Bonga university

Instrumental Analysis II (Chem.2052)

Chapter 7

NUCLEAR MAGNETIC RESONANCE (NMR)

SPECTROSCOPY

2012 E.C

History of NMR Spectroscopy

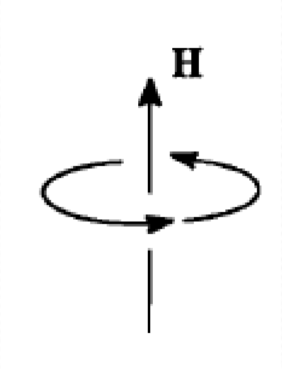
- W. Pauli in 1924- suggested that certain atomic nuclei have the properties of spin and magnetic moment and that as a consequence, exposure to a magnetic field would lead to splitting of their energy levels.
- 1946, that Felix Bloch at Stanford and Edward Purcell at Harvard, working independently, demonstrated that nuclei absorb electromagnetic radiation in a strong magnetic field as a result of the energy level splitting that is induced by the magnetic field.
- The two physicists shared the 1952 Nobel Prize in Physics for their work.
- In 1953 the first high-resolution NMR spectrometer designed for chemical structural studies was marketed by Varian Associates. Since then, the growth of NMR spectroscopy has been explosive, and the technique has had profound effects on the development of organic and inorganic chemistry and biochemistry.
- Continuous Wave (CW) and pulsed, or Fourier transform (FT-NMR), spectrometers.
- *Nearly all NMR instruments produced today are of the FT type.*

Introduction to NMR Spectroscopy

- Nuclear magnetic resonance spectroscopy is a powerful analytical technique used to characterize organic molecules by identifying carbon-hydrogen frameworks within molecules.
- Two common types of NMR spectroscopy are used to characterize organic structure: ^{1}H NMR is used to determine the type and number of H atoms in a molecule; ^{13}C NMR is used to determine the type of carbon atoms in the molecule.
- 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 nuclear spins of some elements, including ^{1}H and ^{13}C.

- All nuclei have charge because they contain protons and some of them also behave as if they spin.

- 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.



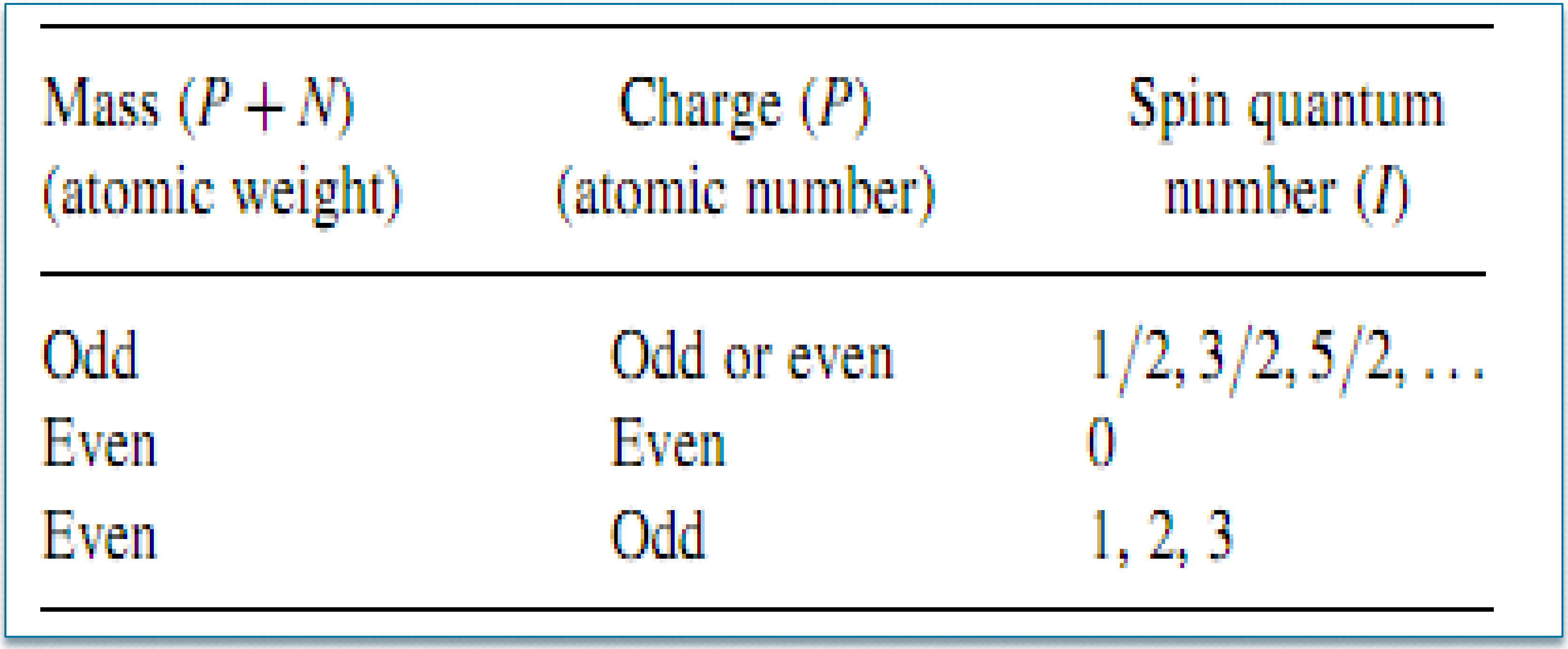
A spinning charge generates a magnetic dipole

- Such nuclear magnetic dipoles are characterized by nuclear magnetic spin quantum numbers which are designated by the letter I and can take up values equal to 0, ½ , 1, 3/2, ... *etc*

Physical principles of NMR

Spin Quantum number

- assume that nuclei rotate about an axis and thus have the property of spin.
- Nuclei with spin have angular momentum *p whose* angular momentum quantum number is quantized and multiple of h/2Π.
- nuclear spin, represented as *I*, the spin quantum number.



Mass ($P + N$) (atomic weight)	Charge (P) (atomic number)	Spin quantum number (I)
Odd	Odd or even	$1/2, 3/2, 5/2, \ldots$
Even	Even	0
Even	Odd	1, 2, 3

- ❑ Odd mass nuclei (i.e. those having an odd number of nucleons) have fractional spins.

Examples are I = 1/2 (^{1}H, ^{13}C, ^{19}F), I = 3/2 (^{11}B) & I = 5/2 (^{17}O).

- ❑ Even mass nuclei composed of odd numbers of protons and neutrons have integral spins.

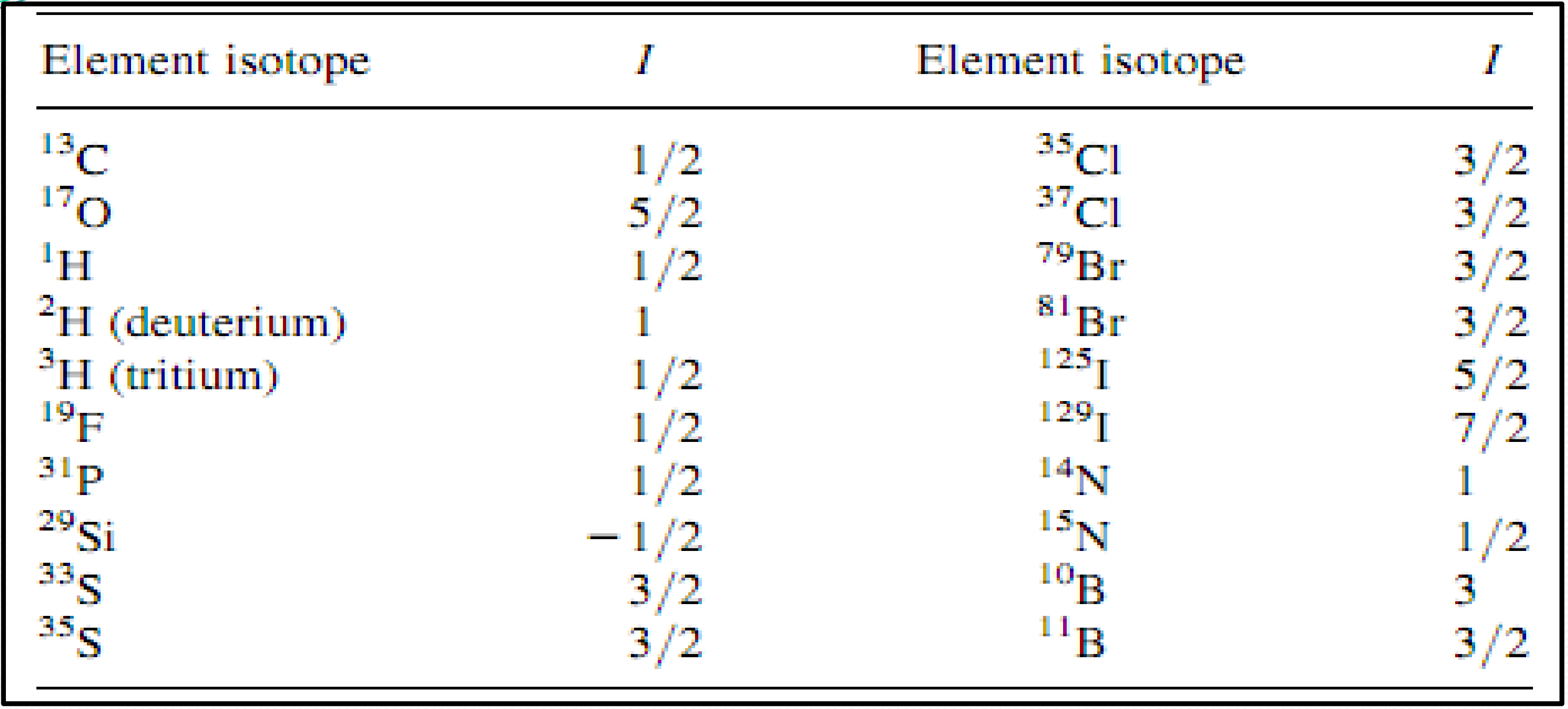
Examples are I = 1 (^{2}H, ^{14}N).

- ❑ Even mass nuclei composed of even numbers of protons and neutrons have zero spin (I = 0).

Examples are ^{12}C, and ^{16}O.

the actual spin number—for example, ½ or 3/2 or 1 or 2—must be determined experimentally.

Table NMR-Active Nuclei and Their Spin Quantum Numbers



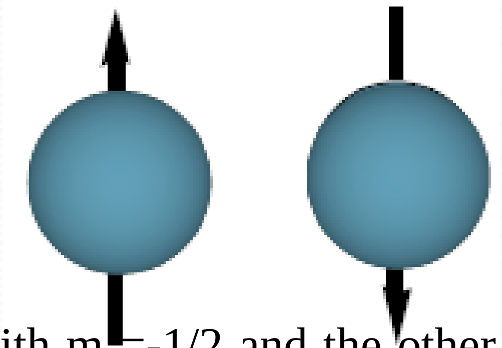
Element isotope	*I*	Element isotope	*I*
^{13}C	1/2	^{35}Cl	3/2
^{17}O	5/2	^{37}Cl	3/2
^{1}H	1/2	^{79}Br	3/2
^{2}H (deuterium)	1	^{81}Br	3/2
^{3}H (tritium)	1/2	^{125}I	5/2
^{19}F	1/2	^{129}I	7/2
^{31}P	1/2	^{14}N	1
^{29}Si	−1/2	^{15}N	1/2
^{33}S	3/2	^{10}B	3
^{35}S	3/2	^{11}B	3/2

For a nucleus to give a signal in an NMR experiment, it must have a nonzero spin quantum number and must have a magnetic dipole moment.

- Nuclei with I = 0 do not absorb RF radiation when placed in a magnetic field and therefore do not give an NMR signal.
- NMR cannot measure ^{12}C,^{16}O, or any other nucleus with both an even atomic mass and an even atomic number.

The number of orientations or number of magnetic quantum states is a function of the physical properties of the nuclei and is numerically equal **to 2I + 1:**

number of orientations =2I+ 1



If *I = 1/2, there are* two allowed spin states.

Consequently, for ^{1}H only two energy levels are permitted, one with m =-1/2 and the other with m =+1/2. The splitting of these energy levels in a magnetic field is called nuclear Zeeman splitting.

The axis of rotation also rotates in a circular manner about the external magnetic field axis,. This rotation is called **precession**. The direction of precession is either with the applied field B_0 or against the applied field

It is useful to consider three types of nuclei:

Type 1:

Nuclei with I = O. These nuclei do not interact with the applied magnetic field and are not NMR chromophores. Nuclei with I = 0 have an even number of protons and even number of neutrons and have no net spin. This means that nuclear spin is a property characteristic of certain isotopes rather than of certain elements. The most prominent examples of nuclei with I = 0 are ^{12}C and ^{16}O, the dominant isotopes of carbon and oxygen. Both oxygen and carbon also have isotopes that can be observed by NMR spectroscopy.

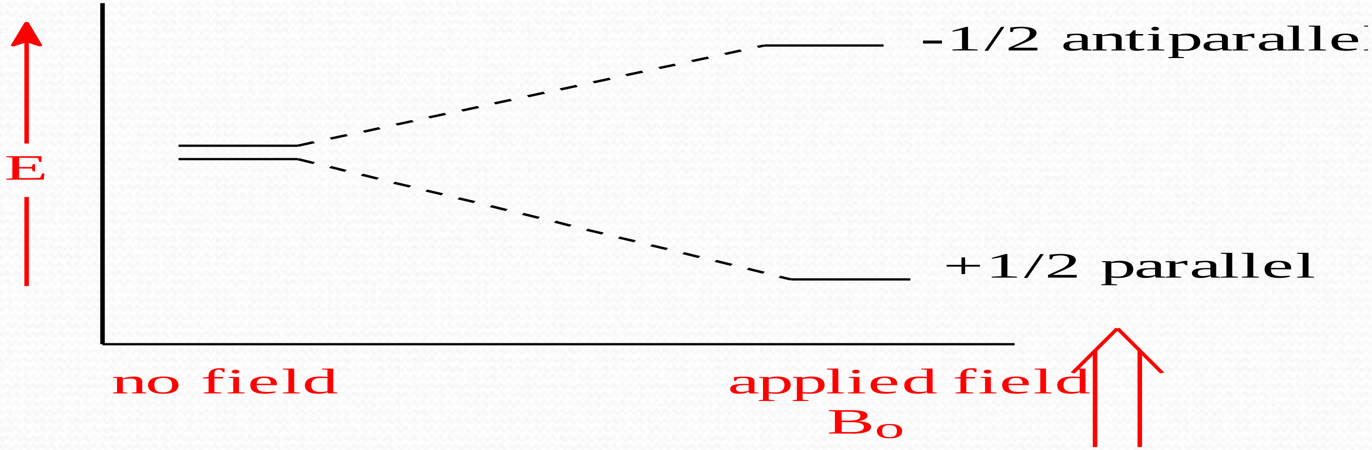
Type 2:

Nuclei with I= 1/2 These nuclei have a non-zero magnetic moment and are NMR visible and have no nuclear electric quadrupole (Q). The two most important nuclei for NMR spectroscopy belong to this category: ^{1}H (ordinary hydrogen) and ^{13}C (a non-radioactive isotope of carbon occurring to the extent of 1.06% at natural abundance). Also, two other commonly observed nuclei ^{19}F and ^{31}P have 1 = ½. Together, NMR data for ^{1}H and ^{13}C account for well over 90% of all NMR observations in the literature and the discussion and examples in this book all refer to these two nuclei. However, the spectra of all nuclei with 1= ½ *can be* understood easily on the basis of common theory.

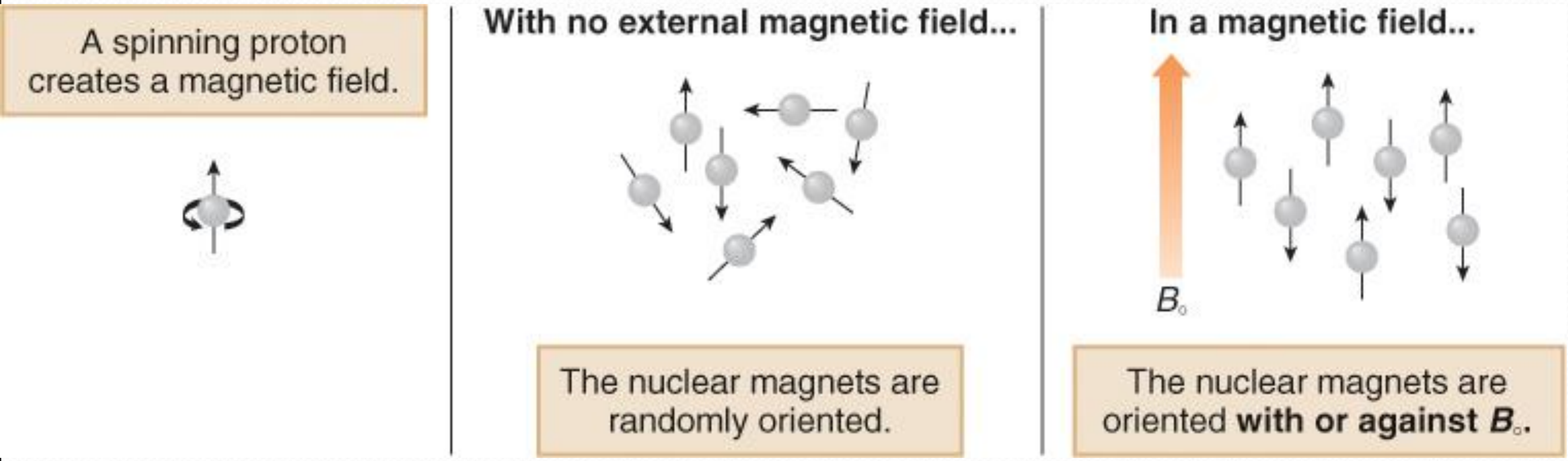
Type 3:

Nuclei with 1> 1/2 These nuclei have both a magnetic moment and an electric quadrupole. This group includes some common isotopes (*e.g.* ^{2}H and ^{14}N) but they are more difficult to observe and spectra are generally very broad. This group of nuclei will not be discussed further.

- The most important consequence of nuclear spin is that in a uniform magnetic field, a nucleus of spin I may assume 2I + 1 orientations. For nuclei with I = 1/2 there are just 2 permissible orientations.
- These two orientations will be of unequal energy (by analogy with the parallel and antiparallel orientations and it is possible to induce a spectroscopic transition (spin-flip) by the absorption of a quantum of electromagnetic energy (ΔE) of the appropriate frequency (v):



- 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



- 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*ν) 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.

In the case of NMR, the energy required to induce the nuclear spin flip (resonance) also depends on the strength of the applied field, *Ho. O*

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

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

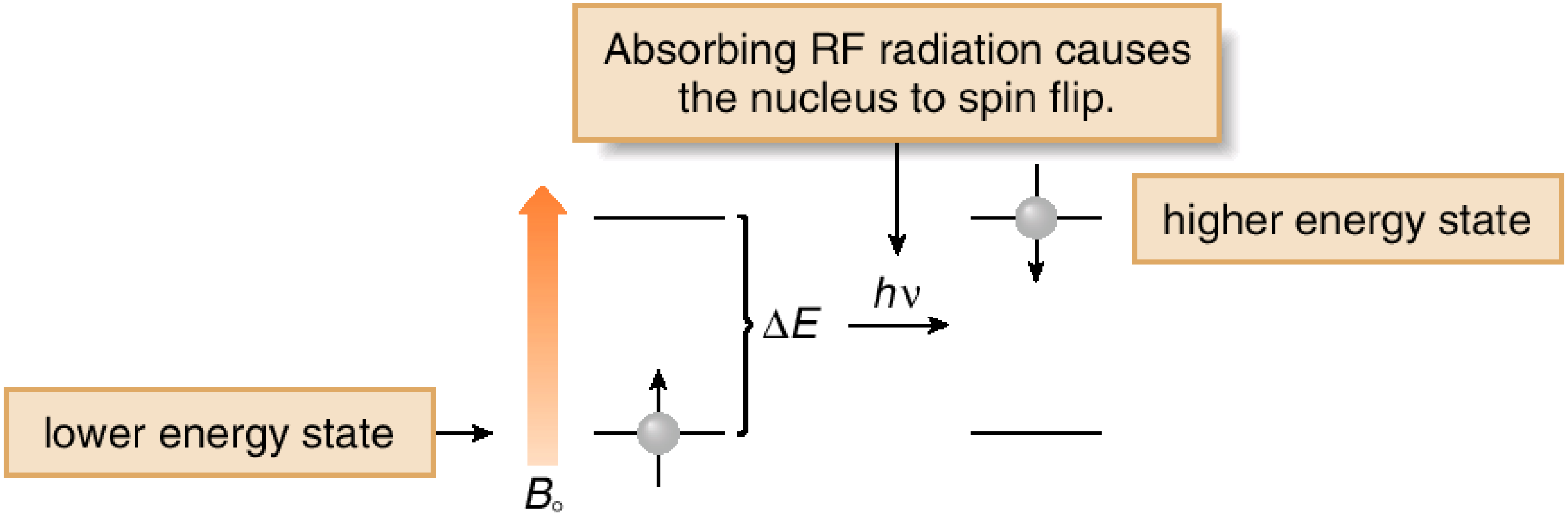
$$\mathbf{V = KH_0}$$

where *K is a constant characteristic of the nucleus observed*

V = resonance frequency.

For every value of *Ho there is a matching value of v corresponding to the condition of*

- 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.

NMR

- ✓ Mainly uses radiation between 1- 100 m wavelength or 3-300 MHz frequency.
- ✓ Absorption of EMR in radio-frequency results in change in orientation of spinning nuclei in a magnetic field
- ✓ Instrumentation-
    - ✓ Powerful and highly homogeneous electromagnet
    - ✓ Radio-frequency signal generator
    - ✓ Glass sample tube
    - ✓ Detector, and signal processor
- ✓ Application- identification and structural analysis of organic compounds
- ✓ Kinetics study

Disadvantage

- Expensive and complex instrumentation
- Limited range of solvents to be used *complete analysis and interpretation of the entire spectrum is normally expected*
- samples weighing less than a milligram

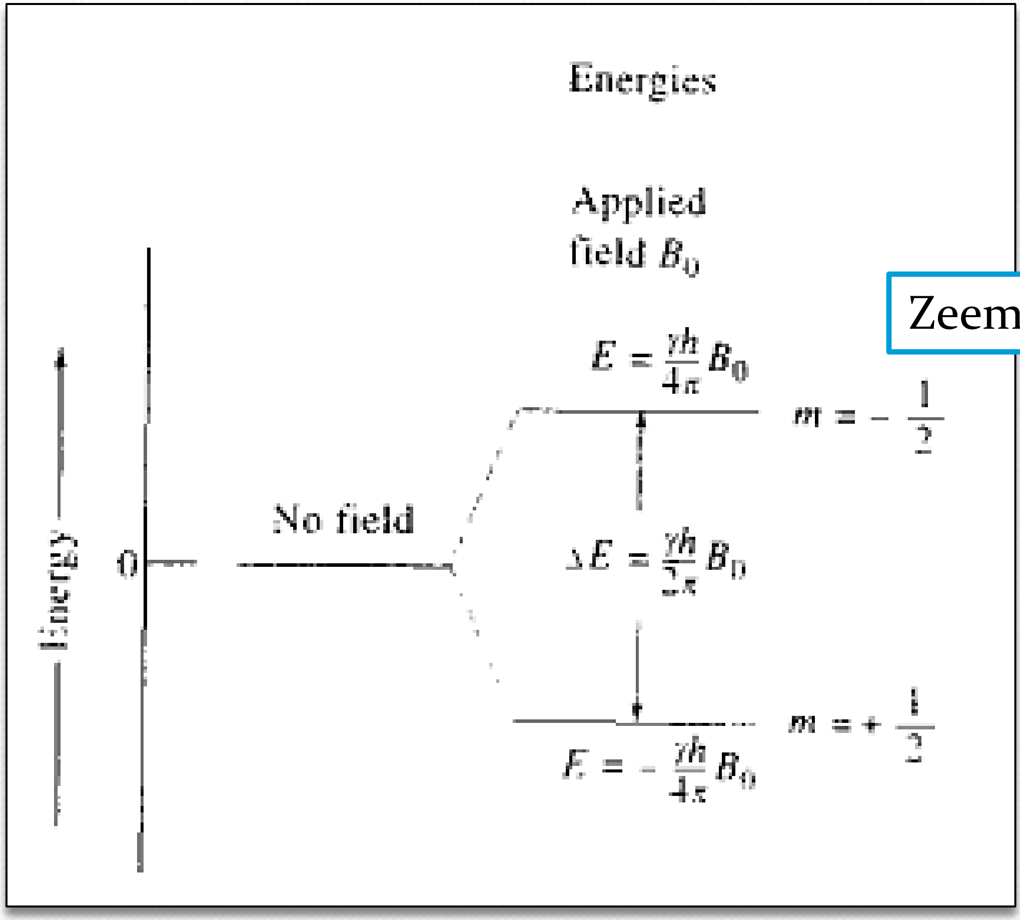
Magnetic energy

- nuclei are charged.
  - The spinning of a charged body produces a magnetic moment along the axis of rotation.
  - The nuclear magnetic moment μ expresses the magnitude of the magnetic dipole.
  - The ratio of the nuclear magnetic moment to the spin quantum number is called the magnetogyric (or gyromagnetic) ratio and is given the symbol g. Therefore γ = m/I. This ratio has a different value for each type of nucleus.
  - The magnetic field of a nucleus that possesses a nuclear magnetic moment can and does interact with other local magnetic fields.
  - The basis of NMR is the study of the response of such magnetically active nuclei to an external applied magnetic field

$$m = I, I - 1, I - 2, \ldots\ldots, -I$$

Zeeman splitting

In the presence of an applied magnetic field, a nucleus with I =1/2 can exist in one of two discrete energy levels. The levels are separated by ΔE. The lower energy level (m =1/2) has the nuclear magnetic moment aligned with the field; in the higher energy state (m =-1/2), the nuclear magnetic moment is aligned against the field.



Zeeman splitting.

Isotope	Natural % Abundance	Spin (I)	Magnetic Moment (μ)*	Magnetogyric Ratio (γ)†
^{1}H	99.9844	1/2	2.7927	26.753
^{2}H	0.0156	1	0.8574	4,107
^{11}B	81.17	3/2	2.6880	--
^{13}C	1.108	1/2	0.7022	6,728
^{17}O	0.037	5/2	-1.8930	-3,628
^{19}F	100.0	1/2	2.6273	25,179
^{29}Si	4.700	1/2	-0.5555	-5,319
^{31}P	100.0	1/2	1.1305	10,840

* **μ** in units of nuclear magnetons = $5.05078 \cdot 10^{-27}$ JT^{-1}

† γ in units of 10^{7} rad T^{-1} sec^{-1}

- 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.

NMR spectrometers

- Components of an NMR spectrometer are a

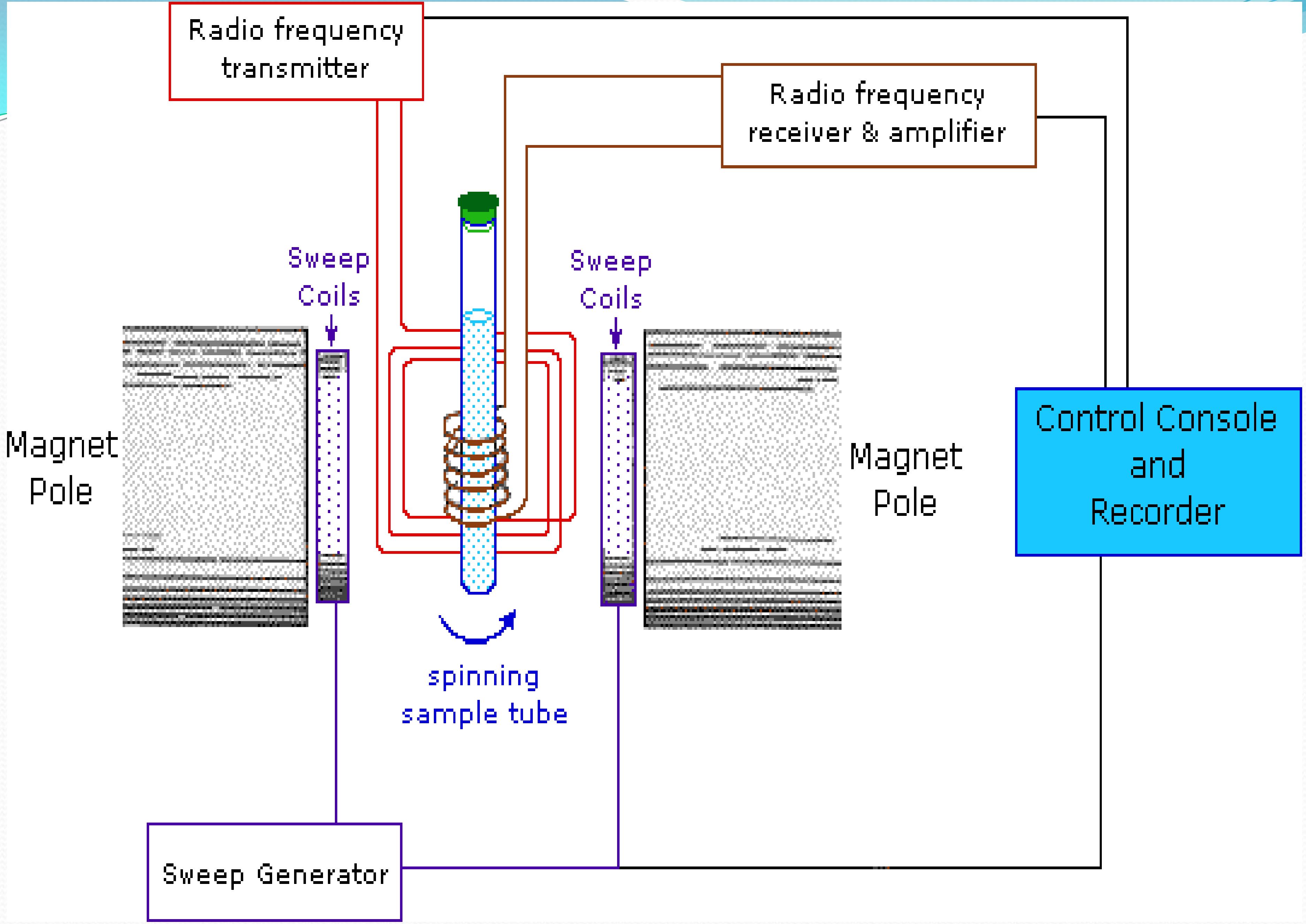
1. powerful magnet that supply range of magnetic fields

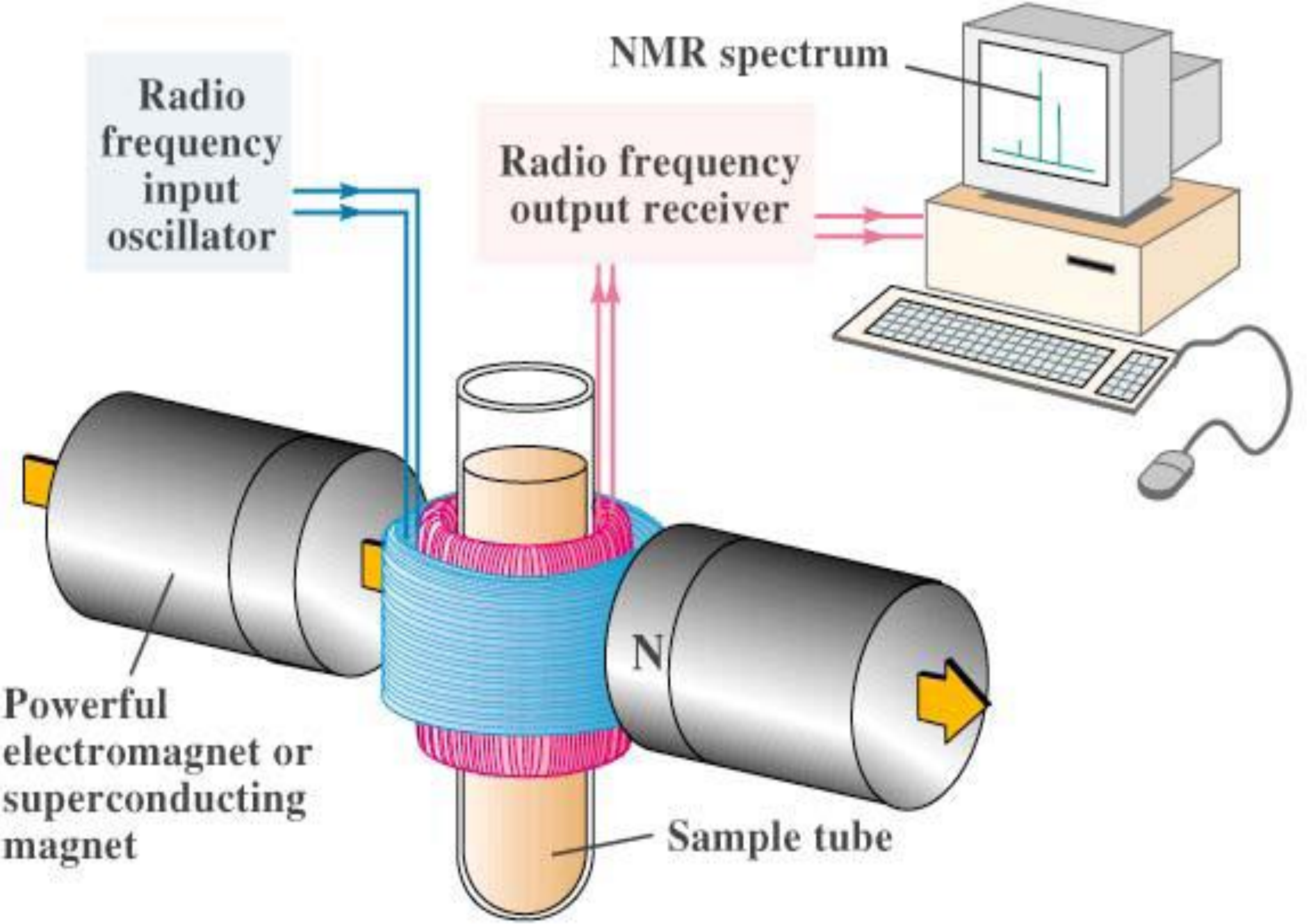
2. a radio-frequency generator

3. a radio-frequency receiver

4. a radio-frequency detector and

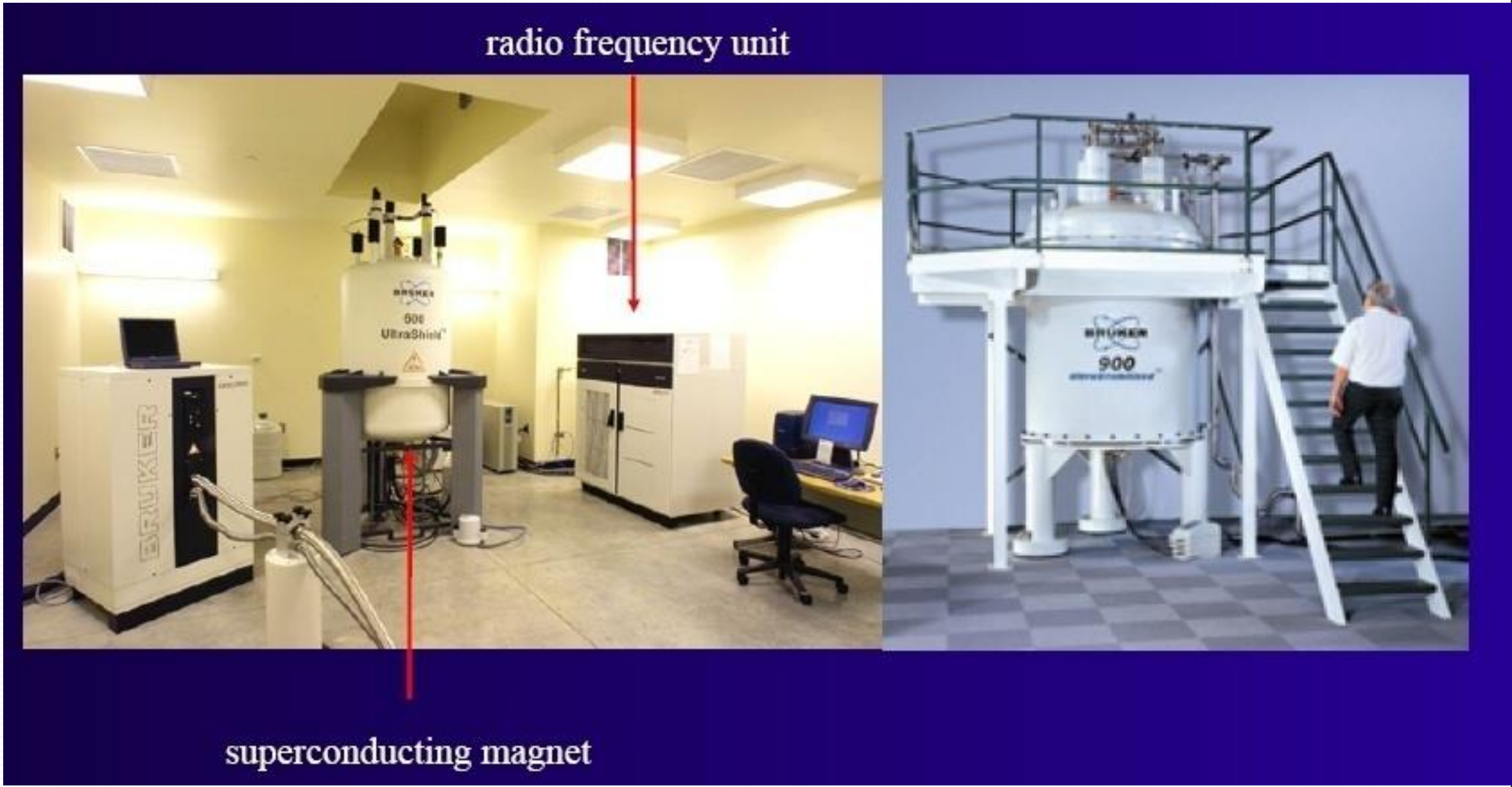
5. a sample holder


Radio frequency transmitter
Radio frequency receiver & amplifier
Sweep Coils
Sweep Coils
Magnet Pole
Magnet Pole
Control Console and Recorder
spinning sample tube
Sweep Generator


Radio frequency input oscillator
NMR spectrum
Radio frequency output receiver
N
Powerful electromagnet or superconducting magnet
Sample tube

1. A magnet to separate the nuclear spin energy states.
2. (a) One Rf channel for field or frequency stabilization, which produces stability for long-term operation, (b) one Rf channel to furnish irradiating energy to the sample, and (c) a third channel that may be added for decoupling nuclei.
3. A sample probe that houses the sample and also coils for coupling the sample with the rf transmitter and the phase-sensitive detector. It is inserted between the pole faces of the magnet.
4. A detector to collect and process the NMR signals.
5. A sweep generator for sweeping the Rf field through the resonance frequencies of the sample. Alternatively, the magnetic field may be swept and the rf field held constant.
6. A recorder to display the spectrum.

An NMR Laboratory



The Acquisition of an NMR spectrum

- As the NMR phenomenon is not observable in the absence of an applied magnetic field, a magnet is an essential component of any NMR spectrometer.
- Magnets for NMR may be **permanent magnets** (as in many low field routine instruments), **electromagnets**, or in most modem instruments they are based on **superconducting solenoids**, cooled by liquid helium.

All magnets used for NMR spectroscopy share . the following characteristics:

- The magnetic field must be strong.
  - This is partly due to the fact that the sensitivity of the NMR experiment increases as the strength of the magnet increases, but more importantly it ensures adequate dispersion of signals and, in the case of 'H NMR, also very important simplification of the spectrum.
- The magnetic field must be extremely homogeneous
  - so that all portions of the sample experience exactly the same magnetic field. Any inhomogeneity of the magnetic field will result in broadening and distortion of spectral bands.
- The magnetic field must be very stable,
  - so that it does not drift during the acquisition of the spectrum, which may take from several seconds to several hours.

- 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.
- 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 ^{1}H, ^{13}C, ^{19}F and ^{31}P) or odd atomic numbers (such as ^{2}H and ^{14}N) give rise to NMR signals.

Most Common types of NMR spectroscopy

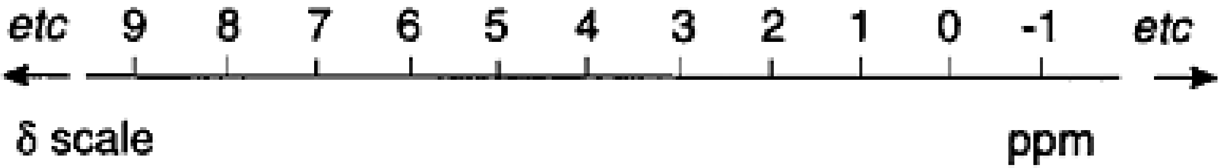
- ^{1}H-NMR: determine the type and number of H atoms in a molecule;
- ^{13}C-NMR: determine the type and number of carbon atoms a molecule.

a) ^{1}H NMR spectrum

- A ^{1}H NMR spectrum is a graph of resonance frequency (the intensity of Rf absorption by the sample vs chemical shift) .
- The spectrum is usually calibrated in dimensionless units called "parts per million" (abbreviated to ppm) although the horizontal scale is a frequency scale, the units are converted to ppm so that the scale has the same numbers irrespective of the strength of the magnetic field in which the measurement was made.
- The scale in ppm, termed the 0 scale, is usually referenced to the resonance of some standard substance whose frequency is chosen as 0.0 ppm. The frequency difference between the resonance of a nucleus and the resonance of the reference compound is **termed the chemical shift.**
- *Every hydrogen and carbon atom in an organic molecule is "a **chromophore**" for NMR spectroscopy*

Chemical shift (σ)

- Unlike infrared and uv-visible spectroscopy, where absorption peaks are uniquely located by a frequency or wavelength, the location of different nmr resonance signals is dependent on both the external magnetic field strength and the RF frequency.
- So it is difficult to assign consistent peak for each magnetic field and frequency variation
- A shielded nucleus resonates or absorbs at a lower frequency than an unshielded nucleus.
- Solution- **reference used**



Reference signal

- Tetramethylsilane, $(CH_3)_4Si$, usually referred to as TMS, reference compound of choice for proton and carbon nmr.
- **Properties of TMS**
  - Low boiling(26.5^0C)   Chemically inert
  - Symmetrical   Soluble in most organic compounds
  - Gives single, intense sharp absorption peak
  - Its protons are more shielded than most organic compounds
  - In TMS all 12 hydrogen nuclei are chemically equivalent; that is, they are all exposed to the same shielding and give a single absorption peak.
- the TMS peak appears at the far right of the spectrum and designated zero
- NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the ‘σ’ scale due to tetramethylsilane (TMS).

Chemical Shift,

- The frequency difference between the resonance of a nucleus and the resonance of the reference compound is termed the chemical shift.
- Chemical shift having units of parts-per-million (ppm), and designated by the symbol δ. The chemical shifts of nuclei are measured (defined) relative to a standard nucleus

- **For convenience, the chemical shift is expressed as follows:**

$$\delta(\text{ppm}) = 10^6 \times \frac{\nu(\text{sample}) - \nu(\text{reference})}{\text{spectrometer frequency}}$$

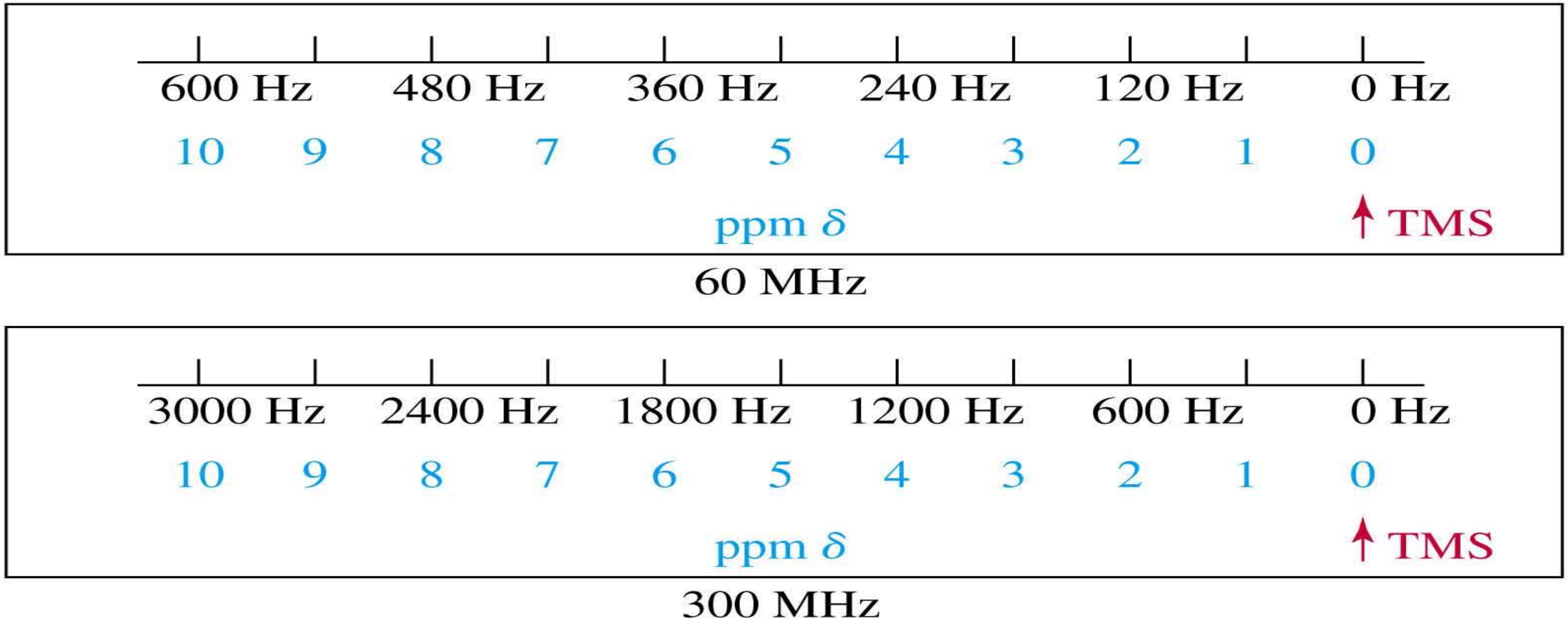
$$\delta = \frac{\nu_S - \nu_R}{\nu_{NMR}} \times 10^6 \text{ ppm}$$

$$= 10^6 \times \frac{\text{Shift in frequency from TMS (Hz)}}{\text{Frequency of spectrometer (Hz)}}$$

The TMS peak, not shown in this figure, would be a single peak located at 0.0 ppm, by definition.

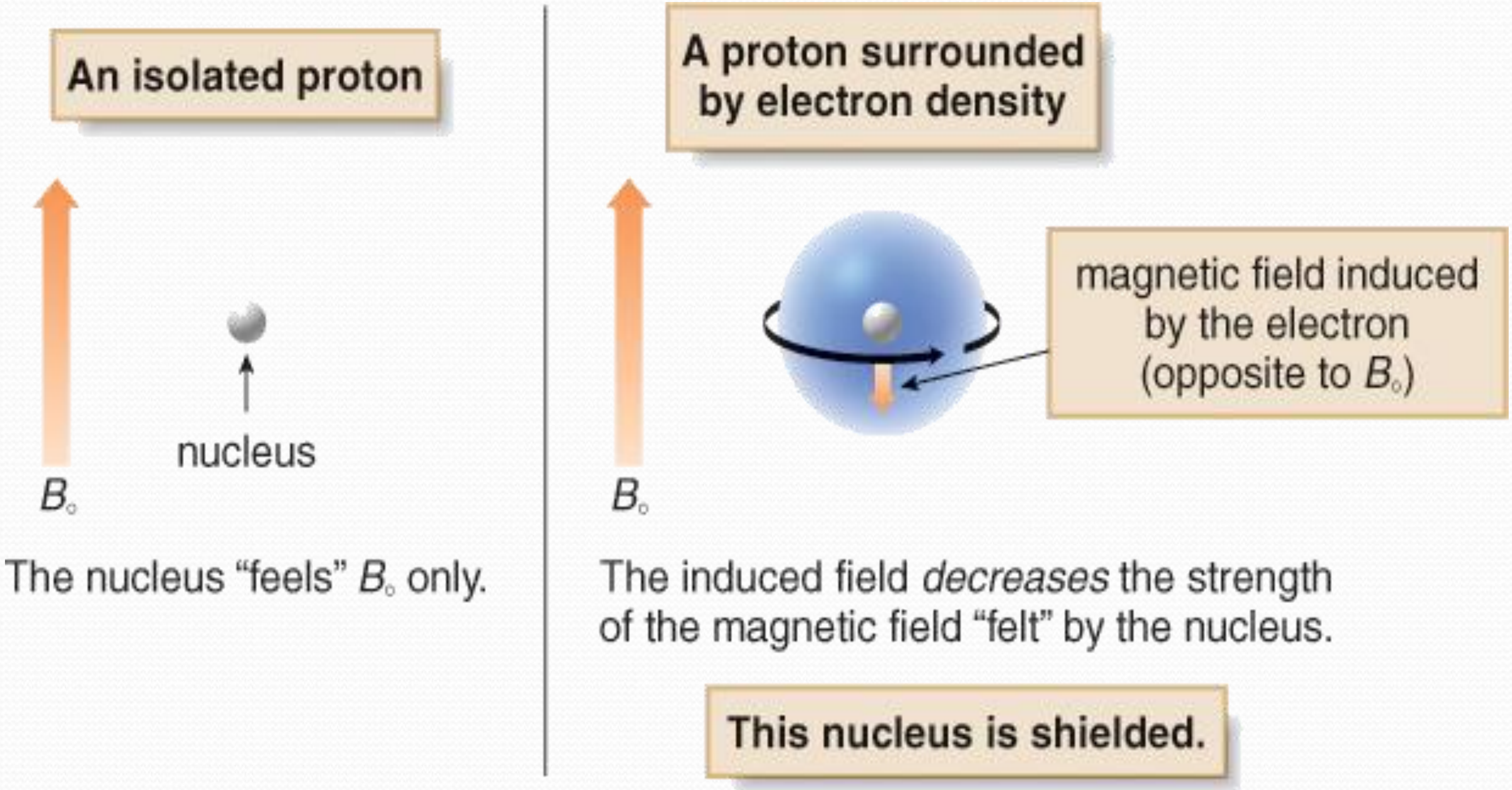
- It is a convention that NMR spectra are presented with the magnetic field increasing from left to right along the x-axis.
- A nucleus that absorbs to the right hand side of the spectrum is said to be more shielded than a nucleus that absorbs to the left side of the **spectrum.**

$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$



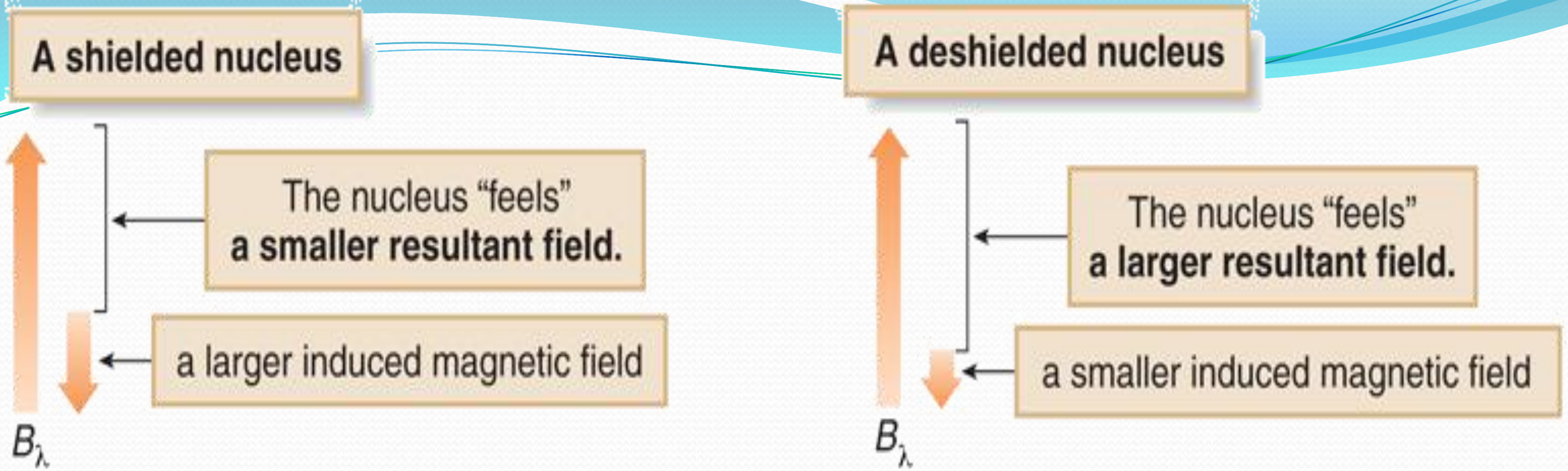
ENVIRONMENTAL EFFECTS ON NMR SPECTRA

- The frequency of RF radiation that is absorbed by a given nucleus is strongly affected by its chemical environment - that is, by nearby electrons and nuclei.



- In the vicinity of the nucleus, the magnetic field generated by the circulating electron decreases the external magnetic field that the proton “feels”.
- Since the electron experiences a lower magnetic field strength, it needs a lower frequency to achieve resonance. Lower frequency is to the right in an NMR spectrum, toward a lower chemical shift, so shielding shifts the absorption upfield.

- 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, so 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 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.**

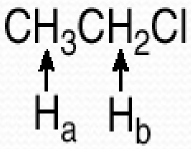
a smaller induced magnetic field

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.**

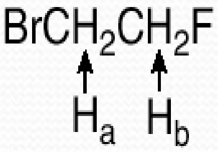
- Most protons absorb between 0-10 ppm.
- The terms "upfield" and "downfield" describe the relative location of peaks.
- Upfield means to the right.
- Downfield means to the left.

The spectra interpretation



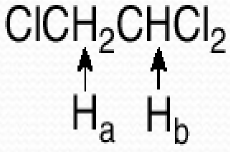
$\underset{\overset{\uparrow}{H_a}}{CH_3}\underset{\overset{\uparrow}{H_b}}{CH_2}Cl$

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



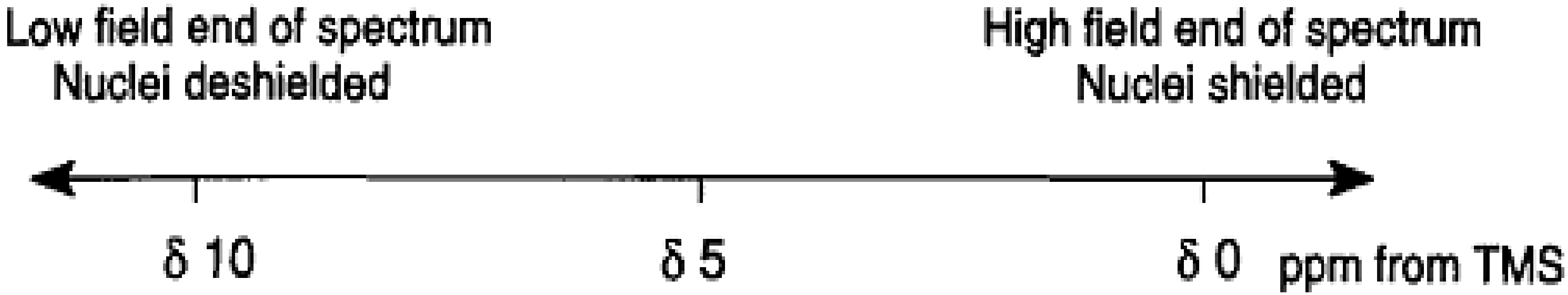
$Br\underset{\overset{\uparrow}{H_a}}{CH_2}\underset{\overset{\uparrow}{H_b}}{CH_2}F$

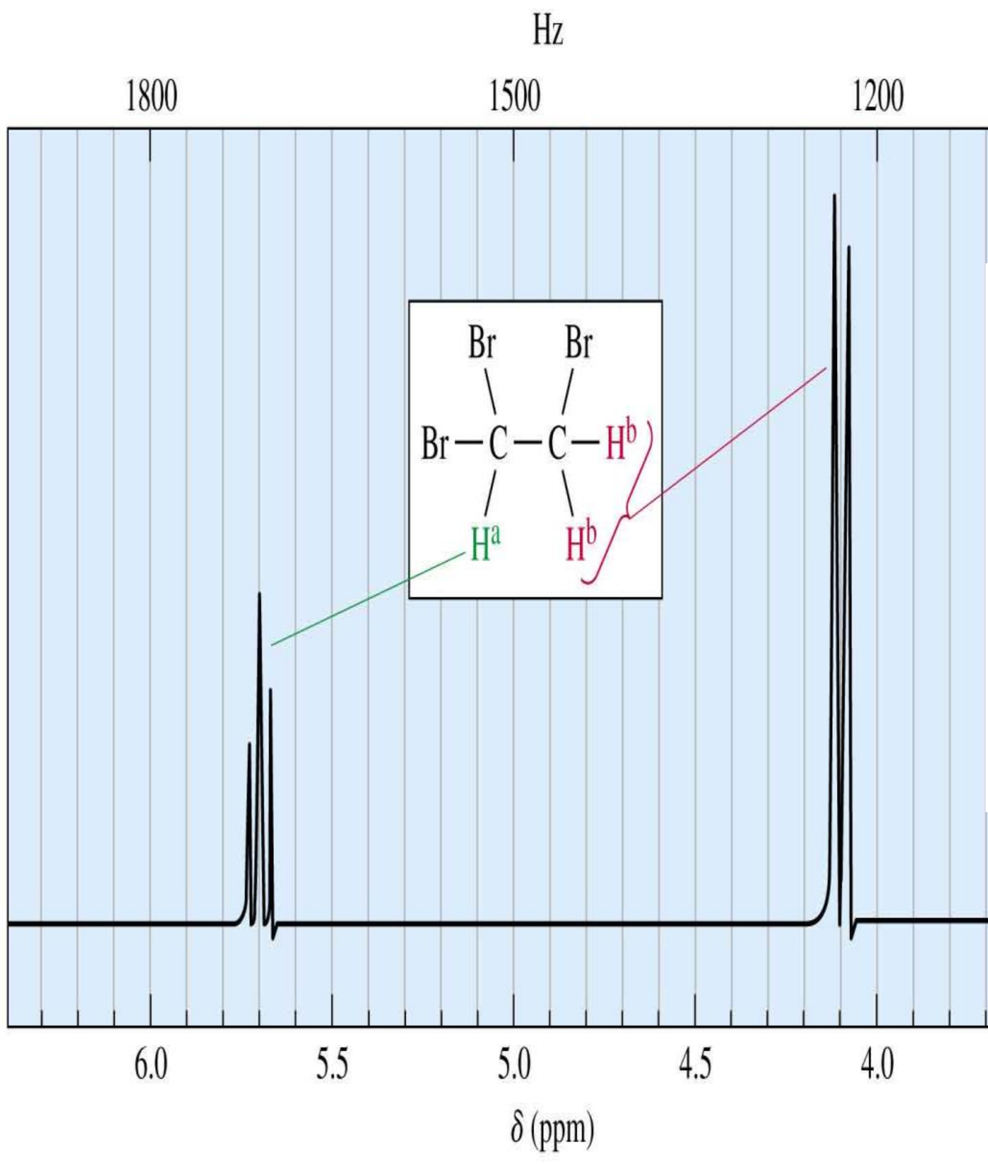
- Because F is more electronegative than Br, the H_b protons are more **deshielded** than the H_a protons and absorb farther **downfield.**



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

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





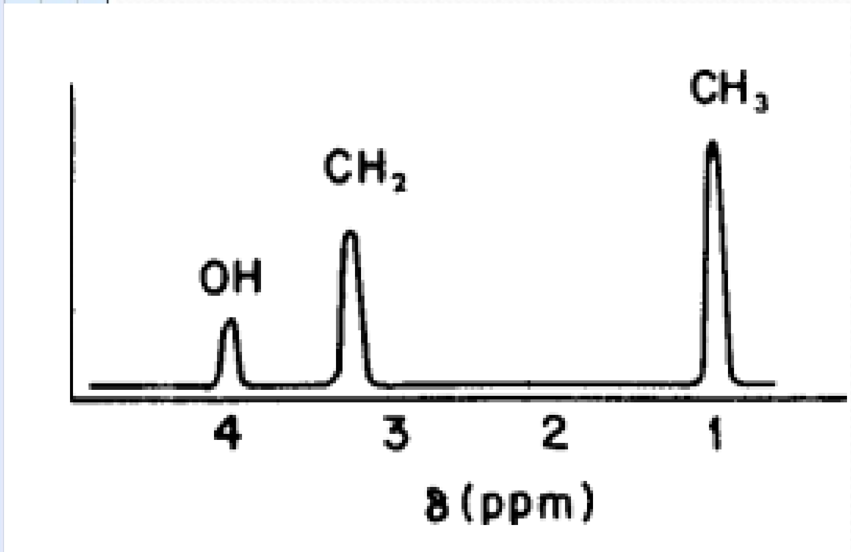


Figure Low resolution proton NMR absorption spectrum of ethanol, CH_3CH_2OH.

Factors affecting chemical shift

A). Intermolecular factor

In dilute solutions, the dominant factor is intermolecular factor

Include

- Inductive effect
- Anisotropy of chemical bond
- Vanderwaal deshilding

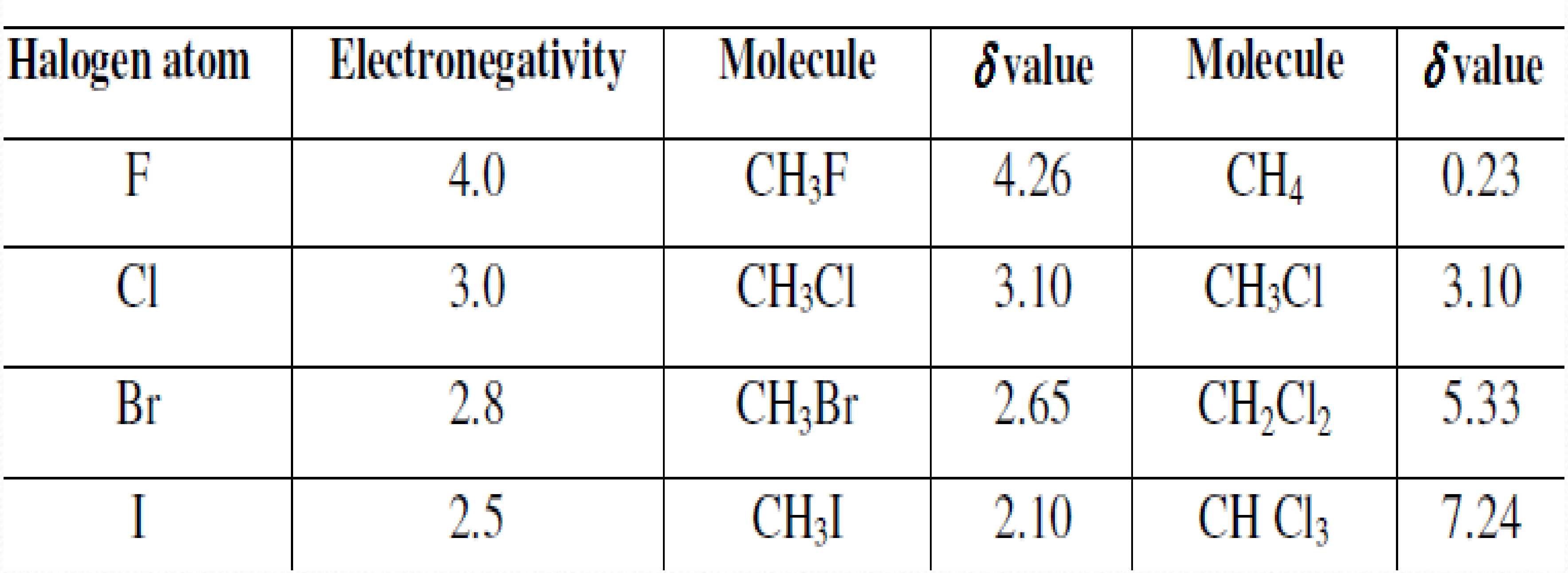
B). Effect of concentration, solvent and temp.

A). Intermolecular factor

Inductive effect

- Electrons under the influence of a magnetic field will circulate and will generate their own magnetic field opposing the applied field
- Shielding of the nucleus
- high electronegativity in a molecule draws electron density towards itself. This causes a decrease in the electron density leading to deshielding of the nucleus
- Thus, with increasing electronegativity values will become high or go downfield.

- The effect of electronegativity and the number of halogen atoms on the chemical shift position of protons in simple methylhalide



Halogen atom	Electronegativity	Molecule	δ value	Molecule	δ value
F	4.0	CH_3F	4.26	CH_4	0.23
Cl	3.0	CH_3Cl	3.10	CH_3Cl	3.10
Br	2.8	CH_3Br	2.65	CH_2Cl_2	5.33
I	2.5	CH_3I	2.10	$CH Cl_3$	7.24

Proton Chemical Shifts of Methyl Derivatives

Compound	$(CH_3)_4C$	$(CH_3)_3N$	$(CH_3)_2O$	CH_3F
δ	0.9	2.1	3.2	4.1
Compound	$(CH_3)_4Si$	$(CH_3)_3P$	$(CH_3)_2S$	CH_3Cl
δ	0.0	0.9	2.1	3.0

Cpd. / Sub.	X=Cl	X=Br	X=I	X=OR	X=SR
CH_3X	3.0	2.7	2.1	3.1	2.1
CH_2X_2	5.3	5.0	3.9	4.4	3.7
CHX_3	7.3	6.8	4.9	5.0	

II Anisotropy of chemical bonds

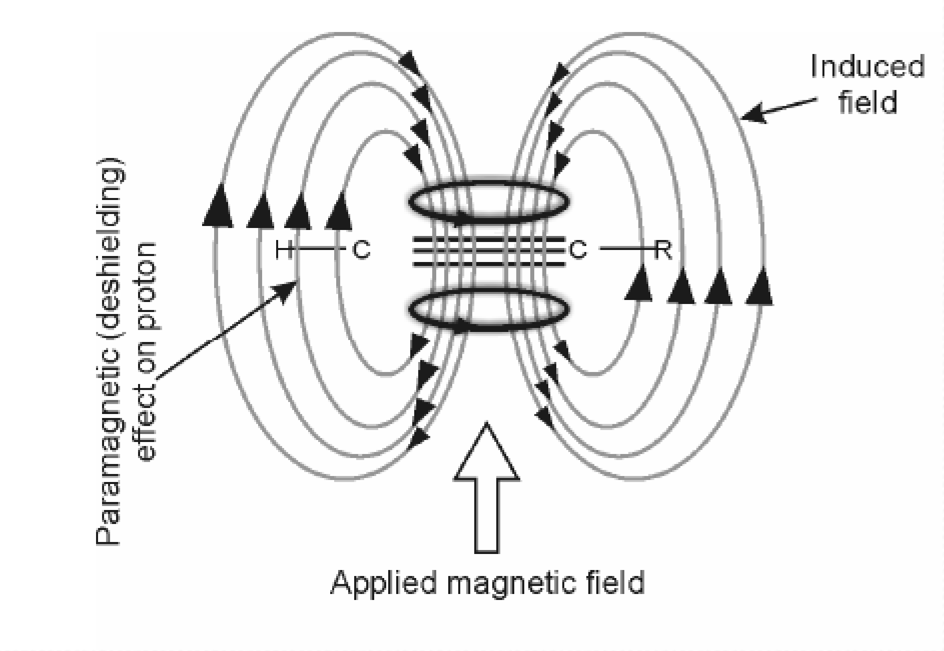
Diamagnetic anisotropy

- Shielding and deshielding depends on the orientation of the molecule wrt the applied magnetic filed

- With π electron cpds, an element of symmetry is lacking and therefore the magnetic field associated with the electron circulation induced by app. Magnetic field do not sum up zero then the neighboring nuclei my be shielded or deshielded

acetylene

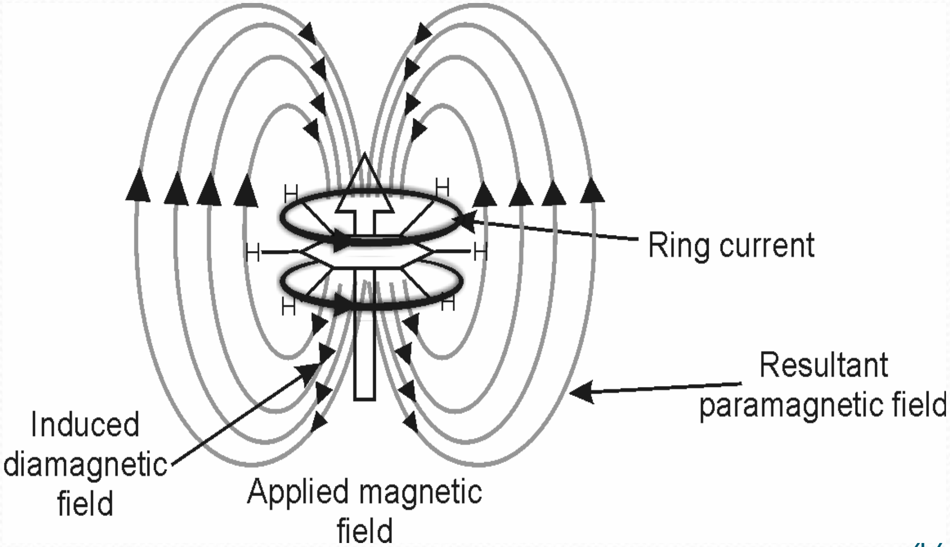
- The molecule is linear and symetrical about its axis
- π electron of the bond can circulate right angle to B_o
- Induce own magnetic field (B) opposing B_o
- The protons lie along the magnetic axis
- Shielding the proton
- Up field



Benzene

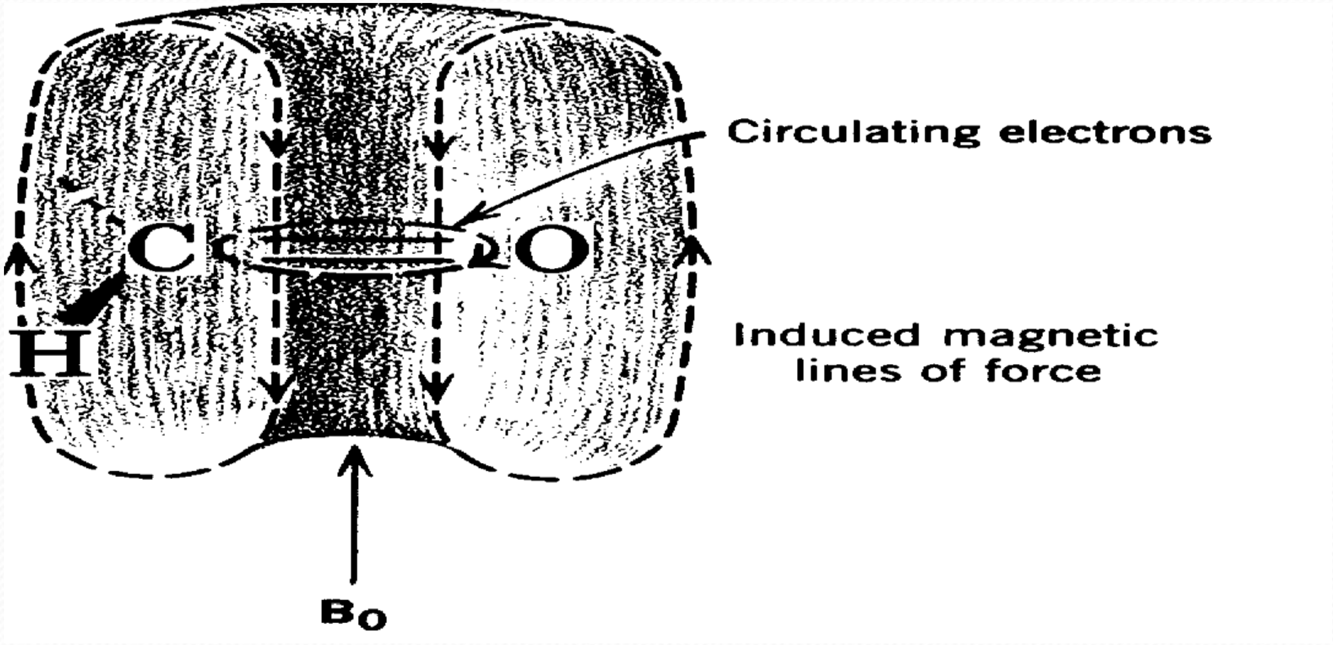
- Benzene diamagnetic anisotropy is also called Ring current effect
- the secondary magnetic field generated by the induced circulation of -electrons in benzene molecule aligned perpendicular to the applied field. The effects of the secondary magnetic field on a rigidly attached proton in the molecule do not average to zero for all possible orientations of the ring with respect to the applied field. You may note here that secondary magnetic field causes pronounced shielding at the centre of the ring but deshielding outside, in the plane of the ring containing protons.

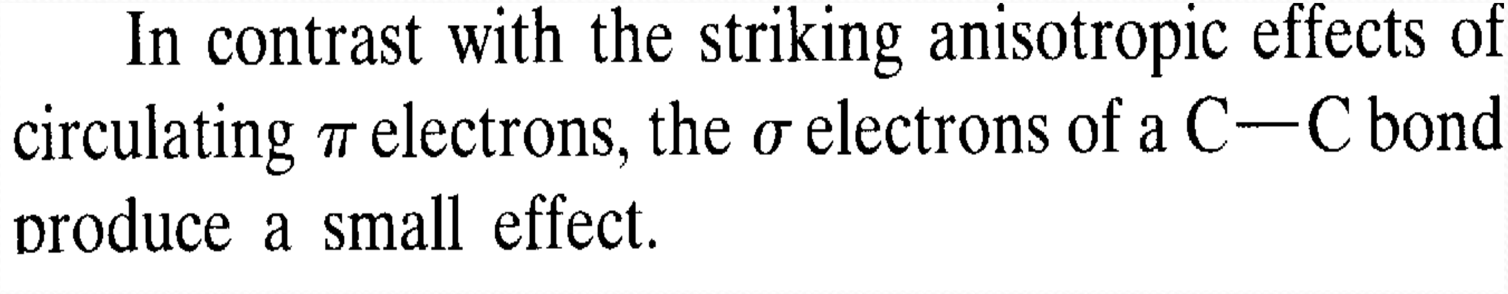
δ 7.22



aldehyde

- The aldehidic proton is in the deshielding portion of the induced magnetic field





In contrast with the striking anisotropic effects of circulating π electrons, the σ electrons of a C—C bond produce a small effect.

- Deshielding effect of successive alkyl substituent's on a proton attached to a carbon atom . The proton are found progressively downfield in the sequence: RCH_3 , R_2CH_2 , and R_3CH

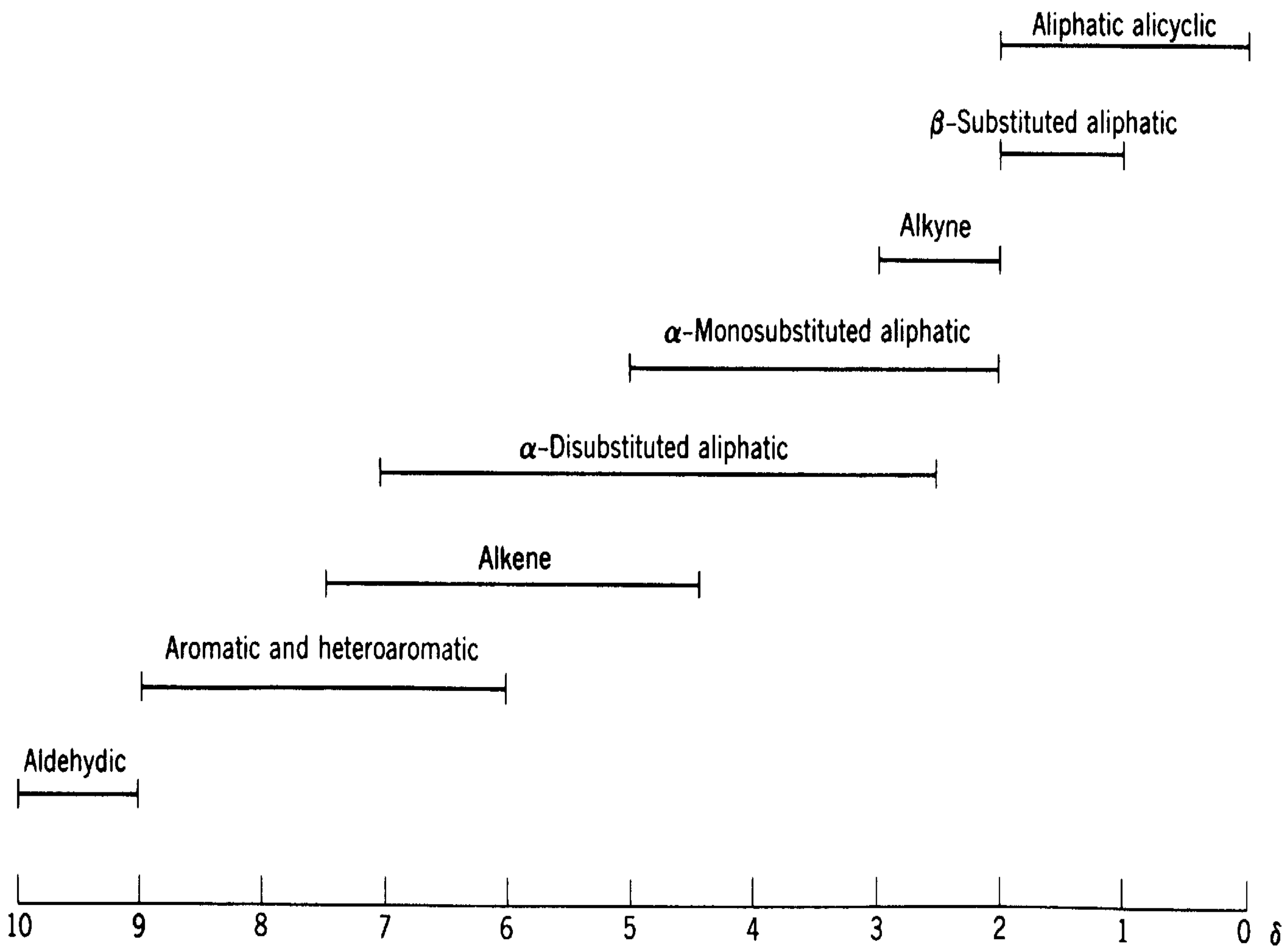


FIGURE 4.21. General regions of chemical shifts.

B) Effect of conc. Solvent and temp

- In conc. 0.05-0.5 M in CCl_4 and deutrated solvent, the resonance position of proton attached to carbon is seldom affected by temp. and conc. But OH. NH and SH proton are markedly affected by temp and conc due to H-bonding.
- All protons are sensitive to solvent change
- Hydrogen bonding is electron cloud transfer to the electronegative atom
- If hydrogen bond is strong then deshielding occurs (higher conc. And lower temp).
- At lower conc. H-bonding diminish and less deshielded

Solvents for NMR Spectroscopy.

- NMR spectra are almost invariably obtained in solution. The solvents of choice:

a) should have adequate dissolving power.

b) should not associate strongly with solute molecules

as this is likely to produce appreciable effects on chemical shifts. This requirement must sometimes be sacrificed to achieve adequate solubility.

c) should be essentially free of interfering signals. T

Thus for IHNMR, the best solvents are proton-free.

d) should preferably contain deuterium, ^{2}H.

Deuterium is an isotope of hydrogen which is relatively easy to obtain and incorporate into common solvents in place of hydrogen with insignificant changes to the properties of the solvent. Almost all NMR instruments use deuterium as a convenient "locking" signal for to stabilise the magnetic field of the NMR magnet

…solvent in NMR

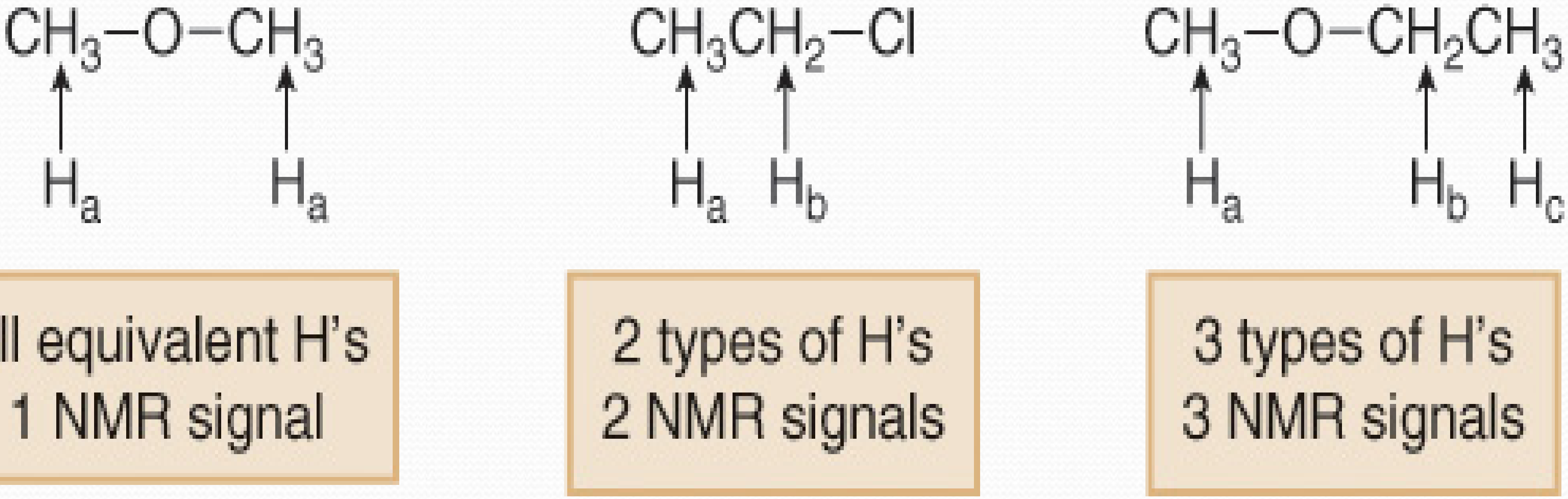
- CCl_4 is ideal whenever possible
- The most commonly used organic solvent is deuterochloroform, $CDCI_3$, which is an excellent solvent and is only weakly associated with most organic substrates. $CDCl_3$ contains no protons and has a deuterium atom.
- For ionic compounds or hydrophilic compounds, the most common solvent is deuterated water, D_2O.
- The sample (5-50 mg) is dissolved in a solvent (~0.5 mL), most commonly $CDCl_3$ or D_2O, and placed in a sample tube (5 mm diam.) which is then suspended in the magnetic field and set spinning.

Information from NMR

- The ***number*** of signals shows how many different kinds of protons are present.
- The ***location*** of the signals shows how shielded or deshielded the proton is.
- The ***intensity*** of the signal shows the number of protons of that type.
- Signal ***splitting*** shows the number of protons on adjacent atoms. =>

1) Number of signals

- **The number of NMR signals equals the number of different types of protons in a compound.**
- **Protons in different environments give different NMR signals.**
- **Equivalent protons give the same NMR signal.**



$CH_3{-}O{-}CH_3$

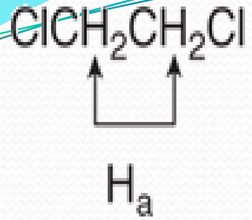
All equivalent H's
1 NMR signal

$CH_3CH_2{-}Cl$

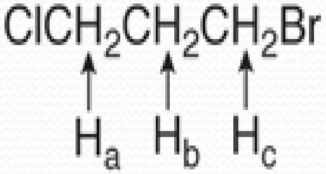
2 types of H's
2 NMR signals

$CH_3{-}O{-}CH_2CH_3$

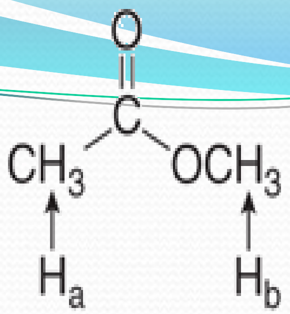
3 types of H's
3 NMR signals



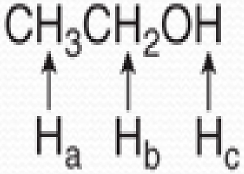
1 type of H
1 NMR signal



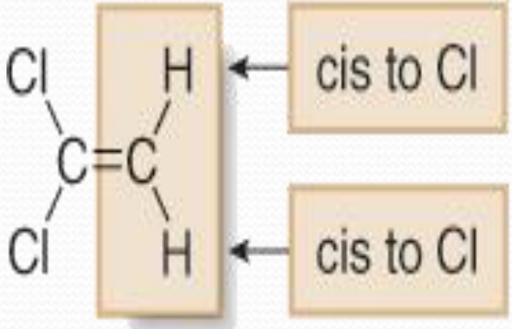
3 types of H's
3 NMR signals



2 types of H's
2 NMR signals

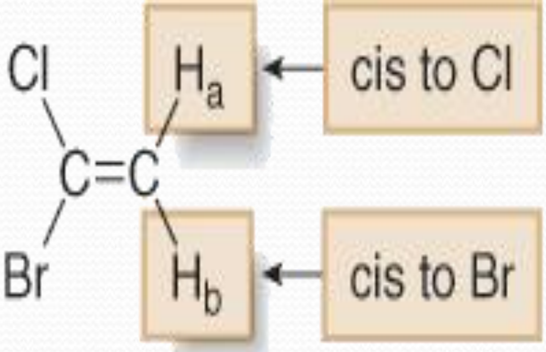


3 types of H's
3 NMR signals



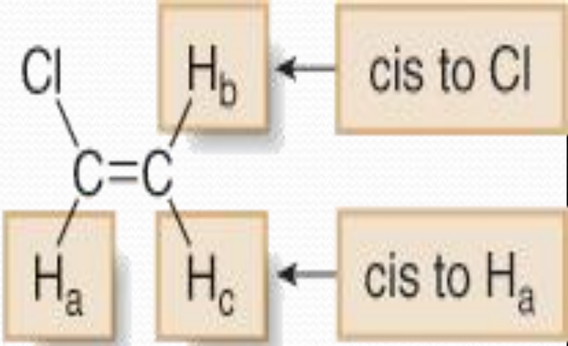
1,1-dichloroethylene

1 type of H
1 NMR signal



1-bromo-1-chloroethylene

2 types of H's
2 NMR signals



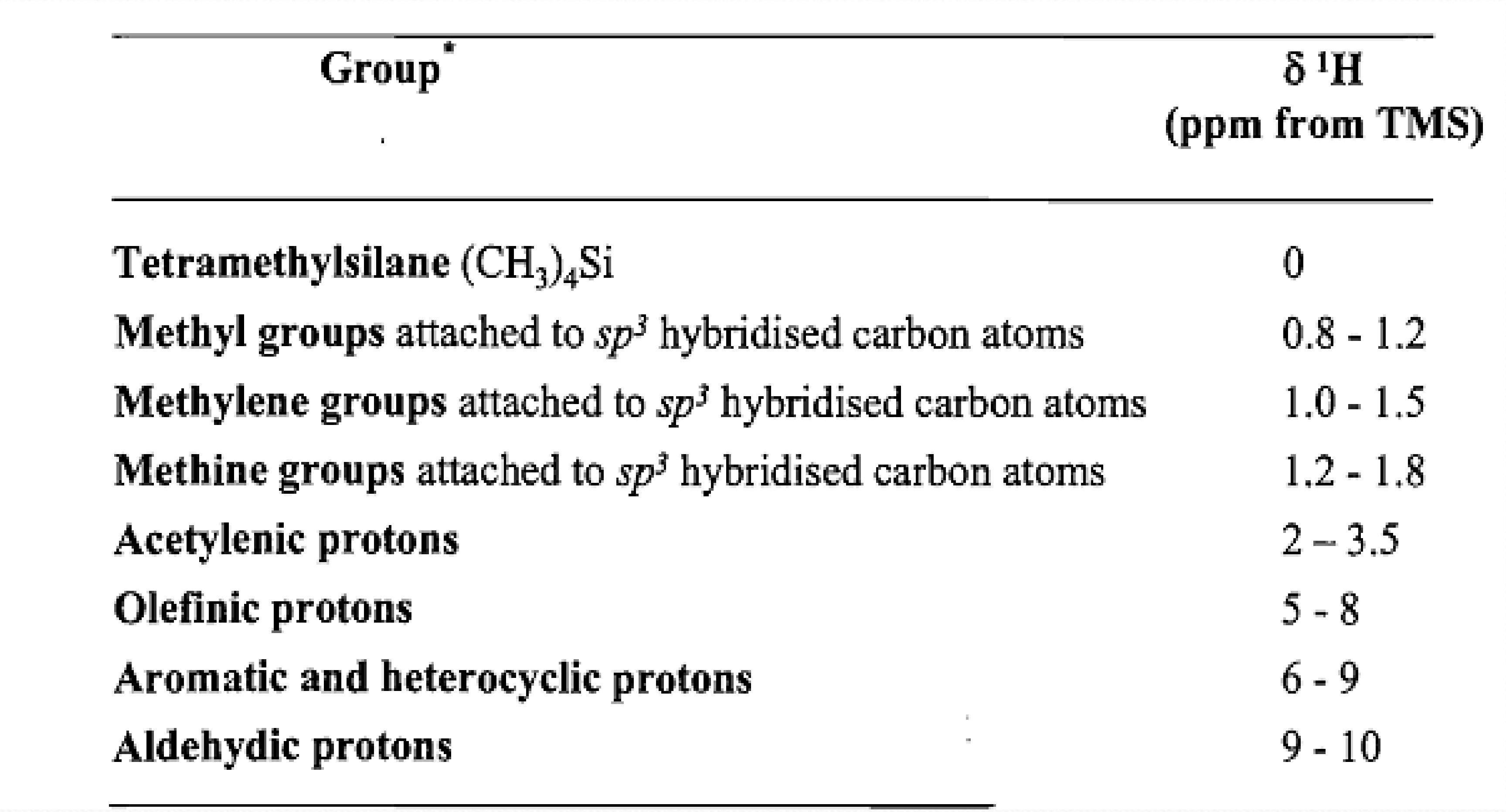
chloroethylene

3 types of H's
3 NMR signals

2) Location of Signal Chemical Shift Ranges in Organic Compounds

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

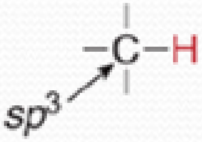
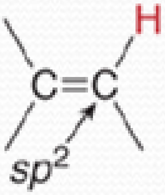
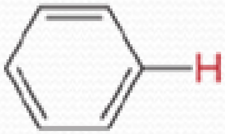
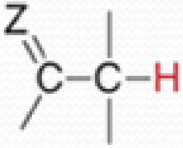
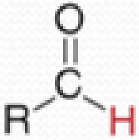
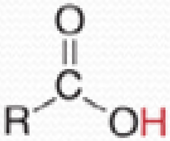
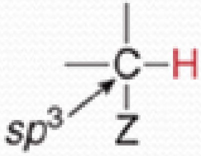
2) Location of Signal Chemical Shift Ranges in Organic Compounds

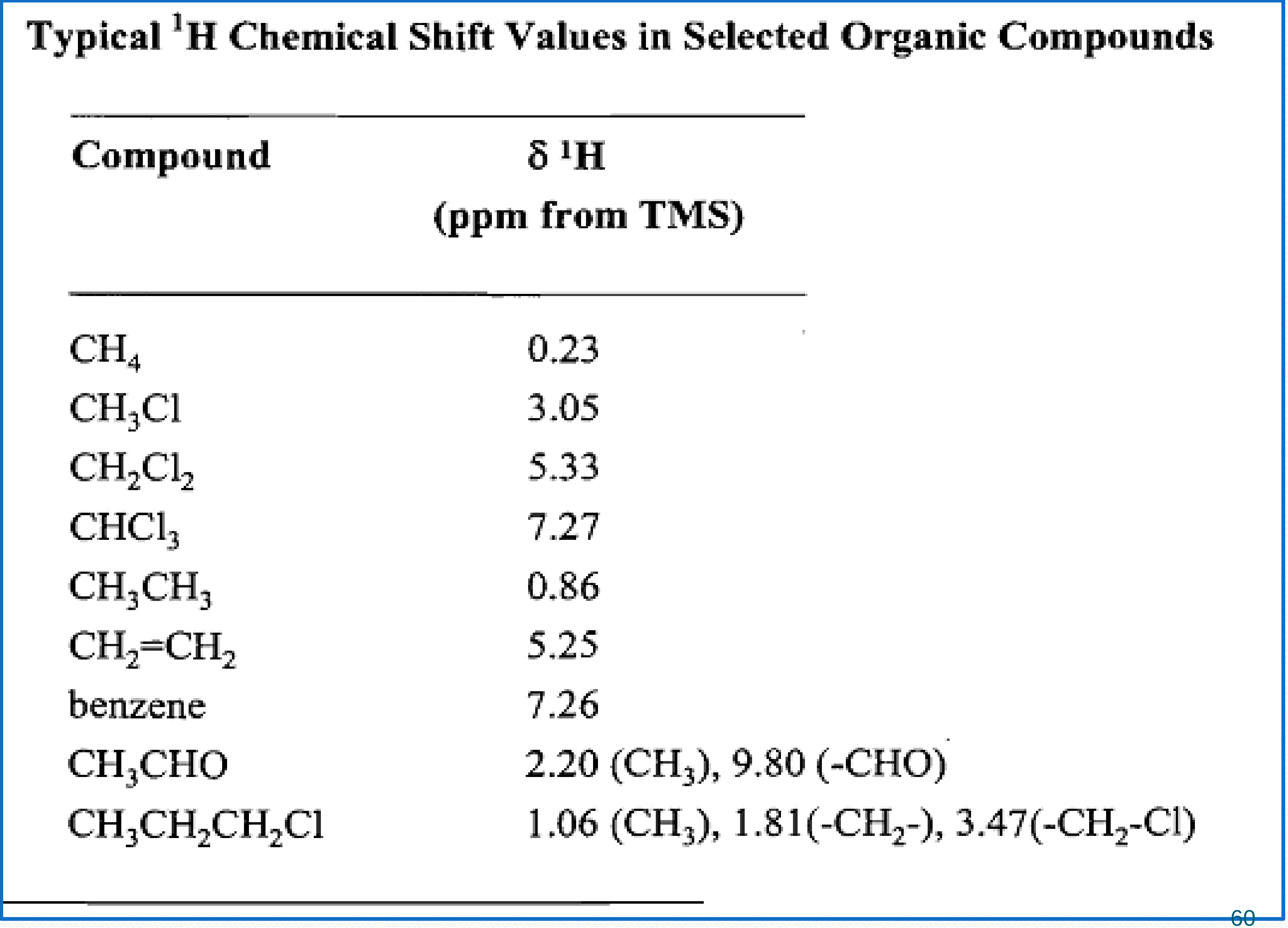


Group*	δ ^{1}H (ppm from TMS)
Tetramethylsilane $(CH_3)_4Si$	0
Methyl groups attached to *sp*^{3} hybridised carbon atoms	0.8 - 1.2
Methylene groups attached to *sp*^{3} hybridised carbon atoms	1.0 - 1.5
Methine groups attached to *sp*^{3} hybridised carbon atoms	1.2 - 1.8
Acetylenic protons	2 – 3.5
Olefinic protons	5 - 8
Aromatic and heterocyclic protons	6 - 9
Aldehydic protons	9 - 10

-OH protons in alcohols, phenols or carboxylic acids; -SH protons in thiols; -NH protons in amines or amides do not have reliable chemical shift ranges

Chemical shifts

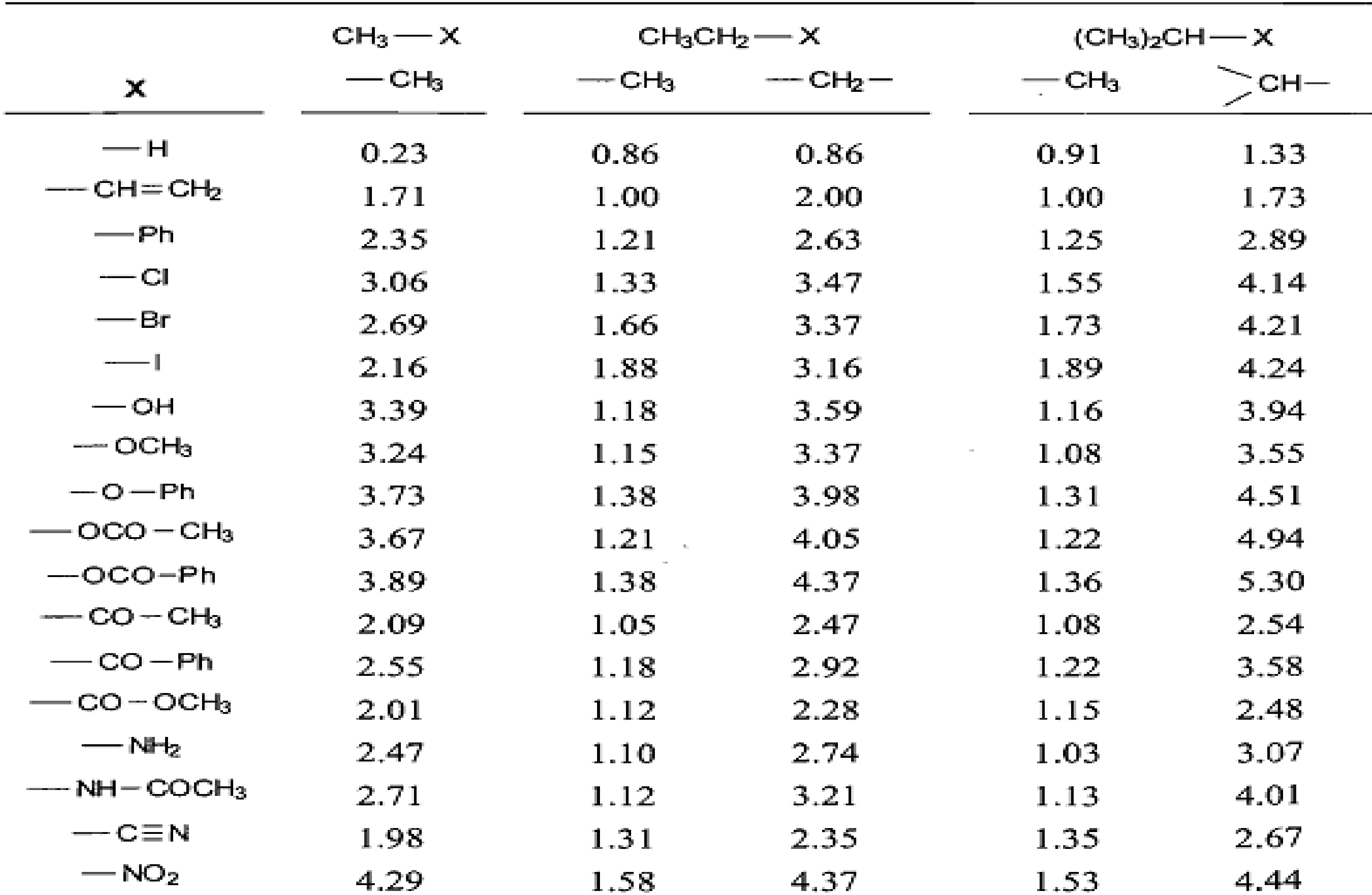
Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
	0.9–2		4.5–6
- RCH_3 - R_2CH_2 - R_3CH	~0.9 ~1.3 ~1.7		6.5–8
 Z = C, O, N	1.5–2.5		9–10
—C≡C—H	~2.5		10–12
 Z = N, O, X	2.5–4	RO–H or $R-\underset{\vert}{N}-H$	1–5



Typical ¹H Chemical Shift Values in Selected Organic Compounds

Compound	δ ¹H (ppm from TMS)
CH_4	0.23
CH_3Cl	3.05
CH_2Cl_2	5.33
$CHCl_3$	7.27
CH_3CH_3	0.86
$CH_2{=}CH_2$	5.25
benzene	7.26
CH_3CHO	2.20 (CH_3), 9.80 (-CHO)
$CH_3CH_2CH_2Cl$	1.06 (CH_3), 1.81(-CH_2-), 3.47(-CH_2-Cl)

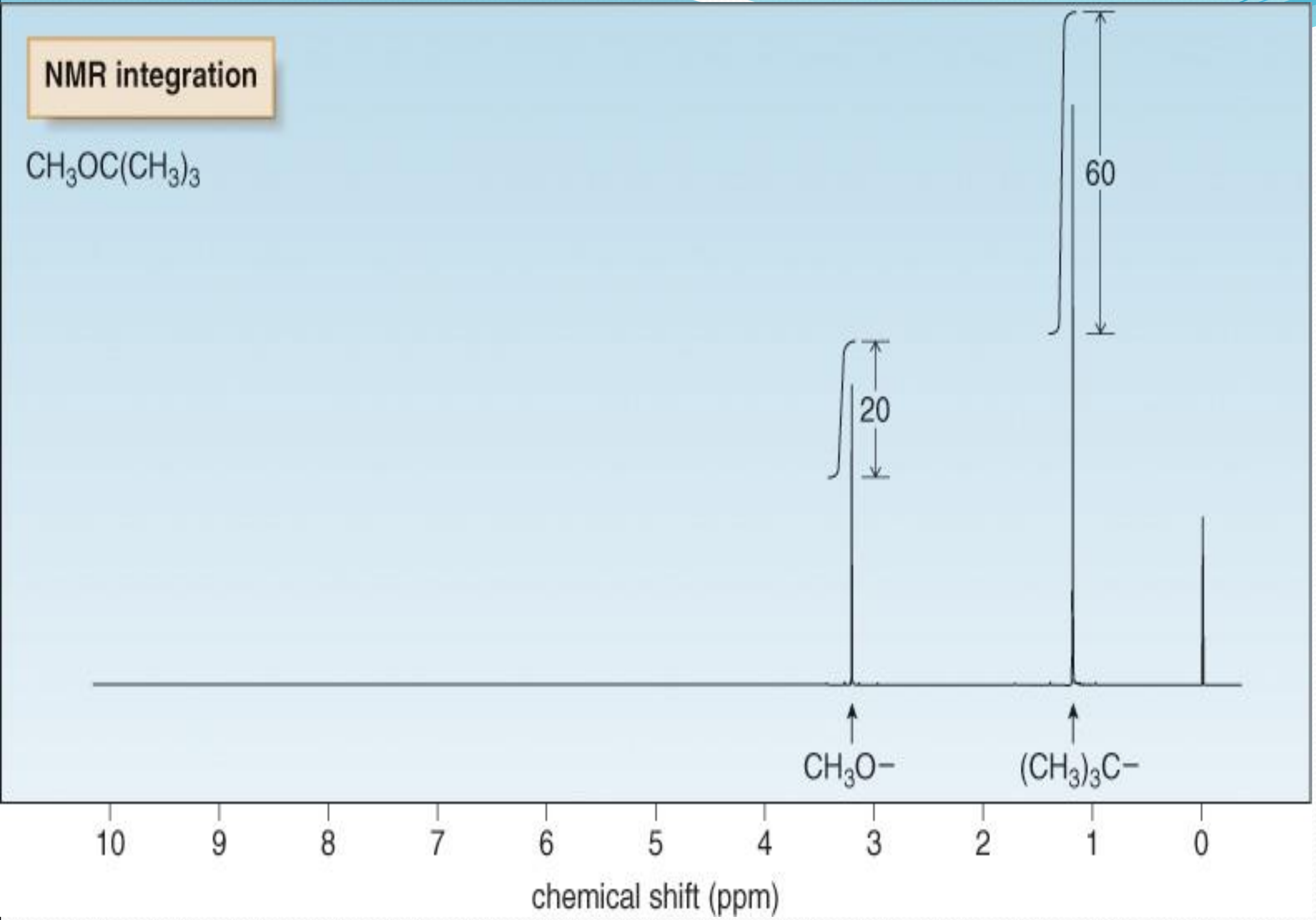
Table 'a Chemical Shifts (6) for Protons in Common Alkyl Derivatives



X	$CH_3—X$	$CH_3CH_2—X$		$(CH_3)_2CH—X$	
	$—CH_3$	$—CH_3$	$—CH_2—$	$—CH_3$	$>CH—$
$—H$	0.23	0.86	0.86	0.91	1.33
$—CH=CH_2$	1.71	1.00	2.00	1.00	1.73
$—Ph$	2.35	1.21	2.63	1.25	2.89
$—Cl$	3.06	1.33	3.47	1.55	4.14
$—Br$	2.69	1.66	3.37	1.73	4.21
$—I$	2.16	1.88	3.16	1.89	4.24
$—OH$	3.39	1.18	3.59	1.16	3.94
$—OCH_3$	3.24	1.15	3.37	1.08	3.55
$—O—Ph$	3.73	1.38	3.98	1.31	4.51
$—OCO—CH_3$	3.67	1.21	4.05	1.22	4.94
$—OCO—Ph$	3.89	1.38	4.37	1.36	5.30
$—CO—CH_3$	2.09	1.05	2.47	1.08	2.54
$—CO—Ph$	2.55	1.18	2.92	1.22	3.58
$—CO—OCH_3$	2.01	1.12	2.28	1.15	2.48
$—NH_2$	2.47	1.10	2.74	1.03	3.07
$—NH—COCH_3$	2.71	1.12	3.21	1.13	4.01
$—C\equiv N$	1.98	1.31	2.35	1.35	2.67
$—NO_2$	4.29	1.58	4.37	1.53	4.44

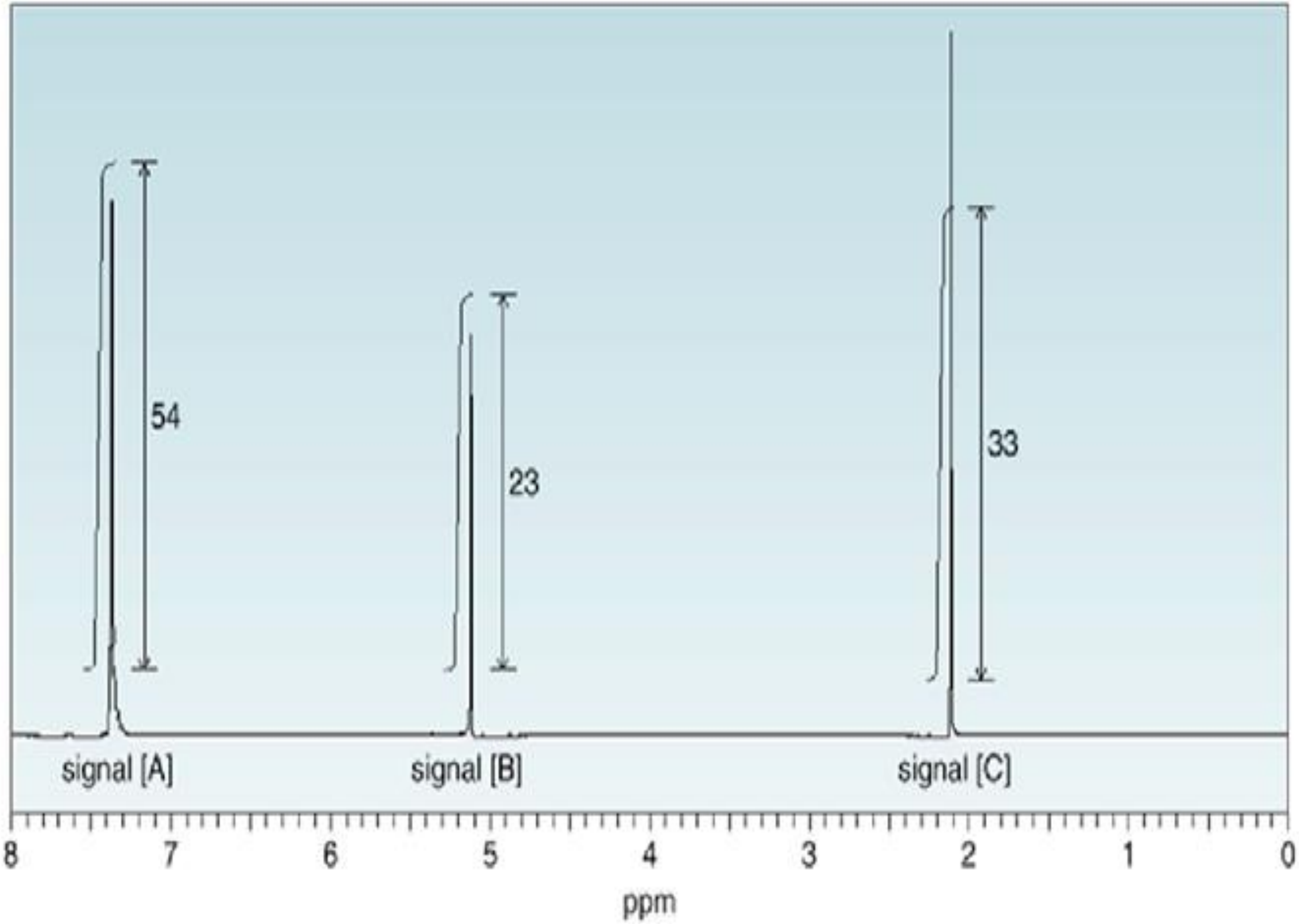
3) ^{1}H NMR—Intensity of Signals

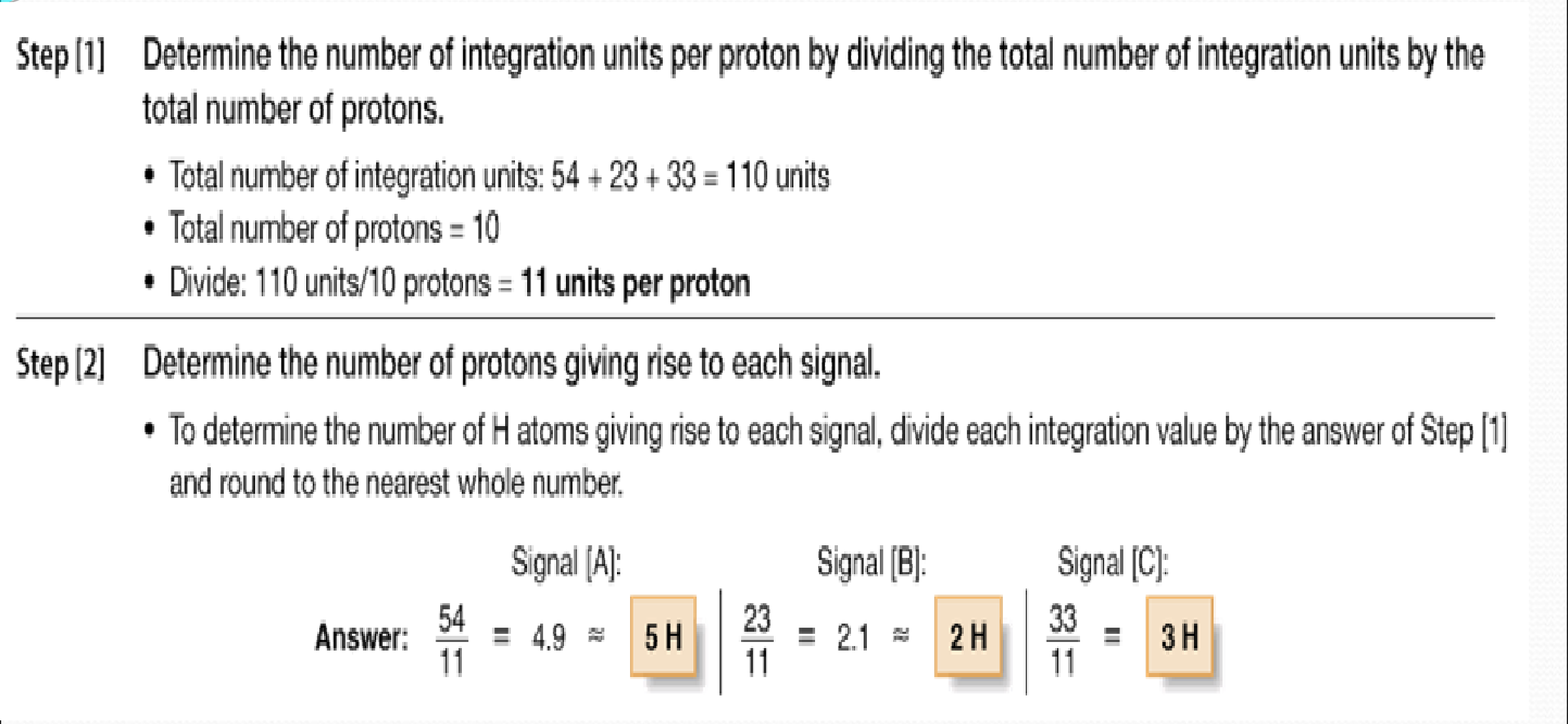
- **The area under an NMR signal is proportional to the number of absorbing protons.**
- **An NMR spectrometer automatically integrates the area under the peaks, and prints out a stepped curve (integral) on the spectrum.**
- **The height of each step is proportional to the area under the peak, which in turn is proportional to the number of absorbing protons.**
- **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 $C_9H_{10}O_2$ gives the following integrated ^1H NMR spectrum. How many protons give rise to each signal?





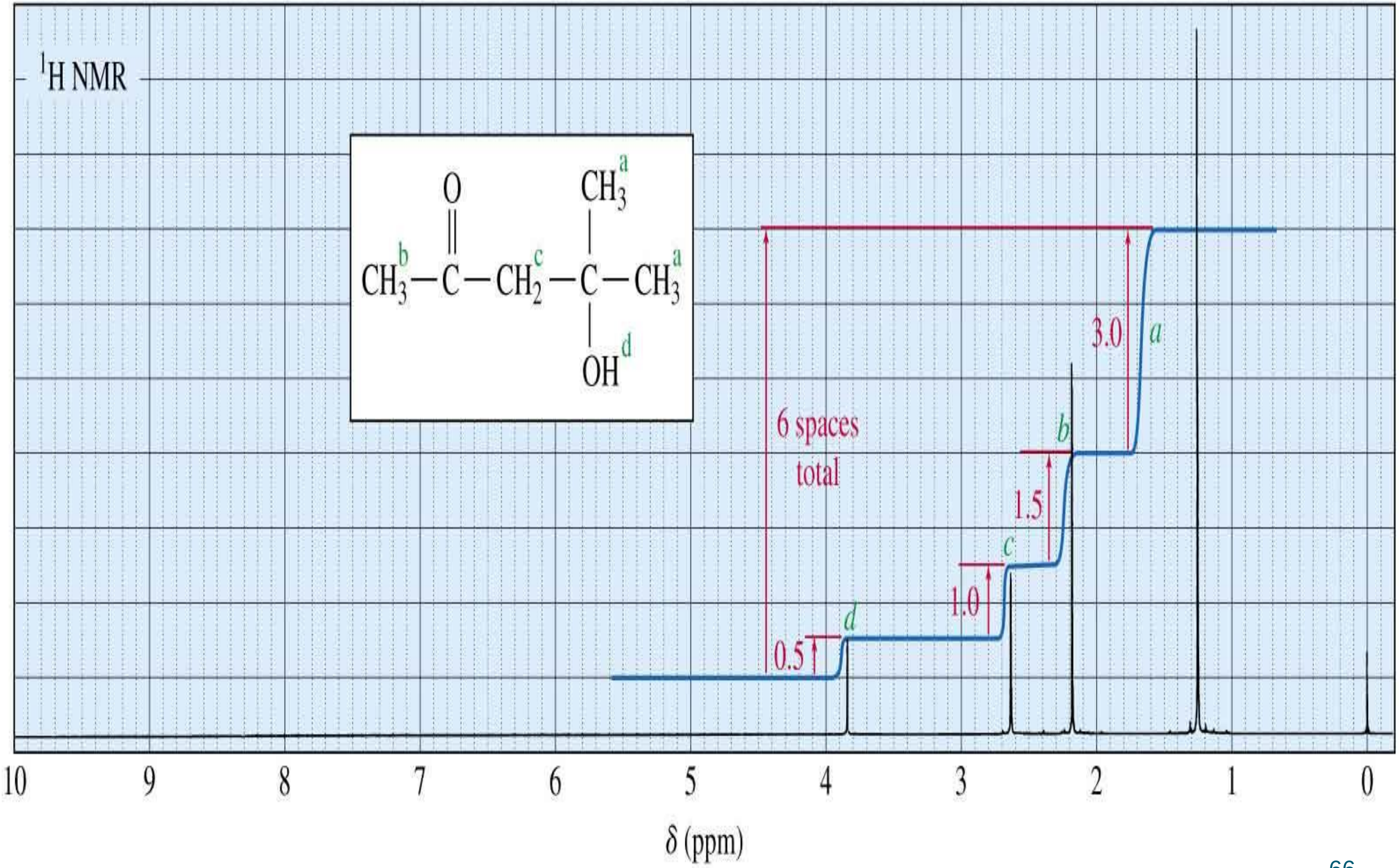
Step [1] Determine the number of integration units per proton by dividing the total number of integration units by the total number of protons.

- 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:	$\frac{54}{11} = 4.9 \approx \boxed{5\text{ H}}$	$\frac{23}{11} = 2.1 \approx \boxed{2\text{ H}}$	$\frac{33}{11} = \boxed{3\text{ H}}$



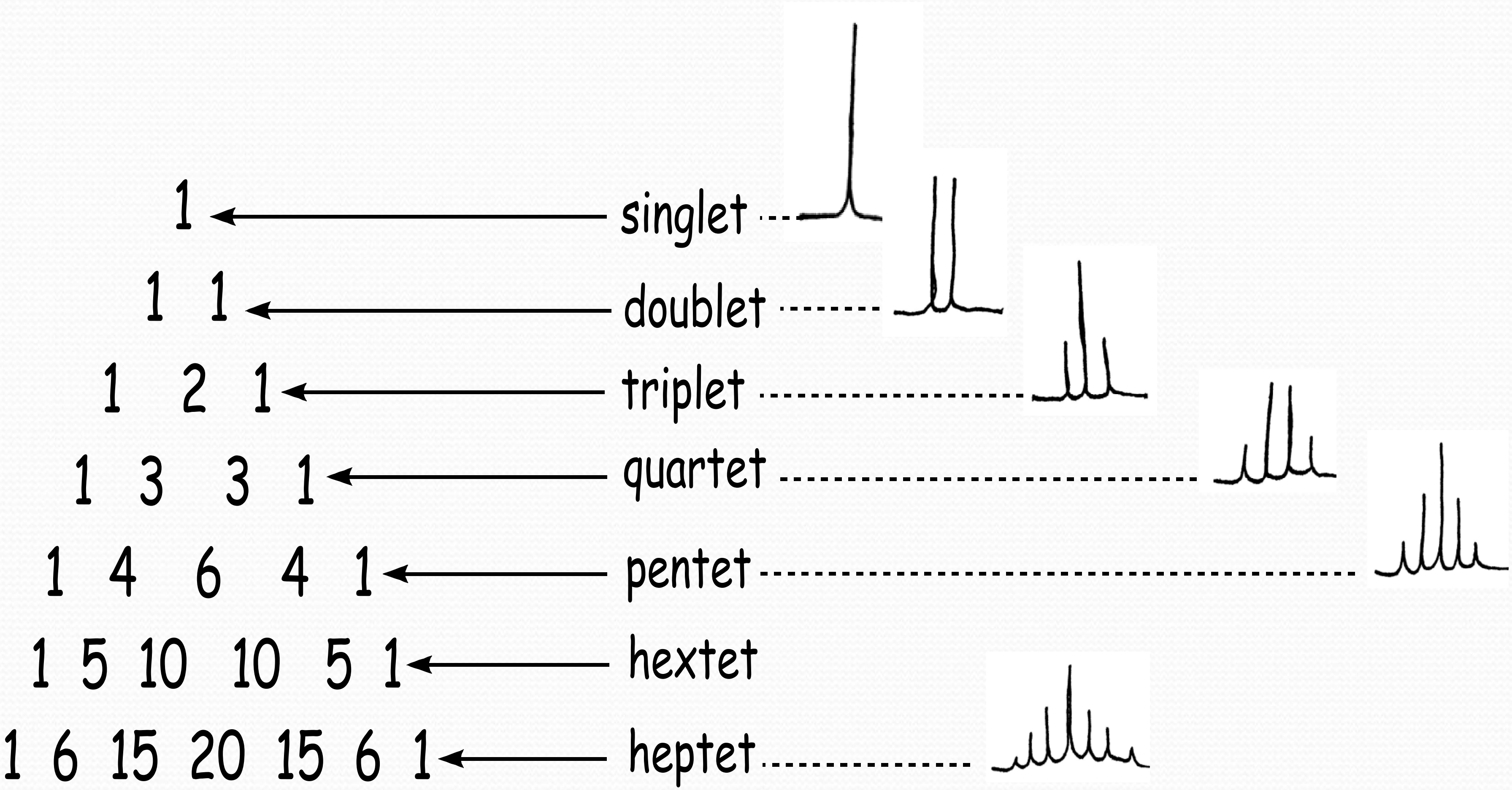
^{1}H NMR
O
CH$_3^a$
CH$_3^b$ — C — CH$_2^c$ — C — CH$_3^a$
OH^d
6 spaces total
0.5
d
1.0
c
1.5
b
3.0
a
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

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

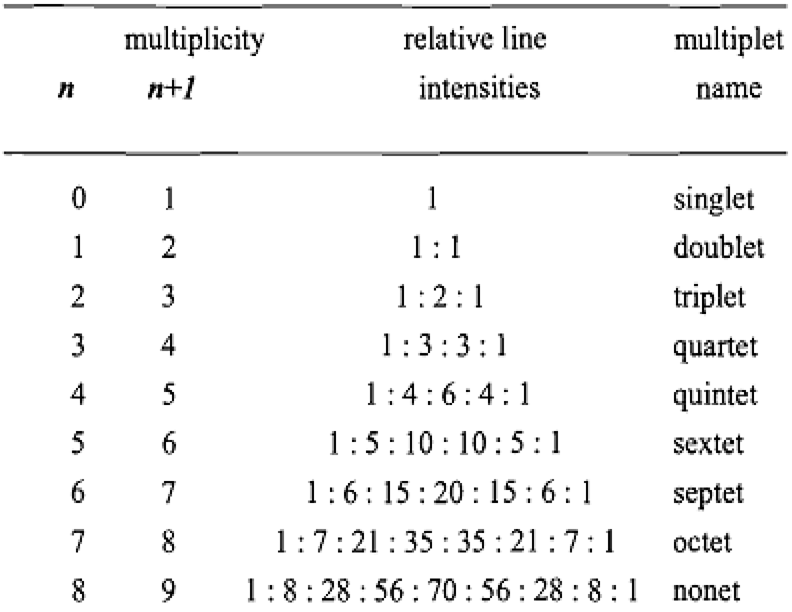
- Spin-spin coupling gives rise to multiplet splitting in ^{1}H NMR spectra. The NMR signal of a nucleus coupled to n equivalent hydrogen's will be split into a multiplet with (n+1) lines.
- Peaks are often split into multiple peaks due to ***magnetic interactions*** between nonequivalent protons on 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 set of peaks is a **multiplet** (2 = doublet, 3 = triplet, 4 = quartet, 5=pentet, 6=hextet, 7=heptet…..)

Pascal's Triangle

- The **relative intensities** are in proportion of a binomial distribution given by Pascal's Triangle

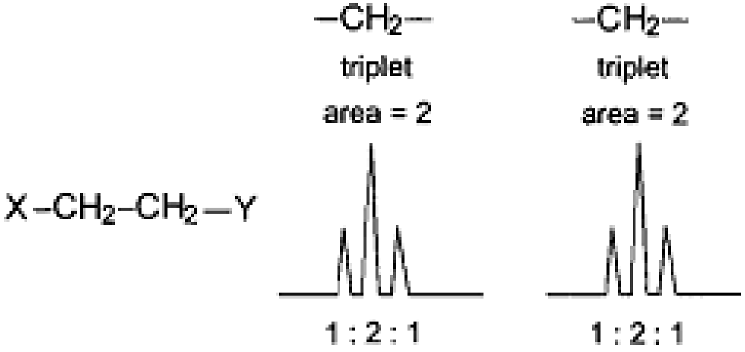


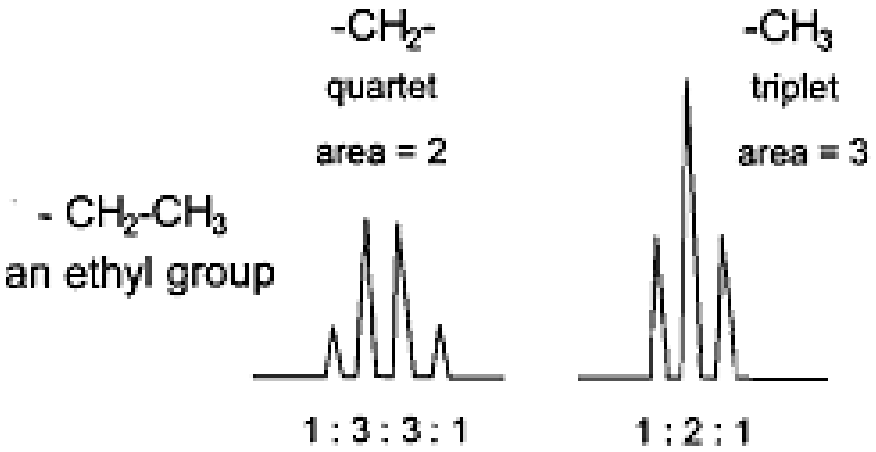
1	singlet
1 1	doublet
1 2 1	triplet
1 3 3 1	quartet
1 4 6 4 1	pentet
1 5 10 10 5 1	hextet
1 6 15 20 15 6 1	heptet

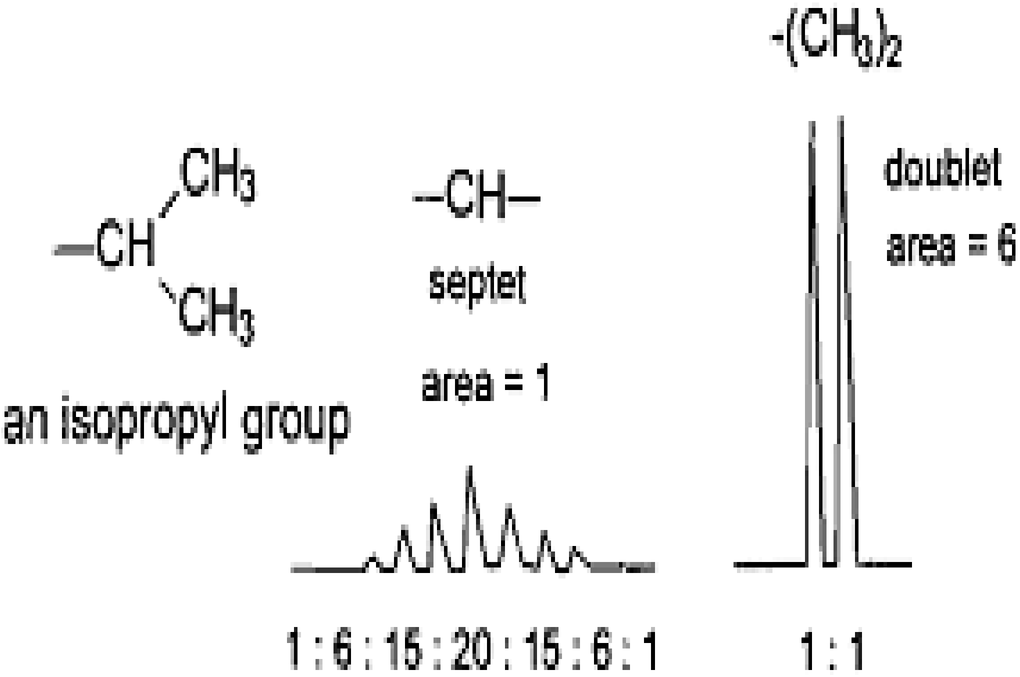


n	multiplicity *n+1*	relative line intensities	multiplet name
0	1	1	singlet
1	2	1 : 1	doublet
2	3	1 : 2 : 1	triplet
3	4	1 : 3 : 3 : 1	quartet
4	5	1 : 4 : 6 : 4 : 1	quintet
5	6	1 : 5 : 10 : 10 : 5 : 1	sextet
6	7	1 : 6 : 15 : 20 : 15 : 6 : 1	septet
7	8	1 : 7 : 21 : 35 : 35 : 21 : 7 : 1	octet
8	9	1 : 8 : 28 : 56 : 70 : 56 : 28 : 8 : 1	nonet

Table - Relative Line Intensities for Simple Multiplets

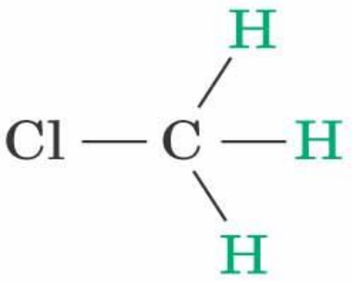






Rules for Spin-Spin Splitting

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



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

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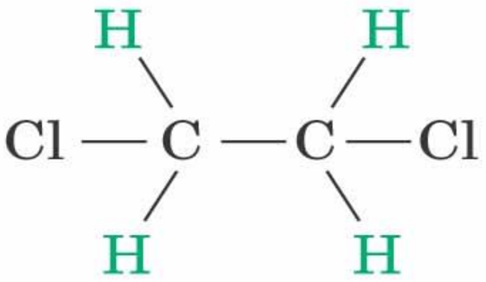
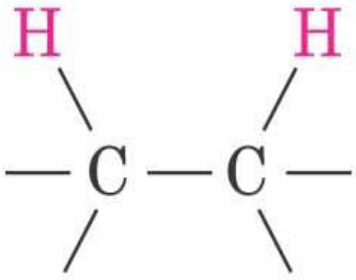


Four C–H protons are chemically equivalent; no splitting occurs.

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



Splitting observed

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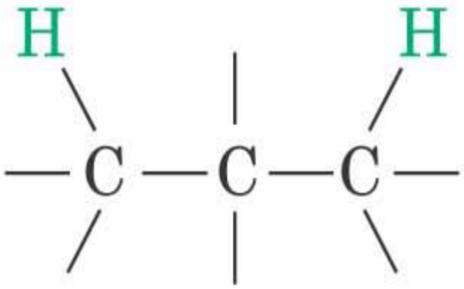
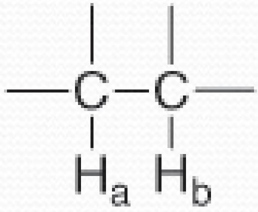


Splitting not usually observed

^1H NMR—Spin-Spin Splitting

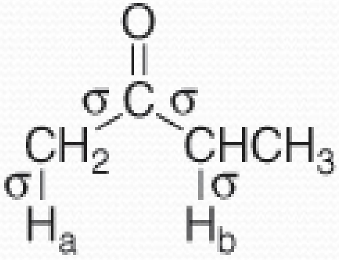
If H_a and H_b are not equivalent, splitting is observed when:

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



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

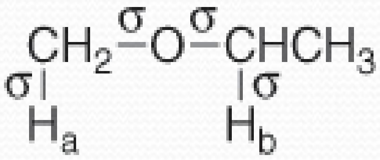
Splitting is not generally observed between protons separated by more than three σ bonds.



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

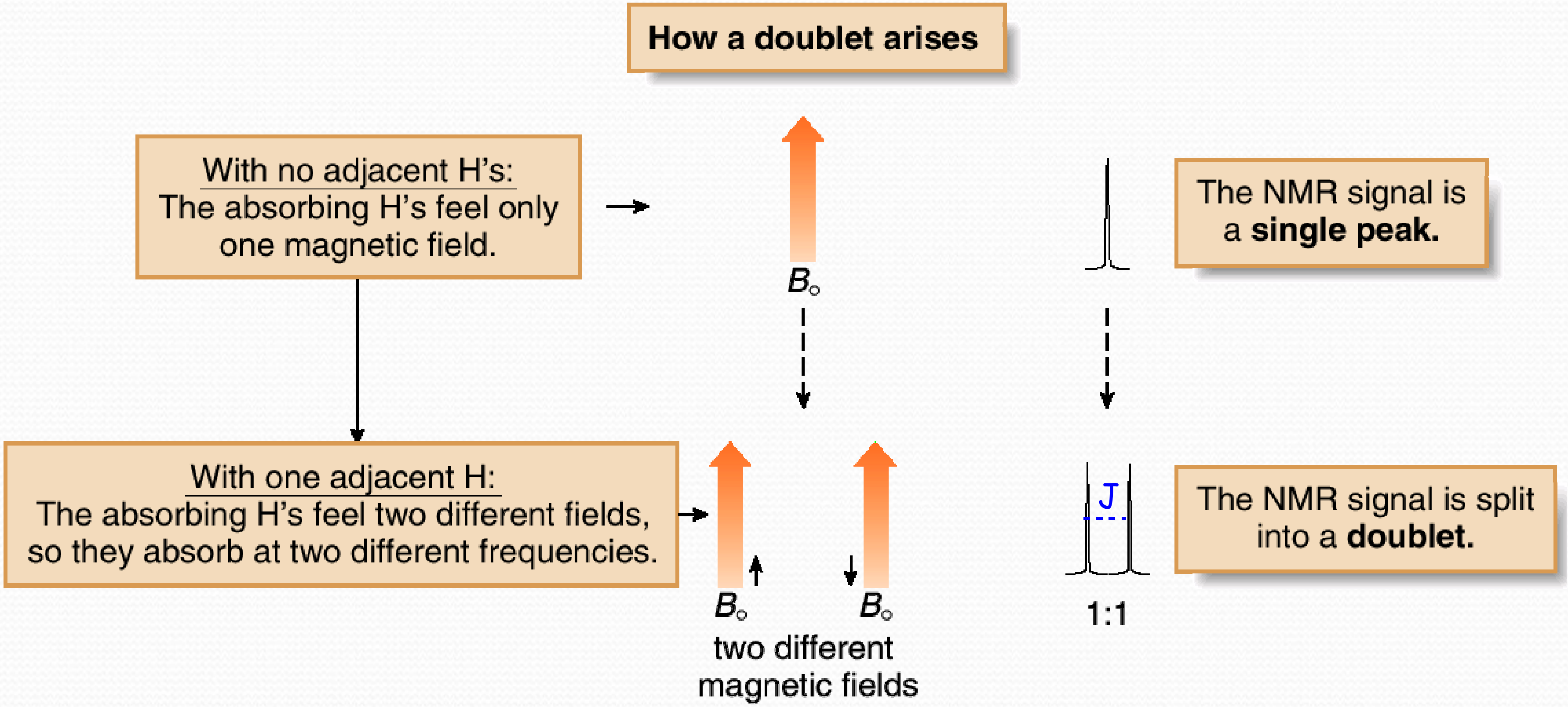
- Spin-spin splitting occurs only between nonequivalent protons on the same carbon or adjacent carbons.

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.



How a doublet arises

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

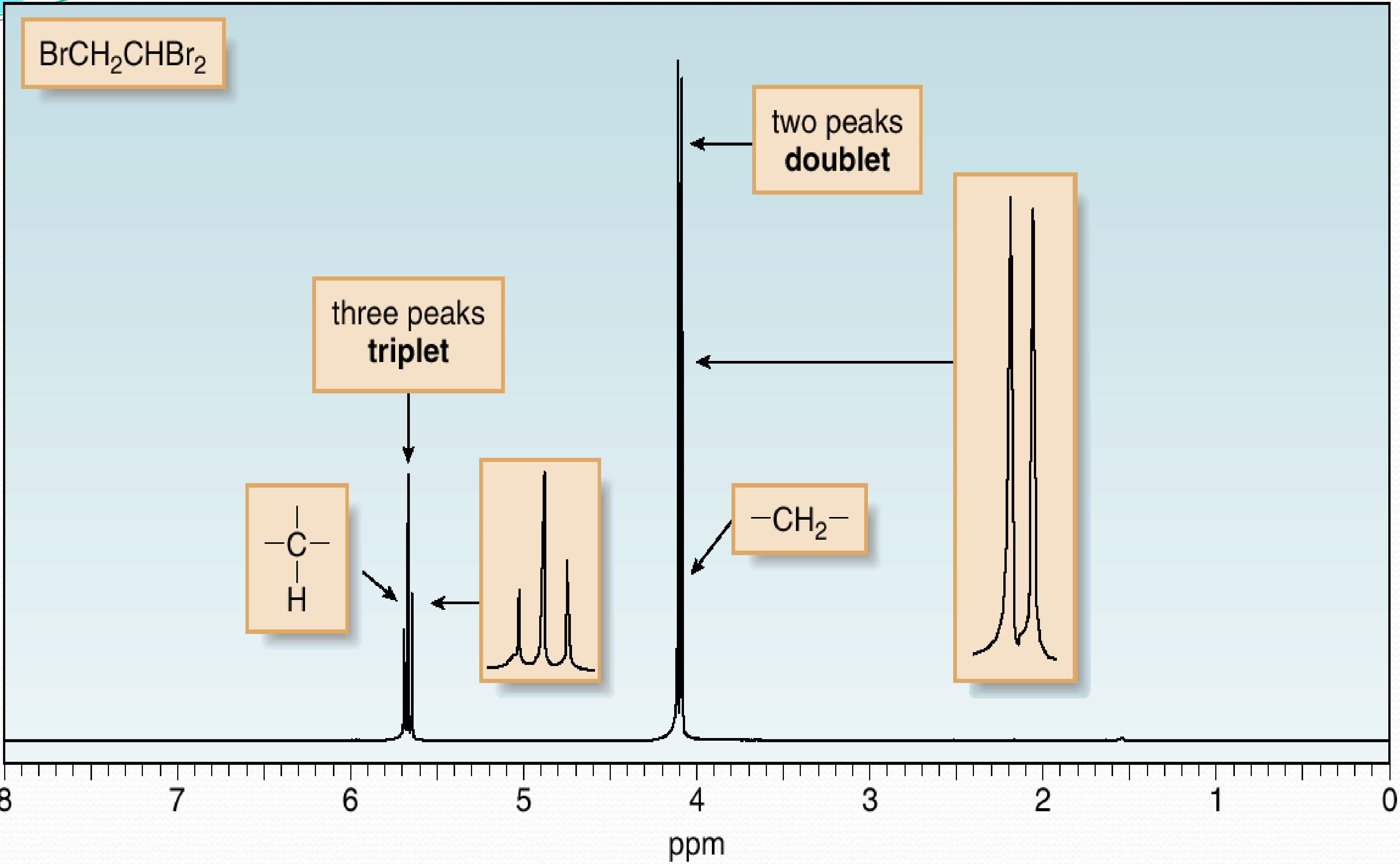
The NMR signal is a **single peak.**

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

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

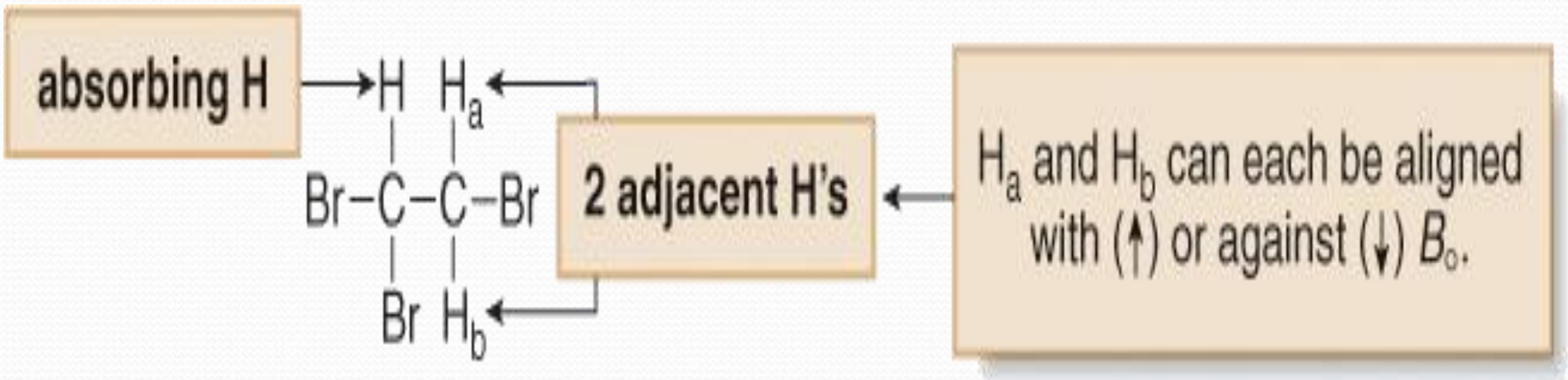
- One adjacent proton splits an NMR signal into a doublet.

^{1}H NMR—Spin-Spin Splitting



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 $(\uparrow_a\downarrow_b)$.

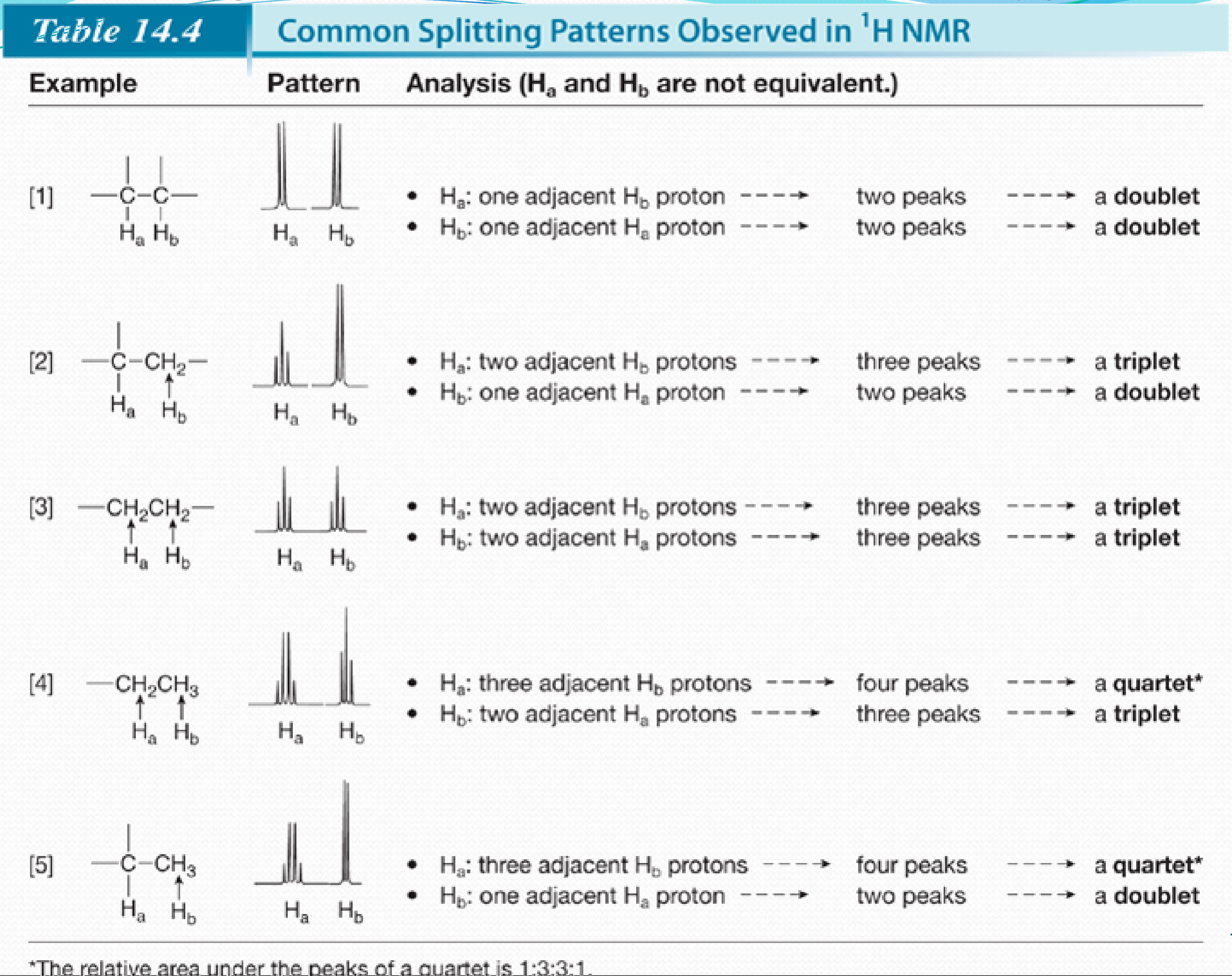


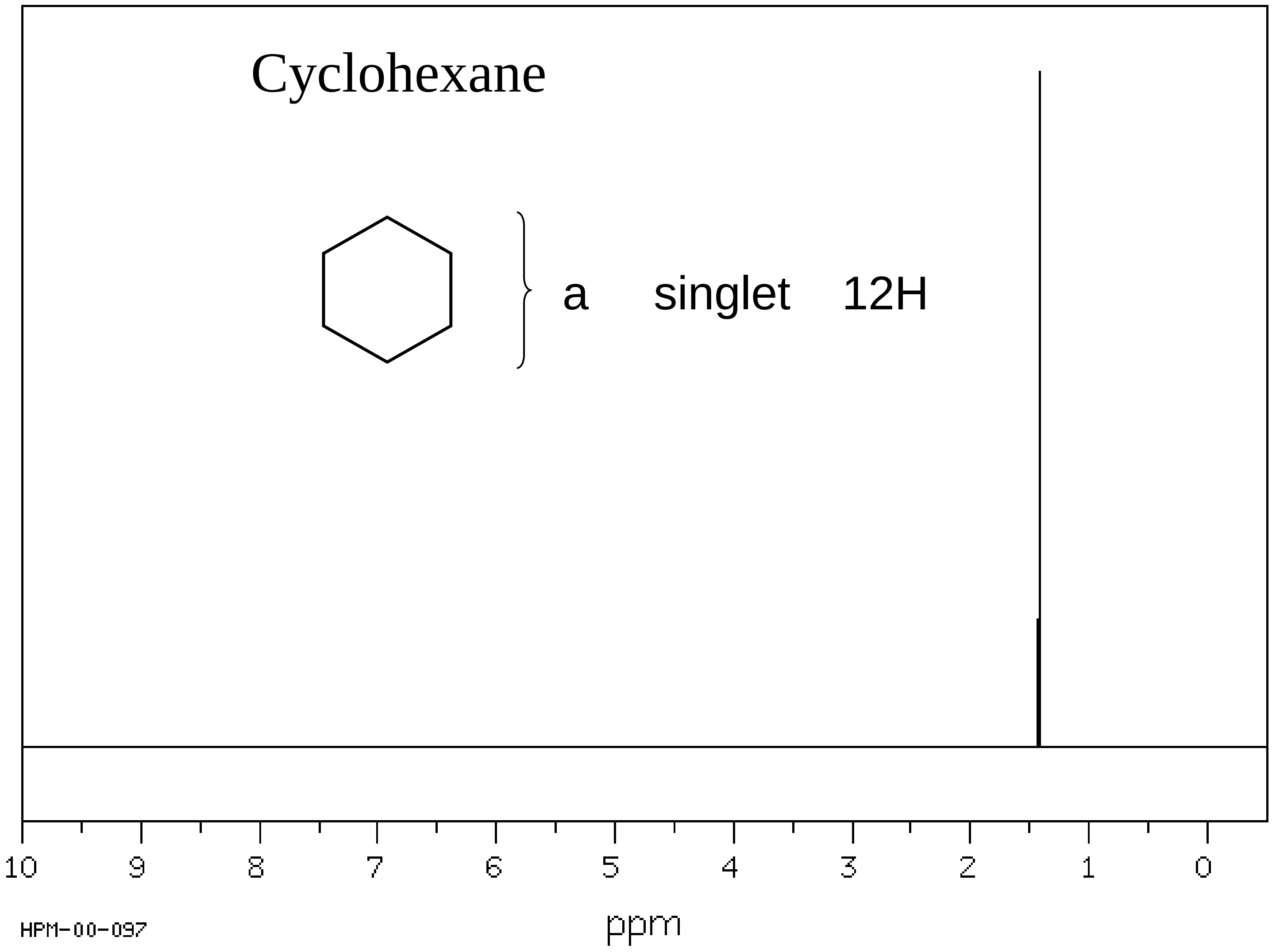
Table 14.4 Common Splitting Patterns Observed in ^{1}H NMR

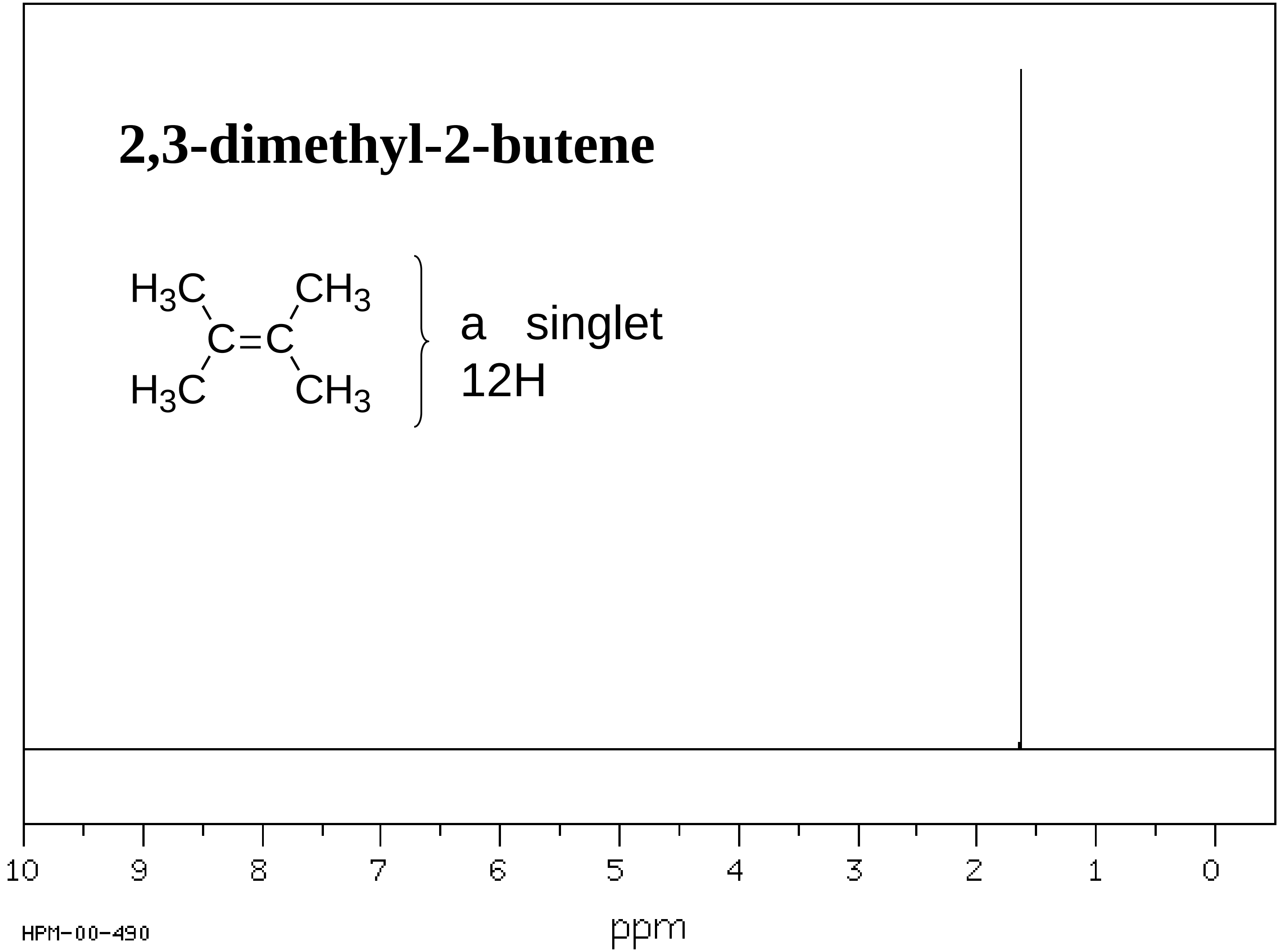
	Example	Pattern	Analysis (H_a and H_b are not equivalent.)		
[1]	$-\underset{H_a}{\overset{\vert}{\underset{\vert}{C}}}-\underset{H_b}{\overset{\vert}{\underset{\vert}{C}}}-$	H_a H_b	• H_a: one adjacent H_b proton ---→ • H_b: one adjacent H_a proton ---→	two peaks ---→ two peaks ---→	a **doublet** a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

---

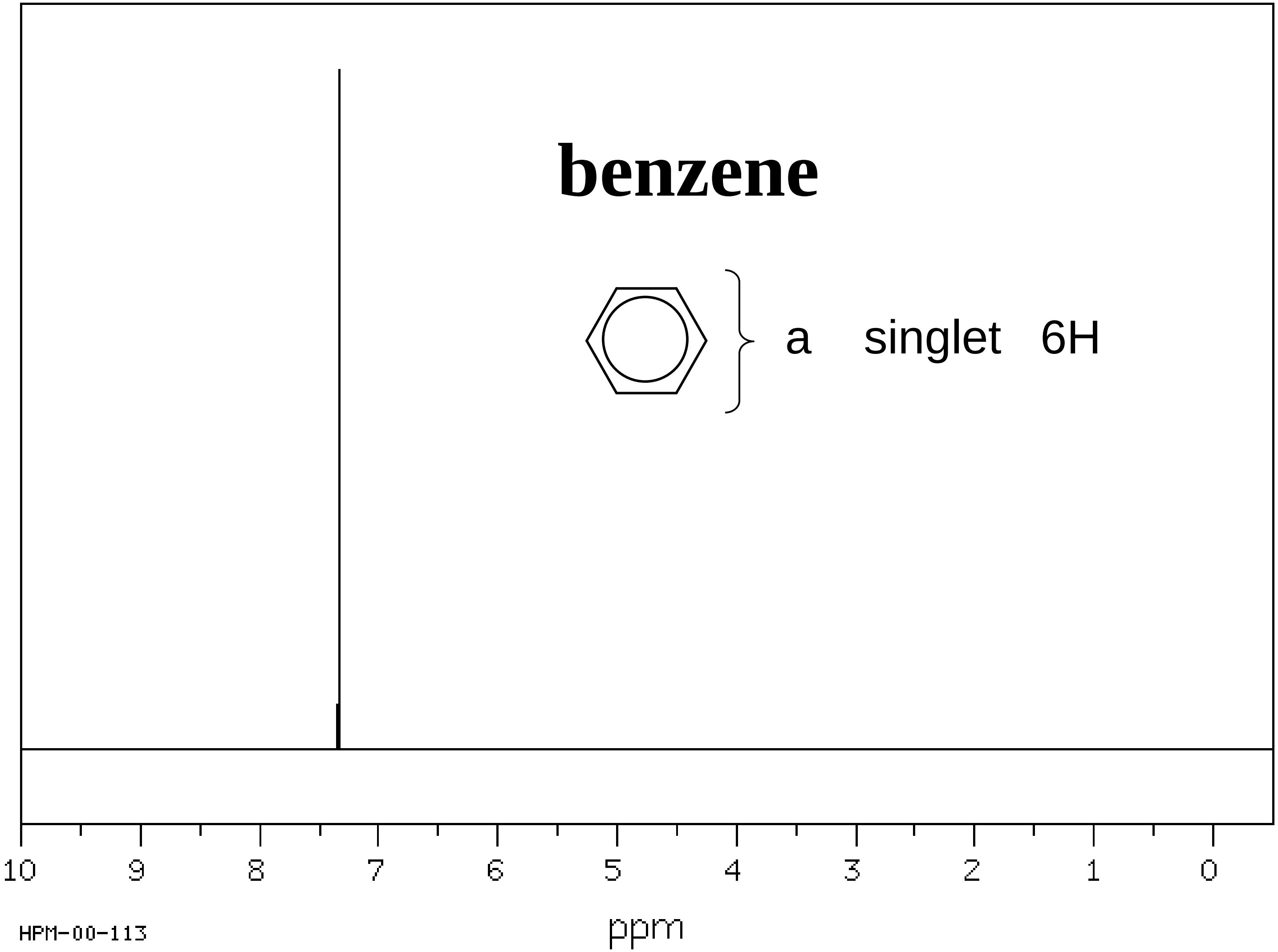
*The relative area under the peaks of a quartet is 1:3:3:1.

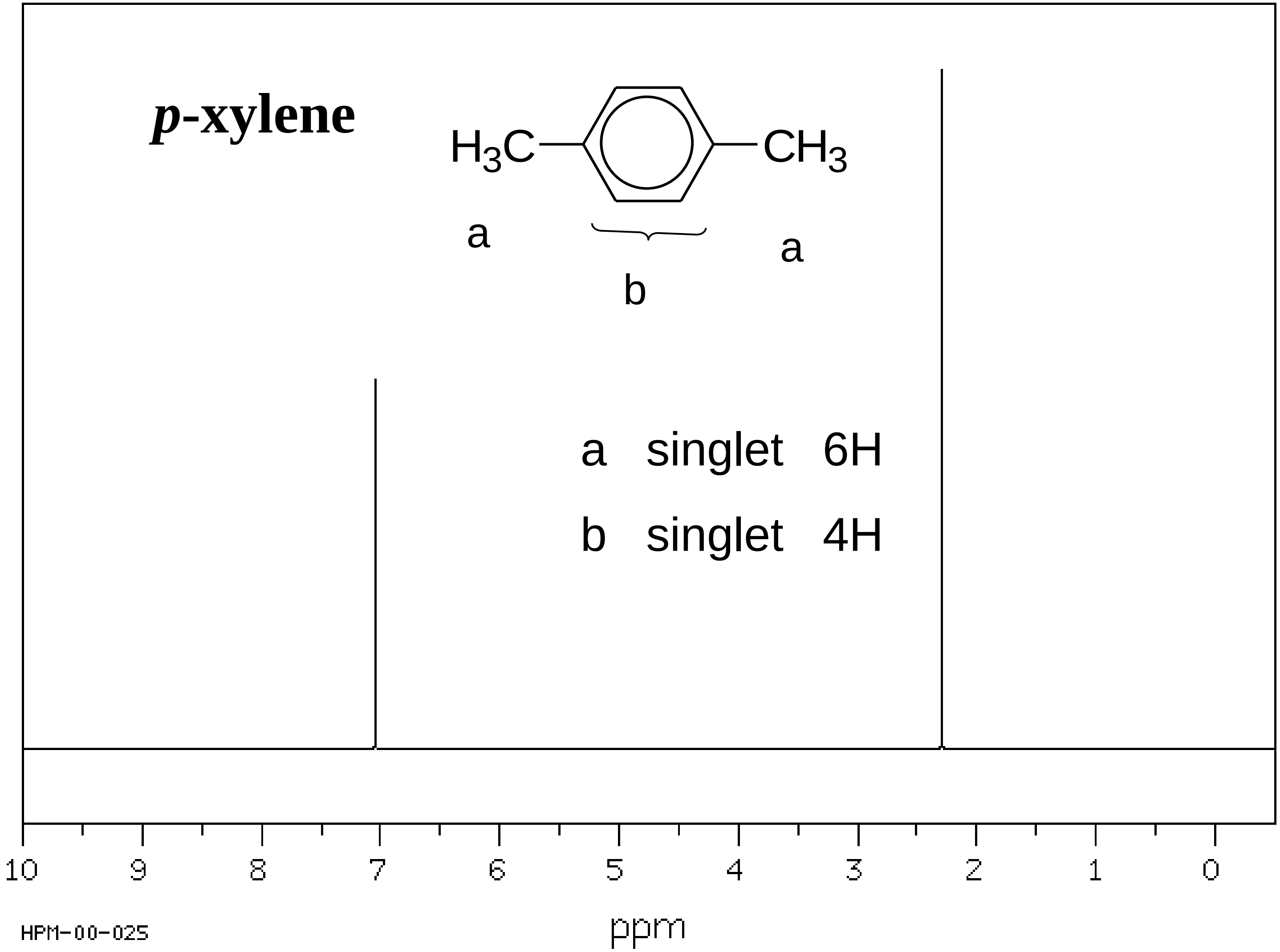
Examples:





2,3-dimethyl-2-butene


benzene
a singlet 6H
10
9
8
7
6
5
4
3
2
1
0
ppm
HPM-00-113

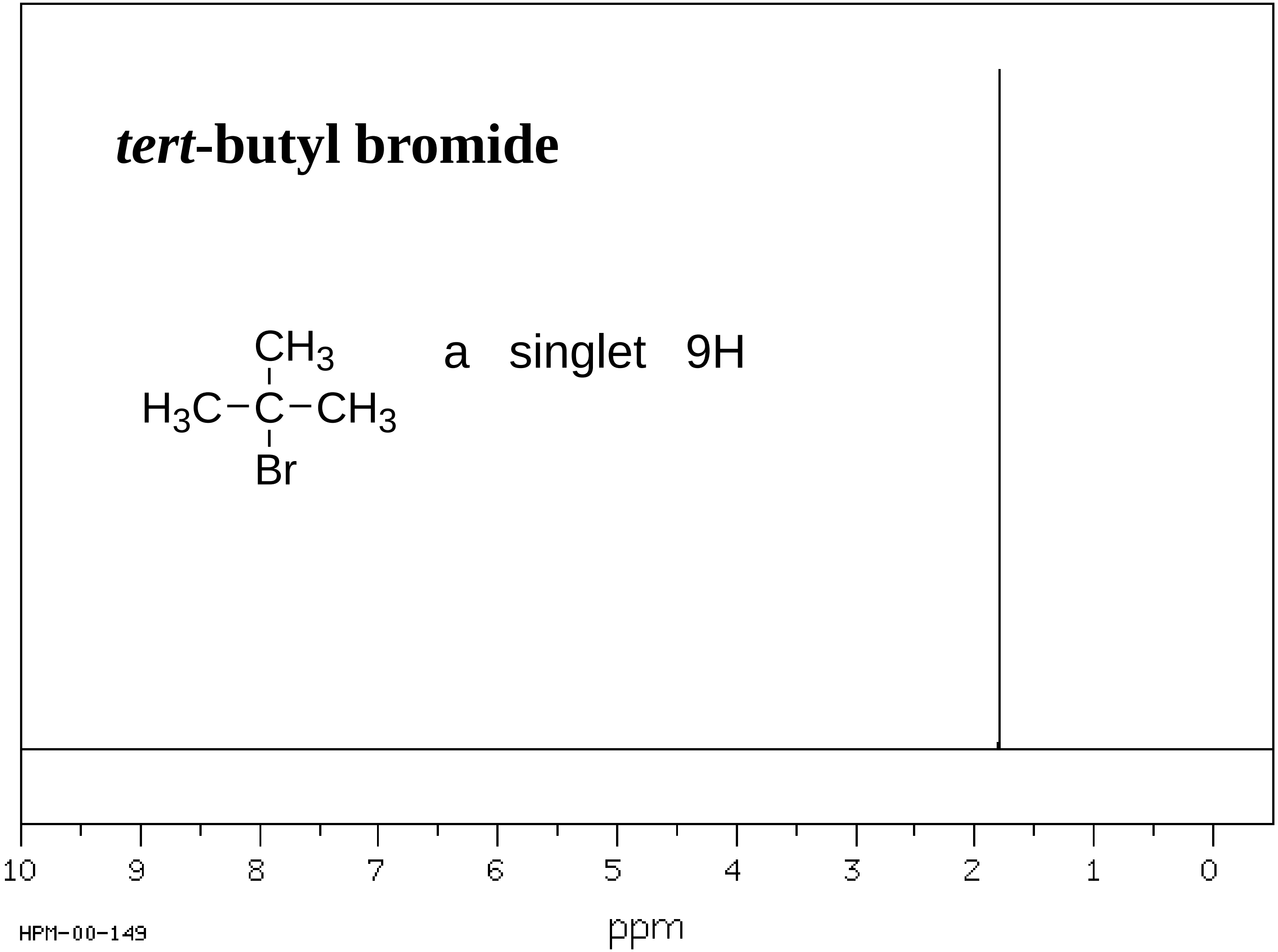


***p*-xylene**

a singlet 6H

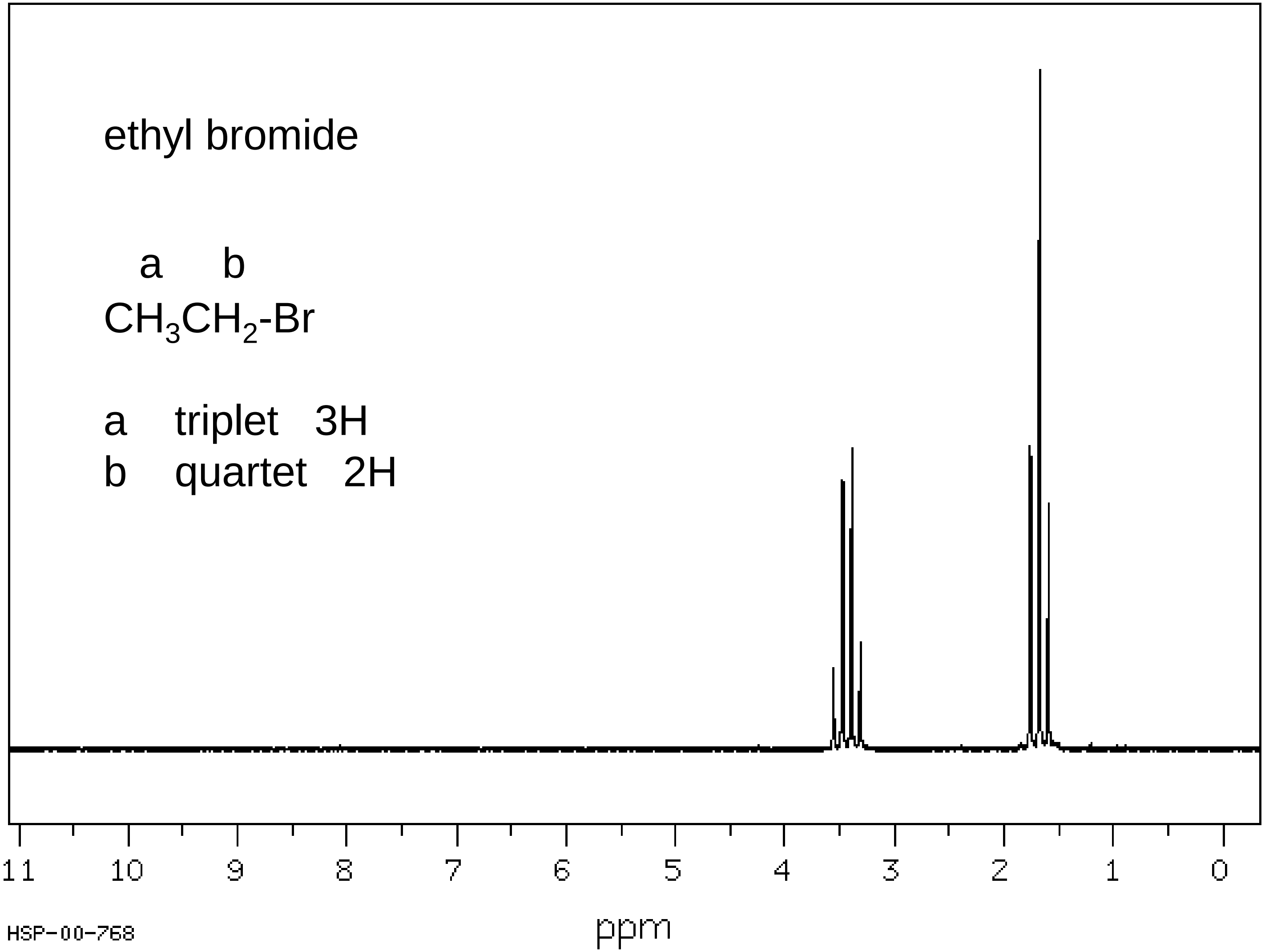
b singlet 4H

tert-butyl bromide



$$(CH_3)_3C{-}Br$$

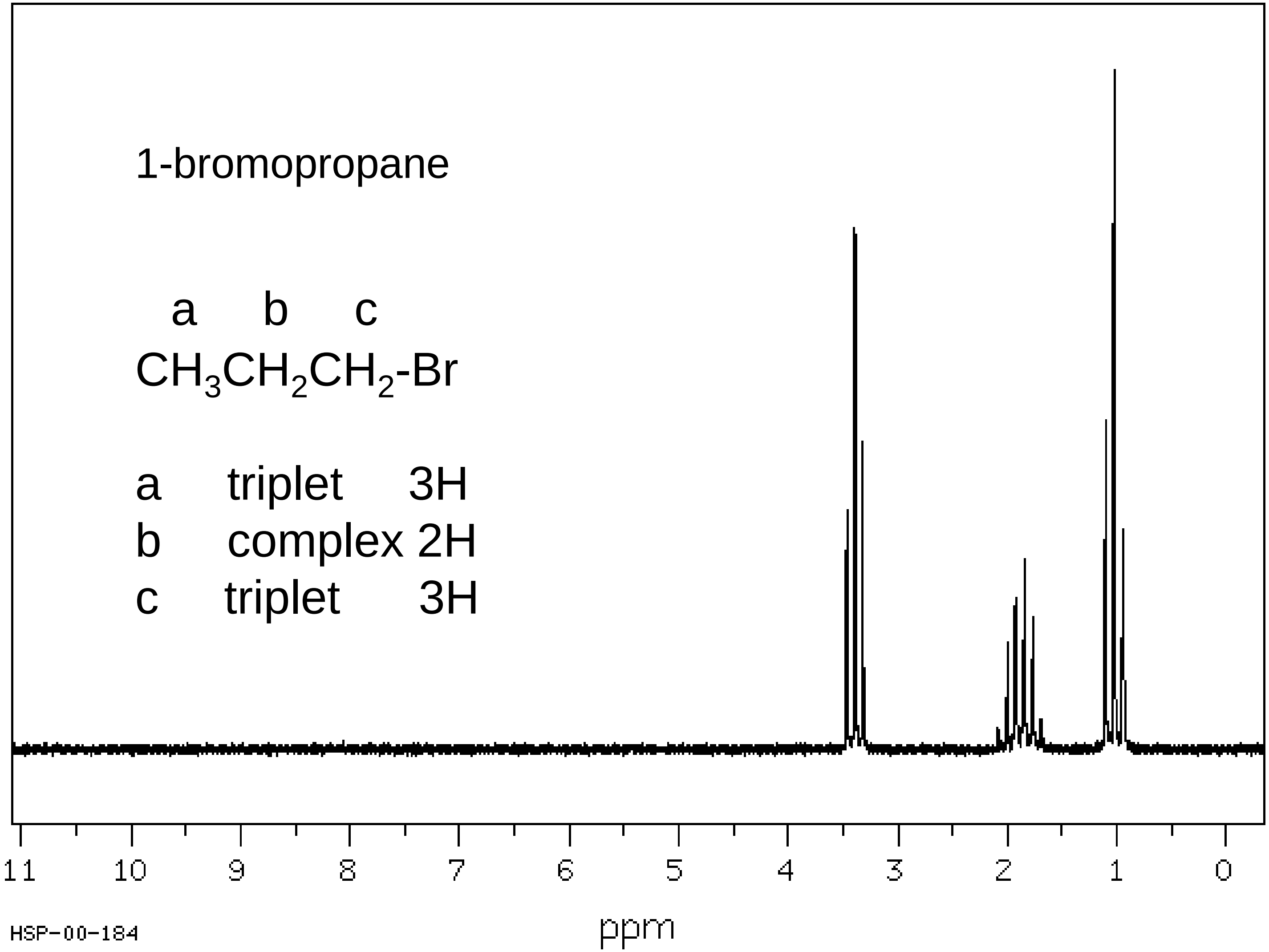
a singlet 9H



ethyl bromide

a b
CH_3CH_2-Br

a triplet 3H
b quartet 2H

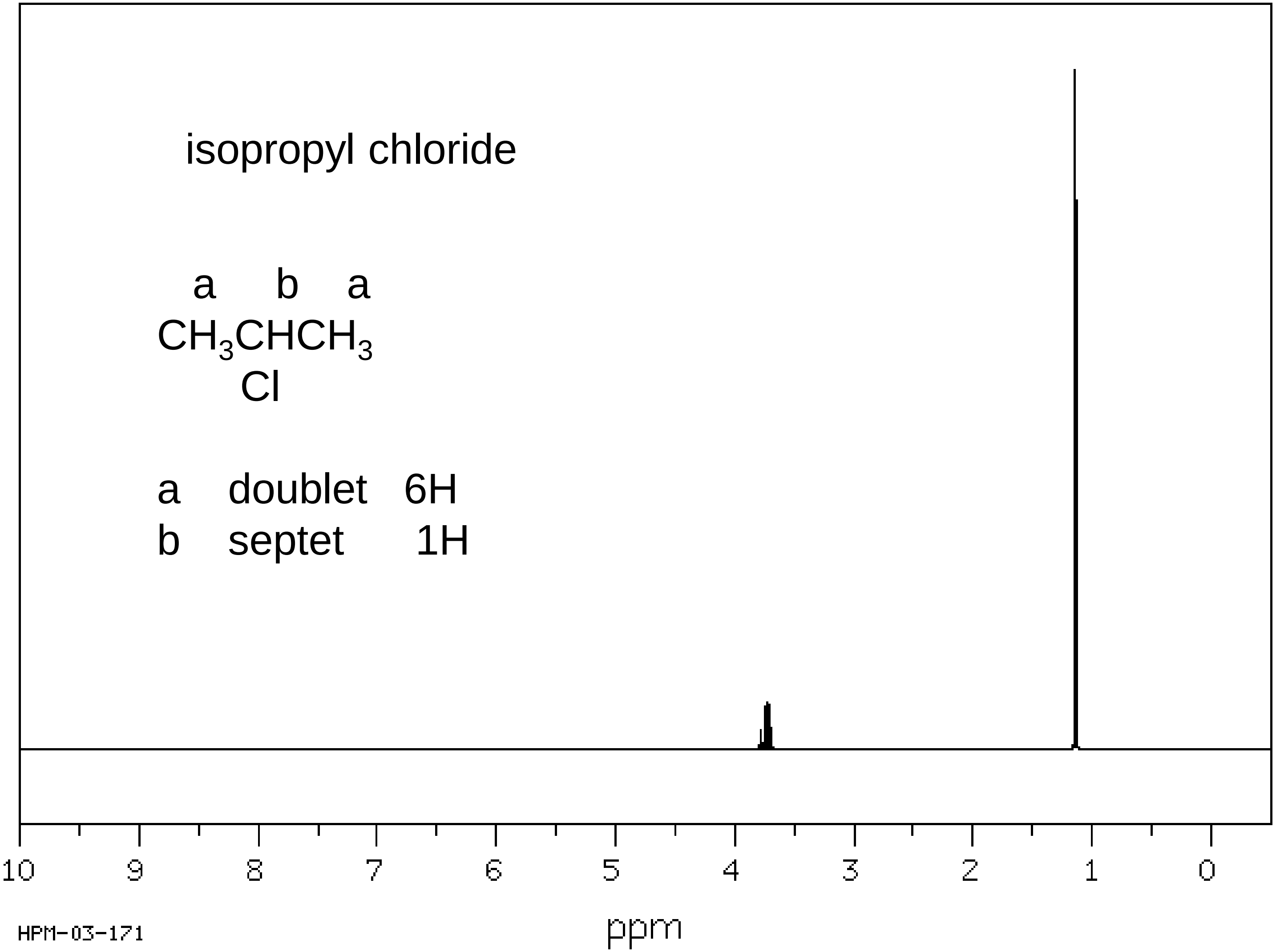


1-bromopropane

a b c

$CH_3CH_2CH_2$-Br

a	triplet	3H
b	complex	2H
c	triplet	3H

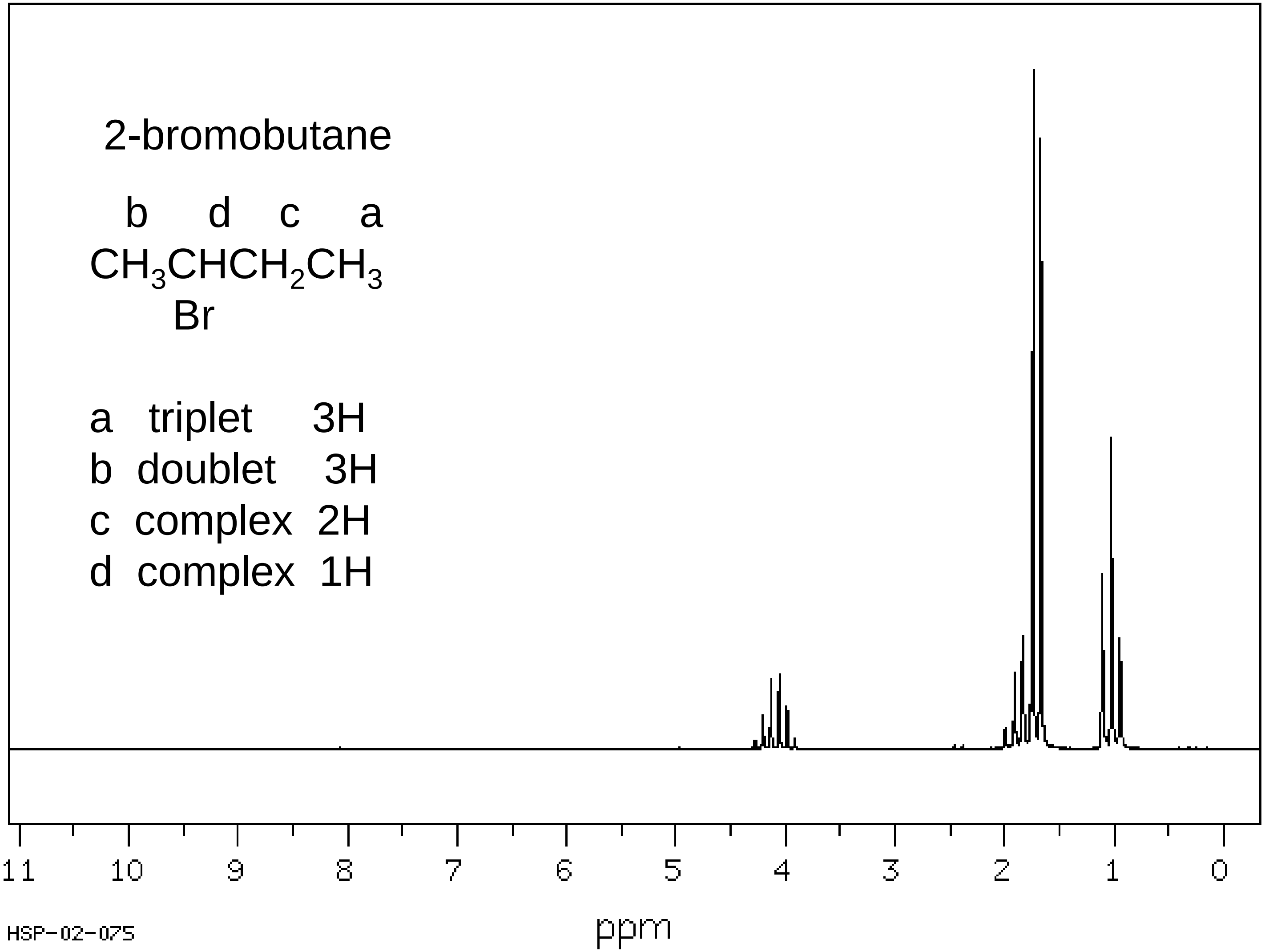


isopropyl chloride

$$\overset{a}{CH_3}\underset{Cl}{\overset{b}{C}H}\overset{a}{CH_3}$$

a doublet 6H

b septet 1H

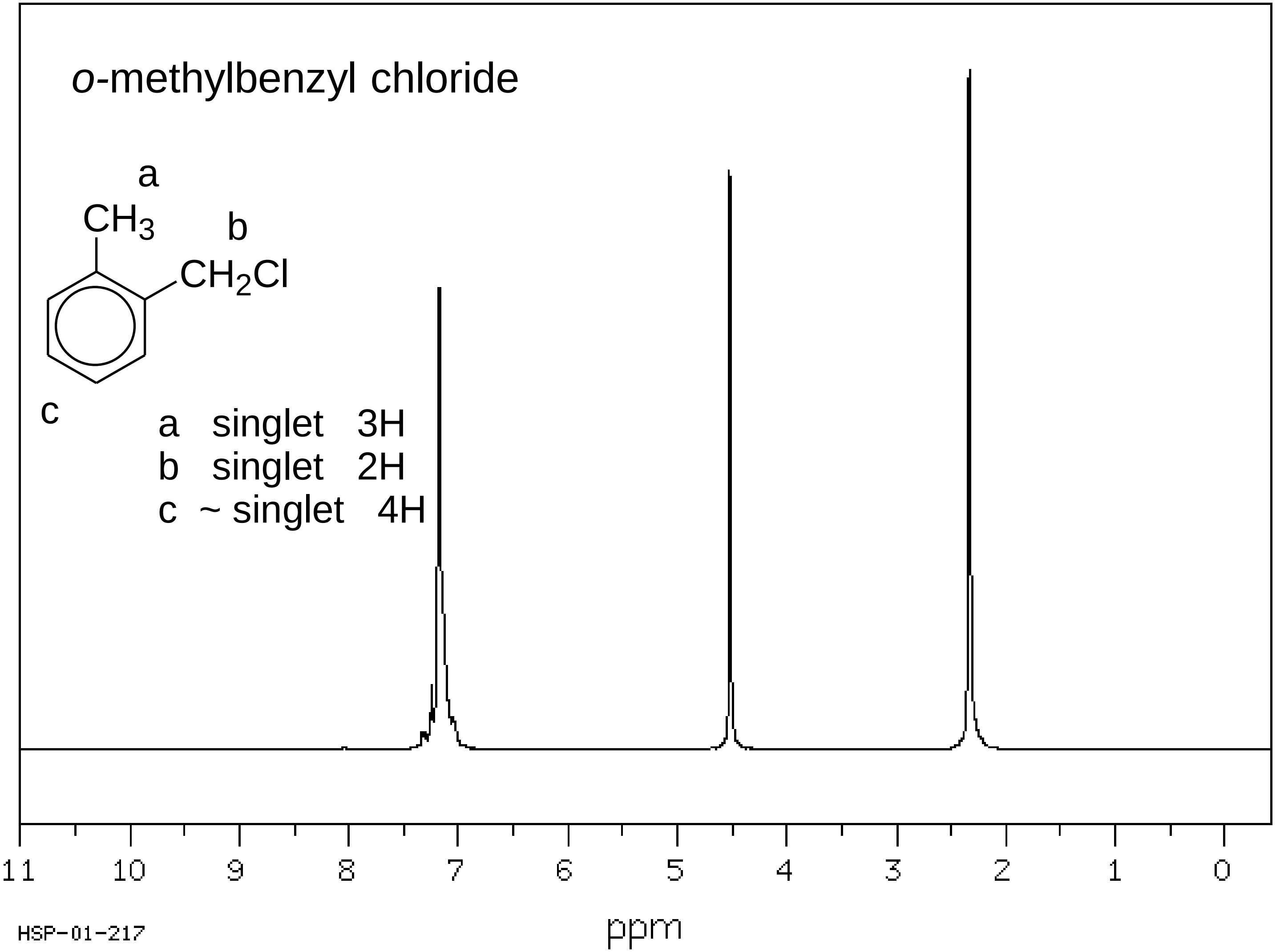


2-bromobutane

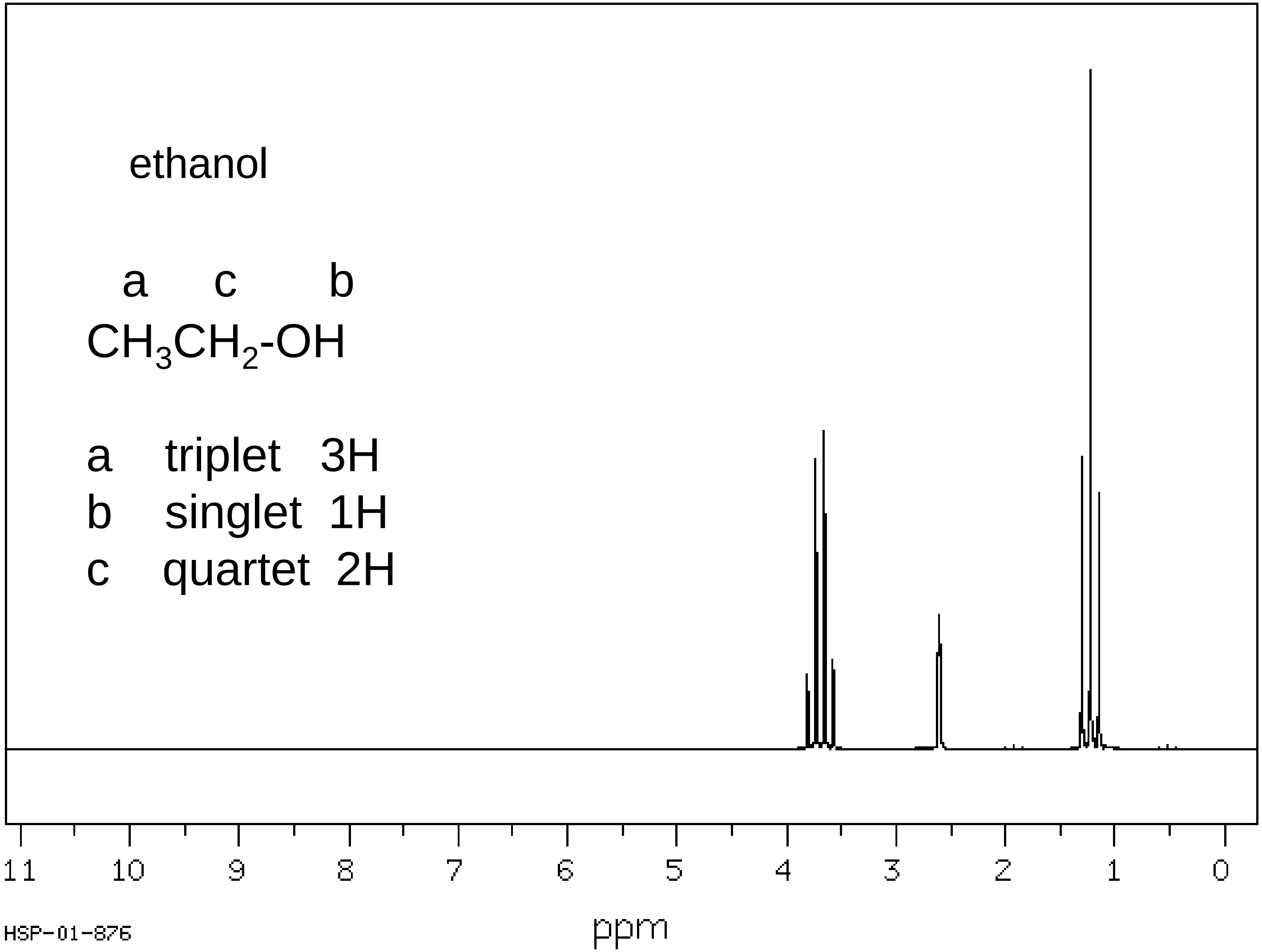
$$\overset{b}{CH_3}\underset{Br}{\overset{d}{CH}}\overset{c}{CH_2}\overset{a}{CH_3}$$

a	triplet	3H
b	doublet	3H
c	complex	2H
d	complex	1H

o-methylbenzyl chloride



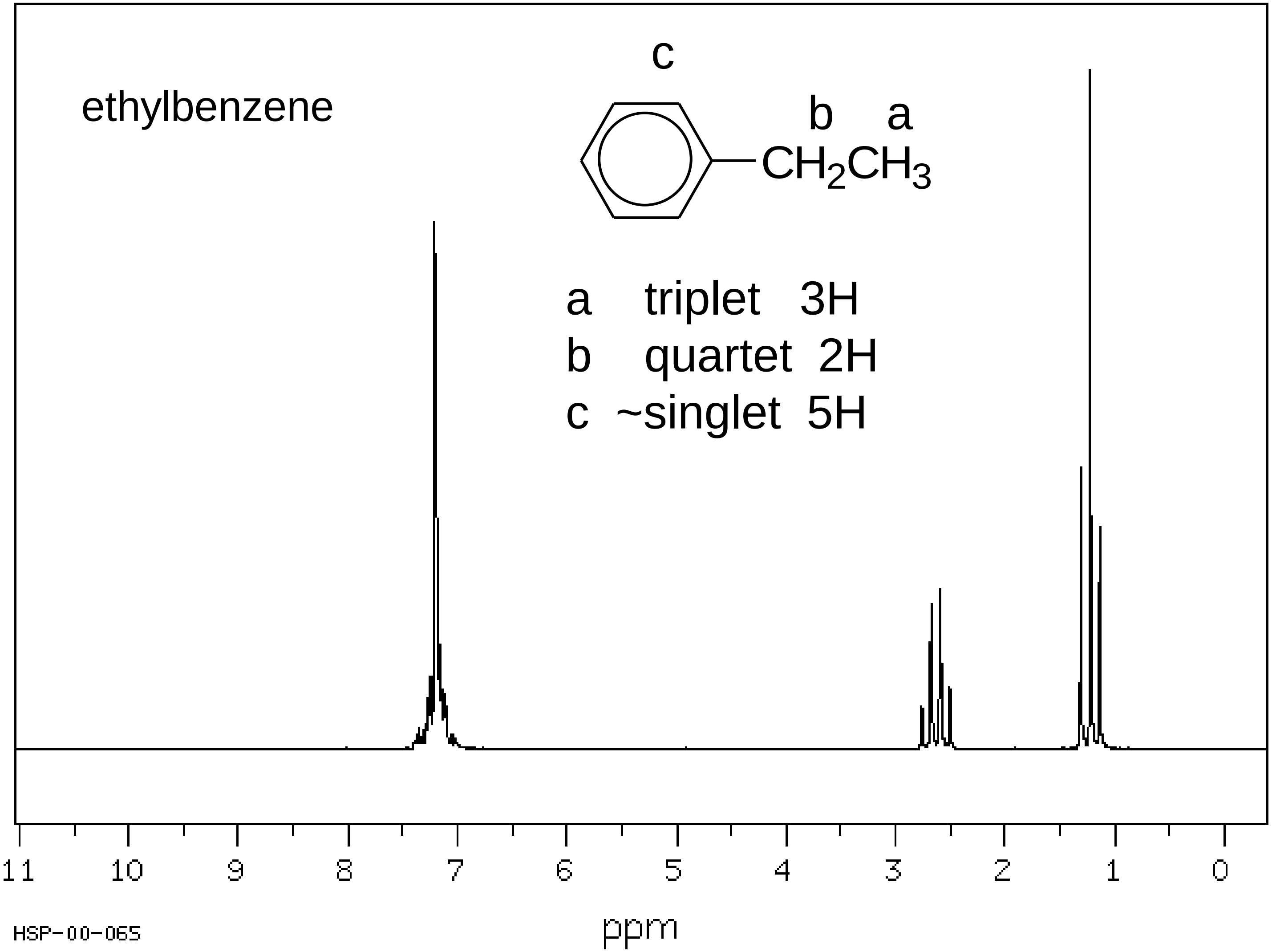
a	singlet	3H
b	singlet	2H
c	~ singlet	4H



ethanol

  a   c   b
CH_3CH_2-OH

a triplet 3H
b singlet 1H
c quartet 2H



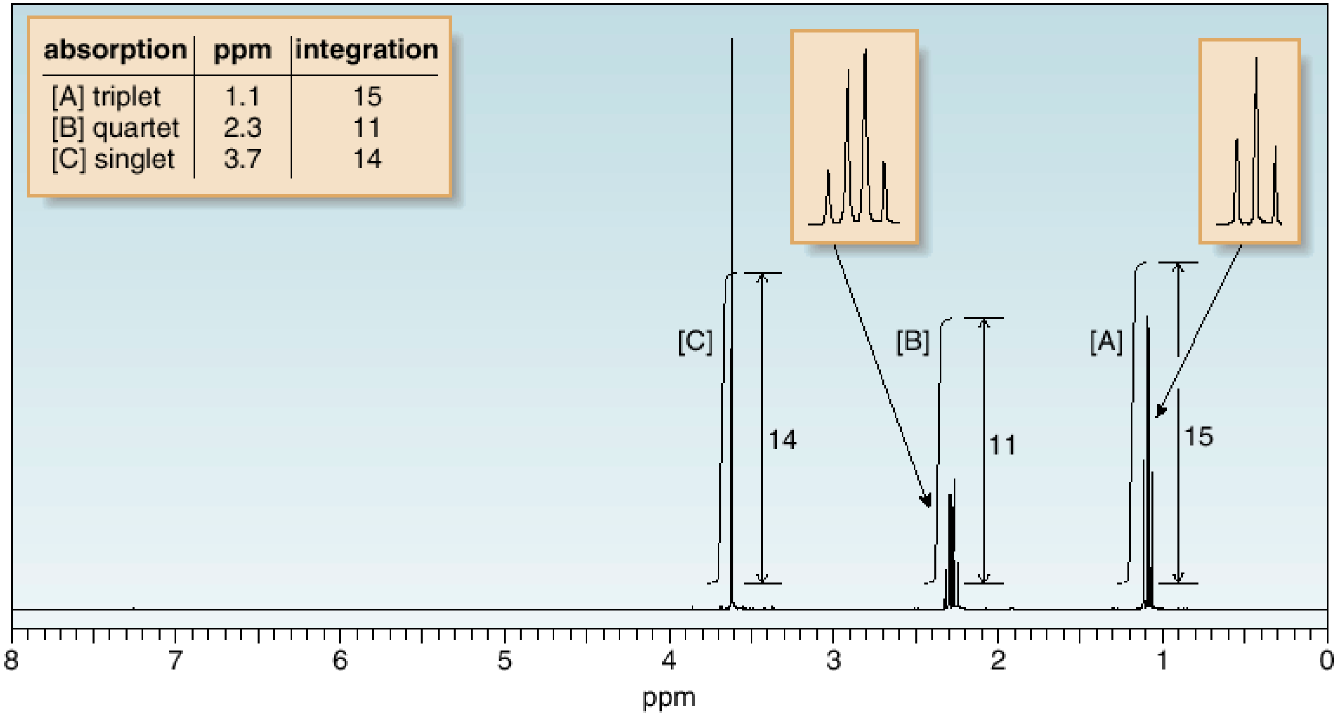
ethylbenzene

a	triplet	3H
b	quartet	2H
c	~singlet	5H

^{1}H NMR—Structure Determination

How To Use ^{1}H NMR Data to Determine a Structure

Example Using its ^{1}H NMR spectrum, determine the structure of an unknown compound **X** that has molecular formula $C_4H_8O_2$ and contains a C=O absorption in its IR spectrum.



absorption	ppm	integration
[A] triplet	1.1	15
[B] quartet	2.3	11
[C] singlet	3.7	14

Step [1] **Determine the number of different kinds of protons.**

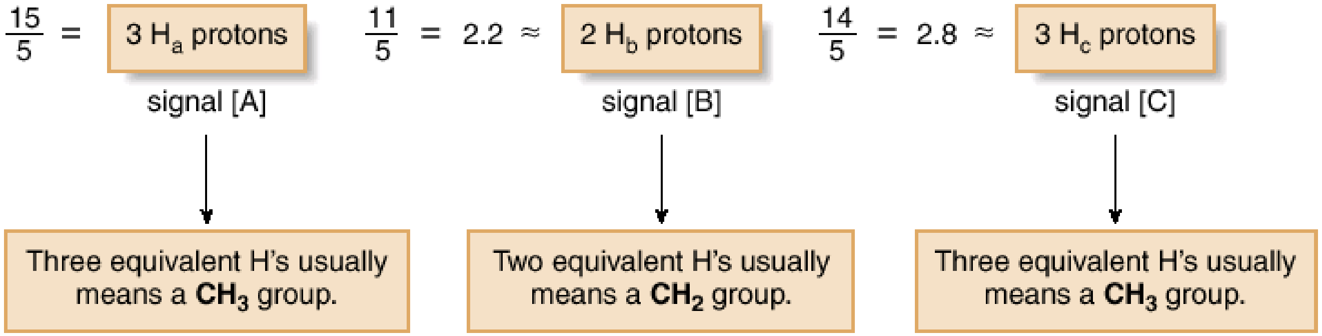
- The number of NMR signals equals the number of different types of protons.
- This molecule has three NMR signals ([A], [B], and [C]) and therefore **three** types of protons (H_a, H_b, and H_c).

^{1}H NMR—Structure Determination

How To, continued . . .

Step [2] Use the integration data to determine the number of H atoms giving rise to each signal (Section 14.5).

- Total number of integration units: 14 + 11 + 15 = 40 units
- Total number of protons = 8
- Divide: 40 units/8 protons = **5 units per proton**
- Then, divide each integration value by this answer (5 units per proton) and round to the nearest whole number.



$\frac{15}{5} = \boxed{3\ H_a\ \text{protons}}$ signal [A]

Three equivalent H's usually means a **CH_3** group.

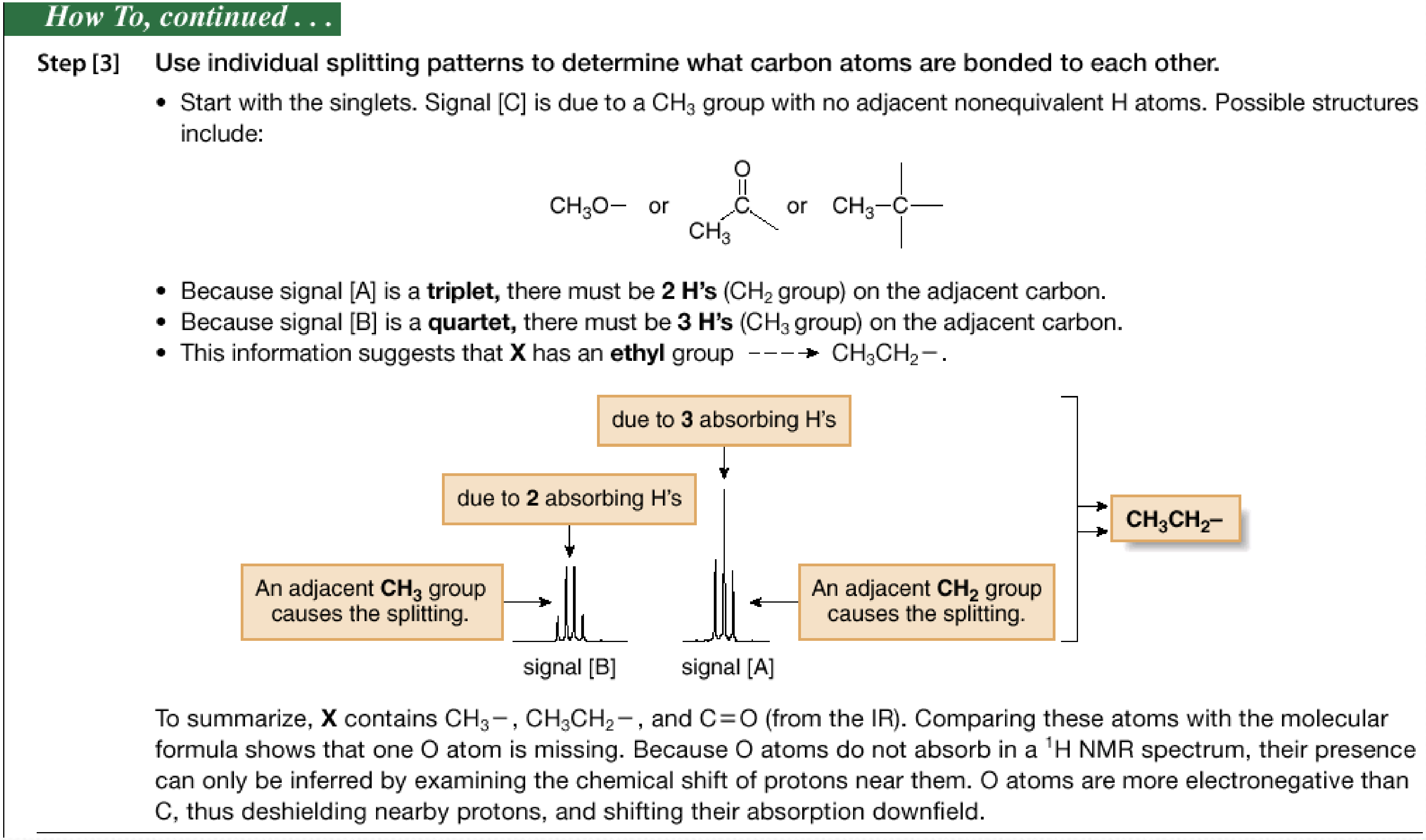
$\frac{11}{5} = 2.2 \approx \boxed{2\ H_b\ \text{protons}}$ signal [B]

Two equivalent H's usually means a **CH_2** group.

$\frac{14}{5} = 2.8 \approx \boxed{3\ H_c\ \text{protons}}$ signal [C]

Three equivalent H's usually means a **CH_3** group.

^{1}H NMR—Structure Determination



How To, continued . . .

Step [3] **Use individual splitting patterns to determine what carbon atoms are bonded to each other.**

- Start with the singlets. Signal [C] is due to a CH_3 group with no adjacent nonequivalent H atoms. Possible structures include:

- Because signal [A] is a **triplet,** there must be **2 H's** (CH_2 group) on the adjacent carbon.
- Because signal [B] is a **quartet,** there must be **3 H's** (CH_3 group) on the adjacent carbon.
- This information suggests that **X** has an **ethyl** group ---→ CH_3CH_2-.

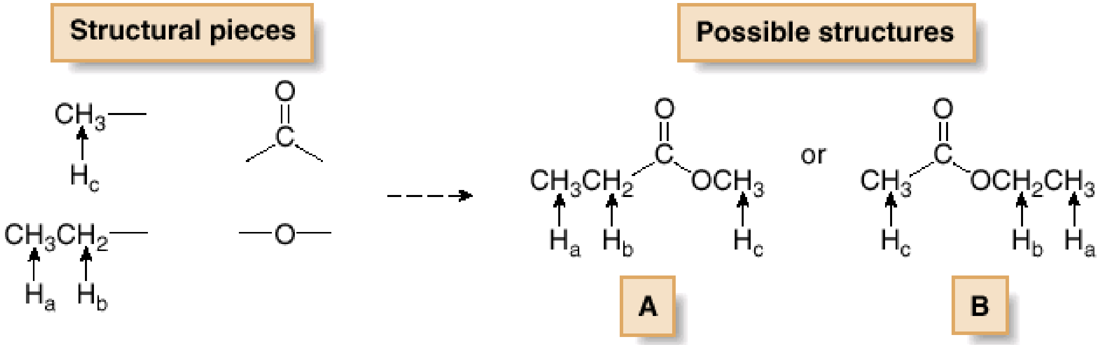
To summarize, **X** contains CH_3-, CH_3CH_2-, and $C=O$ (from the IR). Comparing these atoms with the molecular formula shows that one O atom is missing. Because O atoms do not absorb in a ^{1}H NMR spectrum, their presence can only be inferred by examining the chemical shift of protons near them. O atoms are more electronegative than C, thus deshielding nearby protons, and shifting their absorption downfield.

^{1}H NMR—Structure Determination

How To, continued . . .

Step [4] **Use chemical shift data to complete the structure.**

- Put the structure together in a manner that preserves the splitting data and is consistent with the reported chemical shifts.
- In this example, two isomeric structures (**A** and **B**) are possible for **X** considering the splitting data only:

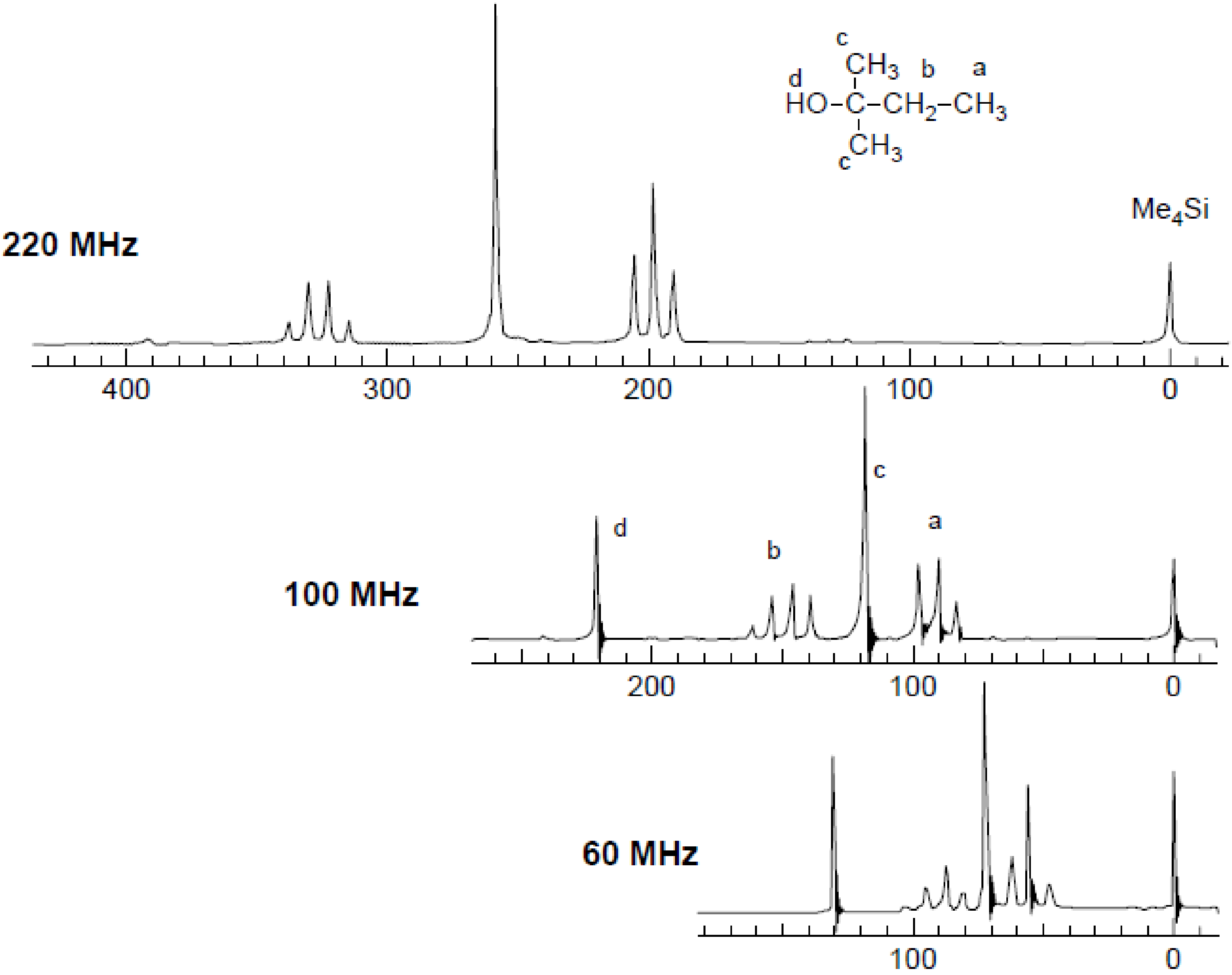


- Chemical shift information distinguishes the two possibilities. The electronegative O atom deshields adjacent H's, shifting them downfield between 3 and 4 ppm. If **A** is the correct structure, the singlet due to the CH_3 group (H_c) should occur downfield, whereas if **B** is the correct structure, the quartet due to the CH_2 group (H_b) should occur downfield.
- Because the NMR of **X** has a singlet (not a quartet) at 3.7, **A is the correct structure.**

Simplification of complex spectra

- Increased field strength can be applied to simplify a complexity of non-first order spectrum and enable more accurate analysis
- Coupling constant are independent of Bo but chemical shift in Hz (v) are field dependent
- Δv/J increased
- Consider the following transformation from complex to first order spectra.

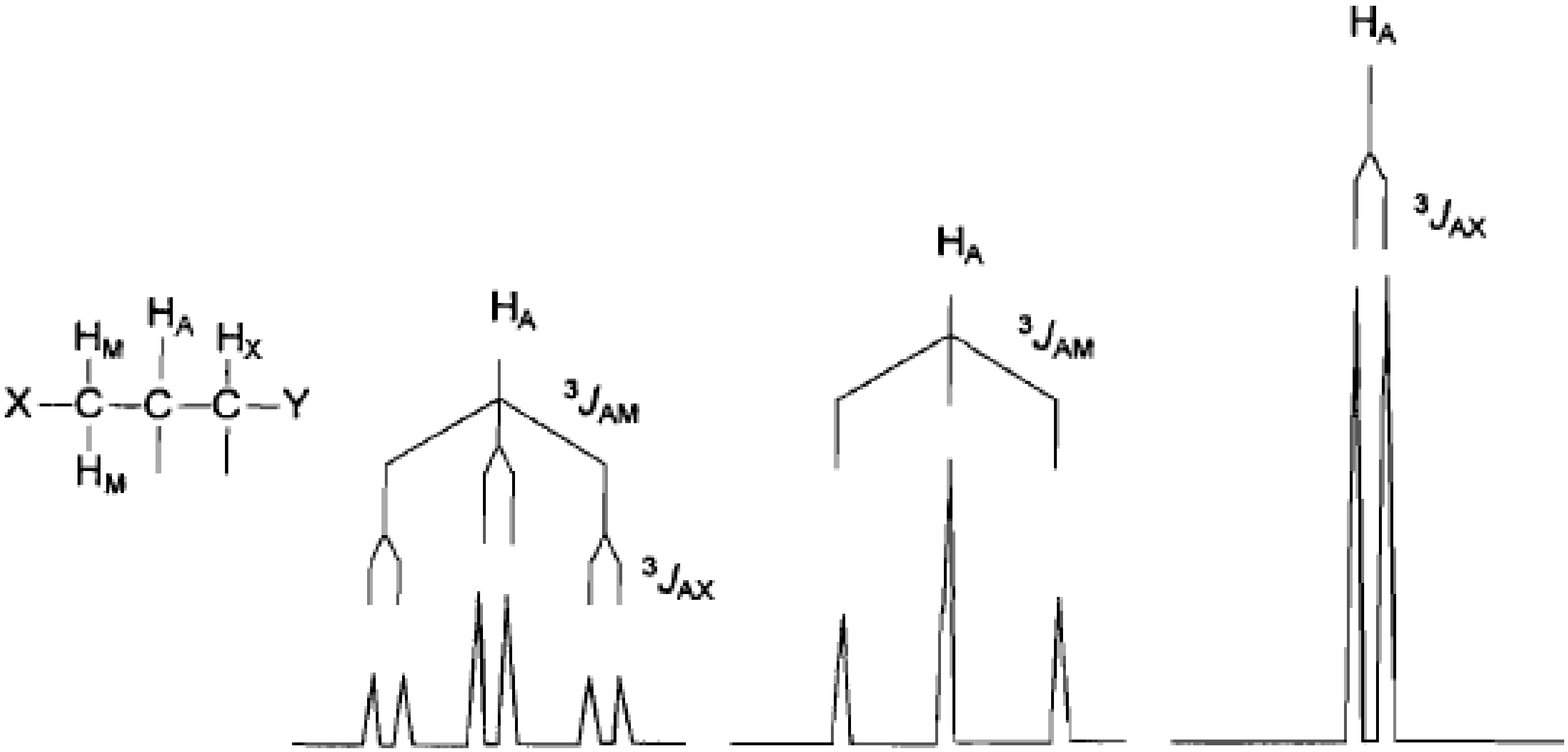
Effect of Spectrometer Magnetic Field Strength



Spin-spin decoupling

- In the signal of a proton that is a multiplet due to spin-spin coupling, it is possible to remove the splitting effects by irradiating the sample with an additional Rf source at the exact resonance frequency of the proton giving rise to the splitting.

- The additional radiofrequency causes rapid flipping of the irradiated nuclei



Basic spectrum of H_A without irradiation of of H_M or H_X

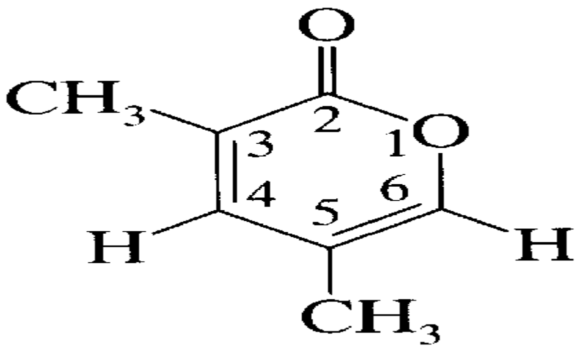
with irradiation of H_X

with irradiation of H_M

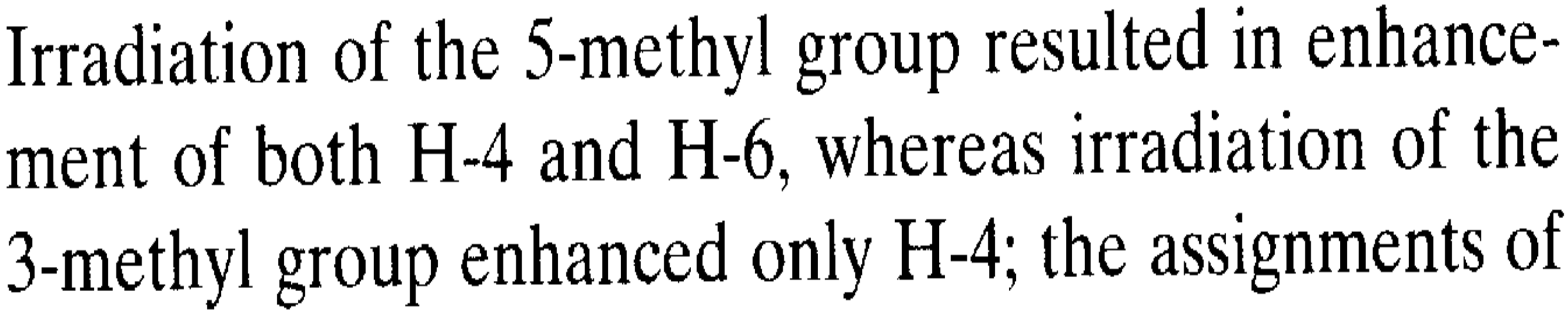
Figure 5.8 Selective Decoupling in a Simple 4-Spin System

The Nuclear Overhauser Effect (NOE)

- Irradiation of one nucleus while observing the resonance of another may result in a change in the **amplitude of the observed resonance** ***i.e. an enhancement of the signal*** intensity. This is known as *(NOE)*.
- *The NOE is a* "through space" effect and its magnitude is inversely proportional to the sixth power of the distance between the interacting nuclei.
- Because of the distance dependence of the NOE, it is an important method for establishing which groups are close together in space and because the NOE can be measured quite accurately it is a very powerful means for determining the three dimensional structure (and stereochemistry) of organic compounds.



III



Irradiation of the 5-methyl group resulted in enhancement of both H-4 and H-6, whereas irradiation of the 3-methyl group enhanced only H-4; the assignments of

A proton that is close in space to the irradiated proton is affected by the NOE *whether or not it is coupled to the irradiated proton;* if it is coupled, it remains at least partially coupled because the irradiation is weak in comparison with that used for a decoupling experiment.

^{13}C - Nuclear Magnetic Resonance Spectroscopy

(^{13}C- NMR)

- Provides a count of the different types of environments of carbon atoms in a molecule

- are measured in ppm (d) from the carbons of TMS

- ^{13}C resonances are 0 to 220 ppm downfield from TMS
- Chemical shift affected by electronegativity of nearby atoms
- O, N, halogen decrease electron density and shielding ("deshield"), moving signal downfield.
- *sp*^{3} C signal is at δ 0 to 9; *sp*^{2} C: δ 110 to 220
- C(=O) at the low field, δ 160 to 220

- ^{13}C is a rare nucleus (1.1% natural abundance)

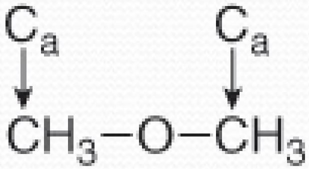
COUPLING AND DECOUPLING IN 13C NMR SPECTRA

- ^{13}C- ^{13}C coupling is not observed
- ➢ there is no signal multiplicity or splitting
- 13C couples strongly to any protons that may be attached
- It is the usual practice to irradiate the 'H nuclei during ^{13}C acquisition so that all ^{1}H are fully decoupled from the ^{13}C nuclei
- ➢ ^{13}C NMR spectra usually appear as a series of singlets if proton decoupled. If no decoupling, then
- CH_3- signals appear as quartets, -CH_2- signals appear as triplets, -CH- groups appear as doublets and quaternary C (no attached H) appear as singlets.

- The lack of splitting in a ^{13}C spectrum is a consequence of the low natural abundance of ^{13}C.
- Recall that splitting occurs when two NMR active nuclei—like two protons—are close to each other. Because of the low natural abundance of ^{13}C nuclei (1.1%), the chance of two ^{13}C nuclei being bonded to each other is very small (0.01%), and so no carbon-carbon splitting is observed.
- A ^{13}C NMR signal can also be split by nearby protons. This ^{1}H-^{13}C splitting is usually eliminated from the spectrum by using an instrumental technique that decouples the proton-carbon interactions, so that every peak in a ^{13}C NMR spectrum appears as a singlet.
- The two features of a ^{13}C NMR spectrum that provide the most structural information are the number of signals observed and the chemical shifts of those signals.

^{13}C NMR—Number of Signals

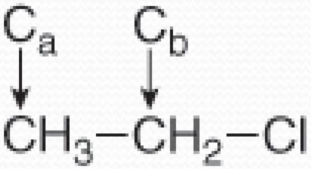
- The number of signals in a ^{13}C spectrum gives the number of different types of carbon atoms in a molecule.
- Because ^{13}C NMR signals are not split, the number of signals equals the number of lines in the ^{13}C spectrum.
- In contrast to the ^{1}H NMR situation, peak intensity is not proportional to the number of absorbing carbons, so ^{13}C NMR signals are not integrated.



dimethyl ether

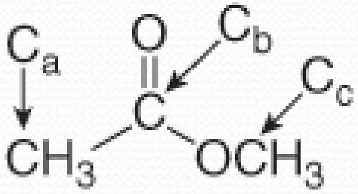
1 ^{13}C NMR signal

Both C's are equivalent.



chloroethane

2 ^{13}C NMR signals

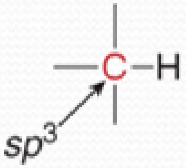
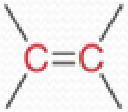
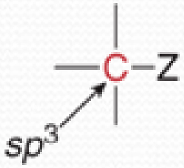
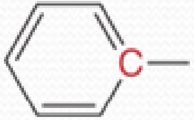
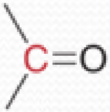


methyl acetate

3 ^{13}C NMR signals

^{13}C NMR—Position of Signals

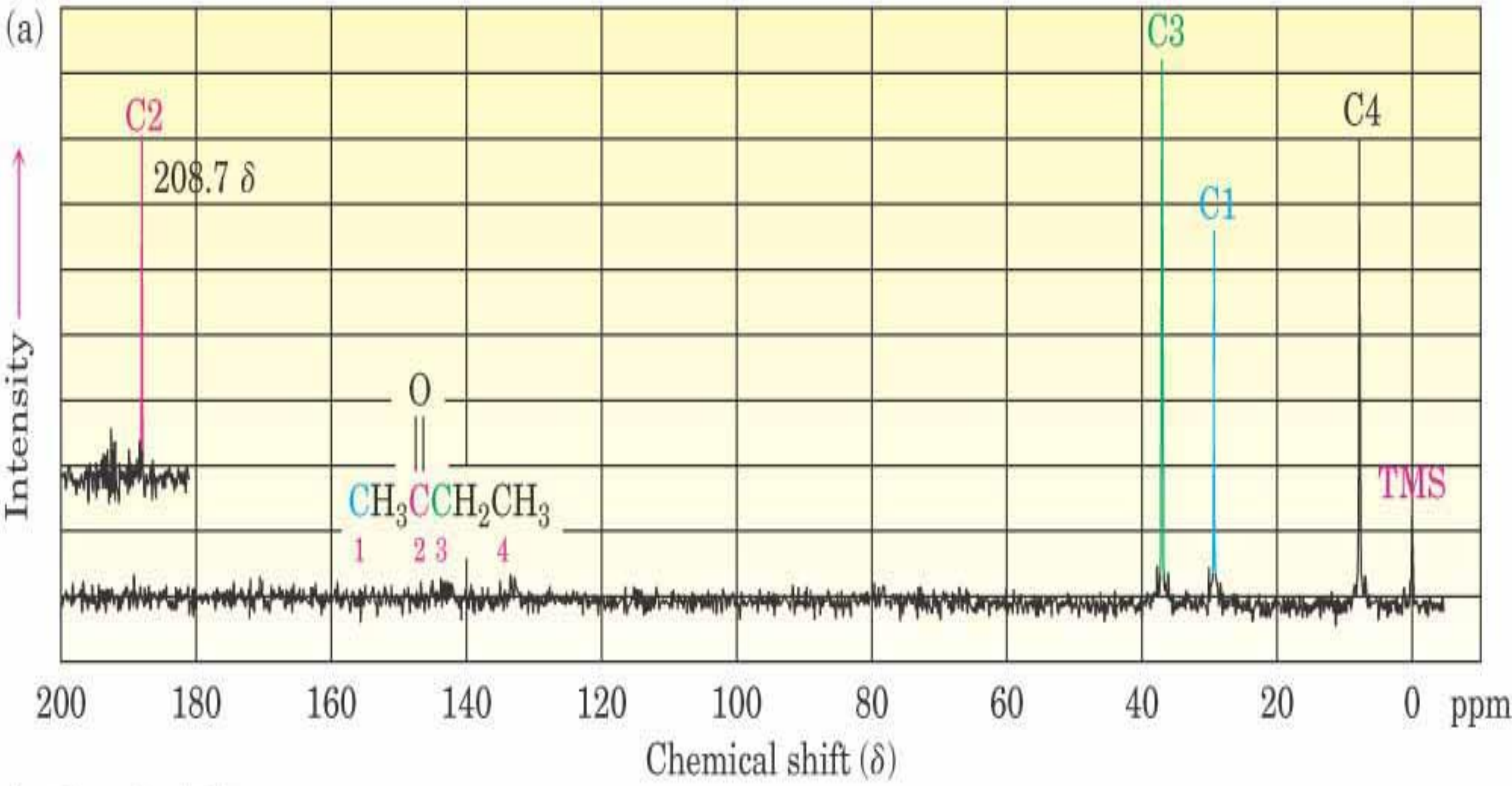
- In contrast to the small range of chemical shifts in ^{1}H NMR (1-10 ppm usually), ^{13}C NMR absorptions occur over a much broader range (0-220 ppm).
- The chemical shifts of carbon atoms in ^{13}C NMR depend on the same effects as the chemical shifts of protons in ^{1}H NMR.

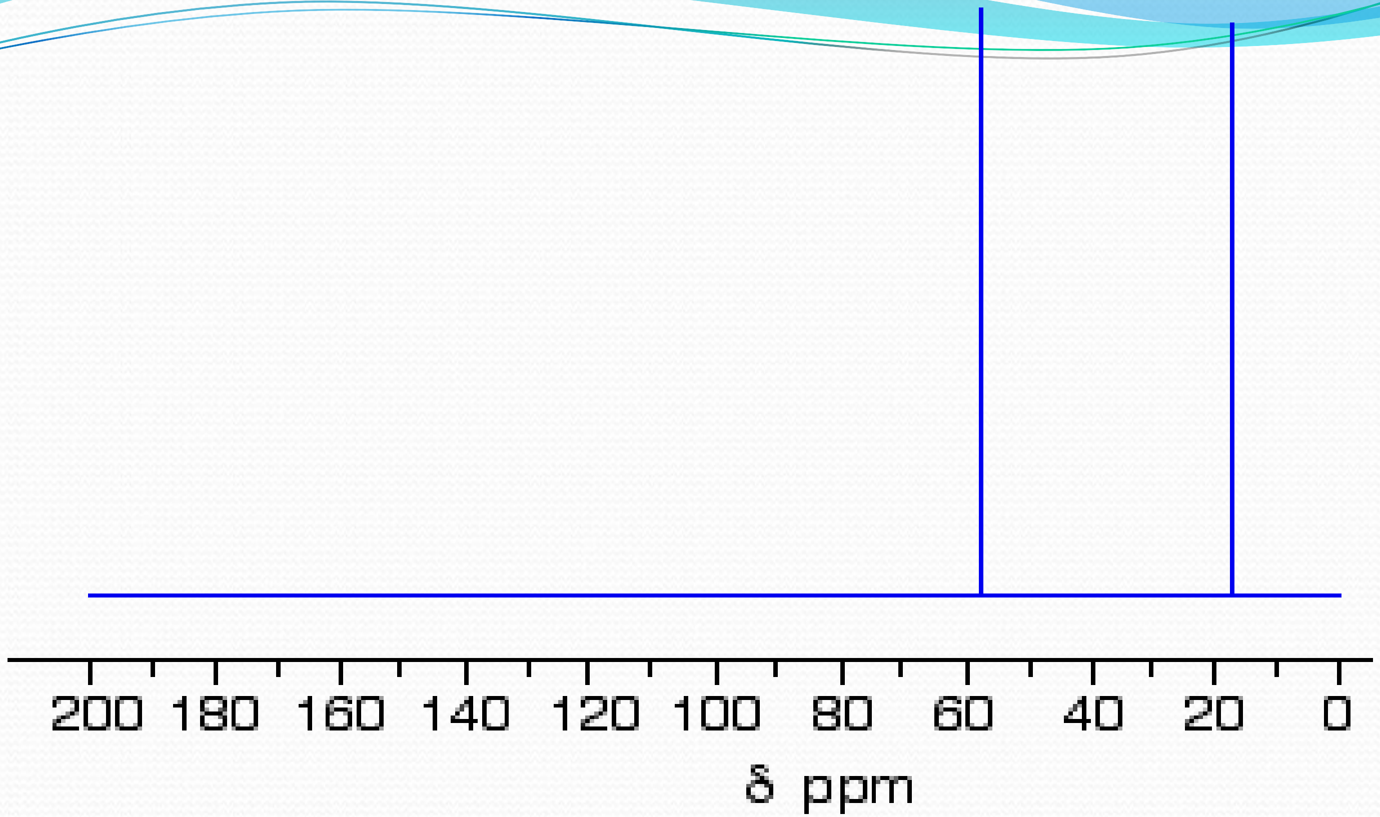
Type of carbon	Chemical shift (ppm)	Type of carbon	Chemical shift (ppm)
	5–45		100–140
 Z = N, O, X	30–80		120–150
$-C\equiv C-$	65–100		160–210

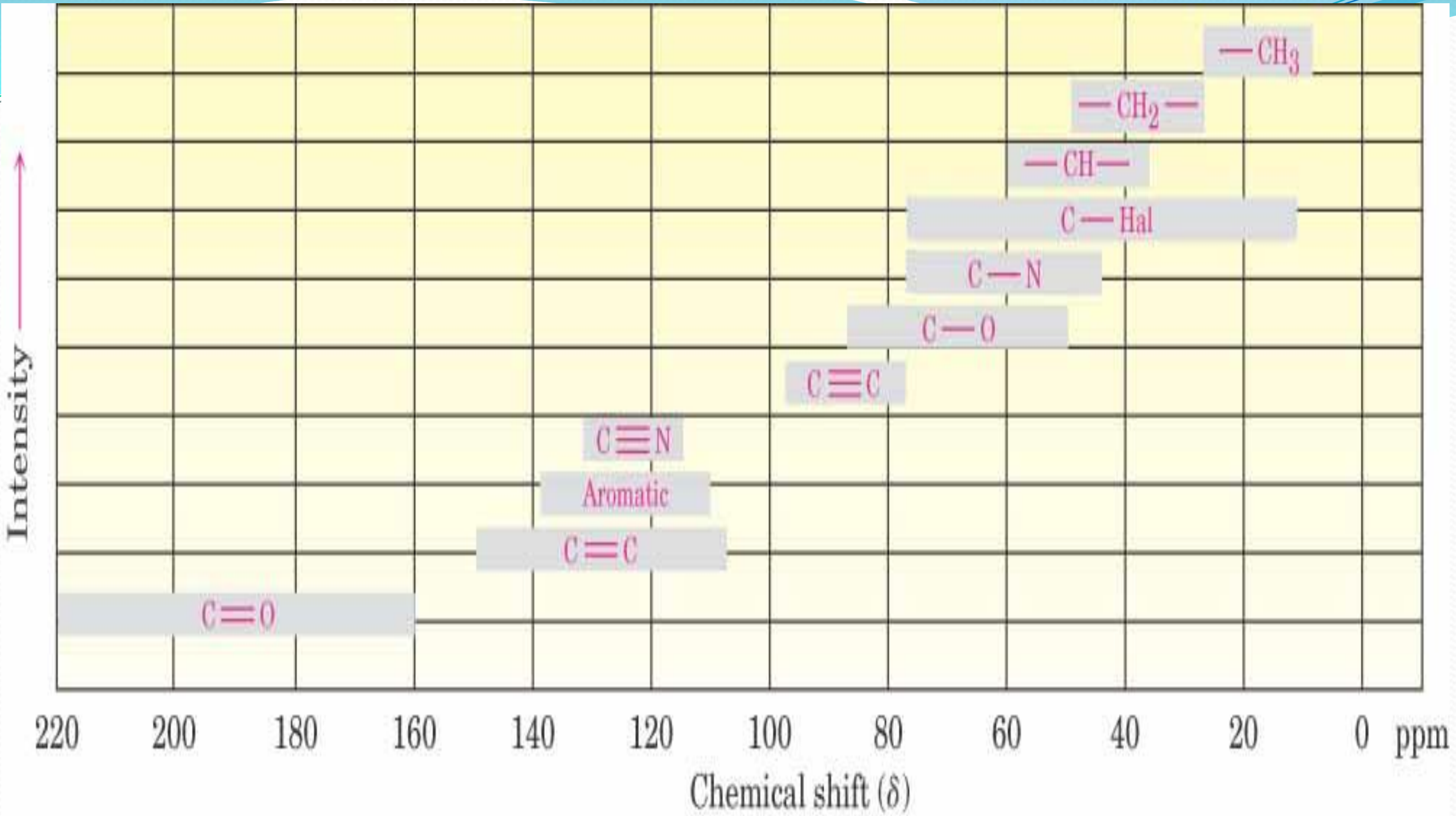
SFORD : Single Frequency Off- Resonance Decoupling

- Another method for obtaining ^{13}C NMR spectra (still retaining the multiplicity information) involves the application of a strong decoupling signal at a single frequency *just outside the range of proton* resonances
- This has the effect of incompletely or partially decoupling protons from the ^{13}C nuclei.

- When a SFORD spectrum is acquired, the effect on the BC spectrum is to *reduce the values of splitting due to all* carbon-proton coupling.
- The multiplicity due to the larger one-bond CH couplings remains. methyl group (quartet), methylene group (triplet), a methine (CH) group (doublet) or a quaternary carbon (a singlet)


(a)
C2
208.7 δ
Intensity
O
CH3CCH2CH3
1 2 3 4
C3
C1
C4
TMS
200 180 160 140 120 100 80 60 40 20 0 ppm
Chemical shift (δ)


200
180
160
140
120
100
80
60
40
20
0
δ ppm



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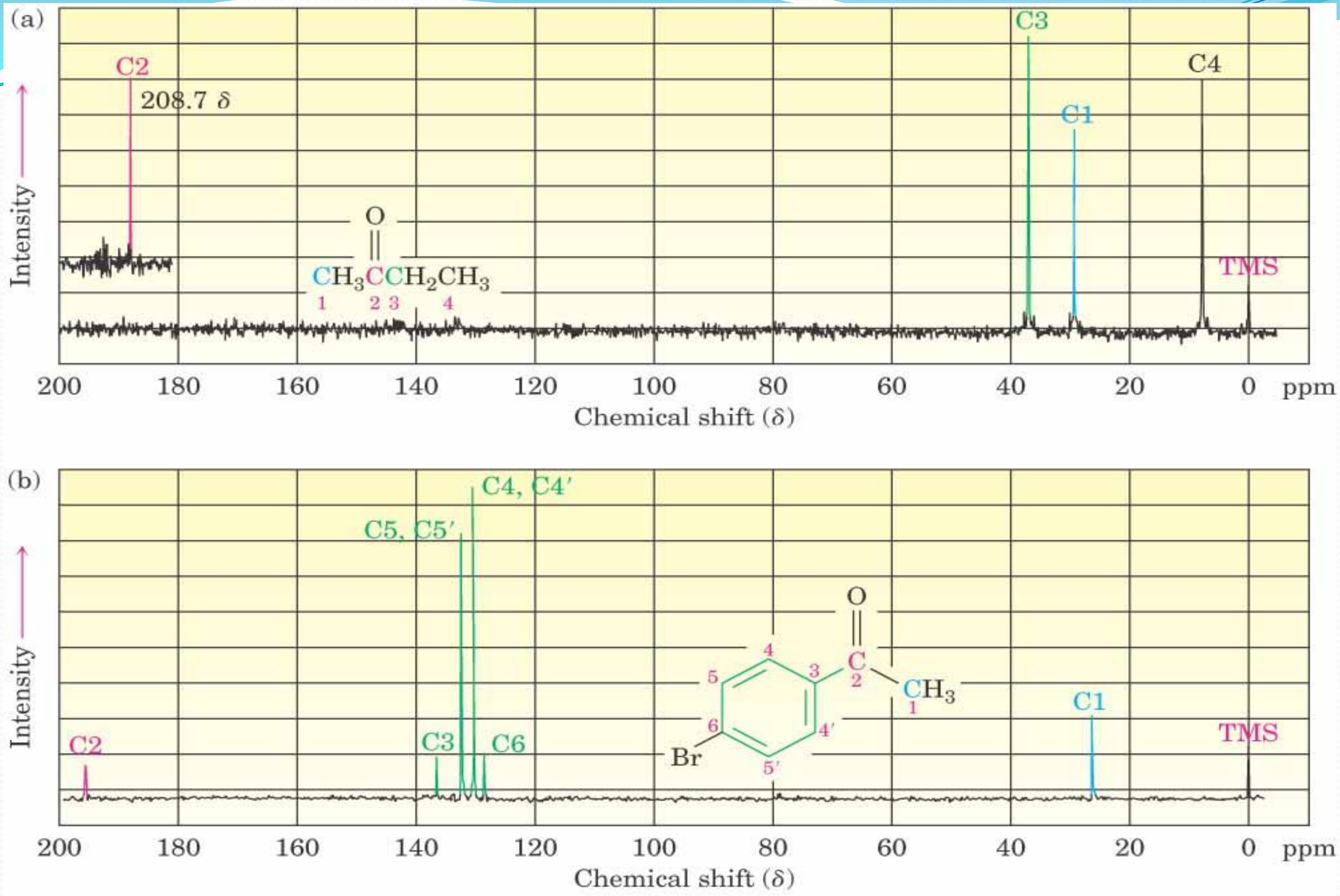
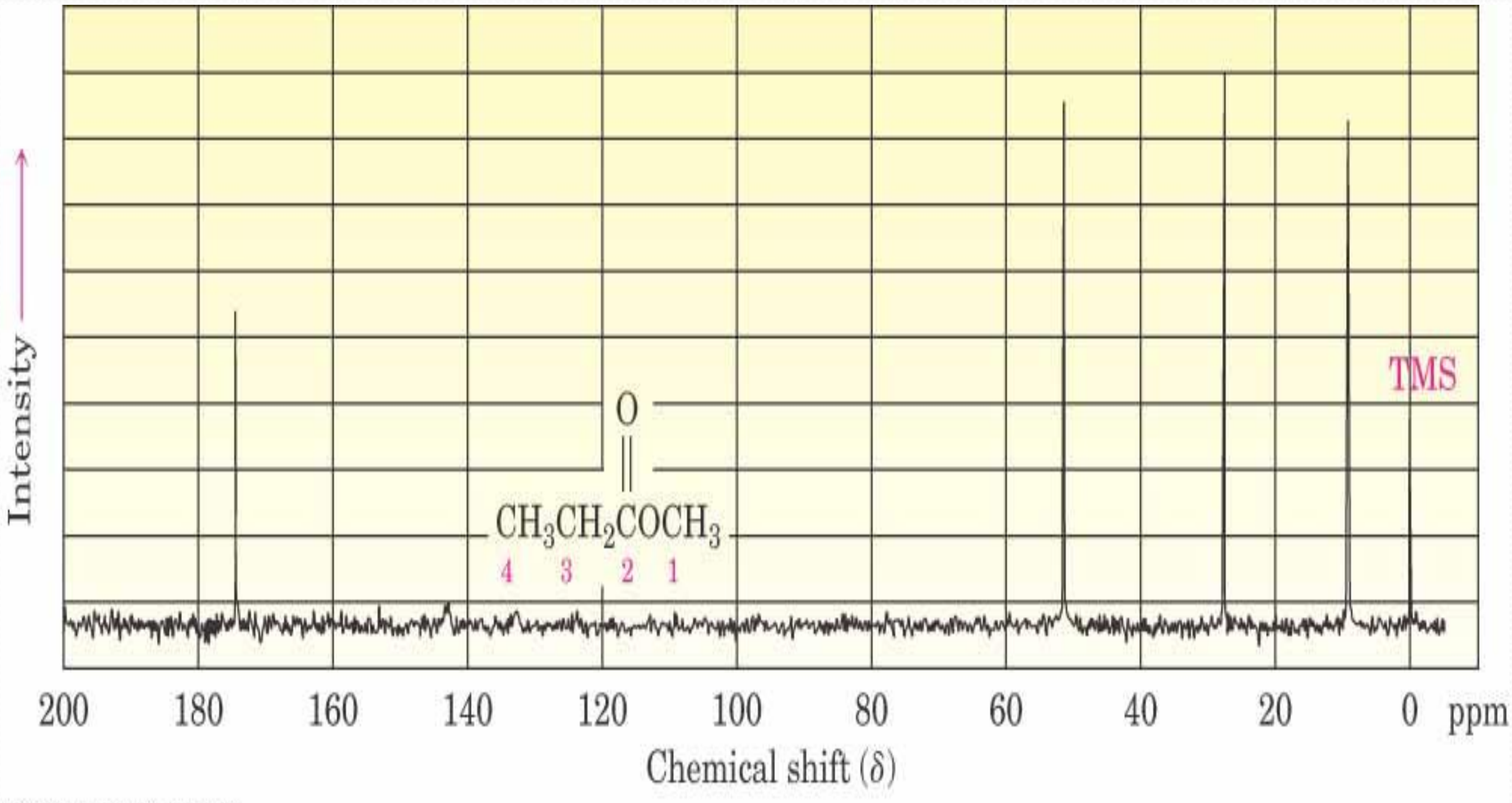
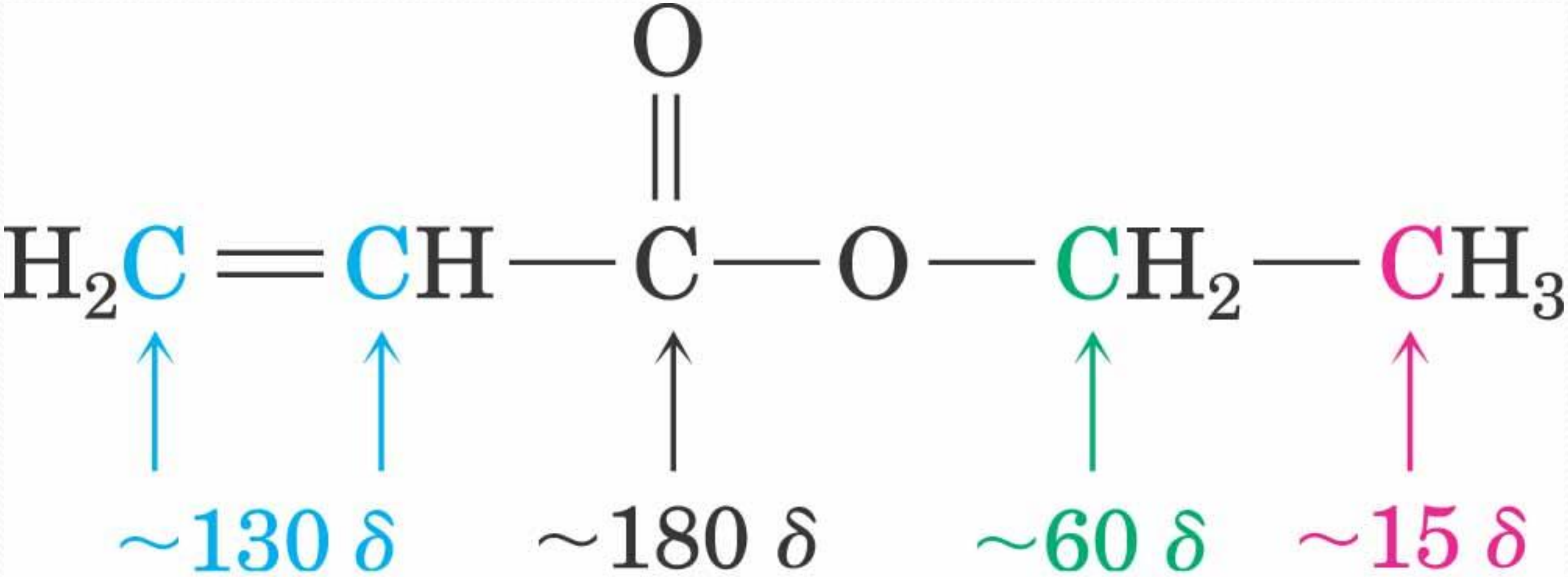

(a)
C2
208.7 δ
C3
C4
C1
TMS
O
CH3CCH2CH3
1 2 3 4
Intensity
200 180 160 140 120 100 80 60 40 20 0 ppm
Chemical shift (δ)
(b)
C4, C4′
C5, C5′
C3
C6
C2
C1
TMS
O
C
CH3
Br
1 2 3 4 5 6 4′ 5′
Intensity
200 180 160 140 120 100 80 60 40 20 0 ppm
Chemical shift (δ)

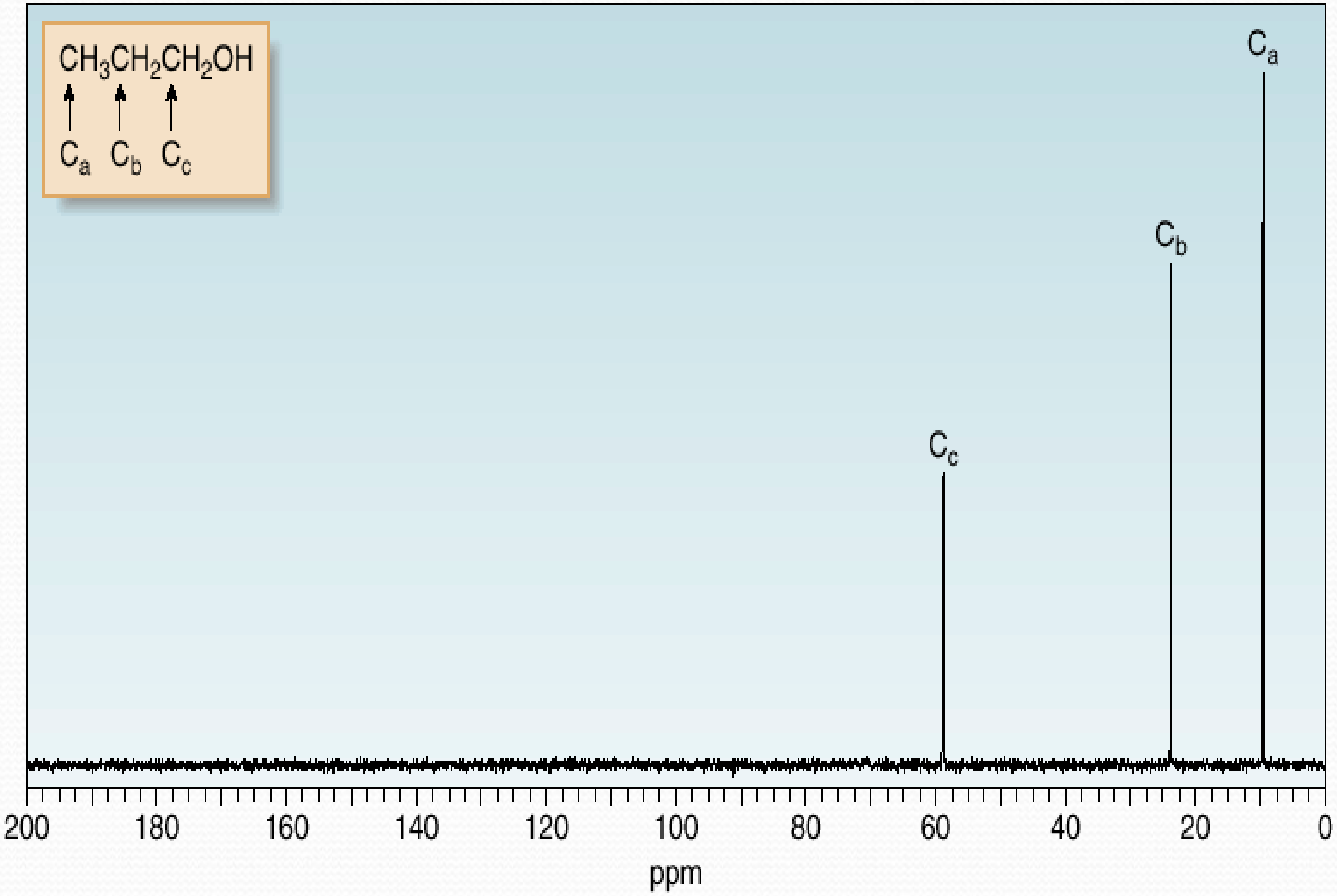

Intensity
TMS
$CH_3CH_2COCH_3$
4 3 2 1
200 180 160 140 120 100 80 60 40 20 0 ppm
Chemical shift (δ)



$$H_2C{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_3$$

- The three types of C's in 1-propanol—identified as C_a, C_b, and C_c—give rise to three ^{13}C NMR signals.
- Deshielding increases with increasing proximity to the electronegative O atom, and the absorption shifts downfield; thus, in order of increasing chemical shift: $C_a < C_b < C_c$.

a. 1-Propanol



Determining ^{13}c Signal Multiplicity Using DEPT

- With most modem NMR instrumentation, the DEPT experiment (Distortionless Enhancement by Polarisation Transfer) is the most commonly used method to determine the multiplicity of ^{13}C signals.

- The DEPT experiment is a pulsed NMR experiment which requires a series of programmed Rf pulses to both the 'H and ^{13}C nuclei in a sample.
- The resulting ^{13}C DEPT spectrum contains only signals arising from protonated carbons (non protonated carbons do not give signals in the ^{13}C DEPT spectrum).

- The signals arising from carbons in CH_3 and CH groups (i.e. those with an odd number of attached protons) appear oppositely phased from those in CH_2 groups (i.e. those with an even number of attached protons) so signals from CH_3 and CH groups point upwards while signals from CH_2 groups point downwards

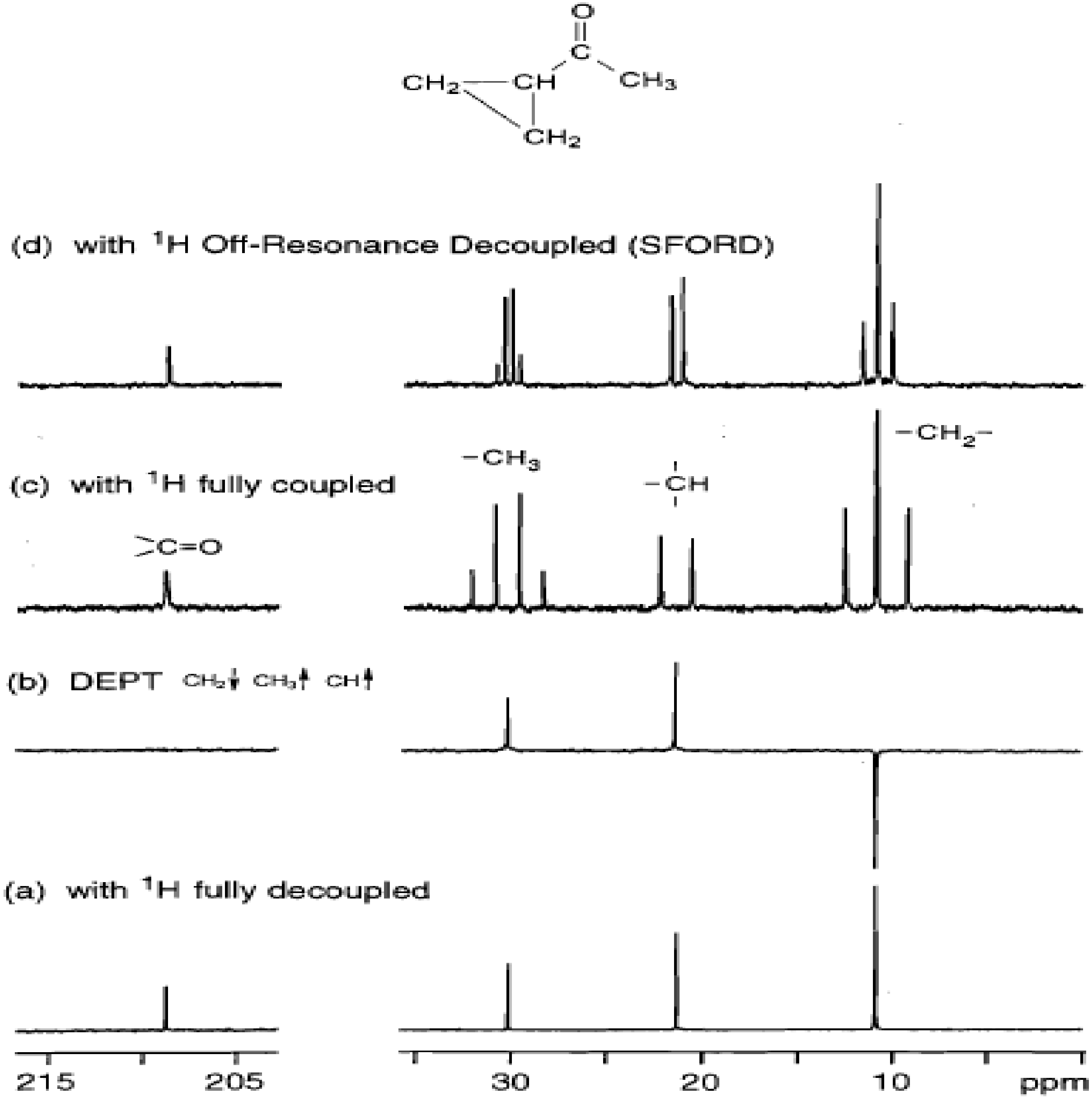
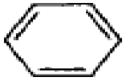
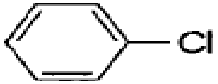
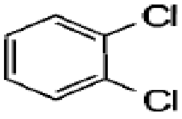
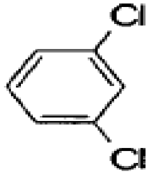
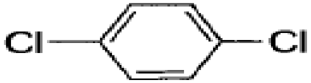
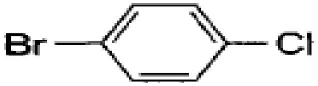
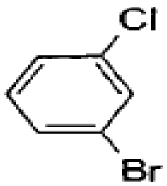
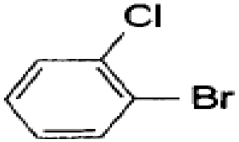
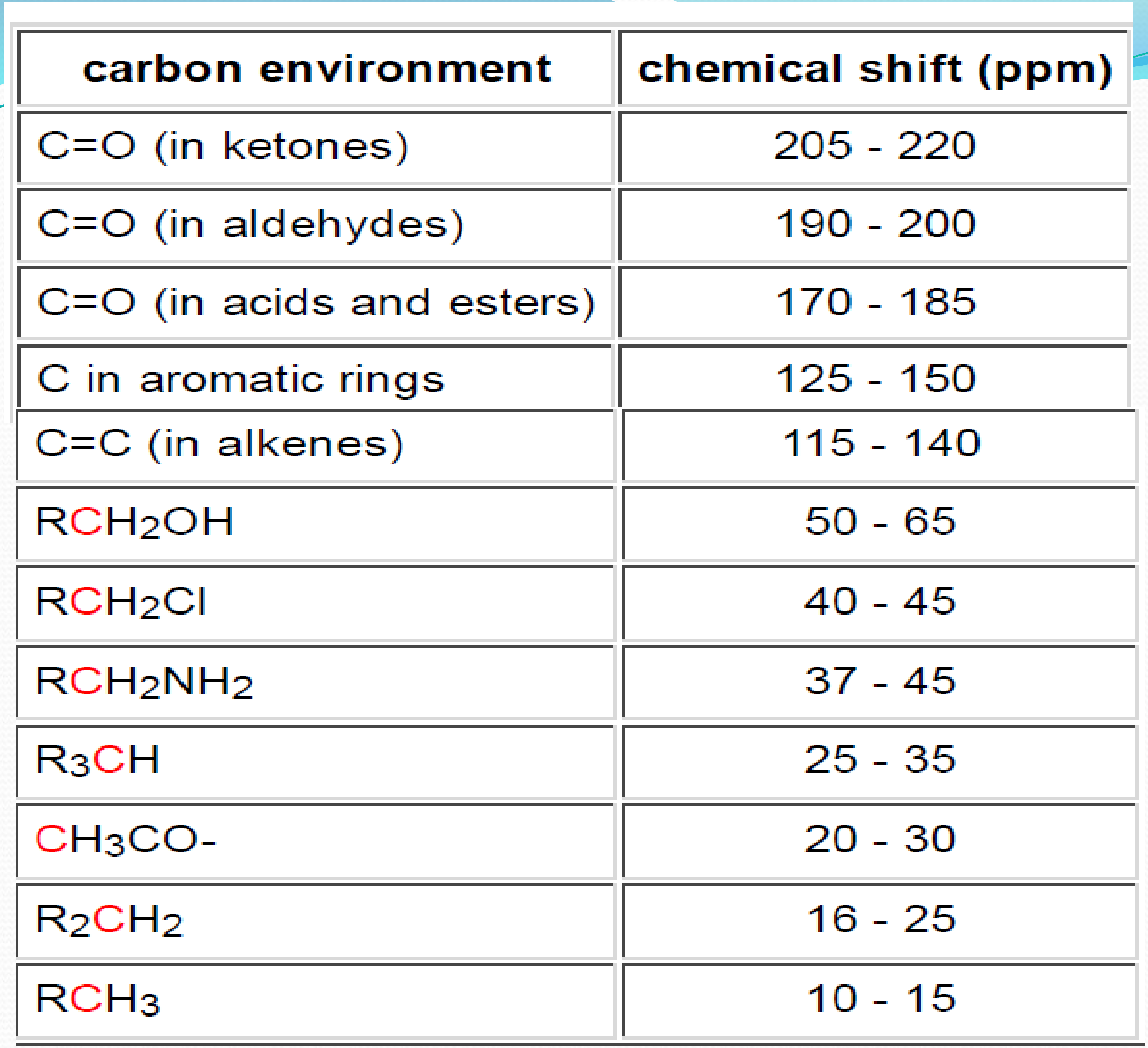

O
C
CH2
CH
CH3
CH2
(d) with ¹H Off-Resonance Decoupled (SFORD)
−CH3
−CH
−CH2−
(c) with ¹H fully coupled
>C=O
(b) DEPT CH2↓ CH3↑ CH↑
(a) with ¹H fully decoupled
215
205
30
20
10
ppm

Table 6.1 The Number of Aromatic ^{13}C Resonances in Benzenes with Different Substitution Patterns

Molecule	Number of aromatic ^{13}C resonances
	1
	4
	3
	4
	2
	4
	6
	6



carbon environment	chemical shift (ppm)
C=O (in ketones)	205 - 220
C=O (in aldehydes)	190 - 200
C=O (in acids and esters)	170 - 185
C in aromatic rings	125 - 150
C=C (in alkenes)	115 - 140
RCH_2OH	50 - 65
RCH_2Cl	40 - 45
RCH_2NH_2	37 - 45
R_3CH	25 - 35
CH_3CO-	20 - 30
R_2CH_2	16 - 25
RCH_3	10 - 15

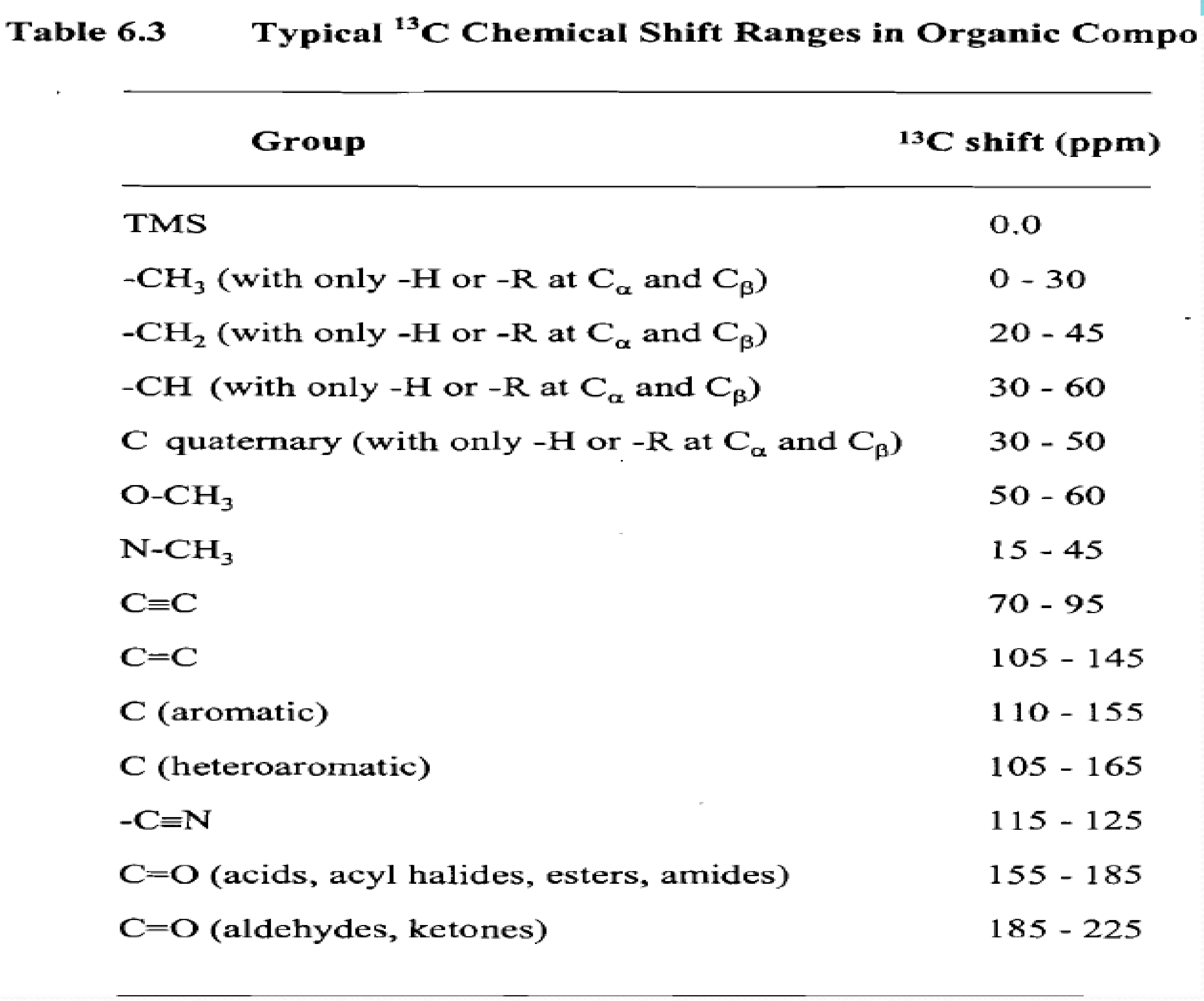


Table 6.3 Typical ^{13}C Chemical Shift Ranges in Organic Compo

Group	^{13}C shift (ppm)
TMS	0.0
$-CH_3$ (with only -H or -R at C_α and C_β)	0 - 30
$-CH_2$ (with only -H or -R at C_α and C_β)	20 - 45
-CH (with only -H or -R at C_α and C_β)	30 - 60
C quaternary (with only -H or -R at C_α and C_β)	30 - 50
$O-CH_3$	50 - 60
$N-CH_3$	15 - 45
$C\equiv C$	70 - 95
C=C	105 - 145
C (aromatic)	110 - 155
C (heteroaromatic)	105 - 165
$-C\equiv N$	115 - 125
C=O (acids, acyl halides, esters, amides)	155 - 185
C=O (aldehydes, ketones)	185 - 225

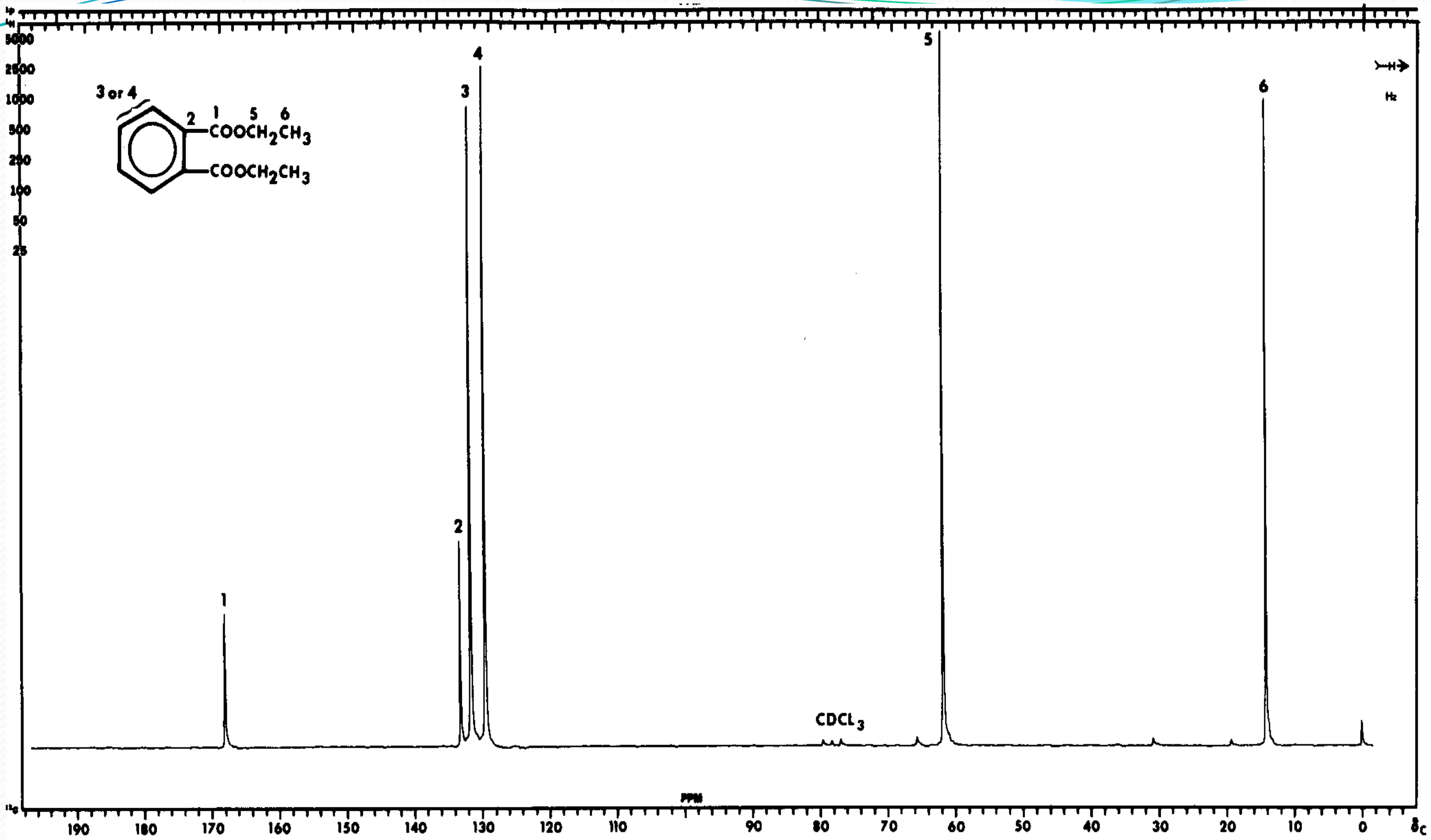


FIGURE 5.1(*c*). The ^{13}C-NMR spectrum of diethyl phthalate with the protons completely decoupled and a 10-s delay between pulses. The solvent used was $CDCl_3$ at 25.2 MHz.

^{1}H and ^{13}C NMR compared:

- **both give us information about the number of chemically nonequivalent nuclei (nonequivalent hydrogens or nonequivalent carbons)**
- **both give us information about the environment of the nuclei (hybridization state, attached atoms, etc.)**

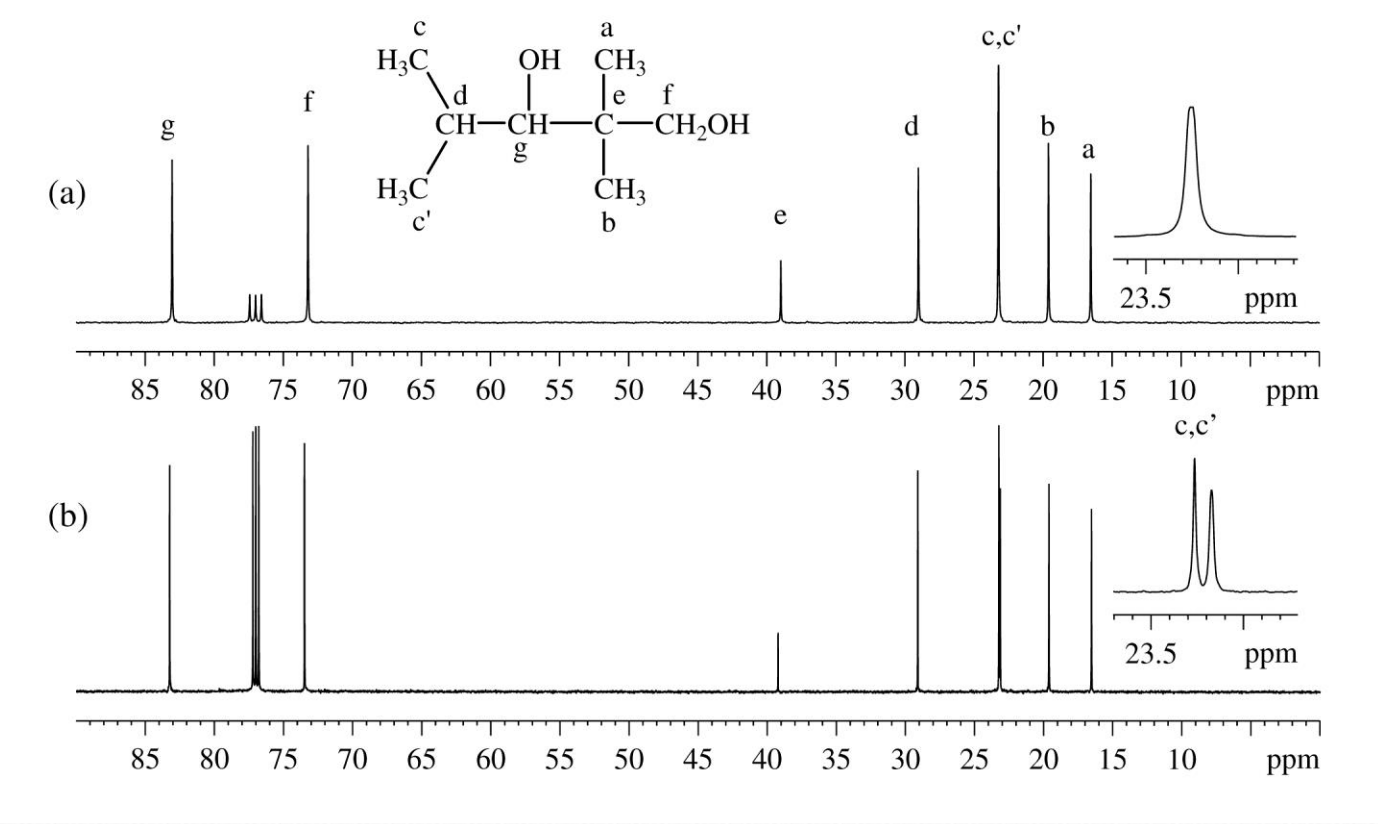
^{1}H and ^{13}C NMR compared:

- the signal for the NMR of a 13 C nucleus is 10^{-4} times weaker than the signal for a hydrogen nucleus
- **a signal for a ^{13}C nucleus is only about 1% as intense as that for ^{1}H because of the magnetic properties of the nuclei, and**
- at the "natural abundance" level only 1.1% of all the C atoms in a sample are ^{13}C (most are ^{12}C)

^{1}H and ^{13}C NMR compared:

- ^{13}C signals are spread over a much wider range than ^{1}H signals making it easier to identify and count individual nuclei
- **Check the spectra on the next slides: Figure 13.20 (a) shows the ^{1}H NMR spectrum of 1-chloropentane; Figure 13.20 (b) shows the ^{13}C spectrum. It is much easier to identify the compound as 1-chloropentane by its ^{13}C spectrum than by its ^{1}H spectrum.**

Spectrum at 75 MHz and 150 MHz



THANK YOU!!!

END OF THE CHAPTER