NMR Spectroscopy

(Part-II)

By

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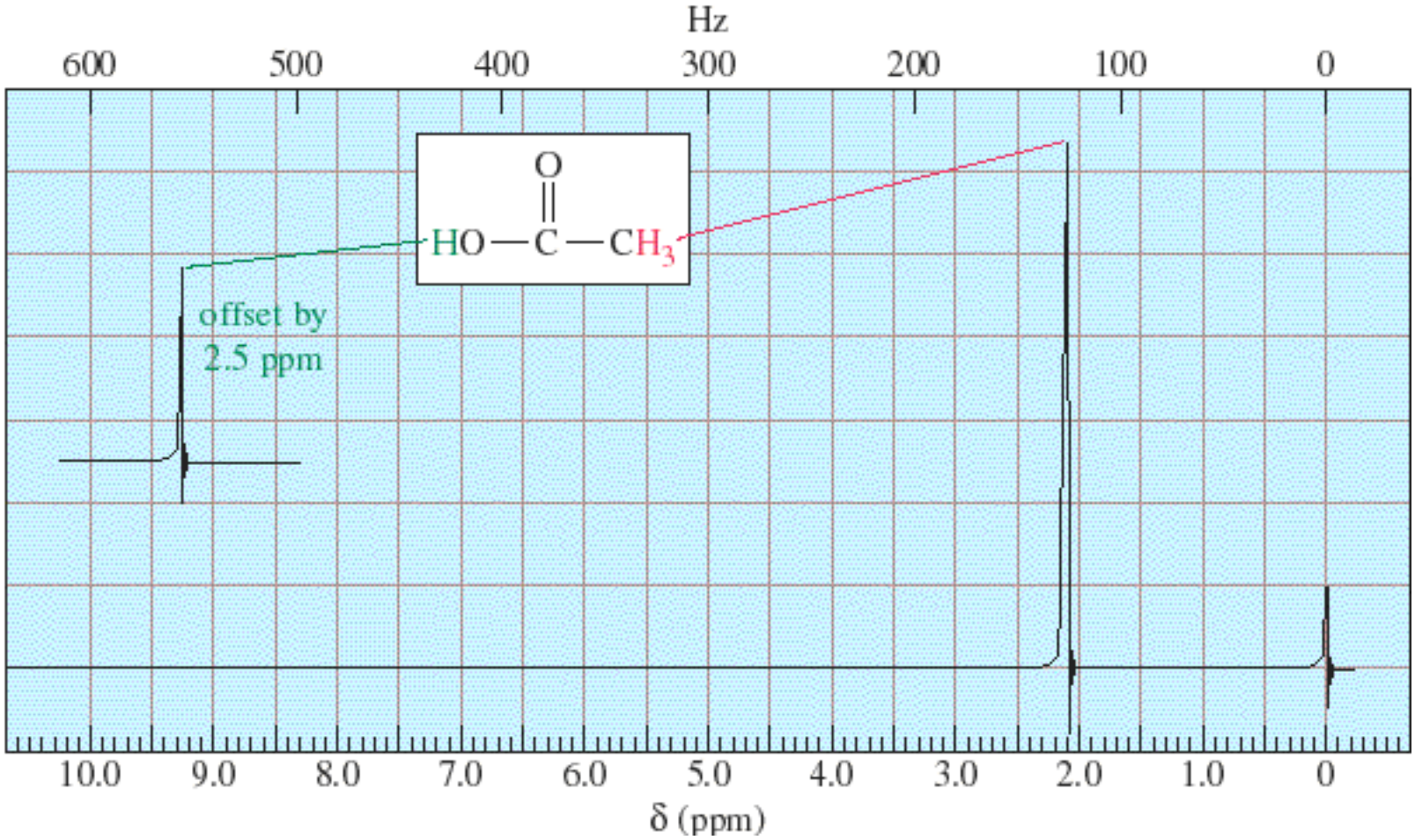
Effect of H-Bonding in Chemical Shift

- **H atom exhibiting Hydrogen bonding resonates at higher delta value.**
- **Less shielded.**
- **Attached to strong electronegative atom, low electron density around the nucleus.**
- **Intra & Inter molecular hydrogen bonding can be distinguished.**
- **Intermolecular H bonding : increasing dilution shifts the signal to lower delta value due to decrease in hydrogen bonding and thereby increase electron density (and shielding effect)**

Carboxylic Acid Proton, δ10+



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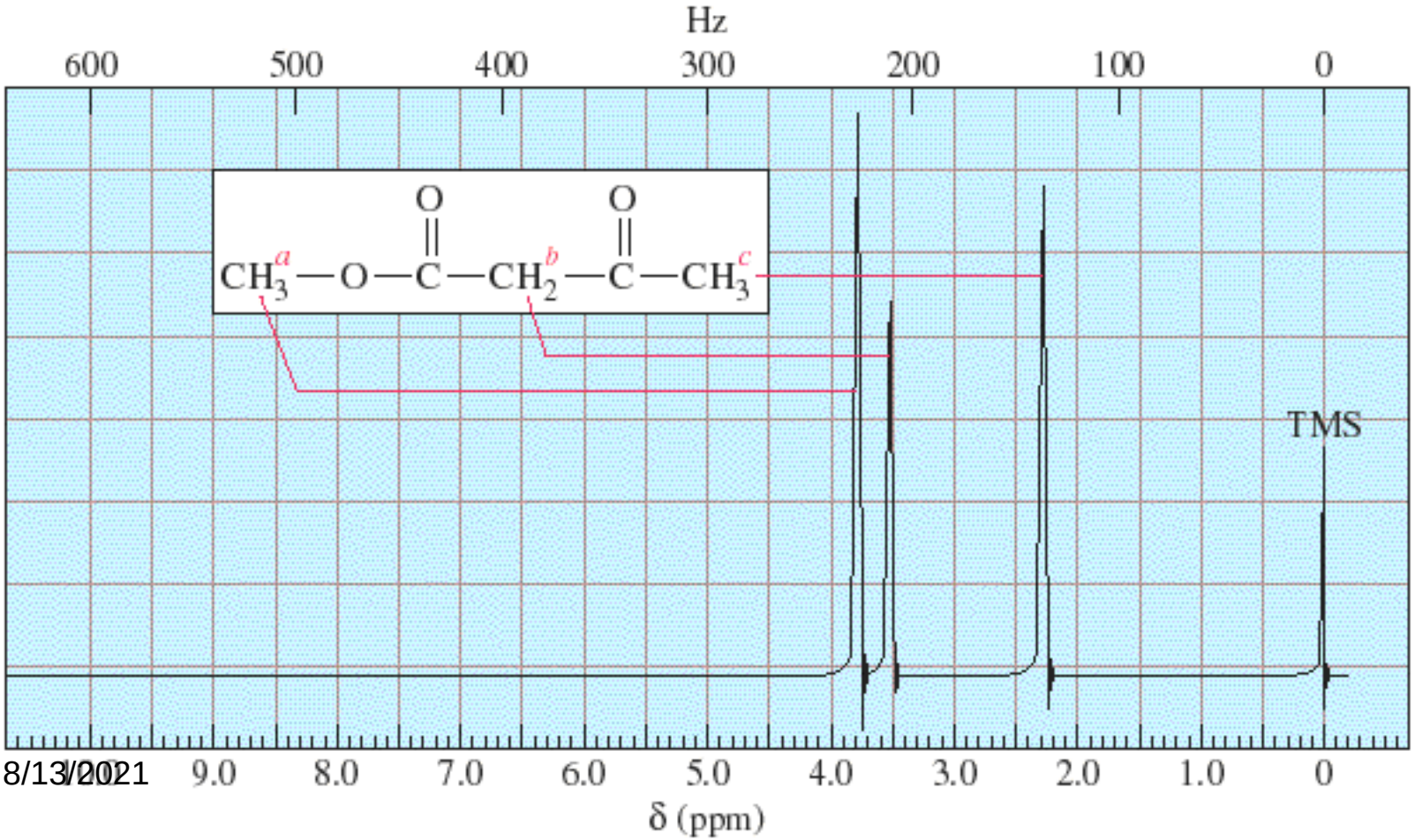
Number of Signals

Equivalent hydrogens have the same chemical shift.



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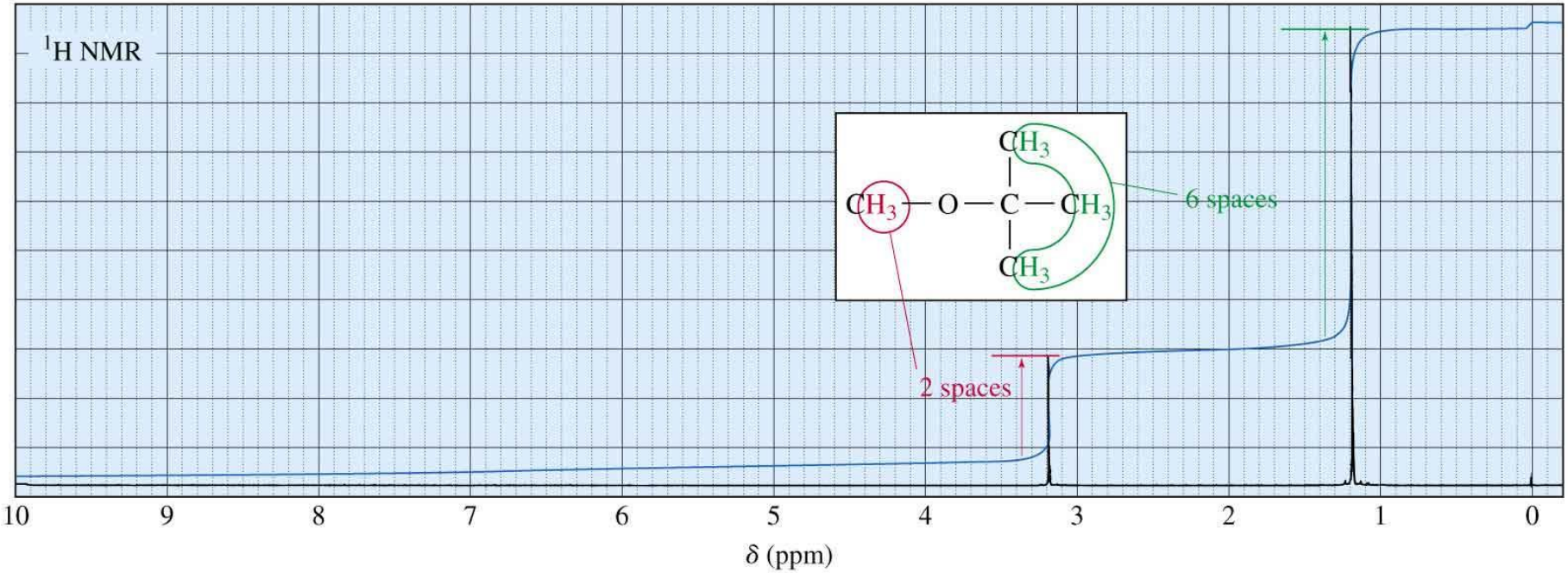
Intensity of Signals

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



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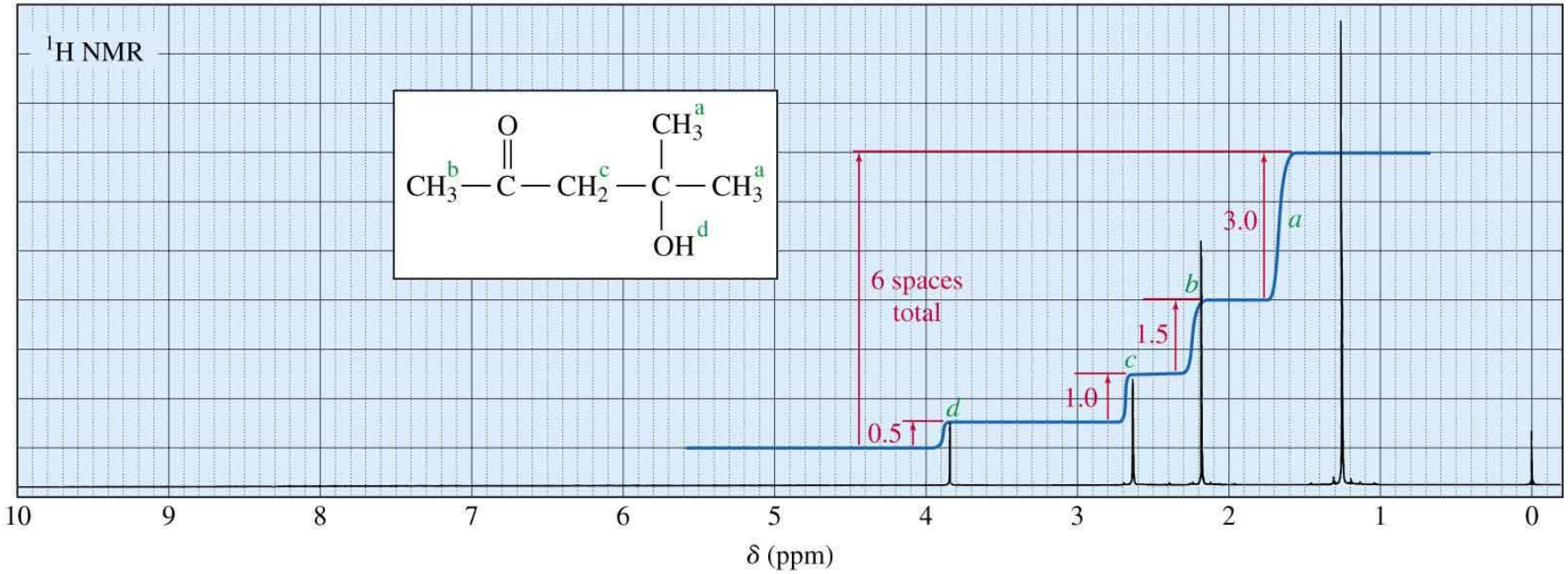
How Many Hydrogens?

When the molecular formula is known, each integral rise can be assigned to a particular number of hydrogens.



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Spin-Spin Splitting

- Nonequivalent protons on adjacent carbons have magnetic fields that may align with or oppose the external field.
- All possibilities exist, so signal is split. =>

Splitting of signals

Thus a neighbouring non equivalent hydrogen would cause another hydrogen to feel two fields

Effective field = Applied field - Electron shielding + /- Neighbouring nuclei field

So instead of seeing one signal, if a neighbouring hydrogen splits the signal you would see two, called a doublet.

It tells you that if you see a doublet that nucleus has a single hydrogen adjacent. Similarly, two neighbouring nuclei yield three peaks, three yield four, etc

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

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The resonance position of A depends on its total magnetic environment: part of it is the nearby proton X, which is itself magnetic, and proton X can either have its nuclear magnet aligned with proton A or opposed to proton A. Thus proton X can either increase (X aligned) or decrease (X opposed) . In fact it does both . The two

spacing is called the *coupling constant*, J.

Why is the signal for proton A split into a doublet? A simplistic explanation is that the resonance position for A depends on its total magnetic environment; part of its magnetic environment is the nearby proton X, which is itself magnetic, and proton X can either have its nuclear magnet *aligned with* proton A or *opposed to* proton A. Thus proton X can either *increase* the net

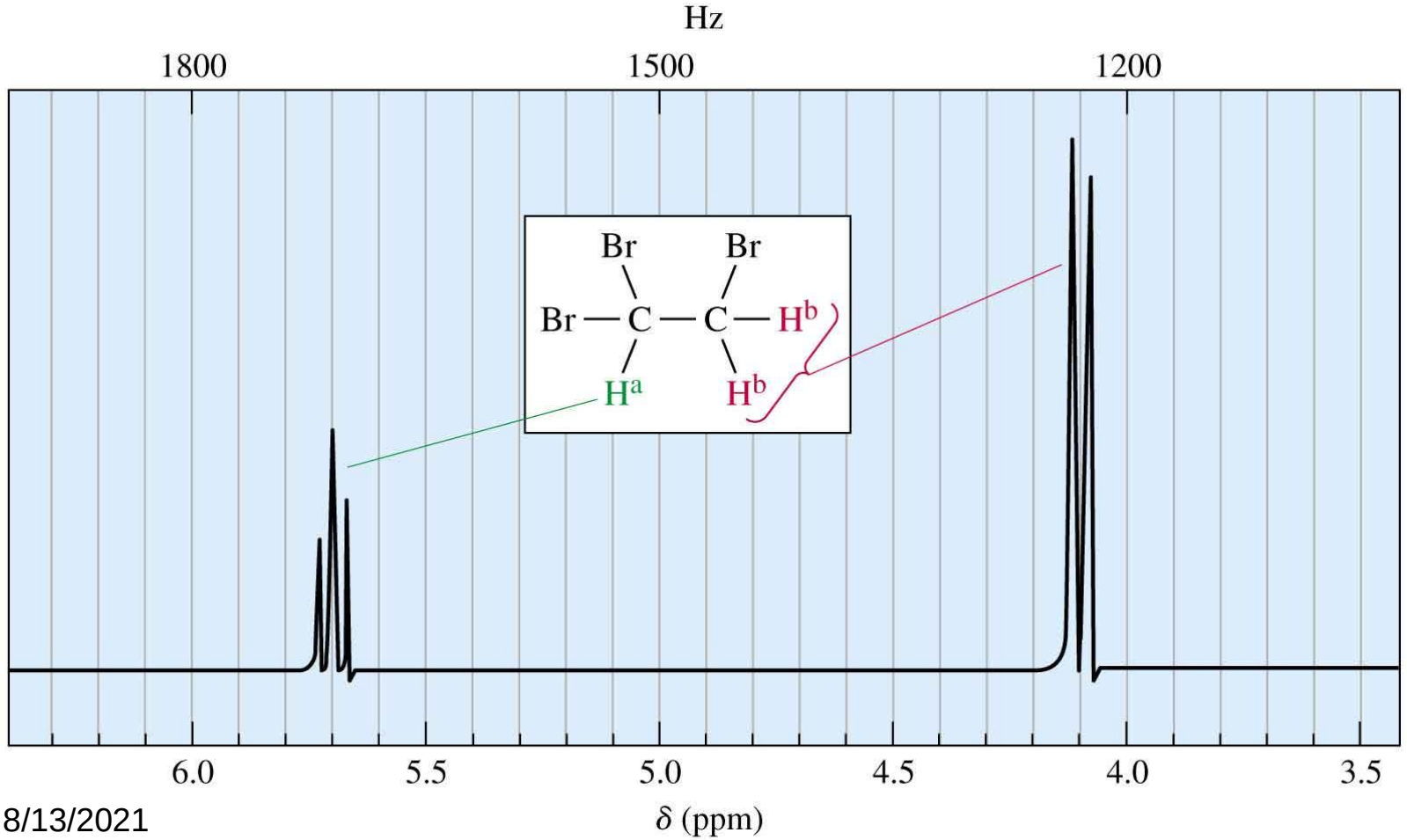
Figure 3.13 *Splitting in the signals of two vicinal protons.*

magnetic field experienced by A (X aligned) or *decrease* it (X opposed); in fact it does both. The two spin orientations of X create two different magnetic fields around proton A. Therefore proton A comes to resonance, not once, but twice, and proton A gives rise to a doublet.

Similarly, proton A is a magnet having two spin orientations with respect to A, and A creates two magnetic fields around X. Proton X comes to resonance twice in the n.m.r. spectrum.

1,1,2-Tribromoethane

Nonequivalent protons on adjacent carbons.



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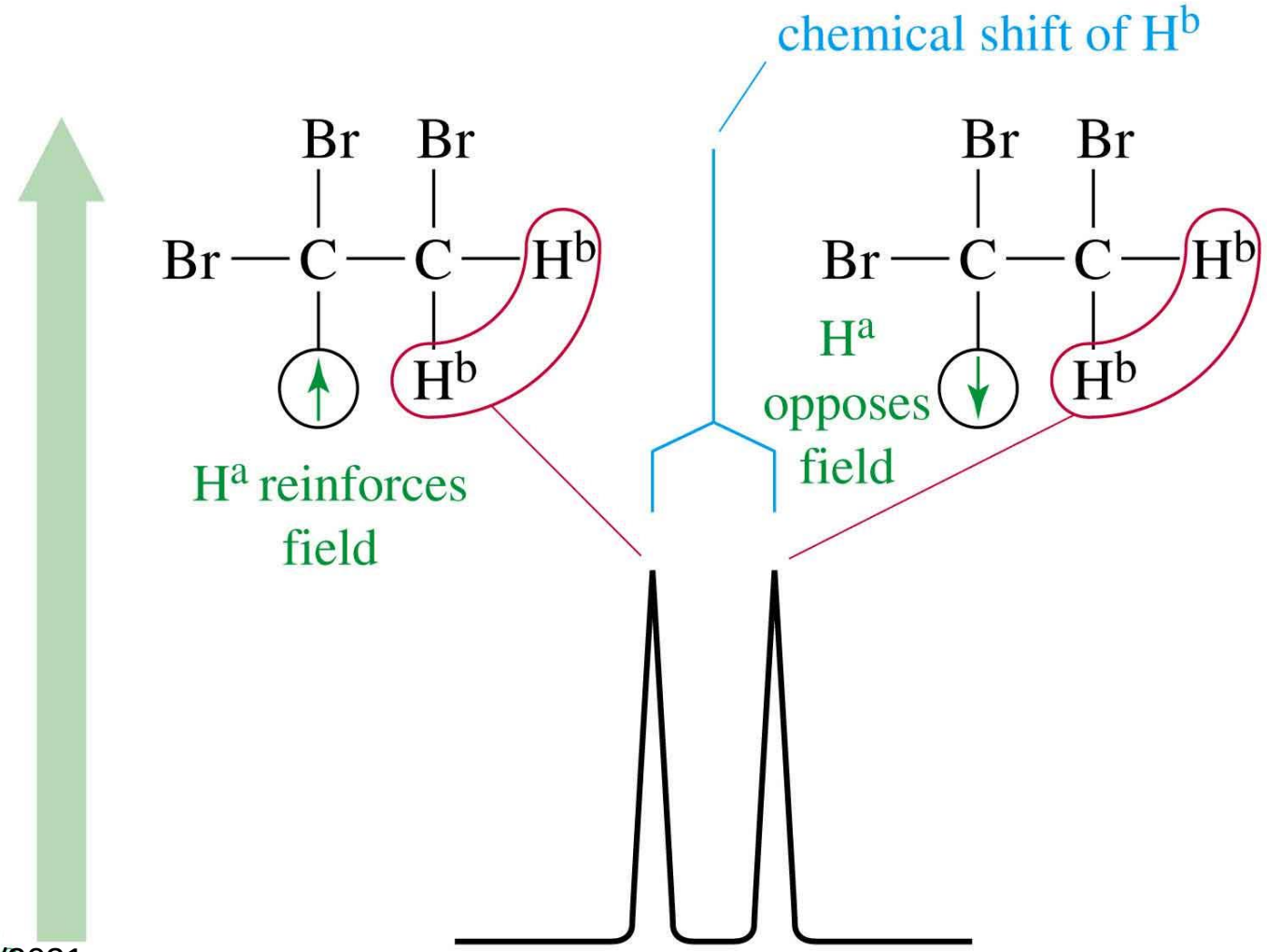
Doublet: 1 Adjacent Proton



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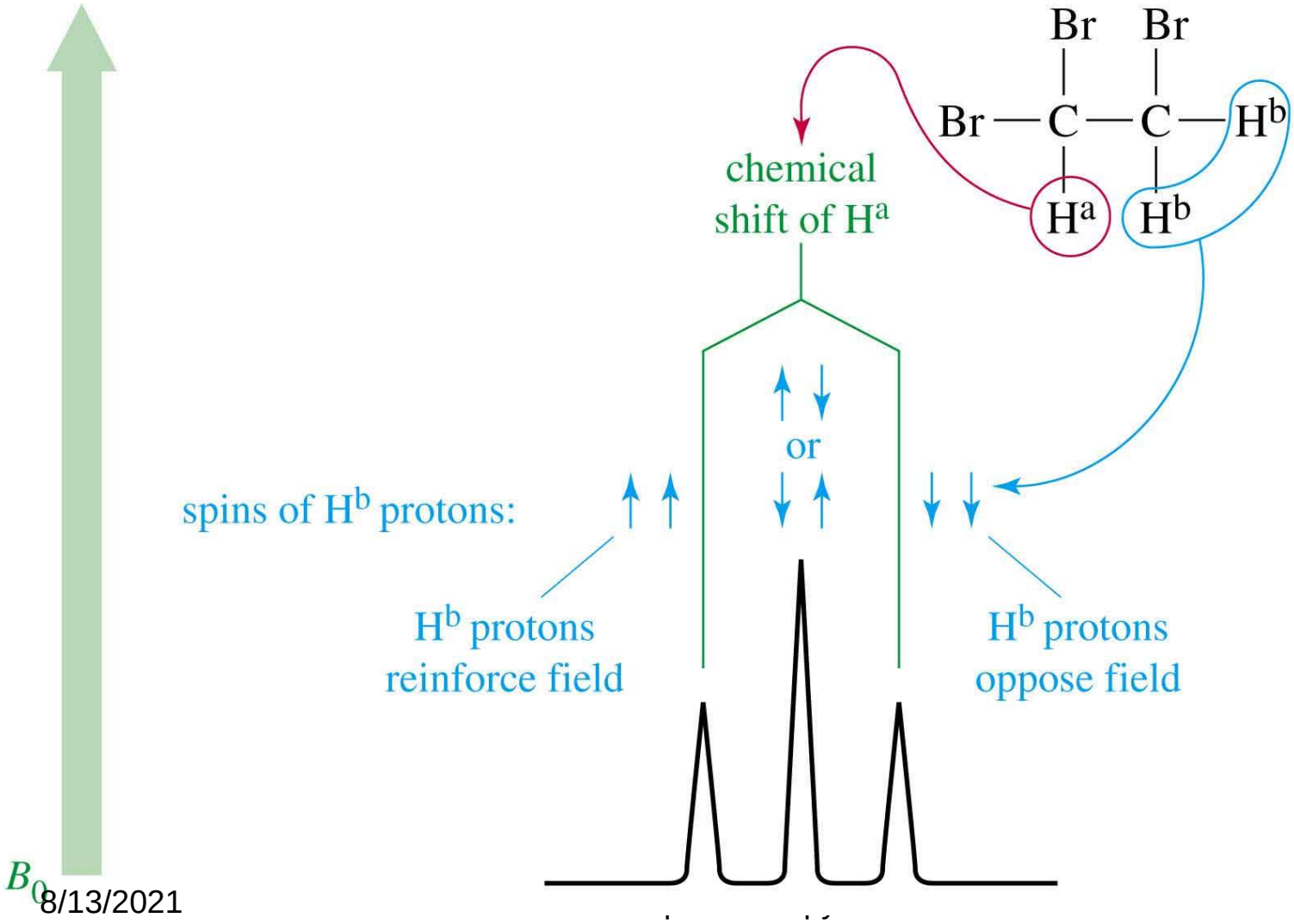
Triplet: 2 Adjacent Protons



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Range of Magnetic Coupling

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

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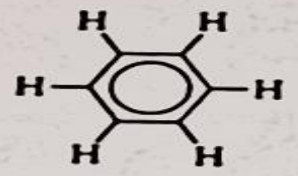
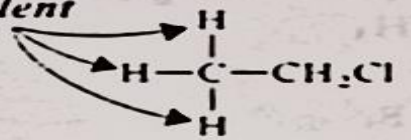
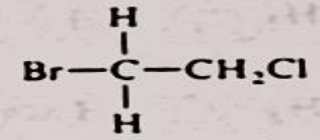


six equivalent H's

Equivalent



ethyl chloride



1-bromo-2-chloroethane

replacement of any of the methyl protons by Br leads to the same compound

three equivalent protons (but nonequivalent to CH_2)

two equivalent protons (but nonequivalent to CH_3)

CH_3-CH_2-Cl

a *b*

2 PMR signals
Ethyl chloride

$CH_3-CHCl-CH_3$

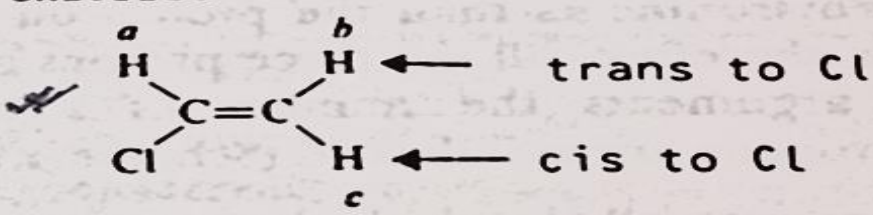
a *b* *a*

2 PMR signals
Isopropyl chloride

$CH_3-CH_2-CH_2-Cl$

a *b* *c*

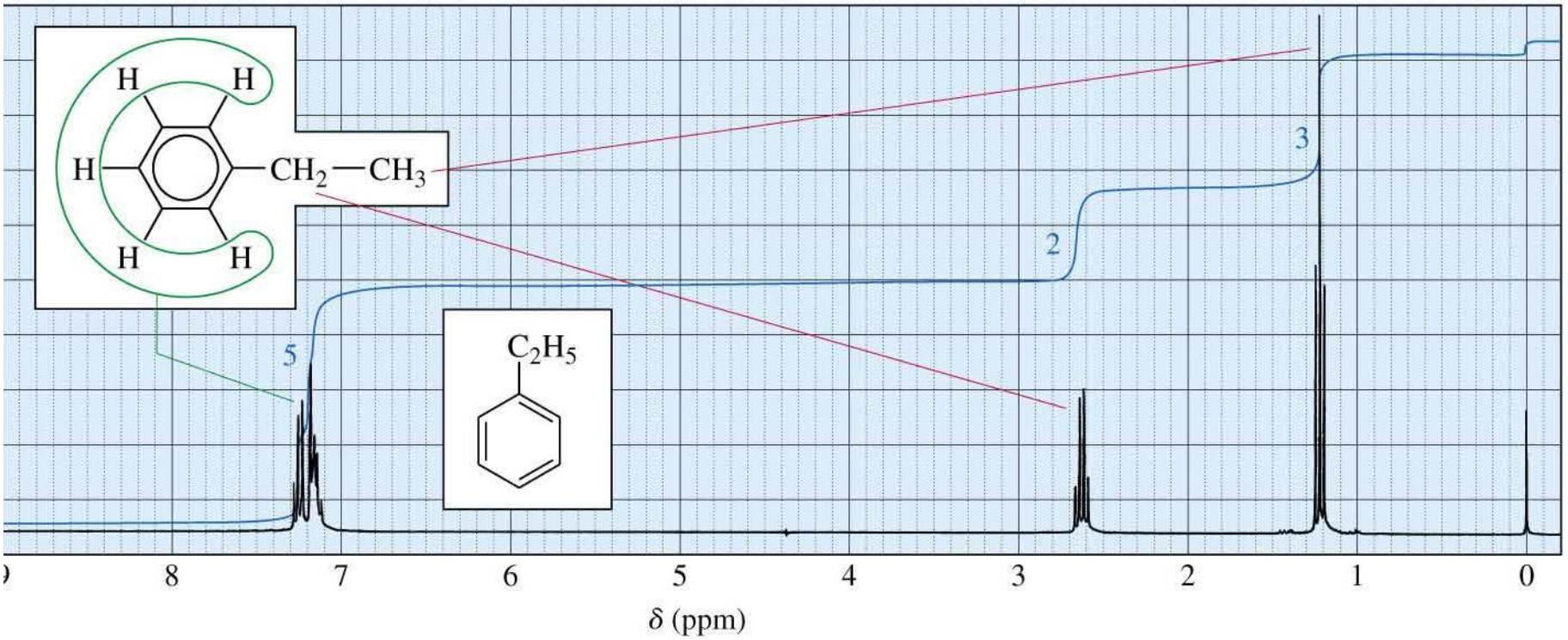
3 PMR signals
n-Propyl chloride



3 PMR signals
Vinyl chloride

the three nonequivalent protons

Splitting for Ethyl Groups



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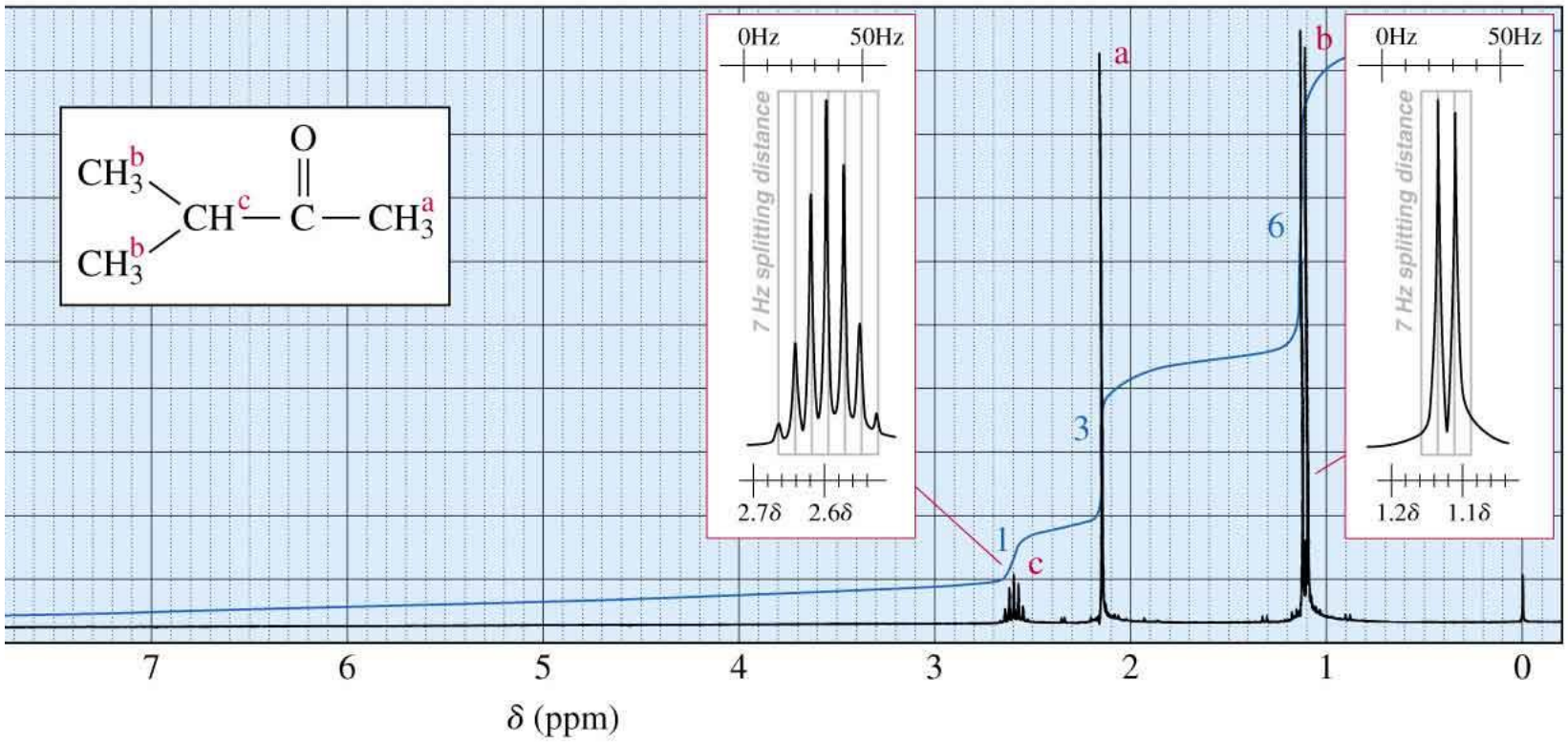
Splitting for Isopropyl Groups



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Coupling Constants

- 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.

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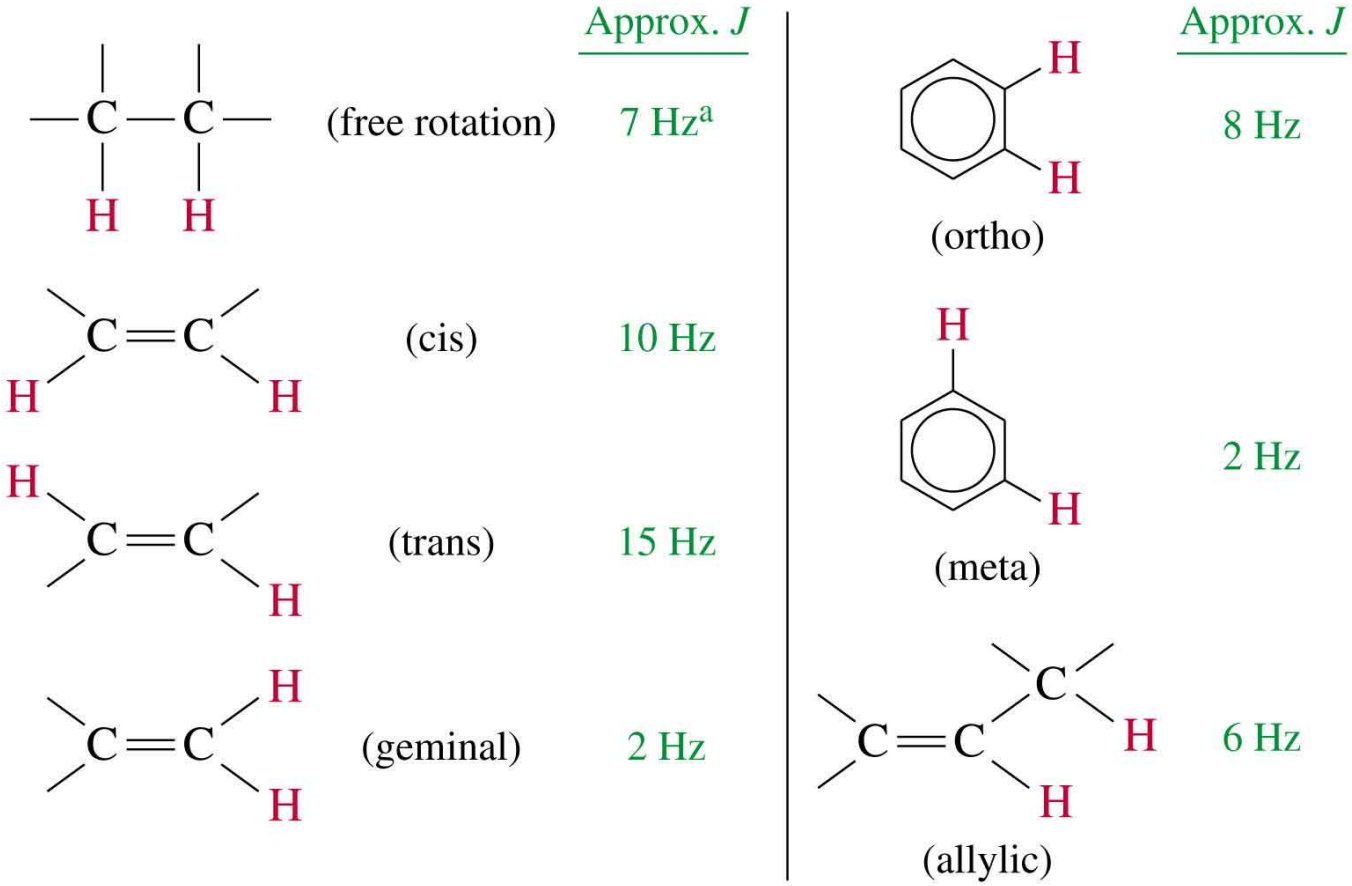
Values for Coupling Constants



[a] The value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon–carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.

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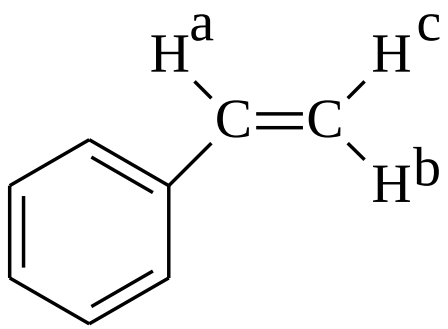
Complex Splitting



- 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).

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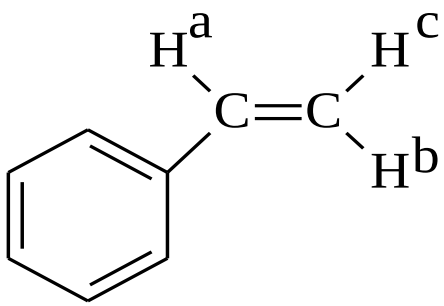
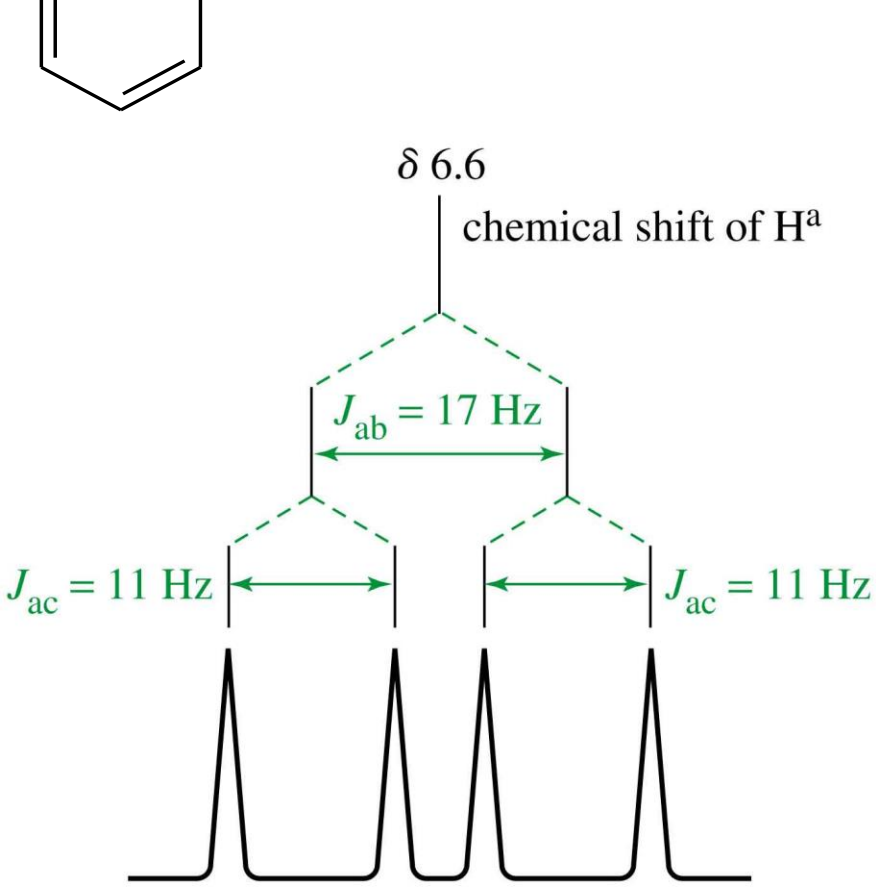
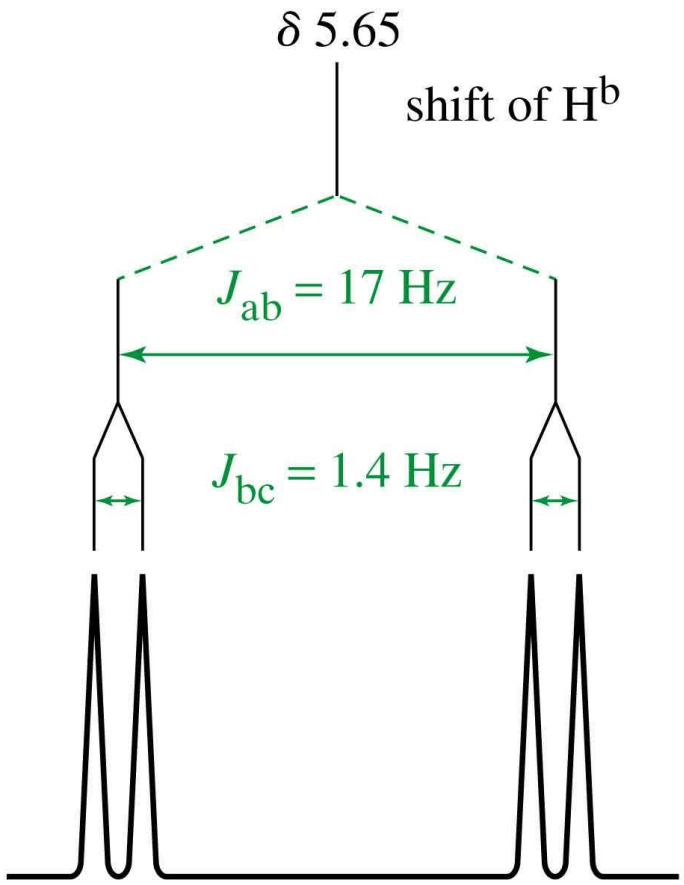
Splitting Tree







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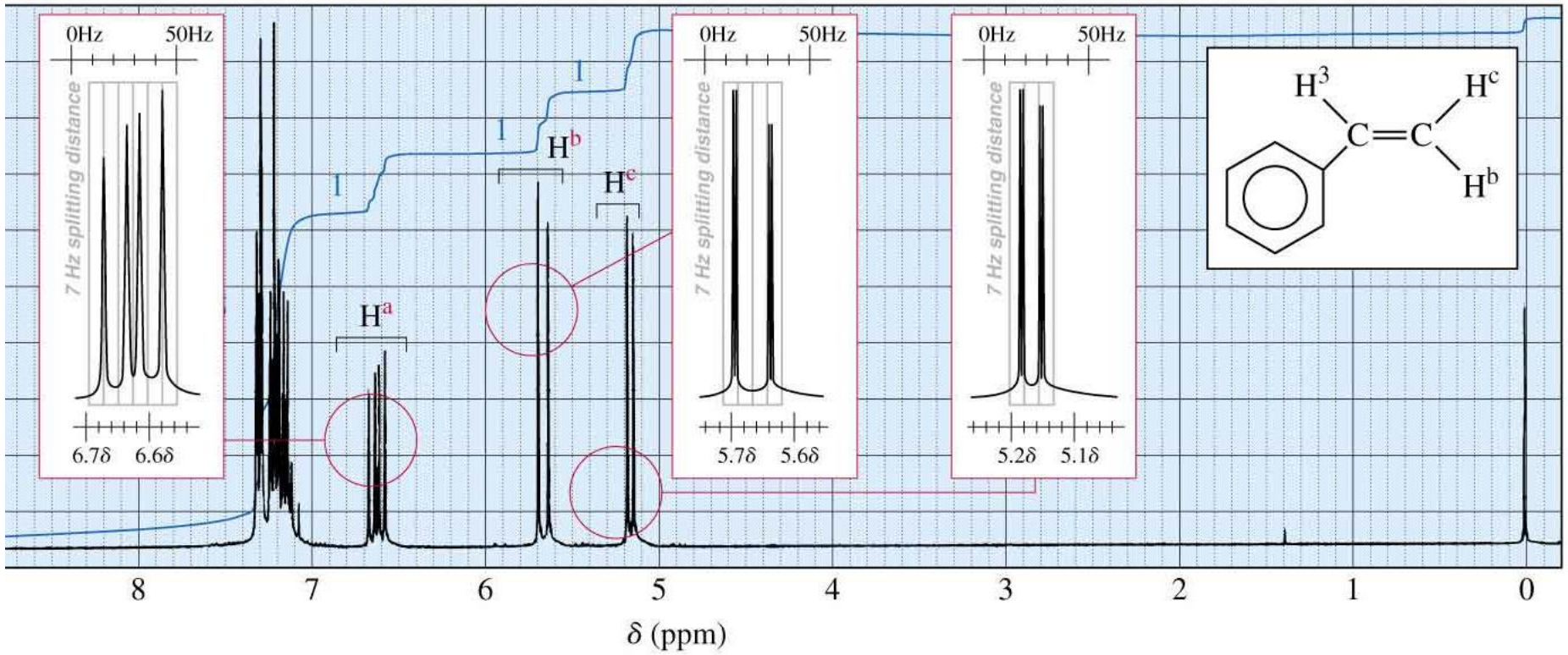
Spectrum for Styrene



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Stereochemical Nonequivalence

- 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.

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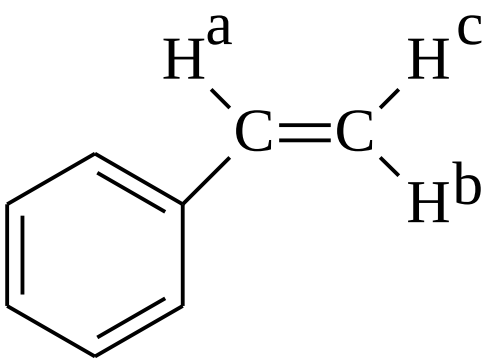
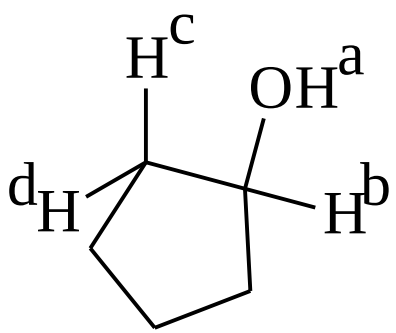
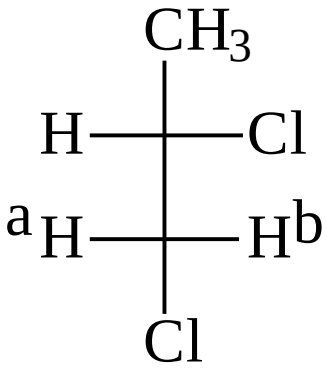
Some Nonequivalent Protons







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Time Dependence

- Molecules are tumbling relative to the magnetic field, so NMR is an averaged spectrum of all the orientations.
- Axial and equatorial protons on cyclohexane interconvert so rapidly that they give a single signal.
- Proton transfers for OH and NH may occur so quickly that the proton is not split by adjacent protons in the molecule.

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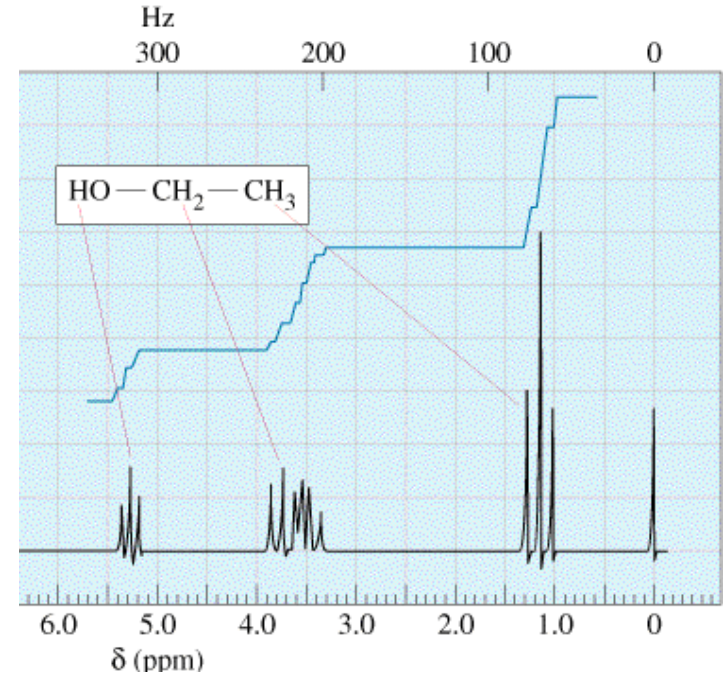

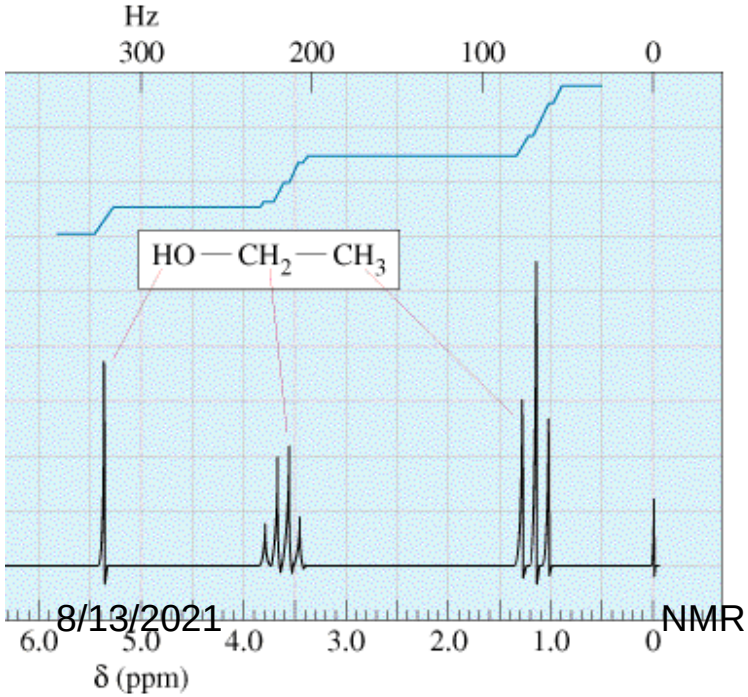

Hydroxyl Proton

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

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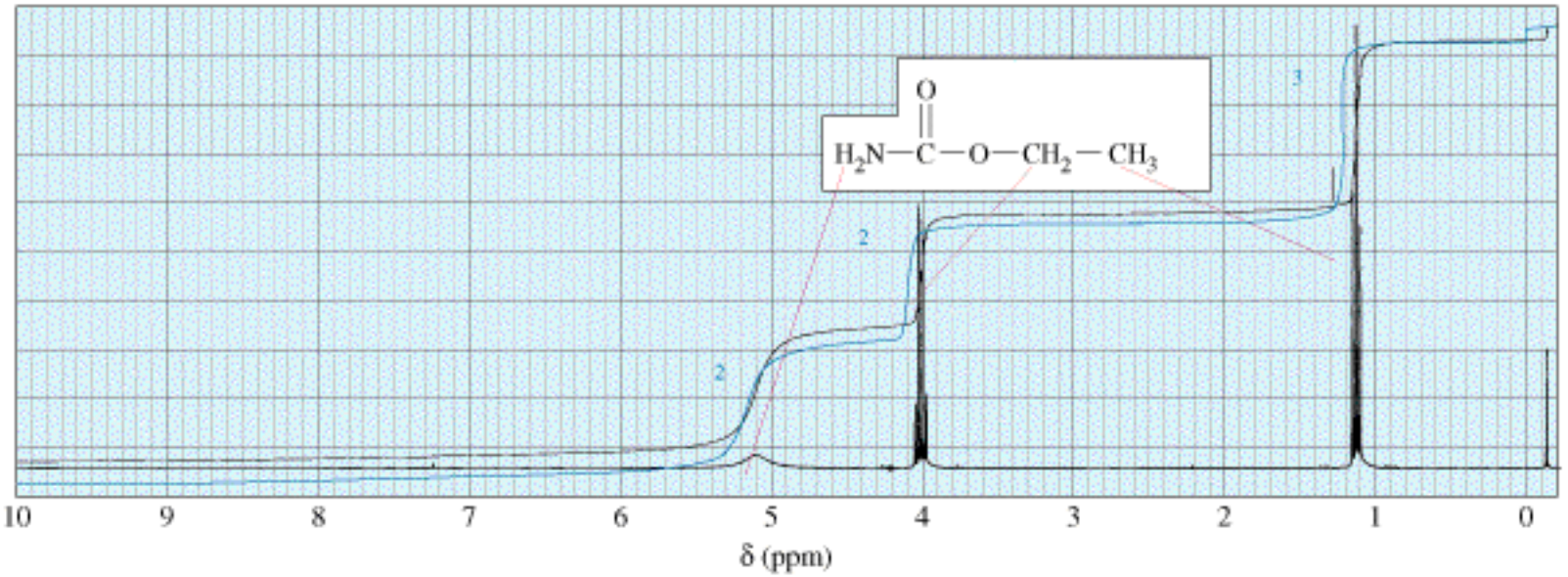
N-H Proton

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



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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.

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Carbon-13

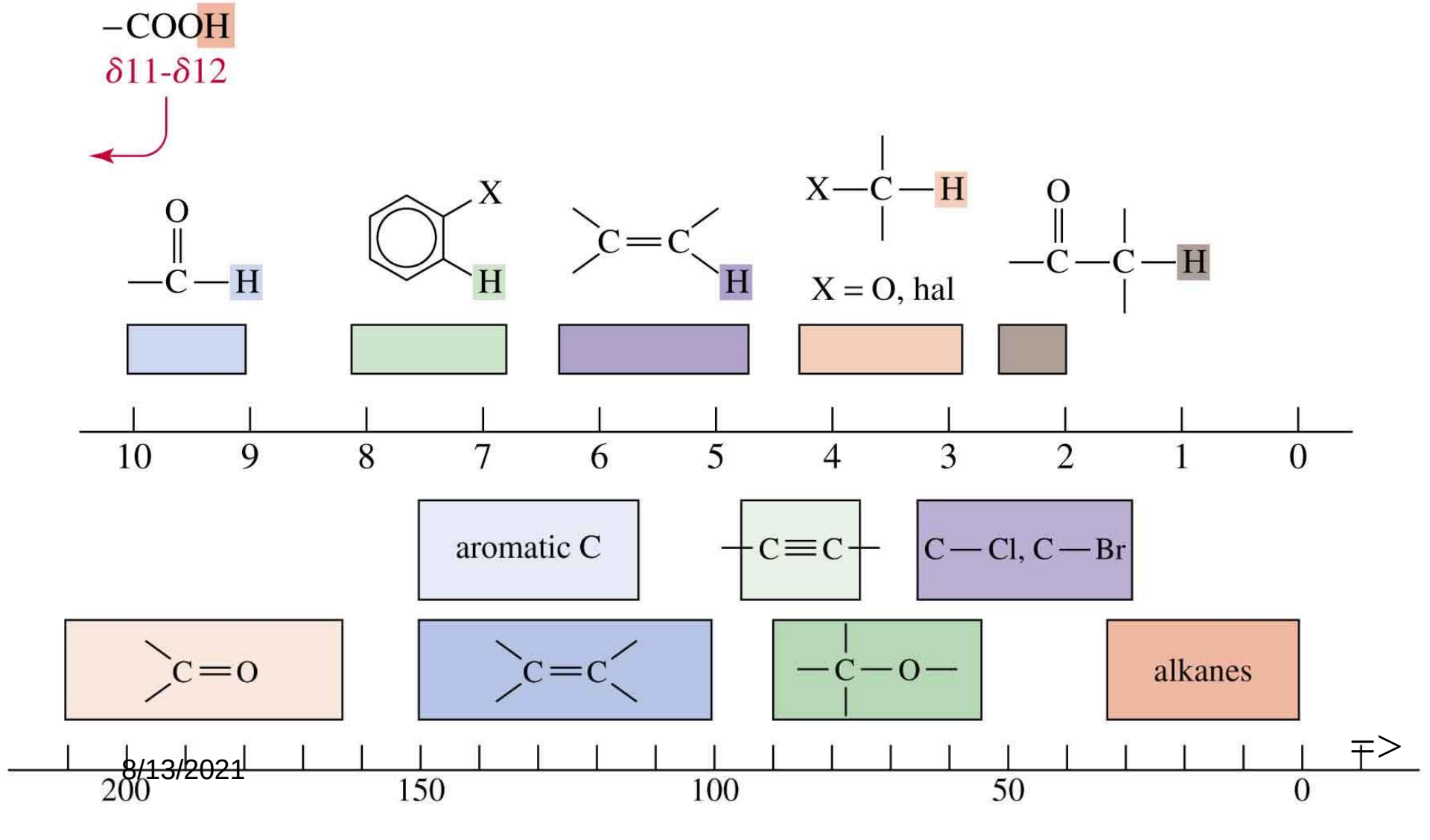
- ^{12}C has no magnetic spin.
- ^{13}C has a magnetic spin, but is only 1% of the carbon in a sample.
- The gyromagnetic ratio of ^{13}C is one-fourth of that of ^{1}H.
- Signals are weak, getting lost in noise.
- Hundreds of spectra are taken, averaged.

=>

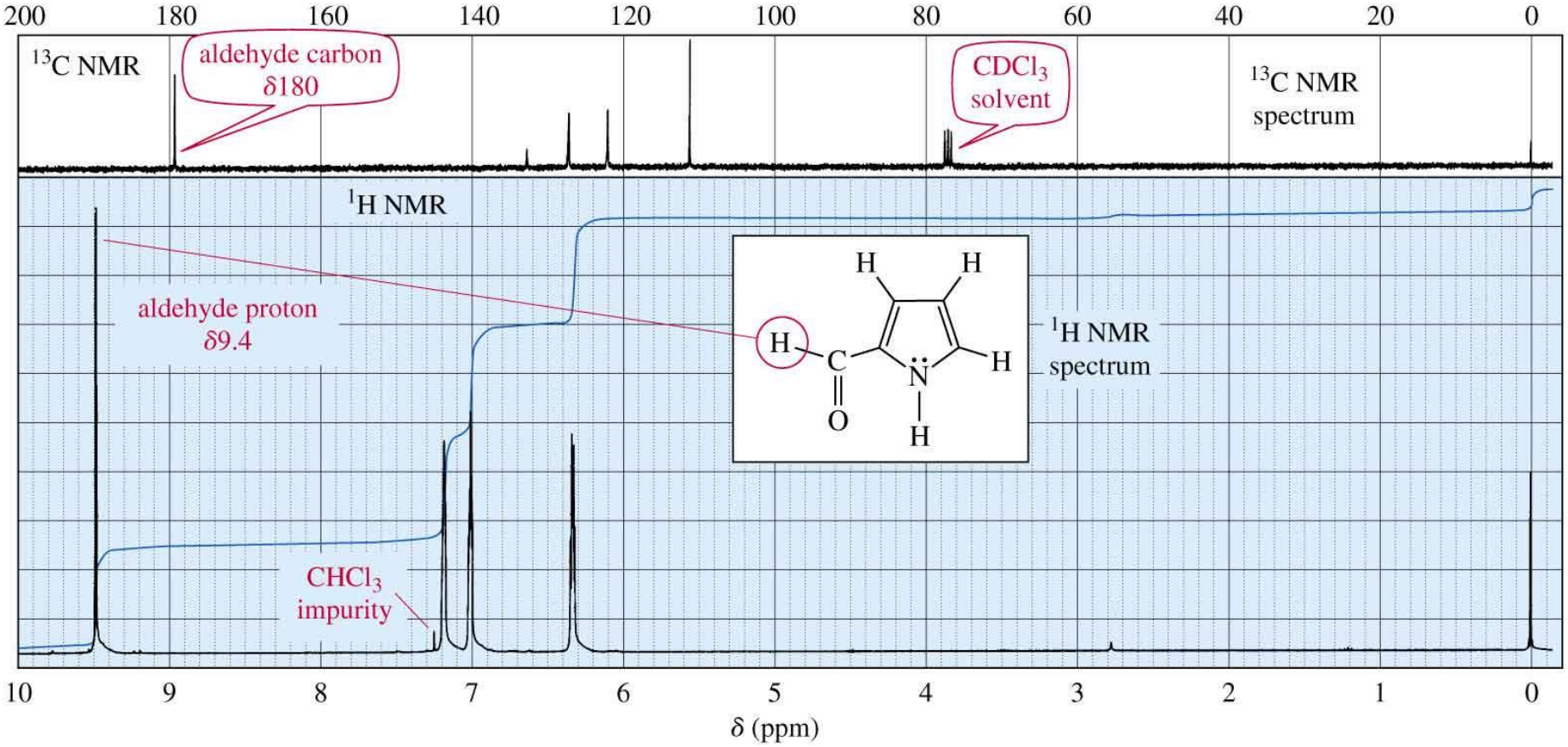
Fourier Transform NMR

- Nuclei in a magnetic field are given a radio-frequency pulse close to their resonance frequency.
- The nuclei absorb energy and precess (spin) like little tops.
- A complex signal is produced, then decays as the nuclei lose energy.
- Free induction decay is converted to spectrum. =>

Hydrogen and Carbon Chemical Shifts



Combined ^{13}C and ^{1}H Spectra



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Differences in ^{13}C Technique

- Resonance frequency is ~ one-fourth, 15.1 MHz instead of 60 MHz.
- Peak areas are not proportional to number of carbons.
- Carbon atoms with more hydrogens absorb more strongly.

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Spin-Spin Splitting

- It is unlikely that a ^{13}C would be adjacent to another ^{13}C, so splitting by carbon is negligible.
- ^{13}C will magnetically couple with attached protons and adjacent protons.
- These complex splitting patterns are difficult to interpret.

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Proton Spin Decoupling

- To simplify the spectrum, protons are continuously irradiated with “noise,” so they are rapidly flipping.
- The carbon nuclei see an average of all the possible proton spin states.
- Thus, each different kind of carbon gives a single, unsplit peak.

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Off-Resonance Decoupling

- ^{13}C nuclei are split only by the protons attached directly to them.
- The $N + 1$ rule applies: a carbon with N number of protons gives a signal with $N + 1$ peaks.

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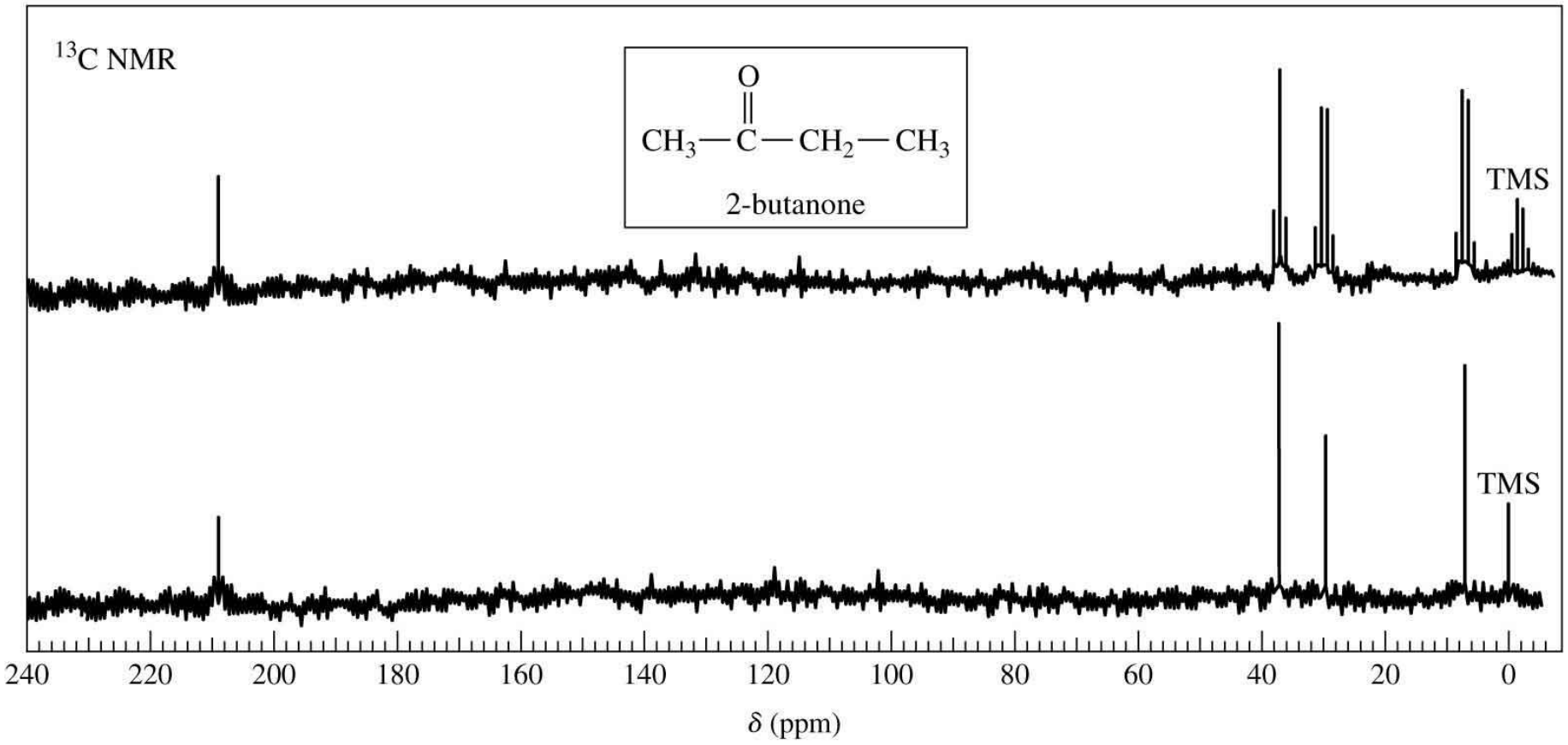
Interpreting ^{13}C NMR

- The number of different signals indicates the number of different kinds of carbon.
- The location (chemical shift) indicates the type of functional group.
- The peak area indicates the numbers of carbons (if integrated).
- The splitting pattern of off-resonance decoupled spectrum indicates the number of protons attached to the carbon. =>

Two ^{13}C NMR Spectra



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MRI

- Magnetic resonance imaging, noninvasive
- “Nuclear” is omitted because of public’s fear that it would be radioactive.
- Only protons in one plane can be in resonance at one time.
- Computer puts together “slices” to get 3D.
- Tumors readily detected.

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