Nuclear Magnetic Resonance Part 2 Number of Signals, Chemical Shift, Coupling and Integration

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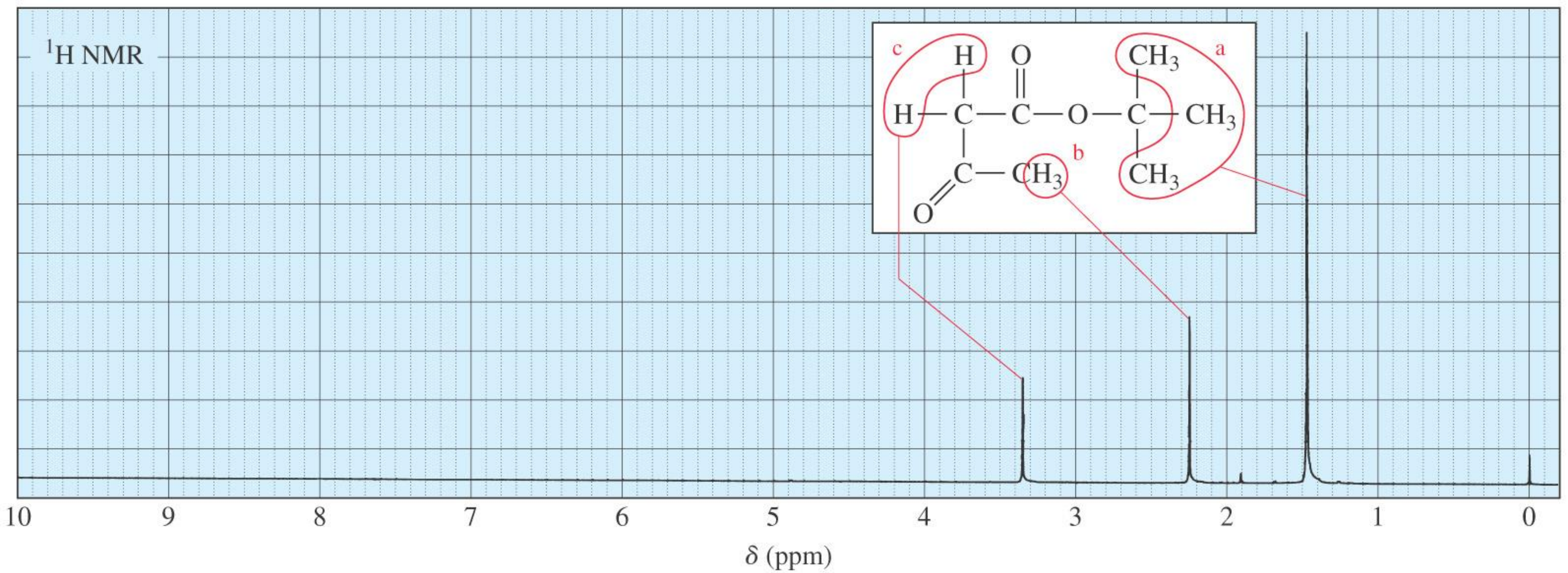
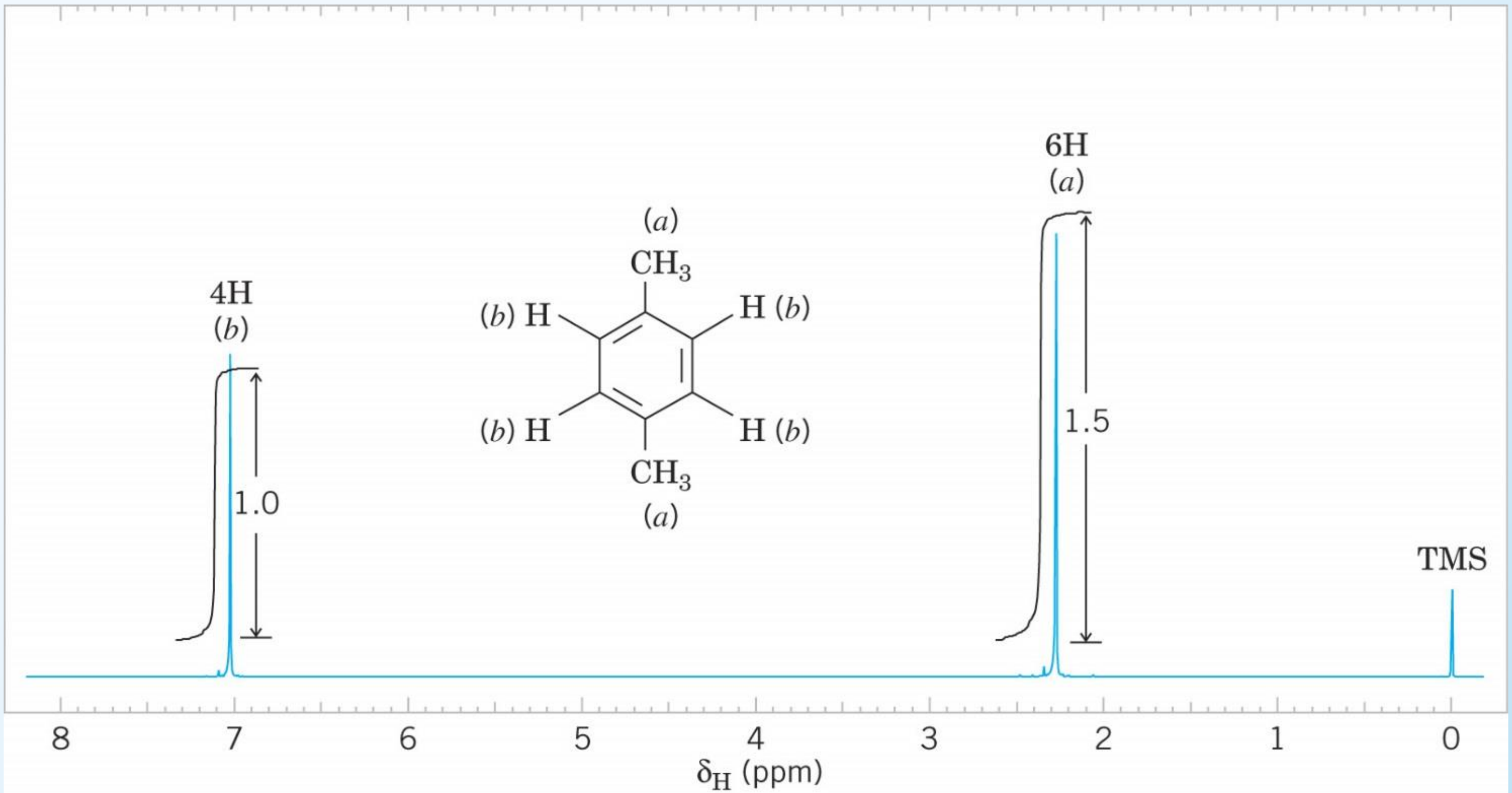
Number of Signals and Chemical Shift

Equivalent hydrogens have the same chemical shift.

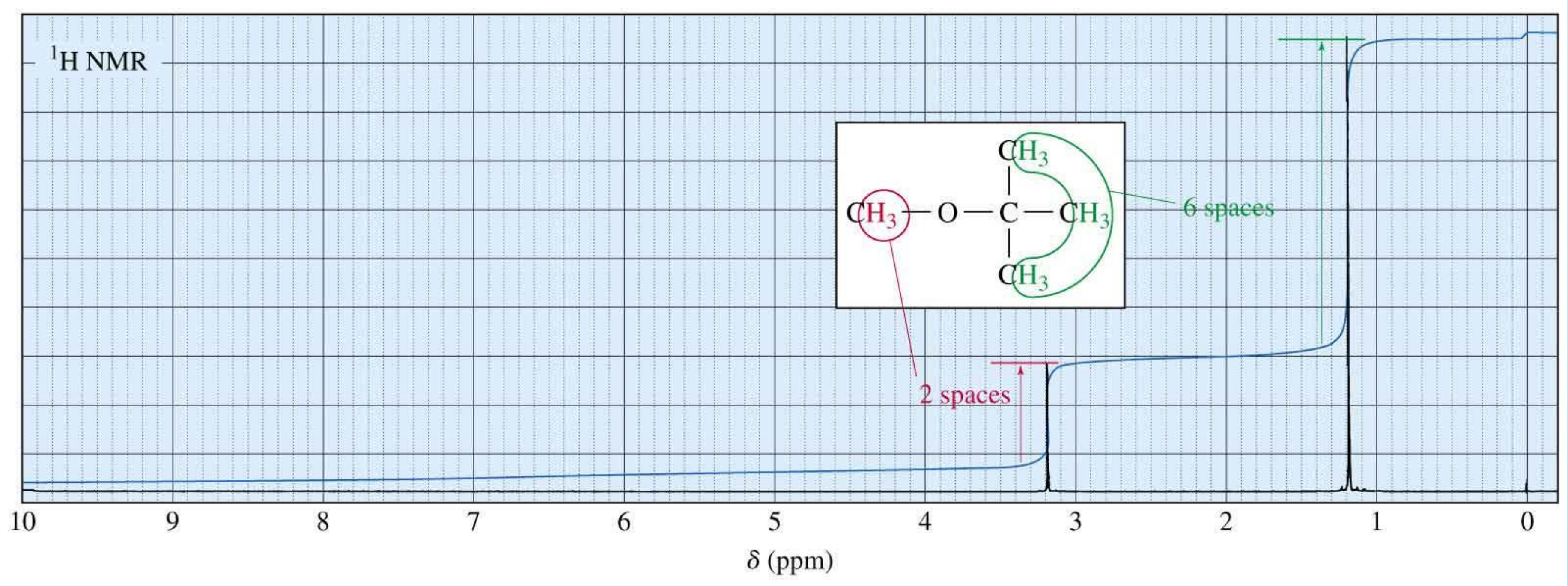
Hydrogens/protons in different environments will show different chemical shifts. In the NMR below: “a” protons are most shielded and “c” protons are most deshielded)




4H
(b)
1.0
(a)
CH3
(b) H
H (b)
(b) H
H (b)
CH3
(a)
6H
(a)
1.5
TMS
8
7
6
5
4
3
2
1
0
δH (ppm)

Intensity of Signals - Integration

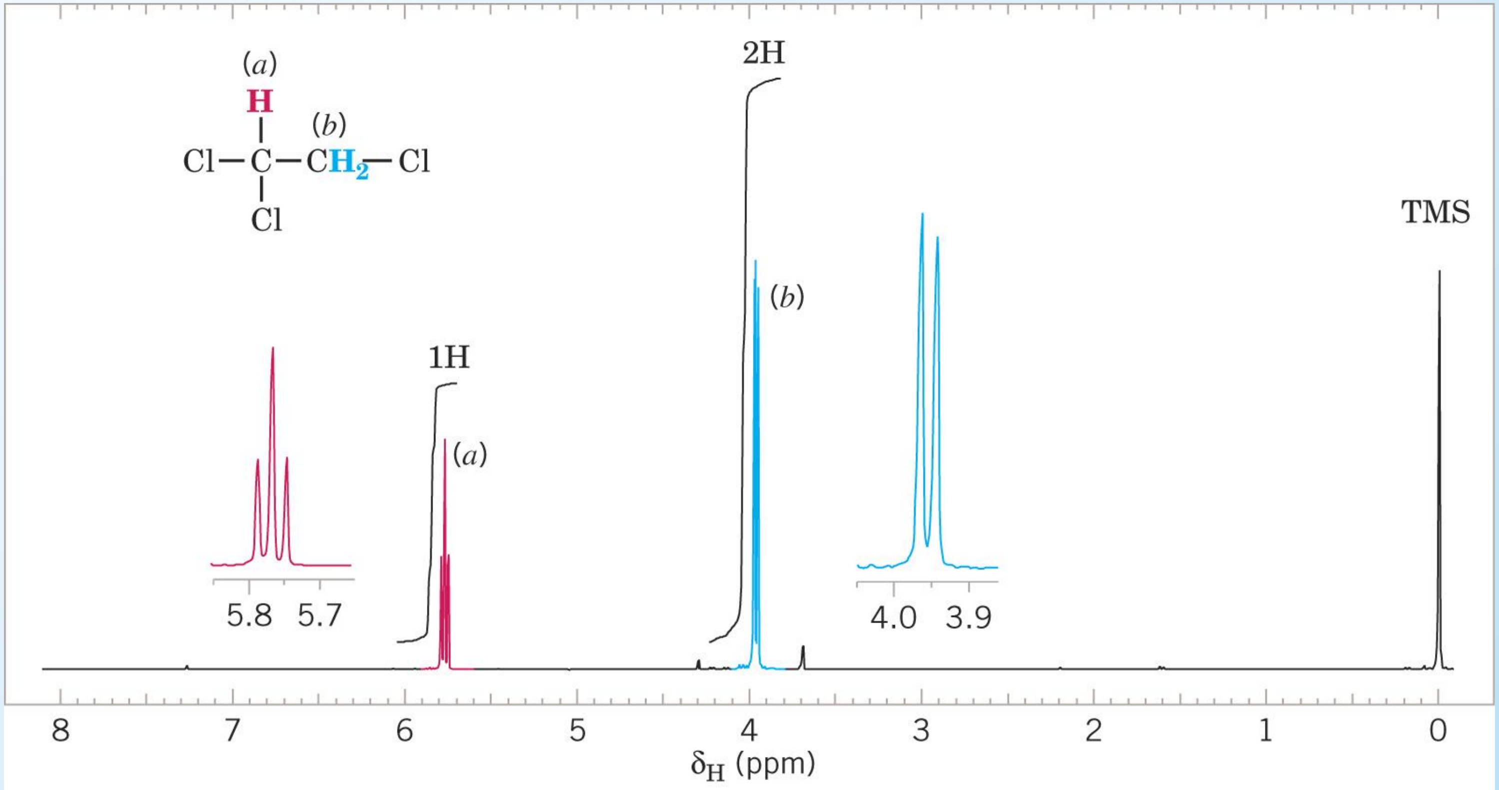
- The area under each peak is proportional to the number of protons.
- Shown by integral trace.



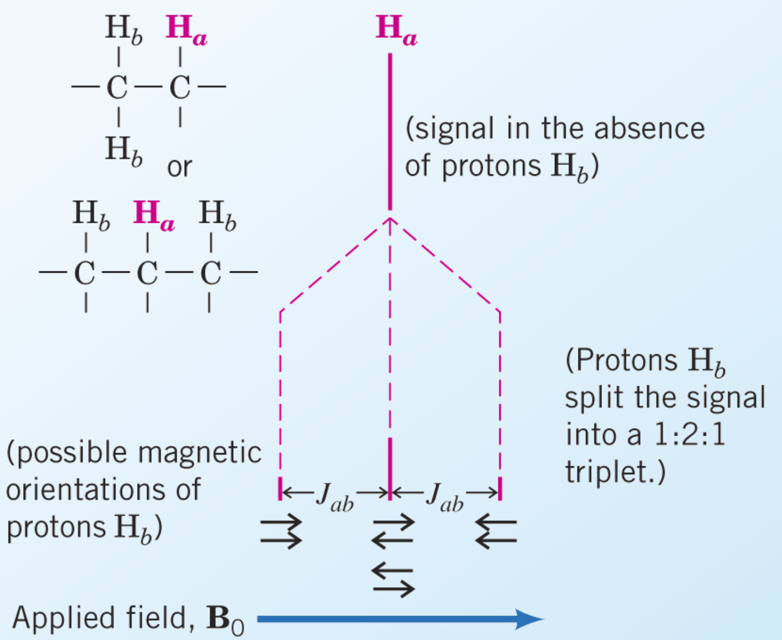
=>

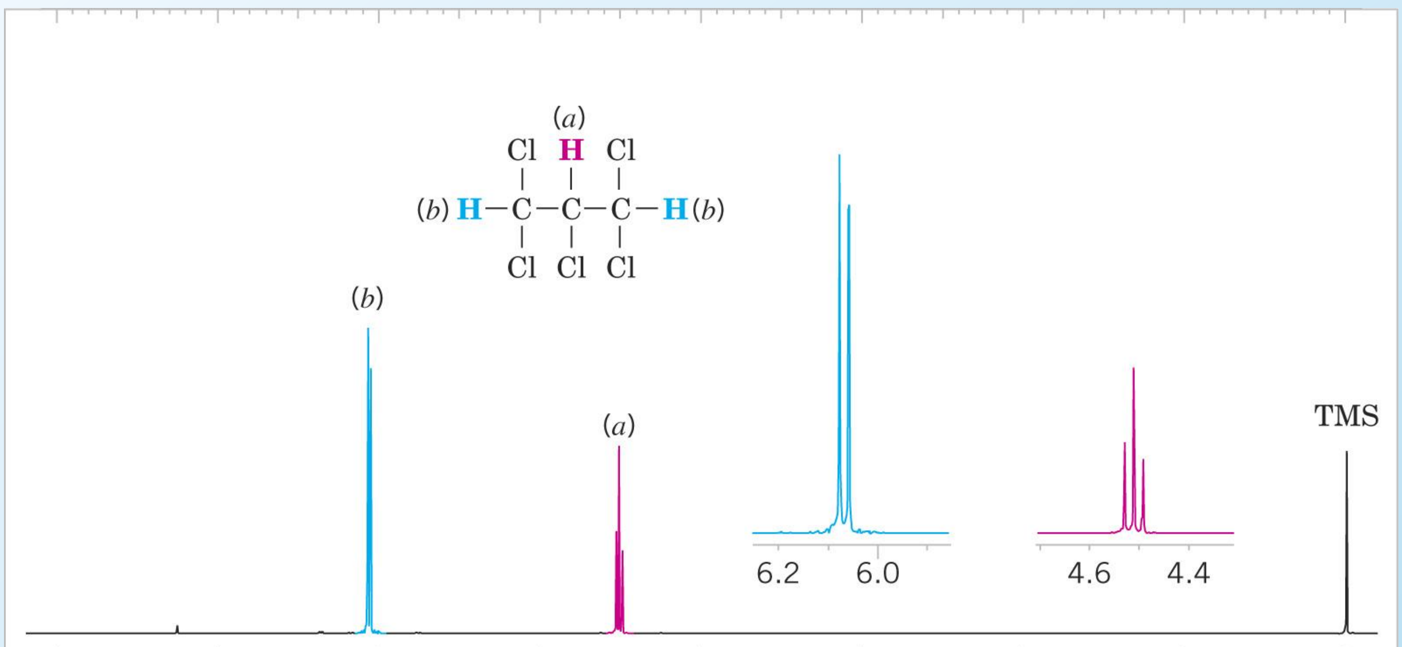
Spin-Spin Splitting (Coupling)

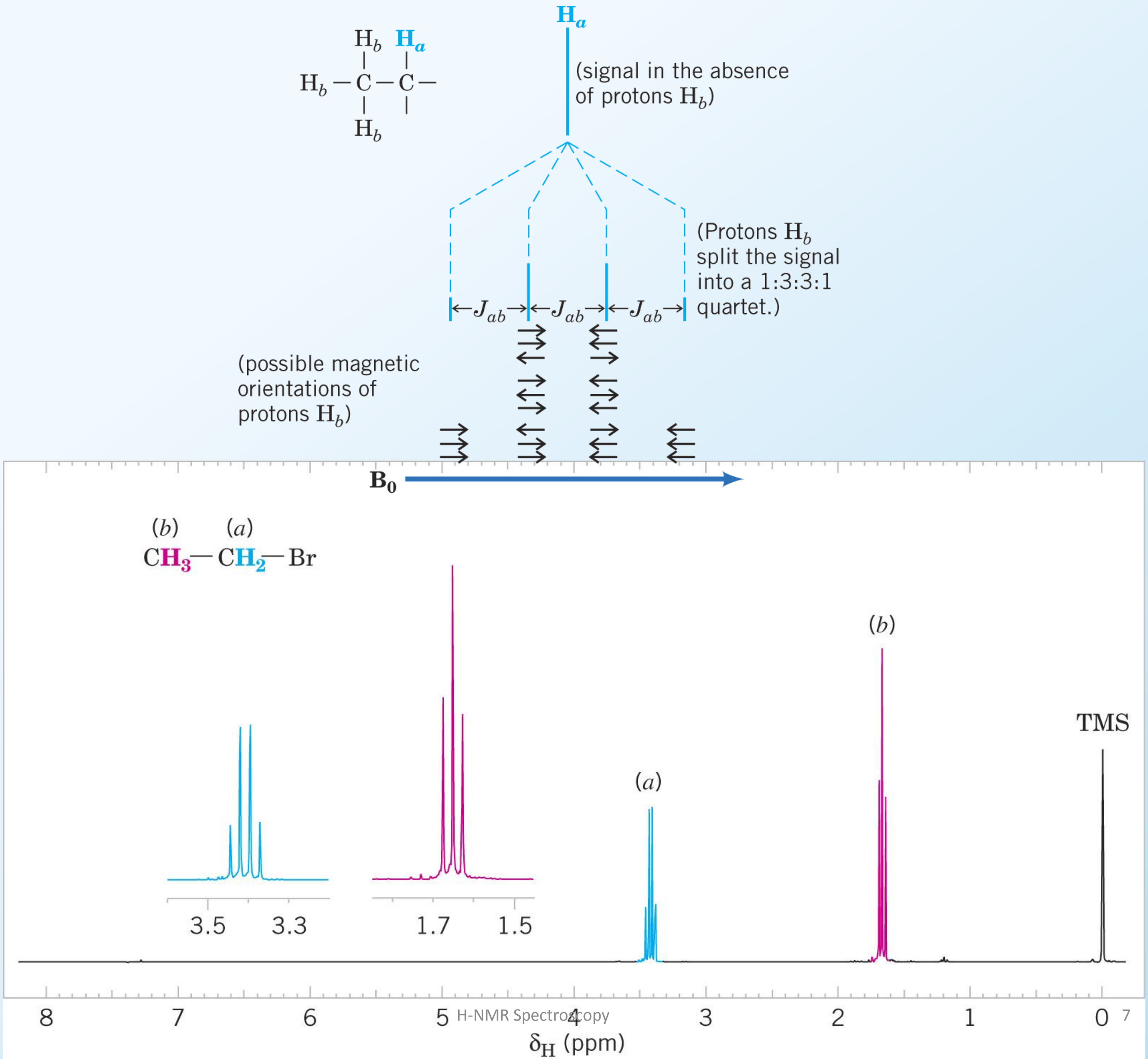
- Signal splitting occurs when there are unequivalent protons (therefore have a different chemical shift) on the neighboring carbons.
- Signal splitting for a proton is neighboring proton +1.
- This has to do with the alignment of the protons to the magnetic field.



More on Coupling







H_a
H_b H_a
H_b — C — C —
H_b
(signal in the absence of protons H_b)
(Protons H_b split the signal into a 1:3:3:1 quartet.)
J_{ab} J_{ab} J_{ab}
(possible magnetic orientations of protons H_b)
B_0
(b) (a)
CH_3—CH_2—Br
3.5 3.3
1.7 1.5
(a)
(b)
TMS
8 7 6 5 4 3 2 1 0
δ_H (ppm)

The $N + 1$ Rule

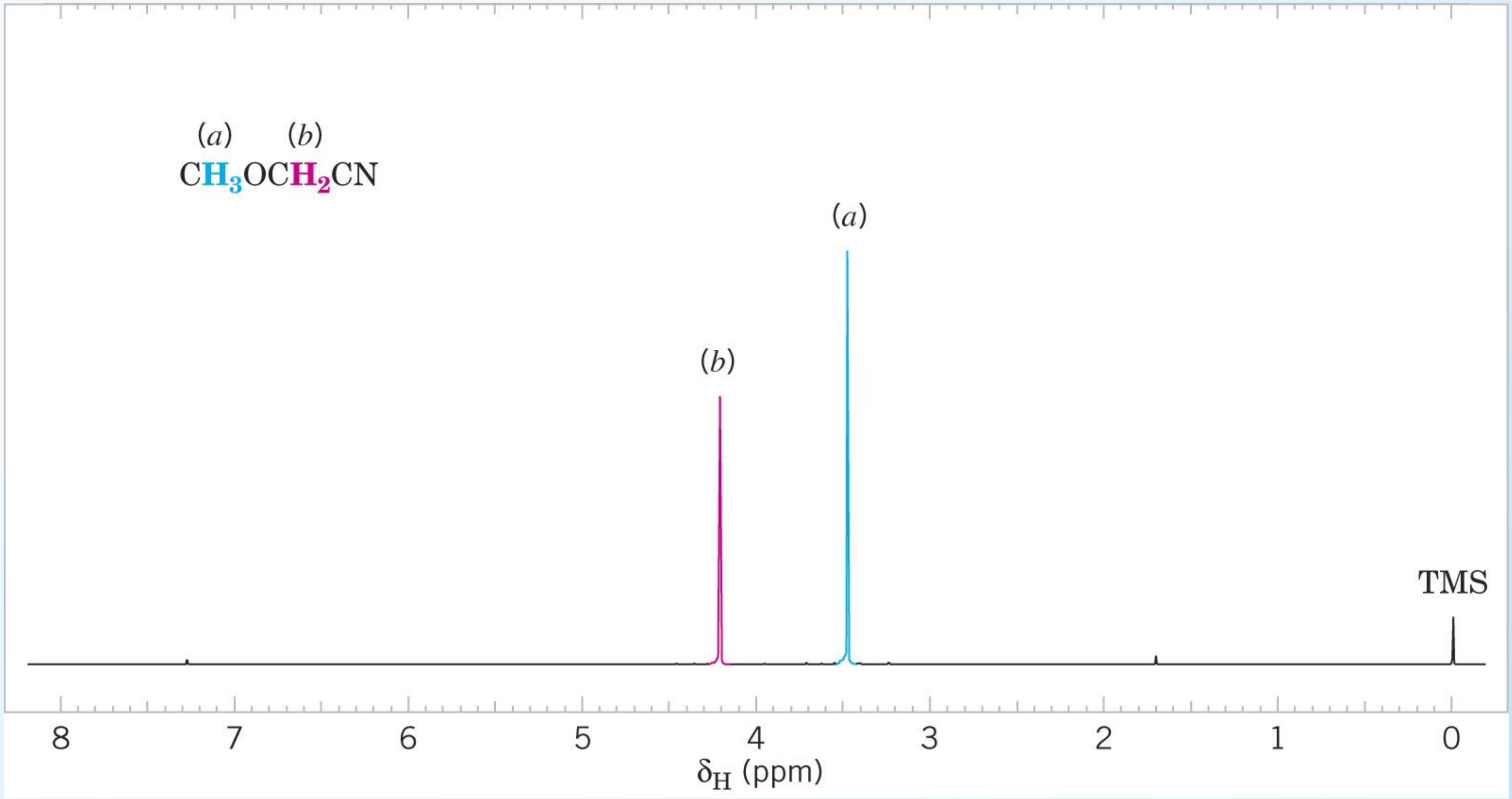
If a signal is split by N equivalent protons, it is split into $N + 1$ peaks.

Relative Peak Intensities of Symmetric Multiplets		
Number of Equivalent Protons Causing Splitting	*Number of Peaks (multiplicity)*	*Area Ratios (Pascal's triangle)*
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

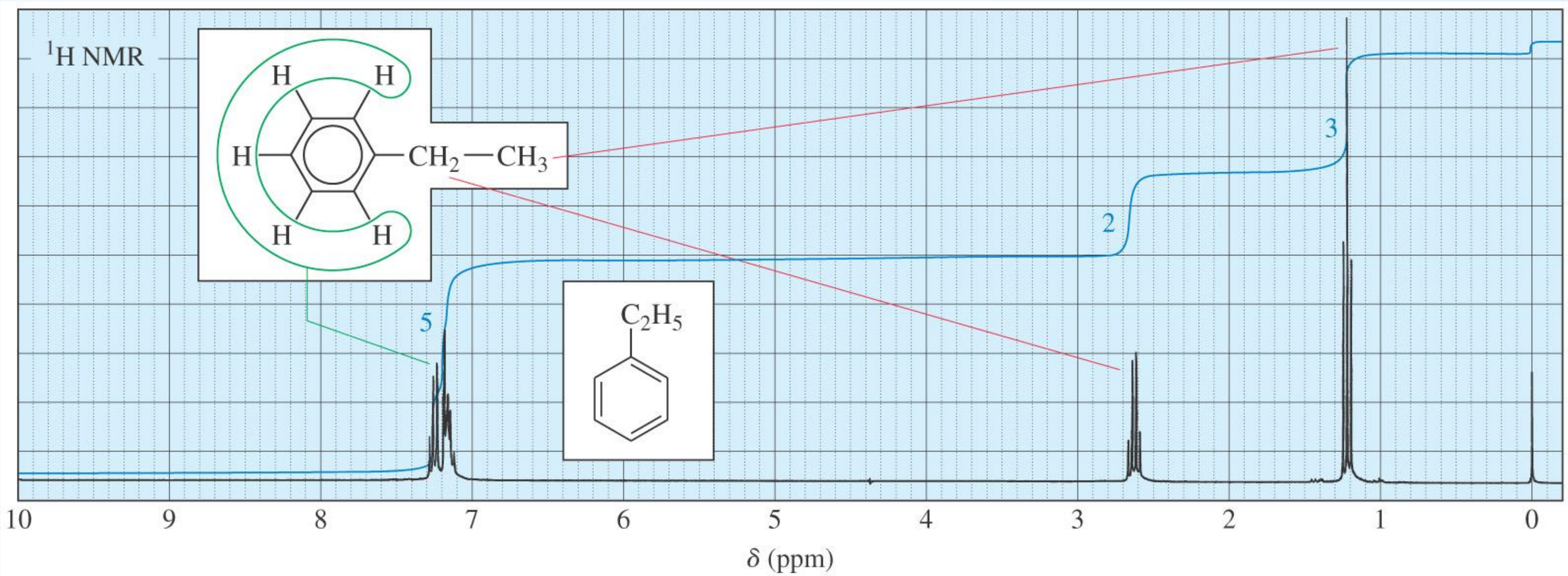
Range of Magnetic Coupling

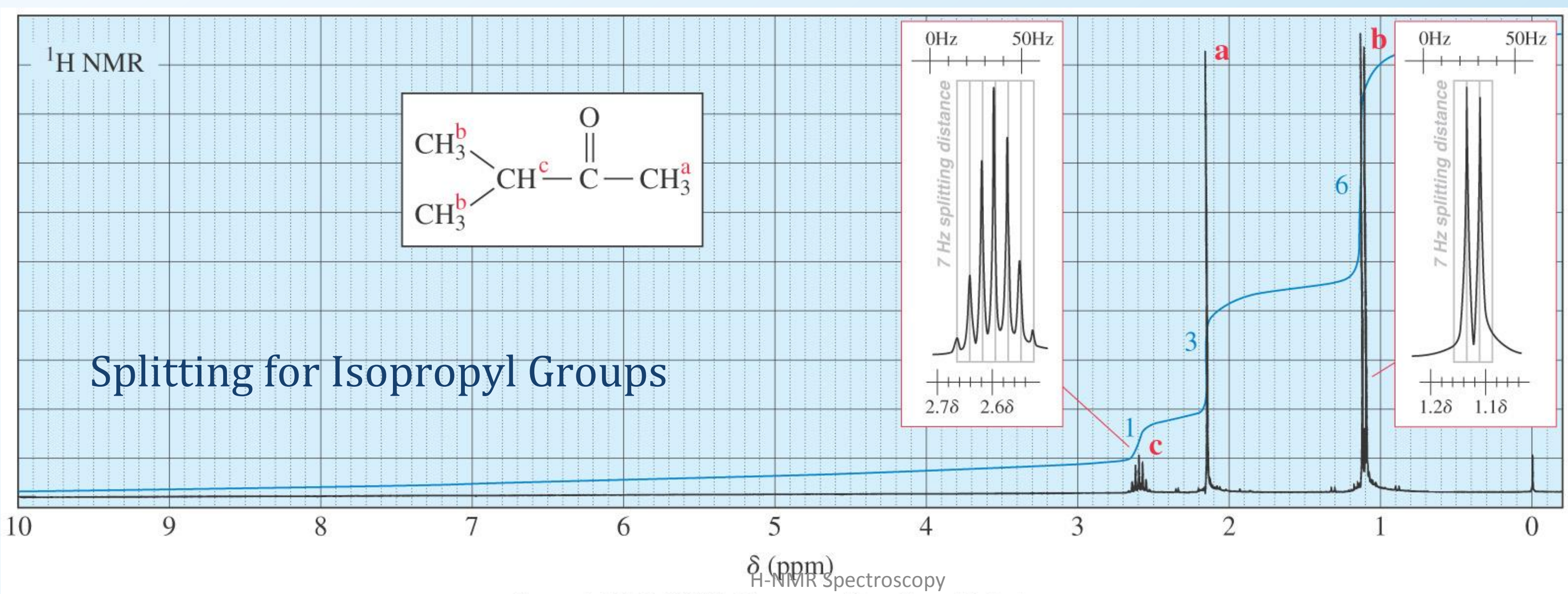
- Equivalent protons do not split each other.
- Protons bonded to the same carbon will split each other <u>only</u> if they are not equivalent.
- Protons on adjacent carbons normally will couple.
- Protons separated by four or more bonds will not couple.

No coupling between Hs because of electronegative O in the middle.



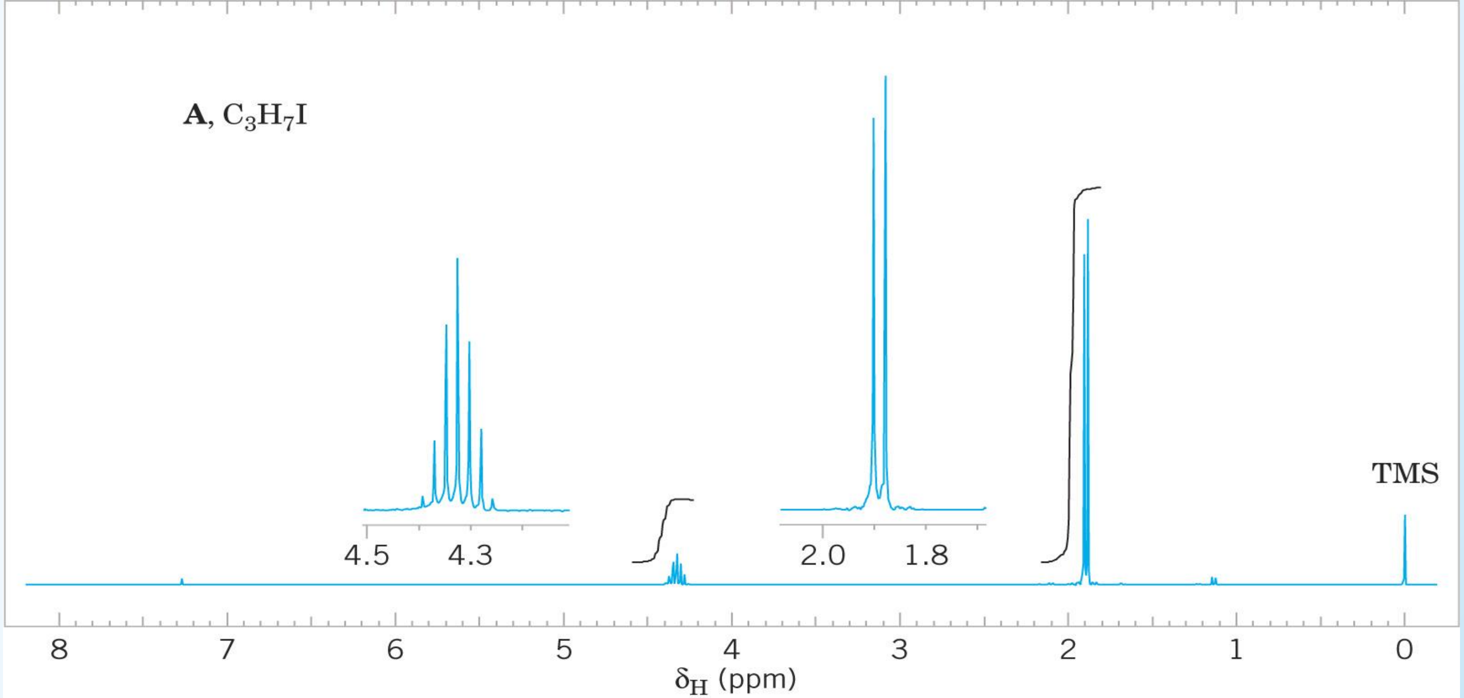
Splitting for Ethyl Groups

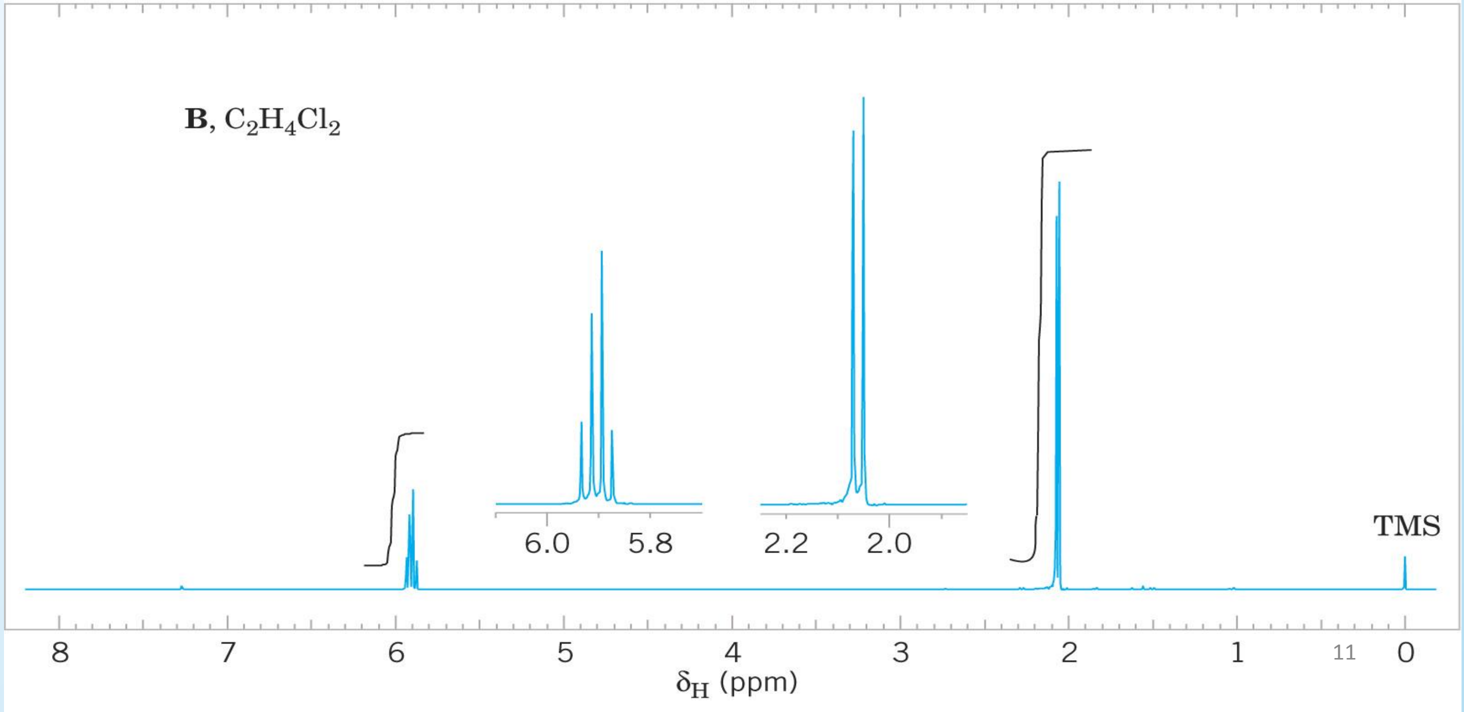




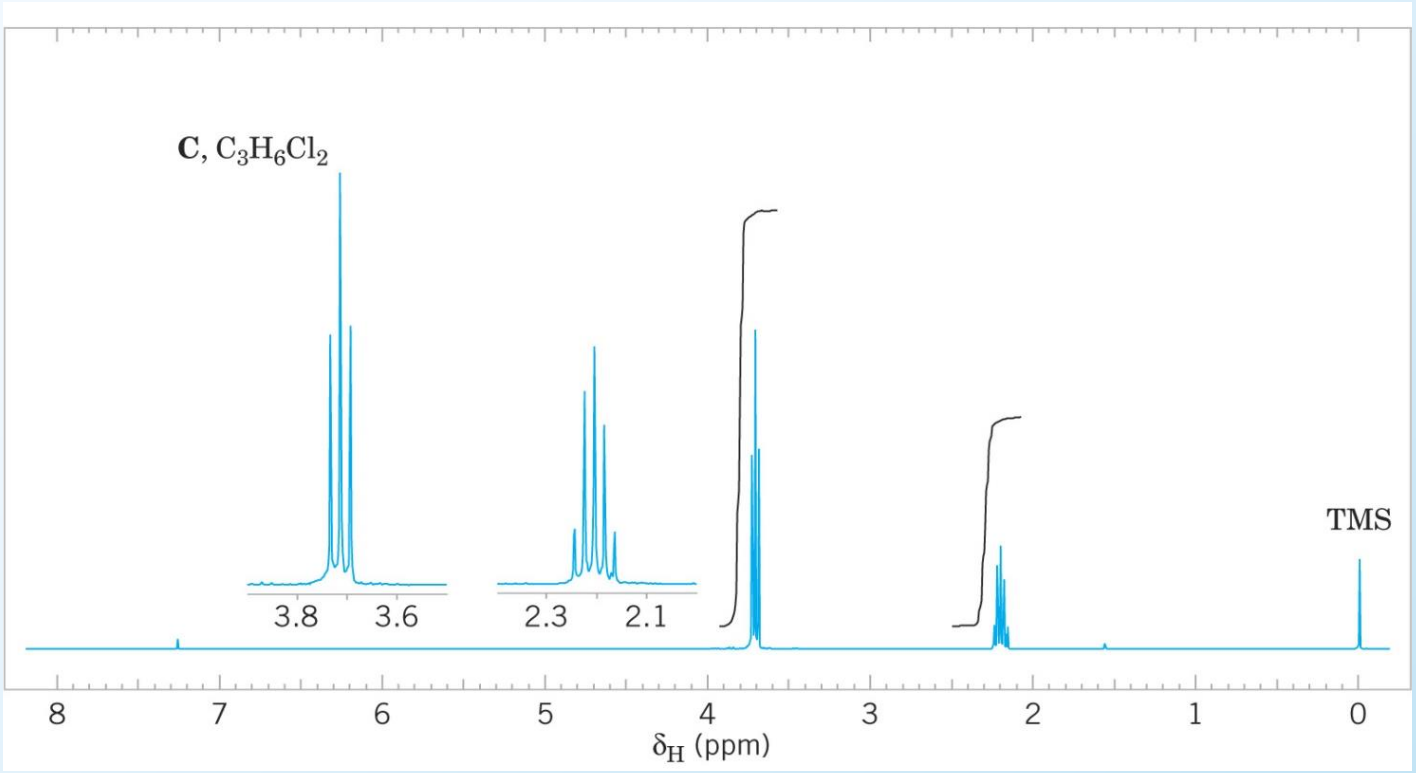
Splitting for Isopropyl Groups

Problems


A, C_3H_7I
4.5
4.3
2.0
1.8
TMS
8
7
6
5
4
3
2
1
0
δ_H (ppm)

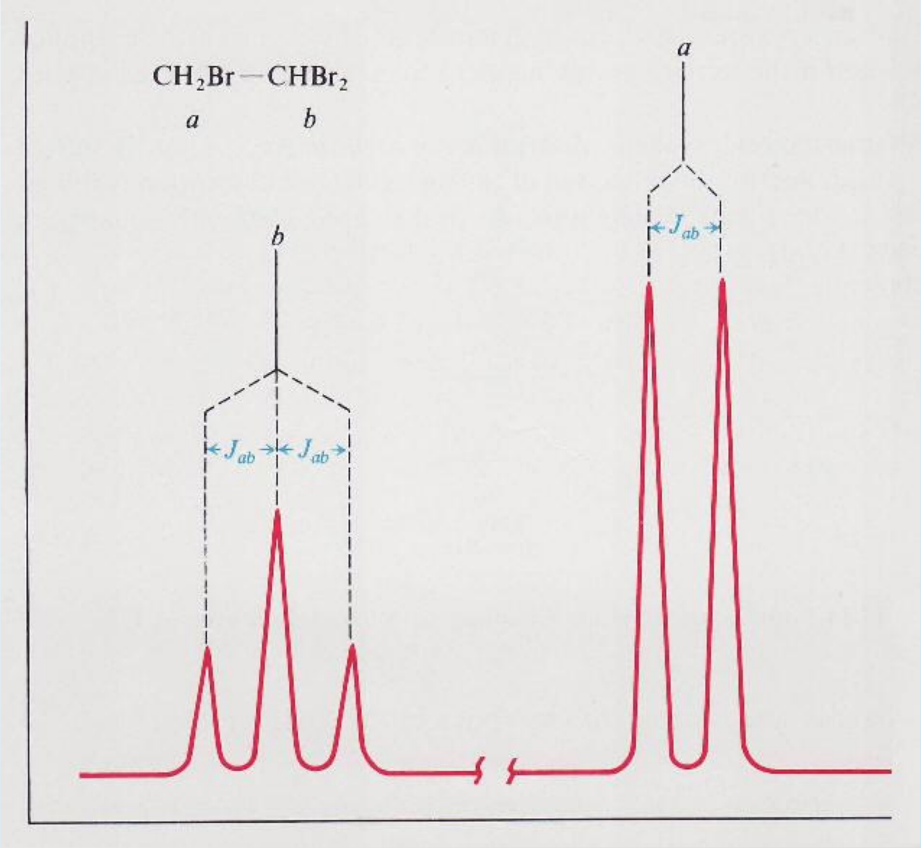

B, $C_2H_4Cl_2$
6.0
5.8
2.2
2.0
TMS
8
7
6
5
4
3
2
1
0
δ_H (ppm)

Problem

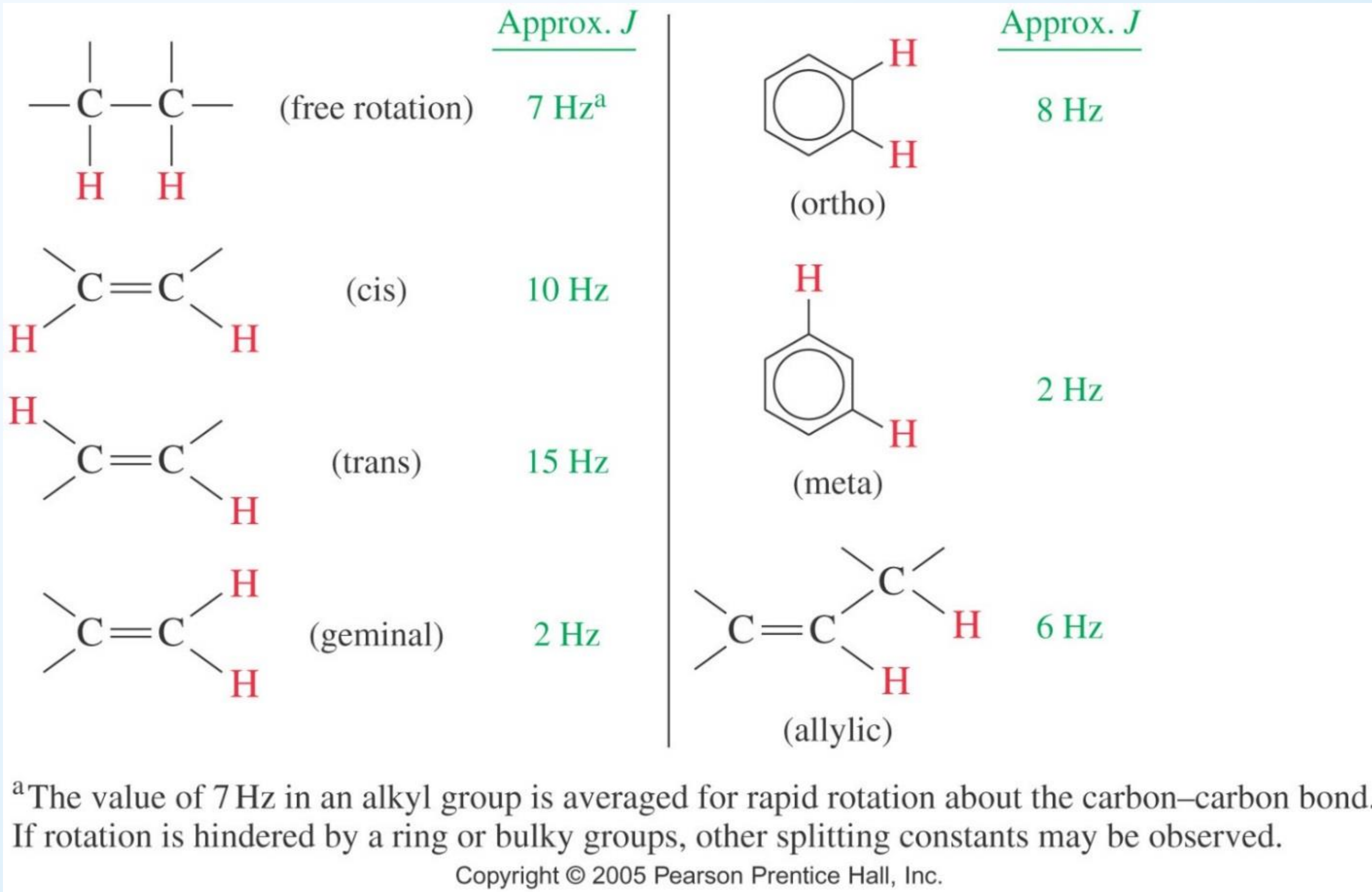


Coupling Constants and Values

- Distance between the peaks of multiplet.
- Measured in Hz.
- Not dependent on strength of the external field.
- Multiplets with the same coupling constants may come from adjacent groups of protons that split each other.

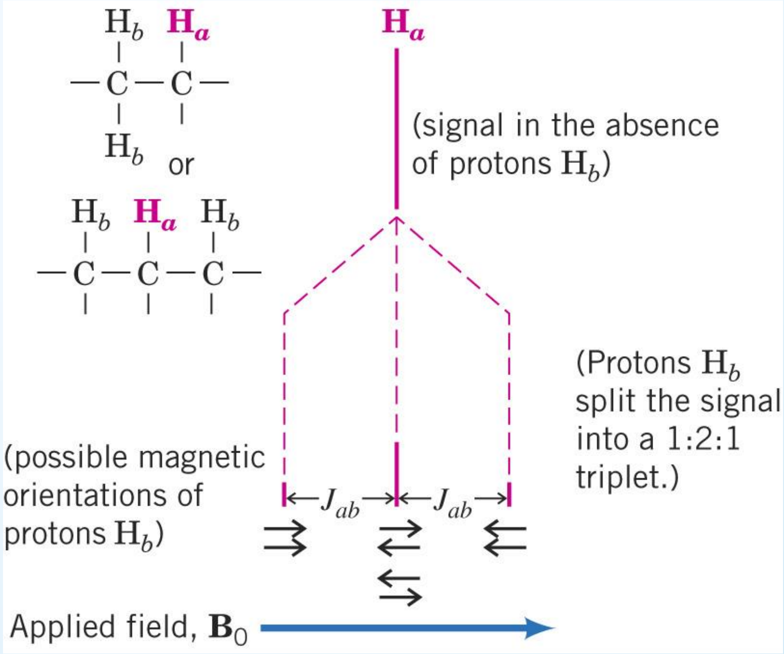


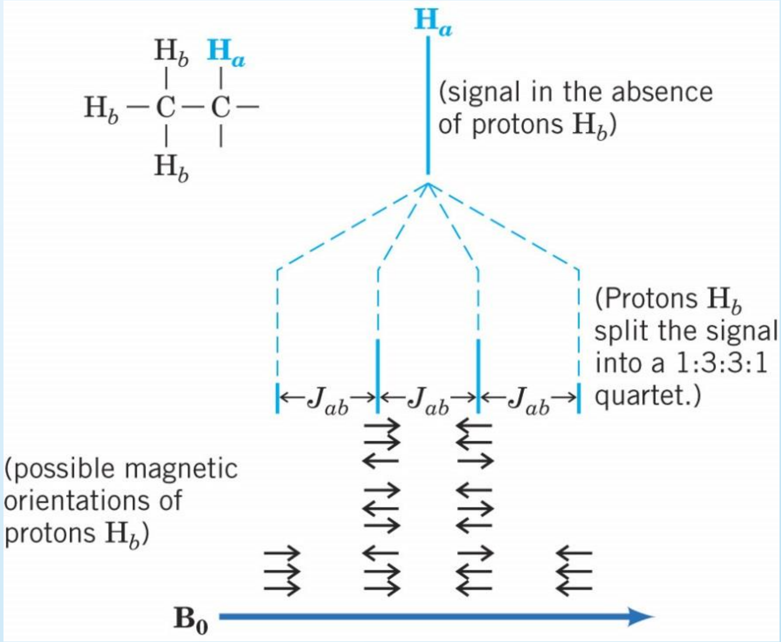
Coupling Constant Values



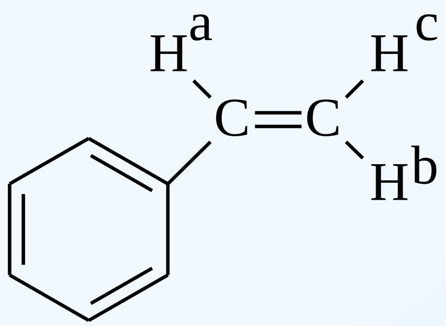
Coupling Constants…contd

- Different for different compounds – depends on the environment of the protons.

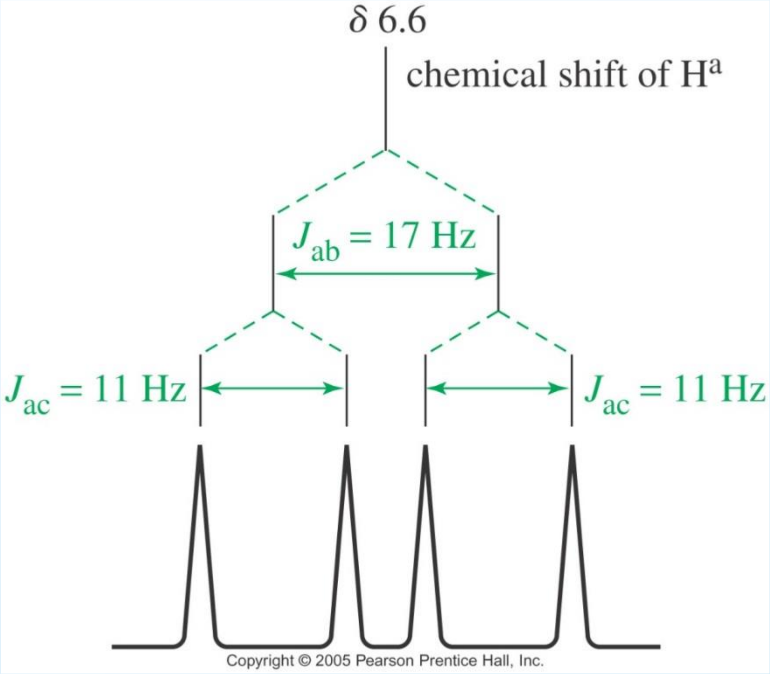


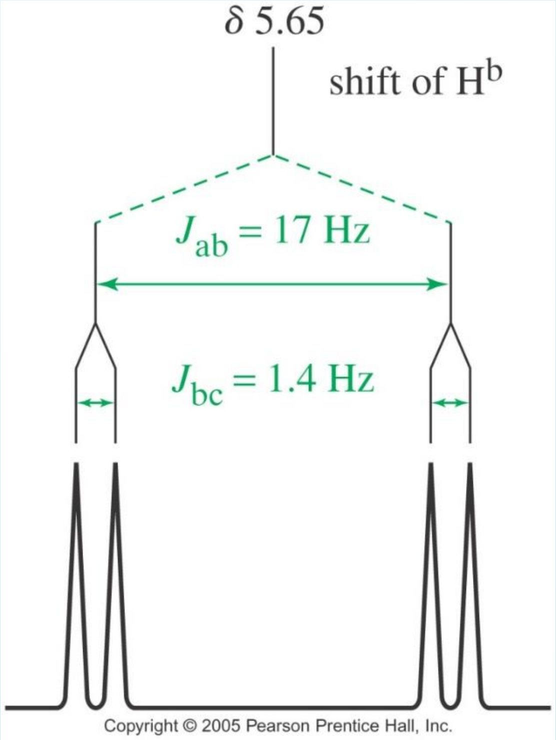


Complex Splitting

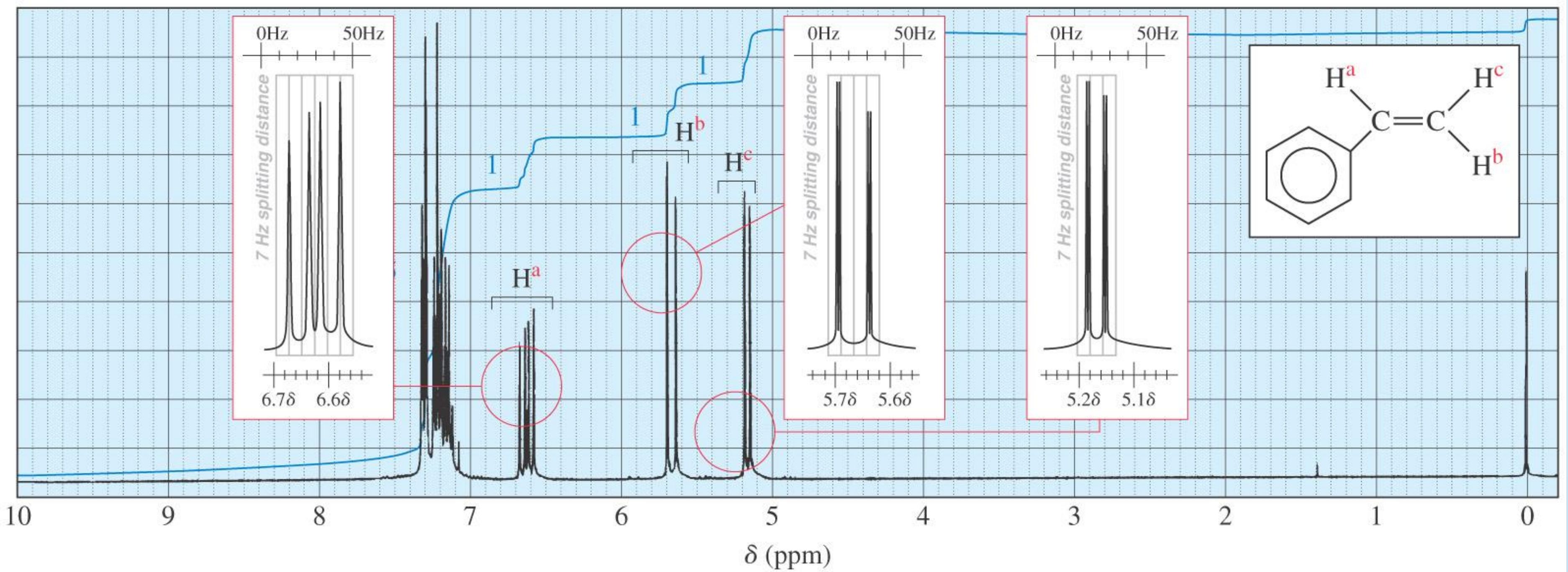


- Signals may be split by adjacent protons, different from each other, with different coupling constants.
- Example: H[a] of styrene which is split by an adjacent H *trans* to it (J = 17 Hz) and an adjacent H *cis* to it (J = 11 Hz).



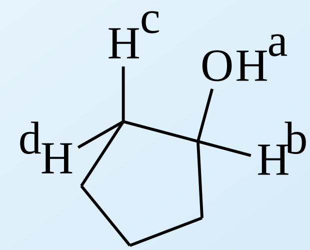


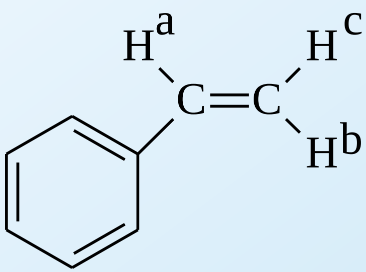
Spectrum for Styrene

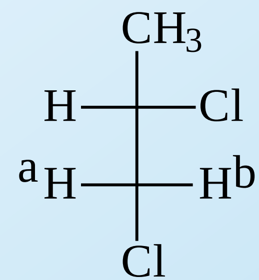


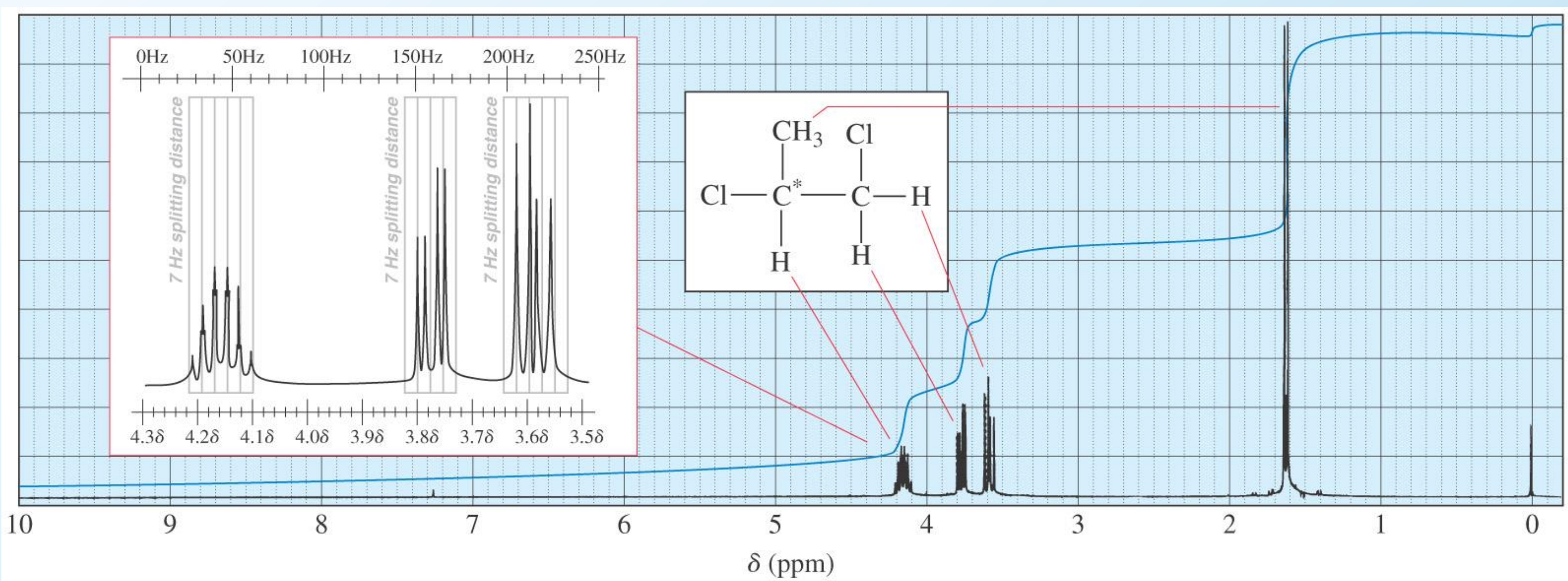
Some Nonequivalent Protons

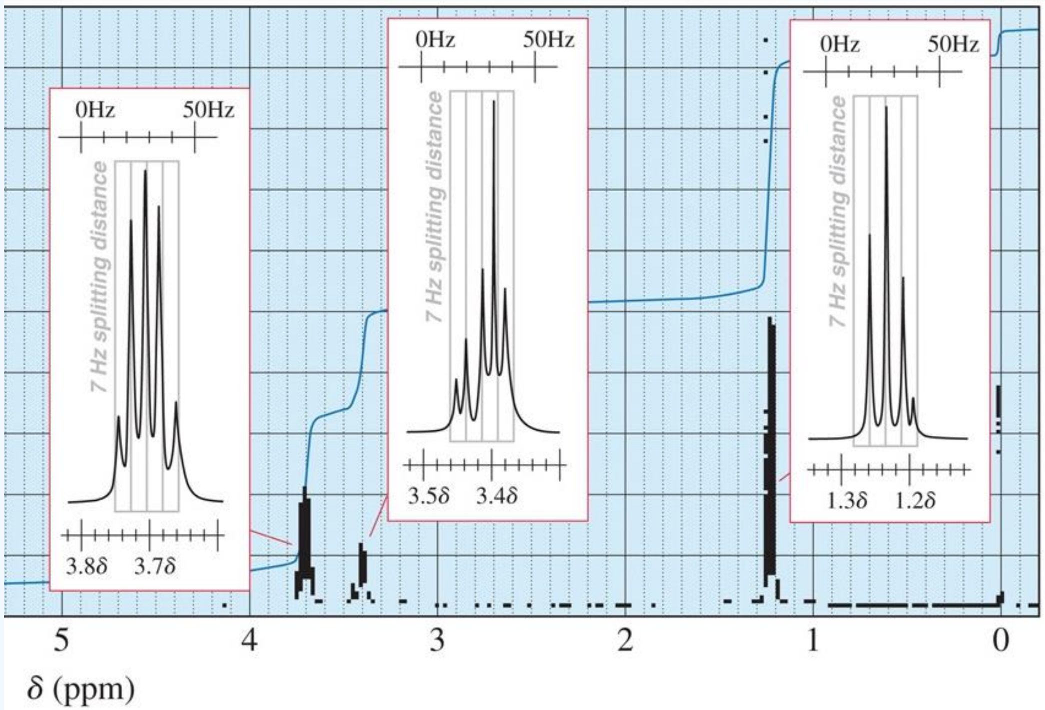
- Usually, two protons on the same C are equivalent and do not split each other.
- If the replacement of each of the protons of a $-CH_2$ group with an imaginary "Z" gives stereoisomers, then the protons are non-equivalent and will split each other.





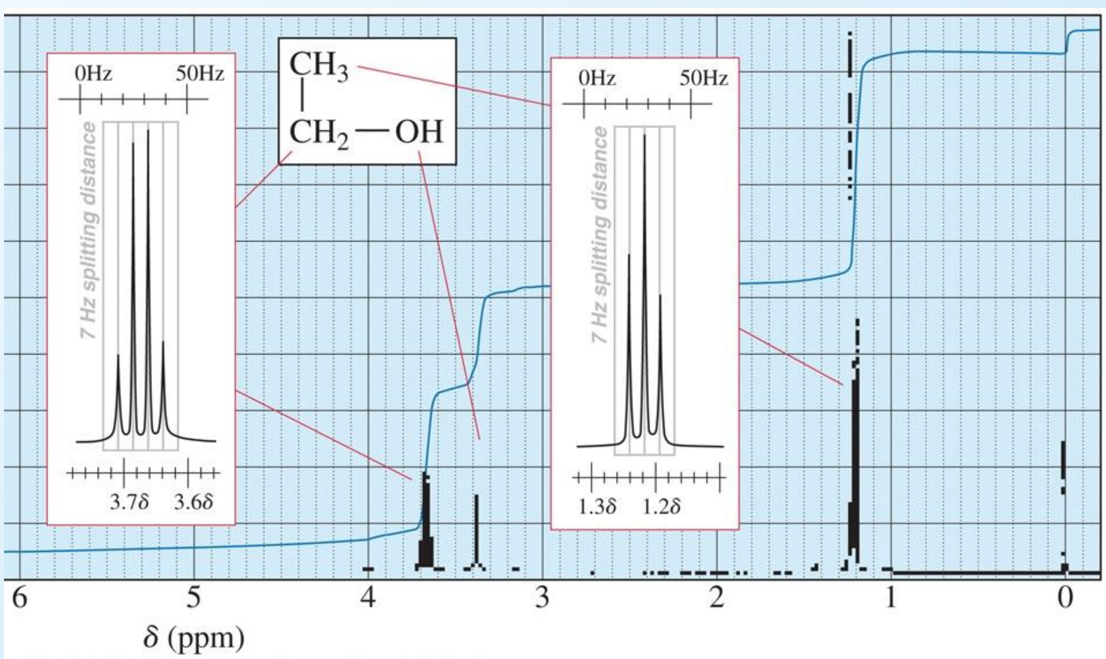






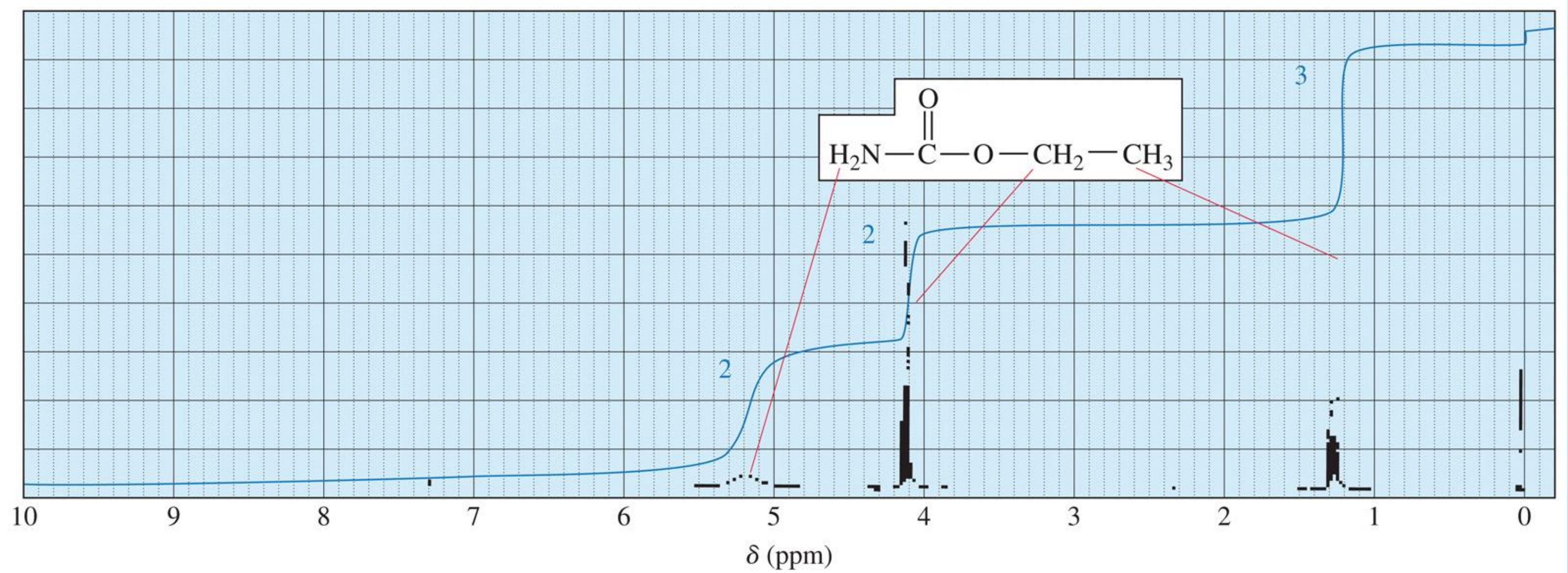
Hydroxyl Proton

- Ultrapure samples of ethanol show splitting.
- Ethanol with a small amount of acidic or basic impurities will not show splitting.



N-H Proton

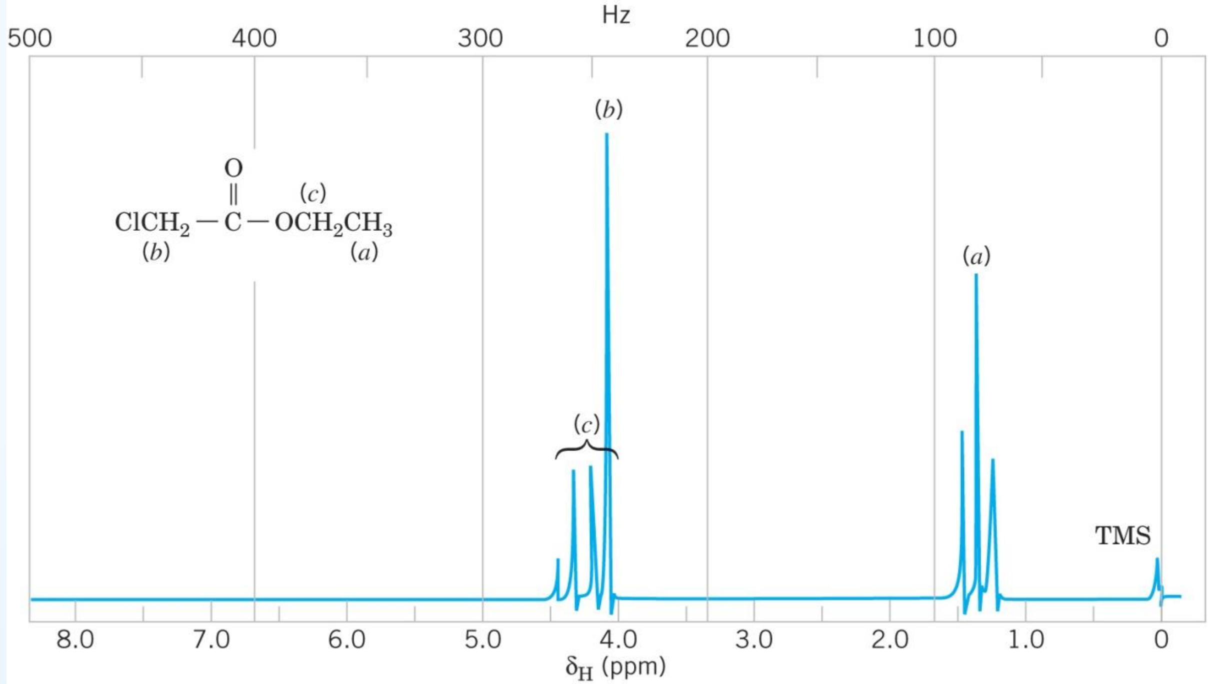
- Moderate rate of exchange.
- Peak may be broad.



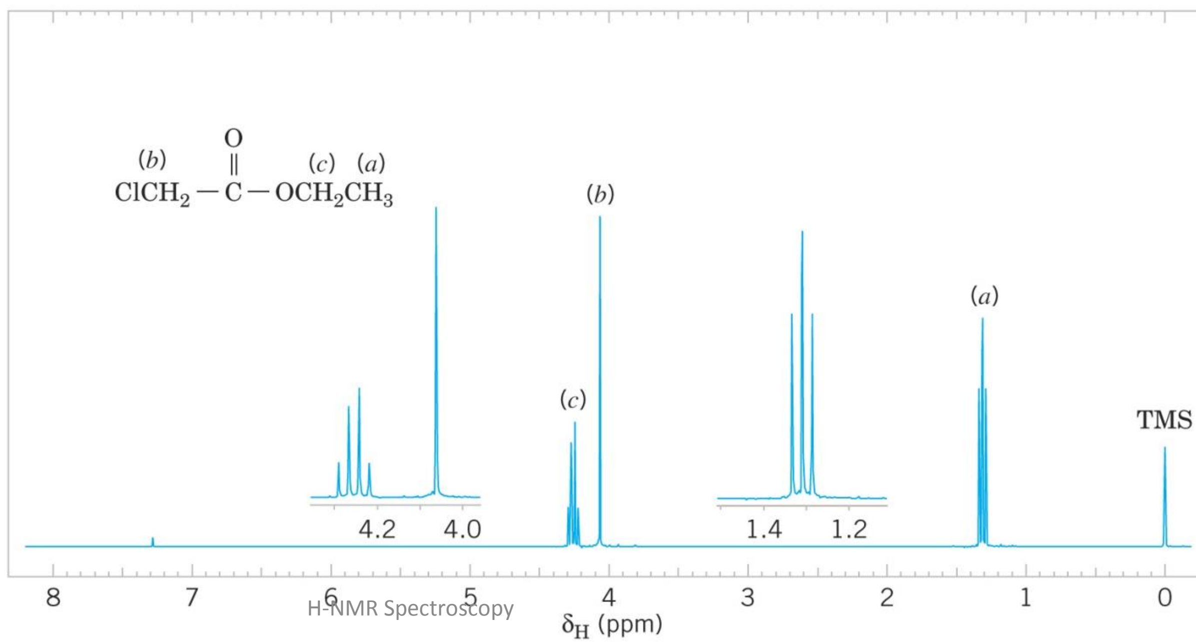
Identifying the O-H or N-H Peak

- Chemical shift will depend on concentration and solvent.
- To verify that a particular peak is due to O-H or N-H, shake the sample with D_2O.
- Deuterium will exchange with the O-H or N-H protons.
- On a second NMR spectrum the peak will be absent, or much less intense.

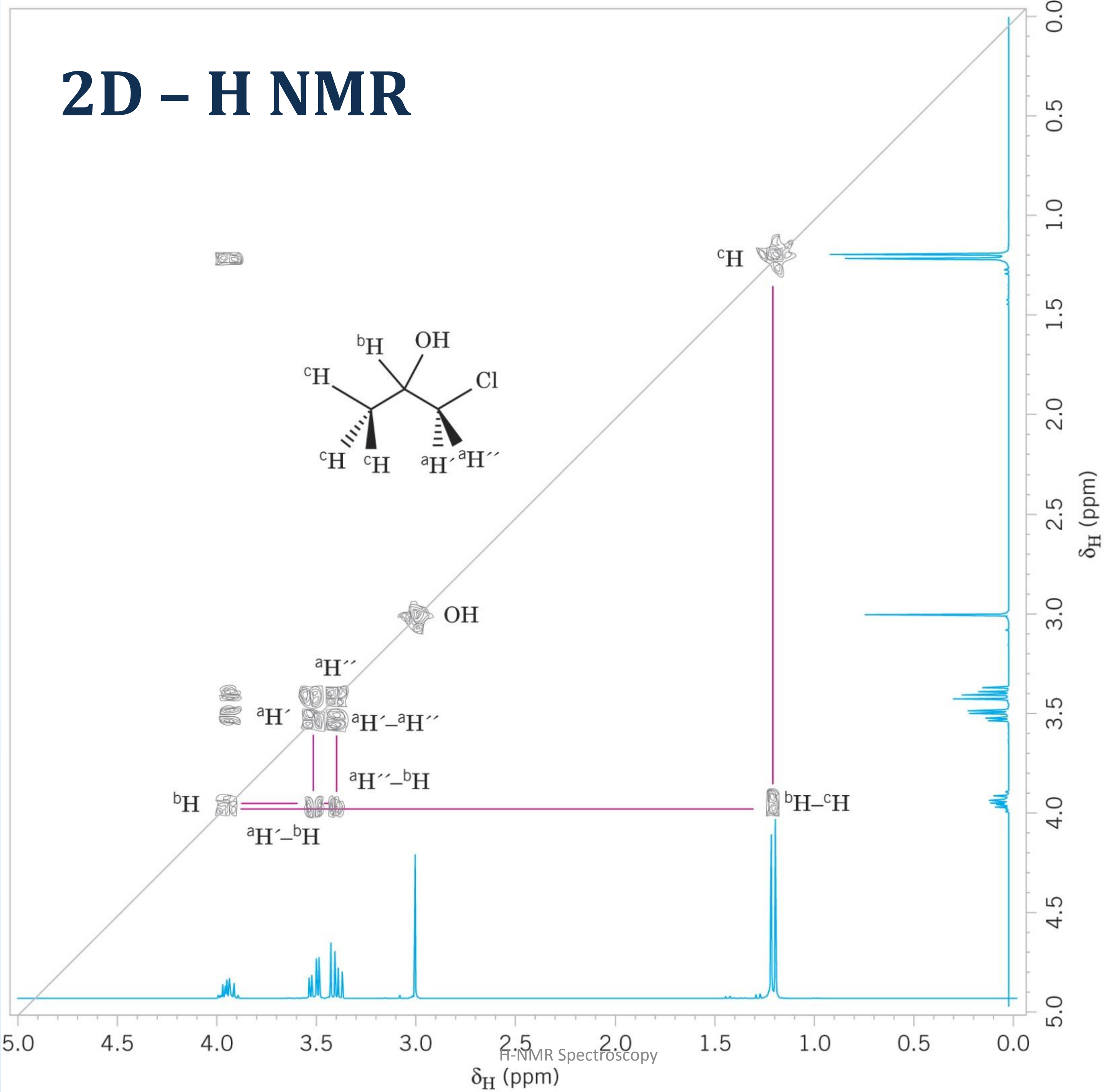
60 MHz NMR



300 MHz NMR



2D – H NMR



ᵇH OH
ᶜH Cl
ᶜH ᶜH ᵃH´ ᵃH´´
ᶜH
OH
ᵃH´´
ᵃH´
ᵃH´–ᵃH´´
ᵃH´´–ᵇH
ᵇH
ᵇH–ᶜH
ᵃH´–ᵇH
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
δH (ppm)
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δH (ppm)

Key Concepts

- Chemical shifts
- Integration
- Coupling
- Interpret a NMR
- Predict NMR for a compound