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CHAPTER 8

NUCLEAR MAGNETIC RESONANCE

Expected Outcomes

Able to explain the theory of NMR
Able to describe the components of NMR spectrometer
Able to explain the chemical shift and spin-spin splitting pattern in NMR spectra effects by different protons environment

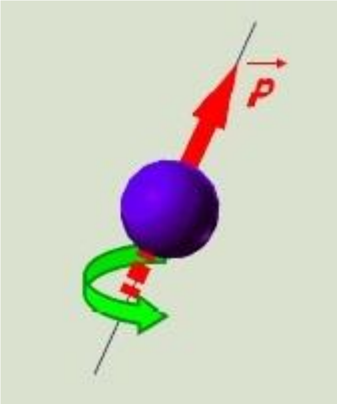
8.1 Theory of NMR

- The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.

- When low-energy radio waves interact with a molecule, they can change the nucleus spins of some elements, including ^{1}H and ^{13}C.

Nucleus Spin

- Nuclei rotate about an axis and spin (angular momentum *p*) – quantized



- A spinning, charged nucleus creates a magnetic field, magnetic moment μ along the axis
- $\mu = \gamma p$

- γ = magnetogyric ratio (specific for different nucleus-constant)

- Relationshp between neclei spin and magnetic moment leads to a set of magnetic quantum number, I= +1/2 and I= -1/2

- Nucleus with spin quantum number ½ is brought to an external magnetic field B_o, its magnetic moment becomes oriented in direction with respect to the field.
- The potential energy of this nucleus
- $E = -(\gamma m h/2\pi)B_o$

Energy level

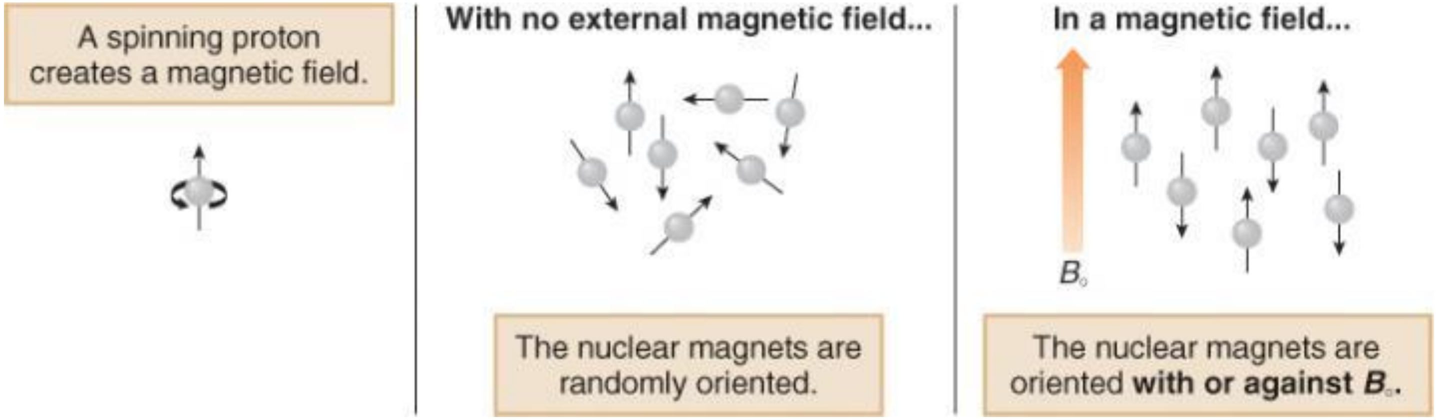
- Lower energy, m = +1/2 (direction of B_o)
- $E = -(\gamma h/4\pi)B_o$

- Higher energy, m = -1/2 (opposing of B_o)
- $E = (\gamma h/4\pi)B_o$

- $\Delta E = (\gamma h/4\pi)B_o - (-\gamma h/4\pi)Bo = (\gamma h/2\pi)B_o$
- $\Delta E = h\nu$ (radiation - RF)
- $\nu = (\gamma/2\pi)B_o$

Nuclear Magnetic Resonance Spectroscopy

- When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet.
- Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a magnetic field B_0, they are oriented with or against this applied field. More nuclei are oriented with the applied field because this arrangement is lower in energy.
- The energy difference between these two states is very small (<0.1 cal).



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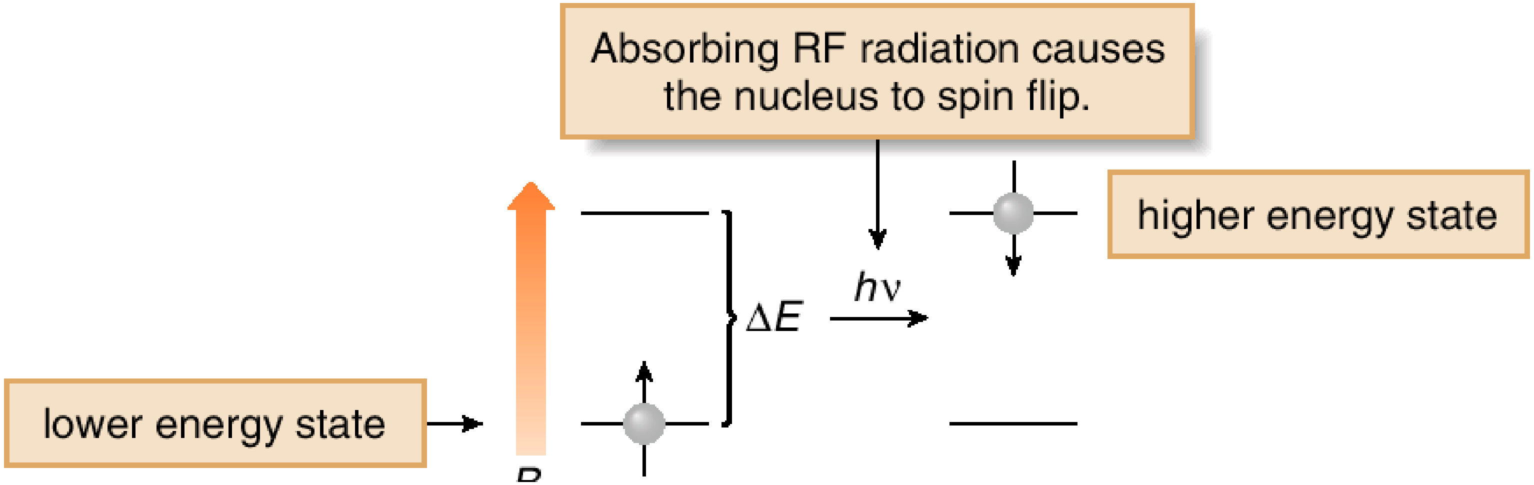
- In a magnetic field, there are now two energy states for a proton: a lower energy state with the nucleus aligned in the same direction as B_0, and a higher energy state in which the nucleus aligned against B_0.
- When an external energy source ($h\nu$) that matches the energy difference (ΔE) between these two states is applied, energy is absorbed, causing the nucleus to "spin flip" from one orientation to another.
- The energy difference between these two nuclear spin states corresponds to the low frequency RF region of the electromagnetic spectrum.

- Thus, two variables characterize NMR: an applied magnetic field B_0, the strength of which is measured in tesla (T), and the frequency ν of radiation used for resonance, measured in hertz (Hz), or megahertz (MHz)—(1 MHz = 10^6 Hz).



Absorbing RF radiation causes the nucleus to spin flip.

higher energy state

lower energy state

- A nucleus is in *resonance* when it absorbs RF radiation and "spin flips" to a higher energy state.

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- The frequency needed for resonance and the applied magnetic field strength are proportionally related:

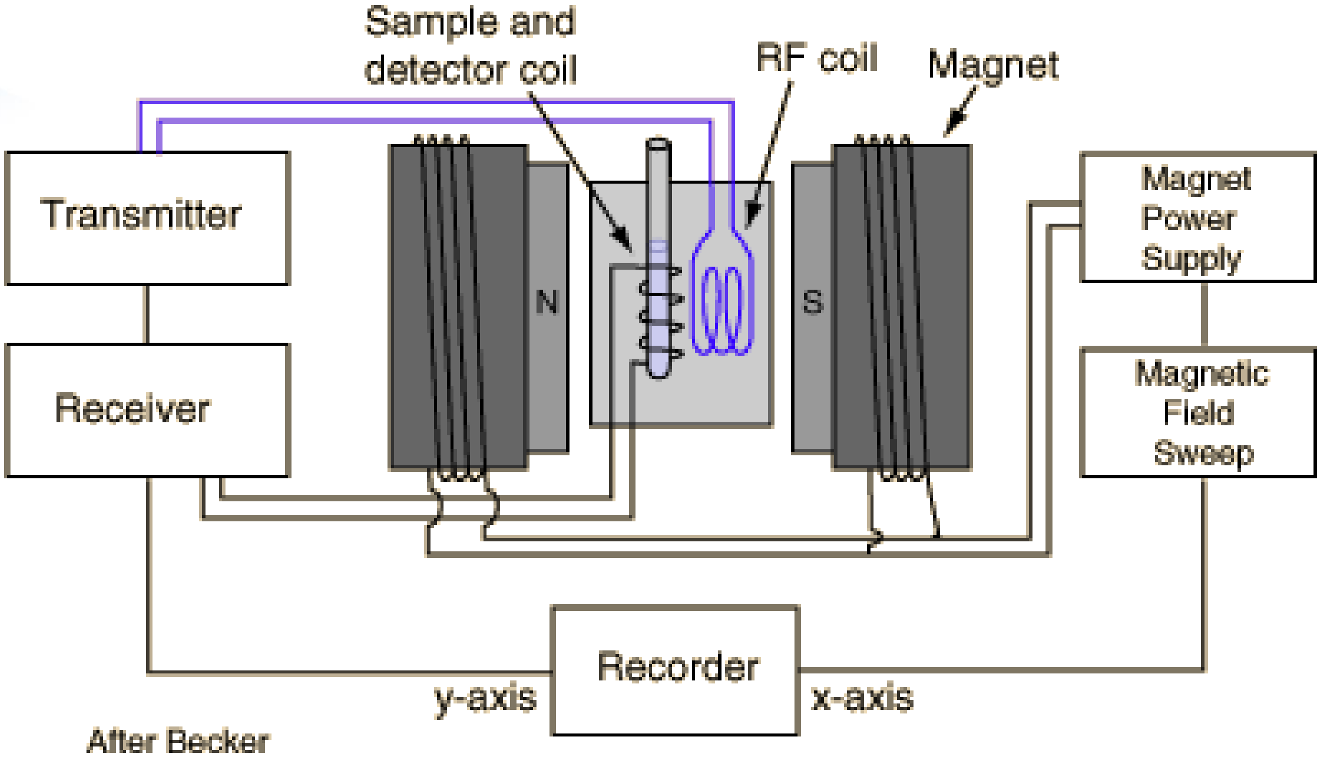
$$\boxed{\nu \propto B_{\circ}}$$

- The stronger the magnetic field, the larger the energy difference between the two nuclear spin states, and the higher the ν needed for resonance.

- NMR spectrometers are referred to as 300 MHz instruments, 500 MHz instruments, and so forth, depending on the frequency of the RF radiation used for resonance.
- These spectrometers use very powerful magnets to create a small but measurable energy difference between two possible spin states.

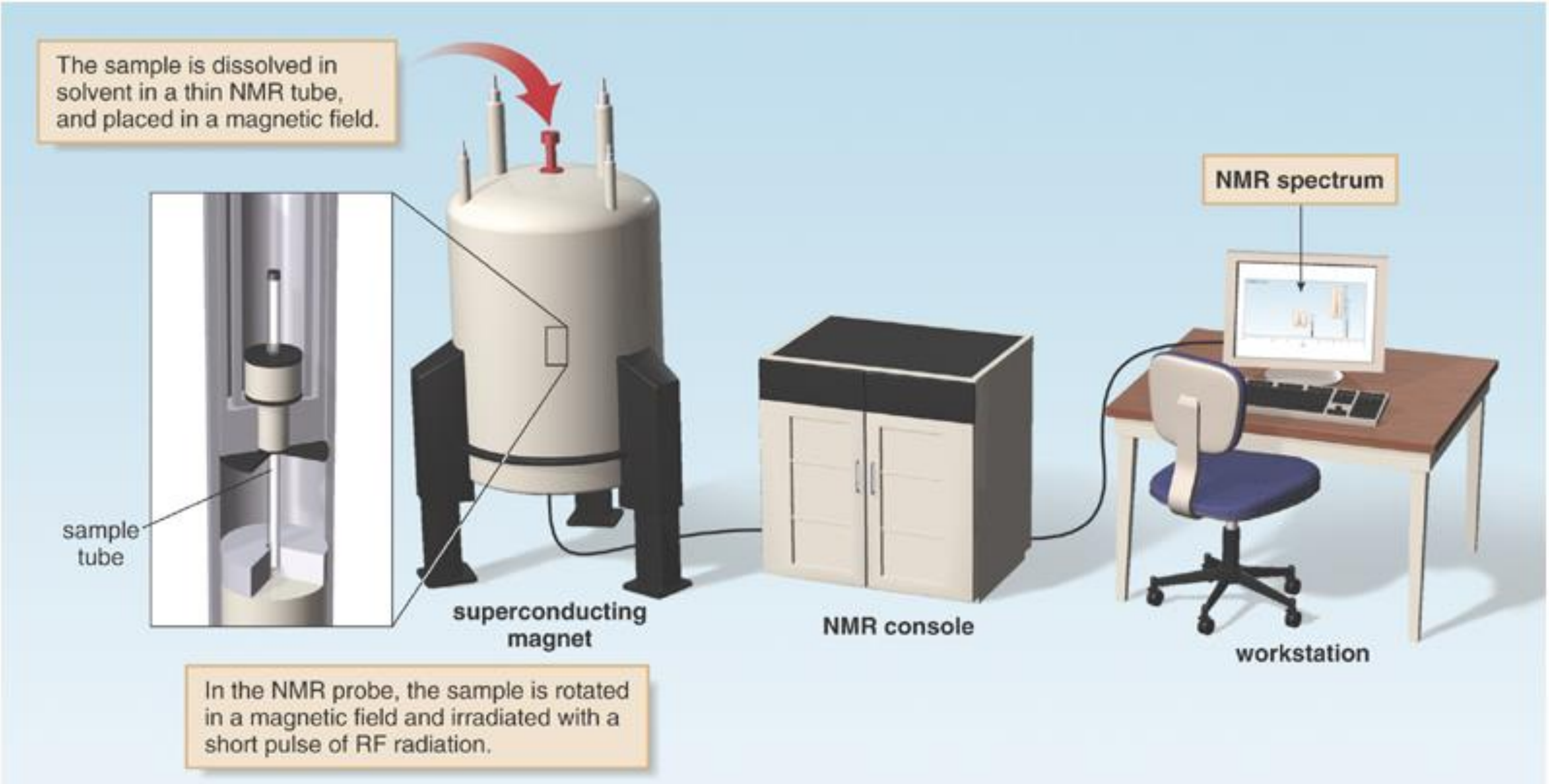
- Protons in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.
- The frequency at which a particular proton absorbs is determined by its electronic environment.
- The size of the magnetic field generated by the electrons around a proton determines where it absorbs.
- Modern NMR spectrometers use a constant magnetic field strength B_0, and then a narrow range of frequencies is applied to achieve the resonance of all protons.
- Only nuclei that contain odd mass numbers (such as ^1H, ^{13}C, ^{19}F and ^{31}P) or odd atomic numbers (such as ^2H and ^{14}N) give rise to NMR signals.

8.2 NMR Spectrometer



Source: http://nmrcentral.com/2011/08/nmr-instrumentation/

Schematic of an NMR spectrometer



The sample is dissolved in solvent in a thin NMR tube, and placed in a magnetic field.

In the NMR probe, the sample is rotated in a magnetic field and irradiated with a short pulse of RF radiation.

An NMR spectrometer. The sample is dissolved in a solvent, usually $CDCl_3$ (deuterochloroform), and placed in a magnetic field. A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance. When the nuclei fall back to their lower energy state, the detector measures the energy released, and a spectrum is recorded. The superconducting magnets in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with essentially no resistance.

Source:http://www2.chemistry.msu.edu/courses/cem251/FS11_HUANG/Chapter14_Smith3e_PPT.pdf

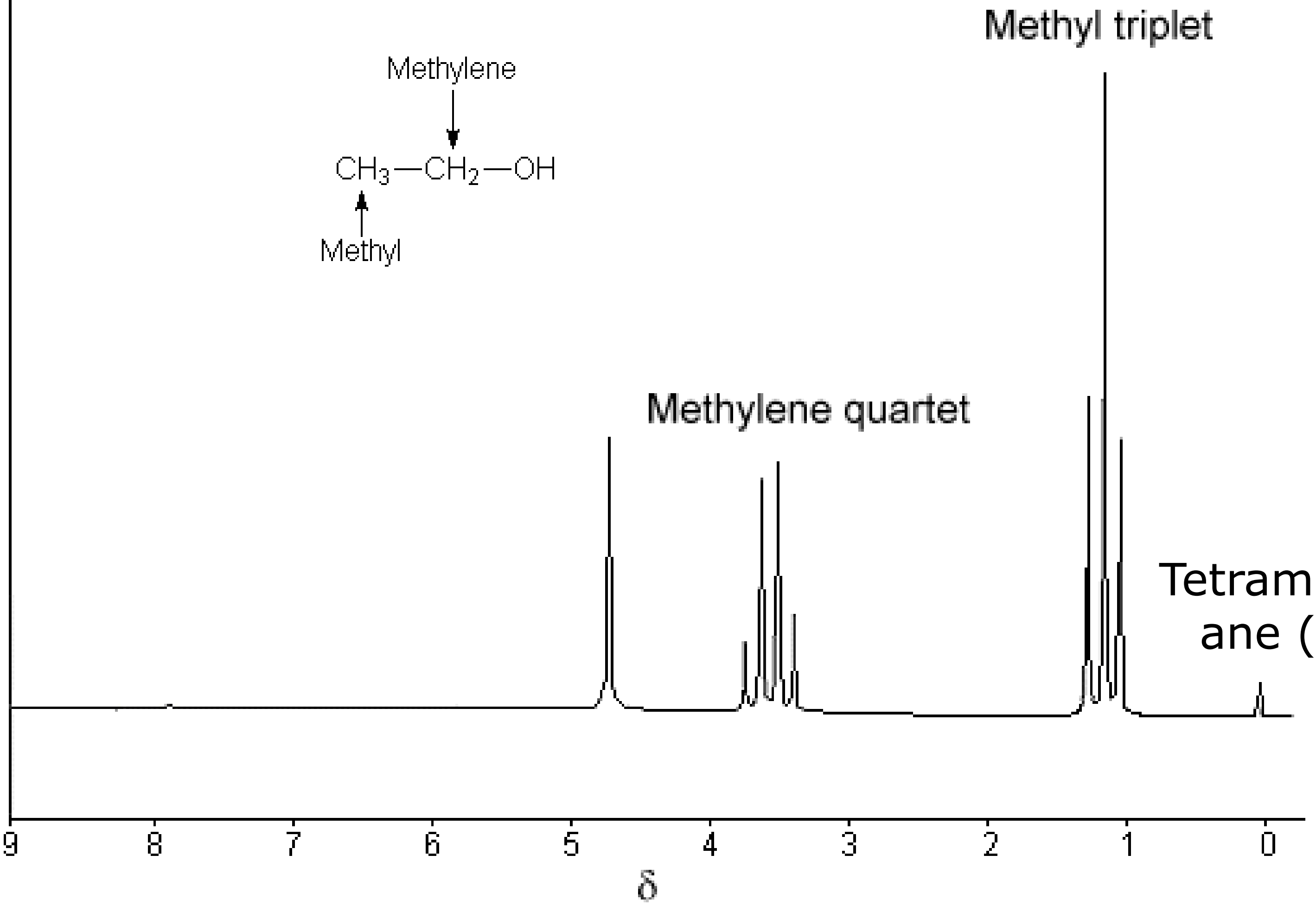
Magnet

- Permanent magnet (low magnetic field)
- Conventional electromagnet (seldom use)
- Superconducting solenoid (high magnetic field)
  - Niobium-tin wire / Niobium-titanium wire in liquid helium (surrounded with liquid nitrogen)
  - Advantages: resolution improves with field strength. sensitivity improves, spectral interpretation becomes easier

8.3 Environmental Effects on NMR spectra

Chemical shift

- One molecules contain multiple proton/ ^{1}H
- Due to different environments the nuclei belong to, these nuclei do not experience the same magnetic influence from Bo.
- This mean that, although they are ^{1}H nuclei, they are not equivalent.
- In the other words, these nuclei will give different NMR signals (will discuss shortly), and hence give rise to what is known as Chemical Shift Differences.



Tetramethylsilane (TMS)

Chemical shift

Low shield ← High shield

^{1}H NMR—Position of Signals

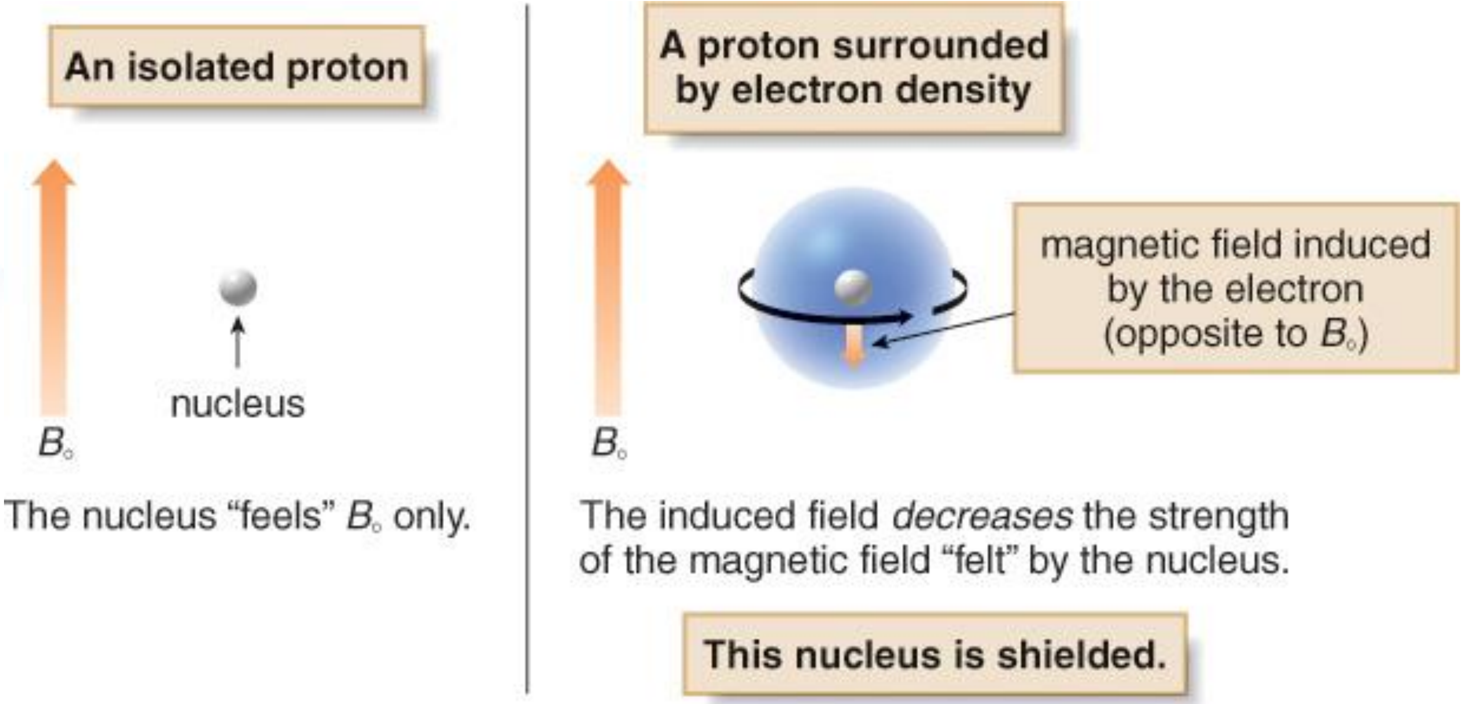
- NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the δ scale due to tetramethylsilane (TMS). TMS is a volatile inert compound, readily soluble in most organic liquids, can be easily remove from sample by distiillation and all protons are identical that gives a single peak upfield from typical NMR absorptions.

- The less shielded the nucleus becomes, the more of the applied magnetic field (B_0) it feels.

- This deshielded nucleus experiences a higher magnetic field strength, to it needs a higher frequency to achieve resonance.

- Higher frequency is to the left in an NMR spectrum, toward higher chemical shift—so deshielding shifts an absorption downfield.

- Protons near electronegative atoms are deshielded, so they absorb downfield**.**



An isolated proton

The nucleus "feels" $B_\circ$ only.

A proton surrounded by electron density

magnetic field induced by the electron (opposite to $B_\circ$)

The induced field *decreases* the strength of the magnetic field "felt" by the nucleus.

This nucleus is shielded.

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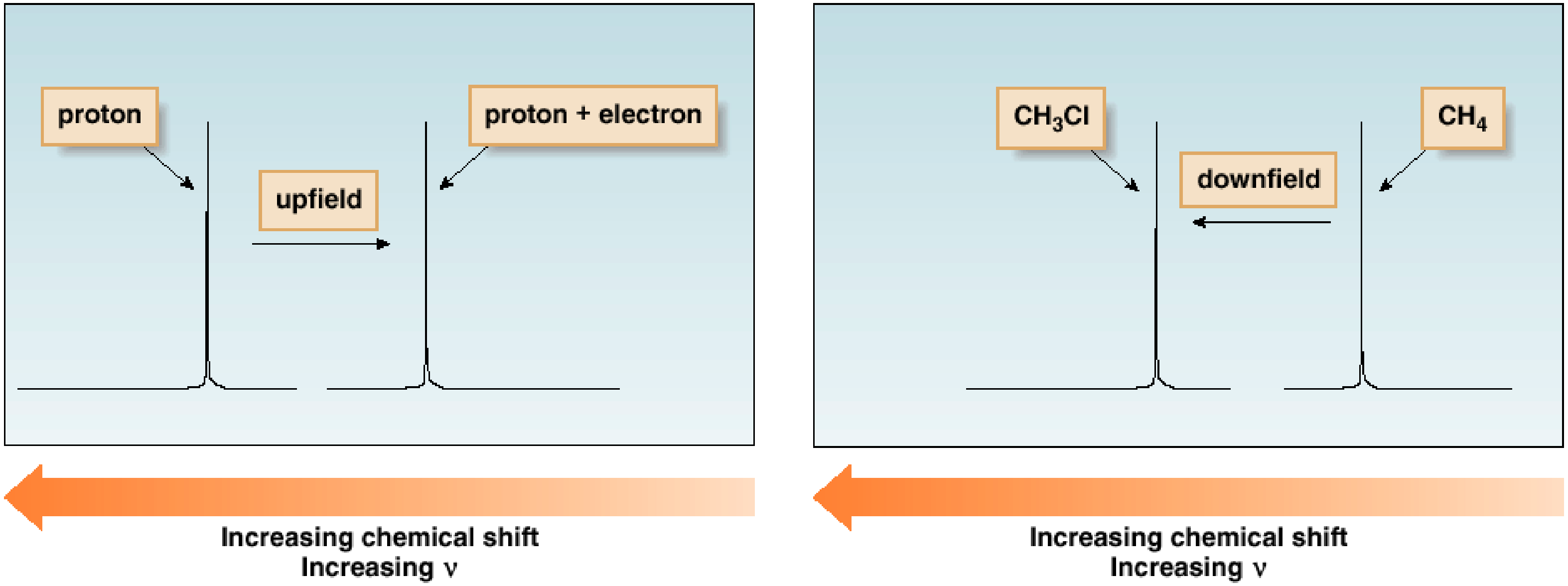
^{1}H NMR—Position of Signals

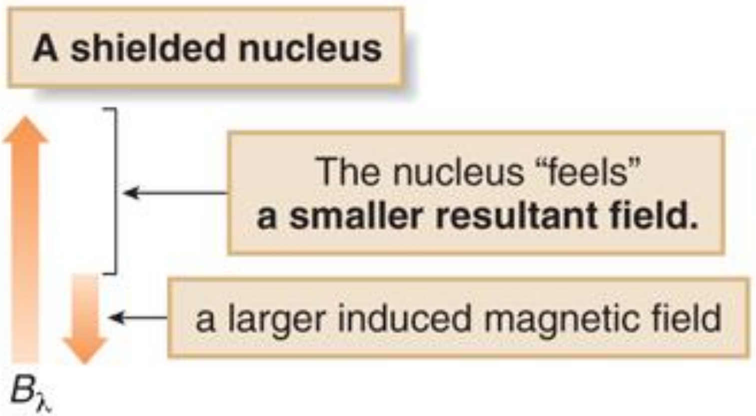
a. Shielding effects
- An electron shields the nucleus.
- The absorption shifts *upfield.*

b. Deshielding effects
- Decreased electron density deshields a nucleus.
- The absorption shifts *downfield.*



Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Position of Signals



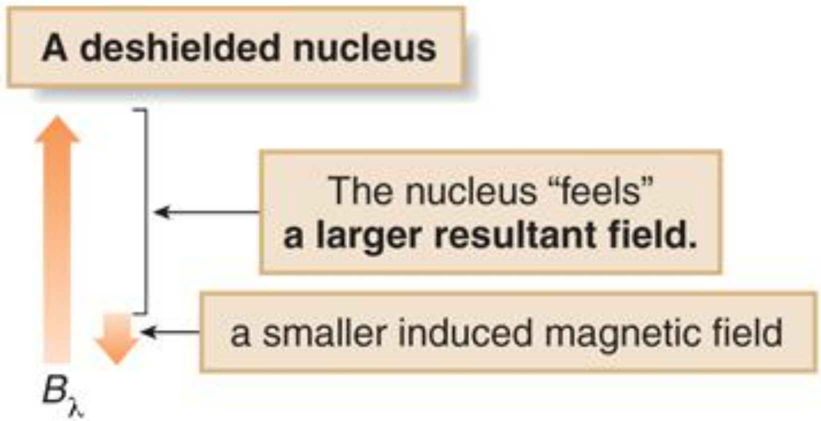
A shielded nucleus

The nucleus "feels" **a smaller resultant field.**

a larger induced magnetic field

B_λ

- As the electron density around the nucleus increases, the nucleus feels a smaller resultant magnetic field, so a lower frequency is needed to achieve resonance.
- **The absorption shifts upfield.**



A deshielded nucleus

The nucleus "feels" **a larger resultant field.**

a smaller induced magnetic field

B_λ

- As the electron density around the nucleus decreases, the nucleus feels a larger resultant magnetic field, so a higher frequency is needed to achieve resonance.
- **The absorption shifts downfield.**

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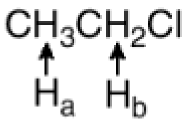
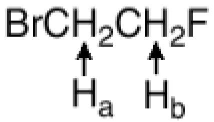
^1H NMR—Position of Signals



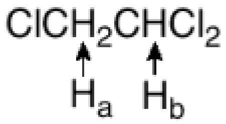
$\underset{\underset{H_a}{\uparrow}}{CH_3}\underset{\underset{H_b}{\uparrow}}{CH_2}Cl$

- The H_b protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from H_a.



$Br\underset{\underset{H_a}{\uparrow}}{CH_2}\underset{\underset{H_b}{\uparrow}}{CH_2}F$

- Because F is more electronegative than Br, the H_b protons are more **deshielded** than the H_a protons and absorb farther **downfield.**

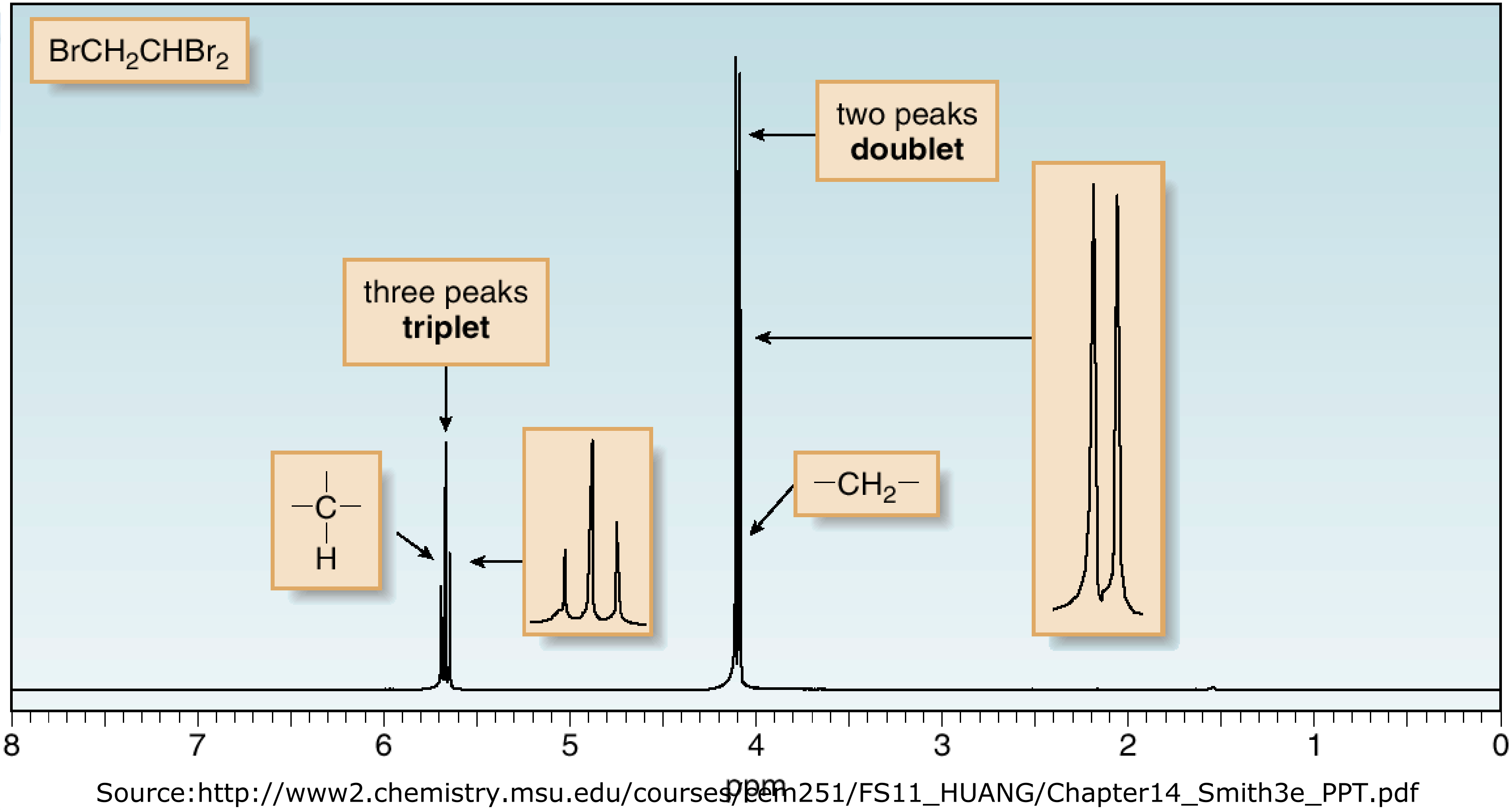


$Cl\underset{\underset{H_a}{\uparrow}}{CH_2}\underset{\underset{H_b}{\uparrow}}{CH}Cl_2$

- The larger number of electronegative Cl atoms (two versus one) **deshields** H_b more than H_a, so it absorbs **downfield** from H_a.

Spin-Spin Splitting

- Consider the spectrum below:



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^{1}H NMR—Spin-Spin Splitting

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

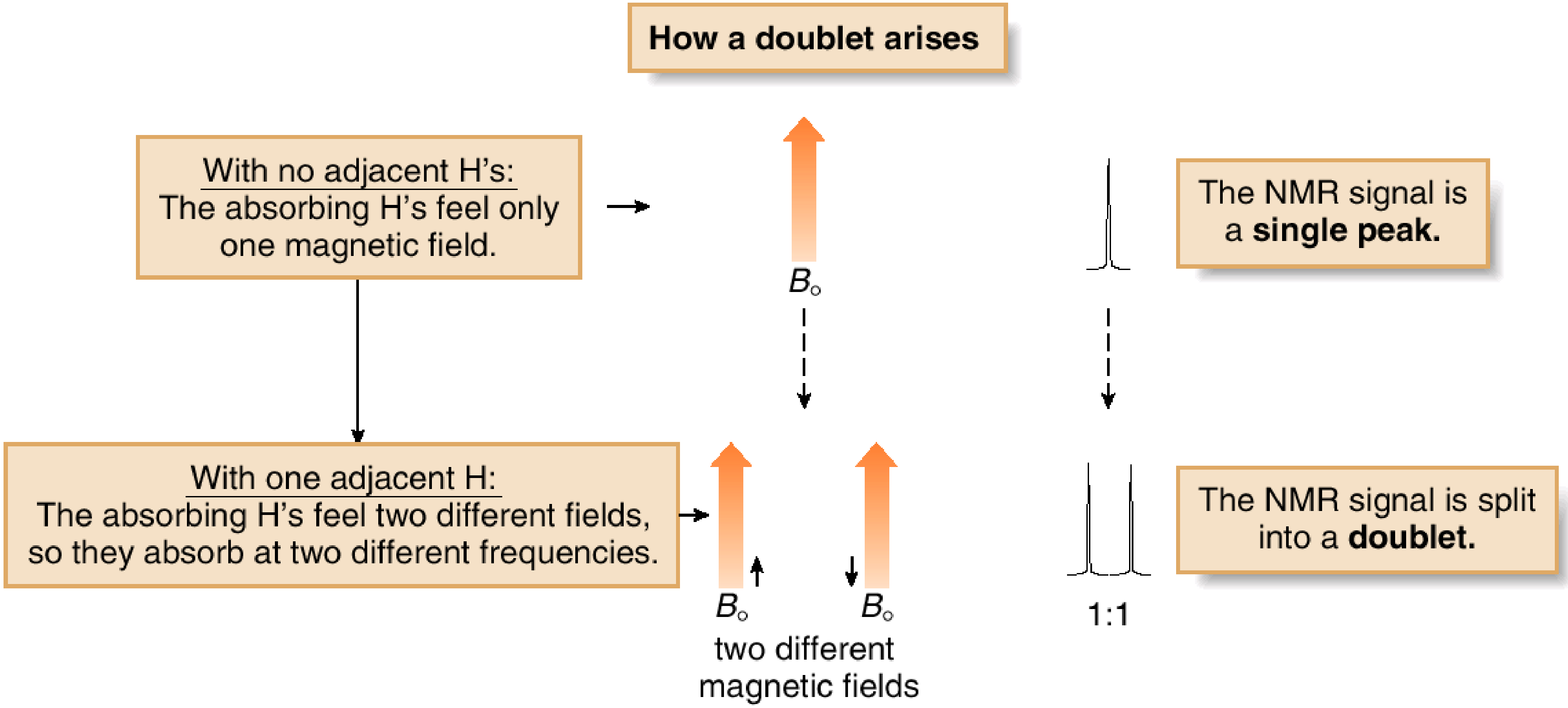
Let us consider how the doublet due to the CH_2 group on $BrCH_2CHBr_2$ occurs:

- When placed in an applied electric field, (B_0), the adjacent proton ($CHBr_2$) can be aligned with (↑) or against (↓) B_0.
- 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.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Spin-Spin Splitting

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



How a doublet arises

With no adjacent H's:
The absorbing H's feel only one magnetic field.

B_o

The NMR signal is a **single peak.**

With one adjacent H:
The absorbing H's feel two different fields, so they absorb at two different frequencies.

B_o B_o
two different magnetic fields

1:1

The NMR signal is split into a **doublet.**

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

^{1}H NMR—Spin-Spin Splitting

Let us now consider how a triplet arises:

absorbing H

2 adjacent H's

H_a and H_b can each be aligned with (↑) or against (↓) B_o.

- 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, one slightly smaller than B_0, and one the same strength as B_0.

^{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.

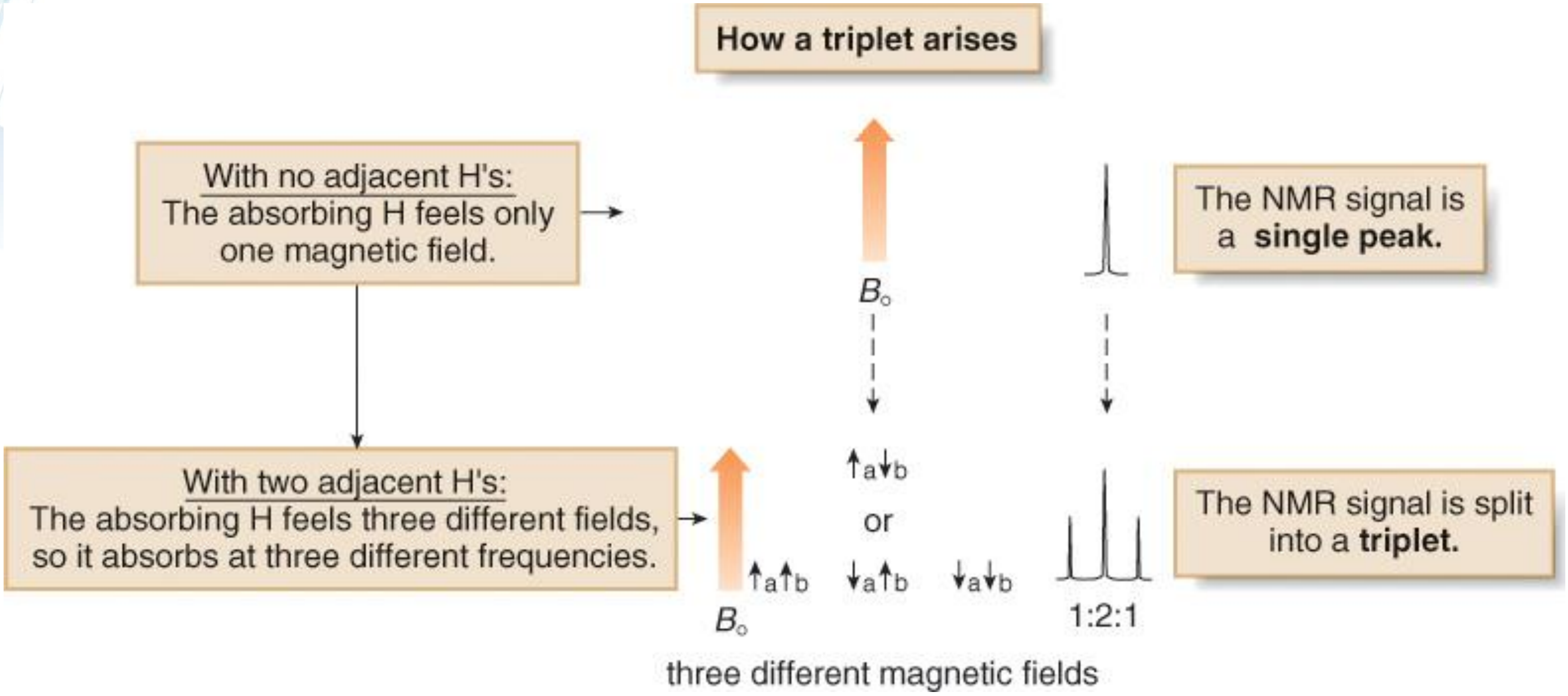
- Because there are two different ways to align one proton with B_0, and one proton against B_0—that is, $\uparrow_a\downarrow_b$ and $\downarrow_a\uparrow_b$—the middle peak of the triplet is twice as intense as the two outer peaks, making the ratio of the areas under the three peaks 1:2:1.

- 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.

^{1}H NMR—Spin-Spin Splitting



How a triplet arises

With no adjacent H's:
The absorbing H feels only one magnetic field.

B_o

The NMR signal is a **single peak.**

With two adjacent H's:
The absorbing H feels three different fields, so it absorbs at three different frequencies.

B_o

↑a↑b

↑a↓b
or
↓a↑b

↓a↓b

three different magnetic fields

1:2:1

The NMR signal is split into a **triplet.**

Source:http://www2.chemistry.msu.edu/courses/cem251/FS11_HUANG/Chapter14_Smith3e_PPT.pdf

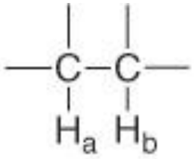
^{1}H NMR—Spin-Spin Splitting

Three general rules describe the splitting patterns commonly seen in the ^{1}H NMR spectra of organic compounds.

1. Equivalent protons do not split each other’s signals.
2. A set of n nonequivalent protons splits the signal of a nearby proton into n + 1 peaks.
3. Splitting is observed for nonequivalent protons on the same carbon or adjacent carbons.

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.

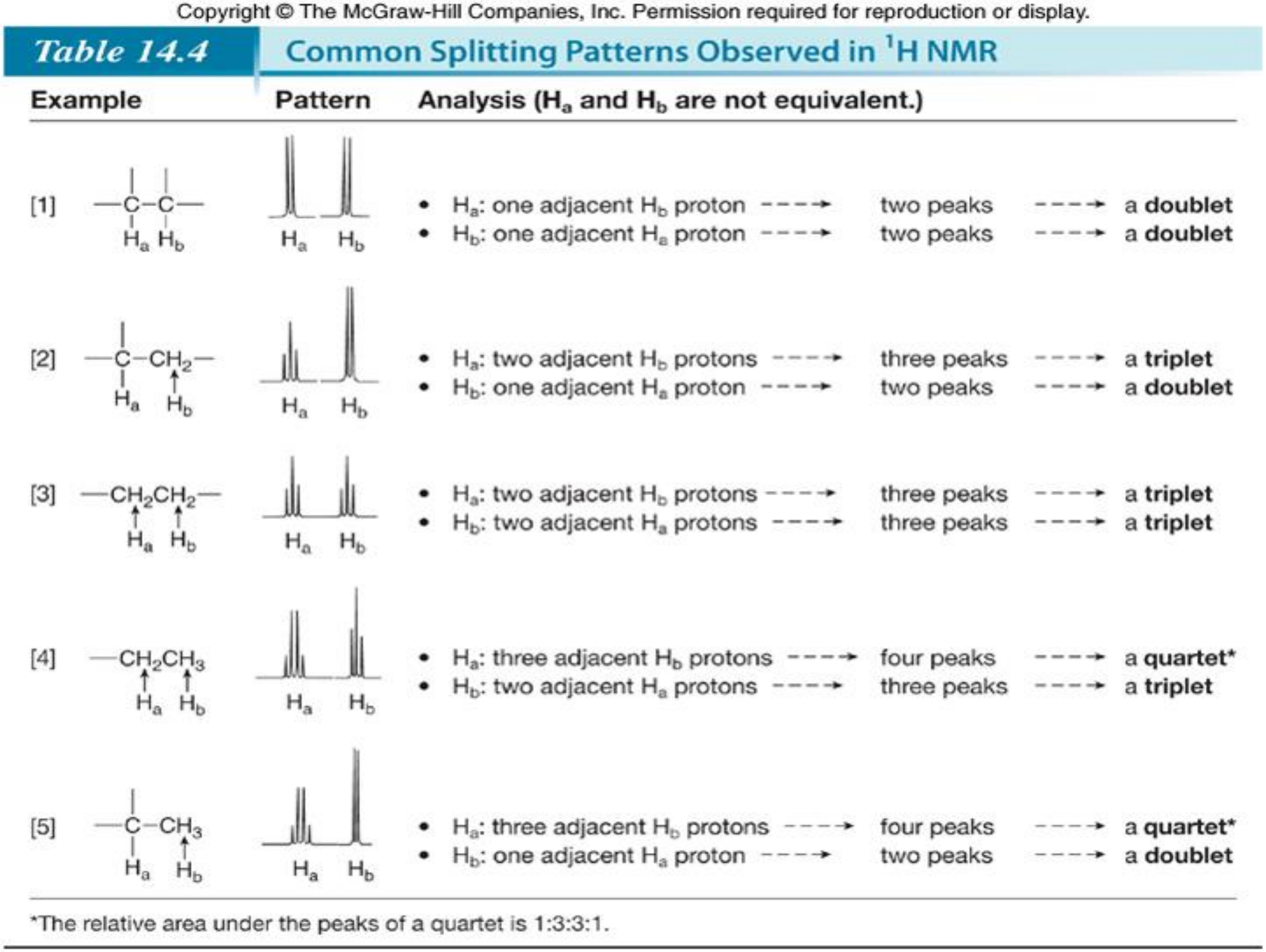


Table 14.4 Common Splitting Patterns Observed in ^1H NMR

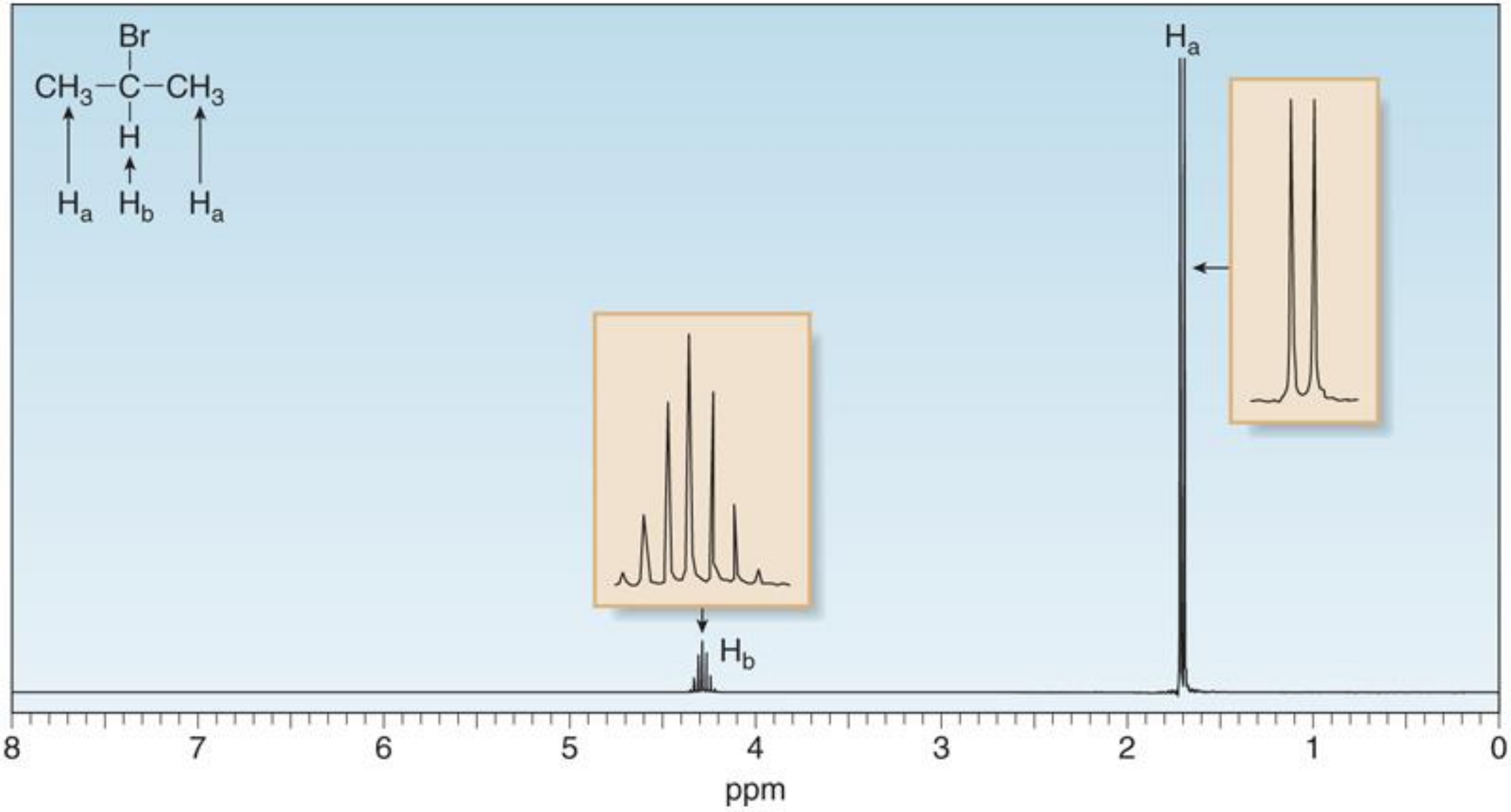
Example	Pattern	Analysis (H_a and H_b are not equivalent.)		
[1] $-\underset{H_a}{\overset{\mid}{C}}-\underset{H_b}{\overset{\mid}{C}}-$	H_a H_b	• H_a: one adjacent H_b proton ---→	two peaks ---→	a **doublet**
		• H_b: one adjacent H_a proton ---→	two peaks ---→	a **doublet**
[2] $-\underset{H_a}{\overset{\mid}{C}}-\underset{H_b}{CH_2}-$	H_a H_b	• H_a: two adjacent H_b protons ---→	three peaks ---→	a **triplet**
		• H_b: one adjacent H_a proton ---→	two peaks ---→	a **doublet**
[3] $-\underset{H_a}{CH_2}\underset{H_b}{CH_2}-$	H_a H_b	• H_a: two adjacent H_b protons ---→	three peaks ---→	a **triplet**
		• H_b: two adjacent H_a protons ---→	three peaks ---→	a **triplet**
[4] $-\underset{H_a}{CH_2}\underset{H_b}{CH_3}$	H_a H_b	• H_a: three adjacent H_b protons ---→	four peaks ---→	a **quartet***
		• H_b: two adjacent H_a protons ---→	three peaks ---→	a **triplet**
[5] $-\underset{H_a}{\overset{\mid}{C}}-\underset{H_b}{CH_3}$	H_a H_b	• 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.

Source:http://www2.chemistry.msu.edu/courses/cem251/FS11_HUANG/Chapter14_Smith3e_PPT.pdf

^{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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