Interpretation of IR Spectra

Interpretation of the IR spectrum of an unknown compound is an art that requires experience and practice. The more spectra you examine, the easier it will become to recognize the absorption due to an $\text{O—H}$ group and to differentiate between that band and one that results from an $\text{N—H}$ group.

Table 13.2 summarizes the positions of the various absorption bands that have been discussed so far. On the basis of these absorptions, it is usually possible to determine the nature of the functional group that is present in the compound whose spectrum is being considered. Many functional groups require the presence of several characteristic absorptions, whereas the absence of a band in a particular region of the spectrum can often be used to eliminate the presence of a particular group.

Infrared spectra of compounds belonging to each of the major functional group classes are provided in the figures in this chapter. Each figure has a summary of the important absorptions for that class.

**Figure 13.14**

The infrared spectrum of 2-nitrotoluene.

**Nitro compounds**: Compounds containing nitro groups are identified by the appearance of two strong bands near 1550 and 1380 cm$^{-1}$. These absorptions appear at lower wavenumbers if the nitro group is conjugated with a benzene ring.

The aromatic ring is responsible for the absorptions due to the $sp^2$ CH stretching vibrations (3100–3000 cm$^{-1}$); the ring skeletal vibrations at 1612, 1577, 1500, and 1461 cm$^{-1}$; and the CH bending vibrations at 859, 788, and 728 cm$^{-1}$.

Two types of CH bonds can be detected in this spectrum:

- $sp^2$-hybridized CH bonds (3100–3000 cm$^{-1}$)
- $sp^3$-hybridized CH bonds (3000–2850 cm$^{-1}$)

The absorption bands due to the nitro group: 1523 and 1347 cm$^{-1}$. They are at lower wavenumbers than usual because the nitro group is conjugated with the benzene ring.
important absorption bands for that functional group. Some of these figures are found on previous pages; others appear on later pages. Table 13.3 provides a list of the important functional groups and the figure(s) that show IR spectra of typical compounds containing that functional group. Now that all of the important absorption bands have been discussed, this is a good time for you to examine all of these spectra to become more familiar with the combination of bands caused by each functional group.

### Table 13.2 Important Absorption Bands in the Infrared Spectral Region

<table>
<thead>
<tr>
<th>Position (cm(^{-1}))</th>
<th>Group</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3550–3200</td>
<td>–O–H</td>
<td>Strong intensity, very broad band</td>
</tr>
<tr>
<td>3400–3250</td>
<td>–N–H</td>
<td>Weaker intensity and less broad than O–H; NH(_2) shows two bands, NH shows one</td>
</tr>
<tr>
<td>3300</td>
<td>≡C–H</td>
<td>Sharp, C is sp hybridized</td>
</tr>
<tr>
<td>3100–3000</td>
<td>=C–H</td>
<td>C is sp(^3) hybridized</td>
</tr>
<tr>
<td>3000–2850</td>
<td>–C–H</td>
<td>C is sp(^3) hybridized; 3000 cm(^{-1}) is a convenient dividing line between this type of C–H bond and the preceding type</td>
</tr>
<tr>
<td>2830–2700</td>
<td>–C–H</td>
<td>Two bands</td>
</tr>
<tr>
<td>2260–2200</td>
<td>≡C–N</td>
<td>Medium intensity</td>
</tr>
<tr>
<td>2150–2100</td>
<td>≡C≡C</td>
<td>Weak intensity</td>
</tr>
<tr>
<td>1820–1650</td>
<td>–C–</td>
<td>Strong intensity; exact position depends on substituents; see Table 13.1</td>
</tr>
<tr>
<td>1660–1640</td>
<td></td>
<td>Often weak intensity</td>
</tr>
<tr>
<td>1600–1450</td>
<td></td>
<td>Four bands of variable intensity</td>
</tr>
<tr>
<td>1550 and 1380</td>
<td>–NO(_2)</td>
<td>Two strong intensity bands</td>
</tr>
<tr>
<td>1300–1000</td>
<td>–C–O</td>
<td>Strong intensity</td>
</tr>
<tr>
<td>900–675</td>
<td></td>
<td>Strong intensity</td>
</tr>
</tbody>
</table>
Table 13.3  IR Spectra of Functional Groups

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane</td>
<td>13.5</td>
<td>509</td>
</tr>
<tr>
<td>Alkyne</td>
<td>13.7</td>
<td>510</td>
</tr>
<tr>
<td>Alcohol</td>
<td>13.9</td>
<td>512</td>
</tr>
<tr>
<td>Ether</td>
<td>13.16</td>
<td>524</td>
</tr>
<tr>
<td>Primary amine</td>
<td>13.11</td>
<td>513</td>
</tr>
<tr>
<td>Secondary amine</td>
<td>13.12</td>
<td>514</td>
</tr>
<tr>
<td>Tertiary amine</td>
<td>13.17</td>
<td>525</td>
</tr>
<tr>
<td>Ketone</td>
<td>13.4</td>
<td>507</td>
</tr>
<tr>
<td>Ester</td>
<td>13.19</td>
<td>527</td>
</tr>
<tr>
<td>Amide</td>
<td>13.21</td>
<td>528</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkene</td>
<td>13.6</td>
<td>510</td>
</tr>
<tr>
<td>Arene</td>
<td>13.8</td>
<td>511</td>
</tr>
<tr>
<td>Nitro compound</td>
<td>13.14</td>
<td>521</td>
</tr>
<tr>
<td>Nitrile</td>
<td>13.13</td>
<td>515</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>13.8</td>
<td>511</td>
</tr>
<tr>
<td>Carboxylic acid</td>
<td>13.10</td>
<td>513</td>
</tr>
<tr>
<td>Anhydride</td>
<td>13.20</td>
<td>528</td>
</tr>
<tr>
<td>Acyl chloride</td>
<td>13.22</td>
<td>529</td>
</tr>
</tbody>
</table>

The aromatic ring skeletal vibrations: 1604, 1580, 1496, and 1450 cm\(^{-1}\). The bending vibrations of the CH bonds of the aromatic ring: 742 and 698 cm\(^{-1}\).

**Figure 13.15**

The infrared spectrum of propylbenzene.

**Arenes:** Arenes that have hydrogens on the aromatic ring show absorptions in the 3100 and 3000 cm\(^{-1}\) region. They also show four absorptions of variable intensity near 1600, 1580, 1500, and 1450 cm\(^{-1}\) due to skeletal vibrations of the benzene ring. In addition, most aromatic compounds have at least one strong absorption in the 900 and 675 cm\(^{-1}\) region due to bending vibrations of the CH bonds of the aromatic ring. Although care must be used in assigning some of these bands because they occur in the fingerprint region, the presence of all of them provides evidence that the compound contains an aromatic ring.
It is usually possible to distinguish among the various carbonyl-containing functional groups by careful examination of the IR spectrum. Of course, all have carbonyl absorptions. However, acid chlorides show this band at unusually high wavenumbers; acid anhydrides have two bands in this region; and amides have this band at unusually low wavenumbers, often have additional bands in this region, and may also show N-H bands. Carboxylic acids are easily recognized by their very broad O-H band, and aldehydes are distinguished by the C-H bands in the 2830 to 2700 cm\(^{-1}\) region. To identify an ester, the strong absorption due to the C=O bands must be located in the 1300 to 1000 cm\(^{-1}\) region. The absence of any of these other features suggests that the compound is a ketone. Recognize, however, that assignment of an unknown to a particular functional group class must sometimes be only tentative. In such cases, confirming evidence must be obtained from other sources, such as other spectroscopic techniques or chemical tests. Be careful not to become so sure of a functional group assignment that other, contradictory evidence is ignored.

In attempting to identify the functional group that is present in an unknown compound from its IR spectrum, it is usually best to begin by examining the region from 4000 to 2700 cm\(^{-1}\) to determine what type of bonds involving hydrogen are present. Then the region from 2300 to 2100 cm\(^{-1}\) should be examined to look for indications of the presence of triple-bond groups. Next, you should look for absorptions due to carbonyl groups,
CC double bonds, aromatic rings, and nitro groups in the 1800 to 1350 cm\(^{-1}\) region. Finally, you should look for C–O absorptions in the 1300 to 1000 cm\(^{-1}\) region and for aromatic ring bands in the 900 to 675 cm\(^{-1}\) region.

Two cautions must be given. First, do not overinterpret the spectrum. Be very careful in assigning the presence of a functional group when only weak bands occur in the appropriate region. It is helpful to compare the spectrum of the unknown to that of a known compound that has that same functional group. Second, make sure that your conclusions are consistent with all of the data. A spectrum that has two bands in the 2830 to 2700 cm\(^{-1}\) region cannot be that of an aldehyde unless it also shows an absorption due to a carbonyl group.

Let’s try a problem. The IR spectrum of an unknown compound is shown in Figure 13.23. First, let’s examine the hydrogen region. The absence of absorptions in the 3600 to 3100 cm\(^{-1}\) region indicates that the compound does not have any O–H or N–H groups. The bands in the 3100 to 3000 cm\(^{-1}\) region indicate the presence of tertiary amines:

Tertiary amines: Tertiary amines do not have a NH bond, so there is no evidence for the amine group in the 3400–3250 cm\(^{-1}\) region. Because the CN bond-stretching vibration is difficult to assign in the fingerprint region, tertiary amines are not readily identified from their IR spectra. Chemical tests are helpful in such cases.

**Figure 13.17**

The infrared spectrum of \(N,N\)-diethylaniline.
hydrogens bonded to \(sp^2\)-hybridized carbons, so the compound must have one or more CC double bonds. The absorptions in the 3000 to 2850 cm\(^{-1}\) region indicate that there are also hydrogens bonded to \(sp^3\)-hybridized carbons in the compound. Next, examination of the triple-bond region shows no indications of the presence of any triple-bonded functional group. Continuing to the double-bond region, the strong absorption at 1722 cm\(^{-1}\) indicates the presence of a carbonyl group. This is not part of a carboxylic acid (no O—H) or an aldehyde (absence of absorptions in the 2830–2700 cm\(^{-1}\) region). Nor does the unknown appear to be an amide (no N—H, carbonyl absorption too high), an anhydride (absence of a second carbonyl band), or an acyl chloride (carbonyl position too low). This leaves a ketone or an ester as possibilities. The strong absorption at 1282 cm\(^{-1}\) suggests that the unknown is an ester. The bands at 1607, 1591, 1489, and 1437 cm\(^{-1}\) along with the absorptions at 3100 to 3000 and 746 cm\(^{-1}\) suggest the presence of an aromatic ring. The carbonyl of the ester
occurs at slightly lower wavenumbers (1722 cm\(^{-1}\)) than the usual position (1740 cm\(^{-1}\)), indicating that it might be conjugated. Therefore, we conclude that the unknown is probably an ester, that it may have an aromatic ring, and that the ester may be conjugated (with the aromatic ring?). However, these conclusions must be considered tentative until confirming evidence is obtained from other sources. The unknown is actually methyl 3-methylbenzoate:

\[
\begin{align*}
H_3C & \quad \text{O} \\
\text{COCH}_3 & \quad \text{Methyl 3-methylbenzoate}
\end{align*}
\]

Esters: Esters show a carbonyl band near 1740 cm\(^{-1}\). They also show a strong absorption in the CO single bond region, from 1300–1000 cm\(^{-1}\), that can be used to differentiate them from ketones. This band is usually of comparable breadth and intensity to the carbonyl band. (However, a compound containing both a ketone and an ether group also has both of these absorptions.) Chemical tests can be very useful in distinguishing a ketone from an ester.

Figure 13.19

The infrared spectrum of ethyl acetate.
Anhydrides: Anhydrides are characterized by the presence of two bands in the carbonyl region, one near 1820 and one near 1750 cm\(^{-1}\).

**Figure 13.20**
The infrared spectrum of propanoic anhydride.

Amides: The absorption for the carbonyl group of an amide appears in the region of 1690–1630 cm\(^{-1}\), lower wavenumbers than most other carbonyl bands. In addition, other relatively strong bands often appear at slightly lower wavenumbers. Amides derived from ammonia or primary amines have bands in the hydrogen region due to their NH bonds.

**Figure 13.21**
The infrared spectrum of \(N,N\)-dimethylacetamide.
The exact identity of an unknown cannot be established only on the basis of its IR spectrum (unless, of course, the spectrum of a known exactly matches the spectrum of the unknown). However, information about the functional group that is present in a compound can be determined:

- **O–H**
- **N–H**
- **Type of C–H**
- **C=O**
- **C≡C**
- **C≡N**

The IR spectrum provides little information about the hydrocarbon part of the compound. However, this is exactly the information provided by nuclear magnetic resonance spectroscopy, discussed in Chapter 14. The combination of these two types of spectroscopy is of enormous value in organic chemistry.

**Figure 13.22**

*The infrared spectrum of o-toluyl chloride.*

The carbonyl group of an acyl chloride appears at unusually high wavenumbers, near 1800 cm⁻¹. Because the carbonyl group is conjugated with the benzene ring in this compound, it is shifted to lower wavenumbers by about 30 cm⁻¹.
Figure 13.23
The infrared spectrum of an unknown compound.

PROBLEM 13.10
Predict the positions of the major absorption bands in the IR spectra of these compounds:

a) $\text{CH}_3\text{CH}==\text{CHCH}_3$

b) $\text{CH}_3\text{CH}_2\text{NH}_2$

c) $\text{CH}_3\text{O}\text{CCH}_3$

d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

e) $\text{CH}_2\text{CH}_2\text{C}==\text{C—H}$

f) $\text{NO}_2\text{CH}_2\text{C}==\text{C—H}$

PROBLEM 13.11
Explain how IR spectroscopy could be used to distinguish between these compounds:

a) $\text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2$ and $\text{CH}_3\text{CH}_2\text{C}==\text{CH}$

b) $\text{CH}_3\text{C}==\text{C—OH}$ and $\text{CH}_2\text{OH}$
PRACTICE PROBLEM 13.2

Explain which functional groups are present in this compound on the basis of its IR spectrum:

\[ \text{Solution} \]

The broad absorption centered near 3300 cm\(^{-1}\) indicates the presence of a hydroxy group. The absorption at 3005 cm\(^{-1}\) suggests the presence of H's bonded to \(sp^2\)-hybridized C's. (Note that you are not expected to read peak positions this exactly from any of these spectra.) This is supported by the absorption for a CC double bond at 1646 cm\(^{-1}\). The absorptions in the region of 3000 to 2850 cm\(^{-1}\) indicate the presence of H's bonded to \(sp^3\)-hybridized C's. Although the compound has a CC double bond, there is no indication of the presence of an aromatic ring due to the absence of the four bands in the 1600 to 1450 cm\(^{-1}\) region and the absence of bands in the 900 to 675 cm\(^{-1}\) region.

In summary, the structural features that can be identified from the IR spectrum are as follows:

\[ \text{O} - \text{H} \quad \text{C} = \text{C} - \text{H} \quad -\text{C} - \text{H} \]
(This is the spectrum of 2-propen-1-ol or allyl alcohol. The structure cannot be determined only from this IR spectrum, but the conclusions reached are consistent with this structure.)

\[
\begin{align*}
\text{OH} \\
\text{CH}_2\equiv\text{CH}–\text{CH}_2
\end{align*}
\]

2-Propen-1-ol (allyl alcohol)

**PROBLEM 13.12**

Explain which functional groups are present in these compounds on the basis of their IR spectra:

a)

b)
Review of Mastery Goals

After completing this chapter, you should be able to:

- Predict the important absorption bands in the IR spectrum of a compound. (Problems 13.13, 13.15, 13.26, 13.27, 13.28, and 13.29)

Additional Problems

**13.13** List the positions of the important absorption bands in the IR spectra of these compounds:

a) \(\text{HC}≡\text{CCH}_2\text{CH}_2\text{NH}_2\)  

b) \(\text{HOCCH}_2\text{CH}_2\text{C}≡\text{N}\)

c) \(\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_3\)  

d) \(\text{[structure image]}\)

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