B.Sc. Semester-VI
Paper CC-XIV
Organic Chemistry-V

III. Nuclear Magnetic Resonance Spectroscopy

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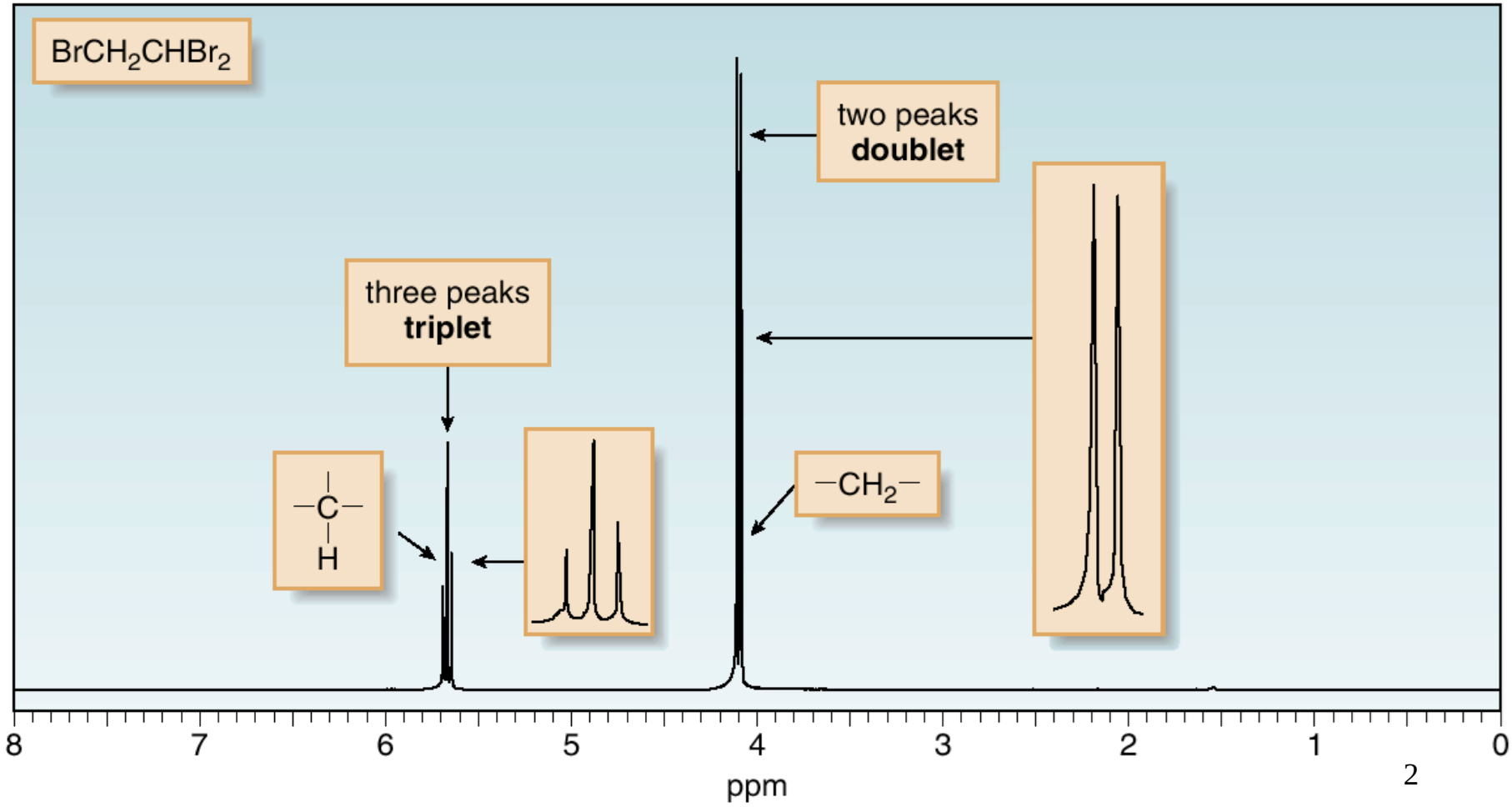
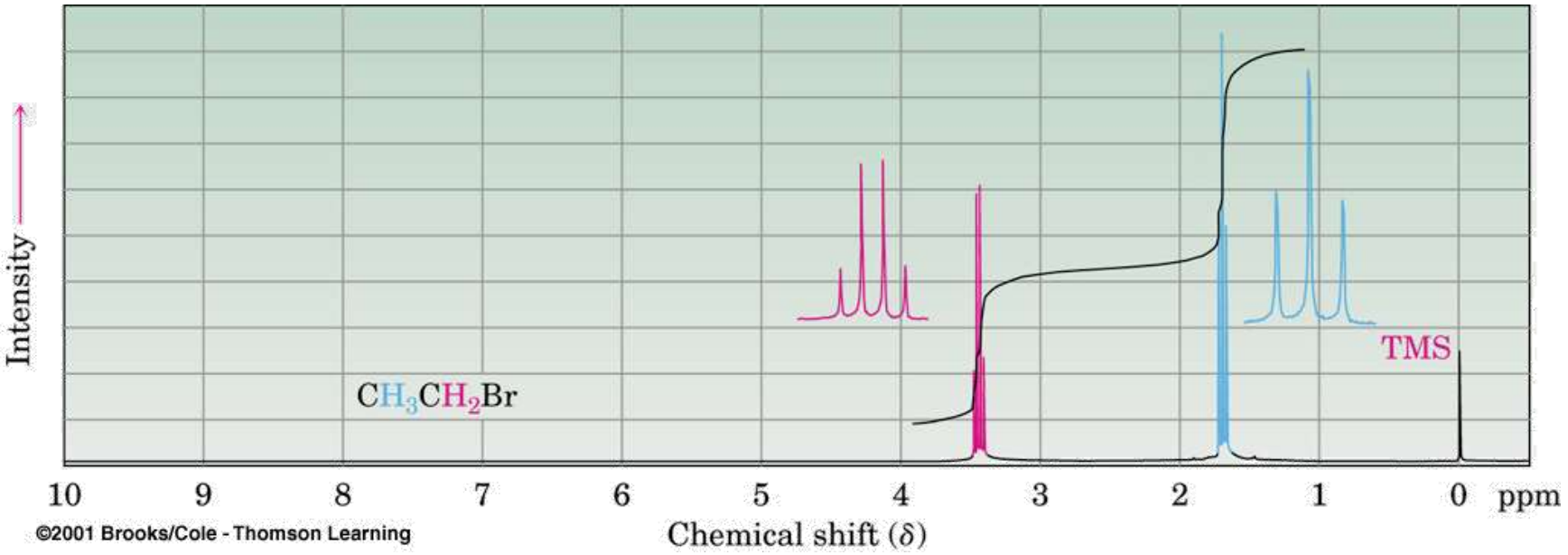
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR–Spin-Spin Splitting

- Consider the spectrum below:

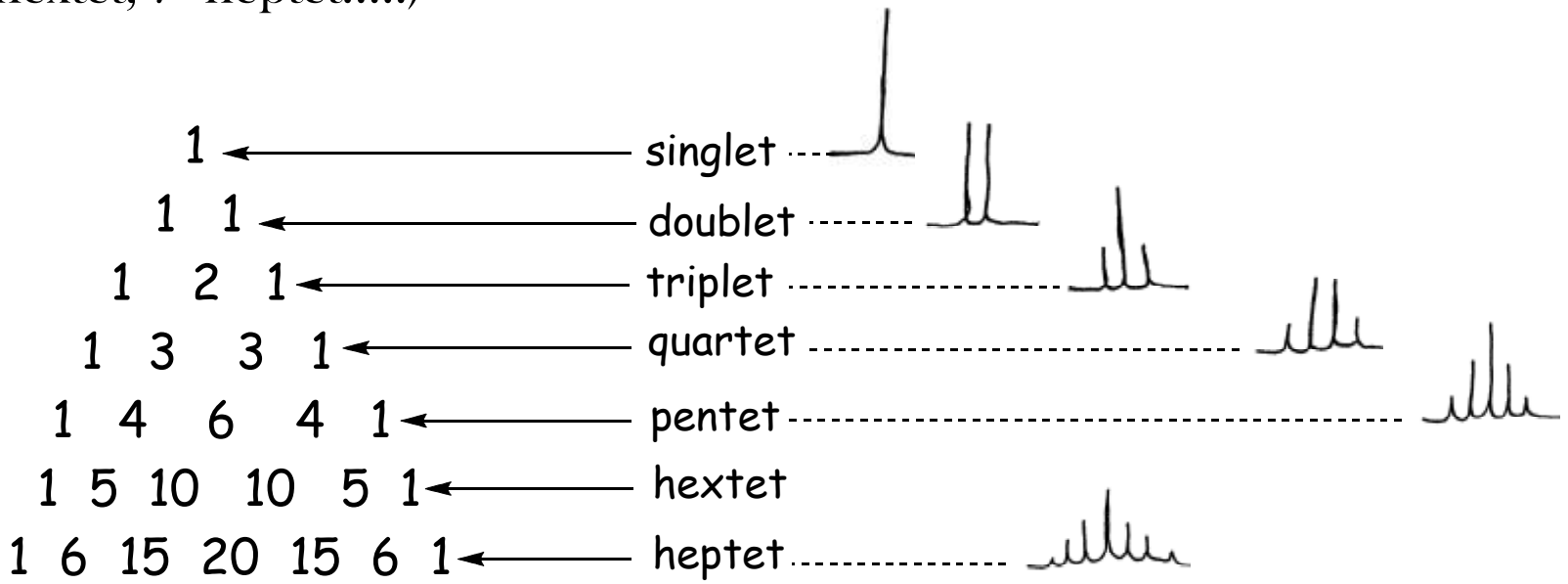


Ethyl Bromide



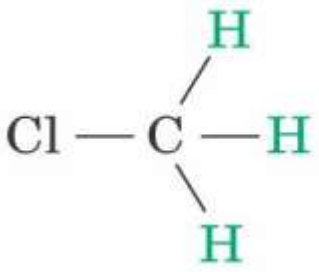
Spin-Spin Splitting in ^{1}H NMR Spectra

- Peaks are often split into multiple peaks due to *magnetic interactions* between nonequivalent protons on adjacent carbons, The process is called **spin-spin splitting**
- The splitting is into one more peak than the number of H's on the adjacent carbon(s), This is the **"n+1 rule"**
- The relative intensities are in proportion of a binomial distribution given by Pascal's Triangle
- The set of peaks is a **multiplet** (2 = doublet, 3 = triplet, 4 = quartet, 5=pentet, 6=hextet, 7=heptet.....)

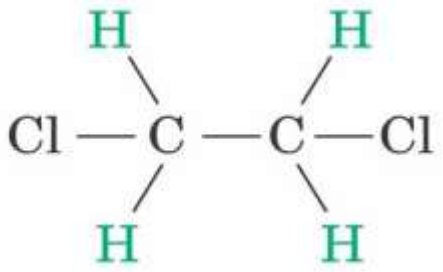


Rules for Spin-Spin Splitting

- **Equivalent** protons **do not** split each other

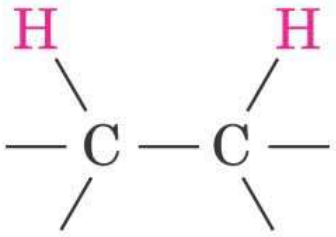


Three C–H protons are chemically equivalent; no splitting occurs.

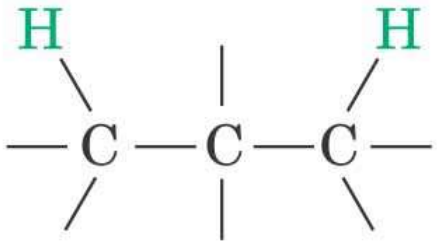


Four C–H protons are chemically equivalent; no splitting occurs.

- Protons that are **farther than two carbon atoms apart do not** split each other



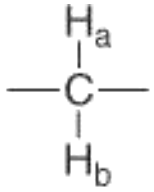
Splitting observed

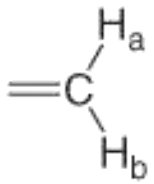


Splitting not usually observed

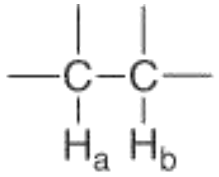
^{1}H NMR—Spin-Spin Splitting

If H_a and H_b are not equivalent, splitting is observed when:



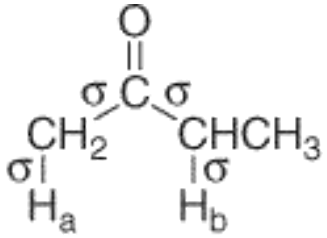


H_a and H_b are on the **same** carbon.



H_a and H_b are on **adjacent** carbons.

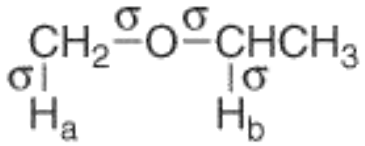
Splitting is not generally observed between protons separated by more than three σ bonds.



2-butanone

H_a and H_b are separated by four σ bonds.

no splitting between H_a and H_b



ethyl methyl ether

H_a and H_b are separated by four σ bonds.

no splitting between H_a and H_b

The Origin of ^{1}H NMR—Spin-Spin Splitting

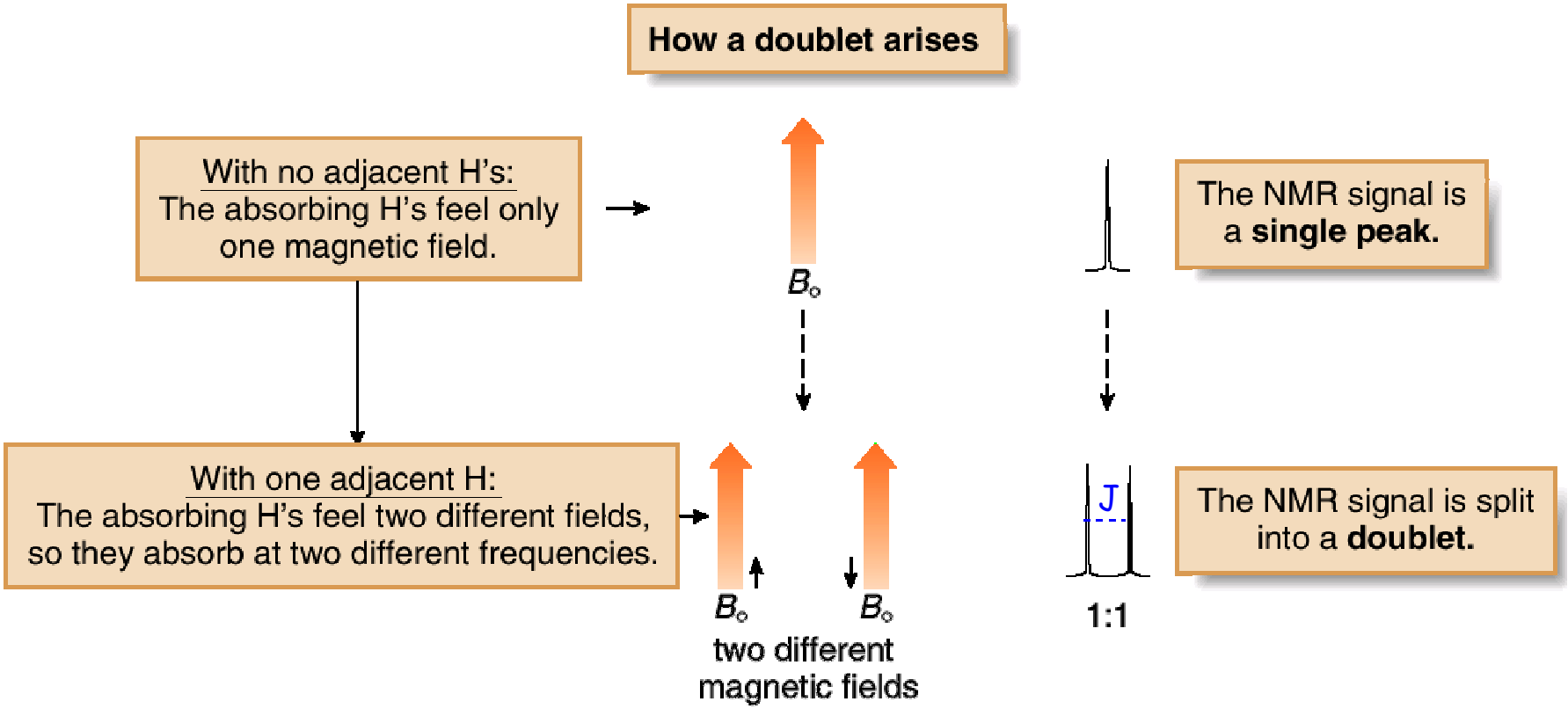
- **Spin-spin splitting occurs only between nonequivalent protons on the same carbon or adjacent carbons.**

  Let us consider how the doublet due to the CH_2 group on $BrCH_2CHBr_2$ occurs:

- When placed in an applied field, (B_0), the adjacent proton ($CHBr_2$) can be aligned with (↑) or against (↓) B_0. The likelihood of either case is about 50% (i.e., 1,000,006↑ vs 1,000,000↓).
- Thus, the absorbing CH_2 protons feel two slightly different magnetic fields—one slightly larger than B_0, and one slightly smaller than B_0.
- Since the absorbing protons feel two different magnetic fields, they absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet, where the two peaks of the doublet have ***equal*** intensity.

The Origin of ^{1}H NMR—Spin-Spin Splitting

The frequency difference, measured in Hz, between two peaks of the doublet is called the coupling constant, *J*.



- One adjacent proton splits an NMR signal into a doublet.

The Origin of ^{1}H NMR—Spin-Spin Splitting

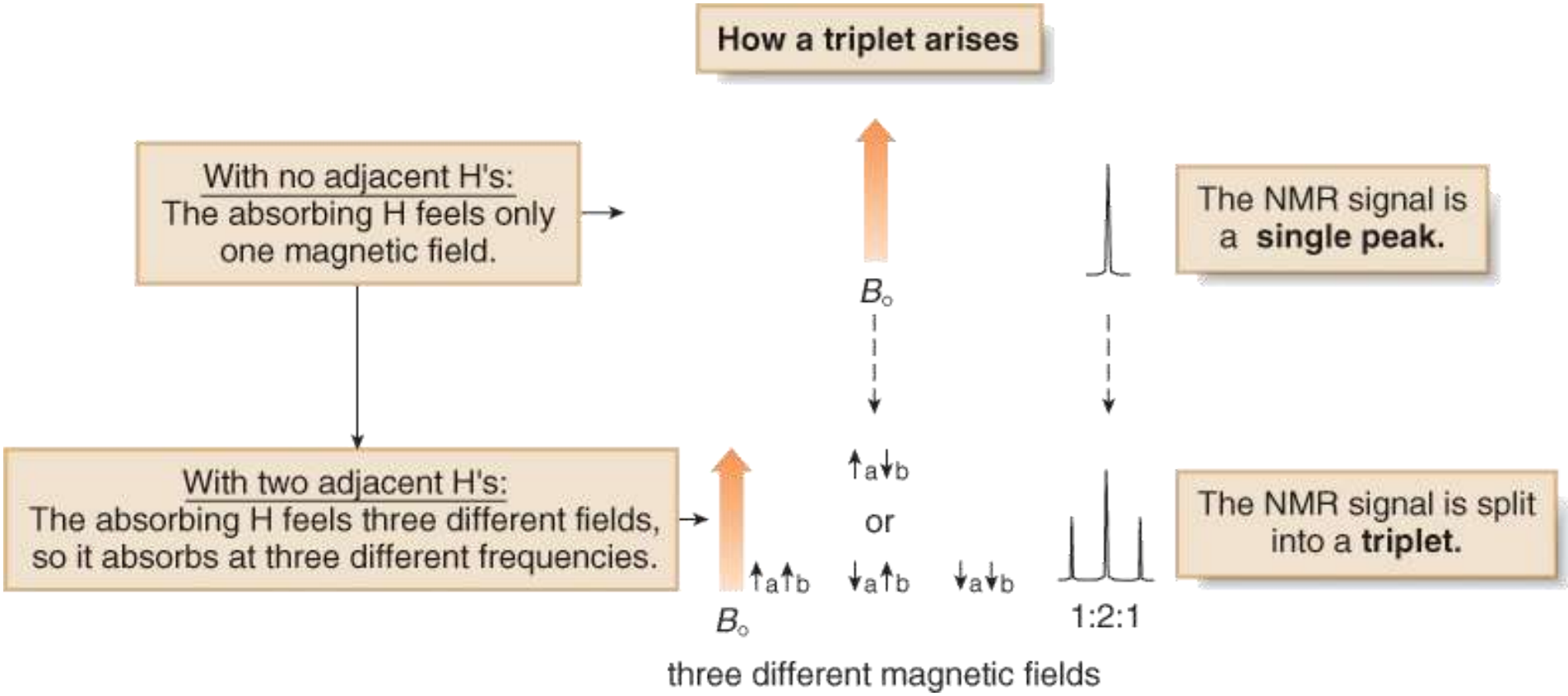
Let us now consider how a triplet arises:

- When placed in an applied magnetic field (B_0), the adjacent protons H_a and H_b can each be aligned with (↑) or against (↓) B_0.
- Thus, the absorbing proton feels three slightly different magnetic fields—one slightly larger than $B_0(\uparrow_a\uparrow_b)$. one slightly smaller than $B_0(\downarrow_a\downarrow_b)$ and one the same strength as B_0 $(\uparrow_a\downarrow_b)$.

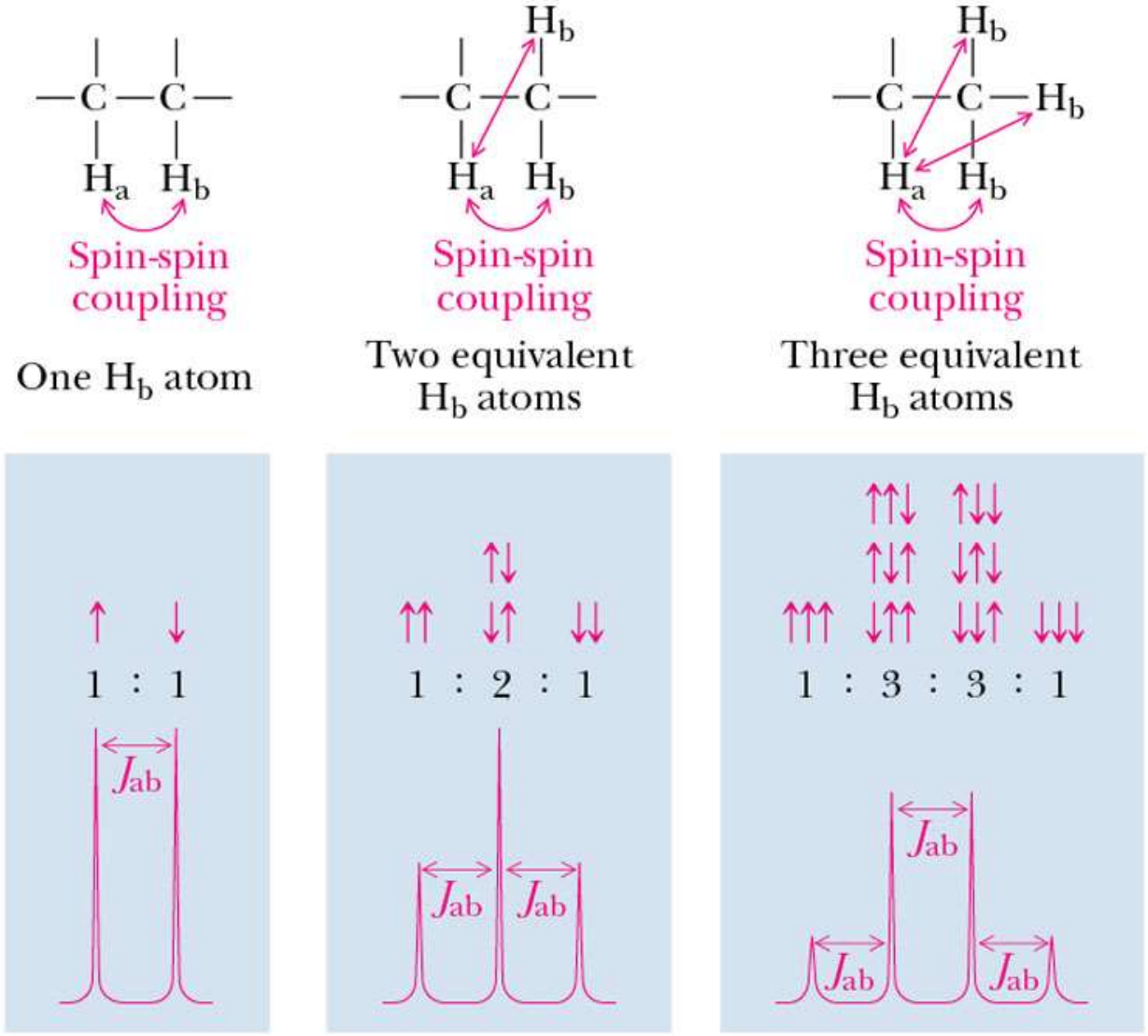
The Origin of ^{1}H NMR—Spin-Spin Splitting

- Because the absorbing proton feels **three** different magnetic fields, it absorbs at **three** different frequencies in the NMR spectrum, thus splitting a single absorption into a **triplet**.
- Because there are **two** different ways to align one proton with B_0, and one proton against B_0—that is, $\uparrow_a\downarrow_b$ and $\downarrow_a\uparrow_b$—the middle peak of the triplet is **twice** as intense as the two outer peaks, making the ratio of the areas under the three peaks 1:**2**:1.
- Two adjacent protons split an NMR signal into a triplet.
- When two protons split each other, they are said to be coupled.
- The spacing between peaks in a split NMR signal, measured by the *J* value, is equal for coupled protons.

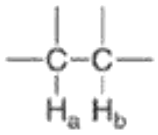
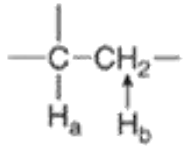
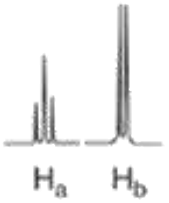
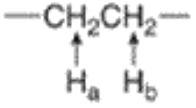
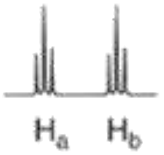
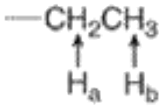
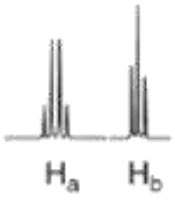
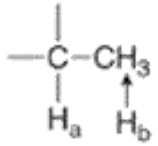
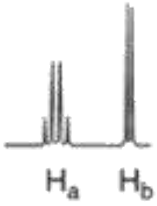
The Origin of ^{1}H NMR—Spin-Spin Splitting



The Origin of ^{1}H NMR—Spin-Spin Splitting



Common Splitting Patterns observed in ^{1}H NMR

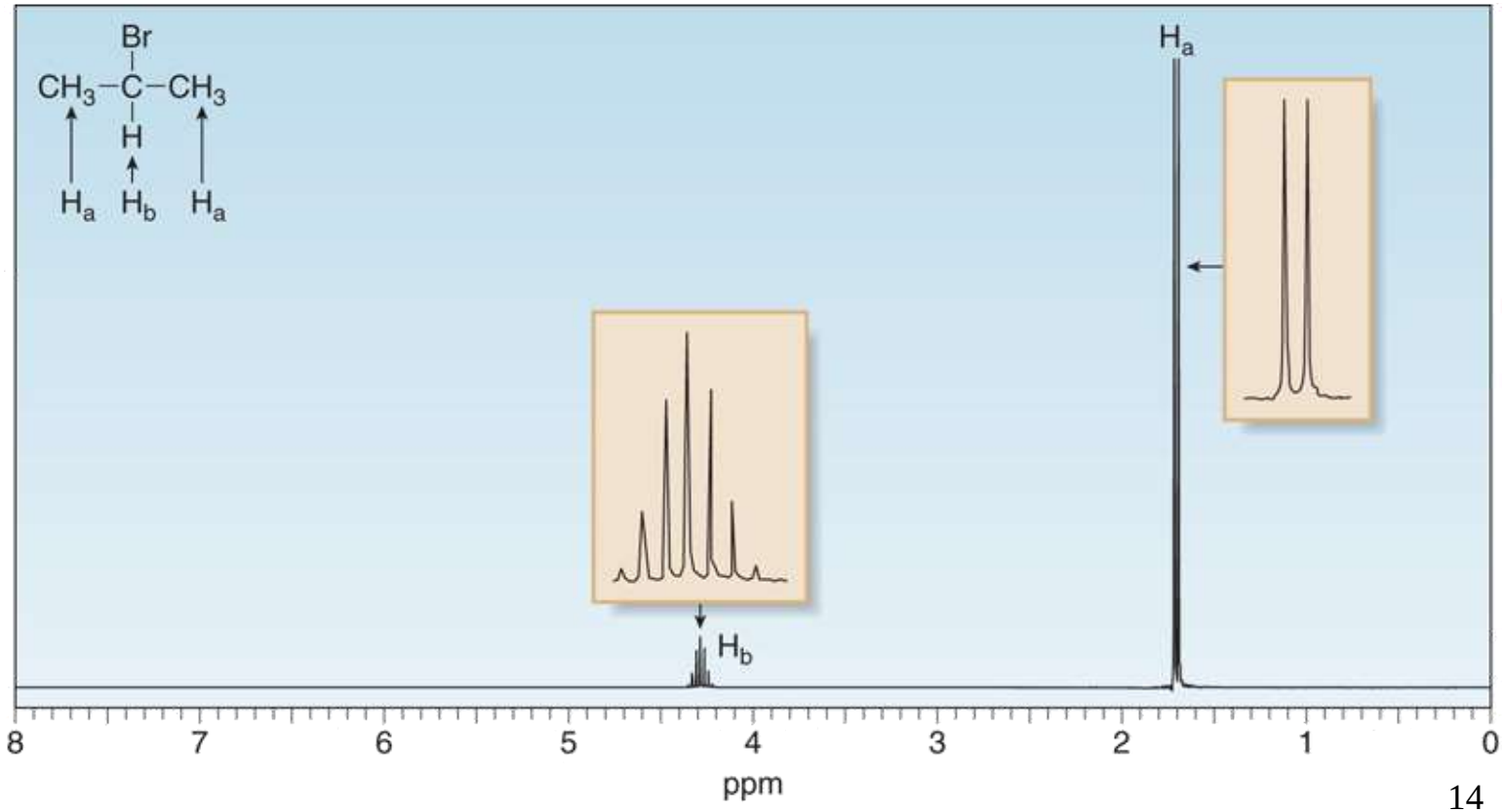
Example	Pattern	Analysis (H_a and H_b are not equivalent.)
[1] 		• H_a: one adjacent H_b proton ----→ two peaks ----→ a **doublet** • H_b: one adjacent H_a proton ----→ two peaks ----→ a **doublet**
[2] 		• H_a: two adjacent H_b protons ----→ three peaks ----→ a **triplet** • H_b: one adjacent H_a proton ----→ two peaks ----→ a **doublet**
[3] 		• H_a: two adjacent H_b protons ----→ three peaks ----→ a **triplet** • H_b: two adjacent H_a protons ----→ three peaks ----→ a **triplet**
[4] 		• H_a: three adjacent H_b protons ----→ four peaks ----→ a **quartet*** • H_b: two adjacent H_a protons ----→ three peaks ----→ a **triplet**
[5] 		• H_a: three adjacent H_b protons ----→ four peaks ----→ a **quartet*** • H_b: one adjacent H_a proton ----→ two peaks ----→ a **doublet**

*The relative area under the peaks of a quartet is 1:3:3:1.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

Whenever two (or three) different sets of adjacent protons are equivalent to each other, use the n + 1 rule to determine the splitting pattern.



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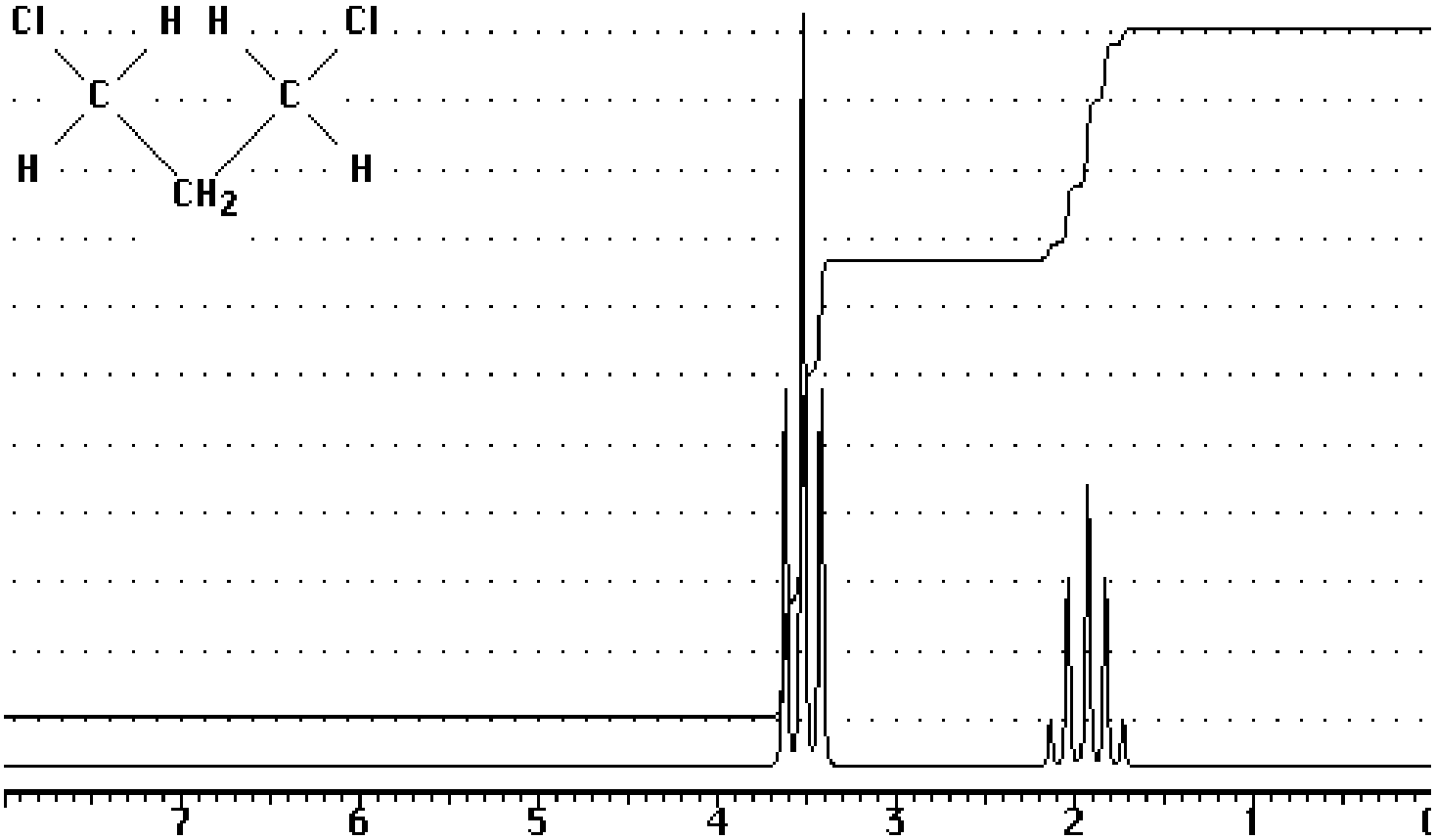
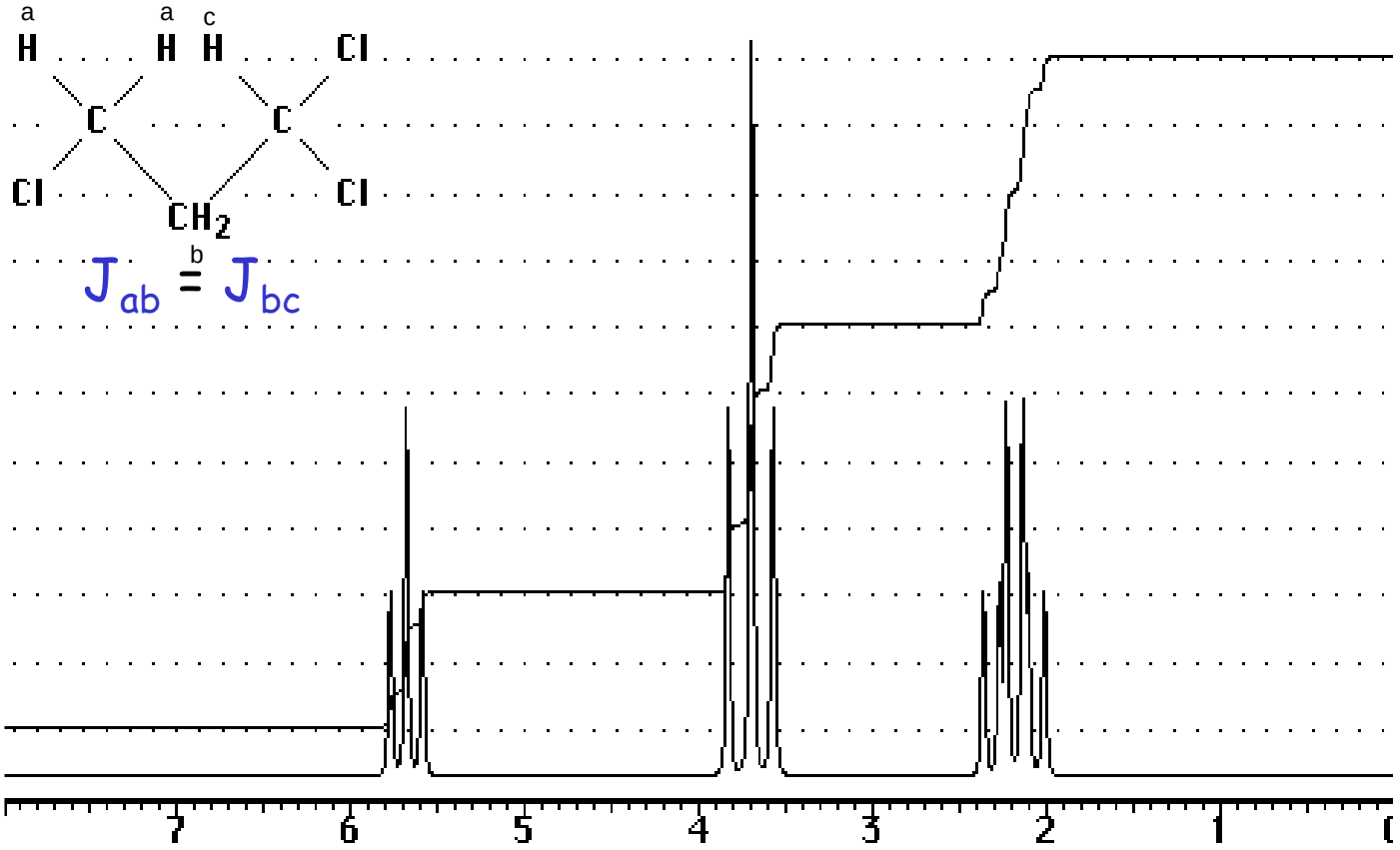


Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR–Spin-Spin Splitting

Whenever two (or three) different sets of adjacent protons are **not equivalent** to each other, use the n + 1 rule to determine the splitting pattern only if the **coupling constants (J) are identical:**

Free rotation around C-C bonds averages coupling constant to J = 7Hz



Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

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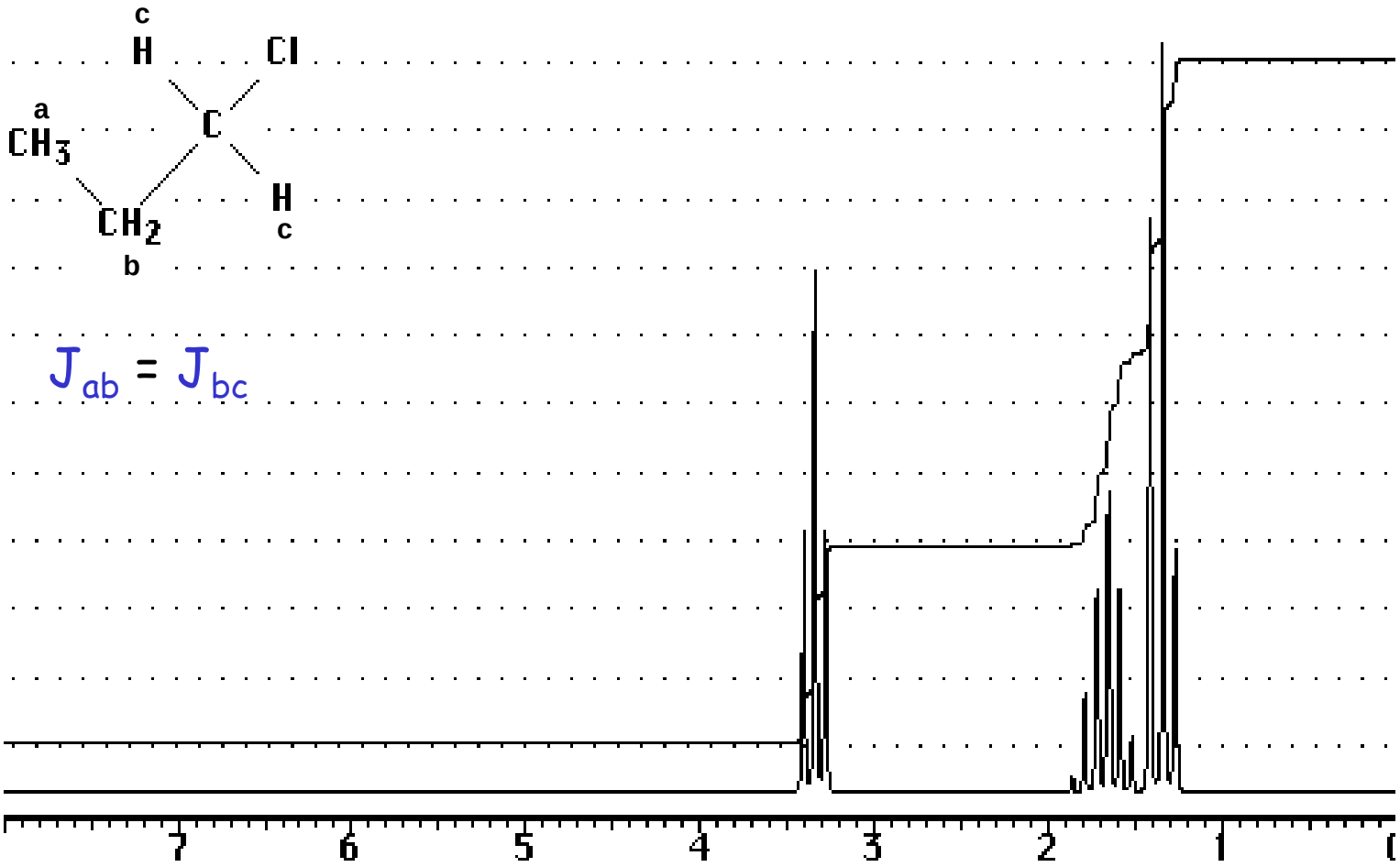
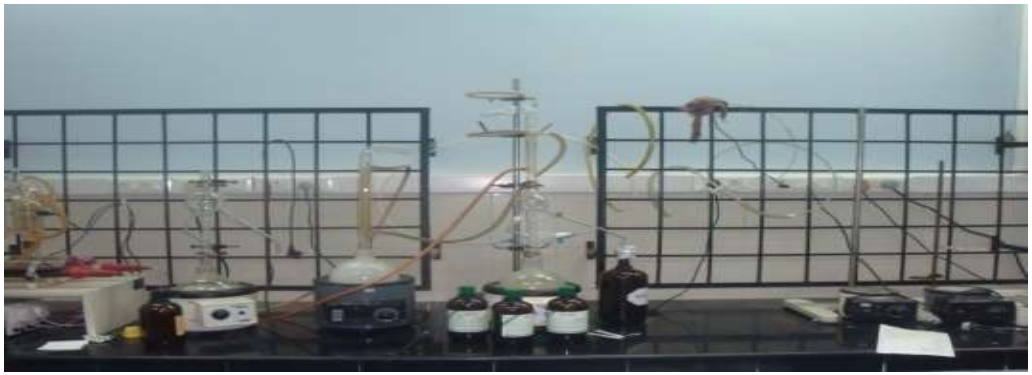


Thank You



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