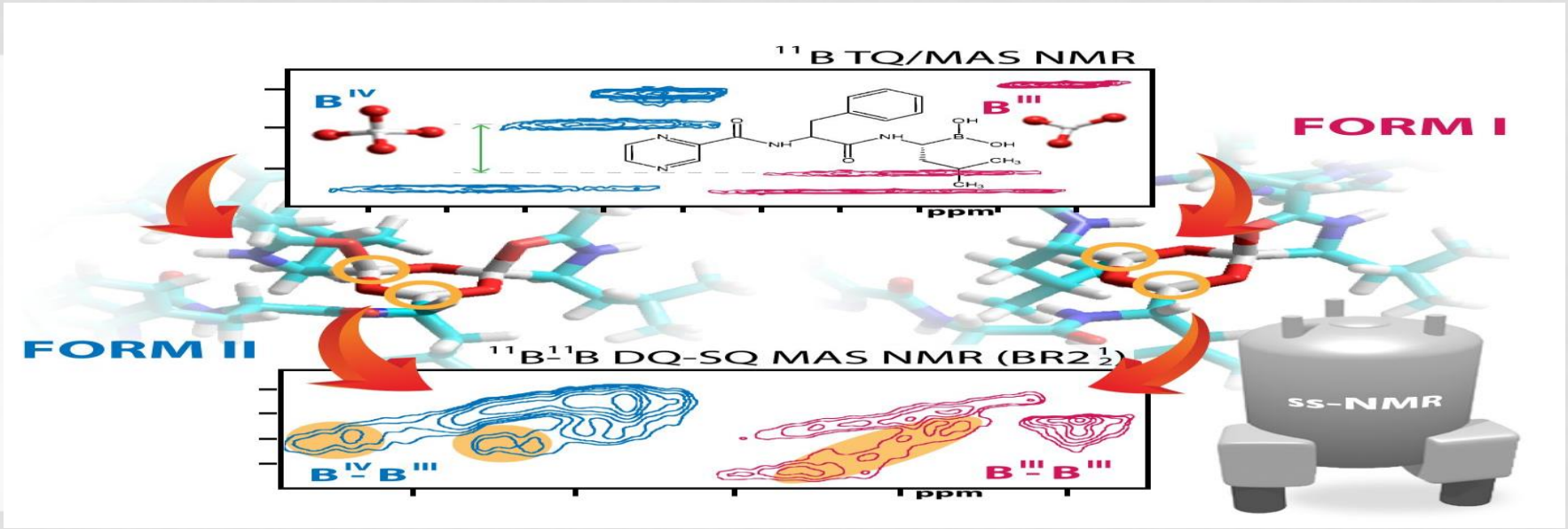
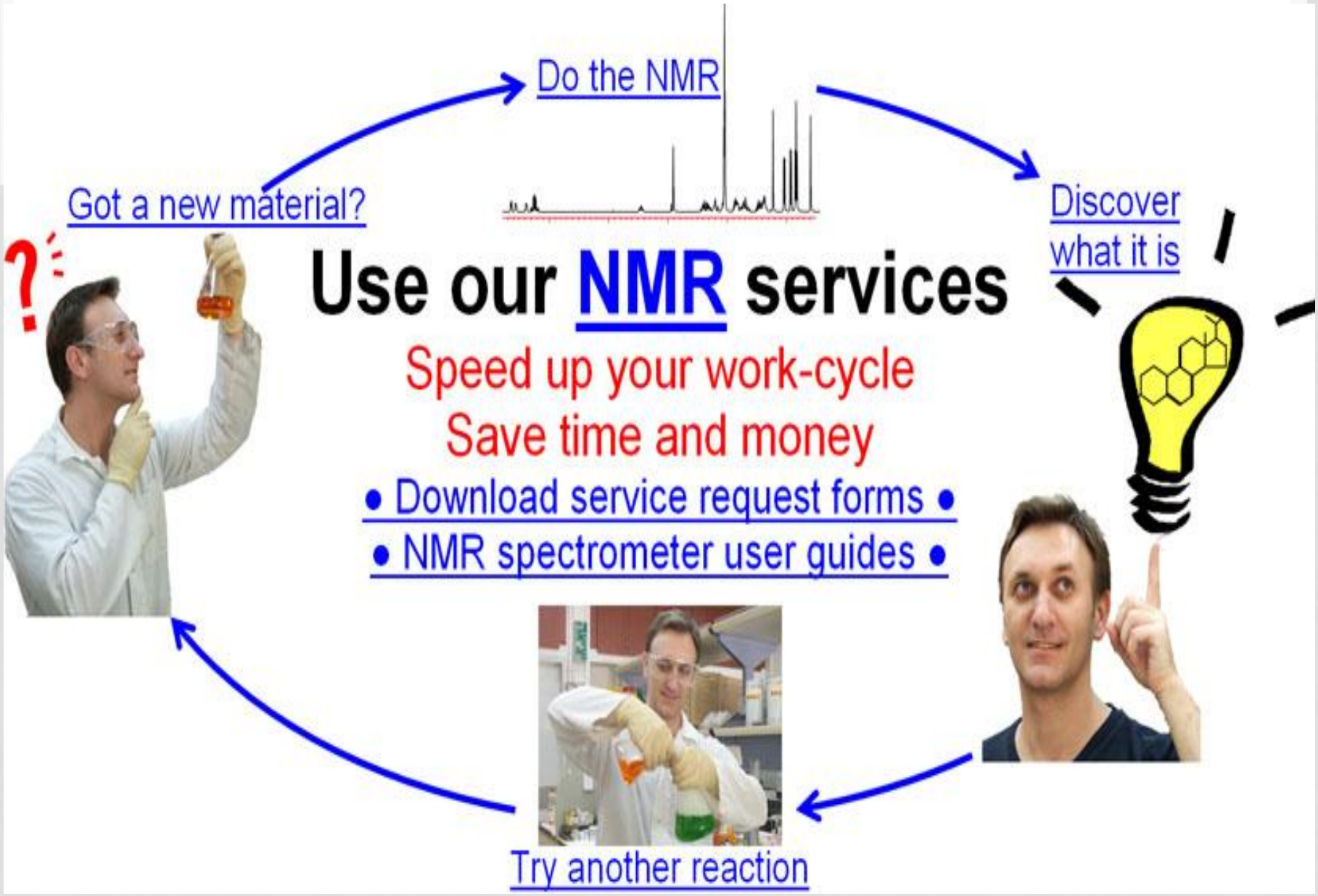
Nuclear Magnetic Resonance (**NMR**)



By:

Asst. Prof. Dr. ***Basma M. Abd Razik***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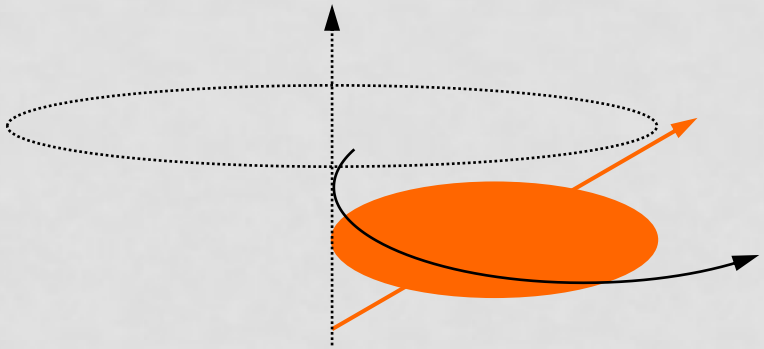
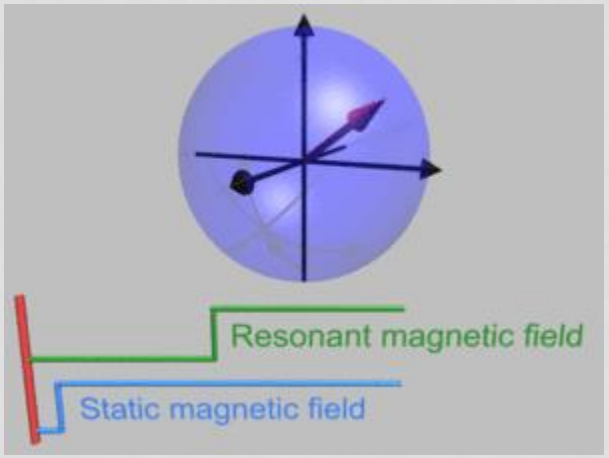
Introduction to NMR Spectroscopy

We begin by describing some magnetic properties of nuclei. All nuclei carry a charge. In some nuclei this charge "spins" on the nuclear axis, and this circulation of nuclear charge generates a magnetic dipole along the axis (Fig. 4.1). The angular momentum of the spinning charge can be described in terms of quantum spin numbers I; these numbers have values of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$, and so on ($I = 0$ denotes no spin). The intrinsic magnitude of the generated dipole is expressed in terms of nuclear magnetic moment, μ.





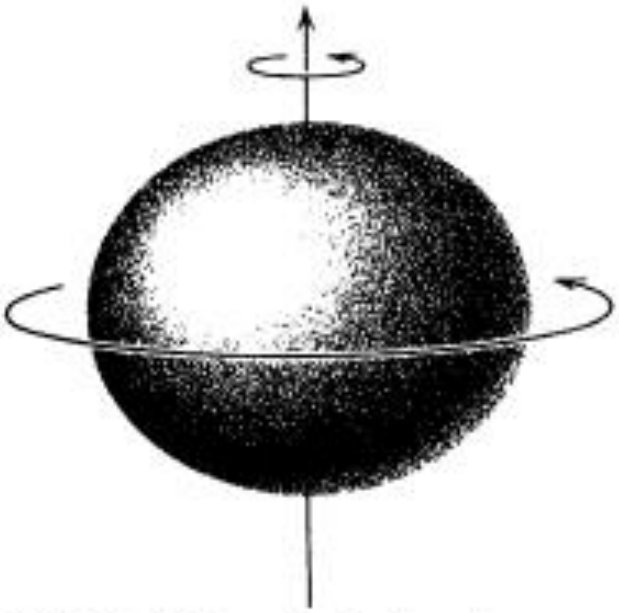
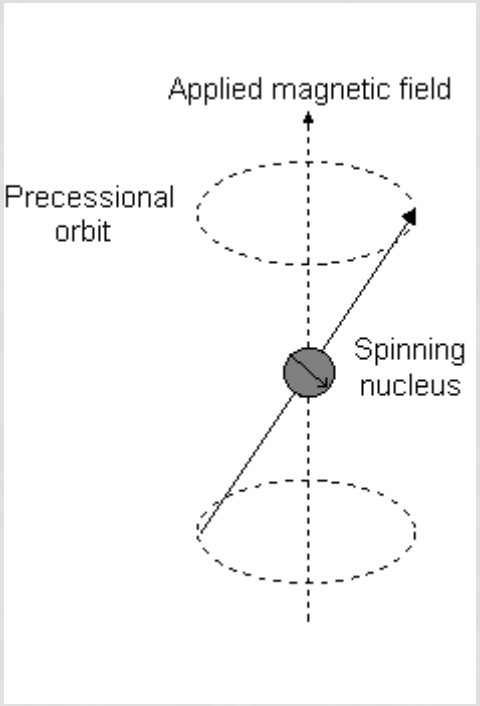


FIGURE 4.1. Spinning charge on proton generates magnetic dipole.



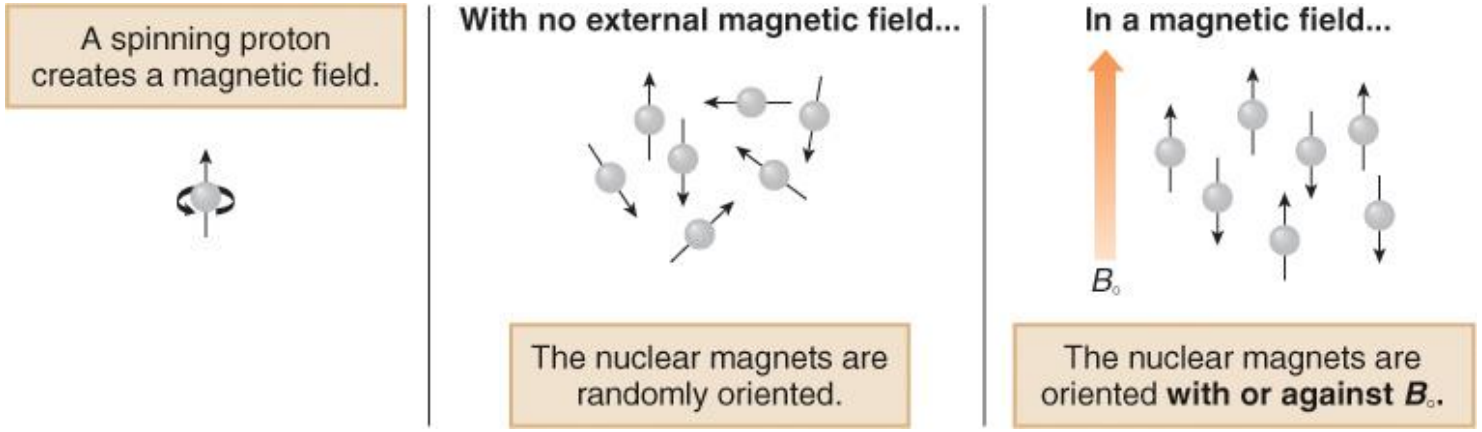
Relevant properties, including the spin number I, of several nuclei are given in Appendix H. The spin number I can be determined from the atomic mass and the atomic number as shown in the next column.

Spectra of several nuclei can be readily obtained (e.g., ${}^{1}_{1}\mathrm{H}$, ${}^{3}_{1}\mathrm{H}$, ${}^{13}_{6}\mathrm{C}$, ${}^{15}_{7}\mathrm{N}$, ${}^{19}_{9}\mathrm{F}$, ${}^{31}_{15}\mathrm{P}$) since they have spin numbers I of $\frac{1}{2}$ and a uniform spherical charge distribution

Nuclear Magnetic Resonance Spectroscopy

Introduction to NMR 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).



Energy Differentiation

Difference in energy between the two states is given by:

$$\Delta E = \gamma h B_o / 2\pi$$

where:

B_o – external magnetic field
h – Planck's constant
γ – gyromagnetic ratio

When the energy of the photon matches the energy difference between the two spin states , an absorption of energy occurs. We call that phenomenon *Resonance*

$$\Delta E = h\upsilon = \gamma h B_o / 2\pi \qquad \text{So, } \upsilon = \gamma B_o / 2\pi$$

THE ORIGIN OF NMR SIGNALS:

(THE NUCLEI OF NMR –"ACTIVE NUCLEI " BEHAVE LIKE TINY BAR MAGNETS)

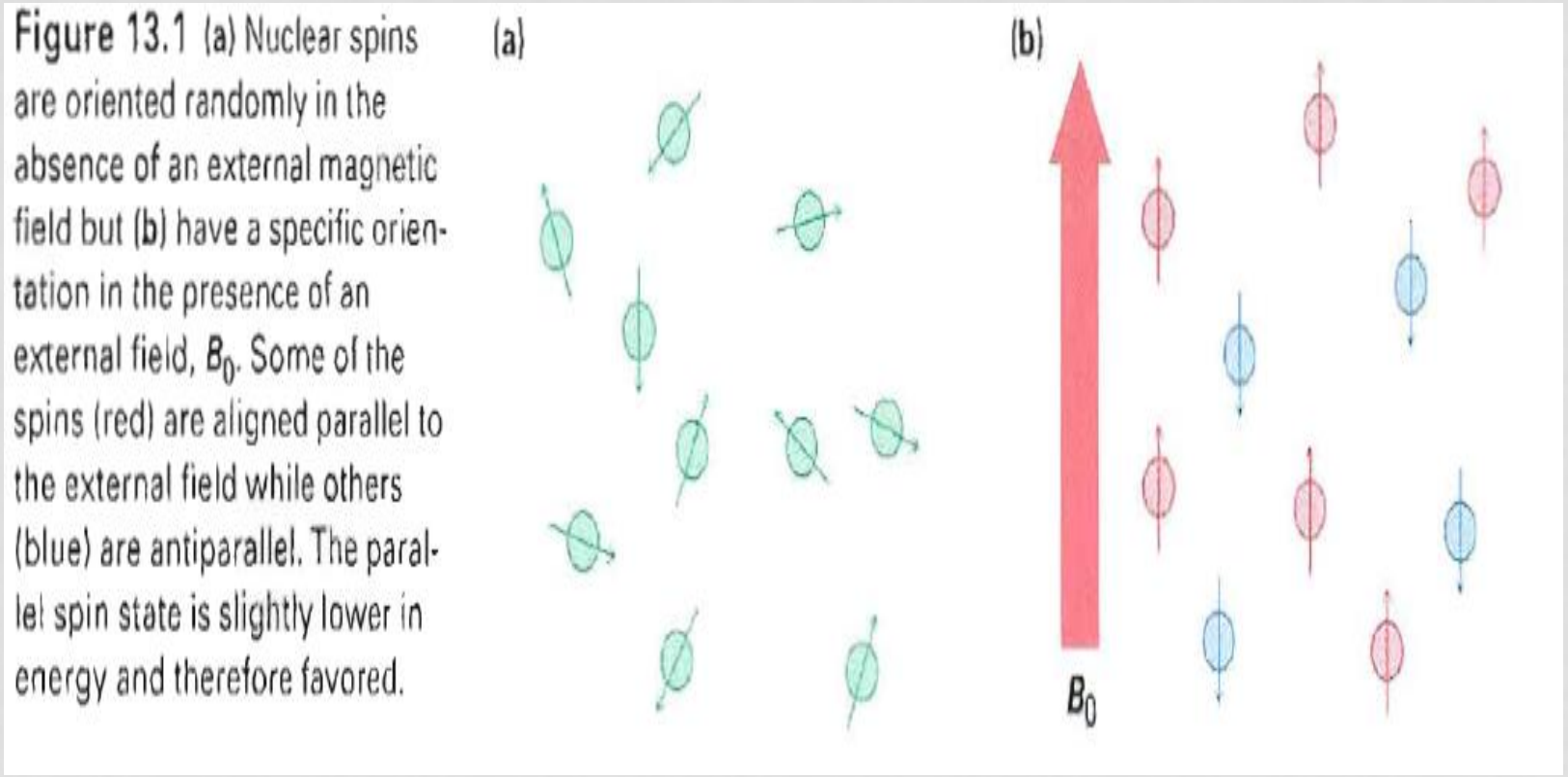
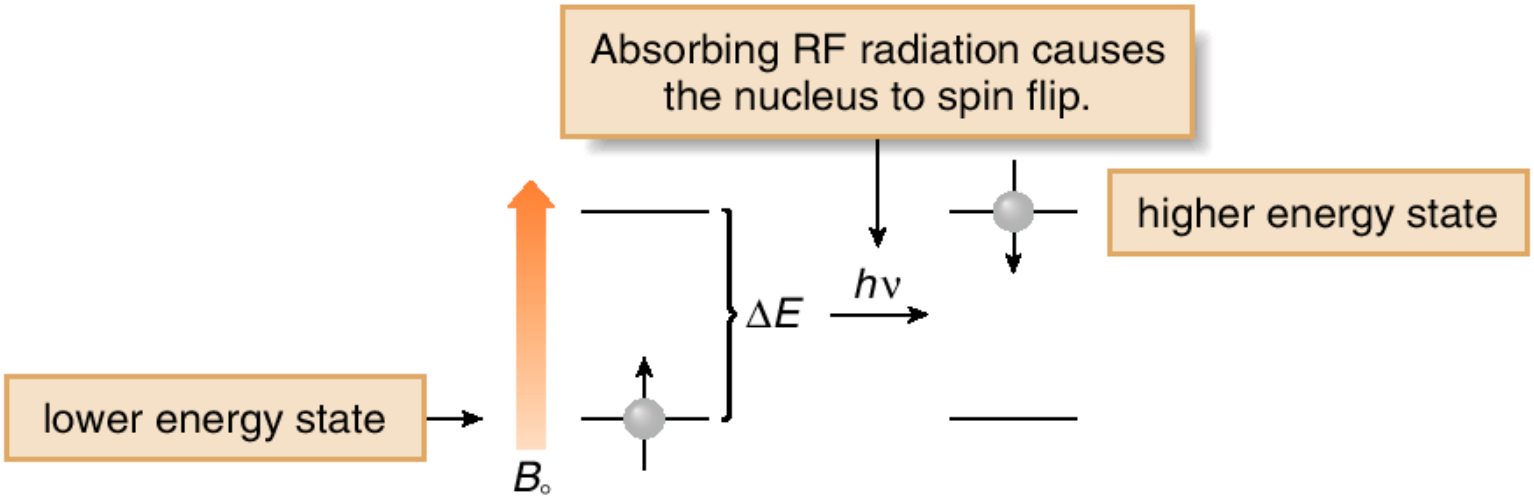


Figure 13.1 (a) Nuclear spins are oriented randomly in the absence of an external magnetic field but (b) have a specific orientation in the presence of an external field, B_0. Some of the spins (red) are aligned parallel to the external field while others (blue) are antiparallel. The parallel spin state is slightly lower in energy and therefore favored.

- Nuclei aligned with the magnetic field are lower in energy than those aligned against the field.
- The nuclei aligned with the magnetic field can be flipped "spin-flip" to the higher-energy state if the right amount of energy is added (DE).
- When this spin-flip occurs, the magnetic nuclei are said to be in resonance with the applied radiation hence the name nuclear magnetic resonance
- The amount of energy required depends on:
- the strength of the external magnetic field
- The identity of the nuclei.

Introduction to NMR Spectroscopy

- **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).**



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

Chemical Shift-δ

The electron density around each nucleus in a molecule varies according to the types of nuclei and bonds in the molecule. The opposing field and therefore the effective field at each nucleus will vary. This is called the chemical shift phenomenon.

the greater the value of B_o, the greater the frequency difference. This relationship could make it difficult to compare NMR spectra taken on spectrometers operating at different field strengths.

The term chemical shift was developed to avoid this problem. The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standard, relative to the standard.

The operation of a basic NMR spectrometer is illustrated in Figure 13.4. An organic sample is dissolved in a suitable solvent (usually deuteriochloroform, $CDCl_3$, which has no hydrogens) and placed in a thin glass tube between the poles of a magnet. The strong magnetic field causes the ^1H and ^{13}C nuclei in the molecule to align in one of the two possible orientations, and the sample is irradiated with rf energy. If the frequency of the rf irradiation is held constant and the strength of the applied magnetic field is varied, each nucleus comes into resonance at a slightly different field strength. A sensitive detector monitors the absorption of rf energy, and the electronic signal is then amplified and displayed as a peak.

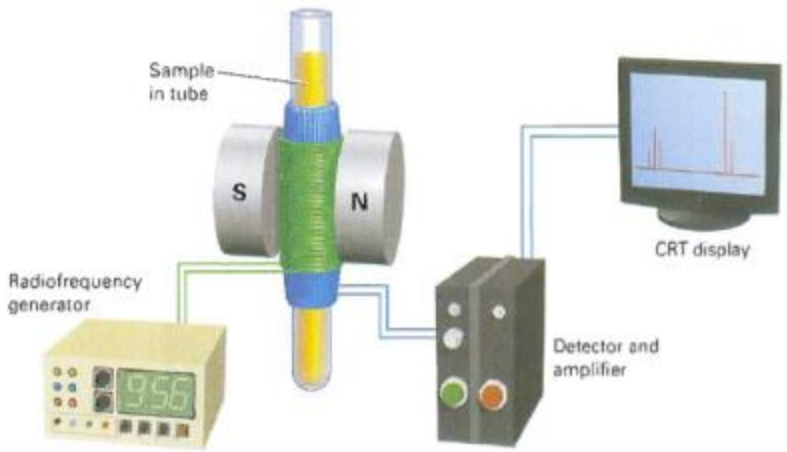
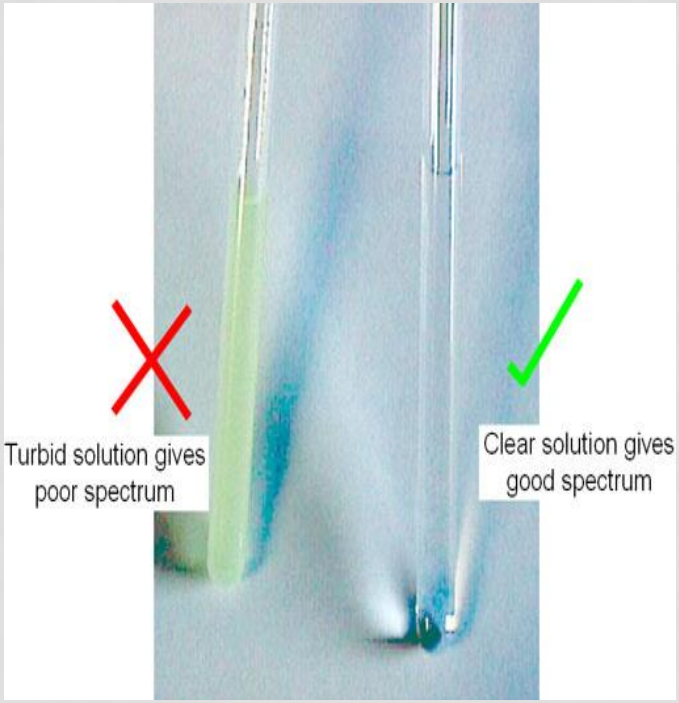
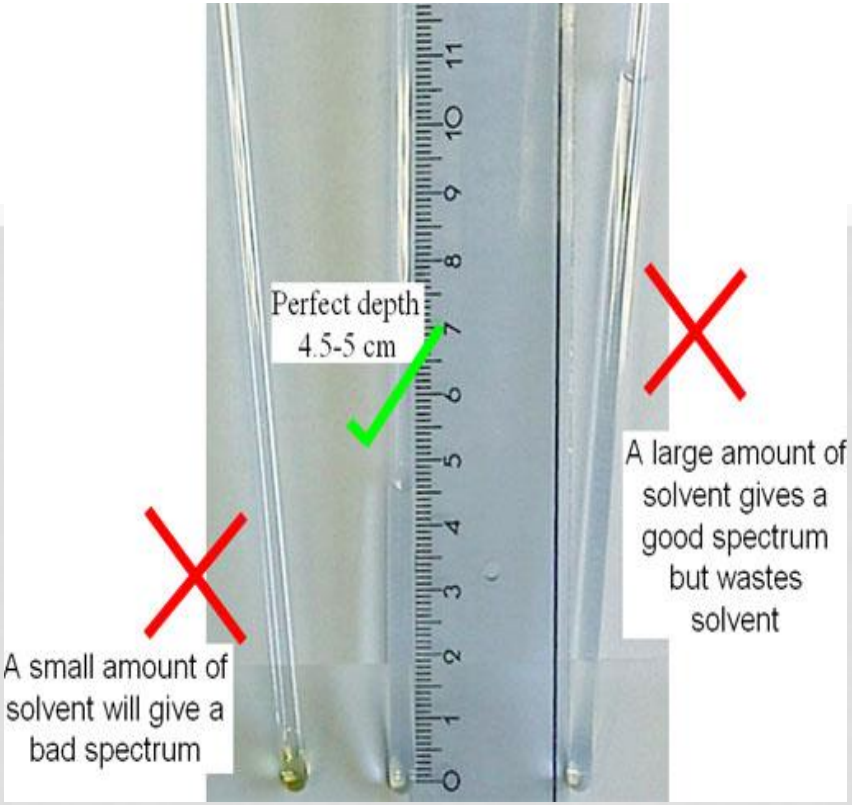


Figure 13.4 Schematic operation of an NMR spectrometer. A thin glass tube containing the sample solution is placed between the poles of a strong magnet and irradiated with rf energy.

NMR SPECTROSCOPY DIFFER FROM" IR" SPECTROSCOPY:

The energy needed for NMR is much smaller than that required for IR Spectroscopy.


Turbid solution gives poor spectrum
Clear solution gives good spectrum


Perfect depth 4.5-5 cm
A small amount of solvent will give a bad spectrum
A large amount of solvent gives a good spectrum but wastes solvent

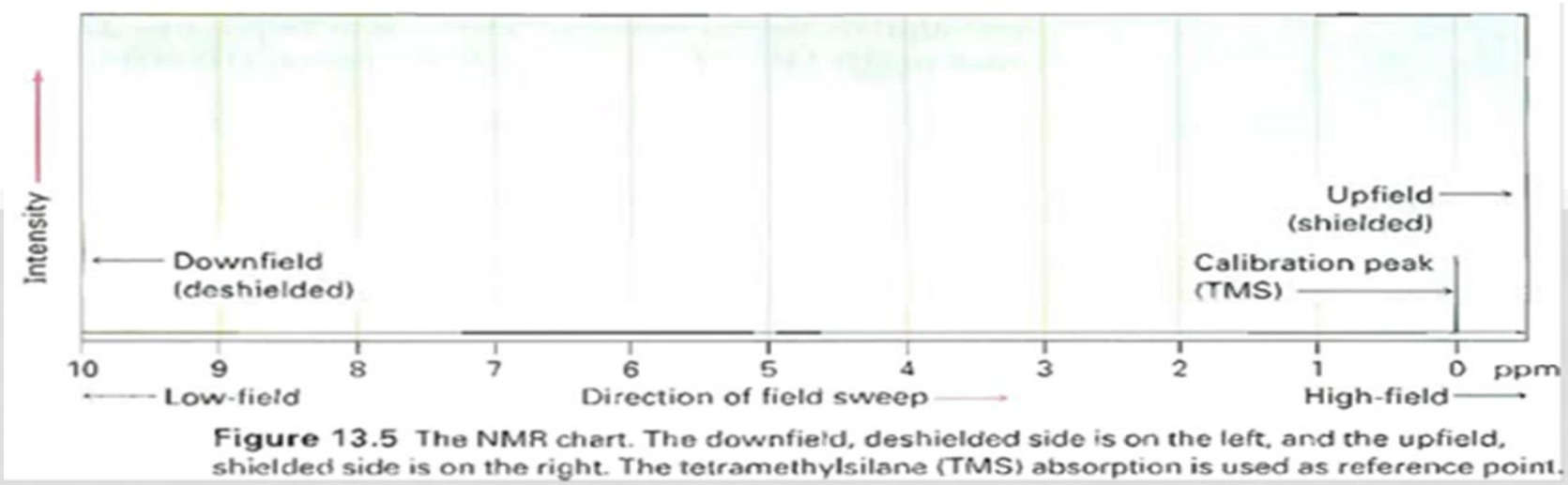
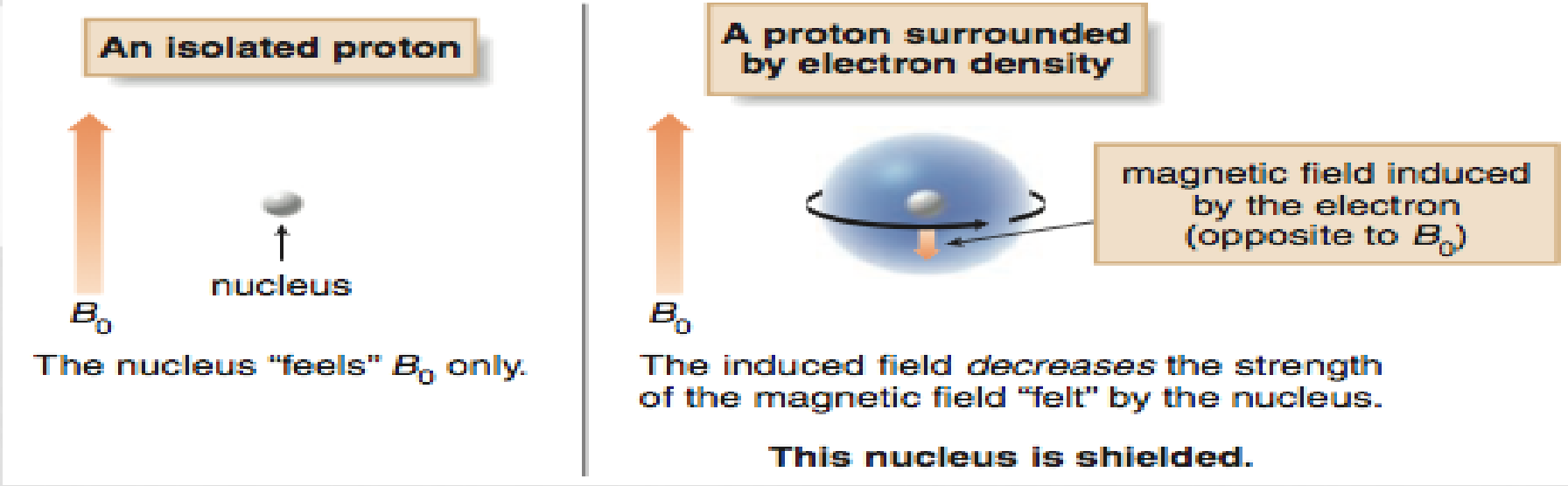


Figure 13.5 The NMR chart. The downfield, deshielded side is on the left, and the upfield, shielded side is on the right. The tetramethylsilane (TMS) absorption is used as reference point.

Shielding requires a higher magnetic field to bring the nucleus into resonance - the signals are up field in the NMR spectrum

Lower electron density around a nucleus deshields the nucleus from the external magnetic field

Deshielding causes absorption of energy at lower frequencies – the signals are downfield in the NMR spectrum



Shielding:
The higher the electron density around the nucleus, the higher the opposing magnetic field to B0 from the electrons, the greater the shielding. Because the proton experiences lower external magnetic field, it needs a lower frequency to achieve resonance, and therefore, the chemical shift shifts **upfield (lower ppms)** .

Deshielding:
If the electron density around a nucleus decreases, the opposing magnetic field becomes small and therefore, the nucleus feels more the external magnetic field B0, and therefore it is said to be deshielded. Because the proton experiences higher external magnetic field, it needs a higher frequency to achieve resonance, and therefore, the chemical shift shifts **downfield (higher ppms)**

- **The less shielded the nucleus becomes, the more of the applied magnetic field (B0) 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.

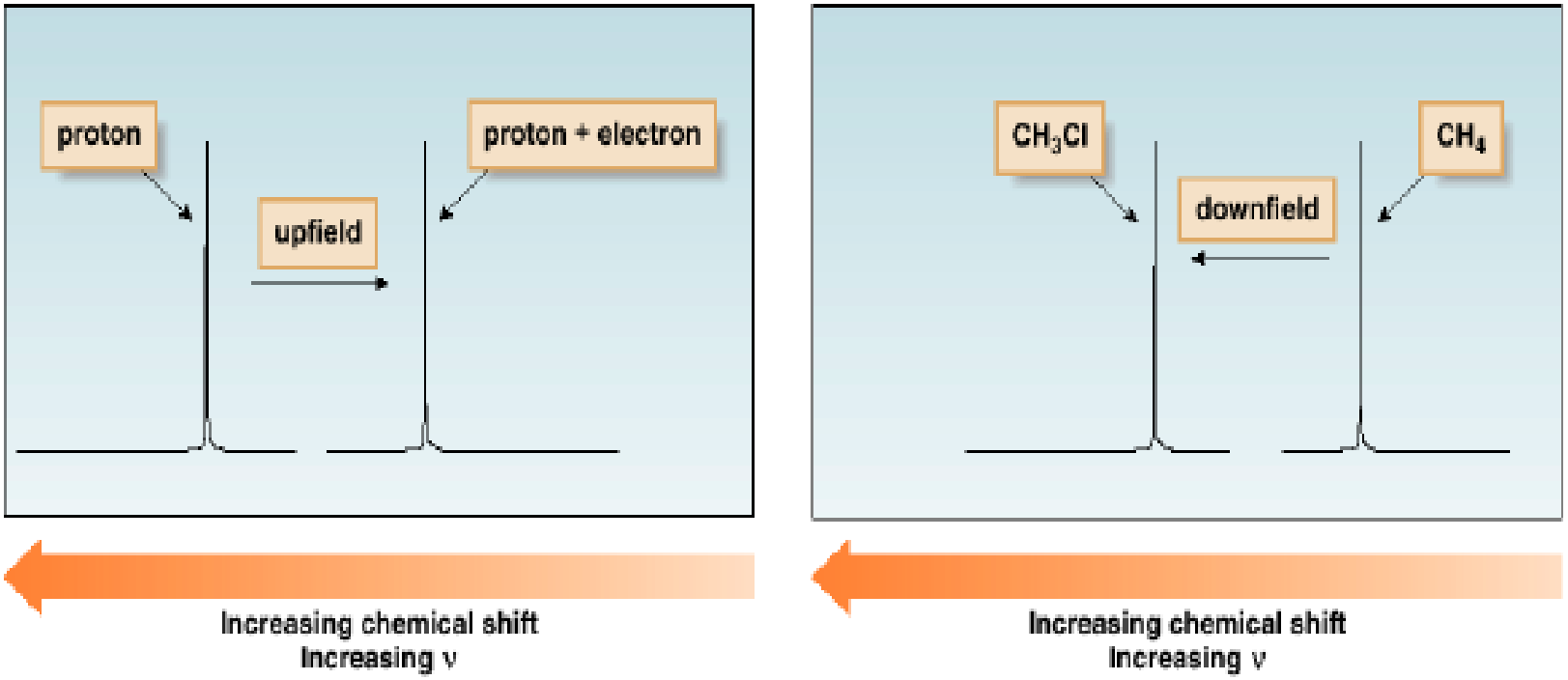
- **Protons near electronegative atoms are deshielded, so they absorb downfield.**

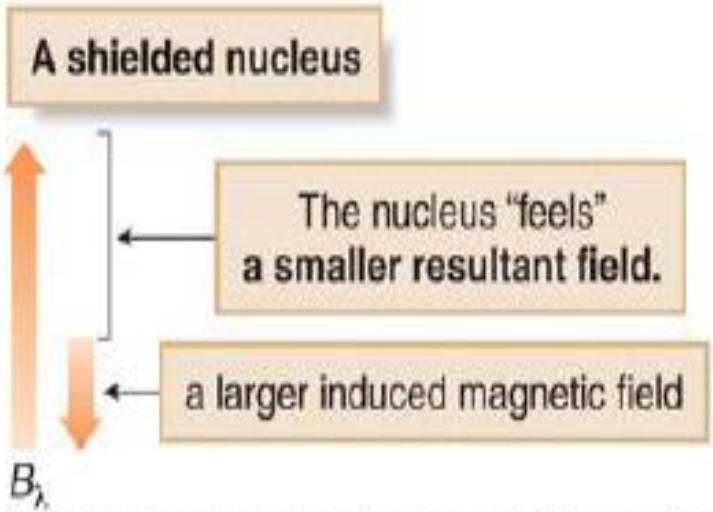
a. Shielding effects

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

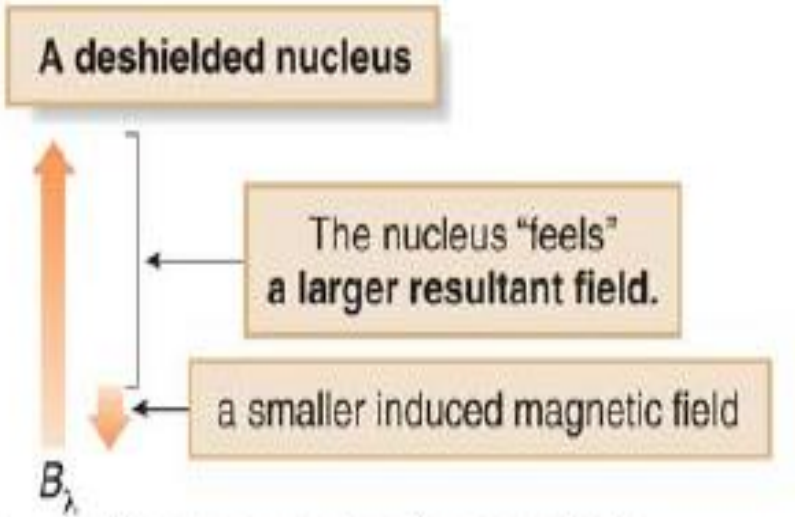
b. Deshielding effects

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

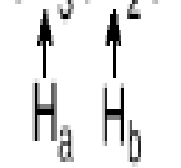




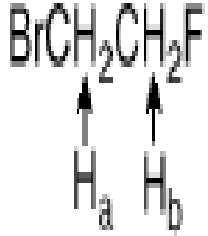
- As the electron density around the nucleus increases, the nucleus feels a smaller resultant magnetic field, so a lower frequency is needed to achieve resonance.
- **The absorption shifts upfield.**



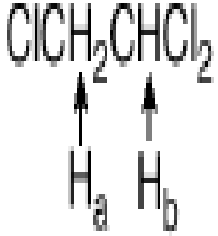
- As the electron density around the nucleus decreases, the nucleus feels a larger resultant magnetic field, so a higher frequency is needed to achieve resonance.
- **The absorption shifts downfield.**



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



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



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

^{1}H NMR—Chemical Shift Values

- **Protons in a given environment absorb in a predictable region in an NMR spectrum.**

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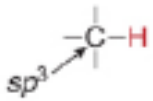
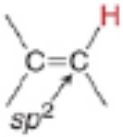
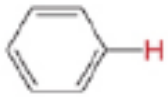
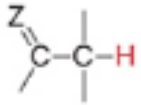
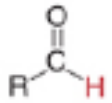
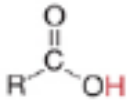
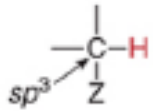
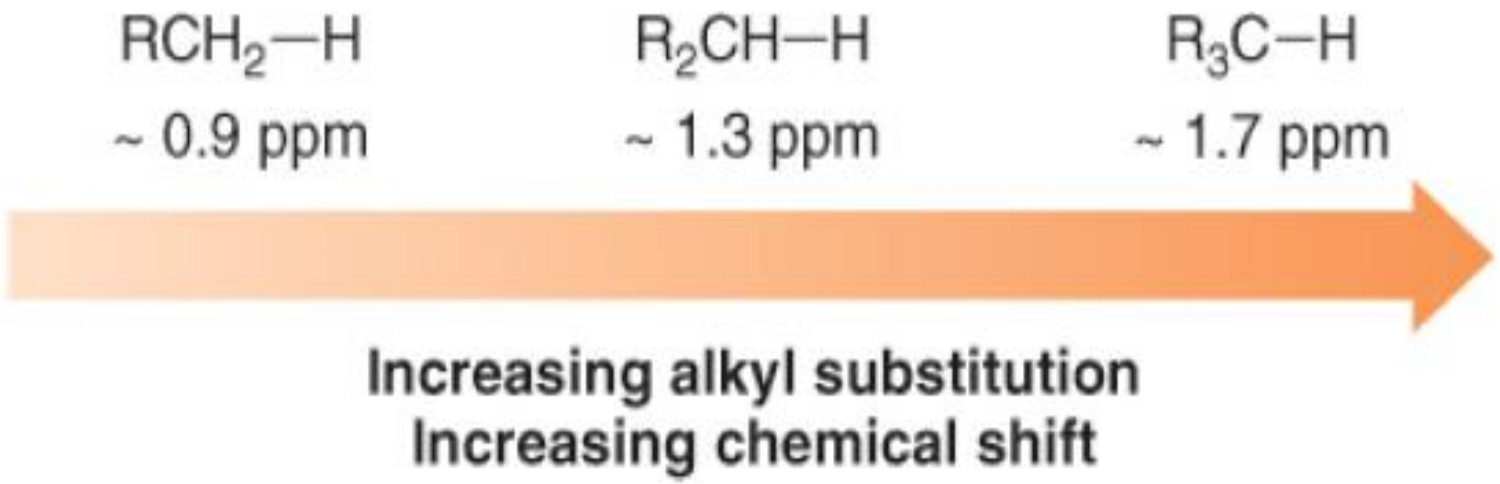
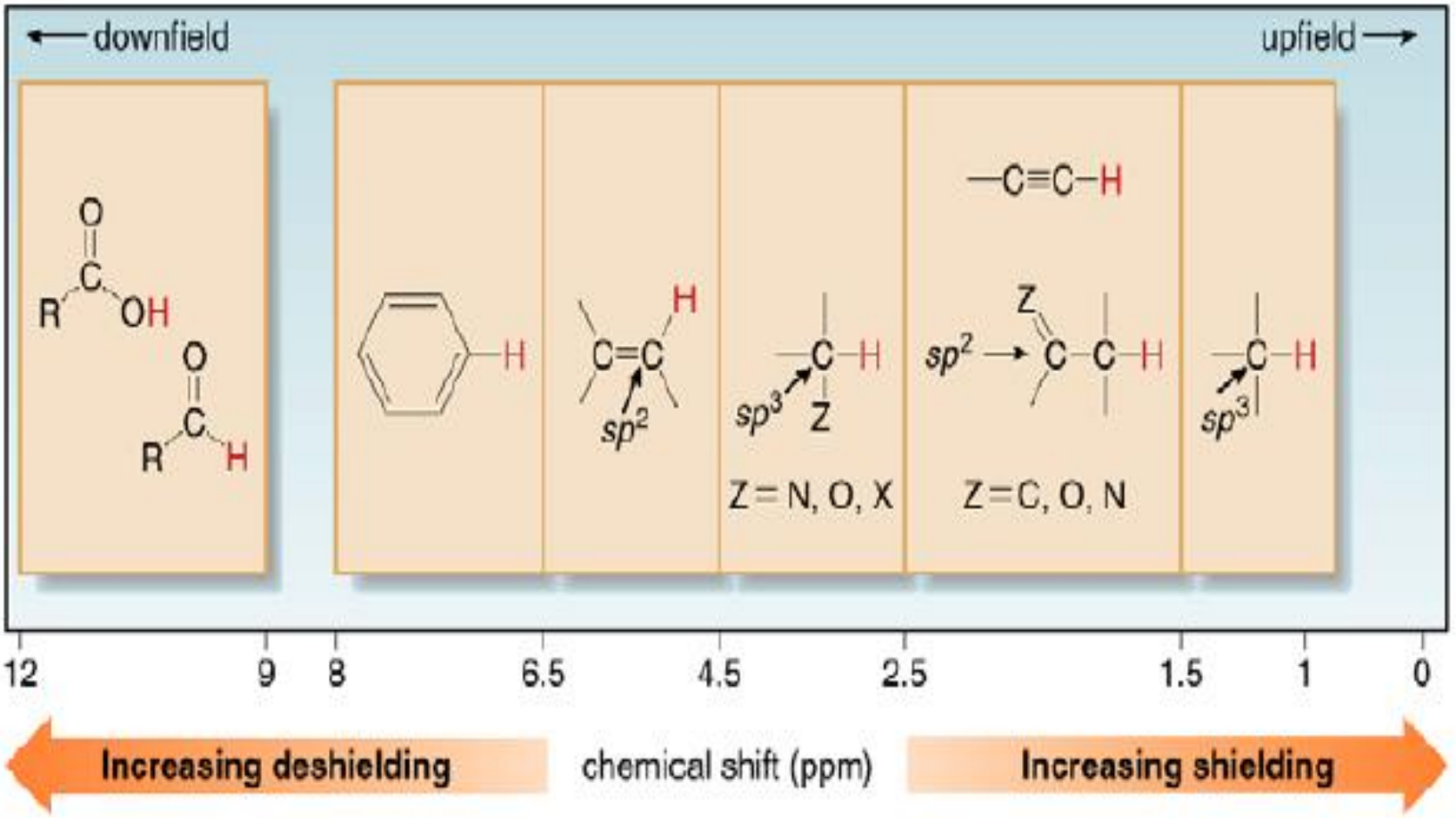
Table 14.1 Characteristic Chemical Shifts of Common Types of Protons

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
	0.9–2		4.5–6
• RCH_3 • R_2CH_2 • R_3CH	~0.9 ~1.3 ~1.7		6.5–8
 Z = C, O, N	1.5–2.5		9–10
—C≡C—H	~2.5		10–12
 Z = N, O, X	2.5–4	RO—H or R—N—H	1–5

- **The chemical shift of a C—H bond increases with increasing alkyl substitution.**

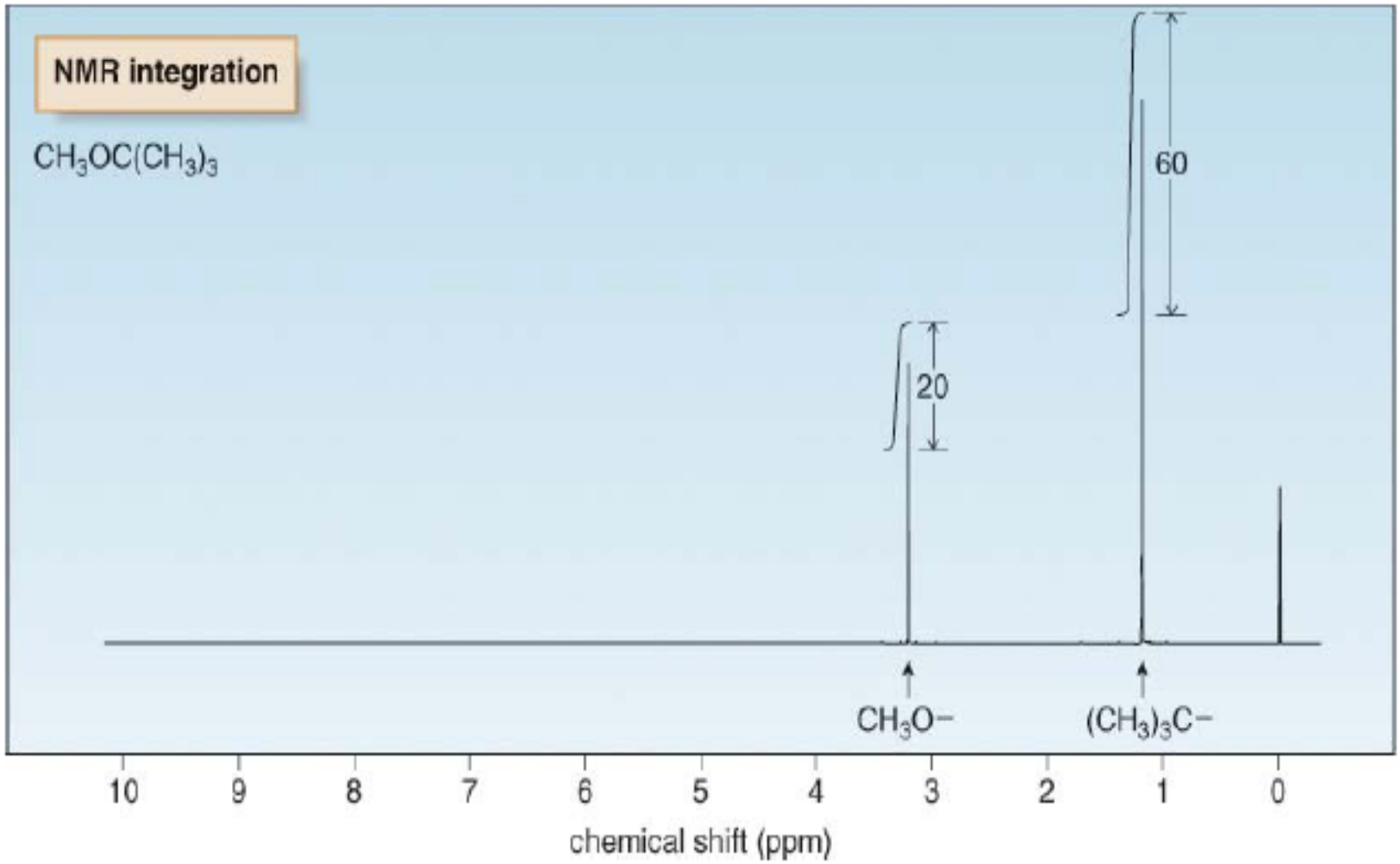




- Shielded protons absorb at lower chemical shift (to the right).
- Deshielded protons absorb at higher chemical shift (to the left).

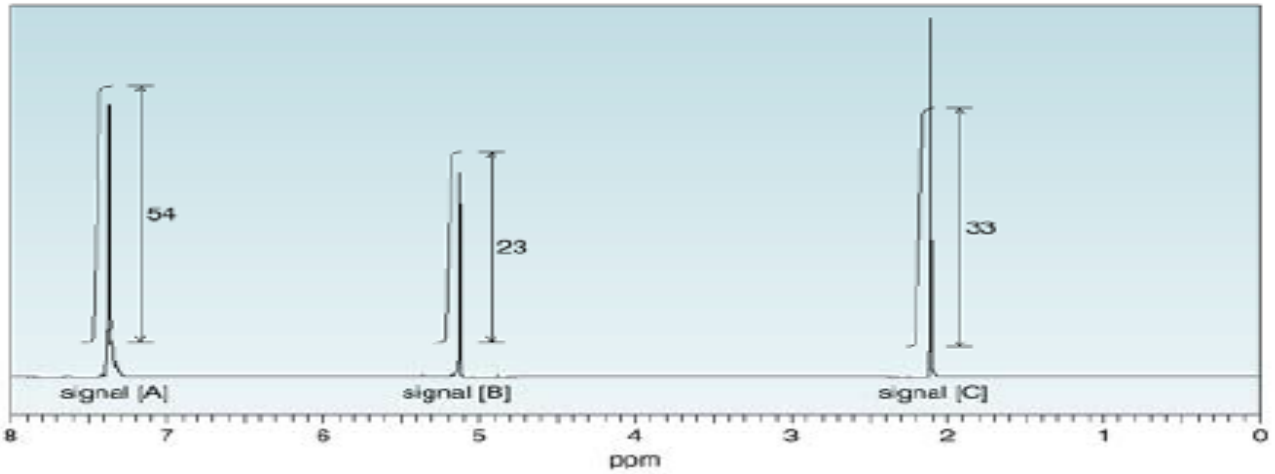
14.5 ^{1}H NMR—Intensity of Signals

- The area under an NMR signal is proportional to the number of absorbing protons.
- An NMR spectrometer automatically integrates the area under the peaks, and prints out a stepped curve (integral) on the spectrum.
- The height of each step is proportional to the area under the peak, which in turn is proportional to the number of absorbing protons.
- Modern NMR spectrometers automatically calculate and plot the value of each integral in arbitrary units.
- The ratio of integrals to one another gives the ratio of absorbing protons in a spectrum. Note that this gives a ratio, and not the absolute number, of absorbing protons.


NMR integration
$CH_3OC(CH_3)_3$
60
20
CH_3O-
$(CH_3)_3C-$
10
9
8
7
6
5
4
3
2
1
0
chemical shift (ppm)

How To Determine the Number of Protons Giving Rise to an NMR Signal

Example A compound of molecular formula $C_5H_{10}O_2$ gives the following integrated ^1H NMR spectrum. How many protons give rise to each signal?



Step [1] Determine the number of integration units per proton by dividing the total number of integration units by the total number of protons.

- Total number of integration units: 54 + 23 + 33 = 110 units
- Total number of protons = 10
- Divide: 110 units/10 protons = **11 units per proton**

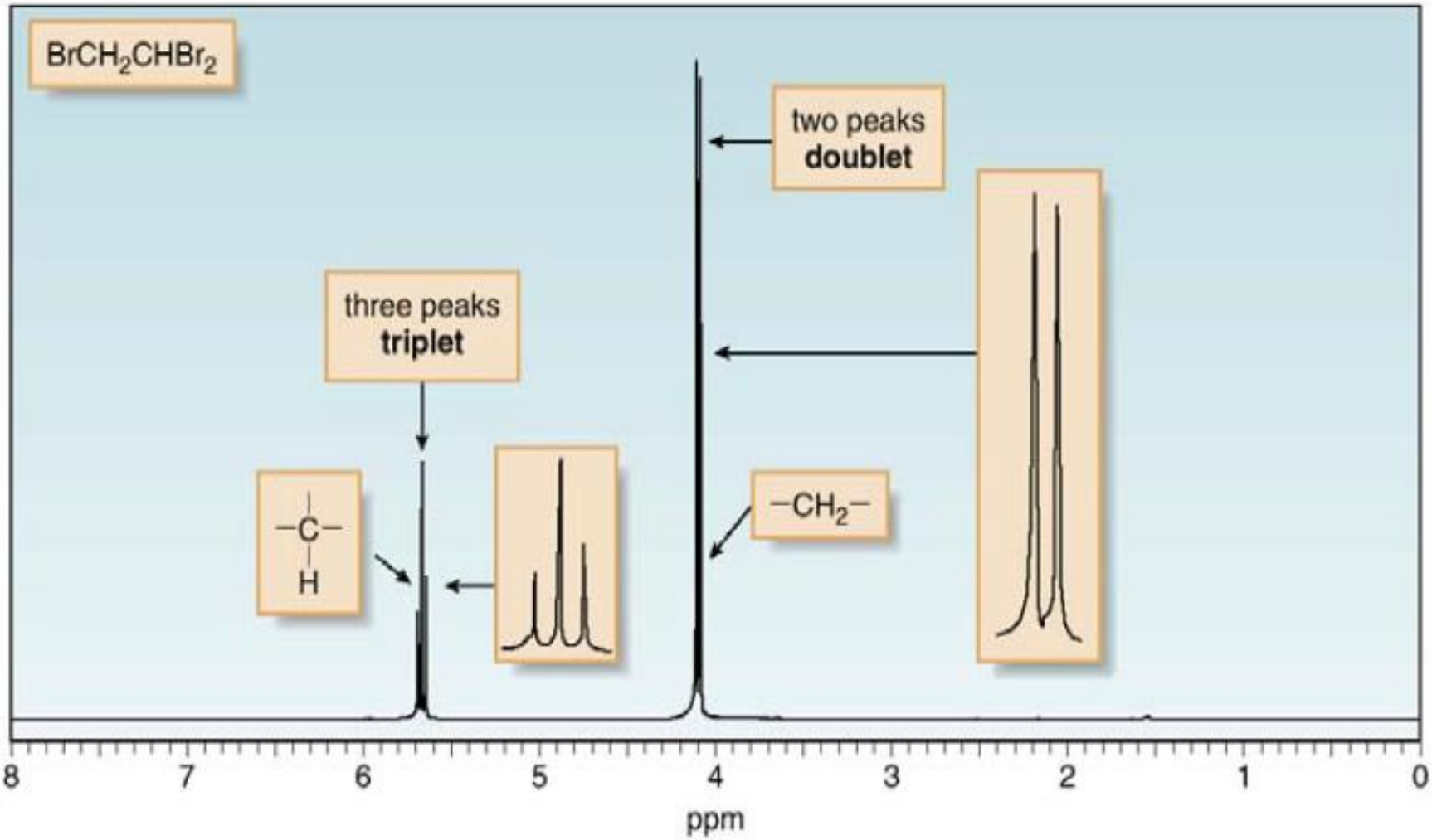
Step [2] Determine the number of protons giving rise to each signal.

- To determine the number of H atoms giving rise to each signal, divide each integration value by the answer of Step [1] and round to the nearest whole number.

Signal [A]:	Signal [B]:	Signal [C]:
Answer: $\frac{54}{11} = 4.9 \approx$ **5 H**	$\frac{23}{11} = 2.1 \approx$ **2 H**	$\frac{33}{11} =$ **3 H**

14.6 ^{1}H NMR—Spin-Spin Splitting

- Consider the spectrum below:



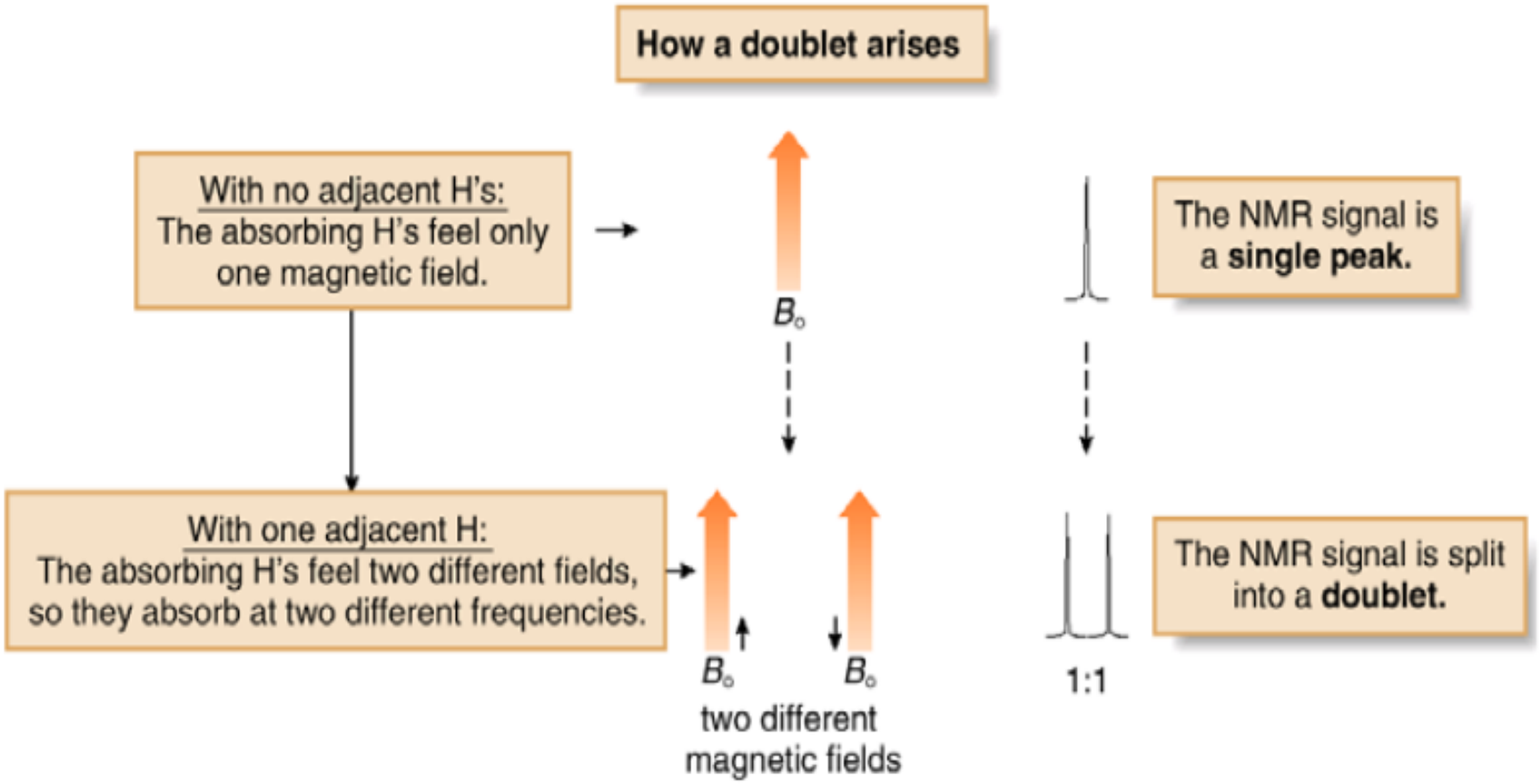
^{1}H NMR—Spin-Spin Splitting

- 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:

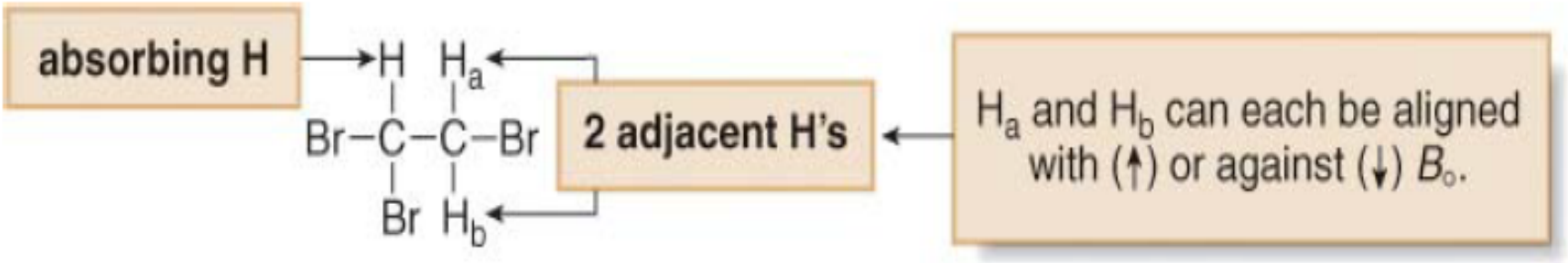
- When placed in an applied electric field, (B_0), the adjacent proton ($CHBr_2$) can be aligned with (↑) or against (↓) B_0.
- Thus, the absorbing CH_2 protons feel two slightly different magnetic fields—one slightly larger than B_0, and one slightly smaller than B_0.
- Since the absorbing protons feel two different magnetic fields, they absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet.

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



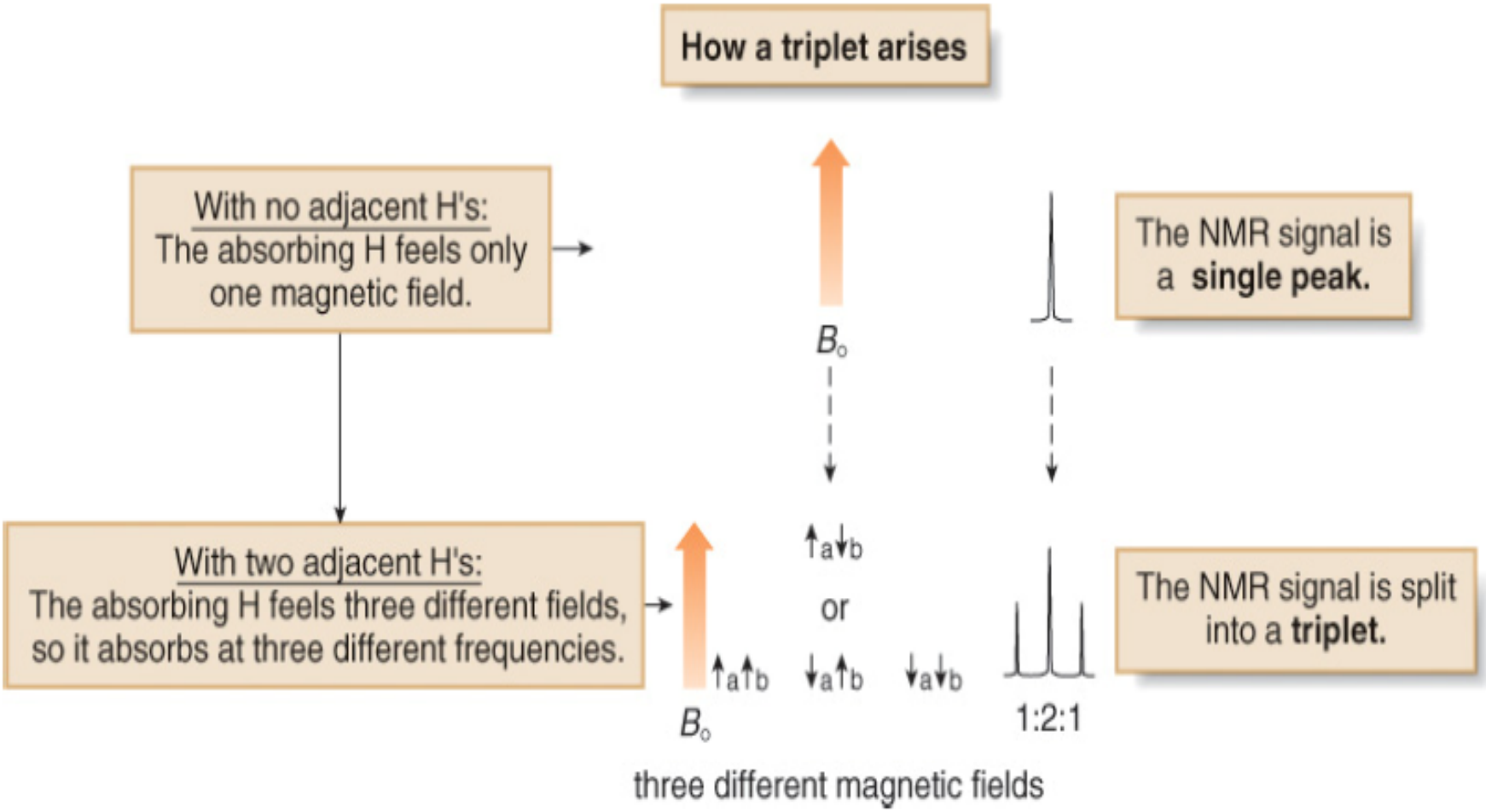
- One adjacent proton splits an NMR signal into a doublet.

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

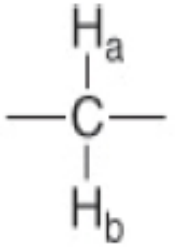
- Because the absorbing proton feels three different magnetic fields, it absorbs at three different frequencies in the NMR spectrum, thus splitting a single absorption into a triplet.
- Because there are two different ways to align one proton with B_0, and one proton against B_0—that is, $\uparrow_a\downarrow_b$ 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.

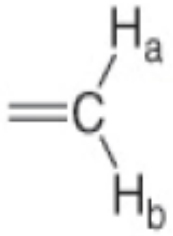

How a triplet arises
With no adjacent H's:
The absorbing H feels only one magnetic field.
B_o
The NMR signal is a single peak.
With two adjacent H's:
The absorbing H feels three different fields, so it absorbs at three different frequencies.
$\uparrow_a\downarrow_b$
or
$\uparrow_a\uparrow_b$ $\downarrow_a\uparrow_b$ $\downarrow_a\downarrow_b$
B_o
1:2:1
The NMR signal is split into a triplet.
three different magnetic fields

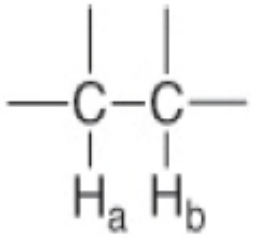
Three general rules describe the splitting patterns commonly seen in the ^{1}H NMR spectra of organic compounds.

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:



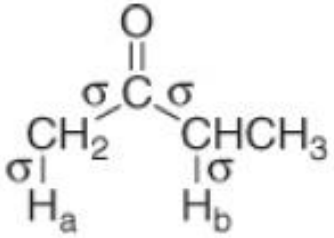




H_a and H_b are on the **same** carbon.

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

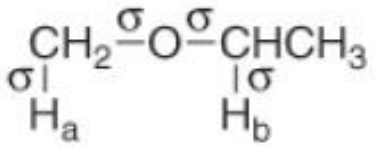
Splitting is not generally observed between protons separated by more than three σ bonds.



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

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Table 14.3 **Names for a Given Number of Peaks in an NMR Signal**

Number of peaks	Name	Number of peaks	Name
1	singlet	5	quintet
2	doublet	6	sextet
3	triplet	7	septet
4	quartet	> 7	multiplet

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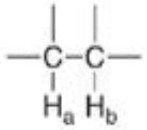
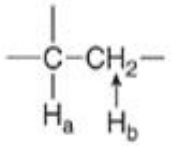
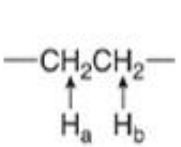
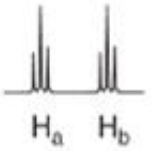
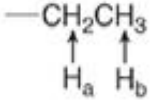
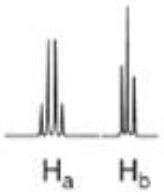
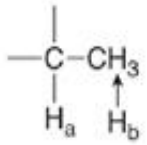
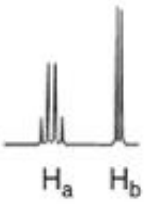
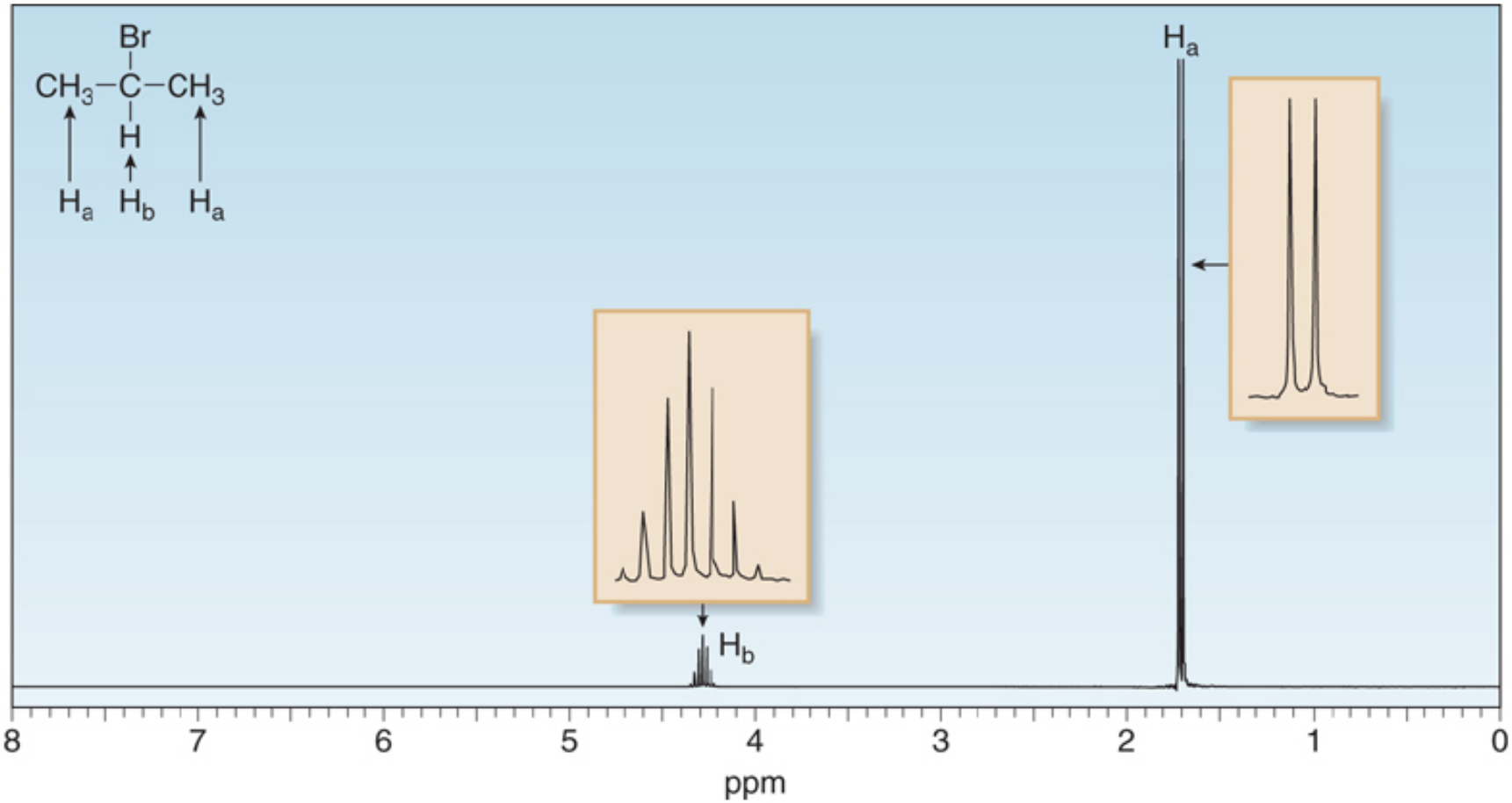
Table 14.4 Common Splitting Patterns Observed in ^{1}H NMR

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**

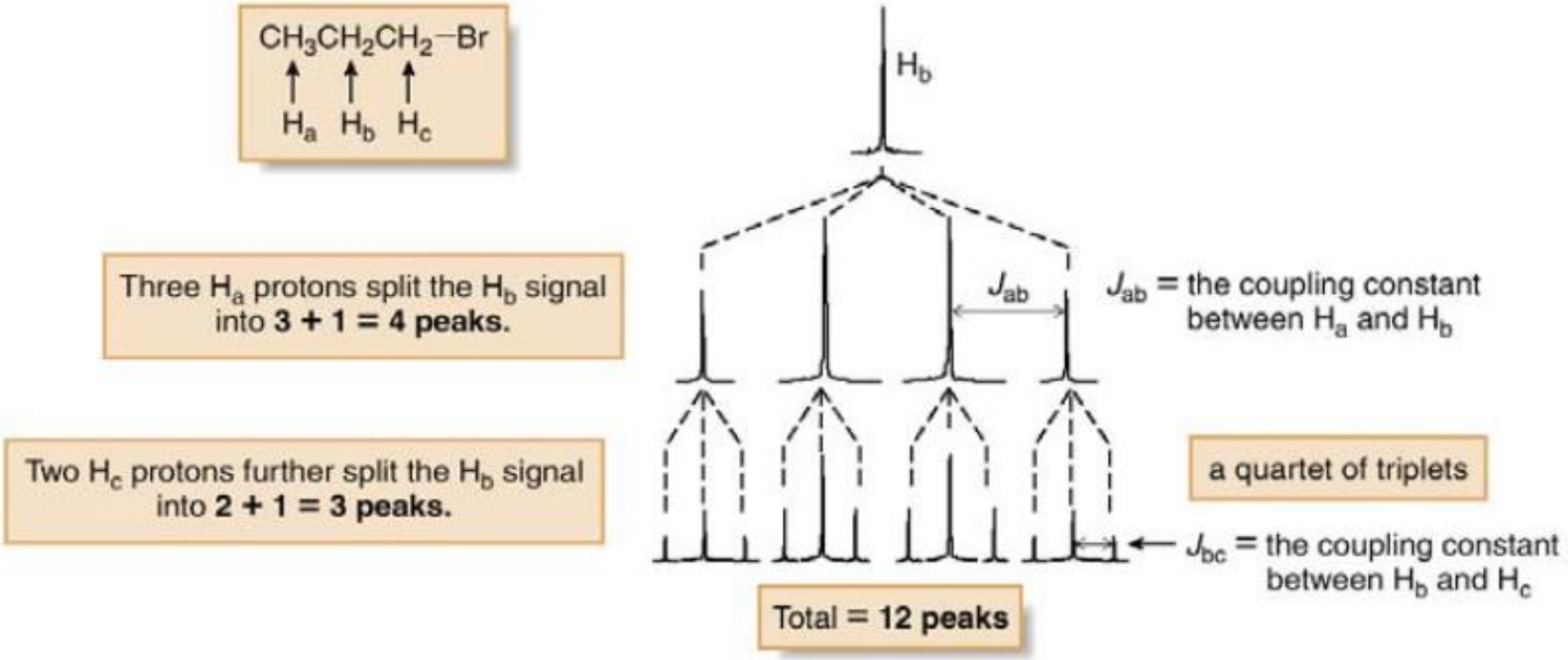
Whenever two (or three) different sets of adjacent protons are equivalent to each other, use the n + 1 rule to determine the splitting pattern.

Figure 14.6 The 1H NMR spectrum of 2-bromopropane, $[(CH_3)_2CHBr]$



When two sets of adjacent protons are different from each other (n protons on one adjacent carbon and m protons on the other), the number of peaks in an NMR signal = (n + 1)(m + 1).

Figure 14.8 A splitting diagram for the H_b protons in 1-bromopropane



- The H_b signal is split into 12 peaks, a quartet of triplets. The number of peaks actually seen for the signal depends on the relative size of the coupling constants, J_{ab} and J_{bc}. When $J_{ab} >> J_{bc}$, as drawn in this diagram, all 12 lines of the pattern are visible. When J_{ab} and J_{bc} are similar in magnitude, peaks overlap and fewer lines are observed.

- Protons on carbon-carbon double bonds often give characteristic splitting patterns.
- A disubstituted double bond can have two geminal protons, two cis protons, or two trans protons.
- When these protons are different, each proton splits the NMR signal of the other so that each proton appears as a doublet.
- The magnitude of the coupling constant *J* for these doublets depends on the arrangement of hydrogen atoms.

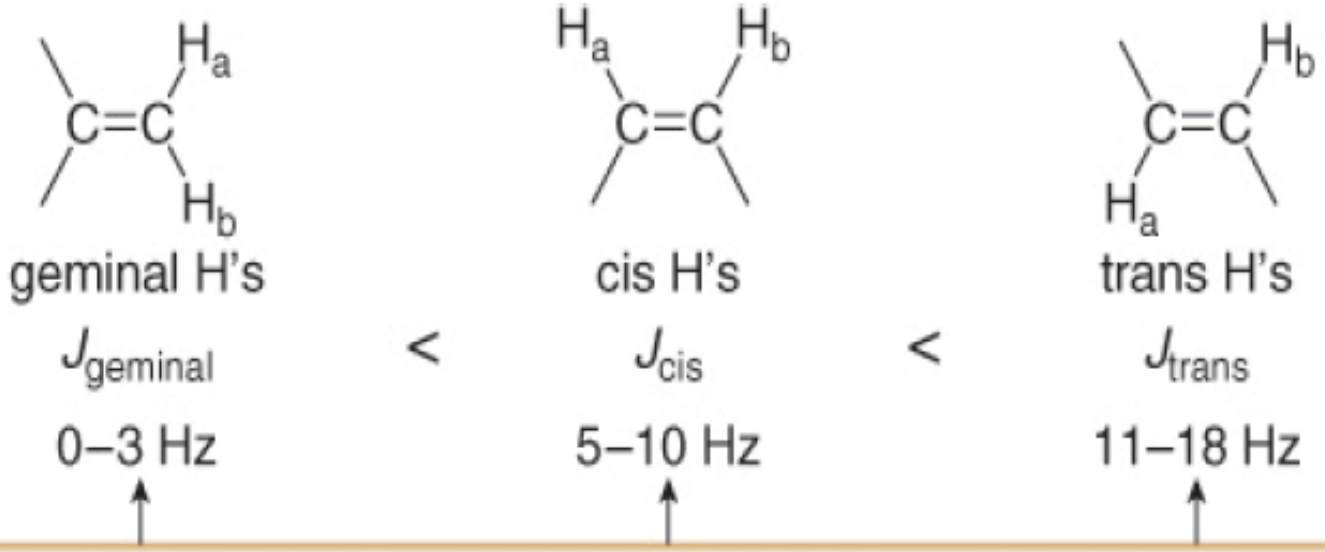
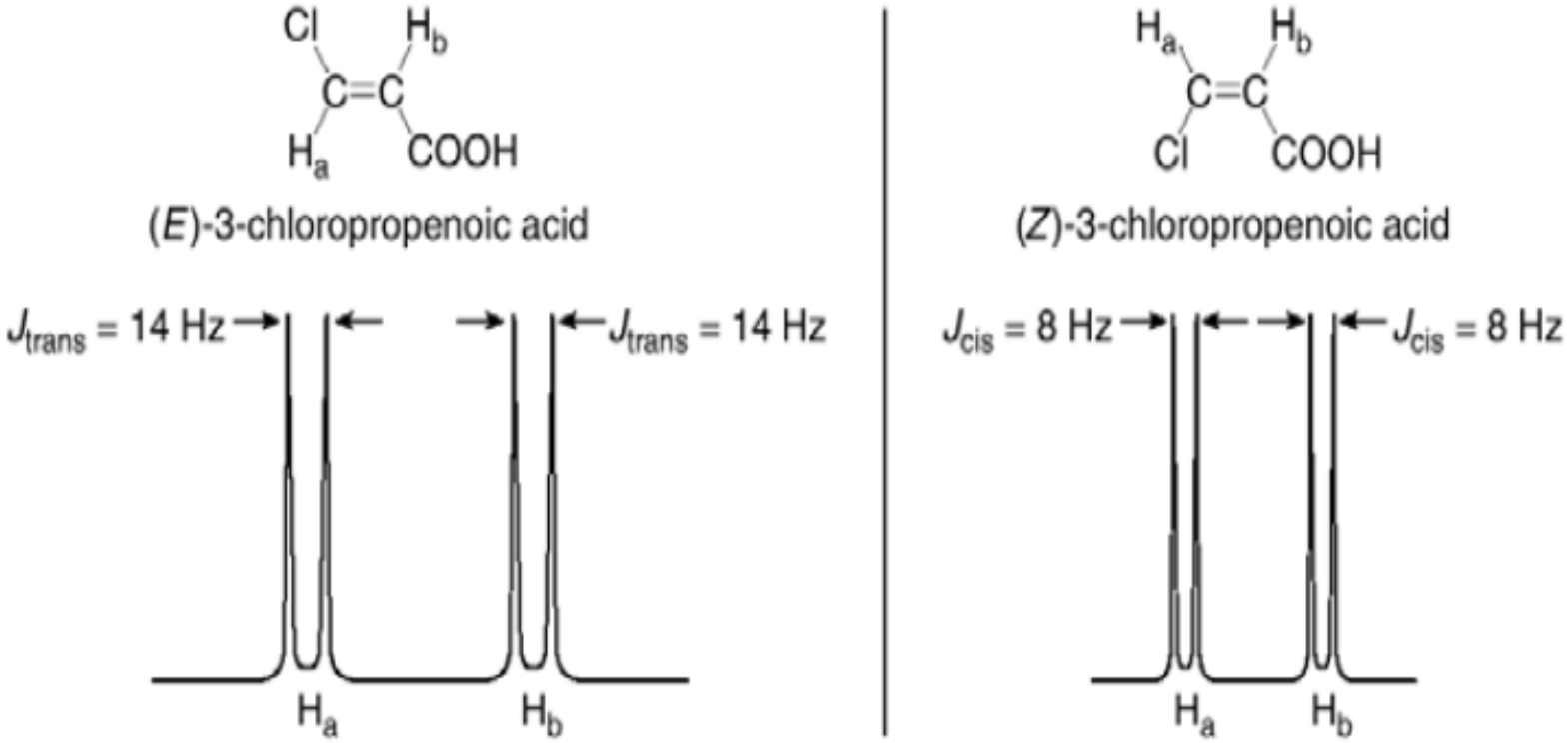


Figure 14.9 ^{1}H NMR spectra for the alkenyl protons of (*E*)- and (*Z*)-3-chloropropenoic acid



- Although both (*E*)- and (*Z*)-3-chloropropenoic acid show two doublets in their ^{1}H NMR spectra for their alkenyl protons, $J_{trans} > J_{cis}$.

Figure 14.10 The ^{1}H NMR spectrum of vinyl acetate (CH_2=$CHOCOCH_3$)

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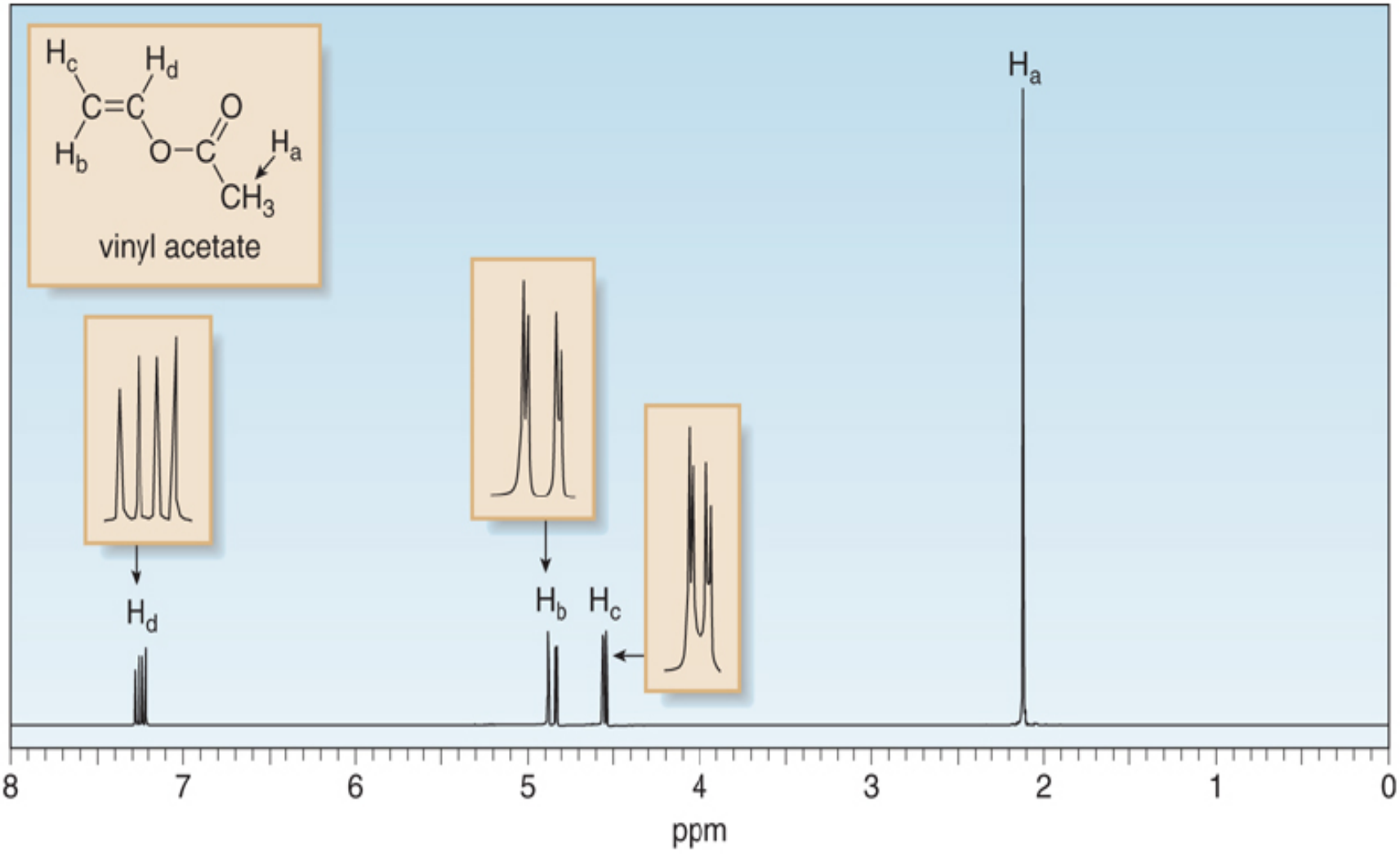

Splitting diagrams for the alkenyl protons in vinyl acetate are shown below. Note that each pattern is different in appearance because the magnitude of the coupling constants forming them is different.

Figure 14.11 Splitting diagram for the alkenyl protons in vinyl acetate (CH_2=CHOCHOCH$_3$)

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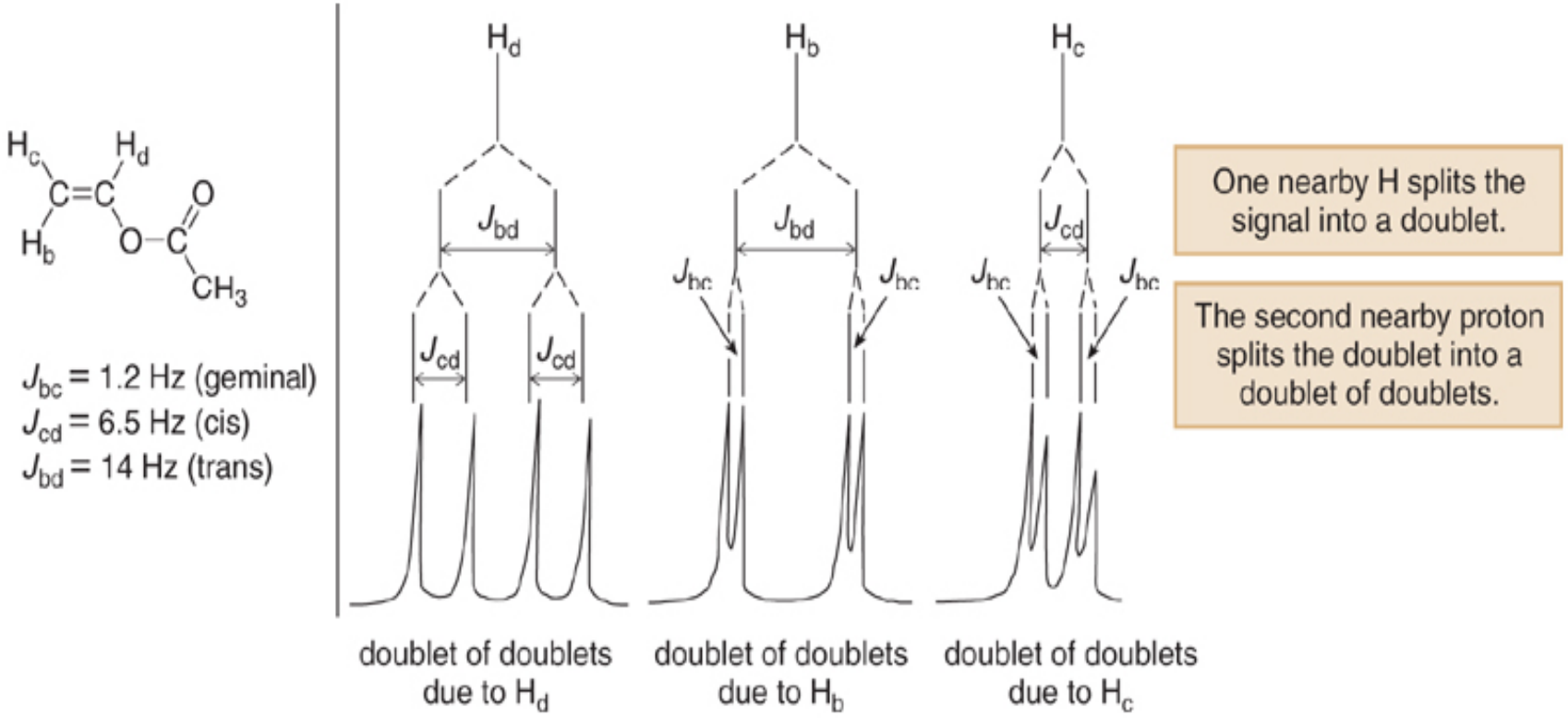

14.9 Other Facts About ^{1}H NMR

14.9A OH Protons

- **Under usual conditions, an OH proton does not split the NMR signal of adjacent protons.**
- **The signal due to an OH proton is not split by adjacent protons.**

Figure 14.12 The ^{1}H spectrum of ethanol (CH_3CH_2OH)

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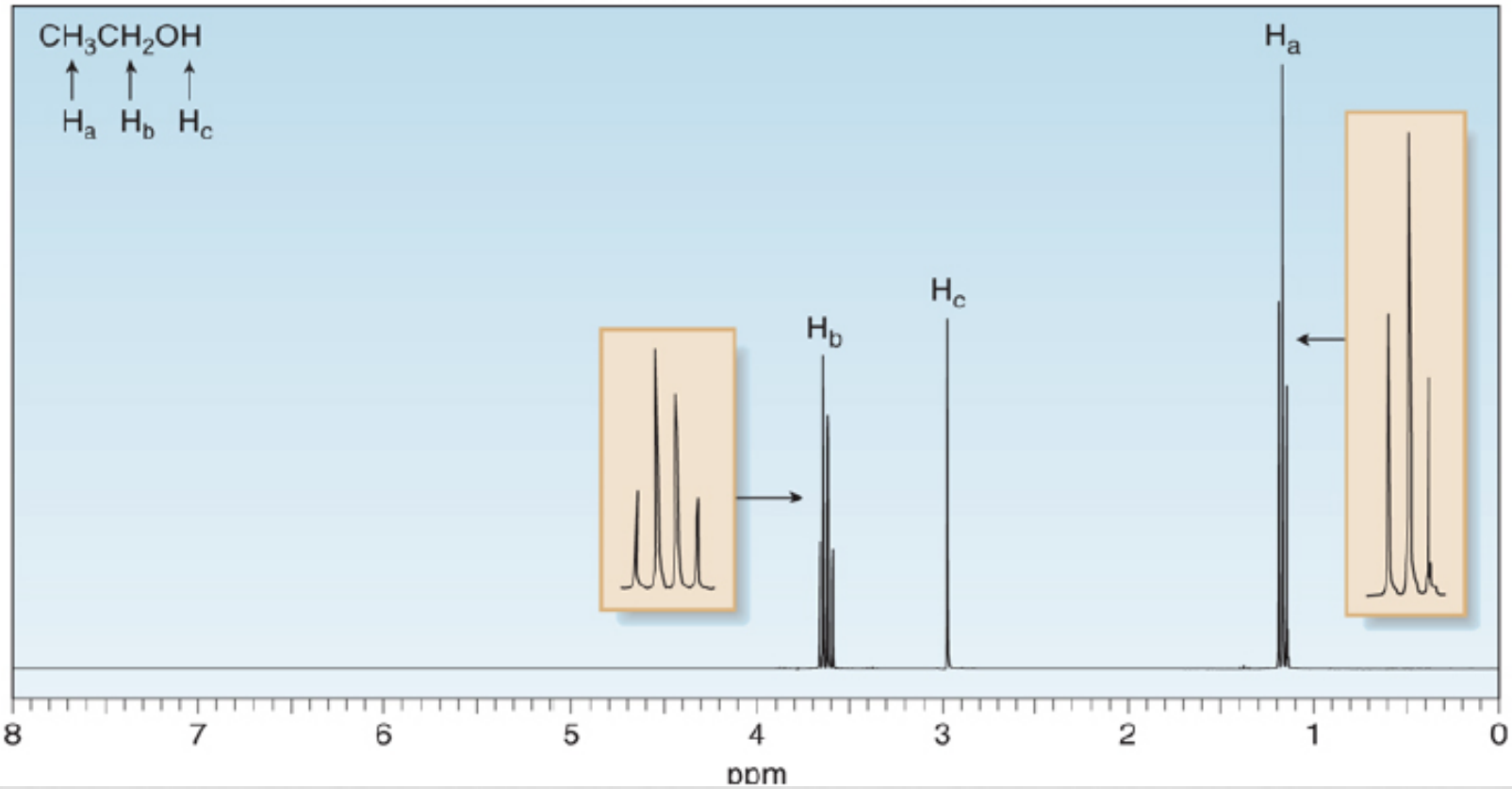
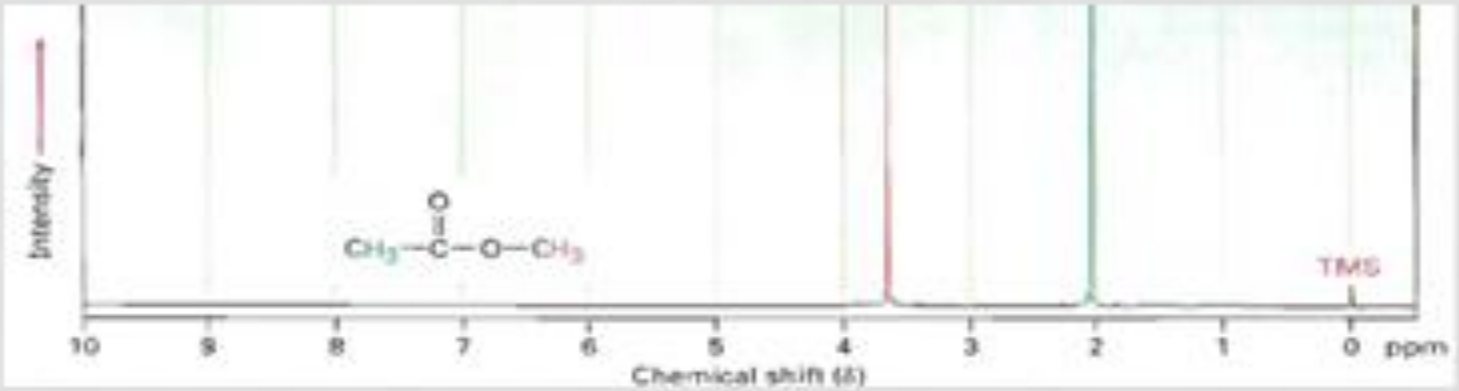


- Ethanol (CH_3CH_2OH) has three different types of protons, so there are three signals in its NMR spectrum.
- The H_a signal is split by the two H_b protons into three peaks (a triplet).
- The H_b signal is split only by the three H_a protons into four peaks, a quartet. The adjacent OH proton does not split the signal due to H_b.
- H_c is a singlet because OH protons are not split by adjacent protons.
- Protons on electronegative atoms rapidly exchange between molecules in the presence of trace amounts of acid or base. Thus, the CH_2 group of ethanol never "feels" the presence of the OH proton, because the OH proton is rapidly moving from one molecule to another.
- This phenomenon usually occurs with NH and OH protons.

^{1}H NMR spectrum in Figure 13.3a shows only two peaks, however, even though methyl acetate has six hydrogens. One peak is due to the $CH_3C{=}O$ hydrogens, and the other to the $-OCH_3$ hydrogens. Because the three hydrogens in each methyl group have the same electronic environment, they are shielded to the same extent and are said to be *equivalent. Chemically equivalent nuclei always show a single absorption.* The two methyl groups themselves, however, are nonequivalent, so the two sets of hydrogens absorb at different positions.

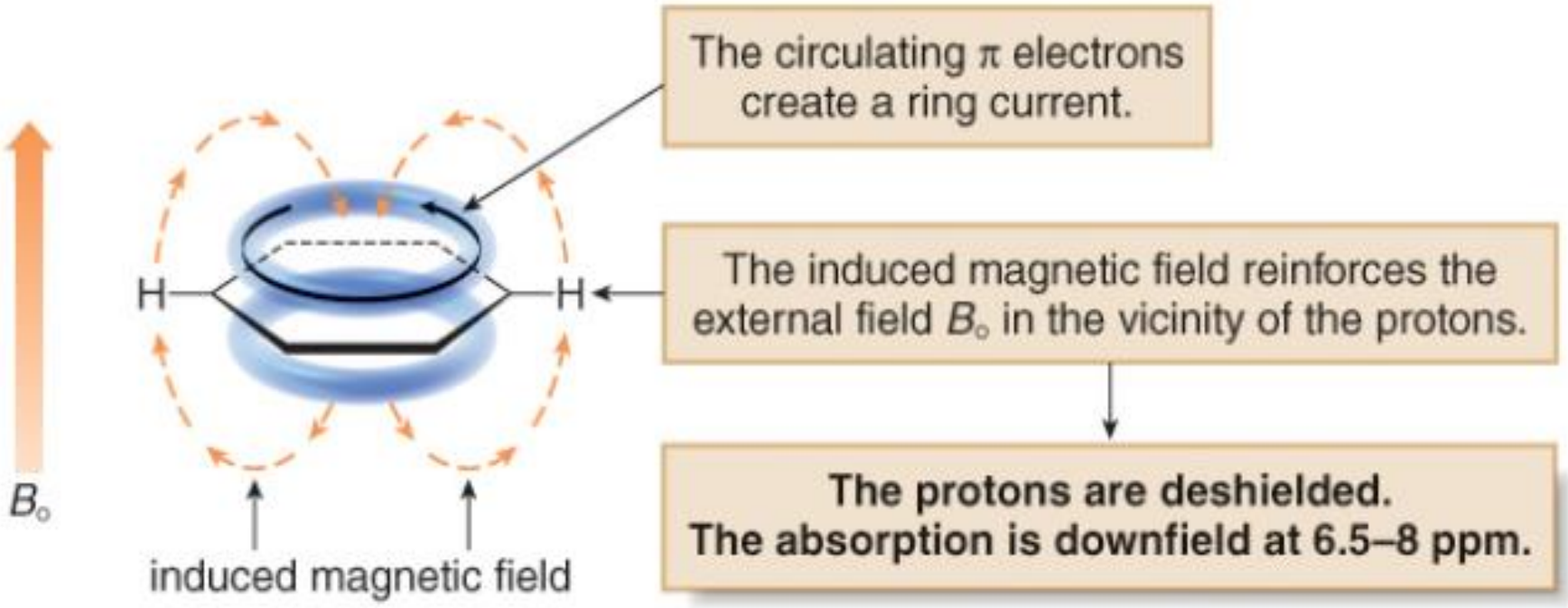


To define the position of an absorption, the NMR chart is calibrated and a reference point is used. In practice, a small amount of tetramethylsilane [TMS; $(CH_3)_4Si$] is added to the sample so that a reference absorption peak is produced when the spectrum is run. TMS is used as reference for both ^1H and ^{13}C mea-

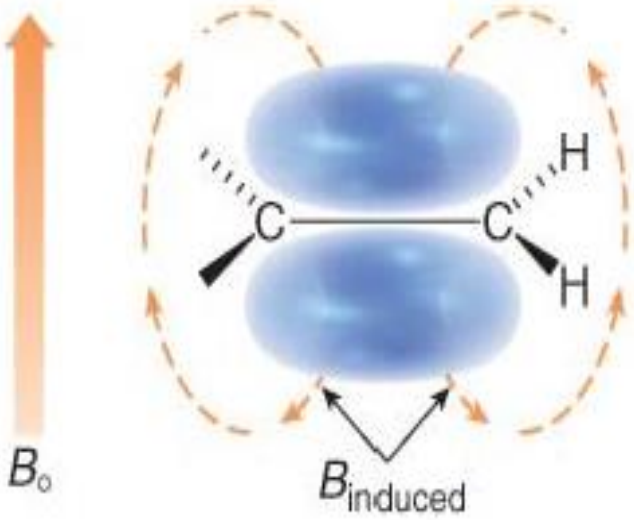
This material has several advantages: it is chemically inert, symmetrical, volatile (bp 27°C), and soluble in most organic solvents; it gives a single, intense, sharp, absorption peak, and its protons are more "shielded" than almost all organic protons. When water or deuterium oxide is the solvent, TMS can be used as an "external reference" in a concentric capillary or the methyl protons of the water-soluble sodium 2, 2-dimethyl-2-silapentane-5-sulfonate (DSS), $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$, are used as an internal reference (0.015 ppm).

14.4 ^{1}H NMR—Chemical Shift Values

- In a magnetic field, the six π electrons in benzene circulate around the ring creating a ring current.
- The magnetic field induced by these moving electrons reinforces the applied magnetic field in the vicinity of the protons.
- The protons thus feel a stronger magnetic field and a higher frequency is needed for resonance. Thus they are deshielded and absorb downfield.



- In a magnetic field, the loosely held π electrons of the double bond create a magnetic field that reinforces the applied field in the vicinity of the protons.
- The protons now feel a stronger magnetic field, and require a higher frequency for resonance. Thus the protons are deshielded and the absorption is downfield.



The induced magnetic field reinforces the external field B_o in the vicinity of the protons.

The protons are deshielded.
The absorption is downfield at 4.5–6 ppm.

- In a magnetic field, the π electrons of a carbon-carbon triple bond are induced to circulate, but in this case the induced magnetic field opposes the applied magnetic field (B_0).
- Thus, the proton feels a weaker magnetic field, so a lower frequency is needed for resonance. The nucleus is shielded and the absorption is upfield.

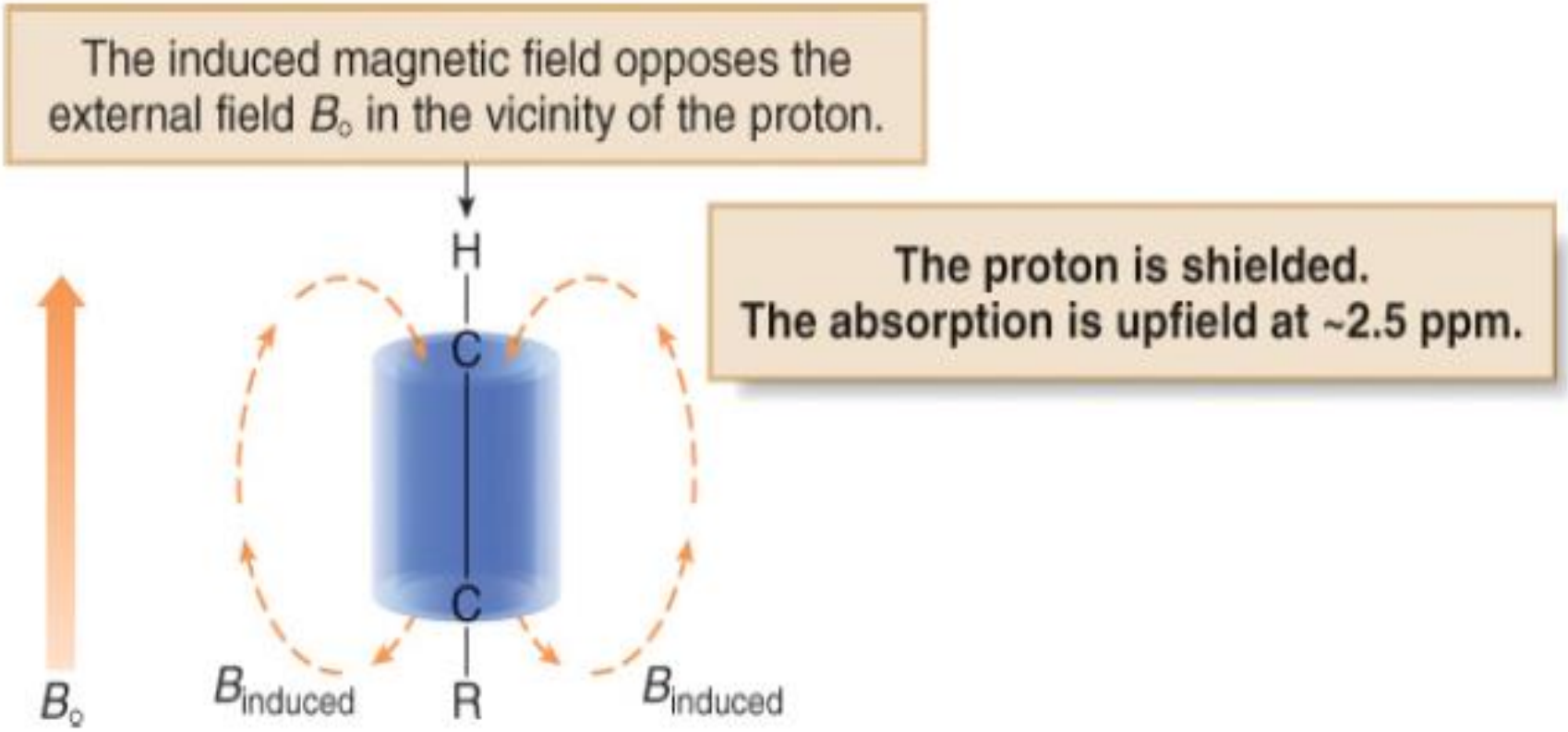


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Table 14.2 Effect of π Electrons on Chemical Shift Values

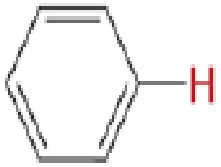
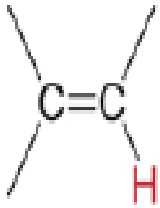
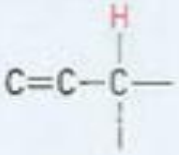
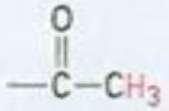
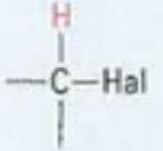
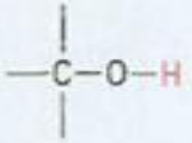
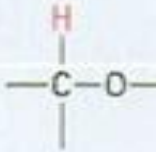
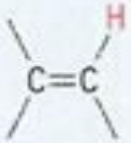
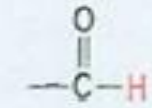
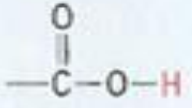
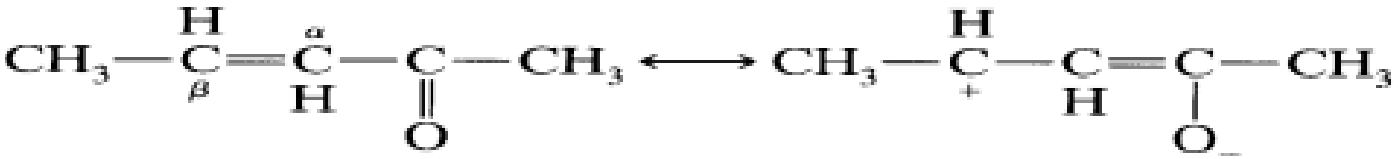
Proton type	Effect	Chemical shift (ppm)
	highly deshielded	6.5–8
	deshielded	4.5–6
—C≡C—H	shielded	~2.5

Table 13.3 | Correlation of ^1H Chemical Shift with Environment

Type of hydrogen		Chemical shift (δ)
Reference	$Si(CH_3)_4$	0
Alkyl (primary)	$-CH_3$	0.7–1.3
Alkyl (secondary)	$-CH_2-$	1.2–1.6
Alkyl (tertiary)		1.4–1.8
Allylic		1.6–2.2
Methyl ketone		2.0–2.4
Aromatic methyl	$Ar-CH_3$	2.4–2.7
Alkynyl	$-C\equiv C-H$	2.5–3.0
Alkyl halide		2.5–4.0
Alcohol		2.5–5.0
Alcohol, ether		3.3–4.5
Vinylic		4.5–6.5
Aryl	$Ar-H$	
Aldehyde		9.7–10.0
Carboxylic acid		11.0–12.0

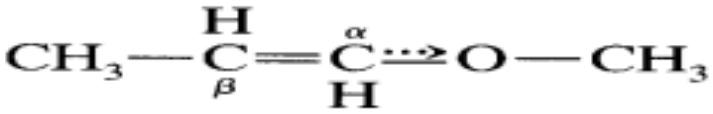
RATIONALIZATION AND PREDICTION OF APPROXIMATE CHEMICAL SHIFT DEPENDING ON INDUCTIVE EFFECT & DIAMAGNETIC ANISOTROPY

1. In an α,β-unsaturated ketone, resonance deshields the β-proton;



α-proton = $\delta \sim 6.2$
β-proton = $\delta \sim 6.8$

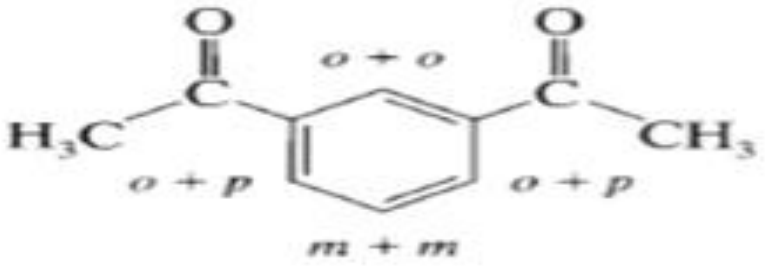
2. In a substituted vinyl ether, the oxygen atom deshields the α-proton by an inductive effect and shields the β-proton by resonance.



α-proton = $\delta \sim 6.2$
β-proton = $\delta \sim 4.6$

3. The shifts of protons *ortho*, *meta*, or *para* to a substituent on an aromatic ring are correlated with electron densities and with the effects of electrophilic reagents (Appendix Chart D.1). For example, the *ortho* and *para* protons of phenol are shielded because of the higher electron density that also accounts for the predominance of *ortho* and *para* substitution by electrophilic reagents. Conversely, the *ortho* and *para* protons of nitrobenzene are deshielded, the *ortho* protons more so (see Figure 3.23).

Since chemical shift increments are approximately additive, it is possible to calculate the ring proton shifts in polysubstituted benzene rings from the monosubstituted values in Appendix Chart D.1. The chemical shift increments for the ring protons of *m*-diacetylbenzene:

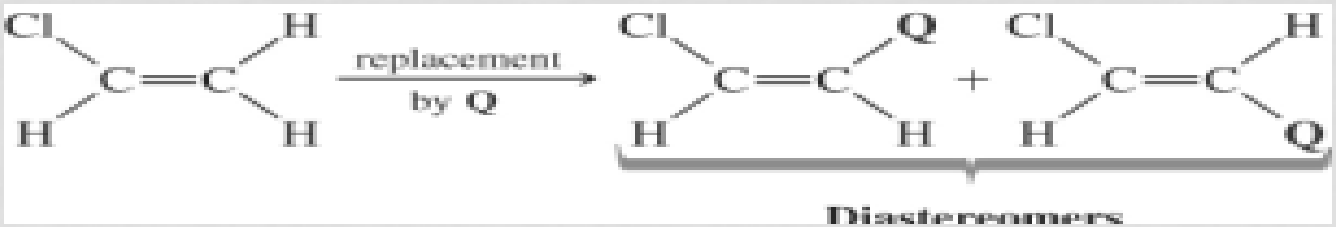


SOLVENT SELECTION:

- Characteristic of the ideal solvent:
- 1. should contain no protons
- 2. inert
- 3. low boiling
- 4. inexpensive
- 5. Deuterated solvents are necessary for modern instruments because they depend on a deuterium signal to lock or stabilize the B° field of the magnet.
- Solvent used in NMR spectroscopy:
- 1. CCl_4: because a/ it is contain no hydrogen.
- b/ good solvent for many organic compounds.
- c/ cheap and readily available.
- 2. $CDCl_3$

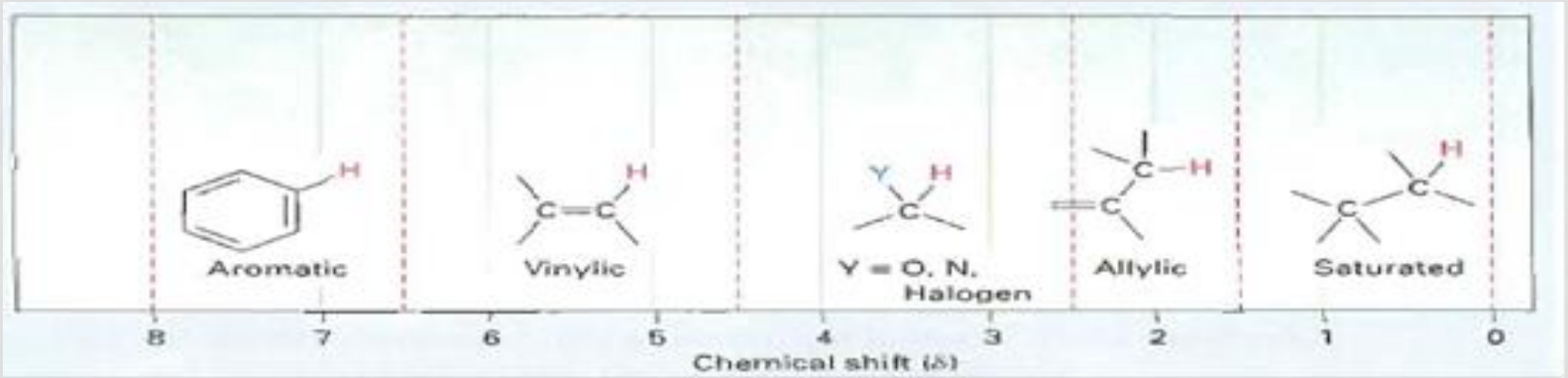
- The protons on a CH_2 group are usually diastereotopic if:

- On an unsymmetrical double bond
- t On opposite sides of a substituted ring
- t There is a chiral center in the molecule



- 2. the position of the signals (chemical shift in H-NMR Spectroscopy)

We said previously that differences in chemical shifts are caused by the small local magnetic fields of electrons surrounding the different nuclei. Nuclei that are more strongly shielded by electrons require a higher applied field to bring them into resonance and therefore absorb on the right side of the NMR chart. Nuclei that are less strongly shielded need a lower applied field for resonance and therefore absorb on the left of the NMR chart.



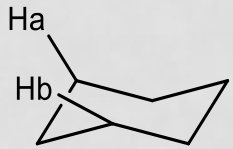
FACTORS EFFECTING CHEMICAL SHIFT:

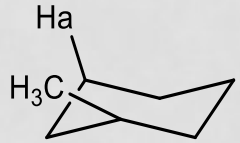
1. inductive effect:

Table 13.3 shows the correlation of ^{1}H chemical shift with electronic environment in more detail. In general, protons bonded to saturated, sp^3-hybridized carbons absorb at higher fields, whereas protons bonded to sp^2-hybridized carbons absorb at lower fields. Protons on carbons that are bonded to electronegative atoms, such as N, O, or halogen, also absorb at lower fields.

2. anisotropic effect

3. vanderwaals deshielding: proton (a) is not effected by proton (b), but if we substituted proton (b) by CH3 → repulsive because of steric effect with the proton (a) → deshielding → down field.





- 4. Hydrogen bonding:

They cause decrease the density around the hydrogen → deshielded by inductive effect.

The intensity of intermolecular hydrogen bonding depending on:

- The concentration: increase concentration → increase H-bonding → increase deshielding.
- The temperature: increase temperature → breakdown the H-bonding → high field.
- The purity.
- Polarity of the solvent: the solvent should be deuterated ($CDCl_3$) and also should not polar.

- Intramolecular H_ bonds are less affected by their environment than are intermolecular H _ bonds.

4. MULTIPLICITY: "SPIN_ SPIN COUPLING" OR SPIN_ SPIN SPLITTING IN H NMR SPECTRA:

pling. This can be described as the indirect coupling of proton spins through the intervening bonding electrons. Very briefly, it occurs because there is some tendency for a bonding electron to pair its spin with the spin of the nearest proton; the spin of a bonding electron having been thus influenced, the electron will affect the spin of the other bonding electron, and so on, through to the next proton. Coupling is ordinarily not important beyond three bonds unless there is ring strain as in small rings or bridged systems, delocalization as in aromatic or unsaturated systems, or four connecting bonds in a W configuration.

As a general rule, called the n + 1 rule, protons that have n equivalent neighboring protons show n + 1 peaks in their NMR spectrum.

In the ^{1}H NMR spectra we've seen thus far, each different kind of proton in a molecule has given rise to a single peak. It often happens, though, that the absorption of a proton splits into multiple peaks, called a **multiplet**. For example, in the ^{1}H NMR spectrum of bromoethane shown in Figure 13.13, the $-CH_2Br$ protons appear as four peaks (a *quartet*) centered at 3.42 δ and the $-CH_3$ protons appear as three peaks (a *triplet*) centered at 1.68 δ.

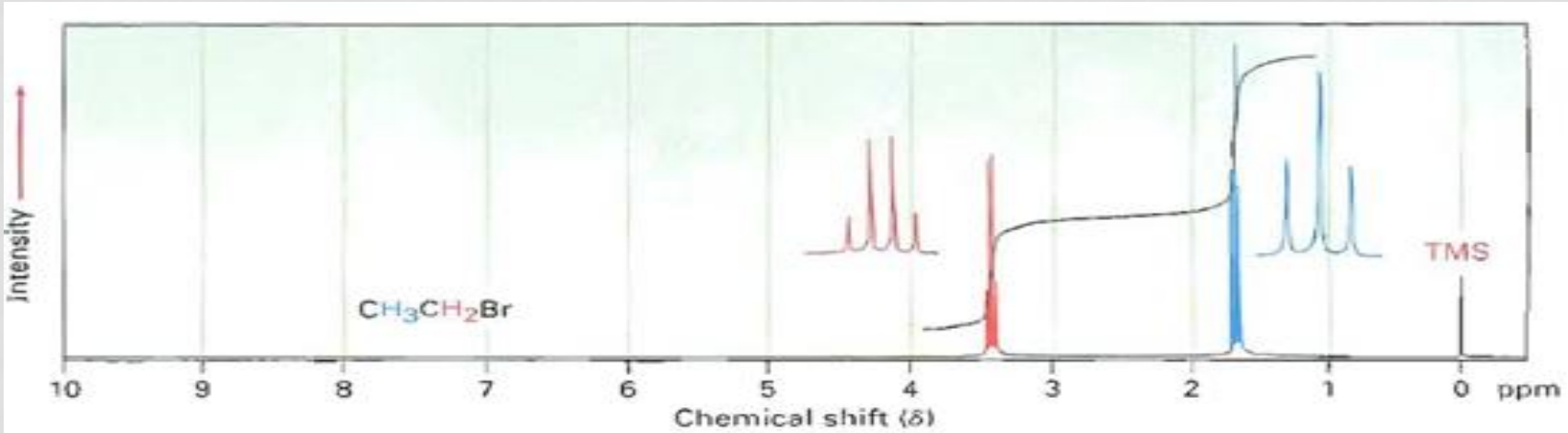


Figure 13.13 The ^{1}H NMR spectrum of bromoethane, CH_3CH_2Br. The $-CH_2Br$ protons appear as a quartet at 3.42 δ, and the $-CH_3$ protons appear as a triplet at 1.68 δ.

spectrum of 2-bromopropane in Figure 13.15 shows a doublet at 1.71 δ and a seven-line multiplet, or *septet*, at 4.28 δ. The septet is caused by splitting of the −CHBr− proton signal by six equivalent neighboring protons on the two methyl groups ($n = 6$ leads to $6 + 1 = 7$ peaks). The doublet is due to signal splitting of the six equivalent methyl protons by the single −CHBr− proton ($n = 1$ leads to 2 peaks). Integration confirms the expected 6:1 ratio.

The distance between peaks in a multiplet is called the **coupling constant**, denoted J. Coupling constants are measured in hertz and generally fall in the range 0 to 18 Hz. The exact value of the coupling constant between two neighboring protons depends on the geometry of the molecule, but a typical value for an open-chain alkane is $J = 6$ to 8 Hz. The same coupling constant is shared by both groups of hydrogens whose spins are coupled and is independent of

Spectrometer field strength

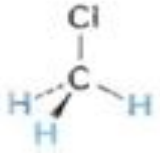
Two_ bond coupling is termed geminal; three _ bond coupling is termed, vicinal;

H—C—H	H—C—C—H
Geminal coupling	Vicinal coupling
2 bonds (^2J)	3 bonds (^3J)

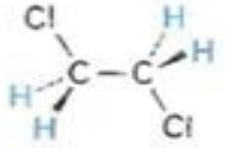
Spin- spin splitting in H NMR can be summarized by:

Rule1:

Chemically equivalent protons do not show spin–spin splitting. The equivalent protons may be on the same carbon or on different carbons, but their signals don't split.



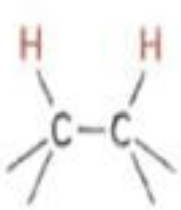
Three C–H protons are chemically equivalent; no splitting occurs.



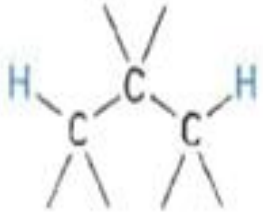
Four C–H protons are chemically equivalent; no splitting occurs.

Rule2:

The signal of a proton that has n equivalent neighboring protons is split into a multiplet of $n + 1$ peaks with coupling constant J. Protons that are farther than two carbon atoms apart don't usually couple, although they sometimes show small coupling when they are separated by a π bond.



Splitting observed



Splitting not usually observed

Rule3: Two groups of protons coupled to each other have the same coupling constant, *J*.

e.g. CH_3CH_2Br multiplets of CH_2Br and CH_3 have the same J value.

- If V1 = chem. Shift of CH_3
  V2 = chem. Shift of CH_2
  ΔV = distance between chem. Shift of non equivalent protons in the molecule.

As ΔV/ J goes down → the distance between different peaks of 2 non equivalent protons smaller (peaks approach each other)

When $\Delta V = J$ → the two peaks of two protons are the same, i,e the two protons are equivalent.

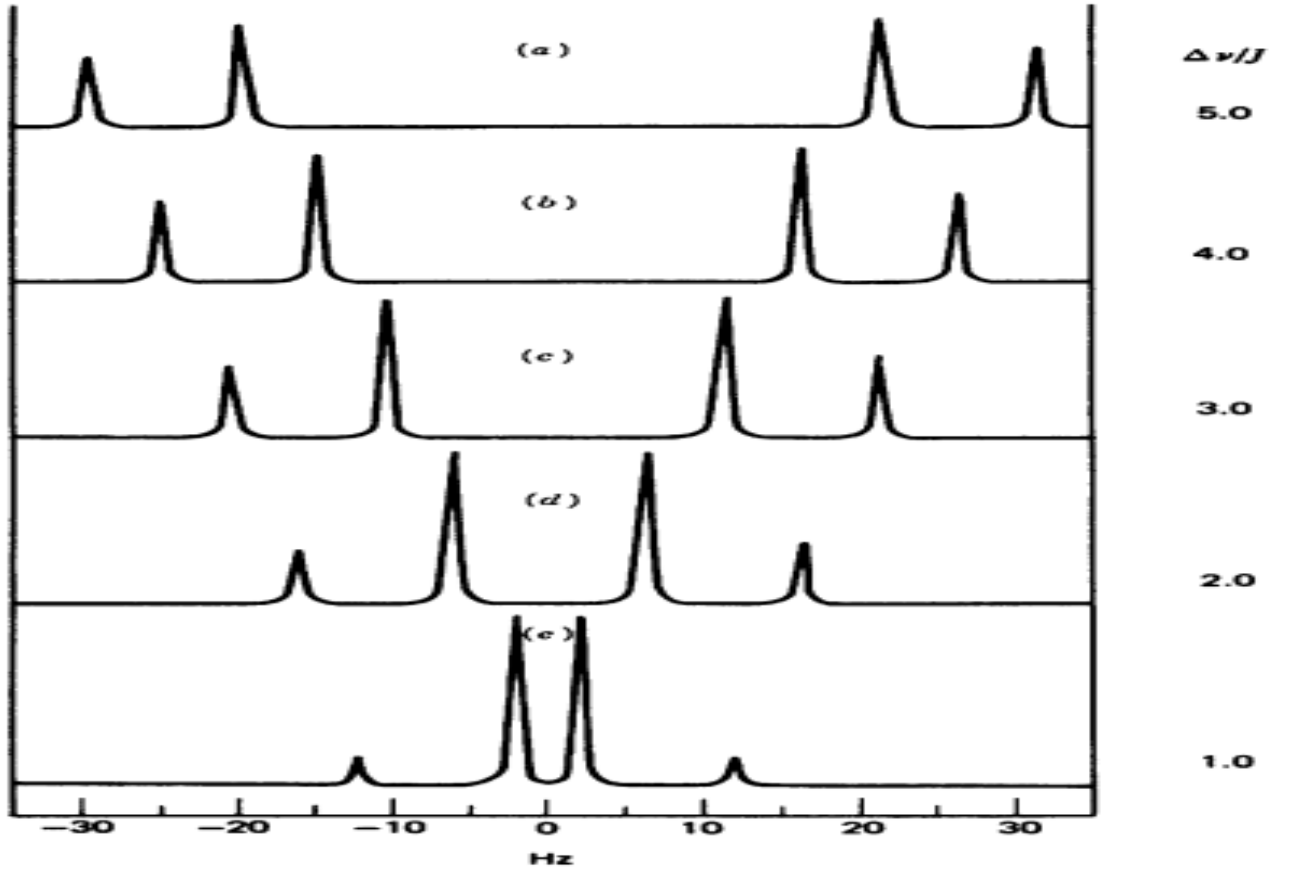


FIGURE 4.24. A two-proton system, spin coupling with a decreasing difference in chemical shifts and a large J value (10 Hz); the difference between AB and AX notation is explained in the text.

Rule4: The relative intensities of the peaks of a multiplet depend on (n):

Table 13.4 Some Common Spin Multiplicities

Number of equivalent adjacent protons	Multiplet	Ratio of intensities
0	Singlet	1
1	Doublet	1:1
2	Triplet	1:2:1
3	Quartet	1:3:3:1
4	Quintet	1:4:6:4:1
6	Septet	1:6:15:20:15:6:1

We can now appreciate the three main features of an NMR spectrum: chemical shifts, peak intensities, and spin splittings that are first order or that approximate first-order patterns. The term "weakly coupled" is used for first-order coupling ($\Delta\nu/J > \sim 8$) and "strongly coupled" is used for couplings whose $\Delta\nu/J$ ratio is less than about eight.

Example: Compound (A) has the chemical formula of $C_{10}H_{12}O_2$:

NMR spectrum showed the following signals (δ) :

7.93 (doublet), 6.91 (doublet), 3.84 (singlet), 2.93(quartet), & 1.20(triplet). The integration for the peaks is as follows: 20:20:30:20:30 respectively. Find the structure of compound (A), and then draw its spectrum chart.

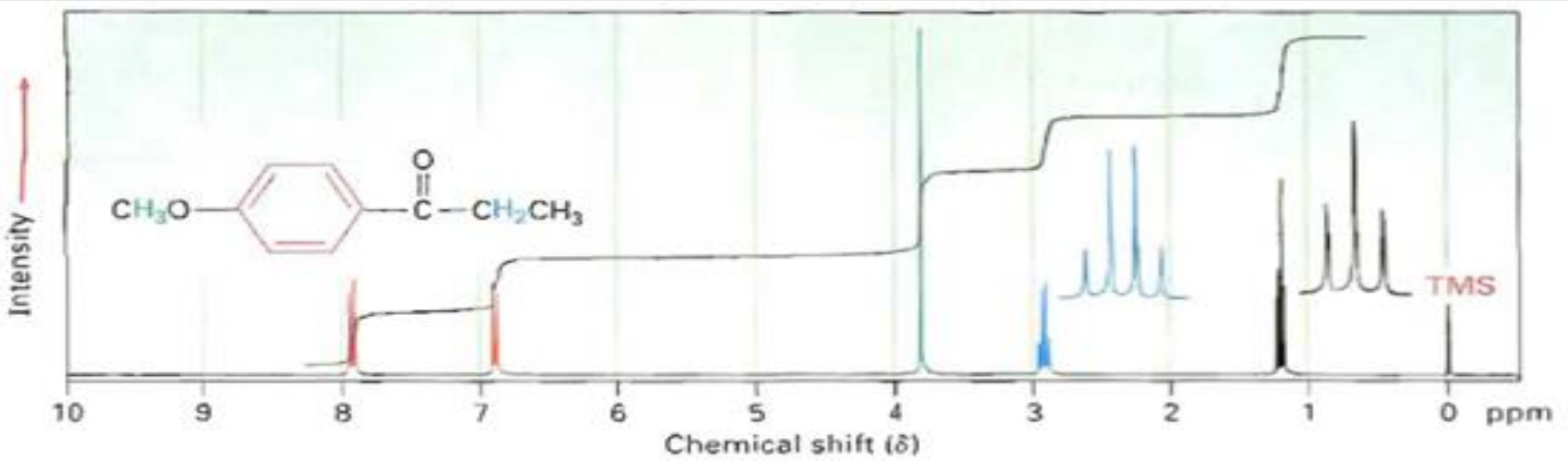
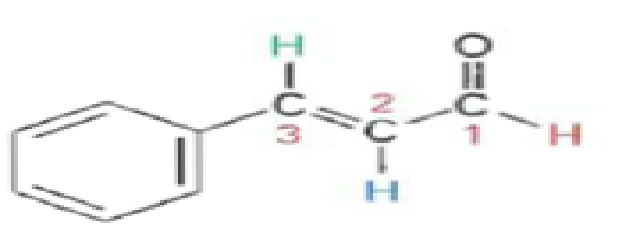


Figure 13.16 The ^{1}H NMR spectrum of *para*-methoxypropiophenone.

Exercise:

Propose a structure for a compound, $C_5H_{12}O$, that fits the following ^{1}H NMR data: 0.92 δ (3 H, triplet, J = 7 Hz), 1.20 δ (6 H, singlet), 1.50 δ (2 H, quartet, J = 7 Hz), 1.64 δ (1 H, broad singlet).

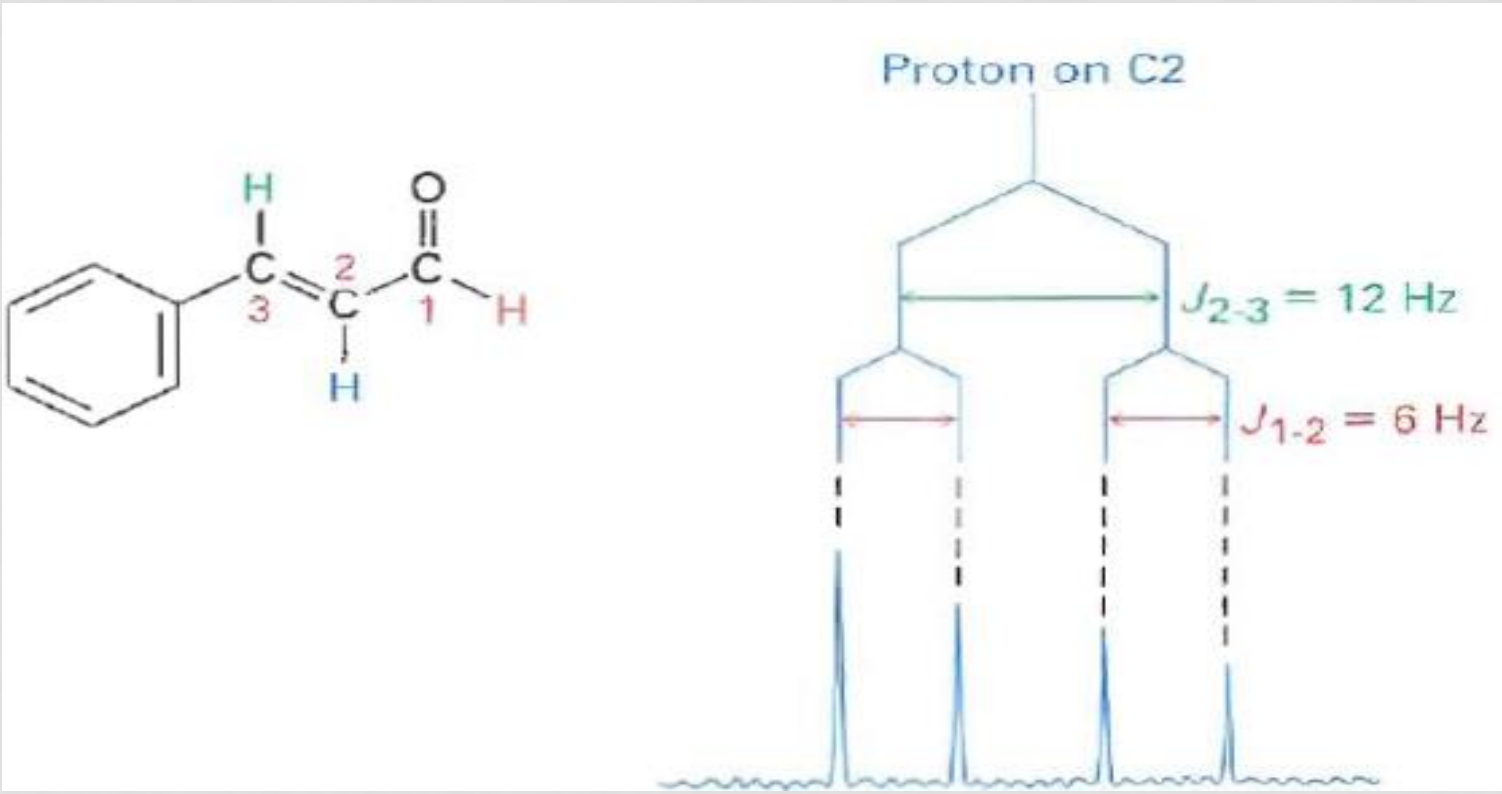


The five aromatic proton signals (black in Figure 13.19) overlap into a complex pattern with a large peak at 7.42 δ and a broad absorption at 7.57 δ.

The aldehyde proton signal at C1 (red) appears in the normal downfield position at 9.69 δ and is split into a doublet with J = 6 Hz by the adjacent proton at C2.

The vinylic proton at C3 (green) is next to the aromatic ring and is therefore shifted downfield from the normal vinylic region. This C3 proton signal appears as a doublet centered at 7.49 δ. Because it has one neighbor proton at C2, its signal is split into a doublet, with J = 12 Hz.

The C2 vinylic proton signal (blue) appears at 6.73 δ and shows an interesting four-line absorption pattern. It is coupled to the two nonequivalent protons at C1 and C3 with two different coupling constants: $J_{1\text{-}2}$ = 6 Hz and $J_{2\text{-}3}$ = 12 Hz.


H
O
C
2
C
C
3
1
H
H
Proton on C2
$J_{2\text{-}3}$ = 12 Hz
$J_{1\text{-}2}$ = 6 Hz

4.9.1.3 Phenols The behavior of a phenolic proton resembles that of an alcoholic proton. The phenolic proton peak is usually a sharp singlet (rapid exchange, no coupling), and its range, depending on concentration, solvent, and temperature, is generally to the left ($\delta \sim 7.5$ to $\delta \sim 4.0$) compared with the alcoholic proton. A car-

3.6.1.5 Carboxylic Acids Carboxylic acids exist as stable hydrogen-bonded dimers in nonpolar solvents even at high dilution. The carboxylic proton therefore absorbs in a characteristic range $\delta \sim 13.2 - \delta \sim 10.0$ and is affected only slightly by concentration. Polar solvents partially disrupt the dimer and shift the peak accordingly.