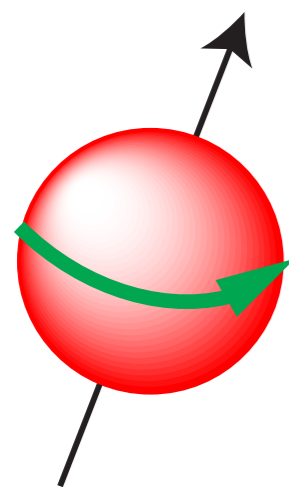


14



**METHODS FOR STRUCTURE
DETERMINATION
NUCLEAR MAGNETIC RESONANCE
AND
MASS SPECTROMETRY**

Figure 14.1 Absorption of Electromagnetic Radiation by a Nucleus

When the magnetic moment of a spinning nucleus (H') is aligned with the magnetic field of an NMR spectrometer, (H_0) low energy results. Absorption of specific frequency causes a change in the spin of the nucleus and results in a magnetic moment opposed to the magnetic field of the instrument. This is a higher energy state.

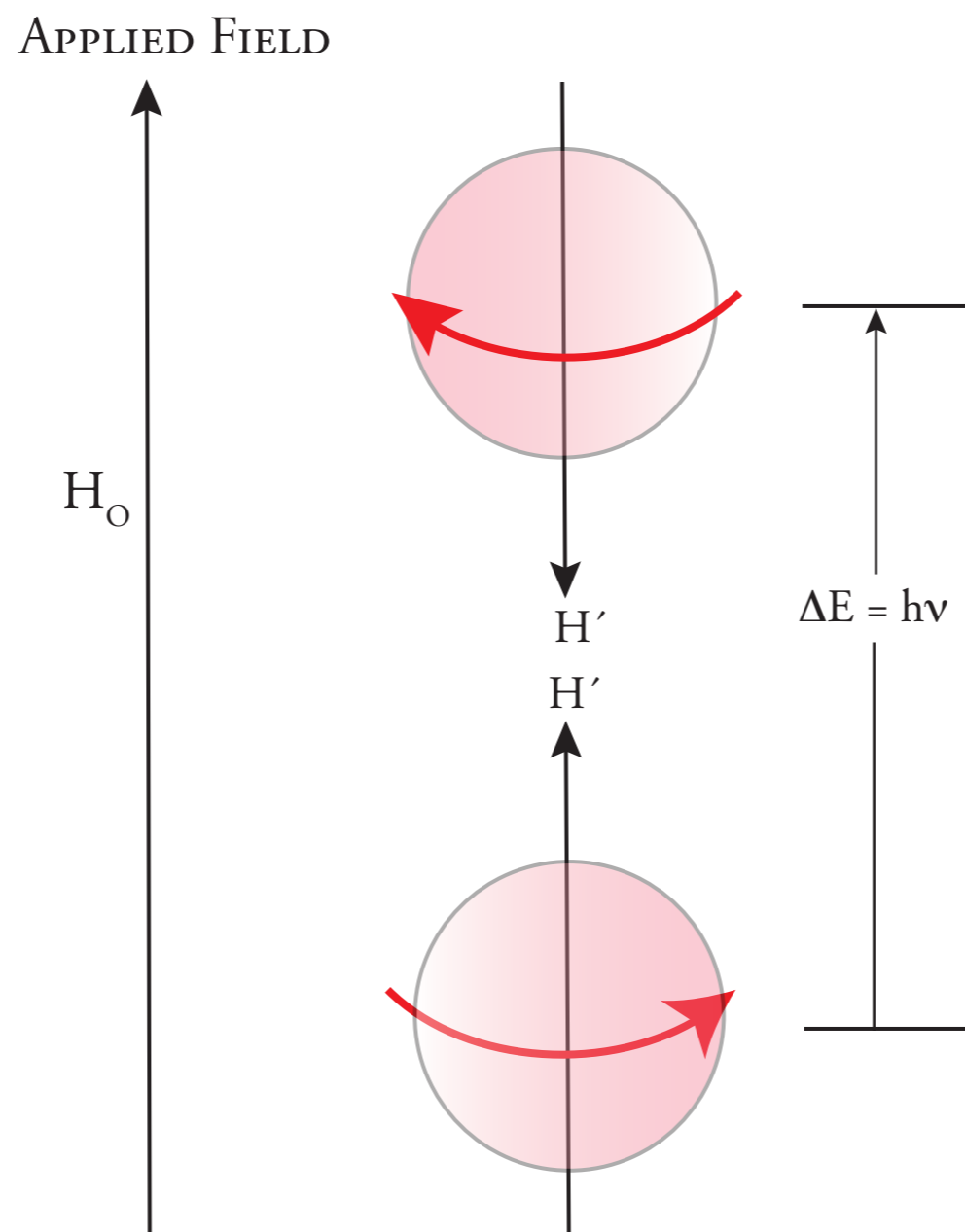


Figure 14.2 Effect of Field Strength on Energy Differences

When the magnetic moment of a nucleus is aligned with the applied magnetic field of an NMR spectrometer, the nucleus is in its ground state. When it absorbs energy, its magnetic field opposes that of the applied field, and the nucleus is in an excited state. The energy difference depends on the strength of the applied field. Although only two spin orientations are possible, the energy difference increases continuously as the applied magnetic field increases.

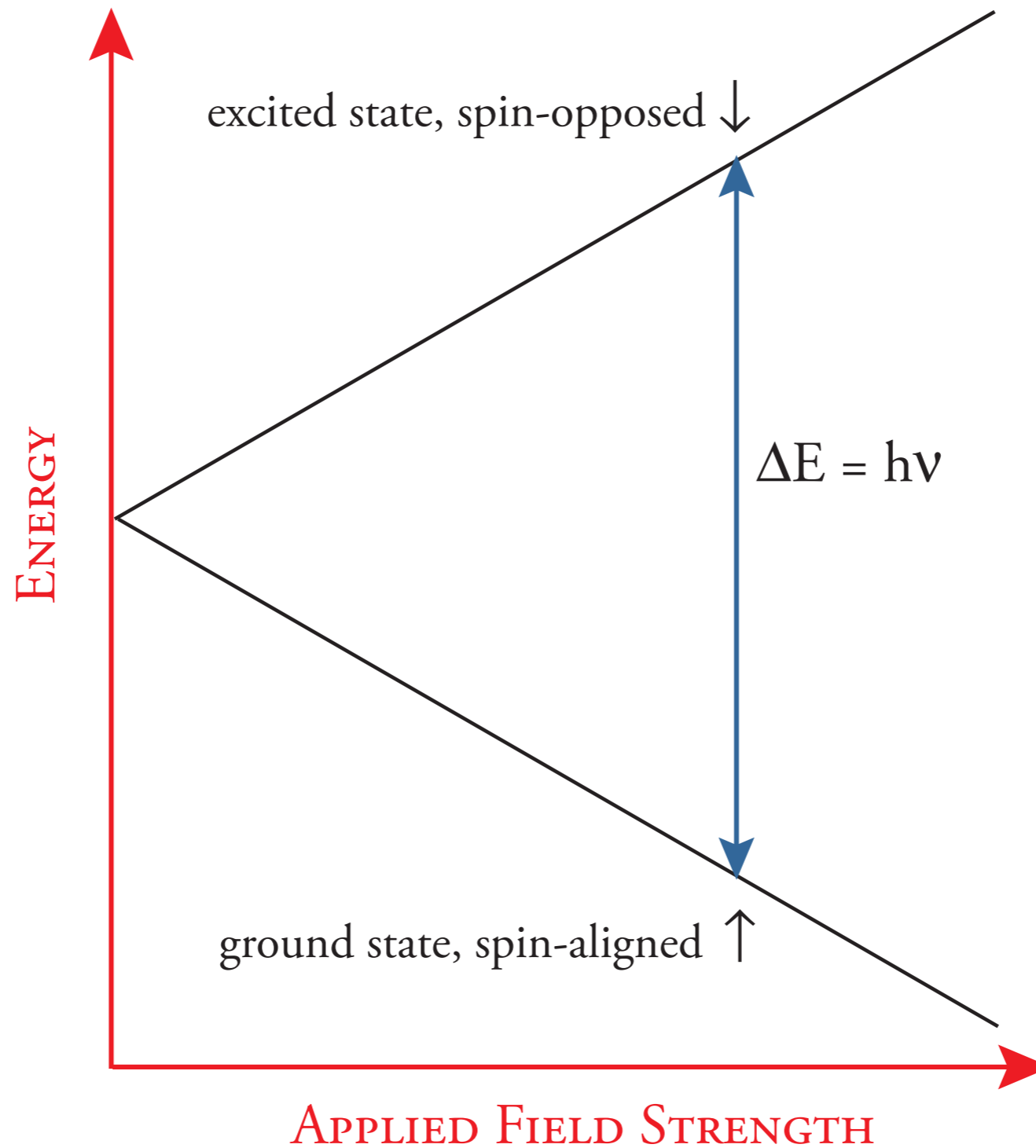
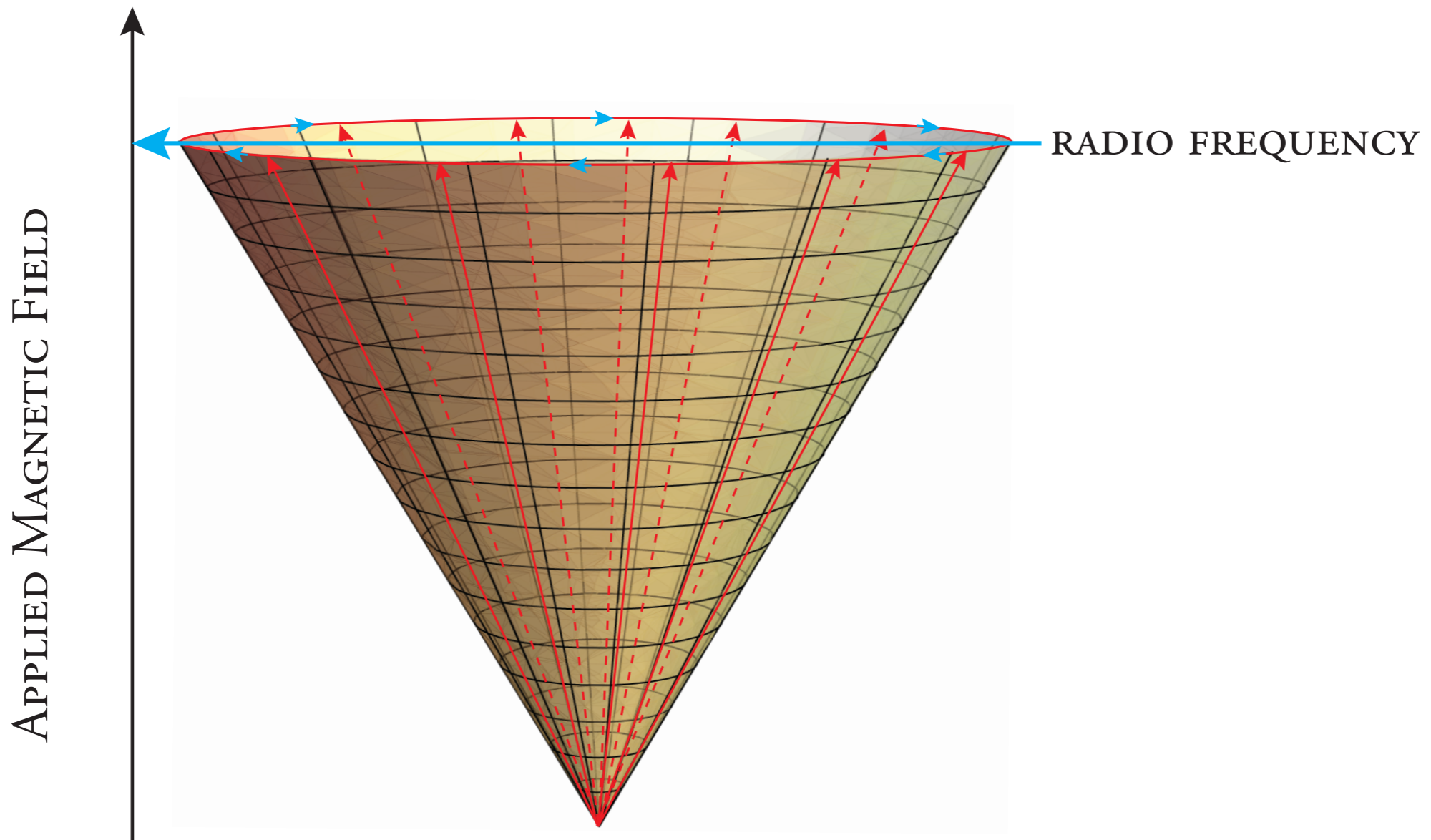


Figure 14.3 The Nuclear Precession Frequency

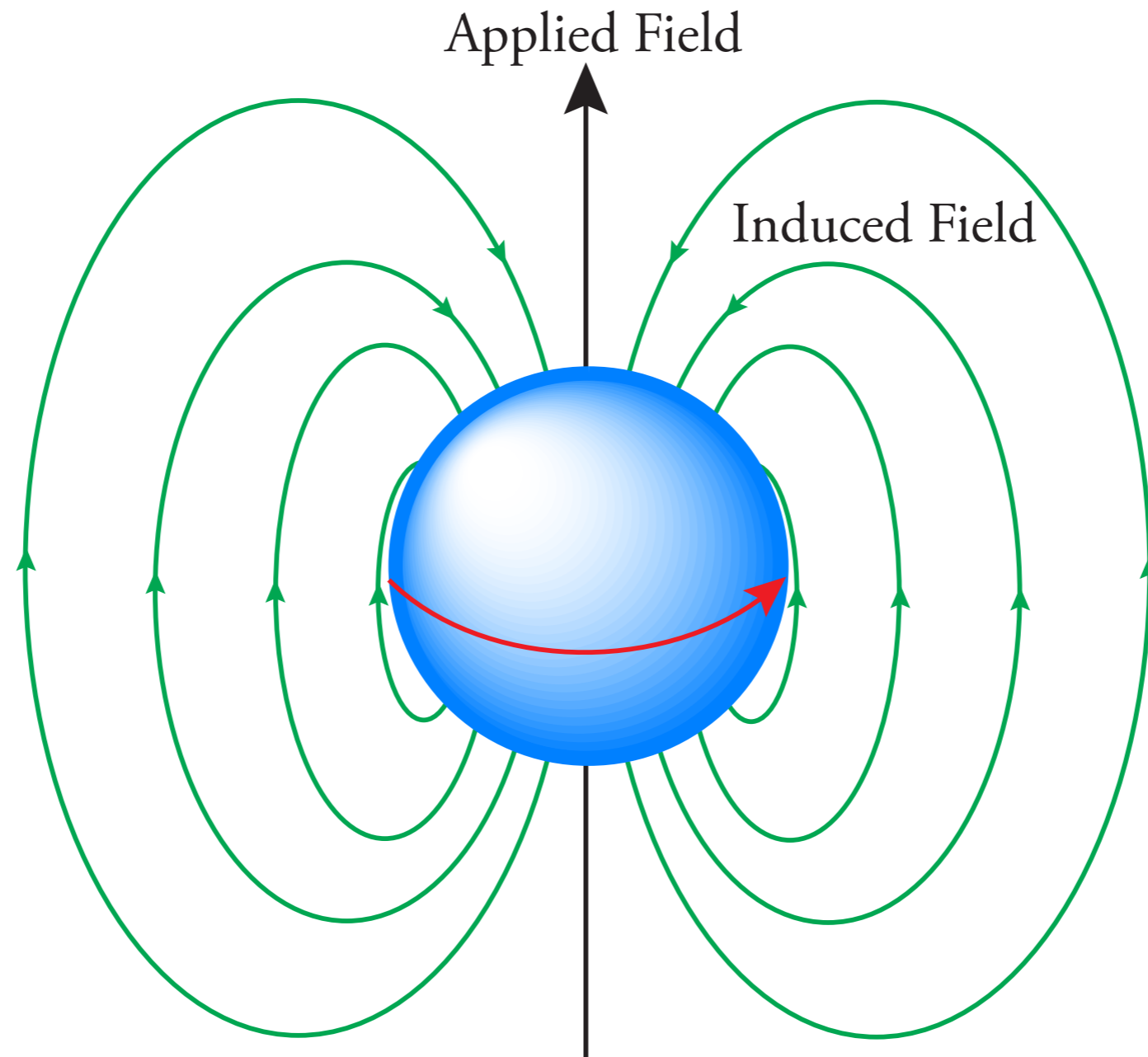
The applied magnetic field of the NMR instrument the field of the nucleus precesses around the axis of the applied field. The rate of precession depends on the strength of the applied field. A radio frequency is applied at right angles to the applied field. When the energy difference between the ground an excited states($\Delta E = h\nu$) of the applied field matches the energy of the radio frequency, the system absorbs energy; that is there is a resonance.



14.3 THE CHEMICAL SHIFT, I

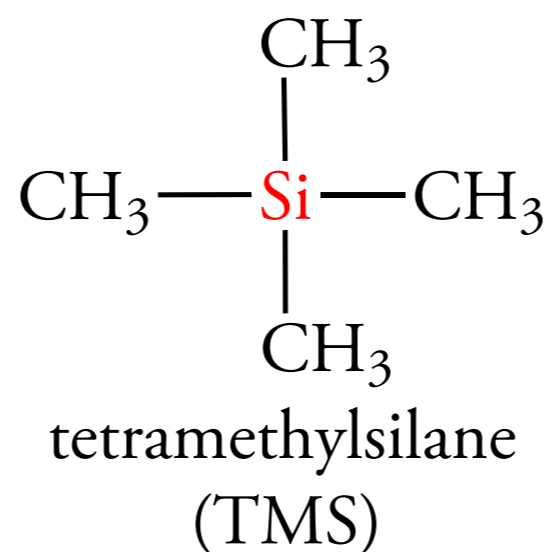
Figure 14.4 Shielding of Nucleus by Electrons

The applied magnetic field induces electron circulation about the nucleus of the hydrogen atom. This generates a small, local magnetic field around the proton that is opposed to applied magnetic field. The induced field shields the nucleus from the applied field.



14.3 THE CHEMICAL SHIFT, II

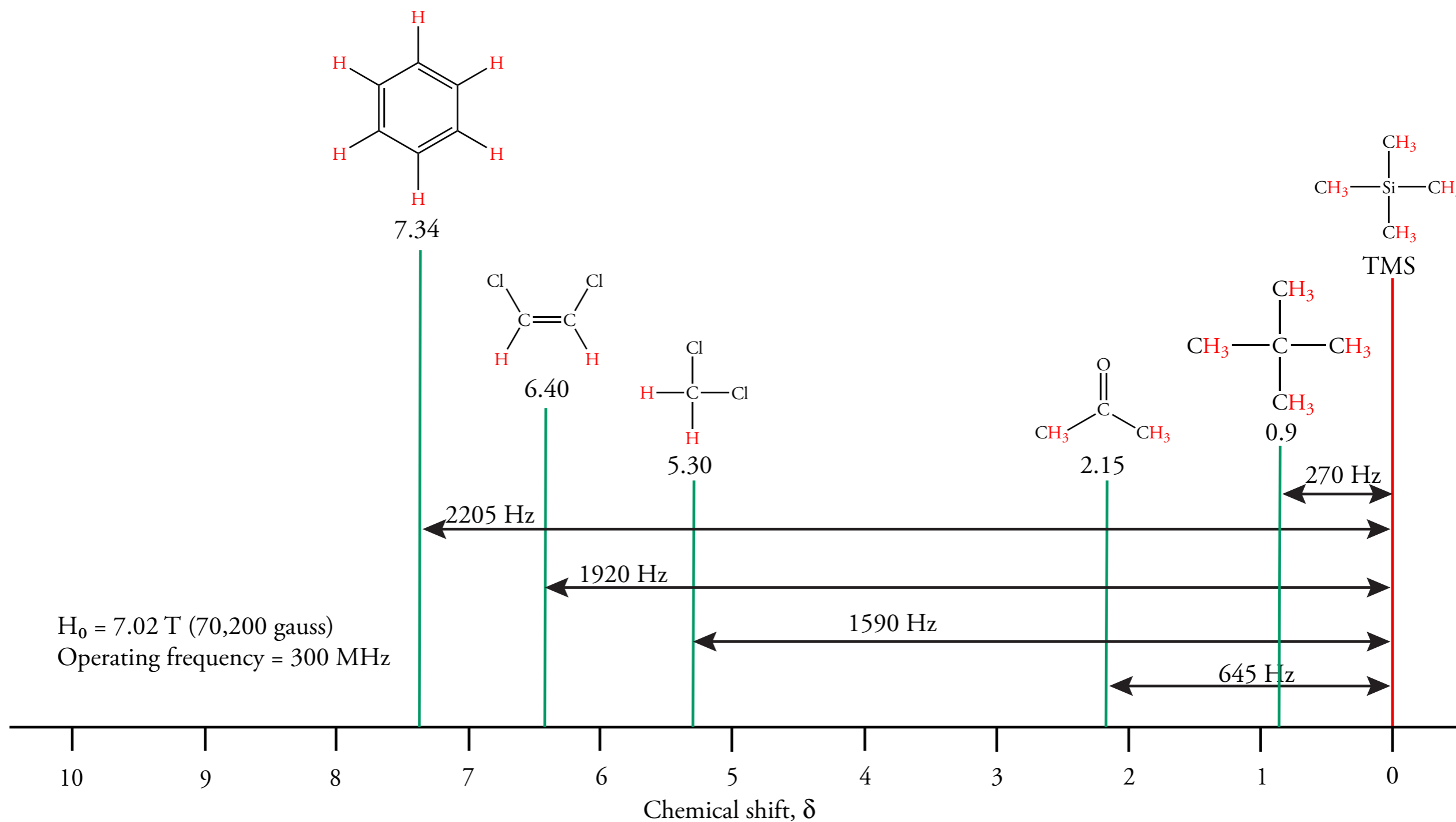
The Delta Scale



$$\delta = \frac{\text{chemical shift (Hz)}}{\text{frequency of NMR (Hz)}} = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\nu_0} \times 10^6$$

Figure 14.5 Chemical Shifts of Equivalent Hydrogens

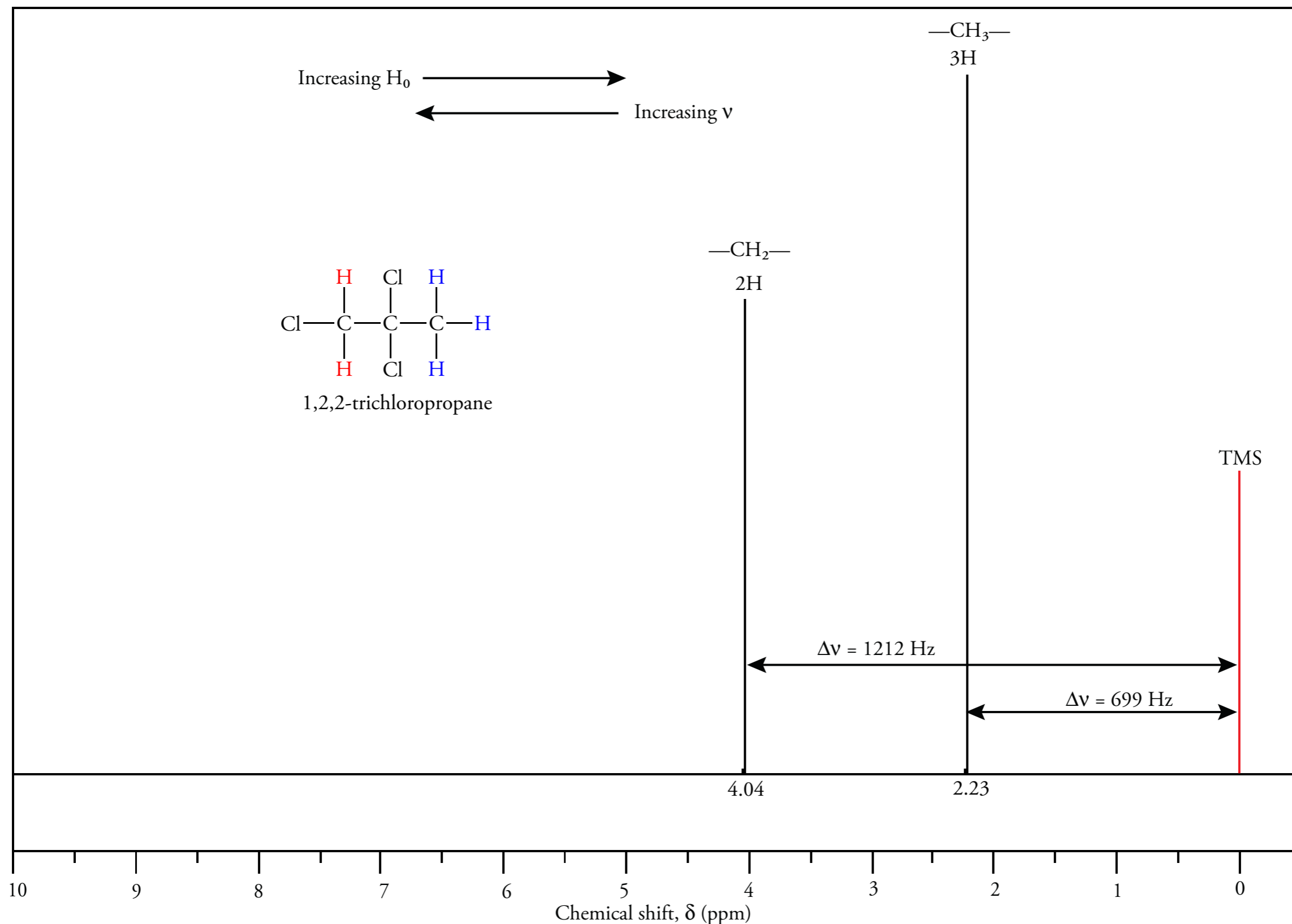
The chemical shift of a given hydrogen atom depends upon the extent to which it is shielded from the applied magnetic field. All of the hydrogens in each compound are equivalent in these examples.



$$\delta = \frac{\text{chemical shift (Hz)}}{\text{frequency of NMR (Hz)}} = \frac{V_{\text{sample}} - V_{\text{TMS}}}{V_0}$$

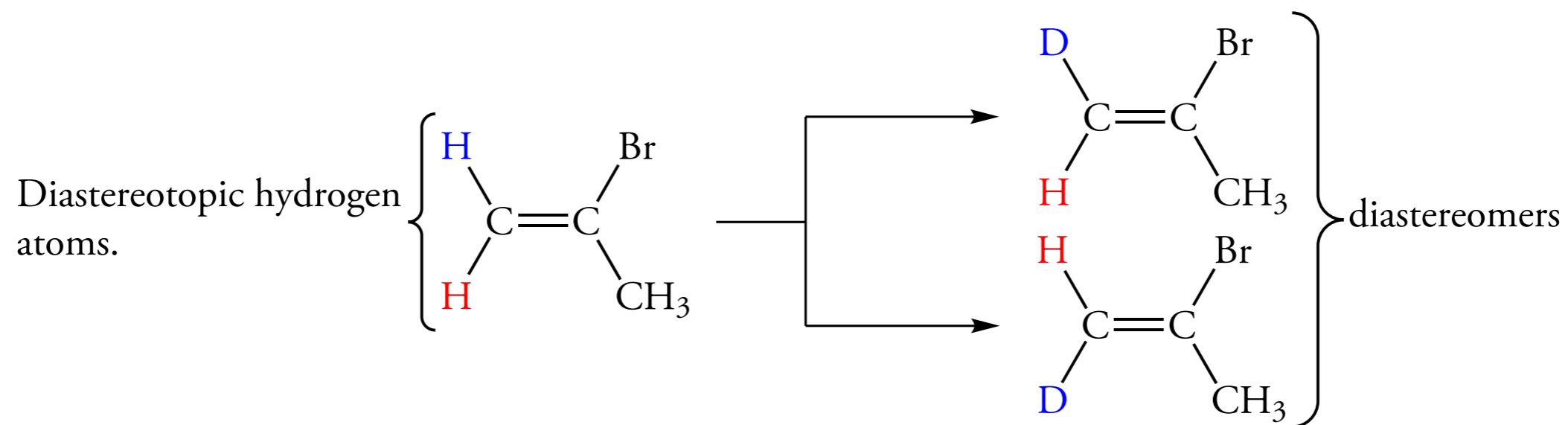
Figure 14.6 NMR Spectrum of 1,2,2-Trichloropropane

The three equivalent hydrogen atoms bonded to C-3 have a chemical shift of 2.23 δ . The two equivalent hydrogen atoms bonded to C-1 have a chemical shift of 4.04 δ .



14.4 DETECTING SETS OF NONEQUIVALENT HYDROGEN ATOMS

Diastereotopic and Enantiotopic Hydrogen Atoms



14.5 EFFECTS OF STRUCTURE ON CHEMICAL SHIFT

Electronegativity Effects

chemical shift δ :	2.1	2.7	3.1	4.3
	CH_3CH_3	$(\text{CH}_3)_3\text{N}$	$(\text{CH}_3)_2\text{O}$	CH_3F
chemical shift δ :	0.9	2.2	3.1	4.3
	CH_4	CH_3Cl	CH_2Cl_2	CHCl_3
chemical shift δ :	0.9	3.1	5.3	7.3

14.5 EFFECTS OF STRUCTURE ON CHEMICAL SHIFT

Effect of π Electrons

Figure 14.7 Effect of π Electrons on Chemical Shift of Benzene Hydrogens

The circulation of the π electrons of benzene results in a substantial ring current that induces a local magnetic field. The induced magnetic field reinforces the external magnetic field. Thus, a lower magnetic field is required to change the spin orientation of the hydrogen atoms that are coplanar with the aromatic ring, and the chemical shift is larger than it is for alkyl hydrogens.

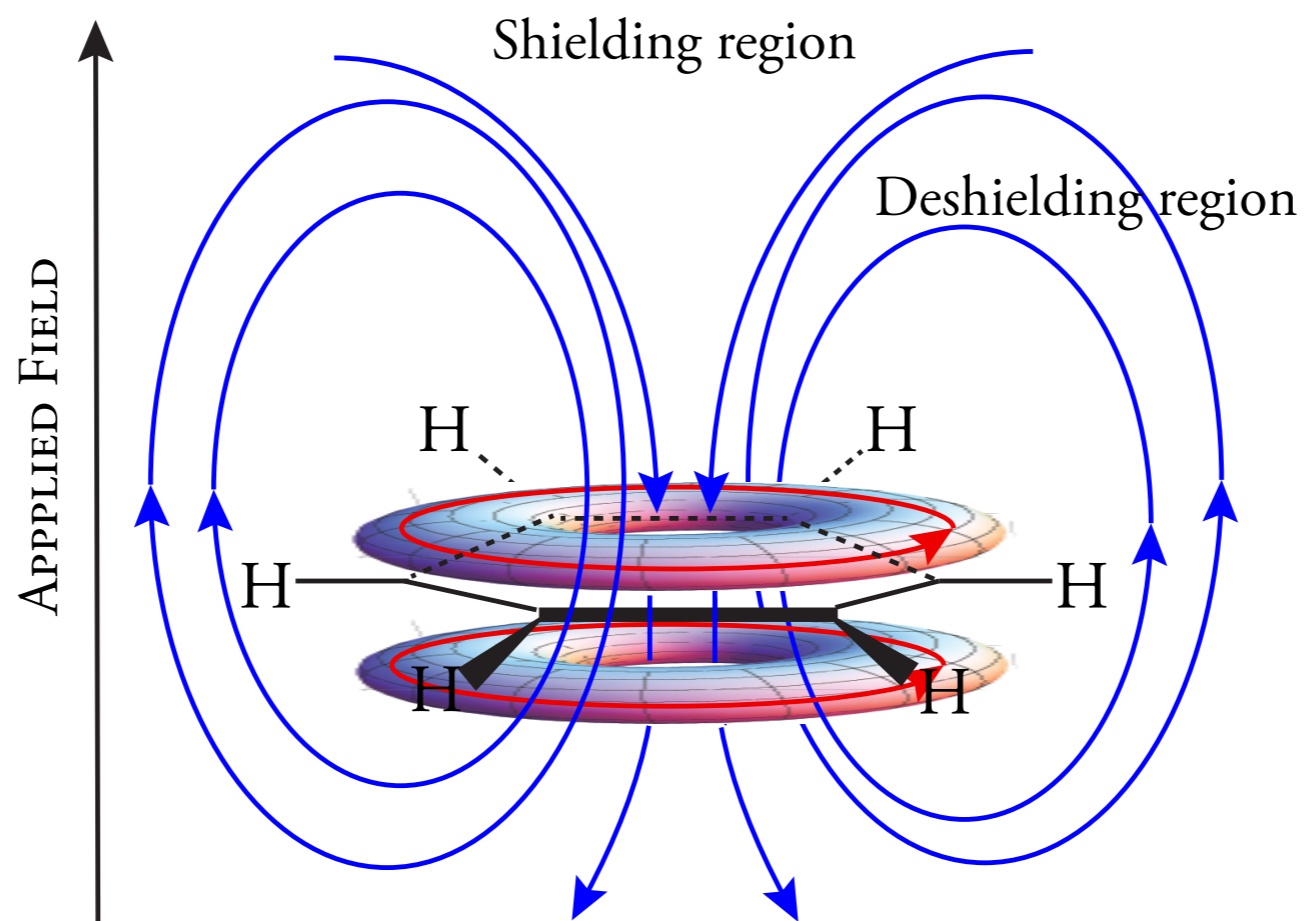
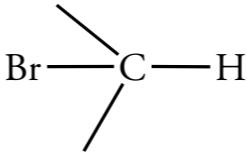
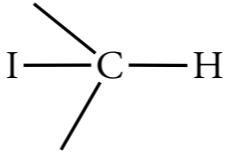
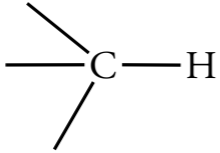
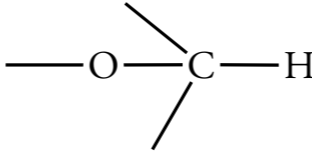
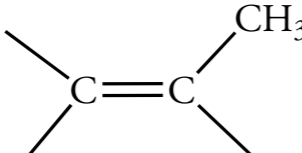
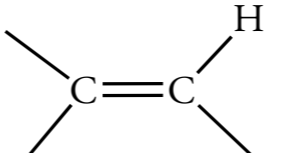
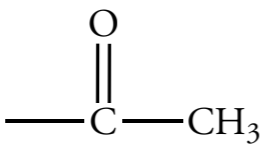
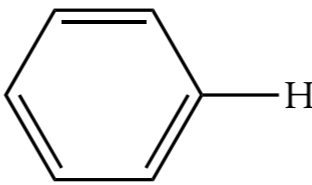
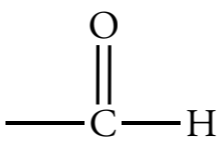
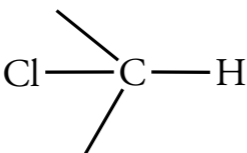
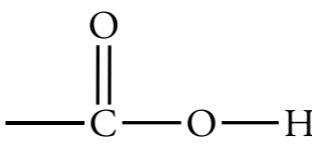


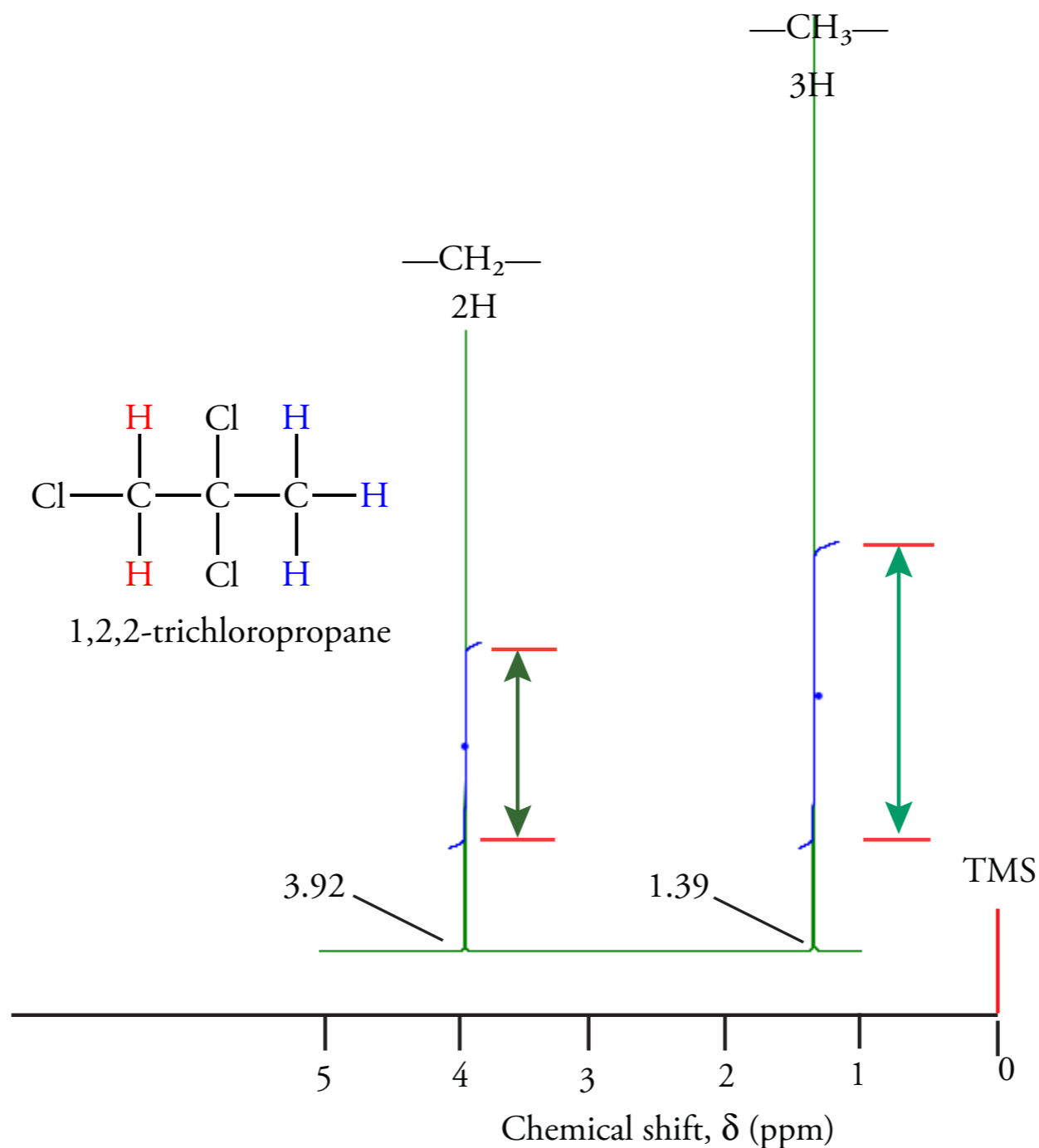
Table 14.1
Chemical Shifts of Hydrogen Atoms

<i>Partial Structural Formula</i>	<i>Chemical Shift (ppm)</i>	<i>Partial Structural Formula</i>	<i>Chemical Shift (ppm)</i>
$-\text{CH}_3$	0.7-1.3		2.5-4.0
$-\text{CH}_2-$	1.2-1.4		2.0-4.0
	1.4-1.7		3.3-4.0
	1.6-1.9		5.0-6.5
	2.1-2.4		6.5-8.0
$-\text{C}\equiv\text{C}-\text{H}$	2.5-2.7		9.7-10.0
	3.0-3.4		10.5-13.0

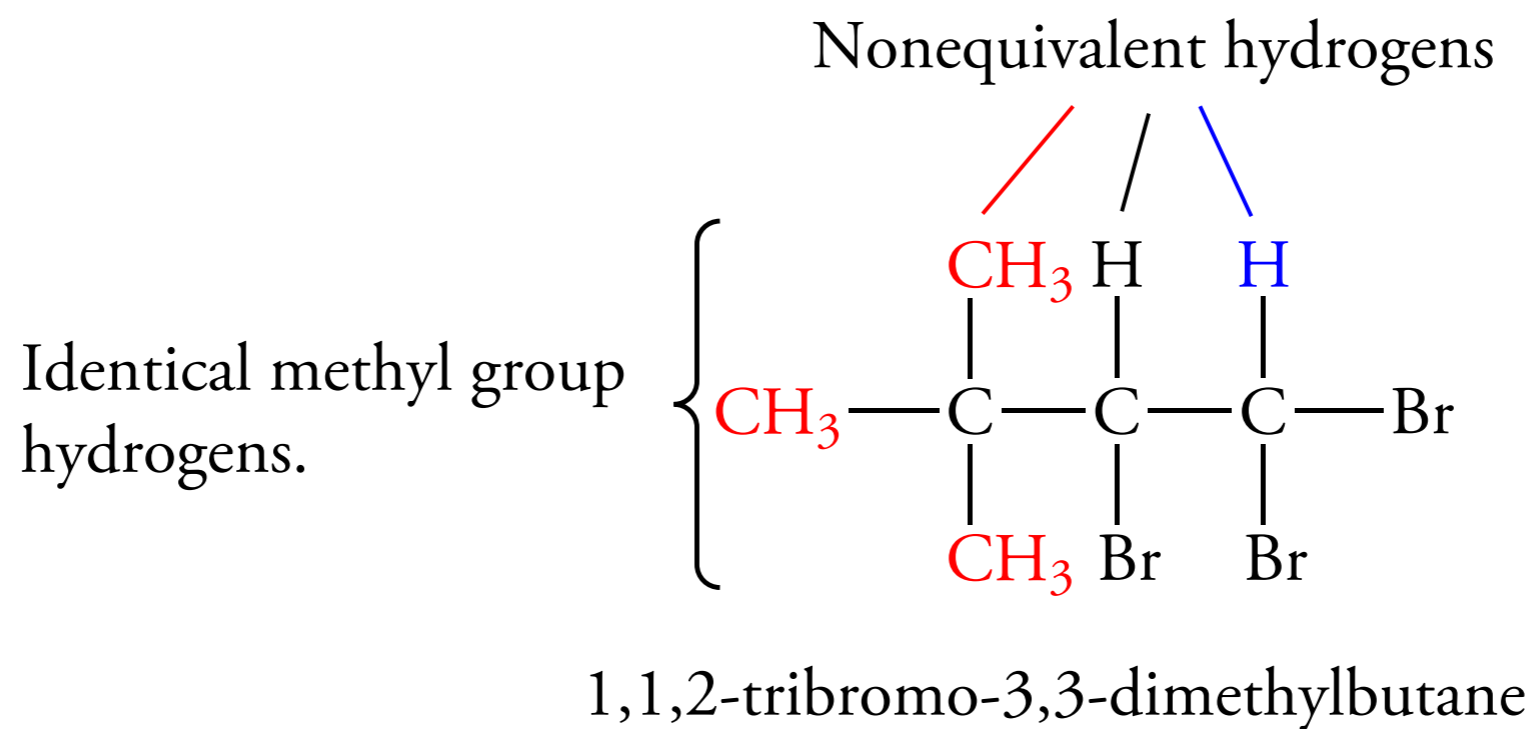
14.6 RELATIVE PEAK AREAS AND PROTON COUNTING

Figure 14.8 Integrated Intensities of an NMR Spectrum

The area of each resonance is proportional to the number of hydrogen atoms. The vertical distances of the "stair steps" shown is a measure those areas. The ratio of peak heights, represented by the green arrows, 3:2, corresponds to the three hydrogen atoms bonded to C-3 and the two hydrogens bonded to C-1 in 1,2,2-trichloropropane.



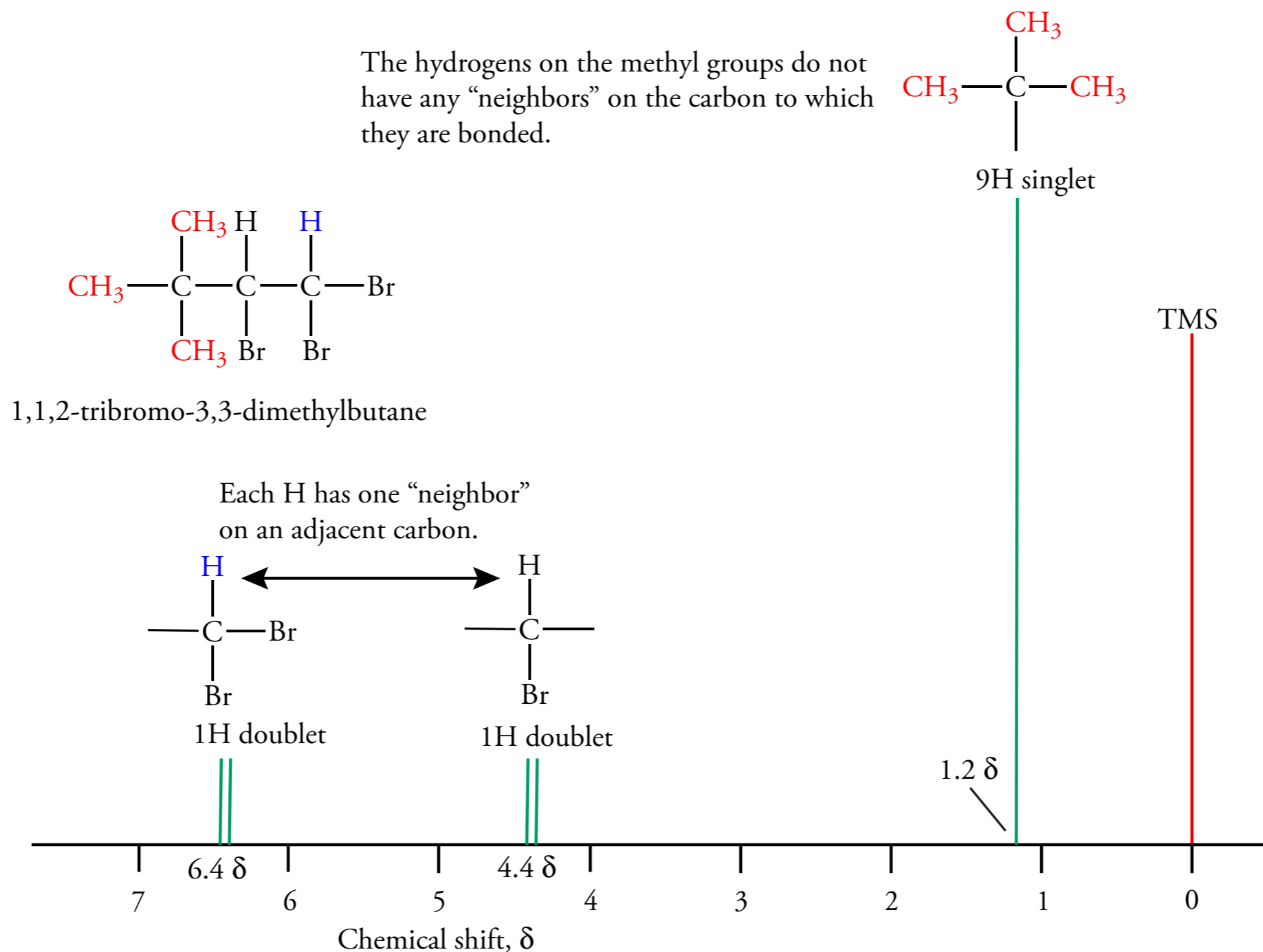
14.7 SPIN-SPIN SPLITTING, I



14.7 SPIN-SPIN SPLITTING, II

Figure 14.9 NMR Spectrum of 1,1,2-Tribromo-3,3-dimethylbutane

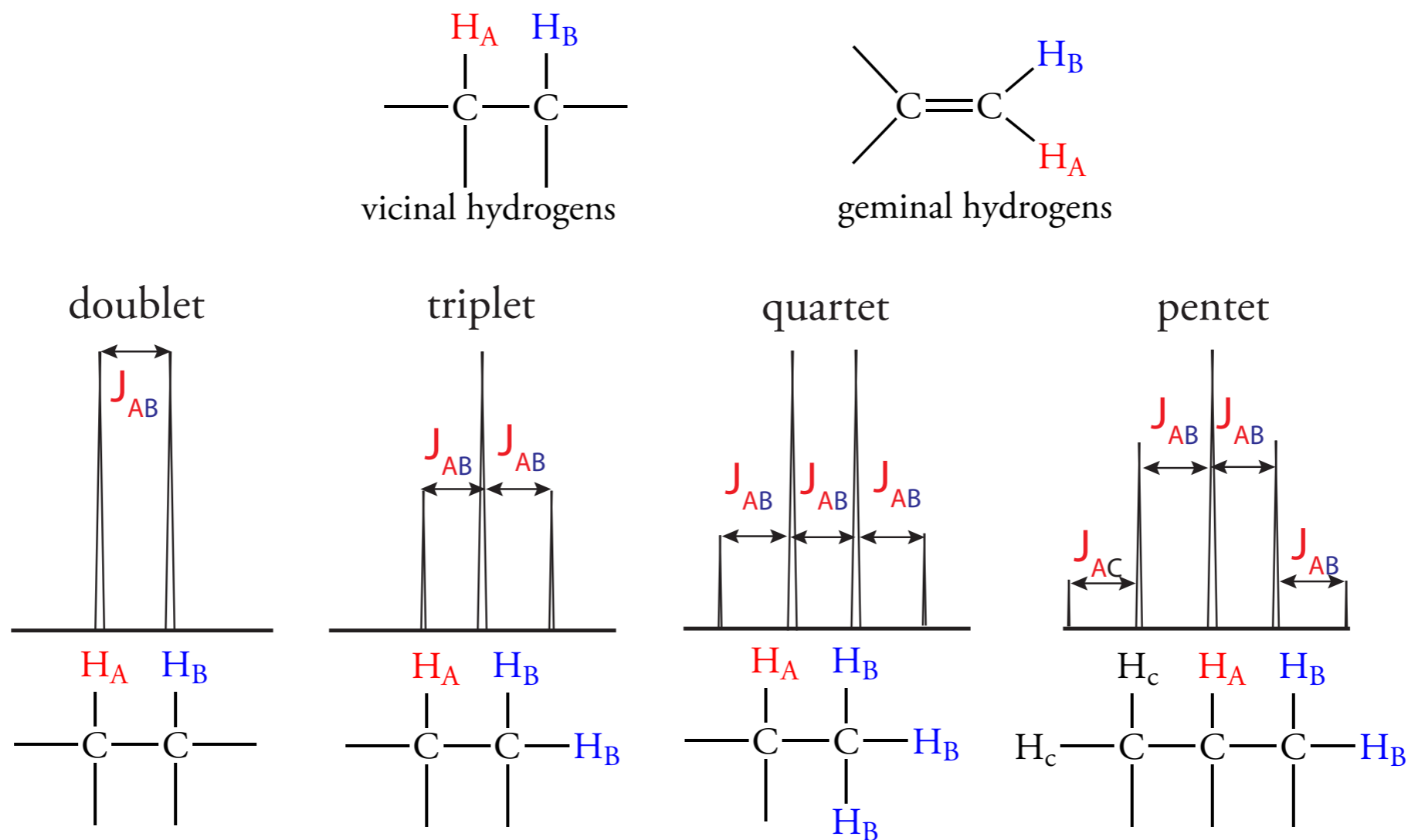
The areas under the peaks are in the ratio of 9:1:1, which corresponds to the ratio of hydrogens at C-3, C-2, and C-1. The hydrogens atom at C-1 and C-2 each have one "neighbor." The nine hydrogens in the methyl groups attached to C-3 do not have any neighboring hydrogen atoms on the quaternary carbon.



14.7 SPIN-SPIN SPLITTING, III

Figure 14.10 NMR Splitting Pattern for Vicinal Hydrogens

The resonance of one hydrogen atom (H_A) with neighboring hydrogens is shown. The number of equivalent neighboring hydrogen atoms is responsible for the multiplicity of the resonance. The number of peaks for H_A equals the number (n) of vicinal hydrogens + 1.



14.7 SPIN-SPIN SPLITTING, IV

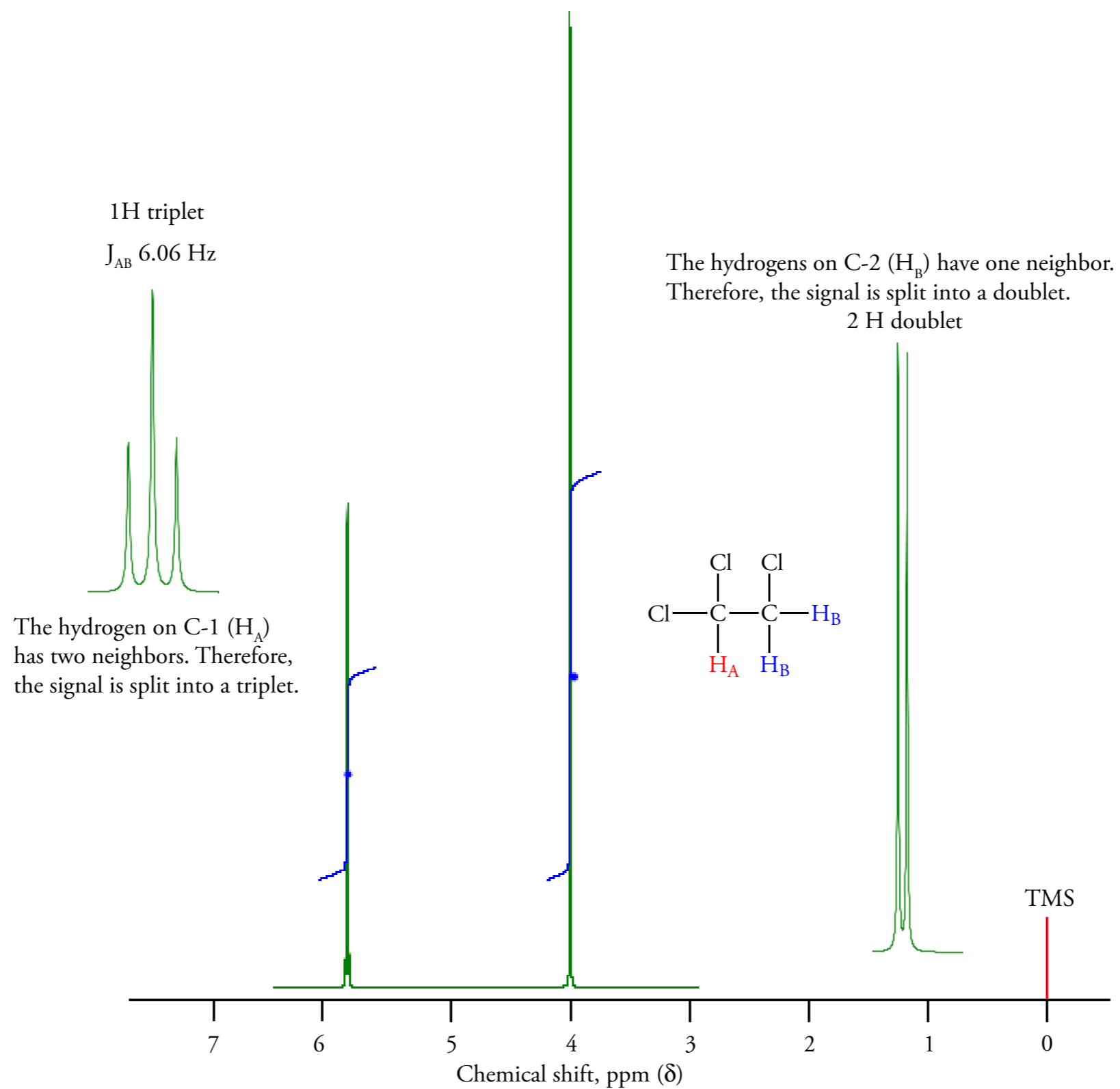
Figure 14.11 Ratios of Peak Heights for NMR Resonances
The ratios of peak heights in NMR multiplets are given by Pascal's Triangle.

Singlet				1				
Doublet			1	1				
Triplet			1	2	1			
Quartet		1	3	3	1			
Pentet		1	4	6	4	1		
Sextet	1	5	10	10	5	1		
Septet	1	6	15	20	15	6	1	

Pascal's Triangle

14.7 SPIN-SPIN SPLITTING, V

Characteristics of Multiplets

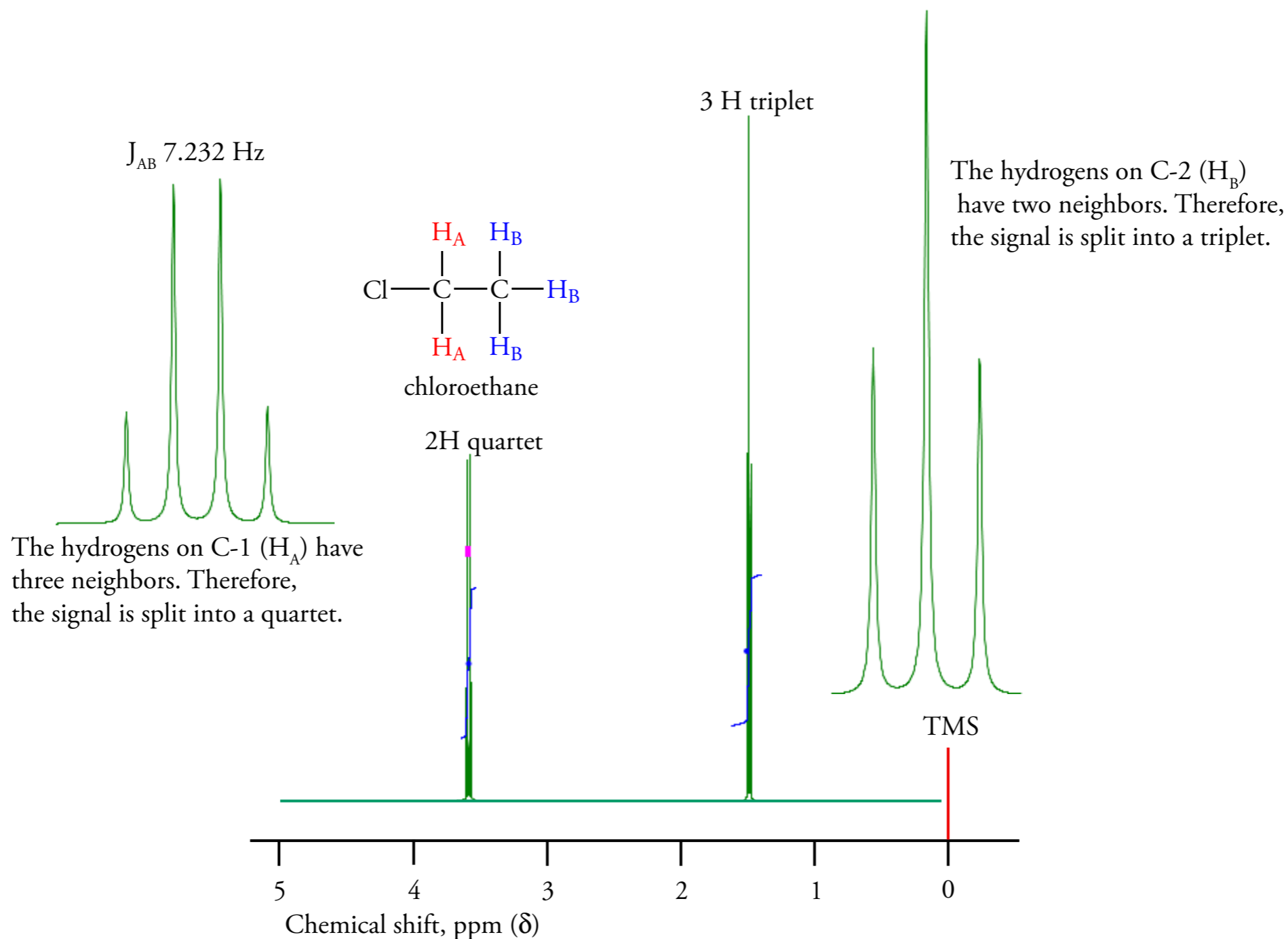


14.7 SPIN-SPIN SPLITTING, VI

Characteristics of Multiplets, II

Figure 14.13 NMR Spectrum of Chloroethane

The spectrum of chloroethane consists of two multiplets: a triplet centered at 1.488 δ for H_B that integrates to three hydrogens, and a quartet centered at 3.505 δ for H_A that integrates to two hydrogens. The insert shows the quartet for H_A . The chlorine atom at C-1 deshields the two H_A protons, so the H_A protons have a larger chemical shift than the H_B protons at C-2.

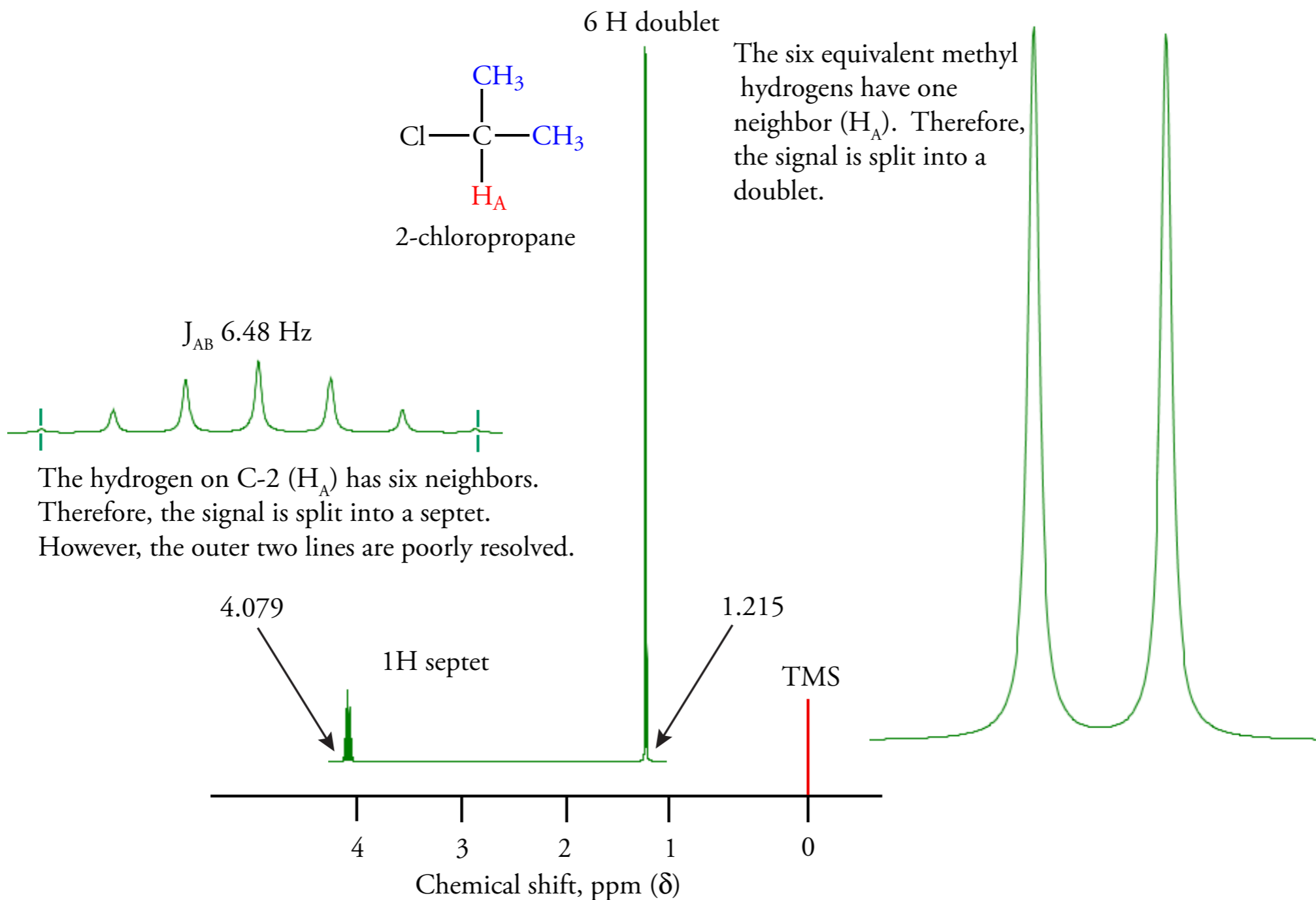


14.7 SPIN-SPIN SPLITTING, VII

Characteristics of Multiplets, III

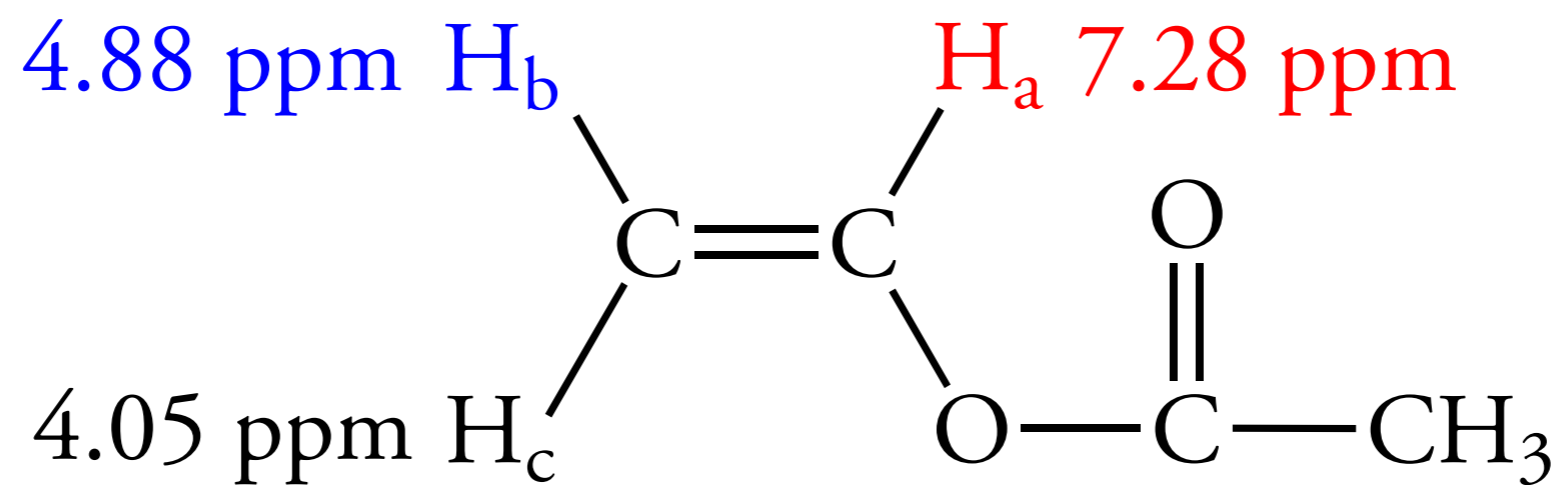
Figure 14.14 NMR Spectrum of 2-Chloropropane

The spectrum consists of two multiplets: a doublet at 1.444 δ that integrates to two hydrogens, and a septet centered at 3.735 δ that integrates to one hydrogen. The insert shows the septet. However, the outer peaks are not highly resolved, so the resonance appears to be a pentet rather than a septet. The chlorine atom at C-2 deshields H_A relative to the methyl hydrogens, so the H_A resonance has a larger chemical shift.



14.7 SPIN-SPIN SPLITTING, VIII

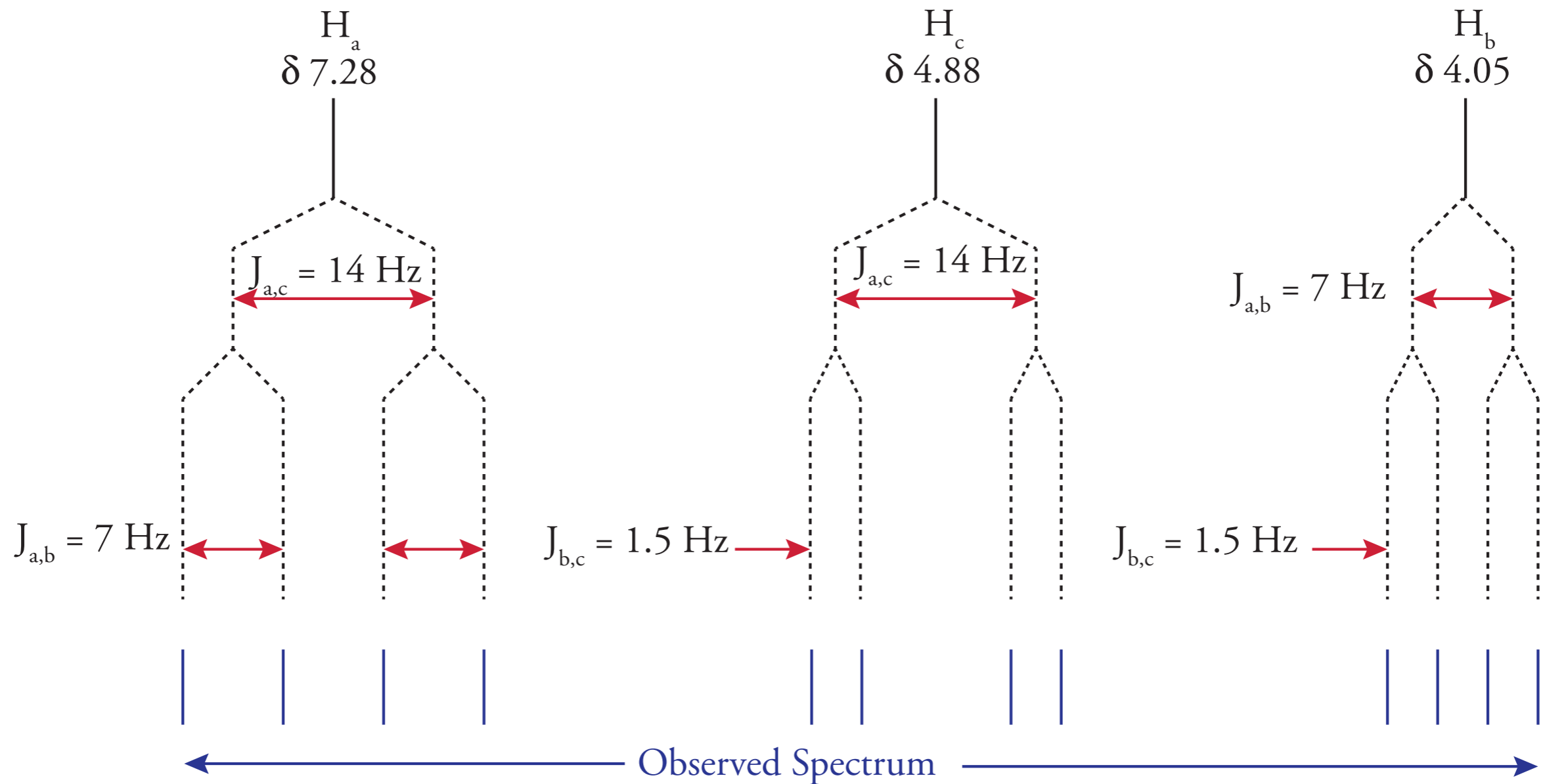
Multiple Splitting: The Vinyl Group



14.7 SPIN-SPIN SPLITTING, IX

Multiple Splitting: The Vinyl Group, II

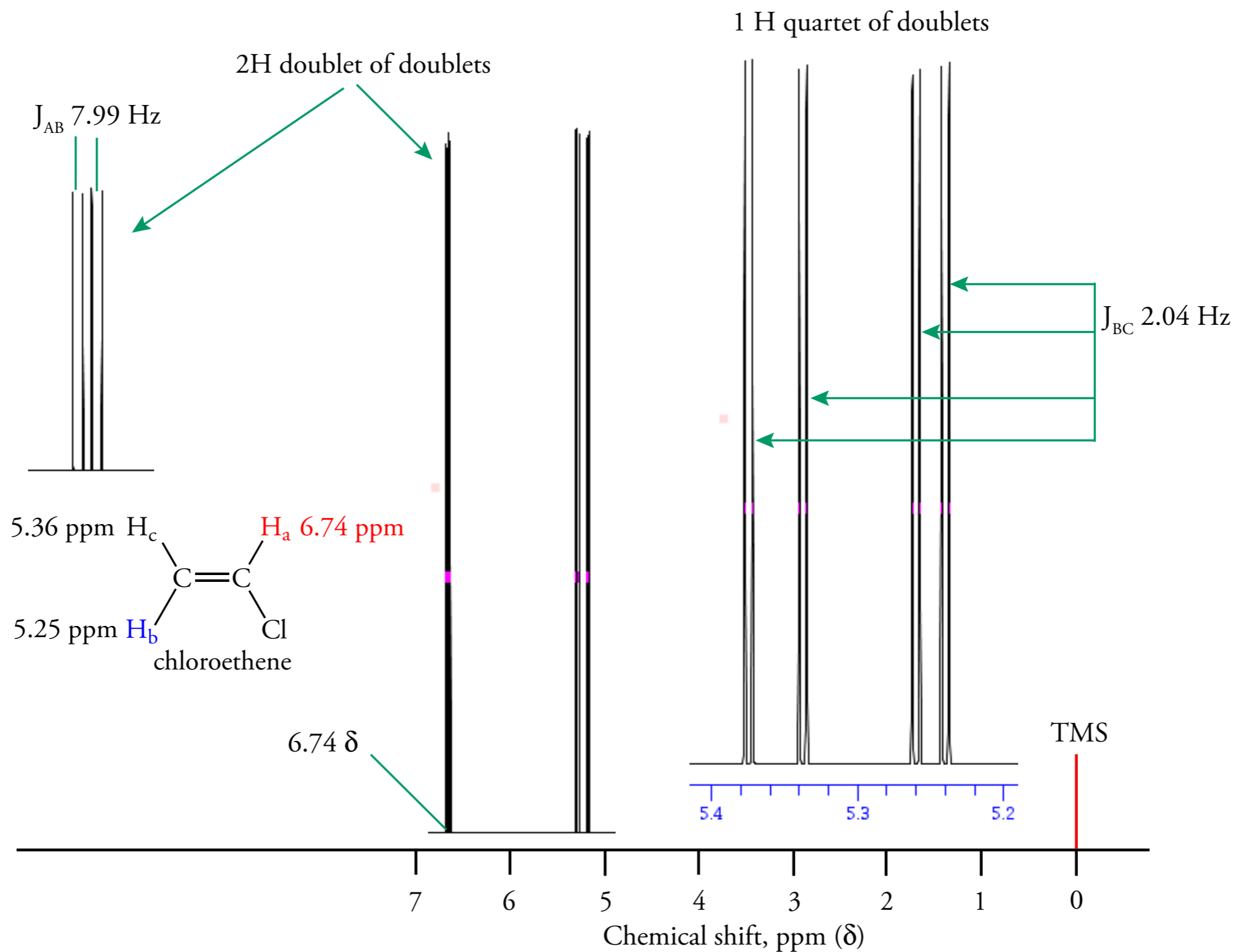
Figure 14.15 Splitting Pattern of a Vinyl Group



14.7 SPIN-SPIN SPLITTING, X

Multiple Splitting: The Vinyl Group, III

Figure 14.16 NMR Spectrum of Chloroethene



14.8 EFFECT OF STRUCTURE ON COUPLING CONSTANTS

Effect of Dihedral Angle on Coupling Constants

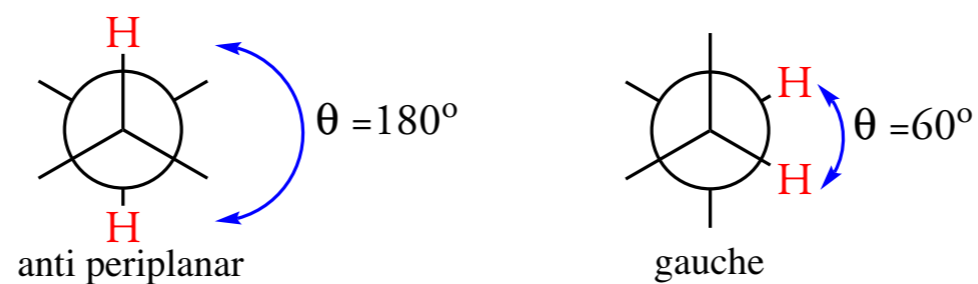
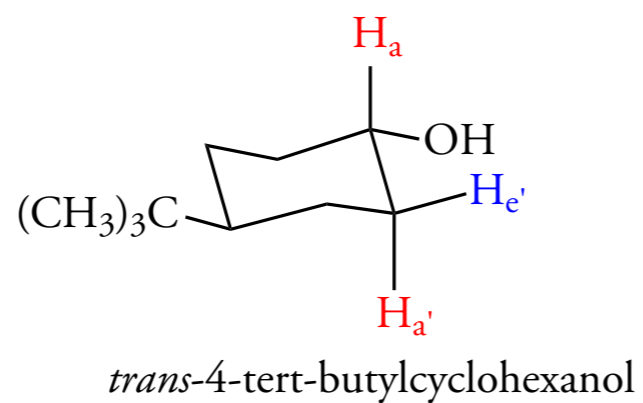


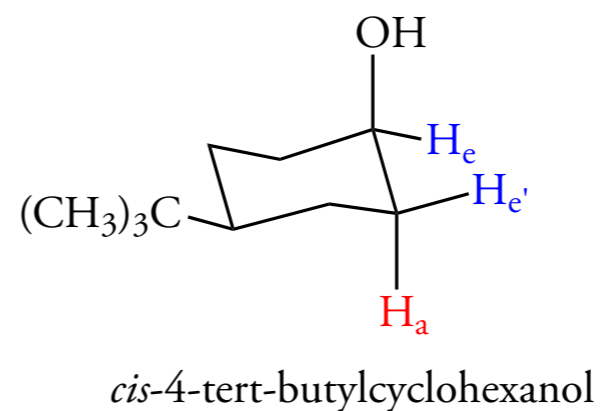
Table 14.2
Relation of Coupling Constants to
Dihedral Angle

Dihedral Angle, θ	Coupling Constant, J (Hz)
0°	8.5
60°	3-4
90°	0
180°	9-14



$$J_{aa'} = 13.1 \text{ Hz}$$

$$J_{ae'} = 4.3 \text{ Hz}$$



$$J_{ee'} = 2.7 \text{ Hz}$$

$$J_{ae'} = 3.0 \text{ Hz}$$

14.8 EFFECT OF STRUCTURE ON COUPLING CONSTANTS, II

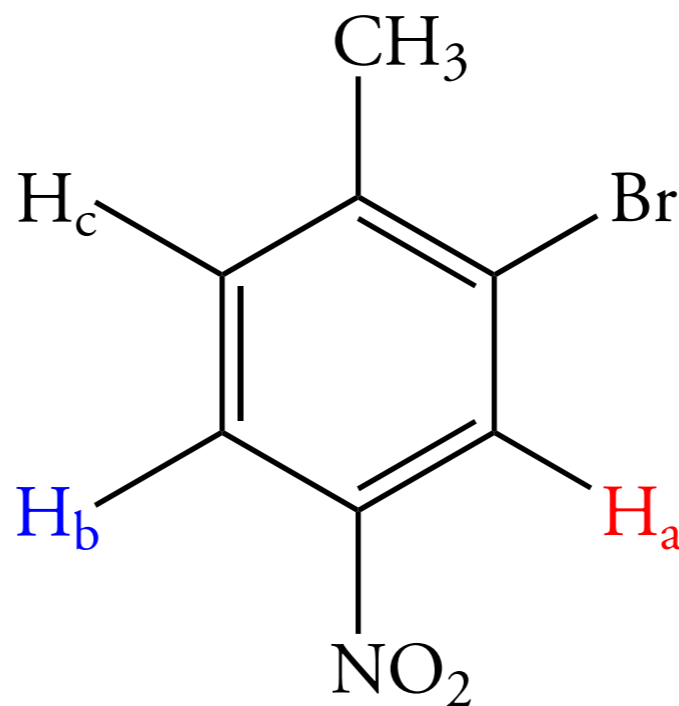
Long-Range Coupling in Aromatic Compounds

$\delta = 7.00$ 1H doublet

$J_{cb} = 8$ Hz

$\delta = 7.60$ 1H doublet of doublets

$J_{cb} = 8$ Hz, $J_{ba} = 2$ Hz



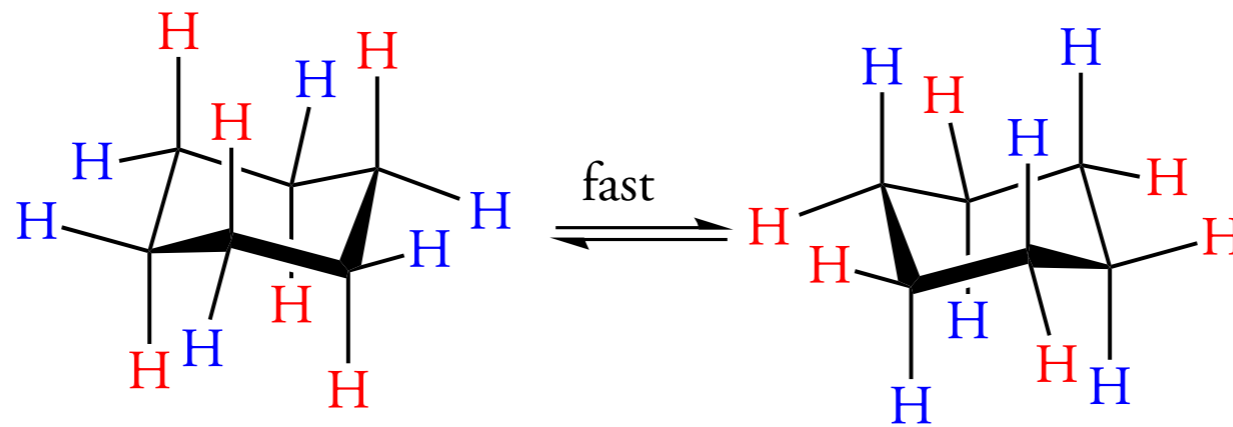
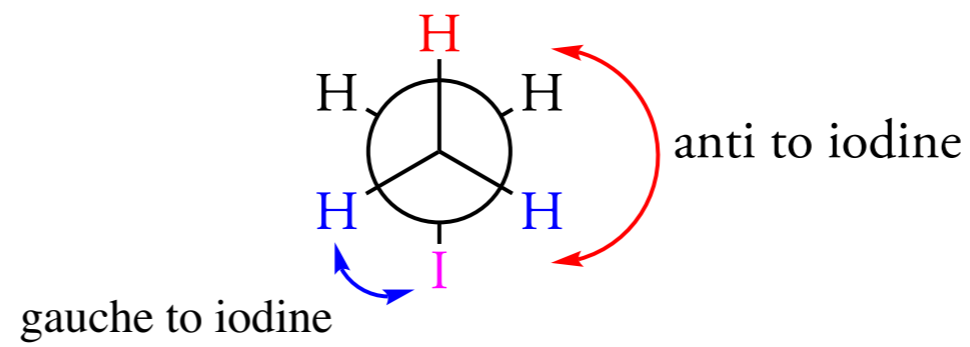
$\delta = 7.85$ 1H doublet

$J_{ba} = 2$ Hz

2-bromo-4-nitrotoluene

14.9 EFFECT OF DYNAMIC PROCESSES, I

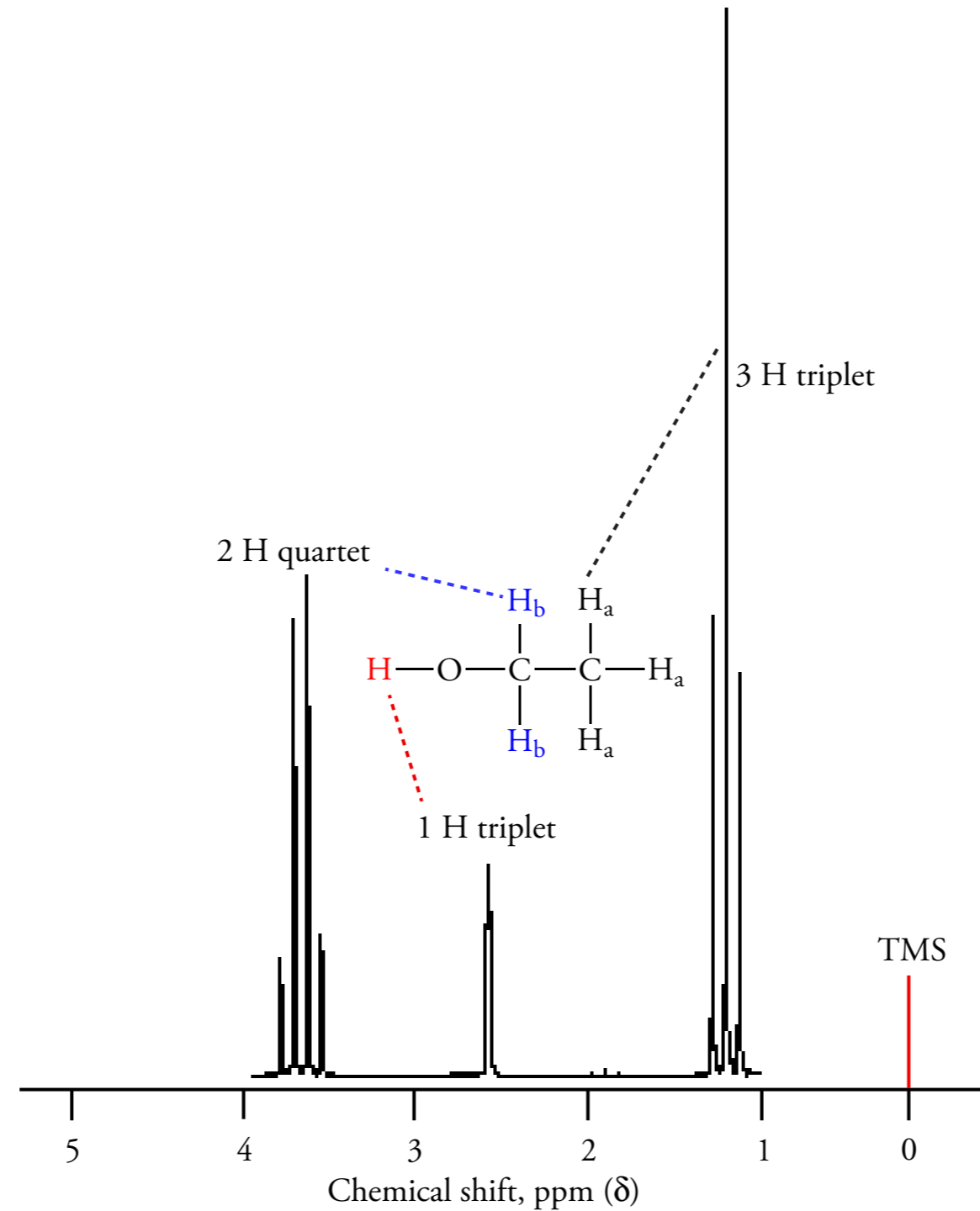
Conformational Changes



14.9 EFFECT OF DYNAMIC PROCESSES, II

Hydroxyl Hydrogens

Figure 14.17 NMR Spectrum of Ethanol



14.10 CARBON-13 NMR SPECTROSCOPY

Characteristics of ^{13}C Spectra

Figure 14.18 ^{13}C NMR Spectrum of 2-Butanol

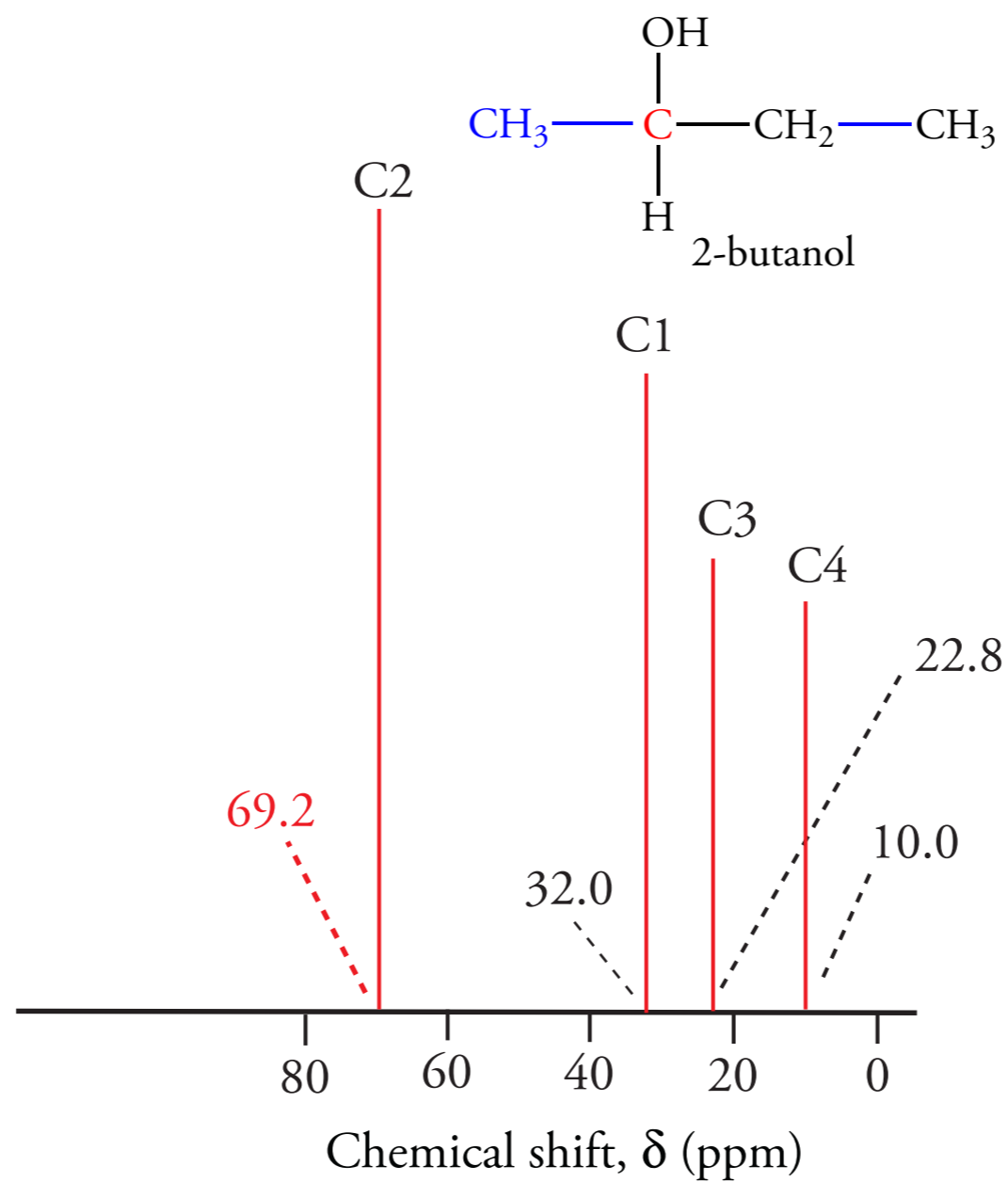


Table 14.3
Chemical Shifts of ^{13}C Atoms

^{13}C Carbon Atom	Chemical Shift (ppm)	^{13}C Carbon Atom	Chemical Shift (ppm)
RCH_2CH_3	12–15	$\text{RCH}=\text{CH}_2$	115–120
R_2CHCH_3	16–25	$\text{RCH}=\text{CH}_2$	125–140
R_3CH	12–35	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR} \end{array}$	170–175
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{CH}_3 \end{array}$	30	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	190–200
RCH_2Cl	40–45	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$	205–220
RCH_2Br	27–35	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$	180
RCH_2OH	50–65	benzene	128

Figure 14.19 ^{13}C NMR Spectrum of 2-Methyl-1-propanol

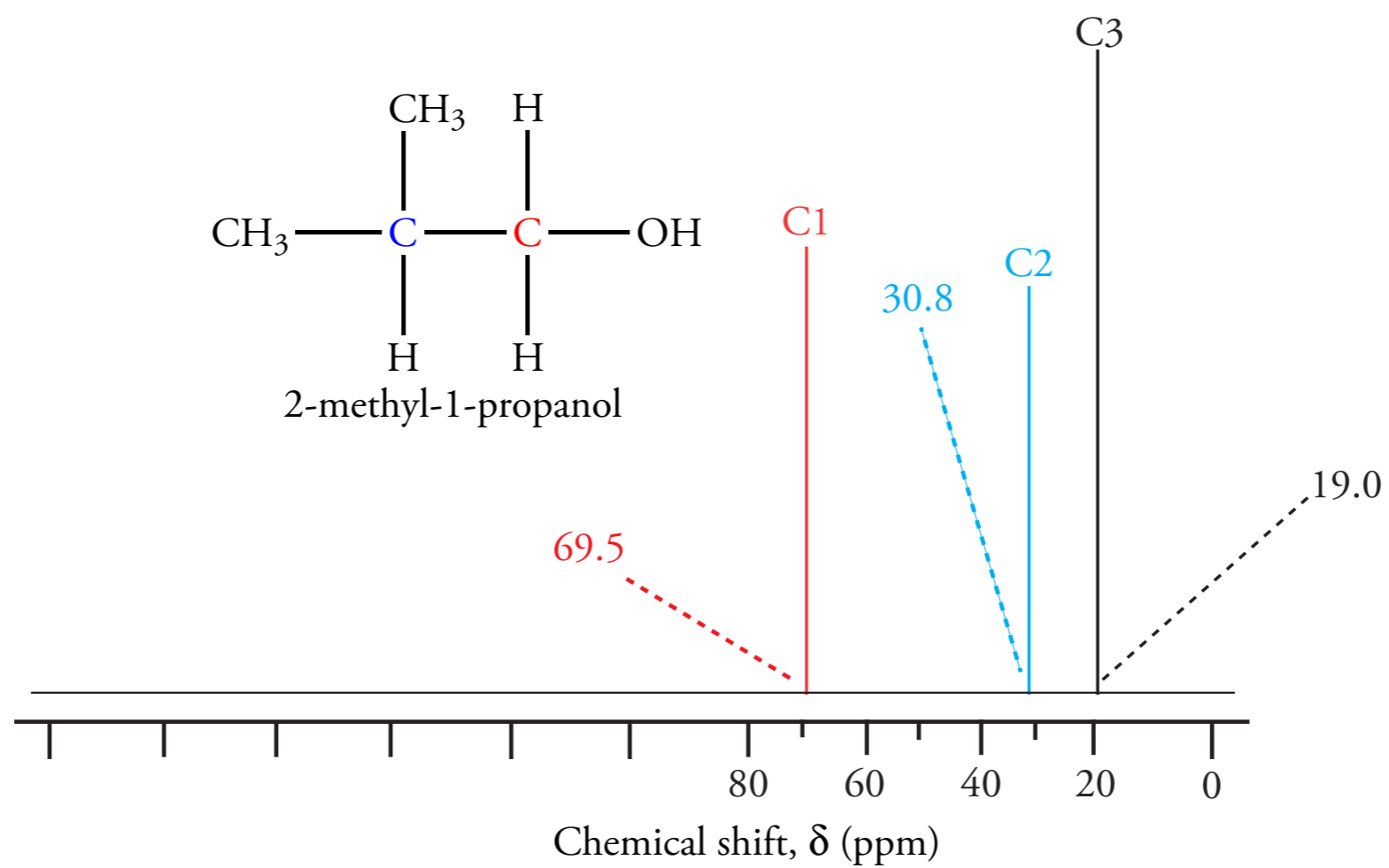


Figure 14.21 ^{13}C NMR Spectrum of 1-cis-3-cis-5-trimethylcyclohexane

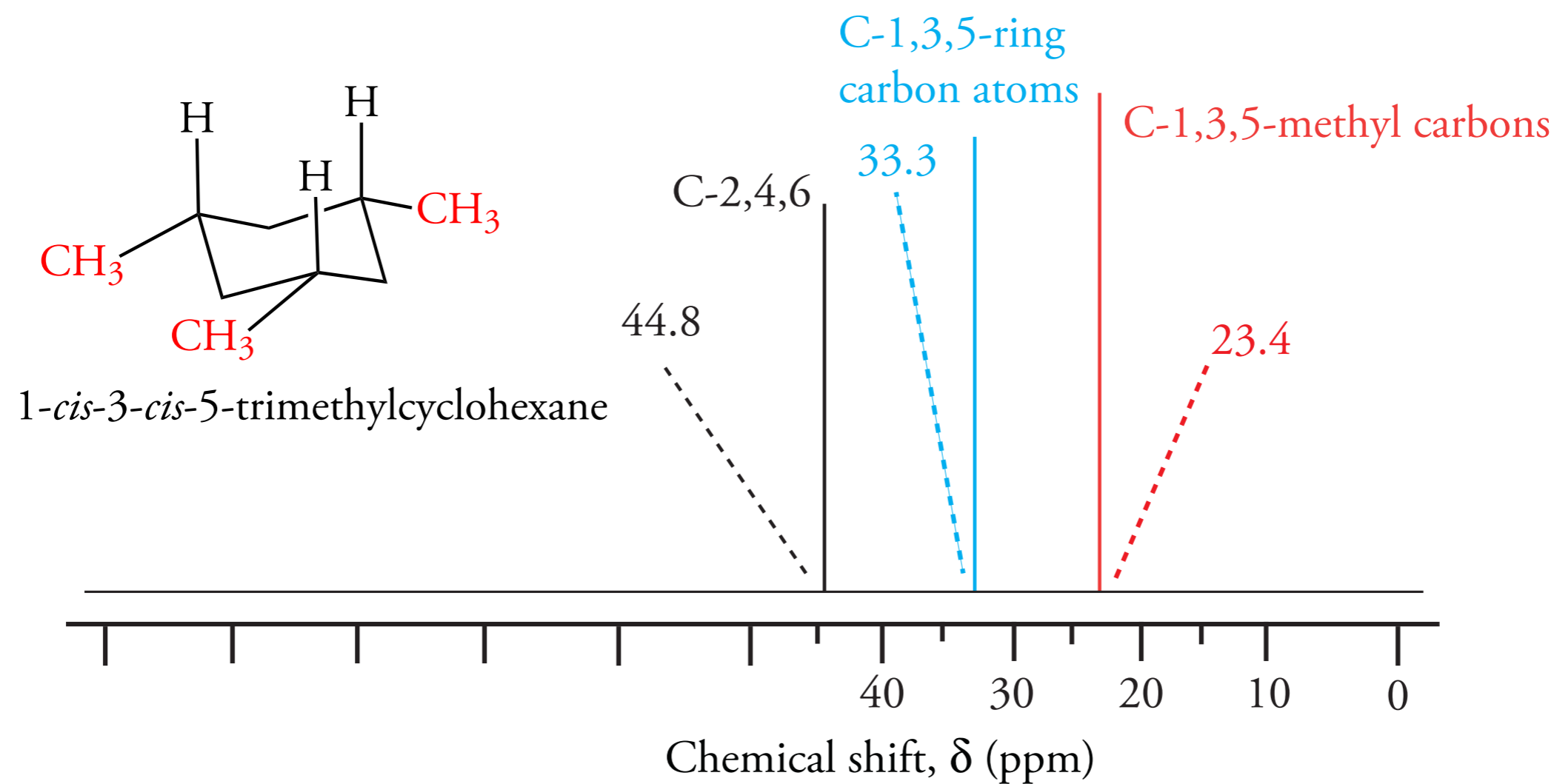
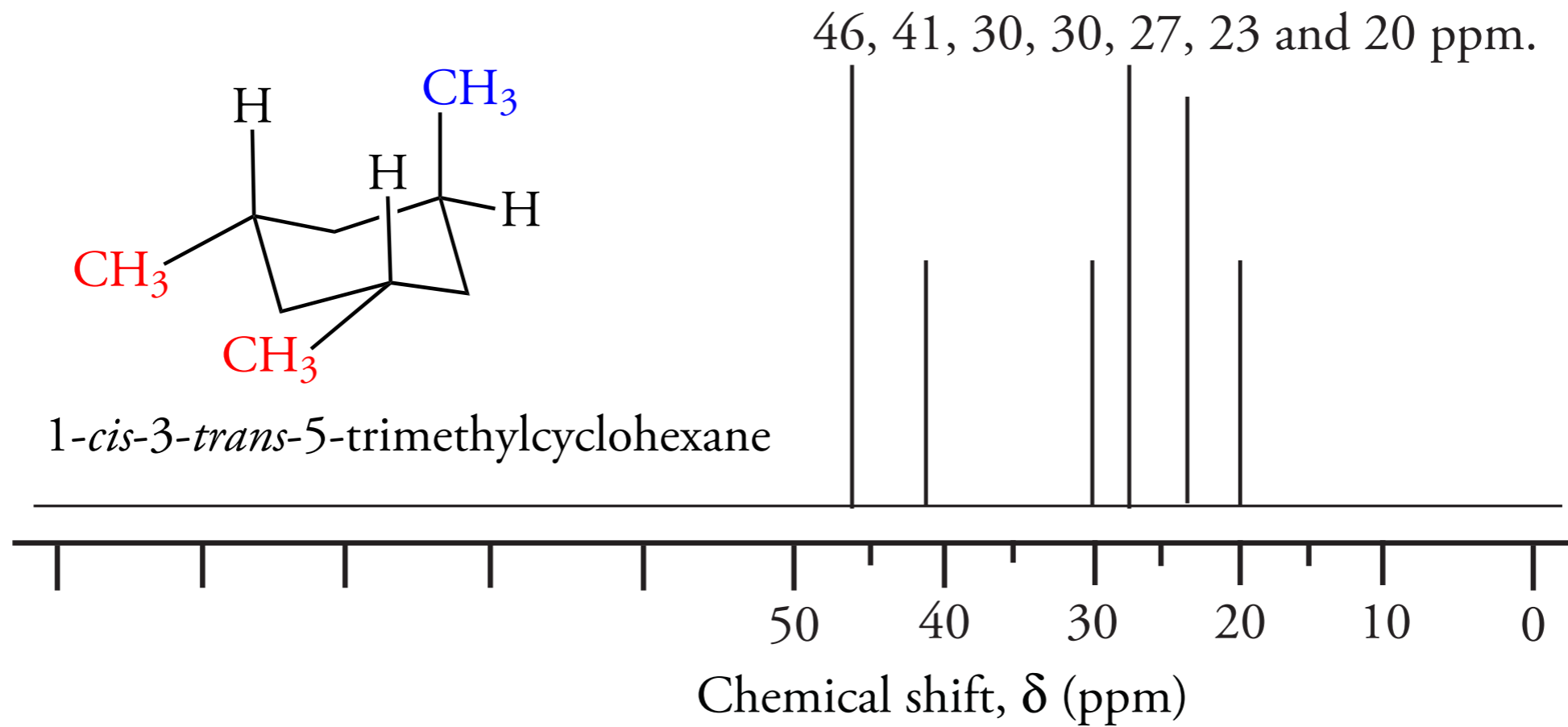


Figure 14.22 ^{13}C NMR Spectrum of 1-cis-3-trans-5-trimethylcyclohexane



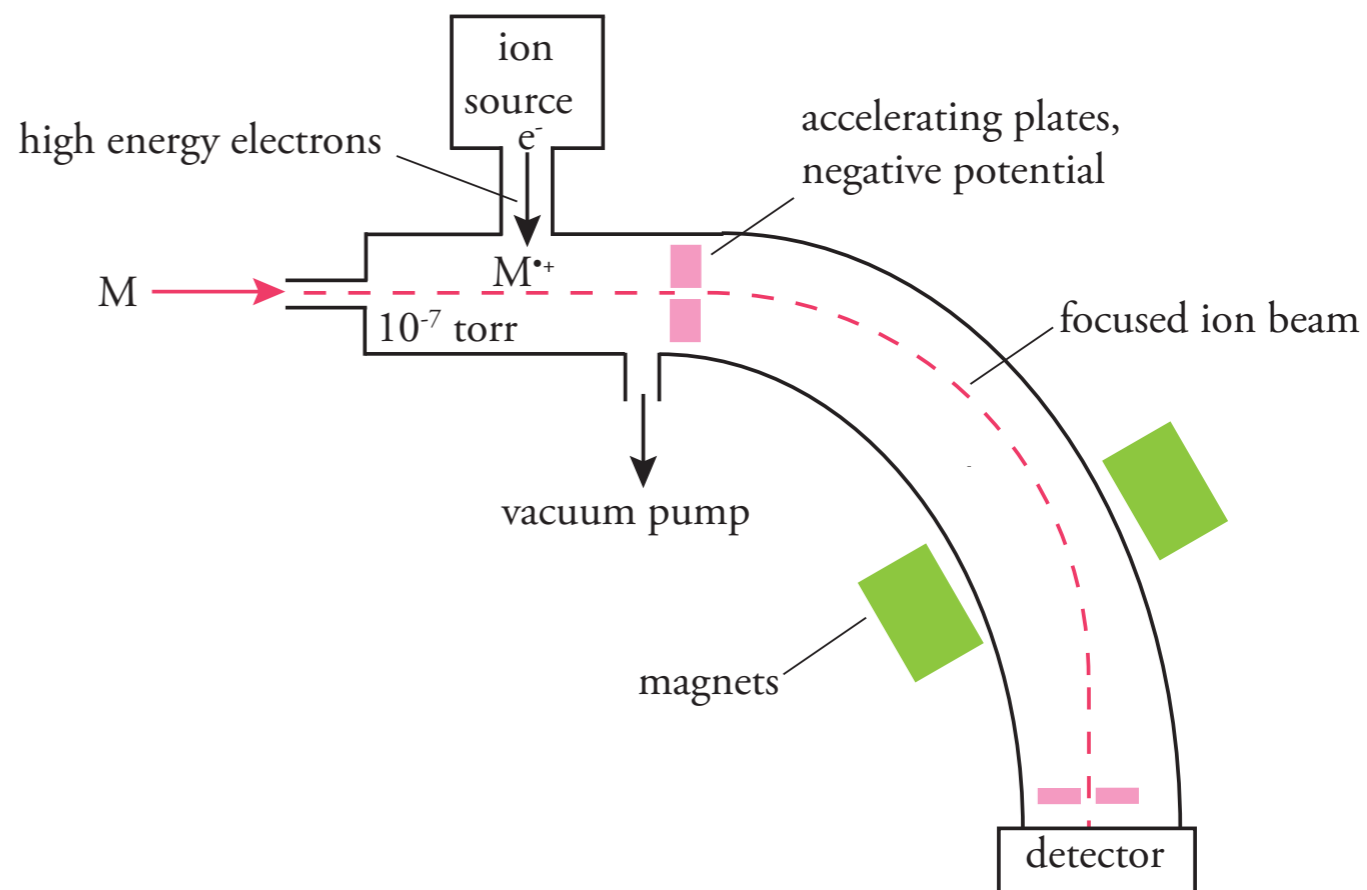
14.11 INTRODUCTION TO MASS SPECTROMETRY

The Mass Spectrometer

Figure 14.23 Block Diagram of a Mass Spectrometer

A mass spectrometer has three major components.

1. The Ion Source. In an **electron impact mass spectrometer**, a sample of the compound is bombarded by electrons. The collision of a high energy electron with a sample molecule converts it into a **radical cation**.
2. The Mass Analyzer. The mass analyzer separates the fragments produced during and after the initial ionization process.
3. The Detector. The fragments that have been sorted are displayed on a computer monitor or printed as a **mass spectrum** that gives the mass of each fragment, and the relative abundance of the fragments.



14.11 INTRODUCTION TO MASS SPECTROMETRY

The Production of Ions in a Mass Spectrometer



Molecular ion
(parent ion)



Parent ion

Most stable ion
(base peak)

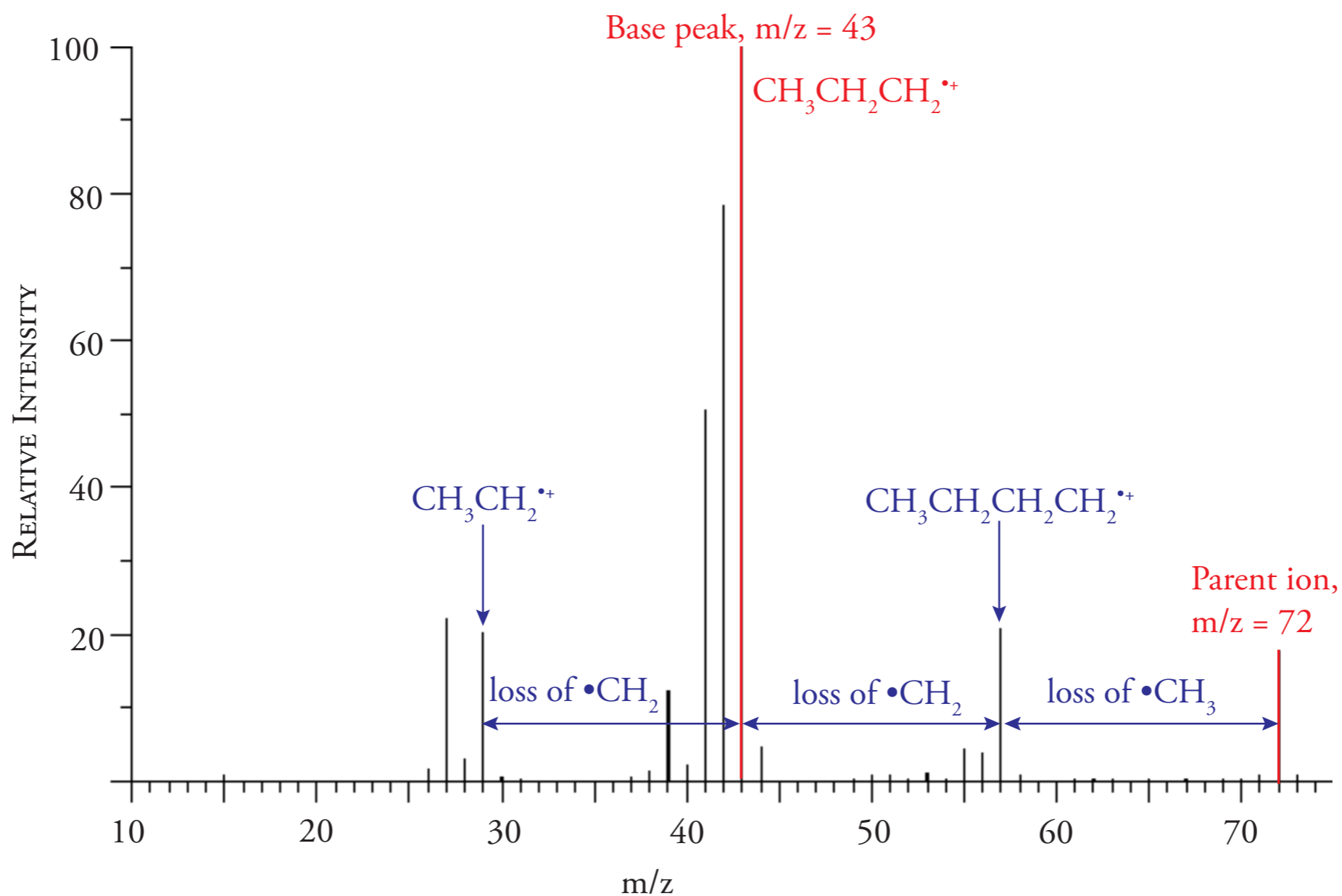
Neutral fragment
(not detected)

14.11 INTRODUCTION TO MASS SPECTROMETRY

Mass Spectrometry of Hydrocarbons

Figure 14.24 Mass Spectrum of n-Pentane

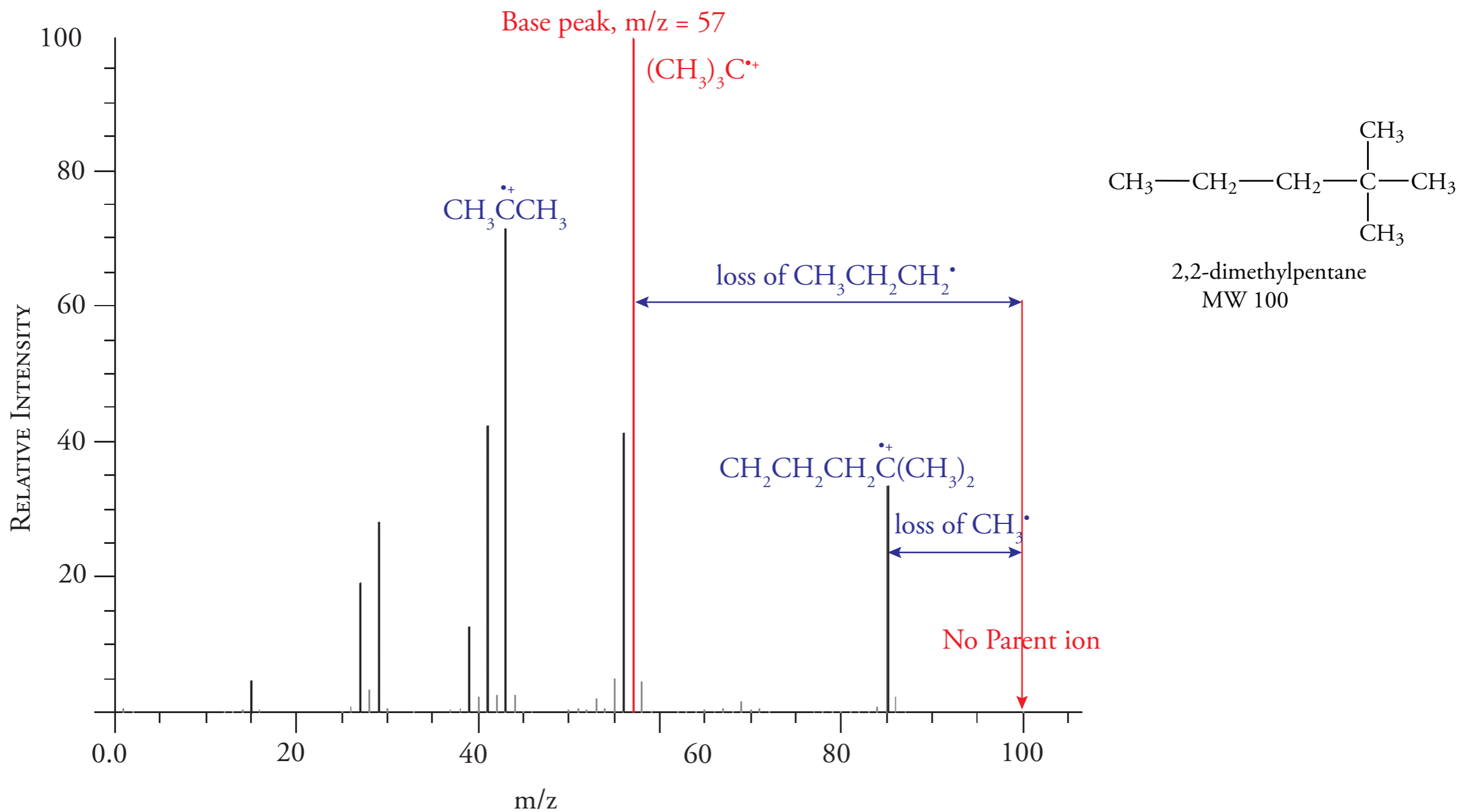
n-Pentane ionizes to give a parent ion whose $m/z = 72$. The parent ion loses a methyl radical to give a peak at $m/z = 57$. This peak loses a neutral $\text{CH}_2\cdot$ group to give the base peak at $m/z = 43$. The general pattern for n-alkyl groups is loss of a $\text{CH}_3\cdot$ group first, followed by successive loss of $\text{CH}_2\cdot$ groups.



14.11 INTRODUCTION TO MASS SPECTROMETRY

Mass Spectrometry of Hydrocarbons

Figure 14.25 Mass Spectrum of 2,2-Dimethylpentane

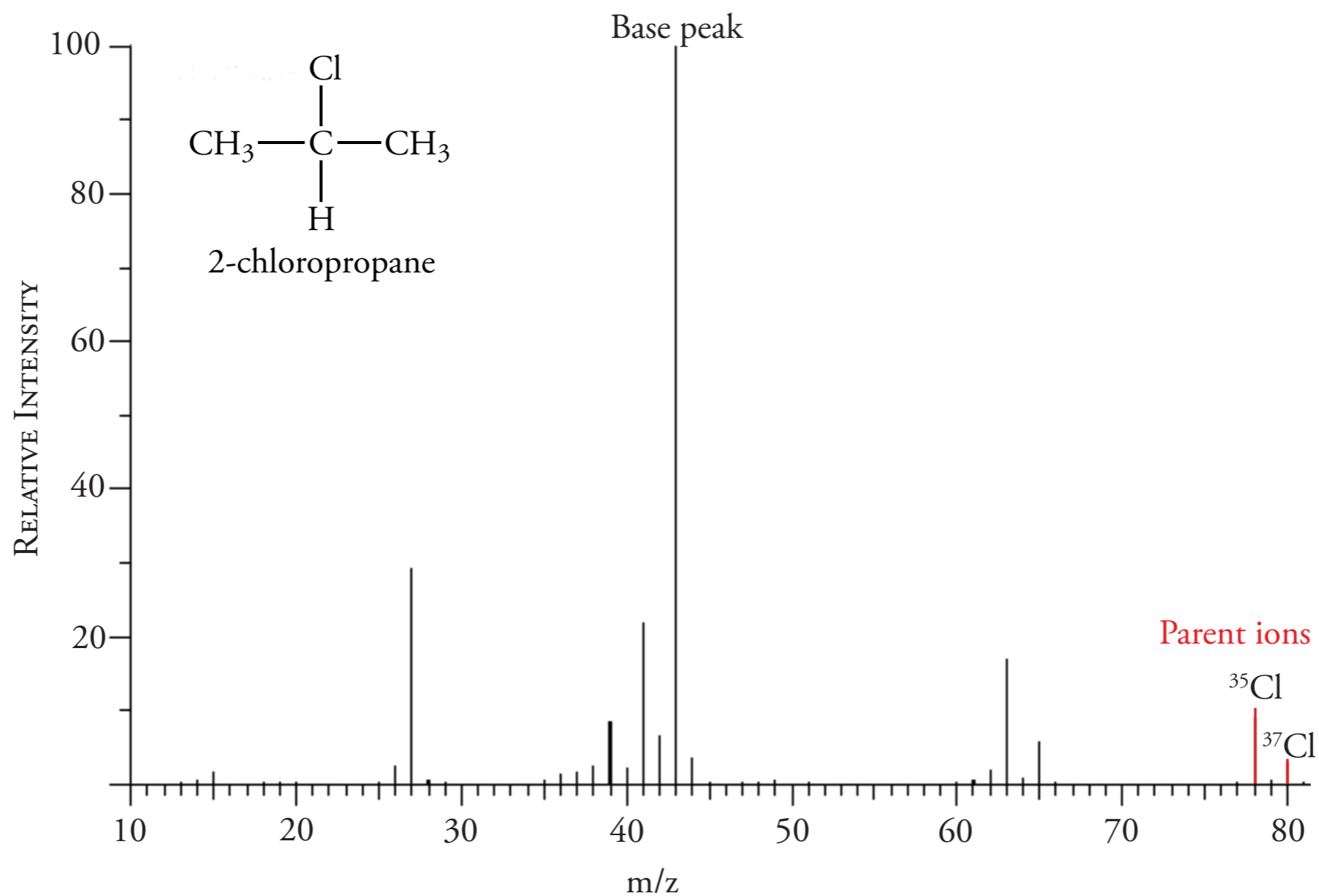


14.11 INTRODUCTION TO MASS SPECTROMETRY

Identifying Chlorine and Bromine-Containing Compounds in a Mass Spectrum

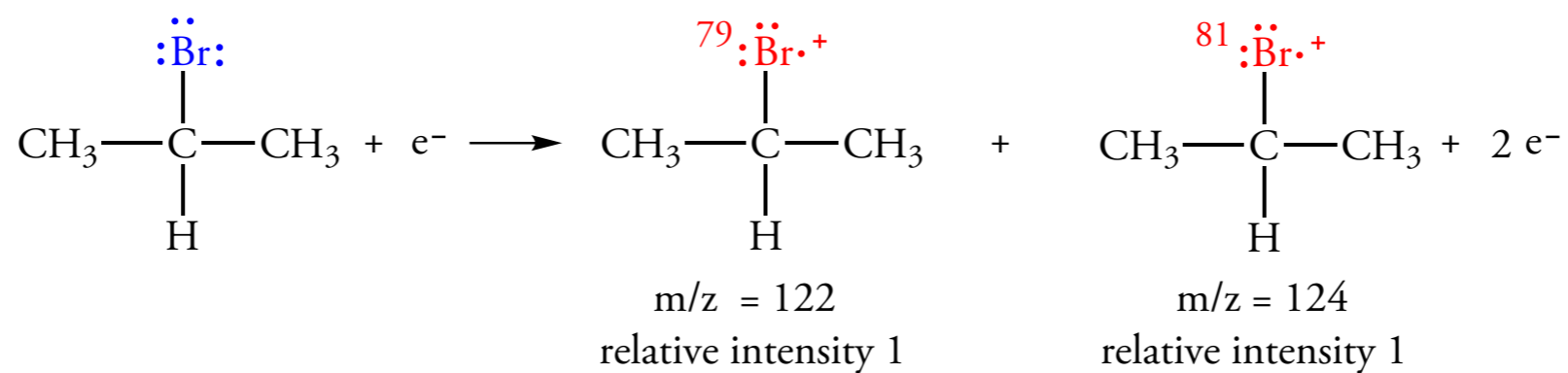
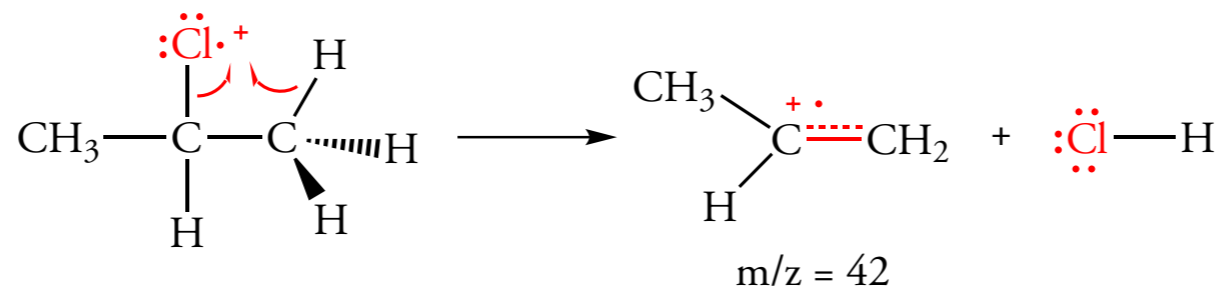
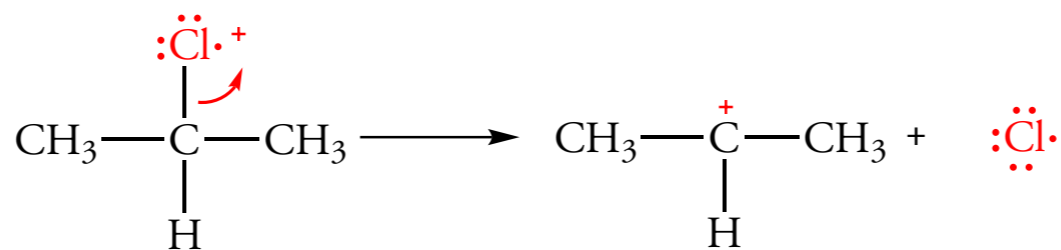
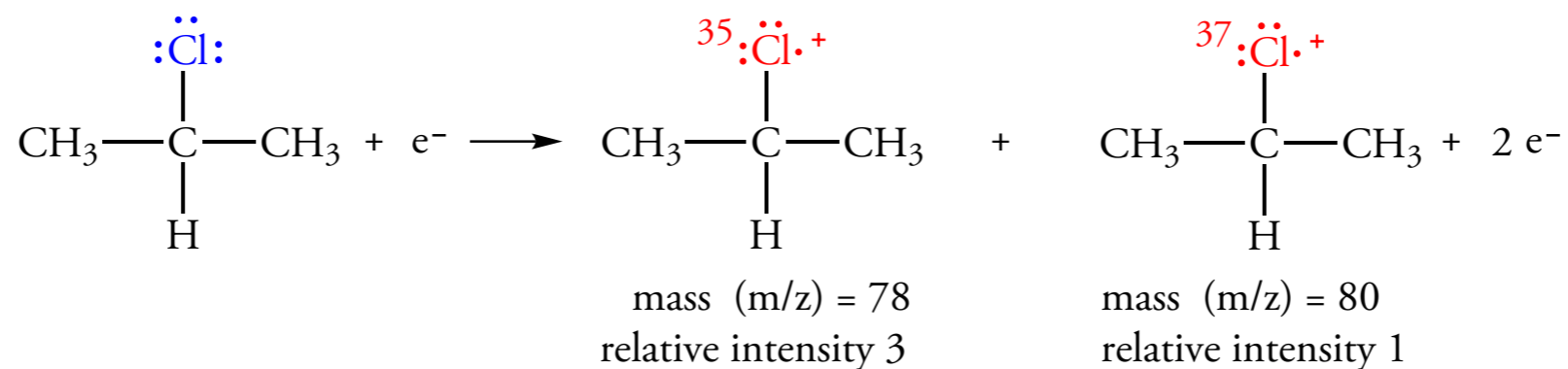
Figure 14.26 Mass Spectrum of 2-Chloropropane

2-Chloropropane ionizes to give two parent ions that differ by two mass units. The ratio of the peak intensities is 3:1, showing one parent ion contains ^{35}Cl and the other one contains ^{37}Cl . Fragmentation of either parent peak by loss of ^{35}Cl or ^{37}Cl gives the base peak of mass 43. It is an isopropyl cation, C_3H_7^+ .



14.11 INTRODUCTION TO MASS SPECTROMETRY

Identifying Chlorine and Bromine-Containing Compounds in a Mass Spectrum



14.11 INTRODUCTION TO MASS SPECTROMETRY
Identifying of Nitrogen-Containing Compounds in a Mass Spectrum

Table 14.4
Molecular Mass as a Function of the
Presence or Absence of Nitrogen

<i>Number of Nitrogen Atoms in Ion</i>	<i>MW</i>
One or Any Odd Number	Odd
Two or Any Even Number	Even
None	Even

14.11 INTRODUCTION TO MASS SPECTROMETRY

Identifying of Nitrogen-Containing Compounds in a Mass Spectrum

Figure 14.28 Mass Spectrum of N-Methyl-diethylamine

This compound has one nitrogen atom, and therefore the parent ion has an odd molecular mass of 87. Loss of a methyl group as a radical gives the base peak, whose mass is 72.

