Chapter 5
Organic Spectrometry

from

Organic Chemistry

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Chapter Outline of the Book

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1. Organic Molecules and Chemical Bonding
2. Alkanes and Cycloalkanes
3. Haloalkanes, Alcohols, Ethers, and Amines
4. Stereochemistry
5. Organic Spectrometry

II. Reactions, Mechanisms, Multiple Bonds

6. Organic Reactions *(*Not yet Posted*)
7. Reactions of Haloalkanes, Alcohols, and Amines. Nucleophilic Substitution
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13. Carbonyl Compounds. Ketones, Aldehydes, and Carboxylic Acids
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V. Bioorganic Compounds

20. Carbohydrates
21. Lipids
22. Peptides, Proteins, and α–Amino Acids
23. Nucleic Acids

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**Note: Chapters marked with an (*) are not yet posted.*

5: Organic Spectrometry

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Preview

This chapter describes four instrumental methods that organic chemists routinely use to determine the structures of organic compounds. They are **Mass Spectrometry (MS)**, **Nuclear Magnetic Resonance Spectrometry (NMR)**, **Infrared Spectrometry (IR)**, and **Ultraviolet-Visible Spectrometry (UV-Vis)**.

These four methods use electronic instruments called **spectrometers** to generate **spectra** that contain the structural information about molecules. We will describe these spectrometers only in the most general terms. This chapter is primarily designed to introduce you to the utility and limitations of these four instrumental methods, and to illustrate how organic chemists use their spectral data to determine structures of organic molecules.

Analytical chemistry is the branch of chemistry that deals with the development and use of instrumental techniques such as these to determine structures of molecules, and it is the subject of other courses in the undergraduate chemistry curriculum. However, these four instrumental methods are of such great importance to organic chemists that we give this early introduction to show the kinds of structural information they provide.

5.1 Spectrometry in Organic Chemistry

Organic chemists must determine structures of the organic compounds that they use in chemical reactions, that form in these chemical reactions, and that they isolate from living organisms. They accomplish this using several instrumental techniques collectively described as **organic spectrometry**. *Organic spectrometry* makes use of electronic instruments called **spectrometers**

that provide energy to molecules and then measure how the molecules respond to that applied energy.

In order to fully understand *spectrometry*, we should learn about the design and construction of *spectrometers*. However we can develop a practical understanding of how these different types of *organic spectrometry* provide information about molecular structure without a detailed knowledge of *spectrometers*. We illustrate this in the following sections using as examples the classes of organic molecules introduced in Chapters 2 and 3.

***Types of Spectrometry* (5.1A)**

The four most important types of spectrometry that organic chemists routinely use are:

Mass Spectrometry (MS)
Nuclear Magnetic Resonance Spectrometry (NMR)
Infrared Spectrometry (IR)
Ultraviolet-Visible Spectrometry (UV-Vis)

Each of these methods provides unique information about organic molecular structure because each monitors the response of an organic molecule to a different type of energy input. In *MS*, a molecule is bombarded with a beam of *high energy electrons*, in *NMR* it is irradiated with *radio waves*, in *IR* it is subjected to *heat energy*, while in *UV-Vis* spectrometry the molecule is placed in a beam of *ultraviolet or visible light*.

We discuss *mass spectrometry* (*MS*) first since it is fundamentally different from the other three types of spectrometry. Of the other three methods, we consider *NMR* in much greater detail than either *IR* or *UV-Vis* because of its overwhelming importance to organic chemists as an aid in structure determination. Our discussions of *IR* and *UV-Vis* in this chapter are brief because these methods are best suited to analyzing types of molecules that we have not yet introduced. We discuss them in more detail in later chapters.

> ***Spectrometry versus Spectroscopy***. You may see other books refer to the techniques in this chapter as **organic spectroscopy** rather than *organic spectrometry*. This is not technically correct, but it is done so often that it has become accepted practice. *Chemical spectroscopy* actually involves the study of the interaction of **electromagnetic energy**, described later in this chapter, with molecules. In contrast, *chemical spectrometry* is the practical use of instruments, including those based on *spectroscopy*, to probe molecular structure.

5.2 Mass Spectrometry (MS)

Mass spectrometry provides information about the *molecular mass* of an organic compound, and about how the organic compound *fragments* when it is has a large amount of excess energy.

***Formation of Molecular and Fragment Ions* (5.2A)**

A **mass spectrometer** bombards a small sample of an organic compound with a beam of high energy electrons (e^-) leading to the formation of positively charged **molecular ions** that subsequently decompose into **fragment ions**.

Organic Compound + e^- → Molecular Ions → Fragment Ions

The *mass spectrometer* detects the mass of the *molecular ions* as well as the masses of the *fragment ions*.

Molecular Ion. A *molecular ion* (**$M^{+\cdot}$**) forms when a high energy electron (**e^-**) collides with a molecule (**M**) in the sample causing it to lose one of its own electrons.

$$e^- + M \rightarrow M^{+\cdot} + 2e^-$$

The two electrons ($2e^-$) that are products of this "reaction" include the electron from the electron beam that hit the molecule as well as the electron ejected from the molecule. The *molecular ion* ($M^{+\cdot}$) is positive because it has lost an electron and therefore has one less electron than it has protons.

Besides its positive (+) charge, we specifically show using the symbol (·) that the *molecular ion* has one *unpaired* (*unshared*) electron. Molecules have even numbers of electrons that exist as *pairs* in chemical bonds, as *pairs* of unshared electrons, or as *pairs* in inner shell atomic orbitals (see Chapter 1). As a result, the loss of one electron (fig?) not only causes *M* to become (+), but also to have an odd number of electrons so that one is unpaired (·).

Fragment Ions. *Molecular ions* ($M^{+\cdot}$) possess a large amount of excess energy when they form. This causes many of them to decompose into smaller fragments that are positively charged *cations* and uncharged (neutral) species called **radicals**. We illustrate *molecular ion formation* and its subsequent *fragmentation* in a mass spectrometer using a generic molecule R_1-R_2 in which the chemical bond between R_1 and R_2 breaks during fragmentation.

$$e^- + \underset{(M)}{R_1\text{-}R_2} \rightarrow \underset{(M)^{+\cdot}}{(R_1\text{-}R_2)^{+\cdot}} + 2e^-$$

$$\underset{(M)^{+\cdot}}{(R_1\text{-}R_2)^{+\cdot}} \rightarrow R_1^+ + R_2^{\cdot} \quad \text{and/or} \quad R_1^{\cdot} + R_2^+$$

Mass spectrometers detect the presence of positively charged ions and measure their masses. As a result, a mass spectrometer provides masses of *molecular ions* ($(R_1\text{-}R_2)^{+\cdot}$) as well as masses of the positive *fragment ions* (R_1^+ and R_2^+) that result from fragmentation of the molecular ion. *Fragment ions* are like pieces of a jig saw puzzle that chemists can often fit back together to give part or all of the detailed molecular structure of the original organic molecule.

Molecular and Fragment Ions from Methane. We use methane (CH_4) to illustrate *molecular ion* formation and *fragmentation* because all of its chemical bonds are identical.

(a) Electron bombardment (formation of the molecular ion)

$$\begin{array}{ccccccc} e^- & + & CH_4 & \rightarrow & CH_4^{+\cdot} & + & 2e^- \\ & & 10p & & 10p & & \\ 1e & & 10e & & 9e & & 2e \end{array}$$

(b) Fragmentation (formation of radical and cation)

$$\begin{array}{ccccc} CH_4^{+\cdot} & \rightarrow & CH_3^{\cdot} & + & H^+ \\ 10p & & 9p & & 1p \\ 9e & & 9e & & \end{array}$$

or

$$\begin{array}{ccccc} CH_4^{+\cdot} & \rightarrow & CH_3^+ & + & H^{\cdot} \\ 10p & & 9p & & 1p \\ 9e & & 8e & & 1e \end{array}$$

Each of these equations is *chemically* and *electrically* balanced. Both the total number of *protons* (*p*) as well as the total number of *electrons* (*e*) are the same on both sides of each equation, and the same is true for the net electrical charge on both sides of each equation. The relative numbers of protons (*p*) and numbers of electrons (*e*) for each species show you why a species has a negative
(-) charge, a positive (+) charge, and/or an unpaired electron (·). The species with single (+) charges have one more *p* than *e*, while those labelled with a (·) have an odd number of *e's*. (By convention, we do not show a (·) on e^- even though it is simply a single electron.)

This detailed analysis is a useful exercise, but you will not need to do it routinely in order to interpret results of *MS* structure determinations of organic compounds. The two important points are that a mass spectrometer (a) generates and detects positively charged ions (*molecular* and *fragment ions*) from the original compound, and (b) determines their masses. We describe this in more detail in the following sections.

***The Mass Spectrometer and Mass Spectrum* (5.2B)**

There are several different designs for mass spectrometers, but all of them form, detect, and measure the mass of positively charged species formed by electron bombardment.

Mass Spectrometer. We show the typical component parts of these mass spectrometers using the simple "block" diagram in Figure 5.4.

Figure 5.4

The mass spectrometer bombards the organic sample in the **sample chamber** (Figure 5.4) with high energy electrons from the **source**, and detects the resulting positive ions in the **analyzer/detector** region of the spectrometer. The *analyzer* and *detector* are usually separate components, but some mass spectrometers, used for routine mass spectral analysis in organic laboratories, analyze and detect positive ions in the *sample chamber* where they form.

Mass Spectrum. The mass spectrometer determines the amount and mass of each positively charged species, stores these data in a computer, and subsequently prints out these results in a table or displays them as a **mass spectrum** (Figure 5.5).

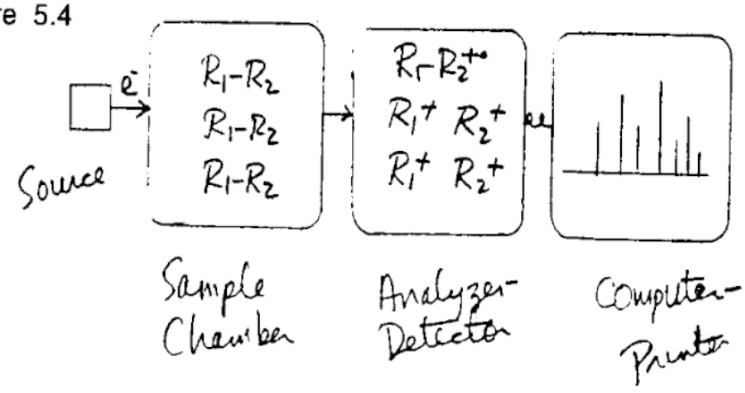
Figure 5.5

A *mass spectrum* consists of a collection of *lines* at different **m/z** values (described below) along the horizontal axis or **base line** of the spectrum. Each line corresponds to a positively charged species detected by the spectrometer.

Mass-to-Charge Ratios (m/z Values). The *m/z values* (**mass-to-charge ratios**) on the horizontal axis of the spectrum correspond to the mass (*m*) (*amu*) of each positively charged species divided by its electrical charge (*z*). Most positive species formed in a mass spectrometer have a charge of +1 (z = +1), so their *m/z values* usually are the same as their masses (*m/z = m/(+1) = m*). The *m/z values* for the taller lines in the *mass spectrum* often appear as labels at the top of those lines.

The height of each *line* (or **signal** or **peak**) corresponds to the relative amount formed of the positive species with a particular *m/z* value. We call the tallest peak in any mass spectrum the

Figure 5.4



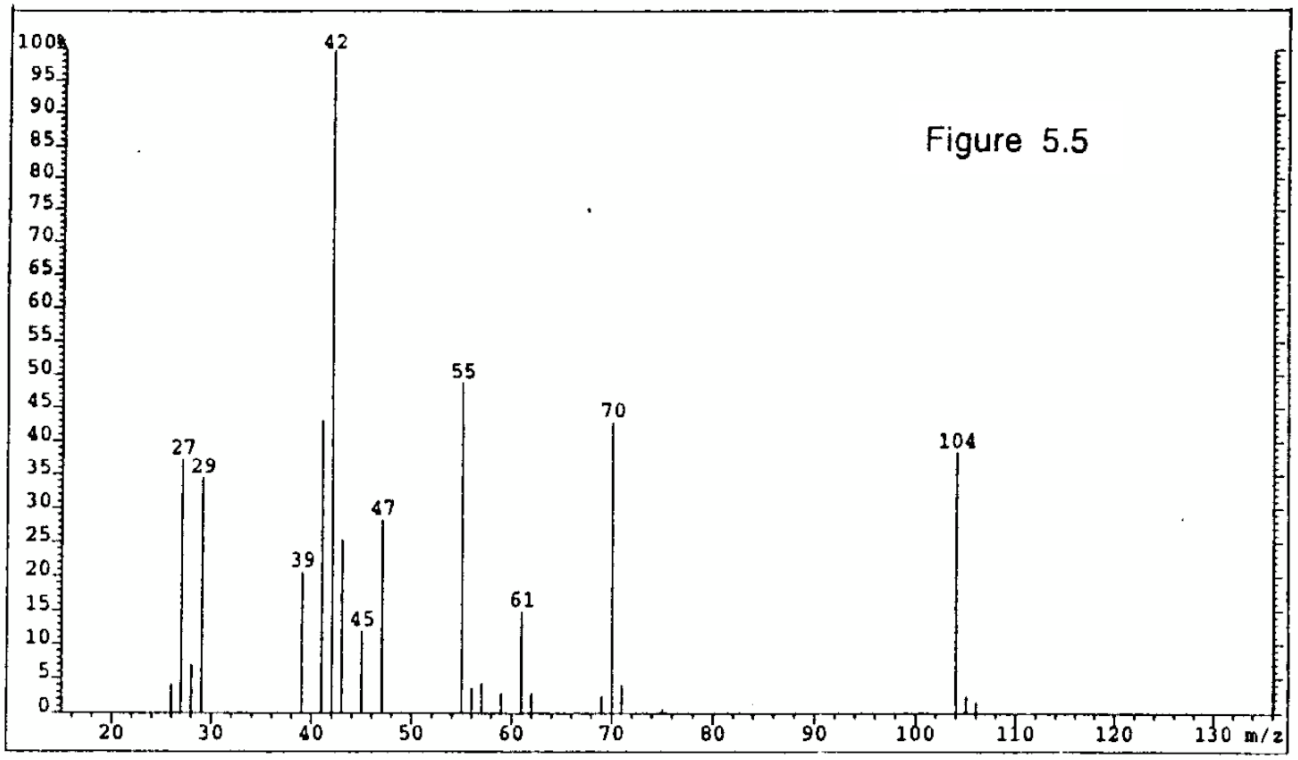


Figure 5.5

base peak and usually assign it a value of 100% on the vertical axis. In the spectrum in Figure 5.5, the *base peak* is the line at m/z = 42. We describe the heights of the other peaks in the spectrum as a percentage of the *base peak*. We will see below that the positive ion giving the base peak is usually not the *molecular ion*, but is a particularly stable *fragment ion* whose structure depends on the particular compound giving the mass spectrum.

Peaks for the Molecular Ion and Fragment Ions. One of the most important lines in a mass spectrum is that of the *molecular ion* since its m/z value gives the *molecular mass* of the original compound. *Fragment ions* are pieces of the original molecule, but a knowledge of their structures is important in deducing the structure of the original molecule since we can often piece them together like pieces of a jigsaw puzzle. Their masses (m/z values) and an understanding of the reactivity of molecules helps us figure out the structures of fragment ions. We illustrate these points and other aspects of the use of MS by considering mass spectral results for several different organic compounds.

***Hexane* (5.2C)**

Our first example is the mass spectrum of the linear alkane *hexane*.

CH_3-CH_2-CH_2-CH_2-CH_2-CH_3
Hexane

Mass Spectrum of Hexane. The hexane mass spectrum (Figure 5.6) has major lines (peaks) at *m/z values* of 15, 27, 29, 39, 41, 42, 43, 56, and 57, and smaller peaks at other *m/z values* including 71 and 86.

Figure 5.6

These m/z values all result from rounding off exact m/z values to **unit resolution** (*e.g.* an m/z value of 35.1 rounded off to *unit resolution* is 35).

What positive ions give these different peaks? Let's first look at the structure of hexane and consider how its *molecular ion* might fragment to form different *fragment ions*, and then see if the masses of these fragments are present in the spectrum.

Molecular Ion and Fragment Ions from Hexane. Bombardment of hexane (C_6H_{14}) with high energy electrons forms the *molecular ion* $(C_6H_{14})^{+\cdot}$ (Figure 5.7).

Figure 5.7

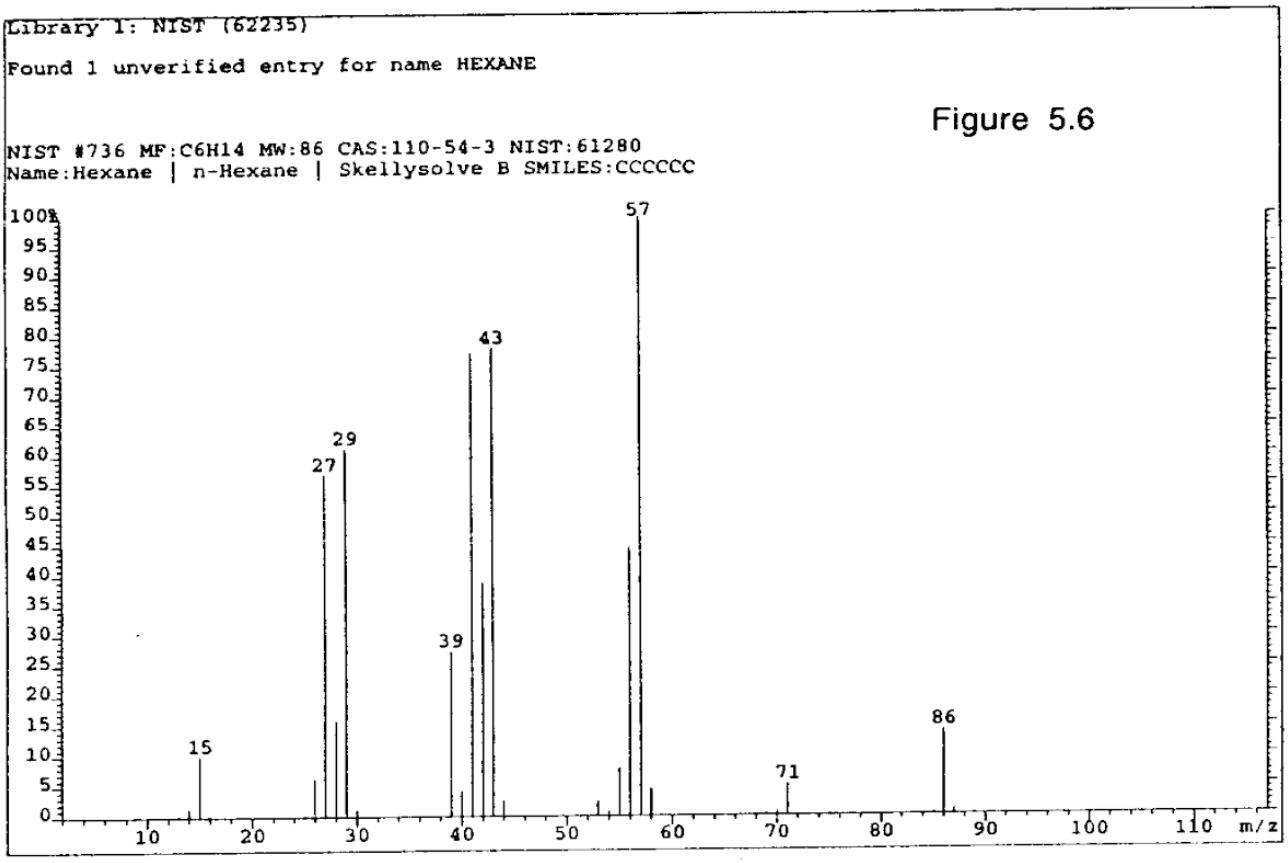


Figure 5.6

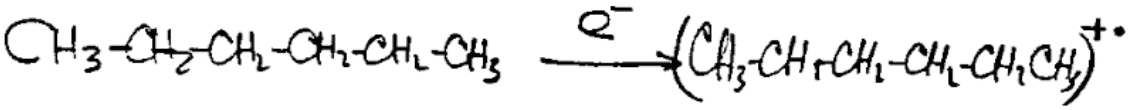
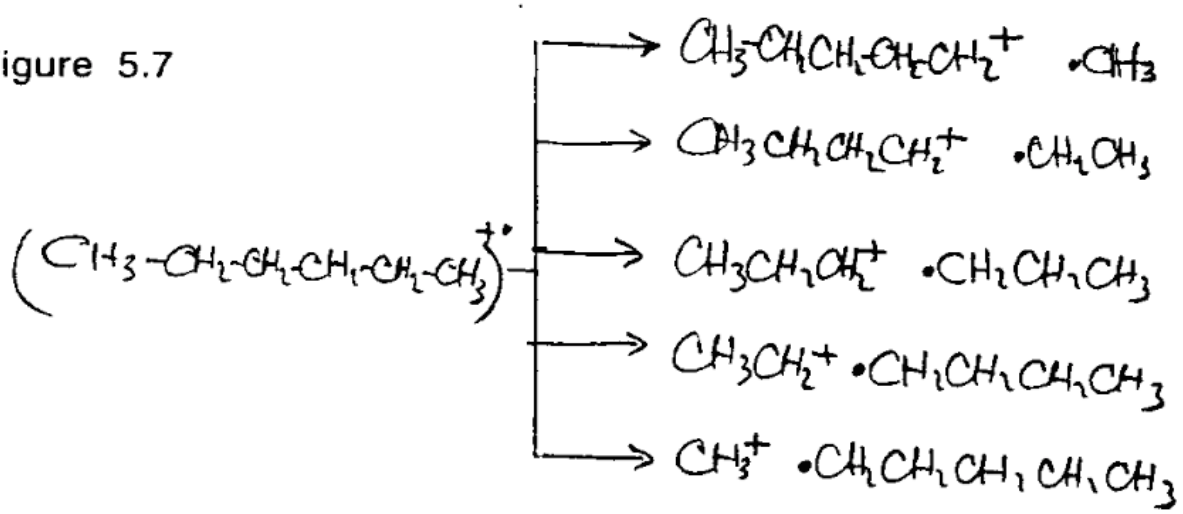


Figure 5.7



This *molecular ion* might then fragment by breaking any of its C-C bonds (Figure 5.7) and we show the *molecular ion* and possible *fragment ions* in Table 5.1 along with their *unit resolution* and exact *m/z values*.

Table 5.1. Exact and Unit Resolution m/z Values for Cations formed from Hexane in a Mass Spectrometer.

		m/z Value (*amu*)	
Ion Structure		**Exact**	**Unit Resolution**
$(C_6H_{14})^{+\cdot}$	$(CH_3CH_2CH_2CH_2CH_2CH_3)^{+\cdot}$	86.1096	86
$C_5H_{11}^+$	$(CH_3CH_2CH_2CH_2CH_2+)$	71.0861	71
$C_4H_9^+$	$(CH_3CH_2CH_2CH_2+)$	57.0705	57
$C_3H_7^+$	$(CH_3CH_2CH_2+)$	43.0548	43
$C_2H_5^+$	(CH_3CH_2+)	29.0391	29
CH_3^+	(CH_3+)	15.0235	15

You can see peaks at all of these m/z values in the hexane mass spectrum (Figure 5.6). In addition, there are prominent peaks for fragments that have m/z values other than those in Table 5.1. Some are 1 or 2 *amu* less than those mentioned in Table 5.1 and they correspond to ions with one or two fewer H atoms than the ions shown in Table 5.1. It is also important to note that there are several "groups" of peaks made up of individual peaks that are each 14 *amu* (the mass of a CH_2 group) larger or smaller than individual peaks in a neighboring group.

Exact Mass Values. The mass values of these peaks are shown at *unit resolution* in Figure 5.6, but **high resolution** mass spectrometers give their *exact mass values*. The exact mass of the hexane molecular ion $(C_6H_{14})^{+\cdot}$ is virtually identical to the exact mass of a hexane molecule (C_6H_{14}) since $(C_6H_{14})^{+\cdot}$ differs from (C_6H_{14}) by just one electron that has negligible mass. However, if you use atomic masses from a periodic table or the *Handbook of Chemistry and Physics* to calculate the molecular mass of hexane, you obtain a value of 86.18 amu rather than the exact mass value of 86.11 (86.1096 rounded off to 4 significant figures). These two values of 86.18 and 86.11 may seem very close to each other, but their difference of 0.07 amu is greater than any experimental or calculational error.

A clue that we may have overlooked something in this analysis of hexane masses is the observation that the mass 86 peak is <u>not</u> the highest mass peak in this mass spectrum. If you look closely at Figure 5.6 you will see a very small peak at mass 87 that is not due to an impurity in our sample. We explain below both the origin of this **M+1 peak**, and why we cannot calculate *exact mass values* using atomic mass data from a *periodic table*.

M+1 Peaks and Isotopes. The *exact mass values* of all of the cations in Table 5.1 are slightly less than we would calculate using atomic mass values from a *periodic table*. This is because atomic masses of C and H from *periodic tables* are *weighted averages* of exact mass values of their naturally occurring *isotopes*. In contrast, mass spectrometers detect individual ions that do not have "average" isotopic distributions as we describe below.

The 12.01 amu atomic mass of C from a periodic table is a weighted average based on the 99% natural abundance of ^{12}C (6 protons, 6 neutrons, atomic mass 12.00000 amu) and 1% ^{13}C (6 protons, 7 neutrons, atomic mass 13.00335 amu). Similarly, the 1.008 amu atomic mass of H from a periodic table is a weighted average based on the 99.985% natural abundance of ^{1}H (1 proton, 0 neutrons, atomic mass 1.007825 amu) and 0.015 % ^{2}H (1 proton, 1 neutron, atomic mass 2.0140 amu). However, the detector of the mass spectrometer determines the masses of individual molecular fragments that cannot contain a statistical distribution of isotopes.

While most hexane molecular ions contain only ^{12}C and ^{1}H and are $(^{12}C_6{}^{1}H_{14})^{+\cdot}$, there are also molecular ions in which one ^{12}C is replaced by a ^{13}C to give $(^{13}C_1{}^{12}C_5{}^{1}H_{14})^{+\cdot}$ that we call the M+1 peak. Their masses are both different from that calculated for $(C_6{}^{1}H_{14})^{+\cdot}$ using atomic masses from a periodic table. In any sample we also expect a few molecular ions of hexane to contain two or more ^{13}C atoms, but their number is so small that they are not visible in the spectrum. While an M+1 peak in the hexane spectrum could also reflect the presence of a ^{2}H atom in the molecular ion $(^{12}C_6{}^{2}H_1{}^{1}H_{13})^{+\cdot}$, the natural abundance of ^{2}H (0.015%) is so small that such ions constitute a trivial part of the M+1 peak.

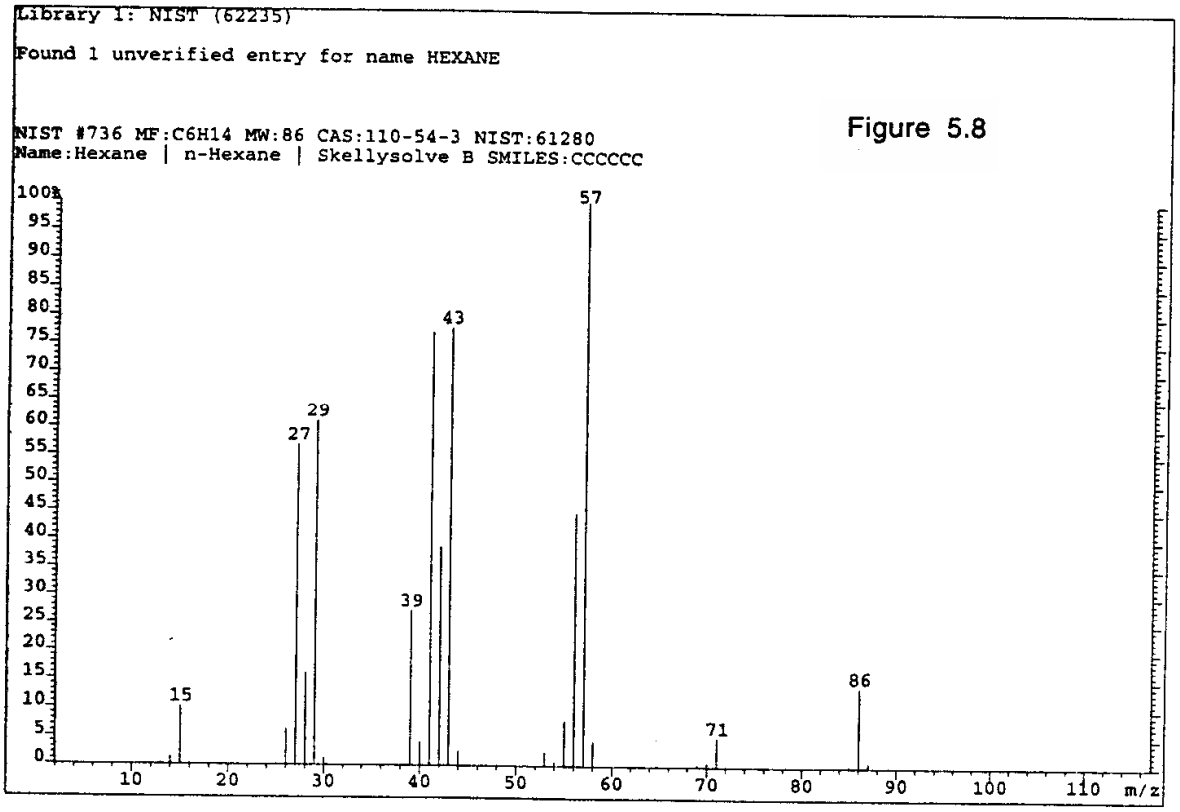
Most *fragment ions* also contain just ^{12}C and ^{1}H, so their exact masses in Table 5.1 are also less than we would calculate using weighted average masses from a periodic table. However like the molecular ion, fragment ions with relatively intense peaks also have neighboring isotopic peaks one mass unit higher due to replacement of a ^{12}C by ^{13}C.

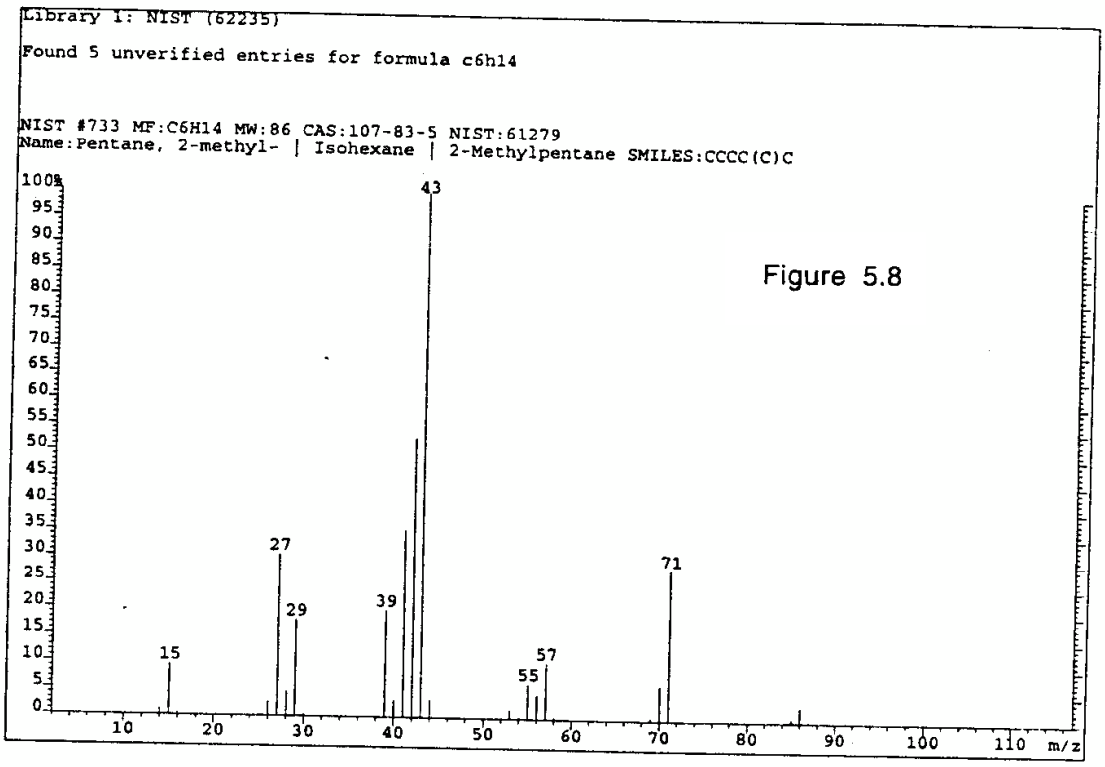
Mass Spectra of Hexane Structural Isomers **(5.2D)**

In order to see how mass spectra can provide information to help distinguish between isomers with the same molecular formula, we compare the mass spectrum of *hexane* with those of its isomers *2-methylpentane*, and *2,2-dimethylbutane* that are all C_6H_{14} (Figure 5.8).

Figure 5.8

The Molecular Ion Peaks. One of the most obvious differences between these spectra in Figure 5.8 is the molecular ion peak at 86. It is much weaker in the spectrum of *2-methylpentane*


Library 1: NIST (62235)
Found 1 unverified entry for name HEXANE
NIST #736 MF:C6H14 MW:86 CAS:110-54-3 NIST:61280
Name:Hexane | n-Hexane | Skellysolve B SMILES:CCCCCC
Figure 5.8
100%
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
57
43
29
27
39
15
71
86
10
20
30
40
50
60
70
80
90
100
110
m/z


Library 1: NIST (62235)
Found 5 unverified entries for formula c6h14
NIST #733 MF:C6H14 MW:86 CAS:107-83-5 NIST:61279
Name:Pentane, 2-methyl- | Isohexane | 2-Methylpentane SMILES:CCCC(C)C
Figure 5.8
100%
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
43
27
71
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100
110
m/z

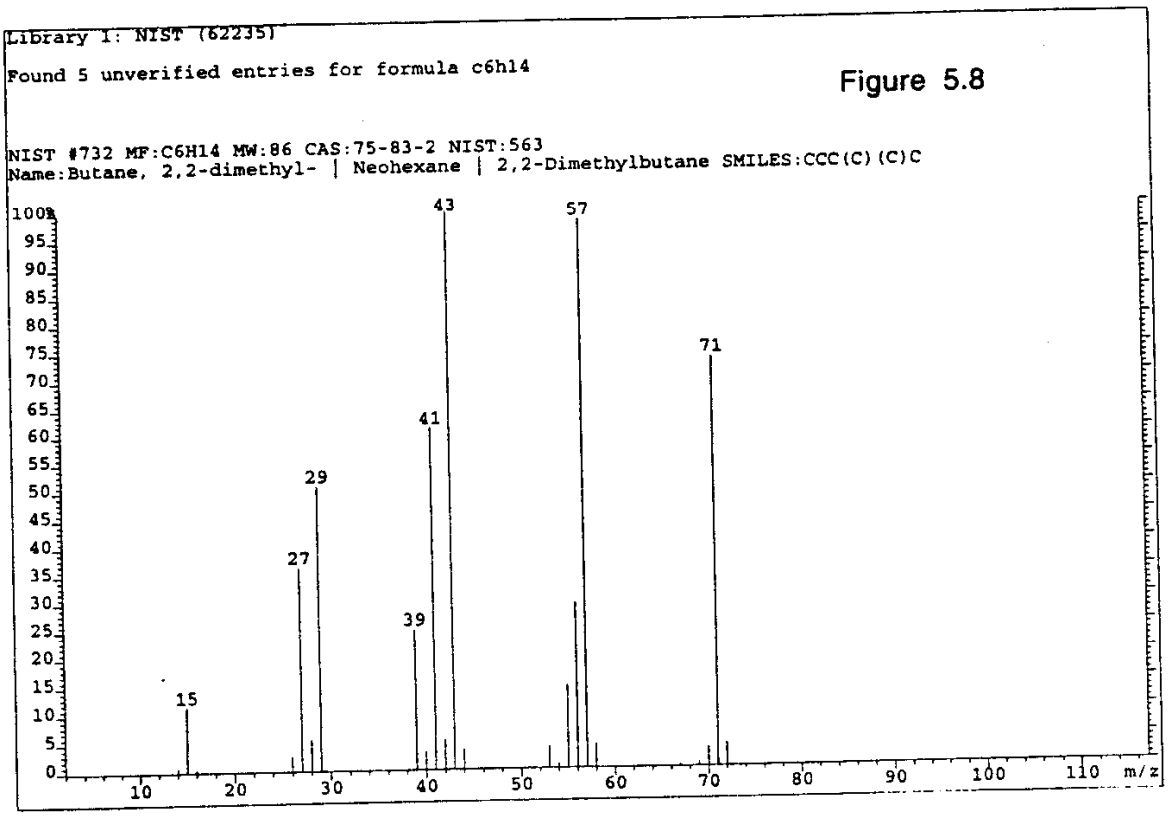
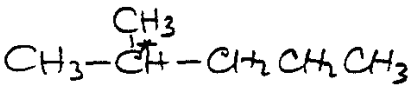


Figure 5.8

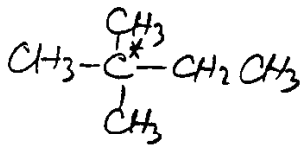
Figure 5.10

Figure 5.9

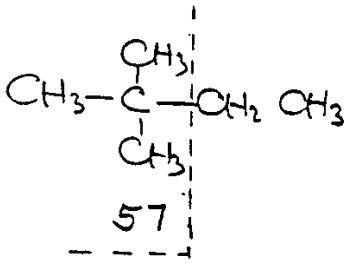
2-methylpentane (C_6H_{14})



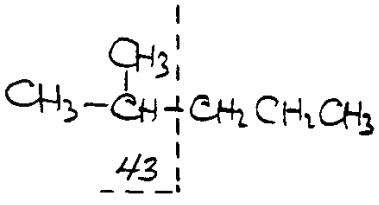
2,2-dimethylbutane (C_6H_{14})



2,2-dimethylbutane



2-methylpentane



than in that of *hexane*, and we cannot see it at all in the spectrum of *2,2-dimethylbutane*. This is an example of a general phenomenon in mass spectrometry that increasing branching in a molecule increases the probability of fragmentation of its molecular ion. An increase in ease of fragmentation of a molecular ion decreases its lifetime and decreases the possibility of observing it in a mass spectrum as we describe below.

Fragmentation. Fragmentation of the molecular ion due to branching occurs primarily at the **points of branching**. We mark these *points of branching* in 2-methylpentane and 2,2-dimethylbutane with the symbol (*) in Figure 5.9

Figure 5.9

If $CH_3^{\cdot}$ is lost from C* in either of those compounds, we expect to see a mass 71 fragment ($C_5H_{11}^+$). Figure 5.8 shows that this mass 71 peak is largest for the most highly branched isomer *2,2-dimethylbutane*, less intense for *2-methylpentane*, and smallest for *hexane* since it is unbranched.

We show other possible C-C fragmentations in Figure 5.10 for *2,2-dimethylbutane* and for *2-methylpentane* at the branch points C*.

Figure 5.10

For *2,2-dimethylbutane*, we might expect to see a mass 57 peak ($C_4H_9^+$), while we might expect to see a mass 43 peak ($C_3H_7^+$) from *2-methylpentane*. We observe each of these in their respective spectra and they illustrate how mass spectra can distinguish between structural isomers.

Mass spectral results are not always easy to interpret in terms of simple fragmentation reactions. For example, while the mass 57 peak ($C_4H_9^+$) for *2-methylpentane* is very small confirming that a C_4 fragment cannot be formed by cleavage at C*, the mass 43 peak ($C_3H_7^+$) from *2,2-dimethylbutane* is unexpectedly large even though there is no obvious way of forming a C_3 fragment by a simple fragmentation reaction at any C-C bond. The molecule "knows what it is doing" and obviously wants to form this ion, but its origin is not easy to understand. Mass spectrometrists say that such unexpected peaks arise by **random rearrangements**.

Why Branching Increases Fragmentation. You will learn later in the text that substitution of an *alkyl group* for an H on a C+ center increases the stability of that C+ center. This is the major reason why the positively charged species formed by C-C cleavage at branch points are so prominent in the mass spectra of branched alkanes.

***Mass Spectra of Compounds with Functional Groups* (5.2E)**

Molecules with functional groups such as OH, NH_2, or a halogen (X) have characteristic mass spectral features that help identify the presence of these functional groups. We illustrate these characteristic features using mass spectra of *1-pentanol*, *1-pentanamine*, *1-chloropentane*, *1-bromopentane*, and *1-iodopentane* (Figure 5.11).

Figure 5.11

General Features. All of these compounds in Figure 5.11 have the general structure $CH_3CH_2CH_2CH_2CH_2$-Y where Y is OH, NH_2, Cl, Br, or I. Electron bombardment in the mass spectrometer first gives molecular ions $(CH_3CH_2CH_2CH_2CH_2\text{-}Y)^{+\cdot}$ and these fragment into smaller cations and radicals. These fragments form by cleavage at C-C bonds as we saw for isomeric hexanes, but the functional group Y influences this fragmentation. We will focus on the *molecular ion peaks*, on the *fragment peaks* corresponding to $^+CH_2\text{-}Y$, and on *fragment peaks* at mass values 55 ($C_4H_7^+$) and 70 ($C_5H_{10}^+$) that form as we show in Figure 5.12.

Figure 5.12

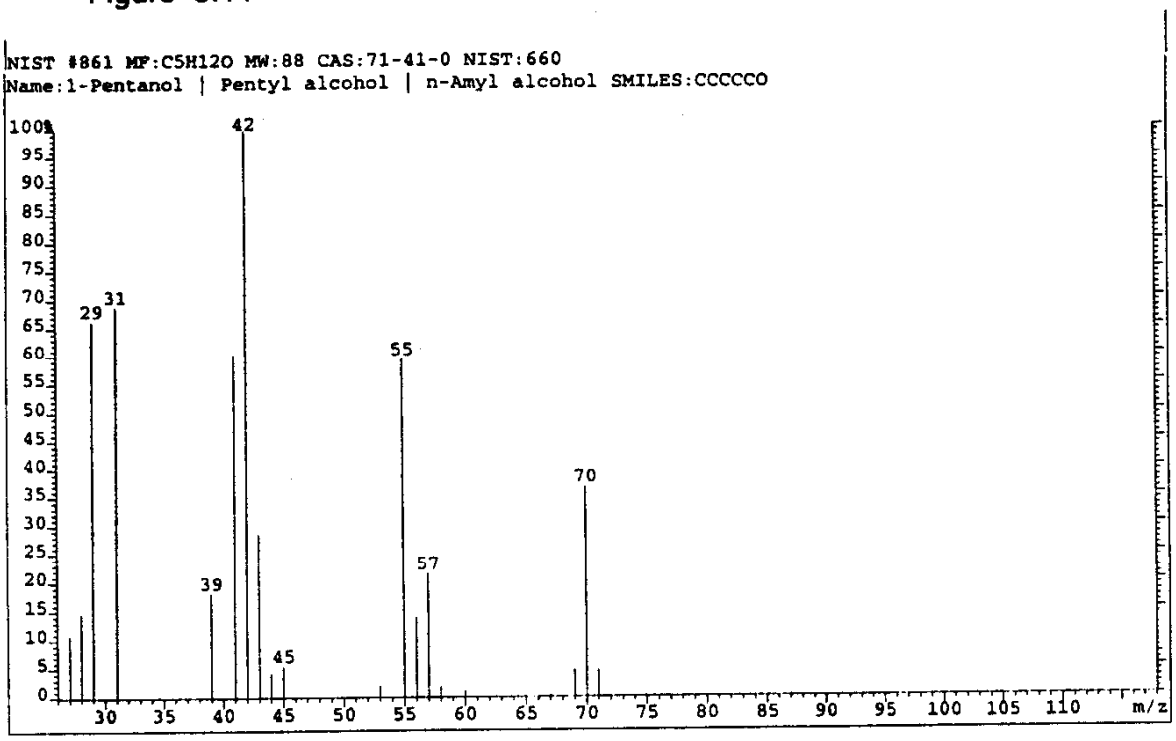
Each Y group causes an unusually large amount of fragmentation at its adjacent C-C bond giving the characteristic $^+CH_2\text{-}Y$ fragment. The peak at m/z = 70 is due to the cation arising from loss of the molecular species H-Y (that is H-OH, H-NH_2, or H-X), while that at m/z = 55 arises from loss of both H-Y and $CH_3^{\cdot}$. We briefly highlight each functional group below.

1-Pentanol (Y = OH). The molecular ion peak (m/z = 88) in the mass spectrum of 1-pentanol ($CH_3CH_2CH_2CH_2CH_2$-OH) is very small and this is characteristic of alcohols (ROH). In contrast, the $^+CH_2\text{-}OH$ peak at m/z = 31 ($^+CH_2\text{-}Y$ where Y = OH) is intense and so are the peaks at m/z = 55 (loss of H-OH and $CH_3^{\cdot}$) and m/z = 70 (loss of H-OH).

1-Pentanamine (Y = NH_2). The molecular ion peak (m/z = 87) for 1-pentamine ($CH_3CH_2CH_2CH_2CH_2$-NH_2) is relatively more intense than the molecular ion peak from 1-pentanol and this is generally true for *amines* (*RNH_2*) compared to *alcohols*(*ROH*). The $M^{+\cdot}$ line is sufficiently intense that its ^{13}C isotopic M+1 peak is also visible in the spectrum. Although the peaks at m/z = 55 and 70 due to loss of H-NH_2 (ammonia) are barely visible, the $^+CH_2\text{-}NH_2$ peak ($^+CH_2\text{-}Y$ where Y = NH_2) is so intense that it is the *base peak* in the spectrum. All of these observations are characteristic of the mass spectra of amines.

1-Chloropentane (Y = Cl). Molecular ions of chloroalkanes undergo extensive fragmentation, so the $M^{+\cdot}$ peak at m/z = 106 for 1-chloropentane ($CH_3CH_2CH_2CH_2CH_2$-Cl) is

Figure 5.11


NIST #861 MF:C5H12O MW:88 CAS:71-41-0 NIST:660
Name:1-Pentanol | Pentyl alcohol | n-Amyl alcohol SMILES:CCCCCO
100%
42
29
31
55
70
57
39
45
m/z

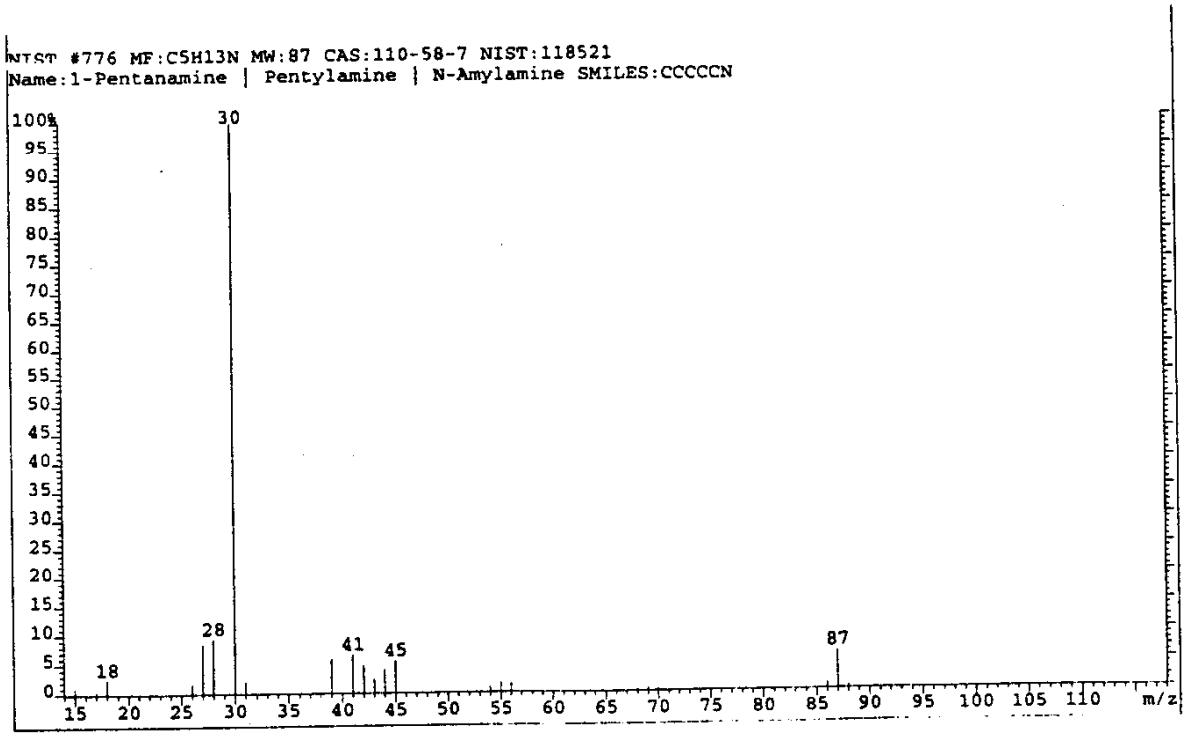
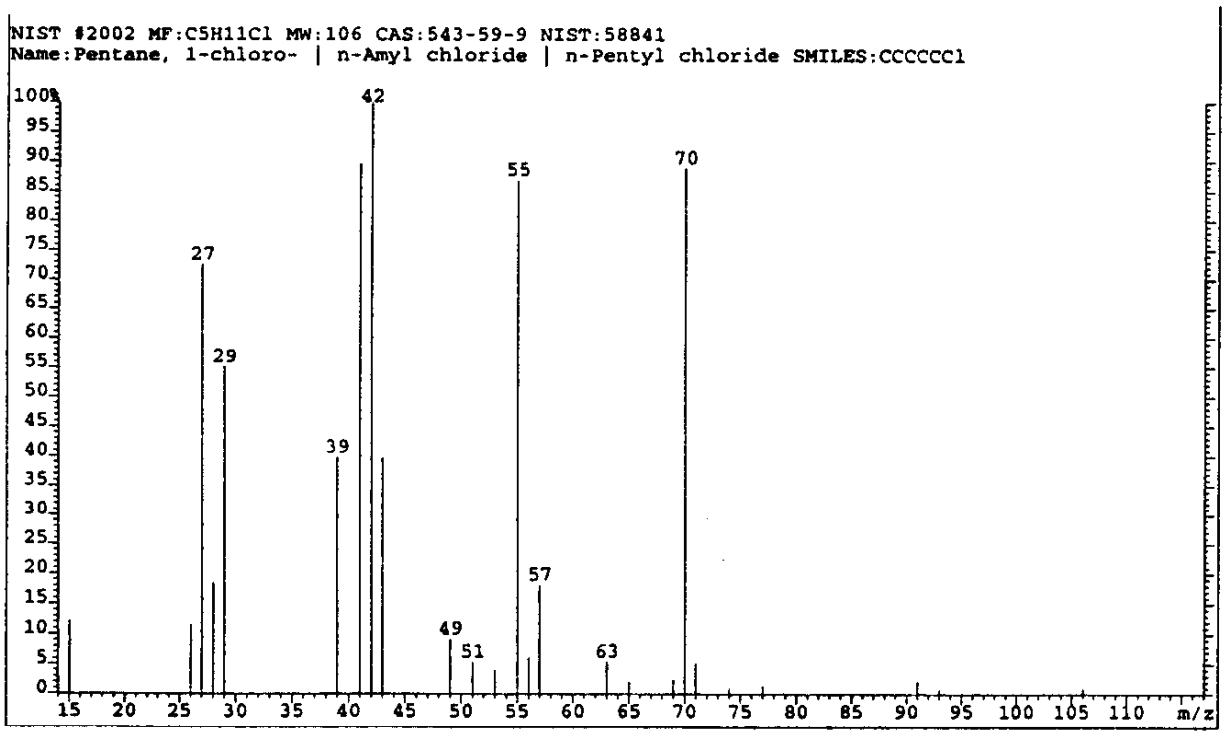

NIST #776 MF:C5H13N MW:87 CAS:110-58-7 NIST:118521
Name:1-Pentanamine | Pentylamine | N-Amylamine SMILES:CCCCCN
100%
30
28
41
45
87
18
m/z

Figure 5.11


NIST #2002 MF:C5H11Cl MW:106 CAS:543-59-9 NIST:58841
Name:Pentane, 1-chloro- | n-Amyl chloride | n-Pentyl chloride SMILES:CCCCCCl
100%
42
55
70
27
29
39
57
49
51
63
m/z

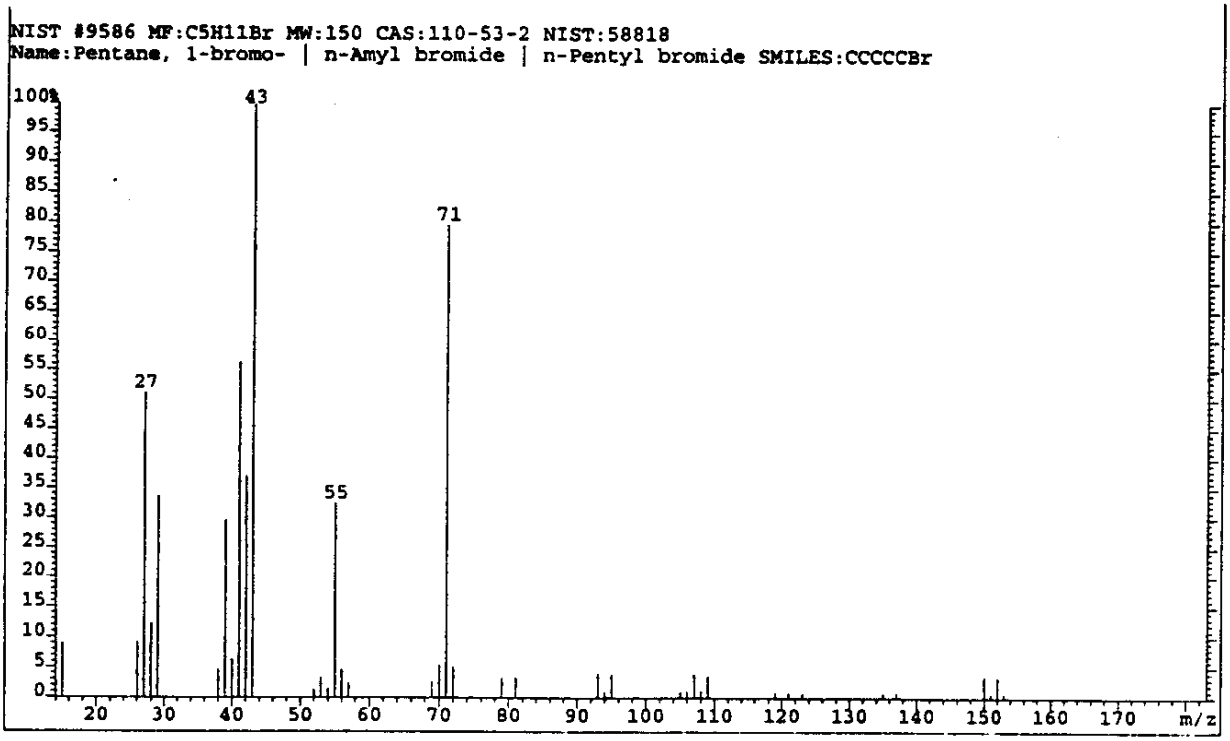

NIST #9586 MF:C5H11Br MW:150 CAS:110-53-2 NIST:58818
Name:Pentane, 1-bromo- | n-Amyl bromide | n-Pentyl bromide SMILES:CCCCCBr
100%
43
71
27
55
m/z

Figure 5.11

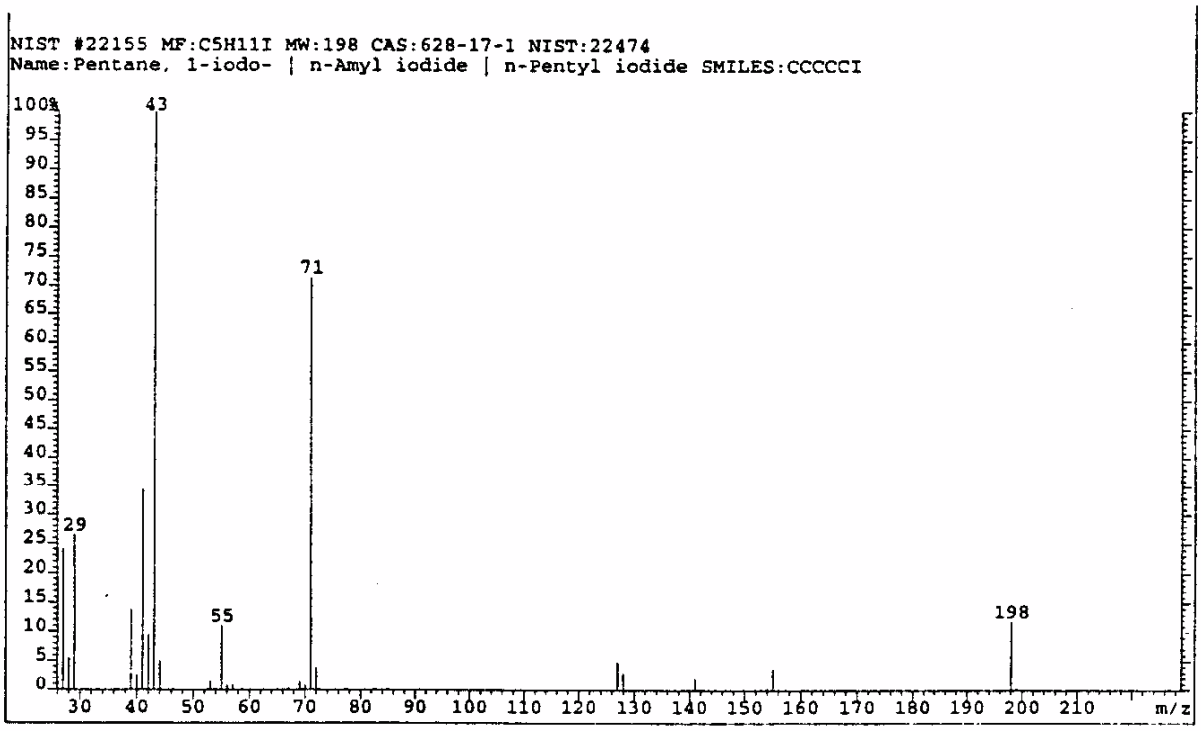
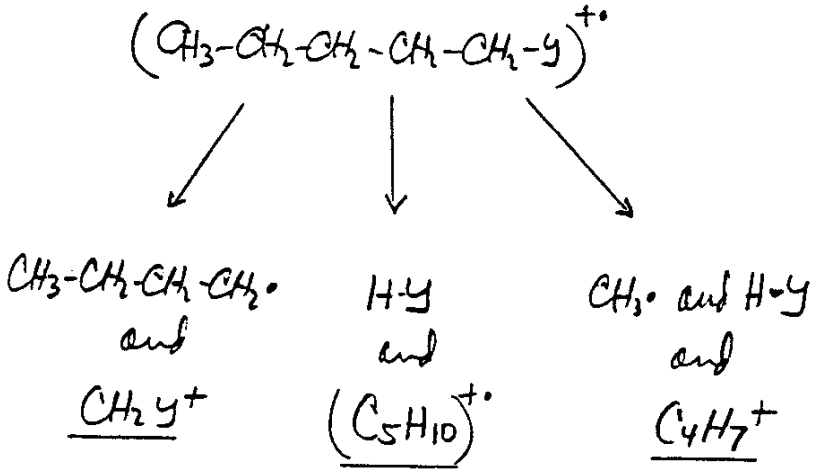


Figure 5.12



just barely visible. Consistent with this, the fragment peaks at m/z = 55 due to loss of both H-Cl and $CH_3^{\cdot}$, and at m/z = 70 due to loss of H-Cl, are very intense.

The $^{+}CH_2$-*Cl* fragment ($^{+}CH_2$-*Y* where Y = Cl) is also visible in this spectrum, but you may be surprised to learn that it corresponds to the <u>two</u> separate peaks at m/z = 49 <u>and</u> 51. Natually occurring Cl is a mixture of the isotopes ^{35}Cl (76%) and ^{37}Cl (24%) so $^{+}CH_2$-*Cl* is an equivalent % mixture of $^{+}CH_2$-^{35}*Cl* (m/z = 49) and $^{+}CH_2$-^{37}*Cl* m/z = 51). The isotopic mixture for Cl also causes every cation containing Cl to give two peaks separated by 2 amu . The molecular ion with the isotope ^{37}Cl (m/z =108) is not visible because it would be only one-fourth the size of the already tiny peak for the ^{35}Cl molecular ion at mass 106, but pairs of fragment ions with ^{35}Cl and ^{37}Cl appear at m/z = 63 and 65 ($C_2H_4Cl^{+}$), and at m/z = 91 and 93 ($C_4H_8Cl^{+}$).

1-Bromopentane (Y = Br). Since naturally occurring Br is almost an equimolar mixture of ^{79}Br (51%) and ^{81}Br (49%), cations containing Br also give two mass spectral peaks with almost equal intensities such as the two weak molecular ion peaks from 1-bromopentane ($CH_3CH_2CH_2CH_2CH_2$-Br) at m/z =150 and 152. You can see other such isotopic pairs of peaks separated by 2 amu including those for $^{+}CH_2$-*Br* ($^{+}CH_2$-*Y* where Y = Br) at m/z = 93 and 95. The characteristic fragment peaks at m/z = 55 and 70 for $C_4H_7^{+}$ and $C_5H_{10}^{+}$ are present, but significantly less intense than those from 1-chloropentane.

1-Iodopentane (Y = I). In contrast to Cl or Br, naturally occuring iodine (I) is almost entirely the single isotope ^{127}I. As a result, 1-iodopentane ($CH_3CH_2CH_2CH_2CH_2$-I) gives just a single molecular ion peak at m/z = 198 along with its small M+1 peak at m/z = 199 due to ^{13}C.

The mass spectrum of 1-iodopentane also illustrates that fragmentation is much less important for *iodoalkanes* than for *bromoalkanes* or *chloroalkanes*. The characteristic fragment peaks at m/z = 55 and 70, and at m/z = 141 for $^{+}CH_2$-*I* ($^{+}CH_2$-*Y* where Y = I) are all relatively small. However, you can see an intense peak at m/z = 71 in the mass spectrum of 1-iodopropane due to $C_5H_{11}^{+}$. This m/z = 71 peak is also present in the mass spectrum of 1-bromopentane and is due to molecular ion fragmentation at C-I or C-Br bonds forming $C_5H_{11}^{+}$ and I· or Br· atoms. We will see in a later chapter that the relative stability of halogen atoms is I· > Br· > Cl· and this explains the very small m/z = 71 peak in the mass spectrum of 1-chloropentane.

Mass Spectrometry Summary **(5.2F)**

If you look back at the mass spectra that we have shown here, you may wonder how a chemist can possibly identify the compound giving that spectrum without knowing the answer in

advance. Each spectrum has many peaks and it is not always clear how some of them formed. These are valid feelings on your part, but chemists who use mass spectrometry as an analytical tool have had extensive training in which they have seen and studied thousands of mass spectra of a variety of different compounds. Like any other skill, the ability to use this technique requires extensive practice.

We have illustrated only a few of the basic concepts that chemists use to interpret mass spectra. It is important to emphasize again that one of the most important uses of mass spectal data by organic chemists is the determination of a molecular mass for a compound from the m/z value of its molecular ion. Fragment ions are also important clues to molecular structure, that chemists use in conjunction with other spectrometric techniques that we describe in the remainder of this chapter. Organic chemists often have some idea of the likely structure of an organic compound before they obtain its mass spectrum so mass spectrometry frequently provides confirmation of a suspected structure. The fragmentation reactions that we have described will be more meaningful after we have studied the reactions of organic molecules in later chapters.

5.3 Spectrometry Using Electromagnetic Radiation

We devote the rest of this chapter to discussions of *NMR*, *IR* and *UV-Vis* spectrometry that rank along with *MS* as the most important spectrometric methods used by organic chemists for molecular structure determination. In contrast with mass spectrometry that uses high energy electrons as its energy source, these additional three methods use **electromagnetic radiation** from different regions of the **electromagnetic spectrum** as their source of energy.

***Electromagnetic Spectrum* (5.3A)**

The *electromagnetic spectrum* includes very high energy *gamma rays* and *x-rays*, intermediate energy *visible light* and *infrared radiation*, and very low energy *radio* and *television waves*. We illustrate the regions of the electromagnetic energy spectrum used for *NMR*, *IR*, and *UV-Vis spectrometry* in Figure 5.13.

Figure 5.13

You may have learned about the *electromagnetic energy spectrum* in other courses such as general physics or general chemistry. It is important for you to be aware that all *electromagnetic energy*, whether from X-rays, UV light, microwaves, or radio and television waves, is provided by packets of energy called **photons** that have no mass or charge.

Photons of Electromagnetic Radiation. What distinguishes X-rays from visible light, for example, is the amount of energy associated with a *photon* of that particular type of

Figure 5.13 Electromagnetic Spectrum

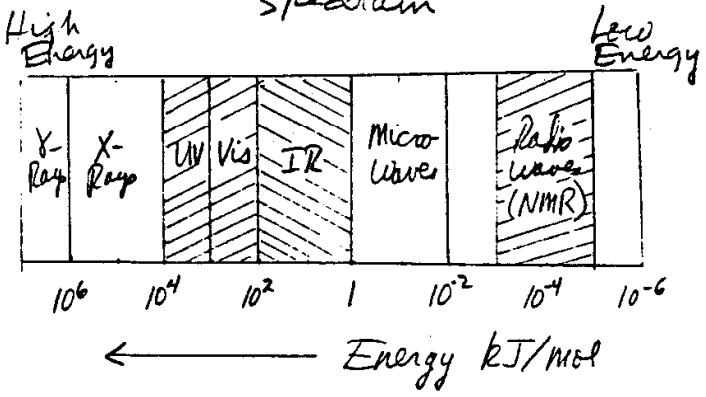


Figure 5.14

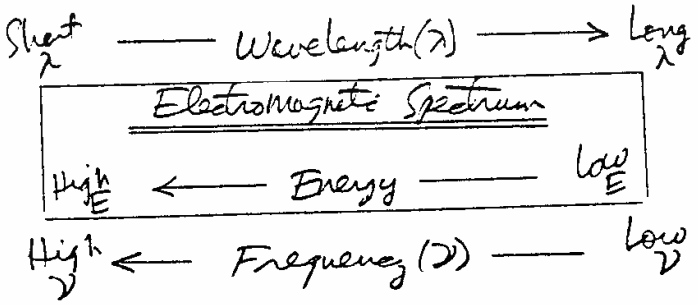


Figure 5.16 Diagram of a Basic Spectrometer

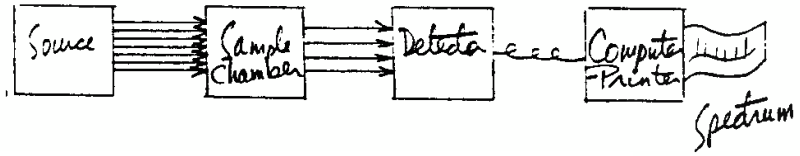
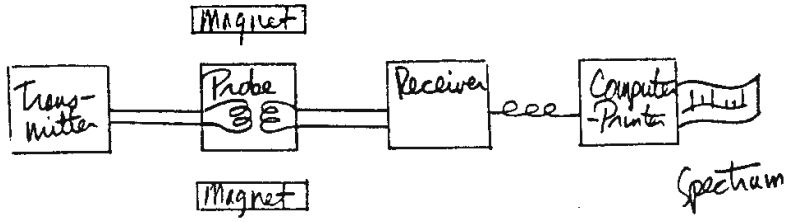


Figure 5.17 Diagram of an NMR Spectrometer



electromagnetic radiation. Radio and television waves are made up of *photons* with very *low energy*, while X-rays and γ-rays are made up of *photons* with very *high energy*. You can see from Figure 5.13 that the relative energy of photons used in the three types of spectrometry that we discuss here decreases in the order $E_{UV\text{-}Vis} > E_{IR} > E_{NMR}$.

> ***Mass Spectrometry Does Not Use Electromagnetic Radiation***. It is important to state again that mass spectrometry (MS) does not use energy from the electromagnetic spectrum! It employs a beam of high energy electrons, not photons, to interact with molecules as we have described earlier. While the MS electron beam destroys the molecular sample in the mass spectrometer, NMR, IR, and UV-Vis spectrometry are non-destructive analytical methods. The energy provided by their photons leads to changes in the molecules, but these changes are almost always rapidly reversible as we will describe in the sections below.

Frequency and Wavelength of Electromagnetic Radiation. We can assign energies in kJ to the photons from different regions of the electromagnetic spectrum (Figure 5.13), but this is not done in practice. Organic chemists typically characterize electromagnetic radiation used in NMR, IR, and UV-Vis spectrometry in terms of its **frequency** or **wavelength**. As a result, you need to understand the general relationships between *energy (E)*, *frequency (ν)*, and *wavelength (λ)* of electromagnetic radiation (Figure 5.14).

Figure 5.14

Our first lesson is that *energy (E)* and *frequency (ν)* are directly proportional to each other as we show in equation (1) where *h* is a proportionality constant called Planck's constant.

$$E = h\nu \qquad (1)$$

Photons with *high energy* (like X-rays and γ-rays) have *high frequencies*, while photons with *low energy* (like microwaves and radiowaves) have *low frequencies*. As a result, the order of relative energies of the photons used in UV-Vis, IR, and NMR spectrometry ($E_{UV\text{-}Vis} > E_{IR} > E_{NMR}$) is the same as the order of their relative frequencies ($\nu_{UV\text{-}Vis} > \nu_{IR} > \nu_{NMR}$).

Our second lesson is that the *wavelength (λ)* of photons is inversely proportional to the *frequency (ν)* of those photons as we show in equation 2 where the proportionality constant *c* is the velocity of light.

$$\nu = c/\lambda \qquad (2)$$

Electromagnetic radiation of *higher* frequency *(higher* energy*)* has *shorter* wavelengths than electromagnetic radiation of *lower* frequency *(lower* energy*)*. This means that the relative order of energies of photons used in NMR, IR, and UV-Vis ($E_{UV\text{-}Vis} > E_{IR} > E_{NMR}$) is opposite to that of their photon wavelengths ($\lambda_{UV\text{-}Vis} < \lambda_{IR} < \lambda_{NMR}$). The *wavelengths* of electromagnetic

radiation used in *UV-Vis* spectrometry are shorter than those used in *IR*, while those of *NMR* are the longest.

Units of Frequency or Wavelength. We could use a single set of units to describe the full range of frequencies (or wavelengths) for the whole electromagnetic spectrum, but again this is not done in practice. Each type of spectrometry traditionally has its own set of units and conventions that describe its portion of the electromagnetic spectrum. This may seem confusing, but these methods evolved during different periods of time and in the laboratories of different types of scientists. This is a fact of organic spectrometry that may never change, so we describe their units and conventions as we present and discuss each of these types of spectrometry. Nevertheless, it is very important for you to keep in mind the relative energy, frequency, and wavelength relationships between UV-Vis, IR, and NMR that we show in Figure 5.13 even if you have difficulty seeing the relationship between the different units of frequency or wavelength that are used for each type of spectrometry.

***Basic Spectrometer Design* (5.3B)**

Each spectrometric technique uses a *spectometer* to (a) provide the electromagnetic energy to the organic compound, and (b) monitor the results of that application of electromagnetic energy.

Spectrometer Components. The detailed design, construction, and overall appearance of NMR, IR, and UV-Vis spectrometers differ greatly, but they share common features that we show using the "block" diagram in Figure 5.16.

Figure 5.16

The *source* provides photons of electromagnetic energy to the *sample* that is enclosed in a *sample chamber*. The *detector* senses energy absorbed (or transmitted) by the *sample*, and this absorption (or transmission) of energy is displayed on a *spectrum* generated by a *computer* that processes data from the *detector*.

Spectral Peaks. The names of the components of these spectrometers sound similar to those of mass spectrometers, but there is a major difference in the nature of the data displayed in spectra from UV-Vis, NMR, and IR spectrometers compared to mass spectra. Individual peaks in a mass spectrum correspond to <u>different</u> molecular species (cations) that have different mass values. In contrast, all of the individual peaks (or signals) in an NMR, IR, or UV-Vis spectrum are due to a <u>single</u> molecular species when a single compound is placed in the sample chamber.

The multiple peaks that we will see in most NMR, IR, or UV-Vis spectra show the response of the molecule to irradiation with energy of a value that corresponds to the position of each peak in the spectrum. As a result, the horizontal axes of NMR, IR, and UV-Vis spectra correspond to the range of energy values for the electromagnetic radiation used in each of these specific types of spectrometry.

5.4 Nuclear Magnetic Resonance Spectrometry

From the standpoint of an organic chemist, probably the single most important tool for structure determination of organic molecules is *Nuclear Magnetic Resonance Spectrometry* (*NMR*) that uses low energy radiation in the radio/television frequency region of the electromagnetic spectrum. We begin with a qualitative description of the technique, and follow this with an extensive discussion of the information about molecular structure that NMR spectra provide.

The NMR Spectrometer (5.4A)

The block diagram of an NMR spectrometer in Figure 5.17 is comparable to the generic spectrometer diagram in Figure 5.16, but it has a number of specialized features.

Figure 5.17

We call the *sample chamber* in the NMR spectrometer the **probe**, and it contains coils of wire that (a) transmit radio frequency radiation to the sample, and (b) detect how the sample deals with that electromagnetic radiation. Since the radiation is radio waves (radio frequency energy) (**rf**), the *source* and *detector* are usually called the **transmitter** and **receiver**, respectively. A special feature of an NMR spectrometer is that the *probe* is surrounded by a powerful **magnet**.

A liquid sample of an organic compound (usually in dilute solution in a solvent), is placed in a glass *sample tube* (sealed on one end like a test tube) that has overall dimensions comparable to a thin ball point pen or pencil (its diameter is typically 5 mm or about 3/8"). This sample tube is placed in the *probe* of the NMR spectrometer and irradiated with *rf energy*.

A *magnet* surrounds the probe because organic compounds do not absorb *radio frequency* (*rf*) radiation unless they are in a magnetic field. When surrounded by the magnetic field, only certain types of atomic nuclei in a molecule are able to absorb rf radiation. The specific energy of the absorbed rf radiation gives information about the type of nucleus absorbing the radiation and where it is located in a molecule.

^{1}H and ^{13}C are NMR Active Nuclei (5.4B)

Atomic nuclei that absorb radio frequency radiation when placed in a magnetic field include ^{1}H and ^{13}C atoms (isotopes). Since organic compounds are primarily composed of carbon (C) and hydrogen (H), NMR identifies the various types of H and C atoms in organic molecules. Organic chemists study ^{1}H atoms and ^{13}C atoms in different NMR experiments. When we study H atoms by NMR, we call the spectrum that we obtain a *Hydrogen* NMR spectrum, or a *Proton* NMR spectrum. When we examine C atoms by NMR, we refer to the resulting spectrum as a *Carbon-13* (or *^{13}C*) NMR spectrum.

Since ^{1}H isotopes of hydrogen have a natural abundance of 99.985%, almost every hydrogen atom in an organic compound is ^{1}H. In contrast, the ^{13}C isotope of carbon has a natural abundance of only about 1% so most carbon atoms are ^{12}C that do not absorb rf energy. In spite of this, any sample of an organic compound contains many molecules with ^{13}C atoms randomly distributed at all possible carbon locations. We will show and discuss ^{13}C and ^{1}H NMR spectra for a variety of different types of organic compounds in the following sections and focus on how organic chemists use these spectra both to determine and to confirm molecular structure.

Other Nuclei that Absorb Radio Frequency Energy. (F, P, B, N, etc)(magnetically active)

5.5 ^{13}C NMR Spectrometry

We begin with ^{13}C NMR spectrometry, but much of what we learn in this section applies directly to the discussion of ^{1}H NMR that will follow.

General Considerations (5.5A)

A typical ^{13}C NMR spectrum of a compound contains a series of *lines* (also called *peaks* or **signals**) that correspond to each type of C atom in the compound. The locations of these *signals* in the spectrum depend on the molecular structure of the organic compound and the types of atoms that are directly and indirectly bonded to each C. We illustrate how these bonded atoms affect the location of ^{13}C NMR *signals* using ^{13}C spectra of several specific compounds as examples.

We present and discuss these spectra before we explain all of the information that they contain. In particular, we will defer our discussion of the horizontal axis labelled **chemical shift** (δ) until later in this section. For now it is enough to know that the *chemical shift δ values* ("delta" values) on the horizontal axis are related to the frequency (or energy) of the rf radiation that each ^{13}C atom absorbs.

Some ^{13}C NMR Spectra (5.5B)

We show ^{13}C NMR spectra for six unbranched alcohols in Figure 5.18 along with their chemical structures.

Figure 5.18

When we ignore the peak at δ 0, and the group of three peaks at about δ 77 that are not due to these alcohols, as we explain later, we see that the spectrum of each alcohol contains the same number of peaks as there are C's in the alcohol. This occurs because each C atom in each alcohol is in a unique environment compared to the other C's in that same alcohol.

Methanol versus Ethanol. Since each *methanol* (CH_3-OH) molecule contains just one C atom, its ^{13}C NMR spectrum has only a single ^{13}C NMR peak or signal and it is located at δ 50.3. In contrast, each *ethanol* molecule (CH_3-CH_2-OH) has two C's that are in different molecular environments from each other. Both C's of ethanol are bonded to each other by a C-C bond, but one is bonded to an O atom while the other has only C-H bonds. This results in a ^{13}C NMR spectrum for ethanol that shows two signals that are located at δ 58.0 and δ 18.2, respectively.

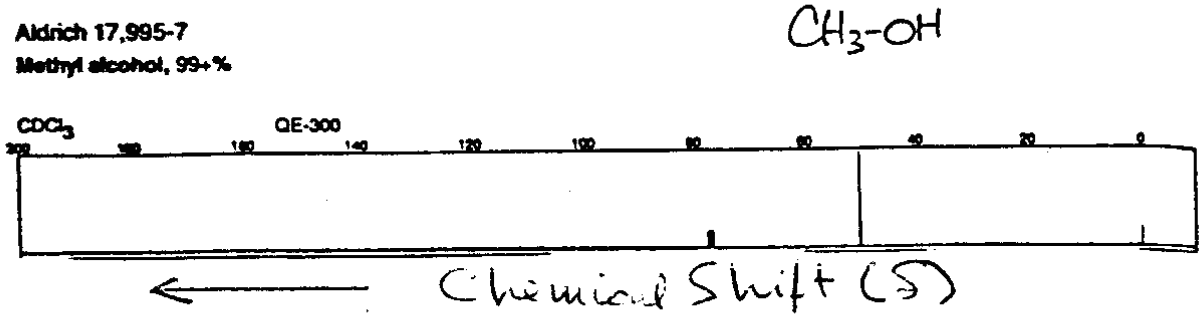
The Other Alcohols. Since C atoms in different molecular environments give discrete signals, we should not be surprised that 1-propanol (CH_3-CH_2-CH_2-OH) has a ^{13}C NMR spectrum with three separate signals (δ 64.3, δ 25.8, and δ 10.2). Successive additions of CH_2 groups to 1-propanol to give 1-butanol, 1-pentanol, and finally 1-hexanol increases the number of signals by one per CH_2 group so that the ^{13}C spectrum for each of these alcohols contains the same number of signals as there are C's in the alcohol.

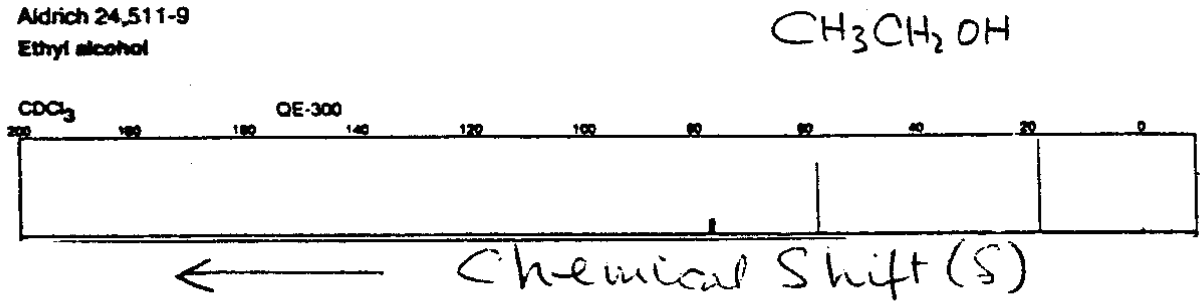
^{13}C NMR Chemical Shifts (δ) (5.5C)

The *chemical shift value* (*δ*) value) of each peak in these alcohols reflects the chemical environment of the C atom giving the peak.

Generalizations for these Alcohols. Besides the fact that ^{13}C NMR spectra for these alcohols have the same number of signals as they have C atoms, you can see that 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol each have one signal at about δ 60, and another just below δ 15. Organic chemists have determined that the δ 60 signals for these four alcohols correspond to <u>C</u> bonded to O in <u>C</u>H_2-OH, while the signals below δ 15 are each due to <u>C</u> in <u>C</u>H_3. From these observations, we can conclude that a ^{13}C NMR signal near δ 60 in a spectrum of a molecule could be due to a CH_2-OH group in the molecule, while the presence of a peak below δ 15 could indicate that the molecule contains a CH_3.

Figure 5.18


Aldrich 17,995-7
Methyl alcohol, 99+%
CH_3-OH
$CDCl_3$
QE-300
Chemical Shift (δ)


Aldrich 24,511-9
Ethyl alcohol
CH_3CH_2OH
$CDCl_3$
QE-300
Chemical Shift (δ)

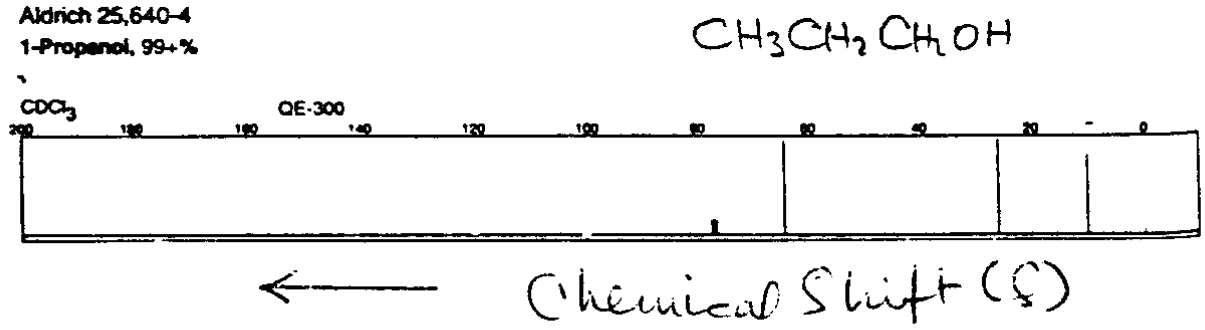
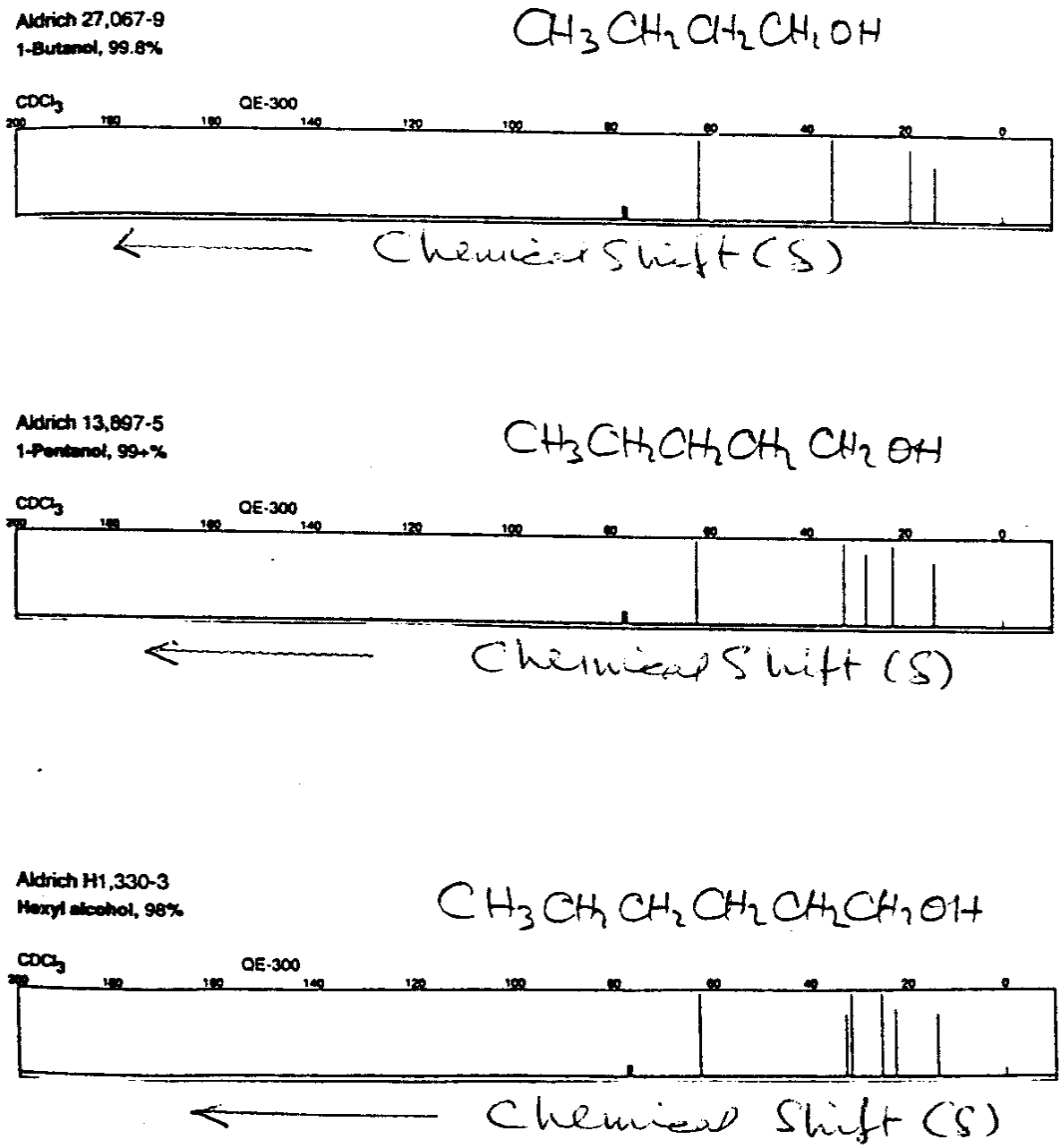

Aldrich 25,640-4
1-Propanol, 99+%
$CH_3CH_2CH_2OH$
$CDCl_3$
QE-300
Chemical Shift (δ)

Figure 5.18


Aldrich 27,067-9
1-Butanol, 99.8%
CH3CH2CH2CH2OH
CDCl3
QE-300
Chemical Shift (S)
Aldrich 13,897-5
1-Pentanol, 99+%
CH3CH2CH2CH2CH2OH
CDCl3
QE-300
Chemical Shift (S)
Aldrich H1,330-3
Hexyl alcohol, 98%
CH3CH2CH2CH2CH2CH2OH
CDCl3
QE-300
Chemical Shift (S)

The signals for the other C's in these molecules have δ values between δ 15 and δ 60. Although each signal corresponds to a C in a CH_2 group between two carbons (C-CH_2-C), the δ value depends on the number of bonds that separate them from the OH group. Because the chemical environment of a C in a molecule determines its ^{13}C δ value, chemists refer to δ values, and the separation between the individual signals in an NMR spectrum, as *chemical shifts*.

Chemical Shifts Depend on Electron Density. The *chemical shift* of the C in C-CH_2-OH is greater than that of the C in any C-CH_2-C because the electron density at the C in C-CH_2-OH is less than that at the C in C-CH_2-C. The highly electronegative O of OH (Chapter 3) decreases electron density on adjacent atoms so that a C directly bonded to O experiences lower electron density than the C's not directly bonded to O. This is reflected in the polar character of C-O bonds that we described in Chapter 3 and show again in Figure 5.19.

Figure 5.19

The effect of O on the electron density at a C decreases as the the number of bonds increases between an O and C as you can see in Figure 5.20 from the chemical shift values for the various C's in hexanol.

Figure 5.20

The CH_3 group in 1-hexanol has the lowest δ value and is separated from the OH group by the most bonds. However this is not the only reason that it has a low δ value. While the δ value for CH_3 increases (?check this versus figs?) going from methanol to ethanol, and then to 1-propanol, it is essentially constant in 1-butanol, 1-pentanol, and 1-hexanol even though it's separation from oxygen continues to increase from 4 to 6 C's (Figure 5.18). Although its chemical shift is partly determined by its relationship to O, a major difference is that it is CH_3 rather than CH_2. The number of C's bonded to a C also influences its electron density contributing to the observed chemical shift difference between CH_2 and CH_3 groups.

Other Factors Effect δ Values. Other structural changes affect the δ values of CH_3 and other C containing groups. We show several alkanes and cycloalkanes in Figure 5.20a and the approximate δ values for each of their C's.

Figure 5.20a

From these δ values, you can see that the chemical shift for a CH_3 group also depends on the number of C's attached to its directly adjacent C. For example, the δ value for the CH_3 groups labelled *(a)* increases from 14 to 22 to 29 as the branching increases on the C to which it is attached.

Figure 5.19

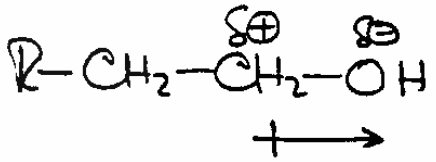


Figure 5.20

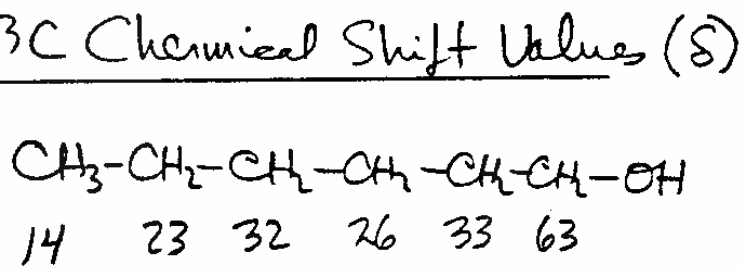


Figure 5.20a

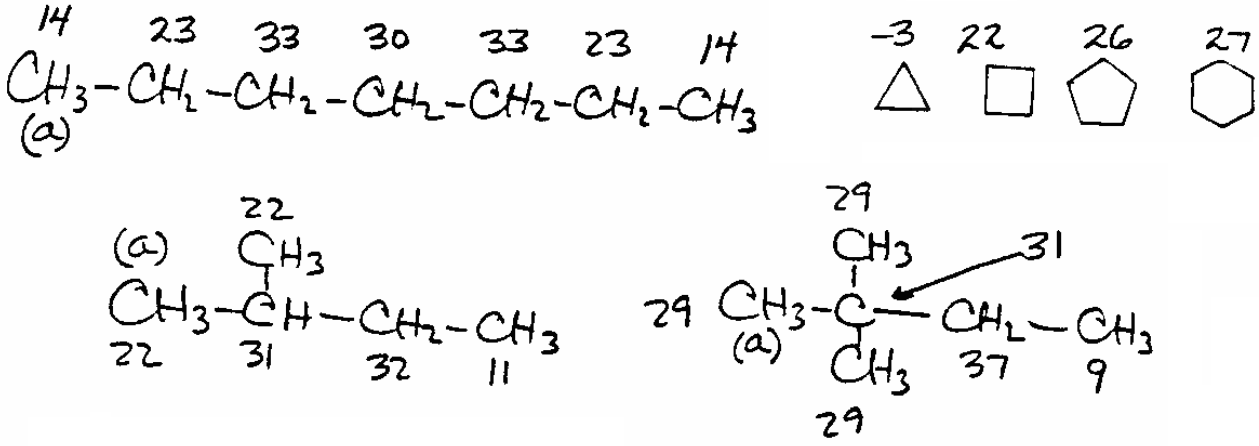
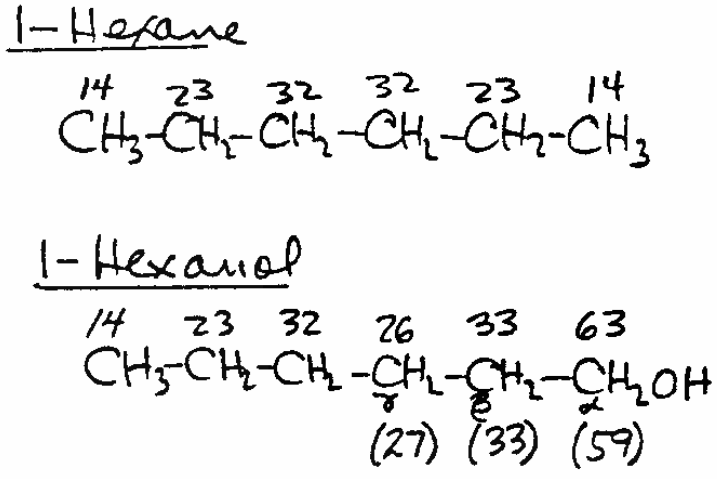


Figure 5.20b



Prediction of ^{13}C δ Values. The data in Table 5.2 show how different functional groups affect the chemical shifts of C atoms. We can use them in combination with δ values for unsubstituted compounds, such as those shown in Figure 5.20a, to estimate δ values of ^{13}C in compounds with halogens (X), OR, or NR_2 groups.

Table 5.2. Additive Effects of Y Groups on ^{13}C Chemical Shift Values of C's in Compounds with the General Structure C(γ)—C(β)—C(α)—Y

Y	C(α)	C(β)	C(γ)
CH_3	+10	+10	-2
O H	+45	+10	-5
O R	+55	+5	-5
NH_2	+25	+10	-5
NHR	+35	+5	-5
NR_2	+40	+5	-3
F	+65	+5	-5
Cl	+30	+10	-5
Br	+25	+10	-3
I	0	+10	0

We can approximate the δ value of C atoms in simple molecules containing these functional groups (Y) by adding the appropriate number from Table 5.2 to the δ value for a comparable C in the corresponding unsubstituted compound where Y = H.

Calculations for 1-Hexanol. (aside?)As an illustration, let's use the data in Table 5.2 and Figure 5.20a to estimate δ values for the C's in 1-hexanol and then compare them to those actually observed. We can imagine that *1-hexanol* originates from *hexane* if we replace an H on one of its CH_3 groups by an OH group. We show these two compounds in Figure 5.20b along with *experimentally* measured δ values for each C atom from ^{13}C NMR spectra (the numbers not in parentheses), and δ values that we *calculate* (the numbers in parentheses) as we illustrate below.

Figure 5.20b
The C of CH_3 in hexane, and the C with the OH group in 1-hexanol, are α carbons and their bonded C's are β, and γ, respectively.

When we add the appropriate numbers from the C(α), C(β), and C(γ) columns for the OH group to the δ values for C(α), C(β), and C(γ) in hexane, we predict a chemical shift for C(α) in hexanol of δ 59 (14 + 45), for C(β) of δ 33 (23 + 10), and for C(γ) of δ 27 (32 + (- 5)). You see that these predicted δ values are very close to those actually observed. You can also see that the observed δ values for C's further from the OH group than C(γ) are the same as those on hexane

since correction for a functional group is usually unnecessary at C atoms more than three C's away from it.

δ Values and Electronegativity. The data in Table 5.2 show that the magnitude of the effect of a functional group on δ values depends on the electronegativity of the atom of that functional group directly bonded to the C skeleton. The effects of OH or OR are greater than those of NH_2, NHR, and NR_2, while they all have greater effects than CH_3 consistent with the order of relative electronegativities O > N > C.

F has the biggest effect since it is the most electronegative atom in the periodic table, and the effect of a halogen on δ values decreases in the electronegativity order F > Cl > Br > I. The magnitude of the effects for Cl, Br, and I are smaller than we might expect based on their actual electronegativity values. The very small effect of I on the δ value on C(α) is particularly striking and there is no simple explanation for this observation.

Chemically Equivalent Carbons. Each C atom in each alcohol in Figure 5.18 gives a separate ^{13}C NMR signal because each C is in a different environment compared to the others in the same molecule. However, when two or more C's in a molecule are **chemically equivalent** they do not give separate peaks. We illustrate this by comparing the ^{13}C NMR spectra of bromoethane, 1-bromopropane and 2-bromopropane in Figure 5.22.

Figure 5.22

Although bromoethane with two C's gives two ^{13}C NMR signals and 1-bromopropane with three C's gives three signals (remember that the small peaks at δ 0 and δ 77 are <u>not</u> due to these bromoalkanes), the spectrum of 2-bromopropane has only <u>two</u> signals even though it has <u>three</u> C atoms.

This occurs because the two CH_3 groups in 2-bromopropane are chemically equivalent! They each have exactly the same relationship to the Br functional group, and the rest of the molecule, and you can even consider them to be mirror images of each other as we illustrate in Figure 5.23.

Figure 5.23

We can identify the C or C's giving rise to each signal in these spectra from their chemical shift values. In each spectrum the signal with the highest δ value corresponds to the C directly attached to the electronegative Br, while those with the lowest δ values are for CH_3 groups analogous to what we observed with the alcohols. The C-<u>C</u>H_2-C signal for 1-bromopropane has an intermediate chemical shift for the same reasons as the C-<u>C</u>H_2-C groups in alcohols (Figure 5.18).

Figure 5.21

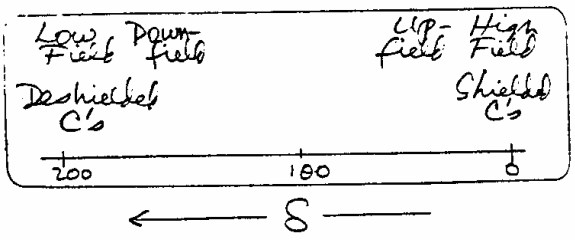


Figure 5.24

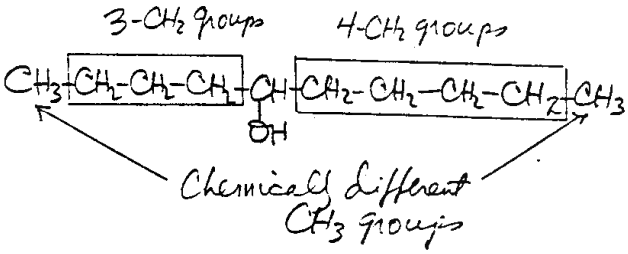


Figure 5.22

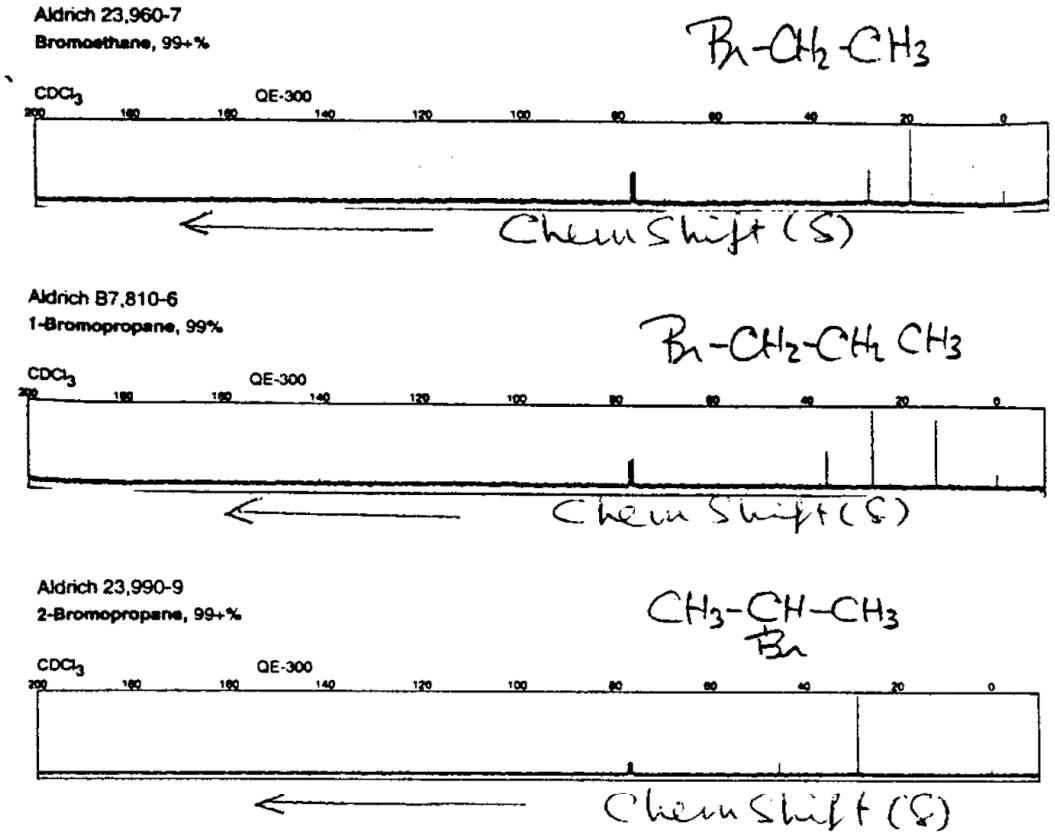


Figure 5.23

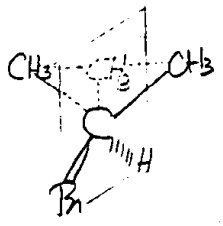
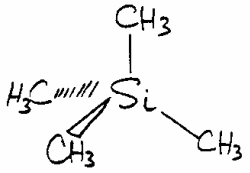


Figure 5.23a



tetramethylsilane (TMS)

***Additional Details about NMR Spectra* (5.5D)**

In order to complete our discussion of ^{13}C NMR spectrometry we introduce some additional terminology and explain those extra signals at δ 0 and δ 77 that we mentioned earlier and have seen in these spectra.

Shielding. When two ^{13}C atoms have different chemical shifts, we say that the C with the smaller δ value is **shielded** compared to the C with the larger δ value. We use this term because *electron density* that **shields** the C atom is *higher* at the C with the *lower* δ value. In any NMR spectrum, the *smaller* the δ value of a signal, the more the atom giving that signal is *shielded*. Conversely, the *larger* the δ value, the more the atom is *deshielded*.

NMR spectra display signals with larger δ values on your left as you face the spectrum and those with smaller δ values on your right (the δ 0 value is at the far right). As a result, signals on the left hand side of the spectrum correspond to atoms that are *deshielded* while those on the right hand side of the spectrum correspond to atoms that are *shielded* (Figure 5.21).

Figure 5.21

High and Low Field. For historical reasons, chemists call the region of the spectrum with low δ values (the *right hand* side of a spectrum) the **high field** or **upfield** region of the spectrum(Figure 5.21). Conversely, the region of the spectrum with large δ values (the *left hand* side of a spectrum) is the **low field** or **downfield** region. These terms arose because of the way that early NMR spectrometers operated. Although these descriptions no longer make sense in terms of the way modern spectrometers operate, chemists continue to routinely use them to describe NMR spectra.

The TMS Reference in ^{13}C NMR. We mentioned at the beginning of our discussion of ^{13}C NMR, that δ values for ^{13}C atoms are related to the amount of rf energy absorbed by ^{13}C atoms. We provide an exact definition of δ values in Appendix xx where we present basic theory for NMR spectrometry. For our purposes here, you simply need to know that a δ value is the difference in the spectral location of the signal for a ^{13}C atom in our compound of interest and the single ^{13}C signal of **tetramethylsilane** (**TMS**) (Figure 5.23a) that we call an **internal reference standard**. The small peak at δ 0 that we have seen in each spectrum is due to *TMS*.

Figure 5.23a

TMS gives a single ^{13}C NMR signal because all four of its C's are chemically equivalent. This signal appears at very *high field* because Si has a lower electronegativity than C so its bonded C atoms are *highly shielded*. Chemists define the chemical shift of the TMS ^{13}C signal as δ 0 and

reference the chemical shifts of all other ^{13}C signals to it since its ^{13}C signal is at higher field than those of most other C atoms in organic compounds. The δ scale increases from the right-hand end (the high field end) to the left-hand end (the low field end) on the spectrum so that ^{13}C signals for C's in other compounds have positive chemical shift values.

TMS is called an **internal reference standard** because it is added to samples whose NMR spectra are being determined and because it defines the δ scale for their spectra. Organic chemists chose TMS as the *internal reference standard* because it has four chemically equivalent C atoms that are highly shielded, and because it does not react with most organic compounds or solvents. It has a low boiling point of 27°C so it is easily removed from most NMR samples.

Solvents Used in NMR Spectrometry. The set of three small peaks at δ 77 that we have seen in NMR spectra, is due to the ^{13}C atom in **D<u>C</u>Cl$_3$** (**deuterochloroform**) used as a solvent for the organic compound. This C atom gives 3 peaks in ^{13}C NMR spectra because of the **deuterium** (**D**) atom. *Deuterium* (*D*) is the common name for the ^{2}H isotope of H that we mentioned along with ^{1}H in our earlier discussion of mass spectrometry. We will explain in our subsequent discussion of ^{1}H NMR why D causes the ^{13}C signal of $DCCl_3$ to be three peaks.

Chemists use $DCCl_3$ ($^{2}HCCl_3$) as an NMR solvent (rather than the less expensive and readily available *undeuterated* chloroform ($^{1}HCCl_3$)) because of its D (^{2}H) atom. ^{13}C NMR spectrometers use the magnetic characteristics of deuterium (D) as a reference point for their electronic systems in a way that is vital to obtaining NMR spectra but not necessary for us to understand at this level. We will see another benefit of the presence of D (^{2}H) instead of ^{1}H in this solvent when we discuss ^{1}H NMR.

While $DCCl_3$ is an excellent solvent for a wide variety of organic compounds, it is not always the best choice. Sometimes other deuterated organic solvents are used and examples are shown in Table 5.xx. Their ^{1}H atoms are replaced by D for the same reasons that we described for $DCCl_3$.

Table 5.xx.

Qualitative Predictions of ^{13}C Spectra (5.5E)

With practice, you will be able to look at the structure of a molecule and predict which C's are *chemically equivalent* (give the same NMR signal) or *non-equivalent* (give different signals). Two carbons are nonequivalent if at least one group on one C differs from one group on the other

C. This difference can occur some distance from the actual C giving rise to the NMR signal as we illustrate with the alcohol *5-undecanol* in Figure 5.24.

Figure 5.24

Although the two terminal C's of this compound are each in CH_3 groups, they are non-equivalent even though both are bonded to several CH_2 groups. C1 is separated from the C-OH group by 3 CH_2 groups, while C11 is separated from that same C-OH by 4 CH_2 groups. In this case the C-OH group is far away from either CH_3 group, so their chemical environments differ only slightly and their δ values are very similar.

In order to predict the chemical shift of a ^{13}C NMR signal for a specific C atom in a molecule, organic chemists make use of extensive chemical shift data that have been compiled in tables and in libraries of NMR spectra. We summarize some of these data in Table 5.yy and include a more extensive compilation with references to other sources of this information in Appendix xx.

Table 5.yy.

5.6 ^{1}H NMR Spectrometry

We have just seen that ^{13}C NMR spectra show a series of signals that correspond to each chemically non-equivalent C in a molecule, so we should not be surprised that ^{1}H NMR (or Proton NMR) spectra show signals for each chemically non-equivalent H atom in a molecule. We illustrate this using examples of Proton NMR spectra that we present and discuss below.

^{1}H versus ^{13}C NMR Chemical Shifts (5.6A)

Before we examine ^{1}H NMR spectra of different organic compounds, it is important for you to understand that these ^{1}H NMR spectra only show signals for ^{1}H atoms. The NMR signals corresponding to ^{13}C atoms do not appear on these spectra since the range of radio frequency (rf) energy that ^{1}H atoms in a magnetic field absorb is significantly different than that absorbed by ^{13}C atoms in the same magnetic field. It is necessary to use different rf transmitters on the spectrometer, or even different spectrometers, to obtain both ^{1}H and ^{13}C NMR spectra.

This difference in radio frequency range for ^{13}C and ^{1}H NMR spectrometry is not apparent from their spectra since both use the symbol δ for the horizontal chemical shift axis and both types of spectra have δ 0 on their far right end of the chemical shift scale. You will see below that δ values in ^{1}H NMR spectra fall in the range of δ 0 to δ 10, and you have already seen that ^{13}C NMR spectra have δ values ranging from δ 0 to δ xx. While it looks like the δ range from 0 to 10 of an^{1}H NMR spectrum might overlap the δ 0 to δ 10 range on a ^{13}C spectrum, this is not the case since these δ scales are separately defined for ^{13}C and ^{1}H NMR spectrometry. We have

discussed the δ scale for ^{13}C spectra above and will describe the ^{1}H δ scale later in this section. We present a more detailed discussion relating these δ scales to absolute rf frequency values in Appendix xx.

^{1}H NMR Spectrum of Bromoethane **(5.6B)**

We illustrate the basic fundamentals of ^{1}H NMR using the ^{1}H NMR spectrum of bromoethane that we show in Figure 5.25.

Figure 5.25

The Origin of the ^{1}H NMR Signals. This spectrum is more complex than the ^{13}C NMR spectrum of the same compound shown in Figure 5.22. When you count the number of peaks (excluding that at δ 0 for the internal reference standard), you see 7 peaks although there are only 5 H's in the molecule. In reality, these 7 individual peaks actually make up only <u>two</u> ^{1}H NMR <u>signals</u> in this ^{1}H NMR spectrum due to the <u>two</u> chemically non-equivalent types of H in 1-bromoethane. One *signal* is the *group of 3 peaks* centered at about δ 1.7 and the *other signal* is the *group of 4 peaks* centered at about δ 3.4.

The signal (group of 3 peaks) centered at δ 1.7 is due to the H's of the CH_3 group, and the other signal centered at δ 3.4 (group of 4 peaks) is due to the H's of the CH_2Br group, as we show on the spectrum in Figure 5.22. These chemical shift values of δ 1.7 and δ 3.4 result from an effect of Br on electron density at these H's that is analogous to the effect of Br on ^{13}C NMR signals that we described earlier. The more electronegative Br atom causes the H's on *CH_2Br* to be *deshielded* and to appear *downfield* from those of the *CH_3* group.

The Shapes of the Signals. Even though there are 3 peaks centered at δ 1.7 for the CH_3 hydrogens, and 3 H's on that carbon, the number of peaks in that signal is <u>not</u> the result of the number of H's on CH_3. Note that there are 4 peaks centered at δ 3.4 for just 2 H's of the CH_2Br group.

All three H's on CH_3 are chemically equivalent to each other because of rapid C-C rotation, so they should give the same NMR signal, and the same is true for the two H's on CH_2Br. We will see in the next section that the 3 peaks in the CH_3 signal are the result of the 2 H's on the <u>adjacent</u> CH_2Br group, and that the 4 peaks in the CH_2Br signal result from the 3 H's on its adjacent CH_3 group.

Figure 5.25

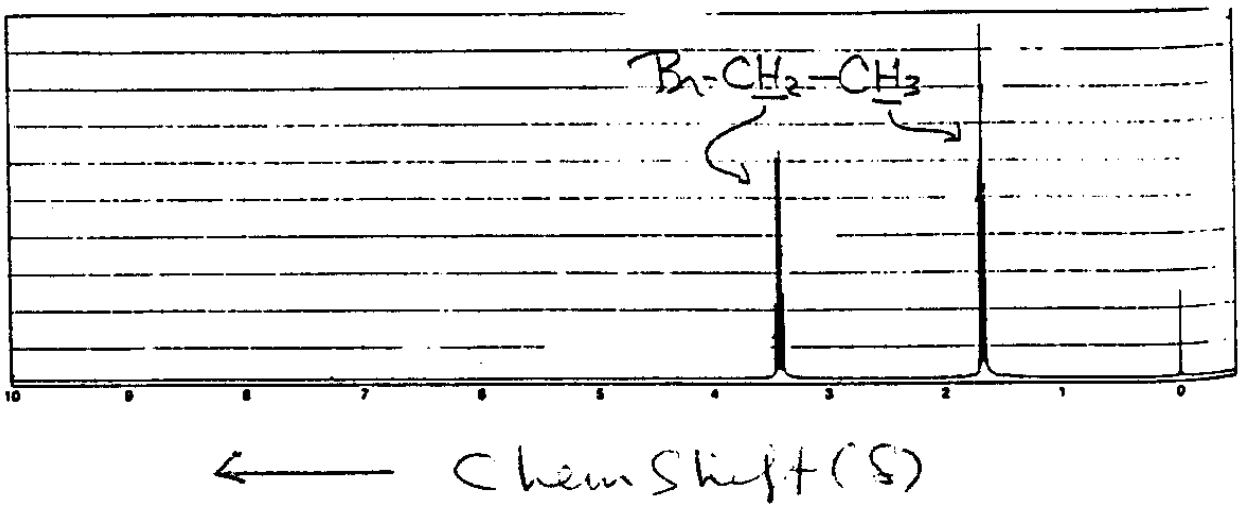
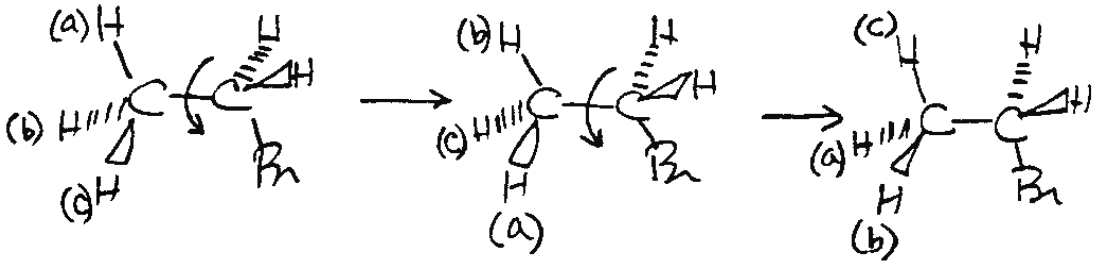


Figure 5.26



C-C Rotation and Chemical Equivalency. The reason for chemical equivalency of the 3 H's of CH_3, and of the 2 H's of CH_2, is rapid rotation about the C-C bond that we described in Chapter 2 and illustrate in Figure 5.26.

Figure 5.26

If C-C rotation did not occur, each of the H's on CH_3 would be in a different environment in the molecule. For example, in the first structure H(a) is *anti* to Br, while both H(b) and H(c) are *gauche* to Br. We would expect *anti* H(a) to give one NMR signal, and *gauche* H(b) and H(c), to give a separate NMR signal. However C-C rotation is rapid compared to the time required for the NMR spectrometer to detect absorption of rf energy by H's, so the environment of each H on CH_3 is averaged and appears to be the same. The same is true for the H's in the CH_2 group.

Signal Splitting in ^{1}H NMR Spectra (5.6C)

In ^{1}H NMR spectra the NMR signal for an H, or group of chemically equivalent H's on the same C (such as the three H's on a CH_3 group), is **split** into multiple peaks by one or more chemically different H atoms on directly bonded C atoms. We call the rule that governs how H's on adjacent C's *split* a ^{1}H NMR signal the **n+1** rule, and we illustrate it below using ^{1}H NMR spectra of *bromoethane*, *1-bromopropane*, and *2-bromopropane*.

1-Bromoethane. The *n+1 rule* predicts that the ^{1}H NMR signal for the H's on CH_3 of 1-bromoethane (Figure 5.25) will be split into a signal of *n+1* peaks by the *n* equivalent H's on the CH_2Br group. Since there are 2 chemically equivalent H's on CH_2Br (n = 2), we expect the CH_3 signal to be 3 peaks (n+1 = 2+1 = 3) and that is what we observe (Figure 5.25). This **triplet** signal for CH_3 has a characteristic shape, that we discuss later in the chapter, where the central peak is about <u>twice</u> the height of each of the outer two peaks (Figure 5.27).

Figure 5.27

The *n+1 rule* also predicts that the ^{1}H NMR signal for the chemically equivalent H's on CH_2Br should be split into 4 peaks by the 3 equivalent H's on the adjacent CH_3 into 4 peaks (n+1 = 3+1 = 4). We call this group of four peaks a **quartet** and it has a characteristic shape where each of the two inner peaks is about <u>three times</u> higher than each of the two outer peaks (Figure 5.28).

Figure 5.28

2-Bromopropane. The compound 2-bromopropane has two different types of H atoms (Figure 5.29).

Figure 5.29

While the H on CHBr is in a different chemical environment than any of the H's on the two CH_3 groups, the two CH_3 groups are chemically identical as we saw earlier from its ^{13}C NMR

Figure 5.27

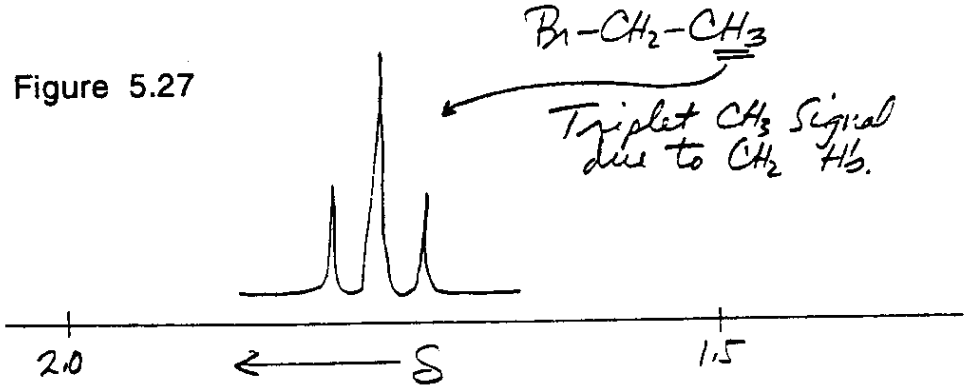


Figure 5.28

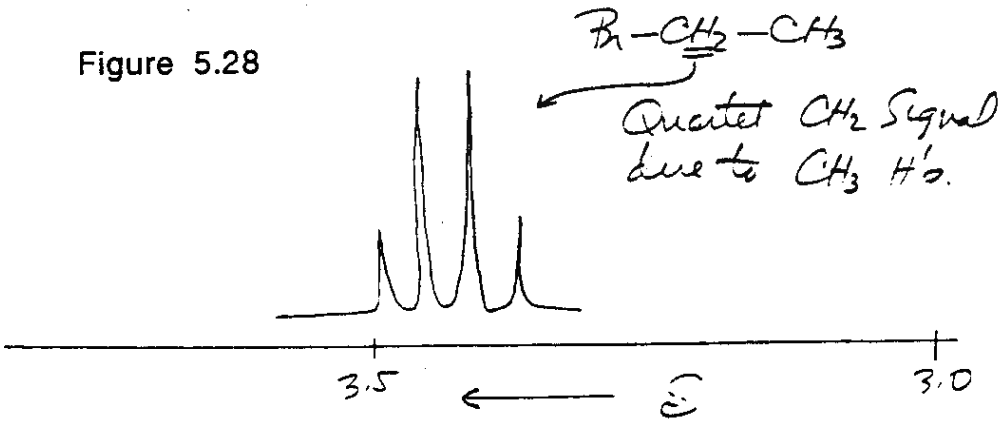
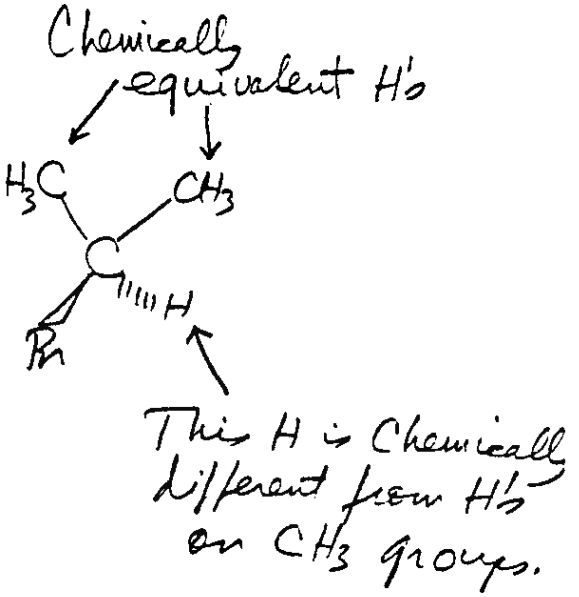


Figure 5.29



spectrum (Figure 5.22). Since C-C rotation makes all of the CH_3 H's chemically equivalent, we expect the ^{1}H NMR spectrum of 2-bromopropane to have separate signals for C<u>H</u>Br and C<u>H</u>$_3$CBr at chemical shift values similar to those of the analogous H's in the spectrum of bromoethane (Figures 5.27 or 5.28).

You can see that in addition to the internal reference peak at δ 0, the ^{1}H NMR spectrum of 2-bromopropane in Figure 5.30 shows the expected two signals. The signal at about δ 1.7 is a **doublet**, while the other signal at about δ 4.3 has seven peaks (a **septet**).

Figure 5.30

The δ 1.7 chemical shift is consistent with that for C<u>H</u>$_3$-CBr (see the spectrum for bromoethane in Figure 5.xx) while the downfield signal at δ 4.3 is deshielded as we would expect for C<u>H</u>Br.

The splitting of these two signals follows the *n+1 rule* and supports their assignment. The H on CHBr is a *septet* (n+1 = 6+1 = 7) because there are 6 (n = 6) chemically equivalent adjacent H's (those on the two CH_3 groups). In contrast, the two CH_3 groups are chemically equivalent, so they give only one NMR signal that is a doublet (n+1 = 1+1 = 2) because of the single H (n = 1) on the adjacent CHBr group.

1-Bromopropane. Based on our analyses of bromoethane and 2-bromopropane, we would predict that 1-bromopropane (Figure 5.31) should give a ^{1}H NMR spectrum with three signals that correspond to the <u>H</u>'s in the C<u>H</u>$_3$-C, C-C<u>H</u>$_2$-C, and C<u>H</u>$_2$Br groups.

Figure 5.31

We also expect Br to affect chemical shifts as we previously observed for bromoethane and 2-bromopropane causing <u>H</u>'s on C<u>H</u>$_2$Br to appear at lowest field (largest δ). Those on C<u>H</u>$_3$-C furthest from Br should appear at the highest field (smallest δ), while those on C-C<u>H</u>$_2$-C should be between these other two signals.

The spectrum of 1-bromopropane in Figure 5.31a confirms these predictions.

Figure 5.31a

The highest field signal is for CH_3 (about δ 1.0) and it is split into a *triplet* by the 2 (n = 2) adjacent chemically equivalent H's on its bonded CH_2 group. Similarly, the lowest field signal, for CH_2Br (about δ 3.4), is also split into a *triplet* by the 2 H's of the same CH_2 group.

Note that the chemical shift of this lowest field signal (δ 3.4) is virtually identical to that of CH_2Br in bromoethane. In contrast, the chemical shift for CH_3 in 1-bromopropane (δ 1.0) is significantly less than that for CH_3 in bromoethane or 2-bromopropane (both about δ 1.7). The

Figure 5.30 $CH_3\overset{Br}{\underset{|}{C}}HCH_3$

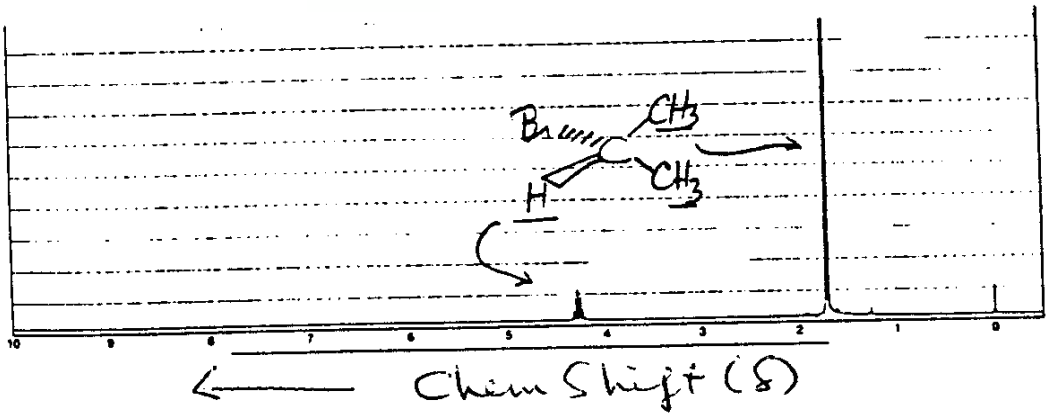


Figure 5.31

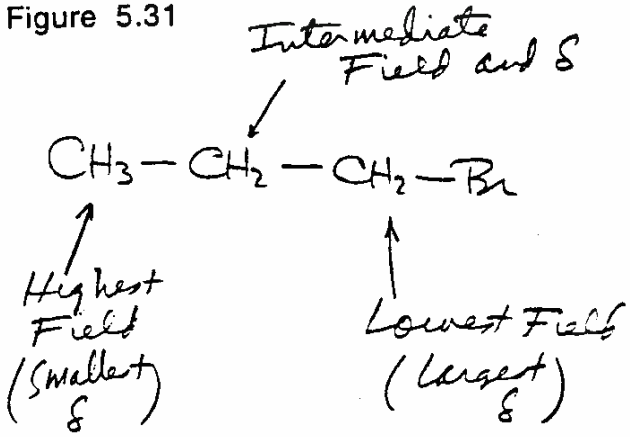
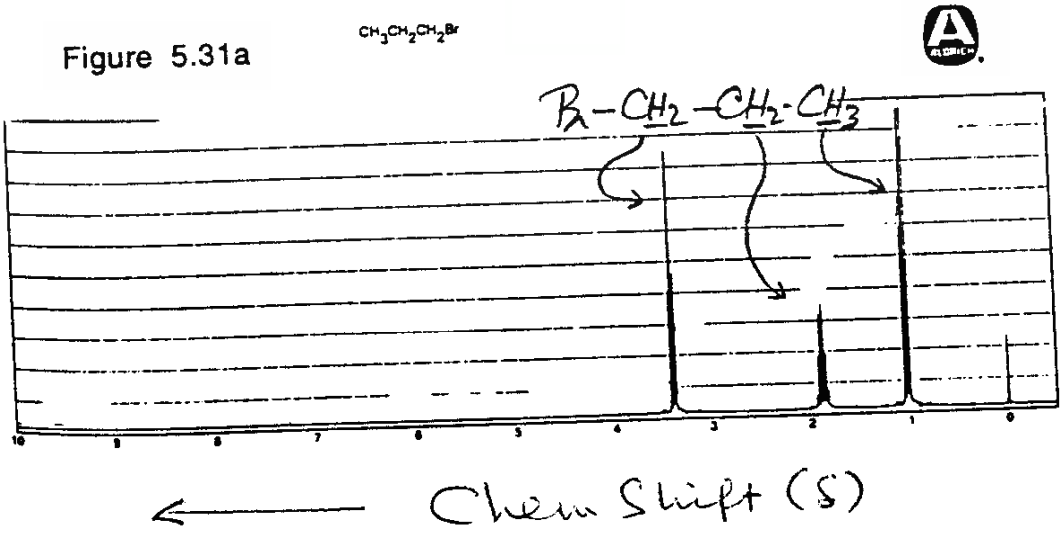


Figure 5.31a $CH_3CH_2CH_2Br$



high electronegativity of Br has less influence on CH_3 in 1-bromopropane than in these other two compounds because Br is further from CH_3 in 1-bromopropane.

The splitting pattern for the CH_2 group results from the H's on <u>both</u> the adjacent CH_3 and CH_2Br groups. While the pattern turns out to be a **sextet** (n+1 = 5+1 = 6) consistent with the total of 5 (n = 5) adjacent H's on these two groups, the *n+1 rule* cannot generally be applied in this way to this type of splitting situation. When the ^1H NMR signal of an H (or set of chemically equivalent H's) on a C is split by H's on two or more adjacent C atoms *that are chemically different*, the observed splitting pattern may not always appear to follow the *n+1 rule*. We discuss this further in Appendix xx.(?)

Aside about this (?) xxxx

The Origin of ^1H NMR Signals. ^1H atoms in organic molecules absorb rf energy and give NMR signals because each ^1H atom has two different **nuclear spin states** that have different energy values in a magnetic field (Figure 5.xx).

Figure 5.xx

The number of ^1H nuclei in each spin state is almost equal because the energy difference between these states is small, but slightly more nuclei are in the lower energy spin state than in the higher energy spin state. The chemical shift of a peak in an NMR spectrum reflects the amount of energy (ΔE) required to excite the specific ^1H nucleus from its lower energy nuclear spin state to its higher energy nuclear spin state. ΔE depends not only on the magnitude of the magnetic field, but also on the chemical environment of each ^1H atom. As a result, chemically non-equivalent ^1H atoms give signals with different chemical shifts.

The Origin of Signal Splitting in ^1H NMR Spectra. The two different spin states of ^1H atoms are also responsible for the n+1 splitting of ^1H NMR signals that we have just described. For example, $HCCl_2$-CBr_2H should give a ^1H NMR spectrum with two ^1H NMR signals since it has two chemically different H's, and the n+1 rule predicts that each signal should be a doublet (n+1 = 1+1 = 2) because each CH group has one H atom (n = 1) on its adjacent C.

The doublet pattern for $\underline{H}_a$ in $\underline{H}_aCCl_2$-CBr_2H_b arises because H_b has two spin states that we symbolize ↑ and ↓. $H_b(\uparrow)$ and $H_b(\downarrow)$ have slightly different effects on the rf energy absorbed by $\underline{H}_a$ so we see two different peaks (a doublet) for $\underline{H}_a$. Similarly, the $\underline{H}_b$ doublet signal arises because $H_a(\uparrow)$ has a slightly different effect than $H_a(\downarrow)$ on the rf energy absorbed by $\underline{H}_b$. Since an NMR signal is due to the existence of *nuclear spin states*, for the atom giving the signal, and

since it is split due to different *nuclear spin states* of adjacent H atoms, this signal splitting phenomenon is generally referred to as **spin-splitting** or **spin-spin-splitting**.

(do a triplet or quartet? as an aside?)

Spin-Spin-Splitting in ^{13}C NMR Spectra

Why did we see no spin-spin-splitting of signals in ^{13}C NMR spectra?

^{1}H-^{13}C Spin-Spin-Splitting. ^{1}H atoms should split ^{13}C NMR signals in ^{13}C NMR spectra for the same reasons that they split ^{1}H peaks in ^{1}H NMR spectra . However we saw no splitting of peaks in the ^{13}C NMR spectra that we showed earlier. The reason that ^{1}H-^{13}C spin-spin-splitting does not occur in these ^{13}C NMR spectra is because they were obtained using the **proton decoupled mode** of the ^{13}C NMR spectrometer. This electronic mode of operation prevents ^{1}H nuclei from splitting ^{13}C NMR signals of ^{13}C atoms in the same molecule. Sometimes it is useful to see this ^{1}H-^{13}C spin-splitting and ^{13}C spectra can be obtained with *proton decoupling* turned off. We show an example of ^{13}C spectra obtained with and without proton decoupling in Figure 5.32.

Figure 5.32

Organic chemists use *proton decoupling* to obtain ^{13}C NMR spectra because ^{1}H-^{13}C splitting is large and complicates a ^{13}C NMR spectrum (Figure 5.32). It is useful to see only one NMR signal for each chemically non-equivalent ^{13}C atom. Because the detailed structural information that spin-spin-splitting provides about neighboring atoms is also present in ^{1}H NMR spectra, the information from both ^{1}H and ^{13}C NMR spectra (along with the mass spectrum of a compound) often lets us determine the chemical structure of an organic compound.

^{13}C-^{13}C Spin-Spin-Splitting in ^{13}C NMR Spectra. ^{13}C atoms in organic compounds give NMR signals because like ^{1}H atoms they have two nuclear spin states with different energies when they are in a magnetic field. This means that ^{13}C atoms should split NMR signals of their bonded ^{13}C atoms, but we do not see such splitting. Because the natural abundance of ^{13}C is only about 1%, each ^{13}C atom in an organic molecule is almost always bonded to ^{12}C atoms that have no nuclear spins. As a result, ^{12}C atoms do not affect the energy difference between the lower and higher spin states of ^{13}C atoms so we see only single peaks for ^{13}C atoms with chemical shifts that depend just on their chemical environment and the magnitude of the magnetic field of the NMR spectrometer (Figure 5.31b).

Figure 5.31b

Figure 5.32

This figure will include two ^{13}C NMR spectra of the same simple organic compound. One spectrum will have been obtained using the spectrometer in the proton spin decoupled mode while the other spectrum will show proton spin coupling to ^{13}C.

Figure 5.31b

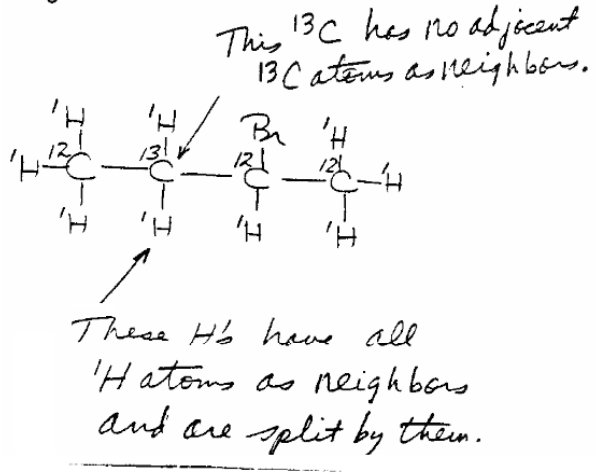


Figure 5.32a $CH_3CH_2\overset{Cl}{\underset{|}{C}}HCH_3$

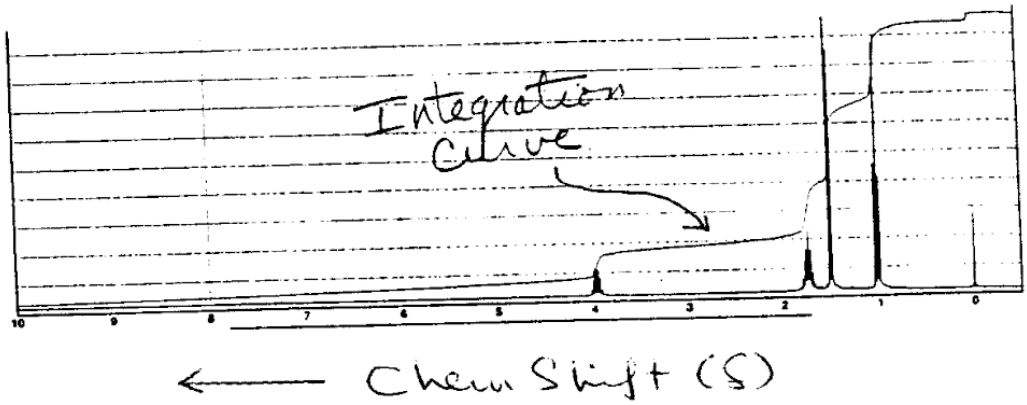
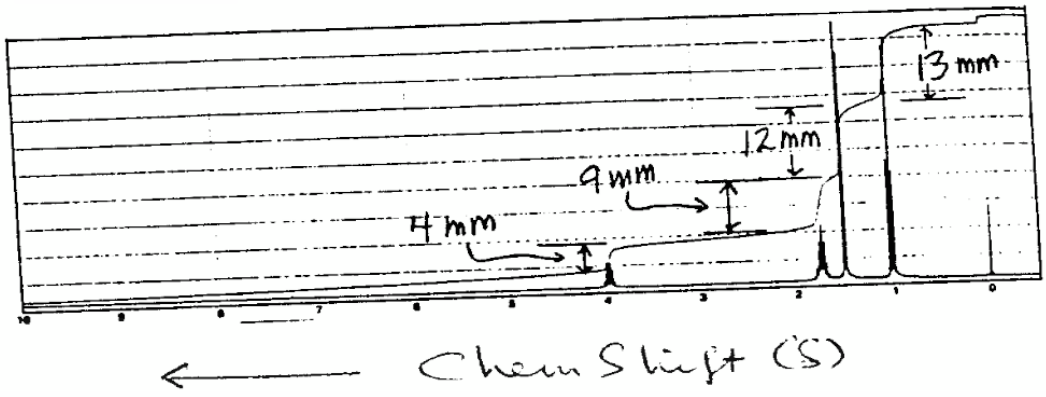


Figure 5.33 $CH_3CH_2\overset{Cl}{\underset{|}{C}}HCH_3$



The Relative Intensity of NMR Signals (5.6D)

So far we have not discussed the significance of the *height* or *intensity* of signals in NMR spectra.

Signal Intensities in ^{1}H NMR Spectra. The *signal intensity* (the total area under a signal) in an ^{1}H NMR spectra is directly proportional to the number of H atoms giving rise to that signal. The computer in a ^{1}H NMR spectrometer that gathers the data also measures signal areas and can be programmed to display them as printed numbers and as **integration curves** on each NMR spectrum as we show in Figure 5.32a.

Figure 5.32a

The *integration curve* is the "stair-step" line superimposed on the normal spectrum. The relative height of each "step" corresponds to the relative area of each signal, and these relative areas are directly proportional to the relative numbers of H's giving rise to each NMR signal.

Integration curves give relative ratios rather than absolute numbers of H atoms In order to use them to estimate the number of H's giving each NMR signal, we need to guess a value for the number of H's giving rise to a particular signal in the NMR spectrum. Based on that initial guess we can calculate a number of H's for each of the other signals from their relative areas. We often begin this process by guessing the number of CH_3 groups of a particular type since we can usually identify CH_3 signals as those with the highest field chemical shifts.

An Example of the Use of Integration Data. We illustrate how organic chemists use an integration curve to calculate numbers of H atoms in a molecule with the ^{1}H NMR spectrum for 2-chlorobutane in Figure 5.32a . We have reproduced that spectrum again in Figure 5.33 showing the height (in mm) of each "stair-step" measured with a ruler.

Figure 5.33

If the high field *signal (a)* is for a CH_3 group, the 12 mm height of its "stair-step" corresponds to 3 H atoms. This means that one H should give a "stair-step height" of 4 mm in this spectrum. Based on this, *signal (b)* (12 mm) is also due to 3 H's (12 mm/4 mm = 3), *signal (d)* (4 mm) is due to 1 H (4 mm/4 mm = 1), while our calculations indicate that *signal (c)* (9 mm) corresponds to 2.25 H's (9 mm/ 4 mm = 2.25).

This non-integral result for *signal (c)* can mean either our initial assumption of 3 H's for *signal (a)* was wrong, or there is inaccuracy in the measurement of the height of the stair-step for *signal (c)* (or for *signal (a)*) In this case, we know that the compound is 2-chlorobutane, and that we have correctly assigned the signals in Figure 5.32a, so one or both of our measurements is probably slightly off.

If we hadn't known the structure, we would have to consider the possibility that *signal (a)* corresponds to 12 H's in a molecular formula because on that basis the integration data then gives the integral values of

12, 9, and 4 H's for *signals (b)*, *(c)*, and *(d)*, respectively. This is a situation where mass spectral data should allow a clear choice between these two possibilities. We would expect the mass spectrum for 2-chlorobutane to show peaks at m/z values for C_4H_9Cl or its fragments, while mass spectral peaks for $C_{16}H_{36}Cl_4$ would be observed at m/z values much greater than C_4H_9Cl.

Signal Intensities in ^{13}C NMR Spectra. In contrast to signals in ^1H NMR spectra, the relative intensities of signals in ^{13}C NMR spectra are not quantitatively related to the number of ^{13}C atoms giving rise to a particular signal. The ^{13}C NMR signal intensities (areas) primarily depend on factors other than the number of atoms giving rise to that signal. These additional factors are relatively unimportant in ^1H NMR spectra, but they become dominant in ^{13}C NMR spectra causing ^{13}C NMR signal intensities to only crudely reflect the relative number of ^{13}C atoms giving rise to a particular ^{13}C NMR signal.

^1H NMR Chemical Shift (δ) Values (5.6E)

We use the symbol δ for chemical shift values in both ^1H and ^{13}C NMR spectra even though chemical shift values in ^{13}C NMR and ^1H NMR are <u>not</u> directly related to each other. In spite of this, relative ^1H NMR δ values do reflect the same type of electronic shielding and deshielding that we described for ^{13}C NMR chemical shifts. For example, we have seen that signals for H's on C-Br carbons all have larger δ values than those for H's on C's without Br just as do the ^{13}C NMR shifts for these different types of C's. The relatively high electronegativity of Br pulls electron density from its bonded C that in turn borrows electron density from attached C-H bonds.

We have summarized the effects of a variety of functional groups on ^1H chemical shifts in Table 5.3.

Table 5.3. Chemical Shift Values (δ) for C-<u>H</u> Atoms in Molecules with Functional Groups.

<u>Y Group</u>	C<u>H</u>$_3$-Y	C<u>H</u>$_3$-C-Y	RC<u>H</u>$_2$-Y	RC<u>H</u>$_2$-C-Y	R$_2$C<u>H</u>-Y	R$_2$C<u>H</u>-C-Y
CH_3	0.8	0.8	1.2	1.2	1.6	1.6
O H	3.2	1.2	3.4	1.5	3.8	1.7
O R	3.2	1.2	3.4	1.5	3.6	1.7
NH_2	2.5	1.1	2.7	1.5	3.0	1.7
NR_2	2.2	1.1	2.4	1.5	2.8	1.7
F	4.2	1.6	4.4	1.9	4.8	2.2
Cl	3.0	1.6	3.4	1.8	4.0	2.0
Br	2.7	1.8	3.4	1.9	4.1	1.9
I	2.2	1.8	3.1	1.8	4.2	2.1

These δ values are for the H atoms in CH_3, RCH_2, and R_2CH groups (the R's are simple alkyl groups) that have a functional group bonded directly to them (-Y) or are separated from the functional group by one C atom (-C-Y). The separating C atom in -C-Y is $-CR_2-$ where R's are H or simple alkyl groups. Chemical shift values for ^1H atoms on cycloalkanes depend on the size of the cycloalkane ring as we show for a series of cycloalkane rings in Figure 5.33a.

Figure 5.33a

We have provided more extensive tables of ^1H NMR δ values for a variety of organic compounds in Apppendix xx.

The TMS Reference in ^1H NMR. A common feature of the δ scales for both ^1H and ^{13}C NMR spectra is that each uses tetramethylsilane (TMS) to define δ 0. The single ^{13}C signal of TMS is the δ 0 position for the ^{13}C NMR scale, while the signal for its H's is δ 0 for the ^1H NMR scale. TMS ($(CH_3)_4Si$) has 12 H atoms that are all chemically equivalent just as all of its C's are chemically equivalent (see Figure 5.23a). As a result, these 12 H's give a single ^1H NMR signal with no spin-splitting. It is very convenient that the single internal standard TMS serves as the δ 0 reference point for both ^{13}C and ^1H NMR spectra.

The Selectivity of NMR Spectrometry. Only nuclei with magnetic moments such as ^{13}C and ^1H absorb radio frequency energy and give NMR spectra. Furthermore, when we obtain an NMR spectrum for ^{13}C, we see no signals for ^1H and *vice-versa*. While this means that we have to take separate spectra to learn about both C and H atoms in an organic molecule, this restriction provides a selectivity that permits us to obtain the maximum amount of information about one type of nucleus with a minimum of competing extraneous information from other nuclei. Neither *Infrared Spectrometry (IR)* nor *Ultraviolet-Visible Spectrometry (UV-Vis)* that we now introduce in the rest of this chapter have this selectivity.

5.7 Infrared Spectrometry

Before NMR spectrometry became routinely available in the late 1950's to study organic compounds, *infrared spectrometry (IR)* was the most important single instrumental method used by organic chemists for structure determination. While it continues to be a useful spectrometric technique, it now plays a decidely secondary role to NMR in organic structure determination.

IR spectra are relatively complex and the structural information that they provide is much less specific than that obtained from NMR spectra. On the other hand, that complexity makes an IR spectrum a "molecular fingerprint" since no two organic compounds have exactly the same IR

Figure 5.33a

Chemical Shift (δ) Values for ^1H Atoms on Cycloalkane Rings

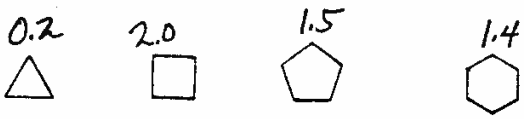


Figure 5.34 Molecular Vibrations

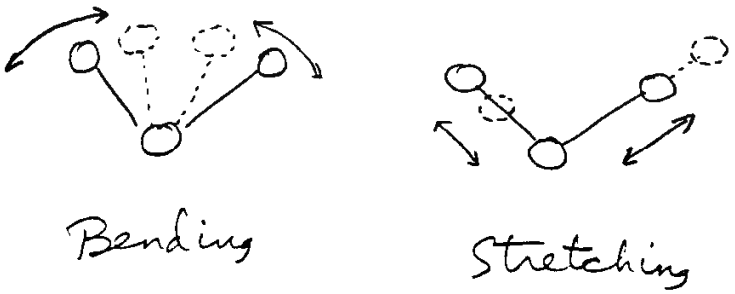
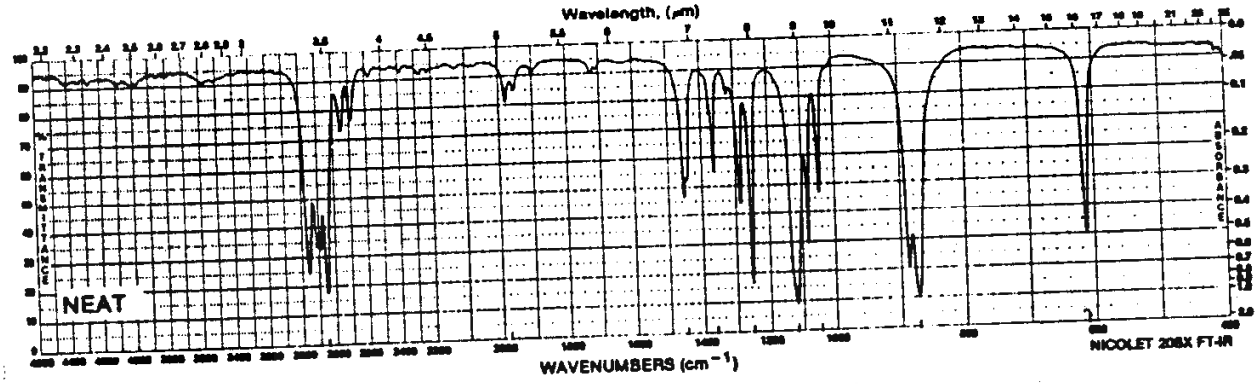


Figure 5.35 15482-2 CAS [123-91-1] 1,4-Dioxane, 99 + %



spectra. As a result, when the IR spectrum of an unknown compound identically matches that of a pure sample of a known compound we can unambiguously conclude that our unknown compound has the same structure as the known compound.

Infrared Energy Causes Molecular Vibrations **(5.7A)**

We obtain infrared spectra of molecules by irradiating them with *infrared energy* of the electromagnetic spectrum (see Figure 5.13). This energy, associated with our sense of heat, causes **molecular vibrations** where chemical bonds in molecules **bend** and **stretch** as we illustrate in Figure 5.34.

Figure 5.34

Different kinds of chemical bonds, such as C-H and C-C bonds, require significantly different amounts of energy to *stretch* and/or *bend*. However, the energy required to stretch various C-H bonds at tetrahedral carbon, for example, shows only a small dependence on molecular structure. For this reason, while it is possible to identify signals in an IR spectrum as C-H stretching, it is difficult to distinguish between different kinds of C-H bonds making IR spectra much less selective than NMR spectra.

The Infrared Spectrometer **(5.7B)**

Chemists obtain IR spectra using an **infrared spectrometer** that has the same fundamental components that we illustrated in Figure 5.16. While their physical appearance differs dramatically from those of NMR spectrometers, the basic components of IR spectrometers also include a *source* of *electromagnetic energy*, the *sample chamber*, a *detector*, and a *computer*. In contrast with NMR spectrometers, IR spectrometers do not have magnets since a magnetic field is not necessary for IR energy absorption by a molecule.

IR Sample Cells. Because IR energy is "heat", the sample container cannot be made of glass. Glass does not absorb radio waves used in ^{13}C and ^{1}H NMR because it is primarily polymeric silicon dioxide ($(SiO_2)_x$) and has no C or H atoms. However it readily absorbs IR energy causing Si-O bonds to bend and stretch. You can convince yourself of this by touching a glass container filled with a hot liquid. As a result, IR sample cells are often made of inorganic salts such as solid NaCl, KCl, or KBr because these salts have no chemical bonds to absorb infrared radiation since they consist of cations (Na^+ and K^+) and anions (Cl^- and Br^-) held together by electrostatic attraction.

Solvents for IR Samples. Since NaCl, KCl, and KBr are partially soluble in a variety of organic solvents, and because organic solvents have chemical bonds that absorb IR radiation,

chemists often obtain IR spectra using pure solid or liquid samples of the organic compound. When this is not possible, they use solvents such as $CHCl_3$ or CCl_4 since they have only a few types of chemical bonds that absorb IR energy in regions of IR spectra that usually do not interfere with the most important spectral regions for other organic compounds.

***IR Spectra* (5.7C)**

The *detector* in an IR spectrometer senses absorption of IR radiation by the organic compound in the sample cell and displays it as a series of "negative" or "upside-down" peaks at the specific energy values absorbed as we show in Figure 5.35 for the cyclic ether *1,4-dioxane*.

Figure 5.35

The Horizontal Axis. The range of electromagnetic radiation that the IR spectrometer uses is displayed on the horizontal axis of the spectrum using a quantity called the **wavenumber** ($\bar{\nu}$) that is defined by equation (3) where λ is the wavelength of the electromagntic radiation (see Figure 5.15).

$$\bar{\nu} = 1/\lambda \qquad (\lambda \text{ in units of cm}) \qquad (3)$$

Since λ in units of centimeters (cm) are used in this equation, *wavenumbers* have units of cm^{-1} that chemists call "reciprocal centimeters" or "centimeters to the -1". *Wavenumbers* are directly proportional to *frequency* (ν) because the frequency of electromagnetic radiation ν is equal to c/λ (c is the speed of light) as we show in equation (4).

$$\bar{\nu} = \nu/c \qquad (4)$$

Energy and frequency are also directly proportional (see equation (1)), so *wavenumbers* are also directly proportional to energy.

Some IR spectra also show the wavelength λ of the electromagnetic radiation on their upper horizontal axis in units of micrometers (μm) that are also called **microns**. Since 1 cm = 10^4 μm, the relationship between $\bar{\nu}$ (in cm^{-1}) and λ (in μm) is given by equation (5).

$$\bar{\nu} = 10^4/\lambda \qquad (\lambda \text{ in units of } \mu m) \qquad (5)$$

The range of wavelengths (λ) for a typical IR spectrum is about 2.2 to 25 μm and this corresponds to a range of $\bar{\nu}$ values from 4600 to 400 cm^{-1}. The highest energy IR radiation is at the left end of the IR spectrum as you view it and the lowest energy IR radiation is at its right

end. While horizontal axes of IR spectra are linear in $\bar{\nu}$, they are usually divided into three separate regions that have different scale factors. This permits greater resolution of all of the IR signals that are closer together in some regions than in others.

The Vertical Axis. The *vertical axis* of an IR spectrum is linear in a quantity called **%-Transmittance** (**%T**) as shown on the left-hand vertical axis in Figure 5.xx. *%T* is the percentage of IR radiation that passes through the sample at each value of λ or $\bar{\nu}$. Organic chemists do not use *%T* values printed directly on the spectrum without correction because for practical reasons they adjust the spectrometer so that the 100%T **baseline** actually appears between the printed values of 90 to 95 %T. The right hand vertical axis of an IR spectrum is calibrated in **Absorbance** (**A**). *Absorbance* doesn't have specific units because it is defined in terms of logarithms as we show in equation (6) where **T** is **Transmittance** ($T = \%T/100$).

.

$$A = \log_{10}(1/T) \qquad (6)$$

For routine purposes, we do not describe the intensity of IR peaks in either %T or A, but simply as *strong* (**s**), *medium* (**m**), or *weak* (**w**). This is because relative peak intensity does not depend on the relative number of bonds that are stretching or bending. Relative peak intensities depend on a number of factors including changes in *molecular dipole moments* (Chapter 3) associated with molecular vibrations so they are not quantitatively useful in making specific structural assignments.

IR Stretching and Bending Signals **(5.7D)**

All chemical bonds bend and stretch, and there is region of infrared radiation corresponding to each of these types of motion for each chemical bond.

Since these regions often overlap, IR spectra are complex even for relatively simple molecules. There are also discrete IR frequencies corresponding to **coupled** molecular vibrations that result from simultaneous motions of two or more bonds connected to the same atom.

These aspects of IR spectra make it difficult to use them to assign specific molecular structures. However, types of chemical bonds or types of functional groups give characteristic IR absorption signals that appear in the same region of an IR spectrum more or less independent of the rest of the molecular structure. This allows us to use IR spectra to confirm the presence or absence of specific types of bonds and functional groups.

Characteristic IR Regions. We illustrate the IR spectral regions corresponding to stretching and bending of some specific types of chemical bonds in Figure 5.38.

Figure 5.38

We described molecules with C-H, N-H, and O-H *single bonds* in Chapters 1-3, and we briefly mentioned organic molecules that contain *double bonds* such as C=C, C=O, and C=N, and *triple bonds* such as C≡C, and C≡N, in Chapter 1.

We will discuss molecules with multiple bonds in greater detail later in the text and discuss their IR spectral characteristics at that time. We will see that the distinct spectral regions for double and triple bond stretching vibrations make IR spectrometry particularly useful for identifying their presence in organic molecules. At this point we use IR spectra for some alkanes, alcohols, and amines to illustrate characteristic differences in C-H, N-H and O-H stretching frequencies that are observed for most of these types of compounds.

Alkanes. The IR spectra of *dodecane* (CH_3-$(CH_2)_{10}$-CH_3) and of *2,2,4-trimethylpentane* ((CH_3)$_3$C-CH_2-$CH(CH_3)_2$) in Figure 5.38a both show strong absorption between 3000 and 2800 cm^{-1} due to C-H stretching.

Figure 5.38a

In addition, they show C-H bending vibrations centered at about 1400 cm^{-1}. There are other absorption peaks in each spectrum that we do not specifically identify that involve complex coupled vibrations specific to the individual molecules.

Alcohols. The alcohol *2,2,4-trimethyl-1-pentanol* in Figure 5.38b contains many C-H bonds similar to those in the two alkanes that we just discussed.

Figure 5.38b

As a result, its IR spectrum shows the characteristic C-H stretching vibrations around 2900 cm^{-1} and the C-H bending vibrations around 1400 cm^{-1}.

In addition, there is also a broad absorption **band** (or signal) centered near 3300 cm^{-1} that we did not see in the IR spectra of the alkanes. This band is the O-H stretching vibration that is characteristic of many O-H bonds as you can see in the IR spectra of methanol and ethanol (Figure 5.38c).

Figure 5.38c

Figure 5.38

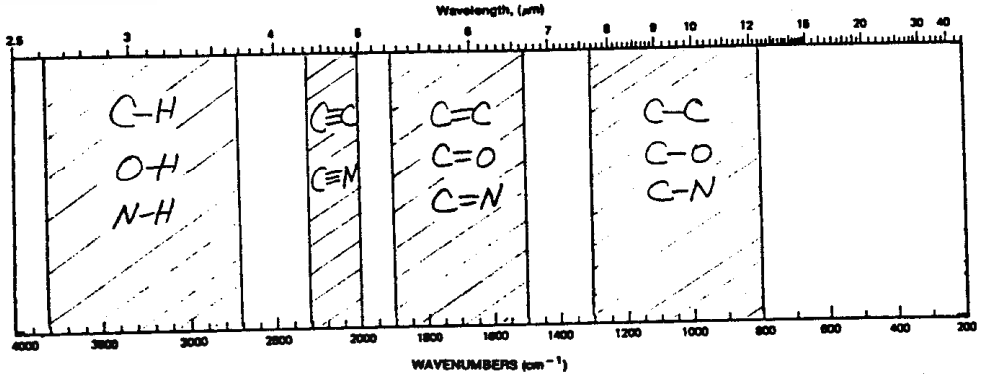
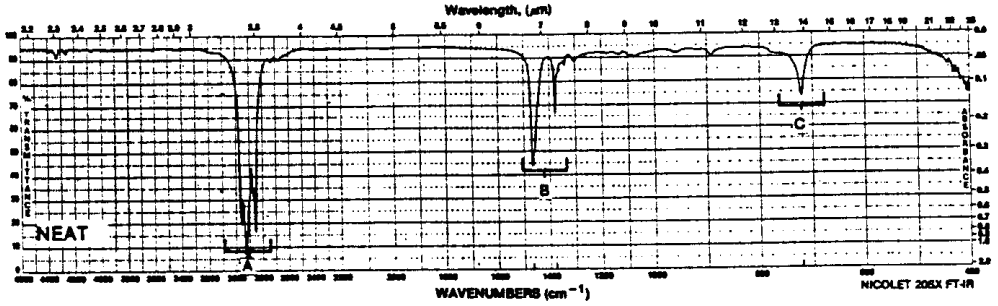


Figure 5.38a D22110-4 *CAS [112-40-3]* $CH_3(CH_2)_{10}CH_3$
Dodecane, 99%



15501-2 *CAS [540-84-1]* $CH_3CH(CH_3)CH_2C(CH_3)_3$
2,2,4-Trimethylpentane, 99%

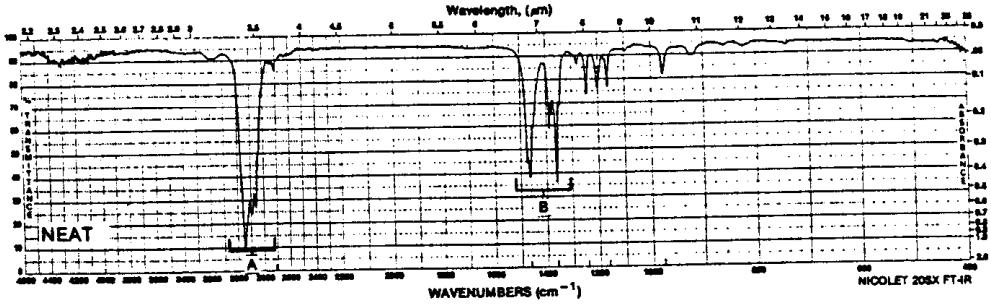


Figure 5.38b 18667-6 *CAS [16325-63-6]* $(CH_3)_3CCH_2CH(CH_3)CH_2OH$
2,4,4-Trimethyl-1-pentanol, 98%

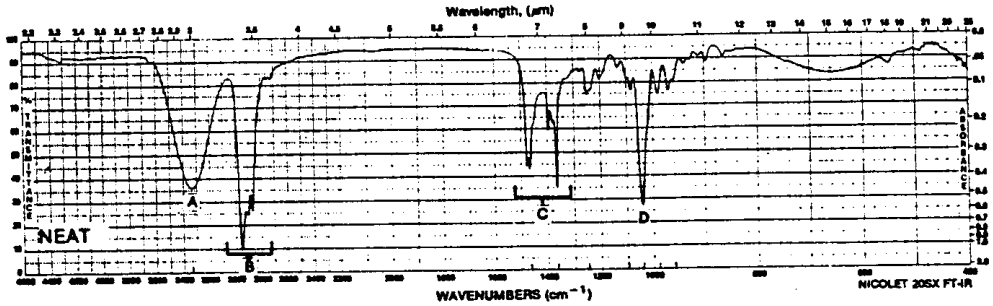
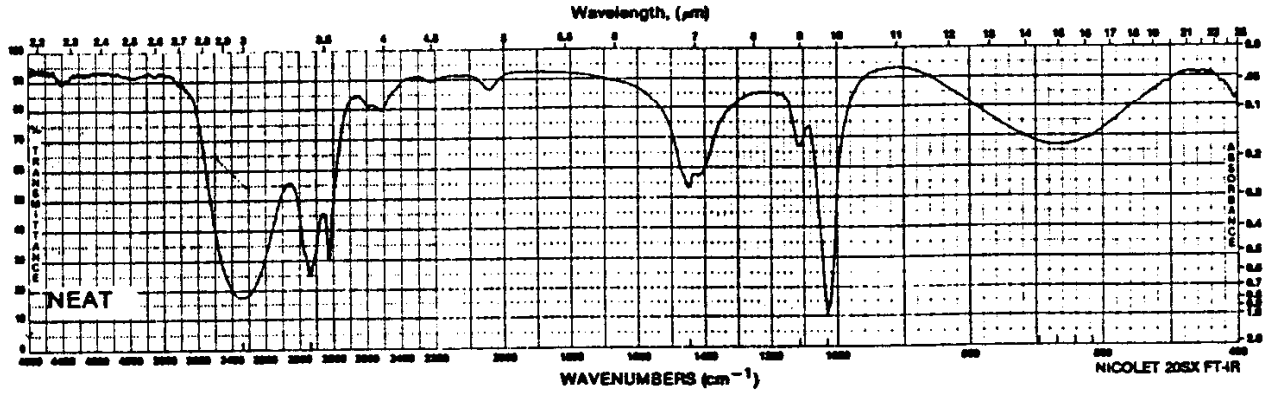


Figure 5.38c 15490-3 *CAS [67-56-1]*
Methyl alcohol, 99.9% CH_3OH



18738-0 *CAS [64-17-5]*
Ethyl alcohol, anhydrous, CH_3CH_2OH

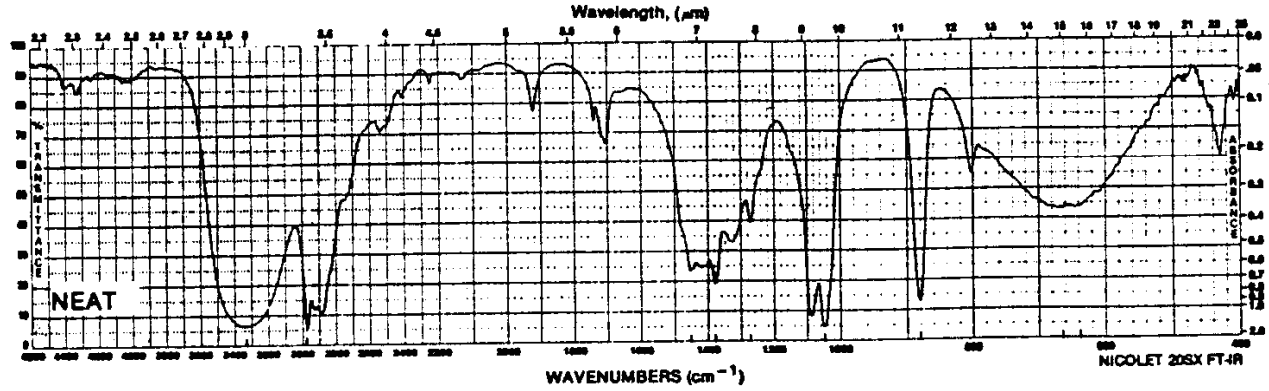
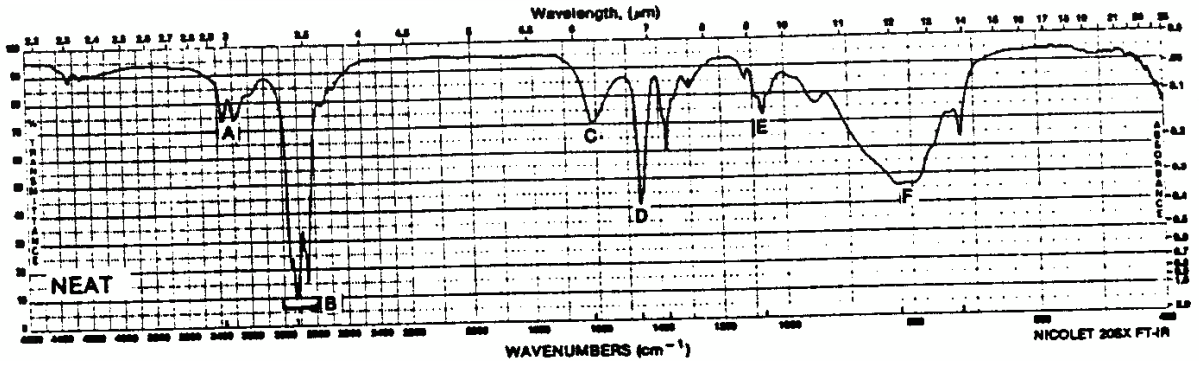


Figure 5.38d O-580-2 *CAS [111-86-4]*
Octylamine, 97% $CH_3(CH_2)_7NH_2$



Although less useful for structure determination purposes, the C-O stretching vibration is relatively strong and appears in the vicinity of 1100 to 1000 cm^{-1} in these alcohol IR spectra.

Amines. The IR spectrum of *octanamine* in Figure 5.38d shows two N-H *stretching vibrations* for the NH_2 group at about 3400 and 3300 cm^{-1}, an N-H *bend* near 1600 cm^{-1}, a weak C-N *stretching* band at about 1100 cm^{-1}, and a broad band at about 800 cm^{-1} due to a vibration called the **N-H wag**.

Figure 5.38d

In addition to these bands, you should be able to pick out the characteristic C-H *stretching* and *bending* bands that we described earlier for alkanes and alcohols.

More IR Later. It is important to repeat that some of the most powerful applications of IR spectrometry involve its use in studying compounds with multiple bonds. The features mentioned above are important and are often used to confirm structures, but they represent only a small sample of the utility of this spectrometric method. Detailed tabulations of IR absorption frequencies (and wavelengths) for all types of chemical bonds are given in a variety of books describing IR spectrometry and some are included in Appendix xx.

5.8 UV-Visible Spectrometry

The final type of spectrometry that we discuss in this chapter uses electromagnetic radiation in the *ultraviolet (UV)* and *visible (Vis)* regions (Figure 5.13). In contrast with the complexity of IR spectra, and the detailed information provided by NMR and Mass spectra, *UV-Vis spectra* are often very simple and sometimes contain only a single broad peak. It is possible for different molecules to have virtually identical *UV-Vis* spectra, while many molecules have no *UV-Vis* spectra because they lack structural features required for a molecule to absorb electromagnetic radiation in the *ultraviolet* or *visible* frequency ranges.

Structural Requirements for UV-Vis Spectra **(5.8A)**

UV-Vis energy absorption occurs most often when a molecule contains two or more *multiple bonds* (C=C, C≡C, C=O, C=N, and/or C≡N) that alternate with single bonds (usually C-C bonds) in an arrangement such as C=C-C=C-C=C. We call molecules with such alternating single and multiple bonds **conjugated**, and they also have special physical and chemical properties, in addition to *UV-Vis* spectra, that we present and discuss in Chapter 11(?). Although we will defer our detailed discussion of *UV-Vis* spectrometry to Chapter 11, we outline its basic principles here so you can compare them with those of the three other major organic spectrometric methods that we have already studied.

***UV and Visible Radiation Excites Electrons* (5.8B)**

The *source* of a *UV-Vis* spectrometer emits electromagnetic energy ranging from *visible* to the more energetic *ultraviolet (UV)* radiation (Figure 5.13). *UV* or *visible* radiation excites electrons from bonding Π molecular orbitals (MO's) into antibonding Π MO's (Chapter 1). However UV or visible light energy of conventional UV-Vis spectrometers is not sufficiently energetic to excite electrons in most C-C, C-O, C-N, C-H, O-H, or N-H single bonds. While excitation of electrons in single bonds usually causes bond breakage and destruction of the molecule, electronic excitation processes involving *conjugated* multiple bonds are usually reversible. After excitation, the excited electrons return to their stable bonding orbitals so the process of taking the UV-Vis spectrum is non-destructive.

***The UV-Vis Spectrometer* (5.8C)**

UV-Vis spectrometers have components analogous to those of other spectrometers using electromagnetic radiation (Figure 5.16) except, like IR spectrometers, they lack a magnet that is unique to NMR spectrometers. Their *wavelength* range extends from 200 nm (200 nanometers) to about 780 nm (1 nm = 10^{-9} meters (m)). The shorter wavelength region below 200 nm is also called UV radiation, but it is not routinely used by organic chemists because atmospheric oxygen absorbs UV radiation below 200 nm. The *UV region* of interest to organic chemists is between 200 and 380 nm, while radiation from 380 nm to 780 defines the *visible region* since the human eye can detect it. We show the colors associated with visible electromagnetic radiation in Figure 5.38e.

Figure 5.38e

UV-Vis Sample Cells. Since the full range of UV-Visible radiation passes through **quartz glass** without being absorbed this material is used for most *UV-Vis cells*. The more common **Pyrex glass**, that most laboratory glassware is made of, transmits electromagnetic radiation with wavelengths longer than 350 nm, but is not routinely used in UV-Vis sample cells because it absorbs light from 200 to 350 nm that is an important range of wavelengths for many organic compounds.

Solvents for UV-Vis Spectrometry. Most organic compounds without multiple bonds do not absorb UV-Visible light, so many solvents are available that do not interfere with UV-Vis spectra of organic compounds. Three that dissolve a wide range of organic compounds are *cyclohexane*, "*95% ethanol*" (95% *ethanol*, 5% *water*), and *1,4-dioxane*. Cyclohexane is non-polar and dissolves non-polar compounds. In contrast, both ethanol and water are highly polar

Figure 5.38e Wavelength Range of Visible Radiation

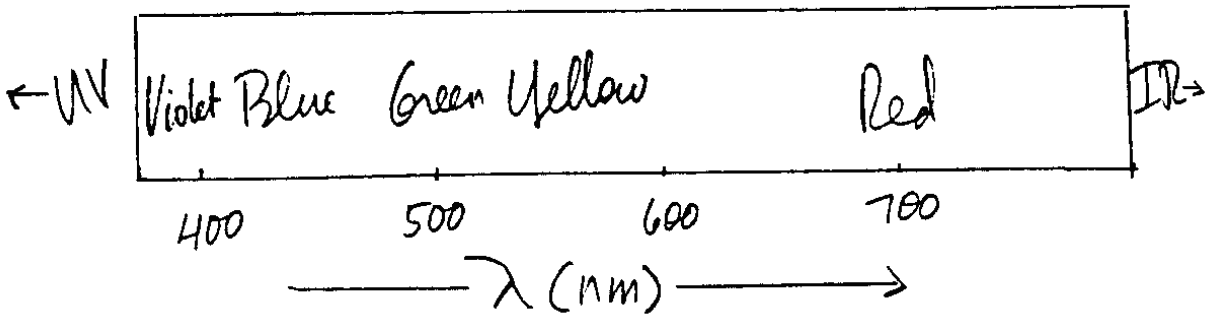
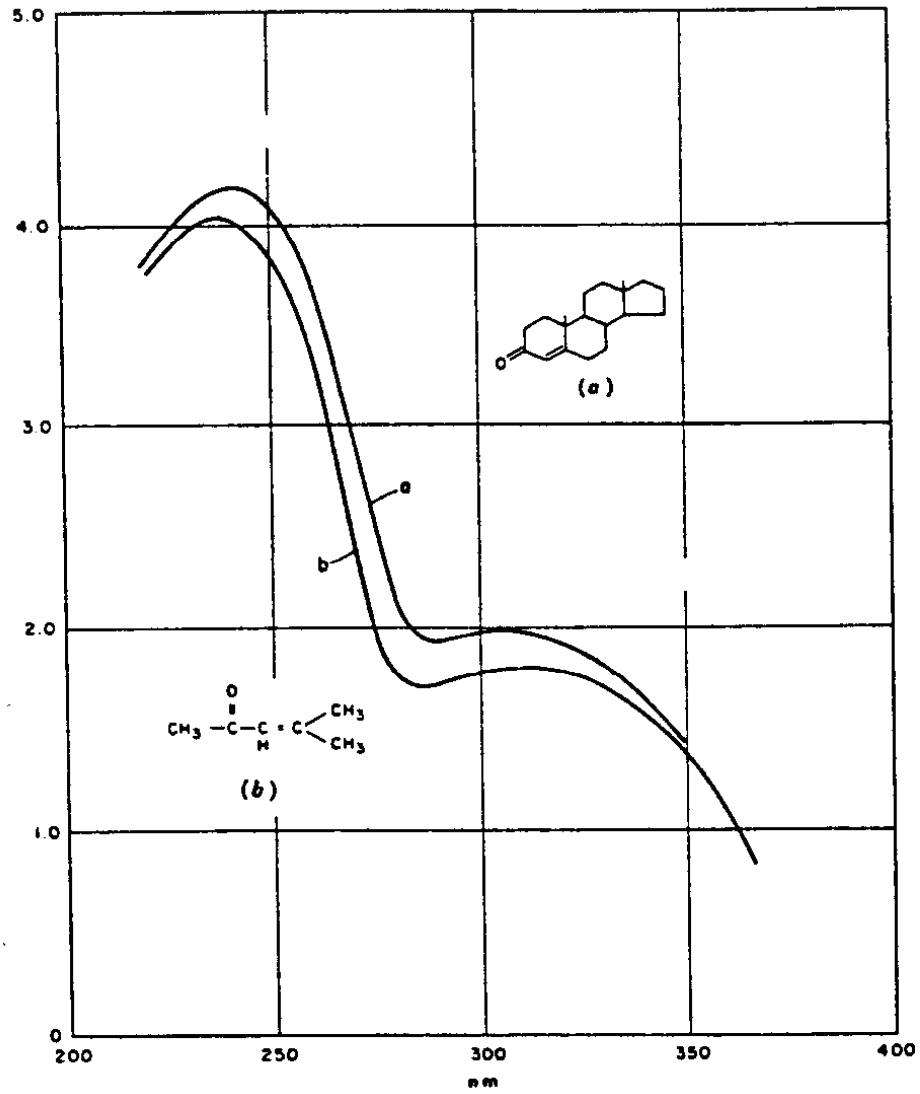


Figure 5.39



so *95% ethanol* dissolves polar compounds as we described in Chapter 3. *Dioxane* is intermediate in polarity and a choice between it or 95% ethanol often depends on whether or not the presence of OH groups in 95% ethanol is of concern.

***UV-Vis Spectra* (5.8D)**

The detector of the UV-Vis spectrometer senses absorption of UV or visible radiation by the organic compound in the sample cell and displays this absorption in a spectrum like those in Figure 5.39.

Figure 5.39

The UV-Vis spectra in this figure are very similar even though they are for two very different molecules. This occurs because they depend primarily on the presence of the same conjugated multiple bond sequence O=C-C=C in each molecule.

The Horizontal Axis. Unlike IR spectra where the baseline (100%-Transmittance of light) is at the top of the spectrum (see Figure 5.35), a typical UV-Vis spectrum has its baseline (100%-T) at the bottom. As a result, peaks increase in intensity as UV-Vis energy is absorbed by the sample. UV-Vis spectra usually display the wavelength of the UV or visible light on the horizontal axis in nanometers (nm) (1 nm = 10^{-9} meters = 10^{-3} μm).

> ***Angstroms***. Older books and chemical literature often describe UV-Vis wavelengths in Å (angstroms). We defined the Å in Chapter 3 as 1 Å = 10^{-8} cm so 1 nm = 10 Å . As a result, the UV-Vis range of 200 to 780 nm is 2000 to 7800 Å.

Since UV-Vis spectra are often very simple with large wavelength regions showing no absorption of UV or visible radiation, they do not have a standard spectral presentation such as those for NMR or IR spectra. NMR spectra always show the same chemical shift range (δ0 to δ10 for ^{1}H NMR or δ0 to δ200 for ^{13}C NMR), and IR spectra usually show the full wavenumber range of 4600 to 400 cm^{-1}. In contrast, UV-Vis spectra generally show only the portion of the wavelength range where there is a significant absorption of electromagnetic radiation.

The Vertical Axis. While IR spectra have vertical axes that are linear in %T, UV-Vis spectra usually have vertical axes that are linear either in *absorbance (A)* or *log A*. We previously showed the relationship between *A* and *T* in equation (6). The use of *A* or *log A* units facilitates our use of UV-Vis spectra to quantitatively measure the amount of a compound giving rise to a

particular peak since the concentration (c) of the compound is linearly related to *A* according to **Beers Law** (equation (7)) .

$$A = \varepsilon\ c\ l \qquad (7)$$

where A = absorbance
c = concentration of sample in mol/L
l = pathlength of the cell
ε = molar absorptivity

Molar absorptivity (ε) is a proportionality constant that makes *A* at a particular wavelength equal to the product of *c* and *l*. The ε value at a particular wavelength is constant over a wide range of concentration values for the sample in a particular solvent so you can consider it a physical property of the sample. Chemists use log A values rather than absorbance (A) values as a matter of convenience to adjust the vertical scale for greater clarity in display.

For organic chemists, important features of a UV-Vis spectrum include the wavelength positions of the peak maxima called the λ_{max} values (pronounced "lambda max" values) for the compound, and the *molar absorptivity* values at each λ_{max} (calculated from *A* or *log A* values), called the ε_{max} values. Since UV-Vis spectra are usually simple, the absorption peaks for a compound are often reported simply as a series of pairs of λ_{max} and ε_{max} values.

> ***UV-Vis Spectrometry in Medicine***. Because of the quantitative relationship between absorbance (A) and concentration (c), UV-Vis spectrometry is the basis of many clinical instruments used for diagnostic medical purposes to determine the presence and concentrations of a variety of substances in the body. This may seem surprising to you because not all compounds give UV-Vis spectra. However, analytical chemists, working with organic chemists and biochemists, have discovered a variety of specific chemical reactions that make medically important organic substances from the body visible by UV-Vis spectrometry.

More UV-Vis Later. We will see later in this text, that both λ_{max} and ε_{max} values give information about the structure of organic compounds. However we do not yet have the necessary chemical background to use UV-Vis spectrometry as an aid to structure determination since its greatest use is with compounds that have *conjugated multiple bonds*. After we introduce these compounds in Chapter 12, we will present and discuss their UV-Vis spectra along with those of other molecules. At that time we will also provide a more detailed presentation of the physical phenomena that occur when a molecule absorbs UV-Vis radiation.

Chapter Review

Spectrometry in Organic Chemistry

(1) Mass spectrometry (MS), nuclear magnetic resonance spectrometry (NMR), infrared spectrometry (IR), and ultraviolet-visible spectrometry (UV-Vis) are used to determine molecular structures of organic compounds. (2) Analysis of a compound using one of these methods of spectrometry generates a spectrum with peaks or signals that give information about molecular structure.

Mass Spectrometry

(1) A mass spectrometer bombards molecules with high energy electrons causing them to lose one electron and become positively charged molecular ions ($M^{+\bullet}$). (2) Molecular ions have excess energy and fragment to lower mass positive ions (fragment ions) and neutral radicals. (3) Mass spectra show a line (peak) for each positive ion at its m/z (mass/charge) value. (4) The m/z value of the molecular ion gives the mass of the original molecule. (5) M/z values of fragment ions, and the molecular ion, aid in determination of molecular structure. (6) The m/z value of a fragment or molecular ion reflects its specific isotopic composition. (7) Natural abundance of 1% ^{13}C in organic compounds gives small M + 1 peaks. (8) Isotopes of other atoms also lead to characteristic "isotope" peaks. (9) Branching and functional groups cause characteristic fragmentation reactions that aid in molecular structure determination.

Spectrometry Using Electromagnetic Radiation

(1) NMR, IR, and UV-Vis spectrometry use energy from the electromagnetic spectrum. (2) The electromagnetic spectrum includes X-rays, ultraviolet radiation, visible light, infrared radiation (heat), microwaves, and radio and television waves listed in order of decreasing energy. (3) Electromagnetic radiation comes in bundles or packets of energy called photons. (4) Photons of electromagnetic radiation are usually described in terms of their frequency (ν) and/or wavelength (λ). (5) Energy of electromagnetic radiation is directly proportional to its frequency (ν) ($E = h\nu$), and inversely proportional to its wavelength (λ) ($E = hc/\lambda$). (6) All spectrometers using electromagnetic radiation have a *source* of electromagnetic radiation, a *sample compartment* for the organic sample, a *detector* to analyze electromagnetic radiation passing through or resulting from the sample, a *computer* to analyze the data from the detector, and a *printer* to print a spectrum.

Nuclear Magnetic Resonance Spectrometry

(1) NMR spectrometers irradiate organic compounds with electromagnetic energy corresponding to the frequency range of radio and television waves. (2) Magnetic nuclei such as ^{13}C and ^{1}H must be in a strong magnetic field in order to absorb this electromagnetic radiation.

^{13}C NMR Spectrometry

(1) ^{13}C NMR spectra that are proton decoupled show a single line (peak) for each chemically non-equivalent carbon atom in an organic molecule. (2) The positions of these lines (their chemical shift values (δ)) depend on the electron density at each C. (3) The range of δ values for a specific type of C is relatively independent of the molecule. (4) ^{13}C signals with small chemical shifts relative to the ^{13}C signal of tetramethylsilane (TMS) are at "high field" (C's are shielded), while those with large chemical shifts relative to TMS are at "low field" (C's are deshielded).

^{1}H NMR Spectrometry

(1) ^{1}H NMR spectra show signals with one or more lines for each chemically non-equivalent H atom in a molecule. (2) Chemical shift scales for ^{1}H and ^{13}C are both referenced to TMS (δ0), but they are not directly related to each other. (3) Chemical shifts of H's depend on electron density in the same way as the chemical shifts of their bonded C's. (4) ^{1}H signals are split into *n + 1* lines by the *n* chemically identical ^{1}H atoms on directly adjacent C's. (5) Relative areas under signals in ^{1}H NMR spectra are directly proportional to the relative number of H's giving those signals. (6) NMR spectra for ^{13}C and for ^{1}H atoms are determined in separate analyses.

Infrared Spectrometry

(1) Infrared spectrometers irradiate organic molecules with electromagnetic radiation that includes wavelengths we sense as heat. (2) IR energy causes chemical bonds to undergo molecular vibrations such as stretching and bending. (3) Energy values of specific molecular vibrations depend on the type of bonded atoms, and whether the bond is single, double, or triple. (4) IR spectrometers use infrared radiation at wavelengths (λ) between about 2.2 and 25 μm that correspond to a "frequency" range in wavenumbers ($\bar{\nu}$) ($\bar{\nu}$ = 1/λ) of 4600 to 400 cm^{-1}. (6) Stretching or bending vibrations of specific types of chemical bonds occur in characteristic regions of IR spectra. (7) The relative intensities of IR signals in a spectrum are <u>not</u> quantitatively related to the relative number of bonds giving the specific molecular vibrations.

UV-Vis Spectrometry

(1) UV-Vis spectrometers irradiate molecules with ultraviolet radiation (λ = 200 to 380 nm), and visible light (λ = 380 to 780 nm). (2) Electromagnetic radiation in these wavelength ranges usually excites π electrons in conjugated multiple bonds from bonding molecular orbitals into higher energy antibonding molecular orbitals. (3) σ electrons in C-H and C-C single bonds, and π electrons in isolated (nonconjugated) C=C and C≡C multiple bonds, are not excited by UV-Vis radiation in these wavelength ranges. (4) UV-Vis spectra often appear identical for different molecules if they contain the same grouping of conjugated multiple bonds.