## WHAT'S AHEAD



# 32

# SOLVING MOLECULAR STRUCTURE

## 32.1 The Electromagnetic Spectrum

In 1666, Isaac Newton used a prism to disperse white light into the colors of the rainbow. He observed that a round beam of white light would produce an oblong image of colors. From this, he concluded that different colors are bent by the prism at different angles. This indicated that color was a property of light rather than of an object that the light illuminates. We now recognize that the electromagnetic spectrum is far more extensive than the visible portion that

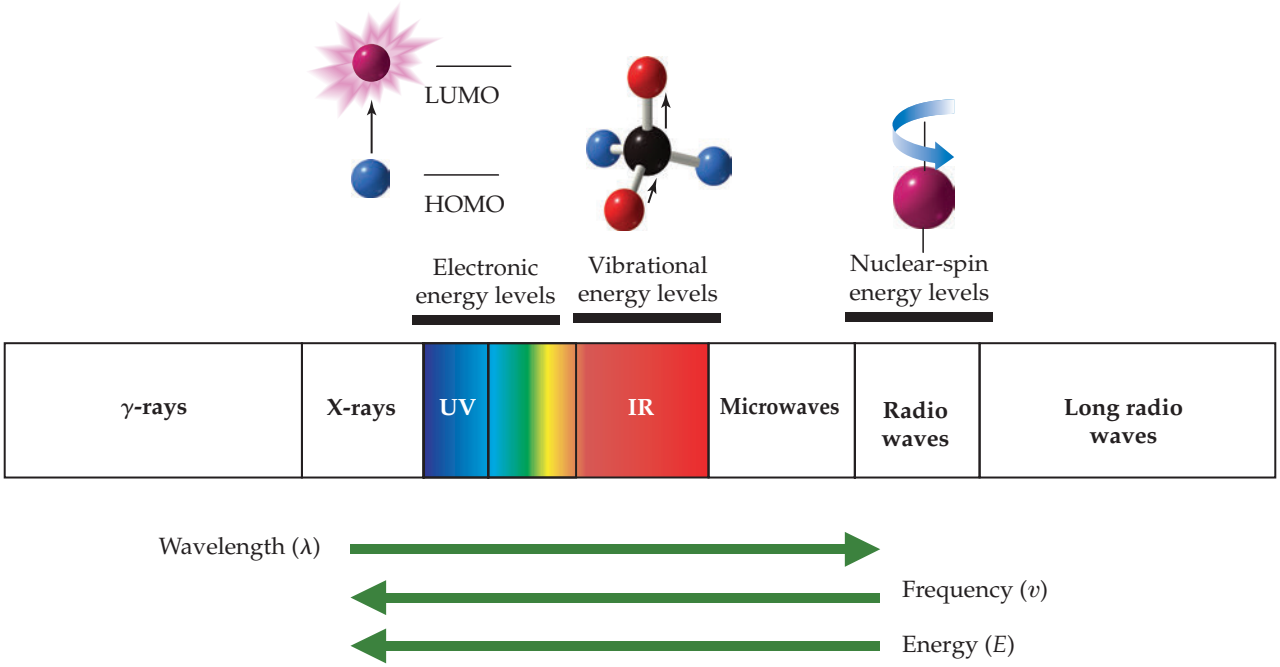
we see and different parts of it correspond to different physical processes that may occur within a molecule. By the end of this section, you should:

- Understand the parts of the spectrum that are used in the analysis of molecules

In Chapter 6, we introduced the electromagnetic spectrum and the concepts of wavelength (λ) and frequency (υ).

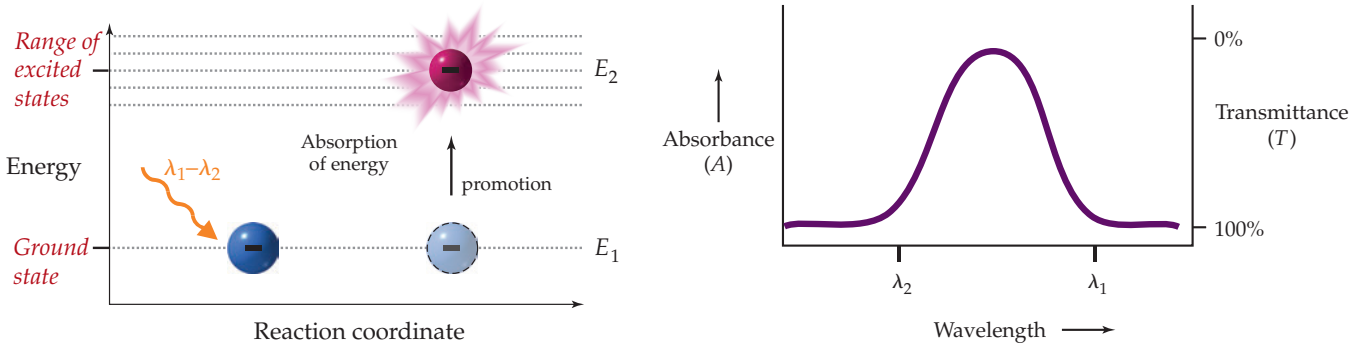
Three regions of the electromagnetic spectrum are particularly important to the organic chemist (**Figure 32.1**). The UV (ultraviolet) and visible region of the spectrum is of an energy that equates to the transition of electrons between electronic energy levels within a molecule (**Figure 32.2**). The technique, aptly named **UV-visible spectroscopy**, is particularly useful for aromatic and π-conjugated compounds. The infrared (IR) region of the spectrum corresponds to transitions between the vibrational energy levels within a molecule. This region of the electromagnetic spectrum is lower in energy than that required to excite an electron from the ground state using ultraviolet radiation, and provides unique information on the types of functional groups present in a molecule. The third region of importance is found at the frequency of radio waves. In this region, the energies relate to transitions between nuclear-spin energy levels. The energies required here are much lower than for either IR- or UV-visible spectroscopy.

When an organic molecule is exposed to a spectrum of electromagnetic radiation, it absorbs energy at certain wavelengths in the ultraviolet and visible region and allows other wavelengths to pass through. Figure 32.2 illustrates the process. A molecule initially in the lower-energy $E_1$ state, referred to as the *ground state*, can undergo a transition to $E_2$, the *excited state*, only by absorption of electromagnetic energy of wavelength λ. This wavelength is related to the difference between $E_1$ and $E_2$ by Equations 6.1 and 6.2, so $\lambda = hc/(E_2 - E_1)$. In atoms, the absorptions occur at very defined energies giving a spectrum of sharp lines. In molecules, each electronic energy level has a stack of much smaller vibrational energy levels associated with it and this results in a broader absorption. The UV-visible absorption spectrum of a molecule is characteristic for each different substance.




▲ **Figure 32.1 The electromagnetic spectrum.** Energy depends upon wavelength. The regions are described in terms of atomic transitions and the type of related spectroscopy.

**Go Figure** The absorption characteristics displayed by molecules have an analogy in everyday life. Why do dark-colored cars get hotter inside than light-colored cars?




▲ **Figure 32.2 An absorption spectrum** is generated when a molecule absorbs electromagnetic radiation of a particular wavelength range ($\lambda_1 - \lambda_2$).

UV-visible spectroscopy is one of several spectroscopic techniques in which energy interacts with a molecule to give a characteristic absorption spectrum. Modern spectroscopic techniques use only minute amounts of material, which in most cases may be recovered unchanged after the analysis. These are called *non-destructive* techniques. Other methods of analysis do destroy the compound and are sometimes unavoidable, for example, mass spectrometry.

In this chapter, we deal with three powerful and complementary techniques that form the cornerstone of modern synthetic organic chemistry. Each technique is useful because it provides a vital piece of evidence, using very small amounts of sample. The chemical detective can draw a logical conclusion to the structural problem by combining two, but usually more, pieces of evidence. The techniques are:

- *infrared (IR) spectroscopy*, which observes the vibrations of covalent bonds and provides useful evidence for the presence of functional groups;

## A CLOSER LOOK Using Spectroscopic Methods to Measure Reaction Rates

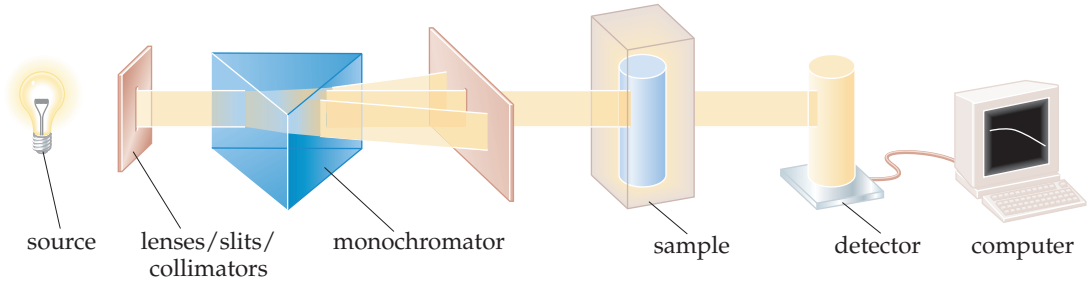
A variety of techniques can be used to monitor the concentration of a reactant or product during a reaction. Spectroscopic methods, which rely on the ability of substances to absorb (or emit) electromagnetic radiation, are some of the most useful. Spectroscopic kinetic studies are often performed with the reaction mixture in the sample compartment of a spectrometer. The spectrometer is set to measure the light absorbed at a wavelength characteristic of one of the reactants or products. In the decomposition of HI(g) into $H_2$(g) and $I_2$(g), for example, both HI and $H_2$ are colorless, whereas $I_2$ is violet. During the course of the reaction, the color increases in intensity as $I_2$ forms. As the concentration of $I_2$ increases and its color becomes more intense, the amount of light absorbed by the reaction mixture increases, causing less light to reach the detector.

**Figure 32.3** shows the basic components of a spectrometer. The spectrometer measures the amount of light absorbed by the sample by comparing the intensity of the light emitted from the light source with the intensity of the light that emerges from the sample.

**Beer–Lambert's law** relates the amount of light being absorbed to the concentration of the substance absorbing the light:

$$A = \varepsilon c l \qquad [32.1]$$

In this equation, $A$ is the measured absorbance, $\varepsilon$ is the molar extinction coefficient (a characteristic of the substance being monitored at a particular wavelength), $l$ is the path length through which the radiation must pass, and $c$ is the molar concentration of the absorbing substance. Thus, for a constant path length, the concentration is directly proportional to absorbance.




▲ **Figure 32.3 Basic components of a spectrometer.**

- *nuclear magnetic resonance (NMR) spectroscopy*, the technique of choice for the organic chemist. This method observes nuclear transitions within a strong magnetic field and yields information on the connectivity of atoms;
- *mass spectrometry (MS)*, which typically bombards a very small amount of sample with electrons to ionize the molecules. Analysis of the mass of these ions gives the molecular mass. Mass spectrometry often provides clues to the structure and functional groups within a molecule, through either fragmentation or isotopic patterns. This technique is often used routinely because it needs only μg amounts of sample.

## Self-Assessment Exercise

**32.1** What portion of the electromagnetic spectrum corresponds to the energy difference between vibrational energy levels?

**(a)** UV-visible light
**(b)** Infrared radiation
**(c)** Radio waves

**Answers to Self-Assessment Exercises**

**32.1** (b)

# 32.2 | Infrared (IR) Spectroscopy


A high body temperature is usually an indicator that the body is fighting an infection. In times of epidemics, such as COVID-19, temperature measuring devices are frequently employed at the entrance to hospitals, at transport hubs and even large shopping centers to screen the general public for the first signs of an infection. It is important these devices do not touch the skin to prevent the risk of transmitting any possible infection from one person to another. Infrared thermometers are often used in these situations and provide a lightweight, robust, and relatively cheap device that is easy for the operator to hold in their hands. The heat we radiate is directly related to our body temperature and is detected as infrared radiation.

In this section, we use infrared radiation in the non-destructive analysis of molecules to determine if they contain some common functional groups. By the end of this section, you should be able

- To recognize if an analyte contains certain functional groups from their characteristic IR frequency of absorption.

Infrared photons (*infra*, Latin, meaning below or beneath) do not have enough energy to cause electronic transitions, but they can cause groups of atoms to vibrate about their respective bonds. These vibration transitions correspond to distinct energy levels. Molecules and, more importantly, the different functional groups contained within them, absorb IR radiation at specific wavelengths to induce the different vibrational modes within a covalent bond (that is, single, double, triple bonds). **Infrared spectroscopy** is the technique that records the absorption of infrared energy of a molecule as a function of energy. It identifies functional groups, but gives little structural information.

The position of an infrared band in an *IR spectrum* is defined by a **wavenumber** value (abscissa) and the band's percentage transmittance (%$T$) (ordinate), as shown in **Figure 32.4**. The wavenumber has traditionally been the most common method of specifying IR absorption, although sometimes the wavelength value (in microns) is also employed. The wavenumber is a type of frequency unit and is the true frequency divided by the speed of light. It corresponds to the number of waves per unit distance, chosen to be centimeters in IR spectroscopy (and, therefore, written in terms of $cm^{-1}$).

The absorbance of a sample is related to the **transmittance** by the equation:

$$\text{Absorbance} = -\log_{10}(\text{transmittance})$$

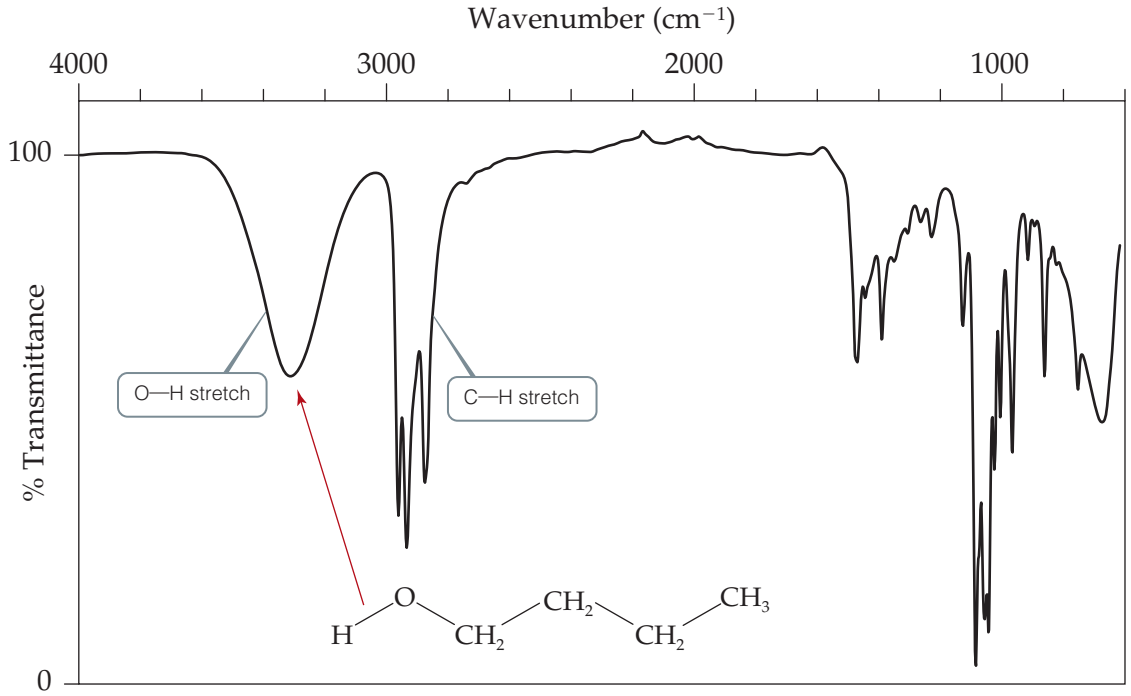
or

$$A = -\log_{10} T \qquad [32.2]$$

The value of transmittance ($T$) always lies between the values of 0 and 1 and the %$T$ between 0 and 100.

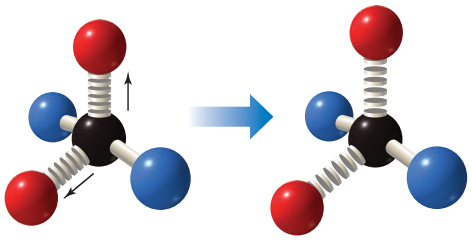
## The Spring Model

Before discussing the characteristics of IR absorptions, it is helpful to understand some theory on molecular vibrations. To do this, let's consider the covalent bond between two atoms as a spring (**Figure 32.5**). This spring can be stretched (shown), compressed, bent or twisted, and then released from the input leading to the distortion. The output, which can be observed as a band within the IR spectrum, is in fact a vibration. The force needed

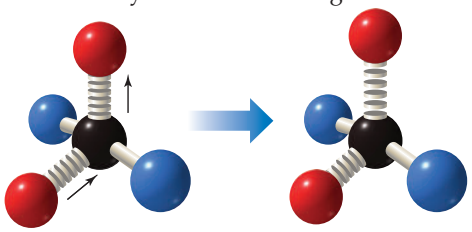



▲ **Figure 32.4 IR spectrum of butan-1-ol.** This IR spectrum is measured as a function of wavenumber ($cm^{-1}$). The ordinate describes the intensity, measured as percentage transmission (%$T$). In this spectrum of butan-1-ol, the broad, strong absorption at 3300 $cm^{-1}$ is due to the strong O—H stretching vibrations that occur at this frequency.

**Go Figure** Do loose springs oscillate with a higher or lower frequency than tight springs?



Symmetric stretching



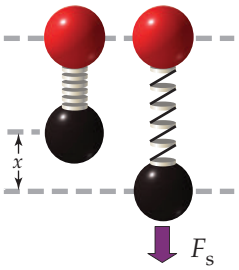
Asymmetric stretching

▲ **Figure 32.5 Spring model.** IR spectroscopy can be more easily understood by thinking of covalent bonds as springs. The stretching, bending or torsion of the spring leads to vibrations of a particular frequency. The vibrations can be modelled using Hooke's law.

to cause the vibration follows **Hooke's law**, which states that the elongation of a spring is proportional to the load applied. Mathematically:

$$F_s = -kx \qquad [32.3]$$

where $F_s$ is the applied force (which equals the force exerted by the spring, only opposite in sign) in units of newtons (N), $k$ is the spring constant (N m$^{-1}$) and $x$ is the deformation of the spring (for example, stretching, with units m) from an equilibrium position (Figure 32.6). The strain in the spring is directly proportional to the load. In any system that can be described by Hooke's law, there exists a fundamental frequency of vibration, $\upsilon = \frac{1}{2}\pi\left(\frac{k}{m}\right)^{\frac{1}{2}}$. This is also true for molecules, so the frequency of vibration of any chemical bond depends on the mass ($m$) of atoms at the moving end of the bond and the stiffness ($k$) of the bond.




▲ **Figure 32.6 Hooke's law** of elasticity applied to a spring system states that the elongation of a spring is proportional to the load applied.

In a group of bonds with similar bond energies, the frequency decreases with an increase in atomic weight of the atoms. Of more interest to the organic chemist is the fact that stronger bonds (for example, double bonds) are generally "stiffer" than single bonds and require more force to stretch or compress them. As a result, stronger bonds usually vibrate faster than weaker bonds. For example, O—H bonds ($D$(O—H = 463 kJ/mol) are stronger than C—H bonds ($D$(C—H = 413 kJ/mol), so O—H bonds vibrate at higher wavenumber. Carbon–carbon triple bonds are stronger than carbon-carbon double bonds, so triple bonds vibrate at higher wavenumbers than do double bonds. In a group of bonds with atoms of similar masses, the frequency increases with increasing bond energy.

The absorption of energy into molecular vibrations is recorded in an IR spectrum. This spectrum gives a record of the energy absorbed as a function of the energy of radiation. An IR spectrum is recorded on an IR spectrophotometer. In the context of this course, we consider only certain vibrations: O—H stretching, C—H stretching, C=C stretching, C—C stretching, N—H stretching and C=O stretching. These stretching vibrations give rise to the easy identification of the most common functional groups in organic chemistry. The low-wavenumber region within the IR spectrum contains most of the complex vibrations and is commonly called the **fingerprint region** of the spectrum (300–1400 cm$^{-1}$). Although it is useful to know of this region, its use in identifying organic molecules is limited because of the complexity of the spectrum in this region. Inorganic chemists

find this region useful for the identification of metal–ligand (M—L) interactions. Organic chemists use the fingerprint region primarily to confirm the identity of a sample, by comparing it with an authentic spectrum of a known compound thought to be the same as the sample under investigation.

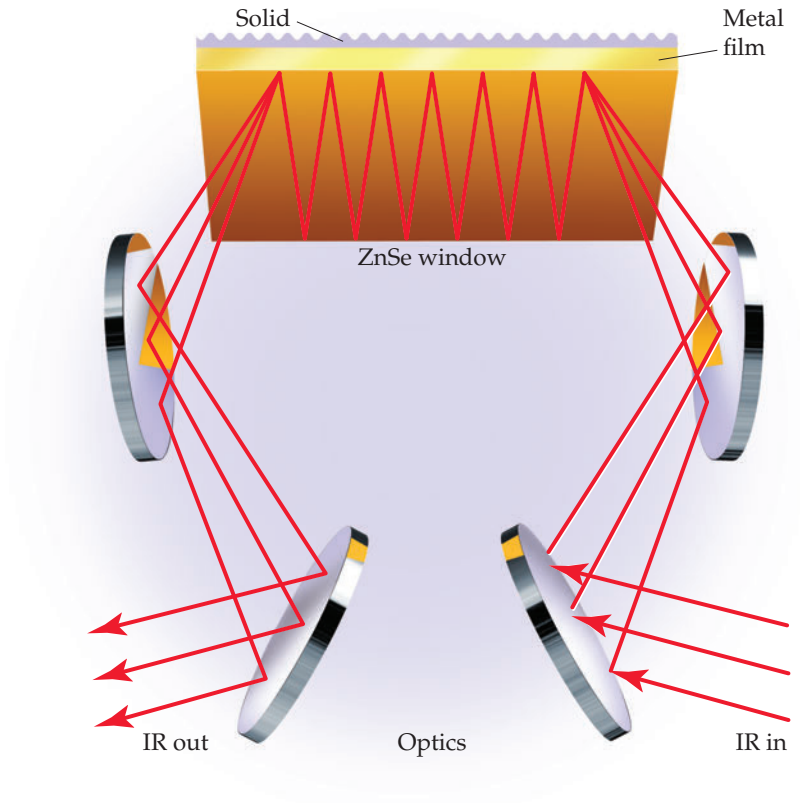
*Stretching vibrations in the region 1550–3800 $cm^{-1}$ are the most characteristic and predictable.*

At this point, we should also recognize that not all molecular vibrations absorb IR radiation. Generally, only bonds with dipole moments (for example, O—H, C═O, N—H bonds) are IR active and hence result in IR absorptions. A dipole moment between two covalently bonded atoms is achieved when the two atoms differ significantly in their electronegativity.

If the molecule is placed in an electromagnetic field, its bonds interact with the field, usually leading to a change in the vibration of the covalent bond, and a change in the dipole moment of the bond. If a bond is symmetrical or has zero dipole moment, the applied field does not interact with the bond as strongly, and this very weak vibration is said to be *IR inactive*.

## Measuring IR Spectra

IR spectra are measured using liquid, solid or gaseous samples placed in a beam of infrared light. Typically, if the sample is a liquid, the compound can be thinly spread *neat* (without solvent) between two thick plates of sodium chloride, which are transparent to infrared light for most of the important wavelength regions. Solid samples are usually prepared by grinding a sample into a paste with an organic oil known as nujol (a type of paraffin oil) forming a mull, which is also sandwiched between two thick NaCl plates. A more modern approach is to place a solid on an ATR diamond or ZnSe window cell and a spectrum taken directly (**Figure 32.7**). ATR stands for attenuated total reflectance. Gases typically require specialized cells.




▲ **Figure 32.7 Attenuated total reflectance (ATR) IR spectroscopy.** Modern IR spectrometers use a direct approach by measuring the transmittance of electromagnetic radiation through a sample placed on a diamond or ZnSe surface.

**TABLE 32.1 Bond-stretching frequencies and their relationship to functional groups**

| Functional group | Stretching vibration frequency ($cm^{-1}$) | Strength of IR band | Bond energy ($kJ\ mol^{-1}$)* |
|---|---|---|---|
| O—H | 3200–3500 | Strong, broad | 465 |
| N—H | 3100–3500 | Medium | 390 |
| C—H | 2700–3100 | Strong to medium | 415 |
| C≡N | 2200–2400 | Strong to medium | 890 |
| C≡C | 2000–2200 | Weak | 840 |
| C=O | 1630–1800 | Strong | 800 |
| C=N | 1630–1680 | Strong | 615 |
| C=C | 1600–1680 | Weak | 615 |

* Bond energies rounded to the nearest 5 kJ mol.

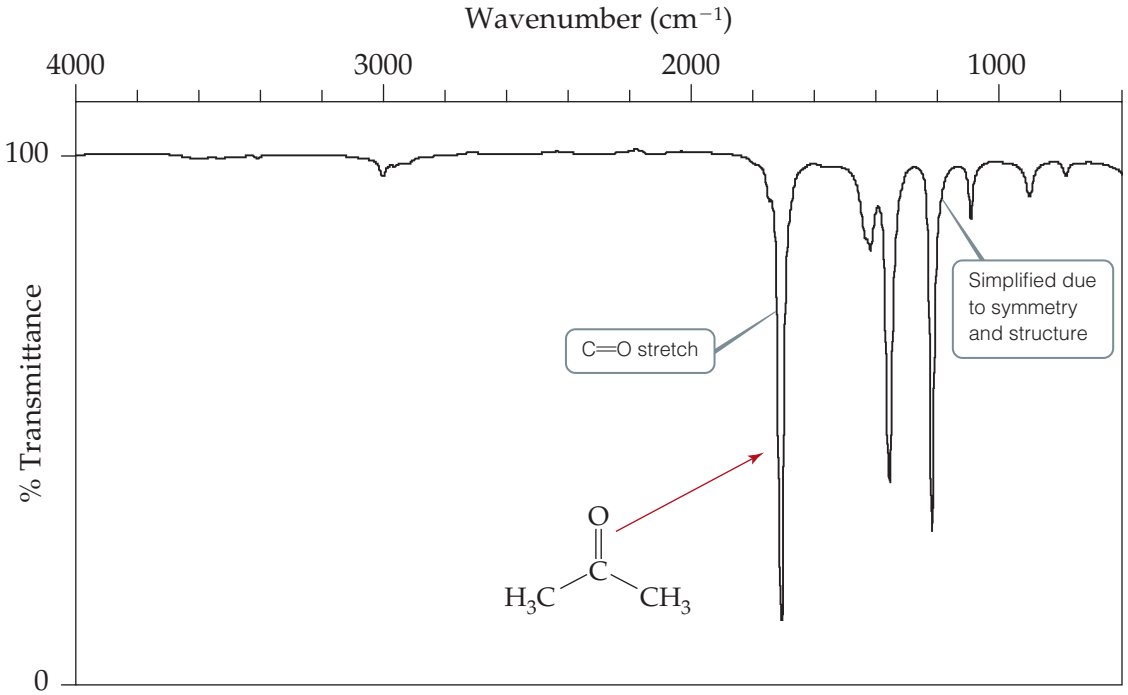
**Table 32.1** illustrates the predicted regions where the most common functional groups absorb IR radiation. As mentioned earlier, strong bonds generally absorb at higher frequencies because of their greater "stiffness." Thus C—C single bonds absorb around 1200 $cm^{-1}$, C=C double bonds around 1600–1680 $cm^{-1}$ and C≡C triple bonds around 2200 $cm^{-1}$. The absorption of C=C double bond vibrations in an IR spectrum are diagnostic and useful for structure determination. The position of C—C single bond absorptions in an IR spectrum are not very diagnostic because they occur in most organic compounds as part of the molecules' framework. Most double bonds produce observable absorptions in the region 1600–1680 $cm^{-1}$. Conjugation of the double bond has the effect of reducing the stretching frequencies from 1620–1640 $cm^{-1}$ (in the case of an aliphatic C=C) to approximately 1600 $cm^{-1}$ for an aromatic C=C. The lowering in frequency can be attributed to the loss of electron density in the double bonds due to the conjugation. As a result, conjugated double bonds are a little less stiff and vibrate a little more slowly than isolated double bonds, giving them lower frequencies of absorption.

Alkanes, alkenes, and alkynes have characteristic C—H stretching bands around 3000 $cm^{-1}$. Because of the prevalence of C—H bonds in organic molecules, the presence of a band at 3000 $cm^{-1}$ makes it easy to identify the presence of an organic compound by IR spectroscopy. However, some organic molecules have very weak absorbances in this area. For example, the C—H stretching band in an IR spectrum of propanone (**Figure 32.8**) is very weak.

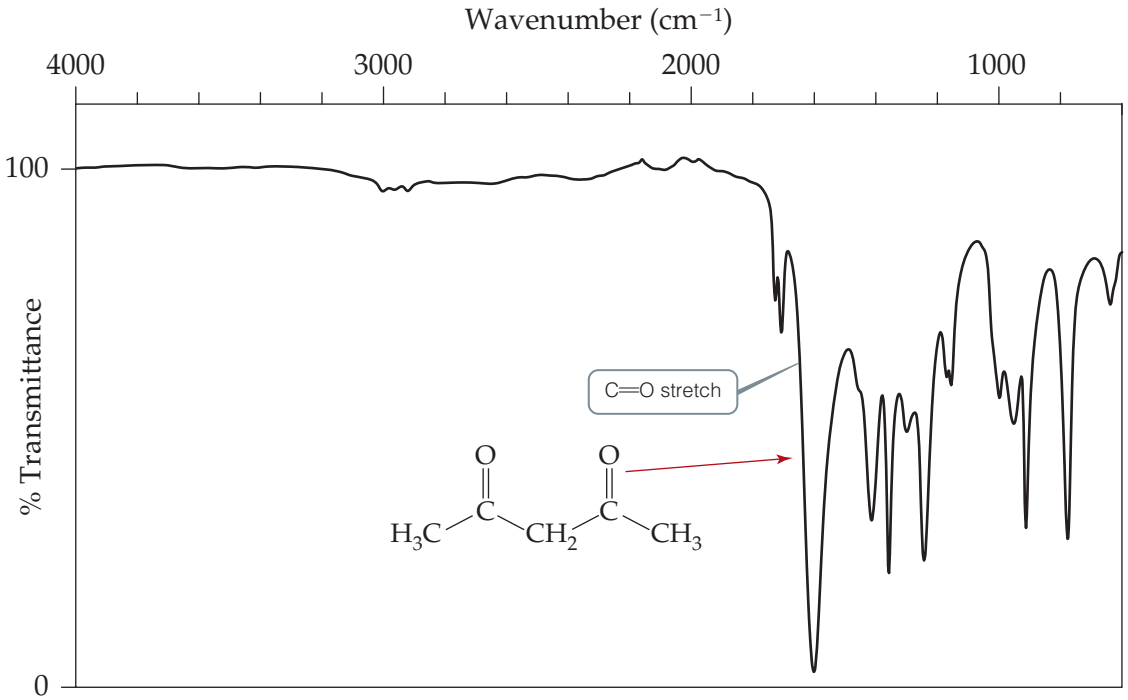
The large dipole moment change associated with the C=O double bond produces a strong IR stretching band around 1700 $cm^{-1}$ as shown in Figure 32.8. The exact position of this band within the IR spectrum depends on the specific functional group present (ketone, aldehyde, amide, carboxylic acid or ester) and the environment created by the rest of the molecule. For these reasons, IR spectroscopy is often the best method for detecting and identifying the type of carbonyl group in an unknown compound.

The C=O double bond stretching vibrations of simple ketones, aldehydes and carboxylic acids occur around 1710 $cm^{-1}$ (**Figure 32.9**). These are slightly higher than those of a C=C double bond because of the relative bond strengths (C=C < C=O, see Table 32.1). Some carbonyl absorptions do occur above 1710 $cm^{-1}$. For example, simple carboxylic esters absorb around 1735 $cm^{-1}$ and ring-strained carbonyl groups, such as those found in cyclobutanone, occur around 1785 $cm^{-1}$. In addition to the C=C stretching band, an aldehyde shows the characteristics of two C—H stretching bands around 2700 $cm^{-1}$ and 2800 $cm^{-1}$ corresponding to the aldehyde C—H stretch, whereas a ketone or an acid does not produce these absorptions. Carboxylic acids produce a characteristic O—H absorption around 3000 $cm^{-1}$ in addition to the intense carbonyl stretching absorption. The position of this O—H stretch within the IR spectrum is usually complicated as a result of the carboxyl group participating in hydrogen bonding, which also results in the broadening of the strong carbonyl absorption.

The carbonyl groups of amides absorb at particularly low IR frequencies (1640–1680 $cm^{-1}$). This very low frequency might be mistaken for an alkene C=C stretch if it weren't for two important features of its IR spectrum. The amide carbonyl absorption is much stronger than that of an alkene bond due to the difference in dipole moment



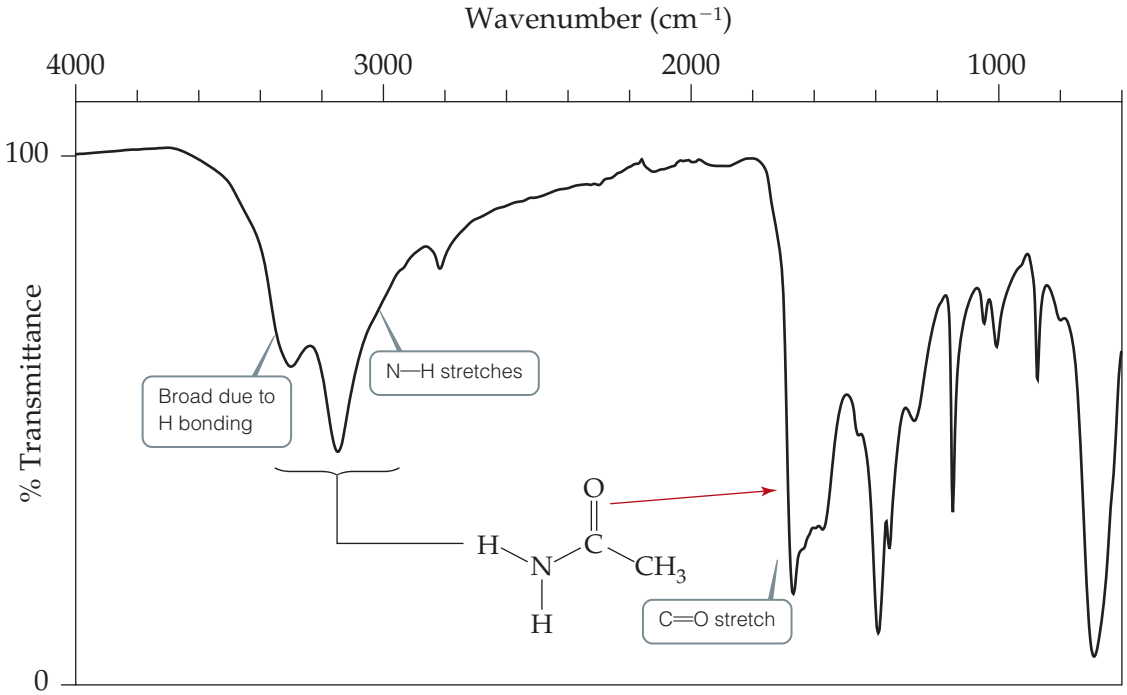

▲ **Figure 32.8 IR spectrum of propanone (acetone).** Note the simplicity of the spectrum and the presence of the dominant C═O stretch at 1710 $cm^{-1}$.



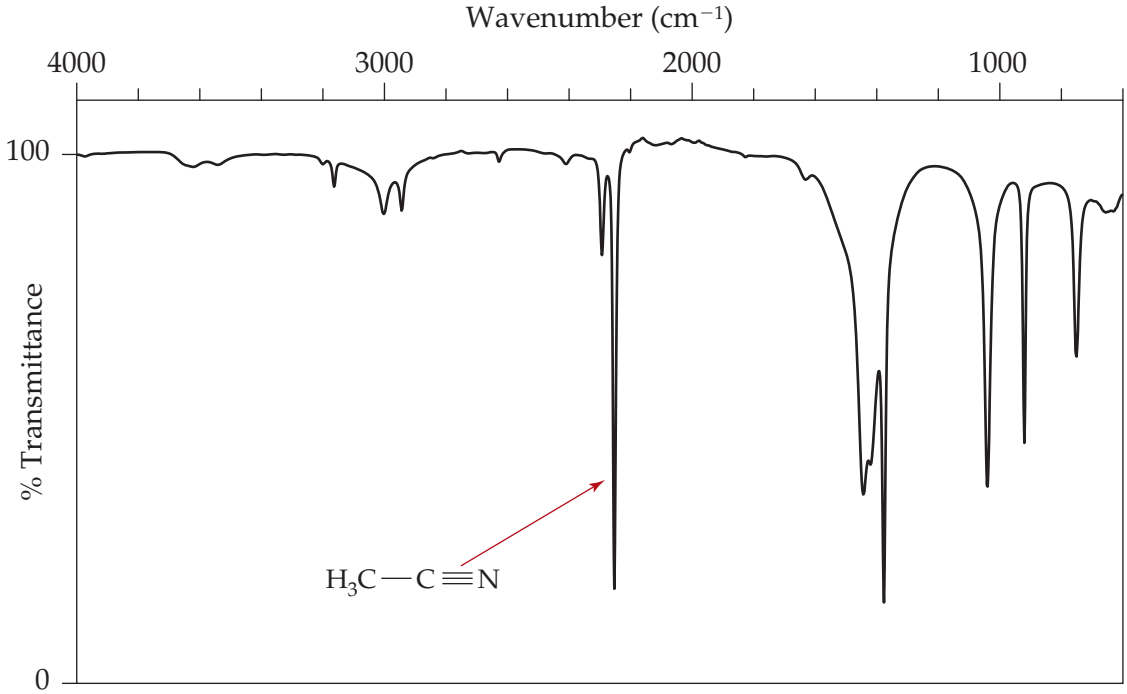

▲ **Figure 32.9 IR spectrum of 2,4-pentanedione.** Note the intense carbonyl stretching band at 1700 $cm^{-1}$.

between the two unsaturated bond types. Primary and secondary amides are also identified by the addition of a N—H stretching absorption around 3200 $cm^{-1}$ (**Figure 32.10**).

The only other multiple bond stretch that we need to consider is that of the nitrile bond (C≡N). Because of the polarity of this C≡N triple bond, nitriles usually exhibit very strong absorbances around 2200 $cm^{-1}$ (**Figure 32.11**) within their IR spectra. This value is similar to that for an alkyne (C≡C) stretch, although nitriles tend to absorb above 2200 $cm^{-1}$ whereas alkynes absorb below 2200 $cm^{-1}$.




▲ **Figure 32.10 IR spectrum of acetamide.** This spectrum was taken of a sample as a crystalline solid, hence there is more information contained within the spectrum than is usually needed for functional group identification.




▲ **Figure 32.11 IR spectrum of acetonitrile.** This simple nitrile shows the characteristic and distinctive IR absorption band for C≡N at 2280 $cm^{-1}$.

The vibrational frequencies of O—H bonds (alcohols) and N—H bonds (amines) occur at higher wavennumbers than for C—H bonds. Alcohol O—H bands are typically broad, absorbing over a wide range of frequencies centered around 3300 $cm^{-1}$. Their broadness is attributed to hydrogen-bonding arrangements between functional groups within the same molecule—that is, they are *intramolecular*—or to interactions with other molecules, including solvent or absorbed water, interactions that are described as *intermolecular*. Therefore, the purity of a sample with respect to absorbed water needs to be taken

## Sample Exercise 32.1

**Distinguishing between constitutional isomers**

How would you be able to use IR spectroscopy to distinguish between the following compounds:
**(a)** butan-1-ol and diethyl ether,
**(b)** ethyl acetate and butanoic acid?

### SOLUTION

**Analyze** We are asked to differentiate between functional groups in compounds using IR.

**Plan** We need to identify the difference in functional groups between the two isomers in each set.

**Solve** Butan-1-ol shows a strong absorption in the O—H stretching frequency region, 3100–3300 $cm^{-1}$. Diethyl ether is devoid of any characteristic functional group absorptions $> 1500\ cm^{-1}$, apart from C—H stretching vibrations. In this case, the absence of the O—H absorption is diagnostic.

Both ethyl acetate and butanoic acid show a strong C=O stretching frequency absorption around 1710–1730 $cm^{-1}$. Although variations in this stretching frequency are possible and somewhat diagnostic, the best answer to this question is the addition of a strong absorption in the O—H stretching frequency region, approximately 3100 $cm^{-1}$ for butanoic acid.

**Practice Exercise**

How would you be able to use IR spectroscopy to distinguish between these compounds:
**(a)** cyclohexane and cyclohexene,
**(b)** acetamide and ethylamine?

into account. Any water that is present will also absorb at these frequencies, complicating the results by giving a false positive for an O—H group. This is usually overcome by extended drying of the sample before analysis by IR spectroscopy.

The amine N—H bond also has a stretching frequency around 3300 $cm^{-1}$ and, like alcohols, these amines participate in *intra-* and *inter*-molecular hydrogen bonding. The difference between O—H and N—H stretches lies in the shape of the band. Although O—H stretches are broad, N—H stretches are sharper. Primary amines typically have two absorptions in their N—H absorption band, whereas secondary amines have only a single absorption band. The presence of water in an amine sample typically leads to one or two sharp spikes superimposed on the broad area of the water O—H stretching absorption. Again, drying the sample distinguishes a wet sample from one containing both an O—H and N—H functional group.

Being able to interpret an IR spectrum is a useful skill. Typically, IR spectra need to be interpreted in conjunction with other techniques. Sections 32.3 and 32.4 deal with two other powerful spectroscopic techniques.

## Self-Assessment Exercise

**32.2** A molecule of formula $C_4H_8O$ has a weak absorption around 1600 $cm^{-1}$, no absorption in the region 1630–1800 $cm^{-1}$ and no absorption in region 3200–3500 $cm^{-1}$. Which of the following compounds would fit this data?

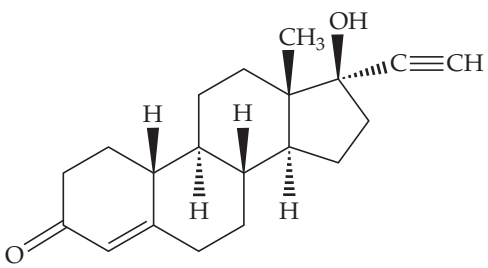
**(a)** but-3-en-1-ol
**(b)** butanal
**(c)** butanone
**(d)** ethoxyethene

## Exercises

**32.3** Identify a possible functional group that might be responsible for the following IR absorptions:

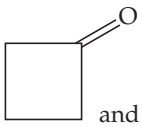
**(a)** 3500 $cm^{-1}$
**(b)** 1705 $cm^{-1}$
**(c)** 1650 $cm^{-1}$
**(d)** 1710 and 3400 $cm^{-1}$
**(e)** 1680 and 3200 $cm^{-1}$

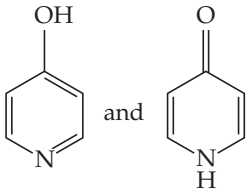
**32.4** Norethidrone is a steroid used primarily as an oral contraceptive. Its synthesis was first achieved in 1951. Indicate which parts of the structure of norethidrone have characteristic absorptions identifiable by IR spectroscopy. Indicate their approximate positions in wavenumbers ($cm^{-1}$).



**32.5** How might you use IR spectroscopy to help distinguish between the following pairs of compounds?

**(a)** $CH_3CH_2OCH_2CH_3$ and $CH_3CH_2CH_2CH_2OH$

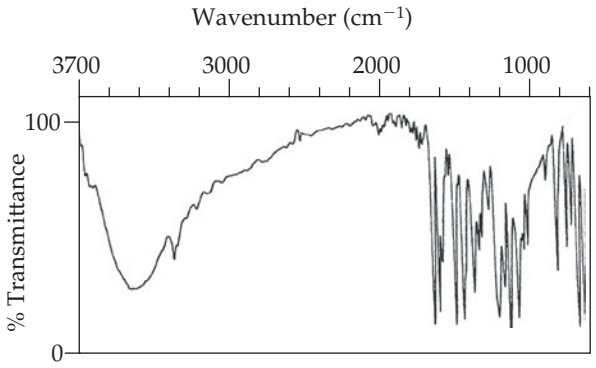
**(b)**  and $CH_2{=}CHCH_2OH$

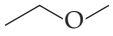
**(c)** 

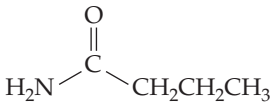
**(d)**  and $CH_3CH{=}CHCH_2CH_3$

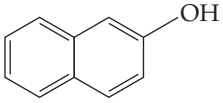
**(e)** $(CH_3)_3N$ and $CH_3CH_2NHCH_3$

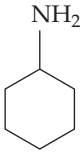
**32.6** Which of the following structures is consistent with the IR spectrum shown here?




**(a)** 

**(b)** 

**(c)** 

**(d)** 

**Answers to Self-Assessment Exercises**

**32.2** (d)

## 32.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

The twin discoveries that led to superconducting magnets were made by Dutch man Heike Kamerlingh Onnes. In 1908, he was the first to liquify helium, and, three years later, he was the first to observe superconductivity in metals cooled to extreme temperatures.

Helium boils at −269 °C, just four degrees above absolute zero, and it was at this temperature that Onnes observed that the resistance of a mercury wire dropped to zero. He adopted the term *superconductivity* to describe this new state and recognized the potential to construct extremely strong magnets. However, it was not for another forty years that a material (niobium) was found that could handle the large current densities present in an ultra-strong magnet. Now, a niobium-titanium or a niobium-tin alloy is used in superconducting magnets. This metal core is cooled by liquid helium, which is surrounded by a jacket of liquid nitrogen. The magnet field produced is typically ten times stronger than can be achieved with traditional iron-core magnets as well as being a more stable, homogenous field.

The discovery of superconducting magnets opened many doors. In this section and the next, we examine two techniques, both of which utilize superconducting magnets in order to achieve very high-resolution analysis. Superconducting magnets are also pivotal to the magnetic resonance imaging of soft body tissue, research into nuclear fusion reactors, and the construction of magnetically levitated trains being developed in Japan.

By the end of this section, you should be able to:

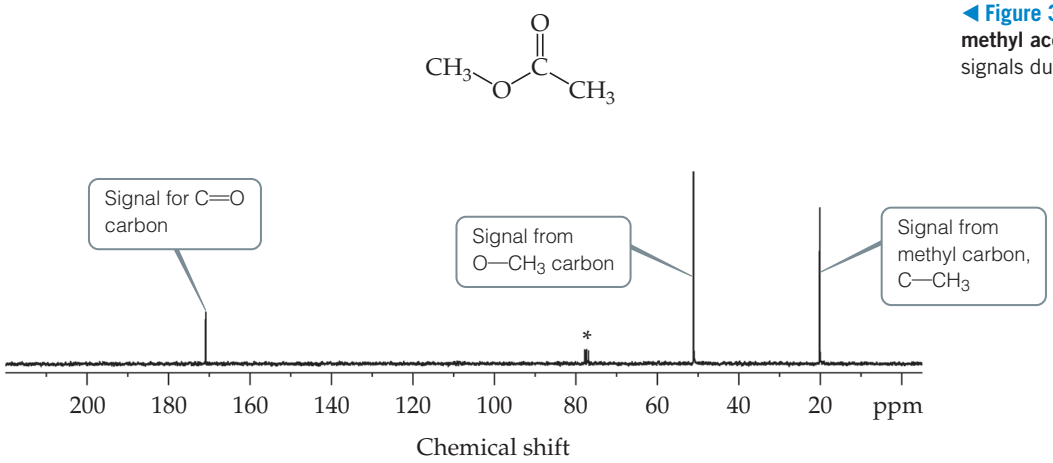
- Identify nuclei that can resonate in a magnetic field (i.e., are NMR active)
- Predict the NMR spectra of simple organic molecules
- Interpret an NMR spectrum to give structural information on a molecule

As a technique, **nuclear magnetic resonance (NMR) spectroscopy** is probably the most powerful tool in the organic chemist's research arsenal. It is a non-destructive technique that requires little sample (typically 2–10 mg for $^{1}$H NMR and 20–40 mg for $^{13}$C NMR spectroscopy). It has become a routine technique, due mainly to the advent of Fourier Transform NMR (FT-NMR), which provides for very rapid data acquisitions (typically 10 minutes), although more demanding experiments take longer (overnight). NMR gives us information about structure, so it is extremely useful for identifying unknown substances or confirming known structures. In the latter case, NMR spectroscopy is also useful for indicating the purity of a sample (to approximately 97%) and for observing the stability of a substance in solution. Even if you are do not intend to study chemistry in future years, the logical nature of the problem-solving skills developed by using this and the other techniques discussed in this chapter will be beneficial for your chosen science.

NMR spectroscopy is a technique that yields important structural information about a molecule by observing the interplay of the different nuclei, such as $^{1}$H, $^{13}$C, $^{15}$N, $^{31}$P, contained within it. The sensitivity of NMR spectroscopy allows us to also identify subtle differences in the same nuclei within a molecule based on their neighboring functional groups, whose influence over a strong magnetic field is measurable. This section concentrates on two forms of NMR spectroscopy: $^{1}$H and $^{13}$C NMR spectroscopy. Information about the number and different types of hydrogen environment within a compound, their connectivity and their relationships will be explored using $^{1}$H NMR spectroscopy. Information on the different types of carbon environment present in a compound will be gained using $^{13}$C NMR spectroscopy.

Let us begin our discussions on NMR spectroscopy by looking at a simple example. The $^{13}$C NMR spectrum shown in **Figure 32.12** has three signals (or peaks), indicating that there are three different types of carbon environments within this compound, methyl acetate. The positions of these signals along the axis yields information about neighboring functional groups that allows us to assign each carbon environment to a signal with confidence. However, to understand the reasons why we can interpret the spectrum shown in Figure 32.12 the way we do, we need to gain an understanding of the background theory to NMR spectroscopy.

From Chapter 6, you should already be familiar with the concept that an electron has an associated magnetic field. Any atomic nucleus that has an odd number of protons or an odd number of neutrons will have a non-zero nuclear *spin* and resulting nuclear magnetic moment ($\mu$). Like electron spin, nuclear spin is quantized. The allowed nuclear magnetic spin states are determined by the nuclear spin quantum number ($I$) of the nucleus.

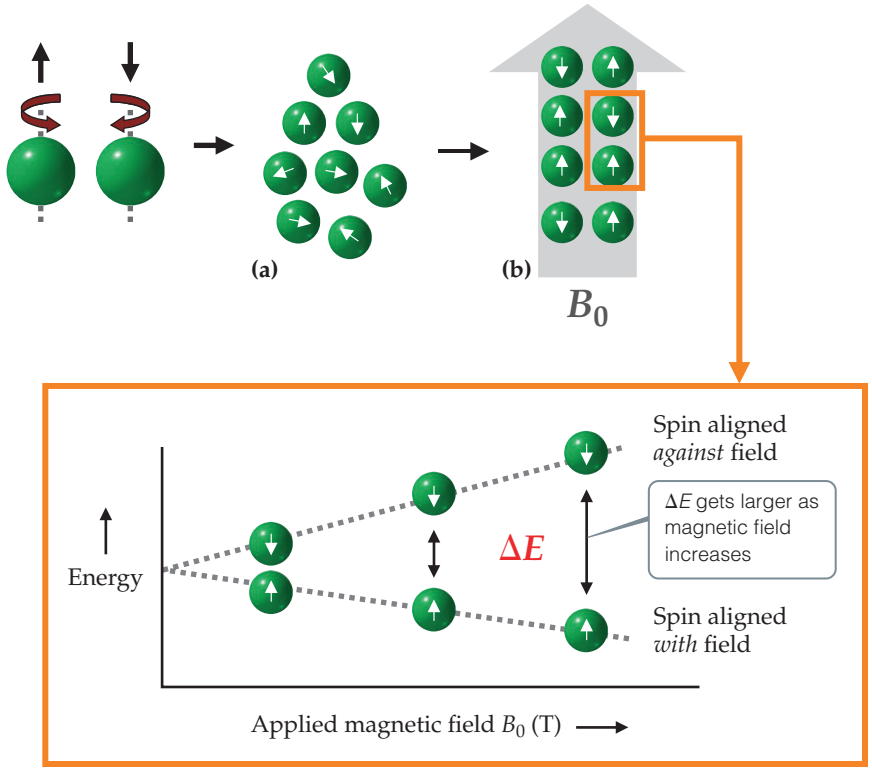



◀ **Figure 32.12 $^{13}$C NMR spectrum of methyl acetate.** The asterisk indicates signals due to $CDCl_3$ solvent.

A nucleus with a spin quantum number of $I$ ($I = 0, \frac{1}{2}, 1, \frac{3}{2}, 2$, etc.) has $(2I + 1)$ spin states. If $I = \frac{1}{2}$, as for $^1$H and $^{13}$C, there are two allowed spin states with values of $+\frac{1}{2}$ and $-\frac{1}{2}$. This spinning charge creates an associated magnetic field that behaves as if it is a tiny bar magnet with a magnetic moment ($\mu$).

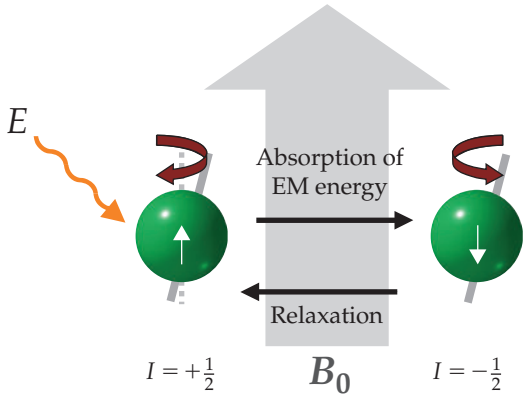
In the absence of external effects, such as an applied magnetic field, the two spin states have the same energy, as shown in **Figure 32.13(a)**, and completely random orientations. However, when the nuclei are placed in a strong external magnetic field, their spins can align parallel (with) or anti-parallel (against) to the field, giving rise to two energy

**Go Figure** Why would an increase in applied magnetic field strength increase the population differences between two spin states?




▲ **Figure 32.13 Nuclear spin.** Like electron spin, nuclear spin generates a small magnetic field and has two allowed values for $^1$H and $^{13}$C. In the absence of an external magnetic field (a), the two spin states have the same energy and a random orientation. If an external magnetic field is applied (b), the parallel alignment of the nuclear spin to the magnetic field is lower in energy than the anti-parallel alignment. The energy difference, $\Delta E$, corresponds to the radiofrequency portion of the electromagnetic spectrum. The weaker the applied magnetic field, the smaller this difference is.

states. The parallel alignment is lower in energy than the anti-parallel one by an amount of energy $\Delta E$, the size of which depends on the strength of the applied magnetic field ($B_0$) and the type of nucleus absorbing the radiation (Figure 32.13). For an applied field strength of 7.05 T (T = Tesla), which is readily available with modern-day superconducting electromagnets, the difference in energy between the two aligned spin states (with and against) is about 0.1 J/mol. This is a very small quantity on the chemical energy scale. NMR spectroscopy is considered a ground-state phenomenon.




▲ **Figure 32.14 Nuclear spin flip.** When Rf radiation of a frequency that corresponds to $\Delta E$ is applied, the parallelspin nuclei absorb this energy and their spins flip to an anti-parallel orientation. Although nuclei are described as aligning in a parallel or anti-parallel fashion, the axis of rotation is tilted, causing the nucleus to precess about its own axis of spin in a similar manner to a spinning top.

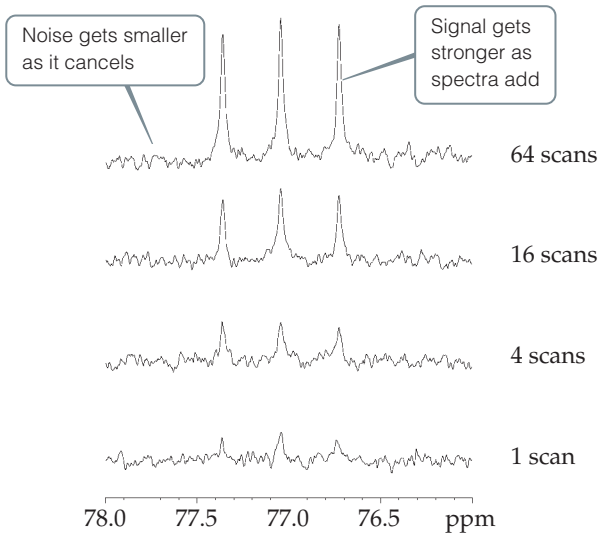
## Nuclear Magnetic Resonance Frequencies

Based on your knowledge of thermodynamics, you would expect that the lower-energy state would have a higher population of nuclear spins aligned with the field compared with those aligned anti-parallel to the field (despite the small value of $\Delta E$) because these aligned spins are lower in energy. If the nuclei being monitored by NMR spectroscopy are irradiated with electromagnetic radiation equal to the difference in energy between the two spin states in the applied magnetic field ($\Delta E$), energy is absorbed and the spin of the nuclei can be "flipped"—that is, excited from a parallel to an anti-parallel alignment, as shown in **Figure 32.14**. The radiation used in $^1$H NMR spectroscopic experiments is in the radiofrequency (Rf) range, typically 200–900 MHz. This radiofrequency is known as the spectrometer's **operating frequency**. The frequency at which the nuclei absorb energy is called the **Larmor frequency**. The absorption of this electromagnetic radiation, and the flip of its nuclear spin from a lower state to a higher state (and *vice versa*), is called **resonance**. Detection of the flipping of nuclei between the two spin states leads, after detection and mathematical manipulation (called Fourier Transform), to the NMR spectrum.

For NMR spectroscopy to be useful, the difference in population between the two aligned spin states needs to be significant. The greater the applied magnetic field, the greater the population difference between the two states (Figure 32.13). The more significant this difference is, the more *sensitive* the technique becomes. A greater sensitivity improves the spectrum acquisition time and lowers the amount of sample needed by providing a better *signal-to-noise ratio*. Acquiring and adding together multiple spectra of the same sample also increases the *signal-to-noise ratio* as shown in **Figure 32.15**. An increase in resolution allows us to gain more information on the connectivity of nuclei within a molecule. This is why chemists desire to have spectrometers with more powerful superconducting magnets (**Figure 32.16**).

From our discussions on NMR theory so far, you might expect that all $^1$H or $^{13}$C nuclei in a molecule would absorb energy at the same frequency. If this were the case, this technique would be of little use for structural determination. Luckily, the absorption frequency is not

▶ **Figure 32.15 75 MHz $^{13}$C NMR spectrum of $CDCl_3$** showing improvement of the signal-to-noise ratio from one scan (bottom spectrum) to 64 scans (top spectrum).



(a) (b)

◀ **Figure 32.16 A modern NMR spectrometer**. This 400 MHz NMR spectrometer shows (a) the superconducting magnet in the foreground with the return lines required to pump the liquid helium into the system to cool the magnet. In the background is the computer mainframe required for Fourier transformations. (b) The desktop computer, showing an initial free induction decay (FID) curve, is interfaced with the spectrometer for data manipulation.

the same for all $^{1}H$ or all $^{13}C$ nuclei because, in organic molecules, these nuclei are not isolated from each other or other atoms. Each nucleus is surrounded by electrons from other atoms, or groups of atoms, that can create local magnetic fields ($B_{local}$) that influence the applied field. This statement can be written in the following way:

$$B_{effective} = B_{applied} - B_{local} \qquad [32.4]$$

The result of the influence of these local magnetic fields is a **shielding** of the nuclei in question from the applied field by reducing its effect. In some instances, the local magnetic field of neighboring electrons can add to the applied field, **deshielding** the nuclei in question. The difference in resonance frequencies for various $^{1}H$ or $^{13}C$ nuclei within a molecule due to shielding or deshielding is generally very small but measurable. Such a difference leads the two nuclei in question to be *magnetically inequivalent*.

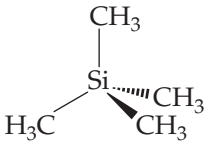
In fact, for a particular magnetic field $B_0$, the resonance frequencies of $^{1}H$ and $^{13}C$ are quite different. This is naturally advantageous when investigating either type of nuclei in isolation.

## The Chemical Shift

Let us now consider the simplest case of a single $^{1}H$ nucleus within an applied magnetic field. Absorption of energy at the resonance frequency, which leads to the nuclear spin flip as shown in Figure 32.14, results in a detectable signal. However, because the resonance frequency depends on several factors, including the magnetic field strength ($B_0$) and the operating frequency of the spectrometer, chemists have developed a dimensionless quantity called the **chemical shift (δ)**, expressed in parts per million (ppm), to quantify the result. The chemical shift scale takes into account the shift in frequency of a particular nucleus from a standard (accepted universally to be tetramethylsilane, TMS), as well as the operating frequency of the spectrometer:

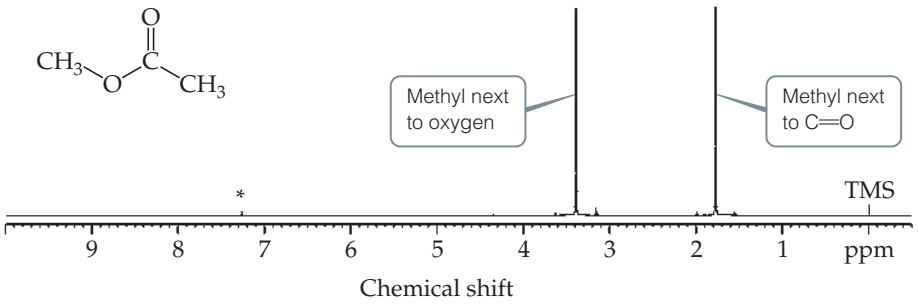
$$\delta = \frac{\text{Shift in resonance frequency from TMS (Hz)}}{\text{Operating frequency of the spectrometer (MHz)}} \qquad [32.5]$$

The chemical shift of an NMR absorption signal is constant, regardless of the operating frequency of the instrument. This is because the chemical shift scale is relative. Using δ allows a comparison between NMR spectra obtained on different spectrometers in different laboratories across the world.




tetramethylsilane

The chemical shift of a $^{1}H$ nucleus that is strongly influenced by the electrons of an adjacent atom has a different chemical shift from a nucleus that is weakly influenced by neighboring electrons. This change in chemical shift is important and is diagnostic. Any competent organic chemist can use the information of functional group effects on




▶ **Figure 32.17 300 MHz $^1$H NMR spectrum of methyl acetate** (inset) acquired in $CDCl_3$ solvent. The residual solvent is marked with an asterisk (*). Compare with the $^{13}$C NMR spectrum of the same compound in Figure 32.12.

chemical shift to identify potential "leads". For example, the $^1$H NMR spectrum of methyl acetate is shown in **Figure 32.17**. This compound has two "different" types of methyl groups: one adjacent to the carbonyl group and the other directly bonded to oxygen. The difference lies in the fact that the two methyl groups are *not* related by symmetry, that is, they are non-identical. Their effective magnetic fields, and hence δ, differ because the effects of the electrons associated with the neighboring carbonyl group and oxygen atom on the applied field are different—this is called *magnetic inequivalence*.

If a hydrogen is partially shielded from the applied field by local magnetic fields, the signal occurs *upfield* towards tetramethylsilane (TMS) (**Figure 32.18**). This is a shift to lower frequency. If the magnetic environment reinforces the applied field, the hydrogen is deshielded and the signal moves *downfield*, away from TMS. This is a shift to higher frequency. So, in the example of methyl acetate, the signal at δ3.39 is *downfield* of the signal at δ1.78.

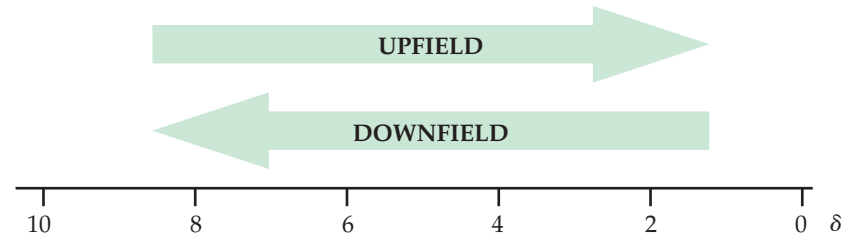
Notice that the hydrogen atoms on each methyl group are equivalent to each other but different from the other methyl hydrogen atom set. Hence only two signals are seen, at 1.78 ppm and 3.39 ppm, in the $^1$H NMR spectrum. The reason why the hydrogens of a methyl group form part of the same signal lies in the speed of rotation about the C—$CH_3$ or O—$CH_3$ bonds in methyl acetate. We mentioned in Chapter 24 that aliphatic alkanes are dynamic molecules, with free rotation about any single bond. This rotation is faster than the timescale of the NMR spectrometer at 300 K (which is the standard operating temperature of a spectrometer), so each hydrogen on the methyl group appears to be equivalent.

A spectrometer with an operating frequency of 400 MHz has a timescale of 400 000 000 times per second. Although several molecular dynamic events, such as rotation about a C—C bond, are faster than this, quite a few are slower—for example, hydrogen exchange rates and some conformational processes. These differences in timescale mean that NMR spectroscopy is a useful technique with which to study kinetic events.

## Sample Preparation

Two other signals in the $^1$H NMR spectrum of methyl acetate need to be accounted for. The first signal is arbitrarily assigned to 0.00 ppm and is a result of the 12 equivalent hydrogens of the reference compound, TMS, which is added to the NMR solvent. Historically, all other

**Go Figure** Is a methyl group resonance at 3.4 ppm shielded or deshielded compared with one at 1.8 ppm?




▲ **Figure 32.18 Chemical shift.** The term *downfield* refers to a higher chemical shift. Nuclei at high chemical shift are relatively *deshielded* by neighboring electron motions. A hydrogen resonance that is *upfield* resonates at a lower chemical shift value. These hydrogens are relatively *shielded* and are the furthest from the resonance of a bare hydrogen atom.

**TABLE 32.2 Common solvents used for sample preparation in $^{1}H$ and $^{13}C$ NMR spectroscopy and the chemical shift of the residual solvent signal**

| Solvent | Residual solvent | $\delta_H$ (ppm) | $\delta_C$ (ppm) |
|---|---|---|---|
| $CDCl_3$ | $CHCl_3$ | 7.26 | 77.16 |
| $CD_3OD$ | $CHD_2OH$ | 3.31 | 49.00 |
| $CD_3COCD_3$ | $CHD_2COCD_3$ | 2.05 | 29.84<br>206.26[a] |
| $D_2O$ | HOD | 4.79 | — |
| $CD_3CN$ | $CHD_2CN$ | 1.94 | 1.32<br>118.26[b] |
| $(CD_3)_2SO$ | $CHD_2SOCD_3$ | 2.50 | 39.52 |

*Data:* H.E. Gottlieb, V. Kotlyar, A. Nudelman, *Journal of Organic Chemistry*, 1997, *62*, 7512.
[a] Value corresponds to carbonyl carbon.
[b] Value corresponds to nitrite carbon.

$^{1}H$ signals are reported by their shift from TMS. Modern NMR spectroscopy, however, typically uses the *residual solvent signal* as the spectrum reference (see **Table 32.2**). There are two reasons for this. The addition of TMS (1% *v*/*v*) to a sample compromises the purity of the sample, even though it is usually removed easily by evaporation. Second, the sample needs to be in solution for this technique to be effective and, as there is usually some source of $^{1}H$ present in the solvent, a marker independent of the sample exists. This leads us to the last signal to be discussed from Figure 32.17, that of solvent.

Recall from our initial discussion on the theory of NMR spectroscopy that any nuclei with a magnetic moment other than zero would produce an NMR spectrum. This means that $^{13}C$ produces an NMR signal while $^{12}C$ does not. Another way of saying this is that $^{12}C$ is *transparent* to the technique of NMR spectroscopy at the frequencies employed.

Typically, organic chemists use solvents to prepare an NMR sample, as a means of making the sample *homogeneous*. The type of solvent used is important because we need to distinguish between signals attributable to the sample and those from the solvent, especially when the solvent is in concentrations greater than 500 times that of the compound of interest in the preparation. This means that any solvent that contains hydrogens will also give rise to a $^{1}H$ NMR signal, which will be at least 500 times stronger than that of the sample. The effect is to "lose" the important sample signals.

To counter this problem, organic chemists use a range of $^{1}H$ NMR transparent (known as *deuterated*) solvents. Solvents such as deuterated chloroform ($CDCl_3$) or $d_4$-methanol ($CD_3OD$) become useful and common solvents in $^{1}H$ NMR spectroscopy because $^{2}H$ absorbs at a completely different frequency from $^{1}H$, so does not interfere. However, although $CHCl_3$ or $CH_3OH$ become unattractive in $^{1}H$ NMR spectroscopy for reasons described earlier, they are acceptable solvents in $^{13}C$ NMR spectroscopy. It is almost impossible (and certainly very expensive) to produce large quantities (liters) of 100% (v/v) pure deuterated solvents. Typically, an NMR spectroscopy laboratory would stock, for example, 99.8% $CDCl_3$ solvent. The extra 0.2% would contain protium rather than deuterium. This amount of $CHCl_3$ is still enough to produce a significant signal (known as the *residual solvent signal*) in the $^{1}H$ NMR spectrum of any sample (see Figure 32.17).

## Interpreting NMR Spectra

Three components of an NMR spectrum provide useful structural information about a molecule. They are:

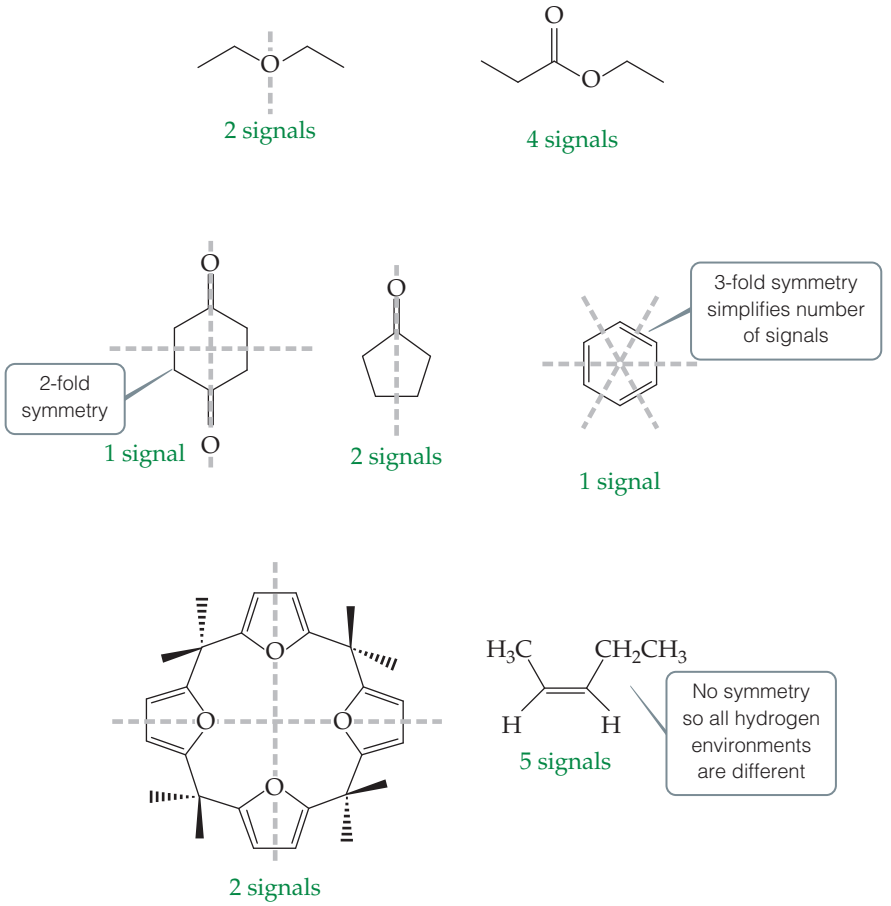
- *chemical shift* (δ)—gives evidence on neighboring functional groups;
- *integration* of the NMR signal—relative areas of signals in a $^{1}H$ NMR spectrum are proportional to the number of hydrogens giving rise to each signal;
- *coupling constant* (*J*)—measured in hertz (Hz), the coupling constant is extremely useful for determining the connectivity of nuclei within a molecule.

As you might expect, the result of an NMR spectroscopic experiment could become very complicated even with simple molecular structures. Luckily, molecular symmetry elements help to simplify matters. These symmetry elements occur in two ways. If the molecule has a plane of symmetry, then the two halves are identical and we need only concern ourselves with one-half of the molecule in order to work out its NMR spectrum. A few examples of the effects of symmetry on $^1H$ are shown in **Figure 32.19**.

The second factor that simplifies a NMR spectrum was introduced in our earlier discussion on rotation about C—$CH_3$ bonds. In fact, this dynamic behaviour of rotation about C—C bonds usually leads to the two hydrogens on a methylene ($CH_2$) group being chemically and magnetically equivalent (Figure 32.19). This simplification using symmetry is a powerful way to differentiate between two constitutional isomers.

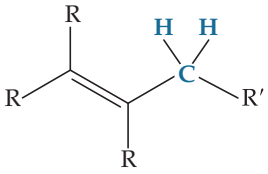
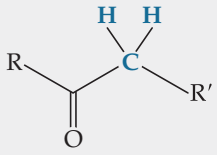
The typical $^1H$ and $^{13}C$ NMR chemical shifts for hydrogens and carbons with neighboring common functional groups are shown in **Table 32.3**. The $^1H$ signal associated with simple alkanes tends to resonate between 0.8 and 1.8 ppm, depending on their classification as primary, secondary or tertiary hydrogen atoms. The general trend for all other organic molecules is that δ depends on the electronegativity of nearby atoms and the hybridization of adjacent atoms. Thus the greater the electronegativity of a neighboring group (F > Cl > Br > I), the more deshielded the $^1H$ nucleus will be and the further downfield (higher δ) the $^1H$ NMR signal will lie. More than one electronegative group influences the signal even more, causing the $^1H$ signal to move further downfield (**Figure 32.20**).

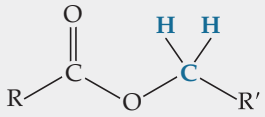
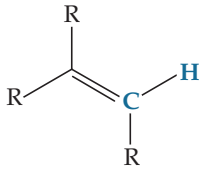
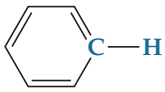
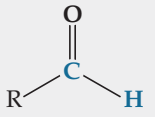
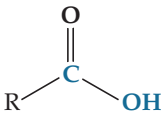
**Go Figure** How many signals would you expect in the $^{13}C$ NMR spectrum of the molecules shown in this figure?



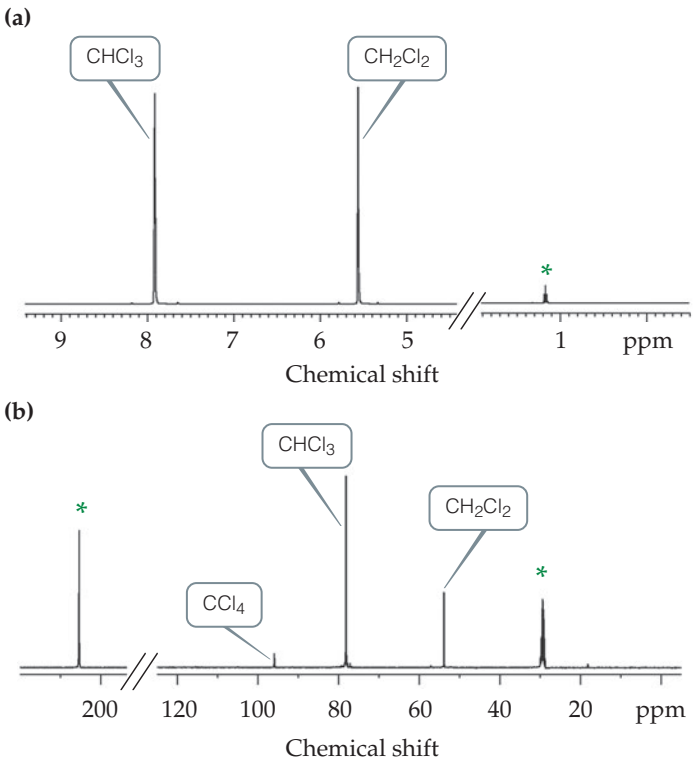

▲ **Figure 32.19 Symmetry.** The number of NMR signals present in a spectrum depends on the symmetry of the compound in question. The higher the symmetry, the smaller the number of signals in the spectrum. Molecules with a single set of equivalent hydrogens will give rise to one $^1H$ NMR signal. Two or more sets of equivalent hydrogens will give different $^1H$ NMR signals for each set. Here, the number of signals seen in the $^1H$ NMR spectrum of each compound is indicated.

**TABLE 32.3 Approximate chemical shift regions for $^1H$ and $^{13}C$ nuclei (colored) neighboring the most common functional groups**

| Type of neighboring group[a] | $\delta_H$[b,c] | $\delta_C$[c] |
|---|---|---|
| R**C**$H_3$, R**C**$H_2$R′, $R_3$**C**H | 0.8–1.6 | 10–55 |
|  | 1.5–2.5 | 40–80 |
|  | 2.0–2.8 | 40–80 |
| Ar**C**$H_3$, Ar**C**$H_2$R | 2.0–3.0 | 20–40 |
| R—C≡C—**H** | 2.0–3.0 | 65–85 |
| R**C**$H_2$X (X=Cl, Br, I) | 3.0–4.0 | 40–80 |
| R**C**$H_2$OR′ | 3.0–4.0 | 40–80 |
| R**C**N | n/a | 110–130 |

| Type of neighboring group[a] | $\delta_H$[c] | $\delta_C$[c] |
|---|---|---|
|  | 3.5–4.5 | 40–80 |
|  | 4.5–6.0 | 100–150 |
| RO**H**, RN$H_2$[d] | 0.5–6.0 | n/a |
|  | 6.5–8.5 | 110–160 |
|  | 9.5–10.5 | 180–210 |
|  | 10–13 | 175–185 |

[a] R and R′ refer to simple aliphatic groups; Ar refers to an aromatic ring.
[b] Note that, when the symbol δ is used, there is no need to add ppm. Remember, chemical shift is dimensionless and ppm is not a dimension.
[c] Chemical shifts referenced to TMS.
[d] Both OH and NH NMR absorptions are typically broad as a result of the hydrogen exchange they exhibit with solvent and traces of water within the solvent.




◀ **Figure 32.20 Effect of electronegative atoms neighboring $^1H$ and $^{13}C$ nuclei on their chemical shift.** (a) 300 MHz $^1H$ NMR spectrum of $CHCl_3$ and $CH_2Cl_2$ in $(CD_3)_2CO$. (b) 75.5 MHz $^{13}C$ NMR spectrum of $CCl_4$, $CHCl_3$ and $CH_2Cl_2$ in $(CD_3)_2CO$. Asterisks indicate solvent or residual solvent signals.

## Sample Exercise 32.2

**Determining the number of NMR signals in a spectrum**

How many absorptions would you expect in the $^1$H NMR spectra of:
**(a)** 1,1-dimethylcyclohexane,
**(b)** ethyl methyl ether?

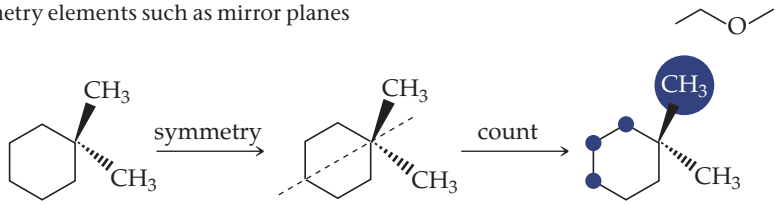
### SOLUTION

**Analyze** We are asked to determine the number of "different" hydrogen environments in two molecules.

**Plan** We need to draw out the structure of each compound and look for symmetry. If no symmetry elements such as mirror planes exist, we then count up the number of *different* hydrogen atoms, remembering that hydrogens on the same carbon are equivalent in an alkane.

**Solve**

**(a)** The answer is four absorptions.
**(b)** The answer is three absorptions. In this case, there is no symmetry across the molecule.

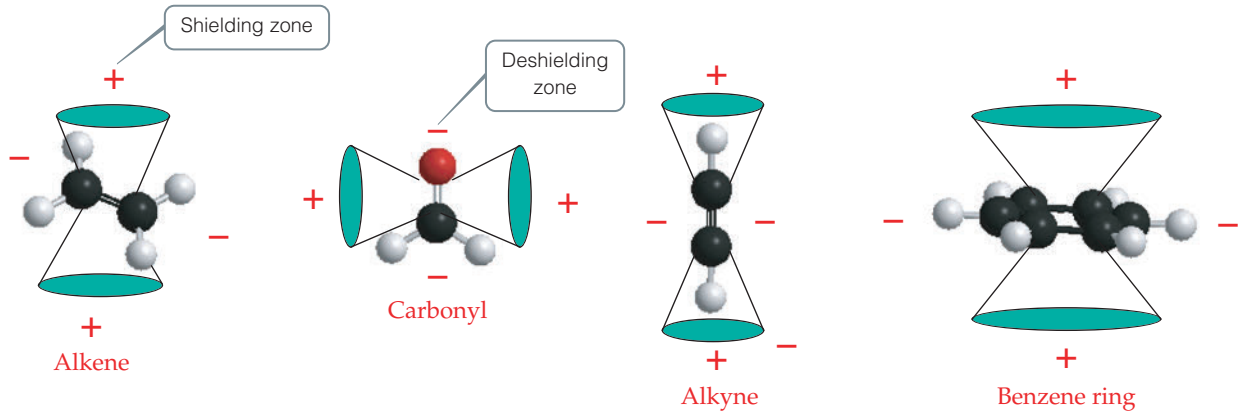



**Practice Exercise**
How many absorptions would you expect in the $^{13}$C NMR spectra of:
**(a)** cyclohexanone
**(b)** 2-methyl-2-butene?

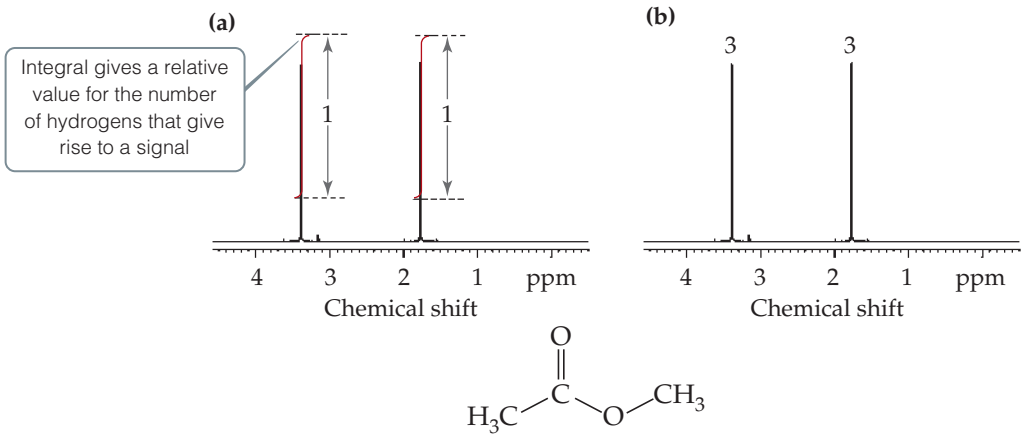
The chemical shift is also influenced by the hybridization of neighboring atoms (Figure 32.21). Generally, the more *p* character in a neighboring atom ($sp > sp^2 > sp^3$), the higher the chemical shift will be for the observed nucleus. This change in δ is due to the deshielding effect from the applied magnetic field produced by these bonds, as indicated in Figure 32.21. Note that orientation is an important factor in this generalization. The hydrogens on benzene are in a deshielding (−) zone, whereas those of ethyne, the carbons of which have more *p* character, are in a shielding (+) zone. In any case, the chemical shift of the signals attributable to either set of hydrogens is higher than that of a simple alkane.

## Integration

Recall that in mathematical terms, **integration** refers to the area under a curve. The term *integration* in NMR is used to describe the area under each signal and is proportional to the number of equivalent nuclei that give rise to that signal. Integration is diagnostic in $^1$H NMR experiments but used rarely in $^{13}$C NMR experiments.




▲ **Figure 32.21** Deshielding effects in alkenes, carbonyls, alkynes and benzene. The magnetic fields associated with the π-electrons of the *sp* and $sp^2$ hybridized atoms cause regions of shielding (+) and deshielding (−) that influence the chemical shift of adjacent nuclei.



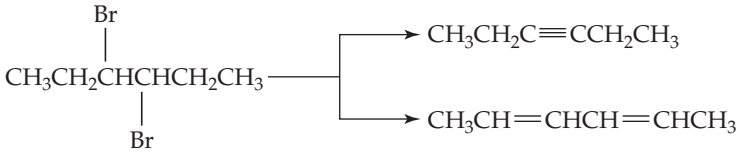

◀ **Figure 32.22 Integration.** (a) Integral lines indicate the area under the signal. This technique doesn't necessarily indicate how many hydrogens each signal accounts for, only their relative areas. (b) This method indicates the number of hydrogens associated with each signal. Both (a) and (b) yield the same information.

Two conventions describing the integration of a signal are used, as shown in **Figure 32.22**. The first method uses the height of the integral to give an area relative to other signals. For example, a ratio of areas that is 1 : 1 may in fact refer to a hydrogen ratio within the compound of 3 : 3, as for methyl acetate. An alternative method (and the one we use more often) does all the hard work for you. The numbers above the signals in Figure 32.22(b) equate to the numbers of protons that give rise to those signals. This result is based on the integration shown in Figure 32.22(a) and its application to the compound in question—methyl acetate in this example. Integration can help in structural analysis, particularly when determining symmetry.

## Sample Exercise 32.3

### Differentiating between products of a reaction

3,4-Dibromohexane can undergo base-induced double dehydrobromination to yield either 3-hexyne or 2,4-hexadiene. How could you use NMR spectroscopy to identify the product formed?

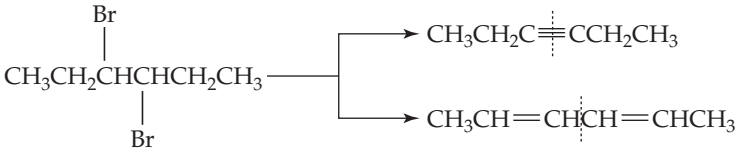



### SOLUTION

**Analyze** We are asked to distinguish between the two possible products using NMR spectroscopy.

**Plan** As with all NMR questions of this kind, start with symmetry. Once identified, or not, count up the number of different carbon or hydrogen environments. Look for differences.

**Solve** Each potential product has a mirror plane, as shown here. Bearing this in mind, both products will exhibit three absorptions in their $^{13}C$ NMR spectrum.

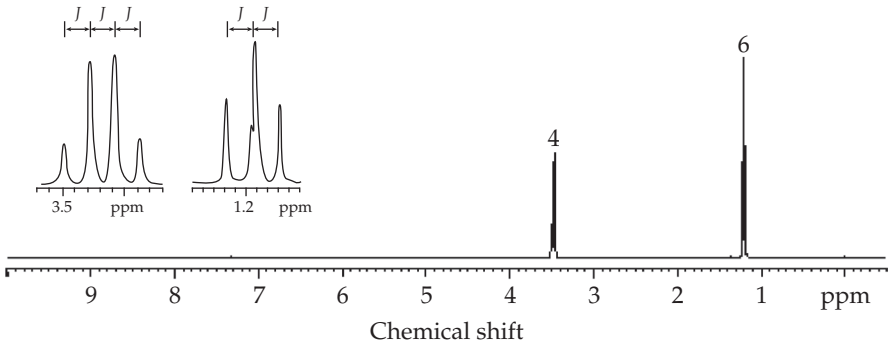



However, the numbers of absorptions in the two $^{1}H$ NMR spectra are different. The alkyne will exhibit two absorptions while the diene exhibits three. Purely on this basis, the two potential products are distinguishable.

**▶ Practice Exercise**

Propene reacts with HBr potentially to produce two alkylbromides. Only one is formed, the outcome following Markovnikov's rule. How could you use NMR to determine which alkylbromide is the Markovnikov product?

**Go Figure** What does the very small signal at 7.3 ppm represent?




▲ **Figure 32.23 300 MHz $^1$H NMR spectrum of diethyl ether in $CDCl_3$.** Inset: Expansions of the two signals showing the multiplicity of each signal.

| | | | | | | |
|---|---|---|---|---|---|---|
| singlet | 1 | | | | | |
| doublet | 1 | 1 | | | | |
| triplet | 1 | 2 | 1 | | | |
| quartet | 1 | 3 | 3 | 1 | | |
| quintet | 1 | 4 | 6 | 4 | 1 | |
| sextet | 1 | 5 | 10 | 10 | 5 | 1 |

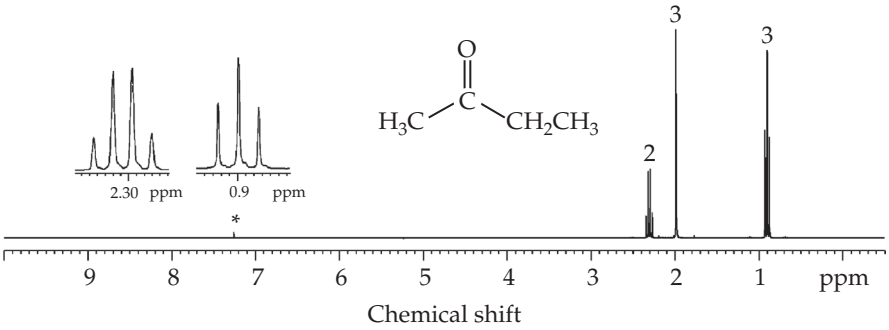
▲ **Figure 32.24 Multiplicity.** $J$ is a quantitative measure of the magnetic interaction of coupled nuclei. The splitting pattern for nuclei with $I = \frac{1}{2}$ follows a binomial distribution. For example, if a signal is split into two peaks of equal intensity, that signal is called a doublet.

## Spin–Spin Coupling

The last piece of NMR evidence we consider is probably the most powerful in determining structure. The concept is called **spin–spin coupling** or *J coupling*. So far we have looked at $^1$H and $^{13}$C nuclei in isolation. When two or more nuclei are close enough for their spins to interact or *couple*, the resulting signals split. This typically occurs if there are hydrogen atoms neigboring the nucleus that you are observing. The **splitting pattern** formed is characteristic of the coupling and yields more information about the nucleus's neighbor than it does about itself. For example, diethyl ether ($CH_3CH_2OCH_2CH_3$) has two sets of different hydrogens (as a result of symmetry), leading to two signals in the $^1$H NMR spectrum (Figure 32.23). The chemical shift of these signals is influenced by the ether oxygen, with the hydrogens of the $CH_2$ being more deshielded. Closer inspection of the signals shows them to be complicated by very uniform patterns. This complicated pattern is a result of the *through-bond* communication between $^1$H nuclei across the $CH_2$ and $CH_3$ groups. For any set of coupled hydrogens, the distance between peaks in each splitting pattern, termed the **coupling constant** ($J$), is identical. The magnitude of the coupling depends on the nature and number of intervening bonds between the two (or more) nuclei. The further away the coupling nuclei are from each other, the smaller the value for $J$. Therefore, a $^4J$ coupling (in which there are four intervening bonds) is smaller than a $^3J$ coupling (in which there are three intervening bonds). The pattern, or **multiplicity**, of the signals is derived from the number of identical nuclei that couple, and follows a binomial distribution, shown in Figure 32.24.

Hydrogen coupling does not usually proceed past a functional group within the carbon framework that doesn't contain $^1$H. Figure 32.25 shows the $^1$H NMR spectrum of 2-butanone to illustrate this point. The spectrum is dominated by three signals at 0.9, 2.0 and 2.3 ppm. An enlarged view of the resonance attributable to the methyl attached to the carbonyl group shows this signal to be a single sharp peak (or *singlet*), demonstrating

▶ **Figure 32.25 300 MHz $^1$H NMR spectrum of butan-2-one in $CDCl_3$.** Despite the four intervening bonds linking $^1$H nuclei, no $^4J$ coupling is observed at this operating frequency due to the carbonyl group. Residual solvent is marked with an asterisk (*).



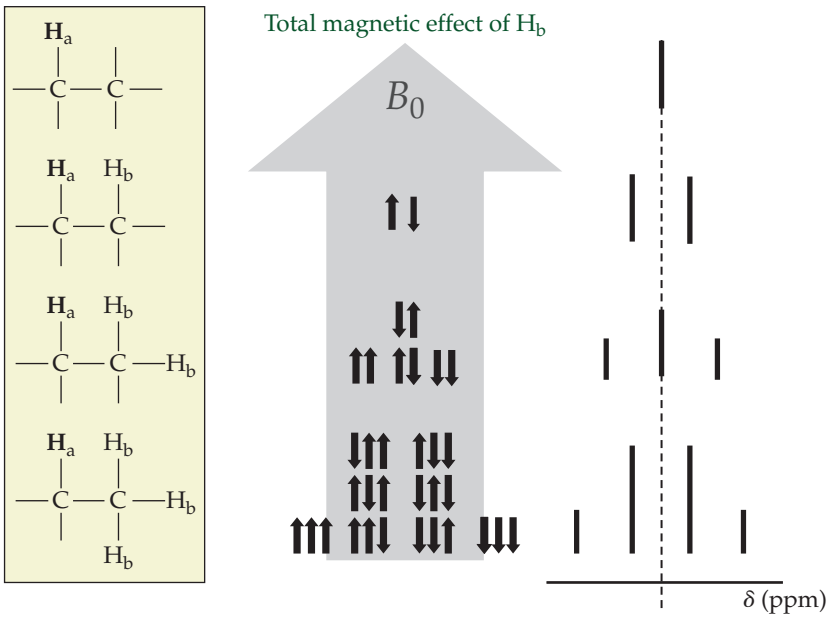
that no coupling across the C═O group from the $CH_2$ group is seen. As with the $^1H$ NMR spectrum of diethyl ether (Figure 32.23), a characteristic splitting pattern is shown for the hydrogens of an ethyl group. Let's now take a more detailed look at this splitting pattern and why it occurs.

A nucleus coupled to $n$ other equivalent nuclei (each with $I = \frac{1}{2}$) appears as a *multiplet* (Figure 32.24). The multiplicity attained for the signal of the coupled nuclei can be described as containing $(n + 1)$ peaks. The origin of this phenomenon, known as the **($n$ + 1) rule**, can be ideally described by considering two non-equivalent hydrogens, $H_a$ and $H_b$, found on adjacent carbons. **Figure 32.26** illustrate the principle as well as the underlying reasoning. The chemical shift of $H_a$ is influenced by $H_b$. In fact, this influence (and hence the multiplicity) is a result of the two possible spin orientations of $H_b$. The parallel orientation of nuclear spins adds to the applied field, causing the signal attributable to $H_a$ to appear at a lower applied field (higher δ), whereas the anti-parallel orientation causes $H_a$ to appear at a higher field (lower δ). These two signals (combined they are termed a *doublet*) occur on either side of the position $H_a$ would occupy in the absence of the influence of $H_b$.

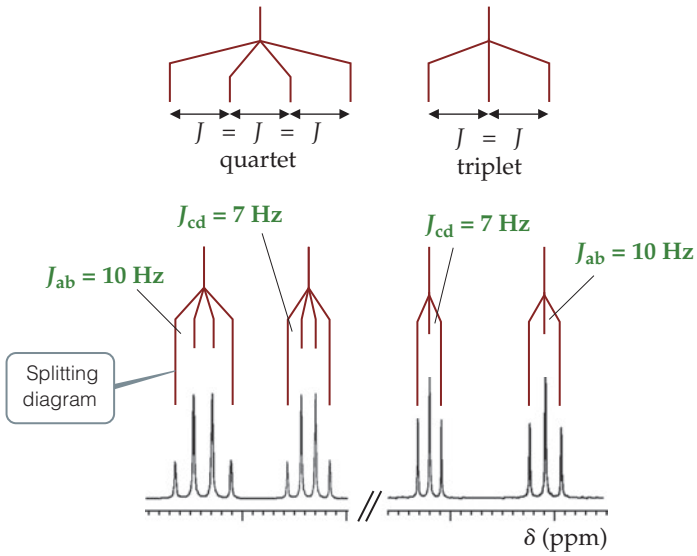
If we turn our attention back to the expanded region of the $^1H$ NMR spectrum of diethyl ether (Figure 32.23), we see that the $CH_2$ group is *coupled* to the three equivalent hydrogens of the methyl group. This coupling causes the signal attributable to the $CH_2$ hydrogens to split into four $(3 + 1)$ peaks with intensities in the ratio 1 : 3 : 3 : 1. This specific pattern is called a *quartet* (see Figure 32.24). Conversely, the methyl group couples

**Go Figure**

Determine the possible connectivity between hydrogen nuclei that show as a doublet and septet multiplicity with integration in the ratio 6 : 1, respectively, within the 1H NMR spectrum.




▲ **Figure 32.26 Origins of complex signal splitting.** The influence of the spin states of $n$ neighboring $H_b$ on the applied field causes the signal for $H_a$ to split into '$n$ + 1' peaks. The splitting pattern and the relative peak heights are attributable to the additive and cancelling effect of $H_b$ spins.



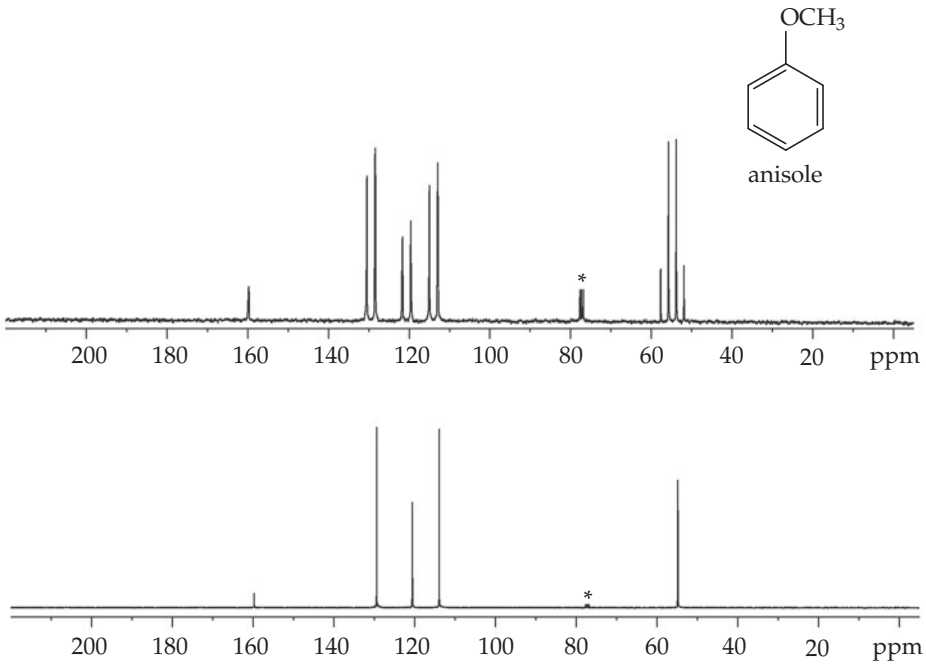

▶ **Figure 32.27 Coupling constants.** The spacing between each peak in a multiplet is called the coupling constant, *J*, expressed in hertz (Hz). Note that the *J* value between two mutually coupled nuclei is the same and different from that attained for other coupled pairs of nuclei. The coupling constant yields information on connectivity.

to the $CH_2$ group, splitting into three (2 + 1) signals in the ratio 1 : 2 : 1, with the distance between each signal in the *triplet* (known as the *J* value) being equivalent to those in the quartet. The permutations of nuclear spin "up" and "down" leading to the triplet and quartet are shown in Figure 32.26.

As organic chemists, we can use the information derived through individual *J* values to determine the connectivity of a carbon framework. **Figure 32.27** illustrates how the connectivity of two nuclei can be expressed by the magnitude of *J*. This spectrum contains two sets of triplets and two sets of quartets for an unknown compound. The triplet/quartet pattern is diagnostic of an ethyl group. So, intuitively, we might expect two sets of ethyl groups within the structure of the unknown. The difficulty lies in distinguishing between the two sets. Determination of the coupling constants, however, soon identifies which triplet is *coupled* to which quartet. We can use this information, together with the chemical shifts of the quartets, to determine the likely connectivity of the ethyl groups to other functional groups. Looking for sets of signals with the same *J* allows information to be extracted from very complex overlapping spectra. Because *J* values do not depend on the spectrometer, a spectrometer with a higher operating frequency will show the splitting of the signal compressed to a shorter distance on a δ scale, one more reason why higher operating frequencies are preferred for studying complex molecules.

## $^{13}$C NMR Spectra

$^{13}$C NMR spectra are often used by chemists to indicate the number of different carbon atoms, as well as to provide some evidence on the nature of the functional groups contained within a molecule. In order to do this, $^{13}$C NMR spectra often remove the multiplicity displayed by C–H coupling—a process called **decoupling**. As shown in **Figure 32.28** coupling of carbon to hydrogen complicates the spectrum to an unnecessary degree. By decoupling the $^1$H and $^{13}$C nuclei, all multiplicity is lost and the signals are simplified to singlets. This type of experiment is called a *heteronuclear decoupling* experiment because it decouples the effect of $^1$H nuclei on $^{13}$C nuclei. Note that the reverse is not necessary, that is, the need to decouple the effects of $^{13}$C coupling on the $^1$H NMR experiment. The reason is that $^1$H is approximately 99% naturally abundant and $^{13}$C is only 1% naturally abundant. Having such a low natural abundance means that, for the most part, the effect of $^{13}$C nuclei contained within the sample is below the level of sensitivity for $^1$H NMR spectroscopy. In $^{13}$C NMR spectra, there are a number of factors that influence the intensity of the signal, not just the number of carbon atoms of a particular environment in the molecule. Consequently, integration is not usually performed on these signals.

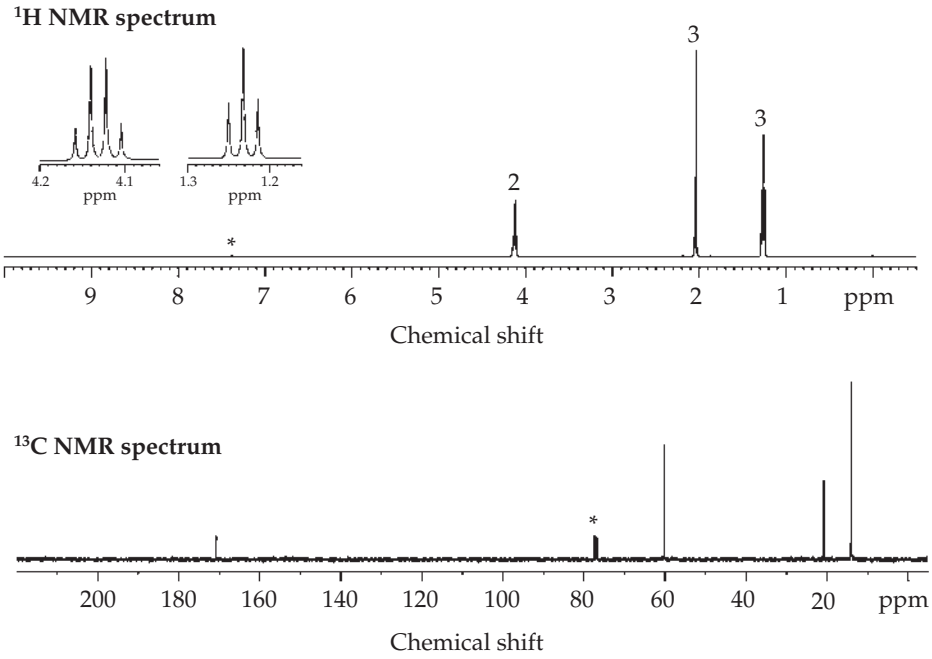



**◀ Figure 32.28 $^{13}$C NMR spectra—when too much information complicates interpretation.** Routinely, organic chemists undertake $^{13}$C NMR experiments that involve decoupling the effect of $^{1}$H to which it is attached. *Top spectrum*: Coupled $^{13}$C NMR spectrum of anisole. *Bottom spectrum*: Decoupled $^{13}$C NMR spectrum of anisole. Asterisks (*) denote $CDCl_3$ solvent.

## Sample Exercise 32.4

### Using NMR to Solve a Chemical Unknown

Compound A, with molecular formula $C_4H_8O_2$, has the following $^{1}$H and $^{13}$C NMR spectra. Deduce its structure using this information.




**Note** Numbers on top of signals represent integration values. Asterisk indicates signals due to solvent.

### SOLUTION

**Analyze** We have been asked to use NMR spectra to deduce the molecular structure of a compound containing C, H and O.

**Plan** Based on chemical shift (δ) and splitting patterns in the $^{1}$H NMR spectrum, we can deduce the structure of compound A. We will use the $^{13}$C NMR spectrum to confirm the choice of structure.

**Solve** The $^{1}$H NMR spectrum contains three signals at about 1.2, 2.0 and 4.1 ppm, with integration in the ratio 3 : 3 : 2. This

*Continued*

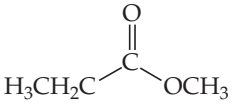
integration totals the number of hydrogens in the molecular formula and so represents the molecule as a whole (no further symmetry).

Two of these hydrogen signals are split, forming a triplet and a quartet. This combined pattern is indicative of an ethyl group ($CH_3CH_2$) following the $n + 1$ rule, a deduction helped by the integration ratio.

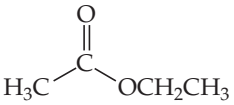
The third signal is a three-hydrogen singlet, which means that the hydrogens on this methyl group (because it integrates for three hydrogens) do not couple. The chemical shift of this resonance implies that this methyl group is bonded to a carbonyl group, consistent with the lack of coupling within the signal (that is, a singlet).

At this stage we have accounted for all atoms in the molecule except for an oxygen atom. This must be linked between the ethyl and carbonyl groups in order to give rise to the chemical shift seen by the $CH_2$ group at 4.10 ppm.

Placing all this information together, suggests our unknown must be ethyl acetate.




Note the other ester




would have a chemical shift of 2.2 ppm for the $CH_2$ group, and a three-hydrogen singlet at 4.10 ppm.

**Check** Our deduction is confirmed by the four signals within the $^{13}C$ NMR spectrum. The signal at 171 ppm indicates the presence of a carbonyl group. The signal at 60 ppm is indicative of a carbon attached to oxygen (in this case, as part of the ester group), with the two other signals at 13 ppm and 21 ppm consistent with the two methyl carbon atoms. Contrast this result with the spectrum of butan-2-one (Figure 32.25).

**▶ Practice Exercise**

A liquid sample has a band in the infrared spectrum at 1710 $cm^{-1}$. The NMR spectrum shows two $^1H$ resonances in the ratio of 3 : 2. The molecular formula of the unknown is $C_5H_{10}O$. Deduce its structure.

## Self-Assessment Exercises

**32.7** Which of the following nuclei will give an NMR spectrum: $^{16}O$, $^{19}F$, $^{31}P$, and $^{32}S$?

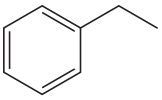
**(a)** $^{16}O$ and $^{19}F$ only

**(b)** $^{19}F$ and $^{31}P$ only

**(c)** $^{16}O$ and $^{32}S$ only

**(d)** $^{19}F$ and $^{31}P$ only

**32.8** Consider ethylbenzene. How many signals do you predict would be in the $^1H$ NMR spectrum and what would be the relative sizes of the signals?

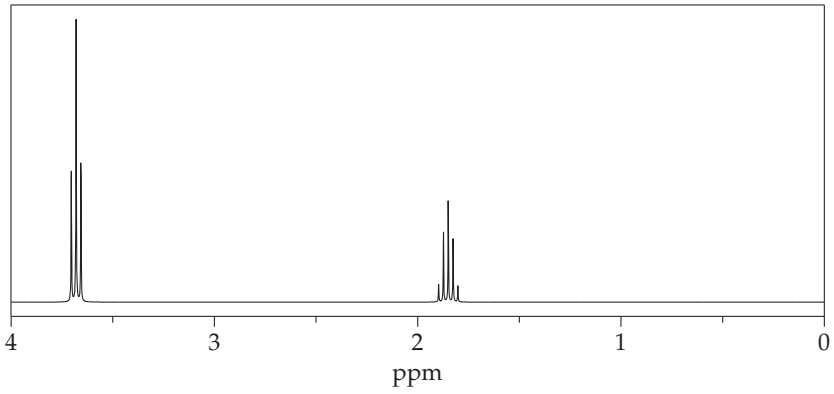


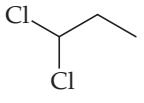
**(a)** Three signals in the ratio 2:2:1

**(b)** Five signals in the ratio 3:2:2:2:1

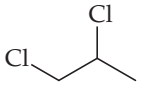
**(c)** Seven signals in the ratio 3:2:1:1:1:1:1

**32.9** There are four constitutional isomers of dichloropropane, $C_3H_6C_{l2}$, shown here. Which one would have the $^1H$ NMR spectrum shown?

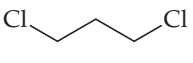



**(a)**




**(b)**




**(c)**


**(d)**

# Exercises

**32.10** Which of the following solvents could be used in $^1$H NMR spectroscopy? Acetone ($CH_3COCH_3$), methanol-$d_4$ ($CD_3OD$), tetrachloromethane ($CCl_4$), water ($H_2O$), diethyl ether ($CH_3CH_2OCH_2CH_3$). Explain your choice.

**32.11** Indicate the number of different absorptions and the relative intensities expected in the $^1$H NMR spectra of:

**(a)** 2,2-dimethylbutane **(b)** ethanol

**(c)** acetone **(d)** 2-chloropropane

**(e)** cyclohexane **(f)** cyclohexanone

**(g)** ethyl methyl ether

**32.12** Indicate the number of different absorptions expected in the $^{13}$C NMR spectra of:

**(a)** 2,2-dimethylbutane **(b)** ethanol

**(c)** acetone **(d)** 2-chloropropane

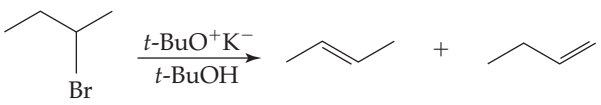
**(e)** cyclohexane **(f)** cyclohexanone

**(g)** ethyl methyl ether

**32.13** Predict the splitting pattern observed in the $^1$H NMR spectrum for each of these compounds:

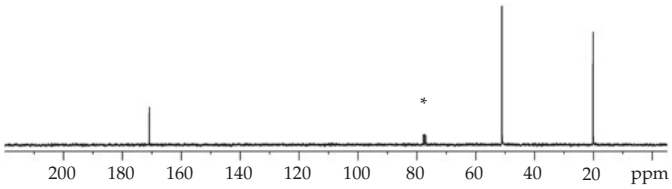
**(a)** $CH_3CHBr_2$ **(b)** $(CH_3)_2CHCl$ **(c)** $(CH_3)_3CBr$

**32.14** 2-Bromobutane undergoes a β-elimination reaction in the presence of potassium *tert*-butoxide to produce one of two isomeric alkenes.




How could you use NMR spectroscopy to determine which alkene is formed as the major product?

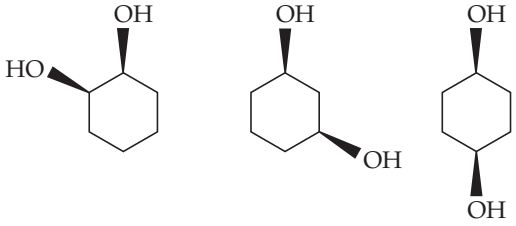
**32.15** The reaction of an unknown with ethanol in the presence of a small amount of $H_2SO_4$ leads to a compound that smells distinctly like rum. The hydrogen-decoupled $^{13}$C NMR spectrum of the product is shown here (* = solvent).




**(a)** What is the structure of the unknown?

**(b)** What other structure(s) would be consistent with this $^{13}$C NMR spectrum?

**32.16** Two bottles labelled *cis*-cyclohexandiol were found in a laboratory. Because of their differing melting points, the bottles clearly contained two different *cis*-cyclohexandiol isomers. To determine which isomer was in which bottle, the chemist decided to run $^{13}$C NMR spectra on a sample of each. The three possible isomers were:

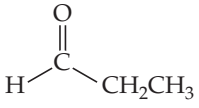



The two $^{13}$C NMR hydrogen-decoupled spectra contained the following data:

- spectrum of sample in bottle A: 20.20, 62.55
- spectrum of sample in bottle B: 16.09, 29.52, 36.15, 63.08

Identify which isomer was present in each bottle.

**32.17** The 200 MHz $^1$H NMR spectrum of propanal (shown) has three distinctive resonances: δ9.5 (1H, singlet), 2.2 (2H, quartet), 1.0 (3H, triplet). Assign each resonance to the structure.




**Answers to Self-Assessment Exercises**

**32.7** (d) **32.8** (b) **32.9** (c)

## 32.4 Mass Spectrometry

All international airports and many of the larger domestic airports require passengers to go through a security screening process. This generally involves two stages, the first being that all passengers pass through a metal detector while their hand luggage passes through an X-ray machine, both of which can detect metallic weapons. The second is a random check of a person's clothes and hand luggage using an explosive trace detector (ETD). Explosives are typically of rather few classes of compound, many of them containing nitro groups. These can be detected in minute quantities, well below that of visible particles. Mass spectrometry provides a fast and accurate means of identifying very small quantities of material. Now that compact 'bench-top' instruments are available, a mass spectrometer tuned to detect certain classes of compounds is a powerful ETD.

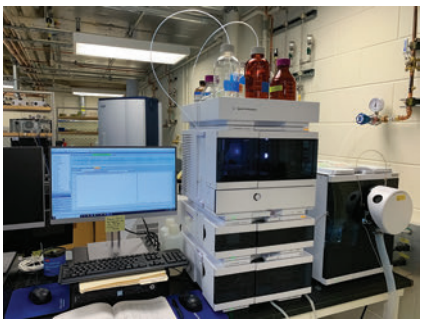
In this section, we examine how this technique can help identify unknown compounds. By the end of it, you should be able to:

- Understand the principle behind mass spectrometry
- Interpret simple spectra to provide some structural knowledge of a molecule

Mass spectrometry is distinctly different from the other characterization techniques introduced in this chapter. This technique does not depend on the absorption of electromagnetic radiation, but instead examines what happens when a molecule is bombarded with high-energy electrons. These electrons are used for two purposes. The molecule is *ionized* by the electrons and the electrons are used to break the molecule apart or **fragment** it, in a similar way to hitting a cricket ball through a pane of glass. The masses of the fragments are measured and brought together (in analysis) in order to reconstruct the molecule. Apart from determining the masses of the fragments, mass spectrometry can also indicate the mass of the *parent structure*, which in most instances, coincides with the signal of highest mass. This signal is called the **molecular ion**, or parent ion peak. Mass spectrometry is a technique used routinely to determine the molecular weight of a compound. The fragmentation pattern can give information on the functional groups present in molecules.

Mass spectrometry employs many different ionization techniques, including electron impact ionization (EI), chemical ionization (CI), fast atom bombardment (FAB) and more advanced techniques such as matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) and electrospray ionization (ESI) methods. Each of these different techniques has certain advantages, and the modern organic chemist uses more than one mass spectrometry technique to solve the structure of an unknown.

Mass spectrometry is also routinely employed in analytical laboratories as part of the identification of compounds in complex reaction mixtures, in the separation and identification of minute quantities of biologically active compounds, or in the identification of drugs in hair samples or trace explosives on luggage. **Figure 32.29** shows an ESI mass spectrometer (right) linked to a high-performance liquid chromatography (LC) unit (left), which is an instrument routinely used for separating complex mixtures. The combination, known as LCMS, is a powerful analytical technique.



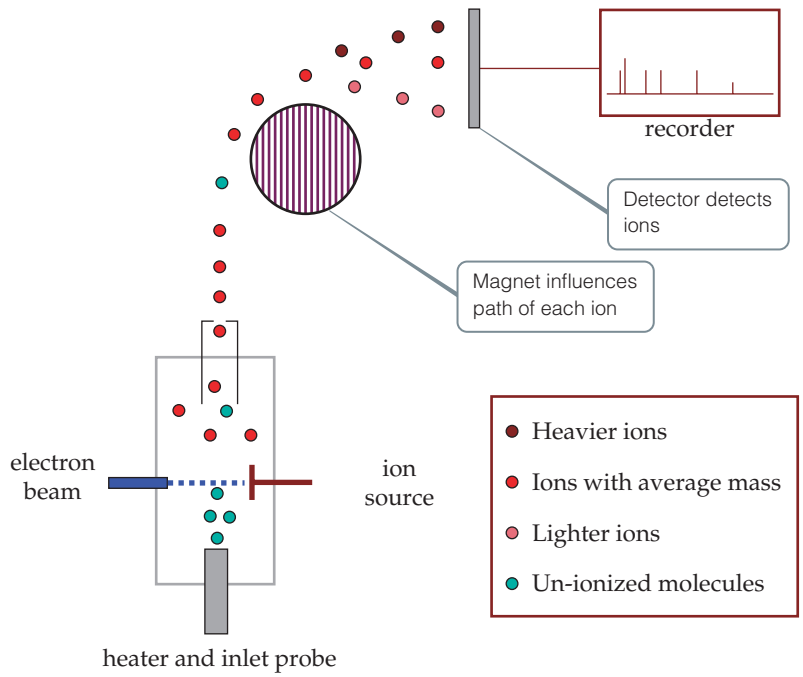
▲ **Figure 32.29 A modern LCMS.** Mass spectrometry is often used in combination with other techniques, typically separation techniques such as liquid chromatography (LC) or gas-phase chromatography (GC). This LCMS is made up of three components: auto-sampler (left), liquid chromatography instrument (center) and electrospray mass spectrometer (right). As different compounds are separated from a mixture by LC, they are analyzed for their molecular mass.

## Electron Impact Ionization Mass Spectrometry

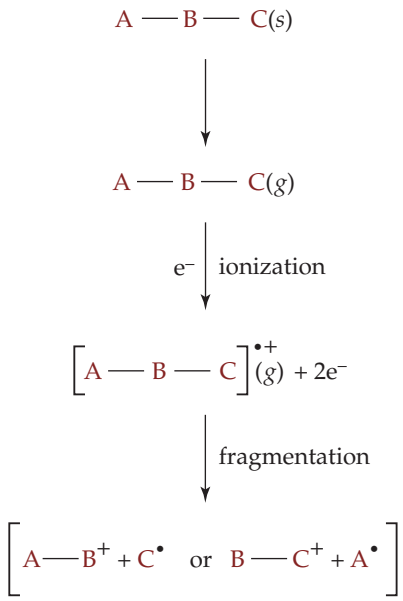
In this section, we concentrate on **electron impact ionization (EI) mass spectrometry (EIMS)** because it most clearly shows the principles of mass spectrometry, even though more complex methods are used more often today. Mass spectrometers using the EI technique operate by determining the *mass-to-charge ratio* ($m/z$) for ions in the gas phase. **Figure 32.30** illustrates how a result is obtained using an EI mass spectrometer. There are three principal components to EIMS: an ion source, which ionizes molecules in a high vacuum and accelerates them to form a beam; a strong magnet to deflect or separate the ions according to their masses; and a detector that records the masses of the ions generated. The intensity of each signal is then plotted as a function of the mass-to-charge ratio ($m/z$).

The sample to be analyzed by EIMS is vaporized by heating to the gas phase within the inlet probe. Ionization of the sample occurs when a beam of high-energy electrons (10–70 eV, 1 eV = 96 kJ/mol) collides with the sample. Energy is transferred as a result of that collision, removing an electron from the molecule and yielding a positive ion. In this case, we say that the organic molecule has been *ionized* by electron impact and the signal that results is called the molecular ion signal ($M^+$). This molecular ion has the same mass

**Go Figure** Why are neutral species not detected by this method?




▲ **Figure 32.30 The principle behind electron impact ionization mass spectrometry.** The technique relies on generating charged species (ions) by bombarding a gas-phase sample with high-energy electrons.



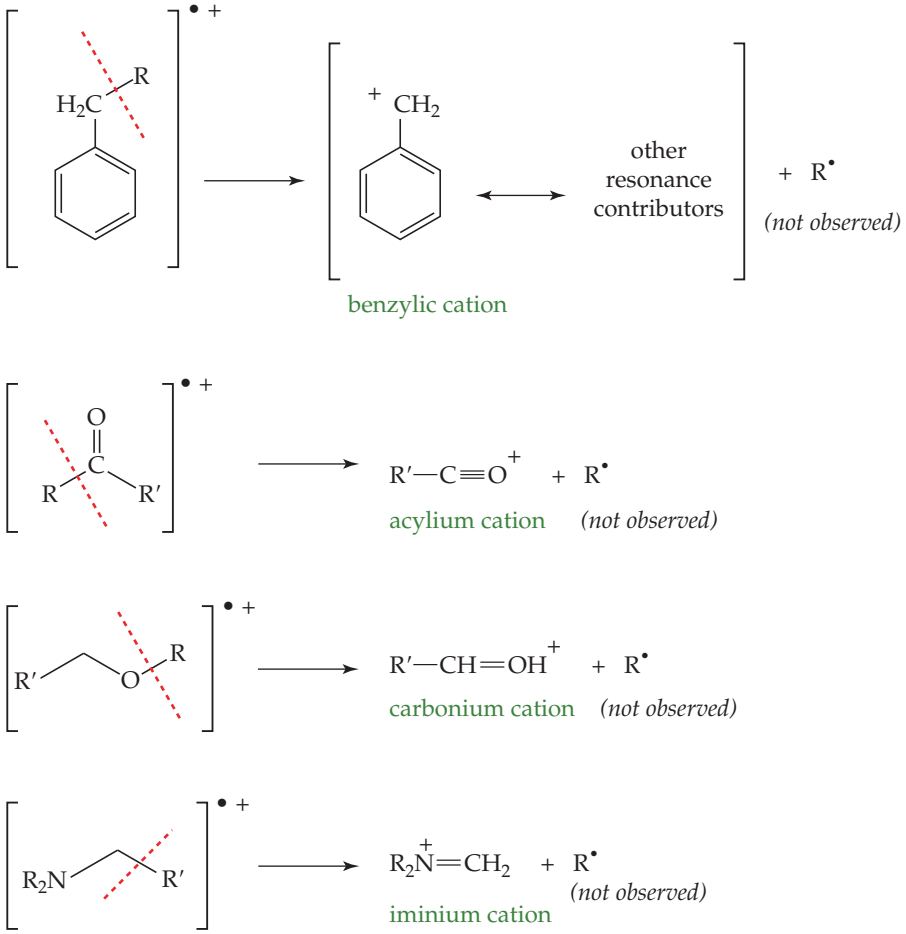

▲ **Figure 32.31** **Ionization and fragmentation.**

as the neutral molecule less the mass of a single electron, which is of course negligible compared with the mass of the molecule.

If the electron collides with the molecule at higher energy (that is, around 70 eV), it not only brings about the ionization of the molecule but also causes dissociation or *fragmentation* of the molecule, as shown in **Figure 32.31**. This fragmentation process gives a characteristic mixture of charged ions and uncharged radicals. The ions are detected easily, whereas the uncharged radicals are neither accelerated nor detected, but can be inferred by the difference in the mass between the molecular ion and the observed fragment. The type of cation (and radical) formed depends on the nature of the functional groups present, so fragmentation becomes diagnostic for functional group types. Those fragments able to stabilize the positive charge, such as allylic cations (derived from alkenes), benzylic cations ($C_6H_5CH_2^+$), acylium cations (derived from aldehydes and ketones), iminium cations (derived from amines) or oxonium cations (derived from alcohols and ethers), are always favored (**Figure 32.32**).

Once the ionization and fragmentation processes have occurred, the ions formed are separated and detected. Initially, the positively charged ions are attracted to a negatively charged accelerator plate that forms a narrow slit, allowing only a stream of ions to pass through. Once past the slit, the positive ion enters an evacuated tube where its flight path is perturbed by the poles of a large magnet. As the positive ion passes through the magnetic field, its path is bent. The degree of bending depends on the mass of the fragments but also on their charge. The detector then converts the signal it receives into a mass spectrum.

**Go Figure** Using resonance contributors, describe how a benzylic cation is able to be stabilized.




▲ **Figure 32.32** **Fragmentation of molecular ions.**

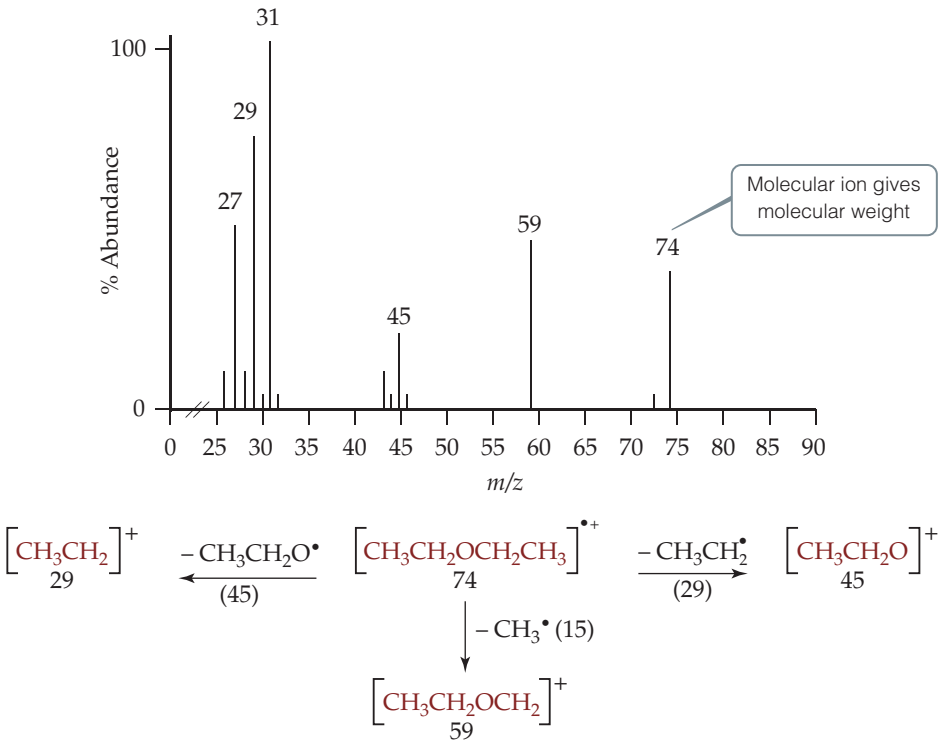
## Interpreting Mass Spectra

Two aspects of a mass spectrum lead the chemical detective to the identity of a compound. The first, called the **mass-to-charge ratio,** is symbolized by $m/z$ (see Figure 32.33), where $m$ equals the mass of the ion (in u) and $z$ is its charge. Typically, organic chemists use the term $m/z$ as a dimensionless quantity. As the charges on ionized or fragmented molecules almost always equate to +1, the mass-to-charge ratio for a particular signal in the mass spectrum is equal to the mass of that ion. These signals are assigned as a percentage abundance with respect to the most intense signal in the spectrum, called the **base peak**. The base signal does not necessarily correspond to the mass of the molecular ion—it is simply the most intense signal in the spectrum. For example, the base peak in Figure 32.33 occurs at $m/z = 31$ and is the result of fragmentation leading to the cation $CH_2OH^+$. The molecular ion is found at $m/z = 74$. Figure 32.33 also illustrates the possible fragmentations leading to each of the signals within the mass spectrum. Note that only the positively charged fragments lead to the signals in the spectrum. All the neutral fragments are unaffected by the magnet and do not impact on the detector.

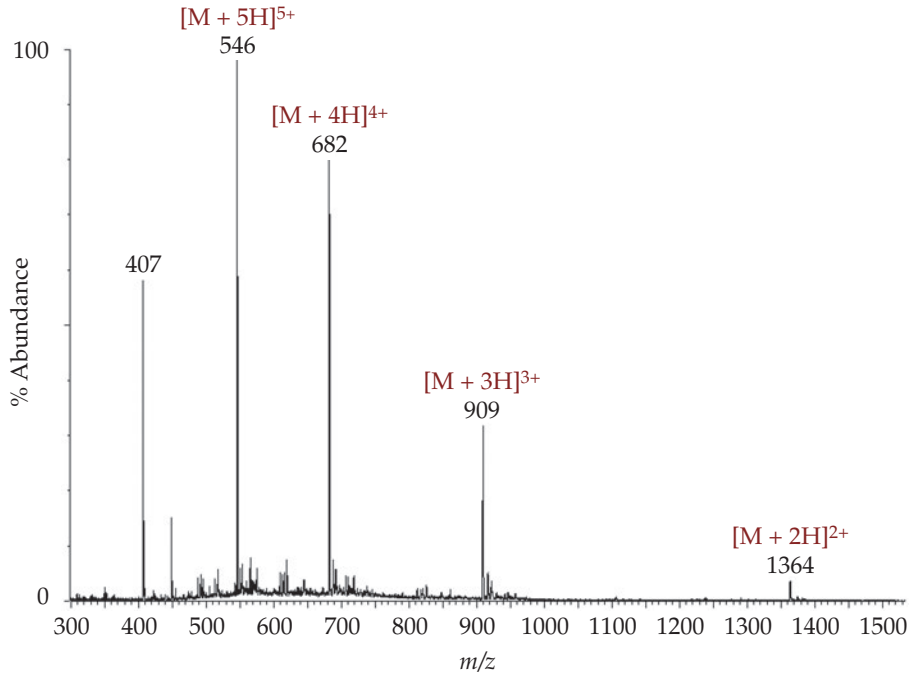
Figure 32.34 illustrates the principle of the mass-to-charge ratio by looking at species containing $z$ values greater than 1. The signals at $m/z = 546, 682, 909$ and 1364 all equate to the same molecular weight, 2726 u. The non-unity charge is due to this molecule's ability to react with $H^+$ at multiple sites, leading to multiple-charged species. This effect is common in subtle techniques such as ESI rather than in the chemically harsher techniques of EI and CI.

Routine mass spectrometry such as the type we have been describing is a low-resolution technique, meaning that the particle masses are rounded typically to a whole number. This means that carbon is taken as 12 u ($^{12}C$), oxygen as 16 u ($^{16}O$) and nitrogen as 14 u ($^{14}N$). However, most elements exist in more than one isotopic form. The heavier isotopes also give rise to small signals in the mass spectrum, higher than that of the molecular ion signal. These signals are sometimes called the $[M + 1]^+$ or $[M + 2]^+$ signals and can be very diagnostic in some instances. Table 32.4 gives the isotopic composition of some common elements, showing how they contribute to $[M + 1]^+$ or $[M + 2]^+$ signals. The isotopes for chlorine and bromine are highlighted as they show the most diagnostic abundance distributions.

For the most part, the $[M + 1]^+$ and $[M + 2]^+$ signals are significantly smaller (less than 1%) than the parent ion or molecular ion signal. However, chlorine exists as two




◀ **Figure 32.33 EI mass spectrum of diethyl ether**. The fragmentation pattern seen within the EI spectrum is also deduced, showing the loss of different radicals from the initially ionized diethyl ether. Remember, uncharged fragments such as $CH_3^•$ and $CH_3CH_2^•$ are not observed.



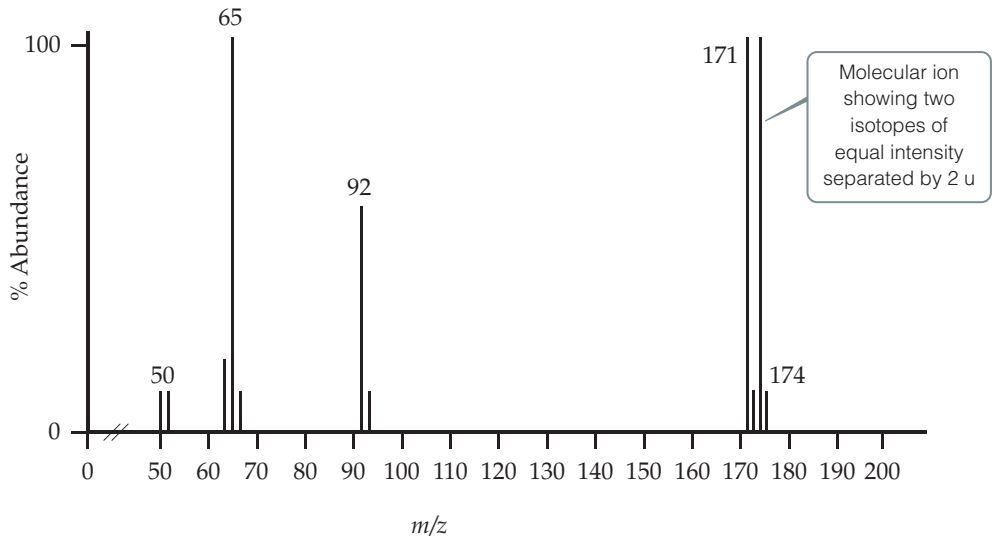

▶ **Figure 32.34 Mass-to-charge ratio.** Multiple charged fragments yield signals within the mass spectrum corresponding to greater masses. For example, a molecule with molecular mass *M* will yield a signal at *M*/2 when doubly charged. This electrospray spectrum is of a new type of therapeutic agent designed to interfere with the translation of the mRNA code to protein. Notice that this type of ionization leads to very little fragmentation, but does allow the sample molecules to accumulate protons, leading to multiple charged ions.

**TABLE 32.4 Isotopic distributions for some common elements**

| Element | M | % Abundance | M + 1 | % Abundance | M + 2 | % Abundance |
|---|---|---|---|---|---|---|
| Hydrogen | $^{1}H$ | 100 | | | | |
| Carbon | $^{12}C$ | 98.9 | $^{13}C$ | 1.1 | | |
| Nitrogen | $^{14}N$ | 99.6 | $^{15}N$ | 0.4 | | |
| Oxygen | $^{16}O$ | 99.8 | | | $^{18}O$ | 0.2 |
| Sulfur | $^{32}S$ | 95.0 | $^{33}S$ | 0.8 | $^{34}S$ | 4.2 |
| Chlorine | $^{35}Cl$ | 75.5 | | | $^{37}Cl$ | 24.5 |
| Bromine | $^{79}Br$ | 50.5 | | | $^{81}Br$ | 49.5 |
| Iodine | $^{127}I$ | 100 | | | | |

isotopes, $^{35}Cl$ and $^{37}Cl$, with respective isotope abundances of 75.5% and 24.5%. Bromine is the most easily recognized of the halogens. It has two signals, one for $^{79}Br$ and one for $^{81}Br$, of near equal intensity (50.5% and 49.5%, respectively). What this means is that, if bromine is present in a molecule, the $[M + 2]^+$ ion has an intensity nearly equal to the molecular ion. This is illustrated in the EIMS spectrum of 4-bromoaniline, shown in **Figure 32.35**. Iodine is typically recognized by the presence of iodine cation ($I^+$) at *m/z* 127. This clue is also combined with a characteristic 127 separation in the mass spectrum between the molecular ion signal and the first fragmentation. If chlorine is present, the $[M + 2]^+$ signal is about one-third as large as the $M^+$ signal.

There is one last aspect of mass spectrometry that we should discuss. To do this, we consider the molecules propane, acetaldehyde and $CO_2$. Each one produces a molecular ion with a mass of 44 u. Under the low-resolution methods we have been applying to date, we would not be able to tell these molecules apart. If, however, we use a high-resolution approach by not considering the mass of atomic hydrogen ($^{1}H$) as 1 u but as 1.0078 u and $^{16}O$ as 15.9949, then the three molecules in question (with different molecular formulas) will correspond to different exact masses—$C_3H_8$, $C_2H_4O$ and $CO_2$ have exact masses of 44.0626, 44.0262 and 43.9898 u. For this high-resolution technique to be useful, accurate masses are always quoted to four decimal places. Analysis requires a highly accurate measurement ($\pm 1$ part in $10^6$). The result can then be compared with exact masses calculated for various element combinations. Note that, by definition, $^{12}C$ has an atomic weight of 12.0000 u.

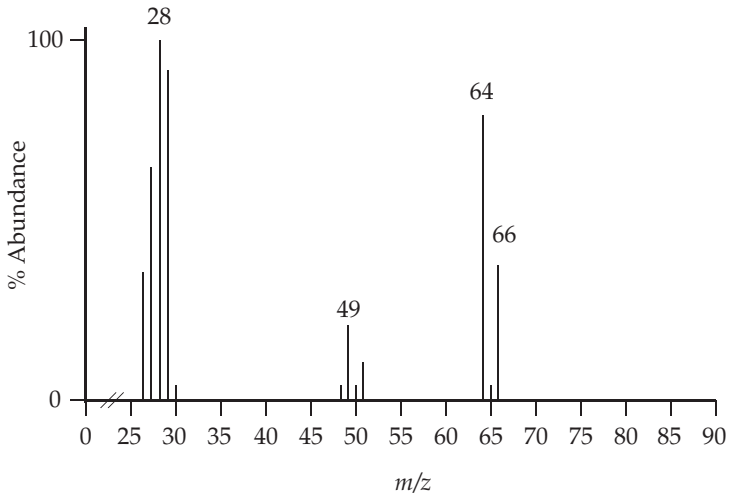



**◀ Figure 32.35 EI mass spectrum of 4-bromoaniline.** Note the diagnostic $M^+$ and $[M + 2]^+$ signals of equal intensity and the spacing of 79 u between the molecular ion and first fragmentation. These clues all indicate that the molecule contains bromine.

## Sample Exercise 32.5

### Interpreting Mass Spectra

An EI mass spectrum of compound B, a simple haloalkane, is shown here. Deduce its structure.




### SOLUTION

**Analyze** We are asked to deduce the structure and hence molecular formula based on the mass spectrum observed.

**Plan** Use the $M^+$ and $[M + 2]^+$ signals to deduce the halide present, as well as the molecular formula. Use the fragmentation patterns to confirm your deduction.

**Solve** The relative abundance of the $M^+$ and $[M + 2]^+$ signals suggests that chlorine is the likely halide, although the observed ratio of these two signals is slightly different from the expected 3 : 1 ratio. The presence of Cl within the structure is confirmed by the difference between the $M^+$ and the second fragmentation of 29 u (difference = 35). The position of this second fragmentation also coincides with the cation $CH_3CH_2^+$. Hence, the structure of our unknown must correspond to *chloroethane*.

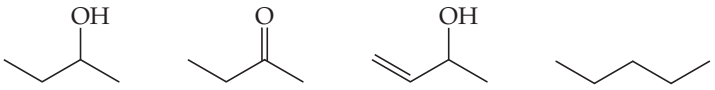
**Check** The fragmentation signal at 49 u corresponds to the loss of a methyl radical (15 u) from $M^+$.

**▶ Practice Exercise**

The mass spectrum of compound C contains major peaks at $m/z$ = 88, 73, 45, 43 and 29. Confirm that this fragmentation pattern is consistent with compound C being ethyl acetate.

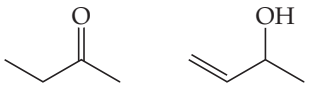
## Self-Assessment Exercises

**32.18** Which molecule will have a molecular ion at $m/z = 74$ in its mass spectrum?




**(a)** **(b)** **(c)** **(d)**

**32.19** A mass spectrum has signals at $m/z$ = 72, 57, 43, 29, and15. Which molecule will give rise to this pattern?




$m/z = 72$ $m/z = 72$

**(a)** **(b)**

## Exercises

**32.20** Carbon tetrabromide shows nine signals in the region $m/z = 328–337$ of the EI mass spectrum. Account for each of these signals.

**32.21** An aliphatic compound gives the following result from microanalysis: C, 66.6%; H, 11.2%. The mass spectrum reveals a molecular ion signal at $m/z = 72$. Determine the compound's molecular formula.

**32.22** **(a)** What are the labels on the axes of a mass spectrum?

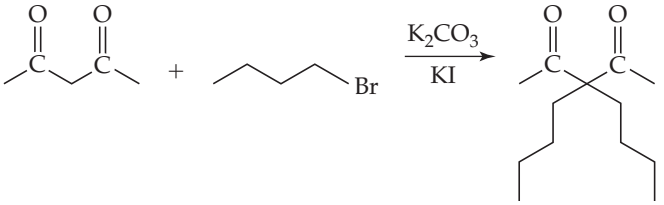
**(b)** In order to measure a mass spectrum of an atom or molecule, the atom or molecule must first lose (or gain) one or more electrons. Why is this so?

**32.23** Illustrate the stability of the following cations by drawing any contributing resonance structures.

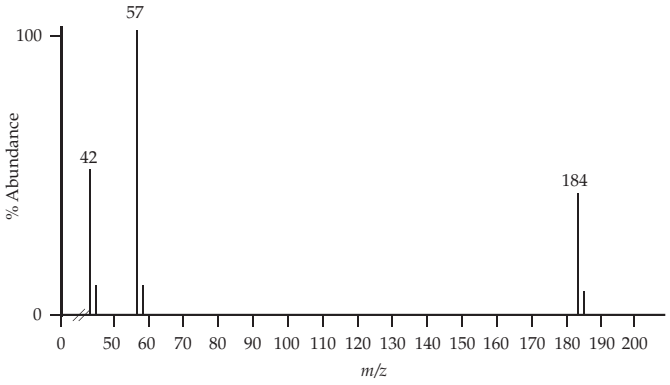
**(a)** acylium cation **(b)** carbonium cation

**(c)** iminium cation

**32.24** Following a literature procedure, a student added butyl bromide (three equivalents) to 2,4-pentanedione in the presence of excess potassium carbonate and potassium iodide, as shown in the following reaction scheme:




As well as isolating the product, the student also isolated a clear oil which she promptly submitted for EIMS. The results are shown here. What is the structure of the by-product? [*Hint:* Look at the difference in mass between the molecular ion and the base peak.]




**32.25** With the aid of a diagram, describe what the EI mass spectrum of 2-chloropropane might look like.

**Answers to Self-Assessment Exercises**

**32.18** (a) **32.19** (a)

# 32.5 Compound Identification Using Spectra

Whether you are a police scientist in a forensic laboratory, a medical scientist in a pathology laboratory, or a research scientist in a synthesis laboratory, you will come across substances that need identifying. More often than not, a combination of techniques including chemical observations as well as instrumental analysis will be needed. Being able to pick the salient information from each bit of data and put it together to generate a structure based on evidence is a skill that takes practice to acquire. Often, an iterative process is useful. First, you "skim" the information to give a "first guess" at the substance. You then use this structure to see if it matches the information from the tests and analysis, refining the structure when the data is inconsistent with your first guess. Eventually, you refine the structure to a point when all the evidence you have is consistent with that structure.

In this section, we introduce this process and show how a combination of chemical tests and instrumental techniques may be used to solve a structure. By the end of this section, you should be able to:

- Identify simple substances based on chemical analysis and instrument data.

## Deducing the Molecular Formula of an Organic Compound

To work out the empirical formula of an organic compound, an organic chemist subjects a small amount of sample to *microanalysis*. This destructive technique combusts the sample and analyses the amount and type of gas released. From these data, a percentage C, H, N is obtained based on weight. The remaining percentage is inferred as the content of O in the sample. Manipulation of these percentages, by taking into account the atomic masses of C, H, N and O leads to an empirical formula, from which a molecular formula can be determined, normally in conjunction with the value for the molecular ion signal in the mass spectrum.

In Chapters 24 and 26, we identified the general molecular formula of an alkane as $C_nH_{2n+2}$, a cycloalkane is $C_nH_{2n}$ and the corresponding alkene also has the same general molecular formula, $C_nH_{2n}$. This difference in molecular formula between, for example, alkanes and alkenes actually yields important structural information. While the example

## Sample Exercise 32.6

### Microanalysis to Molecular Formula

The IR spectrum of a liquid aromatic compound has a broad band in the range 3000–3500 $cm^{-1}$. EIMS indicates a molecular ion signal at $m/z = 108$ and a sample of the unknown does not dissolve in 1 M NaOH. Microanalytical results for this unknown are: C, 78%; H, 7.4%. Deduce the molecular formula of this unknown.

### SOLUTION

**Analyze** We are asked to use a set of analytical and chemical data for an unknown and asked to calculate its molecular formula.

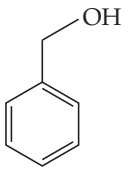
**Plan** Work out the empirical formula and use the molecular ion result from EIMS to yield the molecular formula.

**Solve** The elements present are C = 78%, H = 7.4% and O = 14.6%. Taking into account their atomic weights:

$$\begin{aligned} C : H : O &= \frac{78}{12} : \frac{7.4}{1} : \frac{14.6}{16} \\ &= 6.5 : 7.4 : 0.91 \text{ (divide by smallest number)} \\ &= 7 : 8 : 1 \end{aligned}$$

Therefore the empirical formula is $C_7H_8O$. The empirical mass is equivalent to the molecular ion signal, so the molecular formula is also $C_7H_8O$.

Although this answers the question, let's use the extra information given to us to deduce a structure. We know that the molecule is aromatic (therefore it contains $C_6$) and contains an O—H stretching band in the IR spectrum (therefore it contains OH). Eliminating these fragments from the molecular formula leaves $CH_7$. Not being soluble in 1 M NaOH rules out that the unknown is a phenol. Using the remaining carbon atom to bridge the aromatic and OH groups yields benzyl alcohol as a likely suspect.




**Practice Exercise**

**(a)** An unknown liquid has an IR spectrum with a band at 3330 $cm^{-1}$. EIMS indicates a molecular ion signal at $m/z = 60$. Microanalytical results are: C, 60%; H, 13.4%. Deduce the molecular formula of the unknown.
**(b)** An unknown compound has a band at 1710 $cm^{-1}$ in the IR spectrum. EIMS indicates a molecular ion signal at $m/z = 88$ and a base signal at $m/z = 43$. Microanalysis gives: C, 54.5%; H, 9.15%. Deduce the molecular formula of the unknown.

is trivial, knowing something about the **index of hydrogen deficiency (IHD)**, which is essentially the summation of all π-bonds and rings within a molecule, is useful when determining possible structures of compounds, especially alkenes, ketones and aldehydes, amines, alkyl halides and so on. The IHD quantity is determined by comparing the number of hydrogens in the molecular formula of an unknown with that of an *alkane* reference containing the same number of carbon atoms as the unknown. This last statement can be summarized in the following way:

$$\begin{aligned} \text{IHD} &= \text{Number double bond or ring equivalents} \\ &= \frac{\text{maximum number H possible per C} - \text{actual number H per C}}{2} \end{aligned} \qquad [32.6]$$

Let's investigate the molecular formula, $C_4H_8O_2$, used in Practice Exercise 32.6(b). The index of hydrogen deficiency is

$$\text{IHD} = \frac{\overbrace{(2n+2)}^{\text{maximum number of H atoms possible}} - \overbrace{8}^{\text{actual number}}}{2}$$

where $n = 4$

$$\begin{aligned} \text{IHD} &= \frac{(2 \times 4 + 2) - 8}{2} \\ &= 1 \end{aligned}$$

which means that one double bond (or a ring system) must exist within the molecule. This unknown is ethyl acetate. The presence of a C=O double bond in ethyl acetate supports our IHD calculations. While this calculation works for compounds containing C, H and O, other elements can complicate matters.

To help us, several guidelines have been devised to determine IHD.

1. Work out the molecular formula of the *reference alkane* based on the number of carbon atoms in the unknown's molecular formula.
2. For each halogen in the unknown's molecular formula, *subtract* one hydrogen off the reference's molecular formula.
3. For each nitrogen in the unknown's molecular formula, *add* one hydrogen to the reference's molecular formula.
4. Make no modifications for oxygen or sulfur in the formula.

## Chemical Wet Testing: Tests for Functional Groups

As long as enough of an unknown compound is present, chemical wet tests are useful for providing clues to the types of functional groups present. These tests may be as simple as solubility in aqueous solution or as complex as two- or three-step processes in a micro-test tube. **Figure 32.36** illustrates the process of using functional group tests to offer clues to an unknown's structure. This flow diagram has a significant amount of chemistry, so we will briefly point out the requirements for a positive test for each functional group. Much of this chemistry has been dealt with in the preceding chapters.

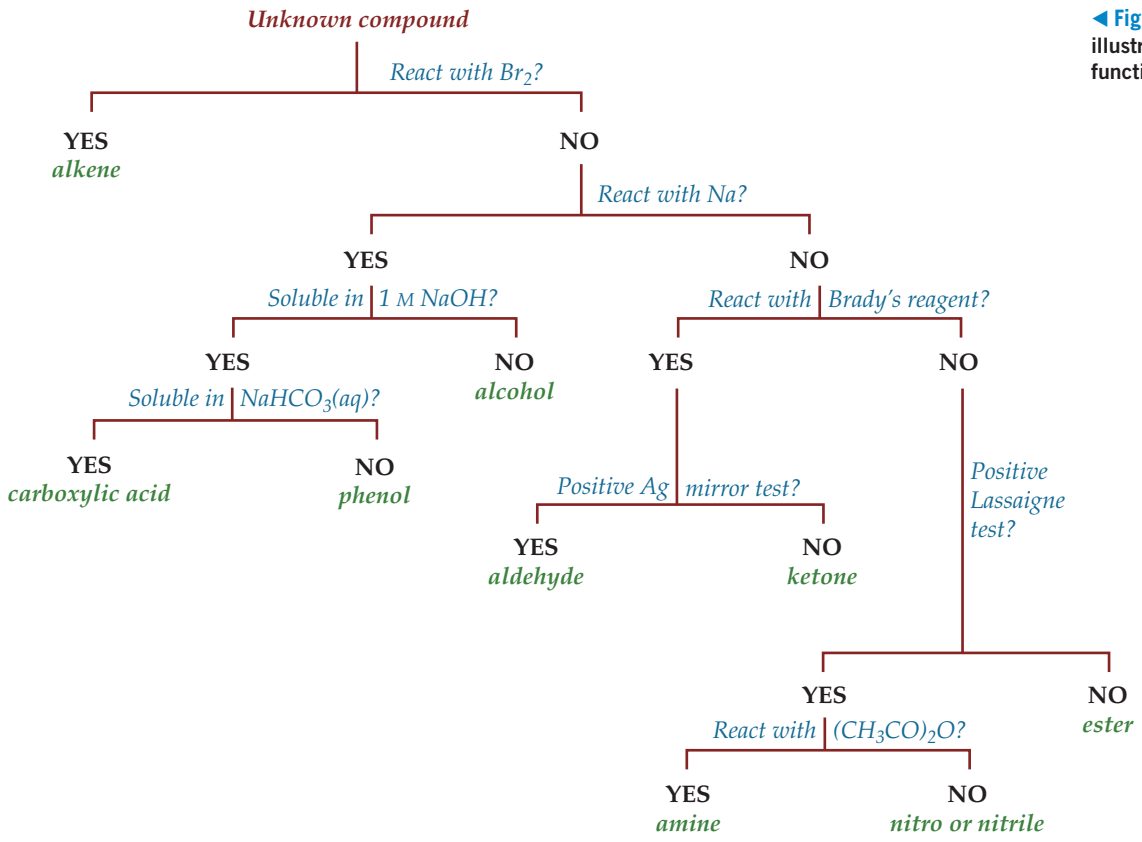
*Alkenes:* The decolorization of a bromine solution when applied to an organic molecule usually indicates the presence of an alkene.

*Alcohols:* Alcohols of low molar mass, such as $CH_3OH$ and $CH_3CH_2OH$, mix completely with water, but those with larger non-polar alkyl groups have low solubility. The addition of sodium metal to alcohols will evolve hydrogen gas (bubbles) generating the alkoxide.

$$2\ ROH + 2\ Na \longrightarrow 2\ RO^- + 2\ Na^+ + H_2(g) \qquad [32.7]$$

Alcohols do not react with aqueous hydroxide.

*Phenols:* Phenols behave as weak acids with $pK_a$ about 10. As a result, they are soluble in 1 M NaOH but not soluble in saturated aqueous sodium bicarbonate solution.




◀ **Figure 32.36** **Flowchart illustrating some simple functional group tests.**

*Carboxylic acids:* Carboxylic acids react with saturated aqueous sodium bicarbonate solution, with the release of $CO_2$ from solution.

$$RCOOH + HCO_3^- (aq) \longrightarrow RCOO^- (aq) + H_2O + CO_2 (g) \quad [32.8]$$

*Aldehydes and ketones:* Both aldehydes and ketones react with 2,4-dinitrophenylhydrazine (DNP), also known as Brady's reagent, to form highly colored precipitates. A generalized equation for this reaction is:

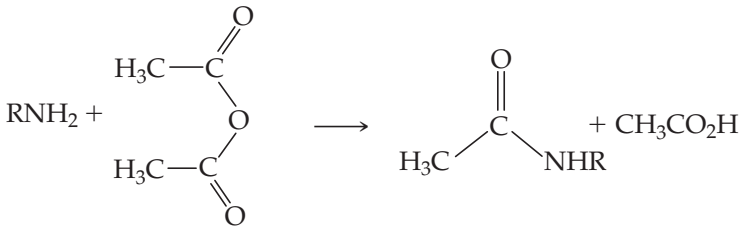
$$R_2C{=}O + H_2NR' \longrightarrow R_2C{=}NR' + H_2O \quad [32.9]$$

To distinguish aldehydes from ketones, a silver mirror test is usually employed.

$$RCHO + 2\ Ag^+ (aq) + 3\ OH^- (aq) \longrightarrow RCOO^- (aq) + 2\ Ag(s) + 2H_2O \quad [32.10]$$

*Nitrogen:* The Lassaigne sodium fusion test is a dramatic test that requires the use of molten sodium metal and ferrous sulfate. The bright blue color of the product, $NaFe[Fe(CN)_6]$ (also known as Prussian blue), indicates a positive test. The nitrogen can be present in amines, nitro compounds, nitriles and amides.

*Amines:* Amines are soluble in 1 M HCl and give alkaline solutions when mixed with water. Primary aromatic amines yield bright red/orange-colored azo-dyes when mixed with nitrous acid and 2-naphthol. Amines form amides by reaction with acetic anhydride.




[32.11]

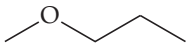
## Using Analysis from Instrumental Techniques

We are now ready to tackle an advanced problem as a chemical detective. To help you to become familiar with the process, here are some guidelines.

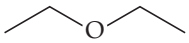
1. *Determine the molecular formula and index of hydrogen deficiency.* Calculate the empirical formula, determine the mass of the molecular ion (from the mass spectrum) and hence calculate the molecular formula and IHD.
2. *Check the IR spectrum.* Look for stretching bands indicative of functional groups O—H, N—H, C=O and so on.
3. *$^1$H NMR spectrum: number of signals and their positioning.* Determine the number of non-equivalent hydrogens by counting the number of signals present. Determine their chemical shift and relate this to potential neighboring functional groups—for example, $CH_2$—O at about 4 ppm, $CH_2C{=}O$ at about 2.5 ppm. Remember, this is only a guide.
4. *$^1$H NMR spectrum: integration.* Determine the relative number of equivalent hydrogens in each signal by measuring the area under each signal. Of course, this may already be done for you (Figure 32.22). The integral value could be exact in terms of the number of hydrogens or, based on extra symmetry within the molecule, may be a fraction of it.
5. *$^1$H NMR spectrum: splitting pattern.* Use your knowledge of splitting patterns and the $(n + 1)$ rule to determine the connectivity between groups of atoms. Learn to recognize ethyl groups by their characteristic splitting pattern.
6. *Deduce the structure.* Using all this information (including chemical tests), try to deduce the structure. Remember, it might not be the first one you draw.
7. *Check.* Use the $^{13}$C NMR spectrum and any distinguishable fragmentation patterns in the mass spectrum to confirm your choice of structure. Use this information to distinguish isomers.

## Self-Assessment Exercise

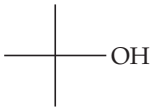
**32.26** After a stocktake in a chemical store, two partially labelled bottles containing liquids with different odours remained. The label on both bottles was $C_4H_xO$ where the value of $x$ was unreadable. The bottles were marked A and B. The store's card index showed that there were five possibilities for A and B, numbered 1–5.



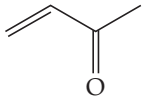

**1**



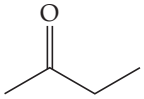

**2**




**3**




**4**




**5**

The $^1$H NMR and IR spectra of A and B were recorded and are described here. For each bottle and its contents, suggest a possible conclusion for the information presented—for example, IR band at 2950 cm$^{-1}$ indicates C—H present—and deduce the structures of A and B.

- *Bottle A:* Strong IR band near 1700 cm$^{-1}$, $^1$H NMR spectrum: three signals in the ratio 3 : 3 : 2.
- *Bottle B:* Strong IR band near 3500 cm$^{-1}$, $^1$H NMR spectrum: two signals in the ratio 9 : 1.

**(a)** Bottle A contains compound 4 and bottle B contains compound 2.

**(b)** Bottle A contains compound 1 and bottle B contains compound 3.

**(c)** Bottle A contains compound 3 and bottle B contains compound 5.

**(d)** Bottle A contains compound 5 and bottle B contains compound 3.

## Exercises

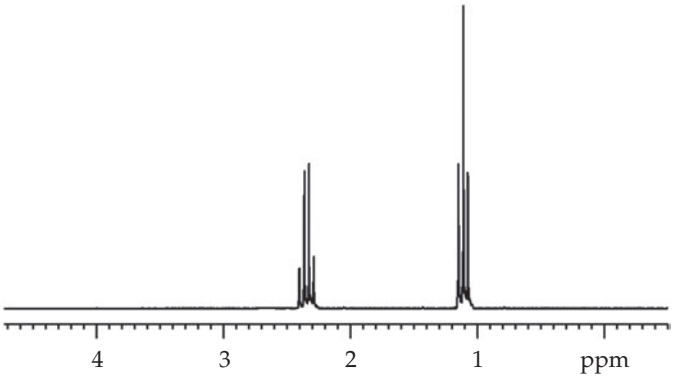
**32.27** Calculate the IHD for the following compounds:

**(a)** cholesterol, $C_{27}H_{46}O$ **(b)** acetic acid, $C_2H_4O_2$

**(c)** aspirin, $C_9H_8O_4$ **(d)** naphthalene, $C_{10}H_8$

**(e)** ascorbic acid, $C_6H_8O_6$ **(f)** cocaine, $C_{17}H_{21}NO_4$

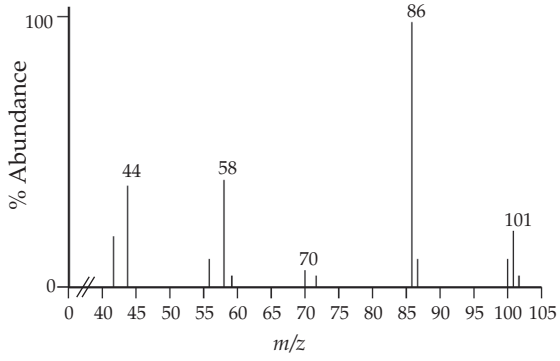
**32.28** The product formed upon oxidation of an unknown organic compound with chromic acid has the molecular formula $C_5H_{10}O$. The $^1$H NMR spectrum of the product is shown here and its IR spectrum has a strong band at 1700 cm$^{-1}$. Using this information, deduce the structure of the product and hence the structure of the unknown compound.



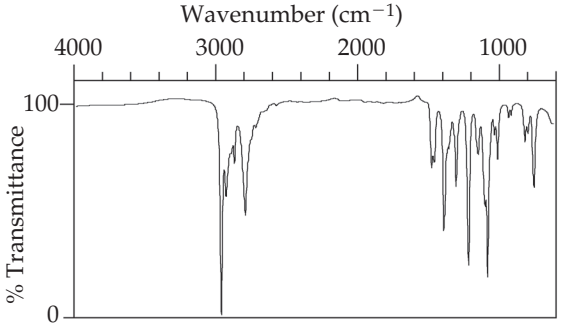

**32.29** An acidic liquid has a broad band at 3300 cm$^{-1}$ and a sharp band at 1710 cm$^{-1}$ in the infrared spectrum. One mole of this unknown reacts with one mole of NaOH. The $^1$H NMR spectrum shows three signals in the ratio 2: 2 : 1. Microanalysis gave C, 33.2%; H, 4.6%; Cl, 32.7%. Deduce the structure of the unknown.

**32.30** This basic compound gives a positive result to the Lassaigne test. Microanalysis gave the following result: C, 71.22; H, 14.94; N, 13.84. Use this information and the accompanying spectra to deduce the structure of the unknown.

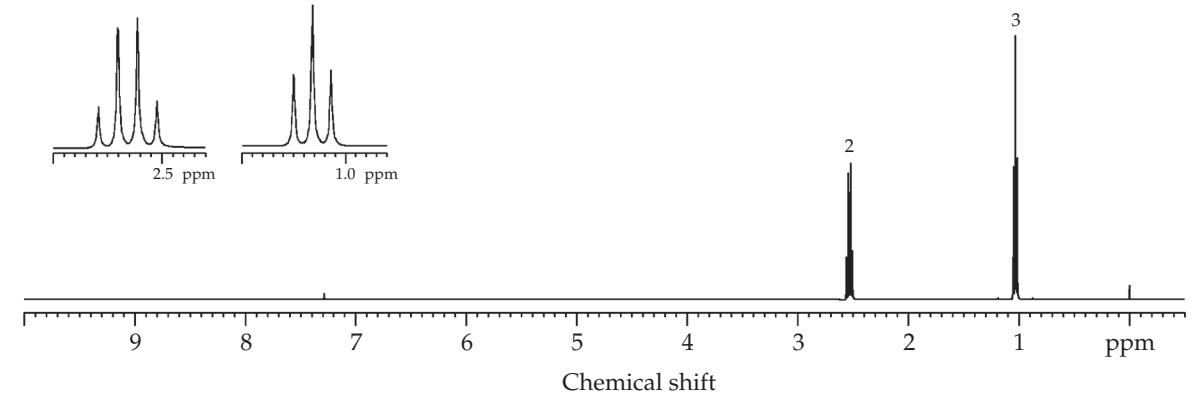
**Mass spectrum**



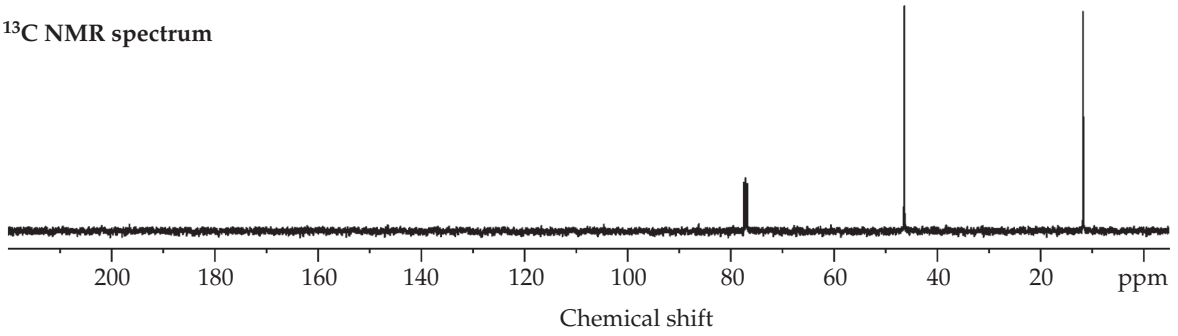

**IR spectrum**



**$^1$H NMR spectrum**

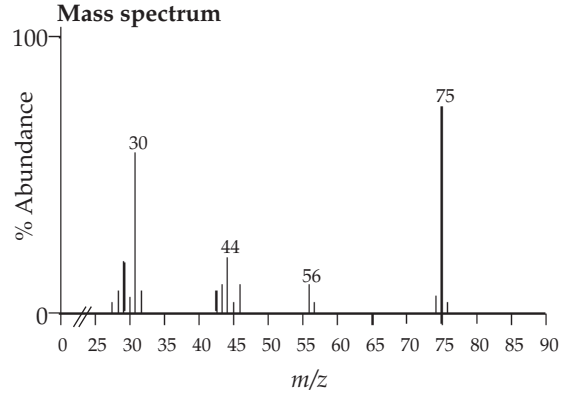



**$^{13}$C NMR spectrum**

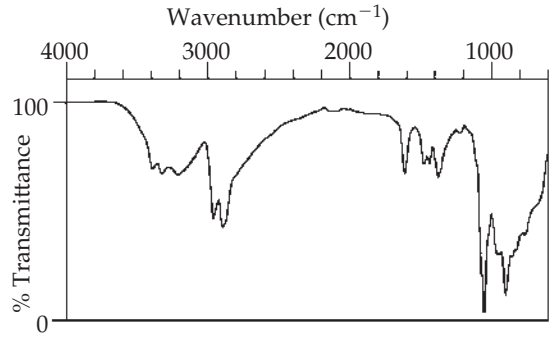


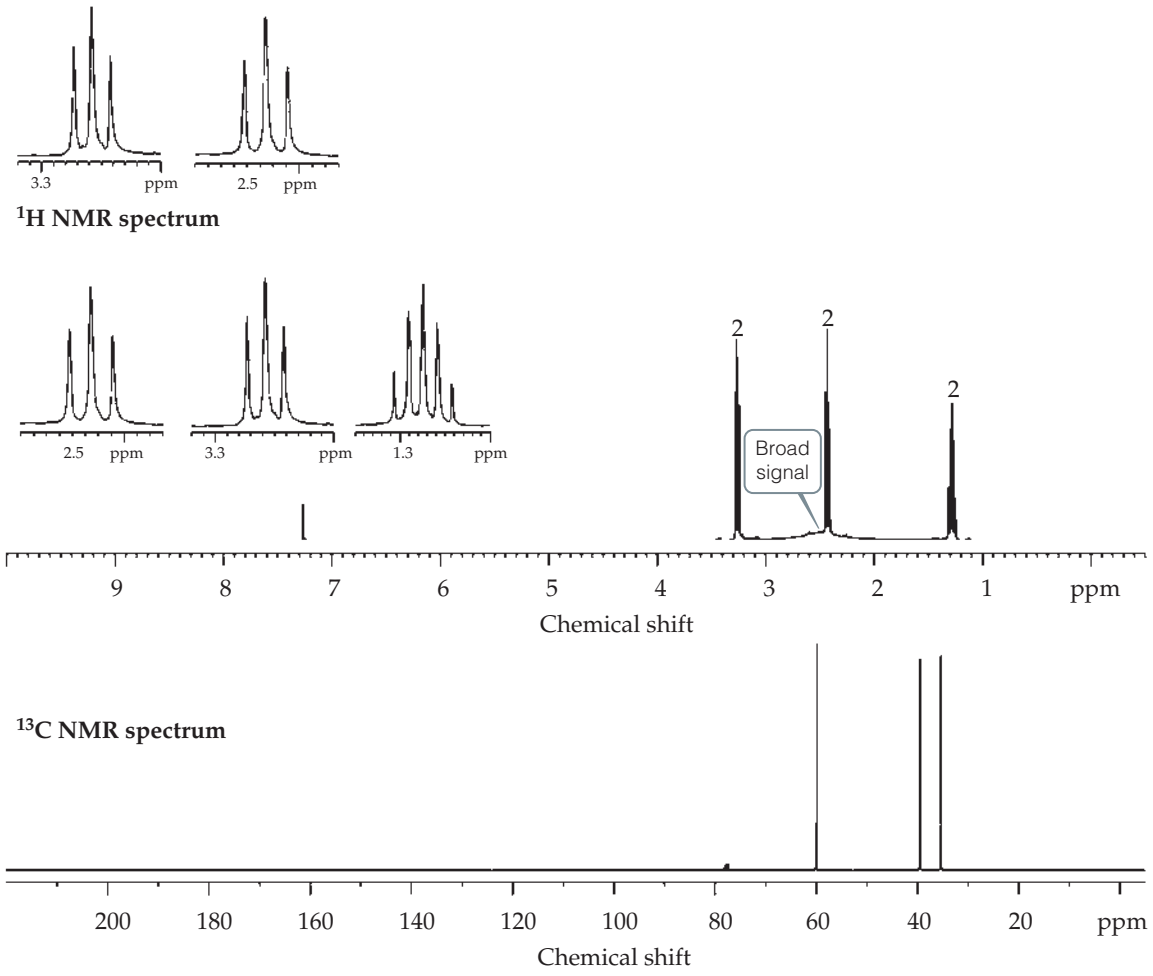

**32.31** This unknown liquid is miscible with water, giving a mildly basic solution. Microanalysis gave the following result: C, 47.97; H, 12.08; N, 18.65. The broad, three-hydrogen signal within the $^1$H NMR spectrum (indicated) disappears on the addition of $D_2O$. Use all the information available to deduce the structure of the unknown.

**Mass spectrum**

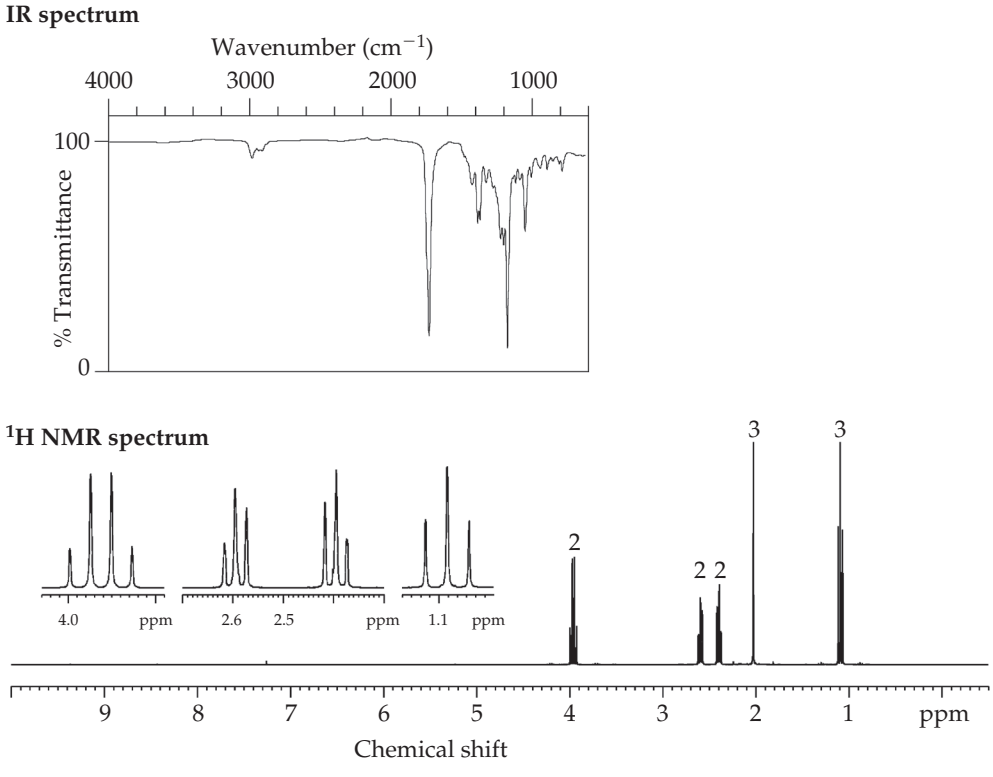



**IR spectrum**

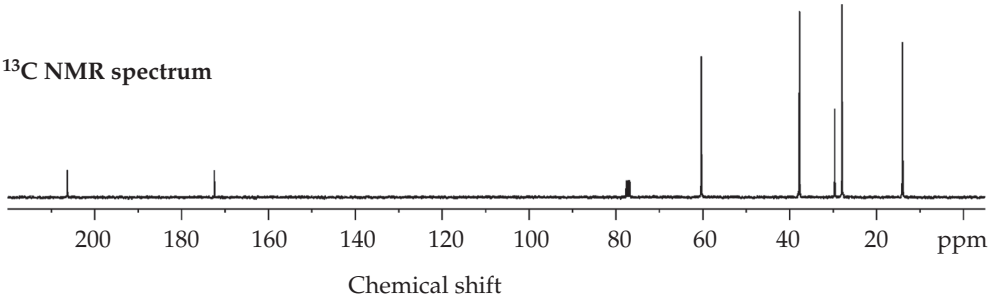





**32.32** This unknown liquid reacts with Brady's reagent to form a highly colored precipitate. The electrospray mass spectrum (not shown) has a signal at $m/z = 145$ corresponding to $[M + H]^+$. Microanalysis gave the following result: C, 58.32; H, 8.39. Use all the information available to deduce the structure of the unknown.



**$^{13}$C NMR spectrum**




**Answers to Self-Assessment Exercise**

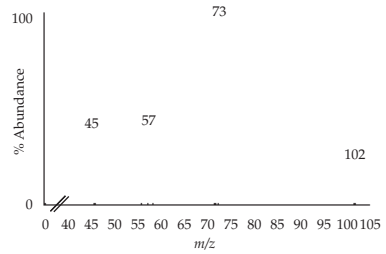
**32.26** Bottle A contains butanone (compound 5); Bottle B contains 2-methylpropan-2-ol (compound 3).

## Sample Integrative Exercise

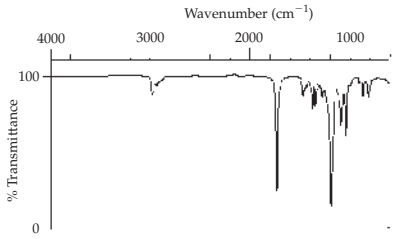
### Putting Concepts Together

Unknown D is a sweet-smelling liquid. Microanalytical results for this unknown give C, 58.80%; H, 9.87%, and the characterization spectra acquired for this unknown are shown here. Use the information to deduce the structure of unknown D.

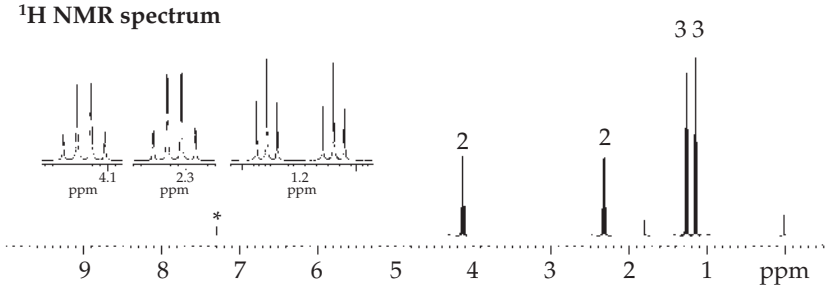
**EI mass spectrum**



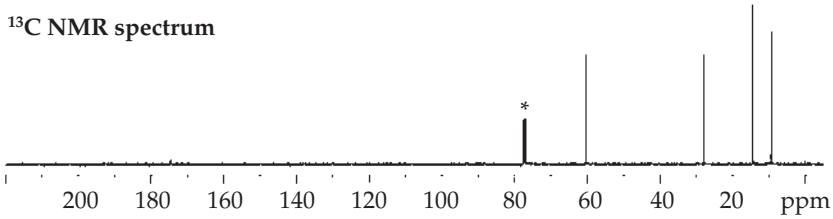

**IR spectrum**




**$^{1}$H NMR spectrum**




**$^{13}$C NMR spectrum**




Asterisks denote solvent signals.

**Analyze** We are asked to use a set of analytical and chemical data for an unknown and asked to determine its structural formula.

**Plan** Use all the information given in the form of spectra and microanalytical data to deduce the structure of the unknown.

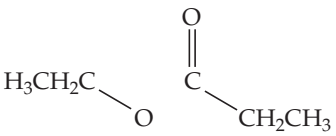
**Solve** The microanalytical data give an empirical formula of $C_5H_{10}O_2$, which has a mass equal to the molecular ion signal. Hence the molecular formula is also $C_5H_{10}O_2$. The IHD is 1, suggesting the presence of either a ring or double bond within the structure, but not both.

The IR spectrum shows a strong band at about 1750 $cm^{-1}$, attributable to a C=O stretching frequency. There is no O—H stretch, which means the extra oxygen atom in the molecular formula must be of ester or ether origin.

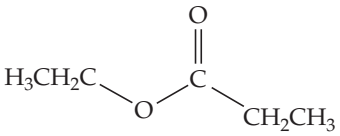
There are four signals in the $^1H$ NMR spectrum with integration in the ratio 2 : 2 : 3 : 3, which accounts for all the hydrogens in the molecular formula.

The chemical shifts of the two sets of quartets indicates that one set (approximately 4 ppm) neighbors oxygen and the other neighbors a carbonyl C=O group. Using the $(n + 1)$ rule, the hydrogens responsible for the quartet splitting patterns must be coupled to methyl groups. Hence, two different ethyl groups exist in this structure.

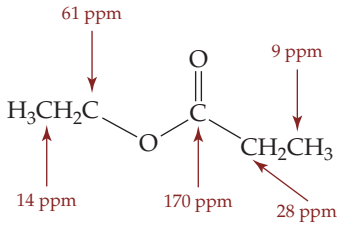
Putting together the clues to date, we have the following fragments:



These fragments make up the molecular formula of the unknown. Knowing that the unknown shows a positive test for esters (and is sweet-smelling) would confirm the choice in structure. Hence, our unknown is *ethyl propanoate*.



**Check** Use the $^{13}C$ NMR data to confirm the structure. The structure of ethyl propanoate has five different carbon atoms, the same number of signals as found in the $^{13}C$ NMR spectrum. In terms of chemical shift, the signals would be distributed as follows:




**Practice Exercise**
A number of these problems can be found in the end-of-chapter Exercises.

# Chapter Summary and Key Terms

**SECTION 32.1** All molecules absorb electromagnetic radiation to some degree and hence give rise to absorption spectra. The amount and type of absorption depends on the energy of radiation and the nature of the molecule, its bond types and its electronic structure. **Beer–Lambert's law** can be used to relate the amount of energy being absorbed to the concentration of the substance absorbing the energy in **UV-visible spectroscopy**.

**SECTION 32.2** **Infrared spectroscopy** observes the vibrations of covalent bonds. The difference in vibration energy is a result of the stiffness of the covalent bond. This principle follows **Hooke's law** and provides useful evidence for the presence of functional groups in molecules. Compounds are measured either as solids, liquids or gases. An **infrared spectrum** is usually plotted as percentage **transmittance** (%$T$) versus **wavenumber** ($cm^{-1}$). The region below 1400 $cm^{-1}$ is known as the **fingerprint region**.

**SECTION 32.3** **Nuclear magnetic resonance (NMR) spectroscopy** is a method for observing nuclear spin transitions, giving information on the connectivity of nuclei (atoms). The technique relies on the difference in energy levels between nuclear spins of $I > 0$ ($I = \frac{1}{2}$ for $^1H$ and $^{13}C$), within a strong magnetic field. The absorption of radiation at the **Larmor frequency**, which leads to an NMR spectrum, is termed **resonance**. The frequency of an NMR spectrometer is called its **operating frequency**.

The electrons within these functional groups also have a spin that creates local magnetic fields that **shield** or **deshield** the neighboring nuclei from the applied magnetic field. Three aspects of an NMR spectrum are important: the **chemical shift** (δ) of a signal, the area under the signal (available by **integration**) and the **splitting pattern** of the signal all yield diagnostic information about the molecular structure. Equivalent hydrogens or carbons within a molecule by symmetry give rise to identical chemical shifts in $^1H$ or $^{13}C$ NMR spectra, respectively.

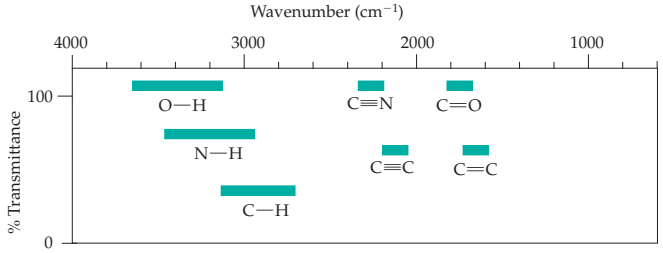
An NMR signal is split by the influence of adjacent atoms on the local magnetic field of the nucleus in question. This splitting is called **spin–spin coupling**. The splitting pattern that results follows the **$(n + 1)$ rule**. Splitting patterns are commonly described in terms of their **multiplicity**—for example, singlets, doublets, triplets, quartets, multiplets. Two (or more) coupled nuclei share the same **coupling constant** ($J$), which allows for easy tracing of the molecule's connectivity. $^{13}C$ NMR spectra are commonly devoid of coupling because they are recorded in a hydrogen-decoupled mode. **Decoupling** is used either to simplify a spectrum or to indicate coupled nuclei.

**SECTION 32.4** **Electron impact ionization mass spectrometry (EIMS)** uses high-energy electrons to bombard a sample compound, causing it to *ionize* or **fragment**. The **molecularion** ($M^+$) formed upon ionization has a **mass-to-charge ratio** ($m/z$) equal in quantity to the molecular weight of the sample being tested. Signals with a mass spectrum are assigned a percentage abundance with respect to the **base peak**. Mass spectrometry often provides clues to the structure and functional groups contained within a molecule through either fragmentation or isotopic patterns.

**SECTION 32.5** Using the **index of hydrogen deficiency (IHD)**, the chemist can determine the number of double bond or ring equivalents within a molecular formula.

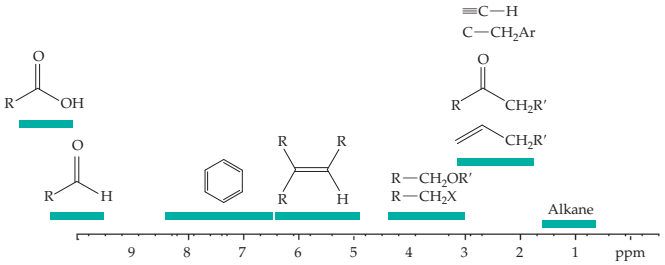
# Key Skills

- Understand how to use Beer–Lambert's law. (Section 32.1)
- Be able to identify O—H, C—H, C≡C, C═C, C═O stretches in IR spectra. (Section 32.2)

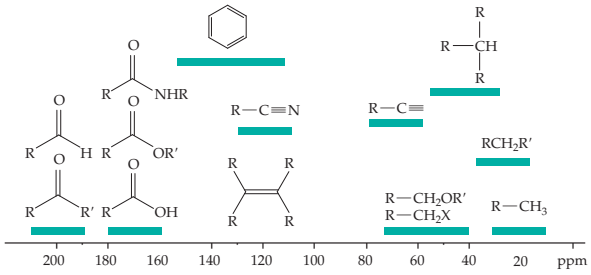



- Apply NMR chemical shifts to determine possible functional group types based on: (Section 32.3)

**(a)** $^{1}$H NMR spectroscopy




**(b)** $^{13}$C NMR spectroscopy




- Apply multiplicity and $J$ in $^{1}$H NMR to determine connectivity within organic molecules. (Section 32.3)
- Be able to identify the molecular ion signal and apply fragmentation patterns to determine functional groups and molecular weight. (Section 32.4)
- Be able to determine molecular formula from percentage composition and mass spectra. (Section 32.5)
- Calculate IHD based on a molecular formula. (Section 32.5)

# Key Equations

- Beer–Lambert's law

$$A = \varepsilon c l \qquad [32.1]$$

- Transmittance

$$\text{Absorbance} = -\log_{10}(\text{transmittance})$$
$$\text{or}$$
$$A = -\log_{10} T \qquad [32.2]$$

- IHD

IHD = Number double bond or ring equivalents

$$= \frac{\text{maximum number H possible per C} - \text{actual number H per C}}{2} \qquad [32.6]$$

- Effective magnetic field

$$B_{\text{effective}} = B_{\text{applied}} - B_{\text{local}} \qquad [32.4]$$

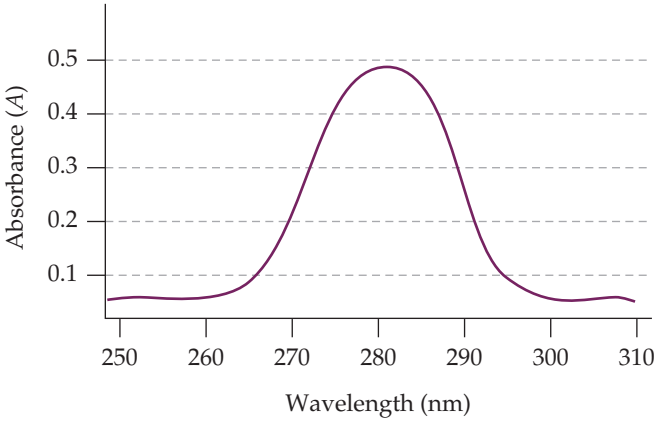
- Chemical shift

$$\delta = \frac{\text{Shift in resonance frequency from TMS (Hz)}}{\text{Operating frequency of the spectrometer (MHz)}} \qquad [32.5]$$

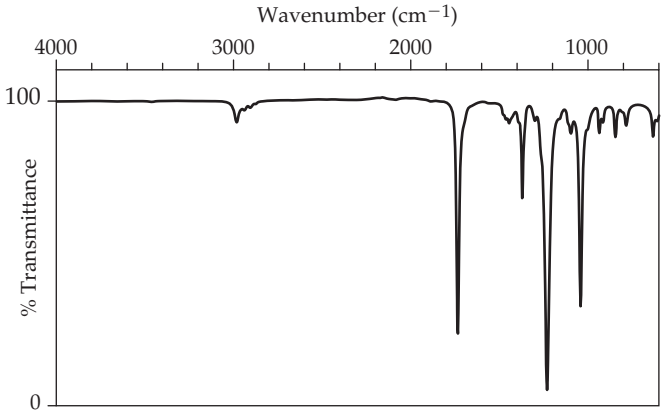
# Exercises

## Visualizing Concepts

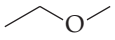
**32.33** **(a)** An aqueous solution of 4-aminobenzoic acid gives a maximum absorbance of 0.21. What is the percentage transmittance? **(b)** The absorption spectrum of a solution of naphthalene ($\varepsilon = 300\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$) in hexane obtained through a path length of 1.0 cm is given here. What is the concentration of the sample? [*Hint:* You will need to estimate the absorbance value by reading off the graph.] [Section 32.1]



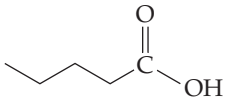
**32.34** Determine which of the following compounds would be likely to give this IR spectrum. [Section 32.2]



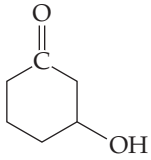

**(a)**



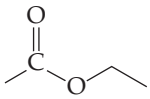
**(b)**



**(c)**



**(d)**

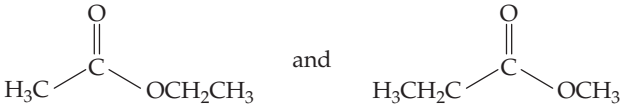


**32.35** Magnetic Resonance Imaging is a medical equivalent to NMR spectroscopy. **(a)** Instruments for obtaining MRI data are typically labelled with a frequency, such as 600 MHz. Why do you suppose this label is relevant to the experiment? **(b)** In general, the stronger the magnetic field, the greater the information obtained from an NMR or MRI experiment. Why do you suppose this is the case? **(c)** What safety precautions do you think are relevant around superconducting magnets? [Section 32.3]


**32.36** How could you use both $^{1}H$ and $^{13}C$ NMR to distinguish between these isomers? [*Hint:* Look for symmetry elements.] [Section 32.3]

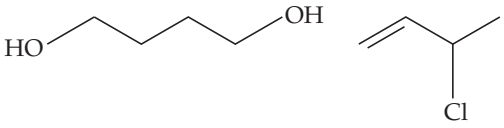
**(a)** $CH_3CH_2OCH_2CH_3$ and $CH_3CH_2CH_2CH_2OH$

**(b)**

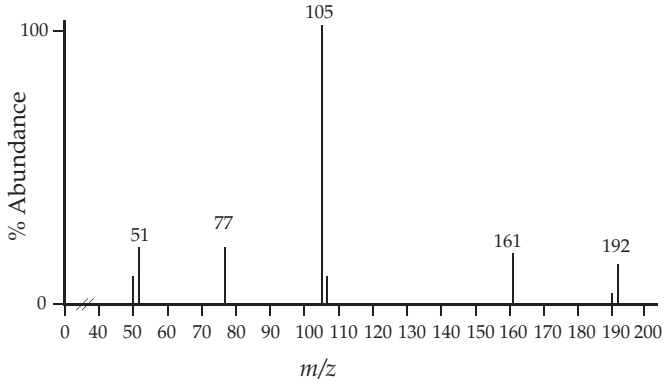


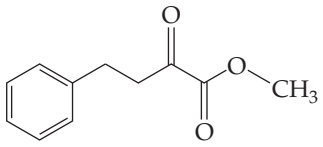

**(c)** $CH_3CH_2CH_2Br$ and $CH_3CHBrCH_3$

**32.37** The two compounds shown here have a molecular ion signal at $m/z = 90$. Describe two ways, using mass spectrometry, of distinguishing between them. [Section 32.4]



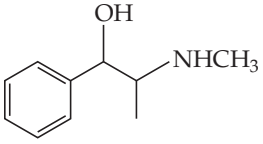
**32.38** Confirm that the fragmentation pattern seen in the following EI mass spectrum is consistent with the structure shown here. What chemical wet test(s) could you perform to support the structure shown? [Sections 32.4 and 32.5]



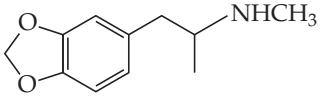



## Infrared Spectroscopy (Section 32.2)

**32.39** Ephedrine is produced by a number of the *Ephedra* species of plants. Its medicinal properties have been related to respiratory conditions since 200 AD. Its structure was elucidated in 1923 and ephedrine began clinical trials in 1926 as a bronchodilator for asthma. In the late 1990s, a new recreational drug, ecstacy, became popular with people in their 20s. Its structure is similar to ephedrine, which also acts as a heart stimulant.



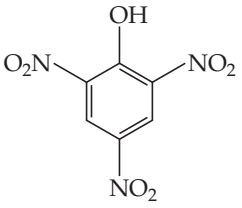
ephedrine



ecstacy

Could police and customs officials use IR spectroscopy to distinguish between the two compounds? Explain.

**32.40** Picric acid is an aromatic compound used extensively before 1960 as an agent for co-crystallising liquid organic samples so that a melting point determination could be made. Picric acid is not a carboxylic acid but instead a phenol bearing nitro substituents at the 2,4, and 6 positions. How could you use IR spectroscopy to determine that picric acid was indeed a phenol and not a carboxylic acid?



**32.41** **(a)** Of the functional groups O—H, C=O, C≡N, which would be most diagnostic for bioimaging? Why? **(b)** Can you name another functional group that could be used for diagnostic purposes using the IR technique? What problems might arise?

## NMR Spectroscopy (Section 32.3)

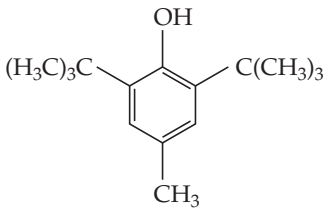
**32.42** The $^1$H NMR spectrum of acetone recorded on a spectrometer with an operating frequency of 200 MHz has a single resonance signal at 2.1 ppm.

**(a)** What is the difference in Hz between this signal and that of tetramethylsilane (TMS)?

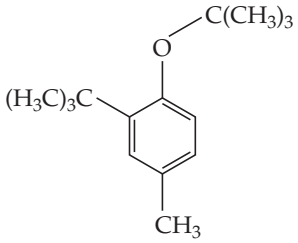
**(b)** At what $\delta$ value does this signal lie if recorded using a 400 MHz spectrometer?

**(c)** How many Hz away from TMS does the absorption in the 400 MHz spectrum correspond to?

**32.43** When the antioxidant BHT was first prepared, chemists were not sure of its structure. The chemical formula was determined by elemental analysis, but NMR, which would have instantaneously revealed the structure, had not yet been discovered. The problem arose because BHT failed the usual tests for phenols; for example, it was not soluble in dilute basic solution. Because of this, chemists thought the second 2-methylpropyl (*t*-butyl) group was linked to oxygen to form an ether. Of course, the reason BHT does not behave like other phenols is because the OH group is hindered by the two neighboring 2- methylpropyl groups, a protective quality that also allows this molecule to be used as a commercial antioxidant.




BHT




Supposed BHT

In terms of the number of equivalent hydrogens present, how could $^1$H NMR spectroscopy be used to verify the correct structure for BHT?

**32.44** Two bottles labelled propanol were found in a laboratory. Because of their differing boiling points, the bottles clearly contained the two propanol constitutional isomers. To determine which propanol was in which bottle, a $^1$H NMR spectrum was obtained on each sample. Draw the two possible isomers and describe how NMR might be used to distinguish between them.

**32.45** Predict the splitting pattern observed in the hydrogen-coupled $^{13}$C NMR spectrum for each of these compounds:

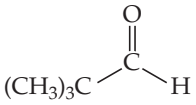
**(a)** $CH_3CHBr_2$ **(b)** $(CH_3)_2CHCl$ **(c)** $(CH_3)_3CBr$

**32.46** The spin of an electron generates a magnetic field, with "spin-up" and "spin-down" electrons having opposite fields. In the absence of a magnetic field, a "spin-up" and a "spin-down" electron have the same energy. **(a)** Why do you think that the use of a magnet was important in the discovery of electron spin? **(b)** A phenomenon called electron spin resonance (ESR) is closely related to nuclear magnetic resonance. In ESR, a compound with an unpaired electron is placed in a magnetic field, causing the unpaired electron to have two different energy states similar to our discussion of nuclear spin (see Figure 32.13). ESR uses microwave radiation instead of radiofrequency radiation to excite the unpaired electron from one state to the other. Does an ESR experiment require photons of greater or lesser energy than an NMR experiment?

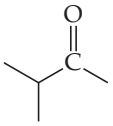
**32.47** 2-methylbut-2-ene contains signals at δ20.3, 22.5, 22.9, 110.3 and 111.5 in the $^{13}$C NMR hydrogen-decoupled spectrum, whereas 2-methylbutane contains only four signals. Explain why this is so.

**32.48** Predict the number of $^1$H NMR signals and also the splitting pattern of each of these compounds in the $^1$H NMR spectrum.

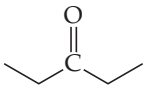
**(a)**



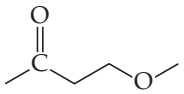

**(b)**




**(c)**

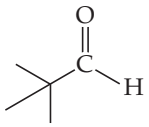



**(d)**

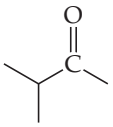



**32.49** Predict the number of $^{13}$C NMR signals in the hydrogen-decoupled spectrum of the following:

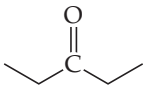
**(a)**



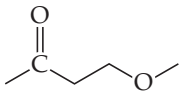

**(b)**




**(c)**

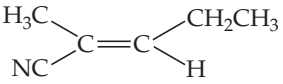



**(d)**




**32.50** $^{31}$P is NMR active ($I = \frac{1}{2}$) and is also the only naturally occurring phosphorus isotope. Describe the splitting you would see in both the $^1$H NMR and $^{31}$P NMR spectra of $PH_2Cl$.

**32.51** The 200 MHz $^1$H NMR spectrum of 2-cyanopent-2-ene has four distinctive resonances: δ5.3 (1H, singlet), 2.1 (2H, quartet), 1.9 (3H, singlet), 1.0 (3H, triplet). Assign each resonance to the structure.

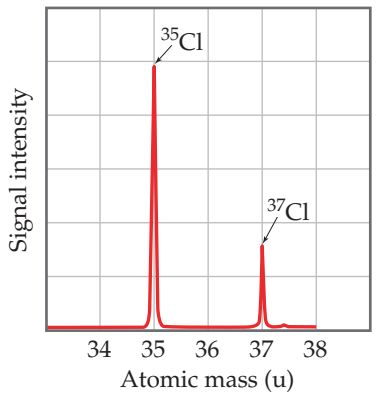



## Mass Spectrometry (Section 32.4)

**32.52** Triethylborane has two signals at *m/z* 97 and 98 in its EI mass spectrum. Account for the two signals.

**32.53** An aliphatic compound contains C, 39.76%, and H, 7.34%, but doesn't contain oxygen. The EI mass spectrum shows a molecular ion at $m/z = 150$ and a second signal of equal intensity at $m/z = 152$. Determine this compound's molecular formula.

**32.54** **(a)** The mass spectrometer in Figure 32.31 has a magnet as one of its components. What is the purpose of the magnet? **(b)** The atomic weight of Cl is 35.5 u. However, the mass spectrum of Cl, shown here, does not have a signal at this mass. Explain.




**32.55** What is meant by these terms?

**(a)** $M^+$ **(b)** $[M+2]^+$ **(c)** base peak

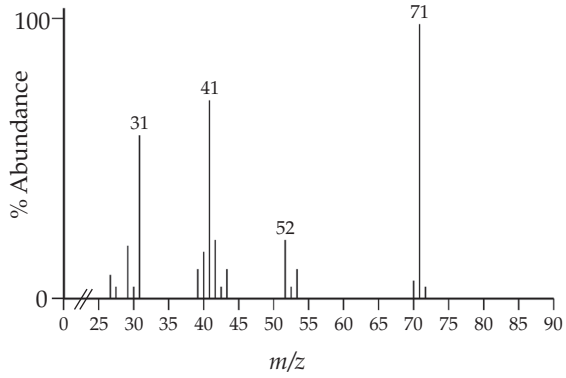
**(d)** *m/z* **(e)** EIMS

## Integrative Exercises

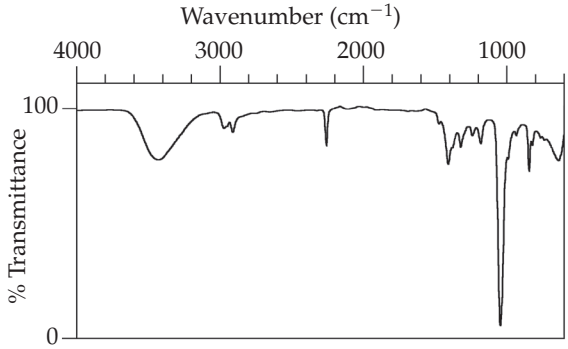
**32.56** The guidelines for determining the IHD of a compound are listed on page 1488. Using examples as appropriate, discuss why, for each nitrogen in the unknown's molecular formula, one hydrogen needs to be added to the reference molecular formula, but for oxygen nothing is added.

**32.57** This unknown evolves gas when a small amount of sodium metal is added. Microanalysis gave the following result: C, 50.69; H, 7.09; N, 19.71. Use all the information available to deduce the structure of the unknown.

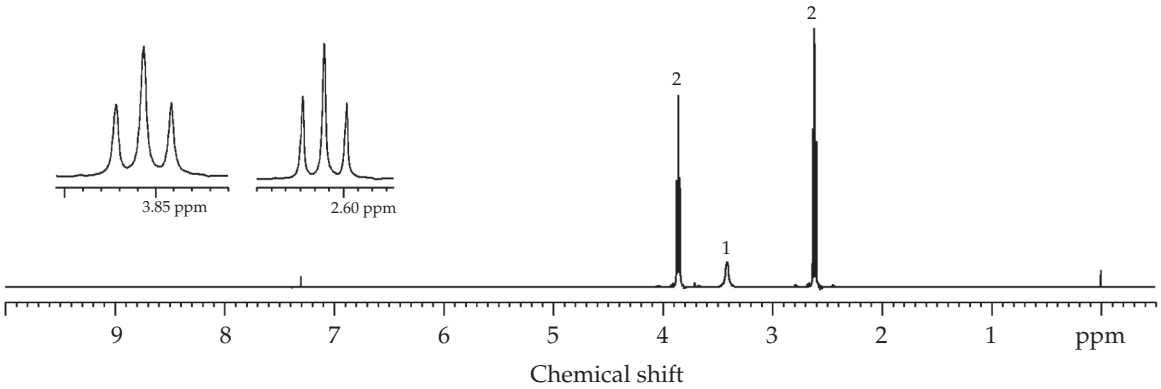
**Mass spectrum**



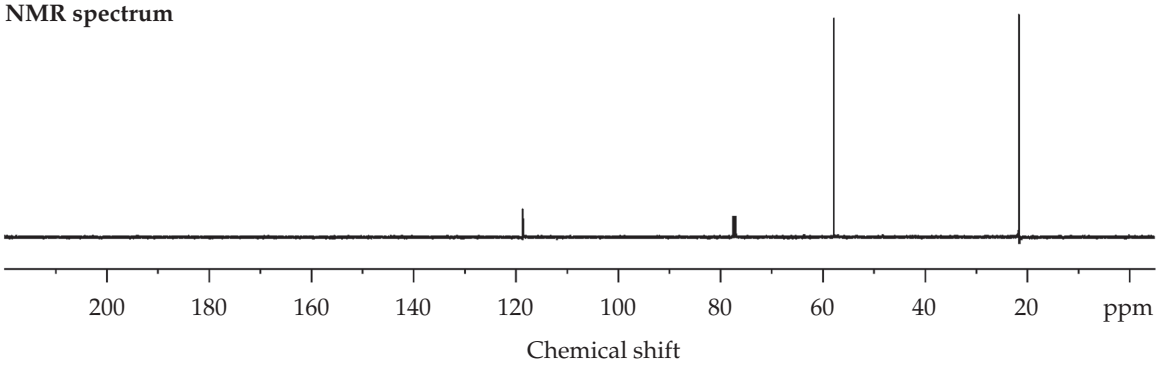

**IR spectrum**




**$^1$H NMR spectrum**

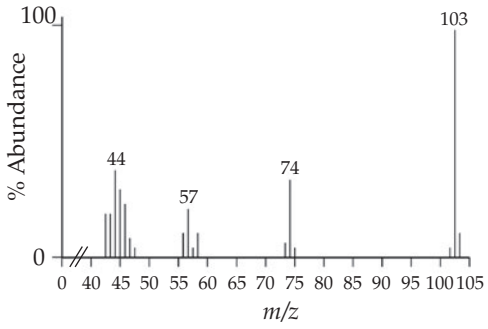


**$^{13}$C NMR spectrum**

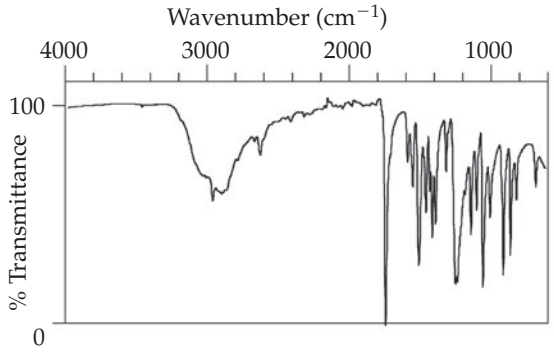



**32.58** This unknown is a derivative of an amino acid. Microanalysis gave the following result: C, 46.59; H, 8.80; N, 13.58. Solvent signals within the $^{1}$H NMR spectrum are labelled with an asterisk. Use all the information available to deduce the structure of the unknown.

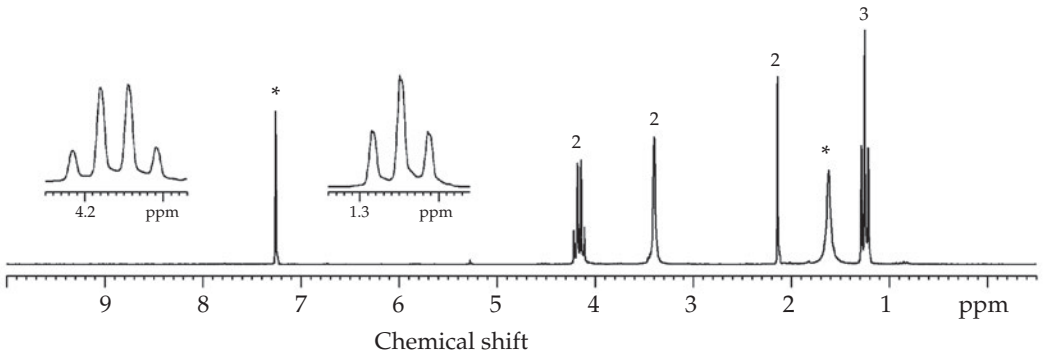
**Mass spectrum**



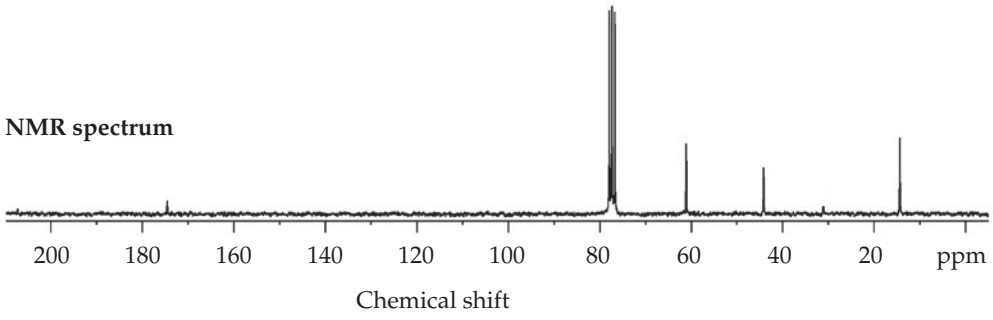

**IR spectrum**




**$^{1}$H NMR spectrum**

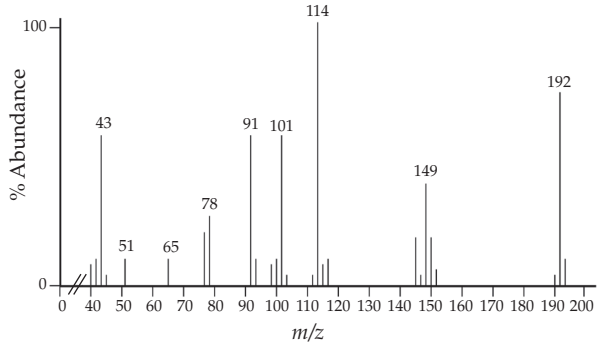



**$^{13}$C NMR spectrum**

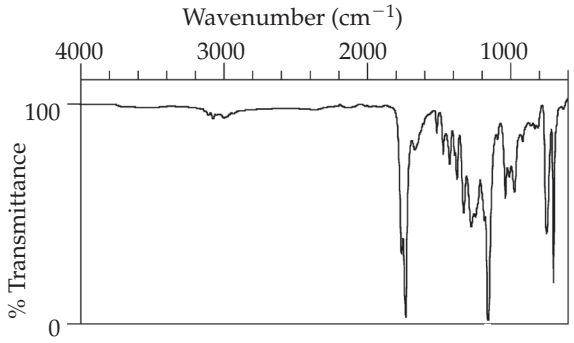



**32.59** When this unknown is saponified, it leads to the isolation of benzyl alcohol as one of the products. Microanalysis gave the following result: C, 68.74; H, 6.29. Use all the information available to deduce the structure of the unknown.

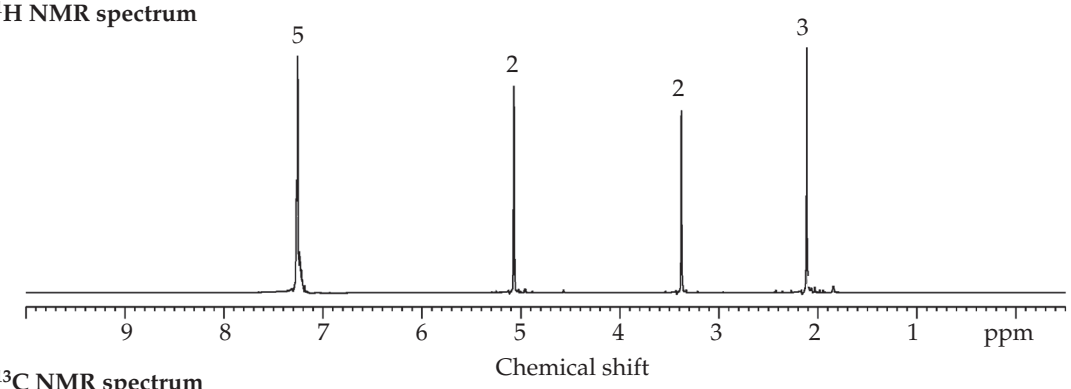
**Mass spectrum**



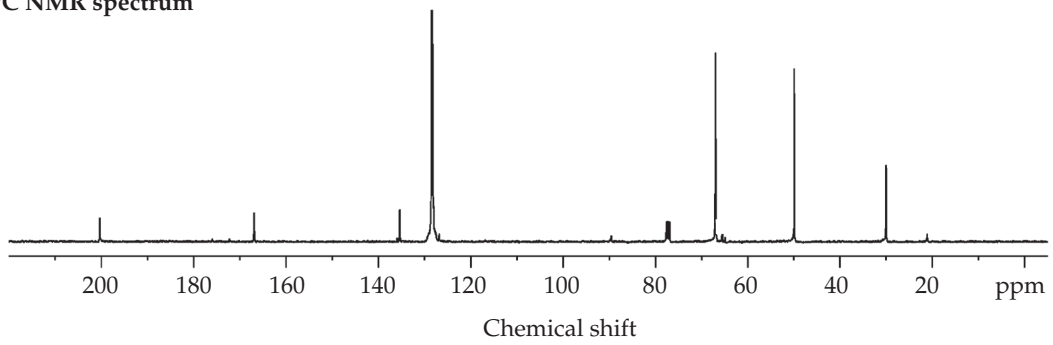

**IR spectrum**




**$^1$H NMR spectrum**

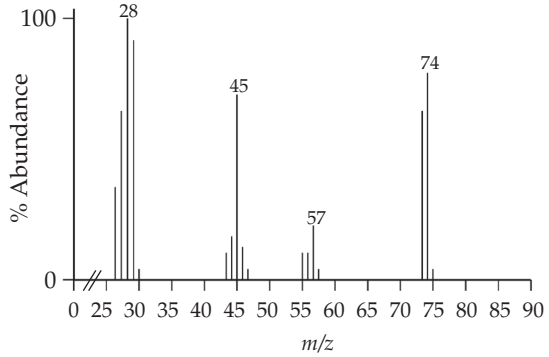



**$^{13}$C NMR spectrum**

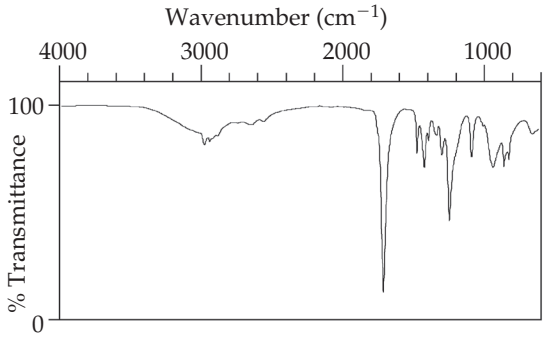



**32.60** This unknown liquid evolves a gas when dissolved in aqueous sodium bicarbonate. Microanalysis gave the following result: C, 48.64; H, 8.16. Use all the information available to deduce the structure of the unknown.

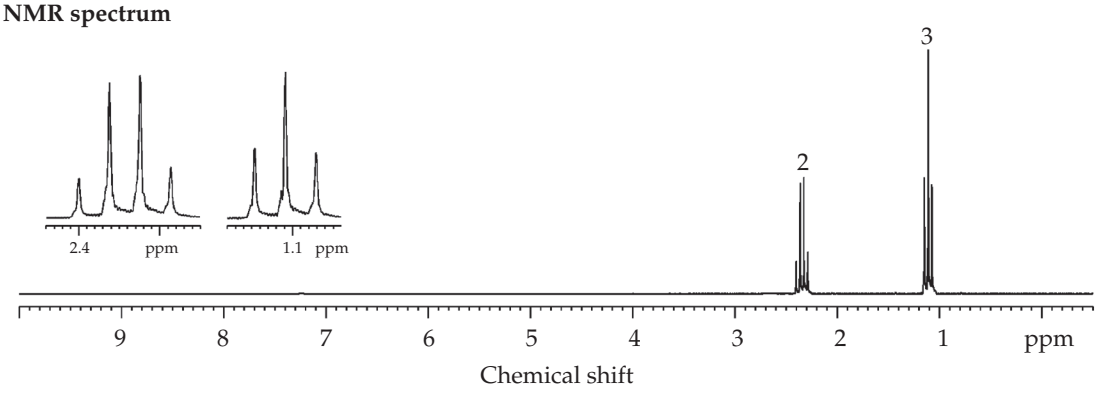
**Mass spectrum**



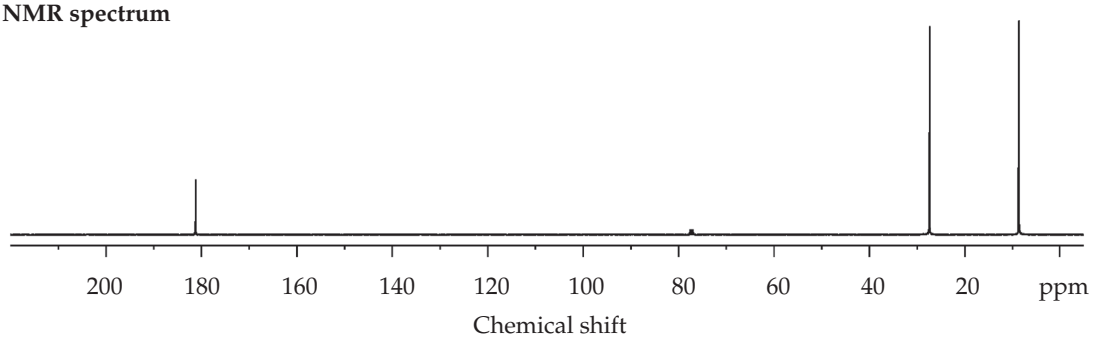

**IR spectrum**



**$^1$H NMR spectrum**

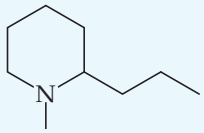



**$^{13}$C NMR spectrum**




## Design an Experiment

The poison hemlock plant (*Conium maculatum*) is toxic to mammals and can be fatal. All parts of the plant are poisonous, and as few as about ten leaves can kill a human. You are asked to help investigate the sudden death of some cattle that are thought to have eaten hemlock, and the vet has provided you with a small sample of a substance taken from the dead animals for you to identify. You suspect the substance to be coniine, one of the active components of hemlock.



Coniine

What precautions would you take when handling this substance? What chemical tests would you perform, and what would you expect them to show? If an elemental analysis were carried out, what percent of C, H, and N would you expect for coniine? What instrumental method would you use to determine the molecular mass of the substance and what would you calculate it to be for coniine? You run an IR spectrum of the substance – which regions of the IR would give you information about what functional groups were, or were not, present in the sample? The $^{13}$C NMR contains eight signals between 10 and 60 ppm. Is this consistent with the structure of coniine? The $^1$H NMR spectrum contains many overlapping signals and is reproduced here. Does it help with your identification? If you are asked how confident you were with your identification, what would you say?