PROBLEMS

12.5 Given that the stretching vibration of a typical C—H bond has a frequency of about \(9 \times 10^{13}\) s\(^{-1}\), which peak(s) in the IR spectrum of nonane (Fig. 12.4) would you assign to the C—H stretching vibrations?

12.6 The physical basis of some carbon monoxide detectors is the infrared detection of the unique C=O stretching vibration of carbon monoxide at 2143 cm\(^{-1}\). How many times per second does this stretching vibration occur?

\[
\text{:C=O:} \\
\text{carbon monoxide}
\]

12.3 INFRARED ABSORPTION AND CHEMICAL STRUCTURE

Each peak in the IR spectrum of a molecule corresponds to the absorption of energy by the vibration of a particular bond or group of bonds. IR spectroscopy is useful for the chemist because in all compounds, a given type of functional group absorbs in the same general region of the IR spectrum. The major regions of the IR spectrum are shown in Table 12.1.

The IR spectrum of a typical organic compound contains many more absorptions than can be readily interpreted. A major part of mastering IR spectroscopy is to learn which absorptions are important. Certain absorptions are diagnostic; that is, they indicate with reasonable certainty that a particular functional group is present. For example, an intense peak in the 1700–1750 cm\(^{-1}\) region indicates the presence of a carbonyl (C=O) group. Other peaks are confirmatory; that is, similar peaks can be found in other types of molecules, but their presence confirms a structural diagnosis made in other ways. For example, absorptions in the 1050–1200 cm\(^{-1}\) region of the IR spectrum due to a C—O bond could indicate the presence of an alcohol, an ether, an ester, or a carboxylic acid, among other things. However, if other evidence (perhaps obtained from other types of spectroscopy) suggests that the unknown molecule is, say, an ether, a peak in this region can serve to support this diagnosis. In the sections that follow, you’ll learn about the relatively few absorptions that are important in IR spectroscopy.

Rarely if ever does an IR spectrum completely define a structure; rather, it provides information that restricts the possible structures under consideration. Once the structure for an unknown compound has been deduced, a comparison of its IR spectrum with that of an authentic sample can be used as a criterion of identity. Even subtle differences in structure generally give discernible differences in the IR spectrum, particularly in the region between 1000 cm\(^{-1}\) and 1600 cm\(^{-1}\). This point is illustrated by the superimposed IR spectra of the two diastereomers cis- and trans-1,3-dimethylcyclohexane (Fig. 12.7). The greatest differences between the two

<table>
<thead>
<tr>
<th>Wavenumber range, cm(^{-1})</th>
<th>Type of absorptions</th>
<th>Name of region</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400–2800</td>
<td>O—H, N—H, C—H stretching</td>
<td>Functional group</td>
</tr>
<tr>
<td>2250–2100</td>
<td>C=N, C=C stretching</td>
<td></td>
</tr>
<tr>
<td>1850–1600</td>
<td>C=O, C=N, C=C stretching</td>
<td></td>
</tr>
<tr>
<td>1600–1000</td>
<td>C=C, C=O, C=N stretching; various bending absorptions</td>
<td>Fingerprint</td>
</tr>
<tr>
<td>1000–600</td>
<td>C—H bending</td>
<td>C—H bending</td>
</tr>
</tbody>
</table>
12.3 INFRARED ABSORPTION AND CHEMICAL STRUCTURE

spectra occur in this region of the spectrum. (That these spectra are different is another illustration of the principle that diastereomers have different physical properties.) Even though absorptions in this region are generally not interpreted in detail, they serve as a valuable “molecular fingerprint.” That is why this region of the spectrum is called the “fingerprint region” in Table 12.1.

A. Factors That Determine IR Absorption Position

One approach to the use of IR spectroscopy is simply to memorize the wavenumbers at which characteristic functional group absorbances appear and to look for peaks at these positions in the determination of unknown structures. However, you can use IR spectroscopy much more intelligently and learn the important peak positions much more easily if you understand a little more about the physical basis of IR spectroscopy. Two aspects of IR absorption peaks are particularly important. First is the position of the peak—the wavenumber or wavelength at which it occurs. Second is the intensity of the peak—how strong it is. Let’s consider each of these aspects in turn.

What factors govern the position of IR absorption? Three considerations are most important.

1. strength of the bond
2. masses of the atoms involved in the bond
3. the type of vibration being observed

Hooke’s law, which comes from the treatment of the vibrating spring by classical physics, nicely accounts for the first two of these effects. Let two atoms with masses $M$ and $m$, respectively, be connected by a bond, which we’ll treat as a spring. The tightness of the spring (bond) is described by a force constant, $\kappa$: the larger the force constant, the tighter the spring, or the stronger the bond.

![Diagram of a spring with masses](image-url)

Figure 12.7 Comparison of the IR spectra of the cis (red) and trans (blue) stereoisomers of 1,3-dimethylcyclohexane. Although these spectra are very similar, discernible differences between them occur in the fingerprint region.
The following equation describes the dependence of the vibrational wavenumber on the masses and the force constant:

\[ \tilde{\nu} = \frac{1}{2 \pi c} \sqrt{\frac{\kappa(m + M)}{mM}} \]  

(12.10)

Before we use this equation, let’s ask what our intuition tells us about how bond strength affects the vibrational frequency. Intuitively, a stronger bond corresponds to a tighter spring. That is, stronger bonds should have larger force constants. Objects connected by a tighter spring vibrate more rapidly—that is, with a higher frequency or wavenumber. Likewise, atoms connected by a stronger bond also vibrate at higher frequency. A simple measure of bond strength is the energy required to break the bond, which is the bond dissociation energy (Table 5.3 on p. 213). It follows, then, that the higher the bond dissociation energy, the stronger the bond. Thus, the IR absorptions of stronger bonds—bonds with greater bond dissociation energies—occur at higher wavenumber. Study Problem 12.1 illustrates this effect.

**Study Problem 12.1**

The typical stretching frequency for a carbon–carbon double bond is 1650 cm\(^{-1}\). Estimate the stretching frequency of a carbon–carbon triple bond.

**Solution** Use Eq. 12.10. We are given \( \tilde{\nu} \) for a double bond, which we’ll call \( \tilde{\nu}_2 \), and we’re asked to estimate \( \tilde{\nu}_3 \), the stretching frequency of the triple bond. Let the force constant for a double bond be \( \kappa_2 \), and that of a triple bond be \( \kappa_3 \). Now take the ratio of \( \tilde{\nu}_3 \) and \( \tilde{\nu}_2 \) as given by Eq. 12.10:

\[ \frac{\tilde{\nu}_3}{\tilde{\nu}_2} = \sqrt{\frac{\kappa_3}{\kappa_2}} \]

(12.11)

All of the mass terms cancel because they are the same in both cases—the mass of a carbon atom. We could complete the problem if we knew the force constants, but these aren’t given. Let’s apply some intuition. As we just learned, force constants are proportional to bond dissociation energies. We could look these up in Table 5.3, but let’s simply assume that the relative strengths of triple and double bonds are in the ratio 3:2. If this were so, then Eq. 12.11 becomes

\[ \frac{\tilde{\nu}_3}{\tilde{\nu}_2} = \sqrt{\frac{3}{2}} = 1.22 \]

(12.12)

With \( \tilde{\nu}_2 = 1650 \text{ cm}^{-1} \), we then estimate \( \tilde{\nu}_3 \) to be \((1.22)(1650 \text{ cm}^{-1}) = 2013 \text{ cm}^{-1}\).

How close are we? See for yourself by jumping ahead to Fig. 14.4, p. 650, which shows the C≡C stretching absorption of an alkyne.

Now let’s consider the effect of mass on the stretching frequency of a bond. Eq. 12.10 also describes this effect. However, a special case of this equation is very important. Suppose the two atoms connected by a bond differ significantly in mass (for example, a carbon and a hydrogen in a C—H bond). The vibration frequency for a bond between two atoms of different mass depends more on the mass of the lighter object than on the mass of the heavier one. The following analogy illustrates this point.
Now let’s use Eq. 12.10 to verify that the smaller mass determines the vibration frequency. Suppose in this equation that $M >> m$. In such a case, the smaller mass can be ignored in the numerator of Eq. 12.10, and the larger mass $M$ then cancels and vanishes from the equation, leaving only the smaller mass $m$ in the denominator. Eq. 12.10 then becomes

$$\tilde{v} = \frac{1}{2\pi c} \sqrt{\frac{\kappa}{m}} \quad \text{(for } M >> m)$$

(12.13)

According to this equation, the vibration frequency of a bond between a heavy and a light atom depends primarily on the mass of the light atom, as our preceding intuitive argument suggested. This is why C—H, O—H, and N—H bonds all absorb in the same general region of the IR spectrum, and why C=O, C=N, and C=C bonds absorb in the same general region (Table 12.1). In fact, the differences that do exist between the vibrational frequencies of these bonds are not primarily mass effects, but mostly bond-strength effects.

### PROBLEMS

**12.7** The following bonds all have IR stretching absorptions in the 4000–2900 cm$^{-1}$ region of the spectrum. Rank the following bonds in order of decreasing stretching frequencies, greatest first, and explain your reasoning. (Hint: Consult Table 5.3 on p. 213.)

- C—H, O—H, N—H, F—H

**12.8** The $\equiv$C—H stretching absorption of 2-methyl-1-pentene is observed at 3090 cm$^{-1}$. If the hydrogen were replaced by deuterium, at what wavenumber would the $\equiv$C—D stretching absorption be observed? Explain. (Assume that the force constants for the C—H and C—D bonds are identical.)

The third factor that affects the absorption frequency is the type of vibration. The two general types of vibrations in molecules are stretching vibrations and bending vibrations. A stretching vibration occurs along the line of the chemical bond. A bending vibration is any vibration that does not occur along the line of the chemical bond. A bending vibration can be envisioned as a ball hanging on a spring and swinging side to side. In general, bending vibrations occur at lower frequencies (higher wavelengths) than stretching vibrations of the same groups.
The only possible type of vibration in a diatomic molecule (for example, H—F) is a stretching vibration. However, when a molecule contains more than two atoms, both stretching and bending vibrations are possible. The allowed vibrations of a molecule are called its normal vibrational modes. The normal vibrational modes for a —CH₂— group are shown in Fig. 12.8. They serve as models for the kinds of vibrations that can be expected for other groups in organic molecules. The bending vibrations can be such that the hydrogens move in the plane of the —CH₂— group, or out of the plane of the —CH₂— group. Furthermore, stretching and bending vibrations can be symmetrical or unsymmetrical with respect to a plane between the two vibrating hydrogens. The bending motions have been given graphic names (scissoring, wagging, and so on) that describe the type of motion involved. Each of these motions occurs with a particular frequency and can have an associated peak in the IR spectrum (although some peaks are weak or absent for reasons to be considered later). The —CH₂— groups in a typical organic molecule undergo all of these motions simultaneously. That is, while the C—H bonds are stretching, they are also bending. The IR spectrum of nonane (Fig. 12.4) shows absorptions for both C—H stretching and C—H bending vibrations. The peak at 2920 cm⁻¹ is due to the C—H stretching vibrations; the peaks at 1470 and 1380 cm⁻¹ are due to various bending modes of both —CH₂— and CH₃— groups; and the peak at 720 cm⁻¹ is due to a different bending mode, the —CH₂— rocking vibration. Notice that all of the bending vibrations absorb at lower wavenumber (and therefore lower energy) than the stretching vibrations.

**B. Factors That Determine IR Absorption Intensity**

The different peaks in an IR spectrum typically have very different intensities. Several factors affect absorption intensity. First, a greater number of molecules in the sample and more absorbing groups within a molecule give a more intense spectrum. Thus, a more concentrated sample gives a stronger spectrum than a less concentrated one, other things being equal. Similarly, at a given concentration, a compound such as nonane, which is rich in C—H bonds, has a stronger absorption for its C—H stretching vibrations than a compound of similar molecular mass with relatively few C—H bonds.

The dipole moment of a molecule also affects the intensity of an IR absorption. We can see why this should be so if we think about the nature of light and how it interacts with a single vibrating bond. A light wave consists of perpendicular vibrating electric and magnetic fields. Only the vibrating electric field is relevant to IR spectroscopy, so we’ll forget about the magnetic field for now. The vibrating electric field of light can be represented as an oscillating vector (Fig. 12.9a, p. 550). An electric field exerts a force on a charge. This means that an electric field affects the motion of a charge. The field imposes an acceleration component on the charge in the direction of the field. In particular, if a charge is moving in the same direction as the electric field, the field increases the velocity of the charge; that is, the field makes the charge “move more.”

Recall from Sec. 1.2D that a polar chemical bond has a bond dipole. This means that we can think of a polar bond as a system of separated positive and negative charges. If a polar bond vibrates with a particular frequency, its bond dipole vibrates with the same frequency (Fig. 12.9b). According to Eq. 1.4 (p. 11), the magnitude of the bond dipole is proportional not
only to the amount of charge on each bonded atom but also to the distance between the
atoms—that is, the bond length. Therefore, as the bond stretches, the bond dipole increases,
and, as the bond compresses, the bond dipole decreases. To a light wave, a polar bond is basi-
cally a system of moving charges. Light interacts with a polar bond because its electric field
exerts a force on the system of moving charges (the vibrating bond dipole). This interaction
can occur only if the light wave and the charges in the bond are oscillating with the same fre-
quency. When the electric field of the light wave exerts a force on the charges in the bond dipole, the bond dipole gains energy, as shown in Fig. 12.6, and consequently the light wave loses energy; this is the process of absorption.

If a bond has no bond dipole, then there are no moving charges with which the electric field of the light wave can interact. For example, the C=C bond in the alkene 2,3-dimethyl-2-butene has no bond dipole because of its symmetrical placement in the molecule. Hence, its stretching vibration does not interact with the electric field of light. The C=C stretching vibration occurs, but it does not absorb energy from light. This means that 2,3-dimethyl-2-butene does not have a C=C stretching absorption in its IR spectrum in the 1600–1700 cm\(^{-1}\) region of its IR spectrum, the region in which many other alkenes have such an absorption.

\[
\text{2,3-dimethyl-2-butene: zero dipole moment}
\]

\[
\text{“stretched” 2,3-dimethyl-2-butene: zero dipole moment}
\]

\[12.14\]
12.3 INFRARED ABSORPTION AND CHEMICAL STRUCTURE

(This compound does have other IR absorptions.) Molecular vibrations that occur but do not give rise to IR absorptions are said to be infrared-inactive. (IR-inactive vibrations can be observed with Raman spectroscopy, another type of spectroscopy.) In contrast, any vibration that gives rise to an IR absorption is said to be infrared-active. We often find in practice that highly symmetrical compounds have less complex IR spectra because their symmetry results in the absence of a molecular dipole moment and a relatively large number of infrared-inactive vibrations.

It is possible for a molecule that has a zero dipole moment to have a molecular vibration that creates a temporary dipole moment in the distorted molecule. Such vibrations are also infrared-active. An example of this situation is found in Study Problem 12.2. This is why some vibrations, even in symmetrical molecules, are infrared-active.

Because the intensity of an IR absorption depends on the size of the dipole moment change that accompanies the corresponding vibration, IR absorptions differ widely in intensity. Chemists do not try to predict intensities; rather, they rely on collective experience to know which absorptions are weaker and which are stronger. Nevertheless, for symmetrical molecules with a zero dipole moment, we must be particularly aware of the possibility of IR-inactive vibrations that would be observed in less symmetrical molecules containing the same functional groups.

Study Problem 12.2

Which one of the following molecular vibrations is infrared-inactive? (a) the C==O symmetrical stretch of CO\(_2\); (b) the C==O unsymmetrical stretch of CO\(_2\). (See Fig. 12.8 on p. 549.)

Solution First be sure you understand what is meant by the terms symmetrical stretch and unsymmetrical stretch. These are defined by analogy to the C—H stretching vibrations in Fig. 12.8. In the symmetrical stretch, the two C==O bonds lengthen (or shorten) at the same time so that the molecule maintains its symmetry with respect to the symmetry plane:

```
O==C==O  O==C==O
```

Symmetrical stretch: maintains the molecular symmetry

In the unsymmetrical stretch, one C==O bond shortens when the other lengthens:

```
O==C==O  O==C==O
```

Unsymmetrical stretch

Which of these vibrational modes results in a change of dipole moment? Because the CO\(_2\) molecule is linear, the two C==O bond dipoles exactly oppose each other. Stretching a bond increases its bond dipole because the size of a bond dipole is proportional not only to the magnitudes of the partial charges at each end of the bond but also to the distance by which the charges are separated (Eq. 1.4, p. 11). Consequently, after the symmetrical stretch, both bond dipoles are increased; but, because they are exactly equal and oppose each other, the dipole moment remains zero. Hence, the symmetrical stretching vibration is IR-inactive.

In an unsymmetrical stretch, one C==O bond is reduced in length while the other is increased. Because the “long” C==O bond has a greater bond dipole than the “short” C==O bond, the two bond dipoles no longer cancel. Thus, the unsymmetrical stretch imparts a temporary dipole moment to the CO\(_2\) molecule. Consequently, this vibration is infrared-active—it gives rise to an IR absorption.
12.4 FUNCTIONAL-GROUP INFRARED ABSORPTIONS

A typical IR spectrum contains many absorptions. Chemists do not try to interpret every absorption in a spectrum. Experience has shown that some absorptions are particularly useful and important in diagnosing or confirming certain functional groups. In this section, we’ll focus on those. We’ll show you sample spectra so that you will begin to see how these absorptions appear in actual spectra.

We’ll consider here only the functional groups covered in Chapters 1–11. Subsequent chapters contain short sections that discuss the IR spectra of other functional groups. These sections, however, can be read and understood at any time with your present knowledge of infrared spectroscopy. In addition, a summary of key IR absorptions is given in Appendix II.

A. IR Spectra of Alkanes

The characteristic structural features of alkanes are the carbon–carbon and carbon–hydrogen single bonds. The stretching of the carbon–carbon single bond is infrared-inactive (or nearly so) because this vibration is associated with little or no change of the dipole moment. The stretching absorptions of alkyl C—H bonds are typically observed in the 2850–2960 cm\(^{-1}\) region. The peaks near 2920 cm\(^{-1}\) in the IR spectrum of nonane (Fig. 12.4) are examples of such absorptions. Various bending vibrations are also observed in the fingerprint region (1380 and 1470 cm\(^{-1}\) in nonane) and in the C—H bending region (720 cm\(^{-1}\) in nonane). Absorptions in these general regions can be expected not only for alkanes but also for any compounds that contain \(\text{H}_3\text{C—C—H}\) and \(\text{C—CH}_2—\) groups. Consequently, these absorptions are not often useful, but it is important to be aware of them so that they are not mistakenly attributed to other functional groups.

B. IR Spectra of Alkyl Halides

The carbon–halogen stretching absorption of alkyl chlorides, bromides, and iodides appear in the low-wavenumber end of the spectrum, but many interfering absorptions also occur in this region. NMR spectroscopy and mass spectrometry are more useful than IR spectroscopy for determining the structures of these alkyl halides.

Alkyl fluorides, in contrast to the other alkyl halides, have useful IR absorptions. A single C—F bond typically has a very strong stretching absorption in the 1000–1100 cm\(^{-1}\) region.