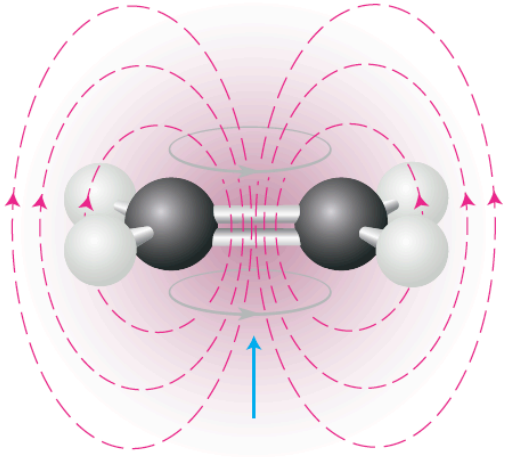
No harmful x-rays:
Magnets and radiowaves

Imaging of biological tissue
Detection of tumors
Visualization of brain function



Gadopentetic acid (Optimark®, Magnevist®)

Ch41b 2018:
Lecture 8 Figures (Part 4)



Nuclear Magnetic Resonance Spectroscopy
(Chapter 13, Loudon)

Steps for Solving Structures

1. Write down the molecular formula, molecular mass (MS) & determine the unsaturation number if possible.
2. Identify functional groups or fragments (IR, NMR).
3. Determine the number of nonequivalent sets of protons or carbons (^{1}H & ^{13}C NMR). Use the integrals and molecular formula to calculate how many protons or carbons correspond to each absorption.
4. Write out partial structures and possible complete structures.
5. Use spectra to confirm or disprove the proposed structure(s).

Practice Problem

The molecular formula for an unknown compound is $C_7H_{16}O_4$. Data for the ^1H NMR are shown below. What is the structure of the compound?

- d 1.93 (t, J = 6 Hz)
- d 3.35 (s)
- d 4.49 (t, J = 6 Hz)
- Relative integral 1:6:1